Supporting Information

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Electrophilic Cleavage of One Silicon-Carbon Bond of Pentacoordinate Tetraorganosilanes. Novel Synthesis of Silalactones

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**General.** $^1$H NMR were measured in CDCl$_3$ solution and referenced to TMS (0.00 ppm) or in d6-acetone solution and referenced to d6-acetone (2.04 ppm). $^{13}$C NMR were measured in CDCl$_3$ solution and referenced to CDCl$_3$ (77.0 ppm). $^{29}$Si NMR were measured in CDCl$_3$ solution and referenced to TMS (0.00 ppm). Chemical shifts are reported in ppm (from TMS). When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sept, septet; m, multiplet; br, broadend. Melting points are uncorrected.

**Materials.** β-Silylacrylic acids 5 were prepared according to the references.¹) Solvents were freshly distilled prior to use: tetrachloromethane (CCl$_4$) was distilled from phosphorus (V) oxide and kept over 4 Å molecular sieves: pyridine was distilled from KOH and kept over KOH: tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl.
Representative procedure (Method A). Synthesis of 2,2,4-trimethyl-3-phenyl-2H-[1,2]oxasilol-5-one (4f) with Iodine (Table 1, entry 7)

To a solution of (Z)-2-methyl-3-trimethylsilylcinnamic acid (30 mg, 0.128 mmol) in CCl₄ (1.5 mL) was added iodine (39 mg, 0.154 mmol) and pyridine (0.021 mL, 0.256 mmol). The reaction mixture was heated at reflux for 19.5 hr. After cooling to room temperature, a saturated Na₂S₂O₃ solution (2 mL) was added and the resulting mixture was extracted with CH₂Cl₂ (15 ml x 3). The organic phase was washed with brine (30 mL), dried over MgSO₄, filtered and concentrated. The resulting residue was chromatographed over silica gel (10% ethyl acetate in hexane) to yield 27 mg (95%) of 4f as a colorless solid, which was recrystallized from pentane to give colorless needles (mp. 73.4 – 74.2 °C). ¹H-NMR (400 MHz, CDCl₃) δ: 0.52 (s, 6H), 2.11 (s, 3H), 7.20-7.25 (m, 2H), 7.33-7.38 (m, 1H), 7.41-7.47 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: -1.9 (q), 13.5 (q), 127.6 (d), 128.1 (d), 128.8 (d), 136.1 (s), 141.4 (s), 155.9 (s), 170.0 (s). IR (CHCl₃): 1730, 1593, 1491, 1442, 1117, 918. MS (EI) m/z 218 (M⁺), 159 (100%). Anal. Calcd for C₁₂H₁₄O₂Si: C, 66.02; H, 6.46, found: C, 65.72; H, 6.55.

Representative procedure (Method B). Synthesis of 4f with N-iodosuccinimide (Table 1, entry 8)

To a solution of (Z)-2-methyl-3-trimethylsilylcinnamic acid (30 mg, 0.128 mmol) in CH₂Cl₂ (2 mL) was added N-iodosuccinimide (43 mg, 0.192 mmol). After stirred at room temperature for 1.5 hr, a saturated Na₂S₂O₃ solution (2 mL) was added and the resulting mixture was extracted with CH₂Cl₂ (15 ml x 3). The organic phase was washed with brine (30 mL), dried over MgSO₄, filtered and concentrated. The resulting residue was chromatographed over silica gel (10% ethyl acetate in hexane) to yield 19 mg of mixture of 2e (65%) and starting material (4%) as a colorless solid.

3-Benzyl-2,2,4-trimethyl-2H-[1,2]oxasilol-5-one (4a)
Colorless prism (Hexane, mp. 68.3-68.8 °C). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 0.03 (s, 6H), 2.05 (t, $J = 0.9$ Hz, 3H), 3.71 (brs, 2H), 7.13-7.17 (m, 2H), 7.24-7.29 (m, 1H), 7.30-7.36 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: -2.3 (q), 12.2 (q), 36.1 (t), 126.9 (d), 128.7 (d), 128.9 (d), 138.5 (s), 140.6 (s), 158.3 (s), 169.8 (s). IR (CHCl$_3$): 1726, 1603, 1149 cm$^{-1}$. MS (EI) $m/z$ 232 (M$^+$, 100%), 173 (M$^+$-CO$_2$-Me).

Anal. Calcd for C$_{13}$H$_{16}$O$_2$Si: C, 67.20; H, 6.94, found: C, 66.97; H, 6.96.

3-Benzyl-2-tert-butyl-2,4-dimethyl-2H-[1,2]oxasilol-5-one (4b)
Colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: -0.06 (s, 3H), 0.87 (s, 9H), 2.09 (d, $J = 1.2$ Hz, 3H), 3.53 (dd, $J = 1.2$ Hz, 15.4 Hz, 1H), 3.94 (d, $J = 15.4$ Hz, 1H), 7.10-7.14 (m, 2H), 7.22-7.34 (m, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: -6.6 (q), 12.2 (q), 25.6 (q), 36.5 (t), 126.9 (d), 128.7 (d), 128.8 (d), 137.9 (s), 142.2 (s), 155.9 (s), 170.2 (s). IR (Neat): 1739, 1602 cm$^{-1}$. MS (EI) $m/z$ 274 (M$^+$), 217 (M$^+$-CMe$_3$, 100%), 173 (M$^+$-CMe$_3$-CO$_2$). Anal. Calcd for C$_{16}$H$_{22}$O$_2$Si: C, 70.03; H, 8.08, found: C, 69.74; H, 8.11.

3-Benzyl-2,2-diethyl-4-methyl-2H-[1,2]oxasilol-5-one (4c)
Colorless needles (pentane, mp. 40.1-40.5 °C). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 0.31 (dq, $J = 7.8$ Hz, 15.6 Hz, 2H), 0.59 (dq, $J = 7.8$ Hz, 15.6 Hz, 2H), 0.75 (t, $J = 7.8$ Hz, 6H), 2.08 (t, $J = 1.0$ Hz, 3H), 3.69 (brs, 2H), 7.13-7.18 (m, 2H), 7.24-7.35 (m, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 4.5 (t), 5.8 (q), 12.2 (q), 36.5 (t), 127.1 (d), 128.7 (d), 128.9 (d), 138.6 (s), 141.7 (s), 156.3 (s), 170.5 (s). IR (CHCl$_3$): 1723, 1602, 1495, 1455, 1149 cm$^{-1}$. MS (EI) $m/z$ 260 (M$^+$), 231 (M$^+$-Et, 100%). Anal. Calcd for C$_{15}$H$_{20}$O$_2$Si: C, 69.19; H, 7.74, found: C, 68.92; H, 7.79.

3-Benzyl-4-methyl-2,2-diisopropyl-2H-[1,2]oxasilol-5-one (4d)
Colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 0.76 (d, $J = 6.3$ Hz, 6H), 0.89-0.99 (m, 8H), 2.10 (s, 3H), 3.71 (s, 2H), 7.12-7.17 (m, 2H), 7.22-7.34 (m, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 11.4 (d), 12.4 (q), 16.3 (q), 16.6 (q), 36.8 (t), 127.0 (d), 128.8 (d), 138.0 (s), 142.4 (s), 155.0 (s), 170.6 (s). IR (Neat):
1737, 1602, 1144 cm$^{-1}$. MS (EI) $m/z$ 288 (M$^+$), 245 (M$^+$-C$_3$H$_7$, 100%), 217 (M$^+$-C$_3$H$_7$-CO). HRMS (EI) Calcd for C$_{17}$H$_{24}$O$_2$Si (M$^+$): 288.1546, found: 288.1540.

**3-Benzyl-4-methyl-2,2-diphenyl-2H-[1,2]oxasilol-5-one (4e)**

Colorless powder (AcOEt-Hexane, mp. 88.4-89.5 °C). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 2.17 (s, 3H), 3.81 (s, 2H), 6.89-6.93 (m, 2H), 7.01-7.12 (m, 3H), 7.28-7.33 (m, 8H), 7.40-7.46 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 12.6 (q), 36.2 (t), 126.7 (d), 128.0 (d), 128.5 (s), 128.5 (d), 129.1 (d), 131.1 (d), 134.9 (d), 137.5 (s), 142.8 (s), 155.4 (s), 169.9 (s). $^{29}$Si-NMR (79.5 MHz, CDCl$_3$) $\delta$: -2.15. IR (CHCl$_3$): 1731, 1121 cm$^{-1}$. MS (EI) $m/z$ 356 (M$^+$), 265 (M$^+$-PhCH$_2$), 221 (M$^+$-PhCH$_2$-CO$_2$, 100%). Anal. Calcd for C$_{23}$H$_{20}$O$_2$Si: C, 77.49; H, 5.65, found: C, 77.41; H, 5.85.

**2-tert-Butyl-3-(2-methoxyethyl)-2,4-dimethyl-2H-[1,2]oxasilol-5-one (4g)**

Colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 0.36 (s, 3H), 0.98 (s, 9H), 1.95 (d, $J$ = 1.5 Hz, 3H), 2.53 (dddq, $J$ = 1.5 Hz, 5.4 Hz, 8.8 Hz, 15.4 Hz, 1H), 2.79 (ddd, $J$ = 4.4 Hz, 5.4 Hz, 15.4 Hz, 1H), 3.34 (s, 3H), 3.36 (ddd, $J$ = 4.4 Hz, 5.4 Hz, 15.4 Hz, 1H), 3.57 (ddd, $J$ = 4.4 Hz, 5.4 Hz, 8.8 Hz, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: -6.7 (q), 12.1 (q), 18.3 (s), 26.1 (q), 31.2 (t), 58.4 (q), 70.5 (t), 142.9 (s), 154.1 (s), 170.4 (s). $^{29}$Si-NMR (79.5 MHz, CDCl$_3$) $\delta$: 23.99. IR (Neat): 1732, 1165, 1102, 903 cm$^{-1}$. MS (FAB) $m/z$ 243 (M$^+$+H), 154 (100%). Anal. Calcd for C$_{12}$H$_{23}$O$_3$Si: C, 59.46; H, 9.15, found: C, 59.16; H, 9.11.

**2,2,4-Trimethyl-3-(4-pentenyl)-2H-[1,2]oxasilol-5-one (4h)**

Colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 0.42 (s, 6H), 1.52-1.61 (m, 2H), 1.91 (t, $J$ = 0.7 Hz, 3H), 2.06-2.15 (m, 2H), 2.38-2.45 (m, 2H), 5.02 (ddt, $J$ = 1.5 Hz, 2.0 Hz, 17.1 Hz, 1H), 5.04 (ddt, $J$ = 1.2 Hz, 2.0 Hz, 10.3 Hz, 1H), 5.80 (ddt, $J$ = 6.6 Hz, 10.3 Hz, 17.1 Hz, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: -1.8 (q), 12.0 (q), 28.4 (t), 29.0 (t), 33.7 (t), 115.4 (t), 137.4 (d), 141.5 (s), 158.9 (s), 169.9 (s). $^{29}$Si-NMR (79.5 MHz, CDCl$_3$) $\delta$: 23.23. IR (Neat): 1732, 1641, 1604, 1167, 911 cm$^{-1}$. MS (EI) $m/z$ 210 (M$^+$), 195 (M$^+$-Me), 169 (M$^+$-C$_3$H$_7$, 100%). HRMS (EI) Calcd for
C$_{11}$H$_{18}$O$_2$Si (M$^+$): 210.1076, found: 210.1073.

4-[(tert-Butyldimethylsiloxy)phenylmethyl]-2,2-dimethyl-2H-[1,2]oxasilol-5-one (4i)
Colorless solid (mp. 55.0-59.0 °C) $^1$H-NMR (400 MHz, CDCl$_3$) δ: -0.10 (s, 3H), 0.04 (s, 3H), 0.38 (s, 3H), 0.45 (s, 3H), 0.89 (s, 9H), 5.61 (d, $J = 1.2$ Hz, 1H), 7.20-7.32 (m, 3H), 7.33 (d, $J = 1.2$ Hz, 1H), 7.39-7.44 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: -5.0 (q), -4.9 (q), -2.0 (q), -2.0 (q), 18.2 (s), 25.7 (q), 72.2 (d), 126.8 (d), 127.5 (d), 128.2 (d), 140.6 (d), 141.9 (s), 157.4 (s), 167.6 (s). $^{29}$Si-NMR (79.5 MHz, CDCl$_3$) δ: 20.99, 25.29. IR (CHCl$_3$): 1738, 1259, 1137, 1106, 839 cm$^{-1}$. MS (FAB) $m/z$ 349 (M$^+$+H), 154 (100%). HRMS (FAB) Calcd for C$_{18}$H$_{28}$O$_3$Si$_2$ (M$^+$): 348.1577, found: 348.1564.

1,1-Dimethyl-1H-benzo[1,2]oxasilol-5-one (4j)
Colorless solid (mp. 128.2-130.0 °C) $^1$H-NMR (400 MHz, d$_6$-Acetone) δ: 0.56 (s, 6H), 7.63-7.74 (m, 2H), 7.92-7.98 (m, 2H). IR (KBr): 1685, 1019, 813 cm$^{-1}$. MS (EI) $m/z$ 178 (M$^+$), 163 (M$^+$-Me, 100%), 119 (M$^+$-Me-CO$_2$).

1-Methyl-1-phenyl-1H-benzo[1,2]oxasilol-5-one (4k)
Colorless solid (mp. 99-105 °C) $^1$H-NMR (400 MHz, CDCl$_3$) δ: 0.87 (s, 3H), 7.38-7.44 (m, 2H), 7.47-7.53 (m, 1H), 7.54-7.59 (m, 2H), 7.63-7.71 (m, 2H), 7.72-7.76 (m, 1H), 8.12-8.16 (m, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: -3.6 (q), 127.5 (d), 128.3 (d), 130.6 (s), 131.4 (d), 131.5 (d), 131.6 (d), 133.4 (d), 134.1 (d), 137.3 (s), 139.4 (s), 168.0 (s). $^{29}$Si-NMR (79.5 MHz, CDCl$_3$) δ: 10.13. IR (KBr): 1687, 1042 cm$^{-1}$. MS (EI) $m/z$ 240 (M$^+$), 225 (M$^+$-Me, 100%). HRMS (EI) Calcd for C$_{14}$H$_{12}$O$_2$Si (M$^+$): 240.0607, found: 240.0623.

References