

## CHAPTER 1

### COTRIMERIZATIONS OF ACETYLENIC COMPOUNDS

NICOLAS AGENET, OLIVIER BUISINE, FRANCK SLOWINSKI, VINCENT GANDON,  
CORINNE AUBERT, AND MAX MALACRIA

*Laboratory of Organic Chemistry (UMR CNRS 7611), Institute for Molecular  
Chemistry (FR 2769), Pierre and Marie Curie University (Paris 6), case 229,  
4 place Jussieu, F-75252, Paris cedex 05, France*

#### CONTENTS

	PAGE
ACKNOWLEDGMENTS . . . . .	3
INTRODUCTION . . . . .	3
MECHANISM AND STEREOCHEMISTRY . . . . .	4
Metallacyclopentadiene Route . . . . .	4
Regioselectivity . . . . .	6
Bimolecular and Intramolecular Cotrimerizations . . . . .	7
Cascade Carbometallation Route . . . . .	7
Intermolecular Cascade Reactions . . . . .	7
Intramolecular Cascade Reactions . . . . .	8
Metathesis Route . . . . .	9
SCOPE AND LIMITATIONS . . . . .	9
Intermolecular Reactions . . . . .	10
Cyclotrimerization of Symmetrical Alkynes . . . . .	10
Regio- and Chemoselectivity in Cotrimerizations of Unsymmetrical Alkynes . . . . .	12
Cyclotrimerization Reactions . . . . .	12
Cotrimerization Reactions . . . . .	13
Bimolecular Reactions . . . . .	17
Regio- and Chemoselectivity in Cotrimerizations . . . . .	17
Tricyclic and Higher Polycyclic Compounds . . . . .	20
Intramolecular Reactions . . . . .	22
Formation of Three Rings . . . . .	22
Formation of Four Rings . . . . .	23
Angular [ <i>N</i> ]-Phenylenes . . . . .	23
Enantioselective Reactions . . . . .	24
Limitations of the Cotrimerization of Acetylenic Compounds . . . . .	25
Catalyst Deactivation . . . . .	25
Side-products . . . . .	26
APPLICATIONS TO THE SYNTHESIS OF NATURAL PRODUCTS . . . . .	27

malacria@ccr.jussieu.fr

*Organic Reactions*, Vol. 68, Edited by Larry E. Overman et al.

© 2007 Organic Reactions, Inc. Published by John Wiley & Sons, Inc.

Intermolecular Reactions . . . . .	27
Derivatives of 2-Nicotinic Acid . . . . .	27
Bimolecular Reactions . . . . .	28
Monocyclic Compounds: Synthesis of Vitamin B <sub>6</sub> . . . . .	28
Biaryls . . . . .	28
Synthesis of 6-Arylpyridines . . . . .	28
A→ABC-Ring Formation: Hyellazole . . . . .	28
AB→ABCD-Ring Formation: Protoberberines . . . . .	29
AB→ABCD-Ring Formation: (±)-Lysergene and (±)-Lysergic Acid Diethylamide (LSD) . . . . .	30
D→ABCD-Ring Formation: <i>rac</i> -Estrone . . . . .	30
D→ABCD-Ring Formation: Phyllocladane and Kaurane Derivatives . . . . .	31
Direct ABCD-Ring Formation: Phyllocladane and Kaurane Derivatives . . . . .	32
Intramolecular Reactions . . . . .	33
Taxoids . . . . .	33
Benz[ <i>a</i> ]anthraquinone Core of Angucyclinone Antibiotics . . . . .	33
Calomelanolactone . . . . .	34
COMPARISON WITH OTHER METHODS . . . . .	35
Dötz Benzannulation . . . . .	35
Palladium-Catalyzed [4+2]-Benzannulations . . . . .	35
Palladium-Catalyzed Cocyclization of Benzynes with Alkynes . . . . .	36
EXPERIMENTAL CONDITIONS . . . . .	37
EXPERIMENTAL PROCEDURES . . . . .	37
( <i>E</i> )- and ( <i>Z</i> )-6-Allyl-2-(2-cyano-1,3-butadienyl)-3,5-dihexylpyridine (Regioselective Stepwise Construction of a Tetrasubstituted Pyridine using Titanium) . . . . .	37
1,2,3,4-Tetraethyl-5,6-dipropylbenzene (Regioselective Stepwise Construction of an Hexasubstituted Benzene using Zirconium) . . . . .	38
5,7-Dihydro-6H-cyclopenta[ <i>c</i> ]pyridine-3,6,6-tricarboxylic Acid 3-Ethyl 6,6-Dimethyl Ester (Construction of a 3,4-Fused Pyridine using Ruthenium) . . . . .	39
3,3'-Bis(cyanomethyl)-5,5',7,7'-tetrahydro-[1,1'-bi-6 <i>H</i> -cyclopenta[ <i>c</i> ]pyridine]-6,6,6',6'-tetracarboxylic Acid Tetramethyl Ester (Construction of a 2,2'-Bipyridine using Ruthenium) . . . . .	39
5-Butyl-1,3,6,8-tetrahydro-1,1,6,6-tetrakis(1-methylethyl)-4-phenylbenzo[1,2- <i>c</i> :3,4- <i>c'</i> ]bis[1,2]oxasilole (Cobalt-Catalyzed Formal Intermolecular Regioselective Construction of a Polysubstituted Benzene using Disposable Silicon Tethers) . . . . .	40
4,5-Dimethyl-1,3,6,8-tetrahydrobenzo[ <i>c</i> ]benzo[5',6']oxepino[3',4':5,6]benzo[ <i>e</i> ]oxepin (Synthesis of a Molecule with Helical Chirality using Cobalt) . . . . .	41
2,3-Bis(Trimethylsilyl)anthraquinone (Cobalt-Catalyzed Anthraquinone Synthesis) . . . . .	41
Tetramethyl 5-( <i>n</i> -Butyl)-1,2,3,4-benzenetetracarboxylate (Chemoselective Construction of a Pentasubstituted Benzene using Iridium) . . . . .	42
1,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(methoxymethyl)isobenzofuran (Enantio- and Diastereoselective Synthesis of an Axially Chiral Teraryl Compound using Iridium) . . . . .	42
2-Butyl-1-(1-hexynyl)-4-methylbenzene (Palladium-Catalyzed [4+2] Cross-Benzannulation Reaction of Enynes with Diynes and Triynes) . . . . .	43
2,3,4,5,6,7,8,9-Octahydro-2,5,8-tris[[2,4,6-tris(1-methylethyl)phenyl]sulfonyl]-1 <i>H</i> -benzo[1,2- <i>c</i> :3,4- <i>c'</i> :5,6- <i>c''</i> ]tripyrrole (Palladium-Mediated Cyclo-trimerization of a Macrocyclic) . . . . .	44
TABULAR SURVEY . . . . .	44
Chart 1. Structure Abbreviations Used in Tables 1-5 . . . . .	47
Chart 2. Porphyrin Abbreviations Used in Table 2 . . . . .	48
Chart 3. Phenylene Abbreviations Used in Table 3 . . . . .	49

Table 1. Monosubstituted Alkynes . . . . .	50
Table 2. Disubstituted Alkynes . . . . .	114
Table 3. Diynes . . . . .	164
Table 4. Triynes . . . . .	219
Table 5. Nitriles . . . . .	248
REFERENCES . . . . .	292

### ACKNOWLEDGMENTS

We wish to thank Professor T. V. RajanBabu for helpful suggestions and Drs. Linda Press and Danielle Soenen for the editing of the manuscript.

### INTRODUCTION

The cyclotrimerization of acetylenic compounds is a useful method for the construction of three new bonds in a one-step process. Although symmetry-allowed, there is a paucity of examples of purely thermal [2+2+2] cycloadditions. Berthelot reported the first example in 1866 which was the cyclization of acetylene to benzene.<sup>1</sup> High temperatures (ca. 400°) are required for this reaction and a mixture of products is formed. In 1948, Reppe discovered the first transition-metal-catalyzed version of this reaction in which nickel was used, leading to the formation of substituted benzenes.<sup>2</sup> Since then, catalysts based on no less than seventeen early to late transition metals (for representative examples see: Ti,<sup>3,4</sup> Zr,<sup>5,6</sup> V,<sup>7</sup> Nb,<sup>8-10</sup> Ta,<sup>9</sup> Cr,<sup>11,12</sup> Mo,<sup>13</sup> W,<sup>12,14</sup> Fe,<sup>15</sup> Ru,<sup>16</sup> Os,<sup>17</sup> Co,<sup>18</sup> Rh,<sup>19-21</sup> Ir,<sup>22,23</sup> Ni,<sup>24</sup> Pd,<sup>25</sup> Cu<sup>26</sup>), two lanthanides (Eu, Yb),<sup>27</sup> one actinide (U),<sup>28</sup> and aluminum<sup>29</sup> have been developed for the cycloaddition of substituted alkynes to benzene derivatives. Alkynes,<sup>18,30-34</sup> alkenes,<sup>18,32</sup> allenes,<sup>34</sup> aldehydes and ketones,<sup>33</sup> imines,<sup>32</sup> isocyanates,<sup>32</sup> isothiocyanates,<sup>35</sup> carbon monoxide,<sup>32</sup> carbon dioxide,<sup>32</sup> carbon disulfide,<sup>35</sup> and carbenes and carbynes<sup>32</sup> can take part in related cyclization reactions to give products with four-, five-, six-, or eight-membered rings. It is well known that nitriles can also be used as alkyne replacements in [2+2+2] cyclotrimerizations to afford pyridines.<sup>18,32,36,37</sup> Many of these reactions proceed with good chemo-, regio-, and stereoselectivities and have found many applications in organic synthesis.

During the last three decades this reaction has been extensively investigated and the topic has been thoroughly reviewed.<sup>18,30-32,37-44</sup> Because of the large number of publications in this area, it is impossible to present more than a limited set of examples, and several very interesting topics will have to be excluded from this chapter. Among them are: cyclizations of acetylenic compounds on low-index metal surfaces, kinetic studies of cyclotrimerizations, cyclizations mediated by metal ions introduced into zeolites, cyclotrimerization of nitriles to triazines, and cocyclization of transient strained cycloalkynes. The latter is mentioned in the "Comparison with Other Methods" section.

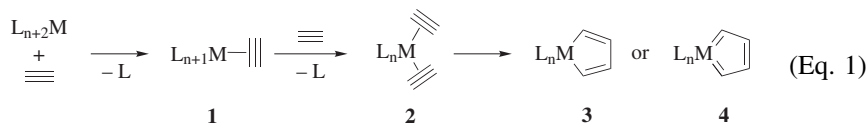
This chapter is devoted to early to late transition metal-mediated cotrimerization of acetylenic compounds directed towards organic synthesis. It addresses the scope and the generality of the reaction as well as the current state of the art with regard to regio- and stereoselectivities. In the context of selectivity, a mechanistic overview is provided. Inter- and intramolecular versions of the cyclizations are presented with an emphasis on applications in synthesis. The literature from 1980 up to the middle of 2004 is covered.

### MECHANISM AND STEREOCHEMISTRY

The cotrimerization of alkynes in the presence of transition metals to produce arenes is probably the most general reaction of these compounds. It is possible to cyclotrimerize acetylene as well as mono- and disubstituted acetylenic compounds. In addition, selective intermolecular cyclizations involving more than one type of alkyne are also possible. A wide variety of homogeneous and heterogeneous catalysts are available for such cyclizations. Therefore, several mechanistic pathways have been proposed, which are mainly dependent on the nature of the catalyst. It seems obvious that the metal may act as a template for the formation of the arenes, by sequentially binding the alkynes and acting as a channel through which electrons flow between the ligands. However, debate about the cyclotrimerization mechanism continues. The emphasis here will be on the most common mechanism involving the intermediacy of metallacyclopentadienes. This mechanism is applicable to most of the metals (for representative examples see: Ti,<sup>3</sup> Zr,<sup>6</sup> Ta,<sup>45</sup> Mo,<sup>46,47</sup> Co,<sup>48,49</sup> Rh,<sup>19</sup> Ir,<sup>22,23</sup> Ru,<sup>50</sup> Ni,<sup>51</sup> and Pd<sup>52</sup>). It also provides a useful model for an understanding of the selectivities. Other types of mechanisms which do not involve the intermediacy of a metallacyclopentadiene will also be mentioned, particularly the Pd(II)-triggered cascade carbometallation route and the Ru(IV) metathesis route.

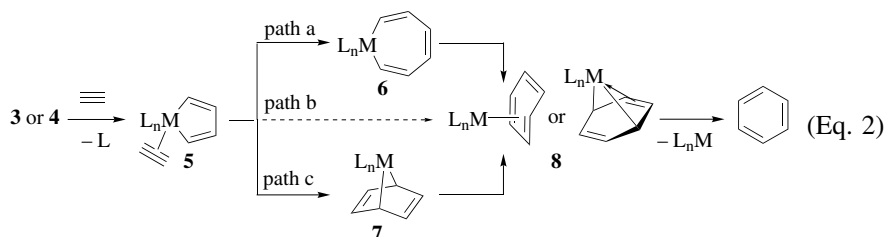
#### Metallacyclopentadiene Route

Initially, one and then two alkyne moieties sequentially displace two ligands of the metal to form alkyne complex **1** and then **2** (Eq. 1). Oxidative coupling may occur to give the coordinatively unsaturated complexes **3** or **4** which have oxidation states of two or four units higher than their precursor **2**.

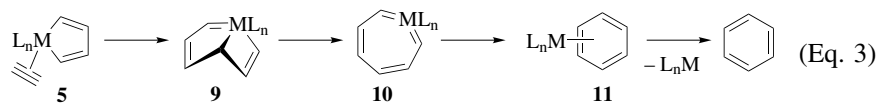


Several pieces of evidence supporting the intermediacy of these metallacycles including calculations and isolation of structurally characterizable molecules have been provided.<sup>50,53–57</sup> Upon opening a vacant coordination site by ligand dissociation, intermediates **3** and **4** may readily complex a third alkyne unit to give the metallacyclopentadiene(alkyne) complex **5** (Eq. 2). Compelling evidence for the accumulation of intermediate **5** in the catalytic cycle has been reported. It

has been observed that blocking the empty coordination site in **3** ( $M = \text{Rh}, \text{Ir}$ ) with an ancillary ligand ( $L = \text{Cl}, \text{PR}_3$ ) inhibits the arene formation or in some cases slows down the rate.<sup>49</sup> In addition, isolated examples of structural motifs such as **5** ( $M = \text{Co}$ ) have been described.<sup>58</sup>



Complex **5** may undergo insertion of the ligated alkyne into a metal-carbon bond to give metallacycloheptatriene **6** (path a). Reductive elimination may occur to provide the complex **8**, which has been isolated occasionally.<sup>23,58–61</sup> Lastly, decomplexation of the arene generates the benzene ring. The intermediacy of the metallacycloheptatriene **6**, which is frequently proposed, is questionable, because the reductive elimination converting **6** to **8** is symmetry forbidden.<sup>62,63</sup> This reaction path is thus expected to be kinetically difficult. Therefore, alternative processes for the formation of the  $\eta^4$ -benzene complex **8** have been proposed. In path c, a [4+2] approach is shown to give an intermediate 7-metallanorbornadiene complex **7** that subsequently leads to **8**. Although kinetic studies support the intermediacy of complex **7**,<sup>49</sup> it appears from more recent studies that the reductive elimination giving the arene formation is also symmetry forbidden.<sup>50,62</sup> For CpCo complexes, calculations support a direct [4+2] cycloaddition pathway (path b) with no intermediate for the conversion of **5** to **8**. This transformation requires a very small activation energy of 0.5 kcal/mol reflecting an extraordinarily large driving force of  $-81.4$  kcal/mol.<sup>62</sup> A fourth suggestion has been made for ruthenium.<sup>50,56,57</sup> A bicyclic ring system **9** is formed from complex **5**. This metallabicyclo[3.2.0]heptatriene rearranges into a metallacycloheptatriene complex **10**, which gives the  $\eta^2$ -cyclohexatriene complex **11** after reductive elimination (Eq. 3). Recently, a relevant iridabicyclo[3.2.0]heptatriene has been isolated and characterized by X-ray crystallography.<sup>64</sup>



It is noteworthy that the metallacyclopentadiene **3** can lead to  $\eta^4$ -cyclobutadiene complex **12**,<sup>63</sup> as illustrated in Eq. 4. For some specific metals such as cobalt, rhodium, and iridium, the mechanism of this transformation has been probed by means of Density Functional Theory (DFT)/B3LYP calculations.<sup>65</sup> A multi-step reaction including a cyclopropylcarbene and a tetrahedrane-type intermediate was computed, supporting the initial proposal made by Vollhardt

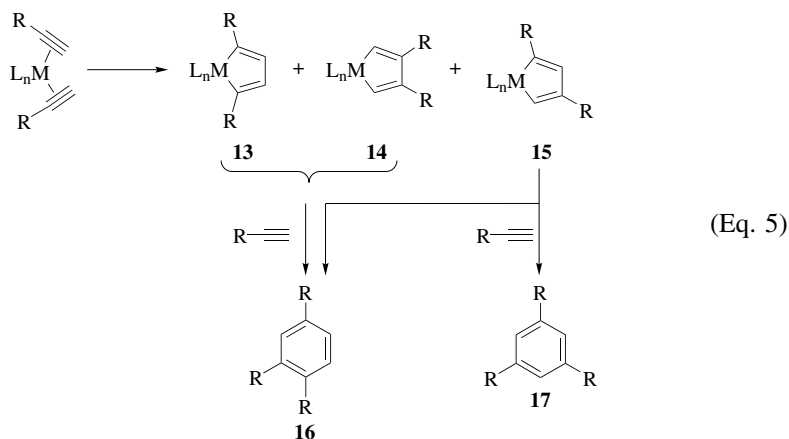
and co-workers.<sup>66</sup> It was shown that, as the substituents on the alkyne get larger, the cyclodimerization reaction becomes easier.<sup>65</sup>



For many years, cyclobutadiene complexes were proposed to be reactive intermediates in the formation of the arenes,<sup>67</sup> despite the high stability of such complexes. Experiments using a number of main group and transition metal catalysts have since provided strong evidence that the cyclotrimerization of alkynes does not take place through cyclobutadiene intermediates.<sup>48</sup> These results support the assertion that complex **12** is an inert byproduct leading to catalyst deactivation, due to the thermodynamic stability of the metal-cyclobutadiene bond.<sup>68,69</sup>

Although not fully clarified, the pyridine syntheses from alkynes and nitriles is thought to proceed according to the same kind of mechanism. The first step would be the formation of a metallacyclopentadiene from two alkyne units, followed by nitrile insertion.<sup>70</sup>

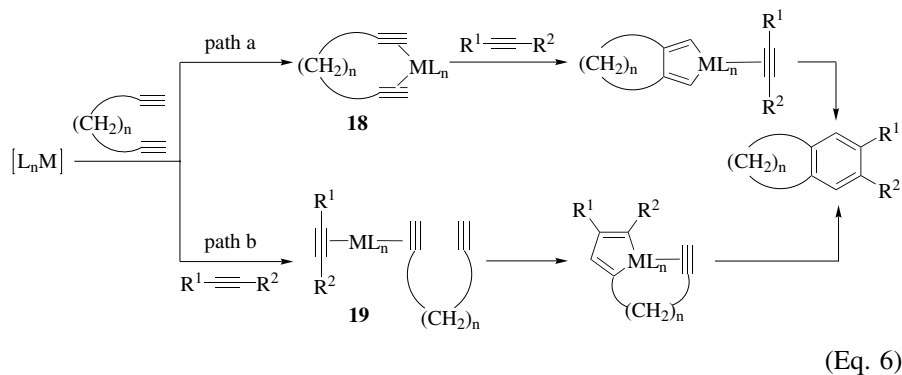
**Regioselectivity.** Whatever the mechanism, the major regiochemical consequence is that the trimerization of unsymmetrically substituted alkynes leads to arenes which display exclusively 1,2,4- or 1,3,5-substitution patterns. In the proposed mechanism, regioselection occurs at two stages: in the formation of the metallacyclopentadiene and in its subsequent reaction with a third alkyne equivalent. The preference for formation of the metallacyclopentadienes **13–15** clearly depends on the catalyst, the substitution pattern on the alkyne, and the reaction conditions (Eq. 5).



Complexes **13** and **14** must lead exclusively to the 1,2,4-product **16**, independent of the orientation of the final insertion. The formation of the 1,3,5-compound **17** requires the intermediacy of the metallacycle **15**. However, complexes of type

**15** can also give rise to 1,2,4-products.<sup>55</sup> Although products of type **17** seem statistically disfavored, many reports dealing with the selective formation of these compounds can be found (see Scope and Limitations).

**Bimolecular and Intramolecular Cotrimerizations.** The bimolecular cyclizations combine a diyne and a monoalkyne. Depending on the substrates, the initial bis-alkyne species is a complex of both alkyne units of the diyne (path a, complex **18**) or a complex of the monoalkyne together with one free alkyne unit (path b, complex **19**) as described in Eq. 6. Either pathway would afford the same arene products. Chemoselectivity is also a potential problem because the cyclizations could involve exclusively the diyne, or exclusively the monoalkyne, or one diyne unit and two monoalkynes. Those could compete with the desired process. In practice, chemoselectivity is readily achieved by employing sterically hindered monoalkynes, for instance, *bis*-trimethylsilylethyne, which is reluctant to undergo autocyclotrimerization.

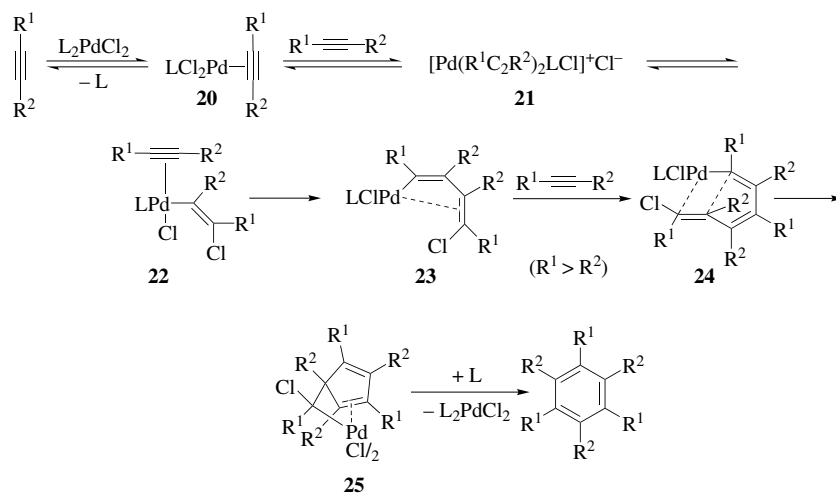


### Cascade Carbometallation Route

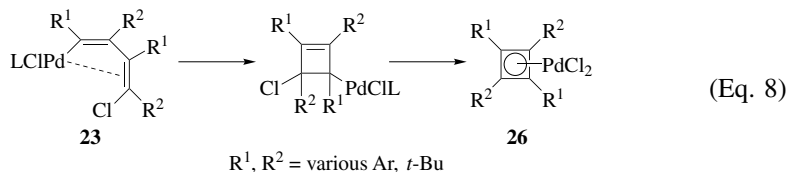
A cascade carbopalladation often occurs with Pd(II) complexes.<sup>71,72</sup>

**Intermolecular Cascade Reactions.** Many palladium(II) complexes are reactive towards alkynes. In intermolecular versions, these Pd-catalyzed cyclizations are complex processes and appear to operate differently from those described above, even though the formation of the arenes is the end result in some of these processes.<sup>38,73</sup> Different intermediates are possible depending on the size of the alkyne substituents or even on the polarity of the solvent in which the reaction is carried out. Metallacyclopentadiene intermediates are not necessarily involved in these sequences. The proposed mechanism presented in Eq. 7 is based on several isolated intermediates.<sup>74</sup> The first step is the formation of the  $\pi$ -acetylene complex **20** after ligand exchange. A second ligand exchange with another alkyne unit provides the transient complex **21**, which is believed to be in equilibrium with the  $\sigma$ -alkenyl intermediate **22**. The irreversible insertion of the second coordinated acetylene into the Pd–C bond then occurs, giving the  $\sigma$ -butadienyl complex

**23.** With small  $R^2$  groups, the next step is an anti-Markovnikov cis-insertion of another acetylene into the Pd–C bond giving a  $\sigma, \pi$ -hexatrienyl complex **24**. The terminal double bond coordinates the metal in such a way that internal cyclization leading to complex **25** becomes straightforward. Palladium in the complex **25** coordinates a cyclopentadiene double bond, which is sterically constrained. Ring expansion in complex **25** will be followed by its decomposition to give the expected arene product regenerating  $\text{PdCl}_2$ .



It is noteworthy that the cyclobutadiene complexes **26**, which are inert to further reaction with alkynes, can be obtained from the  $\sigma$ -( $\eta^2$ -butadienyl) complexes **23** when alkynes are substituted by sterically demanding  $R^1$  groups as shown in Eq. 8.<sup>75</sup>

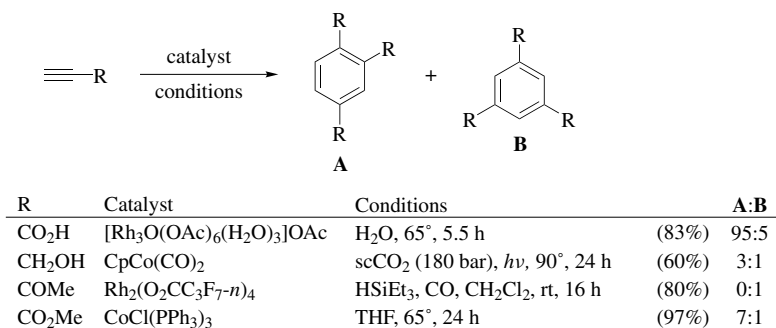


**Intramolecular Cascade Reactions.** The use of palladium(II)-mediated cyclotrimerizations had been scarce until the development of the intramolecular versions. Although the mechanism is not very clear, it is likely that **27** is a putative intermediate as shown in Eq. 9. It is generated by hydropalladation of the less-substituted alkyne function followed by two carbopalladations. The ring closure to the benzene derivatives might occur through a 6-endo-trig cyclization (path a) or an electrocyclic pathway (path b), both followed by a  $\beta$ -hydride elimination.<sup>76,77</sup>





Catalysts based on a very large number of metals have been developed (see Introduction). Polar, non-polar, or even supercritical solvents have been successfully used. This reaction exhibits a high chemoselectivity toward triple bonds and is therefore tolerant of many functional groups (see examples that follow in Eq. 11 and in the Tabular Survey).

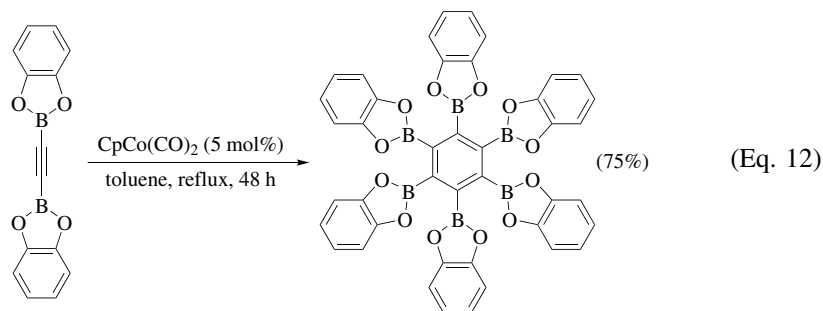


(Eq. 11)

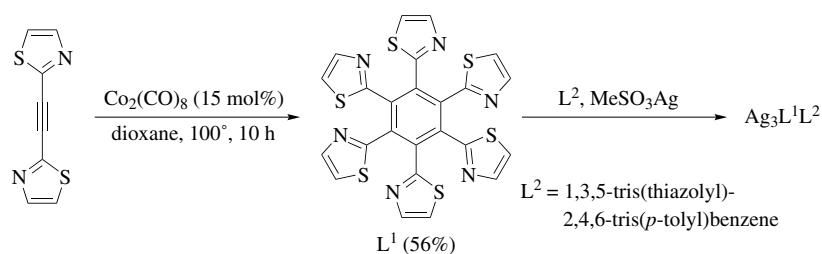
In the following section, an overview of the synthetic potential of the cotrimerization of acetylenic compounds is given. A choice of relevant examples extracted from the recent literature is presented to emphasize the modern applications of this chemistry. Applications for the synthesis of natural products will be described in a separate section.

### Intermolecular Reactions

**Cyclotrimerization of Symmetrical Alkynes.** Symmetrically hexasubstituted benzenes have found applications in many fields such as main-group chemistry, organometallic chemistry, and organic material science. They are readily available from cyclotrimerization of symmetrical alkynes. An example is the cobalt- or nickel-catalyzed cycloaddition of diborylacetylenes for forming hexaborylbenzene derivatives (Eq. 12).<sup>80</sup> These compounds are the only hexa-heteroatom-substituted benzene derivatives obtained by cycloaddition of alkynes.

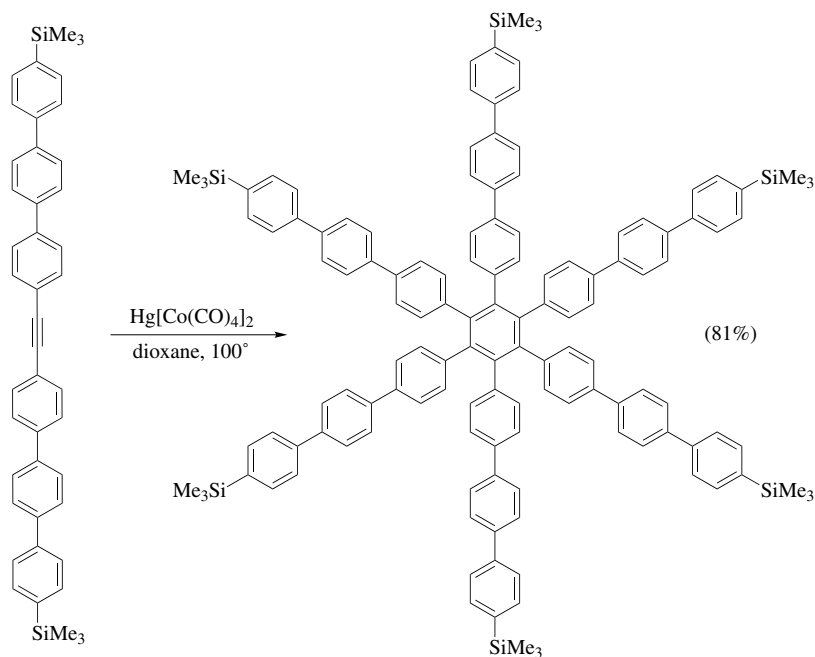


The quest for novel metal-mediated molecular devices has required the preparation of new  $\pi$ -ligands. In that respect, the cobalt-mediated cyclotrimerization of 1,2-bis(2-thiazolyl)ethyne has granted access to the hexa(thiazolyl) disk-shaped ligand  $L^1$  which takes part in the formation of sandwich-shaped heterotopic trinuclear silver(I) complexes of great theoretical interest because of their molecular gear behavior (Eq. 13).<sup>81</sup>



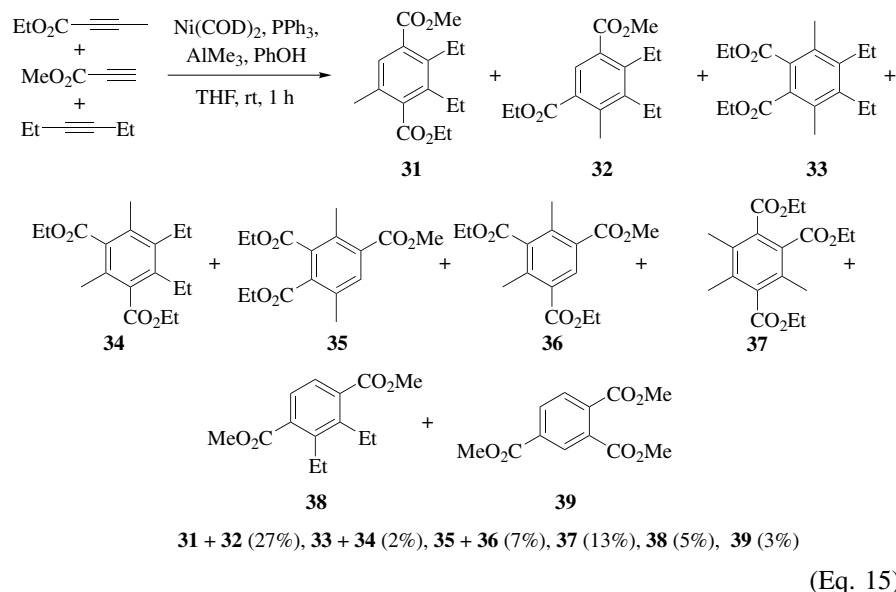
(Eq. 13)

In recent years, the cyclotrimerization of monoalkynes has been employed on many occasions for the short convergent synthesis of dendrimers (see Tabular Survey). Precursors of nanometer-sized dendrimeric materials such as the 6-fold symmetric starlike silylated polyphenylene shown in Eq. 14 have been prepared.<sup>82</sup>

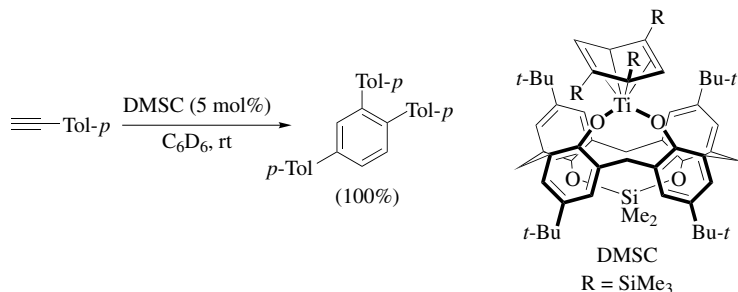


(Eq. 14)

**Regio- and Chemoselectivity in Cotrimerizations of Unsymmetrical Alkynes.** The selective synthesis of polysubstituted benzenes and pyridines from the intermolecular transition-metal-catalyzed [2+2+2] cycloaddition reaction is a challenging problem. Indeed, the cyclotrimerization of an unsymmetrical monoalkyne usually leads to two regioisomers, 1,2,4- and 1,3,5-trisubstituted benzenes (see Eq. 5, Mechanism Section). Cotrimerization of two different unsymmetrical monoalkynes may give up to 9 isomers and cotrimerization of three different unsymmetrical monoalkynes, up to 38 different ones. As illustrated in Eq. 15, a complex mixture was obtained from the cocyclization of ethyl 2-butynoate, methyl propiolate, and 3-hexyne.<sup>83</sup> Recent efforts directed toward selective intermolecular cotrimerization reactions are presented in this section.

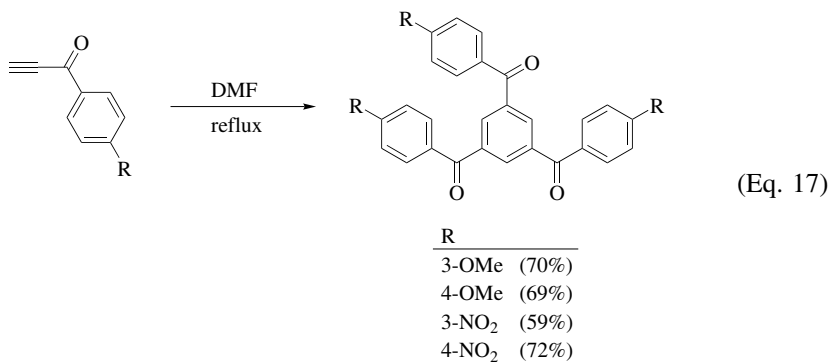


**Cyclotrimerization Reactions.** Only a few methods seem general for success in the selective formation of 1,2,4-trisubstituted benzenes. Among them are the highly selective preparation of 1,2,4-trisubstituted benzenes using a calixarene-bound titanium complex (Eq. 16).<sup>84</sup> The high selectivity may be understood in terms of the directing influence of the DMSC ligand (DMSC = 1,2-alternate Me<sub>2</sub>Si-bridged *p-tert*-butylcalix[4]arene). In the 1,2-alternate conformation, the DMSC ligand favors the formation of the  $\alpha,\beta'$ -substituted titanacyclopentadiene. It also exerts steric control over approach of a substrate to the  $\alpha,\beta'$ -substituted titanacyclopentadiene; the less hindered end of an alkyne is directed into the calixarene cavity.



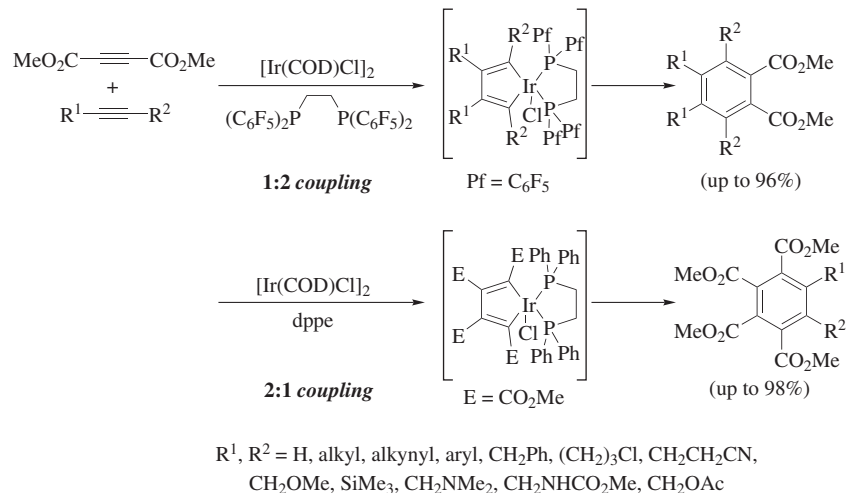
(Eq. 16)

Selective formation of 1,3,5-trisubstituted benzenes has been described (for selected examples see: Ti,<sup>3</sup> Nb,<sup>8</sup> Co,<sup>85</sup> Rh,<sup>86</sup> Pd<sup>87</sup>). There are quite a few examples where the reaction produces the 1,3,5-isomer exclusively, or almost exclusively from HC≡CR where R is SF<sub>5</sub>, CF<sub>3</sub>, CO<sub>2</sub>Me, C(=CH<sub>2</sub>)Me, TMS, Ph, and CHMeBu-*t*. In all examples where R = COAr, only the 1,3,5-isomer is formed, no matter what the conditions (Eq. 17).<sup>88-90</sup>



(Eq. 17)

*Cotrimerization Reactions.* Catalytic regio- and chemoselective assembly of two or three different acetylenic compounds remains rare. The same tendency is observed for the assembly of two different alkynes with nitriles. Recently, an iridium-complex-catalyzed highly selective cotrimerization of two different monoalkynes has been published (Eq. 18).<sup>91</sup> Chelating diphosphine ligands were used and the structure of the ligand had considerable effect on the chemoselectivity of the reaction. Indeed, 1,2-*bis*-(diphenylphosphino)ethane (dppe) promoted the 2 : 1 coupling of dimethyl acetylenedicarboxylate (DMAD) with monoalkynes, whereas with 1,2-*bis*-(dipentafluorophenylphosphino)ethane, the 1 : 2 coupling products were obtained. In the case of the 1 : 2 coupling however, the level of regioselectivity is moderate.

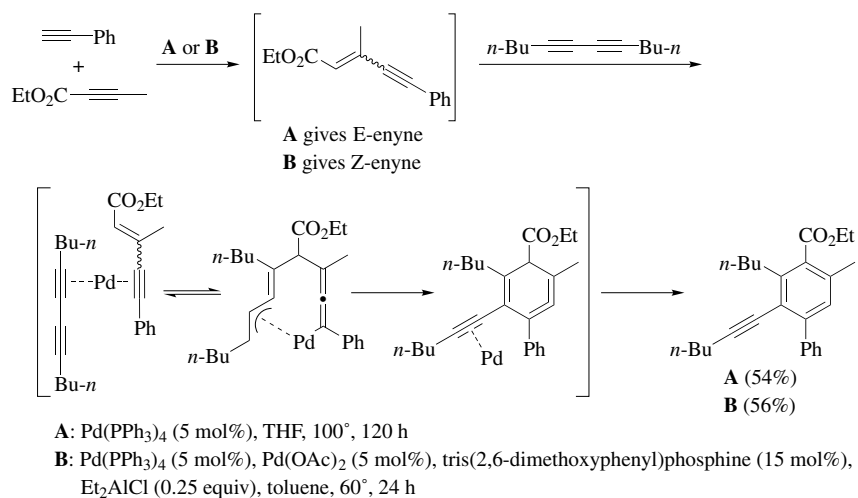


(Eq. 18)

Iridacyclopentadienes are postulated as intermediates. When the ligand is dppe, the coordination of DMAD to the iridium center would be much faster than with other monoynes. The reaction of the resulting tetracarboxy-substituted iridacyclopentadiene with the second monoynone gives the final product. Because DMAD and 1,2-bis(dipentafluorophenylphosphino)ethane are both electron withdrawing, the coordination of DMAD would give an electron-deficient species. Oxidative cyclization of this species would be a relatively difficult process. The formation of the intermediate iridacyclopentadiene from two monoynes, electronically richer than DMAD, is thus preferred.

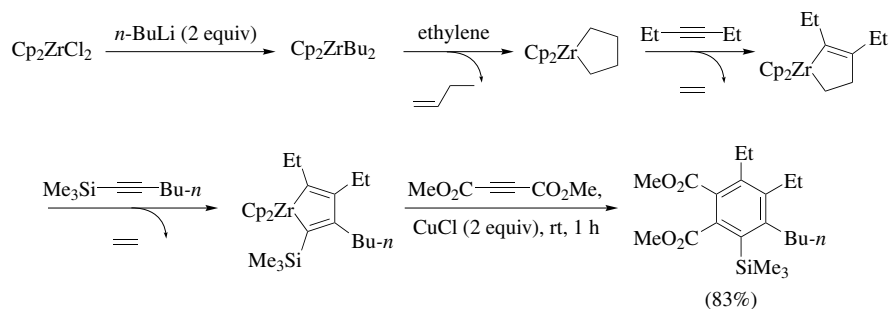
Similarly, ruthenium-catalyzed synthesis of *o*-phthalates from terminal alkynes and DMAD is a highly chemoselective intermolecular [2+2+2] cycloaddition process.<sup>92</sup> Nevertheless, no significant level of regioselectivity is observed. Palladium-catalyzed homodimerization of terminal alkynes and subsequent [4+2] benzannulation with diynes appears a very promising method for the selective cotrimerization of three different alkynes.<sup>93</sup> Tetra- and pentasubstituted benzenes were obtained as single products with excellent levels of regio- and chemoselectivity (Eq. 19). A significant acceleration of the sequential trimerization reaction in the presence of a combined Lewis acid/phosphine system is observed. Mechanistic studies suggest Lewis acid catalysis in the isomerization of the *E*-enyne formed in the first step to the more reactive *Z*-isomer. The employment of a conjugated diyne as cyclization partner has a dramatic influence on the regioselectivity of the cross-cycloaddition.<sup>94</sup> On the basis of deuterium-labeling experiments, the following mechanistic rationale was proposed: the reversible coordination of palladium to the triple bond of the enyne and the diyne produces a  $\sigma$ -allenyl palladium complex, stabilized by the neighboring  $\eta^3$ -propargyl moiety. Reductive elimination occurs affording a strained cyclic cumulene that is transformed into

the desired arene compound via a sigmatropic H-migration.



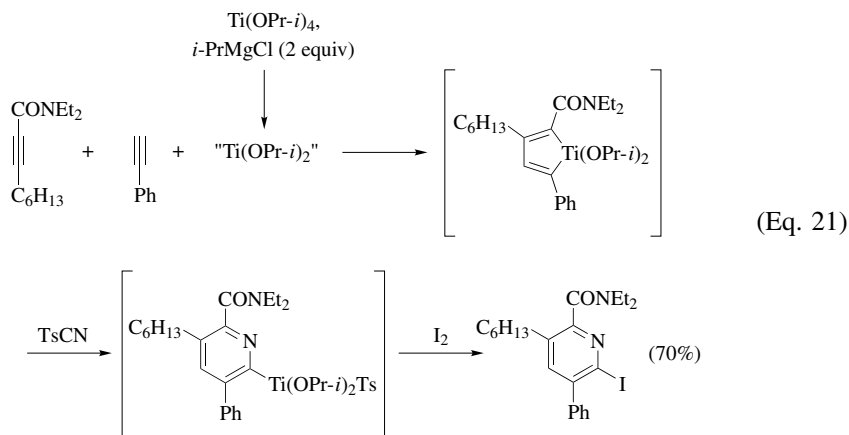
(Eq. 19)

Another way to perform a regio- and chemoselective cotrimerization of acetylenic compounds is to use stoichiometric metal-assisted reactions. The problem of chemoselectivity is circumvented through stepwise addition of all reagents. The key step is the regioselective formation of metallacyclopentadienes. For instance, the cycloaddition reaction of zirconacyclopentadienes to alkynes proved a highly selective method for forming benzene derivatives (Eq. 20).<sup>95,96</sup> ( $\eta^5$ -Cyclopentadienyl)zirconacyclopentane is formed from Cp<sub>2</sub>ZrBu<sub>2</sub> (Negishi reagent) and ethylene. The reagent is regioselectively transformed into a single unsymmetrical zirconacyclopentadiene after successive addition of two different alkynes. This is made possible by the presence of trimethylsilyl or aryl groups which are well known for giving  $\alpha$ -silyl- or  $\alpha$ -arylzirconium complexes. The reaction of the intermediate zirconacyclopentadiene complexes with DMAD in the presence of copper(I) chloride gives hexasubstituted benzenes in good yields.

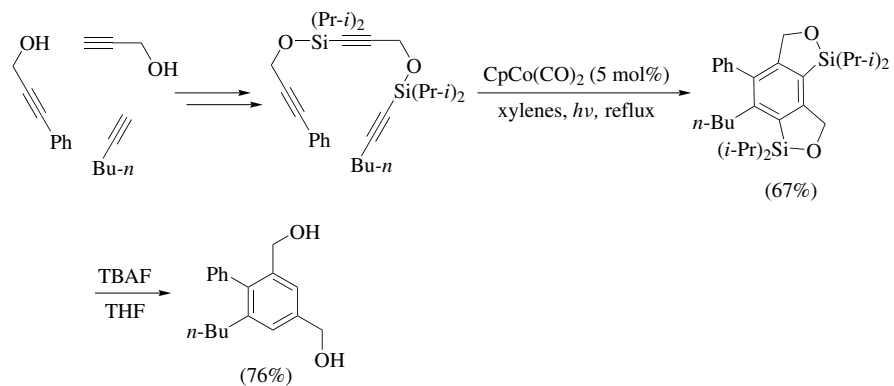


(Eq. 20)

Similarly, the selective assembly of two different alkynes and a nitrile for producing a single pyridine product is worth mentioning.<sup>97</sup> A low-valent titanium(II) alkoxide is generated from titanium(IV) isopropoxide and isopropylmagnesium chloride (Eq. 21). It promotes the selective coupling of two unsymmetrical alkynes to give titanacyclopentadienes regioselectively. Treatment of these intermediates with tosyl cyanide gives 2-metallated pyridines, which are treated with different electrophiles such as I<sub>2</sub> to furnish functionalized 2,3,5,6-tetrasubstituted pyridines in good yields. The amide group is known to be a more potent regiocontrolling element than the silyl or aryl group.<sup>98</sup> However, no rationale for this regioselective nitrile uptake was provided.



Finally, totally chemo- and regioselective formal intermolecular cyclizations of three different monoalkynes via the judicious use of disposable tethers has been disclosed. For instance, the use of silylated tethers in the sequence of cyclization followed by cleavage of the silicon group leads to polysubstituted arenes as unique cycloadducts in good yields (Eq. 22).<sup>99</sup>

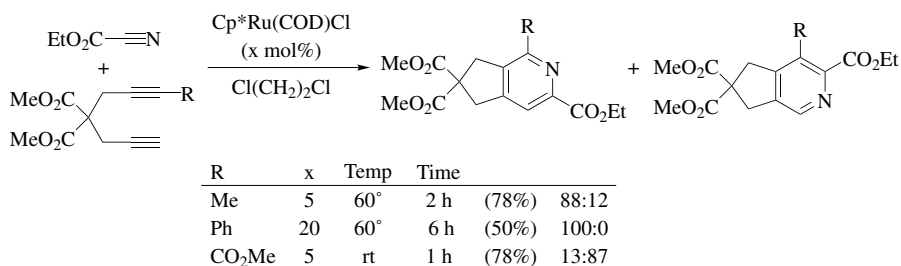


(Eq. 22)



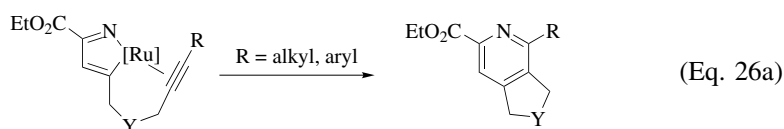


Cp\**Ru*(COD)Cl also gives good to excellent regioselectivities in the [2+2+2] cycloaddition of 1,6-diyne with electron-deficient nitriles<sup>101</sup> and dicyanides (Eq. 25).<sup>102</sup> The desired bicyclic pyridines are obtained in moderate to high yields with significant chemoselectivities. For the cycloaddition of 1,6-diyne with electron-deficient nitriles, the predominant isomer depends on the nature of the alkyne substituents. Electron-withdrawing groups reverse the regioselectivity.

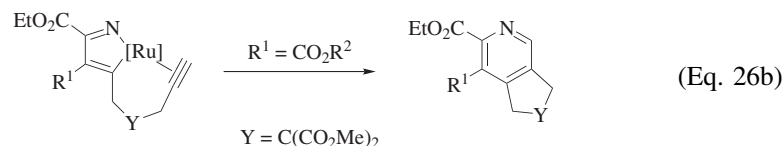


(Eq. 25)

The electron deficiency of the nitrile lowers the antibonding orbital level of the C–N triple bond and facilitates the formation of an azaruthenacyclopentadiene involving the nitrile and the less-hindered alkyne terminus relative to the formation of a ruthenacyclopentadiene involving the starting diyne (Eq. 26a). The subsequent insertion of the remaining alkyne moiety followed by reductive elimination gives the final pyridine. On the other hand, due to its effective delocalization of the d-electrons from the ruthenium center, the presence of an ester group on the diyne directs the oxidative cyclization at the electron-deficient alkyne terminus rather than the less hindered one (Eq. 26b).

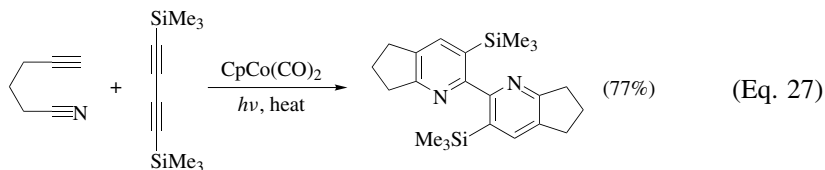


(Eq. 26a)

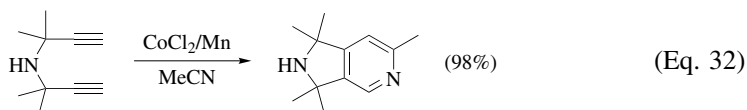
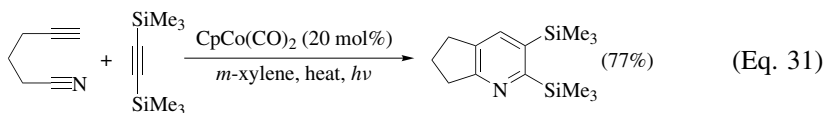
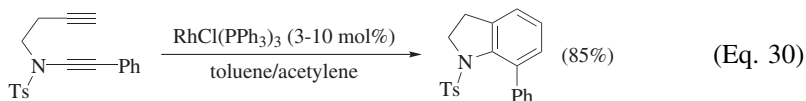
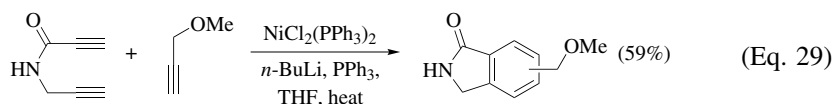
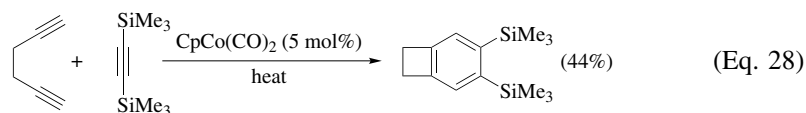


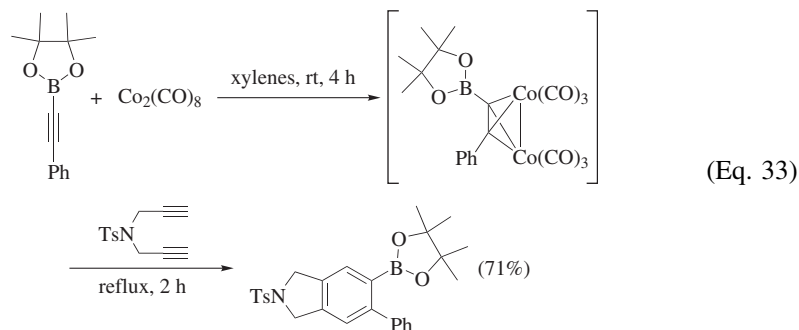
(Eq. 26b)

The regiocontrolled one-step synthesis of annelated 3,3'-disubstituted 2,2'-bipyridine ligands by cobalt(I)-catalyzed cyclotrimerization of 5-hexynenitrile and 1,3-diyne has also been described (Eq. 27).<sup>103</sup> The chemoselectivity was explained by means of semi-empirical LUMO coefficients and the regioselectivity by chelation control.

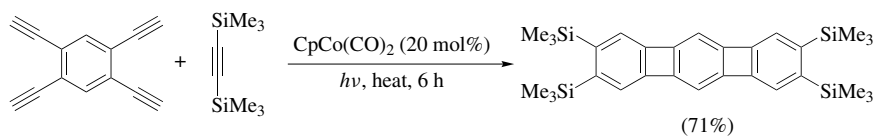
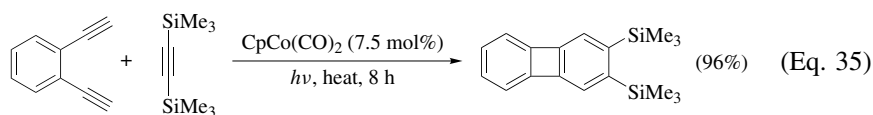
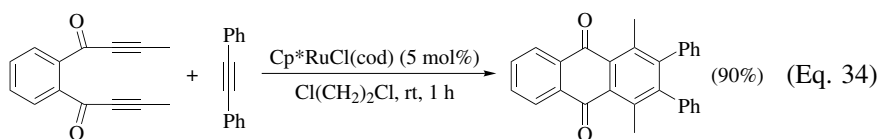


The most common bicyclic compounds obtained by bimolecular cotrimerization reactions are listed in Eqs. 28–32. As illustrated, this powerful strategy allows the preparation of benzocyclobutenes (Eq. 28),<sup>18,104</sup> indanes,<sup>18,104</sup> tetralins,<sup>18,104</sup> and higher homologs such as benzocycloheptenes.<sup>104</sup> Moreover, nitrogen-containing heterocycles have also been prepared frequently with various catalysts. Among them are isoindolinones (Eq. 29),<sup>105</sup> isoindolines and 1,4-dihydroisoquinolinones,<sup>105</sup> indolines (Eq. 30),<sup>106</sup> 2,3-fused pyridines (Eq. 31),<sup>107</sup> 3,4-fused pyridines,<sup>101</sup> and dihydropyrrolopyridines (Eq. 32).<sup>108</sup> Among the recent examples is the synthesis of fused arylboronic esters via cobalt(0)-mediated cycloaddition of alkynylboronates with  $\alpha,\omega$ -diynes (Eq. 33).<sup>109</sup> Alkynes bearing heteroatoms are of particular interest because they might give products amenable to subsequent transformations after the cyclization step. Alkynylsilanes<sup>18,30,104</sup> and alkynylstannanes<sup>110,111</sup> have been used to produce metallated benzene derivatives that allow subsequent electrophilic substitution or metal-halogen exchange. Along these lines, alkyl-, aryl-, and silyl-substituted alkynylboronic esters are successfully converted into arylboronates using  $\text{Co}_2(\text{CO})_8$ .



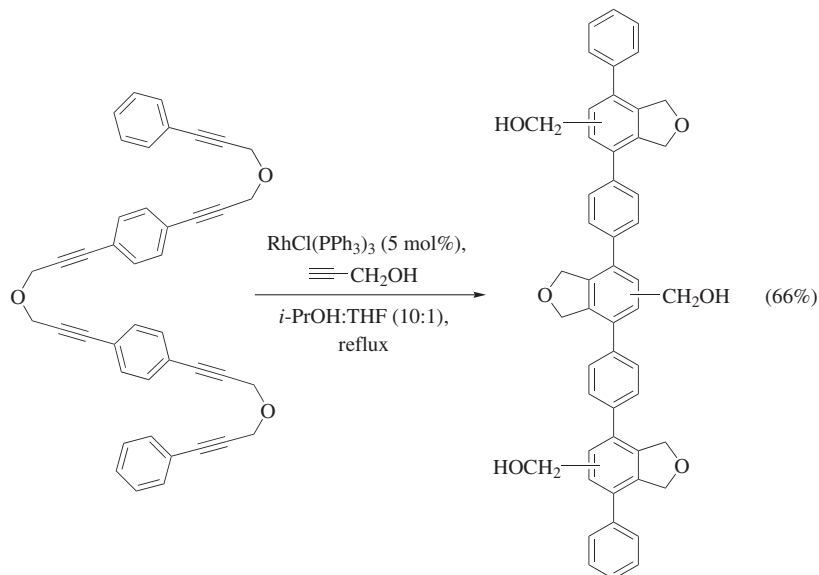


*Tricyclic and Higher Polycyclic Compounds.* The bimolecular cotrimerization of acetylenic compounds is one of the best methods for preparing linear polycyclic compounds. As shown below, the anthraquinone skeleton, which has been a continuing target for synthetic chemists, proves readily accessible from bis-ynones (Eq. 34).<sup>104,112</sup> The [*N*]-phenylenes have also received considerable attention both for their theoretical interest and their potential for the synthesis of fullerenes.<sup>113</sup> Biphenylenes (Eq. 35), linear triphenylenes (Eq. 36), and higher analogs have been prepared from 1,2-bis(alkynyl)arenes or 1,2,4,5-tetra(alkynyl)-arenes.<sup>114</sup> Access to angular [*N*]phenylenes is presented in the “Intramolecular Reactions” section that follows.



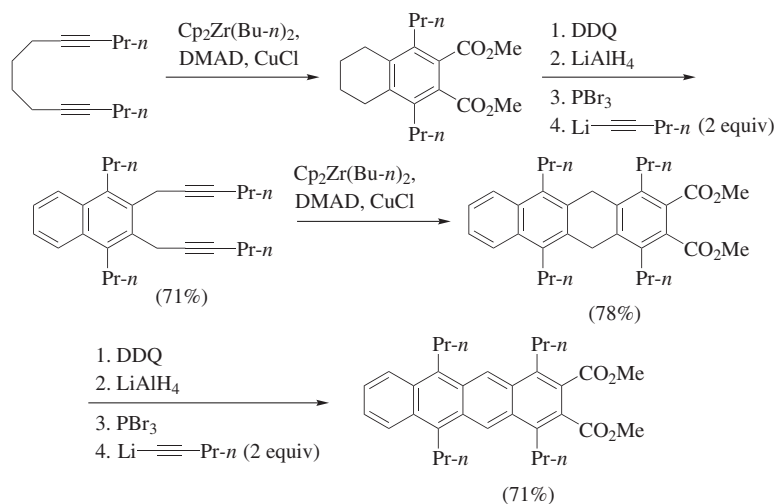
(Eq. 36)

Linear para-phenylenes have also been synthesized by bimolecular cotrimerization of alkynes. Indeed, promising light-emitting soluble poly-para-phenylenes have been prepared from ether-linked para-dialkynylarenes using a rhodium-containing catalyst (Eq. 37).<sup>115</sup>



(Eq. 37)

Finally, linear polycycles can be readily prepared via a homologation procedure.<sup>116</sup> A zirconium-based protocol allows the preparation of soluble acenes such as naphthalenes and pentacenes (Eq. 38).

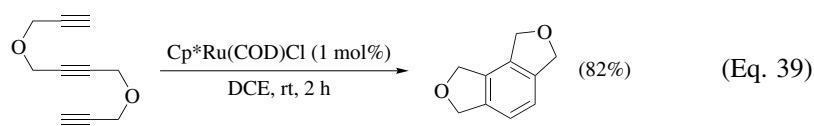


(Eq. 38)

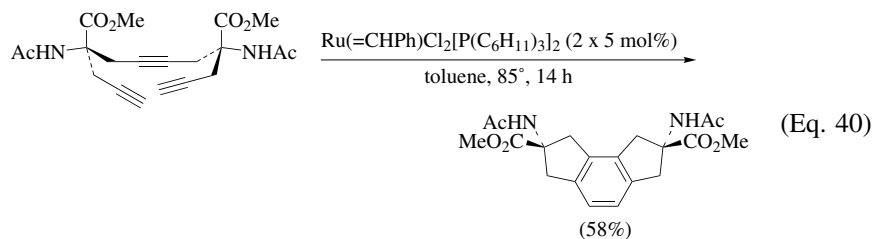
### Intramolecular Reactions

The intramolecular version of the cotrimerization of acetylenic compounds allows the formation of angularly fused polycyclic compounds.

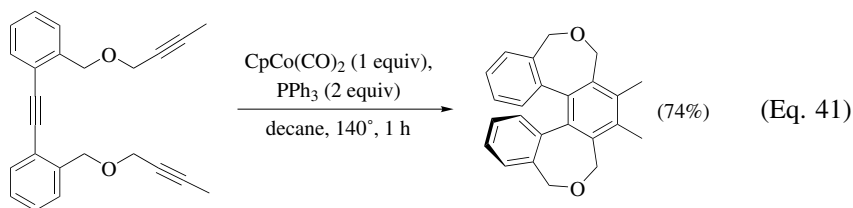
**Formation of Three Rings.** The aforementioned Ru-catalyzed bimolecular [2+2+2]-cycloaddition of 1,6-diyne with monoalkynes is also applicable to selective intramolecular alkyne cyclotrimerization (Eq. 39).<sup>56</sup> Triyne substrates furnish tricyclic aromatic compounds fused with 5–7 membered rings.



An application of the ruthenium-catalyzed ring-closing metathesis cascade reaction (see Mechanism Section, Eq. 10) has also been described (Eq. 40).<sup>117</sup> *as*-Indacene-bridged bis( $\alpha$ -amino acid) derivatives are obtained by the intramolecular [2+2+2] cotrimerization of triynes.

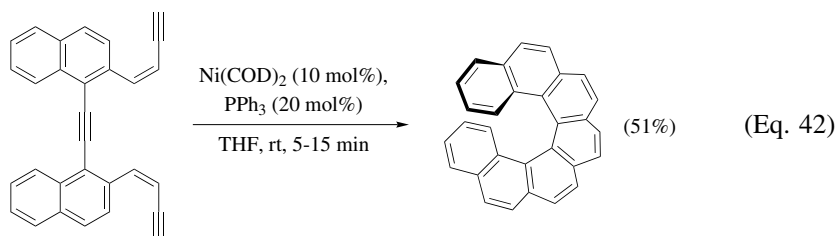


1,2-Diarylacetylenes with two terminal or methyl-substituted tethered acetylene moieties have been used as starting materials for the preparation of a new class of molecules with helical chirality (Eq. 41).<sup>118</sup> Several representatives of this class have been resolved into enantiomers by HPLC on a chiral column. This straightforward synthetic approach involving the formation of three fused rings allows the preparation of a variety of helical molecules.

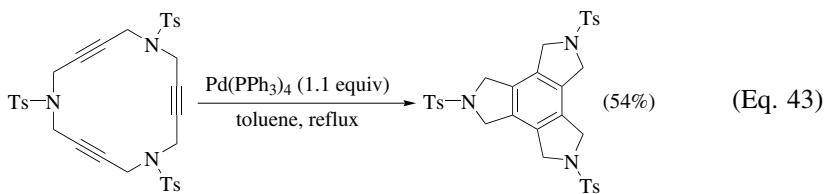


Similarly, the Ni(0)- or Co(I)-catalyzed isomerizations of *cis-cis*-dienetriynes provide access to [5]-, [6]- and [7]-helicenes (Eq. 42).<sup>119</sup> This conversion, which

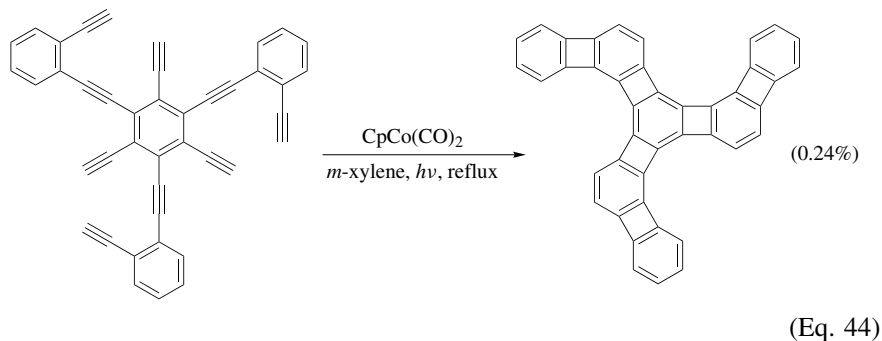
creates three aromatic rings in one step, is highly favored thermodynamically.



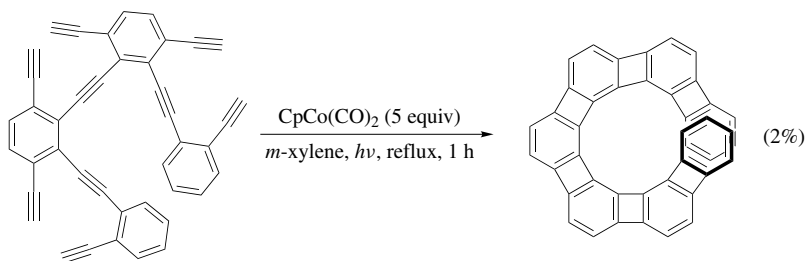
**Formation of Four Rings.** Transannular cotrimerizations of triynes are quite rare (see Tabular Survey). They allow the preparation of tetracyclic compounds such as triazatriindanes obtained from nitrogen-containing 15-membered triacetylenic macrocycles (Eq. 43).<sup>120,121</sup>



**Angular [N]-Phenylenes.** In addition to linear [N]-phenylenes (see above section on Bimolecular Reactions), numerous angular [N]phenylenes are available from the intramolecular version of the cotrimerization of alkynes. For example, a  $C_{3h}$ -symmetric [7]phenylene has been synthesized via cobalt-mediated triple cycloisomerization of a nonayne, albeit in poor yield (Eq. 44).<sup>122</sup> This compound is a promising precursor for  $C_{120}$ -fullerene (Archimedene). The  $\sigma$ - and  $\pi$ -ring strain in triangular  $C_3$ -symmetric [4]phenylenes act in concert rendering their cores to behave spectroscopically and chemically as true cyclohexatrienes.<sup>123,124</sup> The above methodology has also been employed for the preparation of helically extended conjugated  $\pi$  systems.

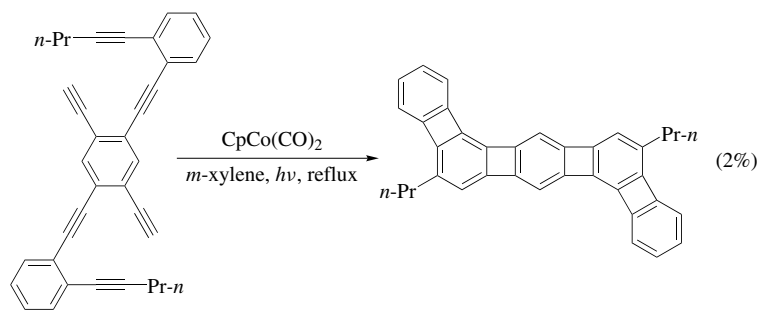


Helical [7]-, [8]-, and [9]phenylenes (heliphenes) have been obtained via cobalt-mediated multiple cycloisomerization of polyynes (Eq. 45).<sup>125,126</sup> The helices prepared to date are not configurationally robust enough to be resolved into their enantiomers.

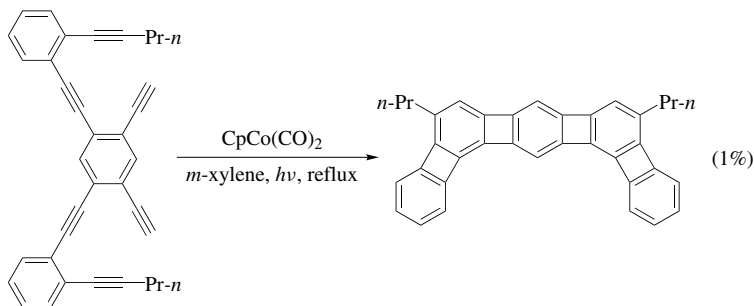


(Eq. 45)

Syn and anti doublebent [5]phenylenes have also been assembled via double cobalt-catalyzed cyclization of hexaynes in which the acetylene units are appropriately positioned (Eq. 46).<sup>127</sup>



(Eq. 46)

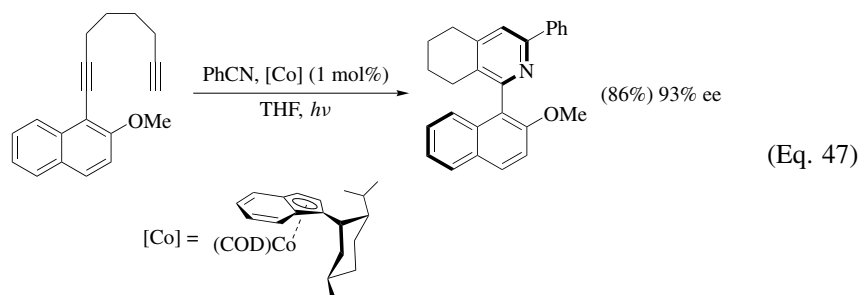


### Enantioselective Reactions

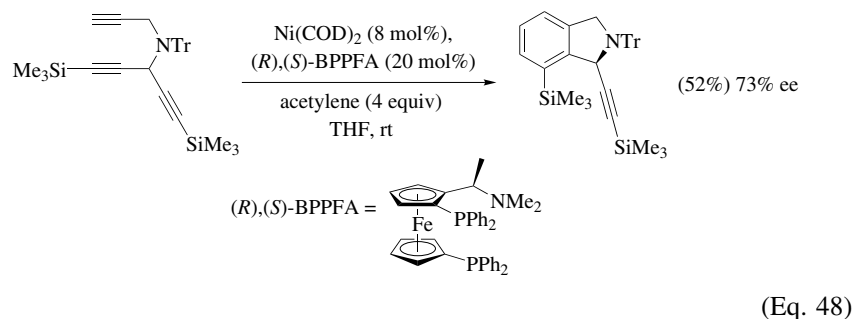
A number of enantioselective cotrimerizations of acetylenic compounds has been reported, such as the bimolecular cobalt(I)-catalyzed asymmetric



cotrimerization of  $\alpha,\omega$ -diynes and nitriles (Eq. 47). Enantiomerically enriched atropoisomers of 2-arylpyridines have been prepared using various chiral cobalt(I) complexes as catalysts.<sup>128</sup>



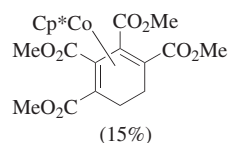
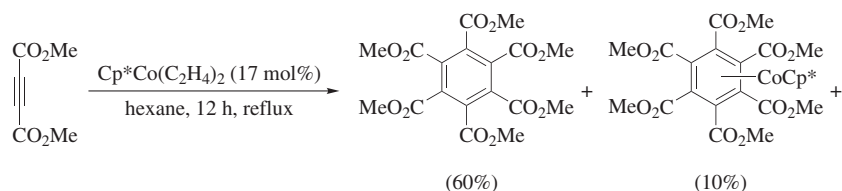
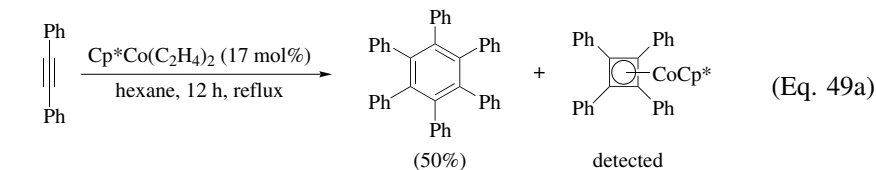
Also, the nickel-catalyzed asymmetric synthesis of isoindolines and isoquinolines has been described (Eq. 48).<sup>129</sup> This cyclization involves a facial stereodifferentiation between two enantiotopic groups and the selective formation of a nickelacyclopentadiene as an intermediate. Several chiral ligands have been tested for this bimolecular process which gives moderate to good enantiomeric excesses.



### Limitations of the Cotrimerization of Acetylenic Compounds

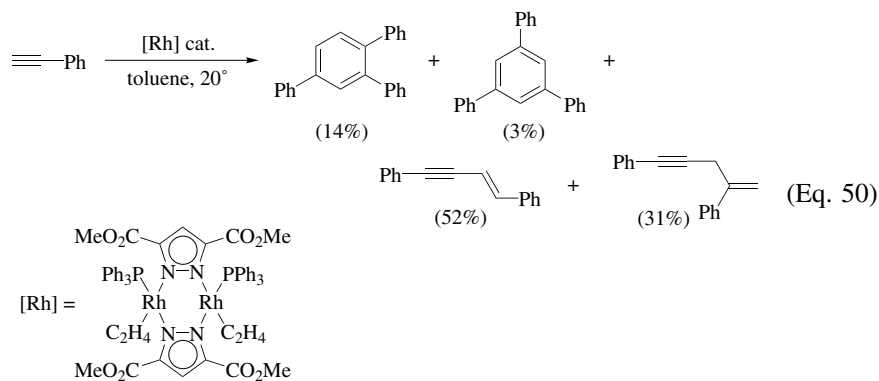
Limitations inherent to some specific catalysts are described in the following section.

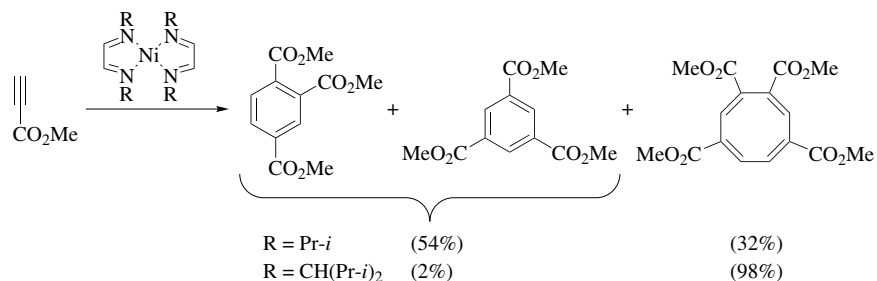
**Catalyst Deactivation.** The formation of stable 18-electron  $\eta^4$ -complexes may impede the turnover of the catalytic process, and may account for low yields in specific cases. In this context,  $\eta^4$ -cyclobutadienyl complexes have already been mentioned (see Mechanism Section). Catalyst deactivation may also arise from stable  $\eta^4$ -cyclohexatriene complex formation as illustrated in Eqs. 49a and 49b. In addition, the ligands associated with certain catalysts may insert into intermediates leading to side-products such as stable  $\eta^4$ -cyclohexadiene complexes (ethene insertion shown in Eq. 49b).<sup>130</sup>



(Eq. 49b)

**Side-products.** In addition to high-order polymers and dimers and trimers, which originate from low regio- and chemoselectivities (see above), some other frequently encountered products are worth mentioning. Some catalysts, especially those based on rhodium, may promote the head-to-head and head-to-tail dimerization of the substrates (Eq. 50).<sup>131</sup> Formation of cyclooctatetraene derivatives is a frequent problem, especially when nickel catalysts are used. These species contaminate the expected benzene products (Eq. 51).<sup>132</sup>





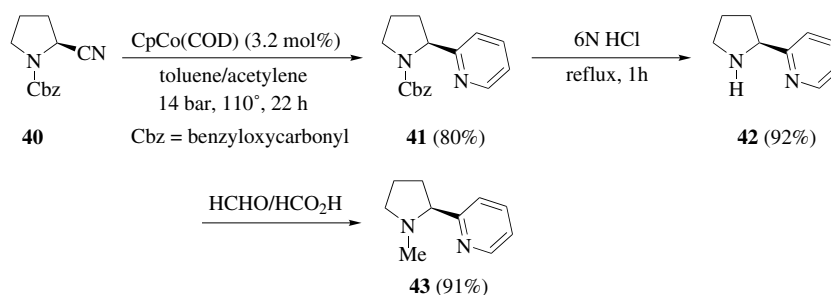
(Eq. 51)

### APPLICATIONS TO THE SYNTHESIS OF NATURAL PRODUCTS

The transition-metal-mediated cotrimerization of acetylenic compounds has been used as a key step in the total synthesis of many natural products and related compounds. Of particular interest, this methodology has allowed the rapid construction of polycyclic frameworks from polyunsaturated substrates, illustrated by the preparation of the ABCD-ring system of steroids and diterpenoids. We have excluded from this section the cobalt-mediated approaches to some steroids derivatives,<sup>133</sup> terpenes,<sup>134,135</sup> sesquiterpenes,<sup>134</sup> and alkaloids such as camptothecin,<sup>136</sup> strychnine,<sup>137</sup> morphine,<sup>138</sup> and lycorane<sup>139</sup> which involve two acetylenic partners and an ethylenic partner.

#### Intermolecular Reactions

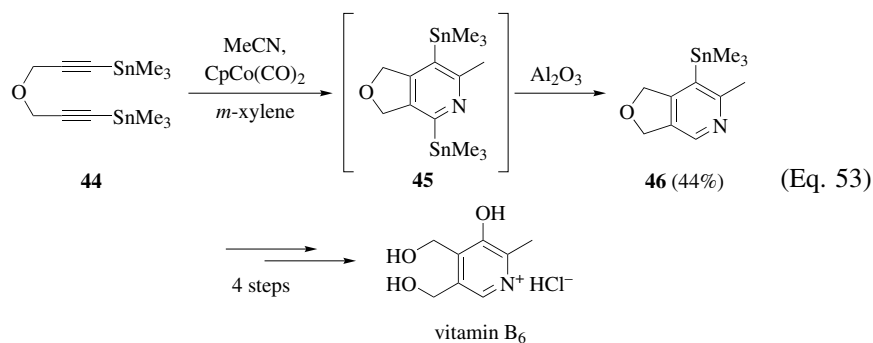
**Derivatives of 2-Nicotinic Acid.** The synthesis of optically active *N*-protected 2-[(2*S*)-2-pyrrolidinyl]pyridine from *L*-proline has been reported.<sup>140</sup> Cobalt(I)-catalyzed cycloaddition of the nitrile **40** with acetylene gives pyridine derivative **41** in good yield (Eq. 52). Deprotection of the *N*-Cbz derivative **41** with 6 N HCl furnishes 2-nornicotine (**42**) in 92% yield. Treatment with formaldehyde and formic acid gives 2-nicotine (**43**) in 91% yield.



(Eq. 52)

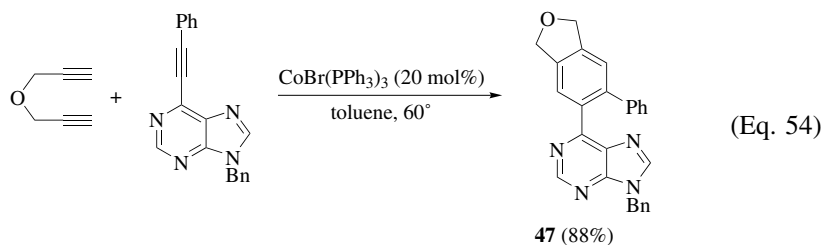
### Bimolecular Reactions

**Monocyclic Compounds: Synthesis of Vitamin B<sub>6</sub>.** The synthetic potential of the cobalt(I)-catalyzed cotrimerization of  $\alpha,\omega$ -bis(trimethylstannyl)diynes was demonstrated by the synthesis of vitamin B<sub>6</sub>.<sup>111</sup> Cyclization of the diyne **44** with acetonitrile gives bis(trimethylstannyl)furo[3,4-*c*]pyridine (**45**) (Eq. 53). The extreme lability of the tin substituent located on the less hindered position of this intermediate provides access to compound **46** via monodestannylation over alumina. Vitamin B<sub>6</sub> is obtained in only four steps from the resulting compound **46**.



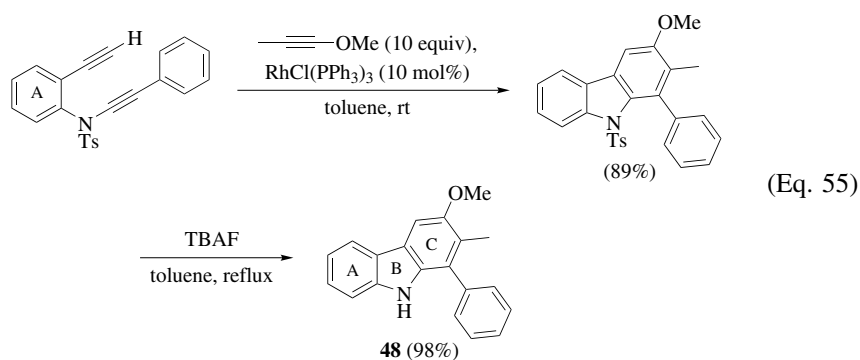
### Biaryls

**Synthesis of 6-Arylpurines.** 6-Arylpurines exhibit antimycobacterial and antibacterial activity, among other biological properties. A novel approach to these compounds based on nickel- or cobalt-catalyzed cotrimerization of 6-alkynylpurines with  $\alpha,\omega$ -diynes has been described.<sup>141</sup> In particular, 2,4,5-trisubstituted 6-phenylpurines such as **47** are obtained in high yields (Eq. 54).

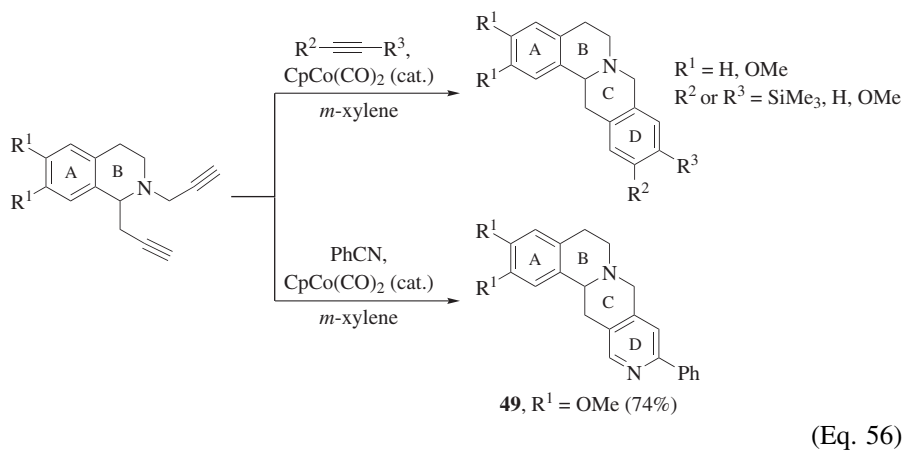


**A→ABC-Ring Formation: Hyellazole.** Hyellazole (**48**) is a marine alkaloid which was prepared in order to illustrate the synthetic potential of the cotrimerization of  $\alpha,\omega$ -diynes with alkynes for the synthesis of substituted carbazoles.<sup>142</sup> The assembly of the carbazole nucleus occurs by an A→ABC ring-formation

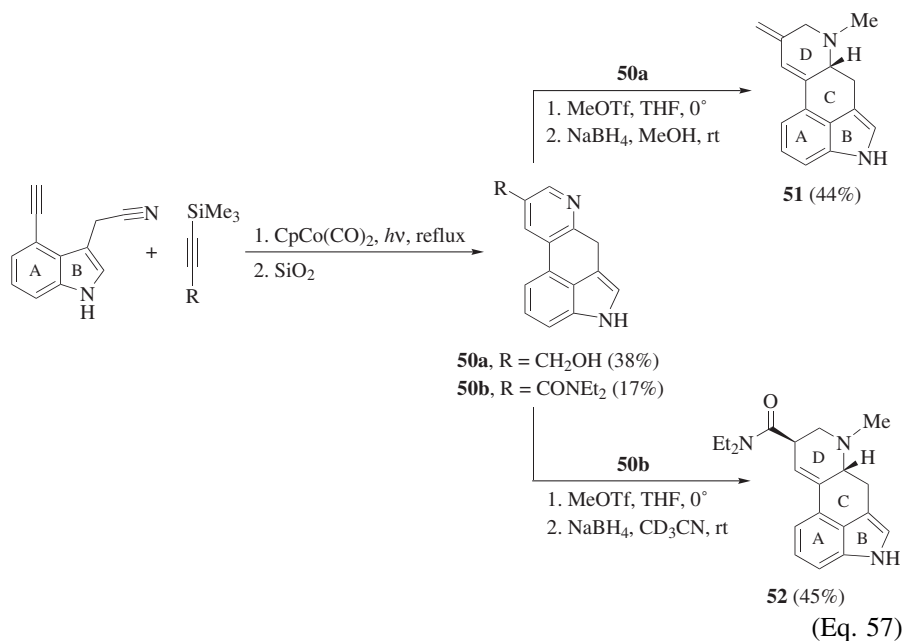
(Eq. 55). It was observed that the use of an electron-rich monoalkyne as cocyclization partner allows a regioselective outcome of the reaction. Isomerically pure hyellazole is obtained through hydrolysis of the tosyl group (Ts) with TBAF in refluxing THF followed by crystallization. The application of the intramolecular version of this reaction to the preparation of the ABCD core of the carbazole nucleus has been reported.<sup>142</sup>



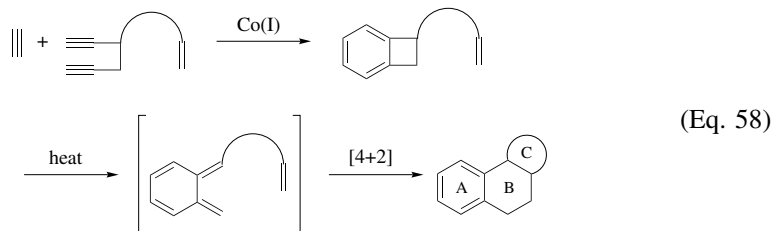
*AB*→*ABCD*-Ring Formation: *Protoberberines*. The protoberberine nucleus has been a continuing target for synthetic chemists because of the varied physiological activities displayed by molecules containing this moiety. The total synthesis of tetrahydroprotoberberines such as **49** has been achieved via cotrimerization of  $\alpha,\omega$ -diynes with monoalkynes and nitriles.<sup>143</sup> The originality of this approach lies in the simultaneous construction of the C and D rings (Eq. 56). The method provides access to varied substitution patterns in the D-ring of the protoberberine structure.



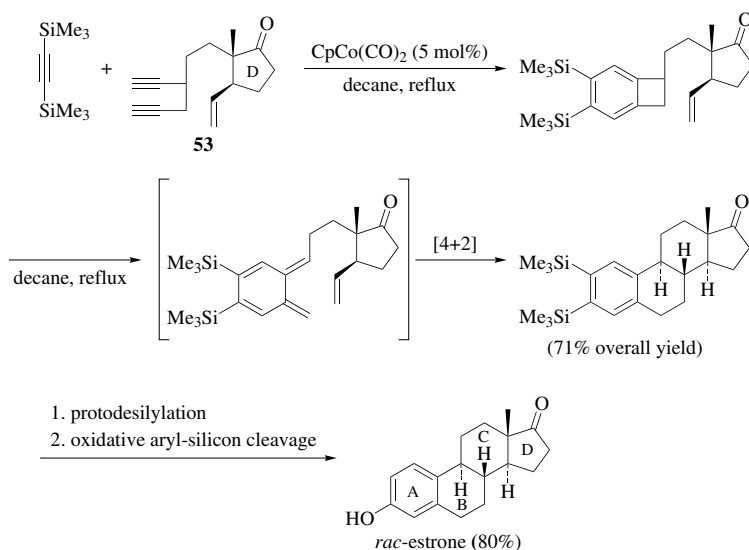
**AB→ABCD-Ring Formation: (±)-Lysergene and (±)-Lysergic Acid Diethylamide (LSD).** Due to their various biological activities and structural features, ergot alkaloids have received great attention from synthetic chemists. The rapid assembly of the C and D rings of the ergolin skeleton using cobalt(I)-mediated cycloaddition of  $\alpha,\omega$ -diynes and monoalkynes has been described.<sup>144</sup> Reaction of 4-ethynyl-3-indoleacetonitrile with silylated alkynes and a slight excess of  $\eta^5$ -cyclopentadienyldicarbonylcobalt [ $\text{CpCo}(\text{CO})_2$ ] followed by protodesilylation over silica affords cycloadducts **50a** and **50b** in moderate yields (38% and 17%, Eq. 57). The corresponding regioisomers are also obtained in 11% ( $\text{R} = \text{CH}_2\text{OH}$ ) and 33% ( $\text{R} = \text{CONEt}_2$ ) yields. Upon treatment with methyl trifluoromethanesulfonate and sodium borohydride, compound **50a** furnishes (±)-lysergene (**51**) in 44% yield, whereas compound **50b** furnishes (±)-LSD (**52**) in 45% yield.



**D→ABCD-Ring Formation: rac-Estrone.** The cobalt(I)-mediated [2+2+2]-cycloaddition of 1,5-diynes with monoalkynes provides access to benzocyclobutene derivatives. Thermal rearrangement of benzocyclobutenes into *o*-quinodimethane, and subsequent Diels-Alder reaction with an alkene moiety results in the formation of tricyclic compounds (Eq. 58). This strategy has been applied to the synthesis of the ABC core of steroid and terpene derivatives.



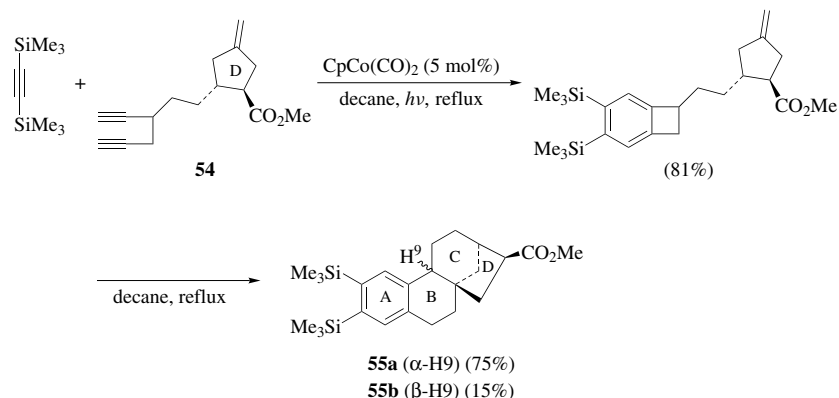
One striking example of this strategy is the total synthesis of estrone which is one of the three naturally occurring estrogens and a primary estrogenic component of several pharmaceutical preparations.<sup>68</sup> Precursor **53** is prepared via consecutive cobalt(I)-mediated diyne–monoalkyne co-oligomerization and a [4+2] cycloaddition reaction (Eq. 59). The in situ generated *o*-quinodimethane undergoes Diels-Alder reaction giving rise to the formation of both B- and C-rings with the correct relative stereochemistry in one step. Racemic estrone is then obtained in two steps in very good yield.



(Eq. 59)

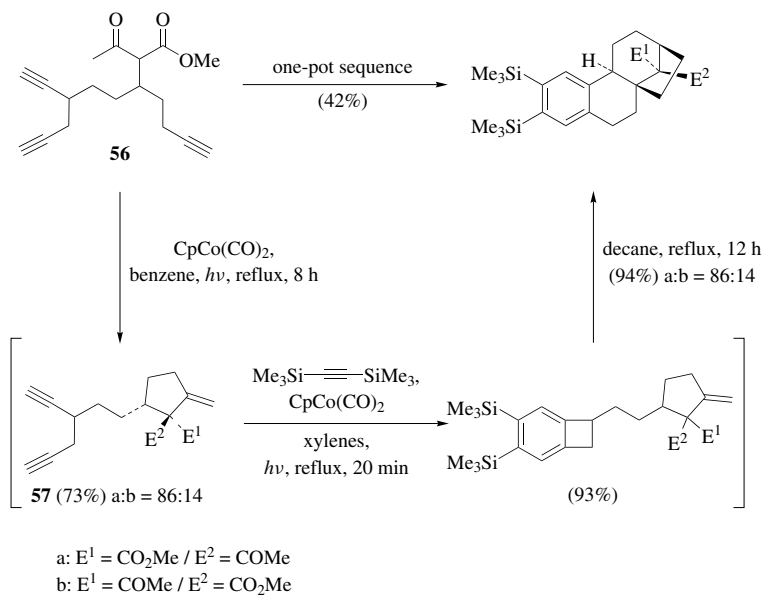
*D*→*ABCD*-Ring Formation: *Phyllocladane* and *Kaurane* Derivatives. A bridged bicyclic C- and D-ring structure is common to several members of the tetracyclic diterpene family of natural products. Such a substituted bicyclo[3.2.1]octane is present in the phyllocladane, kaurane, and gibbane families. There is a wide distribution of natural compounds belonging to these groups and they display important biological activities. In the synthetic approach described in Eq. 60, the cycloaddition reaction occurs between bis(trimethylsilyl)acetylene and an enediene having a methylenecyclopentane unit (**54**).<sup>145</sup> The subsequent [4+2]-cycloaddition reaction affords the basic skeleton

of the tetracyclic diterpenes **55a** ( $\alpha$ -H9) and **55b** ( $\beta$ -H9).



(Eq. 60)

*Direct ABCD-Ring Formation: Phyllocladane and Kaurane Derivatives.* A one-pot access to the ABCD-rings of diterpenes has been described.<sup>146</sup> In the following example (Eq. 61), the  $\varepsilon$ -acetylenic- $\beta$ -ketoester **56** furnishes, through a diastereoselective sequence of [ene type], [2+2+2], and [4+2] cycloadditions, the phyllocladane framework in 42% yield. It is noteworthy that methylene-cyclopentane **57** is generated in situ via a cobalt-catalyzed Conia-ene type reaction.<sup>147</sup> By a subtle change in the position of the  $\beta$ -ketoester substituent relative to the tether, the sequence could be reversed to give the basic skeleton of the kaurane family.<sup>148</sup>



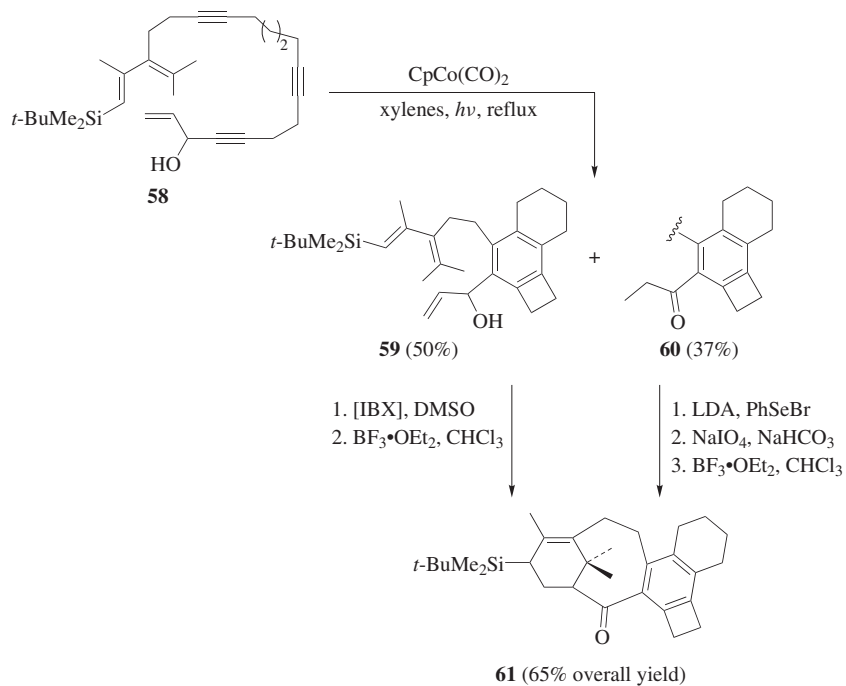
(Eq. 61)



### Intramolecular Reactions

In addition to the aforementioned A→ABCD carbazole ring formation, some relevant examples of intramolecular cotrimerization for the synthesis of natural products are described below.

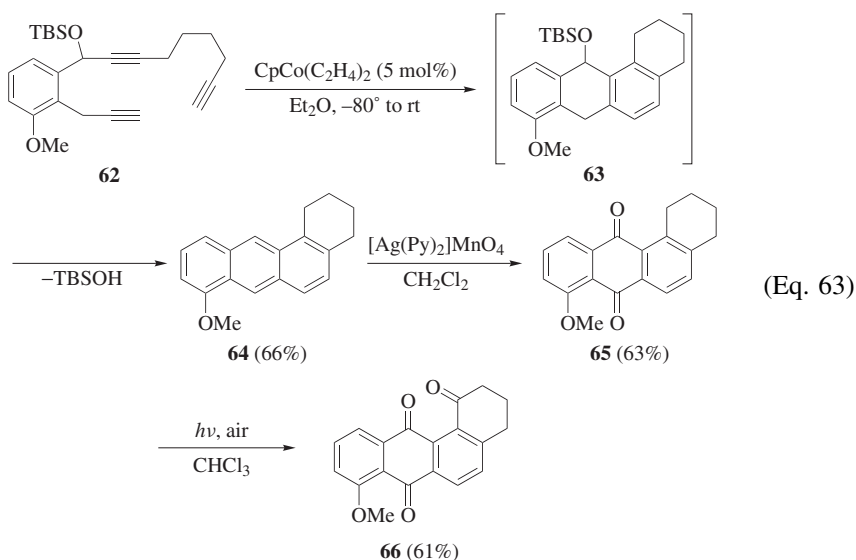
**Taxoids.** Taxane diterpenoids exhibit unusual structural features and considerable therapeutic potential. A short sequence of two consecutive cyclizations, a cobalt(I)-mediated [2+2+2]-cyclootrimerization followed by a Diels-Alder reaction, has been proposed for the formation of the ABC core of the taxoids from the acyclic polyunsaturated precursor **58** (Eq. 62).<sup>149</sup> When compound **58** is exposed to the cobalt mediator, a mixture of benzocyclobutenes **59** and **60** is obtained in 50% and 37% yields, respectively. Compound **60** arises from a (1,3)-migration of the double bond leading to an enol which subsequently undergoes tautomerization to give the ketone. However, the dienophilic alkene is easily introduced via selenation-oxidation. Oxidation of compound **59** is carried out using *o*-iodoxybenzoic acid (IBX). The [4+2] cycloaddition reaction of both **59** and **60** leading to the formation of the pentacyclic structure **61** is promoted by  $\text{BF}_3 \cdot \text{OEt}_2$ .



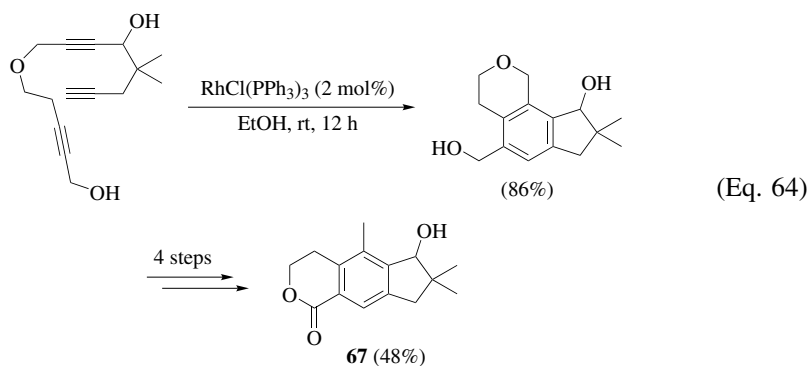
(Eq. 62)

**Benz[*a*]anthraquinone Core of Angucyclinone Antibiotics.** The angucyclines are a large class of antibiotics that display a broad range of biological properties. They feature a unique benz[*a*]anthraquinone structure. A general

method for the synthesis of benz[*a*]anthraquinone has been reported.<sup>150</sup> The key step is an intramolecular cobalt(I)-catalyzed [2+2+2]-cycloaddition of the triyne **62**, which loses the silanol moiety with concomitant aromatization of the intermediate anthracene **63**. Mild oxidation of the resulting compound **64** gives anthraquinone **65** in 63% yield. This compound is then exposed to visible light and air to afford substituted benz[*a*]anthraquinone **66**, the structure of which represents the core of several angucyclinone antibiotics (Eq. 63).



**Calomelanolactone.** Calomelanolactone (**67**) belongs to the illudalane class of sesquiterpenes. A short regioselective synthesis of this natural product, which includes an intramolecular cotrimerization as a key step, has been described (Eq. 64).<sup>151</sup> The tricyclic precursor to calomelanolactone is obtained from a tethered triyne in good yield using Wilkinson's catalyst.

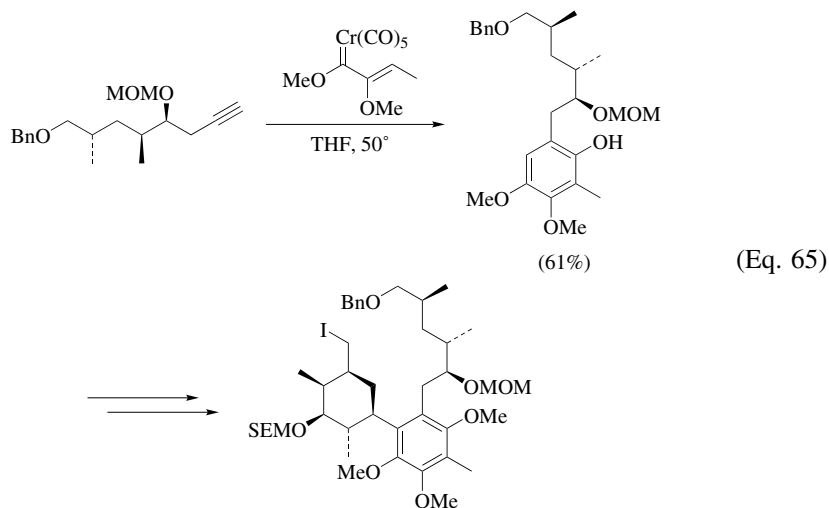


## COMPARISON WITH OTHER METHODS

Most methods for preparing aromatic compounds involve modifications of readily available aromatic precursors.<sup>152–157</sup> However, it is often difficult to control the regioselectivity using classical aromatic substitution reactions. The cycloaddition of unsaturated acyclic compounds thus provides a useful alternative for the construction of polysubstituted benzene derivatives. In that respect, several successful syntheses of benzene derivatives were performed through intramolecular thermal<sup>158–161</sup> or Lewis acid mediated<sup>158,159</sup> [4+2]-benzannulations of enediynes. Bimolecular Lewis acid mediated [4+2]-benzannulations between ortho-alkynylbenzaldehydes and alkynes have also been reported.<sup>162–164</sup> Throughout this chapter we have tried to demonstrate the synthetic potential of the cyclotrimerization of acetylenic compounds. In this section, we will now focus on comparable strategies, namely non-Lewis acid cycloaddition reactions under transition metal mediation.

## Dötz Benzannulation

In this methodology, Fisher-type alkenylchromiumcarbenes undergo addition to terminal alkynes followed by carbonyl insertion to give substituted phenols.<sup>165–167</sup> Several natural products have been prepared that way,<sup>168–170</sup> including a major portion of the ansa macrocycle (–)-kendomycin, a *Streptomyces* metabolite (Eq. 65).<sup>171</sup>

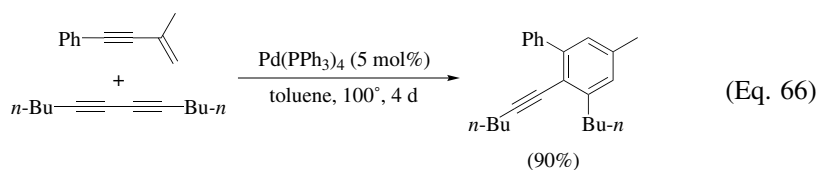


Although highly substituted benzene derivatives can be obtained, this reaction has a number of limitations, particularly with regard to the range of the alkyne substrates that participate in the cyclization process.

## Palladium-Catalyzed [4+2]-Benzannulations

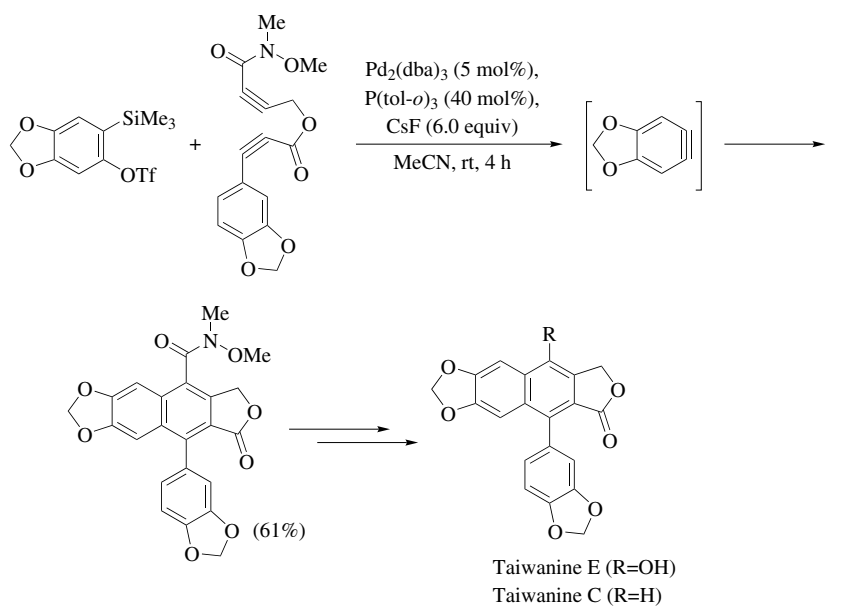
The palladium-catalyzed homodimerization of terminal alkynes and subsequent [4+2]-benzannulation has been discussed in the Scope and Limitations

section as a method for forming benzene rings from three acetylenic partners (see Eq. 19).<sup>93</sup> Since the first step of this reaction is actually an in situ formation of an enyne, this method is also available for [4+2] benzannulations between enynes and alkynes (Eq. 66).<sup>172</sup> This strategy is efficient for forming polysubstituted benzenes regioselectively, even in intermolecular reactions. In that respect, it has advantages over the alkyne cyclotrimerization reaction.



### Palladium-Catalyzed Cocyclization of Benzynes with Alkynes

Transient benzyne species have been used as highly reactive alkynes for forming fused aromatic compounds.<sup>43</sup> Among recent examples are the syntheses of biaryl compounds such as aryl naphthalene lignans for the preparation of biologically active Taiwanins C and E (Eq. 67).<sup>173</sup>

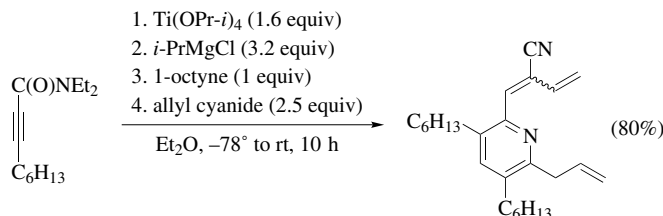


In essence, this strategy complements perfectly the cotrimerization of acetylenic compounds described herein and deserves its own chapter.

## EXPERIMENTAL CONDITIONS

Although various experimental conditions have been used to perform the title reaction, commercially available  $\text{CpCo}(\text{CO})_2$  remains the most common catalyst (see Tabular Survey). It is sold at the technical purity level as a deep red liquid. It decomposes when exposed to air, giving a green residue, but is stable in deoxygenated water. Most cyclotrimerization reactions performed with this catalyst require high temperatures such as those of refluxing toluene or xylenes, and irradiation of the refluxing solution may be necessary. The irradiation conditions vary and include the visible spectrum of a 300W lamp. Irradiation is believed to favor the dissociation of a strongly coordinated carbon monoxide from the complex, leaving a vacant site for the alkyne. It is worthy of note that  $\eta^5$ -cyclopentadienylbis(ethene)cobalt [ $\text{CpCo}(\text{C}_2\text{H}_4)_2$ ] is sometimes a much more active source of  $\text{CpCo}$  than  $\text{CpCo}(\text{CO})_2$ . It is prepared in one step from commercially available cobaltocene, potassium and ethene, on a 25-g scale in 85% yield.<sup>174</sup> An improvement of the purification step has been described.<sup>175</sup>

## EXPERIMENTAL PROCEDURES

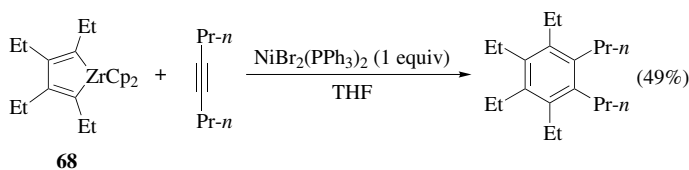


**(E)- and (Z)-6-Allyl-2-(2-cyano-1,3-butadienyl)-3,5-dihexylpyridine (Regioselective Stepwise Construction of a Tetrasubstituted Pyridine using Titanium).**<sup>97</sup> To a stirred solution of  $N,N$ -diethyl-2-nonynamide (40 mg, 0.191 mmol) and  $\text{Ti}(\text{OPr-}i)_4$  (0.071 mL, 0.239 mmol) in 2 mL of  $\text{Et}_2\text{O}$  was added  $i\text{-PrMgCl}$  (1.44 M in  $\text{Et}_2\text{O}$ , 0.345 mL, 0.497 mmol) at  $-78^\circ$  under argon giving a clear yellow solution. The solution was warmed to  $-50^\circ$  over 30 minutes, during which period the color of the solution turned red. After stirring at  $-50^\circ$  for an additional 5 hours, 1-octyne (0.023 mL, 0.153 mmol) was added to the reaction mixture at  $-50^\circ$  and the solution was stirred for another 3 hours. Allylcyanide (0.031 mL, 0.382 mmol) was then added and the reaction mixture was subsequently warmed to  $-30^\circ$ . After being stirred for 5 hours at that temperature, the reaction was quenched by the addition of  $\text{H}_2\text{O}$  (0.2 mL) and the reaction mixture was filtered through Celite. The organic phase was concentrated in vacuo and the crude product was chromatographed on silica gel (hexane-ether) to

afford (*E*)-6-allyl-2-(2-cyano-1,3-butadienyl)-3,5-dihexylpyridine (24 mg, 43%) and (*Z*)-6-allyl-2-(2-cyano-1,3-butadienyl)-3,5-dihexylpyridine (20 mg, 37%) as colorless oils.

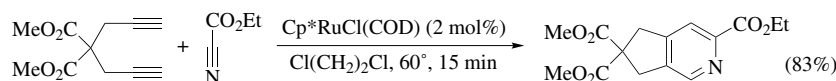
**E isomer:** IR (neat) 3081, 2955, 2928, 2857, 2221 (C≡N), 1637, 1617, 1534, 1466, 1458, 1437, 1412, 1378, 1251, 1196, 1115, 993, 917, 842, 725 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.26–1.40 (m, 12H), 1.49–1.59 (m, 4H), 2.59 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 6.0 Hz, 2H), 3.59 (d, *J* = 6.6 Hz, 2H), 5.08 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 10.5 Hz, 1H), 5.54 (d, *J* = 10.5 Hz, 1H), 5.88 (d, *J* = 17.4 Hz, 1H), 6.09 (ddt, *J* = 10.5, 16.8, 6.6 Hz, 1H), 7.21 (s, 1H), 7.24 (s, 1H), 8.01 (dd, *J* = 10.5, 17.4 Hz, 1H) [Irradiation of the proton at δ 3.59 ppm (PyCH<sub>2</sub>CH) showed 5% nOe enhancement to the peak at δ 2.63 ppm (PyCH<sub>2</sub>), thus confirming the assigned regiochemistry.]; <sup>13</sup>C NMR δ 13.9, 14.0, 22.5, 22.5, 29.0, 29.1, 30.1, 31.1, 31.5, 31.6, 31.9, 32.1, 38.2, 116.1, 116.7, 118.5, 121.9, 130.7, 136.0, 136.6, 136.8, 136.8, 138.5, 148.2, 155.7. Anal. Calcd for C<sub>25</sub>H<sub>36</sub>N<sub>2</sub>: C, 82.36; H, 9.95. Found: C, 82.56; H, 9.81.

**Z isomer:** IR (neat) 3076, 2955, 2928, 2856, 2218 (C≡N), 1638, 1604, 1540, 1466, 1457, 1437, 1405, 1378, 1298, 1258, 1217, 1115, 1082, 976, 913, 726 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.27–1.40 (m, 12H), 1.49–1.59 (m, 4H), 2.62 (t, *J* = 8.1 Hz, 4H), 3.66 (d, *J* = 6.6 Hz, 2H), 5.11 (d, *J* = 10.2 Hz, 1H), 5.13 (d, *J* = 16.8 Hz, 1H), 5.49 (d, *J* = 10.2 Hz, 1H), 5.93 (d, *J* = 17.1 Hz, 1H), 6.43 (ddt, *J* = 10.2, 16.8, 6.6 Hz, 1H), 6.54 (dd, *J* = 10.2, 17.1 Hz, 1H), 7.20 (s, 1H), 7.23 (s, 1H) [Irradiation of proton at δ 6.54 ppm (C(CN)CH=CH<sub>2</sub>) showed 4% nOe enhancement to the peak at δ 7.20 ppm (PyCH=C), thus confirming the *Z*-configuration]; <sup>13</sup>C NMR δ 13.9, 13.9, 22.4, 22.5, 28.9, 29.1, 30.1, 31.2, 31.5, 31.6, 31.7, 31.9, 39.2, 114.5, 115.9, 116.1, 119.6, 134.3, 135.5, 136.3, 137.5, 138.3, 138.9, 146.4, 156.0.



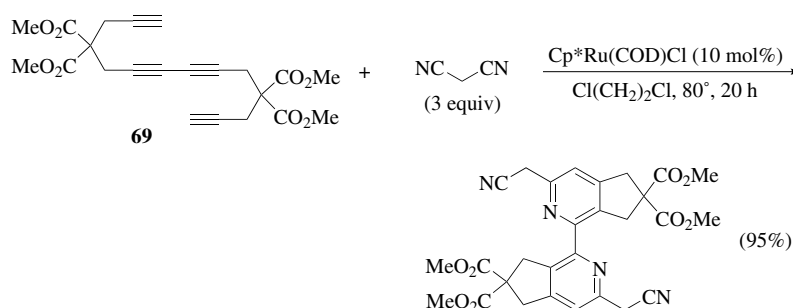
**1,2,3,4-Tetraethyl-5,6-dipropylbenzene (Regioselective Stepwise Construction of an Hexasubstituted Benzene using Zirconium).**<sup>96</sup> To a solution of zirconacyclopentadiene **68** (1.0 mmol) in 20 mL of THF were added the alkyne (1.5 mmol) and NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.74 g, 1.0 mmol) at room temperature. The mixture was stirred for 1 hour, quenched with 3 N HCl, and extracted with hexane. The combined organic extracts were dried (MgSO<sub>4</sub>) and concentrated in vacuo. Column chromatography on silica gel (hexane) afforded the title product as a white solid, GC yield 70%, isolated yield 49%: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.05

(t,  $J = 7.2$  Hz, 6H), 1.18 (t,  $J = 7.3$  Hz, 12H), 1.52–1.58 (m, 4H), 2.49–2.65 (m, 4H), 2.61 (q,  $J = 7.1$  Hz, 4H), 2.63 (q,  $J = 7.0$  Hz, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.2, 15.7, 22.2, 22.3, 24.9, 32.1, 136.8, 137.7, 137.9. Anal. Calcd for  $\text{C}_{20}\text{H}_{34}$ : C, 87.52; H, 12.48. Found: C, 87.38; H, 12.55.



**5,7-Dihydro-6H-cyclopenta[*c*]pyridine-3,6,6-tricarboxylic Acid 3-Ethyl 6,6-Dimethyl Ester (Construction of a 3,4-Fused Pyridine using Ruthenium).**<sup>102</sup>

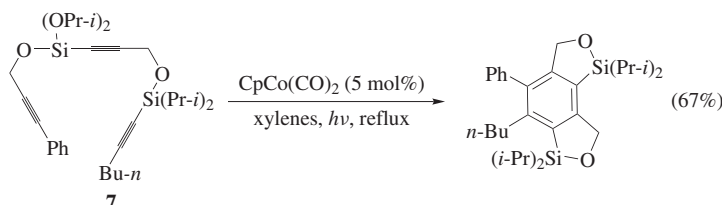
To a solution of ethyl cyanoformate (74 mg, 0.75 mmol) and  $\text{Cp}^*\text{RuCl}(\text{COD})$  (3.8 mg, 0.01 mmol) in dry degassed 1,2-dichloroethane (2 mL) was added a solution of dimethyl 2,2-di(prop-2-ynyl)propanedioate (104 mg, 0.5 mmol) in dry degassed 1,2-dichloroethane (3 mL) over 15 minutes under an argon atmosphere at room temperature. The reaction mixture was stirred at  $60^\circ$  for 0.5 hour. The solvent was evaporated and the crude product was purified by silica gel flash column chromatography (hexane-AcOEt = 1 : 2) to give the title product (128 mg, 83%) as an orange solid; mp  $69.5\text{--}70.0^\circ$ : IR  $1735, 1285\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.40 (t,  $J = 7.2$  Hz, 3H), 3.64 (s, 2H), 3.66 (s, 2H), 3.74 (s, 6H), 4.44 (q,  $J = 7.2$  Hz, 2H), 7.98 (s, 1H), 8.56 (s, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  14.4, 38.4, 40.2, 53.3, 60.0, 61.9, 121.1, 139.7, 145.4, 146.9, 150.6, 165.0, 170.9; MS-FAB  $m/z$  (relative intensity): 308 (100) [ $\text{MH}^+$ ], 234 (37) [ $\text{M}^+ - \text{CO}_2\text{Et}$ ]. Anal. Calcd for  $\text{C}_{15}\text{H}_{17}\text{NO}_6$ : C, 58.63; H, 5.58; N, 4.56. Found: C, 58.88; H, 5.67; N, 4.40.



**3,3'-Bis(cyanomethyl)-5,5',7,7'-tetrahydro-[1,1'-bi-6H-cyclopenta[*c*]pyridine]-6,6,6',6'-tetracarboxylic Acid Tetramethyl Ester (Construction of a 2,2'-Bipyridine using Ruthenium).**<sup>102</sup>

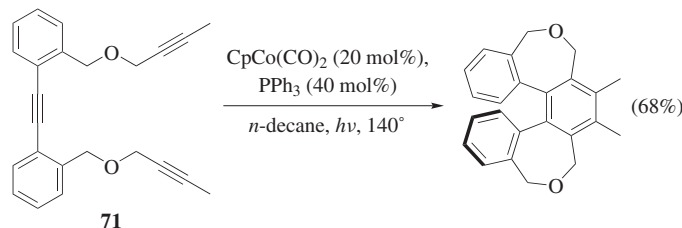
To a solution of malononitrile (50 mg, 0.75 mmol) and  $\text{Cp}^*\text{Ru}(\text{COD})\text{Cl}$  (9.5 mg, 0.025 mmol) in dry degassed 1,2-dichloroethane (2 mL) was added a solution of tetrayne **69** (104 mg, 0.5 mmol) in dry

degassed 1,2-dichloroethane (3 mL) under N<sub>2</sub> atmosphere at room temperature. The reaction mixture was stirred at 80° for 20 hours. The solvent was then evaporated and the crude product was purified by silica-gel flash column chromatography (hexane:AcOEt = 1 : 2) to give the title compound (138 mg, 95%) as white solid; mp 188-189°: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.64 (s, 4H), 3.76 (s, 12H), 3.96 (s, 4H), 7.28 (s, 2H); <sup>13</sup>C NMR (75 MHz) δ 26.5, 40.2, 40.3, 53.2, 59.7, 116.9, 117.7, 135.7, 147.8, 151.8, 153.3, 171.5; MS-FAB *m/z* (relative intensity): 547 (100) [MH<sup>+</sup>], 487 (13), 307 (36), 289 (26). Anal. Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>4</sub>O<sub>8</sub>: C, 61.53; H, 4.80; N, 10.25. Found: C, 61.75; H, 4.93; N, 10.12.



**5-Butyl-1,3,6,8-tetrahydro-1,1,6,6-tetrakis(1-methylethyl)-4-phenylbenzo [1,2-*c*:3,4-*c'*]bis[1,2]oxasilole (Cobalt-Catalyzed Formal Intermolecular Regioselective Construction of a Polysubstituted Benzene using Disposable Silicon Tethers).**<sup>99</sup>

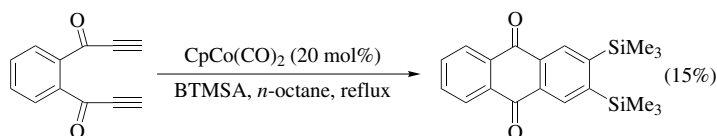
The reaction was carried out under argon in flame-dried glassware. Cyclopentadienyldicarbonylcobalt(I) [CpCo(CO)<sub>2</sub>] (4 μL, 0.05 equiv) was added to a boiling solution of triene **70** (300 mg, 0.6 mmol, 1 equiv) in dry xylenes (30 mL, *c* = 0.05 M) degassed by three freeze-pump-thaw cycles, and was irradiated (light from projector lamp; ELW, 300W, 50% of its power). The reaction was monitored by TLC and, after completion, the reaction mixture was concentrated under vacuum. The crude oil was purified by flash chromatography (petroleum ether:Et<sub>2</sub>O, 9 : 1) to give the title product (200 mg, 67% yield): IR (neat) 2937, 2862, 1461, 1062, 791, 637 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.57 (t, *J* = 14.6 Hz, 3H), 0.95 (m, 28H), 1.15 (m, 4H), 2.38 (m, 2H), 4.61 (s, 2H), 5.04 (s, 2H), 7.13 (m, 2H), 7.28 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 12.2, 12.5, 12.8, 16.0, 16.2, 16.3, 16.4, 22.0, 32.3, 35.4, 71.4, 72.9, 121.4, 126.0, 127.3, 128.2, 129.5, 133.7, 138.1, 145.1, 151.4, 153.1; HRMS (*m/z*): [M + H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>46</sub>O<sub>2</sub>Si<sub>2</sub>, 495.3093; found, 495.3114. HRMS (*m/z*): [M - H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>46</sub>O<sub>2</sub>Si<sub>2</sub>, 493.2966; found, 493.2958.





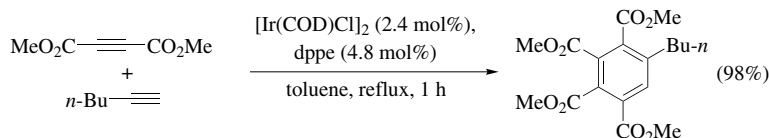
**4,5-Dimethyl-1,3,6,8-tetrahydrobenzo[*c*]benzo[5',6']oxepino[3',4':5,6]benzo[*e*]oxepin (Synthesis of a Molecule with Helical Chirality using Cobalt).**<sup>118</sup>

A mixture of triyne **71** (2.0 g, 5.84 mmol) and *n*-decane (100 mL) under argon was stirred and heated at 100° by means of irradiation with two 250W halogen lamps to dissolve the educt. A hot solution of PPh<sub>3</sub> (613 mg, 2.34 mmol, 40 mol%) in *n*-decane (6 mL) was added, and the mixture was further irradiated to achieve 140°. CpCo(CO)<sub>2</sub> (210 mg, ca. 160 μL, 1.17 mmol, 20 mol%) was added via syringe, and the resulting orange-brown solution was irradiated under stirring while the temperature was maintained at 140° (measured inside the mixture) for 4 hours. A brown-greenish solid gradually deposited on the flask surface. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and loaded onto a silica gel column. The product was eluted with a mixture of petroleum ether-ether-acetone (90:10:0 to 80:10:10). Solvents were evaporated in vacuo to yield the title compound (1.36 g, 68%) as a solid mp, 199–201°: IR (CHCl<sub>3</sub>) 3067, 1603, 1581, 1569, 1559, 1483, 1462, 1372, 1292, 1158, 1081, 1054, 1040, 1023, 948, 551 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.52 (s, 6H), 3.82 (d, *J* = 12.2 Hz, 2H), 4.95 (d, *J* = 12.2 Hz, 2H), 4.42 (d, *J* = 11.0 Hz, 2H), 4.64 (d, *J* = 11.0 Hz, 2H), 6.51 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.98 (dt, *J* = 7.6, 7.6, 1.4 Hz, 2H), 7.25 (dt, *J* = 7.6, 7.6, 1.2 Hz, 2H), 7.41 (dd, *J* = 7.6, 1.4 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 16.7 (q), 62.9 (t), 67.7 (t), 127.3 (d), 27.6 (d), 129.0 (d), 130.8 (d), 133.9 (s), 135.2 (s), 135.6 (s), 136.1 (s), 140.3 (s); EIMS *m/z* (relative intensity): M<sup>+</sup> 342 (100), 327 (8), 309 (19), 295 (12), 281 (27), 269 (12), 253 (20), 239 (10), 146 (10), 126 (9), 66 (10). HRMS (*m/z*): calcd for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>, 342.1619; found, 342.1578.



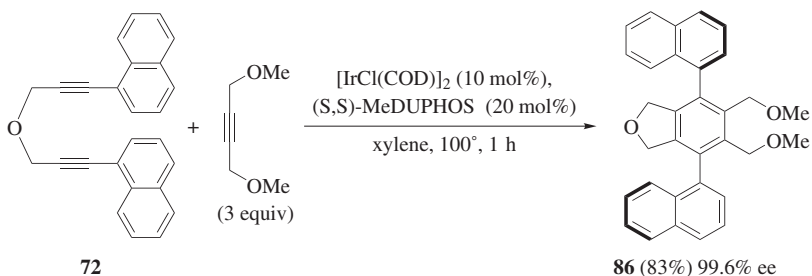
**2,3-Bis(Trimethylsilyl)anthraquinone (Cobalt-Catalyzed Anthraquinone Synthesis).**<sup>104</sup>

1,2-Bis(prop-1-ynyl)benzene (350 mg, 2.3 mmol) was dissolved in diglyme (8 mL) and added over a period of 36 hours (with a syringe pump) to a refluxing solution of BTMSA (5 mL) and CpCo(CO)<sub>2</sub> (60 μL) in *n*-octane (70 mL), under a dry N<sub>2</sub> atmosphere. Removal of the solvent and unreacted BTMSA by vacuum transfer followed by column chromatography on silica gel (100 g) (pentane:ether = 80:20) gave a yellow oil which solidified on standing. Recrystallization of the crude solid from methanol gave orange crystals of the title anthraquinone (120 mg, 15%), mp 69–71.5°: IR (CCl<sub>4</sub>) 2900, 1670, 1540, 1320, 1290, 1250, 1005, 980, 952, 932 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.50 (s, 2H), 1.70 (m, 2H), 2.23 (m, 2H), 9.51 (s, 18H); EIMS *m/z* (relative intensity): M<sup>+</sup> 352 (14), 337 (17), 73 (67), 57 (79), 55 (77), 43 (100), 41 (67).



**Tetramethyl 5-(*n*-Butyl)-1,2,3,4-benzenetetracarboxylate (Chemoselective Construction of a Pentasubstituted Benzene using Iridium).<sup>91</sup>**

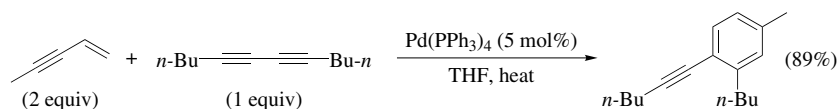
All reagents and the solvents were dried and purified before use by the usual procedures. To a toluene solution (5 mL) of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (13.4 mg, 0.02 mmol) and 1,2-*bis*-diphenylphosphinoethane (15.9 mg, 0.04 mmol) was added 1-hexyne (0.099 g, 1.2 mmol) via syringe. Dimethyl acetylenedicarboxylate (0.284 g, 2 mmol) was then added to the solution via syringe. The reaction mixture was stirred under reflux for 1 hour. The progress of the reaction was monitored by TLC. After the dimethyl acetylenedicarboxylate was consumed, the toluene was evaporated in vacuo. Column chromatography (*n*-hexane:AcOEt = 80:20) of the residue gave the title product as a colorless oil (0.359 g, 98%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J = 7.4$  Hz, 3H), 1.36 (sextet,  $J = 7.4$  Hz, 2H), 1.59 (quintet,  $J = 7.4$  Hz, 2H), 2.69–2.73 (m, 2H), 3.86 (s, 3H), 3.90 (s, 3H), 3.91 (s, 3H), 3.91 (s, 3H), 7.95 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 22.2, 32.9, 33.0, 52.5, 52.7, 52.9, 129.7, 129.9, 132.8, 133.6, 136.6, 142.7, 165.0, 165.7, 167.3, 167.4.



**1,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(methoxymethyl)isobenzofuran (Enantio- and Diastereoselective Synthesis of an Axially Chiral Teraryl Compound using Iridium).<sup>176</sup>**

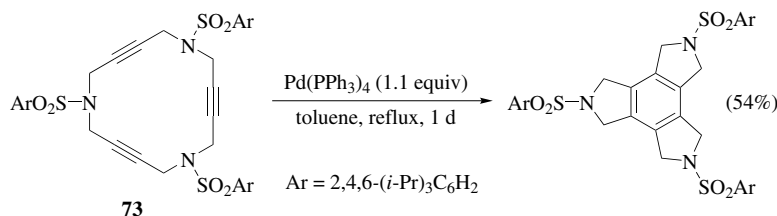
1,2-Bis((*2S,5S*)-2,5-dimethylphospholano)benzene [*(S,S)*-MeDUPHOS] (6.4 mg, 0.021 mmol) and  $[\text{IrCl}(\text{COD})]_2$  (7.1 mg, 0.0105 mmol) were stirred in degassed xylene (1.0 mL) at room temperature resulting in a reddish-yellow solution. After the addition of a xylene solution (1.5 mL) of 1,4-dimethoxy-2-butene (36.0 mg, 0.315 mmol) and a xylene solution (1.5 mL) of diyne **72** (36.5 mg, 0.105 mmol), the resulting mixture was further stirred

under reflux for 1 hour. The solvent was removed under reduced pressure, and purification of the crude products by thin layer chromatography (toluene:AcOEt = 15 : 1) gave pure **86** (40.3 mg, 0.086 mmol, 83% yield). The ratio of *dl/meso* isomers was determined by NMR spectroscopy, and the enantiomeric excess was determined by HPLC analysis using a chiral column. The product was a white solid, mp 161–162°:  $[\alpha]_D^{26} + 43.37^\circ$  (c 1.95, CHCl<sub>3</sub>); IR (CHCl<sub>3</sub>) 2820, 1096, 756 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  3.06 (s, 6H), 4.02 (d, *J* = 9.9 Hz, 2H), 4.46 (d, *J* = 9.9 Hz, 2H), 4.63 (d, *J* = 11.3 Hz, 2H), 4.77 (d, *J* = 11.3 Hz, 2H), 7.40–7.39 (m, 14H); <sup>13</sup>C NMR  $\delta$  58.4, 69.0, 74.1, 125.2, 125.8, 125.9, 126.3, 127.0, 128.0, 128.2, 131.3, 133.4, 134.9, 135.8, 136.2, 139.0. Anal. Calcd for C<sub>32</sub>H<sub>28</sub>O<sub>3</sub>: C, 83.45; H, 6.13. Found: C, 83.29; H, 6.15.



**2-Butyl-1-(1-hexynyl)-4-methylbenzene (Palladium-Catalyzed [4+2] Cross-Benzannulation Reaction of Enynes with Diynes and Triynes).**<sup>172</sup>

To a THF (2 mL) solution of tetrakis(triphenylphosphine)palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>] (28.9 mg, 0.025 mmol) under an Ar atmosphere were added pent-1-en-3-yne (66.1 mg, 1.0 mmol) and dodeca-5,7-diyne (81.1 mg, 0.5 mmol), and the resulting mixture was stirred overnight at 65°. GLC analysis revealed completion of the reaction. The reaction mixture was filtered through a short florisil column, and the product was purified by silica gel column chromatography (hexane). The title product was obtained in 89% yield (101.6 mg): IR (neat) 2957, 2930, 2860, 1611, 1497, 1456, 1379, 1329, 1105, 818 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.938 (t, *J* = 7.3 Hz, 3H), 0.944 (t, *J* = 7.0 Hz, 3H), 1.65–1.32 (m, 8H), 2.30 (s, 3H), 2.43 (t, *J* = 6.7 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.96 (s, 1H), 7.25 (d, *J* = 7.7 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  13.6, 14.0, 19.2, 21.4, 22.0, 22.7, 31.0, 32.9, 34.4, 79.3, 92.8, 120.3, 126.2, 129.4, 131.9, 137.3, 144.6. HRMS (*m/z*): calcd for C<sub>17</sub>H<sub>24</sub>, 228.1877; found, 228.1883.



**2,3,4,5,6,7,8,9-Octahydro-2,5,8-tris[[2,4,6-tris(1-methylethyl)phenyl]sulfonyl]-1*H*-benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tripyrrole (Palladium-Mediated Cyclo-trimerization of a Macrocycle).**<sup>121</sup> A degassed solution of macrocycle **73** (0.05 g, 0.05 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.067 g, 0.06 mmol) in anhydrous toluene (20 mL) was refluxed for 24 hours (TLC monitoring). The solvent was then evaporated and the residue was purified by column chromatography on silica gel with hexane:CH<sub>2</sub>Cl<sub>2</sub> (9:1 to 20:1) to afford the title compound (0.043 g, 54%) as a colorless solid, mp 235–237° dec.; IR (neat) 2957, 2866, 1301, 1151, 1046 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.20–1.29 (m, 54H), 2.92 (sept, *J* = 6.8 Hz, 3H), 4.21 (sept, *J* = 6.6 Hz, 6H), 4.48 (s, 12H), 7.19 (s, 6H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 24.2, 25.5, 30.1, 34.8, 51.6, 124.7, 131.4, 131.7, 152.1, 154.2; ESI-MS (*m/z*) 1017 [M + NH<sub>4</sub>]<sup>+</sup>, 1022 [M + Na]<sup>+</sup>. Anal. Calcd for C<sub>57</sub>H<sub>81</sub>N<sub>3</sub>O<sub>6</sub>S<sub>3</sub>: C, 68.43; H, 8.16; N, 4.20. Found: C, 68.18; H, 8.51; N, 4.06.

#### TABULAR SURVEY

The tables are organized according to increasing carbon count including protecting groups and other abbreviated structures. The tables cover examples of the cotrimerization of acetylenic compounds from 1980 to the middle of 2004. The tables themselves are organized according to the nature and the substitution of the considered acetylenic compound. For transformations involving more than one acetylenic compound, the most relevant was chosen to report the reaction. Table 1 contains the examples of cotrimerization of acetylene and monosubstituted alkynes. Table 2 contains examples of cotrimerization using disubstituted alkynes. Table 3 covers the reactions of diynes. Table 4 consists of transformations using triynes. The reactions involving nitriles are covered in Table 5. When a reaction was reported using several protocols, the references are sorted according to the group of the metal mediator involved. When the products include a complex resulting from the deactivation of the catalyst by a product arising in the reaction or complexed arene, the load of catalyst is reported and the yield of these metallic compounds is calculated with respect to the catalyst.

Charts 1–3 preceding the tables provide structures for abbreviations used in the tables, and not included in the following list.

The following abbreviations are used in the tables:

1,3-C <sub>6</sub> H <sub>8</sub>	cyclohexa-1,3-dienyl
Ac	acetyl
acac	acetylacetonate
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bn	benzyl
Boc	<i>t</i> -butyloxycarbonyl
Brij 56	decaoxyethylenehexadecyl ether
BTMSA	bis(trimethylsilyl)acetylene

Bz	benzoyl
C <sub>3</sub> H <sub>5</sub>	allyl
C <sub>6</sub> H <sub>11</sub>	cyclohexyl
C <sub>5</sub> H <sub>5</sub> N	pyridine
C <sub>7</sub> H <sub>8</sub>	cyclohepta-1,3,5-triene
C <sub>8</sub> H <sub>13</sub>	cyclooctenyl
C <sub>8</sub> H <sub>14</sub>	cycloctene
C <sub>8</sub> H <sub>16</sub>	cyclooctane
C <sub>9</sub> H <sub>7</sub>	indenyl
C <sub>13</sub> H <sub>8</sub>	fluorenyl
C <sub>14</sub> H <sub>10</sub>	anthracenyl
COD	cycloocta-1,5-diene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
dad	2p,3p-dideoxyadenosine-5p-triphosphate
dba	dibenzylideneacetone
DCE	1,2-dichloroethane
dcpe	1,2-bis(dicyclohexyl)phosphinoethane
DIBAL-H	diisobutylaluminium hydride
DIPP	2,6-diisopropylphenoxide
DMAD	dimethyl acetylenedicarboxylate
DME	1,2-dimethoxyethane
dmfm	dimethyl fumarate
dmpe	1,2-bis(dimethyl)phosphinoethane
DMSO	dimethylsulfoxide
dppb	1,4-bis(diphenyl)phosphinobutane
dppe	1,2-bis(diphenyl)phosphinoethane
dppp	1,3-bis(diphenyl)phosphinopropane
MeDUPHOS	1,2-bis((2 <i>S</i> ,5 <i>S</i> )-2,5-dimethylphospholano)benzene
IBX	<i>o</i> -iodoxybenzoic acid
MOM	methoxymethyl
NC <sub>5</sub> H <sub>5</sub>	pyridine
NPMoV	See reference 177 for the preparation of this molybdovanadate.
PTSA	<i>p</i> -toluenesulfonic acid
sc	supercritical
SC <sub>4</sub> H <sub>8</sub>	tetrahydrothiophene
SC <sub>6</sub> H <sub>4</sub> O	1,4-mercaptophenoldioate
SC <sub>6</sub> H <sub>4</sub> NH	1,4-aminothiophenoldioate
SC <sub>6</sub> H <sub>4</sub> S	1,4-benzenedithioldioate
TBS	<i>t</i> -butyldimethylsilyl
TBDPS	<i>t</i> -butyldiphenylsilyl
TES	triethylsilyl

Tf	trifluoromethanesulfonyl
THP	tetrahydropyranyl
TIPS	triisopropylsilyl
TMS	trimethylsilyl
TMSA	trimethylsilylacetylene
TPPTS	triphenylphosphinetrisulfonate
Tr	triphenylmethyl
Ts	<i>p</i> -toluenesulfonyl

CHART 1. STRUCTURE ABBREVIATIONS USED IN TABLES 1-5

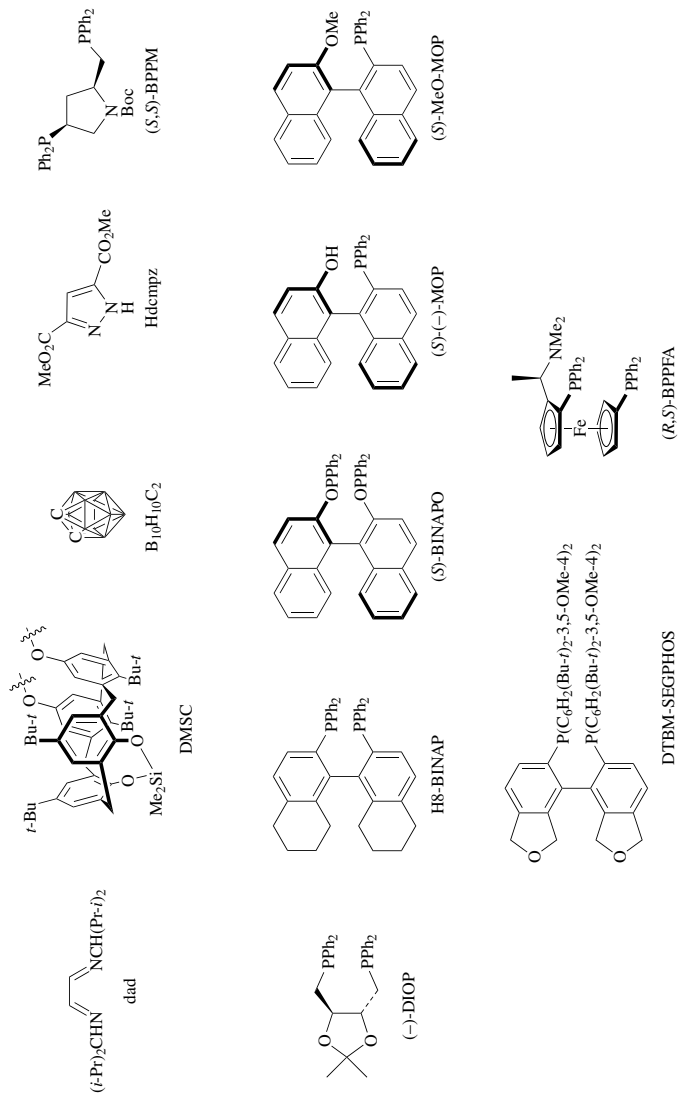
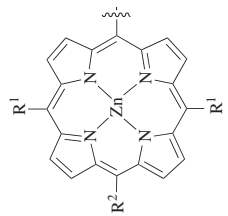
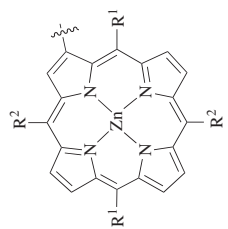
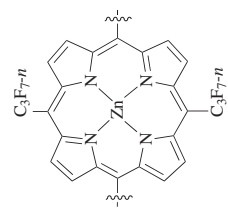


CHART 2. PORPHYRIN ABBREVIATIONS USED IN TABLE 2



R <sup>1</sup>	R <sup>2</sup>	Abbreviation
Ph	Ph	Porph <sup>4</sup>
CF <sub>3</sub>	Ph	Porph <sup>5</sup>
CF <sub>3</sub>	CF <sub>3</sub>	Porph <sup>6</sup>

R <sup>1</sup>	R <sup>2</sup>	Abbreviation
CH <sub>2</sub> Me <sub>2</sub> OMe	H	Porph <sup>1</sup>
	H	Porph <sup>2</sup>
		Porph <sup>3</sup>



CHART 3. PHENYLENE ABBREVIATIONS USED IN TABLE 3

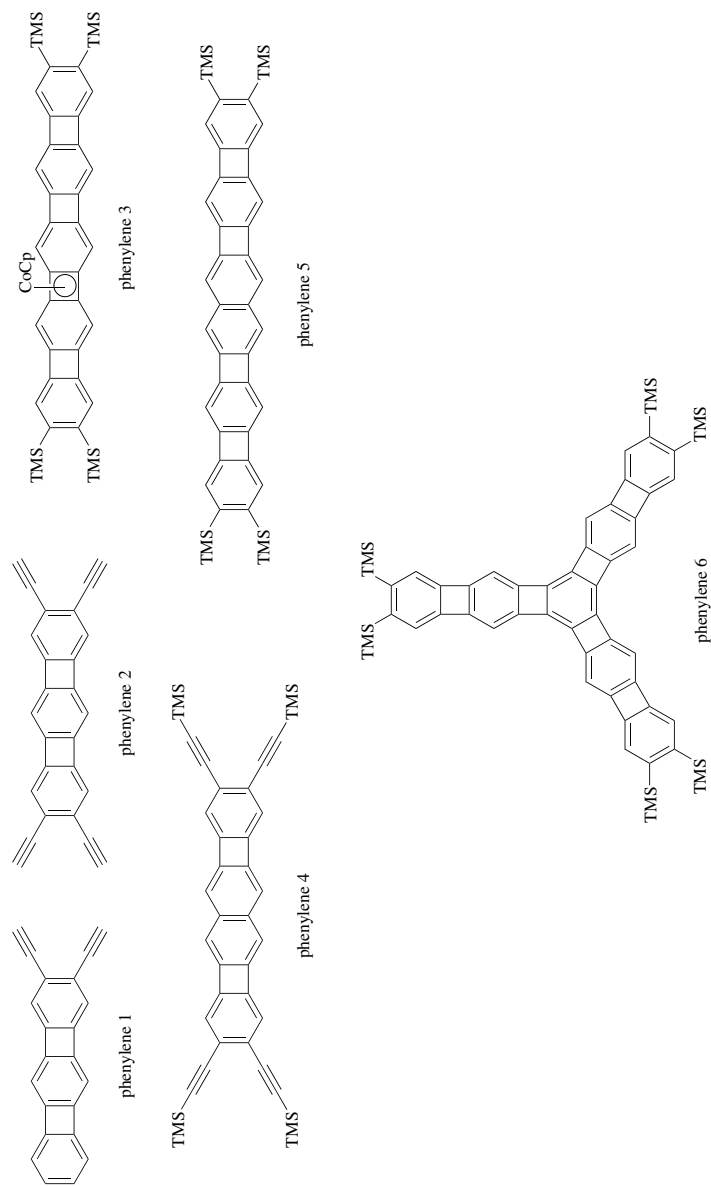
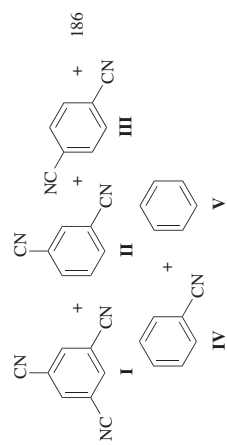


TABLE 1. MONOSUBSTITUTED ALKYNES

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>2</sub> HC≡CH		Sb <sub>2</sub> Cl <sub>6</sub>	210°, 2 d	(90)	178
		Zr, Ti	THF, rt, 3 h	(—)	179
		CpZr(dmpc) <sub>2</sub> Cl	-20°	(—)	6
		CpZr(dmpc) <sub>2</sub> Me	-20°	(—)	6
		NbCl <sub>5</sub>	PhCl, rt	(—)	180
		TaCl <sub>5</sub> , EtAlCl <sub>2</sub>	PhCl, rt	(—)	180
		TaCl <sub>5</sub> , EtAlCl <sub>2</sub> , Na/Hg	PhCl, rt	(—)	180
		Mo <sub>2</sub> (OPr- <i>t</i> ) <sub>6</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> (C <sub>2</sub> H <sub>2</sub> )	C <sub>6</sub> D <sub>6</sub> , 30 min	(5)	181
		Mo <sub>2</sub> (OCH <sub>2</sub> H <sub>2</sub> Bu- <i>t</i> ) <sub>6</sub> (C <sub>6</sub> H <sub>5</sub> N) <sub>2</sub> (C <sub>2</sub> H <sub>2</sub> )	C <sub>6</sub> D <sub>6</sub>	(—)	181
		CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	rt	(—)	174
		[RhCl(CO)(EtSCH <sub>2</sub> SEt) <sub>2</sub> ]	CD <sub>3</sub> CN, rt	(100)	182
			CH <sub>2</sub> Cl <sub>2</sub> , rt, 2 h	(6)	183
			THF, 1 atm, 60°, 24 h	(—)	23
		"	THF, 60°	(—)	61
			4 atm, 100°, 48 h	(—)	184
		NiBr <sub>2</sub> ·Mg	THF	(20)	185



THF, CH<sub>3</sub>CN/C<sub>2</sub>H<sub>5</sub>, *hν*

NiBr<sub>2</sub>, Mg

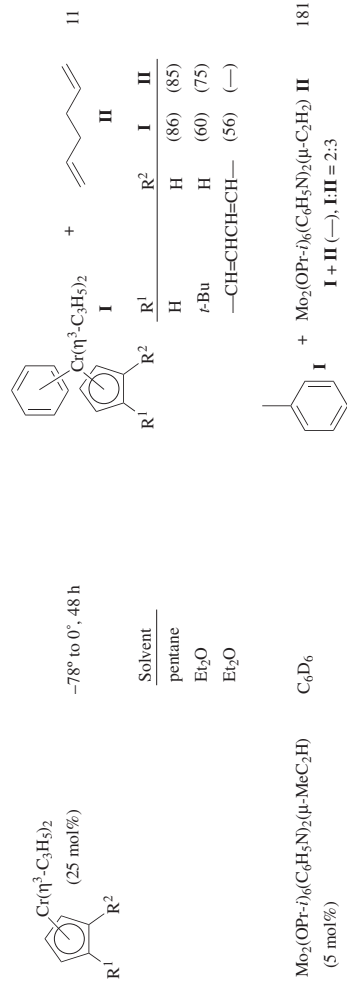
Solv., Pressure	<i>hν</i>	Time	I	II	III	IV	V
20/200 Torr	185, 254 nm	1.5 h	(0)	(0.9)	(0)	(0.9)	(0.04)
50/50 Torr	185, 254 nm	3 h	(0.5)	(1)	(0.07)	(0.1)	(0.03)
100/50 Torr	185, 254 nm	3 h	(0.6)	(0.7)	(0.05)	(0)	(0.05)
20/200 Torr	206 nm	4 h	(0.04)	(1.4)	(0.09)	(1.3)	(0.05)
50/50 Torr	206 nm	3 h	(0.25)	(0.5)	(0.07)	(0)	(0.05)
100/50 Torr	206 nm	3 h	(0.2)	(0.2)	(0.03)	(0)	(0.05)

Ru<sub>3</sub>(CO)<sub>9</sub>(MeCN)<sub>3</sub>

CH<sub>2</sub>Cl<sub>2</sub>, heat, 1 h

Ru<sub>3</sub>(CO)<sub>9</sub>(μ-CO)(C<sub>2</sub>H<sub>2</sub>) I + Ru<sub>3</sub>(CO)<sub>9</sub>(C<sub>6</sub>H<sub>6</sub>) II 13,187

I + II (72), I:II = 70:2



-78° to 0°, 48 h

Solvent  
pentane  
Et<sub>2</sub>O  
Et<sub>2</sub>O

R <sup>1</sup>	R <sup>2</sup>	I	II
H	H	(86)	(85)
<i>t</i> -Bu	H	(60)	(75)
-CH=CHCH=CH-		(56)	(-)

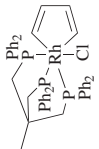
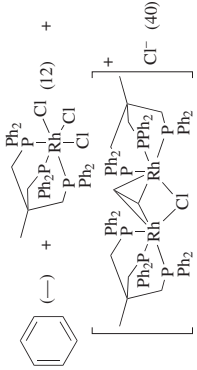

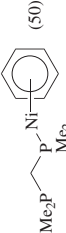

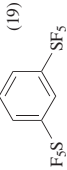

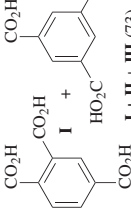
Mo<sub>2</sub>(OPr-*i*)(C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>(μ-MeC<sub>2</sub>H)  
(5 mol%)

C<sub>6</sub>D<sub>6</sub>

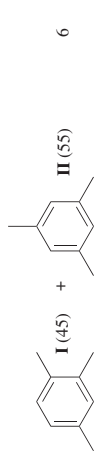
Mo<sub>2</sub>(OPr-*i*)(C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>(μ-C<sub>2</sub>H<sub>2</sub>) II  
I + II (-), I:II = 2:3



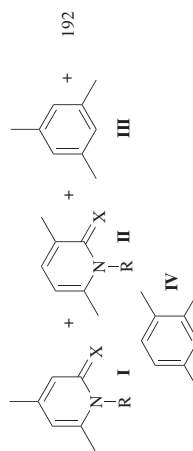
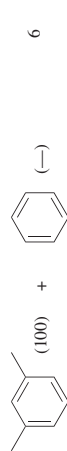
TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>2</sub> HC≡CH	 (5 mol%)	CH <sub>2</sub> Cl <sub>2</sub> , heat	 +	183
	 (25 mol%)	pentane, -78° to -50°	 (50)	188
	SF <sub>5</sub> Cl	<i>hν</i> , 4 h	 (19)	189
C <sub>3</sub> 	[(Cp*)RuCl] <sub>2</sub>	Toluene, 100°, 14 h	 + polymers <b>III</b>	190
	(Cp*)RuCl(COD)	Toluene, 60°, 14 h	<b>I + II + III</b> (56), <b>I:II:III</b> = 43:57:0	190
	(Cp*)RuCl(COD)	DME, 60°, 14 h	<b>I + II + III</b> (-), <b>I:II:III</b> = 74:26:0	190
	RtCl <sub>3</sub>	H <sub>2</sub> O, 65°, 10.5 h	<b>I + II</b> (42), <b>I:II</b> = 93:7	191
	RtCl <sub>3</sub>	THF, 65°, 14 h	<b>I + II</b> (35), <b>I:II</b> = 90:10	191
	RtCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	H <sub>2</sub> O, 65°, 7 h	<b>I + II</b> (54), <b>I:II</b> = 90:10	191
	RtCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	THF, 65°, 9 h	<b>I + II</b> (52), <b>I:II</b> = 90:10	191
	(COD)RtCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	H <sub>2</sub> O, 65°, 9.5 h	<b>I + II</b> (72), <b>I:II</b> = 82:18	191
	(COD)RtCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	THF, 65°, 10 h	<b>I + II</b> (43), <b>I:II</b> = 79:21	191
	[(COD)Rt(μ-Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> -3)] <sub>2</sub>	H <sub>2</sub> O, 65°, 5 h	<b>I + II</b> (54), <b>I:II</b> = 81:19	191

[(COD)Rh(*rac*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>-3)]<sub>2</sub> THF, 65°, 6.5 h 191  
 [(CO)RhCl(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-3)(SPh)]<sub>2</sub> H<sub>2</sub>O, 65°, 7 h 191  
 [(CO)RhCl(Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H-3)(SPh)]<sub>2</sub> THF, 65°, 9 h 191  
 [Rh<sub>3</sub>O(OAc)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]OAc H<sub>2</sub>O, 65°, 5.5 h 191  
 [Rh<sub>3</sub>O(OAc)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]OAc THF, 65°, 6 h 191  
 (Cp\*)RhCl(norbornadiene) Toluene, 60°, 14 h 190  
 (Cp\*)RhCl(norbornadiene) DME, 60°, 14 h 190  
 Pd<sub>2</sub>(dba)<sub>3</sub> Toluene, 100°, 15 h 190



I (83) + II (17) 182



CpCo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> R-N=C=X, C<sub>6</sub>H<sub>6</sub>, 150°

Time	R	X	I + II	E:II	III + IV
8 h	C <sub>6</sub> H <sub>11</sub>	O	(43)	56:44	(-)
8 h	Ph	O	(30)	0:100	(-)
17 h	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	NC <sub>6</sub> H <sub>4</sub> Me- <i>p</i>	(56)	100:0	(32)
17 h	C <sub>6</sub> H <sub>11</sub>	NC <sub>6</sub> H <sub>11</sub>	(85)	58:42	(14)

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)


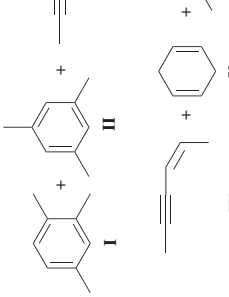

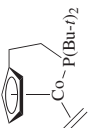
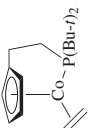
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_3$ 	$Rh_2Cl_2(N\text{-allylamine})_3$	$C_6H_6$ , rt		193
			$I + II + III + IV$ (—), $I:II = 87:13$ , $III:IV = 87:13$	193
	$Rh_2Cl_2(N\text{-allylamine})_3$	Toluene, rt	$I + II + III + IV$ (—), $I:II = 88:12$ , $III:IV = 87:13$	193
	$Rh_2Cl_2(N\text{-allylamine})_3$	$Et_2O$ , rt	$I + II + III + IV$ (—), $I:II = 87:13$ , $III:IV = 86:14$	193
	$Rh_2Cl_2(N\text{-allylamine})_3$	Toluene, $CO_2$ , rt	$I + II + III + IV$ (—), $I:II = 67:33$ , $III:IV = 64:36$	193
	$Rh_2Cl_2(N\text{-allylamine})_3$	$Et_2O$ , $CO_2$ , $60^\circ$	$I + II + V$ (—), $I:II = 70:30$	193
	$Rh_2Cl_2(N\text{-allylamine})_3$	$Et_2O$ , $60^\circ$	$I + II$ (—), $I:II = 87:13$	193
	$Rh_2Cl_2(N\text{-allylamine})_3$	$CH_3CN$ , $120^\circ$	$I + II + V + VI$ (—), $I:II = 78:22$	193
	$Rh_2Cl_2(C_2H_4)_4$	$C_6H_6$ , rt	$I + II$ (—), $I:II = 87:13$	193
		$H_2O$ , $EtOH$ , rt, 7 h		194
	$CpCo(CO)_2$	$seCO_2$ (180 bar), $hv$ , $90^\circ$ , 24 h	$I + II$ (89), $I:II = 39:61$	195
			$I + II$ (60), $I:II = 3:1$	195



TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_3$ 	$[Rh(\mu-SC_6F_3)(COD)]_2$	$C_6H_6$ , rt, 1 h		86
	$[Rh(\mu-SC_6F_4H-4)(COD)]_2$	$C_6H_6$ , rt, 1 h		86
	$[Rh(\mu-SC_6H_4F-4)(COD)]_2$	$C_6H_6$ , rt, 1 h		86
$\equiv$ -CN	—	$CH_2Cl_2$ , 12 kbar, 40°, 48 h		197
	—	$C_6H_6$ , 160°, 22 h	$II + III + IV + V$ (68), $II:III:IV:V = 20:3:1:1$	197
	—	160°, 22 h	$II + III + IV + V$ (27), $II:III:IV:V = 20:3:1:1$	197
	—	50 Torr, <i>h\nu</i> , 185 nm, 254 nm, 2 h		186
$C_4$ 		$H_2O$ , MeOH, 85°, 40 h		198
			$CH_2OH$ (62) (23)	(26)
			NHMe (47)	(26)



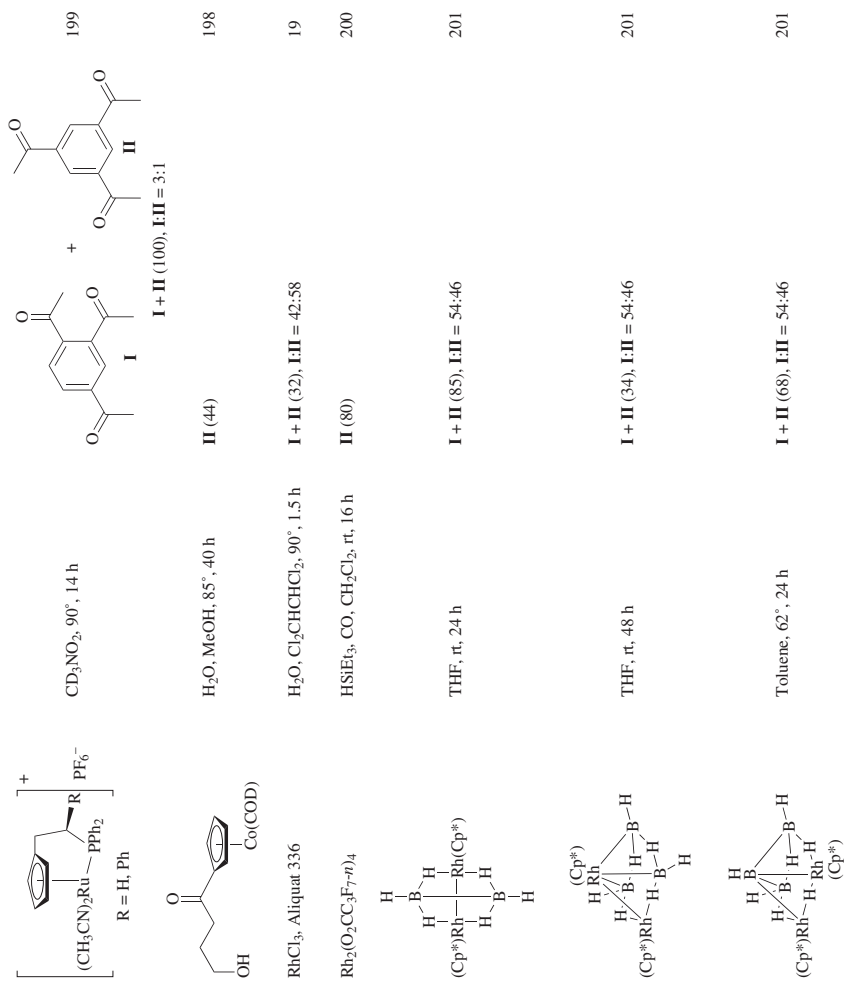


TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

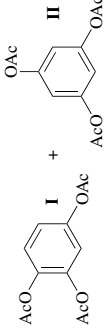
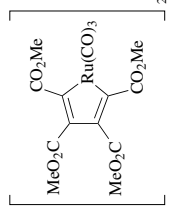
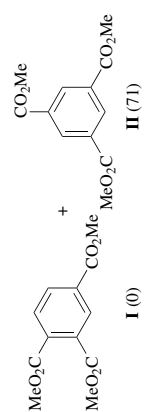
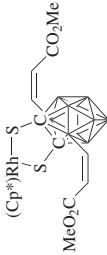
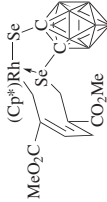
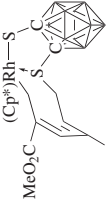
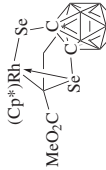
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub> ≡—OAc	RhCl <sub>3</sub> ·Aliquat 336	H <sub>2</sub> O, Cl <sub>2</sub> CHCHCl <sub>2</sub> , 90°, 2 h		19
		160°		202
≡—CO <sub>2</sub> Me	(Cp*)Ru( $\eta^5$ -S) $\mu$ -Cl-Ru(Cp*)	THF, 50°	I + II (95), I:II = 58:42	203
	RuH( $\eta^2$ -H <sub>2</sub> BH <sub>2</sub> )(CO)[P(Pr- <i>i</i> ) <sub>3</sub> ] <sub>2</sub>	Hexane, heat, 13 h	I + II (60), I:II = 1:3	204
	Ru <sub>3</sub> (CO) <sub>12</sub> ·PPhCl <sub>2</sub>	130°, 20 h	I + II (26), I:II = 63:37	205
	Ru <sub>3</sub> (CO) <sub>12</sub> ·PPhCl <sub>2</sub> (3 eq)	130°, 20 h	I + II (32), I:II = 63:37	205
	Ru <sub>3</sub> (CO) <sub>12</sub>	CO <sub>2</sub> (55 bar), 130°, 20 h	I + II (38), I:II = 75:25	205
	Ru <sub>3</sub> (CO) <sub>12</sub>	CH <sub>3</sub> CN, 130°, 20 h	I + II (16), I:II = 75:25	205
	Ru <sub>3</sub> (CO) <sub>12</sub>	70°, 20 h	I + II (28), I:II = 81:19	205
	Ru <sub>3</sub> (CO) <sub>12</sub>	130°, 20 h	I + II (52), I:II = 77:23	205
	Ru <sub>3</sub> (CO) <sub>12</sub> ·PPh <sub>3</sub>	130°, 20 h	I + II (54), I:II = 77:23	204
	Ru <sub>3</sub> (CO) <sub>12</sub> ·PPh <sub>3</sub> (2 eq)	130°, 20 h	I + II (58), I:II = 76:24	205
	Ru <sub>3</sub> (CO) <sub>12</sub> ·PPh <sub>3</sub> (3 eq)	130°, 20 h	I + II (55), I:II = 77:23	205
	Ru <sub>3</sub> (CO) <sub>12</sub> ·P( <i>t</i> -Bu- <i>n</i> ) <sub>3</sub>	130°, 20 h	I + II (28), I:II = 76:24	205
	Ru <sub>3</sub> (CO) <sub>12</sub> ·P( <i>t</i> -Bu- <i>n</i> ) <sub>3</sub> (3 eq)	130°, 20 h	I + II (32), I:II = 64:36	205
	Ru <sub>3</sub> (CO) <sub>12</sub> ·P(OPh) <sub>3</sub>	130°, 20 h	I + II (40), I:II = 63:37	205
	Ru <sub>3</sub> (CO) <sub>12</sub> ·P(OPh) <sub>3</sub> (3 eq)	130°, 20 h	I + II (33), I:II = 64:36	205



TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>4</sub> ≡CO <sub>2</sub> Me	Rh <sub>2</sub> (CO) <sub>6</sub> ( <i>r</i> -BuN=CH=NBu- <i>t</i> )	Toluene, heat, 13 h	<b>II</b> (90)	211	
	Rh <sub>2</sub> (O <sub>2</sub> CC <sub>3</sub> F <sub>7</sub> - <i>m</i> ) <sub>4</sub>	HSIEt <sub>3</sub> , CO, CH <sub>2</sub> Cl <sub>2</sub> , rt, 16 h	<b>I + II</b> (27), <b>I:II</b> = 1:7	200	
	(Cp*)Rh[S <sub>2</sub> C <sub>2</sub> (B <sub>10</sub> H <sub>10</sub> )]	Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212	
	(Cp*)Rh[Se <sub>2</sub> C <sub>2</sub> (B <sub>10</sub> H <sub>10</sub> )]	Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212	
	[(Cp*)Rh(HC <sub>2</sub> CO <sub>2</sub> Me)] <sub>2</sub>	Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212	
	[S <sub>2</sub> C <sub>2</sub> (B <sub>10</sub> H <sub>10</sub> )] <sub>2</sub>	Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212	
	[(Cp*)Rh(HC <sub>2</sub> CO <sub>2</sub> Me)] <sub>2</sub>	Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212	
	[Se <sub>2</sub> C <sub>2</sub> (B <sub>10</sub> H <sub>10</sub> )] <sub>2</sub>	Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212	
			Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212
			Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212
			Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212
			Toluene, 70°, 24 h	<b>I + II</b> (—), <b>I:II</b> = 1:1	212

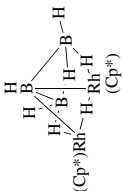
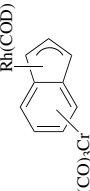
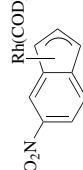
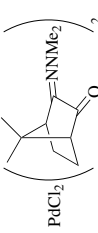
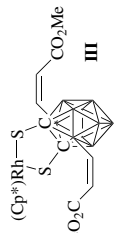
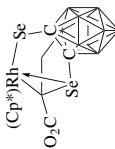
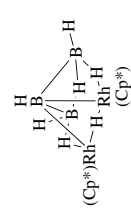
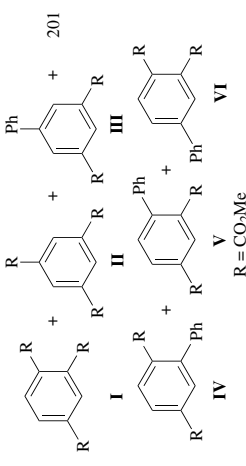
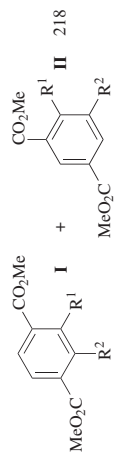
 <p>(Cp*)Rh(BH<sub>3</sub>)<sub>2</sub>(Cp*)</p>	THF, rt, 24 h	<b>I + II (75), I:II = 71:29</b>	201
 <p>(Cp*)Rh(BH<sub>3</sub>)<sub>2</sub></p>	THF, rt, 48 h	<b>I + II (85), I:II = 3:1</b>	213
 <p>(Cp*)Rh(BH<sub>3</sub>)<sub>2</sub></p>	Toluene, 62°, 24 h	<b>I + II (65), I:II = 72:28</b>	201
..	THF, 47°, 24 h	<b>I + II (42), I:II = 5:1</b>	213
 <p>Rh(COD)</p>	50°, 1 h	<b>I + II (23), I:II = 7:3</b>	214
 <p>Rh(COD) (CO)<sub>3</sub>Cr</p>	50°, 1 h	<b>I + II (69), I:II = 7:3</b>	214
 <p>Rh(COD) O<sub>2</sub>N</p>	50°, 1 h	<b>I + II (69), I:II = 7:3</b>	214
 <p>Ph, Ph P=O Ph, Ph P=O Ir(CO)<sub>2</sub> P=O Ph<sub>2</sub></p>	Et <sub>3</sub> SiH, CH <sub>2</sub> Cl <sub>2</sub> , rt, 8 h	<b>I (—)</b>	215

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

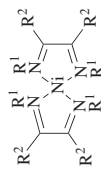
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_4 \equiv CO_2Me$	$NiMe_3Cl(PMe_3)_2$	$-70^\circ$ to $-40^\circ$	<b>I + III</b> (—)	216
	$PdCl_2$ 	$CH_2Cl_2$ , rt	<b>II</b> (21)	217
	$(Cp^*)Rh[S_2C_2(B_{10}H_{10})]$ (0.8 mol%)	$CHCl_3$ , heat, 24 h	<b>I + III</b> + $MeO_2C$ 	212
			<b>I + II + III</b> (—), <b>I:II:III</b> = 1:0.8:2.5	
	$(Cp^*)Rh[Se_2C_2(B_{10}H_{10})]$ (0.8 mol%)	$CHCl_3$ , heat, 24 h	<b>I + II</b> + $MeO_2C$ 	212
			<b>I + II + III + IV</b> (—), <b>I:II:III:IV</b> = 1:1:15:5	
		$Ph \equiv$ (x eq), THF, rt, 2 d	<b>I</b> + <b>II</b> + <b>III</b> + <b>IV</b> + <b>V</b> + <b>VI</b> 	201
			<b>R</b> = $CO_2Me$	
			x <b>I</b> <b>II</b> <b>III</b> <b>IV</b> <b>V</b> <b>VI</b>	
			1 (34) (14) (17) (18) (16) (1)	
			5 (17) (5) (23) (40) (16) (0)	

Ni(acac)<sub>2</sub>, PPh<sub>3</sub>, Et<sub>2</sub>Zn, PhOH

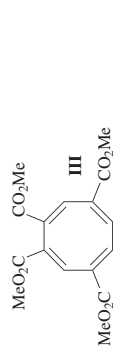
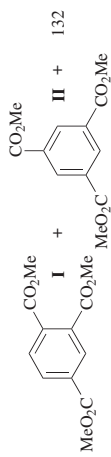
R<sup>1</sup> = R<sup>2</sup>, THF, rt



R <sup>1</sup>	R <sup>2</sup>	I	I:II
CH <sub>2</sub> OTMS	H	(60)	95:5
Et	Et	(41)	100:0
<i>t</i> -Bu	H	(50)	92:8
TMS	H	(64)	90:10
Ph	H	(53)	94:6
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	H	(55)	93:7
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	H	(49)	100:0
C(Me)=CH <sub>2</sub>	H	(68)	93:7



Cyclohexane



Temp	R <sup>1</sup>	R <sup>2</sup>	I+II	III
rt	<i>i</i> -Pr	H	(54)	(32)
rt	C <sub>6</sub> H <sub>11</sub>	H	(29)	(39)
rt	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(16)	(35)
rt	Ph	Me	(35)	(30)
rt	4-MeOC <sub>6</sub> H <sub>4</sub>	Me	(22)	(22)
rt	CH( <i>Pr</i> - <i>t</i> ) <sub>2</sub>	H	(53)	(47)
10°	CH( <i>Pr</i> - <i>t</i> ) <sub>2</sub>	H	(2)	(98)

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)


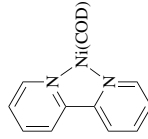
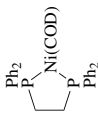
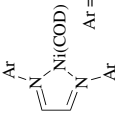
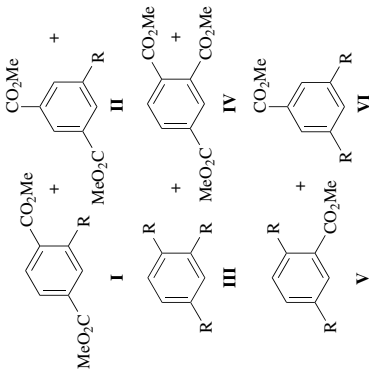

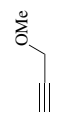
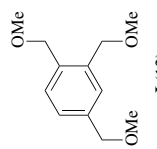
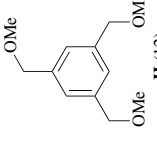

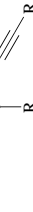






Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub> 		Cyclohexane, rt	<b>I + II (21), III (39)</b>	132
		Cyclohexane, 60°	<b>I + II (38)</b>	132
		Cyclohexane, rt	<b>I + II (7), III (6)</b>	132
	Catalyst Ar = 2,6-(i-Pr) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	$\equiv$ -CH <sub>2</sub> OMe, THF, rt, 5 min		218





TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

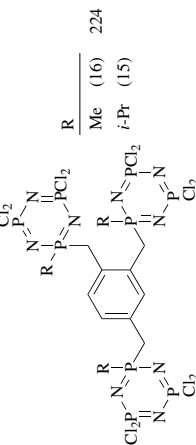
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub> 	Nb <sub>2</sub> Cl <sub>6</sub> (SC <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Ti <sub>2</sub> Cl <sub>6</sub> (SC <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> [RhCl(CO)(EtSCH <sub>2</sub> SEt) <sub>2</sub> ]	Toluene Toluene CD <sub>3</sub> CN, rt	<b>I</b> + <b>II</b> (–), <b>I:II</b> = 1:1 <b>I</b> + <b>II</b> (–), <b>I:II</b> = 1:1 <b>I</b> + <b>II</b> (100), <b>I:II</b> = 5:1	221 221 182
	(Cp*)RuCl(COD)	DCE, rt, 1 d	 <b>I</b> (12) +  <b>II</b> (12)	56
	(Cp*)RuCl(COD)	DCE, 50°, 1 d	<b>I</b> (19) + <b>II</b> (20)	56
	CoCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CN, 82°, 6 h	<b>I</b> + <b>II</b> (75), <b>I:II</b> = 83:17	222
	Pd(PPh <sub>3</sub> ) <sub>4</sub>	R-C≡C-R, THF, 100°, 21 h	 R  R  R 	93
	Ni(COD) <sub>2</sub>	PR <sub>3</sub> (x eq), CO <sub>2</sub> , THF, 80°, 20 h	 <b>I</b> +  <b>II</b>	223
			 <b>III</b>	

R	x	I	II	III
Me	2	(0)	(22)	(—)
Et	2	(18)	(26)	(9)
Et	1	(0)	(26)	(6)
Et	2	(44)	(6)	(0)
Et	4	(31)	(9)	(8)
Et	2	(54)	(3)	(0)
<i>n</i> -Bu	2	(37)	(3)	(0)
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	2	(44)	(5)	(2)
C <sub>6</sub> H <sub>11</sub>	2	(0)	(40)	(14)
Ph	2	(0)	(43)	(—)

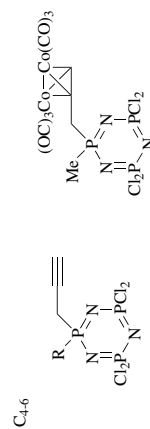
223

Ligand (x eq), CO<sub>2</sub>, THF, 80°, 20 h I + II + III

Ligand	x	I	II	III
dppe	2	(16)	(8)	(0)
dppp	2	(33)	(0)	(3)
dppb	1	(25)	(6)	(0)
dppb	2	(56)	(4)	(0)



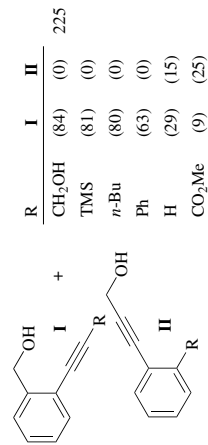
*n*-Octane, 150°, 24 h



C<sub>5-11</sub>


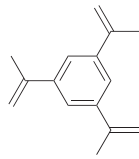

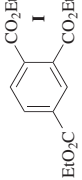
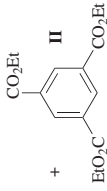
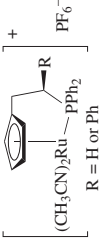
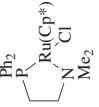


Acetylene, THF, rt



R	I	II
CH <sub>2</sub> OH	(84)	(0)
TMS	(81)	(0)
<i>n</i> -Bu	(80)	(0)
Ph	(63)	(0)
H	(29)	(15)
CO <sub>2</sub> Me	(9)	(25)

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_5$ 	$Mo(CO)_3(N\text{-methylimidazole})$	Toluene, 60°, 8 h	 <b>I</b> (100)	13
	$(CO)_3Co^{\ominus}Co$ 	Toluene, heat, 2 min	<b>I</b> (20)	226
$\equiv CO_2Et$	$Mo(CO)_6$	Toluene, 60°, 8 h	 <b>I</b> +  <b>II</b> <b>I</b> + <b>II</b> (100), <b>I:II</b> = 66:34	13
	$Mo(CO)_6$	$H_2O$ , toluene, 60°, 24 h	<b>I</b> + <b>II</b> (100), <b>I:II</b> = 65:35	13
	$Mo(CO)_3(\text{pyrazole})_3$	$O_2$ , toluene, 60°, 8 h	<b>I</b> + <b>II</b> (5), <b>I:II</b> = 63:37	13
	$Mo(CO)_3(N\text{-methylimidazole})$	Toluene, 60°, 8 h	<b>I</b> + <b>II</b> (—)	13
	 R = H or Ph	Toluene, 60°, 8 h	<b>I</b> + <b>II</b> (100), <b>I:II</b> = 27:73	13
	$(CH_3CN)_2Ru$	$CD_3NO_2$ , 90°, 14 h	<b>I</b> + <b>II</b> (100), <b>I:II</b> = 3:1	199
		Toluene, heat, 20 h	<b>I</b> + <b>II</b> (96), <b>I:II</b> = 1:1	227
	$[CpRu(CH_3CN)_3]PF_6$	$CH_3NO_2$ , 80°, 24 h	<b>I</b> + <b>II</b> (85), <b>I:II</b> = 75:25	228
	$(Cp^*)RuCl(COD)$	DCE, rt, 1 h	<b>I</b> (61) + <b>II</b> (28)	56
	$Co_3(H)(CO)_3(PMe_3)_6$	Toluene, 100°, 5 h	<b>I</b> (90)	229
	$CoCl(PPh_3)_3$	$CH_3CN$ , rt, 30 min	<b>I</b> (96)	222
	$(Cp^*)Co(\eta^2\text{-NO}_2)(OTf)$	Acetone, rt, 24 h	<b>I</b> + <b>II</b> (62)	207

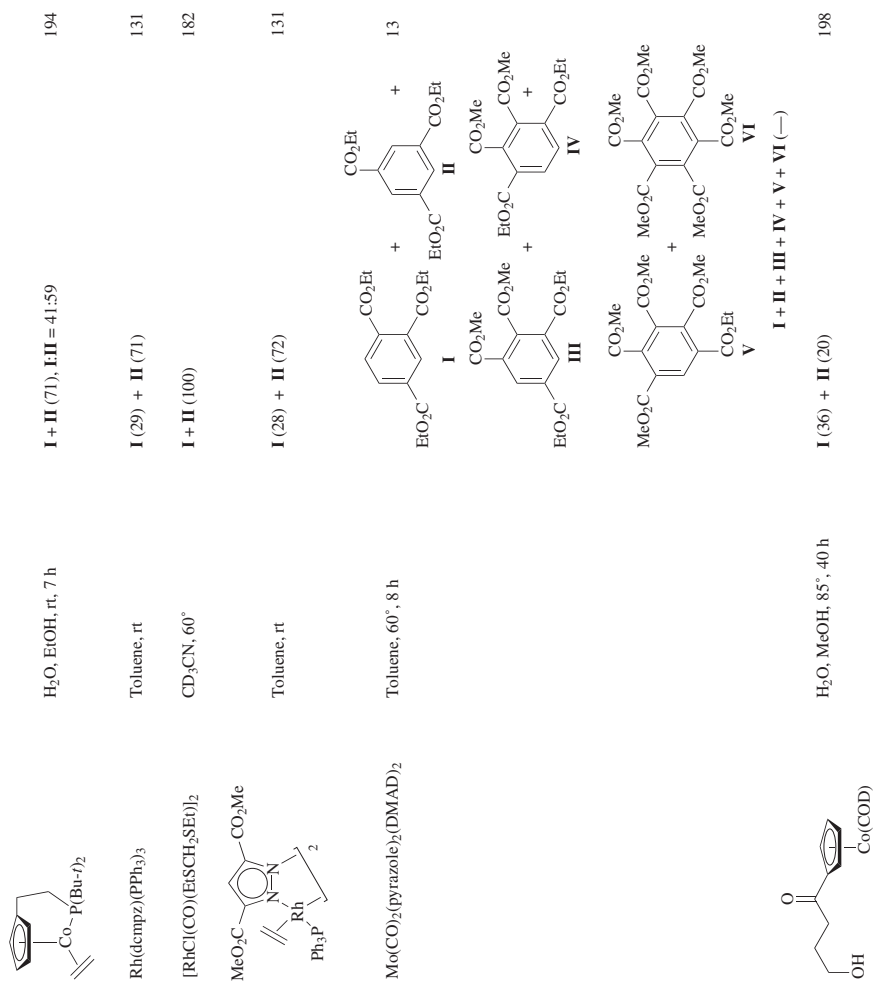
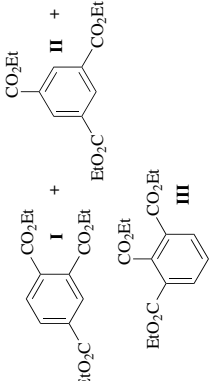
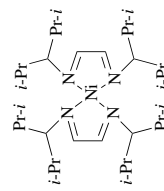
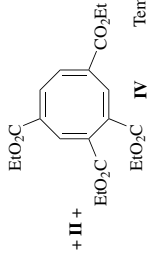
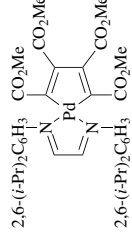
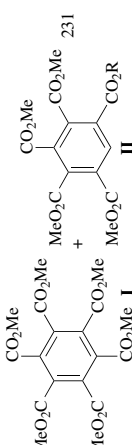


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.											
C <sub>5</sub> ≡—CO <sub>2</sub> Et	CoH(N <sub>2</sub> )(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CN, rt, 23 h	 <b>I + II + III (74), I:II:III = 1:1:1</b>	230											
		Cyclohexane	 <b>I + II + IV</b>	132											
C <sub>5-7</sub> ≡—CO <sub>2</sub> R		DMAD, toluene, 60°, 1 d	 <b>I + II</b>	231											
			<table border="1"> <thead> <tr> <th>R</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>(65)</td> <td>(35)</td> </tr> <tr> <td><i>i</i>-Pr</td> <td>(72)</td> <td>(28)</td> </tr> <tr> <td><i>t</i>-Bu</td> <td>(90)</td> <td>(10)</td> </tr> </tbody> </table>	R	I	II	Et	(65)	(35)	<i>i</i> -Pr	(72)	(28)	<i>t</i> -Bu	(90)	(10)
R	I	II													
Et	(65)	(35)													
<i>i</i> -Pr	(72)	(28)													
<i>t</i> -Bu	(90)	(10)													

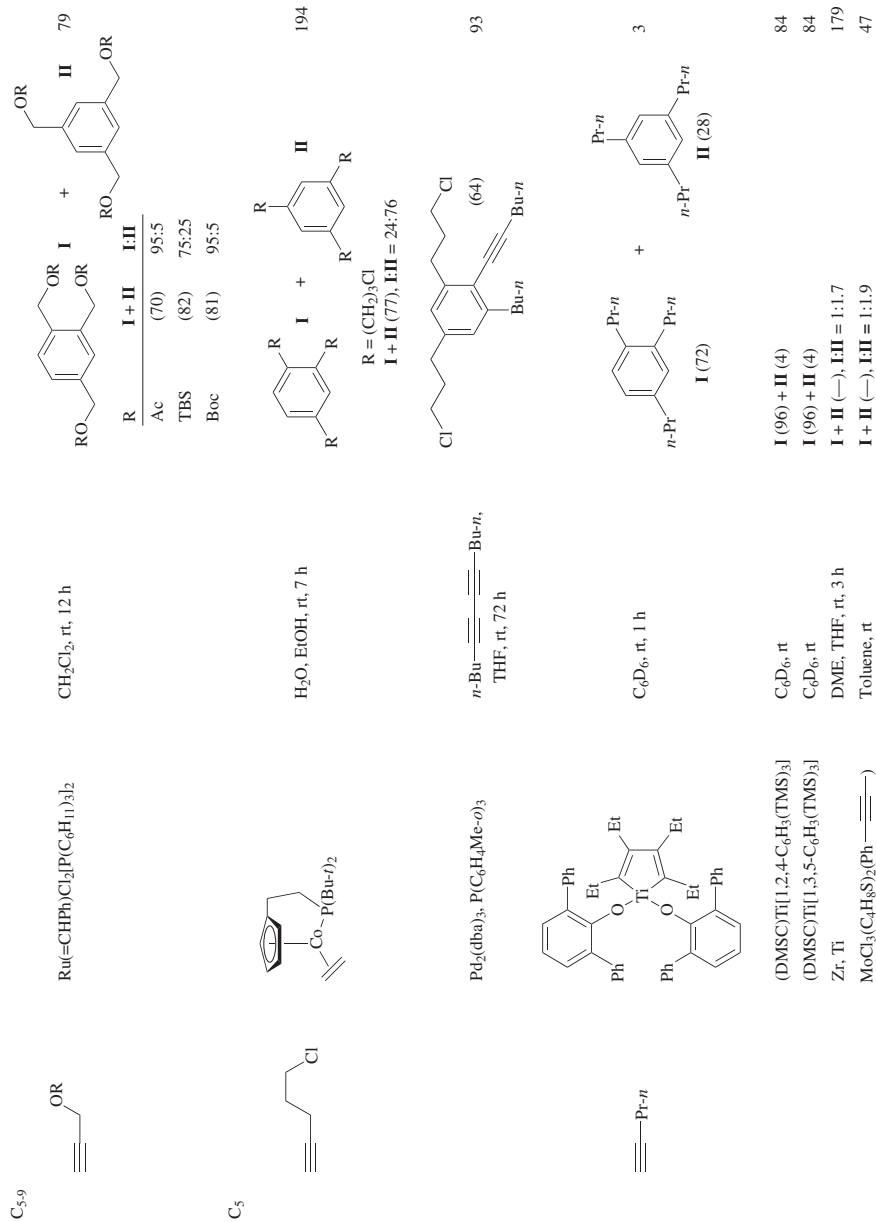

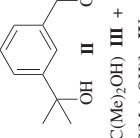

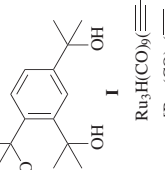
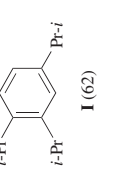
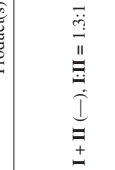




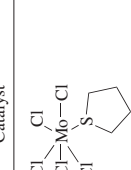
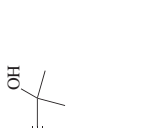


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_3$ 		Toluene, rt	<b>I + II</b> (←), <b>II</b> = 1.3:1	47
$C_3$ 	 Ar = 2,6-Ph <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	C <sub>6</sub> D <sub>6</sub> , rt, 1 h	 <b>I</b> (62) +  <b>II</b> (38)	3
	Nb <sub>2</sub> Cl <sub>6</sub> (THT) <sub>3</sub> Ta <sub>2</sub> Cl <sub>6</sub> (THT) <sub>3</sub>	Toluene, 80° Toluene, 80°	<b>I + II</b> (←), <b>II</b> = 1:1 <b>I + II</b> (←), <b>II</b> = 1:1	221 221
	Ru( $\eta^6$ -naphthalene)(COD) (17 mol%)	THF, rt, 15 h	 <b>I</b> +  <b>II</b> (38) <b>I + II</b> (←), <b>II</b> = 12:88	232
	Ru <sub>3</sub> (CO) <sub>12</sub> (1 eq)	Cyclohexane, heat, 2 h	 <b>I</b> +  <b>II</b> (38) <b>I + II</b> (←), <b>II</b> = 4:1, <b>III</b> (4), <b>IV</b> (30)	233
	 Co(COD)	H <sub>2</sub> O, MeOH, 85°, 40 h	<b>I</b> (53) + <b>II</b> (28)	198



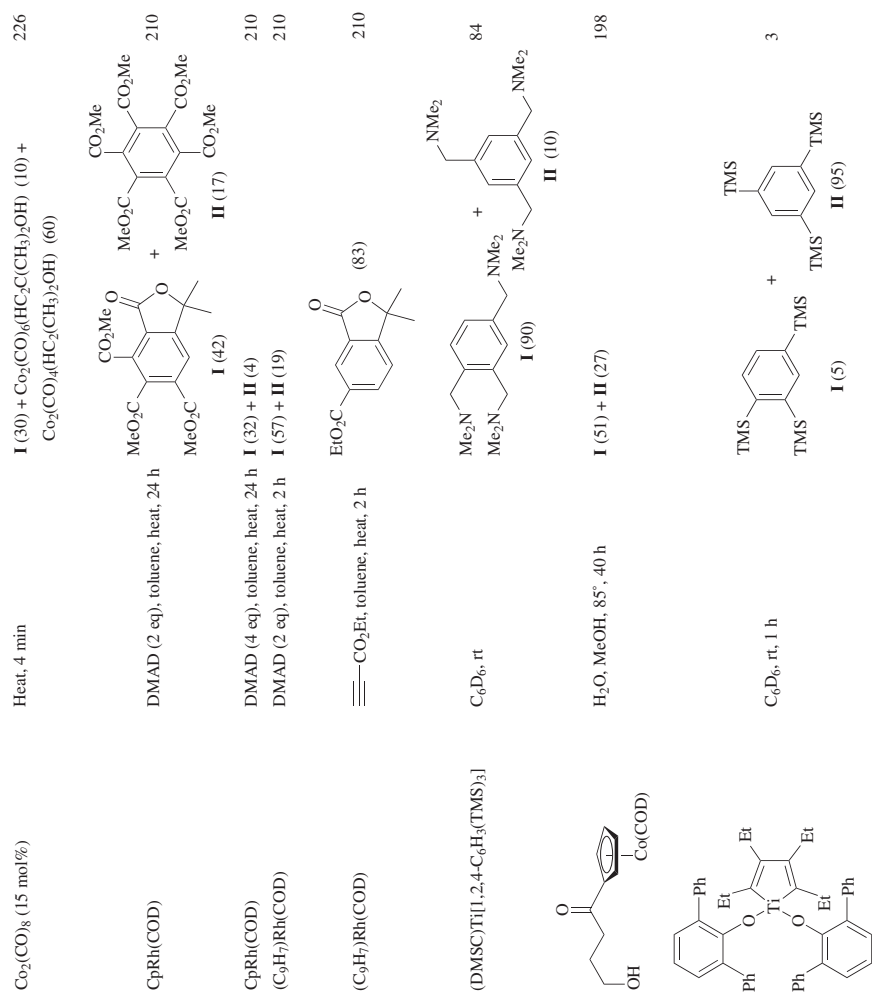
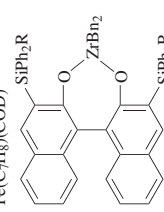
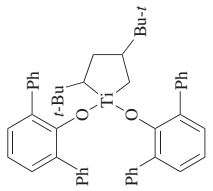
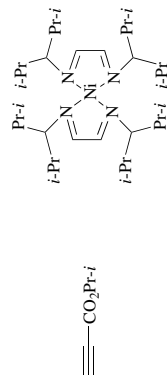
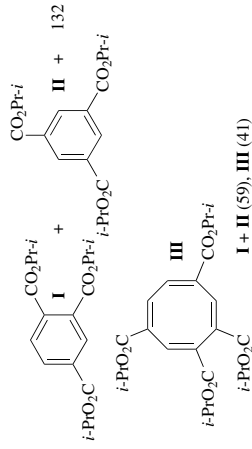


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>5</sub> ≡-TMS	Zr, Ti	DME, THF, rt, 3 h	I + II (—), I:II = 1:15.7	179	
	(DMSO)TiCl <sub>2</sub> , Na	C <sub>6</sub> D <sub>6</sub> , 80°	I (98) + II (2)	234	
	(DMSO)TiCl <sub>2</sub> , Na≡TMS	C <sub>6</sub> D <sub>6</sub> , 80°	I (98) + II (2)	234	
	(DMSO)Ti(≡TMS) <sub>2</sub> (THF)	C <sub>6</sub> D <sub>6</sub> , 80°	I (95) + II (5)	234	
	(DMSO)Ti[1,2,4-C <sub>6</sub> H <sub>3</sub> (TMS) <sub>3</sub> ]	C <sub>6</sub> D <sub>6</sub> , THF, rt	I (95) + II (5)	84	
	(DMSO)Ti[1,2,4-C <sub>6</sub> H <sub>3</sub> (TMS) <sub>3</sub> ]	C <sub>6</sub> D <sub>6</sub> , rt	I (99) + II (1)	84	
	(DMSO)Ti[1,3,5-C <sub>6</sub> H <sub>3</sub> (Bu- <i>t</i> ) <sub>3</sub> ]	C <sub>6</sub> D <sub>6</sub> , rt	I (99) + II (1)	84	
	MeCl <sub>5</sub> , Al	DME, 50°, 24 h	I + II (40), I:II = 1:9	235	
	MeCl <sub>5</sub> , Sn	DME, 50°, 24 h	I + II (51), I:II = 1:3.5	235	
	MeCl <sub>5</sub> , In	DME, 50°, 24 h	I + II (54), I:II = 1:2	235	
	Fe(C <sub>7</sub> H <sub>8</sub> )(COD)	THF, rt, 46 h	I + II (85), I:II = 95:5	236	
					
	Ru(η <sup>6</sup> -naphthalene)(COD) (17 mol%)	C <sub>6</sub> D <sub>6</sub> , rt	R I + II I:II Me (—) 1:1 Ph (—) 4:1	237	
					
	Ru(η <sup>6</sup> -naphthalene)(COD) (17 mol%)	THF, rt, 3.5 h	I + II (23), I:II = 60:40	232	
	RCH=CH <sub>2</sub> , C <sub>6</sub> D <sub>6</sub>	I + II (23), I:II = 60:40 I + II (25), I:II = 60:40 I + II + III I:II:III R Ph TMS (52) 57:25:18 (51) 61:0:39	238		

C<sub>6</sub>

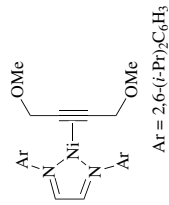
Cyclohexane, rt



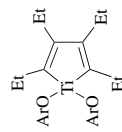
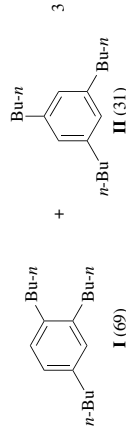
I + II (38), III (62)

132

Cyclohexane, 10°



75

≡—Bu-*n*Ar = 2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>AlEt<sub>3</sub>Ti(η<sup>6</sup>-toluene)(μ-Br)(AlEt<sub>2</sub>)<sub>2</sub>TiCl<sub>4</sub>, AlEt<sub>2</sub>ClTiCl<sub>4</sub>, AlEt<sub>3</sub>VCl<sub>4</sub>, AlEt<sub>2</sub>ClVCl<sub>4</sub>, AlEt<sub>3</sub>VOCl<sub>3</sub>, AlEt<sub>2</sub>ClVOCl<sub>3</sub>, AlEt<sub>3</sub>NbCl<sub>5</sub>C<sub>6</sub>D<sub>6</sub>, rt, 1 h

I (69)

I + II (40), III = 44:57

II (55)

I (53) + II (47)

I (33) + II (37)

I (21) + II (50)

I (26) + II (26)

I (52) + II (38)

I (13) + II (11)

I (78) + II (22)

Toluene, rt, 15h

Toluene, rt, 15h

Toluene, 30°, 24 h

Toluene, 30°, 24 h

Toluene, 30°, 24 h

Toluene, 30°, 24 h

Toluene, 30°, 24 h

Toluene, 30°, 24 h

Toluene, 60°, 2 h

239

239

240

240

240

240

240

240

240

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub> 	TaCl <sub>5</sub>	Toluene, 60°, 2 h	<b>I</b> (78) + <b>II</b> (22)	240	
	NbCl <sub>5</sub>	Toluene, 30°, 24 h	<b>I</b> (76) + <b>II</b> (24)	240	
	CpNbCl <sub>4</sub> , Mg	THF, 0° to rt	<b>I</b> + <b>II</b> (91), <b>I:II</b> = 41:59	8	
	NbCl <sub>5</sub> , EtAlCl <sub>2</sub>	CCl <sub>4</sub>	<b>I</b> + <b>II</b> (58)	241	
	Mo <sub>2</sub> Ac <sub>4</sub> , TiCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	<b>II</b> (74)	242	
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (22)	243	
	Mo <sub>6</sub> (CO) <sub>6</sub>	I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (12)	243	
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (2)	243	
	Mo <sub>6</sub> (CO) <sub>6</sub>	PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (13)	243	
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (8)	243	
	Mo <sub>6</sub> (CO) <sub>6</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (14)	243	
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	I <sub>2</sub> , <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (10)	243	
	Mo <sub>6</sub> (CO) <sub>6</sub>	I <sub>2</sub> , <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (6)	243	
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	I <sub>2</sub> , PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (69)	243	
	Mo <sub>6</sub> (CO) <sub>6</sub>	I <sub>2</sub> , PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 100°, 18 h	<b>I</b> + <b>II</b> (49)	243	
				$\frac{\mathbf{I} + \mathbf{II}}{\mathbf{I} + \mathbf{II}}$	
				$\frac{\mathbf{R}}{\mathbf{Cl}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
				$\frac{\mathbf{I:II}}{\mathbf{I:II}}$	
			$\frac{\mathbf{I:II}}{\mathbf{I:II}}$		
			$\frac{\mathbf{I:II}}{\mathbf{I:II}}$		
			$\frac{\mathbf{I:II}}{\mathbf{I:II}}$		

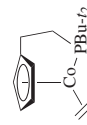
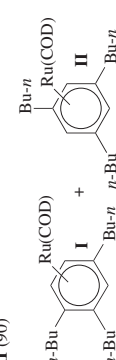
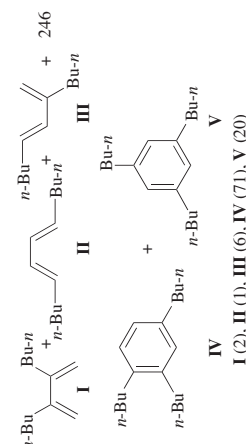
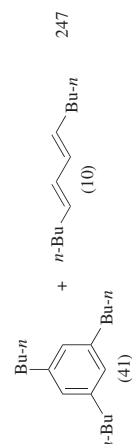
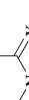
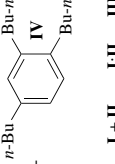
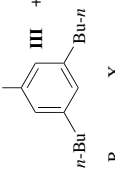
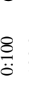

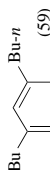



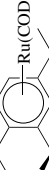
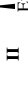



					
(C <sub>9</sub> H <sub>7</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	H <sub>2</sub> O, EtOH, rt, 7 h	<b>I + II (86), I:II = 35:65</b>			194
(C <sub>9</sub> H <sub>7</sub> )Rh(C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub>	<i>o</i> -Xylene, 150°, 109 h	<b>I + II (62), I:II = 70:30</b>			209
(C <sub>9</sub> H <sub>7</sub> )Rh(COD)	<i>o</i> -Xylene, 160°, 111 h	<b>I + II (65), I:II = 70:30</b>			209
(C <sub>9</sub> H <sub>7</sub> )Rh(COD)	<i>o</i> -Xylene, 150°, 93 h	<b>I + II (35), I:II = 68:32</b>			209
(C <sub>13</sub> H <sub>8</sub> )Rh(COD)	<i>o</i> -Xylene, 160°, 109 h	<b>I + II (6), I:II = 71:29</b>			209
RhCl <sub>3</sub> , Aliquat 336	H <sub>2</sub> O, Cl <sub>2</sub> CHCHCl <sub>2</sub> , 60°, 2 h	<b>I + II (17), I:II = 94:6</b>			19
NiBr <sub>2</sub> , Mg	THF	<b>II (90)</b>			185
Ru(η <sup>6</sup> -naphthalene)(COD) (17 mol%)	THF, rt, 1 h				232
Co(C <sub>5</sub> H <sub>5</sub> N)BPh <sub>4</sub>	H <sub>2</sub> (1 atm), pyridine, 10°		<b>I + II (95), I:II = 30:70</b>		246
Co(C <sub>6</sub> H <sub>5</sub> N)BPh <sub>4</sub>	H <sub>2</sub> (90 atm), pyridine, 10°	<b>I (26) + II (4) + III (39) + IV (27) + V (4)</b>			246
Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	Cyclopent-2-enone, THF, rt, 15 min				247

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cp <sub>2</sub> Co(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	R-N=•=X, C <sub>6</sub> H <sub>6</sub> , 150°	 I	192
			 II	
	Pd <sub>2</sub> (dba) <sub>3</sub> , P(C <sub>6</sub> H <sub>4</sub> Me- <i>o</i> ) <sub>3</sub>	Time 8 h 41 h 17 h 17 h	 III	I + II (29) 50:50 (71)
			 IV	
	Pd <sub>2</sub> (dba) <sub>3</sub> , P(C <sub>6</sub> H <sub>4</sub> Me- <i>o</i> ) <sub>3</sub>	 (59) THF, 60°, 72 h	 I	93
			 II	
	Fe(C <sub>7</sub> H <sub>8</sub> )(COD)	THF, rt, 46 h	 I + II (70), I:II = 47:53	236
	Ru(η <sup>6</sup> -naphthalene)(COD) (17 mol%)	THF, rt	 I + II (65), I:II = 10:90	248


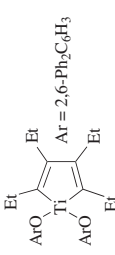
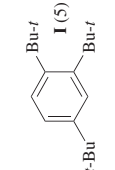
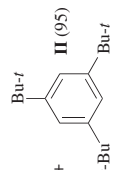
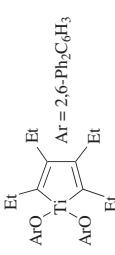
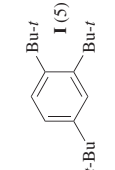
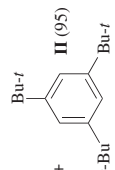
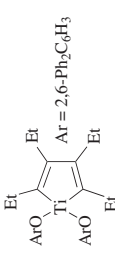
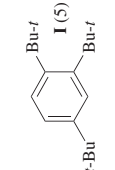
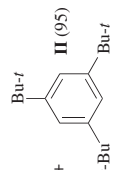
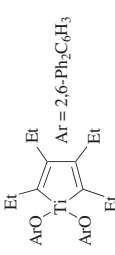
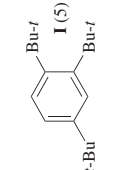
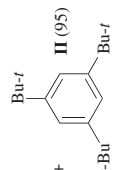
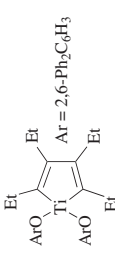
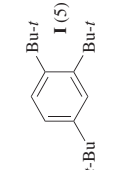
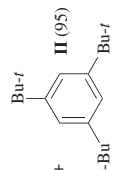
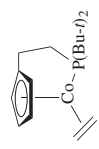




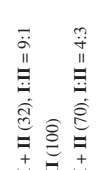


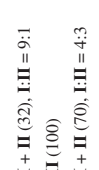


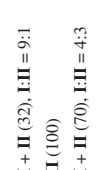


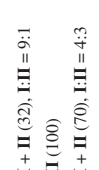

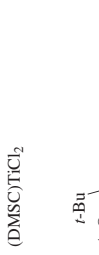
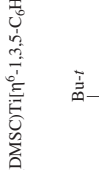

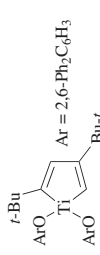
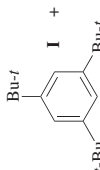
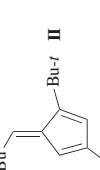




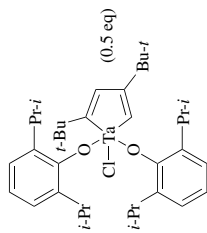
				3
Zr				179
Zr, Ti				179
Fe(C7H8)(COD)				236
CpCo(CO)2				85
				194
RhCl3, Aliquat 336				19
PdCl2				72
Pd/C, TMSCl				87
Pd(OAc)2				249
(DMSC)TiCl2				84
				250
"				250

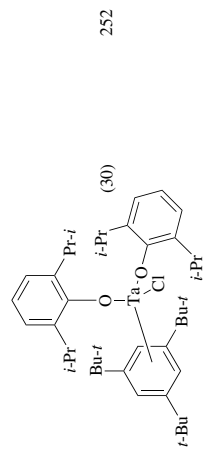
TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_6$ 	$Ti(OC_6H_3Ph_2-2,6)Cl_2$ $Ti[OC_6H_3(Ph-t)_{2-2,6}]Cl_2$ $Ti[OC_6H_3(CH_3)_{2-2,6}]Cl_2$	$Li$ $\equiv$ $Bu-t$ , $C_6H_6$ , $100^\circ$ $Li$ $\equiv$ $Bu-t$ , $C_6H_6$ , $100^\circ$ $Li$ $\equiv$ $Bu-t$ , $C_6H_6$ , $100^\circ$	<b>I + II + III + IV</b> (—), <b>I:II:III:IV</b> = 6:65:19:10 <b>I + II + III + IV</b> (—), <b>I:II:III:IV</b> = 3:71:17:9 <b>I + II + III + IV</b> (—), <b>I:II:III:IV</b> = 3:63:22:12	250 250 250
	$2,6-Ph_2C_6H_3O-Ti$ 	$C_6H_6$ , $100^\circ$	<b>I + II + III + IV</b> (—), <b>I:II:III:IV</b> = 10:78:8:4	250
		$RCH=CH_2$ (x eq), $C_6D_6$	<b>I</b> + <b>II</b> + <b>III</b> + <b>IV</b> + <b>II</b> + <b>III</b> + <b>IV</b> 	
	x	Temp	<b>R</b> <b>I + II + III + IV</b> <b>I:II:III:IV</b>	
	—	rt	H (—) 2:87:7:4	238
	1.4	—	Ph (24) 0:66:28:6	238
	0.25	$90^\circ$	Ph (—) 0:13:47:40	251
	0.5	rt	Ph (—) 0:47:34:19	238, 251
	0.5	$90^\circ$	Ph (—) 0:16:65:19	251
	1	rt	Ph (—) 0:62:30:8	238, 251
	1	$90^\circ$	Ph (—) 0:31:59:10	251
	1.5	rt	Ph (—) 0:74:20:6	238

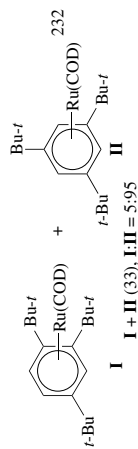




252



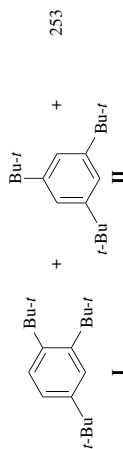
$\text{Ru}(\eta^6\text{-naphthalene})(\text{COD})$  (17 mol%) THF, rt, 15 h



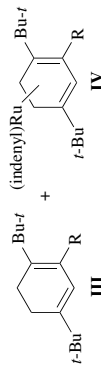
232

$(\text{C}_9\text{H}_7)\text{Ru}(\text{CHR})_2$  (7 mol%)

Hexane, rt, 5 d



253

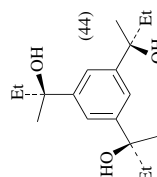


R	I + II + III + IV	III:III:IV	IV
H	(-)	10:1:1:0	(15)
CN	(-)	4:1:0:—	(32)



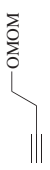
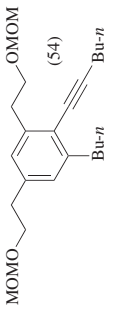
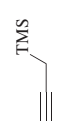
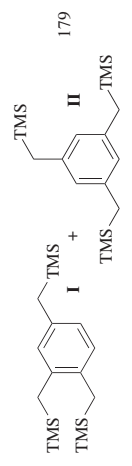
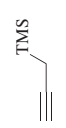
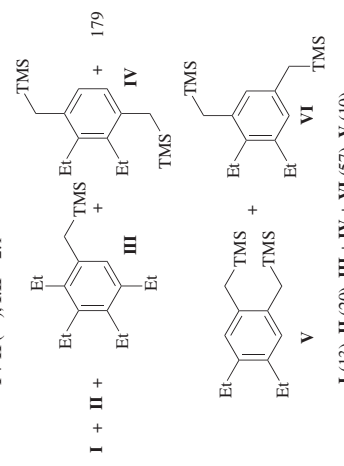
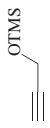
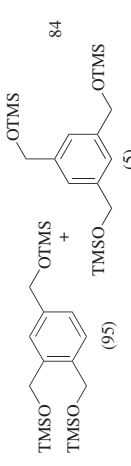
$(\text{t-Bu}_3\text{P})_2\text{NiBr}_2$

Hexane, heat, 15 h



24

TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{Pd}_2(\text{dba})_3, \text{P}(\text{C}_6\text{H}_4\text{Me-}o)_3$	$n\text{-Bu-C}\equiv\text{C-C}\equiv\text{C-Bu-}n$ THF, rt, 72 h	 (54)	93
	$\text{Zr, Ti}^a$	DME, THF, rt, 3 h	 I + II (—), I:II = 2:1	179
	$\text{Zr, Ti}^a$	3-Hexyne, DME, THF, rt, 3 h	 I + II + III + IV + V + VI	179
	$(\text{DMSO})\text{Ti}[1,2\text{-}C_6\text{H}_3(\text{TMS})_2]$	$\text{C}_6\text{D}_6$ , rt	 (95) + (5)	84

C7

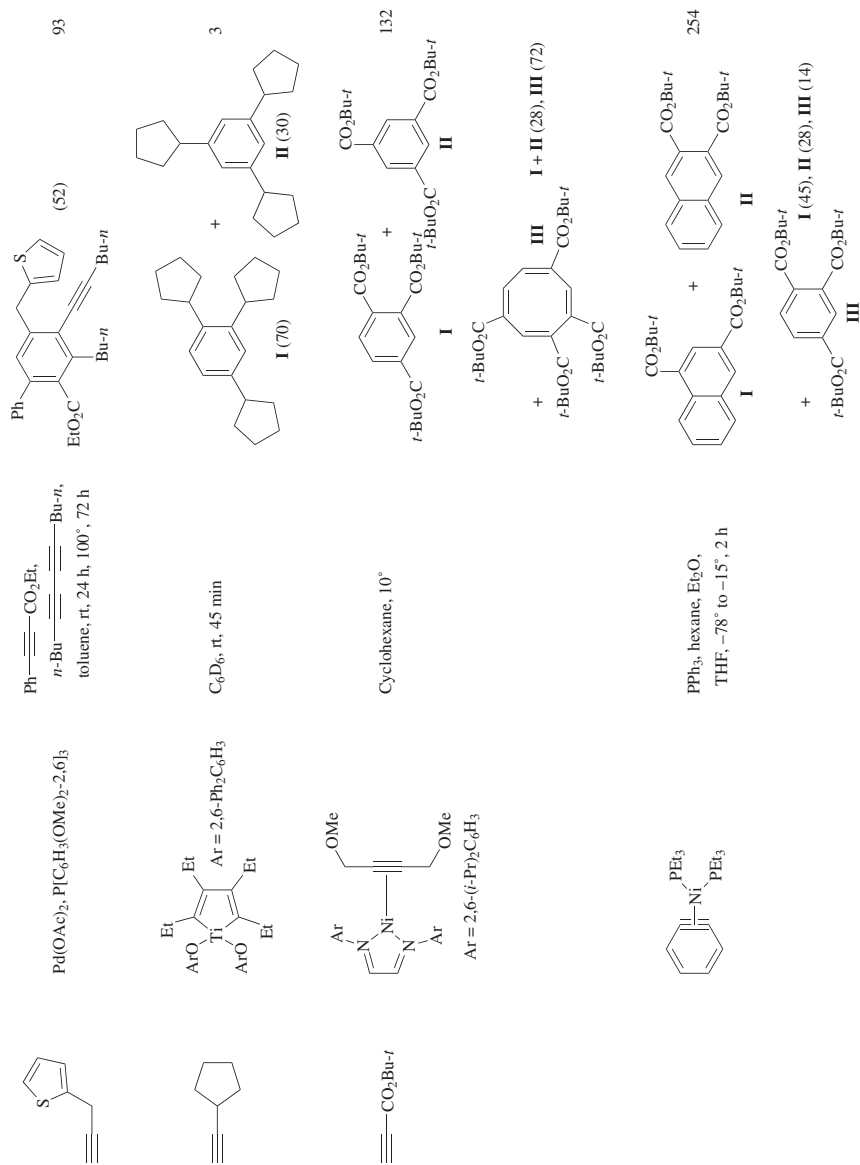
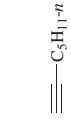
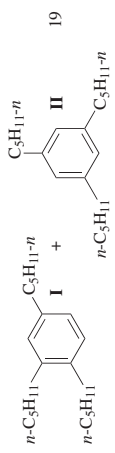
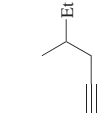
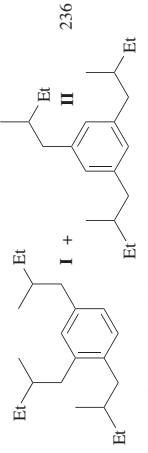
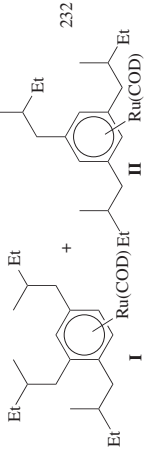
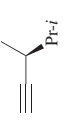
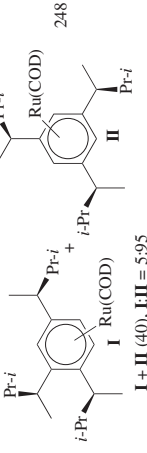
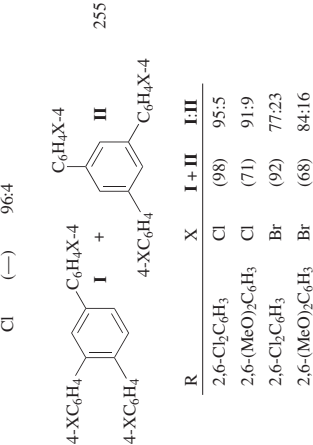
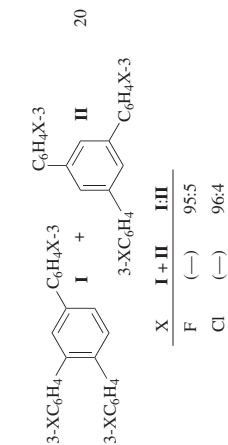
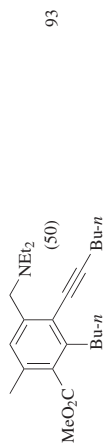
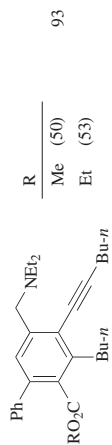


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	RhCl <sub>3</sub> , Aliquat 336	H <sub>2</sub> O, Cl <sub>2</sub> CHCHCl <sub>2</sub> , 90°, 2 h	 <b>I</b> + <b>II</b> (89), <b>I:II</b> = 87:13	19
	PdCl <sub>2</sub>	CuCl <sub>2</sub> , <i>n</i> -BuOH, C <sub>6</sub> H <sub>6</sub> , 40°, 12 h	<b>II</b> (78)	72
	PdCl <sub>2</sub>	CuCl <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> , 40°, 12 h	<b>II</b> (41)	72
	PdCl <sub>2</sub>	CuCl <sub>2</sub> , BuOH, 40°, 12 h	<b>II</b> (35)	72
	Fe(C <sub>7</sub> H <sub>8</sub> )(COD)	THF, rt, 46 h	 <b>I</b> + <b>II</b> (85), <b>I:II</b> = 55:45	236
	Ru(η <sup>6</sup> -naphthalene)(COD) (17 mol%)	THF, rt	 <b>I</b> + <b>II</b> (95), <b>I:II</b> = 25:75	232
	Ru(naphthalene)(COD) (17 mol%)	THF, rt	 <b>I</b> + <b>II</b> (40), <b>I:II</b> = 5:95	248



C<sub>8</sub>


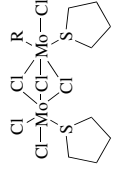
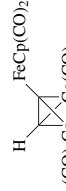
85

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																		
$\text{C}_8$ $\equiv\text{C}-\text{C}_6\text{H}_4\text{X}-4$																						
	X		<table border="1"> <thead> <tr> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>(74)</td> <td>57:43</td> </tr> <tr> <td>(95)</td> <td>9:91</td> </tr> <tr> <td>(—)</td> <td>93:7</td> </tr> <tr> <td>(45)</td> <td>22:78</td> </tr> <tr> <td>(40)</td> <td>25:75</td> </tr> <tr> <td>(90)</td> <td>0:100</td> </tr> <tr> <td>(—)</td> <td>92:8</td> </tr> <tr> <td>(—)</td> <td>96:4</td> </tr> </tbody> </table>	I + II	I:II	(74)	57:43	(95)	9:91	(—)	93:7	(45)	22:78	(40)	25:75	(90)	0:100	(—)	92:8	(—)	96:4	256 256 20 191 191 72 20 20
	I + II	I:II																				
	(74)	57:43																				
	(95)	9:91																				
	(—)	93:7																				
	(45)	22:78																				
	(40)	25:75																				
	(90)	0:100																				
	(—)	92:8																				
	(—)	96:4																				
F	HCl	ZnCl <sub>2</sub> , 7 d																				
F	HCl	85 d																				
F	[1,3-C <sub>6</sub> H <sub>8</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h																				
Cl	RhCl <sub>3</sub> , H <sub>2</sub> O (3 eq)	Toluene, 80°, 8 h																				
Cl	[Rh <sub>3</sub> O(OAc) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ]OAc	Toluene, H <sub>2</sub> O, 92°, 10 h																				
Cl	PdCl <sub>2</sub>	Toluene, H <sub>2</sub> O, 92°, 10 h																				
Cl	[1,3-C <sub>6</sub> H <sub>8</sub> RhCl] <sub>2</sub>	CuCl <sub>2</sub> , <i>n</i> -BuOH, C <sub>6</sub> H <sub>6</sub> , 40°, 15 h																				
Cl	[1,3-C <sub>6</sub> H <sub>8</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h																				
Br	[1,3-C <sub>6</sub> H <sub>8</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h																				
$\text{C}_{8-12}$ $\equiv\text{C}-\text{R}$	CpCo(CO) <sub>2</sub>	Toluene, heat, 24 h		257																		
			 (52)																			
			 (55)																			
			 (52)																			

$C_8$	$\equiv$ Ph	Si <sub>2</sub> Cl <sub>6</sub>	200°, 15 h	I + II (100), I:II = 1:1	178
—	—	HCl, 13 d	200°, 15 h	I + II (100), I:II = 1:1	256
(DMSC)TiCl <sub>2</sub> , Na		C <sub>6</sub> H <sub>6</sub> , rt, 10 min	HCl, 13 d	II (11)	28
(DMSC)Ti[C <sub>6</sub> H <sub>3</sub> (Bu-7) <sub>3</sub> -1,3,5]		C <sub>6</sub> D <sub>6</sub> , 80°	C <sub>6</sub> H <sub>6</sub> , rt, 10 min	I (54) + II (3)	234
(DMSC)Ti[C <sub>6</sub> H <sub>3</sub> (TMS) <sub>3</sub> -1,2,4]		C <sub>6</sub> D <sub>6</sub> , rt	C <sub>6</sub> D <sub>6</sub> , 80°	I (97) + II (3)	84
—	—	C <sub>6</sub> D <sub>6</sub> , rt	C <sub>6</sub> D <sub>6</sub> , rt	I (99) + II (1)	84
—	—	C <sub>6</sub> D <sub>6</sub> , rt	C <sub>6</sub> D <sub>6</sub> , rt	I (99) + II (1)	3
—	—	—	C <sub>6</sub> D <sub>6</sub> , rt	I (93) + II (7)	239
Ti(toluene)[(μ-Br)(AlBr <sub>2</sub> ) <sub>2</sub> ]	—	—	Toluene, rt, 15 h	II (76)	179
Zr, Ti <sup>iv</sup>	—	—	DME, THF, rt, 3 h	I + II (—), I:II = 1:1.4	179
Zr <sup>iv</sup>	—	—	DME, THF	I + II (95)	241
NbCl <sub>5</sub> , EtAlCl <sub>2</sub>	—	—	CCl <sub>4</sub>	I + II (100)	8
CpNbCl <sub>4</sub> , Mg	—	—	THF, 0° to rt	I + II (90), I:II = 22:78	180
NbCl <sub>5</sub>	—	—	CCl <sub>4</sub> , rt	I + II (—)	258
NbCl <sub>5</sub>	—	—	C <sub>6</sub> H <sub>6</sub> , 60°, 1 h	I (90)	221
Nb <sub>2</sub> Cl <sub>6</sub> (SC <sub>4</sub> H <sub>8</sub> ) <sub>3</sub>	—	—	Toluene	I + II (—), I:II = 1:1	259
NbCl <sub>5</sub> (DME)	—	—	CH <sub>2</sub> Cl <sub>2</sub> , rt, 12 h	I + II (87), I:II = 1:1	258
NbBr <sub>5</sub>	—	—	C <sub>6</sub> H <sub>6</sub> , 60°, 1 h	I (71)	180
TaCl <sub>5</sub>	—	—	CCl <sub>4</sub> , rt	I + II (—)	24
Ta <sub>2</sub> Cl <sub>6</sub> (SC <sub>4</sub> H <sub>8</sub> ) <sub>3</sub>	—	—	Toluene	I + II (—), I:II = 1:1	258
TaBr <sub>5</sub>	—	—	1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , 60°, 1 h	I (69)	

TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>8</sub> ≡—Ph	MoCl <sub>5</sub> , Al	DME, 50°, 3 h	I + II (92), I:II = 8:1	235	
	MoCl <sub>5</sub> , Sn	DME, 80°, 3 h	I + II (94), I:II = 12:1	235	
	MoCl <sub>5</sub> , In	DME, 80°, 1 h	I + II (94), I:II = 13:1	235	
	Mo(CO) <sub>3</sub> ( <i>N</i> -methylimidazole)	Toluene, 60°, 8 h	I + II (100), I:II = 6:94	13	
	MoCl <sub>3</sub> (C <sub>4</sub> H <sub>8</sub> S) <sub>2</sub> (Ph—  )	Acetone, 0°, 36 h	II (72)	47	
					
	MoCl <sub>3</sub> (C <sub>4</sub> H <sub>8</sub> S) <sub>3</sub>	Toluene, rt	I + II R Cl I + II Cl (—) 1:3.7 (86) 1.7:1	47	
	WCl( <i>Ge</i> -Cl <sub>3</sub> )(CO) <sub>3</sub> (NCMe) <sub>2</sub>	Toluene, rt	I + II (—), I:II = 1:5.3	47	
	Fe(C <sub>7</sub> H <sub>8</sub> /COD)	CH <sub>2</sub> Cl <sub>2</sub> , rt, 2 h	I + II (71), I:II = 45:26	14	
	CpCo(CO) <sub>2</sub> (3 mol%)	THF, rt, 46 h	I + II (75), I:II = 35:65	236	
	CpCo(CO) <sub>2</sub> (33 mol%)	scCO <sub>2</sub> (180 bar), <i>hν</i> , 90°, 24 h	I + II (22), I:II = 5:1	195	
	CpCo(CO) <sub>2</sub> (3 mol%)	scCO <sub>2</sub> (180 bar), <i>hν</i> , 90°, 24 h	I + II (15)	195	
	CpCo(CO) <sub>2</sub> (3 mol%)	scCO <sub>2</sub> (190 bar), 150°, 24 h	I + II (70)	195	
	CpCo(CO) <sub>2</sub> (3 mol%)	<i>hν</i> , 90°, 24 h	I + II (51)	195	
	CpCo(CO) <sub>2</sub>	Toluene, <i>hν</i> , 90°, 24 h	I + II (84)	195	
CpCo(CO) <sub>2</sub>	scH <sub>2</sub> O, 374°, 2 h	I + II (95), I:II = 6:1	245		
CpCo(CO) <sub>2</sub>	scH <sub>2</sub> O, 2 h	I (71) + II (24)	85		
(C <sub>5</sub> Me <sub>5</sub> )Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	scH <sub>2</sub> O (250 bar), 380°, 2 h	I (71) + II (24)	85		
Co <sub>3</sub> (CO) <sub>9</sub> (μ <sup>3</sup> -CH)	Hexane, 60°	I + II (—)	260		
Co <sub>3</sub> (CO) <sub>9</sub> (μ <sup>3</sup> -CH)	Toluene, heat, 1 h	I (96)	261		
Co <sub>2</sub> (CO) <sub>8</sub>	Toluene, 60°, 1 h	I (52)	261		
	Toluene, heat, 24 h	I + II (90)	262		
	rt, 5 h	I + II (—), I:II = 3:1	263		



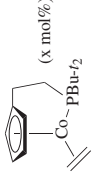
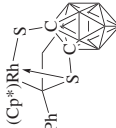

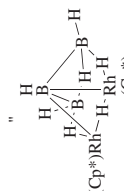
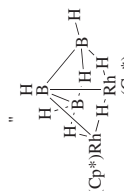
CoCl(PPh <sub>3</sub> ) <sub>3</sub>	THF, 65°, 24 h	<b>II (8)</b>	x	<b>I + II</b>	<b>I:II</b>	264
CoCl(PPh <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub>	THF, 65°, 24 h	<b>II (21)</b>	10	86	34:66	264
CoCl(PMe <sub>3</sub> ) <sub>3</sub>	THF, 65°, 24 h	<b>I (1) + II (19)</b>	5	84	31:69	264
CoCl(PMe <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub>	THF- <i>d</i> <sub>6</sub> , 65°, 18 h	<b>I (1) + II (7)</b>	2	74	25:75	264
	H <sub>2</sub> O, EtOH, rt, 7 h	<b>I + II</b>				194
(Cp*)Co(η <sup>3</sup> -allyl)	Hexane, rt, 72 h	<b>I + II (67)</b>				265
RhCl(dppe)(CO)	THF- <i>d</i> <sub>6</sub> , 40°, 24 h	<b>I (1) + II (5)</b>				191
RhCl(dppe)(CO)	THF- <i>d</i> <sub>6</sub> , 65°, 16 h	<b>I (1) + II (6)</b>				191
RhCl(dppe)(CO)	THF- <i>d</i> <sub>6</sub> , 80°, 4 h	<b>I (2) + II (9)</b>				191
RhCl(PPh <sub>2</sub> Me) <sub>2</sub> (CO)	THF- <i>d</i> <sub>6</sub> , 65°, 18 h	<b>I (3) + II (8)</b>				191
RhCl <sub>3</sub> , H <sub>2</sub> O (3 eq)	Toluene, H <sub>2</sub> O, 92°, 4 h	<b>I (10) + II (2)</b>				191
RhCl <sub>3</sub> , H <sub>2</sub> O (3 eq)	THF, 69°, 6 h	<b>I (25) + II (9)</b>				191
RhCl <sub>3</sub> , H <sub>2</sub> O (3 eq)	CH <sub>3</sub> CN, H <sub>2</sub> O, 80°, 48 h	<b>I (15) + II (3)</b>				191
RhCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	Toluene, H <sub>2</sub> O, 92°, 8 h	<b>I (9) + II (2)</b>				191
RhCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	THF, 69°, 4 h	<b>I + II (1)</b>				191
(COD)RhCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	Toluene, H <sub>2</sub> O, 92°, 4 h	<b>I (3) + II (28)</b>				191
(COD)RhCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na-3)	THF, 69°, 56 h	<b>I (5) + II (11)</b>				191
[(COD)Rh(μ-Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> -3)] <sub>2</sub>	Toluene, H <sub>2</sub> O, 92°, 4 h	<b>I (31) + II (11)</b>				191
[(COD)Rh(μ-Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> -3)] <sub>2</sub>	CH <sub>3</sub> CN, 60°, 10 h	<b>II (8)</b>				191
[(CO)RhCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H-3)(μ-SPh)] <sub>2</sub>	Toluene, H <sub>2</sub> O, 92°, 5 h	<b>I (22) + II (5)</b>				191
[(CO)RhCl(Ph <sub>2</sub> PC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H-3)(μ-SPh)] <sub>2</sub>	THF, 69°, 10 h	<b>I (26) + II (6)</b>				191
[Rh <sub>3</sub> O(OAc) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ]OAc	Toluene, H <sub>2</sub> O, 92°, 4 h	<b>I (27) + II (15)</b>				191
[Rh <sub>3</sub> O(OAc) <sub>6</sub> (H <sub>2</sub> O) <sub>3</sub> ]OAc	THF, 69°, 8 h	<b>I (26) + II (6)</b>				191
[RhCl(CO)(EtSCH <sub>2</sub> SEt)] <sub>2</sub>	CD <sub>3</sub> CN, rt	<b>I + II (100), <b>II</b> = 5:1</b>				182

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub> ≡—Ph	RhH <sub>2</sub> (H <sub>2</sub> NN=CHCH=NNH <sub>2</sub> ) (PPh <sub>3</sub> )ClO <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 3 h	I + II (—)	266
	RhCl <sub>3</sub> , Aliquat 336	H <sub>2</sub> O, Cl <sub>2</sub> CHCHCl <sub>2</sub> , 90°, 2 h	I + II (50), I:II = 84:16	19
	[1,3-C <sub>6</sub> H <sub>8</sub> RhCl] <sub>2</sub>	Toluene, 80°	I + II (—), I:II = 92:8	20
	[1,3-C <sub>6</sub> H <sub>8</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h	I + II (—), I:II = 94:6	20
	[1,3-C <sub>6</sub> H <sub>8</sub> RhCl] <sub>2</sub>	PPh <sub>3</sub> , toluene, 80°	I + II (—), I:II = 38:62	20
	Rh(acac)(CO) <sub>2</sub>	Toluene, 80°	I + II (—), I:II = 91:9	20
	Rh(acac)(CO) <sub>2</sub>	PPh <sub>3</sub> , toluene, 80°	I + II (—), I:II = 58:42	20
	(Cp*)Rh[S <sub>2</sub> C <sub>2</sub> (B <sub>10</sub> H <sub>10</sub> )]	Toluene, 70°, 17 h	I + II (—), I:II = 1:1	212
	(Cp*)Rh[S <sub>2</sub> C <sub>2</sub> (B <sub>10</sub> H <sub>10</sub> )]	Toluene, 70°, 17 h	I + II (—), I:II = 1:1	212
	(Cp*)Rh 	Toluene, 70°, 24 h	I + II (—), I:II = 1:1	212
	(Cp*)Rh 	Hexane, rt, 24 h	I + II (27), I:II = 77:23	201
	" 	THF, rt, 24 h	I + II (27), I:II = 3:1	213
	(Cp*)Rh 	Hexane, rt, 24 h	I + II (39), I:II = 81:19	201
	" "	PPh <sub>3</sub> , hexane, rt, 24 h	I + II (1)	201
	" "	Pyridine, hexane, rt, 24 h	I + II (11)	201
" "	CH <sub>3</sub> CN, hexane, rt, 24 h	I + II (39)	201	
" "	THF, rt, 24 h	I + II (39), I:II = 4:1	213	

<p>(Cp*)Rh(BH<sub>3</sub>)<sub>2</sub></p>	Hexane, rt, 20 h	201	I + II (51), I:II = 82:18																								
<p>RhCl(Phthalocyanine)</p>	180°		<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Et</td> <td>(30)</td> <td>37:63</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>(55)</td> <td>61:39</td> </tr> <tr> <td>2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub></td> <td>H</td> <td>(24)</td> <td>38:62</td> </tr> <tr> <td>2,6-(MeO)<sub>2</sub>-3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub></td> <td>Cl</td> <td>(67)</td> <td>92:8</td> </tr> <tr> <td>2,6-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub></td> <td>H</td> <td>(91)</td> <td>70:30</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	I + II	I:II	H	Et	(30)	37:63	Ph	H	(55)	61:39	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(24)	38:62	2,6-(MeO) <sub>2</sub> -3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Cl	(67)	92:8	2,6-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(91)	70:30
R <sup>1</sup>	R <sup>2</sup>	I + II	I:II																								
H	Et	(30)	37:63																								
Ph	H	(55)	61:39																								
2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(24)	38:62																								
2,6-(MeO) <sub>2</sub> -3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Cl	(67)	92:8																								
2,6-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(91)	70:30																								
<p>Ir(dppe)(CO)Br</p> <p>Ir(PPPh<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>(CO)Cl</p> <p>Cp<sub>2</sub>Ni</p> <p>Ni(CO)<sub>3</sub>(OPr<sup>t</sup>-i<sub>3</sub>)<sub>3</sub></p> <p>(K[18(crown-6)]<sub>2</sub>(η<sup>2</sup>-PhCCPh)Ni(CN)<sub>2</sub> CH<sub>3</sub>CN</p>	<p>THF-<i>d</i><sub>6</sub>, 65°, 16 h</p> <p>THF-<i>d</i><sub>6</sub>, 65°, 18 h</p> <p>115°, 6 h</p> <p>C<sub>6</sub>H<sub>6</sub>, 85°, 2 h</p> <p>CH<sub>3</sub>CN</p>		<p>I (1) + II (4) 264</p> <p>I (1) + II (1) 264</p> <p>I + II (24) 267</p> <p>I (96) 268</p> <p>I (40) 269</p>																								
<p>PdCl<sub>2</sub>(Indene-1,2-dione)</p>	CH <sub>2</sub> Cl <sub>2</sub> , rt		II (20) 217																								
<p>Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub></p>	I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h		<p>I + II (1), III (99) 243</p>																								
<p>Mo(CO)<sub>6</sub></p>	I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h		I + II (1), III (87) 243																								

TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>8</sub> ≡—Ph	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (1), <b>III</b> (87)	243
	Mo(CO) <sub>6</sub>	PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (13), <b>III</b> (86)	243
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (3), <b>III</b> (96)	243
	Mo <sub>2</sub> (CO) <sub>6</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (13), <b>III</b> (86)	243
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	I <sub>2</sub> , <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (7), <b>III</b> (86)	243
	Mo <sub>2</sub> (CO) <sub>6</sub>	I <sub>2</sub> , <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (10), <b>III</b> (84)	243
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (31), <b>III</b> (66)	243
	Mo(CO) <sub>6</sub>	PhOH, CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (38), <b>III</b> (39)	243
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , TiCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	<b>I</b> + <b>II</b> (8), <b>III</b> (4)	270
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , SnCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	<b>I</b> + <b>II</b> (20), <b>III</b> (7)	270
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , TiCl <sub>4</sub>	PhCl, rt, 24 h	<b>I</b> + <b>II</b> (66), <b>III</b> (6)	270
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , SnCl <sub>4</sub>	PhCl, rt, 24 h	<b>I</b> + <b>II</b> (27), <b>III</b> (20)	270
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , TiCl <sub>4</sub>	C <sub>6</sub> H <sub>6</sub> , rt, 24 h	<b>I</b> + <b>II</b> (18), <b>III</b> (5)	270
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , TiCl <sub>4</sub>	C <sub>6</sub> H <sub>6</sub> , rt, 20 h	<b>I</b> + <b>II</b> (15), <b>III</b> (5)	270
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , SnCl <sub>4</sub>	C <sub>6</sub> H <sub>6</sub> , rt, 24 h	<b>I</b> + <b>II</b> (4), <b>III</b> (56)	270
	Mo(NO) <sub>2</sub> (O <sub>2</sub> CPh) <sub>2</sub> , SnCl <sub>4</sub>	Toluene, rt, 24 h	<b>I</b> + <b>II</b> (66), <b>III</b> (3)	270
	Mo <sub>2</sub> Ac <sub>4</sub> , TiCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (99), ( <b>I</b> + <b>II</b> ): <b>III</b> = 96:4	242
	Mo <sub>2</sub> Ac <sub>4</sub> , TiCl <sub>4</sub>	PhCl, rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (89), ( <b>I</b> + <b>II</b> ): <b>III</b> = 93:7	242
	Mo <sub>2</sub> Ac <sub>4</sub> , TiCl <sub>4</sub>	Toluene, rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (70), ( <b>I</b> + <b>II</b> ): <b>III</b> = 91:9	242
	Mo <sub>2</sub> Ac <sub>4</sub> , TiCl <sub>4</sub>	CCl <sub>4</sub> , rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (19), ( <b>I</b> + <b>II</b> ): <b>III</b> = 89:11	242
	Mo <sub>2</sub> Ac <sub>4</sub> , SnCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (87), ( <b>I</b> + <b>II</b> ): <b>III</b> = 49:51	242
	Mo <sub>2</sub> Ac <sub>4</sub> , SnCl <sub>4</sub>	PhCl, rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (66), ( <b>I</b> + <b>II</b> ): <b>III</b> = 63:37	242
	Mo <sub>2</sub> Ac <sub>4</sub> , SnCl <sub>4</sub>	Toluene, rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (61), ( <b>I</b> + <b>II</b> ): <b>III</b> = 28:72	242
	Mo <sub>2</sub> Ac <sub>4</sub> , SnCl <sub>4</sub>	CCl <sub>4</sub> , rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (60), ( <b>I</b> + <b>II</b> ): <b>III</b> = 56:44	242
	Mo <sub>2</sub> Ac <sub>4</sub> , GeCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (82), ( <b>I</b> + <b>II</b> ): <b>III</b> = 93:7	242
	Mo <sub>2</sub> Ac <sub>4</sub> , GeCl <sub>4</sub>	PhCl, rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (70), ( <b>I</b> + <b>II</b> ): <b>III</b> = 93:7	242
	Mo <sub>2</sub> Ac <sub>4</sub> , GeCl <sub>4</sub>	Toluene, rt, 24 h	<b>I</b> + <b>II</b> + <b>III</b> (66), ( <b>I</b> + <b>II</b> ): <b>III</b> = 91:9	242

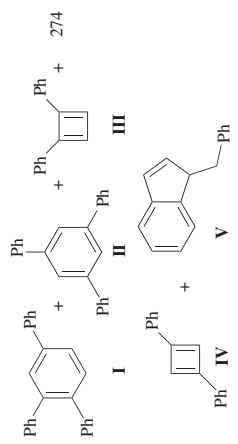
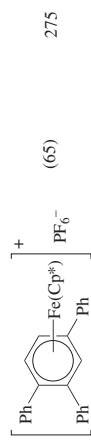
Mo <sub>2</sub> Ac <sub>4</sub> , EtAlCl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	I + II + III (100), (I + II):III = 94:6	242
MoCl(GeCl <sub>3</sub> )(CO) <sub>3</sub> (NCMe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	I + II (—), I:II = 3:1, III (17)	271
Cp*Co(CO) <sub>2</sub>	140°, 4 h	I + III (76), I:II = 66:34	272
[Ir(C <sub>3</sub> H <sub>10</sub> ) <sub>2</sub> Cl] <sub>2</sub>	THF, 60°, 5 h	I + II + III (10), (I + II):III = 100:0	273
[Ir(C <sub>3</sub> H <sub>10</sub> ) <sub>2</sub> Cl] <sub>2</sub>	CHCl <sub>3</sub> , 60°, 5 h	I + II + III (13), (I + II):III = 100:0	273
[Ir(COD) <sub>2</sub> Cl] <sub>2</sub>	THF, 60°, 5 h	I + II + III (45), (I + II):III = 2:98	273
[Ir(COD) <sub>2</sub> Cl] <sub>2</sub>	CHCl <sub>3</sub> , 60°, 5 h	I + II + III (50), (I + II):III = 10:90	273
[Ir(COD) <sub>2</sub> Cl] <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> , 60°, 5 h	I + II + III (48), (I + II):III = 4:96	273
[Ir(COD) <sub>2</sub> Cl] <sub>2</sub>	MeOH, 60°, 5 h	I + II + III (33), (I + II):III = 9:91	273
[Ir(COD)(OMe)] <sub>2</sub>	THF, 60°, 5 h	I + II + III (51), (I + II):III = 4:96	273
[Ir(COD)(OMe)] <sub>2</sub>	CHCl <sub>3</sub> , 60°, 5 h	I + II + III (53), (I + II):III = 5:95	273
[Ir(COD)(OMe)] <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> , 60°, 5 h	I + II + III (49), (I + II):III = 4:96	273
[Ir(COD)(OMe)] <sub>2</sub>	MeOH, 60°, 5 h	I + II + III (37), (I + II):III = 10:90	273
Cp <sub>2</sub> Ni	115°, 6 h	I + II (24), I:II = 84:16, III (69)	272
NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	140°, 4 h	I + II (26), I:II = 81:19, III (47)	272
PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	130°, 5 h	I + III (4), I:II = 0:100, III (86)	272
MoCl(SnCl <sub>3</sub> )(CO) <sub>3</sub> (NCMe) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 2 h	 I (66), II (32), III + IV (1), V (2)	274
MoCl(SnCl <sub>3</sub> )(CO) <sub>3</sub> (NCMe) <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub> , rt, 24 h	I (65), II (32), III + IV (2), V (1)	274
MoCl(SnCl <sub>3</sub> )(CO) <sub>3</sub> (NCPh) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 2 h	I (81), II (18), III + IV (1)	274
(Cp*)Fe(NCCH <sub>3</sub> ) <sub>3</sub> PF <sub>6</sub> (0.33 eq)	CH <sub>2</sub> Cl <sub>2</sub> , rt	 (65)	275

TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{C}_8$ 	$(\text{CO})_4\text{Fe}=\text{C}(\text{NMe}_2)\text{Ph}$ (0.33 eq)	DCE	 I + II + III = 276	
	$(\text{CO})_4\text{Fe}=\text{C}(\text{NMe}_2)\text{Ph}$ (0.33 eq)	THF	 I (16), II (0), III (15), IV (30), V (0)	276
	$(\text{CO})_4\text{Fe}=\text{C}(\text{NMe}_2)\text{Ph}$ (0.33 eq)	THF	 I (12) + II (13) + III (13) + V (18)	232
	$\text{Ru}(\eta^6\text{-naphthalene})(\text{COD})$ (17 mol%)	THF, rt, 5 h	 I + II (95), I:II = 80:20	
	$\text{Co}_2(\text{CO})_8$ (13 eq)	Heat, 1 min	 I (50) + $\text{Co}_2(\text{CO})_8(\text{PhC}_2\text{Me})$ (25) + $\text{Co}_2(\text{CO})_8(\text{HC}_2\text{Ph})_2$ (30)	226
	$\text{CoCl}(\text{PPh}_3)_3$	$\text{CH}_3\text{CN}$ , 82°, 5 h	 I + II (56), I:II = 83:17, III (0), IV (0)	222

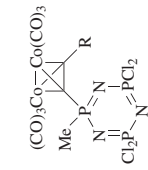
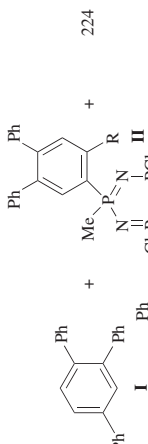
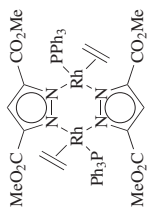
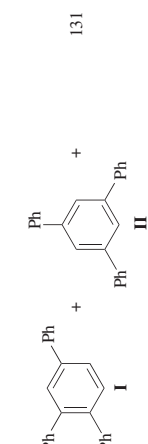
CoCl(PPh <sub>3</sub> ) <sub>3</sub>	NaOMe, CH <sub>3</sub> CN, 82°, 2 h	<b>I</b> + <b>II</b> (51), <b>III</b> (39)	222
CoCl(PPh <sub>3</sub> ) <sub>3</sub>	THF, 65°, 24 h	<b>I</b> (2) + <b>II</b> (2) + <b>III</b> (2) + <b>IV</b> (1)	208
CoCl(PMe <sub>3</sub> ) <sub>3</sub>	THF, 65°, 1 h	<b>I</b> (2) + <b>II</b> (6) + <b>III</b> (9) + <b>IV</b> (2)	208
CoCl(PMe <sub>3</sub> ) <sub>3</sub>	THF, 65°, 24 h	<b>I</b> (2) + <b>II</b> (28) + <b>III</b> (70) + <b>IV</b> (<1)	208
CoCl(PMe <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub>	THF- <i>d</i> <sub>8</sub> , 65°, 24 h	<b>I</b> (1) + <b>II</b> (2) + <b>III</b> (11) + <b>IV</b> (6)	208
RhCl(dpppe)(CO)	THF- <i>d</i> <sub>8</sub> , 65°, 78 h	<b>I</b> (2) + <b>II</b> (18) + <b>III</b> (76) + <b>IV</b> (4)	208
IrBr(dppe)(CO)	THF- <i>d</i> <sub>8</sub> , 65°, 68 h	<b>I</b> (1) + <b>II</b> (2) + <b>III</b> (1) + <b>IV</b> (1)	208
	<i>n</i> -Octane, 150°, 24 h		224
	Toluene, rt		131
Rh(dmpz)(PPh <sub>3</sub> ) <sub>3</sub>	Toluene, rt	<b>I</b> (14), <b>II</b> (3), <b>III</b> (52), <b>IV</b> (31)	131
		<b>I</b> (—) + <b>II</b> (—) + <b>III</b> (82) + <b>IV</b> (17)	131

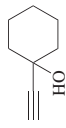
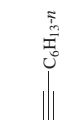
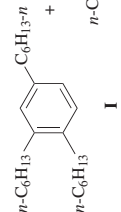
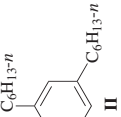

TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{C}_8$ 	$\text{CpCo}(\text{C}_2\text{H}_4)_2$	$\text{R}-\text{N}=\text{X}$ , $\text{C}_6\text{H}_6$ , $150^\circ$	 <b>I</b> + <b>II</b> + 192	192
			 <b>III</b> + <b>IV</b>	
	$6,6,6\text{-}(\text{PPh}_3)_3\text{H-}trido\text{-}6\text{-IrB}_9\text{H}_{13}$ (3 mol%)	$\text{CH}_2\text{Cl}_2$ , microwave, 3.5 min	$2\text{-}(\eta^6\text{-C}_6\text{H}_3\text{Ph}_3)\text{-}c\text{-}los\text{-}2\text{-IrB}_9\text{H}_6\text{-}10\text{-}(\text{PPh}_3)$ (29)	277
	$[(\text{PhCC}_2\text{Ni})_3]$	$\text{C}_6\text{H}_6$ , $70^\circ$	 <b>I</b> + <b>II</b>	278
	Catalyst	$\text{R}-\text{C}\equiv\text{C}-\text{R}$ , THF	$\text{I} + \text{II}$ (90), $\text{I:II} = 1:1$	93
	Catalyst	Temp Time	$\text{R}-\text{C}\equiv\text{C}-\text{R}$	
	$\text{Pd}_2(\text{dba})_3$ , $\text{P}(\text{C}_6\text{H}_4\text{Me-}o)_3$	$60^\circ$ 53 h	$\text{R}-\text{C}\equiv\text{C}-\text{R}$ (65)	
	$\text{Pd}(\text{PPh}_3)_4$	$100^\circ$ 12 h	$n\text{-Bu}$ (89)	
	$\text{Pd}_2(\text{dba})_3$ , $\text{P}(\text{C}_6\text{H}_4\text{Me-}o)_3$	rt 54 h	$n\text{-Bu}$ (82)	





TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $C_8$	$Ni(NCS)_2[P(Bu-n)_3]_2$	$C_6H_6$ , 48 h	<b>I</b> (15)	281
	$Ni(NCS)_2(PPh_3)_2$	$C_6H_6$ , 72 h	<b>I</b> (30)	281
 $n-C_6H_{13-n}$	$MoCl_5$ , metal	DME, 80°	 <b>I</b> + <b>II</b>	235
			 <b>II</b>	
		Time	<b>I</b> + <b>II</b> <b>I:II</b>	
		1 h	(90)	8:1
		3 h	(75)	3.5:1
		3 h	(70)	6:1
		3 h	(44)	1.4:1
		3 h	(34)	1.1:1
		24 h	(32)	3.3:1
			<b>I</b> + <b>II</b> (77), <b>I:II</b> = 83:17	19
	$RhCl_3$ , Aliquat 336	$H_2O$ , $Cl_2CHCHCl_2$ , 90°, 2 h	<b>I</b> + <b>II</b> (39), <b>I:II</b> = 62:38	209
	$(C_9H_7)Rh(C_2H_4)_2$	<i>o</i> -Xylene, 160°, 112 h	<b>I</b> + <b>II</b> (34), <b>I:II</b> = 67:33	209
	$(C_9H_7)Rh(C_8H_{14})_2$	<i>o</i> -Xylene, 160°, 119 h	<b>I</b> + <b>II</b> (30), <b>I:II</b> = 68:32	209
	$(C_9H_7)Rh(COD)$	<i>o</i> -Xylene, 160°, 119 h	<b>I</b> + <b>II</b> (47), <b>I:II</b> = 62:38	209
	$(C_{13}H_8)Rh(COD)$	<i>o</i> -Xylene, 160°, 119 h	<b>II</b> (70)	72
	$PdCl_2$	$CuCl_2$ , <i>n</i> -BuOH, $C_6H_6$ , 40°, 12 h		
	$(Cp^*)Fe(NCCH_2)_3PF_6$ (0.33 eq)	$CH_2Cl_2$ , rt	 <b>(65)</b>	275

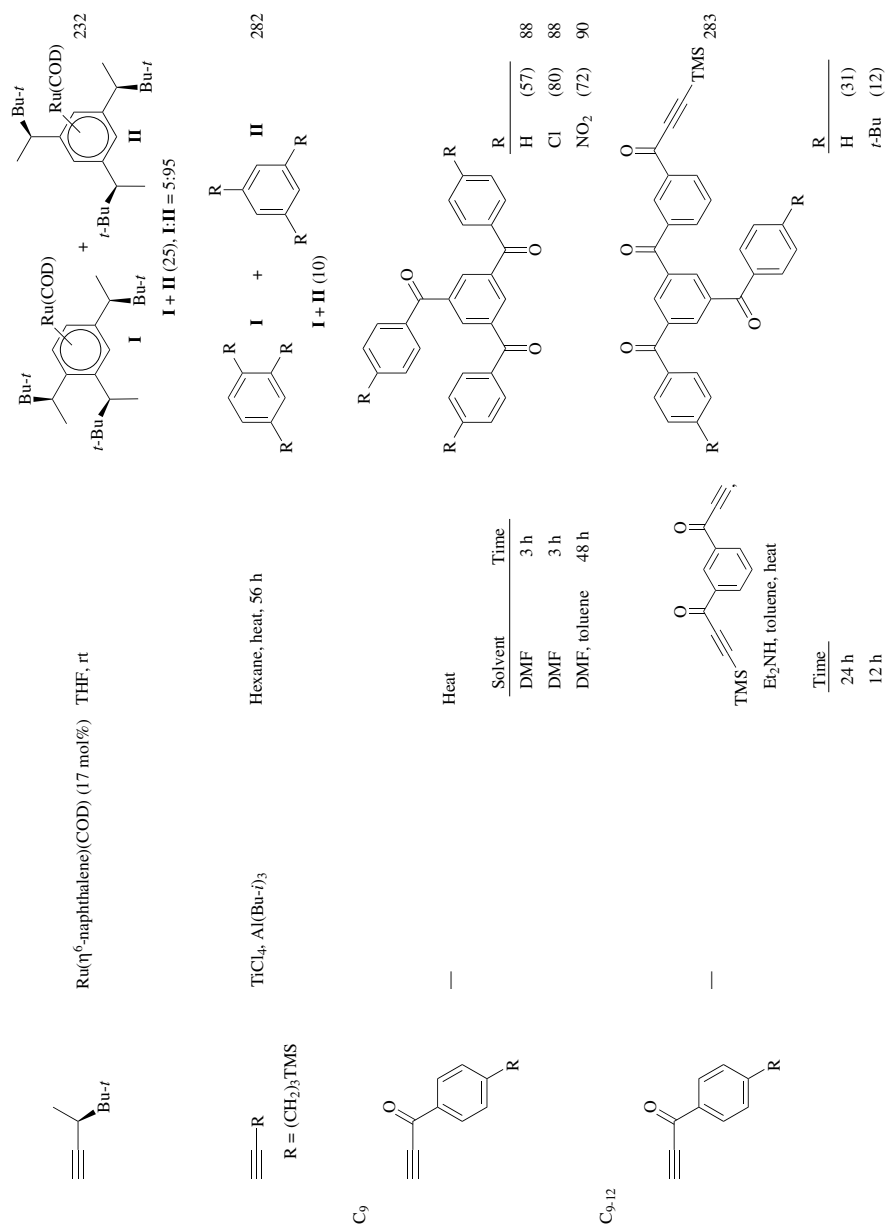
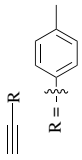
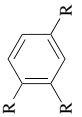
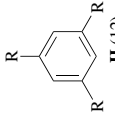

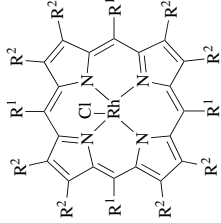
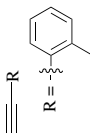
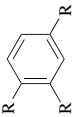
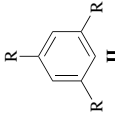


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																
$\text{C}_9$  $\text{R} = \text{---}$	—	4 d	 <b>I (0)</b> +  <b>II (12)</b>	256																
	(DMSO)TiCl <sub>2</sub> , Na 	C <sub>6</sub> D <sub>6</sub> , 80°	<b>I (97) + II (3)</b>	234																
	RhCl <sub>3</sub> , H <sub>2</sub> O (3 eq) Rh <sub>3</sub> (OAc) <sub>9</sub> (H <sub>2</sub> O) <sub>3</sub> OAc	H <sub>2</sub> O, EtOH, 25°, 7 h Toluene, H <sub>2</sub> O, 92°, 6 h Toluene, H <sub>2</sub> O, 92°, 8 h	<b>I + II (81), I:II = 43:57</b> <b>I (10) + II (35)</b> <b>I (27) + II (12)</b>	194 191 191																
	 Rhodium complex with porphyrin ligand and Cl	180°	<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(30)</td> <td>63:37</td> </tr> <tr> <td>2,6-(MeO)<sub>2</sub>-3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub></td> <td>Cl</td> <td>(90)</td> <td>85:15</td> </tr> <tr> <td>2,6-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub></td> <td>H</td> <td>(68)</td> <td>89:11</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	I + II	I:II	H	H	(30)	63:37	2,6-(MeO) <sub>2</sub> -3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Cl	(90)	85:15	2,6-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(68)	89:11	255
R <sup>1</sup>	R <sup>2</sup>	I + II	I:II																	
H	H	(30)	63:37																	
2,6-(MeO) <sub>2</sub> -3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Cl	(90)	85:15																	
2,6-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(68)	89:11																	
	PtCl <sub>2</sub>	CuCl <sub>2</sub> , <i>n</i> -BuOH, C <sub>6</sub> H <sub>6</sub> , 40°, 15 h	<b>II (95)</b>	72																
 $\text{R} = \text{---}$	[1,3-C <sub>6</sub> H <sub>4</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h	 <b>I</b> +  <b>II</b> <b>I + II (—), I:II = 93:7</b>	20																

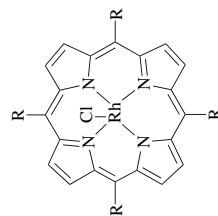
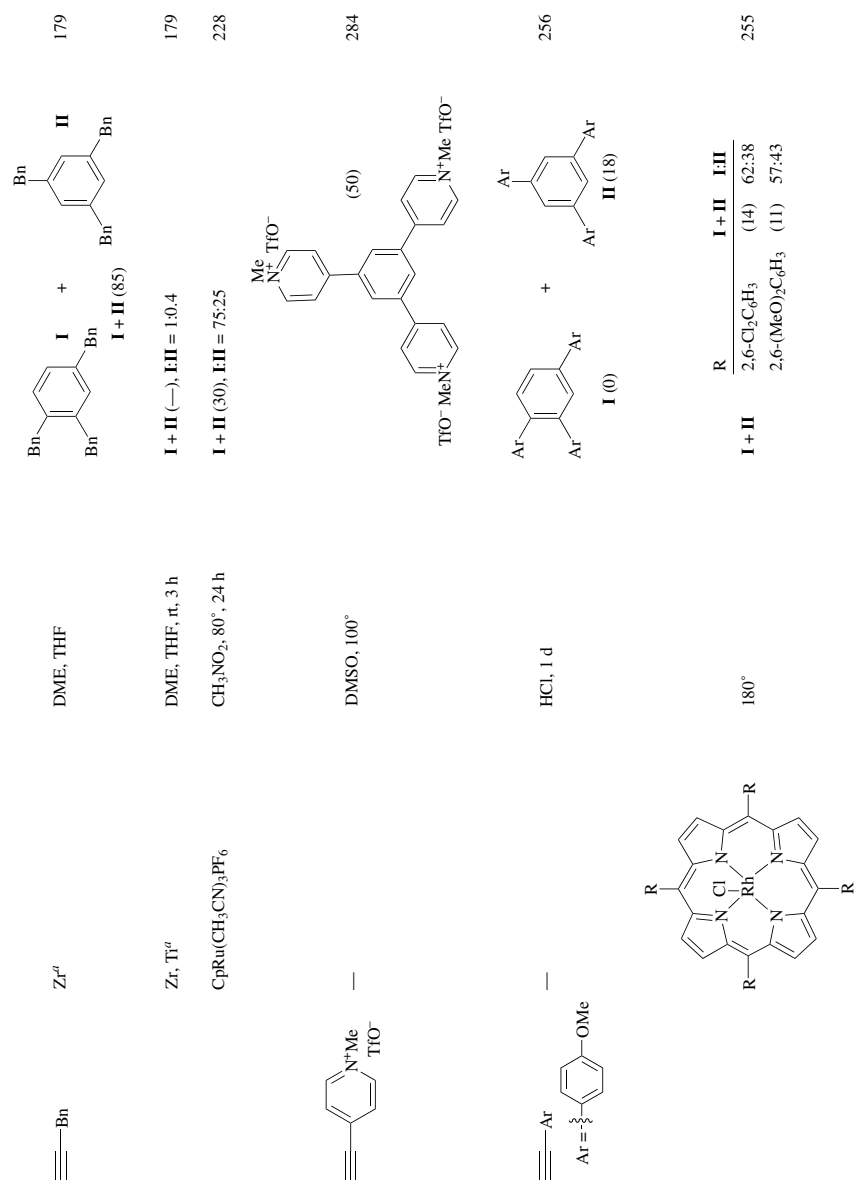


TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																
$\text{C}_9$ 	$[\text{1,5-C}_6\text{H}_9\text{RhCl}]_2$ 	Toluene, 80°, 4 h	 <b>I + II</b> (—), <b>I:II</b> = 92:8	20																
		180°	<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th><b>I + II</b></th> <th><b>I:II</b></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(21)</td> <td>81:19</td> </tr> <tr> <td>2,6-(MeO)<sub>2</sub>-3,5-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub></td> <td>Cl</td> <td>(64)</td> <td>86:14</td> </tr> <tr> <td>2,6-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub></td> <td>H</td> <td>(45)</td> <td>96:4</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	<b>I + II</b>	<b>I:II</b>	H	H	(21)	81:19	2,6-(MeO) <sub>2</sub> -3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Cl	(64)	86:14	2,6-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(45)	96:4	255
R <sup>1</sup>	R <sup>2</sup>	<b>I + II</b>	<b>I:II</b>																	
H	H	(21)	81:19																	
2,6-(MeO) <sub>2</sub> -3,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Cl	(64)	86:14																	
2,6-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	(45)	96:4																	
		THF, 80°, 24 h	<b>I + II</b> (47)	285																
		THF, rt, 3 h	<b>I + II</b> (90), <b>I:II</b> = 30:70	232																
		THF, 0° to rt	<b>I + II</b> (83), <b>I:II</b> = 46:54	8																

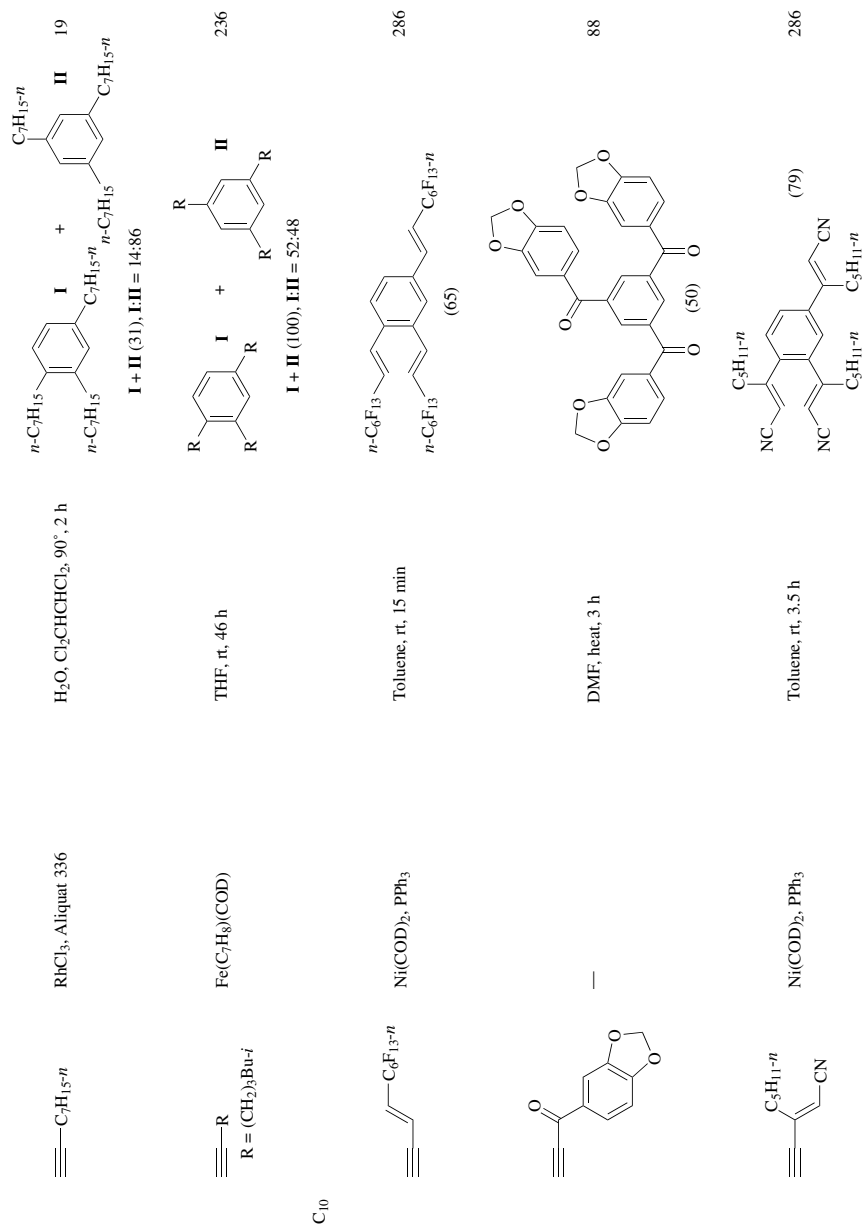
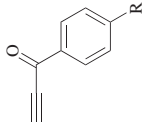
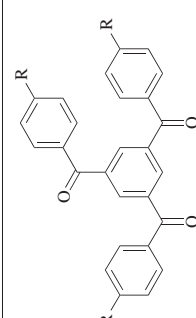

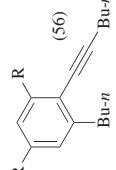
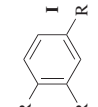
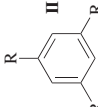
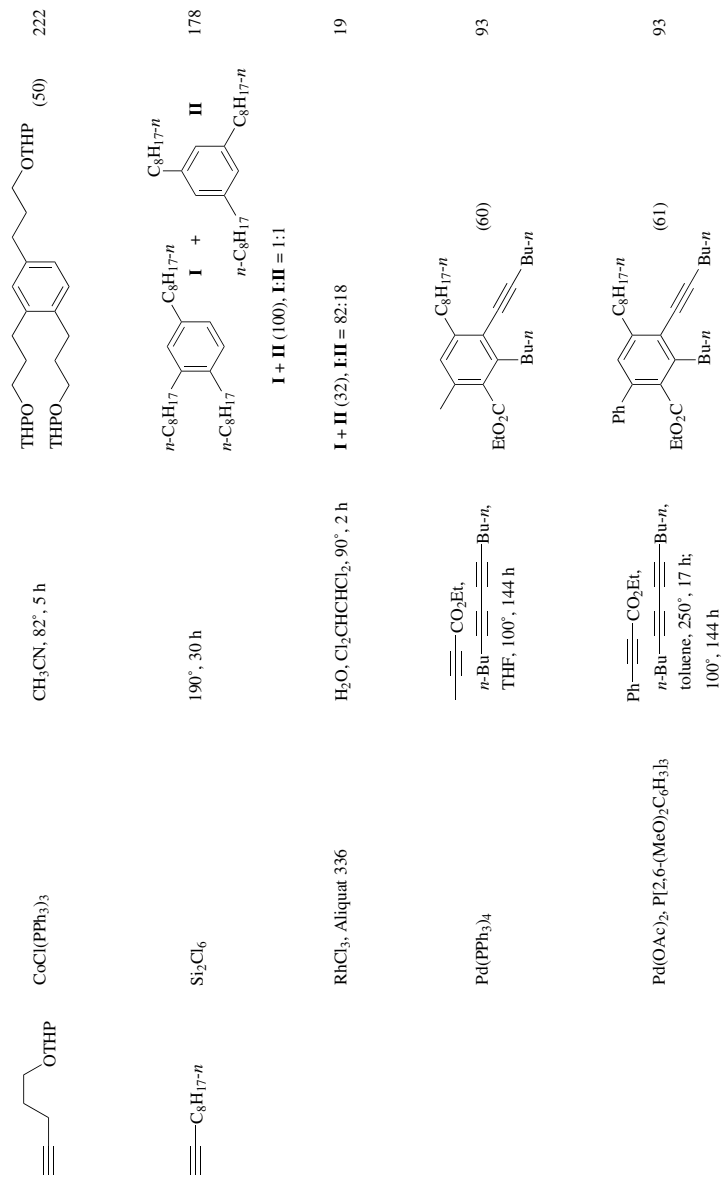


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{10}$ 	—	DMF, heat		88 88 89
 $R = (CH_2)_2Ph$	$Pd_2(dba)_3, P(C_6H_4Me-o)_3$	$n-Bu-C\equiv C-C\equiv C-Bu-n$ THF, rt, 72 h; 60°, 30 h	 (56)	93
	$V(acac)_3$	$AlEt_3$ , toluene, rt, 1 h; 120°, 48 h	 <b>I</b> +  <b>II</b> <b>I (2) + II (2)</b>	7
	$V(acac)_3$	$AlEt_3$ , toluene, 90°, 1 h; 120°, 48 h	<b>I (15) + II (6)</b>	7
	$V(acac)_3$	$AlEt_3$ , hexane-toluene, rt, 1 h; rt, 6 h	<b>I (6) + II (5)</b>	7
	$V(acac)_3$	$AlEt_3$ , hexane, rt, 1 h; rt, 6 h	<b>I (16) + II (4)</b>	7
	$V(acac)_3$	$AlEt_3$ , sonication, rt, 1 h; rt, 6 h	<b>I (5) + II (2)</b>	7
	$V(acac)_3$	$AlEt_3$ , hexane-toluene, rt, 1 h; 50°, 6 h	<b>I (13) + II (7)</b>	7





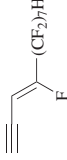
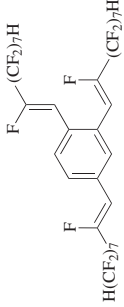

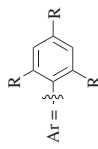
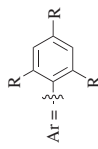
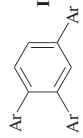
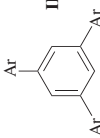

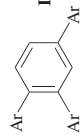
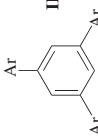

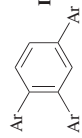
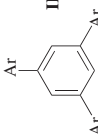
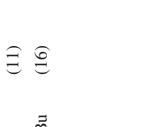
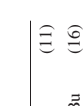
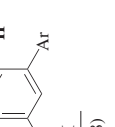
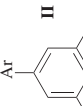
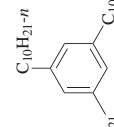

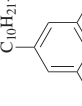
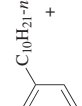
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{11}$ 	Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	Toluene, rt, 5.5 h	 (78)	286
$C_{11-12}$   Ar = 	[1,3-C <sub>6</sub> H <sub>6</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h	 I +  II	20
$C_{11-12}$ 	[1,3-C <sub>6</sub> H <sub>6</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h	 I +  II R    I+II    I:II OMe   (—)   72:28 Me    (—)   67:33	20
$C_{11-12}$  Ar 2-TMSC <sub>6</sub> H <sub>4</sub> 1-naphthyl 2-naphthyl	[1,3-C <sub>6</sub> H <sub>6</sub> RhCl] <sub>2</sub>	Toluene, 80°, 4 h	 I +  II I+II    I:II (—)    76:24 (—)    9:1 (—)    89:11	20



TABLE 1. MONOSUBSTITUTED ALKYNES (Continued)

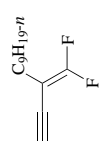
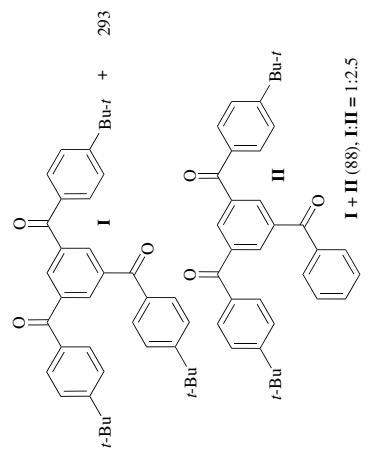
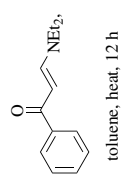
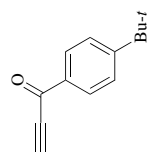
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{12-16}$ 	$CpCo(CO)_2$	$C_8H_{16}$ , heat, 24 h	 R H (11) <i>t</i> -Bu (16)	289
$C_{12-14}$ 	Catalyst $\frac{\text{Catalyst}}{Ni(COD)_2, PPh_3}$ $Ni(COD)_2$ $Ni(COD)_2, PPh_3$	THF, rt, 5 h	 I + II R I II THP (66) (8) THP (33) (8) Bn (50) (5)	290
$C_{12}$ 	$NbCl_5, Zn$ 	$THF, C_6H_6$ , rt, 1 h $H_2O, EtOH$ , rt, 7 h $PPh_3, CH_2Cl_2$ , rt, 18 h $P(Bu-n)_3, CH_2Cl_2$ , rt, 18 h dppe, $CH_2Cl_2$ , rt, 18 h depe, $CH_2Cl_2$ , rt, 18 h Tol-BINAP, $CH_2Cl_2$ , rt, 18 h	 I + II (91), I:II = 23:77  I + II (5) I + II (3) I + II (3) I + II (2) I + II (95), I:II = 64:36	291 194 292 292 292 292 292

[Rh(COD)Cl]<sub>2</sub> 292  
 Rh(COD)<sub>2</sub>BF<sub>4</sub> 292  
 Ir(COD)<sub>2</sub>BF<sub>4</sub> 292

Tol-BINAP, CH<sub>2</sub>Cl<sub>2</sub>, rt, 18 h  
 DTBM-SEGPHOS, CH<sub>2</sub>Cl<sub>2</sub>,  
 rt, 24 h  
 Tol-BINAP, CH<sub>2</sub>Cl<sub>2</sub>, rt, 18 h

**I + II (2)**  
**I + II (91), I:II = 83:17**  
**I + II (2)**

C<sub>13</sub>



Ni(COD)<sub>2</sub>, PPh<sub>3</sub>

Toluene, rt, 20 h

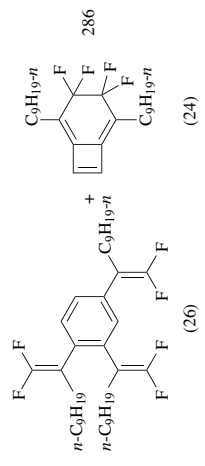
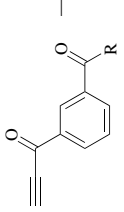
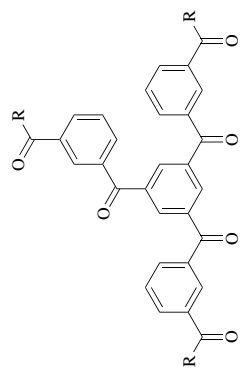

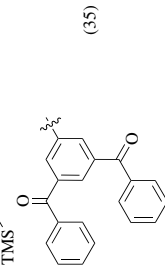
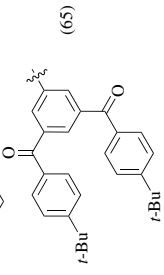
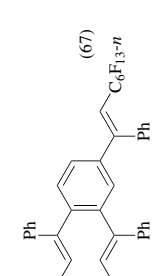
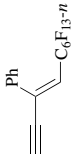
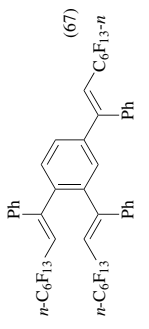


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	—	$\text{Et}_2\text{NH}$ , toluene, heat	 283	
		Time	 (40)	
		12 h	 (35)	
		26 h	 (65)	
		24 h	 (67)	
	$\text{Ni}(\text{COD})_2, \text{PPh}_3$	Toluene, rt, 15 min	 286	

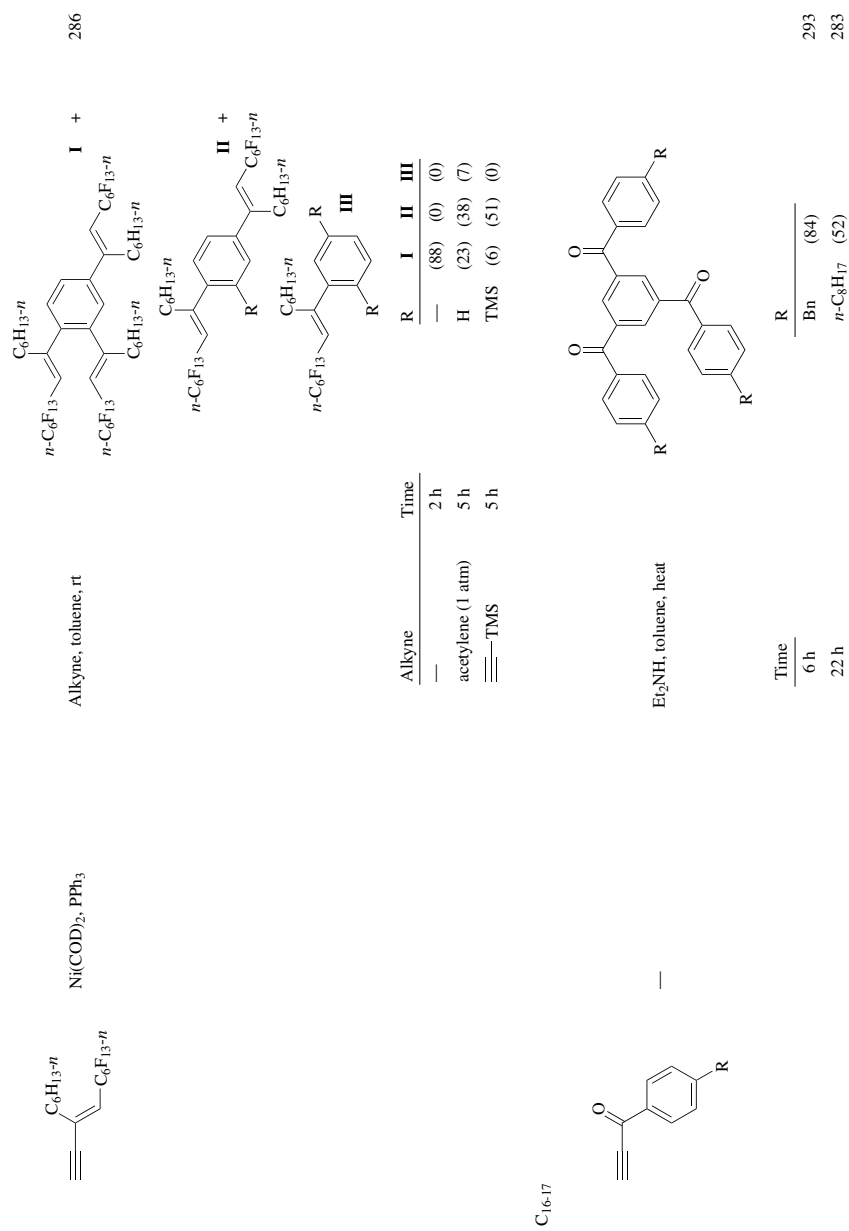
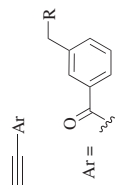
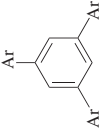
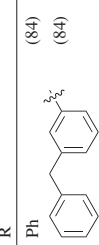
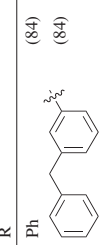
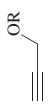
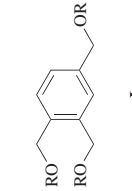
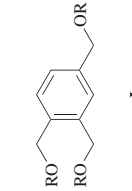
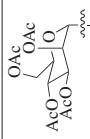
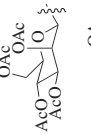
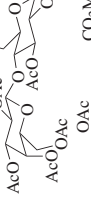
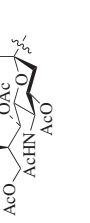
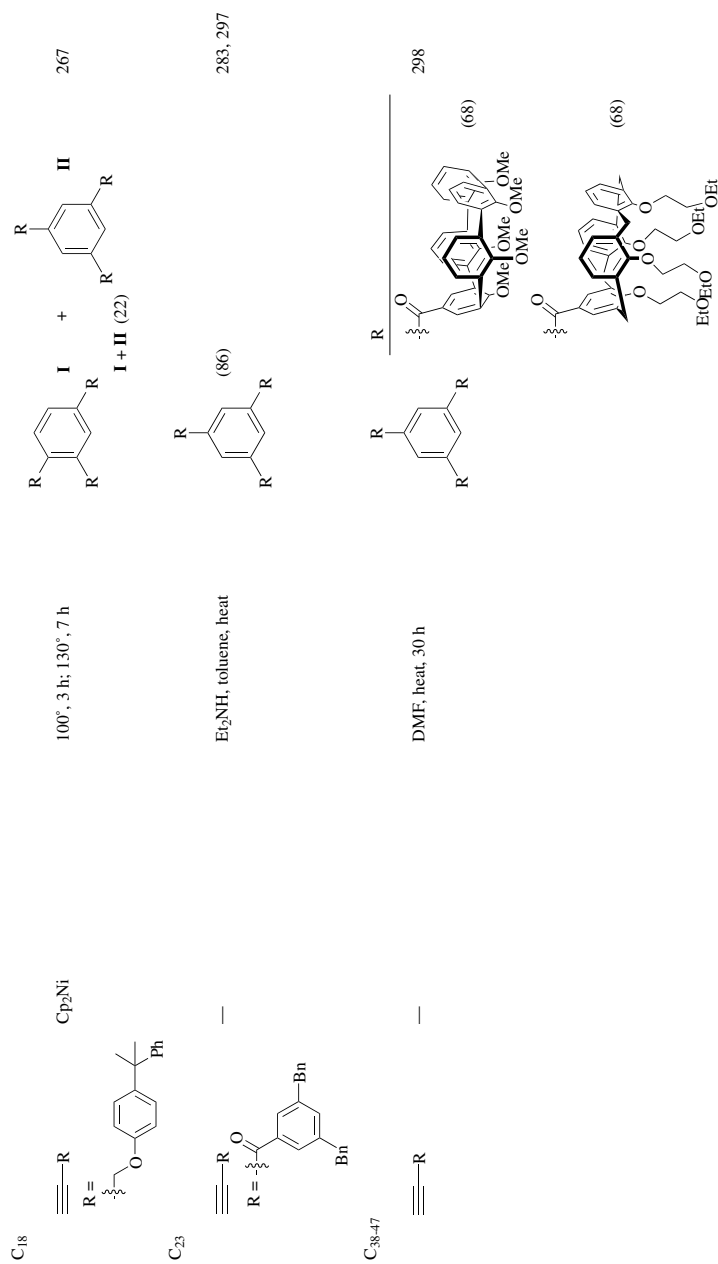


TABLE I. MONOSUBSTITUTED ALKYNES (Continued)

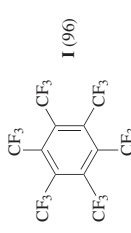
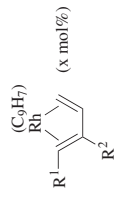
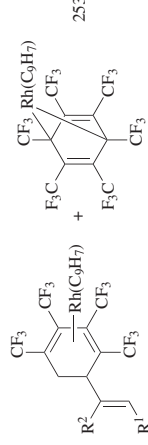
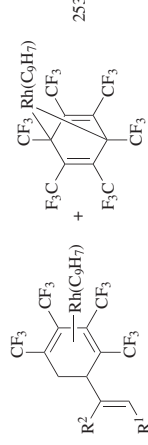
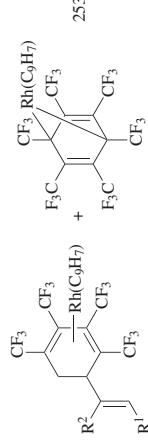
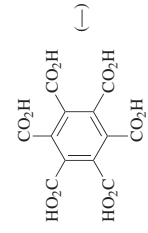
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.				
$\text{C}_{16-23}$  $\text{Ar} =$ 	—	$\text{Et}_2\text{NH}$ , toluene, heat  Time 6 h 12 h	 (84)  (84)	283 294, 283				
$\text{C}_{16-29}$ 	Catalyst		 I  II I + II I:II					
	Catalyst	Solvent	Temp	Time	R	I + II	I:II	
	$\text{Ru}(\equiv\text{CHPh})\text{Cl}_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$	$\text{CH}_2\text{Cl}_2$	rt	12 h	 (75)	(75)	90:10	79
	$\text{Co}_2(\text{CO})_8$	1,4-dioxane	heat	2 h	"	(63)	10:1	295
	$\text{Co}_2(\text{CO})_8$	1,4-dioxane	heat	2 h	 (72)	(72)	90:10	79
	$\text{Co}_2(\text{CO})_8$	1,4-dioxane	heat	2 h	 (66)	(66)	90:10	79
	$\text{Co}_2(\text{CO})_8$	1,4-dioxane	heat	2 h	 (68)	(68)	90:10	296





<sup>a</sup> The catalyst is prepared by reduction of the corresponding chloride salt.

TABLE 2. DISUBSTITUTED ALKYNES

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.															
$\text{CF}_3\text{---}\text{C}\equiv\text{C---CF}_3$	[Rh( $\mu$ -SC <sub>6</sub> F <sub>5</sub> )(COD)] <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> , rt, 1 h	 I (96)	86															
	[Rh( $\mu$ -SC <sub>6</sub> F <sub>5</sub> H-4)(COD)] <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> , rt, 1 h	I (92)	86															
	[Rh( $\mu$ -SC <sub>6</sub> H <sub>4</sub> F)(COD)] <sub>2</sub> [Rh(PPh <sub>3</sub> )]HCTf <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> , rt, 1 h CH <sub>2</sub> Cl <sub>2</sub> , 80°, overnight	I (88) I (—)	86 299															
	 (x mol%)	Hexane, rt	 I	253															
			 II																
$\text{HO}_2\text{C---C}\equiv\text{C---CO}_2\text{H}$	[Cp*] <sub>2</sub> RuCl <sub>2</sub>	<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>x</th> <th>I</th> <th>II</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>H</td> <td>13</td> <td>(12)</td> <td>(23)<sup>a</sup></td> </tr> <tr> <td>H</td> <td>Me</td> <td>20</td> <td>(30)</td> <td>(42)</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	x	I	II	Me	H	13	(12)	(23) <sup>a</sup>	H	Me	20	(30)	(42)		
		R <sup>1</sup>	R <sup>2</sup>	x	I	II													
Me	H	13	(12)	(23) <sup>a</sup>															
H	Me	20	(30)	(42)															
THF, 70°, 14 h	 (—)	190																	

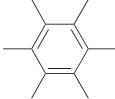

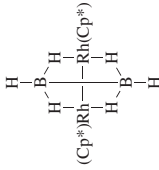
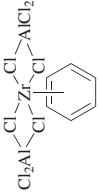
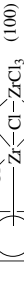
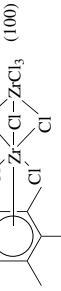


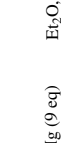


	(58)	Methylcyclohexane, 80°, 1.5 h	Ti( $\eta^6$ -toluene)[( $\mu$ -Br)(AlBr <sub>2</sub> )] <sub>2</sub>	239
	(9)	Methylcyclohexane, rt, 15 h	Ti( $\eta^4$ -C <sub>4</sub> Me <sub>4</sub> )[( $\mu$ -Br)(AlBr <sub>2</sub> )] <sub>2</sub>	239
	(50)	CH <sub>3</sub> CN, rt, 15 h	Mo( $\eta^1$ -NC <sub>2</sub> H <sub>3</sub> (Me) <sub>2</sub> -2,6)	300
	(100)	THF, rt, 28 h	Fe(C <sub>7</sub> H <sub>8</sub> )(COD)	236
	(-)	rt	CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	174
	(5)	scH <sub>2</sub> O, 374°, 2 h	CpCo(CO) <sub>2</sub>	245
	(92)	Pentane, rt, 24 h		301
	(2)	Hexane, rt, 24 h		201
	(70)	H <sub>2</sub> O, Cl <sub>2</sub> CHCHCl <sub>2</sub> , 90°, 29 h	RhCl <sub>3</sub> , Aliquat 336	19
	(35)	THF, 40°	NiBr <sub>2</sub> , Mg	185
	I (61)	CH <sub>2</sub> Cl <sub>2</sub> , 24 h	TiCl <sub>4</sub> (7 eq)	302
	I (60)	1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	TiCl <sub>4</sub> (7 eq)	302
	(-)	—		303

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub> 	ZrCl <sub>4</sub> (2 eq)	Hexane	 (100)	5
	Catalyst	1. Et <sub>2</sub> O, 8 h 2.  -R, rt	 R	6
	Catalyst			
	CpZr(dmpe) <sub>2</sub> Cl		H (100)	
	CpZr(dmpe) <sub>2</sub> Cl		Me (100)	
	CpZr(dmpe) <sub>2</sub> Me		H (100)	
	CpZr(dmpe) <sub>2</sub> Me		Me (100)	
	Ta(DIPP) <sub>2</sub> Cl <sub>3</sub> , Na/Hg (9 eq)	Et <sub>2</sub> O, -30°	 Ta(DIPP) <sub>2</sub> Cl (65)	45
	Ta(DIPP) <sub>2</sub> Cl <sub>3</sub> (2 eq)	—	 Cl(DIPP) <sub>2</sub> Ta (—)	304
	Ru(η <sup>6</sup> -naphthalene)(COD) (17 mol%)	THF, rt, 2 h	 Ru(COD) (95)	232

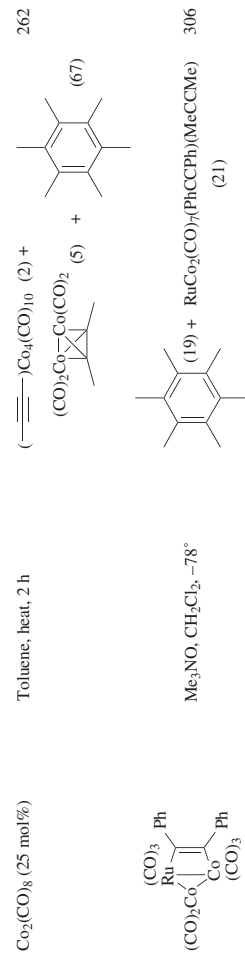
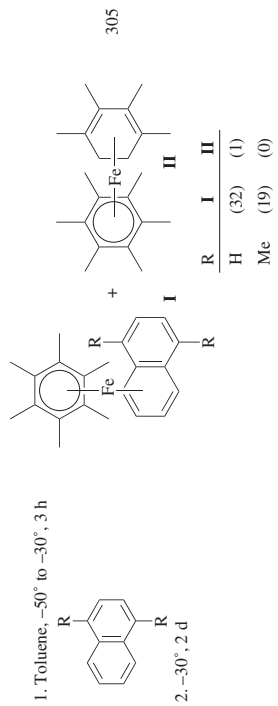
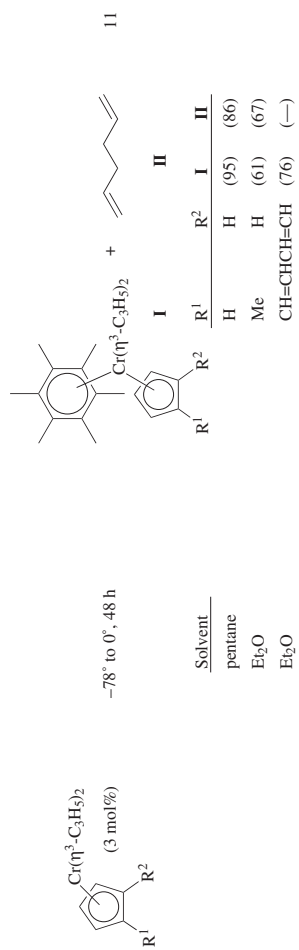

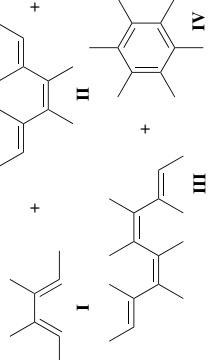
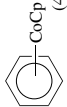
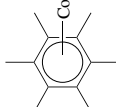
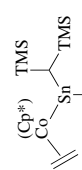
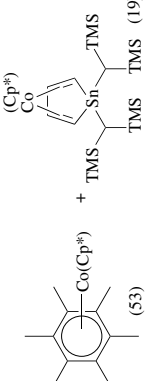


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{Co}(\text{NC}_3\text{H}_5)_2\text{BPh}_4$	$\text{H}_2$ (1 atm), pyridine, rt		246
	$\text{Co}(\text{NC}_3\text{H}_5)_2\text{BPh}_4$	$\text{H}_2$ (50 atm), pyridine, rt	<b>I</b> (1), <b>II</b> (16), <b>III</b> (81), <b>IV</b> (2)	246
	 (4 mol%)	Toluene, 100°, 20 h	<b>I</b> (—)	307
	$\text{CpCo}(\text{C}_2\text{H}_4)_2$	Hexane, -10°	<b>I</b> (46)	174
	$(\text{Cp}^*)\text{Co}(\eta^3\text{-allyl})$ (6 mol%)	Hexane, 80°, 5.5 h	 (100)	265
	 (10 mol%)	$\text{Et}_2\text{O}$ , rt, 1.3 h		308

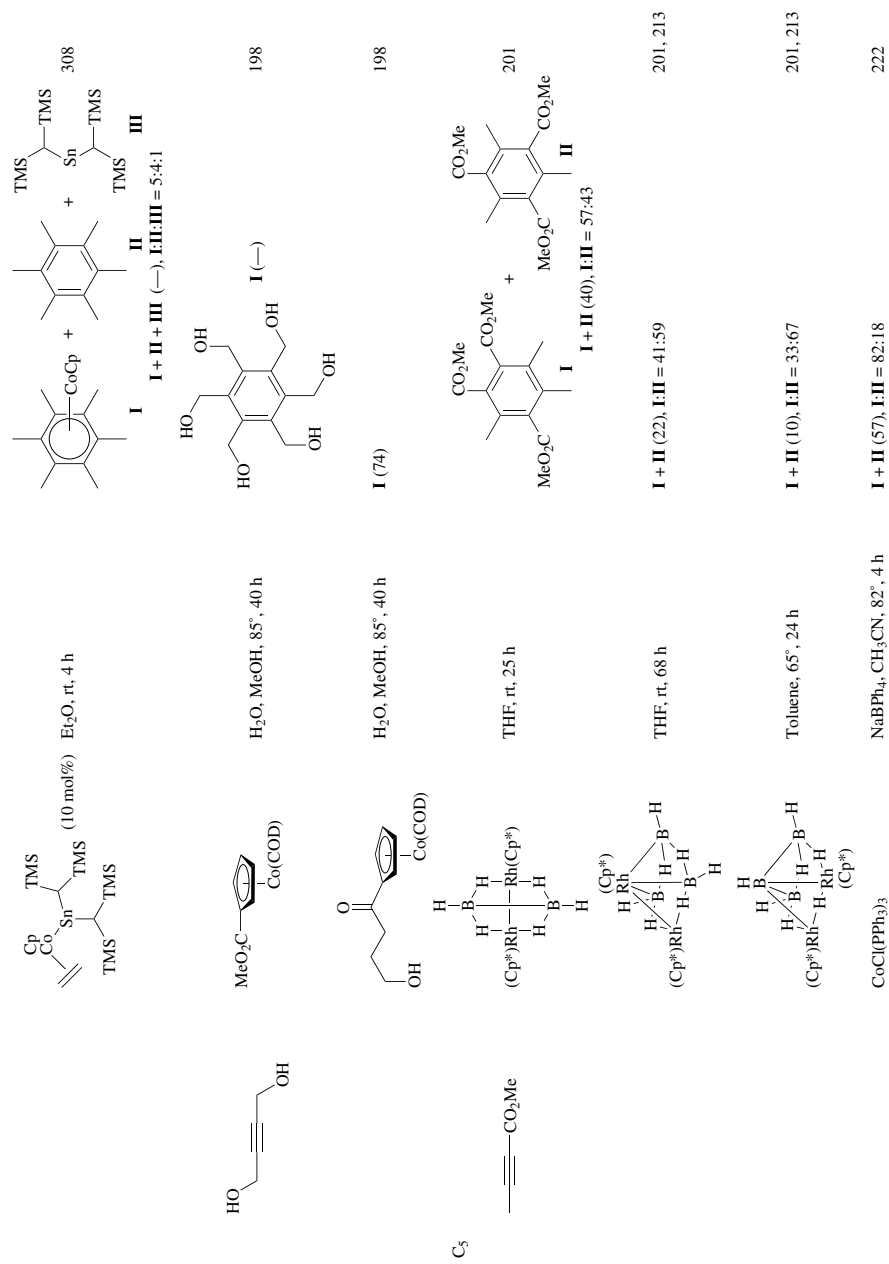
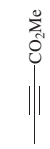
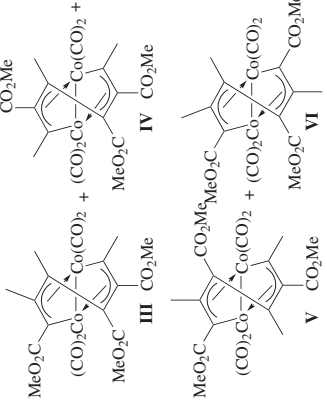

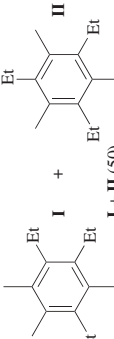


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>5</sub> 	Co <sub>2</sub> (CO) <sub>8</sub> (12 mol%)	Toluene, heat, 24 h	<p><b>I + II +</b></p> 	262
C <sub>6</sub> 	Pd(OAc) <sub>2</sub>	<p>1. Chlorohydroquinone, NPMoV, CH<sub>3</sub>SO<sub>3</sub>H, O<sub>2</sub>, dioxane, 60°, 2 h</p> <p>2. O<sub>2</sub>, 60°, 2 h</p>	<p><b>I + II</b> (95), <b>I:II</b> = 8:1; <b>III + IV</b> (3), <b>V + VI</b> (1)</p> 	249
	Mo(CO) <sub>3</sub> (pyrazole) <sub>3</sub>	Toluene, 60°, 8 h	(—)	13
	Mo(CO) <sub>3</sub> (pyrazole) <sub>3</sub>	Toluene, rt, 8 h	(—)	13
	Mo(CO) <sub>2</sub> (pyrazole) <sub>2</sub> (DMAD) <sub>2</sub>	Toluene, 60°, 8 h	(—)	13
	Mo(CO) <sub>2</sub> (N-methylimidazole)	Toluene, 60°, 8 h	(100)	13



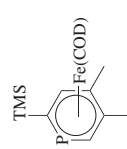
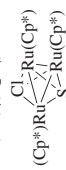
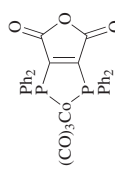
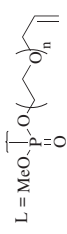
	80°	(—)	309
(Cp*)RuCl(COD)	DCE, rt, 1 h	(88)	56
Ru(CO) <sub>4</sub> (C <sub>2</sub> H <sub>4</sub> )	C <sub>2</sub> H <sub>4</sub> , hexane, rt to 80°	(98)	16
(Cp*)Ru(  )	THF, 50°	(—)	203
CpCo(CO) <sub>2</sub>	seCO <sub>2</sub> (220 bar), <i>hν</i> , 90°, 24 h	(17)	195
CoCl(PPH <sub>3</sub> ) <sub>3</sub>	NaBPh <sub>4</sub> , CH <sub>3</sub> CN, rt, 1 h	(62)	222
CoCl(PPH <sub>3</sub> ) <sub>3</sub>	THF, 65°, 1 h	(87)	208
CoCl(PPH <sub>3</sub> ) <sub>3</sub>	THF, 65°, 24 h	(100)	208
CoCl(PPH <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub>	THF, 65°, 24 h	(95)	208
CoCl(PMe <sub>3</sub> ) <sub>3</sub>	THF, 65°, 24 h	(76)	208
CoCl((PMe <sub>3</sub> ) <sub>2</sub> (CO) <sub>2</sub>	THF- <i>d</i> <sub>6</sub> , 65°, 24 h	(97)	208
	CH <sub>2</sub> Cl <sub>2</sub> , rt, 48 h	(35)	310
"	CH <sub>2</sub> Cl <sub>2</sub> , rt, 96 h	(70)	310
"	CH <sub>2</sub> Cl <sub>2</sub> , 55°, 48 h	(71)	310
CpCoL <sub>3</sub> Na	Toluene, 120°, 24 h	$\frac{n}{1}$	311
L = MeO- 		$\frac{n}{2}$	

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$	 $\text{R} = \text{O}-(\text{CH}_2)_n$	Toluene, 120°, 24 h	 $\text{I}$ $\frac{n}{1 \text{ (57)}}$ $\frac{2 \text{ (23)}}$	311
	RhCl <sub>3</sub> , Aliquat 336	H <sub>2</sub> O, Cl <sub>2</sub> CHCHCl <sub>2</sub> , 90°, 20 h	<b>I</b> (35)	19
	[Rh(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]	C <sub>6</sub> H <sub>6</sub> , heat, 5 h	<b>I</b> (48)	312
	RhCl(dippe)(CO)	THF- <i>d</i> <sub>6</sub> , 65°, 1 h	<b>I</b> (100)	208
	RhCl(dippe)(CO)	THF- <i>d</i> <sub>6</sub> , 65°, 24 h	<b>I</b> (100)	208
	RhCl(PPh <sub>2</sub> Me) <sub>2</sub> (CO)	THF- <i>d</i> <sub>6</sub> , 65°, 48 h	<b>I</b> (63)	208
	(Cp <sup>*</sup> )Rh(COD)	Toluene, heat, 24 h	<b>I</b> (77)	210
	(Cp <sup>*</sup> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	Toluene, heat, 24 h	<b>I</b> (77)	210
	CpRh(COD)	Toluene, heat, 24 h	<b>I</b> (74)	210
	(C <sub>5</sub> Cl <sub>5</sub> )Rh(COD)	Toluene, heat, 24 h	<b>I</b> (39)	210
	(Cp <sup>*</sup> )Rh(CO) <sub>2</sub>	Toluene, heat, 24 h	<b>I</b> (52)	210
	(C <sub>9</sub> H <sub>7</sub> )Rh(COD)	Toluene, heat, 2 h	<b>I</b> (82)	210
	(C <sub>9</sub> H <sub>7</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (0.1%)	C <sub>6</sub> H <sub>6</sub> , 80°, 1 h	<b>I</b> (75)	209
	(C <sub>9</sub> H <sub>7</sub> )Rh(C <sub>8</sub> H <sub>14</sub> ) <sub>2</sub> (0.1%)	C <sub>6</sub> H <sub>6</sub> , 100°, 1 h	<b>I</b> (87)	209
	(C <sub>9</sub> H <sub>7</sub> )Rh(COD) (0.1%)	C <sub>6</sub> H <sub>6</sub> , 80°, 1 h	<b>I</b> (93)	209
	(C <sub>13</sub> H <sub>8</sub> )Rh(COD) (0.1%)	C <sub>6</sub> H <sub>6</sub> , 80°, 1 h	<b>I</b> (86)	209
	Zr(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(η <sup>1</sup> -C <sub>5</sub> H <sub>4</sub> CMe <sub>2</sub> - η <sup>5</sup> -C <sub>13</sub> H <sub>8</sub> Rh(COD))Cl <sub>2</sub>	Toluene, 50°, 1 h	<b>I</b> (4)	313
	Rh <sub>2</sub> (CO) <sub>8</sub> ( <i>n</i> -BuN=CHCH=NBu- <i>r</i> )	Toluene, heat, 12 h	<b>I</b> (80)	211
	Rh(dcmppz)(PPh <sub>3</sub> ) <sub>3</sub>	Toluene, rt	<b>I</b> (100)	131



TABLE 2. DISUBSTITUTED ALKYNES (Continued)

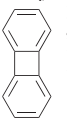
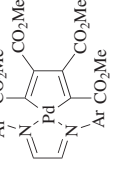
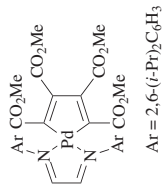
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>6</sub> MeO <sub>2</sub> C—C≡C—CO <sub>2</sub> Me	IrBr(dppe)(CO)	THF-d <sub>8</sub> , 65°, 48 h	<b>I</b> (24)	208	
	IrCl(PPh <sub>2</sub> Me) <sub>2</sub> (CO)	THF-d <sub>8</sub> , 65°, 48 h	<b>I</b> (57)	208	
	<i>trans</i> -MeIr(CO)(PPh <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> , rt, 24 h	<b>I</b> (40)	22	
				<b>I</b> (—)	314
			THF-d <sub>8</sub> , 85°, 24 h		
	NiCl(PPh <sub>3</sub> )	Toluene, 5°, 1 h	<b>I</b> (25)	315	
	NiMeCl(PMe <sub>3</sub> ) <sub>2</sub>	-70° to -40°	<b>I</b> (—)	216	
	Ni(dppe)(SC <sub>6</sub> H <sub>4</sub> O)	Toluene, CH <sub>2</sub> Cl <sub>2</sub> , heat, 48 h	<b>I</b> (6)	316	
	Ni(dppe)(SC <sub>6</sub> H <sub>4</sub> NH-2)	Toluene, CH <sub>2</sub> Cl <sub>2</sub> , heat, 48 h	<b>I</b> (1)	316	
	Ni(dppe)(SC <sub>6</sub> H <sub>4</sub> S-2)	Toluene, CH <sub>2</sub> Cl <sub>2</sub> , heat, 48 h	<b>I</b> (3)	316	
	Ni(dppe)(SC <sub>6</sub> H <sub>3</sub> (Me-4)S-2)	Toluene, CH <sub>2</sub> Cl <sub>2</sub> , heat, 48 h	<b>I</b> (14)	316	
	Pd <sub>2</sub> (Ph) <sub>2</sub> PCH <sub>2</sub> PPPh <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	125°, 1.5 h	<b>I</b> (40)	25	
	Pd <sub>2</sub> (Ph) <sub>2</sub> PCH <sub>2</sub> PPPh <sub>2</sub> )( <i>μ</i> -DMAD)Cl <sub>2</sub>	125°, 1.5 h	<b>I</b> (33)	25	
	Pd <sub>2</sub> (Ph) <sub>2</sub> PCH <sub>2</sub> PPPh <sub>2</sub> ) <sub>2</sub>	125°, 2 h	<b>I</b> (68)	25	
	Pd <sub>2</sub> (Ph) <sub>2</sub> PCH <sub>2</sub> PPPh <sub>2</sub> ) <sub>2</sub> ( <i>μ</i> -DMAD) <sub>2</sub>	125°, 2 h	<b>I</b> (51)	25	
	Pd(PPh <sub>2</sub> PCH <sub>2</sub> PPPh <sub>2</sub> ) <sub>2</sub>	125°, 2 h	<b>I</b> (27)	25	
	Pd <sub>2</sub> (Ph) <sub>2</sub> PCH <sub>2</sub> PPPh <sub>2</sub> ) <sub>3</sub>	125°, 2 h	<b>I</b> (8)	25	
				<b>I</b> (95)	231
			Toluene, 60°, 3 h		
	Cu(O <sub>2</sub> CC <sub>6</sub> H <sub>5</sub> )	MeOH		<b>I</b> (—)	226
[Cu <sub>4</sub> ( <i>μ</i> -O <sub>2</sub> CPh) <sub>4</sub> ( <i>μ</i> -DMAD) <sub>2</sub> ]	MeOH		<b>I</b> (—)	26	



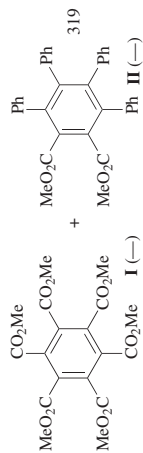
TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$	Catalyst	$\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2$ , toluene, heat		210
	Catalyst CpRh(CO) <sub>2</sub> CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (C <sub>9</sub> H <sub>17</sub> )Rh(COD)			
	[Ir(COD)Cl] <sub>2</sub> , dppe	$\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2$ , heat	I + II	91
		Solvent	R <sup>1</sup> R <sup>2</sup> I II	
		Time		
		toluene	<i>n</i> -Bu H (11) (89)	
		toluene	<i>n</i> -Bu H (2) (98)	
		toluene	<i>n</i> -Bu H (3) (97)	
		toluene	<i>n</i> -C <sub>8</sub> H <sub>17</sub> H (2) (96)	
		xylylene	Ph H (50) (38)	
		toluene	CH <sub>2</sub> Ph H (3) (86)	
		toluene	(CH <sub>2</sub> ) <sub>3</sub> Cl H (2) (83)	
		THF	(CH <sub>2</sub> ) <sub>3</sub> CN H (0) (91)	
		THF	CH <sub>2</sub> OMe H (0) (89)	
		THF	CH <sub>2</sub> OMe H (16) (52)	
		dioxane	TMS H (0) (41)	
		THF	CH <sub>2</sub> NMe <sub>2</sub> H (0) (90)	
		THF	CH <sub>2</sub> NHCO <sub>2</sub> Me H (0) (98)	
		THF	CH <sub>2</sub> OMe CH <sub>2</sub> OMe (0) (93)	
		THF	CH <sub>2</sub> OAc CH <sub>2</sub> OAc (0) (89)	
		THF	Et Et (10) (89)	
		THF	<i>n</i> -Bu $\equiv$ -Bu- <i>n</i> (11) (73)	
		THF	Ph Me (15) (78)	

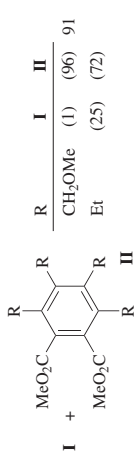


I + II	R <sup>1</sup>	R <sup>2</sup>	I	II	231
	Et	Et	(84)	(16)	
	H	<i>n</i> -Bu	(91)	(9)	
	TMS	TMS	(90)	(10)	
	Ph	Ph	(85)	(15)	
	CH <sub>2</sub> OMe	CH <sub>2</sub> OMe	(60)	(40)	
	H	CH <sub>2</sub> OMe	(90)	(10)	
	Ph	TMS	(48)	(52)	

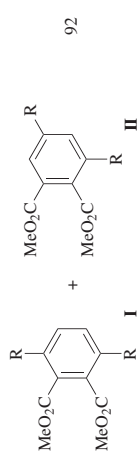
Toluene, 80°, 22 h



Ph  $\equiv$  Ph, 200°, 13 h



R  $\equiv$  R, THF, 50°, 1 h



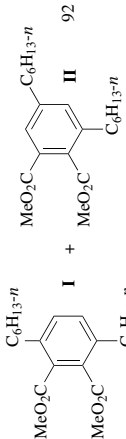
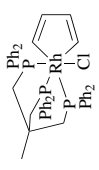
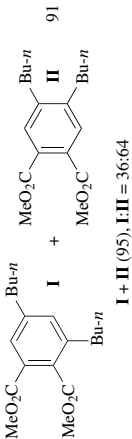
R  $\equiv$  toluene, 110°, 24 h

R	I	II
<i>n</i> -Bu	(26)	(35)
<i>n</i> -C <sub>7</sub> H <sub>15</sub>	(39)	(49)
<i>n</i> -C <sub>8</sub> H <sub>17</sub>	(44)	(55)

[Ir(COD)Cl]<sub>2</sub>

(C<sub>9</sub>H<sub>7</sub>)RuCl(COD)

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{C}_6$ $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$	Catalyst	$n\text{-C}_6\text{H}_{13}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_{13}-n$ $110^\circ, 24\text{ h}$		92
	Solvent			
	(Cp*)RuCl(COD)	toluene	(23)	(30)
	(Cp*)RuCl(COD)	$\text{C}_6\text{H}_{12}$	(12)	(23)
	(Cp*)RuCl(COD)	diglyme	(14)	(15)
	(Cp*)RuCl(COD)	DMF	(3)	(1)
	(Cp*)RuCl(COD)	EtCN	(5)	(2)
	CpRuCl(COD)	toluene	(18)	(17)
	$\text{RuCl}_2(\text{PPh}_3)_3$	toluene	(14)	(9)
	$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	toluene	(8)	(6)
	$\text{RuCl}_3 \cdot \text{H}_2\text{O}$	toluene	(11)	(8)
	$\text{Ru}_3(\text{CO})_{12}$	toluene	(6)	(5)
	$\text{Ru}(\text{COD})(\text{COT})$	toluene	(3)	(3)
	$\text{Ru}(\text{COT})(\text{dmfm})_2$	toluene	(7)	(5)
	$\text{RhH}(\text{CO})(\text{PPh}_3)_3$	toluene	(3)	(6)
$\text{Pd}(\text{dba})_2$	toluene	(6)	(3)	
	$[\text{Ir}(\text{COD})\text{Cl}]_2$	Acetylene, $\text{CH}_2\text{Cl}_2$ , heat, 2 h	I + II (—)	183
		$n\text{-Bu}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{MeO}_2\text{C}$	THF, heat, 1 h	
			I + II (95), I:II = 36:64	



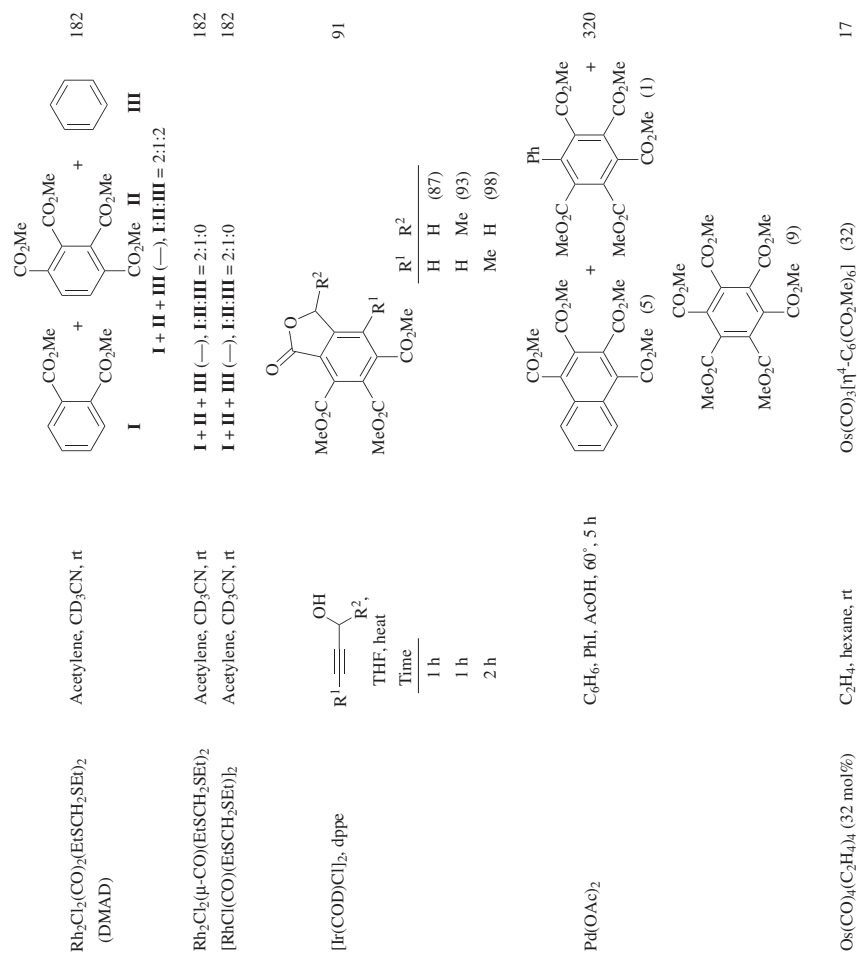
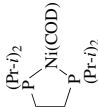
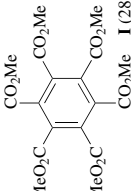
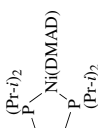
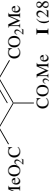

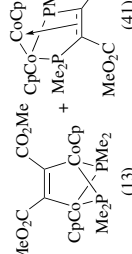
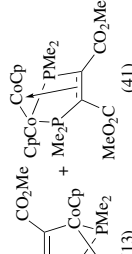
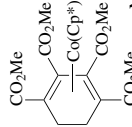
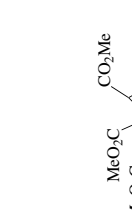
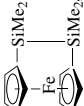
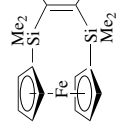
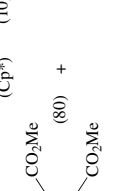

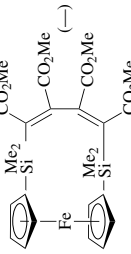


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$	 $(\text{Pr-1})_2\text{Ni}(\text{COD})\text{P}(\text{Pr-1})_2$	THF, rt, 24 h	 +  +  <b>I (28)</b>	314
	 $\text{CpCo}(\text{CO})\text{PMe}_2$ (33 mol%)	$\text{C}_6\text{H}_6$ , $\text{CH}_2\text{Cl}_2$ , rt, 24 h	 <b>I (-)</b> +  <b>(41)</b>	219
	$(\text{Cp}^*)\text{Co}(\text{C}_2\text{H}_4)_2$ (20 mol%)	Hexane, 60°, 12 h	 <b>I (60)</b> +  <b>(15)</b>	260
	$\text{Pd}(\text{PPh}_3)_4$	 toluene, 100°, 27 h	 <b>I (12)</b> +  <b>(80)</b> +  <b>(10)</b>	321
			 <b>(-)</b>	

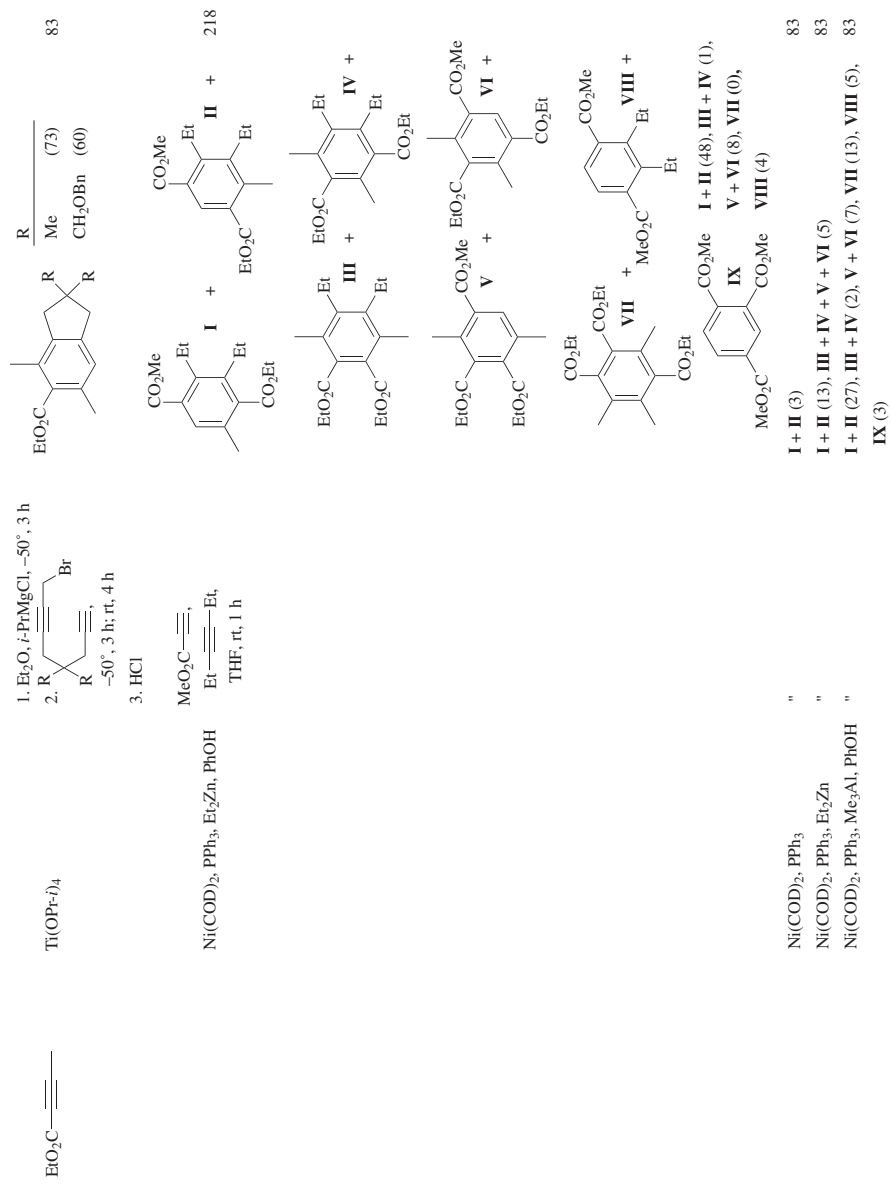
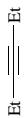
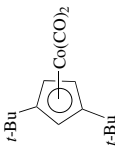


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
$C_6$ 	$Si_2Cl_6$	200°, 2 d	(45)	178	
	$NbCl_5, EtAlCl_2$	$CCl_4$	(34)	241	
	$Nb_2Cl_{10}(SC_2H_5)_3$	Toluene, 80°, 2 h	(70)	221	
	$Fe(C_7H_8)(COD)$	THF, heat, 30 h	(50)	236	
	$Co_3(CO)_9(\mu^3-C_6H_5)$	Toluene, heat, 1 h	(92)	261	
	$Co_3(CO)_9(\mu^3-CMe)$	Toluene, heat, 1 h	(13)	261	
	$Co_3(CO)_9(\mu^3-CPh)$	Toluene, heat, 1 h	(21)	261	
	$Co_3(CO)_9(\mu^3-CCO_2Et)$	Toluene, heat, 1 h	(19)	261	
	$Co_3(CO)_9(\mu^3-CCl)$	Toluene, heat, 1 h	(11)	261	
	$Co_3(CO)_9(\mu^3-CBr)$	Toluene, heat, 1 h	(42)	261	
	$[Co_3(CO)_9(\mu^3-CPh)]_2$	Toluene, heat, 1 h	(38)	261	
	$Co_2(CO)_8$	Toluene, heat, 1 h	(8)	261	
	$Co_4(CO)_{12}$	Toluene, heat, 1 h	(47)	261	
			Toluene, 130°, 2 d	(—)	322
	$(Cp^*)Rh(COD)$		Toluene, heat, 24 h	(14)	210
	$(Cp^*)Rh(C_2H_4)_2$		Toluene, heat, 24 h	(22)	210
	$(C_9H_7)Rh(C_2H_4)_2$		<i>o</i> -Xylene, 160°, 115 h	(49)	209
	$(C_9H_7)Rh(C_8H_{14})_2$		<i>o</i> -Xylene, 160°, 115 h	(39)	209
	$(C_9H_7)Rh(COD)$		<i>o</i> -Xylene, 160°, 113 h	(12)	209
	$(C_{13}H_8)Rh(COD)$		<i>o</i> -Xylene, 160°, 113 h	(13)	209
$NiBr_2, Mg$		THF, heat, 4 h	(90)	323	

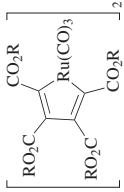
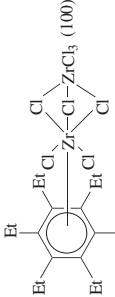

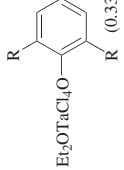
NiBr <sub>2</sub> , Mg	THF, 40°	(100)	185
NiCl <sub>2</sub> , Mg	THF, heat, 4 h	(70)	323
NiI <sub>2</sub> , Mg	THF, heat, 4 h	(40)	323
NiI <sub>2</sub> , Na	THF, heat, 4 h	(50)	323
NiI <sub>2</sub> , Zn	THF, heat, 4 h	(15)	323
Pd/C, TMSCl	THF, heat, 3 h	(100)	87
	120°	$\frac{R}{Me}$ (92) Et (98)	202
Pt(OAc) <sub>2</sub>	1. Chlorohydroquinone, NPMoV CH <sub>2</sub> SO <sub>3</sub> H, O <sub>2</sub> , dioxane, 60°, 2 h 2. O <sub>2</sub> , 60°, 1 h	<b>I</b> (100)	249
ZrCl <sub>4</sub> (2 eq)	Hexane		5
	1. C <sub>2</sub> H <sub>4</sub> , THF, rt, 1 h 2. R <sup>1</sup> ≡R <sup>2</sup> , 50°, 1 h 3. DMAD, CuCl, 0° to rt, 1 h	$\frac{R^1 \quad R^2}{Ph \quad Ph}$ (63) TMS <i>m</i> -Bu (74) Ph H (66)	95
	Et <sub>2</sub> O, rt, 1 h	$\frac{R}{Me}$ (24) <i>i</i> -Pr (10)	324

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
Et—C≡C—Et	( $\eta^6$ -C <sub>6</sub> M <sub>6</sub> )(DIPP) <sub>2</sub> Cl (5 mol%)	Et <sub>2</sub> O, rt, 8 h	  	45
	Et <sub>2</sub> OTa(DIPP) <sub>2</sub> Cl <sub>3</sub> (0.33 eq)	1. Et <sub>2</sub> O, -40° 2. Na/Hg, rt, 1 h	  	325
	CpCr( $\eta^3$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> (29 mol%)	-78° to 0°, 48 h	 	11
	Fe( $\eta^6$ -toluene)(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (0.2 eq)	1. Naphthalene, toluene, -50° to -30°, 3 h 2. -30°, 2 d		305
	Ru( $\eta^6$ -C <sub>10</sub> H <sub>8</sub> )(COD) (17 mol%)	THF, rt, 3 h		326
	Ni(COD) <sub>2</sub> , phosphine	CO <sub>2</sub> (1 MPa), 110°		327

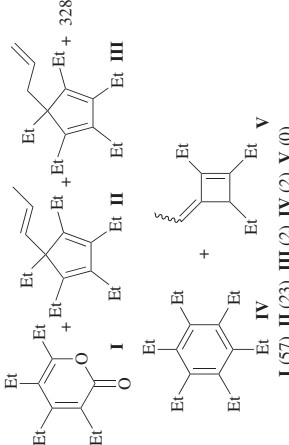
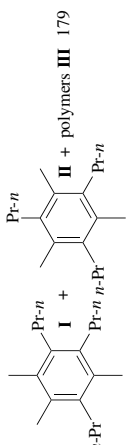
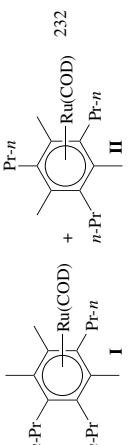
Phosphine	Solvent	Time	I + II + III	I + II + III
PPh <sub>3</sub>	THF	20 h	(96)	5:95
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	THF	20 h	(96)	12:88
PPh <sub>2</sub> Et	THF	20 h	(98)	35:65
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	toluene	20 h	(50)	5:95
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	THF, CH <sub>3</sub> CO <sub>2</sub> Et	20 h	(25)	5:95
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	toluene, CH <sub>3</sub> CN	20 h	(78)	22:78
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	THF, CH <sub>3</sub> CN, 8:2	20 h	(86)	24:76
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	THF, CH <sub>3</sub> CN, 1:1	20 h	(96)	29:71
P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	THF, CH <sub>3</sub> CN, 1:1	16 h	(96)	29:71
PPh <sub>2</sub> Et	THF, CH <sub>3</sub> CN, 1:1	16 h	(95)	75:25
PPhMe <sub>2</sub>	THF, CH <sub>3</sub> CN, 1:1	16 h	(98)	92:8
PEt <sub>3</sub>	THF, CH <sub>3</sub> CN, 1:1	16 h	(100)	96:4
Ni(COD) <sub>2</sub> , Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> PPh <sub>2</sub>	CO <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> , 120°, 20 h			
Ni(COD) <sub>2</sub> , Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>4</sub> PPh <sub>2</sub>	CO <sub>2</sub> , H <sub>2</sub> O, C <sub>6</sub> H <sub>6</sub> , 120°, 20 h		I (57), II (23), III (2), IV (2), V (0)	328
Ni(COD) <sub>2</sub> , Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub>	CO <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> , 120°, 20 h		I (54) + II (25) + III (4) + IV (2)	328
Ni(COD) <sub>2</sub> , Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	CO <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> , 120°, 20 h		I (2) + II (2) + III (1) + IV (0.3)	328
Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	CO <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> , 120°, 20 h		I (13) + II (46) + III (6) + IV (2)	328
Ni(COD) <sub>2</sub> , Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	CO <sub>2</sub> , C <sub>6</sub> H <sub>6</sub> , 120°, 20 h		I (9) + II (66) + III (7) + IV (3)	328
Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	C <sub>6</sub> H <sub>6</sub> , 120°, 5 h		II (1) + IV (1)	328
Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	C <sub>6</sub> H <sub>6</sub> , 120°, 20 h		II (9) + III (4) + IV (39)	328
[HNi(Ph <sub>3</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> ](OTf)	C <sub>6</sub> H <sub>6</sub> , 120°, 5 h		II (4) + III (16) + IV (3) + V (36)	328

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$n\text{-Pr}-\text{C}\equiv\text{C}-\text{R}$	Zr, Ti	DME, THF, rt, 3 h	 <b>I</b> + <b>II</b> = 1:0.4, <b>III</b> (0)	179
	NbCl <sub>5</sub>	EtAlCl <sub>2</sub> , CCl <sub>4</sub>	<b>I</b> + <b>II</b> (52)	241
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (1), <b>III</b> (10)	243
	Mo(CO) <sub>6</sub>	I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (1), <b>III</b> (10)	243
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH, I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (4), <b>III</b> (33)	243
	Mo(CO) <sub>6</sub>	PhOH, I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (4), <b>III</b> (33)	243
	Cp <sub>2</sub> Mo <sub>2</sub> (CO) <sub>6</sub>	PhOH, I <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , 110°, 18 h	<b>I</b> + <b>II</b> (2), <b>III</b> (17)	243
	Pd/C, TMSCI	THF, heat, 2 d	<b>I</b> (65)	87
	Ru(η <sup>6</sup> -naphthalene)(COD)	THF, rt, 3 h	 <b>I</b> + <b>II</b> (95), <b>I:II</b> = 70:30	232
$\text{R}-\text{C}\equiv\text{C}-\text{R}$ R = CH <sub>2</sub> OMe	NiBr <sub>2</sub> , Mg	THF, heat, 10 h	<b>I</b> (50)	232
	Ni[(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ] <sub>2</sub> (C <sub>3</sub> H <sub>4</sub> )	60°, 6 h	<b>I</b> (96)	329



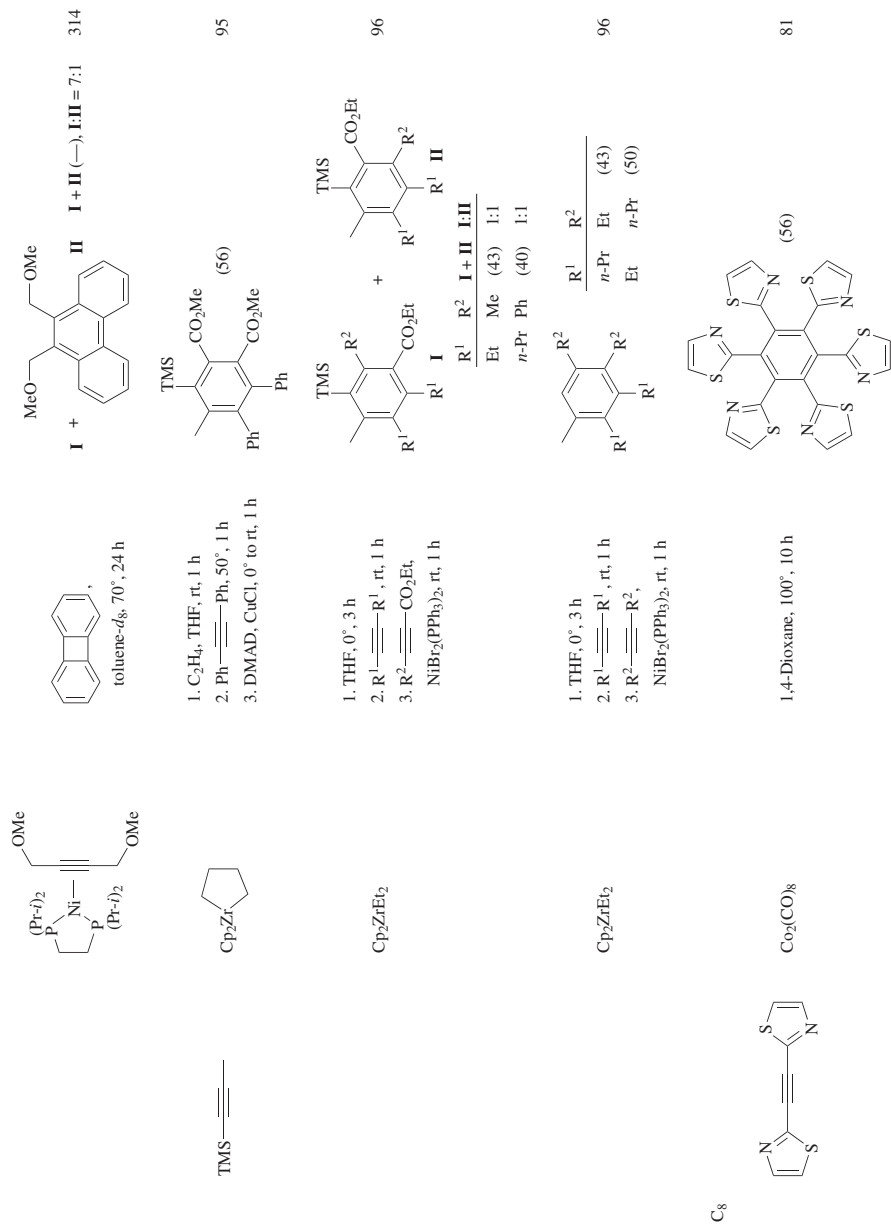
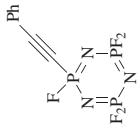
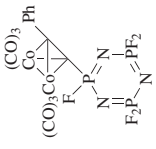
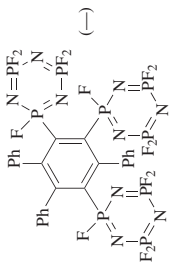

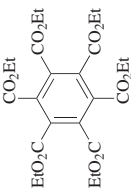
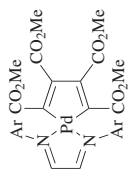
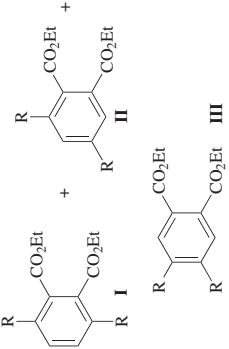
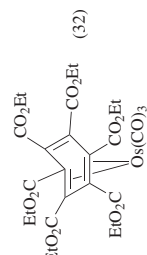
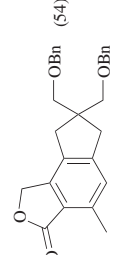
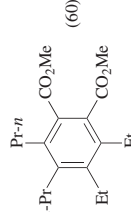


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (—)	330
	Ru(CO) <sub>4</sub> (C <sub>2</sub> H <sub>4</sub> )	C <sub>2</sub> H <sub>4</sub> , hexane, 20–110°	 <b>I (97)</b>	16
	[(Cp*)RuCl <sub>2</sub> ] <sub>2</sub>	Toluene, 100°, 14 h	<b>I (—)</b>	190
	 Ar = 2,6-( <i>i</i> -Pr) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Toluene, 60°, 3 h	<b>I (98)</b>	231
	[Rh(COD) <sub>2</sub> ]BF <sub>4</sub> , H <sub>8</sub> -BINAP	≡—R, CH <sub>2</sub> Cl <sub>2</sub> , rt, 1 h	 <b>I</b> <b>II</b> <b>III</b>	280

R	I + II + III	III:III
$n\text{-C}_{10}\text{H}_{21}$	(88)	92:6:2
$(\text{CH}_2)_3\text{Cl}$	(92)	91:8:1
$\text{CH}_2\text{OMe}$	(61)	86:10:4
Ph	(90)	89:9:2
$o\text{-MeC}_6\text{H}_4$	(77)	89:9:2
1-cyclohexenyl	(90)	91:4:5
TMS	(57)	99:1:0

 (32)	17
 (54)	83
 (60)	95

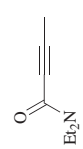
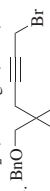
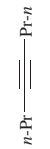
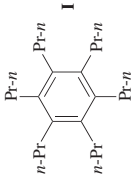
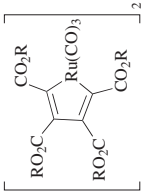
 $\text{Et}_3\text{N}$	$\text{Os}(\text{CO})_4(\text{C}_2\text{H}_4)_4$ (0.33 eq)	$\text{C}_2\text{H}_4$ , hexane, rt, 8 h
	$\text{Ti}(\text{OPr}^i)_4$	<ol style="list-style-type: none"> <li>1. <math>\text{Et}_2\text{O}</math>, <math>i\text{-PrMgCl}</math>, <math>-50^\circ</math>, 5 h</li> <li>2. <math>\text{BnO}</math>, <math>-50^\circ</math>, 3 h</li> <li>3. <math>\text{O}_2</math>, overnight</li> <li>4. HCl</li> <li>5. PTSA, rt, overnight</li> </ol>
 $n\text{-Pr}$	$\text{Cp}_2\text{Zr}$	<ol style="list-style-type: none"> <li>1. 3-hexyne, THF, rt, 1 h</li> <li>2. 2-butyne, <math>50^\circ</math>, 1 h</li> <li>3. DMAD, CuCl, <math>0^\circ</math> to rt, 1 h</li> </ol>

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_8$ $n\text{-Pr}-\text{C}\equiv\text{C}-\text{Pr}-n$	 <b>I</b>	$\text{NbCl}_5, \text{EtAlCl}_2$ $\text{PdCl}_2$	$\text{CCl}_4$ $\text{NaOAc}, \text{CuCl}_2, n\text{-BuOH}, \text{C}_6\text{H}_6,$ $40^\circ, 4 \text{ h}$	(24) 241 (98) 72
		$\text{PdCl}_2$ $\text{PdCl}_2$ $\text{PdCl}_2$ $\text{PdCl}_2$ $\text{PdCl}_2$ $\text{PdCl}_2$	$\text{CuCl}_2, n\text{-BuOH}, \text{C}_6\text{H}_6, 40^\circ, 4 \text{ h}$ $n\text{-BuOH}, \text{C}_6\text{H}_6, 40^\circ, 6 \text{ h}$ $\text{FeCl}_3, n\text{-BuOH}, \text{C}_6\text{H}_6, 40^\circ, 6 \text{ h}$ $\text{LiCl}, n\text{-BuOH}, \text{C}_6\text{H}_6, 40^\circ, 6 \text{ h}$ $\text{Ce}(\text{SO}_4)_2, n\text{-BuOH}, \text{C}_6\text{H}_6,$ $40^\circ, 6 \text{ h}$	(99) 72 (71) 72 (77) 72 (21) 72 (75) 72
		$\text{PdCl}_2(\text{PhCN})_2$ $\text{PdCl}_2$ $\text{PdCl}_2$ $\text{PdCl}_2$ $\text{PdCl}_2$	$\text{CuCl}_2, n\text{-BuOH}, \text{C}_6\text{H}_6, 40^\circ, 4 \text{ h}$ $\text{CuCl}_2, n\text{-BuOH}, 40^\circ, 4 \text{ h}$ $\text{CuCl}_2, \text{CH}_2\text{Cl}_2, 40^\circ, 4 \text{ h}$ $\text{CuCl}_2, s\text{-BuOH}, \text{C}_6\text{H}_6, 40^\circ, 4 \text{ h}$ $\text{CuCl}_2, \text{EtOH}, \text{C}_6\text{H}_6, 40^\circ, 4 \text{ h}$ $\text{CuCl}_2, \text{C}_6\text{H}_6, 40^\circ, 6 \text{ h}$	(77) 72 (70) 72 (98) 72 (99) 72 (98) 72 (66) 72
		$\text{Pd}(\text{OAc})_2$	1. Chlorohydroquinone, NPMoV, $\text{CH}_3\text{SO}_3\text{H}, \text{O}_2, \text{dioxane},$ $60^\circ, 2 \text{ h}$ 2. $\text{O}_2, 60^\circ, 30 \text{ min}$	<b>I</b> (100) 249
			$160^\circ$	<b>I</b> (86) 202 $n\text{-Pr}$ (43)

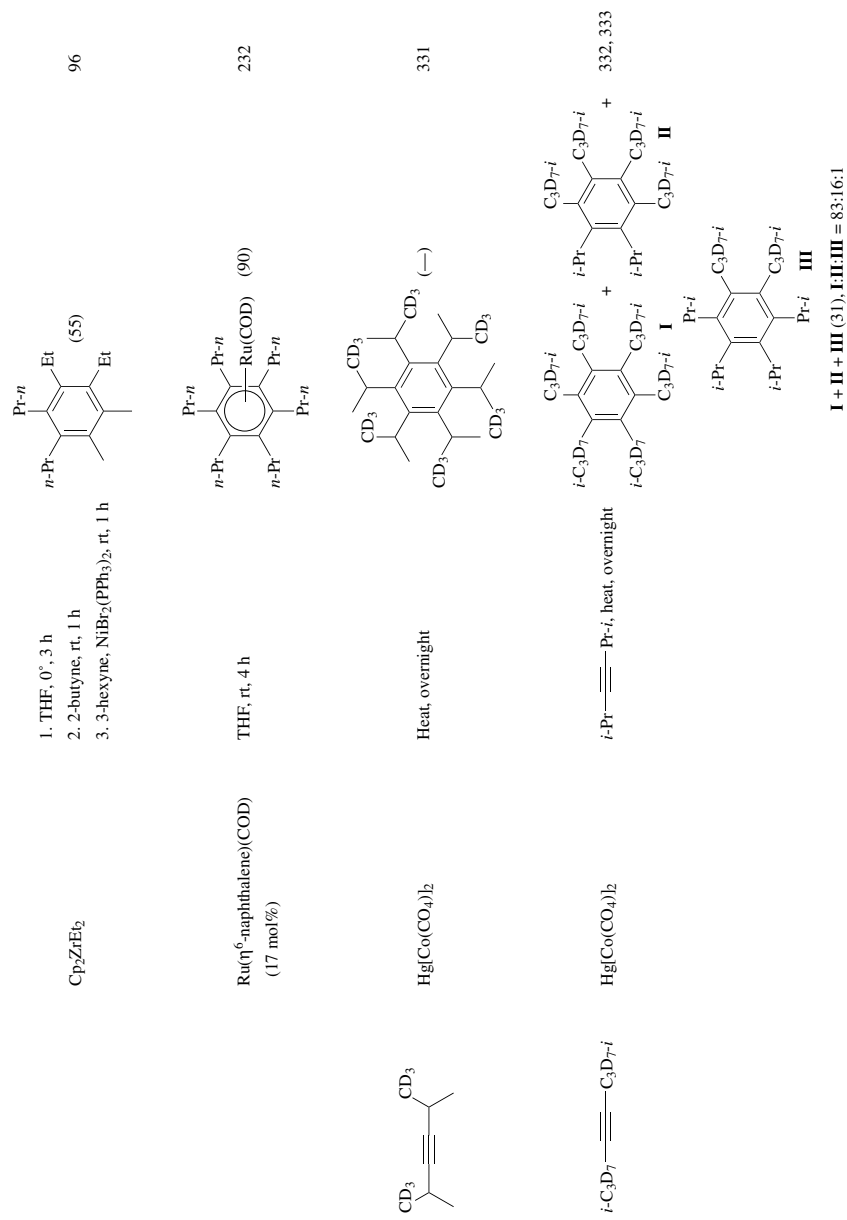
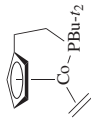
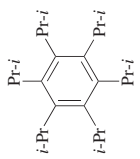
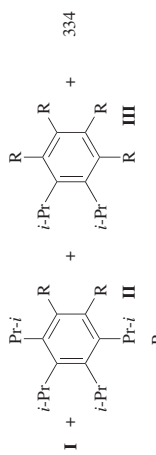
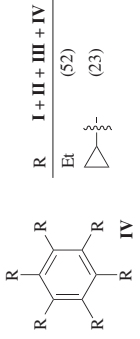
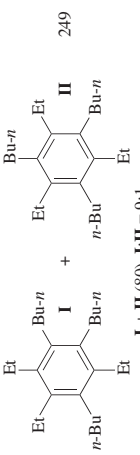
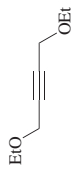
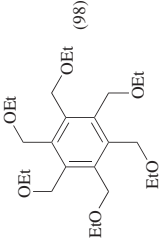


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_8$ $i\text{-Pr}-\text{C}\equiv\text{C}-\text{Pr}-i$	$\text{Hg}[\text{Co}(\text{CO})_4]_2$ 	Heat, overnight	 I (31) 332	
		$\text{H}_2\text{O}$ , EtOH, $60^\circ$ , 7 h	I (51) 194	
	$\text{Hg}[\text{Co}(\text{CO})_4]_2$	$\text{R}-\text{C}\equiv\text{C}-\text{R}$ , heat, 3 d	 I + II + III 334	
			 I + II + III + IV (52) (23)	
$n\text{-Bu}-\text{C}\equiv\text{C}-\text{Et}$	$\text{Pd}(\text{OAc})_2$	1. Chlorohydroquinone, NPMoV, $\text{CH}_3\text{SO}_3\text{H}$ , $\text{O}_2$ , dioxane, $60^\circ$ , 2 h 2. $\text{O}_2$ , $60^\circ$ , 1 h	 I + II (80), I:II = 9:1 249	
	$\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{C}_2\text{H}_4)$	THF, heat	 (98) 329	

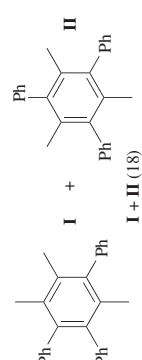
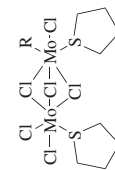



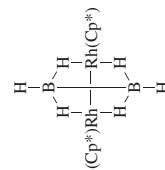


C <sub>9</sub>	Ph—C≡C—	Ta <sub>2</sub> Cl <sub>6</sub> (SC <sub>4</sub> H <sub>8</sub> ) <sub>3</sub>	Toluene, 3 h	221													
			Toluene, rt	47	<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>8 h</td> <td>(98)</td> <td>1:6.7</td> </tr> <tr> <td></td> <td>36 h</td> <td>(99)</td> <td>1:4.3</td> </tr> </tbody> </table>	R	Time	I + II	I:II	Cl	8 h	(98)	1:6.7		36 h	(99)	1:4.3
R	Time	I + II	I:II														
Cl	8 h	(98)	1:6.7														
	36 h	(99)	1:4.3														
		MoCl <sub>3</sub> (SC <sub>4</sub> H <sub>8</sub> ) <sub>2</sub>	Toluene, rt, 8 h	47	I + II (100), I:II = 1:4.1												
		MoCl(SnCl <sub>3</sub> )(CO) <sub>3</sub> (NCPh) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 2 h	274	I + II (—), I:II = 8:1												
		MoCl <sub>3</sub> (SC <sub>4</sub> H <sub>8</sub> ) <sub>2</sub> (Ph—C≡C—)	Acetone, 0°, 36 h	47	II (90)												
			Hexane, rt, 24 h	201, 213	I (21)												
			Hexane, rt, 70 h	201, 213	I (3)												
			Toluene, 70°, 24 h	201, 213	I (36)												


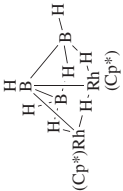
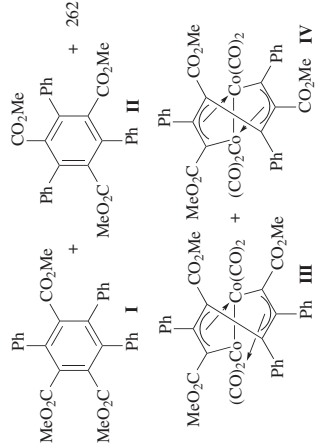

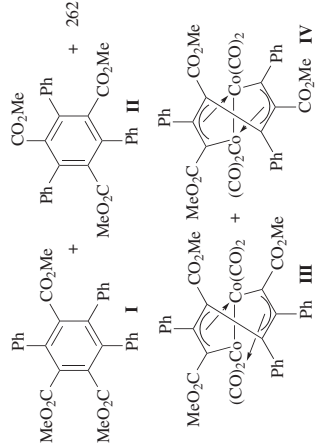

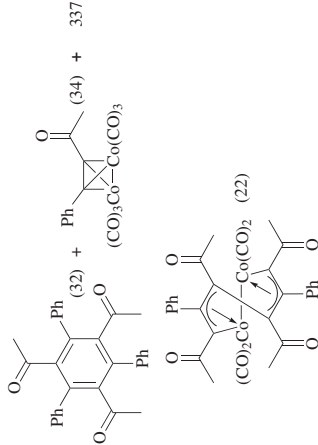
TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{PdCl}_2 \left( \text{C}_2\text{H}_4 \right)_2$	$\text{CH}_2\text{Cl}_2$ , rt, 20 h	<b>II</b> (74)	217
	$\text{Pd/C}$ , TMSCl $\text{PdCl}_2$	THF, heat, 6 d $\text{CuCl}_2$ , <i>n</i> -BuOH, $\text{C}_6\text{H}_6$ , 40°, 12 h	<b>I + II</b> (100), <b>I:II</b> = 4:1 <b>I</b> (80)	87 72
	$\text{Co}_2(\text{CO})_8$ (4.7 eq)	Heat, 15 min	 (-) + $(\text{CO})_3\text{Co} \left( \text{C}_3\text{H}_3 \right) \text{Ph}$ (95)	226
	$(\text{Pr}^i)_2\text{P}(\text{NMe}_2)\text{Ni}(\text{C}\equiv\text{C})\text{Ph}$	$\text{C}_6\text{D}_6$ , 70°, 60 d	 <b>I</b> + <b>II</b> <b>I + II</b> (79), <b>I:II</b> = 7:3	335
	$\text{Mo}(\text{CO})_6$	Toluene, heat, 5 h	 (65)	46
$n\text{-C}_3\text{H}_7\text{C}\equiv\text{CCO}_2\text{Me}$	$[\text{Ir}(\text{COD})\text{Cl}]_2$	$\text{R} \equiv \text{C-C}\equiv\text{C-R}$ , dppp, THF, 50°, 1 h $\text{R} = \text{CH}_2\text{OMe}$	 <b>I</b> + <b>II</b> <b>I + II</b> (82), <b>I:II</b> = 93:7	91





TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.												
$C_{10}$ 	 $(Cp^*)Rh(H)_2(B)_2$ $(Cp^*)$	Toluene, 60°, 24 h	<table border="0"> <tr> <td></td> <td><b>I + II</b></td> <td><b>I + II</b></td> <td><b>III</b></td> </tr> <tr> <td></td> <td>(17)</td> <td>(11)</td> <td>75:25</td> </tr> <tr> <td></td> <td>75:25</td> <td></td> <td>75:25</td> </tr> </table> 		<b>I + II</b>	<b>I + II</b>	<b>III</b>		(17)	(11)	75:25		75:25		75:25	201
	<b>I + II</b>	<b>I + II</b>	<b>III</b>													
	(17)	(11)	75:25													
	75:25		75:25													
	$Co_2(CO)_8$ (20 mol%)	Toluene, heat, 24 h	 <b>I + II</b> (61), <b>I:II</b> = 87:13, <b>III + IV</b> (39)	262												
	$Co_2(CO)_8$ (0.5 eq)	Toluene, heat, 2 min	 <b>I + II</b> (61), <b>I:II</b> = 87:13, <b>III + IV</b> (39)	337												

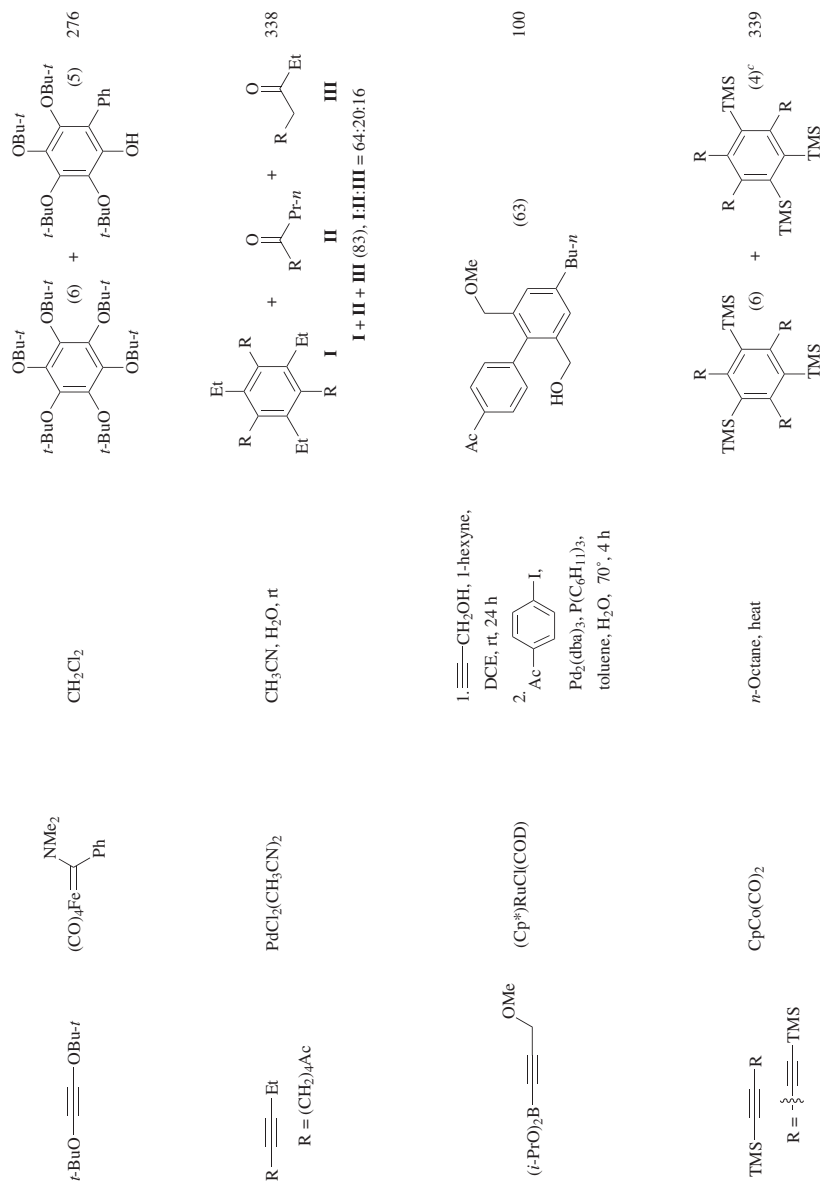
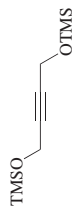
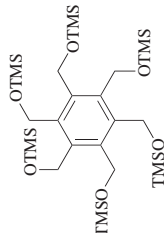
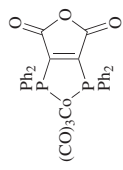

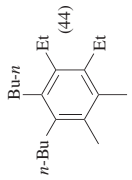
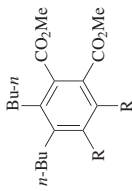
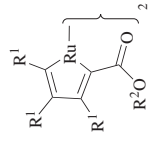
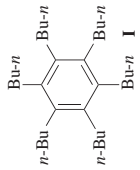


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	NiBr <sub>2</sub> , Mg	THF, heat, 2 h	 <b>I</b> (95)	185
	Ni[P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ] <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )	THF, heat	<b>I</b> (80)	329
	(CO) <sub>3</sub> CrO 	CH <sub>2</sub> Cl <sub>2</sub> , rt, 96 h	<b>I</b> (95)	310
	Cp <sub>2</sub> ZrEt <sub>2</sub>	1. THF, 0°, 3 h 2. 2-Butyne, rt, 1 h 3. 3-Hexyne, NiBr <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , rt, 1 h	 (44)	96
	Cp <sub>2</sub> Zr	1. 3-Hexyne, THF, rt, 1 h 2. R-C≡C-R, 50°, 1 h 3. MeO <sub>2</sub> C-C≡C-CO <sub>2</sub> Me, CuCl, 0° to rt, 1 h	 R Et (71) n-Pr (62)	95
		160°	 R <sup>1</sup> R <sup>2</sup> CO <sub>2</sub> Me Me (72) CO <sub>2</sub> Bu-n n-Bu (41)	202
	Pd/C	TMSCl, THF, heat, 6 h	<b>I</b> (100)	87

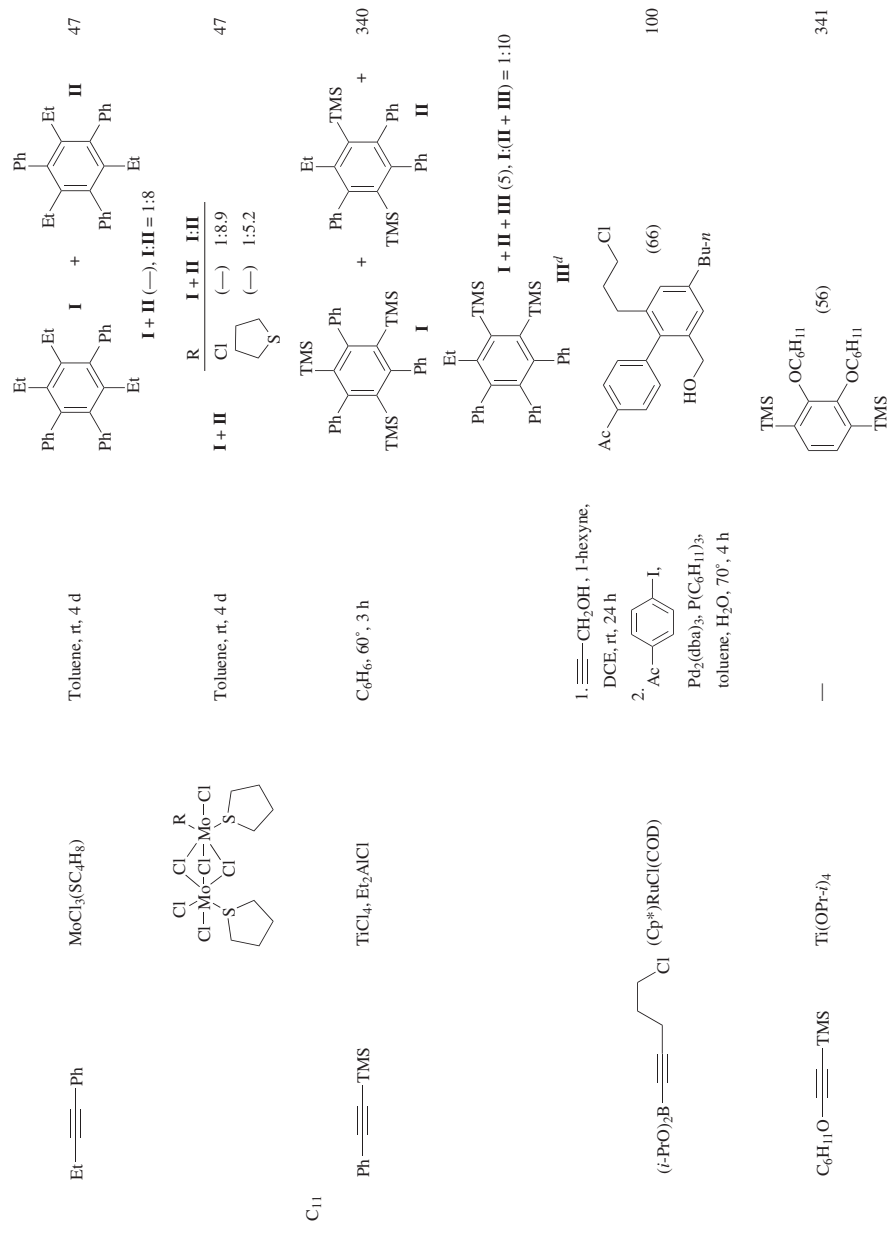
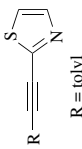
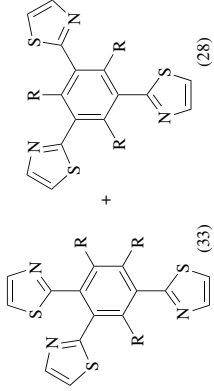
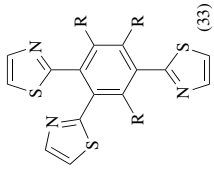
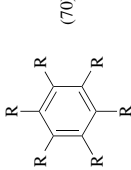
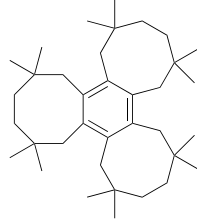
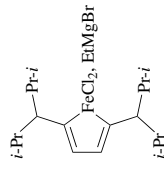
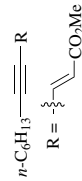
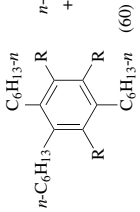
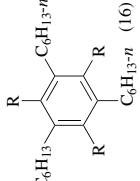


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{12}$  R = tolyl	$Co_2(CO)_8$	1,4-Dioxane, 110°, 4 h	 (28)	342
 (33)				
 (70)	$Ni[P(C_6H_{11})_3]_2(C_2H_4)$	THF, heat, 5 h		329
 (77)	 $i\text{-Pr}$ , $Pr\text{-}i$ , $FeCl_2$ , $EtMgBr$ , $i\text{-Pr}$	Isoprene, $Et_2O$ , 60°, 3 d		343
$n\text{-}C_6H_{13}$  R = $-CH_2-CH_2-CO_2Me$	$Ni(COD)_2, PPh_3$	Toluene, rt, 3.5 h	 (60)	286
			 (16)	

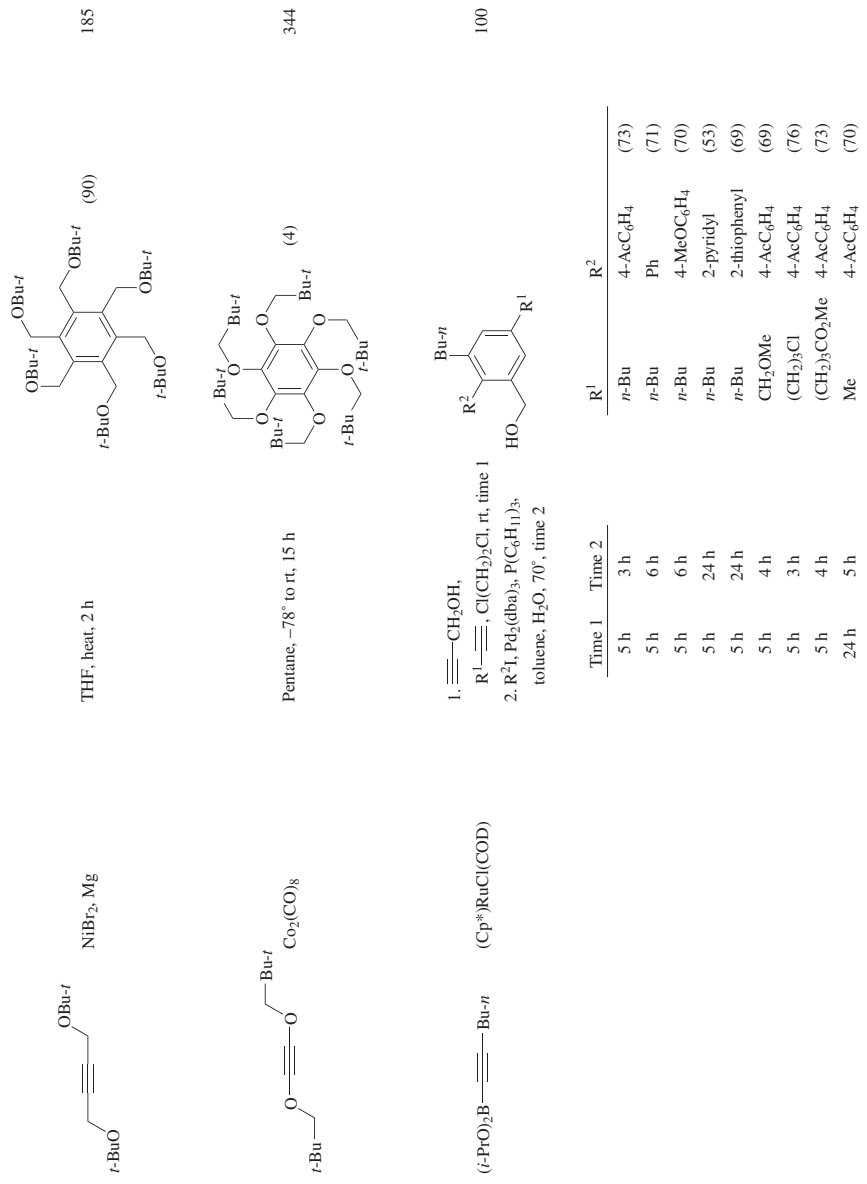


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																																																				
$n\text{-C}_3\text{H}_7\text{C}\equiv\text{C}\text{-C}_3\text{H}_7$	TaCl <sub>5</sub> , Zn	1. DME, C <sub>6</sub> H <sub>6</sub> , 50°, 2 h 2. 1-octyne, rt, 2 h 3. NaOH, H <sub>2</sub> O		345																																																				
$R^1\text{C}\equiv\text{CR}^2$	TaCl <sub>5</sub> , Zn	1. DME, C <sub>6</sub> H <sub>6</sub> , 50°, 2 h 2. THF, pyridine, rt, 0.5 h 3. X-C≡C-R <sup>3</sup> , rt 4. NaOH, H <sub>2</sub> O, rt, 1 h		345																																																				
			<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>R<sup>3</sup></th> <th>X</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-C<sub>6</sub>H<sub>13</sub></td> <td><i>n</i>-C<sub>6</sub>H<sub>11</sub></td> <td>H</td> <td>(CH<sub>2</sub>)<sub>2</sub> (80)</td> </tr> <tr> <td><i>n</i>-C<sub>6</sub>H<sub>13</sub></td> <td>Ph</td> <td>H</td> <td>(CH<sub>2</sub>)<sub>2</sub> (76)</td> </tr> <tr> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td>H</td> <td>CH<sub>2</sub> (74)</td> </tr> <tr> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td>H</td> <td>— (75)</td> </tr> <tr> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td>H</td> <td>O (76)</td> </tr> <tr> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td>H</td> <td>NBn (57)</td> </tr> <tr> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td><i>n</i>-C<sub>6</sub>H<sub>13</sub></td> <td>(CH<sub>2</sub>)<sub>2</sub> (78)</td> </tr> <tr> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td><i>n</i>-C<sub>3</sub>H<sub>11</sub></td> <td>Et</td> <td>CH<sub>2</sub>O (71)</td> </tr> <tr> <td>TMS</td> <td><i>n</i>-C<sub>10</sub>H<sub>21</sub></td> <td>H</td> <td>CH<sub>2</sub> (61)</td> </tr> <tr> <td>TMS</td> <td><i>n</i>-C<sub>10</sub>H<sub>21</sub></td> <td>H</td> <td>O (56)</td> </tr> <tr> <td>SMe</td> <td><i>n</i>-C<sub>10</sub>H<sub>21</sub></td> <td>H</td> <td>CH<sub>2</sub> (69)</td> </tr> <tr> <td>SMe</td> <td><i>n</i>-C<sub>10</sub>H<sub>21</sub></td> <td>H</td> <td>(CH<sub>2</sub>)<sub>2</sub> (64)</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	<i>n</i> -C <sub>6</sub> H <sub>11</sub>	H	(CH <sub>2</sub> ) <sub>2</sub> (80)	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Ph	H	(CH <sub>2</sub> ) <sub>2</sub> (76)	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	CH <sub>2</sub> (74)	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	— (75)	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	O (76)	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	NBn (57)	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	(CH <sub>2</sub> ) <sub>2</sub> (78)	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	Et	CH <sub>2</sub> O (71)	TMS	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	CH <sub>2</sub> (61)	TMS	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	O (56)	SMe	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	CH <sub>2</sub> (69)	SMe	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	(CH <sub>2</sub> ) <sub>2</sub> (64)	
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X																																																					
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	<i>n</i> -C <sub>6</sub> H <sub>11</sub>	H	(CH <sub>2</sub> ) <sub>2</sub> (80)																																																					
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Ph	H	(CH <sub>2</sub> ) <sub>2</sub> (76)																																																					
<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	CH <sub>2</sub> (74)																																																					
<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	— (75)																																																					
<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	O (76)																																																					
<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	H	NBn (57)																																																					
<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	(CH <sub>2</sub> ) <sub>2</sub> (78)																																																					
<i>n</i> -C <sub>3</sub> H <sub>11</sub>	<i>n</i> -C <sub>3</sub> H <sub>11</sub>	Et	CH <sub>2</sub> O (71)																																																					
TMS	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	CH <sub>2</sub> (61)																																																					
TMS	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	O (56)																																																					
SMe	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	CH <sub>2</sub> (69)																																																					
SMe	<i>n</i> -C <sub>10</sub> H <sub>21</sub>	H	(CH <sub>2</sub> ) <sub>2</sub> (64)																																																					



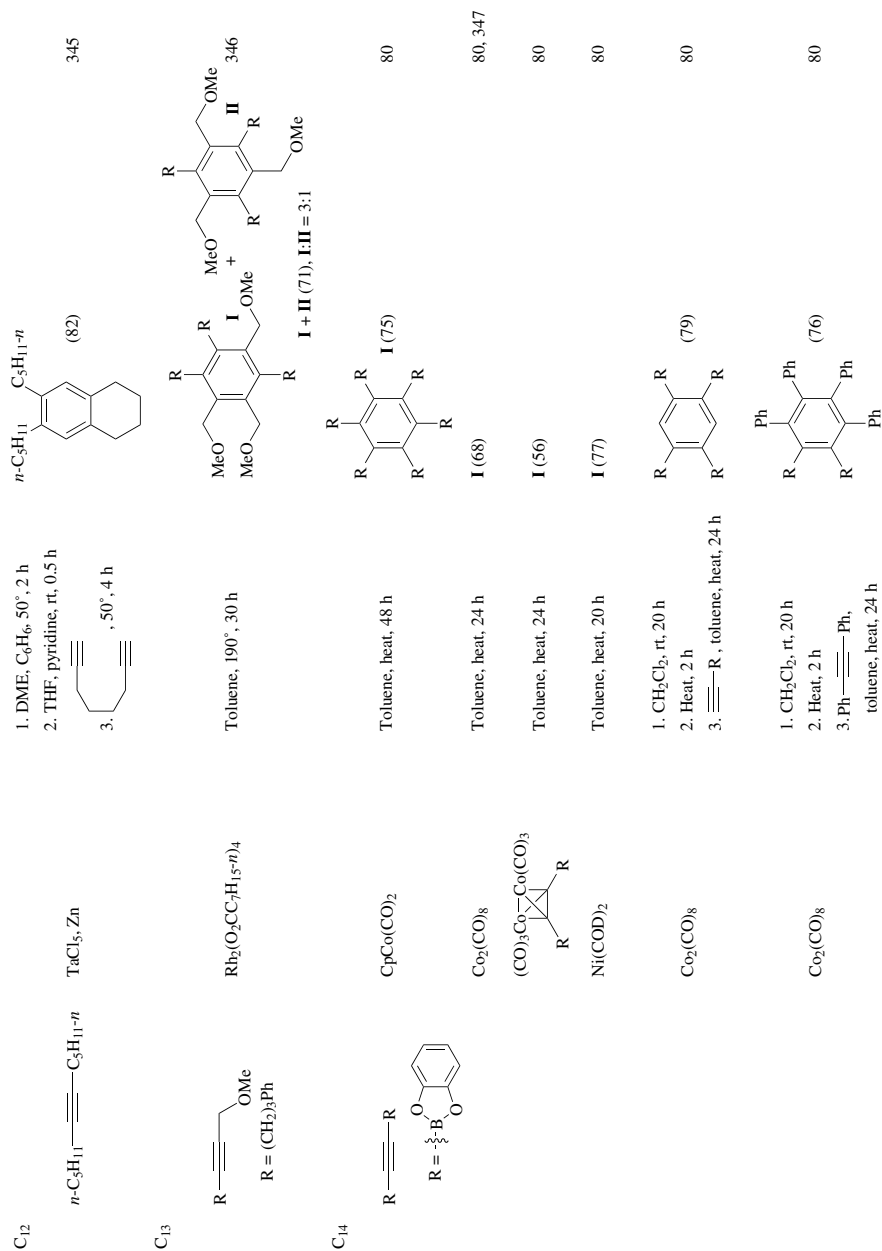
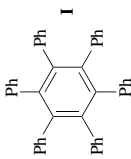
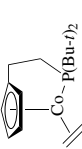
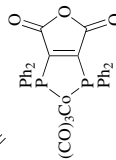
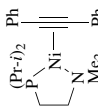
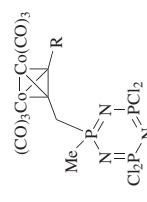


TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}$ $\text{C}_{14}$	$\text{Fe}(\text{C}_7\text{H}_8)(\text{COD})$	THF, rt, 46 h	 (20)	236
	$\text{Fe}(\text{C}_7\text{H}_8)(\text{COD})$	THF, heat, 50 h	(100)	236
	$\text{CoCl}(\text{PPh}_3)_3$	<i>o</i> -Xylene, heat	(97)	348
		$\text{H}_2\text{O}$ , EtOH, 60°, 7 h	(47)	194
		$\text{CH}_2\text{Cl}_2$ , rt, 48°	(5)	310
	$(\text{Cp}^*)\text{Rh}(\text{COD})$	Toluene, heat, 24 h	(6)	210
	$(\text{Cp}^*)\text{Rh}(\text{C}_2\text{H}_4)_2$	Toluene, heat, 24 h	(62)	210
	$\text{Cp}^*\text{Rh}(\text{COD})$	Toluene, heat, 24 h	(1)	210
	$(\text{C}_5\text{Cl}_5)\text{Rh}(\text{COD})$	Toluene, heat, 24 h	(1)	210
	$(\text{Cp}^*)\text{Rh}(\text{CO})_2$	Toluene, heat, 24 h	(34)	210
	$(\text{C}_9\text{H}_7)\text{Rh}(\text{COD})$	Toluene, heat, 24 h	(64)	209
	$(\text{C}_{13}\text{H}_8)\text{Rh}(\text{COD})$	<i>o</i> -Xylene, 160°, 40 h	(18)	209
	$[\text{RhCl}(\text{CO})(\text{EtSCH}_2\text{SEt})_2]$	<i>o</i> -Xylene, 100°, 46 h	(—)	182
	$\text{Ni}(\text{COD})$	$\text{CD}_3\text{CN}$ , 70° THF, heat	(—)	318
		$\text{C}_6\text{D}_6$ , 70°, 60 d	(96)	335

	<b>I</b>	<b>R</b> H 150° (20) Me 200° (20)	<b>Temp</b>	224
$n$ -Octane, 24 h				
	<b>I (75)</b>			318
Toluene, heat, 2 d				
	<b>I (100)</b>			87
	<b>I (93)</b>			239
	<b>I (57)</b>			349
	<b>I (7)</b>			(14)
	<b>I (21)</b>			(14)
	<b>I (62)</b>			96
	<b>I (60)</b>			(58)
	<b>I (58)</b>			(58)

1. Chlorohydroquinone, NPMoV,

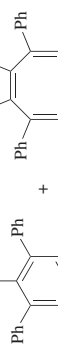
CH<sub>3</sub>SO<sub>3</sub>H, O<sub>2</sub>, dioxane,

60°, 2 h

2. O<sub>2</sub>, 60°, 5 h

TMSCl, THF, heat, 4 d

Ti(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)(μ-Br)(AlBr<sub>2</sub>)<sub>2</sub>



TiCl<sub>4</sub>, Et<sub>2</sub>AlCl

Cycloheptatriene

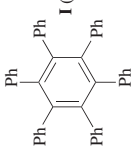
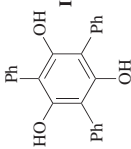
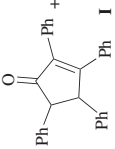
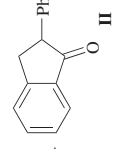
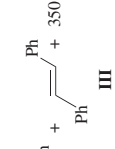
Cp<sub>2</sub>ZrEt<sub>2</sub>

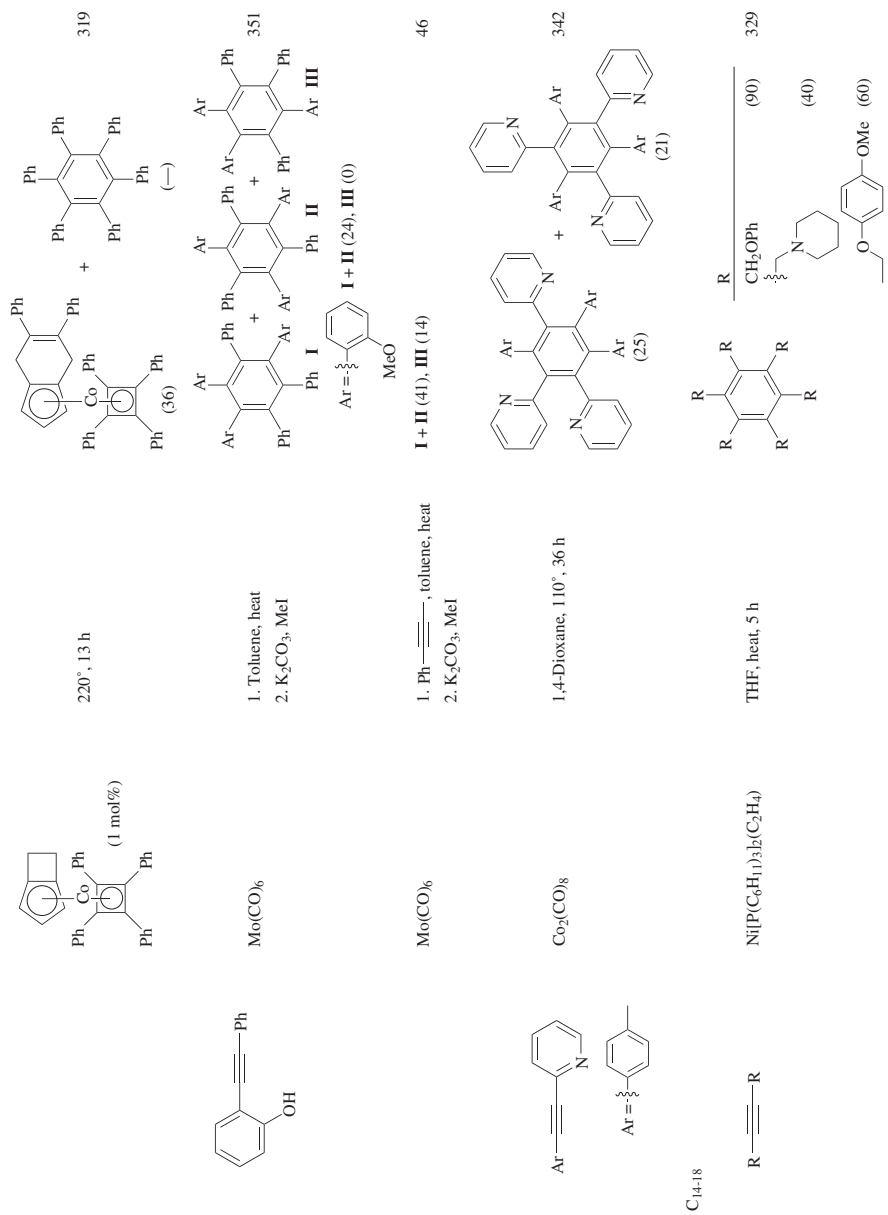
1. THF, 0°, 3 h

2. R<sup>1</sup>-R<sup>1</sup>, rt, 1 h

3. R<sup>2</sup>-R<sup>2</sup>, NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, rt, 1 h

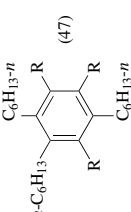
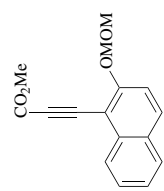
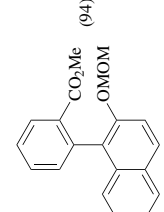
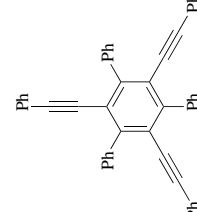
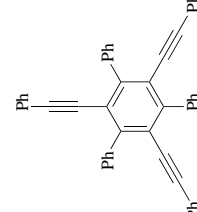
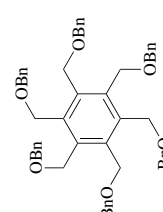
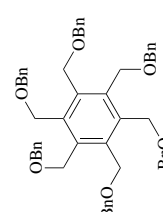
TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}$	$\text{PdCl}_2 \left( \text{NNMMe}_2 \right)_2$	$\text{CH}_2\text{Cl}_2$ , rt	 <b>I</b> (46) +  <b>II</b> (2) 217	217
	$\text{Ti}(\text{COD})(\text{Ph}-\text{C}\equiv\text{C}-\text{Ph})_2$ (8 mol%)	$180^\circ$ , 5 h	<b>I</b> (12) + $(\text{C}_4\text{Ph}_4)\text{Ti}(\text{COD})$ (50)	4
	$\text{TiCl}_3(\text{THF})_3$	<i>i</i> -PrMgCl, $-20^\circ$ , heat, 4 h	<b>I</b> (10)	4
	$(\text{Cp}^*)\text{Co}(\text{C}_2\text{H}_4)_2$	Hexane, $60^\circ$	<b>I</b> (50) + $(\text{Cp}^*)\text{Co}(\eta^4-\text{C}_4\text{Ph}_4)$ (80)	260
	$\text{CpCr}(\eta^3-\text{C}_3\text{H}_5)_2$ (25 mol%)	$-78^\circ$ to $0^\circ$ , 48 h	$\text{CpCo}(\eta^6-\text{C}_6\text{Ph}_6)$ (88) + 1,5-hexadiene (65)	11
	$\text{Ru}(\eta^6\text{-naphthalene})(\text{COD})$ (17 mol%)	THF, rt, 10 h	$\text{Ru}(\text{COD})(\eta^6-\text{C}_6\text{Ph}_6)$ (50)	232
	$\text{Co}(\text{NC}_3\text{H}_5)_2\text{BPh}_4$	Pyridine	$\text{Co}(\eta^6-\text{C}_6\text{Ph}_6)(\eta^2-\text{C}_2\text{Ph}_2)$ (—)	244
	$\text{Co}_4(\text{CO})_{12}$	<i>i</i> -PrOH, $220^\circ$ , 6 h	 <b>I</b> +  <b>II</b> +  <b>III</b> + 350	350
	$\text{Rh}_4(\text{CO})_{12}$	<i>i</i> -PrOH, $220^\circ$ , 6 h	<b>I</b> (41), <b>II</b> (24), <b>V</b> (11), <b>III</b> + <b>VI</b> (5), <b>III:VI</b> = 71:29	350
	$\text{Ir}_4(\text{CO})_{12}$	<i>i</i> -PrOH, $220^\circ$ , 6 h	<b>I</b> (42), <b>IV</b> (35), <b>V</b> (1), <b>III</b> + <b>VI</b> (17), <b>III:VI</b> = 83:17	350
		<i>i</i> -PrOH, $220^\circ$ , 6 h	<b>I</b> (9), <b>IV</b> (51), <b>V</b> (23), <b>III</b> + <b>VI</b> (4), <b>III:VI</b> = 86:14	350



C<sub>14-18</sub>

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

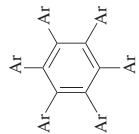
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$n\text{-C}_6\text{H}_{13}\text{—}\text{C}\equiv\text{C—R}$ $\text{R} = \begin{array}{c} \diagup \\ \diagdown \end{array} \text{—C}_6\text{F}_{13}\text{—}n$	Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	Toluene, 50°, 29 h	 (47)	286
 (94)	Ni(acac) <sub>2</sub> , PPh <sub>3</sub>	DIBAL-H, acetylene, THF, rt, 38 h	 (94)	225
 (87)	Co <sub>3</sub> (CO) <sub>9</sub> (t <sup>3</sup> -CH)	Xylene, heat, 30 min	 (87)	261
 (83)	Co <sub>2</sub> (CO) <sub>8</sub>	Toluene, 110°, 30 min	 (83)	352

C<sub>16</sub>

C<sub>18</sub>

C<sub>20-22</sub>

Ar—≡—Ar	PdCl <sub>2</sub> (PhCN) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	Temp	Time	
Ar			60°	6 h	(91)
3-EtOCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub>			heat	5 h	(83)
3,5-(MeOCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>			heat	6 h	(93)
3,5-(MeOCH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>					

C<sub>20-38</sub>

R—≡—R					
R					
4-MeO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, 100°			356
	CpCo(CO) <sub>2</sub>	Toluene, heat, 48 h			80
4- <i>t</i> -BuC <sub>6</sub> H <sub>4</sub>	Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, heat, 20 h			357
4-BzC <sub>6</sub> H <sub>4</sub>	Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, heat, 12 h			358, 359
CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>7</sub> H <sub>15-n</sub> )-4	Cp <sub>2</sub> Co (33 mol%)	Toluene, 80°, 24 h			360
CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>7</sub> H <sub>15-n</sub> )-4	Cp <sub>2</sub> Co (8 mol%)	Toluene, 80°, 24 h			360
CH <sub>2</sub> OC <sub>6</sub> H <sub>4</sub> (C <sub>7</sub> H <sub>15-n</sub> )-4	Cp <sub>2</sub> Co, PPh <sub>3</sub> (6 mol%)	Toluene, 80°, 24 h			360
4-(C <sub>12</sub> H <sub>25-n</sub> )C <sub>6</sub> H <sub>4</sub>	Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, 100°, 6 h			361
4-(C <sub>12</sub> H <sub>25-n</sub> )C <sub>6</sub> H <sub>4</sub>	Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, 100°			362

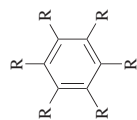
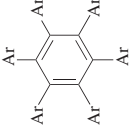

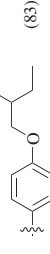
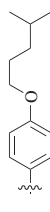
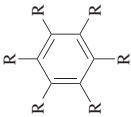
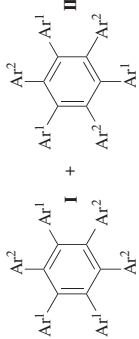


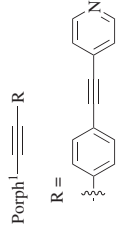
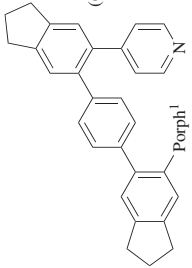
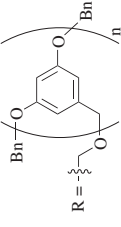
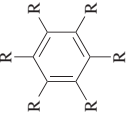

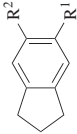
TABLE 2. DISUBSTITUTED ALKYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{24-26}$ $Ar-C\equiv C-Ar$	$PtCl_2(PPhCN)_2$	$C_6H_6$ , rt		360
		Time		
		4 h	 (83)	
		6 h	 (77)	
$C_{24-34}$ $R-C\equiv C-R$ $R = \text{---}O\text{---}C_6H_4\text{---}C_nH_{2n-1}$	$PtCl_2(PPhCN)_2$	$C_6H_6$ , rt		360
		n	Time	
		3	20 h	(32)
		4	11 h	(49)
		5	3 h	(33)
		6	19 h	(46)
		7	6 h	(43)
		8	4 h	(62)
$C_{29}$ $Ar^1-C\equiv C-Ar^2$ $Ar^1 = \text{---}OC_7H_{15-n}$ $Ar^2 = \text{---}OC_7H_{15-n}$	$PtCl_2(PPhCN)_2$	$C_6H_6$ , rt, 19 h		360
			<b>I</b> + <b>II</b> <b>I + II</b> (73)	



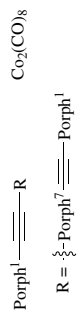
C <sub>30-38</sub>						
		PdCl <sub>2</sub> (PhCN)	C <sub>6</sub> H <sub>6</sub> , rt, 19 h		(57)	360
C <sub>36-74</sub>		Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, heat		(92)	363
		HgCo(CO) <sub>4</sub>	1,4-Dioxane, 100°, 2 d		(81)	82
		Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, 100°, 14 h		(36)	361
		Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane			
			Temp	Time		
			heat	overnight	(85)	364
			heat	overnight	(85)	364
			heat	2 h	(84)	295
			60°	12 h	(53)	365
			100°	5 d	(71)	366

TABLE 2. DISUBSTITUTED ALKYNES (Continued)

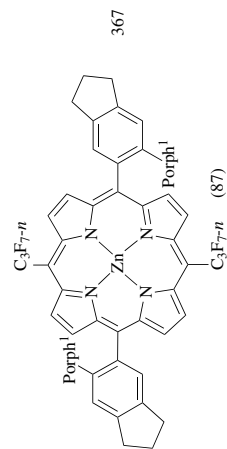
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.								
$C_{45}$ 	$Co_2(CO)_8$	1,6-Hepadiyne, 1,4-dioxane, 100°, 90 min	 (64)	367								
$C_{46-50}$ 	$Co_2(CO)_8$	Toluene, 110°	 <table border="1" data-bbox="862 646 967 793"> <thead> <tr> <th>n</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>2 h (80)</td> </tr> <tr> <td>2</td> <td>20 h (50)</td> </tr> <tr> <td>3</td> <td>48 h (36)</td> </tr> </tbody> </table>	n	Time	1	2 h (80)	2	20 h (50)	3	48 h (36)	352
n	Time											
1	2 h (80)											
2	20 h (50)											
3	48 h (36)											
$C_{50-112}$ 	$Co_2(CO)_8$	1,6-Hepadiyne, 1,4-dioxane, toluene, 100°										

R <sup>1</sup>	R <sup>2</sup>	Time	
Porph <sup>1</sup>	Porph <sup>1</sup>	14 h	(87)
Porph <sup>2</sup>	Porph <sup>4</sup>	17 h	(67)
Porph <sup>2</sup>	Porph <sup>5</sup>	17 h	(41)
Porph <sup>1</sup>	Porph <sup>4</sup>	17 h	(85)
Porph <sup>2</sup>	Porph <sup>2</sup>	—	(94)
Porph <sup>2</sup>	Porph <sup>3</sup>	—	(68)
Porph <sup>3</sup>	Porph <sup>3</sup>	—	(73)
Porph <sup>4</sup>	Porph <sup>4</sup>	17 h	(45)
Porph <sup>4</sup>	Porph <sup>6</sup>	17 h	(35)
Porph <sup>5</sup>	Porph <sup>5</sup>	17 h	(45)
Porph <sup>6</sup>	Porph <sup>6</sup>	17 h	(29)

C<sub>90</sub>



1,6-Hepadiyne, 1,4-dioxane,  
toluene, 100°, 17 h



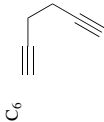
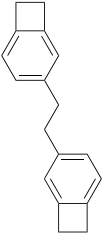
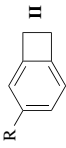
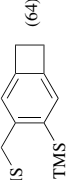
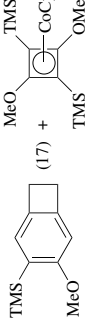
<sup>a</sup> Another product arises in a 20% yield.

<sup>b</sup> The yield is calculated based on catalyst.

<sup>c</sup> Other complexes are isolated in low yields.

<sup>d</sup> Product **I** and either product **II** or **III** are formed in the reaction. Analysis could not determine whether **II** or **III** is the second product, although **II** seems the most reasonable.

TABLE 3. DIYNES

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 C <sub>6</sub>	Catalyst	Toluene, 5 h	 I	9
	Catalyst	Temp		
	NbCl <sub>5</sub>	75°	(71)	
	NbCl <sub>5</sub> , SnPh <sub>4</sub>	35°	(90)	
	NbCl <sub>5</sub> , Sn( <i>Bu-n</i> ) <sub>4</sub>	35°	(91)	
	NbCl <sub>5</sub> , SnMe <sub>3</sub> Cl	35°	(91)	
	NbCl <sub>5</sub> , Sn( <i>Bu-n</i> ) <sub>3</sub> Cl	35°	(88)	
	NbCl <sub>5</sub> , SnI <sub>4</sub>	35°	(82)	
	NbBr <sub>5</sub>	75°	(35)	
	TaCl <sub>5</sub>	75°	(53)	
NbCl <sub>5</sub>	R—C≡C—, toluene, 5 h		 I (—) + II	9
	Temp			
	rt	R	(85)	
	rt	Ph	(18)	
	80°	(CH <sub>2</sub> ) <sub>3</sub> Cl	(38)	
CpCo(CO) <sub>2</sub>	TMSCH <sub>2</sub> —C≡C—TMS, 140°, 72 h		 I (—) + (64)	370
CpCo(CO) <sub>2</sub> (1 eq)	MeO—C≡C—TMS, <i>n</i> -octane, heat, 30 h		 (17) + (99)	68


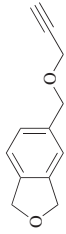

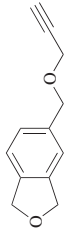

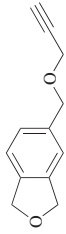

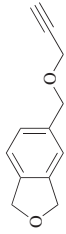

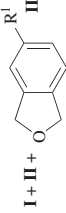

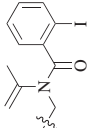

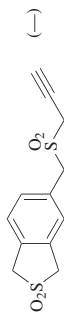
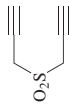
Catalyst	Solvent	Temp	Time	R <sup>1</sup>	<b>I + II</b>	<b>III</b>	
	$C_6D_6$ , rt						84
$Co_2(CO)_8(\mu^3-CH)$	Toluene, heat, 4 h						261
$RhCl(PPh_3)_3$	EtOH, rt, 10 min						21
$RhCl(PPh_3)_3$	EtOH, rt, 20 min						371
Catalyst	$R^1 \equiv \equiv \equiv$						
Catalyst	Solvent	Temp	Time	R <sup>1</sup>	<b>I + II</b>	<b>III</b>	
$(Cp^*)RuCl(COD)$	$Cl(CH_2)_2Cl$	rt	12 h	<i>n</i> -Bu	(18)	(68)	372
$(Cp^*)RuCl(COD)$	$Cl(CH_2)_2Cl$	rt	6 h	<i>n</i> -Bu	(—)	(64)	56
$RhCl(PPh_3)$	EtOH	0°	3 h	<i>n</i> -Pr	(—)	(58)	371
$RhCl(PPh_3)$	EtOH	rt	2 h	H	(—)	(42)	21
$RhCl(PPh_3)$	EtOH	0°	5 h	CH <sub>2</sub> OH	(—)	(44)	21
$RhCl(PPh_3)$	EtOH	0°	4 h	<i>n</i> -Pr	(—)	(58)	21
$RhCl(PPh_3)$	EtOH	0°	2 h	Ph	(—)	(11)	21
$[IrCl(COD)]_2$ , dppe	$C_6H_6$	50°	1 h	<i>n</i> -Bu	(—)	(63)	373
$RhCl(PPh_3)$	toluene	80°	—		(—)	(57)	374
$[RhCl(COD)]_2$ , TPPTS	Solvent	Temp	Time	R <sup>1</sup>	<b>I + II</b>	<b>III</b>	
	$H_2O, Et_2O, NaCl, HCl$ , rt, 24 h				CH <sub>2</sub> OH	(12)	(80)
					(CH <sub>2</sub> ) <sub>2</sub> OH	(1)	(84)
					(CH <sub>2</sub> ) <sub>3</sub> OH	(18)	(76)

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
	Catalyst	$R^1-C\equiv C-R^2$ , toluene		141	
	Catalyst	Temp	$R^1$	$R^2$	<b>I</b>
	CoBr(PPh <sub>3</sub> ) <sub>3</sub>	60°		H	<b>I</b> (55)
	CoBr(PPh <sub>3</sub> ) <sub>3</sub>	60°	"	<i>n</i> -Bu	(55)
	CoBr(PPh <sub>3</sub> ) <sub>3</sub>	60°	"	Ph	(88)
	NiBr <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , Zn	60°	"	H	(12)
	NiBr <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , Zn	60°	"	<i>n</i> -Bu	(5)
	NiBr <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , Zn	60°	"	Ph	(5)
	NiBr <sub>2</sub> (dppe), Zn	60°	"	H	(7)
	NiBr <sub>2</sub> (dppe), Zn	rt	"	<i>n</i> -Bu	(18)
	NiBr <sub>2</sub> (dppe), Zn	rt	"	Ph	(87)
	NiL <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , Zn	60°		Ph	(47)
	Catalyst	$R-C\equiv C$			

Catalyst	Solvent	Temp	Time	X	R
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	rt	11 h	S	H (5)
(Cp*)RuCl(COD)	DCE	rt	1 h	S	<i>n</i> -Bu (68)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	50°	6 h	SO	CH <sub>2</sub> OH (52)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	rt	5.5 h	SO	Ph (58)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	78°	10 min	SO <sub>2</sub>	CH <sub>2</sub> OH (66)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	rt	1 h	SO <sub>2</sub>	H (66)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	55°	1.5 h	SO <sub>2</sub>	Ph (41)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	55°	6 h	SO <sub>2</sub>	<i>n</i> -Pr (42)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	rt	48 h	SO <sub>2</sub>	TMS (5)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	rt	1.5 h	SO <sub>2</sub>	 (30)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH, CHCl <sub>3</sub>	79°	10 min	SO <sub>2</sub>	CH <sub>2</sub> OH (66)



EtOH, rt, 20 min

371

RhCl(PPh<sub>3</sub>)<sub>3</sub>

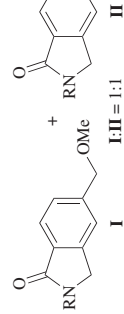
C<sub>6</sub>-19



NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>


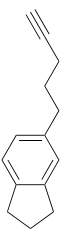
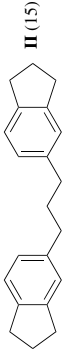
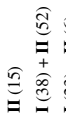
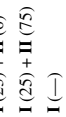
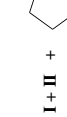


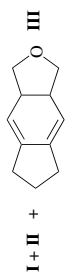
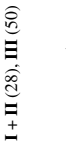
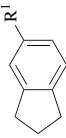
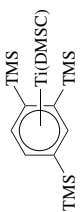
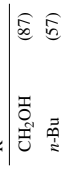
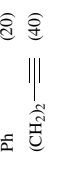
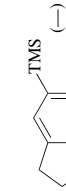
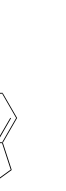
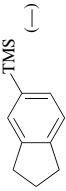


105



R	I+II
H	(59)
Me	(34)
PhCH <sub>2</sub>	(4)
Ph <sub>2</sub> CH	(63)

TABLE 3. DIYNES (Continued)

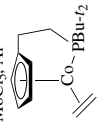
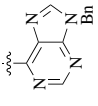
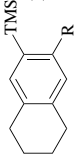
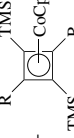

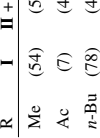
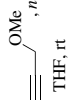
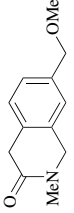
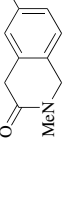
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.											
 C <sub>7</sub>	NbCl <sub>5</sub>	Toluene, 80°, 5 h	 I (0) +	9											
			 II (15)	9											
	TaCl <sub>5</sub>	Toluene, 80°, 5 h	 I (38) + II (52)	228											
			 I (23) + II (6)	19											
			 I (25) + II (75)	21											
			 I (-)	371											
	(Cp*)RuCl(COD)	 , 40°, 24 h	 I + II +	376, 377											
			 I + II (28), III (50)												
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	R <sup>1</sup> -C≡C-EtOH	<table border="1"> <thead> <tr> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>rt</td> <td>1.5 h</td> </tr> <tr> <td>60°</td> <td>2 h</td> </tr> <tr> <td>40°</td> <td>1.5 h</td> </tr> <tr> <td>78°</td> <td>8 h</td> </tr> </tbody> </table>	Temp	Time	rt	1.5 h	60°	2 h	40°	1.5 h	78°	8 h	 R <sup>1</sup>	21
				Temp	Time										
rt				1.5 h											
60°				2 h											
40°				1.5 h											
78°	8 h														
	TMS-C≡C-C <sub>6</sub> H <sub>6</sub> , rt	 CH <sub>2</sub> OH (87)													
		 <i>n</i> -Bu (57)													
		 Ph (20)													
		 (CH <sub>2</sub> ) <sub>2</sub> -C≡C (40)													
			 TMS (-)	84											



Catalyst	R <sup>1</sup> -C≡C-R <sup>2</sup>		Solvent	Temp	Time	R <sup>1</sup>		R <sup>2</sup>	
						R <sup>1</sup>	R <sup>2</sup>		
CpCo(CO) <sub>2</sub>	—	—	—	140°	72 h	CH <sub>2</sub> TMS	TMS	(89)	370
CpCo(CO) <sub>2</sub>			<i>o</i> -xylene	144°	72 h	CH <sub>2</sub> OH	TMS	(—)	370
CpCo(CO) <sub>2</sub>			<i>o</i> -xylene	144°	150 h	EtO <sub>2</sub> C	TMS	(70)	370
RhCl(PPh <sub>3</sub> ) <sub>3</sub>			EtOH	heat	—	CH <sub>2</sub> OH	CH <sub>2</sub> OH	(82)	378
NiBr <sub>2</sub> (dppf), Zn			CH <sub>3</sub> CN	80°	10 h		Ph	(53)	379
NiL <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , Zn (10 mol%)			toluene	60°	96 h		<i>n</i> -Bu	(11)	141
NiL <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , Zn (1 eq)			toluene	60°	48 h	"	<i>n</i> -Bu	(29)	141
RhCl(PPh <sub>3</sub> ) <sub>3</sub>			Acetylene, toluene, rt					(68)	380
RhCl(PPh <sub>3</sub> ) <sub>3</sub>			Acetylene, toluene, rt					(68)	380
NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>			 OMe, <i>n</i> -BuLi, PPh <sub>3</sub> , THF, rt					(46)	105

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst			
$C_{7-8}$				
			$I + II$	
	Catalyst	Solvent	$R^1$ $R^2$ $I + II$ $E:II$	
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	Me <i>n</i> -Bu (35) 1.7:1	381
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	Me C(CH <sub>3</sub> ) <sub>2</sub> OH (54) 1:0	381
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	Me CH <sub>2</sub> OH (53) 1.8:1	381
	(Cp*)RuCl(COD)	DCE	Me <i>n</i> -Bu (75) 95:5	372, 56
	MoCl <sub>5</sub> , Al	PhCl	CO <sub>2</sub> Me Ph (95) 63:37	382
$C_8$	MoCl <sub>5</sub> , Al	DME, 50°, 1 h		235
			$I + II + III$ $R = (CH_2)_4-C \equiv C$	
	Fe(C <sub>7</sub> H <sub>8</sub> )(COD)	THF, rt, 4 d	$I$ (100)	236
	Co	Mesitylene, 100°, 48 h	$I + II + III$ (86), $E:II:III = 86:5:9$	383
	NbCl <sub>5</sub>	Toluene, 80°, 5 h		9
	NbCl <sub>5</sub> , SnPh <sub>4</sub>	Toluene, 80°, 5 h	$I$ (33)	9
	TaCl <sub>5</sub>	Toluene, 80°, 5 h	$I$ (20)	9
	MoCl <sub>5</sub> , Al	DME, 80°, 6 h	$I$ (46)	235

Catalyst	$R^1$ - $\equiv$ - $R^2$	Solvent	Temp	Time	$R^1$	$R^2$	
MoCl <sub>5</sub> , Al		DME	50°	1 h	CO <sub>2</sub> Me	CO <sub>2</sub> Me	(49) 235
MoCl <sub>5</sub> , Al		DME	50°	1 h	<i>n</i> -Pr	<i>n</i> -Pr	(51) 235
MoCl <sub>5</sub> , Al		DME	50°	1 h	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H	(41) 235
		H <sub>2</sub> O, EtOH	rt	7 h	Ph	H	(44) 194
CpCo(CO) <sub>2</sub>		H <sub>2</sub> O, EtOH	rt	7 h	CO <sub>2</sub> Et	H	(40) 194
RhCl(PPh <sub>3</sub> ) <sub>3</sub>		—	140°	72 h	CH <sub>2</sub> TMS	TMS	(92) 370
		EtOH	78°	17 h	CH <sub>2</sub> OH	CH <sub>2</sub> OH	(99) 21
Ni <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , Zn		toluene	60°	24 h		H	(22) 141
CpCo(CO) <sub>2</sub> (5 mol%)	TMS- $\equiv$ -R						<b>I</b> + <b>III</b> <b>II</b> + 370
							<b>I</b> <b>II</b> + <b>III</b> <b>II</b> <b>III</b>
					Me	Me	(54) (5) 0:1
					Ac	Ac	(7) (4) —
					<i>n</i> -Bu	<i>n</i> -Bu	(78) (4) 0:1
NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>						<b>I</b> + <b>II</b>	105
						<b>I</b> + <b>II</b> (59), <b>I</b> : <b>II</b> = 1:1	

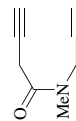
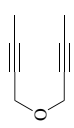
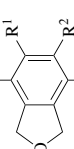
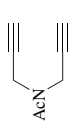
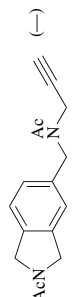
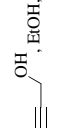
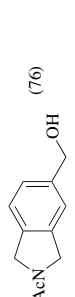
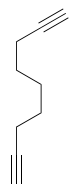
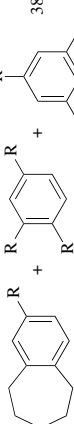
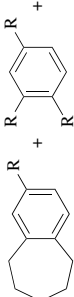
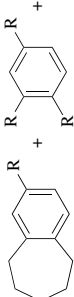
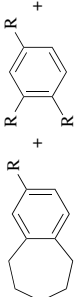
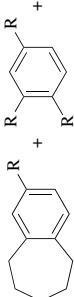

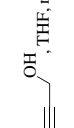
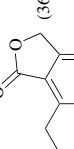


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	R <sup>1</sup> -C≡C-R <sup>2</sup> , EtOH, 83°		21	
		Time	R <sup>1</sup>	R <sup>2</sup>	
		45 min	CH <sub>3</sub> OH	CH <sub>3</sub> OH	(56)
		2 h	CH <sub>3</sub> OH	H	(72)
		2 h	<i>n</i> -Pr	H	(47)
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH, rt, 20 min		371	
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	 , EtOH, 78°, 3.5 h	 (76)	371, 21	
	Co	Mesitylene, 48 h		383	
			 +  + 	388	
				384	
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	 , THF, rt, 17 h	 (36)	384	
		Temp	I + II + III	I:II:III	
		rt	(60)	—:35:65	
	50°	(75)	20:28:52		
	100°	(81)	33:22:45		

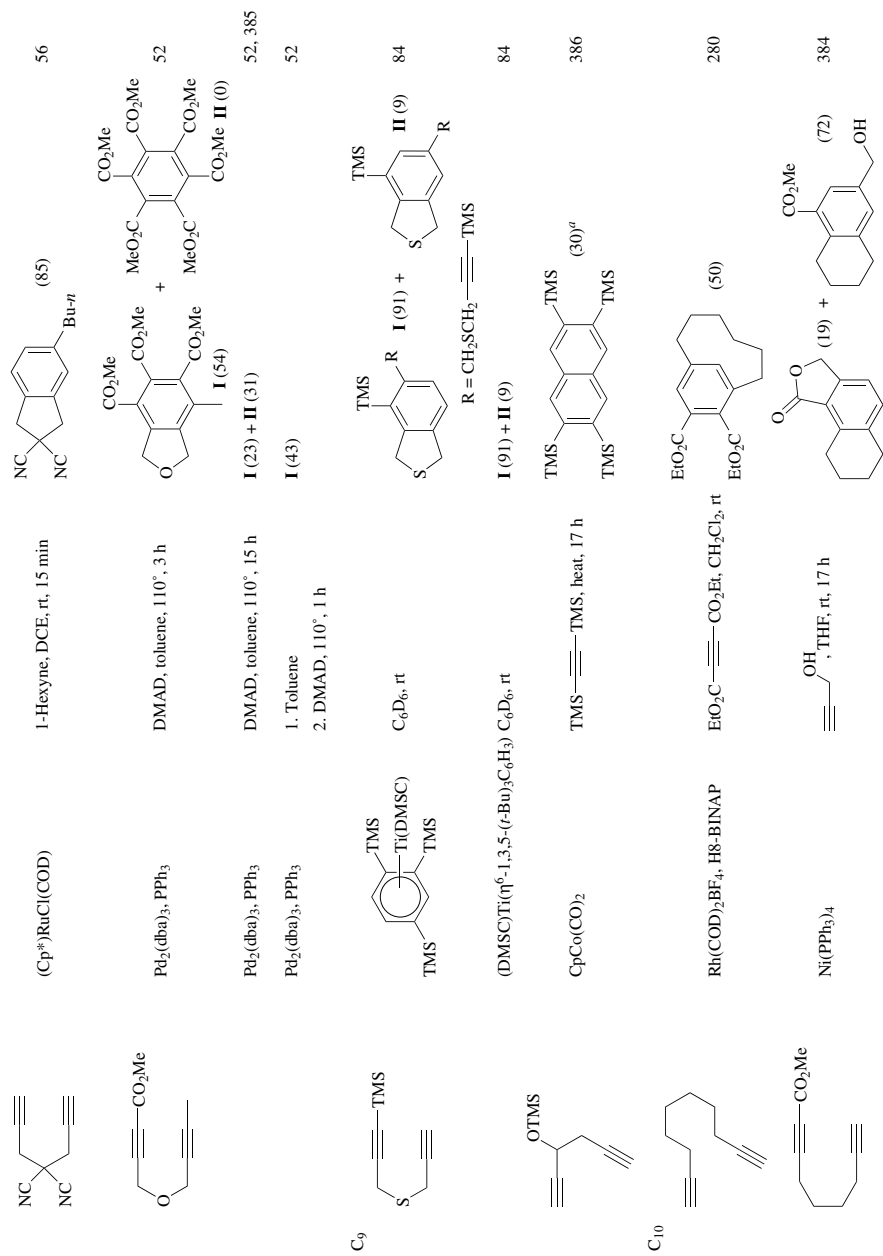


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	Ni(COD) <sub>2</sub> , PR <sub>3</sub>	CO <sub>2</sub> , THF, 120°, 5 h	  I + II Me (19) (4) <i>t</i> -Bu (35) (11) <i>n</i> -C <sub>8</sub> H <sub>17</sub> (46) (44)	218
	NiBr <sub>2</sub> (dppe), Zn	R <sup>1</sup> -C≡C-C≡C-R <sup>2</sup> , CH <sub>3</sub> CN, 80°, 10 h	 I R CO <sub>2</sub> Et R R	379
		Temp. Time	R	
		80° 10 h	Ph (79)	
		80° 10 h	4-AcC <sub>6</sub> H <sub>4</sub> (78)	
		80° 10 h	<i>n</i> -Bu (66)	
		rt 24 h	<i>n</i> -Bu (72)	
		80° 10 h	3,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (72)	
		80° 10 h	TMS (58)	
	CpCo(CO) <sub>2</sub>	R <sup>1</sup> -C≡C-R <sup>2</sup> , <i>hν</i> , heat, 6 h	 I R <sup>1</sup> R <sup>2</sup>	114
		Solvent	R <sup>1</sup> R <sup>2</sup>	
		—	TMS (96)	
		<i>o</i> -xylene	<i>n</i> -Bu (44)	
		<i>o</i> -xylene	Ph (35)	
		<i>o</i> -xylene	CO <sub>2</sub> Me (30)	
		<i>o</i> -xylene	TMS <i>n</i> -C <sub>5</sub> H <sub>11</sub> (58)	
		<i>o</i> -xylene	<i>n</i> -C <sub>6</sub> H <sub>13</sub> H (41)	
		<i>o</i> -xylene	Ph H (25)	

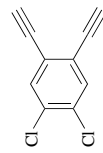
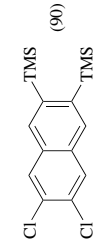
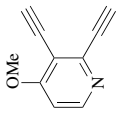
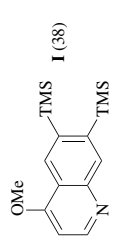
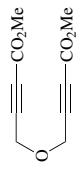
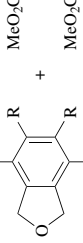
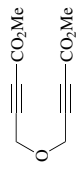
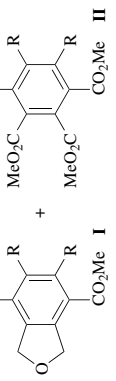
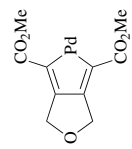
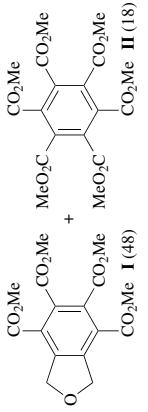
	$\text{CpCo}(\text{CO})_2$	BTMSA, <i>h\nu</i> , heat, 6 h		114
	$\text{CpCo}(\text{CO})_2$	BTMSA, xylenes, <i>h\nu</i> , heat, 6 h		387
	$\text{CpCo}(\text{CO})_2$	BTMSA, toluene, <i>h\nu</i> , heat, 6 h		387
	$\text{Pd}_2(\text{dba})_3$ , $\text{PPh}_3$ $\text{Pd}_2(\text{dba})_3$ , $\text{P}(\text{O}Ph)_3$ $\text{Pd}_2(\text{dba})_3$ , $\text{P}(\text{C}_6\text{H}_{11})_3$ $\text{Pd}_2(\text{dba})_3$ , $\text{PPh}_3$	$\text{R} \equiv \text{R}$		52
	$\text{L}^1$ $\text{L}^2$	Solvent	$\text{R}$	
	— —	toluene	$\text{CO}_2\text{Me}$ (36)	(8)
	$\text{PPh}_3$ —	toluene	$\text{CO}_2\text{Me}$ (68)	(13)
	$\text{PPh}_3$ , $\text{PPh}_3$	toluene	$\text{CO}_2\text{Me}$ (72)	(14)
	dppe	xylylene	$\text{CO}_2\text{Me}$ (40)	(14)
	$\text{PPh}_3$ —	toluene	$\text{CO}_2\text{Et}$ (61)	(30)
	$\text{Pd}_2(\text{dba})_3$ , $\text{PPh}_3$ $\text{Pd}_2(\text{dba})_3$ , $\text{P}(\text{O}Ph)_3$ $\text{Pd}_2(\text{dba})_3$ , $\text{P}(\text{C}_6\text{H}_{11})_3$ $\text{Pd}_2(\text{dba})_3$ , $\text{PPh}_3$	DMAD, toluene, 110°, 9 h		52
		DMAD, toluene, 110°, 30 min	$\text{I}$ (78)	52
		DMAD, toluene, 110°, 10 h	$\text{I}$ (17) + $\text{II}$ (14)	385
		DMAD, toluene, 110°, 18 h	$\text{I}$ (27) + $\text{II}$ (6)	385
		1. Toluene	$\text{I}$ (67)	385
		2. DMAD, 110°, 30 min		

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
	$\text{Pd}_2(\text{dba})_3, \text{PPh}_3$	$\text{EtO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Et}$ , toluene, $110^\circ$ , 1 h		52	
	$\text{Pd}_2(\text{dba})_3, \text{PPh}_3$	$\text{EtO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Et}$ , 1. Toluene 2. DMAD, $110^\circ$ , 1 h	<b>I (61)</b>	52	
	 $[\text{Rh}(\text{cis-cyclooctene})_2]$	$\text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}$ , PhCl, $80^\circ$		Time Ph 5 h (72) TMS 72 h (23)	379
		$\text{R}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}$ , PhCl, $80^\circ$		Time Ph 2 h (84) <i>n</i> -Bu 30 h (68) TMS 72 h (47)	379
	$\text{NiBr}_2(\text{dppe}), \text{Zn}$	$\text{Ph}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{Ph}$ , $\text{CH}_3\text{CN}$ , $80^\circ$ , 10 h		(80)	379
	$\text{Pd}_2(\text{dba})_3, \text{PPh}_3$	1. Toluene 2. DMAD, $110^\circ$ , 1 h		<b>I (13)</b>	385
	$\text{Pd}_2(\text{dba})_3, \text{PPh}_3$	DMAD, toluene, $110^\circ$ , 1 h	<b>I (18)</b>	52, 385	



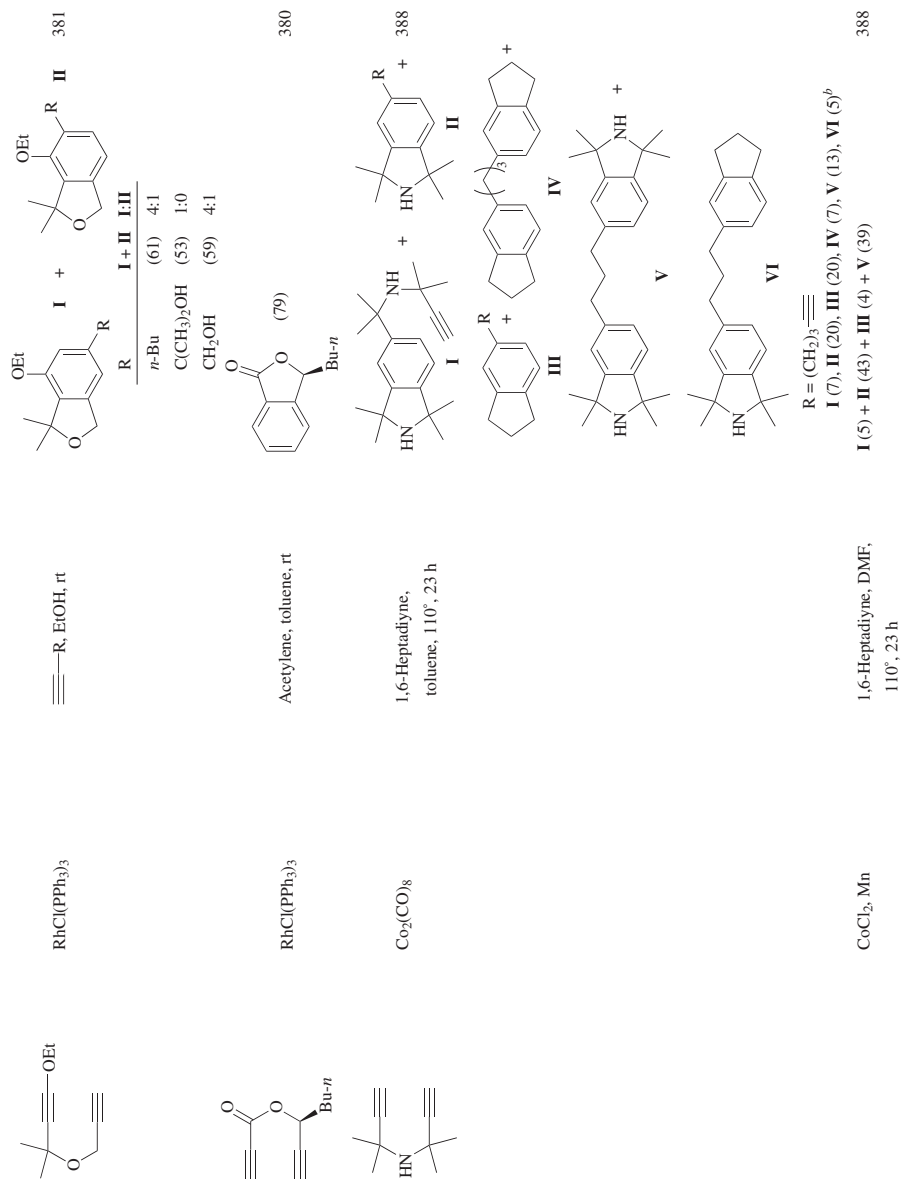
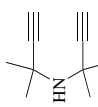
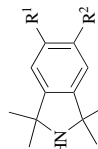
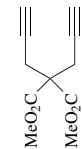
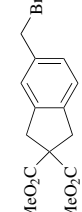
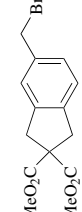


TABLE 3. DIYNES (Continued)

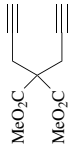
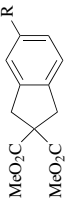

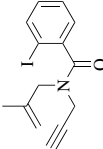
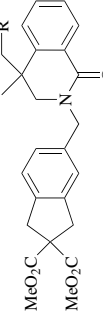

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.						
 C <sub>10</sub>	NiL <sub>4</sub>	R <sup>1</sup> -C≡C-R <sup>2</sup>		108						
					L	Solvent	Temp	Time	R <sup>1</sup>	R <sup>2</sup>
					PPh <sub>3</sub> (OPr- <i>i</i> ) <sub>2</sub>	—	80°	4 h	CMe <sub>2</sub> NH <sub>2</sub>	H (82)
					P(OPr- <i>i</i> ) <sub>3</sub>	—	80°	4 h	CMe <sub>2</sub> NH <sub>2</sub>	H (77)
					P(OPr- <i>i</i> ) <sub>3</sub>	—	80°	72 h	CMe <sub>2</sub> NH <sub>2</sub>	H (30)
					PPh(OPr- <i>i</i> ) <sub>2</sub>	CH <sub>3</sub> CN	80°	20 h	CMe <sub>2</sub> OH	H (20)
					PPh(OPr- <i>i</i> ) <sub>2</sub>	THF	rt	20 h	Ph	H (42)
					PPh(OPr- <i>i</i> ) <sub>2</sub>	THF	80°	4 h	Ph	Ph (63)
					 C <sub>11</sub>	Catalyst			390	
										Ni[PPh(OPr- <i>i</i> ) <sub>2</sub> ] <sub>4</sub>
Ni[PPh(OPr- <i>i</i> ) <sub>2</sub> ] <sub>4</sub>	PhCH=CH <sub>2</sub> , 80°, 72 h	I (7) + II (67)	389							
Ni(COD) <sub>2</sub>	CH <sub>2</sub> =CHCO <sub>2</sub> Et, rt, 8 h	I (11) + II (52)	389							
Ni(COD) <sub>2</sub> , POEt <sub>3</sub>	CH <sub>2</sub> =CHCO <sub>2</sub> Et, rt, 20 h	I (7) + II (63)	389							
Ni(COD) <sub>2</sub> , P(Bu- <i>n</i> ) <sub>3</sub>	CH <sub>2</sub> =CHCO <sub>2</sub> Et, rt, 36 h	I (6) + II (39)	389							
Ni[PPh(OPr- <i>i</i> ) <sub>2</sub> ] <sub>4</sub>	Cyclohexene, rt, 96 h	I (12) + II (36)	389							
	≡-CH <sub>2</sub> Br, THF, heat, 10 h									

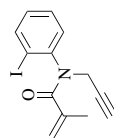
Catalyst	≡R			Reference
	Solvent	Temp	Time	
$\text{Co}_2(\text{CO})_8(\mu^3\text{-CH})$	toluene	heat	4 h	261
$\text{Co}_2(\text{CO})_8(\mu^3\text{-CH})$	$\text{C}_6\text{H}_6$	heat	3 h	261
$\text{RhCl}(\text{PPh}_3)_3$	toluene	heat	4 h	391
$\text{RhCl}(\text{PPh}_3)_3$	toluene	heat	4 h	391
$\text{RhCl}(\text{PPh}_3)_3$	toluene	80°	—	374
$\text{RhCl}(\text{PPh}_3)_3$	toluene	80°	—	374
$\text{RhCl}(\text{PPh}_3)_3$	toluene	110°	2 h	392
$[\text{Ir}(\text{COD})]_2$ , ligand	≡Bu- <i>n</i> , $\text{C}_6\text{H}_6$			373
Ligand	Temp	Time		
—	50°	24 h	(35)	
$\text{PPh}_3$	50°	24 h	(45)	
dppm	50°	24 h	(45)	
dppe	rt	20 min	(84)	
dppp	50°	24 h	(68)	
$\text{P}(\text{OPh})_3$	80°	24 h	(12)	

Reference	Ligand	Temp	Time
(81)		heat	4 h
(64)		heat	3 h
(60)		heat	4 h
(61)		heat	4 h
(58)		80°	—
(52)		80°	—
(—)		110°	2 h

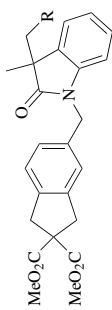
TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																								
	[Ir(COD)] <sub>2</sub> , dppe	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>C<sub>6</sub>H<sub>6</sub></td> <td>rt</td> <td>20 min</td> </tr> <tr> <td>1,4-dioxane</td> <td>heat</td> <td>2 h</td> </tr> <tr> <td>C<sub>6</sub>H<sub>6</sub></td> <td>rt</td> <td>1 h</td> </tr> <tr> <td>1,4-dioxane</td> <td>heat</td> <td>8 h</td> </tr> <tr> <td>C<sub>6</sub>H<sub>6</sub></td> <td>heat</td> <td>10 h</td> </tr> <tr> <td>1,4-dioxane</td> <td>heat</td> <td>2 h</td> </tr> <tr> <td>C<sub>6</sub>H<sub>6</sub></td> <td>rt</td> <td>30 min</td> </tr> </tbody> </table>	Solvent	Temp	Time	C <sub>6</sub> H <sub>6</sub>	rt	20 min	1,4-dioxane	heat	2 h	C <sub>6</sub> H <sub>6</sub>	rt	1 h	1,4-dioxane	heat	8 h	C <sub>6</sub> H <sub>6</sub>	heat	10 h	1,4-dioxane	heat	2 h	C <sub>6</sub> H <sub>6</sub>	rt	30 min	 R n-C <sub>8</sub> H <sub>17</sub> (82) Ph (83) (CH <sub>2</sub> ) <sub>3</sub> Ph (81) CH <sub>2</sub> OH (85) CH <sub>2</sub> OMe (66) CH <sub>2</sub> NMe <sub>2</sub> (65) (CH <sub>2</sub> ) <sub>3</sub> Cl (86)	373
Solvent	Temp	Time																										
C <sub>6</sub> H <sub>6</sub>	rt	20 min																										
1,4-dioxane	heat	2 h																										
C <sub>6</sub> H <sub>6</sub>	rt	1 h																										
1,4-dioxane	heat	8 h																										
C <sub>6</sub> H <sub>6</sub>	heat	10 h																										
1,4-dioxane	heat	2 h																										
C <sub>6</sub> H <sub>6</sub>	rt	30 min																										
		C <sub>6</sub> H <sub>6</sub>	 R (65)																									
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	 1. Toluene, heat, 4 h 2. Additive, Pd(OAc) <sub>2</sub> , PPh <sub>3</sub> , rt, 12 h	 R (39)  R (58) Ph (58) Bz (41)	391																								



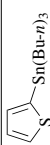
RhCl(PPh<sub>3</sub>)<sub>3</sub>

1. Toluene, heat, 4 h  
2. Additive, Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>,  
rt, 12 h



391

Additive



NaBPh<sub>4</sub>

NaBPh<sub>4</sub>, CO

PhB(OH)<sub>2</sub>

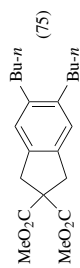
Ph

Bz

Ph

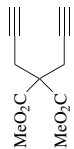
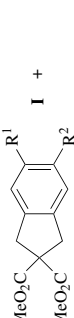
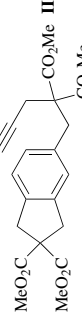
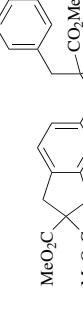

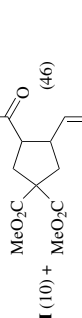
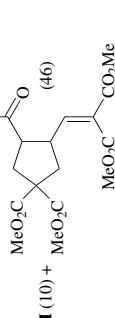
[(Cp\*)RuCl<sub>2</sub>]<sub>2</sub>

1-Hexyne, DCE, rt, 2 h



56

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $\text{C}_{11}$	$(\text{C}_9\text{H}_7)\text{RuCl}(\text{PPh}_3)_2$	$\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2$ , DCE	 <b>I</b> +  <b>II</b> +  <b>III</b>	372, 56 372 56 372 56 372, 56 56 56 56 56 56
		Temp	 <b>II</b> (77) + <b>III</b> (17)	393
	$(\text{Cp}^*)\text{RuCl}(\text{COD})$	 $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$ , DCE, 90°, 1 h	 <b>II</b> (10) + $\text{MeO}_2\text{C}-\text{C}(=\text{O})-\text{Me}$ (46)	394

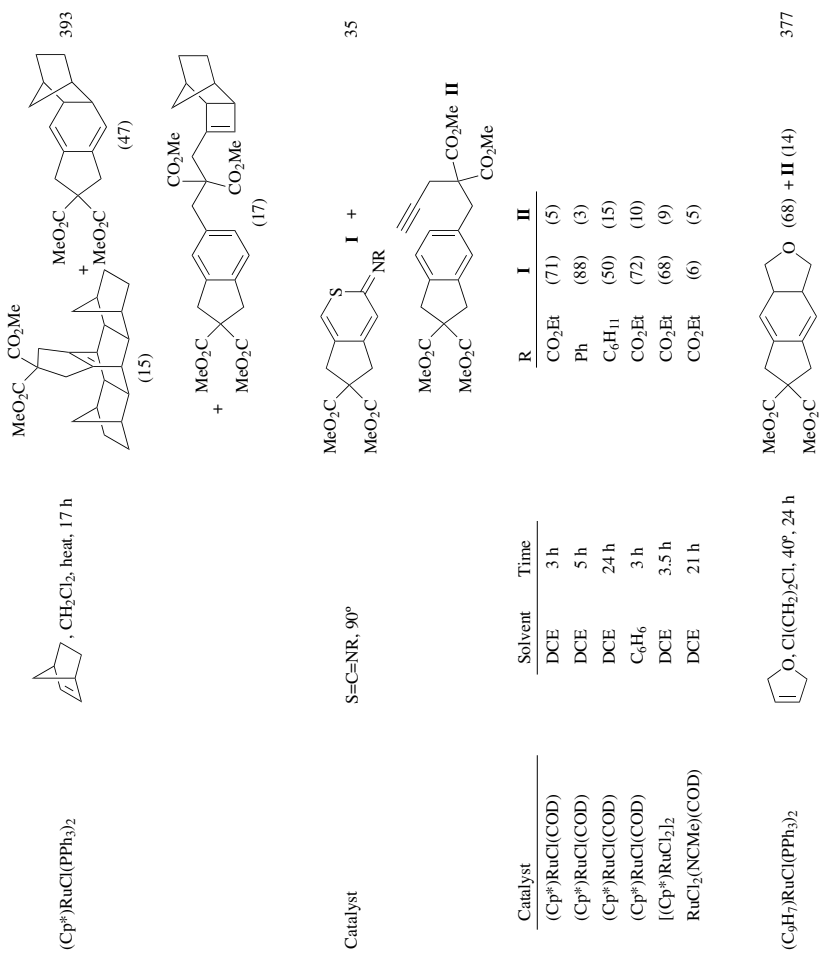
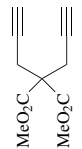

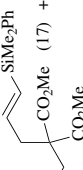
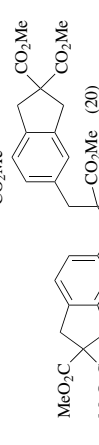
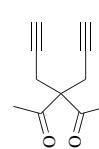
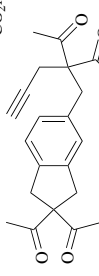


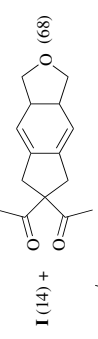

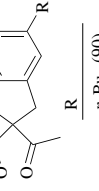
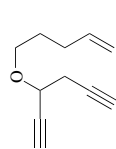
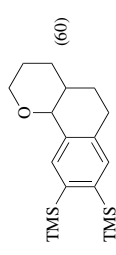


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																		
 $\text{C}_{11}$	$\text{Rh}_4(\text{CO})_{12}$	$\text{Me}_2\text{PhSiH}$ , 80°, 6 h	 (29) +  (17) +  (20)	395																		
	$\text{RhCl}(\text{PPh}_3)_3$	$\text{EtOH}$ , rt, 20 min	 I (-)	371																		
	$(\text{C}_9\text{H}_7)\text{RuCl}(\text{PPh}_3)_2$	 , 40°, 24 h	 I (14) + I (68)	376																		
	Catalyst	$\equiv\text{C}-\text{R}$	<table border="1"> <thead> <tr> <th>Catalyst</th> <th>Solvent</th> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td><math>(\text{Cp}^*)\text{RuCl}(\text{COD})</math></td> <td>DCE</td> <td>rt</td> <td>15 min</td> </tr> <tr> <td><math>\text{RhCl}(\text{PPh}_3)_3</math></td> <td>—</td> <td>—</td> <td>—</td> </tr> </tbody> </table>  R <table border="1"> <thead> <tr> <th>R</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td><i>n</i>-Bu</td> <td>90</td> </tr> <tr> <td>H</td> <td>60</td> </tr> </tbody> </table>	Catalyst	Solvent	Temp	Time	$(\text{Cp}^*)\text{RuCl}(\text{COD})$	DCE	rt	15 min	$\text{RhCl}(\text{PPh}_3)_3$	—	—	—	R	Yield (%)	<i>n</i> -Bu	90	H	60	56 371
Catalyst	Solvent	Temp	Time																			
$(\text{Cp}^*)\text{RuCl}(\text{COD})$	DCE	rt	15 min																			
$\text{RhCl}(\text{PPh}_3)_3$	—	—	—																			
R	Yield (%)																					
<i>n</i> -Bu	90																					
H	60																					
	$\text{CpCo}(\text{CO})_2$	BTMSA, <i>n</i> -octane, heat, 117 h	 (60)	386																		



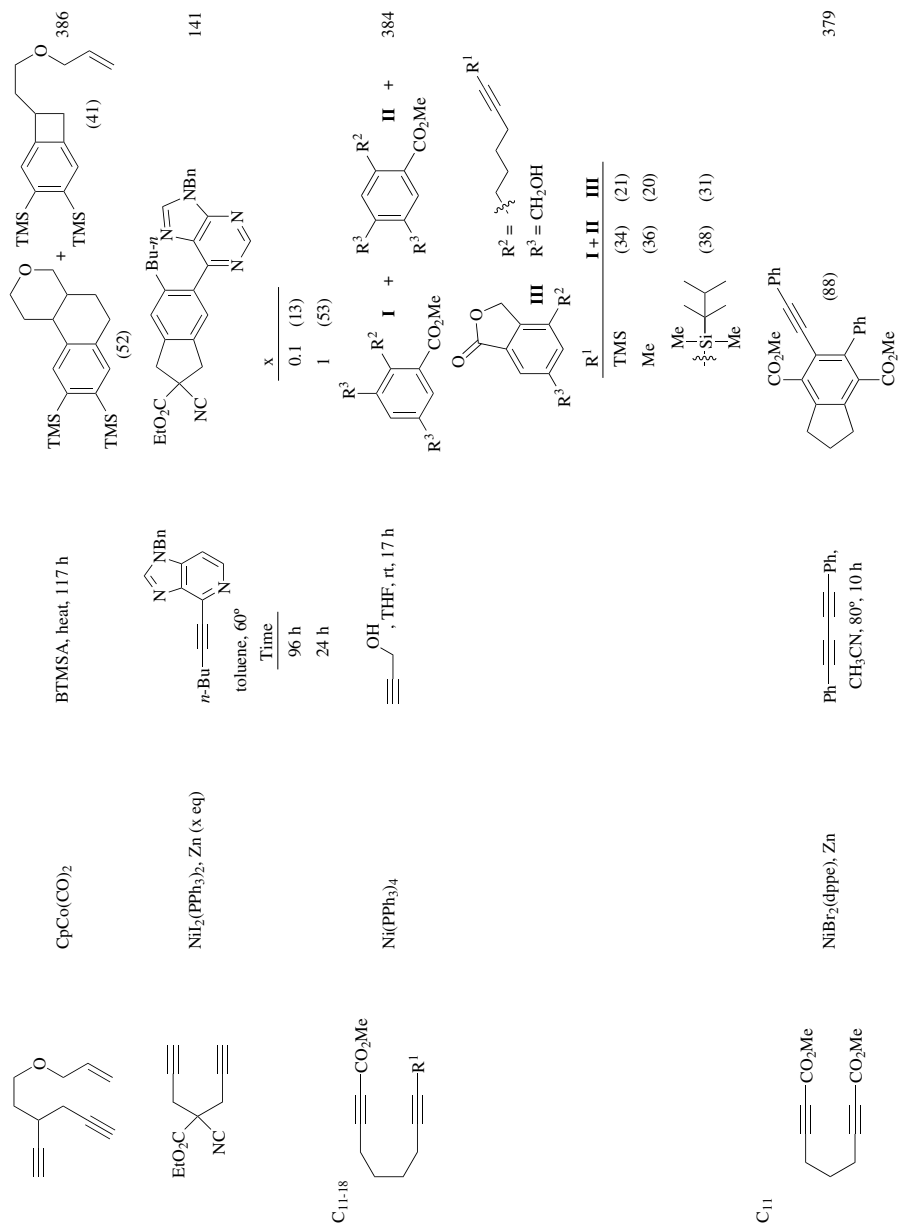


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>12</sub> 	Ni(PPh <sub>3</sub> ) <sub>4</sub>	, THF, rt, 17 h	 I + II + III R = CH <sub>2</sub> OMe I (35), II + III (35)	384
	NiBr <sub>2</sub> (dppe), Zn	<i>n</i> -Bu-C≡C-C≡C-Ph, CH <sub>3</sub> CN, rt, 24 h	 (70) + (3)	379
	Catalyst	R <sup>1</sup> -C≡C-R <sup>2</sup>	 R <sup>1</sup> -C≡C-R <sup>2</sup>	
	Catalyst	Solvent	R <sup>1</sup> CO <sub>2</sub> Me	
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	(CH <sub>2</sub> ) <sub>3</sub> OH	(42)
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	 H	(87)
	NiBr <sub>2</sub> (dppe), Zn	CH <sub>3</sub> CN	Ph	(87)
	NiBr <sub>2</sub> (dppe), Zn	CH <sub>3</sub> CN	<i>n</i> -Bu	(88)
	NiBr <sub>2</sub> (dppe), Zn	CH <sub>3</sub> CN	C <sub>6</sub> H <sub>4</sub> Ac-4	(88)
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	 OH, THF, rt, 17 h	 (24)	384



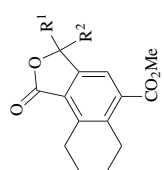
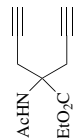
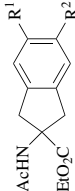
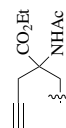
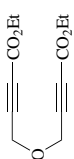
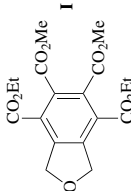

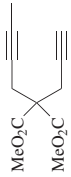
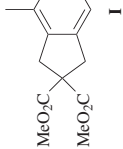
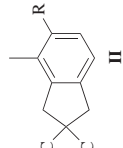
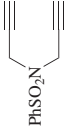
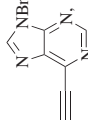
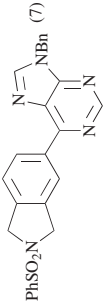
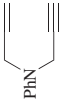
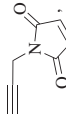
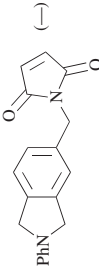
		$R^1, R^2$ , THF, rt, 17 h				$R^1$ H (78) Me (51) Me (58) -CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> - (58)	396, 384
	Catalyst	$R^1, R^2$					
	Catalyst	Solvent	Temp	Time	$R^1$	$R^2$	
	CpCo(CO) <sub>2</sub>	<i>n</i> -octane	heat	14 h	Ph	(22)	397, 398
	CpCo(CO) <sub>2</sub>	<i>n</i> -octane	heat	7 h	Ph	(27)	397, 398
	CpCo(CO) <sub>2</sub>	toluene	heat	11 h	CO <sub>2</sub> Me	(27)	397, 398
	CpCo(CO) <sub>2</sub>	—	140°	5 h	TMS	(12)	399
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	heat	48 h	CH <sub>2</sub> OH	(68)	397, 398
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	heat	6 h	CH <sub>2</sub> OH	(81)	397, 398
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	heat	2.5 h	(CH <sub>2</sub> ) <sub>2</sub> OH	(97)	397, 398
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	heat	50 h	(CH <sub>2</sub> ) <sub>3</sub> OH	(50)	397, 398
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	heat	5 h	C(CH <sub>3</sub> ) <sub>2</sub> OH	(95)	397, 398
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	70°	2 h		(80)	399
	Pd <sub>2</sub> (dba) <sub>3</sub> , PPh <sub>3</sub>	1. Toluene 2. DMAD, 110°, 30 min				<b>I (66)</b>	52, 385
	Pd <sub>2</sub> (dba) <sub>3</sub> , PPh <sub>3</sub>	DMAD, toluene, 110°, 1 h				<b>I (72)</b>	52

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst	$\equiv\equiv\text{R}$	 <b>I</b> +  <b>II</b>	
	Catalyst	Solvent	R	<b>I + II</b>
	(Cp*)RuCl(COD)	DCE	<i>n</i> -Bu	(85) 93:7
	(Cp*)RuCl(COD)	DCE	Me	(80) 94:6
	(Cp*)RuCl(COD)	DCE	CH <sub>2</sub> OMe	(86) 94:6
	(Cp*)RuCl(COD)	DCE	Ph	(82) 88:12
	[(Cp*)RuCl <sub>2</sub> ]	DCE	<i>n</i> -Bu	(81) 94:6
	CpRuCl(COD)	DCE	<i>n</i> -Bu	(76) 87:13
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	<i>n</i> -Bu	(61) 63:37
	Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	THF	<i>n</i> -Bu	(83) 30:70
	CpCo(COD)	xylene	<i>n</i> -Bu	(70) 54:46
		Temp		
		<i>rt</i>		
		18 h		
		3 h		
		24 h		
		2 h		
		24 h		
		60°		
		4 h		
		150°		
		Time		
		1 h		
		372, 56		
		372, 56		
		372, 56		
		372, 56		
		56		
		56		
		56		
		56		
		56		
		56		
	NiBr <sub>2</sub> (dpppe) <sub>2</sub> , PPh <sub>3</sub>		 (7)	141
		toluene, 60°, 96 h		
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>		 (8)	392
		THF, <i>rt</i> , 17 h		

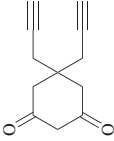
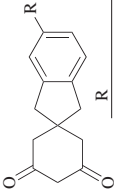
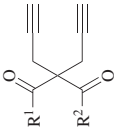
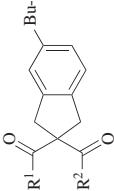
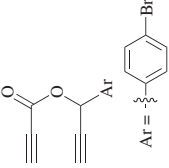
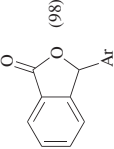
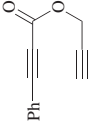
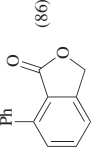
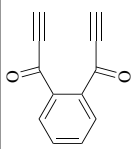
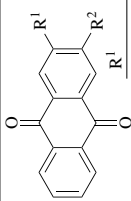
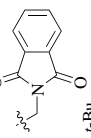
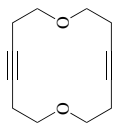
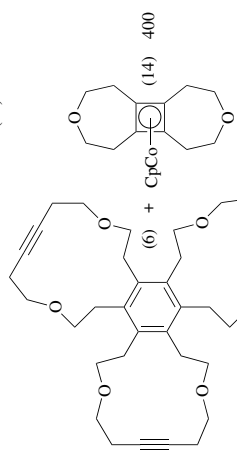
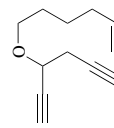
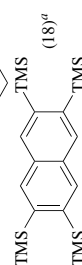
	$\text{RhCl}(\text{PPh}_3)_3$	$\equiv\text{R}$ , EtOH		21
		Temp Time	R	
		40° 1 h	H	(79)
		70° 5 h	CH <sub>2</sub> OH	(64)
		78° 24 h	CH <sub>2</sub> OMe	(61)
		70° 6 h	CH <sub>2</sub> OAc	(70)
		70° 1 h	(CH <sub>2</sub> ) <sub>2</sub> OH	(73)
		40° 4 h	<i>n</i> -Pr	(65)
		40° 2 h	(CH <sub>2</sub> ) <sub>2</sub> -≡	(59)
		60° 6 h	Ph	(55)
		80° 20 h	TMS	(3)
	(Cp*)RuCl(COD)	1-Hexyne, DCE, rt, 15 min		56
	$\text{RhCl}(\text{PPh}_3)_3$	Acetylene, toluene, rt		380
	$\text{RhCl}(\text{PPh}_3)_3$	Acetylene, toluene, rt		380

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.			
	(Cp*)RuCl(COD)	R <sup>1</sup> —C≡C—R <sup>2</sup> , DCE, rt		112			
					Time	R <sup>1</sup>	R <sup>2</sup>
					1.5 h	<i>n</i> -Bu	H (90)
					3 h	CH <sub>2</sub> OMe	H (84)
					1 h	(CH <sub>2</sub> ) <sub>3</sub> Cl	H (81)
30 min	(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> Me	H (84)					
		10 min		(76)			
		—	<i>n</i> -Bu	H (65)			
		—	Ph	H (65)			
		—	H	H (92)			
		—	Et	Et (33)			
	CpCo(COD) (1 eq)	<i>n</i> -Nonane, heat		400			
					(6)	(14)	
	CpCo(CO) <sub>2</sub>	BTMSA, heat, 117 h		386			
					(18) <sup>d</sup>		

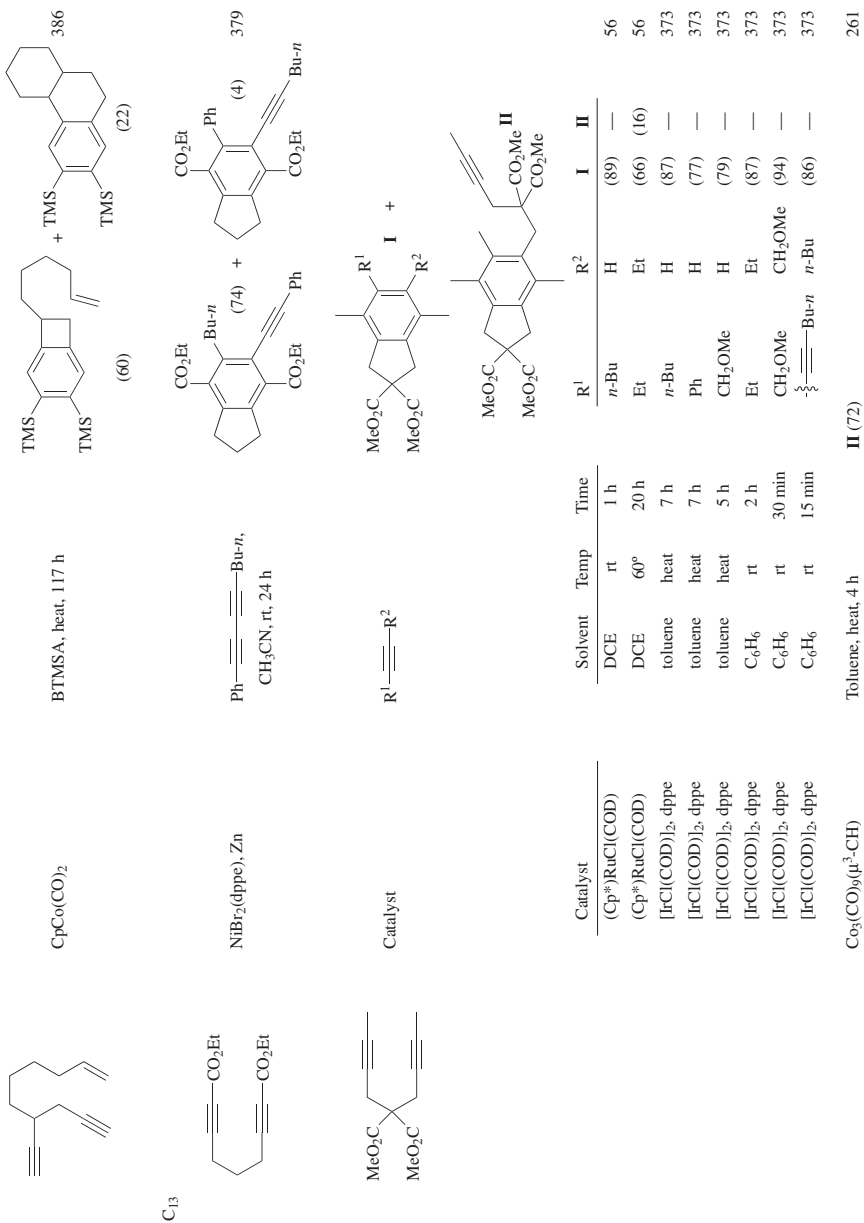


TABLE 3. DIYNES (Continued)

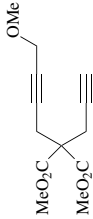
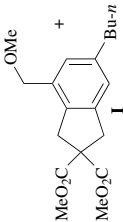
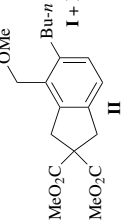
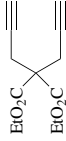

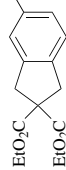
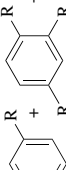
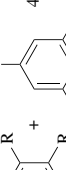



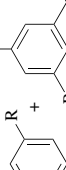


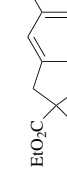




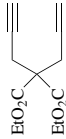
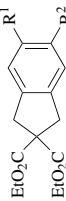

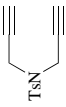

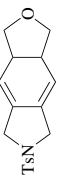
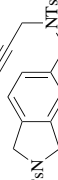
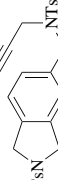




Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $\text{C}_{13}$	(Cp*)RuCl(COD)	1-Hexyne, DCE, rt, 12 h	  <b>I + II (78), I:II = 92:8</b>	56
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	 , THF, rt, 17 h	   <b>I (8), II + III (28)</b>	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	 , THF, rt, 17 h	  <b>(12)</b>	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	 , THF, rt, 17 h	 <b>(20)</b>	401
	Co <sub>2</sub> (CO) <sub>8</sub>	 , CH <sub>2</sub> Cl <sub>2</sub> , 100°, 2 d	 <b>I (85)</b>	402
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH, rt, 20 min	<b>I (→)</b>	371





TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.		
 C <sub>13</sub>	Catalyst	R <sup>1</sup> —C≡C—R <sup>2</sup>				
	Catalyst	Solvent	R <sup>1</sup>	R <sup>2</sup>		
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> NEt <sub>2</sub>	H	(60)	105
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> NMe <sub>2</sub>	H	(62)	105
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> NHMe	H	(72)	105
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> NHAc	H	(40)	105
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> NHBz	H	(42)	105
	NiB <sub>5</sub> (dippe), Zn	CH <sub>3</sub> CN	 -Ph	Ph	(62)	379
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> OH	H	(52)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	(CH <sub>2</sub> ) <sub>2</sub> OH	H	(34)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	(CH <sub>2</sub> ) <sub>3</sub> OH	H	(28)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	(CH <sub>2</sub> ) <sub>4</sub> OH	H	(62)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> OMe	H	(78)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> OTBS	H	(32)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> OTHP	H	(35)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	(CH <sub>2</sub> ) <sub>2</sub> OTHP	H	(16)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	(CH <sub>2</sub> ) <sub>3</sub> OTHP	H	(9)	401
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF	CH <sub>2</sub> OH	CH <sub>2</sub> OH	(15)	401
	Pd(PPh <sub>3</sub> ) <sub>4</sub> , AcOH	DMF	Et	Et	(37)	76
	(Cp*)RuCl(COD)	 O, DCE, rt, 14 h	 + 		376	
	(C <sub>9</sub> H <sub>7</sub> )RuCl(PPh <sub>3</sub> ) <sub>2</sub>	 O, DCE, rt, 14 h	 + 		377	















Catalyst		Solvent	Time	R	Yield (%)
(Cp*)RuCl(COD)		DCE	10 min	<i>n</i> -Bu	372 (80)
(Cp*)RuCl(COD)		DCE	15 min	<i>n</i> -Bu	56 (96)
[RhCl(COD)] <sub>2</sub> , TPPTS		H <sub>2</sub> O, Et <sub>2</sub> O, NaCl, HCl	72 h	CH <sub>2</sub> OH	375 (84)
Ni(acac) <sub>2</sub> , DIBAL-H, PPh <sub>3</sub>		THF	12 h	H	403 (91)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>		Acetylene (1 atm), toluene, rt, 30 min			106
Catalyst				R	
Catalyst		Solvent	Time	R	Yield (%)
(Cp*)RuCl(COD)		DCE	15 min	<i>n</i> -Bu	56 (91)
Ni(PPh <sub>3</sub> ) <sub>4</sub>		THF	12 h	CH <sub>2</sub> OMe	105 (36)
Ni(acac) <sub>2</sub> , PPh <sub>3</sub> , DIBAL-H		Acetylene, THF, rt			225
RhCl(PPh <sub>3</sub> ) <sub>3</sub>		Acetylene, toluene, rt			380
Ni(acac) <sub>2</sub> , PPh <sub>3</sub> , DIBAL-H		1. HO-CH <sub>2</sub> -C≡C-C≡C-CH <sub>2</sub> -OH PPhMe <sub>2</sub> , THF, rt 2. Ac <sub>2</sub> O, pyridine			225 (12)

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Acetylene, toluene, 40°		380
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Acetylene, toluene, 40°		380
	CpCo(CO) <sub>2</sub>	BTMSA, toluene, heat, 117 h		386
	CpCo(CO) <sub>2</sub>	BTMSA, heat		386
	(Cp*)RuCl(COD)	<i>n</i> -octane, 117 h		404
	(Cp*)RuCl(COD)	<i>hν</i> , 6.5 h		372, 56
	(Cp*)RuCl(COD)	1-Hexyne, DCE, rt, 7 h		98, 2

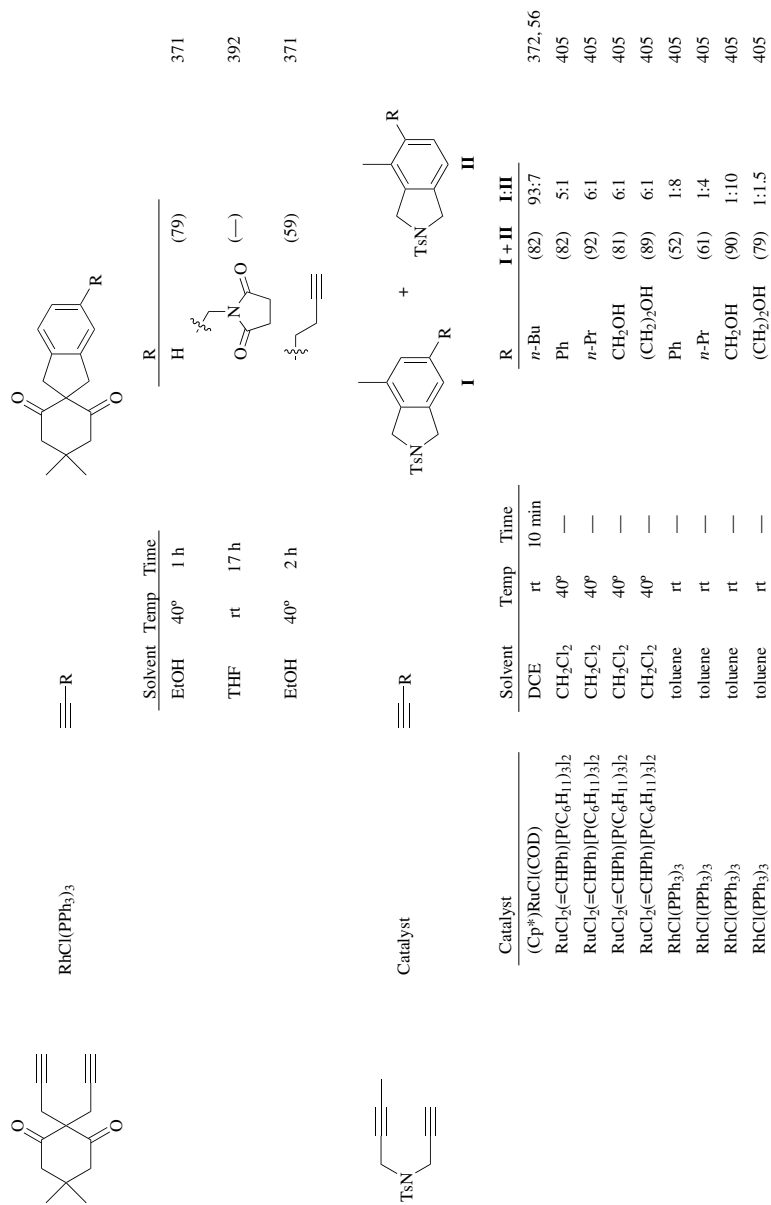
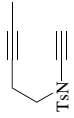

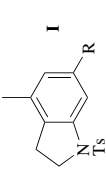
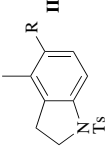
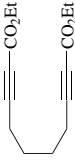

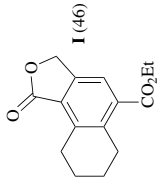
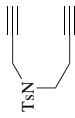


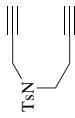
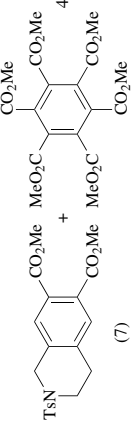
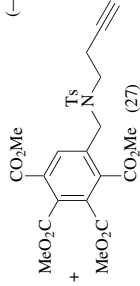
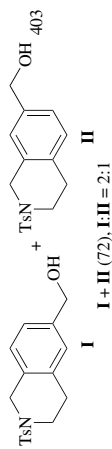
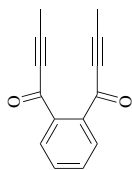


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.			
	Catalyst		 	405			
					Catalyst	Solvent	Temp
					RuCl <sub>2</sub> (=CHPh)(P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	40°
					RuCl <sub>2</sub> (=CHPh)(P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	40°
					RuCl <sub>2</sub> (=CHPh)(P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	40°
					RhCl(PPh <sub>3</sub> )	toluene	rt
RhCl(PPh <sub>3</sub> )	toluene	rt					
RhCl(PPh <sub>3</sub> )	toluene	rt					
	Ni(PPh <sub>3</sub> ) <sub>4</sub>			396			
	Ni(PPh <sub>3</sub> ) <sub>4</sub>			384			
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	DMAD	 	403			

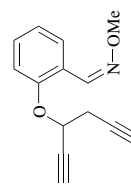


Acetylene, THF, rt, 18 h



$R^1 \text{---} \text{C} \equiv \text{C} \text{---} R^2$

Catalyst	Solvent	Temp	Time	$R^1$	$R^2$
(Cp*)RuCl(COD)	DCE	rt	4 h	Et	H (66)
(Cp*)RuCl(COD)	DCE	rt	20 h	<i>n</i> -Bu	H (80)
(Cp*)RuCl(COD)	DCE	rt	1 h	Ph	Ph (90)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	80°	—		H (35)
RhCl(PPh <sub>3</sub> ) <sub>3</sub>	EtOH	80°	—		H (58)



CpCo(CO)<sub>2</sub>

BTMSA, heat, 117 h

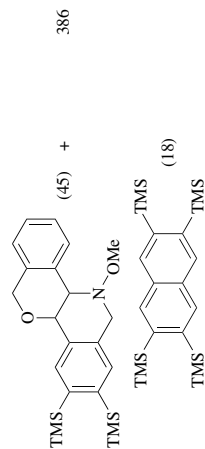
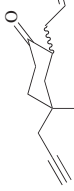

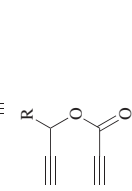

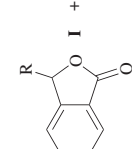
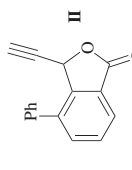
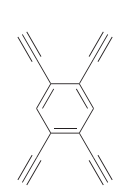
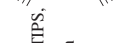
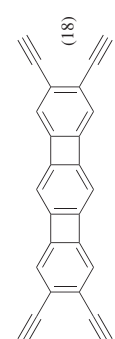


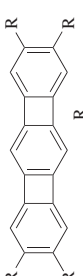
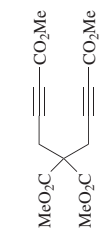
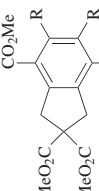
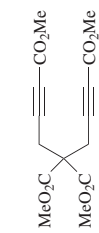

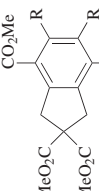
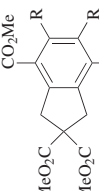


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 C <sub>14</sub>	CpCo(CO) <sub>2</sub>	BTMSA, <i>hν</i> , heat	 (45)	406
 R =  -Ph	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Acetylene, toluene, rt	 I +  II (54), E:II = 6:1	380
	CpCo(CO) <sub>2</sub>	1. TIPS,  , TIPS, DMF, toluene, <i>hν</i> , heat, 16 h 2. Bu <sub>4</sub> NF, THF, EtOH, rt, 1 h	 (18)	407
	CpCo(CO) <sub>2</sub>	R =  , <i>hν</i> , heat	 (71)	114
 C <sub>15</sub>	Pd <sub>2</sub> (dba) <sub>3</sub> , PPh <sub>3</sub>	Solvent: toluene, DMF, <i>o</i> -xylene, THF Time: 6 h, 2 h	 (67)	407
		R =  , 110°, 5 h	 (49)	56
		Conditions: toluene, toluene, 1. toluene, 2. alkyne	 (79)	56



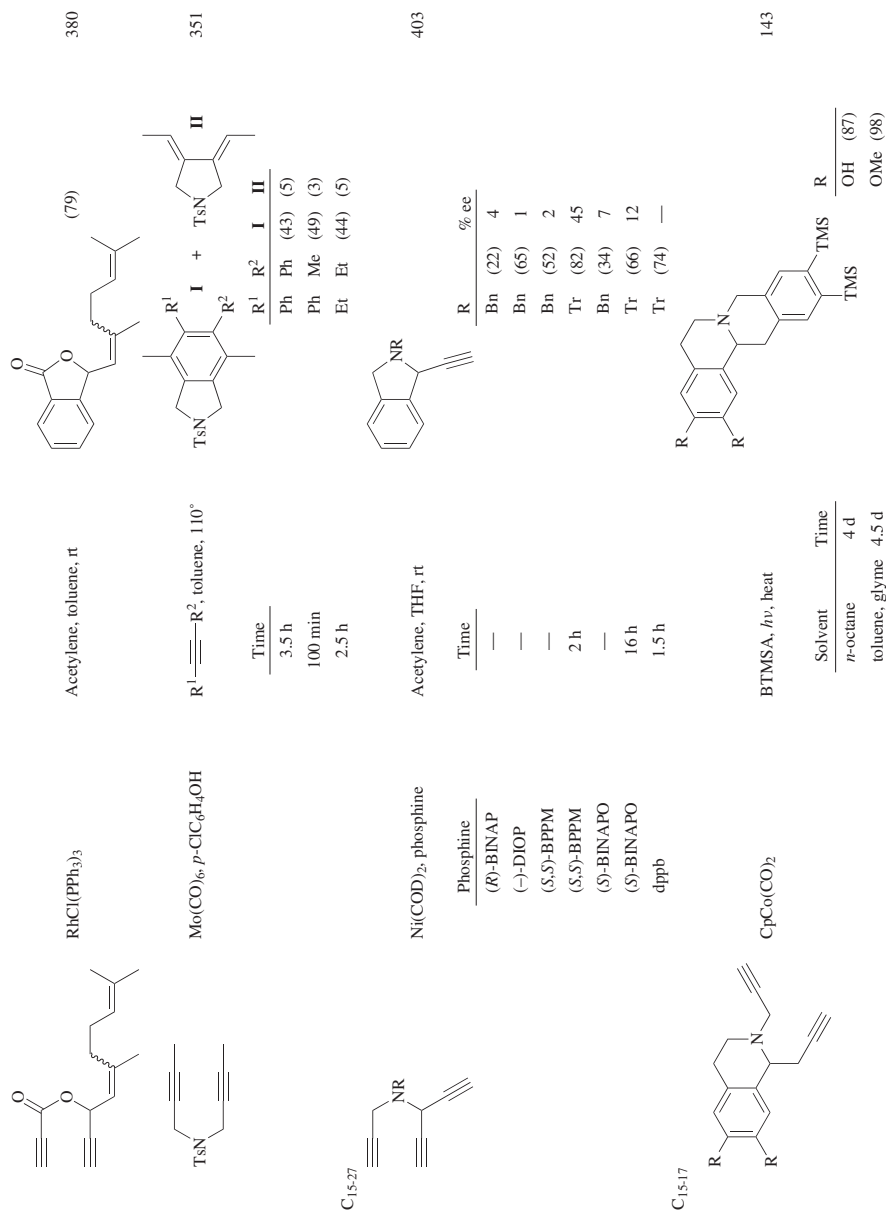
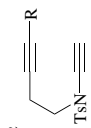
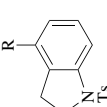
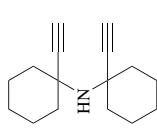

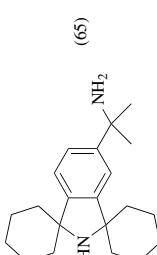
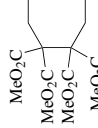
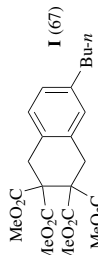
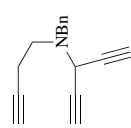
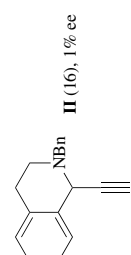
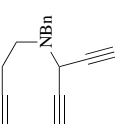
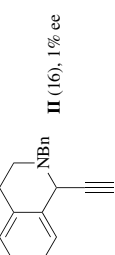
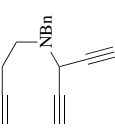
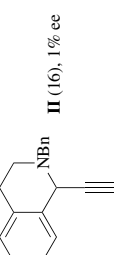


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																
 $C_{15,22}$	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Acetylene (1 atm), toluene <table border="1" data-bbox="568 1029 795 1155"> <thead> <tr> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>110°</td> <td>2 h</td> </tr> <tr> <td>0°</td> <td>5 h</td> </tr> <tr> <td>rt</td> <td>2 h</td> </tr> <tr> <td>rt</td> <td>2 h</td> </tr> <tr> <td>rt</td> <td>2 h</td> </tr> <tr> <td>110°</td> <td>24 h</td> </tr> <tr> <td>110°</td> <td>18 h</td> </tr> </tbody> </table>	Temp	Time	110°	2 h	0°	5 h	rt	2 h	rt	2 h	rt	2 h	110°	24 h	110°	18 h	 R CO <sub>2</sub> Me (43) (CH <sub>2</sub> ) <sub>2</sub> OH (70) (CH <sub>2</sub> ) <sub>2</sub> OBn (55) (CH <sub>2</sub> ) <sub>2</sub> OHP (57) (CH <sub>2</sub> ) <sub>2</sub> NHTs (65) Ph (85) TMS (68)	106
Temp	Time																			
110°	2 h																			
0°	5 h																			
rt	2 h																			
rt	2 h																			
rt	2 h																			
110°	24 h																			
110°	18 h																			
 $C_{16}$	Ni(COD) <sub>2</sub> , P(OPr- <i>i</i> ) <sub>3</sub>	 NH <sub>2</sub> , THF, 80°, 20 h	 (65)	108																
	(Cp*)RuCl(COD)	1-Hexyne, DCE, rt, 6 h	 I (67)	56																
	[IrCl(COD)] <sub>2</sub> , dppe	1-Hexyne, C <sub>6</sub> H <sub>6</sub> , rt, 6 h	 I (53)	373																
	Ni(COD) <sub>2</sub> , (S,S)-BPPM	Acetylene, THF, rt	 II (16), 1% ee	403																
	Ni(COD) <sub>2</sub> , dppe	Acetylene, THF, rt	 II (61)	403																

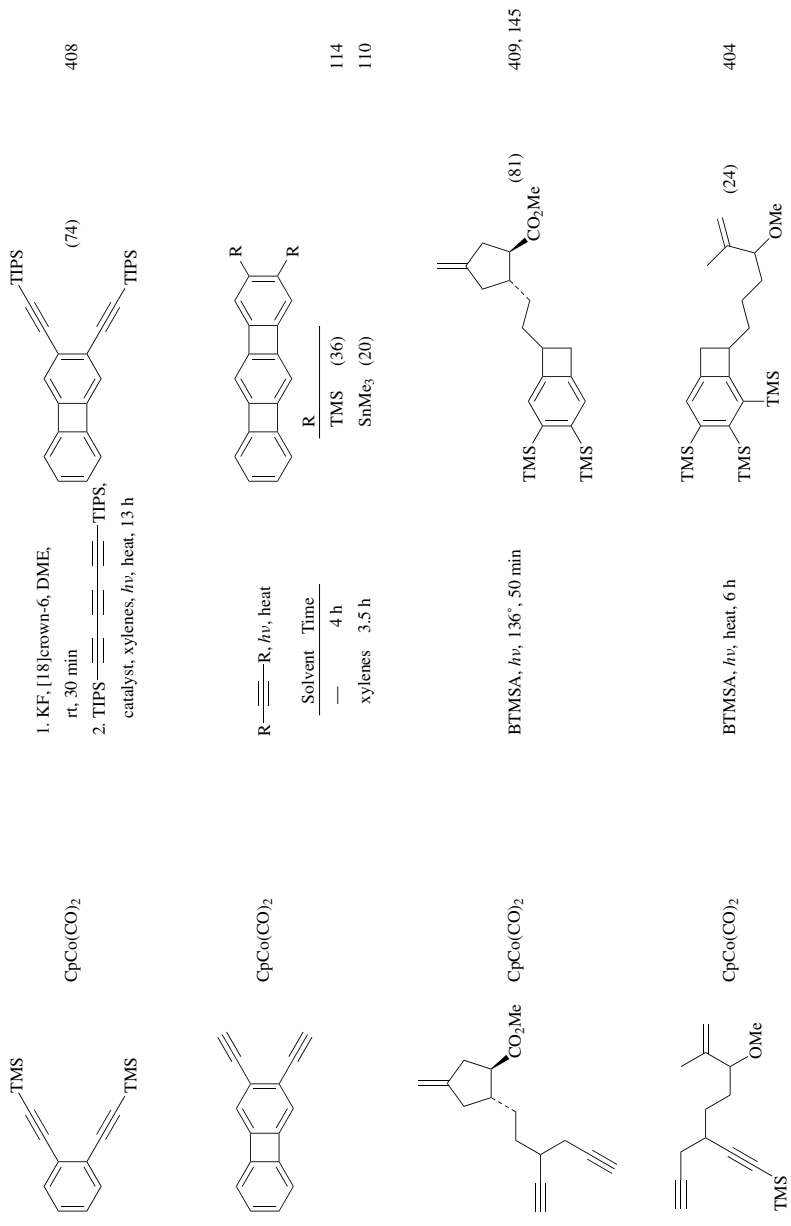
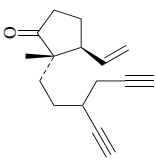
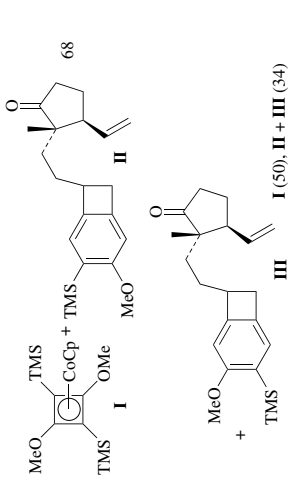
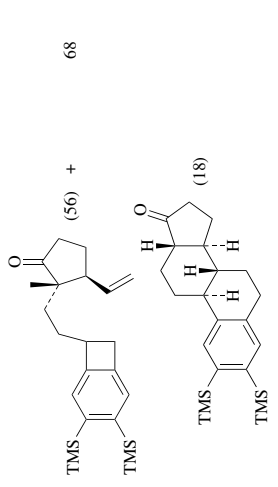
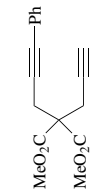
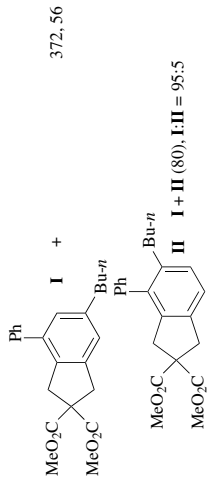


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 C <sub>16</sub>	CpCo(CO) <sub>2</sub> (1 eq)	TMS-C≡C-OMe <i>n</i> -octane, heat, 26 h	 I (50), II + III (34)	68
	CpCo(CO) <sub>2</sub>	BTMSA, heat, 41 h	 (56) + (18)	68
 C <sub>17</sub>	(Cp*)RuCl(COD)	1-Hexyne, DCE, rt, 24 h	 I + II (80), I:II = 95:5	372, 56

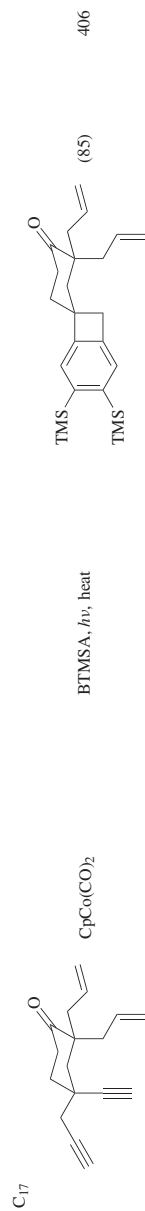
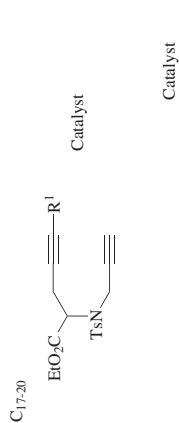
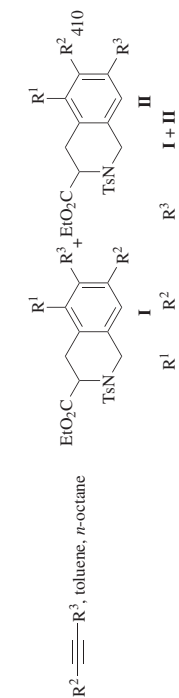
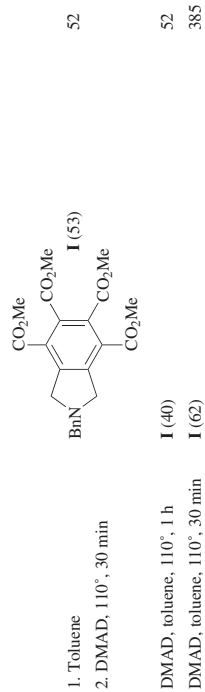


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
<p><math>R^1 = \text{OMe}</math></p>	$\text{CpCo}(\text{CO})_2$	$R^3 \text{---} \text{C} \equiv \text{C} \text{---} R^4$ <i>m</i> -xylene, <i>hv</i> , heat	<p>143</p> <p><b>I</b>   <b>II</b></p>	
		Time	$R^2$ $R^3$ $R^4$	
		8 h	H   OMe   TMS	(34) (34)
		8 h	TMS   TMS   OMe	(58) (0)
		8 h	TMS   TMS $\text{OCH}_2\text{Bu-}t$	(61) (0)
		10 h	TMS   H <i>n</i> -Bu	(3) (3)
	$\text{RhCl}(\text{PPh}_3)_3$	$\text{HO} \text{---} \text{C} \equiv \text{C} \text{---} \text{OH}$ , EtOH, heat	<p>411</p> <p>Leu-OMe (66)                      D-Val-OMe (54)                      D-Leu-NHMe (75)                      D-Val-Leu-OMe (70)                      Leu-Val-NHMe (65)</p>	
	Catalyst	$\text{---} \text{C} \equiv \text{C} \text{---} R$		
	Catalyst	Solvent	$R$	
	$(\text{Cp}^*)\text{RuCl}(\text{COD})$	$\text{CDCl}_3$	H	(32) 56
	$\text{RhCl}(\text{PPh}_3)_3$	toluene	H	(53) 115
	$\text{RhCl}(\text{PPh}_3)_3$	2-propanol, THF	$\text{CH}_2\text{OH}$	(94) 115

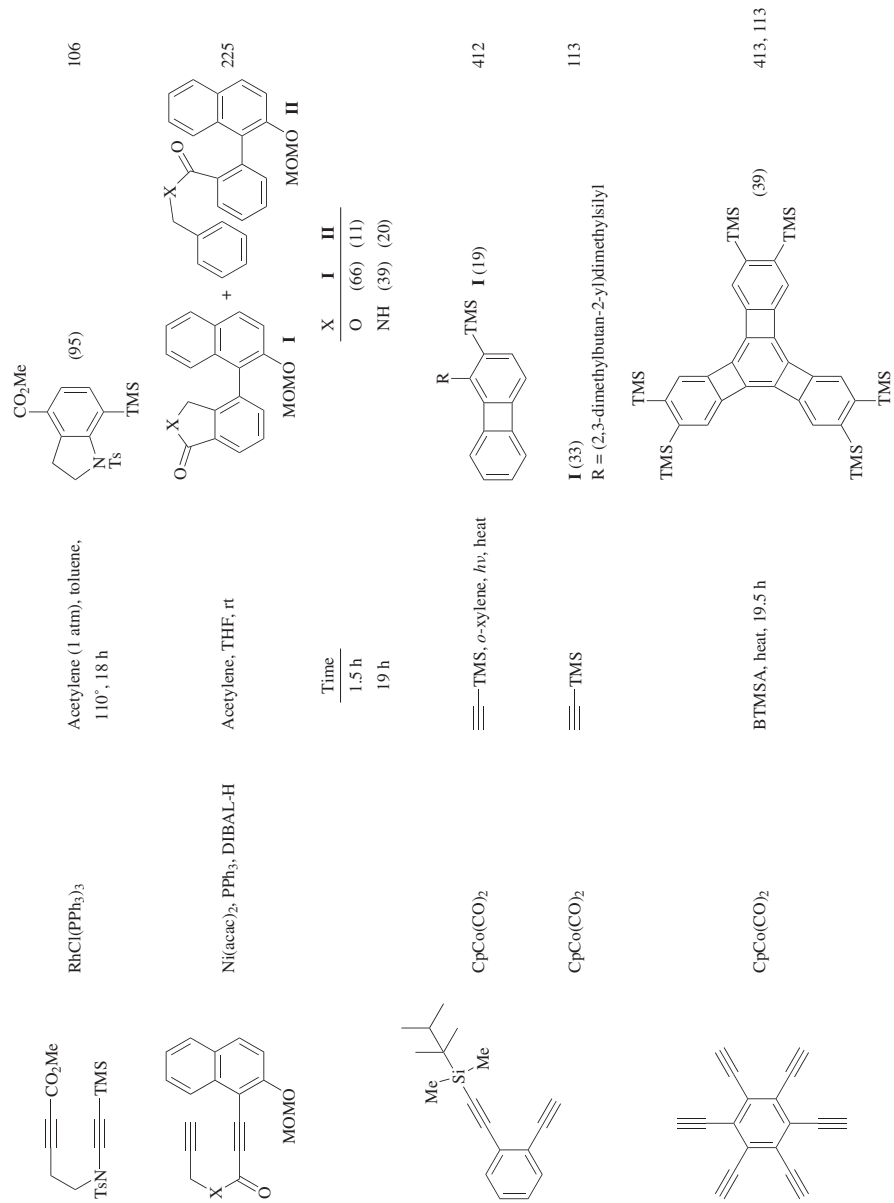


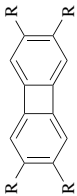
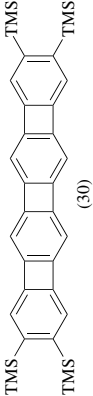
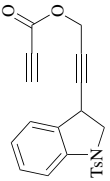
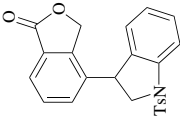
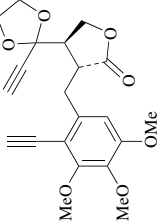
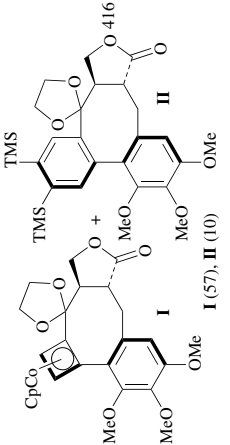

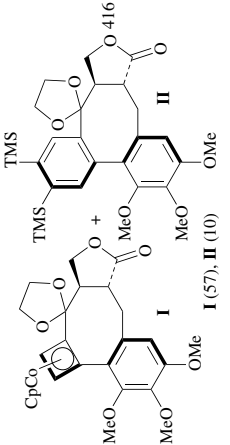

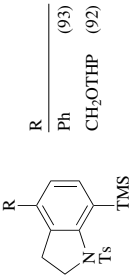
TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
$C_{18-20}$ 	$CpCo(CO)_2$	BTMSA, <i>hν</i>			
		Conditions	X		
		136°, 50 min	 CH <sub>2</sub> (85)	409, 145	
		136°, 50 min	"	O (75)	145
		136°, 50 min	"	 (80)	145
		xylenes, heat, 35 min	 (93)	146	
$C_{18}$ 	$CpCo(CO)_2$	BTMSA, heat, 41 h	 (30) +	68	
			 (28) +		
			 (29)		
		1. $C_6H_6$ , <i>hν</i> , 80°, 8 h 2. BTMSA, <i>hν</i> , 136°, 30 min 3. dppe, decane, 175°, 12 h	 I + II (42), <b>II</b> = 86:14	414	
	$CpCo(CO)_2$		 II		



C19		CpCo(CO) <sub>2</sub>	R <sup>2</sup> =  R <sup>3</sup> , 9 h																		
				<table border="1"> <thead> <tr> <th>Solvent</th> <th>Temp</th> <th>R<sup>2</sup></th> <th>R<sup>3</sup></th> </tr> </thead> <tbody> <tr> <td><i>n</i>-octane</td> <td>heat</td> <td>Ph</td> <td>Ph</td> </tr> <tr> <td><i>n</i>-octane</td> <td>heat</td> <td>Ph</td> <td>H</td> </tr> <tr> <td>—</td> <td>140°</td> <td>TMS</td> <td>TMS</td> </tr> </tbody> </table>	Solvent	Temp	R <sup>2</sup>	R <sup>3</sup>	<i>n</i> -octane	heat	Ph	Ph	<i>n</i> -octane	heat	Ph	H	—	140°	TMS	TMS	398 398 399
Solvent	Temp	R <sup>2</sup>	R <sup>3</sup>																		
<i>n</i> -octane	heat	Ph	Ph																		
<i>n</i> -octane	heat	Ph	H																		
—	140°	TMS	TMS																		
		Co <sub>2</sub> (CO) <sub>8</sub>	Ph, CO (30 atm), CH <sub>2</sub> Cl <sub>2</sub> , 130°, 18 h		415																
		Ti(OPr- <i>i</i> ) <sub>4</sub>	1. Et <sub>2</sub> O, <i>i</i> -PrMgCl, -50°, 4 h 2. Ts-, rt, 4 h 3. HCl		341																
		RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Acetylene (1 atm), toluene, rt, 3 h		106																
		RuCl <sub>2</sub> (=CHPh)(P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub>	OH, CH <sub>2</sub> Cl <sub>2</sub> , 40°	 + <b>I + II (60), I:II = 9.5:1</b>	405																
		RhCl(PPh <sub>3</sub> ) <sub>3</sub>	OH, CH <sub>2</sub> Cl <sub>2</sub> , 40°	<b>I + II (70), I:II = 1:1</b>	405																

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $R = \begin{cases} \text{H} \\ \text{Me} \\ \text{OMe} \\ \text{Me}_2\text{C} \\ \text{Me}_3\text{C} \end{cases}$	$\text{CpCo}(\text{CO})_2$	1. BTMSA, THF, <i>h\nu</i> , heat, 13 h 2. CO (1 atm), 120°, 72 h	 (30)	110
 $R = \begin{cases} \text{H} \\ \text{Me} \\ \text{OMe} \\ \text{Me}_2\text{C} \\ \text{Me}_3\text{C} \end{cases}$	$\text{RhCl}(\text{PPh}_3)_3$	Acetylene, toluene, 40°	 (51)	380
 $R = \begin{cases} \text{H} \\ \text{Me} \\ \text{OMe} \\ \text{Me}_2\text{C} \\ \text{Me}_3\text{C} \end{cases}$	$\text{CpCo}(\text{CO})_2$ (1 eq)	BTMSA, <i>h\nu</i> , heat, 9 h	 I (57), II (10)	416
 $R = \begin{cases} \text{H} \\ \text{Me} \\ \text{OMe} \\ \text{Me}_2\text{C} \\ \text{Me}_3\text{C} \end{cases}$	$\text{CpCo}(\text{CO})_2$	$\text{CH}_3\text{CN}$ , <i>h\nu</i> , heat, 9 h	 I (37) + II (19)	416
 $R = \begin{cases} \text{H} \\ \text{Me} \\ \text{OMe} \\ \text{Me}_2\text{C} \\ \text{Me}_3\text{C} \end{cases}$	$\text{RhCl}(\text{PPh}_3)_3$	Acetylene (1 atm), toluene, 110°, 18 h	 (93) (92)	106

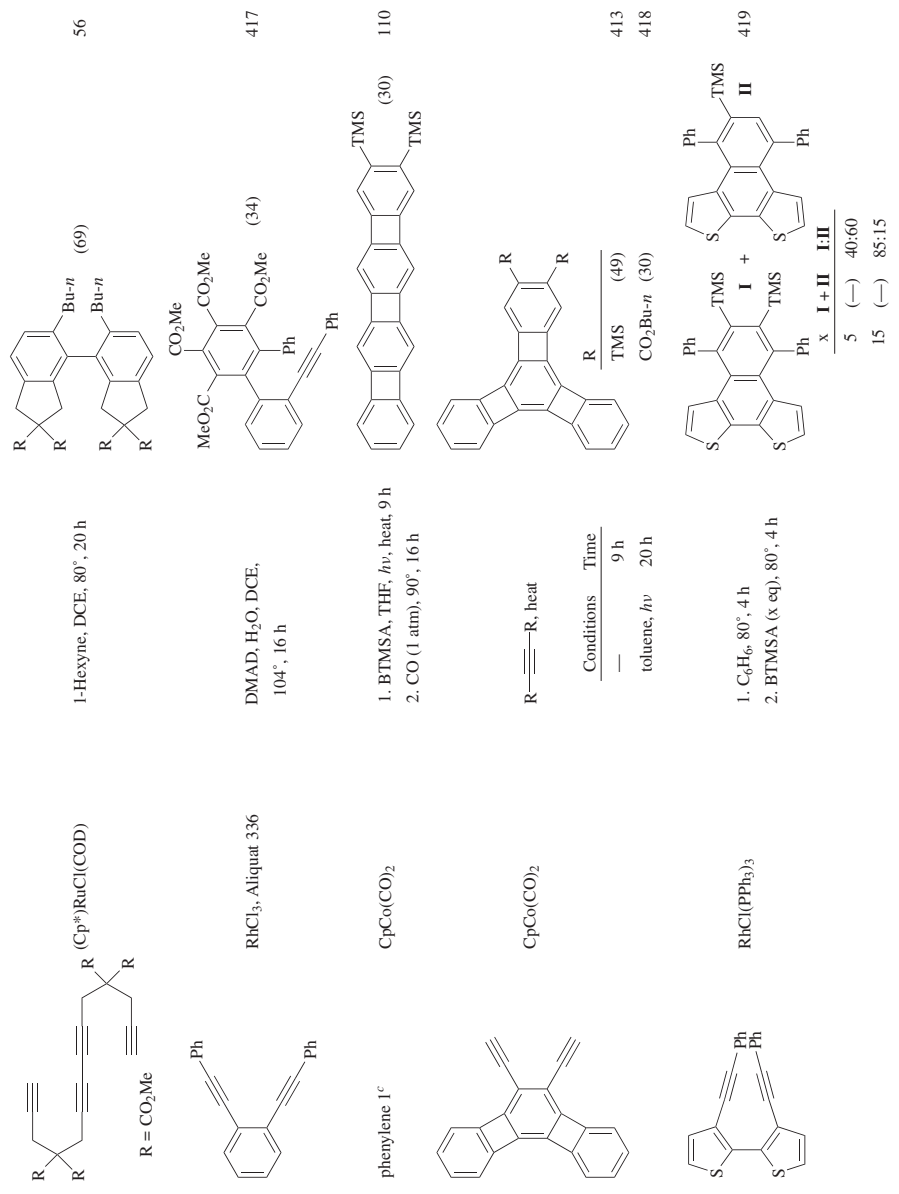
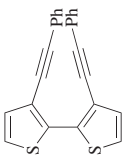
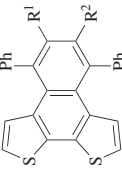
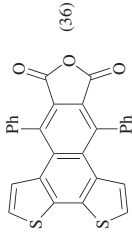
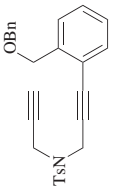
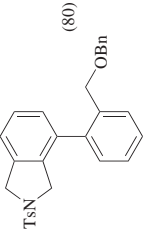
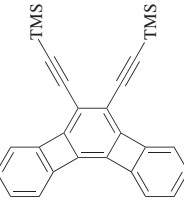
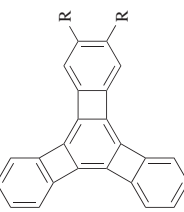


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.										
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	1. C <sub>6</sub> H <sub>6</sub> , 80°, 4 h 2. R <sup>1</sup> -C≡C-R <sup>2</sup> , 80°, 4 h	  (36)	<table border="1"> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> </tr> <tr> <td>H</td> <td>H</td> </tr> <tr> <td>Ph</td> <td>Ph</td> </tr> <tr> <td>CO<sub>2</sub>Me</td> <td>CO<sub>2</sub>Me</td> </tr> <tr> <td>TMS</td> <td>H</td> </tr> </table> (87) 419 (56) (81) (73)	R <sup>1</sup>	R <sup>2</sup>	H	H	Ph	Ph	CO <sub>2</sub> Me	CO <sub>2</sub> Me	TMS	H
R <sup>1</sup>	R <sup>2</sup>													
H	H													
Ph	Ph													
CO <sub>2</sub> Me	CO <sub>2</sub> Me													
TMS	H													
phenylene 2 <sup>c</sup>	CpCo(CO) <sub>2</sub> (1 eq)	1. C <sub>6</sub> H <sub>6</sub> , 80°, 4 h 2. HO <sub>2</sub> C-C≡C-CO <sub>2</sub> H, 80°, 4 h	phenylene 3 <sup>c</sup> (20)	407										
	Ni(acac) <sub>2</sub> , dppb, DIBAL-H	Acetylene, THF, rt	 (80)	225										
	CpCo(CO) <sub>2</sub>	1. (n-Bu) <sub>4</sub> NF, THF, toluene, rt, 2 h 2. R-C≡C-R, catalyst, toluene, hν, heat, 16 h	 R CO <sub>2</sub> Me (32) (18)	420 408										

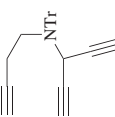
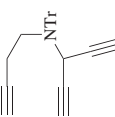


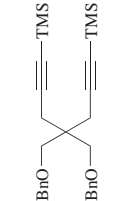
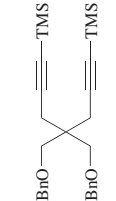


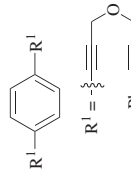

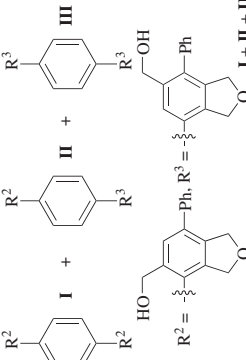
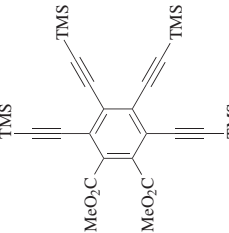
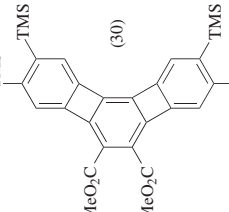
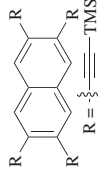
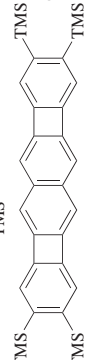
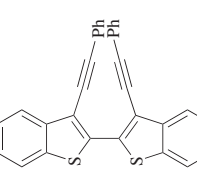
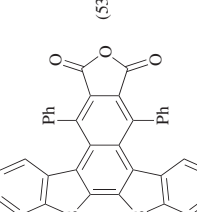
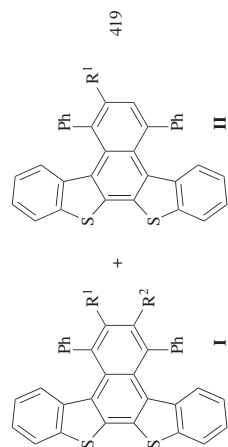
	Ni(COD) <sub>2</sub> , phosphine dppb (S,S)-BPPM (R,S)-BPPFA (S)-MeO-MOP (S)-MeO-MOP	Acetylene (x eq), THF, rt x 4 4 4 4 10		403
	1. Et <sub>2</sub> O, <i>i</i> -PrMgCl, -50°, 4 h 2. Ts-C≡C≡C≡C, rt, 4 h 3. HCl	74		341
	1. Et <sub>2</sub> O, <i>i</i> -PrMgCl, -50°, 4 h 2. Br-C≡C≡C≡C, rt, 4 h 3. Electrophile	R H (73) I (72) OH (66) CH=C-CH <sub>3</sub> (42)		83
	RhCl(PPh <sub>3</sub> ) <sub>3</sub>	Acetylene, 2-propanol, THF, heat, 19 h		115

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $R^1 = \text{---} \text{CH}=\text{CH} \text{---} \text{CH}=\text{CH} \text{---} \text{Ph}$	$\text{RhCl}(\text{PPh}_3)_3$	 2-propanol, THF, heat, 12 h	 I + II + III (66)	115
	$\text{CpCo}(\text{CO})_2$	1. $\text{KF}$ , [18]crown-6, DME, rt, 30 min 2. Catalyst, BTMSA, <i>in vacuo</i> , heat, 14 h	 (30)	408
 $R = \text{---} \text{CH}=\text{CH} \text{---} \text{TMS}$	$\text{CpCo}(\text{CO})_2$	1. $\text{KOH}$ , MeOH 2. BTMSA, catalyst	 (58) (59)	421
 $R = \text{---} \text{CH}=\text{CH} \text{---} \text{TMS}$	$\text{RhCl}(\text{PPh}_3)_3$	1. $\text{C}_6\text{H}_6$ , 80°, 4 h 2. $\text{HO}_2\text{C} \text{---} \text{C} \equiv \text{C} \text{---} \text{CO}_2\text{H}$ , 80°, 4 h	 (53)	419

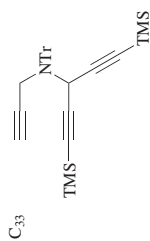


1.  $C_6H_6$ ,  $80^\circ$ , 4 h  
 2.  $R^1 \equiv R^2$  (x eq),  $80^\circ$ , 4 h

$RhCl(PPh_3)_3$

419

$R^1$	$R^2$	x	I + II	III
H	H	—	(85)	1:0
Ph	Ph	5	(62)	1:0
$CO_2Me$	$CO_2Me$	5	(75)	1:0
TMS	H	5	(90)	—
TMS	TMS	1	(—)	1:1
TMS	TMS	15	(—)	9:1



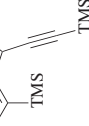
C<sub>33</sub>

$Ni(COD)_2$ , phosphine

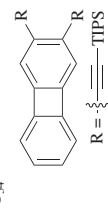
Phosphine  
 dppb  
 (R)-BINAP  
 (S)-BINAP  
 (-)-DIOP  
 (S,S)-BPPM  
 (R,S)-BPPFA

Acetylene, THF, rt

Time	% ee
5 h	(83) 0
140 h	(57) 22
115 h	(52) 18
18 h	(87) 0
18 h	(92) 60
150 h	(52) 73



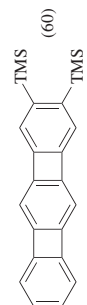
403



C<sub>34</sub>

$CpCo(CO)_2$

1.  $(n-Bu)_4NF$ , THF, rt, 30 min  
 2. Catalyst, BTMSA, hv,  
 heat, 13 h



408

TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C<sub>34</sub></p> <p>R = </p>	CpCo(CO) <sub>2</sub>	1. ( <i>n</i> -Bu) <sub>3</sub> NF, THF, rt 2. BTMSA, catalyst, THF, <i>hν</i> , heat, 16 h	<p>(33)</p> <p>420</p>	
<p>C<sub>36</sub></p> <p>R = </p>	CpCo(CO) <sub>2</sub>	1. KF, [18]crown-6, DME, rt, 30 min 2. HO , catalyst, <i>m</i> -xylenes, <i>hν</i> , heat, 16 h 3. PTSA, MS 4Å, C <sub>6</sub> H <sub>6</sub> , heat, 16 h	<p>(31)</p> <p>408</p>	
<p>R = </p>	CpCo(CO) <sub>2</sub>	1. KF, [18]crown-6, DME, rt 2. R <sup>2</sup> catalyst, toluene, <i>hν</i> , heat, 16 h	<p>(38)</p> <p>R<sup>2</sup> = </p> <p>408</p>	



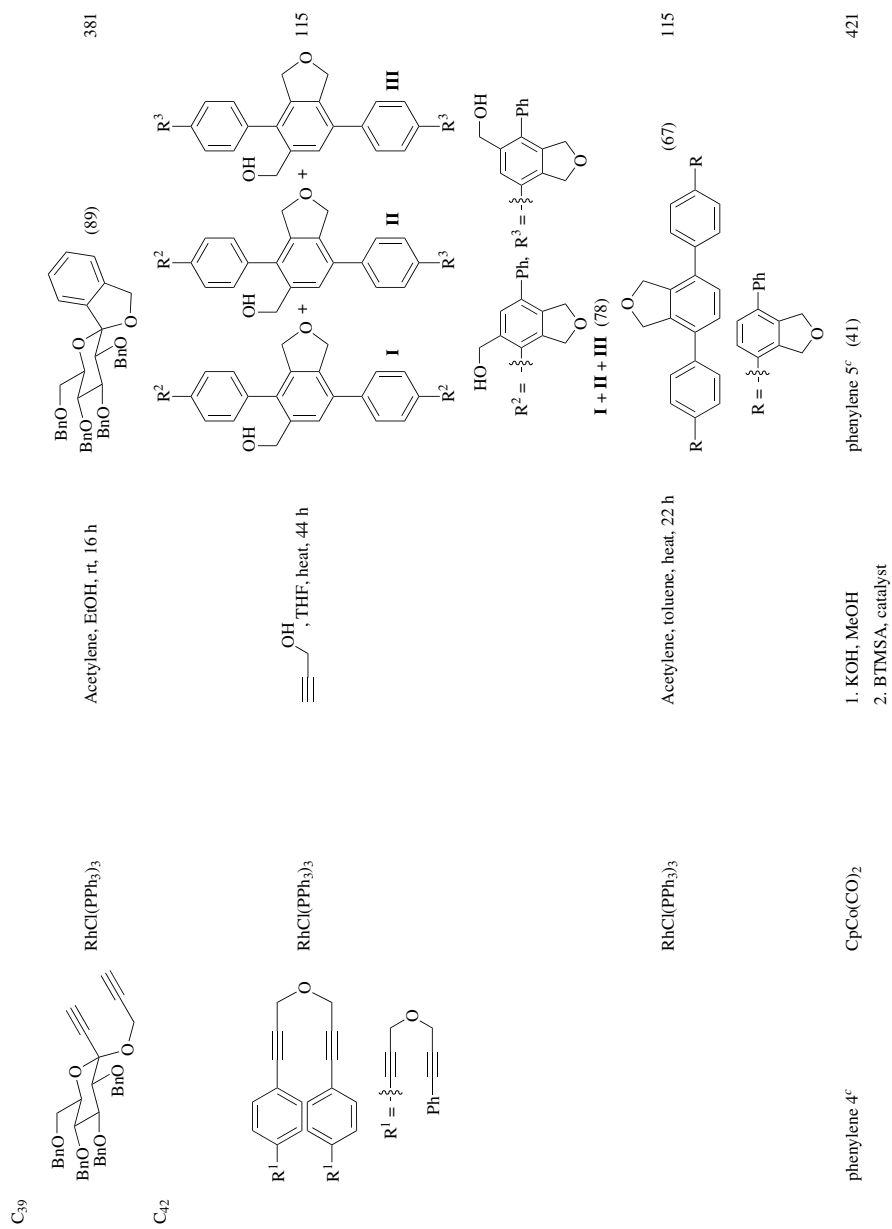
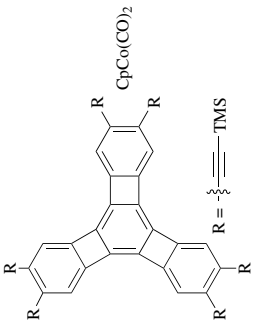


TABLE 3. DIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
		1. ( <i>n</i> -Bu) <sub>4</sub> NF, THF, rt, 30 min 2. BTMSA, catalyst, THF, <i>hν</i> , heat, 16 h	phenylene 6 <sup>c</sup> (37)	420

C<sub>54</sub><sup>a</sup> The [2+2] cycloaddition is followed by another reaction.<sup>b</sup> Other products arise in small amounts.<sup>c</sup> See Chart preceding tables for phenylene structures.

TABLE 4. TRIYNES

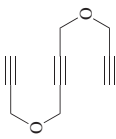
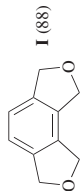

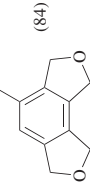
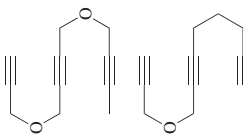
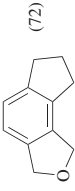
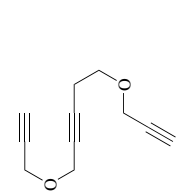
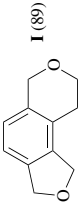
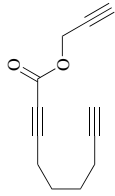
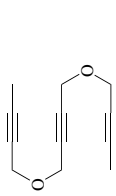
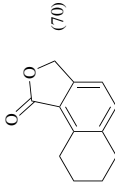
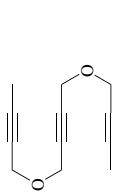
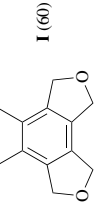
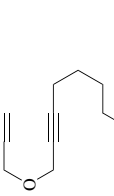
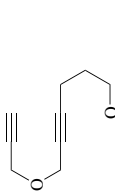
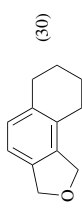
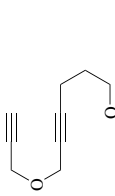
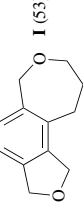
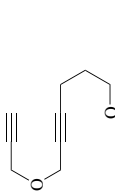
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{Ru}(\text{=CHPh})\text{Cl}_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$	$\text{CH}_2\text{Cl}_2$ , rt, 2 h		78
	$(\text{Cp}^*)\text{RuCl}(\text{COD})$	DCE, rt, 2 h	<b>I</b> (82)	56
	$\text{Co}_3(\text{CO})_9(\mu^3\text{-CH})$	Toluene, heat, 4 h	<b>I</b> (80)	261
	$[\text{RhCl}(\text{COD})]_2$ , TPPTS	$\text{H}_2\text{O}$ , $\text{Et}_2\text{O}$ , rt, 3 h	<b>I</b> (79)	375
	$\text{RhCl}(\text{PPh}_3)_3$	$\text{EtOH}$ , rt, 2 h	<b>I</b> (75)	371
	$\text{Rh}(\text{acac})(\text{CO})_2$	$\text{PhMe}_2\text{SiH}$ , CO (1 atm), toluene, 60°, 21 h	<b>I</b> (57)	422
	$\text{Co}_2(\text{CO})_8$	CO (30 atm), $\text{CH}_2\text{Cl}_2$ , 130°, 18 h	<b>I</b> (70) + 	423
	$\text{Rh}(\text{acac})(\text{CO})_2$	$\text{PhMe}_2\text{SiH}$ , CO (1 atm), toluene, rt, 24 h	$\text{Me}_2\text{PhSi}$ + <b>I</b> + <b>II</b> (98), <b>I:II</b> = 83:17	422
	$\text{Rh}_4(\text{CO})_{12}$	$\text{PhMe}_2\text{SiH}$ , CO (1 atm), toluene, rt, 30 min	<b>I</b> + <b>II</b> (99), <b>I:II</b> = 76:24	422
	$(\text{Cp}^*)\text{RuCl}(\text{COD})$	DCE, rt, 18 h		56
	$\text{Ru}(\text{=CHPh})\text{Cl}_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$	$\text{CH}_2\text{Cl}_2$ , rt, 2 h		78

TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	(Cp*)RuCl(COD)	DCE, rt, 18 h	 <b>I (89)</b>	56
	[RhCl(COD)] <sub>2</sub> , TPPTS	H <sub>2</sub> O, Et <sub>2</sub> O, rt, 10 h	<b>I (93)</b>	375
	Ni(PPh <sub>3</sub> ) <sub>4</sub>	THF, rt, 17 h	 (70)	384
	(Cp*)RuCl(COD)	PhCl, heat, 24 h	 <b>I (60)</b>	56
	Pd <sub>2</sub> (dba) <sub>3</sub> , PPh <sub>3</sub>	Toluene, 110°, 1 h	<b>I (35)</b>	56
	Ru(=CHPh)Cl <sub>2</sub> [P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ] <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> , rt, 2 h	 (30)	78
	(Cp*)RuCl(COD)	DCE, rt, 20 h	 <b>I (53)</b>	56
	[RhCl(COD)] <sub>2</sub> , TPPTS	H <sub>2</sub> O, Et <sub>2</sub> O, rt, 10 h	<b>I (84)</b>	375

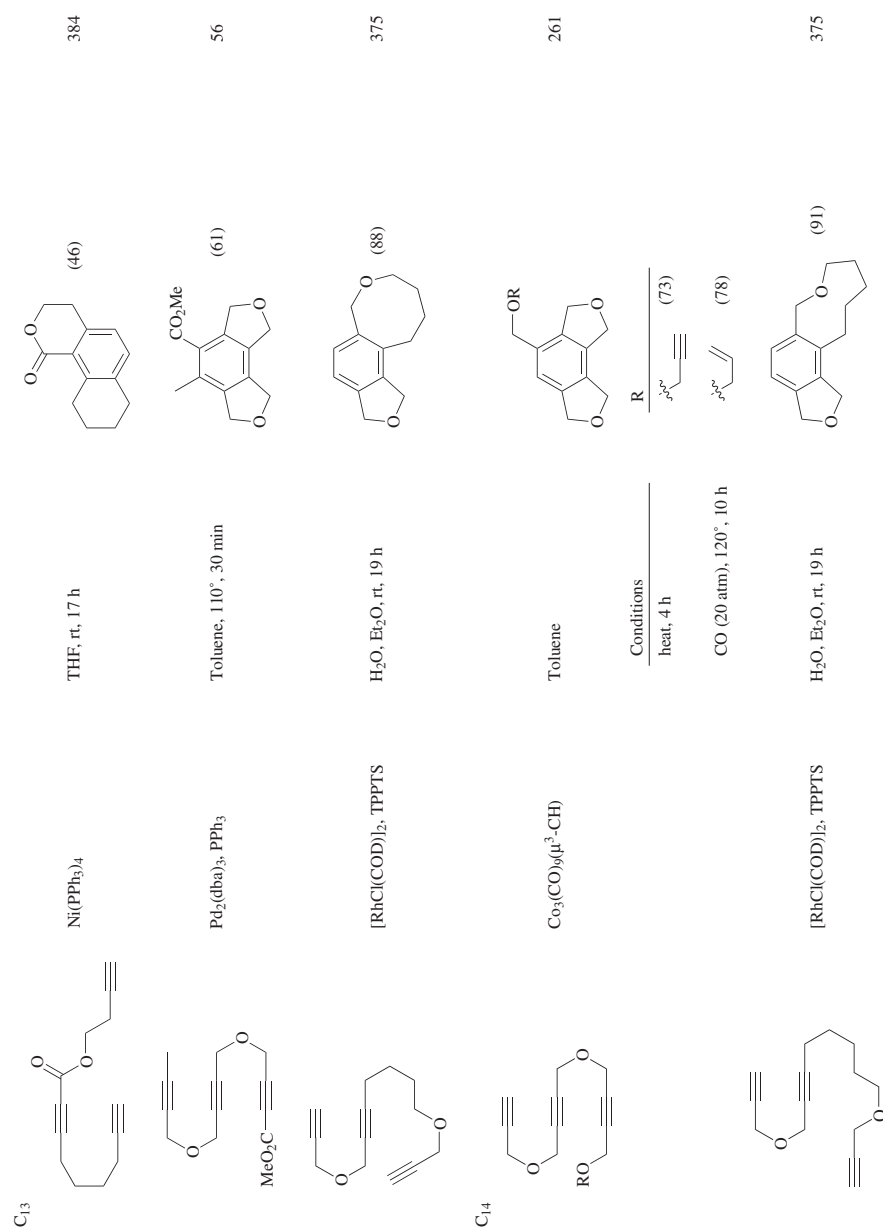
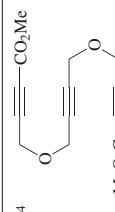
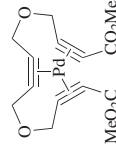
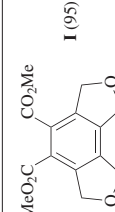
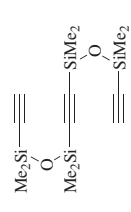
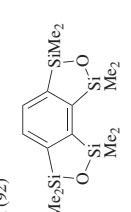
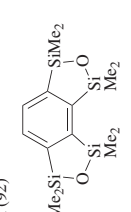
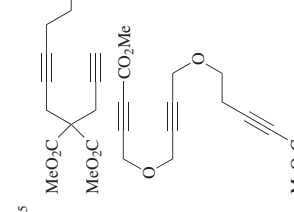
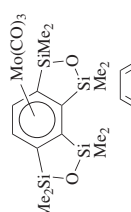
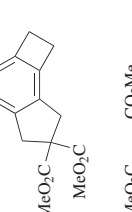
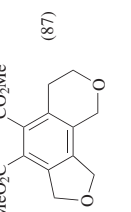


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C<sub>14</sub></p>	<p>Pd<sub>2</sub>(dba)<sub>3</sub>, PPh<sub>3</sub></p>  <p>I (99)</p>	<p>Toluene, 110°, 30 min</p> <p>Toluene, 110°, 5 h</p>	 <p>I (95)</p>	<p>56, 372 385</p> <p>56</p>
	<p>"</p> <p>"</p> <p>Cr(CO)<sub>6</sub></p>	<p>PPh<sub>3</sub>, toluene, 50°, 7 h</p> <p>PPh<sub>3</sub>, toluene, 110°, 30 min</p>	 <p>I (80)</p>  <p>I (92)</p>	<p>56</p> <p>56</p> <p>12</p>
 <p>C<sub>15</sub></p>	<p>Mo(CO)<sub>6</sub></p> <p>CoI<sub>2</sub>, Mn, PPh<sub>3</sub></p> <p>Pd<sub>2</sub>(dba)<sub>3</sub>, PPh<sub>3</sub></p>	<p>—</p> <p>—</p> <p>CH<sub>2</sub>Cl<sub>2</sub>, rt</p> <p>Toluene, 110°, 15 min</p>	 <p>(16)</p>  <p>(78)</p>  <p>(87)</p>	<p>12</p> <p>424</p> <p>56</p>

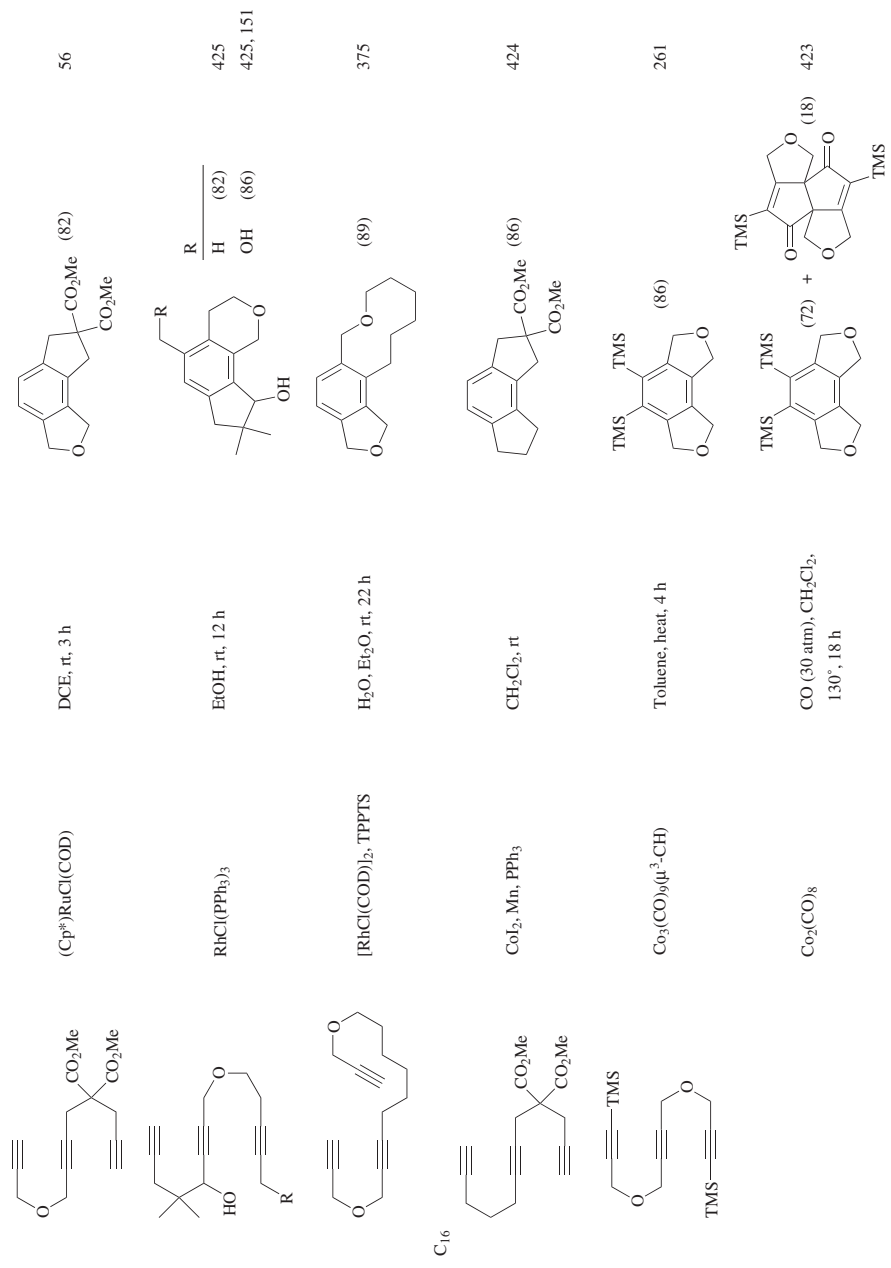
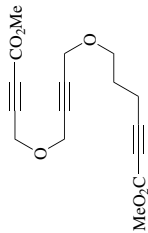
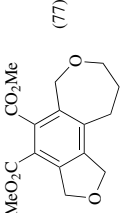
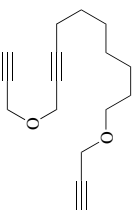
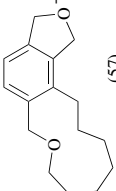
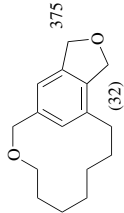
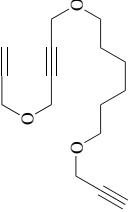
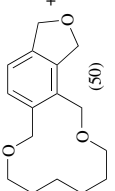
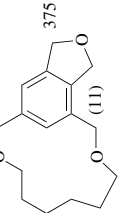
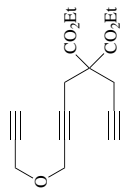
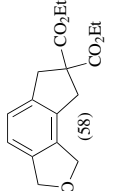
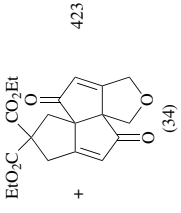
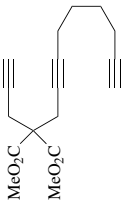
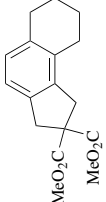


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $\text{MeO}_2\text{C}$	$\text{Pd}_2(\text{dba})_3, \text{PPh}_3$	Toluene, $110^\circ$ , 1.5 h	 (77)	56
 $\text{MeO}_2\text{C}$	$[\text{RhCl}(\text{COD})]_2, \text{TPPTS}$	$\text{H}_2\text{O}, \text{Et}_3\text{O}$ , rt, 20 h	 (57) +  (32)	375
 $\text{MeO}_2\text{C}$	$[\text{RhCl}(\text{COD})]_2, \text{TPPTS}$	$\text{H}_2\text{O}, \text{Et}_3\text{O}$ , rt, 24 h	 (50) +  (11)	375
 $\text{MeO}_2\text{C}$	$\text{Co}_2(\text{CO})_8$	$\text{CO}$ (30 atm), $\text{CH}_2\text{Cl}_2$ , $130^\circ$ , 18 h	 (58) +  (34)	423
 $\text{MeO}_2\text{C}$	$\text{CoI}_2, \text{Mn}, \text{PPh}_3$	$\text{CH}_2\text{Cl}_2$ , rt	 (83)	424



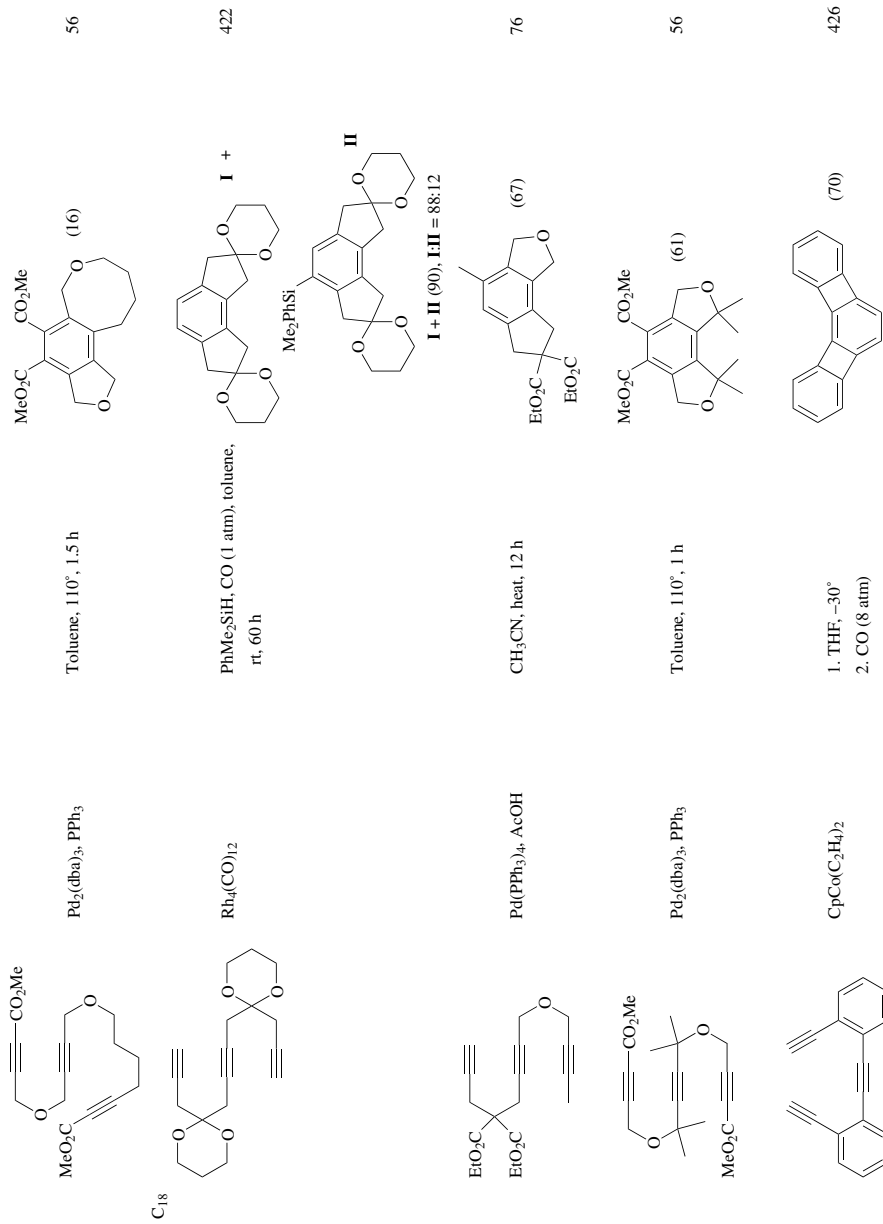
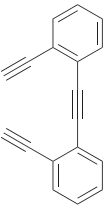
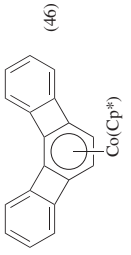
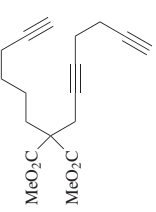
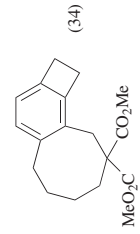
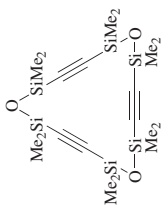
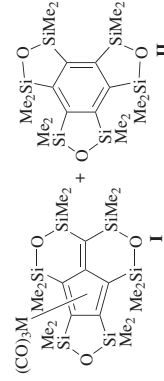
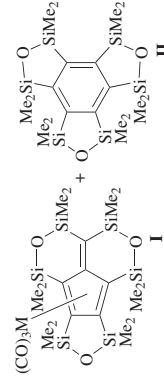
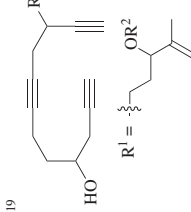
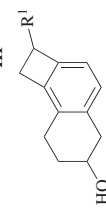


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.												
	(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> (1 eq)	1. THF, rt, 3 d 2. 85°, 2 h	 (46)	58												
	CpCo(CO) <sub>2</sub>	Toluene, <i>hν</i> , heat	 (34)	424												
	M(CO) <sub>6</sub>	<i>n</i> -Octane, 140°	 I  II	12, 404												
	CpCo(CO) <sub>2</sub>	<i>o</i> -Xylene, <i>hν</i> , heat, 1 h	 III <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>M</td> <td>I</td> <td>II</td> <td>III</td> </tr> <tr> <td>Cr</td> <td>(50)</td> <td>(29)</td> <td>(—)</td> </tr> <tr> <td>W</td> <td>(18)</td> <td>(2)</td> <td>(0)</td> </tr> </table>	M	I	II	III	Cr	(50)	(29)	(—)	W	(18)	(2)	(0)	427
M	I	II	III													
Cr	(50)	(29)	(—)													
W	(18)	(2)	(0)													

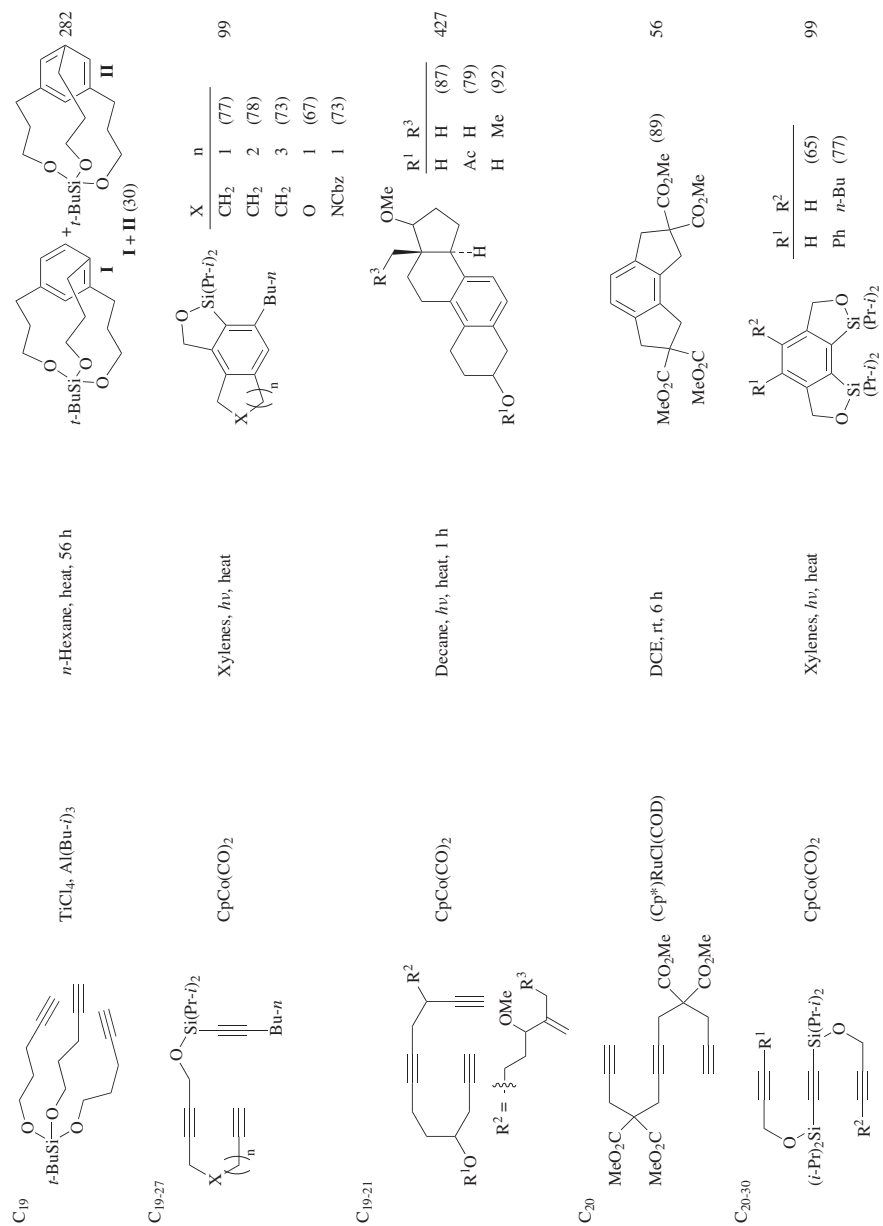


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $R = \text{NHAc}$	$\text{Ru}(\text{=CHPh})\text{Cl}_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$	Toluene, 85°, 14 h	 (58)	117
	$\text{Co}_2(\text{CO})_8$	$\text{CO}$ , 30 min; $\text{CH}_2\text{Cl}_2$ , 130°, 18 h	 (30) +	423
 $R = \text{CH}_2\text{OMe}$	$\text{Rh}_4(\text{CO})_{12}$	$\text{PhMe}_2\text{SiH}$ , $\text{CO}$ (1 atm), toluene, rt, 35 h	 (61)	
 $R = \text{CH}_2\text{OMe}$	$\text{Rh}_4(\text{CO})_{12}$	$\text{PhMe}_2\text{SiH}$ , $\text{CO}$ (1 atm), toluene, rt, 35 h	 <b>I + II (75), I:II = 8:92</b>	422
	$\text{CpCo}(\text{CO})_2$	Xylenes, <i>hv</i> , heat	 (70)	99
	$\text{Pd}_2(\text{dba})_3, \text{PPh}_3$	Toluene, 110°, 30 min	 (91)	56

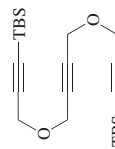
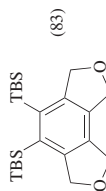
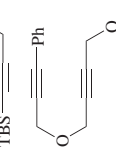
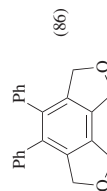
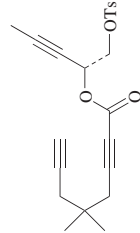
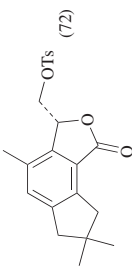
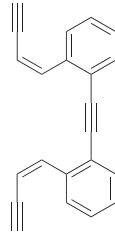
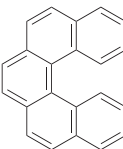
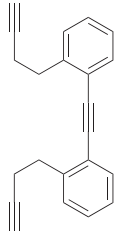
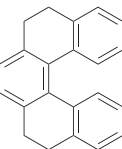
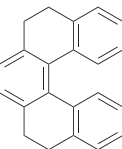
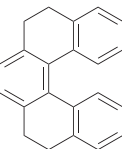
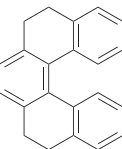
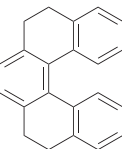
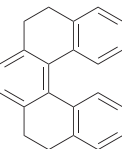
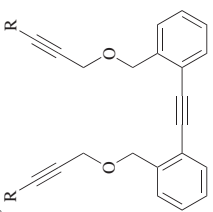
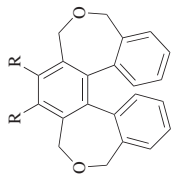
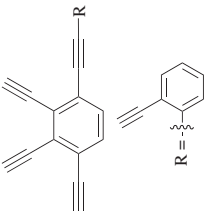
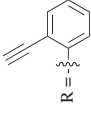
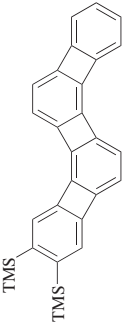
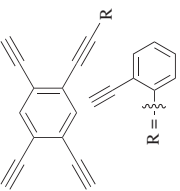
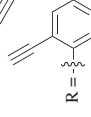
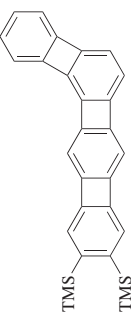
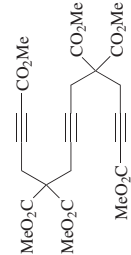
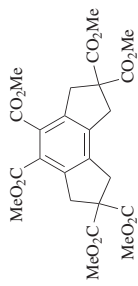
C <sub>22</sub>		Co <sub>2</sub> (CO) <sub>8</sub>	CO (30 atm), CH <sub>2</sub> Cl <sub>2</sub> , 130°, 18 h	 (83)	423
		Co <sub>3</sub> (CO) <sub>9</sub> (μ <sup>3</sup> -CH)	Toluene, heat, 4 h	 (86)	261
		RhCl(PPh <sub>3</sub> ) <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> , 40°	 (72)	428
		Co <sub>2</sub> (CO) <sub>8</sub>	1,4-Dioxane, heat, 40 min	 I (8)	119
		CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	1,4-Dioxane, <i>hν</i> , heat, 22 h	 I (30)	119
		CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	<i>n</i> -Decane, <i>hν</i> , heat, 70 min	 I (43)	119
		Ni(COD) <sub>2</sub>	THF, rt, 15 min	 I (83)	119
		Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	THF, rt, 15 min	 I (64)	119
		CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	<i>n</i> -Decane, <i>hν</i> , 140°, 1 h	 II (72)	119
		Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	THF, rt, 30 min	 II (66)	294

TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C<sub>22-28</sub></p> 	CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	<i>n</i> -Decane, <i>hν</i> , 140°	 R                      R H    30 min    (89) TMS 5.5 h    (23)	118
<p>C<sub>22</sub></p>  R = 	CpCo(CO) <sub>2</sub>	BTMSA, <i>hν</i> , heat, 10 h	 TMS                      TMS	(15) 429
 R = 	CpCo(CO) <sub>2</sub>	BTMSA, <i>hν</i> , heat, 16 h	 TMS                      TMS	(15) 127
<p>C<sub>24</sub></p> 	Pd <sub>2</sub> (dba) <sub>3</sub> , PPh <sub>3</sub>	Toluene, 110°, 5 h	 MeO <sub>2</sub> C                      MeO <sub>2</sub> C MeO <sub>2</sub> C                      MeO <sub>2</sub> C MeO <sub>2</sub> CMe                      MeO <sub>2</sub> CMe	(95) 56

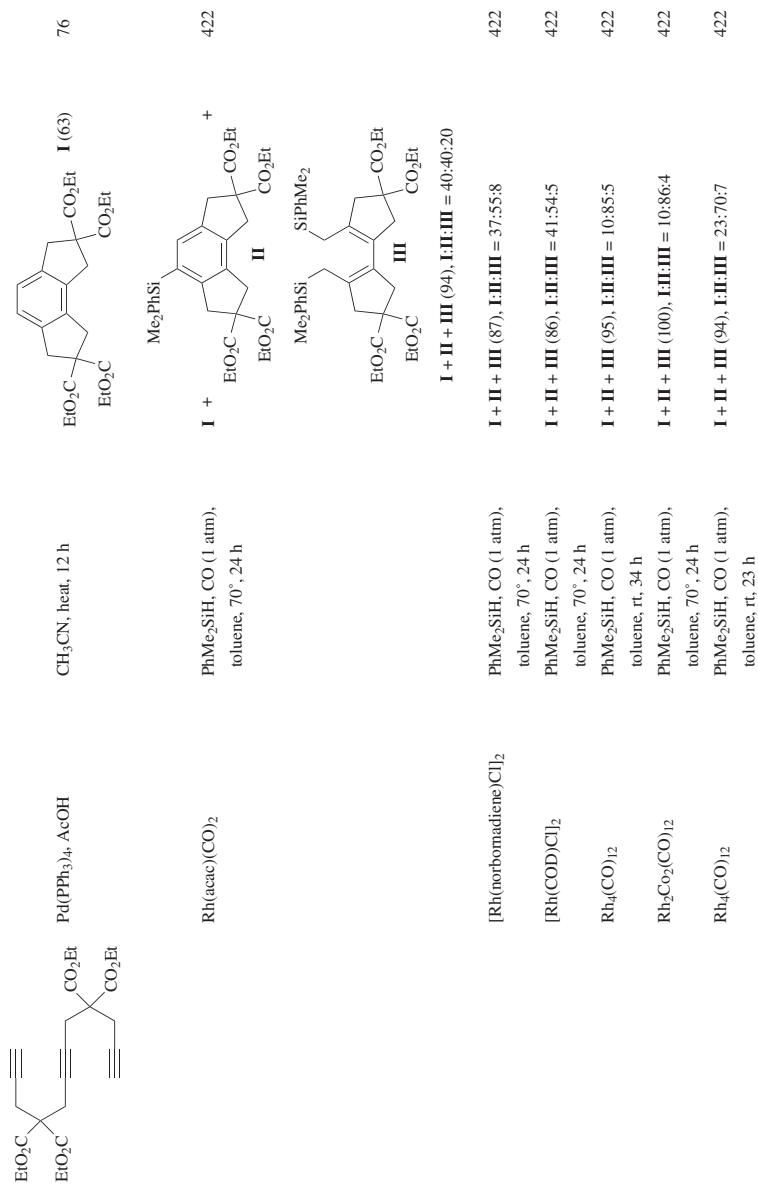


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																												
	$\text{Rh}_4(\text{CO})_{12}$	$\text{R}^1\text{R}^2\text{SiH}_2$ , CO (1 atm), toluene, rt	 	422																												
	$\text{Ru}(\text{=CHPh})(\text{Cl})_2[\text{P}(\text{C}_6\text{H}_{11})_3]_2$	Time 20 h 18 h 46 h 60 h 43 h 55 h	<table border="1"> <thead> <tr> <th><math>\text{R}^1</math></th> <th><math>\text{R}^2</math></th> <th>I + II</th> <th>E:II</th> </tr> </thead> <tbody> <tr> <td>OEt</td> <td>Me</td> <td>(97)</td> <td>16:84</td> </tr> <tr> <td>OEt</td> <td>OEt</td> <td>(88)</td> <td>11:89</td> </tr> <tr> <td>Et</td> <td>Et</td> <td>(90)</td> <td>10:90</td> </tr> <tr> <td>Me</td> <td><i>t</i>-Bu</td> <td>(80)</td> <td>7:93</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>(95)</td> <td>12:88</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(57)</td> <td>7:93</td> </tr> </tbody> </table> 	$\text{R}^1$	$\text{R}^2$	I + II	E:II	OEt	Me	(97)	16:84	OEt	OEt	(88)	11:89	Et	Et	(90)	10:90	Me	<i>t</i> -Bu	(80)	7:93	Ph	Me	(95)	12:88	Ph	Ph	(57)	7:93	78
$\text{R}^1$	$\text{R}^2$	I + II	E:II																													
OEt	Me	(97)	16:84																													
OEt	OEt	(88)	11:89																													
Et	Et	(90)	10:90																													
Me	<i>t</i> -Bu	(80)	7:93																													
Ph	Me	(95)	12:88																													
Ph	Ph	(57)	7:93																													
	$\text{Rh}(\text{acac})(\text{CO})_2$	$\text{PhMe}_2\text{SiH}_2$ , CO (1 atm), toluene, 50°, 10 h		422																												
	$\text{Rh}(\text{acac})(\text{CO})_2$	$\text{PhMe}_2\text{SiH}_2$ , CO (1 atm), toluene, rt, 24 h		422																												
	$\text{Rh}_4(\text{CO})_{12}$	$\text{PhMe}_2\text{SiH}_2$ , CO (1 atm), toluene, rt, 7 h		422																												



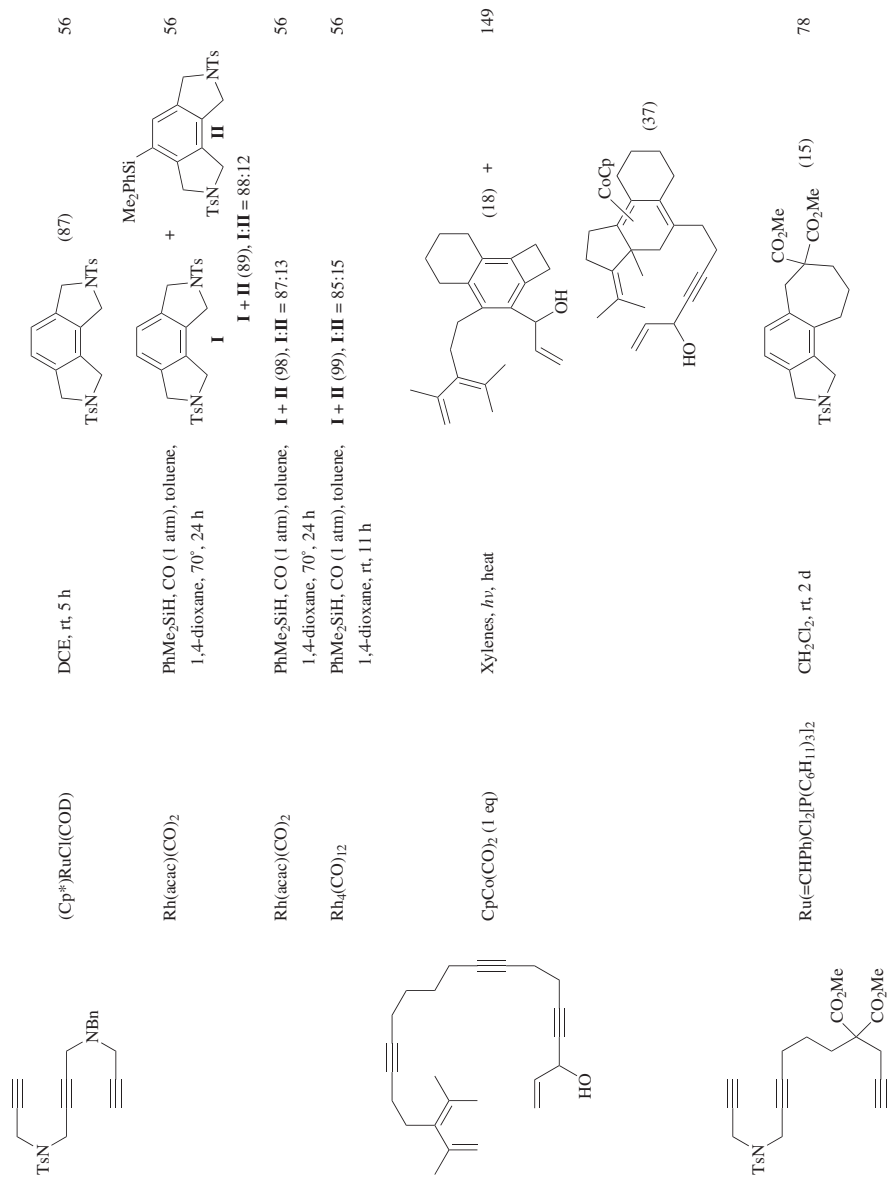
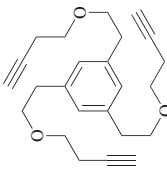
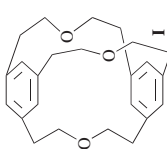
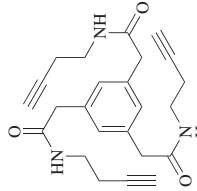
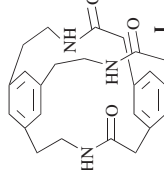
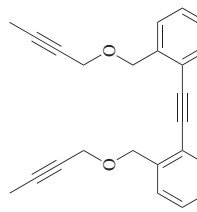
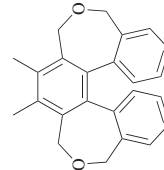


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 C <sub>24</sub>	CpCo(CO) <sub>2</sub>	<i>o</i> -Xylene, 155°, 21 h	 I + II (52), <b>II</b> = 1:1.7 430	430
	CpCo(CO) <sub>2</sub>	<i>o</i> -Xylene, 155°, 21 h	 I + II (54), <b>II</b> = 1:1.3 430	430
	CpCo(CO) <sub>2</sub>	<i>i</i> -Octane, 99°, 3.5 h	 I (41)	118
	CpCo(CO) <sub>2</sub>	<i>i</i> -Octane, <i>hv</i> , 99°, 3.5 h	I (47)	118
	CpCo(CO) <sub>2</sub>	<i>n</i> -Decane, <i>hv</i> , 120°, 1 h	I (64)	118
	CpCo(CO) <sub>2</sub>	PhCl, <i>hv</i> , 120°, 30 min	I (48)	118
	CpCo(CO) <sub>2</sub>	CO (1 atm), <i>n</i> -decane, <i>hv</i> , 120°, 1 h	I (16)	118
	CpCo(CO) <sub>2</sub>	<i>n</i> -Decane, <i>hv</i> , 120°, 4 h	I (31)	118
	CpCo(CO) <sub>2</sub>	<i>n</i> -Decane, <i>hv</i> , 120°, 2 h	I (70)	118
	CpCo(CO) <sub>2</sub>	<i>n</i> -Decane, <i>hv</i> , 140°, 1 h	I (74)	118

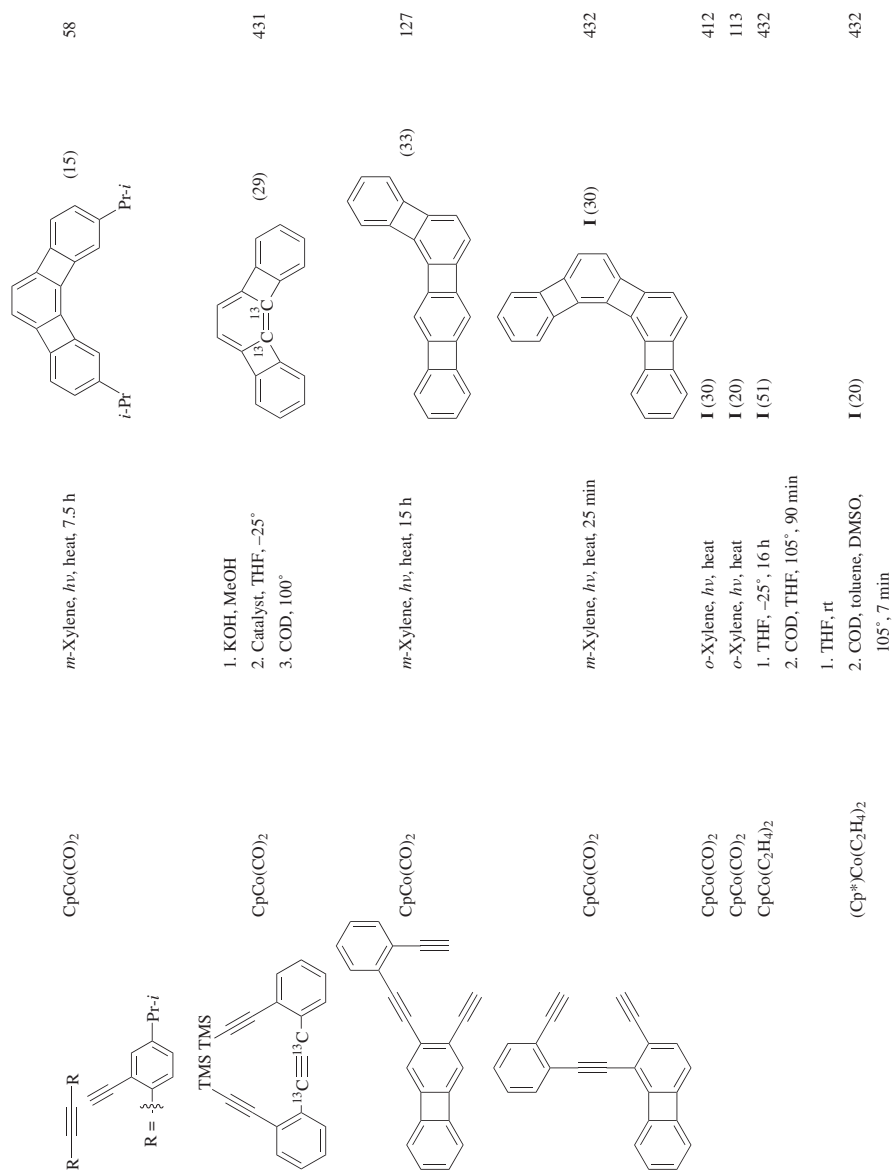
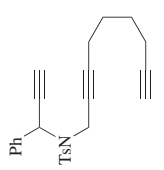
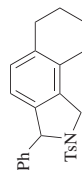
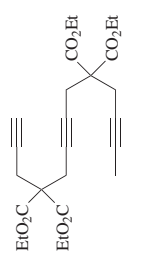
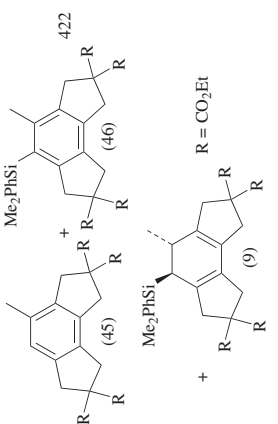
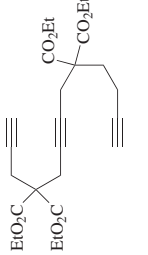
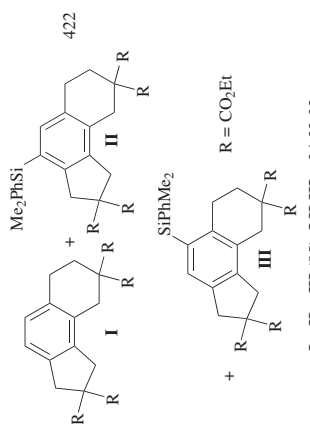


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 $\text{C}_{25}$	$\text{Ru}(\text{=CHPh})(\text{Cl})_2\text{P}(\text{C}_6\text{H}_{11})_2$	$\text{CH}_2\text{Cl}_2$ , rt	 (35)	78
	$\text{Rh}_4(\text{CO})_{12}$	$\text{PhMe}_2\text{SiH}$ , CO (1 atm), toluene, rt, 7 h		422
	$\text{Rh}_4(\text{CO})_{12}$	$\text{PhMe}_2\text{SiH}$ , CO (1 atm), toluene, rt, 40 h	 <b>I + II + III</b> (85), <b>III</b> = 34:33:33	422

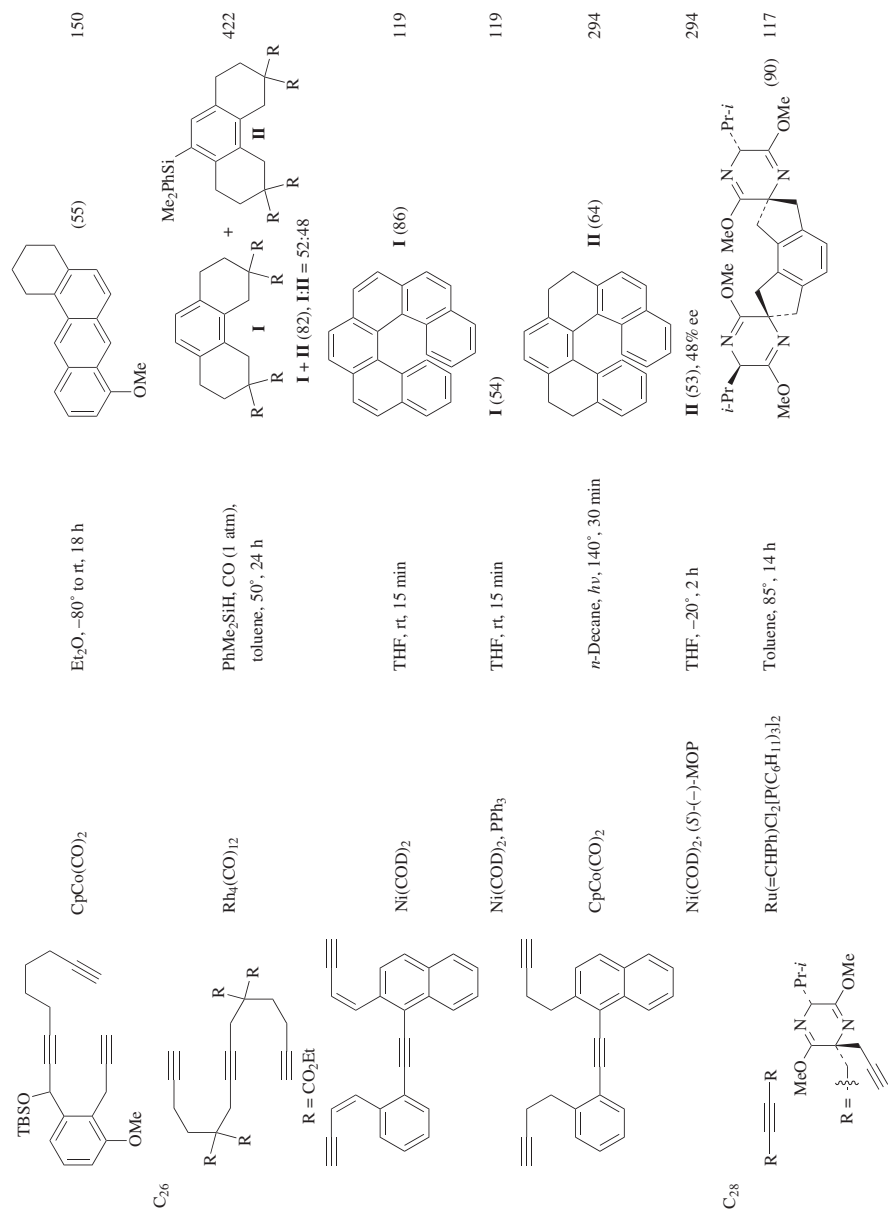
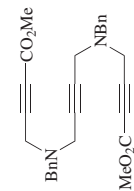
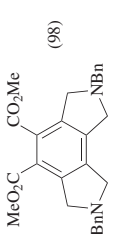
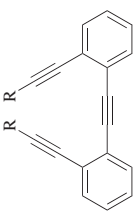
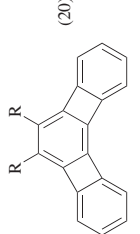
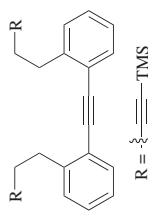
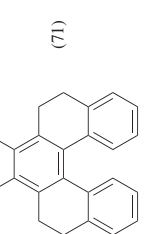
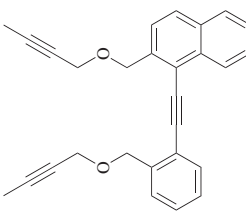
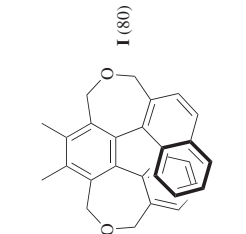


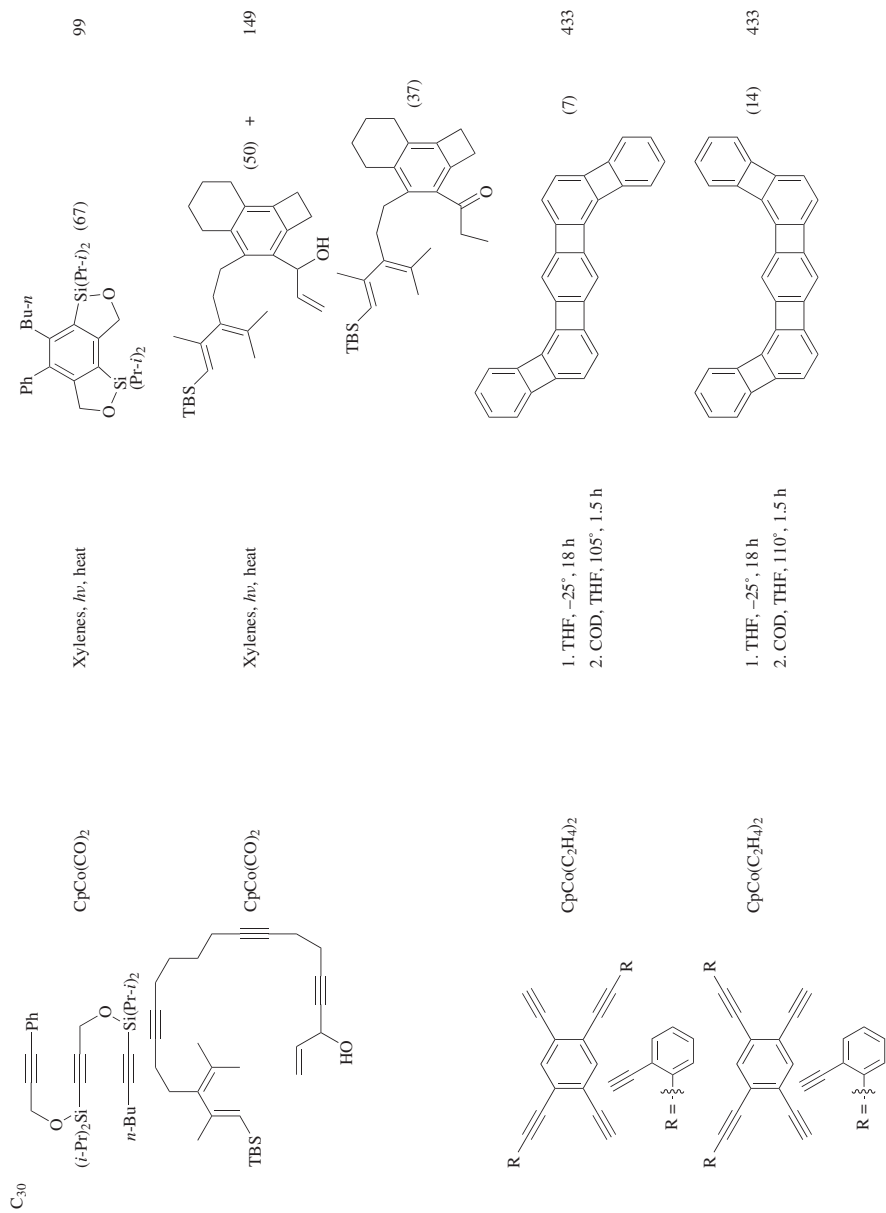


TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
 C <sub>28</sub>	Pd <sub>2</sub> (dba) <sub>3</sub> , PPh <sub>3</sub>	Toluene, 110°, 30 min	 (98)	56
 R R TMS	CpCo(CO) <sub>2</sub>	<i>o</i> -Xylene, heat, 7 h	 (20)	413
 R R TMS	CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	<i>n</i> -Decane, <i>hν</i> , 140°, 2.5 h	 (71)	118
 R R TMS	CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	<i>n</i> -Decane, <i>hν</i> , 140°, 2 h	 I (80)	118
 R R TMS	CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	<i>n</i> -Decane, <i>hν</i> , 140°, 2 h	 I (71)	118



99

149

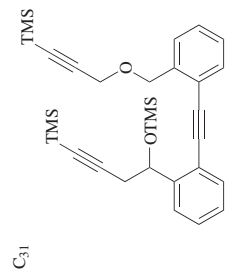
433

433

TABLE 4. TRIYNES (Continued)

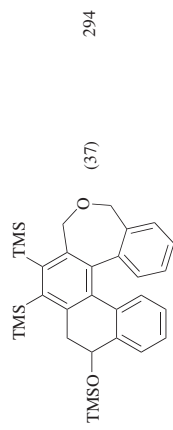
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C<sub>30-42</sub></p> <p> <math>R^1 = \begin{cases} \text{H} &amp; (2) \\ \text{Ph} &amp; (15) \\ n\text{-Pr} &amp; (23) \end{cases}</math> </p>	CpCo(CO) <sub>2</sub>	<i>m</i> -Xylene, <i>hν</i> , heat, 2 h	<p>429</p>	
<p>C<sub>30</sub></p> <p>R = <math>\begin{cases} \text{H} \\ n\text{-Bu} \end{cases}</math></p>	Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	THF, rt, 15 min	<p>(76)</p>	119
	Ni(COD) <sub>2</sub>	THF, rt, 15 min	<p>I (60)</p>	119
	Ni(COD) <sub>2</sub> , PPh <sub>3</sub>	THF, rt, 15 min	<p>I (51)</p>	119
	CpCo(CO) <sub>2</sub> , PPh <sub>3</sub>	<i>n</i> -Decane, <i>hν</i> , 140°, 2 h	<p>(64)</p>	294



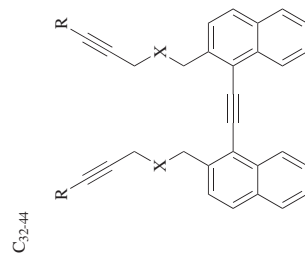


CpCo(CO)<sub>2</sub>, PPh<sub>3</sub>

*n*-Decane, *hν*, 140°, 4 h

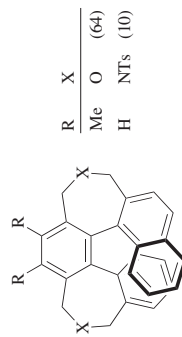


294



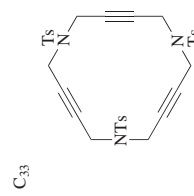
CpCo(CO)<sub>2</sub>, PPh<sub>3</sub>

*n*-Decane, *hν*, 140°, 3 h



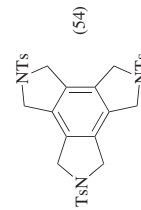
118

R	X
Me	O (64)
H	NTs (10)



Pd(PPh<sub>3</sub>)<sub>4</sub>

Toluene, heat, 22 h



120

TABLE 4. TRYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	<p>CpCo(CO)<sub>2</sub>, PPh<sub>3</sub></p>	<p><i>n</i>-Decane, <i>hν</i>, 140°, 1 h</p>	<p><b>I (72)</b> 118</p>	118
	<p>CpCo(CO)<sub>2</sub>, PPh<sub>3</sub> (1 eq)</p>	<p><i>n</i>-Decane, <i>hν</i>, 140°, 1.3 h</p>	<p><b>I (83)</b></p>	118
	<p>CpCo(CO)<sub>2</sub></p>	<p>1. (<i>n</i>-Bu)<sub>4</sub>NF, THF, rt, 40 min 2. Catalyst, <i>m</i>-xylene, <i>hν</i>, heat, 18 h</p>	<p>(29)</p>	429
	<p>CpCo(CO)<sub>2</sub></p>	<p>Xylenes, <i>hν</i>, heat, 1 h</p>	<p>(4)</p>	434

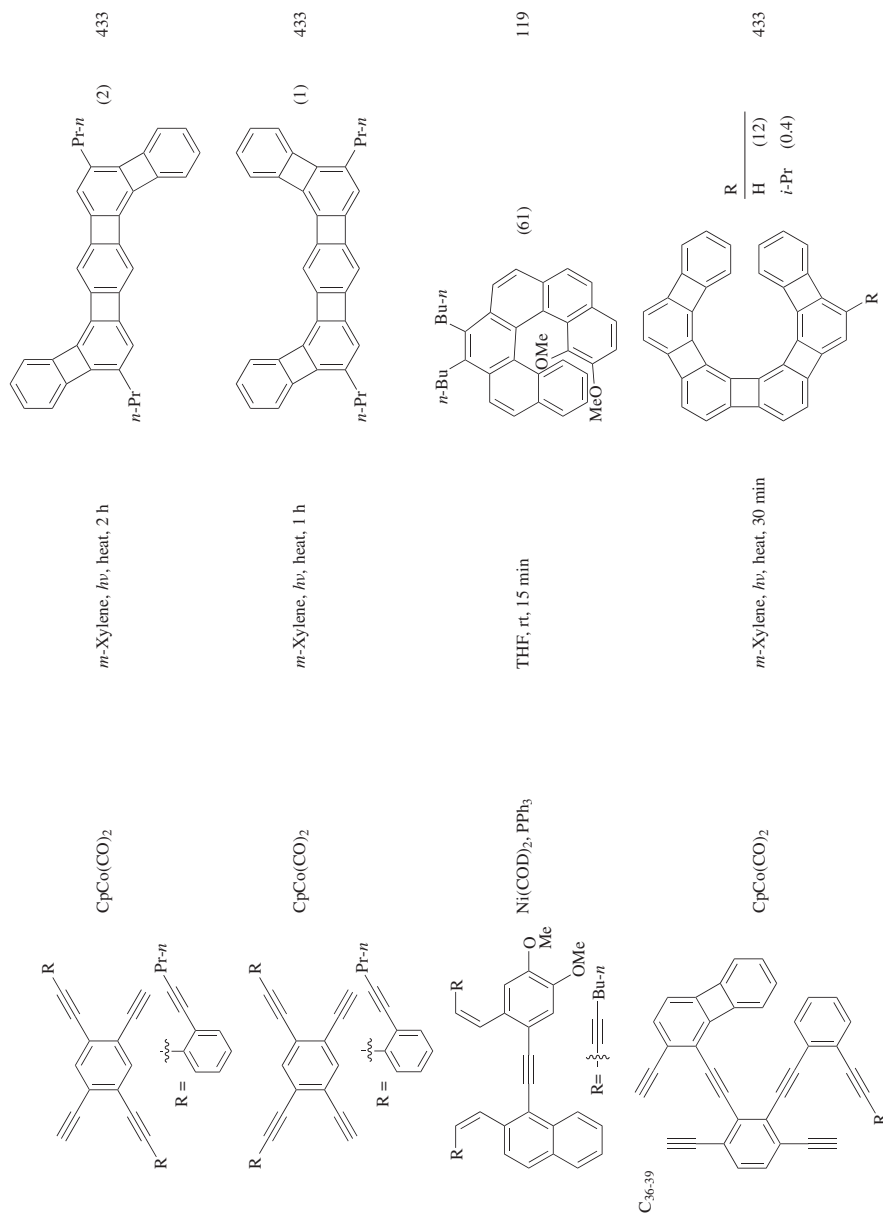
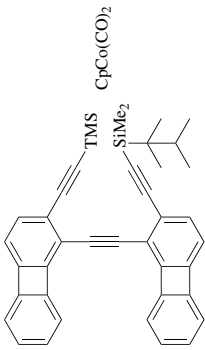
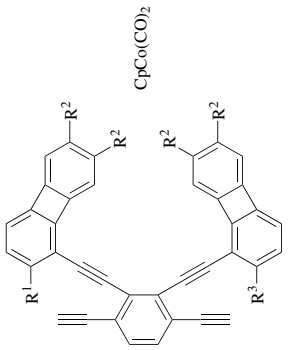
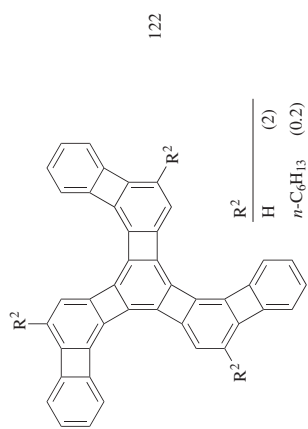


TABLE 4. TRIYNES (Continued)

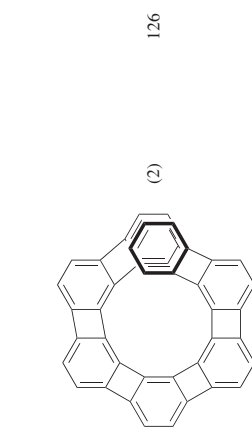
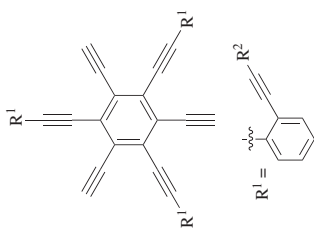
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C<sub>41</sub></p> 	CpC <sub>9</sub> (CO) <sub>2</sub>	1. ( <i>n</i> -Bu) <sub>4</sub> NF, THF 2. Catalyst, <i>o</i> -xylene, <i>hν</i> , heat	(5)	412, 113
<p>C<sub>42-53</sub></p>  <p> <math>R^1 = \begin{cases} \text{---} \\ \text{---} \\ \text{---} \end{cases} R^4</math>  <math>R^3 = \begin{cases} \text{---} \\ \text{---} \\ \text{---} \end{cases} R^5</math> </p>	CpC <sub>9</sub> (CO) <sub>2</sub>	<i>m</i> -Xylene, <i>hν</i> , heat, 30 min	125	

R <sup>2</sup>	R <sup>4</sup>	R <sup>5</sup>
H	H	H
H	CH <sub>2</sub> OMe	H
Me	H	H
Me	CH <sub>2</sub> OMe	CH <sub>2</sub> OMe
Me	CH <sub>2</sub> OMe	H



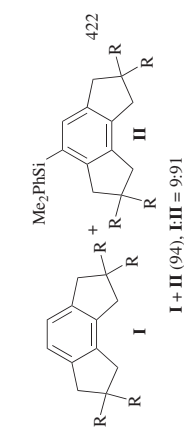
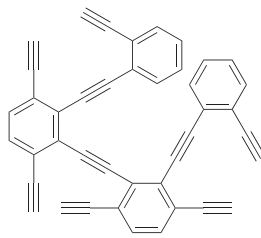
*m*-Xylene, *hν*, heat

CpC<sub>9</sub>(CO)<sub>2</sub>



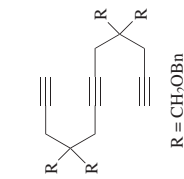
*m*-Xylene, *hν*, heat, 30 min

CpC<sub>9</sub>(CO)<sub>2</sub>



Me<sub>2</sub>PhSiH, CO (1 atm),  
toluene, rt, 38 h

Rh<sub>4</sub>(CO)<sub>12</sub>

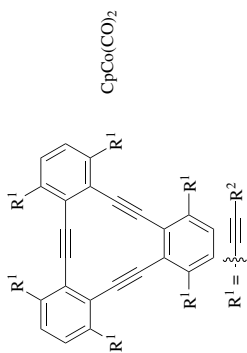


I + II (94%), I:II = 9:91

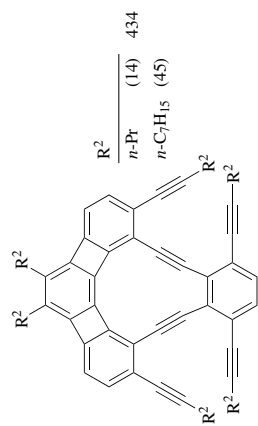
TABLE 4. TRIYNES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.				
<p>C<sub>88-50</sub></p> <p>CpCo(CO)<sub>2</sub></p>		<i>m</i> -Xylene, <i>hν</i> , heat, 1 h	<p>R</p> <table border="1"> <tr> <td>H</td> <td>(2)</td> </tr> <tr> <td>CH<sub>2</sub>OMe</td> <td>(3.5)</td> </tr> </table> <p>126</p>	H	(2)	CH <sub>2</sub> OMe	(3.5)	
H	(2)							
CH <sub>2</sub> OMe	(3.5)							
<p>C<sub>50</sub></p> <p>CpCo(CO)<sub>2</sub></p> <p>TBSO</p> <p>OTBDDPS</p> <p>TBDDPS</p>		1. Xylene, <i>hν</i> , heat 2. ( <i>n</i> -Bu) <sub>4</sub> NF, THF, -78° to 0°	<p>TBSO</p> <p>OTBDDPS</p> <p>(88)</p> <p>99</p>					
<p>C<sub>54-56</sub></p> <p>CpCo(CO)<sub>2</sub></p> <p>R</p>		<i>m</i> -Xylene, <i>hν</i> , heat, 25 min	<p>R</p> <table border="1"> <tr> <td>H</td> <td>(2)</td> </tr> <tr> <td>CH<sub>2</sub>OMe</td> <td>(3.5)</td> </tr> </table> <p>126</p>	H	(2)	CH <sub>2</sub> OMe	(3.5)	
H	(2)							
CH <sub>2</sub> OMe	(3.5)							

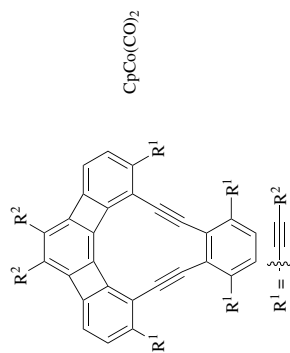
C<sub>54</sub>78



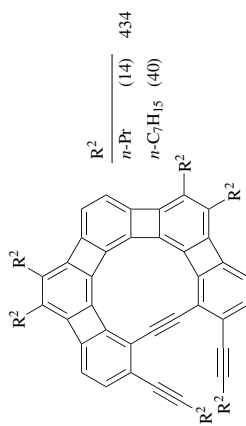
*m*-Xylene, *hν*, heat, 20 min



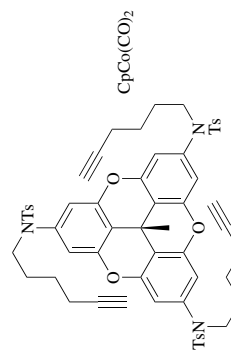
247



1,2,4-Cl<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, *hν*, 160°, 3 h



C<sub>59</sub>



*o*-Xylene, *hν*, heat, 18 h

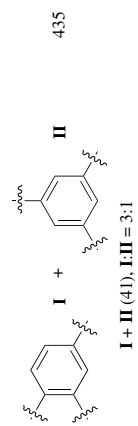


TABLE 5. NITRILES

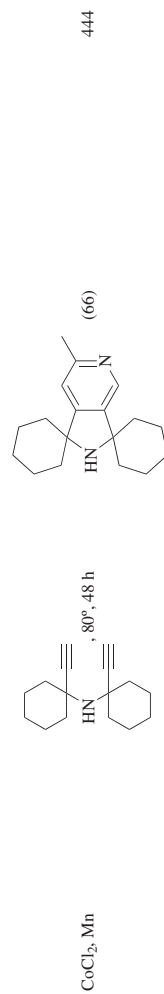
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_2$ $CCl_3-C\equiv N$	$(Cp^*)RuCl(COD)$	$MeO_2C-CH_2-C\equiv C-CH_2-C(OMe)_2$ $MeO_2C-CH_2-C\equiv C-CH_2-C(OMe)_2$ DCE, 60°, 30 min	 (-)	101
$Cl-CH_2-C\equiv N$	$(Cp^*)Ru(MeCN)_3PF_6$	$MeO_2C-CH_2-C\equiv C-CH_2-C(OMe)_2$ $MeO_2C-CH_2-C\equiv C-CH_2-C(OMe)_2$ DMF, rt, 1.5 h	 (-)	436
$-C\equiv N$	Catalyst	$R^1-C\equiv C-R^2$	 $R^1$ $R^2$	
	Catalyst	Solvent	Temp	Time
	$CpZr(dmppe)_2Cl$	$Et_2O$	rt	-
	$(Cp^*)Ru(MeCN)_3PF_6$	-	rt	-
	 $Co(COD)O$	$H_2O, MeOH$	85°	24 h
	$(Cp^*)Co(\eta^3\text{-allyl})$	hexane	rt	72 h
	$(Cp^*)Co(\eta^3\text{-allyl})$	hexane	rt	72 h
	$(MeC_6H_5)Fe(C_2H_4)_2$	Acetylene, -30°		
	$CpCo(COD)$	Acetylene, $H_2O$ , Brij 56, <i>hv</i> , 4 h		
			$R^1$ $R^2$	
			Me H (100)	6
			$CO_2Et$ H (73)	275
			$CH_2OH$ $CH_2OH$ (76)	437
			Me Me (100)	438
			Ph Ph (57)	438
			 <b>I</b> + <b>II</b>	439
			<b>I</b> + <b>II</b> (-), <b>I:II</b> = 88:12	
			 (18)	440



Catalyst	Acetylene	Temp Time	441
CpCo(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	<i>hν</i>	40° 3 h	(1)
CpCo(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	in the dark	40° 3 h	(1)
CpCo(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	diffuse daylight	40° 3 h	(1)
CpCo(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	sunlight	40° 3 h	(1)
CpCo(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	Hg-lamp	rt 1 h	(2)
CpCo(COD)	Hg-lamp (254-580 nm)	40° 2 h	(2)
CpCo(COD)	Hg-lamp (320-370 nm)	40° 2 h	(2)
CpCo(COD)	Hg-lamp (>400 nm)	40° 2 h	(4)



Catalyst	Acetylene	Temp Time	442
Cp <sub>2</sub> Zr(Bu- <i>n</i> ) <sub>2</sub>	1. R <sup>1</sup> -C≡C-R <sup>2</sup> , THF, catalyst	50° 3 h	(59)
	2. Nitriole, 50°	3 h	(66)
	3. R <sup>3</sup> -C≡C-R <sup>4</sup> , NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , 50°	9 h	(65)
			(86)
			(89)
			(41)
			(58)





Catalyst	Solvent	Temp	Time	X	R	I	II	III	
CpCo(CO) <sub>2</sub>	—	80°	100 h	CH <sub>2</sub>	H	(25)	(3)	(0)	445
	toluene	rt	48 h	(CH <sub>2</sub> ) <sub>2</sub>	H	(—)	(—)	(—)	448
Catalyst	toluene	80°	48 h	(CH <sub>2</sub> ) <sub>2</sub>	H	(—)	(—)	(—)	448
	—	100 bar, 145°	1 h	O	TMS	(73)	(1)	(0)	447
	CH <sub>3</sub> CN	120°	24 h	NMe	H	(34)	(12)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NPr- <i>i</i>	H	(61)	(4)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NBu- <i>n</i>	H	(36)	(3)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NBn	H	(65)	(0)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NCO <sub>2</sub> Me	H	(22)	(20)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NCO <sub>2</sub> Et	H	(49)	(0)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NAc	H	(36)	(17)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NCOCH <sub>2</sub> Et	H	(34)	(0)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NBz	H	(34)	(0)	(0)	449
	CH <sub>3</sub> CN	120°	24 h	NTs	H	(47)	(0)	(0)	449

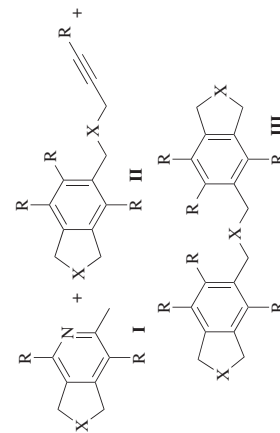
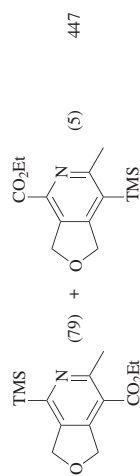
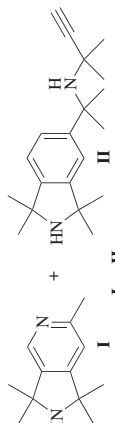
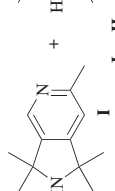
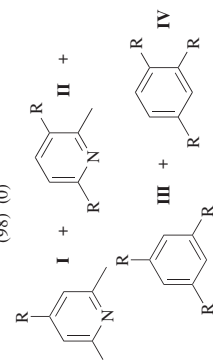
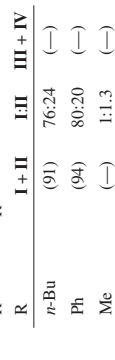
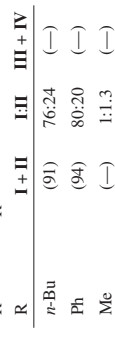
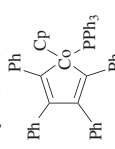








TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.	
C <sub>2</sub> —C≡N	Catalyst	Time 72 h		445	
	Catalyst Co(CH <sub>3</sub> CN) <sub>2</sub> (Z-MeO <sub>2</sub> CC=CCO <sub>2</sub> Me) <sub>2</sub> CpCo(CO) <sub>2</sub> CoCl <sub>2</sub> , Mn	80° 100 h 6 h		(8) (8) (10) (0) (98) (0)	
C <sub>2</sub> R—C≡N	Catalyst	R—C≡N			
	Catalyst	Solvent Temp Time			
C <sub>2</sub> —C≡N	Catalyst (Cp*)Co(η <sup>3</sup> -allyl) (Cp*)Co(η <sup>3</sup> -allyl) CpCo(COD)	hexane rt 72 h hexane rt 72 h toluene <i>h</i> v, rt 2 h		438 438 450	
	Catalyst 	THF 80° 24 h		(85) — (3)	285
	"	THF 80° 24 h		(34) — (15)	285
	"	THF 80° 24 h		(54) — (5)	285
	"	THF 80° 24 h		(79) — (6)	285
	"	THF 80° 24 h		(8) — (1)	285
	CpCo(CO) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub> 50° 48 h		(77) 54:46 (12)	451

(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	110°	48 h	<i>n</i> -Bu	(83)	69:31	(5)	451
Co	—	120°	48 h	<i>n</i> -Pr	(—)	87:13	(—)	448
Co	—	120°	48 h	<i>n</i> -Bu	(—)	88:12	(—)	448
CpCo(COD)	—	120°	48 h	<i>n</i> -Bu	(—)	89:11	(—)	448
CoCl <sub>2</sub> · H <sub>2</sub> O (6 eq), NaBH <sub>4</sub>	—	120°	48 h	<i>n</i> -Bu	(—)	55:45	(—)	448
Cp <sub>2</sub> Co	toluene	150°	20 h	(CH <sub>2</sub> ) <sub>6</sub> ≡	(14)	—	(8)	342
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	15 h	H	(5)	—	(—)	452
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	15 h	Et	(40)	55:45	(5)	452
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	15 h	<i>n</i> -Bu	(63)	55:45	(15)	452
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	90 h	<i>n</i> -Bu	(4)	86:14	(10)	452
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	90 h	Ph	(21)	87:13	(58)	452

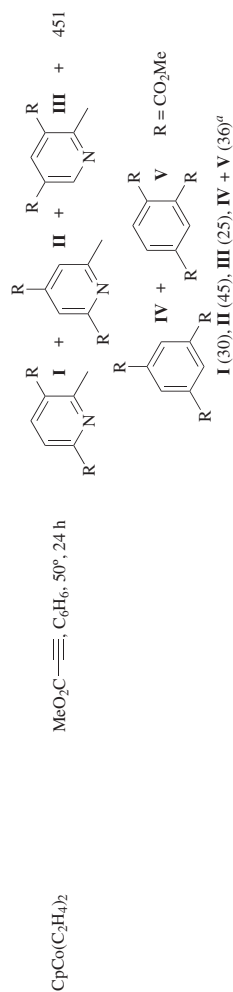
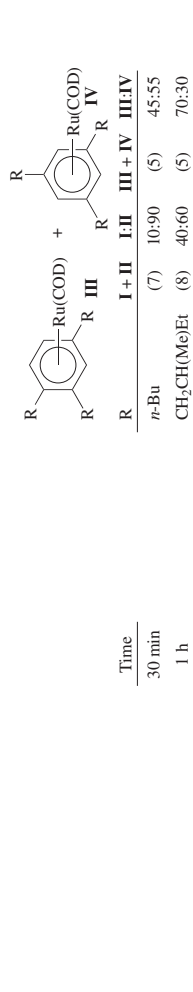
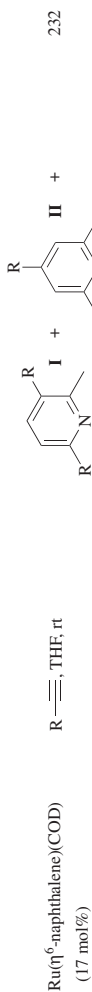

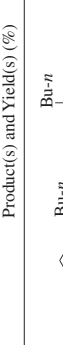
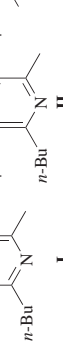

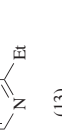



TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.									
C <sub>2</sub> 	CpCo(CO) <sub>2</sub>	1-Hexyne, <i>sc</i> H <sub>2</sub> O, 37/4°, 2 h	 +  +  I + II (15), I:II = 1:1, III (—)	245									
			C <sub>3</sub> Et—C≡C—N	Catalyst Catalyst	Acetylene lamp		Temp	Time	Hg (125 W)	rt	2 h	(13)	441
									Hg (125 W)	−60°	2 h	(19)	441
									Hg (125 W)	15°	2 h	(14)	441
									Hg (125 W)	15°	2 h	(12)	441
									Hg (125 W)	15°	2 h	(11)	441
									halogen (250 W)	15°	30 min	(20)	441
									halogen (800 W)	15°	30 min	(43)	441
									—	rt	—	(—)	174
									CpZrEt <sub>2</sub>	1. R <sup>1</sup> —C≡C—R <sup>2</sup> , THF 2. Nitrile, 50°, 3 h 3. R <sup>3</sup> —C≡C—R <sup>4</sup> , NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , 50°, 9 h		R <sup>1</sup>	R <sup>2</sup>
Et	Et	Et										Ph	Ph
Et	Et	Et	Ph	Ph	(75)								
	<i>n</i> -Bu	TMS	Me	Ph	Ph	(52)							
	Ph	Ph	<i>n</i> -Pr	<i>n</i> -Pr	<i>n</i> -Pr	(77)							
	Ph	Ph	<i>n</i> -Pr	<i>n</i> -Pr	<i>n</i> -Pr	(58)							


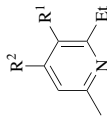

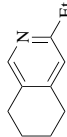



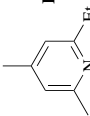
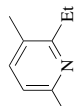
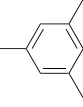
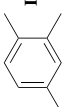
Cp <sub>2</sub> ZrEt <sub>2</sub>	1. R <sup>1</sup> -C≡C-R <sup>2</sup> , THF, 0°, 3 h 2. Nitrile, 50°, 3 h 3.  , CuCl, 50°, 1 h		$\frac{R^1 \quad R^2}{n\text{-Pr} \quad m\text{-Pr} \quad (43)}$ Ph SiEt <sub>3</sub> (81)	442
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	 , 150°, 15 h	 (20)		452
(CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> )Fe(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	Acetylene, -30°	 +  (—)		439
Catalyst	 , toluene	 <b>I</b> +  <b>II</b> +  <b>III</b> +  <b>IV</b>	$\frac{\mathbf{I:II}}{\mathbf{I + II (-), III + IV (-)}}$	453
Catalyst	Temp			
CpCo(η <sup>2</sup> -η <sup>2</sup> -COD)	147°		63:37	
CpCo(η <sup>1</sup> -η <sup>3</sup> -COD)	147°		63:37	
(η <sup>3</sup> -C <sub>8</sub> H <sub>13</sub> )Co(η <sup>2</sup> -η <sup>2</sup> -COD)	130°		70:30	
(η <sup>1</sup> -η <sup>3</sup> -cyclohexenyl)Co(C <sub>6</sub> Me <sub>6</sub> )	165°		72:28	
(η <sup>3</sup> -cyclohexenyl)Co(C <sub>6</sub> H <sub>6</sub> )	155°		72:28	
(η <sup>3</sup> -cyclohexenyl)Co(C <sub>6</sub> Me <sub>6</sub> )	162°		72:28	
(η <sup>3</sup> -crotyl)Co(C <sub>6</sub> Me <sub>6</sub> )	169°		72:28	
(η <sup>3</sup> -cyclopentenyl)Co(C <sub>6</sub> H <sub>5</sub> Me <sub>3</sub> )	158°		66:34	
(η <sup>3</sup> -cyclopentenyl)Co(C <sub>6</sub> Me <sub>6</sub> )	160°		68:32	

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>3</sub> Et—C≡N	Catalyst	R ≡		
	R ≡			
	Catalyst	Solvent	I:II (84)	451
	CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	<i>n</i> -Bu (84)	451
	CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	<i>i</i> -Bu (9)	451
	CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	Ph (72)	451
	CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	CH <sub>2</sub> OH (40)	451
	CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	CH <sub>2</sub> OMe (73)	451
	(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	<i>n</i> -Bu (82)	451
	(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	<i>i</i> -Bu (5)	451
	(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	Ph (15)	451
	(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	CH <sub>2</sub> OH (38)	451
	(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	CH <sub>2</sub> OMe (80)	451
	CpCo(COD)	—	<i>n</i> -Bu (65)	454
		—	<i>n</i> -Bu (88)	454
		—	<i>n</i> -Bu (78)	455, 454
	CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	<i>n</i> -Bu (67)	455, 454
	CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	Me (62)	452
	CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	<i>n</i> -Pr (70)	452



CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	15 h	<i>n</i> -Bu	(75)	56:44	(19)	452
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	90 h	<i>n</i> -C <sub>8</sub> H <sub>13</sub>	(72)	50:50	(22)	452
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	15 h	CH <sub>2</sub> OH	(57)	47:53	(13)	452
(C <sub>3</sub> H <sub>4</sub> NO <sub>2</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>n</i> -Bu	(8)	—	(14)	456
(C <sub>3</sub> H <sub>4</sub> CF <sub>3</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>n</i> -Bu	(66)	—	(15)	456
(C <sub>3</sub> H <sub>4</sub> CF <sub>3</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>t</i> -Bu	(9)	—	(12)	456
(C <sub>3</sub> H <sub>4</sub> CF <sub>3</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	Ph	(32)	—	(46)	456
(C <sub>3</sub> H <sub>4</sub> CF <sub>3</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	CH <sub>2</sub> OMe	(73)	—	(19)	456
(C <sub>3</sub> H <sub>4</sub> CF <sub>3</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	TMS	(25)	—	(11)	456
(C <sub>3</sub> H <sub>4</sub> Cl)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>n</i> -Bu	(32)	—	(20)	456
(C <sub>3</sub> H <sub>4</sub> Cl)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>t</i> -Bu	(5)	—	(17)	456
(C <sub>3</sub> H <sub>4</sub> Cl)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	Ph	(14)	—	(49)	456
(C <sub>3</sub> H <sub>4</sub> Cl)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	CH <sub>2</sub> OMe	(11)	—	(14)	456
(C <sub>3</sub> H <sub>4</sub> Cl)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	TMS	(10)	—	(24)	456
(C <sub>3</sub> H <sub>4</sub> CO <sub>2</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	150°	3 h	<i>n</i> -Bu	(68)	—	(18)	456
(C <sub>3</sub> H <sub>4</sub> CO <sub>2</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>t</i> -Bu	(8)	—	(14)	456
(C <sub>3</sub> H <sub>4</sub> CO <sub>2</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	Ph	(30)	—	(52)	456
(C <sub>3</sub> H <sub>4</sub> CO <sub>2</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	CH <sub>2</sub> OMe	(67)	—	(12)	456
(C <sub>3</sub> H <sub>4</sub> CO <sub>2</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	TMS	(32)	—	(31)	456
(C <sub>3</sub> H <sub>4</sub> CO <sub>2</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	6 h	<i>n</i> -Bu	(68)	43:57	(19)	455
(C <sub>3</sub> H <sub>4</sub> CO <sub>2</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>n</i> -Bu	(65)	—	(19)	456
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>t</i> -Bu	(5)	—	(14)	456
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	Ph	(36)	—	(45)	456
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	CH <sub>2</sub> OMe	(42)	—	(11)	456
CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	TMS	(5)	—	(25)	456
(C <sub>3</sub> H <sub>4</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>n</i> -Bu	(62)	—	(20)	456
(C <sub>3</sub> H <sub>4</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>t</i> -Bu	(8)	—	(10)	456
(C <sub>3</sub> H <sub>4</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	Ph	(20)	—	(54)	456
(C <sub>3</sub> H <sub>4</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	CH <sub>2</sub> OMe	(60)	—	(22)	456
(C <sub>3</sub> H <sub>4</sub> Me)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	TMS	(7)	—	(38)	456
(C <sub>3</sub> H <sub>4</sub> Bu- <i>n</i> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	—	130°	3 h	<i>n</i> -Bu	(68)	—	(17)	456

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.		
C <sub>3</sub> Et—C≡N	Catalyst	R—C≡				
	Catalyst	R—C≡				
	Catalyst	Temp	I + II	I:II	III + IV	
	(C <sub>3</sub> H <sub>4</sub> Bu- <i>γ</i> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	<i>t</i> -Bu (5)	—	(19)	456
	(C <sub>3</sub> H <sub>4</sub> Bu- <i>o</i> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	Ph (16)	—	(23)	456
	(C <sub>3</sub> H <sub>4</sub> Bu- <i>l</i> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	CH <sub>2</sub> OMe (58)	—	(21)	456
	(C <sub>3</sub> H <sub>4</sub> Bu- <i>l</i> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	TMS (9)	—	(35)	456
	(C <sub>3</sub> H <sub>4</sub> NMe <sub>2</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	80° 3 h	<i>n</i> -Bu (30)	—	(39)	456
	(C <sub>3</sub> H <sub>4</sub> NMe <sub>2</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	<i>t</i> -Bu (5)	—	(24)	456
	(C <sub>3</sub> H <sub>4</sub> NMe <sub>2</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	Ph (7)	—	(27)	456
	(C <sub>3</sub> H <sub>4</sub> NMe <sub>2</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	CH <sub>2</sub> OMe (40)	—	(41)	456
	(C <sub>3</sub> H <sub>4</sub> NMe <sub>2</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 3 h	TMS (17)	—	(60)	456
	CpRh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 15 h	<i>n</i> -Bu (75)	56:44	(19)	452
	(Cp*)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 24 h	<i>n</i> -Bu (37)	81:19	(25)	452
	CpRh(CO) <sub>2</sub>	130° 15 h	<i>n</i> -Bu (38)	60:40	(8)	452
	CpRh(COD)	130° 15 h	<i>n</i> -Bu (16)	58:42	(6)	452
	(C <sub>9</sub> H <sub>7</sub> )Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 90 h	<i>n</i> -Bu (19)	76:24	(36)	452
	(C <sub>9</sub> H <sub>7</sub> )Rh(COD)	130° 140 h	<i>n</i> -Bu (10)	74:26	(55)	452
	(C <sub>3</sub> Ph <sub>4</sub> Cl)Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	130° 48 h	<i>n</i> -Bu (26)	56:44	(11)	452
	(C <sub>13</sub> H <sub>8</sub> )Rh(COD)	130° 72 h	<i>n</i> -Bu (9)	69:31	(44)	452

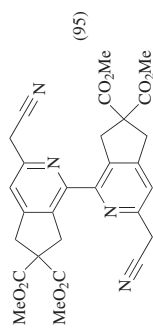
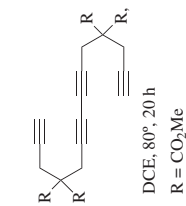
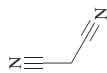
Catalyst	Solvent	Temp	Time	X	R <sup>1</sup>	R <sup>2</sup>	I + II	I:II
(Cp*)RuCl(COD)	DCE	60°	7 h	C(CO <sub>2</sub> Me) <sub>2</sub>	H	H	(91)	—
(Cp*)RuCl(COD)	DCE	rt	2.5 h	C(CO <sub>2</sub> Me) <sub>2</sub>	H	H	(95)	—
[(Cp*)RuCl <sub>2</sub> ]	DCE	rt	2.5 h	C(CO <sub>2</sub> Me) <sub>2</sub>	H	H	(92)	—
(Cp*)Rh(CH <sub>3</sub> CN) <sub>3</sub> PF <sub>6</sub>	DMF	rt	10 min	C(CO <sub>2</sub> Me) <sub>2</sub>	H	H	(84)	—
(Cp*)RuCl(COD)	DCE	60°	5 h	C(CO <sub>2</sub> Me) <sub>2</sub>	Me	H	(97)	95:5
(Cp*)RuCl(COD)	DCE	80°	20 h	C(CO <sub>2</sub> Me) <sub>2</sub>	Me	Me	(77)	—
(Cp*)RuCl(COD)	DCE	60°	24 h	C(CO <sub>2</sub> Me) <sub>2</sub>	Ph	H	(78)	100:0
(Cp*)RuCl(COD)	DCE	60°	5.5 h	C(CO <sub>2</sub> Me) <sub>2</sub>	TMS	H	(92)	100:0
(Cp*)RuCl(COD)	DCE	rt	24 h	C(CO <sub>2</sub> Me) <sub>2</sub>	CO <sub>2</sub> Me	H	(80)	100:0
(Cp*)RuCl(COD)	DCE	60°	30 min	NTs	Me	H	(95)	100:0
(Cp*)RuCl(COD)	DCE	60°	16 h	O	Me	H	(97)	95:5

(Cp*)RuCl(COD)	DCE, 80°, 20 h R = CO <sub>2</sub> Me	102
----------------	--	-----

CpCo(COD)	Acetylene, toluene, hv, rt, 5 h	457
-----------	---------------------------------	-----

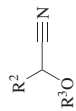


C<sub>3</sub>

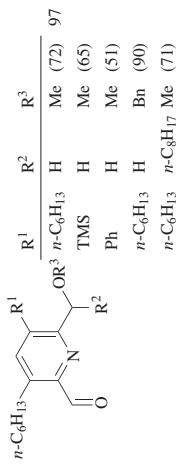


TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$\text{Me}_2\text{N}-\text{C}\equiv\text{N}$	$\text{CpRh}(\text{C}_2\text{H}_4)_2$	1-Hexyne, 150°, 90 h	 <b>I</b> + <b>II</b> (60), <b>I:II</b> = 57:43, <b>III + IV</b> (29)	452
			 (46)	458
$\text{Me}-\text{X}-\text{C}\equiv\text{N}$	 $\text{CpCo}(\text{COD})$	Acetylene, <i>hv</i> , rt, 2 h	 <b>X</b>	437
		$\text{H}_2\text{O}$ , $\text{MeOH}$ , 85°, 24 h	 <b>O</b> (32) <b>S</b> (38)	437
$\text{EtS}-\text{C}\equiv\text{N}$	$(\text{Cp}^*)\text{Ru}(\text{CH}_3\text{CN})_3\text{PF}_6$	 $\text{DMF}$ , 80°, 4 h	 (53)	436
$\text{Me}-\text{C}(=\text{O})-\text{C}\equiv\text{N}$	$(\text{Cp}^*)\text{RuCl}(\text{COD})$	 $\text{DCE}$ , 80°, 1 h	 (90)	101

C<sub>3,11</sub>Ti(OPr-*i*)<sub>4</sub>

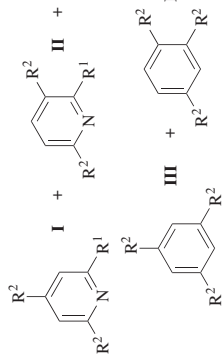
1.  $\text{Et}_3\text{N}-\text{C} \equiv \text{C}-\text{C}_6\text{H}_{13-n}-\text{Et}_2\text{O}$ ,  $n-\text{C}_6\text{H}_{13}$
2.  $\text{R}^1-\text{C} \equiv \text{C}-\text{Cl}$ ,  $-50^\circ$ , 5 h
3. Nitrile,  $-30^\circ$ , 3 h
4.  $\text{H}_2\text{O}$



R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield (%)
$n-\text{C}_6\text{H}_{13}$	H	Me	97 (72)
TMS	H	Me	65 (65)
Ph	H	Me	51 (51)
$n-\text{C}_6\text{H}_{13}$	H	Bn	90 (90)
$n-\text{C}_6\text{H}_{13}$	$n-\text{C}_8\text{H}_{17}$	Me	71 (71)

C<sub>4</sub>

Catalyst



Catalyst	Solvent	Temp	Time
(MeC <sub>4</sub> H <sub>5</sub> ) <sub>2</sub> Fe(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	$i$ -Pr	$-30^\circ$	—
(MeC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Fe(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	$n$ -Pr	$-30^\circ$	—
CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	toluene	rt	48 h
(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	$50^\circ$	48 h
CpRh(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	$110^\circ$	48 h
CpRh(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	—	$150^\circ$	1.5 h
CpRh(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	—	$150^\circ$	1.5 h

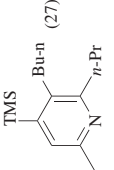
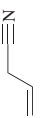
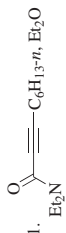
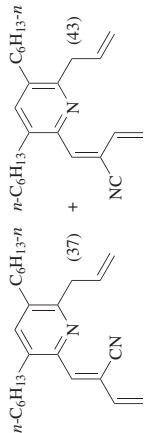
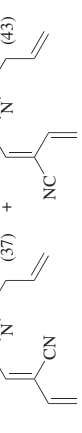
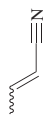
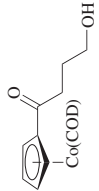
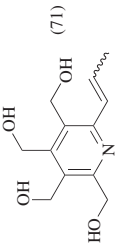
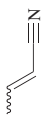


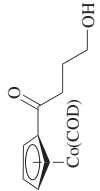
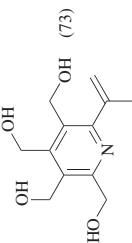

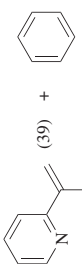

R <sup>1</sup>	R <sup>2</sup>	I + II	I:II	III + IV	Yield (%)
$i$ -Pr	H	(—)	—	—	439
$n$ -Pr	H	(—)	—	—	439
$n$ -Pr	CH <sub>2</sub> OMe	(5)	—	(7)	309
$i$ -Pr	$n$ -Bu	(71)	55:45	(11)	451
$i$ -Pr	$n$ -Bu	(69)	70:30	(8)	451
$n$ -Pr	$n$ -Bu	(65)	56:44	(23)	452
$i$ -Pr	$n$ -Bu	(62)	58:42	(35)	452

1. TMS-C≡C-Bu-*n*, THF, rt, 1 h
2. Nitrile,  $50^\circ$ , 3 h
3. Ph-C≡C-Et, NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>,  $50^\circ$ , 12 h

CpZrEt<sub>2</sub>

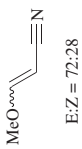


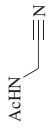
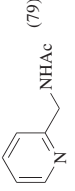
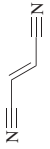

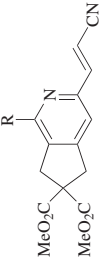

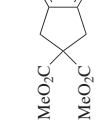

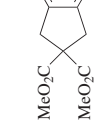
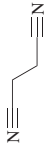
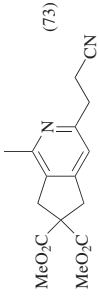
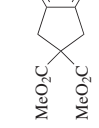
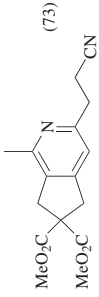
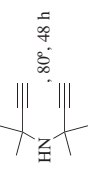
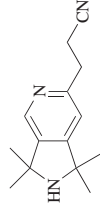


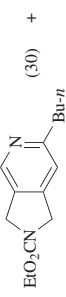
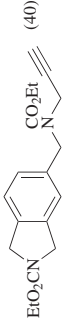
442

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$n\text{-Pr-C}\equiv\text{N}$	$\text{Cp}^*\text{ZrEt}_2$	1. TMS-C≡C-Bu- <i>n</i> , THF, 0°, 3 h 2. Nitrile, 50°, 1 h 3. Br-C≡C- <i>n</i> -Pr	 (27)	442
	$\text{Ti}(\text{OPr-}i)$ <sub>4</sub>	1.  $n\text{-C}_6\text{H}_{13}$ , Et <sub>2</sub> O <i>i</i> -PrMgCl, -50°, 5 h 2. 1-Octyne, -50°, 3 h 3. Nitrile, -30°, 5 h 4. H <sub>2</sub> O	 (37) +  (43)	97
		H <sub>2</sub> O, MeOH, 85°, 24 h	 (71)	437
 E:Z = 69:31	$\text{CpCo}(\text{COD})$	Acetylene, toluene, <i>h\nu</i> , rt, 5 h	 (23)	457
		H <sub>2</sub> O, MeOH, 85°, 24 h	 (73)	437
	$\text{CpCo}(\text{COD})$	Acetylene, toluene, <i>h\nu</i> , rt, 5 h	 (39) +  (26)	457

	<b>AlBr<sub>3</sub></b>	1. <i>t</i> -Bu-C≡C, CH <sub>2</sub> Cl <sub>2</sub> , -90°, 45 min 2. Nitrite, -90°, 25 min		459
	<b>AlBr<sub>3</sub></b>	1. <i>t</i> -Bu-C≡C, CH <sub>2</sub> Cl <sub>2</sub> , -90°, 2 h 2. Nitrite, -90°, 2 h	<b>I (8)</b>	459
	<b>(Cp*)RuCl(COD)</b>			101
	<b>Catalyst</b>	<b>Temp</b> <b>Time</b>	<b>X</b> <b>R</b> <b>I + II</b> <b>I:II</b>	
		60° 30 min	C(CO <sub>2</sub> Me) <sub>2</sub> H (83) —	
		60° 2 h	C(CO <sub>2</sub> Me) <sub>2</sub> Me (78) 88:12	
		60° 6 h	C(CO <sub>2</sub> Me) <sub>2</sub> Ph (50) 100:0	
		rt 1 h	C(CO <sub>2</sub> Me) <sub>2</sub> CO <sub>2</sub> Me (78) 13:87	
		60° 30 min	NTs H (75) —	
		60° 2 h	O H (49) —	
	<b>Catalyst</b>	Acetylene, <i>hν</i> (W), rt		460
	<b>Catalyst</b>	<b>W</b> <b>Time</b>		
	CpCo(COD)	125 2 h	(14)	
	CpCo(COD)	625 1 h	(26)	
	CpCo(COD)	800 30 min	(46)	
	(C <sub>5</sub> H <sub>9</sub> Ph) <sub>2</sub> Co(COD)	125 2 h	(16)	
	(C <sub>5</sub> H <sub>4</sub> Ac)Co(COD)	125 2 h	(14)	
	(C <sub>5</sub> H <sub>4</sub> Ac)Co(COD)	625 2 h	(15)	
	(C <sub>5</sub> H <sub>4</sub> COPh)Co(COD)	125 2 h	(15)	
	(C <sub>5</sub> H <sub>4</sub> COPh)Co(COD)	800 2 h	(11)	
	<b>CpCo(COD)</b>	Acetylene, H <sub>2</sub> O, Brij 56, <i>hν</i> , 4 h	<b>I (20)</b>	440

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>4</sub>  E:Z = 72:28	CpCo(COD)	Acetylene, toluene, <i>hν</i> , rt, 3.5 h	 (24) E:Z = -- +  (11)	457
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , 35°, 4 h	 (79)	461
	Catalyst		 (73)	102
	Catalyst		 (50)	436
	Catalyst		 (88)	102
	(Cp*)RuCl(COD)	DCE, 60°, 7 h	 (73)	102
	(Cp*)RuCl(COD)	DMF, 80°, 2 h	 (50)	436
	(Cp*)RuCl(COD)	DCE, 60°, 1.5 h	 (73)	102
	CoCl <sub>2</sub> , Mh	 , 80°, 48 h	 (90)	444
C <sub>5</sub> 	CoCl <sub>2</sub> , Mh	 , 120°, 24 h	 (30) +  (40)	449



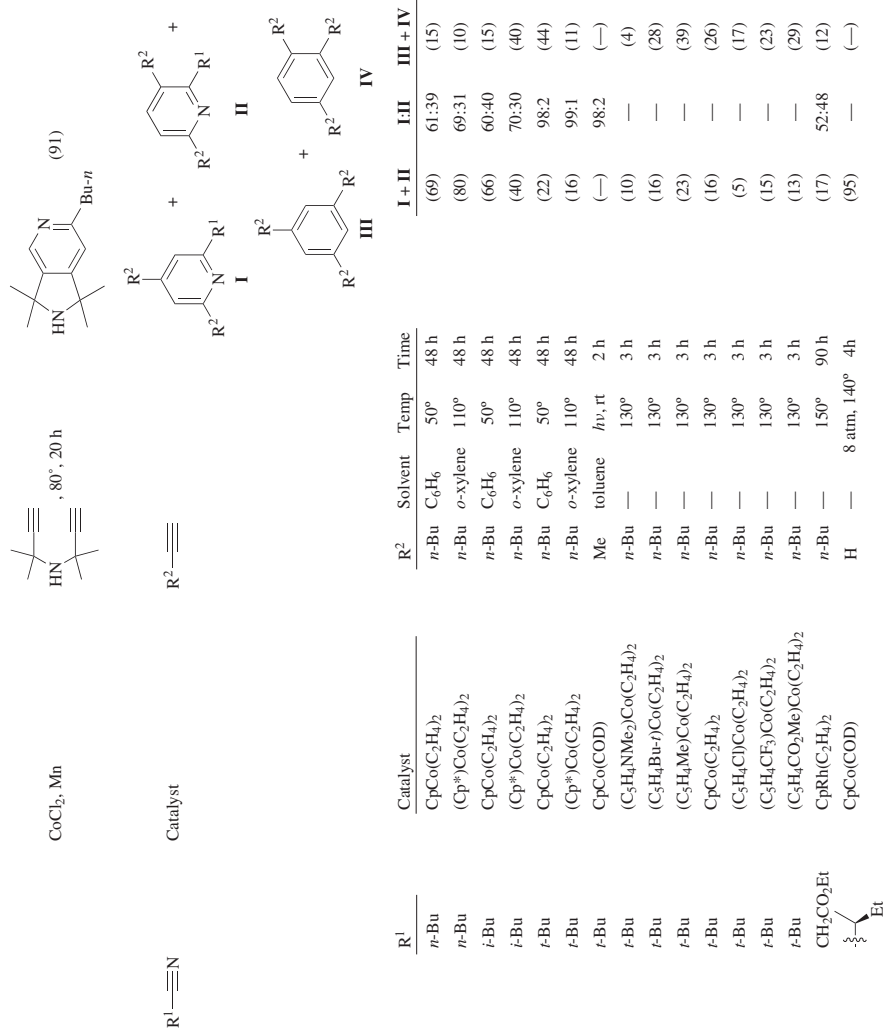
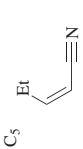
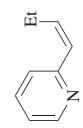
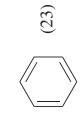
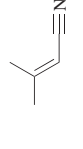
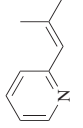
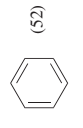
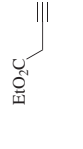


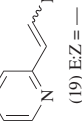
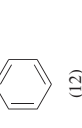
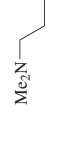
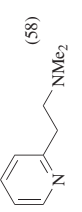
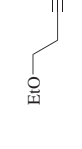
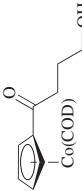
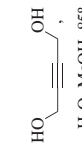
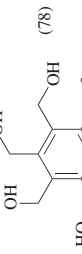
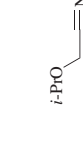

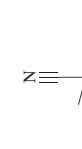
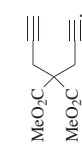
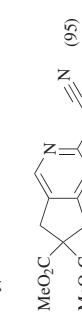


TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , rt, 5 h	 (32) +  (23)	457
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , rt, 5 h	 (55) +  (52)	457
	CpCo(COD)	Acetylene, <i>hν</i> , rt, 2 h	 (29)	458
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , rt, 4 h	 (19) E:Z = — +  (12)	457
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , 35°, 4 h	 (58)	461
	 Co(COD)	 H <sub>2</sub> O, MeOH, 85°, 24 h	 (78)	437
	CpCo(COD)	Acetylene, <i>hν</i> , rt, 2 h	 (17)	458
	(Cp*)Ru(CH <sub>3</sub> CN) <sub>3</sub> PF <sub>6</sub>	 DMF, rt, 10 min	 (95)	436

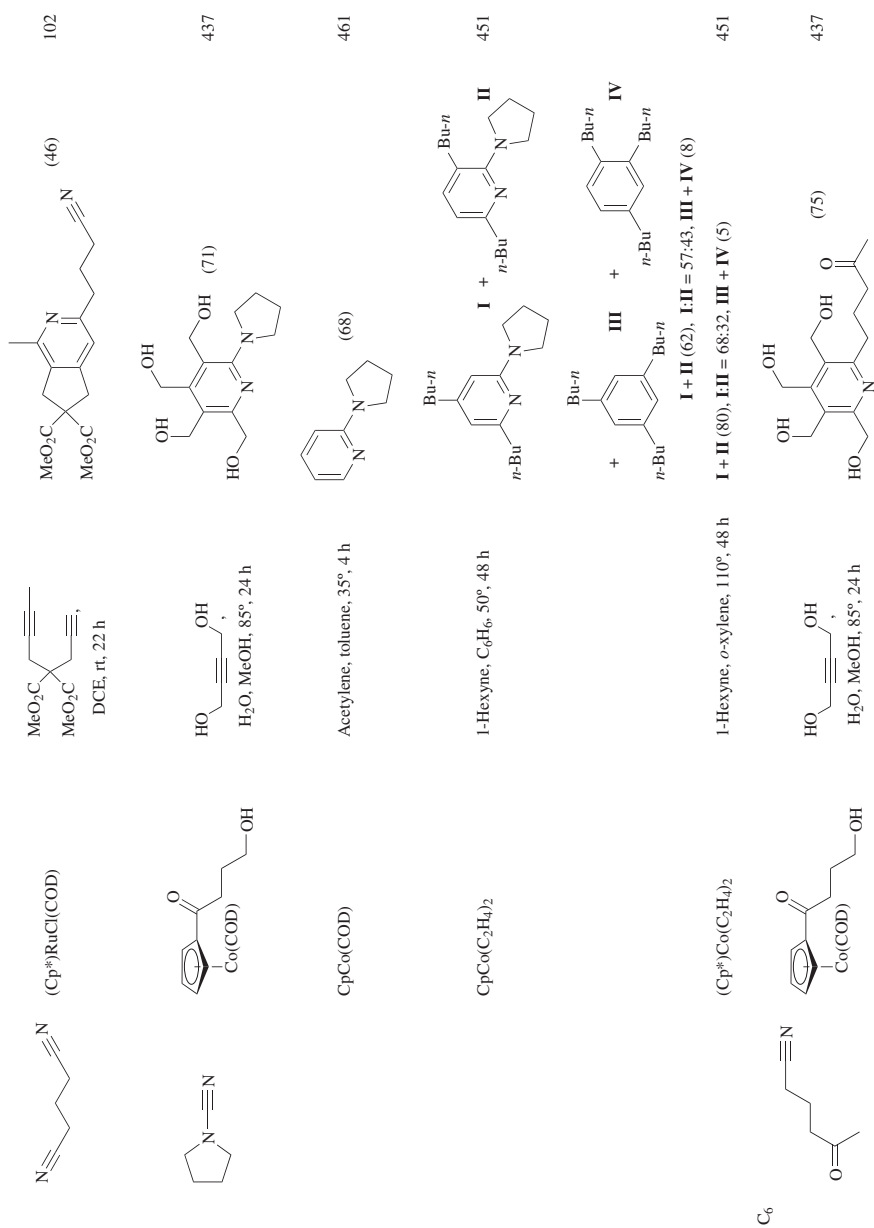
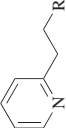
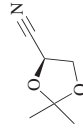
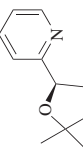
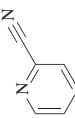
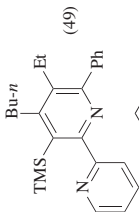
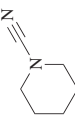
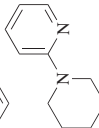

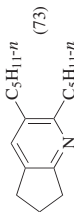
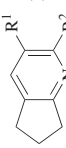
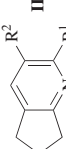
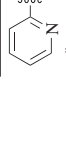
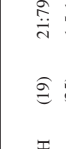


TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
C <sub>6-12</sub> R-CH <sub>2</sub> -C≡N	CpCo(COD)	Acetylene, <i>hν</i> Solvent Temp Time hexane 35° 4 h toluene 35° 4 h toluene 35° 4 h toluene 35° 4 h toluene 35° 4 h toluene 35° 4 h — rt 2 h toluene 35° 4 h — rt 2 h	 (70) (77) (75) (77) (80) (78) (83) (55) (88)	461 461 461 461 461 461 458 461 458
C <sub>6</sub> 	CpCo(COD)	Acetylene, toluene, 120°, 24 h	 (85)	463
	Cp <sub>2</sub> ZrEt <sub>2</sub>	1. TMS-C≡C-Bu- <i>n</i> , THF, rt, 1 h 2. Nitrile, 50°, 2 h 3. Ph-C≡C-Et, NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , 50°, 12 h	 (49)	442
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , 35°, 24 h	 (75)	461
	TaCl <sub>5</sub> , Zn	1. <i>n</i> -C <sub>3</sub> H <sub>11</sub> -C≡C-C <sub>3</sub> H <sub>11</sub> - <i>n</i> , DME, C <sub>6</sub> H <sub>6</sub> , 50°, 2 h 2. THF, pyridine 3. Nitrile, 50°, 4 h 4. NaOH, H <sub>2</sub> O	 (73)	345

CpCo(CO) <sub>2</sub>	R <sup>1</sup> —C≡C—R <sup>2</sup> , <i>hν</i> , heat	I		II		
		R <sup>1</sup>	R <sup>2</sup>	I + II	I:II	
—	toluene			(19)	21:79	464
0.8	toluene, slow addition of alkyne			(25)	1.5:1	464
0.8	toluene	"	TMS	(51)	1.4:1	464
1.2	toluene	"	TMS	(35)	1.3:1	464
1.5	toluene	"	TMS	(43)	1.3:1	464
2.0	toluene	"	TMS	(74)	1.1:1	464
1.5	toluene, slow addition of catalyst	"	TMS	(61)	1.2:1	464
—	toluene	"	H	(15)	27:73	464
—	<i>m</i> -xylene	TMS	TMS	(77)	—	107
—	<i>m</i> -xylene	CO <sub>2</sub> Me	CO <sub>2</sub> Me	(68)	—	107
—	<i>m</i> -xylene	Me	TMS	(70)	100:0	107

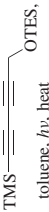
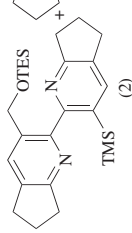
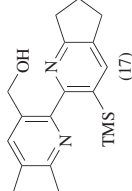
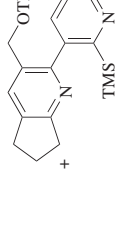
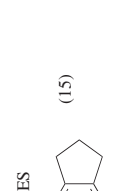



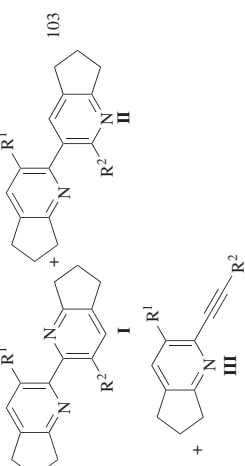



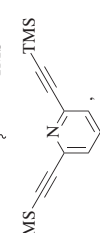
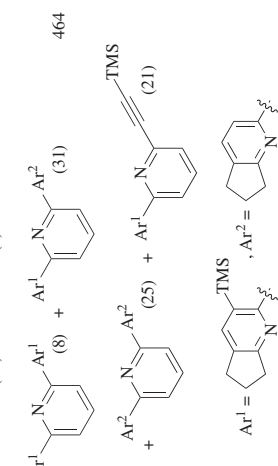
CpCo(CO) <sub>2</sub>				(2)	(17)	103
—	toluene, <i>hν</i> , heat			(15)	—	—

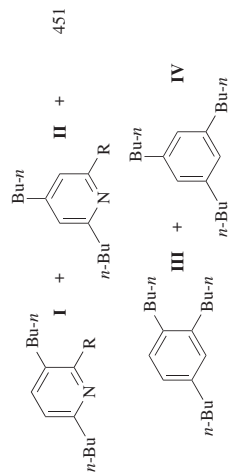
TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																																																						
 C <sub>6</sub>	CpCo(CO) <sub>2</sub>	R <sup>1</sup> =  , R <sup>2</sup> =  , toluene, hν, heat, 1 h	 103																																																							
			<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>Time</th> <th>I + II</th> <th>I:II</th> <th>III</th> </tr> </thead> <tbody> <tr> <td>TMS</td> <td>TMS</td> <td>1 h</td> <td>(0)</td> <td>—</td> <td>(77)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>1 h</td> <td>(48)</td> <td>63:37</td> <td>(0)</td> </tr> <tr> <td>CH<sub>2</sub>OH</td> <td>CH<sub>2</sub>OH</td> <td>1 h</td> <td>(9)</td> <td>100:0</td> <td>(0)</td> </tr> <tr> <td>CH<sub>2</sub>OMe</td> <td>CH<sub>2</sub>OMe</td> <td>1 h</td> <td>(63)</td> <td>73:27</td> <td>(0)</td> </tr> <tr> <td>CH<sub>2</sub>OTES</td> <td>CH<sub>2</sub>OTES</td> <td>1 h</td> <td>(45)</td> <td>80:20</td> <td>(0)</td> </tr> <tr> <td>CO<sub>2</sub>Me</td> <td>CO<sub>2</sub>Me</td> <td>1 h</td> <td>(18)</td> <td>58:42</td> <td>(0)</td> </tr> <tr> <td>CH<sub>2</sub>NMe<sub>2</sub></td> <td>CH<sub>2</sub>NMe<sub>2</sub></td> <td>1 h</td> <td>(49)</td> <td>100:0</td> <td>(0)</td> </tr> <tr> <td>TMS</td> <td></td> <td>TMS 2 h</td> <td>(31)</td> <td>32:68</td> <td>(0)</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	Time	I + II	I:II	III	TMS	TMS	1 h	(0)	—	(77)	Me	Me	1 h	(48)	63:37	(0)	CH <sub>2</sub> OH	CH <sub>2</sub> OH	1 h	(9)	100:0	(0)	CH <sub>2</sub> OMe	CH <sub>2</sub> OMe	1 h	(63)	73:27	(0)	CH <sub>2</sub> OTES	CH <sub>2</sub> OTES	1 h	(45)	80:20	(0)	CO <sub>2</sub> Me	CO <sub>2</sub> Me	1 h	(18)	58:42	(0)	CH <sub>2</sub> NMe <sub>2</sub>	CH <sub>2</sub> NMe <sub>2</sub>	1 h	(49)	100:0	(0)	TMS		TMS 2 h	(31)	32:68	(0)	
R <sup>1</sup>	R <sup>2</sup>	Time	I + II	I:II	III																																																					
TMS	TMS	1 h	(0)	—	(77)																																																					
Me	Me	1 h	(48)	63:37	(0)																																																					
CH <sub>2</sub> OH	CH <sub>2</sub> OH	1 h	(9)	100:0	(0)																																																					
CH <sub>2</sub> OMe	CH <sub>2</sub> OMe	1 h	(63)	73:27	(0)																																																					
CH <sub>2</sub> OTES	CH <sub>2</sub> OTES	1 h	(45)	80:20	(0)																																																					
CO <sub>2</sub> Me	CO <sub>2</sub> Me	1 h	(18)	58:42	(0)																																																					
CH <sub>2</sub> NMe <sub>2</sub>	CH <sub>2</sub> NMe <sub>2</sub>	1 h	(49)	100:0	(0)																																																					
TMS		TMS 2 h	(31)	32:68	(0)																																																					
	CpCo(CO) <sub>2</sub>	 toluene, hν, heat, 7 h	 464																																																							



CpCo(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>

1-Hexyne, C<sub>6</sub>H<sub>6</sub>, 50°, 48 h



R = (CH<sub>2</sub>)<sub>4</sub>CN  
**I + II** (76), **I:II** = 44:56, **III + IV** (6)

451

**I + II** (55), **I:II** = 31:69, **III + IV** (5)

1-Hexyne, *o*-xylene, 110°, 48 h

(Cp\*)Co(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>

C<sub>7</sub>

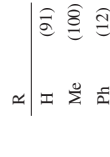


Catalyst

CpCo(COD)  
 (Cp\*)Co(η<sup>3</sup>-allyl)  
 (Cp\*)Co(η<sup>3</sup>-allyl)

R —≡ R, rt

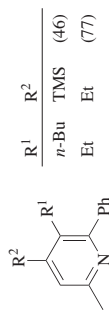
Solvent	Temp	Time
toluene	<i>hν</i> , rt	1 h
hexane	rt	72 h
hexane	rt	72 h
H <sub>2</sub> O, MeOH	85°	24 h



458  
438  
438  
437


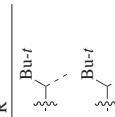
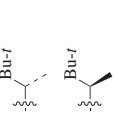






Cp<sub>2</sub>ZrEt<sub>2</sub>

1. R<sup>1</sup> —≡ R<sup>2</sup>, THF, 0°, 3 h  
 2. Nitrile, 50°, 1 h  
 3. , CuCl, 50°, 1 h

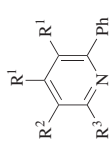


442

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions			Product(s) and Yield(s) (%)	Refs.
		Solvent	Temp	Time		
$R-C\equiv N$	CpCo(COD)	Acetylene				
$R-\text{C}\equiv\text{N}$		—	140°	12 h	(20)	465
		toluene	160°	7 h	(50)	465
		toluene	140°	20 h	(77)	465
$CH_2CH(OEt)_2$		$H_2O$ , toluene	$h\nu$ , 35°	4 h	(85)	461
$(CH_2)_2OBu-f$		—	$h\nu$ , rt	2 h	(80)	458
$CH_2CO_2Bu-f$		hexane	$h\nu$ , 35°	4 h	(81)	461
		—	140°	12 h	(72)	462
		toluene	$h\nu$ , 35°	4 h	(75)	461
		toluene	$h\nu$ , 35°	4 h	(75)	461
		toluene	$h\nu$ , 35°	4 h	(69)	461
$(CH_2)_2NEt_2$		—	$h\nu$ , 35°	2 h	(39)	458
		—	$h\nu$ , 35°	2 h	(41)	458
		—	$h\nu$ , 35°	2 h	(52)	458



Catalyst	1. R <sup>1</sup> -C≡C-R <sup>1</sup> , THF			R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	2. Niirile, 50°, 1 h	3. R <sup>2</sup> -C≡C-R <sup>3</sup> , NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , 50°, 1 h															
	Cp <sub>2</sub> ZrEt <sub>2</sub>	Me	<i>n</i> -Pr								<i>n</i> -Pr	Me	<i>n</i> -Pr	Et	Ph	Et	Me	Ph	Et	<i>n</i> -Pr	Et	Me	Ph
										(52)	443												
										(86)	443												
										(64)	443												
										(73)	443												
										(52)	443												
										(53)	442												
										(42)	442												
										(57)	442												
										(49)	443												
										(63)	443												

Catalyst	Acetylene, <i>hν</i>	I + II		Solvent	Temp	Time	Yield (%)
		I	II				
CpCo(COD)	toluene	101 Torr, rt	—	toluene	45°	—	(—)
CpCo(COD)	toluene	45°	—	hexane	45°	1 h	(—)
CpCo(COD)	H <sub>2</sub> O	—	3 h	H <sub>2</sub> O, Brij 56	—	4 h	(75)
CpCo(COD)	(C <sub>9</sub> H <sub>7</sub> )Co(COD)	—	3 h	H <sub>2</sub> O	—	3 h	(51)
(C <sub>9</sub> H <sub>7</sub> )Co(COD)	(C <sub>9</sub> H <sub>7</sub> )Co(COD)	—	4 h	H <sub>2</sub> O	—	3 h	(62)
(C <sub>9</sub> H <sub>7</sub> )Co(COD)	(C <sub>9</sub> H <sub>7</sub> )Co(COD)	—	4 h	H <sub>2</sub> O, Brij 56	—	4 h	(67)

TABLE 5. NITRILES (Continued)

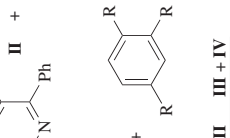
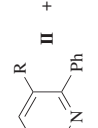
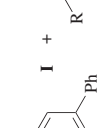
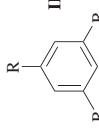

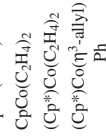

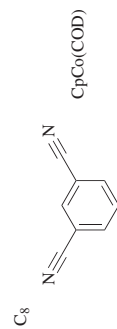
Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.																																																											
$\text{Ph}-\text{C}\equiv\text{N}$ 	Catalyst	R $\equiv$	 <b>I</b> +  <b>II</b> +  <b>III</b> +  <b>IV</b>																																																												
	Catalyst	R $\equiv$	<table border="1"> <thead> <tr> <th>R</th> <th><b>I</b> + <b>II</b></th> <th><b>I:II</b></th> <th><b>III</b> + <b>IV</b></th> </tr> </thead> <tbody> <tr><td>Me</td><td>(—)</td><td>1.3:1</td><td>(—)</td></tr> <tr><td>Me</td><td>(95)</td><td>2.6:1</td><td>(—)</td></tr> <tr><td>Me</td><td>(95)</td><td>2.1:1</td><td>(—)</td></tr> <tr><td>Me</td><td>(95)</td><td>1.8:1</td><td>(—)</td></tr> <tr><td>Me</td><td>(95)</td><td>1.4:1</td><td>(—)</td></tr> <tr><td>Me</td><td>(95)</td><td>1.1:1</td><td>(—)</td></tr> <tr><td>Me</td><td>(—)</td><td>—</td><td>(—)</td></tr> <tr><td>Me</td><td>(—)</td><td>—</td><td>(—)</td></tr> <tr><td>Me</td><td>(—)</td><td>—</td><td>(—)</td></tr> <tr><td>Me</td><td>(—)</td><td>—</td><td>(—)</td></tr> <tr><td><i>n</i>-Bu</td><td>(48)</td><td>54:46</td><td>(22)</td></tr> <tr><td><i>n</i>-Bu</td><td>(71)</td><td>72:28</td><td>(13)</td></tr> <tr><td>Ph</td><td>(68)</td><td>60:40</td><td>(—)</td></tr> <tr><td><i>n</i>-Bu</td><td>(83)</td><td>—</td><td>(—)</td></tr> </tbody> </table>	R	<b>I</b> + <b>II</b>	<b>I:II</b>	<b>III</b> + <b>IV</b>	Me	(—)	1.3:1	(—)	Me	(95)	2.6:1	(—)	Me	(95)	2.1:1	(—)	Me	(95)	1.8:1	(—)	Me	(95)	1.4:1	(—)	Me	(95)	1.1:1	(—)	Me	(—)	—	(—)	Me	(—)	—	(—)	Me	(—)	—	(—)	Me	(—)	—	(—)	<i>n</i> -Bu	(48)	54:46	(22)	<i>n</i> -Bu	(71)	72:28	(13)	Ph	(68)	60:40	(—)	<i>n</i> -Bu	(83)	—	(—)
R	<b>I</b> + <b>II</b>	<b>I:II</b>	<b>III</b> + <b>IV</b>																																																												
Me	(—)	1.3:1	(—)																																																												
Me	(95)	2.6:1	(—)																																																												
Me	(95)	2.1:1	(—)																																																												
Me	(95)	1.8:1	(—)																																																												
Me	(95)	1.4:1	(—)																																																												
Me	(95)	1.1:1	(—)																																																												
Me	(—)	—	(—)																																																												
Me	(—)	—	(—)																																																												
Me	(—)	—	(—)																																																												
Me	(—)	—	(—)																																																												
<i>n</i> -Bu	(48)	54:46	(22)																																																												
<i>n</i> -Bu	(71)	72:28	(13)																																																												
Ph	(68)	60:40	(—)																																																												
<i>n</i> -Bu	(83)	—	(—)																																																												
	Catalyst	Solvent	Temp	Time																																																											
	CpCo(COD)	toluene	<i>hν</i> , rt	2 h																																																											
	(C <sub>5</sub> HPh <sub>4</sub> )Co(COD)	toluene	<i>hν</i> , rt	2 h																																																											
	(PhBC <sub>3</sub> H <sub>5</sub> )Co(COD)	toluene	<i>hν</i> , rt	2 h																																																											
	(η <sup>3</sup> -C <sub>8</sub> H <sub>13</sub> )Co(COD)	toluene	<i>hν</i> , rt	2 h																																																											
	CpCo(COD)	toluene	<i>hν</i> , rt	2 h																																																											
	(C <sub>9</sub> H <sub>7</sub> )Co(COD)	toluene	<i>hν</i> , rt	2 h																																																											
	CpCo(COD)	H <sub>2</sub> O	<i>hν</i> , rt	3 h																																																											
	CpCo(COD)	MgSO <sub>4</sub> , H <sub>2</sub> O	<i>hν</i> , rt	3 h																																																											
	CpCo(COD)	NaCl, H <sub>2</sub> O	<i>hν</i> , rt	3 h																																																											
	CpCo(COD)	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> O	<i>hν</i> , rt	3 h																																																											
	CpCo(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	50°	48 h																																																											
	(Cp*)Co(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	<i>o</i> -xylene	110°	48 h																																																											
	(Cp*)Co(η <sup>3</sup> -allyl)	hexane	rt	72 h																																																											
		THF	80°	20 h																																																											
	CpRh(C <sub>3</sub> H <sub>4</sub> ) <sub>2</sub>	THF	80°	20 h																																																											



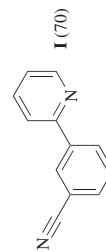
TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	Catalyst	$n\text{-Bu}\equiv$ , 110°, 48 h	 <b>I</b> + <b>II</b>	451
			 <b>III</b> + <b>IV</b>	
	Catalyst	Solvent	<b>I + II</b> / <b>III + IV</b>	
	$\text{CpCo}(\text{C}_2\text{H}_4)_2$	$\text{C}_6\text{H}_6$	(22) 50:50 (43)	
	$(\text{Cp}^*)\text{Co}(\text{C}_2\text{H}_4)_2$	<i>o</i> -xylene	(43) 23:77 (3)	
	$\text{CpCo}(\text{COD})$	Acetylene, $\text{H}_2\text{O}$ , <i>h\nu</i> , 3 h	 <b>I</b> (50) + <b>II</b> (1)	440
	$(\text{C}_9\text{H}_7)\text{Co}(\text{COD})$	Acetylene, $\text{H}_2\text{O}$ , <i>h\nu</i> , rt	<b>I</b> (79) + <b>II</b> (1)	450
	$\text{CpCo}(\text{COD})$	Acetylene, toluene, <i>h\nu</i> , rt, 5.5 h	 <b>I</b> + <b>II</b>	457
	$\text{CpCo}(\text{COD})$	Acetylene, hexane, <i>h\nu</i> , rt, 5 h	 (82)	468
	$\text{CpCo}(\text{CO})_2$	$\text{R}^1\text{-}\equiv\text{-}\text{R}^2$ , <i>h\nu</i> , heat	 <b>I</b> + <b>II</b>	

$n$	Solvent	$R^1$	$R^2$	<b>I + II</b>	<b>I:II</b>	
1	$C_6H_6$	TMS	$CO_2Me$	(82)	1:1.1	144
1	$C_6H_6$	TES	$CO_2Me$	(78)	1:1	144
1	$C_6H_6$	TES	$CO_2Me$	(67)	1:1.7	144
1	$C_6H_6$	TMS	$CONEt_2$	(87)	1:1.4	144
1	<i>m</i> -xylene	TES	OMe	(43)	1:99	144
1	<i>m</i> -xylene	TES	H	(26)	1:99	144
1	<i>m</i> -xylene	TMS	Me	(70)	1:99	144
1	toluene		H	(54)	83:17	464
1	<i>m</i> -xylene	TMS	TMS	(77)	—	107
1	<i>m</i> -xylene	$CO_2Me$	$CO_2Me$	(83)	—	107
1	<i>m</i> -xylene	$CH_2OMe$	$CH_2OMe$	(33)	—	107
1	<i>m</i> -xylene	Ph	Ph	(4)	—	107
1	<i>m</i> -xylene	Me	TMS	(80)	1:0	107
1	<i>m</i> -xylene	H	<i>n</i> -Bu	(41)	98:2	107
1	<i>m</i> -xylene	<i>n</i> -Bu	TMS	(56)	1:0	107
1	<i>m</i> -xylene	Me	<i>n</i> -Bu	(80)	56:44	107
1	<i>m</i> -xylene	H	TMS	(29)	1:0	107
1	<i>m</i> -xylene	Me	<i>n</i> -Bu	(54)	80:20	107
2	<i>m</i> -xylene	TMS	TMS	(25)	—	107
2	<i>m</i> -xylene	$CO_2Me$	$CO_2Me$	(95)	—	107
2	<i>m</i> -xylene	Me	TMS	(66)	1:0	107



Acetylene, toluene, 100°, 48 h



466



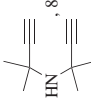

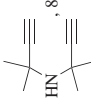
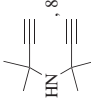
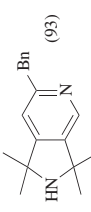
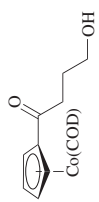
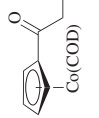
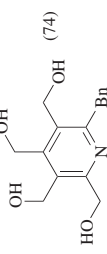
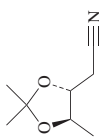
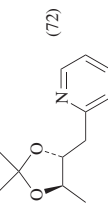

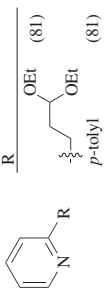

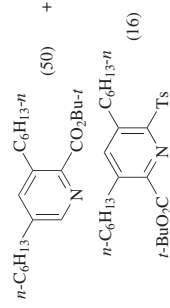


**I (72)**

Acetylene, DMF, 80°, 4 h

436

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	CpCo(COD)	Acetylene, H <sub>2</sub> O, <i>hν</i> , rt, 3 h		440, 450
	(AcC <sub>3</sub> H <sub>4</sub> )Co(COD)	Acetylene, H <sub>2</sub> O, Brij 56, <i>hν</i> , rt, 3 h		440
	CoCl <sub>2</sub> , Mn	 , 80°		444
	 Co(COD)	H <sub>2</sub> O, MeOH, 85°, 24 h		437
	CpCo(COD)	Acetylene, toluene, 140°, 36 h		462
	CpCo(COD)	Acetylene, H <sub>2</sub> O, toluene, <i>hν</i> , 35°, 4 h		461
	Ti(OPr- <i>i</i> ) <sub>4</sub>	1. <i>n</i> -C <sub>6</sub> H <sub>13</sub> -C≡C-CO <sub>2</sub> Bu- <i>t</i> , Et <sub>2</sub> O, <i>i</i> -PrMgCl, -50°, 5 h 2. 1-Octyne, -50°, 3 h 3. Nitriole, -10°, 3 h 4. H <sub>2</sub> O		97

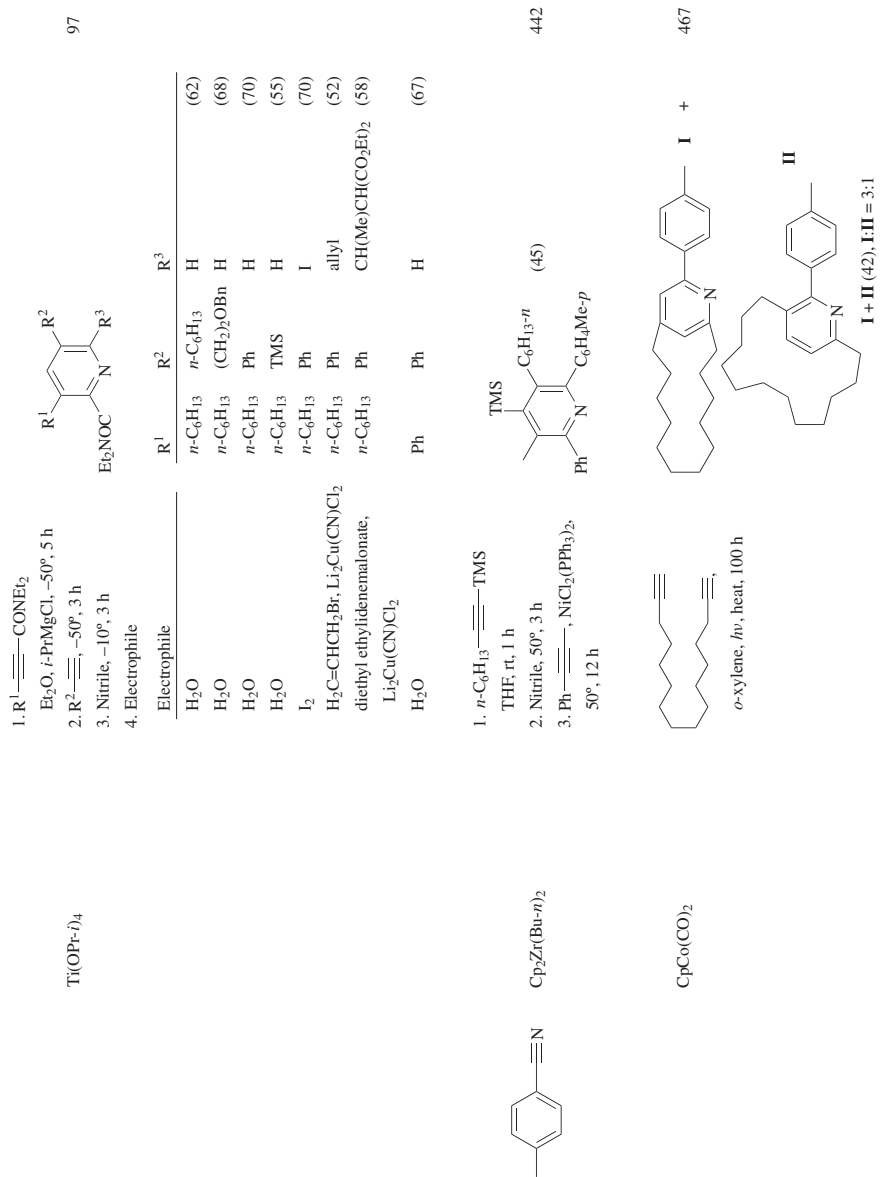


TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	CpCo(CO) <sub>2</sub>	 <i>o</i> -xylene, <i>hν</i> , heat, 100 h	 <b>I</b> + 467	
	 (x mol%)	R —≡≡	 <b>II</b>	
	(Cp*)Ru(CH <sub>3</sub> CN) <sub>3</sub> PF <sub>6</sub>	Acetylene, DMF, rt, 1.5 h	 <b>I</b> + <b>II</b> 285	436

R <sup>1</sup>	R <sup>2</sup>	n	X	<b>I</b> + <b>II</b>	<b>I:II</b>
Me	CO <sub>2</sub> Me	2	H <sub>2</sub>	(22)	3:1
Me	H	1	H <sub>2</sub>	(61)	1:5
Me	H	1	O	(34)	1:7
Me	H	2	H <sub>2</sub>	(57)	1:1
OMe	H	2	H <sub>2</sub>	(38)	1:1

R	<b>I</b> + <b>II</b>
<i>n</i> -Bu	(91)
CH <sub>2</sub> OPh	(56)
CH <sub>2</sub> OPh	(97)



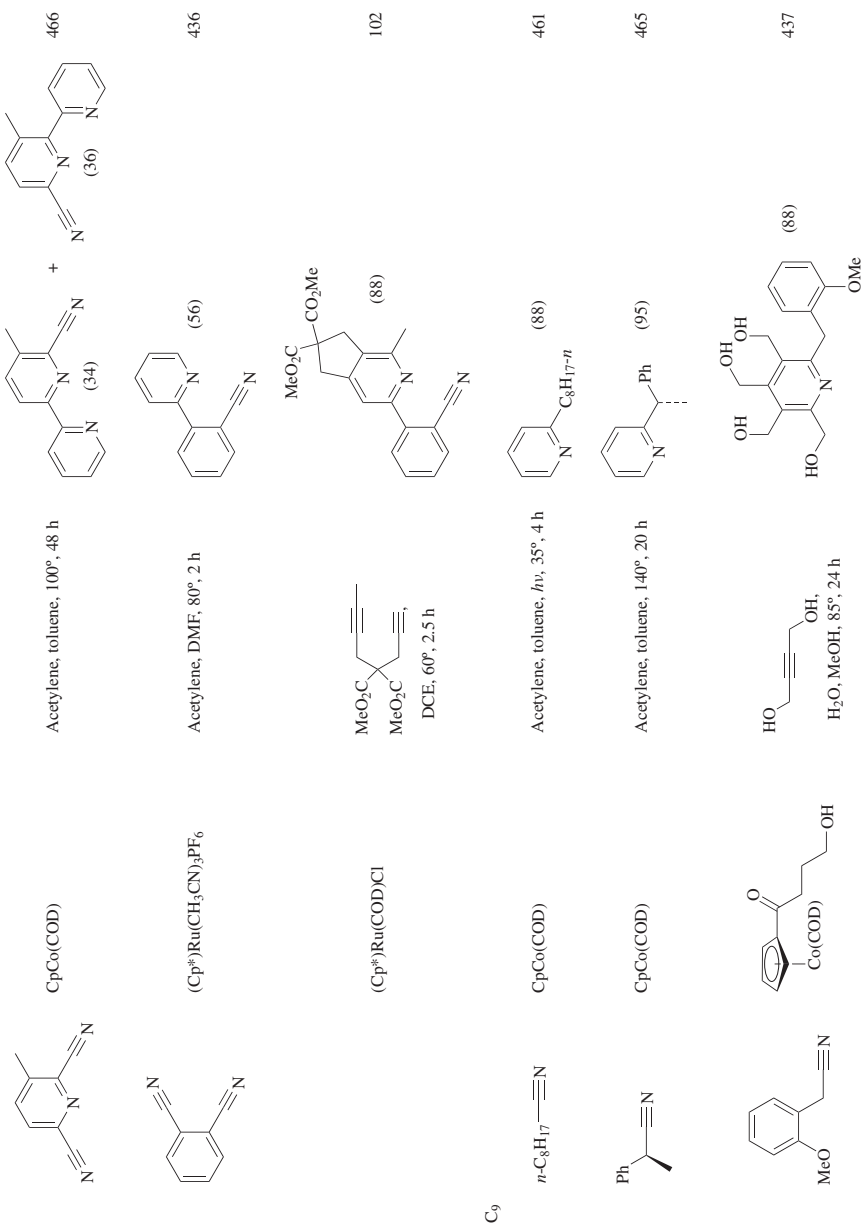
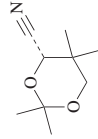
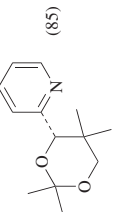
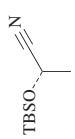
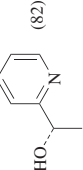
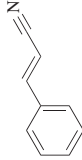

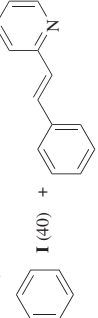

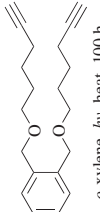
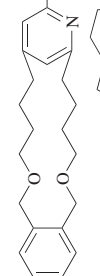
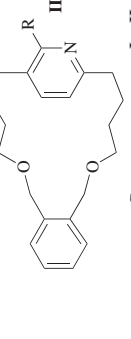
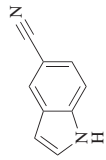
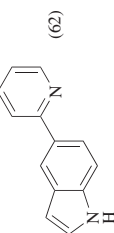
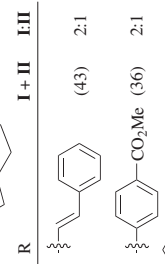


TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , rt, 5 h	 (85)	468
	CpCo(COD)	1. Acetylene, toluene, 120°, 24 h 2. HCl, 5 h	 (82)	463
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , rt, 5 h	 I (40) +  II (469) I:II = 1.77:1	469
	CpCo(CO) <sub>2</sub>	 <i>o</i> -xylene, <i>hν</i> , heat, 100 h	 I +  II	467
	CpCo(COD)	Acetylene, 35°, 4 h	 (62)	461



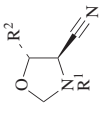
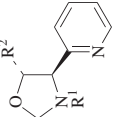
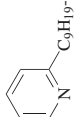
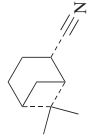
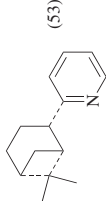
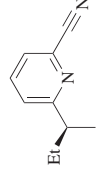
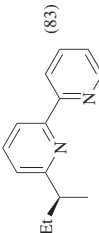

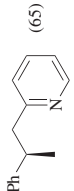
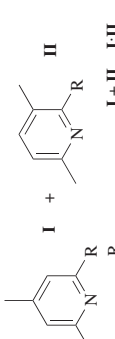
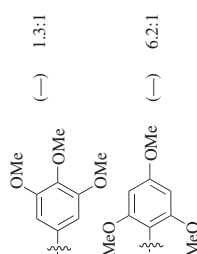
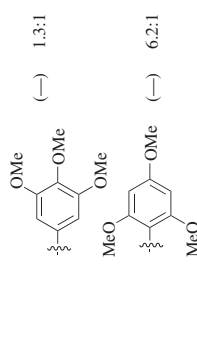
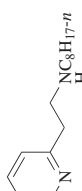

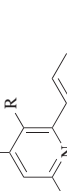
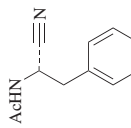
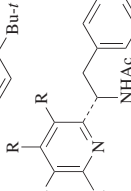
$C_{9-11}$		CpCo(COD)	Acetylene, toluene, 120°, 2 h		R <sup>1</sup> R <sup>2</sup> Boc H (90) Bz H (90) Boc Me (90)	470
$C_{10}$	$n-C_9H_{19}-C\equiv N$	CpCo(COD)	Acetylene, H <sub>2</sub> O, <i>hν</i> , 3 h		<b>I</b> (73) + <b>II</b> (1)	440
		CpCo(COD)	Acetylene, H <sub>2</sub> O, Tween 20, <i>hν</i> , 8 h	<b>I</b> (38) + <b>II</b> (38)		440
		CpCo(COD)	Acetylene, toluene, <i>hν</i> , rt, 1 h	<b>I</b> (74)		458
		CpCo(COD)	Acetylene, toluene, 100°, 20 h		(53)	471, 472
		CpCo(COD)	Acetylene (13 atm), toluene, 120°, 20 h		(83)	473
		CpCo(COD)	Acetylene, toluene, 140°, 70 h		(65)	462

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
$R-C\equiv N$ C <sub>10</sub>	CpCo(COD)	$\equiv$ , toluene, <i>h\nu</i> , rt, 2 h	 I + II I:II (→) 1.3:1	450
 R = tolyl, E:Z = 24:76 C <sub>11</sub>	CpCo(COD)	Acetylene, toluene, <i>h\nu</i> , rt, 2 h	 I + II I:II (→) 6.2:1	457
$n-C_8H_{17}N\equiv C$ C <sub>11</sub>	CpCo(COD)	Acetylene, toluene, <i>h\nu</i> , 35°, 4 h	 (50)	461
$i-Bu-C\equiv N$ C <sub>11</sub>	Cp <sub>2</sub> ZrEt <sub>2</sub>	1. $R-C\equiv R$ , THF, 0°, 3 h 2. Nitrile, 50°, 1 h 3.  , CuCl, 50°, 1 h	 R (50)	442
 C <sub>11</sub>	CpCo(COD)	$R-C\equiv R$ , toluene, <i>h\nu</i> , rt, 6 h	 R (64) Et (83)	468


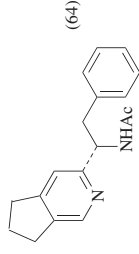

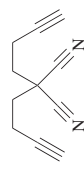
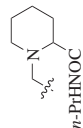
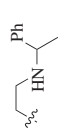
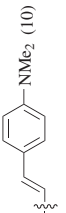
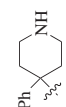
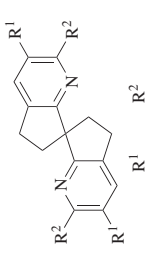

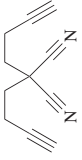
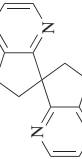
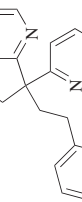


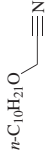


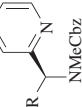
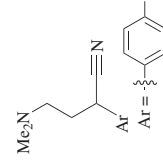
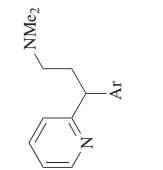
C <sub>11-12</sub> R—C≡N	CpCo(COD)		toluene, <i>hν</i> , rt, 6 h		468
	CpCo(COD)	Acetylene, toluene, <i>hν</i>			
C <sub>11</sub>	CpCo(CO) <sub>2</sub>		R <sup>1</sup> —C≡C—R <sup>2</sup> , toluene, <i>hν</i> , heat		(78)
					(49)
					(10)
				adamantyl	(90)
					(49)
					
			Time	R <sup>1</sup> R <sup>2</sup>	
			4.5 h	TMS TMS	(33)
			2 h	Ph Ph	(9)
			2 h	CO <sub>2</sub> Me CO <sub>2</sub> Me	(7)
			6 h	TMS  Ph	(8)

TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	CpCo(COD)	Acetylene (2.3 bar), toluene, 137°, overnight	 <b>I</b> (32) +  <b>II</b> (14)	474
	CpCo(COD)	Acetylene (1.2 bar), toluene, 137°, overnight	<b>I</b> (9) + <b>II</b> (—)	474
	CpCo(COD)	Acetylene (1.2 bar), toluene, 137°, overnight	<b>I</b> (20) + <b>II</b> (—)	474
	CpCo(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub>	Acetylene (1 bar), toluene, rt, 4 h	<b>I</b> (21) + <b>II</b> (11)	474
	CpCo(CO) <sub>2</sub>	Acetylene, toluene, <i>hν</i> , heat, 5 h	<b>I</b> (7)	474
	CpCo(COD)	Acetylene, toluene, <i>hν</i> , 35°, 4 h	 (89)	474
	CpCo(COD)	Acetylene, <i>hν</i> , rt, 2 h	 (35)	458
	CpCo(COD)	Acetylene, toluene, 110°, 72 h		475
			R Me (65) <i>i</i> -Pr (65) <i>i</i> -Bu (75) <i>s</i> -Bu (63) Bn (76) R	
	CpCo(COD)	Acetylene, toluene, 140°, 36 h		469
			H (85) Cl (75) Br (70)	

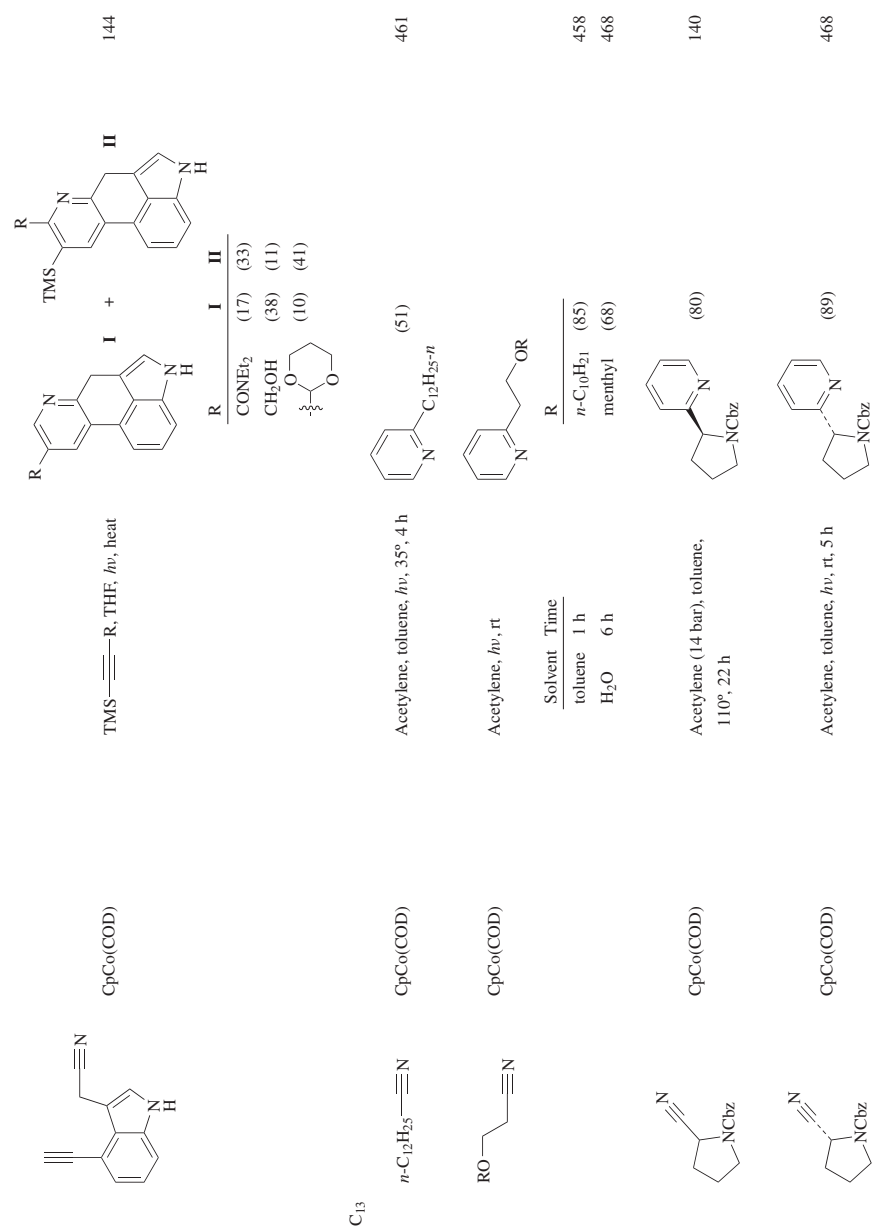
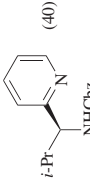
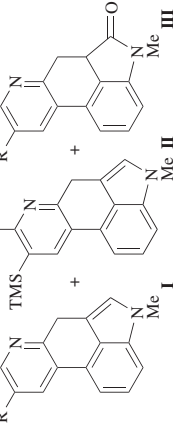
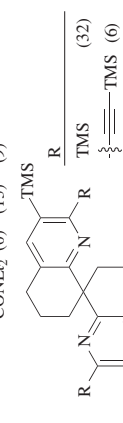
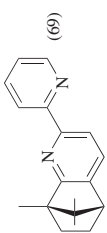
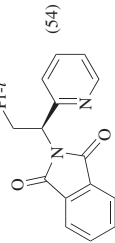
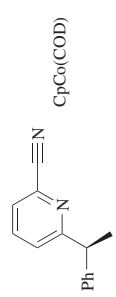
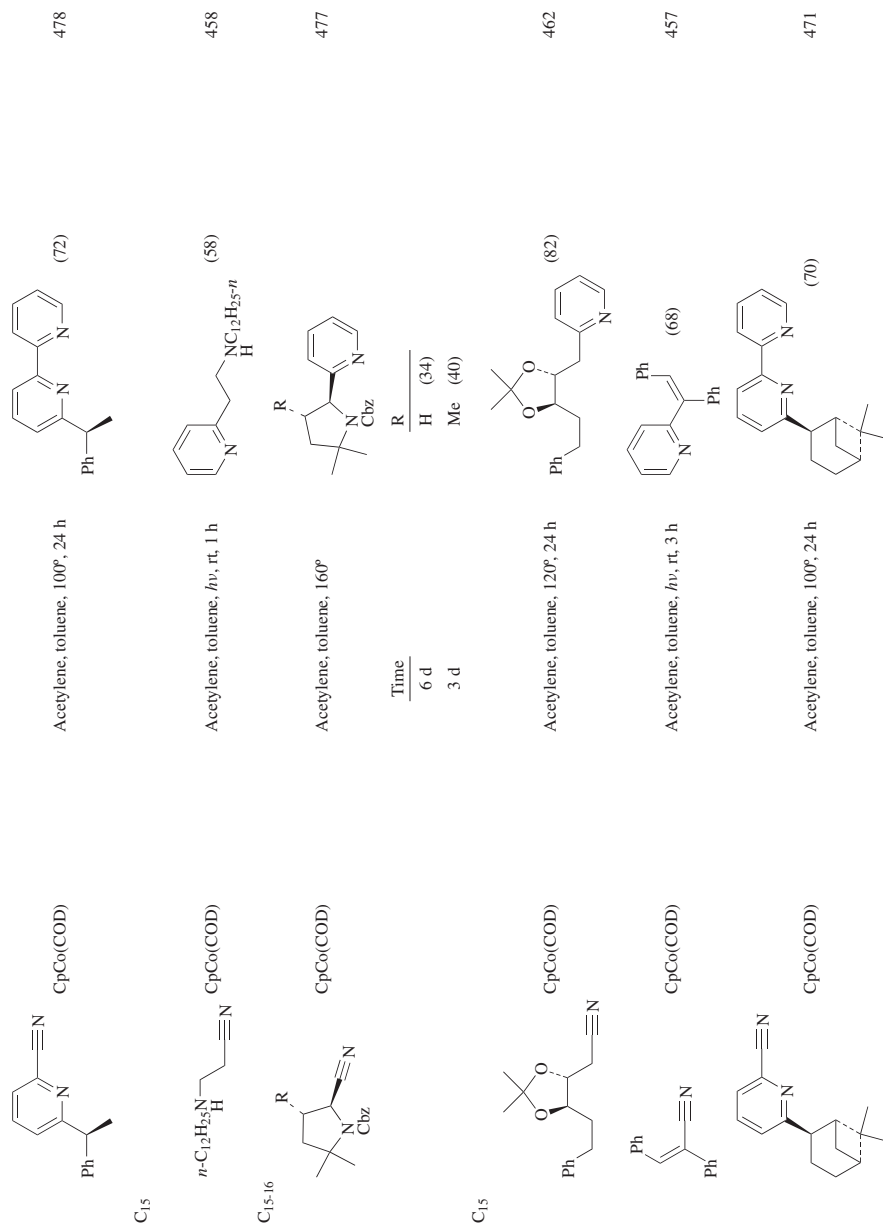


TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
	CpCo(COD)	Acetylene, toluene, 110°, 72 h	(40)	475
	CpCo(COD)	TMS-C≡C-R, THF, hν, heat	I (6) + II (0) + III (33) Me (0) (0) (12) CONEt <sub>2</sub> (0) (13) (9)	144
	CpCo(CO) <sub>2</sub>	TMS-C≡C-R, toluene, hν, heat	R-TMS (32) TMS-C≡C-TMS (6)	474
	CpCo(COD)	Acetylene, toluene, 130°, 10 h	(69)	476
	CpCo(COD)	Acetylene, toluene, 110°, 72 h	(54)	475

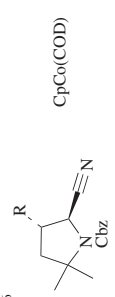




C<sub>15</sub>



C<sub>15-16</sub>



C<sub>15</sub>

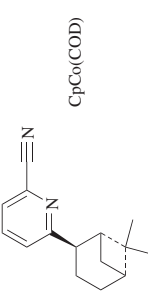
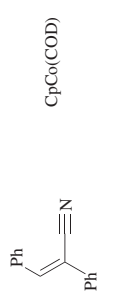
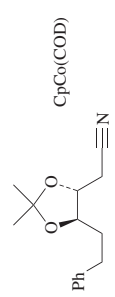
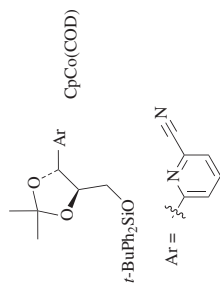


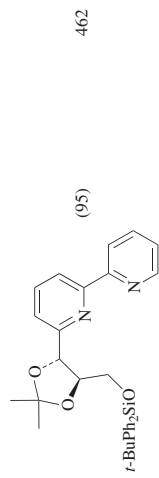
TABLE 5. NITRILES (Continued)

Substrate	Catalyst	Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C<sub>17</sub></p> <p>R = </p>	CpCo(COD)	Acetylene, toluene, 140°, 48 h	<p>(-)</p> <p>462</p>	462
<p>C<sub>19</sub></p> <p>R = </p>	CpCo(COD)	Acetylene, toluene, 120°, 24 h	<p>(82)</p> <p>462</p>	462
<p>R<sup>1</sup> = </p> <p>R<sup>2</sup> = </p>	CpCo(CO) <sub>2</sub>	 <i>o</i> -Xylene, <i>hv</i> , heat, 100 h	<p>(44)</p> <p>467</p>	467
<p>C<sub>23</sub></p> <p>TBDFPSO</p>	CpCo(COD)	Acetylene, toluene, 120°, 24 h	<p>(44)</p> <p>479</p>	479

C<sub>29</sub>



Acetylene, toluene, 120°, 24 h



<sup>a</sup> The yields for **I**, **II**, **III** are calculated based on nitrile; the yields for **IV** and **V** are calculated based on alkyne.

<sup>b</sup> Other products are isolated in small amounts.

## REFERENCES

- <sup>1</sup> Berthelot, M. C. R. *Hebd. Seances Acad. Sci.* **1866**, 62, 905.
- <sup>2</sup> Reppe, W.; Schweckendiek, W. J. *Liebigs Ann. Chem.* **1948**, 560, 104.
- <sup>3</sup> Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, 12, 2911.
- <sup>4</sup> Meijer-Veldman, M. E. E.; Meijer, H. J. D. L. *J. Organomet. Chem.* **1984**, 260, 199.
- <sup>5</sup> Musso, F.; Solari, E.; Floriani, C. *Organometallics* **1997**, 16, 4889.
- <sup>6</sup> Wielstra, Y.; Gambarotta, S.; Meetsma, A.; De Boer, J. L.; Chiang, M. Y. *Organometallics* **1989**, 8, 2696.
- <sup>7</sup> Rodriguez, J. G.; Martin-Villamil, R.; Fonseca, I. *J. Chem. Soc., Perkin Trans. 1* **1997**, 945.
- <sup>8</sup> Williams, A. C.; Sheffels, P.; Sheehan, D.; Livinghouse, T. *Organometallics* **1989**, 8, 1566.
- <sup>9</sup> Srinivasan, R.; Faron, M. F. *J. Mol. Catal.* **1989**, 53, 203.
- <sup>10</sup> Du Toit, C. J.; Du Plessis, A. K.; Lachmann, G. *J. Mol. Catal.* **1989**, 53, 67.
- <sup>11</sup> Angermund, K.; Betz, P.; Döhring, A.; Jolly, P. W.; Krüger, C.; Schönfelder, K. U. *Polyhedron* **1993**, 12, 2663.
- <sup>12</sup> Sakurai, H.; Nakadaira, Y.; Hosomi, A.; Eriyama, Y.; Hiram, K.; Kabuto, C. *J. Am. Chem. Soc.* **1984**, 106, 8315.
- <sup>13</sup> Ardizzioia, G. A.; Brenna, S.; LaMonica, G.; Maspero, A.; Masciocchi, N. *J. Organomet. Chem.* **2002**, 649, 173.
- <sup>14</sup> Szymanska-Buzar, T.; Glowiak, T. *J. Organomet. Chem.* **1998**, 564, 143.
- <sup>15</sup> Reppe, W.; Vetter, H. *Liebigs Ann. Chem.* **1953**, 585, 133.
- <sup>16</sup> Lindner, E.; Jansen, R. M.; Mayer, H. A.; Hiller, W.; Fawzi, R. *Organometallics* **1989**, 8, 2355.
- <sup>17</sup> Lindner, E.; Kuebauch, H.; Mayer, H. A. *Chem. Ber.* **1994**, 127, 1343.
- <sup>18</sup> Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 539.
- <sup>19</sup> Amer, I.; Bernstein, T.; Eisen, M.; Blum, J.; Vollhardt, K. P. C. *J. Mol. Catal.* **1990**, 60, 313.
- <sup>20</sup> Wendt, J.; Klinger, U.; Singer, H. *Inorg. Chim. Acta* **1991**, 183, 133.
- <sup>21</sup> Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1357.
- <sup>22</sup> Rappoli, B. J.; Churchill, M. R.; Janik, T. S.; Rees, W. M.; Atwood, J. D. *J. Am. Chem. Soc.* **1987**, 109, 5145.
- <sup>23</sup> Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, 13, 2010.
- <sup>24</sup> Schoenfelder, W.; Snatzke, G. *Chem. Ber.* **1980**, 113, 1855.
- <sup>25</sup> Lee, C.-L.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, 20, 2498.
- <sup>26</sup> Aalten, H. L.; van Koten, G.; Riethorst, E.; Stam, C. H. *Inorg. Chem.* **1989**, 28, 4140.
- <sup>27</sup> Imamura, H.; Suda, E.; Konishi, T.; Sakata, Y.; Tsuchiya, S. *Chem. Lett.* **1995**, 215.
- <sup>28</sup> Wen, T. C.; Chang, C. C.; Chuang, Y. D.; Cheng, C. P.; Chiu, J. P.; Chang, C. T. *J. Am. Chem. Soc.* **1981**, 103, 4576.
- <sup>29</sup> Hogeveen, H.; Kingma, R. F.; Kok, D. M. *J. Org. Chem.* **1982**, 47, 989.
- <sup>30</sup> Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, 10, 1.
- <sup>31</sup> Winter, M. J. In *The Chemistry of the Metal-Carbon Bond. Carbon-Carbon Bond Formation Using Organometallic Compounds*; Patai, S., Ed.; John Wiley & Sons Ltd: Chichester, 1985; Vol. 3, pp 259–294.
- <sup>32</sup> Schore, N. E. *Chem. Rev.* **1988**, 88, 1081.
- <sup>33</sup> Harvey, D. F.; Johnson, B. M.; Ung, C. S.; Vollhardt, K. P. C. *Synlett* **1989**, 15.
- <sup>34</sup> Llerena, D.; Buisine, O.; Aubert, C.; Malacria, M. *Tetrahedron* **1998**, 54, 9373.
- <sup>35</sup> Yamamoto, Y.; Takagishi, H.; Itoh, K. *J. Am. Chem. Soc.* **2002**, 124, 28.
- <sup>36</sup> Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1973**, 280.
- <sup>37</sup> Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1978**, 17, 505.
- <sup>38</sup> Maitlis, P. *Acc. Chem. Res.* **1976**, 9, 93.
- <sup>39</sup> Schore, N. E. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon Press: Oxford, 1991; Vol. 5, pp 1129–1162.
- <sup>40</sup> Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Hegedus, L., Ed.; Pergamon Press: Oxford, 1995; Vol. 12, pp 741–770.
- <sup>41</sup> Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, 96, 49.

- <sup>42</sup> Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635.
- <sup>43</sup> Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901.
- <sup>44</sup> Malacria, M.; Aubert, C.; Renaud, J. L. In *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations*; Trost, B. M., Ed.; Georg Thieme Verlag: Stuttgart, 2001; Vol. 1, pp 439–530.
- <sup>45</sup> Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.
- <sup>46</sup> Kaneta, N.; Hirai, T.; Mori, M. *Chem. Lett.* **1995**, 627.
- <sup>47</sup> Boorman, P. M.; Wang, M.; Parvez, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4533.
- <sup>48</sup> Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 3800.
- <sup>49</sup> McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666.
- <sup>50</sup> Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 11721.
- <sup>51</sup> Eisch, J. J.; Aradi, A. A.; Lucarelli, A.; Qian, Y. *Tetrahedron* **1998**, *54*, 1169.
- <sup>52</sup> Yamamoto, Y.; Nagata, A.; Nagata, H.; Ando, Y.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Chem. Eur. J.* **2003**, *9*, 2469.
- <sup>53</sup> Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298.
- <sup>54</sup> Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549.
- <sup>55</sup> Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.
- <sup>56</sup> Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143.
- <sup>57</sup> Yamamoto, Y.; Kinpara, K.; Saigoku, T.; Takagishi, H.; Okuda, S.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 605.
- <sup>58</sup> Diercks, R.; Eaton, B. E.; Guertzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *120*, 8247.
- <sup>59</sup> Bowyer, W. J.; Merkert, J. W.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191.
- <sup>60</sup> Bell, T. W.; Helliwell, M.; Partridge, M. G.; Perutz, R. N. *Organometallics* **1992**, *11*, 1911.
- <sup>61</sup> Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Foltling, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127.
- <sup>62</sup> Hardesty, J. H.; Koerner, J. B.; Albright, T. A.; Lee, G. B. *J. Am. Chem. Soc.* **1999**, *121*, 6055.
- <sup>63</sup> Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431.
- <sup>64</sup> Paneque, M.; Poveda, M. L.; Rendon, N.; Mereiter, K. *J. Am. Chem. Soc.* **2004**, *126*, 1610.
- <sup>65</sup> Veiros, L. F.; Dazinger, G.; Kirchner, K.; Calhorda, M. J.; Schmid, R. *Chem. Eur. J.* **2004**, *10*, 5860.
- <sup>66</sup> Ville, G. A.; Vollhardt, K. P. C.; Winter, M. J. *Organometallics* **1984**, *3*, 1177.
- <sup>67</sup> Meriwhether, L. S.; Leto, M. F.; Colthup, E. C.; Kennerly, G. W. *J. Org. Chem.* **1962**, *27*, 3930.
- <sup>68</sup> Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5253.
- <sup>69</sup> Chang, C. A.; Francisco, C. G.; Gadek, T. R.; King, J. J. A.; Sternberg, E. D.; Vollhardt, K. P. C. In *Organic Synthesis Today and Tomorrow*; Hutchinson, C. R., Ed.; Pergamon Press: Oxford, 1981; pp 71–83.
- <sup>70</sup> Varela, J. A.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787.
- <sup>71</sup> Dietl, H.; Reinheimer, J.; Moffat, P.; Maitlis, M. *J. Am. Chem. Soc.* **1970**, *92*, 2276.
- <sup>72</sup> Li, J.; Jiang, H.; Chen, M. *J. Org. Chem.* **2001**, *66*, 3627.
- <sup>73</sup> Maitlis, P. *Pure Appl. Chem.* **1973**, *33*, 489.
- <sup>74</sup> Maitlis, P. *J. Organomet. Chem.* **1980**, *200*, 161.
- <sup>75</sup> Kelley, E. A.; Maitlis, P. *J. Chem. Soc., Dalton Trans.* **1979**, 167.
- <sup>76</sup> Negishi, E.; Harring, L. S.; Owczarczyk, Z.; Mohamud, M. M.; Ay, M. *Tetrahedron Lett.* **1992**, *33*, 3253.
- <sup>77</sup> de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379.
- <sup>78</sup> Peters, J.-U.; Blechert, S. *Chem. Commun.* **1997**, 1983.
- <sup>79</sup> Das, S. K.; Roy, R. *Tetrahedron Lett.* **1999**, *40*, 4015.
- <sup>80</sup> Ester, C.; Maderna, A.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem.* **2000**, 1177.
- <sup>81</sup> Hiraoka, S.; Shiro, M.; Shionoya, M. *J. Am. Chem. Soc.* **2004**, *126*, 1214.
- <sup>82</sup> Xianfeng, S.; Douglas, M. H.; Robert, A. P. *J. Am. Chem. Soc.* **2004**, *126*, 5798.
- <sup>83</sup> Tanaka, R.; Nakano, Y.; Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2002**, *124*, 9682.
- <sup>84</sup> Ozerov, O. V.; Patrick, B. O.; Ladipo, F. T. *J. Am. Chem. Soc.* **2000**, *122*, 6423.
- <sup>85</sup> Borwieck, H.; Walter, O.; Dinjus, E.; Rebizant, J. *J. Organomet. Chem.* **1998**, *570*, 121.

- <sup>86</sup> Garcia, J. J.; Sierra, C.; Torrens, H. *Tetrahedron Lett.* **1996**, 37, 6097.
- <sup>87</sup> Jhingan, A. K.; Maier, W. F. *J. Org. Chem.* **1987**, 52, 1161.
- <sup>88</sup> Balasubramanian, K. K.; Selvaraj, S.; Venkataramani, P. S. *Synthesis* **1980**, 29.
- <sup>89</sup> Pigge, F. C.; Ghasedi, F.; Rath, N. P. *Tetrahedron Lett.* **1999**, 40, 8045.
- <sup>90</sup> Pigge, F. C.; Zheng, Z.; Rath, N. P. *Nouv. J. Chem.* **2000**, 24, 183.
- <sup>91</sup> Takeuchi, R.; Nakaya, Y. *Org. Lett.* **2003**, 5, 3659.
- <sup>92</sup> Ura, Y.; Sato, Y.; Shiotsuki, M.; Kondo, T.; Mitsudo, T.-a. *J. Mol. Catal. A: Chemical* **2004**, 209, 35.
- <sup>93</sup> Gevorgyan, V.; Radhakrishnan, U.; Takeda, A.; Rubina, M.; Rubin, M.; Yamamoto, Y. *J. Org. Chem.* **2001**, 66, 2835.
- <sup>94</sup> Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, 119, 11313.
- <sup>95</sup> Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kitora, M. *J. Am. Chem. Soc.* **1998**, 120, 1672.
- <sup>96</sup> Takahashi, T.; Tsai, F.-Y.; Li, Y.; Nakajima, K.; Kitora, M. *J. Am. Chem. Soc.* **1999**, 121, 11093.
- <sup>97</sup> Suzuki, D.; Tanaka, R.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2002**, 124, 3518.
- <sup>98</sup> Hamada, T.; Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **1999**, 121, 7342.
- <sup>99</sup> Chouraqui, G.; Petit, M.; Aubert, C.; Malacria, M. *Org. Lett.* **2004**, 6, 1519.
- <sup>100</sup> Yamamoto, Y.; Ishii, J.-i.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2004**, 126, 3712.
- <sup>101</sup> Yamamoto, Y.; Okuda, S.; Itoh, K. *Chem. Commun.* **2001**, 1102.
- <sup>102</sup> Yamamoto, Y.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2001**, 123, 6189.
- <sup>103</sup> Varela, J. A.; Castedo, L.; Maestro, M.; Mahia, J.; Saa, C. *Chem. Eur. J.* **2001**, 7, 5203.
- <sup>104</sup> Hillard III, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, 99, 4058.
- <sup>105</sup> Duckworth, D. M.; Lee-Wong, S.; Slawin, A. M. Z.; Smith, E. H.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 815.
- <sup>106</sup> Witulski, B.; Stengel, T. *Angew. Chem., Int. Ed. Engl.* **1999**, 38, 2426.
- <sup>107</sup> Brien, D. J.; Naiman, A.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1982**, 133.
- <sup>108</sup> Chiusoli, G. P.; Pallini, L.; Terenghi, G. *Transition Met. Chem.* **1983**, 8, 189.
- <sup>109</sup> Gandon, V.; Leca, D.; Aechtner, T.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *Org. Lett.* **2004**, 6, 3405.
- <sup>110</sup> Hirthammer, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, 108, 2481.
- <sup>111</sup> Parnell, C. A.; Vollhardt, K. P. C. *Tetrahedron* **1985**, 41, 5791.
- <sup>112</sup> Yamamoto, Y.; Hata, K.; Arakawa, T.; Itoh, K. *Chem. Commun.* **2003**, 1290.
- <sup>113</sup> Vollhardt, K. P. C. *Pure Appl. Chem.* **1993**, 65, 153.
- <sup>114</sup> Berris, B. C.; Hovakeemian, G. H.; Lai, Y.-H.; Mestdag, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, 107, 5670.
- <sup>115</sup> McDonald, F. E.; Smolentsev, V. *Org. Lett.* **2002**, 4, 745.
- <sup>116</sup> Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, 122, 12876.
- <sup>117</sup> Hoven, G. B.; Efskind, J.; Romming, C.; Undheim, K. *J. Org. Chem.* **2002**, 67, 2459.
- <sup>118</sup> Stara, I. G.; Sary, I.; Kollarovic, A.; Teply, F.; Saman, D.; Tichy, M. *J. Org. Chem.* **1998**, 63, 4046.
- <sup>119</sup> Teply, F.; Stara, I. G.; Sary, I.; Kollarovic, A.; Saman, D.; Rulisek, L.; Fiedler, P. *J. Am. Chem. Soc.* **2002**, 124, 9175.
- <sup>120</sup> Pla-Quintana, A.; Roglans, A.; Torrent, A.; Moreno-Mañas, M.; Benet-Buchholz, J. *Organometallics* **2004**, 23, 2762.
- <sup>121</sup> Torrent, A.; Gonzalez, I.; Pla-Quintana, A.; Roglans, A.; Moreno-Manas, M.; Parella, T.; Benet-Buchholz, J. *J. Org. Chem.* **2005**, 70, 2033.
- <sup>122</sup> Bruns, D.; Miura, H.; Vollhardt, K. P. C.; Stanger, A. *Org. Lett.* **2003**, 5, 549.
- <sup>123</sup> Beckhaus, H.-D.; Faust, R.; Matzger, A. J.; Mohler, D. L.; Rogers, D. W.; Rüchardt, C.; Sawhney, A. K.; Verevkin, S. P.; Vollhardt, K. P. C.; Wolff, S. *J. Am. Chem. Soc.* **2000**, 122, 7819.
- <sup>124</sup> Kumaraswamy, S.; Jalisatitgi, S. S.; Matzger, A. J.; Miljanic, O. S.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **2004**, 43, 3711.
- <sup>125</sup> Han, S.; Bond, A. D.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed. Engl.* **2002**, 41, 3223.

- <sup>126</sup> Han, S.; Anderson, D. R.; Bond, A. D.; Chu, H. V.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 3227.
- <sup>127</sup> Bong, D. T. Y.; Gentric, L.; Holmes, D.; Matzger, A. J.; Scherhag, F.; Vollhardt, K. P. C. *Chem. Commun.* **2002**, 278.
- <sup>128</sup> Gutnov, A.; Heller, B.; Fisher, C.; Drexler, H.-J.; Spannenberg, A.; Sundermann, B.; Sundermann, C. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 2.
- <sup>129</sup> Sato, Y.; Nishimata, T.; Mori, M. *Heterocycles* **1997**, *44*, 443.
- <sup>130</sup> Kölle, U.; Fuss, B. *Chem. Ber.* **1986**, *119*, 116.
- <sup>131</sup> Ardizzioia, G. A.; Brenna, S.; Cenini, S.; LaMonica, G.; Masciocchi, N.; Maspero, A. *J. Mol. Catal. A: Chemical* **2003**, *204–205*, 333.
- <sup>132</sup> Diercks, R.; Tom Dieck, H. *Chem. Ber.* **1985**, *118*, 428.
- <sup>133</sup> Vollhardt, K. P. C. *Pure Appl. Chem.* **1985**, *57*, 1819.
- <sup>134</sup> Johnson, E. P.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1991**, *119*, 381.
- <sup>135</sup> Germamas, J.; Aubert, C.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1991**, *113*, 4006.
- <sup>136</sup> Earl, R. A.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 4786.
- <sup>137</sup> Eichberg, M. J.; Dorta, R. L.; Grotjahn, D. B.; Lamottke, K.; Martin, S.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **2001**, *123*, 9324.
- <sup>138</sup> Perez, D.; Siesel, B. A.; Malaska, M. J.; David, E.; Vollhardt, K. P. C. *Synlett* **2000**, 306.
- <sup>139</sup> Grotjahn, D. B.; Vollhardt, K. P. C. *Synthesis* **1993**, 579.
- <sup>140</sup> Chelucci, G.; Falorni, M.; Giacomelli, G. *Synthesis* **1990**, 1121.
- <sup>141</sup> Turek, P.; Kotor, M.; Hocek, M.; Cisarova, I. *Tetrahedron Lett.* **2003**, *44*, 785.
- <sup>142</sup> Witulski, B.; Alayrac, C. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 3281.
- <sup>143</sup> Hillard III, R. L.; Parnell, C. A.; Vollhardt, K. P. C. *Tetrahedron* **1983**, *39*, 905.
- <sup>144</sup> Saa, C.; Crotts, D. D.; Hsu, G.; Vollhardt, K. P. C. *Synlett* **1994**, 487.
- <sup>145</sup> Aubert, C.; Gotteland, J. P.; Malacria, M. *J. Org. Chem.* **1993**, *58*, 4298.
- <sup>146</sup> Cruciani, P.; Stammmler, R.; Aubert, C.; Malacria, M. *J. Org. Chem.* **1996**, *61*, 2699.
- <sup>147</sup> Stammmler, R.; Malacria, M. *Synlett* **1994**, 92.
- <sup>148</sup> Cruciani, P.; Aubert, C.; Malacria, M. *Synlett* **1996**, 105.
- <sup>149</sup> Petit, M.; Chouraqui, G.; Phansavath, P.; Aubert, C.; Malacria, M. *Org. Lett.* **2002**, *4*, 1027.
- <sup>150</sup> Kalogerakis, A.; Groth, U. *Org. Lett.* **2003**, *5*, 843.
- <sup>151</sup> Neeson, S. J.; Stevenson, P. J. *Tetrahedron Lett.* **1988**, *29*, 813.
- <sup>152</sup> Calloway, N. O. *Chem. Rev.* **1935**, *17*, 327.
- <sup>153</sup> Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, **1990**.
- <sup>154</sup> Zoltewicz, J. A. *Top. Curr. Chem.* **1975**, *59*, 33.
- <sup>155</sup> Kobrina, L. S. *Russ. Chem. Rev. (Engl. Trans.)* **1977**, *46*, 348.
- <sup>156</sup> Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327.
- <sup>157</sup> Narasimhan, N. S.; Mali, R. S. *Synthesis* **1983**, 957.
- <sup>158</sup> Danheiser, R. L.; Gould, A. E.; Fernandez de la Predilla, R.; Helgason, A. L. *J. Org. Chem.* **1994**, *59*, 5514.
- <sup>159</sup> Wills, M. S. B.; Danheiser, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 9378.
- <sup>160</sup> Burrell, R. C.; Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1996**, *118*, 4218.
- <sup>161</sup> Bradley, A. Z.; Johnson, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 9917.
- <sup>162</sup> Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650.
- <sup>163</sup> Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921.
- <sup>164</sup> Barluenga, J.; Vasquez-Villa, H.; Ballesteros, A.; Gonzales, J. M. *Org. Lett.* **2003**, *5*, 4121.
- <sup>165</sup> Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517.
- <sup>166</sup> Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.
- <sup>167</sup> de Meijere, A.; Schrimmer, H.; Duetsch, M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3964.
- <sup>168</sup> Wulff, W. D.; Tang, P.-C. *J. Am. Chem. Soc.* **1984**, *106*, 434.
- <sup>169</sup> Wulff, W. D.; Xu, Y. C. *J. Am. Chem. Soc.* **1988**, *110*, 2312.
- <sup>170</sup> Manish, R.; Wulff, W. D. *Org. Lett.* **2004**, *6*, 329.
- <sup>171</sup> White, J. D.; Helmars, S. *Org. Lett.* **2005**, *7*, 235.

- 172 Gevorgyan, V.; Takeda, A.; Homma, M.; Sadayori, N.; Radhakrishnan, U.; Yamamoto, Y. *J. Am. Chem. Soc.* **1999**, *121*, 6391.
- 173 Sato, Y.; Tamura, T.; Mori, M. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 2436.
- 174 Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716.
- 175 Cammack, J. K.; Jalisatgi, S.; Matzger, A. J.; Negron, A.; Vollhardt, K. P. C. *J. Org. Chem.* **1996**, *61*, 4798.
- 176 Shibata, T.; Fujimoto, T.; Yokota, K.; Takagi, K. *J. Am. Chem. Soc.* **1994**, *126*, 8382.
- 177 Yong, L.; Fujibayashi, S.; Nishiyama, Y.; Sakaguchi, S.; Ishii, Y. *J. Mol. Catal. A: Chemical* **1996**, *114*, 113.
- 178 Yang, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, *120*, 6834.
- 179 Chio, K. S.; Park, M. K.; Han, B. H. *J. Chem. Res. (S)* **1998**, 518.
- 180 Du Plessis, J. A. K.; Smulders, P.; Du Toit, C. J. *J. Mol. Catal.* **1987**, *42*, 105.
- 181 Chisholm, M. H.; Foltling, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389.
- 182 Song, H.; Haltiwanger, R. C.; DuBois, M. R. *Organometallics* **1987**, *6*, 2021.
- 183 Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 645.
- 184 Bianchini, C.; Graziani, M.; Kaspar, J.; Meli, A.; Vizza, F. *Organometallics* **1994**, *13*, 1165.
- 185 Alphonse, P.; Moyon, F.; Mazerolles, P. *J. Organomet. Chem.* **1988**, *345*, 209.
- 186 Ferris, J. P.; Guillemin, J. C. *J. Org. Chem.* **1990**, *55*, 5601.
- 187 Edwards, A. J.; Leadbeater, N. E.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1995**, 3785.
- 188 Nickel, T.; Goddard, R.; Krueger, C.; Poeschke, K. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 879.
- 189 Wessel, J.; Hartl, H.; Seppelt, K. *Chem. Ber.* **1986**, *119*, 453.
- 190 Yamaguchi, I.; Osakada, K.; Yamamoto, T. *Inorg. Chim. Acta* **1994**, *220*, 35.
- 191 Baidossi, W.; Goren, N.; Blum, J. *J. Mol. Catal.* **1993**, *85*, 153.
- 192 Diversi, P.; Ingrosso, G.; Lucherini, A.; Malquori, S. *J. Mol. Catal.* **1987**, *40*, 267.
- 193 Aresta, M.; De Fazio, M. *J. Organomet. Chem.* **1980**, *186*, 109.
- 194 Yong, L.; Butenschoen, H. *Chem. Commun.* **2002**, 2852.
- 195 Montilla, F.; Aviles, T.; Casimiro, T.; Ricardo, A. A.; Nunes da Ponte, M. *J. Organomet. Chem.* **2001**, *632*, 113.
- 196 Tom Dieck, H.; Lauer, A. M.; Stamp, L.; Diercks, R. *J. Mol. Catal.* **1986**, *35*, 317.
- 197 Breitung, V.; Hopf, H.; Klaerner, F.-G.; Witulski, B.; Zimny, B. *Liebigs Ann. Chem.* **1995**, 613.
- 198 Sigman, M. S.; Fatland, A. W.; Eaton, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 5130.
- 199 Becker, E.; Mereiter, K.; Puchberger, M.; Schmid, R.; Kirchner, K.; Doppiu, A.; Salzer, A. *Organometallics* **2003**, *22*, 3164.
- 200 Doyle, M. P.; Shanklin, M. S. *Organometallics* **1994**, *13*, 1081.
- 201 Yan, H.; Beatty, A. M.; Fehlner, T. P. *Organometallics* **2002**, *21*, 5029.
- 202 Lindner, E.; Kuehbauch, H. *J. Organomet. Chem.* **1991**, *403*, C9.
- 203 Hashizume, K.; Mizobe, Y.; Hidai, M. *Organometallics* **1995**, *14*, 5367.
- 204 Bohanna, C.; Esteruelas, M. A.; Herrero, J.; Lopez, A. M.; Oro, L., A. *J. Organomet. Chem.* **1995**, *498*, 199.
- 205 Ren, C. Y.; Cheng, W. C.; Chan, W. C.; Yeung, C. H.; Lau, C. P. *J. Mol. Catal.* **1990**, *59*, L1.
- 206 Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 1714.
- 207 Han, W. S.; Lee, S. W. *J. Organomet. Chem.* **2003**, *678*, 102.
- 208 Field, L. D.; Ward, A. J.; Turner, P. *Aust. J. Chem.* **1999**, *52*, 1085.
- 209 Borrini, A.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181.
- 210 Abdulla, K.; Booth, B. L.; Stacey, C. *J. Organomet. Chem.* **1985**, *293*, 103.
- 211 Staal, L. H.; Van Koten, G.; Vrieze, K.; Van Santen, B.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 3598.
- 212 Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Organometallics* **2000**, *19*, 4289.
- 213 Yan, H.; Beatty, A. M.; Fehlner, T. P. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4498.
- 214 Cecon, A.; Gambaro, A.; Santi, S. *J. Mol. Catal.* **1991**, *69*, L1.
- 215 Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984.
- 216 Bochmann, M.; Hawkins, I.; Sloan, M. P. *J. Organomet. Chem.* **1987**, *332*, 371.
- 217 Carvalho, M. F. N. N.; Almeida, F. M. T.; Galvao, A. M.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2003**, *679*, 143.



- <sup>218</sup> Mori, N.; Ikeda, S.-i.; Odashima, K. *Chem. Commun.* **2001**, 181.
- <sup>219</sup> Werner, H.; Zolk, R. *Chem. Ber.* **1987**, *120*, 1003.
- <sup>220</sup> Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.
- <sup>221</sup> Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233.
- <sup>222</sup> Rhyoo, H.-Y.; Lee, B. Y.; Yu, H. K. B.; Chung, Y. K. *J. Mol. Catal.* **1994**, *92*, 41.
- <sup>223</sup> Tsuda, T.; Kunisada, K.; Nagahama, N.; Morikawa, S.; Saegusa, T. *Synth. Commun.* **1989**, *19*, 1575.
- <sup>224</sup> Allcock, H. R.; Nissan, R. A.; Harris, P. J.; Whittle, R. R. *Organometallics* **1984**, *3*, 432.
- <sup>225</sup> Sato, Y.; Ohashi, K.; Mori, M. *Tetrahedron Lett.* **1999**, *40*, 5231.
- <sup>226</sup> Giordano, R.; Sappa, E.; Predieri, G. *Inorg. Chim. Acta* **1995**, *228*, 139.
- <sup>227</sup> Mauthner, K.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 1956.
- <sup>228</sup> Rüba, E.; Schmid, R.; Kirchner, K.; Calhorda, M. J. *J. Organomet. Chem.* **2003**, *682*, 204.
- <sup>229</sup> Klein, H.-F.; Mager, M. *Organometallics* **1992**, *11*, 3174.
- <sup>230</sup> Herrmann, R.; Pombeiro, A. J. L. *Monatsh. Chem.* **1988**, *119*, 583.
- <sup>231</sup> Tom Dieck, H.; Munz, C.; Mueller, C. *J. Organomet. Chem.* **1990**, *384*, 243.
- <sup>232</sup> Pertici, P.; Verrazzani, A.; Vitulli, G.; Baldwin, R.; Bennett, M. A. *J. Organomet. Chem.* **1998**, *551*, 37.
- <sup>233</sup> Aime, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 828.
- <sup>234</sup> Ozerov, O. V.; Ladipo, F. T.; Patrick, B. O. *J. Am. Chem. Soc.* **1999**, *121*, 7941.
- <sup>235</sup> Hara, R.; Guo, Q.; Takahashi, T. *Chem. Lett.* **2000**, 140.
- <sup>236</sup> Breschi, C.; Piparo, L.; Pertici, P.; Caporusso, A. M.; Vitulli, G. *J. Organomet. Chem.* **2000**, *607*, 57.
- <sup>237</sup> van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.
- <sup>238</sup> Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685.
- <sup>239</sup> Calderazzo, F.; Marchetti, F.; Pampaloni, G.; Hiller, W.; Antropiusova, H.; Mach, K. *Chem. Ber.* **1989**, *122*, 2229.
- <sup>240</sup> Masuda, T.; Deng, Y. X.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2798.
- <sup>241</sup> Du Plessis, J. A. K.; Viljoen, J. S.; Du Toit, C. J. *J. Mol. Catal.* **1991**, *64*, 269.
- <sup>242</sup> Matusiak, R.; Keller, A. *J. Mol. Catal. A: Chemical* **2003**, *195*, 29.
- <sup>243</sup> Du Plessis, J. A. K.; Vosloo, H. C. M. *J. Mol. Catal.* **1991**, *65*, 51.
- <sup>244</sup> Biagini, P.; Funaioli, T.; Fachinetti, G.; Laschi, F.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1989**, 405.
- <sup>245</sup> Jerome, K. S.; Parsons, E. J. *Organometallics* **1993**, *12*, 2991.
- <sup>246</sup> Biagini, P.; Caporusso, A. M.; Funaioli, T.; Fachinetti, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1009.
- <sup>247</sup> Mori, N.; Ikeda, S.-i.; Sato, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2722.
- <sup>248</sup> Pertici, P.; Verrazzani, A.; Pitzalis, E.; Caporusso, A. M.; Vitulli, G. *J. Organomet. Chem.* **2001**, *621*, 246.
- <sup>249</sup> Yokota, T.; Sakurai, Y.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1997**, *38*, 3923.
- <sup>250</sup> Johnson, E. S.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 11086.
- <sup>251</sup> Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1993**, *115*, 1581.
- <sup>252</sup> Strickler, J. R.; Bruck, M. A.; Wigley, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 2814.
- <sup>253</sup> Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 962.
- <sup>254</sup> Bennett, M. A.; Wenger, E. *Organometallics* **1996**, *15*, 5536.
- <sup>255</sup> Tagliatesta, P.; Floris, B.; Galloni, P.; Leoni, A.; D'Arcangelo, G. *Inorg. Chem.* **2003**, *42*, 7701.
- <sup>256</sup> Griesbaum, K.; Rao, R.; Leifker, G. *J. Org. Chem.* **1982**, *47*, 4975.
- <sup>257</sup> Gu, Y.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem.* **2001**, 373.
- <sup>258</sup> Masuda, T.; Mouri, T.; Higashimura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1152.
- <sup>259</sup> Hartung, J. B., Jr.; Pedersen, S. F. *Organometallics* **1990**, *9*, 1414.
- <sup>260</sup> Koelle, U.; Fuss, B. *Chem. Ber.* **1986**, *119*, 116.

- 261 Sugihara, T.; Wakabayashi, A.; Nagai, Y.; Takao, H.; Imagawa, H.; Nishizawa, M. *Chem. Commun.* **2002**, 576.
- 262 Baxter, R. J.; Knox, G. R.; Moir, J. H.; Pauson, P. L.; Spicer, M. D. *Organometallics* **1999**, *18*, 206.
- 263 Akita, M.; Terada, M.; Ishii, N.; Hirakawa, H.; Moro-oka, Y. *J. Organomet. Chem.* **1994**, *473*, 175.
- 264 Field, L. D.; Ward, A. J. *J. Organomet. Chem.* **2003**, *681*, 91.
- 265 Nehl, H. *Chem. Ber.* **1993**, *126*, 1519.
- 266 Iglesias, M.; Del Pino, C.; Ros, J.; Garcia Blanco, S.; Carrera, S. M. *J. Organomet. Chem.* **1988**, *338*, 89.
- 267 Douglas, W. E.; Overend, A. S. *J. Organomet. Chem.* **1993**, *444*, C62.
- 268 Mantovani, A.; Marcomini, A.; Belluco, U. *J. Mol. Catal.* **1985**, *30*, 73.
- 269 Del Rosario, R.; Stuhl, L. S. *Organometallics* **1986**, *5*, 1260.
- 270 Keller, A.; Matusiak, R. *J. Mol. Catal. A: Chemical* **1999**, *142*, 317.
- 271 Szymanska-Buzar, T.; Glowiak, T.; Czelusniak, I. *J. Organomet. Chem.* **1999**, *585*, 215.
- 272 Douglas, W. E.; Overend, A. S. *J. Mater. Chem.* **1994**, *4*, 1167.
- 273 Marigo, M.; Marsich, N.; Farnetti, E. *J. Mol. Catal. A: Chemical* **2002**, *187*, 169.
- 274 Szymanska-Buzar, T.; Glowiak, T. *J. Organomet. Chem.* **1999**, *575*, 98.
- 275 Ferre, K.; Toupet, L.; Guerchais, V. *Organometallics* **2002**, *21*, 2578.
- 276 Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550.
- 277 Bould, J.; Clegg, W.; Spalding, T. R.; Kennedy, J. D. *Inorg. Chem. Commun.* **1999**, *2*, 315.
- 278 Lawrie, C. J.; Gable, K. P.; Carpenter, B. K. *Organometallics* **1989**, *8*, 2274.
- 279 Deeming, A. J.; Hogarth, G.; Lee, M.-y.; Saha, M.; Redmond, S. P.; Phetmung, H.; Orpen, A. G. *Inorg. Chim. Acta* **2000**, *309*, 109.
- 280 Tanaka, K.; Shirasaka, K. *Org. Lett.* **2003**, *5*, 4697.
- 281 Carusi, P.; Cerichelli, G.; Furlani, A.; Russo, M. V.; Suber, L. *Appl. Organomet. Chem.* **1987**, *1*, 555.
- 282 Damrauer, R.; Hankin, J. A.; Haltiwanger, R. C. *Organometallics* **1991**, *10*, 3962.
- 283 Matsuda, K.; Nakamura, N.; Iwamura, H. *Chem. Lett.* **1994**, 1765.
- 284 Rubinsztajn, S.; Fife, W. K.; Zeldin, M. *Tetrahedron Lett.* **1992**, *33*, 1821.
- 285 Lee, J.-C.; Tomita, I.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1999**, *37*, 1979.
- 286 Saito, S.; Kawasaki, T.; Tsuboya, N.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 796.
- 287 Ito, S.; Inabe, H.; Okujima, T.; Morita, N.; Watanabe, M.; Harada, N.; Imafuku, K. *J. Org. Chem.* **2001**, *66*, 7090.
- 288 Ito, S.; Inabe, H.; Okujima, T.; Morita, N.; Watanabe, M.; Harada, N.; Imafuku, K. *Tetrahedron Lett.* **2001**, *42*, 1085.
- 289 Elwahy, A. H. M.; Hafner, K. *Tetrahedron Lett.* **2000**, *41*, 2859.
- 290 Hocek, M.; Stara, I. G.; Stary, I.; Dvorakova, H. *Tetrahedron Lett.* **2001**, *42*, 519.
- 291 Kataoka, Y.; Takai, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1992**, *57*, 1615.
- 292 Chelucci, G. *Synth. Commun.* **1992**, *22*, 2645.
- 293 Matsuda, K.; Nakamura, N.; Takahashi, K.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1995**, *117*, 5550.
- 294 Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872.
- 295 Roy, R.; Das, S. K.; Dominique, R.; Trono, M. C.; Hernandez-Mateo, F.; Santoyo-Gonzalez, F. *Pure Appl. Chem.* **1999**, *71*, 565.
- 296 Gan, Z.; Roy, R. *Can. J. Chem.* **2002**, *80*, 908.
- 297 Matsuda, K.; Nakamura, N.; Inoue, K.; Koga, N.; Iwamura, H. *Chem. Eur. J.* **1996**, *2*, 259.
- 298 Wang, J.; Gutsche, C. D. *J. Org. Chem.* **2002**, *67*, 4423.
- 299 Siedle, A. R.; Newmark, R. A.; Howells, R. D. *Inorg. Chem.* **1988**, *27*, 2473.
- 300 Mehnert, C. P.; Chernega, A. N.; Green, M. L. H. *J. Organomet. Chem.* **1996**, *513*, 247.
- 301 Schmid, G.; Schuetz, M. *J. Organomet. Chem.* **1995**, *492*, 185.
- 302 Solari, E.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, C.; Rosi, M.; Sgamellotti, A. *Inorg. Chem.* **1994**, *33*, 2018.

- <sup>303</sup> Calderazzo, F.; Pampaloni, G.; Pallavicini, P.; Straehle, J.; Wurst, K. *Organometallics* **1991**, *10*, 896.
- <sup>304</sup> Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.
- <sup>305</sup> Brodt, C.; Niu, S.; Pritzkow, H.; Stephan, M.; Zenneck, U. *J. Organomet. Chem.* **1993**, *459*, 283.
- <sup>306</sup> Bantel, H.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1990**, *123*, 1607.
- <sup>307</sup> Lee, W.-S.; Koola, J. D.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *206*, C4.
- <sup>308</sup> Schneider, J. J.; Hagen, J.; Heinemann, O.; Kruger, C.; Fabrizi de Biani, F.; Zanello, P. *Inorg. Chim. Acta* **1998**, *281*, 53.
- <sup>309</sup> Knoch, F.; Kremer, F.; Schmidt, U.; Zenneck, U.; Le Floch, P.; Mathey, F. *Organometallics* **1996**, *15*, 2713.
- <sup>310</sup> Fei, M.; Schut, D. M.; Tyler, D. R. *Organometallics* **1996**, *15*, 4770.
- <sup>311</sup> Krampe, O.; Song, C. E.; Klaui, W. *Organometallics* **1993**, *12*, 4949.
- <sup>312</sup> Booth, B. L.; Haszeldine, R. N.; Perkins, I. *J. Chem. Soc., Dalton Trans.* **1981**, 2593.
- <sup>313</sup> Broussier, R.; Laly, M.; Perron, P.; Gautheron, B.; M'Koyan, S.; Kalck, P.; Wheatley, N. *J. Organomet. Chem.* **1999**, *574*, 267.
- <sup>314</sup> Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1999**, *18*, 4040.
- <sup>315</sup> Hernandez, E.; Saez, I.; Royo, P. *J. Organomet. Chem.* **1985**, *293*, 249.
- <sup>316</sup> Thomas, M. S.; Darkwa, J. *Polyhedron* **1998**, *17*, 1811.
- <sup>317</sup> Kobayashi, T.; Nitta, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 152.
- <sup>318</sup> Eisch, J. J.; Ma, X.; Han, K. I.; Gitua, J. N.; Kruger, C. *Eur. J. Inorg. Chem.* **2001**, 77.
- <sup>319</sup> Butenschon, H. *Chem. Ber.* **1993**, *126*, 1651.
- <sup>320</sup> Sakakibara, T.; Tanaka, Y.; Yamasaki, S. *Chem. Lett.* **1986**, 797.
- <sup>321</sup> Finckh, W.; Tang, B. Z.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904.
- <sup>322</sup> Caffyn, A. J. M.; Carmichael, D.; Mathey, F.; Ricard, L. *Organometallics* **1997**, *16*, 2049.
- <sup>323</sup> Mauret, P.; Alphonse, P. *J. Organomet. Chem.* **1984**, *276*, 249.
- <sup>324</sup> Arney, D. J.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 1282.
- <sup>325</sup> Wexler, P. A.; Wigley, D. E. *Organometallics* **1991**, *10*, 2319.
- <sup>326</sup> Baldwin, R.; Bennett, M. A.; Hockless, D. C. R.; Pertici, P.; Verrazzani, A.; Uccello Barretta, G.; Marchetti, F.; Salvadori, P. *J. Chem. Soc., Dalton Trans.* **2002**, 4488.
- <sup>327</sup> Walther, D.; Schoenberg, H.; Dinjus, E.; Sieler, J. *J. Organomet. Chem.* **1987**, *334*, 377.
- <sup>328</sup> Inoue, Y.; Ito, Y.; Kazama, H.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3329.
- <sup>329</sup> Rosenthal, U.; Schulz, W. *J. Prakt. Chem.* **1986**, *328*, 335.
- <sup>330</sup> Allen, C. W.; Malik, P.; Bridges, A.; Desorcie, J.; Pellon, B. *Phosphorus, Sulfur, Silicon, Relat. Elem.* **1990**, *49-50*, 433.
- <sup>331</sup> Biali, S. E.; Gutierrez, A.; Mislow, K. *J. Org. Chem.* **1988**, *53*, 1316.
- <sup>332</sup> Siegel, J.; Gutierrez, A.; Schweizer, W. B.; Ermer, O.; Mislow, K. *J. Am. Chem. Soc.* **1986**, *108*, 1569.
- <sup>333</sup> Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 7763.
- <sup>334</sup> Weissensteiner, W.; Gutierrez, A.; Radcliffe, M. D.; Siegel, J.; Singh, M. D.; Tuohey, P. J.; Mislow, K. *J. Org. Chem.* **1985**, *50*, 5822.
- <sup>335</sup> Mueller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1975.
- <sup>336</sup> Gleiter, R.; Schelmann, V. *Tetrahedron Lett.* **1989**, *30*, 2893.
- <sup>337</sup> Gervasio, G.; Sappa, E.; Marko, L. *J. Organomet. Chem.* **1993**, *444*, 203.
- <sup>338</sup> Imi, K.; Imai, K.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 3127.
- <sup>339</sup> Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590.
- <sup>340</sup> Klein, R.; Schmid, G.; Sedmera, P.; Hanus, V.; Mach, K. *J. Organomet. Chem.* **1994**, *466*, 125.
- <sup>341</sup> Suzuki, D.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2001**, *123*, 7925.
- <sup>342</sup> Hiraoka, S.; Harano, K.; Tanaka, T.; Shiro, M.; Shionoya, M. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 5182.
- <sup>343</sup> Tom Dieck, H.; Diercks, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 778.
- <sup>344</sup> Pericas, M. A.; Riera, A.; Serratos, F. *Tetrahedron* **1982**, *38*, 1505.
- <sup>345</sup> Takai, K.; Yamada, M.; Utimoto, K. *Chem. Lett.* **1995**, 851.
- <sup>346</sup> Taber, D. F.; Rahimizadeh, M. *Tetrahedron Lett.* **1994**, *35*, 9139.
- <sup>347</sup> Maderna, A.; Pritzkow, H.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1501.

- 348 Angermund, K. P.; Betz, P.; Butenschoen, H. *Chem. Ber.* **1993**, *126*, 713.
- 349 Mach, K.; Antropiusova, H.; Sedmera, P.; Hanus, V.; Turecek, F. *J. Chem. Soc., Chem. Commun.* **1983**, 805.
- 350 Hong, P.; Mise, T.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 247.
- 351 Nishida, M.; Shiga, H.; Mori, M. *J. Org. Chem.* **1998**, *63*, 8606.
- 352 Hecht, S.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1999**, *121*, 4084.
- 353 Sendhoff, N.; Kissener, W.; Voegtle, F.; Franken, S.; Puff, H. *Chem. Ber.* **1988**, *121*, 2179.
- 354 Duchene, K. H.; Voegtle, F. *Synthesis* **1986**, 659.
- 355 Dijkstra, H. P.; Meijer, M. D.; Patel, J.; Kreiter, R.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; Cauty, A. J.; van Koten, G. *Organometallics* **2001**, *20*, 3159.
- 356 Kobayashi, K.; Shirasaka, T.; Horn, E.; Furukawa, N. *Tetrahedron Lett.* **2000**, *41*, 89.
- 357 Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Mullen, K. *Chem. Eur. J.* **2000**, *6*, 1834.
- 358 Rathore, R.; Burns, C. L.; Guzei, I. A. *J. Org. Chem.* **2004**, *69*, 1524.
- 359 Rathore, R.; Burns, C. L.; Abdelwahed, S. A. *Org. Lett.* **2004**, *6*, 1689.
- 360 Pugh, C.; Percec, V. *J. Mater. Chem.* **1991**, *1*, 765.
- 361 Doetz, F.; Brand, J. D.; Ito, S.; Gherghel, L.; Muellen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7707.
- 362 Stabel, A.; Herwig, P.; Muellen, K.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1609.
- 363 Wu, J.; Watson, M. D.; Muellen, K. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 5329.
- 364 Mamane, V.; Gref, A.; Lefloch, F.; Riant, O. *J. Organomet. Chem.* **2001**, *637-639*, 84.
- 365 Dominique, R.; Liu, B.; Das, S. K.; Roy, R. *Synthesis* **2000**, 862.
- 366 Simpson, C. D.; Brand, J. D.; Berresheim, A. J.; Przybilla, L.; Rader, H. J.; Mullen, K. *Chem. Eur. J.* **2002**, *8*, 1424.
- 367 Fletcher, J. T.; Therien, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12393.
- 368 Fletcher, J. T.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 4298.
- 369 Fletcher, J. T.; Therien, M. J. *Inorg. Chem.* **2002**, *41*, 331.
- 370 Gesing, E. R. F.; Sinclair, J. A.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1980**, 286.
- 371 Grigg, R.; Scott, R.; Stevenson, P. *Tetrahedron Lett.* **1982**, *23*, 2691.
- 372 Yamamoto, Y.; Ogawa, R.; Itoh, K. *Chem. Commun.* **2000**, 549.
- 373 Takeuchi, R.; Tanaka, S.; Nakaya, Y. *Tetrahedron Lett.* **2001**, *42*, 2991.
- 374 Grigg, R.; Savic, V.; Tambyrajah, V. *Tetrahedron Lett.* **2000**, *41*, 3003.
- 375 Kinoshita, H.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2003**, *125*, 7784.
- 376 Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Kawaguchi, H.; Tatsumi, K.; Itoh, K. *J. Am. Chem. Soc.* **2000**, *122*, 4310.
- 377 Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. *J. Org. Chem.* **1998**, *63*, 9610.
- 378 Magnus, P.; Witty, D.; Stamford, A. *Tetrahedron Lett.* **1993**, *34*, 23.
- 379 Jeevanandam, A.; Korivi, R. P.; Huang, I. W.; Cheng, C.-H. *Org. Lett.* **2002**, *4*, 807.
- 380 Witulski, B.; Zimmermann, A. *Synlett* **2002**, 1855.
- 381 McDonald, F. E.; Zhu, H. Y. H.; Holmquist, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 6605.
- 382 Nishiyama, H.; Niwa, E.; Inoue, T.; Ishima, Y.; Aoki, K. *Organometallics* **2002**, *21*, 2572.
- 383 Vitulli, G.; Bertozzi, S.; Lazzaroni, R.; Salvadori, P. *J. Mol. Catal.* **1988**, *45*, 155.
- 384 Bhatarah, P.; Smith, E. H. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2163.
- 385 Yamamoto, Y.; Nagata, A.; Itoh, K. *Tetrahedron Lett.* **1999**, *40*, 5035.
- 386 Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5245.
- 387 Gibson, K. J.; D'Alarcao, M.; Leonard, N. J. *J. Org. Chem.* **1985**, *50*, 2462.
- 388 Battaglia, L. P.; Delledonne, D.; Nardelli, M.; Predieri, G.; Chiusoli, G. P.; Costa, M.; Pelizzi, C. *J. Organomet. Chem.* **1989**, *363*, 209.
- 389 Chiusoli, G. P.; Pallini, L.; Terenghi, M. G. *Transition Met. Chem.* **1985**, *10*, 350.
- 390 Sugihara, T.; Yamada, M.; Nishizawa, M. *J. Indian Chem. Soc.* **1998**, *75*, 645.
- 391 Grigg, R.; Sridharan, V.; Zhang, J. *Tetrahedron Lett.* **1999**, *40*, 8277.
- 392 Grigg, R.; Sridharan, V.; Wang, J.; Xu, J. *Tetrahedron* **2000**, *56*, 8967.
- 393 Yamamoto, Y.; Kitahara, H.; Hattori, R.; Itoh, K. *Organometallics* **1998**, *17*, 1910.
- 394 Yamamoto, Y.; Takagishi, H.; Itoh, K. *J. Am. Chem. Soc.* **2002**, *124*, 6844.
- 395 Muraoka, T.; Matsuda, I.; Itoh, K. *Tetrahedron Lett.* **1998**, *39*, 7325.
- 396 Bhatarah, P.; Smith, E. H. *J. Chem. Soc., Chem. Commun.* **1991**, 277.

- <sup>397</sup> Kotha, S.; Brahmachary, E. *Tetrahedron Lett.* **1997**, *38*, 3561.
- <sup>398</sup> Kotha, S.; Brahmachary, E. *Bioorg. Med. Chem.* **2002**, *10*, 2291.
- <sup>399</sup> Kotha, S.; Brahmachary, E. *J. Organomet. Chem.* **2004**, *689*, 158.
- <sup>400</sup> Wolfart, V.; Rammig, M.; Gleiter, R.; Nuber, B.; Pritzkow, H.; Rominger, F. *Eur. J. Inorg. Chem.* **1999**, 499.
- <sup>401</sup> Bhatarah, P.; Smith, E. H. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2603.
- <sup>402</sup> Hong, S. H.; Kim, J. W.; Choi, D. S.; Chung, Y. K.; Lee, S.-G. *Chem. Commun.* **1999**, 2099.
- <sup>403</sup> Sato, Y.; Nishimata, T.; Mori, M. *J. Org. Chem.* **1994**, *59*, 6133.
- <sup>404</sup> Halterman, R. L.; Nguyen, N. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1379.
- <sup>405</sup> Witulski, B.; Stengel, T.; Fernandez-Hernandez, J. M. *Chem. Commun.* **2000**, 1965.
- <sup>406</sup> Stammer, R.; Halvorsen, K.; Gotteland, J. P.; Malacria, M. *Tetrahedron Lett.* **1994**, *35*, 417.
- <sup>407</sup> Blanco, L.; Helson, H. E.; Hirthammer, M.; Mestdagh, H.; Spyroudis, S.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1246.
- <sup>408</sup> Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399.
- <sup>409</sup> Gotteland, J. P.; Malacria, M. *Tetrahedron Lett.* **1989**, *30*, 2541.
- <sup>410</sup> Kotha, S.; Sreenivasachary, N. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1413.
- <sup>411</sup> Kotha, S.; Mohanraja, K.; Durani, S. *Chem. Commun.* **2000**, 1909.
- <sup>412</sup> Schmidt-Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 9713.
- <sup>413</sup> Diercks, R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 3150.
- <sup>414</sup> Cruciani, P.; Aubert, C.; Malacria, M. *J. Org. Chem.* **1995**, *60*, 2664.
- <sup>415</sup> Son, S. U.; Choi, D. S.; Chung, Y. K.; Lee, S.-G. *Org. Lett.* **2000**, *2*, 2097.
- <sup>416</sup> Bradley, A.; Motherwell, W. B.; Ujjainwalla, F. *Chem. Commun.* **1999**, 917.
- <sup>417</sup> Badrieh, Y.; Greenwald, A.; Schumann, H.; Blum, J. *Chem. Ber.* **1992**, *125*, 667.
- <sup>418</sup> Nambu, M.; Mohler, D. L.; Hardcastle, K.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 6138.
- <sup>419</sup> Dahlmann, U.; Neidlein, R. *Helv. Chim. Acta* **1997**, *80*, 111.
- <sup>420</sup> Boese, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1478.
- <sup>421</sup> Helson, H. E.; Vollhardt, K. P. C.; Yang, Z. Y. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 114.
- <sup>422</sup> Ojima, I.; Vu, A. T.; McCullagh, J. V.; Kinoshita, A. *J. Am. Chem. Soc.* **1999**, *121*, 3230.
- <sup>423</sup> Son, S. U.; Paik, S.-J.; Lee, S. I.; Chung, Y. K. *J. Chem. Soc., Perkin Trans. 1* **2000**, 141.
- <sup>424</sup> Slowinski, F.; Aubert, C.; Malacria, M. *Adv. Synth. Catal.* **2001**, *343*, 64.
- <sup>425</sup> Neeson, S. J.; Stevenson, P. J. *Tetrahedron* **1989**, *45*, 6239.
- <sup>426</sup> Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266.
- <sup>427</sup> Lecker, S. H.; Nguyen, N. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 856.
- <sup>428</sup> Witulski, B.; Zimmermann, A.; Gowans, N. D. *Chem. Commun.* **2002**, 2984.
- <sup>429</sup> Eickmeier, C.; Holmes, D.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 800.
- <sup>430</sup> Hansen, J.; Blake, A. J.; Li, W.-S.; Mascal, M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3371.
- <sup>431</sup> Dosa, P. I.; Schleifenbaum, A.; Vollhardt, K. P. C. *Org. Lett.* **2001**, *3*, 1017.
- <sup>432</sup> Dosa, P. I.; Whitener, G. D.; Vollhardt, K. P. C.; Bond, A. D.; Teat, S. J. *Org. Lett.* **2002**, *4*, 2075.
- <sup>433</sup> Bong, D. T. Y.; Chan, E. W. L.; Diercks, R.; Dosa, P. I.; Haley, M. M.; Matzger, A. J.; Miljanic, O. S.; Vollhardt, K. P. C. *Org. Lett.* **2004**, *6*, 2249.
- <sup>434</sup> Eickmeier, C.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2103.
- <sup>435</sup> Lofthagen, M.; Chadha, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 8785.
- <sup>436</sup> Varela, J. A.; Castedo, L.; Saa, C. *J. Org. Chem.* **2003**, *68*, 8595.
- <sup>437</sup> Fatland, A. W.; Eaton, B. E. *Org. Lett.* **2000**, *2*, 3131.
- <sup>438</sup> Nehl, H. *Chem. Ber.* **1994**, *127*, 2535.
- <sup>439</sup> Schmidt, U.; Zenneck, U. *J. Organomet. Chem.* **1992**, *440*, 187.
- <sup>440</sup> Heller, B.; Oehme, G. *J. Chem. Soc., Chem. Commun.* **1995**, 179.
- <sup>441</sup> Schulz, W.; Pracejus, H.; Oehme, G. *Tetrahedron Lett.* **1989**, *30*, 1229.
- <sup>442</sup> Takahashi, T.; Tsai, F.-Y.; Li, Y.; Wang, H.; Kondo, Y.; Yamanaka, M.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 5059.

- 443 Takahashi, T.; Tsai, F.-Y.; Kotora, M. *J. Am. Chem. Soc.* **2000**, *122*, 4994.
- 444 Chiusoli, G. P.; Pallini, L.; Terenghi, G. *Transition Met. Chem.* **1983**, *8*, 250.
- 445 Chiusoli, G. P.; Pallini, L.; Terenghi, G. *Transition Met. Chem.* **1984**, *9*, 360.
- 446 Vitulli, G.; Bertozzi, S.; Vignali, M.; Lazzaroni, R.; Salvadori, P. *J. Organomet. Chem.* **1987**, *326*, C33.
- 447 Geiger, R. E.; Lalonde, M.; Stoller, H.; Schleich, K. *Helv. Chim. Acta* **1984**, *67*, 1274.
- 448 Vitulli, G.; Bertozzi, S.; Lazzaroni, R.; Salvadori, P. *J. Organomet. Chem.* **1986**, *307*, C35.
- 449 Chiusoli, G. P.; Costa, M.; Reverberi, S.; Terenghi, M. G. *Transition Met. Chem.* **1989**, *14*, 238.
- 450 Heller, B.; Heller, D.; Wagler, P.; Oehme, G. *J. Mol. Catal. A: Chemical* **1998**, *136*, 219.
- 451 Diversi, P.; Ingrosso, G.; Lucherini, A.; Vanacore, D. *J. Mol. Catal.* **1987**, *41*, 261.
- 452 Cioni, P.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Ronca, P. *J. Mol. Catal.* **1987**, *40*, 337.
- 453 Bönneemann, H.; Goddard, R.; Grub, J.; Mynott, R.; Raabe, E.; Wendel, S. *Organometallics* **1989**, 1941.
- 454 Costa, M.; Dalcanale, E.; Dias, F. S.; Graiff, C.; Tiripicchio, A.; Bigliardi, L. *J. Organomet. Chem.* **2001**, *619*, 179.
- 455 Costa, M.; Dias, F. S.; Chiusoli, G. P.; Gazzola, G. L. *J. Organomet. Chem.* **1995**, *488*, 47.
- 456 Diversi, P.; Ermini, L.; Ingrosso, G.; Lucherini, A. *J. Organomet. Chem.* **1993**, *447*, 291.
- 457 Karabet, F.; Heller, B.; Kortus, K.; Oehme, G. *Appl. Organomet. Chem.* **1995**, *9*, 651.
- 458 Heller, B.; Reihsig, J.; Schulz, W.; Oehme, G. *Appl. Organomet. Chem.* **1993**, *7*, 641.
- 459 Wedinger, R.; Hogeveen, H.; Le Noble, W. J. *J. Org. Chem.* **1984**, *49*, 1338.
- 460 Schulz, W.; Pracejus, H.; Oehme, G. *J. Mol. Catal.* **1991**, *66*, 29.
- 461 Heller, B.; Sundermann, B.; Buschmann, H.; Drexler, H.-J.; You, J.; Holzgrave, U.; Heller, E.; Oehme, G. *J. Org. Chem.* **2002**, *67*, 4414.
- 462 Chelucci, G. *Tetrahedron: Asymmetry* **1995**, *6*, 811.
- 463 Chelucci, G.; Cabras, M. A.; Saba, A. *Tetrahedron: Asymmetry* **1994**, *5*, 1973.
- 464 Varela, J. A.; Castedo, L.; Saa, C. *J. Org. Chem.* **1997**, *62*, 4189.
- 465 Salvadori, P.; Rosini, C.; Bertucci, C.; Pini, D.; Marchetti, M. *J. Chem. Soc., Perkin Trans. 2* **1983**, 399.
- 466 Chelucci, G.; Cabras, M. A.; Saba, A. *J. Heterocycl. Chem.* **1994**, *31*, 1289.
- 467 Moretto, A. F.; Zhang, H.-C.; Maryanoff, B. E. *J. Am. Chem. Soc.* **2001**, *123*, 3157.
- 468 Heller, B.; Sundermann, B.; Fischer, C.; You, J.; Chen, W.; Drexler, H.-J.; Knochel, P.; Bonrath, W.; Gutnov, A. *J. Org. Chem.* **2003**, *68*, 9221.
- 469 Botteghi, C.; Chelucci, G.; Del Ponte, G.; Marchetti, M.; Paganelli, S. *J. Org. Chem.* **1994**, *59*, 7125.
- 470 Conti, S.; Cossu, S.; Giacomelli, G.; Falorni, M. *Tetrahedron* **1994**, *50*, 13493.
- 471 Botteghi, C.; Schionato, A.; Chelucci, G.; Brunner, H.; Kuerzinger, A.; Obermann, U. *J. Organomet. Chem.* **1989**, *370*, 17.
- 472 Chelucci, G. *Synth. Commun.* **1993**, *23*, 1897.
- 473 Botteghi, C.; Caccia, G.; Chelucci, G.; Soccolini, F. *J. Org. Chem.* **1984**, *49*, 4290.
- 474 Varela, J. A.; Castedo, L.; Saa, C. *Org. Lett.* **1999**, *1*, 2141.
- 475 Falorni, M.; Chelucci, G.; Conti, S.; Giacomelli, G. *Synthesis* **1992**, 972.
- 476 Gladiali, S.; Chelucci, G.; Soccolini, F.; Delogu, G. *Appl. Organomet. Chem.* **1988**, *2*, 227.
- 477 Cossu, S.; Conti, S.; Giacomelli, G.; Falorni, M. *Synthesis* **1994**, 1429.
- 478 Botteghi, C.; Chelucci, G.; Chessa, G.; Delogu, G.; Gladiali, S.; Soccolini, F. *J. Organomet. Chem.* **1986**, *304*, 217.
- 479 Chelucci, G.; Cabras, M. A.; Botteghi, C.; Marchetti, M. *Tetrahedron: Asymmetry* **1994**, *5*, 299.