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Brønsted acid-mediated ring-opening reactions of methylenecyclopropanes: a dramatic counter ion effect

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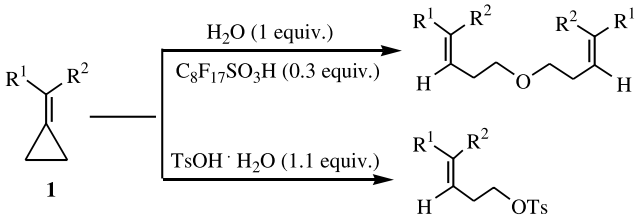
Abstract—We report herein two different ring-opening patterns of methylenecyclopropanes (MCPs) in the presence of two Brønsted acids heptadecafluorooctane-1-sulfonic acid ($C_8F_{17}SO_3H$) and toluene *p*-sulfonic acid (TsOH) under mild conditions: (a) the ring-opening of MCPs by H_2O and subsequent etherification give the corresponding homoallylic ethers in the presence of heptadecafluorooctane-1-sulfonic acid; (b) the direct ring-opening of MCPs by the Brønsted acid gives the corresponding homoallylic alcohol derivatives in the presence of toluene *p*-sulfonic acid.

1. Introduction

Transition metal-catalyzed reactions of methylenecyclopropanes (MCPs) **1** have been widely explored in this area of study over the past decades.[1] The attractive feature of these compounds is their surprising stability along with a high level of strain.[2–4] Strangely, less attention has been paid for the Lewis acid or Brønsted acid-mediated reactions of MCPs.[5] In the continuum of Lewis acid or Brønsted acid-mediated transformations of MCPs **1**, we have found that MCPs **1** can react with various reagents such as alcohols, amines, and imines in a different ring-opening pattern.[6] These progresses stimulate us to investigate further the Lewis acid or Brønsted acid-mediated ring-opening reactions of MCPs **1**. Recently, Yamamoto and co-workers reported that the cyclopropyl ring of MCPs can be opened by water to give the homoallylic alcohol under severe reaction conditions, such as the use of a sealed pressure vial under an inert gas atmosphere and at higher temperature (80 °C) without organic solvent.[7] In the recent program of Brønsted acid-mediated transformations of MCPs **1**, we found that the corresponding anion (counter ion) of the employed Brønsted acid played a significant role in the ring-opening reactions under milder conditions: a) the cyclopropyl ring of MCPs **1** can be opened by H_2O and subsequent etherification to give the homoallylic ethers in the presence of heptadecafluorooctane-1-sulfonic acid ($C_8F_{17}SO_3H$) in which the corresponding anion $C_8F_{17}SO_3^-$ is a weak nucleophile; (b) the cyclopropyl ring of MCPs **1** can be opened directly by the Brønsted acid toluene *p*-sulfonic acid (TsOH) to give the homoallylic alcohol derivatives (sulfonated homoallylic alcohols) in which the corresponding anion TsO^- is a strong nucleophile. In this paper we wish to report the full details of these interesting results (Scheme 1).



Scheme 1. Ring-opening reactions of MCPs **1** in the presence of $C_8F_{17}SO_3H/H_2O$ and $TsOH{\cdot}H_2O$.

2. Results and discussion

At the outset of our investigation, the reaction of MCP **1a** with H_2O (1 equiv) was chosen as a model reaction and carried out under various reaction conditions to confirm the optimum reaction conditions. Table 1 shows the representative results. After several trials and errors, we were pleased to find out that the reaction of MCP **1a** with H_2O in the presence of $C_8F_{17}SO_3H$ (0.1 equiv) gave the homoallylic ether **2a** in 63% yield along with the homoallylic

Keywords: Methylenecyclopropanes (MCPs); Brønsted acid; Ring-opening reaction; Toluene *p*-sulfonic acid (TsOH); Heptadecafluorooctane-1-sulfonic acid ($C_8F_{17}SO_3H$).
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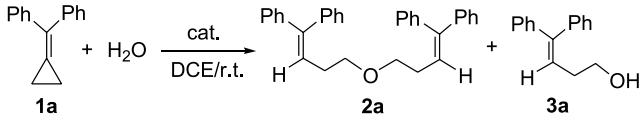
Table 1. The screening of the catalysts of the ring-opening of MCPs by H_2O and subsequent etherification



1a 2a 3a

Entry[a]	Catalyst	Time/(h)	Yield/(%)[b]	
			2a	**3a**
1	$Zn(OTf)_2$	72	—	—
2	$Cu(OTf)_2$	72	Trace	Trace
3	$Eu(OTf)_3$	72	—	—
4	$Sc(OTf)_3$	72	Trace	—
5	$Yb(OTf)_3$	72	Trace	—
6	BF_3OEt_2	72	Trace	11
7	CF_3SO_3H	72	49	5
8	$Zr(OTf)_4$	72	21	Trace
9	$C_8F_{17}SO_3H$	72	63	8
10[c]	$Zr(OTf)_4$	48	48	Trace
11[c]	$C_8F_{17}SO_3H$	24	71	—
12[d]	$C_8F_{17}SO_3H$	24	67	Trace
13[c,e]	$C_8F_{17}SO_3H$	24	11	25
14[c,f]	$C_8F_{17}SO_3H$	24	36	18

[a] Otherwise specified, 0.1 equiv of catalysts were used.
[b] Isolated yields.
[c] 0.3 equiv of catalysts were used.
[d] 1.0 equiv of catalyst was used.
[e] CH_3CN as the solvent.
[f] *n*-Hexane as the solvent.

alcohol **3a** in 8% yield within 72 h (Table 1, entry 9). The product **2a** was also obtained in somewhat lower yields, either in the catalysis of CF_3SO_3H (0.1 equiv) or $Zr(OTf)_4$ (0.1 equiv) (Table 1, entries 7 and 8). Investigation into other catalysts showed that $Zn(OTf)_2$, $Cu(OTf)_2$, $Eu(OTf)_3$, $Sc(OTf)_3$, $Yb(OTf)_3$ and $BF_3{\cdot}OEt_2$ were not effective promoters for this reaction (Table 1, entries 1–6). Further screening showed that this reaction can complete within 24 h to give **2a** as a sole product in 71% yield when 0.3 equiv of $C_8F_{17}SO_3H$ was used (Table 1, entry 11) and increasing the amount of $C_8F_{17}SO_3H$ to 1.0 equiv gave **2a** in comparable yield also as a sole product (Table 1, entry 12). In addition, product **2a** was obtained in somewhat lower yields along with **3a** when CH_3CN and *n*-hexane were used as the solvents (Table 1, entries 13 and 14). Of the solvents screened, 1,2-dichloroethane (DCE) proved to be a suitable solvent, giving the best results.

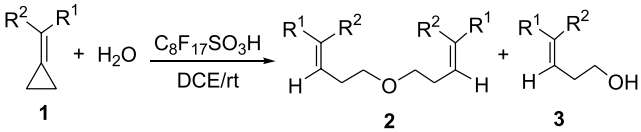
The equivalents of H_2O were investigated for this ring-opening reaction of MCPs. The results are summarized in Table 2. As can be seen from Table 2, the best result was obtained when 1.0 equiv H_2O was used (Table 2, entry 1). Increasing the amount of H_2O to 2.0–4.0 equiv gave product **2a** in somewhat lower yields along with the formation of

Table 2. The effects of the amount of water used

Entry[a]	H_2O (equiv)	Yield (%)[b]	
		2a	**3a**
1	1.0	71	—
2	2.0	62	4
3	3.0	46	14
4	4.0	28	9
5	5.0	Trace	Trace
6	90.0	—	—

[a] All reactions were carried out for 24 h.
[b] Isolated yields.

Table 3. Reaction of MCPs **1** with H_2O (1.0 equiv) under the catalysis of $C_8F_{17}SO_3H$ (0.3 equiv) in DCE



1 2 3

Entry	R^1/R^2	Time/h	Yield (%)[a]	
			2	**3**
1	**1b**, *p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$	1	**2b**, 52	—
2	**1c**, *p*-$MeOC_6H_4$/C_6H_5	2	**2c**, 60	Trace
3	**1d**, *p*-MeC_6H_4/*p*-MeC_6H_4	4	**2d**, 56	—
4	**1e**, *o*-ClC_6H_4/C_6H_5	24	**2e**, 63	**3e**, 9
5	**1f**, *p*-ClC_6H_4/*p*-ClC_6H_4	24	**2f**, 42	—
6	**1g**, *p*-FC_6H_4/*p*-FC_6H_4	24	**2g**, 94	**3g**, 6

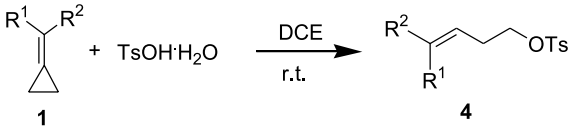
[a] Isolated yields.

homoallylic alcohol **3a** (Table 2, entries 2–4). Traces of **2a** and **3a** were obtained when 5.0 equiv of H_2O was used and no reaction took place when 90.0 equiv of H_2O was used (Table 2, entries 5, 6). Thus, these optimized reaction conditions were 1.0 equiv of H_2O as the reagent, 0.3 equiv of $C_8F_{17}SO_3H$ as the catalyst and DCE as the solvent.

In the following series of reactions, we examined the reactivity of a variety of MCPs **1** under these optimized conditions to surrey the generality of this reaction. The results are shown in Table 3. We were delighted to find out that the reactions proceeded smoothly to give the corresponding homoallylic ether **2** as a sole product in good to excellent yields in most cases except for MCP **1e** and **1g** in which less than 10% of the homoallylic alcohol were obtained (Table 3, entries 4 and 6). For MCPs **1b**, **1c** and **1d**, in which electron-donating groups on the phenyl ring, the reaction time was dramatically reduced (Table 3, entries 1–3). For the unsymmetric MCPs **1c** and **1e**, only one isomer of the product **2** were obtained and we cannot explain these phenomena at present stage (Table 3, entries 2 and 4) (see their ^1H and ^{13}C NMR spectra in Supporting Information).

Interestingly, we found that the ring of MCPs **1** can be opened by the corresponding anion when toluene *p*-sulfonic acid monohydrate ($TsOH{\cdot}H_2O$) was used as the Brønsted acid reagent in 1,2-dichloroethane (DCE). The results are shown in Table 4. As can be seen from Table 4, all reactions

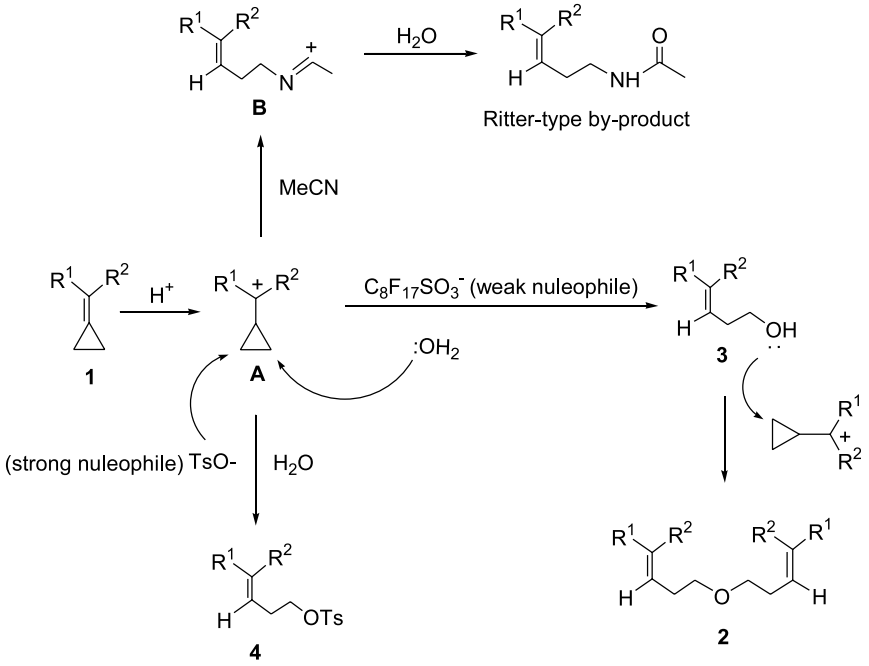
Table 4. The reaction of toluene-4-sulfonic acid with various MCPs **1**



1 4

Entry	R^1/R^2	Time/min	Yield/%[a], **4** (*E*/*Z*)
1	**1a**, C_6H_5/C_6H_5	4	98
2	**1b**, *p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$	5	96
3[b]	**1c**, *p*-$MeOC_6H_4/C_6H_5$	5	99 (1:1)
4	**1d**, *p*-MeC_6H_4/*p*-MeC_6H_4	5	77
5[b]	**1e**, *o*-ClC_6H_4/C_6H_5	25	93 (7.8:1)
6	**1f**, *p*-ClC_6H_4/*p*-ClC_6H_4	20	92
7	**1g**, *p*-FC_6H_4/*p*-FC_6H_4	30	96
8[b]	**1h**, *p*-$EtOC_6H_4$/Me	5	97 (2.5:1)

[a] Isolated yields.
[b] Mixtures of (*Z*)- and (*E*)-isomers.



Scheme 2. Plausible reaction mechanism.

proceeded smoothly to give the homoallylic alcohol derivatives **4** in excellent yields within 30 min. In this case, the ambient H_2O did not participate in the ring-opening reaction. For the unsymmetric MCPs **1b**, **1e** and **1h**, the products **4b**, **4e** and **4h** were obtained as mixtures of *Z*- and *E*-isomers (Table 4, entries 3, 5 and 8). Using MeCN as the solvent, a Ritter reaction product was obtained as the by-product (Scheme 2).[8]

The structures of products **2**, **3** and **4** were determined by ^{1}H NMR and ^{13}C NMR spectroscopic data, microanalysis and HRMS.

A plausible mechanism for these two different ring-opening reactions of MCPs **1** is shown in Scheme 2. The initial protonation of MCPs **1** with Brønsted acid gives the intermediate **A**. The cyclopropylmethyl cation intermediate **A** is further stabilized by two substituents on the double bond.[9] The intermediate **A** is attacked by H_2O if the corresponding anion of the Brønsted acid is a weak nucleophile (in the case of $C_8F_{17}SO_3^-$) to give product **3**. Subsequent ring-opening nucleophilic attack of **3** to another cation intermediate **A** gives product **2**. The intermediate A can also be attacked by the corresponding anion of the Brønsted acid if it is a strong nucleophile (in the case of TsO^-) to furnish product **4**. In the case of MeCN as the solvent, the cation intermediate **A** will be attacked by the solvent (MeCN) to give the cation intermediate **B** which is quenched by H_2O to give the Ritter-type by-product (Scheme 2).

3. Conclusion

In conclusion, we have found two different ring-opening patterns of MCPs **1** in different Brønsted acid-mediated systems. The nucleophilicity of the anion of the employed Brønsted acid has dramatic effect on the ring-opening modes of MCPs **1**: the cyclopropyl ring of MCPs **1** can be opened by water when the corresponding anion is a weak nucleophile such as heptadecafluorooctane-1-sulfonic acid ($C_8F_{17}SO_3H$) as the Brønsted acid mediator; and the cyclopropyl ring of MCPs **1** also can be opened by the corresponding anion when it is a strong nucleophile such as toluene *p*-sulfonic acid (TsOH) as the Brønsted acid mediator. Other Brønsted acids will be investigated in this ring-opening system in the near future. In addition, efforts are underway to elucidate the mechanistic details and subsequent transformation thereof. Work along these lines is currently in progress.

4. Experimental

4.1. General remarks

^{1}H NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA^+ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points are uncorrected. 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.

4.2. General procedure for the ring-opening of MCPs by H_2O and subsequent etherification in the catalysis of heptadecafluorooctane-1-sulfonic acid ($C_8F_{17}SO_3H$)

Under an argon atmosphere, MCPs **1** (0.30 mmol), H_2O (0.30 mmol) and $C_8F_{17}SO_3H$ (0.1 mmol), were added into a

flame-dried Schlenk tube with freshly distilled 1,2-dichloroethane (DCE) (1.0 mL). The obtained white solid suspended reaction mixture was stirred at room temperature. The solvent was removed under reduced pressure and then the residue was purified by a flash column chromatography.

4.2.1. Di(4,4-diphenyl-but-3-en-1-yl) ether (2a). A white solid, Mp: 103–106 °C; IR (neat): ν 3078, 3054, 3023, 2856, 2778, 1945, 1889, 1734, 1597, 1494, 1443 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.43 (dt, $J=6.3$, 7.2 Hz, 4H), 3.51 (t, $J=6.3$ Hz, 4H), 6.61 (t, $J=7.2$ Hz, 2H), 7.20–7.39 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 30.4, 70.4, 126.0, 126.90, 126.93, 127.2, 128.0, 128.2, 129.9, 139.9, 142.5, 143.1. MS (%) *m/z* 430 (M^+, 0.25), 237 (50.68), 206 (75.71), 91 (100). HRMS Calcd. for $C_{32}H_{30}ONa^+$ (Maldi)[10]: 453.2201, Found: 453.2189 ($M+Na^+$).

4.2.2. 4,4-diphenyl-but-3-en-1-ol (3a). A colorless liquid; IR (neat): ν 3344, 3055, 2926, 1493, 1443, 1047, 1031 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.40 (dt, $J=6.6$, 7.5 Hz, 2H), 3.72 (t, $J=6.6$ Hz, 2H), 6.11 (t, $J=7.5$ Hz, 1H), 7.17–7.40 (m, 10H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 33.3, 62.6, 125.2, 127.07, 127.09, 127.2, 128.1, 128.2, 129.8, 139.8, 142.4, 144.2. MS (%) *m/z* 224 (M^+), 193, 178, 165, 115. HRMS Calcd. for $C_{16}H_{16}O$ (EI): 224.1201, Found: 224.1215.

4.2.3. Di[4,4-bis(4-methoxyphenyl)-but-3-en-1-yl] ether (2b). A colorless liquid, IR (CH_2Cl_2): ν 3002, 2956, 2933, 2907, 2836, 2052, 1730, 1645, 1604, 1510, 1462, 1248 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.39 (dt, $J=6.6$, 6.9 Hz, 4H), 3.48 (t, $J=6.6$ Hz, 4H), 3.78 (s, 3H, CH_3O), 3.81 (s, 3H, CH_3O), 5.99 (t, $J=6.9$ Hz, 2H), 6.77 (d, $J=$ 8.7 Hz, 4H, Ar), 6.87 (d, $J=8.7$ Hz, 4H, Ar), 7.10 (d, $J=$ 8.7 Hz, 4H, Ar), 7.14 (d, $J=8.7$ Hz, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 30.4, 55.17, 55.21, 70.5, 113.3, 113.4, 113.5, 124.0, 128.38, 131.0, 132.2, 142.0, 158.4, 162.8. MS (%) *m/z* 550 (M^+, 0.55), 266 (66.78), 236 (100). HRMS Calcd. for $C_{32}H_{30}ONa^+$ (Maldi): 573.2615, Found: 573.2612 ($M+Na^+$).

4.2.4. Di{4,4-[1-phenyl-1-(4-methoxyphenyl)]-but-3-en-1-yl} ether (2c). A colorless liquid, IR (CH_2Cl_2): ν 3054, 3030, 3003, 2955, 2935, 2904, 2859, 2837, 2793, 2548, 2311, 2059, 1893, 1719, 1654, 1606, 1575, 1510, 1493 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.31 (dt, $J=6.6$, 7.5 Hz, 4H), 3.36–3.44 (m, 4H), 3.69 (s, 3H, CH_3O), 3.72 (s, 3H, CH_3O), 5.96 (t, $J=7.5$ Hz, 1H), 6.00 (t, $J=7.5$ Hz, 1H), 6.68 (d, $J=9.0$ Hz, 2H, Ar), 6.80 (d, $J=8.4$ Hz, 2H, Ar), 7.16–7.40 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 30.4, 30.5, 55.16, 55.19, 70.46, 70.49, 113.4, 113.5, 124.2, 125.7, 126.8, 126.9, 127.3, 128.0, 128.1, 128.3, 129.8, 131.0, 132.2, 135.3, 140.2, 142.5, 142.7, 143.0, 158.5, 158.7. MS (%) *m/z* 490 (M^+, 0.50), 267 (20.58), 236 (100). HRMS Calcd. for $C_{34}H_{34}O_3Na^+$ (Maldi): 513.2429, Found: 513.2400 ($M+Na^+$).

4.2.5. Di[4,4-bis-(4-methylphenyl)-but-3-en-1-yl] ether (2d). A colorless liquid, IR (CH_2Cl_2): ν 3023, 2946, 2920, 2865, 2733, 1900, 1719, 1656, 1608, 1511, 1449, 1278 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.30–2.46 (m, 16H), 3.51 (t, $J=6.9$ Hz, 4H), 6.61 (t, $J=7.2$ Hz, 2H), 7.04–7.20 (m, 16H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 21.1, 21.2, 30.4, 70.5, 124.9, 125.7, 127.2, 128.7, 128.8, 129.8, 136.5, 137.1, 140.0, 142.8. MS (%) *m/z* 486 (M^+, 1.5), 265 (28.11), 234 (100). HRMS Calcd. for $C_{36}H_{38}ONa^+$ (Maldi): 509.2817, Found: 509.2815 ($M+Na^+$).

4.2.6. Di{4,4-[1-phenyl-1-(2-chlorophenyl)]-but-3-en-1-yl} ether (2e). A yellow liquid, IR (CH_2Cl_2): ν 3080, 3055, 3024, 2947, 2858, 2791, 1937, 1800, 1730, 1597, 1494, 1473, 1445, 1434, 1360 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.14 (dt, $J=6.9$, 7.5 Hz, 4H), 3.39 (t, $J=6.9$ Hz, 4H), 6.23 (t, $J=7.5$ Hz, 2H), 7.09–7.21 (m, 16H, Ar), 7.33–7.36 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 30.4, 69.9, 126.1, 126.7, 127.0, 127.1, 128.2, 128.6, 129.7, 131.7, 133.8, 138.5, 140.1, 140.3. MS (%) *m/z* 498 (M^+, 0.20), 271 (83.66), 201 (100). HRMS Calcd. for $C_{32}H_{28}Cl_2ONa^+$ (Maldi): 521.1416, Found: 521.1409 ($M+Na^+$).

4.2.7. 1-Phenyl-1-(2-chlorophenyl)-but-3-en-1-ol (3e). A yellow liquid, IR (CH_2Cl_2): ν 3321, 3056, 3024, 2928, 2881, 1945, 1712, 1594, 1560, 1494, 1473, 1445, 1434 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.19 (dt, $J=6.6$, 7.2 Hz, 2H), 3.65 (t, $J=6.6$ Hz, 2H), 6.23 (t, $J=7.2$ Hz, 1H), 7.12–7.25 (m, 8H, Ar), 7.37–7.40 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 33.4, 62.1, 126.17, 126.24, 126.5, 126.8, 127.3, 128.3, 128.8, 129.7, 131.6, 133.7, 138.4, 140.0. MS (%) *m/z* 258 (M^+, 46.87), 227 (100). HRMS Calcd. for $C_{16}H_{15}ClONa^+$ (Maldi): 281.0733, Found: 281.0704 ($M+Na^+$).

4.2.8. Di[4,4-bis(4-chlorophenyl)-but-3-en-1-yl] ether (2f). A bright yellow liquid, IR (CH_2Cl_2): ν 3044, 2857, 2785, 1893, 1778, 1586, 1491, 1405 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.38 (dt, $J=6.6$, 7.5 Hz, 4H), 3.49 (t, $J=6.6$ Hz, 4H), 6.12 (t, $J=7.5$ Hz, 2H), 7.095 (d, $J=7.8$ Hz, 4H, Ar), 7.103 (d, $J=7.8$ Hz, 4H, Ar), 7.21 (d, $J=7.8$ Hz, 4H, Ar), 7.31 (d, $J=7.8$ Hz, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 30.4, 70.2, 127.2, 128.3, 128.4, 128.5, 131.2, 133.0, 133.1, 137.8, 140.6, 141.0. MS (%) *m/z* 566 (M^+, 0.20), 305 (41.37), 275 (10.83), 125 (100). HRMS Calcd. for $C_{32}H_{27}Cl_4O^+$ (Maldi): 567.0815, Found: 567.0811 ($M+H^+$).

4.2.9. Di[4,4-bis(4-fluorophenyl)-but-3-en-1-yl] ether (2g). A colorless liquid, IR (CH_2Cl_2): ν 3045, 2955, 2863, 2778, 2030, 1893, 1782, 1715, 1656, 1601, 1508, 1401, 1225 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.39 (dt, $J=6.0$, 6.9 Hz, 4H), 3.51 (t, $J=6.9$ Hz, 4H), 6.07 (t, $J=$ 6.0 Hz, 2H), 6.92 (d, $J=6.9$ Hz, 4H, Ar), 6.97 (d, $J=$ 6.9 Hz, 4H, Ar), 7.03 (d, $J=6.9$ Hz, 4H, Ar), 7.07–7.18 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 30.4, 70.3, 115.0 (d, $J_{C-F}=21.60$ Hz), 115.2 (d, $J_{C-F}=20.25$ Hz), 126.3, 127.4 (d, $J_{C-F}=7.28$ Hz), 128.7 (d, $J_{C-F}=7.58$ Hz), 131.4 (d, $J_{C-F}=7.28$ Hz), 135.6 (d, $J_{C-F}=3.68$ Hz), 138.6 (d, $J_{C-F}=3.08$ Hz), 141.2, 161.9 (d, $J_{C-F}=246.68$ Hz), 162.1 (d, $J_{C-F}=244.65$ Hz). MS (%) *m/z* 502 (M^+, 0.15), 273 (27.26), 242 (60.00), 109 (100). HRMS Calcd. for $C_{32}H_{26}F_4ONa^+$ (Maldi): 525.1805, Found: 525.1812 ($M+Na^+$).

4.2.10. Di[4,4-bis(fluorophenyl)-but-3-en-1-ol (3g). A yellow liquid, IR (CH_2Cl_2): ν 3341, 3045, 2928, 2881,

1893, 1719, 1602, 1508, 1409, 1225 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.31 (dt, $J=6.3$, 7.2 Hz, 2H), 3.66 (t, $J=6.3$ Hz, 2H), 5.98 (t, $J=7.2$ Hz, 1H), 6.85–7.13 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ 33.2, 62.5, 115.0 (d, $J_{C-F}=21.15$ Hz), 115.3 (d, $J_{C-F}=42.9$ Hz), 125.6, 128.8 (d, $J_{C-F}=7.88$ Hz), 131.4 (d, $J_{C-F}=8.03$ Hz), 135.4 (d, $J_{C-F}=3.75$ Hz), 142.2, 162.0 (d, $J_{C-F}=244.95$ Hz), 162.1 (d, $J_{C-F}=244.80$ Hz). MS (%) *m/z* 260 (M^+, 29.31), 229 (100). HRMS Calcd. for $C_{16}H_{14}F_2O$ (EI): 260.1013, Found: 260.0989.

4.3. The direct ring-opening of MCPs by toluene *p*-sulfonic acid (TsOH)

Under an argon atmosphere, MCPs **1** (0.50 mmol) and toluene *p*-sulfonic acid ($TsOH\cdot H_2O$) (0.55 mmol) were added into a Schlenk tube with 1,2-dichloroethane (DCE) (2.0 mL). After gentle heating to make TsOH soluble in DCE, the reaction mixture was stirred at room temperature. The solvent was removed under reduced pressure and then the residue was purified by a flash column chromatography.

4.3.1. Toluene-4-sulfonic acid 4,4-diphenyl-but-3-en-1-yl ester (4a). A white solid, Mp: 84–86 °C; IR (thin film): ν 3027, 1958, 1494, 1444, 1360, 1189, 1176, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.42–2.47 (m, 5H), 4.08 (t, $J=6.6$ Hz, 2H), 5.90 (t, $J=7.2$ Hz, 1H), 7.07–7.15 (m, 4H, Ar), 7.23–7.35 (m, 8H, Ar), 7.76 (d, $J=8.1$ Hz, 2H. Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.6, 29.4, 69.8, 122.7, 127.17, 127.23, 127.8, 128.1, 128.3, 129.6, 129.8, 133.0, 139.2, 141.8, 142.2, 144.7, 144.9; MS (%) *m/z* 377 (M^+-1, 0.84), 206 (100), 191 (25.36); Anal. Calcd. for $C_{23}H_{22}O_3S$ requires C, 72.99; H, 5.86; Found: C, 72.91; H, 5.86%.

4.3.2. Toluene-4-sulfonic acid 4,4-bis(4-methoxyphenyl) but-3-en-1-yl ester (4b). A colorless oil, IR (thin film): ν 2956, 2837, 1606, 1575, 1541, 1463, 1359, 1290, 1247, 1176, 1079, 1033 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.40–2.47 (m, 5H), 3.79 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 4.06 (t, $J=6.6$ Hz, 2H), 5.75 (t, $J=7.5$ Hz, 1H), 6.78 (d, $J=8.7$ Hz, 2H, Ar), 6.87 (d, $J=8.7$ Hz, 2H, Ar), 6.99 (d, $J=9.0$ Hz, 2H, Ar), 7.06 (d, $J=9.0$ Hz, 2H, Ar), 7.28 (d, $J=8.4$ Hz, 2H, Ar), 7.76 (d, $J=8.4$ Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.6, 29.4, 55.21, 55.25, 70.0, 113.4, 113.6, 120.6, 127.9, 128.4, 129.8, 130.7, 131.7, 133.0, 135.0, 144.0, 144.6, 158.7, 158.9; MS (%) *m/z* 438 (M^+, 14.83), 266 (100), 253 (49.35), 235 (92.98); HRMS Calcd. for $C_{25}H_{27}O_5S^+$ (Maldi): 439.1572, Found: 439.1574 ($M+H^+$).

4.3.3. Toluene-4-sulfonic acid 4-(4-methoxyphenyl)-4-phenylbut-3-en-1-yl ester (4c). A yellow oil, IR (thin film): ν 2957, 2837, 1606, 1510, 1360, 1291, 1248, 1176, 1097, 1033 cm^{-1}; (*Z*- or *E*-isomer) ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.39–2.48 (m, 5H), 3.78 (s, 3H, CH_3O), 4.06 (t, $J=6.9$ Hz, 2H), 5.81 (t, $J=6.9$ Hz, 1H), 6.78 (d, $J=8.7$ Hz, 2H, Ar), 6.99–7.15 (m, 4H, Ar), 7.23–7.36 (m, 5H, Ar), 7.75 (d, $J=8.1$ Hz, 2H, Ar); (*E*- or *Z*-isomer) ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.39–2.48 (m, 5H), 3.83 (s, 3H, CH_3O), 4.08 (t, $J=6.6$ Hz, 2H), 5.83 (t, $J=6.9$ Hz, 1H), 6.87 (d, $J=8.7$ Hz, 2H, Ar), 6.99–7.15 (m, 4H, Ar), 7.23–7.36 (m, 5H, Ar), 7.76 (d, $J=8.1$ Hz, 2H, Ar); (*Z*- or *E*-isomer) ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.5, 29.2, 55.0, 69.8, 113.3, 120.7, 127.0, 127.7, 128.1, 129.4, 130.6, 132.8, 139.4, 144.2, 144.6, 158.6. (*E*- or *Z*-isomer) ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.5, 29.3, 55.0, 69.9, 113.5, 122.4, 127.1, 127.9, 128.1, 129.7, 131.3, 134.4, 142.2, 144.4, 144.6, 158.8. MS (%) *m/z* 408 (M^+, 4.59), 236 (72.85), 91 (100); HRMS Calcd. for $C_{24}H_{25}O_4S^+$ (Maldi): 409.1488, Found: 409.1468 ($M+H^+$).

4.3.4. Toluene-4-sulfonic acid 4,4-di-p-tolyl-but-3-en-1-yl ester (4d). A white solid, Mp: 93–95 °C; IR (thin film): ν 2957, 2930, 1606, 1510, 1494, 1444, 1360, 1291, 1247, 1176, 1097, 1033 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.32 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.43 (td, $J=6.6$, 7.2 Hz, 2H), 4.06 (t, $J=6.6$ Hz, 2H), 5.82 (t, $J=7.2$ Hz, 1H), 6.96 (d, $J=8.1$ Hz, 2H, Ar), 7.01–7.07 (m, 4H, Ar), 7.14 (d, $J=7.5$ Hz, 2H, Ar), 7.28 (d, $J=8.1$ Hz, 2H, Ar), 7.76 (d, $J=8.1$ Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.0, 21.1, 21.5, 29.3, 69.9, 121.5, 127.0, 127.8, 128.7, 128.9, 129.4, 129.7, 130.1, 132.8, 136.3, 136.7, 136.9, 139.2, 144.6; MS (%) *m/z*: 406 (M^+, 1), 346 (3.72), 234 (38.64), 219 (50.67), 59 (100); Anal. Calcd. for $C_{25}H_{26}O_3S$ requires C, 73.86; H, 6.45; Found: C, 73.79; H, 6.46%.

4.3.5. Toluene-4-sulfonic acid 4-(2-chlorophenyl)-4-phenylbut-3-en-1-yl ester (4e). A white solid, Mp: 101–103 °C; IR (thin film): ν 2924, 1598, 1494, 1468, 1444, 1360, 1177, 1189, 1097, 1056, 1035 cm^{-1}; (*Z*-isomer) ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.27 (dt, $J=6.3$, 7.2 Hz, 2H), 2.38 (s, 3H, CH_3), 4.06 (t, $J=6.3$ Hz, 2H), 6.07 (t, $J=7.2$ Hz, 1H), 7.06–7.13 (m, 3H, Ar), 7.17–7.27 (m, 8H, Ar), 7.38–7.41 (m, 1H, Ar), 7.75 (d, $J=8.1$ Hz, 2H, ArH); (*Z*-isomer) ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.5, 29.3, 69.3, 123.9, 126.1, 126.8, 127.1, 127.3, 127.72, 128.1, 128.8, 129.7, 131.26, 132.7, 137.7, 139.5, 141.7, 144.7; (*E*-isomer) ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.61 (dt, $J=6.3$, 7.2 Hz, 2H), 2.38 (s, 3H, CH_3), 4.11 (t, $J=6.3$ Hz, 2H), 5.60 (t, $J=7.2$ Hz, 1H), 7.06–7.13 (m, 3H, Ar), 7.17–7.27 (m, 8H, Ar), 7.38–7.41 (m, 1H, Ar), 7.75 (d, $J=8.1$ Hz, 2H, Ar); (*E*-isomer) ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 22.1, 28.8, 69.5, 126.4, 126.7, 127.70, 127.9, 128.5, 129.0, 129.58, 129.61, 131.34, 132.9, 133.3, 138.4, 139.5, 141.8, 142.6. MS (%) *m/z* 240 (M^+–TsOH) (100), 205 (89.98); Anal. Calcd. for $C_{23}H_{21}ClO_3S$ requires C, 66.90; H, 5.13; Found: C, 66.80; H, 5.11%.

4.3.6. Toluene-4-sulfonic acid 4,4-bis-(4-chlorophenyl)-but-3-en-1-yl ester (4f). A white solid, Mp: 83–85 °C; IR (thin film): ν 2919, 2850, 1596, 1491, 1464, 1401, 1360, 1188, 1175, 1091, 1014 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.40–2.45 (m, 5H) 4.10 (t, $J=6.6$ Hz, 2H), 5.92 (t, $J=7.8$ Hz, 1H), 7.01–7.08 (m, 4H, Ar), 7.21–7.36 (m, 6H, Ar), 7.75 (d, $J=8.4$ Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.6, 29.4, 69.4, 124.0, 127.8, 128.3, 128.4, 128.7, 129.8, 130.9, 132.9, 133.37, 133.43, 137.2, 139.9, 142.7, 144.8; MS (%) *m/z* 274 (M^+–TsOH) (31.72), 239 (100); Anal. Calcd. for $C_{23}H_{20}Cl_2S$ requires C, 61.75; H, 4.51; Found: C, 61.60; H, 4.67%.

4.3.7. Toluene-4-sulfonic acid 4,4-bis-(4-fluorophenyl) but-3-en-1-yl ester (4g). A yellow oil, IR (thin film): ν 2926, 1601, 1508, 1361, 1223, 1189, 1177, 1096 cm^{-1}; ^1H

NMR ($CDCl_3$, TMS, 300 MHz): δ 2.38–2.45 (m, 5H), 4.08 (t, J=6.6 Hz, 2H), 5.85 (t, J=7.2 Hz, 1H), 6.94 (dd, J=9.0, J_{HF}=9.0 Hz, 2H, Ar), 7.03–7.11 (m, 6H, Ar), 7.29 (d, J=8.1 Hz, 2H, Ar), 7.76 (d, J=8.1 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.6, 29.3, 69.6, 115.0 (d, J_{C-F}=21.5 Hz), 115.4 (d, J_{C-F}=21.5 Hz), 123.1, 127.8, 128.8 (d, J_{C-F}=7.9 Hz), 129.8, 131.2, 133.0, 134.9 (d, J_{C-F}=36.9 Hz), 137.9 (d, J_{C-F}=36.9 Hz), 143.0, 144.8, 163.1 (d, J_{C-F}=245.8 Hz), 162.3 (d, J_{C-F}=245.8 Hz); MS (%) m/z 242 (M^+–TsOH) (100), 227 (19.43), 133 (30.78), 109 (59.91); HRMS Calcd. for $C_{23}H_{20}F_2O_3SNa^+$ (Maldi): 437.1008, Found: 437.0993 ($M+Na^+$).

4.3.8. Toluene-4-sulfonic acid 4-(4-ethoxyphenyl)pent-3-en-1-yl ester (4h). A colorless oil, IR (thin film): ν 2978, 2928, 1607, 1511, 1478, 1360, 1245, 1188, 1177, 1117, 1097 cm^{-1}; (Z- or E-isomer) ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.37–1.44 (m, 3H, CH_3), 1.95 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.44–2.60 (m, 2H), 3.98–4.11 (m, 4H), 5.45–5.53 (m, 1H), 6.80–6.86 (m, 2H, Ar), 7.20–7.31 (m, 4H, Ar), 7.66–7.82 (m, 2H, Ar); (E- or Z-isomer) ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.37–1.44 (m, 3H, CH_3), 1.50 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.44–2.60 (m, 2H), 3.98–4.11 (m, 4H), 5.45–5.53 (m, 1H), 6.80–6.86 (m, 2H, Ar), 7.20–7.31 (m, 4H, Ar), 7.66–7.82 (m, 2H, Ar); (Z- or E-isomer) ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.6, 28.4, 63.25, 63.33, 69.7, 113.8, 114.0, 125.7, 127.7, 127.8, 129.69, 129.74, 135.3, 144.6, 157.3. (E- or Z-isomer) ^{13}C NMR ($CDCl_3$, TMS, 75 MHz): δ 21.6, 29.6, 63.3, 67.4, 70.1, 114.0, 119.3, 126.5, 127.8, 128.7, 129.7, 132.9, 137.6, 144.6, 158.0. MS (%) m/z 360 (M^+, 12.45), 188 (72.15), 173 (100); HRMS Calcd. for $C_{20}H_{26}O_4S^+$ (Maldi): 361.1504, Found: 361.1468 ($M+H^+$).

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Supplementary data

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References and notes

1. Binger, P.; Schuchardt, U. *Chem. Ber.* **1981**, *114*, 3313–3324.
2. For the synthesis of MCPs (a) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589–635. (b) *Carbocyclic Three-membered Ring Compounds*; de Meijere, A., Ed.; Houben-Weyl; Thieme: Stuttgart, 1996; Vol. E17a-c.
3. For recent reviews, please see: (a) Nakamura, I.; Yamamoto, Y. *Adv. Synth. Catal.* **2002**, *344*, 111–129. (b) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, *103*, 1213–1269.
4. For some more recent related papers, please see: (a) de Meijere, A.; Leonov, A.; Heiner, T.; Noltemeyer, M.; Bes, M. T. *Eur. J. Org. Chem.* **2003**, 472–478. (b) Belov, V. N.; Savchenko, A. I.; Sokolov, V. V.; Straub, A.; de Meijere, A. *Eur. J. Org. Chem.* **2003**, 551–561. (c) de Meijere, A.; Kuchuk, I. D.; Sokolov, V. V.; Labahn, T.; Rauch, K.; Es-Sayed, M.; Krämer, T. *Eur. J. Org. Chem.* **2003**, 985–997. (d) Huang, X.; Zhou, H.-W.; Chen, W.-L. *J. Org. Chem.* **2004**, *69*, 839–842. (e) Zhou, H.-W.; Huang, X.; Chen, W.-L. *Synlett* **2003**, 2080–2082. (f) Huang, Z.; Zhou, H.-W. *Org. Lett.* **2002**, *4*, 4419–4422. (g) Zhou, H-W. ; Huang, X.; Chen, W.-L. *J. Org. Chem.* **2004**, *69*, 5471–5472. (h) Huang, X.; Chen, W.-L.; Zhou, H.-W. *Synlett* **2004**, 329–331. (i) Siriwardana, A. I.; Nakamura, I.; Yamamoto, Y. *J. Org. Chem.* **2004**, *69*, 3202–3204. (j) Oh, B. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Heterocycles* **2003**, *61*, 247–257.
5. For some related Lewis acid or Brønsted acid-mediated reactions of MCPs, please see: (a) Peron, G. L. N.; Kitteringham, J.; Kilburn, J. D. *Tetrahedron Lett.* **1999**, *40*, 3045–3048. (b) Miura, K.; Takasumi, M.; Hondo, T.; Saito, H.; Hosomi, A. *Tetrahedron Lett.* **1997**, *38*, 4587–4590. (c) Peron, G. L. N.; Kitteringham, J.; Kilburn, J. D. *Tetrahedron Lett.* **2000**, *41*, 1615–1618. (d) Patient, L.; Berry, M. B.; Kilburn, J. D. *Tetrahedron Lett.* **2003**, *44*, 1015–1017. (e) Peron, G.; Norton, D.; Kitteringham, J.; Kilburn, J. D. *Tetrahedron Lett.* **2001**, *42*, 347–349. (f) Nakamura, I.; Kamada, M.; Yamamoto, Y. *Tetrahedron Lett.* **2004**, *45*, 2903–2906. (g) Patient, L.; Berry, M. B.; Coles, S. J.; Hursthouse, M. B.; Kilburn, J. D. *Chem. Commun.* **2003**, 2552–2553.
6. For some of the Lewis acid or Brønsted acid-mediated transformations of MCPs in our laboratory, please see: (a) Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145–2148. (b) Huang, J.-W.; Shi, M. *Tetrahedron* **2004**, *60*, 2057–2062. (c) Shao, L.-X.; Shi, M. *Eur. J. Org. Chem.* **2004**, 426–430. (d) Chen, Y.; Shi, M. *J. Org. Chem.* **2004**, *69*, 426–431. (e) Shao, L.-X.; Shi, M. *Adv. Synth. Catal.* **2003**, *345*, 963–966. (f) Shi, M.; Chen, Y. *J. Fluoro. Chem.* **2003**, *122*, 219–227. (g) Huang, J.-W.; Shi, M. *Tetrahedron Lett.* **2003**, *44*, 9343–9347. (h) Shi, M.; Chen, Y.; Xu, B.; Tang, J. *Green Chem.* **2003**, *5*, 85–88. (i) Shi, M.; Xu, B. *Tetrahedron Lett.* **2003**, *44*, 3839–3842. (j) Xu, B.; Shi, M. *Org. Lett.* **2003**, *5*, 1415–1418. (k) Shi, M.; Shao, L.-X.; Xu, B. *Org. Lett.* **2003**, *5*, 579–582. (l) Shi, M.; Chen, Y.; Xu, B.; Tang, J. *Tetrahedron Lett.* **2002**, *43*, 8019–8024. (m) Shi, M.; Xu, B.; Huang, J.-W. *Org. Lett.* **2004**, *6*, 1175–1178.
7. Siriwardana, A. I.; Nakamura, I.; Yamamoto, Y. *Tetrahedron Lett.* **2003**, *44*, 4547–4550.
8. Ritter-type reaction product was obtained as a byproduct if the reaction was carried out in CH_3CN (a) Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045–4048. (b) Ritter, J. J.; Kalish, J. *J. Am. Chem. Soc.* **1948**, *70*, 4048–4050. (c) Reddy, K. L. *Tetrahedron Lett.* **2003**, *44*, 1453–1455. (d) Krimen, L. I.; Cota, D. J. *Org. React.* **1969**, *17*, 213–325. (e) Nair, V.; Rajan, R.; Rath, N. P. *Org. Lett.* **2002**, *4*, 1575–1577.
9. The rearrangement of cyclopropylmethyl cation has already been studied extensively. It is reasonable that the substituents on the double further stabilize the cation. Please seeCarey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 5th ed.; Plenum: New York, 1998; pp 221 and 419.

10. Matrix-assisted laser desorption/ionization (MALDI) is a more soft and sensitive ionization technique than others. Among the chemical and physical ionization pathways suggested for MALDI are gas-phase photoionization, ion-molecule reactions, etc. The most widely accepted ion formation mechanism involves gas-phase proton transfer or alkali metal transfer in the expanding plume with photoionized matrix molecules. The matrix will serve to minimize sample damage from the laser pulse and inhibit the appearance of molecular ionsde Hoffmann, E.; Stroobant, V. *Mass Spectrometry: Principles and Applications*, 2nd ed.; Wiley: Chichester, 2001; pp 28–32.