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Supporting Information

Consecutive β,β′-Selective C(sp^3)−H Silylation of Tertiary Amines with Dihydrosilanes Catalyzed by $B(C_6F_5)_3$

*Huaquan Fang, Kaixue Xie, Sebastian Kemper, and Martin Oestreich**

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Supporting Information

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1 General Experimental Information

Reagents and Solvents

Toluene, benzene, chlorobenzene, chlorobenzene, and *p*-xylene were purified by distillation over $LiAlH_4$ and freshly distilled prior to use. CH_2Cl_2 was dried over CaH_2 and freshly distilled prior to use. $B(C_6F_5)_3$ was purchased from Boulder Scientific Company, sublimed under vacuum at 130 °C prior to use, and stored in a nitrogen-filled glovebox. Di-*p*-tolylsilane (**2b**),[1] bis(4-(*tert*-butyl)phenyl)silane (**2c**),[2] bis(4-fluorophenyl)silane (**2d**),[2] 2,3-dihydro-1*H*-benzo[*b*]silole (**2g**),[3] and dimesitylsilane (**2k**)[4] were prepared according to literature procedures. Ph_2SiD_2[5] was prepared according to literature procedures. All other reagents were purchased from commercial sources and used as received unless specified otherwise.

Reactions

All manipulations were carried out in a nitrogen-filled glovebox or under an atmosphere of dry nitrogen using standard Schlenk techniques, unless otherwise stated.

Chromatography

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Grace* using the indicated solvents.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker AV500 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^1H NMR and $CDCl_3$: δ = 77.16 ppm for ^{13}C NMR; toluene: δ = 7.09, 7.01, 6.97, 2.08 ppm for ^1H NMR). Data are reported as follows: chemical shift, multiplicity (br = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration.

Gas Chromatography (GC)

Gas chromatography (GC) was performed on an *Agilent Technologies* 7820A gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm, 0.25 *µ*m film

thickness) by *Agilent Technologies/ CS-Chromatographie Service* using the following program: nitrogen carrier gas, injection temperature 250 °C, detector temperature 300 °C, flow rate: 1.7 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min.

Gas Chromatography–Mass Spectrometry (GC-MS)

Gas chromatography–mass spectrometry (GC-MS) was performed on an *Agilent Technologies* 5975C gas chromatograph equipped with an *Agilent Technologies* HP-5 column (30 m × 0.32 mm, 0.25 µm film thickness) using the following program: nitrogen carrier gas, injection temperature 280 °C, detector temperature 280 °C, flow rate: 0.8 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min.

Infrared Spectroscopy

Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer equipped with an ATR unit or a Jasco FT/IR-4100 spectrometer, and the bands are reported in wavenumbers (cm^{-1}).

Mass Spectrometry

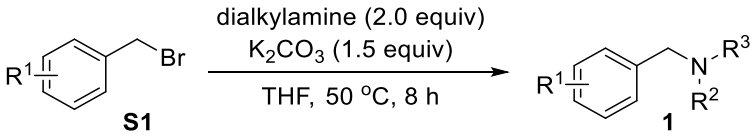
High resolution mass spectrometry (HRMS) analysis was performed by the Analytical Facility at the *Institut für Chemie, Technische Universität Berlin*.

Compound Nomenclature

The compound names were generated by the computer program *ChemDraw* according to the guidelines specified by the *International Union of Pure and Applied Chemistry* (IUPAC).

2 Experimental Details for the Preparation of *N*,*N*-Dialkyl Benzylamines

2.1 General Procedure for the Preparation of *N*,*N*-Dialkyl Benzylamines

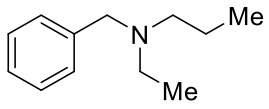


A mixture of benzyl bromides **S1** (10.0 mmol), dialkylamine (20.0 mmol), K_2CO_3 (15.0 mmol) in THF (30 mL) was heated at 50 °C for 8 h. The mixture was cooled to room temperature and diluted with methyl *tert*-butyl ether (20 mL) and H_2O (20 mL). Then the mixture was extracted with methyl *tert*-butyl ether (10 mL×3). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane to afford *N*,*N*-dialkyl benzylamines as a colorless liquid.

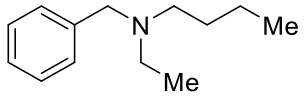
N,*N*-Dialkyl Benzylamines **1a**, **1o**–**q**, **1t**, and **1u** were purchased from commercial sources and used as received unless specified otherwise.

N,*N*-Dialkyl Benzylamines **1b**,[6] **1c**,[7] **1d**–**e**,[8] **1f**,[6] **1g**,[8] **1h**,[6] **1i**–**j**,[8] **1k**,[7] **1l**,[6] **1m**,[7] **1n**[6], and **1v**[9] were prepared according to the general procedure and data were consistent with that reported.

2.2 Charaterization Data of New *N*,*N*-Dialkyl Benzylamines



***N*-Benzyl-*N*-ethylpropan-1-amine (1r).** The general procedure was followed with benzyl bromide (1.19 mL, 10.0 mmol), *N*-ethylpropan-1-amine (2.42 mL, 20.0 mmol), K_2CO_3 (2.10 g, 15.0 mmol) in THF (30 mL) at 50 °C for 8 h. The residue was purified by flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent to afford **1r** as a colorless liquid (1.60 g, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 4H), 7.24 (t, *J* = 7.0 Hz, 1H), 3.58 (s, 2H), 2.52 (q, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 1.54 – 1.47 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.3, 129.0, 128.2, 126.7, 58.2, 55.4, 47.4, 20.3, 12.0, 11.9 ppm. **HRMS** (APCI): Calculated for $C_{12}H_{20}N^+$ $[M+H]^+$: 178.1596; Found: 178.1586. **IR** (ATR): ṽ 2961, 2931, 2871, 2794, 1492, 1452, 1368, 1193, 1163, 1073, 1026, 727, 696.



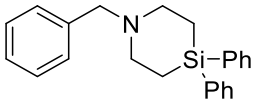
***N*-Benzyl-*N*-ethylbutan-1-amine (1s).** The general procedure was followed with benzyl bromide (1.19 mL, 10.0 mmol), *N*-ethylbutan-1-amine (2.73 mL, 20.0 mmol), K_2CO_3 (2.10 g, 15.0 mmol) in THF (30 mL) at 50 °C for 8 h. The residue was purified by flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent to afford **1s** as a colorless liquid (1.80 g, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 – 7.33 (m, 4H), 7.25 – 7.21 (m, 1H), 3.57 (s, 2H), 2.51 (q, *J* = 7.1 Hz, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 1.50 – 1.44 (m, 2H), 1.35 – 1.27 (m, 2H), 1.04 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.3, 129.0, 128.2, 126.8, 58.2, 53.1, 47.4, 29.4, 20.8, 14.2, 11.9 ppm. **HRMS** (APCI): Calculated for $C_{13}H_{22}N^+$ $[M+H]^+$: 192.1752; Found: 192.1743. **IR** (ATR): ṽ 2957, 2929, 2869, 2793, 1493, 1452, 1368, 1187, 1160, 1071, 1027, 728, 696.

3 Experiment Details for the Two-Fold C(sp^3)–H Silylation

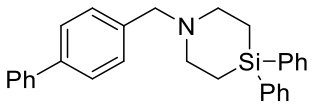
3.1 General Procedure for the Two-Fold C(sp^3)–H Silylation

In a nitrogen-filled glovebox, a 10-mL sealed tube equipped with a magnetic stir bar was charged with the desired amount of amine, hydrosilane, solvent, additive, and $B(C_6F_5)_3$. The sealed tube was fitted with a cap, and the reaction stirred at required temperature for indicated time in a preheated oil bath. After the resulting reaction mixture was cooled to room temperature, the volatile were removed under reduced pressure. *In the case of R_3SiOTf as an additive, the solution was neutralized upon stirring with NaOH (5 mL, 10% aq.) for 30 min. The mixture was extracted with methyl tert-butyl ether (10 mL×3). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure.* Mesitylene (0.500 equiv) was added as an internal standard, and the yield was determined by ^{1}H NMR spectroscopy. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane for *N*-benzyl-substituted 4-silapiperidines or MeOH / methyl *tert*-butyl ether for *N*-alkyl-substituted 4-sila-piperidines as the eluent and Kugelrohr distillation.

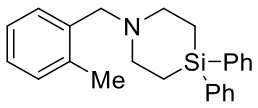
3.2 Characterization Data of the 4-Silapiperidines



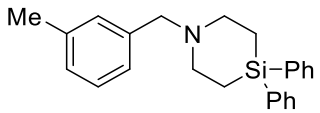
1-Benzyl-4,4-diphenyl-1,4-azasilinane (3aa). The general procedure was followed with *N*-benzyl-*N*-ethylethanamine (**1a**, 8.20 mg, 0.0500 mmol), Ph_2SiH_2 (**2a**, 18.4 mg, 0.100 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (3.60 µL, 20.0 µmol) and $B(C_6F_5)_3$ (5.10 mg, 10.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (200 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (12.5 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60 – 7.57 (m, 4H), 7.44 – 7.33 (m, 10H), 7.29 – 7.25 (m, 1H), 3.62 (s, 2H), 2.86 (t, *J* = 6.3 Hz, 4H), 1.40 (t, *J* = 6.3 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.6, 136.0, 134.8, 129.5, 128.9, 128.3, 128.0, 126.9, 62.8, 52.4, 11.5 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.60 – 7.57/–15.4, 2.86/–15.4, 1.40/–15.4 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{26}NSi^+$ $[M+H]^+$: 344.1835; Found: 344.1828. **IR** (ATR): ṽ 2920, 2891, 2794, 2758, 1452, 1226, 1185, 1109, 968, 864, 724, 694. Spectral data is in agreement with published data.[10]



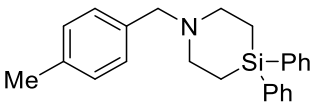
1-([1,1'-Biphenyl]-4-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ba). The general procedure was followed with *N*-([1,1'-biphenyl]-4-ylmethyl)-*N*-ethylethanamine (**1b**, 23.9 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (240 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (23.9 mg, 57% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.65 – 7.58 (m, 8H), 7.48 – 7.35 (m, 11H), 3.66 (s, 2H), 2.89 (t, *J* = 6.5 Hz, 4H), 1.43 (t, *J* = 6.5 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 141.2, 139.9, 138.7, 136.0, 134.8, 129.5, 129.3, 128.9, 128.1, 127.2, 127.2, 127.1, 62.5, 52.5, 11.5 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.58/–15.5, 2.89/–15.5, 1.43/–15.5 ppm. **HRMS** (APCI): Calculated for $C_{29}H_{30}NSi^+$ $[M+H]^+$: 420.2148; Found: 420.2138. **IR** (ATR): ṽ 2920, 2892, 2792, 2758, 1485, 1426, 1226, 1185, 1110, 1007, 970, 867, 727, 695.



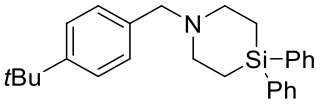
1-(2-Methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ca). The general procedure was followed with *N*-ethyl-*N*-(2-methylbenzyl)ethanamine (**1c**, 17.7 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (21.1 mg, 59% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.58 – 7.55 (m, 4H), 7.42 – 7.33 (m, 7H), 7.18 – 7.14 (m, 3H), 3.52 (s, 2H), 2.83 (t, *J* = 5.2 Hz, 4H), 2.37 (s, 3H), 1.36 (t, *J* = 5.2 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.8, 137.5, 136.1, 134.8, 130.3, 129.5, 128.1, 126.9, 125.6, 60.7, 52.6, 19.4, 11.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.58 – 7.55/–15.4, 2.83/–15.4, 1.36/–15.4 ppm. **HRMS** (APCI): Calculated for $C_{24}H_{28}NSi^+$ $[M+H]^+$: 358.1991; Found: 358.1984. **IR** (ATR): ṽ 2920, 2889, 2795, 2758, 1459, 1426, 1226, 1185, 1110, 969, 865, 728, 697.



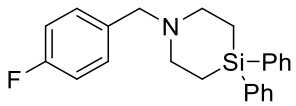
1-(3-Methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3da). The general procedure was followed with *N*-ethyl-*N*-(3-methylbenzyl)ethanamine (**1d**, 17.7 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (20.8 mg, 58% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.58 – 7.56 (m, 4H), 7.42 – 7.36 (m, 6H), 7.24 – 7.16 (m, 3H), 7.08 (d, *J* = 7.3 Hz, 1H), 3.58 (s, 2H), 2.85 (t, *J* = 6.0 Hz, 4H), 2.37 (s, 3H), 1.40 (t, *J* = 6.1 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.9, 136.0, 134.8, 129.8, 129.5, 128.2, 128.1, 127.8, 126.1, 62.7, 52.4, 21.6, 11.3 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.58 – 7.56/–15.8, 2.85/–15.8, 1.40/–15.8 ppm. **HRMS** (APCI): Calculated for $C_{24}H_{28}NSi^+$ $[M+H]^+$: 358.1991; Found: 358.1983. **IR** (ATR): ṽ 3045, 2921, 2794, 1427, 1389, 1227, 1112, 970, 865, 728, 698.



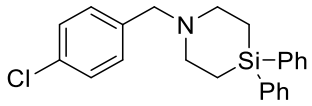
1-(4-Methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ea). The general procedure was followed with *N*-ethyl-*N*-(4-methylbenzyl)ethanamine (**1e**, 17.7 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (21.8 mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.58 – 7.56 (m, 4H), 7.42 – 7.36 (m, 6H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 3.58 (s, 2H), 2.84 (t, *J* = 6.1 Hz, 4H), 2.36 (s, 3H), 1.39 (t, *J* = 6.2 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 136.6, 136.1, 135.9, 134.8, 129.5, 129.0 (2C), 128.1, 62.5, 52.3, 21.2, 11.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.58 – 7.56/–15.6, 2.84/–15.6, 1.39/–15.6 ppm. **HRMS** (APCI): Calculated for $C_{24}H_{28}NSi^+$ $[M+H]^+$: 358.1991; Found: 358.1985. **IR** (ATR): ṽ 3045, 2920, 2792, 1426, 1186, 1111, 970, 867, 728, 698.



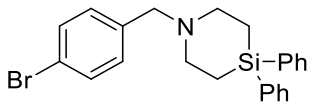
1-(4-(*tert*-Butyl)benzyl)-4,4-diphenyl-1,4-azasilinane (3fa). The general procedure was followed with *N*-(4-(*tert*-butyl)benzyl)-*N*-ethylethanamine (**1f**, 21.9 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (230 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (26.7 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.59 – 7.57 (m, 4H), 7.43 – 7.35 (m, 8H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.60 (s, 2H), 2.86 (t, *J* = 5.7 Hz, 4H), 1.41 (t, *J* = 5.7 Hz, 4H), 1.35 (s, 9H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.9, 136.0, 135.9, 134.8, 129.5, 128.7, 128.1, 125.2, 62.4, 52.4, 34.6, 31.5, 11.3 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.59 – 7.57/–15.5, 2.86/–15.5, 1.41/–15.5 ppm. **HRMS** (APCI): Calculated for $C_{27}H_{34}NSi^+$ $[M+H]^+$: 400.2461; Found: 400.2451. **IR** (ATR): ṽ 3066, 2958, 2792, 1465, 1426, 1389, 1226, 1109, 970, 906, 867, 726, 696.



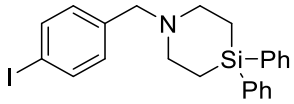
1-(4-Fluorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ga). The general procedure was followed with *N*-ethyl-*N*-(4-fluorobenzyl)ethanamine (**1g**, 18.1 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (25.3 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 4H), 7.41 – 7.35 (m, 6H), 7.32 – 7.29 (m, 2H), 7.02 – 6.98 (m, 2H), 3.55 (s, 2H), 2.81 (t, *J* = 6.1 Hz, 4H), 1.37 (t, *J* = 5.9 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 162.0 (d, *J* = 244.6 Hz), 135.9, 135.3, 134.8, 130.3 (d, *J* = 7.9 Hz), 129.5, 128.1, 115.0 (d, *J* = 21.1 Hz), 62.0, 52.3, 11.5 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ –116.2 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.56 – 7.54/–15.6, 2.81/–15.6, 1.37/–15.6 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{25}FNSi^+$ $[M+H]^+$: 362.1740; Found: 362.1727. **IR** (ATR): ṽ 3066, 2922, 2793, 1602, 1506, 1427, 1221, 1112, 971, 866, 729, 700.



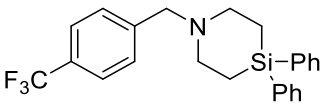
1-(4-Chlorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ha). The general procedure was followed with *N*-ethyl-*N*-(4-chlorobenzyl)ethanamine (**1h**, 19.7 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (230 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (24.6 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 4H), 7.42 – 7.35 (m, 6H), 7.30 – 7.27 (m, 4H), 3.56 (s, 2H), 2.82 (t, *J* = 6.0 Hz, 4H), 1.38 (t, *J* = 6.0 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.8, 135.7, 134.8, 132.7, 130.3, 129.6, 128.5, 128.1, 62.0, 52.4, 11.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.56 – 7.54/–16.0, 2.82/–16.0, 1.38/–16.0 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{25}ClNSi^+$ $[M+H]^+$: 378.1445; Found: 378.1440. **IR** (ATR): ṽ 3066, 2922, 2796, 1488, 1427, 1112, 1015, 971, 868, 699.



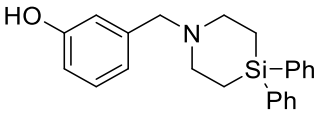
1-(4-Bromobenzyl)-4,4-diphenyl-1,4-azasilinane (3ia). The general procedure was followed with *N*-ethyl-*N*-(4-bromobenzyl)ethanamine (**1i**, 24.2 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 μL, 40.0 μmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (230 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (28.8 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.57 – 7.54 (m, 4H), 7.45 – 7.36 (m, 8H), 7.24 (d, *J* = 8.3 Hz, 2H), 3.54 (s, 2H), 2.82 (t, *J* = 6.2 Hz, 4H), 1.38 (t, *J* = 6.2 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.3, 135.7, 134.8, 131.4, 130.6, 129.6, 128.1, 120.8, 62.1, 52.4, 11.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.57 – 7.54/–15.7, 2.82/–15.5, 1.38/–15.5 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{25}BrNSi^+$ $[M+H]^+$: 422.0940; Found: 422.0933. **IR** (ATR): ṽ 3066, 2922, 2795, 1485, 1427, 1388, 1112, 1011, 971, 699.



1-(4-Iodobenzyl)-4,4-diphenyl-1,4-azasilinane (3ja). The general procedure was followed with *N*-ethyl-*N*-(4-iodobenzyl)ethanamine (**1j**, 28.9 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 μL, 40.0 μmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (30.1 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.55 (m, 4H), 7.43 – 7.36 (m, 6H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.53 (s, 2H), 2.82 (t, *J* = 6.1 Hz, 4H), 1.38 (t, *J* = 6.2 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.3, 137.4, 135.8, 134.8, 130.9, 129.5, 128.1, 92.3, 62.2, 52.4, 11.5 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.57 – 7.55/–15.8, 2.82/–15.8, 1.38/–15.8 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{25}INSi^+$ $[M+H]^+$: 470.0801; Found: 470.0782. **IR** (ATR): ṽ 3065, 2920, 2792, 1586, 1480, 1425, 1386, 1110, 969, 906, 865, 726, 695.

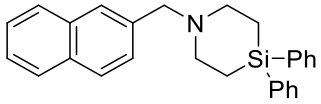


4,4-Diphenyl-1-(4-(trifluoromethyl)benzyl)-1,4-azasilinane (3ka). The general procedure was followed with *N*-ethyl-*N*-(4-(trifluoromethyl)benzyl)ethanamine (**1k**, 23.1 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (21.1 mg, 51% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.60 – 7.57 (m, 6H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.38 (m, 6H), 3.65 (s, 2H), 2.84 (t, *J* = 6.2 Hz, 4H), 1.41 (t, *J* = 6.2 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.9, 135.7, 134.8, 129.6, 129.2 (q, *J* = 32.4 Hz), 128.9, 128.1, 125.3 (q, *J* = 3.6 Hz), 124.5 (q, *J* = 271.9 Hz), 62.3, 52.6, 11.5 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ –62.3 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.60 – 7.57/–15.8, 2.84/–15.8, 1.41/–15.8 ppm. **HRMS** (APCI): Calculated for $C_{24}H_{25}F_3NSi^+$ $[M+H]^+$: 412.1708; Found: 412.1694. **IR** (ATR): ṽ 3067, 2922, 2795, 1426, 1321, 1159, 1110, 1063, 1017, 970, 867, 697.

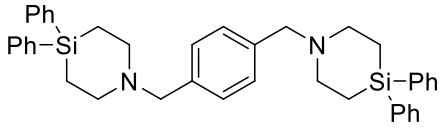


3-((4,4-Diphenyl-1,4-azasilinan-1-yl)methyl)phenol (3la). The general procedure was followed with *N*-ethyl-*N*-(3-methoxybenzyl)ethanamine (**1l**, 19.3 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 1 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (18.1 mg, 50% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.53 – 7.51 (m, 4H), 7.41 – 7.34 (m, 6H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.84 – 6.81 (m, 2H), 6.76 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.07 (br, 1H), 3.56 (s, 2H), 2.87 (t, *J* = 6.2 Hz, 4H), 1.39 (t, *J* = 6.2 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 156.7, 139.3, 135.3, 134.9, 129.6, 129.5, 128.1, 121.5, 117.0, 115.2, 62.6, 52.4, 10.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.53 – 7.51/–16.0, 2.87/–16.0, 1.39/–16.0 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{26}NOSi^+$

$[M+H]^+$: 360.1784; Found: 360.1778. **IR** (ATR): ṽ 3295, 3045, 2924, 2084, 1588, 1454, 1265, 1112, 972, 908, 861, 699.

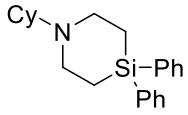


1-(Naphthalen-2-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ma). The general procedure was followed with *N*-ethyl-*N*-(naphthalen-2-ylmethyl)ethanamine (**1m**, 21.3 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (240 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (18.2 mg, 46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86 – 7.83 (m, 3H), 7.78 (s, 1H), 7.60 – 7.56 (m, 5H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 6H), 3.78 (s, 2H), 2.91 (t, *J* = 6.2 Hz, 4H), 1.43 (t, *J* = 6.3 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.1, 136.0, 134.8, 133.5, 132.9, 129.5, 128.1, 128.0, 127.8, 127.8, 127.4, 127.4, 126.0, 125.6, 62.9, 52.5, 11.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.60 – 7.56/–15.7, 2.91/–15.7, 1.43/–15.7 ppm. **HRMS** (APCI): Calculated for $C_{27}H_{28}NSi^+$ $[M+H]^+$: 394.1991; Found: 394.1982. **IR** (ATR): ṽ 3046, 2920, 2798, 1426, 1328, 1110, 971, 864, 727, 698.

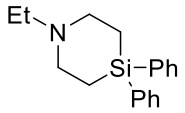


1,4-Bis((4,4-diphenyl-1,4-azasilinan-1-yl)methyl)benzene (3na). The general procedure was followed with *N,N′*-(1,4-phenylenebis(methylene))bis(*N*-ethylethanamine) (**1n**, 24.8 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 73.6 mg, 0.400 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (14.4 µL, 80.0 µmol) and $B(C_6F_5)_3$ (20.4 mg, 40.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 1 as the eluent and Kugelrohr distillation (250 °C, 0.2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (28.7 mg, 47% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.4 Hz, 8H), 7.41 – 7.36 (m, 12H), 7.29 (s, 4H), 3.59 (s, 4H), 2.84 (t, *J* = 5.5 Hz, 8H), 1.38 (t, *J* = 5.5 Hz, 8H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.0, 136.0, 134.8, 129.5, 128.8, 128.1, 62.5, 52.4, 11.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K,

optimized for J = 7 Hz): δ 7.56/–15.8, 2.84/–15.8, 1.38/–15.8 ppm. **HRMS** (APCI): Calculated for $C_{40}H_{45}N_2Si_2^+$ $[M+H]^+$: 609.3121; Found: 609.3119. **IR** (ATR): ṽ 2921, 2893, 2792, 2757, 1426, 1387, 1226, 1185, 1110, 969, 906, 866, 725, 696.

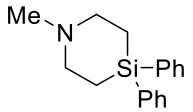


1-Cyclohexyl-4,4-diphenyl-1,4-azasilinane (3oa). The general procedure was followed with *N,N*-diethylcyclohexanamine (**1o**, 15.5 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with MeOH / methyl *tert*-butyl ether = 1 : 10 as the eluent and Kugelrohr distillation (180 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (12.8 mg, 38% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 4H), 7.40 – 7.34 (m, 6H), 2.97 (t, J = 6.5 Hz, 4H), 2.52 (t, J = 7.7 Hz, 1H), 1.86 – 1.77 (m, 4H), 1.62 (d, J = 13.8 Hz, 1H), 1.38 (t, J = 6.5 Hz, 4H), 1.28 – 1.17 (m, 4H), 1.11 – 1.03 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 136.0, 134.9, 129.5, 128.1, 64.4, 48.8, 29.1, 26.5, 26.3, 11.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.56 – 7.54/–14.6, 2.97/–14.6, 1.38/–14.6 ppm. **HRMS** (APCI): Calculated for $C_{22}H_{30}NSi^+$ $[M+H]^+$: 336.2148; Found: 336.2142. **IR** (ATR): ṽ 3065, 2922, 2850, 2795, 1374, 1227, 1110, 987, 863, 728, 698.

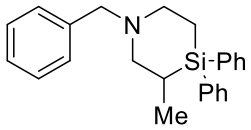


1-Ethyl-4,4-diphenyl-1,4-azasilinane (3pa). The general procedure was followed with triethylamine (**1p**, 10.1 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with MeOH / methyl *tert*-butyl ether = 1 : 10 as the eluent and Kugelrohr distillation (150 °C, 2 mbar) to afford th e 4-silapiperidine product as a colorless viscous liquid (16.9 mg, 60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 4H), 7.42 – 7.35 (m, 6H), 2.93 (t, J = 6.1 Hz, 4H), 2.64 (q, J = 7.2 Hz, 2H), 1.47 (t, J = 6.1 Hz, 4H), 1.14 (t, J = 7.2 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 135.0, 134.9, 129.7, 128.2, 52.0, 51.9, 11.7, 10.8 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.56 – 7.54/–15.6, 2.93/–15.6, 1.47/–15.6 ppm.

HRMS (APCI): Calculated for $C_{18}H_{24}NSi^+$ $[M+H]^+$: 282.1678; Found: 282.1669. **IR** (ATR): ṽ 3066, 2923, 2799, 1427, 1229, 1111, 984, 867, 707.

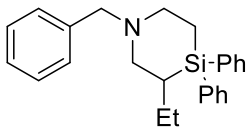


1-Methyl-4,4-diphenyl-1,4-azasilinane (3qa). The general procedure was followed with *N*-ethyl-*N*-methylethanamine (**1q**, 8.70 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with MeOH / methyl *tert*-butyl ether = 1 : 10 as the eluent and Kugelrohr distillation (150 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (12.9 mg, 48% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 4H), 7.42 – 7.35 (m, 6H), 2.77 (t, *J* = 6.2 Hz, 4H), 2.34 (s, 3H), 1.42 (t, *J* = 6.2 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 135.3, 134.9, 129.6, 128.1, 54.9, 47.2, 11.7 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.56 – 7.53/–16.5, 2.77/–16.5, 1.42/–16.5 ppm. **HRMS** (APCI): Calculated for $C_{17}H_{22}NSi^+$ $[M+H]^+$: 268.1522; Found: 268.1514. **IR** (ATR): ṽ 3066, 2924, 2781, 1464, 1374, 1246, 1181, 1112, 968, 729, 707.

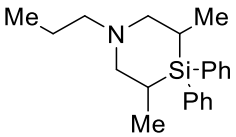


1-Benzyl-3-methyl-4,4-diphenyl-1,4-azasilinane (3ra). The general procedure was followed with *N*-benzyl-*N*-ethylpropan-1-amine (**1r**, 17.7 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (16.5 mg, 46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.62 – 7.57 (m, 4H), 7.44 – 7.34 (m, 10H), 7.29 – 7.26 (m, 1H), 3.63 (q, *J* = 15.7 Hz, 2H), 3.04 – 2.99 (m, 1H), 2.92 – 2.88 (m, 1H), 2.86 – 2.81 (m, 1H), 2.52 – 2.47 (m, 1H), 1.72 – 1.68 (m, 1H), 1.49 – 1.44 (m, 1H), 1.37 – 1.31 (m, 1H), 1.11 (dd, *J* = 7.6, 2.3 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.8, 136.0, 135.9, 135.0, 134.6, 129.5, 129.4, 128.9, 128.3, 128.0, 127.8, 126.9, 63.3, 61.1, 53.2, 17.8, 14.9, 11.1 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz):

δ 7.62 – 7.57/–13.7, 3.04 – 2.99/–13.7, 2.92 – 2.88/–13.7, 1.49 – 1.44/–13.7, 1.37 – 1.31/–13.7, 1.11/–13.7 ppm. **HRMS** (APCI): Calculated for $C_{24}H_{28}NSi^+$ $[M+H]^+$: 358.1991; Found: 358.1982. **IR** (ATR): ṽ 2921, 2863, 2794, 2756, 1452, 1426, 1314, 1186, 1107, 993, 960, 886, 695.

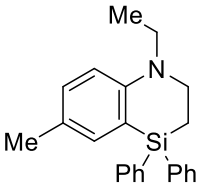


1-Benzyl-3-ethyl-4,4-diphenyl-1,4-azasilinane (3sa). The general procedure was followed with *N*-benzyl-*N*-ethylbutan-1-amine (**1s**, 19.1 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 μL, 40.0 μmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (14.2 mg, 38% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.57 – 7.53 (m, 4H), 7.41 – 7.30 (m, 10H), 7.26 – 7.23 (m, 1H), 3.64 – 3.54 (m, 2H), 2.90 – 2.78 (m, 3H), 2.53 (t, *J* = 8.0 Hz, 1H), 1.60 – 1.53 (m, 1H), 1.44 – 1.40 (m, 3H), 1.28 (s, 1H), 0.79 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.8, 136.1, 135.8, 135.1, 134.6, 129.4, 129.0, 128.3, 128.0, 127.9, 127.0, 63.4, 57.5, 53.2, 25.7, 22.2, 13.9, 11.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.57 – 7.53/–14.5, 2.90 – 2.78/–14.5, 2.53/–14.5, 1.60 – 1.53/–14.5, 1.44 – 1.40/–14.5 ppm. **HRMS** (APCI): Calculated for $C_{25}H_{30}NSi^+$ $[M+H]^+$: 372.2148; Found: 372.2137. **IR** (ATR): ṽ 2955, 2922, 2869, 2796, 1453, 1427, 1109, 973, 865, 699.

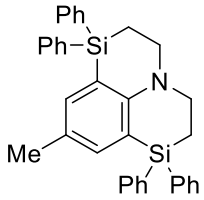


3,5-Dimethyl-4,4-diphenyl-1-propyl-1,4-azasilinane (3ta, *cis*:*trans* = 58:42). The general procedure was followed with tripropylamine (**1t**, 14.3 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 μL, 40.0 μmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with MeOH / methyl *tert*-butyl ether = 1 : 30 as the eluent and Kugelrohr distillation (180 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless

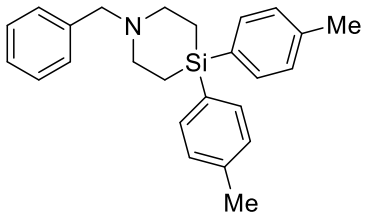
viscous liquid (13.3 mg, 41% yield, *cis*:*trans* = 58:42). The stereochemistry of **3ta** was determined by 2D-NOESY. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.62 – 7.51 (m, 4H), 7.44 – 7.33 (m, 6H), 3.07 – 2.83 (m, 2H), 2.58 – 2.49 (m, 3H), 2.45 – 2.32 (m, 1H), 1.76 – 1.69 (m, 1H), 1.64 – 1.56 (m, 2H), 1.55 – 1.48 (m, 1H), 1.03 – 0.98 (m, 6H), 0.94 – 0.90 (m, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 137.0, 136.0, 135.3, 134.9, 134.5, 132.4, 129.6, 129.4, 129.3, 128.0, 127.8, 127.7, 61.9, 61.7, 61.5, 60.7, 20.6, 20.3, 18.3, 15.9, 15.4, 13.9, 12.2, 12.1 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.62 – 7.51/–10.6, 3.07 – 2.83/–10.6, 2.58 – 2.49/–10.6, 1.76 – 1.69/–10.6, 1.03 – 0.98/–10.6 ppm. **HRMS** (APCI): Calculated for $C_{21}H_{30}NSi^+$ $[M+H]^+$: 324.2148; Found: 324.2137. **IR** (ATR): ṽ 2935, 2863, 2766, 1457, 1425, 1376, 1195, 1108, 997, 885, 696.



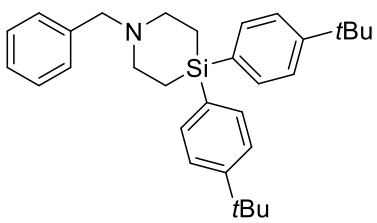
1-Ethyl-6-methyl-4,4-diphenyl-1,2,3,4-tetrahydrobenzo[*b*][1,4]azasiline (4ua). The general procedure was followed with *N,N*-diethyl-4-methylaniline (**1u**, 16.3 mg, 0.100 mmol), Ph_2SiH_2 (**2a**, 36.8 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 μL, 40.0 μmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 100 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (19.0 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.66 – 7.64 (m, 4H), 7.46 – 7.39 (m, 6H), 7.22 (s, 1H), 7.13 (dd, J = 8.5, 2.2 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 3.53 – 3.46 (m, 4H), 2.24 (s, 3H), 1.53 (t, J = 6.3 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 153.7, 137.7, 136.2, 135.7, 131.8, 129.5, 127.9, 125.3, 116.5, 112.9, 48.7, 47.4, 20.4, 12.6, 11.4 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.66 – 7.64/–20.7, 7.22/–20.7, 6.77/–20.7, 3.53 – 3.46/–20.7, 1.53/–20.7 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{26}NSi^+$ $[M+H]^+$: 344.1835; Found: 344.1828. **IR** (ATR): ṽ 3065, 2969, 2926, 1604, 1487, 1426, 1332, 1277, 1108, 1068, 802, 699.



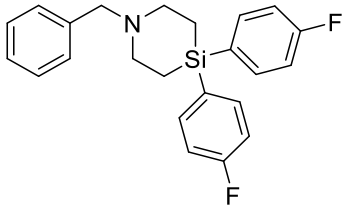
8-Methyl-1,1,6,6-tetraphenyl-2,3,5,6-tetrahydro-1*H*,4*H*-3a-aza-1,6-disilaphenalene (5ua). The following residue was further purified by Kugelrohr distillation (250 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (4.30 mg, 8% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 – 7.59 (m, 8H), 7.39 – 7.34 (m, 12H), 7.22 (s, 2H), 3.49 – 3.45 (m, 4H), 2.12 (s, 3H), 1.51 – 1.49 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ162.2, 139.6, 136.3, 135.7, 129.5, 128.0, 125.7, 117.3, 52.8, 20.5, 12.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.61 – 7.59/–19.5, 7.39 – 7.34/–19.5, 7.22/–19.5, 3.49 – 3.45/–19.5, 1.51 – 1.49/–19.5 ppm. **HRMS** (APCI): Calculated for $C_{35}H_{34}NSi_2^+$ $[M+H]^+$: 524.2230; Found: 524.2215. **IR** (ATR): ṽ 3066, 2934, 2809, 2134, 1536, 1483, 1427, 1262, 1109, 827, 733, 698.



1-Benzyl-4,4-di-*p*-tolyl-1,4-azasilinane (3ab). The general procedure was followed with *N*-benzyl-*N*-ethylethanamine (**1a**, 16.3 mg, 0.100 mmol), di-*p*-tolylsilane (**2b**, 42.5 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (24.1 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.45 (d, J = 7.9 Hz, 4H), 7.37 – 7.30 (m, 4H), 7.26 – 7.23 (m, 1H), 7.19 (d, J = 7.5 Hz, 4H), 3.60 (s, 2H), 2.83 (t, J = 5.8 Hz, 4H), 2.37 (s, 6H), 1.35 (t, J = 5.7 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.5, 139.3, 134.9, 132.4, 129.0, 128.9, 128.3, 127.0, 62.8, 52.5, 21.6, 11.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.45/–16.0, 2.83/–16.0, 1.35/–16.0 ppm. **HRMS** (APCI): Calculated for $C_{25}H_{30}NSi^+$ $[M+H]^+$: 372.2148; Found: 372.2135. **IR** (ATR): ṽ 3027, 2920, 2796, 1601, 1452, 1391, 1188, 1107, 970, 866, 799, 727.

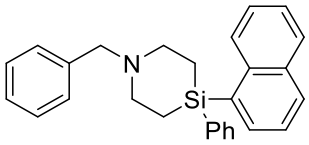


1-Benzyl-4,4-bis(4-(*tert*-butyl)phenyl)-1,4-azasilinane (3ac). The general procedure was followed with *N*-benzyl-*N*-ethylethanamine (**1a**, 16.3 mg, 0.100 mmol), bis(4-(*tert*-butyl)phenyl)silane (**2c**, 59.3 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (240 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (29.6 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 4H), 7.41 (d, *J* = 8.2 Hz, 4H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 3.62 (s, 2H), 2.85 (t, *J* = 6.2 Hz, 4H), 1.37 (t, *J* = 6.1 Hz, 4H), 1.35 (s, 18H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 152.3, 139.8, 134.7, 132.6, 128.9, 128.3, 126.9, 125.0, 62.7, 52.5, 34.8, 31.4, 11.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.52/–16.8, 2.85/–16.8, 1.37/–16.8 ppm. **HRMS** (APCI): Calculated for $C_{31}H_{42}NSi^+$ $[M+H]^+$: 456.3087; Found: 456.3071. **IR** (ATR): ṽ 3066, 2959, 2797, 1598, 1458, 1387, 1267, 1136, 1086, 970, 866, 820, 724.

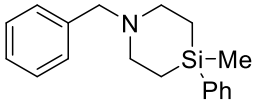


1-Benzyl-4,4-bis(4-fluorophenyl)-1,4-azasilinane (3ad). The general procedure was followed with *N*-benzyl-*N*-ethylethanamine (**1a**, 16.3 mg, 0.100 mmol), bis(4-fluorophenyl)silane (**2d**, 44.1 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (220 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (25.5 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52 – 7.48 (m, 4H), 7.36 – 7.30 (m, 4H), 7.27 – 7.24 (m, 1H), 7.10 – 7.05 (m, 4H),

3.59 (s, 2H), 2.81 (t, *J* = 6.3 Hz, 4H), 1.34 (t, *J* = 6.1 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.1 (d, *J* = 248.8 Hz), 139.4, 136.7 (d, *J* = 7.3 Hz), 131.2, 128.9, 128.3, 127.1, 115.4 (d, *J* = 19.8 Hz), 62.9, 52.3, 11.8 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ –111.1 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.52 – 7.48/–15.0, 2.81/–15.0,1.34/–15.0 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{24}F_2NSi^+$ $[M+H]^+$: 380.1646; Found: 380.1635. **IR** (ATR): ṽ 3026, 2922, 2797, 1585, 1497, 1388, 1230, 1161, 1105, 971, 867, 821, 728.

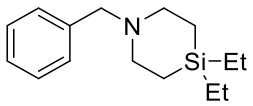


1-Benzyl-4-(naphthalen-1-yl)-4-phenyl-1,4-azasilinane (3ae). The general procedure was followed with *N*-benzyl-*N*-ethylethanamine (**1a**, 16.3 mg, 0.100 mmol), naphthalen-1-yl(phenyl)silane (**2e**, 46.9 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (230 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (26.8 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.81 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.53 (dd, *J* = 8.2, 6.9 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.39 – 7.31 (m, 8H), 7.27 – 7.24 (m, 1H), 3.63 (s, 2H), 2.95 – 2.85 (m, 4H), 1.65 – 1.54 (m, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.6, 137.3, 136.9, 135.2, 134.8, 133.7, 133.5, 130.5, 129.4, 129.1, 128.9, 128.6, 128.3, 128.1, 127.0, 125.9, 125.6, 125.2, 62.9, 52.6, 12.6 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.81/–15.8, 7.60/–15.8, 2.95 – 2.85/–15.8, 1.65 – 1.54/–15.8, ppm. **HRMS** (APCI): Calculated for $C_{27}H_{28}NSi^+$ $[M+H]^+$: 394.1991; Found: 394.1978. **IR** (ATR): ṽ 2923, 2895, 2796, 2759, 1426, 1389, 1317, 1226, 1106, 969, 905, 867, 795, 776, 723, 696.



1-Benzyl-4-methyl-4-phenyl-1,4-azasilinane (3ag). The general procedure was followed with *N*-benzyl-*N*-ethylethanamine (**1a**, 16.3 mg, 0.100 mmol), methyl(phenyl)silane (**2g**, 24.4 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol) and $B(C_6F_5)_3$ (10.2 mg,

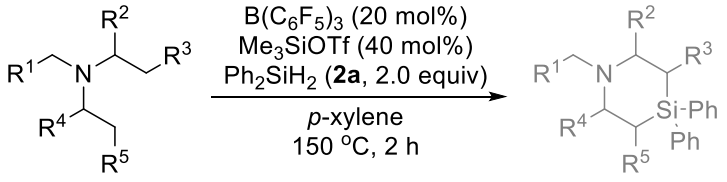
20.0 μmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (180 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (11.3 mg, 40% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.57 – 7.56 (m, 2H), 7.38 – 7.31 (m, 7H), 7.27 – 7.24 (m, 1H), 3.62 (s, 2H), 2.87 – 2.82 (m, 2H), 2.79 – 2.74 (m, 2H), 1.21 – 1.16 (m, 2H), 0.99 – 0.96 (m, 2H), 0.32 (s, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.1, 138.1, 134.0, 129.3, 129.1, 128.3, 128.0, 127.0, 62.8, 52.5, 12.6, –4.0 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.57 – 7.56/–11.5, 2.87 – 2.82/–11.5, 1.21 – 1.16/–11.5, 0.99 – 0.96/–11.5, 0.32/–11.5, ppm. **HRMS** (APCI): Calculated for $C_{18}H_{24}NSi^+$ $[M+H]^+$: 282.1678; Found: 282.1673. **IR** (ATR): ṽ 2919, 2794, 2756, 1391, 1250, 1110, 972, 868, 788, 730, 697.



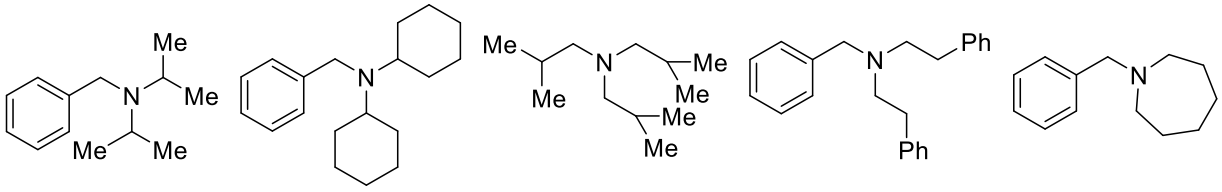
1-Benzyl-4,4-diethyl-1,4-azasilinane (3ai). The general procedure was followed with *N*-benzyl-*N*-ethylethanamine (**1a**, 16.3 mg, 0.100 mmol), diethylsilane (**2i**, 17.6 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 μL, 40.0 μmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol) at 150 °C for 2 h. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether / cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (140 °C, 2 mbar) to afford the 4-silapiperidine product as a colorless viscous liquid (10.5 mg, 42% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 4H), 7.26 – 7.23 (m, 1H), 3.60 (s, 2H), 2.73 (t, J = 6.3 Hz, 4H), 0.96 (t, J = 8.0 Hz, 6H), 0.79 (t, J = 6.4 Hz, 4H), 0.57 (t, J = 8.0 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.9, 129.2, 128.3, 127.1, 62.7, 52.6, 9.9, 7.4, 3.7 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 2.73/–3.1, 0.96/–3.1, 0.79/–3.1, 0.57/–3.1, ppm. **HRMS** (APCI): Calculated for $C_{15}H_{26}NSi^+$ $[M+H]^+$: 248.1835; Found: 248.1831. **IR** (ATR): ṽ 2950, 2910, 2794, 1465, 1391, 1230, 1010, 976, 865, 730, 697.

3.3 Unsuccessful Substrates

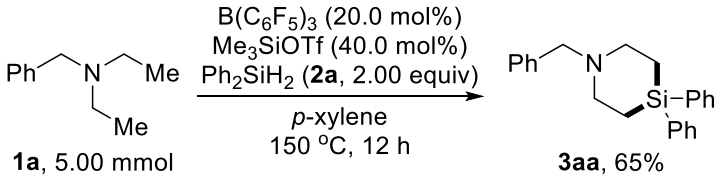
Further investigation of the substrate scope revealed that tertiary benzylamines having two isopropyl, cyclohexyl, isobutyl, or phenethyl groups as well as 1-benzylazepane failed to furnish the corresponding 4-silapiperidine derivative.



not detected



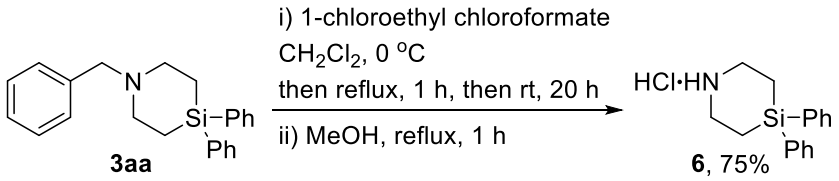
4 Scale-Up Experiment



In a nitrogen-filled glovebox, a 50-mL single-neck round bottom flask equipped with a magnetic stir bar was charged with *N*-benzyl-*N*-ethylethanamine (**1a**, 0.820 g, 5.00 mmol), Ph_2SiH_2 (**2a**, 1.84 g, 10.0 mmol), *p*-xylene (20.0 mL), Me_3SiOTf (362 µL, 2.00 mmol) and $B(C_6F_5)_3$ (512 mg, 1.00 mmol). The single-neck round bottom flask was fitted with a cap, and the reaction was then removed from the glovebox. After a condenser was attached to the flask, the mixture was stirred at 150 °C for 12 h in a preheated oil bath with a continous flow of nitrogen gas. After the resulting reaction mixture was cooled to room temperature, NaOH (20.0 mL, 10% aq.) was added and the mixture stirred for 30 min. The mixture was extracted with methyl *tert*-butyl ether (20 mL×3). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether : cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (200 °C, 2 mbar) to afford **3aa** as a colorless viscous liquid (1.12 g, 65% yield).

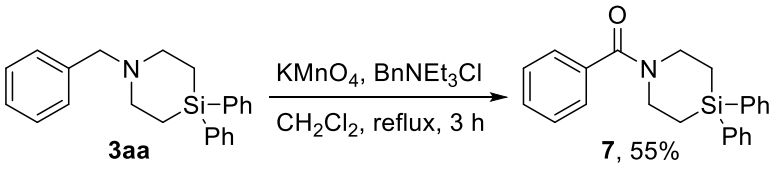
5 Elaboration of an *N*-Benzylated 4-Silapiperidine

5.1 Debenzylation of Product 3aa[11]



A flame-dried 50-mL two-neck flask equipped with a magnetic stir bar and a reflux condenser was charged with **3aa** (0.340 g, 1.00 mmol) and CH_2Cl_2 (15 mL) under an atmosphere of nitrogen. Then, 1-chloroethyl chloroformate (0.135 mL, 1.25 mmol) was added dropwise at 0 °C within 5 min. The mixture was heated at reflux for 1 h and was then stirred at room temperature for a further 20 h. After that, the solvent was removed under reduced pressure. The resluting oily residue was dissolved in MeOH (10 mL), and the mixture was heated at reflux for 1 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure to give viscous oil which was triturated with diethyl ether to obtain the product **6** as a white solid (217 mg, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.63 (br, 2H), 7.56 – 7.55 (m, 4H), 7.46 – 7.38 (m, 6H), 3.44 (t, *J* = 6.2 Hz, 4H), 1.74 (t, *J* = 6.3 Hz, 4H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 134.8, 132.0, 130.5, 128.6, 44.3, 9.1 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.56 – 7.55/–16.5, 3.44/–16.5, 1.74/–16.5 ppm. Spectral data is in agreement with published data.[12]

5.2 Oxidation of Product 3aa[13]



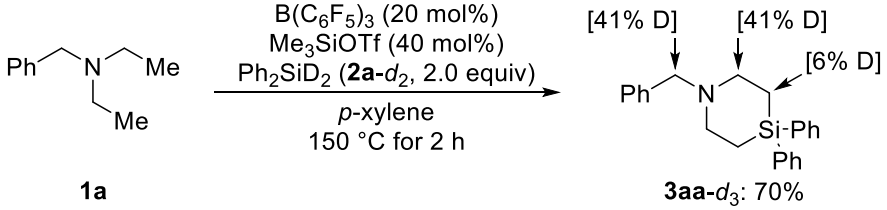
A flame-dried 50-mL two-neck flask equipped with a magnetic stir bar and a reflux condenser was charged with **3aa** (0.340 g, 1.00 mmol) and CH_2Cl_2 (20 mL) under a atmosphere of nitrogen. Then benzyltriethylammoniumchlorid (0.680 g, 3.00 mmol) and $KMnO_4$ (0.470 g, 3.00 mmol) was added, and the reaction mixture was heated at reflux for 3 h. After the reaction mixture was cooled to room temperature, the suspension was quenched by aq. sodium thiosulphate and filtered. The resulting solution was extracted with CH_2Cl_2 (20 mL×3),

and the combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified by flash column chromatography on silica gel with methyl *tert*-butyl ether : cyclohexane = 1 : 3 as the eluent to afford **7** as a white solid (197 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 – 7.54 (m, 4H), 7.45 – 7.38 (m, 11H), 4.00 (br, 2H), 3.64 (br, 2H), 1.56 (br, 2H), 1.27 (br, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.1, 136.9, 134.6, 134.5, 130.0, 129.4, 128.5, 128.3, 126.5, 47.1, 42.0, 13.0, 11.3 ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz): δ 7.56 – 7.54/–14.2 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{24}NOSi^+$ $[M+H]^+$: 358.1627; Found: 358.1618. **IR** (ATR): ṽ 2927, 2894, 1626, 1426, 1296, 1112, 969, 831, 731, 701.

6 Mechanistic Investigations

6.1 ^{2}H-Labeling Experiments

6.1.1 Reaction of **1a** with Ph_2SiD_2 (**2a**-d_2) Under Standard Conditions



1a **3aa**-d_3: 70%

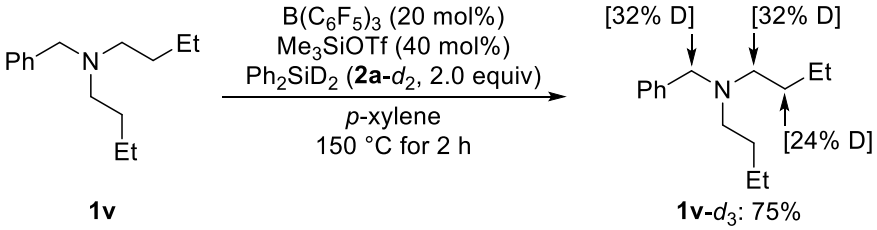
In a nitrogen-filled glovebox, a 10-mL sealed tube equipped with a magnetic stir bar was charged with *N*-benzyl-*N*-ethylethanamine (**1a**, 16.3 mg, 0.100 mmol), Ph_2SiH_2 (**2a**-d_2, 37.2 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 µL, 40.0 µmol), and $B(C_6F_5)_3$ (10.2 mg, 20.0 µmol). The sealed tube was fitted with a cap, and the reaction stirred at 150 °C for 2 h in a preheated oil bath. After the resulting reaction mixture was cooled to room temperature, NaOH (5.00 mL, 10% aq.) was added and the mixture stirred for 30 min. The mixture was extracted with methyl *tert*-butyl ether (20 mL×3). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether : cyclohexane = 1 : 10 as the eluent and Kugelrohr distillation (200 °C, 2 mbar) to afford **3aa**-d_3 as a colorless viscous liquid (24.2 mg, 70% yield). Deuterium incorporation: 2.70 D/molecule (^{1}H NMR). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.57 – 7.56 (m, 4H), 7.42 – 7.31 (m, 10H), 7.27 – 7.24 (m, 1H), 3.60 (d, *J* = 13.8 Hz, 1.18H, 41%D), 2.89 – 2.78 (m, 2.36H, 41%D), 1.40 – 1.35 (m, 3.74H, 6%D) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 139.4, 135.9, 134.8, 129.5, 129.0, 128.3, 128.1, 127.0, 62.7 –62.2 (m), 52.4 – 51.8 (m), 11.2 (t, *J* = 16.1 Hz) ppm. **^{1}H/^{29}Si HMQC NMR** (500/99 MHz, $CDCl_3$, 298 K, optimized for *J* = 7 Hz): δ 7.57 – 7.56/–15.8, 2.89 – 2.78/–15.8, 1.40 – 1.35/–15.8 ppm. **HRMS** (APCI): Calculated for $C_{23}H_{23}D_3NSi^+$ $[M+H]^+$: 347.2023; Found: 347.2009. **IR** (ATR): ṽ 3064, 3021, 2919. 2786, 1491, 1427, 1214, 1110, 962, 874, 698.

Table S1. Ratio of different deuterated products **3aa**-d_n (n = 0~6) determined by mass spectroscopy.

3aa-d_n	Compared to each other in %(intensity : sum of all intensity * 100%)
3aa	2
3aa-d_1	10
3aa-d_2	22
3aa-d_3	28
3aa-d_4	22
3aa-d_5	11
3aa-d_6	1

The overall deuteration grades of **3aa**-d_3 determined by mass spectrometry is 2.87 D.

6.1.2 Reaction of **1v** with Ph_2SiD_2 (**2a**-d_2) Under Standard Conditions



1v **1v**-d_3: 75%

In a nitrogen-filled glovebox, a 10-mL sealed tube equipped with a magnetic stir bar was charged with *N*-benzyl-*N*-butylbutan-1-amine (**1v**, 21.9 mg, 0.100 mmol), Ph_2SiH_2 (**2a**-d_2, 37.2 mg, 0.200 mmol), *p*-xylene (0.800 mL), Me_3SiOTf (7.20 μL, 40.0 μmol) and $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol). The sealed tube was fitted with a cap, and the reaction stirred at 150 °C for 2 h in a preheated oil bath. After the resulting reaction mixture was cooled to room temperature, NaOH (5.00 mL, 10% aq.) was added and the mixture stirred for 30 min. The mixture was extracted with methyl *tert*-butyl ether (20 mL×3). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by a sequence of flash column chromatography on silica gel with methyl *tert*-butyl ether : cyclohexane = 1 : 5 as the eluent to afford **1v**-d_3 as a colorless liquid (16.8 mg, 75% yield). Deuterium incorporation: 2.85 D/molecule (^{1}H NMR). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 4H), 7.22 (t, *J* = 7.0 Hz, 1H), 3.58 – 3.50 (m, 1.37H, 32%D), 2.42 – 2.38 (m, 2.71H, 32%D), 1.48 – 1.42 (m, 4H), 1.33 – 1.26 (m, 3.06H, 24%D), 0.88 (t, *J* = 7.4 Hz, 6H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.2, 129.0, 128.2, 126.8, 58.7 –58.2 (m), 53.6 – 53.1 (m), 29.3 – 29.0 (m), 20.7 – 20.2 (m), 14.2 – 14.0 (m) ppm. **HRMS** (APCI): Calculated for

$C_{15}H_{23}D_3N^+$ $[M+H]^+$: 223.2254; Found: 223.2244. **IR** (ATR): ṽ 2955, 2928, 2869, 2795, 1453, 1376, 1170, 731, 697.

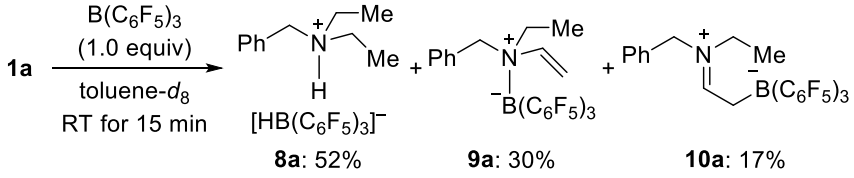
Table S2. Ratio of different deuterated products **1v**-d_n (n = 0~7) determined by mass spectroscopy.

1v-d_n	Compared to each other in %(intensity : sum of all intensity * 100%)
1v	3
1v-d_1	12
1v-d_2	23
1v-d_3	27
1v-d_4	21
1v-d_5	10
1v-d_6	3
1v-d_7	1

The overall deuteration grades of **1v**-d_3 determined by mass spectrometry is 2.98 D.

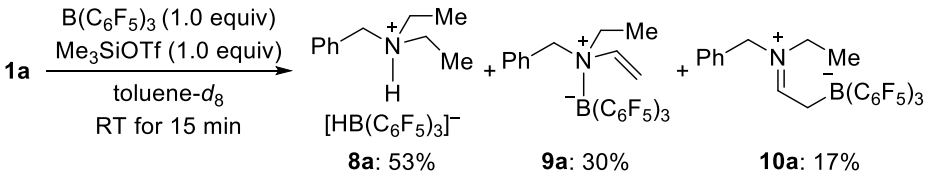
6.2 Stoichiometric Experiments

6.2.1 Stoichiometric Reaction of **1a** and $B(C_6F_5)_3$ (1:1)



In a nitrogen-filled glovebox, a J-Young tube was charged with **1a** (8.20 mg, 0.0500 mmol), mesitylene (3.50 µL, 0.0250 mmol), toluene-d_8 (0.5 mL), and $B(C_6F_5)_3$ (25.6 mg, 0.0500 mmol). After shaking 15 min at RT, the reaction mixture was analyzed by NMR spectroscopy (internal standard material: mesitylene, 3.50 µL, 0.0250 mmol). *Crude NMR data of **8a***: **^{11}B NMR** (161 MHz, toluene-d_8; selected data of **8a**): δ –23.8 (d, *J* = 81.2 Hz) ppm; **^{19}F NMR** (471 MHz, toluene-d_8; selected data of **8a**): δ –133.8 (d, *J* = 30.0 Hz), –161.2 (t, *J* = 20.8 Hz), –165.4 – –165.5 (m) ppm. *Crude NMR data of **9a***: **^{11}B NMR** (161 MHz, toluene-d_8; selected data of **9a**): δ –13.9 ppm; **^{19}F NMR** (471 MHz, toluene-d_8; selected data of **9a**): δ –132.5 (d, *J* = 28.0 Hz), –159.4 (t, *J* = 21.4 Hz), –164.2 – –164.4 (m) ppm. *Crude NMR data of **10a***: **^{11}B NMR** (161 MHz, toluene-d_8; selected data of **10a**): δ –13.5 ppm; **^{19}F NMR** (471 MHz, toluene-d_8; selected data of **10a**): δ –132.1 (d, *J* = 28.6 Hz), –159.2 (t, *J* = 21.4 Hz), –164.1 – –164.2 (m) ppm.

6.2.2 Stoichiometric Reaction of **1a**, Me_3SiOTf, and $B(C_6F_5)_3$ (1:1:1)



In a nitrogen-filled glovebox, a J-Young tube was charged with **1a** (8.20 mg, 0.0500 mmol), mesitylene (3.50 µL, 0.0250 mmol), toluene-d_8 (0.5 mL), and $B(C_6F_5)_3$ (25.6 mg, 0.0500 mmol). After shaking 15 min at RT, the reaction mixture was analyzed by NMR spectroscopy (internal standard material: mesitylene, 3.50 µL, 0.0250 mmol).

7 NMR Spectra

Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***N*-benzyl-*N*-ethylpropan-1-amine (1r)**.

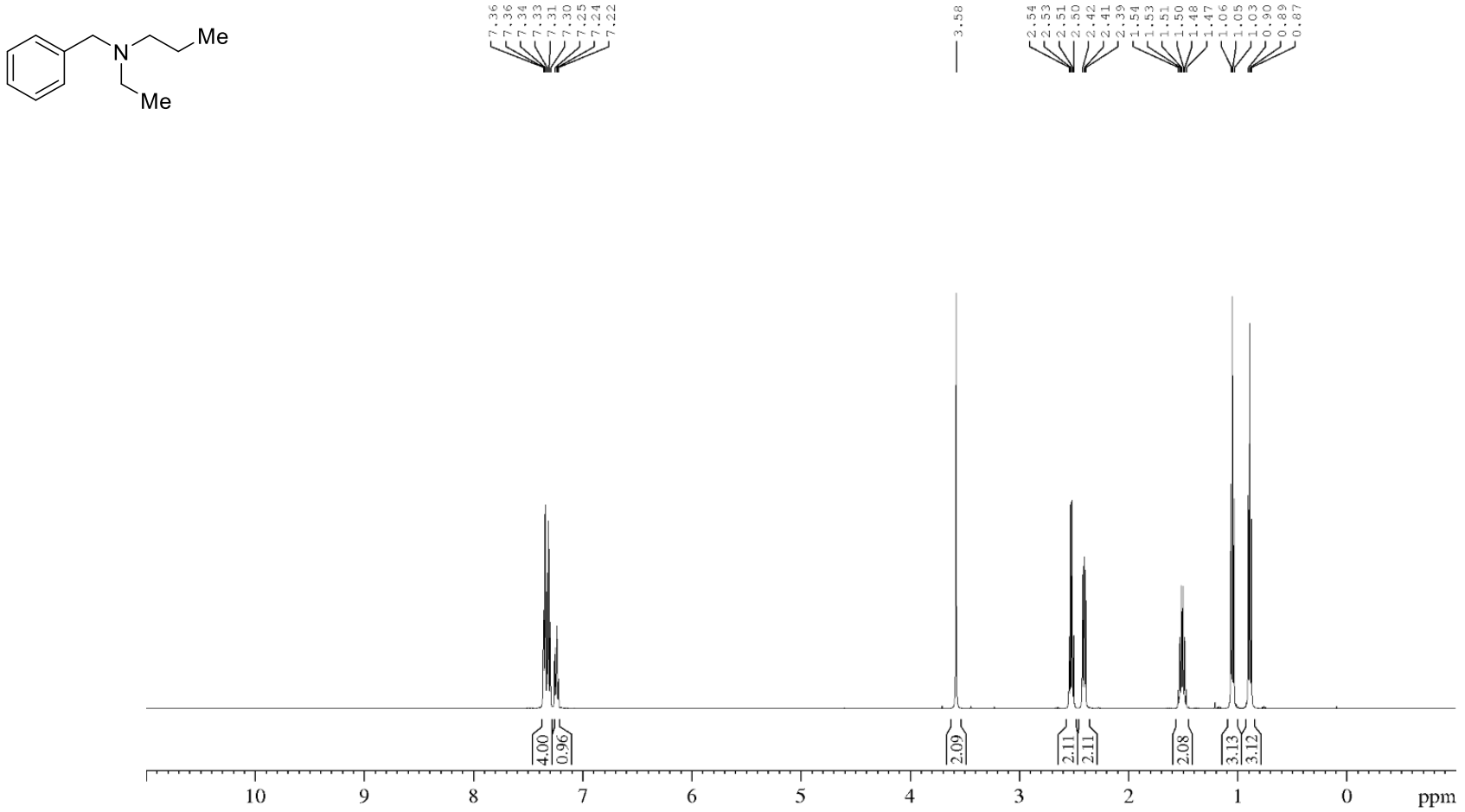


Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of ***N*-benzyl-*N*-ethylpropan-1-amine (1r)**.

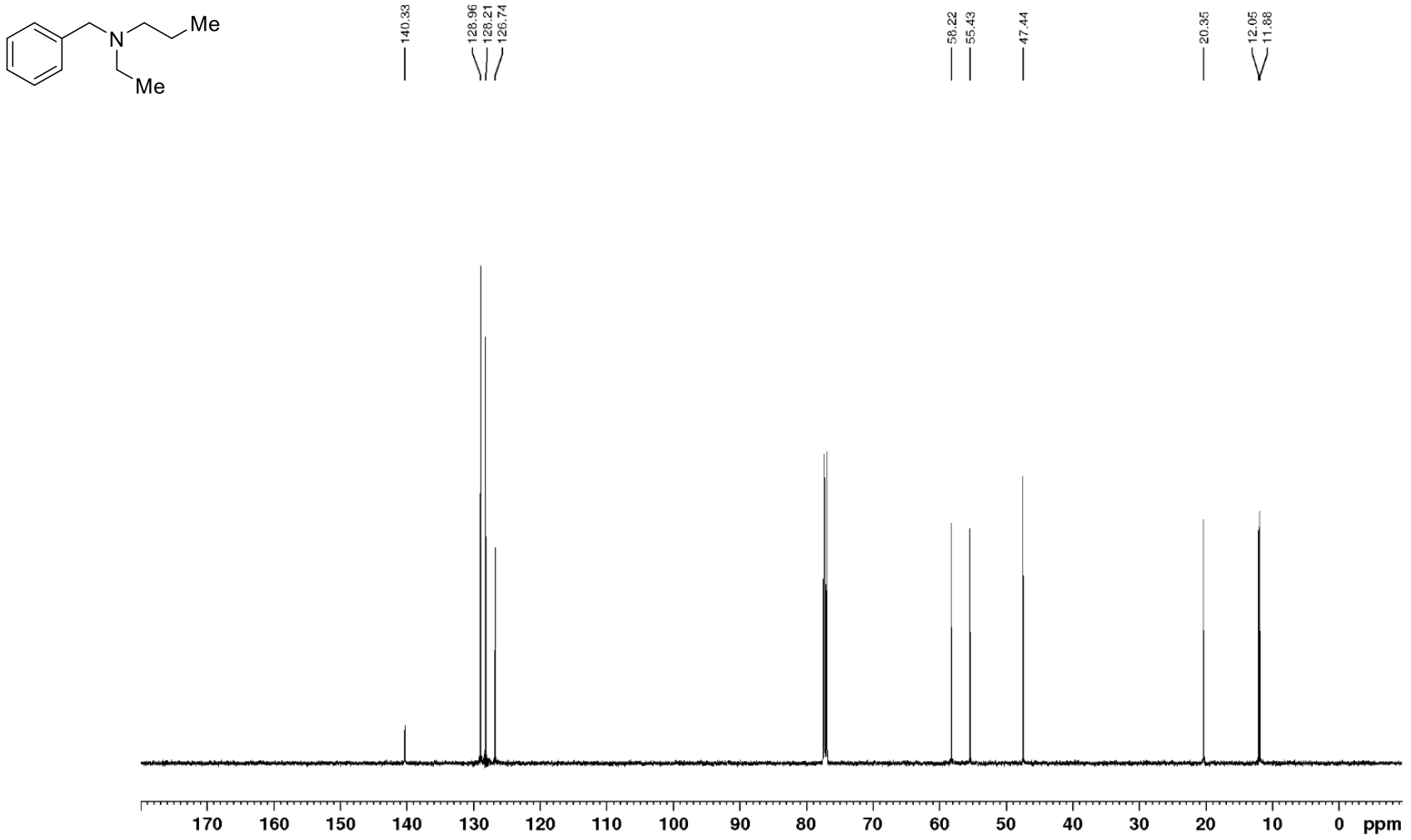


Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***N*-benzyl-*N*-ethylbutan-1-amine (1s)**.

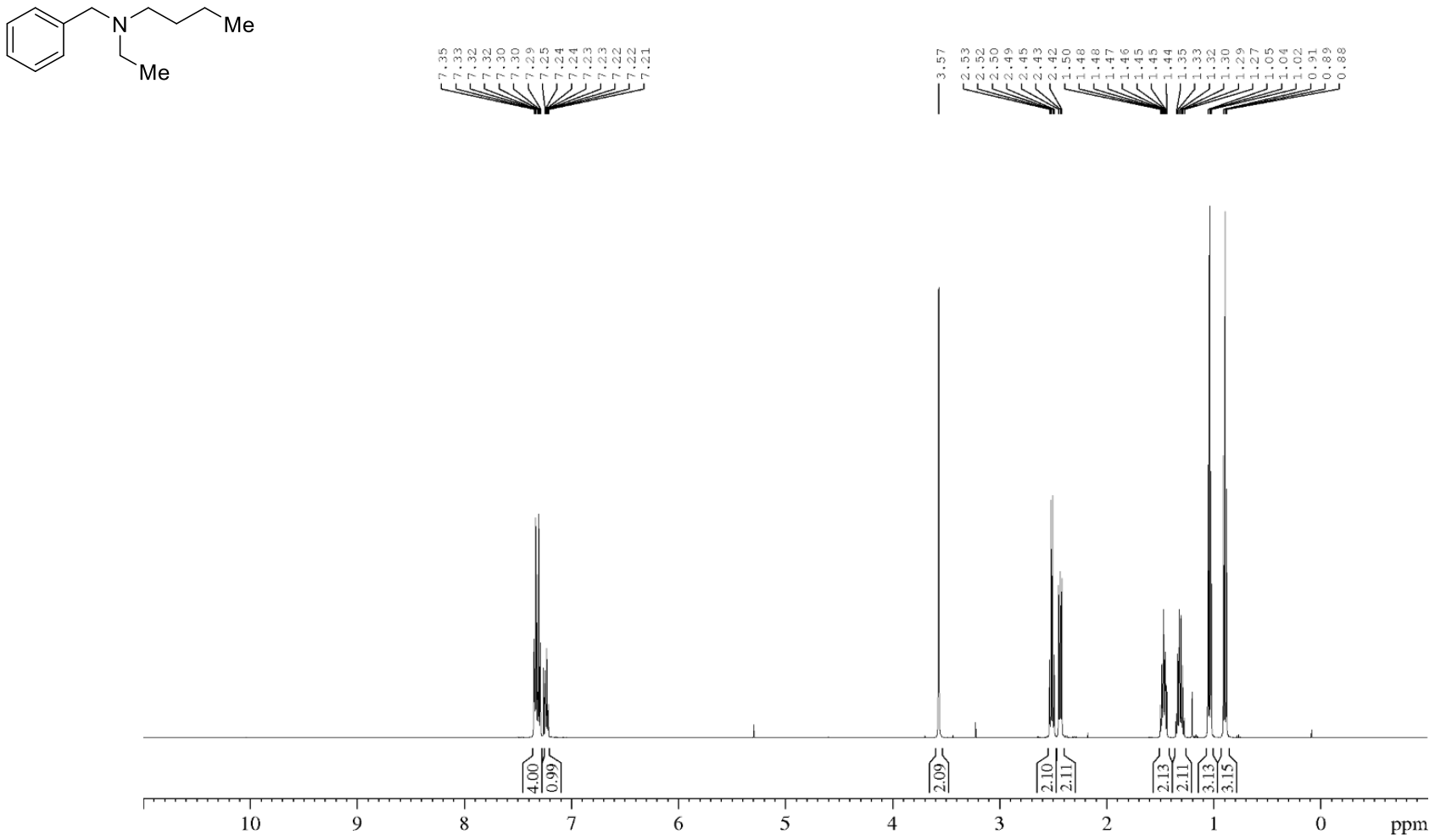


Figure S4. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of ***N*-benzyl-*N*-ethylbutan-1-amine (1s)**.

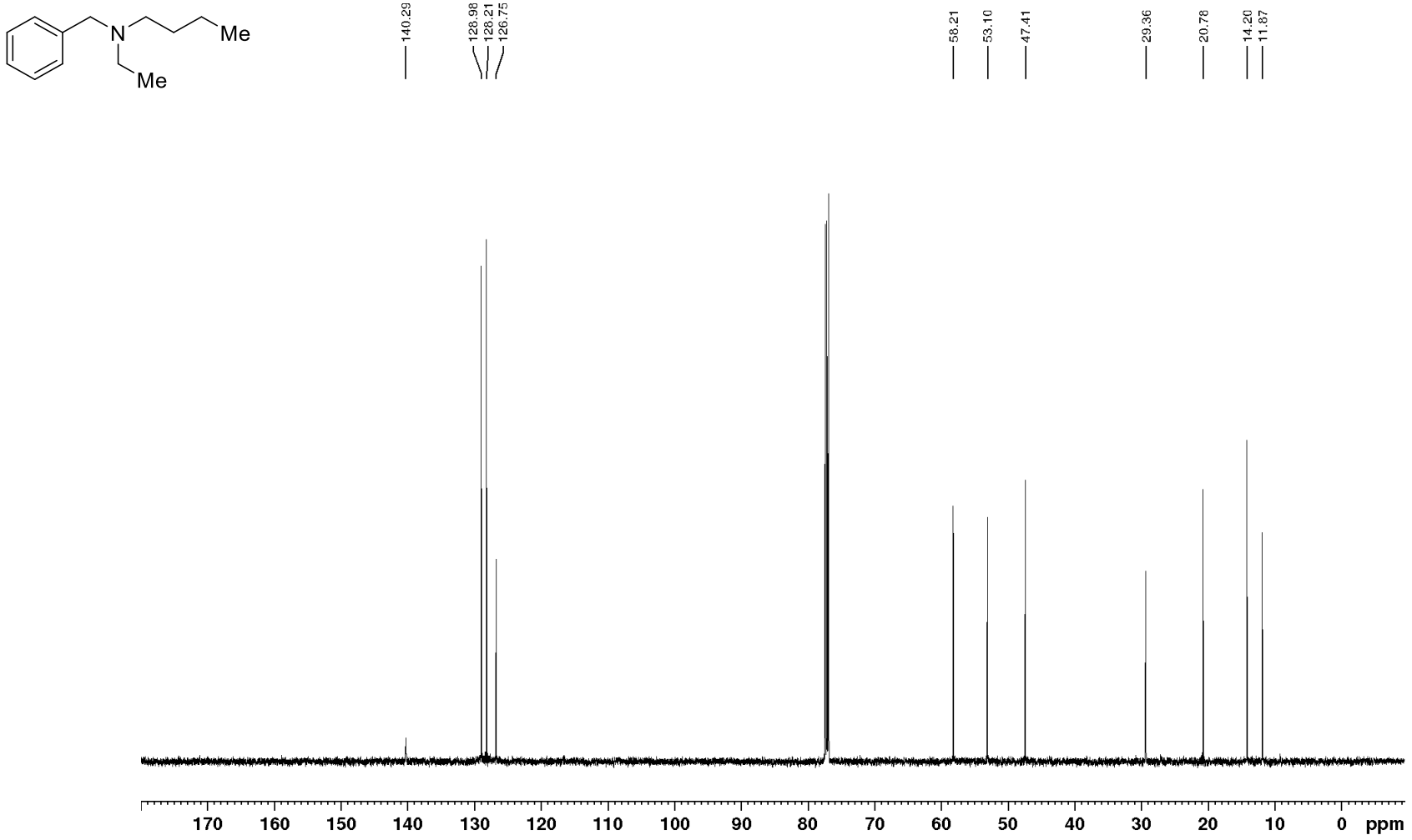


Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-diphenyl-1,4-azasilinane (3aa)**.

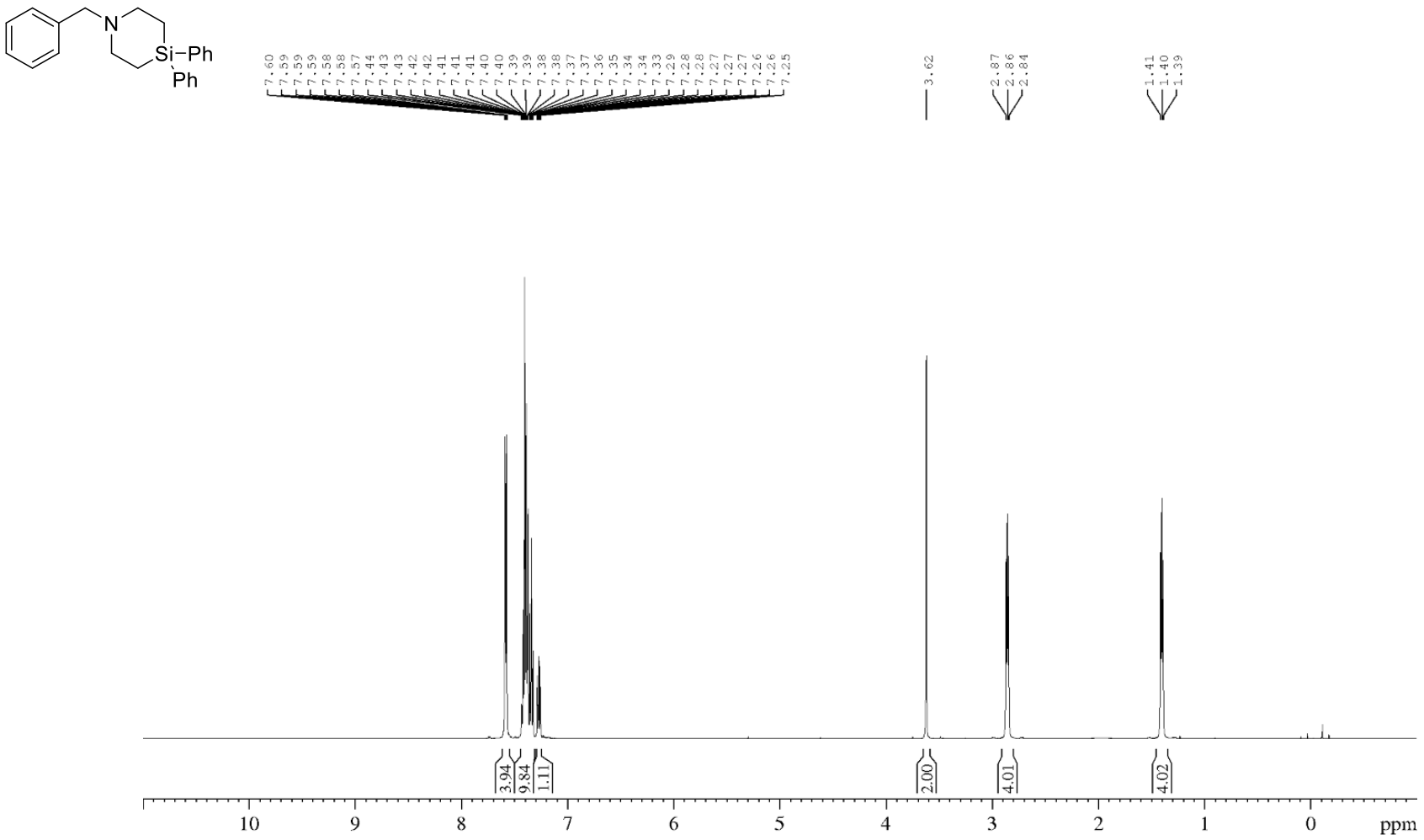


Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-diphenyl-1,4-azasilinane (3aa)**.

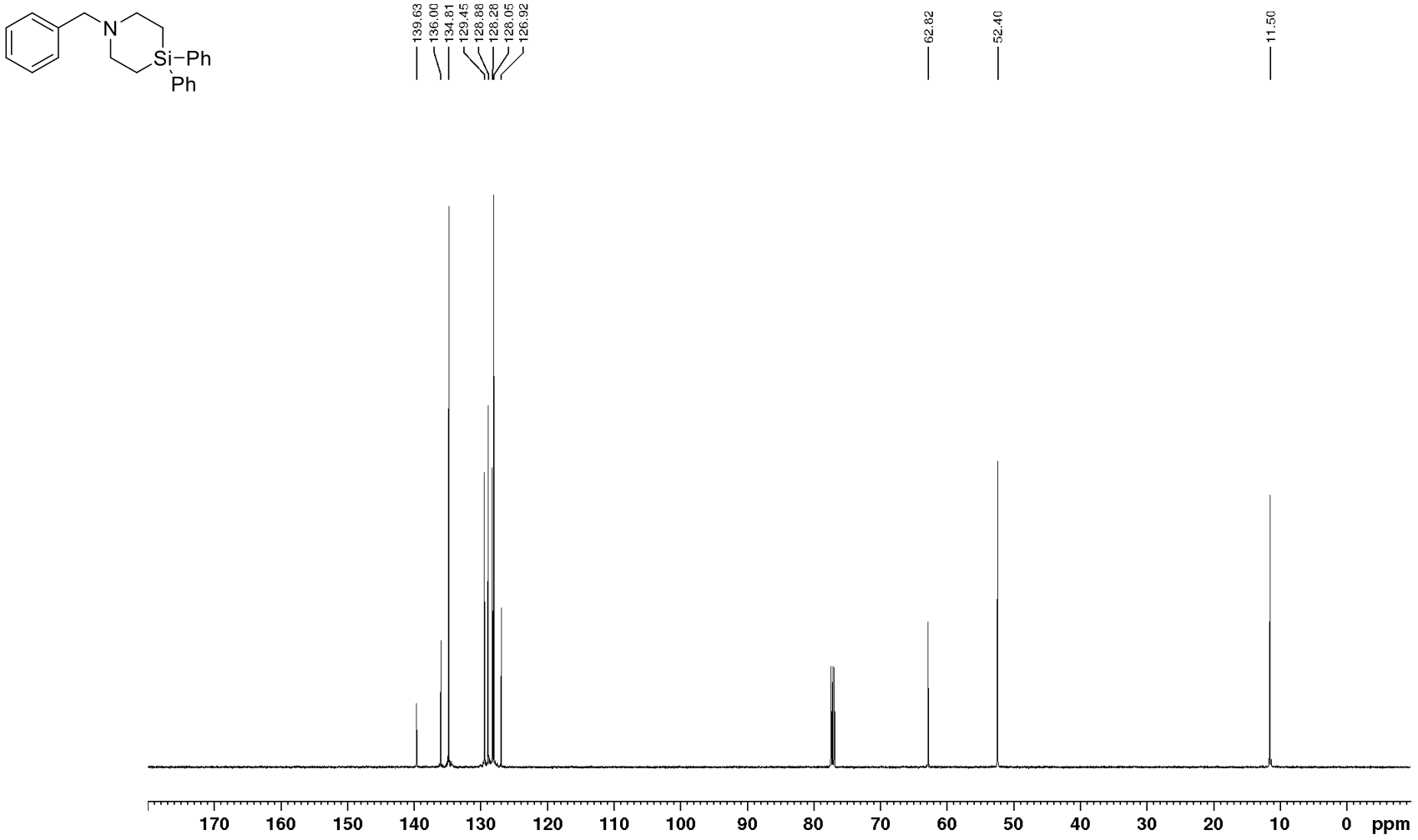


Figure S7. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-4,4-diphenyl-1,4-azasilinane (3aa)**.

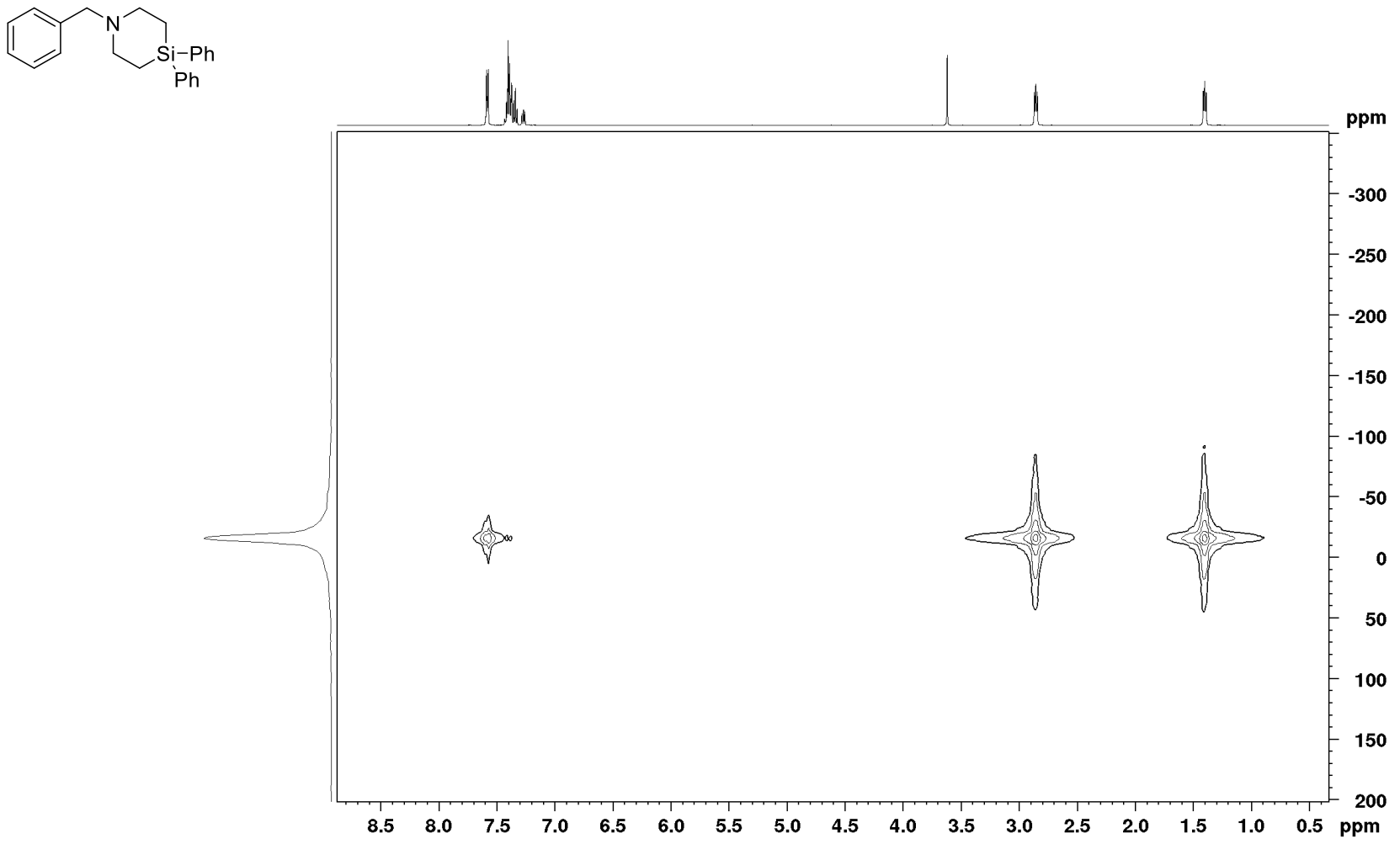


Figure S8. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-([1,1'-biphenyl]-4-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ba)**.

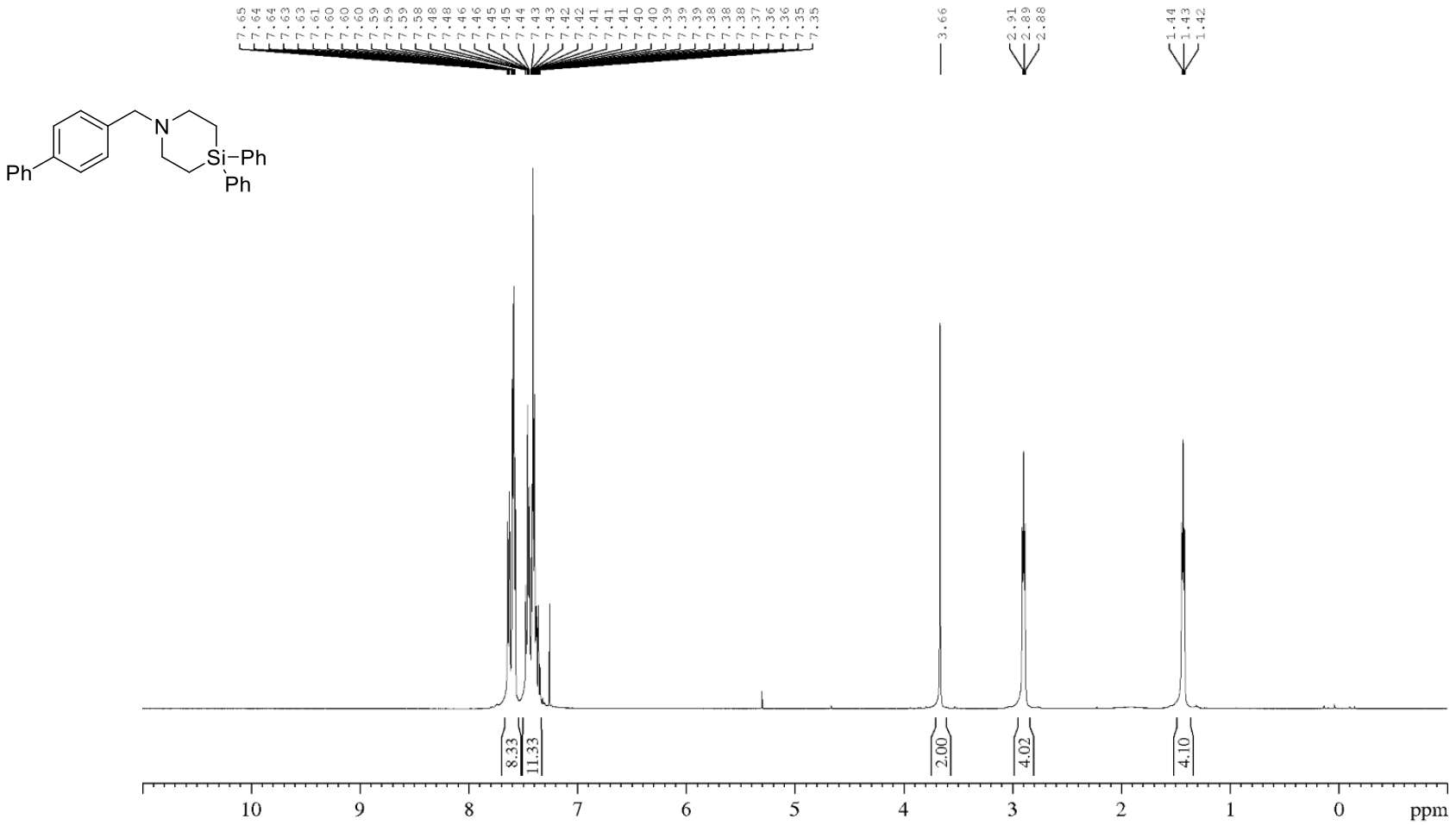


Figure S9. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-([1,1'-biphenyl]-4-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ba)**.

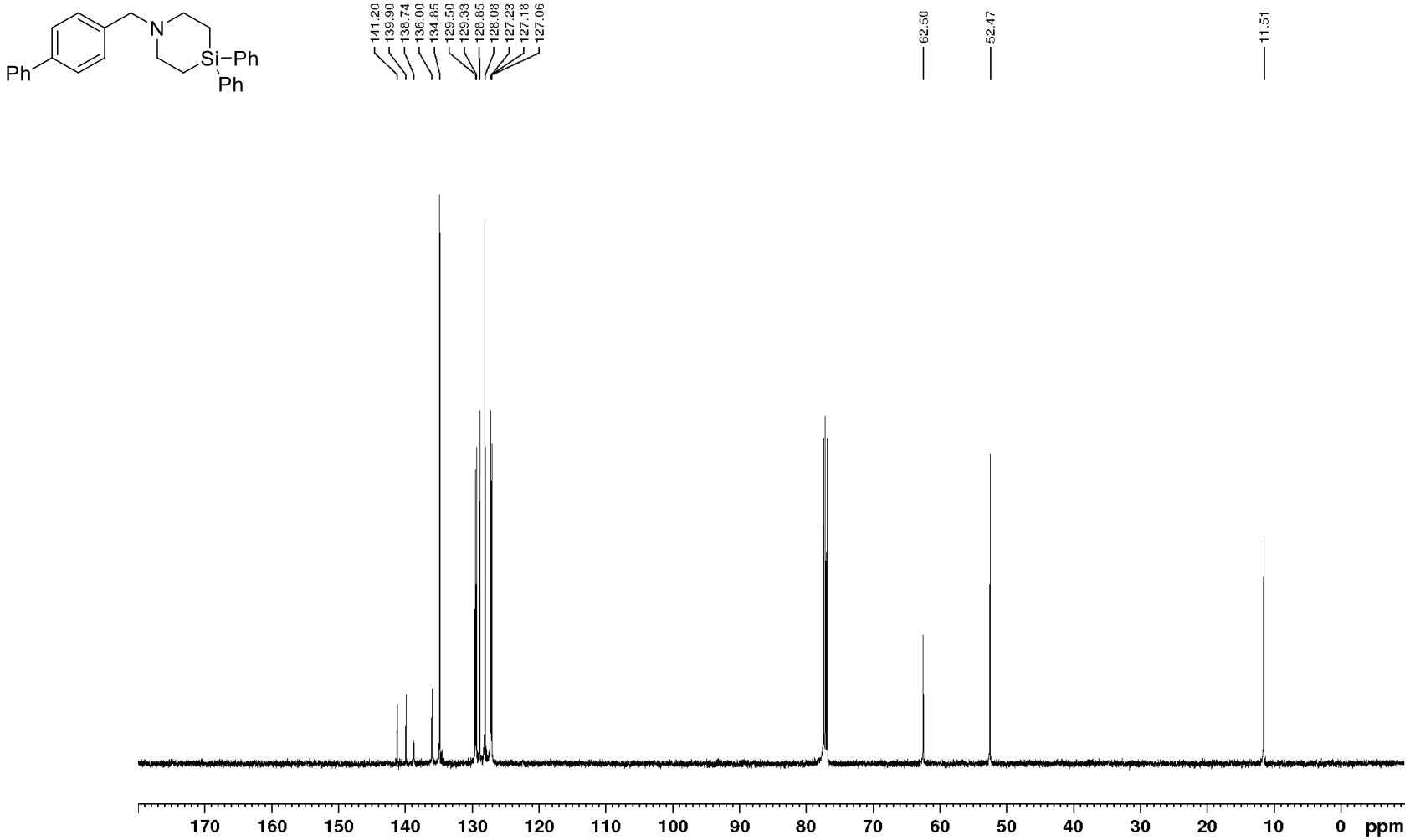


Figure S10. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-([1,1'-biphenyl]-4-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ba)**.

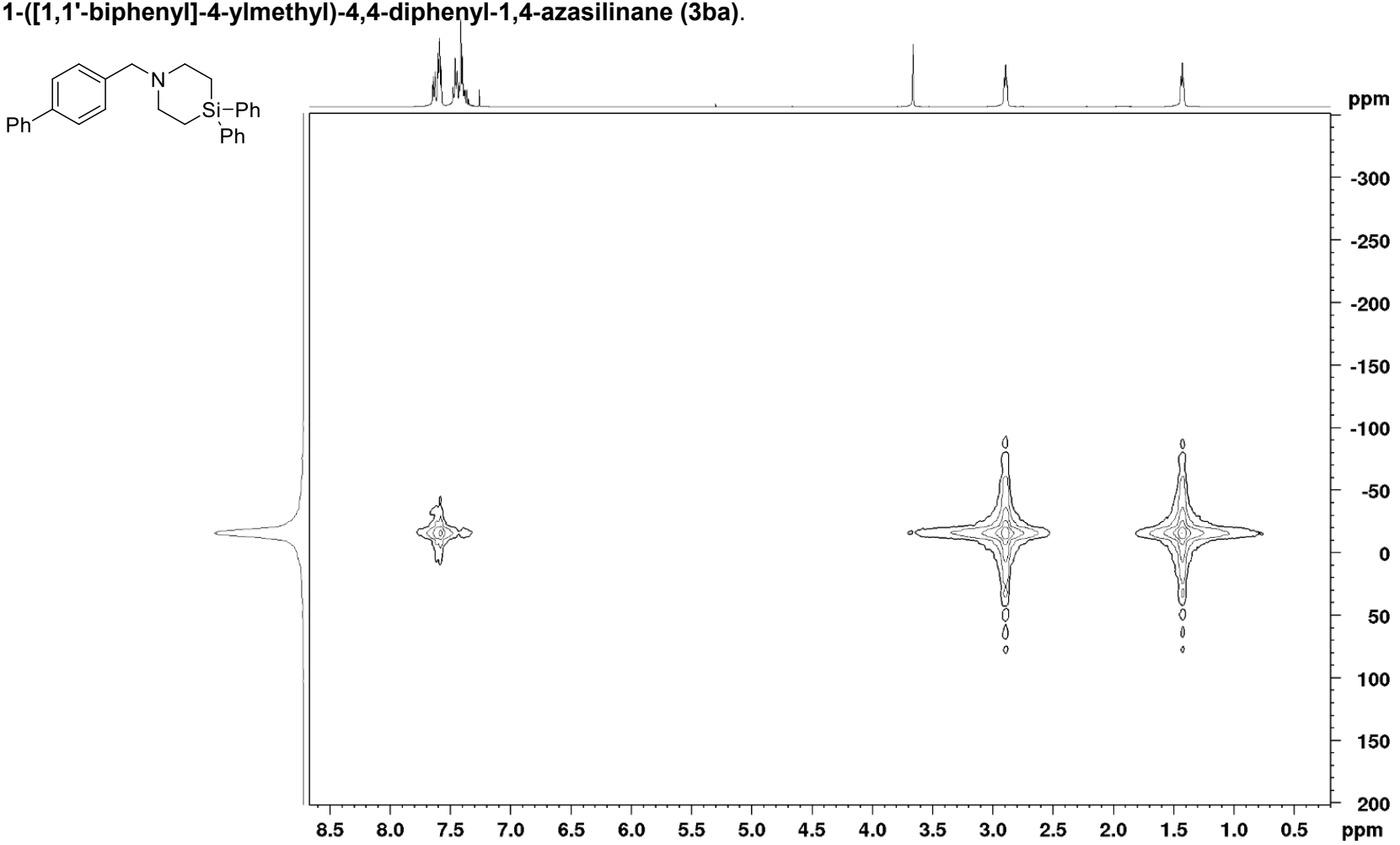


Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(2-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ca)**.

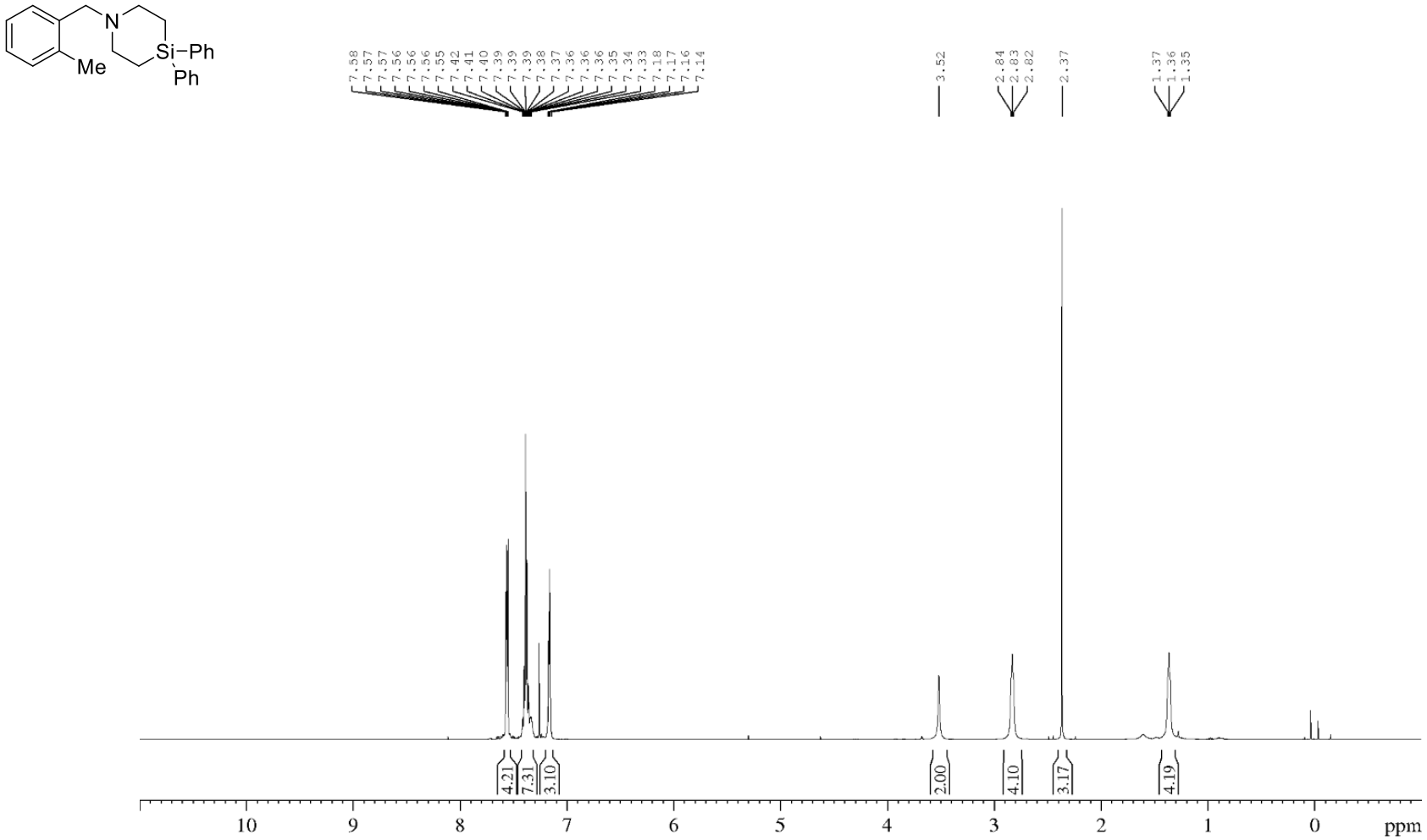


Figure S12. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(2-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ca)**.

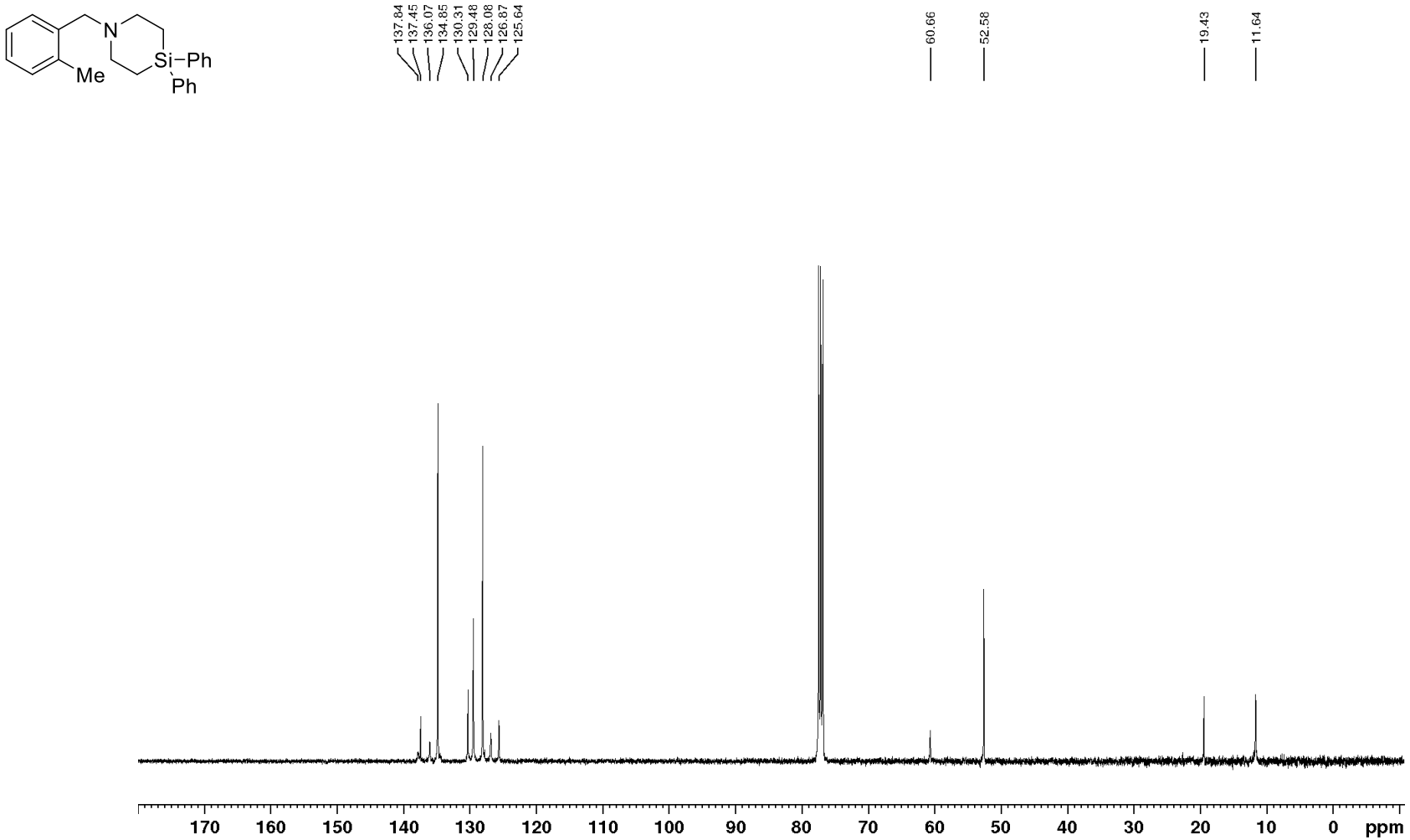


Figure S13. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(2-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ca)**.

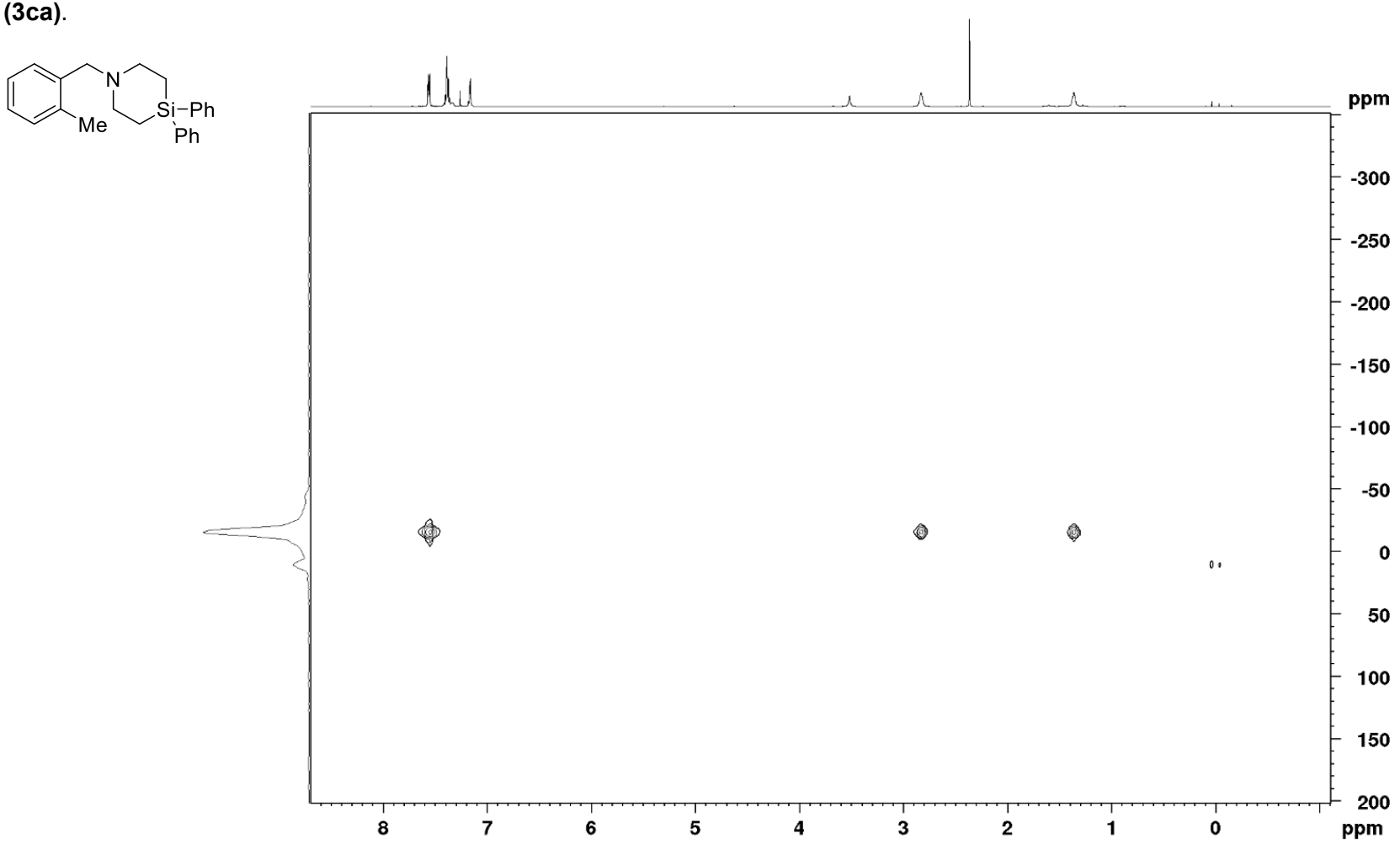


Figure S14. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(3-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3da)**.

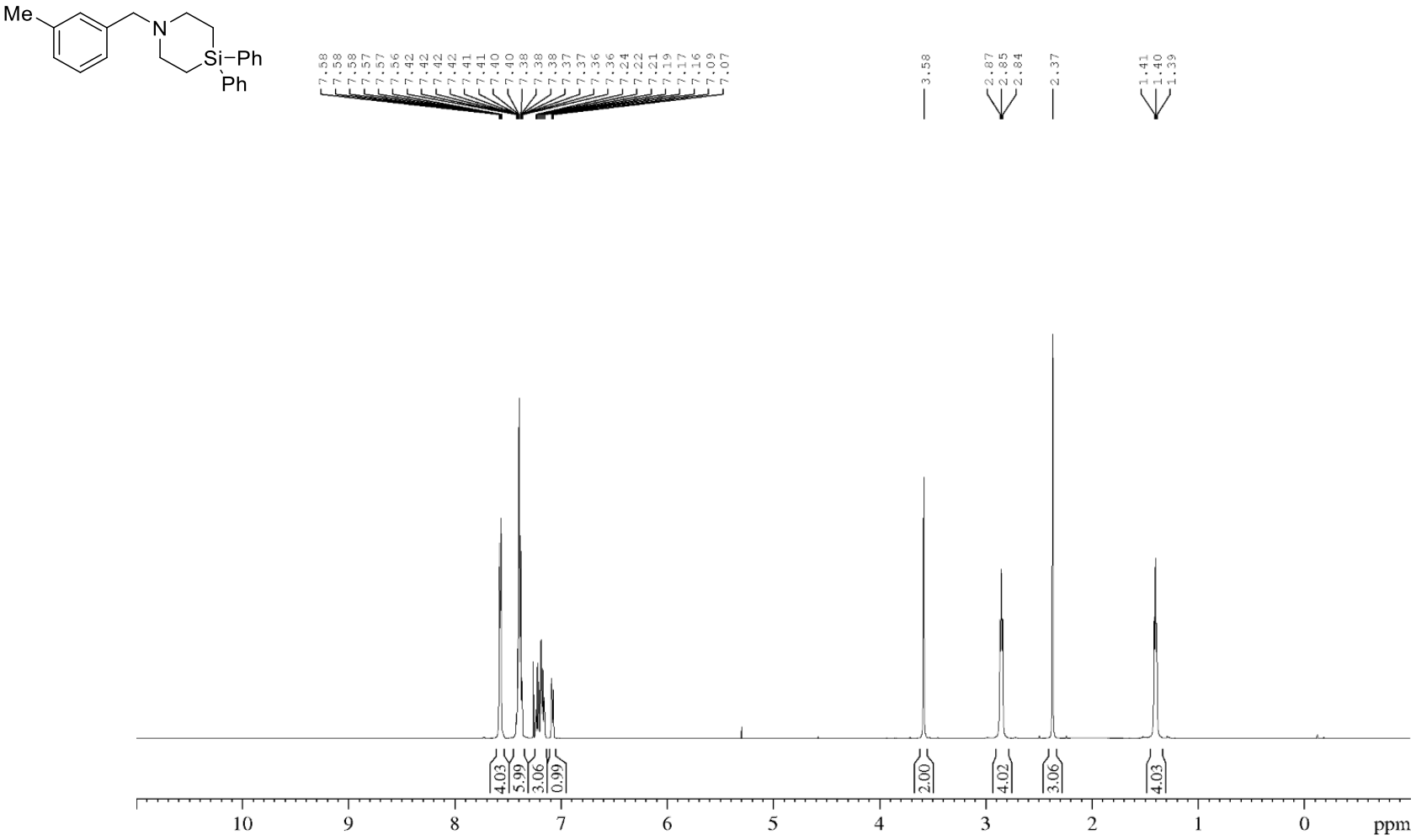


Figure S15. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(3-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3da)**.

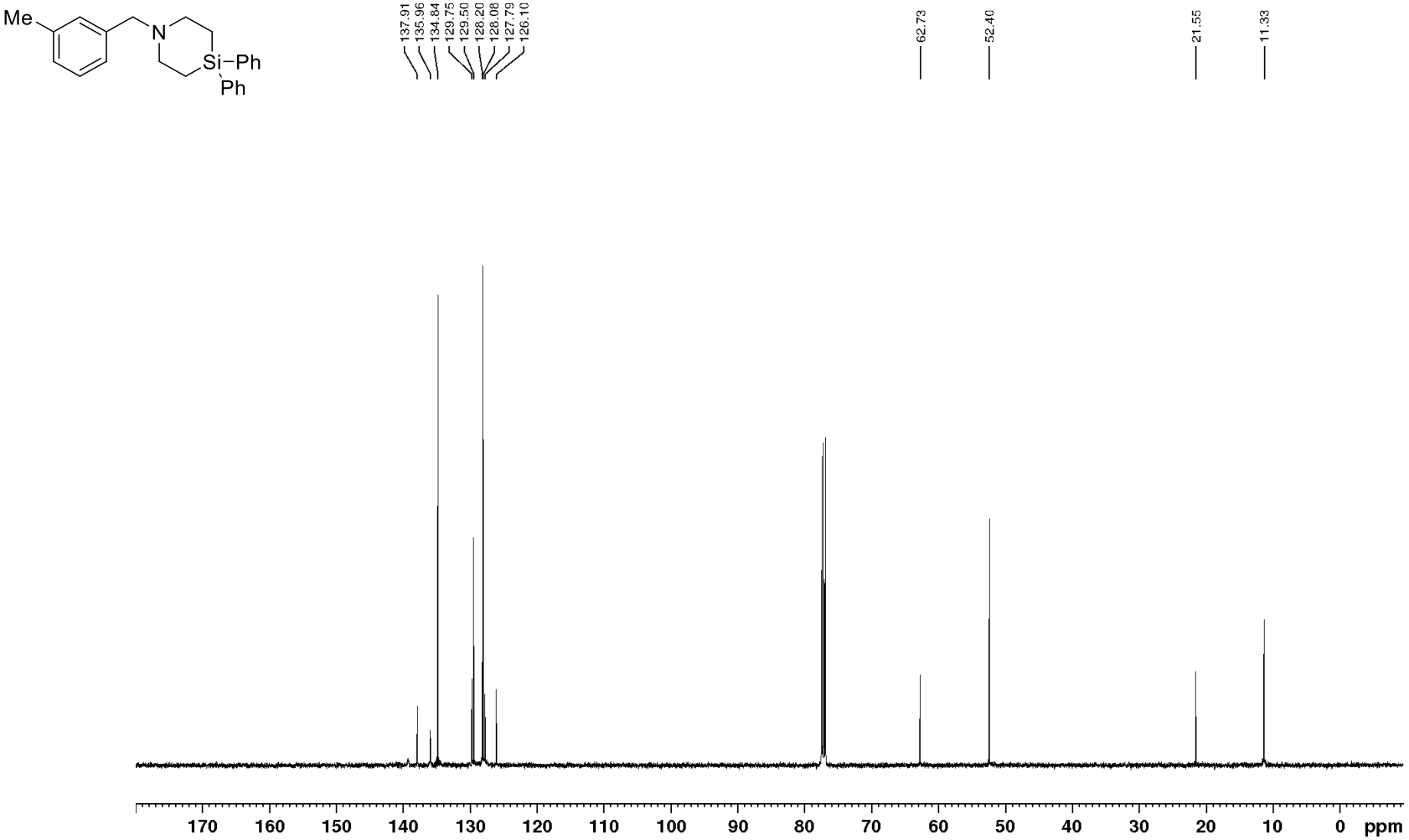


Figure S16. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(3-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3da)**.

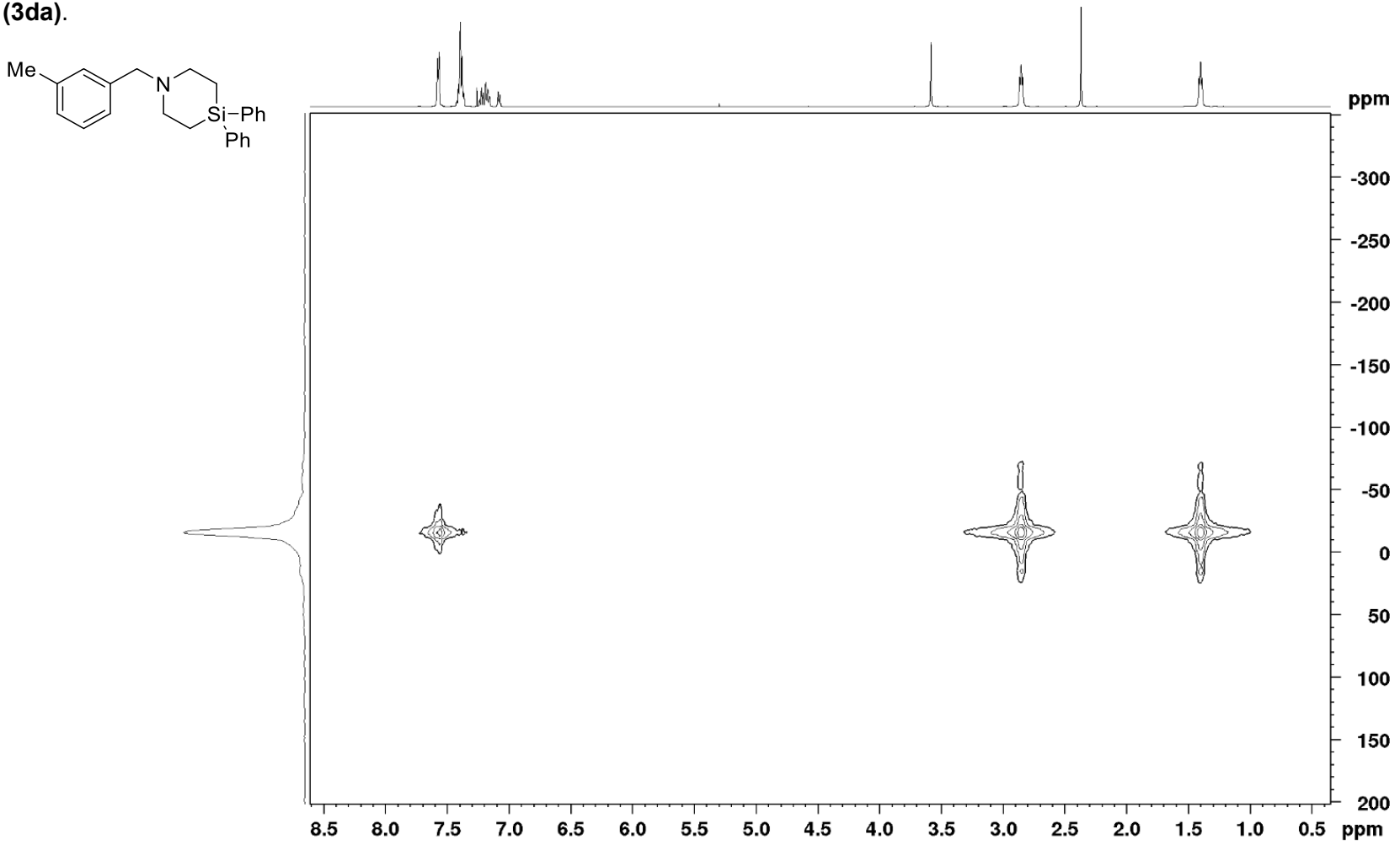


Figure S17. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(4-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ea)**.

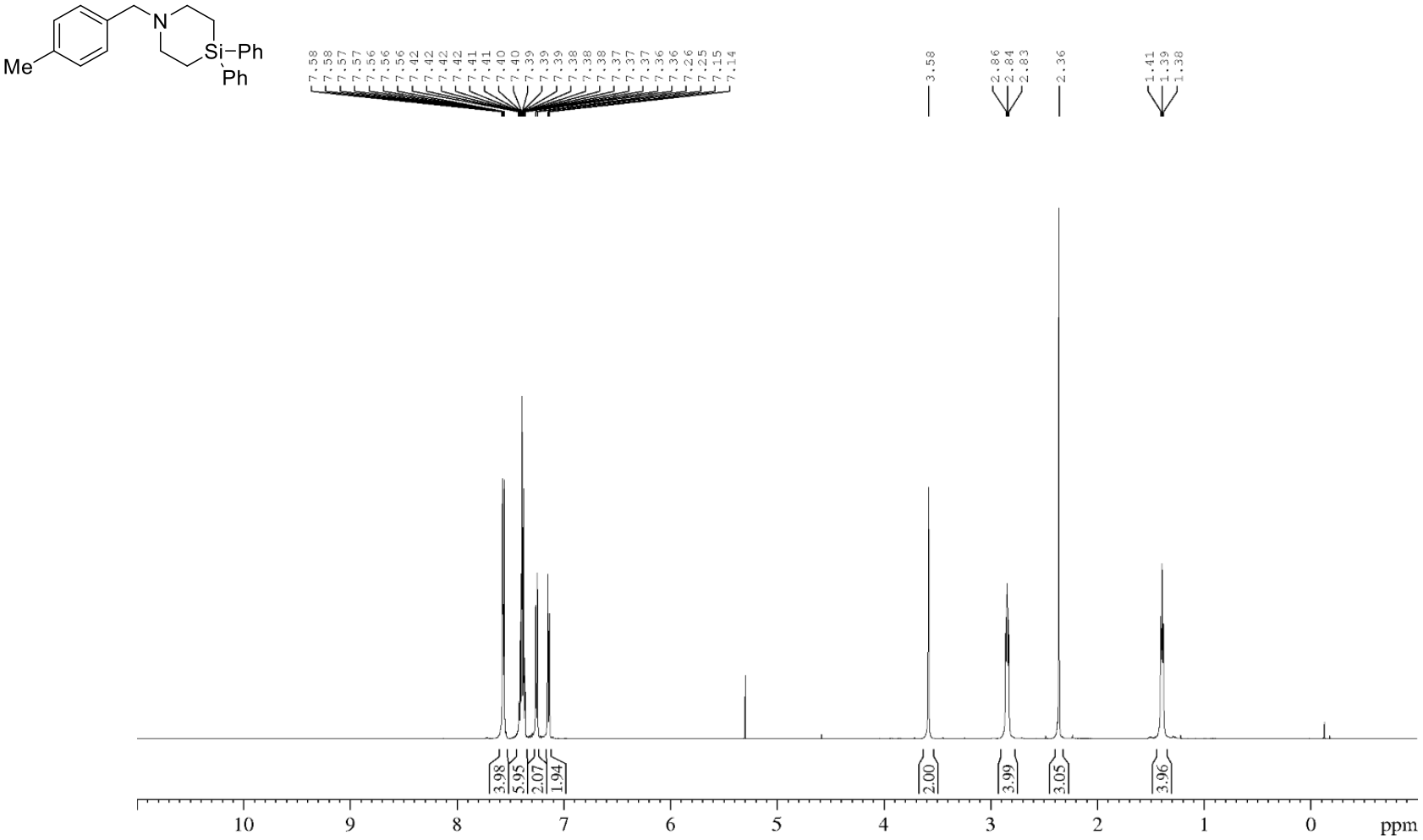


Figure S18. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(4-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ea)**.

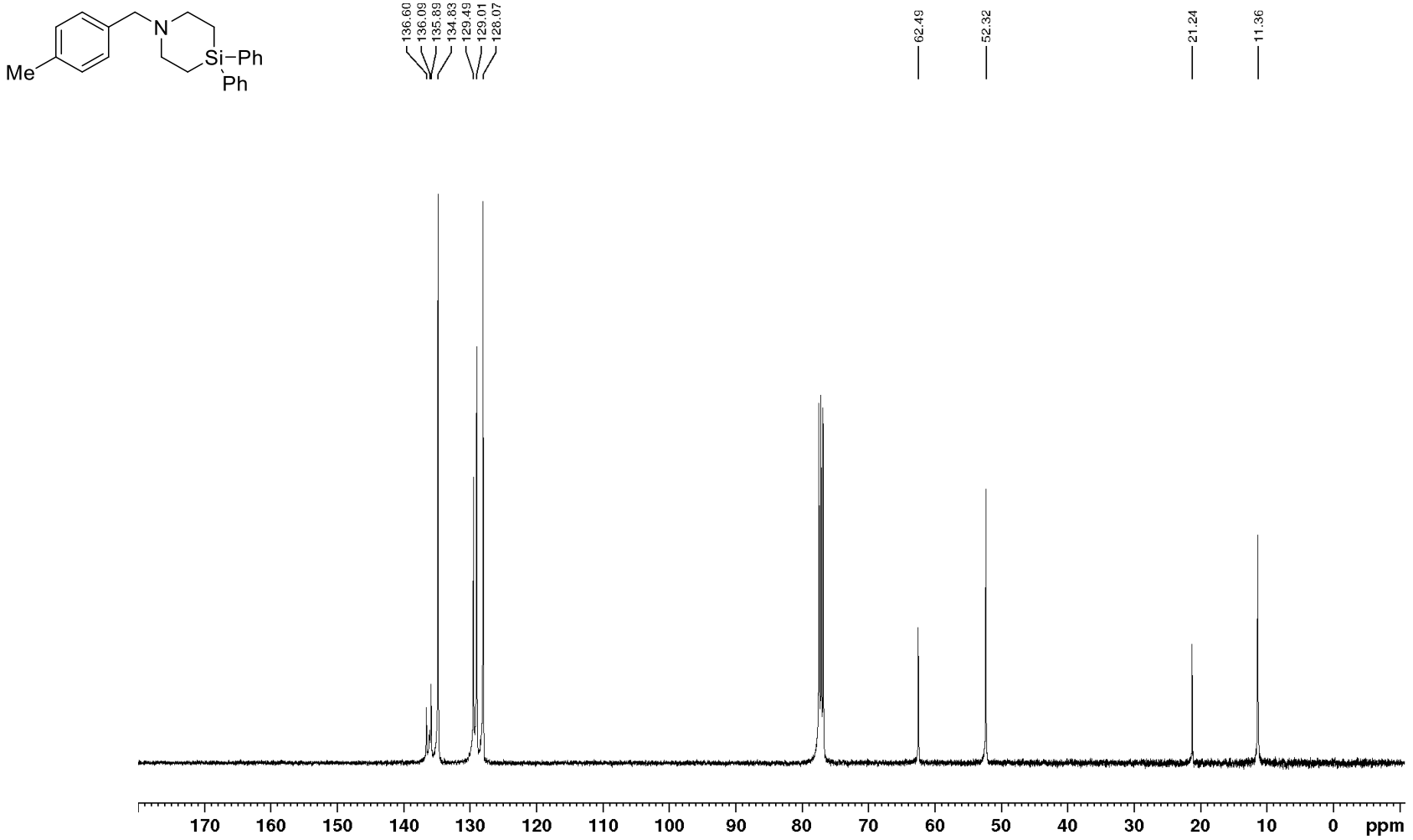


Figure S19. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(4-methylbenzyl)-4,4-diphenyl-1,4-azasilinane (3ea)**.

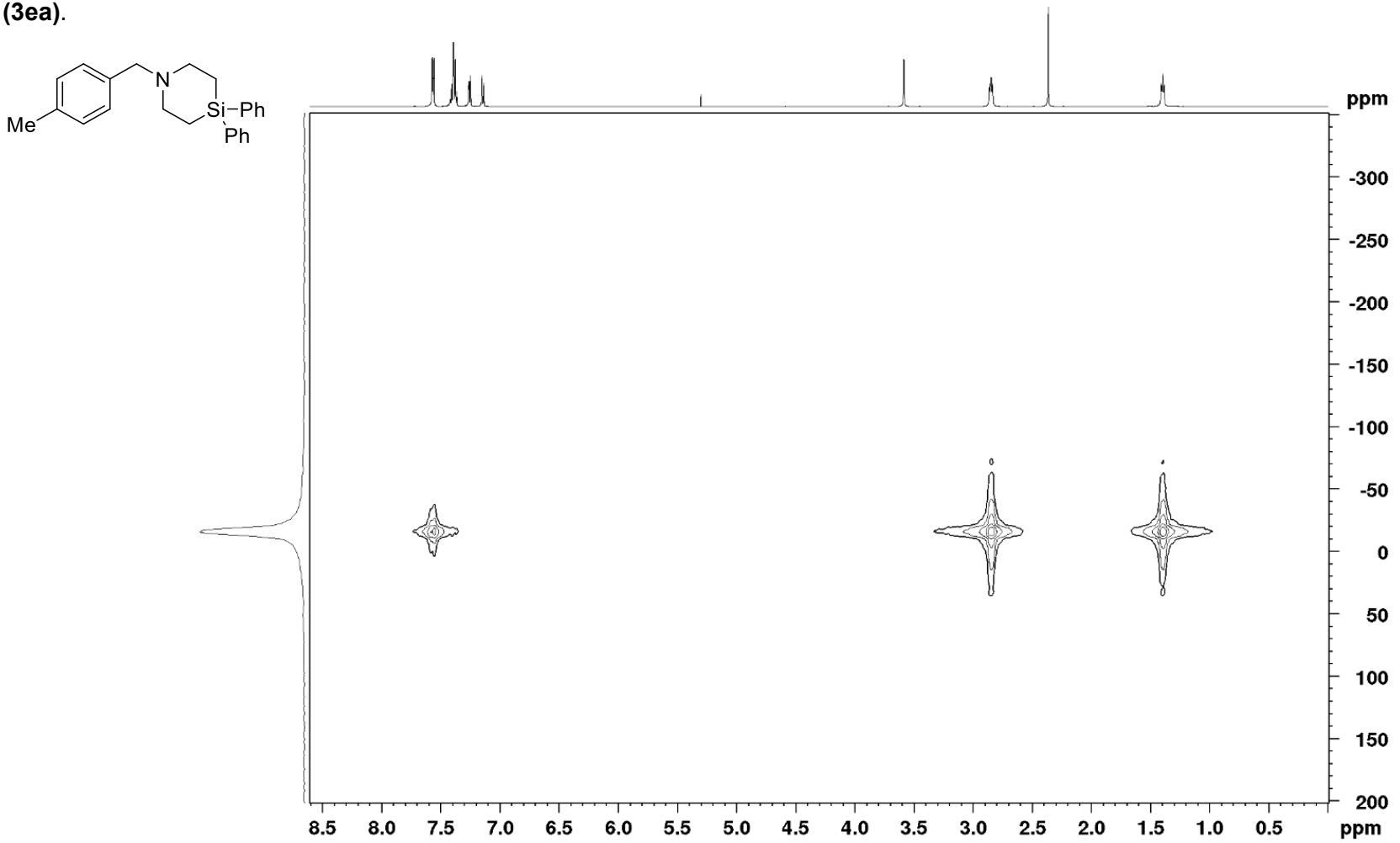


Figure S20. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(4-(*tert*-butyl)benzyl)-4,4-diphenyl-1,4-azasilinane (3fa)**.

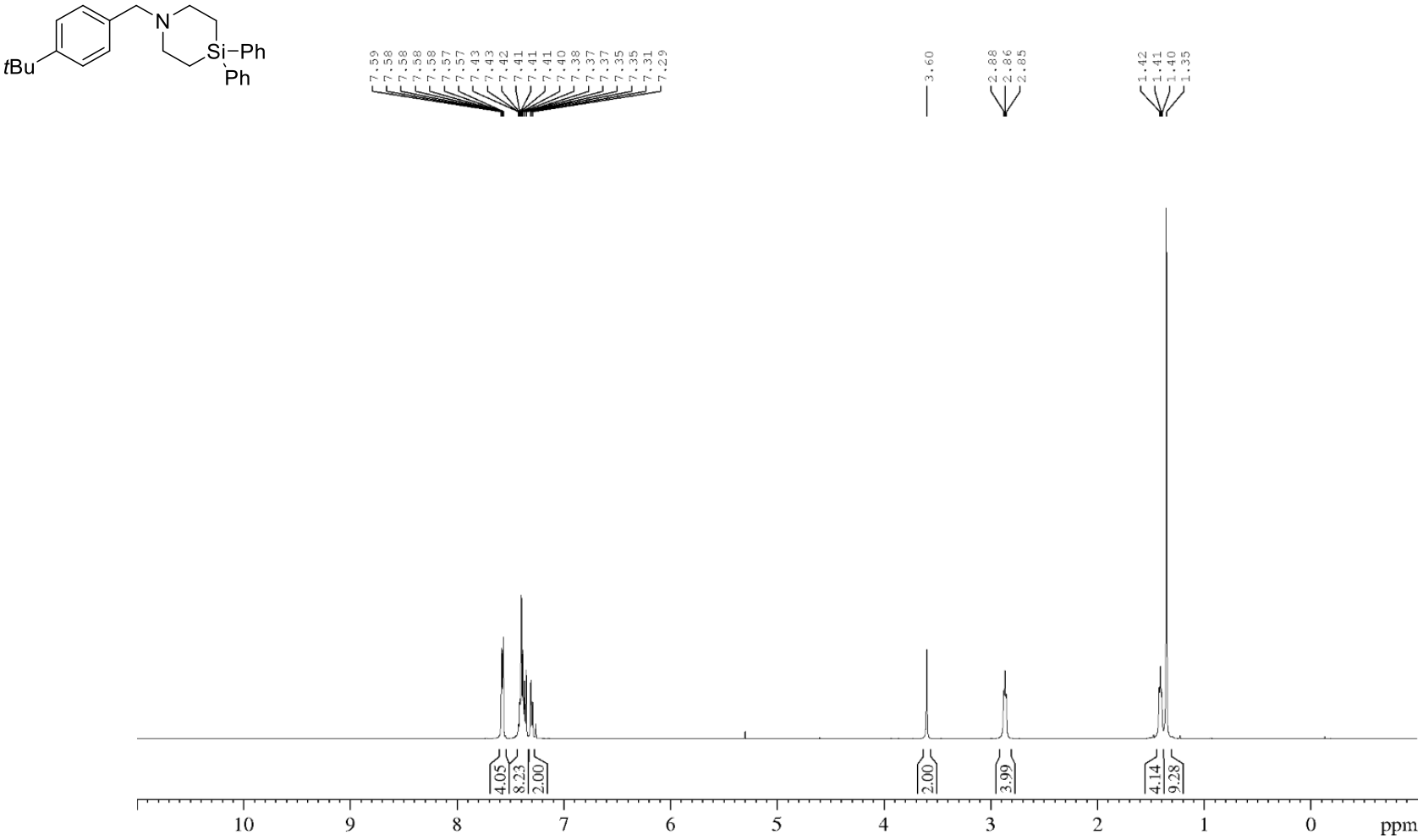


Figure S21. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(4-(*tert*-butyl)benzyl)-4,4-diphenyl-1,4-azasilinane (3fa)**.

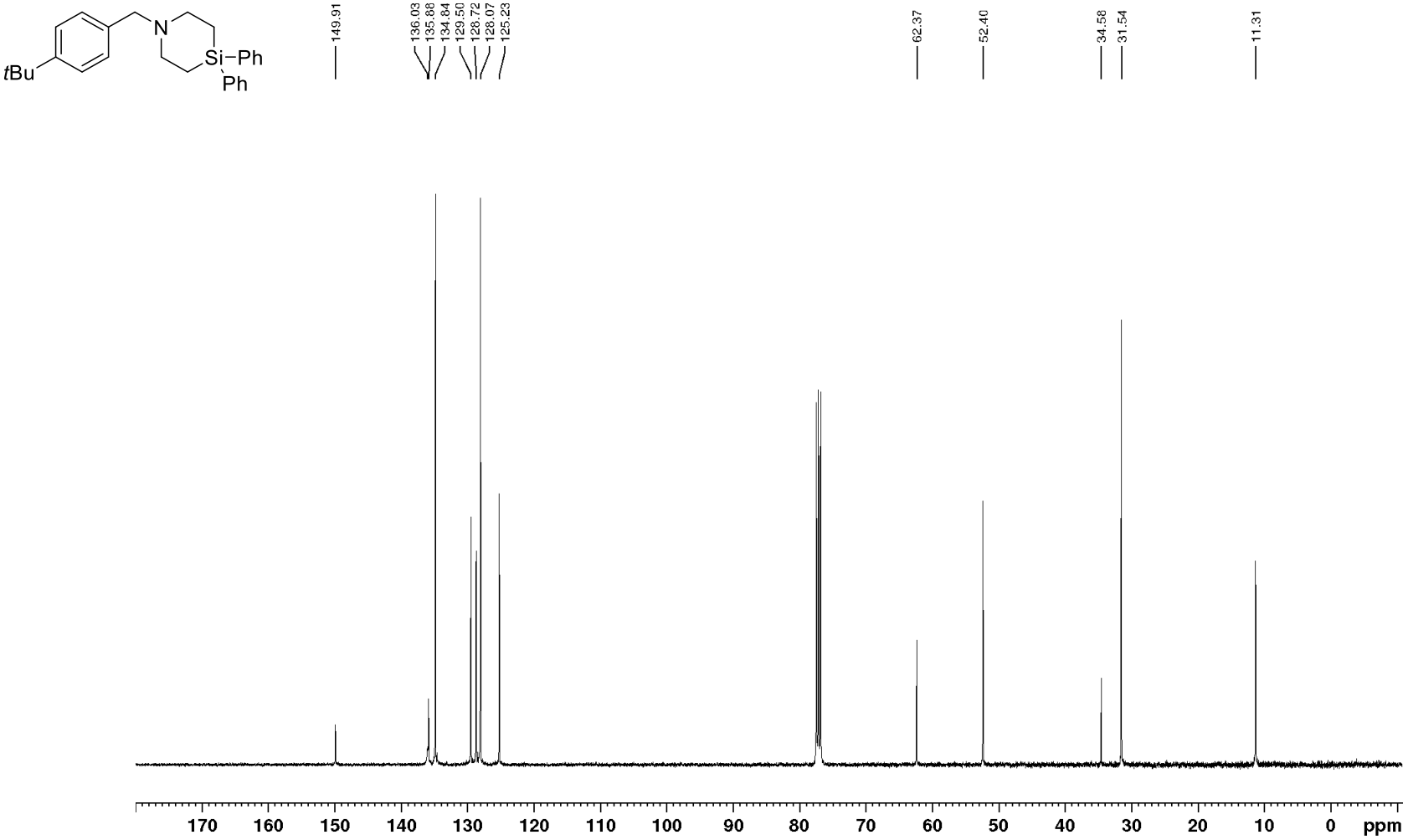


Figure S22. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(4-(*tert*-butyl)benzyl)-4,4-diphenyl-1,4-azasilinane (3fa)**.

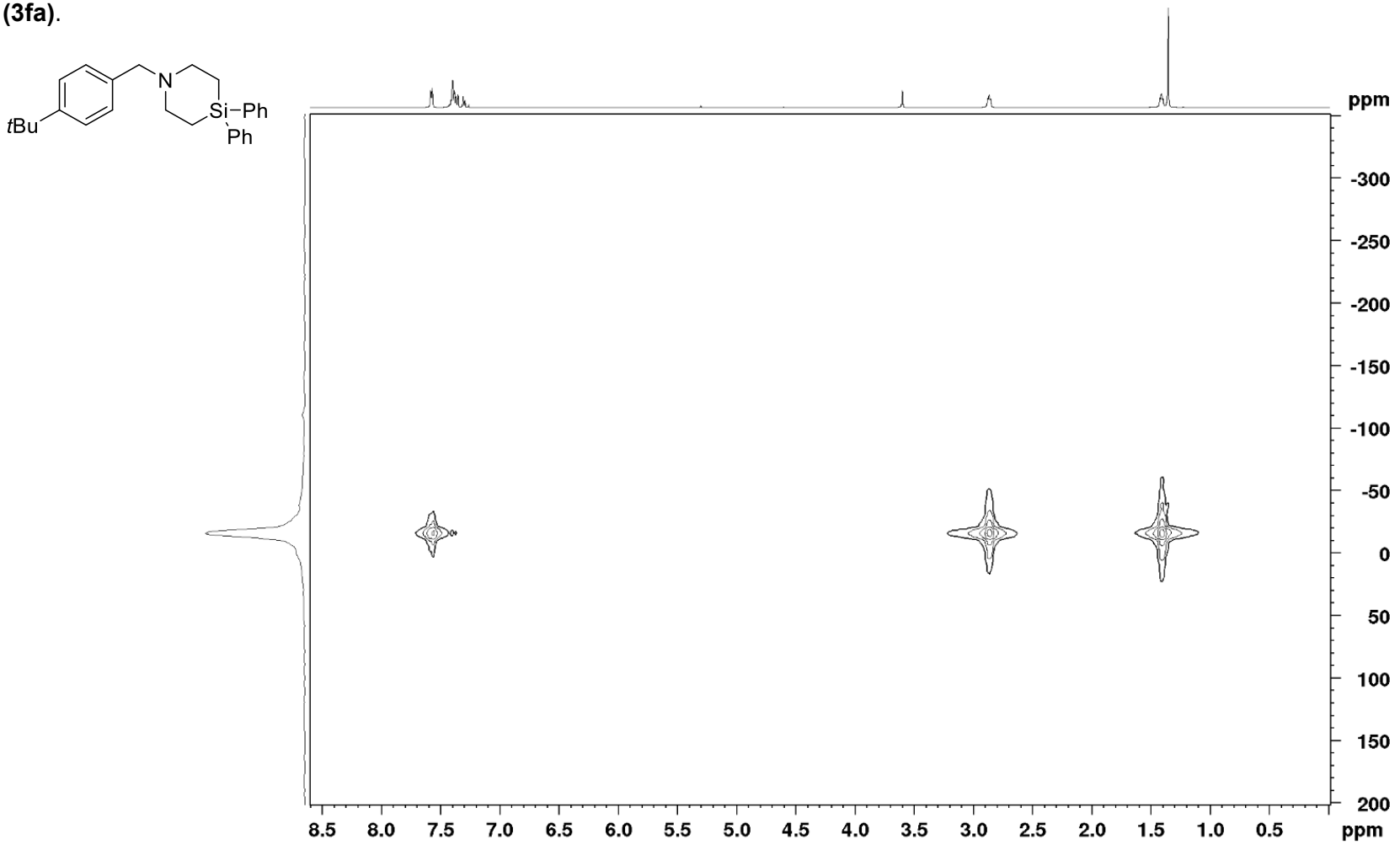


Figure S23. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(4-fluorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ga)**.

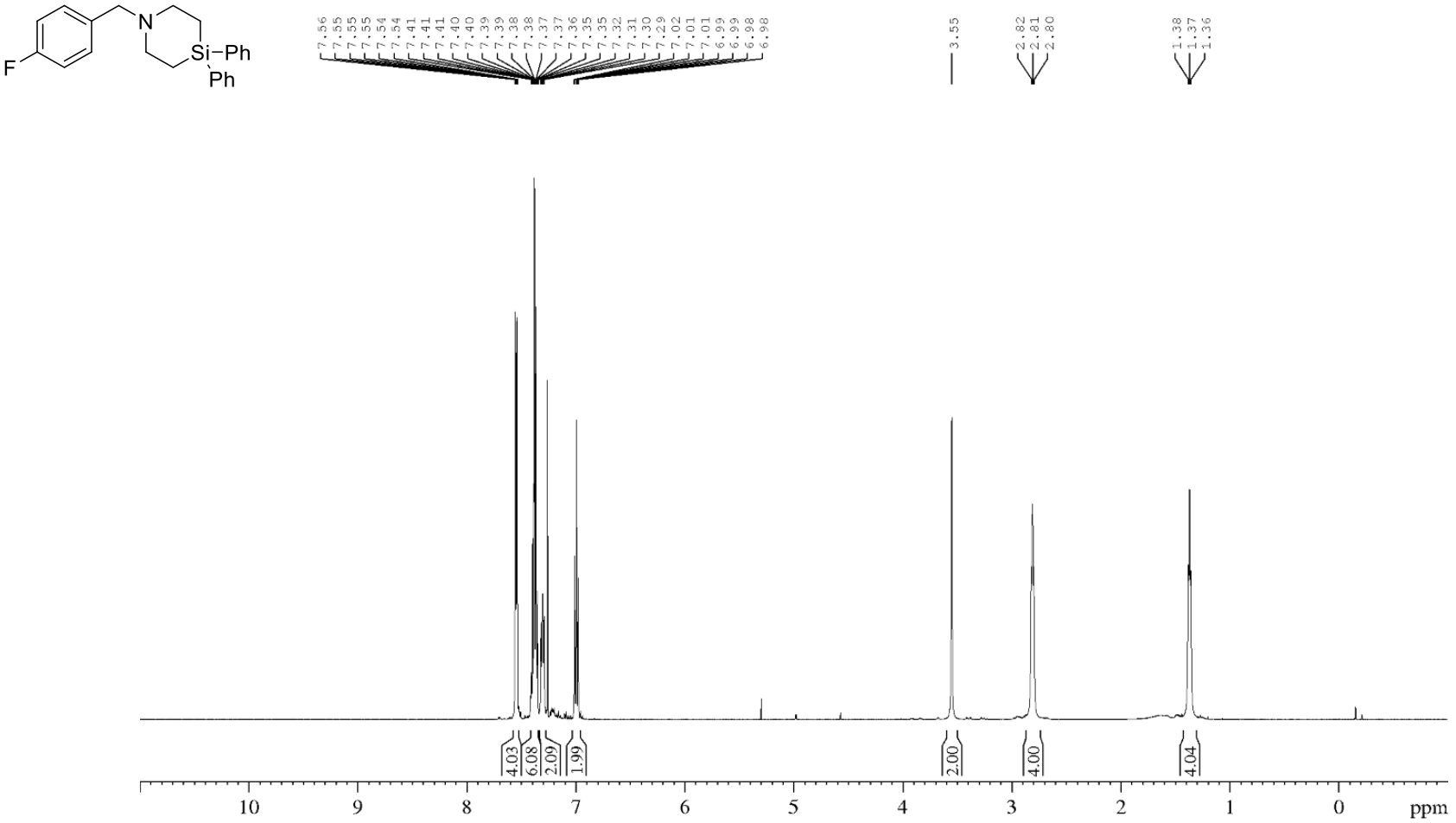


Figure S24. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(4-fluorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ga)**.

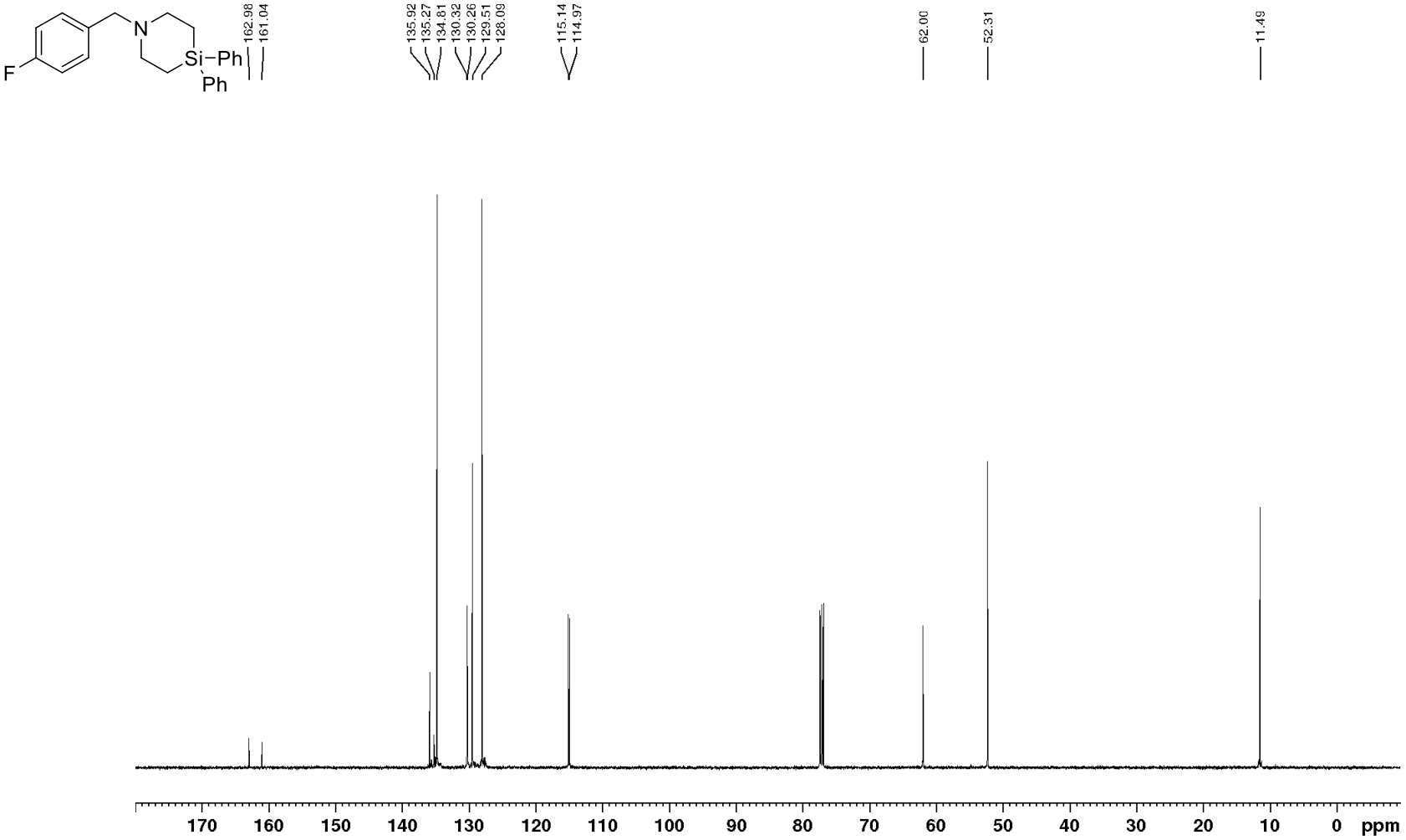
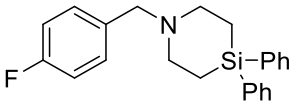


Figure S25. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of **1-(4-fluorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ga)**.



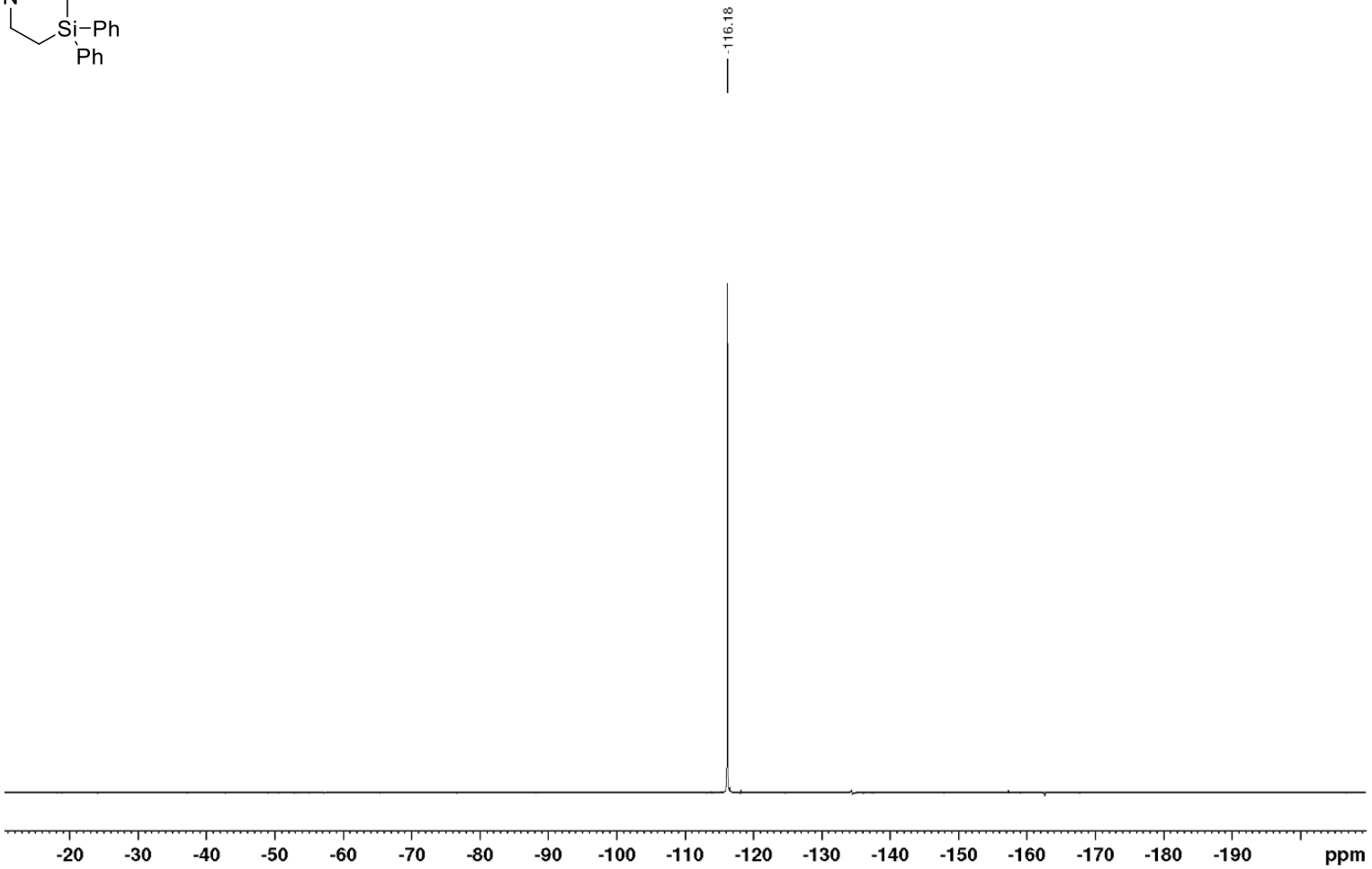


Figure S26. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(4-fluorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ga)**.

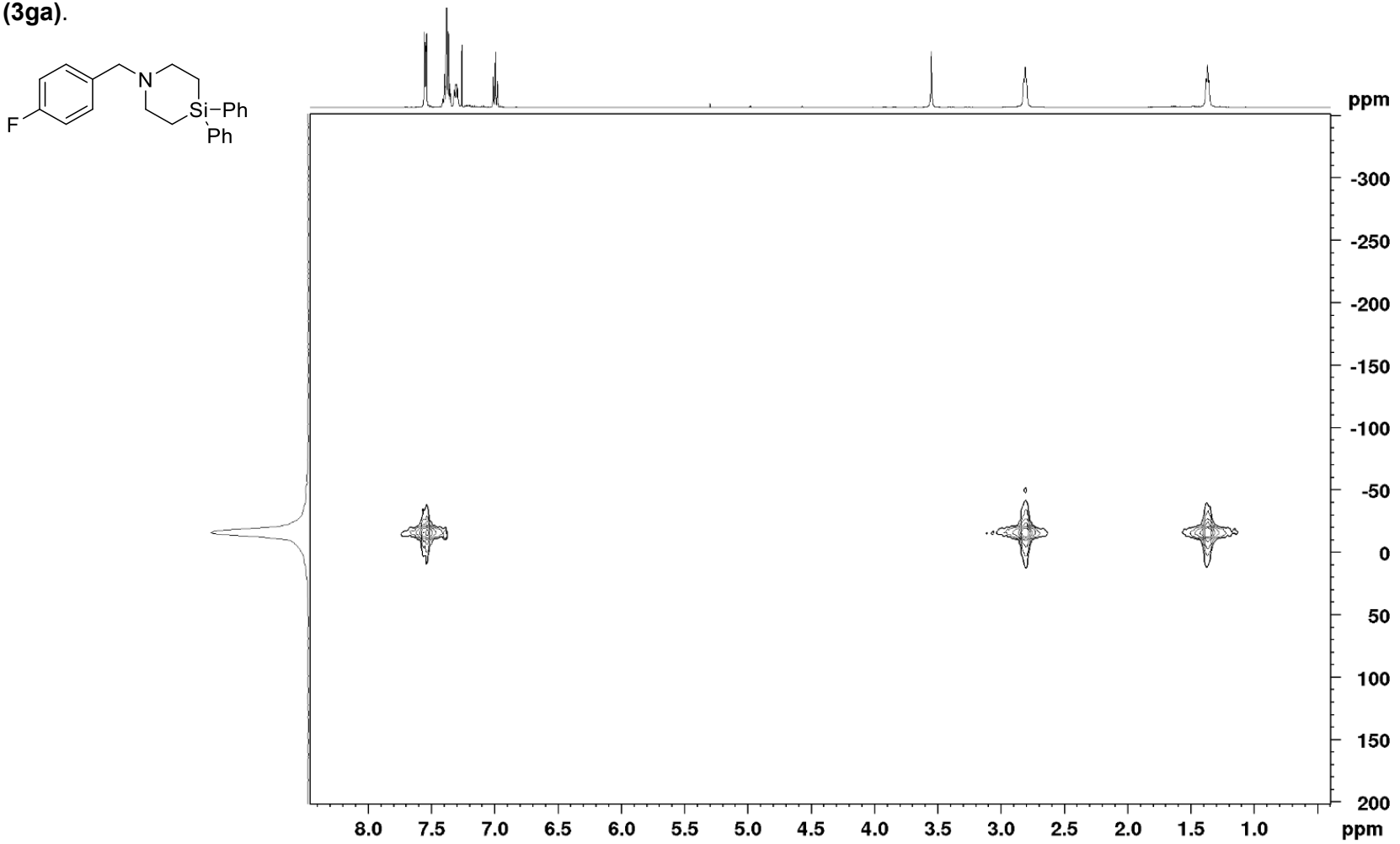


Figure S27. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(4-chlorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ha)**.

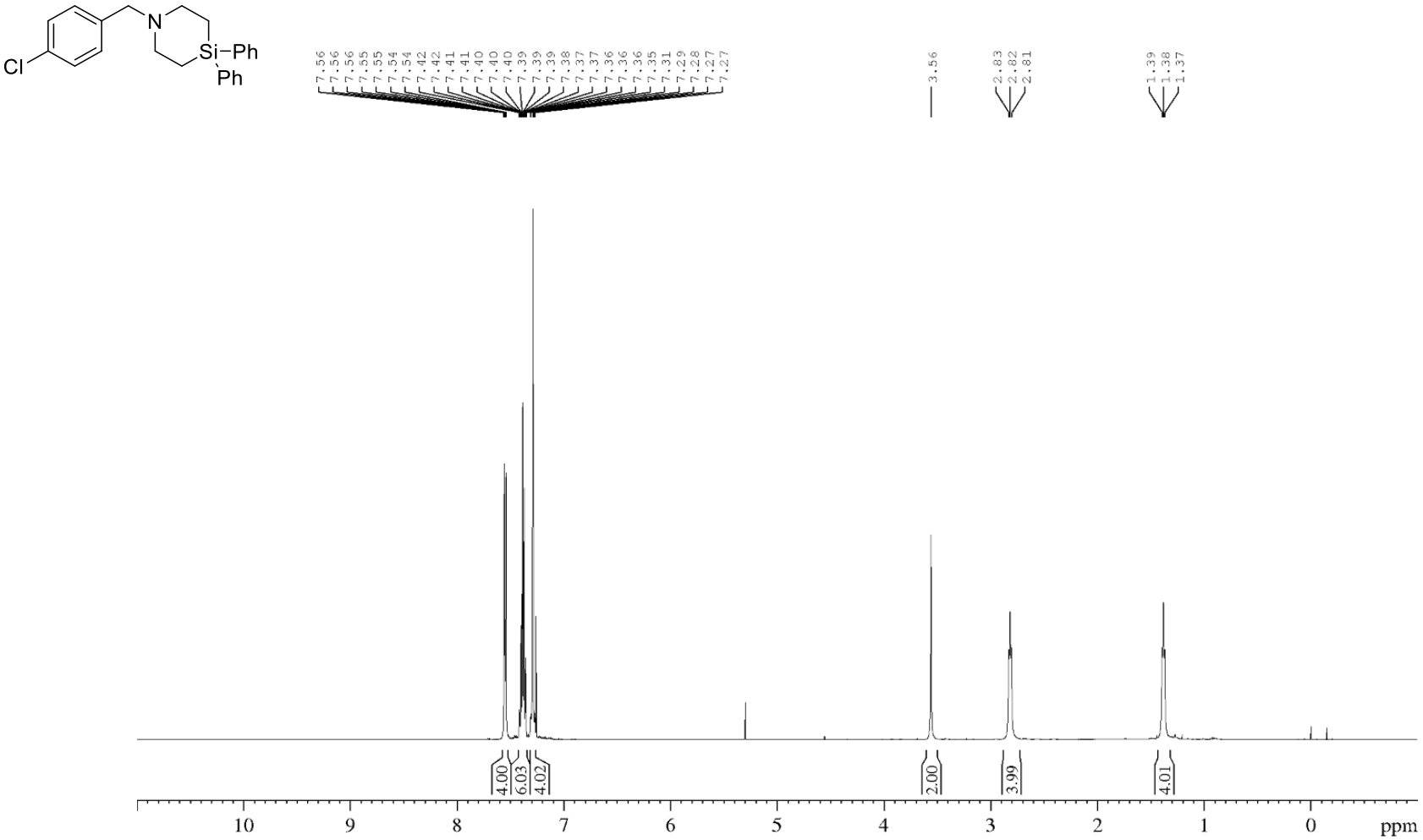


Figure S28. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(4-chlorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ha)**.

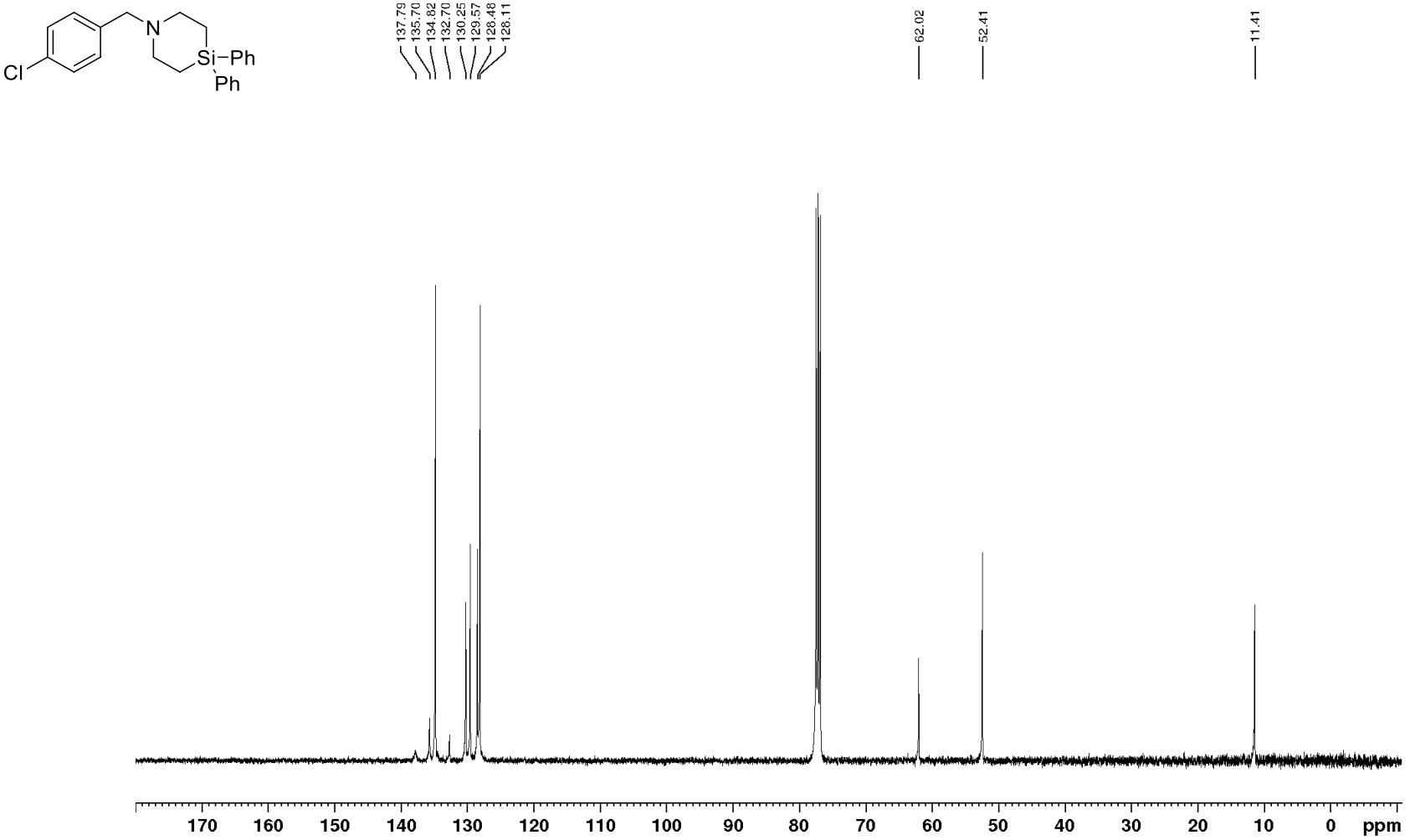


Figure S29. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(4-chlorobenzyl)-4,4-diphenyl-1,4-azasilinane (3ha)**.

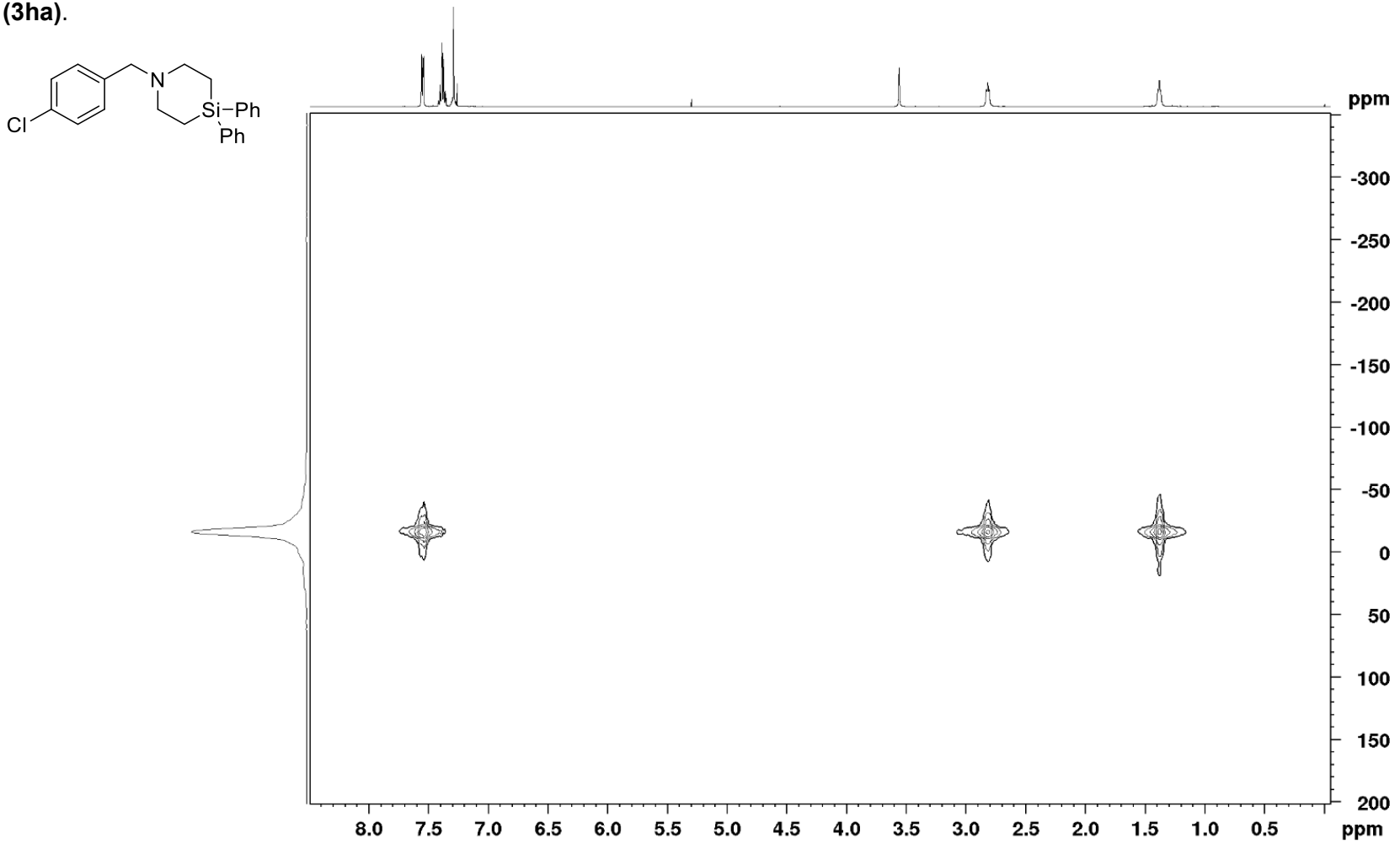


Figure S30. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(4-bromobenzyl)-4,4-diphenyl-1,4-azasilinane (3ia)**.

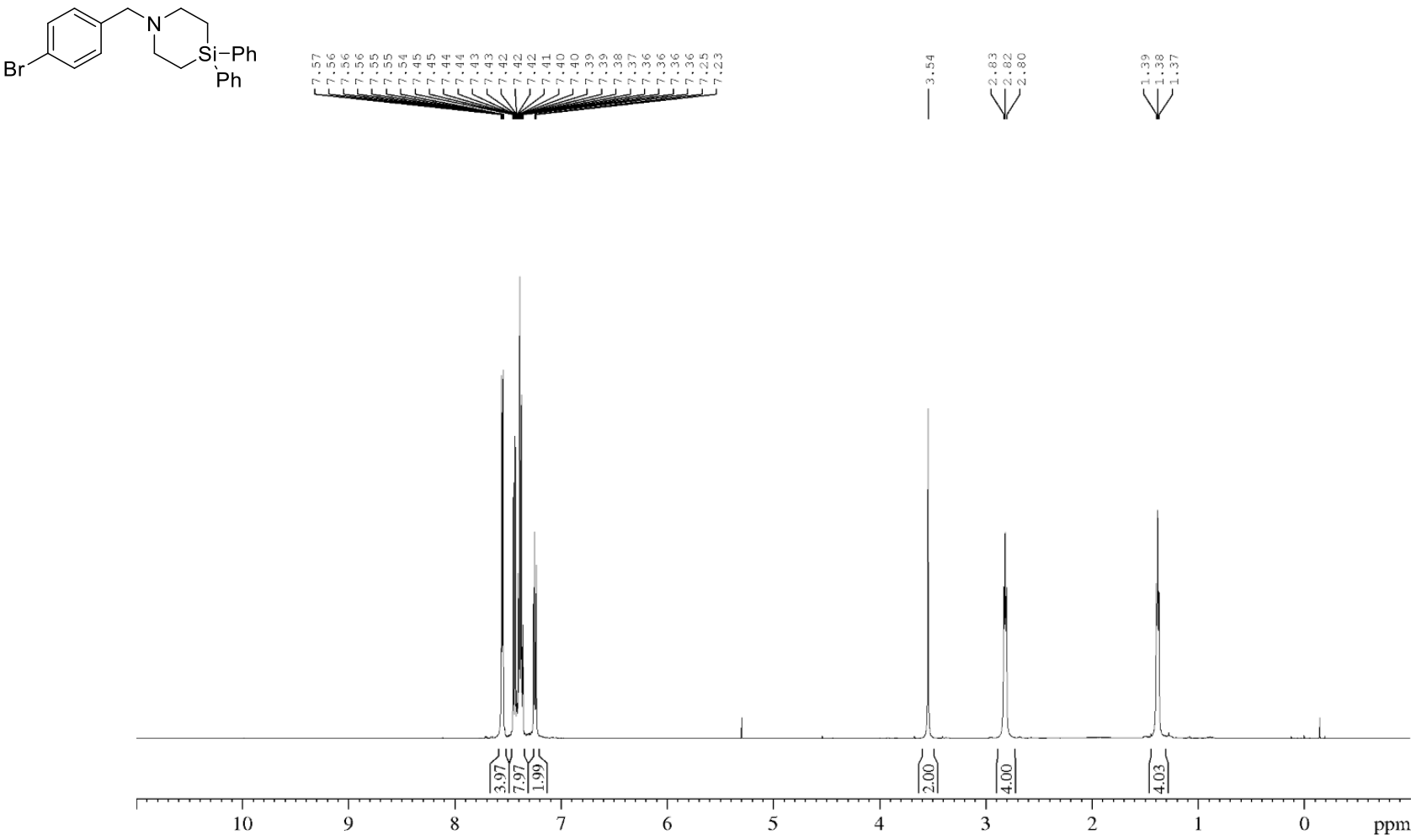


Figure S31. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(4-bromobenzyl)-4,4-diphenyl-1,4-azasilinane (3ia)**.

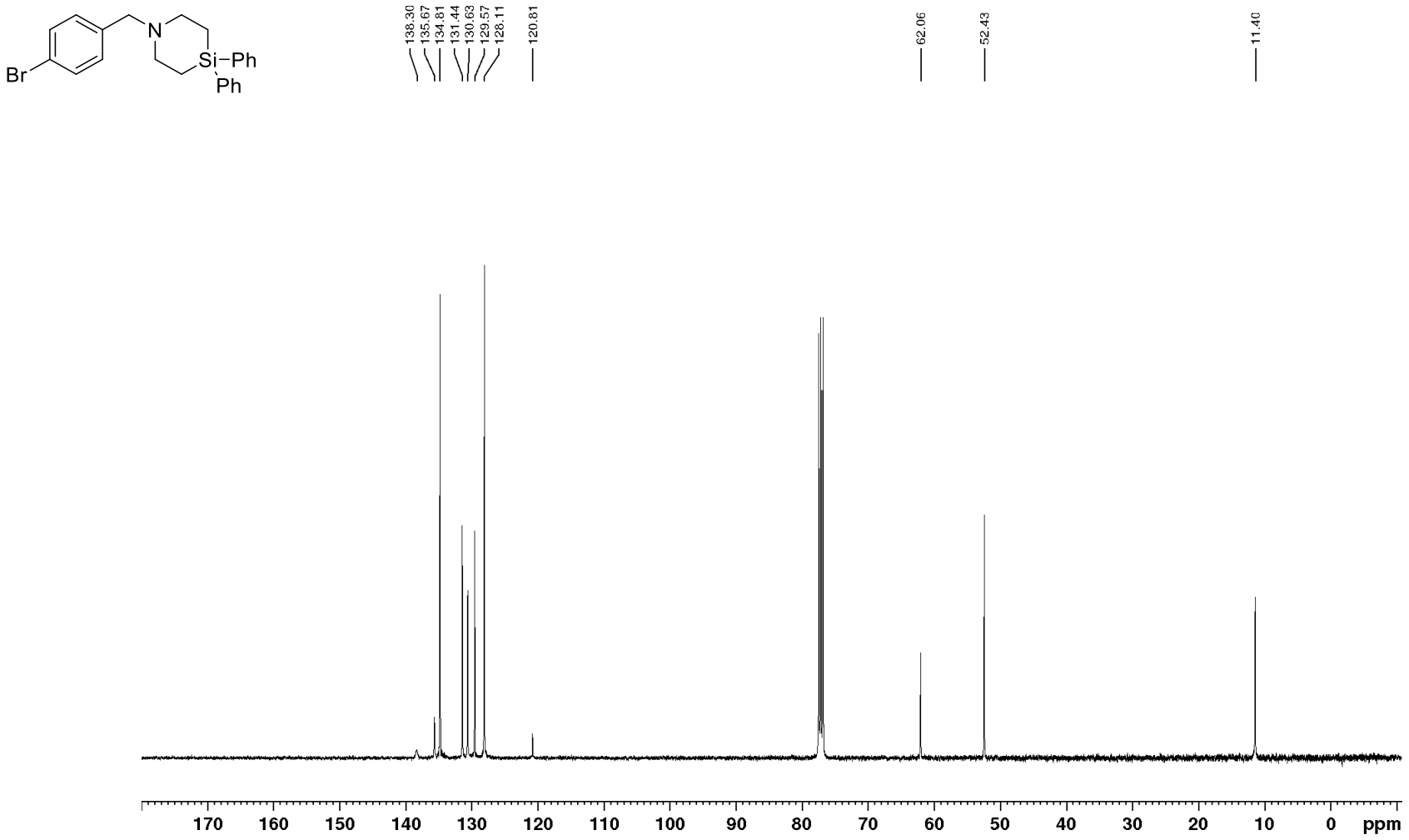


Figure S32. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(4-bromobenzyl)-4,4-diphenyl-1,4-azasilinane (3ia)**.

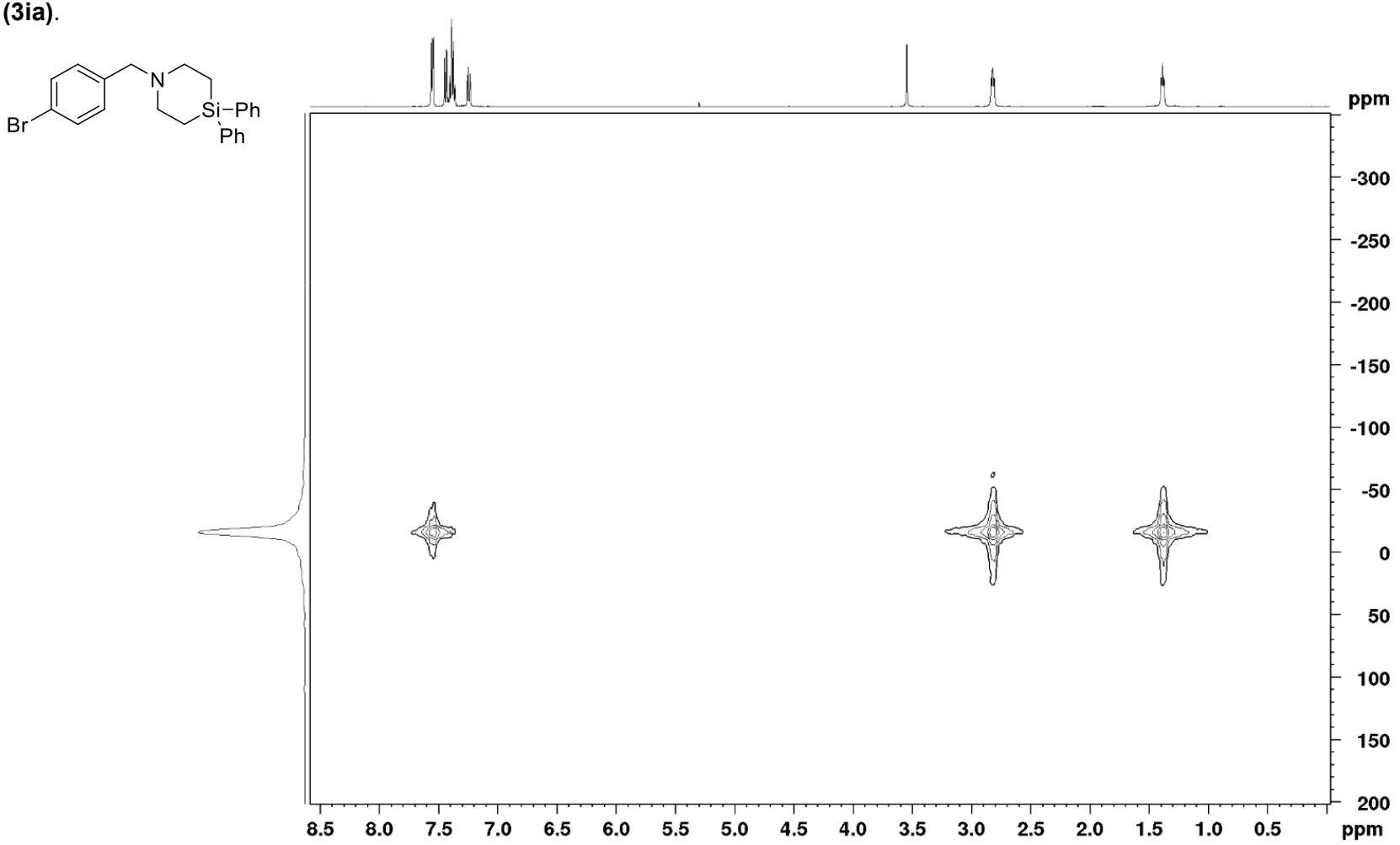


Figure S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(4-iodobenzyl)-4,4-diphenyl-1,4-azasilinane (3ja)**.

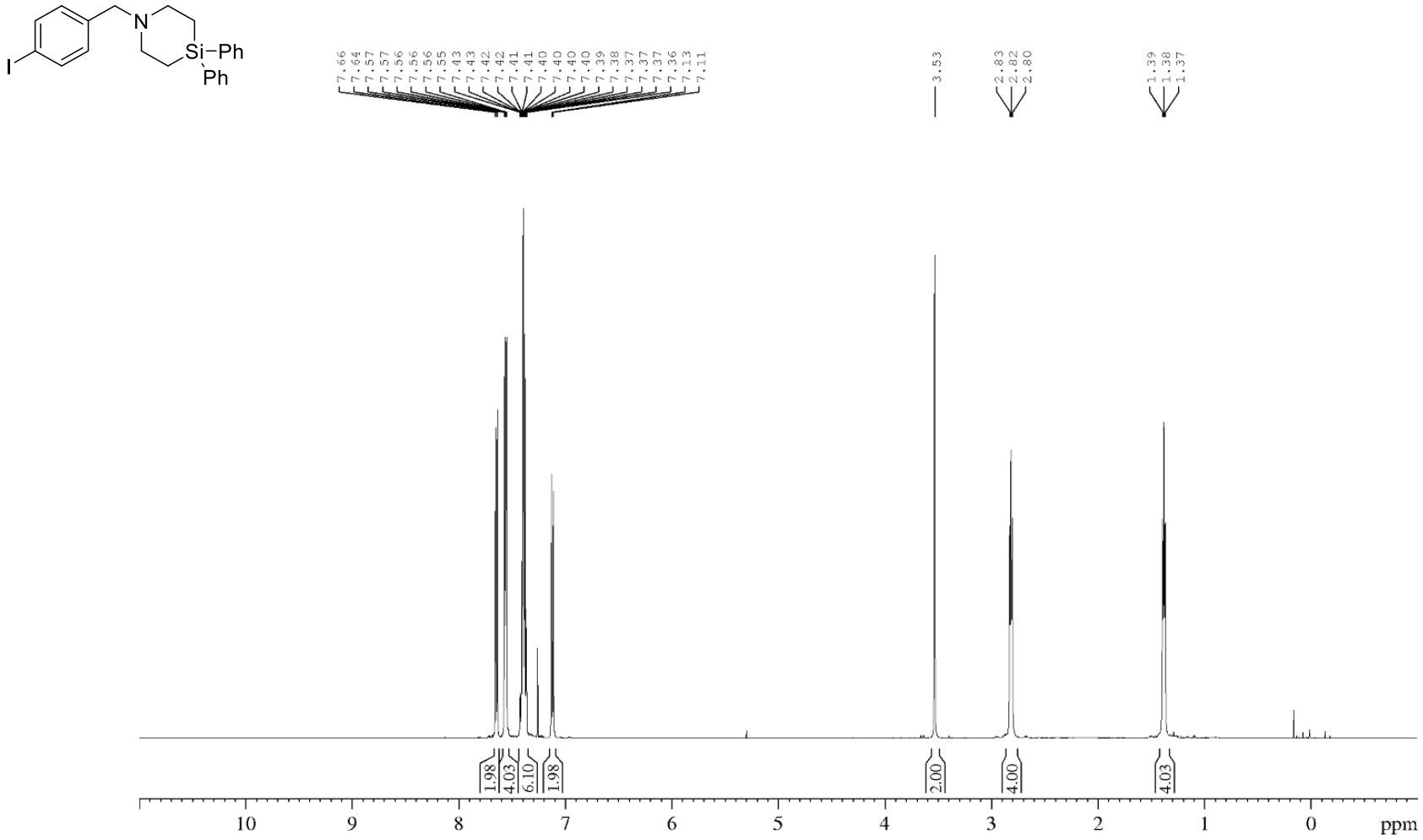


Figure S34. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(4-iodobenzyl)-4,4-diphenyl-1,4-azasilinane (3ja)**.

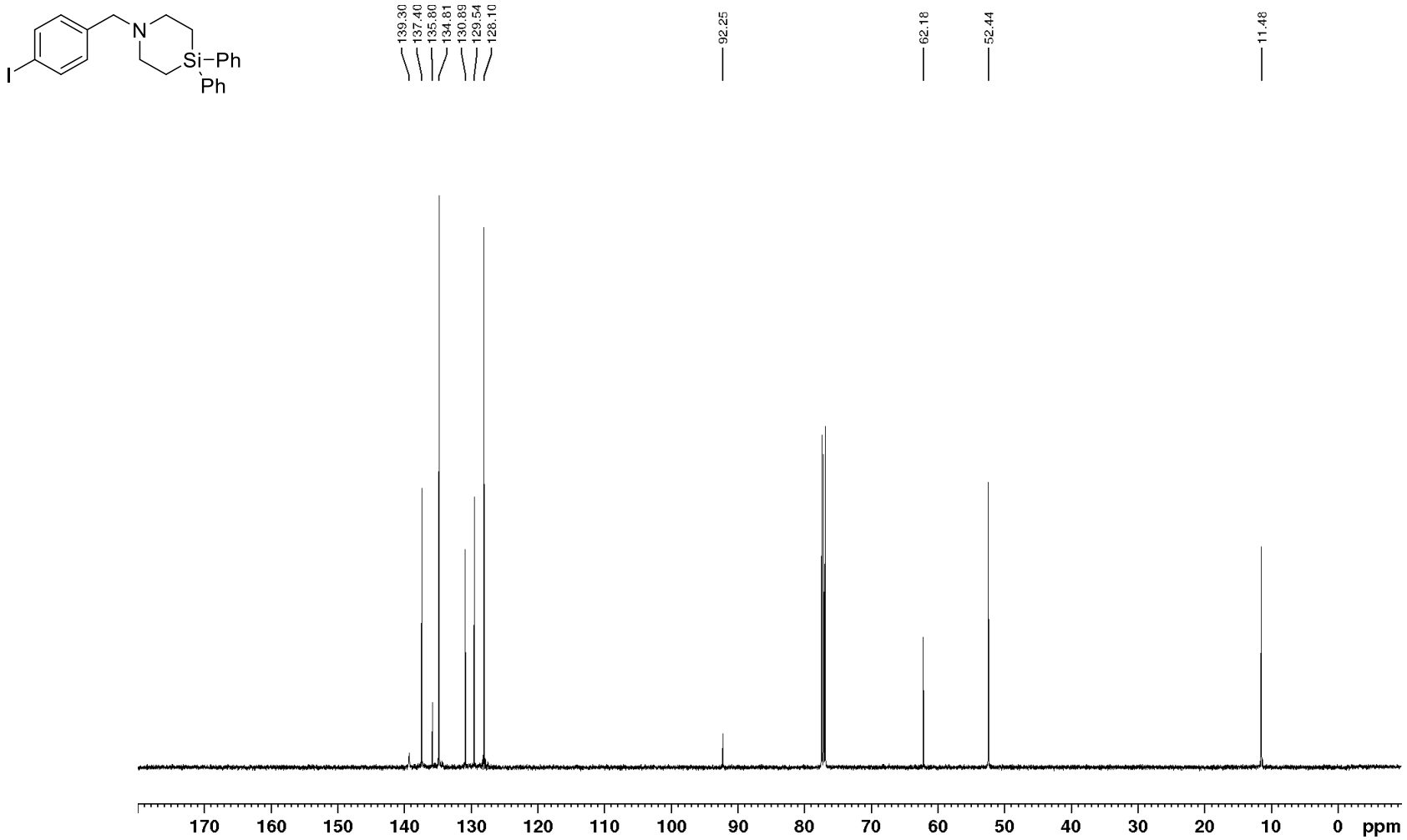


Figure S35. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(4-iodobenzyl)-4,4-diphenyl-1,4-azasilinane (3ja)**.

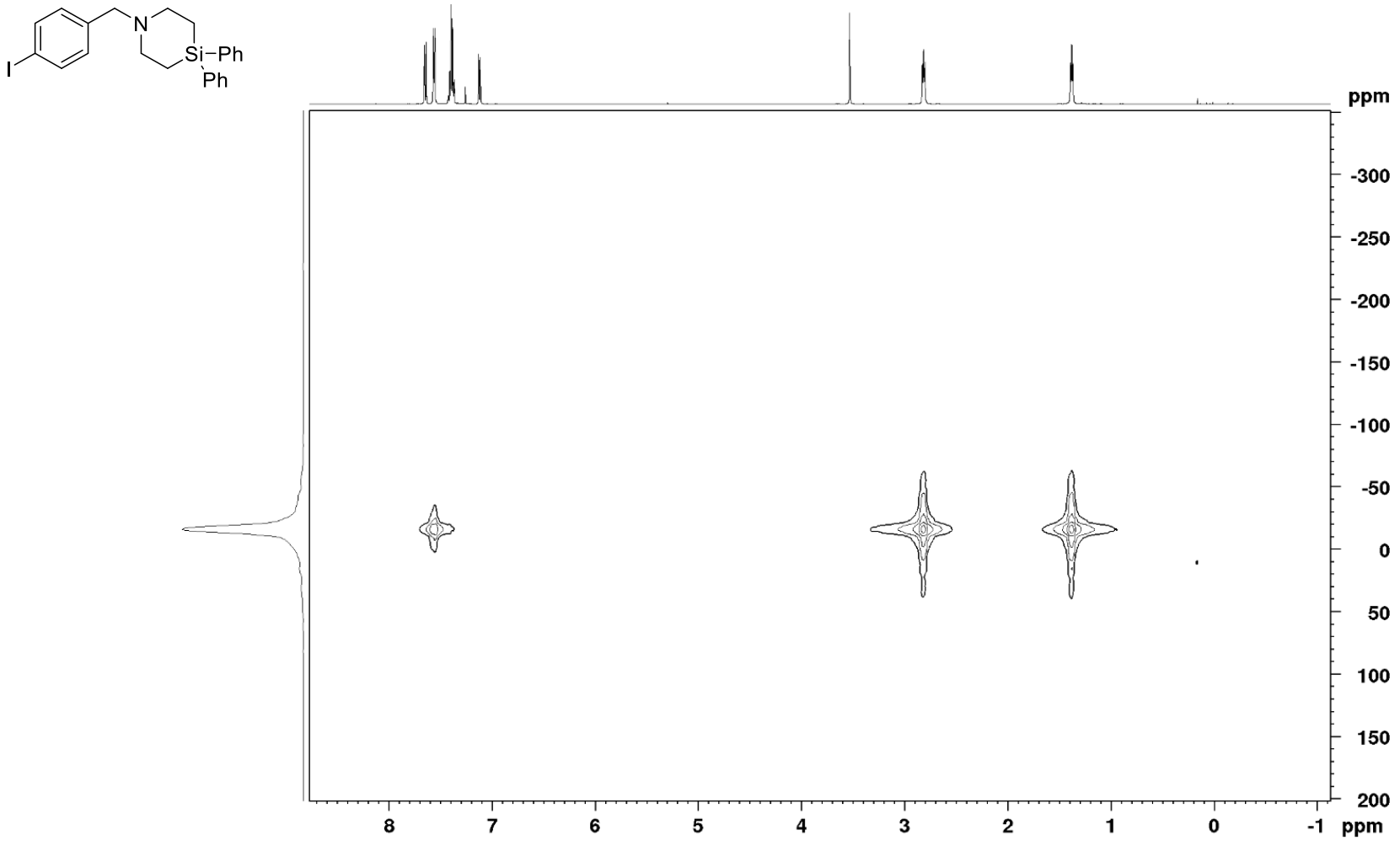


Figure S36. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4,4-diphenyl-1-(4-(trifluoromethyl)benzyl)-1,4-azasilinane (3ka)**.

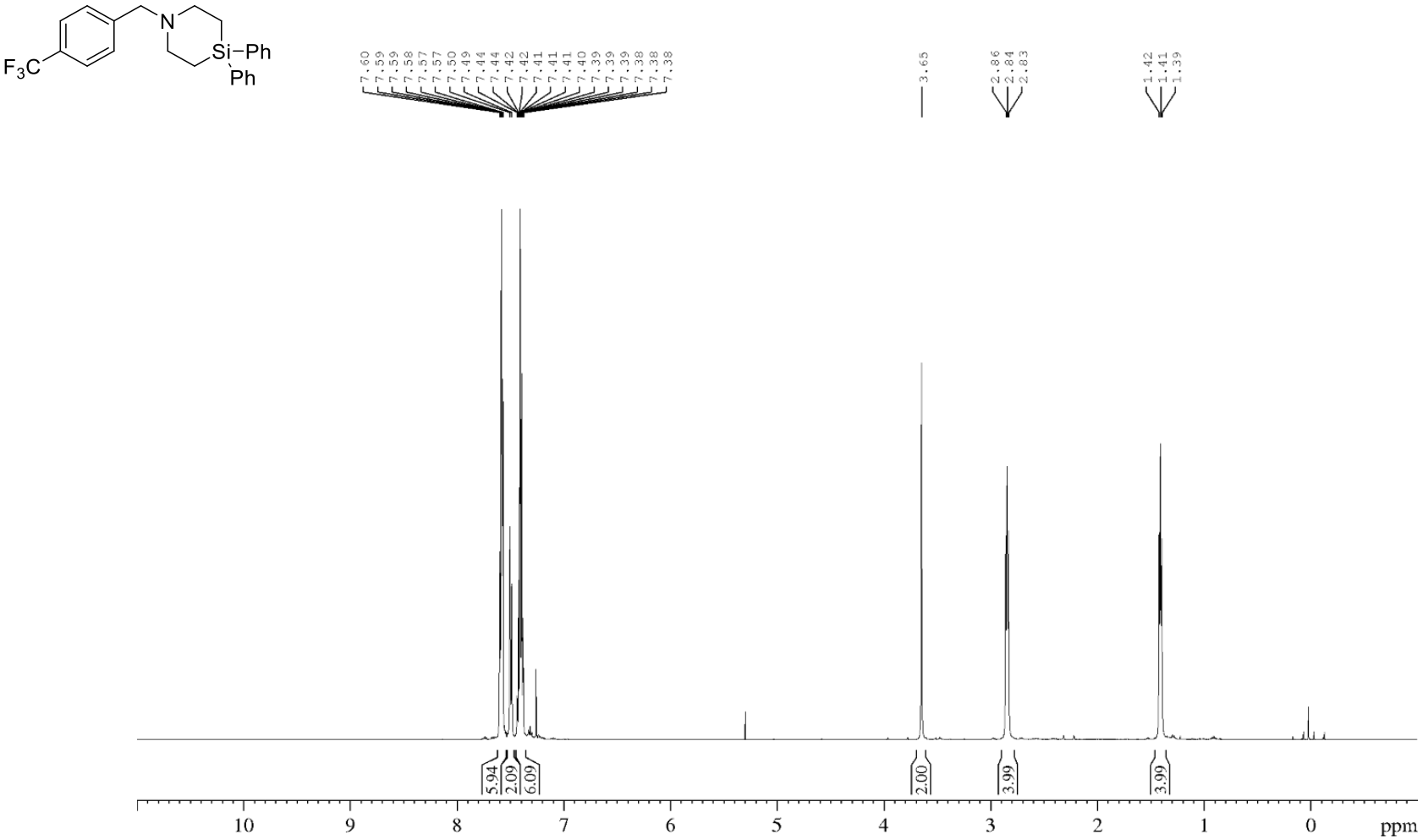


Figure S37. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **4,4-diphenyl-1-(4-(trifluoromethyl)benzyl)-1,4-azasilinane (3ka)**.

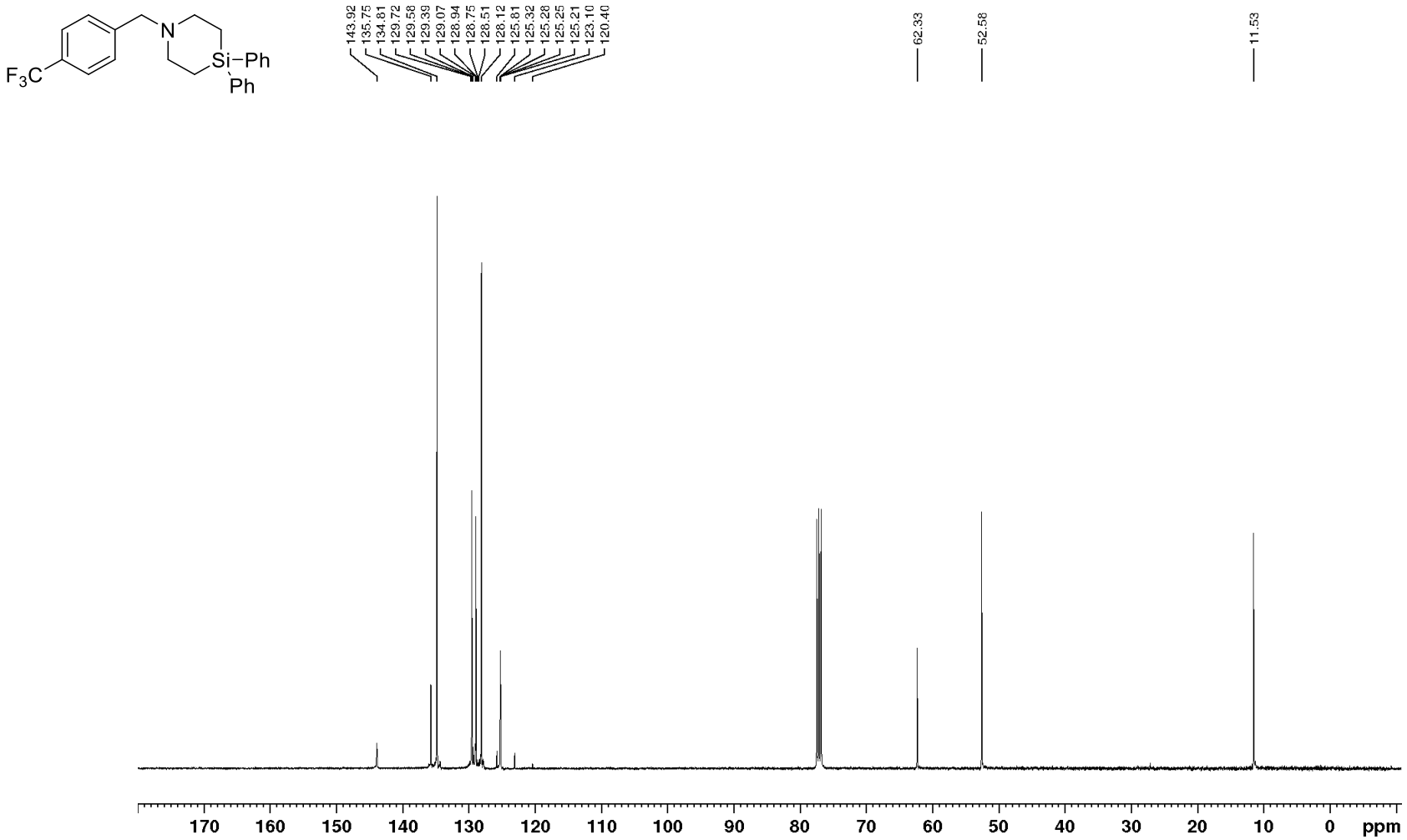


Figure S38. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of **4,4-diphenyl-1-(4-(trifluoromethyl)benzyl)-1,4-azasilinane (3ka)**.

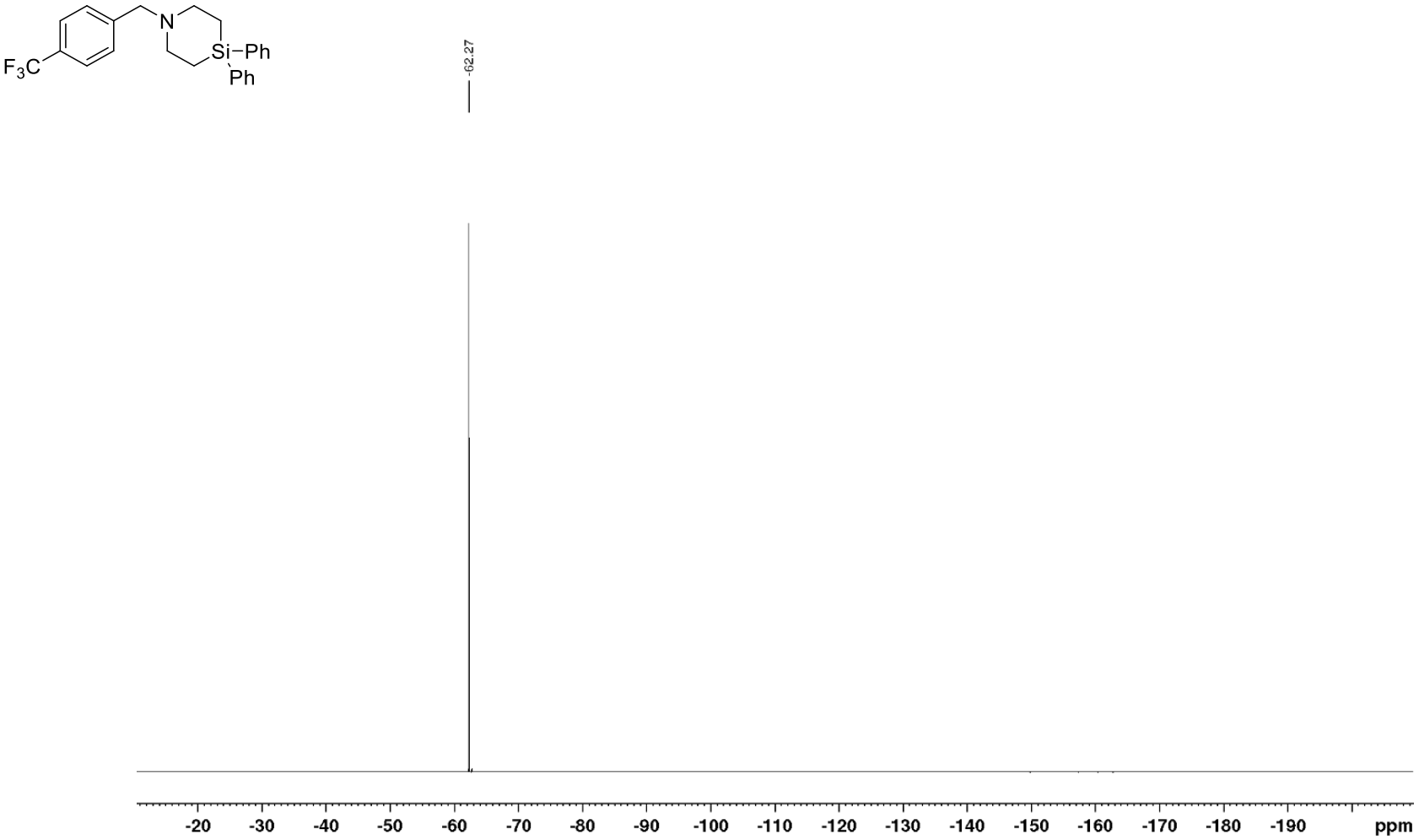


Figure S39. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4,4-diphenyl-1-(4-(trifluoromethyl)benzyl)-1,4-azasilinane (3ka)**.

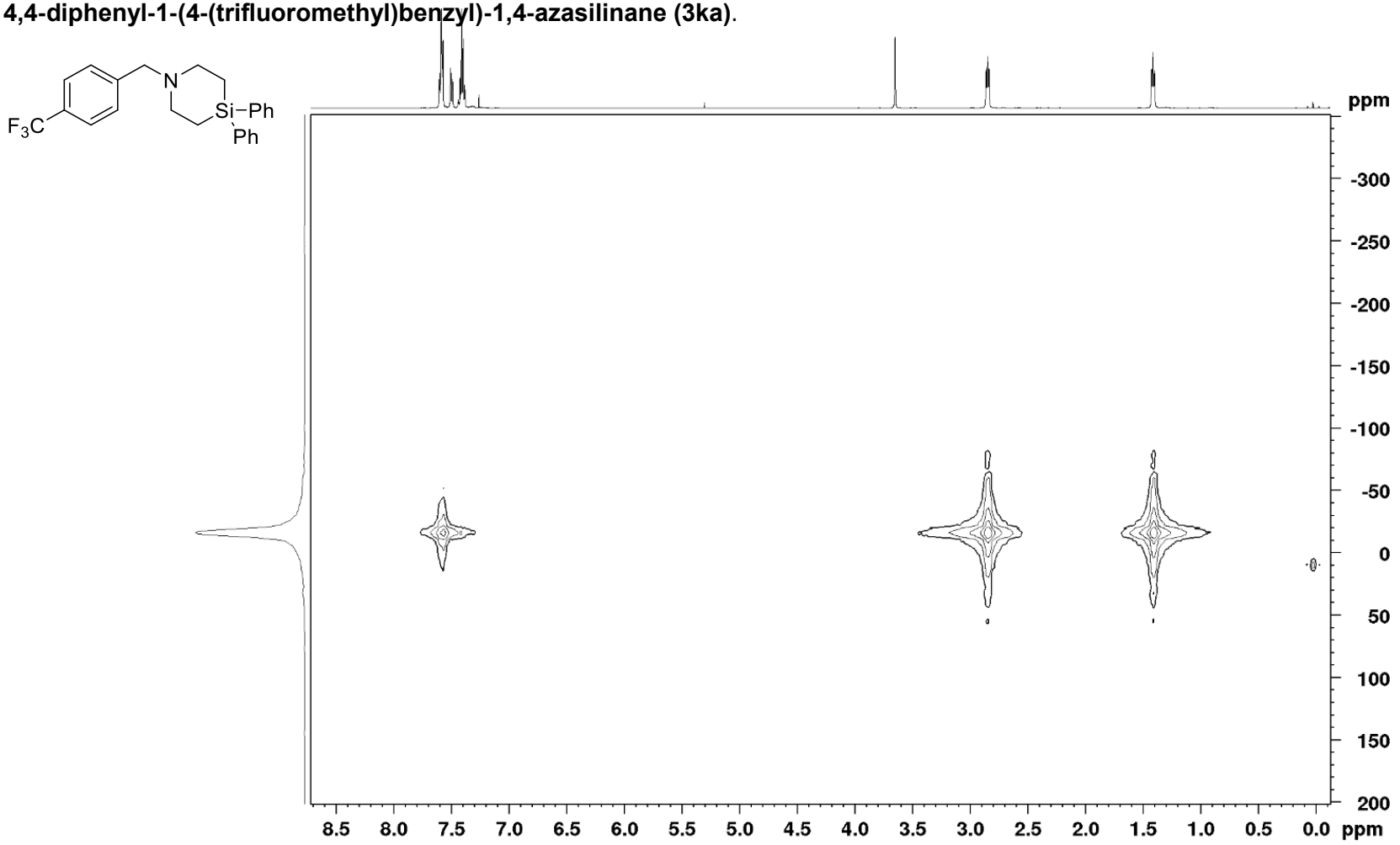


Figure S40. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **3-((4,4-diphenyl-1,4-azasilinan-1-yl)methyl)phenol (3la)**.

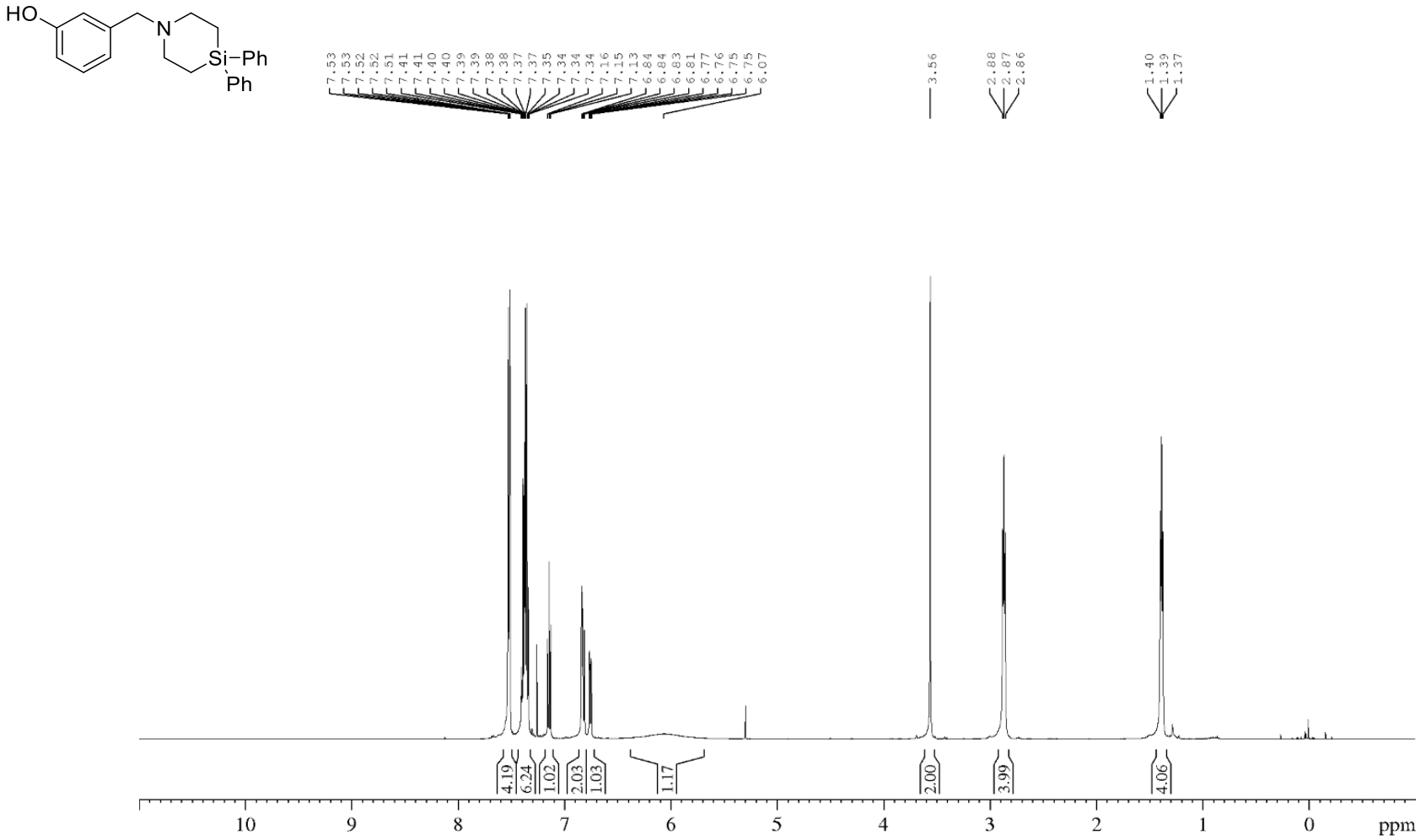


Figure S41. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **3-((4,4-diphenyl-1,4-azasilinan-1-yl)methyl)phenol (3la)**.

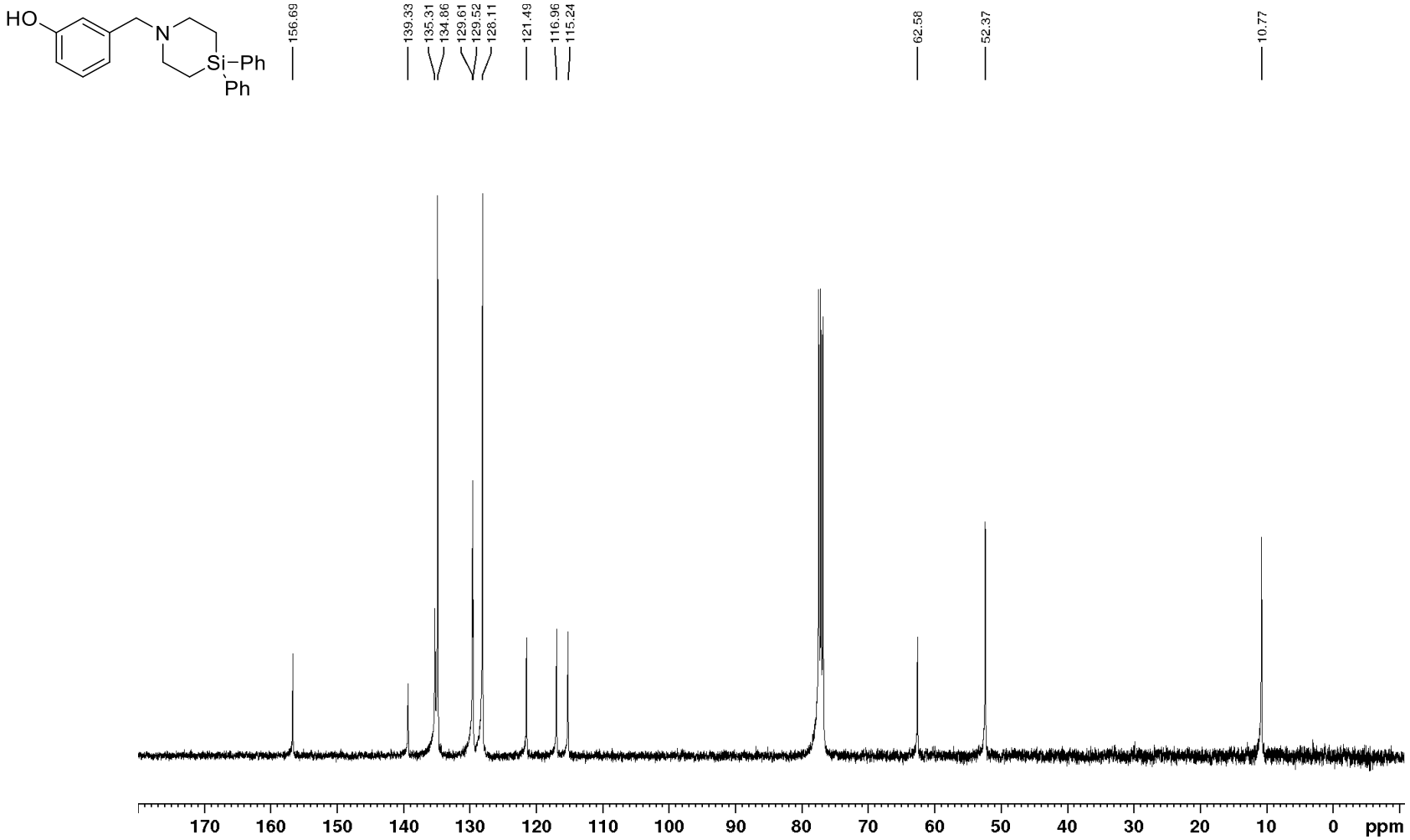


Figure S42. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3-((4,4-diphenyl-1,4-azasilinan-1-yl)methyl)phenol (3la)**.

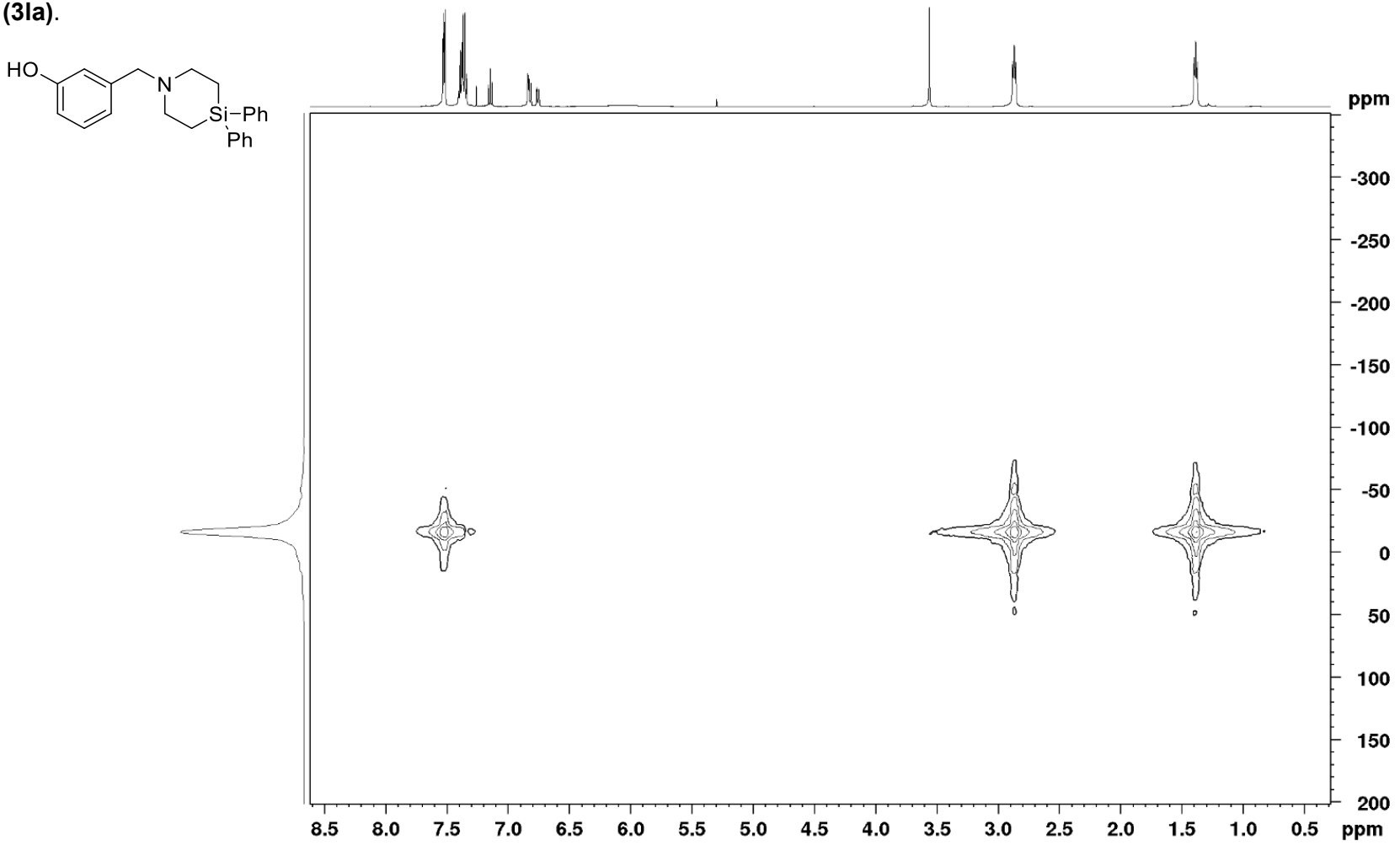


Figure S43. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-(naphthalen-2-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ma)**.

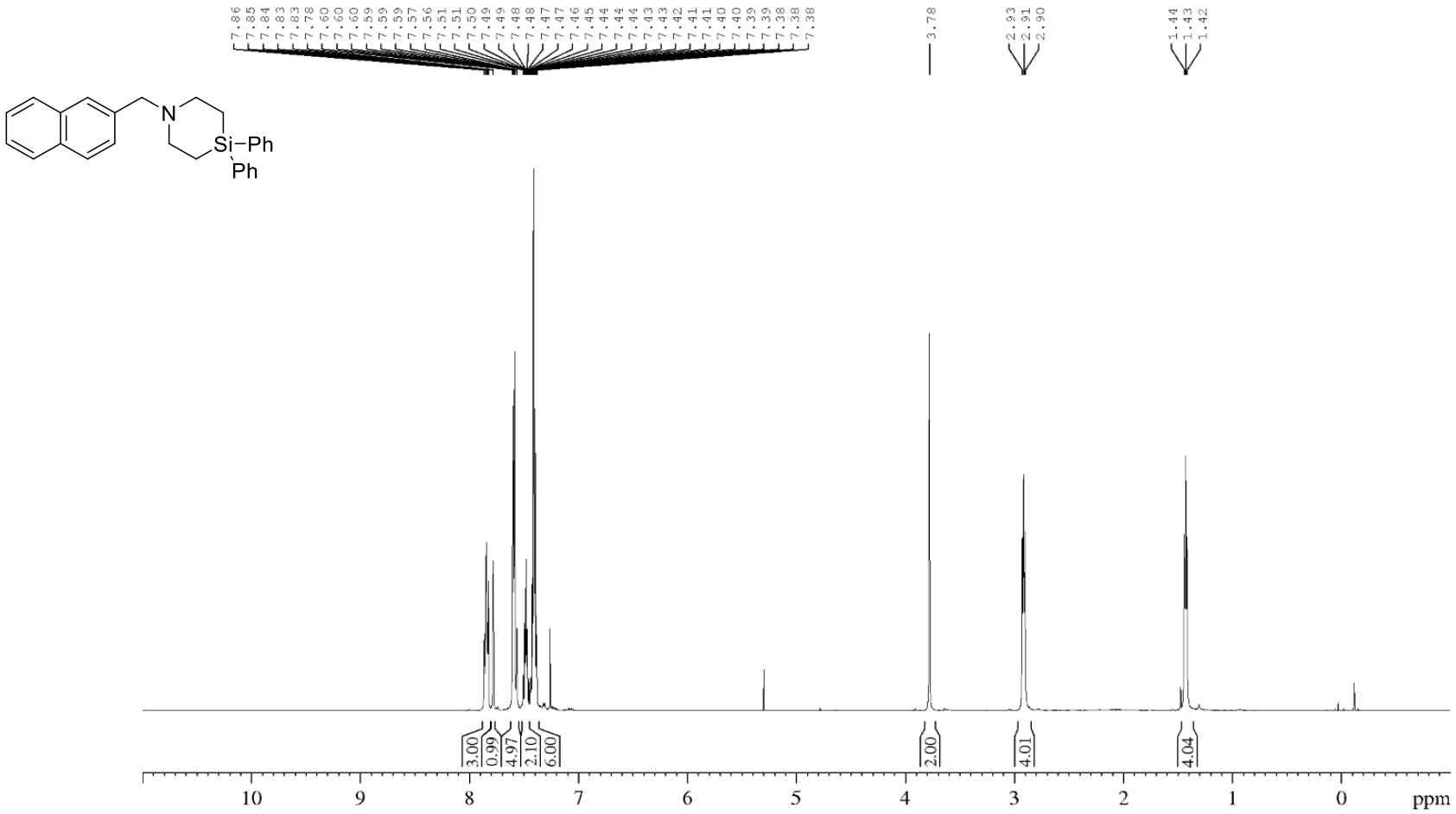


Figure S44. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-(naphthalen-2-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ma)**.

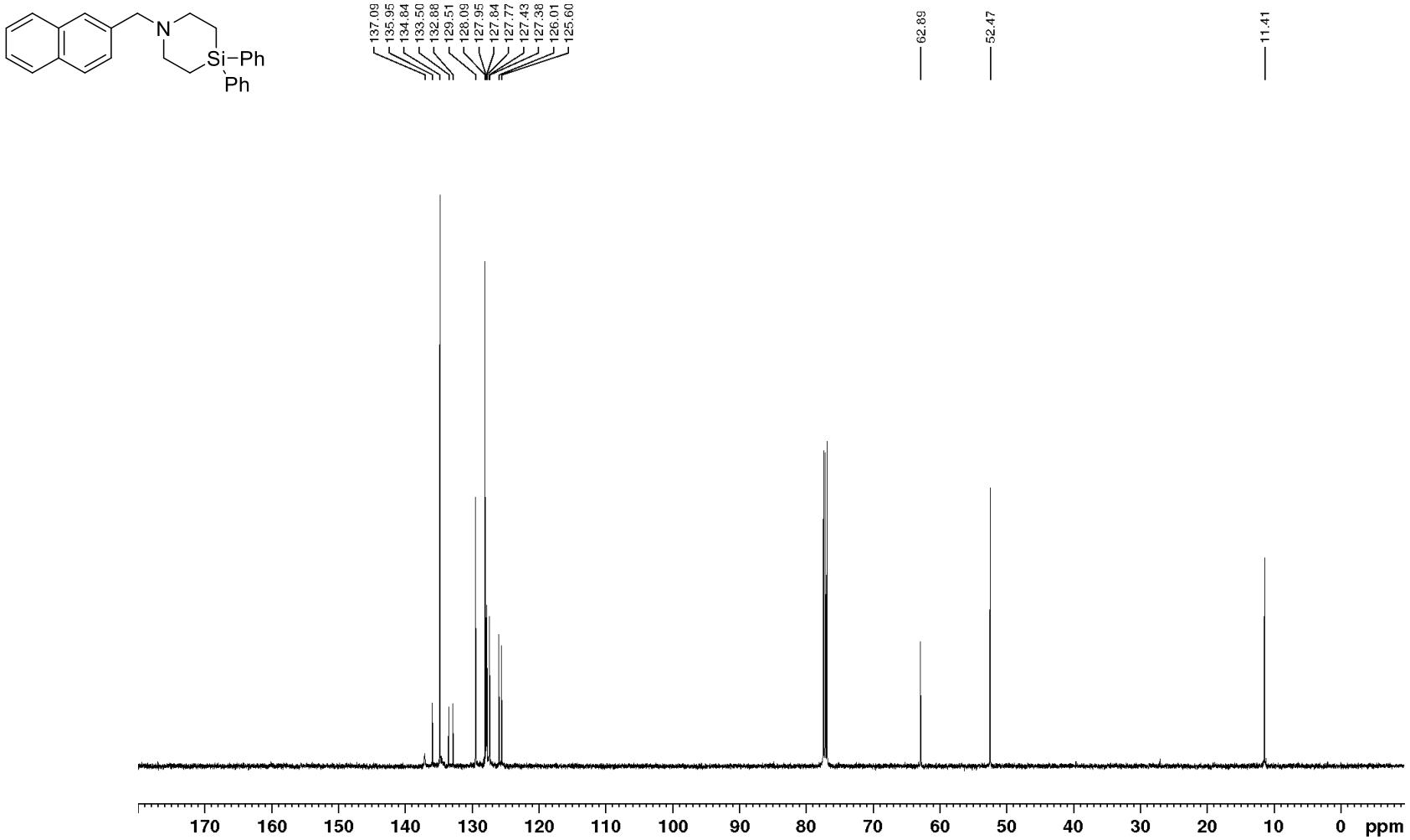


Figure S45. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-(naphthalen-2-ylmethyl)-4,4-diphenyl-1,4-azasilinane (3ma)**.

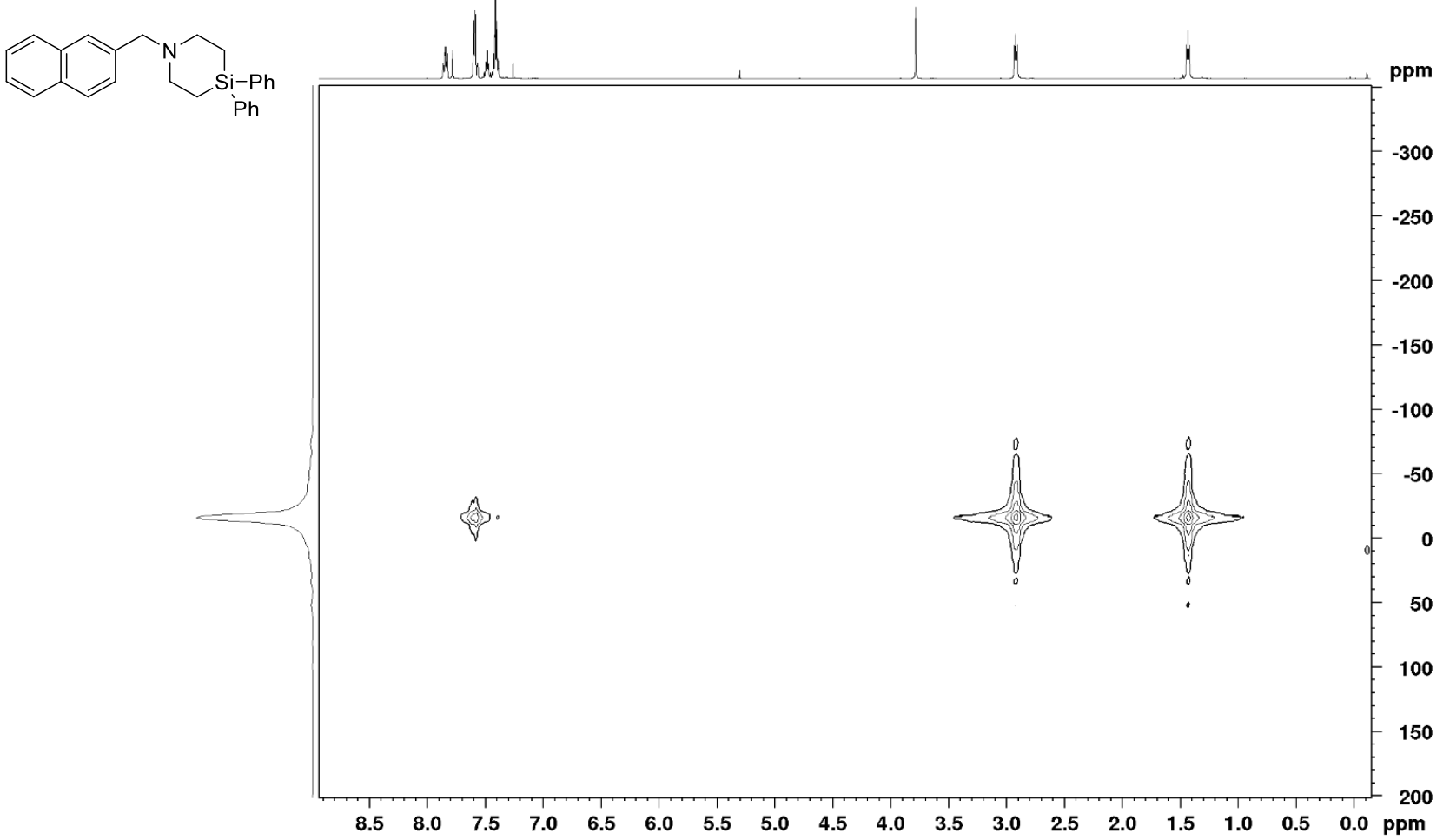


Figure S46. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1,4-bis((4,4-diphenyl-1,4-azasilinan-1-yl)methyl)benzene (3na)**.

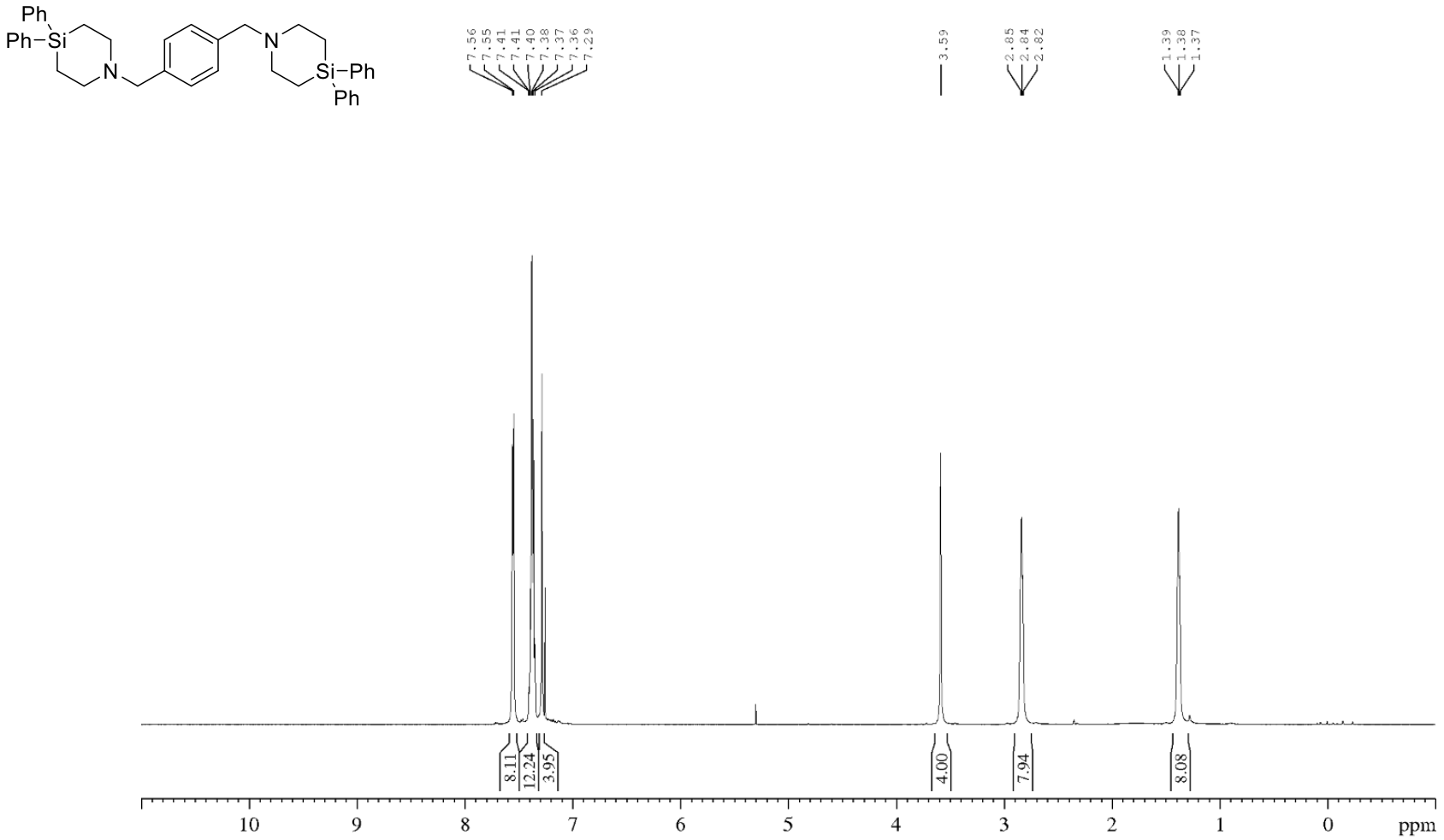


Figure S47. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1,4-bis((4,4-diphenyl-1,4-azasilinan-1-yl)methyl)benzene (3na)**.

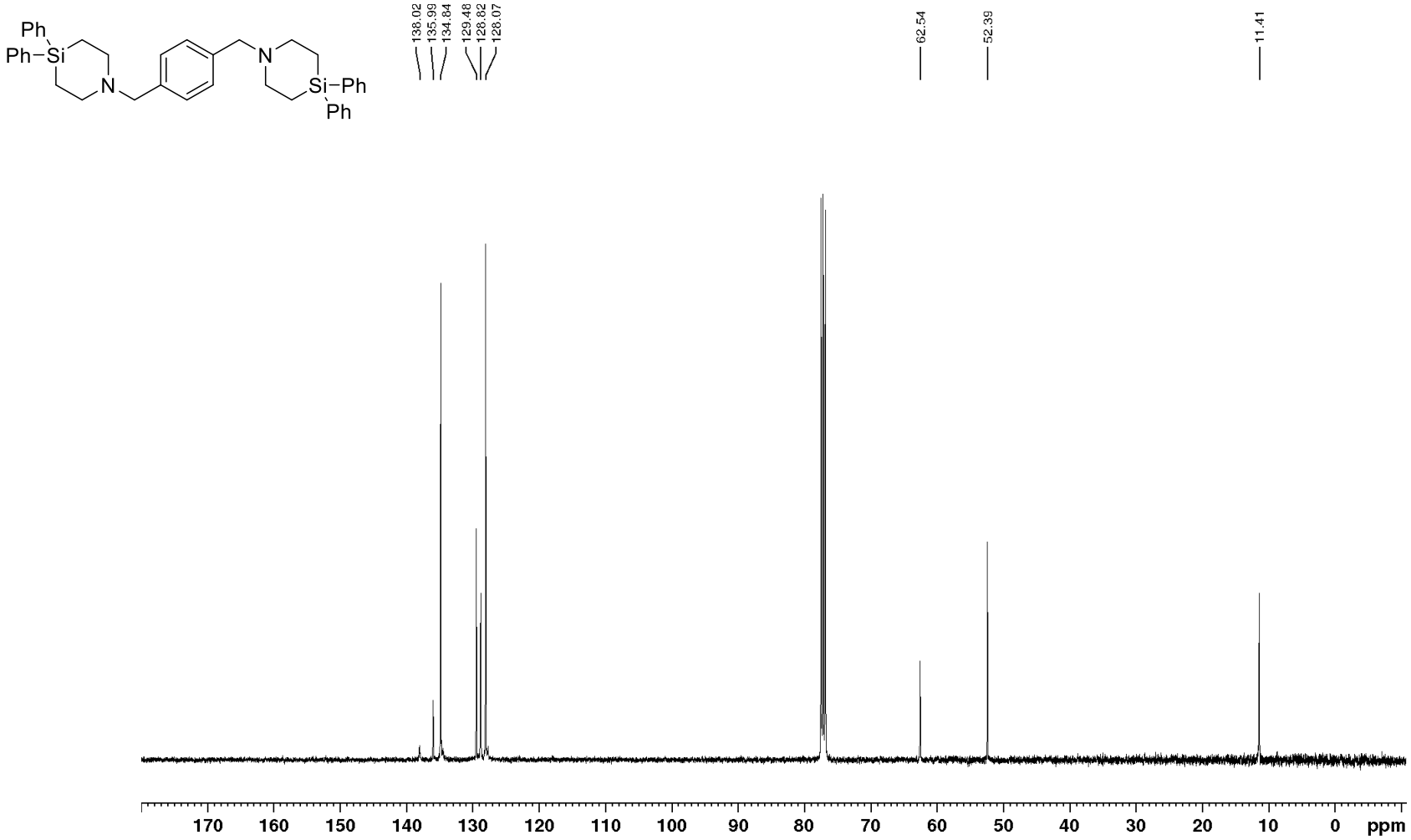


Figure S48. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1,4-bis((4,4-diphenyl-1,4-azasilinan-1-yl)methyl)benzene (3na)**.

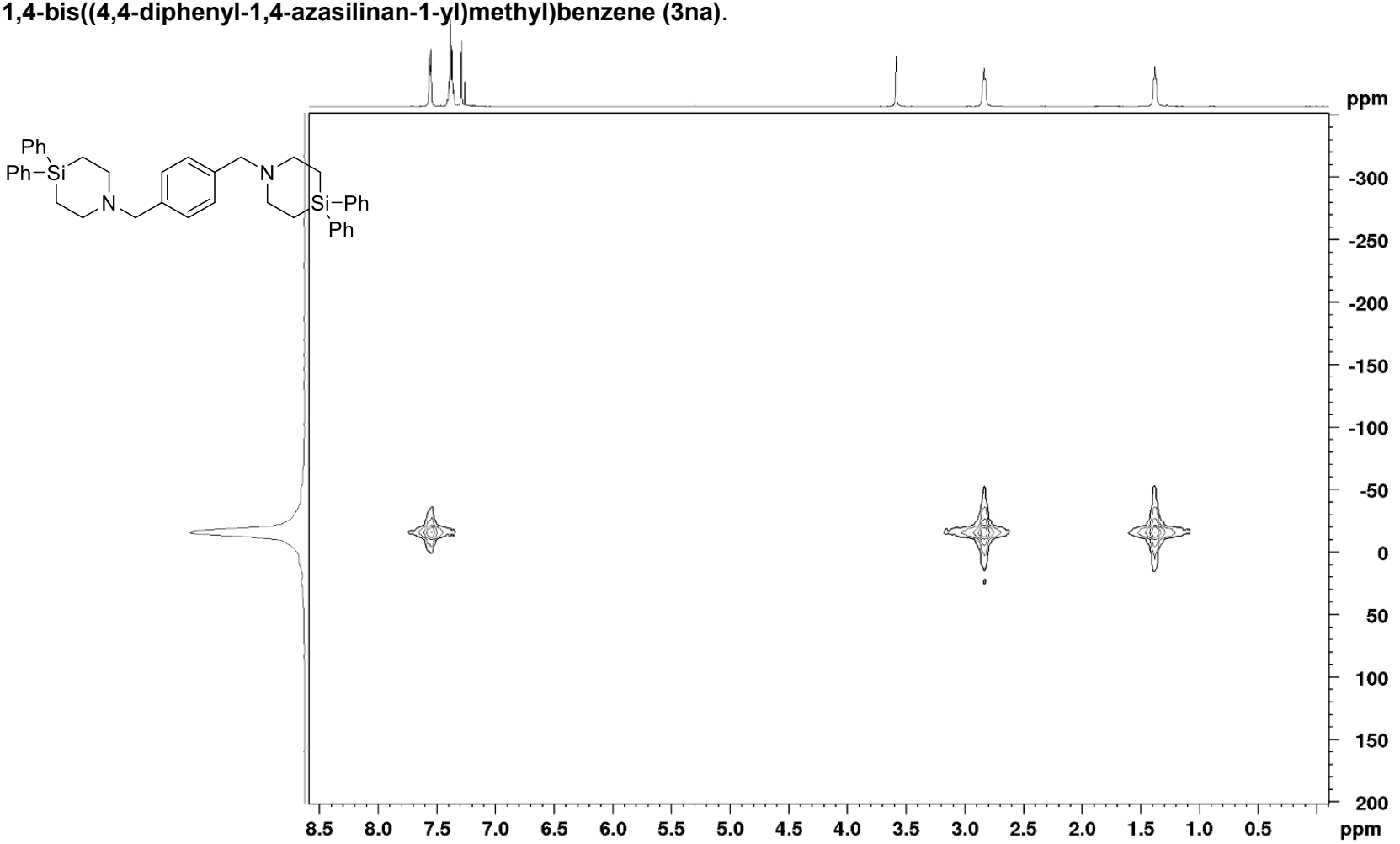


Figure S49. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-cyclohexyl-4,4-diphenyl-1,4-azasilinane (3oa)**.

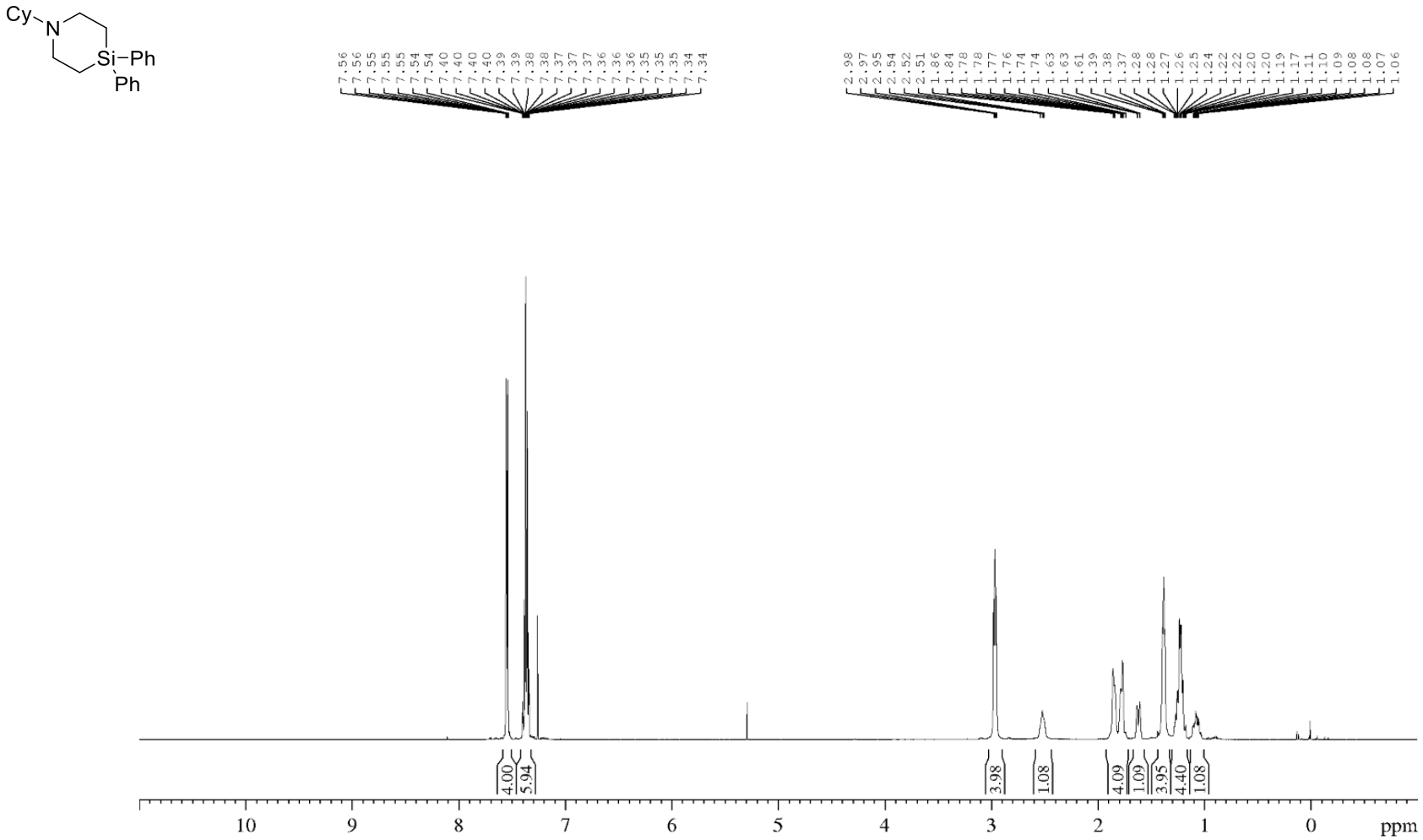


Figure S50. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-cyclohexyl-4,4-diphenyl-1,4-azasilinane (3oa)**.

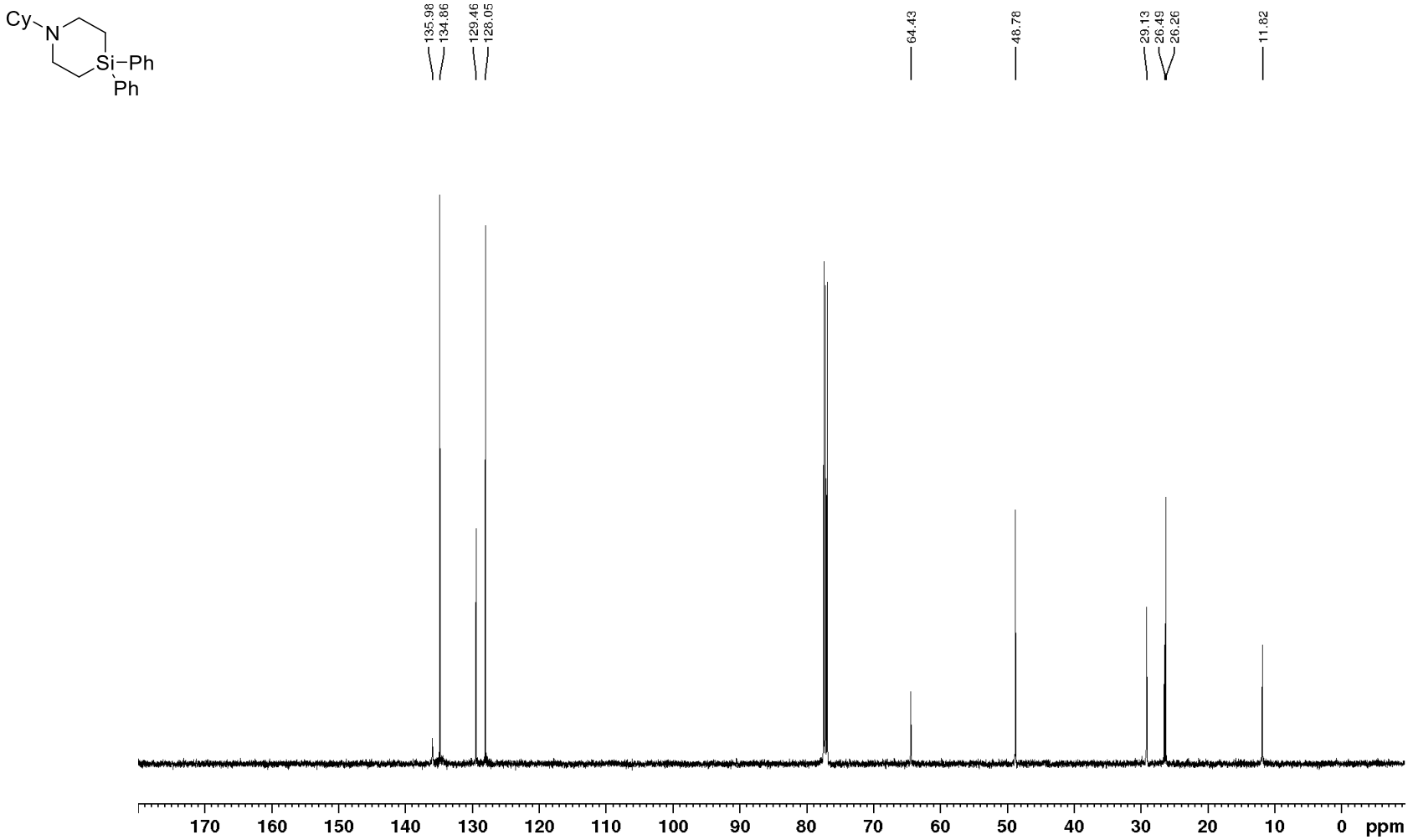


Figure S51. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-cyclohexyl-4,4-diphenyl-1,4-azasilinane (3oa)**.

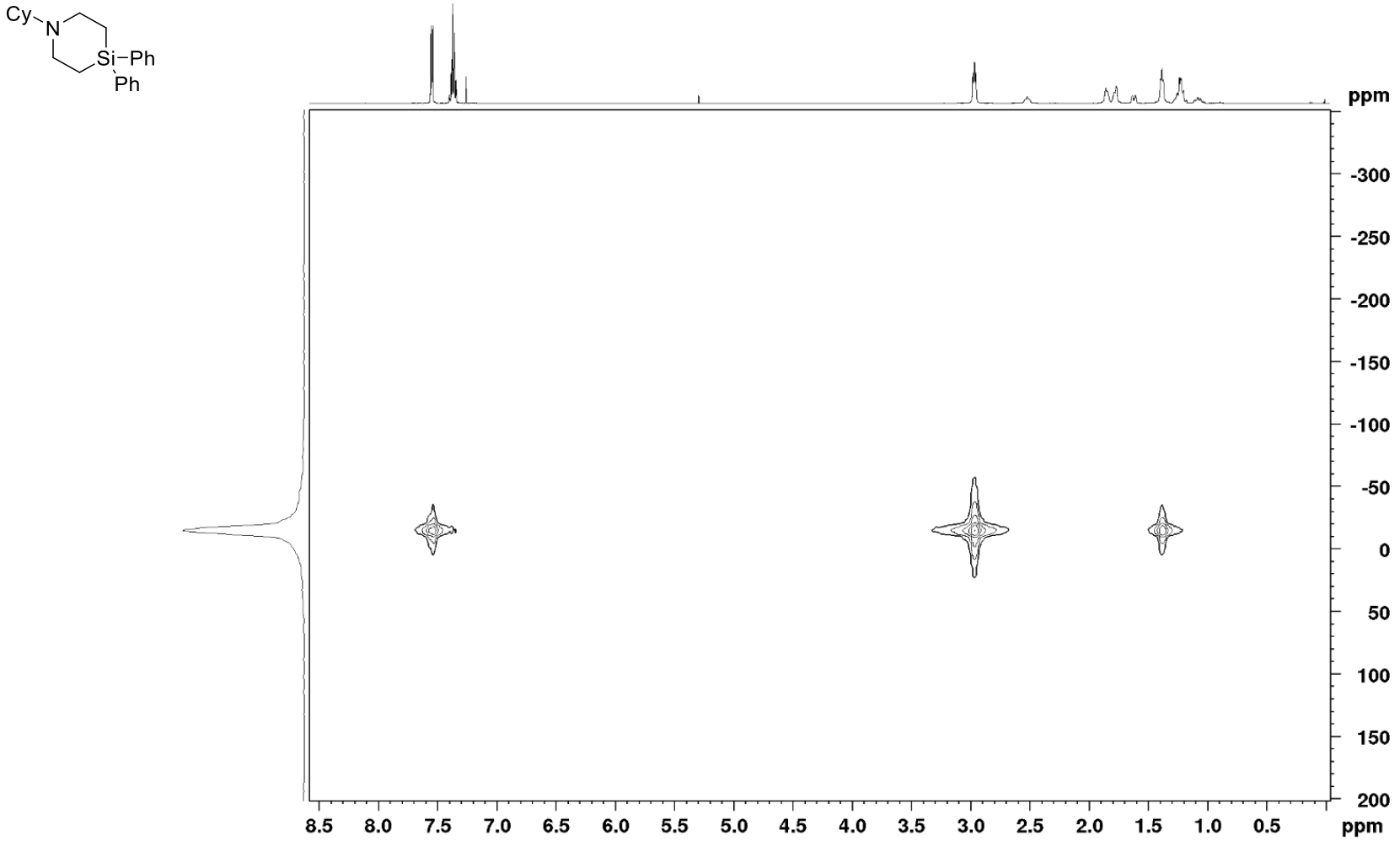


Figure S52. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-ethyl-4,4-diphenyl-1,4-azasilinane (3pa)**.

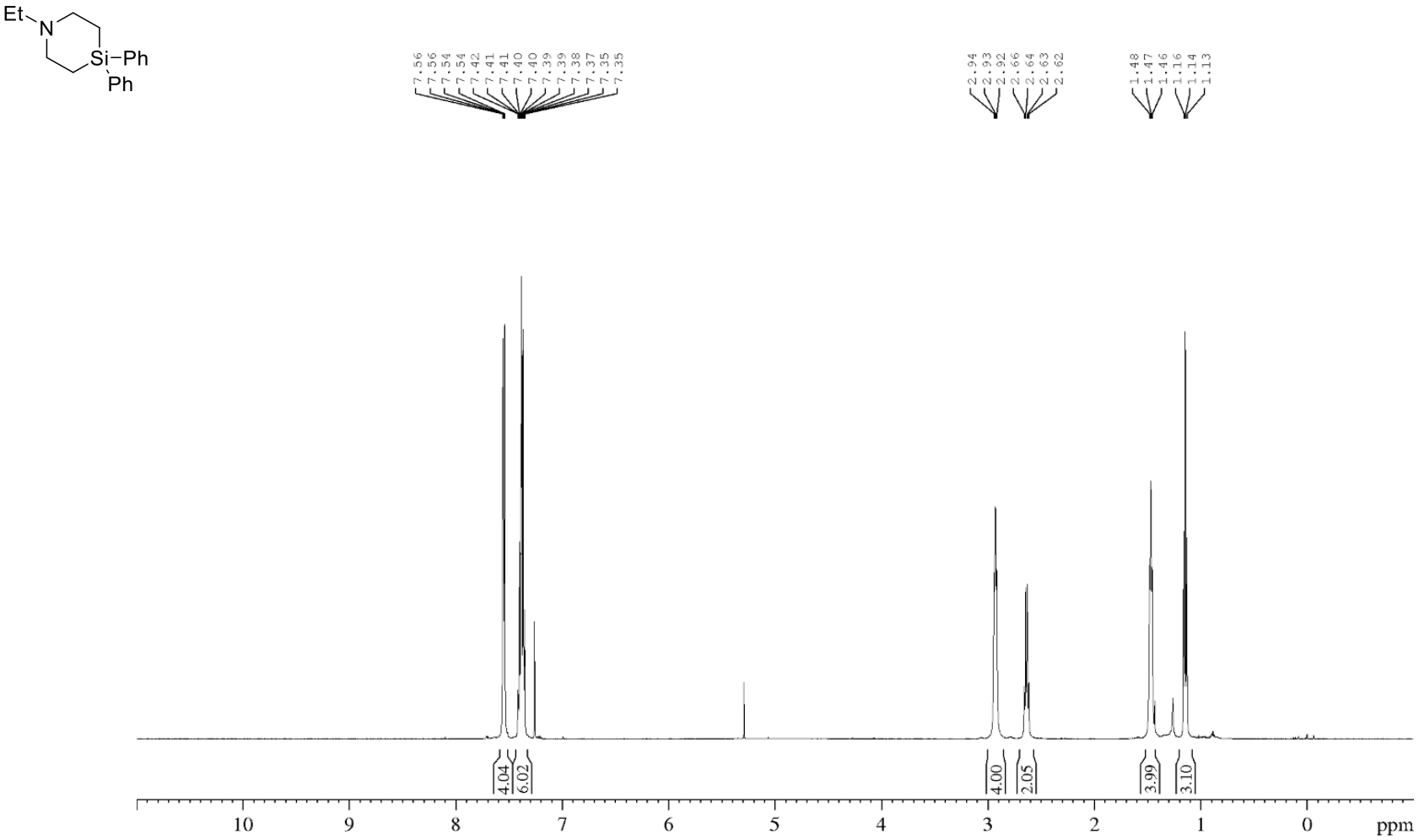


Figure S53. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-ethyl-4,4-diphenyl-1,4-azasilinane (3pa)**.

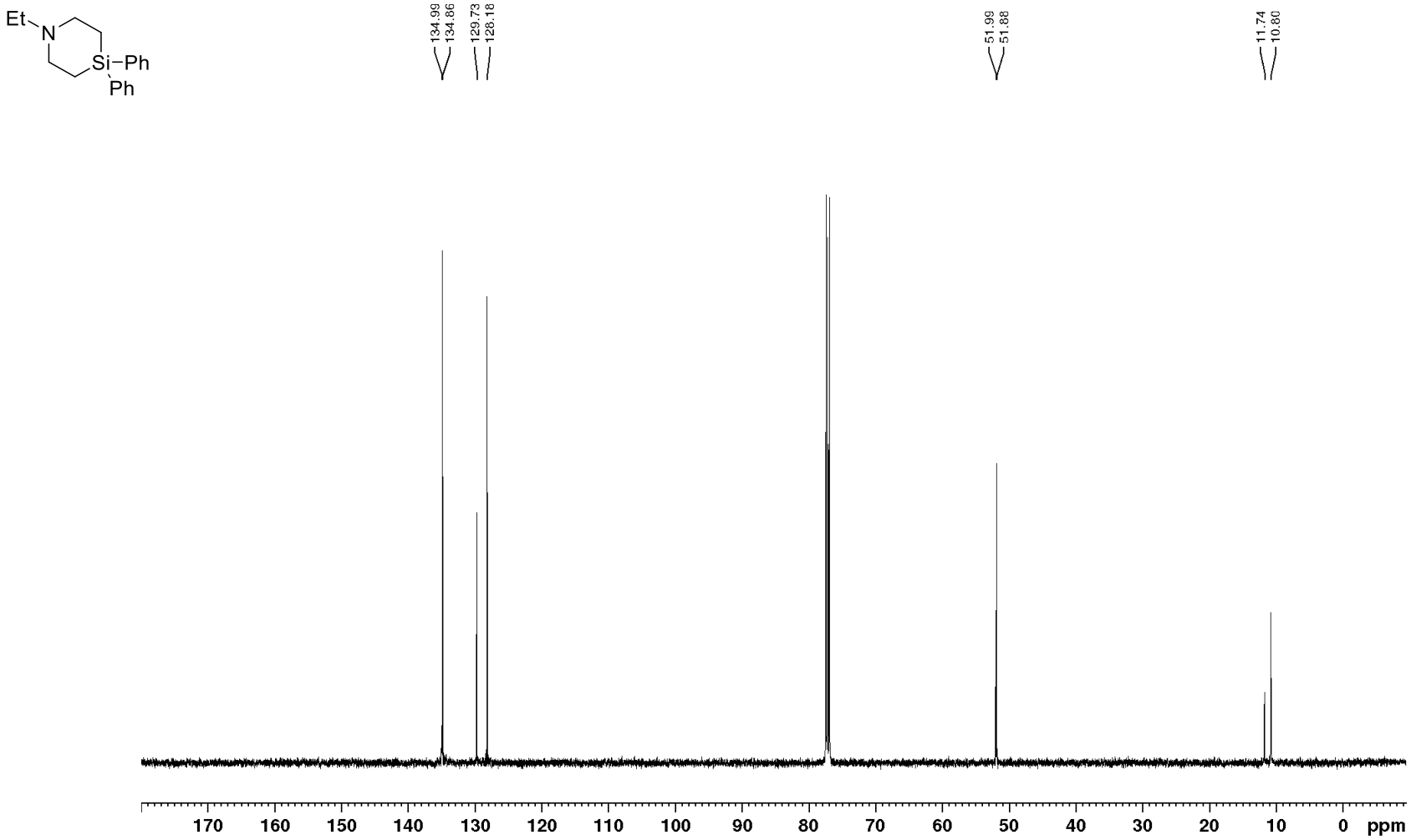


Figure S54. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-ethyl-4,4-diphenyl-1,4-azasilinane (3pa)**.

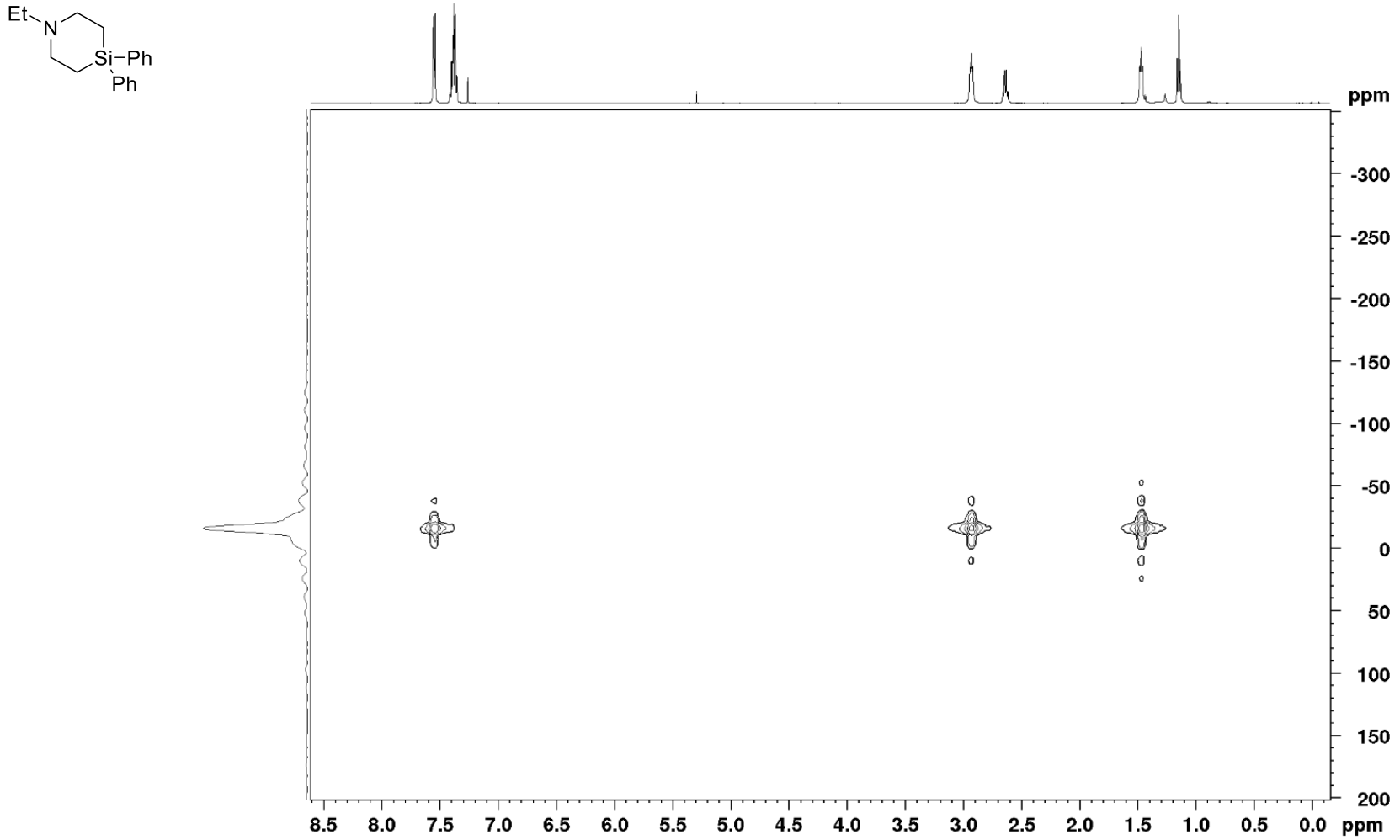


Figure S55. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-methyl-4,4-diphenyl-1,4-azasilinane (3qa)**.

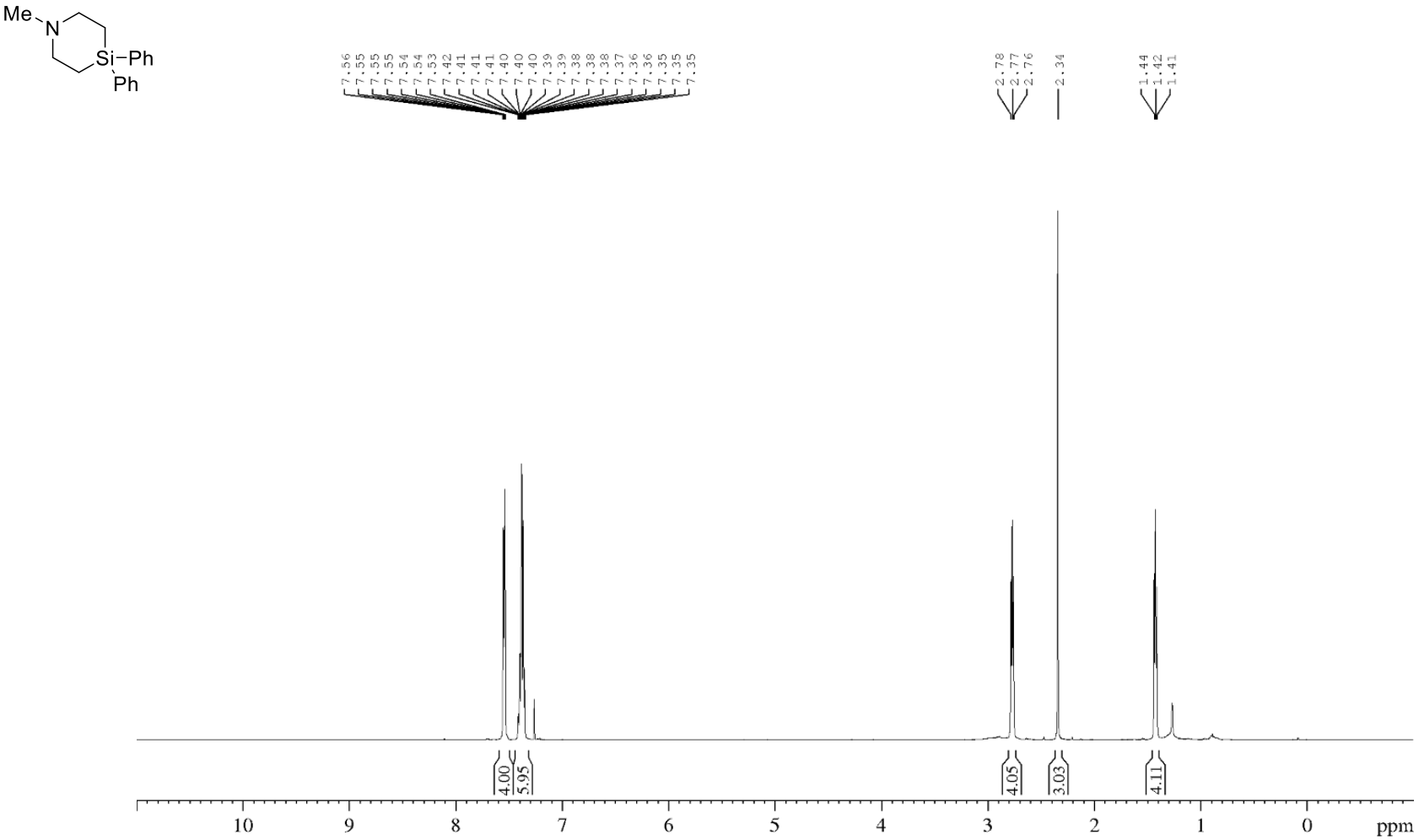


Figure S56. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-methyl-4,4-diphenyl-1,4-azasilinane (3qa)**.

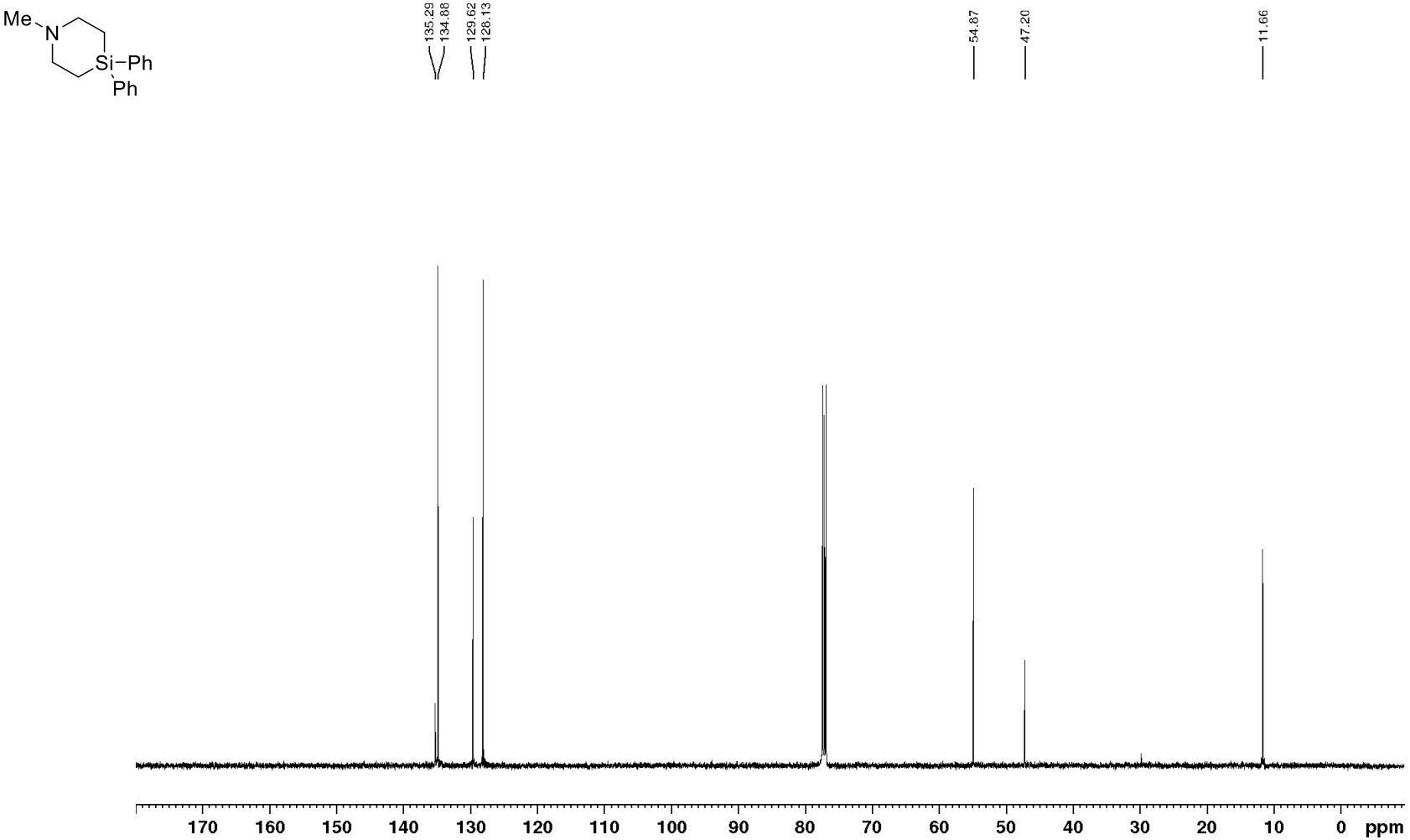


Figure S57. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-methyl-4,4-diphenyl-1,4-azasilinane (3qa)**.

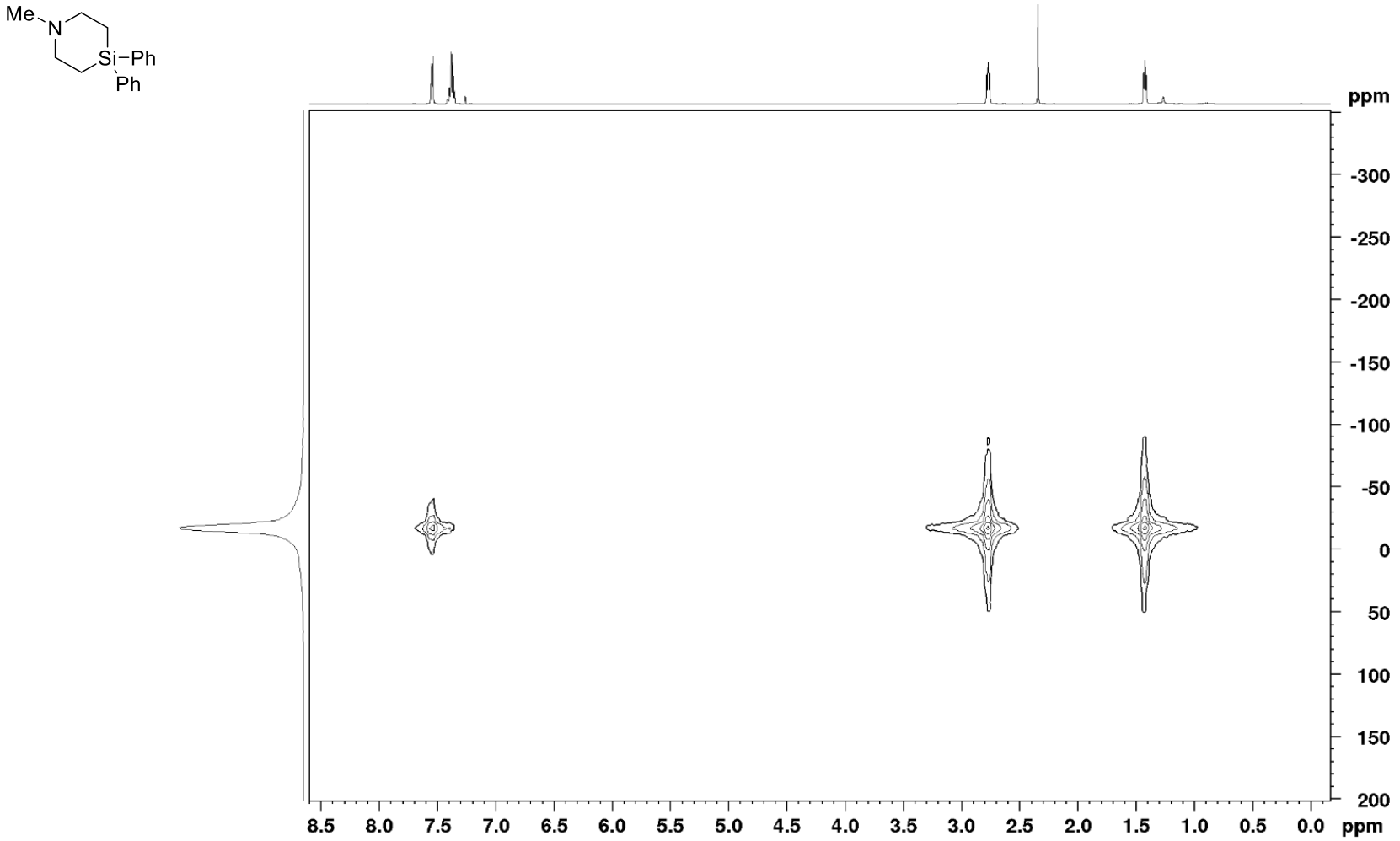


Figure S58. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-3-methyl-4,4-diphenyl-1,4-azasilinane (3ra)**.

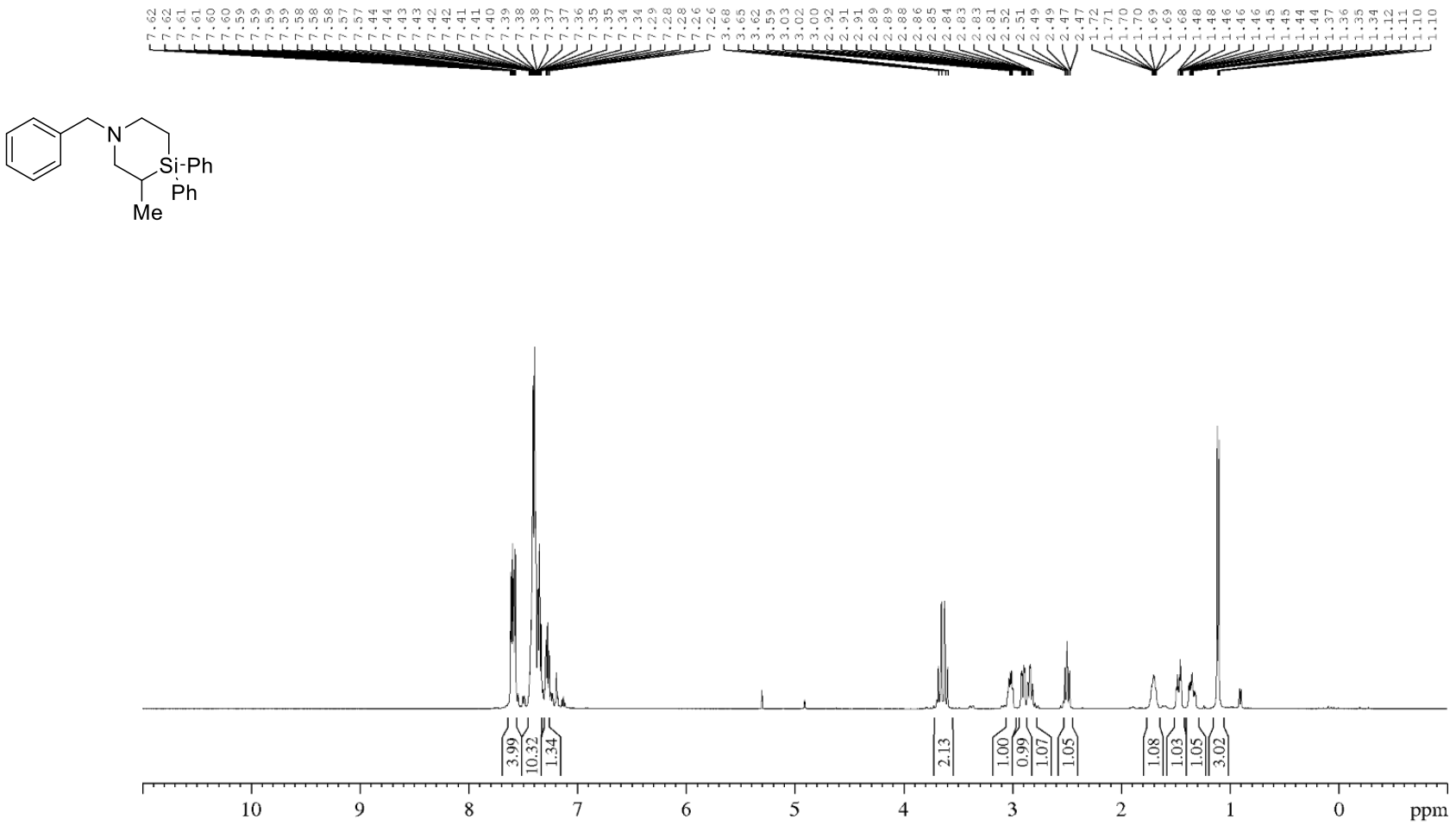


Figure S59. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-3-methyl-4,4-diphenyl-1,4-azasilinane (3ra)**.

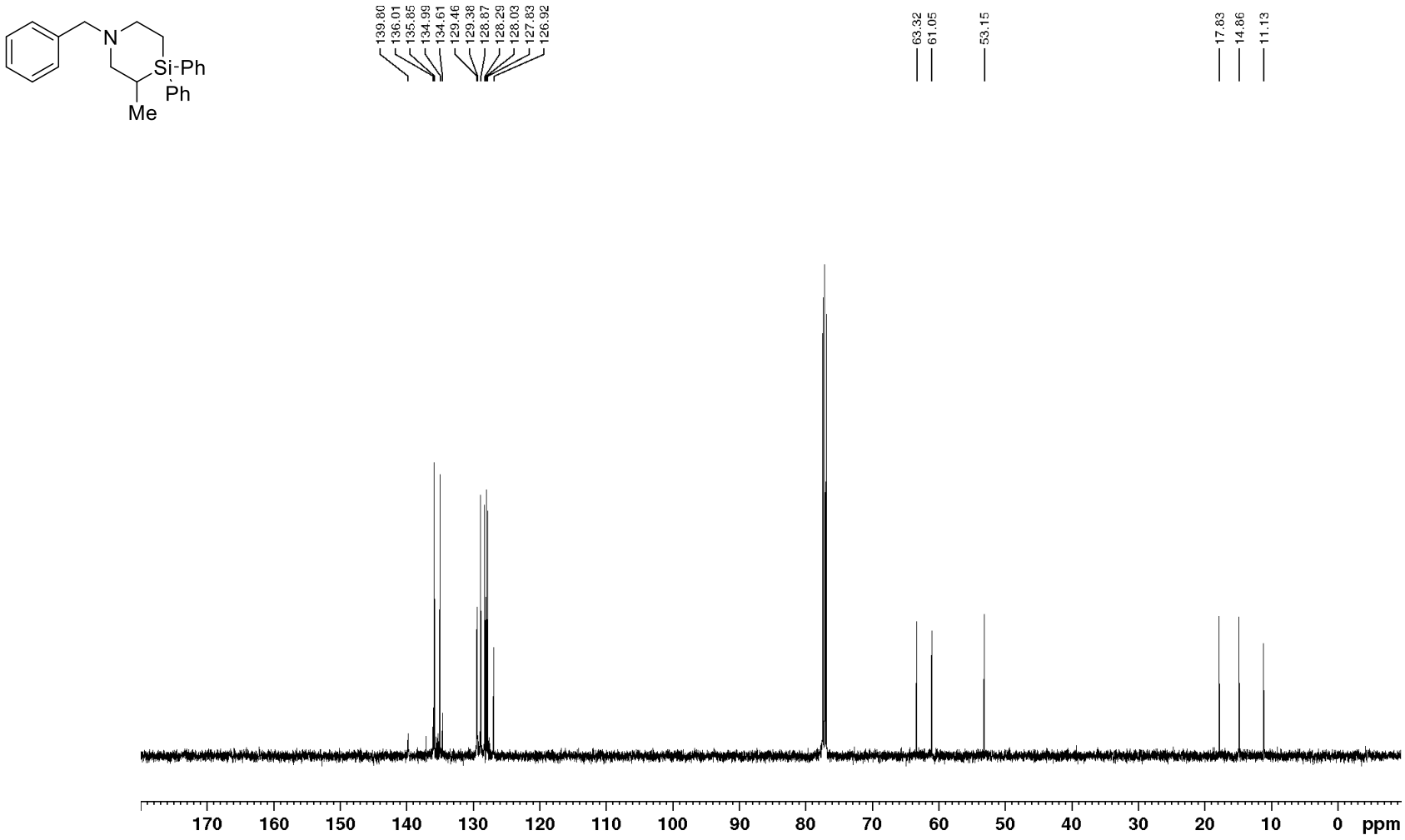


Figure S60. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-3-methyl-4,4-diphenyl-1,4-azasilinane (3ra)**.

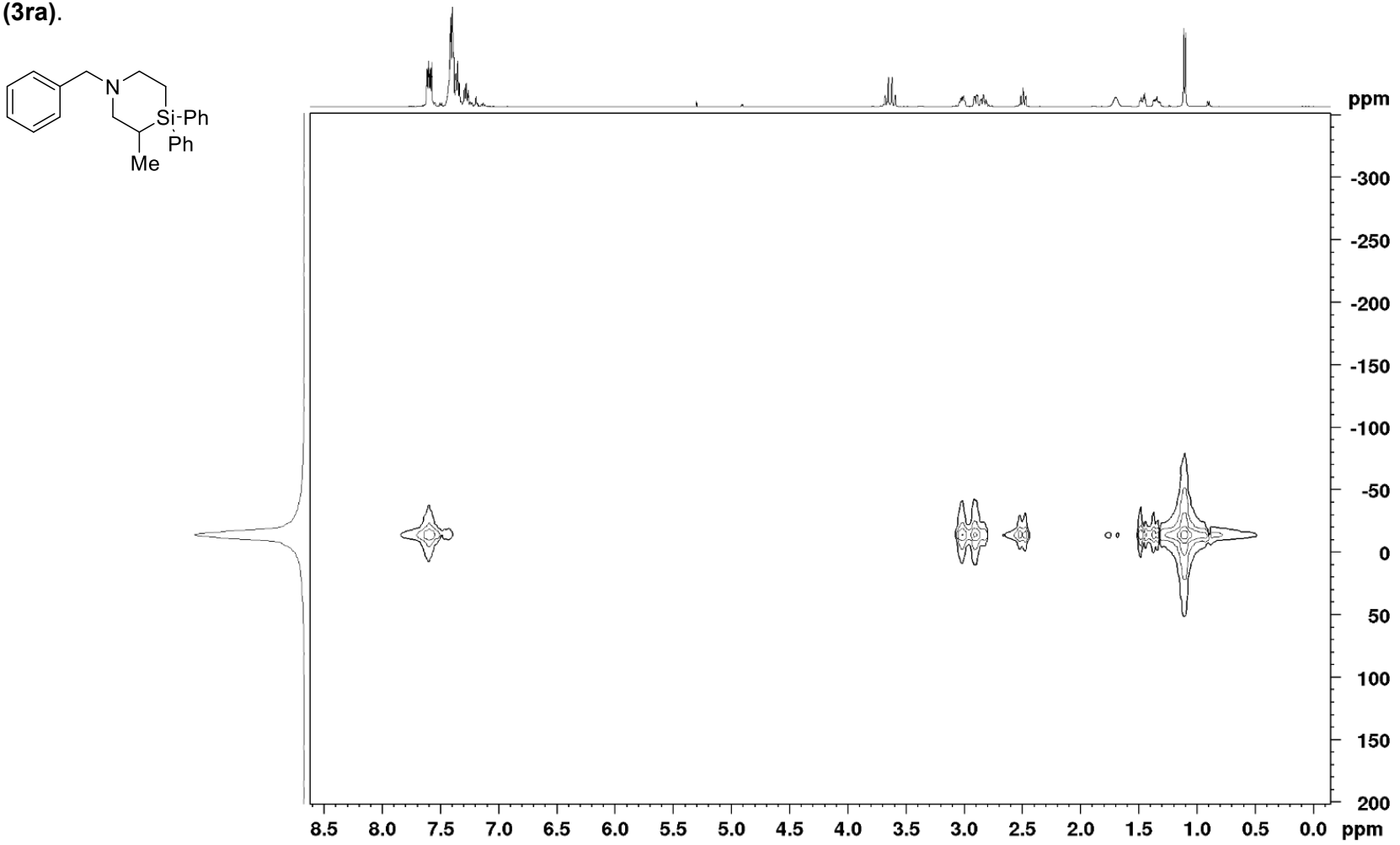


Figure S61. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-3-ethyl-4,4-diphenyl-1,4-azasilinane (3sa)**.

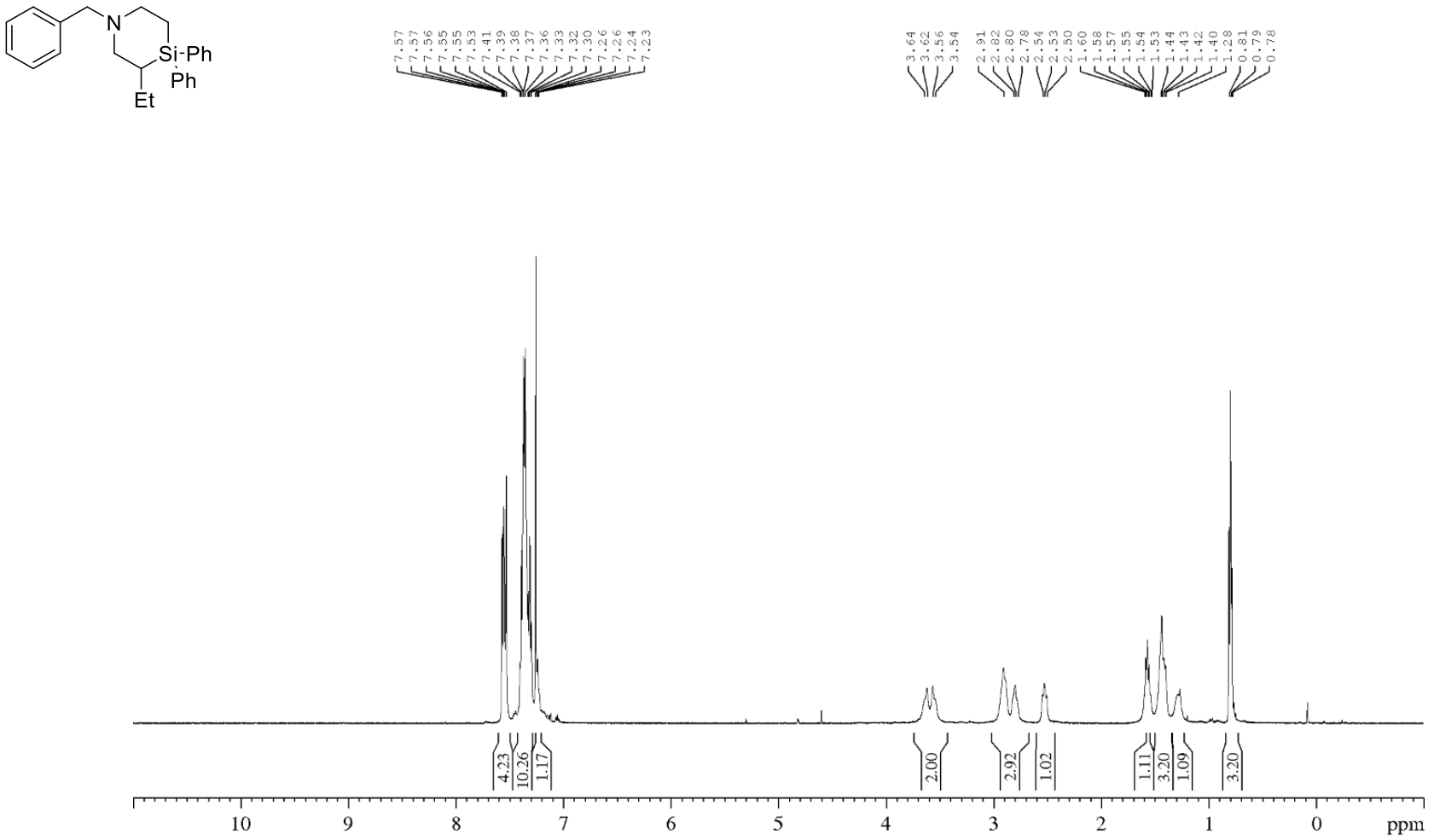


Figure S62. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-3-ethyl-4,4-diphenyl-1,4-azasilinane (3sa)**.

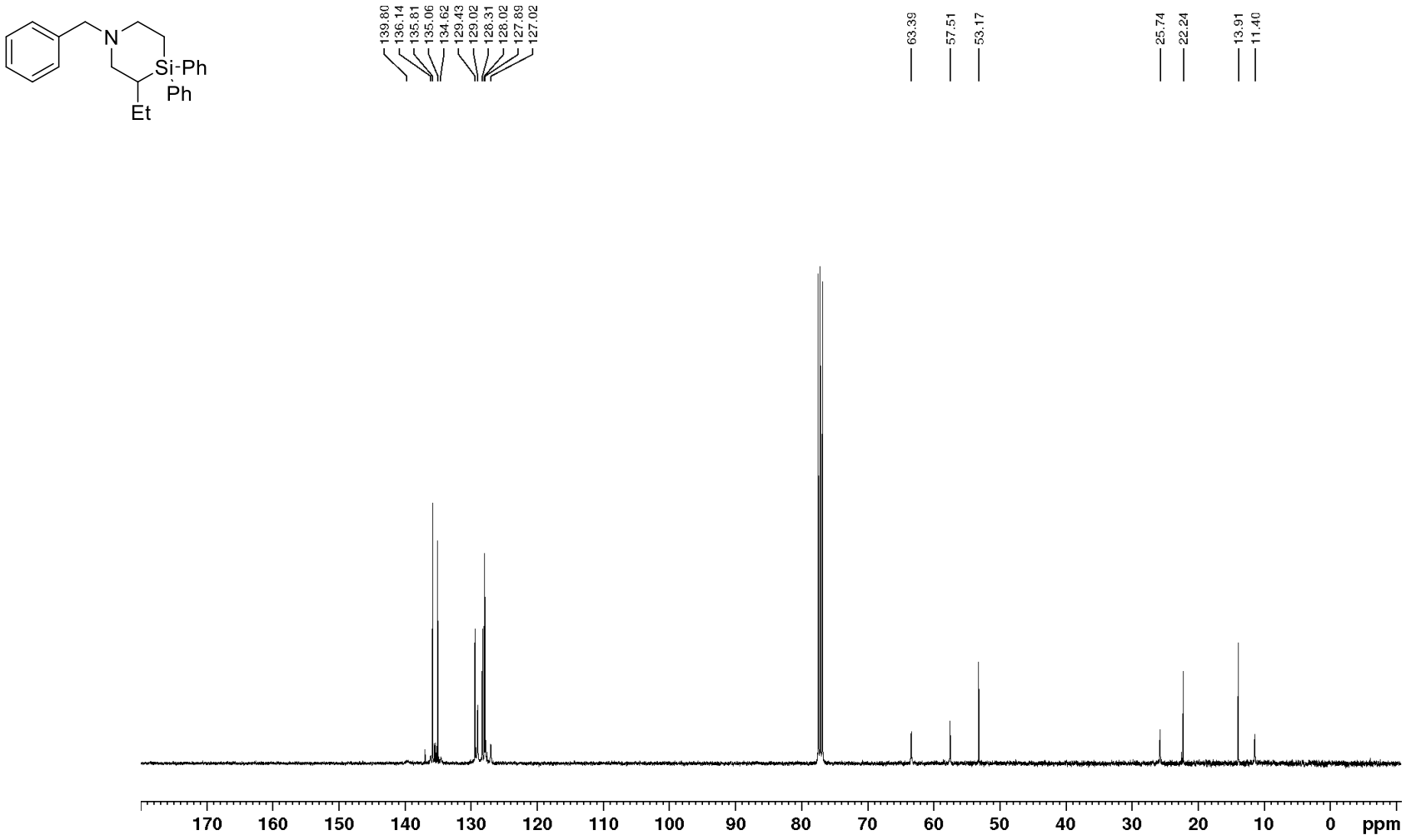


Figure S63. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-3-ethyl-4,4-diphenyl-1,4-azasilinane (3sa)**.

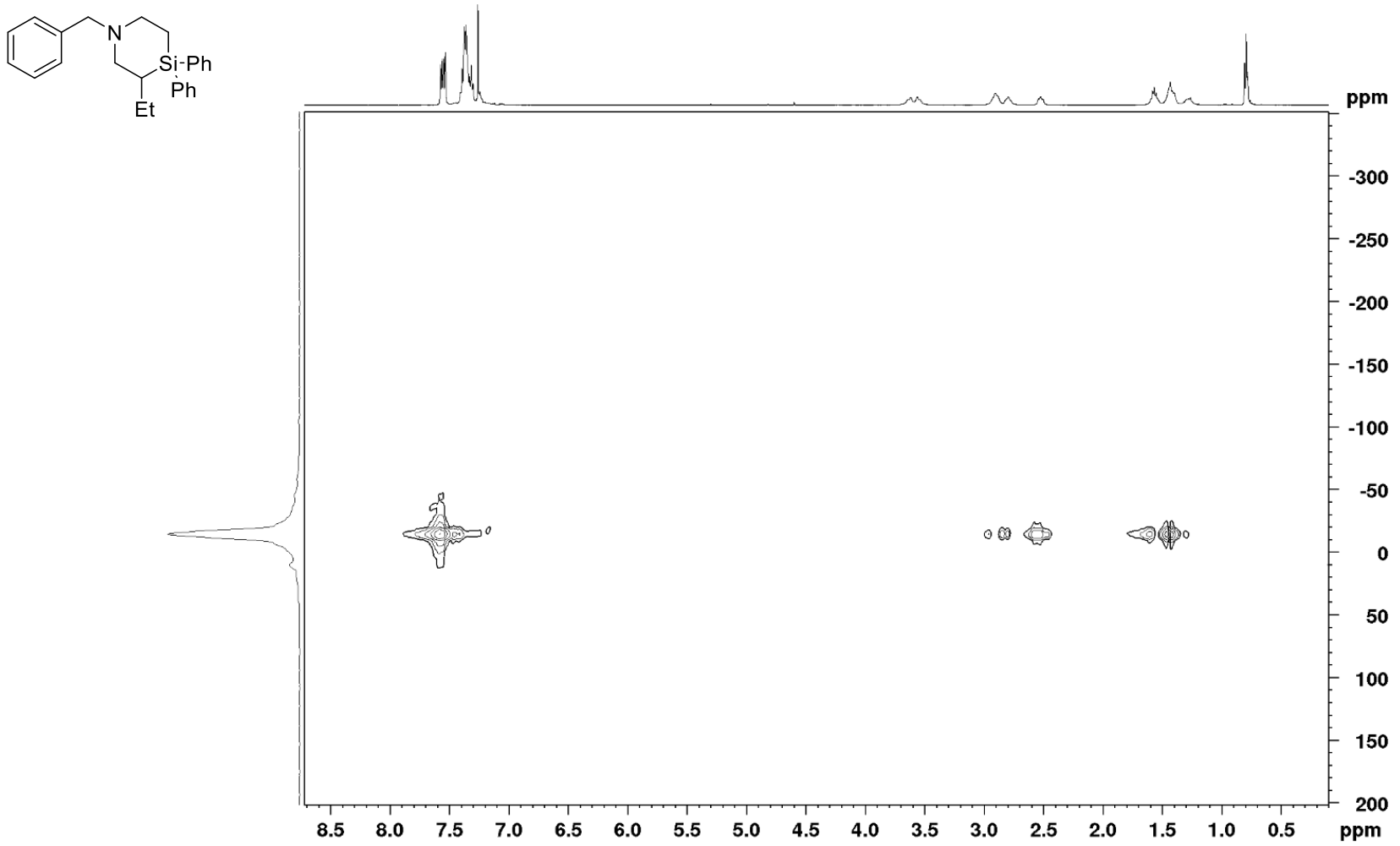


Figure S64. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **3,5-dimethyl-4,4-diphenyl-1-propyl-1,4-azasilinane (3ta) (d.r. = 58:42)**.

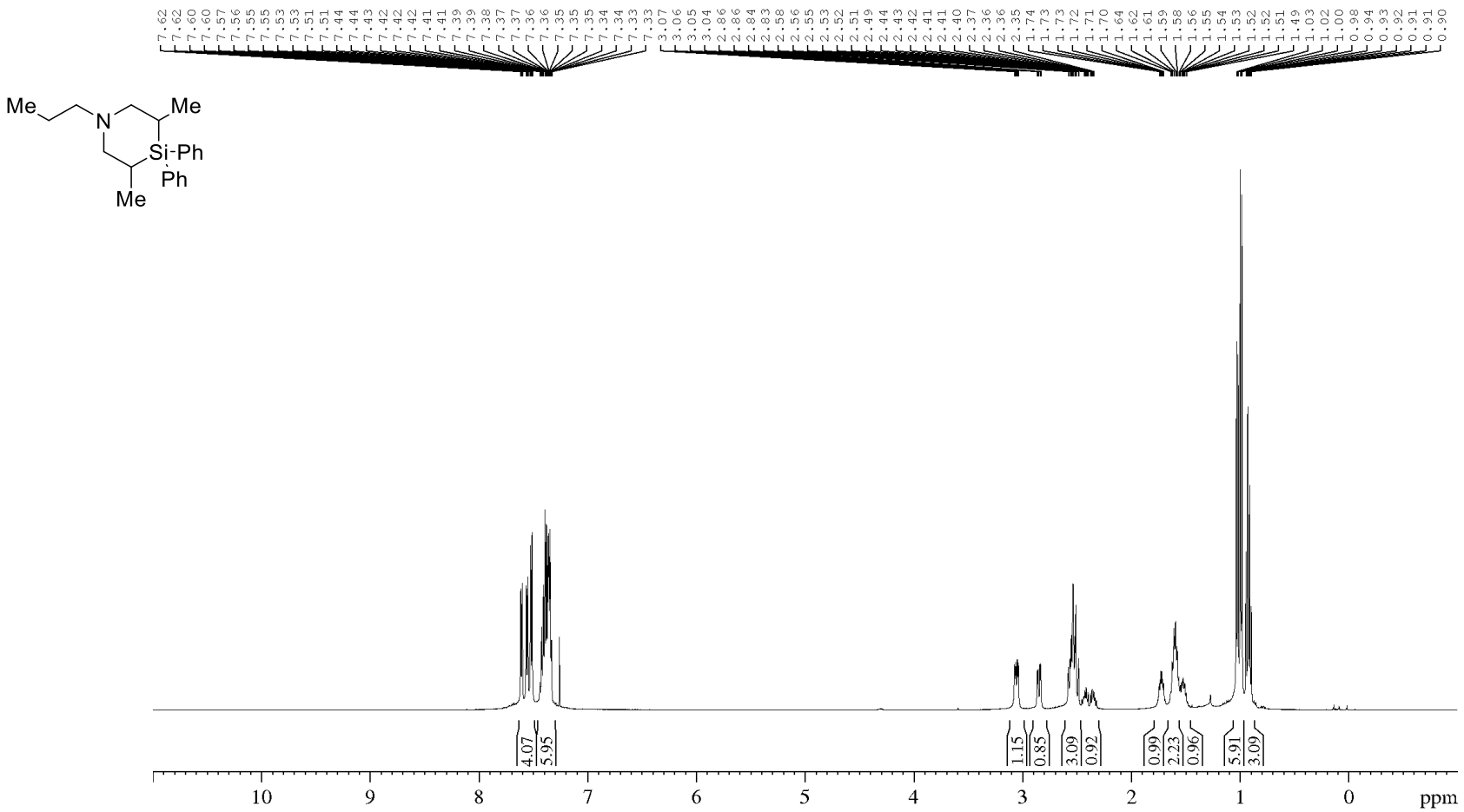


Figure S65. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **3,5-dimethyl-4,4-diphenyl-1-propyl-1,4-azasilinane (3ta) (d.r. = 58:42)**.

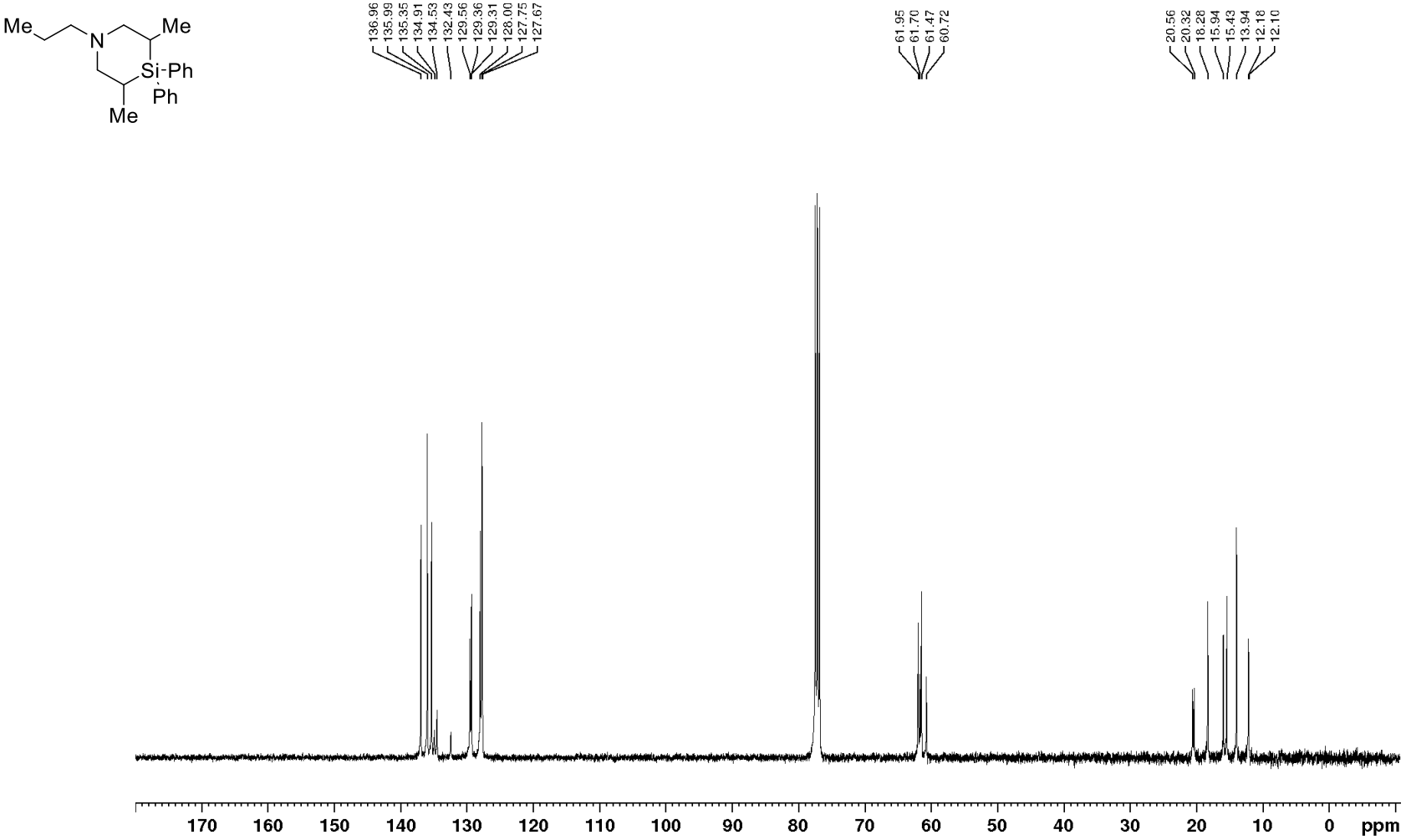


Figure S66. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **3,5-dimethyl-4,4-diphenyl-1-propyl-1,4-azasilinane (3ta) (d.r. = 58:42)**.

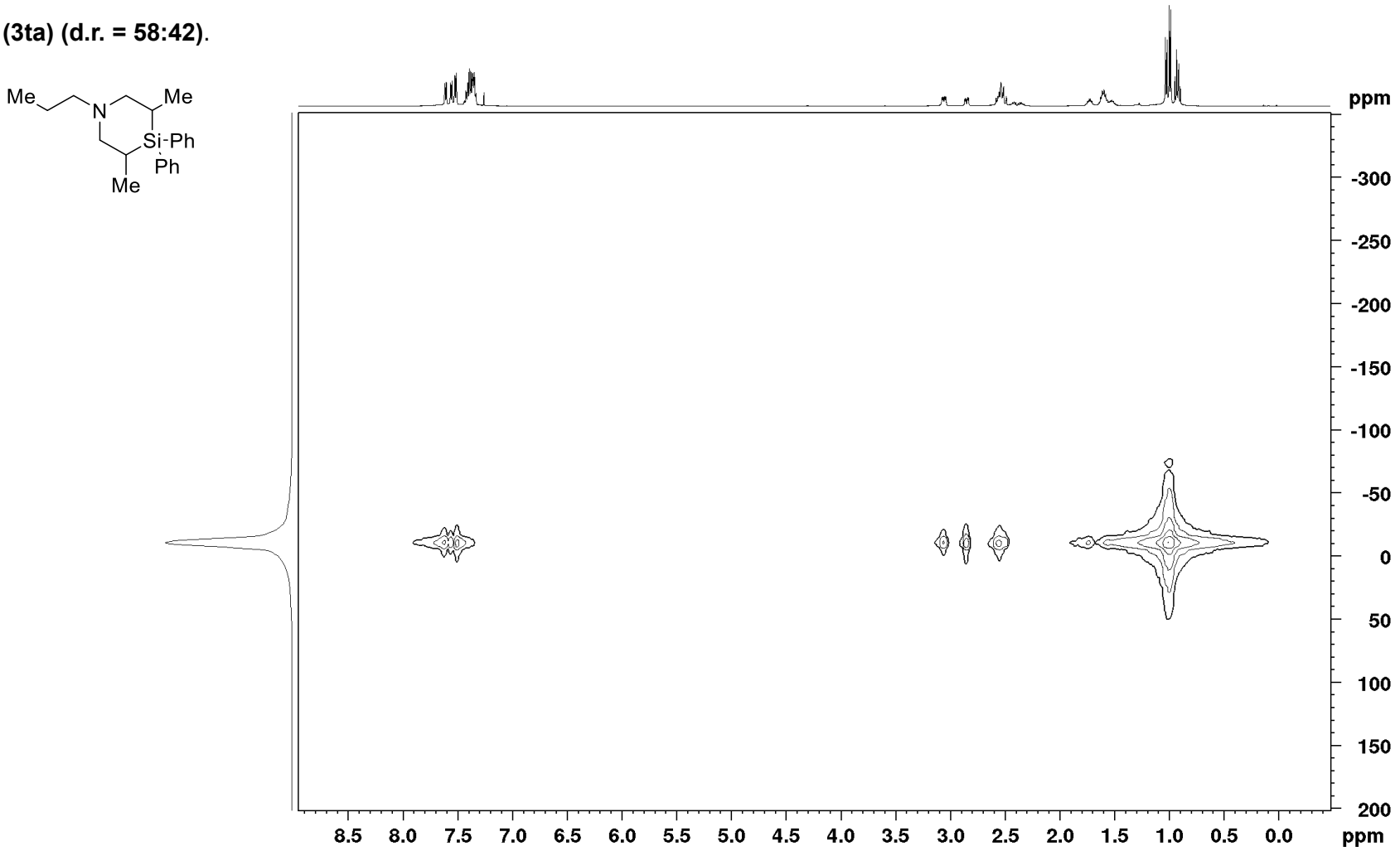


Figure S67. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-ethyl-6-methyl-4,4-diphenyl-1,2,3,4-tetrahydrobenzo[*b*][1,4]azasiline (4ua)**.

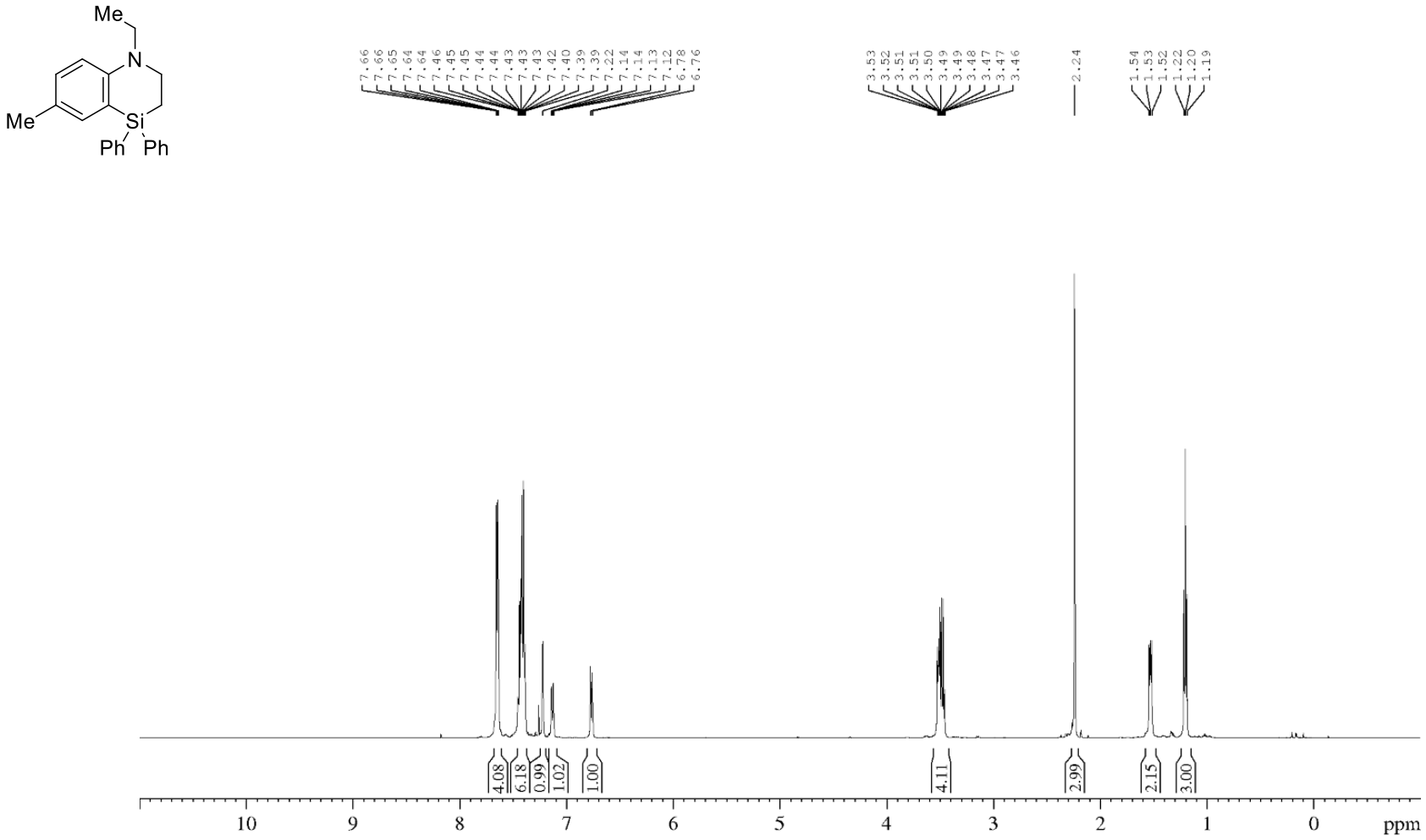


Figure S68. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-ethyl-6-methyl-4,4-diphenyl-1,2,3,4-tetrahydrobenzo[*b*][1,4]azasiline (4ua)**.

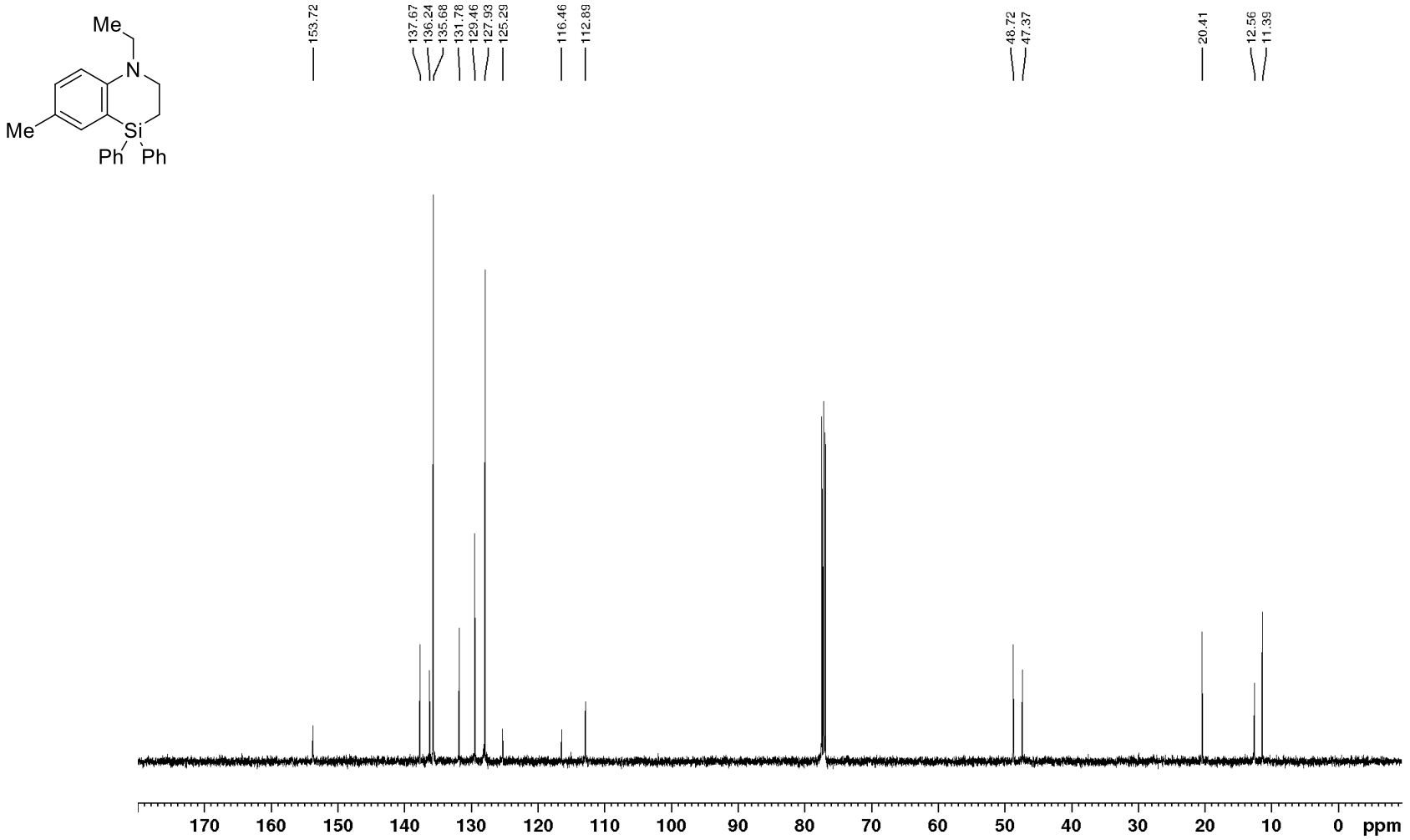


Figure S69. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-ethyl-6-methyl-4,4-diphenyl-1,2,3,4-tetrahydrobenzo[*b*][1,4]azasiline (4ua)**.

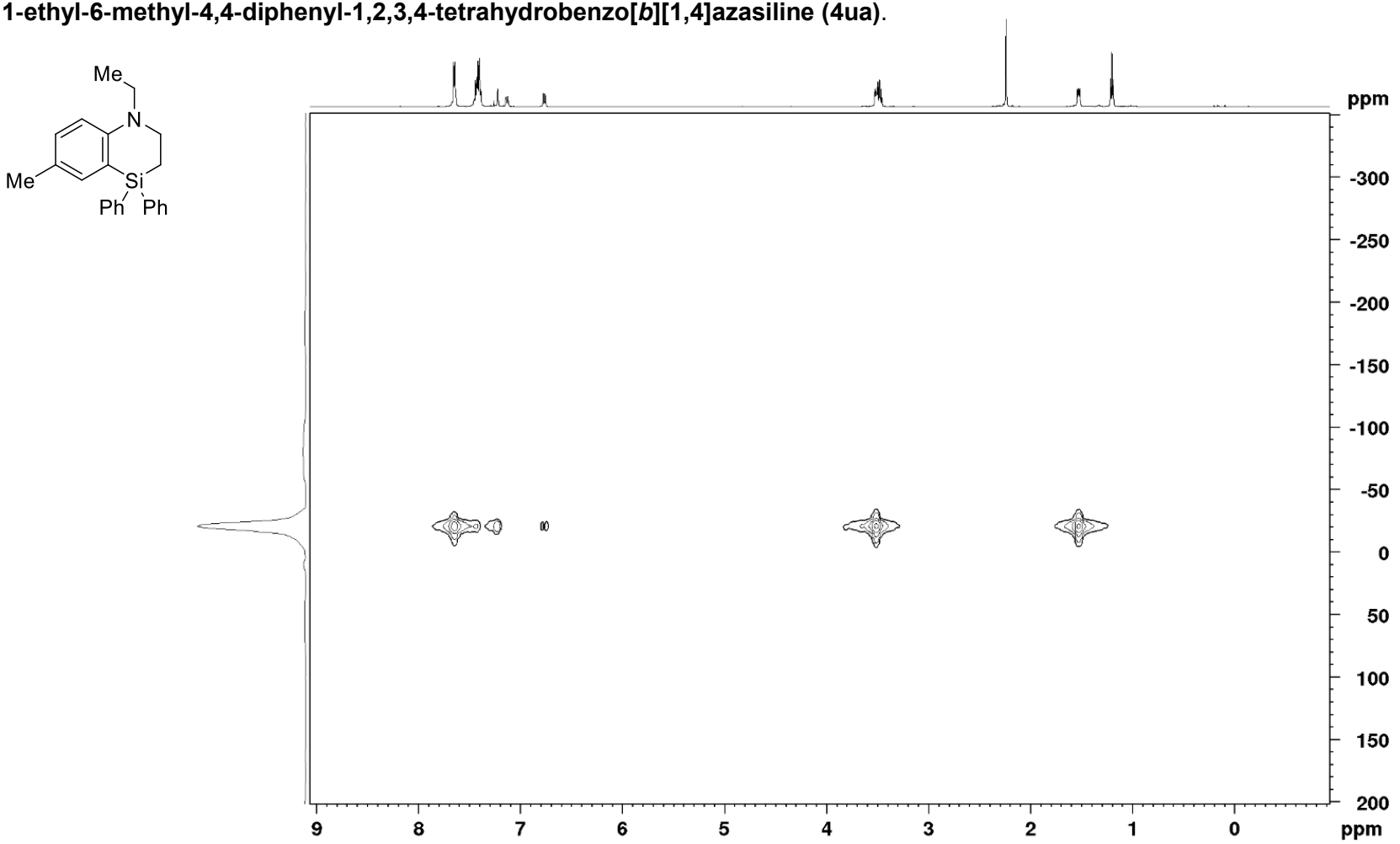


Figure S70. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of

8-methyl-1,1,6,6-tetraphenyl-2,3,5,6-tetrahydro-1*H*,4*H*-3a-aza-1,6-disilaphenalene (5ua).

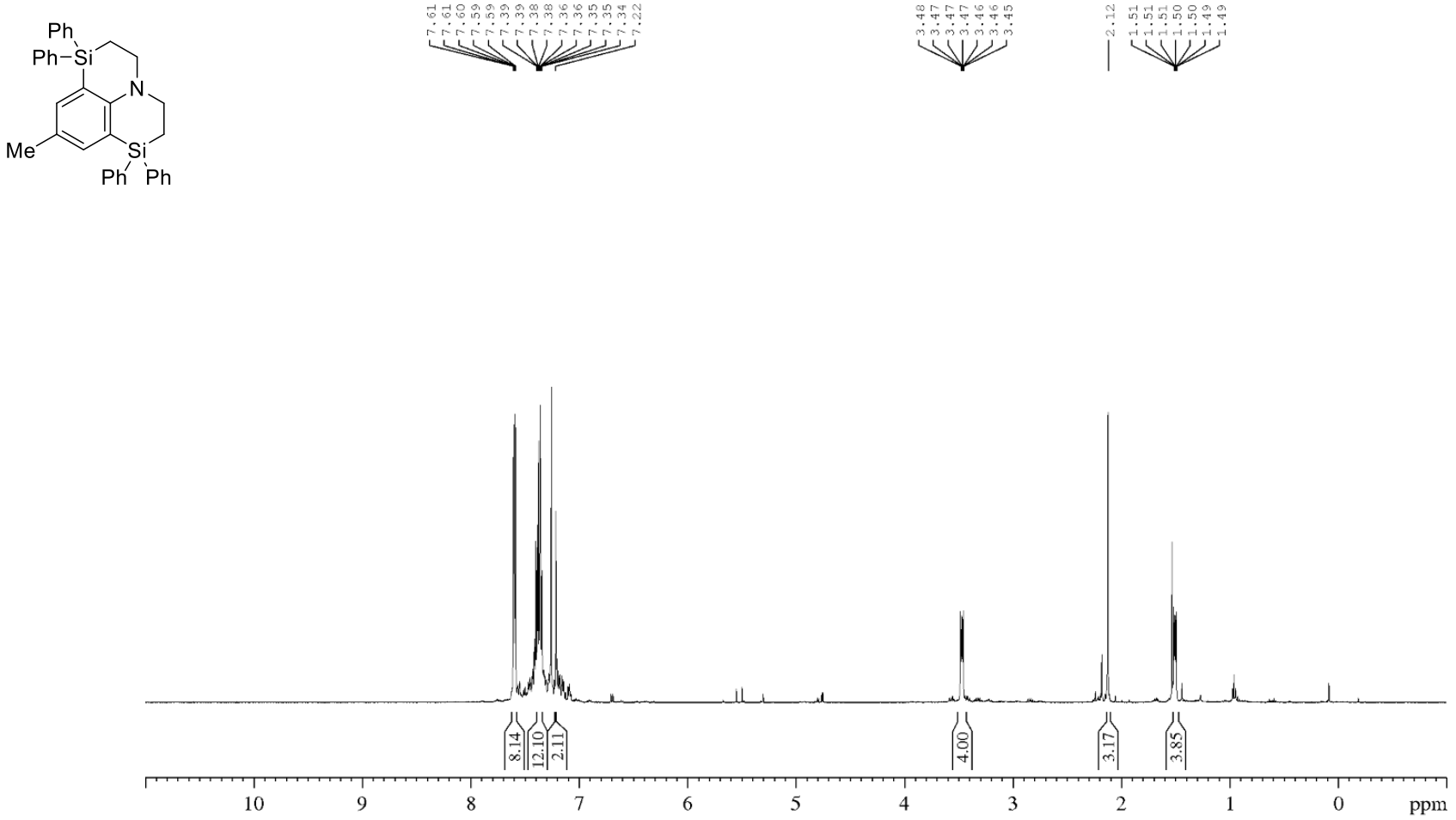


Figure S71. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of

8-methyl-1,1,6,6-tetraphenyl-2,3,5,6-tetrahydro-1*H*,4*H*-3a-aza-1,6-disilaphenalene (5ua).

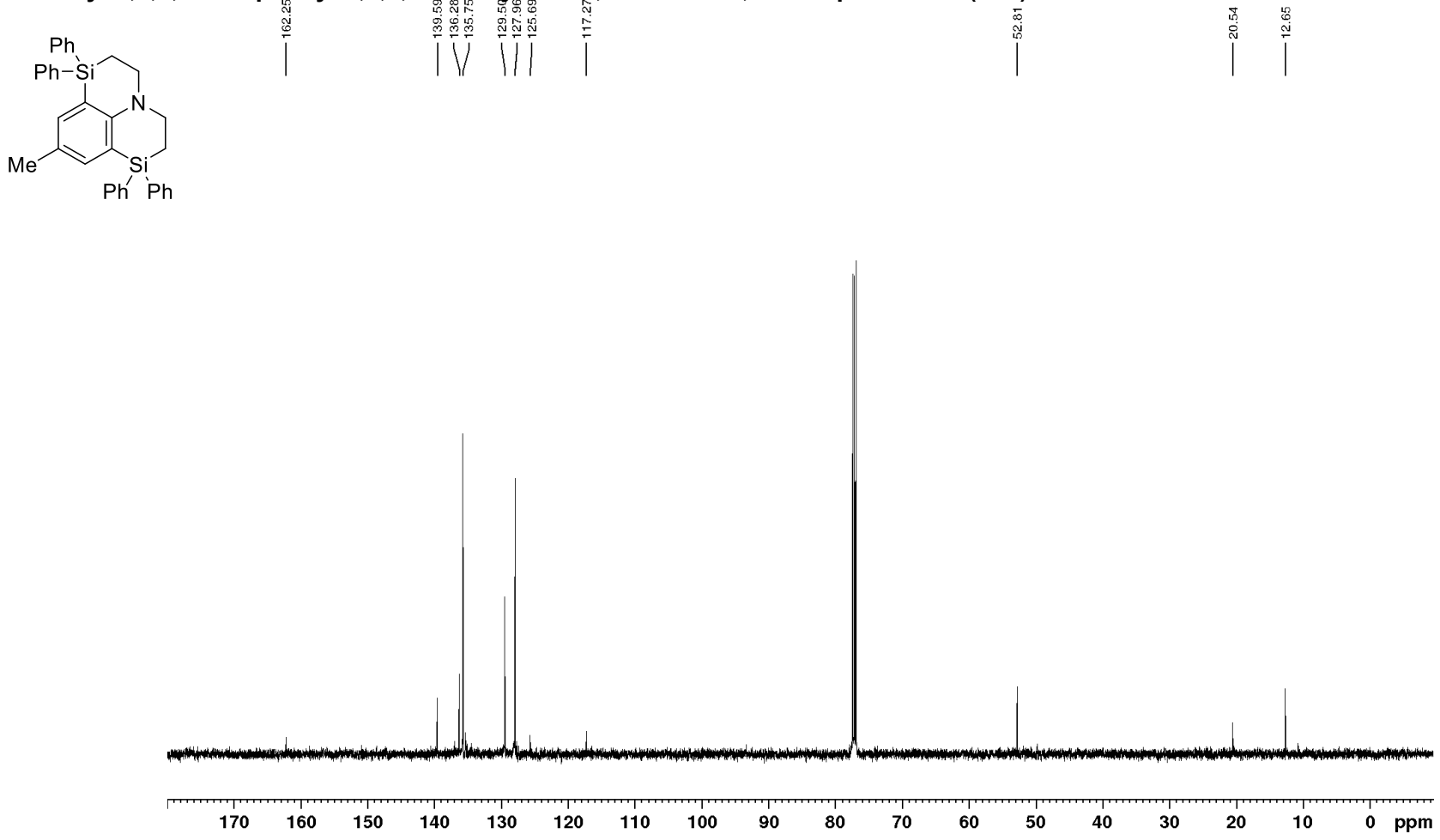


Figure S72. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of

8-methyl-1,1,6,6-tetraphenyl-2,3,5,6-tetrahydro-1*H*,4*H*-3a-aza-1,6-disilaphenalene (5ua).

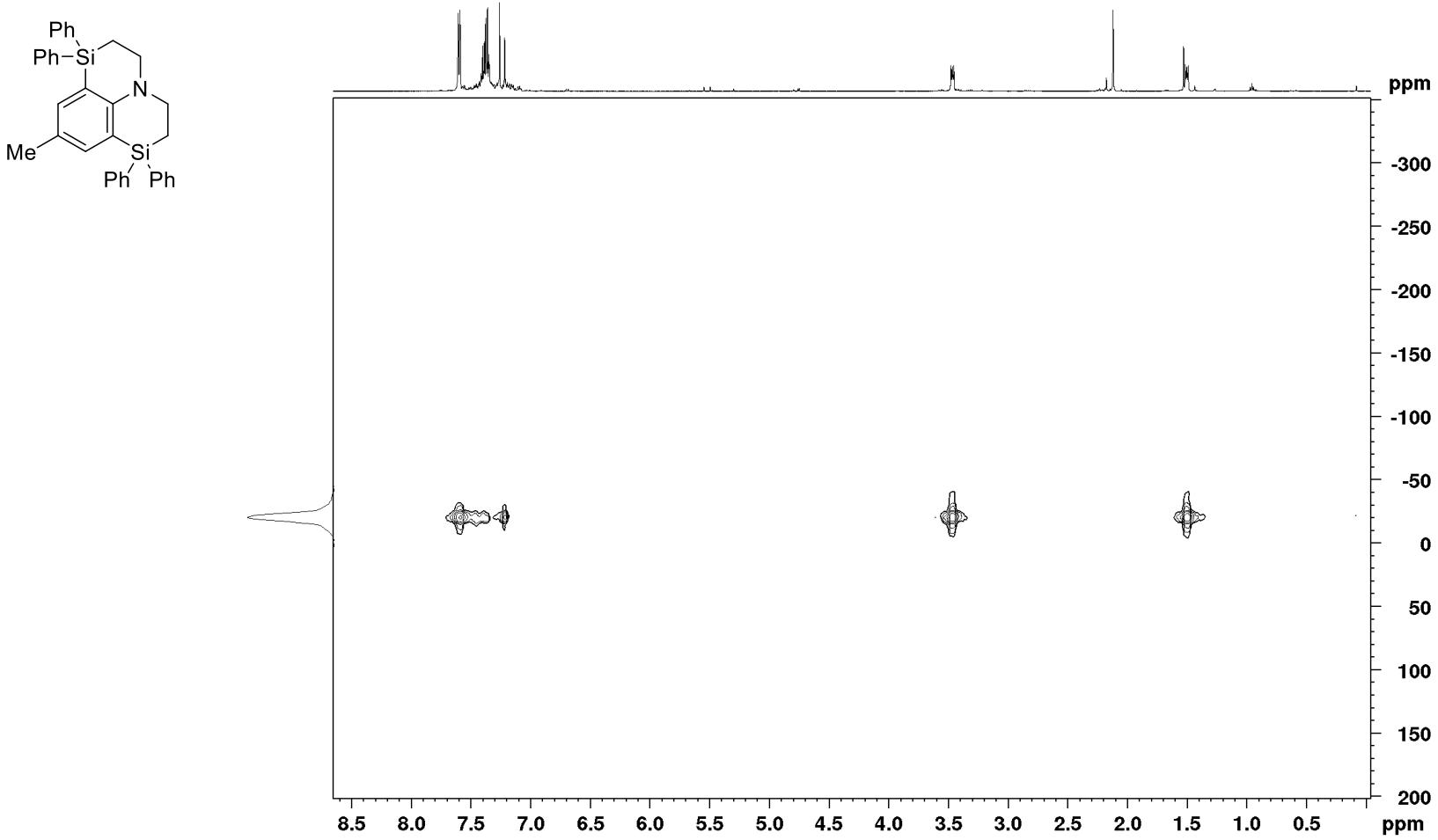


Figure S73. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-di-*p*-tolyl-1,4-azasilinane (3ab)**.

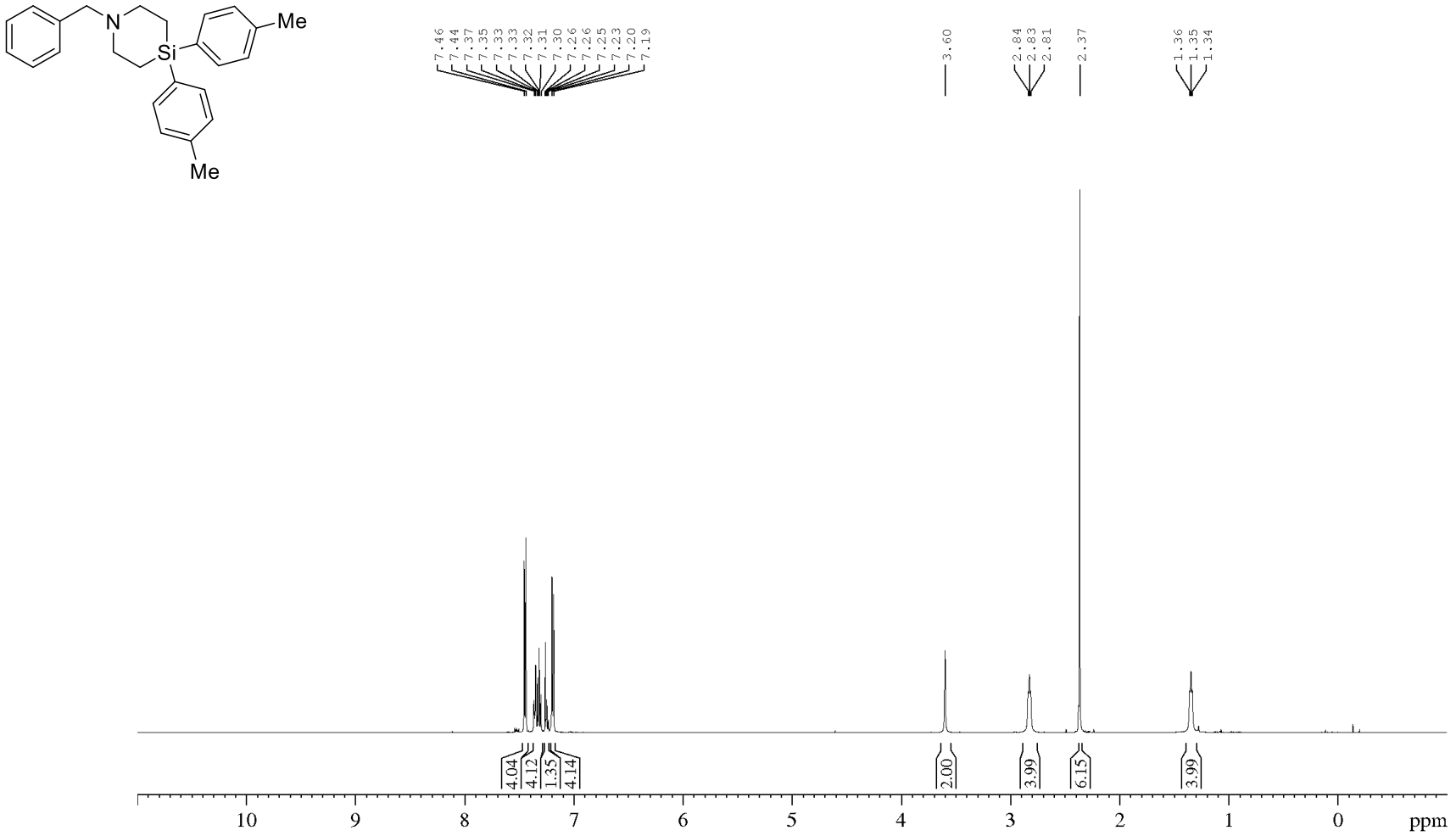


Figure S74. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-di-*p*-tolyl-1,4-azasilinane (3ab)**.

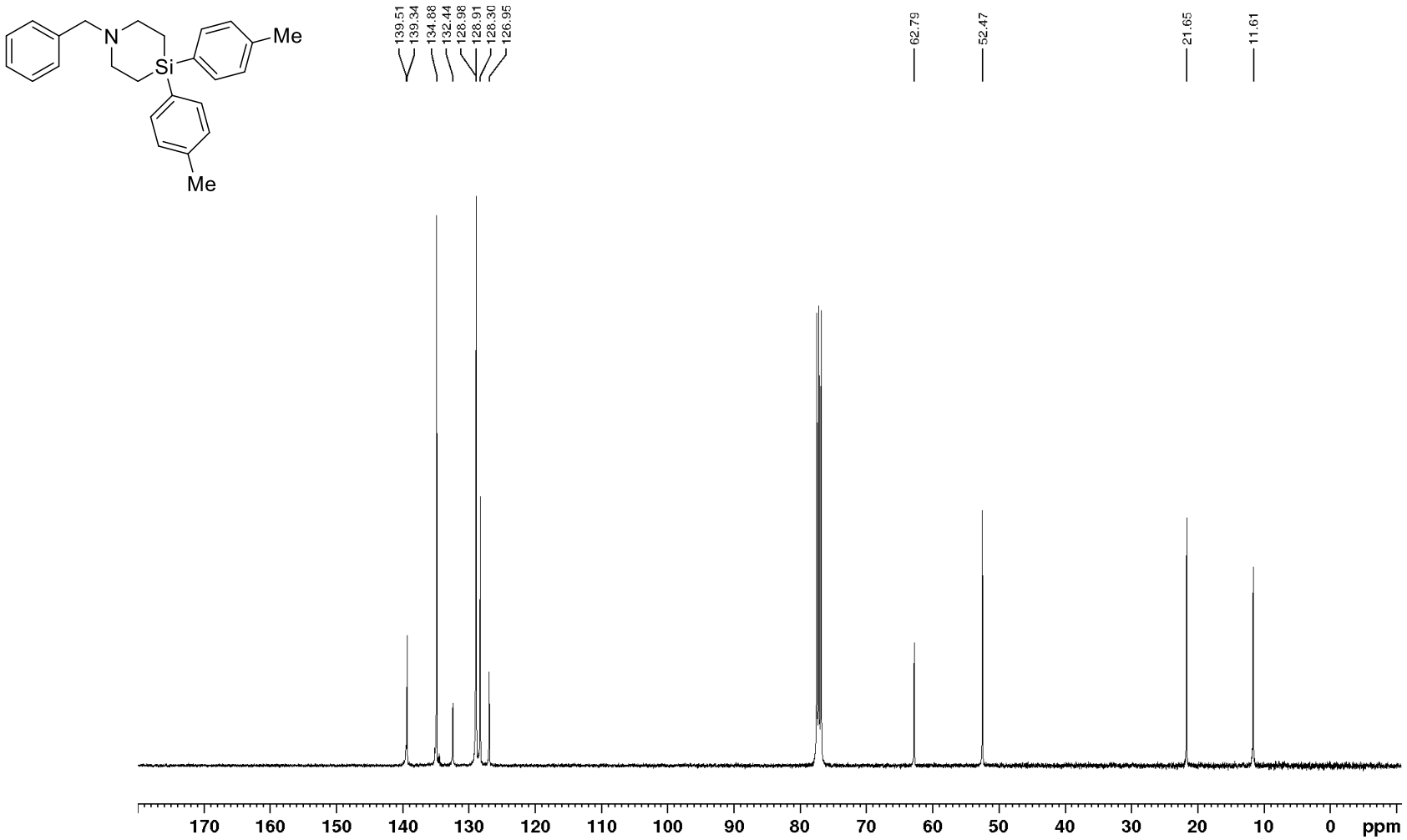


Figure S75. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-4,4-di-*p*-tolyl-1,4-azasilinane (3ab)**.

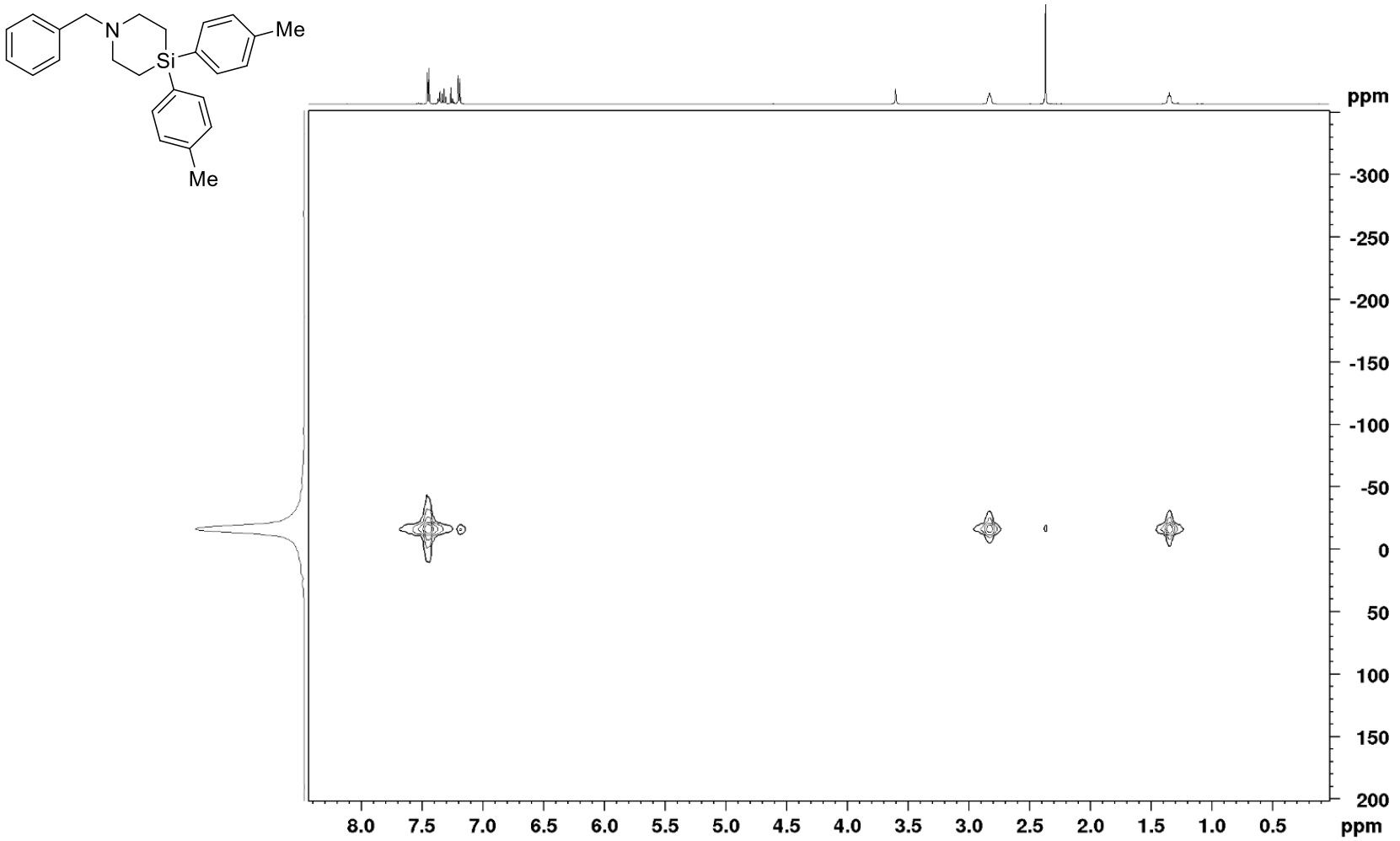


Figure S76. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-bis(4-(*tert*-butyl)phenyl)-1,4-azasilinane (3ac)**.

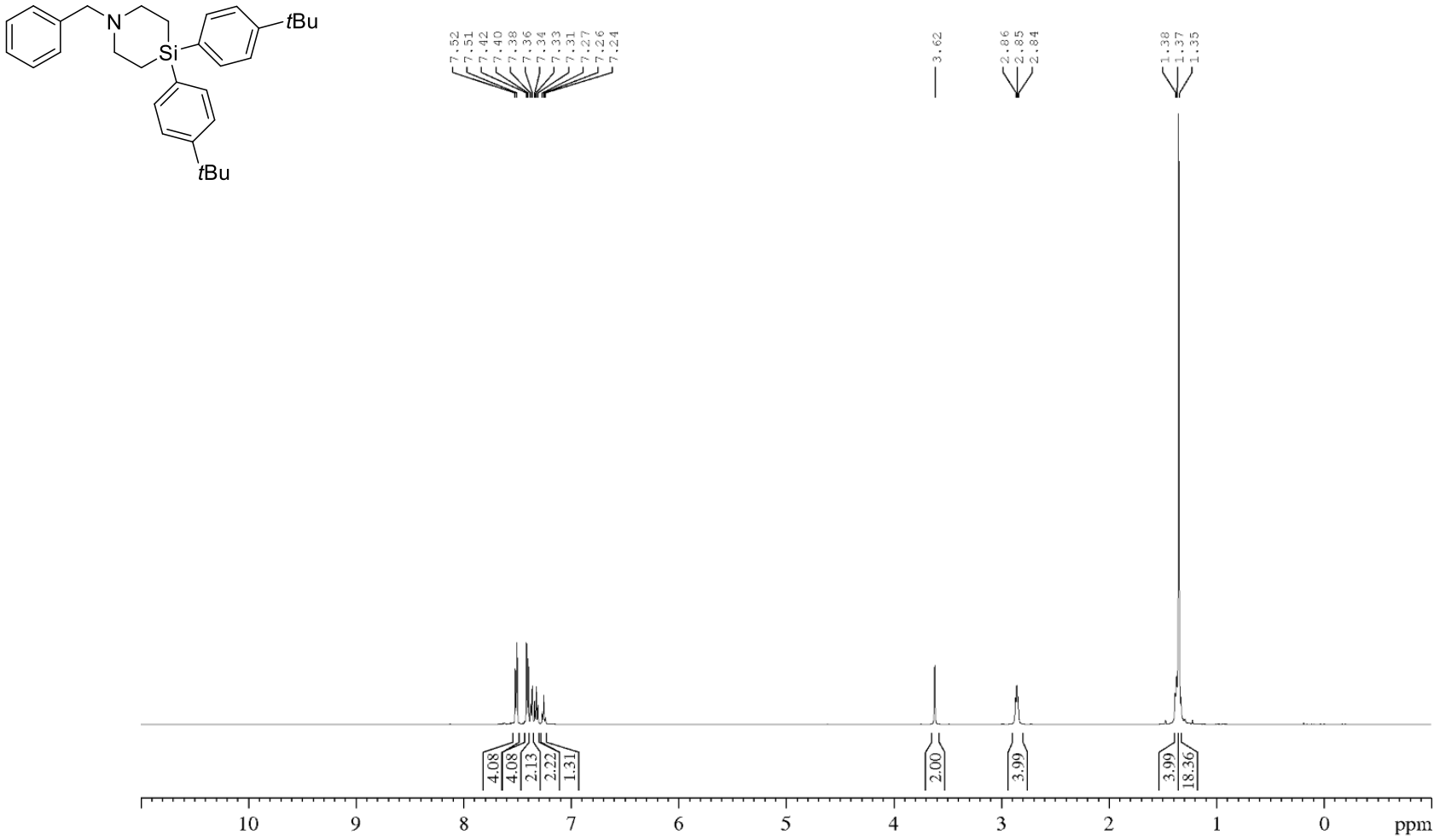


Figure S77. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-bis(4-(*tert*-butyl)phenyl)-1,4-azasilinane (3ac)**.

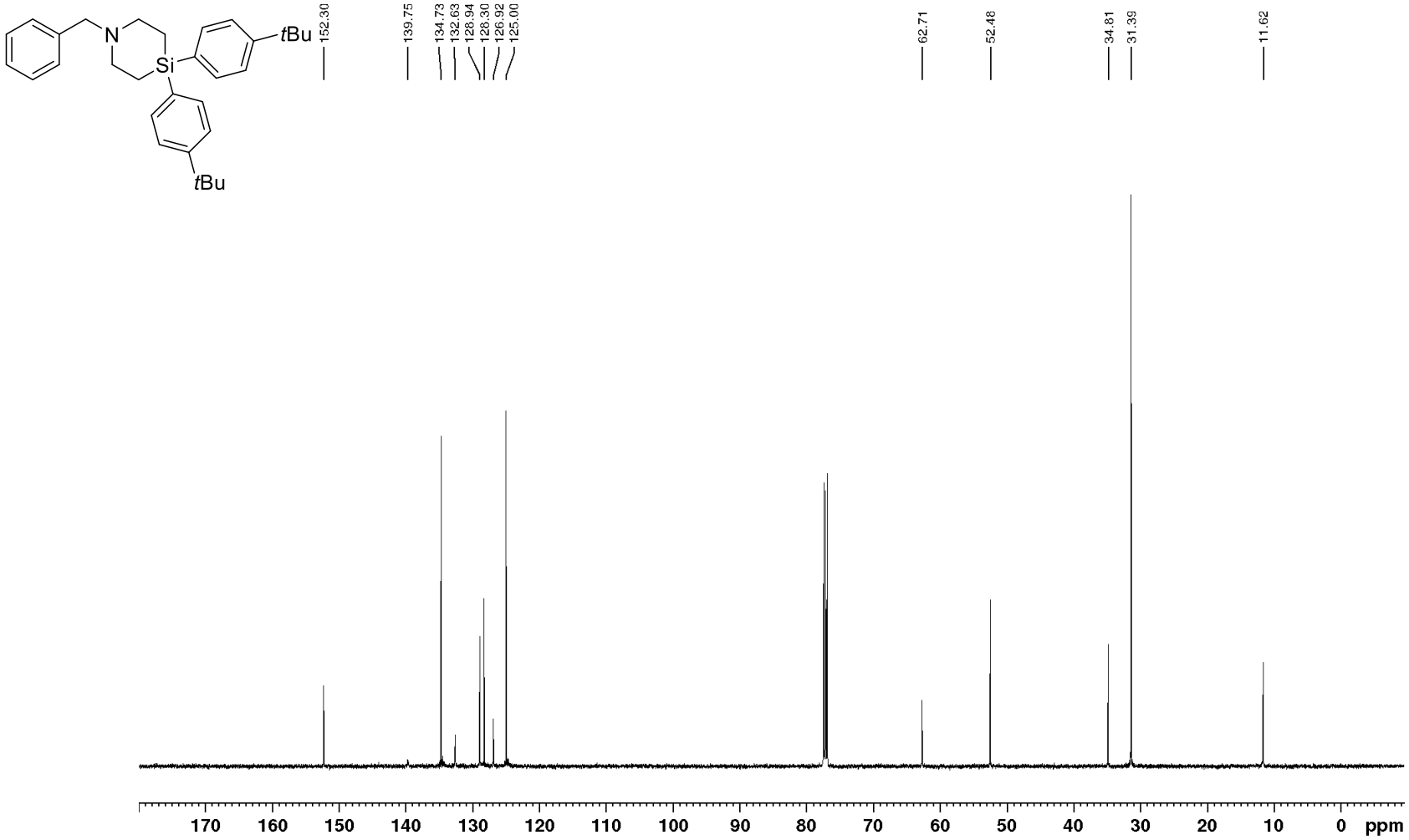


Figure S78. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of

1-benzyl-4,4-bis(4-(*tert*-butyl)phenyl)-1,4-azasilinane (3ac).

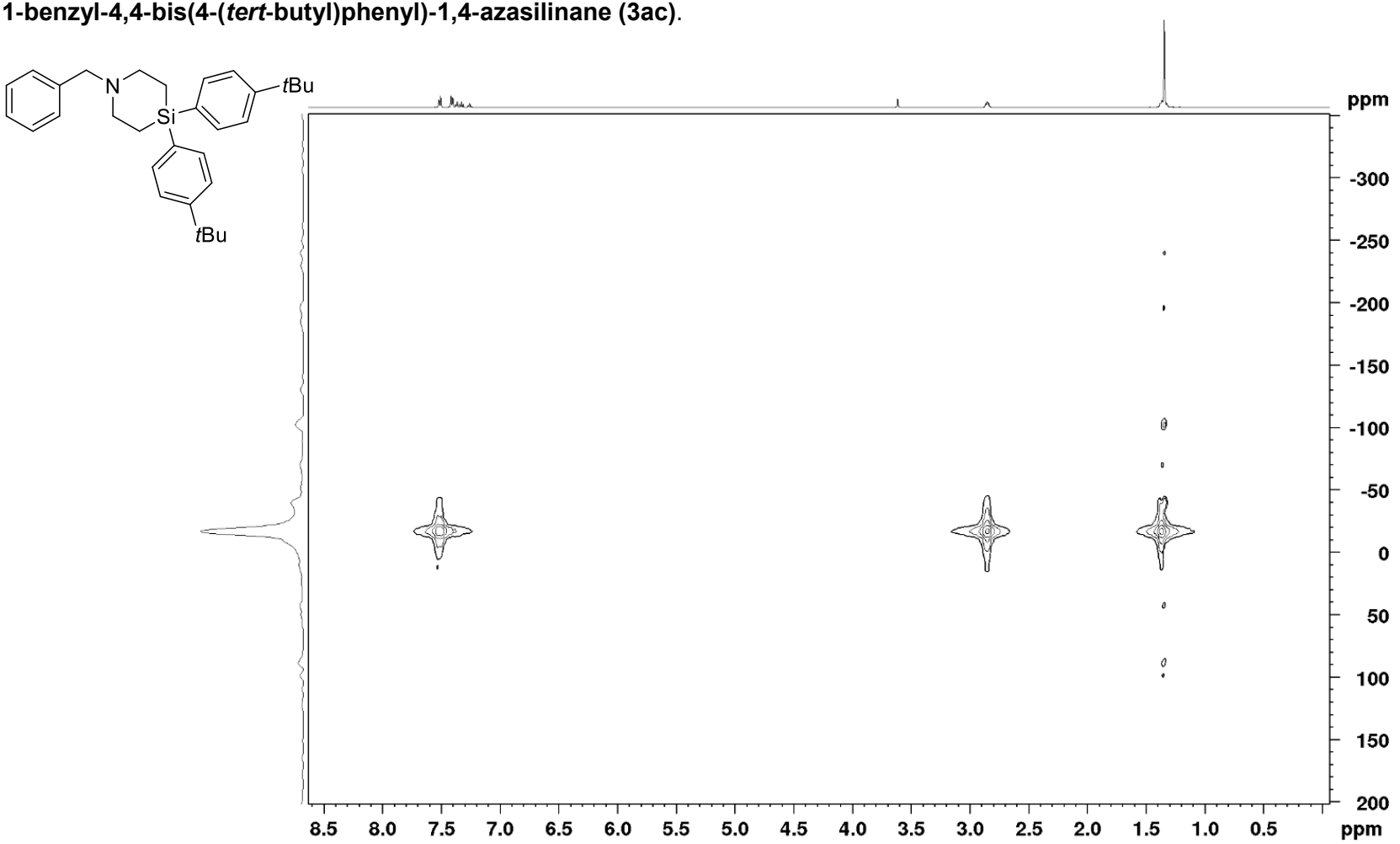


Figure S79. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-bis(4-fluorophenyl)-1,4-azasilinane (3ad)**.

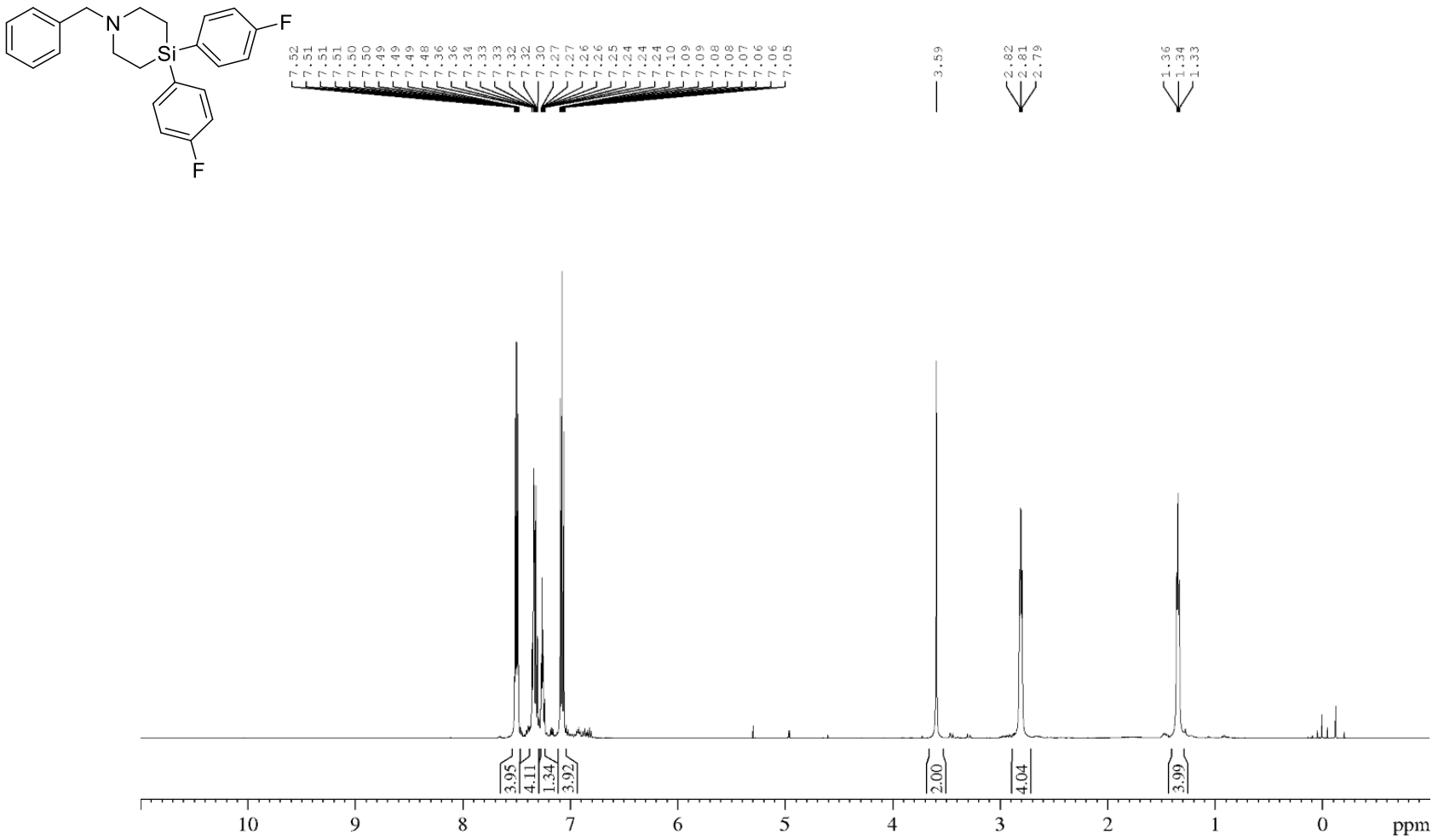


Figure S80. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-bis(4-fluorophenyl)-1,4-azasilinane (3ad)**.

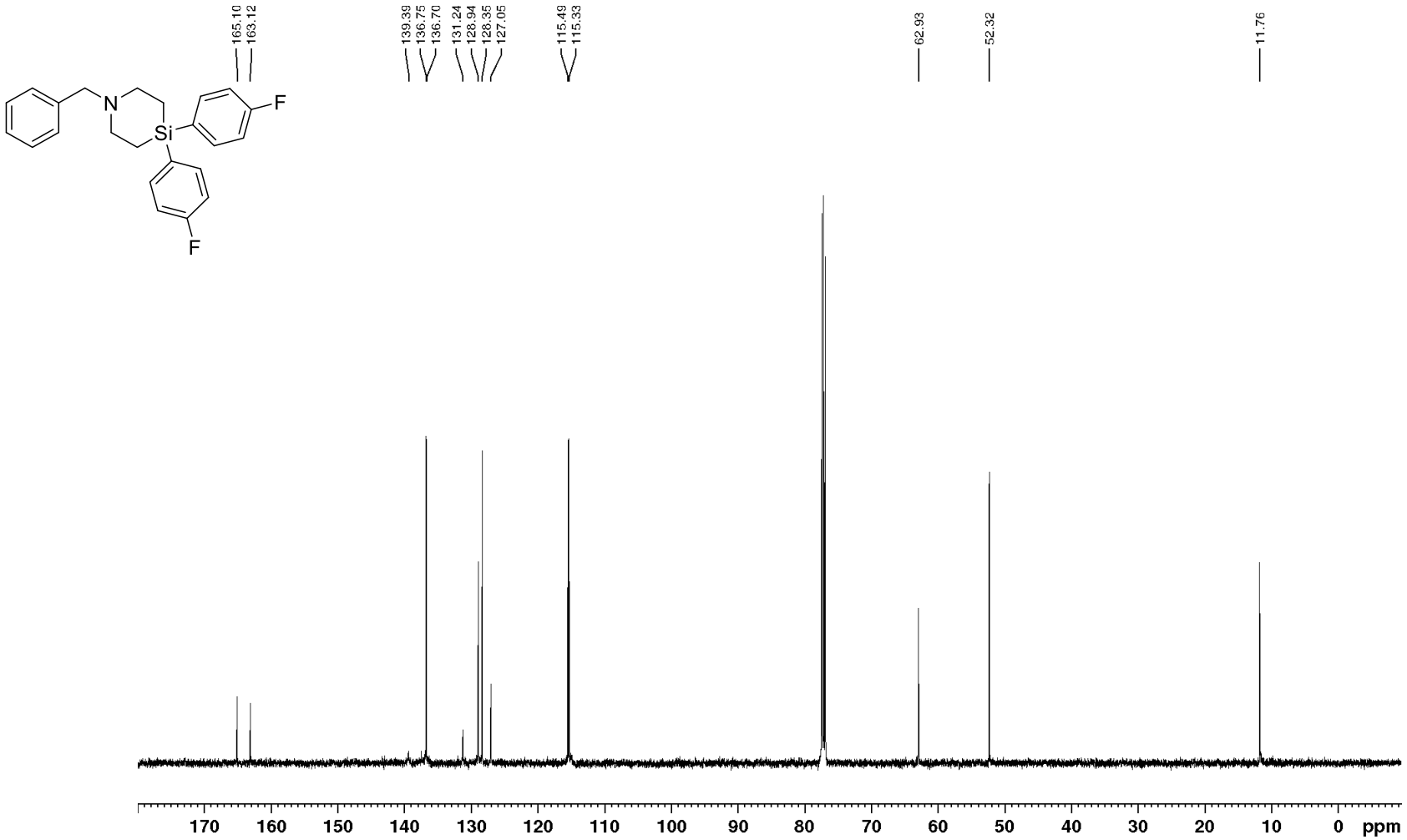


Figure S81. ^{19}F NMR spectrum (471 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-bis(4-fluorophenyl)-1,4-azasilinane (3ad)**.

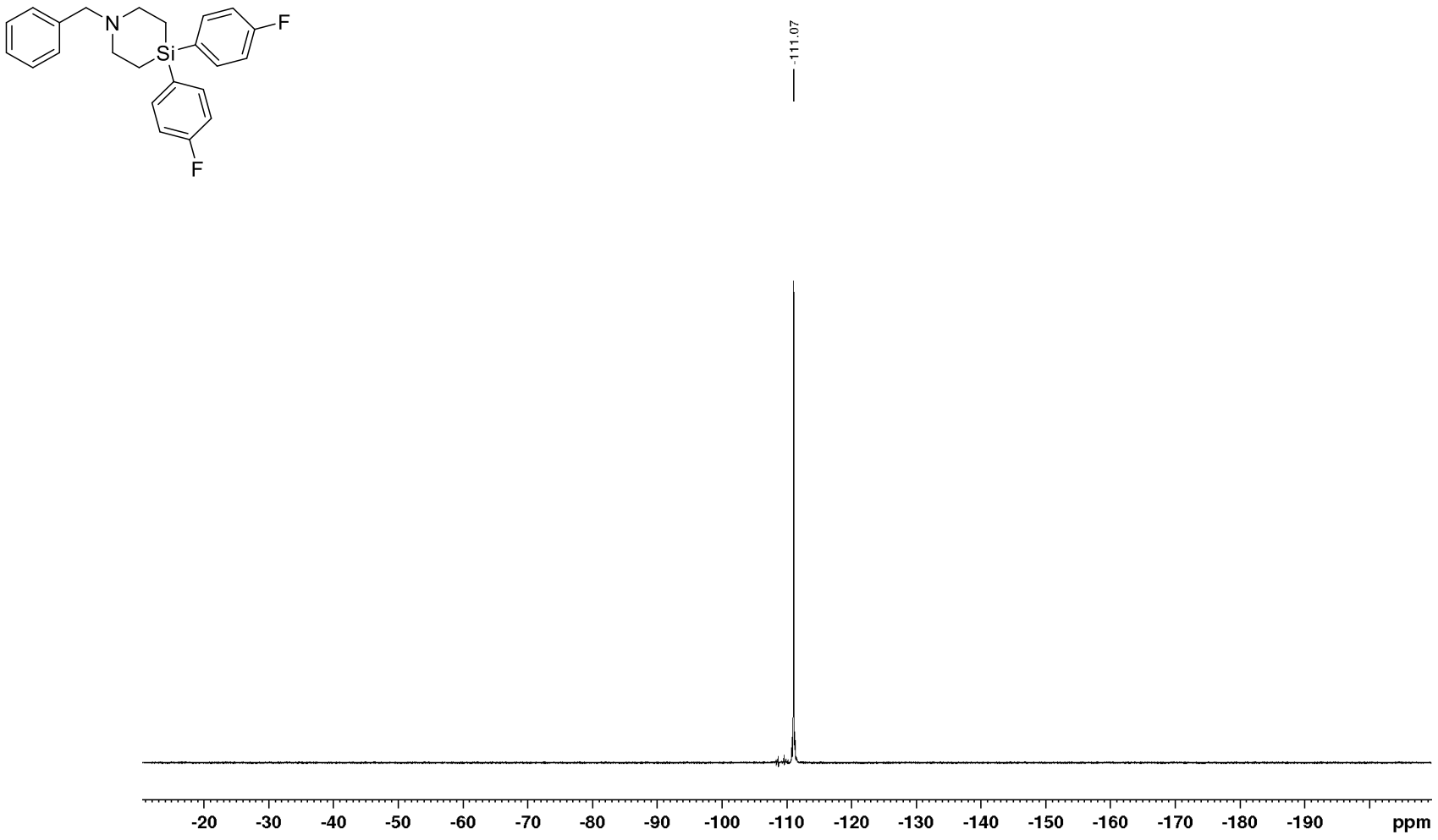


Figure S82. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-4,4-bis(4-fluorophenyl)-1,4-azasilinane (3ad)**.

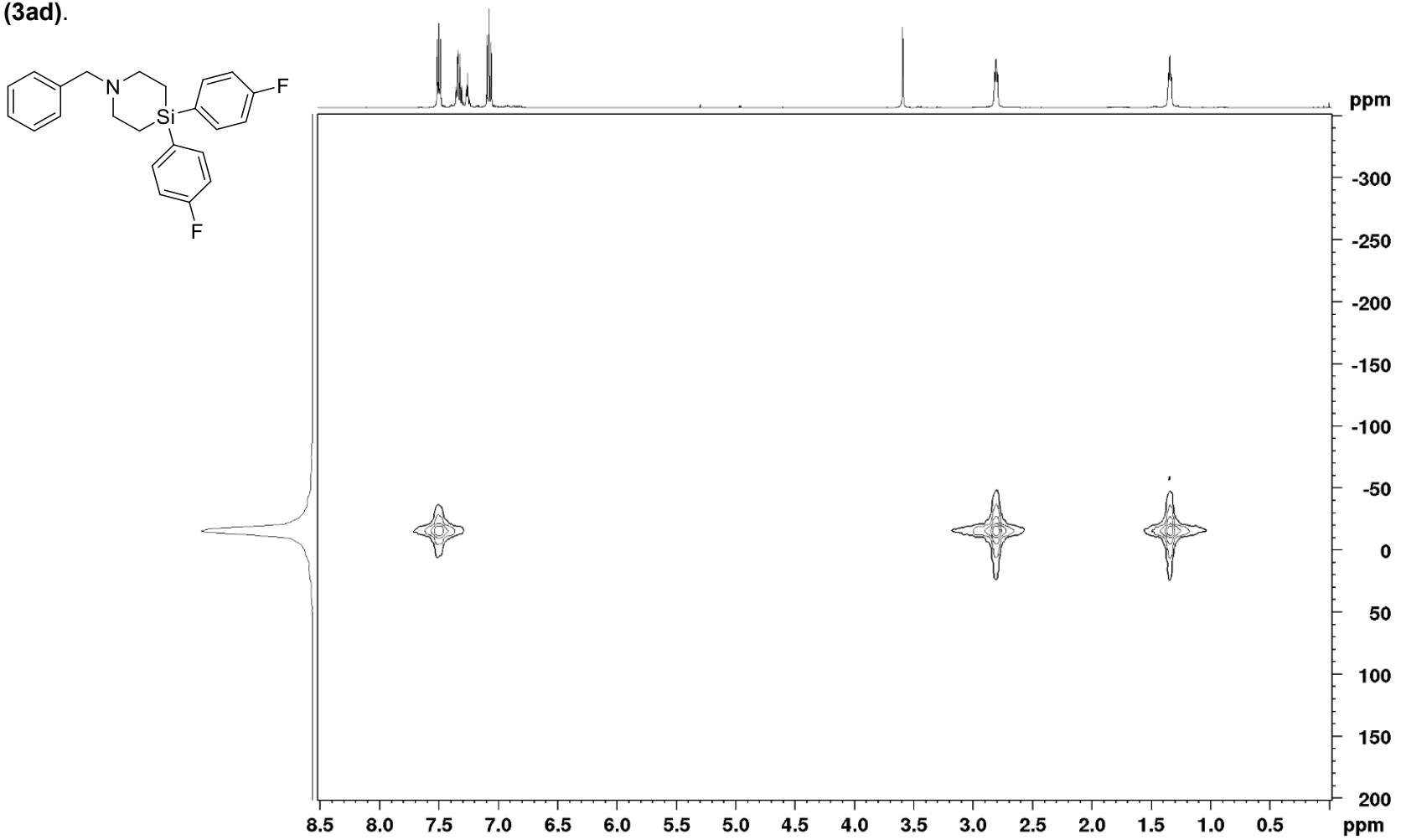


Figure S83. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-4-(naphthalen-1-yl)-4-phenyl-1,4-azasilinane (3ae)**.

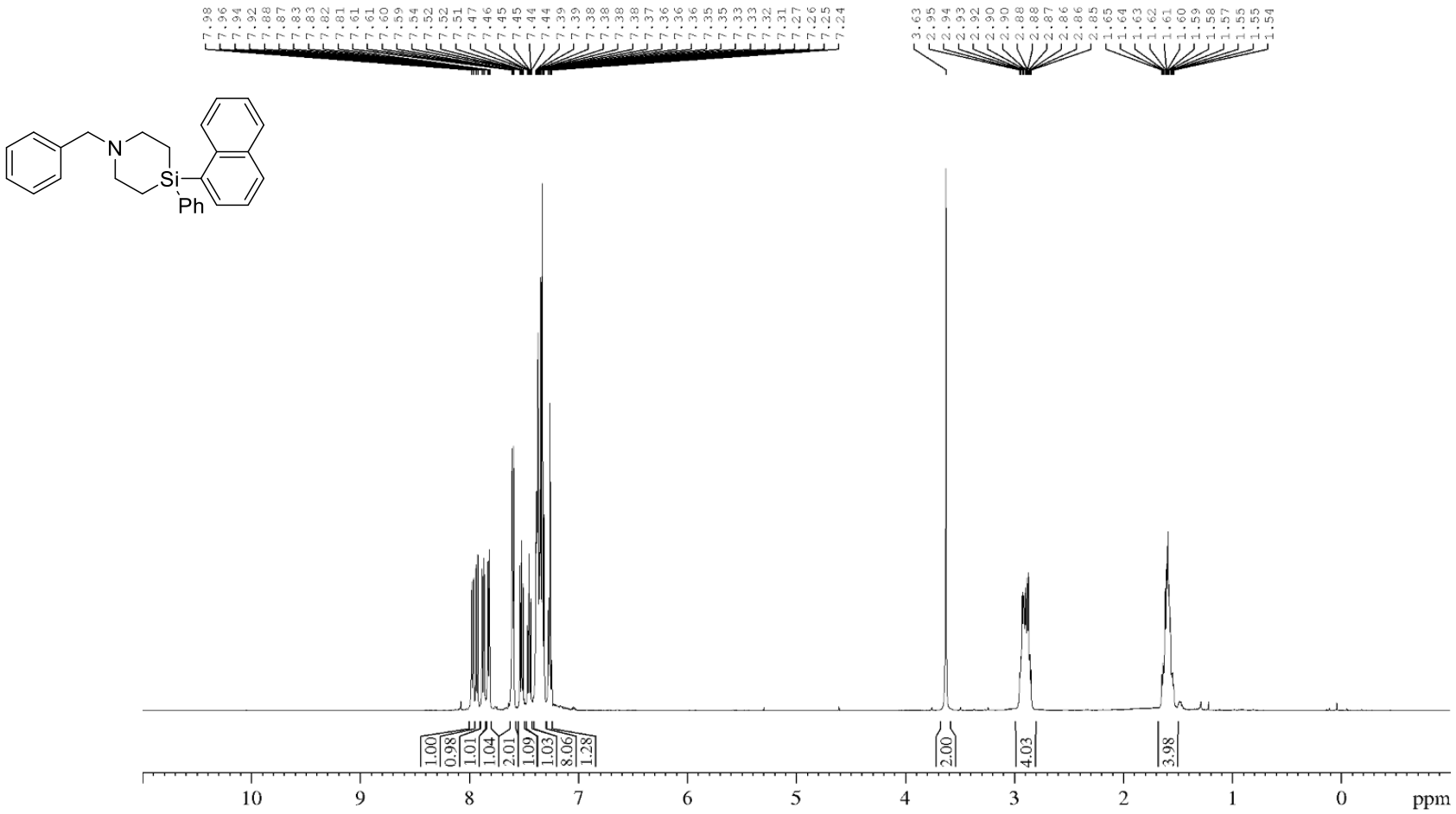


Figure S84. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-4-(naphthalen-1-yl)-4-phenyl-1,4-azasilinane (3ae)**.

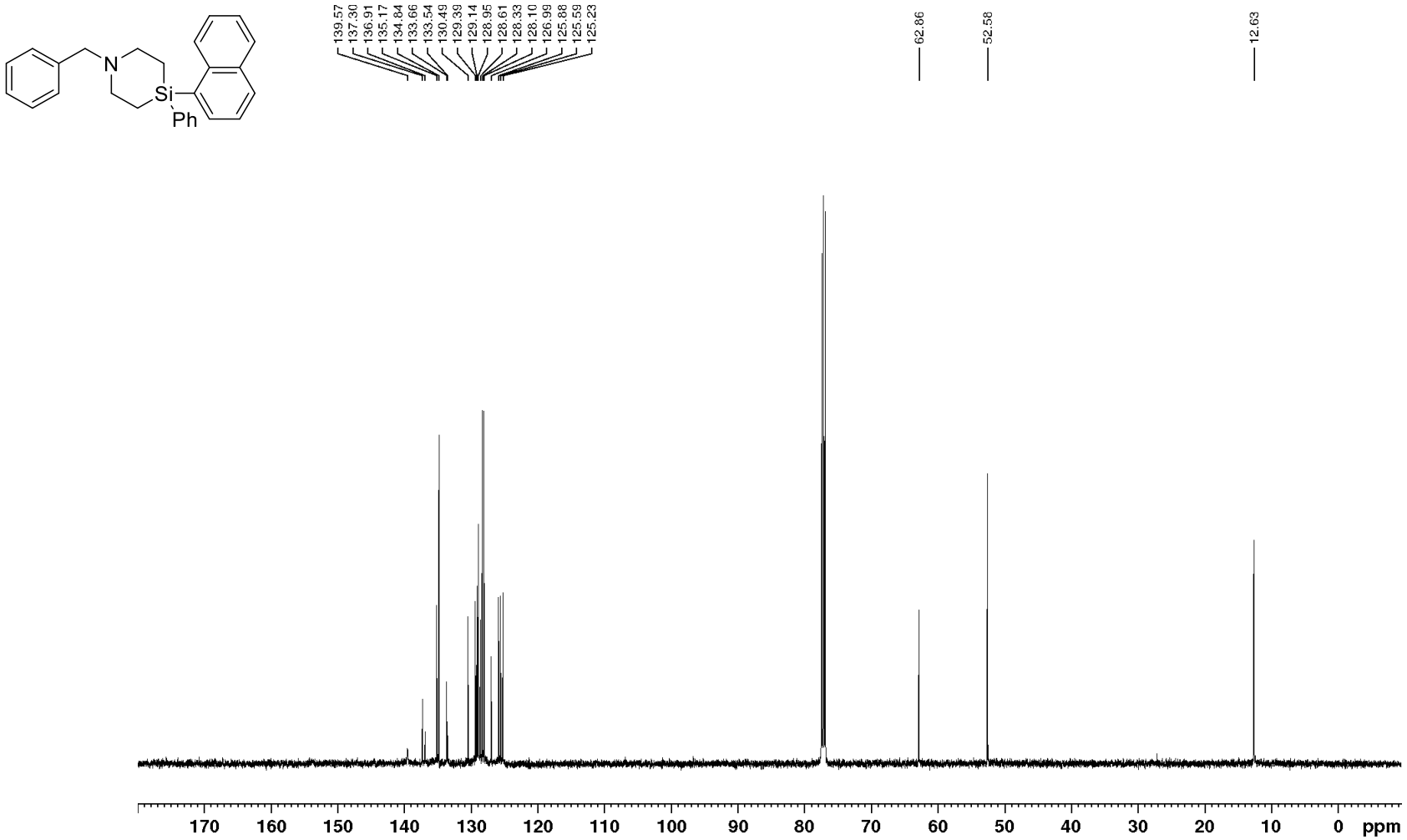


Figure S85. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-4-(naphthalen-1-yl)-4-phenyl-1,4-aza-silinane (3ae)**.

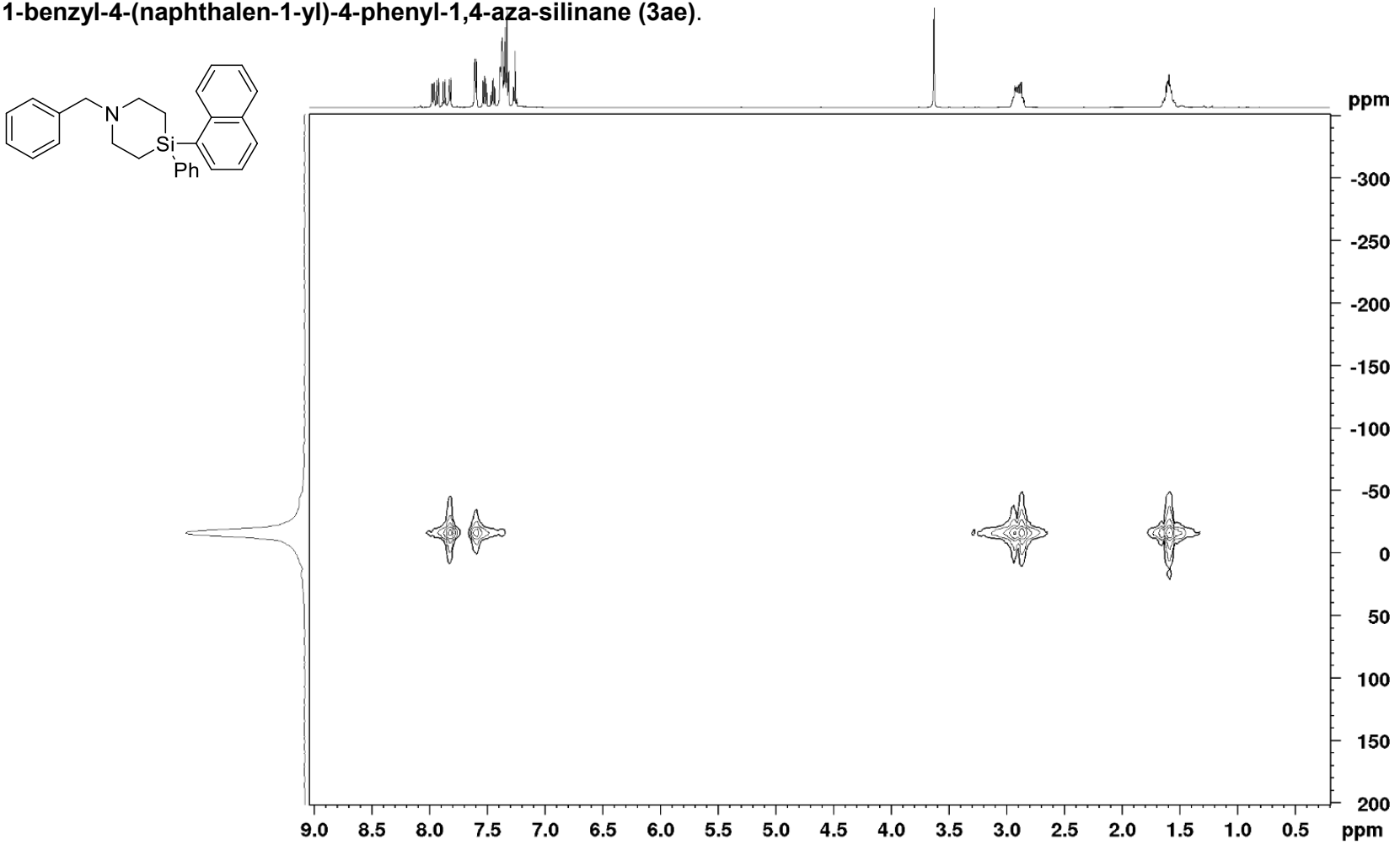


Figure S86. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-4-methyl-4-phenyl-1,4-azasilinane (3ag)**.

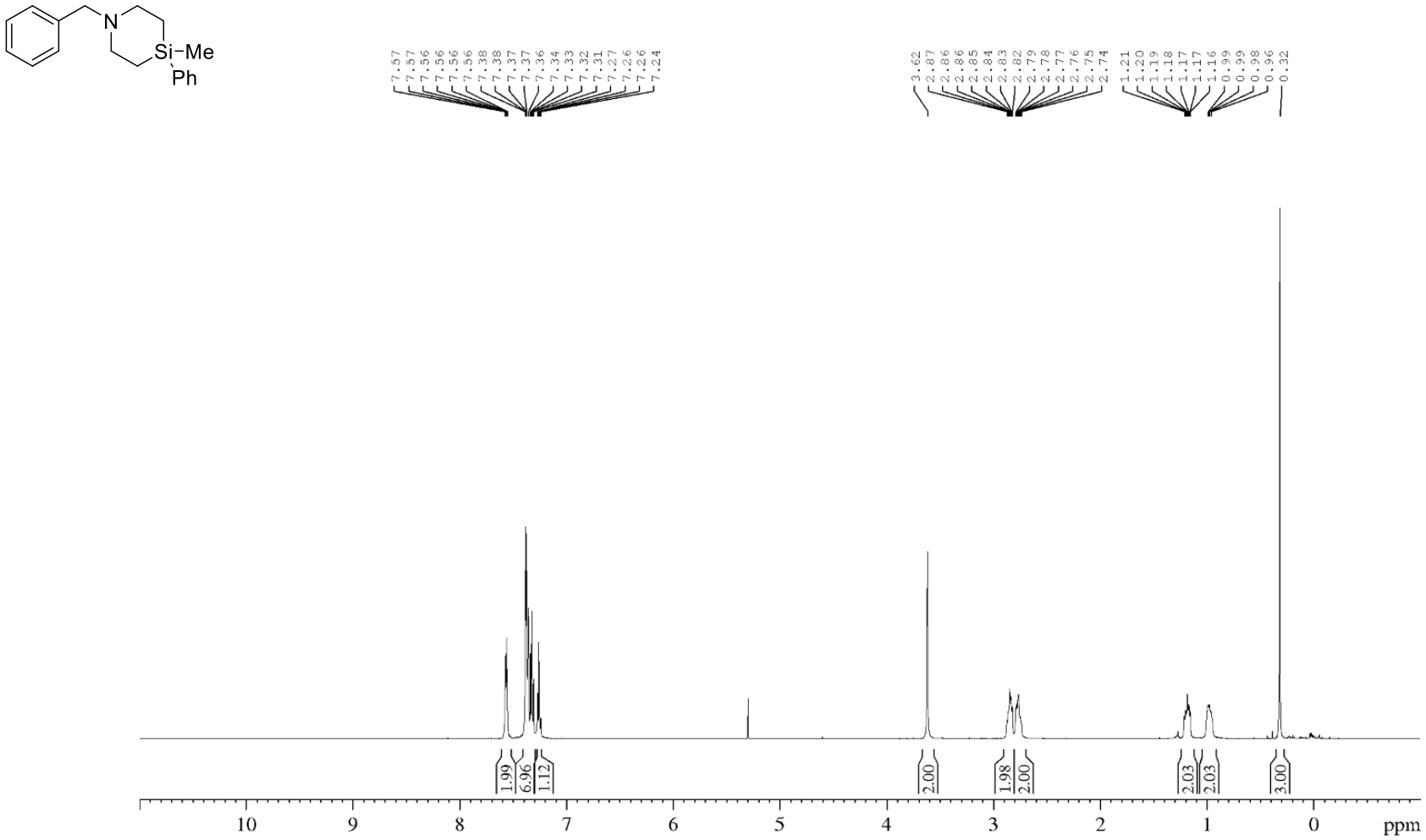


Figure S87. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-4-methyl-4-phenyl-1,4-azasilinane (3ag)**.

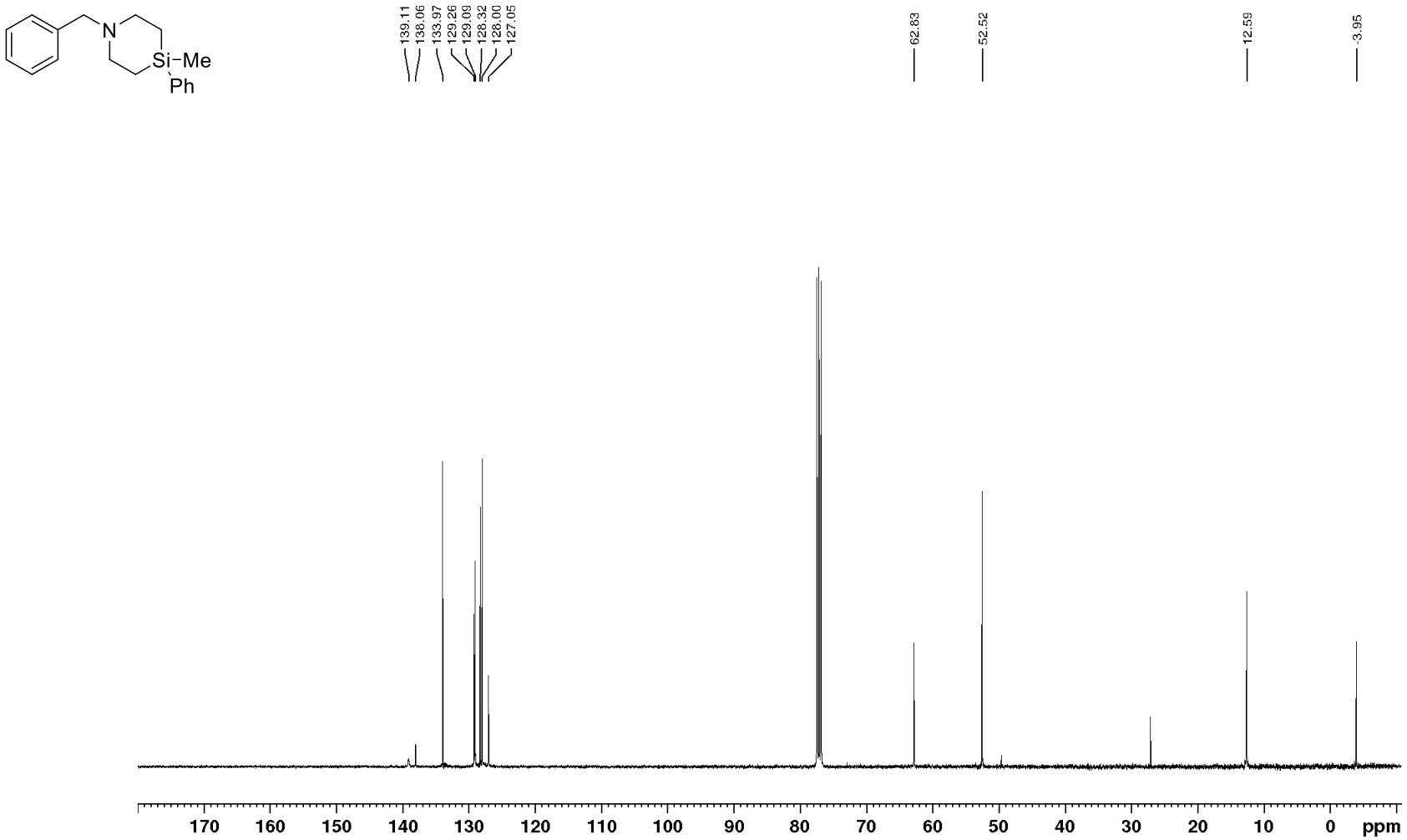


Figure S88. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-4-methyl-4-phenyl-1,4-azasilinane (3ag)**.

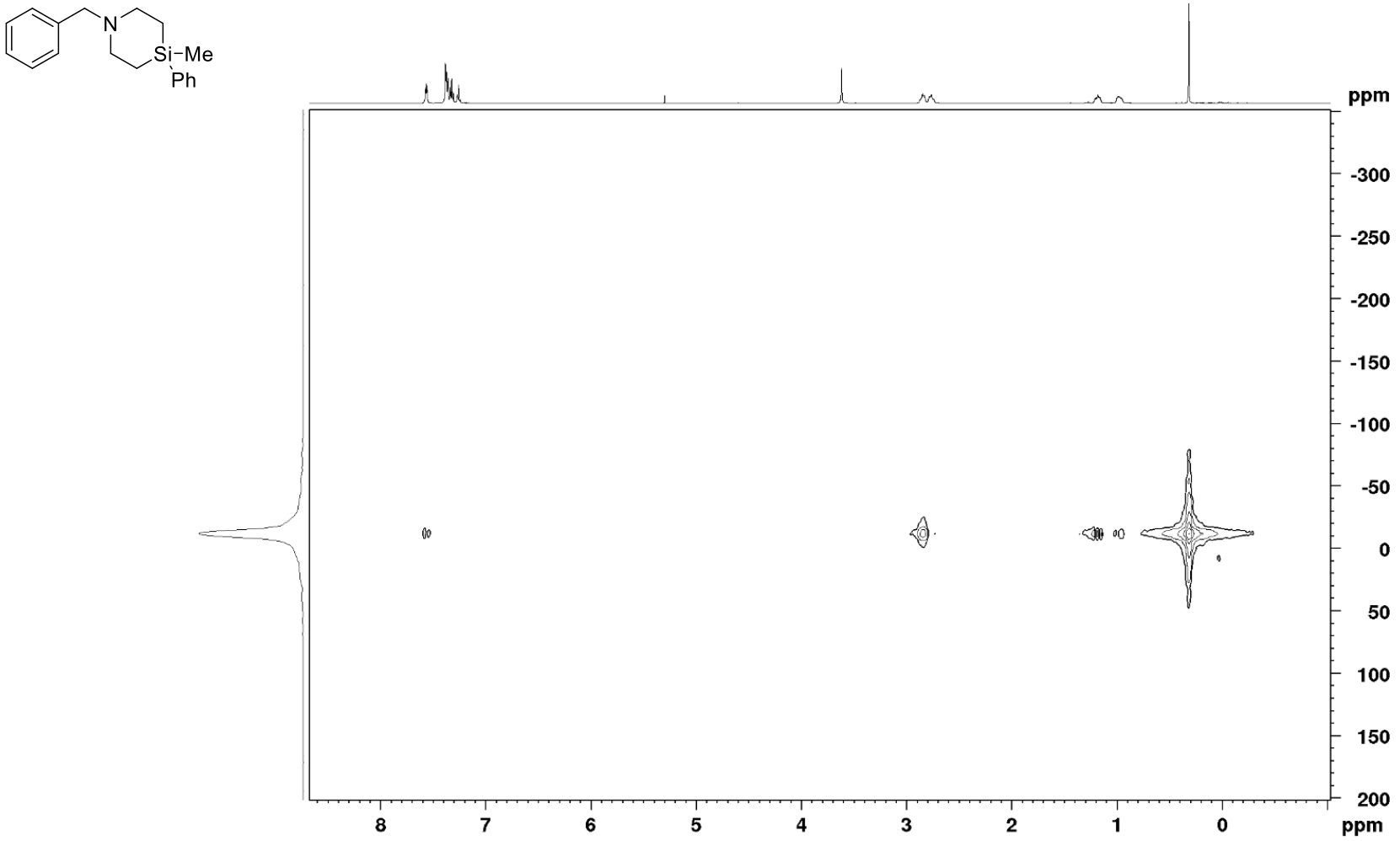


Figure S89. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-diethyl-1,4-azasilinane (3ai)**.

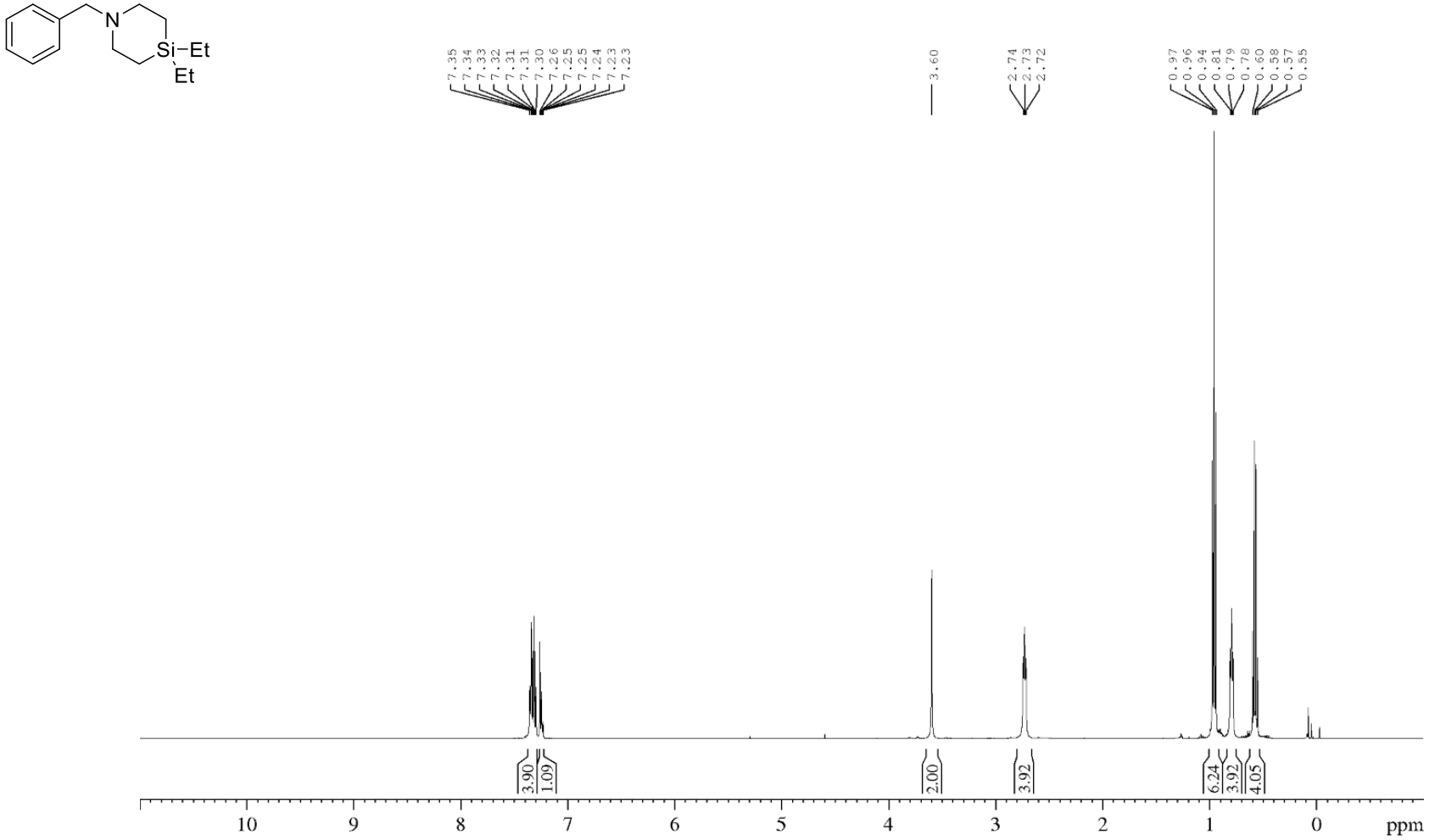


Figure S90. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1-benzyl-4,4-diethyl-1,4-azasilinane (3ai)**.

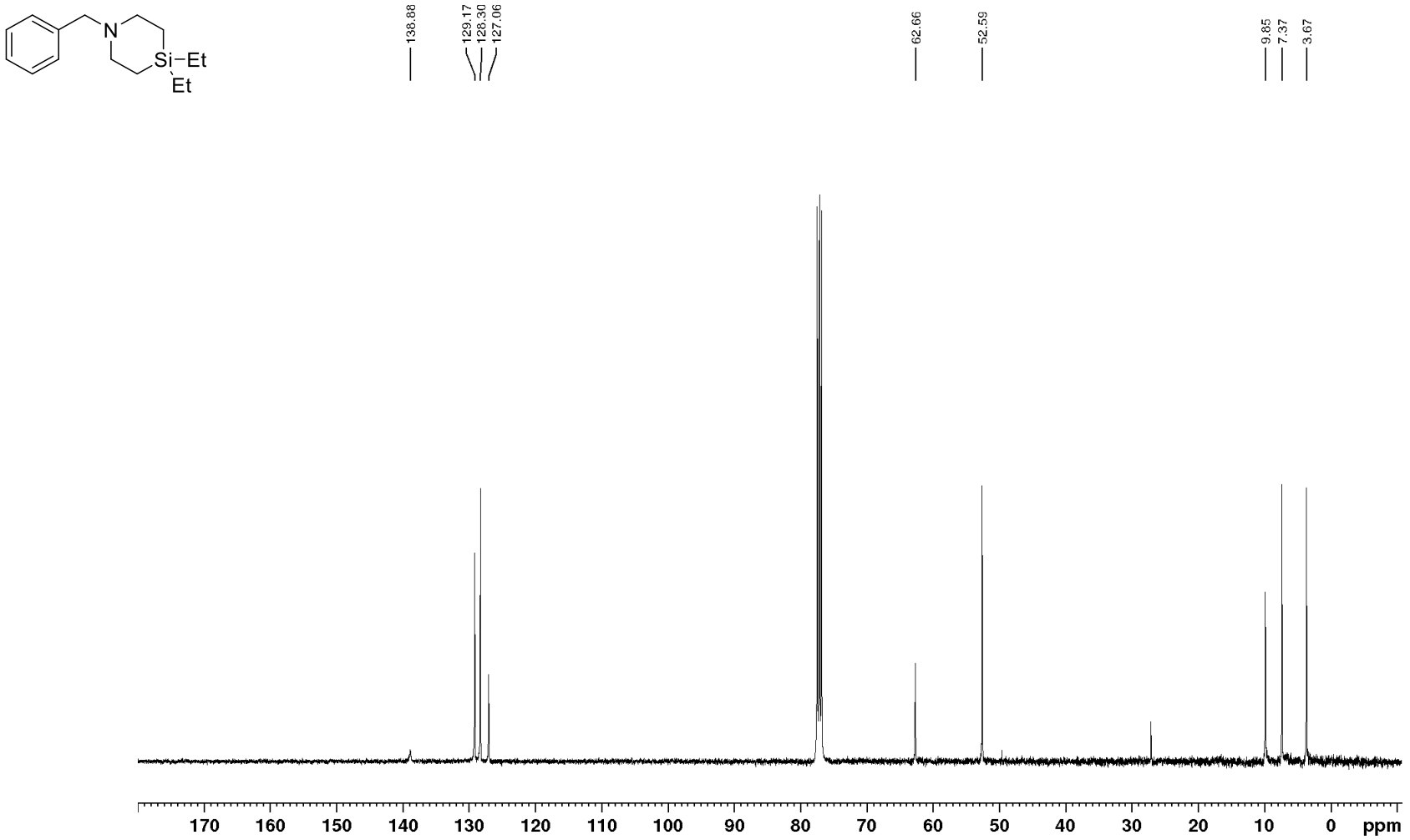


Figure S91. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **1-benzyl-4,4-diethyl-1,4-azasilinane (3ai)**.

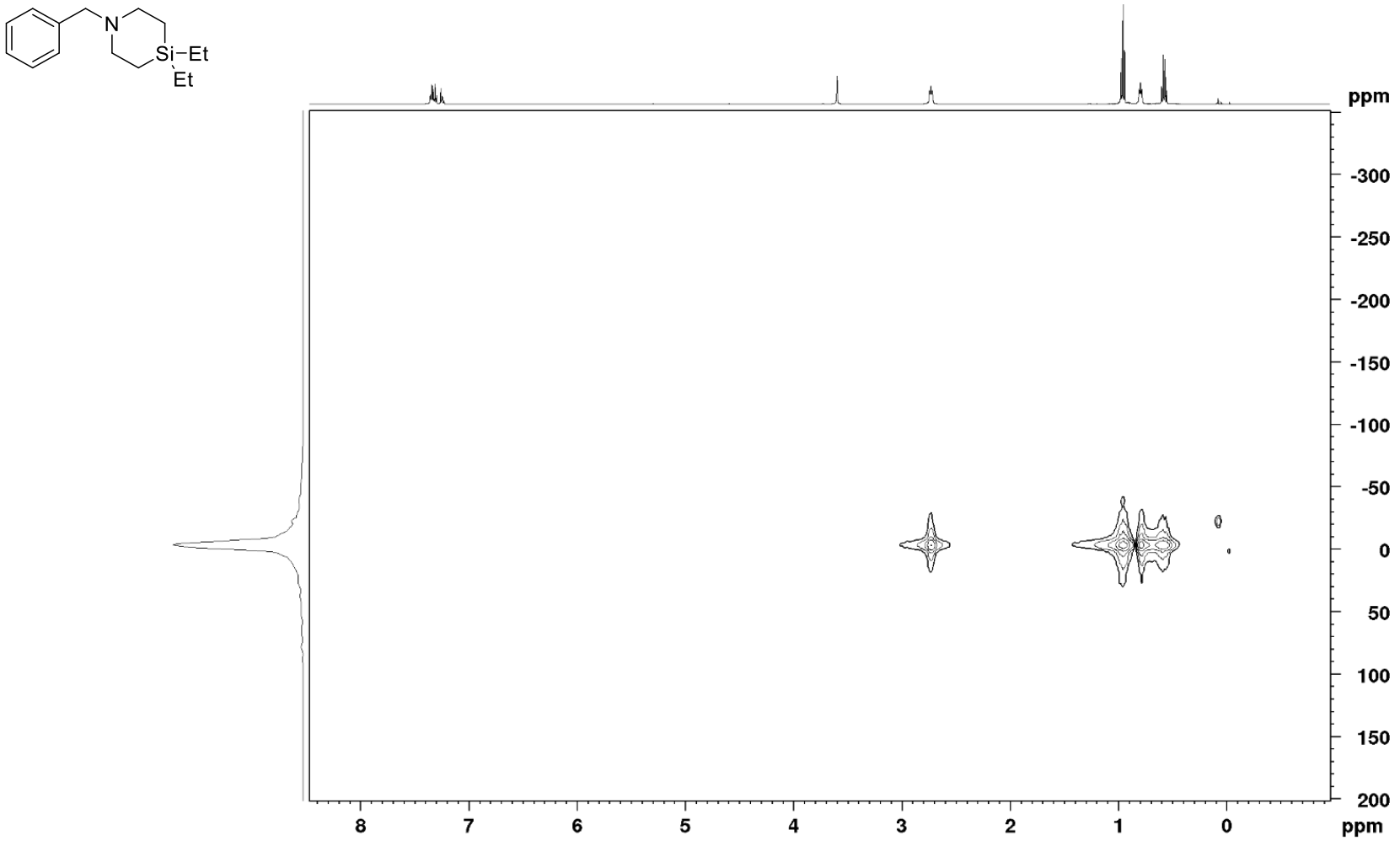


Figure S92. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4,4-diphenyl-1,4-azasilinane hydrochloride (6)**.

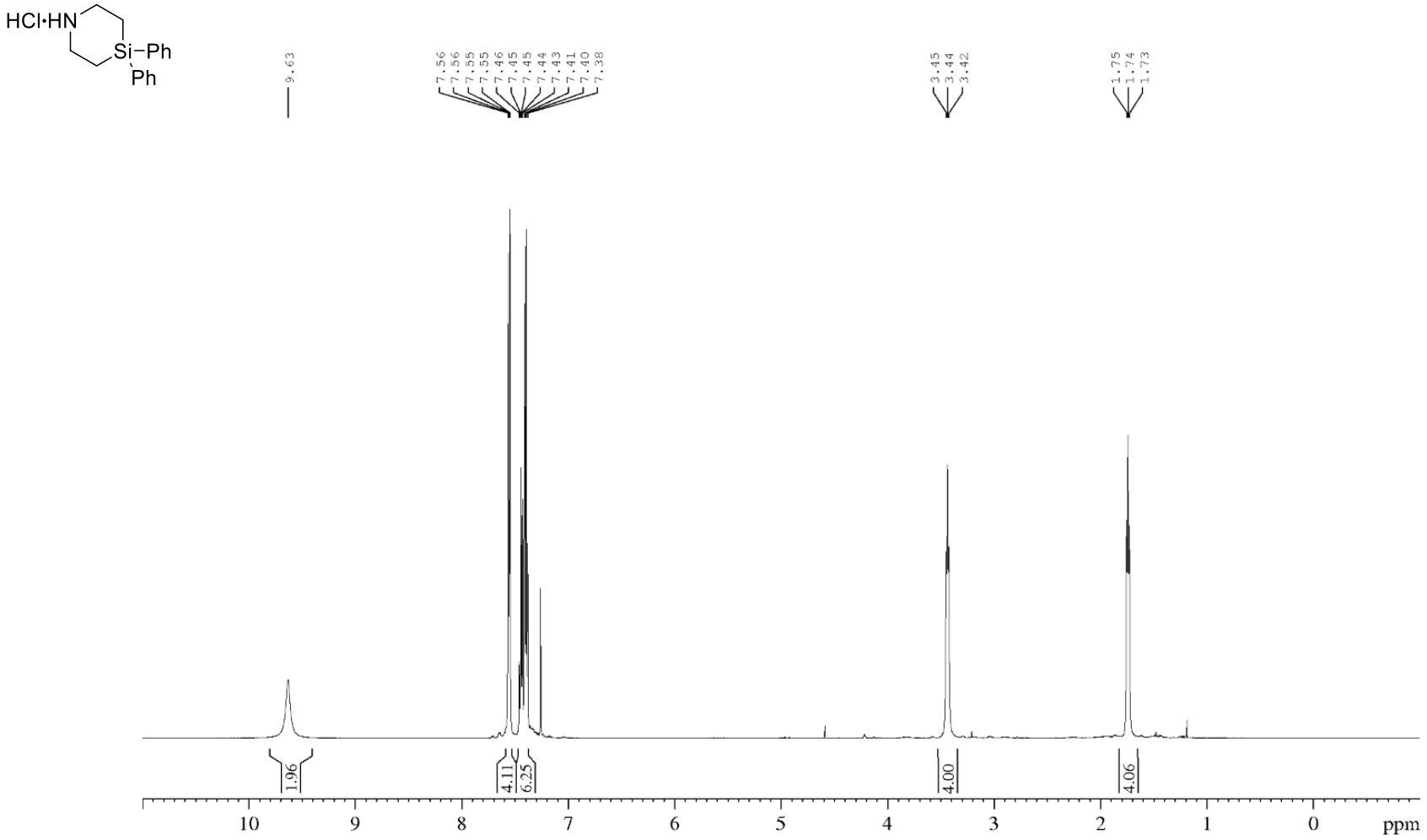


Figure S93. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **4,4-diphenyl-1,4-azasilinane hydrochloride (6)**.

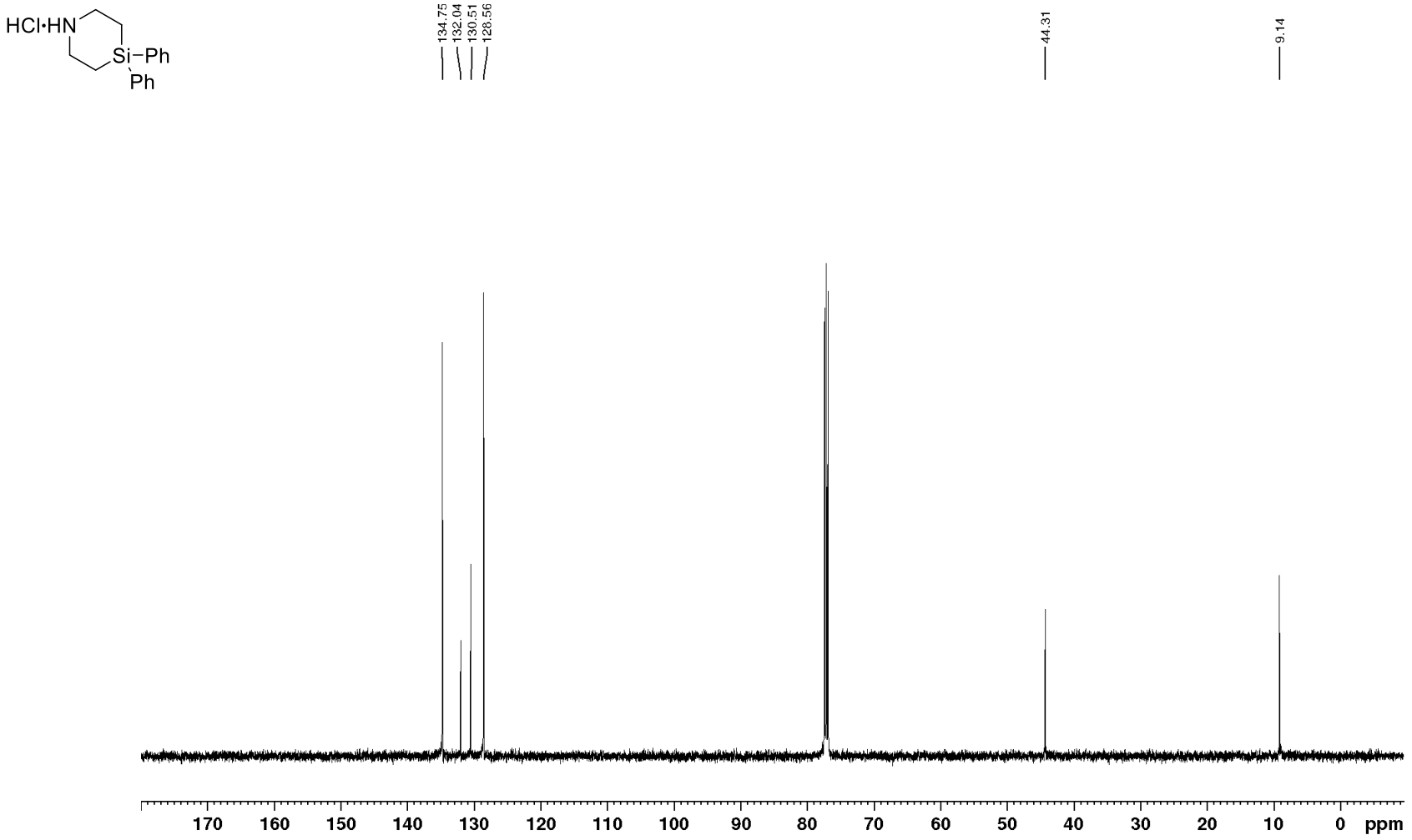


Figure S94. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4,4-diphenyl-1,4-azasilinane hydrochloride (6)**.

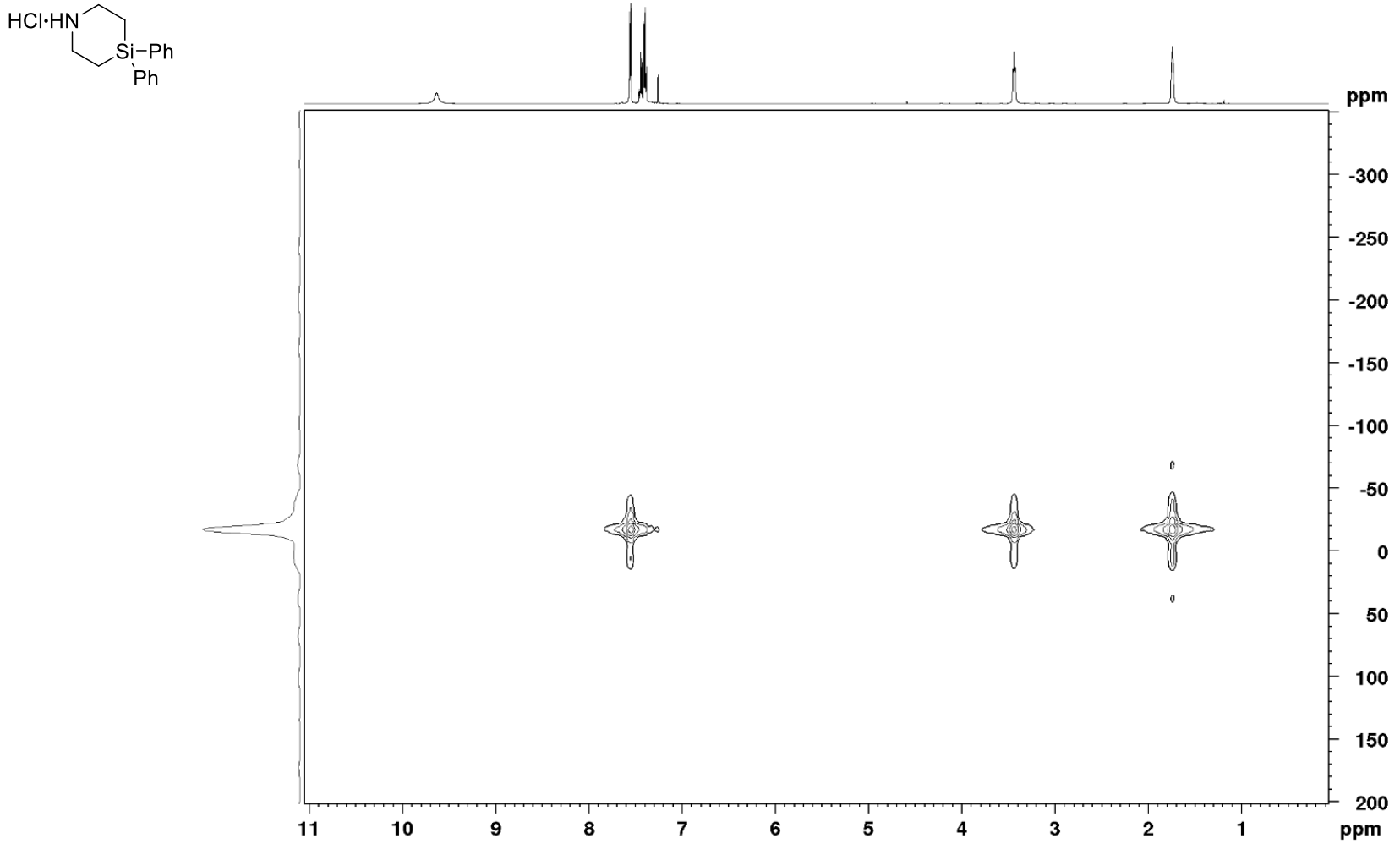


Figure S95. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **(4,4-diphenyl-1,4-azasilinan-1-yl)(phenyl)methanone (7)**.

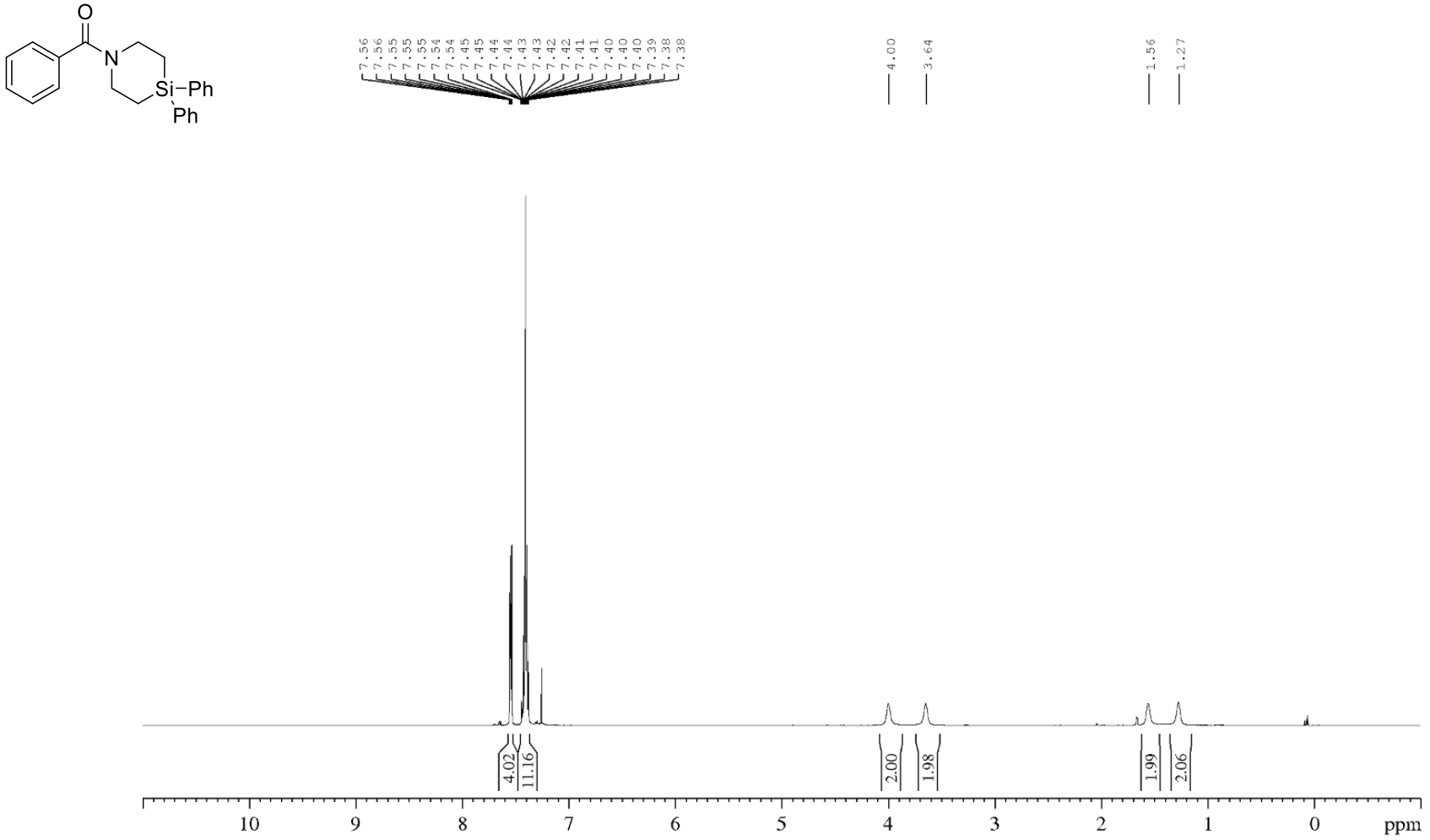


Figure S96. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **(4,4-diphenyl-1,4-azasilinan-1-yl)(phenyl)methanone (7)**.

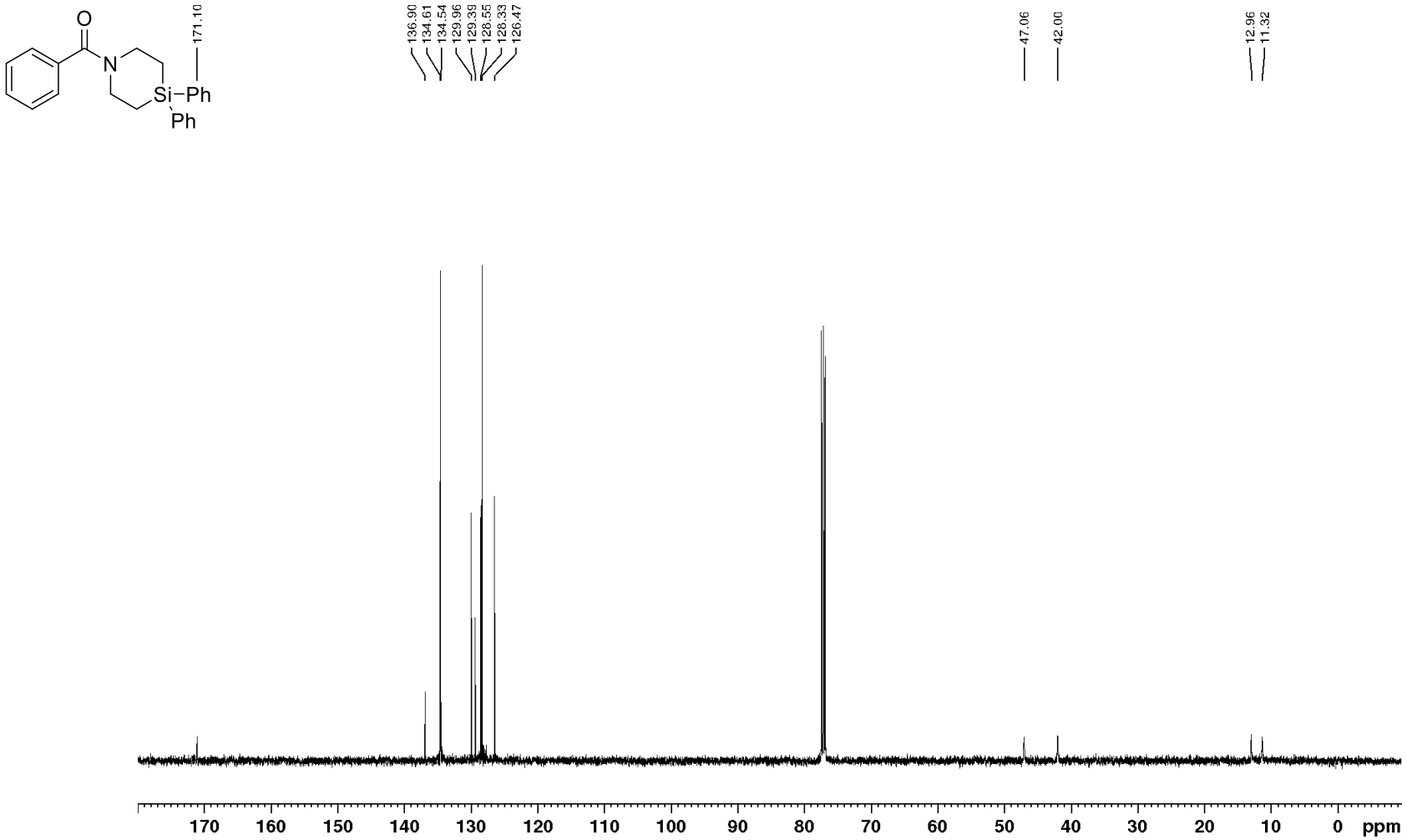


Figure S97 $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **(4,4-diphenyl-1,4-azasilinan-1-yl)(phenyl)methanone (7)**.

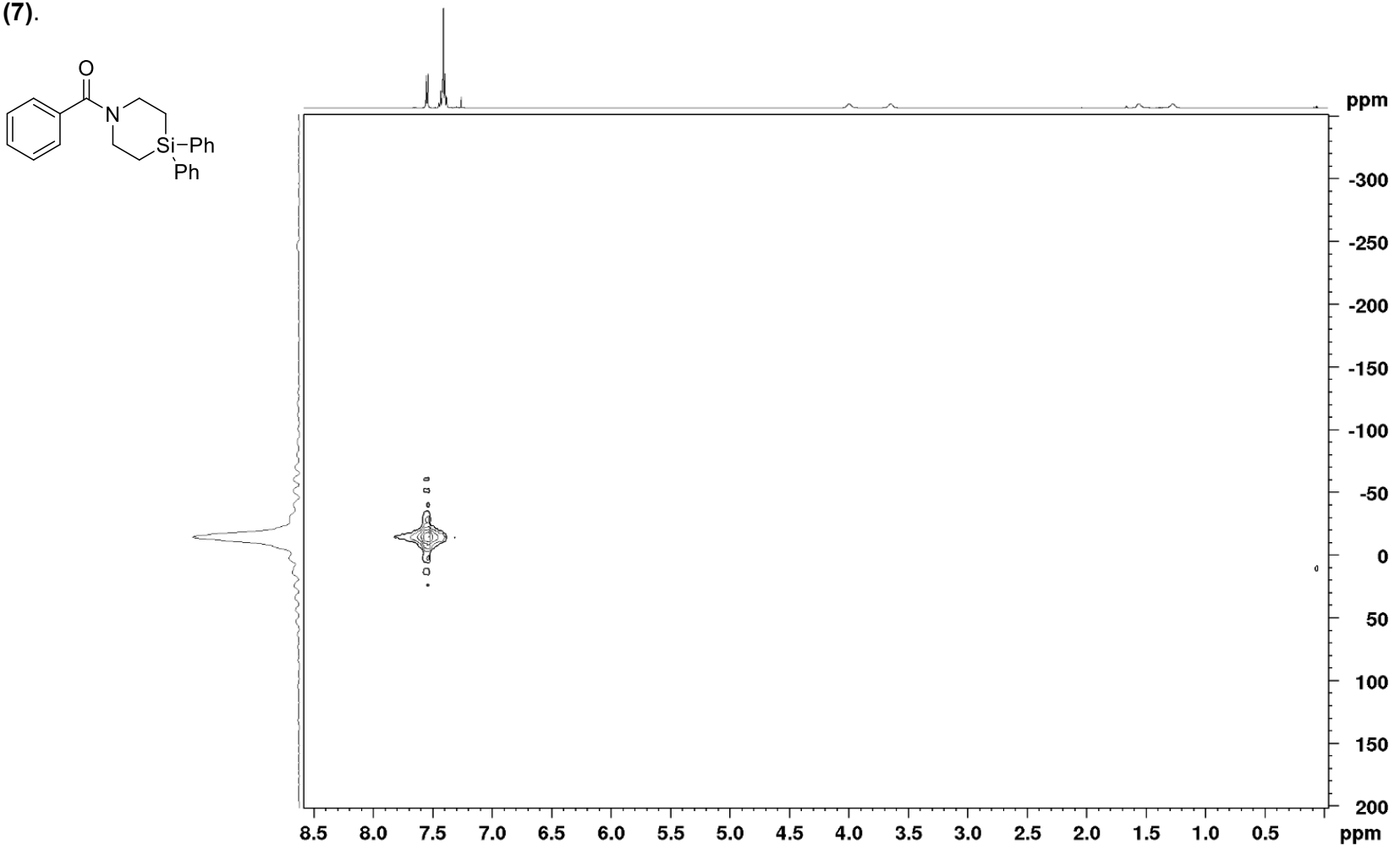


Figure S98. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **4,4-diphenyl-1-(phenylmethyl-d)-1,4-azasilinane-2,6-d_2 (3aa-d_3)**.

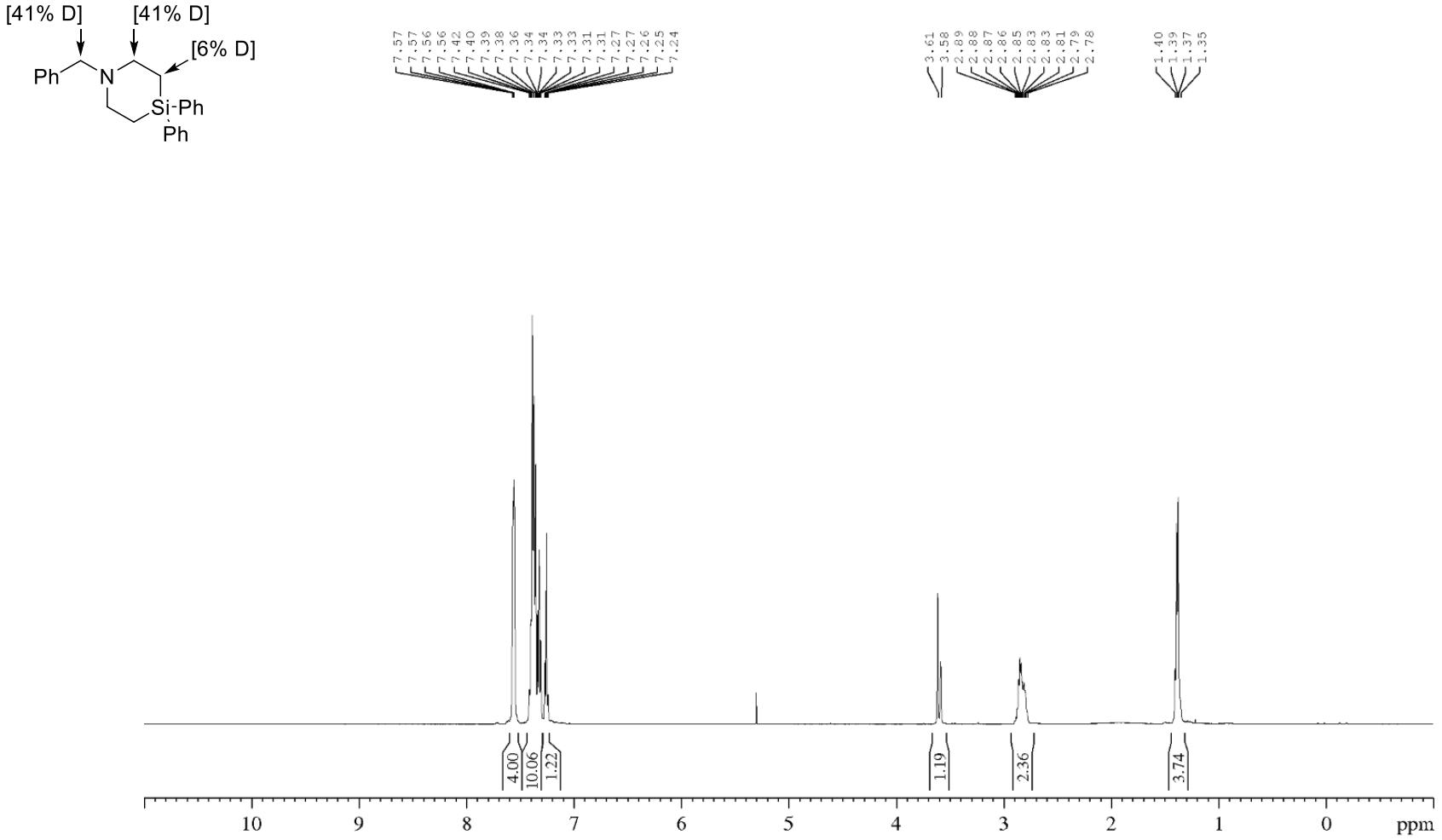


Figure S99. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **4,4-diphenyl-1-(phenylmethyl-d)-1,4-azasilinane-2,6-d_2 (3aa-d_3)**.

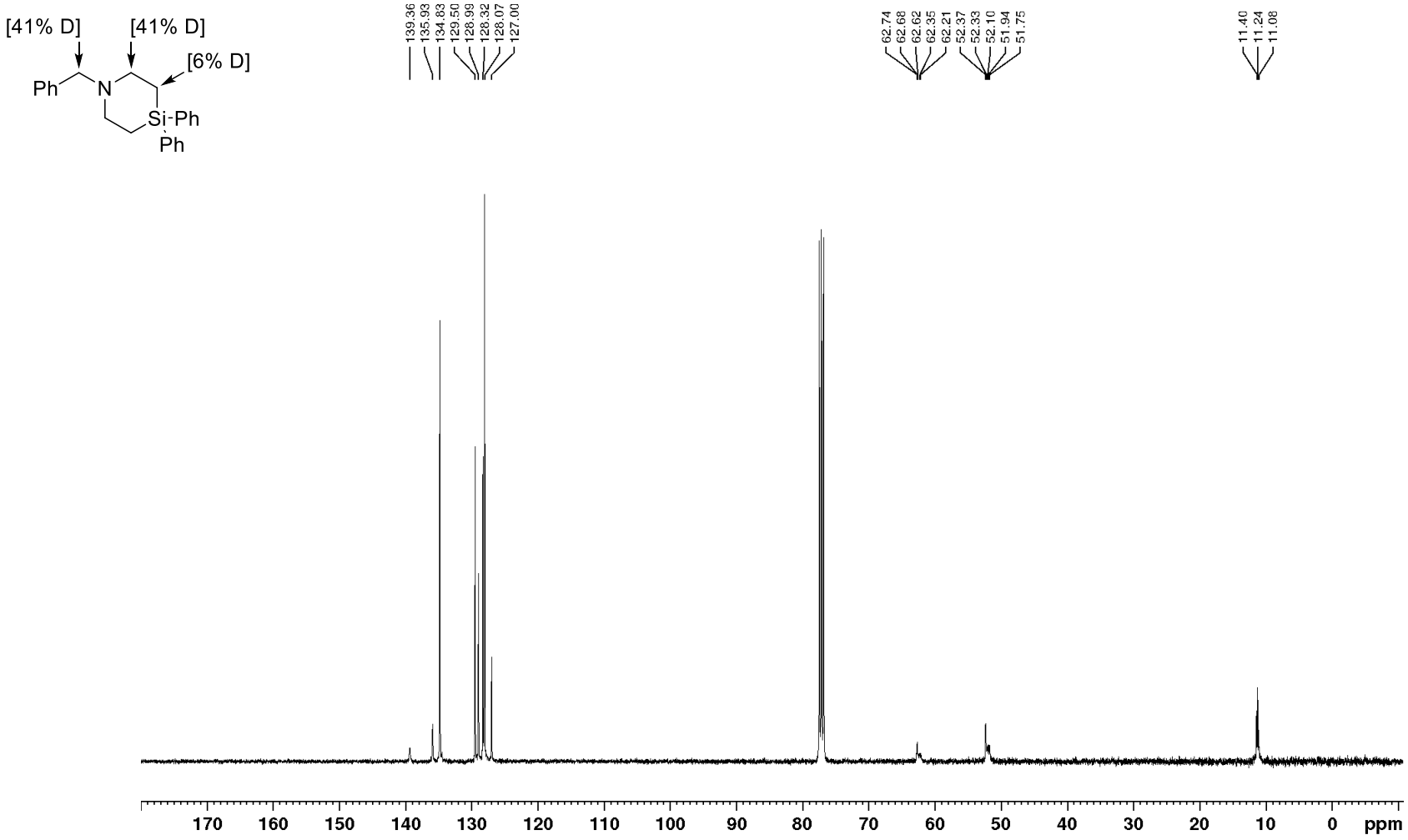


Figure S100. $^{1}H/^{29}Si$ HMQC NMR (500/99 MHz, $CDCl_3$, 298 K, optimized for J = 7 Hz) of **4,4-diphenyl-1-(phenylmethyl-d)-1,4-azasilinane-2,6-d_2 (3aa-d_3)**.

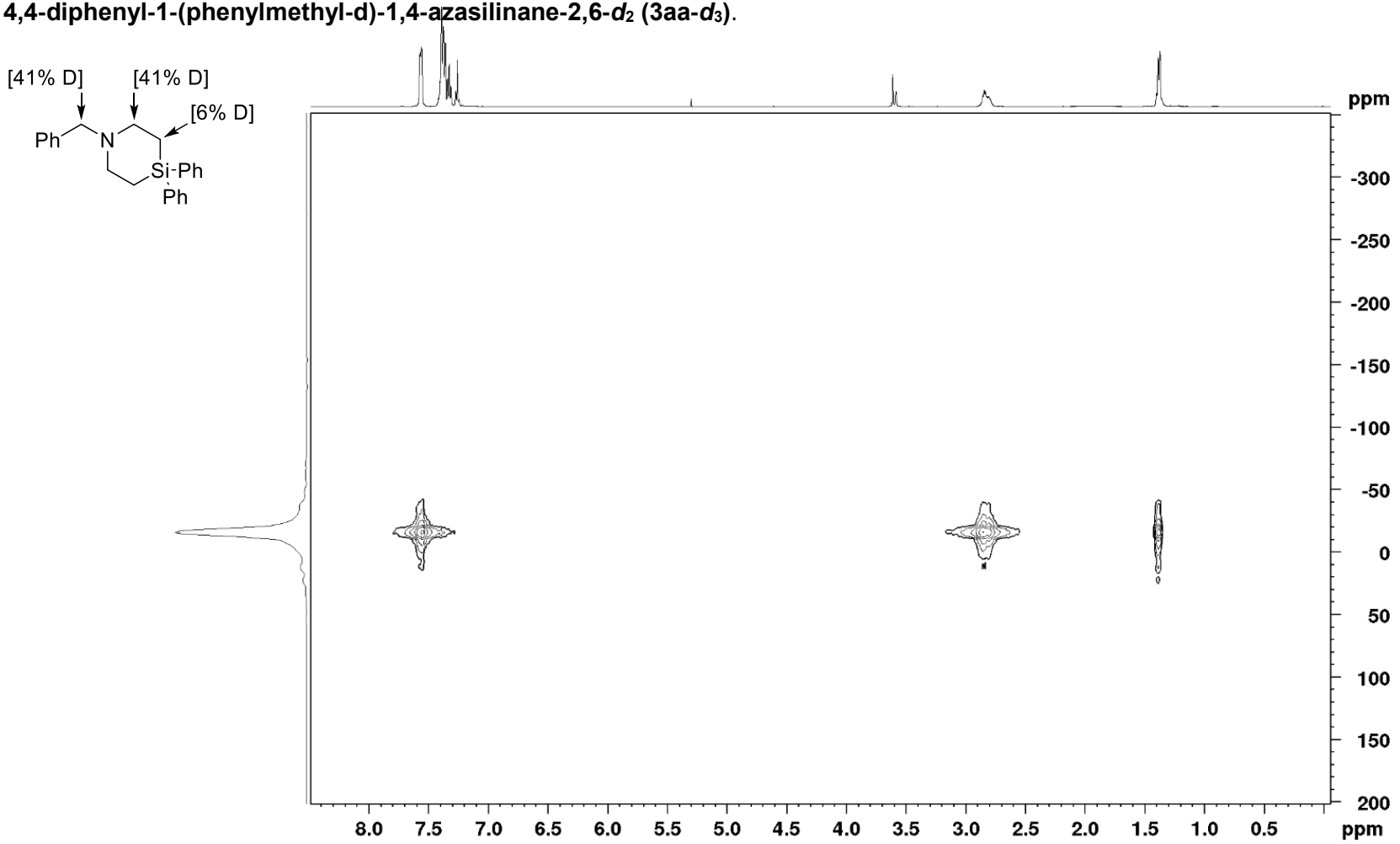


Figure S101. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of ***N*-benzyl-*N*-butylbutan-1-amine-d_3 (1v-d_3)**.

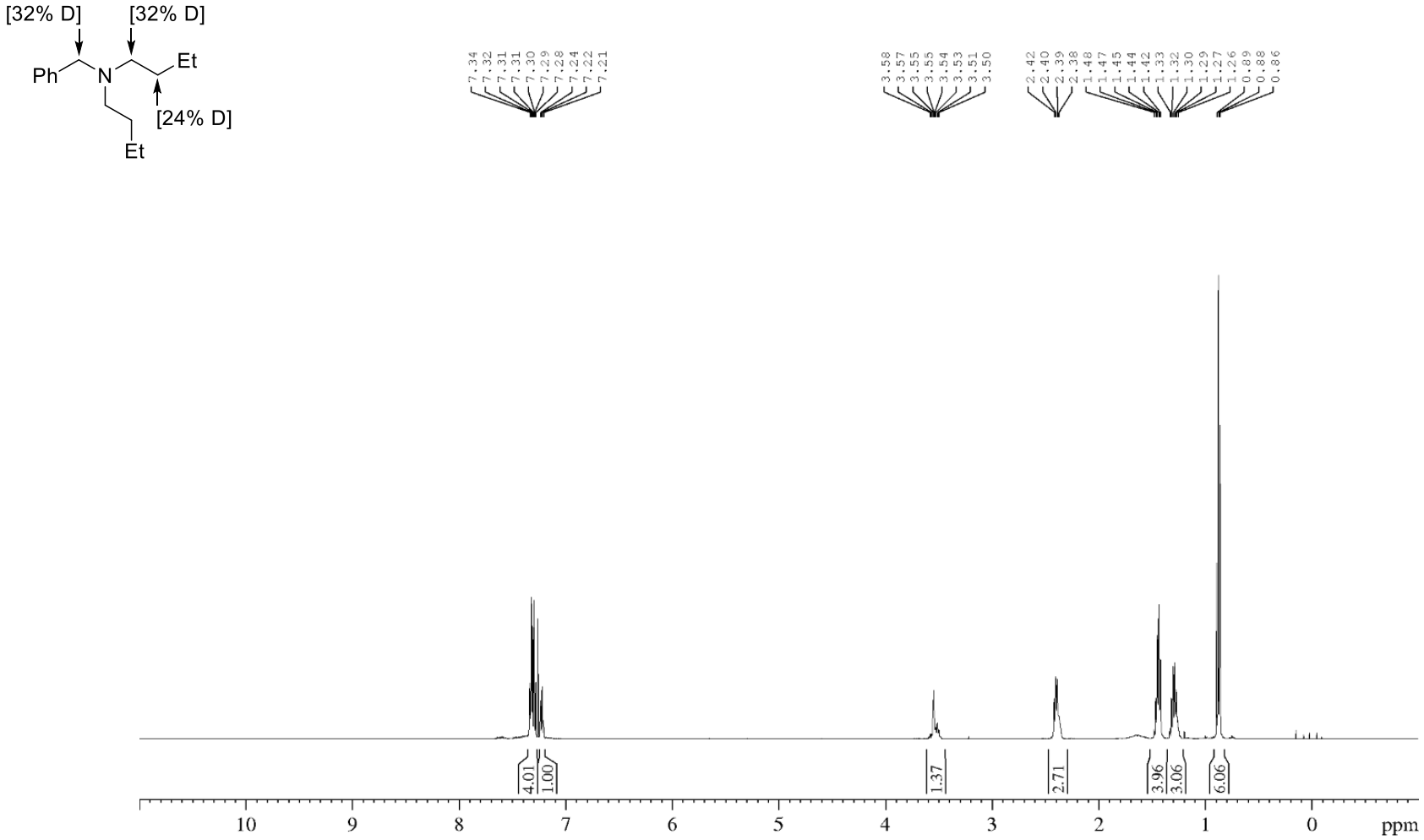


Figure S102. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of ***N*-benzyl-*N*-butylbutan-1-amine-d_3 (1v-d_3)**..

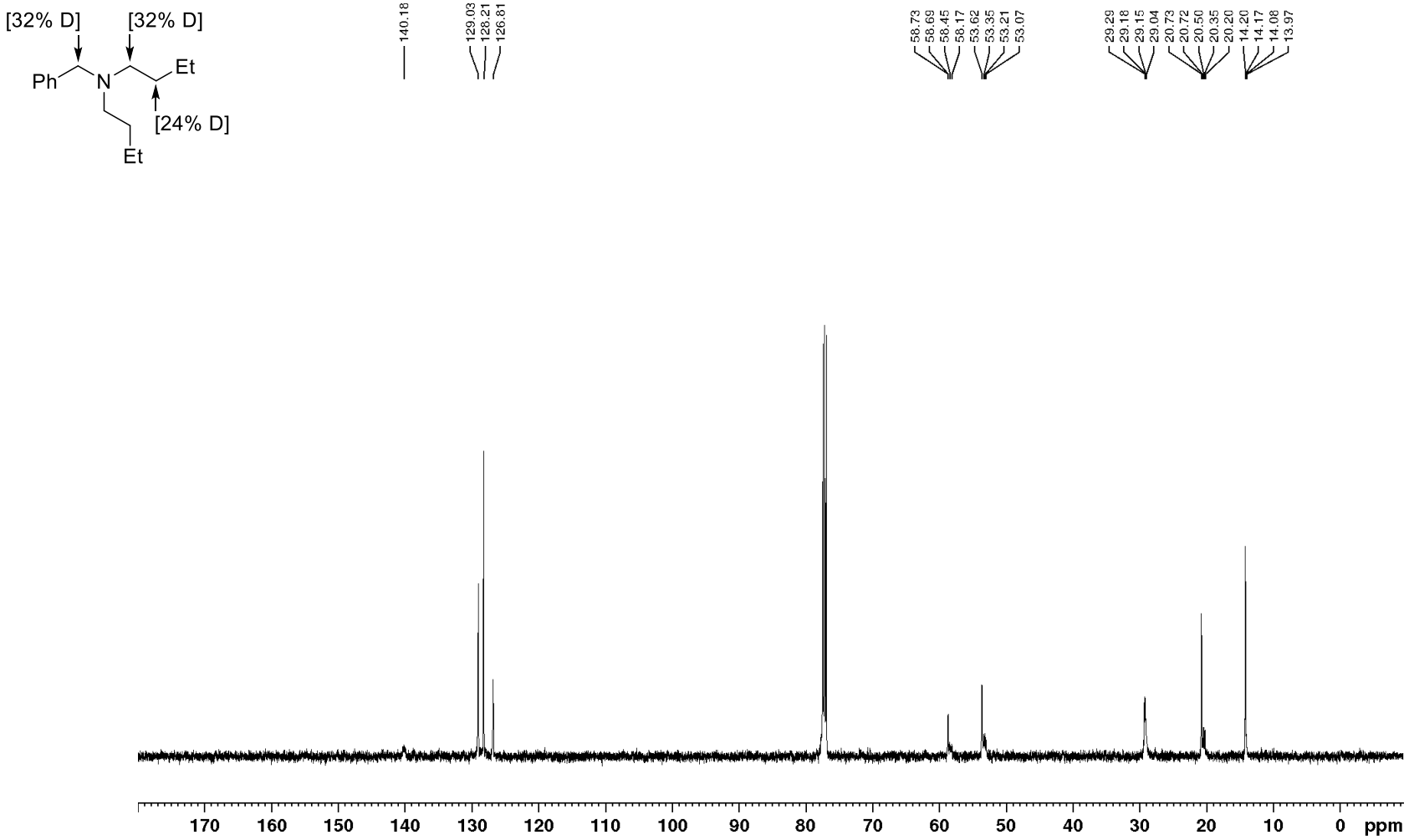


Figure S103. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of the stoichiometric reaction of **1a** and $B(C_6F_5)_3$ (1:1).

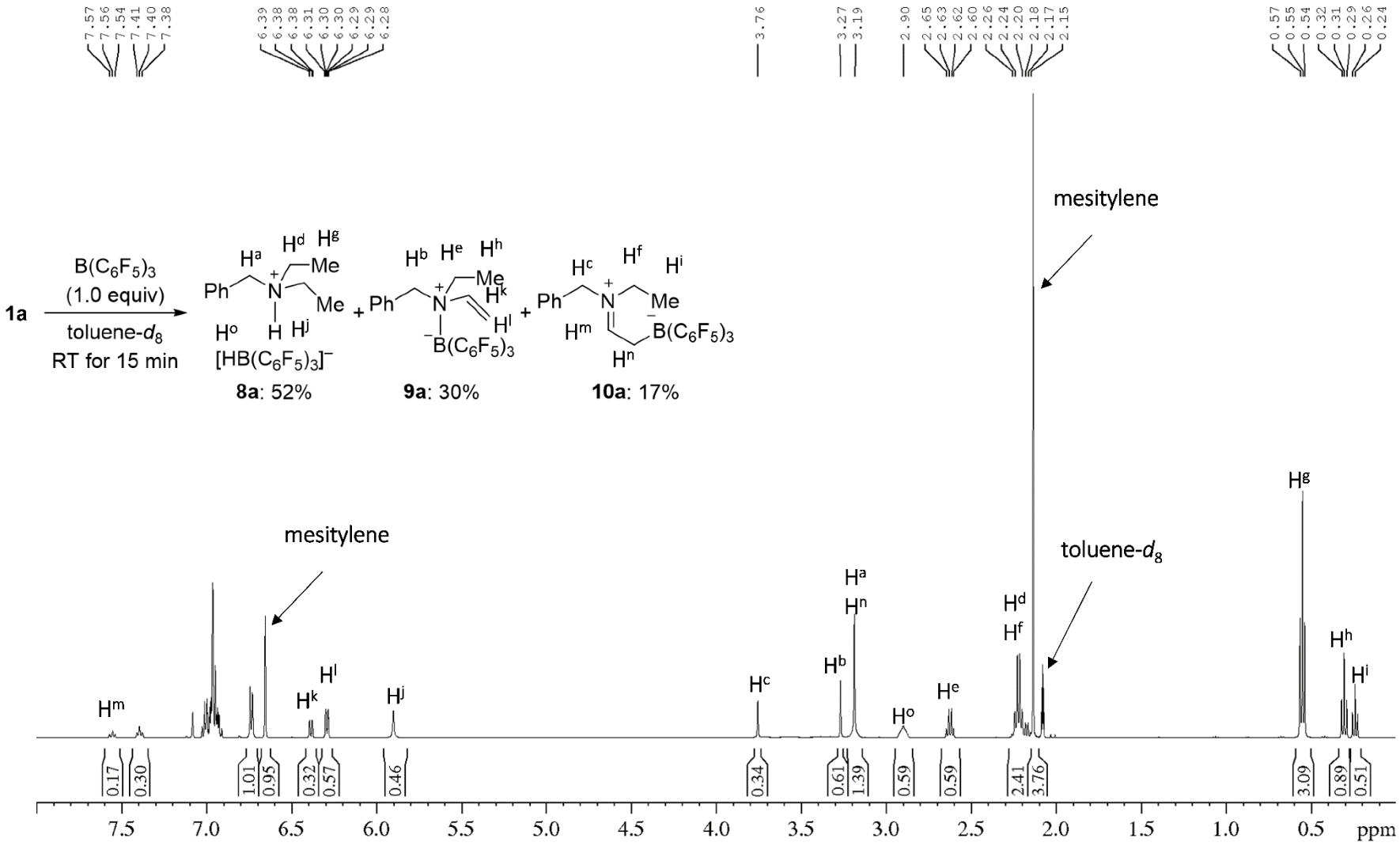


Figure S104. ^{11}B NMR spectrum (161 MHz, 1,2-$C_6D_4Cl_2$, 298 K) of the stoichiometric reaction of **1a** and $B(C_6F_5)_3$ (1:1).

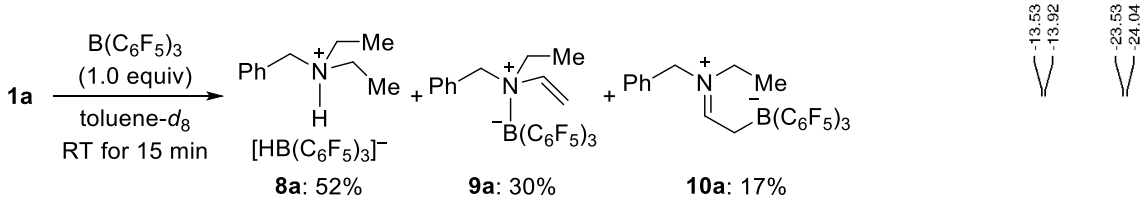


Figure S105. ^{19}F NMR spectrum (471 MHz, 1,2-$C_6D_4Cl_2$, 298 K) of the stoichiometric reaction of **1a** and $B(C_6F_5)_3$ (1:1).

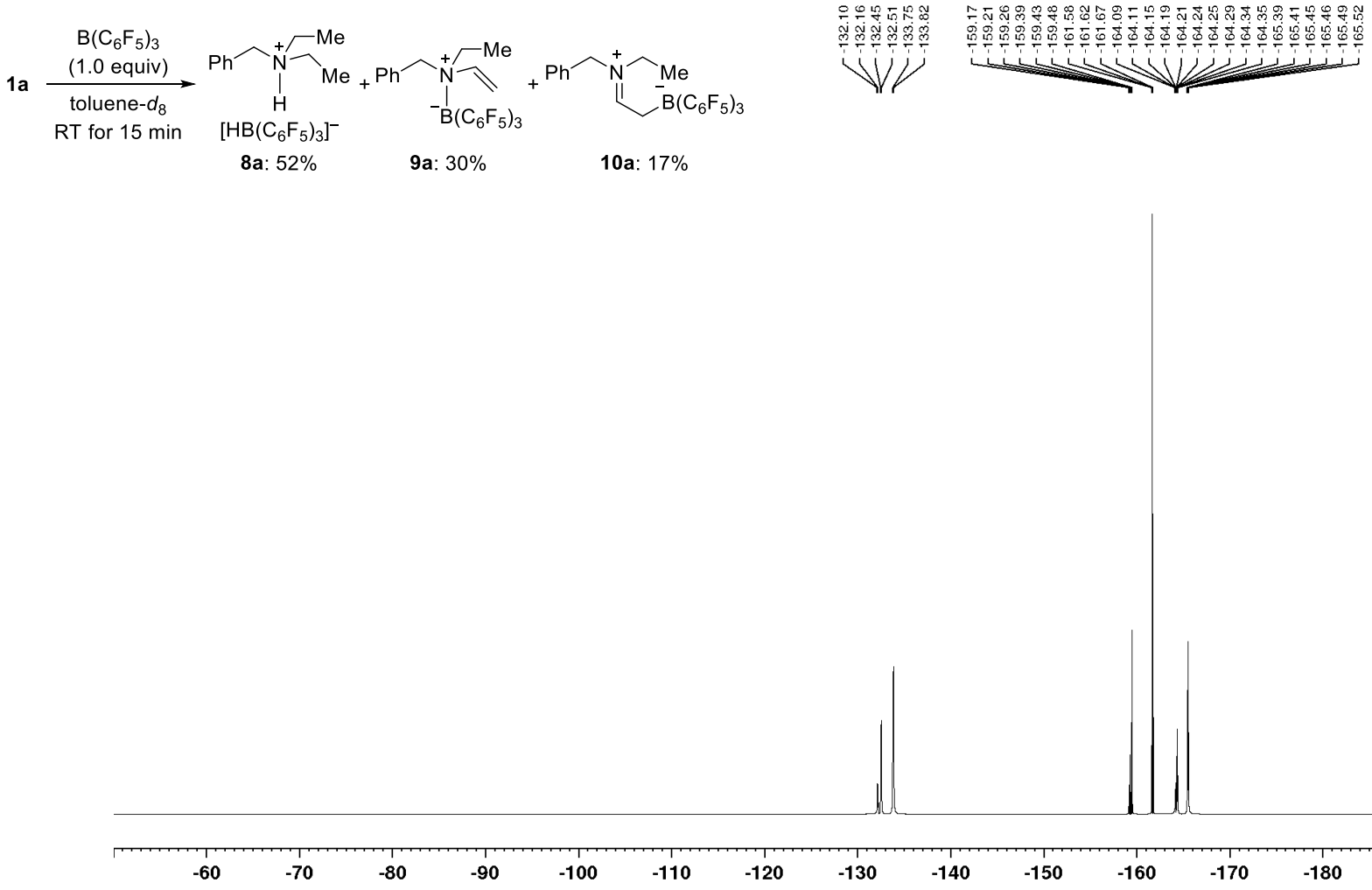


Figure S106. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of the stoichiometric reaction of **1a**, Me_3SiOTf, and $B(C_6F_5)_3$ (1:1:1).

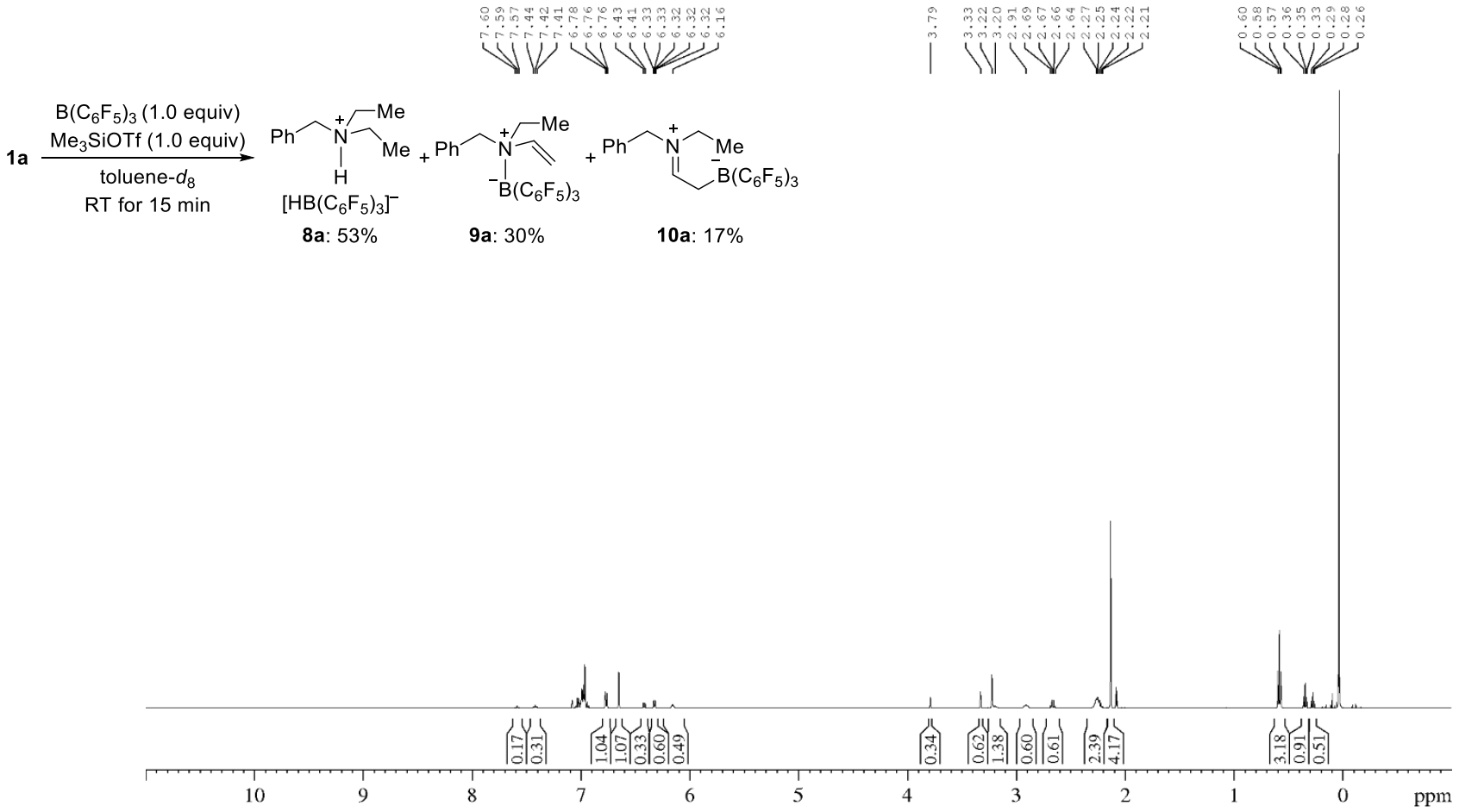
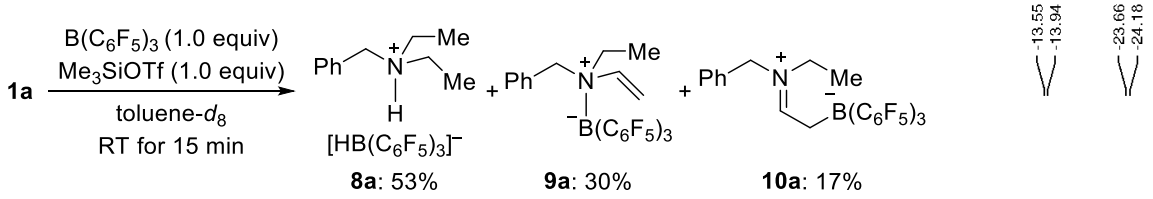


Figure S107. ^{11}B NMR spectrum (161 MHz, 1,2-$C_6D_4Cl_2$, 298 K) of the stoichiometric reaction of **1a**, Me_3SiOTf, and $B(C_6F_5)_3$ (1:1:1).



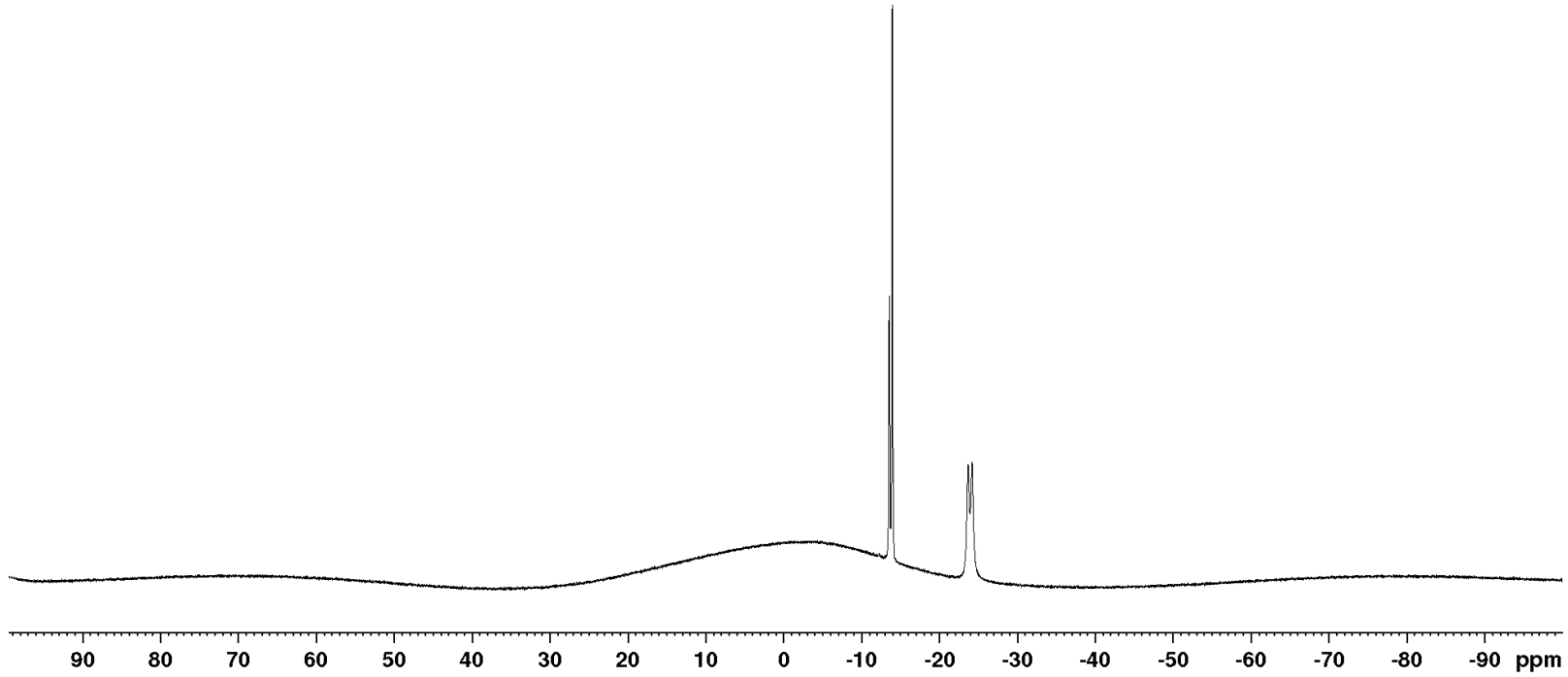
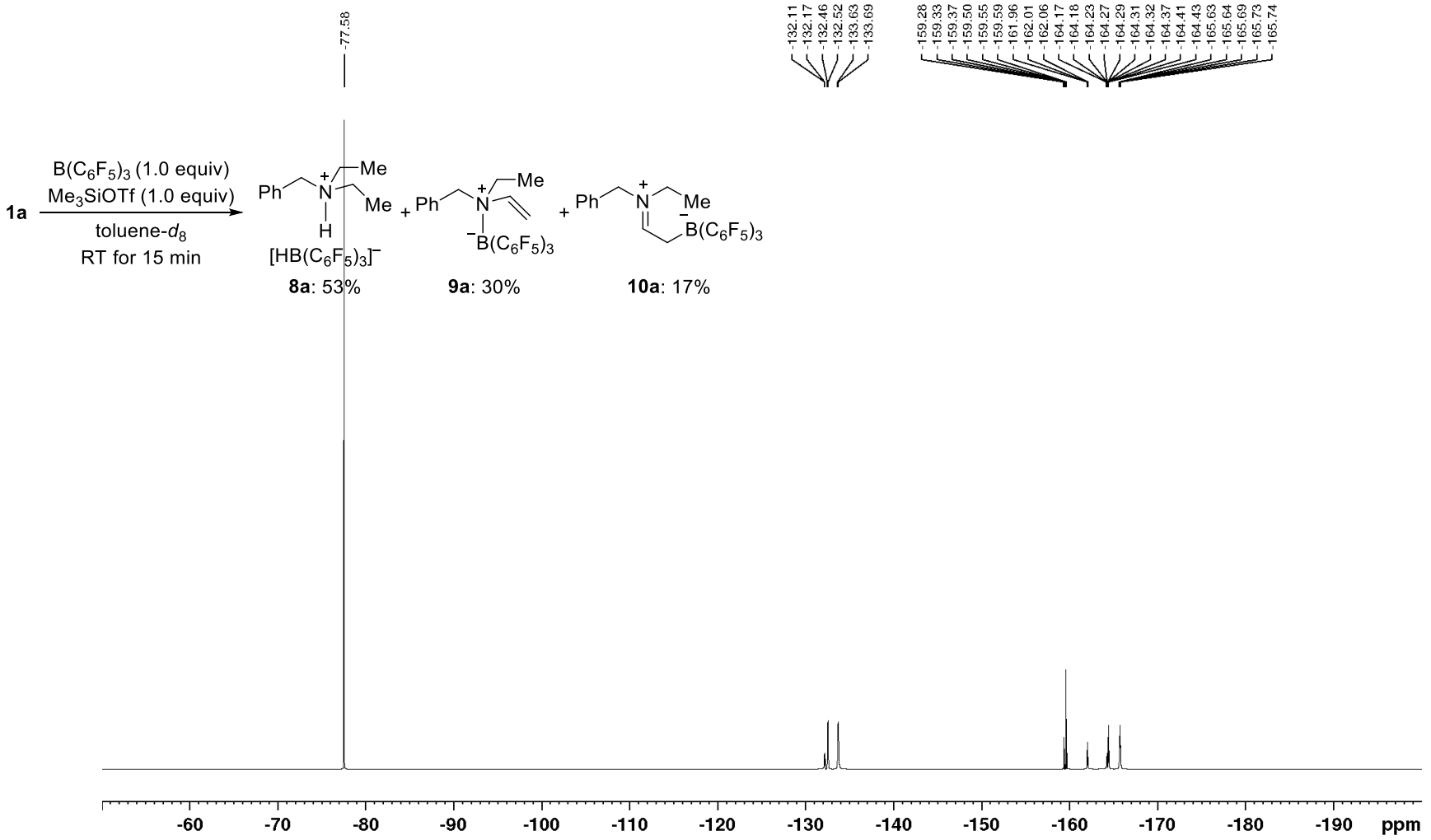


Figure S108. ^{19}F NMR spectrum (471 MHz, 1,2-$C_6D_4Cl_2$, 298 K) of the stoichiometric reaction of **1a**, Me_3SiOTf, and $B(C_6F_5)_3$ (1:1:1).



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