SUPPORTING INFORMATION

Synthesis of silacylopent-2-en-4-ols via intramolecular [2+2] photocycloaddition of benzoyl(allyl)silanes

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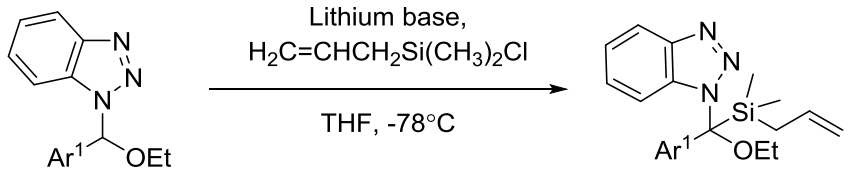
General information

Reactions were monitored through thin-layer chromatography (TLC) with commercial silica gel plates (Merck silica gel, 60 F254). Visualization of the developed plates was performed under UV light at 254 nm and by staining with cerium ammonium molybdate, phosphomolybdic acid and vanillin stains. Flash column chromatography was performed on silica gel 60 (40−63 μm) as stationary phase. Preparative TLCs were conducted on silica gel 60 F254, 1 mm. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz in a 300 MHz Varian Mercury spectrometer, using $CDCl_3$ as solvent. Alternatively, ^{1}H and ^{13}C spectra were recorded at 500 MHz and 125 MHz respectively in a JEOL ECZR 500 instrument. Chemical shifts (δ) are reported in ppm referenced to the $CDCl_3$ residual peak (δ7.26) or TMS peak (δ 0.00) for ^{1}H NMR and to $CDCl_3$ (δ 77.16) for ^{13}C NMR. The following abbreviations were used to describe peak splitting patterns: s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants J were reported in Hertz (Hz). High-resolution mass spectra were recorded on a Waters ESI-TOF MS spectrometer or in a Thermo Scientific Orbitrap LC-MS. Irradiation experiments were performed with a Rayonet RPR-200 Photoreactor (419 nm). THF, Et_2O and DCM were obtained by passing deoxygenated solvents through activated alumina columns (PureSolv micro solvent purification system). Benzotriazole derivatives **1** were prepared as reported elsewhere.[1]

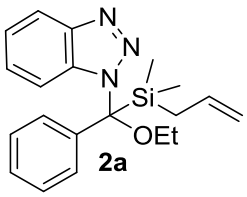
Synthesis of benzotriazole silyl derivatives 2:



1 **2**

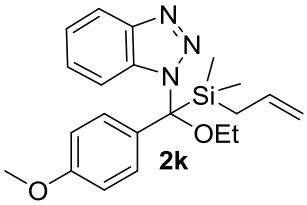
Method A: Benzotriazole derivative **1** (5 mmol) was dissolved in 30 mL of dry THF, in an Argon filled round-bottom flask. The solution was cooled to -78 °C with an acetone/liquid nitrogen bath. *n*BuLi, *t*BuLi or LDA (1.1 equiv.) was added dropwise at this temperature. After addition, the solution was left stirring for 10 minutes at -78 °C. Allyl(chloro)dimethylsilane (1.1 eq.) was then added dropwise at the same temperature. The solution was left at this temperature for 15 minutes and then slowly warmed to room temperature for one hour. The reaction was quenched with 30 mL of saturated aqueous $NaHCO_3$ and transferred to an extraction funnel. The phases were allowed to separate and the top organic phase collected. The aqueous phase was extracted with Et_2O (2 × 30 mL) and the organic phases combined, dried over $MgSO_4$ and filtered. The solvent was evaporated and the resulting crude oil purified through silica chromatography (hexane/ethyl acetate mixture as eluent) to give silyl derivatives **2** as yellow tainted clear oils.

Method B: Benzotriazole derivative **1** (5 mmol) was dissolved in 30 mL of dry THF, in an argon filled round-bottom flask. The solution was cooled to -78 °C with an acetone/liquid nitrogen bath and allyl(chloro)dimethylsilane (1.1 eq.) added dropwise. Immediately after addition, *t*BuLi (1.1 equiv.) was slowly added dropwise, over a period of 10 minutes. After addition, the solution was left stirring for additional 10 minutes at -78 °C and then slowly warmed to room temperature for one hour. The reaction was quenched with 30 mL of saturated aqueous $NaHCO_3$ and transferred to an extraction funnel. The phases were allowed to separate and the top organic phase collected. The aqueous phase was extracted with Et_2O (2 × 30 mL) and the organic phases combined, dried over $MgSO_4$ and filtered. The solvent was evaporated and the resulting crude oil purified through silica chromatography (hexane/ethyl acetate mixture as eluent) to give silyl derivatives **2** as yellow tainted clear oils.



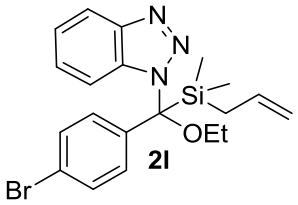
2a

2a: Method A with *n*BuLi as base. 86% yield (1.517 g, 4.3 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (95:5). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.06 (d, J = 8.3 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.19 (t, J = 7.6 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.93 (d, J = 8.3 Hz, 1H), 5.82 – 5.67 (m, 1H), 4.90 – 4.84 (m, 2H), 3.56 – 3.46 (m, 1H), 3.28 – 3.18 (m, 1H), 1.81 (t, J = 8.1 Hz, 2H), 1.12 (t, J = 6.9 Hz, 3H), 0.30 (s, 3H), 0.25 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 146.5, 139.7, 134.5, 132.9, 128.2, 127.7, 127.1, 126.4, 124.2, 120.0, 114.2, 113.3, 93.7, 61.2, 22.5, 15.5, -3.0, -3.1.



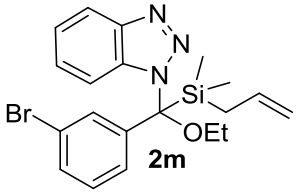
2k

2k: Method B. 71% yield (1.362 g, 3.6 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (92:8). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.05 (dt, *J* = 8.3, 0.8 Hz, 1H), 7.31 – 7.28 (m, 1.0 Hz, 1H), 7.21 – 7.18 (m, 1H), 6.98 – 6.96 (m, 1H), 6.91 (d, J = 8.2 Hz, 2H), 6.81 – 6.80 (m, 2H), 5.75 (ddt, J = 16.7, 10.1, 8.2 Hz, 1H), 4.90 – 4.85 (m, 2H), 3.79 (s, 3H), 3.53 – 3.45 (m, 1H), 3.22 – 3.16 (m, 1H), 1.85 – 1.75 (m, 2H), 1.10 (t, J = 6.9 Hz, 3H), 0.29 (s, 3H), 0.24 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 159.0, 146.5, 134.6, 132.8, 131.7, 127.6, 127.0, 124.2, 119.9, 114.1, 113.4, 113.4, 93.6, 61.1, 55.3, 22.5, 15.6, -3.0, -3.1.



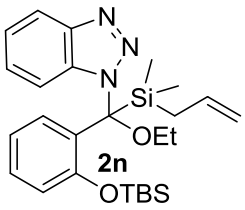
2l

2l: Method A with LDA as base. 87% yield (1.862 g, 4.3 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.07– 8.05 (m, 1H), 7.41 – 7.40 (m, 2H), 7.33 – 7.30 (m, 1H), 7.25 –7.21 (m, 1H), 6.97 (dt, J = 8.3, 0.9 Hz, 1H), 6.88 (d, J = 7.8 Hz, 2H), 5.79 – 5.70 (m, 1H), 4.91 – 4.87 (m, 2H), 3.55 (dq, J = 8.6, 6.9 Hz, 1H), 3.16 (dq, J = 8.6, 7.1 Hz, 1H), 1.85 – 1.74 (m, 2H), 1.11 (t, J = 6.9 Hz, 3H), 0.29 (s, 3H), 0.25 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 146.6, 139.1, 134.1, 132.5, 131.3, 128.1, 127.4, 124.4, 121.8, 120.1, 114.5, 113.0, 93.4, 61.4, 22.4, 15.5, -3.1, -3.1.



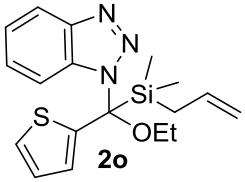
2m

2m: Method A with LDA as base. 89% yield (1.910 g, 4.4 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.07 (d, J = 8.4 Hz, 1H), 7.41–7.40 (m, 2H), 7.34 – 7.31 (m, 1H), 7.26 – 7.23 (m, 1H), 7.10 (t, J = 8.1 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.70 (d, J = 7.9 Hz, 1H), 5.79 – 5.71 (m, 1H), 4.92 – 4.88 (m, 2H), 3.56 (dq, J = 8.7, 6.9 Hz, 1H), 3.15 (dq, J = 8.7, 7.0 Hz, 1H), 1.86 – 1.76 (m, 2H), 1.13 (t, J = 6.9 Hz, 3H), 0.31 (s, 3H), 0.27 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 146.5, 142.3, 134.0, 132.5, 130.8, 129.7, 129.3, 127.4, 124.9, 124.4, 122.6, 120.1, 114.6, 113.0, 93.1, 61.4, 22.4, 15.5, -3.0, -3.1.



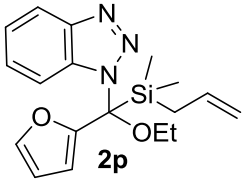
2n

2n: Method B. 75% yield (1.817 g, 3.8 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (96:4). Column chromatography yielded the compound with only 80% purity, which was used as such in the next synthetic step. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.04 – 8.01 (m, 1H), 7.71 – 7.69 (m, 1H), 7.27 – 7.08 (m, 6H), 5.80 – 5.72 (m, 1H), 4.89 – 4.83(m, 2H), 3.18 (dq, J = 8.6, 6.9 Hz, 1H), 2.97 (dq, J = 8.7, 6.9 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.02 (t, J = 6.9 Hz, 3H), 0.56 (s, 9H), 0.32 (s, 3H), 0.25 (s, 3H), -0.32 (s, 3H), -0.45 (s, 3H).



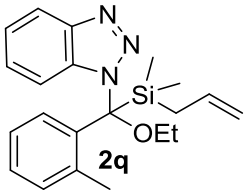
2o

2o: Method B. 79% yield (1.418 g, 4.0 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.06 (dt, J = 8.3, 1.0 Hz, 1H), 7.34 – 7.25 (m, 3H), 7.11 (dt, J = 8.3, 1.0 Hz, 1H), 6.90 (dd, J = 5.1, 3.7 Hz, 1H), 6.38 (dd, J = 3.6, 1.2 Hz, 1H), 5.82 – 5.73(m, 1H), 4.93 – 4.87 (m, 2H), 3.56 (dq, J = 8.6, 6.9 Hz, 1H), 3.21 (dq, J = 8.6, 7.0 Hz, 1H), 1.91 (dd, J = 13.5, 8.0 Hz, 1H), 1.83 (dd, J = 13.5, 8.3 Hz, 1H), 1.10 (t, J = 7.0 Hz, 3H), 0.38 (s, 3H), 0.33 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 146.4, 144.2, 134.3, 132.7, 127.3, 127.0, 125.2, 124.4, 124.3, 120.0, 114.3, 113.1, 92.3, 61.7, 22.5, 15.5, -3.0.



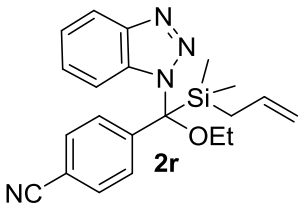
2p

2p: Method B. 77% yield (1.321 g, 3,9 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.08 – 8.02 (m, 1H), 7.35 – 7.28 (m, 3H), 6.93 – 6.87 (m, 1H), 6.46 (dd, J = 3.3, 1.8 Hz, 1H), 6.38 (dd, J = 3.3, 0.7 Hz, 1H), 5.84 – 5.70 (m, 1H), 4.93 – 4.84 (m, 2H), 3.46 (dq, J = 8.6, 7.0 Hz, 1H), 3.31 (dq, J = 8.7, 6.9 Hz, 1H), 1.90 – 1.76 (m, 2H), 1.06 (t, J = 7.0 Hz, 3H), 0.30 (s, 3H), 0.25 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 151.8, 146.1, 142.5, 134.4, 134.0, 127.6, 124.1, 120.0, 114.1, 112.2, 110.9, 108.6, 89.8, 61.3, 22.3, 15.5, -3.5, -3.6.



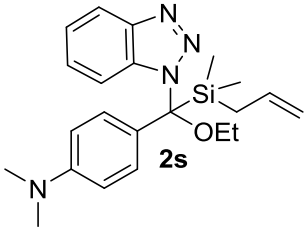
2q

2q: Method B. 79% yield (1.439 g, 3,9 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.05 (d, J = 8.3 Hz, 1H), 7.32 – 7.15 (m, 5H), 7.01 (d, J = 7.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 5.83 – 5.69 (m, 1H), 4.91 – 4.85 (m, 2H), 3.40 – 3.11 (m, 1H), 3.21 – 3.11 (m, 1H), 1.96 – 1.80 (m, 2H), 1.09 (t, J = 6.9 Hz, 3H), 0.34 (s, 3H), 0.27 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 146.3, 136.7, 135.2, 134.7, 133.8, 132.8, 128.1, 127.7, 127.3, 125.9, 124.2, 120.0, 114.2, 112.5, 60.8, 23.0, 15.4, -2.3, -x\2.6.



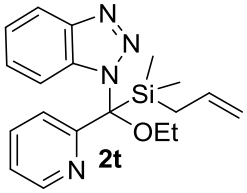
2r

2r: Method A with *t*BuLi as base. 80% yield (1.508 g, 4.0 mmol) as yellow tainted oil. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.08 (dt, J = 8.3, 1.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.36 – 7.21 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.91 (dt, J = 8.2, 1.0 Hz, 1H), 5.80 – 5.65 (m, 1H), 4.91 – 4.86 (m, 2H), 3.61 (dq, J = 8.6, 6.9 Hz, 1H), 3.16 (dq, J = 8.6, 7.0 Hz, 1H), 1.86 – 1.73 (m, 2H), 1.14 (t, J = 6.9 Hz, 3H), 0.30 (s, 3H), 0.26 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 146.5, 145.4, 133.5, 132.2, 131.9, 127.5, 126.9, 124.5, 120.2, 118.5, 114.8, 112.4, 111.6, 93.3, 61.5, 22.2, 15.4, -3.1, -3.2.



2s

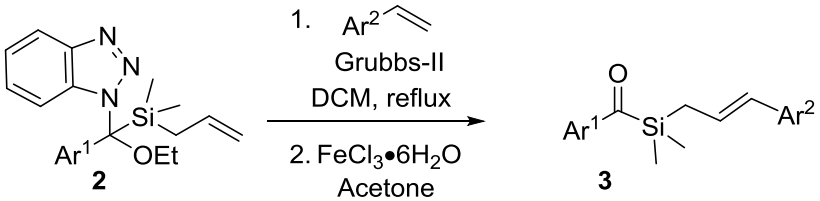
2s: Method B. 80% yield (1.578 g, 4.0 mmol) as yellow tainted oil. Column eluent hexane/ethyl acetate/Et_3N (93:5:2). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.03 (d, J = 8.3 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.21 – 7.15 (m, 1H), 7.00 (d, J = 8.3 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 9.2 Hz, 2H), 5.86 – 5.70 (m, 1H), 4.90 – 4.83 (m, 2H), 3.50 – 3.41 (m, 1H), 3.30 – 3.16 (m, 1H), 2.93 (s, 6H), 1.88 – 1.76 (m, 2H), 1.09 (t, J = 6.9 Hz, 3H), 0.29 (s, 3H), 0.24 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 149.8, 146.5, 134.9, 133.0, 127.2, 126.9, 126.8, 124.0, 119.8, 113.8, 113.8, 111.8, 93.8, 61.0, 40.5, 27.1, 22.6, 15.6, -3.0, -3.1.



2t

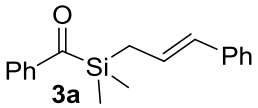
2t: Method A with *n*BuLi as base. 65% yield (1.143 g, 3.2 mmol) as a brown amorphous solid. Column eluent hexane/ethyl acetate/Et_3N (90:8:2). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.42 – 8.39 (m, 1H), 8.04 (dt, J = 8.3, 1.0 Hz, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.67 (dt, J = 8.0, 1.0 Hz, 1H), 7.28 – 7.11 (m, 3H), 6.58 (d, J = 8.3 Hz, 1H), 5.81 – 5.67 (m, 1H), 4.90 – 4.82 (m, 2H), 3.43 (dq, J = 8.8, 7.3 Hz, 1H), 3.27 (dq, J = 8.8, 7.0 Hz, 1H), 1.92 – 1.77 (m, 2H), 1.10 (t, J = 7.0 Hz, 3H), 0.28 (s, 3H), 0.27 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 158.8, 149.2, 146.3, 136.4, 134.5, 133.3, 127.0, 123.8, 122.5, 121.6, 120.1, 114.1, 112.4, 93.5, 61.3, 22.5, 15.6, -3.1, -3.2.

Synthesis of aroylsilanes 3:



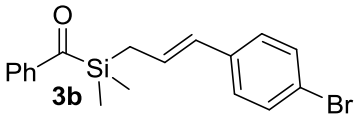
Silyl derivative **2** (1 mmol) was dissolved in 6 mL of dry DCM, in an argon filled round-bottom flask. The substituted styrene (5 mmol, 5 equiv.) was added to the solution, followed by 2nd generation Grubbs catalyst (1-5 mol %). The solution was refluxed overnight. The solvent was evaporated and 10 mL of hexane/ethyl acetate (9:1) mixture was added. The suspension was stirred for 10 minutes and filtered through cotton. The off-white solid, mostly composed by undesired stilbene, was

washed two more times with hexane/ethyl acetate (9:1) mixture (10 mL) and filtered again. The filtrate was combined and the solvents evaporated. The crude was passed through a small silica column (hexane/ethyl acetate mixture as eluent) to remove the remaining stilbene (highly mobile on silica). $FeCl_3 \bullet 6H_2O$ (0.3 mmol, 0.3 equiv.) was added in one portion to an acetone solution (6 mL) of the resulting crude oil. The solution was stirred for 30 minutes and the solvent evaporated under reduced pressure. Hexane (6 mL) was added and the solution stirred for 10 minutes. The bright yellow liquid was filtered through cotton and the reaction flask washed with hexane (2 x 6 mL) and filtered. The filtrate was combined and the hexane evaporated to give bright yellow oil as crude, which was purified through silica chromatography (hexane/ethyl acetate mixture as eluent) to give aroylsilanes **3** as bright yellow clear oils.



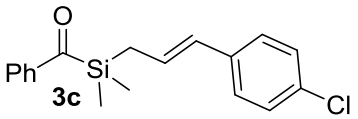
3a

3a: 53% yield (154 mg, 0.53 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.84 – 7.81 (m, 2H), 7.57 – 7.44 (m, 3H), 7.26 – 7.25 (m, 4H), 7.20 – 7.13 (m, 1H), 6.31 – 6.14 (m, 2H), 2.02 (d, J = 7.0 Hz, 2H), 0.42 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 234.7, 141.7, 138.1, 133.0, 130.1, 128.9, 128.6, 127.8, 126.7, 125.8, 125.8, 21.8, -2.9. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{21}OSi^+$ $[M+H]^+$ 281.1356, found 281.1362.



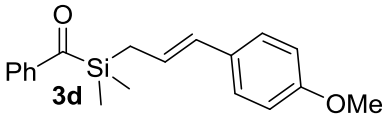
3b

3b: 55% yield (198 mg, 0.55 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (97:3). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.84 – 7.80 (m, 2H), 7.58 – 7.44 (m, 3H), 7.39 – 7.34 (m, 2H), 7.12 – 7.08 (m, 2H), 6.21 – 6.18 (m, 2H), 2.01 (dd, J = 4.8, 2.1 Hz, 2H), 0.42 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 234.5, 141.6, 137.0, 133.1, 131.6, 128.9, 128.8, 127.7, 127.3, 126.8, 120.3, 21.9, -2.8. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{20}BrOSi^+$ $[M+H]^+$ 359.0461, found 359.0451.



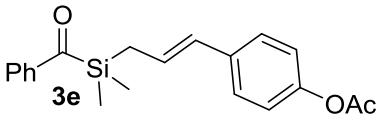
3c

3c: 83% yield (261 mg, 0.83 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (97:3). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.83 – 7.80 (m, 2H), 7.58 – 7.44 (m, 3H), 7.23 – 7.14 (m, 4H), 6.25 – 6.12 (m, 2H), 2.02 – 2.00 (m, 2H), 0.43 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 234.5, 141.6, 136.5, 133.1, 132.2, 128.9, 128.8, 128.7, 127.7, 127.0, 126.7, 21.9, -2.9. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{20}ClOSi^+$ $[M+H]^+$ 315.0966, found 315.0970.



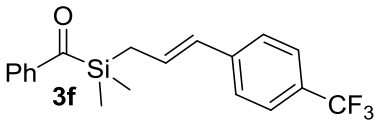
3d

3d: 30% yield (93 mg, 0.3 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (95:5). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.84 – 7.81 (m, 2H), 7.54 – 7.44 (m, 3H), 7.20 – 7.17 (m, 2H), 6.82 – 6.79 (m, 2H), 6.22 (d, J = 15.8 Hz, 1H), 6.04 (dt, J = 15.8, 8.1 Hz, 1H), 3.78 (s, 3H), 1.99 (d, J = 8.0 Hz, 2H), 0.41 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 235.1, 158.7, 141.8, 133.1, 131.1, 129.6, 129.0, 127.8, 127.0, 123.5, 114.1, 55.5, 21.7, -2.8. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{23}O_2Si^+$ $[M+H]^+$ 311.1462, found 311.1464.



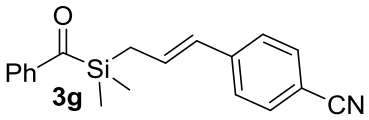
3e

3e: 26% yield (89 mg, 0.26 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (85:15). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.84 – 7.80 (m, 2H), 7.58 – 7.44 (m, 3H), 7.27 – 7.22 (m, 2H), 7.00 – 6.95 (m, 2H), 6.28 – 6.09 (m, 2H), 2.28 (s, 3H), 2.01 (d, J = 7.2 Hz, 2H), 0.42 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 234.6, 169.7, 149.4, 141.6, 135.9, 133.0, 129.0, 128.9, 127.7, 126.7, 126.1, 121.6, 21.8, 21.3, -2.9. **HR-MS** (ESI) *m/z* calculated for $C_{20}H_{23}O_3Si^+$ $[M+H]^+$ 339.1411, found 339.1423.



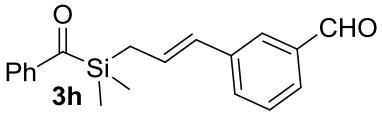
3f

3f: 47% yield (163 mg, 0.47 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (92:8). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.83 – 7.81 (m, 2H), 7.57 – 7.54 (m, 1H), 7.51 – 7.47 (m, 4H), 7.33 – 7.32 (d, J = 7.7 Hz, 2H), 6.37 – 6.27 (m, 2H), 2.06 (d, J = 7.2 Hz, 2H), 0.44 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 234.4, 141.6, 141.5, 133.2, 129.0, 128.9, 128.7, 127.7, 125.8, 125.6, 125.6, 125.5, 125.5, 22.1, -2.8. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{20}F_3OSi^+$ $[M+H]^+$ 349.4477, found 349.4470.



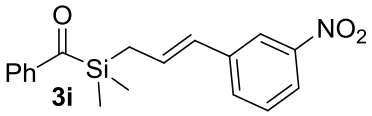
3g

3g: 7% yield (22 mg, 0.07 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (90:10). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.82 – 7.80 (m, 2H), 7.57 – 7.46 (m, 5H), 7.30 (d, J = 8.3 Hz, 2H), 6.38 (dt, J = 16.3, 8.2 Hz, 1H), 6.26 (d, J = 15.7 Hz, 1H), 2.07 (dd, J = 8.2, 0.8 Hz, 2H), 0.44 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 234.1, 142.5, 141.5, 133.2, 132.4, 130.7, 128.9, 128.4, 127.6, 126.1, 119.3, 109.7, 22.4, -2.8. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{20}NOSi^+$ $[M+H]^+$ 306.1309, found 306.1315.



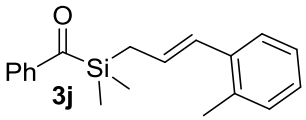
3h

3h: 43% yield (132 mg, 0.43 mmol), bright yellow oil. 1 mol% of G-II used. Gradient column eluent hexane/ethyl acetate (98:2 to 85:15). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 9.98 (s, 1H), 7.84 – 7.39 (m, 10H), 6.34 – 6.31 (m, 2H), 2.07 – 2.05 (m, 2H), 0.44 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 234.4, 192.6, 141.6, 139.0, 136.8, 133.1, 131.7, 129.3, 128.9, 128.6, 128.1, 128.0, 127. 7, 126.7, 22.0, -2.8. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{21}O_2Si^+$ $[M+H]^+$ 309.1305, found 309.1310.



3i

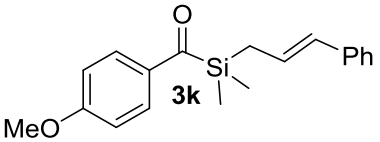
3i: 26% yield (84 mg, 0.26 mmol), bright yellow oil. 1 mol% of G-II used. Gradient column eluent hexane/ethyl acetate (90:10 to 85:15). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.06 (t, J = 1.9 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.84 – 7.81 (m, 2H), 7.58 – 7.38 (m, 5H), 6.43 – 6.26 (m, 2H), 2.07 (d, J = 7.2 Hz, 2H), 0.45 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 234.1, 148.7, 141.6, 139.8, 133.2, 131.6, 129.7, 129.4, 128.9, 127.8, 127.7, 121.3, 120.3, 22.1, -2.7. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{20}NO_3Si^+$ $[M+H]^+$ 326.1207, found 326.1192.



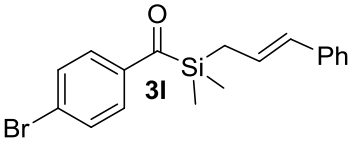
3j

3j: 45% yield (133 mg, 0.45 mmol), bright yellow oil. 1 mol% of G-II used. Column eluent hexane/ethyl acetate (97:3). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.86 – 7.83 (m, 2H), 7.58 – 7.45 (m, 3H), 7.32 – 7.29 (m, 1H), 7.15 – 7.09 (m, 3H), 6.46 (d, J = 15.6 Hz, 1H), 6.07 (dt, J = 15.7, 8.2 Hz, 1H), 2.25 (s, 3H), 2.06 (dd, J = 8.2, 1.2 Hz, 2H), 0.44 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 234.7, 141.7, 137.3,

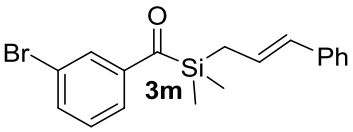
134.7, 133.0, 130.2, 128.9, 128.1, 127.7, 127.0, 126.7, 126.1, 125.4, 22.2, 20.0, -2.9. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{23}OSi^+$ $[M+H]^+$ 295.1513, found 295.1512.



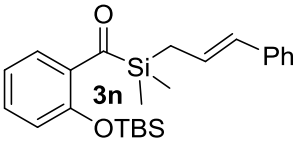
3k: 53% yield (164 mg, 0.53 mmol), pale yellow oil. 1.5 mol% of G-II used. Column eluent hexane/ethyl acetate (94:6). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.84 (dd, J = 8.7, 1.5 Hz, 2H), 7.26 (d, J = 4.2 Hz, 4H), 7.18 – 7.15 (m, 1H), 6.95 (dd, J = 8.6, 1.4 Hz, 2H), 6.30 – 6.18 (m, 2H), 3.87 (s, 3H), 2.01 (d, J = 7.7 Hz, 2H), 0.41 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 231.8, 163.5, 138.1, 135.5, 130.1, 129.9, 128.6, 126.7, 126.0, 125.8, 114.0, 55.6, 21.9, -2.8. **HR-MS** (ESI) *m/z* calculated for $C1_9H_{23}O_2Si^+$ $[M+H]^+$ 311.1462, found 311.1449.



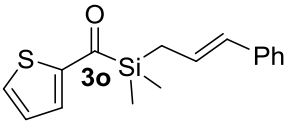
3l: 46% yield (164 mg, 0.46 mmol), bright yellow oil. 2 mol% of G-II used. Column eluent hexane/ethyl acetate (97:3). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.69 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.29 – 7.24 (m, 4H), 7.19 – 7.16 (m, 1H), 6.27 (d, J = 15.8 Hz, 1H), 6.18 (dt, J = 15.8, 8.0 Hz, 1H), 2.01 (d, J = 8.0 Hz, 2H), 0.42 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 233.6, 140.2, 137.9, 132.2, 130.2, 129.1, 128.6, 128.2, 126.8, 125.8, 125.4, 21.7, -3.0. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{20}BrOSi^+$ $[M+H]^+$ 359.0461, found 359.0474.



3m: 37% yield (132 mg, 0.37 mmol), bright yellow oil. 2 mol% of G-II used. Column eluent hexane/ethyl acetate (97:3). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.91 (s, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.19 – 7.15 (m, 1H), 6.28 (d, J = 15.8 Hz, 1H), 6.18 (dt, J = 15.8, 8.0 Hz, 1H), 2.01 (d, J = 8.0 Hz, 2H), 0.42 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 233.5, 143.1, 137.9, 135.8, 130.5, 130.3, 130.2, 128.6, 126.8, 126.7, 125.8, 125.3, 123.5, 21.6, -3.0. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{20}BrOSi^+$ $[M+H]^+$ 359.0461, found 359.0483.

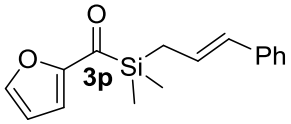


3n: 42% yield (171 mg, 0.42 mmol), bright yellow oil. 2 mol% of G-II used. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.29 – 7.22 (m, 5H), 7.17 – 7.11 (m, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.21 (d, J = 15.7 Hz, 1H), 6.12 (dt, J = 15.8, 8.0 Hz, 1H), 1.92 (d, J = 7.9 Hz, 2H), 0.95 (s, 9H), 0.29 (s, 3H), 0.20 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 241.8, 152.6, 138.2, 137.7, 131.5, 129.7, 128.5, 127.3, 126.6, 125.9, 125.8, 121.4, 120.6, 26.0, 21.3, 18.7, -3.8, -4.0. **HR-MS** (ESI) *m/z* calculated for $C_{24}H_{35}O_2Si_2^+$ $[M+H]^+$ 411.2170, found 411.2169.

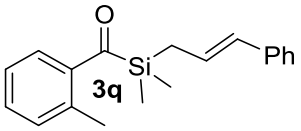


3o: 36% yield (106 mg, 0.36 mmol), bright yellow oil. 2 mol% of G-II used. Column eluent hexane/ethyl acetate (97:3). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.75 – 7.74 (m, 1H), 7.66 – 7.65 (m, 1H), 7.27 (d, J = 4.3 Hz, 4H), 7.18 – 7.14 (m, 2H), 6.30 (d, J = 15.7 Hz, 1H), 6.21 (dt, J = 15.8, 7.9 Hz, 1H),

2.02 (d, J = 7.9 Hz, 2H), 0.43 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 223.5, 150.9, 138.0, 133.5, 133.2, 130.1, 128.6, 128.4, 126.7, 125.8, 125.5, 21.5, -3.3. **HR-MS** (ESI) *m/z* calculated for $C_{16}H_{19}OSSi^+$ $[M+H]^+$ 287.0920, found 287.0918.

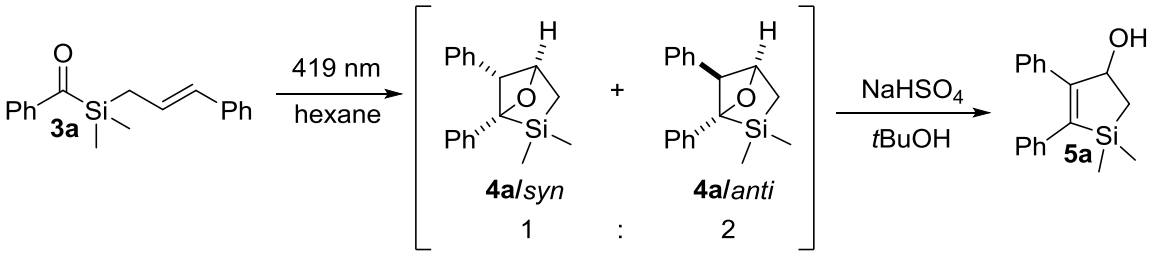


3p: 39% yield (105, 0.39 mmol), bright yellow oil. 5 mol% of G-II used. Column eluent hexane/ethyl acetate (96:4). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.61 – 7.60 (m, 1H), 7.27 (d, J = 4.0 Hz, 4H), 7.20 – 7.13 (m, 1H), 7.09 (dt, J = 3.6, 0.7 Hz, 1H), 6.54 (ddd, J = 3.6, 1.7, 0.7 Hz, 1H), 6.32 – 6.15 (m, 2H), 2.02 (d, J = 7.6 Hz, 2H), 0.39 (d, J = 0.7 Hz, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 220.2, 158.4, 146.3, 138.1, 129.9, 128.6, 126.7, 125.7, 125.6, 115.0, 112.3, 21.0, -4.1. **HR-MS** (ESI) *m/z* calculated for $C_{16}H_{19}O_2Si^+$ $[M+H]^+$ 271.1149, found 271.1143.



3q: 59% yield (175 mg, 0.59 mmol), bright yellow oil. 2 mol% of G-II used. Column eluent hexane/ethyl acetate (98:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.57 (dd, J = 7.5, 1.2 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.30 – 7.22 (m, 6H), 7.18 – 7.14 (m, 1H), 6.25 – 6.13 (m, 2H), 2.40 (s, 3H), 1.97 (d, J = 7.5 Hz, 2H), 0.36 (s, 6H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 241.1, 142.1, 138.1, 135.9, 132.2, 130.9, 129.9, 129.8, 128.6, 126.7, 125.7, 125.7, 125.6, 21.6, 20.7, -3.2. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{23}OSi^+$ $[M+H]^+$ 295.1513, found 295.1527.

Irradiation of acylsilane 3a:

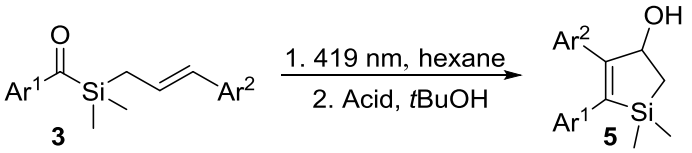


Acylsilane **3a** (81 mg, 0.29 mmol) was dissolved in dry hexane (7 mL) under argon atmosphere, in a glass test tube. The solution was degassed with argon (until a final volume of 6 mL) and then irradiated for 5 hours. During this time the solution's bright yellow colour disappeared to give a colourless liquid. The solution was transferred to a round-bottom flask and the hexane evaporated under reduced pressure. NMR analysis of the crude at this stage showed the presence of **4a** as a 1:2 mixture of diastereoisomers. **4a/*syn***: **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.60 – 6.88 (m, 10H), 5.17 (t, J = 4.8 Hz, 1H), 4.32 (d, J = 5.1 Hz, 1H), 1.53 –1.28 (m, 2H), 0.20 (s, 3H), -0.06 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 141.9, 138.2, 128.7, 128.2, 127.6, 127.4, 126.8, 126.6, 94.1, 81.2, 59.19, 19.7, -1.7, -3.4. **4a/*anti***: **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.39 – 6.86 (m, 10H), 4.97 (d, J = 4.3 Hz, 1H), 3.54 (s, 1H), 1.65 (dd, J = 14.0, 4.3 Hz, 1H), 1.43 (d, J = 14.0 Hz, 1H), 0.54 (s, 3H), 0.22 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 140.4, 138.4, 128.8, 128.1, 127.9, 126.6, 125.2, 123.2, 93.4, 84.3, 60.3, 23.3, -3.0, -4.8.

The oily crude was solubilized in *t*butanol (6 mL) at 27 °C, followed by addition of $NaHSO_4$ (0.03 mmol, 0.1 equiv.) and stirring at that temperature for 6 hours. The reaction was quenched with saturated aqueous K_2CO_3 (10 mL) and the product extracted with ethyl acetate (3 × 10 mL). The organic phases were combined, dried over $MgSO_4$ and filtered. The solvent was evaporated and the

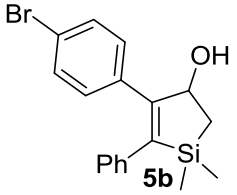
product isolated through silica column chromatography using hexane/ethyl acetate/Et_3N (90:8:2) and eluent, to give silacyclopentenol **5a** as an amorphous solid in 82% yield (66.1 mg, 0.236 mmol). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.24 – 7.04 (m, 8H), 6.91 – 6.89 (m, 2H), 5.26 (dd, J = 7.6, 4.9 Hz, 1H), 1.81 (s, 1H), 1.61 (dd, J = 14.9, 7.7 Hz, 1H), 1.08 – 0.99 (m, 1H), 0.44 (s, 3H), 0.17 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 157.2, 144.2, 140.5, 138.2, 129.1, 128.4, 128.2, 128.1, 127.3, 125.7, 77.3, 21.2, 0.1, -2.2. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{19}OSi^+$ $[M]^+$ 279.1200, found 279.1213.

Synthesis of silacyclopentenols 5:

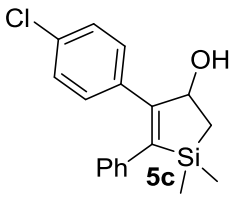


Acylsilane **3** (0.3 mmol) was dissolved in dry hexane (7 mL) under argon atmosphere, in a glass test tube. The solution was degassed with argon (until a final volume of 6 mL) and then irradiated for 5 hours. The solution was transferred to a round-bottom flask and the hexane evaporated under reduced pressure. The residue was solubilized in *t*butanol (6 mL) at 27 °C, followed by addition of $NaHSO_4$ or pyridinium *p*-toluenesulfonate (0.03 mmol, 0.1 equiv.) and stirring at that temperature for 6 hours. The reaction was quenched with saturated aqueous K_2CO_3 (10 mL) and the product extracted with ethyl acetate (3 × 10 mL). The organic phases were combined, dried over $MgSO_4$ and filtered. The solvent was evaporated and the product isolated through silica column chromatography to give silacyclopentenols **5**.

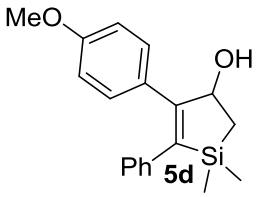
Note: Some reactions were performed in different scale due to availability of starting material **3**.



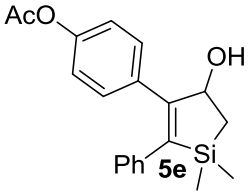
5b: 73% yield (79.0 mg, 0.220 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (82:10:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.34 – 7.31 (m, 2H), 7.17 (ddd, J = 7.5, 6.4, 1.2 Hz, 2H), 7.12 – 7.09 (m, 1H), 7.03 – 7.00 (m, 2H), 6.89 – 6.87 (m, 2H), 5.23 (dt, J = 8.0, 4.4 Hz, 1H), 1.73 (d, J = 4.2 Hz, 1H), 1.62 (dd, J = 14.9, 7.7 Hz, 1H), 1.01 (dd, J = 14.9, 4.9 Hz, 1H), 0.43 (s, 3H), 0.17 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.8, 145.4, 140.1, 137.1, 131.5, 130.8, 128.4, 127.9, 125.9, 121.4, 77.2, 21.6, 0.0, -2.2. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{18}BrOSi^+$ $[M]^+$ 357.0305, found 357.0297.



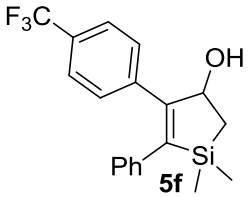
5c: 63% yield (59.2 mg, 0.183 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (90:8:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.19 – 7.16 (m, 4H), 7.12 – 7.06 (m, 3H), 6.89 – 6.87 (m, 2H), 5.24 – 5.23 (m, 1H), 1.74 – 1.73 (m, 1H), 1.63 (dd, J = 14.9, 7.6 Hz, 1H), 1.01 (dd, J = 15.1, 4.8 Hz, 1H), 0.43 (s, 3H), 0.17 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.8, 145.3, 140.2, 136.6, 133.1, 130.5, 128.5, 128.4, 127.9, 125.9, 77.2, 21.6, 0.0, -2.2. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{18}ClOSi^+$ $[M]^+$ 313.0810, found 313.0803.



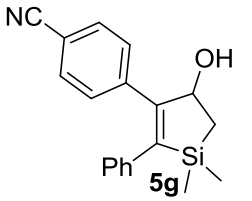
5d: 60% yield (53.1 mg, 0.171 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (86:12:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.18 – 7.15 (m, 2H), 7.10 – 7.06 (m, 3H), 6.92 – 6.91 (m, 2H), 6.76 – 6.73 (m, 2H), 5.27 – 5.24 (m, 1H), 3.75 (s, 3H), 1.81 (s, 1H), 1.60 (dd, *J* = 14.9, 7.7 Hz, 1H), 1.01 (dd, J = 15.0, 4.9 Hz, 1H), 0.43 (s, 3H), 0.15 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 158.8, 156.5, 143.2, 140.8, 130.4, 130.1, 128.3, 128.1, 125.6, 113.8, 77.1, 55.3, 21.1, 0.2, -2.2. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{21}O_2Si^+$ $[M]^+$ 309.1305, found 309.1318.



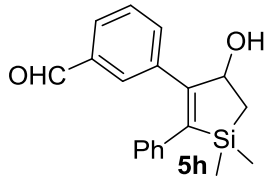
5e: 71% yield (72.5 mg, 0.214 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (78:20:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.17 – 7.14 (m, 4H), 7.10 – 7.07 (m, 1H), 6.95 – 6.93 (m, 2H), 6.90 – 6.88 (m, 2H), 5.24 (dd, J = 7.6, 4.8 Hz, 1H), 2.26 (s, 3H), 1.82 (s, 1H), 1.60 (dd, J = 14.9, 7.7 Hz, 1H), 1.02 (dd, J = 14.9, 4.7 Hz, 1H), 0.42 (s, 3H), 0.17 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 169.4, 156.0, 149.8, 144.8, 140.3, 135.7, 130.2, 128.3, 128.0, 125.8, 121.4, 77.3, 21.3, 21.3, 0.0, -2.1. **HR-MS** (ESI) *m/z* calculated for $C_{20}H_{21}O_3Si^+$ $[M]^+$ 337.1254, found 279.1268.



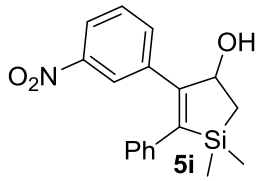
5f: 79% yield (83.1 mg, 0.239 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (83:15:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.45 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.12 – 7.09 (m, 1H), 6.88 – 6.86 (m, 2H), 5.28 (dt, J = 7.7, 4.6 Hz, 1H), 1.71 (d, J = 4.6 Hz, 1H), 1.66 (dd, J = 14.9, 7.6 Hz, 1H), 1.03 (dd, J = 14.9, 4.9 Hz, 1H), 0.44 (s, 3H), 0.19 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.6, 146.5, 142.2, 139.8, 129.5, 128.4, 127.9, 126.1, 125.2, 125.2, 125.2, 125.1, 77.3, 21.9, -0.1, -2.2. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{18}F_3OSi^+$ $[M]^+$ 347.1074, found 347.1060.



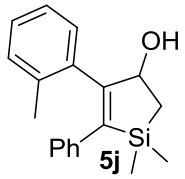
5g: 64% yield (14.3 mg, 0.047 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (68:30:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.47 – 7.45 (m, 2H), 7.25 – 7.22 (m, 2H), 7.18 – 7.09 (m, 3H), 6.84 – 6.83 (m, 2H), 5.25 (dd, J = 7.4, 5.0 Hz, 1H), 1.69 (s, 1H), 1.66 (dd, J = 14.9, 7.6 Hz, 1H), 1.02 (dd, J = 14.9, 4.9 Hz, 1H), 0.42 (s, 3H), 0.18 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.1, 147.6, 143.6, 139.6, 131.9, 129.9, 128.5, 127.8, 126.3, 119.1, 110.7, 77.1, 22.2, -0.2, -2.3. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{18}NOSi^+$ $[M]^+$ 304.1152, found 304.1151.



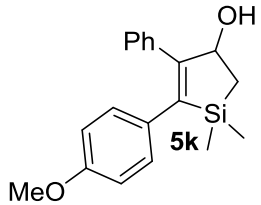
5h: 84% yield (78.0 mg, 0.252 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (78:20:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 9.86 (s, 1H), 7.69 – 7.67 (m, 2H), 7.37 – 7.1 (m, 2H), 7.17 – 7.13 (m, 2H), 7.10 – 7.07 (m, 1H), 6.90 – 6.85 (m, 2H), 5.34 – 5.29 (m, 1H), 1.84 (s, 1H), 1.67 (dd, J = 14.9, 7.6 Hz, 1H), 1.04 (dd, J = 14.9, 4.9 Hz, 1H), 0.44 (s, 3H), 0.20 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 192.4, 155.6, 146.2, 139.9, 139.4, 136.3, 135.6, 130.5, 128.9, 128.4, 128.3, 127.9, 126.0, 77.2, 21.9, -0.1, -2.2. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{19}O_2Si^+$ $[M]^+$ 307.1149, found 307.1160.



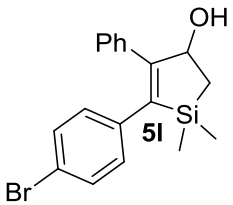
5i: 73% yield (62.4 mg, 0.192 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (73:15:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.08 – 8.07 (m, 1H), 8.01 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 7.42 – 7.40 (m, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.19 – 7.16 (m, 2H), 7.12 – 7.09 (m, 1H), 6.88 – 6.86 (m, 2H), 5.31 (dd, J = 7.5, 4.8 Hz, 1H), 1.78 (s, 1H), 1.69 (dd, J = 14.9, 7.6 Hz, 1H), 1.05 (dd, J = 14.9, 4.9 Hz, 1H), 0.44 (s, 3H), 0.21 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 154.4, 148.1, 147.6, 140.2, 139.5, 135.7, 128.9, 128.6, 127.8, 126.3, 123.9, 122.1, 77.1, 22.3, -0.3, -2.3. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{19}NO_3Si^-$ $[M]^-$ 325.1140, found 325.1136.



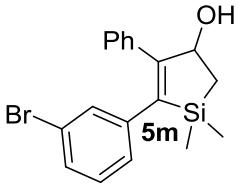
5j: 61% yield (53.5 mg, 0.182 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (90:8:2). **^{1}H NMR** (C_6D_6, 500 MHz) δ 7.07 (dd, J = 8.2, 1.2 Hz, 2H), 7.00 – 6.96 (m, 4H), 6.92 (d, J = 7.8 Hz, 1H), 6.86 – 6.84 (m, 1H), 4.87 (s, 1H), 2.03 (s, 3H), 1.42 (dd, J = 14.8, 7.5 Hz, 2H), 1.10 (dd, J = 14.8, 4.9 Hz, 1H), 0.36 (s, 3H), 0.16 (s, 3H). **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{21}OSi^+$ $[M]^+$ 293.1356, found 293.1344.



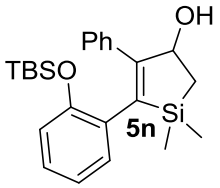
5k: 58% yield (53.8 mg, 0.172 mmol) as an amorphous solid. Pyridinium *p*-toluenesulfonate used as acid. Column eluent hexane/ethyl acetate/Et_3N (83:15:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.25 – 7.14 (m, 5H), 6.85 – 6.82 (m, 2H), 6.70 – 6.67 (m, 2H), 5.25 – 5.21 (m, 1H), 3.73 (s, 3H), 1.79 (d, J = 4.0 Hz, 1H), 1.59 (dd, J = 14.9, 7.7 Hz, 1H), 1.00 (dd, J = 14.9, 4.9 Hz, 1H), 0.45 (s, 3H), 0.18 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 157.7, 156.4, 143.2, 138.5, 132.5, 129.4, 129.1, 128.5, 127.3, 113.7, 77.4, 55.2, 21.1, 0.3, -2.1. **HR-MS** (ESI) *m/z* calculated for $C_{19}H_{21}O_2Si^+$ $[M]^+$ 309.1305, found 309.1295.



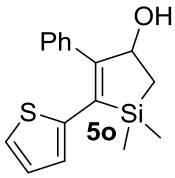
5l: 69% yield (74.3 mg, 0.207 mmol) as an amorphous solid. Pyridinium *p*-toluenesulfonate used as acid. Column eluent hexane/ethyl acetate/Et_3N (84:14:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.26 – 7.17 (m, 5H), 7.11 – 7.09 (m, 2H), 6.77 – 6.74 (m, 2H), 5.24 – 5.21 (m, 1H), 1.79 (d, J = 3.8 Hz, 1H), 1.60 (dd, J = 14.9, 7.7 Hz, 1H), 1.01 (dd, J = 14.9, 4.9 Hz, 1H), 0.41 (s, 3H), 0.15 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 158.1, 143.0, 139.5, 137.8, 131.4, 129.8, 129.0, 128.5, 127.6, 119.6, 77.2, 21.2, 0.0, -2.2. **HR-MS** (ESI) *m/z* calculated for $C_{18}H_{18}BrOSi^+$ $[M]^+$ 357.0305, found 357.0317.



5m: 59% yield (64.2 mg, 0.179 mmol) as an amorphous solid. Pyridinium *p*-toluenesulfonate used as acid. Column eluent hexane/ethyl acetate/Et_3N (84:14:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.25 – 7.19 (m, 4H), 7.12 – 7.10 (m, 2H), 7.05 (t, J = 1.8 Hz, 1H), 7.00 (t, J = 7.8 Hz, 1H), 6.79 (dt, J = 7.7, 1.3 Hz, 1H), 5.27 – 5.23 (m, 1H), 1.82 (d, J = 3.9 Hz, 1H), 1.62 (dd, J = 14.9, 7.7 Hz, 1H), 1.03 (dd, J = 14.9, 5.0 Hz, 1H), 0.44 (s, 3H), 0.18 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 158.5, 142.9, 142.8, 137.6, 130.8, 129.8, 129.0, 128.7, 128.5, 127.7, 126.7, 122.3, 77.2, 21.2, -0.0, -2.2.**HR-MS** (ESI) *m/z* calculated for $C_{18}H_{18}BrOSi^+$ $[M]^+$ 357.0305, found 357.0297.

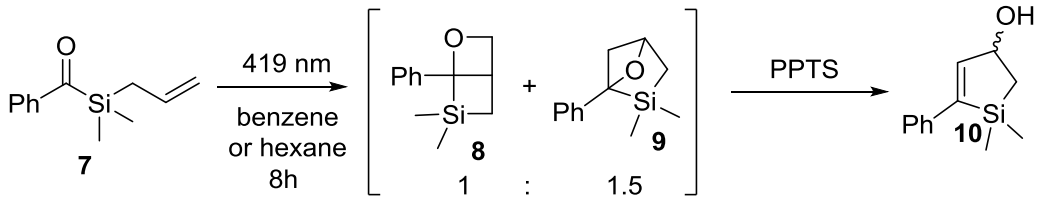


5n: 50% yield (62.0 mg, 0.151 mmol) as an amorphous solid. $NaHSO_4$ used as acid. Column eluent hexane/ethyl acetate/Et_3N (90:8:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.20 – 7.09 (m, 5H), 7.02 – 6.99 (m, 1H), 6.84 – 6.81 (m, 2H), 6.70 (d, J = 8.1 Hz, 1H), 5.38 – 5.36 (m, 1H), 1.76 (s, 1H), 1.65 (dd, J = 14.8, 7.6 Hz, 1H), 1.01 (dd, J = 14.8, 5.2 Hz, 1H), 0.90 (s, 9H), 0.34 (s, 3H), 0.15 (s, 3H), 0.12 (s, 3H), 0.00 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 156.4, 137.8, 132.0, 129.5, 128.4, 128.0, 127.3, 126.6, 120.8, 118.6, 76.6, 26.1, 21.6, 18.4, -0.4, -2.1, -3.8, -4.3. **HR-MS** (ESI) *m/z* calculated for $C_{24}H_{35}O_2Si_2^+$ $[M]^+$ 411.2170, found 411.2162.



5o: 85% yield (68.0 mg, 0.237 mmol) as an amorphous solid. **8o** was directly obtained without acid treatment. Column eluent hexane/ethyl acetate/Et_3N (84:14:2). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.44 – 7.36 (m, 3H), 7.26 – 7.23 (m, 2H), 7.04 (dd, J = 5.1, 1.2 Hz, 1H), 6.87 – 6.85 (m, 1H), 6.82 (dd, *J* = 3.6, 1.1 Hz, 1H), 5.02 (ddd, J = 7.9, 5.2, 3.8 Hz, 1H), 1.77 (d, J = 3.8 Hz, 1H), 1.60 (dd, J = 14.9, 7.8 Hz, 1H), 1.01 (dd, J = 14.9, 5.3 Hz, 1H), 0.52 (s, 3H), 0.35 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 156.4, 142.1, 139.1, 134.3, 129.2, 129.1, 128.1, 127.3, 126.3, 125.8, 78.1, 20.9, 0.1, -1.5. **HR-MS** (ESI) *m/z* calculated for $C_{16}H_{17}OSSi^+$ $[M]^+$ 285.0764, found 285.0766.

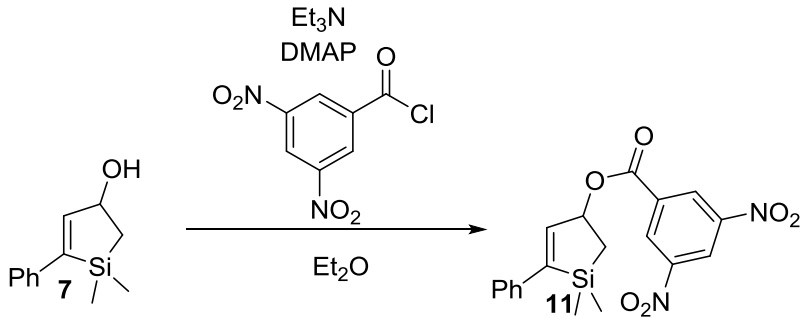
Irradiation of acylsilane 7:



Acylsilane **7** (50 mg, 0.245 mmol) was dissolved in dry benzene or hexane (5 mL). The solution was irradiated for 5-8h, until complete disappearance of the bright yellow colour. NMR analysis of the reaction crude at this point showed a mixture of the unstable intermediates **8** and **9**, which structures were elucidated based on spectroscopic characterization of previously reported related bicyclic structures.[2] **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.38 – 7.12 (m, 10H, **8**/**9**), 5.20 (t, J = 7.2 Hz, 1H, **8**), 4.81 (d, J = 4.6 Hz, 1H, **9**), 4.61 (dd, J = 6.4, 3.5 Hz, 1H, **8**), 3.40 – 3.33 (m, 1H, **8**), 2.90 – 2.84 (m, 1H, **9**), 2.22 (d, J = 8.3 Hz, 1H, **9**), 1.58 – 1.38 (m, 3H, **8**/**9**), 1.26 (d, J = 13.8 Hz, 1H, **9**), 0.60 (s, 3H, **8**), 0.40 (s, 3H, **9**), 0.27 (s, 3H, **8**), 0.24 (s, 3H, **9**). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 144.5, 143.2, 128.4, 128.2, 125.9, 125.3, 123.1, 123.0, 96.3 (**8**), 89.9 (**9**), 79.3 (**8**), 79.2 (**9**), 44.6 (**9**), 42.2 (**8**), 23.5 (**9**), 17.3 (**8**), -1.3 (**8**), -3.0 (**9**), -3.0 (**8**), -4.9 (**9**).

The solution was transferred to a round-bottom flask and pyridinium *p*-toluenesulfonate (65 mg, 0.257 mmol, 1.05 equiv.) was added. The reaction was stirred at room temperature for 15 minutes. The solvent was evaporated and the product purified through alumina column chromatography, eluent hexane/ethyl acetate (80:20) to give silacyclopentenol **10** (20 mg, 0,099 mmol) as an oil in 40% yield. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.37 – 7.30 (m, 4H), 7.25 – 7.22 (m, 1H), 6.86 (d, J = 2.3 Hz, 1H), 4.92 (s, 1H), 1.69 (s, 1H), 1.59 (dd, J = 14.6, 7.6 Hz, 1H), 0.84 (dd, J = 14.6, 5.7 Hz, 1H), 0.39 (s, 3H), 0.31 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 147.3, 146.5, 139.1, 128.7, 127.3, 126.9, 126.9, 74.7, 23.7, -0.2, -1.3. HR-MS (ESI) *m/z* calculated for $C_{12}H_{15}OSi^+$ $[M]^+$ 203.0887, found 203.0905.

Synthesis of silacyclopentenol ester 11:

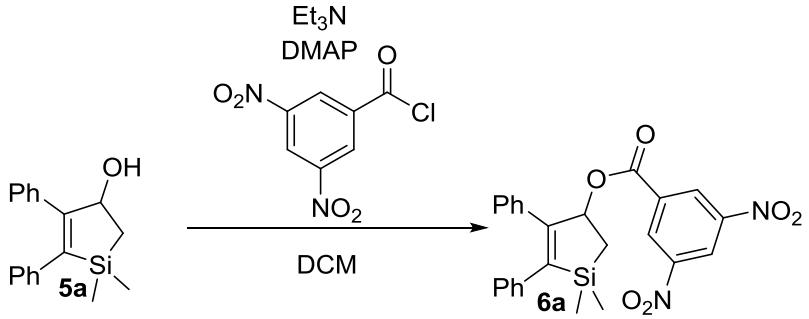


Alcohol **7** (38 mg, 0.186 mmol) was dissolved in dry Et_2O (1 mL). Triethylamine (31 µL, 0.223 mmol, 1.2 equiv.) was added, followed by 3,5-dinitrobenzoyl chloride (42 mg, 0.205, 1.1 equiv.). Then, dimethylaminopyridine (2 mg, 0.02 mmol, 0.1 equiv.) was added. The reaction was left stirring at room temperature for 30 minutes. The reaction was quenched with water (5 mL). DCM (5 mL) was added and the layers separated. The organic layer was collected and the aqueous layer washed with DCM (2 × 5 mL). The organic phases were combined and dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The crude was purified by silica column chromatography, eluent hexane/ethyl acetate (95:5), to give ester **11** as a white solid (39 mg. 0.098 mmol) in 53% yield. The compound was further recrystallized from hexane/DCM to give suitable crystals for X-ray diffraction analysis. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 9.23 (t, J = 2.1 Hz, 1H), 9.20 (d, J = 2.1 Hz, 2H), 7.42 – 7.35 (m, 4H), 7.31 – 7.27 (m, 1H), 6.89 (d, J = 2.4 Hz, 1H), 6.20 (ddd, J = 8.1, 6.0, 2.4 Hz, 1H), 1.79 (dd, J = 14.7, 7.9 Hz, 1H), 1.16 (dd, J = 14.7, 6.0 Hz, 1H), 0.50 (s, 3H), 0.40 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125

MHz) δ 162.4, 149.8, 148.7, 141.5, 138.2, 134.5, 129.6, 128.9, 127.9, 127.0, 122.4, 80.5, 19.8, -0.5, -1.5.

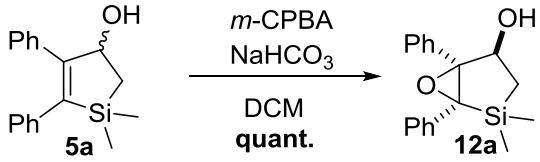
Transformation reactions of 5a:

Synthesis of silacyclopentenol ester 6a:



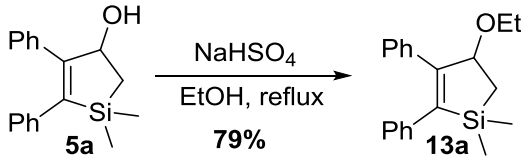
Alcohol **5a** (42 mg, 0.15 mmol) was dissolved in dry DCM (2 mL). Triethylamine (27 µL, 0.19 mmol, 1.3 equiv.) was added, followed by 3,5-dinitrobenzoyl chloride (42 mg, 0.18, 1.2 equiv.). Then, dimethylaminopyridine (2 mg, 0.02 mmol, 0.1 equiv.) was added. The reaction was left stirring at room temperature for 30 minutes. The reaction was quenched with water (5 mL). DCM (5 mL) was added and the layers separated. The organic layer was collected and the aqueous layer washed with DCM (2 × 5 mL). The organic phases were combined and dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The crude was purified by silica column chromatography, eluent hexane/ethyl acetate (94:6), to give ester **6a** as a white solid (55 mg. 0.12 mmol) in 77% yield. The compound was further recrystallized from hexane/DCM to give suitable crystals for X-ray diffraction analysis. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 9.12 (t, J = 2.1 Hz, 1H), 8.84 (d, J = 2.1 Hz, 2H), 7.22 – 7.07 (m, 8H), 7.00 – 6.98 (m, 2H), 6.61 (dd, J = 7.9, 5.7 Hz, 1H), 1.93 (dd, J = 14.9, 8.0 Hz, 1H), 1.20 (dd, J = 14.9, 5.6 Hz, 1H), 0.55 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 162.3, 153.2, 148.6, 147.1, 139.5, 137.5, 134.5, 129.3, 128.6, 128.4, 128.2, 128.0, 127.4, 126.2, 122.2, 82.4, 19.3, -0.1, -2.4.

Synthesis of silacyclopentenol oxide 12a:



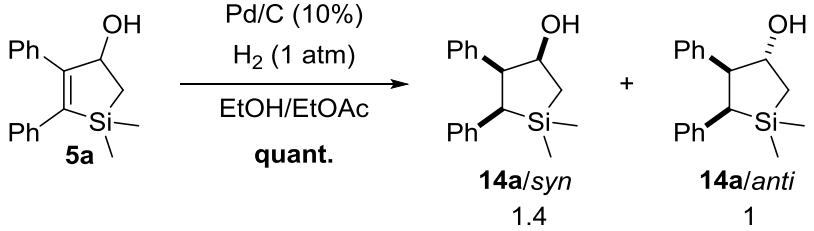
Silacyclopentenol **5a** (28 mg, 0.1 mmol) was dissolved in DCM (2 mL). Then, $NaHCO_3$ (20 mg, 0.24 mmol, 2.4 equiv.) was added, followed by *m*CPBA (38 mg, 0.22 mmol, 2.2 equiv.). After stirring for two hours at room temperature, the reaction was quenched with a saturated aqueous solution of Na_2SO_3 (2 mL). The layers were separated and the organic phase collected. The aqueous phase was extracted with DCM (2 × 2 mL) and the organic fractions were combined, dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure to give epoxide **12a** as oil in quantitative yield. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.26 (t, J = 3.6 Hz, 2H), 7.18 (t, J = 7.4 Hz, 2H), 7.11 (dd, J = 13.1, 7.3 Hz, 3H), 7.04 – 7.00 (m, 3H), 4.97 (dd, J = 9.3, 7.8 Hz, 1H), 1.44 – 1.40 (m, 1H), 1.25 (s, 1H), 0.88 (dd, J = 14.0, 9.4 Hz, 1H), 0.36 (s, 3H), 0.30 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 137.0, 134.9, 128.1, 127.9, 127.6, 127.3, 126.3, 126.3, 76.0, 74.2, 68.8, 17.4, -2.7, -5.0. HR-MS (ESI) *m/z* calculated for $C_{18}H_{19}OSi^+$ $[M\text{-}OH]^+$ 279.11997, obtained 279.11870.

Synthesis of silacyclopentenol ether 13a:



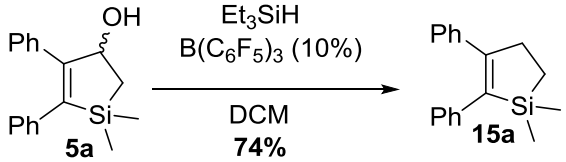
Silacyclopentenol **5a** (10 mg, 0.036 mmol) was dissolved in dry ethanol (2 mL). Then, $KHSO_4$ (10 mg, 0.073 mmol, 2 equiv.) was added and the solution was heated to 70 °C for one hour. The reaction was quenched with saturated aqueous $NaHCO_3$ (2 mL) and the product was extracted with EtOAc (3 × 2 mL). The organic phases were combined, dried over $MgSO_4$ and filtered. The solvent was evaporated and the resulting crude purified by silica column chromatography, eluent hexane/EtOAc (97:3) to give the ether **13a** in 88% yield (8.8 mg, 0.029 mmol). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.15 – 7.05 (m, 8H), 6.90 (d, J = 7.8 Hz, 2H), 4.93 (dd, J = 7.5, 4.3 Hz, 1H), 3.60 (dq, J = 14.1, 7.0 Hz, 1H), 3.41 – 3.35 (m, 1H), 1.46 (dd, J = 14.8, 7.6 Hz, 1H), 1.07 (t, J = 7.0 Hz, 3H), 1.03 – 0.99 (m, 1H), 0.39 (s, 3H), 0.18 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 155.9, 144.9, 140.8, 139.0, 129.2, 128.2, 128.1, 127.6, 126.7, 125.5, 84.3, 63.8, 17.8, 15.5, -0.2, -1.8. HR-MS (ESI) *m/z* calculated for $C_{20}H_{23}OSi^+$ $[M\text{-}H^-]^+$ 307.1531, found 307.1520.

Synthesis of silacyclopentanol 14a:



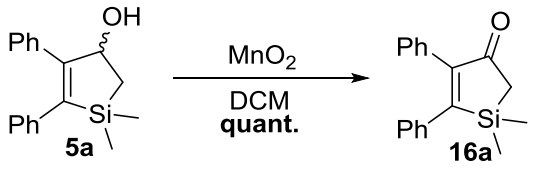
Silacyclopentenol **5a** (28 mg, 0.1 mmol) was dissolved in 1.5 mL of an ethanol/ethyl acetate mixture (3:2), under argon atmosphere, followed by addition of Pd/C (10%) (5.3 mg, 5 mol%). The argon balloon was then replaced for a hydrogen-filled balloon. The solution was stirred at room temperature for 30 min and then filtered over celite. The solvents were evaporated to give **14a** as mixture of two non-isolable diastereoisomers in quantitative yield (28 mg, 0.1 mmol). **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.22 – 6.73 (m, 10H+10H), 4.85 (dt, J = 11.0, 8.6 Hz, 1H/*anti*), 4.70 – 4.57 (m, 1H/*syn*), 3.74 (dd, J = 8.0, 4.6 Hz, 1H/*syn*), 3.30 (dd, J = 11.1, 7.6 Hz, 1H, *anti*), 3.00 (d, J = 8.0 Hz, 1H, *syn*), 2.71 (d, J = 7.6 Hz, 1H, *anti*), 1.77 (s, 1H,), 1.64 (dd, J = 14.7, 7.8 Hz, 1H, *anti*), 1.54 (s, 1H), 1.26 (dd, J = 14.4, 6.0 Hz, 1H/*syn*), 1.03 – 0.97 (m, 1H+1H/*syn* and *anti*), 0.40 (s, 3H, *anti*), 0.37 (s, 3H/*syn*), 0.25 (s, 3H/*syn*), 0.11 (s, 3H, *anti*). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.3, 141.0, 140.0, 139.0, 130.2, 130.0, 129.5, 128.5, 128.1, 128.0, 127.8, 127.8, 126.3, 126.3, 124.8, 124.2, 74.9(*syn*), 74.6(*anti*), 58.7(*anti*), 54.6(*syn*), 41.7(*anti*), 38.3(*syn*), 23.4(syn), 22.1(*anti*), 0.6(*syn*), 0.4(*anti*), -1.7(*syn*), -2.5(anti). HR-MS (ESI) *m/z* calculated for $C_{18}H_{21}OSi^+$ $[M\text{-}H^-]^+$ 281.1356, found 281.1364.

Synthesis of silacyclopentene 15a:

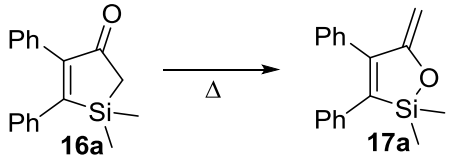


Silacyclopentenol **5a** (28 mg, 0.1 mmol) was dissolved in dry DCM (1.5 mL), under argon atmosphere. Borane catalyst $B(C_6F_5)_3$ (0.01 mmol, 10 mol%) was added to the solution, followed by dropwise addition of triethylsilane (48 µL, 0.3 mmol, 3 equiv.). The solution was left stirring at room temperature for 3 hours. The solvent was evaporated and the product purified by silica column chromatography, eluted with hexane to give **15a** as a white amorphous solid in 74% yield (19.5 mg, 0,074 mmol). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.18 – 7.04 (m, 8H), 6.93 – 6.90 (m, 2H), 3.01 – 2.96 (m, 2H), 1.02 – 0.97 (m, 2H), 0.27 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 155.3, 141.6, 141.3, 140.9, 128.5, 128.3, 128.1, 127.9, 126.8, 125.1, 36.5, 9.5, -1.0.

Synthesis of silacyclopentenone 16a:



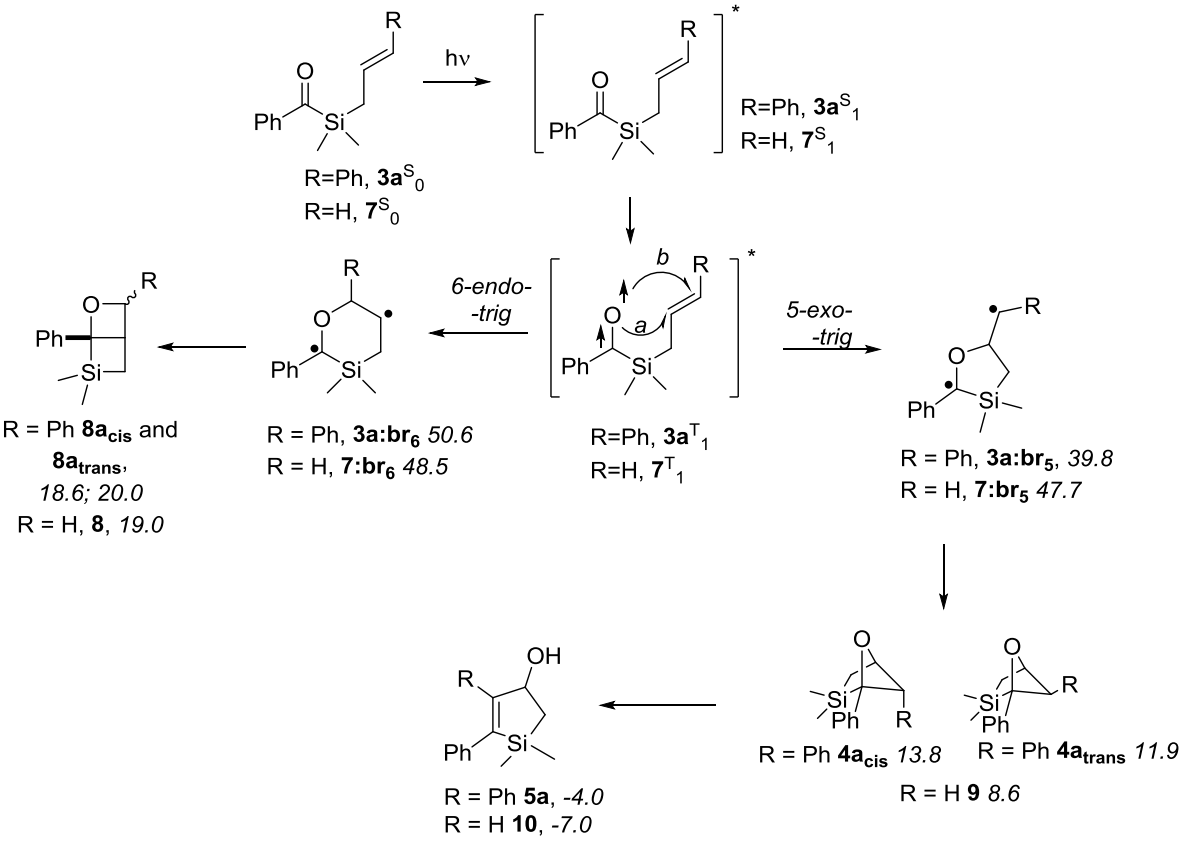
Silacyclopentenol **5a** (20 mg, 0.071 mmol) was dissolved in dry DCM (1.5 mL), under argon atmosphere. The solution was cooled to 0 °C and MnO_2 (186 mg, 2.13 mmol, 30 equiv.) was added. After stirring at 0 °C for 1 hour, the solution was filtered through celite to remove excess MnO_2. The solvent was evaporated to give pentenone **16a** in quantitative yield (20 mg, 0.071 mmol). **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.27 – 7.19 (m, 6H), 7.10 – 7.07 (m, 2H), 7.04 – 7.00 (m, 2H), 2.04 (s, 2H), 0.47 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 203.8, 166.1, 154.3, 138.9, 134.8, 130.2, 128.5, 128.1, 127.8, 127.7, 27.6, -2.4. HR-MS (ESI) *m/z* calculated for $C_{18}H_{19}OSi^+$ $[M+H]^+$ 279.11997, obtained 279.11850.



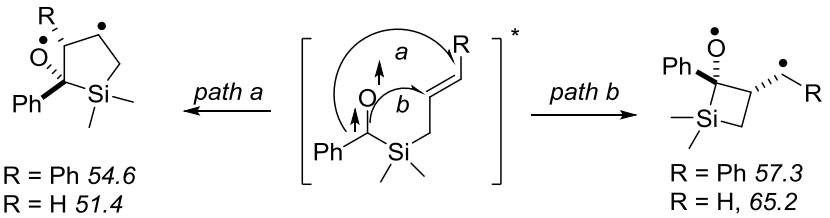
Pentenone **16a** was observed to isomerize under thermal conditions to the silyl enol ether **17a**, which could be isolated by passing it through a short silica column using hexane:ethyl acetate (9:1) as the eluent. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.34 – 7.30 (m, 3H), 7.20 – 7.10 (m, 5H), 6.93 – 6.89 (m, 2H), 4.67 (d, J = 1.3 Hz, 1H), 4.15 (d, J = 1.2 Hz, 1H), 0.53 (s, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 163.4, 149.5, 141.7, 137.4, 136.8, 129.8, 128.6, 128.4, 128.4, 127.6, 126.8, 91.9, -0.1. HR-MS (ESI) *m/z* calculated for $C_{18}H_{19}OSi^+$ $[M+H]^+$ 279.11997, obtained 279.11844.

Computational Details:

All calculations were performed using the Gaussian 09 software package,[3] without symmetry constraints in gas-phase. The BMK (Boese-Martin for kinetics)[4] density functional (42% HF-exchange) in conjunction with the 6-31+G (d, p)[5] basis set was employed in the geometry optimizations. The nature of all stationary points were confirmed by absence of imaginary vibrational frequencies. The geometries of the biradical species was optimized at (U)BMK/6-31+G (d, p) level of theory, where values for $<S^2>$ were typically consistent with two unpaired electrons for triplets. Vertical excitations energies were calculated at the TD-BMK level with the 6-31+G (d, p) basis set.



Scheme S1: Biradical intermediates in the photoreaction of **3a** and **7**. Free energies of the species are indicated in italics (kcal/mol), referring to corresponding acylsilanes in ground state. This scheme is an extended version of Scheme 6 in the manuscript.



Scheme S2: Biradical intermediates derived from carbonyl carbon attack on olefin moiety of **3a** and **7**. Free energies of the species are indicated in italics (kcal/mol), referring to corresponding acylsilanes in ground state.

Atomic coordinates for all the optimized species (BMK/6-31G)**

3a

SCF Done: E(RBMK) = -1062.12391871

6	-2.582905	-0.228388	-4.472356
6	-2.527379	-1.559374	-4.026744
6	-3.286002	-1.961558	-2.920409
6	-4.100435	-1.032998	-2.259615
6	-4.161761	0.300246	-2.699604
6	-3.395328	0.696074	-3.812787
6	-5.033375	1.322086	-2.005662
14	-6.159298	0.928172	-0.479774
8	-5.050852	2.473775	-2.417858
6	-7.488109	-0.309313	-0.964808
6	-5.143272	0.302853	0.969711
6	-6.942880	2.583609	-0.032122
6	-8.034386	2.426579	0.995170
6	-7.925265	2.763033	2.294550
1	-1.992131	0.082253	-5.331883
1	-1.894001	-2.279754	-4.541239
1	-3.244417	-2.992079	-2.573865
1	-4.684634	-1.354384	-1.400005
1	-3.455403	1.732321	-4.138701
1	-8.156518	-0.491488	-0.111487
1	-7.068475	-1.275681	-1.272398
1	-8.096747	0.071352	-1.796239
1	-5.753063	0.357974	1.883285
1	-4.251219	0.924446	1.124881
1	-4.813669	-0.736584	0.848804
1	-7.331630	3.032857	-0.957658
1	-6.150396	3.250967	0.336102
1	-8.969499	1.988955	0.637818
6	-8.960066	2.590606	3.339911
1	-6.999481	3.236837	2.630824
6	-8.811477	3.270151	4.565819
6	-9.767566	3.150312	5.581431
6	-10.894346	2.340344	5.394079
6	-11.050717	1.648523	4.183201
6	-10.094541	1.768476	3.170994
1	-7.938949	3.904762	4.717575
1	-9.631765	3.691086	6.516318
1	-11.637396	2.241580	6.182788
1	-11.916452	1.006382	4.031396
1	-10.222386	1.206455	2.247904

$3a^{S}_{1}$

SCF Done: E(RBMK) = -1062.11580178

Total Energy, E(TD-HF/TD-KS) = -1062.02014529

6	-0.407422	-0.500576	-1.902096
6	-0.051156	-1.471081	-0.949652
6	-0.880518	-1.665695	0.168751
6	-2.041850	-0.916009	0.340099
6	-2.415428	0.066733	-0.621853
6	-1.563173	0.261557	-1.754094
6	-3.610284	0.870925	-0.510933
14	-4.907440	0.713330	0.942874
8	-3.984645	1.759291	-1.324210
6	-5.590946	-1.031440	0.920301
6	-4.053641	1.146606	2.551091
6	-6.263226	1.962575	0.562458
6	-7.425617	1.800595	1.510316
6	-7.683837	2.612994	2.553096
1	0.225112	-0.337044	-2.773181
1	0.851642	-2.063738	-1.075276
1	-0.617553	-2.411549	0.916886
1	-2.657951	-1.089632	1.217220
1	-1.832063	1.008978	-2.496004
1	-6.249047	-1.179167	1.789213
1	-4.801654	-1.791161	0.957171
1	-6.180142	-1.200772	0.009476
1	-4.789112	1.111086	3.368392
1	-3.643922	2.163967	2.505275
1	-3.233464	0.461935	2.795664
1	-6.584849	1.816728	-0.478953
1	-5.836780	2.973473	0.630974
1	-8.078413	0.945010	1.325443
6	-8.795692	2.483351	3.521924
1	-7.034753	3.478714	2.706753
6	-9.021955	3.528098	4.440111
6	-10.068996	3.463859	5.367378
6	-10.912695	2.347165	5.397516
6	-10.694744	1.294816	4.494595
6	-9.648865	1.360317	3.571048
1	-8.371516	4.401934	4.420022
1	-10.225168	4.287203	6.061855
1	-11.729156	2.293273	6.114741
1	-11.340543	0.418899	4.514084
1	-9.491531	0.528449	2.887519

$3a^{T}_{1}$

SCF Done: E(UBMK) = -1062.03419253

6	-0.404817	-0.497768	-1.916991
6	-0.044576	-1.478436	-0.976115
6	-0.862283	-1.679383	0.149955
6	-2.017670	-0.923809	0.338908
6	-2.396154	0.068441	-0.609967
6	-1.555915	0.268186	-1.747721
6	-3.588688	0.874867	-0.465732
14	-4.884382	0.720725	0.963116
8	-3.943900	1.780450	-1.288203
6	-5.576232	-1.021659	0.943724
6	-4.046198	1.137990	2.584547
6	-6.241575	1.971084	0.585691
6	-7.412623	1.803233	1.522340
6	-7.691112	2.620639	2.555565
1	0.220264	-0.330337	-2.792551
1	0.854062	-2.074500	-1.116287
1	-0.594631	-2.433180	0.888361
1	-2.628130	-1.097517	1.220833
1	-1.829686	1.024961	-2.479320
1	-6.231931	-1.166705	1.814766
1	-4.789467	-1.784475	0.978977
1	-6.168339	-1.190859	0.034734
1	-4.785028	1.082888	3.397529
1	-3.643311	2.158726	2.557662
1	-3.221571	0.455247	2.821732

1	-6.557201	1.832283	-0.458835
1	-5.819401	2.983185	0.663836
1	-8.054777	0.940095	1.335418
6	-8.813678	2.489701	3.512111
1	-7.050799	3.492487	2.711148
6	-9.050291	3.534838	4.427165
6	-10.106937	3.470930	5.343536
6	-10.950719	2.354114	5.365474
6	-10.723118	1.301636	4.465111
6	-9.667574	1.366852	3.552478
1	-8.399906	4.408839	4.413605
1	-10.270447	4.294614	6.035935
1	-11.774729	2.300329	6.074024
1	-11.369220	0.425790	4.477597
1	-9.504109	0.534979	2.870368

3a:br$_5$

SCF Done: E(UBMK) = -1062.06152200

6	-3.129557	1.855872	-0.816029
6	-2.860226	-1.185153	-0.005010
14	-1.042788	-0.757209	-0.006288
6	-1.282061	0.279059	-1.567972
6	-2.798911	0.591541	-1.572690
8	-3.522873	-0.530920	-0.999452
6	-0.484261	0.215414	1.499679
6	0.107889	-2.215562	-0.277495
6	-3.633183	-2.116765	0.766881
6	-5.032557	-2.292311	0.565510
6	-5.752168	-3.205253	1.336097
6	-5.115620	-3.971521	2.327420
6	-3.734696	-3.809770	2.540150
6	-3.004911	-2.901814	1.776308
6	-4.407641	2.485005	-0.846814
6	-4.619337	3.707452	-0.138677
6	-5.852451	4.351579	-0.167062
6	-6.921653	3.805406	-0.900635
6	-6.739041	2.599401	-1.600643
6	-5.510263	1.943622	-1.576046
1	-2.347355	2.309634	-0.205819
1	-1.027843	-0.331308	-2.445645
1	-0.697326	1.204835	-1.622960
1	-3.192516	0.653054	-2.595226
1	0.558619	0.545694	1.394081
1	-0.549028	-0.403537	2.405306
1	-1.114513	1.099682	1.658747
1	1.124318	-1.866428	-0.509029
1	-0.239439	-2.837682	-1.112372
1	0.173452	-2.854254	0.613487
1	-5.531275	-1.697451	-0.194610
1	-6.821589	-3.320637	1.166466
1	-5.683226	-4.682672	2.923745
1	-3.229623	-4.397534	3.304694
1	-1.935050	-2.793573	1.953163
1	-3.794086	4.133949	0.430350
1	-5.988710	5.280977	0.382818
1	-7.885098	4.310437	-0.921778
1	-7.565749	2.169201	-2.162955
1	-5.390653	0.998544	-2.100697

3a:br$_6$

SCF Done: E(UBMK) = -1062.04260417

8	-3.561310	0.079071	-1.215804
6	-4.630459	-0.771932	-1.157352
6	-2.680367	-1.013647	-3.233776
6	-2.383880	-0.295631	-1.939747
14	-5.262018	-1.473140	-2.785366
6	-3.960028	-0.751182	-3.956294
6	-5.228655	-3.349828	-2.842728
6	-6.987338	-0.849469	-3.200536
6	-5.285744	-0.816222	0.126642
6	-4.796703	-0.077930	1.244209
6	-5.439778	-0.142820	2.479385
6	-6.584229	-0.939841	2.654289
6	-7.080246	-1.677118	1.565056
6	-6.448719	-1.617132	0.324438
1	-1.782186	-0.953343	-1.290766
1	-1.986064	-1.782658	-3.565853
6	-1.586135	0.984933	-2.197390
1	-3.976185	-1.208192	-4.952370
1	-4.155202	0.329537	-4.064681
1	-5.568190	-3.710750	-3.824043
1	-5.882168	-3.791938	-2.078899
1	-4.212585	-3.727866	-2.670044
1	-7.280836	-1.190680	-4.203669
1	-7.017423	0.247988	-3.190925
1	-7.741874	-1.210162	-2.489125
1	-3.913707	0.541012	1.114860
1	-5.047663	0.432561	3.316428
1	-7.080778	-0.986007	3.621173
1	-7.962782	-2.302332	1.688104
1	-6.848489	-2.204366	-0.500131
6	-2.230233	2.204997	-2.458394
6	-1.478286	3.349645	-2.753083
6	-0.078659	3.287294	-2.790665
6	0.567665	2.072297	-2.525133
6	-0.184076	0.928682	-2.228920
1	-3.315295	2.256370	-2.405929
1	-1.987270	4.291933	-2.948117
1	0.503802	4.178426	-3.015783
1	1.654555	2.017072	-2.539547
1	0.322541	-0.012631	-2.015514

4a*$_{cis}$*

SCF Done: E(RBMK) = -1062.11085739

6	-1.814117	0.519631	0.230016
6	-2.915484	-0.463662	-0.322111
14	-2.232336	-1.097418	-1.997255
6	-1.683232	0.689178	-2.329611
6	-2.260450	1.313012	-1.026393
8	-3.581060	0.730726	-0.873456
6	-0.843465	-2.359991	-1.980320
6	-3.647079	-1.686395	-3.071074
6	-3.775955	-1.268093	0.608393

6	-3.430268	-2.595050	0.926356
6	-4.200093	-3.336858	1.829988
6	-5.341499	-2.768216	2.412336
6	-5.704380	-1.455215	2.083467
6	-4.925548	-0.706779	1.191086
1	-2.250094	1.012666	1.111648
6	-0.387486	0.109528	0.514020
1	-2.181594	1.142134	-3.196034
1	-0.601084	0.831032	-2.432365
1	-2.291671	2.407712	-0.995314
1	-0.469284	-2.514172	-3.002838
1	-1.192015	-3.335333	-1.612421
1	-0.003262	-2.035621	-1.353501
1	-3.342531	-1.760475	-4.124259
1	-4.487814	-0.984630	-3.002187
1	-3.997601	-2.677584	-2.752153
1	-2.552961	-3.047135	0.463696
1	-3.913585	-4.358700	2.071919
1	-5.944616	-3.344946	3.110841
1	-6.595343	-1.010705	2.523632
1	-5.204057	0.311260	0.929301
6	0.701654	0.849443	0.023878
6	2.018447	0.477969	0.330619
6	2.264439	-0.640129	1.136926
6	1.184228	-1.376624	1.644157
6	-0.128844	-1.001107	1.338674
1	0.522065	1.724162	-0.599203
1	2.848768	1.063219	-0.060380
1	3.285430	-0.932591	1.373666
1	1.363807	-2.241737	2.279828
1	-0.963546	-1.572039	1.742913

4a*trans*

SCF Done: E(RBMK) = -1062.11184000

6	-2.960314	1.113154	-0.474314
6	-2.812319	-0.449702	-0.286885
14	-0.912546	-0.676302	-0.282874
6	-0.875509	0.511443	-1.769081
6	-2.413641	0.707715	-1.874276
8	-2.998947	-0.608878	-1.735356
6	-0.050194	-0.060945	1.266333
6	-0.434886	-2.438309	-0.682228
6	-3.742897	-1.259426	0.556516
6	-4.538520	-2.267813	-0.011086
6	-5.377484	-3.045058	0.800067
6	-5.435460	-2.820039	2.180994
6	-4.646094	-1.809461	2.750785
6	-3.802935	-1.037358	1.945014
6	-4.358148	1.688167	-0.415329
6	-4.614728	2.780458	0.431343
6	-5.894530	3.346176	0.514152
6	-6.941523	2.823504	-0.253302
6	-6.697948	1.732154	-1.099903
6	-5.420518	1.167707	-1.181572
1	-2.281907	1.729172	0.129280
1	-0.491359	0.051759	-2.688405
1	-0.350661	1.461817	-1.605165
1	-2.783639	1.228854	-2.764632
1	1.041098	-0.055916	1.137281
1	-0.278954	-0.716701	2.118270
1	-0.359949	0.959108	1.530193
1	0.625224	-2.512829	-0.961127
1	-1.037503	-2.805563	-1.522812
1	-0.606097	-3.098189	0.178896
1	-4.498123	-2.431065	-1.085708
1	-5.990458	-3.823235	0.348612
1	-6.092710	-3.419650	2.807523
1	-4.688881	-1.621633	3.822106
1	-3.193924	-0.250590	2.391134
1	-3.804406	3.194357	1.031149
1	-6.068833	4.193135	1.175326
1	-7.937386	3.258208	-0.193450
1	-7.507082	1.316172	-1.697504
1	-5.238304	0.314600	-1.830967

8a*cis*

SCF Done: E(RBMK) = -1062.09915459

8	-4.207390	0.958980	-0.839284
6	-4.234479	-0.485486	-0.924648
6	-2.656645	-0.551487	-0.940305
6	-2.772311	1.002656	-0.871119
14	-4.191708	-1.084338	-2.749273
6	-2.335502	-1.136156	-2.355629
6	-4.963438	-2.757803	-3.082952
6	-4.762443	0.214770	-3.968527
6	-5.059961	-1.132946	0.146343
6	-4.814783	-2.464526	0.531688
6	-5.608130	-3.084363	1.504034
6	-6.660018	-2.381065	2.108602
6	-6.905492	-1.052915	1.735070
6	-6.111517	-0.430672	0.762606
6	-2.166153	1.687220	0.335163
6	-1.011315	2.471321	0.190658
6	-0.410785	3.065647	1.309148
6	-0.968478	2.885487	2.581296
6	-2.128540	2.110173	2.730010
6	-2.724379	1.513502	1.613120
1	-2.138919	-1.011844	-0.091071
1	-2.415609	1.494837	-1.790220
1	-1.939468	-2.158590	-2.292345
1	-1.626690	-0.530709	-2.933577
1	-4.670938	-3.129460	-4.075115
1	-6.059848	-2.694934	-3.053504
1	-4.653184	-3.500090	-2.336223
1	-4.396060	0.000132	-4.981758
1	-4.396355	1.204336	-3.665713
1	-5.859290	0.260781	-4.005227
1	-3.989321	-3.014735	0.079225
1	-5.399451	-4.111851	1.796599
1	-7.275594	-2.861329	2.866487
1	-7.714087	-0.495265	2.204559
1	-6.290821	0.604067	0.478681
1	-0.584697	2.623592	-0.800638
1	0.481988	3.675676	1.184960

1	-0.507400	3.350775	3.450510
1	-2.568599	1.972615	3.715973
1	-3.631187	0.919994	1.720395

8a*trans*

SCF Done: E(RBMK) = -1062.09885766

8	-4.385571	0.765187	-1.254302
6	-4.511335	-0.680936	-1.143310
6	-2.962271	-0.838131	-1.443348
6	-2.956647	0.696039	-1.185086
14	-4.850428	-1.407818	-2.877582
6	-2.962563	-1.288926	-2.945310
6	-5.483785	-3.173861	-2.871967
6	-5.868208	-0.329898	-4.017981
6	-5.094051	-1.124223	0.167652
6	-4.970101	-2.463854	0.586186
6	-5.520087	-2.887382	1.800826
6	-6.205839	-1.977863	2.619571
6	-6.331953	-0.644231	2.211222
6	-5.780248	-0.218199	0.995128
1	-2.623648	0.906967	-0.154924
1	-2.350420	-1.444877	-0.767903
6	-2.239857	1.619214	-2.143871
1	-2.442976	-2.243528	-3.092076
1	-2.512717	-0.547143	-3.615691
1	-5.563718	-3.549344	-3.902180
1	-6.479736	-3.233261	-2.411902
1	-4.816189	-3.850049	-2.322919
1	-5.790526	-0.671856	-5.059288
1	-5.521707	0.709840	-3.968984
1	-6.928703	-0.350727	-3.732023
1	-4.433363	-3.177441	-0.038419
1	-5.410123	-3.925133	2.110760
1	-6.630893	-2.305317	3.566188
1	-6.856640	0.071327	2.842127
1	-5.865672	0.818331	0.678549
6	-2.942439	2.443175	-3.033937
6	-2.246478	3.283280	-3.916522
6	-0.846915	3.300177	-3.920703
6	-0.140020	2.476867	-3.030597
6	-0.833921	1.645764	-2.145171
1	-4.029531	2.428839	-3.021444
1	-2.799984	3.923675	-4.600992
1	-0.309750	3.950334	-4.608472
1	0.948360	2.485521	-3.025642
1	-0.283347	1.010457	-1.450663

5a

SCF Done: E(RBMK) = -1062.13480003

6	-2.556733	0.745836	-0.313998
6	-3.915866	0.827593	-0.299729
14	-4.473528	2.540486	-0.822871
6	-2.751459	3.018714	-1.415749
6	-1.793982	2.025216	-0.707713
6	-5.787838	2.515546	-2.159701
6	-5.060214	3.609990	0.610387
8	-0.681297	1.677832	-1.514594
6	-1.761877	-0.421904	0.188299
6	-1.964968	-0.881908	1.504531
6	-1.238161	-1.967943	2.005293
6	-0.300049	-2.619190	1.193387
6	-0.091993	-2.171888	-0.118130
6	-0.809649	-1.077225	-0.616650
6	-4.843192	-0.280821	0.068575
6	-4.691065	-1.583224	-0.451225
6	-5.596962	-2.597109	-0.123710
6	-6.677663	-2.335004	0.730559
6	-6.848145	-1.044409	1.247114
6	-5.945239	-0.027785	0.910841
1	-2.455181	4.061470	-1.242637
1	-2.687137	2.820568	-2.495748
1	-1.424080	2.471557	0.233576
1	-6.041069	3.531073	-2.494191
1	-6.708915	2.046525	-1.786159
1	-5.449484	1.940401	-3.031504
1	-5.125385	4.661436	0.295688
1	-4.370090	3.554062	1.462996
1	-6.057840	3.311621	0.960317
1	-0.139854	2.461307	-1.648234
1	-2.703582	-0.385798	2.131514
1	-1.408342	-2.306288	3.025719
1	0.264088	-3.466257	1.579214
1	0.635002	-2.672056	-0.755630
1	-0.635798	-0.723809	-1.628579
1	-3.857753	-1.795726	-1.117092
1	-5.458104	-3.595132	-0.535512
1	-7.379621	-3.126503	0.985692
1	-7.684736	-0.826542	1.908694
1	-6.085240	0.972286	1.318963

7

SCF Done: E(RBMK) = -831.213452093

6	-0.486953	-0.427308	-1.852254
6	0.077498	-1.040584	-0.721567
6	-0.661975	-1.143995	0.463220
6	-1.964018	-0.630093	0.518969
6	-2.535451	-0.014468	-0.607724
6	-1.786271	0.080721	-1.796505
6	-3.937361	0.551291	-0.575107
14	-5.060610	0.578391	1.003324
8	-4.413364	1.029640	-1.595382
6	-5.553211	-1.175163	1.463805
6	-4.209878	1.442122	2.436749
6	-6.571069	1.576216	0.481211
6	-7.683352	1.492542	1.497571
6	-8.007415	2.449614	2.379278
1	0.090103	-0.347413	-2.771533
1	1.091438	-1.434008	-0.765014
1	-0.227532	-1.620811	1.339546
1	-2.529964	-0.712801	1.444515
1	-2.245331	0.558535	-2.659357
1	-6.203222	-1.159642	2.350088
1	-4.684725	-1.805174	1.695868

1	-6.107139	-1.656799	0.646647
1	-4.970099	1.719129	3.181821
1	-3.711070	2.363903	2.108461
1	-3.462793	0.814402	2.938247
1	-6.899326	1.202961	-0.499351
1	-6.255956	2.619540	0.334095
1	-8.245478	0.555294	1.517787
1	-8.812373	2.308397	3.097708
1	-7.485103	3.406562	2.396885

7^{S}_{1}

SCF Done: E(RBMK) = -831.205126335

Total Energy, E(TD-HF/TD-KS) = -831.109566312

6	-0.501274	-0.448858	-1.810909
6	0.049657	-1.104118	-0.695997
6	-0.711901	-1.204189	0.481691
6	-1.993358	-0.663464	0.555593
6	-2.560036	0.005616	-0.567652
6	-1.780086	0.099150	-1.763023
6	-3.877994	0.594540	-0.557916
14	-5.067193	0.609859	0.993022
8	-4.432488	1.190352	-1.521643
6	-5.493295	-1.163874	1.419066
6	-4.200128	1.515033	2.382051
6	-6.606589	1.553183	0.462812
6	-7.685874	1.459912	1.516358
6	-7.997291	2.423239	2.395256
1	0.076492	-0.363042	-2.729946
1	1.050696	-1.525889	-0.741926
1	-0.300671	-1.711109	1.352962
1	-2.555718	-0.758128	1.480090
1	-2.199177	0.606008	-2.628475
1	-6.112423	-1.181261	2.328377
1	-4.605432	-1.781062	1.598786
1	-6.066396	-1.626780	0.605024
1	-4.901220	1.634314	3.221363
1	-3.888364	2.514573	2.052551
1	-3.312201	0.985769	2.746248
1	-6.956527	1.140791	-0.494269
1	-6.326230	2.600605	0.281963
1	-8.230068	0.513477	1.564359
1	-8.775912	2.277590	3.141173
1	-7.490996	3.388763	2.385011

7^{T}_{1}

SCF Done: E(UBMK) = -831.123613336

6	-0.488557	-0.410529	-1.816405
6	0.064665	-1.090119	-0.717035
6	-0.698427	-1.229353	0.455747
6	-1.985467	-0.701897	0.538412
6	-2.555179	-0.008388	-0.566976
6	-1.773477	0.123471	-1.755183
6	-3.883166	0.563860	-0.533111
14	-5.067428	0.597393	0.996730
8	-4.421163	1.176883	-1.512443
6	-5.508875	-1.165198	1.456166
6	-4.213267	1.507833	2.391476
6	-6.605892	1.539141	0.455658
6	-7.686088	1.469888	1.510141
6	-7.995523	2.451265	2.369416
1	0.091646	-0.295176	-2.730525
1	1.069958	-1.501182	-0.771264
1	-0.284815	-1.756406	1.313758
1	-2.553874	-0.827948	1.455965
1	-2.194691	0.650990	-2.607926
1	-6.130549	-1.158487	2.363792
1	-4.626546	-1.785568	1.653086
1	-6.082443	-1.642199	0.650652
1	-4.917835	1.620969	3.228553
1	-3.905506	2.509766	2.065546
1	-3.323400	0.983422	2.759334
1	-6.960288	1.112785	-0.493864
1	-6.321801	2.582369	0.256778
1	-8.233158	0.526204	1.576682
1	-8.774773	2.322447	3.117805
1	-7.486081	3.414768	2.341035

7:br_5

SCF Done: E(UBMK) = -831.137798873

6	-3.000839	1.904492	-0.977106
6	-2.846579	-1.102675	-0.073823
14	-1.019781	-0.711843	-0.035892
6	-1.186991	0.245612	-1.656017
6	-2.699199	0.614466	-1.686396
8	-3.466426	-0.449037	-1.096887
6	-0.496334	0.346535	1.422811
6	0.095021	-2.215585	-0.168377
6	-3.671138	-1.999200	0.684502
6	-5.057077	-2.168204	0.398838
6	-5.835009	-3.049132	1.149229
6	-5.271235	-3.787707	2.204011
6	-3.905295	-3.630532	2.500965
6	-3.116868	-2.754629	1.757892
1	-3.925855	2.004715	-0.414292
1	-2.370661	2.777141	-1.136222
1	-0.951071	-0.412998	-2.503653
1	-0.566798	1.145258	-1.741448
1	-3.063198	0.662539	-2.725687
1	0.554045	0.656332	1.329655
1	-0.600017	-0.208235	2.365621
1	-1.118880	1.247855	1.493573
1	1.143564	-1.912417	-0.297676
1	-0.190045	-2.844494	-1.021478
1	0.038731	-2.834602	0.737200
1	-5.493074	-1.596302	-0.416032
1	-6.891551	-3.163635	0.911741
1	-5.883383	-4.475410	2.783535
1	-3.457728	-4.197199	3.315620
1	-2.060333	-2.646109	2.001793

7:br_6

SCF Done: E(UBMK) = -831.137950912

8	-3.471774	-0.012437	-1.114140
6	-4.577993	-0.813957	-1.099626
6	-2.587786	-1.026902	-3.188531
6	-2.307475	-0.431675	-1.835727
14	-5.194511	-1.453231	-2.758748
6	-3.868636	-0.706199	-3.887953
6	-5.186442	-3.327845	-2.877219
6	-6.903426	-0.792261	-3.182322
6	-5.285160	-0.832812	0.157851
6	-4.823838	-0.096580	1.287995
6	-5.518938	-0.132372	2.496096
6	-6.688638	-0.899741	2.630839
6	-7.156350	-1.637160	1.529191
6	-6.472956	-1.605090	0.315254
1	-1.747328	-1.147356	-1.212209
1	-1.962464	-1.850174	-3.529528
1	-1.705295	0.487400	-1.910733
1	-3.898228	-1.108531	-4.907262
1	-4.047979	0.381049	-3.932723
1	-5.516877	-3.654028	-3.873633
1	-5.857751	-3.783233	-2.136821
1	-4.179131	-3.727298	-2.701227
1	-7.184874	-1.101216	-4.199318
1	-6.917210	0.304795	-3.142482
1	-7.675244	-1.161388	-2.494319
1	-3.921946	0.500330	1.188110
1	-5.148085	0.442667	3.343044
1	-7.226643	-0.923721	3.576128
1	-8.056915	-2.241553	1.622202
1	-6.850106	-2.193485	-0.519189

9

SCF Done: E(RBMK) = -831.207601942

6	-3.000857	1.064452	-0.546489
6	-2.803411	-0.471402	-0.309101
14	-0.900136	-0.648826	-0.271626
6	-0.869255	0.507416	-1.780290
6	-2.411229	0.663814	-1.919593
8	-2.971196	-0.661663	-1.757171
6	-0.077301	0.033948	1.271922
6	-0.361732	-2.404552	-0.621471
6	-3.748964	-1.266594	0.535256
6	-4.653550	-2.167582	-0.049969
6	-5.530367	-2.909518	0.754310
6	-5.519140	-2.754908	2.146057
6	-4.618812	-1.853633	2.734680
6	-3.736066	-1.119249	1.935484
1	-4.066006	1.315944	-0.606118
1	-2.454284	1.782028	0.076493
1	-0.453531	0.041618	-2.682681
1	-0.372781	1.474246	-1.623288
1	-2.762919	1.147004	-2.837019
1	1.013808	0.082076	1.150171
1	-0.283759	-0.608740	2.139274
1	-0.432522	1.046592	1.505973
1	0.703344	-2.453220	-0.886475
1	-0.943416	-2.808786	-1.459843
1	-0.523255	-3.049636	0.252589
1	-4.663761	-2.272026	-1.132202
1	-6.226057	-3.605687	0.289046
1	-6.205278	-3.326818	2.767574
1	-4.603683	-1.725467	3.815610
1	-3.036885	-0.421831	2.397899

8

SCF Done: E(RBMK) = -831.189967306

8	-4.157537	0.940758	-0.935327
6	-4.219248	-0.508991	-0.979750
6	-2.632273	-0.586956	-0.980421
6	-2.742380	0.928091	-0.710596
14	-4.183723	-1.085042	-2.801392
6	-2.319306	-0.983220	-2.466631
6	-4.797364	-2.833131	-3.092343
6	-4.929747	0.126511	-4.014671
6	-5.042569	-1.106134	0.122868
6	-4.889531	-2.460768	0.477162
6	-5.677554	-3.029591	1.483828
6	-6.634864	-2.252811	2.153008
6	-6.789344	-0.903585	1.809344
6	-5.998990	-0.331951	0.803254
1	-2.505256	1.219510	0.322963
1	-2.131147	-1.188295	-0.214713
1	-2.210964	1.586480	-1.412198
1	-1.797486	-1.945725	-2.539795
1	-1.721988	-0.230986	-2.996478
1	-4.595090	-3.146917	-4.126193
1	-5.881213	-2.897109	-2.923855
1	-4.311770	-3.553813	-2.421895
1	-4.580382	-0.066193	-5.038344
1	-4.649479	1.149846	-3.734482
1	-6.026292	0.062290	-4.011838
1	-4.141968	-3.070549	-0.030289
1	-5.542098	-4.076402	1.750234
1	-7.247813	-2.694264	2.936264
1	-7.525369	-0.290759	2.327136
1	-6.105257	0.717707	0.540148

10

SCF Done: E(RBMK) = -831.230721510

6	-2.409150	0.877268	-0.651697
6	-3.730413	0.920130	-0.367573
14	-4.345716	2.674230	-0.647452
6	-2.769989	3.176856	-1.560439
6	-1.703574	2.148877	-1.092689
6	-5.906101	2.770355	-1.683470
6	-4.582139	3.643469	0.947437
8	-0.766265	1.793568	-2.096181
1	-1.788299	-0.014654	-0.539002
6	-4.513971	-0.259903	0.084976
1	-2.439171	4.213647	-1.415779
1	-2.929932	3.015614	-2.637095
1	-1.157677	2.557725	-0.222505
1	-6.141964	3.808905	-1.954191

1	-6.767496	2.364431	-1.135189
1	-5.796029	2.190961	-2.609468
1	-4.741482	4.709192	0.729829
1	-3.699836	3.556637	1.595540
1	-5.452397	3.289458	1.516617
1	-0.267925	2.576293	-2.350005
6	-5.648318	-0.090241	0.904062
6	-6.398053	-1.189304	1.340668
6	-6.034799	-2.485812	0.955321
6	-4.917532	-2.670833	0.127928
6	-4.168947	-1.571705	-0.304326
1	-5.937958	0.912285	1.216865
1	-7.265185	-1.031918	1.979458
1	-6.619208	-3.341185	1.288158
1	-4.634403	-3.672714	-0.189953
1	-3.319071	-1.724633	-0.966845

Single crystal x-ray diffraction

The crystal data for **6a** and **11** were collected at 120(2) K on an Agilent SuperNova dual wavelength diffractometer with micro-focus x-ray source and Atlas detector and using multilayer optics monochromatized Cu-Kα (λ = 1.54184 Å) radiation. Data collection (ω scans) and reduction was performed using the program *CrysAlisPro*.[6] The gaussian face-indexing-based absorption correction method was applied. The structure was solved by intrinsic phasing methods (*SHELXT*)[7] and refined by full-matrix least squares on F^2 using *SHELXL*-2018/3.[8] Anisotropic displacement parameters were assigned to non-H atoms. All hydrogen atoms were constrained to their idealised positions and refined using riding models with U_{eq}(H) of 1.5U_{eq}(C) for terminal methyl groups and of 1.2U_{eq}(C) for other groups. More details and parameters are presented in Table S1. Deposition Numbers CCDC- 1935510 and 1935511 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table S1: Crystal data and parameters of **11** and **6a**.

	11	**6a**
CCDC	1935510	1935511
Empirical formula	$C_{19}H_{18}N_2O_6Si$	$C_{25}H_{22}N_2O_6Si$
Formula weight	398.44	474.53
Crystal system	Monoclinic	Orthorhombic
Space group	*Cc*	$P2_12_12_1$
Unit cell dimensions		
a [Å]	10.8289(2)	5.98640(10)
b [Å]	10.4035(2)	18.2027(4)
c [Å]	17.1866(3)	21.5323(4)
β [°]	103.190(2)	90
Volume [Å^3]	1885.14(6)	2346.35(8)
Z	4	4
Density (calculated) [Mg/m^3]	1.404	1.343
Absorption coefficient [mm^{-1}]	1.456	1.262
F(000)	832	992
Crystal size [mm]	0.22 × 0.18 × 0.11	0.25 × 0.06 × 0.03
Theta range [°]	5.28 – 73.44	3.18 – 73.64
Reflections collected	15023	16171
Independent reflections	3720	4669
Reflections [$I>2\sigma(I)$]	3668	4348
R_{int}	0.0271	0.0471
Data completeness [%]	99.9	100.0
Restraints / parameters	2[a] / 253	0 / 308
Goodness-of-fit on F^2	1.025	1.022
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0274, wR2 = 0.0735	R1 = 0.0344, wR2 = 0.0848
R indices (all data)	R1 = 0.0279, wR2 = 0.0741	R1 = 0.0383, wR2 = 0.0875
Absolute structure parameter	-0.011(14)	- [b]
Largest diff. peak & hole [e.Å^{-3}]	0.165 & -0.157	0.255 & -0.204

[a] Floating origin restraints; [b] Compound is a two-component inversion twin, BASF = 0.32

Although **6a** crystallized in chiral space group $P2_12_12_1$, it is not a pure enantiomer, but the crystal is approximately 2:1 inversion twin (ESI) containing both enantiomers.

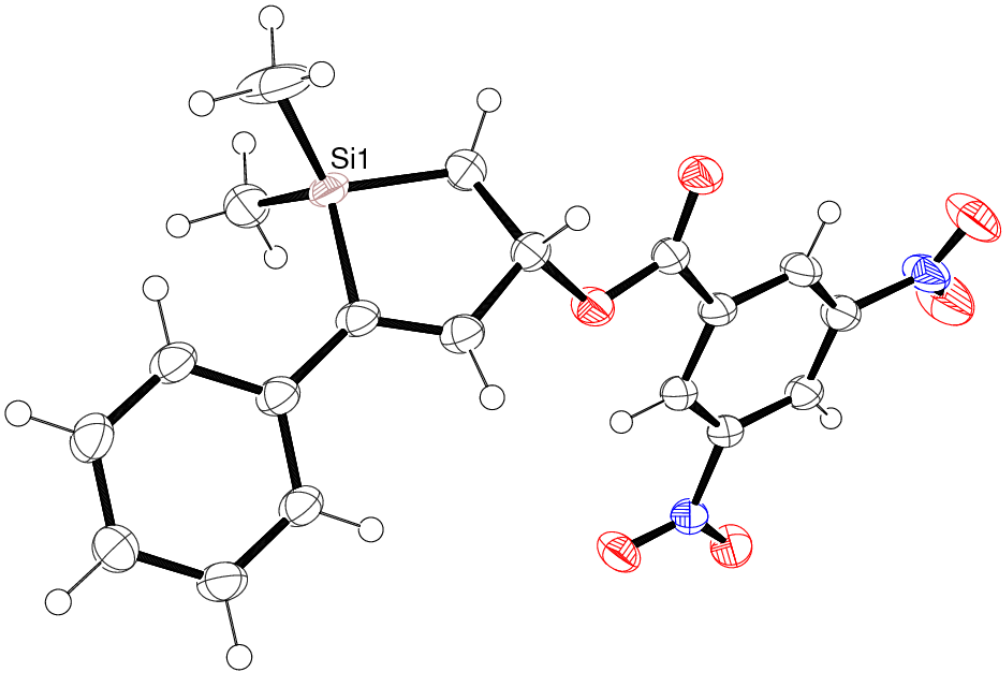


Figure S1: Thermal ellipsoid diagram of **11** (ellipsoid probability 50 %).

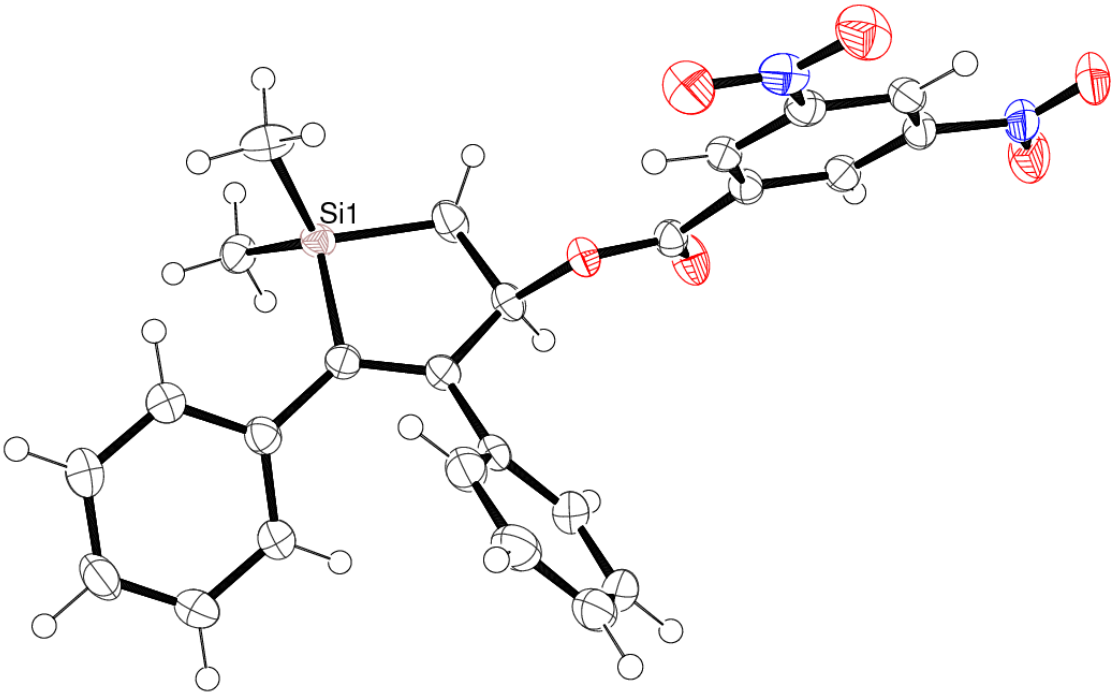


Figure S2: Thermal ellipsoid diagram of **6a** (ellipsoid probability 50 %).

References

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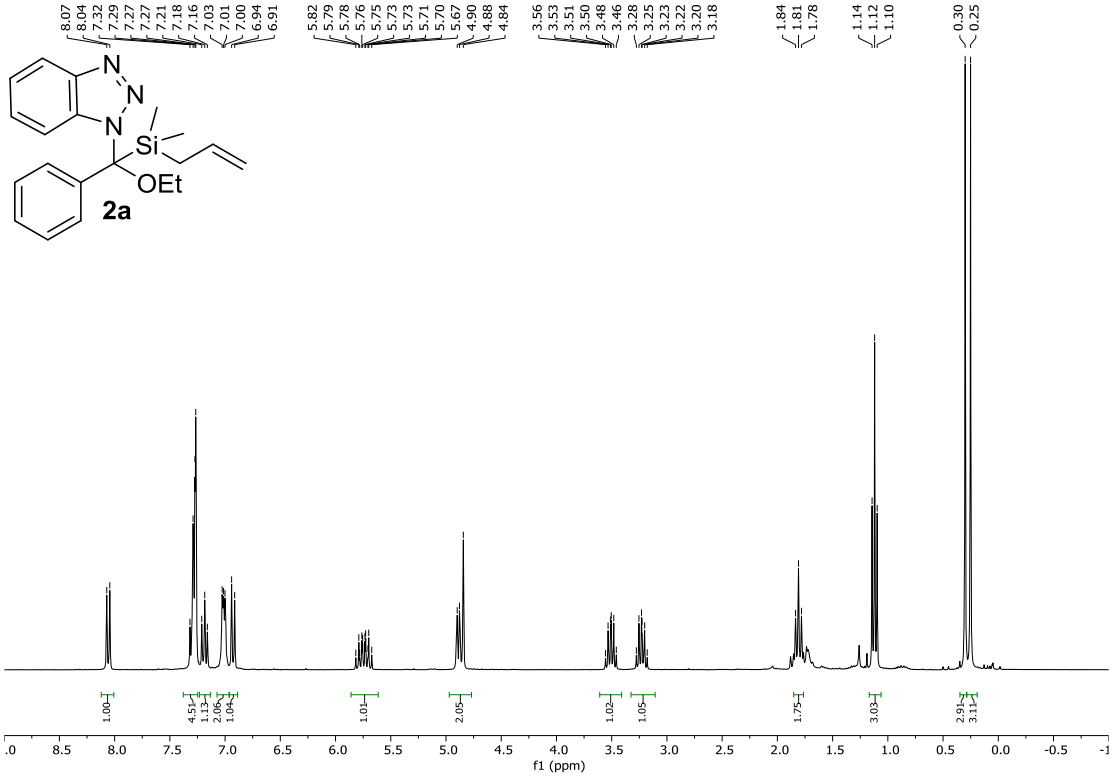
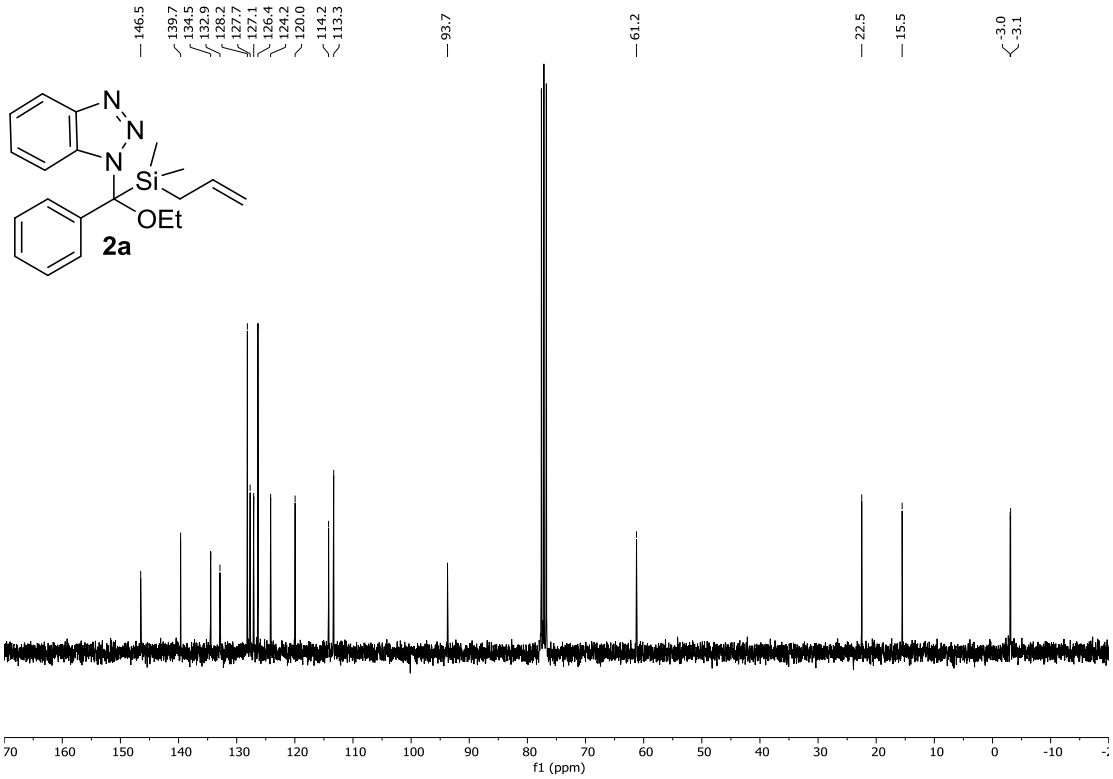
[8] Sheldrick, G. M., Acta Crystallogr., *Sect. C: Struct. Chem.*, **2015**, 71, 3-8.

NMR Spectra

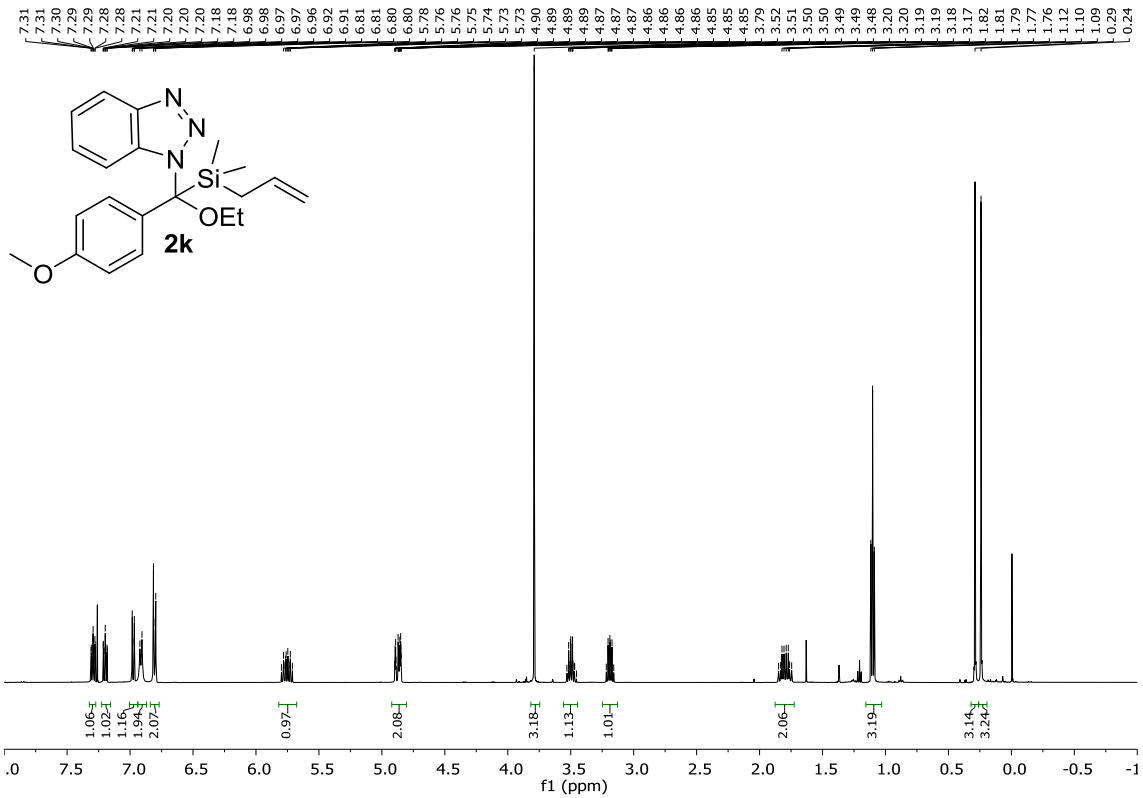
^{1}H NMR ($CDCl_3$, 300 MHz) of
1-((allyldimethylsilyl)(ethoxy)(phenyl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2a**)



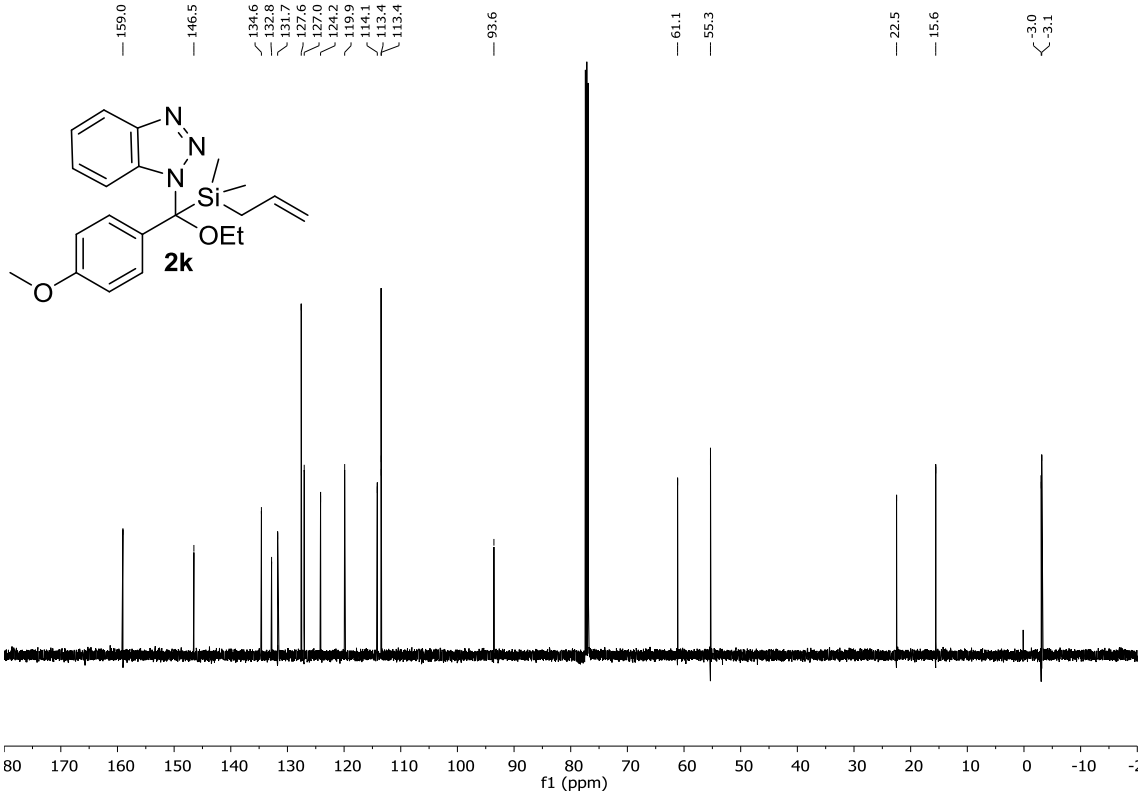
^{13}C NMR ($CDCl_3$, 75 MHz) of
1-((allyldimethylsilyl)(ethoxy)(phenyl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2a**)



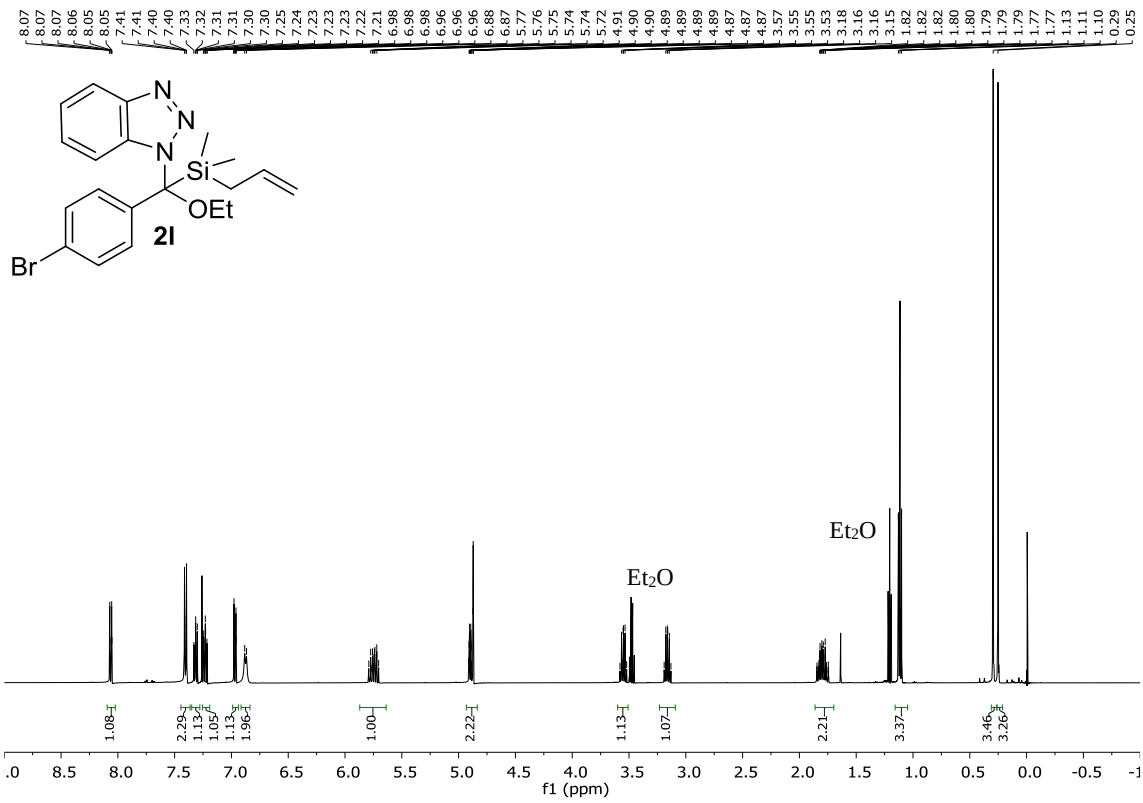
^{1}H NMR ($CDCl_3$, 500 MHz) of
1-((allyldimethylsilyl)(ethoxy)(4-methoxyphenyl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2k**)



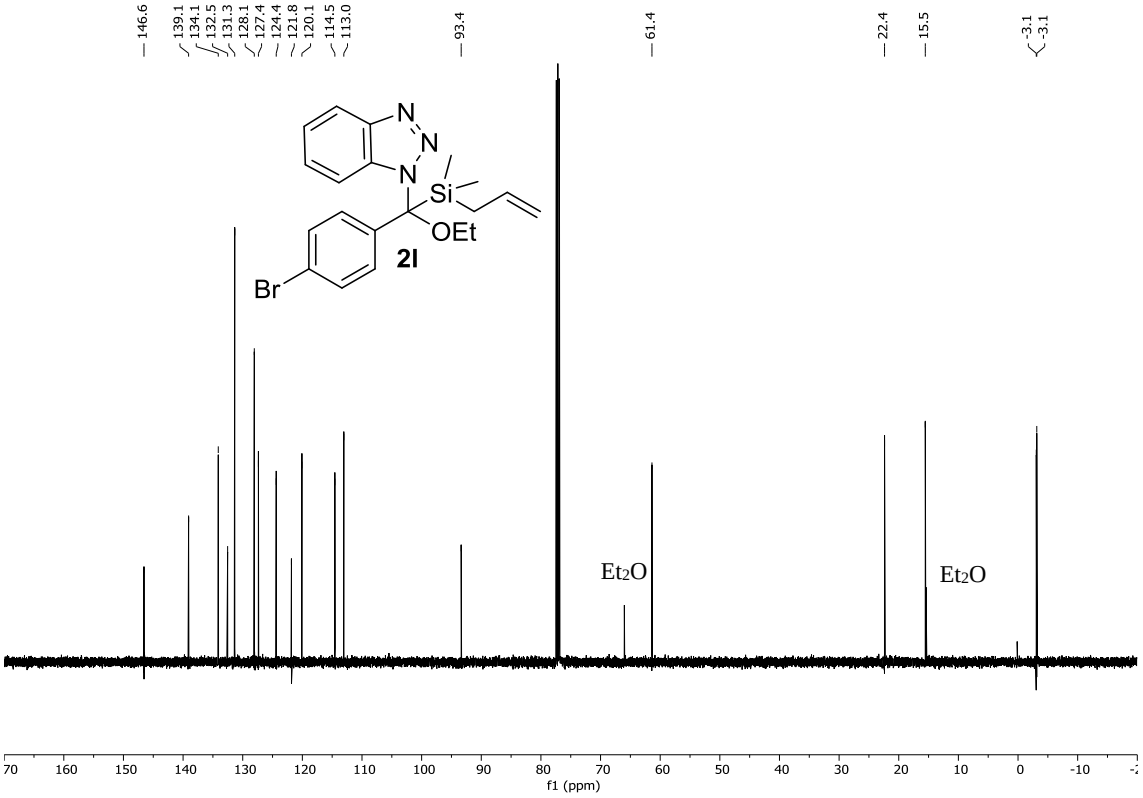
^{13}C NMR ($CDCl_3$, 125 MHz) of
1-((allyldimethylsilyl)(ethoxy)(4-methoxyphenyl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2k**)



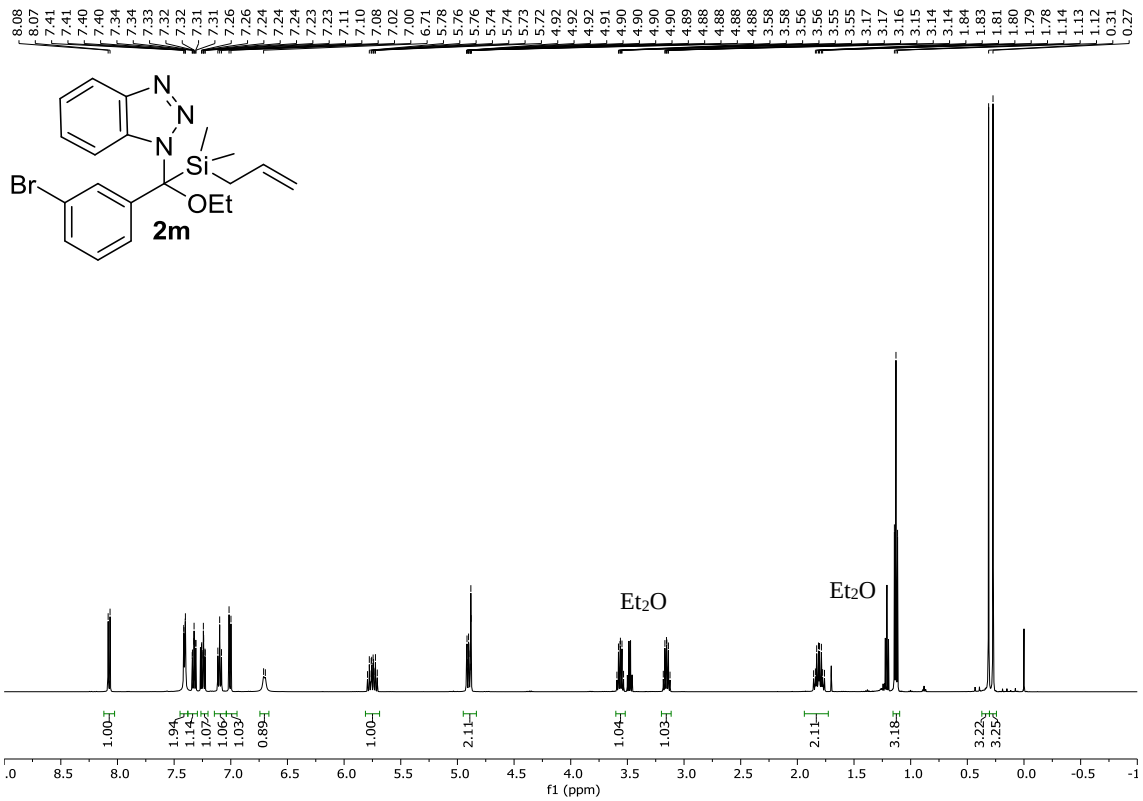
^{1}H NMR ($CDCl_3$, 500 MHz) of
1-((allyldimethylsilyl)(4-bromophenyl)(ethoxy)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2l**)



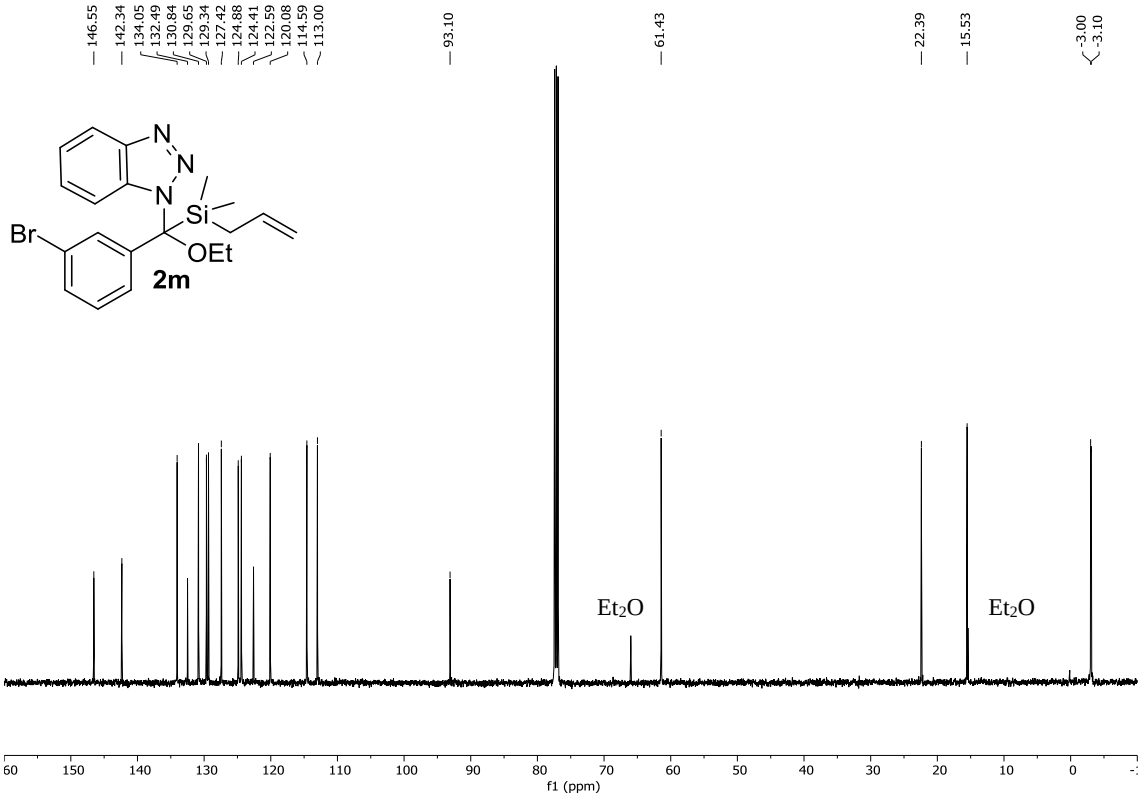
^{13}C NMR ($CDCl_3$, 125 MHz) of
1-((allyldimethylsilyl)(4-bromophenyl)(ethoxy)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2l**)



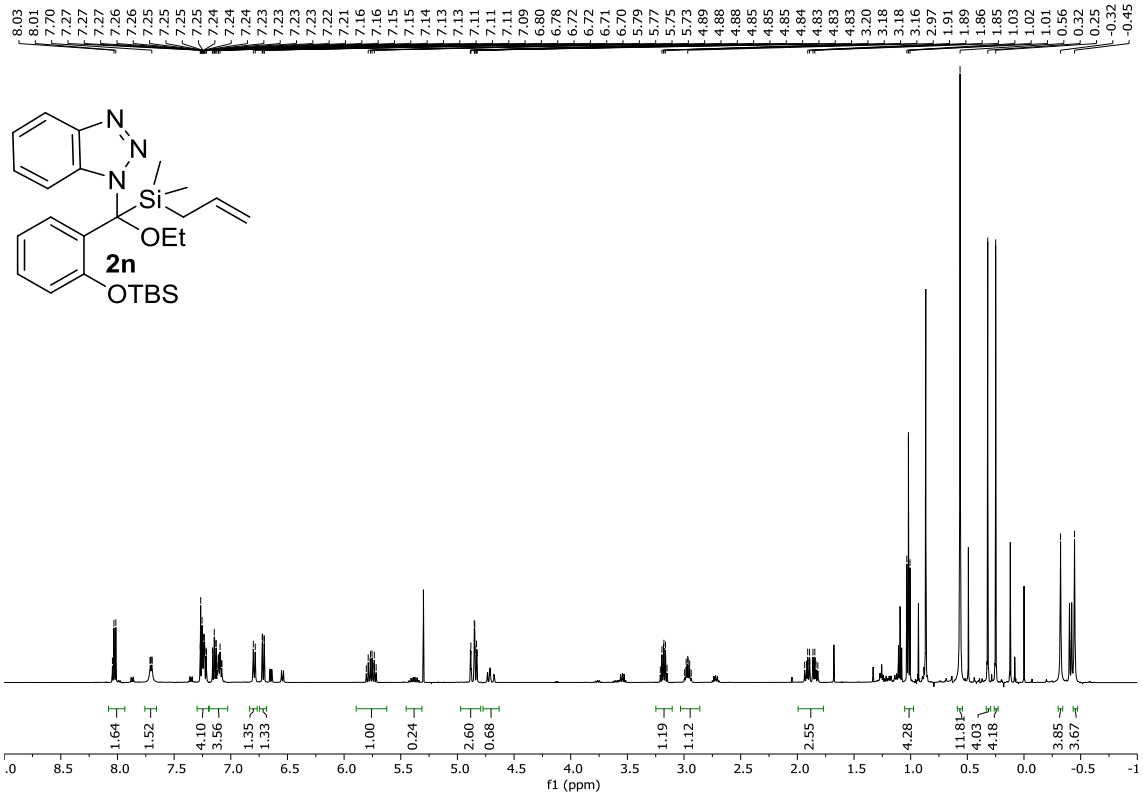
^{1}H NMR ($CDCl_3$, 500 MHz) of
1-((allyldimethylsilyl)(3-bromophenyl)(ethoxy)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2m**)



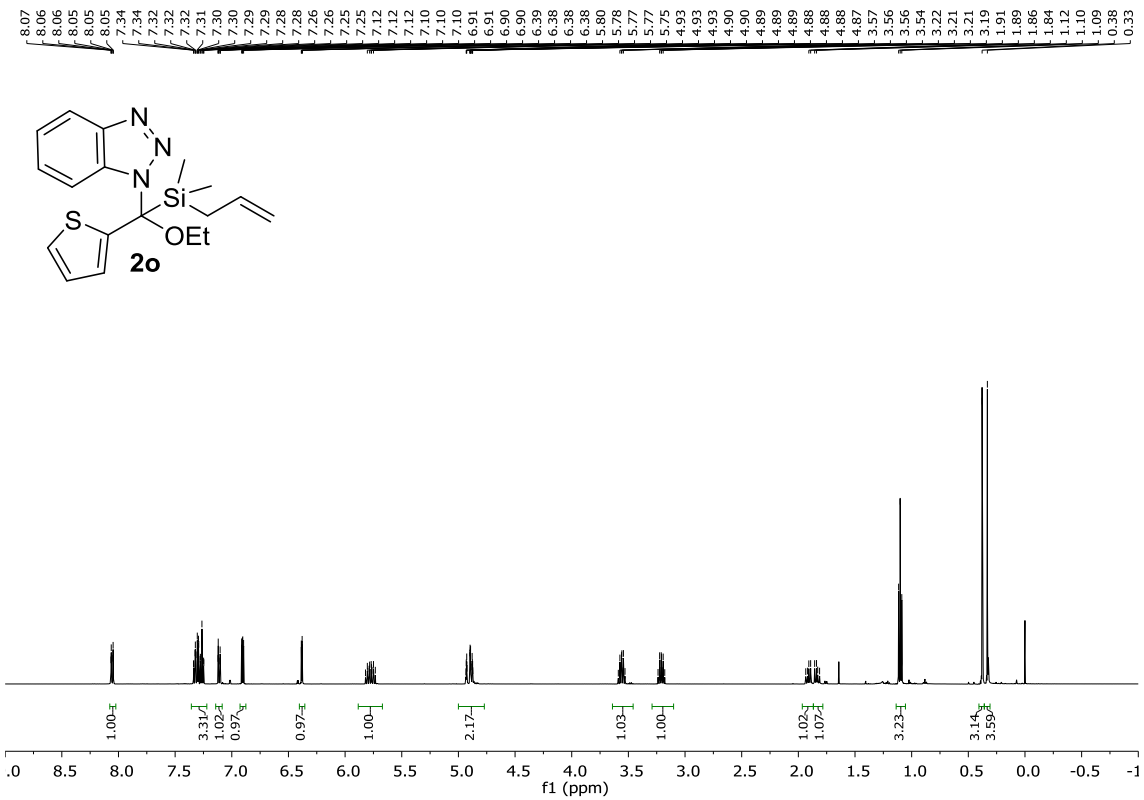
^{13}C NMR ($CDCl_3$, 125 MHz) of
1-((allyldimethylsilyl)(3-bromophenyl)(ethoxy)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2m**)



^{1}H NMR ($CDCl_3$, 500 MHz) of 1-((allyldimethylsilyl)(2-((*tert*-butyldimethylsilyl)oxy)phenyl)(ethoxy)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2n**)



^{1}H NMR ($CDCl_3$, 500 MHz) of
1-((allyldimethylsilyl)(ethoxy)(thiophen-2-yl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2o**)



^{13}C NMR ($CDCl_3$, 125 MHz) of
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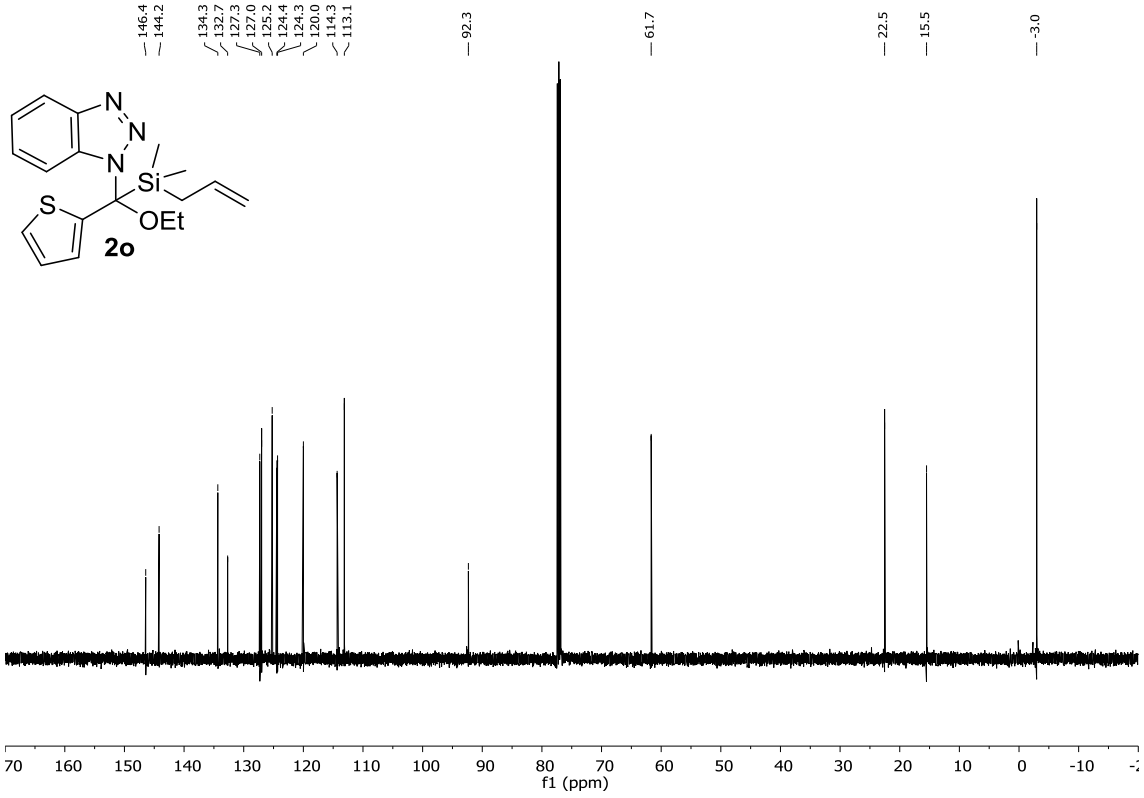

^{1}H NMR ($CDCl_3$, 300 MHz) of
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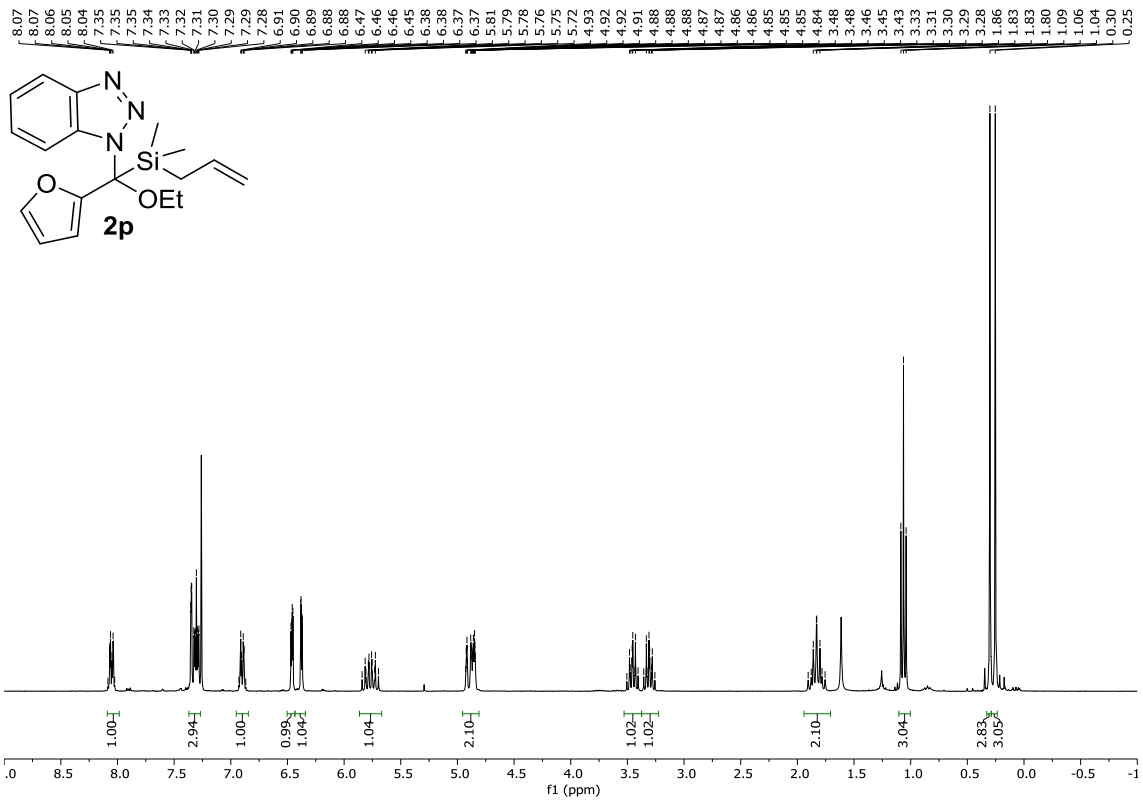

^{13}C NMR ($CDCl_3$, 75 MHz) of
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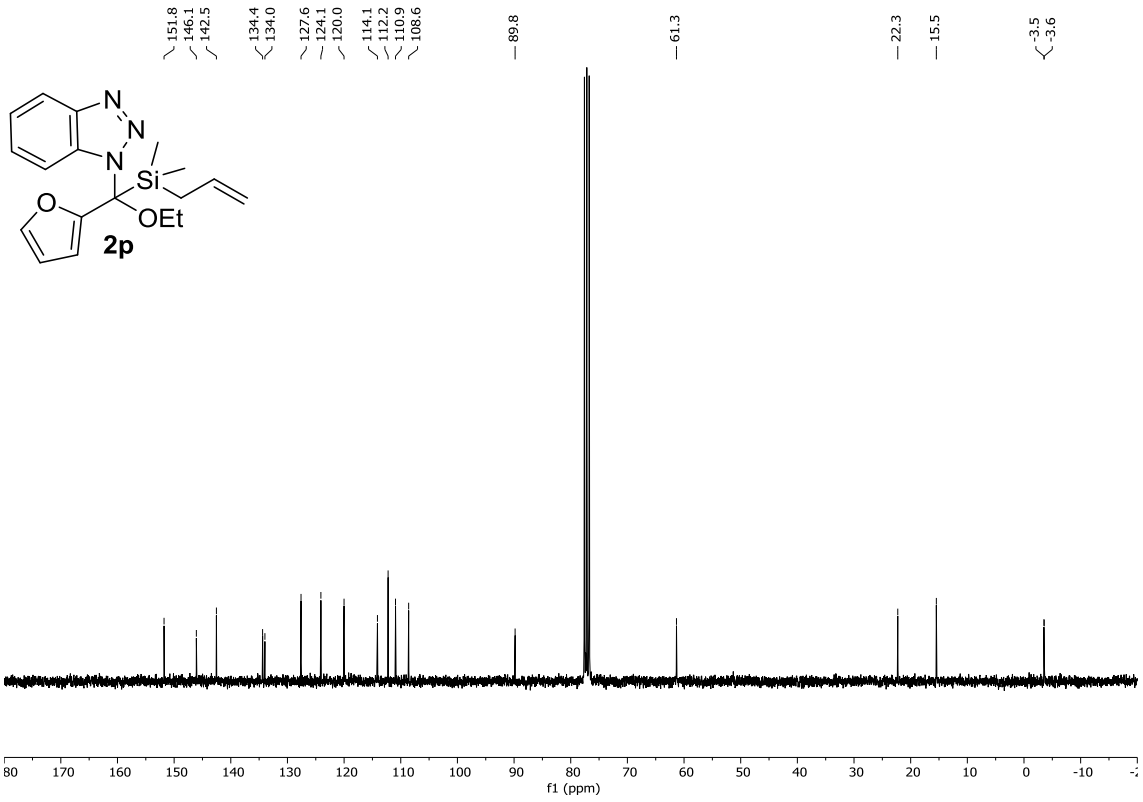
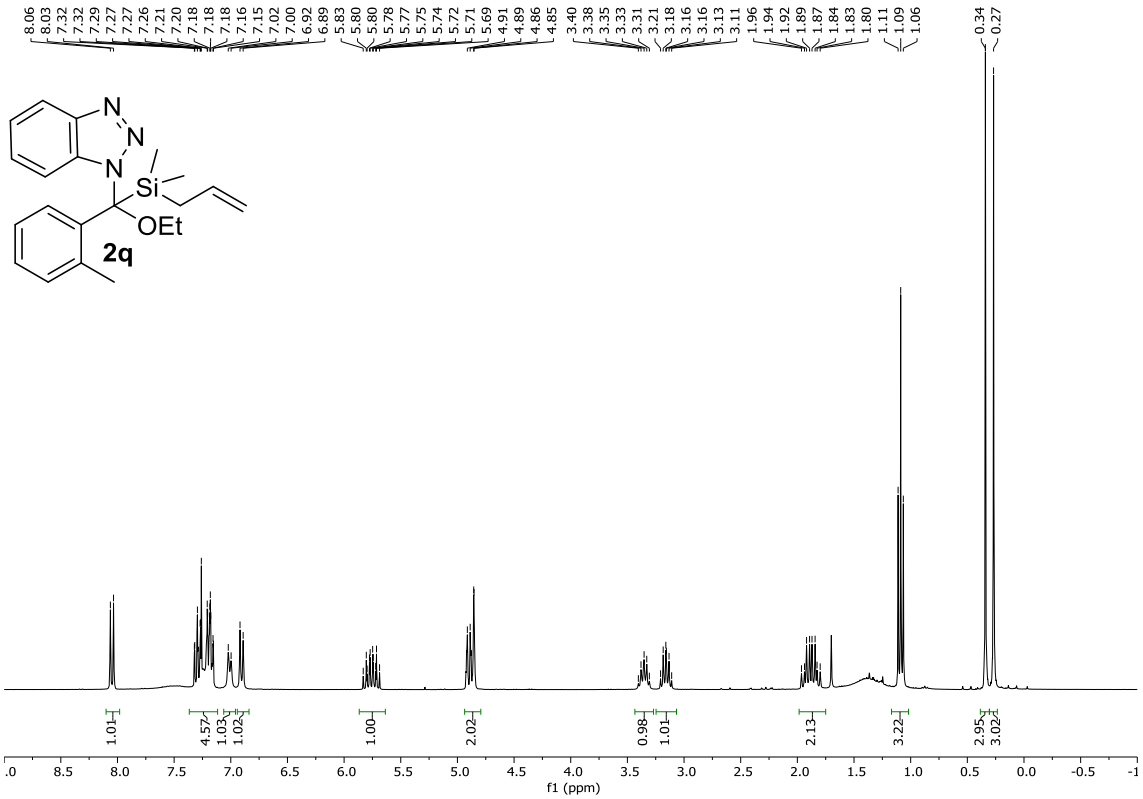
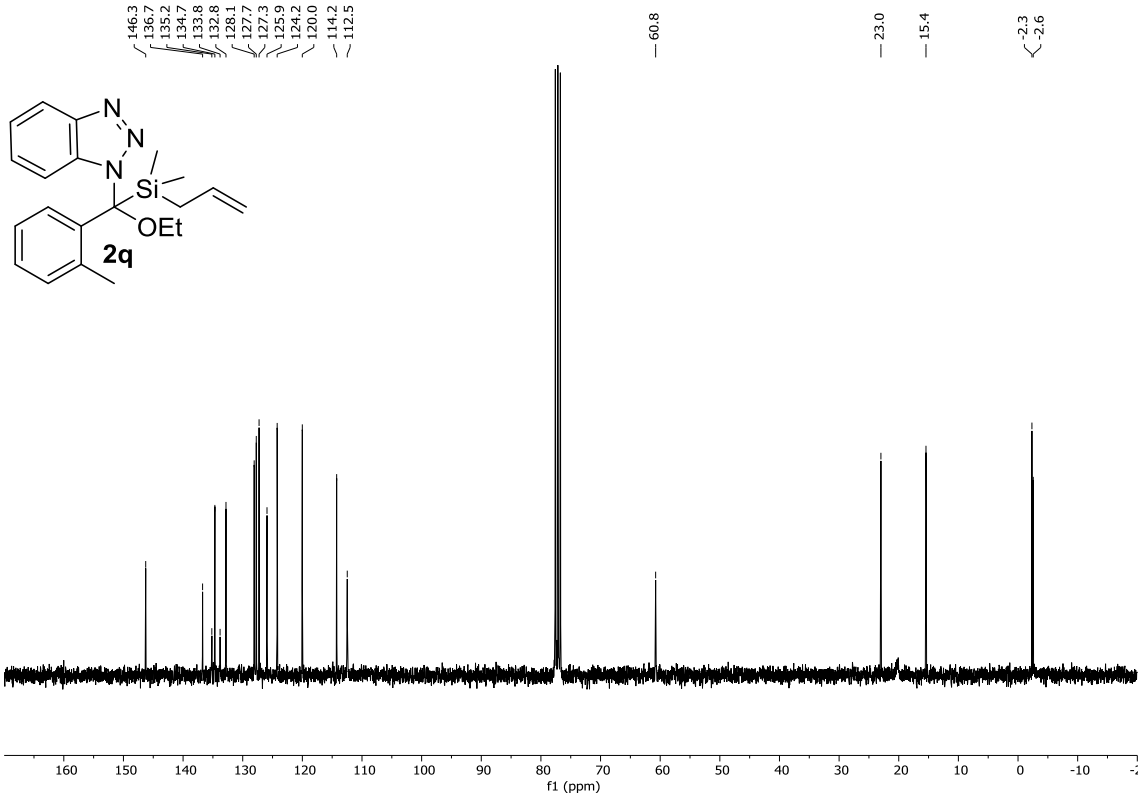


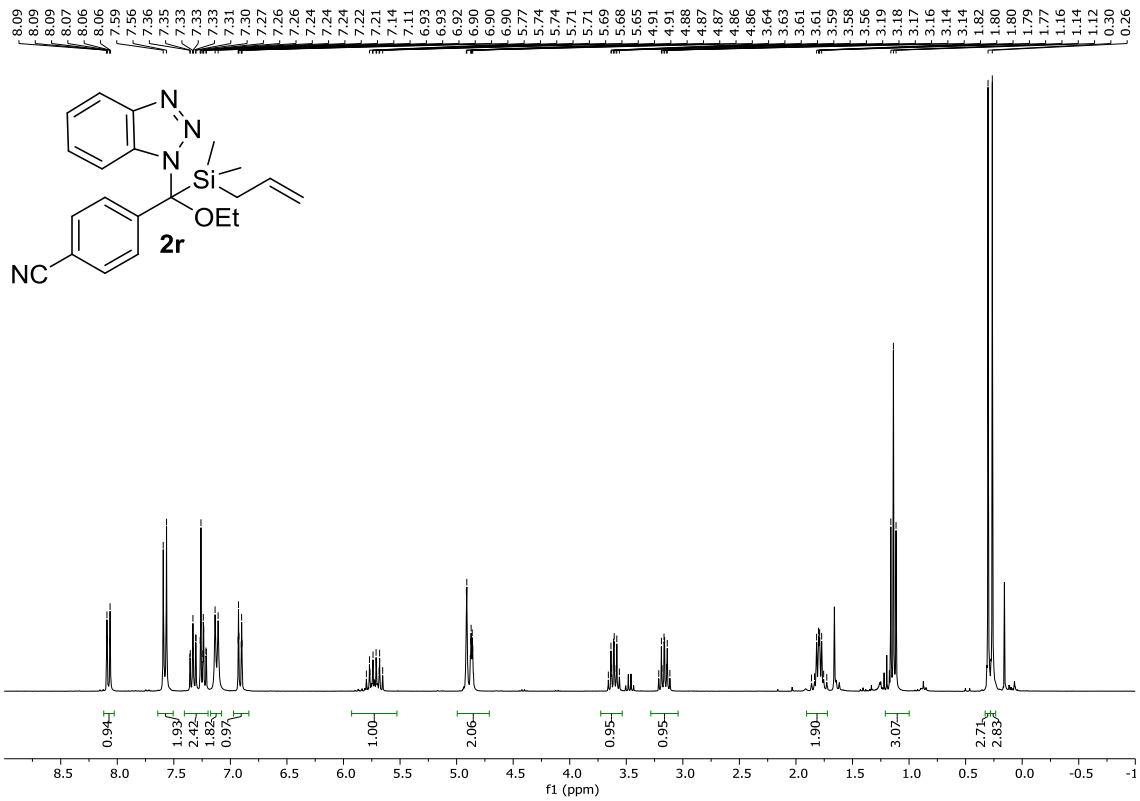
^{1}H NMR ($CDCl_3$, 300 MHz) of
1-((allyldimethylsilyl)(ethoxy)(o-tolyl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2q**)



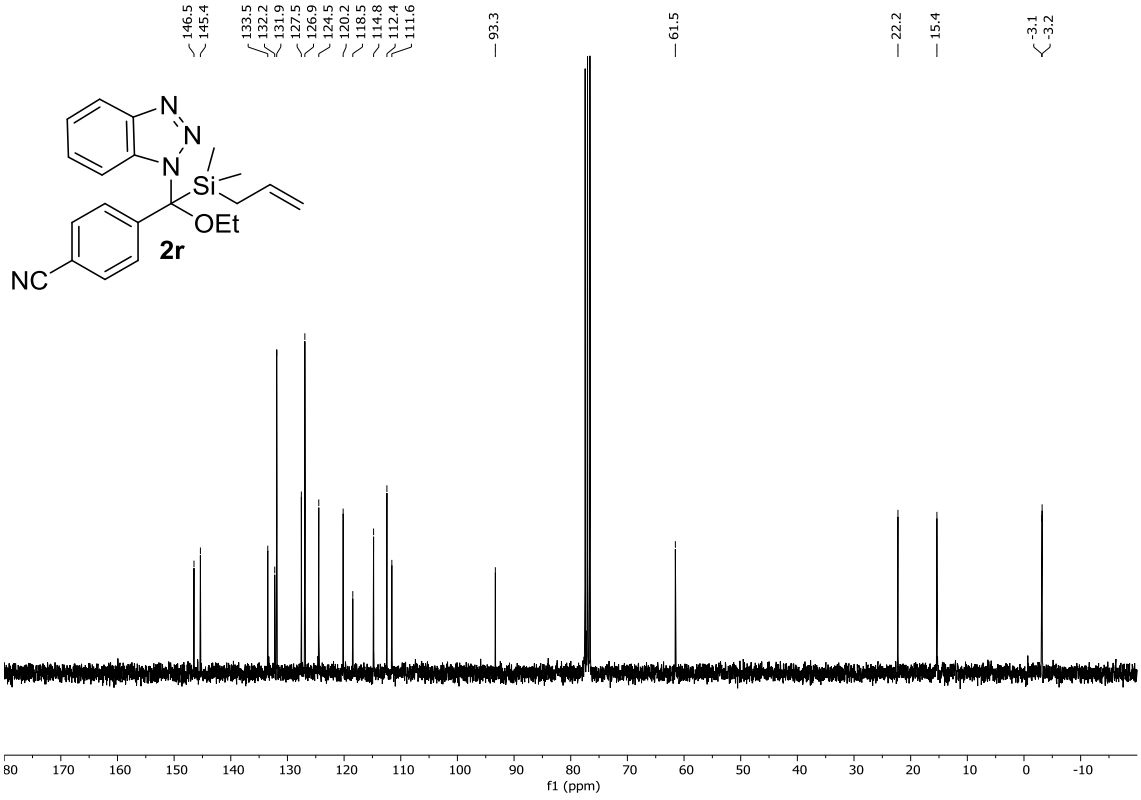
^{13}C NMR ($CDCl_3$, 75 MHz) of
1-((allyldimethylsilyl)(ethoxy)(o-tolyl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (**2q**)



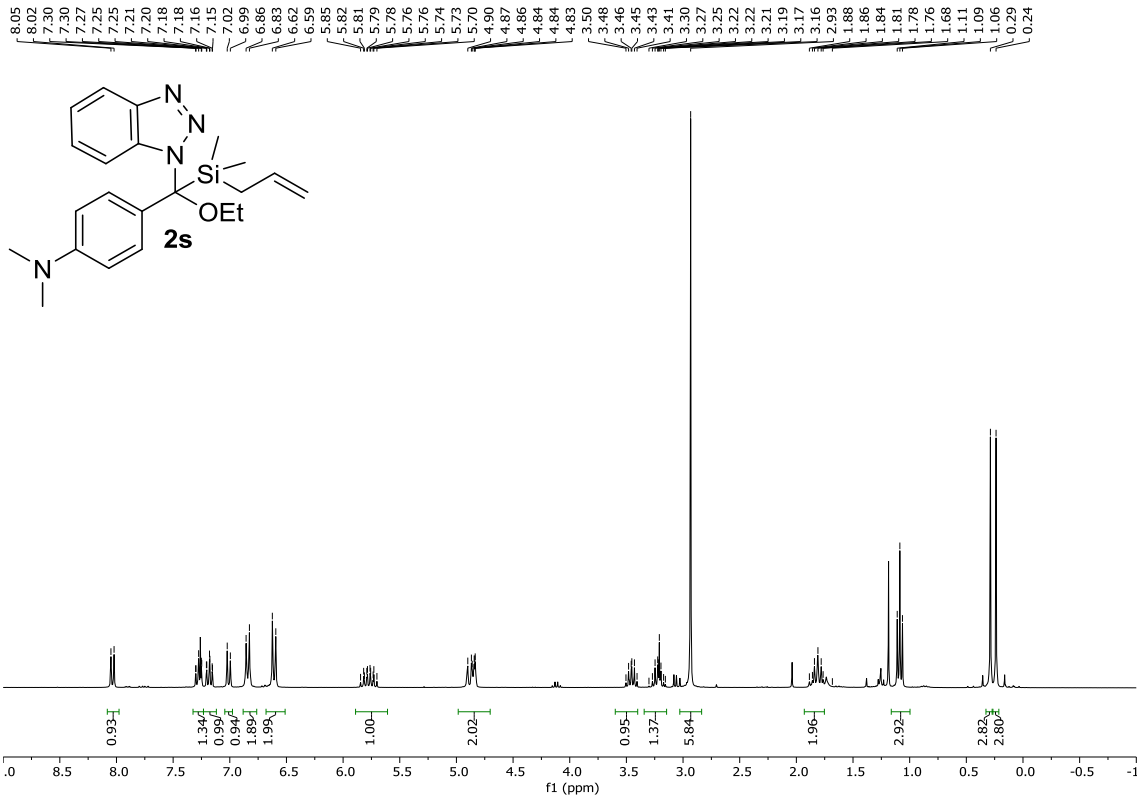
^{1}H NMR ($CDCl_3$, 300 MHz) of
4-((allyldimethylsilyl)(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(ethoxy)methyl)benzonitrile (**2r**)



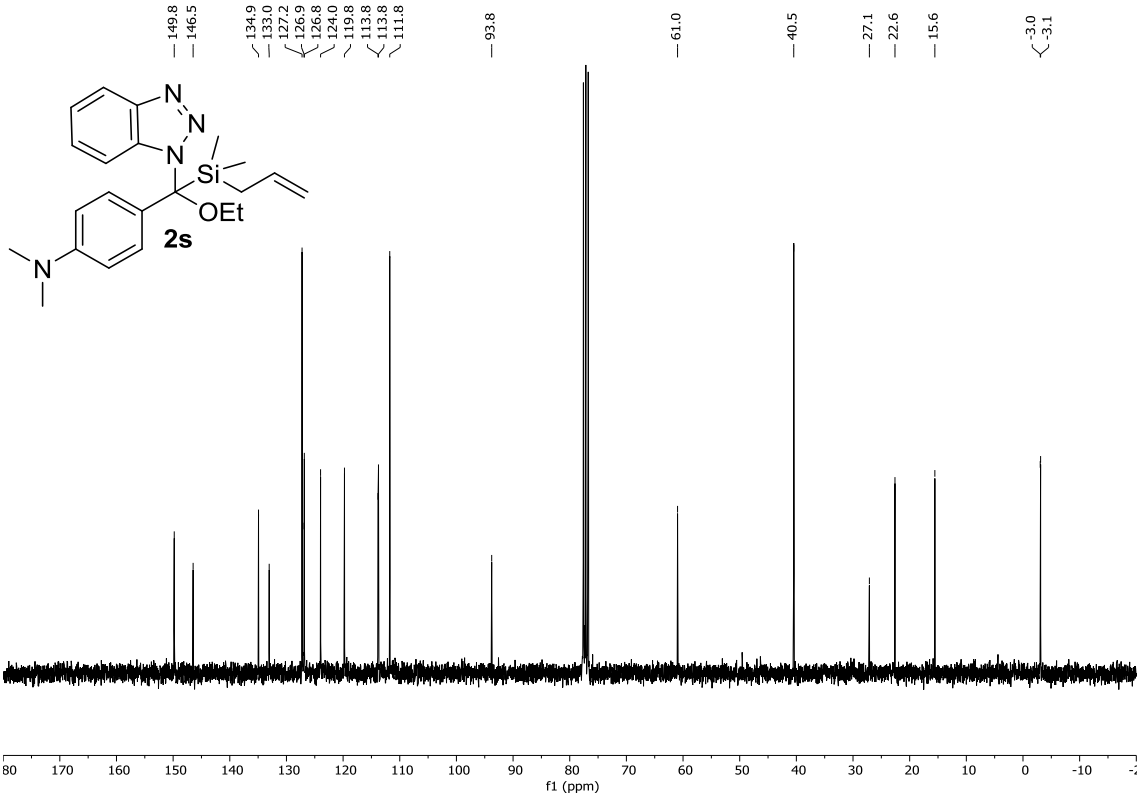
^{13}C NMR ($CDCl_3$, 74 MHz) of
4-((allyldimethylsilyl)(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(ethoxy)methyl)benzonitrile (**2r**)



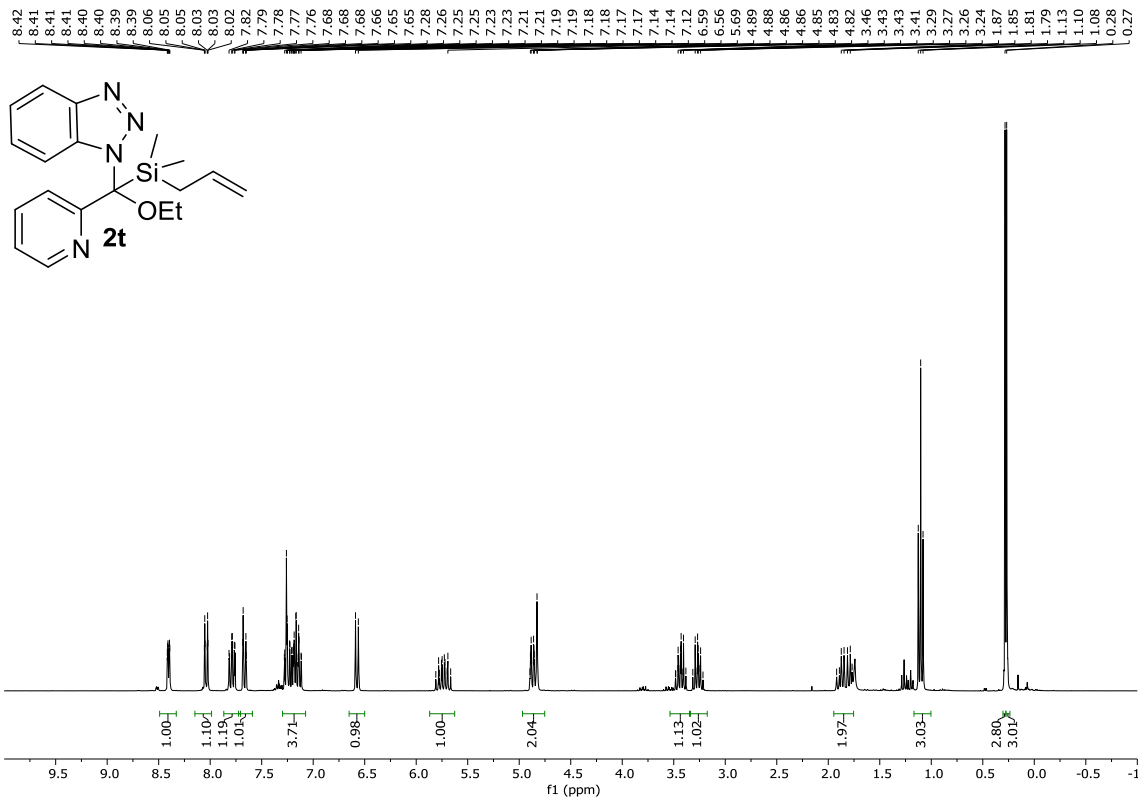
^{1}H NMR ($CDCl_3$, 300 MHz) of 4-((allyldimethylsilyl)(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(ethoxy)methyl)-N,N-dimethylaniline (**2s**)



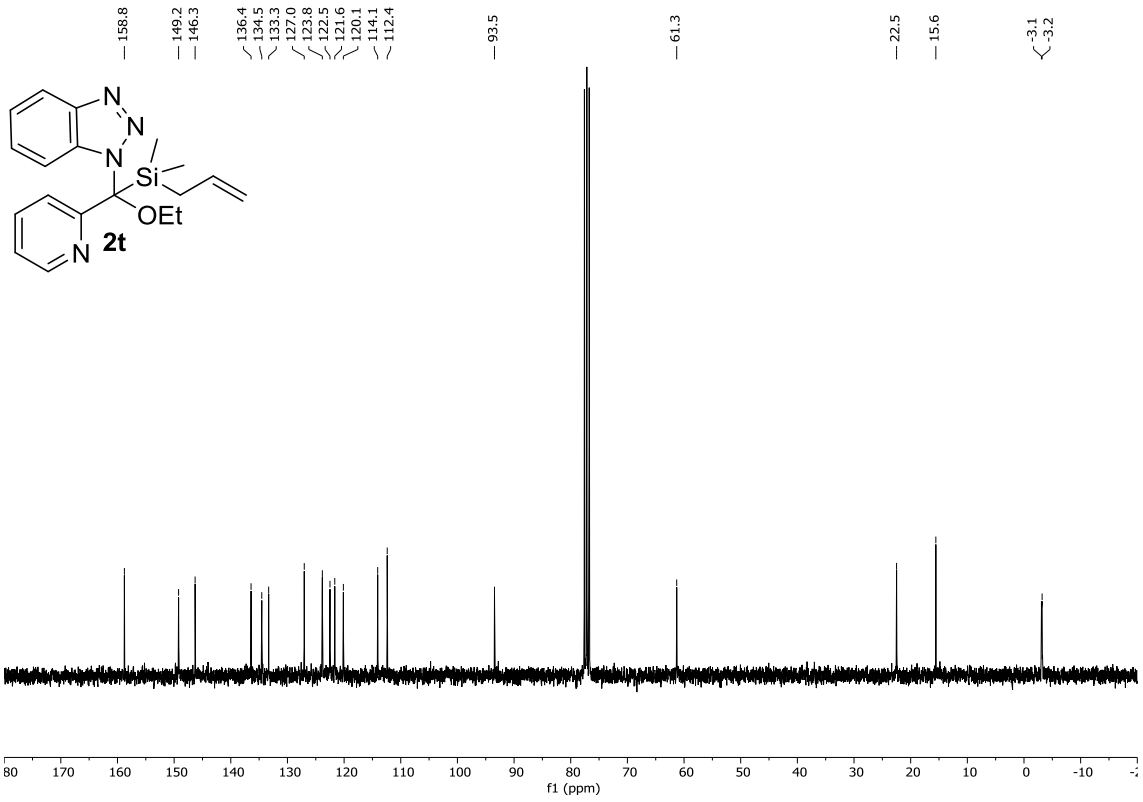
^{13}C NMR ($CDCl_3$, 75 MHz) of 4-((allyldimethylsilyl)(1*H*-benzo[*d*][1,2,3]triazol-1-yl)(ethoxy)methyl)-*N*,*N*-dimethylaniline (**2s**)



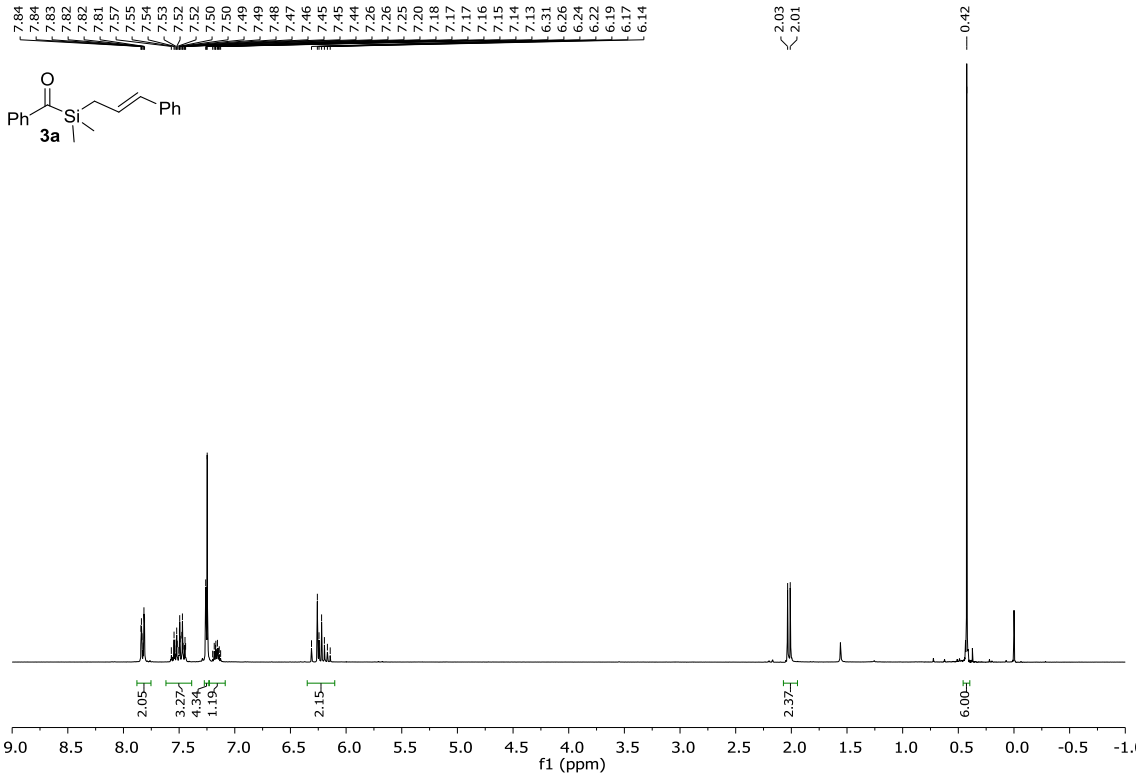
^{1}H NMR ($CDCl_3$, 300 MHz) of
1-((allyldimethylsilyl)(ethoxy)(pyridin-2-yl)methyl)-1H-benzo[*d*][1,2,3]triazole (**2t**)



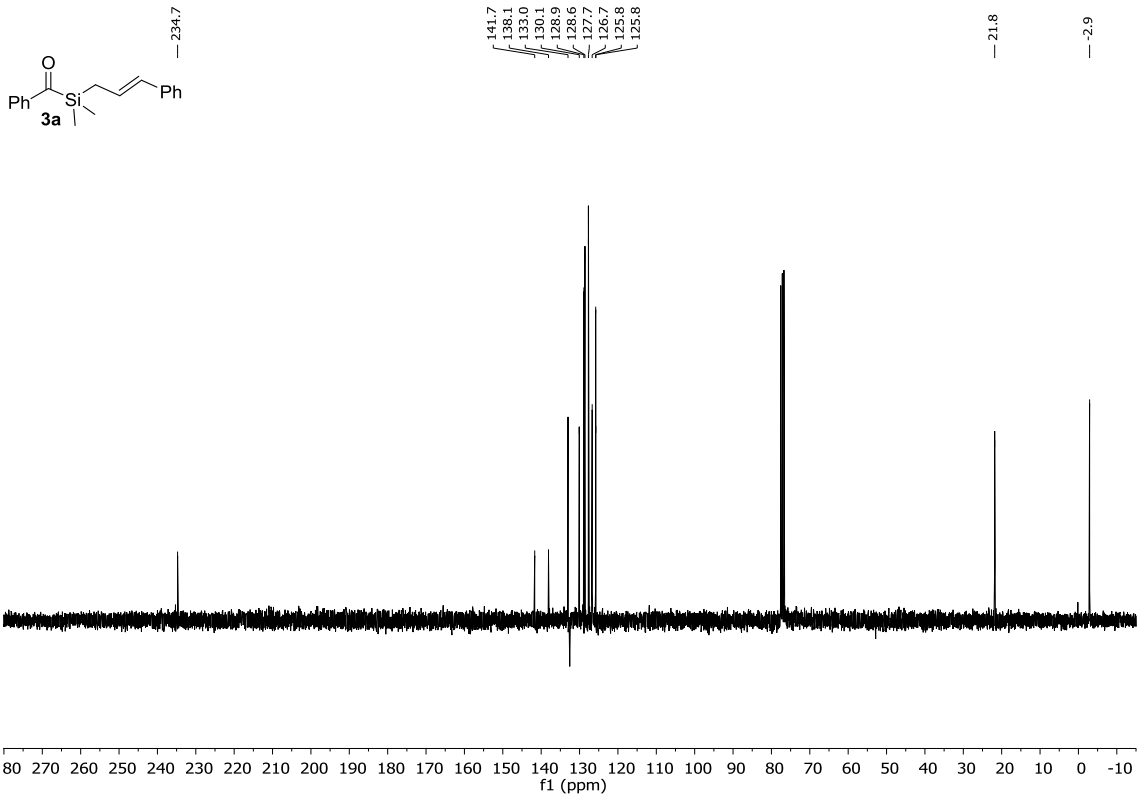
^{13}C NMR ($CDCl_3$, 75 MHz) of
1-((allyldimethylsilyl)(ethoxy)(pyridin-2-yl)methyl)-1H-benzo[*d*][1,2,3]triazole (**2t**)



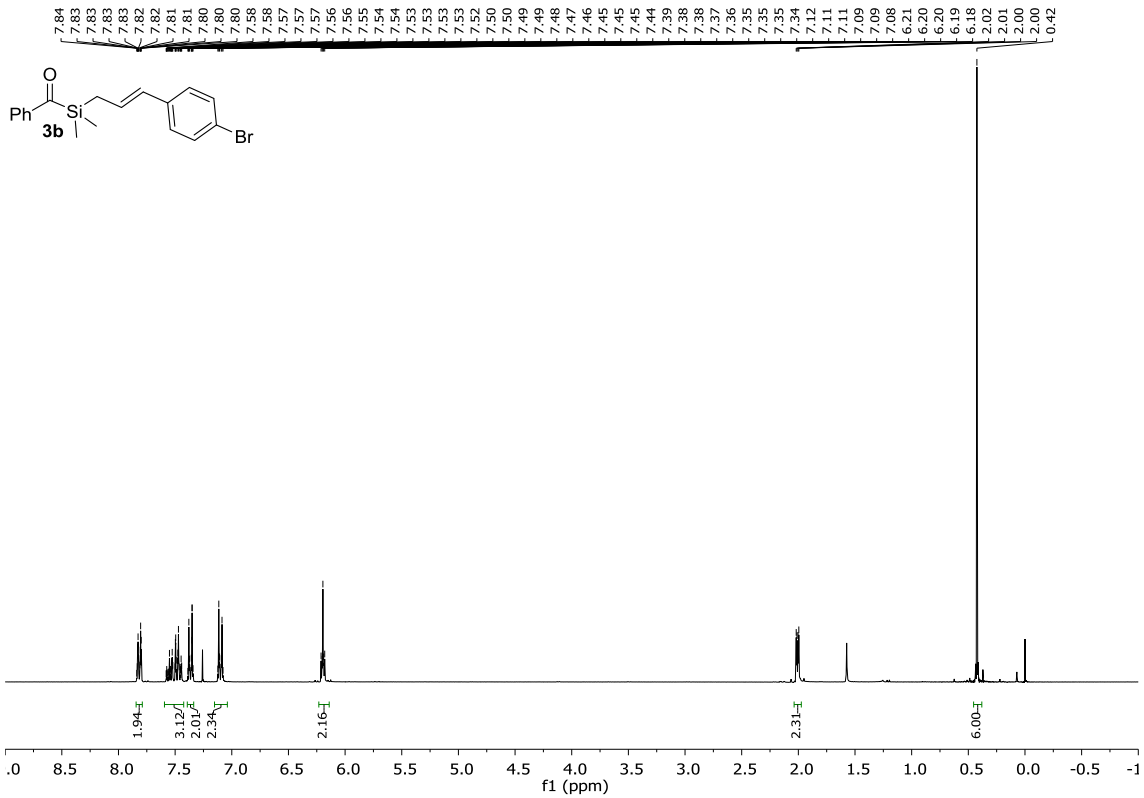
^{1}H NMR ($CDCl_3$, 300 MHz) of (cinnamyldimethylsilyl)(phenyl)methanone (**3a**)



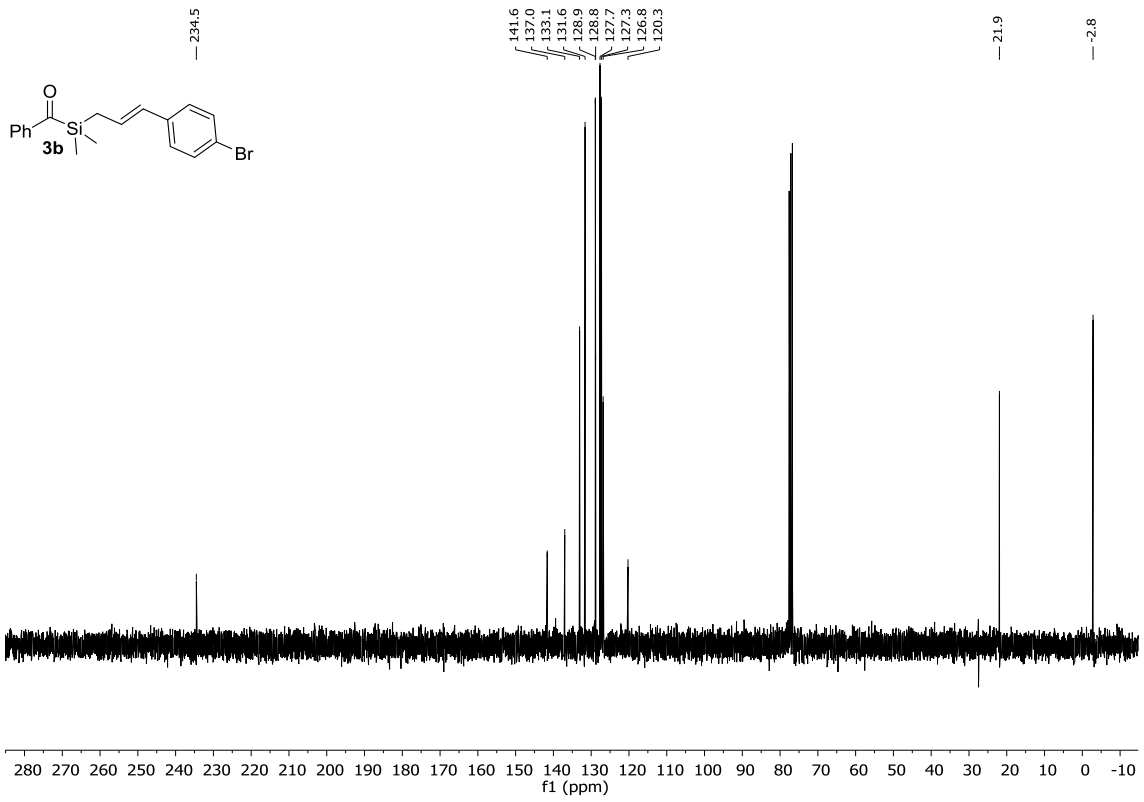
^{13}C NMR ($CDCl_3$, 75 MHz) of (cinnamyldimethylsilyl)(phenyl)methanone (**3a**)



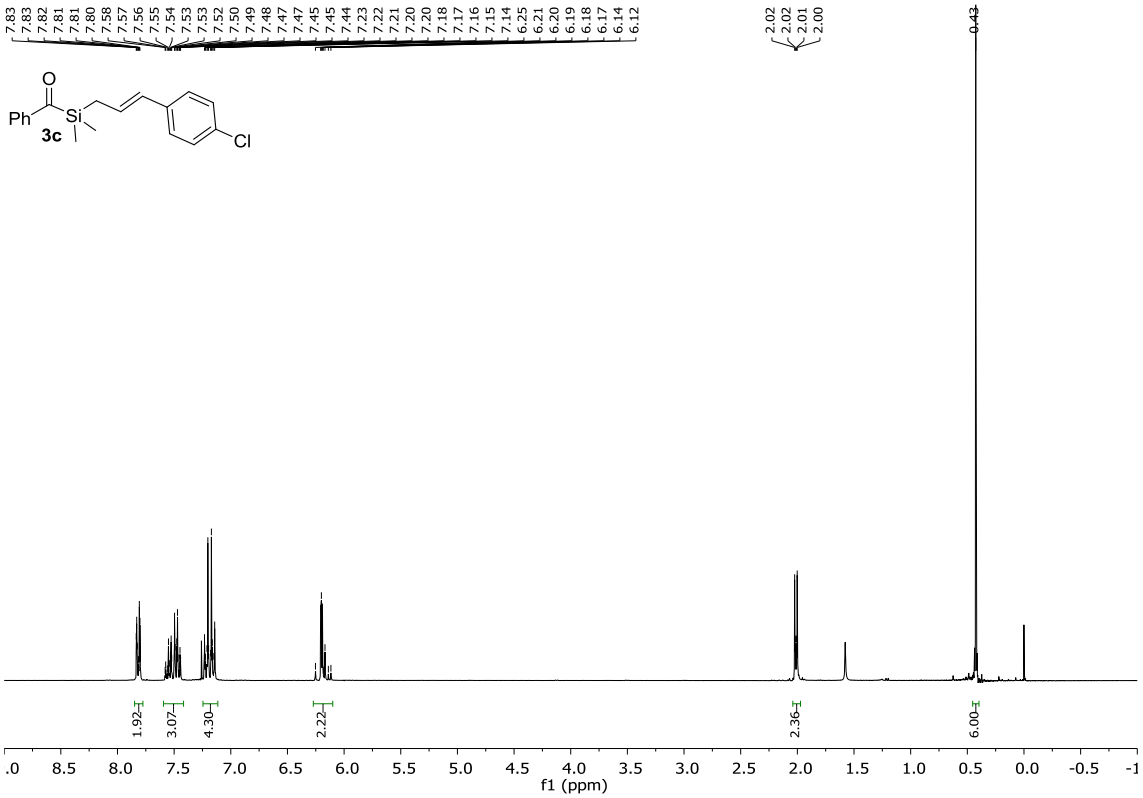
^{1}H NMR ($CDCl_3$, 300 MHz) of (*E*)-((3-(4-bromophenyl)allyl)dimethylsilyl)(phenyl)methanone (**3b**)



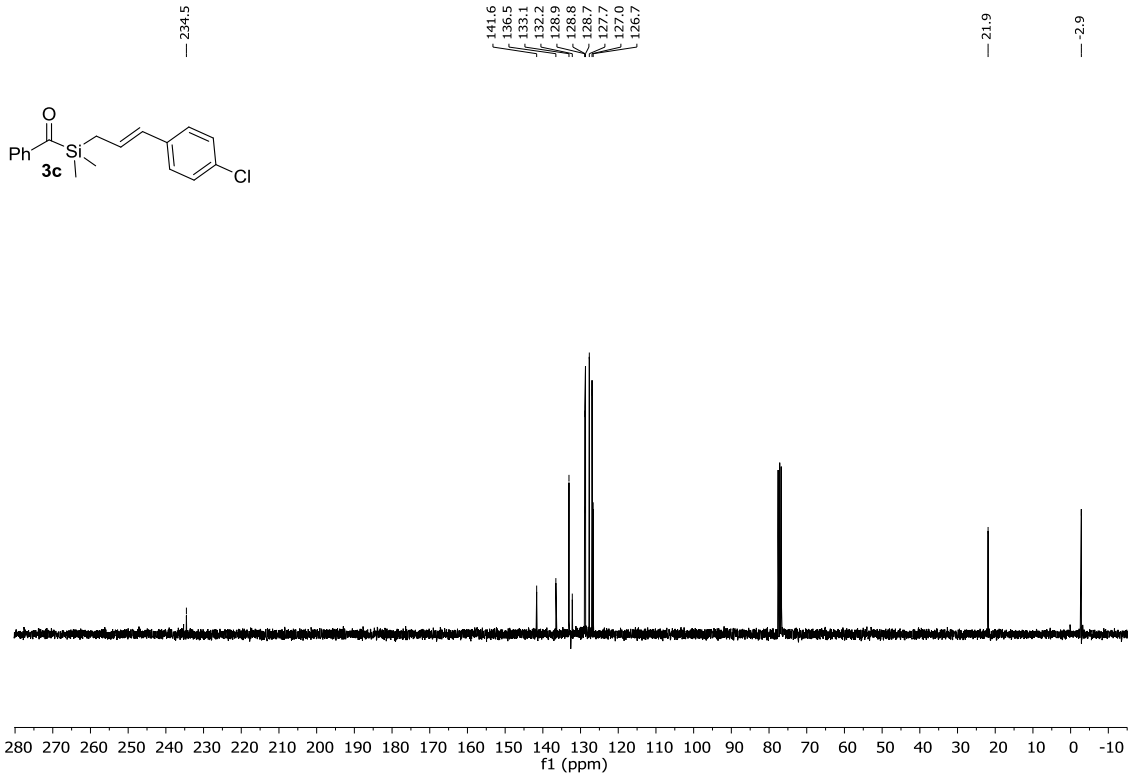
^{13}C NMR ($CDCl_3$, 75 MHz) of (*E*)-((3-(4-bromophenyl)allyl)dimethylsilyl)(phenyl)methanone (**3b**)



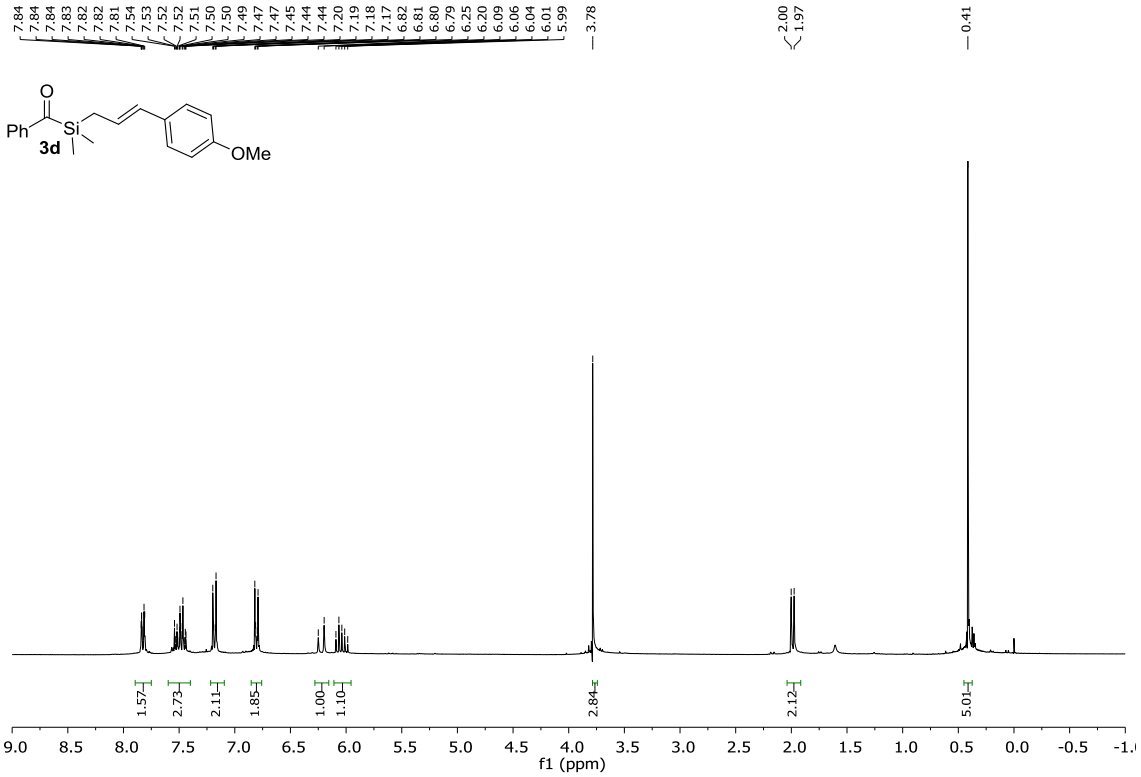
^{1}H NMR ($CDCl_3$, 300 MHz) of (*E*)-((3-(4-chlorophenyl)allyl)dimethylsilyl)(phenyl)methanone (**3c**)



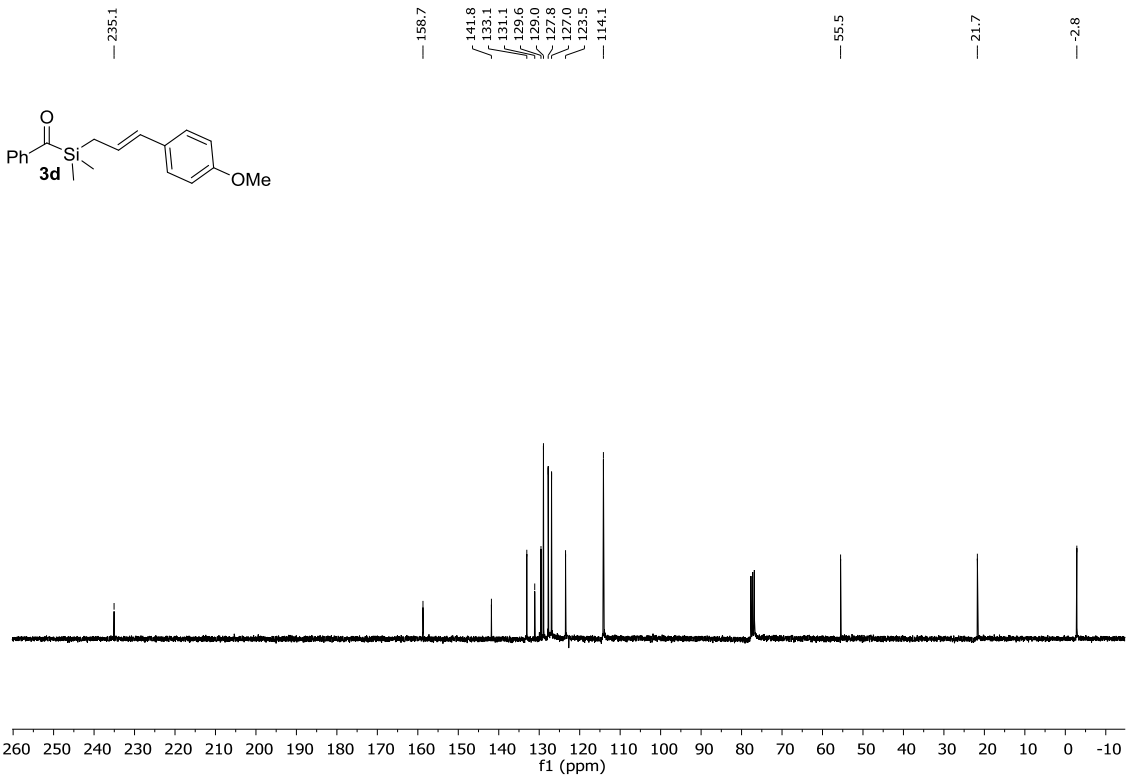
^{13}C NMR ($CDCl_3$, 75 MHz) of (*E*)-((3-(4-chlorophenyl)allyl)dimethylsilyl)(phenyl)methanone (**3c**)



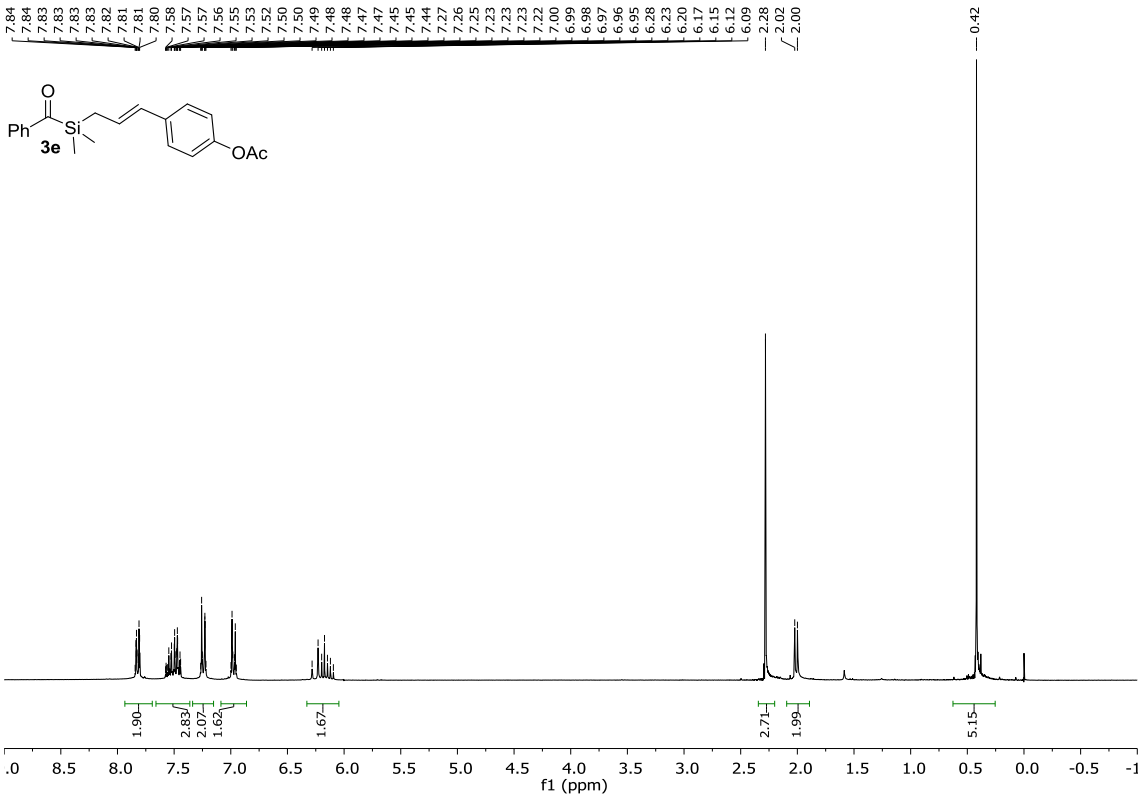
^{1}H NMR ($CDCl_3$, 300 MHz) of (*E*)-((3-(4-methoxyphenyl)allyl)dimethylsilyl)(phenyl)methanone (**3d**)



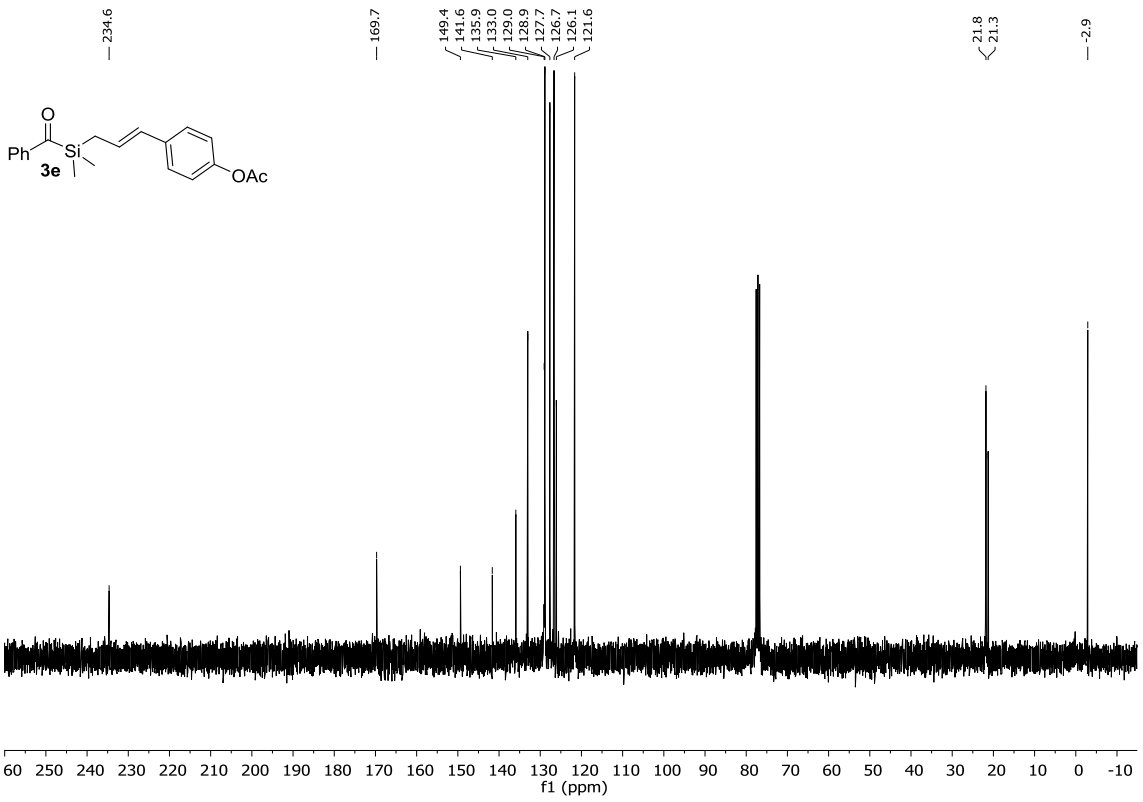
^{13}C NMR ($CDCl_3$, 75 MHz) of (*E*)-((3-(4-methoxyphenyl)allyl)dimethylsilyl)(phenyl)methanone (**3d**)



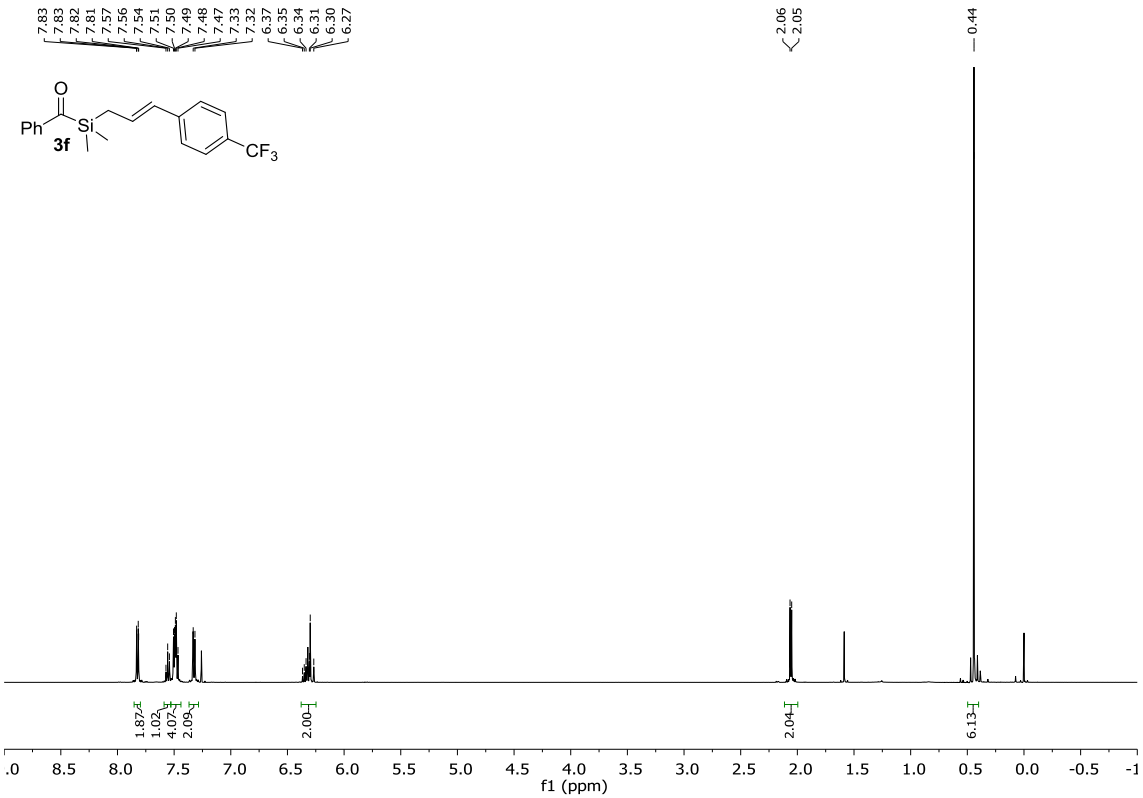
^{1}H NMR ($CDCl_3$, 300 MHz) of (*E*)-4-(3-(benzoyldimethylsilyl)prop-1-en-1-yl)phenyl acetate (**3e**)



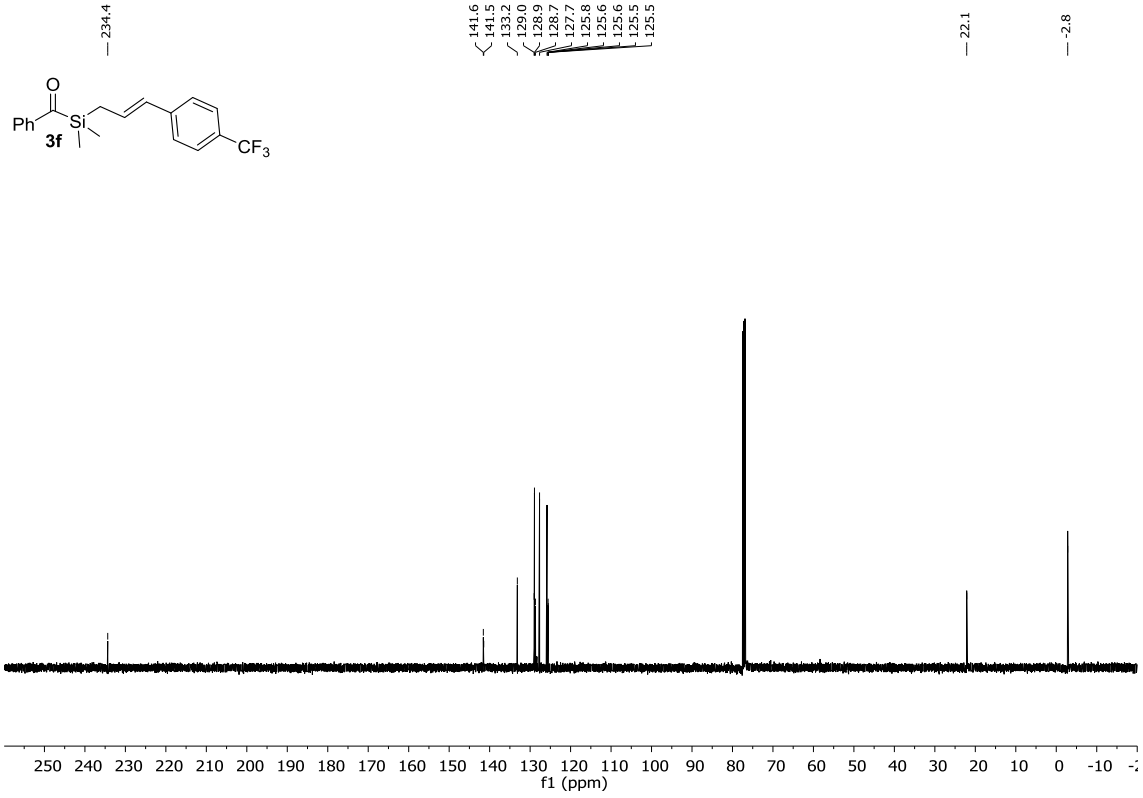
^{13}C NMR ($CDCl_3$, 75 MHz) of (*E*)-4-(3-(benzoyldimethylsilyl)prop-1-en-1-yl)phenyl acetate (**6e**)



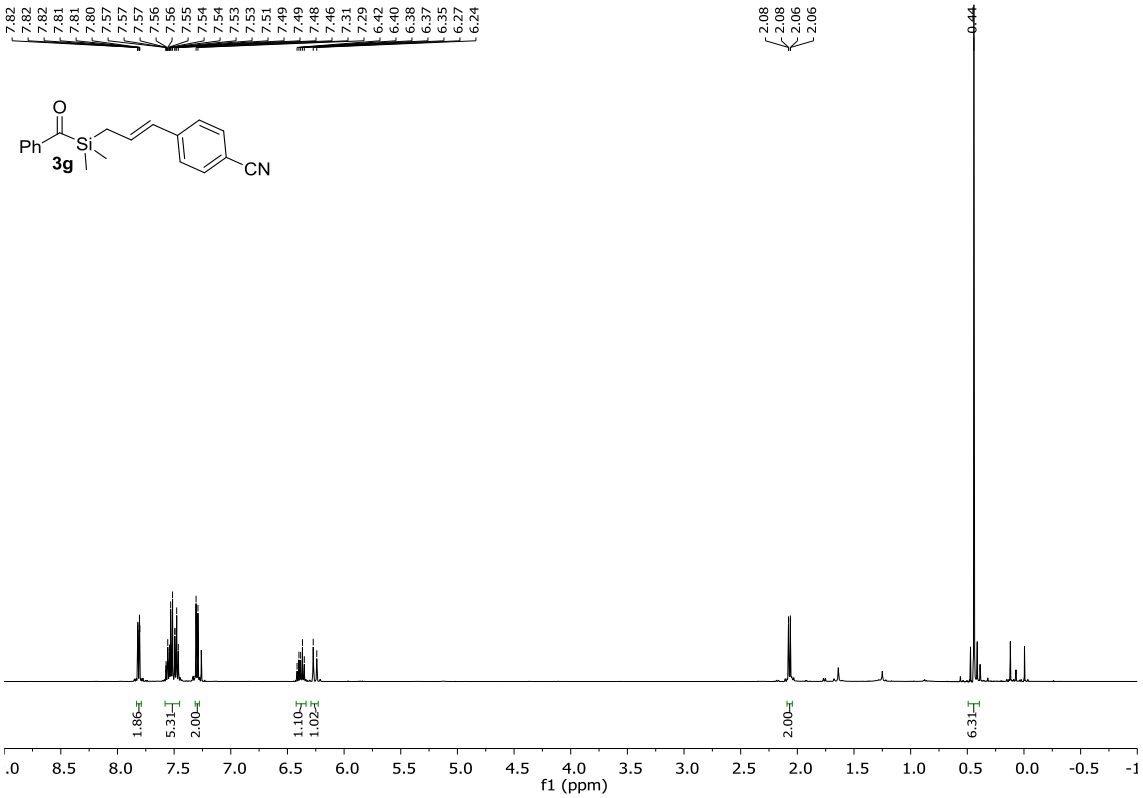
^{1}H NMR ($CDCl_3$, 500 MHz) of
(*E*)-(dimethyl(3-(4-(trifluoromethyl)phenyl)allyl)silyl)(phenyl)methanone (**3f**)



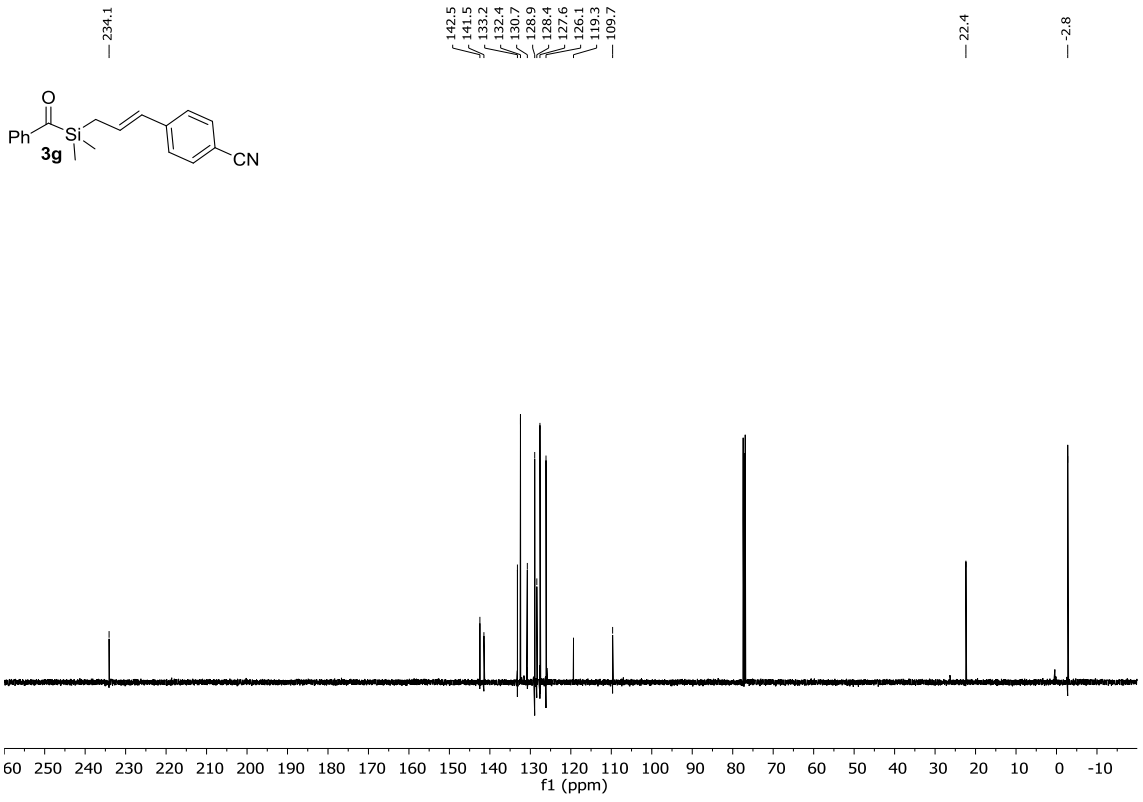
^{13}C NMR ($CDCl_3$, 125 MHz) of
(*E*)-(dimethyl(3-(4-(trifluoromethyl)phenyl)allyl)silyl)(phenyl)methanone (**3f**)



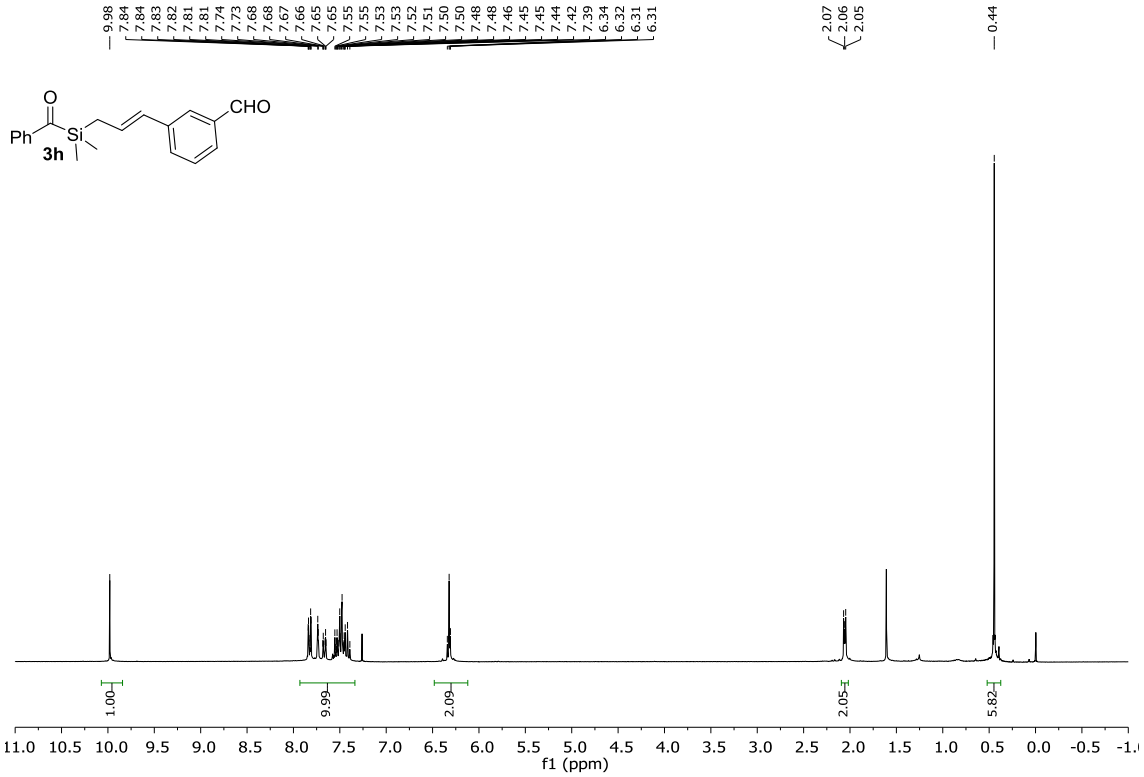
^{1}H NMR ($CDCl_3$, 500 MHz) of (*E*)-4-(3-(benzoyldimethylsilyl)prop-1-en-1-yl)benzonitrile (**3g**)



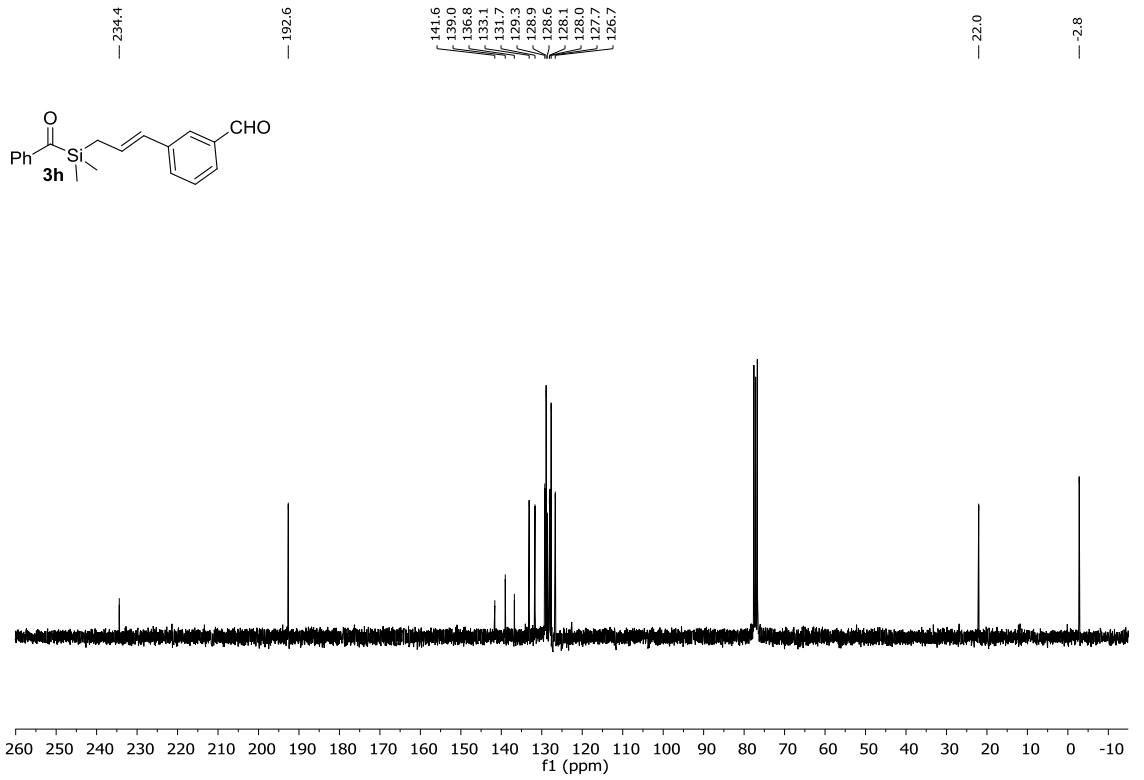
^{13}C NMR ($CDCl_3$, 125 MHz) of (*E*)-4-(3-(benzoyldimethylsilyl)prop-1-en-1-yl)benzonitrile (**3g**)



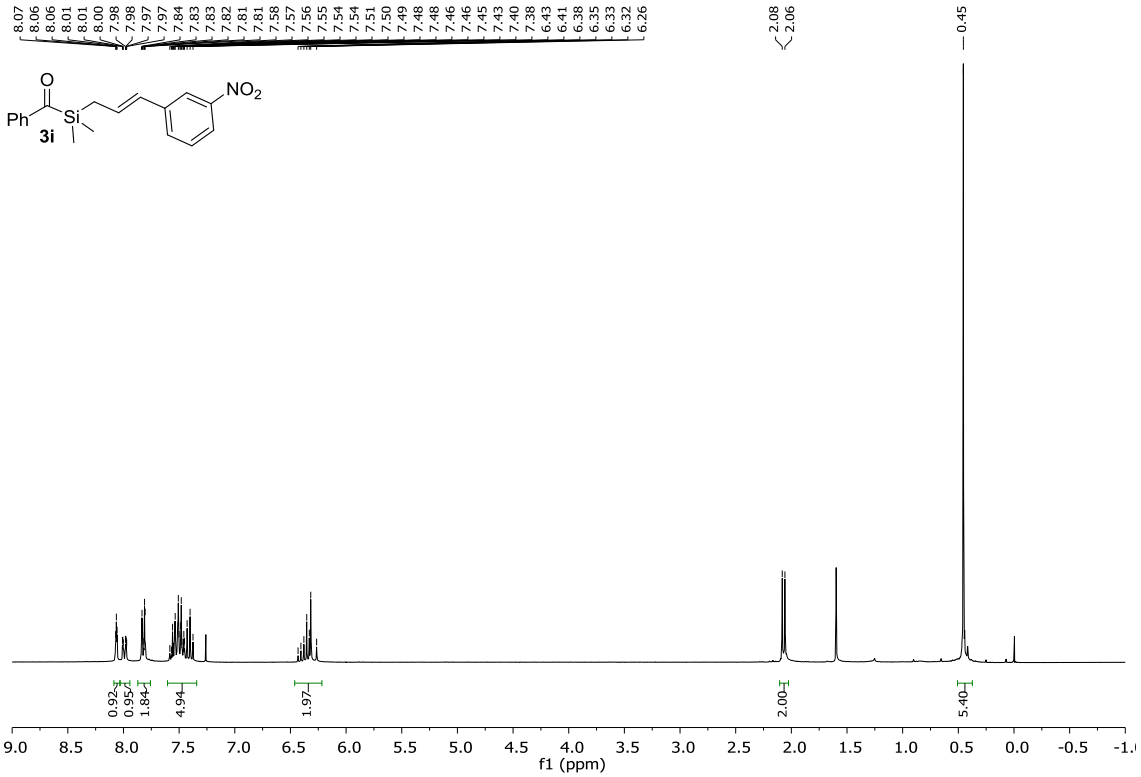
^{1}H NMR ($CDCl_3$, 300 MHz) of
(*E*)-3-(3-(benzoyldimethylsilyl)prop-1-en-1-yl)benzaldehydeacetate (**3h**)



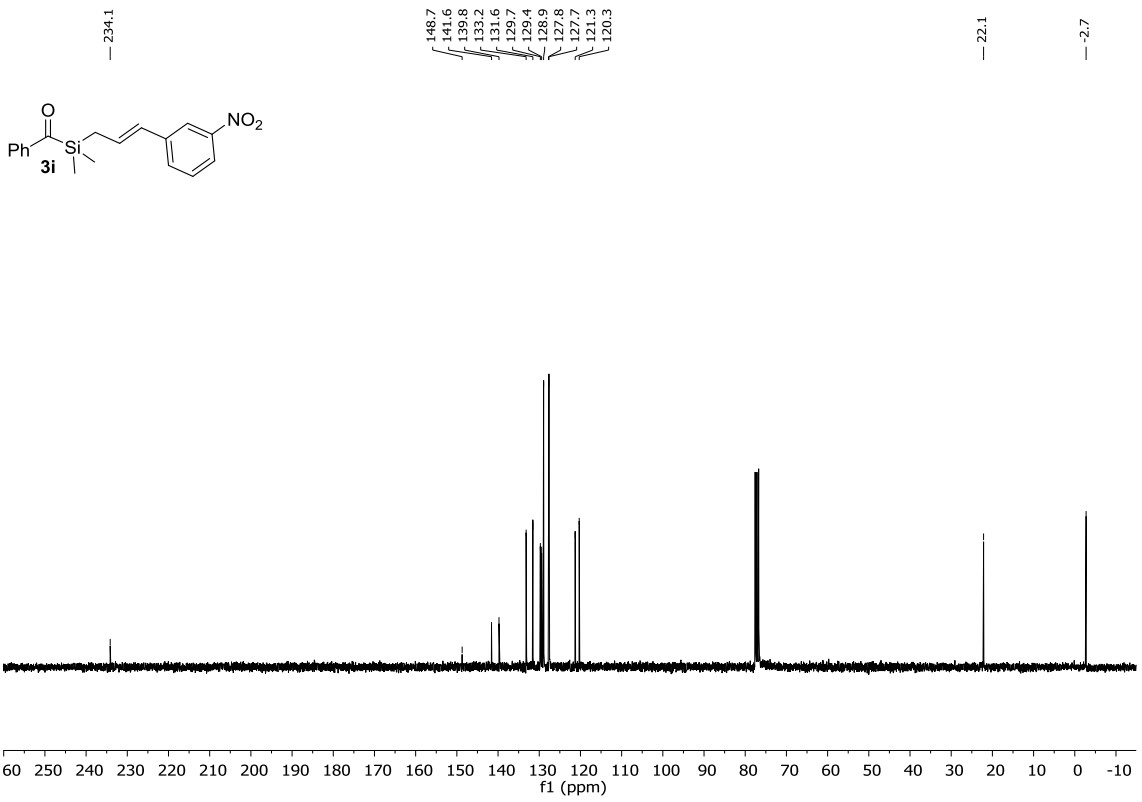
^{13}C NMR ($CDCl_3$, 75 MHz) of
(*E*)-3-(3-(benzoyldimethylsilyl)prop-1-en-1-yl)benzaldehydeacetate (**3h**)



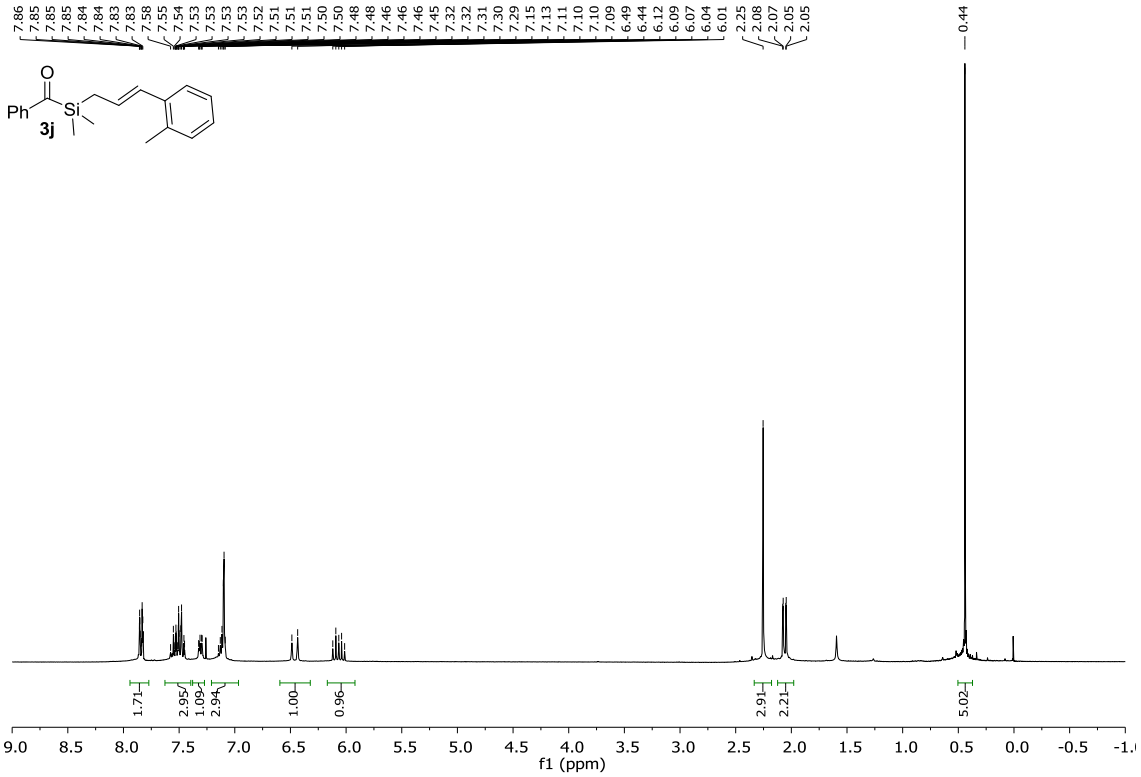
^{1}H NMR ($CDCl_3$, 300 MHz) of (*E*)-(dimethyl(3-(3-nitrophenyl)allyl)silyl)(phenyl)methanone (**3i**)



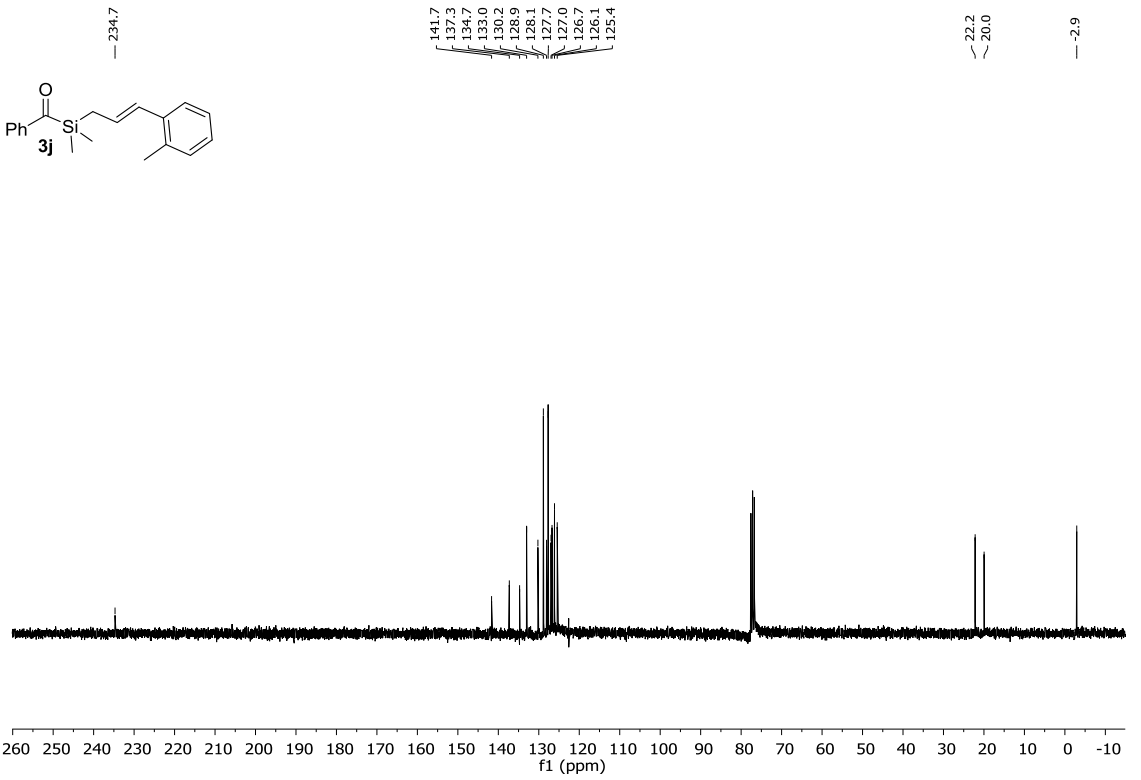
^{13}C NMR ($CDCl_3$, 75 MHz) of (*E*)-(dimethyl(3-(3-nitrophenyl)allyl)silyl)(phenyl)methanone (**3i**)



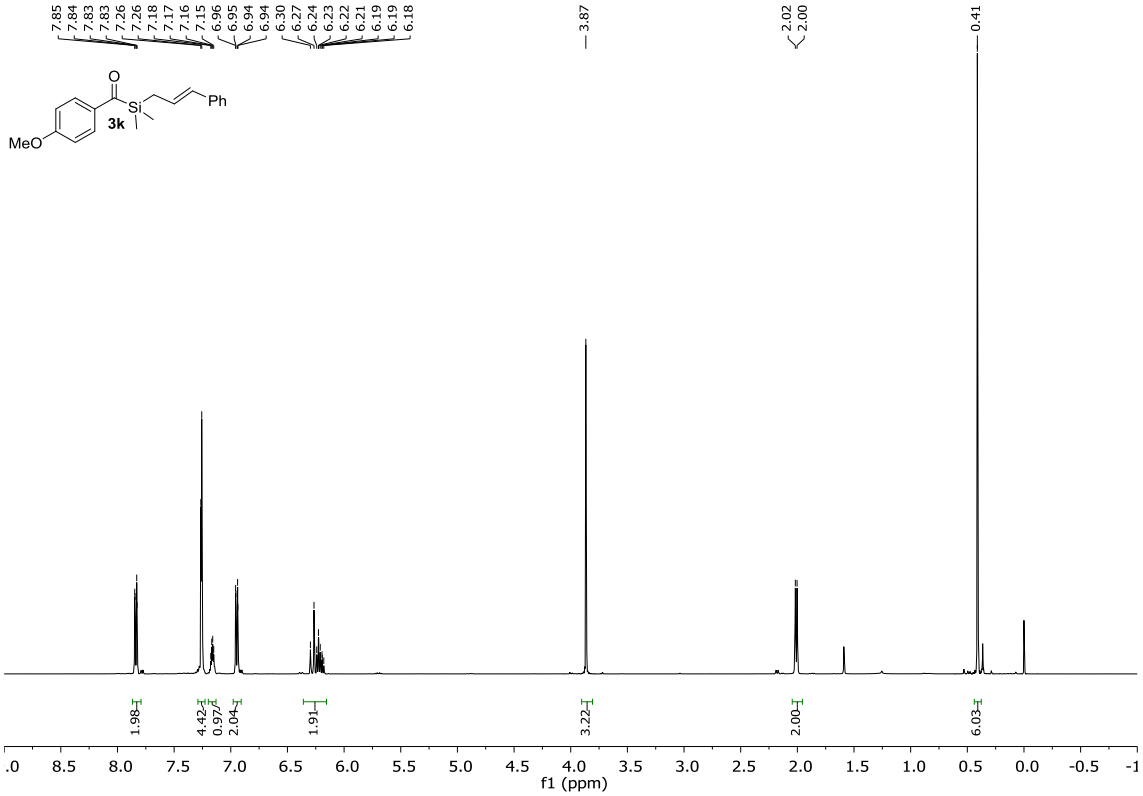
^{1}H NMR ($CDCl_3$, 300 MHz) of (*E*)-(dimethyl(3-(o-tolyl)allyl)silyl)(phenyl)methanonemethanone (**3j**)



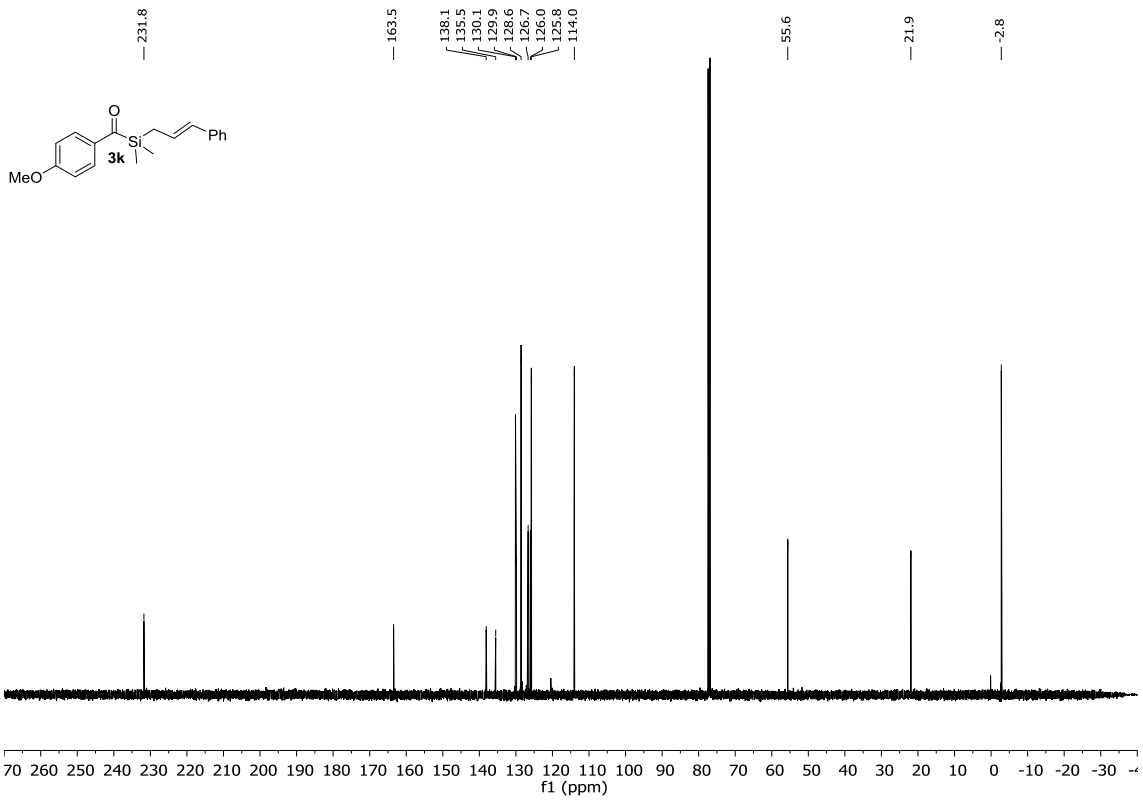
^{13}C NMR ($CDCl_3$, 75 MHz) of (*E*)-(dimethyl(3-(o-tolyl)allyl)silyl)(phenyl)methanonemethanone (**3j**)



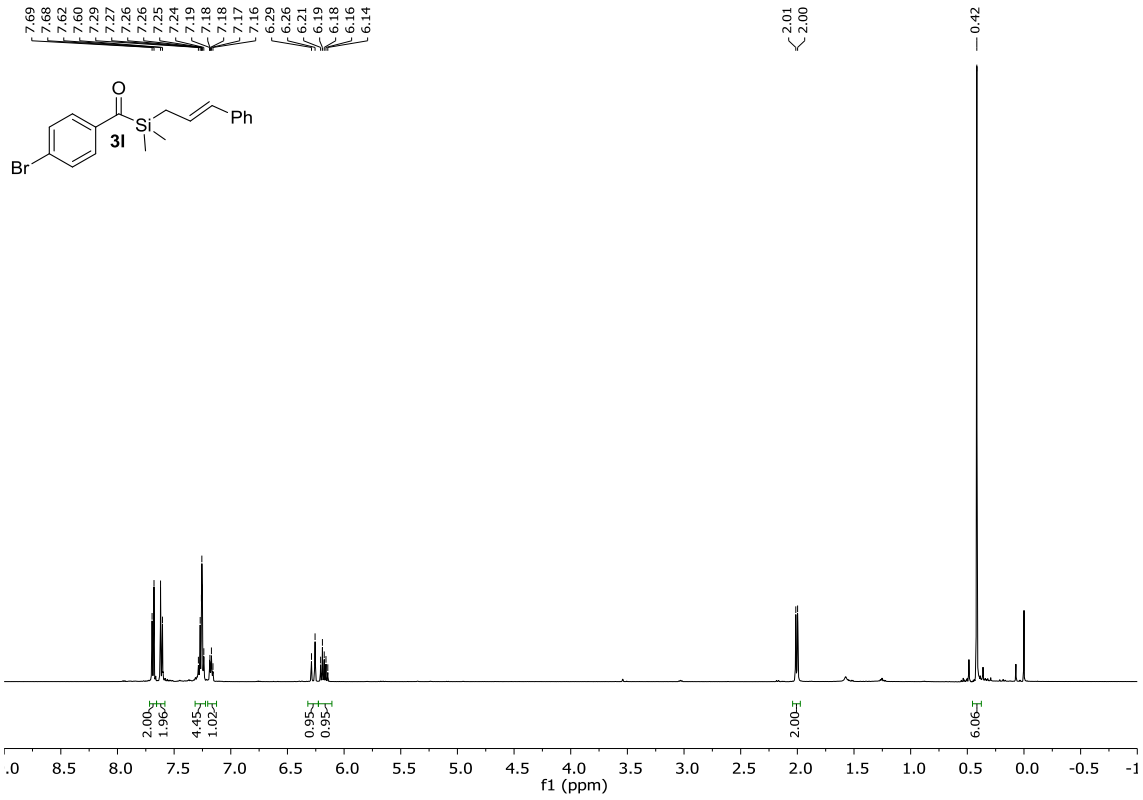
^{1}H NMR ($CDCl_3$, 500 MHz) of (cinnamyldimethylsilyl)(4-methoxyphenyl)methanone (**3k**)



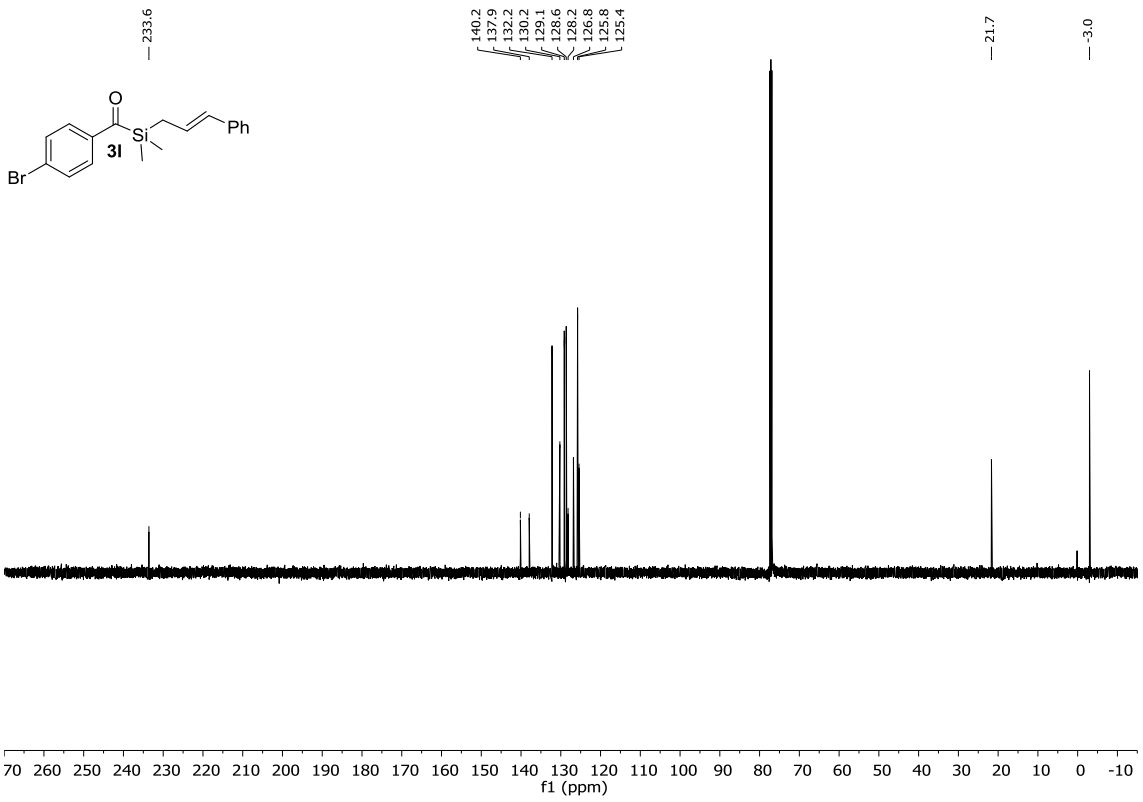
^{13}C NMR ($CDCl_3$, 125 MHz) of (cinnamyldimethylsilyl)(4-methoxyphenyl)methanone (**3k**)



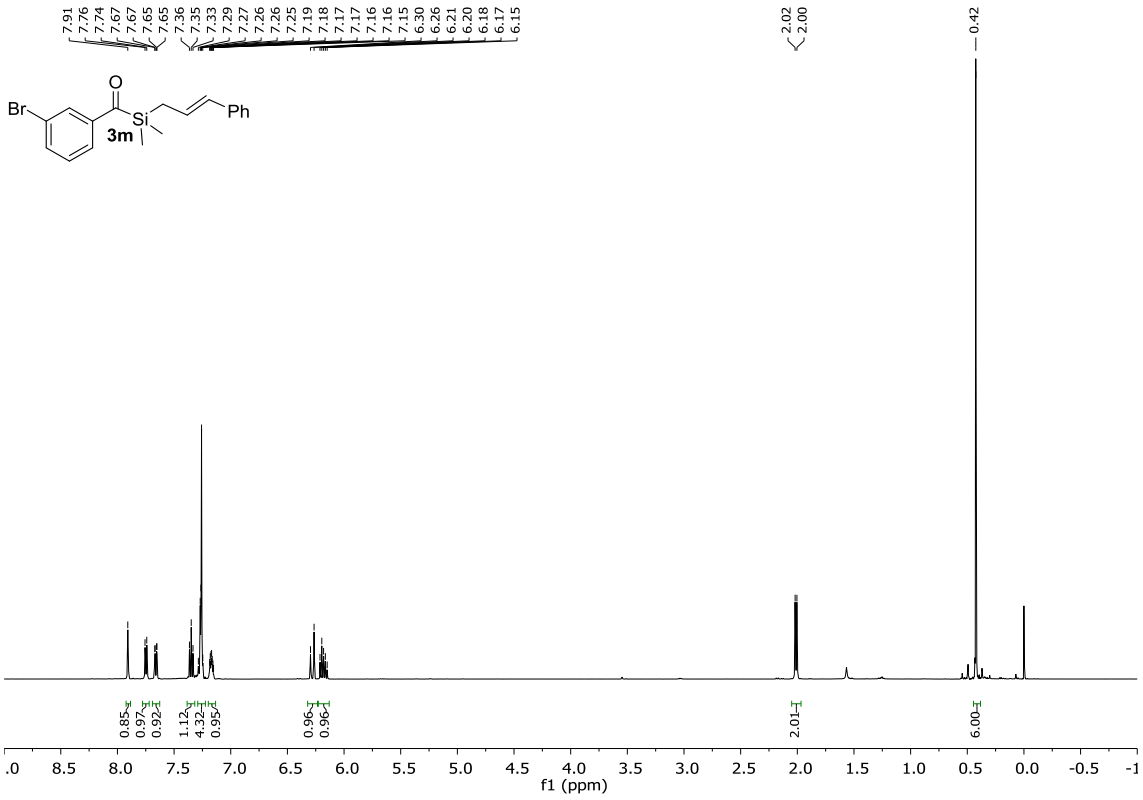
^{1}H NMR ($CDCl_3$, 500 MHz) of (4-bromophenyl)(cinnamyldimethylsilyl)methanone (**3l**)



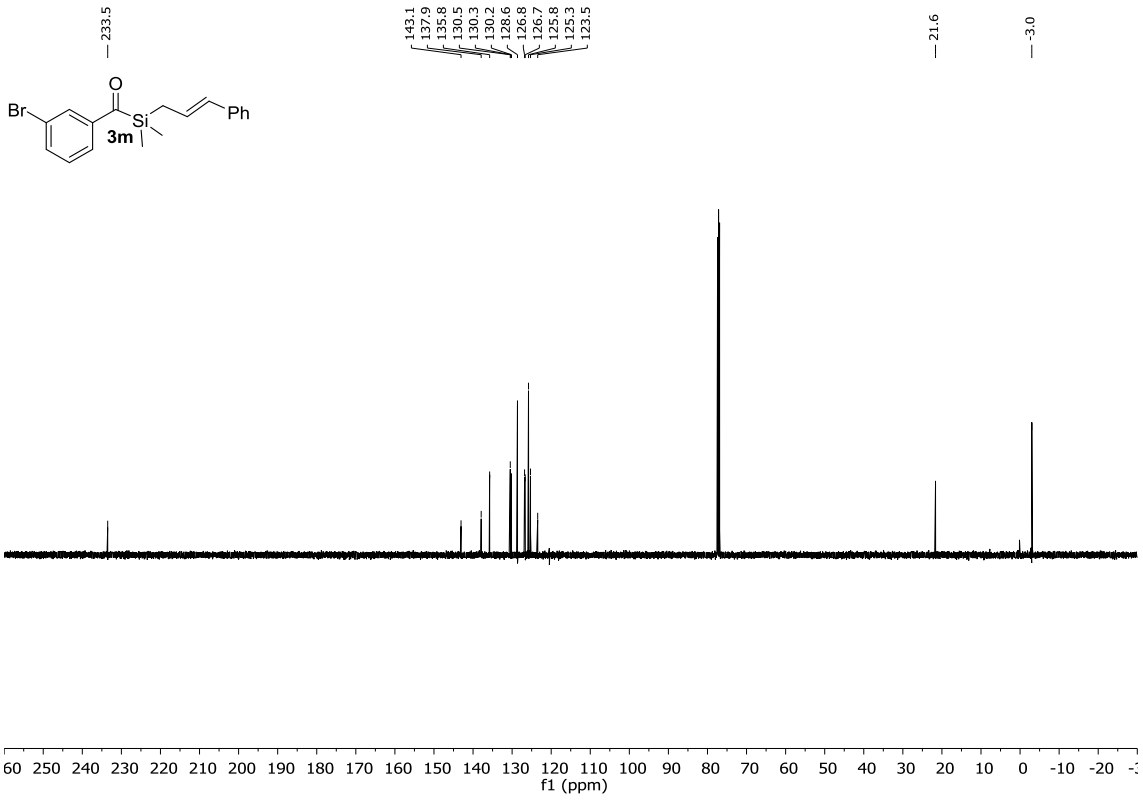
^{13}C NMR ($CDCl_3$, 125 MHz) of (4-bromophenyl)(cinnamyldimethylsilyl)methanone (**3l**)



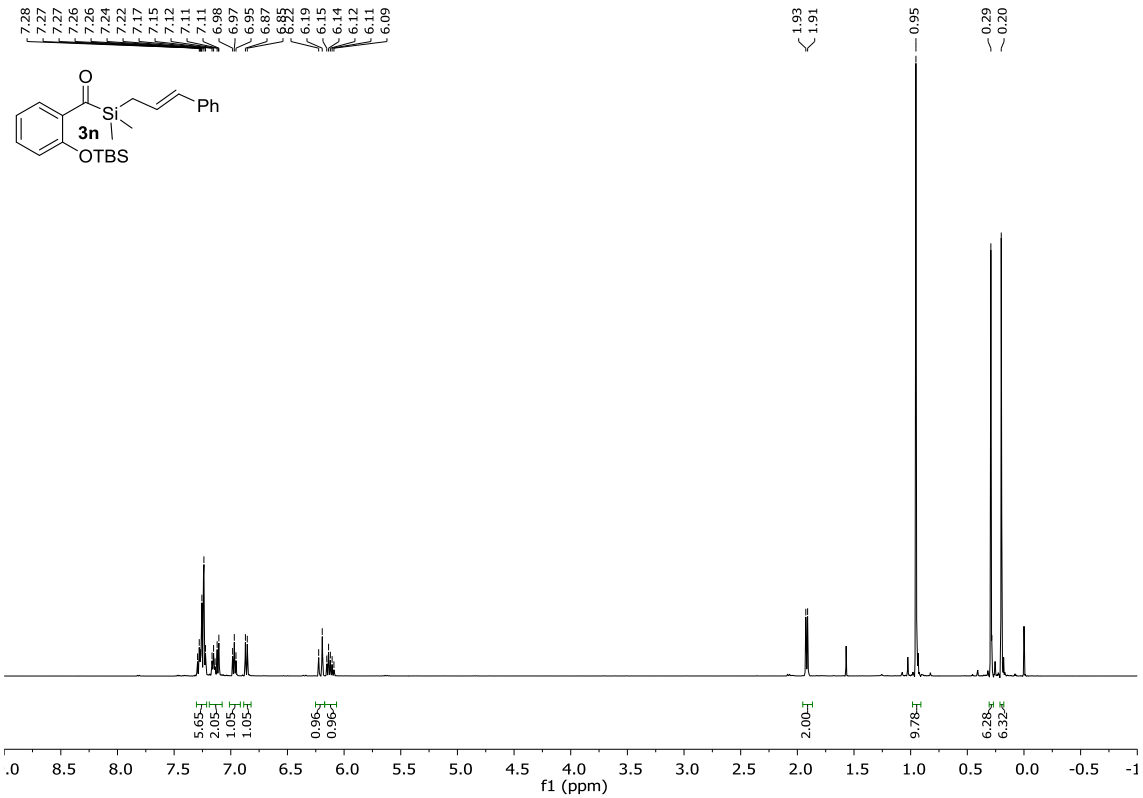
^{1}H NMR ($CDCl_3$, 500 MHz) of (3-bromophenyl)(cinnamyldimethylsilyl)methanone (**3m**)



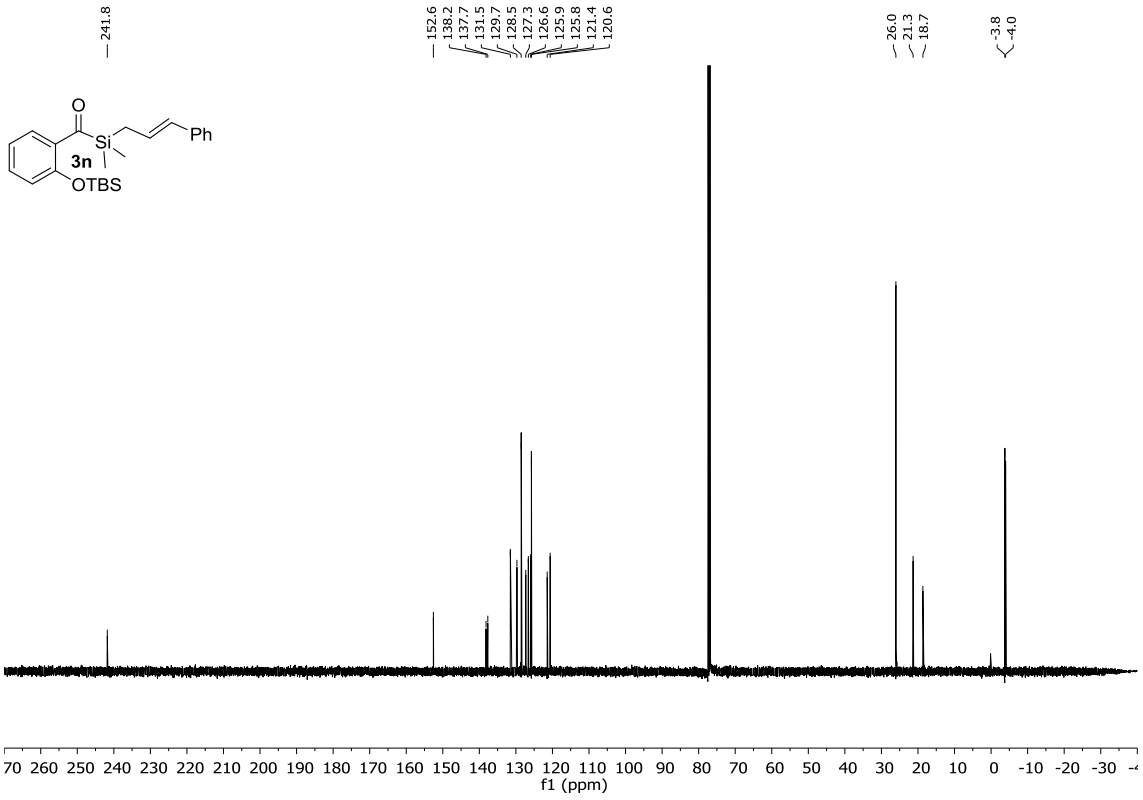
^{13}C NMR ($CDCl_3$, 125 MHz) of (3-bromophenyl)(cinnamyldimethylsilyl)methanone (**3m**)



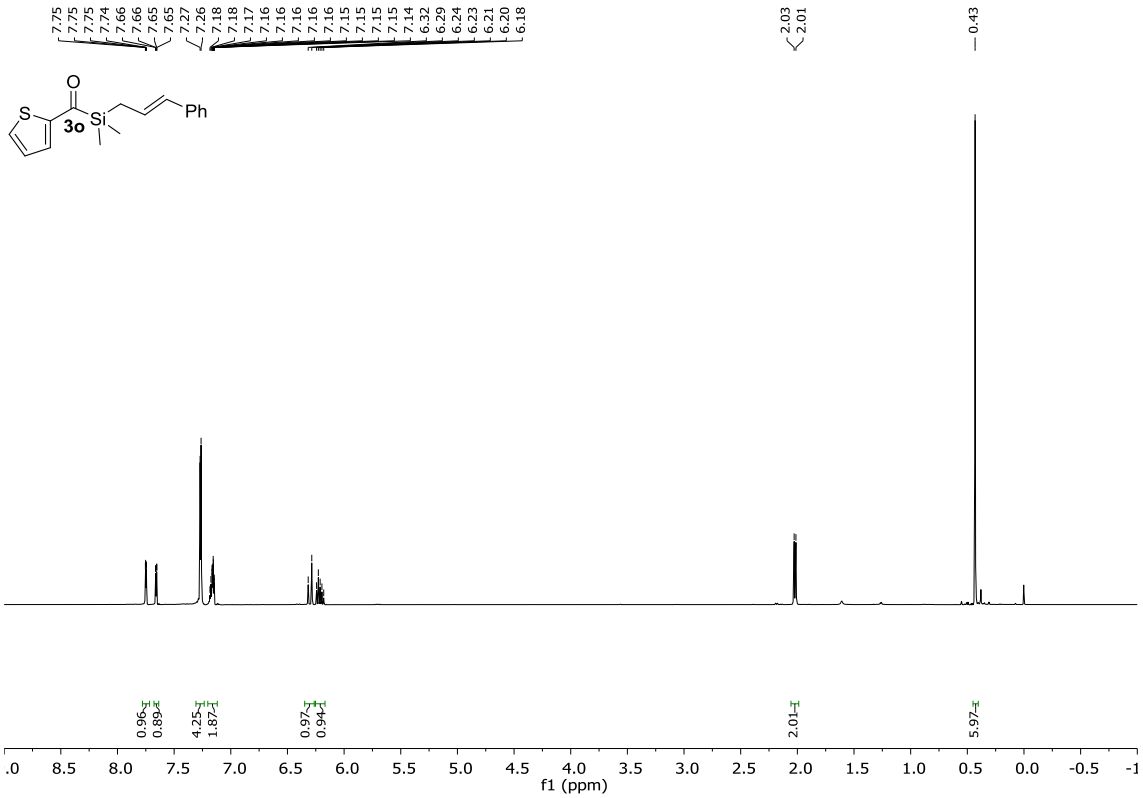
^{1}H NMR ($CDCl_3$, 500 MHz) of
(2-((tert-butyldimethylsilyl)oxy)phenyl)(cinnamyldimethylsilyl)methanone (**3n**)



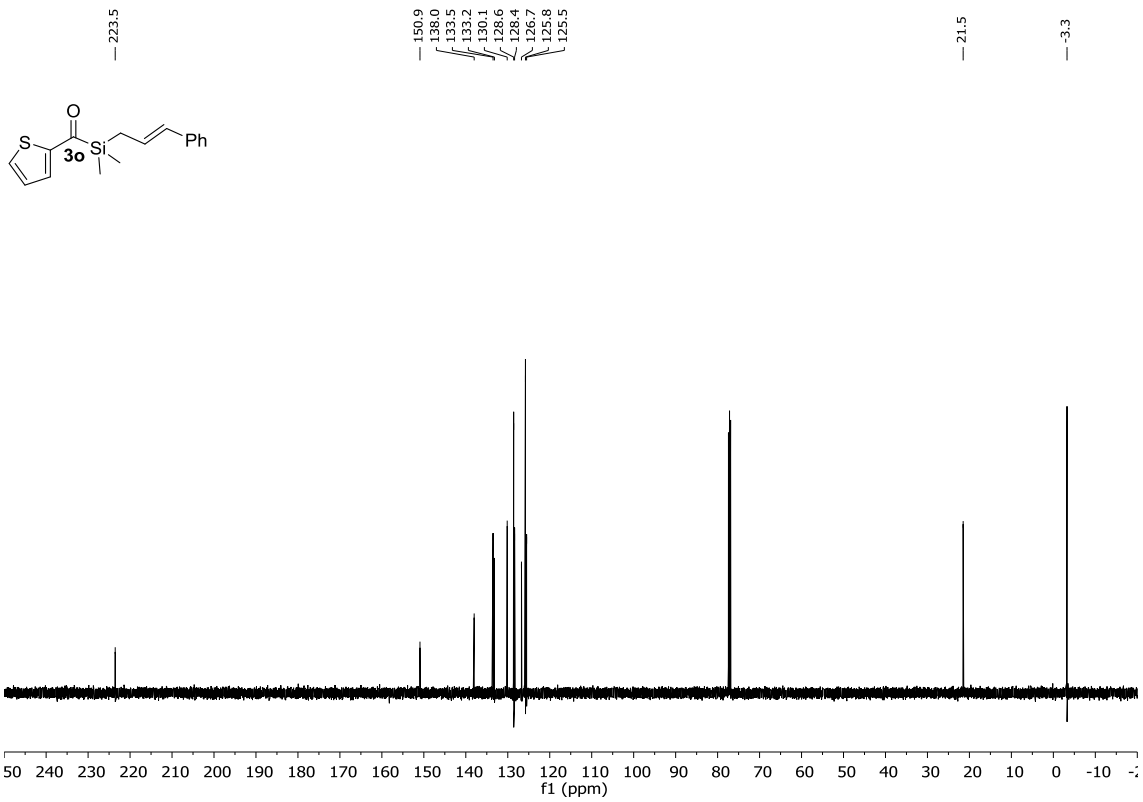
^{13}C NMR ($CDCl_3$, 125 MHz) of
(2-((tert-butyldimethylsilyl)oxy)phenyl)(cinnamyldimethylsilyl)methanone (**3n**)



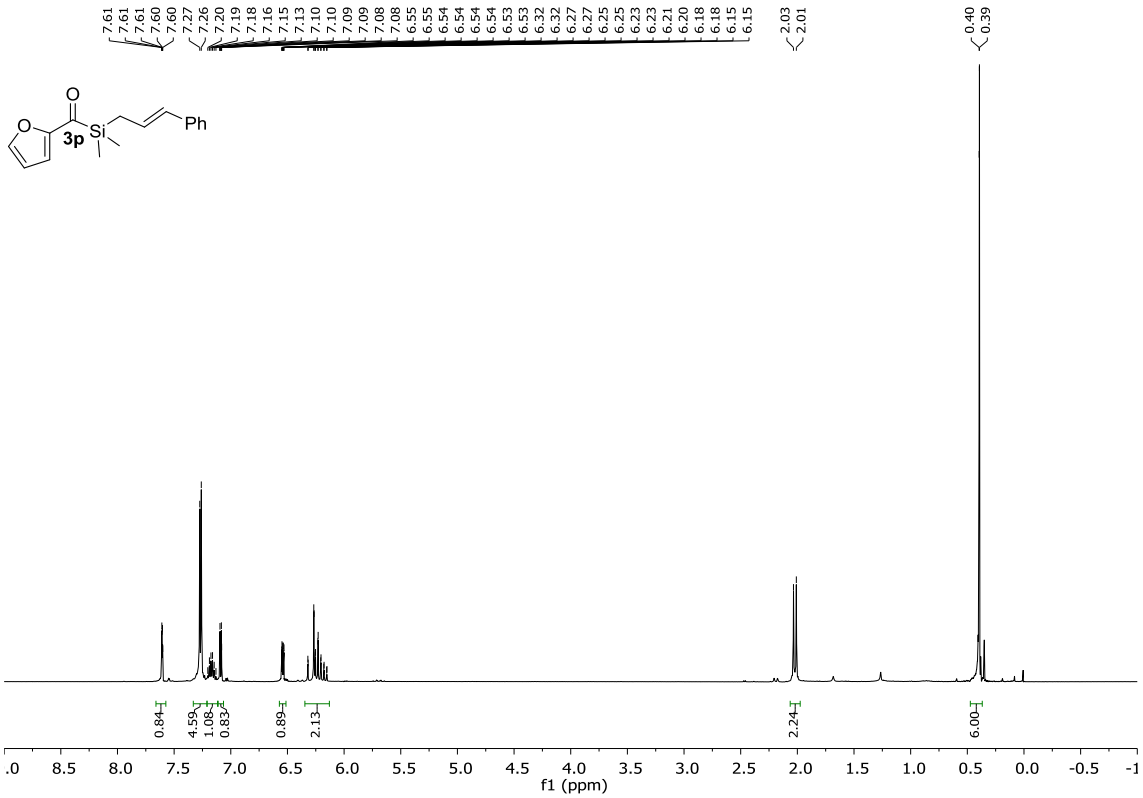
^{1}H NMR ($CDCl_3$, 500 MHz) of (cinnamyldimethylsilyl)(thiophen-2-yl)methanone (**3o**)



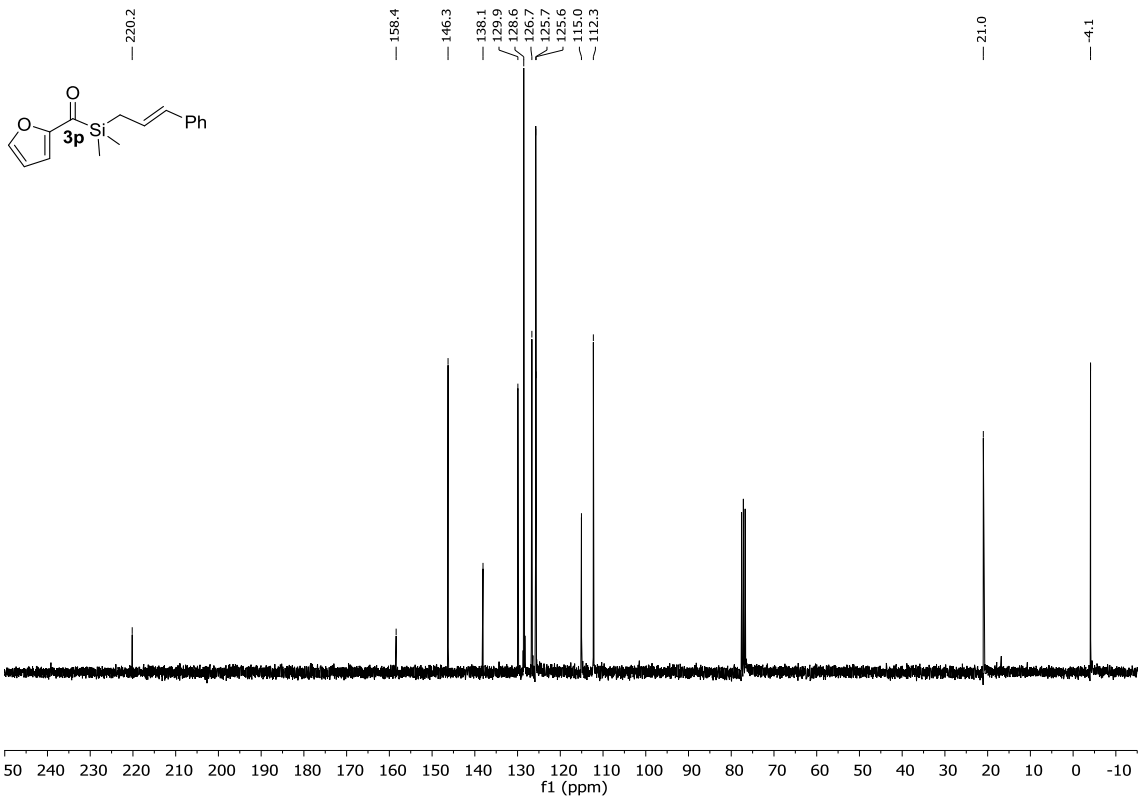
^{13}C NMR ($CDCl_3$, 125 MHz) of (cinnamyldimethylsilyl)(thiophen-2-yl)methanone (**3o**)



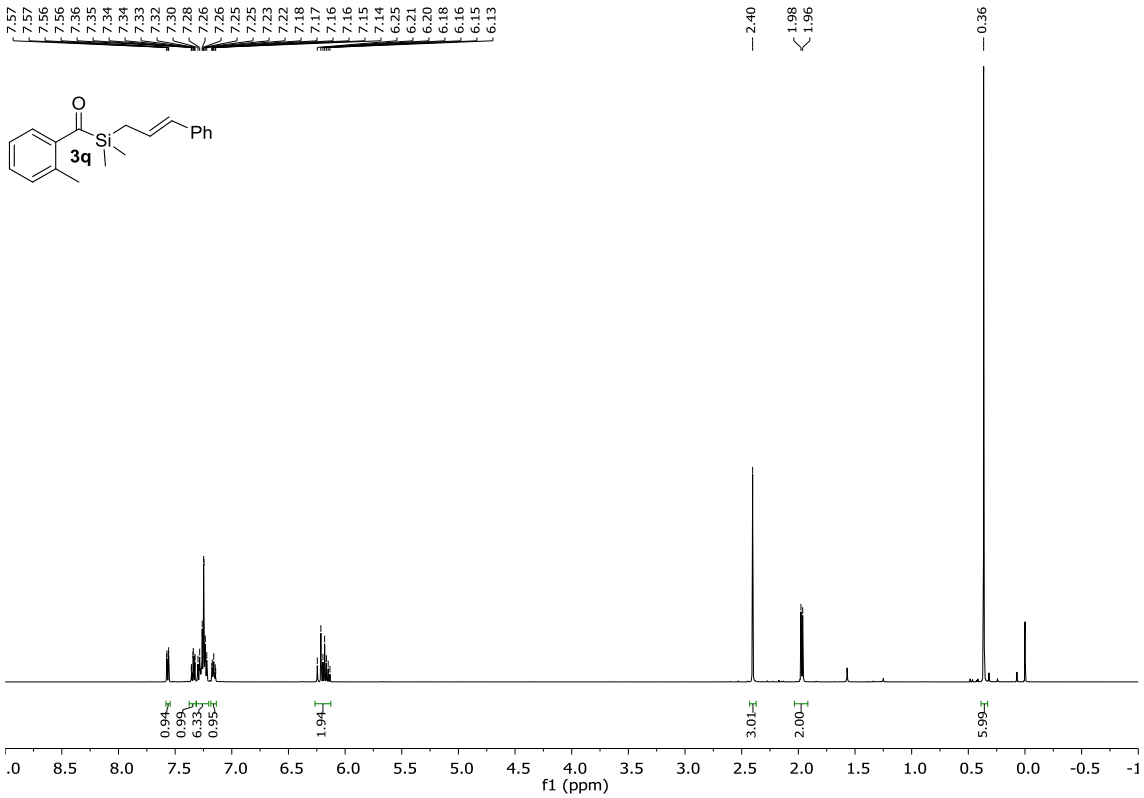
^{1}H NMR ($CDCl_3$, 300 MHz) of (cinnamyldimethylsilyl)(furan-2-yl)methanone (**3p**)



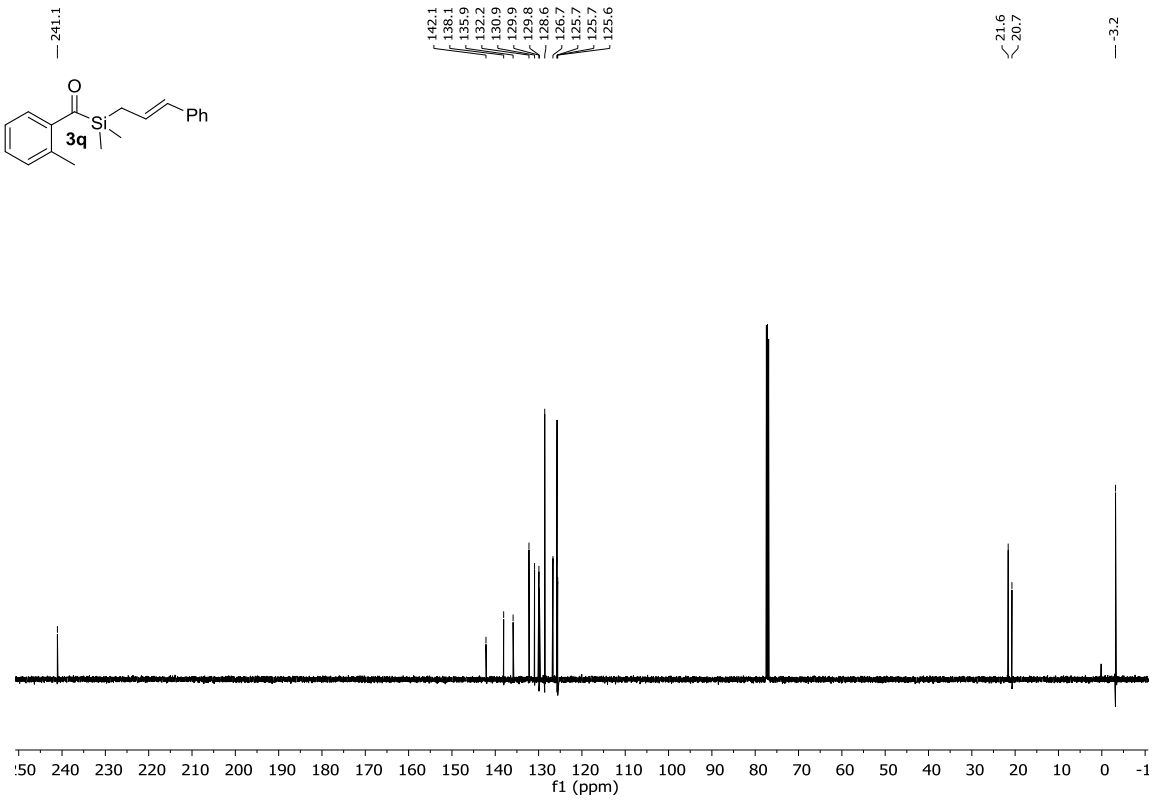
^{13}C NMR ($CDCl_3$, 75 MHz) of (cinnamyldimethylsilyl)(furan-2-yl)methanone (**3p**)



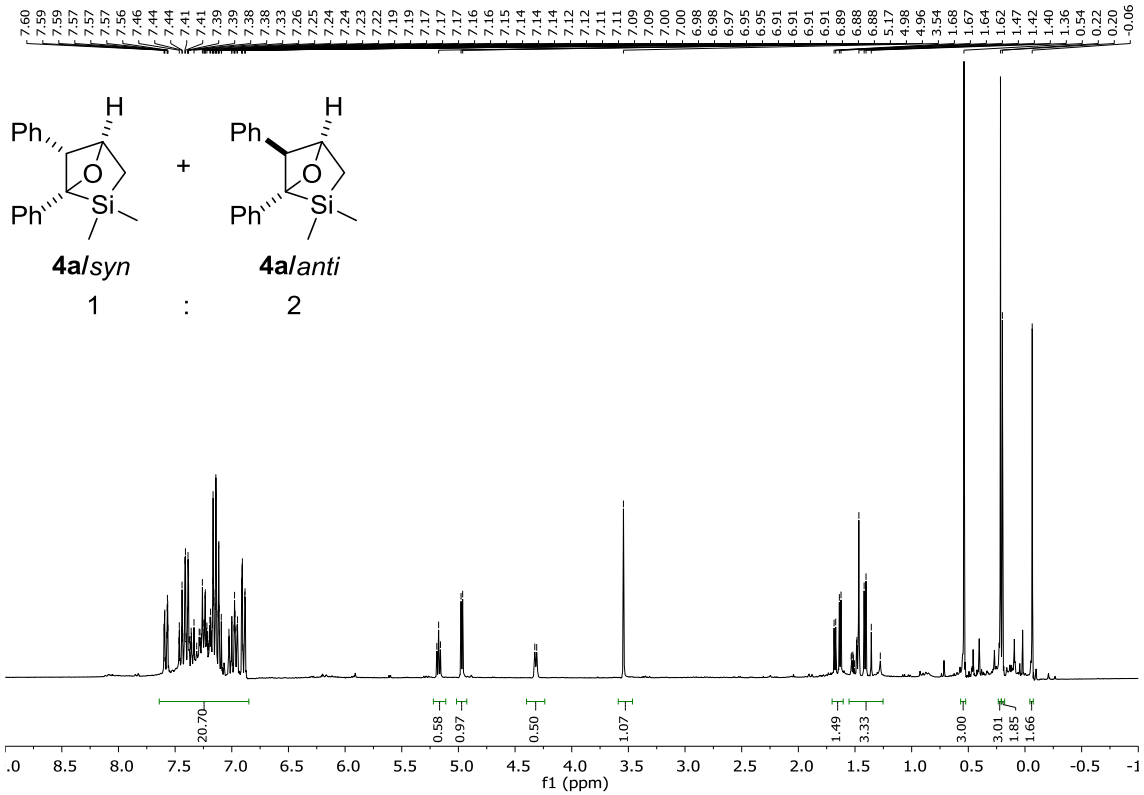
^{1}H NMR ($CDCl_3$, 500 MHz) of (cinnamyldimethylsilyl)(o-tolyl)methanone (**3q**)



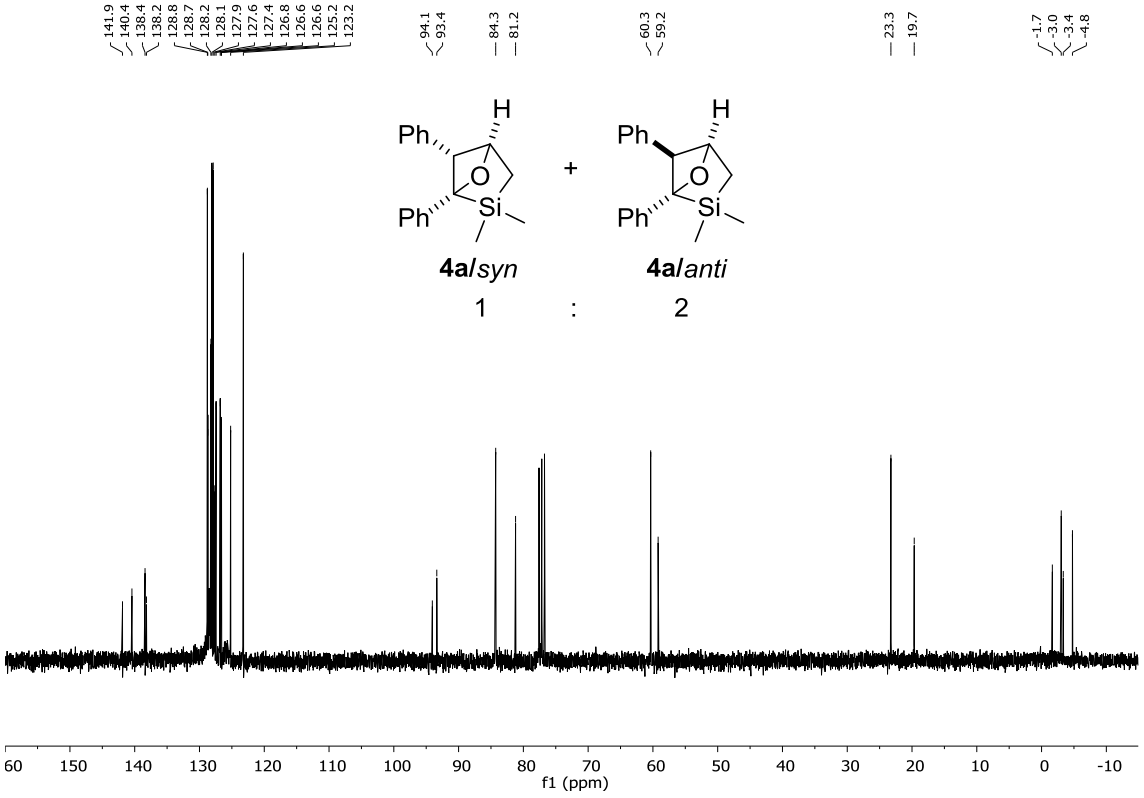
^{13}C NMR ($CDCl_3$, 125 MHz) of (cinnamyldimethylsilyl)(o-tolyl)methanone (**3q**)



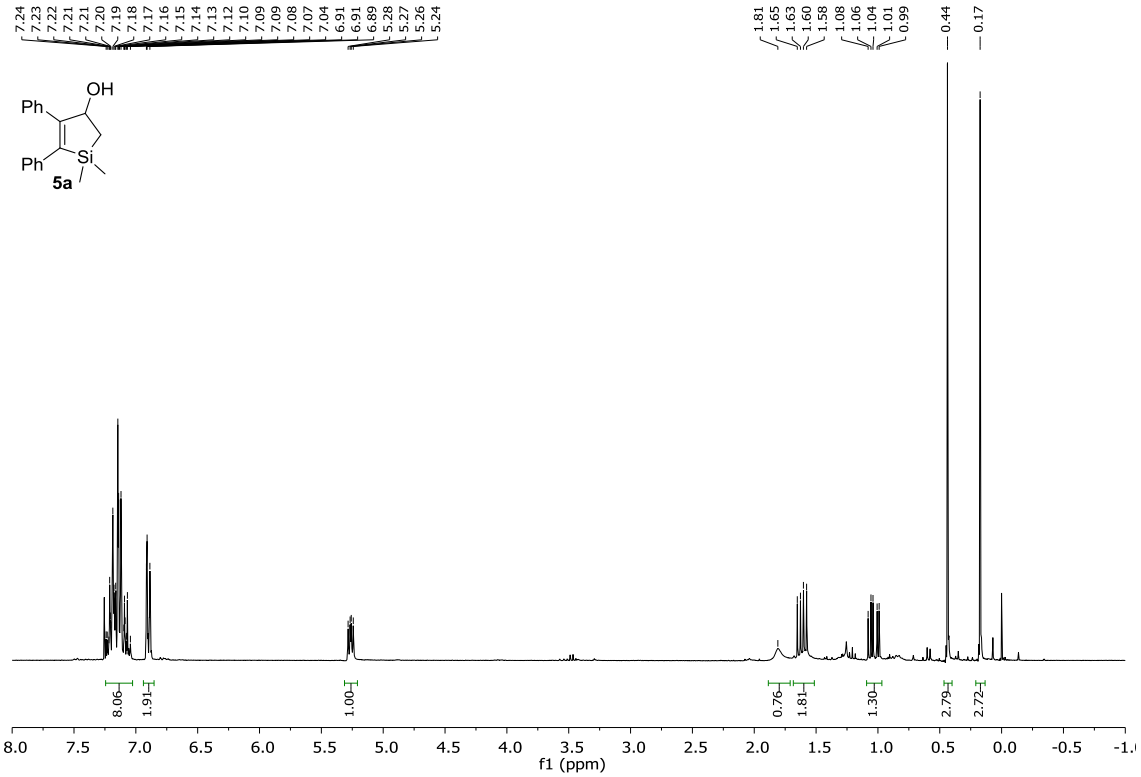
^{1}H NMR ($CDCl_3$, 300 MHz) of
2,2-dimethyl-1,6-diphenyl-5-oxa-2-silabicyclo[2.1.1]hexane (**4a**/*syn* and **4a**/*anti*)



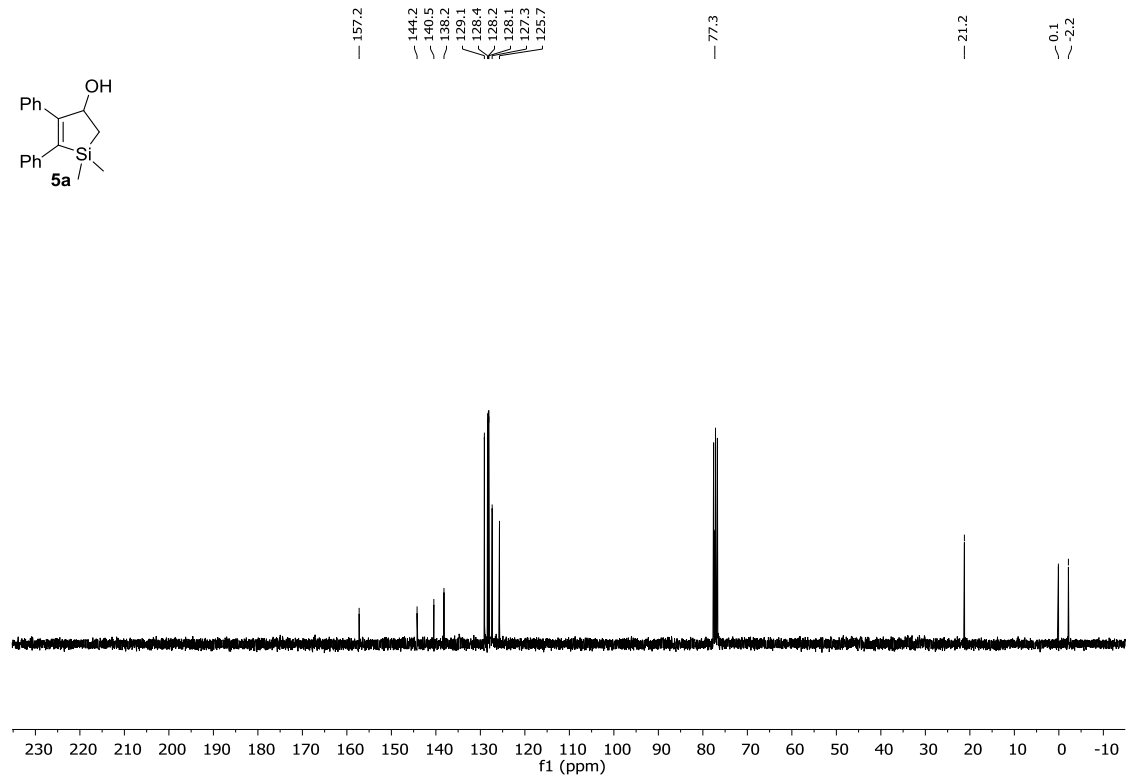
^{13}C NMR ($CDCl_3$, 75 MHz) of
2,2-dimethyl-1,6-diphenyl-5-oxa-2-silabicyclo[2.1.1]hexane (**4a**/*syn* and **4a**/*anti*)



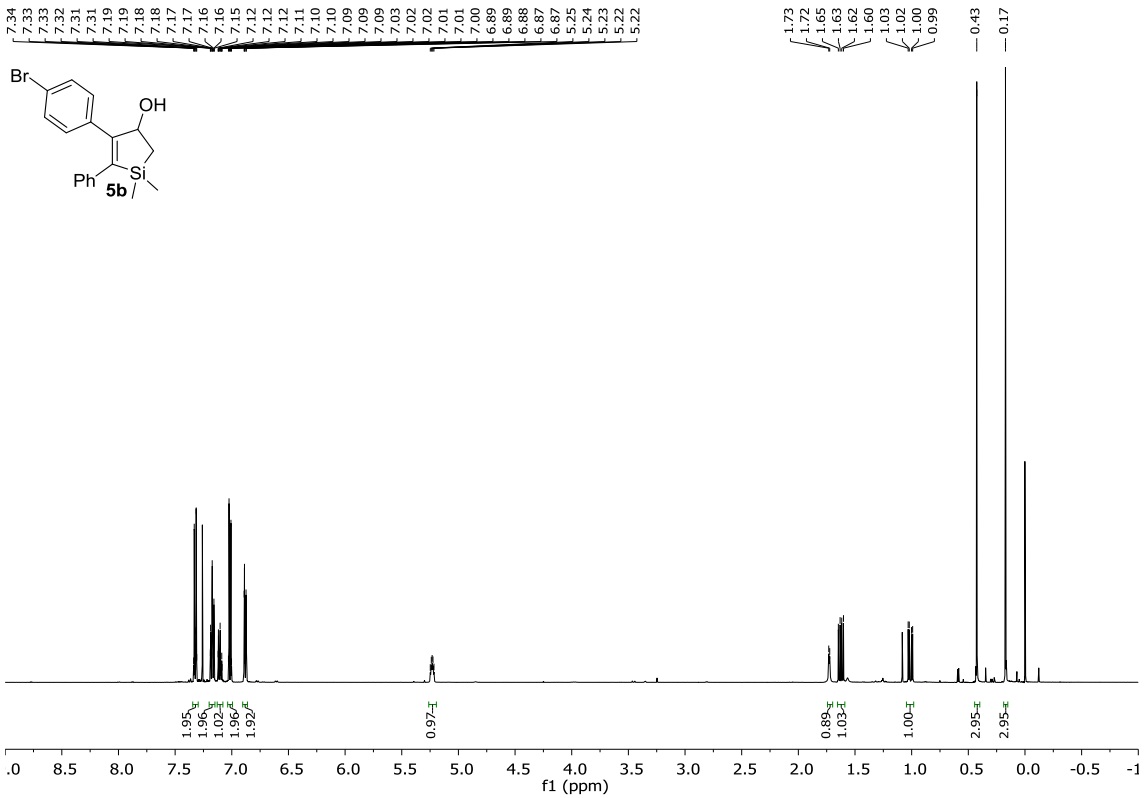
^{1}H NMR ($CDCl_3$, 300 MHz) of 1,1-dimethyl-4,5-diphenyl-2,3-dihydro-1*H*-silol-3-ol (**5a**)



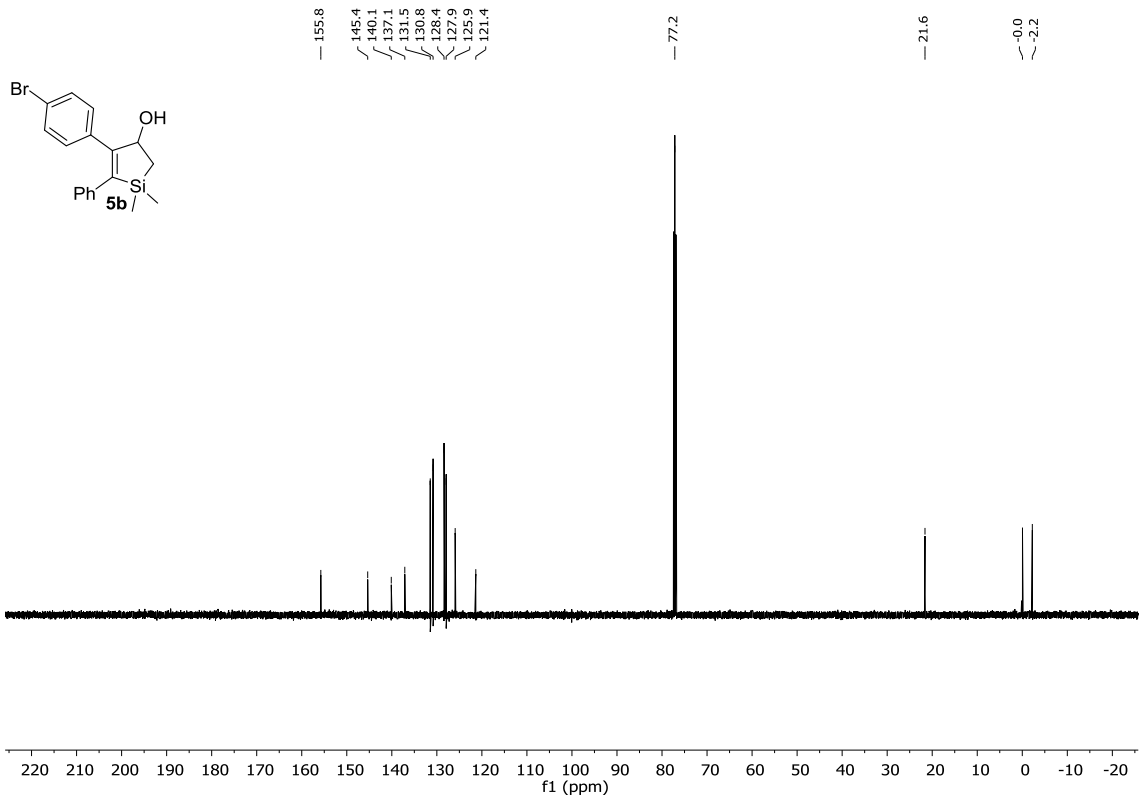
^{13}C NMR ($CDCl_3$, 75 MHz) of 1,1-dimethyl-4,5-diphenyl-2,3-dihydro-1*H*-silol-3-ol (**5a**)



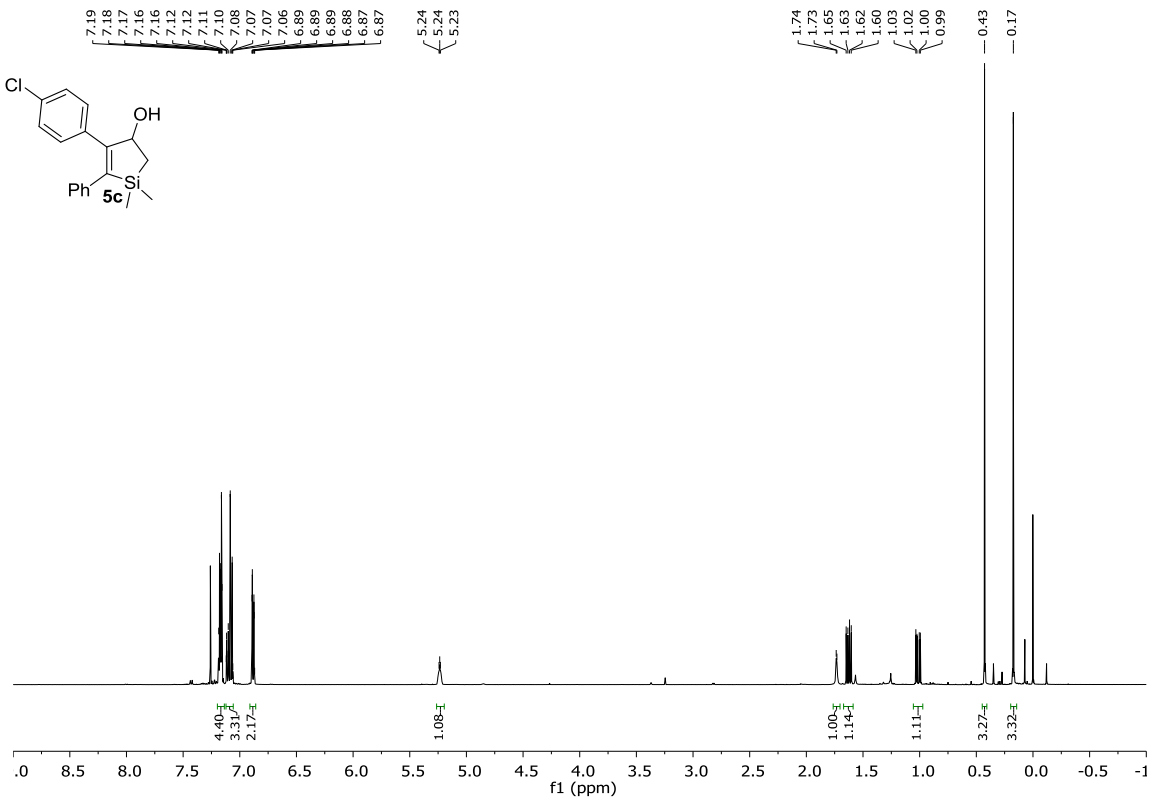
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(4-bromophenyl)-1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5b**)



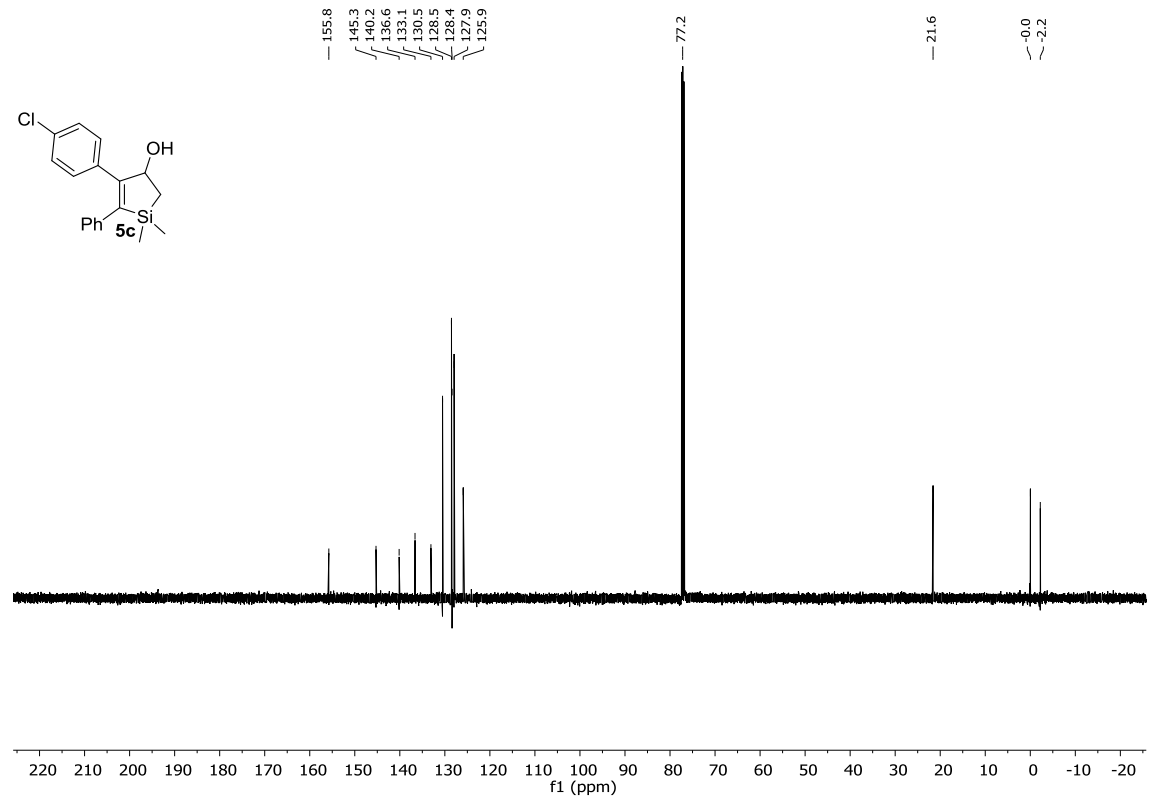
^{13}C NMR ($CDCl_3$, 125 MHz) of 4-(4-bromophenyl)-1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5b**)



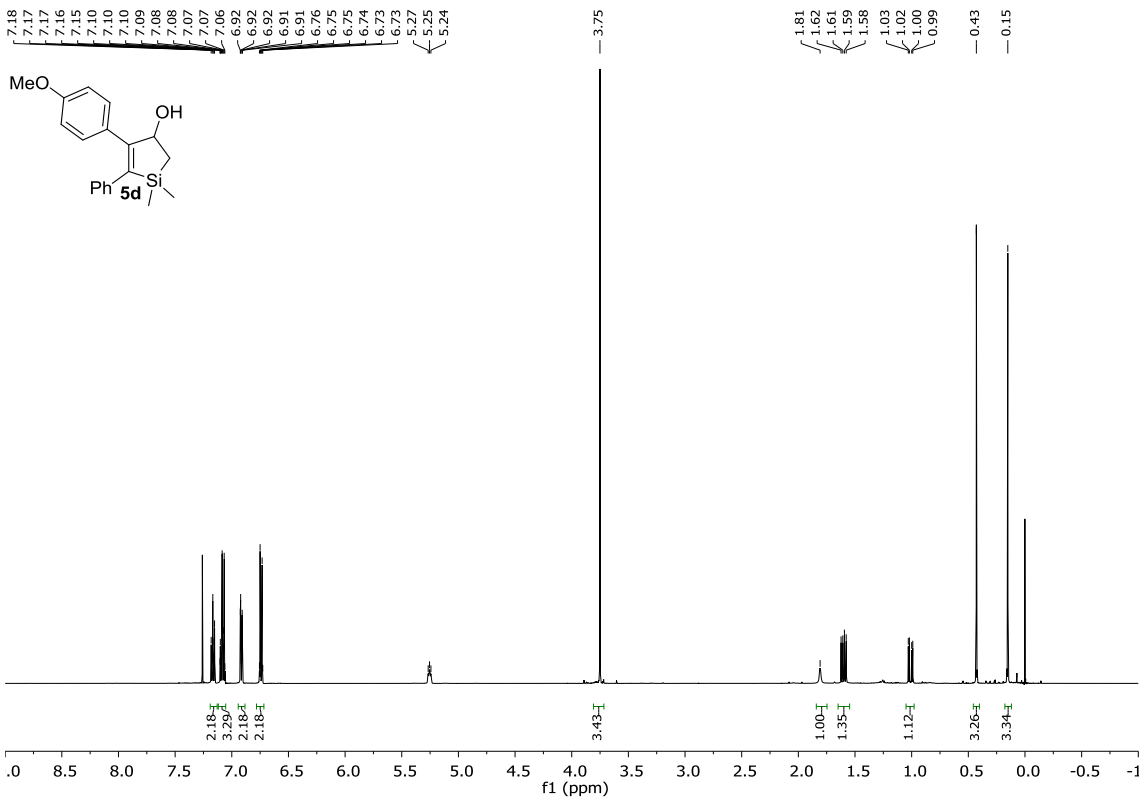
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(4-chlorophenyl)-1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5c**)



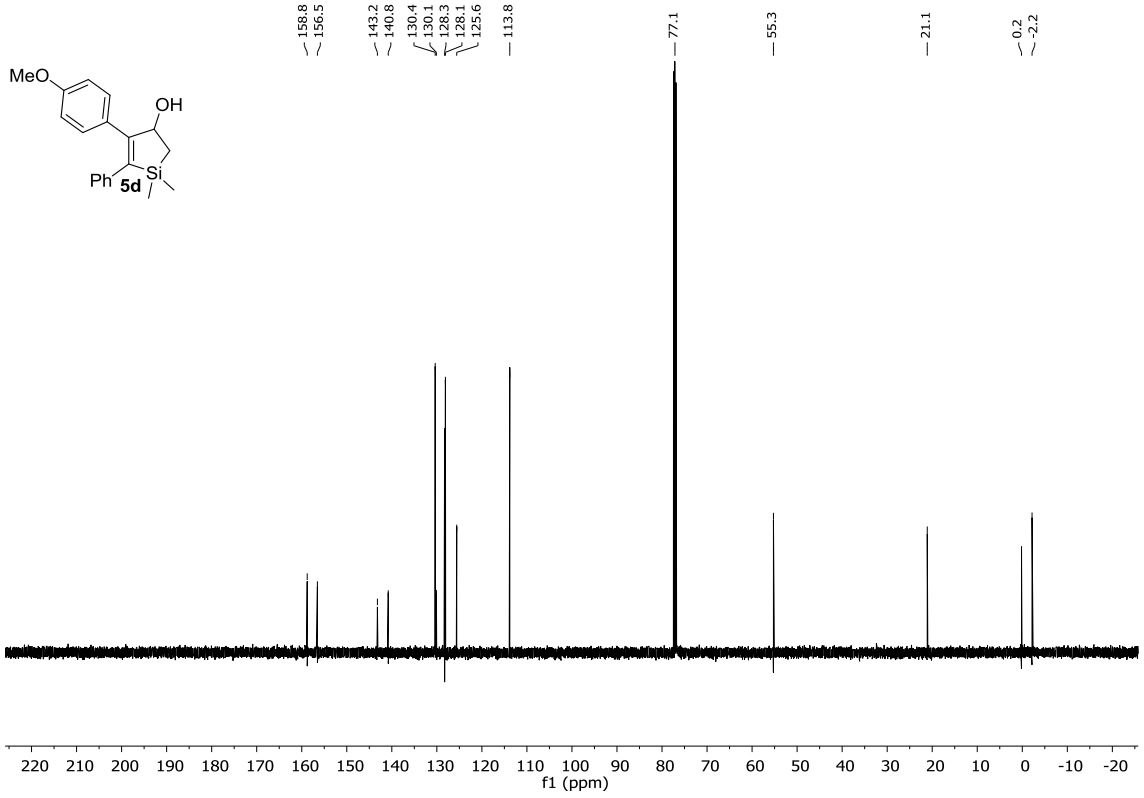
^{13}C NMR ($CDCl_3$, 125 MHz) of 4-(4-chlorophenyl)-1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5c**)



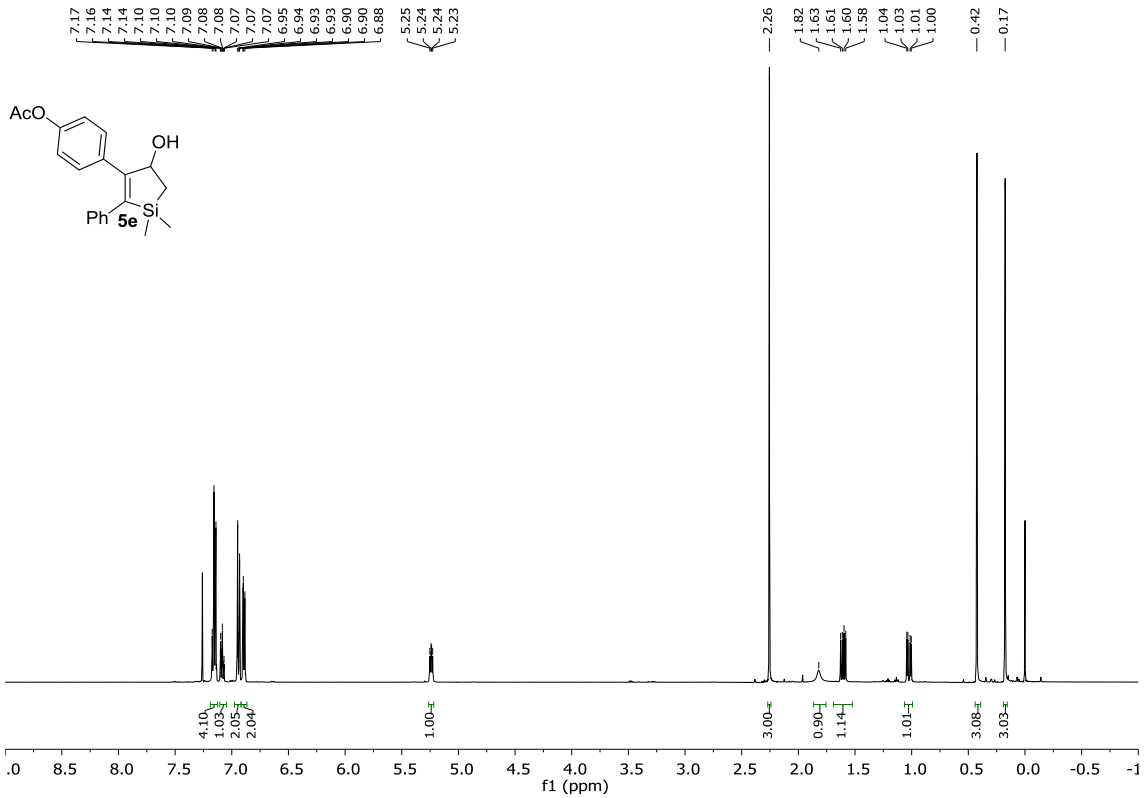
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(4-methoxyphenyl)-1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5d**)



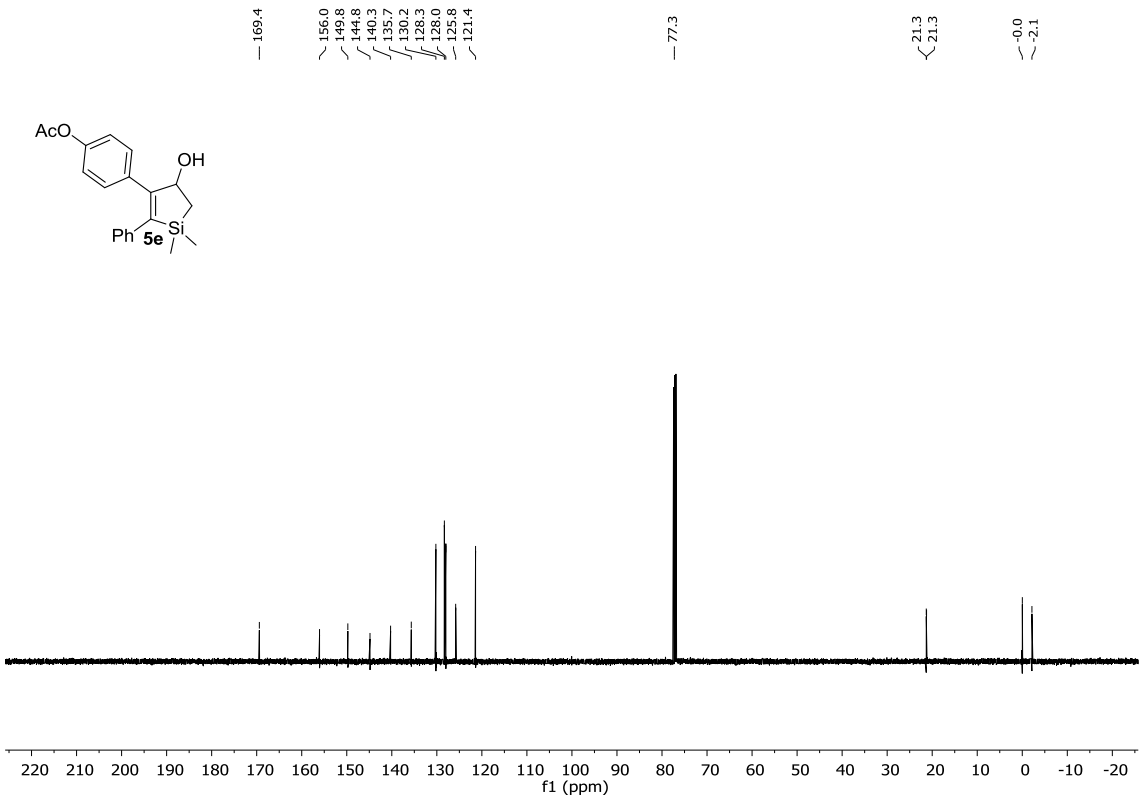
^{13}C NMR ($CDCl_3$, 125 MHz) of 4-(4-methoxyphenyl)-1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5d**)



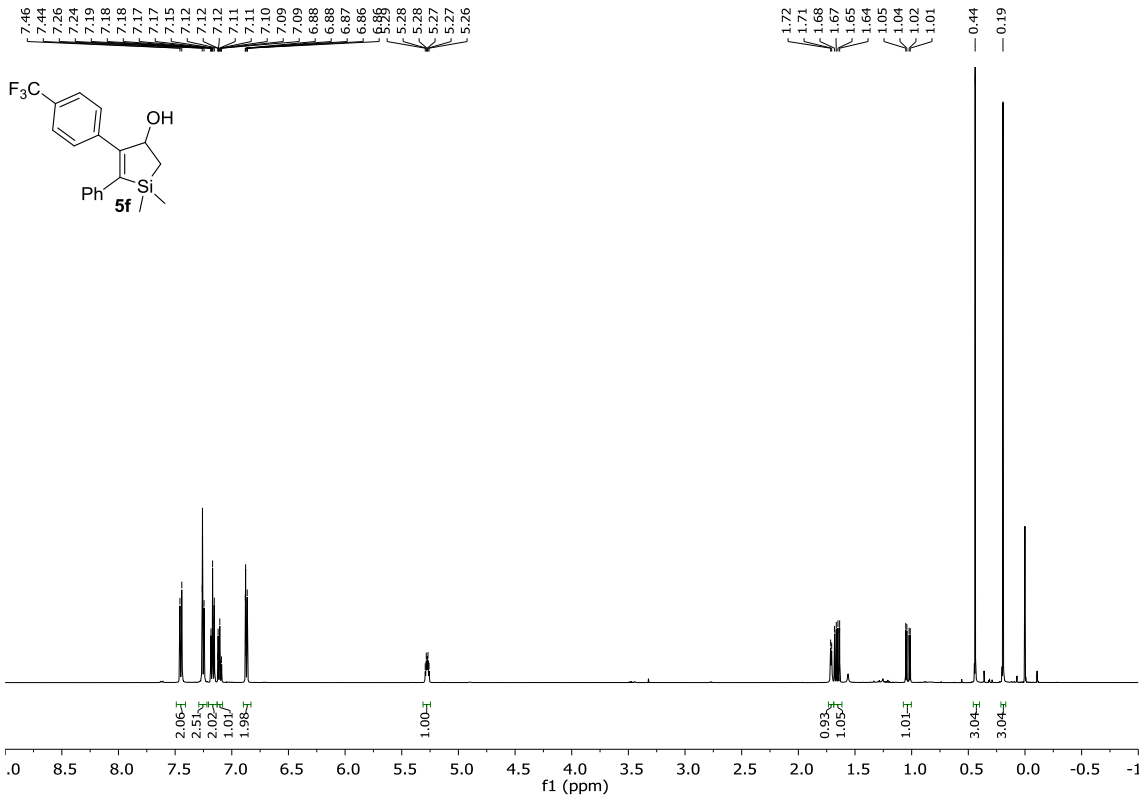
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(4-hydroxy-1,1-dimethyl-2-phenyl-4,5-dihydro-1*H*-silol-3-yl)phenyl acetate (**5e**)



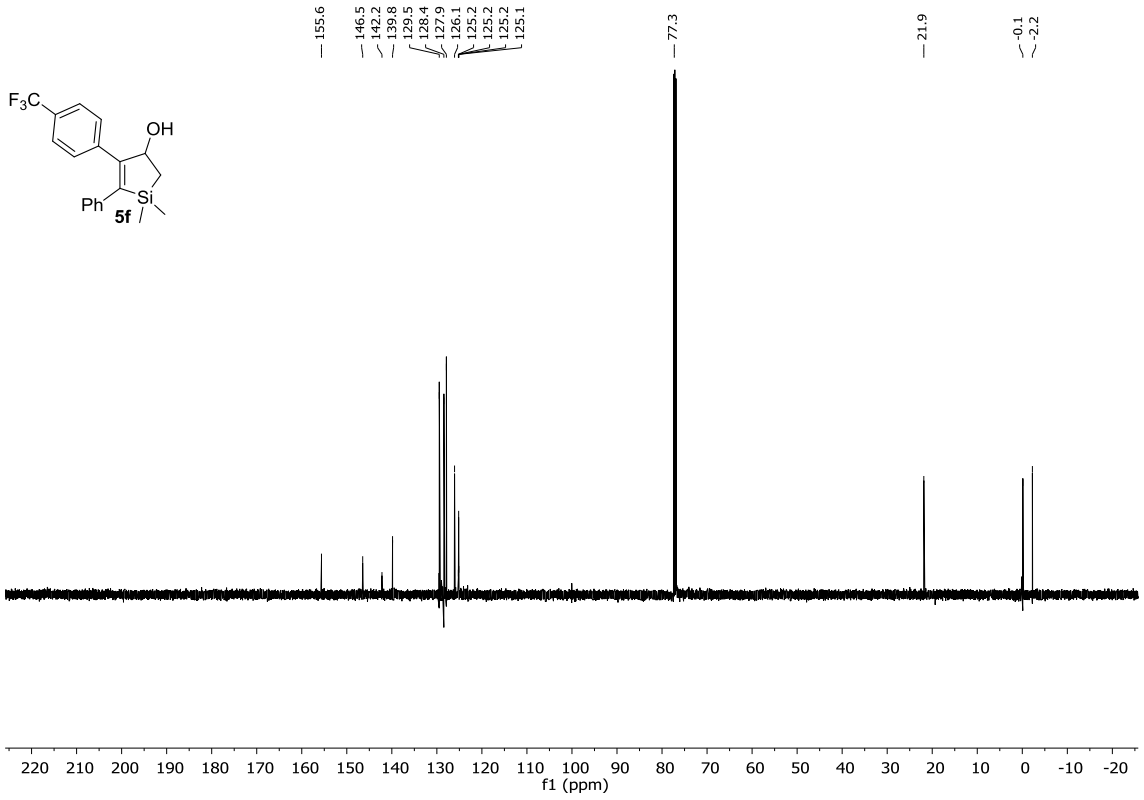
^{13}C NMR ($CDCl_3$, 125 MHz) of 4-(4-hydroxy-1,1-dimethyl-2-phenyl-4,5-dihydro-1*H*-silol-3-yl)phenyl acetate (**5e**)



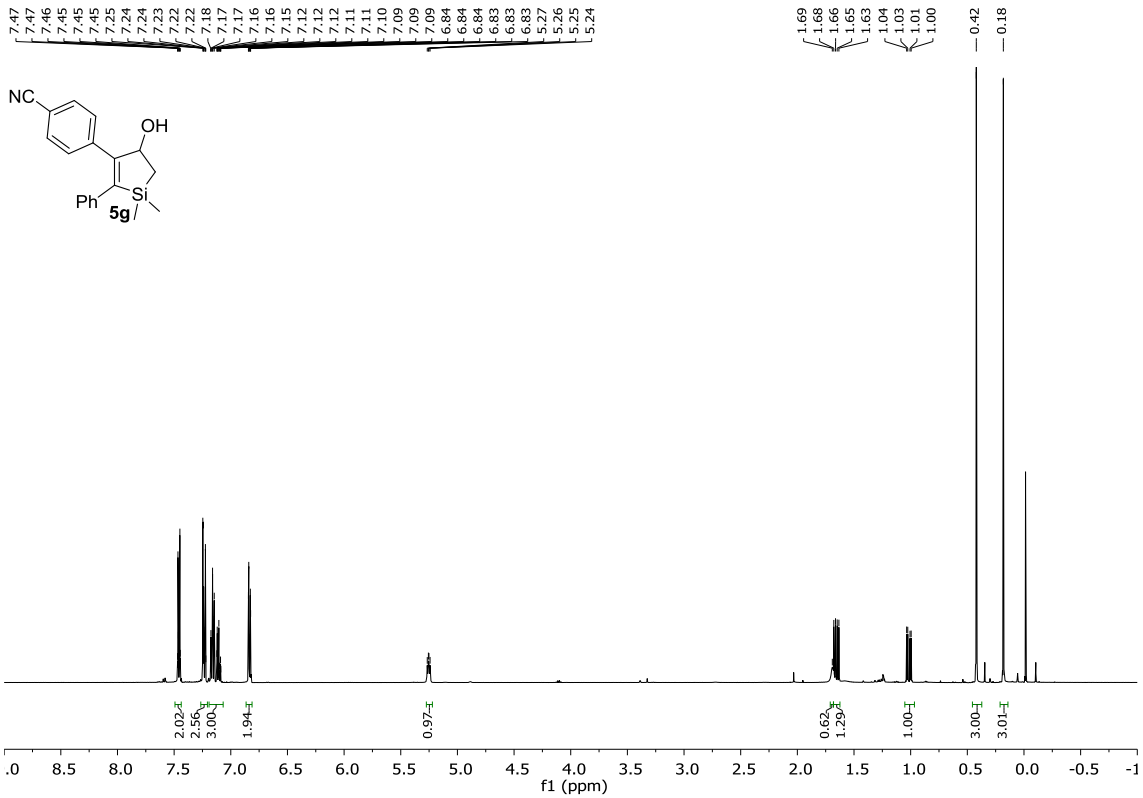
^{1}H NMR ($CDCl_3$, 500 MHz) of 1,1-dimethyl-5-phenyl-4-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-silol-3-ol (**5f**)



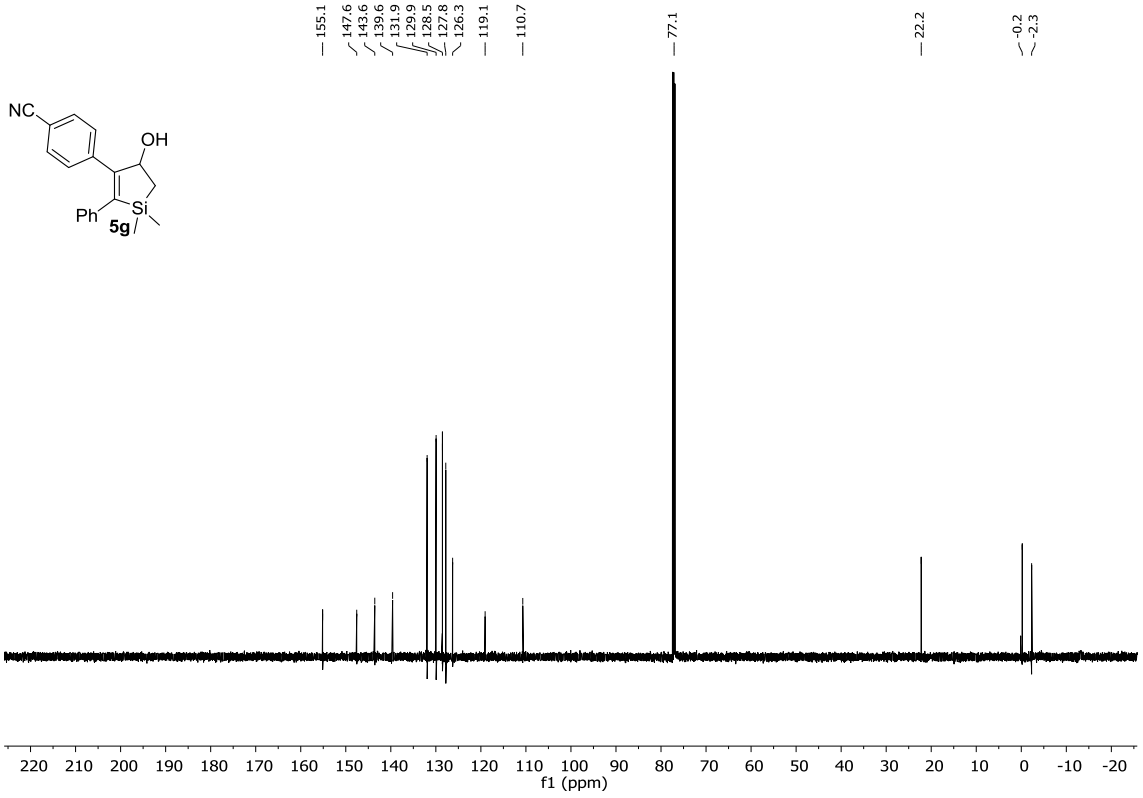
^{13}C NMR ($CDCl_3$, 125 MHz) of 1,1-dimethyl-5-phenyl-4-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-silol-3-ol (**5f**)



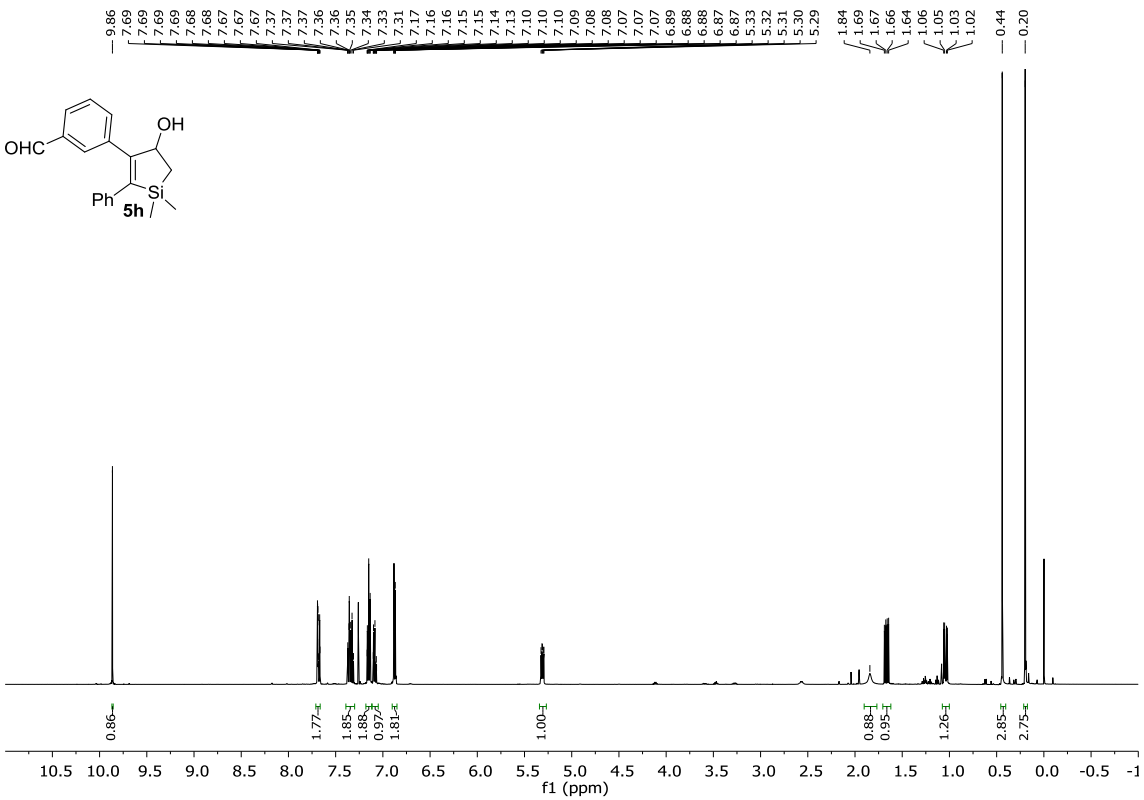
^{1}H NMR ($CDCl_3$, 500 MHz) of 4-(4-hydroxy-1,1-dimethyl-2-phenyl-4,5-dihydro-1*H*-silol-3-yl)benzonitrile (**5g**)



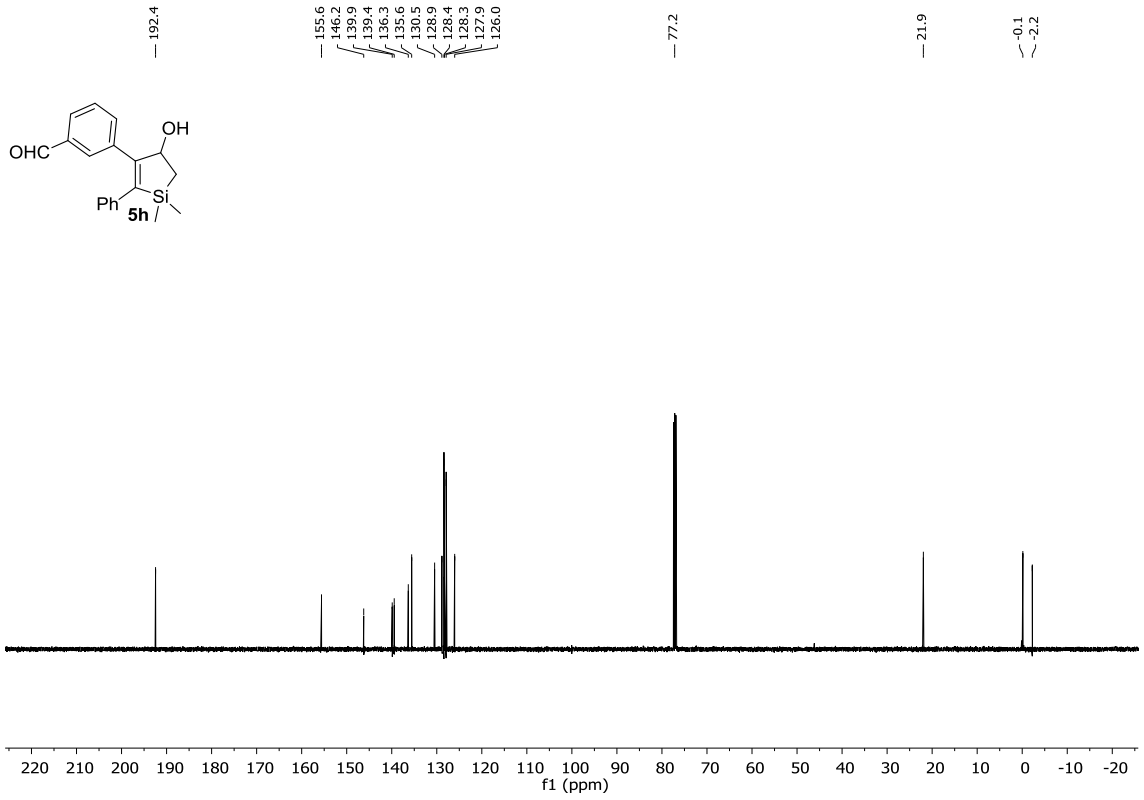
^{13}C NMR ($CDCl_3$, 125 MHz) of 4-(4-hydroxy-1,1-dimethyl-2-phenyl-4,5-dihydro-1*H*-silol-3-yl)benzonitrile (**5g**)



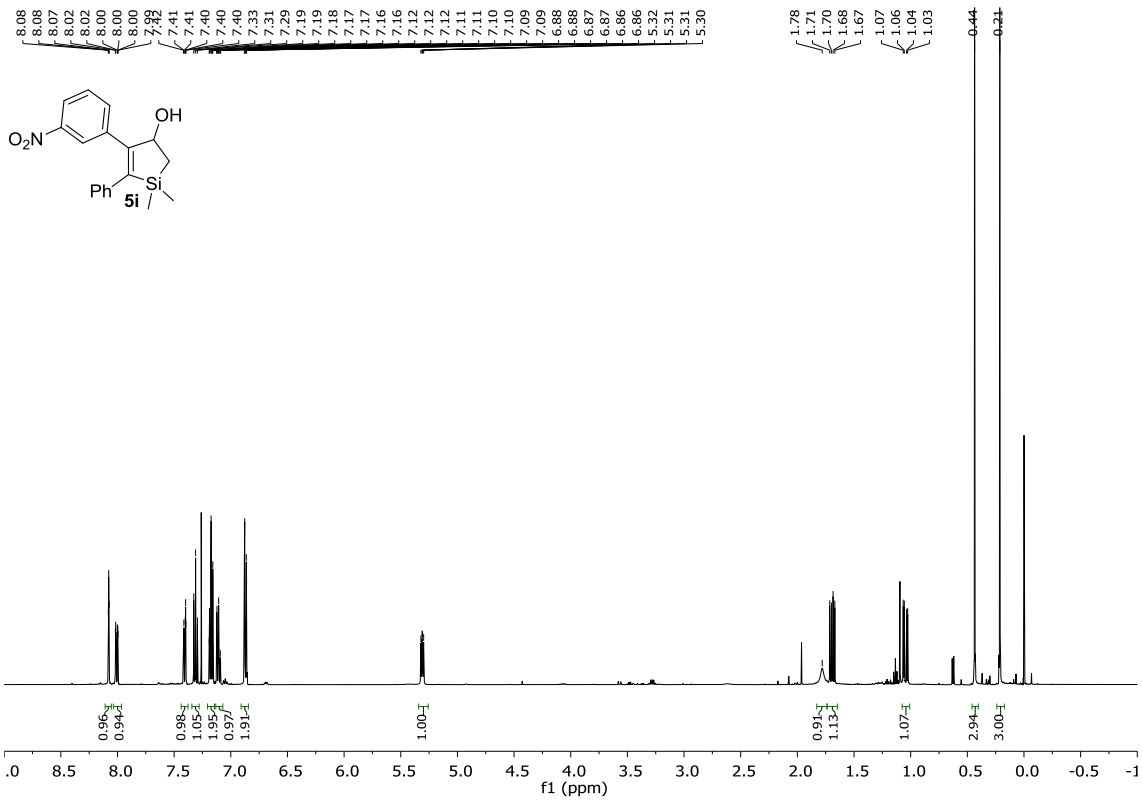
^{1}H NMR ($CDCl_3$, 500 MHz) of 3-(4-hydroxy-1,1-dimethyl-2-phenyl-4,5-dihydro-1*H*-silol-3-yl)benzaldehyde (**5h**)



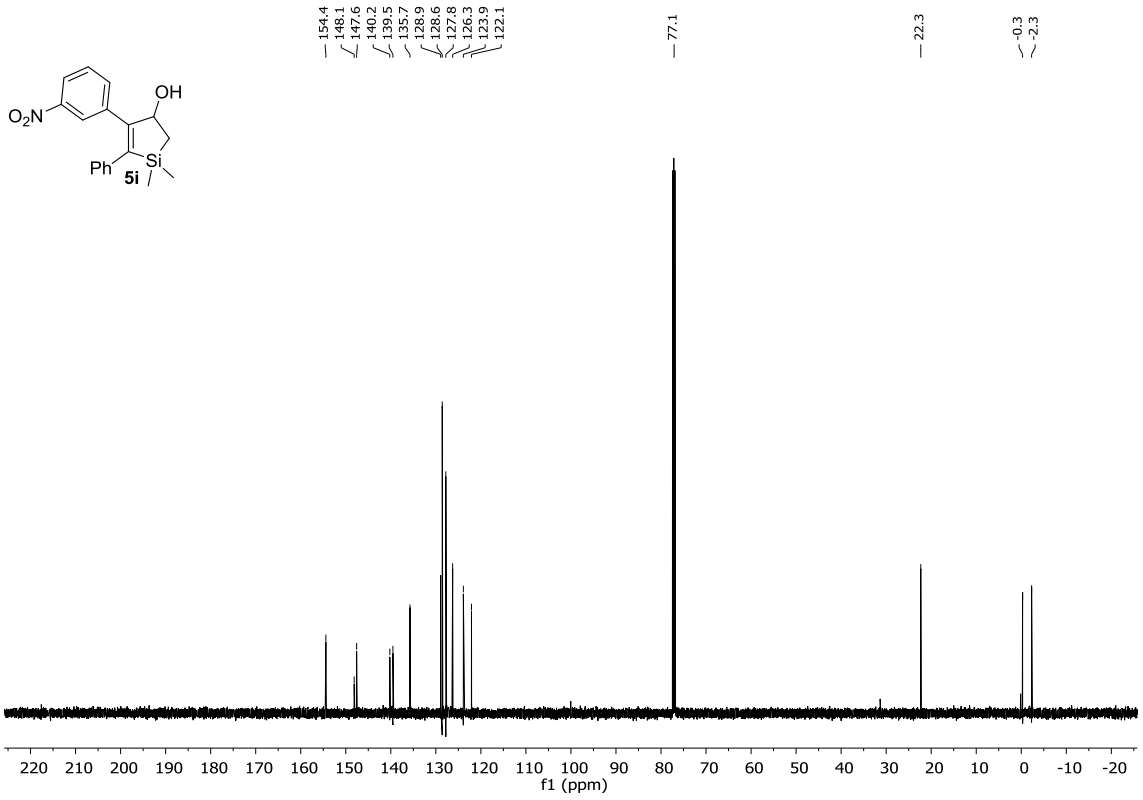
^{13}C NMR ($CDCl_3$, 125 MHz) of 3-(4-hydroxy-1,1-dimethyl-2-phenyl-4,5-dihydro-1*H*-silol-3-yl)benzaldehyde (**5h**)



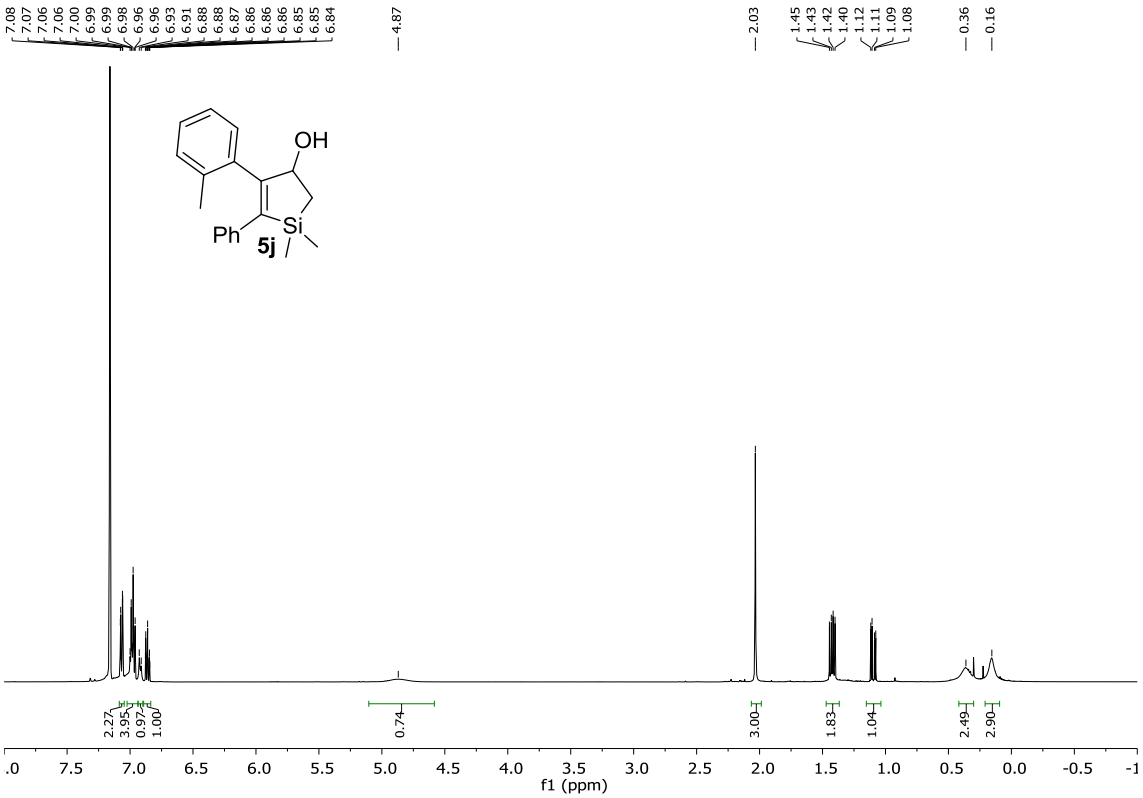
^{1}H NMR ($CDCl_3$, 500 MHz) of 1,1-dimethyl-4-(3-nitrophenyl)-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5i**)



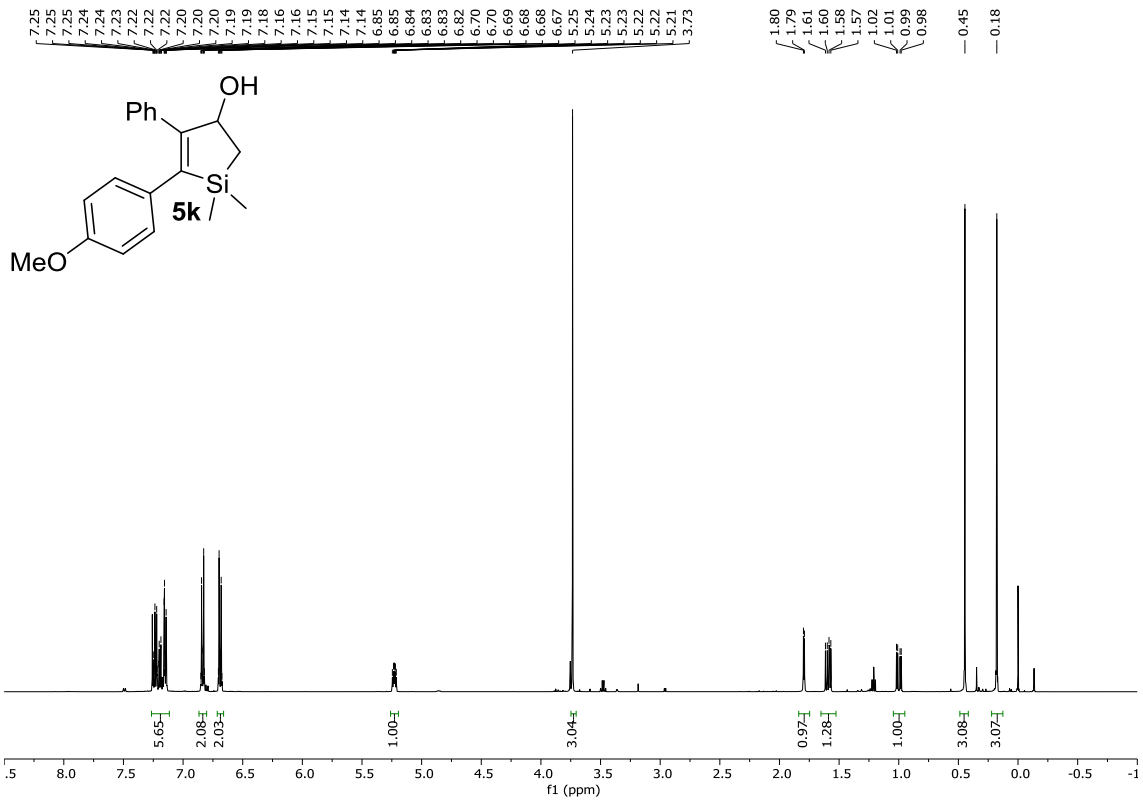
^{13}C NMR ($CDCl_3$, 125 MHz) of 1,1-dimethyl-4-(3-nitrophenyl)-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5i**)



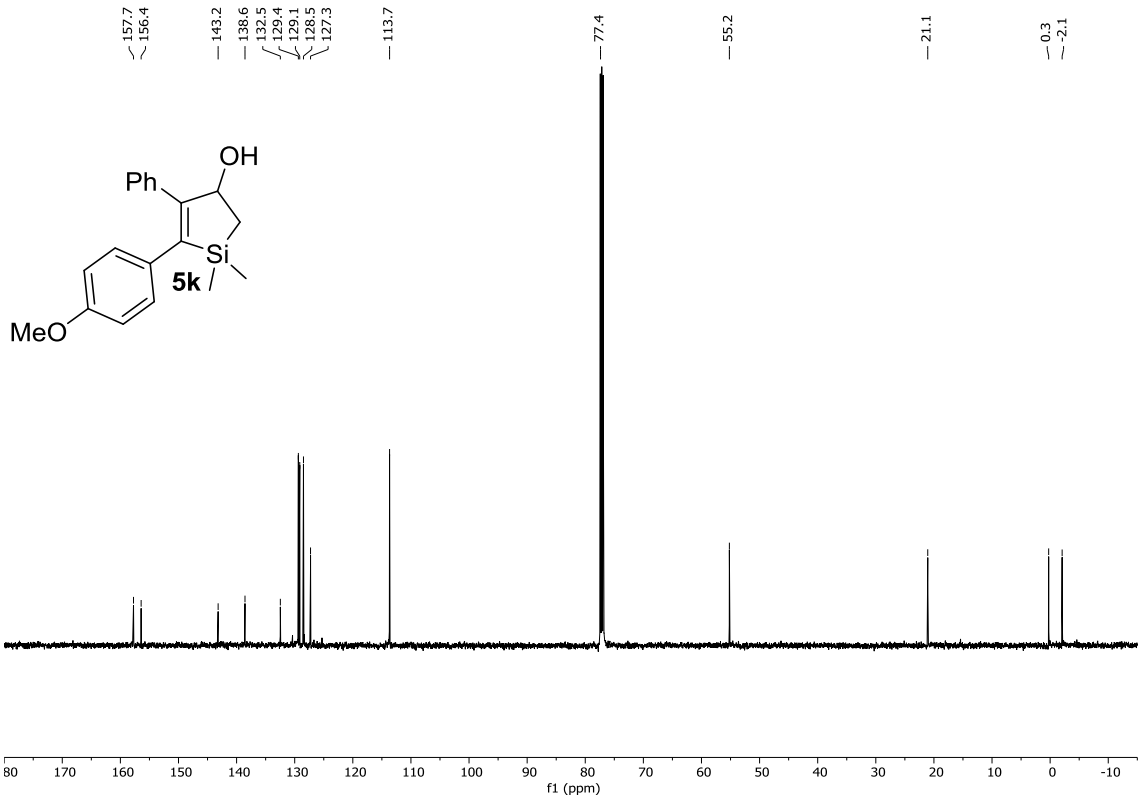
^{1}H NMR (C_6D_6, 500 MHz) of 1,1-dimethyl-5-phenyl-4-(*o*-tolyl)-2,3-dihydro-1*H*-silol-3-ol (**5j**)



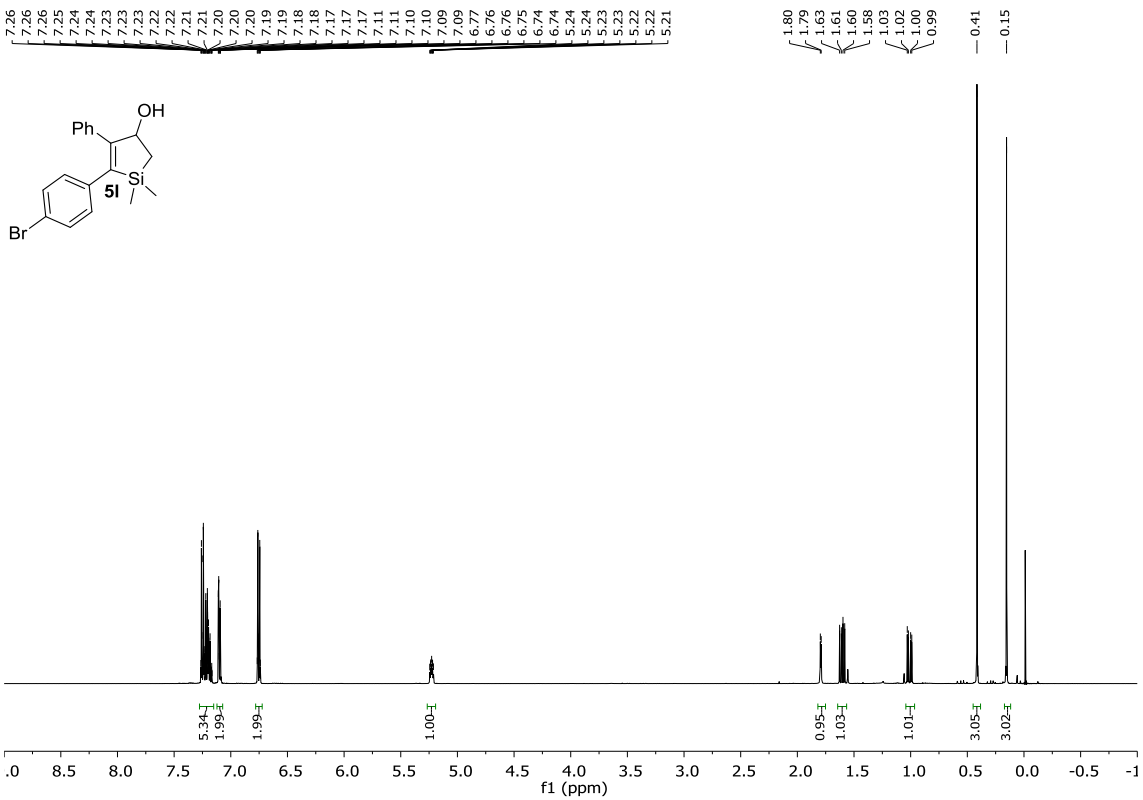
^{1}H NMR ($CDCl_3$, 500 MHz) of 5-(4-methoxyphenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5k**)



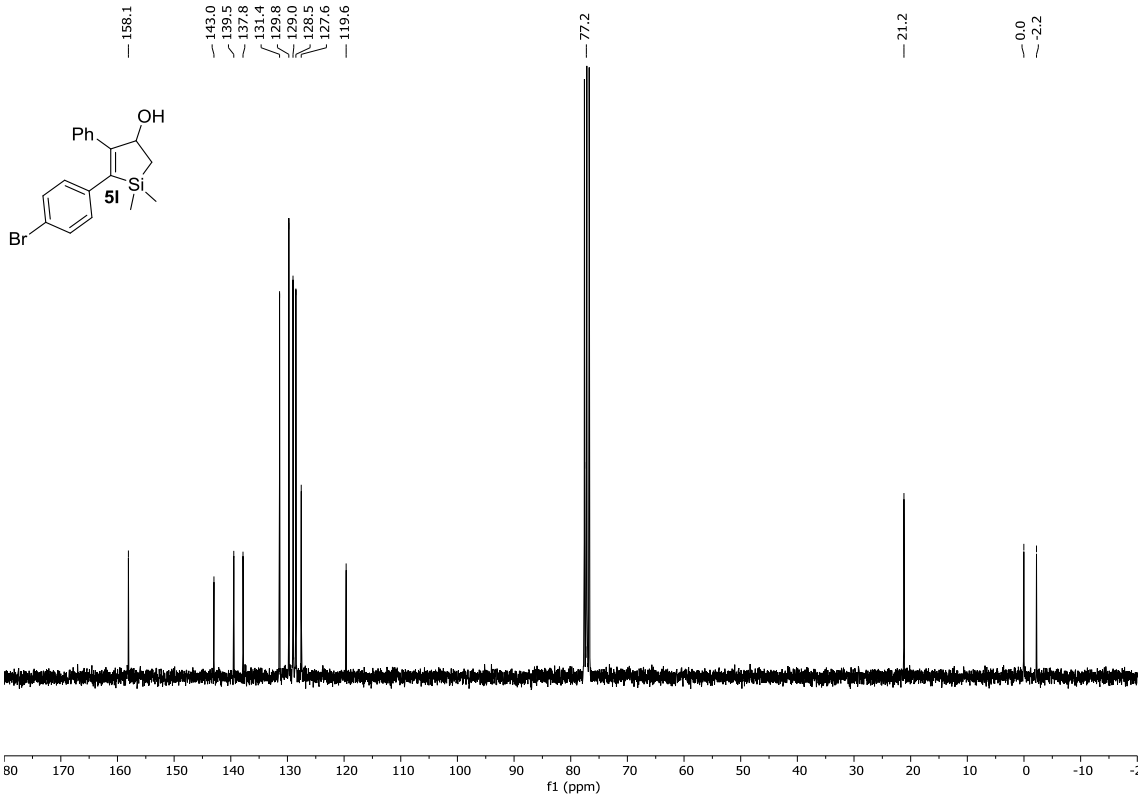
^{13}C NMR ($CDCl_3$, 125 MHz) of 5-(4-methoxyphenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1*H*-silol-3-ol (**5k**)



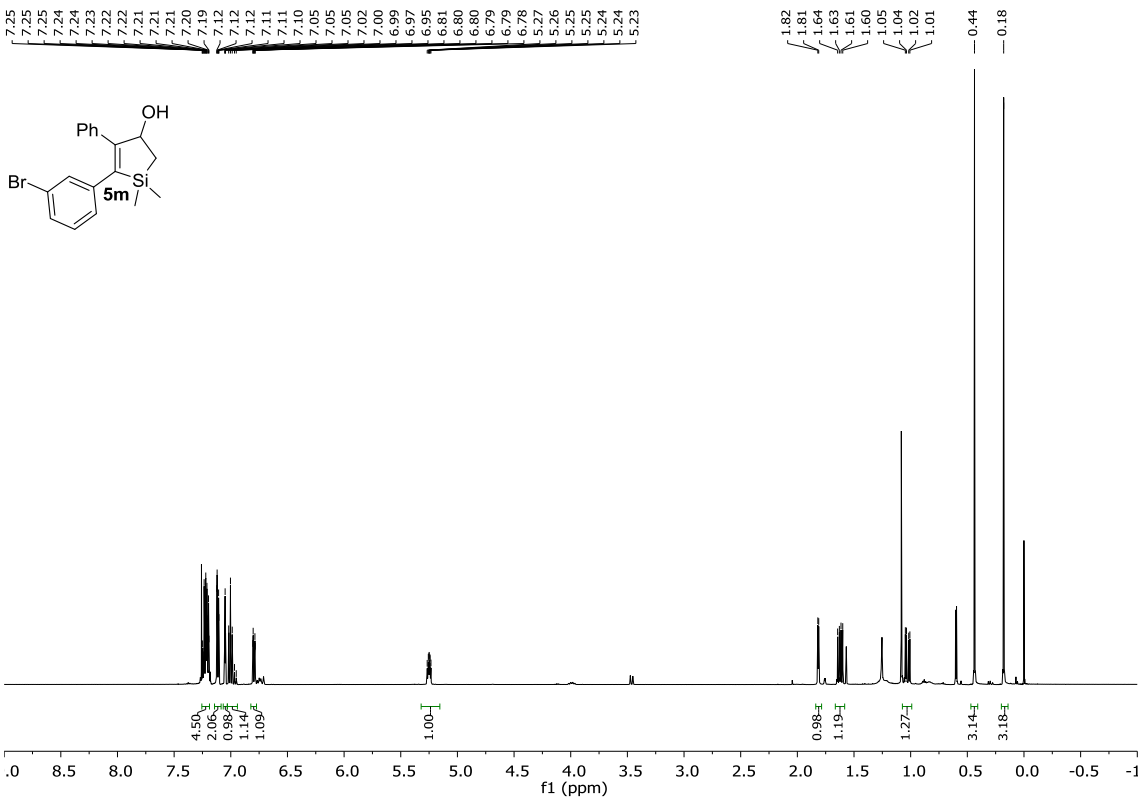
^{1}H NMR ($CDCl_3$, 500 MHz) of 5-(4-bromophenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1H-silol-3-ol (**5l**)



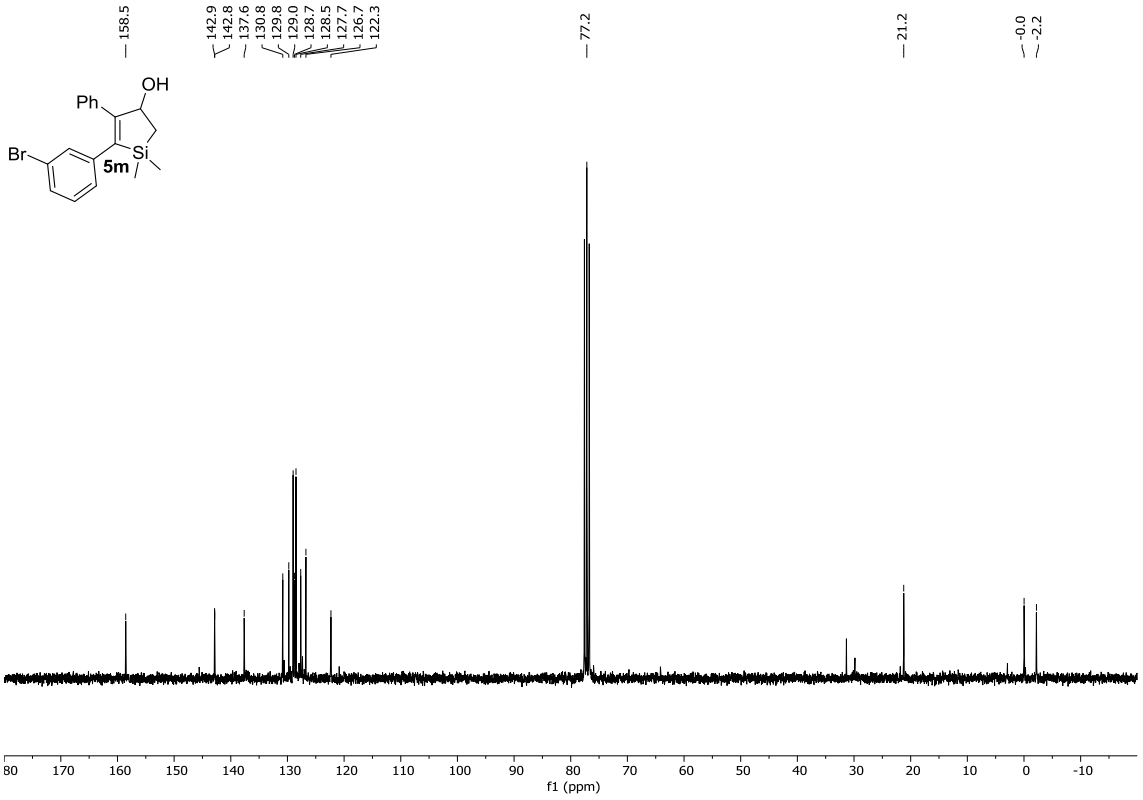
^{13}C NMR ($CDCl_3$, 75 MHz) of 5-(4-bromophenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1H-silol-3-ol (**5l**)



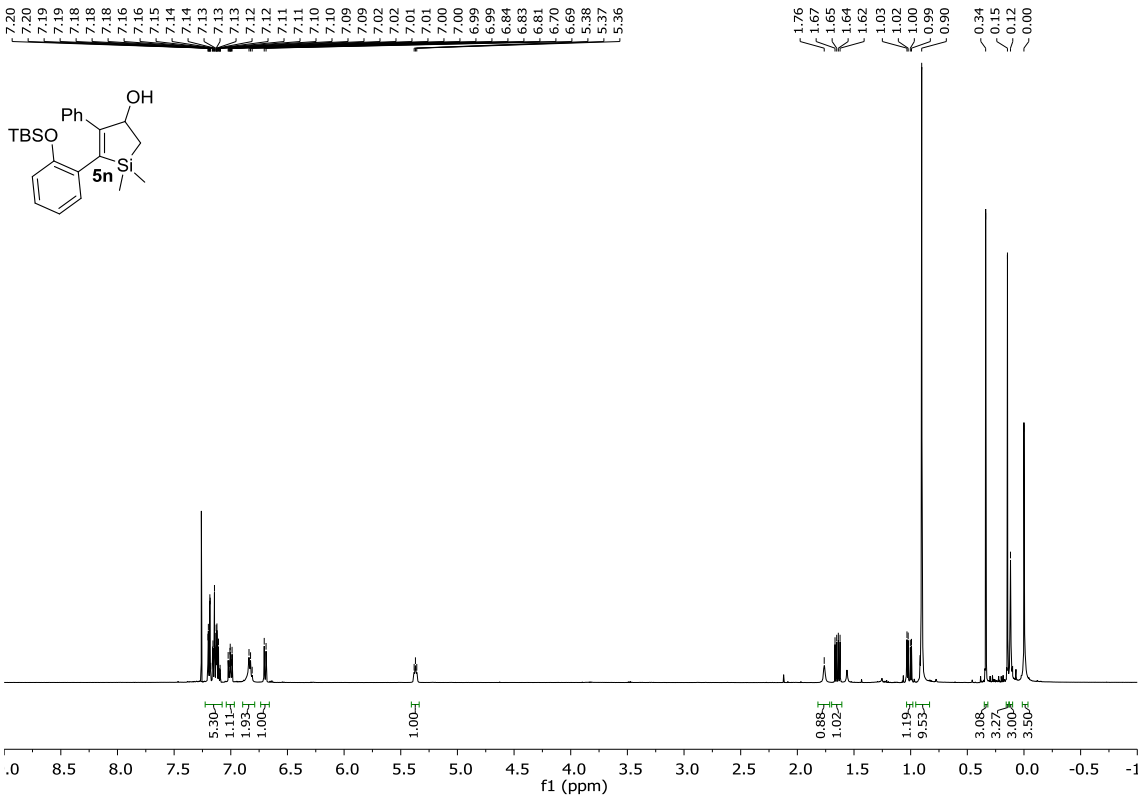
^{1}H NMR ($CDCl_3$, 500 MHz) of 5-(3-bromophenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1H-silol-3-ol (**5m**)



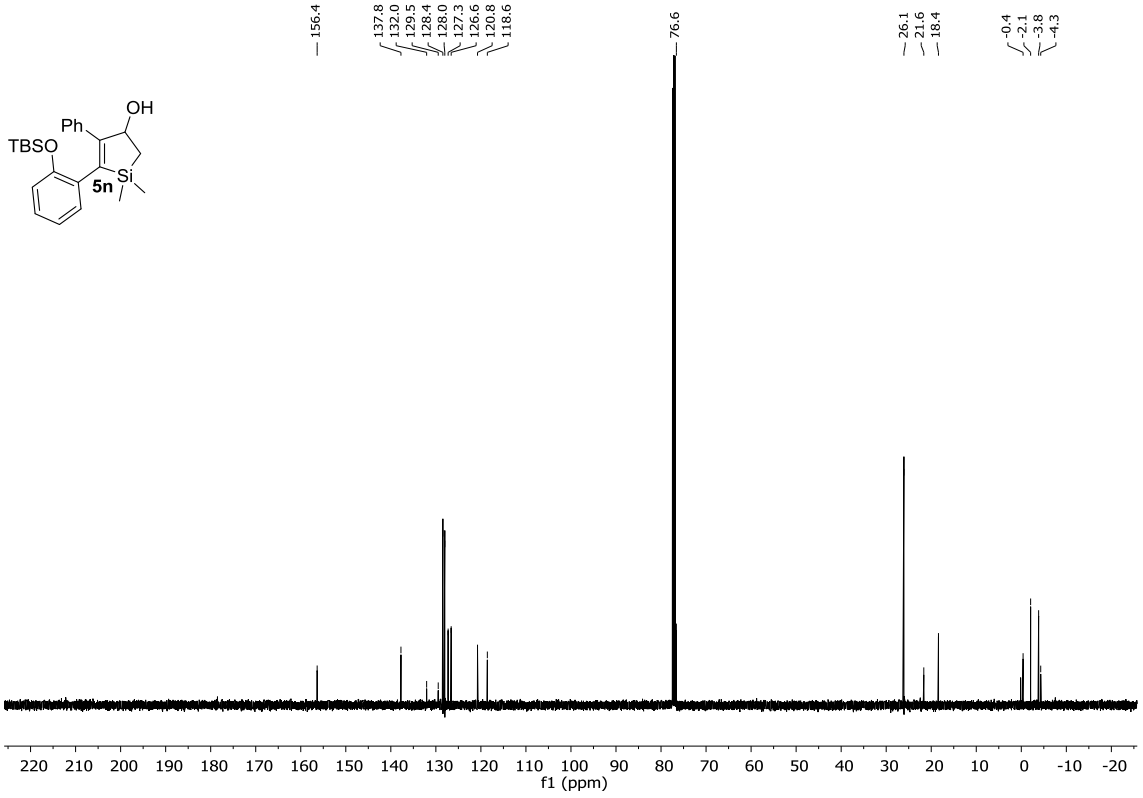
^{13}C NMR ($CDCl_3$, 75 MHz) of 5-(3-bromophenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1H-silol-3-ol (**5m**)



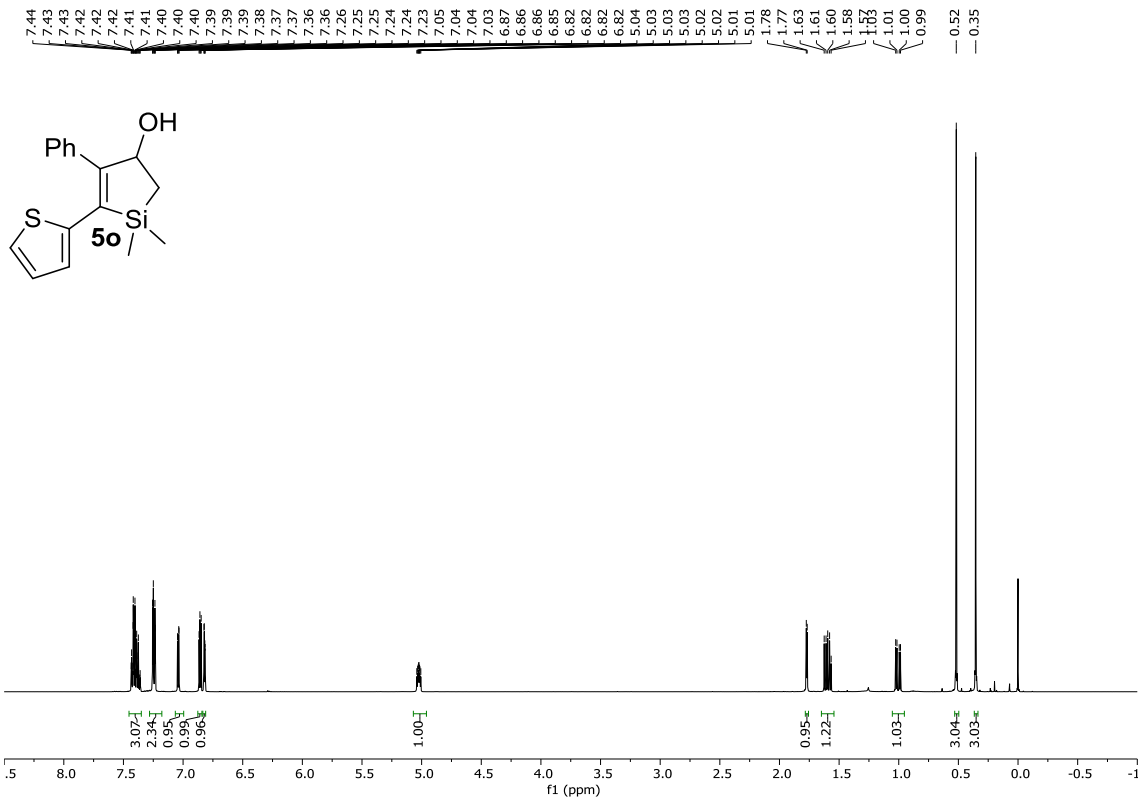
^{1}H NMR ($CDCl_3$, 500 MHz) of 5-(2-((tert-butyldimethylsilyl)oxy)phenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1H-silol-3-ol (**5n**)



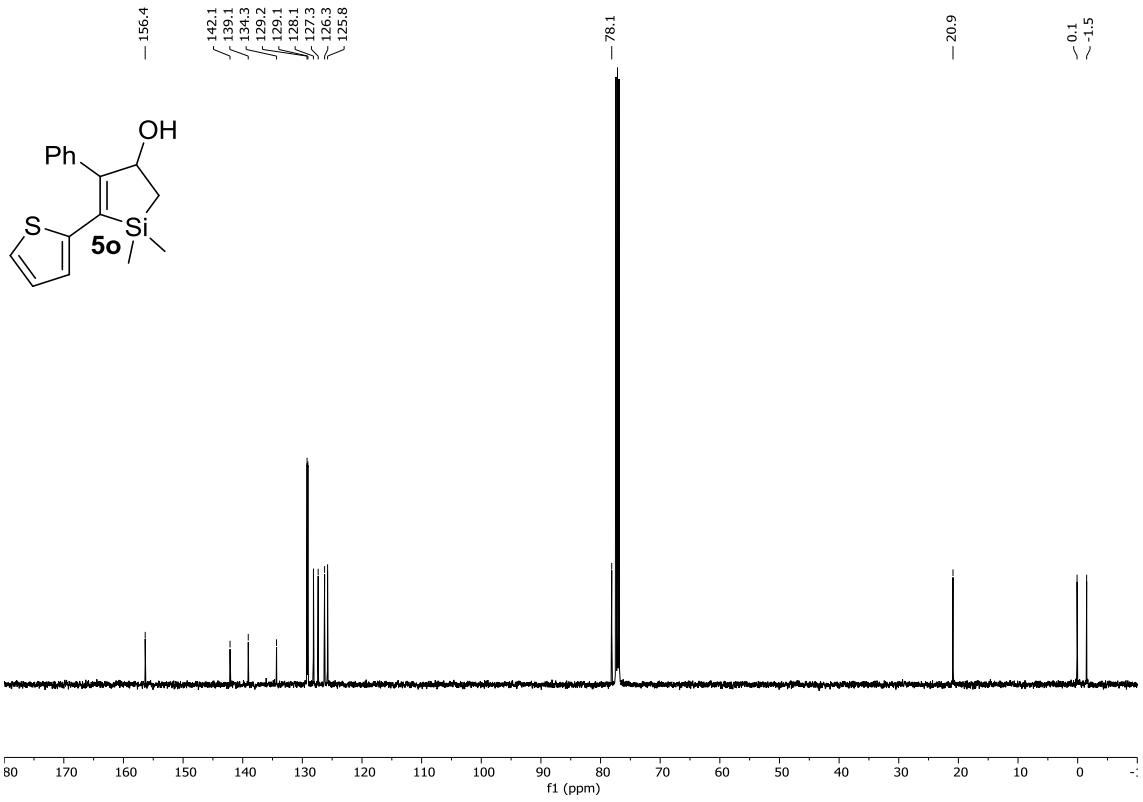
^{13}C NMR ($CDCl_3$, 125 MHz) of 5-(2-((tert-butyldimethylsilyl)oxy)phenyl)-1,1-dimethyl-4-phenyl-2,3-dihydro-1H-silol-3-ol (**5n**)



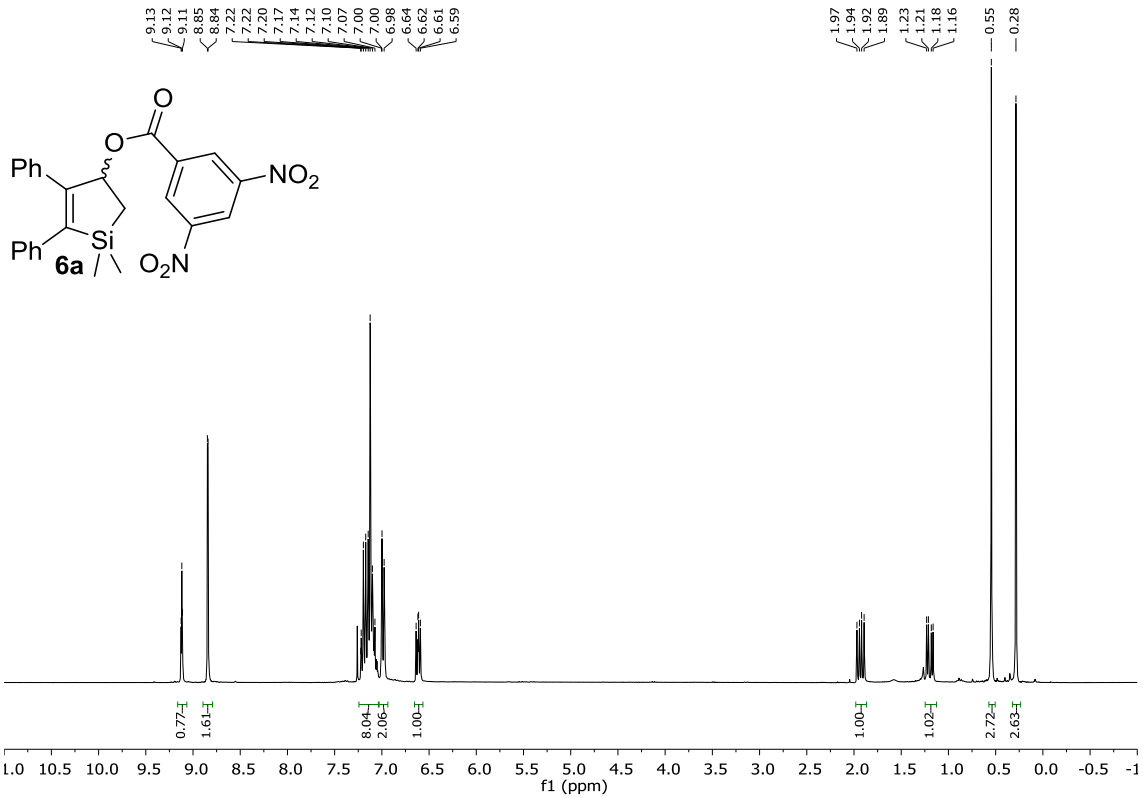
^{1}H NMR ($CDCl_3$, 500 MHz) of 1,1-dimethyl-4-phenyl-5-(thiophen-2-yl)-2,3-dihydro-1*H*-silol-3-ol (**5o**)



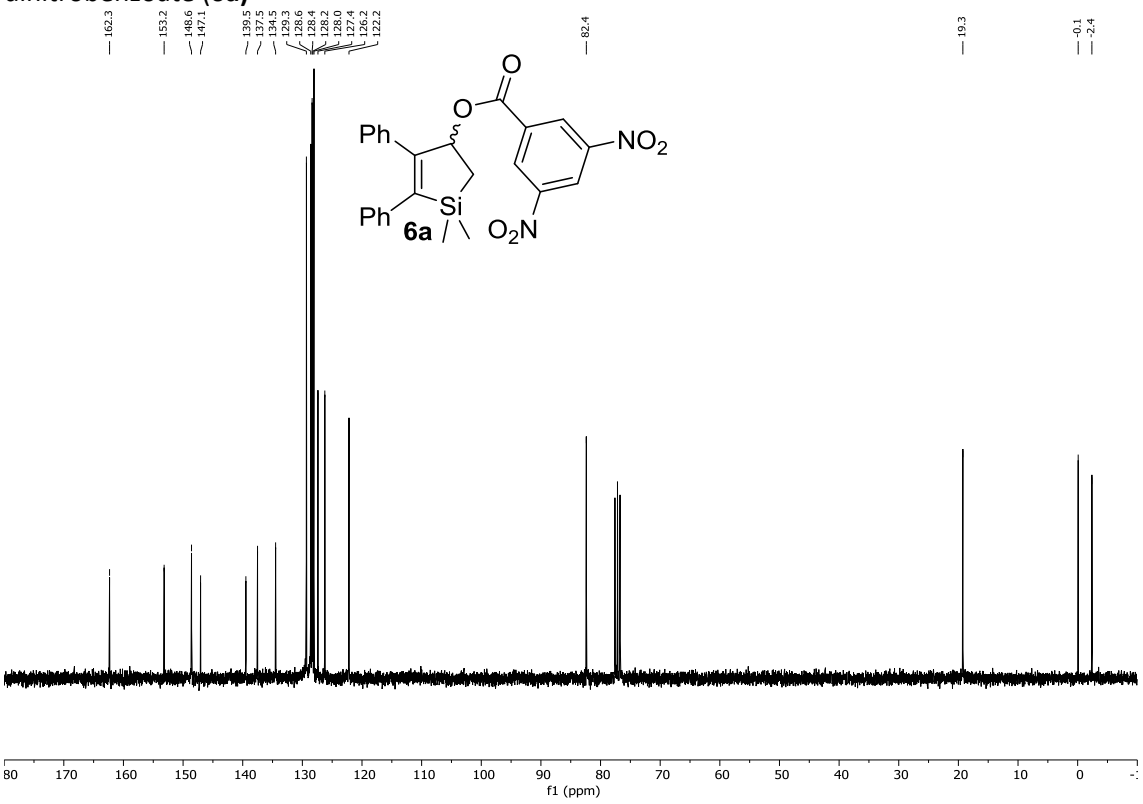
^{13}C NMR ($CDCl_3$, 125 MHz) of 1,1-dimethyl-4-phenyl-5-(thiophen-2-yl)-2,3-dihydro-1*H*-silol-3-ol (**5o**)



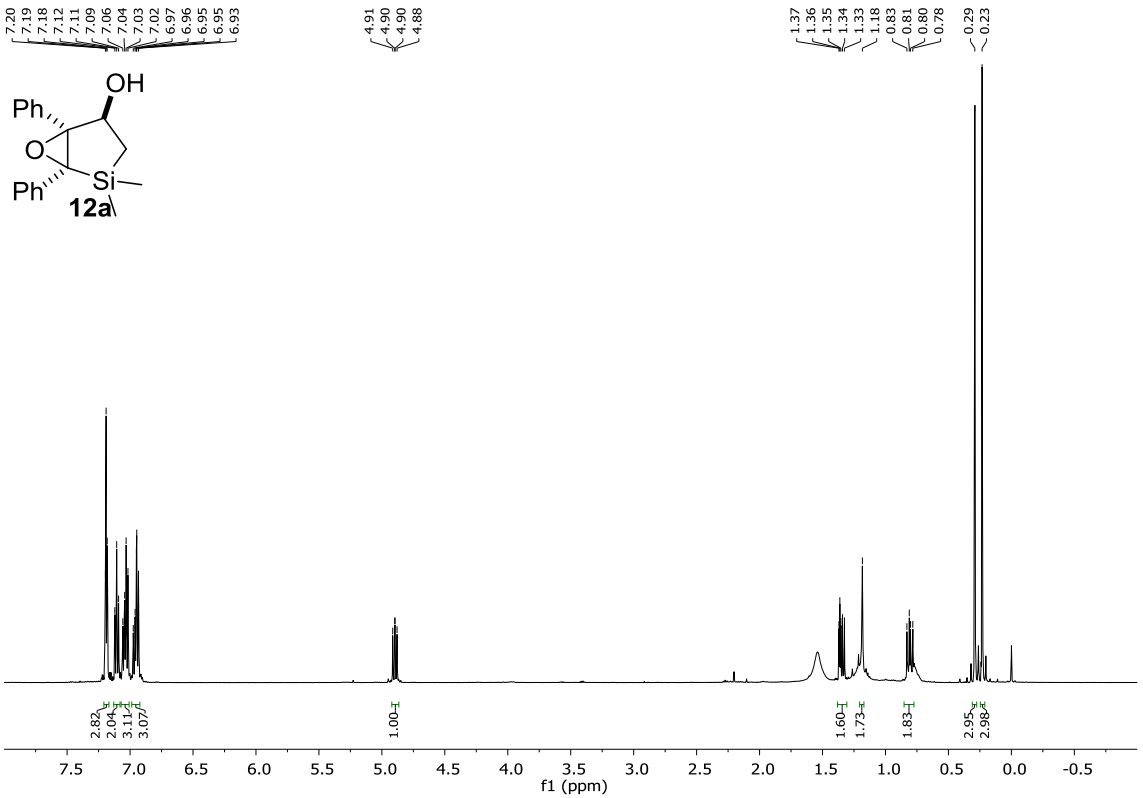
^{1}H NMR ($CDCl_3$, 300 MHz) of 1,1-dimethyl-4,5-diphenyl-2,3-dihydro-1*H*-silol-3-yl 3,5-dinitrobenzoate (**6a**)



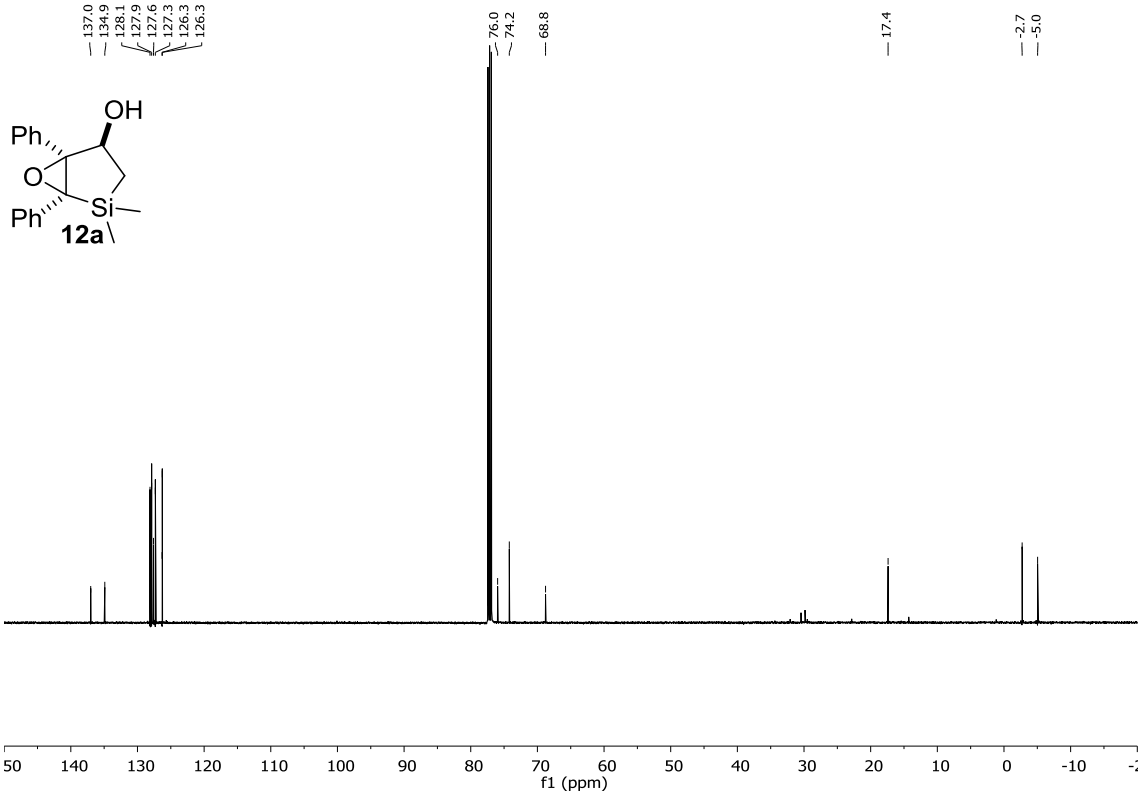
^{13}C NMR ($CDCl_3$, 75 MHz) of 1,1-dimethyl-4,5-diphenyl-2,3-dihydro-1*H*-silol-3-yl 3,5-dinitrobenzoate (**6a)**



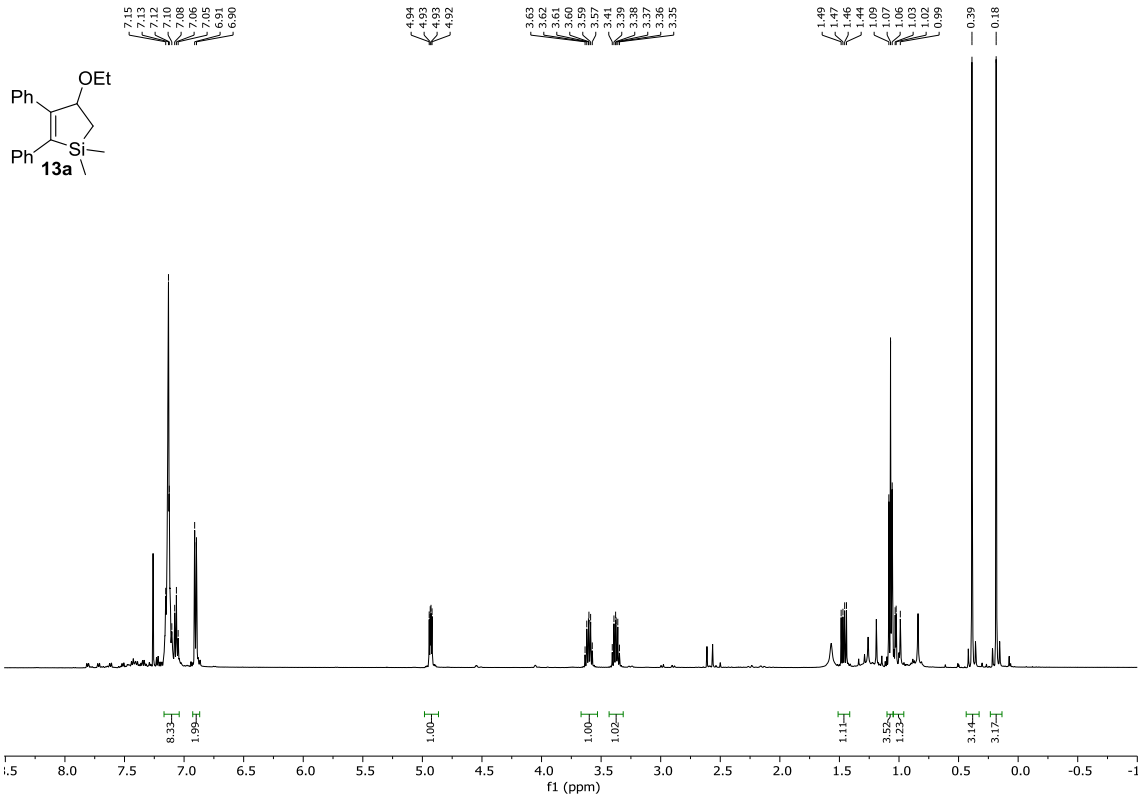
^{1}H NMR ($CDCl_3$, 500 MHz) of 2,2-dimethyl-1,5-diphenyl-6-oxa-2-silabicyclo[3.1.0]hexan-4-ol (**12a**)



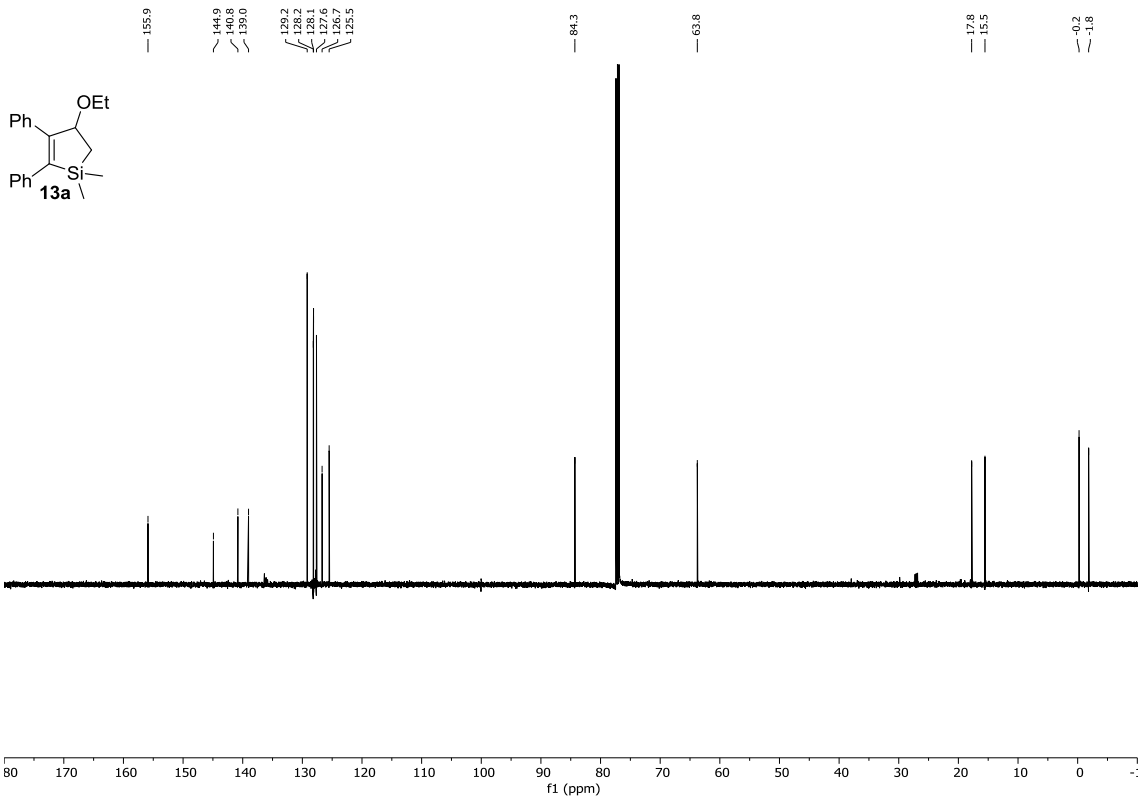
^{13}C NMR ($CDCl_3$, 125 MHz) of 2,2-dimethyl-1,5-diphenyl-6-oxa-2-silabicyclo[3.1.0]hexan-4-ol (**12a**)



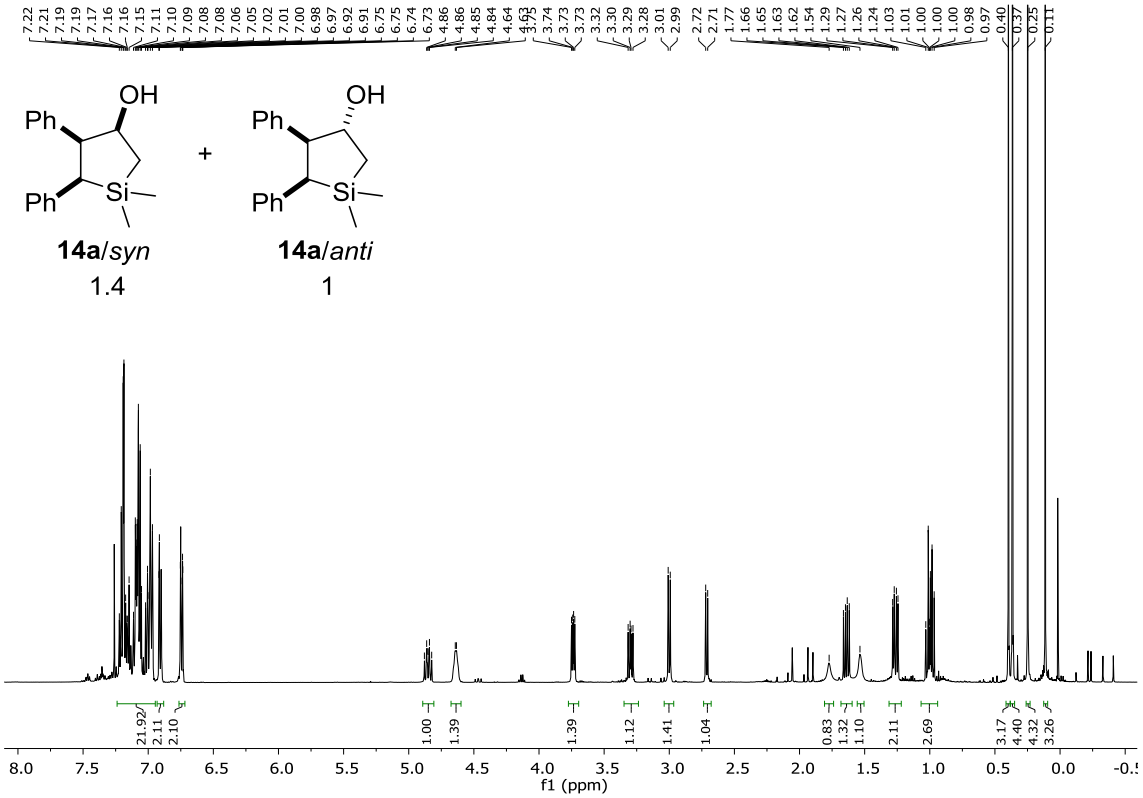
^{1}H NMR ($CDCl_3$, 500 MHz) of 3-ethoxy-1,1-dimethyl-4,5-diphenyl-2,3-dihydro-*1H*-silole (**13a**)



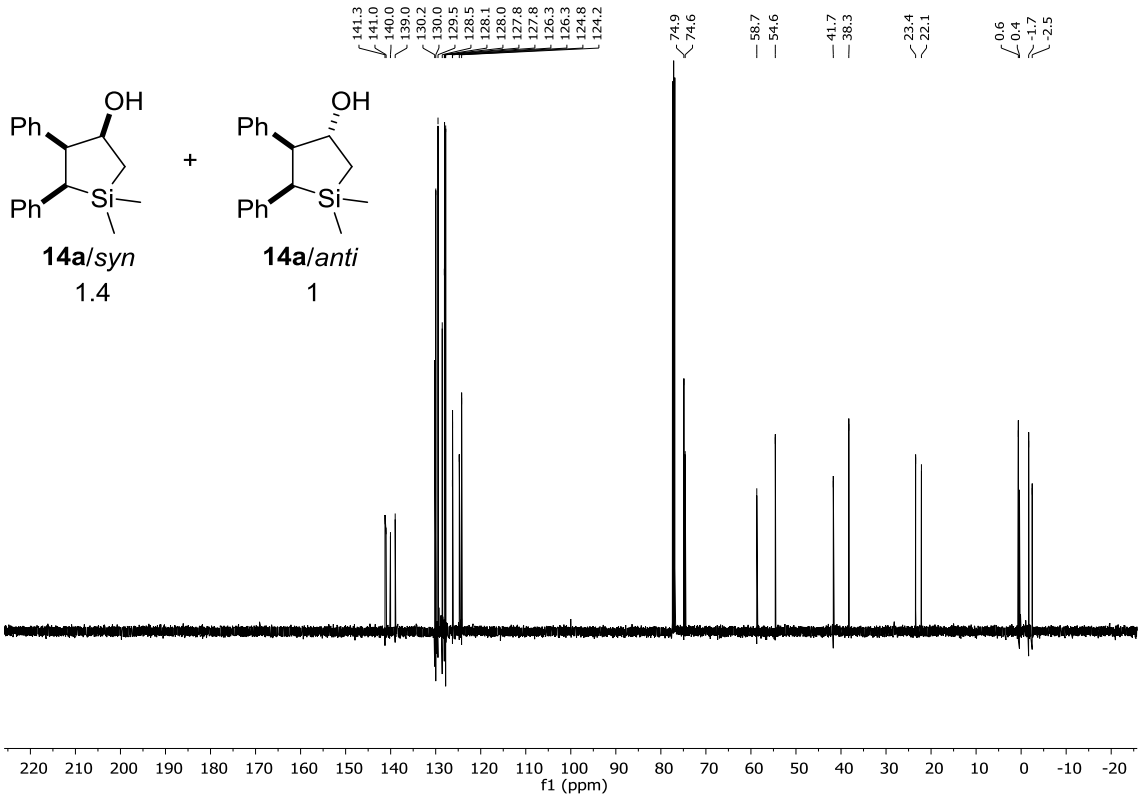
^{13}C NMR ($CDCl_3$, 125 MHz) of 3-ethoxy-1,1-dimethyl-4,5-diphenyl-2,3-dihydro-*1H*-silole (**13a**)



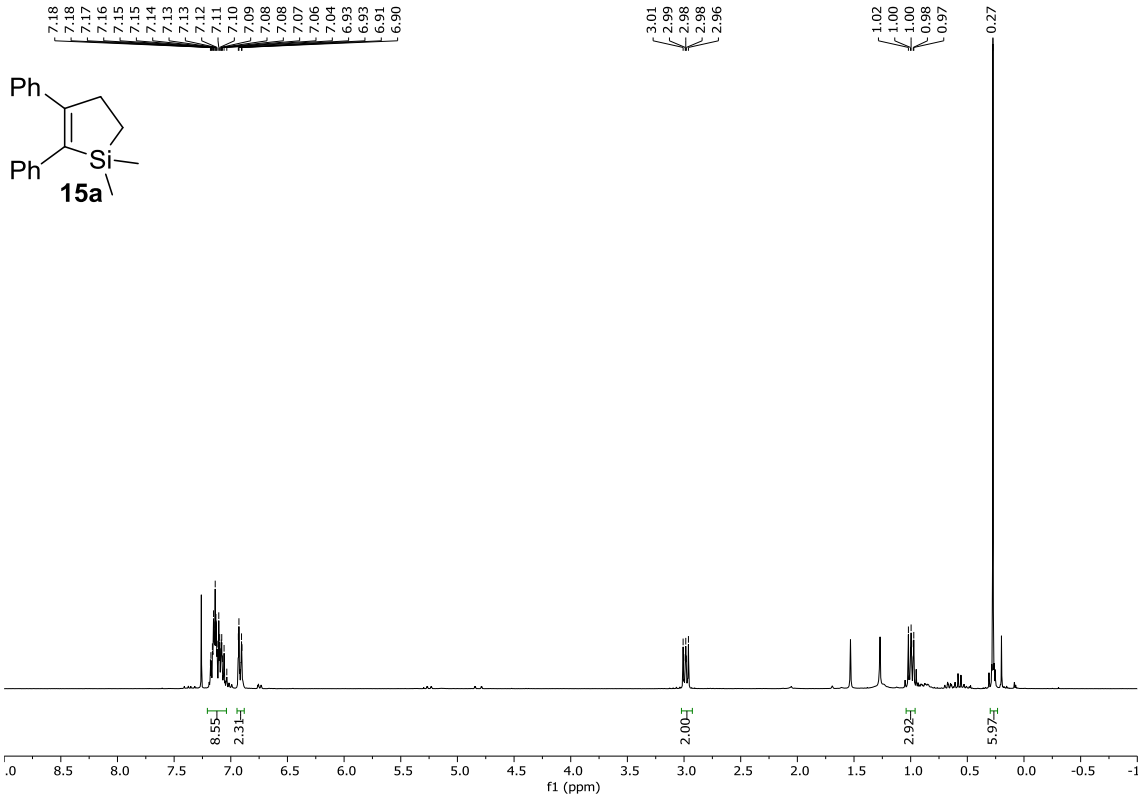
^{1}H NMR ($CDCl_3$, 500 MHz) of 1,1-dimethyl-4,5-diphenylsilolan-3-ol (**14a**/syn **and 14a**/anti)



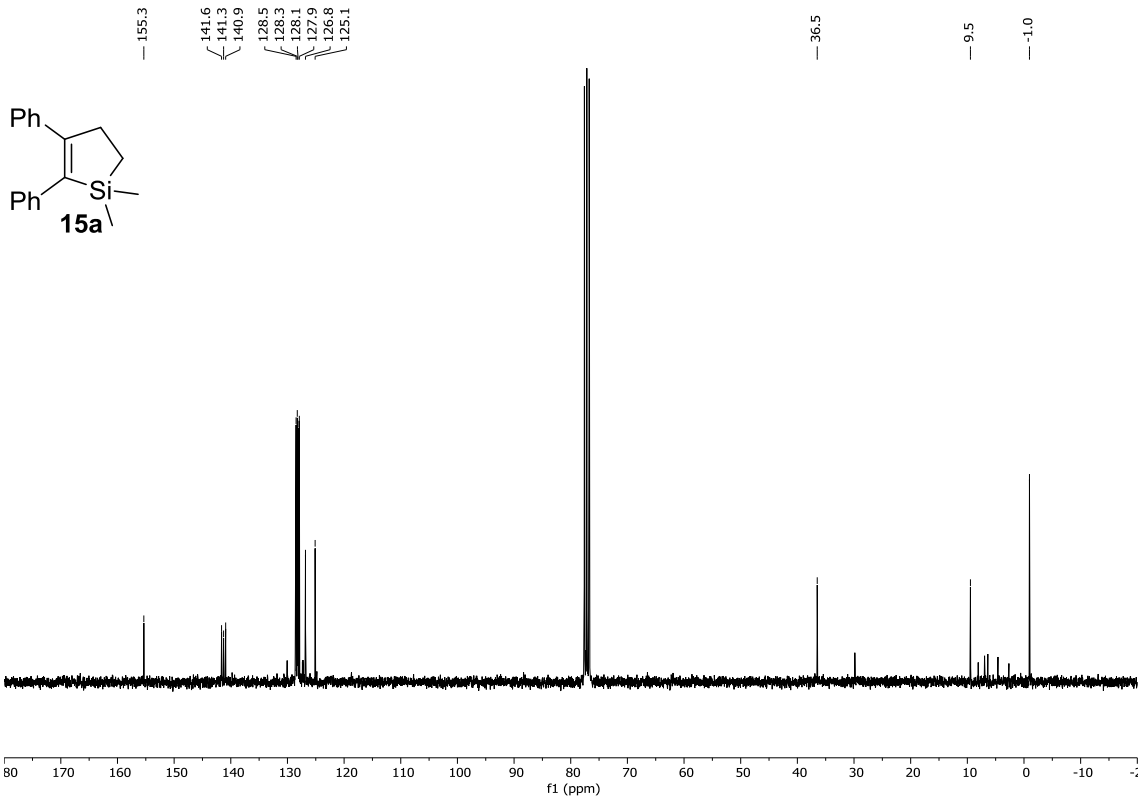
^{13}C NMR ($CDCl_3$, 125 MHz) of 1,1-dimethyl-4,5-diphenylsilolan-3-ol (**14a**/syn **and 14a**/anti)



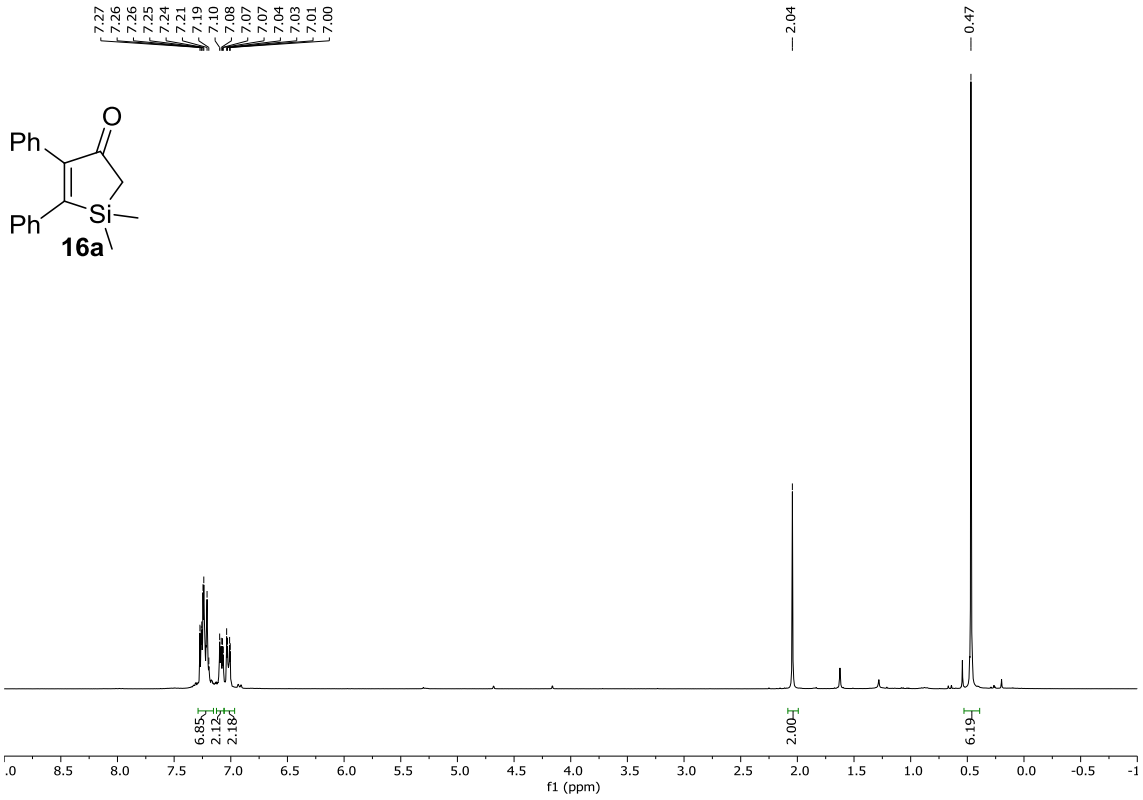
^{1}H NMR ($CDCl_3$, 300 MHz) of 1,1-dimethyl-4,5-diphenyl-2,3-dihydro-1*H*-silole (**15a**)



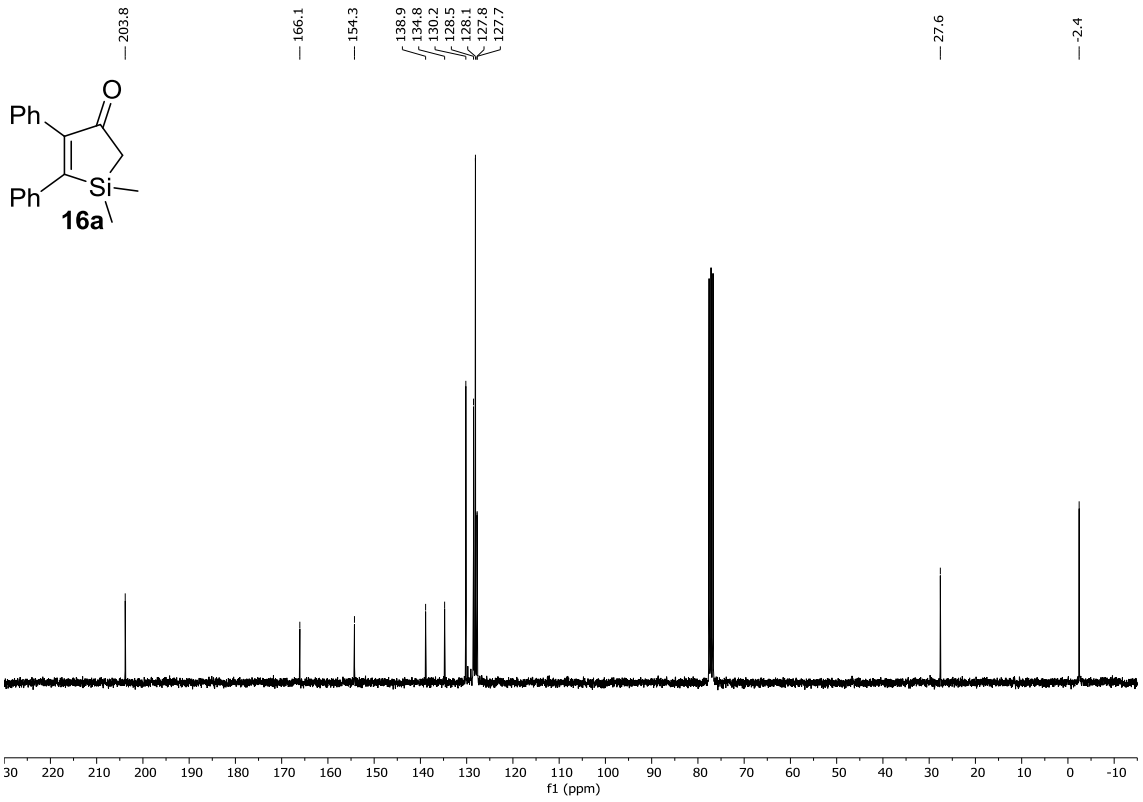
^{13}C NMR ($CDCl_3$, 75 MHz) of 1,1-dimethyl-4,5-diphenyl-2,3-dihydro-1*H*-silole (**15a**)



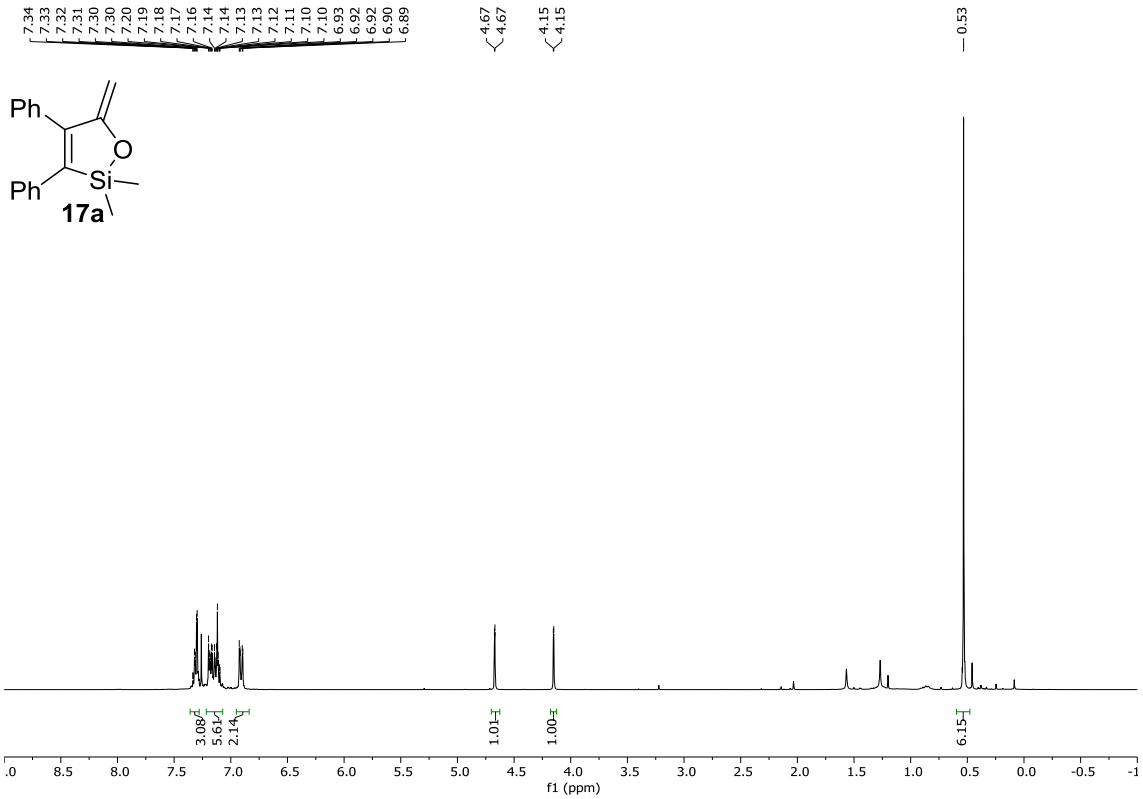
^{1}H NMR ($CDCl_3$, 300 MHz) of 1,1-dimethyl-4,5-diphenyl-1,2-dihydro-3*H*-silol-3-one (**16a**)



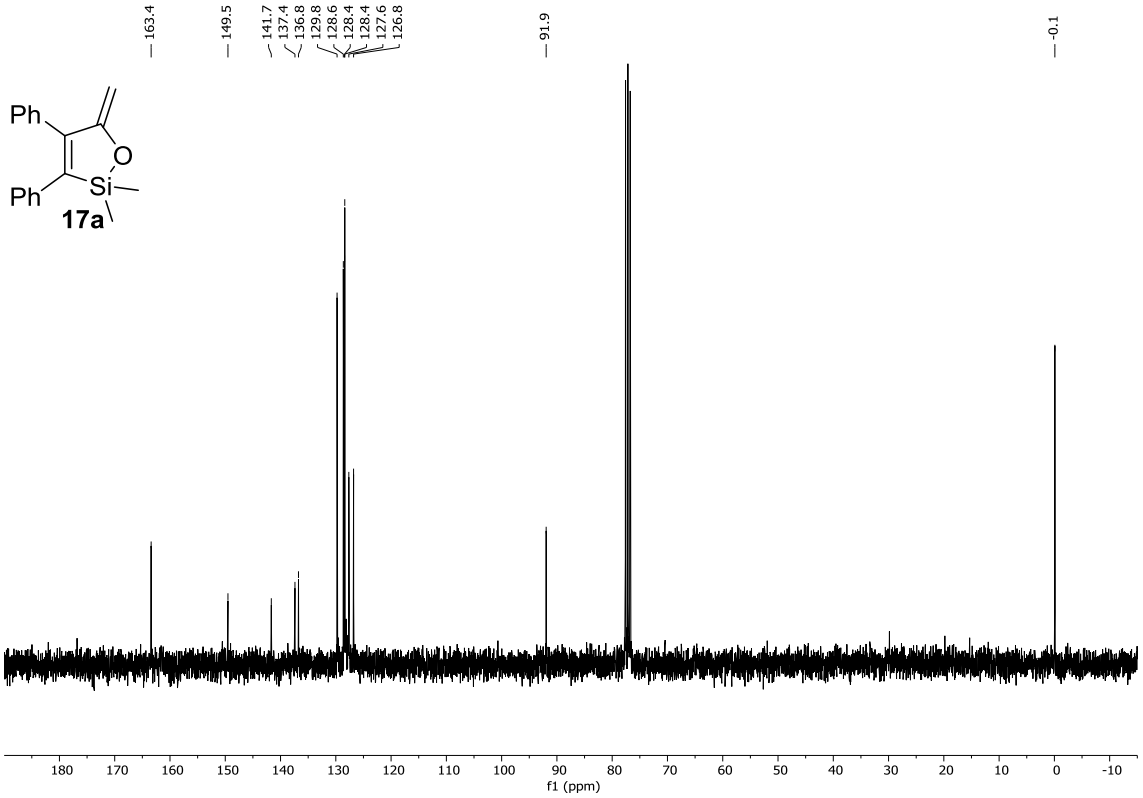
^{13}C NMR ($CDCl_3$, 75 MHz) of 1,1-dimethyl-4,5-diphenyl-1,2-dihydro-3*H*-silol-3-one (**16a**)



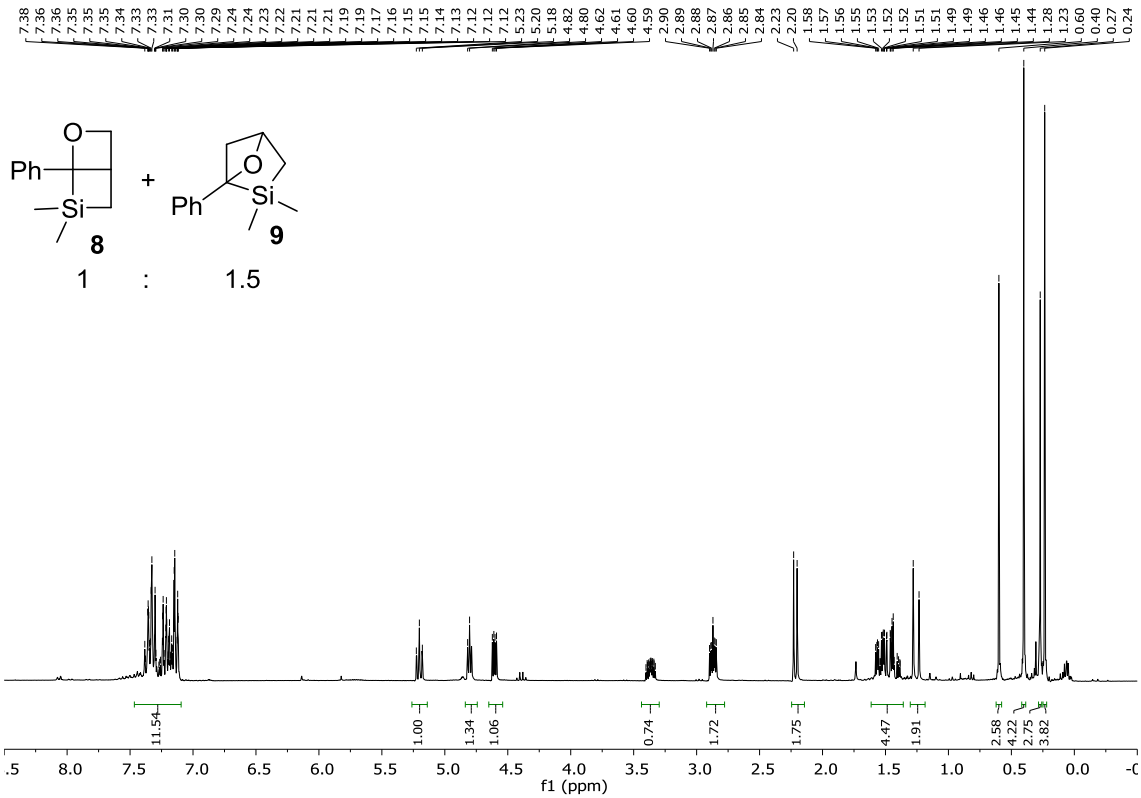
^{1}H NMR ($CDCl_3$, 300 MHz) of 2,2-dimethyl-5-methylene-3,4-diphenyl-2,5-dihydro-1,2-oxasilole (**17a**)



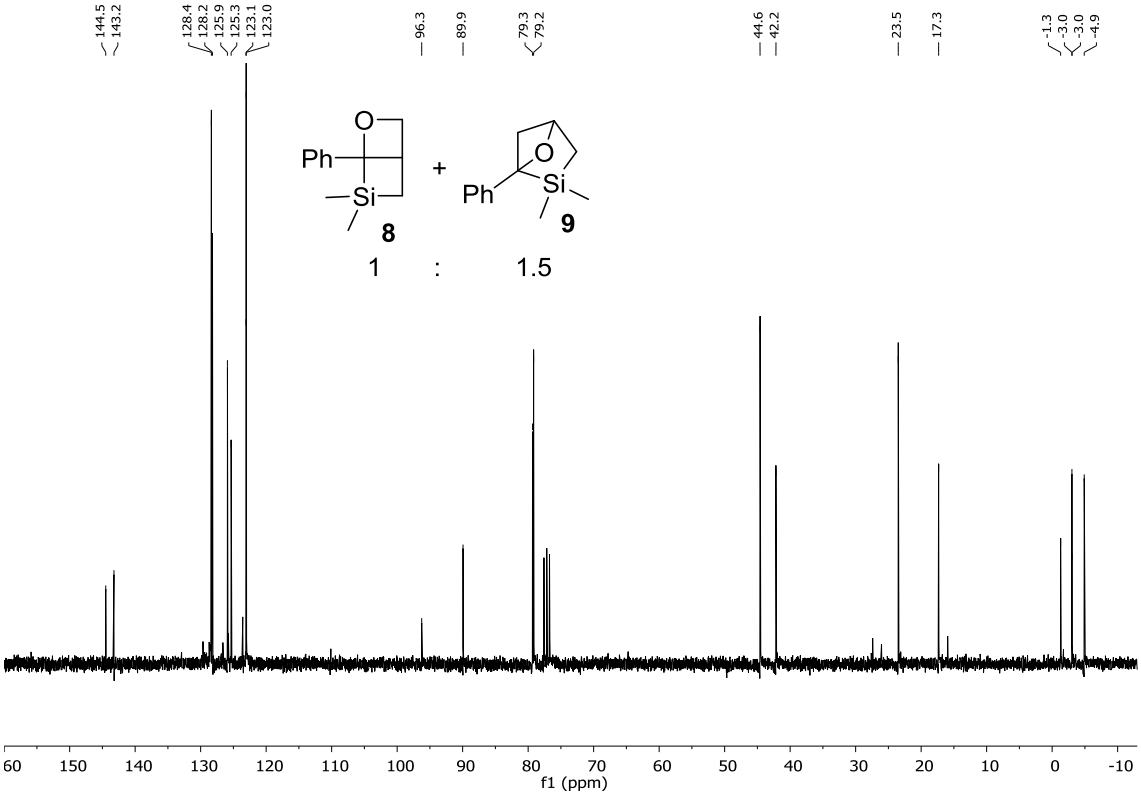
^{13}C NMR ($CDCl_3$, 75 MHz) of 2,2-dimethyl-5-methylene-3,4-diphenyl-2,5-dihydro-1,2-oxasilole (**17a**)



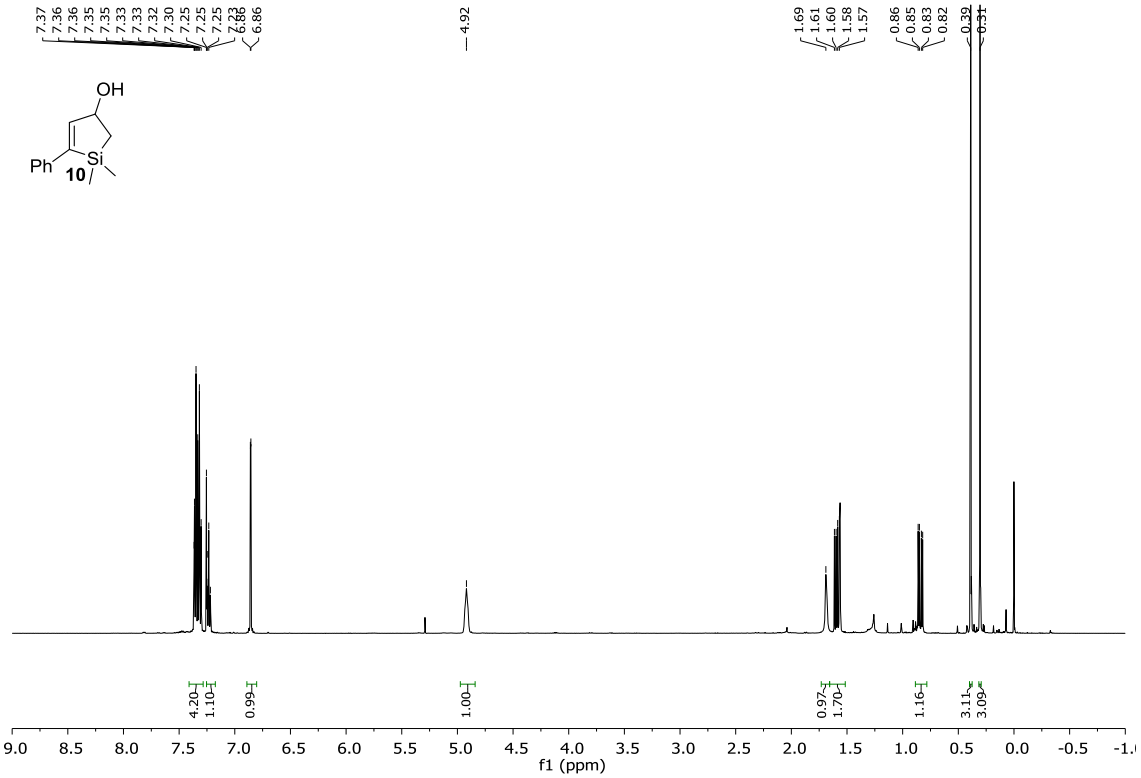
^{1}H NMR ($CDCl_3$, 300 MHz) of 6,6-dimethyl-1-phenyl-2-oxa-6-silabicyclo[2.2.0]hexane (**8**) and 2,2-dimethyl-1-phenyl-5-oxa-2-silabicyclo[2.1.1]hexane (**9**)



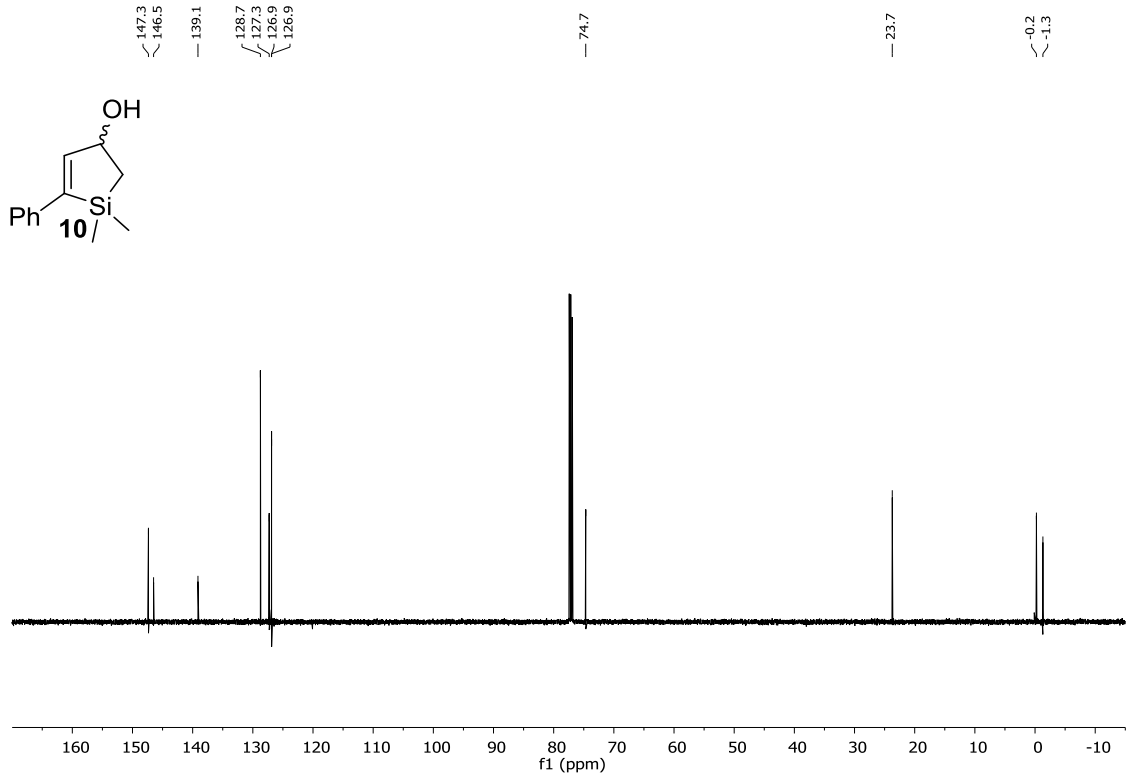
^{13}C NMR ($CDCl_3$, 75 MHz) of 6,6-dimethyl-1-phenyl-2-oxa-6-silabicyclo[2.2.0]hexane (**8**) and 2,2-dimethyl-1-phenyl-5-oxa-2-silabicyclo[2.1.1]hexane (**9**)



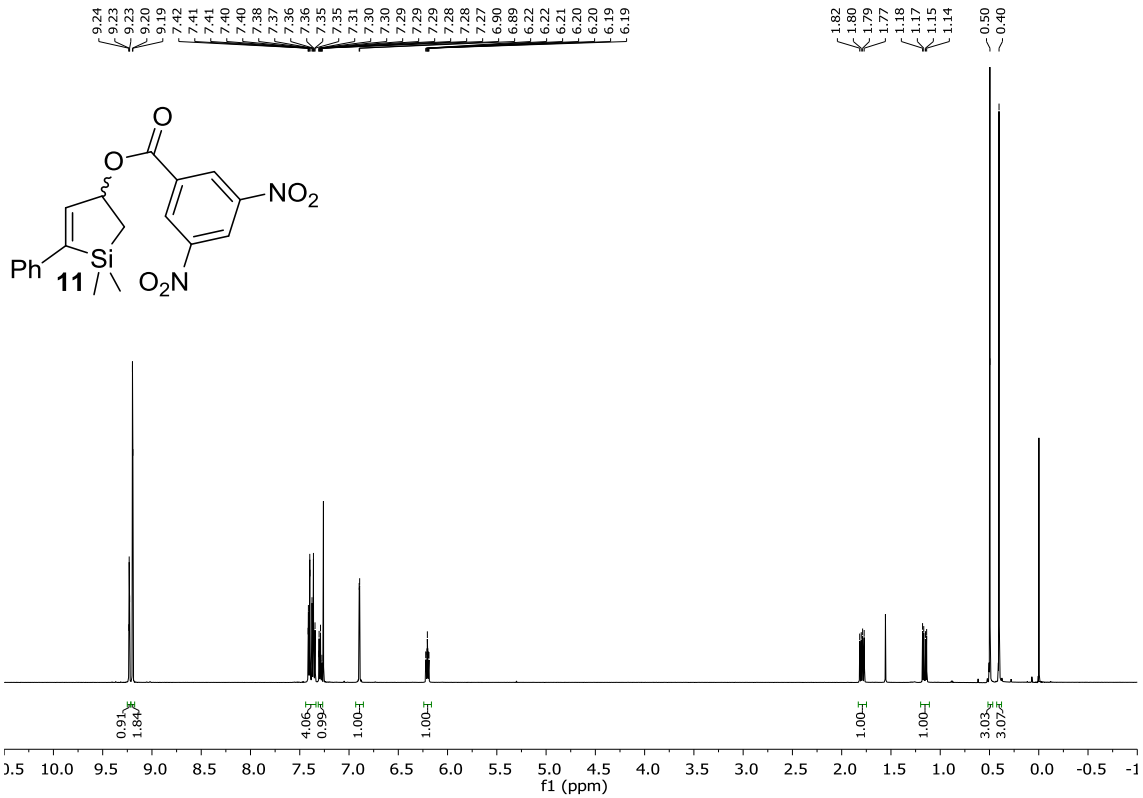
^{1}H NMR ($CDCl_3$, 500 MHz) of 1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**10**)



^{13}C NMR ($CDCl_3$, 125 MHz) of 1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-ol (**10**)



^{1}H NMR ($CDCl_3$, 500 MHz) of 1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-yl 3,5-dinitrobenzoate (**11**)



^{13}C NMR ($CDCl_3$, 125 MHz) of 1,1-dimethyl-5-phenyl-2,3-dihydro-1*H*-silol-3-yl 3,5-dinitrobenzoate (**11**)