DOI: 10.1002/chem.200800421

Lewis Acid Catalyzed Cascade Reactions of Diarylvinylidenecyclopropanes and 1,1,3-Triarylprop-2-yn-1-ols or Their Methyl Ethers

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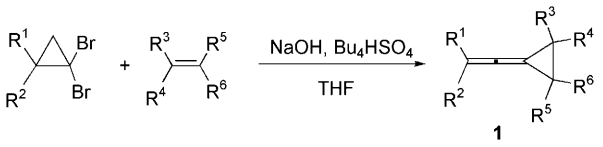
Abstract: The reactions of vinylidenecyclopropanes **1** with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers **2** in the presence of a Lewis acid selectively produce 4-dihydro-1H-cyclopenta[*b*]-naphthalene derivatives **3** or 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives **4** depending on the substituents on the cyclopropane. Good to high yields are obtained under mild conditions. A plausible cascade Meyer–Schuster rearrangement and Friedel–Crafts reaction mechanism has been proposed. Moreover, novel functionalized methylenecyclobutene derivatives **5** could also be obtained in moderate to good yields under similar conditions when strongly electron-donating methoxy groups were introduced into the benzene rings of **2**.

Keywords: alkynes · domino reactions · Friedel–Crafts reaction · indenes · Meyer–Schuster rearrangement · naphthalenes

Introduction

Vinylidenecyclopropanes (VDCPs) are highly strained but readily accessible and stable molecules that can serve as useful building blocks in organic synthesis (Scheme 1).[1] It is known that VDCPs can undergo a variety of ring-opening–cycloaddition reactions upon heating or photoirradiation and by using Lewis acids as the catalysts because the relief of ring strain can provide a powerful thermodynamic driving force.[2,3] Thus far, a number of interesting skeletal conversions of VDCPs have been explored. For example, we have recently reported an interesting Lewis acid catalyzed *intramolecular* rearrangement of diarylvinylidenecyclopropanes containing one, two, or three substituents at the 1- and/or 2-position of the corresponding cyclopropane, which gave 6a*H*-benzo[*c*]fluorine derivatives in a double-intramolecular Friedel–Crafts reaction or indene or naphthalene derivatives via an intramolecular Friedel–Crafts reaction (Scheme 2).[3a,b,c] In addition, we have also succeeded in an effective Lewis acid catalyzed synthesis of substituted indene derivatives by the *intermolecular* reactions of arylvinylidenecyclopropanes **1** with acetals under mild conditions, which is believed to proceed via regioselective addition of an oxonium intermediate to an arylvinylidenecyclopropane and a subsequent intramolecular Friedel–Crafts reaction (Scheme 3).[3d] These results stimulated us to further explore the transformation of VDCPs under mild conditions. Previously, we reported that arylmethylenecyclopropanes (MCPs) 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 a Lewis acid (BF_3·OEt_2) under mild conditions.[4a] Herein, we wish to present a highly efficient Lewis acid catalyzed cascade *intermolecular* reaction of VDCPs **1** with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers **2** that selectively produces 4-dihydro-1H-cyclopenta[*b*]naphthalene derivatives **3** and 1,2,3,8-tetrahydrocyclo-



Scheme 1. Preparation of vinylidenecyclopropanes.

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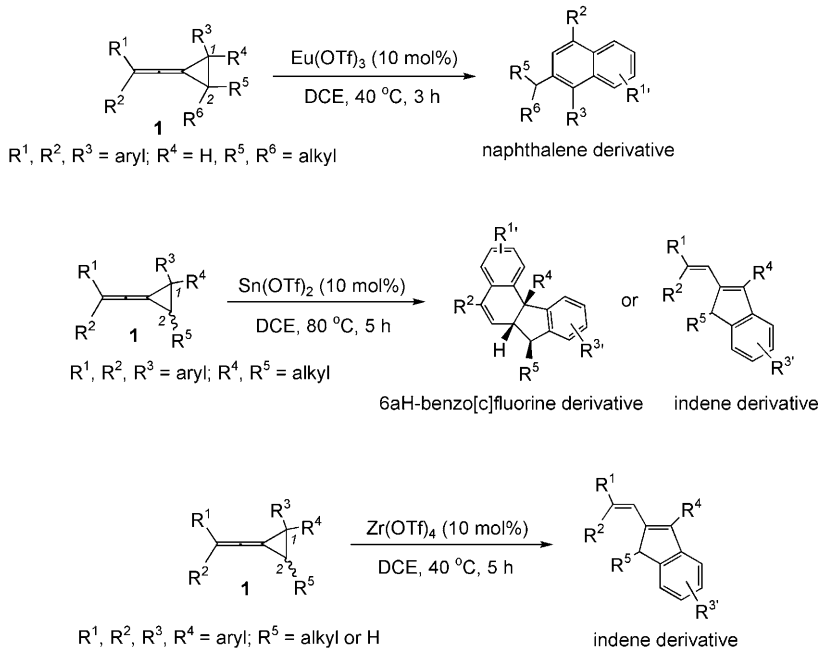
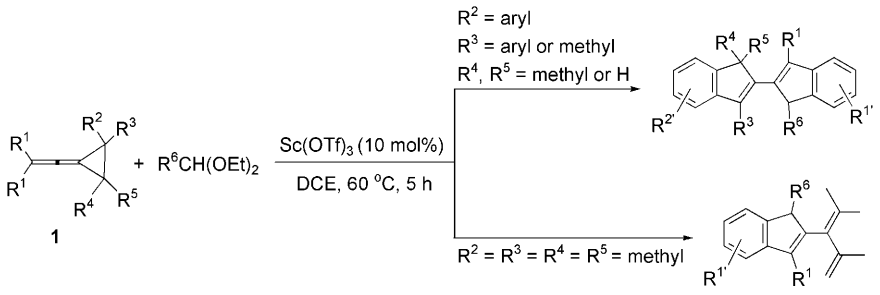
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200800421. It includes spectroscopic data (^1H and ^{13}C NMR spectroscopic data) and analytic data of the compounds shown in Tables 1–5, the X-ray crystal structures of **3a** and **4d**, and detailed descriptions of experimental procedures.



Scheme 2. Lewis acid catalyzed intramolecular rearrangement of VDCPS **1**.



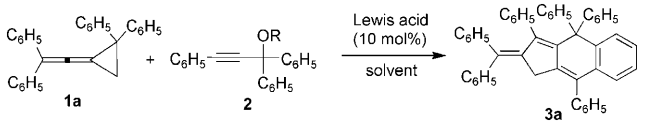
Scheme 3. Lewis acid catalyzed intermolecular reaction of VDCPs **1** with acetals.

penta[*a*]indene derivatives **4** in good to high yields under mild conditions.

Results and Discussion

Lewis acid catalyzed reactions of VDCPs 1 with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers 2: Initial examinations with diphenylvinylidenecyclopropane (**1a**) and 1,1,3-triphenylprop-2-yn-1-ol (**2a**) or its methyl ether (**2b**) as the substrates in the presence of various Lewis acids or a Brønsted acid (TfOH) in a variety of solvents were aimed at determining the optimal conditions and the results of these experiments are summarized in Table 1. We found that the reaction proceeded smoothly in 1,2-dichloroethane (DCE) to afford 2-benzhydrylidene-3,4,4,9-tetraphenyl-2,4-dihydro-1H-cyclopenta[*b*]naphthalene **3a** in 93% yield within 6 h at −20°C in the presence of $Zr(OTf)_4$ (10 mol%, OTf = trifluoromethanesulfonate) (Table 1, entry 2). When the reactions were carried out in dichloromethane and acetonitrile under identical conditions, **3a** was obtained in 86 and 53% yields, respectively (Table 1, entries 7 and 8). In THF, a trace of **3a** was obtained (Table 1, entry 9) and, in toluene, complex product mixtures were formed (Table 1, entry 10). Other Lewis acids such as $BF_3{\cdot}OEt_2$, $Sc(OTf)_3$, $Nd(OTf)_3$, $Sn(OTf)_2$, and the Brønsted acid (TfOH) were not as effective as $Zr(OTf)_4$ under the standard conditions (Table 1, entries 1–6). When **2b** was used as a reactant, complex product mixtures were obtained at room temperature (20°C) or even at 0°C by using $Yb(OTf)_3$ or $BF_3{\cdot}OEt_2$ as a Lewis acid in DCE (Table 1, entries 12–14). However, the Lewis acids $BF_3{\cdot}OEt_2$ and $Zr(OTf)_4$ (10 mol%) produced **3a** in 78 and 85% yields, respectively at −20°C (Table 1, entries 15 and 16). Therefore, on the basis of the above results, the best reaction conditions for the formation of **3** were to carry out the reaction of VDCPs **1** with **2a** in DCE at −20°C with $Zr(OTf)_4$ (10 mol%) as a Lewis acid.

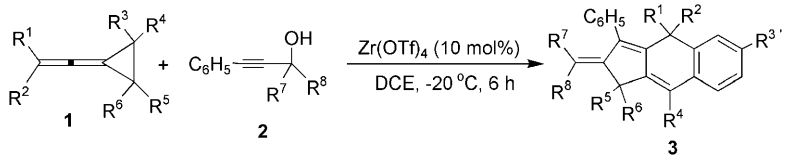
Table 1. Optimization of the reaction conditions of **1a** with **2a** or **2b**.



Entry[a]	Lewis acid	Solvent	T [°C]	t [h]	R	2	Yield of **3a** [%][b]
1	$BF_3{\cdot}OEt_2$	DCE	−20	8	H	**2a**	80
2	$Zr(OTf)_4$	DCE	−20	6	H	**2a**	93
3	$Sc(OTf)_3$	DCE	−20	8	H	**2a**	70
4	TfOH	DCE	−20	6	H	**2a**	85
5	$Nd(OTf)_3$	DCE	−20	6	H	**2a**	84
6	$Sn(OTf)_2$	DCE	−20	10	H	**2a**	75
7	$Zr(OTf)_4$	CH_2Cl_2	−20	6	H	**2a**	86
8	$Zr(OTf)_4$	MeCN	−20	6	H	**2a**	53
9	$Zr(OTf)_4$	THF	−20	24	H	**2a**	trace
10	$Zr(OTf)_4$	toluene	−20	12	H	**2a**	complex
11	$Zr(OTf)_4$	DCE	−25	6	H	**2a**	77
12	$Yb(OTf)_3$	DCE	RT	6	Me	**2b**	complex
13	$Yb(OTf)_3$	DCE	0	6	Me	**2b**	complex
14	$BF_3{\cdot}OEt_2$	DCE	RT	6	Me	**2b**	complex
15	$BF_3{\cdot}OEt_2$	DCE	−20	6	Me	**2b**	78
16	$Zr(OTf)_4$	DCE	−20	6	Me	**2b**	85

[a] All reactions were carried out by using **1a** (0.2 mmol), **2** (0.24 mmol) and Lewis acid (10 mol%) in various solvents (2.0 mL). [b] Isolated yields.

Table 2. $Zr(OTf)_4$ catalyzed reactions of VCPs with 1,1,3-triphenyl-prop-2-yn-1-ols.



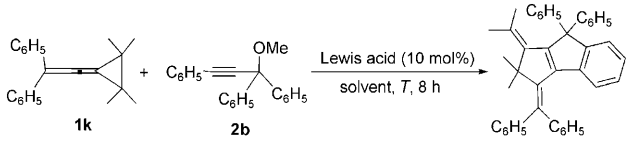
Entry	1	R^1	R^2	R^3	R^4	R^5	R^6	2	R^7	R^8	Yield of 3 [%][a]
1	**1b**	C_6H_5	C_6H_5	C_6H_5	C_6H_5	Me	H	**2a**	Ph	Ph	**3b**, 80
2	**1c**	C_6H_5	C_6H_5	*p*-FC_6H_4	*p*-FC_6H_4	H	H	**2a**	Ph	Ph	**3c**, 80
3	**1d**	C_6H_5	C_6H_5	*p*-ClC_6H_4	*p*-ClC_6H_4	H	H	**2a**	Ph	Ph	**3d**, 65
4	**1e**	C_6H_5	C_6H_5	*p*-MeC_6H_4	*p*-MeC_6H_4	H	H	**2a**	Ph	Ph	**3e**, 80
5	**1f**	*p*-MeC_6H_4	*p*-MeC_6H_4	C_6H_5	C_6H_5	H	H	**2a**	Ph	Ph	**3f**, 52
6	**1g**	*p*-FC_6H_4	*p*-FC_6H_4	C_6H_5	C_6H_5	H	H	**2a**	Ph	Ph	**3g**, 91
7	**1h**	*p*-ClC_6H_4	C_6H_5	C_6H_5	C_6H_5	H	H	**2a**	Ph	Ph	**3h**, 88
8	**1a**	C_6H_5	C_6H_5	C_6H_5	C_6H_5	H	H	**2c**	*p*-MeC_6H_4	*p*-MeC_6H_4	**3i**, 65
9	**1a**	C_6H_5	C_6H_5	C_6H_5	C_6H_5	H	H	**2d**	*p*-ClC_6H_4	*p*-ClC_6H_4	**3j**, 80[b]
10	**1a**	C_6H_5	C_6H_5	C_6H_5	C_6H_5	H	H	**2e**	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**3k**, 45
11	**1i**	Me	Me	C_6H_5	C_6H_5	H	H	**2a**	Ph	Ph	**3l**, 30
12	**1j**	C_6H_5	C_6H_5	*p*-ClC_6H_4	C_6H_5	H	H	**2a**	Ph	Ph	**3m**, 81 (1:1)[c]

[a] Isolated yields. [b] 24% of **1a** was recovered. [c] Ratio of two stereoisomers ($R^{3'}$=H, R^4=*p*-ClC_6H_4)/($R^{3'}$=Cl, R^4=C_6H_5).

Under these optimal reaction conditions, we next carried out this interesting reaction by using a variety of starting materials **1** and 1,1,3-triarylprop-2-yn-1-ols **2**. The results are summarized in Table 2. As can be seen in Table 2, these reactions proceeded smoothly to afford the corresponding 4-dihydro-1H-cyclopenta[*b*]naphthalene derivatives **3** in moderate to high yields (Table 2). Substituents on the aromatic rings of **1** have a modest influence on the reaction outcomes. Adding a moderately electron-donating group, such as a methyl group, on the aromatic ring of **1** afforded the corresponding 4-dihydro-1H-cyclopenta[*b*]naphthalene derivative **3f** in somewhat lower yield (52%) (Table 2, entry 5). Similarly, introducing a strongly electron-donating methoxy group onto the aromatic ring of **2** produced the corresponding 4-dihydro-1H-cyclopenta[*b*]naphthalene derivative **3k** in 45% yield (Table 2, entry 10). The presence of electron-withdrawing groups, such as fluoro- or chloro-substituents, on the benzene rings in R^1 and R^2 of **1** or at the benzene rings R^7 and R^8 of **2** gave the corresponding 4-dihydro-1H-cyclopenta[*b*]naphthalene derivatives **3g** or **3j** in higher yields (Table 2, entries 6 and 9). A similar result was obtained by using unsymmetrical VDCP **1h** (R^1=*p*-ClC_6H_4, R^2=C_6H_5) as the substrate (Table 2, entry 7). In the case of aliphatic VDCP substrate **1i** (R^1=R^2=Me), the corresponding product **3l** was obtained in 30% yield (Table 2, entry 11). As for VDCP **1j** in which R^3 and R^4 are not identical, two stereoisomeric mixtures were obtained in a ratio of 1:1 (Table 2, entry 12). Product structures were determined from ^1H and ^{13}C NMR spectroscopic data, HRMS, and microanalysis. Furthermore, the X-ray crystal structure of **3a** was determined (Figure 1).[5]

Lewis acid catalyzed reactions of VDCPs 1 containing four methyl groups on the cyclopropane with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers 2: Interestingly, by using VDCPs **1k–r** with four methyl groups on the cyclopropane as the substrates under the standard conditions, 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives **4** were obtained in good yields. The reaction conditions have been carefully examined in a similar way (Table 3). The examination of Lewis acids and solvent effects revealed that $Sc(OTf)_3$ is the best catalyst in the reaction of **1k** with **2b** and DCE is the solvent of choice (Table 3, entries 1–15). Examination of the reaction temperature also indicated that this reaction should

Table 3. Optimization of the reaction conditions of **1k** with **2b** or **2a**.



Entry[a]	Lewis acid	Solvent	*T* [°C]	Yield of **4a** [%][b]
1	$Yb(OTf)_3$	DCE	40	83
2	$Sc(OTf)_3$	DCE	40	87
3	$BF_3.OEt_2$	DCE	40	85
4	$Sn(OTf)_2$	DCE	40	68
5	$Zr(OTf)_4$	DCE	40	81
6	TfOH	DCE	40	82
7	$La(OTf)_3$	DCE	40	68
8	$Nd(OTf)_3$	DCE	40	69
9	$Gd(OTf)_3$	DCE	40	72
10	$Sc(OTf)_3$	CH_2Cl_2	40	83
11	$Sc(OTf)_3$	THF	40	NR
12	$Sc(OTf)_3$	MeCN	40	47
13	$Sc(OTf)_3$	toluene	40	40
14	$Sc(OTf)_3$	EtOH	40	28
15	$Sc(OTf)_3$	hexane	40	51
16	$Sc(OTf)_3$	DCE	RT	trace
17	$Sc(OTf)_3$	DCE	60	86
18	$Sc(OTf)_3$	DCE	40	93[c]
19	$Sc(OTf)_3$	DCE	40	68[d]

[a] All reactions were carried out by using **1k** (0.2 mmol), **2b** (0.24 mmol), and catalyst (10 mol%) in various solvents (2.0 mL). [b] Isolated yields. [c] **2b** (0.3 mmol) was used. [d] **2a** was used.

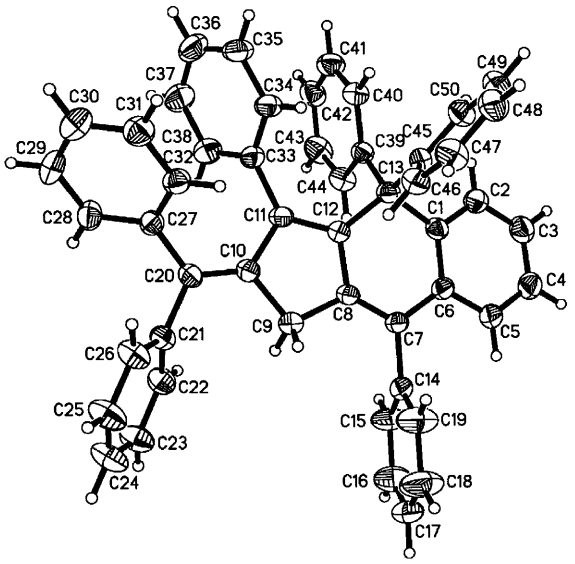
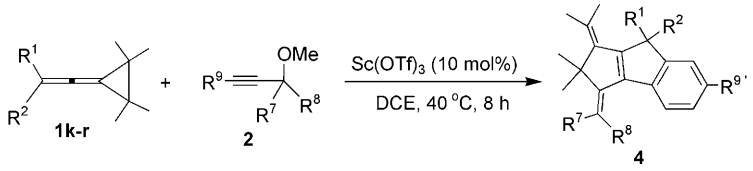


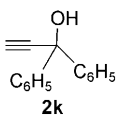
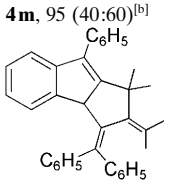
Figure 1. ORTEP drawing of **3a**.

be carried out at 40 °C (Table 3, entries 16 and 17). Moreover, **4a** could be obtained in 93 % yield by using 1.5 equiv of **2b** under the standard conditions (Table 3, entry 18). By using **2a** as a reactant, **4a** was formed in 68 % yield under otherwise identical conditions (Table 3, entry 19). Therefore, we found that the best reaction conditions for the formation of **4** were to carry out the reactions of VDCPs **1k–r** with **2b** (1.5 equiv) in DCE at 40 °C by using $Sc(OTf)_3$ (10 mol %) as a Lewis acid. Subsequently, we also examined the generality of this reaction under these optimized conditions, and the results of these experiments are summarized in Table 4. As for the reaction of **1k** with **2g** and **2i**, in which R^7 and R^8 or R^9 are electron-rich aromatic groups, the corresponding 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives **4c** and **4e** were obtained in somewhat lower yields (40 and 55 %) (Table 4, entries 3 and 5). In other cases, the corresponding 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives **4** were obtained in 66–92 % yields (Table 4, entries 1–9). As for the substrates **1p–r** containing substituents at the *meta*- and/or *ortho*-position of the benzene ring, the corresponding products **4j–l** were obtained in 70, 75, and 25 % yields, respectively, suggesting that the sterically encumbered VDCP did not facilitate the formation of **4** (Table 4, entries 10–12). In the reaction of **1k** with **2j**, in which R^7 and R^8 are not identical, the corresponding product **4m** was formed as *E*- and *Z*-isomeric mixtures (Table 4, entry 13). The product **4n** was formed in 60 % yield by using 1,1-diphenyl-prop-2-yn-1-ol **2k** as a substrate (Table 4, entry 14). The crystal structure of **4d** was determined by X-ray diffraction (Figure 2).[5]

It should be noted that in the reactions of VDCP **1a** with 1,1-diphenyl-non-2-yn-1-ol **2l** and VDCP **1k** with 2-methyl-4-phenyl-but-3-yn-2-ol **2m** under these optimized conditions, complex product mixtures were formed, respectively, suggesting that R^7, R^8, and R^9 in **2** should be aromatic groups (Scheme 4).

Table 4. $Sc(OTf)_3$-catalyzed reactions of VCPs **1k–r** with 3-methoxy-1,3,3-triarylprop-1-yne.



Entry	**1**	R^1	R^2	**2**	R^9	R^7	R^8	Yield of **4** [%][a]
1	**1k**	C_6H_5	C_6H_5	**2b**	C_6H_5	C_6H_5	C_6H_5	**4a**, 93
2	**1k**	C_6H_5	C_6H_5	**2f**	C_6H_5	*p*-ClC_6H_4	*p*-ClC_6H_4	**4b**, 79
3	**1k**	C_6H_5	C_6H_5	**2g**	C_6H_5	*p*-MeC_6H_4	*p*-MeC_6H_4	**4c**, 40
4	**1k**	C_6H_5	C_6H_5	**2h**	C_6H_5	*p*-FC_6H_4	*p*-FC_6H_4	**4d**, 67
5	**1k**	C_6H_5	C_6H_5	**2i**	*p*-$MeOC_6H_4$	C_6H_5	C_6H_5	**4e**, 55
6	**1l**	*p*-FC_6H_4	*p*-FC_6H_4	**2b**	C_6H_5	C_6H_5	C_6H_5	**4f**, 74
7	**1m**	*p*-MeC_6H_4	*p*-MeC_6H_4	**2b**	C_6H_5	C_6H_5	C_6H_5	**4g**, 82
8	**1n**	*p*-ClC_6H_4	*p*-ClC_6H_4	**2b**	C_6H_5	C_6H_5	C_6H_5	**4h**, 66
9	**1o**	*p*-MeC_6H_4	C_6H_4	**2b**	C_6H_5	C_6H_5	C_6H_5	**4i**, 92
10	**1p**	*m*,*p*-$Cl_2C_6H_3$	C_6H_5	**2b**	C_6H_5	C_6H_5	C_6H_5	**4j**, 70
11	**1q**	*m*,*p*-$(CH_3)_2C_6H_3$	C_6H_5	**2b**	C_6H_5	C_6H_5	C_6H_5	**4k**, 75
12	**1r**	*p*-ClC_6H_4	*o*-ClC_6H_4	**2b**	C_6H_5	C_6H_5	C_6H_5	**4l**, 25
13	**1k**	C_6H_5	C_6H_5	**2j**	C_6H_5	C_6H_5	*p*-ClC_6H_4	**4m**, 95 (40:60)[b]
14	**1k**							 **4n**, 60

[a] Isolated yields. [b] Ratio of *E*/*Z* or *Z*/*E* 40:60.

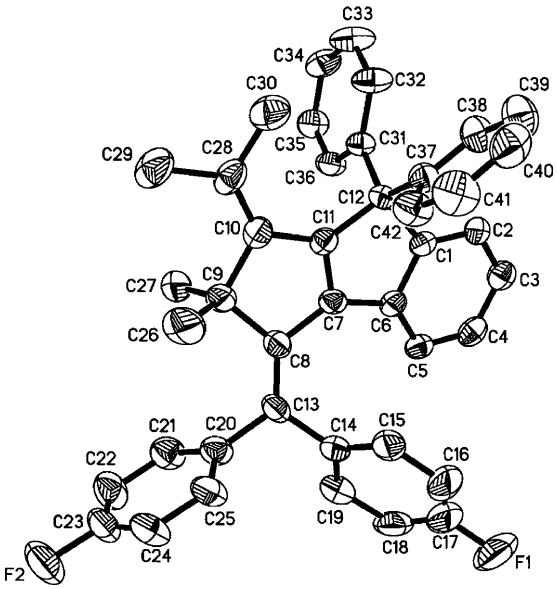
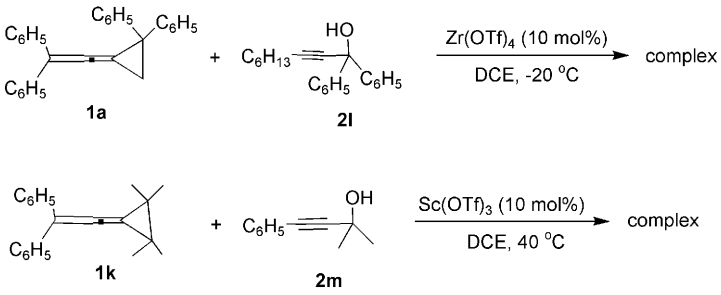
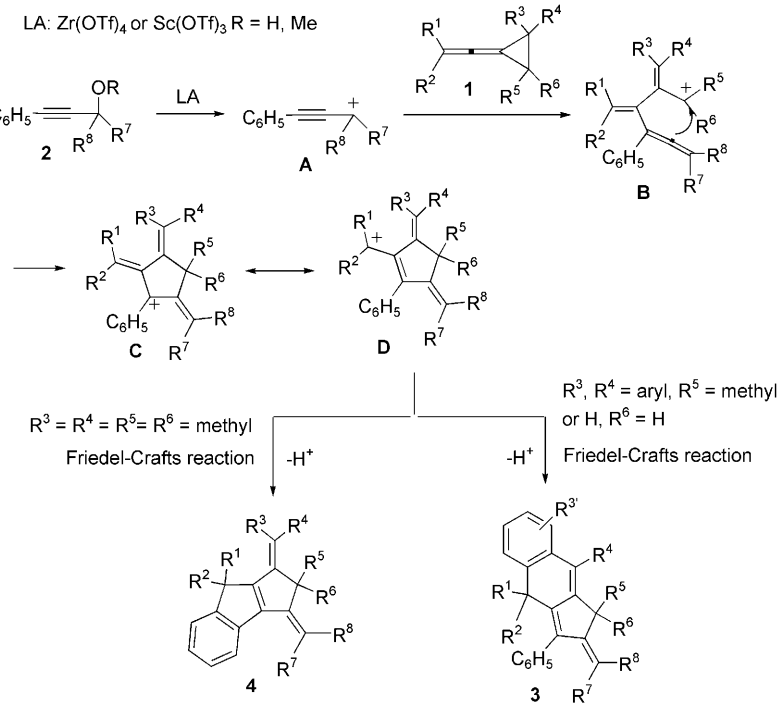


Figure 2. ORTEP drawing of **4d**.



Scheme 4. Lewis acid catalyzed reaction of VDCP **1a** with 1,1-diphenylnon-2-yn-1-ol **2l** and VDCP **1k** with 2-methyl-4-phenyl-but-3-yn-2-ol **2m**.



Scheme 5. Plausible reaction mechanism.

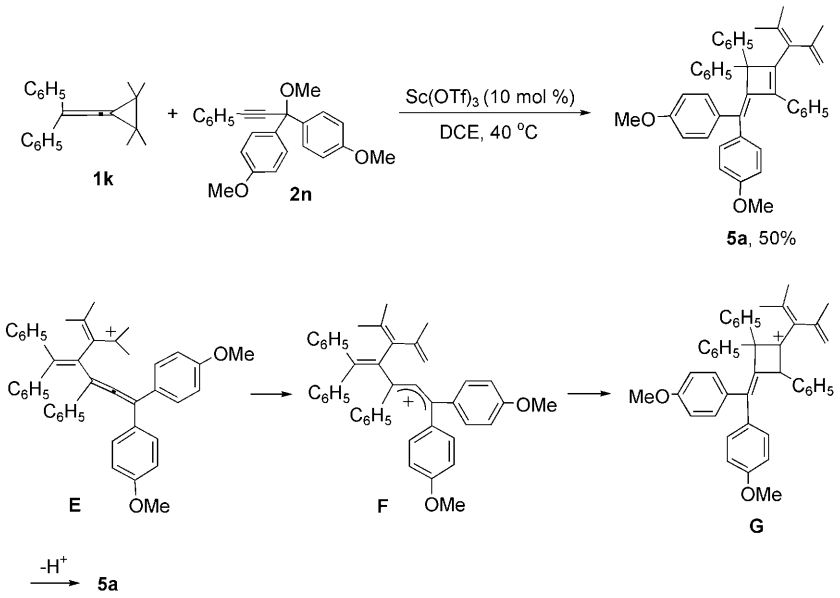
Exploration of the reaction mechanism: A plausible mechanism based on a Meyer–Schuster rearrangement is outlined in Scheme 5.[6] In the presence of a Lewis acid, an intermediate propargylic cation **A** is produced from 1,1,3-triarylprop-2-yn-1-ol or its methyl ether **2**. Nucleophilic attack of the central carbon in **1** on intermediate **A**, along with allylic rearrangement affords cationic intermediate **B**.[7] Cyclization of intermediate **B** produces cationic intermediates **C** and **D** via an allylic rearrangement.[8] When $R^3=R^4=R^5=R^6=$Me, a Friedel–Crafts reaction with the adjacent aromatic group takes place to afford 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivative **4**. When R^3 and $R^4=$aromatic groups, a Friedel–Crafts reaction with R^3 or R^4 takes place, presumably due to steric effects, to afford 4-dihydro-1H-cyclopenta[*b*]naphthalene derivative **3**. The formation of a stable cationic intermediate **A** is the key step in this reaction because when R^7, R^8 or R^9 are aliphatic groups, complex mixtures of products are formed (Scheme 4).

Moreover, we found that, as for the reaction of **1k** with **2n,** which contains two *p*-methoxyphenyl groups, a novel functionalized methylenecyclobutene derivative **5a** was formed in 50% yield instead of the 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivative (Scheme 6). The structure of **5a** was determined by ^{1}H and ^{13}C NMR spectroscopic data and from the DEPT spectrum (see the Supporting Information). This might be because the intermediate formed, cation **E**, produces allyl cationic intermediate **F**, which can be stabilized by two electron-rich aromatic groups, through an intramolecular proton transfer. Subsequent cyclization and deprotonation afford methylenecyclobutene derivative **5a** (Scheme 6).

Because this functionalized methylenecyclobutene derivative is quite interesting, we next examined the generality of this reaction. The results are shown in Table 5. As can be seen from Table 5, the corresponding functionalized methylenecyclobutene derivatives **5b–f** were obtained in moderate to high yields for a variety of symmetrical or unsymmetrical VDCPs **1l–p** (Table 5, entries 1–5). A sterically hindered unsymmetrical VDCP **1p** produced the corresponding functionalized methylenecyclobutene derivative **5f** in 50% yield (Table 5, entry 5).

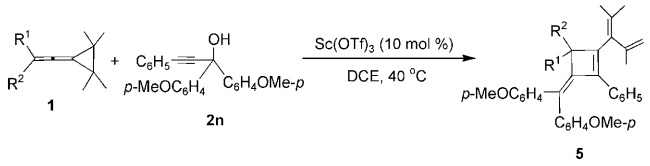
Conclusion

We have found an interesting Lewis acid catalyzed *intermolecular* reaction procedure, in which VDCPs **1** react with 1,1,3-triarylprop-2-yn-1-ols or



Scheme 6. $Sc(OTf)_3$-catalyzed reaction of **1k** with **2n**.

Table 5. $Sc(OTf)_3$-catalyzed reaction of VDCPs **1l–1p** with **2n**.



Entry	R^1	R^2	**1**	Yield of **5** [%][a]
1	*p*-FC_6H_4	*p*-FC_6H_4	**1l**	**5b**, 86
2	*p*-MeC_6H_4	*p*-MeC_6H_4	**1m**	**5c**, 84
3	*p*-ClC_6H_4	*p*-ClC_6H_4	**1n**	**5d**, 96
4	*p*-MeC_6H_4	C_6H_5	**1o**	**5e**, 98
5	*m*,*p*-$Cl_2C_6H_3$	C_6H_5	**1p**	**5f**, 50

[a] Isolated yields.

their methyl ethers **2** to provide 4-dihydro-1H-cyclopenta[*b*]naphthalene derivatives **3** and 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives **4** in good to high yields. A plausible reaction mechanism has been proposed that is based on a cascade Meyer–Schuster rearrangement and Friedel–Crafts reaction pathway. On the basis of this synthetic protocol, a series of novel functionalized naphthalene and indene derivatives were obtained selectively depending on the substituents on the cyclopropane, by using easily available reagents under mild conditions and in moderate to good yields. Moreover, novel functionalized methylenecyclobutene derivatives **5** could also be obtained in moderate to good yields when strongly electron-donating methoxy groups were introduced into the benzene rings of **2** under similar conditions. Further studies regarding the mechanistic details and scope of this process are in progress.

Experimental Section

General methods: Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI, ESI, or Maldi methods, and HRMS measurements were made on a Finnegan MA^+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with a Carlo–Erba 1106 analyzer. The commercially obtained reagents were used directly without further purification. All reactions were monitored by TLC with Huanghai GF254 silica-gel-coated plates. Flash column chromatography was carried out by using 300–400 mesh silica gel at increased pressure.

General procedure for Lewis acid catalyzed reactions of arylvinylidenecyclopropanes with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers: Arylvinylidenecyclopropane **1** (0.2 mmol), 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers **2** (0.4 mmol) and $Zr(OTf)_4$ or $Sc(OTf)_3$ (10 mol%) were added into a Schlenk tube under an argon atmosphere. The reaction mixture was stirred at −20 °C for 6 h in DCE, then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography.

Compound **3a**: A yellow solid, m.p. 141–143 °C; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 3.48$ (s, 2H, CH_2), 6.02 (d, $J = 7.5$ Hz, 2H, Ar), 6.34 (t, $J = 7.5$ Hz, 2H, Ar), 6.51–6.73 (m, 6H, Ar), 6.89–6.90 (m, 3H, Ar), 7.04–7.21 (m, 16H, Ar), 7.26 (d, $J = 7.8$ Hz, 2H, Ar), 7.32 (d, $J = 7.8$ Hz, 1H, Ar), 7.41 ppm (t, $J = 7.2$ Hz, 2H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): $\delta = 36.7$, 57.4, 124.6, 125.0, 125.2, 125.67, 125.72, 125.9, 126.28, 126.31, 126.8, 127.1, 127.3, 127.6, 128.2, 128.7, 129.0, 129.7, 129.8, 130.07, 130.12, 130.5, 133.8, 134.9, 136.5, 138.7, 139.1, 141.2, 141.9, 144.63, 144.66, 146.0, 149.3, 152.0 ppm; IR(CH_2Cl_2): $\tilde{\nu} = 3055$, 3023, 1597, 1489, 1441, 1265, 1074, 1030, 1003, 912, 771, 740, 697, 669, 649, 627, 619, 572 cm^{-1}; MS (MALDI): *m*/*z* (%): 636 [M^+]; elemental analysis calcd (%) for $C_{50}H_{36}{\cdot}0.75CH_3(CH_2)_4CH_3$: C 93.22, H 6.68, found: C 93.55, H 6.54.

Compound **4a**: A yellow solid, m.p. 203–205 °C; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 1.49$ (s, 3H, CH_3), 1.51 (s, 6H, CH_3), 1.70 (s, 3H, CH_3), 5.45 (d, $J = 7.2$ Hz, 1H, Ar), 6.57 (t, $J = 7.8$ Hz, 1H, Ar), 6.80 (t, $J = 7.8$ Hz, 1H, Ar), 7.07–7.10 (m, 5H, Ar), 7.19–7.47 (m, 12H, Ar), 7.51 ppm (d, $J = 7.2$ Hz, 4H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): $\delta =$ 23.0, 26.8, 27.0, 55.4, 63.5, 122.7, 123.9, 125.4, 125.5, 125.8, 126.4, 126.6, 126.7, 127.5, 127.8, 128.1, 129.0, 131.0, 131.6, 133.3, 136.5, 141.7, 142.2, 143.7, 146.0, 146.8, 149.5, 159.7, 163.9 ppm; IR (CH_2Cl_2): $\tilde{\nu} = 3057$, 2911, 2840, 1597, 1490, 1440, 1361, 1265, 1077, 1035, 763, 740, 700, 623, 558, 551, 535, 527, 513, 506 cm^{-1}; MS *m*/*z* (%): 540 (100) [M^+], 541 (47), 44 (17), 167 (13), 165 (11), 542 (11), 43 (9), 91 (9); HRMS (EI): *m*/*z*: calcd for $C_{42}H_{36}$: 529.2817; found: 529.2816.

Compound **5a**, A yellow oil; ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 0.88$ (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 3.65 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 4.52 (s, 1H, =CH), 4.71 (s, 1H, =CH), 6.42 (d, $J =$ 8.7 Hz, 2H, Ar), 6.47 (d, $J = 8.7$ Hz, 2H, Ar), 6.66 (d, $J = 8.7$ Hz, 2H, Ar), 6.90–7.03 (m, 7H, Ar), 7.13–7.24 (m, 6H, Ar), 7.36–7.39 ppm (m, 4H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): $\delta = 20.8$, 21.0, 23.3, 55.0, 55.2, 68.7, 112.56, 112.61, 115.3, 125.7, 126.3, 126.4, 127.2, 129.0, 130.1, 131.3, 131.6, 133.5, 133.8, 133.9, 134.0, 141.8, 143.5, 144.2, 146.9, 155.8, 157.7, 158.2 ppm; IR (CH_2Cl_2): $\tilde{\nu} = 3075$, 3062, 3032, 2996, 2965, 2947, 2933, 2905, 2837, 2059, 1957, 1886, 1809, 1659, 1638, 1601, 1573, 1516, 1506, 1494, 1456, 1444, 1433, 1409, 1379, 1369, 1330, 1292, 1269, 1244, 1206, 1185, 1170, 1159, 1146, 1111, 1085, 1072, 1049, 1045, 1038, 1003, 989, 984,

974, 958, 941, 925, 909, 897, 885, 866, 849, 843, 825, 801, 787, 777, 766, 758, 746, 740, 729, 715, 701, 692, 683, 668, 658, 642, 631, 614, 600, 593, 580, 575, 569, 549, 540, 535, 526, 507 cm^{-1}; MS (MALDI): m/z: 612 [M^+]; HRMS (MALDI): m/z: calcd for $C_{44}H_{40}O_2Na^+$: 623.2920 [M+Na]$^+$; found: 623.2920.

Acknowledgements

We thank the Shanghai Municipal Committee of Science and Technology (04 JC14083, 06XD14005), Chinese Academy of Sciences (KGCX2–210–01), and the National Natural Science Foundation of China for financial support (20472096, 203900502, 20672127, and 20732008).

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[5] Crystallographic data for **3a**: Empirical Formula: $C_{107}H_{81}$; Formula Weight: 1372.72; Crystal Color, Habit: colorless, prismatic; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters: a= 14.5403(17 Å, b=14.9680(18 Å, c=20.922(3) Å, α=103.976(3)°, β= 103.541(2)°, γ=105.537(3)°, V=4033.9(8) Å^3; Space group: $P1$; Z=2; ρ_{calc}=1.130 g cm^{-3}; F_{000}=1452; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0778, 0.1998. Crystallographic data for **4d**: Empirical Formula: $C_{42}H_{34}F_2$; Formula Weight: 576.69; Crystal Color, Habit: colorless, prismatic; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters: a=11.3929(15 Å, b=15.0062(19 Å, c=29.245(4) Å, α=98.661(3)°, β=100.657(3)°, γ=92.025(3)°, V= 4847.3(11 Å^3; Space group: $P1$; Z=6; ρ_{calc}=1.185 g cm^{-3}; F_{000}=1824; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0556, 0.0904. CCDC 646896 (**3a**) 651602 (**4d**) and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Received: March 8, 2008
Published online: August 7, 2008

