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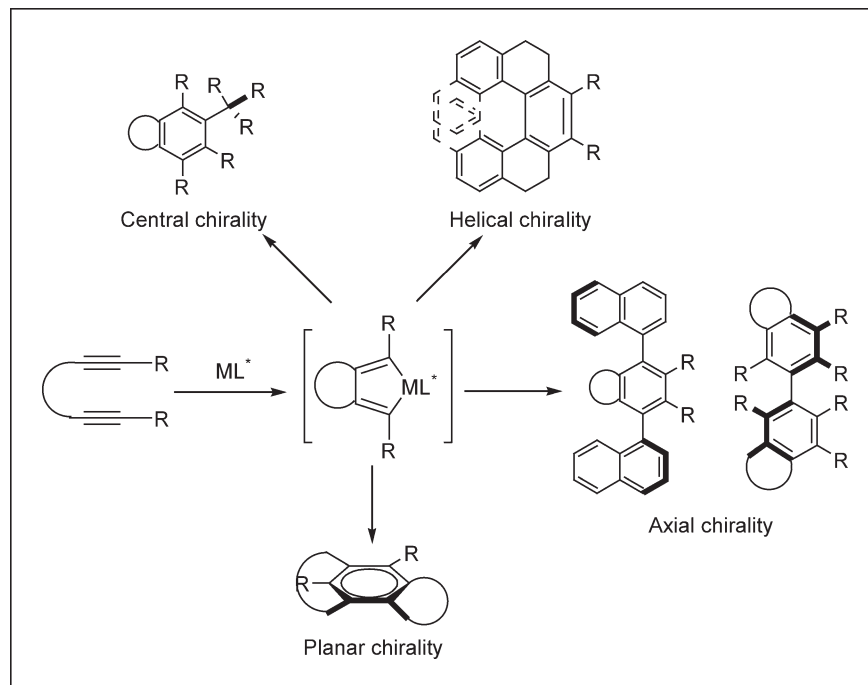
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Metallacyclopentadiene, which is recognized as a metallo-heterocycle, is an important intermediate for the formation of aromatic derivatives. In this short review, we summarized the recent advance on construction of axial, central, planar, and helical chirality by transition-metal-catalyzed aromatic compounds formation *via* metallacyclopentadienes.

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## INTRODUCTION

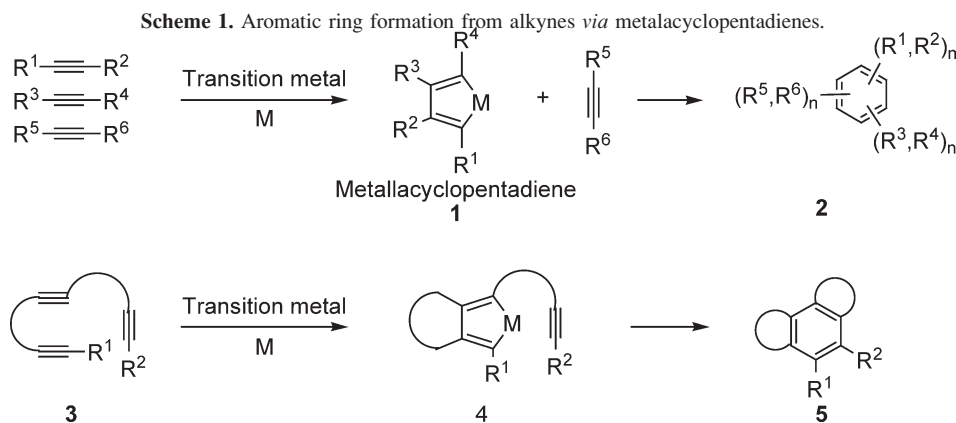
Transition-metal-catalyzed cycloadditions of alkynes provided an efficient method for construction of aromatic derivatives. Metallacyclopentadiene, which is recognized as cyclic compound with a metal (metallo-heterocycle), is an important intermediate for the formation of aromatic derivatives. Reactions of two alkynes with low valent transition metals generally provide metallacyclopentadienes **1**. Stepwise reaction of the metallacyclopentadienes **1** with the third alkyne affords the corresponding benzene derivatives **2** (Scheme 1). Application of the method for triynes **3** affords benzenes **5** having polycyclic skeletons *via* metallacyclopentadienes **4**.

A number of transition-metal-catalyzed cycloadditions have been developed for the synthesis of aromatic compounds [1]. Most of them focus on the chemo- and regio-selective formation of aromatic compounds. The development of enantioselective cycloaddition is still

limited. In 1994, Mori and coworkers reported the first example as an enantioselective desymmetrization of triynes for the formation of isoindoline and isoquinoline derivatives using a chiral nickel complex-catalyzed [2 + 2 + 2] cycloaddition [2]. After their report, several transition metal complexes, mainly containing group 9 and 10 elements, have been reported as efficient catalysts for asymmetric cycloaddition of alkynes. Some review articles have appeared on this topic [3]. This review introduces some recent development of enantioselective formation of aromatic derivatives from alkynes using transition metal complexes as catalysts.

## CONSTRUCTION OF AXIAL CHIRALITY

**One axial chirality formation by single [2 + 2 + 2] cycloaddition.** Axially chiral biaryls are widely used as the key structure of effective chiral ligands and



biologically active compounds. Transition-metal-catalyzed cycloaddition of 1,*n*-diynes **6**, possessing an *ortho*-substituted aryl groups and a substituted alkyne would give an axially chiral biaryls **8** due to steric hindrance between R<sup>1</sup> and R<sup>2</sup> *via* metallacyclopentadienes **7** (Scheme 2).

Transition-metal-catalyzed asymmetric [2 + 2 + 2] cycloaddition of alkynes as a new approach for obtaining axially chiral compounds had been achieved using Co, Ir, and Rh catalysts [4]. The typical examples were summarized in Table 1.

Heller *et al.* discovered that chiral cobalt(I) catalyst **11** under irradiation with visible light could be used for preparation of axially chiral 2-arylpyridines **10** in good yields and optical purities (entry 1).[4a] The reaction could proceed with very low catalyst loading at ambient temperature and pressure. Axially chiral biaryls bearing phosphoryl moieties such as **13** were also constructed from acetylene and phosphinoyl alkyne **12** in the presence of chiral cobalt(I) catalyst **14** (entry 2) [5]

Tanaka and coworkers found that the reaction of electron-deficient 1,6-diyne **15** with 1,4-diacetoxybut-2-yne in the presence of 5 mol % [Rh(cod)<sub>2</sub>]BF<sub>4</sub>/(*S*)-H<sub>8</sub>-BINAP gave axially chiral phthalide **16** in high yield and with excellent enantioselectivity (entry 3) [4b]. By using the same rhodium(I) catalyst, not only partial intramolecular reaction, but complete intermolecular asymmetric [2 + 2 + 2] cycloaddition was accomplished. The reaction of naphthylalkyne **17** with diethyl acetylenedicarboxylate gave the corresponding axially chiral biaryl **18** in high yield and with high enantioselectivity (entry 4) [6a]. The use of alkynylphosphonate

**20** extended this methodology for synthesis of chiral biaryl phosphorus compound **21**. The electron-deficient, coordinating, and sterically demanding characteristics of the phosphorus moiety would be the key points to achieve high yields and enantioselectivity (entry 5) [6b]. Use of isocyanates instead of monoalkynes furnished axially chiral pyridones. The reaction of unsymmetrical 1,6-diyne **22** with benzyl isocyanate in the presence of a cationic rhodium(I)/(*R*)-DTBM-segphos complex gave the corresponding axially chiral pyridone **23** as a sole regioisomer in high yield and with high enantioselectivity (entry 6) [6c]. Not only a chiral carbon–carbon axis but also a chiral carbon–nitrogen axis was constructed by the rhodium-catalyzed cycloaddition of 1,6-diynes **24** and ynamide **25** (entry 7) [6d,e]. Enantioselective construction of aryl-carbonyl axial chirality in *N,N*-dialkylbenzamide **29** was achieved in outstanding yields and enantiomeric excess through cycloaddition of 1,6-diynes **27** and *N,N*-dialkylalkynylamide **28** (entry 8) [7] The substituents on the nitrogen and at the *ortho* position of *N,N*-dialkylbenzamide **29** significantly affect the thermal stability of axial chirality.

Shibata *et al.* reported iridium(I)/(*S,S*)-MeDUPHOS catalyzed [2 + 2 + 2] cycloaddition of unsymmetrical diyne **30** gave an axially chiral biaryl **31** in a good yield and *ee* (entry 9) [8]. The bulkiness of substituents on the alkyne was very important. Methyl group in place of phenyl group in diyne **30** decreased both of the product yield and enantioselectivity (49% yield, 41% *ee*).

**One axial chirality formation by double [2 + 2 + 2] Cycloaddition.** There are two strategies for synthesis of axially chiral biaryls *via* double [2 + 2 + 2]

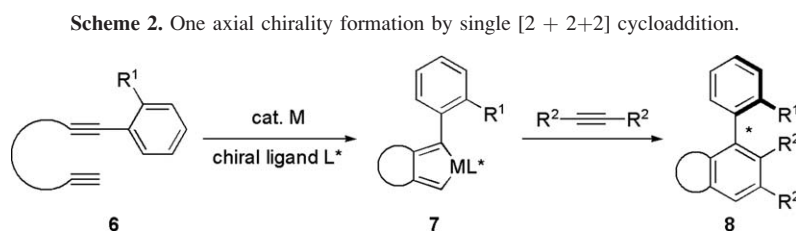


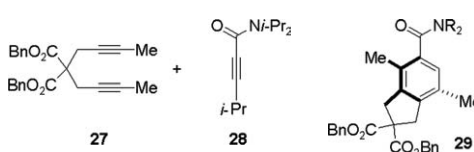
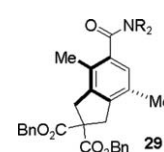
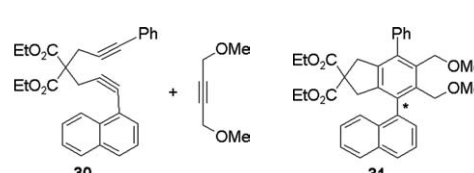
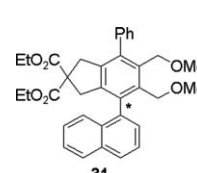
Table 1

Construction of one axial chirality by transition-metal-catalyzed single [2 + 2 + 2] cycloaddition.

Entry	Alkynes	Product	Catalyst	Conditions	Yield/%	ee/%	Refs.
1				$h\nu$ THF, $-20^\circ\text{C}$ , 3 d	86	93	4(a)
2				$h\nu$ THF, $-25^\circ\text{C}$ , 48 h	61	82	5
3			[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> (S)-H <sub>8</sub> -BINAP 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t. 3 h	73	>99	4(b)
4			[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> (S)-H <sub>8</sub> -BINAP 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t. 16 h	89	95	6(a)
5			[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> (R)-H <sub>8</sub> -BINAP 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t. 1 h	>99	97	6(b)
6			[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> (R)-DTBM-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> $-20^\circ\text{C}$ 12–36 h	89	92	6(c)
7			[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> (S)-xyl-BINAP 10 mol %	CH <sub>2</sub> Cl <sub>2</sub> r.t. 15–42 h	79	97	6(d,e)

(Continued)

**Table 1**  
(Continued)

Entry	Alkynes	Product	Catalyst	Conditions	Yield/%	ee/%	Refs.
8			[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> ( <i>S</i> )-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> r.t. 1 h	>99	>99	7
9			[IrCl(cod)] <sub>2</sub> ( <i>S,S</i> )-MeDUPHOS 10 mol %	xylene 100°C, 1 h	99	94	8

cycloaddition as shown in Scheme 3. One is a reaction of 1,3-diyne **32** with  $\alpha,\omega$ -diyne **33** in the presence of a chiral metal catalyst. The other is a reaction of tetrayne **37** containing suitable spacers and conjugated diyne unit and monoynes. In each case, the enantioselection of axial chirality would occur at the second cyclization step. Such examples were summarized in Table 2.

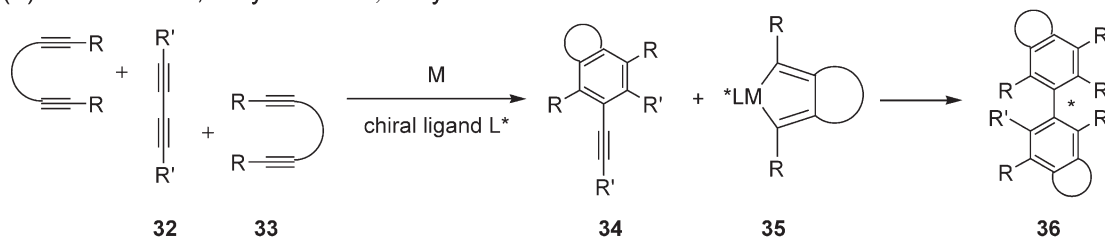
A reaction of electron-deficient 1,6-diyne **40** and 1,3-diyne **41** in the presence of 5 mol % [Rh(cod)<sub>2</sub>]BF<sub>4</sub>/*S*-Segphos complex afforded the corresponding C<sub>2</sub> symmetric chiral biaryl **42** in moderate yield and with excellent enantioselectivity (entry 1) [9]. The reaction of 1,6-

diyne **43** with phosphonate-substituted 1,3-butadiyne **44** in the presence of the similar catalyst gave the corresponding chiral biaryl diphosphonate **45** in high yield with outstanding *ee* (entry 2) [10]. The similar biaryl diphosphonate **47** was also synthesized using a Rh(I)BI-NAP catalyst in good yield and with high enantioselectivity (entry 3) [11].

Double [2 + 2 + 2] cycloaddition strategy for synthesis of chiral biaryls has been applied for the reactions of tetraynes with monoalkynes successfully as shown in entries 4–7. The reaction with tetrayne **48** in the presence of 5 mol % chiral rhodium catalyst gave the

**Scheme 3.** Two strategies for asymmetric biaryl synthesis *via* double [2 + 2 + 2] cycloaddition.

(a) reaction of 1,3-diyne and  $\alpha,\omega$ -diyne



(b) reaction of tetrayne and monoynes

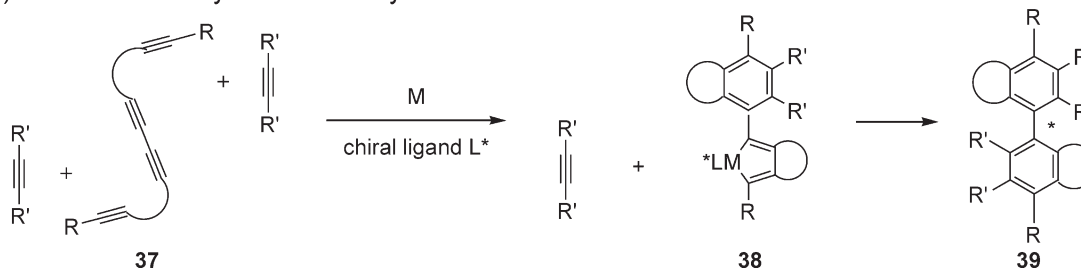
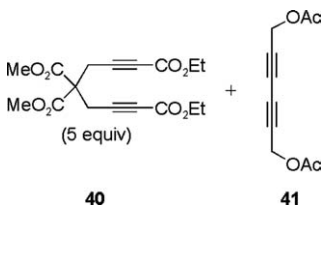
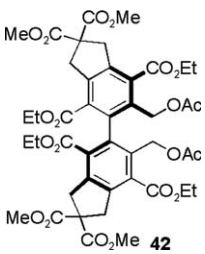
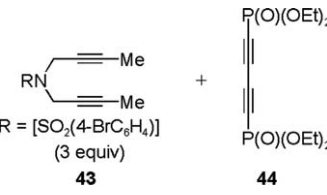
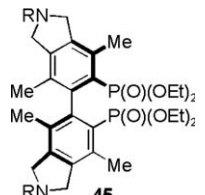
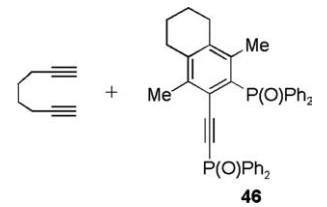
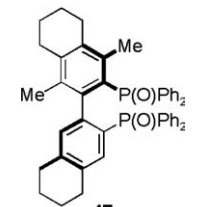
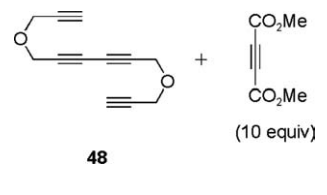
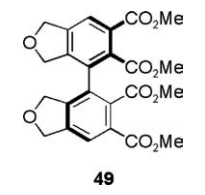
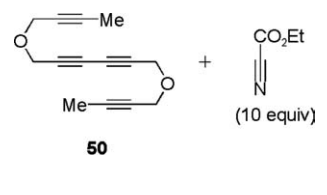
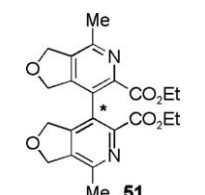
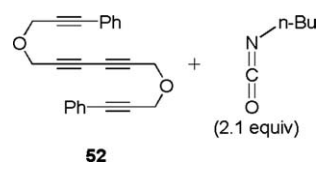
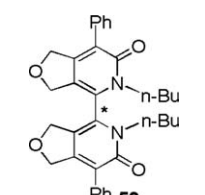


Table 2

Construction of one axial chirality by double [2 + 2 + 2] cycloaddition.

Entry	Alkynes	Product	Catalyst	Conditions	Yield/%	ee/%	Refs.
1	 <p>40 (5 equiv) + 41</p>	 <p>42</p>	[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> /( <i>S</i> )-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 16 h	59	>99	9
2	 <p>43 (3 equiv) + 44</p>	 <p>45</p>	[Rh(cod) <sub>2</sub> ]BF <sub>4</sub> ( <i>R</i> )-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> r.t., 3 h	81	>99	10
3	 <p>46 + 47</p>	 <p>48</p>	[Rh{( <i>R</i> )-BINAP}] [SbF <sub>6</sub> ] (10 mol %)	1,2-C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> 80°C, 16 h	84	96	11
4	 <p>49 + 50 (10 equiv)</p>	 <p>51</p>	[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> /( <i>S</i> )-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> r.t., 16 h	24	98	9
5	 <p>52 + 53 (10 equiv)</p>	 <p>54</p>	[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> /( <i>S</i> )-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 16 h	38	98	9
6	 <p>55 + 56 (2.1 equiv)</p>	 <p>57</p>	[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> /( <i>S</i> )-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t., 16 h	89	52	9

(Continued)

**Table 2**  
(Continued)

Entry	Alkynes	Product	Catalyst	Conditions	Yield/%	ee/%	Refs.
7	 <b>54</b>	 <b>55</b>	[IrCl(cod)] <sub>2</sub> 2CHIRAPHOS 20 mol %	xylene, 100°C reflux, 3 h	49	89	12
8	 <b>56</b>	 <b>57</b>	[IrCl(cod)] <sub>2</sub> 2xylylBINAP 10 mol %	xylene, r. t. 15 min	81	97	12

corresponding  $C_2$ -symmetric, axially chiral biaryl **49** with excellent enantioselectivity (entry 4) [9]. Interestingly, the double [2 + 2 + 2] cycloaddition was applied to the synthesis of axially chiral bipyridine **51** and bipyridone **53** using ethyl cyanofornate (entry 5) and butyl isocyanate (entry 6), respectively.

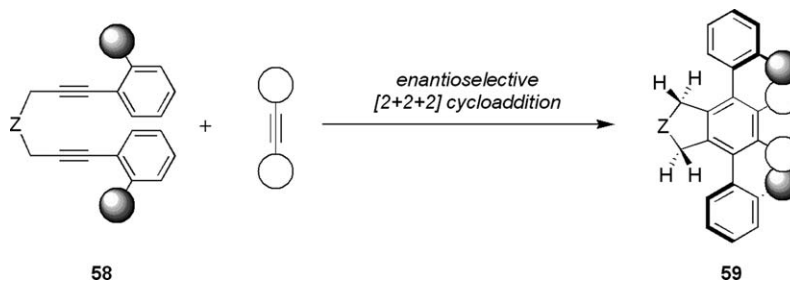
Shibata *et al.* also achieved the enantioselective cycloaddition by mean of iridium(I) catalysts. [2 + 2 + 2] Cycloaddition of tetrayne **54** and TBS-protected but-2-yne-1,4-diol afforded axially chiral biaryl **55** (entry 7) [12]. They also reported the completely intramolecular version of the [2 + 2 + 2] cycloaddition using hexayne **56**. The reaction proceeded consecutive double [2 + 2 + 2] cycloadditions to produce the corresponding chiral biaryl **57** with excellent enantioselectivity (entry 8) [12].

**Multiaxial chirality formation.** Shibata *et al.* proposed the intermolecular coupling of diynes **58**, possessing *ortho*-substituted aryl groups on their termini, and substituted internal alkynes would provide teraryls **59** with two axial chiralities due to the steric hindrance between

two substituents (Scheme 4). In the case of symmetrical diynes and symmetrical monoynes,  $C_2$ -symmetrical chiral compounds will be obtained. Such examples were summarized in Table 3.

The reaction of oxygen tethered 1,6-diyne **60** with naphthyl groups at their termini and 1,4-dimethoxybut-2-yne gave the corresponding  $C_2$  symmetrical teraryl **61** with two axial chiralities was obtained in high diastereo- and enantioselectivity by using a chiral iridium complex (entry 1) [4c]. The similar cycloaddition of 1,6-diyne **62** with unsymmetrical alkyne **63** possessing a tosylamino group proceeded quantitatively to produce axially chiral monoamine **64** in diastereomerically and enantiomerically pure form (entry 2) [8]. The reaction with alkyne **65** having a phosphorus functionality gave the corresponding chiral teraryl **66**. Although the product yield of **66** was not satisfactory, the diastereo- and enantioselectivities were almost perfect (entry 3) [8]. The iridium-catalyzed cycloaddition was successfully applied for synthesis of first example of axially chiral pentacene derivative **68** with

**Scheme 4.** Construction of multiaxial chirality by single [2 + 2 + 2] cycloaddition.



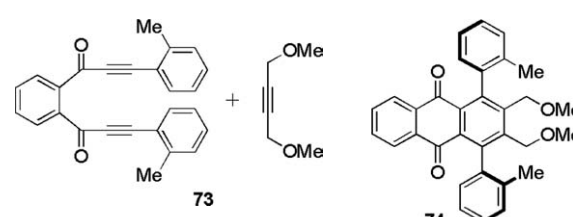
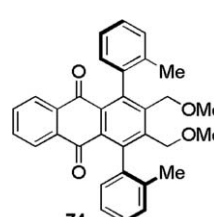
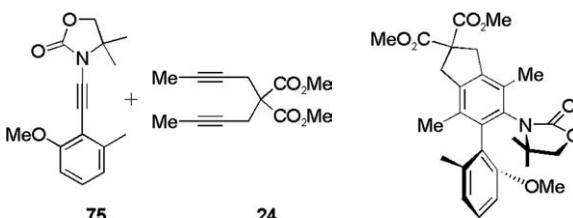
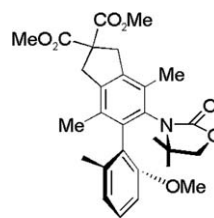
**Table 3**  
Construction of multiaxial chirality.

Entry	Alkynes	Product	Catalyst	Conditions	Yield/%	<i>dr</i>	<i>ee</i> / <i>%</i> <sup>a</sup>	Refs.
1			$[\text{IrCl}(\text{cod})_2]$ 2( <i>S,S</i> )-MeDUPHOS (10 mol %)	xylene, 100°C, 1 h	83	>95/5 <sup>b</sup>	99.6	4(c)
2			$[\text{IrCl}(\text{cod})_2]$ 2( <i>S,S</i> )-MeDUPHOS (10 mol %)	xylene, 100°C, 0.3 h	Quant.	>20/1	>99	8
3			$[\text{IrCl}(\text{cod})_2]$ 2( <i>S,S</i> )-MeDUPHOS (10 mol %)	xylene, 60°C, 3 h	24	>20/1	>99	8
4			$[\text{IrCl}(\text{cod})_2]$ 2( <i>S,S</i> )-MeDUPHOS (10 mol %)	DME Reflux, 1 h	57	–	>99 <sup>c</sup>	12
5			$[\text{IrCl}(\text{cod})_2]$ 2( <i>S,S</i> )-MeDUPHOS (10 mol %)	xylene, 60°C, 0.5 h	95	12/1	90	13
6			$[\text{IrCl}(\text{cod})_2]$ 2( <i>S,S</i> )-MeDUPHOS (20 mol %)	xylene 100°C, 20 min	92	–	>99	14

(Continued)



**Table 3**  
(Continued)

Entry	Alkynes	Product	Catalyst	Conditions	Yield/%	dr	ee/% <sup>a</sup>	Refs.
7			[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> /(S)-Segphos 10 mol %	CH <sub>2</sub> Cl <sub>2</sub> r.t., 16 h	80	8:1	97	15
8			[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> /(S)-xylyl-BINAP 10 mol %	ClCH <sub>2</sub> CH <sub>2</sub> Cl 85°C, 4 Å MS	93	1:6	99	16

<sup>a</sup>The *ee* of major diastereomer.

<sup>b</sup>*dl/meso*.

<sup>c</sup>*Ee* was determined after bromination and aromatization.

excellent *ee* (entry 4) [12]. Completely intramolecular reaction of triyne **69** with *ortho*-substituted aryl groups gave the corresponding *ortho*-diarylbenzene derivative **70** with high enantiomeric excess (entry 5) [13]. The consecutive [2 + 2 + 2] cycloaddition of oxygen-tethered octayne **71** connected with a naphthalen-1,4-diyl spacer efficiently proceeded. The corresponding nonaaryl compound **72** with consecutive eight axial chiralities was obtained with more than 99% *ee* (entry 6) [14].

The cationic rhodium(I)/segphos complex could be applied to asymmetric [2 + 2 + 2] cycloaddition of acyl-functionalized diyne **73**. The corresponding 1,4-diaxially substituted quinone **74** having two axial chiralities was obtained in a good yield and with good enantio- and diastereoselectivity (entry 7) [15].

The Rh(I)-catalyzed asymmetric [2 + 2 + 2] cycloaddition of achiral ynamide **75** with diyne **24** was also reported. This work demonstrates a unique concept of stereochemical control of both the C—C and C—N axial chirality and provides an approach to the synthesis of chiral *N,O*-biaryl **76** (entry 8) [16].

### CONSTRUCTION OF CENTRAL CHIRALITY

Construction of central chirality by transition-metal-catalyzed asymmetric [2 + 2 + 2] cycloaddition was summarized in Table 4. The pioneering work was

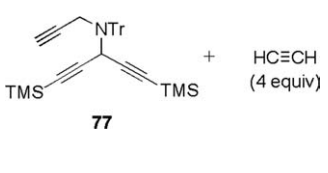
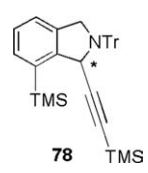
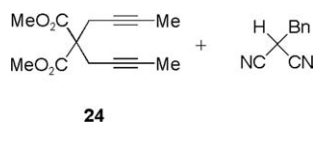
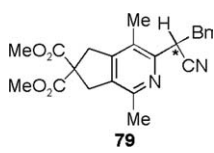
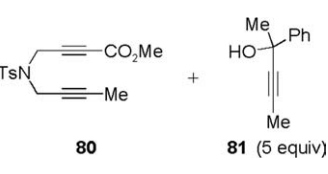
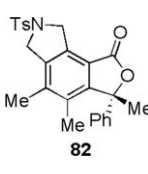
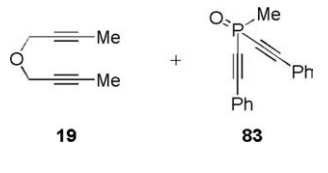
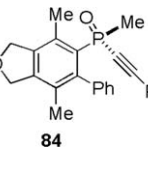
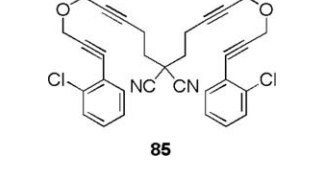
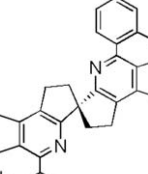
reported by Sato *et al.* as an enantioselective desymmetrization of triynes leading to isoindoline and isoquinoline with benzylic chiral carbon centers using chiral nickel(0) complex [2]. The reaction of triyne **77** and acetylene in the presence of Ni(cod)<sub>2</sub> and (*R*)-(*S*)-BPPFA gave isoindoline **78** (entry 1) [2]. It was found that bulky substituents on nitrogen and alkyne termini affected the enantiomeric excess of the cyclized products.

Several successful examples of enantioselective desymmetrization of alkynes by using the chiral Rh(I) complex catalyzed [2 + 2 + 2] cycloaddition were reported by Tanaka *et al.* As shown in entry 2, 1,6-diyne **24** smoothly reacted with benzylmalononitrile in the presence of 5 mol % [Rh(cod)<sub>2</sub>]BF<sub>4</sub>/(*R*)-*xyl*-solphos to give enantio-enriched bicyclic pyridine **79** containing a tertiary stereocenter [17a]. Cyclization of diyne **80** with alkynol **81** in the presence of a chiral rhodium catalyst produced chiral lactone **82** (entry 3). This is sequential two-step reaction: first step is transesterification and the second is [2 + 2 + 2] cyclization of thus formed triyne. The enantioselection occurred at the first step as kinetic resolution of racemic alcohol **81** catalyzed by the same chiral rhodium catalyst because of its high Lewis acidity of cationic rhodium [17b].

The cationic chiral rhodium(I)-catalyzed cycloaddition was applied for desymmetrization of dialkynylphosphine oxide **83** with 1,6-diyne **19** (entry 4) [18]. The *P*-stereogenic alkynylphosphine oxide **84** was obtained in high yield and high enantiomeric excess.



**Table 4**  
Construction of central chirality by [2 + 2 + 2] cycloaddition.

Entry	Alkynes	Product	Catalyst	Conditions	Yield/%	ee/%	Refs.
1			Ni(cod) <sub>2</sub> , 8 mol % ( <i>R</i> )-( <i>S</i> )-BPPFA 20 mol %	THF, 23°C	52	73	2
2			[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> / <i>R</i> )-xyl-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t. 12 h	91	64	17(a)
3			[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> / <i>R</i> )-Solphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> , r.t. 1 h	89	93	17(b)
4			[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> / <i>R</i> )-dtbm-segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> r.t., 1 h	>99	93	18
5			[Rh(cod) <sub>2</sub> ] BF <sub>4</sub> / <i>R</i> )-Segphos 5 mol %	CH <sub>2</sub> Cl <sub>2</sub> r.t., 16–24 h	89	71	17(c)

The successful enantioselective pyridine formation was also reported by using dicyano-substituted tetrayne **85** to give the expected *C*<sub>2</sub>-symmetric spirobipyridine **86** in 89% yield and 71% *ee* (entry 5) [17c].

### CONSTRUCTION OF PLANAR CHIRALITY

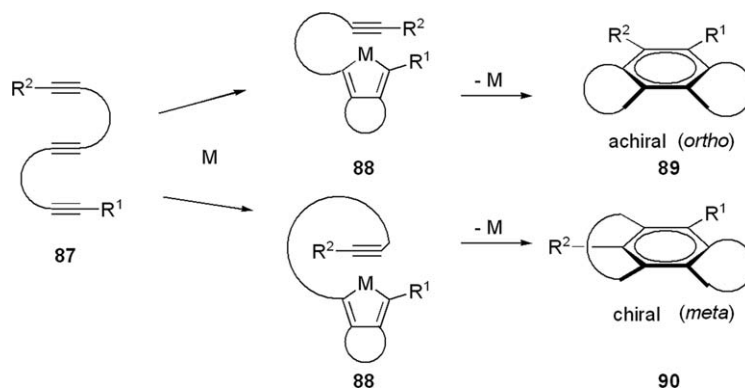
Few examples were reported about enantioselective construction of planar-chiral aromatic rings from alkynes catalyzed by transition metals. Tanaka *et al.* designed an intramolecular [2 + 2 + 2] cycloaddition of triynes **87**, bearing substituents at two alkyne termini, which could form the corresponding *ortho*- or *meta*-cyclophanes **89** and

**90**. *Meta*-cyclophane **90** would possess stable planar chirality because of no ring flip occurring (Scheme 5) [19].

The reaction of substituted triyne **91** in the presence of 5 mol % [Rh(cod)<sub>2</sub>]BF<sub>4</sub>/*R*)-H<sub>8</sub>-BINAP complex gave the desired [7–10] metacyclophanes **92** with high enantioselectivity (Scheme 6) [19a].

The intermolecular variant of this reaction was also investigated. The reaction of bis(methoxymethyl)-substituted diyne **93** with di-*tert*-butyl acetylenedicarboxylates in the presence of 10 mol % [Rh(cod)<sub>2</sub>]BF<sub>4</sub>/*S*)-xyl-H<sub>8</sub>-BINAP at room temperature gave the desired [9]-metacyclophane **94** in 15% yield and 92% *ee*, along with [9]-paracyclophane **95** in 5% yield (Scheme 7) [19a].

Scheme 5. Planar chirality formation by [2 + 2 + 2] cycloaddition.

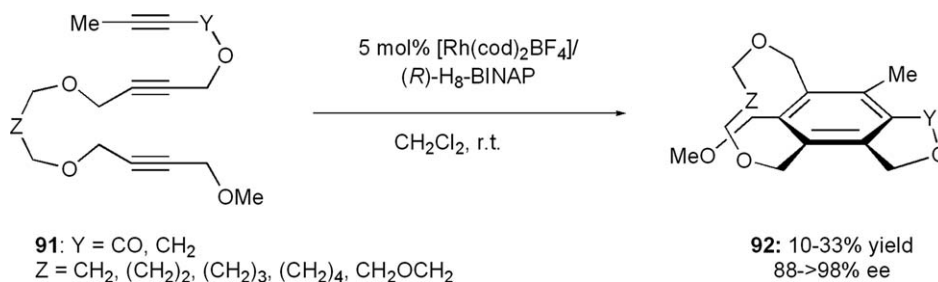


### CONSTRUCTION OF HELICAL CHIRALITY

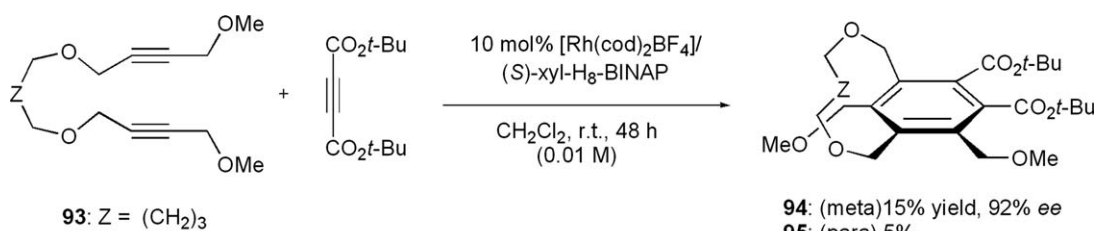
Helicenes and helicene-like molecules possessing nonplanar *ortho*-fused scaffolds exhibit helical chirality. So far, catalytic synthesis of enantioenriched helicenes by [2 + 2 + 2] cycloaddition of alkynes was achieved by three transition metals such as Ni, Pd, and Rh. Stará

and coworkers reported the pioneering chiral helicene formation as a nickel-catalyzed enantioselective [2 + 2 + 2] cycloaddition of triynes **96** leading to a [6] helicene-like molecule **97** (Scheme 8) [20]. However, 20 mol % of the catalyst is necessary and *ee* value of product **97** is lower (42–48% *ee*).

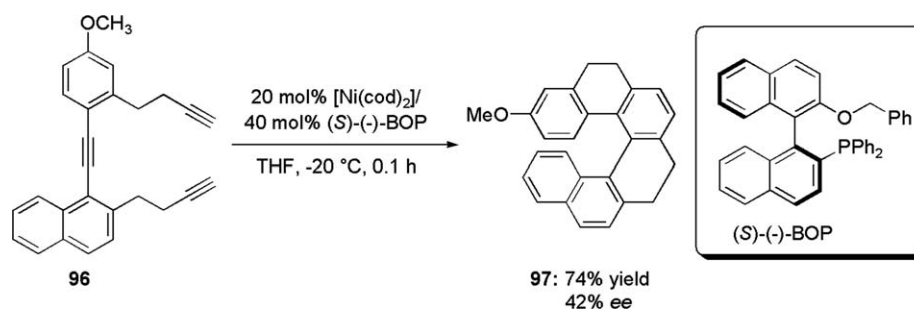
Scheme 6. Planar chirality formation by [2 + 2 + 2] cycloaddition of triynes.

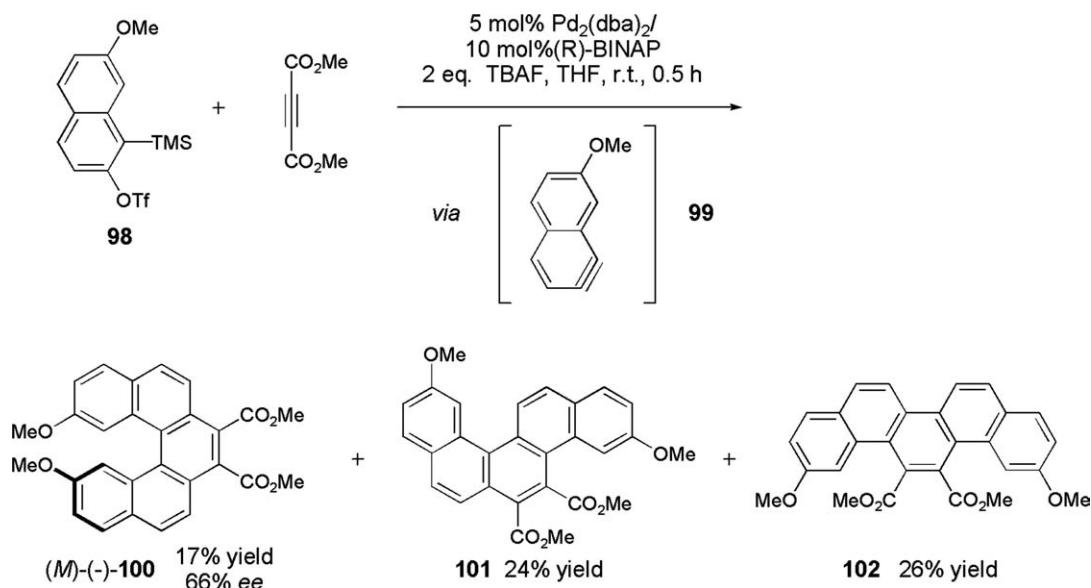
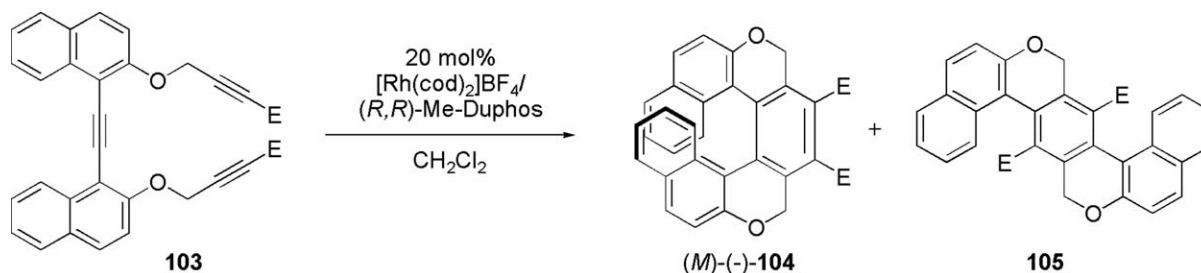


Scheme 7. Planar chirality formation by [2 + 2 + 2] cycloaddition of diyne and monoene.



Scheme 8. Helical chirality formation by Ni-catalyzed [2 + 2 + 2] cycloaddition of triyne.



**Scheme 9.** Helical chirality formation by Pd-catalyzed [2 + 2 + 2] cycloaddition of benzynes and monoynne.**Scheme 10.** Helical chirality formation by Rh-catalyzed [2 + 2 + 2] cycloaddition of triyne.

E	conditions	<b>104</b> /% yield (%ee)	<b>105</b> /% yield
CO <sub>2</sub> Me	r.t., 15 h	80 (71)	<1
CO <sub>2</sub> <i>n</i> -Bu	r.t., 15 h	71 (77)	<1
<i>n</i> -Bu	40 °C, 140 h	71 (85)	10

Another example was reported by Caeiro *et al.* using chiral BINAP-based Pd(0) catalysts in the cyclotrimerization of naphthyl triflate **98** and dimethyl acetylenedicarboxylate. Naphthyl triflate **98** was used as an adequate precursor for aryne **99**. Nonracemic 9,12-dimethoxypentahelicene **100** with moderate *ee* was afforded in a low yield along with other regioisomers **101** and **102** (Scheme 9) [21]. This is the first example of an enantioselective, metal-catalyzed cycloaddition involving arynes.

In 2007, Tanaka and coworkers reported highly enantioselective synthesis of [7] helicene-like molecules **104** *via* their Rh-catalyzed [2 + 2 + 2] cycloaddition of triynes **103** [22]. The sterically more demanding [7] hel-

icene-like molecules **104** were obtained in a good yield and enantiomeric excess (71–80% yield, 71–85% *ee*). The ladder-type molecule **105** was formed as minor byproduct (<5% yield) *via* unprecedented Rh-catalyzed formal [2 + 1 + 2 + 1] cycloaddition involving C-C triple bond cleavage (Scheme 10).

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