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Lewis Acid Catalyzed Cascade Reactions of 1,6-Diynes and 1,6-Enynes with Vinylidenecyclopropanes

Liang-Feng Yao and Min Shi*[a]

Abstract: Lewis acid catalyzed reactions of *N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methyl-*N*-prop-2-ynylbenzenesulfonamides or 1,1-diphenyl-4-prop-2-ynyloxybut-2-yn-1-ol (1,6-diynes) **1** and *N*-allyl-*N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methylbenzenesulfonamides (1,6-enynes) **2** with vinylidenecyclopropanes **3** selectively produce polycyclic compounds **4**, **5** and **10** as well as isopropylidene-3,3-diarylcyclobut-1-enylmethyl derivatives **6** or **7** in good to high yields depending on the substituents on the benzene ring of **3** under mild conditions. An interesting $PtCl_2$-catalyzed cyclization of **6** and a $Cu(OAc)_2{\cdot}H_2O$ catalyzed Eglinton coupling reaction of **5** and **10** to produce the corresponding 5-isopropylidene-6-methyl-1-(toluene-4-sulfonyl)-7-vinyl-1,2,3,4,5,8-hexahydroazocine derivatives **8** and the coupling products **9** and **11** in good yields have been disclosed, respectively. Plausible mechanisms of these processes have been proposed that belong to a cascade rearrangement followed by the Friedel–Crafts reaction, an intramolecular proton transferring and a cyclization reaction.

Keywords: cyclization · cyclopropanes · Friedel–Crafts reaction · Lewis acids · platinum

Introduction

Metal-catalyzed reactions of 1,6-diynes and 1,6-enynes have emerged as efficient and useful methods for the construction of cyclic or polycyclic organic skeletons from rather simple substrates under mild conditions.[1] Recently, we have been investigating the Lewis acid catalyzed skeletal conversions of vinylidenecyclopropanes (VDCPs) and methylenecyclopropanes (MCPs), two kinds of highly strained and readily accessible molecules, into various cyclic compounds under mild conditions through the formation of cationic intermediates.[2–4] Thus far, a number of interesting intramolecular and intermolecular skeletal conversions of VDCPs and MCPs into cyclic functional compounds have been explored. For example, previously, we reported that arylmethylenecyclopropanes can react with 3-methoxy-1,3,3-triarylprop-1-yne or 1,1,3-triarylprop-2-yn-1-ol to give the corresponding functionalized methylenecyclobutene, cyclobutane, and cyclopropane derivatives in the presence of Lewis acid $BF_3{\cdot}OEt_2$ under mild conditions as well as vinylidenecyclopropanes can react with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers to produce 4-dihydro-1*H*-cyclopenta[*b*]naphthalene derivatives and 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives in good to high yields in the presence of Lewis acid, respectively, depending on the substituents on the cyclopropane (Scheme 1).[5] These results inspired us to investigate the intermolecular reactions of 1,6-diynes and 1,6-enynes with VDCPs in the presence of metal catalysts. On the basis of above results, we envisaged that a diphenylmethanol containing 1,6-diyne or 1,6-enyne would produce cationic intermediate **A** similarly in the presence of Lewis acids via an allenyl cationic rearrangement; this intermediate is anticipated to react with VDCPs to afford very useful polycyclic compounds through a tandem reaction pathway (Scheme 2). Moreover, it is conceivable that through the extra C=C double bond or C≡C triple bond in 1,6-diyne or 1,6-enyne, the further transformation could be realized. Polysubstituted aromatic compounds have played an important role in the chemical and pharmaceutical industries as well as in the fields of optical and electronic materials. Recently, there has been a considerable interest in synthesizing

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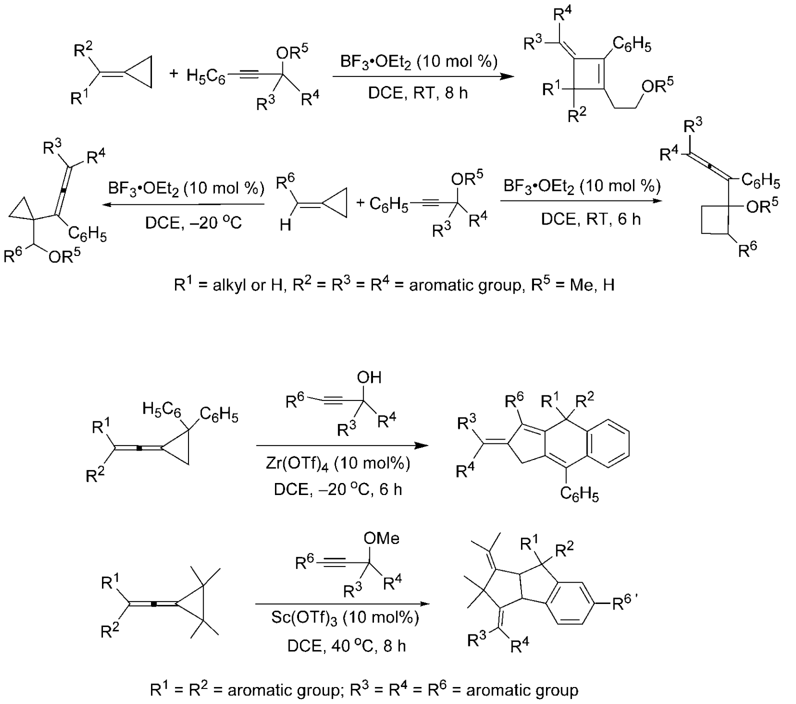
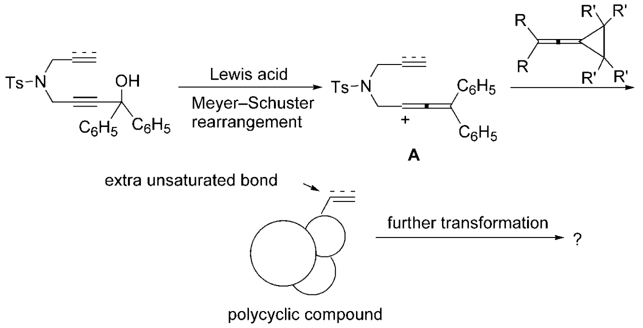
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200802284: The spectroscopic data (^1H and ^{13}C NMR spectroscopic data) and analytic data of the compounds shown in Tables 1–3 and Scheme 2, the X-ray crystal structures of **4a**, **6a**, **8a** and **10a** and the detailed description of experimental procedures



Scheme 1. Lewis acid catalyzed reactions of arylmethylenecyclopropanes with 3-methoxy-1,3,3-triarylprop-1-yne or 1,1,3-triarylprop-2-yn-1-ol.



Scheme 2. Proposal on the intermolecular reactions of 1,6-diyne and 1,6-enyne with VDCPs in the presence of Lewis acid.

naphthalene, indene derivatives and other extended aromatic systems, which are extremely useful benzenoid compounds for biological studies and material applications.[6] The most important methods for these compounds include annulation via Fischer carbene (the Dötz reaction)[7] and palladium-catalyzed cyclization of alkynes with arylsilyl triflate via highly reactive benzynes (generated in situ).[8] Herein, we wish to report highly efficient Lewis acid catalyzed cascade intermolecular reactions of *N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methyl-*N*-prop-2-ynylbenzenesulfonamides or 1,1-diphenyl-4-prop-2-ynyloxybut-2-yn-1-ol (1,6-diynes) **1** and *N*-allyl-*N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methylbenzenesulfonamides (1,6-enynes) **2** with VDCPs **3** that selectively produce polycyclic derivatives **4** and **5** as well as isopropylidene-3,3-diarylcyclobut-1-enylmethyl derivatives **6** or **7** in good to high yields under mild conditions; the resulting products depend on the substituents on the benzene rings of **3** along with an interesting PtCl$_2$-catalyzed cyclization and a Cu(OAc)$_2$•H$_2$O catalyzed Eglinton coupling reaction.

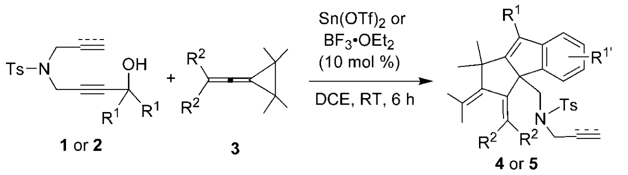
Results and Discussion

Initial examinations using *N*-(4-hydroxy-4,4-diphenylbut-2-ynyl)-4-methyl-*N*-prop-2-ynylbenzenesulfonamide (1,6-diyne) (**1a**, R^1 = C$_6$H$_5$, 0.1 or 0.12 mmol) or *N*-allyl-*N*-(4-hydroxy-4,4-diphenylbut-2-ynyl)-4-methylbenzenesulfonamide (1,6-enyne) (**2a**, R^1 = C$_6$H$_5$, 0.1 or 0.12 mmol) and diphenylvinylidenecyclopropane (**3a**, R^2 = C$_6$H$_5$, 0.1 or 0.2 mmol) having four methyl groups at the cyclopropane ring as the substrates in the presence of various Lewis acids in a variety of solvents were aimed at determining the optimal conditions. The results of these experiments are provided in the Supporting Information as Tables S1 and S2. We found that the corresponding polycyclic compounds **4a** or **5a** were formed in the presence of Sn(OTf)$_2$ (10 mol % for the formation of **4a**) and BF$_3$•OEt$_2$ (10 mol % for the formation of **5a**) in 1,2-dichloroethane (DCE) at room temperature (20 °C), which serves as the best condition for the following experiments.

Under this optimal condition, we next carried out this reaction using a variety of starting materials **1** (1,6-diynes) or **2** (1,6-enyne) and **3** (diarylvinylidenecyclopropanes) attached by different aromatic groups. The selected results are summarized in Table 1. As can be seen in Table 1, the corresponding polycyclic compounds **4** and **5** were obtained in good to high yields (50 to 99 %, Table 1, entries 1–15). Substituents on the aromatic ring of **1**, **2** and **3** have little influence on the reaction outcomes. As for unsymmetrical 1,6-enyne **2c** (R^1 = C$_6$H$_5$. R^1 = Me), the corresponding polycyclic product **5f** was obtained in 50 % yield (Table 1, entry 15). In the case of unsymmetrical vinylidenecyclopropanes **3e** and **3f**, polycyclic products **4h** and **4i** were produced stereospecifically in 75 and 70 % yield with *E*/*Z* or *Z*/*E* > 99:1 on the basis of their NMR spectroscopic data (see Supporting Information), respectively (Table 1, entries 8 and 9). Product structures were determined by ^{1}H and ^{13}C NMR spectroscopic data, HRMS and microanalysis. Furthermore, the X-ray crystal structure of **4a** was determined and its CIF data are presented in the Supporting Information (Figure 1).[9]

Using 1,1-diphenyl-4-prop-2-ynyloxy-but-2-yn-1-ol (**1a′**) to replace **1a** in the reaction with **3a** afforded the corre-

Table 1. $Sn(OTf)_2$ or $BF_3{\cdot}OEt_2$-catalyzed reactions of **1** or **2** with VDCPs **3**.



Entry[a]	R^1/R^1	R^2/R^2	Yield of **4** or **5** [%][b]
1	C_6H_5/ C_6H_5, **1a**	C_6H_5/ C_6H_5, **3a**	**4a**, 80[c]
2	*p*-ClC_6H_4/ *p*-ClC_6H_4, **1b**	**3a**	**4b**, 80[c]
3	*p*-MeC_6H_4/ *p*-MeC_6H_4, **1c**	**3a**	**4c**, 93[c]
4	*p*-FC_6H_4/ *p*-FC_6H_4, **1d**	**3a**	**4d**, 95[c]
5	**1a**	*p*-FC_6H_4/ *p*-FC_6H_4, **3b**	**4e**, 91[c]
6	**1a**	*p*-MeC_6H_4/ *p*-MeC_6H_4, **3c**	**4f**, 99[c]
7	**1a**	*p*-ClC_6H_4/ *p*-ClC_6H_4, **3d**	**4g**, 94[c]
8	C_6H_5/ C_6H_5, **2a**	*p*-ClC_6H_4/ C_6H_5, **3e**	**4h**, 75[e]
9	**2a**	*m*,*p*-$Cl_2C_6H_3$/ C_6H_5, **3f**	**4i**, 70[e]
10	**2a**	**3a**	**5a**, 97[d]
11	**2a**	**3d**	**5b**, 86[d]
12	**2a**	**3b**	**5c**, 85[d]
13	**2a**	**3c**	**5d**, 90[d]
14	*p*-MeC_6H_4/ *p*-MeC_6H_4, **2b**	**3a**	**5e**, 88[d]
15	*p*-MeC_6H_4/ Me, **2c**	**3a**	**5f**, 50[d]

[a] All reactions were carried out using **1** or **2** (0.4 mmol), **3** (0.2 mmol) and catalyst (10 mol%) in DCE (2 mL). [b] Isolated yields. [c] $Sn(OTf)_2$ was used a Lewis acid. [d] $BF_3{\cdot}OEt_2$ was used as a Lewis acid. [e] *E*/*Z* or *Z*/*E* > 99:1.

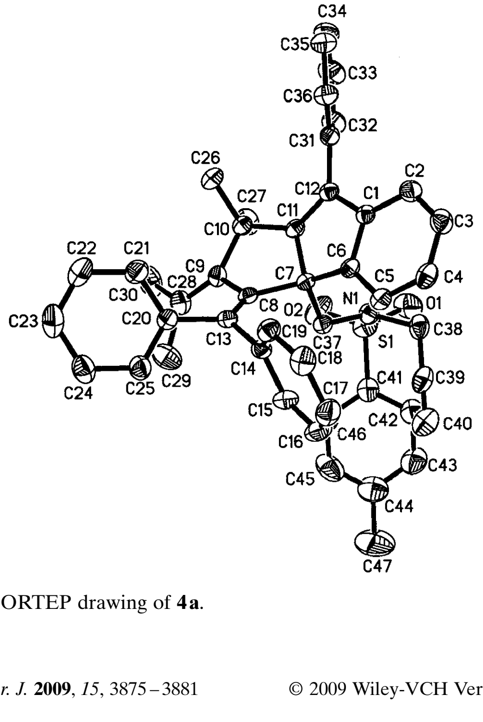
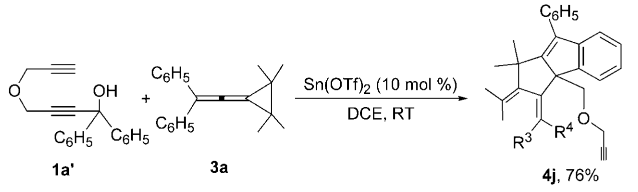


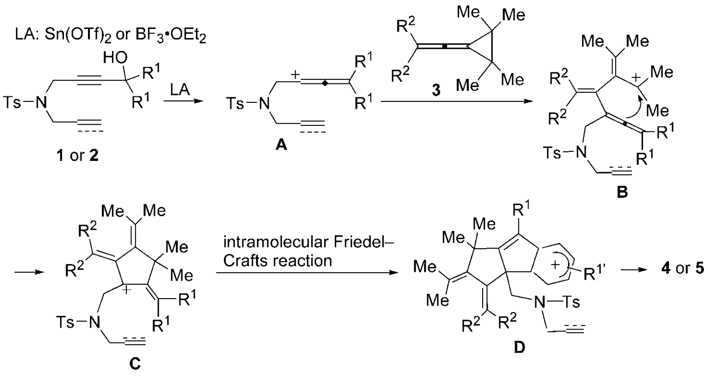
Figure 1. ORTEP drawing of **4a**.

sponding polycyclic product **4j** in 76% yield under identical conditions, rendering the significant diversity of this interesting reaction (Scheme 3).



Scheme 3. $Sn(OTf)_2$-catalyzed reaction of **1a'** with **3a**.

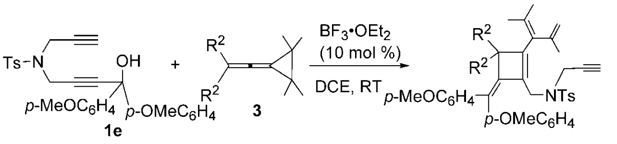
A plausible mechanism based on a cascade rearrangement is outlined in Scheme 4.[10] In the presence of a Lewis acid (LA), a cationic intermediate **A** is produced from **1** or **2**, which adds to the central carbon in allenic moiety of **3** to afford cationic intermediate **B**.[10] Cyclization of intermediate **B** produces cationic intermediate **C**, which affords cationic intermediate **D** via the intramolecular Friedel–Crafts reaction with the adjacent aromatic R^1 group. Aromatization of intermediate **D** produces polycyclic compounds **4** and **5**.



Scheme 4. Plausible reaction mechanism.

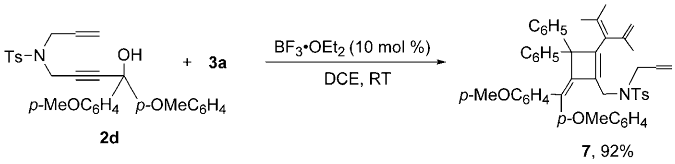
Interestingly, we found that as for the reaction of **1e** or **2d**, bearing two *p*-methoxyphenyl groups, with **3a**, isopropylidene-3,3-diphenylcyclobut-1-enylmethyl derivative **6a** or **7** was formed in 75 or 92% yield, respectively, rather than polycyclic derivative **4** or **5** (Table 2, entry 1 and Scheme 5). The generality of this reaction was found to be satisfactory for a variety of VDCPs **3** under the standard condition (Table 2). The structure of **6a** was unambiguously disclosed by X-ray diffraction and its CIF data are also provided in the Supporting Information (Figure 2).[9] This might be due to the fact that the formed cationic intermediate **E** produces intermediate **F** via an intramolecular proton transferring, which can be stabilized by two electron-rich aromatic groups (two *p*-methoxyphenyl groups). The subsequent intramolecular cyclization and deprotonation afford **6** or **7** (Scheme 6).

Table 2. $BF_3{\cdot}OEt_2$-catalyzed reaction of **1e** with VDCPs **3**.



Entry	R^2/R^2	Yield of **6** [%][a]
1	**3a**	**6a**, 75
2	**3d**	**6b**, 84
3	**3c**	**6c**, 88
4	**3b**	**6d**, 97
5	p-$MeOC_6H_4$/p-$MeOC_6H_4$, **3e**	**6e**, 82

[a] Isolated yields.



Scheme 5. $BF_3{\cdot}OEt_2$-catalyzed reaction of **2d** with **3a**.

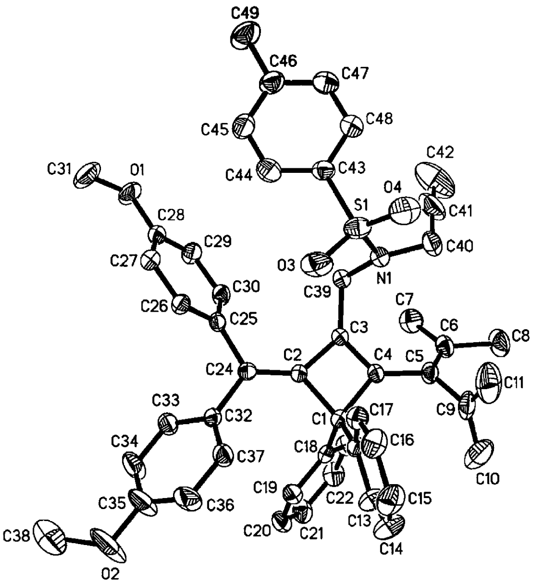
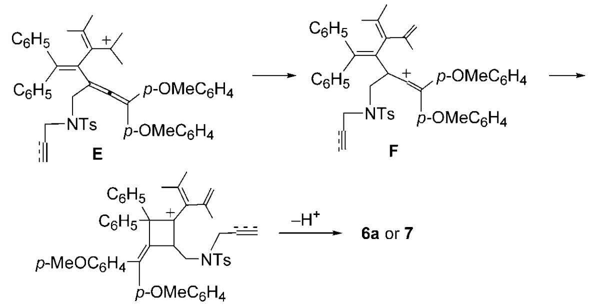


Figure 2. ORTEP drawing of **6a**.

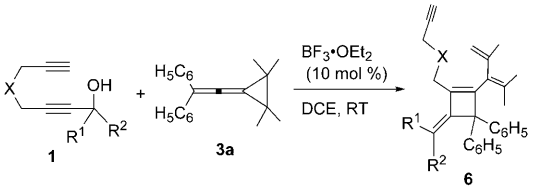


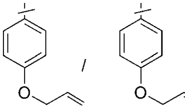
Scheme 6. Plausible reaction mechanism.

To clarify other strongly electron-donating substituents that can provide such isopropylidene-3,3-diphenylcyclobut-1-enylmethyl derivative **6**, a variety of 1,6-diynes **1f**–**1i** containing electron-donating alkoxy groups on the benzene rings were prepared and successively employed in this reaction and the results of these experiments are summarized in Table 3. As can be seen, the corresponding isopropylidene-3,3-diphenylcyclobut-1-enylmethyl derivatives **6g** and **6h** were formed in 67 and 52 % yield, respectively, although *O*-benzyl group substituted 1,6-diyne **1f** afforded the corresponding isopropylidene-3,3-diphenylcyclobut-1-enylmethyl derivative **6f** in trace along with other complex product mixtures presumably due to the lability of *O*-benzyl group under identical conditions (Table 3, entries 1–3). As for 1,1-bis(4-methoxyphenyl)-4-prop-2-ynyloxybut-2-yn-1-ol **1i**, a similar result was obtained, affording **6i** in 77 % yield under the standard conditions (Table 3, entry 4).

Next, we attempted to utilize $PtCl_2$ as a catalyst for the cyclization of **6**[12] to construct another series of useful butadiene derivatives.[13,14] As shown in Table 4, the corresponding 5-isopropylidene-6-methyl-1-(toluene-4-sulfonyl)-7-vinyl-1,2,3,4,5,8-hexahydroazocine derivatives **8** were obtained in good yields of 77 to 96 % in toluene within 5 h at 60 °C (Table 4, entries 1–3). The structure of **8a** has been confirmed by X-ray diffraction (Figure 3).[9]

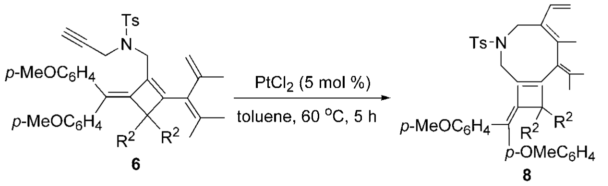
Table 3. $BF_3{\cdot}OEt_2$-catalyzed reaction of a variety of electron-rich **1** with **3a**.



Entry	X	R^1/R^2	Yield of **6** [%][a]
1	TsN	p-$BnOC_6H_4$/p-$BnOC_6H_4$, **1f**	**6f**, trace[b]
2	TsN	p-$EtOC_6H_4$/p-$EtOC_6H_4$, **1g**	**6g**, 67
3	TsN	 , **1h**	**6h**, 52
4	O	p-$MeOC_6H_4$/p-$MeOC_6H_4$, **1i**	**6i**, 77

[a] Isolated yields. [b] Complex product mixture.

Table 4. $PtCl_2$-catalyzed cyclization of **6**.



Entry	R^2/R^2	Yield of **8** [%][a]
1	C_6H_5/C_6H_5, **6a**	**8a**, 80
2	p-MeC_6H_4/p-MeC_6H_4, **6c**	**8b**, 77
3	p-$MeOC_6H_4$/p-$MeOC_6H_4$, **6e**	**8c**, 96

[a] Isolated yields.

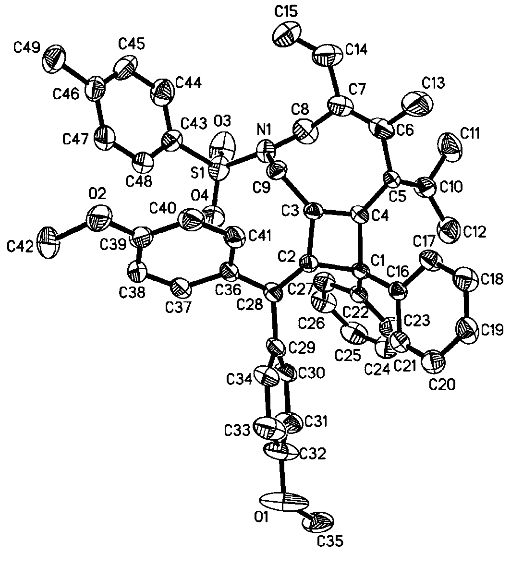
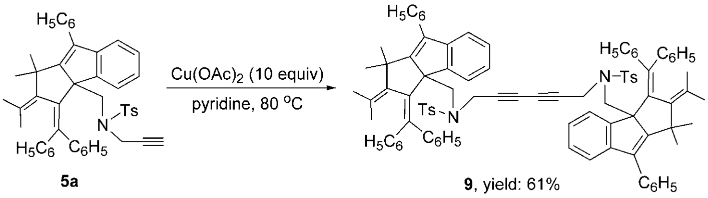


Figure 3. ORTEP drawing of **8a**.

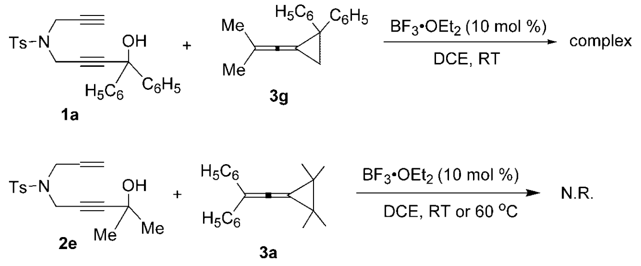
Furthermore, we attempted to use ruthenium–carbene catalyst (Grubbs 1st-generation catalyst) instead of $PtCl_2$ in this interesting cyclization. However, it was found that no reaction occurred along with the recovery of the starting materials.

Moreover, the Eglinton coupling reaction of **5a** catalyzed by Cu^{II} in pyridine afforded 1,3-diyne **9** in 61 % yield (Scheme 7).[15] This is because product **9** contains diyne moiety, which is extremely useful for organometallic studies. The most important utility of this compound is to form zirconocene complexes via cyclization with Cp_2ZrPh_2.[16] Therefore, the polycyclic products **5** and **6** derived from the reaction of VDCPs with 1,6-enyne **2** can be transformed into more interesting products via the $PtCl_2$-catalyzed cyclization and the Eglinton coupling reaction with another free triple bond.



Scheme 7. Eglinton coupling reaction of compound **5a** to produce **9**.

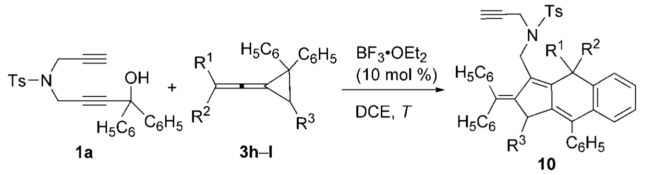
As for the $BF_3{\cdot}OEt_2$-catalyzed reaction of **1a** with dimethylvinylidenecyclopropane **3g**, complex product mixtures were obtained under the standard conditions, suggesting that two aromatic groups in substrate **3** are required (Scheme 8). Moreover, it was found that no reaction occurred at room temperature or at 60 °C between enyne **2e** containing dimethylmethylmethanol moiety and **3a**, indicating that one aromatic group is essential for the generation of a cationic intermediate (Scheme 8).



Scheme 8. Lewis acid catalyzed reaction of **1a** with VDCP **3g** and **2e** with VDCP **3a**.

On the other hand, the $BF_3{\cdot}OEt_2$-catalyzed reaction of **1a** with VDCPs **3h–l** having two phenyl groups at one carbon of cyclopropane produced the corresponding 2-benzhydrylidene-4,4,9-triphenyl-2,4-dihydro-1*H*-cyclopenta[*b*]naphthalene derivatives **10**, another type of interesting polycyclic compounds, in moderate yields, indicating the interesting reaction diversity depending on the substituents at the cyclopropane in **1** (Table 5). The structure of **10a** has been confirmed by X-ray diffraction and the CIF data have been presented in the Supporting Information (Figure 4).[9] A plausible reaction mechanism is indicated in Scheme 9. Similarly, intermediates **A**, **B**, and **C** are formed in the Lewis acid catalyzed reaction of **1a** with VDCPs **3h–l**. The allylic rearrangement of cationic intermediate **C** gives cationic intermediate **D**, which is stabilized by two aromatic groups and undergoes intramolecular Friedel–Crafts reaction with the adjacent phenyl ring to produce the corresponding product **10**. The intramolecular Friedel–Crafts reaction with the adjacent phenyl ring in intermediate **D** can take place more easily than that of intermediate **C** since the cyclic cation in intermediate **C** is a sterically tight species which should be more difficult to go through an intramolecular Friedel–Crafts reaction. This is the reason why 2-benzhydrylidene-4,4,9-triphenyl-2,4-dihydro-1*H*-cyclopenta[*b*]naphthalene derivatives **10** are formed in the $BF_3{\cdot}OEt_2$-catalyzed reaction of **1a** with VDCPs **3h–l**.

Table 5. $BF_3{\cdot}OEt_2$-catalyzed reaction of **1a** with VDCPs **3h–l**.



Entry[a]	R^1/R^2R^3	T [°C]	Yield of **10** [%][b]
1	**3h**, $C_6H_5/C_6H_5/H$	0	**10a**, 58
2	**3i**, p-MeC_6H_4/p-MeC_6H_4/H	−10	**10b**, 51
3	**3j**, p-ClC_6H_4/p-ClC_6H_4/H	−10	**10c**, 60
4	**3k**, p-FC_6H_4/p-FC_6H_4/H	0	**10d**, 58
5	**3 L**, $C_6H_5/C_6H_5/Me$	0	**10e**, 58

[a] All reactions were carried out in DCE (2 mL) using **1** (0.2 mmol), **2a** (0.24 mmol) and $BF_3{\cdot}OEt_2$ (10 mol %). [b] Isolated yields.

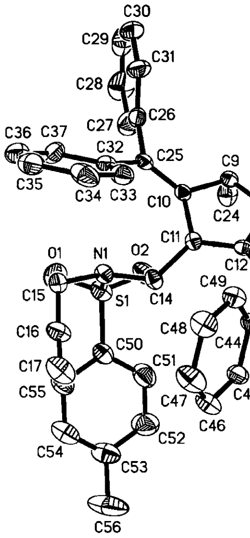
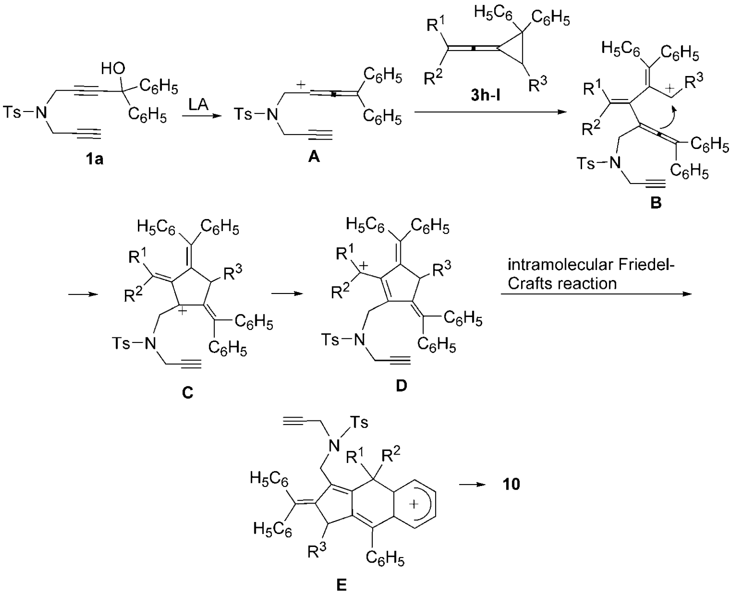
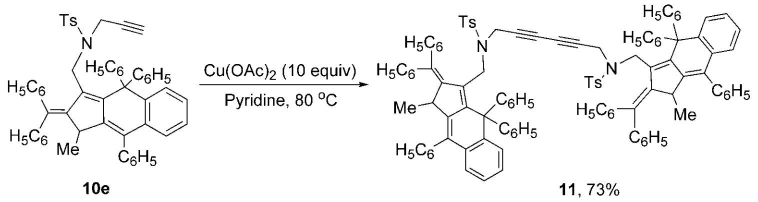


Figure 4. ORTEP drawing of **10a**.



Scheme 9. Plausible reaction mechanism.

Similarly, the Eglinton coupling reaction of **10e** catalyzed by Cu^{II} in pyridine afforded 1,3-diyne **11** in 73% yield (Scheme 10).



Scheme 10. Eglinton coupling reaction of compound **10e** to produce **11**.

Conclusion

We have established a new Lewis acid catalyzed intermolecular reaction in which *N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methyl-*N*-prop-2-ynyl-benzenesulfonamides or 1,1-diphenyl-4-prop-2-ynyloxybut-2-yn-1-ol (1,6-diynes) **1** and *N*-allyl-*N*-(4-hydroxy-4,4-diarylbut-2-ynyl)-4-methylbenzenesulfonamides (1,6-enynes) **2** react with VDCPs **3** to provide polycyclic compounds **4**, **5**, and **10** as well as isopropylidene-3,3-diarylcyclobut-1-enylmethyl derivatives **6** or **7** selectively and efficiently along with an interesting $PtCl_2$-catalyzed cyclization of **6** and a $Cu(OAc)_2{\cdot}H_2O$ catalyzed Eglinton coupling reaction of **5** and **10** to produce the corresponding 5-isopropylidene-6-methyl-1-(toluene-4-sulfonyl)-7-vinyl-1,2,3,4,5,8-hexahydroazocine derivatives **8** and the coupling products **9** and **11** in good yields. Plausible mechanisms of these processes have been proposed that belong to a cascade rearrangement followed by the Friedel–Crafts reaction, an intramolecular proton transferring and a cyclization reaction. Using this method, a series of novel polycyclic and isopropylidene-3,3-diarylcyclobut-1-enylmethyl derivatives can be conveniently obtained by starting with easily available reagents under mild conditions. Further studies regarding the mechanistic details and scope of this process are in progress.

Experimental Section

General remarks: ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J* values are in Hz. Mass spectra were recorded by EI and MALDI methods, and HRMS was measured on a Finnigan MA$^+$ mass spectrometer. CHN microanalyses were recorded on a Carlo-Erba 1106 analyzer. THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN and 1,2-dichloroethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

General procedure for the Lewis acid catalyzed reaction of arylvinylidienecyclopropanes with 1,6-diynes-ols: Under an argon atmosphere, arylvinylidenecyclopropane **3** (0.4 mmol), 1,6-diynes-ols **1** (0.2 mmol), $Sn(OTf)_2$ (10 mol%) were added into a Schlenk tube. The reaction mixture was stirred at room temperature for 6 h in DCE, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

Product **4a**: A white solid, m.p. 144–146 °C; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 1.27$ (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.88 (t, 1H, $J = 2.1$ Hz, CH), 1.93 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.49 (dd, 1H, $J = 2.1$, 18.3 Hz, CH_2), 3.73 (dd, 1H, $J = 2.1$, 18.3 Hz, CH_2), 3.91 (d, 1H, $J = 13.8$ Hz, CH_2), 4.39 (d, 1H, $J = 13.8$ Hz, CH_2), 5.86 (d, 1H, $J = 8.1$ Hz, Ar), 6.44–6.50 (m, 2H, Ar), 6.90–7.19 (m, 8H, Ar), 7.18 (d, 2H, $J = 8.1$ Hz, Ar), 7.27–7.57 (m, 9H, Ar), 7.68 ppm (d, 1H, $J = 7.5$ Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): $\delta = 21.0$, 21.5, 25.3, 27.7, 30.2, 37.0, 41.3, 50.4, 67.9, 73.8, 77.4, 119.4, 124.1, 126.0, 126.1, 127.2, 127.4, 128.0, 128.2, 128.3, 129.1, 129.4, 129.6, 130.2, 130.9, 131.1, 135.8, 136.4, 137.0, 138.6, 139.5, 142.4, 143.2, 144.1, 145.0, 145.1, 146.9, 160.0 ppm; IR (CH_2Cl_2): $\tilde{\nu}$ = 3095, 3058, 3024, 2969, 2926, 2853, 1629, 1596, 1568, 1490, 1456, 1442, 1348, 1330, 1307, 1288, 1266, 1162, 1118, 1103, 1090, 1073, 1059, 1031, 1019, 973, 893, 879, 815, 800, 778, 764, 750, 702, 683, 662, 635, 603, 579, 563, 545, 531 cm^{-1}; MS (MALDI): m/z: 708 [M^++Na]; elemental analysis calcd (%) for $C_{47}H_{43}NO_2SNa^+$: 708.2918; found: 708.2907.

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