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Acid-Catalyzed Cascade Reactions of Arylvinylcyclopropenes with Acetals and Aldehydes for the Construction of Different Aromatic Systems

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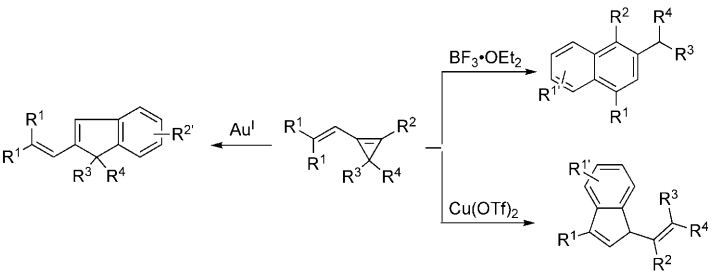
Cyclopropenes,[1] as the smallest cycloolefins, are highly strained[2] but readily accessible substances, which have been serving as useful building blocks in many organic reactions.[3] In the past several years, catalyzed/noncatalyzed addition reactions, substitution reactions and metathesis reactions of cyclopropenes as well as thermolysis and pyrolysis of cyclopropenes have been extensively investigated.[4] However, acid-catalyzed reactions of cyclopropenes have been seldom reported.[5]

Recently, our group has explored a new kind of highly substituted arylvinylcyclopropenes stabilized by multi-aromatic rings. These interesting arylvinylcyclopropenes tolerate strong bases and weak acids. Rearrangements of these arylvinylcyclopropenes can easily construct naphthalene and indene skeletons in the presence of Lewis acids (Scheme 1).[5b] On the other hand, gold(I)-catalyzed rearrangement of **1** can produce another type of indene derivatives in good yields (Scheme 1).[6] These interesting rearrangements of **1** have attracted our attention to investigate the reactions of **1** with some other substrates catalyzed by Lewis acids, which could lead to the construction of interesting aromatic skeletons. In this paper, we wish to report the Lewis acid-catalyzed cascade reactions of arylvinylcyclopropenes with acetals **2** and aldehydes **3** for the construction of different aromatic systems.

Initially we employed arylvinylcyclopropene **1a** to react with acetal **2a** with two different Lewis acids as the catalysts.[5b] We found that $BF_3{\cdot}OEt_2$ could promote the intermolecular addition of **1a** with **2a** to produce 8,8-dimethyl-2,2,3-triphenyl-2,8-dihydrocyclopenta[*a*]indene (**4a**), which was unambiguously determined by X-ray diffraction (Figure 1),[7] in 74% yield as well as the naphthalene derivative **7a** derived from the intramolecular rearrangement of **1a** in 13% yield in 1,2-dichloroethane (DCE) at 50°C within 1 h



Scheme 1. Lewis acid and Au^I-catalyzed rearrangement of arylvinylcyclopropenes.

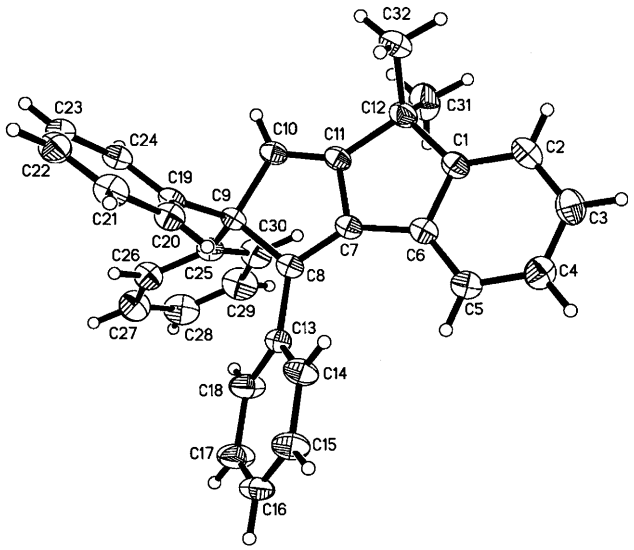


Figure 1. ORTEP drawing of compound **4a**.

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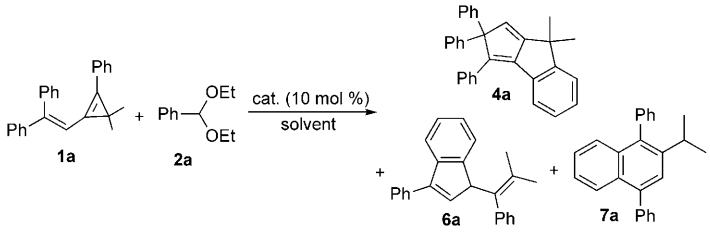
(entry 1, Table 1). However, only indene derivative **6a** derived from the intramolecular rearrangement of **1a** was obtained in 81% yield when $Cu(OTf)_2$ was employed as the catalyst (entry 2, Table 1). The investigation of other Lewis acids such as $Sn(OTf)_2$, $Ln(OTf)_3$ (various lanthanide triflates) and TMSOTf as well as Brønsted acid trifluoromethanesulfonic acid (TfOH) in this reaction revealed that adduct **4a** was produced in most cases as the major products along with **6a** and **7a** as the minor products in DCE at 50°C (entries 3–12, Table 1). $BF_3{\cdot}OEt_2$ is the best catalyst to give **4a** in higher yield. The examination of solvent effects using $BF_3{\cdot}OEt_2$ as the catalyst revealed that DCE was the best one for this addition reaction (entries 13–16, Table 1). Moreover, two control experiments were carried out to evaluate the importance of the catalyst as well as the optimized reaction conditions and the results of the two experiments are summarized in entries 17 and 18 of Table 1. In the absence of catalyst, no reaction occurred (entry 17, Table 1). Lowering the reaction temperature to 20°C (room temperature) afforded **4a** in lower yield under identical conditions (entry 18, Table 1).

Table 1. Optimization of the reaction conditions of **1a** with **2a**.[a]

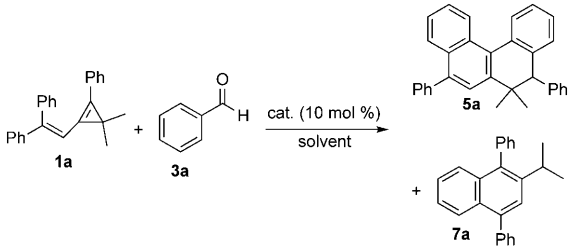


Entry	Catalyst	Solvent	t [h]	T [°C]	Yield [%][b]		
					4a	**6a**	**7a**
1	**$BF_3{\cdot}OEt_2$**	**DCE**	**1**	**50**	**74**	**–**	**13**
2	$Cu(OTf)_2$	DCE	3	50	–	81	–
3	$Sc(OTf)_3$	DCE	3	50	63	3	–
4	$Sn(OTf)_2$	DCE	3	50	46	trace	–
5	$Gd(OTf)_3$	DCE	1	50	11	trace	–
6	$Nd(OTf)_3$	DCE	1	50	5	–	–
7	$Yb(OTf)_3$	DCE	1	50	17	–	–
8	$La(OTf)_3$	DCE	10	50	trace	–	–
9	CuOTf	DCE	2	50	–	60	–
10	$Eu(OTf)_3$	DCE	9	50	46	18	–
11	TMSOTf	DCE	1	50	61	–	trace
12	TfOH	DCE	1	50	63	8	10
13	$BF_3{\cdot}OEt_2$	THF	5	50	–	–	–
14	$BF_3{\cdot}OEt_2$	CH_3CN	0.5	20	53	–	trace
15	$BF_3{\cdot}OEt_2$	toluene	0.5	50	24	–	24
16	$BF_3{\cdot}OEt_2$	Et_2O	0.5	50	22	–	–
17	–	DCE	24	50	–	–	–
18	$BF_3{\cdot}OEt_2$	DCE	1	20	40	–	20

[a] All reactions were carried out using **1a** (0.2 mmol) and **2a** (0.4 mmol) in the presence of the listed catalysts (10 mol%) and solvents (2.0 mL); best result highlighted in bold. [b] Isolated yields.

Interestingly, using benzaldehyde **3a** to replace acetal **2a**, we found that 6,6-dimethyl-5,8-diphenyl-5,6-dihydrobenzo[*c*]phenanthrene (**5a**) was obtained in 69% yield along with **7a** in 17% yield in the presence of $BF_3{\cdot}OEt_2$ (10 mol%) in DCE at 20°C (room temperature) (entry 1, Table 2), whereas using $Cu(OTf)_2$ (10 mol%) as the catalyst produced the rearrangement product **6a** exclusively in 80% yield at room temperature (entry 2, Table 2). In the presence of Brønsted acid TfOH, **5a** was formed in 70% yield along with **7a** in 20% yield (entry 3, Table 2). Using Brønsted acid $TsOH{\cdot}H_2O$ (10 mol%) as the catalyst in DCE at 20°C afforded **5a** in 30% yield (entry 4, Table 2). Optimization of the reaction conditions was undertaken to minimize the amount of unwanted product **7a**. We examined a variety of solvents in this reaction using TfOH as the catalyst, and found that DCE is the best solvent for this reaction (entries 5-8, Table 2). Variation of temperature revealed that at 10°C, **5a** could be formed in 76% yield along with 13% of **7a** in DCE using TfOH as the catalyst (entries 9 and 10, Table 2). This is the best reaction condition to give **5a** in higher yield.

Table 2. Optimization of the reaction conditions of **1a** with **3a**.[a]



Entry	Catalyst	Solvent	t [h]	T [°C]	Yield [%][b]	
					5a	**7a**
1	$BF_3{\cdot}OEt_2$	DCE	3	20	69	17
2	$Cu(OTf)_2$	DCE	2	20	**6a**, 80	
3	TfOH	DCE	1	20	70	20
4	$TsOH{\cdot}H_2O$	DCE	3	20	30	trace
5	TfOH	CH_3CN	1	20	67	30
6	TfOH	toluene	1	20	trace	–
7	TfOH	THF	1	20	complex	
8	TfOH	DCM	1	20	51	49
9	TfOH	DCE	1	20	25	50
10	**TfOH**	**DCE**	**1**	**10**	**76**	**13**

[a] All reactions were carried out using **1a** (0.2 mmol) and **3a** (0.4 mmol) in the presence of the listed catalysts (10 mol%) and solvents (2.0 mL); best result highlighted in bold. [b] Isolated yields.

Using the optimized reaction conditions, we examined a variety of arylvinylcyclopropenes **1**, acetals **2** and aldehydes **3** in these reactions and the results of these experiments are shown in Tables 3 and 4, respectively. Acetals **2b–d** and **2f** with an electron-withdrawing group on the benzene ring produced the products **4** in 48 to 62% yields along with minor products **7** in 15 to 19% yield. However, acetal **2e** with a methyl group instead of an electron-withdrawing group on the benzene ring reacted with **1a** to produce the corresponding adduct **4e** in higher yield (67%) along with less amount of the rearrangement product **7e** (5% yield) (entries 1–5, Table 3). The X-ray crystal structure of **4f**[8] further supported the formation of product **4** (Figure 2). As for arylvinylcyclopropenes **1b** and **1c** having a substituent on

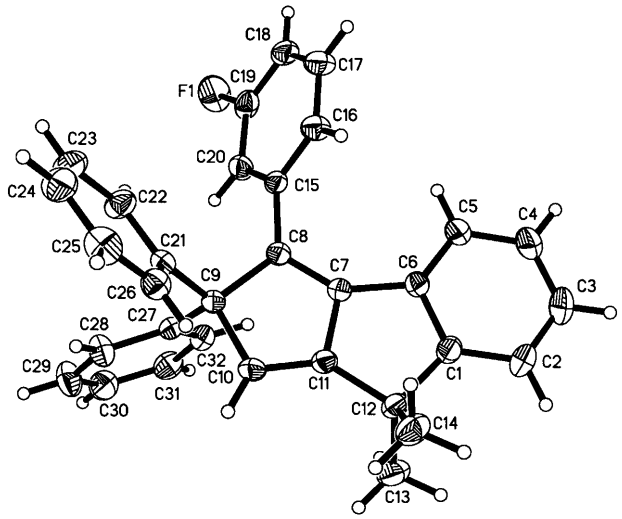
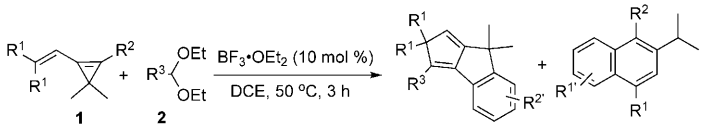


Figure 2. ORTEP drawing of compound **4f**.

the aromatic R^2 ring, products **4g** and **4h** were obtained as sole products in good yields (entries 6 and 7, Table 3). The substitution on the aromatic R^1 rings of arylvinylcyclopropenes did not significantly change the reaction outcomes. In the cases of **1d** and **1e**, adducts **4i** and **4j** were afforded in 61 and 65% yield as the major products along with minor products **7i** and **7j** in 4 and 10% yield, respectively (entries 8 and 9, Table 3).

Table 3. Scope of the reactions of arylvinylcyclopropenes **1** with acetals **2**.[a]



$R^1 = R^{1'} = C_6H_4$, $R^2 = R^{2'} = C_6H_4$

$R^{1'}$ or $R^{2'}$ is the substitution on the R^1 or R^2 aromatic ring

Entry	**1** (R^1/R^2)	**2** (R^3)	Yield [%][b] **4**	**7**
1	**1a** (C_6H_5/C_6H_5)	**2b** (p-ClC_6H_4)	**4b**, 57	**7a**, 19
2	**1a**	**2c** (p-BrC_6H_4)	**4c**, 51	**7a**, 15
3	**1a**	**2d** (p-FC_6H_4)	**4d**, 62	**7a**, 17
4	**1a**	**2e** (p-MeC_6H_4)	**4e**, 67	**7a**, 5
5	**1a**	**2f** (m-FC_6H_4)	**4f**, 48	**7a**, 19
6	**1b** (C_6H_5/p-MeC_6H_4)	**2a** (C_6H_5)	**4g**, 89	–
7	**1c** (C_6H_5/p-ClC_6H_4)	**2a**	**4h**, 73	–
8	**1d** (p-MeC_6H_4/C_6H_5)	**2a**	**4i**, 61	**7d**, 4
9	**1e** (p-ClC_6H_4/C_6H_5)	**2a**	**4j**, 65	**7e**, 10

[a] All reactions were carried out using **1** (0.2 mmol) and **2** (0.4 mmol) and $BF_3{\cdot}OEt_2$ (10 mol%) in DCE (2.0 mL) at 50°C. [b] Isolated yields.

The reactions of **1a** with electron-rich arylaldehydes **3d**, **3e** and **3f** produced the corresponding adducts **5d**, **5e** and **5f** in higher yields than those with electron-deficient arylaldehydes **3b** and **3c** (entries 1–5, Table 4). The reactions of **3a** with various substituted arylvinylcyclopropenes **1b–f** produced the corresponding phenanthrenes derivatives **5g–k** in moderate yields similarly (entries 6–10, Table 4). 1-Naphthaldehyde (**3g**) also could be used as the substrate in this reaction, affording **5l** in 47% yield (entry 11, Table 4). In all these cases, the minor products **7** were formed in 4 to 23% yield (entries 1–11, Table 4). The structures of **5f** and **5k** were further determined by X-ray diffraction and their ORTEP drawings are shown in Figure 3.[9]

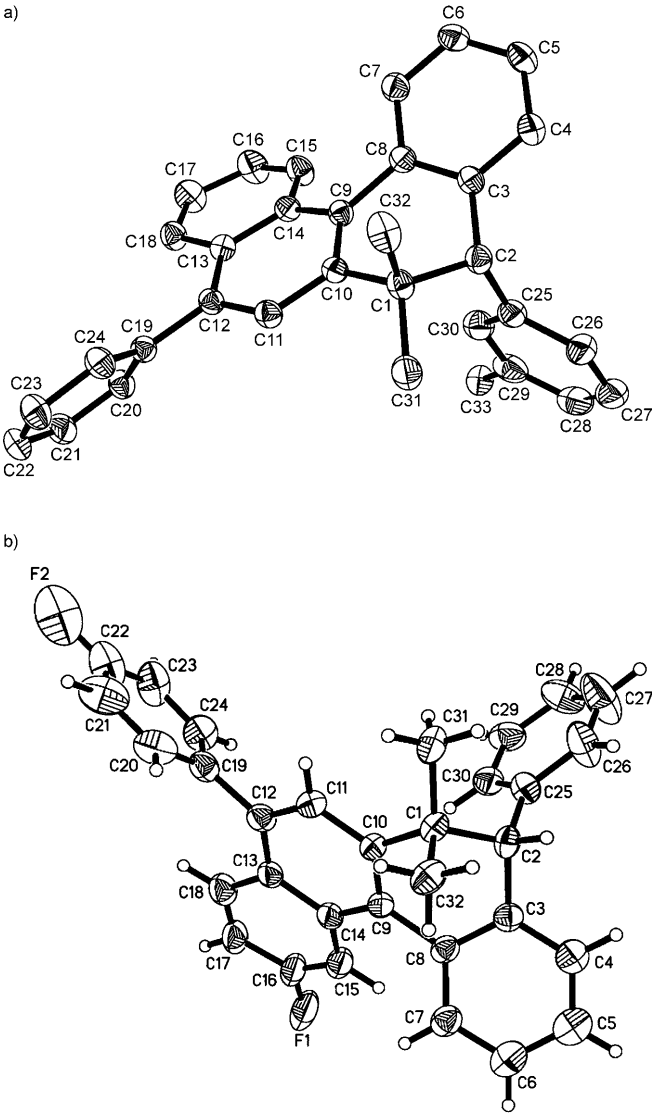
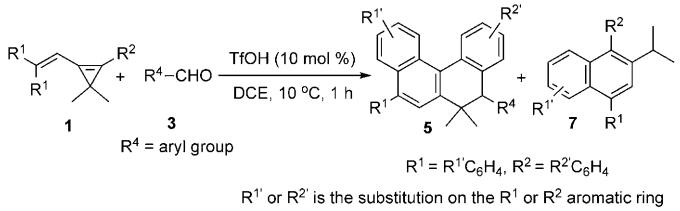


Figure 3. ORTEP drawings of **5f** (top) and **5k** (bottom).

Notably we did not obtain the similar products when aliphatic aldehydes were used as the substrates under identical conditions. The examination of the reaction between arylvinylcyclopropene **1a** (1.0 equiv) and 3-phenylpropanal **3h** (3.0 equiv) in the presence of TfOH (10 mol%) revealed that naphthalene derivative **8a** was obtained in 51% yield along with the rearrangement product **7a** in 16% yield within 24 h in DCE at 10°C (entry 1, Table 5). The structure of **8a** was unambiguously determined by X-ray diffraction

Table 4. Scope of the reactions of arylvinylcyclopropenes **1** with aldehydes **3**.[a]



Entry	**1** (R^1/R^2)	**3** (R^4)	Yield [%][b] **5**	**7**
1	**1a** (C_6H_5/C_6H_5)	**3b** (*p*-BrC_6H_4)	**5b**, 52	**7a**, 15
2	**1a**	**3c** (*p*-ClC_6H_4)	**5c**, 51	**7a**, 12
3	**1a**	**3d** (*p*-MeC_6H_4)	**5d**, 62	**7a**, 14
4	**1a**	**3e** (*p*-MeOC_6H_4)	**5e**, 61	**7a**, 15
5	**1a**	**3f** (*m*-MeC_6H_4)	**5f**, 67	**7a**, 14
6	**1b** (C_6H_5/*p*-MeC_6H_4)	**3a** (C_6H_5)	**5g**, 59	**7b**, 4
7	**1c** (C_6H_5/*p*-ClC_6H_4)	**3a**	**5h**, 65	**7c**, 13
8	**1d** (*p*-MeC_6H_4/C_6H_5)	**3a**	**5i**, 62	**7d**, 14
9	**1e** (*p*-ClC_6H_4/C_6H_5)	**3a**	**5j**, 45	**7e**, 11
10	**1f** (*p*-FC_6H_4/C_6H_5)	**3a**	**5k**, 51	**7e**, 20
11	**1a**	**3g** (1-naphthaldehyde)	**5l**, 47	**7e**, 23

[a] All reactions were carried out using **1** (0.2 mmol) and **3** (0.4 mmol) and TfOH (10 mol%) in DCE (2.0 mL) at 10°C. [b] Isolated yields.

and its ORTEP drawing is shown in Figure 4.[10] Similarly, a variety of arylvinylcyclopropenes **1** and aliphatic aldehydes can be used in this reaction to give the products in good

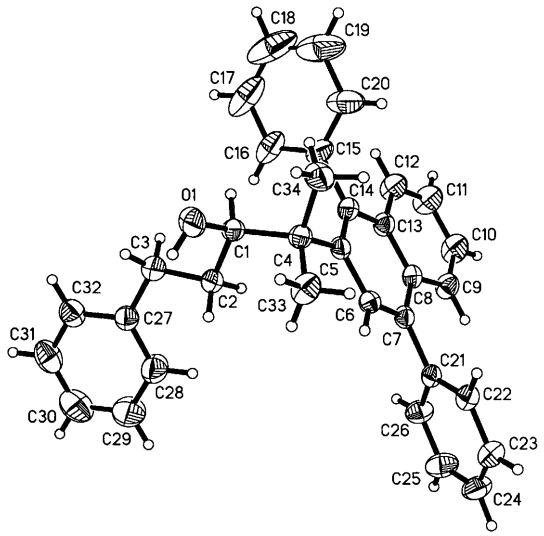
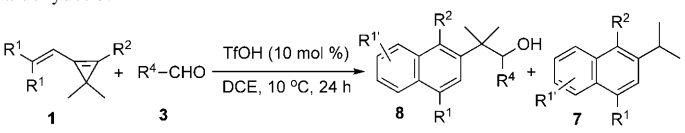
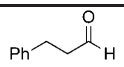
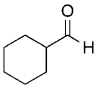
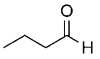
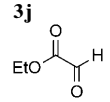
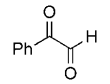


Figure 4. ORTEP drawing of compound **8a**.

total yields and the results of these experiments are summarized in Table 5. The steric hindrance is probably the reason leading to adduct **8b** in 17% yield and the rearrangement product **7n** in 51% yield when the aliphatic aldehyde **3i** reacted with **1a** (entry 2, Table 5). In other cases, the corresponding products were obtained in good total yields with **8c** and **8d** as the major products (entries 3 and 4, Table 5). The investigation of the reactions of arylvinylcyclopropenes **1** with activated aldehyde ethyl 2-oxoacetate **3k** or oxo-phenylacetaldehyde **3l** revealed that the corresponding naphthalene products **8** were obtained in good yields as the major products along with naphthalene derivatives **7** as the minor products in most cases (entries 5–9, Table 5). Only in the case of arylvinylcyclopropene **1e** having electron-withdrawing substituent on the benzene ring, the corresponding product **8h** was obtained in 25% yield along with **7t** in 34% yield, presumably due to the electronic nature of the aromatic group (entry 8, Table 5).

Table 5. Scope of the reactions of arylvinylcyclopropenes **1** with aliphatic aldehydes **3**.[a]

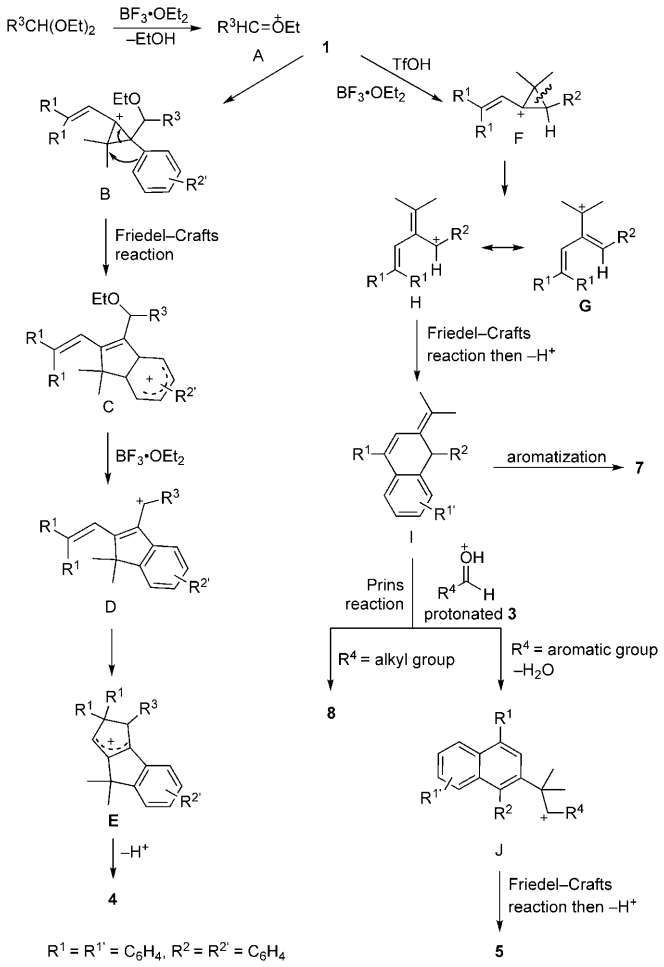


Entry	**1** (R^1/R^2)	**3**	Yield [%][b] **8**	**7**
1	**1a** (C_6H_5/C_6H_5)	 **3h**	**8a**, 51	**7a**, 16
2	**1a**	 **3i**	**8b**, 17	**7a**, 51
3	**1a**	 **3j**	**8c**, 42	**7a**, 26
4	**1a**	 **3k**	**8d**, 92	**7a**, 5
5	**1b** (C_6H_5/*p*-MeC_6H_4)	**3k**	**8e**, 94	**7b**, trace
6	**1c** (C_6H_5/*p*-ClC_6H_4)	**3k**	**8f**, 76	**7c**, 5
7	**1d** (*p*-MeC_6H_4/C_6H_5)	**3k**	**8g**, 89	**7d**, trace
8	**1e** (*p*-ClC_6H_4/C_6H_5)	**3k**	**8h**, 25	**7e**, 34
9	**1a**	 **3l**	**8i**, 62	**7a**, 12

[a] All reactions were carried out using **1** (0.2 mmol) and **3** (0.6 mmol) and TfOH (10 mol%) in DCE (2.0 mL) at 10°C. [b] Isolated yields.

A plausible mechanism for the formation of **4** and **5** is illustrated in Scheme 2. When acetal **2** is used as the substrate, acetal **2** initially generates oxonium intermediate **A** in the presence of Lewis acid.[11] Alternatively, the carbocation **F** could also be formed in the presence of Lewis acid. We have theoretically investigated the relative stabilities of intermediates **A** and **F** in the gas phase and in solution. The intermediate **A** is slightly more stable than the carbocation **F** in solution (for computational details, see Supporting Information). Thus, a possible mechanism is suggested as follows. The reaction of intermediate **A** with arylvinylcyclopropene **1** produces cyclopropane cationic intermediate **B** via

intramolecular Friedel–Crafts reaction to give intermediate **C**. In the presence of $BF_3{\cdot}OEt_2$, intermediate **C** undergoes the release of an ethoxy group and aromatization to give the corresponding cationic intermediate **D**. Intramolecular cyclization to the *exo*-vinyl group produces intermediate **E** through deprotonation to furnish the product **4**.



Scheme 2. A plausible reaction mechanism of arylvinylcyclopropene **1** with acetal **2** and aldehyde **3** in the presence of acids.

When aldehyde **3** (R = aromatic ring) is employed as the substrate, the carbocation **F** and protonated aldehyde **3** could be formed in the presence of Lewis acid initially. Their relative stabilities are also investigated theoretically. The carbocation **F** is more stable than protonated aldehyde **3** in the gas phase and in solution (for computational details, see Supporting Information). Based on theoretical investigation results, one possible mechanism starting from the carbocation **F** is proposed here. When aldehyde **3** is used in the reaction, **1** undergoes protonation, ring-opening, allylic migration, and intramolecular Friedel–Crafts reaction via intermediates **F**, **G**, and **H** to generate intermediate **I**.[5b] The Prins-type reaction of intermediate **I** with protonated aldehyde **3** produces final products **8** (R^4 = alkyl group) or intermediate **J** (R^4 = aryl group). Further intermolecular Friedel–Crafts reaction of intermediate **J** produces adducts **5**.[12] On the other hand, aromatization of intermediate **I** produces naphthalene derivative **7** as the by-product.[5b] It should be noted that the π attack and the σ attack of H^+ to cyclopropene could be both possible in this reaction. However, since the structures of arylvinylcyclopropenes **1** are planar and highly hindered,[5b] the direct π attack could be favorable and the sigma-attack could be blocked out.

In conclusion, we have succeeded in the construction of a variety of aromatic systems via different regioselective addition of arylvinylcyclopropenes to acetals and aldehydes in the presence of Lewis or Brønsted acid under mild conditions. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

Experimental Section

General procedure for $BF_3{\cdot}OEt_2$-catalyzed reaction of arylvinylcyclopropenes with acetals: Under an argon atmosphere, arylvinylcyclopropenes **1** (0.2 mmol), acetal **2** (0.4 mmol), $BF_3{\cdot}OEt_2$ (0.02 mmol) and DCE (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 50 °C until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2).

General procedure for TfOH-catalyzed reaction of arylvinylcyclopropenes with aldehyde: Under an argon atmosphere, arylvinylcyclopropenes **1** (0.2 mmol), aldehyde **3** (0.4 or 0.6 mmol), TfOH (0.02 mmol) and DCE (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 10 °C until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2).

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[1] For a review, see: M. S. Baird in *Cyclopropenes: Synthesis by Construction of the System, Vol. E17d/2* (Ed.: A. de Meijere), Houben-Weyl, Stuttgart, **1996**, pp. 2695–2744.

[2] a) R. D. Bach, O. Dmitrenko, *J. Am. Chem. Soc.* **2006**, *128*, 4598–4611; b) P. R. Khoury, J. D. Goddard, W. Tam, *Tetrahedron* **2004**, *60*, 8103–8112; c) A. Fattahi, R. E. McCarthy, M. R. Ahmad, S. R. Kass, *J. Am. Chem. Soc.* **2003**, *125*, 11746–11750.

[3] For reviews, see: a) P. Binger, H. M. Büch, *Top. Curr. Chem.* **1987**, *135*, 77–151; b) P. W. Jennings, L. L. Johnoson, *Chem. Rev.* **1994**, *94*, 2241–2290; c) M. S. Baird in *Cyclopropenes: Transformations, Vol. E17d/2*, (Ed.: A. de Meijere), Houben-Weyl, Stuttgart, **1996**, pp. 2781–2860; d) M. Nakamura, H. Isobe, E. Nakamura, *Chem. Rev.* **2003**, *103*, 1295–1326.

[4] For recent reviews, see: a) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117–3179; b) M. Rubin, M. Rubina, V. Ge-

vorgyan, *Synthesis* **2006**, 1221–1245; c) J. M. Fox, N. Yan, *Curr. Org. Chem.* **2005**, *9*, 719–732; d) R. Walsh, *Chem. Soc. Rev.* **2005**, *34*, 714–732; e) W. R. Dolbier, Jr., M. A. Battiste, *Chem. Rev.* **2003**, *103*, 1071–1098; f) A. Sekiguchi, V. Y. Lee, *Chem. Rev.* **2003**, *103*, 1429–1448; g) K. C. Chen, G. A. Lee, *Huaxue* **2006**, *64*, 73–95; h) M. S. Baird, *Chem. Rev.* **2003**, *103*, 1271–1294.

[5] a) A. Padwa, M. W. Wannamaker, A. D. Dyszlewski, *J. Org. Chem.* **1987**, *52*, 4760–4767; b) L.-X Shao, Y.-P. Zhang, M.-H. Qi, M. Shi, *Org. Lett.* **2007**, *9*, 117–120.

[6] a) Z.-B. Zhu, M. Shi, *Chem. Eur. J.* **2008**, *14*, 10219–10222; b) J.-M. Lu, Z.-B. Zhu, M. Shi, *Chem. Eur. J.* **2009**, *15*, 963–971; c) J.-M. Lu, M. Shi, *Chem. Eur. J.* **2009**, *15*, 6065–6073; d) M. Shi, L.-F. Yao, *Chem. Eur. J.* **2008**, *14*, 8725–8731; e) L.-F. Yao, M. Shi, *Chem. Eur. J.* **2009**, *15*, 3875–3881; f) Z.-B. Zhu, L.-X. Shao, M. Shi, *Eur. J. Org. Chem.* **2009**, 2576–2580; g) F.-F. Yu, W.-G. Yang, M. Shi, *Chem. Commun.* **2009**, 1392–1394.

[7] CCDC 653043 (**4a**) contains 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. Empirical formula: $C_{32}H_{26}$; formula weight: 410.53; crystal color, habit: colorless, prismatic; crystal system: triclinic; lattice type: primitive; lattice parameters: $a=9.1980(14)$, $b=10.2335(16)$, $c=13.778(2)$ Å, $\alpha=111.343(2)$, $\beta=91.614(3)$, $\gamma=103.590(3)°$, $V=1164.8(3)$ Å^3; space group: $P\bar{1}$; $Z=2$; $\rho_{calcd}=1.170$ g cm^{-3}; $F_{000}=436$; diffractometer: Rigaku AFC7R; residuals: R, R_w = 0.0645, 0.1495.

[8] CCDC 679735 (**4f**) contains 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. Empirical formula: $C_{32}H_{25}F$; formula weight: 428.52; crystal color, habit: colorless, prismatic; crystal dimensions: $0.480\times0.402\times0.317$ mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a=10.2391(10)$, $b=18.0161(17)$, $c=13.0623(13)$ Å, $\alpha=90$, $\beta=102.724(9)$, $\gamma=90°$, $V=2350.4(4)$ Å^3; space group: $P21/n$; $Z=4$; $\rho_{calcd}=1.211$ g cm^{-3}; $F_{000}=904$; diffractometer: Rigaku AFC7R; residuals: R, R_w = 0.0549, 0.1269.

[9] In order to identify the various aromatic rings, we have carried out the X-ray diffraction of two different substituted adducts; a) CCDC 724594 (**5f**) contains 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. Empirical formula: $C_{33}H_{28}$; formula weight: 424.55; crystal color, habit: colorless, prismatic; crystal dimensions: $0.306\times0.179\times0.137$ mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a=9.8477(12)$, $b=23.856(3)$, $c=10.9866(13)$ Å, $\alpha=90$, $\beta=113.883(2)$, $\gamma=90°$, $V=2360.0(5)$ Å^3; space group: $P21/n$; $Z=4$; $\rho_{calcd}=1.195$ g cm^{-3}; $F_{000}=904$; diffractometer: Rigaku AFC7R; residuals: R, R_w = 0.0665, 0.1677; b) CCDC 657295 (**5k**) contains 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. Empirical formula: $C_{32}H_{24}F_2$; formula weight: 446.51; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: $a=10.5985(12)$, $b=12.9847(15)$, $c=17.034(2)$ Å, $\alpha=90$, $\beta=97.139(3)$, $\gamma=90°$, $V=2325.9(5)$ Å^3; space group: $P21/n$; $Z=4$; $\rho_{calcd}=1.275$ g cm^{-3}; $F_{000}=936$; diffractometer: Rigaku AFC7R; residuals: R, R_w: 0.0487, 0.0826.

[10] CCDC 704849 (**8a**) contains 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. Empirical formula: $C_{34}H_{32}O$; formula weight: 456.60; crystal color, habit: colorless, prismatic; crystal dimensions: $0.303\times0.216\times0.147$ mm; crystal system: triclinic; lattice type: primitive; lattice parameters: $a=13.0705(16)$, $b=13.8252(18)$, $c=15.995(2)$ Å, $\alpha=77.673(3)$, $\beta=72.742(3)$, $\gamma=79.133(3)°$, $V=2672.2(6)$ Å^3; space group: $P\bar{1}$; $Z=4$; $\rho_{calcd}=1.135$ g cm^{-3}; $F_{000}=976$; diffractometer: Rigaku AFC7R; residuals: R, R_w: 0.0717, 0.1514.

[11] H. Meerwein, W. Florian, N. Schön, G. Stopp, *Justus Liebigs Ann. Chem.* **1961**, *641*, 1–39.

[12] For an example of 1,4-addition of intermediate **I** with α,β-unsaturated compounds, see: Z.-B. Zhu, M. Shi, *J. Org. Chem.* **2009**, *74*, 2481–2485.

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