Supporting Information

“Cation Pool” Method Based on C-C Bond Dissociation. Effective Generation of Monocations and Dications

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General Remarks. GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused silica capillary. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Varian Gemini 2000, MERCURYplus-400 or JEOL ECA-600 spectrometer with Me_4Si as an internal standard unless otherwise noted. Mass spectra were obtained on JEOL JMS SX-102A or GC mate mass spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F₂₅₄ plates (thickness 0.25 mm). Flash chromatography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel 60 N, spherical, neutral, 40-100 μm). All reactions were carried out under Ar atmosphere unless otherwise noted.

Voltammetry. Rotating-disk electrode voltammetry was carried out using BAS 100B and Nikko Keisoku RDE-1 rotating disk electrode with Nikko Keisoku SC-5 controller. Measurements were carried out in 0.1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ using a glassy carbon disk working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode with sweep rate of 10 mV/s at 1000 r.p.m.

Materials. Dichloromethane was washed with water, distilled from P_2O_5 , redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. *meso*-1,2-dimethoxy-1,2-diphenylethane (**1**), *d,l*-1,2-dimethoxy-1,2-diphenylethane (**4**), 1-methoxy-1,2-diphenylethane (**7**), (1,2-dimethoxy-ethyl)-benzene (**8**), (1-methoxy-2,2-dimethyl-propyl)-benzene (**9**) and 2,2'-bis-methoxymethyl-biphenyl (**15**) were prepared by the reaction of the corresponding alcohol, NaH, and methyl iodide in THF. *trans*-2,3-Diphenyl-1,4-dioxane (**17**) was prepared according to the literature.¹

Methoxyphenyltrimethylsilylmethane² (**6**). To a solution of benzyl methyl ether (**5**) (1.21 g, 9.93 mmol) in THF (15 mL) was added *n*-butyllithium (1.59 M solution in hexane, 7.50 mL, 11.9 mmol) at $-40\text{ }^\circ\text{C}$. The reaction mixture was stirred for 40 min at $-40\text{ }^\circ\text{C}$. Chlorotrimethylsilane (1.29 g, 11.9 mmol) was added at $-40\text{ }^\circ\text{C}$. After stirring at the same temperature for 1.5 h, the reaction mixture was poured into water. The mixture was extracted with ether and the organic phase was dried over Na_2SO_4 and concentrated by evaporation. The crude product was purified with flash chromatography (hexane/EtOAc 30/1) to obtain the title compound (0.925 mg, 48%): TLC R_f 0.62 (hexane/EtOAc 10/1); ^1H NMR (400 MHz, CDCl_3) δ -0.01 (s, 9H), 3.30 (s, 3H), 3.94 (s, 1H), 7.10-7.32 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.81, 59.2, 80.8, 125.5, 125.7, 127.9, 141.1; IR (neat) 1248, 1088, 870, 841 cm^{-1} ; LRMS (CI) m/z 195 (MH^+), 179 (M^+-CH_3), 163 (M^+-OCH_3); HRMS (CI) calcd for $\text{C}_{11}\text{H}_{19}\text{OSi}$ 195.1205, found 195.1205.

***trans*-9,10-Dimethoxy-9,10-dihydro-phenanthrene** (**10**). Phenanthrenequinone (4.11 g, 19.7 mmol) was added to the stirred suspension of sodium borohydride (7.60 g, 201 mmol) in ethanol (300 mL) and water (40 mL). The mixture was stirred at room temperature for 24 h. Then ice-water and 1 M *aq* HCl were added to the white suspension. The mixture was extracted with dichloromethane. The organic phase was washed with aqueous NaHCO_3 , and dried over MgSO_4 . After removal of the solvent, the crude product was recrystallized

from methanol to obtain *trans*-9,10-dihydro-phenanthrene-9,10-diol³ (2.94 g, 13.8 mmol, 70%). The reaction of *trans*-9,10-dihydro-phenanthrene-9,10-diol (2.17 g, 10.2 mmol), sodium hydride (55% dispersion in paraffin liquid, 1.10 g, 25.3 mmol) and methyl iodide (3.65 g, 25.7 mmol) in THF followed by recrystallization from ethyl acetate/hexane gave the title compound (1.87 g, 7.78 mmol, 76%): ¹H NMR (400 MHz, CDCl₃) δ 3.73 and 3.74 (s, 6H), 4.39 (s, 2H), 7.27-7.31 (m, 2H), 7.37-7.43 (m, 4H), 7.81 (d, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 57.3, 80.0, 124.0, 127.5, 129.1, 129.8, 132.9, 133.0; IR (neat) 1464, 1179, 1096, 745 cm⁻¹; LRMS (EI) *m/z* 240 (M⁺), 209 (M⁺-OCH₃); HRMS (EI) calcd for C₁₆H₁₆O₂ 240.1150, found 240.1150.

Generation and Reactions of Methoxyphenylcarbenium Ion Pool. Typical Procedure. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 2 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of benzyl ether (0.400 mmol) in 0.3 M Bu₄NBF₄/CH₂Cl₂ (8.0 mL). In the cathodic chamber were placed 0.3 M Bu₄NBF₄/CH₂Cl₂ (8.0 mL) and trifluoromethanesulfonic acid (150.1 mg, 1.00 mmol). The constant current electrolysis (10 mA) was carried out at -78 °C with magnetic stirring until 2.5 F/mol of electricity was consumed. To the “cation pool” thus generated in the anodic chamber was added carbon nucleophile (1.00 mmol). Then the reaction mixture was stirred for 20 min and quenched by Et₃N. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column of silica gel to remove Bu₄NBF₄. The silica gel was washed with ether (200 mL). The combined filtrate was concentrated in *vacuo* and purified using flash chromatography to give corresponding product.

NMR Analysis of Methoxyphenylcarbenium Ion 2. ¹H and ¹³C NMR spectra were recorded in CD₂Cl₂ on a JEOL ECA-600 spectrometer. Chemical shifts are reported using methylene signals at δ 5.32 (¹H NMR) and δ 53.80 (¹³C NMR) as standards. The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber were placed a solution of **1** (48.4 mg, 0.200 mmol) in 4 mL of 0.3 M Bu₄NBF₄/CD₂Cl₂. In the cathodic chamber were placed trifluoromethanesulfonic acid (76.3 mg, 0.509 mmol) and 0.3 M Bu₄NBF₄/CD₂Cl₂ (4.0 mL). The constant current electrolysis (4 mA) was carried out at -48 °C with magnetic stirring. After 2.5 F/mol of electricity was consumed, the reaction mixture was transferred to a 5 mm NMR tube with a septum cap under Ar atmosphere at -78 °C. The NMR measurement was carried out at 0 °C: ¹H NMR (600 MHz, CD₂Cl₂) δ 5.11 (s, 3H), 7.77-7.80 (m, 2H), 8.16-8.20 (m, 1H), 8.39 (d, *J* = 7.6 Hz, 2H), 9.87 (s, 1H); ¹³C NMR (150 MHz, CD₂Cl₂) δ 74.6, 128.4, 131.1, 145.7, 207.8.

^1H NMR spectrum of methoxyphenylcarbnium ion **2** (0 °C).

^{13}C NMR spectrum of methoxyphenylcarbnium ion **2** (0 °C).

NMR Analysis of Dication **11.** ^1H and ^{13}C NMR spectra were recorded in CD_2Cl_2 on a JEOL ECA-600 spectrometer. Chemical shifts are reported using methylene signals at δ 5.32 (^1H NMR) and δ 53.80 (^{13}C NMR) as standards. The anodic oxidation was carried out in a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber were placed a solution of **10** (48.6 mg, 0.202 mmol) in 4 mL of 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CD}_2\text{Cl}_2$. In the cathodic chamber were placed trifluoromethanesulfonic acid (76.3 mg, 0.509 mmol) and 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CD}_2\text{Cl}_2$ (4.0 mL). The constant current electrolysis (4 mA) was carried out at -78°C with magnetic stirring. After 2.5 F/mol of electricity was consumed, the reaction mixture was transferred to a 5 mm NMR tube with a septum cap under Ar atmosphere at -78°C . The NMR measurement was carried out at -80°C : ^1H NMR (600 MHz, CD_2Cl_2) δ 4.88 (s, 6H), 7.85-7.91 (m, 4H), 8.21 (t, $J = 7.6$ Hz, 2H), 8.52 (d, $J = 8.2$ Hz, 2H), 9.04 (s, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 74.3, 126.4, 131.1, 133.4, 134.3, 143.6, 145.5, 205.0.

^1H NMR spectrum of dication **11** (-80°C).

^{13}C NMR spectrum of dication **11** (-80 °C).

4-Methoxy-4-phenyl-1-butene (3).

Prepared from **1** (97.5 mg, 0.402 mmol) and allyltrimethylsilane (225.6 mg, 1.97 mmol). The GC analysis of the crude product indicated that the title compound was formed in 90% yield (118.0 mg, 0.727 mmol, t_R 5.1 min., column, OV-1; 0.25 mm x 25 m; oven temperature, 100 °C; rate of temperature increase, 10 °C/min): TLC R_f 0.59 (hexane/EtOAc 10/1); ^1H NMR (300 MHz, CDCl_3) δ 2.35-2.46 (m, 1H), 2.50-2.63 (m, 1H), 3.22 (s, 3H), 4.17 (dd, J = 5.9, 7.7 Hz, 1H), 4.98-5.10 (m, 2H), 5.70-5.84 (m, 1H), 7.24-7.40 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 42.6, 56.7, 83.6, 116.7, 126.6, 127.4, 128.2, 134.6, 141.5; IR (neat) 1455, 1102, 914, 758, 702 cm^{-1} ; LRMS (GCMS, CI) m/z 163 (MH^+), 131 ($\text{M}^+ - \text{OMe}$) 121 ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$); HRMS (GCMS, CI) calcd for $\text{C}_{11}\text{H}_{15}\text{O}$ (MH^+): 163.1123, found: 163.1121.

¹H NMR spectrum of **3**.

¹³C NMR spectrum of **3**.

2,2'-Bis(1-methoxy-3-butenyl)biphenyl (12).

Prepared from **10** (96.7 mg, 0.402 mmol) and allyltrimethylsilane (240.0 mg, 2.100 mmol). The crude product was purified with flash column chromatography (hexane/EtOAc 50/1) to obtain the title compound in 80% yield (104.2 mg, 0.323 mmol): This compound was characterized as a mixture of isomers: TLC R_f 0.57 (hexane/EtOAc 5/1); ^1H NMR (600 MHz, CDCl_3 , 25 °C) δ 2.18-2.53 (m, 4H), 3.16 (s) and 3.17 (s) and 3.22 (s) (total 6H), 3.97 (dd, $J = 4.1, 7.6$ Hz) and 4.08 (dd, $J = 4.1, 7.6$ Hz) and 4.10 (dd, $J = 3.5, 8.9$ Hz) and 4.15 (dd, $J = 3.1, 9.3$ Hz) (total 2H), 4.86-5.00 (m, 4H), 5.65-5.68 (m, 2H), 7.05-7.19 (m, 2H), 7.27-7.33 (m, 2H), 7.38-7.45 (m, 2H), 7.53-7.60 (m, 2H); ^1H NMR (600 MHz, CDCl_3 , 50 °C) δ 2.18-2.51 (m, 4H), 3.145 (s) and 3.154 (s) and 3.17 (s) and 3.22 (s) (total 6H), 3.97 (dd, $J = 4.1, 7.6$ Hz) and 4.09 (dd, $J = 4.1, 7.6$ Hz) and 4.11 (dd, $J = 3.4, 8.9$ Hz) and 4.16 (dd, $J = 3.5, 8.9$ Hz) (total 2H), 4.84-4.98 (m, 4H), 5.65-5.66 (m, 2H), 7.05-7.17 (m, 2H), 7.24-7.31 (m, 2H), 7.37-7.42 (m, 2H), 7.53-7.58 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3 , 50 °C) δ 40.78, 40.82, 41.7, 42.0, 56.3, 56.4, 56.8, 78.6, 78.7, 79.8, 79.9, 116.4, 116.5, 116.6, 126.0, 126.2, 126.6, 126.7, 126.9, 127.8 (two signals), 128.0 (two signals), 130.2 (two signals), 130.5, 130.7, 134.9 (two signals), 135.1, 135.2, 138.8, 138.9, 139.5, 139.6, 139.7, 139.8, 140.2, 140.5; IR (neat) 1474, 1447, 1040, 1096, 914, 764 cm^{-1} ; LRMS (FAB) m/z 323 (MH^+), 281 ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$); HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{27}\text{O}_2$ (MH^+): 323.2011, found: 323.2012.

^1H NMR spectrum of **12** (25 °C).

2,2'-Bis(1-methoxyethyl)biphenyl (13).

Prepared from **10** (96.3 mg, 0.401 mmol) and methylmagnesium bromide (3.00 M in ether, 0.53 mL, 1.590 mmol). The crude product was purified with flash column chromatography (hexane/EtOAc 30/1) to obtain the title compound in 77% yield (83.8 mg, 0.310 mmol): This compound was characterized as a mixture of isomers: TLC R_f 0.39 (hexane/EtOAc 5/1); ^1H NMR (600 MHz, CDCl_3 , 25 $^\circ\text{C}$) δ 1.30 (d, $J = 6.2$ Hz) and 1.31 (d, $J = 6.8$ Hz) 1.32 (d, $J = 6.2$ Hz) and 1.33 (d, $J = 6.2$ Hz) (total 6H), 3.13 (s) and 3.16 (s) and 3.19 (s) (total 6H), 4.02 (q, $J = 6.4$ Hz) and 4.14 (q, $J = 6.2$ Hz) and 4.17 (q, $J = 6.4$ Hz) and 4.25 (q, $J = 6.4$ Hz) (total 2H), 7.04-7.18 (m, 2H), 7.25-7.32 (m, 2H), 7.40-7.44 (m, 2H), 7.57-7.62 (m, 2H); ^1H NMR (600 MHz, CDCl_3 , 50 $^\circ\text{C}$) δ 1.29 (d, $J = 6.2$ Hz) and 1.30 (d, $J = 6.2$ Hz) 1.31 (d, $J = 6.2$ Hz) and 1.32 (d, $J = 6.2$ Hz) (total 6H), 3.121 (s) and 3.124 (s) and 3.15 (s) and 3.19 (s) (total 6H), 4.02 (q, $J = 6.4$ Hz) and 4.14 (q, $J = 6.2$ Hz) and 4.17 (q, $J = 6.4$ Hz) and 4.24 (q, $J = 6.2$ Hz) (total 2H), 7.02-7.17 (m, 2H), 7.24-7.30 (m, 2H), 7.38-7.42 (m, 2H), 7.56-7.61 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3 , 50 $^\circ\text{C}$) δ 22.3, 23.2 (two signals), 56.0 (two signals), 56.1, 56.2, 74.7, 74.8, 75.9, 76.0, 125.4, 125.5, 125.9, 126.0, 126.4, 126.5, 126.6, 126.8, 128.0, 128.1 (two signals), 129.9, 130.0, 130.2, 138.6, 138.7, 139.5, 139.7, 141.1, 141.6, 141.9, 142.5; IR (neat) 1370, 1211, 1111, 1076, 760 cm^{-1} ; LRMS (FAB) m/z 271 (MH^+), 239 ($\text{M}^+ - \text{OMe}$); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2$ (MH^+): 271.1698, found: 271.1696.

^1H NMR spectrum of **13** (25 $^\circ\text{C}$).

^1H NMR spectrum of **13** (50 °C).

^{13}C NMR spectrum of **13** (50 °C).

2,2'-Bis[1-methoxy-2-methyl-2-(methoxycarbonyl)propyl]biphenyl (14).

Prepared from **10** (97.5 mg, 0.406 mmol) and dimethylketene methyl trimethylsilyl acetal (345.8 mg, 1.984 mmol). The crude product was purified with flash column chromatography (hexane/EtOAc 20/1) to obtain the title compound in 74% yield (126.2 mg, 0.298 mmol): This compound was characterized as a mixture of isomers: TLC R_f 0.36 (hexane/EtOAc 5/1); The major isomer was separated by recrystallization (hexane/EtOAc 10/1); ^1H NMR (400 MHz, CDCl_3) δ 0.52 (s, 6H), 1.02 (s, 6H), 3.44 (s, 6H), 3.53 (s, 6H), 5.11 (s, 2H), 7.10 (dd, $J = 1.6, 7.6$ Hz, 2H), 7.31 (dt, $J = 1.5, 7.5$ Hz, 2H), 7.38 (dt, $J = 1.5, 7.6$ Hz, 2H), 7.55 (dd, $J = 1.4, 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7, 24.7, 49.5, 51.6, 56.4, 82.1, 126.8, 127.4, 128.3, 133.2, 134.7, 142.2, 176.8; IR (neat) 1740, 1262, 1132, 1103 cm^{-1} ; LRMS (FAB) m/z 443 (MH^+), 341 ($\text{M}-\text{C}_5\text{H}_9\text{O}_2$); HRMS (FAB) calcd for $\text{C}_{26}\text{H}_{35}\text{O}_6$ (MH^+): 443.2434, found: 443.2432. The minor isomer; ^1H NMR (400 MHz, CDCl_3) δ 0.89 (s) and 1.07 (s) (total 6H), 1.20 (s) and 1.34 (s) (total 6H), 3.09 (s) and 3.17 (s) (total 6H), 3.58 (s) and 3.63 (s) (total 6H), 4.71 (s) and 4.79 (s) (total 2H), 7.17 (dd, $J = 1.6, 7.6$ Hz, 2H), 7.28-7.40 (m, 4H), 7.64 (dt, $J = 1.2, 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.1, 20.8, 23.3, 26.0, 48.0, 48.4, 51.7, 51.9, 57.8, 57.9, 82.3, 82.9, 126.3, 127.1, 128.1, 128.4, 131.4, 131.8, 136.7, 137.4, 139.7, 141.5, 177.0, 177.7.

^1H NMR spectrum of **14** (a mixture of isomers).

^{13}C NMR spectrum of the major isomer of **14**.

2-[1-Methoxy-2-methyl-2-(methoxycarbonyl)propyl]-2'-(methoxymethyl)-biphenyl (16).

Prepared from **15** (96.8 mg, 0.399 mmol) and dimethylketene methyl trimethylsilyl acetal (353.7 mg, 2.029 mmol). The crude product was purified with flash column chromatography (hexane/EtOAc 15/1) to obtain the title compound in 30% yield (40.7 mg, 0.119 mmol): This compound was characterized as a mixture of isomers: TLC R_f 0.39 (hexane/EtOAc 5/1); ^1H NMR (400 MHz, CDCl_3) δ 0.563 (s) and 0.758 (s) (total 3H), 1.07 (s) and 1.11 (s) (total 3H), 3.17 (s) and 3.18 (s) and 3.18 (s) and 3.20 (s) (total 6H), 3.58 (s) and 3.59 (s) (total 3H), 4.04 (d, $J = 12$ Hz) and 4.14 (d, $J = 11.2$ Hz) (total 1H), 4.31 (d, $J = 11.2$ Hz) and 4.32 (d, $J = 12$ Hz) (total 1H), 4.41 (s) and 4.95 (s) (total 1H), 7.10-7.43 (m, 6H), 7.53-7.62 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.2, 18.6, 23.1, 24.8, 48.6, 49.0, 51.8, 56.9, 57.1, 58.2, 58.5, 71.9, 72.5, 82.1, 83.2, 126.6, 126.8, 127.0, 127.4, 127.5, 127.7, 128.4, 129.1, 129.5, 130.1, 130.4, 130.5, 131.6, 135.1, 135.5, 135.6, 136.3, 139.3, 139.4, 141.0, 141.2, 176.8, 176.9; IR (neat) 1732, 1470, 1266, 1132, 1090, 768 cm^{-1} ; LRMS (FAB) m/z 343 (MH^+); HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{27}\text{O}_4$ (MH^+): 343.1909, found: 343.1911.

^1H NMR spectrum of **16**.

^{13}C NMR spectrum of **16**.

Prepared from **17** (97.2 mg, 0.404 mmol) and allyltrimethylsilane (254.5 mg, 2.227 mmol). The crude product was purified with flash column chromatography (hexane/EtOAc 30/1) to obtain the title compound in 61% yield (79.8 mg, 0.247 mmol): This compound was characterized as a mixture of two diastereomers: TLC R_f 0.68 (hexane/EtOAc 5/1); ^1H NMR (400 MHz, CDCl_3) δ 2.35-2.44 (m, 2H), 2.53-2.64 (m, 2H), 3.35-3.50 (m, 4H), 4.31 (t, $J = 6.8$ Hz, 2H), 4.97-5.08 (m, 4H), 5.72-5.83 (m, 2H), 7.22-7.35 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 42.7 (two signals), 68.0, 68.1, 82.1, 82.2, 116.6, 126.6, 127.3, 128.1, 134.8, 141.9; IR (neat) 1453, 1098, 914, 758, 700 cm^{-1} ; LRMS (FAB) m/z 323 (MH^+), 281 ($\text{M}-\text{CH}_2\text{CH}=\text{CH}_2$); HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{27}\text{O}_2$ (MH^+): 323.2011, found: 323.2009.

^1H NMR spectrum of **18**.

^{13}C NMR spectrum of **18**.

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