Supporting Information

Reaction of *N*-Acyliminium Ion Pool with Benzylsilanes. Implication of a Radical/Cation/Radical Cation Chain Mechanism Involving Oxidative C-Si Bond Cleavage

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General Remarks. ^1H and ^{13}C NMR spectra were recorded on Varian MERCURYplus-400 (^1H 400 MHz, ^{13}C 100MHz) and JEOL ECA-600 (^1H 600 MHz, ^{13}C 150 MHz) spectrometers in CDCl_3 . NMR spectra of carbamates were usually very broad and sometimes separated to two signals due to the existence of two rotamers. EI and CI mass spectra were recorded on JMS-SX102A spectrometer. IR spectra were measured with a SHIMADZU FTIR 1600 spectrometer. GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused silica capillary. Gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using CHCl_3 as eluent.

Materials. Dichloromethane was washed with water and distilled from P_2O_5 , then removal of a trace amount of acid was carried out by distillation from dried K_2CO_3 and the distillate was stored over molecular sieves 4A. Trifluoromethanesulfonic acid (TfOH) was purchased from Nacalai and was used without purification. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was purchased from TCI and dried with P_2O_5 under vacuum. All reactions were carried out under Ar atmosphere unless otherwise noted. *N*-Methoxycarbonyl-2-trimethylsilylpyrrolidine was prepared according to the literature procedure.¹

Voltammetry. OSWV was carried out using BAS 100B (step E: 4mV; S. W. amplitude: 25 mV; S. W. frequency: 15 Hz (**2** and **8b**), 90 Hz (**8e**)). Measurements were carried out in a 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ using a glassy carbon working electrodes (3.0 mm diameter), a platinum wire counter electrode, and an SCE reference electrode.

Generation of Cation Pool of *N*-Acyliminium Ion (1**).** 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 1 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (563.8 mg, 2.8 mmol) in 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ (56 mL). In the cathodic chamber were placed 0.3 M

Bu₄NBF₄/CH₂Cl₂ (56 mL) and trifluoromethanesulfonic acid (0.62 mL, 7.0 mmol). The constant current electrolysis (20 mA) was carried out at -78 °C with magnetic stirring until 2.5 F/mol of electricity was consumed.

General Procedure for Synthesis of Benzylsilanes 2 and Benzylstannanes 8. To a well-dried round-bottomed flask equipped with a condenser, a dropping funnel, a magnetic stirring bar, and a septum, Mg (55 mmol), chlorotrimethylsilane (75 mmol), and THF (50 mL) were added. Then, a substituted benzyl chloride (50 mmol) in THF (50 mL) was added dropwise over 10 min under reflux. After the mixture was stirred for 30 min, the reaction was quenched by adding water. The resulting mixture was extracted with ether (3 x 30 mL). The combined organic extract was washed with saturated NaCl (20 mL) and was dried over MgSO₄. The solvent was removed under reduced pressure. The crude product thus obtained was purified by distillation.

Benzylsilanes 2 and Benzylstannanes 8. Benzylsilanes **2** were prepared according to the general procedure described above. Benzylstannanes **8** were prepared in a similar fashion using chlorotributylstannane instead of chlorotrimethylsilane. Known compounds (**2b**,³ **2c**,² **2d**,² **2e**,² **2g**,³ **8b**,³ **8e**³) were identified by comparison of their spectra with those reported in the literature.^{2,3}

Trimethyl((4-fluorophenyl)methyl)silane (2a). ¹H NMR (400 MHz, CDCl₃) δ 0.00 (s, 9H), 2.05 (s, 2H), 6.86-6.96 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ -1.8, 26.2, 114.6 and 114.8, 128.8 and 128.9, 135.8 and 135.8, 158.9 and 161.2; IR (KBr) 2957, 851 cm⁻¹; LRMS (EI) *m/z* 182 (M⁺); HRMS (EI) calcd for C₁₀H₁₅FSi (M⁺): 182.0927, found: 182.0929.

Trimethyl((2,4,6-trimethylphenyl)methyl)silane (2f). ¹H NMR (400 MHz, CDCl₃) δ 0.06 (s, 9H), 2.14 (s, 2H), 2.23 (s, 6H), 2.26 (s, 3H), 6.82 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ -0.2, 19.7, 20.8, 21.2, 130.2, 130.4, 132.0, 134.6; IR (neat) 2958, 841 cm⁻¹; LRMS (EI) *m/z* 206 (M⁺); HRMS (EI) calcd for C₁₃H₂₂Si (M⁺): 206.1491, found: 206.1489.

Trimethyl((2,3,4,5,6-pentamethylphenyl)methyl)silane (2h). ^1H NMR (400 MHz, CDCl_3) δ 0.04 (s, 9H), 2.20 (s, 6H), 2.24 (s, 6H), 2.25 (s, 3H), 2.27 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 0.1, 16.9, 17.1, 18.0, 21.1, 128.5, 132.5, 134.4, 134.7; IR (neat) 2955, 857 cm^{-1} ; LRMS (EI) m/z 234 (M^+); HRMS (EI) calcd for $\text{C}_{15}\text{H}_{26}\text{Si}$ (M^+): 234.1804, found: 234.1803.

General Procedure for the Reaction of Cation Pool of 1 with Benzylsilanes (2) or Benzylstannanes (8). The electrolysis of *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (0.375 mmol) was carried out as described above. To the cation pool of **1** thus obtained, was added benzylsilane (**2**) or benzylstannane (**8**) (0.250 mmol) at $-50\text{ }^\circ\text{C}$ and the reaction mixture was stirred for 1.5 h. Triethylamine was added to the stirred solution at $-50\text{ }^\circ\text{C}$. The mixture was warmed to room temperature. Solvent was removed under reduced pressure and the residue was quickly filtered through a short column (3 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (100 mL). The crude product thus obtained was purified using flash chromatography.

Procedure for Reaction of 1 and 2e Using Benzylstannane 8e as an Initiator. The electrolysis of *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (0.375 mmol) was carried out as described above. To the cation pool of **1** thus obtained, was added benzylsilane **2e** (0.250 mmol) at $-50\text{ }^\circ\text{C}$. Then, benzylstannane **8e** (0.025 mmol) was added and the mixture was stirred for 1.5 h at the same temperature. Triethylamine was added at $-50\text{ }^\circ\text{C}$. The resulted mixture was warmed to room temperature. Solvent was removed under reduced pressure and the residue was quickly filtered through a short column (3 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (100 mL). The filtrate and washings were combined and the solvent was removed under reduced pressure. The crude product thus obtained was purified using flash chromatography to obtain **3e** in 97% yield. The yield based on the total amount of **2e** and **8e** was 88%.

Procedure the Reaction of 1 and 2a with Slow Addition of Benzylstannane Initiator 8e. The electrolysis of *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (0.60 mmol) was carried out as described above. To the cation pool of **1** thus obtained, was added benzylsilane **2a** (0.20 mmol) at $-50\text{ }^\circ\text{C}$. Then, 0.4 M dichloroethane solution of benzylstannane **8e** (0.20 mmol) was added dropwise over a period of 30 min and the mixture was stirred for 1.5 h at the same temperature. Triethylamine was added at $-50\text{ }^\circ\text{C}$. The mixture was warmed to room temperature. Solvent was removed under reduced pressure and the residue was quickly filtered through a short column (3 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (100 mL). The filtrate and washings were combined and the solvent was removed under reduced pressure. The crude product thus obtained was purified using flash chromatography to obtain **3a** (97%) and **3e** (82%).

***N*-Methoxycarbonyl-2-((4-fluorophenyl)methyl)pyrrolidine (3a).** Prepared from a cation pool of **1** generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (120.8 mg, 0.60 mmol), trimethyl((4-fluorophenyl)methyl)silane (**2a**) (36.9 mg, 0.202 mmol), and 0.4 M dichloroethane solution of tributyl((4-methylphenyl)methyl)stannane (**8e**) (0.5 mL, 0.20 mmol) as an initiator (slow addition), and purified by flash chromatography (hexane/EtOAc 4:1) (97% yield, determined by GC analysis): ¹H NMR (400 MHz, CDCl₃) δ 1.62-1.84 (m, 4H), 2.56 (dd, *J* = 13.2, 9.2 Hz, 1H), 2.89-3.16 (m, 1H), 3.25-3.46 (m, 2H), 3.71 (s, 3H), 3.92-4.06 (m, 1H), 6.91-6.98 (m, 2H), 7.05-7.18 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 22.7 and 23.5, 28.9 and 29.8, 38.7 and 39.7, 46.5 and 46.8, 52.1, 58.5 and 59.2, 114.8 and 115.0, 130.6, 134.4, 155.3, 160.1 and 162.5; IR (neat) 2955, 1705 cm⁻¹; LRMS (CI) *m/z* 238 (M⁺ + H); HRMS (CI) calcd for C₁₃H₁₆FN₂ (M⁺ + H): 238.1243, found: 238.1243.

***N*-Methoxycarbonyl-2-benzylpyrrolidine (3b).** Prepared from a cation pool of **1** generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (50.3 mg, 0.25 mmol) and tributylbenzylstannane (**8b**) (62.8 mg, 0.165 mmol) and purified by flash chromatography (hexane/EtOAc 9:1) and GPC (18.6 mg, 0.085 mmol, 51% yield): ¹H NMR (400 MHz, CDCl₃) δ 1.69-1.89 (m, 4H), 2.58 (dd, *J* = 13.2, 9.6 Hz, 1H), 2.96-3.09 (m, 0.5H), 3.16-3.26 (m, 0.5H), 3.31-3.50 (m, 2H), 3.73 (s, 3H), 3.99-4.14 (m, 1H), 7.12-7.30 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 22.8 and 23.6, 29.0 and 29.9, 39.6 and 40.6, 46.6, 52.2, 58.6 and 59.3, 126.0, 128.2, 129.3, 138.8, 155.4; IR (neat) 2953.4, 1699.5, 702.2 cm⁻¹; LRMS (CI) *m/z* 220 (M⁺ + H); HRMS (CI) calcd for C₁₃H₁₈NO₂ (M⁺ + H): 220.1338, found: 220.1337.

***N*-Methoxycarbonyl-2-((3,5-dimethylphenyl)methyl)pyrrolidine (3d).** Prepared from a cation pool of **1** generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (60.4 mg, 0.30 mmol) and trimethyl((3,5-dimethylphenyl)methyl)silane (**2d**) (38.1 mg,

0.198 mmol), and purified by flash chromatography (hexane/EtOAc 5.7:1) and GPC (9.2 mg, 0.037 mmol, 19% yield): ^1H NMR (400 MHz, CDCl_3) δ 1.69-1.88 (m, 4H), 2.31 (s, 6H), 2.38-2.49 (m, 1H), 2.93-3.25 (m, 1H), 3.29-3.49 (m, 2H), 3.75 (s, 3H), 3.95-4.11 (m, 1H), 6.75-6.91 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 22.7 and 23.6, 29.0 and 29.7, 39.5 and 40.3, 46.5 and 46.8, 52.1, 58.6 and 59.5, 127.1 and 127.6, 128.9, 135.6, 138.7, 155.3; IR (neat) 2953, 1703 cm^{-1} ; LRMS (CI) m/z 248 ($\text{M}^+ + \text{H}$); HRMS (CI) calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2$ ($\text{M}^+ + \text{H}$): 248.1651, found: 248.1652.

***N*-Methoxycarbonyl-2-((4-methylphenyl)methyl)pyrrolidine (3e).** Prepared from a cation pool of **1** generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (75.5 mg, 0.375 mmol), trimethyl((4-methylphenyl)methyl)silane (**2e**) (44.5 mg, 0.25 mmol), and tributyl((4-methylphenyl)methyl)stannane (**8e**) (10.5 mg, 0.0266 mmol) as an initiator, and purified by flash chromatography (hexane/EtOAc 4:1) (97% yield based on **2e**, determined by GC analysis): ^1H NMR (400 MHz, CDCl_3) δ 1.64-1.86 (m, 4H), 2.33 (s, 3H), 2.54 (dd, $J = 13.2, 9.6$ Hz, 1H), 2.92-3.22 (m, 1H), 3.27-3.49 (m, 2H), 3.74 (s, 3H), 3.95-4.12 (m, 1H), 7.02-7.15 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.1, 22.7 and 23.6, 28.9 and 29.8, 39.1 and 40.0, 46.5 and 46.8, 52.1, 58.6 and 59.4, 128.8, 129.1, 135.4, 135.6, 155.3; IR (neat) 2953, 1705 cm^{-1} ; LRMS (CI) m/z 234 ($\text{M}^+ + \text{H}$); HRMS (CI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ ($\text{M}^+ + \text{H}$): 234.1493, found: 234.1493.

***N*-Methoxycarbonyl-2-((2,4,6-trimethylphenyl)methyl)pyrrolidine (3f).** Prepared from a cation pool of **1** generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (60.4 mg, 0.30 mmol) and trimethyl((2,4,6-trimethylphenyl)methyl)silane (**2f**) (41.2 mg, 0.20 mmol), and purified by flash chromatography (hexane/EtOAc 9:1) and GPC (45.0 mg, 0.172 mmol, 86% yield): ^1H NMR (400 MHz, CDCl_3) δ 1.60-1.83 (m, 2H), 1.87-1.98 (m, 1H), 1.98-2.12 (m, 1H), 2.26 (s, 3H), 2.34 (s, 3H), 2.42 (s, 3H), 2.62 (dd, $J = 23.6, 12.0$ Hz, 1H), 2.93-3.27 (m, 1H), 3.28-3.48 (m, 1H), 3.49-3.60 (m, 1H), 3.60-3.79 (m, 3H), 4.07-4.21 (m, 1H), 6.85 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.3 and 20.4, 20.9, 23.0 and 23.8, 28.3 and 29.5, 32.1 and 33.3, 46.4 and 46.7, 52.1, 56.9 and 57.8, 128.9, 132.5, 135.2, 136.7 and 136.9, 155.4; IR (neat) 2953, 1705 cm^{-1} ; LRMS (CI) m/z 262 ($\text{M}^+ + \text{H}$); HRMS (CI) calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_2$ (M^+

+ H): 262.1807, found: 262.1808.

N-Methoxycarbonyl-2-((4-methoxyphenyl)methyl)pyrrolidine (3g). Prepared from a cation pool of **1** generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (75.5 mg, 0.375 mmol) and trimethyl((4-methoxyphenyl)methyl)silane (**2g**) (50.9 mg, 0.262 mmol), and purified by flash chromatography (hexane/EtOAc 4:1) (57.4 mg, 0.230 mmol, 88% yield): ^1H NMR (400 MHz, CDCl_3) δ 1.62-1.85 (m, 4H), 2.53 (dd, J = 13.2, 9.2 Hz, 1H), 2.86-3.18 (m, 1H), 3.24-3.47 (m, 2H), 3.72 (s, 3H), 3.77 (s, 3H), 3.92-4.10 (m, 1H), 6.81 (d, J = 8.4 Hz, 2H), 7.02-7.13 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 22.5 and 23.4, 28.7 and 29.6, 38.4 and 39.4, 46.4 and 46.7, 52.0 and 52.2, 55.1, 58.6 and 59.3, 113.7, 130.2 and 130.3, 130.8 and 130.9, 155.4 and 155.6, 158.0; IR (neat) 2953, 1708 cm^{-1} ; LRMS (CI) m/z 250 (M^+ + H); HRMS (CI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3$ (M^+ + H): 250.1443, found: 250.1443.

N-Methoxycarbonyl-2-((2,3,4,5,6-pentamethylphenyl)methyl)pyrrolidine (3h). Prepared from a cation pool of **1** generated from *N*-methoxycarbonyl-2-trimethylsilylpyrrolidine (60.4 mg, 0.30 mmol) and trimethyl((2,3,4,5,6-pentamethylphenyl)methyl)silane (**2h**) (46.9 mg, 0.20 mmol), and purified by flash chromatography (hexane/EtOAc 5.7:1) and GPC (50.9 mg, 0.176 mmol, 88% yield): ^1H NMR (400 MHz, CDCl_3) δ 1.62-1.74 (m, 2H), 1.96-2.00 (m, 1H), 2.00-2.17 (m, 1H), 2.19-2.52 (m, 15H), 2.79 (dd, J = 24.4, 12.8 Hz, 1H), 3.06-3.49 (m, 2H), 3.52-3.66 (m, 1H), 3.66-3.84 (m, 3H), 4.01-4.20 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.0, 17.0, 17.4, 23.0 and 23.9, 28.0 and 29.0, 32.8 and 33.9, 46.4 and 46.7, 52.1, 57.5 and 58.5, 132.5, 132.7, 155.5; IR (KBr) 2975, 1709 cm^{-1} ; LRMS (CI) m/z 290 (M^+ + H); HRMS (CI) calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2$ (M^+ + H): 290.2120, found: 290.2120.

References

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- 3) Hirao, T.; Morimoto, C.; Takeda, T.; Sakurai, H. *Tetrahedron*, **2001**, 57, 5073.

^1H and ^{13}C NMR spectra of unknown compounds:

^1H NMR spectrum of trimethyl((4-fluorophenyl)methyl)silane (2a).

^{13}C NMR spectrum of trimethyl((4-fluorophenyl)methyl)silane (2a).

¹H NMR spectrum of trimethyl((2,4,6-trimethylphenyl)methyl)silane (2f).

¹³C NMR spectrum of trimethyl((2,4,6-trimethylphenyl)methyl)silane (2f).

¹H NMR spectrum of trimethyl((2,3,4,5,6-pentamethylphenyl)methyl)silane (2h).

¹³C NMR spectrum of trimethyl((2,3,4,5,6-pentamethylphenyl)methyl)silane (2h).

¹H NMR spectrum of *N*-methoxycarbonyl-2-((4-fluorophenyl)methyl)pyrrolidine (3a).

¹³C NMR spectrum of *N*-methoxycarbonyl-2-((4-fluorophenyl)methyl)pyrrolidine (3a).

¹H NMR spectrum of *N*-methoxycarbonyl-2-((3,5-dimethylphenyl)methyl)pyrrolidine (3d).

¹³C NMR spectrum of *N*-methoxycarbonyl-2-((3,5-dimethylphenyl)methyl)pyrrolidine (3d).

¹H NMR spectrum of *N*-methoxycarbonyl-2-((4-methylphenyl)methyl)pyrrolidine (3e).

¹³C NMR spectrum of *N*-methoxycarbonyl-2-((4-methylphenyl)methyl)pyrrolidine (3e).

¹H NMR spectrum of *N*-methoxycarbonyl-2-((4-methoxyphenyl)methyl)pyrrolidine (3g).

¹³C NMR spectrum of *N*-methoxycarbonyl-2-((4-methoxyphenyl)methyl)pyrrolidine (3g).

¹H NMR spectrum of *N*-methoxycarbonyl-2-((2,3,4,5,6-pentamethylphenyl)methyl)pyrrolidine (3h**).**

¹³C NMR spectrum of *N*-methoxycarbonyl-2-((2,3,4,5,6-pentamethylphenyl)methyl)pyrrolidine (3h**).**