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Ruthenium-Catalyzed Propargylation of Aromatic Compounds with Propargylic Alcohols

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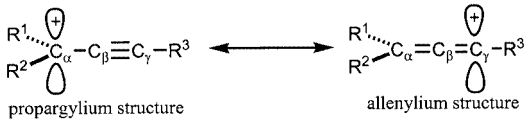
Reactions of propargylic alcohols bearing a terminal alkyne moiety with aromatic compounds in the presence of a catalytic amount of thiolate-bridged diruthenium complexes give the corresponding propargylated aromatic compounds in high yields with complete selectivity. Intramolecular reactions of propargylic alcohols bearing an aromatic moiety proceed smoothly to afford the cyclized products in high yields with complete selectivity. The stoichiometric reaction of the ruthenium–allenylidene complex $[Cp^*RuCl(\mu_2\text{-}SMe)_2RuCp^*(=C=C=CHPh)]BF_4$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with 10 equiv. 2-methylfuran results in the formation of 2-methyl-5-(1-phenyl-2-propynyl)furan in 34 % yield, indicating that these catalytic reactions proceed via ruthenium–allenylidene intermediates. The reaction is considered to be an electrophilic substitution of aromatic compounds by the ruthenium-stabilized propargyl cation.

Introduction

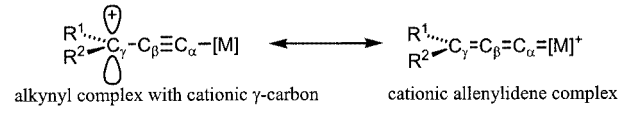
The chemical features of propargyl cations as reactive intermediates as well as persistent species have attracted interest in organic and physical chemistry.[1–2] The electronic ground state of propargyl cations is delineated by propargylium and allenylium resonance structures, where the positive charge is distributed over sp^2- and sp-hybridized carbon atoms [Equation (1)].



(1)

The electronic and structural properties of propargyl cations have been extensively investigated by Olah and coworkers, who concluded that propargyl cations can be considered to be alkynyl-substituted carbenium ions, and their reactivity depends much on the kind of substituents at the α- and γ-positions,[2] affording either propargyl or allenyl products by nucleophilic trapping of propargyl cations.[3]

Discovery of the stabilization of reactive intermediates by transition metals not only stimulated a theoretical interest remarkably, but also gave a tremendous impact for the application of such species in organic synthesis.[4] Introduction of a transition metal at the γ-position of a propargyl cation without complexation of the triple bond can realize the stabilization and conformational fixation of the propargyl cation [Equation (2)].



(2)

It has been reported that the electrophilic aromatic substitution reaction of a *free* propargyl cation gives some polymers as predominant products together with a small amount of a mixture of propargylated and allenylated aromatic compounds.[5] In contrast, the positive charge at the γ-position of the metal complex may promote a desirable electrophilic aromatic substitution reaction. After a detailed investigation, we have actually succeeded in the selective propargylation of aromatic compounds with propargylic alcohols by using a diruthenium complex as a catalyst; the results are summarized in this paper.[6,7] In this catalytic reaction, a stabilized propargyl cation assisted by the diruthenium complex reacted directly with aromatic compounds.

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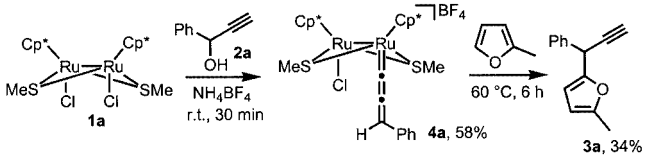
Results and Discussion

As shown in Equation (2), a metal–allenylidene complex exists as another resonance structure of a metal–alkynyl complex with a positive charge at the γ-position. At first, the stoichiometric reaction of the ruthenium–allenylidene complex with aromatic compounds was investigated. Heating the allenylidene complex [Cp*RuCl(μ$_2$-SMe)$_2$RuCp*(=C=C=CHPh)]BF$_4$ (Cp* = η^5-C$_5$Me$_5$; **4a**) with 10 equiv. 2-methylfuran in ClCH$_2$CH$_2$Cl at 60 °C for 6 h led to the formation of 2-methyl-5-(1-phenyl-2-propynyl)furan (**3a**) in 34% yield as the sole product [Equation (3)].



(3)

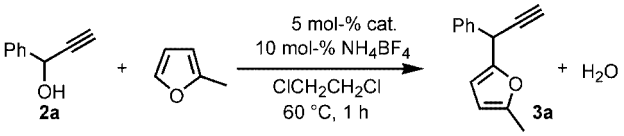
This unprecedented result indicates that an electrophilic aromatic substitution reaction occurs at the γ-carbon of an allenylidene ligand. Reactions of allenylidene complexes with various heteroatom- and carbon-centered nucleophiles at the α- and γ-carbons have already been reported,[8] but there is no example of the *direct* reaction of the allenylidene ligand with aromatic compounds until now.[9]

The result of the stoichiometric reaction above prompted us to investigate the catalytic reaction of aromatic compounds with propargylic alcohols in the presence of the thiolate-bridged diruthenium complex[10] [Cp*RuCl(μ$_2$-SMe)$_2$RuCp*Cl] (**1a**) as catalyst, because the ruthenium–allenylidene complex **4a** can be readily prepared from the reaction of **1a** with 1 equiv. 1-phenyl-2-propyn-1-ol (**2a**) in the presence of NH$_4$BF$_4$.[10n] Treatment of **2a** with 2-methylfuran in ClCH$_2$CH$_2$Cl in the presence of **1a** (5 mol-%) and NH$_4$BF$_4$ (10 mol-%) at 60 °C for 1 h afforded the furan **3a** in quantitative yield (Table 1, entry 1). Typical results are shown in Table 1. Neither other products nor regioisomers of **3a** were observed by GLC and ^{1}H NMR spectroscopy. The reaction proceeded smoothly even at room temperature for 1 h, **3a** being obtained in 90% yield. It is noteworthy that only thiolate-bridged diruthenium complexes **1a**–**1d** worked as catalysts (Table 1, entries 2–4). The ruthenium–allenylidene complex [Cp*RuCl(μ$_2$-SMe)$_2$RuCp*(=C=C=CHPh)]BF$_4$ (**4a**) was also effective in this catalytic reaction (Table 1, entry 5). Unfortunately, other conventional mono- and diruthenium complexes such as [Cp*RuCl(PPh$_3$)$_2$] (Cp* = η^5-C$_5$Me$_5$), [RuCl$_2$(PPh$_3$)$_3$], [RuCl$_2$(*p*-cymene)]$_2$, and [(indenyl)RuCl(PPh$_3$)$_2$], which were known to react with propargylic alcohols to produce the corresponding allenylidene complexes, did not work at all as catalysts (Table 1, entries 6–9).

Reactions of other furans with 1-aryl-, 1-alkenyl-, and 1-alkyl-substituted propargylic alcohols in the presence of **1a** proceeded smoothly to give the corresponding propargylated furans **3** in high yields with complete selectivity. Typical results are summarized in Table 2. A slightly lower yield of 2-(1-phenyl-2-propynyl)furan (**3j**) was obtained when furan was used as a substrate (Table 2, entry 10). Pyrrole, *N*-methylpyrrole, and 2-methylthiophene can be propargylated with **2a** (Table 2, entries 11–17). In all cases, propargylation occurred selectively at the α-position of the heterocyclic rings, and the reaction of indole with **2a** afforded the β-propargylated indole **3n** in 52% yield with complete selectivity (Scheme 1). These results are exactly in agreement with the regioselectivity of electrophilic substitution reactions of heterocyclic compounds.[11] Interestingly, the reaction of indoline with **2a** selectively gave *N*-(1-phenyl-2-propenyl)indole in 74% yield (Scheme 2).

N,*N*-Dimethylaniline (**5a**) reacted with several 1-aryl-2-propyn-1-ols **2** at 60 °C for 2–6 h to give the corresponding *N*,*N*-dimethyl-4-(1-aryl-2-propynyl)anilines **6a**–**6f** in good yields with complete regioselectivity. Typical results are summarized in Table 3. In this case, the aryl groups in **2** were found to have a strong influence on the catalytic activity. Introduction of an electron-withdrawing group such as *p*-CF$_3$ and *p*-Cl increased the product yield slightly, while the introduction of an electron-releasing group such as *p*-

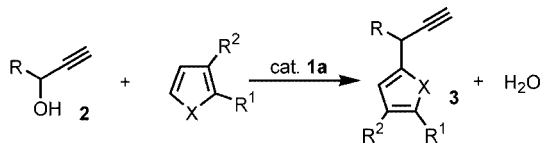
Table 1. Propargylation of 2-methylfuran with propargylic alcohol (**2a**).[a]



Entry	Catalyst	Conv. of **2a** [%][b]	Yield of **3a** [%][b]
1	[Cp*RuCl(μ$_2$-SMe)]$_2$ (**1a**)	100	>95 (85)[c]
2	[Cp*RuCl(μ$_2$-S*n*Pr)]$_2$ (**1b**)	100	87
3	[Cp*RuCl(μ$_2$-S*i*Pr)]$_2$ (**1c**)	100	78
4	[Cp*RuCl(μ$_2$-S*i*Pr)2Ru(OH2)Cp*]OTf (**1d**)[d]	100	>95
5	[Cp*RuCl(μ$_2$-SMe)$_2$Ru(=C=C=CHPh)Cp*]BF$_4$ (**4a**)[d]	100	>95
6	[Cp*RuCl(PPh$_3$)$_2$]	36	0
7	[RuCl$_2$(PPh$_3$)$_3$]	18	0
8	[RuCl$_2$(*p*-cymene)]$_2$	40	0
9	[(indenyl)RuCl(PPh$_3$)$_2$]	44	0

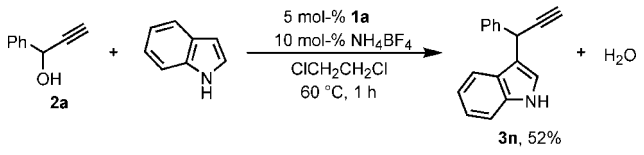
[a] All reactions of 2-methylfuran (1.0 mmol) with 1-phenyl-2-propyn-1-ol (**2a**) (0.10 mmol) were carried out in the presence of catalyst in ClCH$_2$CH$_2$Cl at 60 °C for 1 h. [b] Determined by GLC. [c] Isolated yield. [d] In the absence of NH$_4$BF$_4$.

Table 2. Propargylation of heterocyclic compounds with propargylic alcohols.[a]

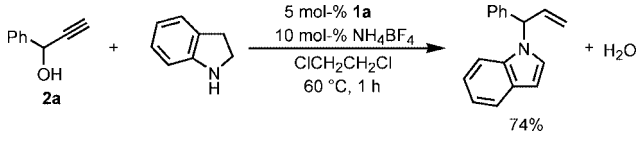


Entry	Propargylic alcohol	Heterocyclic compound	Yield of product [%][b]
1	**2a**, R = Ph	X = O, R^1 = Me, R^2 = H	**3a**, 85 (>95)[c]
2	**2b**, R = *p*-MeC_6H_4	X = O, R^1 = Me, R^2 = H	**3b**, 83
3	**2c**, R = *p*-FC_6H_4	X = O, R^1 = Me, R^2 = H	**3c**, 70
4	**2d**, R = 2,4,6-$Me_3C_6H_2$	X = O, R^1 = Me, R^2 = H	**3d**, 77
5	**2e**, R = 1-naphthyl	X = O, R^1 = Me, R^2 = H	**3e**, 84
6	**2a**, R = Ph	X = O, R^1 = Et, R^2 = H	**3f**, 75
7	**2a**, R = Ph	X = O, R^1 = OMe, R^2 = H	**3g**, 51
8	**2f**, R = Ph_2C=CH-	X = O, R^1 = Me, R^2 = H	**3h**, 59
9	**2g**, R = cyclohexyl	X = O, R^1 = Me, R^2 = H	**3i**, 61
10	**2a**, R = Ph	X = O, R^1 = H, R^2 = H	**3j**, 68
11	**2a**, R = Ph	X = NH, R^1 = H, R^2 = H	**3k**, 67
12	**2a**, R = Ph	X = NMe, R^1 = H, R^2 = H	**3l**, 94
13	**2a**, R = Ph	X = S, R^1 = Me, R^2 = H	**3m**, 86
14	**2g**, R = cyclohexyl	X = NMe, R^1 = H, R^2 = H	**3o**, 95
15	**2b**, R = *p*-MeC_6H_4	X = NMe, R^1 = H, R^2 = H	**3p**, 92
16	**2c**, R = *p*-FC_6H_4	X = NMe, R^1 = H, R^2 = H	**3q**, 92
17	**2h**, R = 2-naphthyl	X = NMe, R^1 = H, R^2 = H	**3r**, 90
18	**2a**, R = Ph	X = O, R^1 = Me, R^2 = Me	**3s**, 91
19	**2h**, R = 2-naphthyl	X = O, R^1 = Me, R^2 = H	**3t**, 79

[a] All reactions of **2** (0.60 mmol) with heterocyclic compound (6.0 mmol) were carried out in the presence of **1a** (0.03 mmol) and NH_4BF_4 (0.06 mmol) in $ClCH_2CH_2Cl$ (15–30 mL) at 60 °C for 1 h. [b] Isolated yield. [c] GLC yield.



Scheme 1.



Scheme 2.

Me and *p*-MeO decreased it (Table 3, entries 1–5). It is worth noting that electrophilic substitution reactions occurred exclusively at the *para* position of anilines. These results support a reaction pathway that proceeds by an electrophilic attack of the cationic γ-carbon of the alkynyl complex, which is considered to be a resonance structure of the allenylidene complex (vide supra). Reactions of **2a** with other aniline derivatives proceeded to give the corresponding propargylated anilines in moderate to good yields. A mixture of **6j** and **6k** was obtained in a ratio of 1 to 5 by the reaction of **2a** with *N*-phenylpyrrole (**5e**) (Table 3, entry 10).

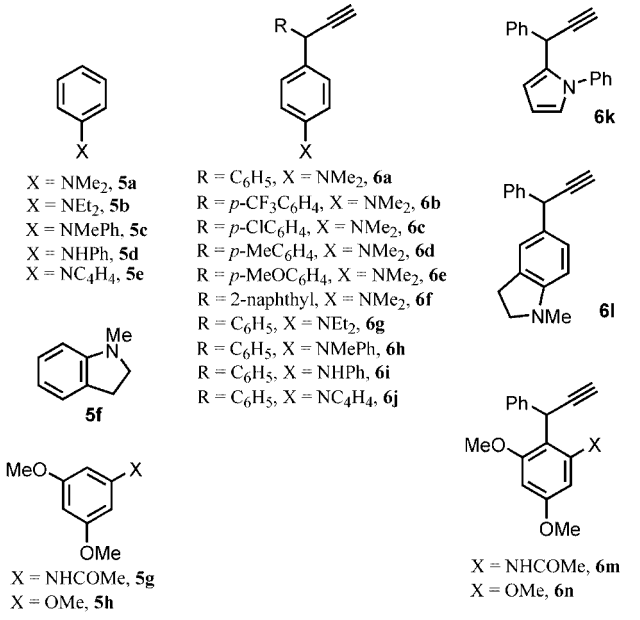
Reactions of 3,5-dimethoxyacetanilide (**5g**) and 1,3,5-trimethoxybenzene (**5h**) with **2a** proceeded smoothly and selectively, and afforded the corresponding propargylated aromatic compounds **6m** and **6n** in moderate yields (Table 3, entries 12 and 13). The molecular structure of **6n** is unambiguously clarified by X-ray analysis (Figure 1). In contrast, no propargylation occurred when acetanilide, 1,3-dimethoxybenzene, 1,3,5-trimethylbenzene, *p*-xylene, and toluene, besides many other aromatic compounds, were used (Figure 2).[11] Thus, this catalytic propargylation proceeded only when highly electron-rich arenes[12] were used. Interestingly, 1-propargylated azulenes **6o** and **6p** were formed in reactions of propargylic alcohols with azulene (Scheme 3).

Next, catalytic intramolecular cyclization reactions were investigated. Typical results are summarized in Table 4. Treatment of propargylic alcohols **7a** bearing a furan moiety in $ClCH_2CH_2Cl$ at 60 °C for 24 h in the presence of **1a** afforded the corresponding seven-membered tricyclic compound **8a** in >93% yield (GLC, 82% isolated yield) (Table 4, entry 1). Noteworthy is that only thiolate- and selenolate-bridged diruthenium complexes worked effectively as catalysts (Table 4, entries 2–5). On the other hand, tellurolate-bridged diruthenium complexes and other conventional mono- and diruthenium complexes such as $[Cp^*RuCl(\mu_2\text{-}TeMe)]_2$, $[CpRuCl(PPh_3)_2]$ (Cp = η^5-C_5H_5), $[RuCl_2(PPh_3)_3]$, $[RuCl_2(p\text{-cymene})]_2$, $[(indenyl)RuCl(PPh_3)_2]$, and $[Cp^*RuCl_2]_2$ did not work at all as in the case of intermolecular reactions of propargylic alcohols with furan (Table 4, entries 6–11).

Table 3. Propargylation of aromatic compounds with propargylic alcohols.[a]

Entry	Propargylic alcohol	Aromatic compound	Reaction time [h]	Yield of product [%][b]
1	**2a**, R = Ph	**5a**	2	**6a**, 50
2	**2i**, R = *p*-$CF_3C_6H_4$	**5a**	2	**6b**, 58
3	**2j**, R = *p*-ClC_6H_4	**5a**	2	**6c**, 53
4	**2b**, R = *p*-MeC_6H_4	**5a**	5	**6d**, 23
5	**2k**, R = *p*-$MeOC_6H_4$	**5a**	3	**6e**, –[c]
6	**2h**, R = 2-naphthyl	**5a**	6	**6f**, 30
7	**2a**, R = Ph	**5b**	5	**6g**, 23
8	**2a**, R = Ph	**5c**	3	**6h**, 49
9	**2a**, R = Ph	**5d**	2	**6i**, 63
10	**2a**, R = Ph	**5e**	3	**6j** + **6k**, 60[d]
11	**2a**, R = Ph	**5f**	1	**6l**, 48
12	**2a**, R = Ph	**5g**	3	**6m**, 52
13	**2a**, R = Ph	**5h**	2	**6n**, 38

[a] All reactions of **2** (0.60 mmol) with aromatic compound (6.0 mmol) were carried out in the presence of **1a** (0.03 mmol) and NH_4BF_4 (0.060 mmol) in $ClCH_2CH_2Cl$ (15–30 mL) at 60 °C. [b] Isolated yield. [c] A small amount of **6e** was detected by GC–MS. [d] **6j**:**6k** = 1:5.



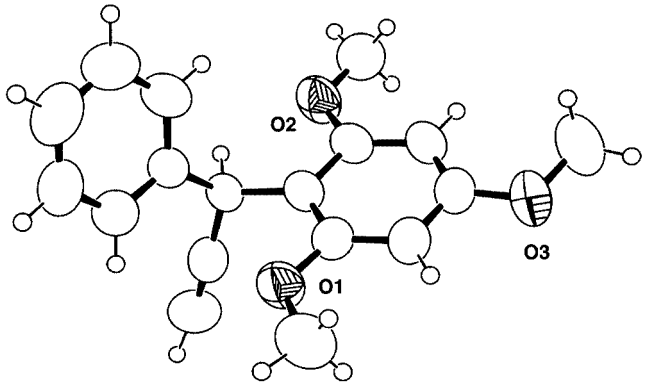


Figure 1. Crystal structure of **6n**.

Other intramolecular cyclization reactions of the various propargylic alcohols **7b**–**7e** bearing a furan moiety were carried out. Cyclized products **8b**–**8e** were obtained in moderate to good yields (Table 4, entries 12–15). The presence of substituents on a phenyl ring was found to decrease the product yield. As a further extension of the intramolecular cyclization reaction, reactions of propargylic alcohols **9a**–**9c** bearing an electron-rich benzene moiety were investigated (Scheme 4). Although the reactions proceeded to give the corresponding cyclized products **10a**–**10c**, their yields were relatively low. The molecular structure of **10c** was unambiguously determined by X-ray crystallographic analysis (Figure 3). Reactions of propargylic alcohols **7f** and **9d** bearing a bulky naphthyl moiety also gave the corresponding products **8f** and **10d** in moderate yields (Scheme 5).

Finally, in order to obtain some mechanistic information, [D_5]pyrrole was allowed to react with **2a** under similar reaction conditions (Scheme 6). 2-(1-Phenyl-2-propynyl)pyrrole (**3l′**) was formed with a high deuterium incorporation (80%) at the C-3 position, indicating that this catalytic propargylation of aromatic compounds proceeded via a ruthenium–allenylidene intermediate such as **4a**. However, at the present stage we cannot exclude the possibility that the reaction proceeded by a charge-transfer mechanism including radical cation intermediates.

In conclusion, we have found a novel ruthenium-catalyzed inter- and intramolecular propargylation of aromatic compounds with propargylic alcohols to afford the corresponding propargylated aromatic products in good to high yields with complete selectivity. The Nicholas reaction has been known to be effective for propargylation of aromatic compounds by use of a *stoichiometric* amount of $Co_2(CO)_8$, where several steps are necessary to obtain propargylated products from propargylic alcohols via cationic propargyl complexes $[(propargyl)Co_2(CO)_6]^+$.[13] The *catalytic* reaction presented in this paper may be potentially useful for practical application in organic synthesis, because the selective propargylation of aromatic compounds is so far known to be quite difficult.[5,14] It is also noteworthy that some

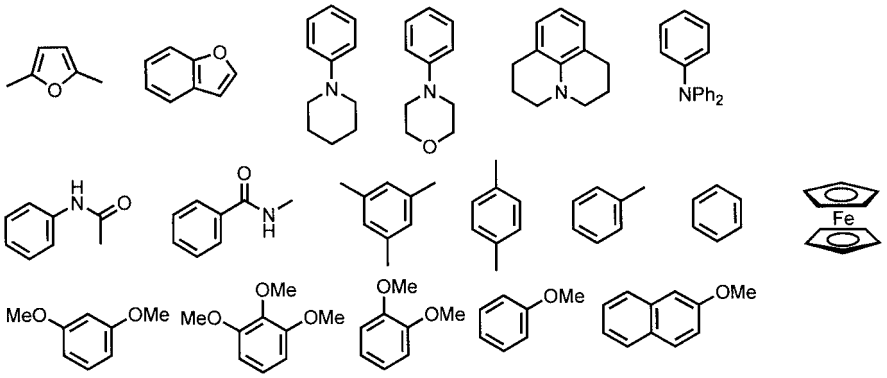
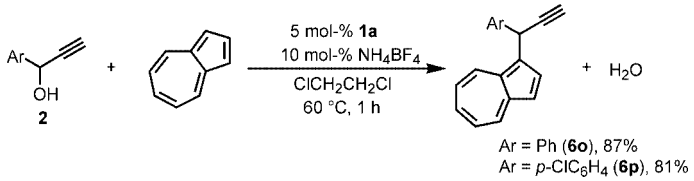
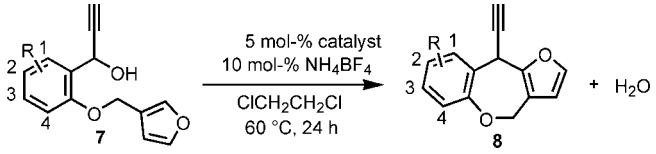


Figure 2. Unreactive aromatic compounds for propargylation.



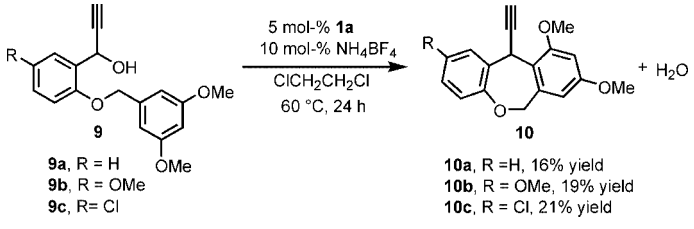
Scheme 3.

Table 4. Intramolecular cyclization of propargylic alcohols bearing a furan moiety (**7**).[a]



Entry	Propargylic alcohol	Catalyst	Yield of **8** [%][b]
1	**7a**, R = H	$[Cp^*RuCl(\mu_2\text{-SMe})]_2$ (**1a**)	**8a**, >93 (82)[c]
2	**7a**, R = H	$[Cp^*RuCl(\mu_2\text{-S}n\text{Pr})]_2$ (**1b**)	**8a**, 92
3	**7a**, R = H	$[Cp^*RuCl(\mu_2\text{-S}i\text{Pr})]_2$ (**1c**)	**8a**, 84
4	**7a**, R = H	$[Cp^*RuCl(\mu_2\text{-S}i\text{Pr})_2Ru(OH_2)Cp^*]OTf$ (**1d**)[d]	**8a**, 25
5	**7a**, R = H	$[Cp^*RuCl(\mu_2\text{-SeMe})]_2$	**8a**, 38
6	**7a**, R = H	$[Cp^*RuCl(\mu_2\text{-TeMe})]_2$	**8a**, 0
7	**7a**, R = H	$[CpRuCl(PPh_3)_2]$	**8a**, 0
8	**7a**, R = H	$[RuCl_2(PPh_3)_3]$	**8a**, 0
9	**7a**, R = H	$[RuCl_2(p\text{-cymene})]_2$	**8a**, 0
10	**7a**, R = H	$[(indenyl)RuCl(PPh_3)_2]$	**8a**, 0
11	**7a**, R = H	$[Cp^*RuCl_2]_2$	**8a**, 0
12	**7b**, R = 2-Me	$[Cp^*RuCl(\mu_2\text{-SMe})]_2$ (**1a**)	**8b**, 63[c]
13	**7c**, R = 2-Cl	$[Cp^*RuCl(\mu_2\text{-SMe})]_2$ (**1a**)	**8c**, 40[c]
14	**7d**, R = 4-Me	$[Cp^*RuCl(\mu_2\text{-SMe})]_2$ (**1a**)	**8d**, 72[c]
15	**7e**, R = 4-MeO	$[Cp^*RuCl(\mu_2\text{-SMe})]_2$ (**1a**)	**8e**, 56[c]

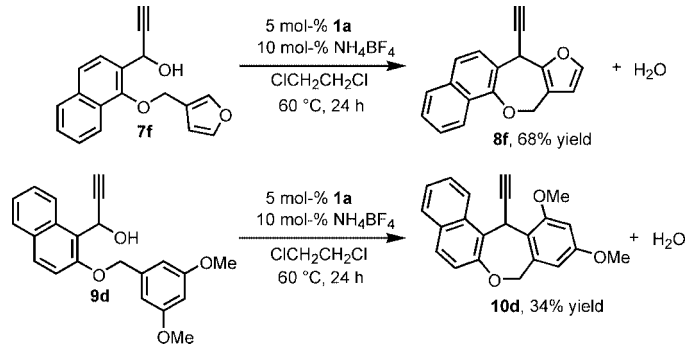
[a] All reactions of **7** (0.10 mmol) were carried out in the presence of catalyst (0.005 mmol) and NH_4BF_4 (0.01 mmol) in $ClCH_2CH_2Cl$ at 60 °C for 24 h. [b] Determined by GLC. [c] Isolated yield. [d] In the absence of NH_4BF_4.



9a, R = H
9b, R = OMe
9c, R= Cl

10a, R =H, 16% yield
10b, R = OMe, 19% yield
10c, R = Cl, 21% yield

Scheme 4.



Scheme 5.

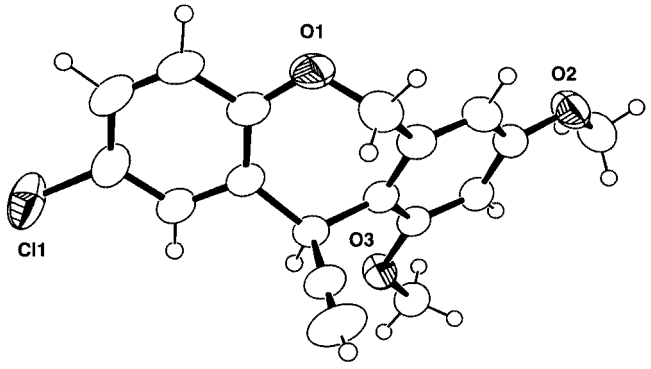
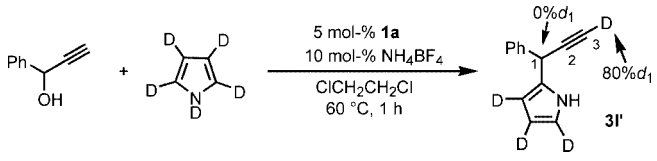


Figure 3. Crystal structure of **10c**.



Scheme 6.

propargylated aromatic products are useful monomers in the field of material science.

Experimental Section

General Methods: ^{1}H NMR (400, 300, and 270 MHz) and ^{13}C NMR (100, 75, and 67.8 MHz) spectra were recorded using $CDCl_3$ as solvent. Quantitative GLC analyses were performed with a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. GC–MS analyses were carried out with a Shimadzu GC–MS QP-5000 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Mass spectra were measured with a JEOL JMS600H mass spectrometer. All reactions were carried out under dry nitrogen. Solvents were dried by the usual methods and distilled before use.

Ruthenium-Catalyzed Propargylation of Aromatic Compounds with Propargylic Alcohols: A typical experimental procedure for the reaction of 2-methylfuran with 1-phenyl-2-propyn-1-ol (**2a**) catalyzed by [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1a**) is described below. In a 20-mL flask were placed **1a** (19 mg, 0.03 mmol) and NH_4BF_4 (6 mg, 0.06 mmol) under nitrogen. Anhydrous $ClCH_2CH_2Cl$ (15 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (79 mg, 0.60 mmol) and 2-methylfuran (492 mg, 6.00 mmol), the reaction flask was kept at 60 °C for 1 h. The solvent was concentrated under reduced pressure maintained by an aspirator, and then the residue was purified by TLC (SiO_2) with EtOAc/*n*-hexane (1:9) to give 2-methyl-5-(1-phenyl-2-propynyl)furan (**3a**) as a pale yellow oil (100 mg, 0.51 mmol; 85% yield).

3a: ^{1}H NMR δ = 2.23 (s, 3 H), 2.41 (d, J = 3.0 Hz, 1 H), 5.00 (s, 1 H), 5.88 (s, 1 H), 6.06 (d, J = 3.0 Hz, 1 H), 7.25–7.43 (m, 5 H) ppm. ^{13}C NMR δ = 13.6, 37.0, 71.8, 82.3, 106.2, 107.4, 127.3, 127.7, 128.6, 138.5, 151.3, 152.0 ppm. $C_{14}H_{12}O$ (196.24): calcd. C 85.68, H 6.16; found C 85.41, H 5.88.

3b: Yield 83% (105 mg). Pale yellow oil. ^{1}H NMR δ = 2.22 (s, 3 H), 2.33 (s, 3 H), 2.39 (s, 1 H), 4.96 (s, 1 H), 5.86 (s, 1 H), 6.06 (s, 1 H), 7.13 (d, J = 7.5 Hz, 2 H), 7.29 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR δ = 13.6, 21.0, 36.7, 71.6, 82.5, 106.2, 107.3, 127.6, 129.3, 135.6, 137.0, 151.5, 151.9 ppm. $C_{15}H_{14}O$ (210.27): calcd. C 85.68, H 6.71; found C 85.44, H 6.59.

3c: Yield 70% (90 mg). Pale yellow oil. ^{1}H NMR δ = 2.23 (s, 3 H), 2.42 (d, J = 2.4 Hz, 1 H), 4.98 (s, 1 H), 5.88 (s, 1 H), 6.06 (d, J = 2.4 Hz, 1 H), 7.01 (t, J = 8.8 Hz, 2 H), 7.38 (dd, J = 8.8 and 5.4 Hz, 2 H) ppm. ^{13}C NMR δ = 13.6, 36.3, 72.0, 82.0, 106.2, 107.5, 115.3 (d, J = 22 Hz), 129.3 (d, J = 9 Hz), 134.2 (d, J = 4 Hz), 151.0, 152.1, 162.0 (d, J = 246 Hz) ppm. $C_{14}H_{11}FO$ (214.23): calcd. C 78.49, H 5.18; found C 78.30, H 5.07.

3d: Yield 77% (110 mg). Pale yellow oil. ^{1}H NMR δ = 2.21 (s, 3 H), 2.26 (s, 3 H), 2.29 (d, J = 2.7 Hz, 1 H), 2.35 (s, 6 H), 5.43 (s, 1 H), 5.86 (s, 1 H), 6.03 (s, 1 H), 6.85 (s, 2 H) ppm. ^{13}C NMR δ = 13.6, 20.4, 20.8, 31.7, 70.6, 81.7, 106.0, 107.3, 129.9, 131.5, 136.8, 136.9, 150.3, 151.5 ppm. $C_{17}H_{18}O$ (238.32): calcd. C 85.67, H 7.61; found C 85.45, H 7.28.

3e: Yield 84% (124 mg). Pale yellow oil. ^{1}H NMR δ = 2.24 (s, 3 H), 2.45 (d, J = 3.0 Hz, 1 H), 5.71 (s, 1 H), 5.88 (s, 1 H), 6.04 (d, J = 3.0 Hz, 1 H), 7.50 (m, 3 H), 7.62 (d, J = 7.0 Hz, 1 H), 7.80 (d, J = 8.0 Hz, 1 H), 7.87 (d, J = 7.0 Hz, 1 H), 8.12 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR δ = 13.6, 37.2, 72.1, 82.2, 106.2, 107.6, 125.9, 125.9, 126.2, 126.4, 127.6, 127.9, 128.4, 132.7, 133.4, 135.8, 151.2, 152.1 ppm. $C_{18}H_{14}O$ (246.3): calcd. C 87.78, H 5.73; found C 87.53, H 5.64.

3f: Yield 75% (95 mg). Pale yellow oil. ^{1}H NMR δ = 1.17 (t, J = 7.5 Hz, 3 H), 2.40 (d, J = 2.5 Hz, 1 H), 2.58 (q, J = 7.5 Hz, 2 H), 5.00 (d, J = 2.5 Hz, 1 H), 5.88 (d, J = 3.0 Hz, 1 H), 6.07 (d, J = 3.0 Hz, 1 H), 7.23–7.42 (m, 5 H) ppm. ^{13}C NMR δ = 12.0, 21.3, 37.0, 71.7, 82.2, 104.5, 107.2, 127.3, 127.7, 128.6, 138.5, 151.1, 157.7 ppm. $C_{15}H_{14}O$ (210.27): calcd. C 85.68, H 6.71; found C 85.43, H 6.69.

3g: Yield 51% (65 mg). Pale yellow oil. ^{1}H NMR δ = 2.40 (d, J = 1.2 Hz, 1 H), 3.75 (s, 3 H), 4.93 (s, 1 H), 5.04 (d, J = 3.0 Hz), 6.07 (d, J = 3.0 Hz, 1 H), 7.25–7.42 (m, 5 H) ppm. ^{13}C NMR δ = 36.9, 57.6, 71.9, 79.8, 81.9, 107.6, 127.3, 127.7, 128.6, 138.2, 142.8, 161.3 ppm. $C_{14}H_{12}O_2$ (212.24): calcd. C 79.22, H 5.70; found C 78.99, H 5.51.

3h: Yield 59% (106 mg). Yellow oil. ^{1}H NMR δ = 2.23 (s, 3 H), 2.30 (d, J = 2.4 Hz, 1 H), 4.47 (dd, J = 9.9 and 2.4 Hz, 1 H), 5.88 (d, J = 3.0 Hz, 1 H), 6.09 (d, J = 3.0 Hz, 1 H), 6.15 (d, J = 9.9 Hz, 1 H), 7.25–7.40 (m, 10 H) ppm. ^{13}C NMR δ = 13.6, 31.7, 70.6, 82.4, 106.2, 106.6, 124.9, 127.6, 128.1, 128.4, 129.8, 138.7, 150.5, 151.9 ppm. $C_{22}H_{18}O$ (298.38): calcd. C 88.56, H 6.08; found C 88.40, H 5.85.

3i: Yield 61% (74 mg). Pale yellow oil. ^{1}H NMR δ = 1.10–1.90 (m, 10 H), 2.18 (d, J = 2.7 Hz, 1 H), 2.27 (s, 3 H), 3.55 (m, 1 H), 5.48 (dd, J = 11 and 2.7 Hz, 1 H), 5.88 (d, J = 3.0 Hz, 1 H), 6.06 (d, J = 3.0 Hz, 1 H) ppm. ^{13}C NMR δ = 13.6, 26.1, 26.2, 27.5, 29.2, 31.0, 70.9, 82.4, 105.9, 107.0, 150.9, 151.1 ppm. $C_{14}H_{18}O$ (202.29): calcd. C 83.12, H 8.97; found C 83.05, H 8.83.

3j: Yield 68% (74 mg). Pale yellow oil. ^{1}H NMR δ = 2.42 (d, J = 3.0 Hz, 1 H), 5.04 (d, J = 3.0 Hz, 1 H), 6.21 (d, J = 3.0 Hz, 1 H), 6.30 (m, 1 H), 7.25–7.43 (m, 6 H) ppm. ^{13}C NMR δ = 37.0, 72.0, 81.9, 106.7, 110.3, 127.5, 127.7, 128.6, 138.2, 142.3, 153.1 ppm. $C_{13}H_{10}O$ (182.22): calcd. C 85.69, H 5.53; found C 85.56, H 5.35.

3k: Yield 67% (73 mg). Brown oil. ^{1}H NMR δ = 2.45 (d, J = 2.4 Hz, 1 H), 5.06 (d, J = 2.4 Hz, 1 H), 6.00 (s, 1 H), 6.13 (q, J = 2.8 Hz, 1 H), 6.68 (q, J = 2.3 Hz, 1 H), 7.21–7.39 (m, 5 H), 8.11 (s, 1 H) ppm. ^{13}C NMR δ = 36.3, 72.2, 83.1, 106.5, 108.6, 117.4, 127.3, 127.6, 128.7, 129.9, 139.5 ppm. IR (neat): $\tilde{\nu}$ = 2118 ($C{\equiv}C$), 3289 ($\equiv C$–H), 3430 (N–H) cm^{-1}. $C_{13}H_{11}N$ (181.23): calcd. C 86.15, H 6.12, N 7.73; found C 85.88, H 5.93, N 7.50.

3l: Yield 94% (110 mg). Yellow oil. ^{1}H NMR δ = 2.43 (d, J = 2.4 Hz, 1 H), 3.43 (s, 3 H), 5.06 (d, J = 2.4 Hz, 1 H), 6.02 (s, 1 H), 6.07 (s, 1 H), 6.55 (s, 1 H), 7.22–7.44 (m, 5 H) ppm. ^{13}C NMR δ = 34.2, 35.4, 72.2, 83.0, 106.7, 108.5, 122.9, 127.1, 127.7, 128.6, 130.4, 139.0 ppm. $C_{14}H_{13}N$ (195.26): calcd. C 86.12, H 6.72, N 7.17; found C 85.85, H 6.55, N 6.99.

3m: Yield 86% (110 mg). Pale yellow oil. ^{1}H NMR δ = 2.40 (s, 3 H), 2.48 (s, 1 H), 5.13 (s, 1 H), 6.55 (s, 1 H), 6.74 (s, 1 H), 7.25–7.54 (m, 5 H) ppm. ^{13}C NMR δ = 15.3, 38.7, 72.3, 83.9, 124.6, 124.9, 128.6, 128.8, 130.9, 139.5, 140.6, 142.3 ppm. $C_{14}H_{12}S$ (212.31): calcd. C 79.20, H 5.70; found C 79.11, H 5.64.

3n: Yield 52% (72 mg). White crystals. ^{1}H NMR δ = 2.41 (d, J = 2.6 Hz, 1 H), 5.23 (s, 1 H), 7.02–7.52 (m, 10 H), 7.87 (br., 1 H) ppm. ^{13}C NMR δ = 34.6, 71.3, 84.8, 111.2, 116.2, 119.4, 119.6, 122.2, 122.6, 125.8, 126.9, 127.8, 128.5, 136.6, 140.6 ppm. $C_{17}H_{13}N$ (231.29): calcd. C 88.28, H 5.67, N 6.06; found C 88.12, H 5.51, N 5.95.

3o: Yield 95% (115 mg). Pale yellow oil. ^{1}H NMR δ = 0.90–1.25 (m, 5 H), 1.58–1.74 (m, 5 H), 2.18 (d, J = 2.7 Hz, 1 H), 3.47 (dd, J = 2.7 and 7.0 Hz, 1 H), 3.60 (s, 3 H), 6.04 (m, 2 H), 6.52 (t, J = 2.4 Hz, 1 H) ppm. ^{13}C NMR δ = 26.1, 26.2, 30.0, 31.5, 34.1, 36.2, 42.0, 70.7, 83.8, 106.6, 107.5, 122.0, 130.5 ppm. $C_{14}H_{19}N$ (201.31): calcd. C 83.53, H 9.51, N 6.96; found C 83.45, H 9.34, N 6.83.

3p: Yield 92% (116 mg). Pale yellow oil. ^{1}H NMR δ = 2.33 (s, 3 H), 2.41 (d, J = 3.0 Hz, 1 H), 3.43 (s, 3 H), 5.02 (d, J = 3.0 Hz, 1 H), 6.05 (m, 2 H), 6.55 (t, J = 2.4 Hz, 1 H), 7.12 (d, J = 8.1 Hz, 2 H), 7.23 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR δ = 21.0, 34.1, 35.1, 71.9, 83.2, 106.6, 108.4, 122.8, 127.4, 129.2, 130.6, 136.0, 136.7 ppm. $C_{15}H_{15}N$ (209.29): calcd. C 86.08, H 7.22, N 6.69; found C 85.85, H 7.19, N 6.61.

3q: Yield 92% (118 mg). Yellow oil. ^{1}H NMR δ = 2.45 (d, J = 2.0 Hz, 1 H), 3.44 (s, 3 H), 5.04 (s, 1 H), 5.98 (d, J = 2.0 Hz, 1 H), 6.06 (t, J = 3.0 Hz, 1 H), 6.57 (s, 1 H), 7.01 (dd, J = 8.7 and 8.7 Hz, 2 H), 7.32 (dd, J = 8.7 and 8.7 Hz) ppm. ^{13}C NMR δ = 34.1, 34.7, 72.4, 82.8, 100.5, 106.7, 108.5, 115.3 (d, J = 21 Hz), 123.1, 129.1 (d, J = 8 Hz), 130.2, 134.7 (d, J = 3 Hz), 163.5 (d, J = 265 Hz) ppm. $C_{14}H_{12}NF$ (213.25): calcd. C 78.85, H 5.67, N 6.57; found C 78.74, H 5.55, N 6.42.

3r: Yield 90% (132 mg). Yellow oil. ^{1}H NMR δ = 2.49 (d, J = 3.0 Hz, 1 H), 3.45 (s, 3 H), 5.22 (d, J = 3.0 Hz, 1 H), 6.08 (m, 2 H), 6.58 (t, J = 2.4 Hz, 1 H), 7.42 (m, 3 H), 7.83 (m, 4 H) ppm. ^{13}C NMR δ = 34.2, 35.6, 72.6, 82.9, 106.7, 108.7, 123.1, 125.9, 125.9, 126.1, 126.2, 127.6, 127.9, 128.4, 130.3, 132.6, 133.3, 136.4 ppm. $C_{18}H_{15}N$ (245.32): calcd. C 88.13, H 6.16, N 5.71; found C 88.01, H 5.99, N 5.68.

3s: Yield 91% (115 mg). Yellow oil. ^{1}H NMR δ = 1.87 (s, 3 H), 2.14 (s, 3 H), 2.40 (d, J = 3.0 Hz, 1 H), 4.96 (d, J = 3.0 Hz, 1 H), 5.94 (s, 1 H), 7.23–7.43 (m, 5 H) ppm. ^{13}C NMR δ = 9.81, 11.3, 37.0, 71.7, 82.4, 109.9, 114.6, 127.3, 127.8, 128.6, 138.5, 147.2, 150.0 ppm. $C_{15}H_{14}O$ (210.27): calcd. C 85.68, H 6.71; found C 85.52, H 6.47.

3t: Yield 79% (117 mg). Pale yellow oil. ^{1}H NMR δ = 2.24 (s, 3 H), 2.45 (d, J = 2.4 Hz, 1 H), 5.70 (d, J = 2.0 Hz, 1 H), 5.87 (d, J = 2.4 Hz, 1 H), 6.03 (d, J = 3.6 Hz, 1 H), 7.44–7.53 (m, 3 H), 7.62 (d, J = 6.8 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 8.12 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR δ = 13.6, 34.2, 72.0, 82.4, 106.3, 108.2, 123.5, 125.5, 125.7, 126.0, 126.2, 128.4, 128.8, 130.9, 134.0, 150.8, 151.9 ppm. $C_{18}H_{14}O$ (246.30): calcd. C 87.78, H 5.73; found C 87.60, H 5.64.

***N*-(1-Phenyl-2-propenyl)indole:** Yield 74% (103 mg). Pale yellow oil. ^{1}H NMR δ = 5.01 (d, J = 16.9 Hz, 1 H), 5.36 (d, J = 10.3 Hz, 1 H), 6.09 (d, J = 5.7 Hz, 1 H), 6.30–6.39 (m, 1 H), 6.52 (d, J = 3.3 Hz, 1 H), 7.07–7.29 (m, 9 H), 7.62 (d, J = 7.7 Hz, 1 H) ppm. ^{13}C NMR δ = 61.9, 101.5, 110.1, 118.5, 119.6, 120.9, 121.5, 126.2, 127.5, 127.9, 128.7, 128.8, 136.0, 139.0 ppm.

6a: Yield 50% (71 mg). White crystals. ^{1}H NMR δ = 2.44 (d, J = 2.7 Hz, 1 H), 2.89 (s, 6 H), 4.93 (s, 1 H), 6.67 (d, J = 8.6 Hz, 2 H), 7.19–7.38 (m, 7 H) ppm. ^{13}C NMR δ = 40.6, 41.9, 72.2, 85.3, 112.8, 126.7, 127.7, 128.4, 128.5, 129.1, 141.7, 149.5 ppm. $C_{17}H_{17}N$ (235.32): calcd. C 86.77, H 7.28, N 5.95; found C 86.47, H 7.19, N 5.82.

6b: Yield 58% (106 mg). Brown solid. ^{1}H NMR δ = 2.49 (d, J = 2.6 Hz, 1 H), 2.91 (s, 6 H), 4.96 (s, 1 H), 6.67 (d, J = 8.8 Hz, 2 H), 7.19 (d, J = 8.8 Hz, 2 H), 7.47–7.56 (m, 4 H) ppm. ^{13}C NMR δ = 40.7, 41.9, 73.0, 84.3, 112.6, 125.3, 125.4, 127.8, 127.9, 128.3, 128.9, 145.7, 149.6 ppm. $C_{18}H_{16}NF_3$ (303.32): calcd. C 71.28, H 5.32, N 4.62; found C 71.55, H 5.28, N 4.42.

6c: Yield 53% (86 mg). Yellow oil. ^{1}H NMR δ = 2.45 (s, 1 H), 2.90 (s, 6 H), 4.88 (s, 1 H), 6.6 (d, J = 8.4 Hz, 2 H), 7.16–7.2 (m, 6 H) ppm. ^{13}C NMR δ = 40.5, 41.3, 72.6, 84.8, 112.7, 128.3, 128.6, 129.1, 132.5, 140.4, 149.7 ppm. $C_{17}H_{16}NCl$ (269.77): calcd. C 75.69, H 5.98, N 5.19; found C 75.91, H 5.93, N 4.89.

6d: Yield 23% (34 mg). Yellow crystals. ^{1}H NMR δ = 2.30 (s, 3 H), 2.43 (d, J = 2.6 Hz, 1 H), 2.89 (s, 6 H), 4.89 (s, 1 H), 6.66 (d, J = 6.6 Hz, 2 H), 7.07–7.26 (m, 6 H) ppm. ^{13}C NMR δ = 21.1, 40.7, 41.6, 72.1, 85.5, 112.6, 127.5, 128.2, 129.1, 129.1, 136.1, 138.8, 149.4 ppm. $C_{18}H_{19}N$ (249.35): calcd. C 86.70, H 7.68, N 5.62; found C 86.43, H 7.58, N 5.44.

6f: Yield 30% (51 mg). Yellow crystals. ^{1}H NMR δ = 2.52 (s, 1 H), 2.88 (s, 6 H), 5.09 (s, 1 H), 6.66 (d, J = 8.8 Hz, 2 H), 7.25 (d, J = 8.8 Hz, 2 H), 7.41–7.88 (m, 7 H) ppm. ^{13}C NMR δ = 40.6, 42.1, 72.7, 85.1, 112.6, 125.6, 125.8, 125.9, 126.1, 127.5, 127.8, 128.2, 128.4, 128.6, 132.3, 133.3, 139.0, 149.5 ppm. HRMS: *m*/*z* calcd. for $C_{21}H_{19}N$ [M] 285.1517; found 285.1516.

6g: Yield 23% (36 mg). Reddish brown oil. ^{1}H NMR δ = 1.13 (t, J = 7.0 Hz, 6 H), 2.45 (s, 1 H), 3.31 (q, J = 7.0 Hz, 4 H), 4.91 (s, 1 H), 6.61 (d, J = 7.9 Hz, 2 H), 7.16–7.40 (m, 7 H) ppm. ^{13}C NMR δ = 12.5, 41.9, 44.3, 72.1, 85.4, 111.7, 126.6, 127.7, 128.5, 129.2, 141.8, 146.7 ppm. $C_{19}H_{21}N$ (263.38): calcd. C 86.65, H 8.04, N 5.32; found C 86.62, H 8.24, N 5.14.

6h: Yield 49% (87 mg). Pale brown oil. ^{1}H NMR δ = 2.46 (d, J = 2.6 Hz, 1 H), 3.26 (s, 3 H), 4.95 (s, 1 H), 6.91–7.40 (m, 14 H) ppm. ^{13}C NMR δ = 40.2, 42.2, 72.5, 84.9, 120.1, 120.7, 121.4, 126.9, 127.7, 128.5, 128.6, 129.1, 133.6, 141.3, 147.8, 148.8 ppm. $C_{22}H_{19}N$ (297.36): calcd. C 88.85, H 6.44, N 4.71; found C 88.75, H 6.56, N 4.59.

6i: Yield 63% (107 mg). Red solid; m.p. 57.0–57.8 °C. ^{1}H NMR δ = 2.46 (d, J = 2.0 Hz, 1 H), 4.95 (d, J = 2.0 Hz, 1 H), 5.64 (br. s, 1 H), 6.87 (t, J = 7.6 Hz, 2 H), 7.00 (m, 4 H), 7.02–7.26 (m, 5 H), 7.30 (m, 2 H), 7.38 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR δ = 42.1, 72.6, 84.9, 117.7, 117.8, 120.9, 126.9, 127.7, 128.6, 128.6, 129.3, 133.5, 141.3, 141.9, 142.9 ppm. IR (neat): $\tilde{\nu}$ = 2114 (*C*≡*C*), 3289 (≡*C*–*H*), 3399 (*N*–*H*) cm^{-1}. $C_{21}H_{17}N$ (283.37): calcd. C 89.01, H 6.05, N 4.94; found C 88.79, H 6.10, N 5.27.

6j and 6k: Yield 60% (93 mg) (a mixture of **6j** and **6k** was obtained in a ratio of 1 to 5). Yellow oil. **6k**. ^{1}H NMR δ = 2.35 (d, J = 3.0 Hz, 1 H), 4.94 (d, J = 3.0 Hz, 1 H), 6.24 (t, J = 3.0 Hz, 1 H), 6.30 (m, 1 H), 6.73 (t, J = 3.0 Hz, 1 H), 7.11–7.38 (m, 10 H) ppm. ^{13}C NMR δ = 35.3, 71.6, 84.0, 108.1, 108.9, 120.1, 122.8, 126.7, 127.4, 128.2, 128.9, 132.1, 139.5, 139.9 ppm. **6j**. ^{1}H NMR δ = 2.41 (d, J = 3.0 Hz, 1 H), 6.22 (m, 1 H), 7.00 (m, 2 H) ppm. $C_{19}H_{15}N$ (257.33): calcd. C 88.68, H 5.88, N 5.44; found C 88.88, H 5.84, N 5.37.

6l: Yield 48% (71 mg). Green oil. ^{1}H NMR δ = 2.44 (d, J = 2.6 Hz, 1 H), 2.69 (s, 3 H), 2.86 (t, J = 8.1 Hz, 2 H), 3.23 (t, J = 8.1 Hz, 2 H), 4.89 (s, 1 H), 6.38 (d, J = 7.7 Hz, 1 H), 7.04–7.39 (m, 7 H) ppm. ^{13}C NMR δ = 28.6, 36.2, 42.3, 56.2, 72.2, 85.4, 106.8, 123.7, 126.6, 126.7, 127.6, 128.4, 130.4, 130.9, 141.8, 152.4 ppm. $C_{18}H_{17}N$ (247.33): calcd. C 87.41, H 6.93, N 5.66; found C 87.31, H 6.98, N 5.65.

6m: Yield 52% (97 mg). Pale yellow oil. ^{1}H NMR δ = 1.85 (s, 3 H), 2.04 (s, 1 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 5.90 (s, 1 H), 6.36 (s, 1 H), 7.24–7.39 (m, 6 H), 7.55 (br. s, 1 H) ppm. ^{13}C NMR δ = 24.2, 30.2, 55.4, 56.0, 72.7, 83.1, 95.4, 100.6, 111.3, 126.4, 126.8, 128.5, 137.6, 138.5, 156.9, 159.8, 167.8 ppm. $C_{19}H_{19}NO_3$ (309.36): calcd. C 73.77, H 6.19, N 4.53; found C 73.55, H 6.27, N 4.46.

6n: Yield 38% (64 mg). Pale yellow oil. ^{1}H NMR δ = 2.26 (dd, J = 1.3 and 2.6 Hz, 1 H), 3.73 (s, 6 H), 3.78 (s, 3 H), 5.69 (s, 1 H), 6.13 (s, 2 H), 7.15 (d, J = 7.3 Hz, 1 H), 7.23 (t, J = 7.3 Hz, 2 H), 7.43 (d, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR δ = 30.5, 55.3, 55.9, 68.9, 84.8, 91.5, 110.8, 125.8, 127.1, 127.7, 140.9, 158.5, 160.4 ppm. $C_{18}H_{18}O_3$ (282.33): calcd. C 76.57, H 6.43; found C 76.48, H 6.44.

6o: Yield 87% (126 mg). Blue solid. ^{1}H NMR δ = 2.45 (s, 1 H), 5.66 (s, 1 H), 7.03–8.33 (m, 12 H) ppm. ^{13}C NMR δ = 35.8, 71.7, 85.2, 116.9, 122.4, 123.0, 126.7, 127.5, 128.5, 133.5, 134.5, 137.1, 137.6, 141.3 ppm. $C_{19}H_{14}$ (242.31): calcd. C 94.18, H 5.82; found C 94.31, H 5.74.

6p: Yield 81% (135 mg). Blue oil. ^{1}H NMR δ = 2.48 (d, J = 2.6 Hz, 1 H), 5.64 (d, J = 2.6 Hz, 1 H), 7.11–7.35 (m, 7 H), 7.59 (t, J = 9.7 Hz, 1 H), 7.86 (d, J = 3.9 Hz, 1 H), 8.31 (dd, J = 5.3 and 9.7 Hz, 2 H) ppm. ^{13}C NMR δ = 35.2, 72.1, 84.7, 117.0, 122.6, 123.3, 127.7, 128.6, 128.9, 132.5, 133.4, 134.5, 137.0, 137.2, 137.8, 140.0, 141.4 ppm. $C_{19}H_{13}Cl$ (276.76): calcd. C 82.46, H 4.73; found C 82.20, H 4.72.

Preparation of [Cp*RuCl(μ$_2$-SMe)$_2$RuCp*(C=C=CHPh)]BF$_4$ (4a): A typical experimental procedure for the preparation of the title compound is described below. In a 200-mL flask were placed **1a** (510 mg, 0.80 mmol), NH_4BF_4 (109 mg, 1.04 mmol) and $MgSO_4$ (1 g) under nitrogen. Anhydrous tetrahydrofuran (THF) (100 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (219 mg, 1.66 mmol), the reaction flask was kept at room temperature for 30 min. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2/diethyl ether to give black crystals of **4a** (378 mg, 0.467 mmol; 58%).

4a: Black crystals. ^{1}H NMR δ = 1.66 (s, 15 H), 1.85 (s, 15 H), 2.73 (s, 6 H), 7.39 (t, J = 7.5 Hz, 2 H), 7.66 (t, J = 7.5 Hz, 1 H), 7.72 (d, J = 7.5 Hz, 2 H), 8.89 (s, 1 H) ppm. ^{13}C NMR δ = 10.4, 10.6, 20.1, 99.4, 105.6, 130.2, 132.4, 134.0, 142.6, 151.2, 198.0, 319.7 ppm. IR (KBr): $\tilde{\nu}$ = 1945 (*C*=*C*=*C*) cm^{-1}. $C_{31}H_{42}BClF_4Ru_2S_2$ (803.19): calcd. C 46.36, H 5.27; found C 46.00, H 5.15.

Reaction of 2a with [D$_5$]Pyrrole in the Presence of 1a and NH$_4$BF$_4$: In a 20-mL flask were placed **1a** (0.03 mmol) and NH_4BF_4 (0.06 mmol) under nitrogen. Anhydrous $ClCH_2CH_2Cl$ (18 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **1a** (0.60 mmol) and [D$_5$]pyrrole (3.00 mmol), the reaction flask was kept at 60 °C for 1 h. The solvent was concentrated under reduced pressure maintained by an aspirator, and then the residue was purified by TLC (SiO_2) with EtOAc/*n*-hexane (3:7) to give 2-(1-phenyl-2-propynyl)pyrrole (**3l′**) as a brown oil (83 mg, 0.46 mmol; 77% yield).

2-(1-Phenyl-2-propynyl)pyrrole (3l′): Brown oil. ^{1}H NMR ($CDCl_3$): δ = 2.45 (d, J = 2.4 Hz, 0.20 H), 5.06 (d, J = 2.4 Hz, 1 H), 7.21–7.39 (m, 5 H), 8.11 (s, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 2585 (≡*C*–*D*), 3428 (*N*–*H*) cm^{-1}. This result indicates the 80% deuterium content at the C-3 position.

Ruthenium-Catalyzed Intramolecular Cyclization Reactions of Propargylic Alcohols: A typical experimental procedure for the intramolecular cyclization reaction of **7a** catalyzed by [Cp*RuCl(μ$_2$-SMe)$_2$RuCp*Cl] (**1a**) is described below. In a 50-mL flask were placed **1a** (19 mg, 0.03 mmol) and NH_4BF_4 (6 mg, 0.06 mmol) under nitrogen. Anhydrous $ClCH_2CH_2Cl$ (30 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **7a** (136.8 mg, 0.6 mmol), the reaction flask was kept at 60 °C for 24 h. The solvent was concentrated under reduced pressure maintained by an aspirator, and then the residue was purified by TLC (SiO_2) with EtOAc/*n*-hexane (1:9) to give 4-ethynyl-4,10-dihydro-3,9-dioxabenzo[*f*]azulene (**8a**) as a pale yellow oil (102.9 mg, 0.49 mmol; 82% yield).

4-Ethynyl-4,10-dihydro-3,9-dioxabenzo[*f*]azulene (8a): ^{1}H NMR δ = 2.52 (t, J = 1.5 Hz, 1 H), 4.90 (t, J = 15.6 Hz, 2 H), 5.23 (s, 1 H), 6.10 (d, J = 1.5 Hz, 1 H), 7.10–7.21 (m, 2 H), 7.25–7.31 (m, 2 H), 7.47 (d, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR δ = 33.5, 69.2, 73.0, 80.2, 108.8, 117.4, 122.8, 124.8, 127.7, 129.3, 132.9, 141.1, 145.2, 157.3 ppm. HRMS: *m*/*z* calcd. for $C_{14}H_{10}O_2$ [M] 210.0681; found 210.0680.

4-Ethynyl-6-methyl-4,10-dihydro-3,9-dioxabenzo[*f*]azulene (8b): Yield 63% (85 mg). Yellow oil. ^{1}H NMR δ = 2.31(s, 3 H), 2.52 (d, J = 2.7 Hz, 1 H), 4.87 (q, J = 14.7 Hz, 2 H), 5.18 (s, 1 H), 6.10 (d, J = 2.7 Hz, 1 H), 7.06 (s, 2 H), 7.27 (t, J = 2.7 Hz, 2 H) ppm. ^{13}C

NMR δ = 20.8, 33.6, 69.2, 72.9, 80.4, 108.8, 117.5, 122.5, 128.2, 129.7, 132.4, 134.4, 141.1, 145.4, 155.0 ppm. HRMS: *m*/*z* calcd. for $C_{15}H_{12}O_2$ [M] 224.0837; found 224.0836.

6-Chloro-4-ethynyl-4,10-dihydro-3,9-dioxabenzo[*f*]azulene (8c): Yield 40% (59 mg). Yellow solid; m.p. 65.8–66.8 °C. ^{1}H NMR δ = 2.58 (d, *J* = 2.4 Hz, 1 H), 4.88 (dq, *J* = 1.8 and 14.7 Hz, 2 H), 5.26 (s, 1 H), 6.12 (d, *J* = 1.8 Hz, 1 H), 7.10 (d, *J* = 8.4 Hz, 1 H), 7.23–7.31 (m, 2 H), 7.50 (d, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR δ = 33.2, 69.4, 73.9, 79.1, 108.8, 117.2, 124.1, 127.6, 129.2, 129.9, 134.6, 141.4, 144.5, 155.8 ppm. $C_{14}H_9ClO_2$ (244.67): calcd. C 68.72, H 3.71; found C 68.47, H 4.00.

4-Ethynyl-8-methyl-4,10-dihydro-3,9-dioxabenzo[*f*]azulene (8d): Yield 72% (97 mg). Yellow oil. ^{1}H NMR δ = 2.33 (s, 3 H), 2.50 (d, *J* = 2.8 Hz, 1 H), 4.85 (q, *J* = 14.8 Hz, 2 H), 5.18 (s, 1 H), 6.10 (d, *J* = 2.8 Hz, 1 H), 6.99 (t, *J* = 7.6 Hz, 1 H), 7.14 (d, *J* = 7.6 Hz, 1 H), 7.27 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR δ = 15.8, 33.6, 67.5, 72.6, 80.5, 108.7, 117.4, 117.5, 124.4, 125.3, 130.7, 131.6, 132.9, 140.9, 145.5, 154.9 ppm. HRMS: *m*/*z* calcd. for $C_{15}H_{12}O_2$ [M] 224.0837; found 224.0833.

4-Ethynyl-8-methoxy-4,10-dihydro-3,9-dioxabenzo[*f*]azulene (8e): Yield 56% (81 mg). Yellow solid; m.p. 114.8–116.0 °C. ^{1}H NMR δ = 2.44 (d, *J* = 2.7 Hz, 1 H), 3.79 (t, *J* = 15.4 Hz, 3 H), 4.83 (d, *J* = 14.7 Hz, 2 H), 5.21 (s, 1 H), 6.04 (s, 1 H), 6.82 (d, *J* = 7.2 Hz, 1 H), 6.96 (m, 2 H), 7.20 (s, 1 H) ppm. ^{13}C NMR δ = 33.4, 55.9, 68.2, 73.0, 79.9, 108.8, 112.0, 117.5, 119.1, 124.9, 134.7, 141.0, 145.2, 145.5, 152.8 ppm. HRMS: *m*/*z* calcd. for $C_{15}H_{12}O_3$ [M] 240.0786; found 240.0781.

7-Ethynyl-7,11-dihydro-8,12-dioxanaphtho[2,1-*f*]azulene (8f): Yield 68% (106 mg). Orange solid; m.p. 120.0–121.2 °C. ^{1}H NMR δ = 2.51 (d, *J* = 2.7 Hz, 1 H), 4.96 (q, *J* = 15.8 Hz, 2 H), 5.25 (s, 1 H), 6.04 (t, *J* = 15.8 Hz, 1 H), 7.28 (d, *J* = 1.5 Hz, 1 H), 7.41–7.59 (m, 4 H), 7.77 (d, *J* = 7.8 Hz, 1 H), 8.22 (d, *J* = 7.8 Hz, 1 H) ppm. ^{13}C NMR 33.8, 68.3, 72.7, 80.6, 108.8, 118.0, 121.8, 124.4, 125.4, 126.3, 127.8, 128.2, 128.3, 134.4, 141.1, 145.4, 152.4 ppm. HRMS: *m*/*z* calcd. for $C_{18}H_{12}O_2$ [M] 260.0837; found 260.0841.

11-Ethynyl-8,10-dimethoxy-6,11-dihydrodibenzo[b,e]oxepine (10a): Yield 16% (27 mg). Yellow solid; m.p. 135.5–137.0 °C. ^{1}H NMR δ = 2.37 (d, *J* = 2.7 Hz, 1 H), 3.80 (d, *J* = 14.1 Hz, 6 H), 4.77 (d, *J* = 12.9 Hz, 1 H), 5.47 (d, *J* = 2.7 Hz, 1 H), 6.17 (d, *J* = 12.9 Hz, 1 H), 6.45 (d, *J* = 2.7 Hz, 2 H), 6.84 (q, *J* = 7.8 Hz, 2 H), 7.11 (t, *J* = 7.8 Hz, 1 H), 7.23 (m, 1 H) ppm. ^{13}C NMR δ = 30.9, 55.4, 55.9, 70.5, 70.9, 86.2, 98.6, 105.5, 120.5, 121.6, 125.1, 128.9, 132.0, 137.9, 156.5, 156.9, 160.0 ppm. HRMS: *m*/*z* calcd. for $C_{18}H_{16}O_3$ [M] 280.1099; found 280.1097.

11-Ethynyl-2,8,10-trimethoxy-6,11-dihydrodibenzo[b,e]oxepine (10b): Yield 19% (35 mg). White solid; m.p. 140.2–141.6 °C. ^{1}H NMR δ = 2.27 (d, *J* = 3.0 Hz, 1 H), 3.68 (d, *J* = 7.8 Hz, 6 H), 3.77 (s, 3 H), 4.68 (d, *J* = 13.4 Hz, 1 H), 5.33 (d, *J* = 3.0 Hz, 1 H), 5.90 (d, *J* = 13.4 Hz, 1 H), 6.32 (d, *J* = 3.0 and 13.0 Hz, 2 H), 6.62 (m, 3 H) ppm. ^{13}C NMR δ = 31.2, 55.4, 55.8, 56.1, 70.5, 71.2, 86.0, 98.4, 104.9, 114.8, 116.0, 116.4, 118.8, 121.4, 126.9, 138.2, 151.0, 154.2, 156.6, 159.9 ppm. HRMS: *m*/*z* calcd. for $C_{19}H_{18}O_4$ [M] 310.1205; found 310.1205.

2-Chloro-11-ethynyl-8,10-dimethoxy-6,11-dihydrodibenzo[b,e]oxepine (10c): Yield 21% (40 mg). White crystals, m.p. 149.8–150.8 °C. ^{1}H NMR δ = 2.31 (d, *J* = 2.4 Hz, 1 H), 3.73 (d, *J* = 16.0 Hz, 6 H), 4.69 (d, *J* = 13.2 Hz, 1 H), 5.33 (d, *J* = 2.4 Hz, 1 H), 6.10 (d, *J* = 13.2 Hz, 1 H), 6.38 (s, 2 H), 6.69 (d, *J* = 8.4 Hz, 1 H), 6.99 (dd, *J* = 2.4 and 8.4 Hz, 1 H), 7.16 (d, *J* = 2.4 Hz, 1 H) ppm. ^{13}C NMR δ = 30.6, 55.4, 55.9, 70.5, 71.4, 85.5, 98.7, 105.6, 118.8, 121.9, 125.8, 126.2, 128.7, 131.4, 137.4, 155.4, 156.3, 160.1 ppm. $C_{18}H_{15}ClO_3$ (314.76): calcd. C 68.68, H 4.80; found C 68.50, H 4.83.

13-Ethynyl-10,12-dimethoxy-8,13-dihydrobenzo[*e*]-naphtho[1,2-*b*]oxepine (10d): Yield 34% (67 mg). White solid; m.p. 175.1–176.3 °C. ^{1}H NMR δ = 2.32 (d, *J* = 2.8 Hz, 1 H), 3.82 (d, *J* = 5.6 Hz, 6 H), 4.85 (d, *J* = 12.8 Hz, 1 H), 6.24 (d, *J* = 12.8 Hz, 1 H), 6.31 (d, *J* = 2.8 Hz, 1 H), 6.47 (d, *J* = 2.4 Hz, 1 H), 6.52 (d, *J* = 2.4 Hz, 1 H), 7.02 (d, *J* = 8.8 Hz, 1 H), 7.36 (t, *J* = 7.2 Hz, 1 H), 7.58–7.63 (m, 2 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 8.29 (d, *J* = 8.4 Hz, 1 H) ppm. ^{13}C NMR δ = 24.8, 55.4, 56.0, 70.0, 70.8, 86.1, 98.6, 105.0, 116.1, 119.1, 121.9, 122.6, 123.5, 126.9, 128.4, 129.3, 129.8, 133.3, 138.6, 155.2, 156.6, 160.0 ppm.

X-ray Crystallographic Studies of 6n and 10c: Colorless crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane. CCDC-196412 (**6n**) and CCDC-288345 (**10c**) contain the supplementary crystallographic data for these crystals. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{13}C NMR spectra of **8a**, **8b**, **8d**, **8e**, **8f**, **10a**, **10b**, and **10d**.

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