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Biscarbene−Ruthenium Complexes in Catalysis: Novel Stereoselective Synthesis of (1*E*,3*E*)-1,4-Disubstituted-1,3-dienes via Head-to-Head Coupling of Terminal Alkynes and Addition of Carboxylic Acids

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Abstract: The reaction of a variety of alkynes RC≡CH with a variety of carboxylic acids R^1CO_2H, in the presence of 5% of $RuCl(COD)C_5Me_5$, selectively leads to the dienylesters (1*E*,3*E*)-$RCH^1{=}CH^2{-}CH^3{=}C(R){-}(O_2CR^1)$. The reaction also applies to amino acid and dicarboxylic acid derivatives. It is shown that the first step of the reaction consists of the head-to-head alkyne coupling and of the formation of the metallacyclic biscarbene−ruthenium complex $(C_5Me_5)(Cl)Ru{:}\overline{C(R){-}CH{=}CH{-}C}{:}(R)$, isolated for R = Ph and catalyzing the formation of dienylester. D-labeled reactions show that the alkyne protons remain at the alkyne terminal carbon atoms and carboxylic acid protonates the C^1 carbon atom. QM/MM (ONIOM) calculations, supporting a mixed Fischer−Schrock-type biscarbene complex, show that protonation occurs preferentially at the carbene carbon C^1 adjacent to Ru, in the relative cis position with respect to the Ru−Cl bond, to give a mixed C(1)alkyl−C(4)carbene complex in which the C^4 carbene is conjugated with the noncoordinated $C^2{=}C^3$ double bond. This 16-electron intermediate has a weak stabilizing α agostic C−H bond. This most stable isomer appears to have a C^4 center more accessible to the nucleophilic addition which accounts for the experimentally observed product.

Introduction

The selective combinations of several molecules into only one added value product are attracting an increasing interest for the development of clean syntheses with atom economy. Metal catalysts especially promote the discovery of such new processes.[1,2] Although selective palladium catalyzed cross-coupling and Heck reactions cannot be overlooked, they usually require preliminary halogenation or metalation of substrates and release a salt as byproduct.[3] By contrast, ruthenium catalysts have recently promoted a variety of carbon−heteroatom[2] and carbon−carbon[1,4] bond formation reactions by the coupling of simple unsaturated substrates, such as alkynes.[5]

The catalyzed dimerization of alkynes offers a set of versatile and target products.[6] The dimerization of acetylene itself, catalyzed by the alkynylcopper derivative, constitutes an industrial access to but-1-en-3-yne and to neoprene rubber.[7] Whereas palladium catalysts provide the dimerization of functional alkynes with selective (terminal)C−(internal)C bond coupling,[8] ruthenium catalysts preferentially lead to 1,3-enynes with terminal carbon couplings.[9−13] By contrast, $RuH_2(CO)(PPh_3)_3$[14] and $RuH_3(PCy_3)C_5Me_5$[15] dimerize terminal alkynes

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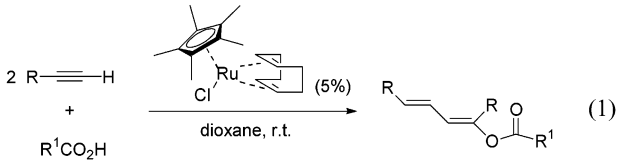
into the butatriene derivatives RCH═C═C═CHR. Ruthenium vinylidene intermediates Ru═C═CHR are known to control these 1,3-enyne and butatriene formations via mixed (vinylidene)(alkynyl)ruthenium intermediates, followed by formal vinylidene insertion into the (alkynyl)carbon−ruthenium bond.[12−15]

By contrast, a completely different stoichiometric head-to-head coupling of alkynes has been discovered by Singleton et al., affording a metallacyclic biscarbene complex.[16] Despite the interest to selectively produce functional dienes from alkynes, such a stoichiometric coupling has not yet been used to initiate the RC(Y)═CH−CH═C(Y)R backbone catalytic formation.

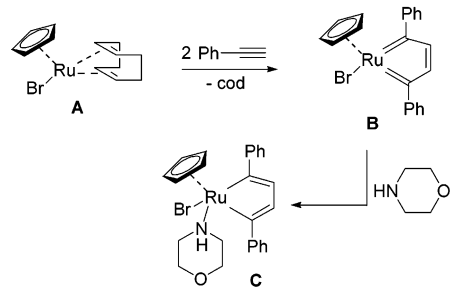
We now report a new chemical transformation, catalyzed by $RuCl(COD)C_5Me_5$, involving the combination of two molecules of alkynes and one molecule of carboxylic acid to selectively afford functional conjugated dienes (eq 1). It is established that this general catalytic reaction involves the head-to-head coupling of 2 mol of terminal alkyne at a ruthenium site and the formation of a metallacyclic biscarbene−ruthenium as the key catalytic species. It takes place with stereoselective formal addition of proton and carboxylate at C^1 and C^4 carbon atoms with concomitant C−C, C−H, and C−O bond formation. Computational studies show that the biscarbene−ruthenium complex, which is consistent with a complex containing both Fischer- and Schrock-type carbene moieties, on protonation does not lead to the expected η^3-allylcarbene ruthenium intermediate,[17,18] but rather gives a mixed C^1 alkyl, C^4 carbene ruthenium intermediate stabilized by a very weak agostic C^1−H bond.



(1)

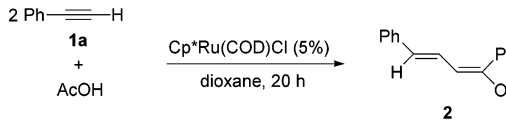
Results and Discussion

(1) Catalytic Combination of 2 mol of Alkynes with Carboxylic Acids. The reaction of phenylacetylene with $RuBr(COD)C_5H_5$ (**A**) was previously shown to lead to a metallacyclic biscarbene complex **B** which adds a two-electron nitrogen ligand to afford a classical metallacyclopentadiene complex **C**[16] (eq 2). This stoichiometric head-to-head coupling of alkynes analogous to intermediate **B** has been supported by similar observations with several C_5R_5Ru complexes and osmium derivatives.[18,19] The displacement of the 1,4-disubstituted C_4 biscarbene ligand from the metal, as a step toward catalysis, was considered. It is well known that the carbene ligand can insert into a metal−hydride bond, arising from the protonation of an 18-electron Fischer-type metal carbene complex.[20] Thus, the activation of alkynes, in the presence of carboxylic acid, with the more electron-rich ruthenium precursor $RuCl(COD)(C_5Me_5)$ than complex **A** has been investigated.



(2)

The reaction of 2 equiv of phenylacetylene (2.5 mmol) with 1 equiv of acetic acid in the presence of 5 mol % of catalyst precursor $RuCl(COD)C_5Me_5$[21] in 5 mL of dioxane leads, after 20 h at room temperature, to 77% conversion of phenylacetylene **1a** and to the formation of only one stereoisomer, (1*E*,3*E*)-1,3-dienyl acetate **2**[22] (eq 3). The 1*E*,3*E* stereochemistry was established by the ^1H NMR ($CDCl_3$) spectra of **2** and model derivatives.[23]



(3)

The reaction is very sensitive to the nature of the solvent as under similar conditions the conversion of phenylacetylene into derivative **2** was 75% in THF, 53% in DMF, 49% in acetonitrile, 40% in dichloromethane, 37% in toluene, and 30% in ethanol

(9) Ru(trispyrazolylborate)Cl$(PPh_3)_2$[10] and $RuCl(═C═CHPh)(PPh_3)C_5Me_5$[11] lead to the *E* isomer of 1,3-enynes, whereas $RuH_2[P(CH_2CH_2PPh_2)_3]$[12a] and $RuH(H_2)[P(CH_2CH_2PPh_2)_3]^+$[12b] afford the *Z* isomer. However, the nature of the alkyne itself can differently orientate the configuration of the 1,3-enyne.[10b,11,13]

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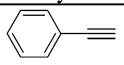
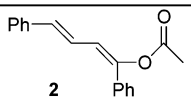
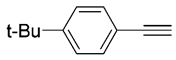
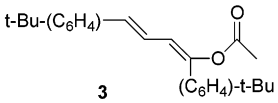
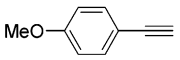
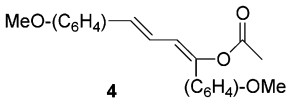
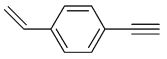
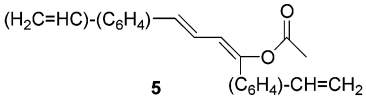
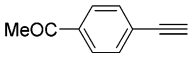
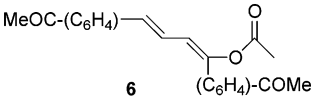
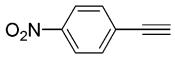
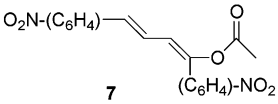
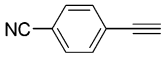
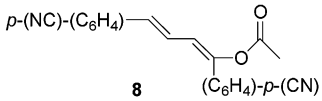
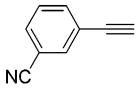
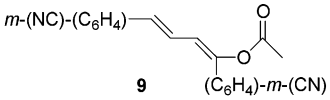
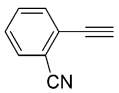
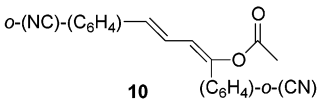
(23) The stereochemistry of derivatives **2** was established by ^1H NMR ($CDCl_3$) of [$PhCH^3═CH^2−CH^1═C(Ph)OAc$] **2** and model compounds. The NOE experiments performed on **2** were not conclusive as they do not show a significant increase (2%) of the H^1 signal ($\delta = 6.29$ ppm) on irradiation of the acetate protons ($\delta = 2.21$ ppm). The 1*E* configuration of $H^1C═CH$-(Ph)OAc was established by comparison of the ^1H NMR data of a mixture of *E* and *Z* isomers $PhCH^3═CH^2−CH^1═C(Ph)OAc$ to that of the acetoxystilbene *E* and *Z* isomers. As the transvinylation of vinylester is known to be catalyzed by $Ru_3(CO)_{12}$ under an atmosphere of carbon monoxide,[24] the derivative **2** was reacted with acetic acid in the presence of $Ru_3(CO)_{12}$ at 150 °C for 3 h, and both isomers $PhCH^3═CH^2−CH^1═C(Ph)OAc$ were then present in the ratio 80/20. They showed $H^1C═C(OAc)$ signals, respectively, at $\delta = 6.29$ ppm, as the starting product **2**, and at $\delta = 6.61$ ppm for the new isomer. These two isomers can be directly compared to those of acetoxystilbene. The *E* acetoxystilbene isomer shows an alkenyl proton signal at low field chemical shift ($\delta = 6.42$ ppm) with respect to its *Z* isomer ($\delta = 6.62$ ppm).[25] These respective chemical shifts allow one to attribute the configuration 1*E* to the $H^1C═C(Ph)OAc$ bond of **2** which shows the lower field signal of both isomers.

Table 1. Combination of Arylacetylene and Acetic Acid into Dienyl Acetates **2**−**10**

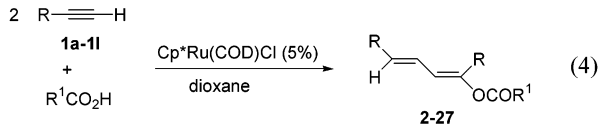
Alkynes	Dienes	Yields a)	Reaction time b)
 **1a**	 **2**	90%	20 h
 **1b**	 **3**	70%	45h
 **1c**	 **4**	85%	42 h
 **1d**	 **5**	60%	20 h
 **1e**	 **6**	91%	2 h
 **1f**	 **7**	85%	30 min
 **1g**	 **8**	81%	15 min
 **1h**	 **9**	85%	40 min
 **1i**	 **10**	80%	120 min

[a] Reaction conditions: alkyne (2.5 mmol), catalyst $RuCl(C_5Me_5)COD$ (0.125 mmol), dioxane (1 mL), acetic acid (1.25 mmol), stirred at room temperature for 15 min to 45 h. Isolated yields. [b] Determined for complete conversion of alkyne by gas chromatography.

yields. Thus, the reaction appears to be favored in cyclic ethers that are potentially two-electron weak ligands. Although the reaction cannot be performed in neat acetic acid, an increase of the reagent concentration favors the catalytic reaction, and the best conditions for the transformation **1a** → **2** were found for 2.5 mmol of alkyne and 1.25 mmol of acetic acid in 1 mL of dioxane at room temperature for 20 h. The alkyne conversion was thus completed, and derivative **2** was isolated in 90% yield. These basic conditions were retained for the following studies. Under the same conditions, the less sterically hindered complex $RuCl(COD)C_5H_5$ only partially converts (40%) the alkyne **1a** into diene **2**. The electron richness of the catalyst precursor $RuCl(COD)C_5Me_5$ appears to favor the reaction, likely by promoting the oxidative coupling of the alkyne.

A variety of arylacetylenes **1a**−**1i** were reacted with acetic acid in 1 mL of dioxane at room temperature for 15 min to 45 h according to the nature of the aryl group, and the results in the formation of dienes **2**−**10** (eq 4) are given in Table 1.

Table 1 shows that good yields are obtained (60−90%) when the reaction is performed at room temperature. It is noteworthy that the reaction is faster for alkynes containing electron-withdrawing groups at the aryl para position **1g** (NC) > **1f** (O_2N) > **1e** (MeCO) > **1a** (H) for which the completed alkyne conversion occurs after 0.25, 0.5, 2, and 20 h, respectively. The reaction is disfavored for electron-donating groups **1b** (^{t}Bu) < **1c** (MeO) < **1a** (H). The electron-withdrawing group at the phenyl para position favors the reaction over the meta and ortho positions (**1g** > **1h** > **1i**).

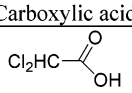
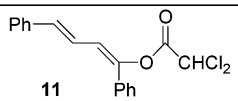
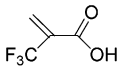
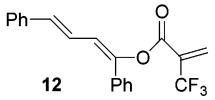
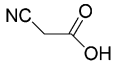
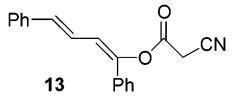
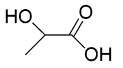
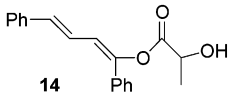
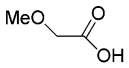
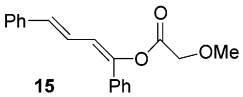
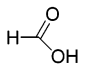
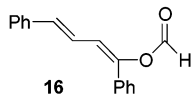
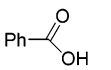
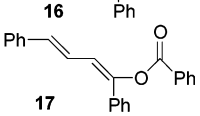
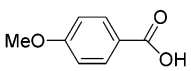
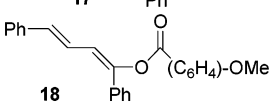
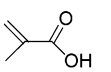
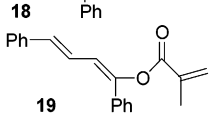
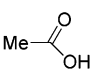
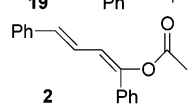
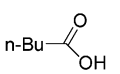
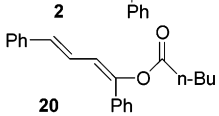
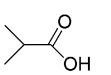
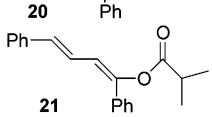
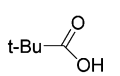
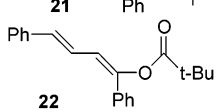


(4)

It is noteworthy that the reaction does not apply to 2-pyridylacetylene and 4-aminophenylacetylene, and this is likely due to the in situ deprotonation of the acetic acid. Indeed, the transformation **1a** → **2** is completely inhibited when 1 equiv of base such as aniline is added to the reaction medium or when $Et_4N^+AcO^-$ is used instead of acetic acid.

The combination of phenylacetylene with a variety of carboxylic acids in the presence of 5 mol % of $RuCl(COD)C_5Me_5$ takes place under the same conditions (eq 4). The results,

Table 2. Catalytic Reaction of Phenylacetylene with Carboxylic Acid

Carboxylic acid	pKa	Dienes	Yields a)	Reaction time b)
	1.48	 **11**	30%	15 h
	2.07	 **12**	70%	22 h
	2.45	 **13**	85%	17 h30
	3.08	 **14**	80%	18 h
	3.55	 **15**	93%	18 h
	3.75	 **16**	62%	20 h
	4.19	 **17**	98%	20 h
	4.47	 **18**	45%	18 h
	4.58	 **19**	91%	20 h
	4.75	 **2**	90%	20 h
	4.82	 **20**	60%	24 h
	4.84	 **21**	70%	23 h
	5.03	 **22**	91%	20 h

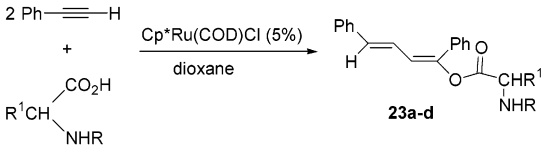
[a] Reaction conditions: phenylacetylene (2.5 mmol), catalyst $RuCl(C_5Me_5)COD$ (0.125 mmol), dioxane (1 mL), acid (1.25 mmol), stirred at room temperature for 15 to 24 h. Isolated yields. [b] Determined for complete conversion of alkyne by gas chromatography.

summarized in Table 2, show that this new synthesis of dienes is general and tolerates a large variety of functional groups and carboxylic acids. This one-step reaction allows the direct access to diene monomer containing methacrylate group (**12**, **19**) and the introduction of small (**16**) or bulky (**22**) carboxylic acid. However, the strongest acids do not lead to the dienes, as only 30% yield of **11** could be obtained with Cl_2CHCO_2H (pK_a = 1.48). CF_3CO_2H (pK_a = 0.25) does not lead to the conversion of alkynes. This is likely due to the protonation of the ruthenium catalyst which is expected to inhibit the oxidative coupling of two molecules of alkyne at the ruthenium site. As a consequence, the head-to-head coupling of alkynes does not result from double insertion of alkyne into the Ru−H and then into the resulting Ru−C bonds, as confirmed later by labeled experiments.

The direct reaction of arylacetylenes with amino acids does not allow the conversion of alkynes. However, when the amino group is protected with a BOC or a CBz group (BOC = CO_2-^{t}Bu, CBz = CO_2CH_2Ph), the combination of phenylacetylene with different amino acids leads to the synthesis of dienylaminoesters **23a**−**d** (Scheme 1).

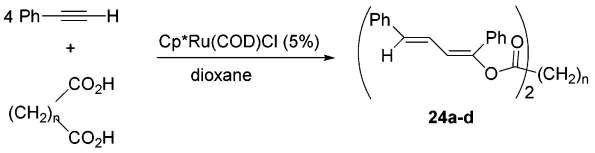
The reaction of arylacetylenes with dicarboxylic acids can be performed in the presence of 4 equiv of phenylacetylene, under similar conditions (Scheme 2). Oxalic acid (n = 0) (pK_{a1} = 1.38) does not allow the formation of diester, whereas for diacids with a longer carbon chain (n > 1), the reaction leads to only one isomer of dienylesters **24a**−**d** with good yields (Scheme 2). This synthesis tolerates functional groups, as the reaction of (L)-tartaric acid or (L)-glutamic acid, respectively, leads to the products **24e** and **24f** in 50% yield (Scheme 3).

Scheme 1



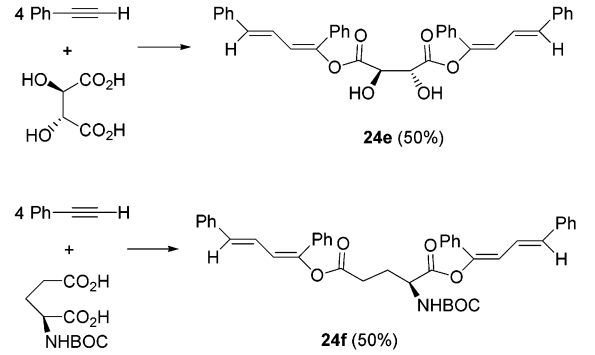
Amino acid		Compound **23** (yield)
R^1	R	
CH_3	CBz	**23a** (84%)
$PhCH_2$	BOC	**23b** (75%)
H	BOC	**23c** (55%)
$HOCH_2$	BOC	**23d** (33%)

Scheme 2



Diacid		Compound **24** (yield)
n	pKa_1	
1	2.92	**24a** (50%)
2	4.24	**24b** (75%)
4	4.39	**24c** (70%)
6	4.46	**24d** (70%)

Scheme 3



The above reaction can be extended to alkylacetylenes; however, the transformation leads to moderate yields in dienes (Table 3). From hex-1-yne, oct-1-yne, and trimethylsilylacetylene are obtained the dienes **25** (20%), **26** (40%), and **27** (20%), respectively (eq 4).

This novel reaction, performed with electron-rich ruthenium(II) precatalysts, contrasts well with the regioselective addition of carboxylic acids to alkynes with electrophilic ruthenium(II) catalysts promoting the formation, without preliminary head-to-head coupling of the alkynes, of enol esters via either Markovnikov addition with $RuCl_2(PR_3)$(arene)[2b] or anti-Markovnikov addition with Ru(methallyl)$_2$(diphosphine)[2a,26] catalysts.

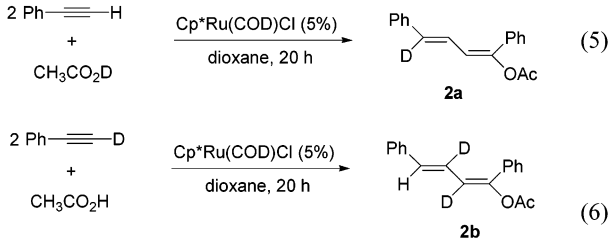
(2) Mechanism Study. To propose a reaction mechanism and its catalytic cycle, several key experiments involving labeled reagents and stoichiometric reactions were designed. The reaction of 2 equiv of phenylacetylene with deuterated acetic acid with 5 mol % of RuCl(COD)C_5Me_5 at room temperature

Table 3. Combination of Alkylacetylene and Acetic Acid into Dienyl Acetates **25**−**27**

Alkynes	Dienes	Yields a)	Reaction time b)
n-Bu—≡ **1j**	n-Bu, O, n-Bu **25**	20%	22 h
n-Hex—≡ **1k**	n-Hex, O, n-Hex **26**	40%	19 h
TMS—≡ **1l**	TMS, O, TMS **27**	20%	16 h

[a] Reaction conditions: alkyne (2.5 mmol), catalyst RuCl(C_5Me_5)COD (0.125 mmol), dioxane (1 mL), acetic acid (1.25 mmol), stirred at room temperature for 16 to 22 h. Isolated yields. [b] Determined for complete conversion of alkyne by gas chromatography.

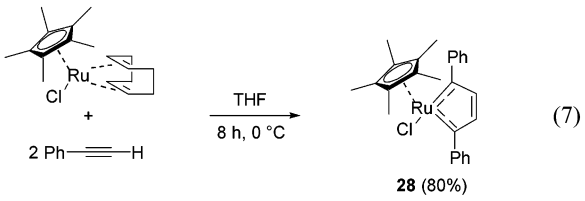
for 22 h afforded only derivative **2a**, selectively deuterated at carbon C^1, isolated in 85% yield (eq 5). The C^1 deuterated phenylacetylene and acetic acid were reacted under the same conditions and afforded only derivative **2b** in 68% which showed complete retention of deuterium at carbons C^2 and C^3 (eq 6). These experiments definitively show a head-to-head coupling of the alkynes, with retention of both terminal C−H (C−D) bonds, and that the carboxylic acid formally adds to carbon C^1 (proton) and to carbon C^4 (carboxylate). Thus, a mechanism involving a vinylidene intermediate with 1,2-migration of the terminal hydrogen atom cannot be considered.[12]



The catalyst precursor RuCl(COD)C_5Me_5 (0.37 mmol) was reacted with 2 equiv of phenylacetylene (1.85 mmol) in 5 mL of degassed THF. After 8 h of reaction at 0 °C, the complex **28** was formed and isolated in 80% yield and contained a biscarbene ligand (^{13}C NMR, δ (Ru)C = 262.4 ppm, δ (=CH) = 155.1 ppm) (eq 7). The same complex **28** was recently obtained by reaction of RuCl($Me_2NCH_2CH_2NMe_2$)C_5Me_5 with phenylacetylene in diethyl ether,[27] whereas RuCl(PPh_3)$_2C_5Me_5$ with acetylene by contrast leads to the ruthenacyclopentadiene complex $C_5Me_5(PPh_3)(Cl)Ru\overline{CH{=}CH{-}CH{=}CH}$.[5g] This complex **28** can be viewed as a mixed Fischer−Schrock-type biscarbene−ruthenium(IV) complex as discussed later (Scheme 5). We can adopt for this biscarbene representation the formula **28** (eq 7), which is the average situation between the two Scheme 5 canonical forms.

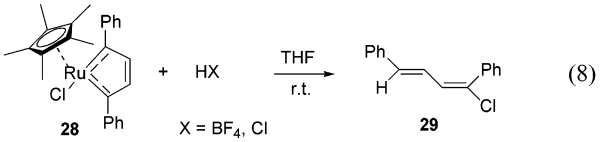
The isolated complex **28** was reacted with 1 equiv of acetic acid in CD_2Cl_2 in an NMR tube and led to the complete formation of derivative **2**. Complex **28** was used as a catalyst precursor (5 mol %) in the reaction of 2 equiv of phenylacetylene (2.5 mmol) with 1 equiv of acetic acid (1.25 mmol) in

(24) Murray, R. E. European Patent, 0351 603 A2, 1989.
(25) Bach, R. D.; Woodard, R. A.; Anderson, T. J.; Glick, M. D. *J. Org. Chem.* **1982**, *47*, 3707.
(26) (a) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247. (b) Doucet, H.; Höfer, J.; Derrien, N.; Bruneau, C.; Dixneuf, P. H. *Bull. Soc. Chim. Fr.* **1996**, *133*, 939.
(27) Gemel, C.; Le Pensee, A.; Mauthner, K.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **1997**, *128*, 1189.



(7)

dioxane (1 mL) at 25 °C for 20 h. The reaction affords the diene **2** and shows that complex **28** has a catalytic activity similar to that of its precursor $RuCl(COD)C_5Me_5$. Complex **28** was reacted with 1 equiv of HBF_4 in Et_2O and was immediately transformed into several organometallic salts which could not be identified but led to an organic product which has been identified as the chlorinated 1*E*,3*E*-diene **29** in 50% yield (eq 8). The same reaction performed with HCl in Et_2O and **28** also affords the same chlorinated diene **29** isolated but in 33% yield. By contrast, complex **28** does not react with $AcO^-NEt_4^+$ in dioxane at room temperature. These experiments support that the initial reaction of intermediate **28** takes place with the proton and then with carboxylate and not the reverse.



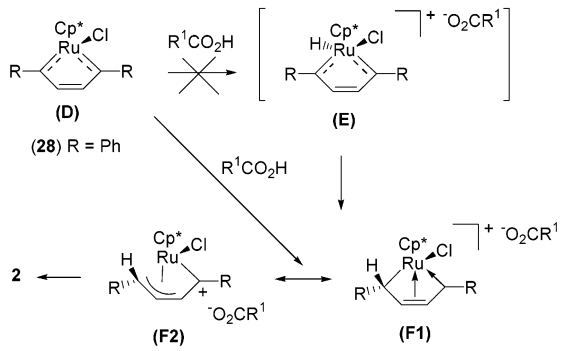
(8)

Consequently, the above experiments and classical organometallic concepts would suggest that an intermediate of type **F** could be a catalytic intermediate (Scheme 4). The key catalytic intermediate is the biscarbene−ruthenium complex of type **D**, that has been isolated, characterized, and shown to catalyze the diene formation when R = Ph (**28**). The carboxylic acid first protonates the complex to give the transient ruthenium intermediate **E** or **F**, as ammonium acetate does not react with **28**. Carbene ligands readily insert into the metal−hydride bond to give an alkyl group,[20] and this insertion is favored by the addition of a two-electron ligand. Thus, species **F**, with a coordinated C=C bond, corresponding to a mixed carbene allyl species which can be represented by the canonical forms **F1** and **F2**, might be expected from ruthenium hydride species (**E**). It is likely, as a Ru−H species was never observed by ^1H NMR on addition of acids to complex **28** at low temperature, that the protonation of the biscarbene **D** directly led to a mixed allyl carbene ruthenium species (**F**), by direct protonation of the carbene carbon.

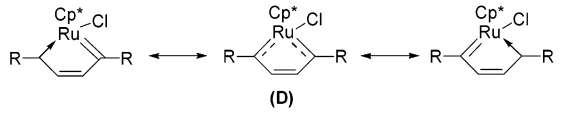
Indeed, mixed allyl carbene−ruthenium complexes are well known.[17] Furthermore, recently Kirchner et al.[18] showed that intramolecular migration of a two-electron ligand (PR_3) to the adjacent carbene carbon takes place, in related cationic biscarbene complexes $C_5H_5(Ph_3)Ru(:C(Me)\text{-}CR{=}CR\text{-}(Me)C:)^+X^-$ to afford an allyl carbene ligand.

The remaining carbene atom in the cationic ruthenium(IV) intermediate (**F**) should be more electrophilic than that in neutral biscarbene (**D**), and then the carboxylate on addition to this electrophilic carbon atom should lead to the release of the diene of type **2**. The formation of the chlorinated diene **29** on protonation of **28** by HBF_4 can thus be explained by the internal 1,2-migration of the chloride ligand of **F** species to the carbene carbon atom (eq 8).

Scheme 4



Scheme 5



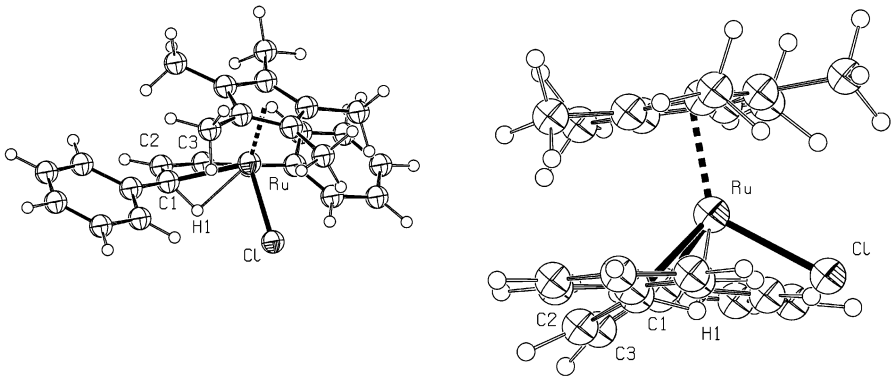
As an attempt to identify the most stable protonated species of biscarbene complex **D** and the relative cis or trans position of the incoming proton with respect to the chlorine atom, theoretical calculations, using the hybrid QM/MM (ONIOM) method with Gaussian 98, were thus undertaken.

(3) Computational Studies. The electronic structure and geometrical features of the biscarbene complex **D** have been fully discussed by Calhorda et al.[28] with a level of calculation similar to that used in this work, and no further comment is needed on this species. We thus focus our study on the structure and reactivity of the protonated species of **D**. Protonation can occur at several sites leading to different isomers which can themselves generate various diene products after reaction with the carboxylate.

We have optimized the structure of a protonated biscarbene complex with various initial positions for the proton. Two resulting minima were obtained, and their structures are shown as **T1** and **T2** (Figures 1 and 2). In the two species, the C−H bond is fully formed. No minimum with a protonation exclusively at the ruthenium atom could be located on the potential energy surface. The two isomers **T1** and **T2** differ by the relative position of the C−H and Ru−Cl bonds relative to the $C^1-C^2-C^3-C^4$ backbone. In the most stable structure, **T1**, the C−H and Ru−Cl bonds are cisoïd, the less stable isomer **T2** with transoïd C−H and Ru−Cl bonds being 15.2 kcal mol^{-1} above **T1**.

In **T1**, the C^1−H bond of 1.120 Å is just slightly longer than a normal $C(sp^3)$−H bond. Protonation of C^1 has significantly elongated the Ru−C^1 bond (2.315 Å) as compared to Ru−C^4 (1.981 Å) and that in the biscarbene complex **A** (1.942 Å) (eq 2).[16] The Ru···H distance, equal to 1.952 Å, is on the long side for an agostic interaction. These features are characteristic of the formation of an alkyl group at C^1 in which the new C−H bond makes a weak agostic bond with the ruthenium center. Protonation to C^1 has not modified the carbon backbone of the metallacycle. A double bond is clearly identified between C^2 and C^3 with a typical C^2-C^3 distance of 1.388 Å, and this double bond remains conjugated with the π carbene orbital of C^4 as shown by the rather short C^3-C^4 distance (1.412 Å) for

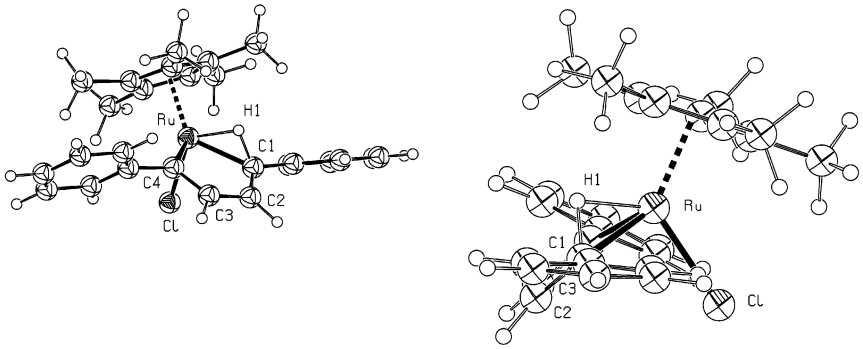
(28) Rüba, E.; Mereiter, K.; Schmid, R.; Sapunov, V. N.; Kirchner, K.; Schottenberger, H.; Calhorda, M. J.; Veiros, L. F. *Chem.-Eur. J.* **2002**, *8*, 3948.



C1-H1 = 1.120 Å
Ru-C1 = 2.315 Å
C1-C2 = 1.412 Å
C2-C3 = 1.388 Å
C3-C4 = 1.412 Å

Ru-C4 = 1.981 Å
H...Cl = 2.407 Å

Figure 1. Two views of the optimized (B3PW91) structure of $Cp^*Ru(C_4Ph_2H_2)(Cl)(H)^+$, isomer **T1**. Distances in angstroms.



C1-H1 = 1.226 Å
Ru-H1 = 1.702 Å
Ru-C1 = 2.110 Å

Ru-C4 = 1.971 Å
Ru-Cl = 2.298 Å

Figure 2. Two views of the optimized (B3PW91) structure of $Cp^*Ru(C_4Ph_2H_2)(Cl)(H)^+$, isomer **T2**. Distances in angstroms.

a single bond. A key feature of this species is that the π orbitals of the allylic $C^2-C^3-C^4$ system do not interact directly with Ru as is often observed in allyl complexes. A mixed $C^1-C^2-C^3$ allyl C^4 carbene ligand as observed in some molybdenum[17] or ruthenium[18] complexes cannot be retained. Thus, the hypothetical intermediate such as **F1** or **F2** can no longer be retained. This appears from the dihedral angle of $Ru-C^4-C^3-C^2$ which is essentially 0°. It should be noted furthermore that surprisingly the entire metallacycle has remained planar. This protonated complex is best described as having a carbene group at C^4 stabilized by the $C^2=C^3$ double bond and by the phenyl ring and an alkyl group at C^1 with a very weak C−H agostic interaction. This weak agostic bond allows one to satisfy the 18-electron environment of the ruthenium atom in **T1** as it is clear that the $C^2=C^3$ bond does not contribute to this. Another stabilizing interaction can be identified in this complex, although it cannot be quantified. The distance between the negatively charged chlorine center and the H of C^1 is only 2.407 Å, which is short enough for a weak $Cl^{\delta-}\cdots H^{\delta+}-C$ interaction.[29]

The less stable isomer, **T2**, has the C^1-H and Ru−Cl bonds transoïd relative to the $C^1-C^2-C^3-C^4$ backbone. The C^1-H bond, equal to 1.226 Å, is long for a C−H bond, and the hydrogen is only 1.702 Å from the ruthenium which indicates a definite interaction between Ru and H. In contrast to what has been obtained for **T1**, the presence of H on C^1 leads to a short $Ru-C^1$ distance of 2.110 Å. The incoming proton bridges the $Ru-C^1$ π orbital (the dihedral angle $H-C^1-Ru-C^4$ is 84°) and interacts strongly with the two Ru and C^1 sites. The remaining part of the metallacycle is identical in **T1** and **T2**, in particular, the $C^2-C^3-C^4$ system with no interaction between the $C^2=C^3$ double bond and the ruthenium atom. Therefore, **T2** also has a carbene group stabilized by a double bond and a phenyl ring.

The energy preference for **T1** over **T2** is not negligible, and several factors can contribute to it. Although the ruthenium formal oxidation numbers in the above intermediates should be considered only with extra caution, several comments can be made. There are several ways to consider the oxidation state of species **D**. If **D** is viewed as a biscarbene with a noncoordinated $C^2=C^3$ double bond, the ruthenium atom should be considered as having the formal oxidation state II. The π system of the metallacycle thus has only two electrons. An alternative extreme viewpoint is to consider that each of the two carbenes becomes an alkylidene ligand which requires a transfer of two electrons from the ruthenium atom per carbene. In this limit, the ruthenium would have the higher oxidation state of VI. An intermediate

(29) Jeffrey, G. A.; Saenger, W. In *H-Bonding in Biological Structures*; Springer: Weinheim, 1994.

situation is obtained by considering that the π system $C^1-C^2-C^3-C^4$ is occupied by a total of four electrons corresponding to the classical metallacyclopentadiene system. The ruthenium center is then at the formal oxidation state IV. This latter point of view agrees best with the analysis of the electron wave function as done by Calhorda et al.[28] However, these calculations[28] reveal that both Ru−C bonds have actually a strong double bond character, while retaining a formal Ru(IV) moiety. By doing so, the RuC_4 cycle is better described as a Ru(IV) metallacyclopentatriene than a metallacyclopentadiene. Thus, the biscarbene−ruthenium carbene is better described with the canonical forms in Scheme 5 rather than by representation **B** (eq 2). This is why the biscarbene **D** is represented as resulting from these two canonical forms. In metal complex chemistry language, it means that the biscarbene−ruthenium(IV) species **D** (or **28**) gathers in the same complex both Fischer and Schrock types of metal−carbene complexes. In molecular orbital language, it means that one of three orbitals originating from the formal t_{2g} is strongly delocalized in the π system of the $C^1-C^2-C^3-C^4$ skeleton. This has two consequences: accumulation of electron density on the carbon π system, in particular between Ru and C^1 (and Ru and C^4); thus the Ru=C becomes an obvious site for protonation. However, the formal oxidation state of Ru(IV) intrinsically decreases the ruthenium ability to be protonated. Therefore, the protonation of the Ru atom only is clearly unfavorable. This results in the formation of a strong C−H bond, with at best a weak interaction with Ru (**T1**). One can even push the formal oxidation langage to account for why **T1** is more stable than **T2**. In **T1**, the electronic density of Ru has not changed by the protonation, and only the carbon has given electronic density to the proton. In **T2**, the Ru would be more implicated in the protonation process and is required to give more density which is not favorable for a Ru(IV) system.

Because **T1** is likely to be the dominant species in solution, it is now necessary to examine its reactivity toward an incoming nucleophile. Computational methods are not well set for such studies. There is no transition state for approaching ions in the vacuum, and the solvent would play a major role in determining the position and height of the activation barrier. To understand qualitatively the regioselectivity, one is forced to consider the isolated ion and use some structural/reactivity pattern to acquire some information. In the present case, the situation is reasonably clear on steric grounds. From the views in Figures 1 and 2, it appears that no nucleophile is likely to come from the side of the C_5Me_5 ligand, and it is also evident that the direct access to the four carbon atom ligand on the opposite side of the ruthenium atom is facile even for rather large nucleophiles. The approach of the carboxylate to the π system, and to the C^4 carbon atom at which the addition takes place, on the opposite side of the ruthenium is expected to be favored. It is also rewarding to notice that the same steric considerations clearly show that **T2** would not be as reactive as **T1**. One sees from Figure 3 that in **T2** the access to C^4 is considerably more hindered by the position of Cl and the orientation taken by the phenyl rings than in **T1**. This also eliminates **T2** as an intermediate to produce the final product. As a final remark, it is frustrating not to understand how the diene is formed by decomposition of the metallacycle after the addition of the nucleeophile, but such complex decomposition on a large size system is beyond our present computational possibilities.

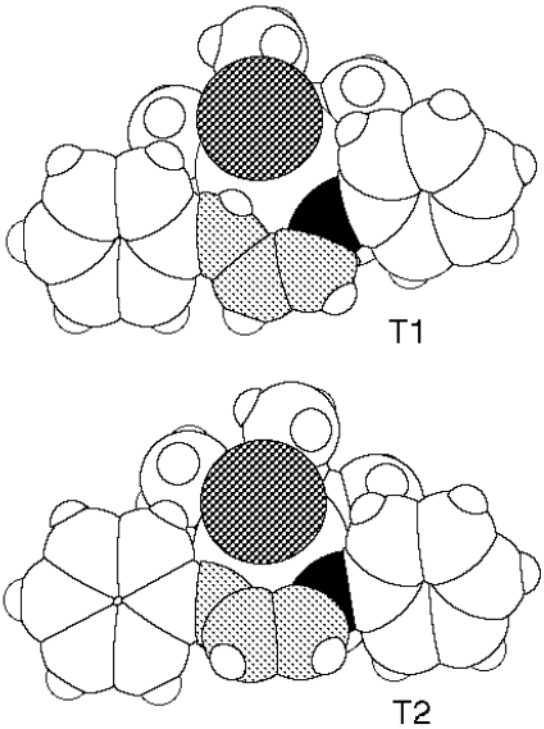
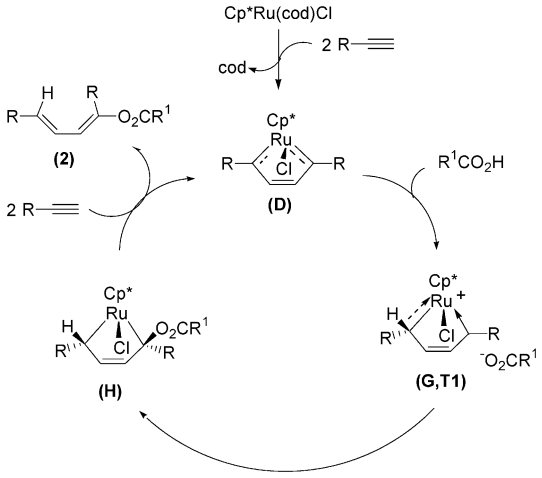


Figure 3. Space-filling models of the optimized structures of **T1** and **T2** isomers of $Cp^*Ru(C_4Ph_2H_2)(Cl)(H)^+$. In black is the carbon where the nucleophile adds. In light gray are the three other carbons of the RuC_4 ring. In intermediate gray is the chlorine atom.

Scheme 6



(4) Catalytic Cycle. On the basis of theoretical studies, the catalytic cycle as described in Scheme 6 can be proposed. It involved (i) the direct protonation of intermediate **D** carbene carbon C^1 to give **G**, with a very weak $H-C^1$ agostic bond stabilization corresponding to the calculated species **T1**, and (ii) the addition of carboxylate to the C^4 carbene carbon atom to give the intermediate **H** releasing the diene **2** and the catalyst. Expected intermediates as species **F1** or **F2** are now ruled out.

It was observed (Table 1) that the formation of the dienes **2** is much faster with electron-withdrawing groups at the para position of phenylacetylene (NC, O_2N, RCO) than with the electron-donating groups (MeO, ^{t}Bu). This strong influence can be rationalized in terms of the stability of the mixed alkyl carbene complexes **(G = T1)**. Indeed, electron-releasing substituents on aryl groups are known to stabilize Fischer-type

carbene complexes. The alkyne *p*-$MeOC_6H_4C{\equiv}CH$ is expected to lead to a more stable carbene and a less electrophilic C^4 carbene carbon in intermediate **G** than *p*-$NCC_6H_4C{\equiv}CH$. Thus, the former is expected to lead to a slower carboxylate addition reaction than the latter as observed in Table 1.

Conclusion

The above result shows a novel catalytic reaction which combines, in one step, two molecules of alkynes and one of carboxylic acid to afford only one diene isomer, thus with high stereoselectivity and atom economy. This unique catalytic formation of (1*E*,3*E*)-1,4-disubstituted-1,3-dienes is highly regioselective in the head-to-head coupling of alkynes and stereoselective in the concomitant formation of the three C−C, C−H, and C−O bonds. The existence of the metallacyclic biscarbene intermediate as the key catalytic species is demonstrated, for which reactivity and calculations are consistent with a mixed Fischer−Schrock-type biscarbene ruthenium(IV). Computational studies do not support the stereoselective formation of a mixed carbene allyl intermediate (**F**) on protonation. They suggest, via direct protonation at the C^1 carbene carbon atom of the biscarbene **D** rather than at the ruthenium site, that a chelating mixed C(1)alkyl, C(4)carbene ligand is formed. This chelating ligand−ruthenium system is stabilized by a very weak agostic H−C^1 bond interaction and clearly not by the $C_2{=}C_3$ double bond coordination which would rather lead to the allyl $C^1-C^2-C^3$ group.

The concept of the reactive biscarbene intermediate should allow further development via addition of pronucleophiles, and the reaction shows potential for access to new unsaturated polymers from diynes.

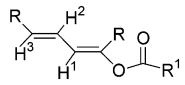
Experimental Section

All catalytic reactions were carried out under inert atmosphere in Schlenk tubes. Chemicals were obtained commercially and used as supplied. The complex $RuCl(cod)(C_5Me_5)$ was prepared according to the reported method.[21] Products were isolated by silica gel (70−230 mesh) flash column chromatography with mixed solvents (pentane/diethyl ether mixtures). ^1H and ^{13}C NMR spectra were recorded on Bruker AM 3000 WB and DPX 200 spectrometers in deuterated chloroform solutions at 298 K. IR spectra were recorded on a Bruker IFS28 spectrometer. Mass spectra were obtained on a VARIAN MATT 311 high-resolution spectrometer in Centre Regional de Mesures de l'Ouest (CRMPO), University of Rennes 1. Diethyl ether and THF were distilled from a mixture of sodium/benzophenone. Pentane, hexane, and toluene were distilled from CaH_2, and the dichloromethane was distilled from P_2O_5.

Computational Details. The full system was calculated using the hybrid QM/MM (ONIOM)[30] method with Gaussian 98.[31] The metal and all atoms in the direct vicinity of Ru are part of the quantum domain and are represented with the hybrid B3PW91[32] density functional. To maintain conjugation between the carbene and the phenyl ring, two carbons of each phenyl are part of the quantum domain (the phenyl is a vinyl at the QM level). The five methyl groups of C_5Me_5 as well as the remaining atoms of the two phenyl rings are represented at the MM(UFF) level.[33] The Ru atom was represented by the relativistic effective core potential (RECP) from the Dolg group (16 valence electrons) and its associated (8s7p5d)/[6s5p3d] basis set[34] supplemented by an f polarization function ($\alpha = 1.235$).[35] The Cl atom was represented also with the Stuttgart RECP[36] and basis set supplemented by a d polarization function ($\alpha = 0.640$).[37] A 6-31G (d,p) basis set[38] was used for the remaining atoms. Optimizations were performed without any symmetry constraint and were followed by analytical computation of the Hessian matrix to confirm the nature of the located minima on the potential energy surface.

To test the influence of the partition between the QM and MM parts within the phenyl substituent, we have optimized isomers **T1** and **T2** at the ONIOM(B3PW91/UFF) level with the phenyl ring entirely in the QM part with the same basis set as described above. This resulted in a significant increase of the computational cost: 443 versus 311 basis functions and 166 versus 114 electrons to treat at the DFT level. However, the two partitions (phenyl QM vs vinyl QM) gave virtually the same results with a difference in energy between the two isomers of 15.5 versus 15.2 kcal mol^{-1}. The geometrical parameters were also hardly altered, which validates the use for the phenyl ring of the vinyl partition scheme yielding much less expensive calculations with a comparable accuracy.

Typical Procedure for Ruthenium-Catalyzed Dimerization of Terminal Alkynes with Monocarboxylic Acids. To a solution of terminal alkyne (2.5 mmol, 1 equiv) in degassed dioxane (1 mL) were added $RuCl(cod)(C_5Me_5)$ (0.125 mmol, 5%) and carboxylic acid (1.25 mmol, 0.5 equiv) under inert atmosphere at room temperature. The reaction mixture was stirred at room temperature for 15 min to 45 h. The solvent was removed, and the product was purified by silica gel flash column chromatography (eluent pentane−diethyl ether mixtures) to give dimerization adduct as a white solid in 20−98% yield. The compounds were analyzed by NMR (^1H and ^{13}C), IR, and mass spectroscopy.



2. Yield: 90%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.21 (s, 3H, MeCO), 6.29 (d, $J = 11.1$ Hz, 1H, H^1), 6.67 (d, $J = 15.5$ Hz, 1H, H^3), 6.99 (dd, $J = 11.1$ Hz, $J = 15.5$ Hz, 1H, H^2), 7.21−7.53 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.6, 148.4, 137.2, 134.7, 134.5, 128.9, 128.7, 128.5, 128.4, 127.8, 126.5, 123.3, 120.5, 21.1. MS (EI): *m*/*z* 264.1148 (calc for $C_{18}H_{16}O_2$ 264.1150). FT-IR (KBr) ν (cm^{-1}): 3060, 3035, 3022, 1758, 1636, 1594.

3. Yield: 70%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.32 (s, 9H, ^{t}Bu), 1.36 (s, 9H, ^{t}Bu), 2.20 (s, 3H, Me), 6.25 (d, $J = 11.2$ Hz, 1H, H^1), 6.65 (d, $J = 15.5$ Hz, 1H, H^3), 7.00 (dd, $J = 11.2$ Hz, $J = 15.5$ Hz, 1H, H^2), 7.31 (m, 4H, Ar), 7.45 (m, 4H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.70, 151.9, 150.9, 148.0, 134.7, 134.0, 131.8,

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128.1, 126.3, 125.6, 125.5, 122.9, 120.3, 31.4, 21.2. MS (EI): *m/z* 376.2392 (calc for $C_{26}H_{32}O_2$ 376.2402). FT-IR (KBr) ν (cm^{-1}): 3050, 2964, 1758, 1608, 1367.

4. Yield: 85%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.17 (s, 3H, Me), 3.77 (s, 3H, Me), 3.82 (s, 3H, Me), 6.15 (d, J = 10.9 Hz, 1H, H^1), 6.56 (d, J = 15.6 Hz, 1H, H^3), 6.80 (dd, J = 10.9 Hz, J = 15.6 Hz, 1H, H^2), 6.81 (dm, J = 9.0 Hz, 2H, Ar), 6.91 (dm, J = 9.0 Hz, 2H, Ar), 7.25 (dm, J = 9.0 Hz, 2H, Ar), 7.39 (dm, J = 9.0 Hz, 2H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.7, 159.8, 159.3, 147.3, 133.3, 130.2, 129.7, 127.6, 127.2, 121.4, 119.6, 114.1, 113.9, 55.3, 55.3, 21.1. MS (EI): *m/z* 324.1367 (calc for $C_{20}H_{20}O_4$ 324.1361). FT-IR (KBr) ν (cm^{-1}): 3035, 3002, 1757, 1603, 1573. mp: 92 °C.

5. Yield: 60%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.19 (s, 3H, Me), 5.21 (d, J = 11.0 Hz, 1H, $=CH_2$), 5.30 (d, J = 11.0 Hz, 1H, $=CH_2$), 5.71 (d, J = 17.0 Hz, 1H, $=CH_2$), 5.80 (d, J = 16.6 Hz, 1H, $=CH_2$), 6.25 (d, J = 11.2 Hz, 1H, H^1), 6.63 (d, J = 15.6 Hz, 1H, H^3), 6.65−6.80 (m, 2H, =CH), 6.98 (dd, J = 11.2 Hz, J = 15.6 Hz, 1H, H^2), 7.30 (m, 4H, Ar), 7.40 (m, 4H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.6, 148.1, 138.1, 137.1, 136.8, 136.4, 136.3, 134.1, 134.0, 128.6, 126.7, 126.6, 126.4, 123.3, 120.6, 115.0, 113.9, 21.2.

6. Yield: 91%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.19 (s, 3H, Me), 2.55 (s, 3H, $ArCOCH_3$), 2.62 (s, 3H, $ArCOCH_3$), 6.35 (d, J = 11.2 Hz, 1H, H^1), 6.71 (d, J = 15.6 Hz, 1H, H^3), 7.02 (dd, J = 11.2 Hz, J = 15.6 Hz, 1H, H^2), 7.37 (d, J = 8.5 Hz, 2H, Ar), 7.54 (d, J = 8.6 Hz, 2H, Ar), 7.85 (d, J = 8.5 Hz, 2H, Ar), 7.98 (d, J = 8.6 Hz, 2H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 197.4, 169.3, 148.4, 141.4, 138.9, 137.2, 136.2, 134.2, 128.9, 128.6, 128.5, 126.6, 125.3, 121.6, 26.7, 26.6, 21.0. MS (EI): *m/z* 348.1365 (calc for $C_{22}H_{20}O_4$ 348.1361). FT-IR (KBr) ν (cm^{-1}): 3053, 3002, 1758, 1681, 1637, 1598, 1560.

7. Yield: 85%. ^1H NMR (200.131 MHz, CD_2Cl_2) δ ppm: 2.22 (s, 3H, Me), 6.43 (d, J = 11.1 Hz, 1H, H^1), 6.76 (d, J = 15.4 Hz, 1H, H^3), 6.98 (dd, J = 11.1 Hz, J = 15.4 Hz, 1H, H^2), 7.44 (d, J = 8.8 Hz, 2H, Ar), 7.62 (d, J = 8.8 Hz, 2H, Ar), 8.15 (d, J = 8.8 Hz, 2H, Ar), 8.29 (d, J = 8.8 Hz, 2H, Ar). ^{13}C NMR (50.329 MHz, CD_2Cl_2) δ ppm: 171.1, 150.1, 149.0, 145.0, 142.6, 135.7, 131.2, 129.1, 128.4, 126.0, 125.8, 124.0, 22.7. MS (EI): *m/z* 354.0867 (calc for $C_{18}H_{14}O_6N_2$ 354.0852). FT-IR (KBr) ν (cm^{-1}): 3055, 1758, 1653, 1589, 1507, 1340.

8. Yield: 81%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.20 (s, 3H, Me), 6.36 (d, J = 11.1 Hz, 1H, H^1), 6.68 (d, J = 15.6 Hz, 1H, H^3), 6.91 (dd, J = 11.1 Hz, J = 15.6 Hz, 1H, H^2), 7.37 (dm, J = 8.2 Hz, 2H, Ar), 7.54 (m, 4H, Ar), 7.70 (dm, J = 8.6 Hz, 2H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.2, 148.0, 141.0, 138.7, 134.0, 132.5, 132.4, 129.0, 127.0, 125.6, 121.6, 118.8, 118.3, 112.8, 111.2, 21.0. MS (EI): *m/z* 314.1043 (calc for $C_{20}H_{14}O_2N_2$ 314.1055). FT-IR (KBr) ν (cm^{-1}): 3054, 2226, 1760, 1634, 1599.

9. Yield: 85%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.20 (s, 3H, Me), 6.34 (d, J = 10.6 Hz, 1H, H^1), 6.65 (d, J = 15.6 Hz, 1H, H^3), 6.80 (dd, J = 10.6 Hz, J = 15.6 Hz, 1H, H^2), 7.3−7.7 (m, 8H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.3, 147.3, 137.9, 135.7, 133.4, 132.9, 132.6, 131.8, 131.2, 130.6, 130.1, 129.6, 129.6, 124.4, 121.5, 118.6, 118.3, 113.2, 113.0, 21.0. MS (EI): *m/z* 314.1059 (calc for $C_{20}H_{14}O_2N_2$ 314.1055). Anal. Calcd for $C_{20}H_{14}O_2N_2$: C, 71.00; H, 4.31. Found: C, 70.75; H, 4.40. FT-IR (KBr) ν (cm^{-1}): 3068, 2231, 1765, 1636, 1594, 1573.

10. Yield: 80%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.21 (s, 3H, Me), 6.54 (d, J = 11.1 Hz, 1H, H^1), 6.74 (dd, J = 11.1 Hz, J = 15.2 Hz, 1H, H^2), 7.02 (d, J = 15.2 Hz, 1H, H^3), 7.25 (m, 1H, Ar), 7.4−7.8 (m, 7H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.1, 146.9, 139.8, 137.6, 133.8, 133.3, 132.8, 132.7, 131.3, 131.1, 129.6, 128.1, 126.8, 125.8, 122.6, 117.8, 117.4, 112.1, 111.1, 20.8. MS (EI): *m/z* 314.1043 (calc for $C_{20}H_{14}O_2N_2$ 314.1055). FT-IR (KBr) ν (cm^{-1}): 3057, 2227, 1757, 1636, 1593.

11. Yield: 30%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 6.07 (s, 1H, $CHCl_2$), 6.40 (d, J = 11.1 Hz, 1H, H^1), 6.74 (d, J = 15.6 Hz, 1H, H^3), 7.00 (dd, J = 11.1 Hz, J = 15.6 Hz, 1H, H^2), 7.24−7.57 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 162.9, 147.6, 136.8, 135.9, 133.0, 129.5, 128.7, 128.6, 128.4, 128.2, 126.7, 122.4, 120.8, 64.3. MS (EI): *m/z* 332.0386 (calc for $C_{18}H_{14}O_2{}^{35}Cl_2$ 332.0371). FT-IR (KBr) ν (cm^{-1}): 3058, 3024, 1779, 1678, 1615, 1596.

12. Yield: 70%. ^{19}F NMR (188.31 MHz, $CDCl_3$) δ ppm: −65.8. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 6.42 (d, J = 11.2 Hz, 1H, H^1), 6.57 (m, 1H, H^4), 6.74 (d, J = 15.6 Hz, 1H, H^3), 6.88 (m, 1H, H^5), 7.04 (dd, J = 11.2 Hz, J = 15.6 Hz, 1H, H^2), 7.25−7.56 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 160.0, 147.6, 137.0, 135.4, 134.3, 133.8, 131.2, 129.3, 128.8, 128.7, 128.4, 128.0, 126.7, 122.8, 121.3, 121.0. MS (EI): *m/z* 344.1022 (calc for $C_{20}H_{15}O_2F_3$ 344.1024). FT-IR (KBr) ν (cm^{-1}): 3062, 1750, 1683, 1598.

13. Yield: 85%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 3.55 (s, 2H, CH_2CO), 6.35 (d, J = 11.0 Hz, 1H, H^1), 6.70 (d, J = 15.6 Hz, 1H, H^3), 6.93 (dd, J = 11.0 Hz, J = 15.6 Hz, 1H, H^2), 7.22−7.49 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 161.6, 147.7, 136.8, 135.8, 133.4, 129.4, 128.7, 128.7, 128.4, 128.1, 126.7, 122.4, 121.1, 112.7, 24.9. MS (EI): *m/z* 289.1112 (calc for $C_{19}H_{15}O_2N$ 289.1103). FT-IR (KBr) ν (cm^{-1}): 3058, 3040, 2261, 1766, 1636, 1595.

14. Yield: 80%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.52 (d, J = 7.0 Hz, 3H, Me), 2.82 (d, J = 5.0 Hz, 1H, OH), 4.44 (m, 1H, CHOH), 6.29 (d, J = 11.1 Hz, 1H, H^1), 6.67 (d, J = 15.6 Hz, 1H, H^3), 6.95 (dd, J = 11.1 Hz, J = 15.6 Hz, 1H, H^2), 7.20−7.37 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 174.4, 147.8, 137.1, 135.1, 133.9, 129.2, 128.7, 128.6, 128.3, 127.9, 126.6, 122.8, 120.6, 66.9, 20.4. MS (EI): *m/z* 294.1256 (calc for $C_{19}H_{18}O_3$ 294.1256). FT-IR (KBr) ν (cm^{-1}): 3445, 3058, 3024, 1755, 1634, 1595.

15. Yield: 93%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 3.47 (s, 3H, Me), 4.18 (s, 2H, CH_2CO), 6.31 (d, J = 11.1 Hz, 1H, H^1), 6.66 (d, J = 15.6 Hz, 1H, H^3), 6.95 (dd, J = 11.1 Hz, 1H, J = 15.6 Hz, H^2), 7.22−7.47 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 168.9, 147.7, 137.1, 134.8, 134.2, 129.1, 128.6, 128.5, 128.4, 127.8, 126.5, 123.1, 120.7, 69.8, 59.5. MS (EI): *m/z* 294.1262 (calc for $C_{19}H_{18}O_3$ 294.1256). FT-IR (KBr) ν (cm^{-1}): 3058, 3024, 1772, 1684, 1636, 1595.

16. Yield: 65%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 6.31 (d, J = 11.0 Hz, 1H, H^1), 6.69 (d, J = 15.5 Hz, 1H, H^3), 6.96 (dd, J = 11.0 Hz, J = 15.5 Hz, 1H, H^2), 7.23−7.47 (m, 10H, Ph), 8.20 (s, 1H, CHO). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 159.6, 147.6, 136.9, 135.2, 133.3, 129.3, 128.7, 128.5, 128.4, 127.5, 126.3, 122.8, 120.4. MS (EI): *m/z* 250.0987 (calc for $C_{17}H_{14}O_2$ 250.0994). FT-IR (KBr) ν (cm^{-1}): 3058, 3040, 2850, 1735, 1684, 1636, 1595.

17. Yield: 98%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 6.44 (d, J = 11.2 Hz, 1H, H^1), 6.71 (d, J = 15.7 Hz, 1H, H^3), 7.09 (dd, J = 11.2 Hz, J = 15.7 Hz, 1H, H^2), 7.22−7.62 (m, 13H, Ph), 8.14−8.19 (m, 2H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 165.3, 148.5, 137.2, 134.6, 134.5, 133.6, 130.1, 129.6, 128.9, 128.7, 128.6, 128.5, 128.4, 127.8, 126.5, 123.3, 120.6. MS (EI): *m/z* 326.1343 (calc for $C_{23}H_{18}O_2$ 326.1306). FT-IR (KBr) ν (cm^{-1}): 3059, 3037, 1732, 1636, 1595.

18. Yield: 45%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 3.86 (s, 3H, Me), 6.39 (d, J = 11.0 Hz, 1H, H^1), 6.67 (d, J = 15.6 Hz, 1H, H^3), 6.94 (dm, J = 9.0 Hz, 2H, Ar), 7.05 (dd, J = 11.0 Hz, J = 15.6 Hz, 1H, H^2), 7.22−7.40 (m, 8H, Ph), 7.52−7.57 (m, 2H, Ph), 8.09 (dm, J = 9.0 Hz, 2H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 165.1, 163.9, 148.6, 137.4, 134.8, 134.3, 132.2, 128.8, 128.6, 128.5, 128.4, 127.7, 126.5, 123.3, 121.9, 120.6, 113.8, 55.5. MS (EI): *m/z* 356.1407 (calc for $C_{24}H_{20}O_3$ 356.1412). FT-IR (KBr) ν (cm^{-1}): 3045, 1727, 1636 (f, $\nu_{C=C}$), 1605, 1580.

19. Yield: 91%. ^1H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.02 (m, 3H, Me), 5.72 (m, 1H, H^4), 6.31 (s, 1H, H^5), 6.34 (d, J = 11.2 Hz, 1H, H^1), 6.68 (d, J = 15.6 Hz, 1H, H^3), 7.04 (dd, J = 11.2 Hz, J = 15.6 Hz, 1H, H^2), 7.24−7.54 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 166.1, 148.5, 137.2, 136.1, 134.7, 134.4, 128.9, 128.7, 128.5, 128.4, 127.7, 127.1, 126.5, 123.4, 120.5, 18.4. MS (EI): *m/z* 290.1304 (calc for $C_{20}H_{18}O_2$ 290.1307). FT-IR (KBr) ν (cm^{-1}): 3082, 3058, 1733, 1636, 1595.

20. Yield: 60%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.04 (t, J = 7.3 Hz, 3H, CH_3), 1.48 (m, 2H, CH_2), 1.78 (m, 2H, CH_2), 2.57 (t, J = 7.5 Hz, 2H, CH_2), 6.38 (d, J = 11.2 Hz, 1H, H^1), 6.76 (d, J = 15.6 Hz, 1H, H^3), 7.09 (dd, J = 11.2 Hz, J = 15.6 Hz, 1H, H^2), 7.3−7.6 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 172.9, 148.9, 137.7, 135.2, 134.8, 129.3, 129.1, 129.0, 128.9, 128.2, 127.0, 123.9, 120.8, 34.6, 27.4, 22.7, 14.3. MS (EI): *m*/*z* 306.1603 (calc for $C_{21}H_{22}O_2$, 306.1620). FT-IR (KBr) ν (cm^{-1}): 3058, 2958, 1757, 1636, 1595.

21. Yield: 70%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.40 (d, J = 7.0 Hz, 6H, $(CH_3)_2$), 2.87 (hept, J = 7.0 Hz, 1H, CH), 6.43 (d, J = 11.2 Hz, 1H, H^1), 6.81 (d, J = 15.6 Hz, 1H, H^3), 7.15 (dd, J = 11.2 Hz, J = 15.6 Hz, 1H, H^2), 7.3−7.7 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 176.1, 149.0, 137.7, 135.3, 134.8, 129.4, 129.2, 129.0, 128.9, 128.2, 127.0, 123.9, 120.8, 19.4. MS (EI): *m*/*z* 292.1469 (calc for $C_{20}H_{20}O_2$, 292.1463). FT-IR (KBr) ν (cm^{-1}): 2973, 1752.

22. Yield: 91%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.28 (s, 9H, ^{t}Bu), 6.64 (d, J = 11.1 Hz, 1H, H^1), 6.98 (d, J = 15.5 Hz, 1H, H^3), 6.98 (dd, J = 11.1 Hz, J = 15.5 Hz, 1H, H^2), 7.18−7.40 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 177.1, 148.6, 137.2, 134.7, 134.1, 128.8, 128.7, 128.4, 128.3, 127.7, 126.5, 123.4, 120.5, 38.9, 27.1. MS (EI): *m*/*z* 306.1618 (calc for $C_{21}H_{22}O_2$ 306.1620). FT-IR (KBr) ν (cm^{-1}): 3059, 3034, 3024, 1747, 1636, 1595.

23a. Yield: 84%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.55 (d, J = 7.2 Hz, 3H, Me), 4.66 (m, 1H, CH), 5.21 (s, 2H, CH_2O), 5.77 (d, J = 7.7 Hz, 1H, NH), 6.40 (d, J = 11.2 Hz, 1H, H^1), 6.74 (d, J = 15.5 Hz, 1H, H^3), 7.08 (dd, J = 11.2 Hz, J = 15.5 Hz, 1H, H^2), 7.26−7.58 (m, 15H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 172.4, 156.4, 148.4, 137.6, 136.9, 135.5, 134.6, 129.6, 129.2, 129.1, 128.9, 128.7, 128.6, 128.4, 127.1, 123.5, 121.2, 67.5, 50.3, 18.7. MS (EI): *m*/*z* 427.1795 (calc for $C_{27}H_{25}O_4N$ 427.1784). FT-IR (KBr) ν (cm^{-1}): 3431, 3337, 3064, 1710, 1646, 1598.

23b. Yield: 75%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.49 (s, 9H, Me), 3.21 (m, 2H, CH_2), 4.81 (m, 1H, CH), 5.20 (m, 1H, NH), 6.24 (d, J = 11.2 Hz, 1H, H^1), 6.79 (d, J = 15.6 Hz, 1H, H^3), 7.00 (dd, J = 11.2 Hz, J = 15.6 Hz, 1H, H^2), 7.20−7.51 (m, 15H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 171.3, 155.6, 148.6, 137.5, 136.3, 135.3, 134.5, 130.0, 129.5, 129.1, 129.0, 128.9, 128.3, 127.6, 127.0, 123.5, 121.1, 80.6, 55.1, 38.6, 28.8. MS (EI): *m*/*z* 222.1040 (calc for $C_{16}H_{14}O$ 222.1045). MS (LSIMS): *m*/*z* 414.1711 (calc for $C_{26}H_{24}O_4N$ 414.1705). FT-IR (KBr) ν (cm^{-1}): 3430, 3337, 3061, 3038, 3022, 1748, 1701, 1646, 1598.

23c. Yield: 55%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.49 (s, 9H, Me), 4.09 (d, J = 5.5 Hz, 2H, CH_2), 5.30 (m, 1H, NH), 6.35 (d, J = 11.1 Hz, 1H, H^1), 6.69 (d, J = 15.5 Hz, 1H, H^3), 7.00 (dd, J = 11.1 Hz, J = 15.5 Hz, 1H, H^2), 7.22−7.53 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.7, 156.2, 148.3, 137.5, 135.4, 134.6, 129.5, 129.1, 129.0, 128.9, 128.3, 127.0, 123.4, 121.1, 80.6, 43.1, 28.8. MS (EI): *m*/*z* 379.1784 (calc for $C_{23}H_{25}O_4N$ 379.1784). FT-IR (KBr) ν (cm^{-1}): 3367, 3065, 1759, 1708, 1627, 1596.

23d. Yield: 33%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.47 (s, 9H, Me), 2.82 (s, 1H, OH), 4.03 (m, 2H, CH_2), 4.57 (m, 1H, CH), 5.59 (d, J = 8.0 Hz, 1H, NH), 6.34 (d, J = 11.0 Hz, 1H, H^1), 6.67 (d, J = 15.7 Hz, 1H, H^3), 6.98 (dd, J = 11.0 Hz, J = 15.7 Hz, 1H, H^2), 7.21−7.53 (m, 10H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 170.4, 156.3, 148.3, 137.5, 135.5, 134.4, 129.5, 129.1, 129.0, 128.9, 128.3, 127.0, 123.3, 121.2, 80.9, 63.8, 56.4, 28.8. MS (EI): *m*/*z* 222.1037 (calc for $C_{16}H_{14}O$ 222.1045). FT-IR (KBr) ν (cm^{-1}): 3432, 3294, 3054, 1757, 1715, 1632, 1596.

25. Yield: 20%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 0.82−0.90 (m, 6H, CH_3), 1.22−1.42 (m, 8H, CH_2−CH_2), 2.04−2.11 (m, 2H, =C−CH_2), 2.09 (s, 3H, Me), 2.32 (t, J = 7.7 Hz, 2H, =C(OAc)−CH_2), 5.62 (dt, J = 15.0 Hz, J = 7.5 Hz, 1H, H^3), 5.70 (d, J = 11.1 Hz, 1H, H^1), 6.02 (ddt, J = 11.1 Hz, J = 15.0 Hz, J = 1.3 Hz, 1H, H^2). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.7, 149.3, 135.4, 123.5, 118.8, 32.7, 31.4, 29.2, 29.1, 22.2, 22.2, 21.0, 13.9, 13.8. MS (EI): *m*/*z* 224.1774 (calc for $C_{14}H_{24}O_2$ 224.1776). FT-IR (KBr) ν (cm^{-1}): 3032, 2958, 1756, 1669, 1626.

26. Yield: 40%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 0.84 (m, 6H, CH_3), 1.24−1.36 (m, 16H, −$(CH_2)_4$−), 2.03−2.13 (m, 2H, =C−CH_2), 2.09 (s, 3H, Me), 2.31 (t, J = 7.5 Hz, 2H, =C(OAc)−CH_2), 5.67 (dt, J = 15.0 Hz, J = 7.3 Hz, 1H, H^3), 5.71 (d, J = 11.0 Hz, 1H, H^1), 6.03 (ddt, J = 11.0 Hz, J = 15.0 Hz, J = 1.3 Hz, 1H, H^2). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.7, 149.2, 135.4, 123.5, 118.8, 33.0, 31.7, 31.6, 29.4, 29.2, 28.9, 28.8, 26.9, 22.7, 22.6, 21.0, 14.1, 14.0. MS (EI): *m*/*z* 280.2412 (calc for $C_{18}H_{32}O_2$ 280.2402). FT-IR (KBr) ν (cm^{-1}): 3032, 2927, 1757, 1668, 1626.

27. Yield: 20%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 0.05 (s, 9H, CH_3), 0.20 (s, 9H, CH_3), 2.09 (s, 3H, CH_3), 5.87 (dd, J = 18.0 Hz, J = 6.0 Hz, 1H, H^3), 6.35 (dd, J = 11.3 Hz, J = 0.6 Hz, 1H, H^1), 6.67 (dd, J = 11.3 Hz, J = 18.0 Hz, 1H, H^2). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 170.3, 159.4, 138.0, 137.2, 136.3, 20.8, −0.8, −1.4. MS (EI): *m*/*z* 256.1347 (calc for $C_{12}H_{24}Si_2O_2$ 256.1315). FT-IR (KBr) ν (cm^{-1}): 3023, 2955, 1741, 1614, 1560, 830.

Typical Procedure for Ruthenium-Catalyzed Dimerization of Phenylacetylene with Dicarboxylic Acids. To a solution of phenylacetylene (2.5 mmol, 1 equiv) in degassed dioxane (1 mL) were added $RuCl(cod)(C_5Me_5)$ (0.125 mmol, 5%) and carboxylic acid (0.625 mmol, 0.25 equiv) under inert atmosphere at room temperature. The reaction mixture was stirred at room temperature for 20 h. The solvent was removed, and the product was purified by silica gel flash column chromatography (eluent pentane−diethyl ether mixtures) to give dimerization adduct as a white solid in 50−75% yield.

24a. Yield: 50%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 3.73 (s, 2H, CH_2), 6.41 (d, J = 11.2 Hz, 2H, =CH), 6.74 (d, J = 15.6 Hz, 2H, =CH), 7.06 (dd, J = 11.2 Hz, J = 15.6 Hz, 2H, =CH), 7.27−7.59 (m, 20H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 165.1, 148.4, 137.5, 135.6, 134.3, 129.6, 129.1, 129.0, 128.9, 128.4, 127.0, 123.3, 121.3, 42.1. MS (EI): *m*/*z* 290.0931 (calc for $C_{19}H_{14}O_3$ 290.0943). FT-IR (KBr) ν (cm^{-1}): 3059, 1755, 1624, 1598.

24b. Yield: 75%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.88 (s, 4H, CH_2), 6.29 (d, J = 11.2 Hz, 2H, =CH), 6.68 (d, J = 15.6 Hz, 2H, =CH), 7.01 (dd, J = 11.2 Hz, J = 15.6 Hz, 2H, =CH), 7.23−7.51 (m, 20H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 171.2, 148.6, 137.6, 135.1, 134.8, 129.4, 129.1, 129.0, 128.8, 128.2, 127.0, 123.6, 121.0, 29.7. MS (EI): *m*/*z* 526.2141 (calc for $C_{36}H_{30}O_4$ 526.2144). FT-IR (KBr) ν (cm^{-1}): 3064, 3032, 1757, 1640, 1594.

24c. Yield: 70%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.75 (m, 4H, CH_2), 2.51 (m, 4H, CH_2), 6.27 (d, J = 11.2 Hz, 2H, =CH), 6.66 (d, J = 15.6 Hz, 2H, =CH), 6.97 (dd, J = 11.2 Hz, J = 15.6 Hz, 2H, =CH), 7.24−7.47 (m, 20H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 172.3, 148.7, 137.6, 135.0, 134.8, 129.3, 129.0, 128.9, 128.8, 128.1, 126.9, 123.7, 120.8, 34.3, 24.6. MS (EI): *m*/*z* 554.2459 (calc for $C_{38}H_{34}O_4$ 554.2457). FT-IR (KBr), ν (cm^{-1}): 3054, 1752, 1636, 1595.

24d. Yield: 70%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.40 (m, 4H, CH_2), 1.71 (m, 4H, CH_2), 2.49 (t, J = 7.4 Hz, 4H, CH_2), 6.29 (d, J = 11.2 Hz, 2H, =CH), 6.69 (d, J = 15.6 Hz, 2H, =CH), 7.00 (dd, J = 11.2 Hz, J = 15.6 Hz, 2H, =CH), 7.22−7.52 (m, 20H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 172.7, 148.8, 137.6, 135.1, 134.8, 129.3, 129.1, 128.9, 128.8, 128.2, 127.0, 123.8, 120.8, 34.7, 29.1, 25.1. MS (EI): *m*/*z* 582.2784 (calc for $C_{40}H_{38}O_4$ 582.2770). FT-IR (KBr) ν (cm^{-1}): 3054, 1752, 1636, 1595.

24e. Yield: 50%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 3.41 (m, 2H, OH), 4.95 (d, J = 6.1 Hz, 2H, CH), 6.41 (d, J = 11.1 Hz, 2H, =CH), 6.72 (d, J = 15.6 Hz, 2H, =CH), 7.02 (dd, J = 11.1 Hz, J = 15.6 Hz, 2H, =CH), 7.22−7.66 (m, 20H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 170.8, 148.1, 137.4, 135.9, 134.0, 129.7, 129.1, 129.0, 128.9, 128.4, 127.1, 123.1, 121.4, 72.4. MS (EI): *m*/*z* 222.1037 (calc for $C_{16}H_{14}O$ 222.1045). FT-IR (KBr) ν (cm^{-1}): 3496, 3058, 1762, 1685, 1596.

24f. Yield: 50%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.49 (s, 9H,Me), 1.99−2.17 (m, 1H, CH_2), 2.30−2.52 (m, 1H, CH_2), 2.62 (m, 2H, CH_2), 4.56 (m, 1H, CH), 5.11 (d, J = 8.7 Hz, 1H, NH), 6.32 (d, J = 10.9 Hz, 2H, =CH), 6.69 (d, J = 15.6 Hz, 2H, =CH), 6.96 (dd, J = 10.9 Hz, J = 15.6 Hz, 1H, =CH), 6.99 (dd, J = 10.9 Hz, J = 15.6 Hz, 1H, =CH), 7.22−7.53 (m, 20H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 171.8, 171.4, 155.8, 148.6, 148.4, 137.6, 137.5, 135.5, 135.1, 134.9, 134.5, 129.6, 129.4, 129.1, 129.0, 129.0, 128.9, 128.3, 128.2, 127.0, 127.0, 123.6, 123.3, 121.2, 121.0, 80.8, 53.4, 30.8, 28.8, 27.9. MS (EI): *m*/*z* 222.1037 (calc for $C_{16}H_{14}O$ 222.1045). FT-IR (KBr) ν (cm^{-1}): 3413, 3358, 3058, 3032, 1755, 1713, 1637, 1595.

Procedure for Deuterated Products. 2a. To a solution of phenylacetylene (2.5 mmol, 1 equiv) in degassed dioxane (2 mL) were added RuCl(cod)(C_5Me_5) (0.125 mmol, 5%) and acetic acid-*d* (1.25 mmol, 0.5 equiv) under inert atmosphere at room temperature. The reaction mixture was stirred at room temperature for 20 h. The solvent was removed, and the product was purified by silica gel flash column chromatography (eluent pentane−diethyl ether mixtures) to give dimerization adduct **2a** as a white solid in 60% yield with 70% deuterium incorporation.

Yield: 70%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.20 (s, 3H, MeCO), 6.28 (d, J = 11.3 Hz, 1H, H^1), 6.96 (d, J = 11.4 Hz, 1H, H^2), 7.18−7.53 (m, 10H, Ph).

2b. To a solution of phenylacetylene-*d* (2.5 mmol, 1 equiv) in degassed dioxane (2 mL) were added RuCl(cod)(C_5Me_5) (0.125 mmol, 5%) and acetic acid (1.25 mmol, 0.5 equiv) under inert atmosphere at room temperature. The reaction mixture was stirred at room temperature for 22 h. The solvent was removed, and the product was purified by silica gel flash column chromatography (eluent pentane−diethyl ether mixtures) to give dimerization adduct **2b** as a white solid in 68% yield with 98% deuterium incorporation.

Yield: 68%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 2.22 (s, 3H, Me), 6.69 (s, 1H, H^3), 7.2−7.6 (m, 10H, Ar). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 169.6, 148.3, 137.2, 134.7, 134.4, 129.0, 128.7, 128.6, 128.5, 127.8, 126.6, 21.2. MS (EI): *m*/*z* 266.1269 (calc for $C_{18}H_{14}O_2D_2$ 266.1276). FT-IR (KBr) ν (cm^{-1}): 3022, 1768, 1594.

Synthesis of Biscarbene−Ruthenium Complex 28. To a solution of 0.188 g of RuCl(cod)(C_5Me_5) (0.5 mmol, 1 equiv) in degassed THF (15 mL) was added at 0 °C 0.22 mL of phenylacetylene (5 mmol, 10 equiv) under inert atmosphere. The reaction mixture was stirred 20 h and allowed to warm to rooom temperature. The solvent was removed in vacuo, and the residue was washed with 15 mL of cold (0 °C) heptane to give 0.130 g of a dark red powder.

Yield: 51%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 1.19 (s, 15H, Me), 7.06−7.23 (m, 8H, Ph), 7.26 (s, 2H, =CH), 7.53−7.60 (m, 2H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 262.4 (C=Ru), 158.6 (C Ph), 155.1 (=CH), 129.1, 126.9, 124.7 (CH Ph), 106.6 (C C_5Me_5), 10.1 (Me C_5Me_5). FT-IR (KBr) ν (cm^{-1}): 3045, 3024, 3008, 2905, 1590.

Synthesis of Compound 29. To a solution of biscarbene complex **28** (0.240 g, 0.5 mmol, 1 equiv) in degassed THF (5 mL) was added at room temperature 0.42 mL of HBF_4 (0.5 mmol, 1 equiv, 1.2 M in MeOH) under inert atmosphere. The reaction mixture was stirred 20 h. The solvent was removed in vacuo, and the product was purified by silica gel flash column chromatography (eluent pentane−diethyl ether mixtures).

Yield: 51%. ^{1}H NMR (200.131 MHz, $CDCl_3$) δ ppm: 6.80 (d, J = 15.8 Hz, 1H, H^1), 6.94 (d, J = 10.4 Hz, 1H, H^3), 7.26−7.41 (m, 7H, 6H Ph and H^2), 7.49−7.54 (m, 2H, Ph), 7.66−7.71 (m, 2H, Ph). ^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 136.1 (=CH), 131.4 (CPh), 129.3 (C Ph), 129.2, 129.1, 128.8, 128.6, 127.2, 126.7 (CH Ph), 126.4, 125.5 (=CH), 114.4 (=C−Cl).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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