Supporting Information

The ring-opening reaction of methylenecyclopropanes promoted by metal halides

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Experimental Procedures.

General Methods. Melting points are uncorrected. ^{1}H 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 used were dried by standard methods when necessary. Commercially obtained 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 at increased pressure. The starting materials **1** were prepared according to the literature.[1]

Ref. 1. Utimoto, K.; Tamura, M.; Sisido, K. *Tertrahedron* **1973**, *2*9, 1169.

1. General Procedure for the reactions of MCPs with metal chlorides or bromides.

Under argon atmosphere, MCPs **1** (0.5 mmol) was dissolved in 1.5 mL of anhydrous dichloromethane (DCM) and then metal chlorides or bromides (1.0 M solution in DCM) 0.75 mL (0.75 mmol) was added. The reaction mixture was stirred for 2~24 h at room temperature and the reaction was quenched with water. The organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and residue was purified by a silica gel column (hexane/ethyl acetate as an eluent) to afford the product **2** or **3**.

2. General Procedure for the reactions of MCPs 1 with $BF_3{\cdot}Et_2O$/n-$Bu_4N^+I^-$ system.

Under argon atmosphere, MCPs **1** (0.5 mmol) and n-$Bu_4N^+I^-$ (0.75 mmol) was dissolved in 1.5 mL of DCM and then $BF_3 \cdot Et_2O$ was added. The reaction mixture was stirred for 24 h at room temperature and the reaction was quenched with water. The organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a silica gel column (hexane/ethyl acetate as an eluent) to afford product **4**.

4,4-Diphenyl-1-chloro-but-3-ene (**2a**): **2a** was obtained as a colorless oil, yield 82%. IR (neat): ν 3079, 3024, 2956, 1598, 1494, 1444, 1296, 1029 cm^{-1}; ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.56 (td, J = 7.2, 7.2 Hz, 2H), 3.55 (t, J = 7.2 Hz, 2H), 6.12 (t, J = 7.2 Hz, 1H), 7.23-7.47 (m, 10H, Ar); ^{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^+), 193, 180, 165, 115, 104, 91; HRMS (EI) Calcd. for $C_{16}H_{15}Cl$: 242.0862, found: 242.0829.

4-Phenyl-4-(4-chloro-phenyl)-1-chloro-but-3-ene (**2b**): **2b** was obtained as a colorless oil (*E*/*Z*-mixture, *E*/*Z* = 1:1), yield 77%. IR (neat): ν 3055, 2950, 1598, 1489, 1444, 1092 cm^{-1}; *E*-**2b**: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.59 (td, J = 7.2, 7.2 Hz, 2H), 3.57 (t, J = 7.2 Hz, 2H), 6.09 (t, J = 7.2 Hz, 1H), 6.95-7.40 (m, 9H, Ar); *Z*-**2b**: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.55 (td, J = 7.2, 7.2 Hz, 2H), 3.55 (t, J = 7.2 Hz, 2H), 6.07 (t, J = 7.2 Hz, 1H), 6.95-7.40 (m, 9H, Ar); MS (EI) m/z: 276 (M^+), 227, 205, 192, 165, 149, 115; HRMS (EI) Calcd. for $C_{16}H_{14}Cl_2$: 276.0473, found: 276.0493.

4,4-Bis-(4-chloro-phenyl)-1-chloro-but-3-ene (**2c**): **2c** was obtained as a colorless oil, yield 84%. 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), 3.58 (t, J = 6.6 Hz, 2H), 6.11 (t, J = 6.6 Hz, 1H), 7.09-7.38 (m, 8H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$): 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.

4,4-Bis-(4-methoxy-phenyl)-1-chloro-but-3-ene (**2d**): **2d** was obtained as a colorless oil, yield 93%. 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), 3.53 (t, *J* = 7.2 Hz, 2H), 3.75 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.94 (t, *J* = 7.2 Hz, 1H), 6.77-7.16 (m, 8H, Ar); ^{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, 132.35, 132.52, 1325.46, 143.69, 158.96, 159.24; MS (EI) m/z: 302 (M^+), 267, 253, 242, 211, 145, 135; HRMS (EI) Calcd. for $C_{18}H_{19}ClO_2$: 302.1074, found: 302.1118.

1-Chloro-pentadec-3-ene (**2e**): **2e** was obtained as a colorless oil (*E*/*Z* mixture, *E*/*Z* = 3.4:1), yield 35%. IR (neat): ν 2924, 2853, 1465, 1377, 968 cm^{-1}; *E*-**2e**: ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 0.87 (t, *J* = 6.3 Hz, 3H, CH_3), 1.28-1.41 (m, 18H), 1.96-2.00 (m, 2H), 2.40-2.47 (m, 2H), 3.49 (dd, *J* = 7.2, 7.2 Hz, 2H), 5.38-5.42 (m, 1H), 5.49-5.52 (m, 1H); *Z*-**2e**: ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 0.87 (t, *J* = 6.3 Hz, 3H, CH_3), 1.28-1.41 (m, 18H), 1.96-2.00 (m, 2H), 2.47-2.51 (m, 2H), 3.49 (t, *J* = 7.2 Hz, 2H), 5.74-5.82 (m, 1H), 5.82-5.89 (m, 1H); MS (EI) m/z: 244 (M^+), 209, 159, 145; HRMS (EI) Calcd. for $C_{16}H_{29}Cl$: 244.1958, found: 244.1968.

1-Chloro-4-methyl-undec-3-ene (**2f**): **2f** was obtained as a colorless oil (*E*/*Z* mixture, *E*/*Z* = 3.4:1), yield 75%. IR (neat): ν 2956, 2926, 1457, 1377, 1292, 721 cm^{-1}; *E*-**2f**: ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 0.87 (t, *J* = 7.2 Hz, 3H, CH_3), 1.26-1.40 (m, 10H), 1.61 (s, 3H), 1.96-2.10 (m, 2H), 2.42-2.49 (m, 2H), 3.47 (t, *J* = 7.8 Hz, 2H), 5.11 (tt, *J* = 7.2, 1.2 Hz, 1H); *Z*-**2f**: ^{1}H 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), 1.90-1.96 (m, 2H), 2.05-2.20 (m, 2H), 3.57 (t, *J* = 7.8 Hz, 2H), 5.14 (tq, *J* = 7.2, 1.2 Hz); MS (EI) m/z: 202 (M^+), 202, 167, 125, 118, 95; HRMS (EI) Calcd. for $C_{12}H_{23}Cl$: 202.1488, found: 202.1462.

4,4-Diphenyl-1-bromo-but-3-ene (**3a**): **3a** was obtained as a colorless oil, yield 80%. 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), 3.41 (t, *J* = 7.2 Hz, 2H), 6.08 (t, *J* = 7.2 Hz, 1H), 7.15-7.37 (m, 10H, Ar); ^{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^+), 207, 193, 189, 182, 178; HRMS (EI) Calcd. for $C_{16}H_{15}Br$: 286.0357, found: 285.9449.

4-Phenyl-4-(4-chloro-phenyl)-1-bromo-but-3-ene (**3b**): **3b** was obtained as a colorless oil (*E*/*Z*-mixture, *E*/*Z* = 1:1), yield 89%. IR (neat): ν 3056, 2962, 1661, 1597, 1489, 1091, 1014 cm^{-1}. *E*-**3b**: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.65 (td, *J* = 7.2, 7.2 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 6.05 (t, *J* = 7.2 Hz, 1H), 7.10-7.38 (m, 9H, Ar); *Z*-**3b**: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.63 (td, *J* = 7.2, 7.2 Hz, 2H), 3.38 (t, *J* = 6.8 Hz, 2H), 6.03 (t, *J* = 7.2 Hz, 1H), 7.10-7.38 (m, 9H, Ar); MS (EI) m/z: 320 (M^+), 241, 227, 192, 178, 163, 149, 129; HRMS (EI) Calcd. for $C_{16}H_{14}Br_2$: 319.9967, found: 319.9984.

4,4-Bis-(4-chloro-phenyl)-1-bromo-but-3-ene (**3c**): **3c** was obtained as a colorless oil, yield 84%. 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), 3.42 (t, *J* = 6.6 Hz, 2H), 6.06 (t, *J* = 7.2 Hz, 1H), 7.08-7.37 (m, 8H, Ar); ^{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.

1-Bromo-4-methyl-undec-3-ene (**3f**): **3f** was obtained as a colorless oil (*E*/*Z* mixture, *E*/*Z* = 1.7:1), yield 45%. IR (neat): ν 2957, 2855, 1456, 1378, 1268, 723 cm^{-1}; *E*-**3f**: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 0.86 (t, *J* = 7.2 Hz, 3H, CH_3), 1.26-1.40 (m, 10H), 1.61 (s, 3H), 1.90-2.05 (m, 2H), 2.10-2.20 (m, 2H), 3.38 (t, *J* = 7.8 Hz, 2H), 5.18 (tt, *J* = 7.2, 1.0 Hz, 1H); *Z*-**3f**: ^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), 1.90-1.96 (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^+), 191, 177, 162, 125, 95, 83, 55; HRMS (EI) Calcd. for $C_{12}H_{23}Br$: 246.0983, found: 246.0960.

4,4-Diphenyl-1,3-diiodo-but-3-ene (**4**): **4** was obtained as a colorless oil. IR (neat): ν

3045, 2877, 1954, 1597, 1490, 1245 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 3.06 (t, J = 6.9 Hz, 2H), 3.37 (t, J = 6.9 Hz, 2H), 7.18-7.32 (m, 10H, Ar); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 6.24, 44.21, 106.58, 127.46, 127.48, 128.16, 128.17, 128.45, 128.46, 128.51, 139.88, 146.27, 150.57; MS (EI) m/z: 460 (M^+), 333, 254, 206, 178; HRMS (EI) Calcd. for $C_{16}H_{14}I_2$: 459.9185, found: 459.9189.

4,4-Diphenyl-1-iodo-but-3-ene (**5a**): **5a** was obtained as a colorless oil. yield 95%. 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), 3.16 (t, J = 7.2 Hz, 2H), 6.01 (t, J = 7.2 Hz, 1H), 7.15-7.36 (m, 10H, Ar); ^{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^+), 207, 191, 178, 129; HRMS (EI) Calcd. for $C_{16}H_{15}I$: 334.0218, found: 334.0194.

4-Phenyl-4-(4-chloro-phenyl)-1-iodo-but-3-ene (**5b**): **5b** was obtained as a colorless oil (*E*/*Z*-mixture, *E*/*Z* = 1:1), yield 100%. IR (neat): ν 3024, 2924, 1489, 1091, 702 cm^{-1}; *E*-**5b**: ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.65 (td, J = 7.2, 7.2 Hz, 2H), 3.19 (t, J = 7.2 Hz, 2H), 6.01 (t, J = 7.2 Hz, 1H), 7.09-7.35 (m, 9H, Ar); *Z*-**5b**: ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.63 (td, J = 7.2, 7.2 Hz, 2H), 3.16 (t, J = 7.2 Hz, 2H), 6.02 (t, J = 7.2 Hz, 1H), 7.09-7.35 (m, 9H, Ar); MS (EI) m/z: 368 (M^+), 256, 241, 216, 163; HRMS (EI) Calcd. for $C_{16}H_{14}ClI$: 367.9829, found: 367.9809.

4,4-Bis-(4-chloro-phenyl)-1-iodo-but-3-ene (**5c**): **5c** was obtained as a colorless oil, yield 98%. IR (neat): ν 3030, 2957, 1591, 1491, 1400, 1091 cm^{-1}; ^{1}H NMR (300 MHz, TMS, $CDCl_3$): δ 2.65 (td, J = 7.2, 7.2 Hz, 2H), 3.17 (t, J = 7.2 Hz, 2H), 5.99 (t, J = 7.2 Hz, 1H), 7.07-7.36 (m, 8H, Ar); ^{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.

4,4-Bis-(4-methoxy-phenyl)-1-iodo-but-3-ene (**5d**): **5d** was obtained as a colorless oil, yield 53%. 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), 3.18 (t, J = 7.2 Hz, 2H), 3.79 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 5.88 (t, J = 7.2 Hz, 1H), 6.79-7.18 (m, 8H, Ar); ^{13}C NMR (75 MHz, TMS, $CDCl_3$): δ 5.86, 33.33, 55.08, 55.12, 113.31, 113.46, 113.67, 125.58, 128.33, 128.38, 128.66, 130.68, 131.94, 135.05, 142.66, 158.52, 158.79; HRMS (EI) Calcd. for $C_{18}H_{19}IO_2$: 394.0430, found: 394.0446.

By-product in the reaction of MCP **1d** with $BF_3{\cdot}OEt_2/Bu_4N^+I^-$ was obtained as a colorless oil (*E*/*Z* mixture, *E*/*Z*= 1/1), yield 36%. IR (neat): ν 3385, 2955, 2834, 1607, 1510, 1245, 834 cm^{-1}; *E*-isomer: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.66 (td, J = 7.2, 7.2 Hz, 2H), 3.17 (t, J = 7.2 Hz, 2H), 3.79 (s, 3H, OCH_3), 5.35 (brs, 1H, OH), 5.86 (t, J = 7.2 Hz, 1H), 6.79-7.18 (m, 8H, Ar); *Z*-isomer: ^1H NMR (300 MHz, TMS, $CDCl_3$): δ 2.66 (td, J = 7.2, 7.2 Hz, 2H), 3.17 (t, J = 7.2 Hz, 2H), 3.84 (s, 3H, OCH_3), 5.39 (br.s., 1H, OH), 5.87 (t, J = 7.2 Hz, 1H), 6.79-7.18 (m, 8H, Ar); MS (EI) m/z: 380 (M^+), 253, 213, 181, 159, 84; HRMS (EI) Calcd. for $C_{17}H_{17}IO_2$: 380.0273, found: 380.0254.