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Ring-opening reaction of methylenecyclopropanes with LiCl, LiBr or NaI in acetic acid

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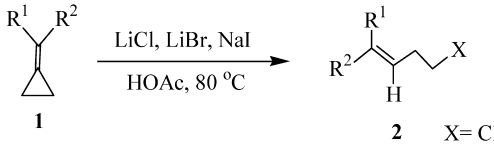
Abstract—The methylenecyclopropanes **1** react with LiCl, LiBr or NaI at 80 °C to give the corresponding *gem*-disubstituted homoallylic halides **2** in good to excellent yields in acetic acid. In some cases, the ring-opening reaction can be completed within 5 min to give the corresponding *gem*-disubstituted homoallylic halides in high yields.

1. Introduction

Methylenecyclopropanes (MCPs) **1** are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis.[1] Strain in organic molecules often correlates with increased reactivity because the relief of ring strain provides a potent thermodynamic driving force.[2] Recently, Yamamoto reported that the reaction of alkylidenecyclopropanes with HCl or with HBr proceeds very smoothly at 120 °C to produce the corresponding *gem*-disubstituted homoallylic chlorides and bromides in good to excellent yields.[3] However, the reactions were carried out in a well sealed, pressured vial with 4 M hydrogen chloride in 1,4-dioxane or 1 M hydrogen bromide in acetic acid. Obviously, the severe reaction conditions limited its use in organic synthesis. In addition, the preparation of *gem*-disubstituted homoallylic iodides has not been mentioned.

In this paper, we wish to describe a more convenient and useful synthetic method for the preparation of *gem*-disubstituted homoallylic halides including *gem*-disubstituted homoallylic iodides in good yields from the ring-opening reaction of MCPs with LiCl, LiBr, NaI (alkali metal halides) in acetic acid under milder conditions (Scheme 1).



1 **2** X= Cl, Br, I

Scheme 1. The ring-opening reaction of MCPs **1** with LiCl, LiBr, NaI in acetic acid.

2. Results and discussion

Using diphenylmethylenecyclopropane **1a** (0.5 mmol) as a substrate, we first attempted the hydrohalogenation of **1a** using sodium halides (0.75 mmol) in acetic acid (Table 1). We found that using NaCl or NaBr as a hydrohalogenating reagent in acetic acid at 80 °C,[4] only trace of the corresponding homoallylic chloride **2a** or bromide **2b** was formed (Table 1, entries 1 and 2). Using NaI as a hydrohalogenating reagent at 80 °C in acetic acid, the corresponding *gem*-disubstituted homoallylic iodide **2c** was produced in quantitative yield within 10 min, although no reaction occurred at room temperature and only trace of **2c** was formed at 50 °C under the same conditions (Table 1, entries 3–5). This is simply because NaI has higher nucleophilicity than NaCl or NaBr and is soluble in acetic acid at 80 °C. On the other hand, using LiCl or $LiBr{\cdot}H_2O$ as a nucleophile instead of NaCl and NaBr, the ring-opening reaction of **1a** takes place smoothly to give the corresponding *gem*-disubstituted homoallylic chloride **2a** and bromide **2c** in excellent yields within 20 and 60 min, respectively, under identical conditions (Table 1, entries 9 and 10). The other nucleophiles such as NaN_3, KF and NaOAc showed no reactivities to this ring-opening reaction under the same conditions (Table 1, entries 6–8).

Keywords: Methylenecyclopropanes; LiCl; LiBr; NaI; *gem*-Disubstituted homoallylic halides; Ring-opening reaction; Acetic acid.
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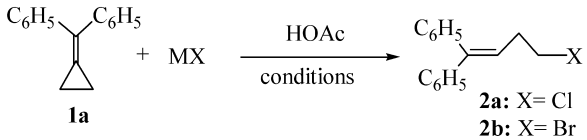
Table 1. The reaction of MCP **1a** with metal halides in acetic acid



1a

2a: X= Cl
2b: X= Br
2c: X= I

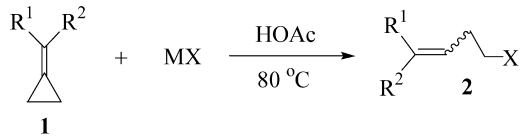
Entry	MX	Temperature (°C)	Time	Yield[a]
1	NaCl	80	48 h	**2a**, trace
2	NaBr	80	48 h	**2b**, trace
3	NaI	15	48 h	**2c**, NR
4	NaI	50	48 h	**2c**, trace
5	NaI	80	10 min	**2c**, 100
6	NaN_3	80	48 h	Trace
7	KF	80	48 h	Trace
8	NaOAc	80	48 h	Trace
9	LiCl	80	60 min	**2a**, 96
10	LiBr·H_2O	80	20 min	**2b**, 98

[a] Isolated yield.

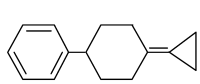
Using various MCPs **1** (0.5 mmol) as the substrates, we carried out the ring-opening reaction of **1** with LiCl, LiBr·H_2O and NaI (0.75 mmol) under the optimized conditions. The results were summarized in Table 2. As shown in Table 2, homoallylic halides **2** were obtained in good to excellent yields (Table 2, entries 1–15). The substituents on the benzene ring significantly affected the reaction. For MCP **1b** having a strongly electron-donating group on the benzene ring, the ring-opening reaction of MCP **1b** could be completed within 5 min in the presence of either LiCl, LiBr or NaI to give the corresponding halides in excellent yields (Table 2, entries 1–3). The electron-withdrawing groups such as F- or Cl- on the benzene ring slowed down the reaction rates. Thus, a prolonged reaction time (1–5 h) was required to complete the reaction for MCPs **1d** and **1e** (Table 2, entries 7–12). For unsymmetric MCP **1f** (R^1=*p*-$MeOC_6H_4$, R^2=C_6H_5), the *gem*-disubstituted homoallylic halides **2p** was obtained as a mixture of *Z*/*E*-isomer (Table 2, entry 13). For aliphatic MCPs **1f-i**, the corresponding homoallylic halides could be obtained under the same conditions for a prolonged reaction time (12 h) in high yields as well (Table 2, entries 14–20). In the case of aliphatic MCP **1g**, the corresponding homoallylic halides were obtained as a mixture of α,β-isomers (Scheme 2).

In conclusion, we disclosed in this paper a more efficient transformation of MCPs **1** to the corresponding *gem*-disubstituted homoallylic chlorides, bromides, and iodides under milder conditions using LiCl, LiBr, and NaI as hydrohalogenating reagents.[5] The reaction was carried out under ambient atmosphere. Inert atmosphere and high pressure reaction vessel are not required. In some cases, the ring-opening reaction can be completed within 5 min to give the corresponding *gem*-disubstituted homoallylic halides in high yields. The rearrangement of cyclopropyl carbinyl cation to a homoallylic cation induced by acetic acid is likely the key step of this ring-opening reaction.[6] The experiments are underway to elucidate the mechanistic details, expand the scope and define the limitations of this reaction.

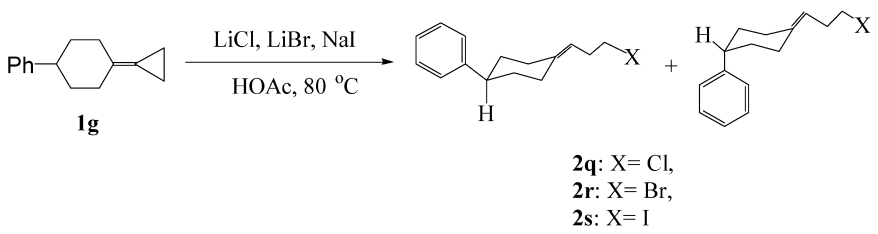
Table 2. The reactions of various MCPs **1** with alkali metal halides in acetic acid



1 **2**

Entry	R^1/R^2	N	MX	Time	Yield[a]
1	*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$	**1b**	LiCl	<5 min	**2d**, 99
2	*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$	**1b**	LiBr·H_2O	<5 min	**2e**, 100
3	*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$	**1b**	NaI	<5 min	**2f**, 100
4	*p*-MeC_6H_4/*p*-MeC_6H_4	**1c**	LiCl	20 min	**2g**, 98
5	*p*-MeC_6H_4/*p*-MeC_6H_4	**1c**	LiBr·H_2O	20 min	**2h**, 96
6	*p*-MeC_6H_4/*p*-MeC_6H_4	**1c**	NaI	10 min	**2i**, 96
7	*p*-FC_6H_4/*p*-FC_6H_4	**1d**	LiCl	5 h	**2j**, 97
8	*p*-FC_6H_4/*p*-FC_6H_4	**1d**	LiBr·H_2O	5 h	**2k**, 92
9	*p*-FC_6H_4/*p*-FC_6H_4	**1d**	NaI	1 h	**2l**, 95
10	*p*-ClC_6H_4/*p*-ClC_6H_4	**1e**	LiCl	4 h	**2m**, 91
11	*p*-ClC_6H_4/*p*-ClC_6H_4	**1e**	LiBr·H_2O	3 h	**2n**, 94
12	*p*-ClC_6H_4/*p*-ClC_6H_4	**1e**	NaI	1 h	**2o**, 98
13	*p*-$MeOC_6H_4$/C_6H_5	**1f**	LiBr·H_2O	20 min	**2p**, 100 (2.0:1)[b]
14		**1g**	LiCl	12 h	**2q**, 100 (1:0.9)[c]
15		**1g**	LiBr·H_2O	12 h	**2r**, 94 (1.47:1)[c]
16			NaI	12 h	**2s**, 89 (4:1)[c]
17	*n*-C_7H_{15}/CH_3	**1h**	LiBr·H_2O	12 h	**2t**, 90 (1.7:1)[b]
18	*n*-C_4H_9/*n*-C_4H_9	**1i**	LiCl	12 h	**2u**, 89
19	*n*-C_4H_9/*n*-C_4H_9	**1i**	LiBr·H_2O	12 h	**2v**, 80
20	*n*-C_4H_9/*n*-C_4H_9	**1i**	NaI	12 h	**2w**, 73

[a] Isolated yield.
[b] *Z*/*E*-mixture.
[c] α/β-mixture.



1g

2q: X= Cl,
2r: X= Br,
2s: X= I

Scheme 2. The ring-opening reaction of aliphatic MCP **1g** with LiCl, LiBr, NaI in acetic acid.

3. Experimental

3.1. General methods

Melting points are uncorrected. ^{1}H NMRs and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Commercial reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel. The starting materials (MCPs) **1** were prepared according to the literature.[7]

3.2. General procedure for the reactions of MCPs with alkali metal chlorides, bromides or iodides

MCPs **1** (0.5 mmol) was dissolved in 1.0 mL of acetic acid and then a metal iodide, chloride or bromide (0.75 mmol) was added into the solution. The reaction mixture was heated to 80 °C and was stirred for 5–300 min. The reaction was monitored by TLC plate. After the reaction was completed, it was quenched by the addition of water, the organic compounds were extracted with petroleum ether. The organic layer was washed with saturated aqueous Na_2CO_3, brine, and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography eluenting with hexane/ethyl acetate (5:1) to afford the product **2**.

3.2.1. 4,4-Diphenyl-1-chloro-but-3-ene (2a). This compound was obtained as a colorless oil in 96% yield. IR (neat): ν 3079, 3024, 2956, 1598, 1494, 1444, 1296, 1029 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.56 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.55 (t, J=7.2 Hz, 2H, CH_2), 6.12 (t, J=7.2 Hz, 1H, C=CH), 7.23–7.47 (m, 10H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 32.96, 44.42, 124.83, 127.30, 127.33, 127.35, 128.21, 128.39, 129.77, 139.65, 142.15, 144.44; MS (EI) *m/z*: 242 (M^+) (41), 193 (100), 180 (95), 165 (70), 115 (90), 104 (68), 91 (49); HRMS (EI) Calcd for $C_{16}H_{15}Cl$: 242.0862. Found: 242.0829.

3.2.2. 4,4-Diphenyl-1-bromo-but-3-ene (2b). This compound was obtained as a colorless oil in 98% yield. IR (neat): ν 3056, 3024, 1660, 1598, 1494, 1444, 1269 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.66 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.41 (t, J=7.2 Hz, 2H, CH_2), 6.08 (t, J=7.2 Hz, 1H, C=CH), 7.15–7.37 (m, 10H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 32.65, 32.84, 125.62, 125.65, 127.23, 127.26, 128.10, 128.27, 129.64, 139.52, 142.02, 144.19; MS (EI) *m/z*: 286 (M^+) (31), 207 (10), 193 (56), 189 (10), 182 (16), 178 (34), 165 (27), 129 (100); HRMS (EI) Calcd for $C_{16}H_{15}Br$: 286.0357. Found: 285.9449.

3.2.3. 4,4-Diphenyl-1-iodo-but-3-ene (2c). This compound was obtained as a colorless oil in 100% yield. IR (neat): ν 3055, 3022, 1598, 1494, 1443, 1239, 759 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.67 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.16 (t, J=7.2 Hz, 2H, CH_2), 6.01 (t, J=7.2 Hz, 1H, C=CH), 7.15–7.36 (m, 10H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 5.62, 33.29, 127.22, 127.24, 127.64, 128.11, 129.26, 129.63, 139.54, 142.05, 143.72; MS (EI) *m/z*: 334 (M^+) (20), 207 (75), 191 (16), 178 (23), 129 (100); HRMS (EI) Calcd for $C_{16}H_{15}I$: 334.0218. Found: 334.0194.

3.2.4. 4,4-Bis(4-methoxyphenyl)-1-chloro-but-3-ene (2d). This compound was obtained as a colorless oil in 99% yield. IR (neat): ν 3000, 2956, 1605, 1510, 1287, 1031 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.55 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.53 (t, J=7.2 Hz, 2H, CH_2), 3.75 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.94 (t, J=7.2 Hz, 1H, C=CH), 6.77–7.16 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 33.24, 44.80, 55.50, 55.71, 113.74, 113.94, 123.02, 128.73, 131.12, 132.52, 135.46, 143.69, 158.96, 159.24; MS (EI) *m/z*: 302 (M^+) (44), 267 (6), 253 (100), 242 (31), 211 (15), 145 (42), 135 (82); HRMS (EI) Calcd for $C_{18}H_{19}ClO_2$: 302.1074. Found: 302.1118.

3.2.5. 1-[4-Bromo-1-(4-methoxyphenyl)but-1-enyl]-4-methoxybenzene (2e). This compound was obtained as a colorless oil in 100% yield. IR (neat): ν 2920, 2850, 1605, 1509, 1460, 1244, 1172, 1107, 1033 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.68 (td, J=6.6, 7.2 Hz, 2H, CH_2), 3.42 (t, J=7.2 Hz, 2H, CH_2), 3.78 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.94 (t, J=6.9 Hz, 1H, C=CH), 6.81 (d, J=8.7 Hz, 2H, ArH), 6.88 (d, J=8.7 Hz, 2H, ArH), 7.09 (d, J=8.7 Hz, 2H, ArH), 7.16 (d, J=8.7 Hz, 2H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 32.90, 33.00, 55.23, 55.27, 113.46, 113.66, 123.67, 128.46, 130.81, 132.07, 135.16, 143.30, 158.76, 158.98; MS (EI) *m/z*: 346 (M^+) (40), 267 (18), 253 (86), 242 (43), 211 (20), 159 (35), 145 (38), 135 (100), 121 (41); HRMS (EI) Calcd for $C_{18}H_{19}BrO_2$: 346.0568. Found: 346.0578.

3.2.6. 4,4-Bis(4-methoxyphenyl)-1-iodo-but-3-ene (2f). This compound was obtained as a colorless oil in 100% yield. IR (neat): ν 2954, 2834, 1606, 1511, 1246, 833 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.67 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.18 (t, J=7.2 Hz, 2H, CH_2), 3.79 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.88 (t, J=7.2 Hz, 1H, C=CH), 6.79–7.18 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 5.86, 33.33, 55.08, 55.12, 113.31, 113.46, 125.58, 128.33, 130.68, 131.94, 135.05, 142.66, 158.52,

158.79; MS (EI) *m/z*: 394 (M^+) (8), 267 (28), 227 (9), 205 (13), 159 (19), 121 (23), 84 (100); HRMS (EI) Calcd for $C_{18}H_{19}IO_2$: 394.0430. Found: 394.0446.

3.2.7. 1-[4-Chloro-1-(4-methylphenyl)but-1-enyl]-4-methylbenzene (2g). This compound was obtained as a colorless oil in 98% yield. IR (neat): ν 3023, 2921, 1606, 1511, 1448, 1295, 1110, 1021 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.32 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.57 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.54 (t, J=7.2 Hz, 2H, CH_2), 6.03 (t, J=7.2 Hz, 1H, C=CH), 7.03–7.19 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 21.05, 21.21, 32.92, 44.43, 123.62, 127.17, 128.78, 128.94, 129.56, 136.72, 136.78, 136.97, 139.51, 144.12; MS (EI) *m/z*: 270 (M^+) (14), 221 (25), 210 (46), 119 (100), 91 (41); HRMS (EI) Calcd for $C_{18}H_{19}Cl$: 270.1175. Found: 270.1197.

3.2.8. 1-[4-Bromo-1-(4-methylphenyl)but-1-enyl]-4-methylbenzene (2h). This compound was obtained as a colorless oil in 96% yield. IR (neat): ν 3022, 2920, 1609, 1511, 1445, 1267, 1207, 1020 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.30 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.66 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.38 (t, J=7.2 Hz, 2H, CH_2), 6.00 (t, J=7.2 Hz, 1H, C=CH), 7.03–7.18 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 21.04, 21.21, 32.77, 32.93, 124.62, 127.15, 128.77, 128.93, 129.52, 136.66, 136.75, 136.95, 139.46, 143.96; MS (EI) *m/z*: 316 (M^+) (73), 221 (100), 205 (42), 143 (97), 129 (55), 105 (60); HRMS (EI) Calcd for $C_{18}H_{19}Br$: 314.0670. Found: 314.0653.

3.2.9. 1-[4-Iodo-1-(4-methylphenyl)but-1-enyl]-4-methylbenzene (2i). This compound was obtained as a colorless oil in 96% yield. IR (neat): ν 3021, 2919, 1609, 1511, 1444, 1239, 1169, 1110, 1020 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.30 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.66 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.15 (t, J=7.2 Hz, 2H, CH_2), 5.94 (t, J=7.2 Hz, 1H, C=CH), 7.02–7.18 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 6.78, 21.06, 21.22, 33.39, 126.56, 127.16, 128.77, 128.90, 129.51, 136.71, 136.75, 136.93, 139.50, 143.48; MS (EI) *m/z*: 362 (M^+) (14), 235 (68), 219 (17), 205 (20), 143 (100), 128 (34), 105 (72); HRMS (EI) Calcd for $C_{18}H_{19}I$: 362.0531. Found: 362.0500.

3.2.10. 1-[4-Chloro-1-(4-fluorophenyl)but-1-enyl]-4-fluorobenzene (2j). This compound was obtained as a colorless oil in 97% yield. IR (neat): ν 2958, 2926, 1602, 1508, 1445, 1409, 1297, 1225, 1094, 1015 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.56 (td, J=6.8, 7.2 Hz, 2H, CH_2), 3.57 (t, J=6.8 Hz, 2H, CH_2), 6.04 (t, J=7.2 Hz, 1H, C=CH), 6.92–7.20 (m, 8H, ArH); ^{19}F NMR (282 MHz, TMS, $CDCl_3$): −115.47, −115.02; MS (EI) *m/z*: 278 (M^+) (55), 229 (100), 214 (20), 147 (14), 133 (41), 109 (30); HRMS (EI) Calcd for $C_{16}H_{13}ClF_2$: 278.0674. Found: 278.0664.

3.2.11. 1-[4-Bromo-1-(4-fluorophenyl)but-1-enyl]-4-fluorobenzene (2k). This compound was obtained as a colorless oil in 92% yield. IR (neat): ν 2968, 1602, 1508, 1225, 1158, 1094, 1015 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.67 (td, J=7.2, 7.3 Hz, 2H, CH_2), 3.43 (t, J=7.2 Hz, 2H, CH_2), 6.02 (t, J=7.3 Hz, 1H, C=CH), 6.93–7.20 (m, 8H, ArH); ^{19}F NMR (282 MHz, TMS, $CDCl_3$): −115.47, −115.02; MS (EI) *m/z*: 322 (M^+) (64), 229 (100), 214 (30), 147 (82), 133 (54), 109 (85); HRMS (EI) Calcd for $C_{16}H_{13}BrF_2$: 322.0169. Found: 322.0177.

3.2.12. 1-Fluoro-4-[1-(4-fluorophenyl)-4-iodobut-1-enyl]benzene (2l). This compound was obtained as a colorless oil in 95% yield. IR (neat): ν 3043, 2958, 1601, 1508, 1225, 1158, 1094, 1014 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.67 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.19 (t, J=7.2 Hz, 2H, CH_2), 5.95 (t, J=7.2 Hz, 1H, C=CH), 6.93–7.20 (m, 8H, ArH); ^{19}F NMR (282 MHz, TMS, $CDCl_3$): −115.47, −114.99; ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 5.46, 33.14, 114.89, 115.18, 115.23, 115.51, 127.92, 127.95, 128.78, 128.88, 131.20, 131.31, 135.20, 138.13, 138.85, 141.79, 160.39, 163.66, 163.86; MS (EI) *m/z*: 370 (M^+) (24), 243 (100), 227 (11), 214 (14), 201 (14), 147 (93), 109 (95); HRMS (EI) Calcd for $C_{16}H_{13}F_2I$: 370.0030. Found: 370.0036.

3.2.13. 4,4-Bis(4-chlorophenyl)-1-chloro-but-3-ene (2m). This compound was obtained as a colorless oil in 91% yield. IR (neat): ν 3030, 2956, 2925, 1592, 1492, 1401, 1091 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.57 (td, J=6.6, 6.6 Hz, 2H, CH_2), 3.58 (t, J=6.6 Hz, 2H, CH_2), 6.11 (t, J=6.6 Hz, 1H, C=CH), 7.09–7.38 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 33.03, 44.36, 126.20, 128.64, 128.77, 128.99, 131.31, 133.63, 133.71, 137.77, 140.41, 142.49; MS (EI) *m/z*: 310 (M^+), 275, 261, 226, 191, 163; HRMS (EI) Calcd for $C_{16}H_{13}Cl_3$: 310.0083. Found: 310.0047.

3.2.14. 4,4-Bis-(4-chlorophenyl)-1-bromo-but-3-ene (2n). This compound was obtained as a colorless oil in 95% yield. IR (neat): ν 3030, 2963, 1661, 1590, 1491, 1268, 1091 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.65 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.42 (t, J=6.6 Hz, 2H, CH_2), 6.06 (t, J=7.2 Hz, 1H, C=CH), 7.08–7.37 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 40.42, 41.67, 126.37, 128.26, 128.31, 128.46, 130.96, 131.26, 133.37, 137.39, 140.04, 141.97; MS (EI) *m/z*: 354 (M^+), 261, 250, 235, 226, 202, 191, 163; HRMS (EI) Calcd for $C_{16}H_{13}BrCl_2$: 353.9578. Found: 353.9569.

3.2.15. 4,4-Bis(4-chlorophenyl)-1-iodo-but-3-ene (2o). This compound was obtained as a colorless oil in 98% yield. IR (neat): ν 3030, 2957, 1591, 1491, 1400, 1091 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.65 (td, J=7.2, 7.2 Hz, 2H, CH_2), 3.17 (t, J=7.2 Hz, 2H, CH_2), 5.99 (t, J=7.2 Hz, 1H, C=CH), 7.07–7.36 (m, 8H, ArH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 5.20, 33.08, 128.35, 128.49, 128.57, 128.66, 128.75, 130.97, 133.31, 137.46, 140.12, 141.57; MS (EI) *m/z*: 402 (M^+), 275, 250, 204, 163; HRMS (EI) Calcd for $C_{16}H_{13}Cl_2I$: 401.9439. Found: 401.9482.

3.2.16. 1-(4-Bromo-1-phenyl-but-1-enyl)-4-methoxybenzene (2p). This compound was obtained as a colorless oil (*Z*/*E*-mixture, 2:1) in 100% yield. IR (neat): ν 3028, 2958, 2835, 1606, 1575, 1510, 1493, 1443, 1247, 1179, 1034 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): for *Z*- or *E*-**2p**: δ 2.60–2.75 (m, 2H, CH_2), 3.38–3.43 (m, 2H, CH_2), 3.78 (s, 3H, OCH_3), 5.99 (t, J=7.2 Hz, 1H), 6.78–7.38 (m,

9H, ArH); for *E*- or *Z*-**2p**: δ 2.60–2.75 (m, 2H, CH_2), 3.38–3.43 (m, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.02 (t, *J*=7.2 Hz, 1H), 6.78–7.38 (m, 9H, ArH); MS (EI) *m/z*: 316 (M^+) (77), 277 (3), 237 (15), 223 (100), 208 (10), 191 (10), 178 (17), 165 (19), 129 (42), 121 (24), 115 (37), 91 (28); HRMS (EI) Calcd for $C_{17}H_{17}BrO$: 316.0463. Found: 316.0454.

3.2.17. [4-(3-Chloropropylidene)cyclohexyl]benzene (2q). This compound was obtained as a colorless oil (α/β-mixture, 1:0.9) in 100% yield. IR (neat): ν 3027, 2925, 1603, 1493, 1452, 1292, 1242 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): ^1H NMR (300 MHz, TMS, $CDCl_3$): for α- or β-isomer: δ 1.40–2.40 (m, 9H, CH_2), 2.47–2.56 (m, 1H, CH_2), 2.64–2.75 (m, 1H, CH_2), 3.47–3.58 (m, 2H, CH_2), 5.18 (t, *J*=6.9 Hz, 1H, C═CH), 7.15–7.36 (m, 5H, ArH); for β- or α-isomer: δ 1.40–2.40 (m, 9H, CH_2), 2.47–2.56 (m, 1H, CH_2), 2.64–2.75 (m, 1H, CH_2), 3.47–3.58 (m, 2H, CH_2), 5.54 (t, *J*=6.9 Hz, 1H, C═CH), 7.15–7.36 (m, 5H, ArH); MS (EI) *m/z*: 234 (M^+) (34), 157 (10), 143 (10), 104 (100), 91 (20); HRMS (EI) Calcd for $C_{15}H_{19}Cl$: 234.1175. Found: 234.1168.

3.2.18. [4-(3-Bromopropylidene)cyclohexyl]benzene (2r). This compound was obtained as a colorless oil (α/β-mixture, 1.47:1) in 94% yield. IR (neat): ν 3026, 2925, 1602, 1493, 1452, 1268, 1245, 1206, 1031 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): for α- or β-isomer: δ 1.40–2.40 (m, 9H, CH_2), 2.57–2.71 (m, 2H, CH_2), 3.35–3.44 (m, 2H, CH_2), 5.16 (t, *J*=7.2 Hz, 1H, C═CH), 7.18–7.31 (m, 5H, ArH); for β- or α-isomer: δ 1.40–2.40 (m, 9H, CH_2), 2.57–2.71 (m, 2H, CH_2), 3.35–3.44 (m, 2H, CH_2), 5.54 (d, *J*=4.2 Hz, 1H, C═CH), 7.18–7.31 (m, 5H, ArH); MS (EI) *m/z*: 278 (M^+) (4), 199 (5), 157 (10), 143 (11), 129 (16), 115 (21), 104 (100), 91 (52); HRMS (EI) Calcd for $C_{15}H_{19}Br$: 278.0670. Found: 278.0673.

3.2.19. [4-(3-Iodopropylidene)cyclohexyl]benzene (2s). This compound was obtained as a colorless oil (α/β-mixture, 4:1) in 90% yield. IR (neat): ν 3025, 2924, 1602, 1493, 1451, 1227, 1166 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): for α- or β-isomer: δ 1.42–1.60 (m, 2H, CH_2), 1.80–2.40 (m, 5H, CH_2), 2.58–2.80 (m, 4H, CH_2), 3.05–3.11 (m, 2H, CH_2), 5.13 (t, *J*=7.5 Hz, 1H, C═CH), 7.07–7.18 (m, 5H, ArH); for β- or α-isomer: δ 1.42–1.60 (m, 2H, CH_2), 1.80–2.40 (m, 5H, CH_2), 2.58–2.80 (m, 4H, CH_2), 3.05–3.11 (m, 2H, CH_2), 5.55 (d, *J*=4.2 Hz, 1H, C═CH), 7.07–7.18 (m, 5H, ArH); MS (EI) *m/z*: 326 (M^+) (23), 222 (6), 199 (100), 157 (34), 143 (20), 129 (23), 117 (50), 104 90), 95 (52), 91 (100); HRMS (EI) Calcd for $C_{15}H_{19}I$: 326.0531. Found: 326.0521.

3.2.20. 1-Bromo-4-methyl-undec-3-ene (2t). This compound was obtained as a colorless oil (*Z*/*E*-mixture, 1.7:1) in 90% yield. IR (neat): ν 2957, 2855, 1456, 1378, 1268, 723 cm^{-1}; *Z*- or *E*-**2t**: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.86 (t, *J*=7.2 Hz, 3H, CH_3), 1.26–1.40 (m, 10H, CH_2), 1.61 (s, 3H, CH_3), 1.80–1.96 (m, 2H, CH_2), 2.10–2.20 (m, 2H, CH_2), 3.38 (t, *J*=7.8 Hz, 2H, CH_2), 5.18 (tt, *J*=7.2, 1.0 Hz, 1H, C═CH); *E*- or *Z*-**2t**: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.87 (t, *J*=7.2 Hz, 3H, CH_3), 1.26–1.40 (m, 10H), 1.71 (s, 3H), 1.96–2.20 (m, 2H), 2.55–2.60 (m, 2H), 3.34 (t, *J*=7.8 Hz, 2H), 5.12 (tq, *J*=7.2, 1.0 Hz); MS (EI) *m/z*: 246 (M^+) (25), 162 (51), 125 (16), 95 (35), 83 (72), 55 (100); HRMS (EI) Calcd for $C_{12}H_{23}Br$: 246.0983. Found: 246.0960.

3.2.21. 5-(2-Chloroethylidene)nonane (2u). This compound was obtained as a colorless oil in 89% yield. IR (neat): ν 2957, 2928, 2859, 1465, 1378, 1293, 1138 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.85–0.93 (m, 6H, CH_3), 1.27–1.34 (m, 8H, CH_2), 1.97–2.03 (m, 4H, CH_2), 2.48 (dt, *J*=7.2, 7.2 Hz, 2H, CH_2), 3.48 (t, *J*=7.2 Hz, 2H, CH_2), 5.11 (t, *J*=7.2 Hz, CH, C═CH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 14.00, 14.03, 22.46, 22.85, 29.95, 30.30, 30.69, 31.33, 36.54, 44.57, 119.55, 143.31; MS (EI) *m/z*: 202 (M^+) (65), 160 (20), 145 (5), 118 (54), 97 (26), 81 (42), 69 (58), 55 (100); HRMS (EI) Calcd for $C_{12}H_{23}Cl$: 202.1488. Found: 202.1519.

3.2.22. 5-(2-Bromoethylidene)nonane (2v). This compound was obtained as a colorless oil in 80% yield. IR (neat): ν 2957, 2928, 2859, 1465, 1378, 1293, 1138 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.88–0.92 (m, 6H, CH_3), 1.30–1.41 (m, 8H, CH_2), 1.96–2.03 (m, 4H, CH_2), 2.57 (dt, *J*=7.2, 7.2 Hz, 2H, CH_2), 3.34 (t, *J*=7.2 Hz, 2H, CH_2), 5.10 (t, *J*=7.2 Hz, CH, C═CH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 13.99, 14.02, 22.45, 22.84, 29.95, 30.28, 30.68, 31.48, 32.93, 36.51, 120.57, 143.21; MS (EI) *m/z*: 246 (M^+) (7), 206 (8), 162 (6), 109 (9), 97 (21), 83 (69), 69 (67), 55 (100) HRMS (EI) Calcd for $C_{12}H_{23}Br$: 246.0983. Found: 246.1002.

3.2.23. 5-(2-Iodoethylidene)nonane (2w). This compound was obtained as a colorless oil in 73% yield. IR (neat): ν 2956, 2927, 2858, 1465, 1378, 1244, 1164 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.87–0.93 (m, 6H, CH_3), 1.28–1.35 (m, 8H, CH_2), 1.94–2.01 (m, 4H, CH_2), 2.58 (dt, *J*=7.5, 7.5 Hz, 2H, CH_2), 3.11 (t, *J*=7.5 Hz, 2H, CH_2), 5.06 (t, *J*=7.5 Hz, CH, C═CH); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 6.23, 14.01, 14.03, 22.45, 22.83, 29.97, 30.23, 30.65, 32.15, 36.18, 122.71, 142.74; MS (EI) *m/z*: 294 (M^+) (2), 210 (4), 167 (16), 111 (20), 97 (37), 83 (41), 69 (84), 55 (100); HRMS (EI) Calcd for $C_{11}H_{21}I$: 294.0844. Found: 294.0868.

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