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Supporting Information

Visible Light Catalyzed Arylsilylation of Alkenes to Construct Silicon-Containing 1,1-Diaryl Moieties

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1. General Information

All reactions were carried out with standard Schlenk techniques in an argon-filled glove-box. (Dimethylphenylsilyl)boronic acid pinacol ester ($PhMe_2SiBpin_2$), 4-canopyridine, base, photocatalysis, substituted styrenes bearing Me, MeO, CF_3, F, CN, Cl, Br, CO_2Me group on the benzene ring as well as 1.1-diphenylethylene, 2-phenyl-1-propene, trans-stilbene, ethyl acrylate and 2-methyl-2-propenoic acid cyclohexyl ester were purchased and used without purification. Additionally, (hetero)aryl nitriles including 2-cyclopropylisonicotinonitrile, 2-tert-butylisonicotinonitrile, 2,6-dimethyl-4-cyanopyridine, 2-fluoroisonicotinonitrile, 3-methoxy-isonicotinonitrile, 4-cyano-3-methylpyridine, 4-cyano-3-fluoropyridine, 5-cyanoquinoline, 1.2-dicyanobenzene, 1.4-dicyanobenzene,2,5-dimethylterephthalonitrile, 4-(4-cyanophenyl)benzonitrile and 2,5-dichloroterephthalonitrile were also purchased and used without purification. Commercial chemicals were purchased from TCI, Acros, Sigma-Aldrich, J&K, and Alfa Aesar Chemical Companies and used as received. Anhydrous CH_3CN was purchased from J&K and used as received (water < 30 ppm, J&KSeal). Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum sheets from Qingdao Haiyang Chemical Co., Ltd. Flash chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd). Other substituted alkenes[1] and 3-aryl subustituted canopyridines[2] were prepared according to the literature. Silylboronates (1b–1f) were prepared according to the literatures.[3]

^1H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE Avance III 400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^1H NMR, and 77.16 ppm for $^{13}C\{^1H$ NMR). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using a neat thin-film technique. High-resolution mass spectra (HRMS) were recorded on the Thermo Quest Finnigan LCQDECA system equipped with an ESI ionization source and a TOF detector mass spectrometer.

All the photochemical reactions were performed with Blue LED strip (8 W, λ = 450 nm).

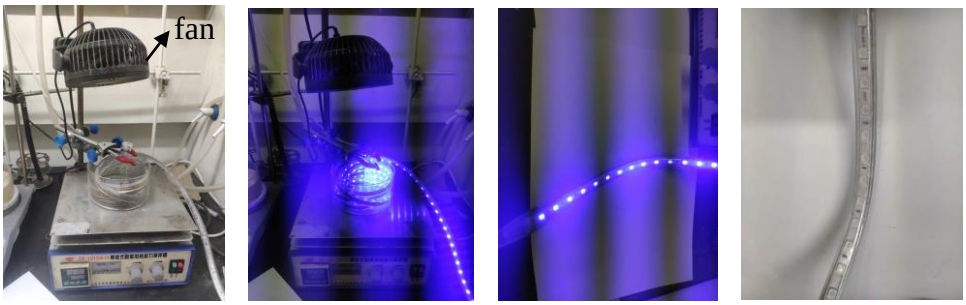
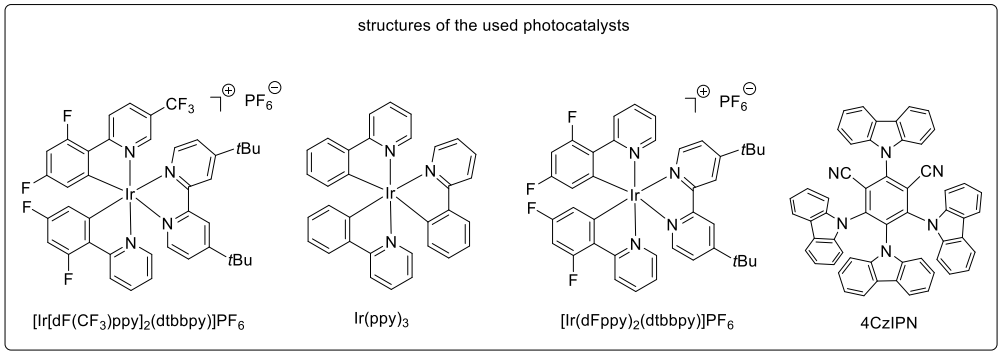


Figure S1. Photoreactor setup

2. Experimental Details for the Photoredox Catalyzed 1.2-Silylarylation of Alkenes

2.1 Reaction Optimization Studies

Experimental procedure: according to the general procedure, in an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.), 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), and $PhMe_3SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), Rb_2CO_3 (0.2 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 2 mol%) and anhydrous acetonitrile (1 mL) in an argon-filled glove box. After stirring under blue LED irradiation at room temperature for 24 h (The temperature of the reaction was maintained at room temperature *via* a fan). Then, the reaction mixture was diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding silylpyridylation of alkenes product.

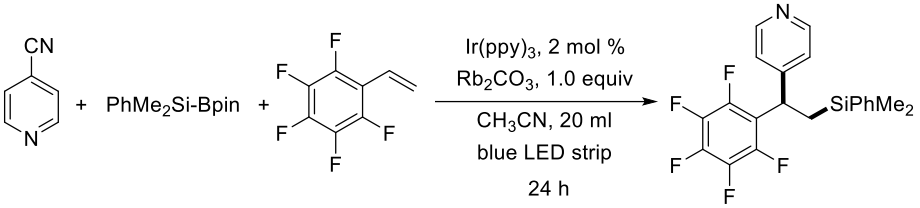


2.2 Experimental Procedure for the Photoredox Catalyzed 1.2-Silylarylation of Alkenes

2.2.1 General procedure for the photoredox catalyzed 1.2-silylarylation of alkenes

In an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with (hetero)aryl nitrile derivatives (0.2 mmol, 1.0 equiv.), alkene (0.3 mmol, 1.5 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), Rb_2CO_3 (0.2 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 2 mol%) and anhydrous acetonitrile (1 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under 8 W blue LED strip irradiation at room temperature for 24 h (The temperature of the reaction was maintained at room temperature *via* a fan). Upon completion, the reaction mixture was diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding silylpyridylation of alkenes product.

2.2.2 Gram scale experiments

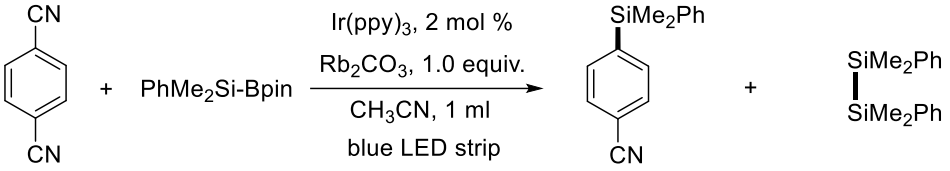


1b (4 mmol) **2a** (1.5 equiv) **3l** (1.5 equiv) **4bl,** 1.3 g, 78%

In an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with 4-canopyridine (4 mmol, 1.0 equiv.), alkene (1.5 equiv.), $PhMe_2SiBpin$ (1.5 equiv.), Rb_2CO_3 (1.0 equiv.), $Ir(ppy)_3$ (2 mol%) and anhydrous acetonitrile (20 mL) in an argon-filled glove box. The vial was tightly sealed, then removed from the glovebox. After stirring under 8 W blue LED strip irradiation at room temperature for 24 h (The temperature of the reaction was maintained at room temperature *via* a fan). Upon completion, the reaction mixture was diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding product **4bl** in 78% yield.

2.3 Experimental Studies on Reaction Mechanism

2.3.1 Radical-radical coupling experiment



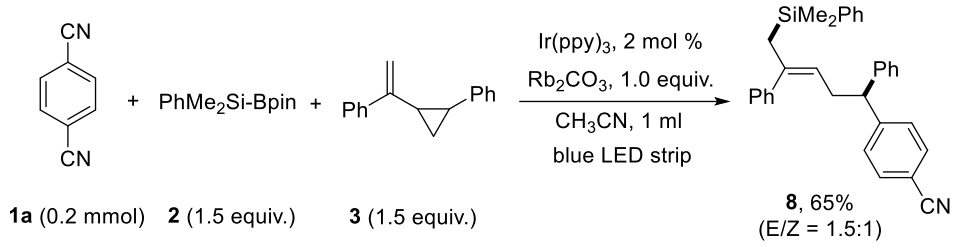
1a (0.2 mmol) **2** (1.5 equiv.) **6**, 14% **7**, 35%

We performed the reaction of 1.4-dicyanobenzene and $PhMe_3SiBpin$ under standard conditions. The cross-coupling product **6** between $PhMe_2Si$ radical and (hetero)aryl nitrile radical anion as well as the product $PhMe_2Si$-$SiMe_2Ph$ from dimeric $PhMe_2Si$ radical were produced. These results indicated both the $PhMe_2Si$ radical and (hetero)aryl nitrile radical anion was formed in the photocatalyzed process.

Experimental procedure: according to the general procedure, in an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), and $PhMe_3SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), Rb_2CO_3 (0.2 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 2 mol%) and anhydrous acetonitrile (1 mL) in an argon-filled glove box. After stirring under blue LED irradiation at room temperature for 24 h (The temperature of the reaction was maintained at room temperature *via* a fan). Upon completion, the reaction mixture was diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl

acetate) to afford the corresponding product. Compound **6** as oil (14% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 – 7.60 (m, 4H), 7.51 – 7.47 (m, 2H), 7.42 – 7.35 (m, 3H), 0.57 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.5, 136.6, 134.7, 134.2, 131.1, 129.7, 128.2, 119.1, 112.8, -2.6 ppm. Spectra datas of compound **6** are consistent with literature data.[4] Compound **7** as oil (35% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 – 7.51 (m, 4H), 7.43 – 7.35 (m, 6H), 0.37 (s, 12H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.9, 132.1, 128.4, 126.8, 0.0 ppm. Spectra data of compound **7** are consistent with literature data.[5]

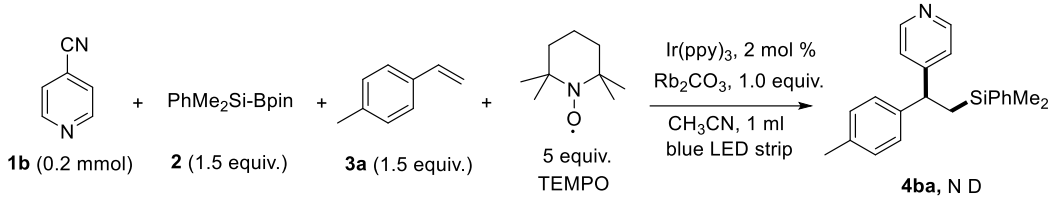
2.3.2 Radical clock experiments



We performed a radical-clock experiment using the reaction of (1-(2-phenylcyclopropyl)-vinyl)-benzene **3**, 1.4-dicyanobenzene, and $PhMe_3SiBpin$ with $Ir(ppy)_3$ as photocatalyst and Rb_2CO_3 as a base, the corresponding ring-opening product **8** was obtained in 65% yield, which supports a radical mechanism.

Experimental procedure: according to the general procedure, in an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with (1-(2-phenylcyclopropyl)-vinyl)-benzene **3**, 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), and $PhMe_3SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), Rb_2CO_3 (0.2 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 2 mol%) and anhydrous acetonitrile (1 mL) in an argon-filled glove box. After stirring under blue LED irradiation at room temperature for 24 h (The temperature of the reaction was maintained at room temperature *via* a fan). Upon completion, the reaction mixture was diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding product **8** as colorless oil (65% yield, E/Z = 1.5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 – 7.42 (m, 3H), 7.41 – 7.17 (m, 13H), 7.12 – 7.05 (m, 2H), 7.00 – 6.97 (m, 1H), 5.15 (td, J = 7.1, 2.1 Hz, 1H), 3.98 – 3.89 (m, 1H), 2.72 – 2.68 (m, 1H), 2.67 – 2.54 (m, 1H), 2.18 (s, 1H), 2.03 (s, 1H), 0.13 – 0.07 (m, 3H), 0.06 – 0.01 (m, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 150.3, 150.2, 144.3, 143.2, 143.2, 141.9, 139.9, 139.3, 139.0, 138.9, 133.7, 133.6, 132.2, 132.1, 129.1, 128.9, 128.9, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 126.9, 126.7, 126.6, 123.3, 122.8, 119.1, 110.0, 109.9, 52.1, 51.2, 34.9, 34.8, 29.0, 21.1, -2.4, -2.8 ppm. **IR** (film): 3066, 3024, 2954, 2896, 2226, 1599, 1492, 1426, 1247, 1112, 1020, 910, 834, 697 cm^{-1}. **HRMS (ESI)**: calculated for $C_{32}H_{32}NSi^+$ $[M+H]^+$ 458.2299; found 458.2290.

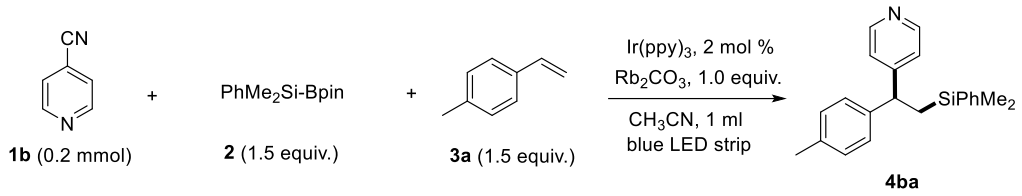
2.3.3 TEMPO trapping experiment



When adding the 2,2,6,6-Tetramethyl-1-piperinedinyloxy (TEMPO) into the reaction of 4-canopyridine, 4-methyl styrene and $PhMe_3SiBpin$ in presence of $Ir(ppy)_3$ and Rb_2CO_3, the desired product 4ba was inhibited, suggesting a radical mechanism.

Experimental procedure: according to the general procedure, in an oven-dried reaction vial (10 mL) containing a magnetic stir bar was charged with 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.), 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), 2,2,6,6-Tetramethyl-1-piperinedinyloxy (TEMPO, 5.0 equiv.) and $PhMe_3SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), Rb_2CO_3 (0.2 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 2 mol%) and anhydrous acetonitrile (1 mL) in an argon-filled glove box. After stirring under blue LED irradiation at room temperature for 24 h. Then, the reaction mixture was analysis by GC-MS.

2.3.4 Light on/off experiment



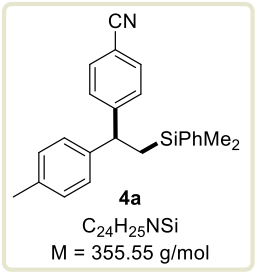
We carried out the light on/off experiments by the reaction of 4-canopyridine, 4-methylstyrene and $PhMe_3SiBpin$ under standard conditions, indicating light irradiation is essential for this protocol.

Experimental procedure: according to the general procedure, six oven-dried reaction vials were charged respectively 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.), 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), and $PhMe_3SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), Rb_2CO_3 (0.2 mmol, 1.0 equiv.), $Ir(ppy)_3$ (2.6 mg, 0.004 mmol, 2 mol%) and anhydrous acetonitrile (1 mL) in an argon-filled glove box. The vials were irritated under blue LED irradiation. After 2 hour, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining five vials were stirred in the absence of light for an additional 1 hour. Then, one vial was removed for analysis, and the other lamps were turned back on to irradiate. After an additional 2 hours of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining vials were stirred in the absence of light for an additional 1 hour. Then, a vial was removed for analysis, and the other lamps were turned back on to irradiate the remaining one reaction mixture. After an additional 2 hours of irradiation, the lamps were turned off, and the last vial was removed for analysis. The reaction mixtures were diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was

concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding product.

2.4 Characterization Data of alkene silylarylation products

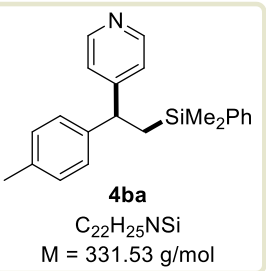
2.4.1 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)benzonitrile (**4a**)



4a
$C_{24}H_{25}NSi$
M = 355.55 g/mol

Prepared according to general procedure from 1,4-dicyanobenzene **1a** (26 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4aa** as colorless oil (49 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 – 7.46 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.34 (m, 2H), 7.32 – 7.29 (m, 2H), 7.10 – 7.05 (m, 4H), 4.08 – 4.03 (m, 1H), 2.32 – 2.31 (m, 3H), 1.67 – 1.60 (m, 2H), 0.11 (s, 3H), 0.08 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.7, 142.1, 138.5, 136.3, 133.6, 132.2, 129.3, 129.0, 128.3, 127.8, 127.5, 119.1, 109.7, 47.0, 23.2, 21.0, -2.4, -2.7 ppm. **IR** (film): 3028, 2253, 2232, 1607, 1255, 1122, 903, 674 cm^{-1}. **HRMS (ESI)**: calculated for $C_{24}H_{26}NSi^+$ $[M+H]^+$ 356.1829; found 356.1822.

2.4.2 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)pyridine (**4ba**)

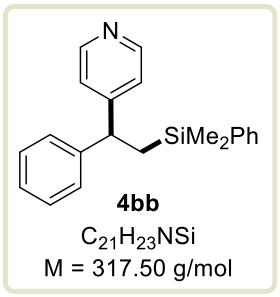


4ba
$C_{22}H_{25}NSi$
M = 331.53 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4ba** as colorless oil (69 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): 8.30 (d, *J* = 5.3 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 7.02 – 6.99 (m, 2H), 6.98 – 6.91 (m, 4H), 3.86 – 3.80 (m, 1H), 2.18 (s, 3H), 1.52 – 1.44

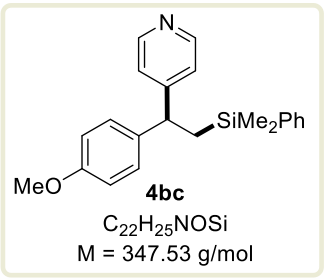
(m, 2H), 0.06 (s, 3H), 0.03 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.2, 149.7, 141.8, 138.6, 136.4, 133.6, 129.3, 129.1, 127.9, 127.6, 122.9, 46.4, 22.8, 21.1, -2.3, -2.7 ppm. **IR** (film): 3043, 3020, 2953, 2918, 1593, 1511, 1426, 1248, 1112, 993, 837, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{26}NSi^+$ $[M+H]^+$ 332.1839; found 332.1927.

2.4.3 4-(2-(dimethyl(phenyl)silyl)-1-phenylethyl)pyridine (**4bb**)



Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), styrene **3b** (32 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bb** as colorless oil (50 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 5.3 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.18 – 7.13 (dm, 3H), 7.12 – 7.09 (m, 2H), 3.96 (t, *J* = 8.0 Hz, 1H), 1.63 – 1.56 (m, 2H), 0.05 (s, 3H), 0.03 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 155.9, 149.7, 144.8, 138.5, 133.6, 129.1, 128.7, 127.9, 127.8, 126.8, 122.9, 46.8, 22.8, -2.3, -2.7 ppm. **IR** (film)**:** 3067, 3024, 1953, 2917, 1680, 1593, 1493, 1414, 1249, 1112, 837, 733, 699 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{24}NSi^+$ $[M+H]^+$ 318.1673; found 318.1667. Spectra data are consistent with literature data.[1]

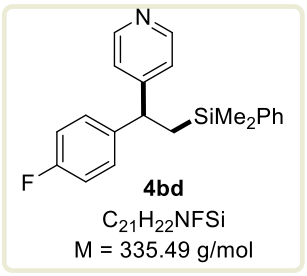
2.4.4 4-(2-(dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)ethyl)pyridine (**4bc**)



Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methoxystyrene **3c** (40 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bc** as colorless oil (54 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 5.0 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.28 – 7.20 (m, 3H), 7.04 – 6.99 (m, 4H), 6.72 – 6.69 (m, 2H), 3.88 – 3.82 (n, 1H), 3.67 (s, 3H), 1.56 – 1.47

(m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 158.4, 156.3, 149.7, 138.6, 136.8, 133.5, 129.0, 128.7, 127.8, 122.8, 114.0, 55.3, 45.9, 22.9, -2.4, -2.7 ppm. **IR** (film): 3067, 3021, 2953, 2905, 2834, 1608, 1593, 1426, 1246, 1176, 1126, 1073, 993, 835, 731 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{26}NOSi^+$ $[M+H]^+$ 348.1778; found 348.1779. Spectra data are consistent with literature data.[1,6]

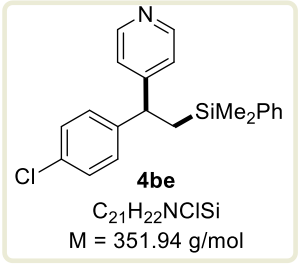
2.4.5 4-(2-(dimethyl(phenyl)silyl)-1-(4-fluorophenyl)ethyl)pyridine (**4bd**)



4bd
$C_{21}H_{22}NFSi$
M = 335.49 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methoxystyrene **3d** (37 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bd** as colorless oil (54 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.5 Hz, 2H), 7.43 – 7.26 (m, 5H), 7.14 – 7.08 (m, 4H), 6.96 – 6.88 (m, 2H), 3.97 (t, *J* = 8.0 Hz, 1H), 1.62 – 1.57 (m, 2H), 0.09 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.6 (d, *J* = 245.2 Hz), 155.6, 149.8, 140.4 (d, *J* = 3.3 Hz), 138.3, 133.5, 129.2, 129.1, 127.9, 122.7, 115.4 (d, *J* = 21.3 Hz), 46.0, 23.0, -2.4, -2.7 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.1. **IR** (film): 3068, 2954, 2897, 1594, 1507, 1426, 1411, 1249, 1221, 1157, 1112, 835, 813, 699 cm^{-1}. **HRMS (ESI)**: calculated for $C_2H_{23}NFSi^+$ $[M+H]^+$ 336.1578; found 336.1573. Spectra data are consistent with literature data.[1]

2.4.6 4-(1-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)ethyl)pyridine (**4be**)

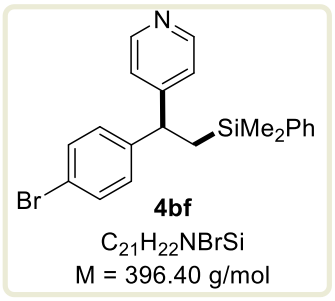


4be
$C_{21}H_{22}NClSi$
M = 351.94 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-chlorostyrene **3e** (42 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4be** as colorless oil (58 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 – 8.42 (m, 2H), 7.42 – 7.29 (m, 5H), 7.24 –

7.16 (m, 2H), 7.10 – 7.07 (m, 4H), 3.95 (t, *J* = 8.0 Hz, 1H), 1.61 – 1.56 (m, 2H), 0.09 (s, 6H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 155.3, 149.8, 143.2, 138.1, 133.5, 132.5, 129.2, 129.1, 128.7, 127.9, 122.8, 46.1, 22.8, -2.4, -2.6 ppm. **IR** (film): 3068, 3022, 2954, 2916, 1426, 1249, 1090, 1113, 873, 728, 699 cm^{-1}. **HRMS (ESI)**: calculated for $C_2H_{23}NClSi^+$ $[M+H]^+$ 352.1283; found 352.1280.

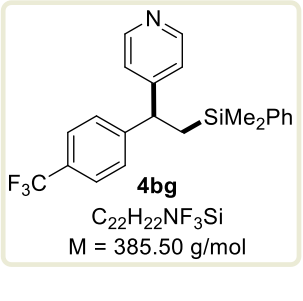
2.4.7 4-(1-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)ethyl)pyridine (**4bf**)



4bf
$C_{21}H_{22}NBrSi$
M = 396.40 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4- bromostyrene **3f** (55 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bf** as colorless oil (39 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 – 8.40 (m, 2H), 7.44 – 7.26 (m, 7H), 7.11 – 7.07 (m, 2H), 7.05 – 7.00 (m, 2H), 3.93 (t, *J* = 8.0 Hz, 1H), 1.63 – 1.53 (m, 2H), 0.09 (s, 6H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 155.2, 149.8, 143.7, 138.1, 133.5, 131.7, 129.5, 129.2, 127.9, 122.8, 120.6, 46.2, 22.7, -2.4, -2.6 ppm. **IR** (film): 3067, 3046, 3021, 2916, 1678, 1593, 1486, 1426, 1249, 1112, 1009, 872, 836, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{23}NBrSi^+$ $[M+H]^+$ 396.0778; found 396.0777.

2.4.8 4-(2-(dimethyl(phenyl)silyl)-1-(4-(trifluoromethyl)phenyl)ethyl)pyridine (**4bg**)

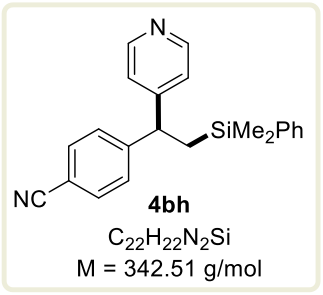


4bg
$C_{22}H_{22}NF_3Si$
M = 385.50 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-bromostyrene **3g** (52 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bg** as colorless oil (51 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 5.2 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.39

– 7.33 (m, 3H), 7.33 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.11 – 7.08 (m, 2H), 4.02 (t, *J* = 8.0 Hz, 1H), 1.64 – 1.59 (m, 2H), 0.10 (s, 3H), 0.09 (s, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 154.7, 149.9, 148.7, 138.0, 133.5, 129.2, 128.9, 128.1, 127.9, 125.6 (q, *J* = 3.8 Hz), 125.5, 122.8, 46.6, 22.7, -2.6, -2.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4. **IR** (film): 3069, 2956, 1618, 1595, 1416, 1250, 1163, 1120, 1067, 1016, 834, 731 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{23}NF_3Si^+$ $[M+H]^+$ 386.1546; found 386, 1540.

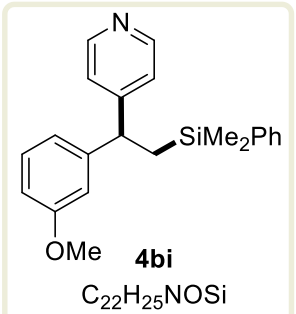
2.4.9 4-(2-(dimethyl(phenyl)silyl)-1-(pyridin-4-yl)ethyl)benzonitrile (**4bh**)



4bh
$C_{22}H_{22}N_2Si$
M = 342.51 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-cyanostyrene **3h** (39 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bh** as colorless oil (34 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 5.0 Hz, 2H), 7.47 – 7.39 (m, 2H), 7.34 – 7.19 (m, 5H), 7.18 – 7.15 (m, 2H), 7.02 – 6.98 (m, 2H), 3.93 (t, *J* = 8.0 Hz, 1H), 1.55 – 1.50 (m, 2H), 0.10 (s, 3H), 0.09 (s, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$):154.1, 150.2, 150.0, 137.7, 133.5, 132.5, 129.4, 128.5, 128.0, 122.8, 118.7, 110.7, 46.9, 22.6, -2.5, -2.5 ppm. **IR** (film): 3068, 3047, 2954, 2923, 2227, 2182, 2015, 1980, 1677, 1570, 1426, 1250, 1112, 904, 837, 731 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{23}N_2Si^+$ $[M+H]^+$ 343.1625; found 349.1622.

2.4.10 4-(2-(dimethyl(phenyl)silyl)-1-(3-methoxyphenyl)ethyl)pyridine (**4bi**)

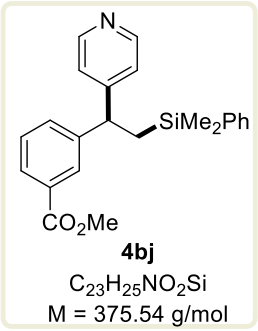


4bi
$C_{22}H_{25}NOSi$
M = 347.53 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 3-methoxystyrene **3i** (40 mg, 0.3 mmol, 1.5 equiv.) and

anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bi** as colorless oil (53 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.7 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.39 – 7.30 (m, 3H), 7.21 – 7.16 (m, 1H), 7.15 – 7.12 (m, 2H), 6.81 – 6.78 (m, 1H), 6.74 – 6.71 (m, 2H), 3.95 (t, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 1.66 – 1.57 (m, 2H), 0.11 (s, 3H), 0.09 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 159.7, 155.6, 149.7, 146.3, 138.5, 133.5, 129.6, 129.1, 127.8, 122.9, 120.2, 113.9, 111.6, 55.2, 46.7, 22.7, -2.4, -2.7 ppm. **IR** (film): 3068, 2953, 2834, 1593, 1487, 1426, 1249, 1112, 1048, 993, 827, 730, 697 cm^{-1}. **HRMS (ESI):** calculated for $C_{22}H_{26}NOSi^+$ $[M+H]^+$ 348.1778; found 348.1773.

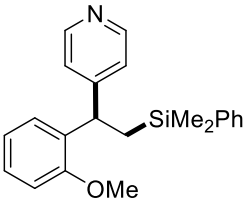
2.4.11 methyl-3-(2-(dimethyl(phenyl)silyl)-1-(pyridin-4-yl)ethyl)benzoate (**4bj**)



4bj
$C_{23}H_{25}NO_2Si$
M = 375.54 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), methyl 3-vinylbenzoate **3j** (49 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bj** as colorless oil (39 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 – 8.28 (m, 2H), 7.77 – 7.68 (m, 2H), 7.25 – 7.15 (m, 7H), 7.00 – 6.97 (m, 2H), 3.90 (t, *J* = 8.0 Hz, 1H), 3.77 (s, 3H), 1.57 – 1.45 (m, 2H), 0.05 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 166.9, 155.2, 149.9, 145.1, 138.1, 133.5, 132.4, 130.5, 129.1, 128.8, 128.7, 128.1, 127.9, 122.8, 52.2, 46.6, 22.7, -2.5, -2.6 ppm. **IR** (film): 3068, 3021, 2951, 1700, 1594, 1427, 1284, 1251, 1196, 1175, 1110, 993, 905, 834 cm^{-1}. HRMS (ESI): calculated for $C_{23}H_{26}NO_2Si^+$ $[M+H]^+$ 376.1727; found 376.1725.

2.4.12 4-(2-(dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)ethyl)pyridine (**4bk**)



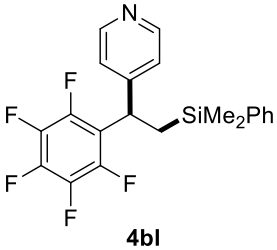
4bk

$C_{22}H_{25}NOSi$

M = 347.53 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 2-methoxystyrene **3k** (40 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bk** as colorless oil (52 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 5.1 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.28 – 7.12 (m, 4H), 7.12 – 7.06 (m, 3H), 6.84 – 6.79 (m, 1H), 6.72 – 6.69 (m, 1H), 4.48 – 4.41 (m, 1H), 3.65 (s, 3H), 1.63 – 1.55 (m, 1H), 1.50 – 1.44 (m, 1H), 0.03 (s, 3H), 0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.6, 156.0, 149.4, 139.0, 133.5, 133.1, 128.9, 128.0, 127.7, 127.5, 123.2, 120.6, 110.7, 55.2, 38.8, 21.6, -2.5, -2.6 ppm. **IR** (film): 3068, 3022, 2953, 2836, 1973, 1593, 1489, 1413, 1242, 1111, 1029, 905, 835, 728 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{26}NOSi^+$ $[M+H]^+$ 348.1778; found 348.1772.

2.4.13 4-(2-(dimethyl(phenyl)silyl)-1-(perfluorophenyl)ethyl)pyridine (**4bl**)



4bl

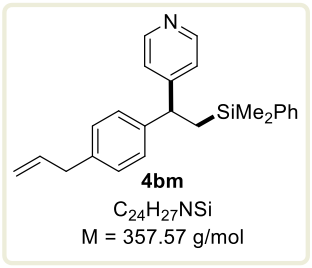
$C_{21}H_{18}NF_5Si$

M = 407.45 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 1,2,3,4,5-Pentafluoro-6-vinylbenzene **3l** (58 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bk** as colorless oil (60 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.51 – 8.47 (m, 2H), 7.38 – 7.28 (m, 3H), 7.28 – 7.22 (m, 2H), 7.20 (d, *J* = 5.3 Hz, 2H), 4.46 (dd, *J* = 11.8, 4.9 Hz, 1H), 1.97 – 1.89 (m, 1H), 1.58 – 1.52 (m, 1H), 0.30 (s, 3H), 0.23 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.0, 150.0, 146.2 – 145.8 (m, 1C), 143.7 – 143.3 (m, 1C), 141.4 – 140.9 (m, 1C), 138.9 – 138.4 (m, 1C), 137.1, 136.4 – 135.9 (m, 1C), 133.1, 129.1, 127.7, 122.4, 117.5 – 116.9 (m, 1C), 35.4, 18.7, -2.3, -4.2

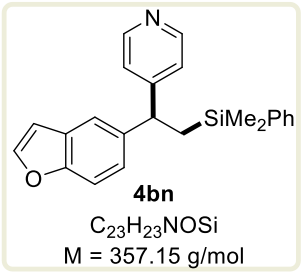
ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -141.3 – -141.4 (m, 2F), -156.2 – -156.4 (m, 1F), -161.7 – -161.9 (m, 2F) ppm. **IR** (film): 3076, 3018, 2956, 1654, 1595, 1520, 1499, 1415, 1251, 1114, 983, 836, 717 cm^{-1}. **HRMS (ESI)**: calculated for $C_{21}H_{19}F_5NSi^+$ $[M+H]^+$ 408.1201; found 408.1194.

2.4.14 4-(1-(4-allylphenyl)-2-(dimethyl(phenyl)silyl)ethyl)pyridine (**4bm**)



Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 1-allyl-4-vinylbenzene **3m** (43 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bm** as colorless oil (47 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 4.7 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.31 – 7.25 (m, 3H), 7.09 – 7.05 (m, 4H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.95 – 5.81 (m, 1H), 5.03 – 5.00 (m, 1H), 4.99 – 4.97 (m, 1H), 3.93 – 3.87 (m, 1H), 3.29 (dd, J = 6.6, 1.6 Hz, 2H), 1.63 – 1.49 (m, 2H), 0.30 (s, 3H), 0.23 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.0, 149.7, 142.6, 138.6, 138.5, 137.4, 133.6, 129.1, 128.9, 127.9, 127.8, 122.9, 115.8, 46.4, 39.8, 22.9, -2.4, -2.7 ppm. **IR** (film): 3068, 3021, 2953, 2901, 2215, 2040, 1975, 1679, 1557, 1426, 1413, 1248, 1112, 993, 837, 730 cm^{-1}. HRMS (ESI): calculated for $C_{24}H_{28}NSi^+$ $[M+H]^+$ 358.1986; found 358.1983.

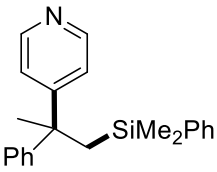
2.4.15 4-(1-(benzofuran-5-yl)-2-(dimethyl(phenyl)silyl)ethyl)pyridine (**4bn**)



Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 5-vinylbenzofuran **3n** (43 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bn** as colorless oil (52 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 – 8.28 (m, 2H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.26 – 7.17 (m, 4H), 7.05 (d, J = 5.0 Hz, 2H), 7.00 – 6.96 (m, 1H), 6.59 – 6.56 (m, 1H),

4.02 – 3.98 (m, 1H), 1.63 – 1.50 (m, 2H), -0.02 (s, 3H), -0.04 (s, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 156.2, 153.9, 149.7, 145.5, 139.4, 138.5, 133.5, 129.1, 127.8, 127.6, 124.3, 122.9, 120.0, 111.4, 106.6, 46.6, 23.2, -2.4, -2.7 ppm. **IR** (film): 3068, 3020, 2953, 2897, 2161, 1594, 1465, 1426, 1414, 1248, 1196, 1110, 1031, 885, 810, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{24}NOSi^+$ $[M+H]^+$ 358.1622; found 358.1619.

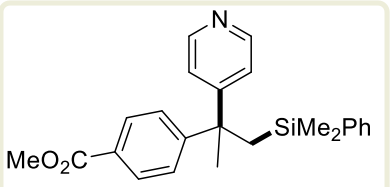
2.4.16 4-(1-(dimethyl(phenyl)silyl)-2-phenylpropan-2-yl)pyridine (**4bo**)



4bo
$C_{22}H_{25}NOSi$
M = 331.53 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 2-Phenyl-1-propene **3o** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bo** as colorless oil (39 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.8 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.37 – 7.29 (m, 3H), 7.28 – 7.24 (m, 2H), 7.21 – 7.16 (m, 3H), 7.13 – 7.10 (m, 2H), 1.88 – 1.77 (m, 2H), 1.58 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 160.8, 149.5, 149.1, 139.7, 133.5, 128.9, 128.2, 127.8, 127.2, 126.3, 122.3, 45.3, 30.6, 29.7, -1.4, -1.5 ppm. **IR** (film): 3058, 3022, 2966, 2896, 1591, 1549, 1493, 1409, 1248, 1111, 906, 821, 727 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{24}NOSi^+$ $[M+H]^+$ 332.1829; found 332.1826.

2.4.17 methyl 4-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)benzoate (**4bp**)

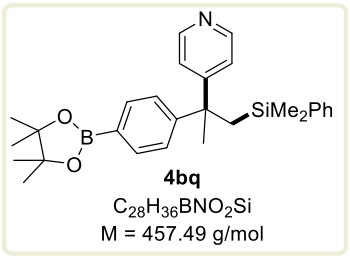


4bp
$C_{24}H_{27}NO_2Si$
M = 389.57 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 5-vinylbenzofuran **3p** (53 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bp** as colorless

oil (53 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 4.9 Hz, 2H), 7.91 – 7.87 (m, 2H), 7.35 – 7.32 (m, 2H), 7.31 – 7.24 (m, 3H), 7.22 – 7.20 (m, 2H), 7.07 – 7.04 (m, 2H), 3.89 (s, 3H), 1.82 – 1.78 (m, 2H), 1.56 (s, 3H) 0.00 (s, 3H), 0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 166.9, 159.9, 154.3, 149.6, 139.2, 133.4, 129.5, 129.0, 128.2, 127.9, 127.2, 122.2, 52.1, 45.6, 30.5, 29.5, -1.4, -1.4. **IR** (film): 3068, 2952, 2362, 1700, 1592, 1434, 1408, 1281, 1190, 1112, 1016, 830, 775, 710 cm^{-1}**. HRMS (ESI)**: calculated for $C_{24}H_{28}NO_2Si^+$ $[M+H]^+$ 390.1884; found 390.1881. Spectra data are consistent with literature data.[1]

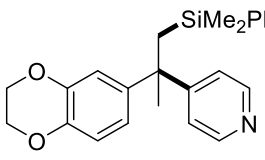
2.4.18 methyl 4-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)benzoate (**4bq**)



4bq
$C_{28}H_{36}BNO_2Si$
M = 457.49 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4,4,5,5-tetramethyl-2-(4-(prop-1-en-2-yl)phenyl)-1,3,2-dioxaborolane **3q** (73 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bq** as colorless oil (73 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 – 8.30 (m, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.21 (m, 3H), 7.16 – 7.13 (m, 2H), 7.08 – 7.02 (m, 2H), 1.84 – 1.74 (m, 2H), 1.54 (s, 3H), 1.32 (s, 12H), 0.01 (s, 3H), -0.05 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 162.6, 152.2, 149.5, 139.7, 134.7, 133.5, 128.9, 128.5, 127.8, 126.6, 122.3, 83.9, 45.6, 30.5, 29.6, 25.0, -1.35, -1.43. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 31.8. **IR** (film): 3074, 3022, 2976, 1610, 1592, 1550, 1399, 1300, 1249, 1144, 1093, 1018, 962, 831, 730 cm^{-1}. **HRMS (ESI)**: calculated for $C_{28}H_{36}NBO_2Si^+$ $[M+H]^+$ 458.2681; found 458.2676. Spectra data are consistent with literature data.[1]

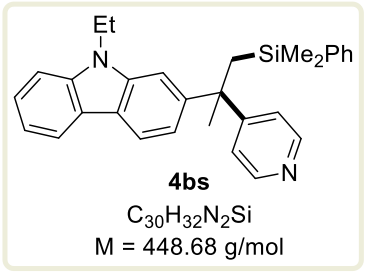
2.4.19 4-(2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1-(dimethyl(phenyl)silyl)propan-2-yl)pyridine (**4br**)



4br
$C_{24}H_{27}NO_2Si$
M = 389.57 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 6-(prop-1-en-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine **3u** (53 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4br** as colorless oil (58 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 5.0 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.24 (m, 3H), 7.12 – 7.09 (m, 2H), 6.73 – 6.65 (m, 2H), 6.62 – 6.57 (m, 1H), 4.23 – 4.19 (m, 4H), 1.76 – 1.73 (m, 2H), 1.53 (s, 3H), -0.05 (s, 3H), 0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 160.8, 149.4, 143.0, 142.6, 141.8, 139.7, 133.5, 128.8, 127.8, 122.2, 120.2, 116.8, 116.2, 64.5, 64.4, 44.7, 30.8, 29.8, -1.3 ppm. **IR** (film): 3068, 2972, 2876, 2362, 2115, 1592, 1500, 1410, 1287, 1250, 1070, 904, 837 cm^{-1}. **HRMS (ESI)**: calculated for $C_{24}H_{28}NO_2Si^+$ $[M+H]^+$ 390.1884; found 390.1880. Spectra data are consistent with literature data.[1]

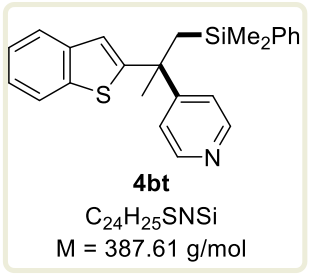
2.4.20 2-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)-9-ethyl-9H-carbazole (**4bs**)



4bs
$C_{30}H_{32}N_2Si$
M = 448.68 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 9-ethyl-2-(prop-1-en-2-yl)-9H-carbazole **3v** (70 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bs** as colorless oil (61 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 5.7 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.44 – 7.33 (m, 4H), 7.27 – 7.17 (m, 5H), 7.16 – 7.08 (m, 3H), 4.33 – 4.25 (m, 2H), 1.98 – 1.85 (m, 2H), 1.67 (s, 3H), 1.42 – 1.35 (m, 3H), -0.05 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.9, 149.4, 140.3, 139.8, 139.4, 138.5, 133.5, 128.8, 127.7, 125.9, 125.6, 123.0, 122.4, 122.3, 120.3, 118.8, 118.3, 108.6, 108.2, 45.3, 37.6, 31.3, 30.3, 13.9, -1.3, -1.4 ppm. **IR** (film): 3067, 3020, 2972, 2932, 2893, 1677, 1594, 1490, 1346, 1248, 1111, 906, 831, 730 cm^{-1}. **HRMS (ESI)**: calculated for $C_{30}H_{33}N_2Si^+$ $[M+H]^+$ 449.2408; found 449.2403. Spectra data are consistent with literature data.[1]

2.4.21 4-(2-(benzo[b]thiophen-2-yl)-1-(dimethyl(phenyl)silyl)propan-2-yl)pyridine (**4bt**)



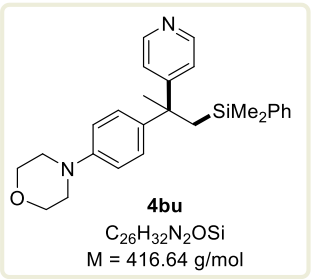
4bt

$C_{24}H_{25}SNSi$

M = 387.61 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 2-(prop-1-en-2-yl)benzo[b]thiophene **3w** (52 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bt** as colorless oil (38 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (s, 2H), 7.83 – 7.77 (m, 1H), 7.36 – 7.28 (m, 7H), 7.22 – 7.19 (m, 2H), 7.08 – 7.05 (m, 1H), 7.02 – 6.97 (m, 1H), 2.15 – 2.04 (s, 1H), 1.91 – 1.82 (s, 1H), 1.63 (s, 3H), -0.07 (s, 3H), -0.15 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 159.7, 149.8, 142.8, 141.3, 139.2, 137.5, 133.5, 129.0, 127.8, 124.4, 123.9, 123.6, 123.1, 122.4, 121.6, 43.9, 31.4, 28.6, -1.9, -2.2 ppm. **IR** (film): 3068, 2965, 2109, 2014, 1594, 1426, 1248, 1112, 900, 835 cm^{-1}. **HRMS (ESI)**: calculated for $C_{24}H_{26}SNSi^+$ $[M+H]^+$ 388.1550; found 388.1547. Spectra data are consistent with literature data.[1]

2.4.22 4-(4-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)phenyl)morpholine (**4bu**)



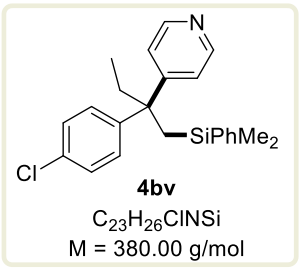
4bu

$C_{26}H_{32}N_2OSi$

M = 416.64 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), and 4-(4-(prop-1-en-2-yl)phenyl)morpholine **3u** (61 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bu** as colorless oil (51 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): 8.42 – 8.34 (m, 2H), 7.38 – 7.32 (m, 2H), 7.32 – 7.22 (m, 3H), 7.08 (d, *J* = 5.9 Hz, 2H), 7.04 – 7.01 (m, 2H), 6.77 – 6.73 (m, 2H), 3.84 – 3.81 (m, 4H), 3.12 – 3.09 (m, 4H), 1.80 – 1.71 (m, 2H), 1.52 (s, 3H), 0.01 (s, 3H), -0.03 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 161.2, 149.5, 149.4, 140.4, 139.9, 133.5, 128.9, 127.9, 127.8, 122.3, 115.2, 67.0, 49.3, 44.6, 30.7, 29.8, -1.35.ppm. **IR** (film): 3068, 2963, 2891, 2820, 2362, 2185, 2040, 1592, 1513, 1232, 1121, 930, 827, 750 cm^{-1}. **HRMS (ESI)**: calculated for $C_{26}H_{33}ON_2Si^+$ $[M+H]^+$ 417.2357; found 417.2353. Spectra data are consistent with literature data.[1]

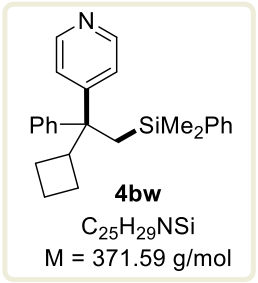
2.4.23 4-(2-(4-chlorophenyl)-1-(dimethyl(phenyl)silyl)butan-2-yl)pyridine (**4bv**)



4bv
$C_{23}H_{26}ClNSi$
M = 380.00 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 1-(but-1-en-2-yl)-4-chlorobenzene **3v** (50 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bv** as colorless oil (59 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 5.7 Hz, 2H), 7.32 – 7.14 (m, 5H), 7.12 – 6.99 (m, 2H), 6.96 – 6.92 (m, 4H), 1.93 (q, J = 7.3 Hz, 2H), 1.62 (d, J = 10.0 Hz, 2H), 0.45 (t, J = 7.3 Hz, 3H), -0.10 (s, 3H), -0.11 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 159.0, 149.4, 147.1, 139.1, 133.4, 132.07, 129.1, 129.0, 128.1, 127.8, 123.0, 48.6, 31.9, 26.2, 8.7, -1.7 ppm. **IR** (film): 3068, 3021, 2967, 2881, 1594, 1489, 1426, 1406, 1249, 1111, 1012, 930, 800, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{27}NClSi^+$ $[M+H]^+$ 380.1596; found 380.1594.

2.4.24 4-(1-cyclobutyl-2-(dimethyl(phenyl)silyl)-1-phenylethyl)pyridine (**4bw**)

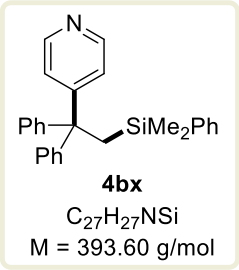


4bw
$C_{25}H_{29}NSi$
M = 371.59 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), and 1-(but-1-en-2-yl)-4-chlorobenzene **3w** (47 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bw** as colorless oil (57 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 4.8 Hz, 2H), 7.46 – 7.36 (m, 2H), 7.37 – 7.28 (m, 3H), 7.28 – 7.16 (m, 3H), 7.10 – 7.02 (m, 4H), 3.19 – 3.10 (m, 1H), 1.92 – 1.78 (m, 2H), 1.77 – 1.62 (m, 2H), 1.59 – 1.44 (m, 2H), 1.44 – 1.07 (m, 2H), -0.04 (s, 3H), -0.09 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 157.6, 148.9, 146.8, 139.9, 133.4, 129.0, 128.9, 127.8, 127.8, 126.4, 124.7, 51.61, 42.21, 27.48, 24.84, 24.53, 17.48, -1.73, -1.87 ppm. **IR** (film): 3076, 3021,

2976, 2866, 1593, 1444, 1407, 1250, 1112, 1072, 997, 904, 842, 729 cm^{-1}. **HRMS (ESI)**: calculated for $C_{25}H_{30}NSi^+$ $[M+H]^+$ 372.2142; found 372.2139.

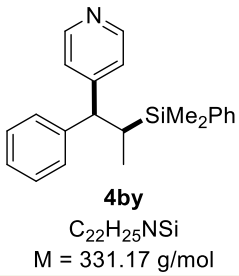
2.4.25 4-(2-(dimethyl(phenyl)silyl)-1,1-diphenylethyl)pyridine (**4bx**)



4bx
$C_{27}H_{27}NSi$
M = 393.60 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), and 1,1-Diphenylethylene **3x** (54 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bx** as colorless oil (51 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 5.2 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.35 (m, 3H), 7.34 – 7.29 (m, 8H), 7.29 – 7.24 (m, 4H), 2.42 – 2.38 (m, 2H), -0.03 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 158.2, 149.3, 147.0, 140.2, 133.4, 129.1, 128.9, 128.0, 12.87, 126.5, 124.1, 55.5, 30.9, -1.3 ppm. **IR** (film): 3054, 3021, 2954, 2924, 1948, 1600, 1492, 1426, 1249, 1111, 821, 699 cm^{-1}. HRMS (ESI): calculated for $C_{27}H_{28}NSi^+$ $[M+H]^+$ 394.1986; found 394.1980.

2.4.26 4-(2-(dimethyl(phenyl)silyl)-1-phenylpropyl)pyridine (**4by**)

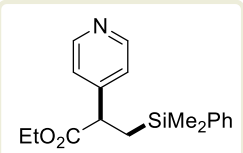


4by
$C_{22}H_{25}NSi$
M = 331.17 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), *β*-methylstyrene **3y** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4by** as colorless oil (23 mg, 35% yield, d. r. = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 4.6 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.30 (m, 3H), 7.28 – 7.24 (m, 3H), 7.24 – 7.20 (m, 3H), 7.20 – 7.14 (m, 1H), 3.71 (s, 0.5H), 3.68 (s, 0.5H), 2.03 – 1.97 (m, 1H), 0.90 – 0.85 (m, 3H), 0.08 (s, 3H), 0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.2, 149.9, 143.6, 138.3, 134.0, 128.9, 128.7, 128.3, 127.7, 127.0, 123.4,

55.3, 24.0, 14.9, -2.7, -4.2 ppm. **IR** (film): 3067, 3024, 2954, 2870, 1594, 1493, 1415, 1249, 1111, 903, 834, 734 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{26}NSi^+$ $[M+H]^+$ 332.1829; found 332.1826.

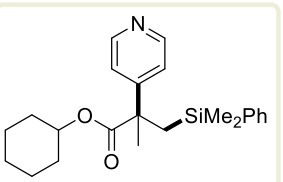
2.4.27 ethyl-3-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propanoate (**4bz**)



4bz
$C_{18}H_{23}NO_2Si$
M = 313.47 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), ethyl acrylate (30 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bz** as colorless oil (23 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.39 – 8.24 (m, 2H), 7.27 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 7.01 – 6.99 (m, 2H), 3.85 – 3.75 (m, 2H), 3.41 – 3.35 (m, 1H), 1.54 – 1.49 (m, 1H), 1.11 (s, 1H), 0.99 – 0.94 (m, 3H), 0.04 (s, 3H), 0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 173.5, 150.1, 149.9, 137.7, 133.7, 129.3, 128.0, 123.2, 61.3, 47.0, 20.4, 14.0, -2.6, -2.7 ppm. **IR** (film): 3069, 3052, 1700, 1597, 1426, 1250, 1175, 1113, 1030, 905, 838, 730 cm^{-1}. **HRMS (ESI)**: calculated for $C_{18}H_{24}NO_2Si^+$ $[M+H]^+$ 314.1571; found 314.1568.

2.4.28 cyclohexyl 3-(dimethyl(phenyl)silyl)-2-methyl-2-(pyridin-4-yl)propanoate (**4baa**)

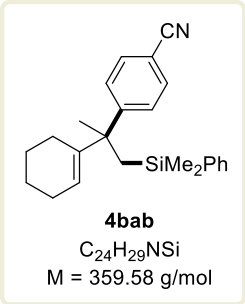


4baa
$C_{23}H_{31}NO_2Si$
M = 381.59 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), cyclohexyl methacrylate **3aa** (50 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4baa** as colorless oil (40 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 – 8.21 (m, 2H), 7.27 – 7.22 (m, 2H), 7.17 – 7.08 (m, 3H), 7.03 (d, *J* = 6.0 Hz, 2H), 4.51 – 4.43 (m, 1H), 1.53 – 1.42 (m, 2H), 1.39 – 1.29 (m, 6H), 1.27 – 1.22 (m, 1H), 1.15 – 1.04 (m, 5H), 1.02 – 0.94 (m, 1H), 0.04 (s, 3H), 0.00 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 174.9, 154.9, 149.7, 139.2, 133.6, 129.1, 127.9, 121.2, 73.4, 48.8,

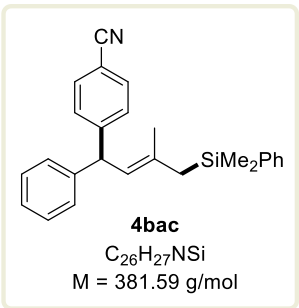
31.1, 27.5, 25.3, 24.9, 23.4, -1.3, -1.3 ppm. **IR** (film): 2937, 2859, 1722, 1593, 1250, 1210, 1112, 905, 837 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{32}NO_2Si^+$ $[M+H]^+$ 382.2197; found 382.2193.

2.4.29 4-(2-(cyclohex-1-en-1-yl)-1-(dimethyl(phenyl)silyl)propan-2-yl)benzonitrile (**4bab**)



Prepared according to general procedure from 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 1-(prop-1-en-2-yl)cyclohex-1-ene (37 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bab** as colorless oil (40 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 2H), 7.28 – 7.20 (m, 2H), 7.19 – 7.07 (m, 5H), 5.61 – 5.57 (m, 1H), 1.95 – 1.88 (m, 2H), 1.42 – 1.19 (m, 8H), 1.14 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 156.0, 143.4, 140.0, 133.5, 131.8, 128.8, 127.8, 127.2, 121.4, 119.3, 109.3, 46.8, 27.9, 27.8, 25.8, 25.5, 23.0, 22.2 ppm. **HRMS (ESI)**: calculated for $C_{24}H_{30}NSi^+$ $[M+H]^+$ 360.2142; found 360.2131.

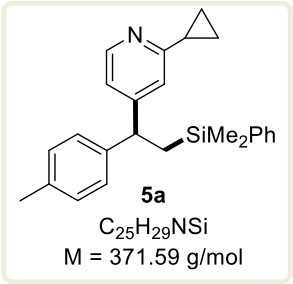
2.4.30 4-(4-(dimethyl(phenyl)silyl)-3-methyl-1-phenylbut-2-en-1-yl)benzonitrile (**4bac**)



Prepared according to general procedure from 1.4-dicyanobenzene (0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 1-(prop-1-en-2-yl)cyclohex-1-ene (37 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4bac** as colorless oil (***E***, 34 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 – 7.24 (m, 2H), 7.21 – 7.16 (m, 2H), 7.11 – 6.94 (m, 6H), 6.90 – 6.87 (m, 2H), 6.81 – 6.77 (m, 2H), 5.07 (d, J = 9.4 Hz, 1H), 4.59 (d, J = 9.3 Hz, 1H), 1.57 – 1.54 (m, 2H), 1.33 (d, J = 1.4 Hz, 3H) ppm. NOE difference

measurement: When the chemical shift of olefin proton was identified at δ 5.09 ppm, NOE was observed at the methylene (-CH_2-$SiMe_2Ph$) proton resonances at δ 1.55 ppm, whereas no NOE appeared at the methyl proton resonance at δ 1.33 ppm. Irradiation at the methyl proton resonance at δ 1.33 ppm caused enhancement of the benzyl [-CH-(Ph)(4-CNPh), δ 4.59 ppm] and the olefin (δ 5.16) proton resonances, while no NOE was observed at the olefin proton resonance at 5.09 ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 151.1, 144.0, 138.6, 135.1, 133.7, 132.2, 129.1, 129.0, 128.6, 128.2, 127.8, 126.5, 124.6, 119.2, 109.7, 49.8, 29.6, 19.2, -2.3, -2.5 ppm. **HRMS (ESI)**: calculated for $C_{26}H_{27}NSiNa^+$ $[M+Na]^+$ 404.1805; found 404.1795.

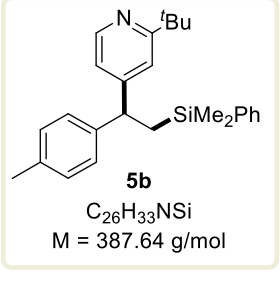
2.4.31 2-cyclopropyl-4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)pyridine (**5a**)



5a
$C_{25}H_{29}NSi$
M = 371.59 g/mol

Prepared according to general procedure from 2-cyclopropyl-4-cyanopyridine **1ba** (29 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5a** as colorless oil (48 mg, 65% yield). **^1H NMR** (400 MHz, $CDCl_3$): δ8.12 (d, *J* = 5.1 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.25 – 7.12 (m, 3H), 6.98 – 6.92 (m, 4H), 6.84 (d, *J* = 1.7 Hz, 1H), 6.76 (dd, *J* = 5.2, 1.7 Hz, 1H), 3.79 (t, *J* = 7.9 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.52 – 1.45 (m, 2H), 0.87 – 0.77 (m, 4H), -0.03 (s, 3H), -0.05 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 162.7, 155.8, 149.2, 142.1, 138.8, 136.2, 133.6, 129.3, 129.0, 127.8, 127.6, 120.6, 119.8, 46.4, 22.8, 21.1, 17.2, 9.8, 9.7, -2.3, -2.7 ppm. **IR** (film): 3007, 2953, 2918, 1598, 1512, 1478, 1426, 1249, 1113, 900, 836 cm^{-1}. **HRMS (ESI)**: calculated for $C_{25}H_{30}NSi^+$ $[M+H]^+$ 372.2142; found 372.2136.

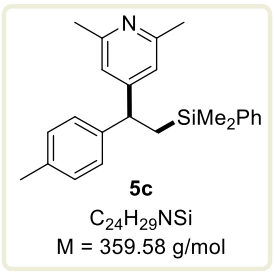
2.4.32 2-(tert-butyl)-4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)pyridine (**5b**)



5b
$C_{26}H_{33}NSi$
M = 387.64 g/mol

Prepared according to general procedure from 2-tert-butylisonicotinonitrile **1bb** (32 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5b** as colorless oil (38 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 5.1 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.25 – 7.17 (m, 3H), 7.06 (s, 1H), 7.00 – 6.97 (m, 2H), 6.95 – 6.91 (m, 2H), 6.82 – 6.79 (m, 1H), 3.81 (t, *J* = 8.0 Hz, 1H), 2.18 (s, 3H), 1.52 – 1.44 (m, 2H), 1.21 (s, 9H), -0.04 (s, 3H), -0.07 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 169.29 155.9, 148.6, 142.3, 138.7, 136.1, 133.6, 129.3, 129.0, 127.8, 127.5, 120.0, 118.3, 46.8, 37.4, 30.3, 23.1, 21.0, -2.4, -2.5 ppm. **IR** (film): 3028, 2961, 2253, 1599, 1251, 1114, 902, 722, 649 cm^{-1}. **HRMS (ESI)**: calculated for $C_{26}H_{34}NSi^+$ $[M+H]^+$ 388.2455; found 388.2449.

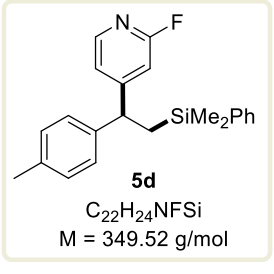
2.4.33 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-2,6-dimethylpyridine (**5c**)



5c
$C_{24}H_{29}NSi$
M = 359.58 g/mol

Prepared according to general procedure from 2,6-dimethyl-4-cyanopyridine **1bc** (27 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5c** as colorless oil (35 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 7.09 – 7.04 (m, 4H), 6.77 (s, 2H), 3.86 (t, J = 8.0 Hz, 1H), 2.41 (s, 6H), 2.29 (s, 3H), 1.62 – 1.50 (m, 2H), 0.08 (s, 3H), 0.05 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 157.6, 156.5, 142.2, 138.8, 136.2, 133.6, 129.3, 129.0, 127.8, 127.6, 119.5, 46.3, 24.5, 22.8, 21.1, -2.2, -2.7 ppm. **IR** (film): 3070, 3019, 2954, 2919, 2203, 2172, 1602, 1566, 1426, 1249, 1112, 907, 843, 731 cm^{-1}. **HRMS (ESI)**: calculated for $C_{24}H_{30}NSi^+$ $[M+H]^+$ 360.2142; found 360.2136.

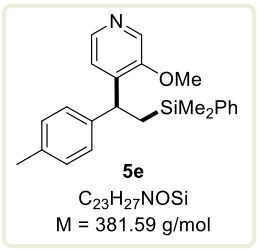
2.4.34 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-2-fluoropyridine (**5d**)



5d
$C_{22}H_{24}NFSi$
M = 349.52 g/mol

Prepared according to general procedure from 4-cyano-2-fluoropyridine **1bd** (25 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), and 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5d** as colorless oil (32 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.92 (d, *J* = 5.3 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.29 – 7.23 (m, 3H), 6.98 (t, J = 1.1 Hz, 4H), 6.92 – 6.89 (m, 1H), 6.67 (s, 1H), 3.89 (dd, J = 9.1, 6.8 Hz, 1H), 2.22 (s, 3H), 1.57 – 1.47 (m, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 164.1 (d, $J_{C\text{-}F}$ = 238.4 Hz), 162.4 (d, *J* = 7.3 Hz), 147.4 (d, $J_{C\text{-}F}$ = 15.3 Hz), 141.0, 138.3, 136.7, 133.6, 129.5, 129.1, 127.9, 127.6, 120.7 (d, $J_{C\text{-}F}$ = 3.9 Hz), 108.1 (d, $J_{C\text{-}F}$ = 37.2 Hz), 46.3, 22.8, 21.1, -2.3, -2.8 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.6 ppm. **IR** (film): 3070, 3020, 2953, 2921, 1595, 1512, 1410, 1249, 1112, 838, 731. **HRMS (ESI)**: calculated for $C_{22}H_{25}FNSi^+$ $[M+H]^+$ 350.1735; found 350.1732.

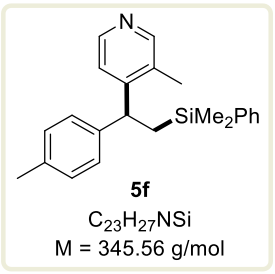
2.4.35 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-3-methoxypyridine (**5e**)



5e
$C_{23}H_{27}NOSi$
M = 381.59 g/mol

Prepared according to general procedure from 3-methoxy-isonicotinonitrile **1be** (27 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5e** as colorless oil (55 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 – 7.99 (m, 2H), 7.35 – 7.28 (m, 2H), 7.27 – 7.15 (m, 3H), 7.06 – 7.03 (m, 3H), 6.95 (d, *J* = 7.8 Hz, 2H), 4.41 (t, *J* = 7.9 Hz, 1H), 3.73 (s, 3H), 2.20 (s, 3H), 1.47 (d, *J* = 8.0 Hz, 2H), 0.02 (s, 3H), -0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.8, 144.0, 142.7, 141.6, 139.0, 135.9, 133.5, 133.1, 129.0, 128.8, 127.9, 127.7, 122.1, 55.9, 38.2, 22.1, 21.0, -2.3, -2.8 ppm. **IR** (film): 3067, 3019, 2953, 2921, 1972, 1588, 1511, 1494, 1415, 1293, 1112, 1025, 830, 731, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{28}NOSi^+$ $[M+H]^+$ 362.1935; found 362.1933.

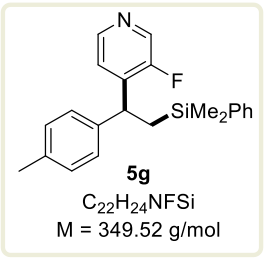
2.4.36 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-3-methylpyridine (**5f**)



5f
$C_{23}H_{27}NSi$
M = 345.56 g/mol

Prepared according to general procedure from 4-cyano-3-methylpyridine **1bf** (36 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5f** as colorless oil (49 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (d, J = 5.3 Hz, 1H), 8.19 (s, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.25 (m, 3H), 7.23 (d, J = 4.8 Hz, 1H), 6.98 (s, 4H), 4.08 (t, J = 7.8 Hz, 1H), 2.23 (s, 3H), 2.04 (s, 3H), 1.59 – 1.46 (m, 2H), 0.06 (s, 3H), 0.02 (s, 3H). ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.5, 151.0, 147.7, 141.2, 138.6, 136.1, 134.0, 133.6, 131.1, 129.2, 129.1, 127.8, 121.5, 42.0, 23.6, 21.0, 16.5, -2.2, -2.5 ppm. **IR** (film): 3046, 3019, 2952, 2922, 1590, 1511, 1426, 1248, 1112, 904, 831, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{23}H_{28}NSi^+$ $[M+H]^+$ 346.1986; found 346.1981.

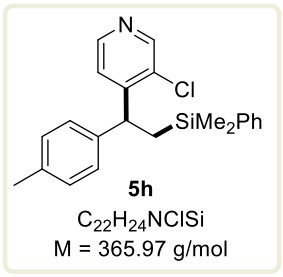
2.4.37 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-3-fluoropyridine (**5g**)



5g
$C_{22}H_{24}NFSi$
M = 349.52 g/mol

Prepared according to general procedure from 4-cyano-3-fluoropyridine **1bg** (25 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5g** as colorless oil (48 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 – 8.21 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.23 (m, 3H), 7.22 – 7.18 (m, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.36 (t, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 1.65 – 1.55 (m, 2H), 0.12 (s, 3H), 0.09 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 157.3 (d, $J_{C\text{-}F}$ = 254.3 Hz), 145.7 (d, $J_{C\text{-}F}$ = 5.0 Hz), 142.73 (d, $J_{C\text{-}F}$ = 12.2 Hz), 140.5, 138.4, 138.0 (d, $J_{C\text{-}F}$ = 25.6 Hz), 136.6, 133.5, 129.3, 129.1, 127.9, 127.7, 122.9, 38.9, 22.0, 21.1, -2.4, -2.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -131.9 ppm. **IR** (film): 3070, 3050, 2952, 2927, 2015, 1881, 1512, 1484, 1414, 1248, 1112, 904, 834, 700 cm^{-1}**. HRMS (ESI)**: calculated for $C_{22}H_{25}FNSi^+$ $[M+H]^+$ 350.1735; found 350.1730.

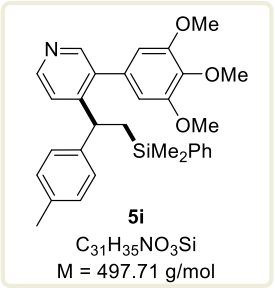
2.4.38 3-chloro-4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)pyridine (**5h**)



5h
$C_{22}H_{24}NClSi$
M = 365.97 g/mol

Prepared according to general procedure from 3-Chloro-4-cyanopyridine **1bh** (28 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5h** as colorless oil (35 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.30 (d, *J* = 5.0 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.35 – 7.29 (m, 3H), 7.23 (d, J = 5.1 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 4.53 (dd, J = 8.8, 7.0 Hz, 1H), 2.30 (s, 3H), 1.62 – 1.53 (m, 2H), 0.15 (s, 3H), 0.10 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.1, 149.5, 147.8, 140.0, 138.5, 136.6, 133.5, 131.4, 129.3, 129.1, 128.0, 127.8, 123.1, 42.0, 22.8, 21.1, -2.3, -2.8 ppm. **IR** (film): 3047, 3020, 2953, 2922, 1678, 1580, 1512, 1426, 1399, 1249, 1112, 1034, 903, 835, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{22}H_{25}NClSi^+$ $[M+H]^+$ 366.1439; found 366.1434.

2.4.39 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-3-(3,4,5-trimethoxyphenyl)pyridine (**5i**)

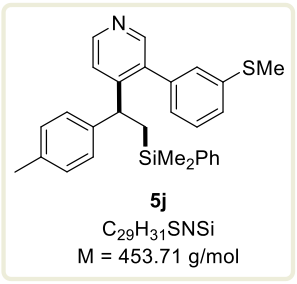


5i
$C_{31}H_{35}NO_3Si$
M = 497.71 g/mol

Prepared according to general procedure from 3-(3,4,5-trimethoxyphenyl)-4-cyanopyridine **1bi** (54 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5i** as colorless oil (50 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 5.3 Hz, 1H), 8.38 (s, 1H), 7.46 (d, J = 5.2 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.29 (d, *J* = 3.5 Hz, 4H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.86 – 6.83 (m, 2H), 6.26 (s, 1H), 4.23 (dd, *J* = 8.9, 6.8 Hz, 1H), 3.94 (s, 3H), 3.72 (s, 6H), 2.29 (s, 3H), 1.62 – 1.47 (m, 2H), 0.00 (s, 3H), -0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.0, 152.9, 150.1, 148.8, 141.8, 138.5, 137.5, 137.3, 135.9, 133.4, 133.3, 129.0, 129.0, 127.9, 127.7, 122.0,

106.8, 61.0, 56.0, 42.1, 24.6, 21.0, -2.2, -2.8 ppm. **IR** (film): 3066, 3001, 2937, 2836, 1583, 1510, 1479, 1412, 1347, 1238, 1238, 1172, 1112, 1007, 907, 834, 731 cm^{-1}. **HRMS (ESI)**: calculated for $C_{31}H_{36}NO_3Si^+$ $[M+H]^+$ 498.2459; found 498.2449.

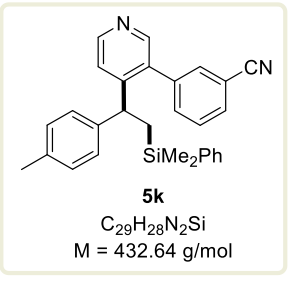
2.4.40 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-3-(3-(methylthio)phenyl)pyridine (**5j**)



5j
$C_{29}H_{31}SNSi$
M = 453.71 g/mol

Prepared according to general procedure from 3-(3-(methylthio)phenyl)-4-cyanopyridine **1bj** (45 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5j** as colorless oil (53 mg, 59% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.32 (s, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.27 – 7.25 (m, 3H), 7.24 – 7.22 (m, 3H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.89 (s, 1H), 6.82 (t, *J* = 6.4 Hz, 3H), 4.17 (dd, J = 9.2, 6.4 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.59 – 1.53 (m, 1H), 1.46 – 1.40 (m, 1H), -0.05 (s, 3H), -0.06 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.3, 150.1, 148.9, 141.5, 138.8, 138.6, 138.5, 136.7, 136.1, 133.4, 129.1, 129.0, 128.7, 128.6, 127.8, 127.3, 126.2, 125.8, 122.1, 41.9, 24.4, 21.0, 15.5, -2.3, -2.8 ppm. **IR** (film): 3070, 3019, 2953, 2920, 2184, 1588, 1512, 1426, 1112, 900, 837, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{29}H_{32}SNSi^+$ $[M+H]^+$ 454.2019; found 454.2013.

2.4.41 3-(4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)pyridin-3-yl)benzonitrile (**5k**)

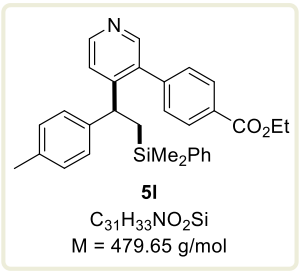


5k
$C_{29}H_{28}N_2Si$
M = 432.64 g/mol

Prepared according to general procedure from 3-(3-cyanophenyl)-4-cyanopyridine **1bk** (41 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5k** as colorless oil (65 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 5.3 Hz, 1H), 8.24 (s,

1H), 7.62 (dt, J = 7.7, 1.4 Hz, 1H), 7.47 (d, *J* = 5.2 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.35 – 7.32 (m, 1H), 7.29 – 7.22 (m, 4H), 7.20 – 7.14 (m, 2H), 6.97 (d, J = 7.8 Hz, 2H), 6.71 – 6.68 (m, 2H), 3.97 – 3.91 (m, 1H), 2.26 (s, 3H), 1.61 – 1.52 (m, 1H), 1.42 – 1.37 (m, 1H), -0.01 (s, 3H), -0.07 (s, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 153.2, 149.8, 149.6, 140.9, 139.0, 138.0, 136.4, 135.0, 134.0, 133.4, 133.0, 131.3, 129.3, 129.2, 129.0, 127.9, 127.6, 122.2, 118.4, 112.6, 42.3, 24.3, 21.0, -2.1, -2.7 ppm. **IR** (film): 3060, 3028, 2254, 1589, 1249, 1116, 900, 724, 649 cm^{-1}. **HRMS (ESI)**: calculated for $C_{29}H_{29}N_2Si^+$ $[M+H]^+$ 433.2095; found 433.2087.

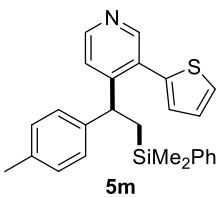
2.4.42 ethyl-4-(4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)pyridin-3-yl)benzoate (**5l**)



5l
$C_{31}H_{33}NO_2Si$
M = 479.65 g/mol

Prepared according to general procedure from ethyl 4-(4-cyanopyridin-3-yl)benzoate **1bl** (51 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5l** as colorless oil (62 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 5.0 Hz, 1H), 8.46 (s, 1H), 8.16 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.44 – 7.38 (m, 4H), 7.27 (d, J = 8.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 4.61 (q, J = 7.1 Hz, 2H), 4.31 (dd, J = 9.5, 6.1 Hz, 1H), 2.43 (s, 3H), 1.81 – 1.74 (m, 1H), 1.62 (q, J = 7.3 Hz, 4H), 0.15 (s, 3H), 0.08 (s, 3H). **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 166.4, 153.3, 149.9, 149.3, 142.5, 141.2, 138.3, 136.2, 136.0, 133.5, 129.7, 129.7, 129.5, 129.2, 129.0, 127.8, 127.7, 122.1, 61.2, 41.8, 24.4, 21.0, 14.5, -2.2, -2.8 ppm. **IR** (film): 3070, 3046, 2980, 2954, 2362, 2157, 1981, 1718, 1609, 1585, 1230, 1178, 1111, 1024, 838, 769, 709 cm^{-1}. **HRMS (ESI)**: calculated for $C_{31}H_{34}NO_2Si^+$ $[M+H]^+$ 480.2353; found 480.2345.

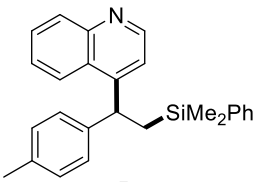
2.4.43 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-3-(thiophen-2-yl)pyridine (**5m**)



5m
$C_{26}H_{27}SNSi$
M = 413.65 g/mol

Prepared according to general procedure from 3-(thiophen-2-yl)isonicotinonitrile **1bm** (37 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5m** as colorless oil (42 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1 8.38 – 8.33 (m, 2H), 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.22 – 7.19 (m, 3H), 7.17 (dt, *J* = 7.0, 1.4 Hz, 1H), 6.96 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.92 (d, J = 7.9 Hz, 2H), 6.86 – 6.83 (m, 2H), 6.71 (dd, J = 3.5, 1.2 Hz, 1H), 4.42 (dd, J = 9.4, 6.3 Hz, 1H), 2.19 (s, 3H), 1.56 – 1.50 (m, 1H), 1.38 – 1.33 (m, 1H), -0.09 (s, 3H), -0.11 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 154.8, 151.2, 149.3, 141.2, 138.7, 138.1, 136.2, 133.5, 129.6, 129.2, 128.9, 128.2, 127.8, 127.8, 127.4, 126.5, 122.2, 41.6, 24.3, 21.1, -2.3, -2.8 ppm. **IR** (film): 3072, 3044, 3019, 2924, 2203, 1585, 1426, 1249, 1112, 900, 836, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{26}H_{28}SNSi^+$ $[M+H]^+$ 414.1706; found 414.1702.

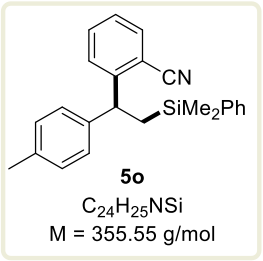
2.4.44 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)quinoline (**5n**)



5n
$C_{26}H_{27}NSi$
M = 381.59 g/mol

Prepared according to general procedure from quinoline-4-carbonitrile **1bn** (31 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5n** as colorless oil (24 mg, 32% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.78 (d, J = 4.6 Hz, 1H), 8.07 (dd, J = 8.5, 1.3 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.66 – 7.60 (m, 1H), 7.48 – 7.38 (m, 3H), 7.37 – 7.26 (m, 4H), 7.16 – 7.11 (m, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 4.82 – 4.77 (m, 1H), 2.28 (s, 3H), 1.76 – 1.66 (m, 2H), 0.10 (s, 3H), 0.07 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.7, 150.2, 148.6, 141.4, 138.6, 136.3, 133.7, 130.3, 129.3, 129.1, 128.9, 127.9, 127.8, 126.9, 126.4, 123.5, 119.2, 41.3, 24.1, 21.1, -2.2, -2.7 ppm. **IR** (film): 3092, 3020, 2950, 2924, 2362, 2176, 2011, 1587, 1510, 1426, 1249, 1112, 838, 734 cm^{-1}. **HRMS (ESI)**: calculated for $C_{26}H_{28}NSi^+$ $[M+H]^+$ 382.1986; found 382.1982.

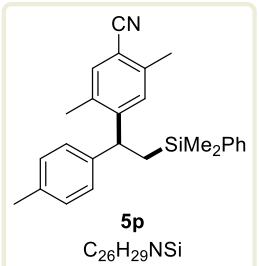
2.4.45 2-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)benzonitrile **(5o**)



5o
$C_{24}H_{25}NSi$
M = 355.55 g/mol

Prepared according to general procedure from phthalonitrile **1bo** (26 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5o** as colorless oil (46 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δδ 7.45 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 7.23 (qd, J = 6.1, 4.3 Hz, 3H), 7.16 – 7.08 (m, 3H), 6.99 (dd, J = 8.2, 2.3 Hz, 2H), 4.52 – 4.46 (m, 1H), 2.21 (s, 3H), 1.67 – 1.50 (m, 2H), 0.09 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 150.9, 141.5, 138.6, 136.3, 133.5, 133.0, 132.9, 129.3, 129.0, 127.8, 127.6, 127.6, 126.5, 118.4, 111.9, 44.6, 23.6, 21.0, -2.4, -2.9 ppm. **IR** (film): 3072, 3052, 2954, 2222, 1598, 1511, 1426, 1249, 1111, 904, 728 cm^{-1}. **HRMS (ESI)**: calculated for $C_{24}H_{26}NSi^+$ $[M+H]^+$ 356.1829; found 356.1821.

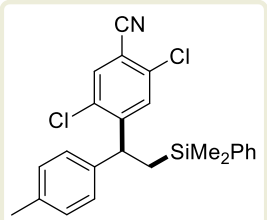
2.4.46 4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-2,5-dimethylbenzonitrile (**5p**)



5p
$C_{26}H_{29}NSi$
M = 383.61 g/mol

Prepared according to general procedure from 2,5-dimethylterephthalonitrile **1bp** (31 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5p** as colorless oil (39 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 4.8, 2.6 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.22 – 7.19 (m, 2H), 6.99 (d, *J* = 4.2 Hz, 4H), 4.16 – 4.10 (m, 1H), 2.38 (s, 3H), 2.25 (s, 3H), 2.06 (s, 3H), 1.57 – 1.50 (m, 2H), 0.09 (s, 3H), 0.04 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 149.9, 141.9, 139.3, 138.7, 136.0, 134.0, 133.9, 133.5, 129.2, 129.0, 129.0, 127.8, 127.7, 118.6, 109.9, 42.4, 24.2, 21.0, 20.2, 19.1, -2.2, -2.7 ppm. **IR** (film): 3068, 3019, 2952, 2923, 2362, 2220, 1611, 1529, 1426, 1248, 1112, 861, 731 cm^{-1}. **HRMS (ESI)**: calculated for $C_{26}H_{30}NSi^+$ $[M+H]^+$ 384.2142; found 384.2140.

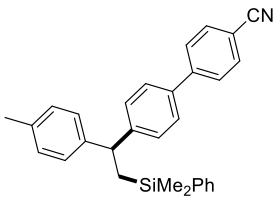
2.4.47 2,5-dichloro-4-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)benzonitrile (**5q**)



5q
$C_{23}H_{24}NCl_2Si$
M = 424.44 g/mol

Prepared according to general procedure from 2,5-dichloroterephthalonitrile **1bq** (40 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5q** as colorless oil (25 mg, 30% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.32 – 7.28 (m, 3H), 7.27 – 7.21 (m, 3H), 7.03 (d, J = 5.3 Hz, 4H), 4.50 (t, J = 7.9 Hz, 1H), 2.25 (s, 3H), 1.54 (s, 1H), 1.47 – 1.42 (m, 1H), 0.13 (s, 3H), 0.06 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 151.7, 139.7, 138.1, 136.9, 135.2, 134.3, 133.5, 132.2, 130.1, 129.5, 129.1, 127.8, 115.0, 111.8, 42.7, 23.3, 21.1, -2.2, -3.1 ppm. **IR** (film): 3072, 3026, 2954, 2235, 1589, 1512, 1467, 1250, 1112, 1084, 903, 835, 700 cm^{-1}. **HRMS (ESI)**: calculated for $C_{24}H_{24}Cl_2NSi^+$ $[M+H]^+$ 424.1050; found 424.1052.

2.4.48 3-(2-(dimethyl(phenyl)silyl)-1-(p-tolyl)ethyl)-2-naphthonitrile **(5r**)

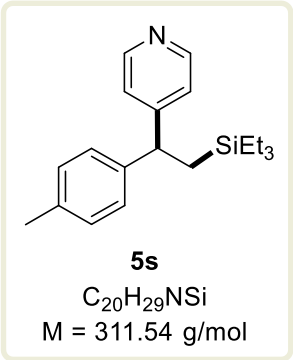


5r
$C_{30}H_{29}NSi$
M = 431.65 g/mol

Prepared according to general procedure from [1,1'-biphenyl]-4,4'-dicarbonitrile **1br** (41 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5r** as colorless oil (51 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.39 – 7.30 (m, 5H), 7.17 (dd, J = 8.2, 2.2 Hz, 2H), 7.11 – 7.06 (m, 2H), 4.13 – 4.06 (m, 1H), 2.32 (s, 3H), 1.71 – 1.66 (m, 2H), 0.12 (s, 3H), 0.10 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 148.0, 145.5, 143.4, 139.0, 136.7, 135.8, 133.6, 132.6, 129.2, 128.9, 128.3, 127.8, 127.5, 127.5, 127.2, 119.1, 110.6, 46.6, 23.5, 21.0, -2.4, -2.6 ppm. **IR** (film): 3060, 3032, 2253,

1067, 1491, 1249, 1114, 903, 840, 700. **HRMS (ESI)**: calculated for $C_{30}H_{30}NSi^+$ $[M+H]^+$ 432.2142; found 432.2139.

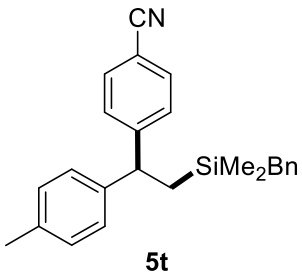
2.4.49 4-(1-(p-tolyl)-2-(triethylsilyl)ethyl)pyridine **(5s**)



5s
$C_{20}H_{29}NSi$
M = 311.54 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $Et_3SiBpin$ (73 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5s** as colorless oil (45 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (d, J = 5.3 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.16 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.99 (t, J = 7.8 Hz, 1H), 2.30 (s, 3H), 1.42 – 1.33 (m, 2H), 0.84 (t, J = 7.9 Hz, 9H), 0.39 – 0.33 (m, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 156.6, 149.8, 142.3, 136.3, 129.3, 127.5, 122.8, 46.3, 21.0, 18.4, 7.4, 3.5 ppm. **HRMS (ESI)**: calculated for $C_{20}H_{30}NSi^+$ $[M+H]^+$ 312.2142; found 312.2133.

2.4.50 4-(2-(benzyldimethylsilyl)-1-(p-tolyl)ethyl)benzonitrile **(5t**)

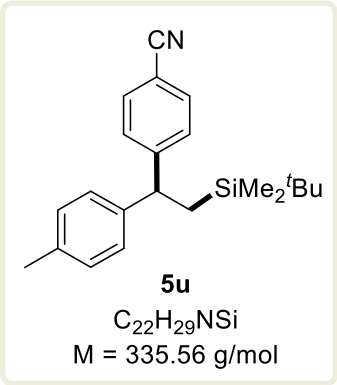


5t
$C_{25}H_{27}NSi$
M = 369.58 g/mol

Prepared according to general procedure from 1,4-dicyanobenzene **1a** (26 mg, 0.2 mmol, 1.0 equiv.), $Me_2BnSiBpin$ (83 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5t** as colorless oil (47 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): 7.75 – 7.66 (m, 2H), 7.51 – 7.47 (m, 2H),

7.42 – 7.36 (m, 2H), 7.28 – 7.22 (m, 5H), 7.13 – 7.07 (m, 2H), 4.20 (t, J = 8.0 Hz, 1H), 2.46 (s, 3H), 2.13 (s, 2H), 1.65 – 1.58 (m, 1H), 1.54 – 1.49 (m, 1H), -0.04 (s, 6H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): 153.0, 142.1, 139.9, 136.4, 132.3, 129.4, 128.3, 128.2, 128.2, 127.4, 124.2, 119.1, 109.8, 46.9, 26.0, 22.2, 21.0, -2.9 ppm. **HRMS (ESI)**: calculated for $C_{25}H_{28}NSi^+$ $[M+H]^+$ 370.1986; found 370.1998.

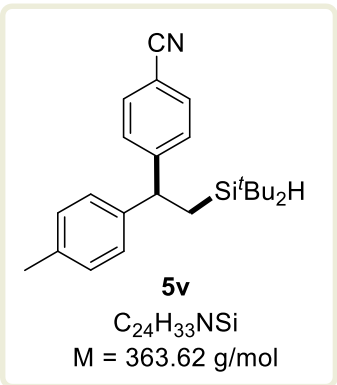
2.4.51 4-(2-(tert-butyldimethylsilyl)-1-(p-tolyl)ethyl)benzonitrile **(5u**)



5u
$C_{22}H_{29}NSi$
M = 335.56 g/mol

Prepared according to general procedure from 1,4-dicyanobenzene **1a** (26 mg, 0.2 mmol, 1.0 equiv.), $Me_2{}^tBuSiBpin$ (73 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5u** as colorless oil (43 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 – 7.61 (m, 2H), 7.51 – 7.48 (m, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 4.18 (t, J = 7.9 Hz, 1H), 2.41 (s, 3H), 1.54 – 1.44 (m, 2H), 0.97 (s, 9H), -0.16 (s, 3H), -0.20 (s, 3H) ppm. **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 153.3, 142.5, 136.3, 132.4, 129.4, 128.3, 127.4, 119.1, 109.8, 47.3, 26.5, 21.0, 19.3, 16.7, -5.7, -5.8 ppm. **HRMS (ESI)**: calculated for $C_{22}H_{30}NSi^+$ $[M+H]^+$ 336.2142; found 336.2132.

2.4.52 4-(2-(di-tert-butylsilyl)-1-(p-tolyl)ethyl)benzonitrile **(5v**)

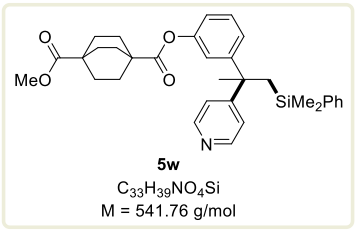


5v
$C_{24}H_{33}NSi$
M = 363.62 g/mol

Prepared according to general procedure from 1,4-dicyanobenzene **1a** (26 mg, 0.2 mmol, 1.0 equiv.), $H^tBu_2SiBpin$ (81 mg, 0.3 mmol, 1.5 equiv.), 4-methylstyrene **3a** (36 mg, 0.3 mmol, 1.5 equiv.)

and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5v** as colorless oil (53 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (dd, J = 8.2, 1.4 Hz, 2H), 7.39 (dd, J = 8.4, 2.0 Hz, 2H), 7.16 (dd, J = 8.3, 2.2 Hz, 2H), 7.11 (dd, J = 8.1, 1.8 Hz, 2H), 4.19 (t, J = 7.9 Hz, 1H), 3.18 (q, J = 2.7 Hz, 1H), 2.31 (s, 3H), 1.47 – 1.37 (m, 2H), 0.98 (s, 9H), 0.96 (s, 9H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.6, 142.3, 136.2, 132.3, 129.3, 128.7, 127.6, 119.1, 109.8, 48.7, 28.8, 28.8, 21.1, 18.9, 18.8, 16.4 ppm. **HRMS (ESI)**: calculated for $C_{24}H_{34}NSi^+$ $[M+H]^+$ 364.2455; found 364.2444.

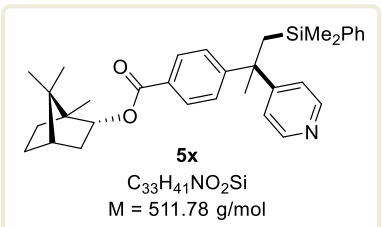
2.4.53 1-(3-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)phenyl) 4-methyl bicyclo[2.2.2]octane-1,4-dicarboxylate (**5w**)



5w
$C_{33}H_{39}NO_4Si$
M = 541.76 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), 1-methyl 4-(3-(prop-1-en-2-yl)phenyl) bicyclo[2.2.2]octane-1,4-dicarboxylate (99 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **6w** as colorless oil (54 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (d, J = 5.8 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.24 (m, 3H), 7.20 (t, J = 7.9 Hz, 1H), 7.08 – 7.05 (m, 2H), 6.93 (d, J = 8.5 Hz, 1H), 6.86 – 6.80 (m, 2H), 3.64 (s, 3H), 1.98 – 1.91 (m, 6H), 1.89 – 1.82 (m, 6H), 1.75 (s, 2H), 1.52 (s, 3H), 0.01 (s, 3H), -0.02 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 177.7, 175.9, 160.1, 150.9, 150.9, 149.5, 139.5, 133.5, 129.1, 128.9, 127.8, 124.7, 122.2, 120.1, 119.4, 51.8, 45.3, 39.1, 38.7, 30.6, 29.6, 27.8, 27.8, -1.4, -1.5 ppm. **IR** (film): 3072, 2953, 2873, 2253, 1724, 1595, 1427, 1250, 1200, 1112, 904, 837, 649 cm^{-1}. **HRMS (ESI)**: calculated for $C_{33}H_{39}NO_4Si^+$ $[M+H]^+$ 542.2721; found 542.2714. Spectra data are consistent with literature data.[1]

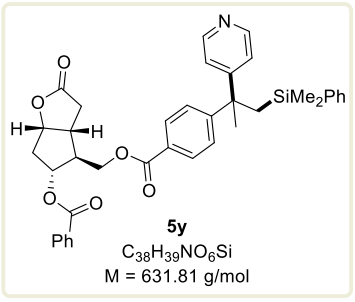
2.4.54 (1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)benzoate (**5x**)



5x
$C_{33}H_{41}NO_2Si$
M = 511.78 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(prop-1-en-2-yl)benzoate (90 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5x** as colorless oil (46 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.42 (d, J = 5.8 Hz, 2H), 7.89 (d, J = 8.3 Hz, 2H), 7.39 – 7.24 (m, 5H), 7.23 – 7.18 (m, 2H), 7.09 – 7.04 (m, 2H), 5.12 – 5.06 (m, 1H), 2.50 – 2.41 (m, 1H), 2.13 – 2.05 (m, 1H), 1.82 (d, J = 3.9 Hz, 2H), 1.72 (t, J = 4.5 Hz, 1H), 1.58 (s, 3H), 1.43 – 1.25 (m, 3H), 1.10 (dd, J = 13.8, 3.5 Hz, 1H), 0.96 (s, 3H), 0.91 – 0.88 (m, 6H), 0.02 (s, 3H), -0.04 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 166.6, 159.9, 154.2, 149.6, 139.2, 133.4, 129.5, 129.0, 128.9, 127.9, 127.2, 122.2, 80.5, 49.2, 48.0, 45.6, 45.1, 37.0, 30.5, 29.6, 28.2, 27.5, 19.8, 19.0, 13.7, -1.3, -1.3 ppm. **IR** (film): 3072, 2954, 2878, 2253, 1712, 1593, 1407, 1426, 1281, 1113, 1016, 904, 700, 649 cm^{-1}. **HRMS (ESI)**: calculated for $C_{33}H_{41}NO_2Si^+$ $[M+H]^+$ 512.2979; found 512.2976. Spectra data are consistent with literature data.[1]

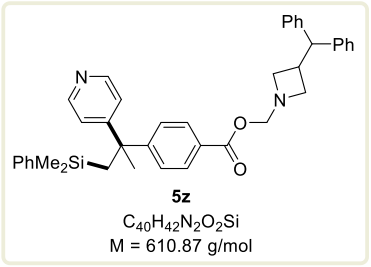
2.4.55 (5-(benzoyloxy)-2-oxohexahydro-2H-cyclopenta[b]furan-4-yl)methyl 4-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)benzoate **(5y**)



5y
$C_{38}H_{39}NO_6Si$
M = 631.81 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), ((3aR,4S,5R,6aS)-5-(benzoyloxy)-2-oxohexahydro-2H-cyclopenta[b]furan-4-yl)methyl 4-(prop-1-en-2-yl)benzoate (157 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5y** as colorless oil (40 mg, 31% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44 (d, J = 5.3 Hz, 2H), 8.06 – 7.94 (m, 2H), 7.89 – 7.84 (m, 2H), 7.57 – 7.51 (m, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.24 – 7.20 (m, 2H), 7.08 – 7.04 (m, 2H), 5.48 – 5.43 (m, 1H), 5.14 – 5.08 (m, 1H), 4.42 – 4.32 (m, 2H), 2.99 – 2.86 (m, 2H), 2.66 – 2.55 (m, 3H), 2.42 – 2.36 (m, 1H), 1.81 (s, 2H), 1.58 (s, 3H), 0.02 (s, 3H), 0.00 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 176.2, 166.1, 166.0, 159.6, 155.1, 149.6, 139.1, 133.4, 129.8, 129.7, 129.6, 129.5, 129.0, 128.6, 128.6, 127.9, 127.4, 122.2, 84.0, 77.4, 64.5, 51.7, 45.7, 40.7, 38.3, 35.8, 30.5, 29.5, -1.3, -1.4 ppm. **IR** (film): 3060, 3020, 2298, 2254, 1773, 1719, 1269, 1108, 1269, 1194, 1108, 903, 734, 649 cm^{-1}. **HRMS (ESI)**: calculated for $C_{38}H_{40}NO_6Si^+$ $[M+H]^+$ 634.2619; found 634.2607. Spectra data are consistent with literature data.[1]

2.4.56 (3-benzhydrylazetidin-1-yl)methyl 4-(1-(dimethyl(phenyl)silyl)-2-(pyridin-4-yl)propan-2-yl)benzoate (**5z**)



5z
$C_{40}H_{42}N_2O_2Si$
M = 610.87 g/mol

Prepared according to general procedure from 4-cyanopyridine **1b** (21 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (79 mg, 0.3 mmol, 1.5 equiv.), (1-benzhydrylazetidin-3-yl)methyl 4-(prop-1-en-2-yl)benzoate (119 mg, 0.3 mmol, 1.5 equiv.) and anhydrous acetonitrile (1 mL) in the presence of $Ir(ppy)_3$ (2 mol%, 2.6 mg, 004 mmol) and Rb_2CO_3 (0.2 mmol, 1.0 equiv.). Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **5z** as colorless oil (41 mg, 34% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 – 8.39 (m, 2H), 7.94 – 7.86 (m, 2H), 7.44 – 7.39 (m, 4H), 7.37 – 7.16 (m, 13H), 7.08 – 7.05 (m, 2H), 4.48 (d, J = 6.8 Hz, 2H), 4.37 (s, 1H), 3.34 (t, J = 7.6 Hz, 2H), 3.01 (dd, J = 7.6, 5.9 Hz, 2H), 2.92 – 2.82 (m, 1H), 1.83 (d, J = 1.9 Hz, 2H), 0.04 (s, 3H), 0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 166.3, 159.9, 154.4, 149.7, 142.1, 139.2, 133.4, 129.5, 129.0, 128.5, 128.2, 127.9, 127.5, 127.3, 127.2, 122.2, 78.1, 66.9, 56.3, 45.6, 30.5, 29.5, 29.1, -1.3, -1.4 ppm. **IR** (film): 3068, 3025, 2952, 2831, 2252, 1716, 1593, 1490, 1408, 1250, 1111, 1016, 906, 704 cm^{-1}. **HRMS (ESI)**: calculated for $C_{40}H_{43}N_2O_2Si^+$ $[M+H]^+$ 611.3088; found 611.3080. Spectra data are consistent with literature data.[1]

3. Computational Investigations

All calculations were performed with the Gaussian 16 package.[7] Geometry optimizations were performed at M06-2X[8]/6-31G(d,p) level of theory in conjugation with the polarizable continuum model (PCM) solvation model for acetonitrile.[9] To get more accurate energies, single-point energy calculations were done with the same functional and solvation model using the cc-pVTZ basis set. The 3D structures of the optimized species were generated using CYLview.[10]

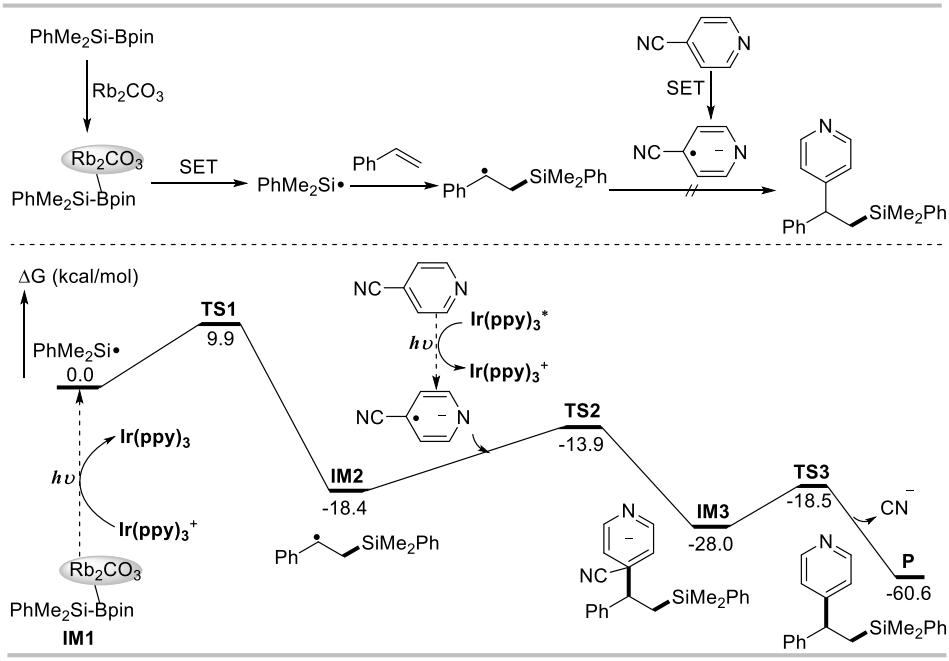


Figure S2. Gibbs free energy profile of $PhMe_2Si$ radical, styrene and 4-canopyridine radical anion.

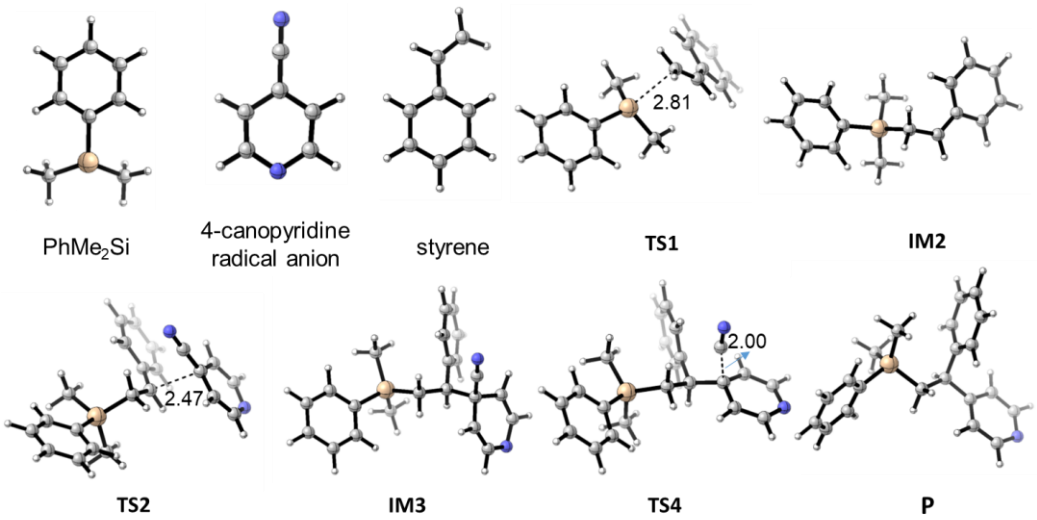
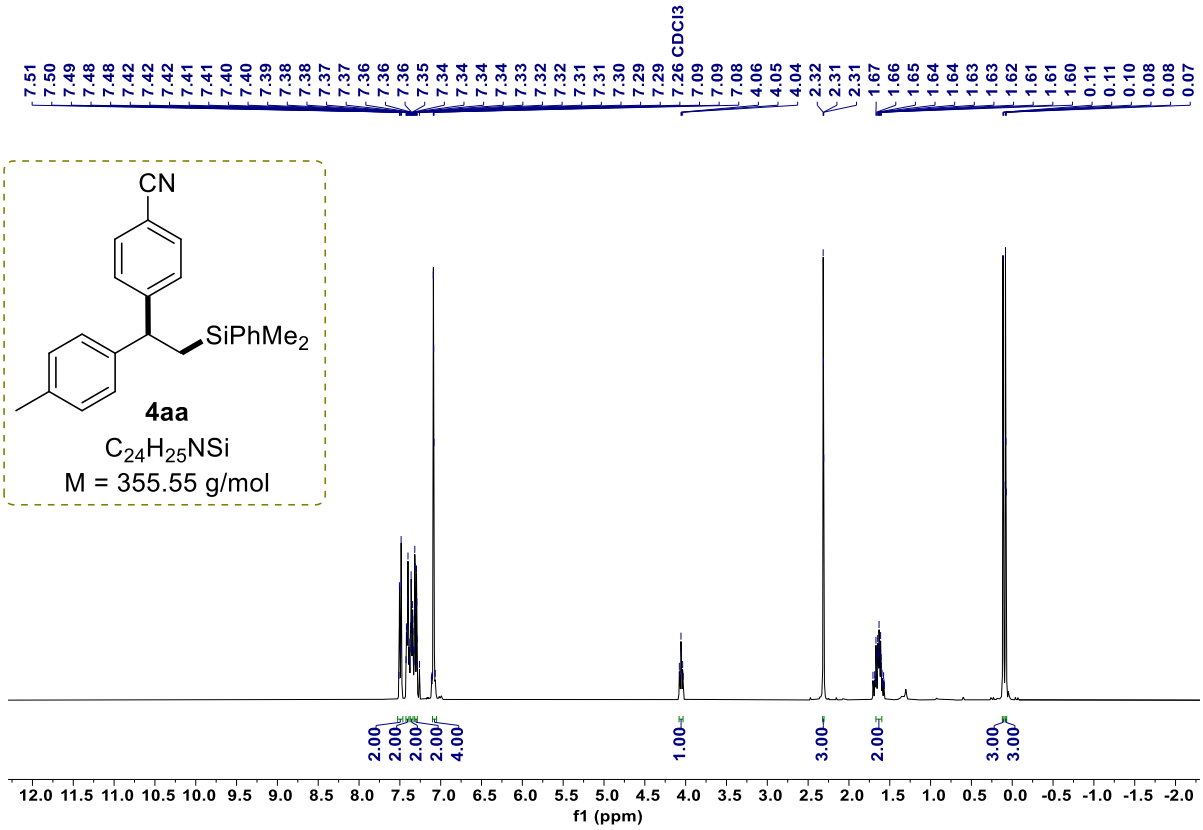
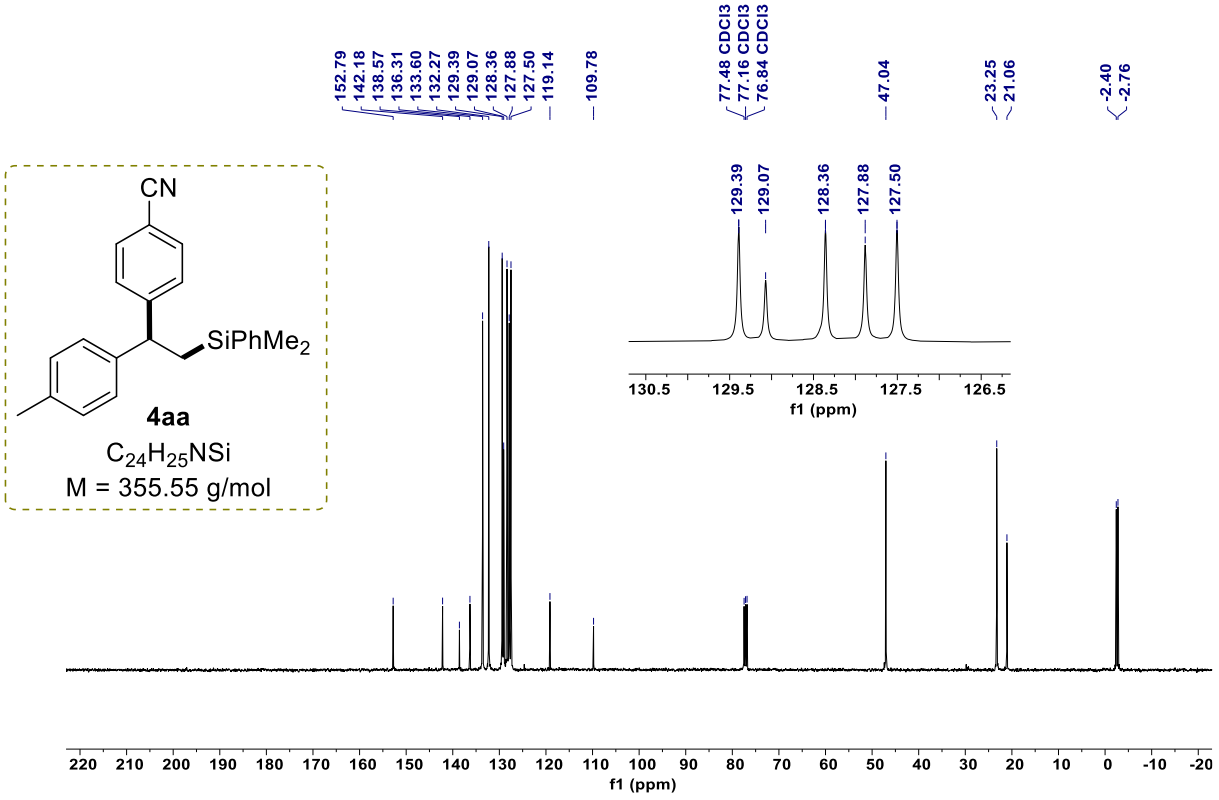


Figure S3. Optimized structures of reactants, transition states, intermediates and product for the reaction of $PhMe_2Si$ radical, styrene and 4-canopyridine radical anion (atom-atom distances in Å).

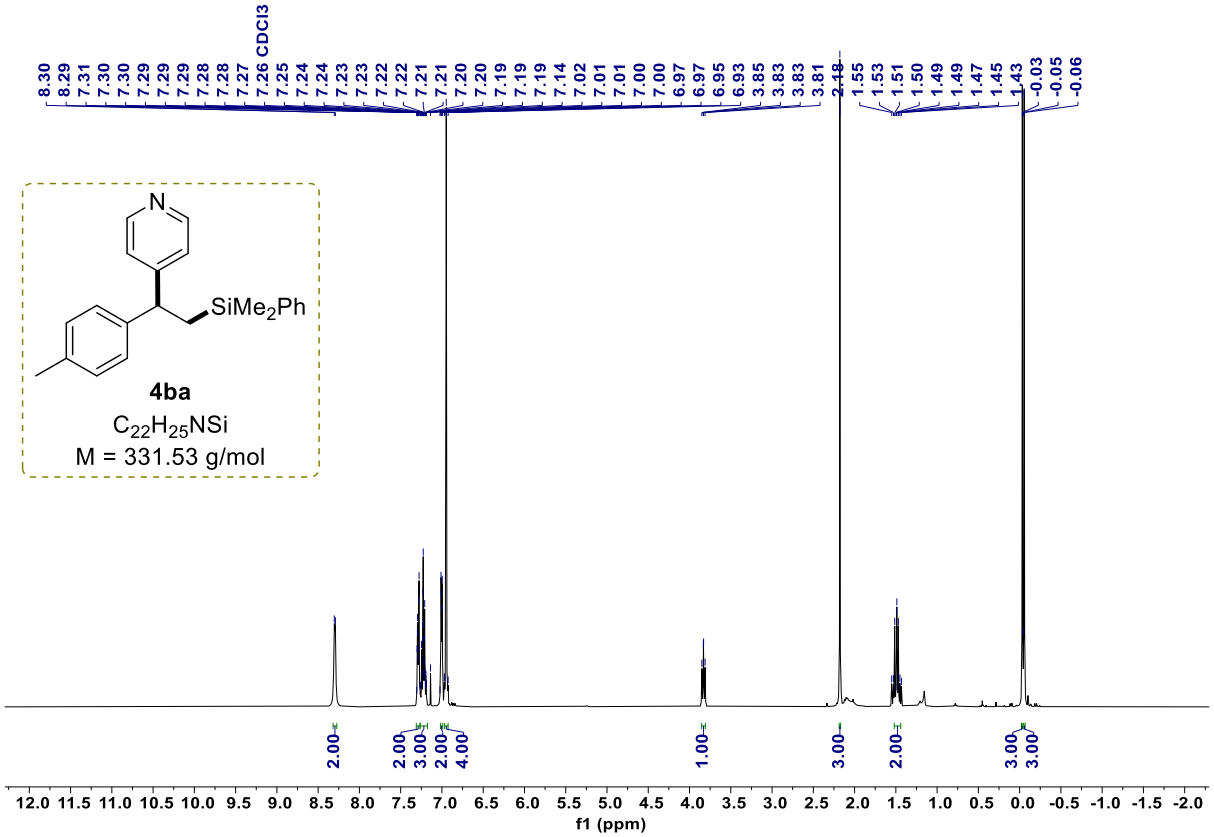
4. NMR Spectra



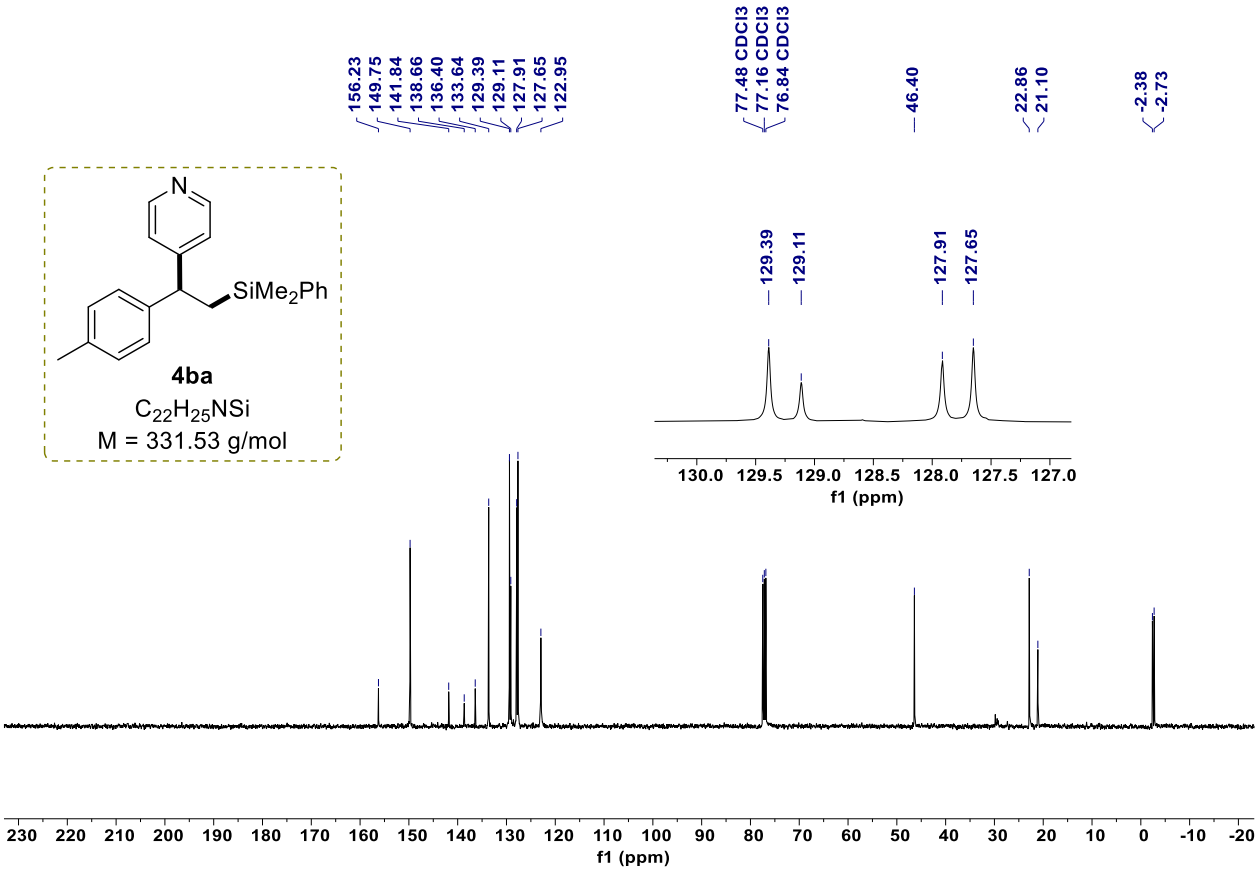
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4aa**.



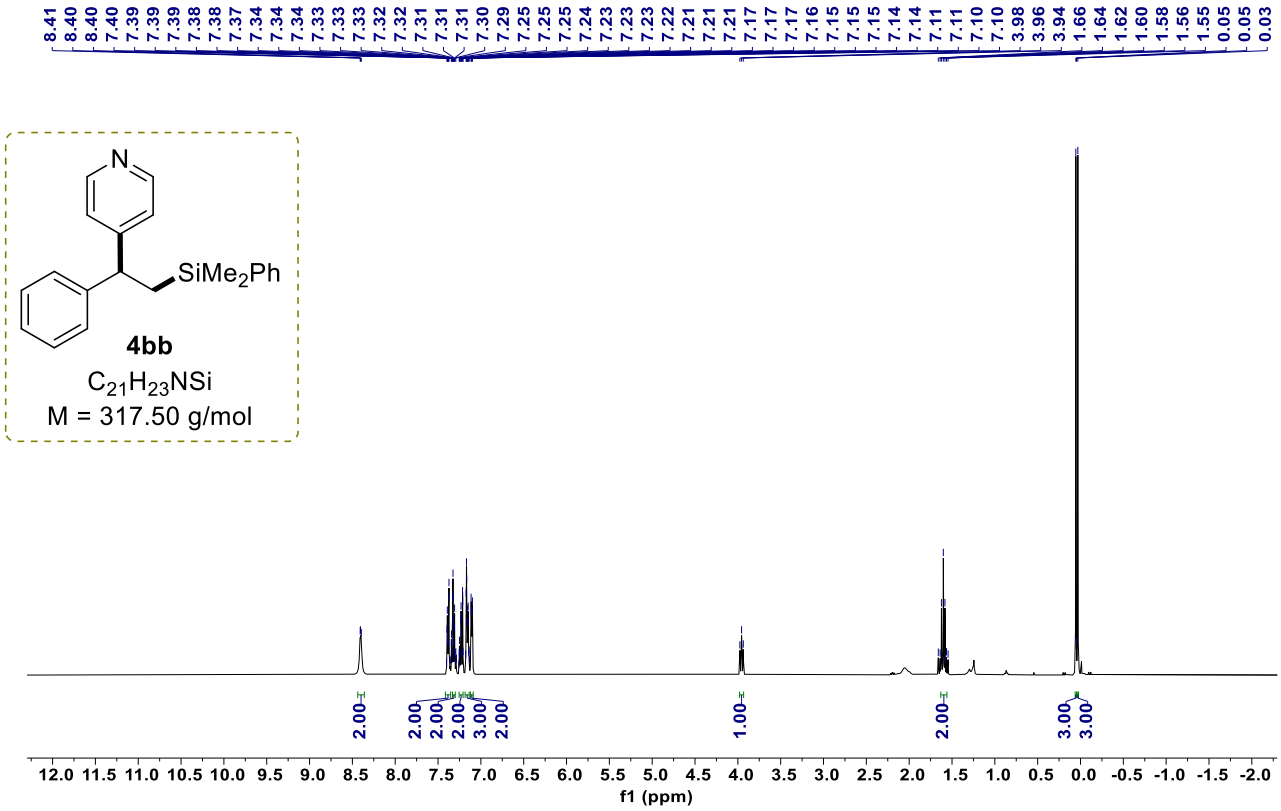
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4aa**.



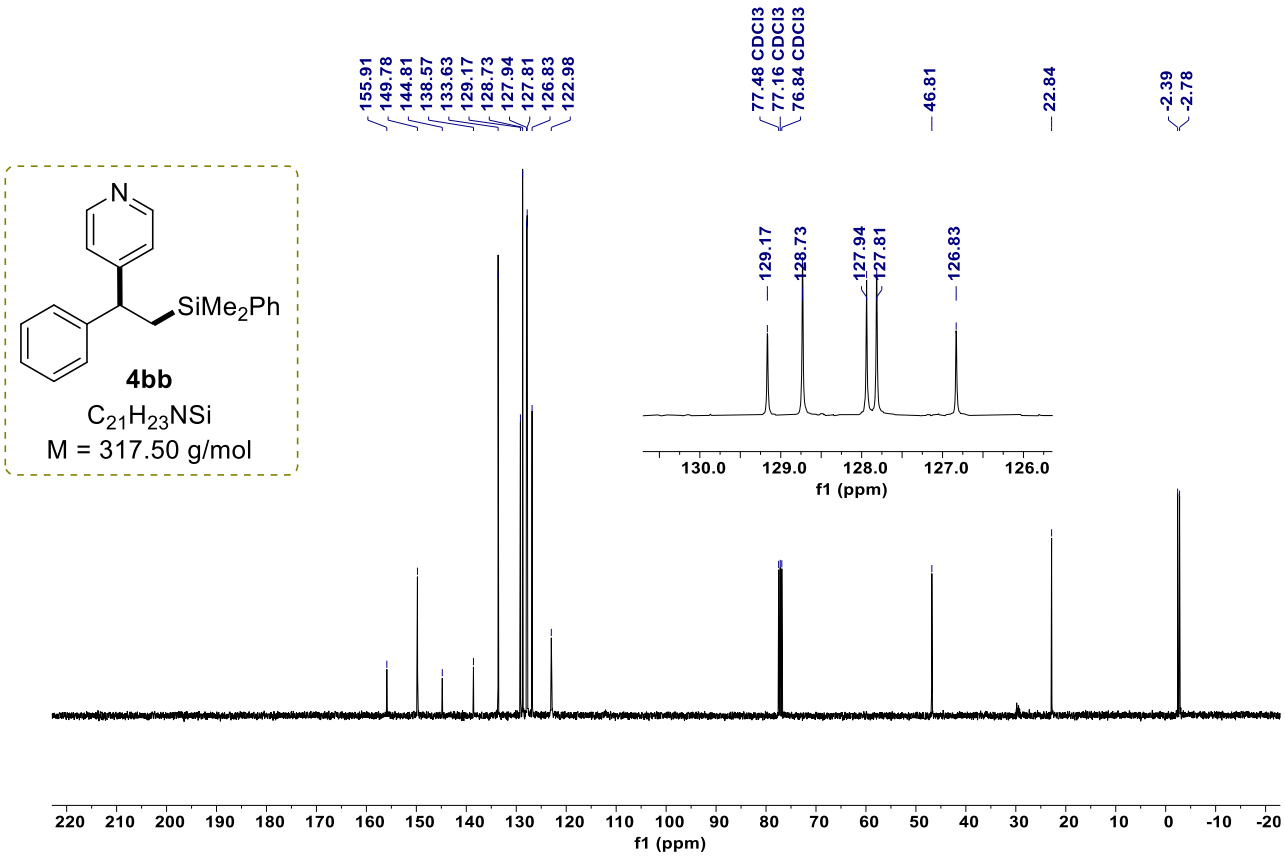
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4ba**.



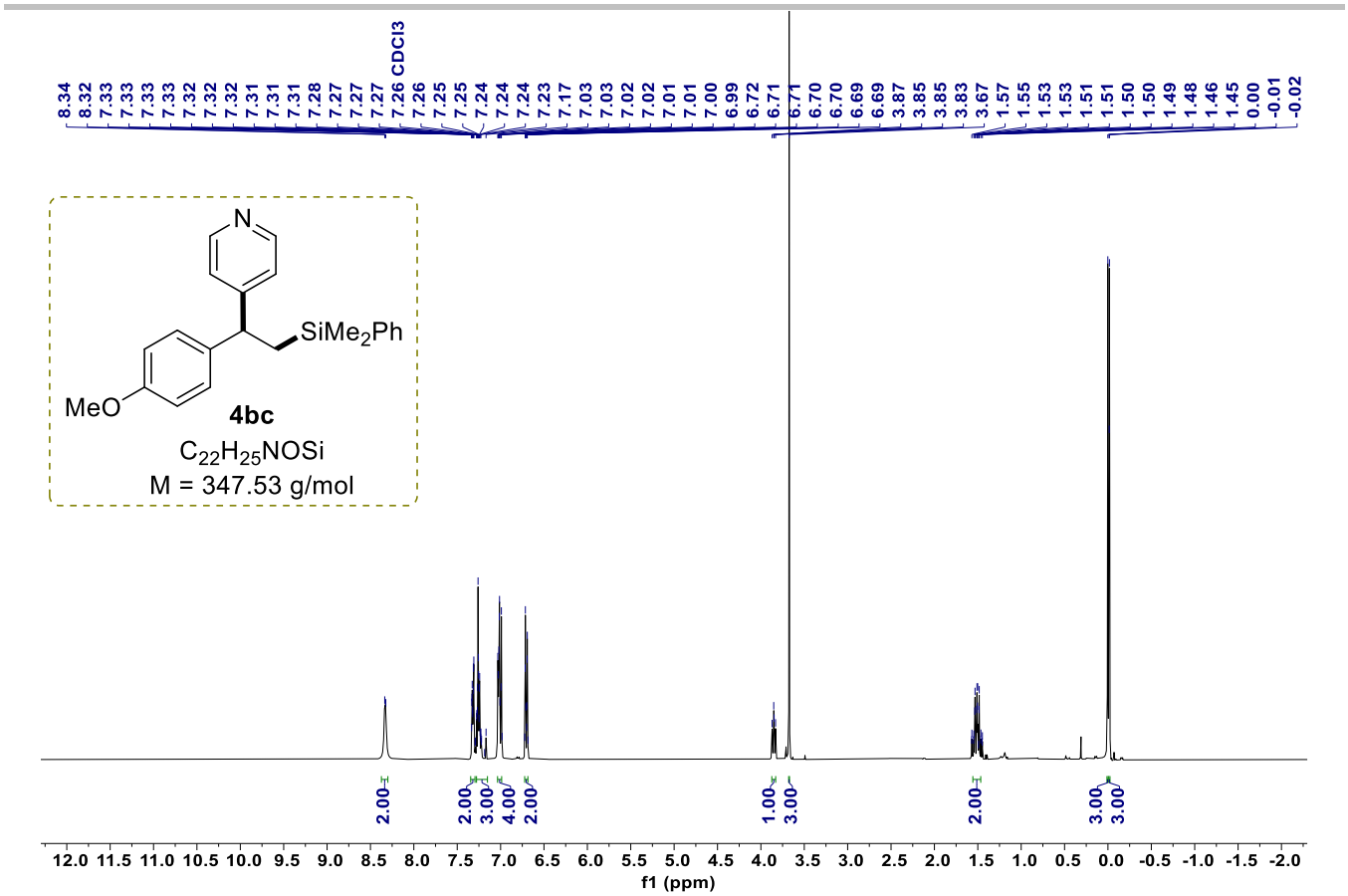
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4ba**.



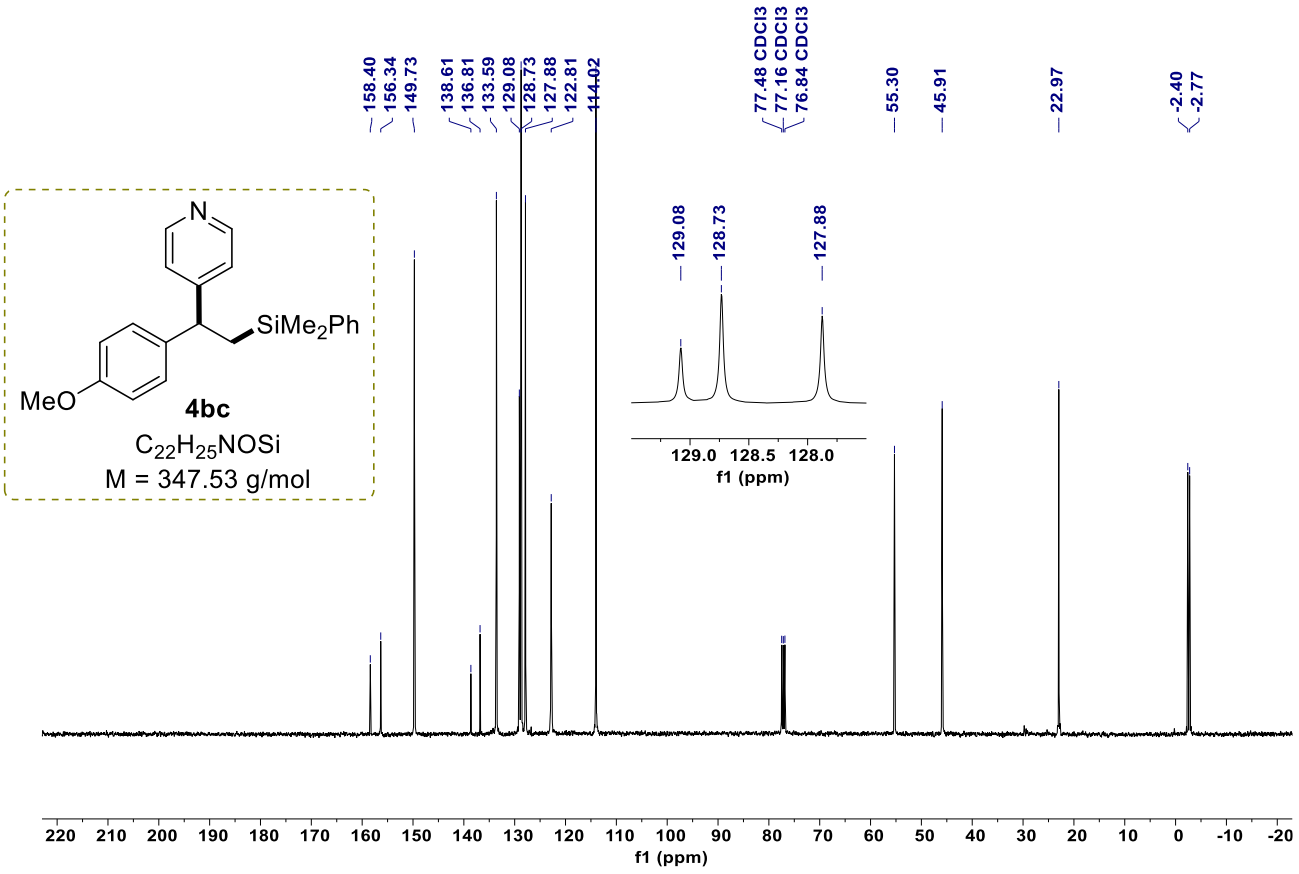
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bb**.



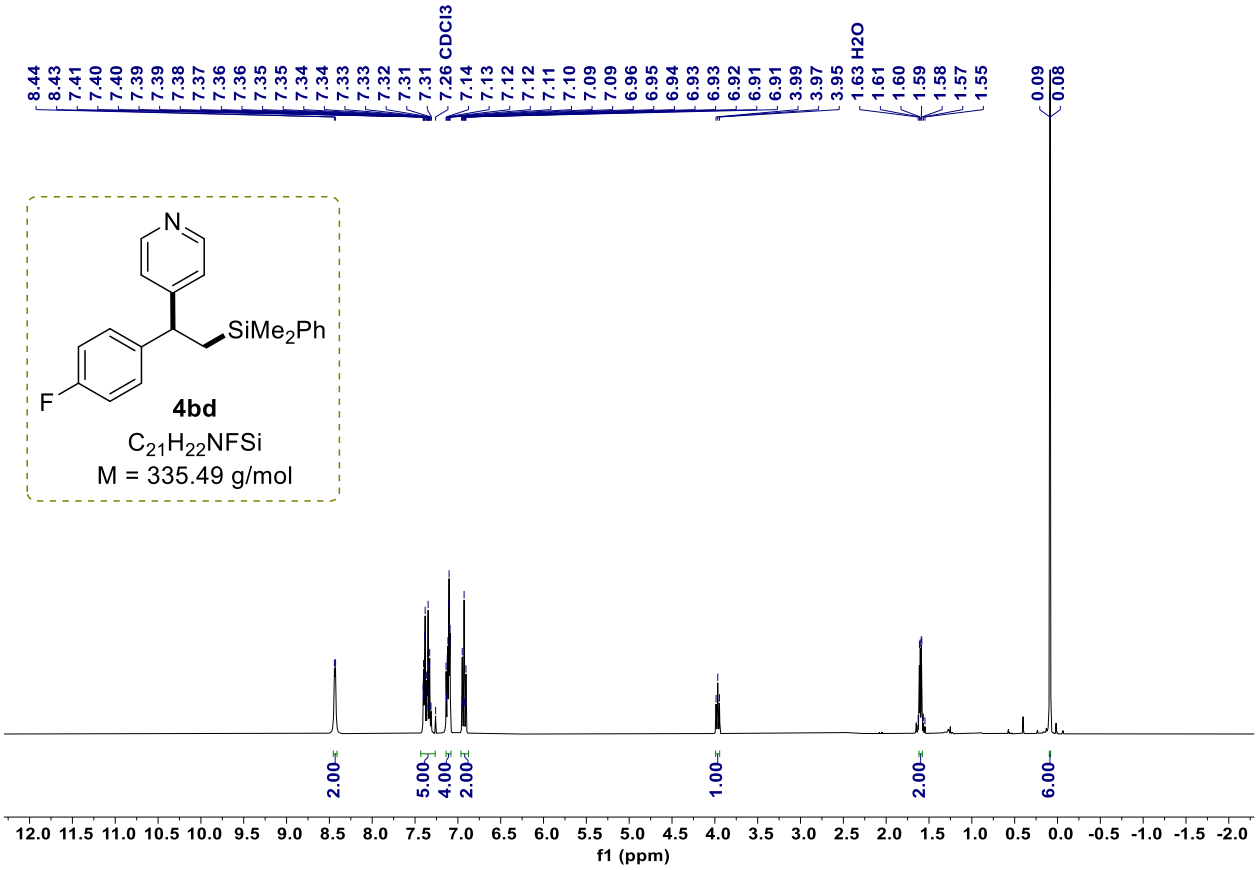
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bb**.



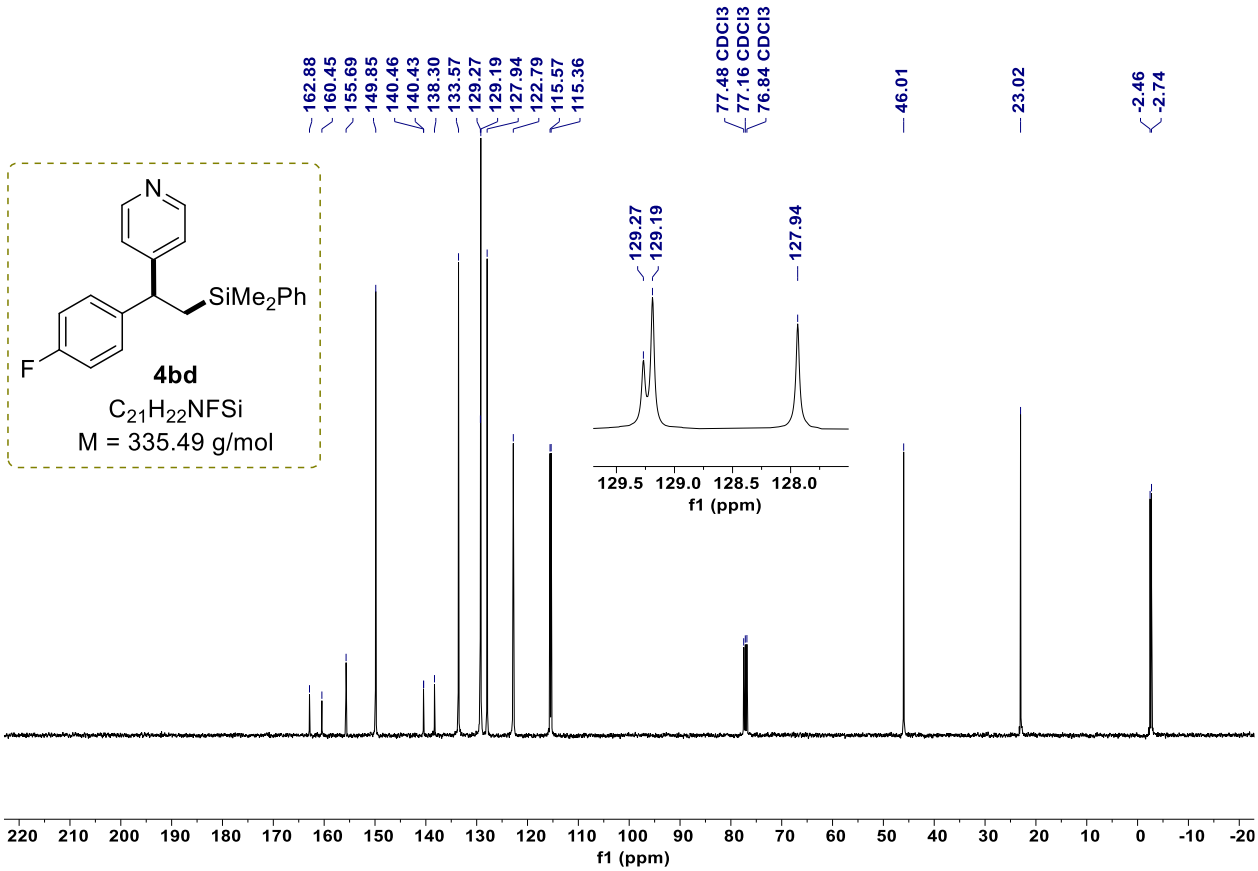
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bc**.



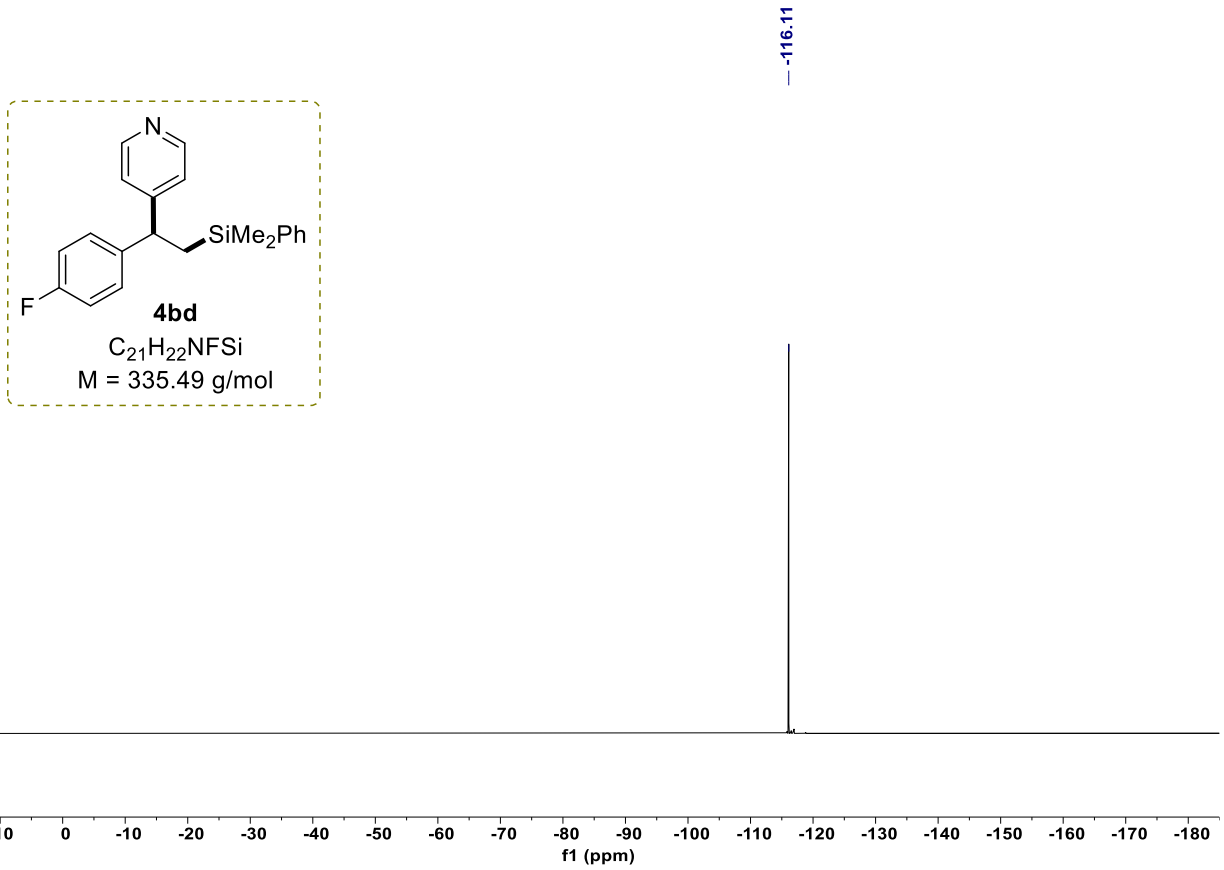
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bc**.



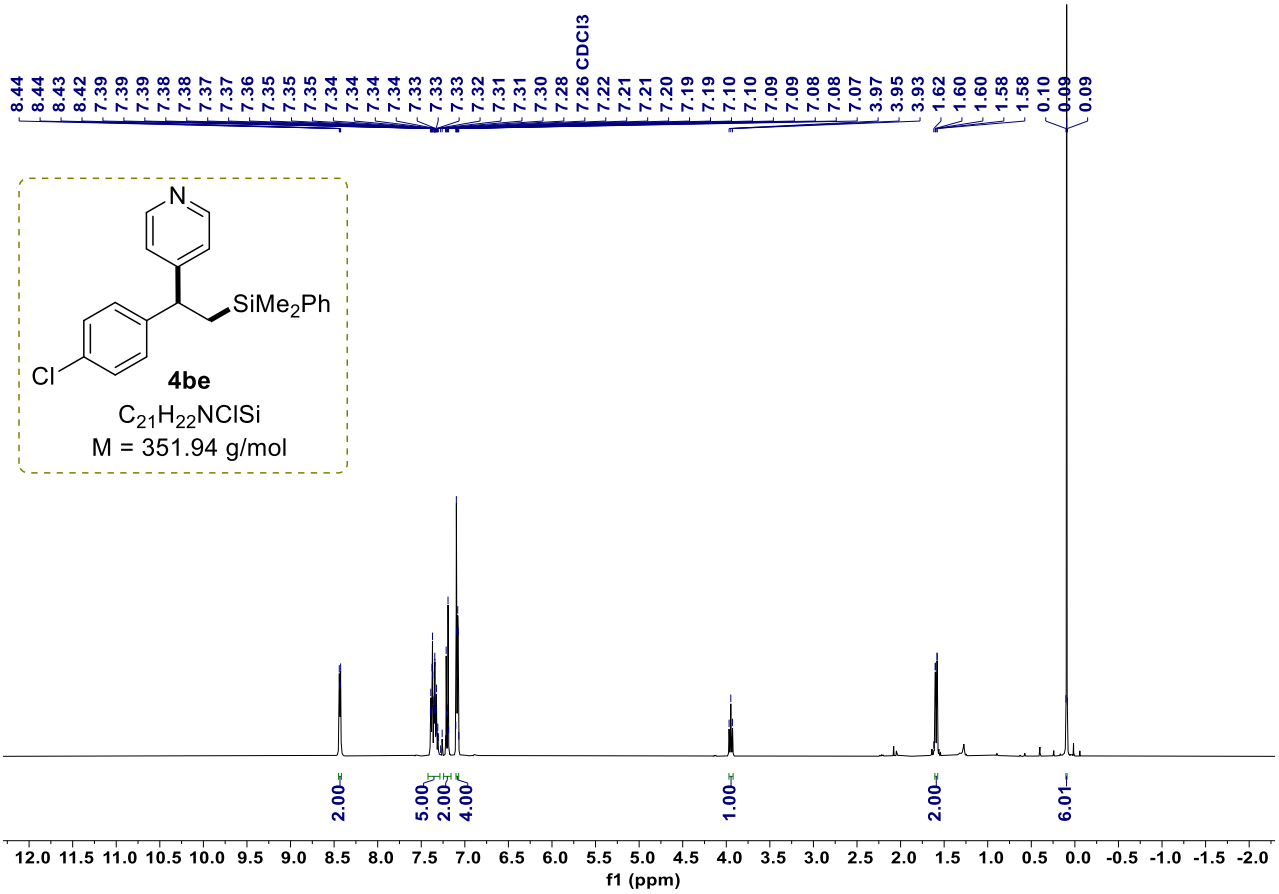
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bd**.



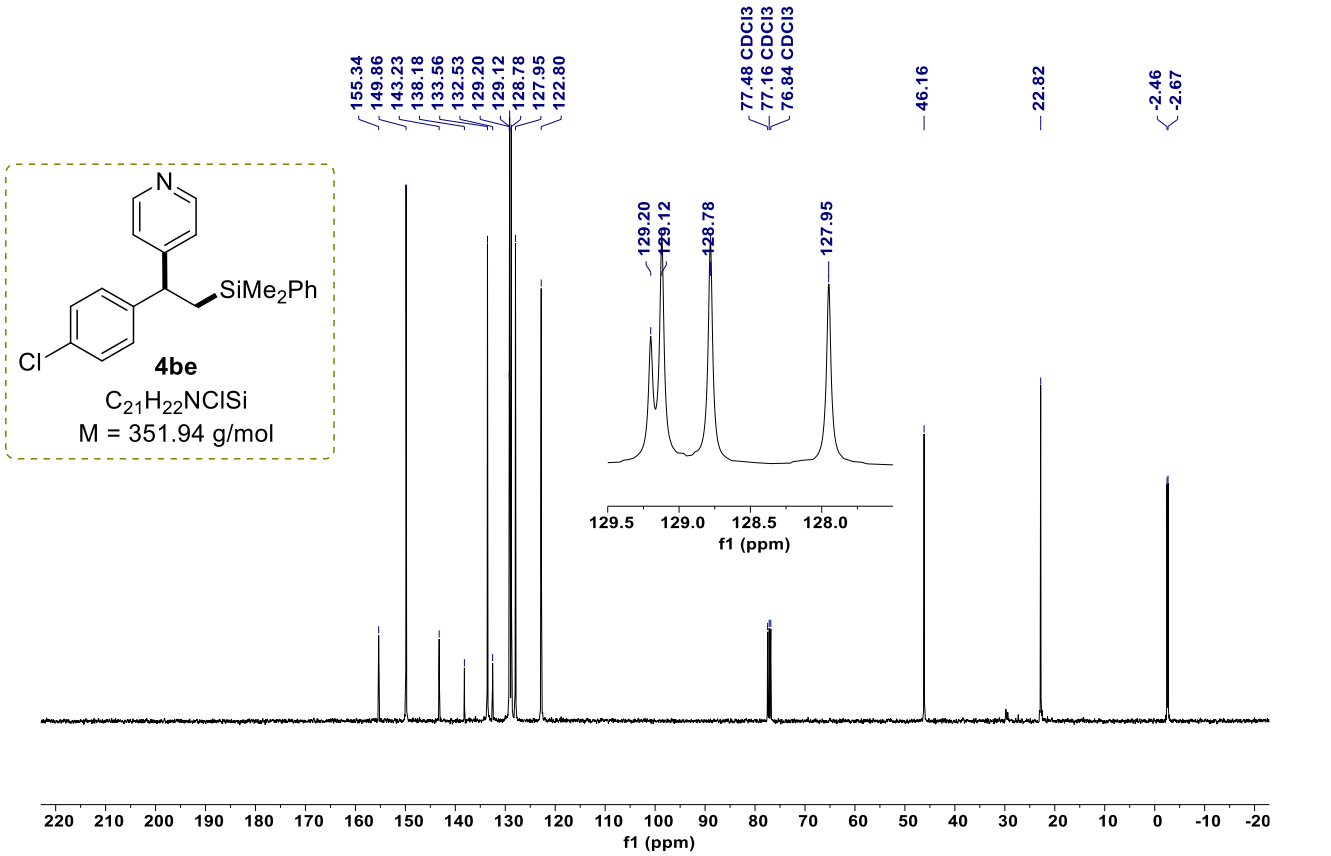
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bd**.



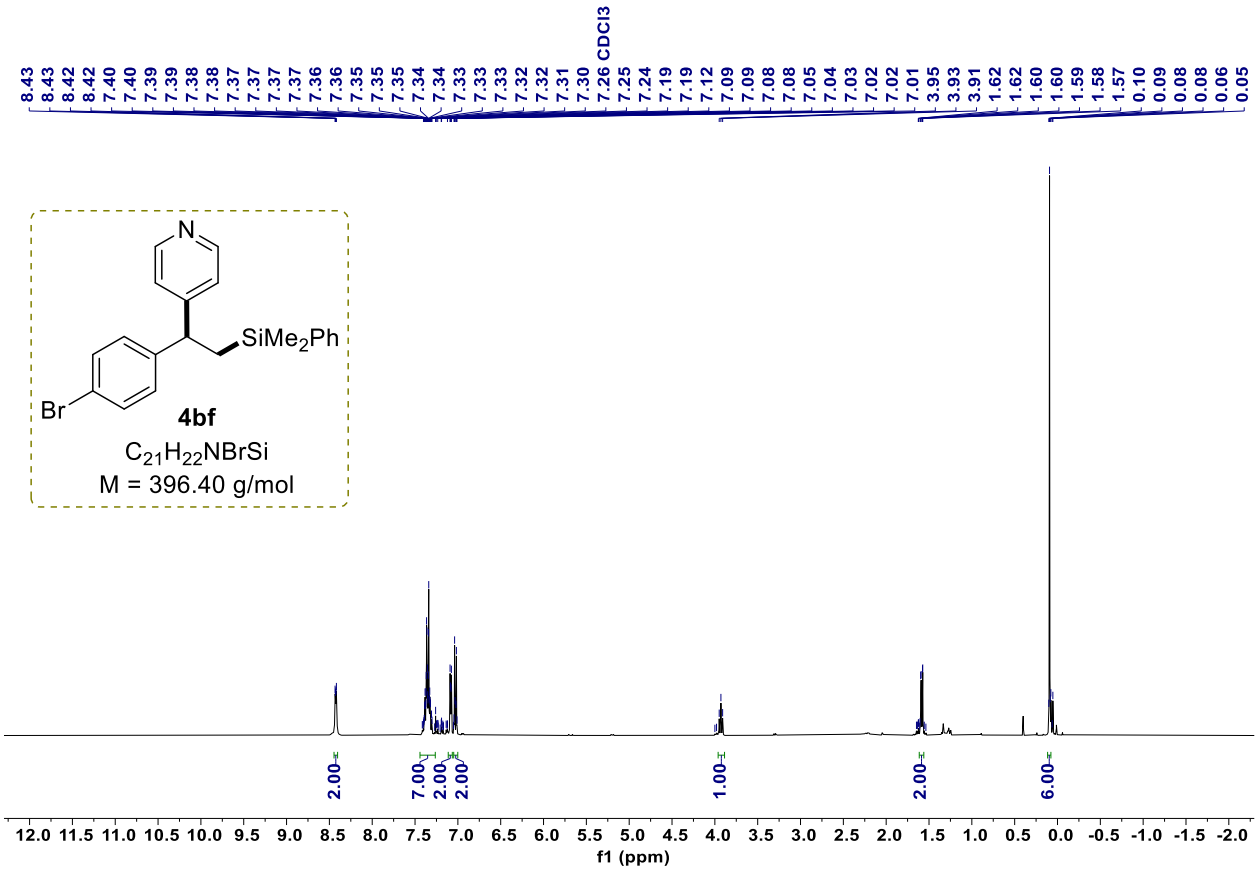
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4bd**.



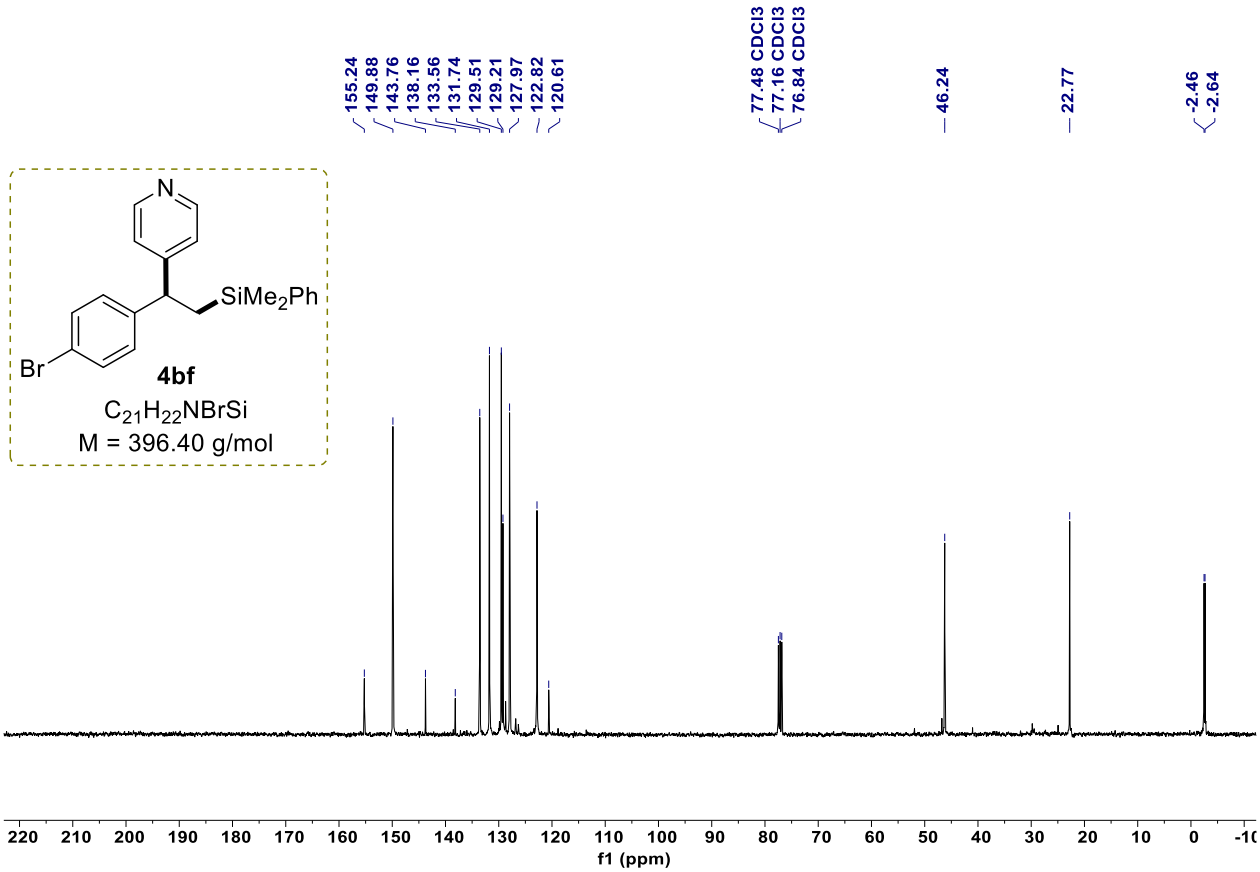
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4be**.



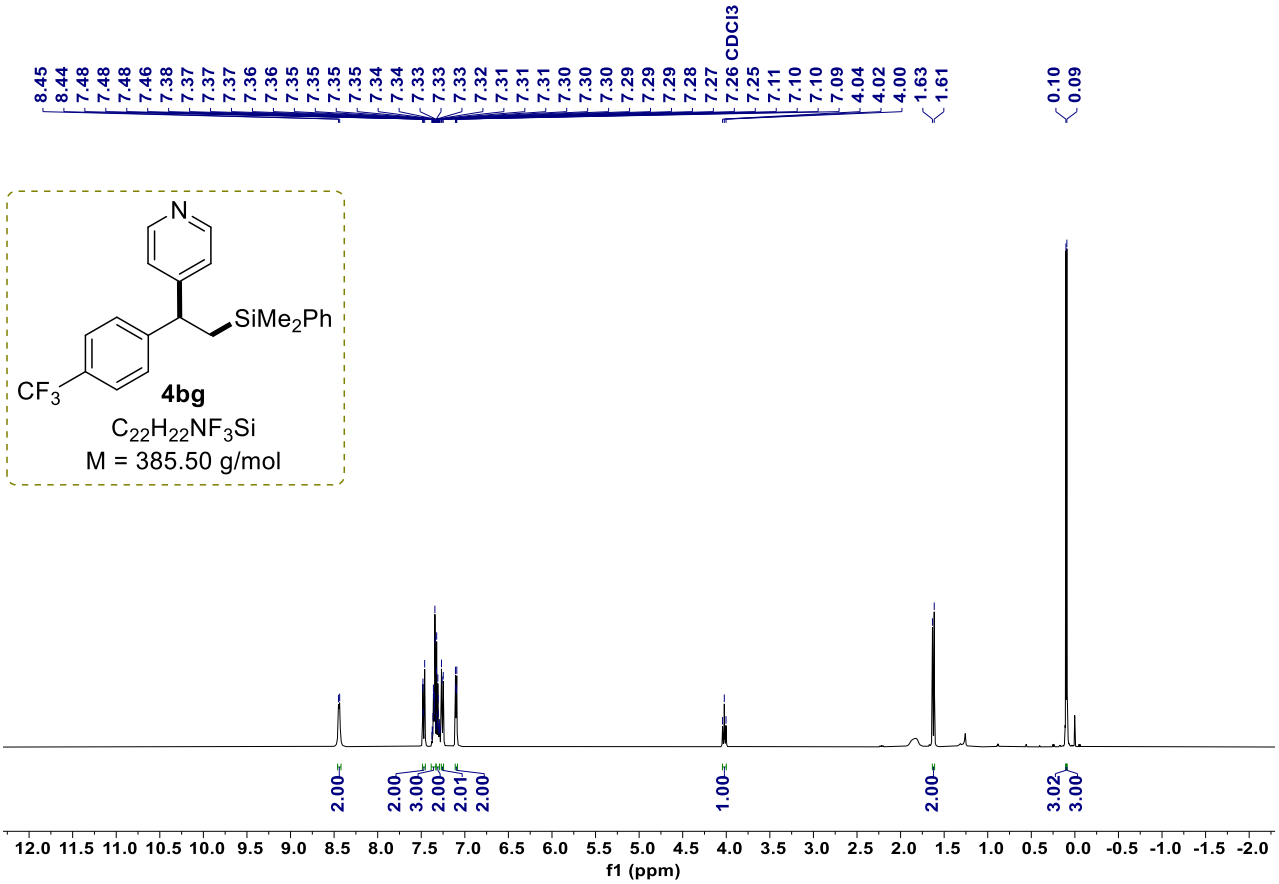
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4be**.



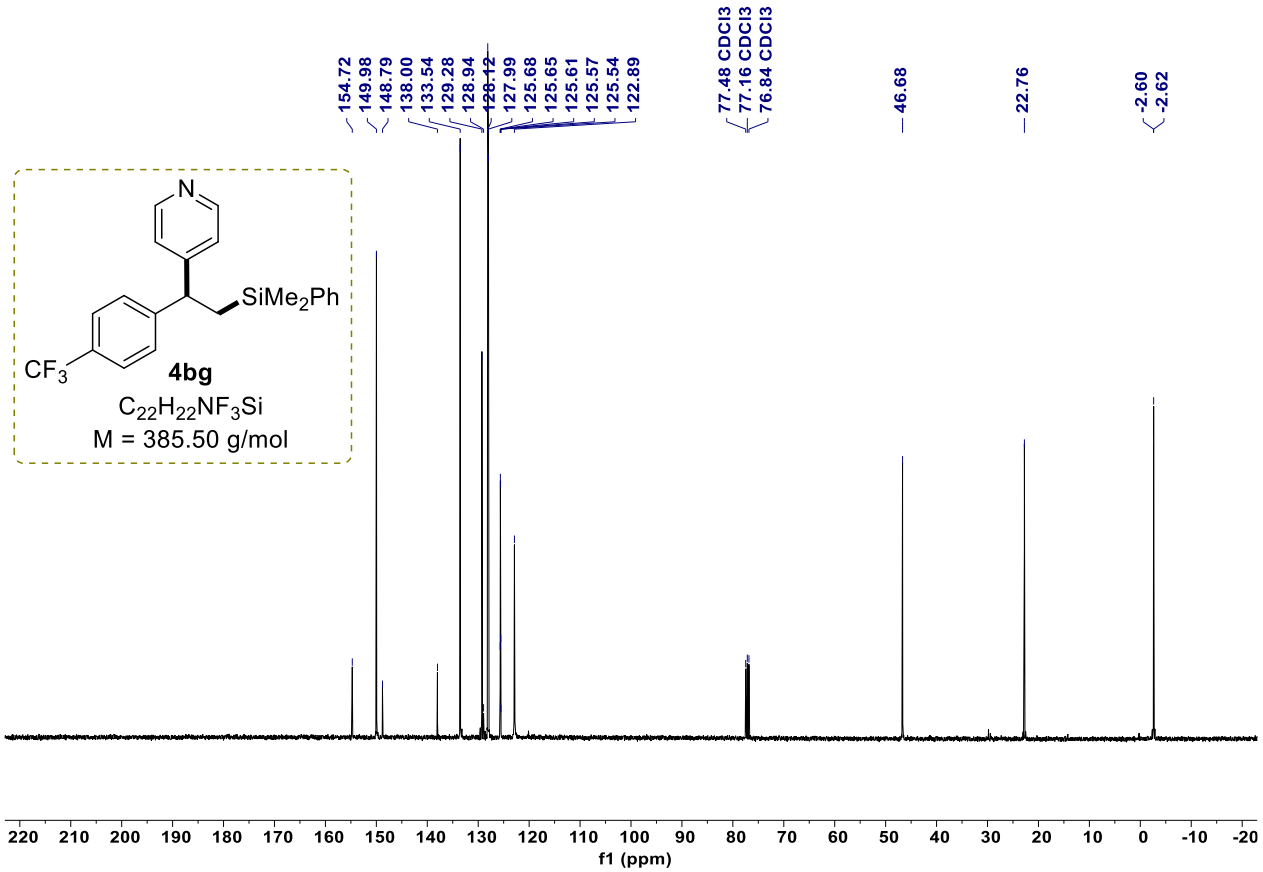
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bf**.



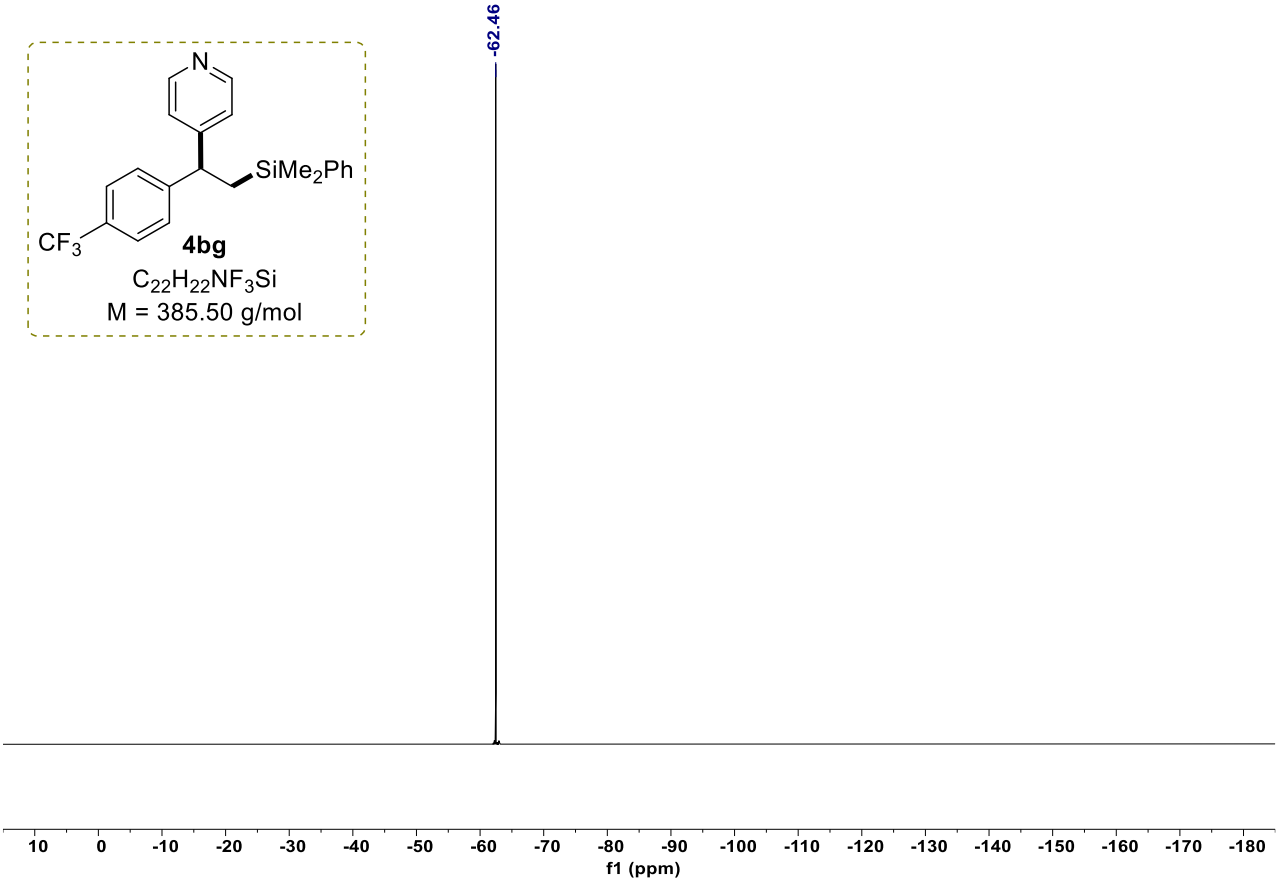
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4bf**.



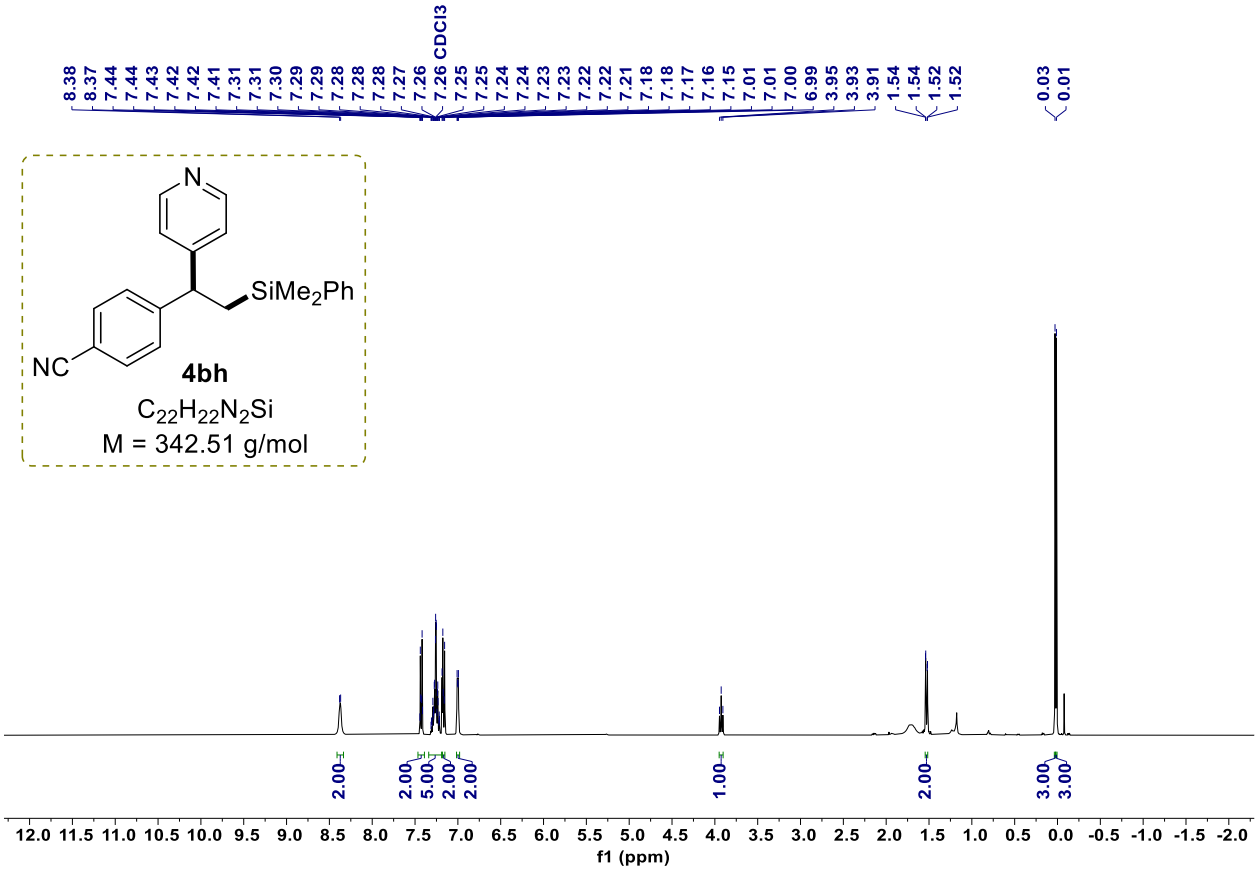
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bg**.



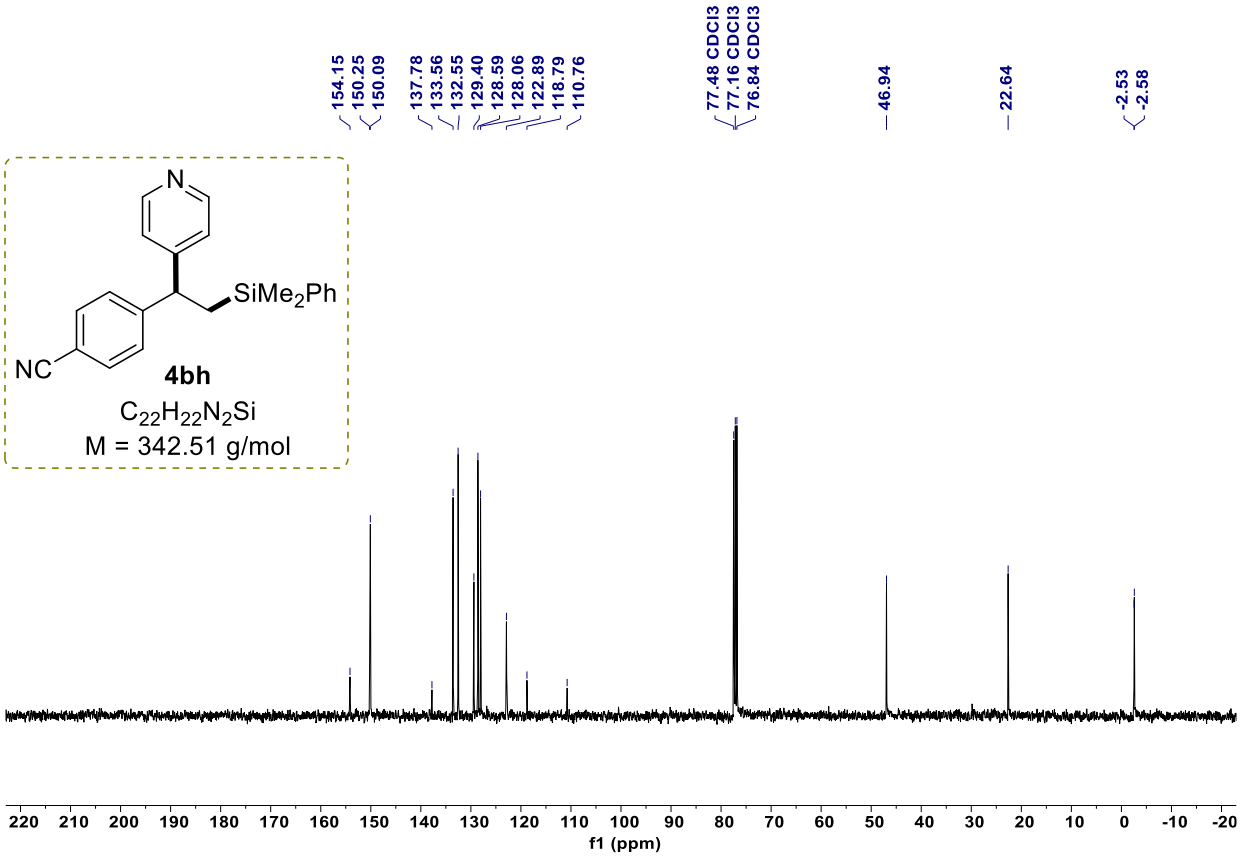
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4bg**.



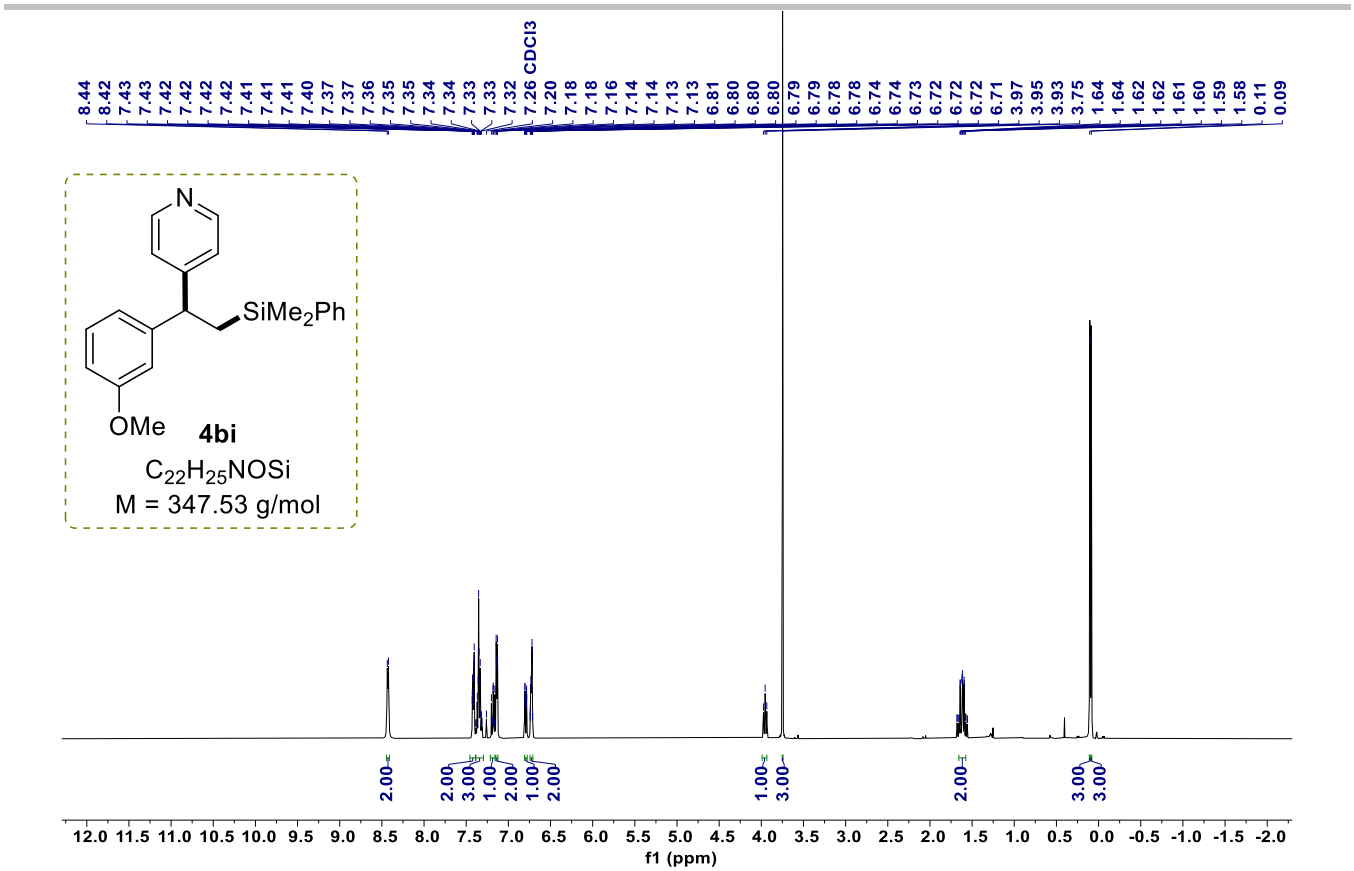
^{19}F NMR (376 MHz, $CDCl_3$) of compound **4bg**.



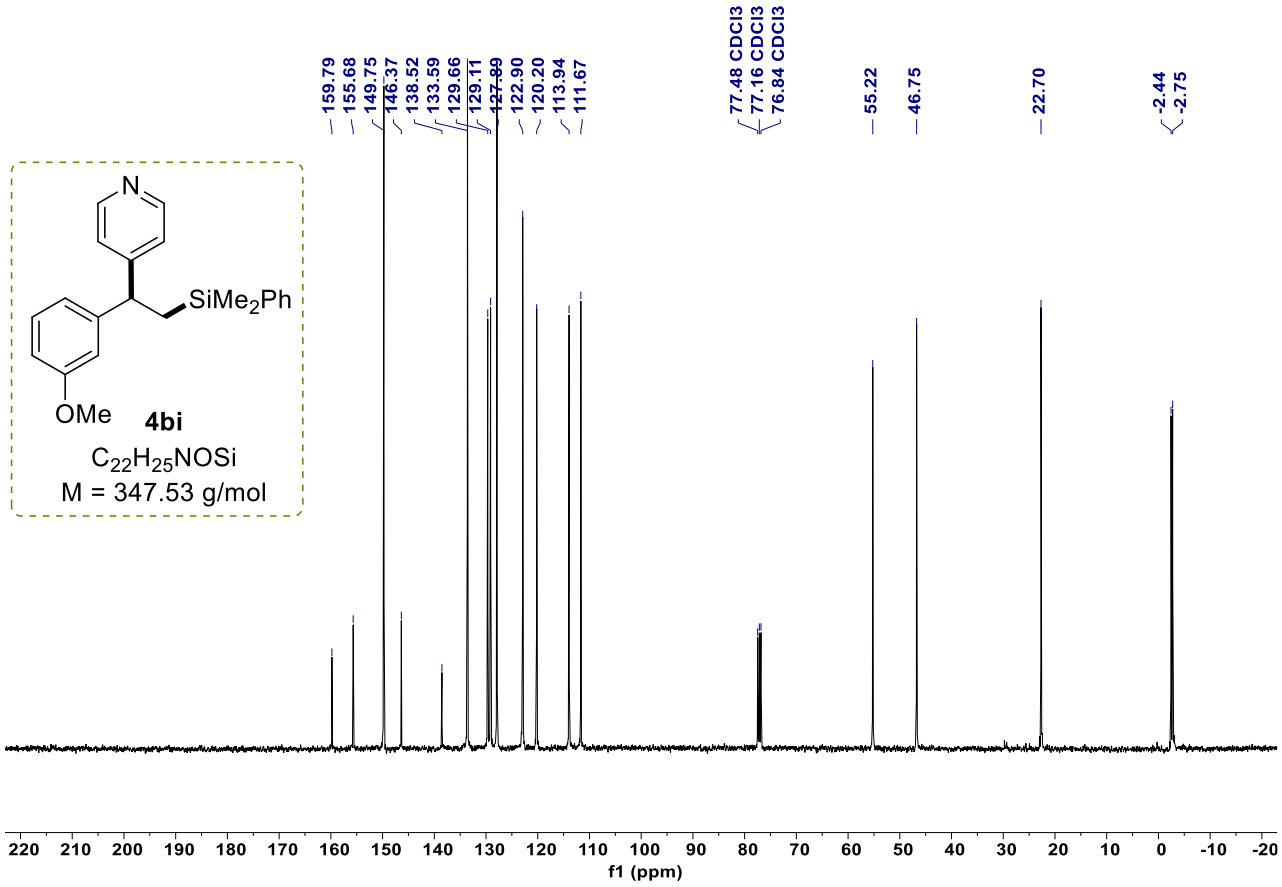
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bh**.



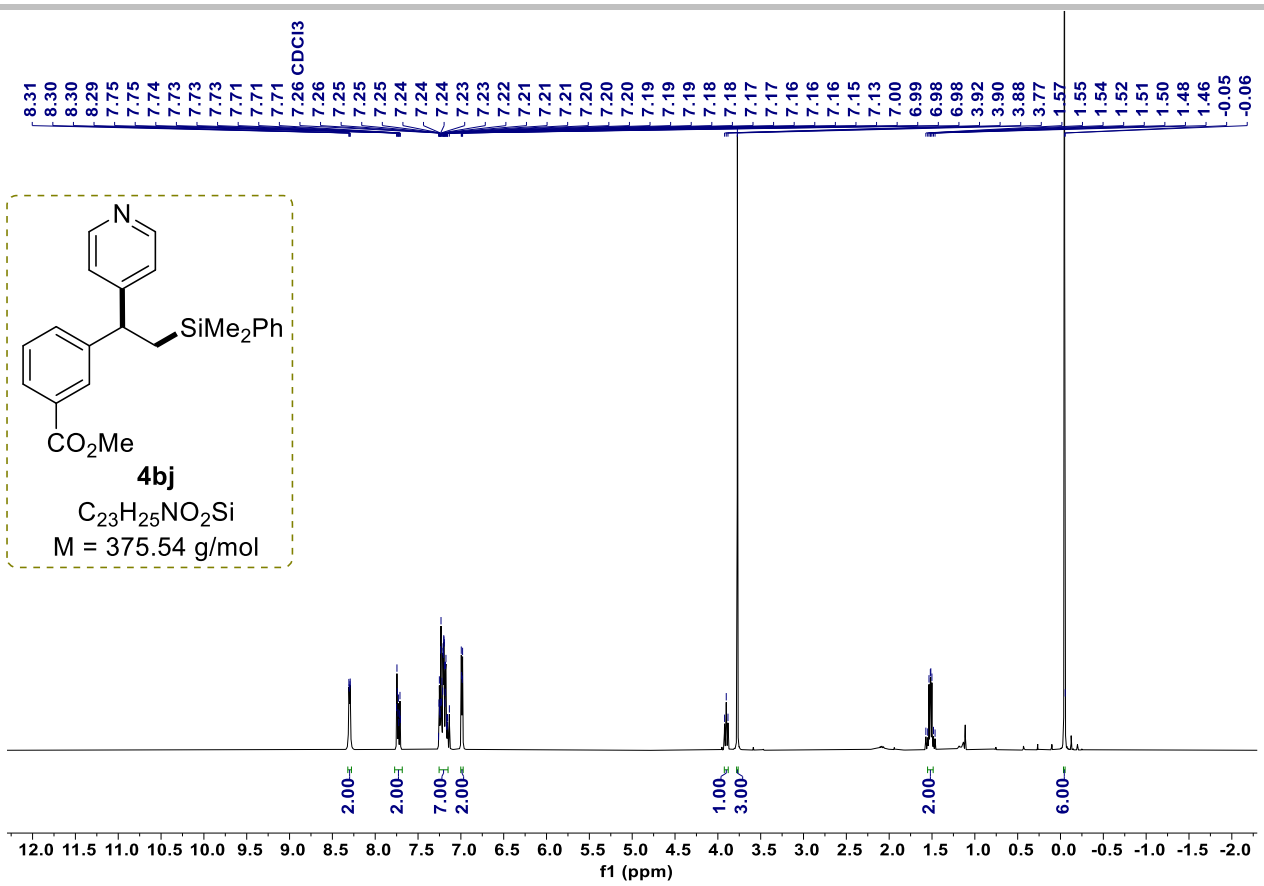
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bh**.



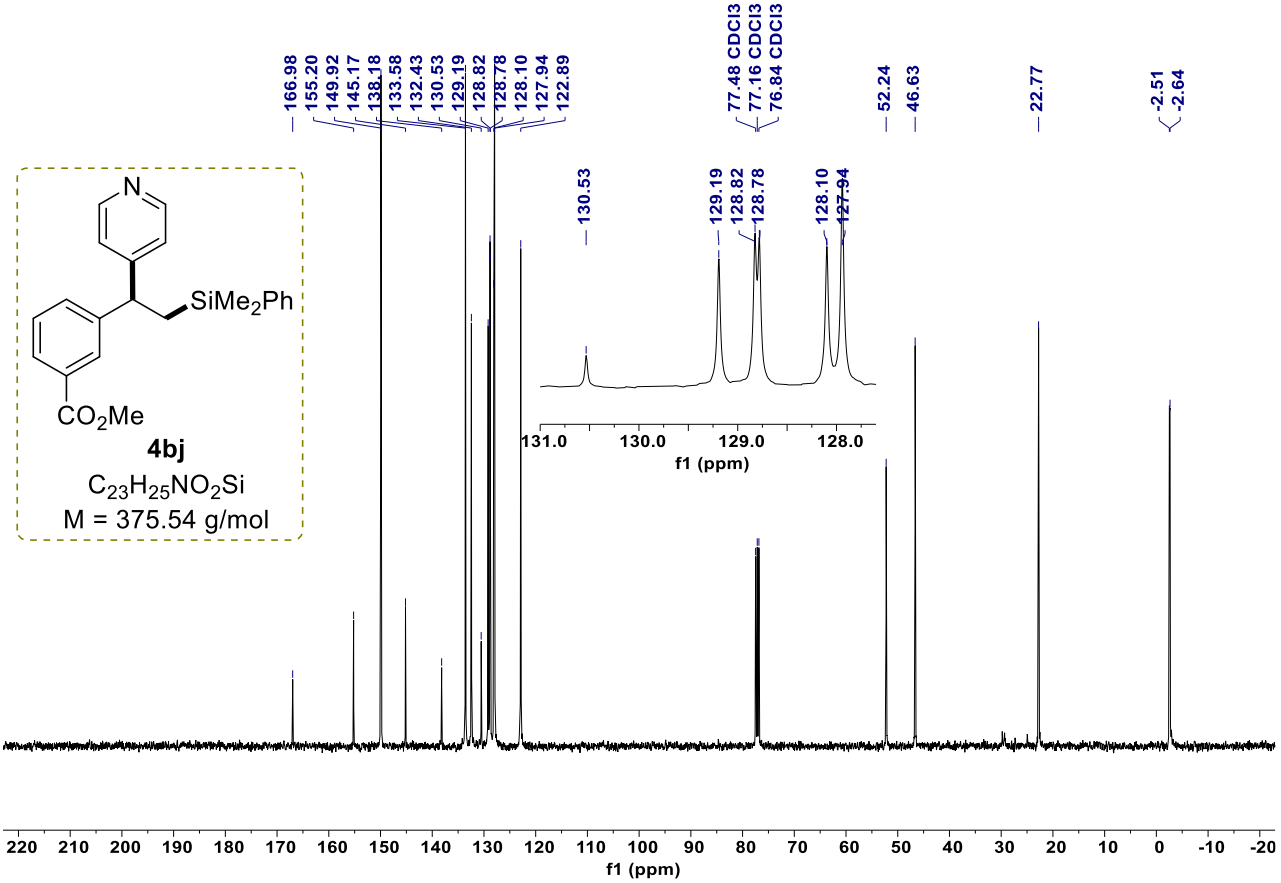
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bi**.



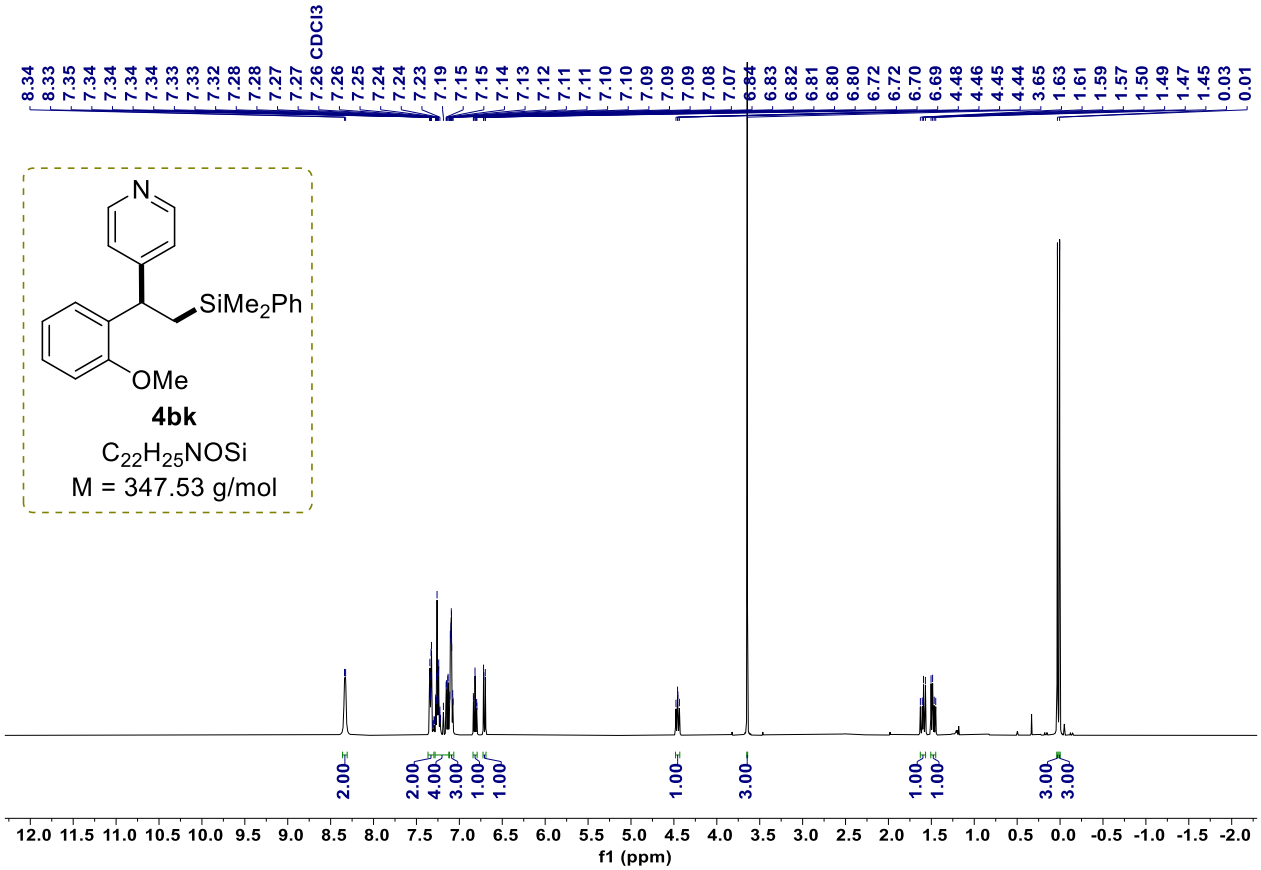
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bi**.



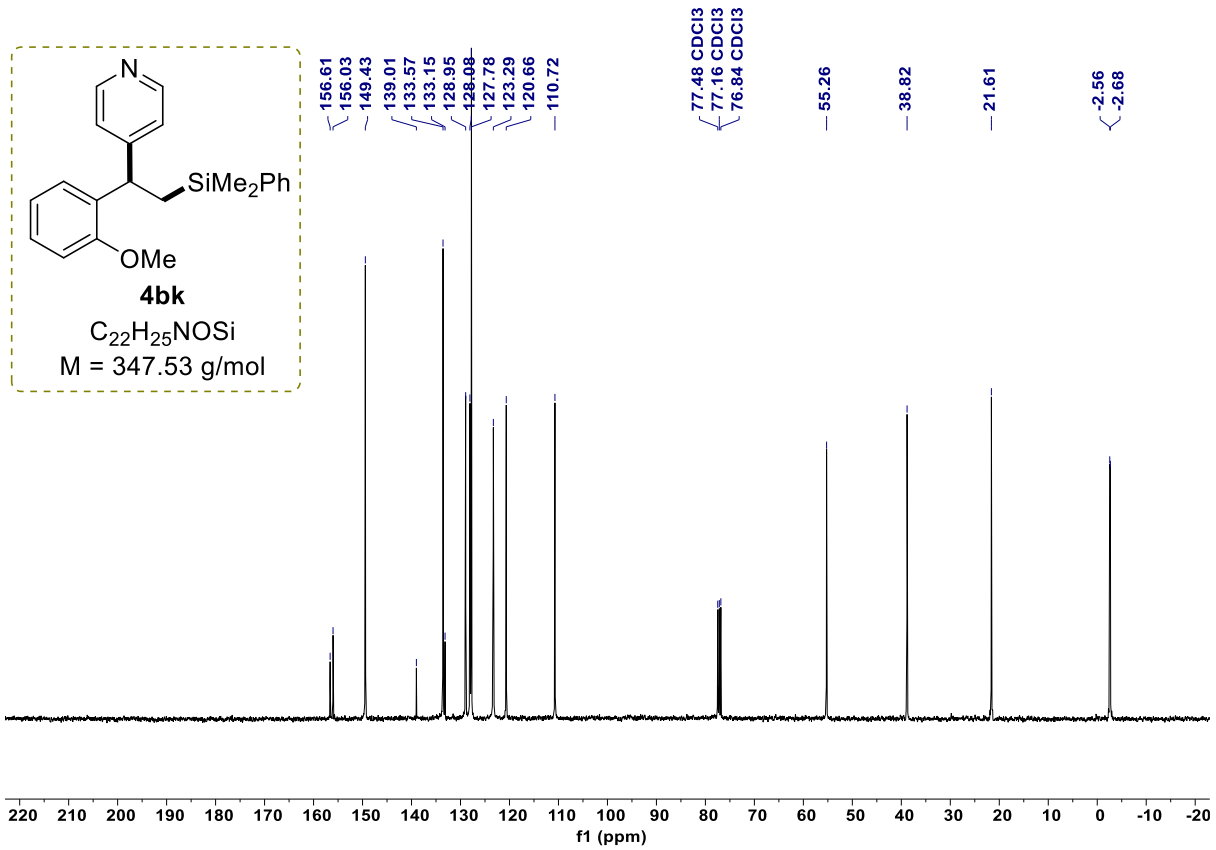
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bj**.



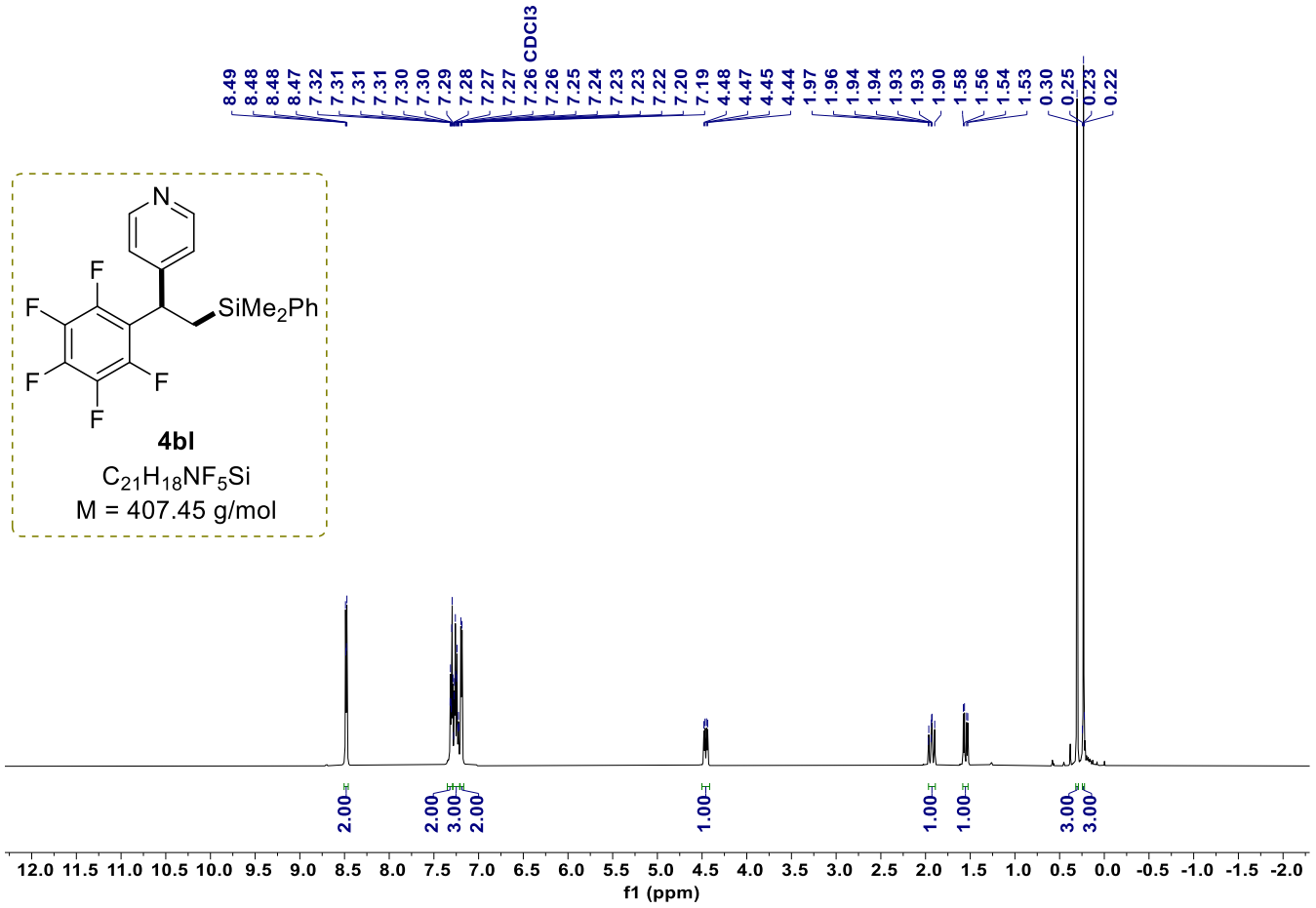
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bj**.



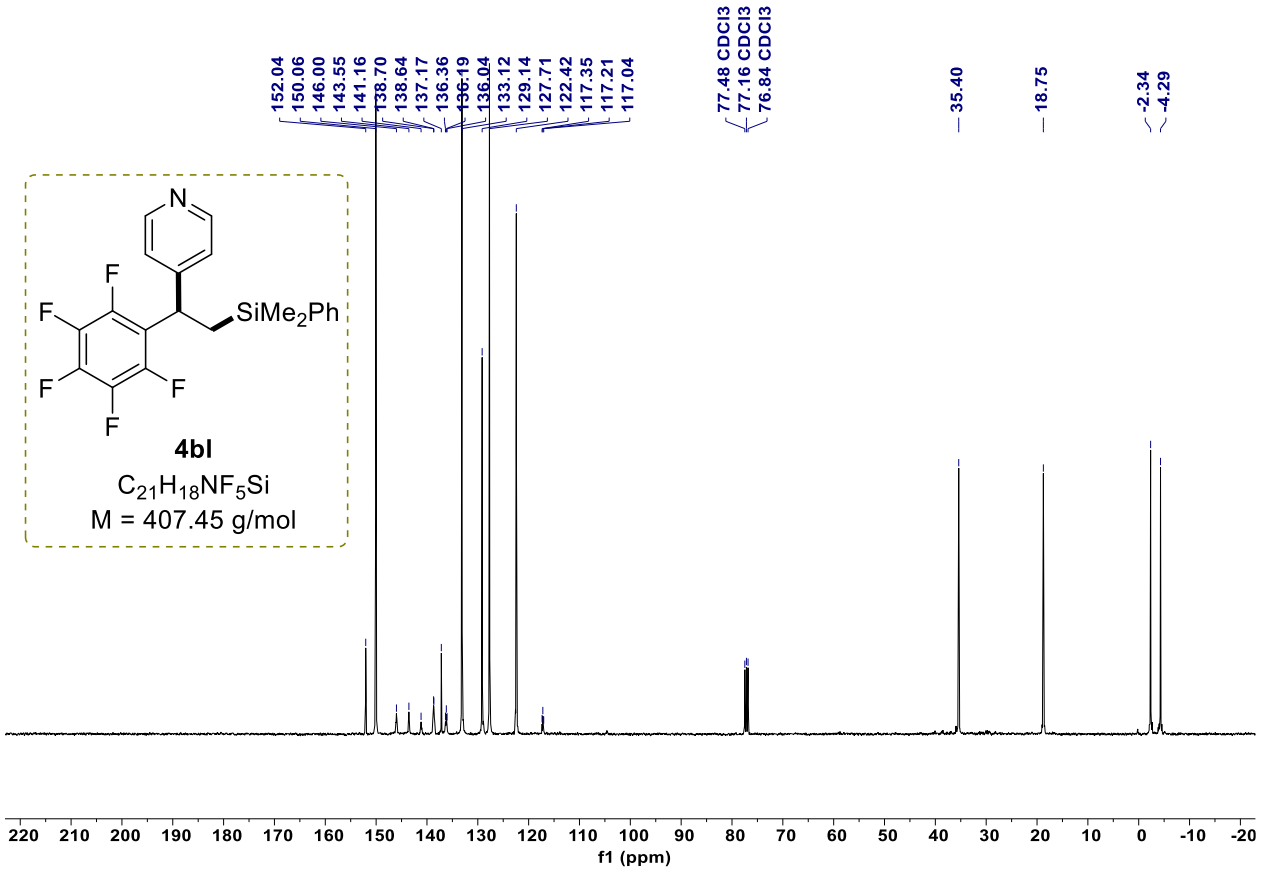
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bk**.



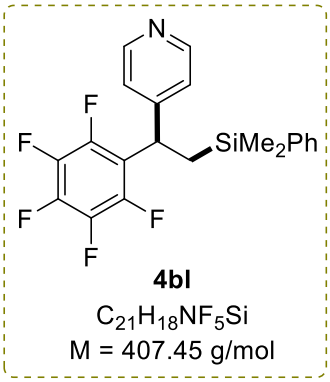
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bk**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bl**.



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bl**.

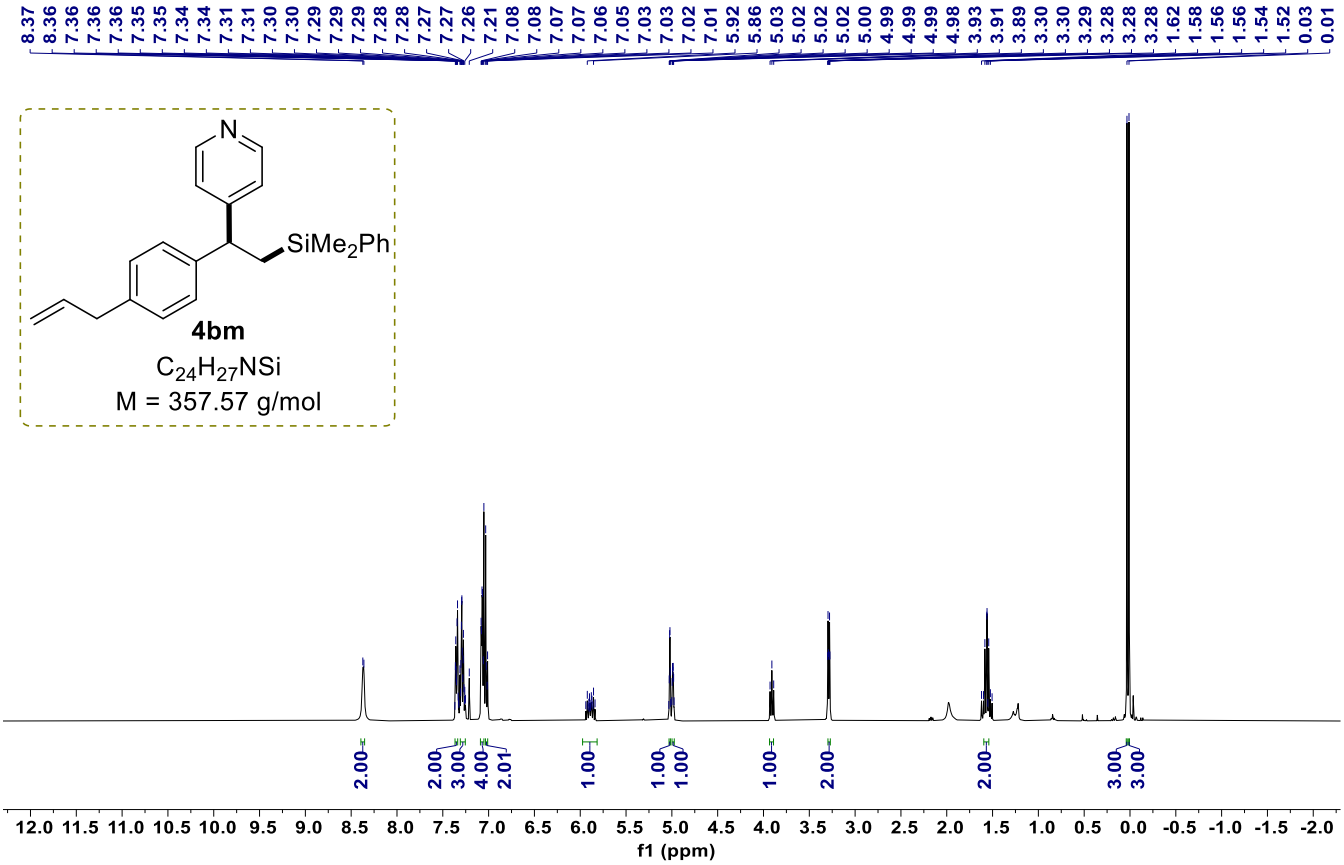


4bl

$C_{21}H_{18}NF_5Si$

M = 407.45 g/mol

^{19}F NMR (376 MHz, $CDCl_3$) of compound **4bl**.

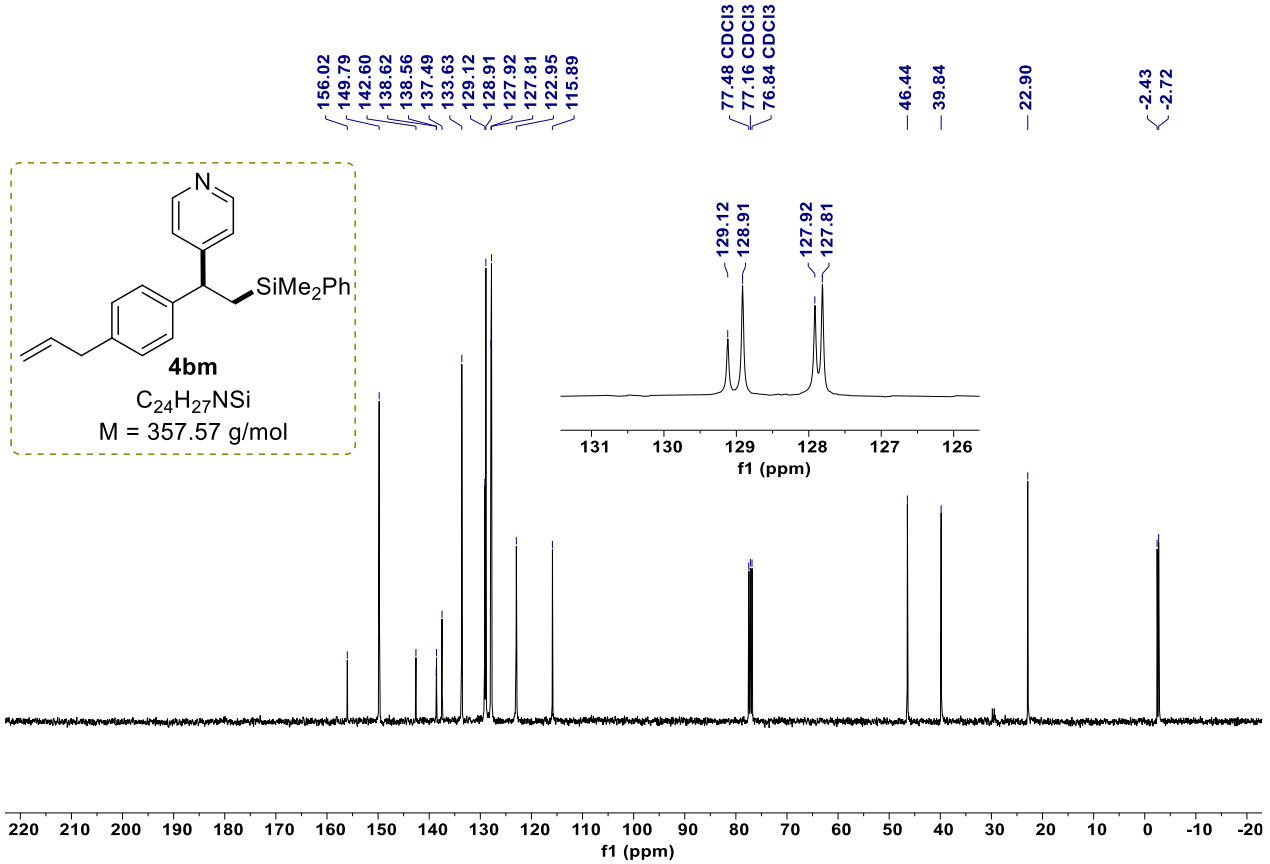


4bm

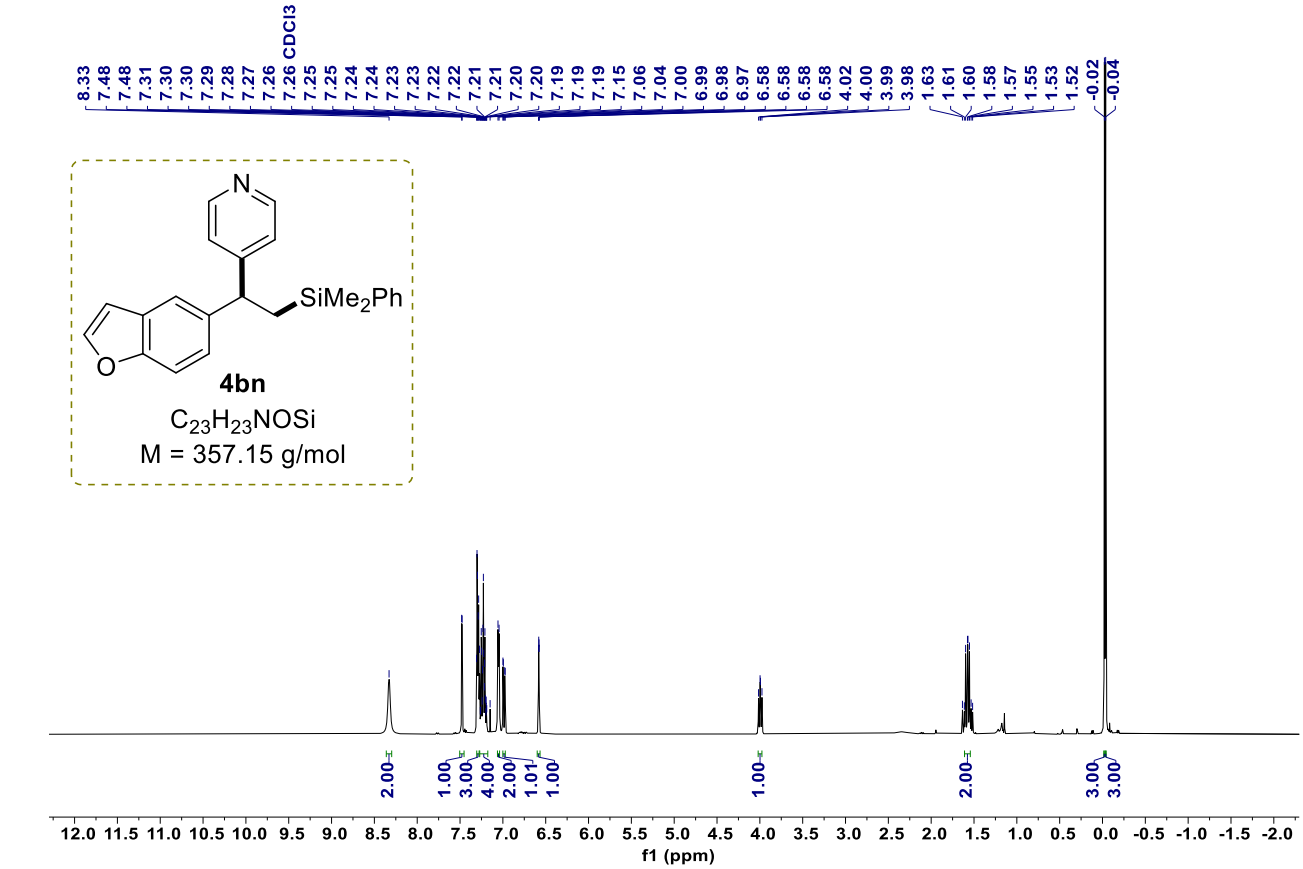
$C_{24}H_{27}NSi$

M = 357.57 g/mol

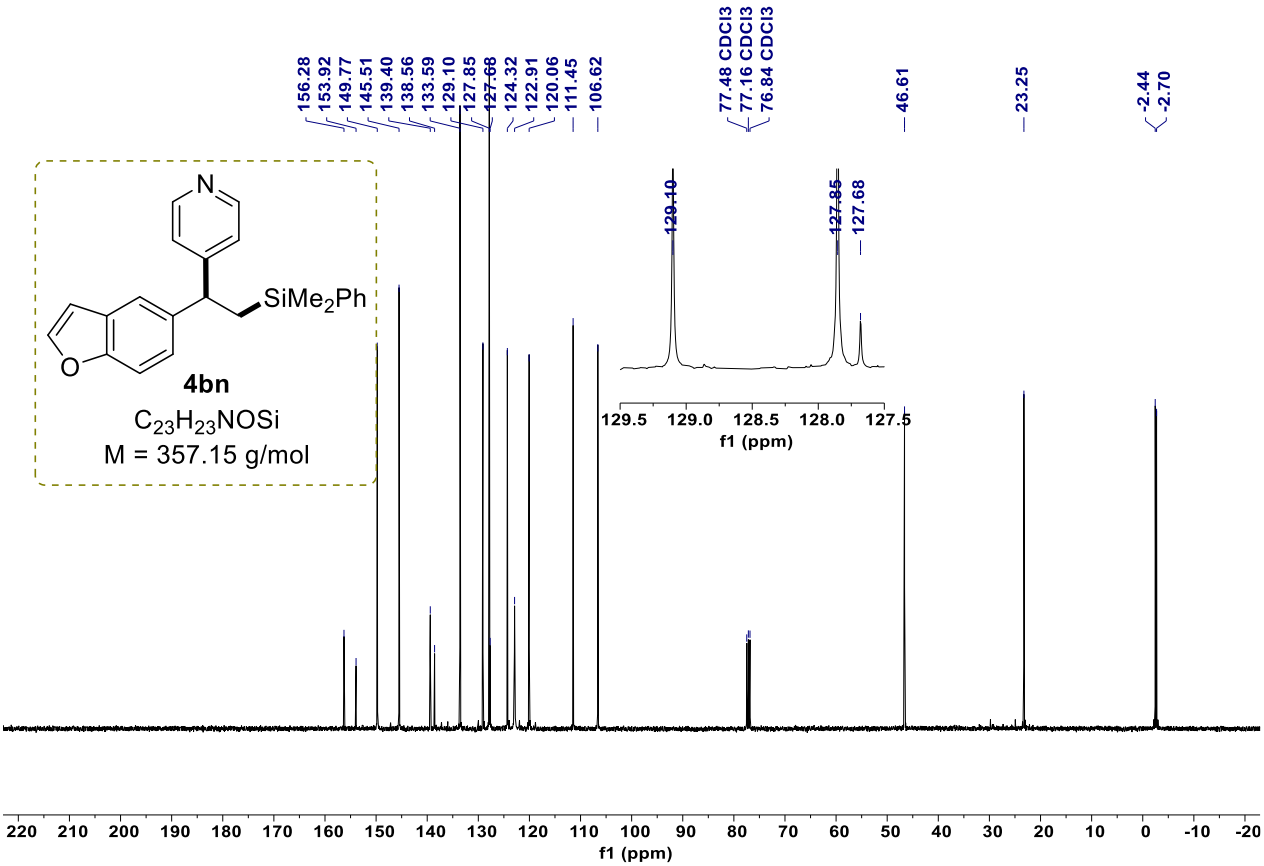
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bm**.



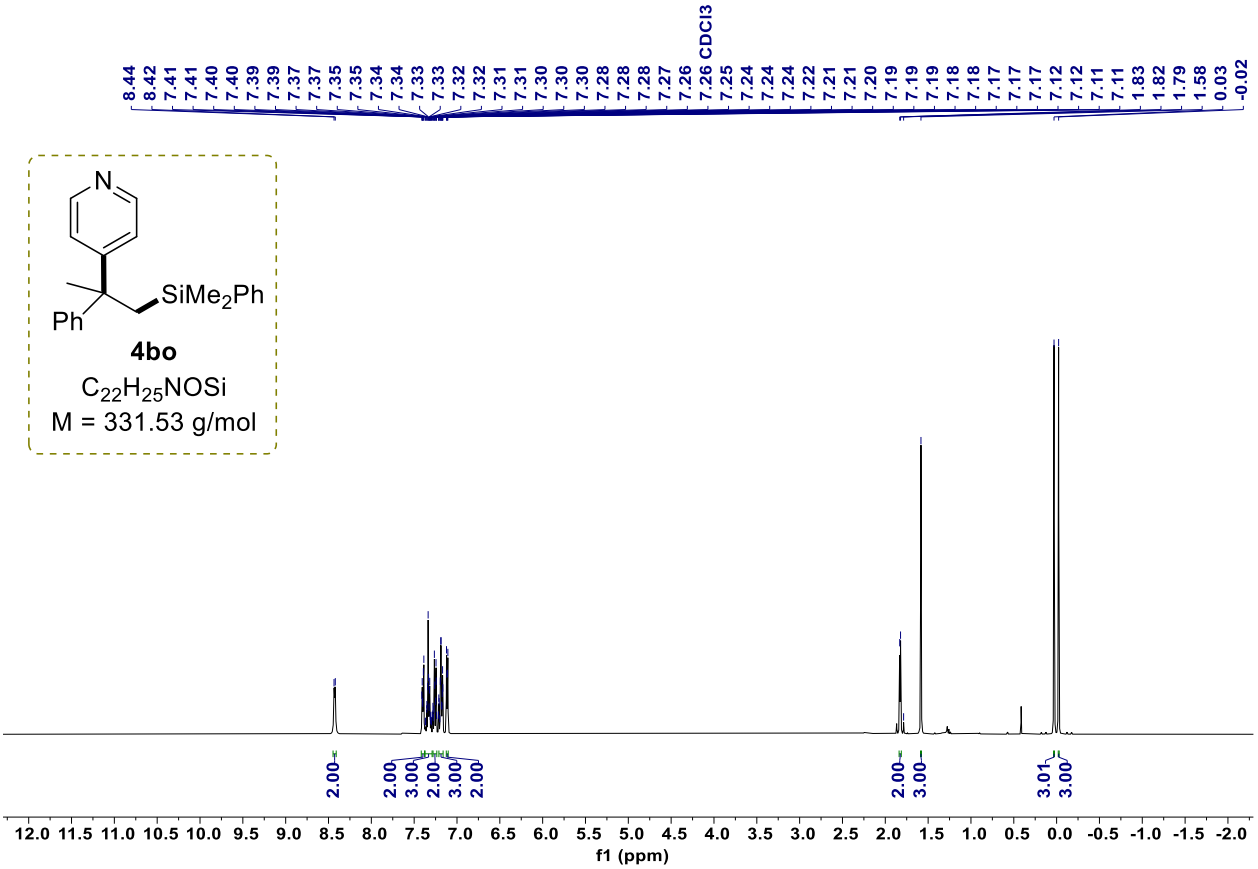
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4bm**.



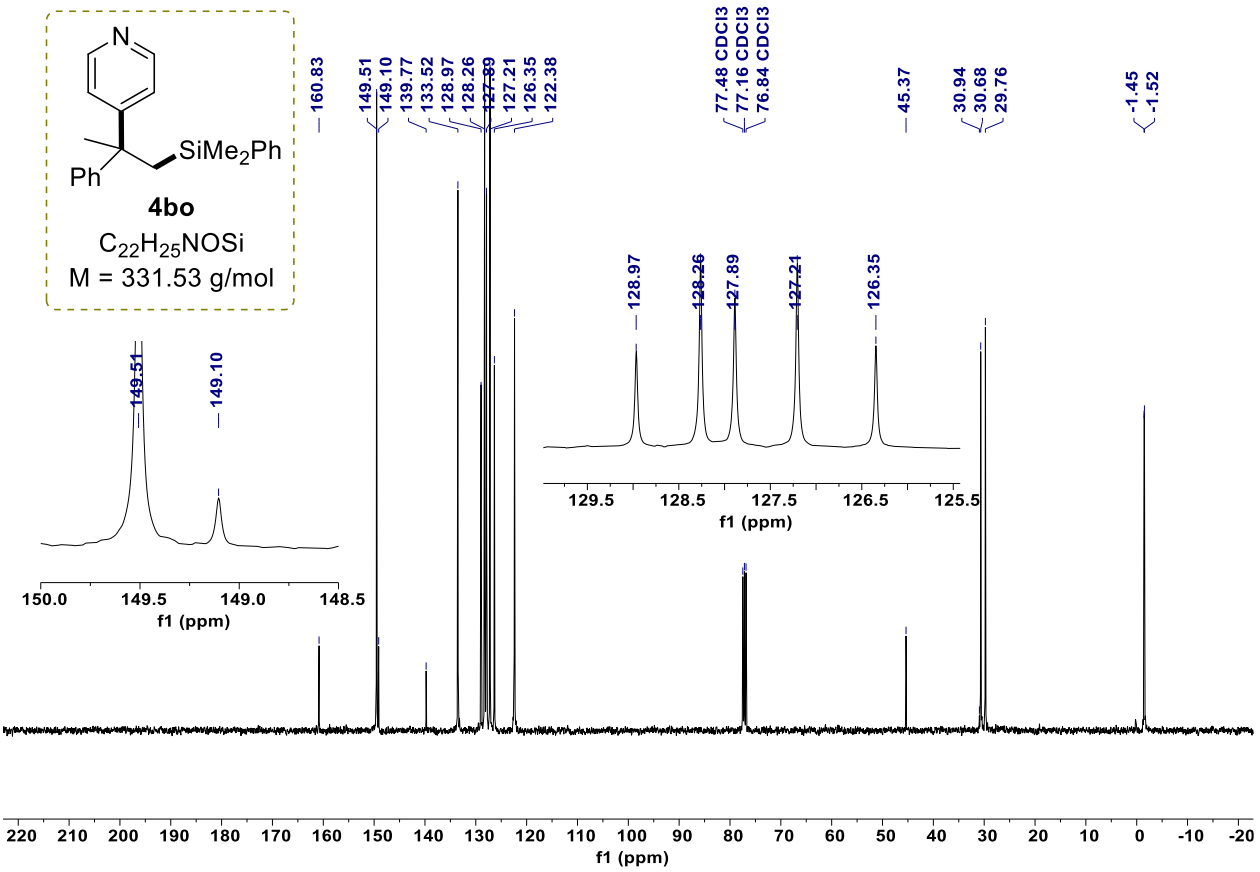
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bn**.



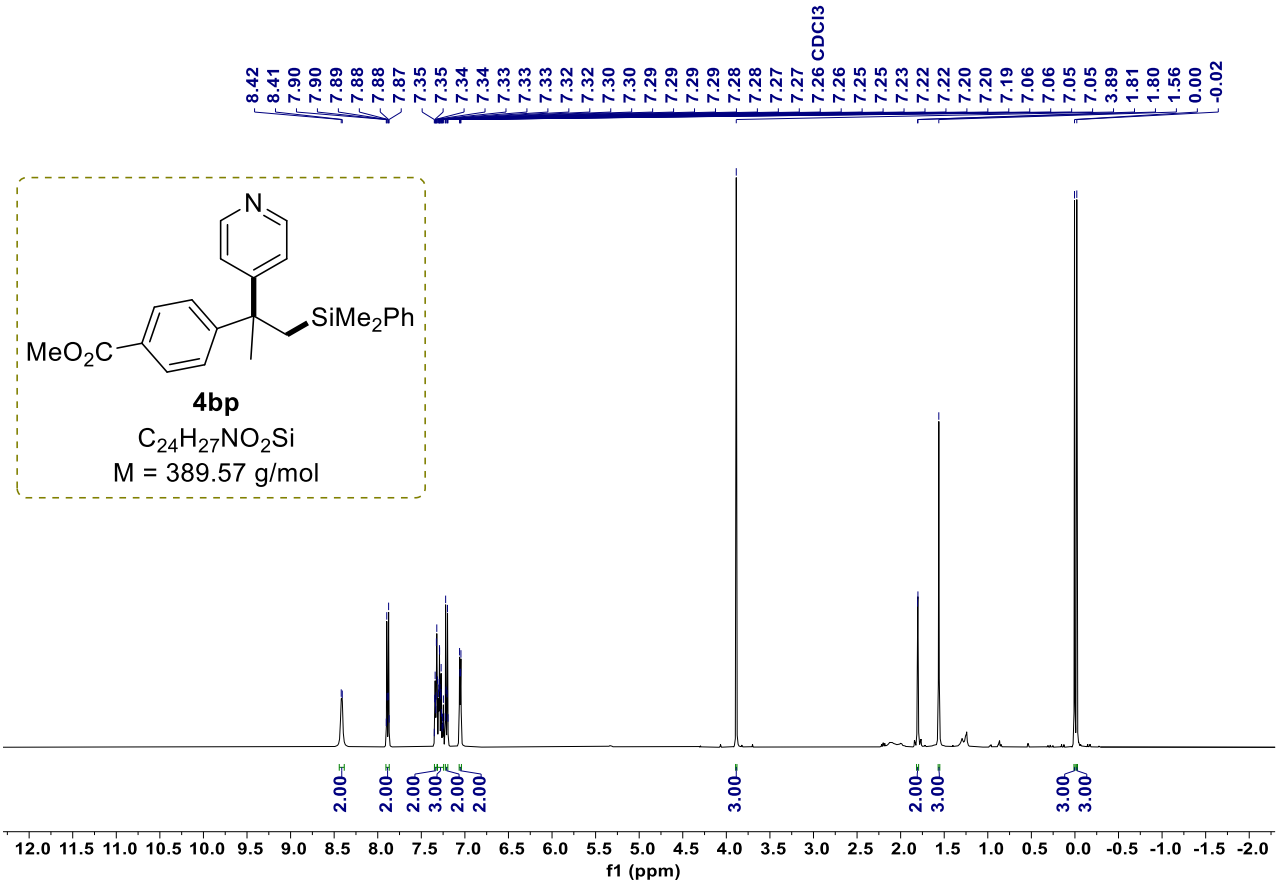
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4bn**.



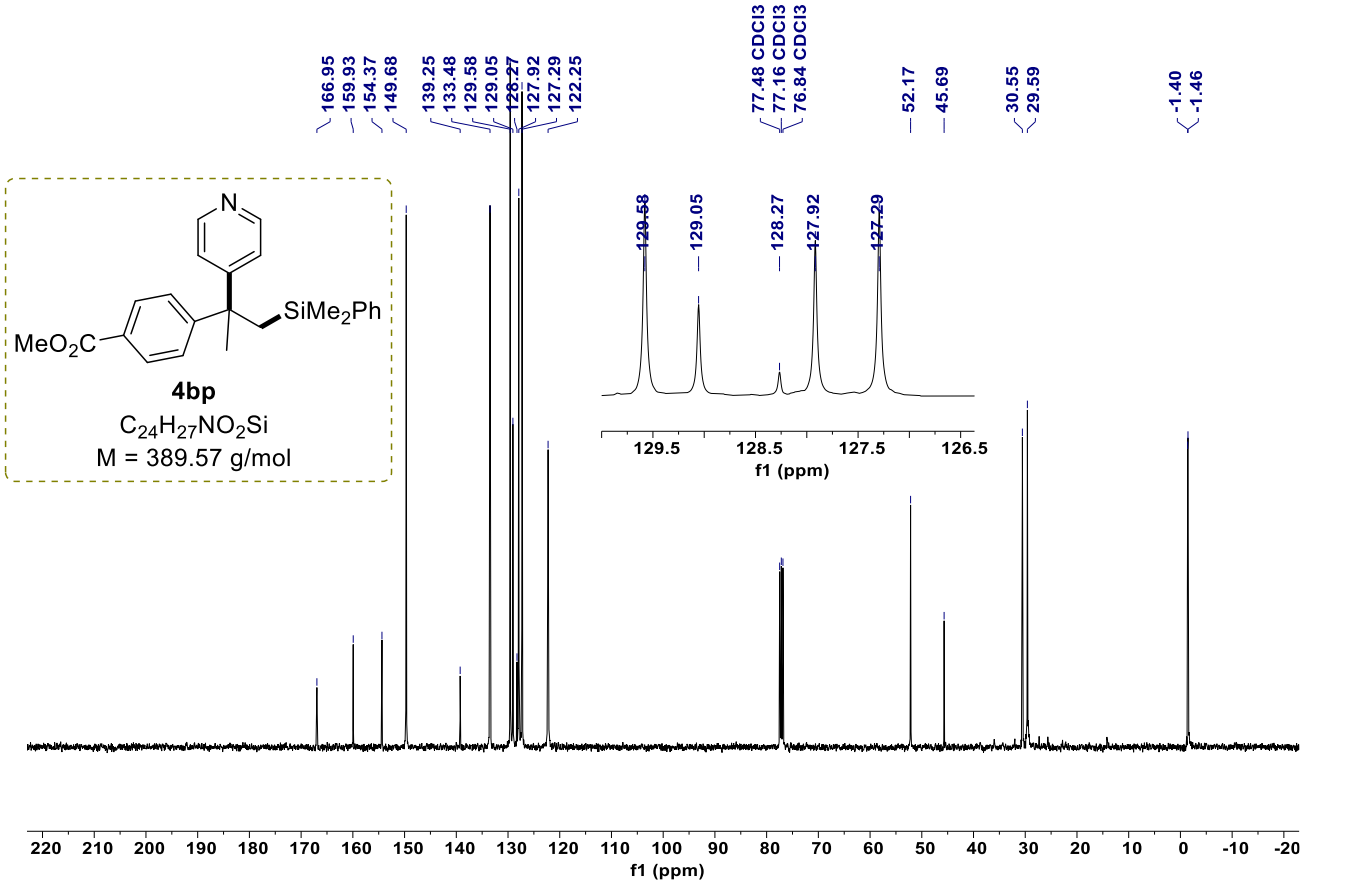
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bo**.



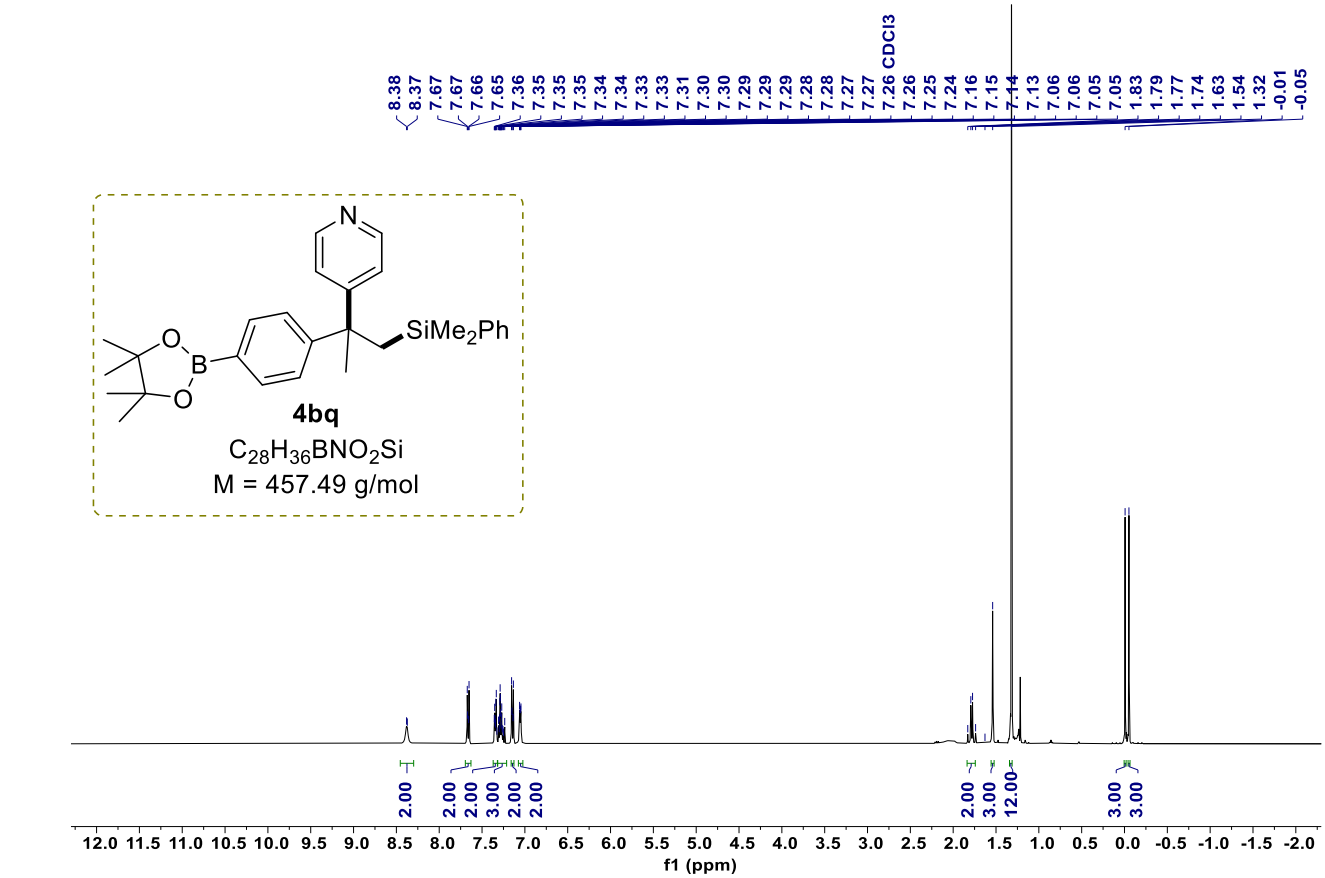
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4bo**.



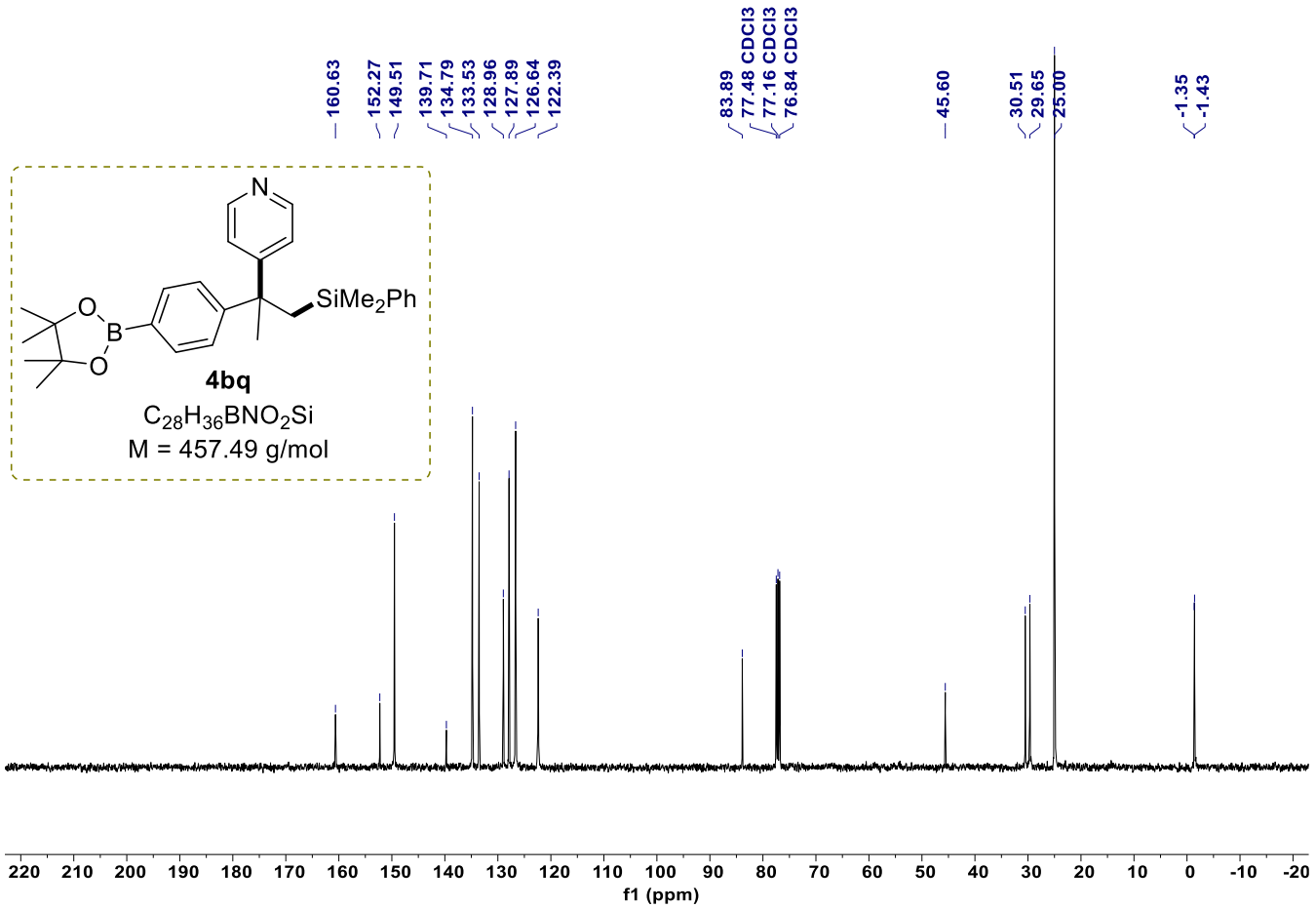
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bp**.



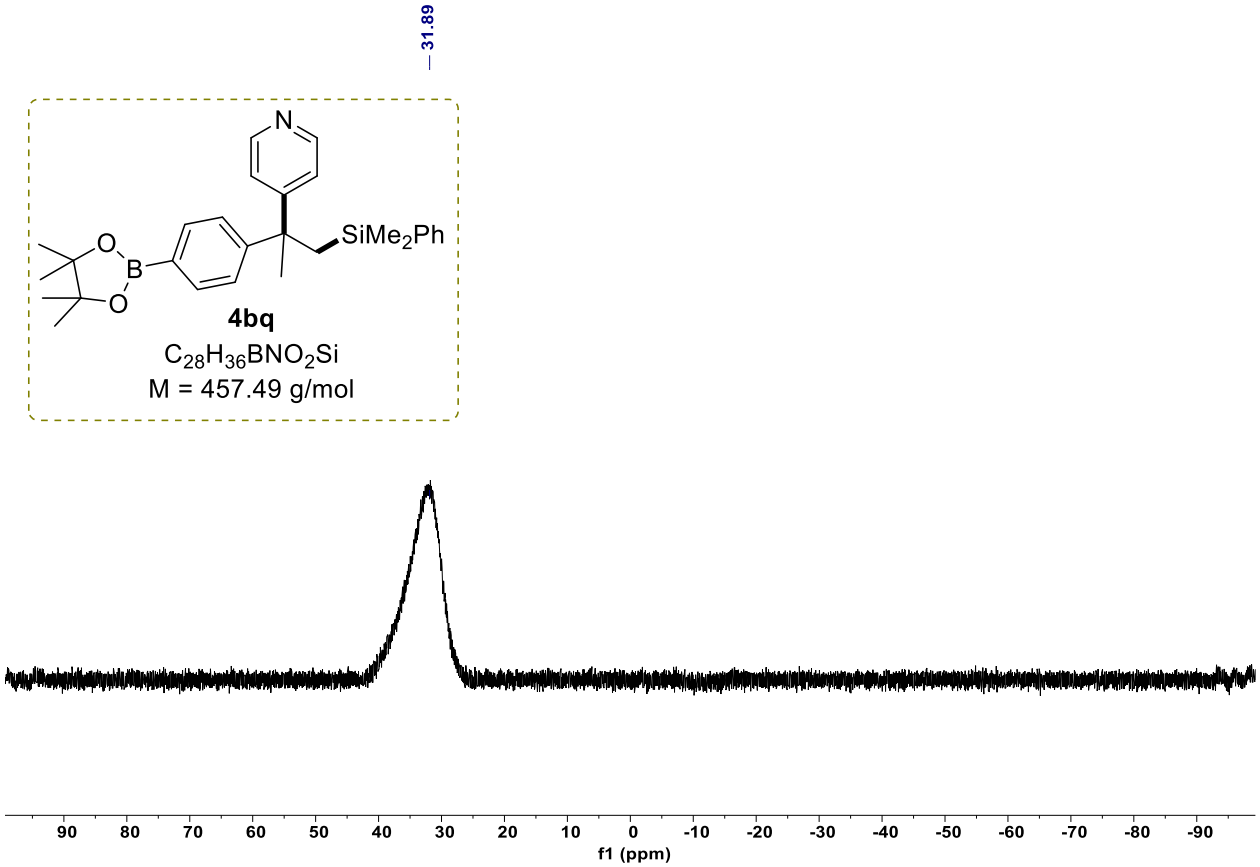
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4bp**.



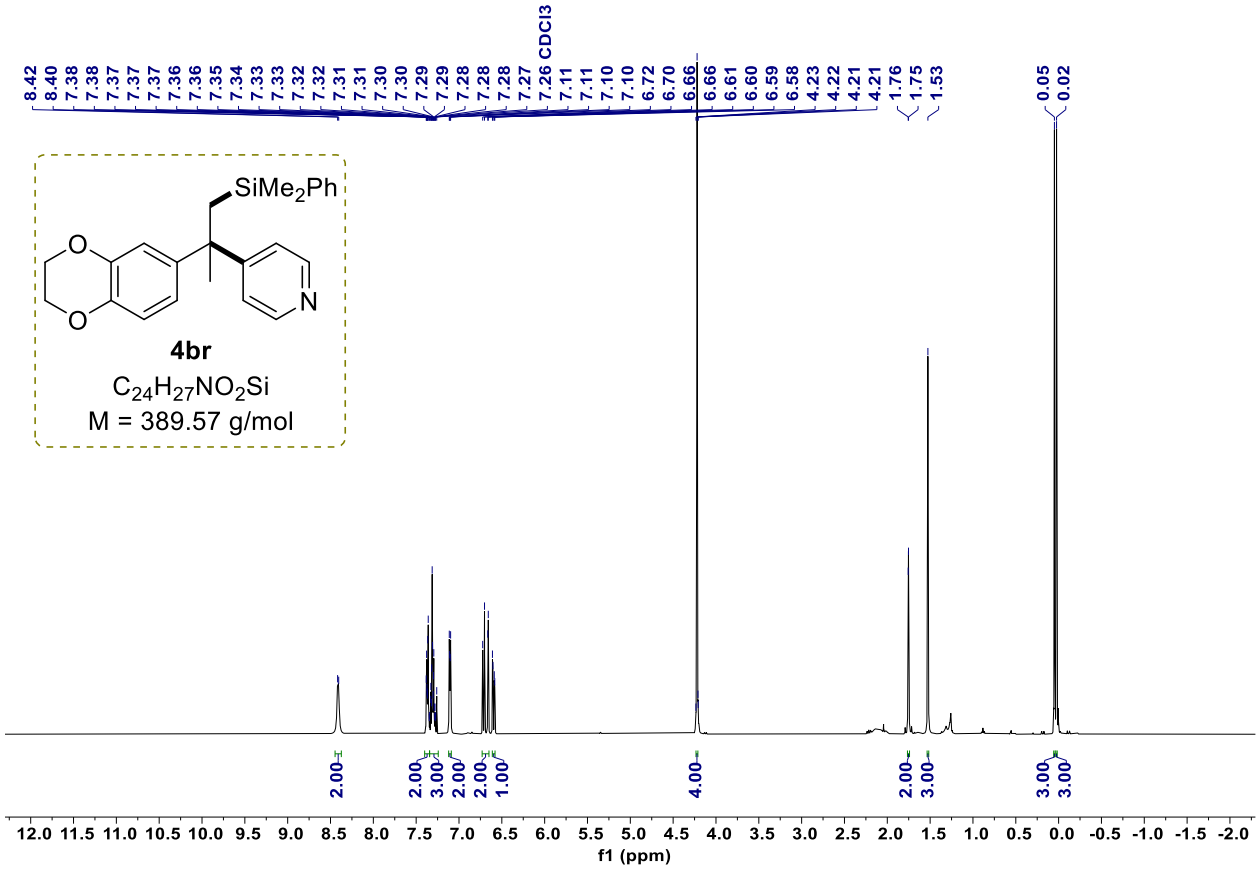
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bq**.



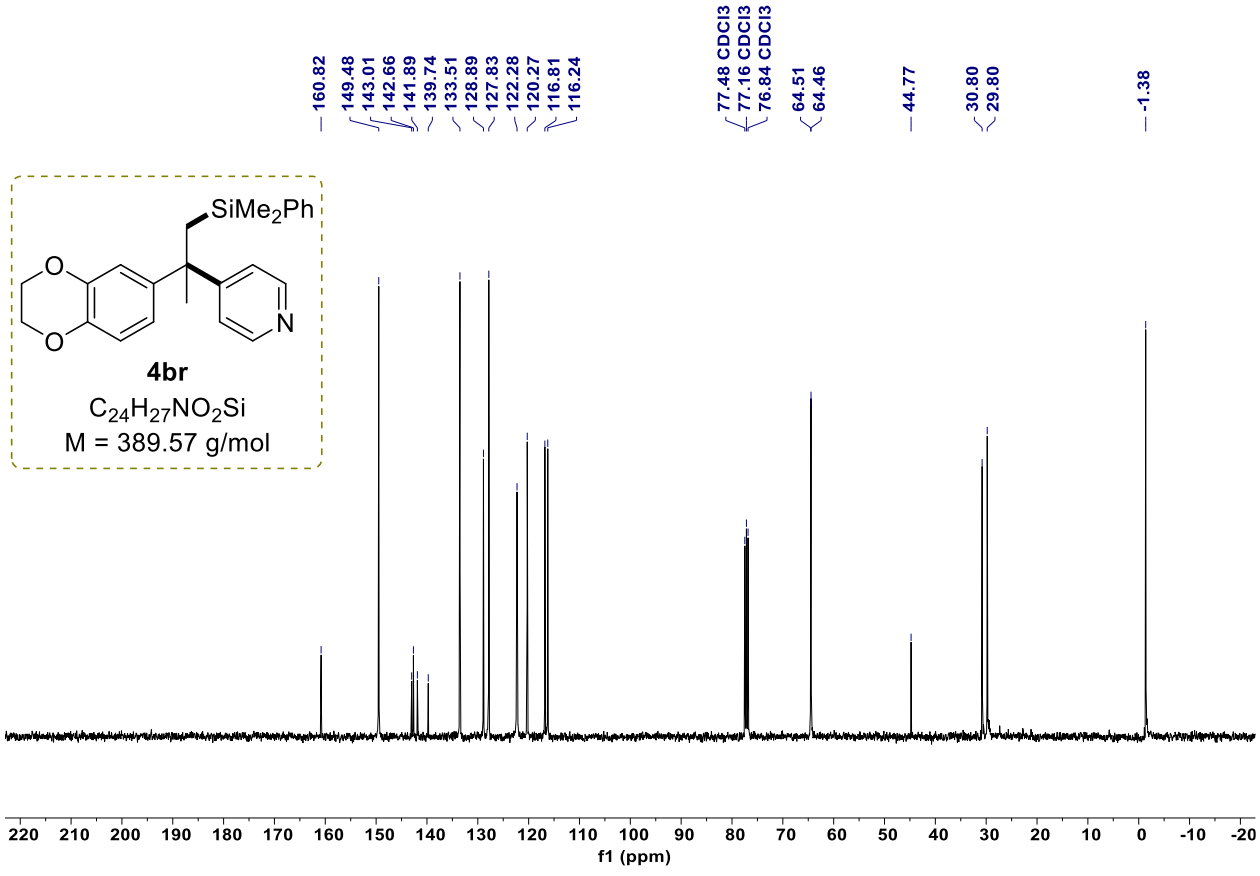
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4bq**.



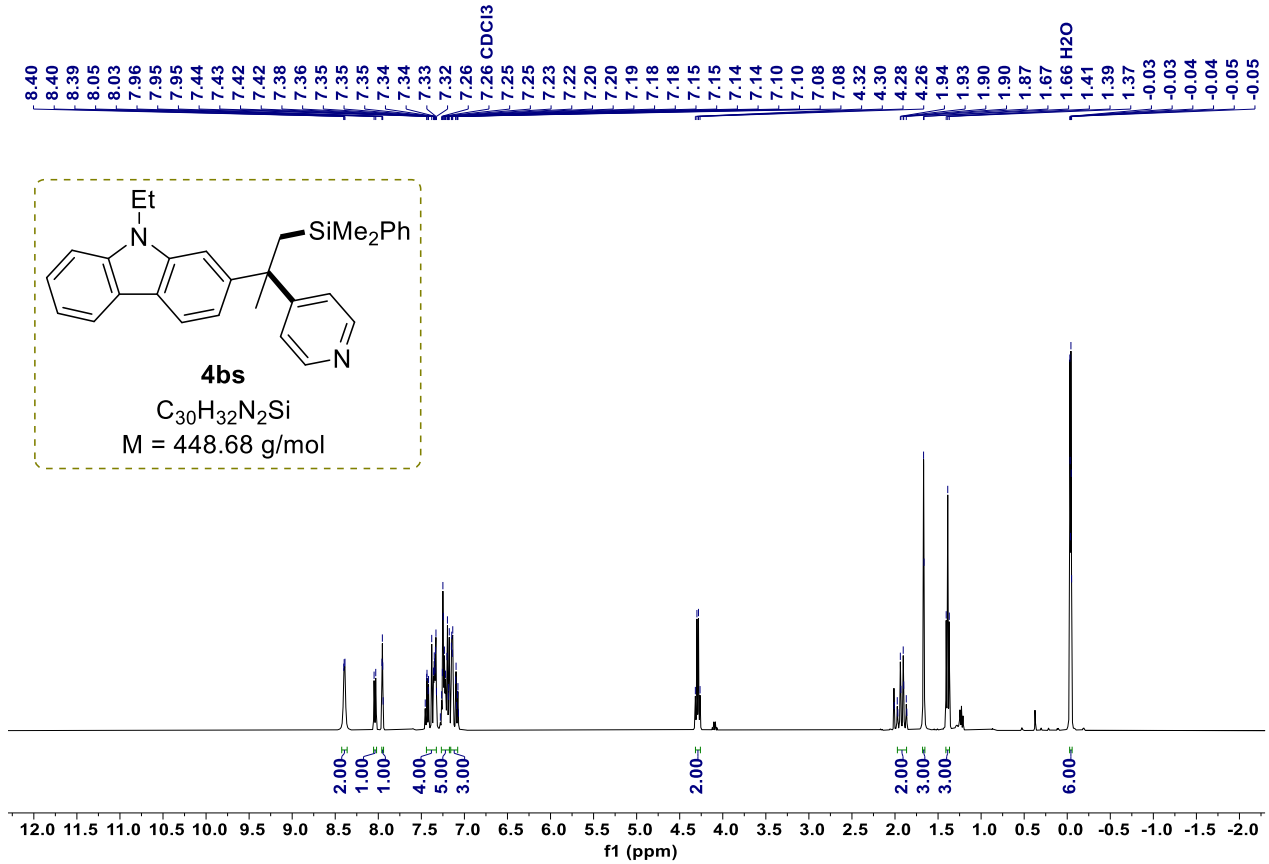
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of compound **4bq**.



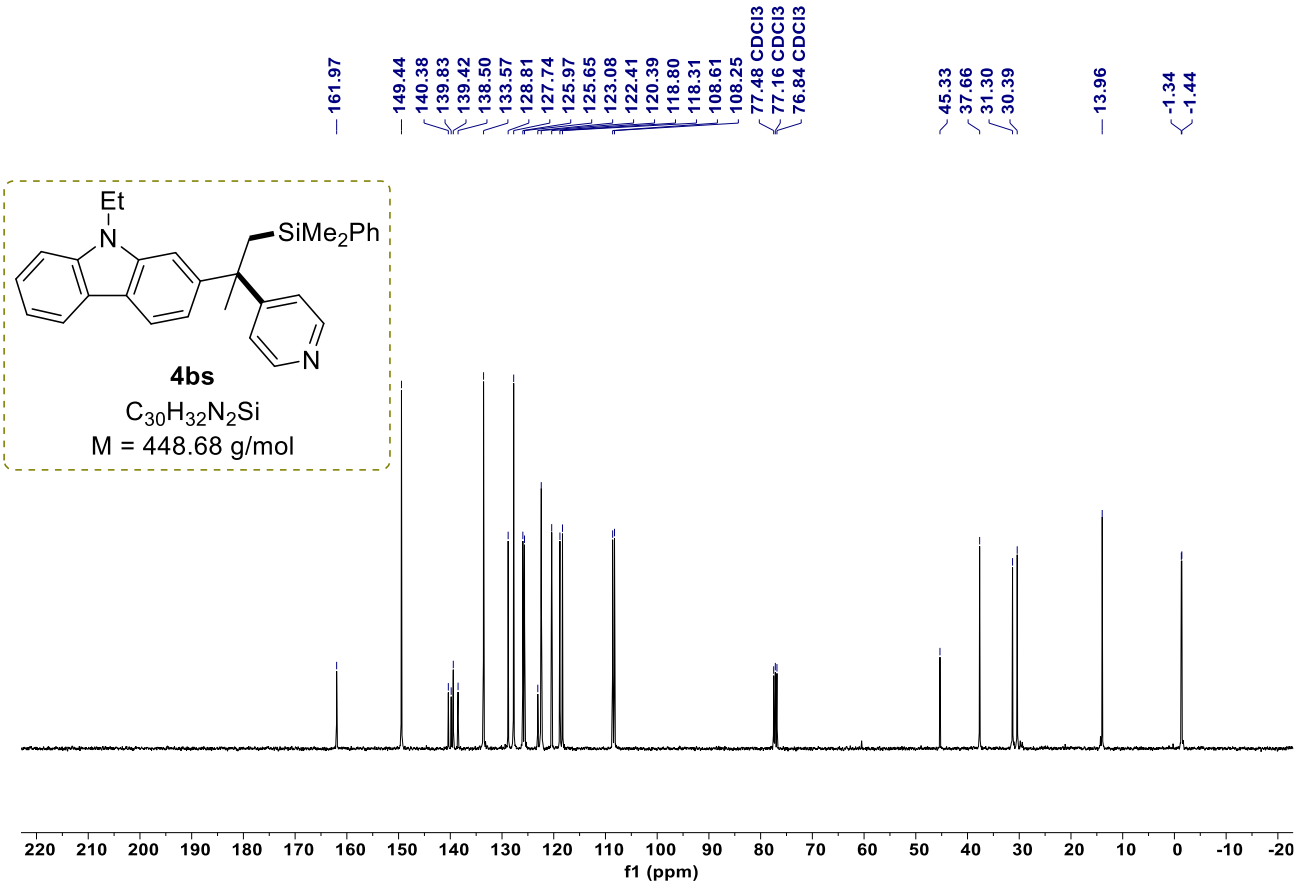
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4br**.



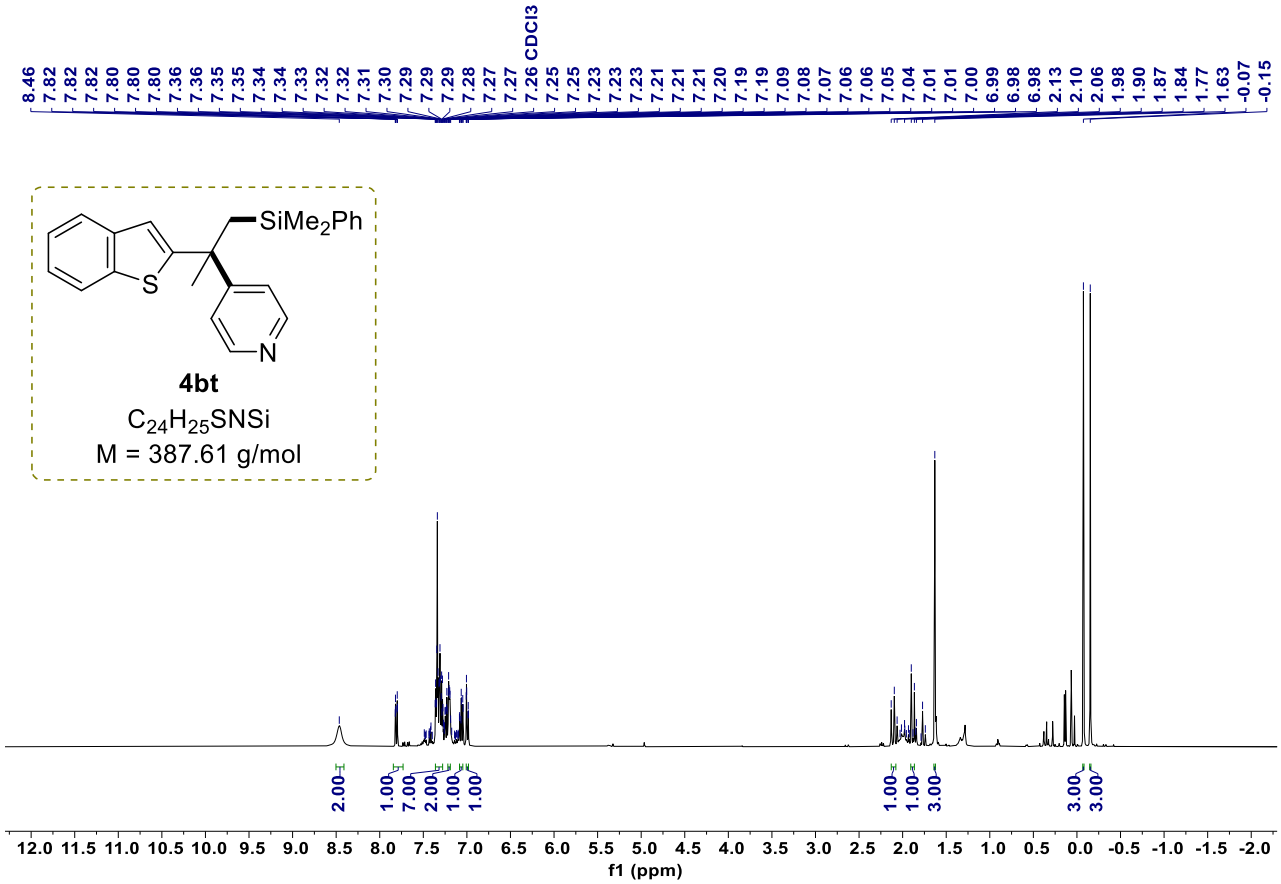
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4br**.



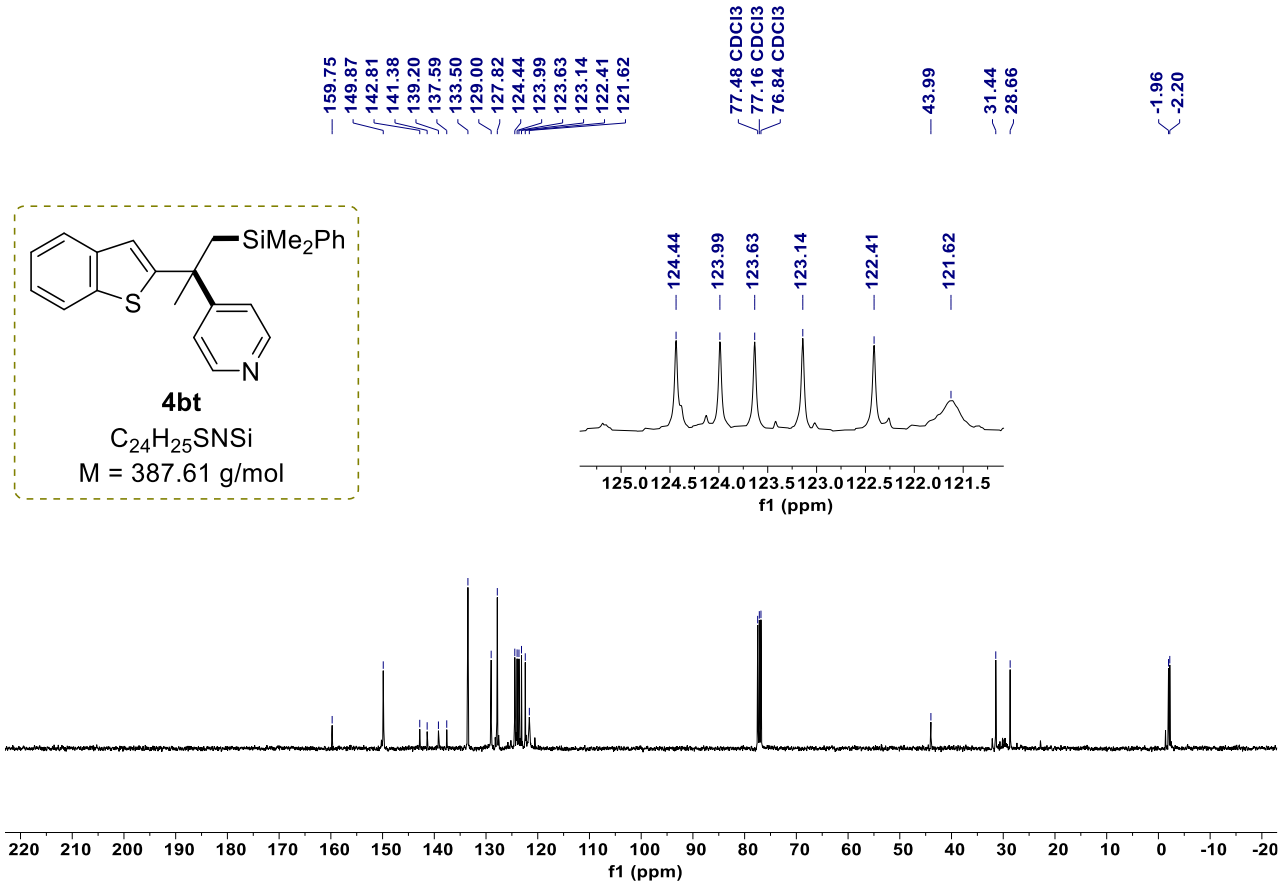
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bs**.



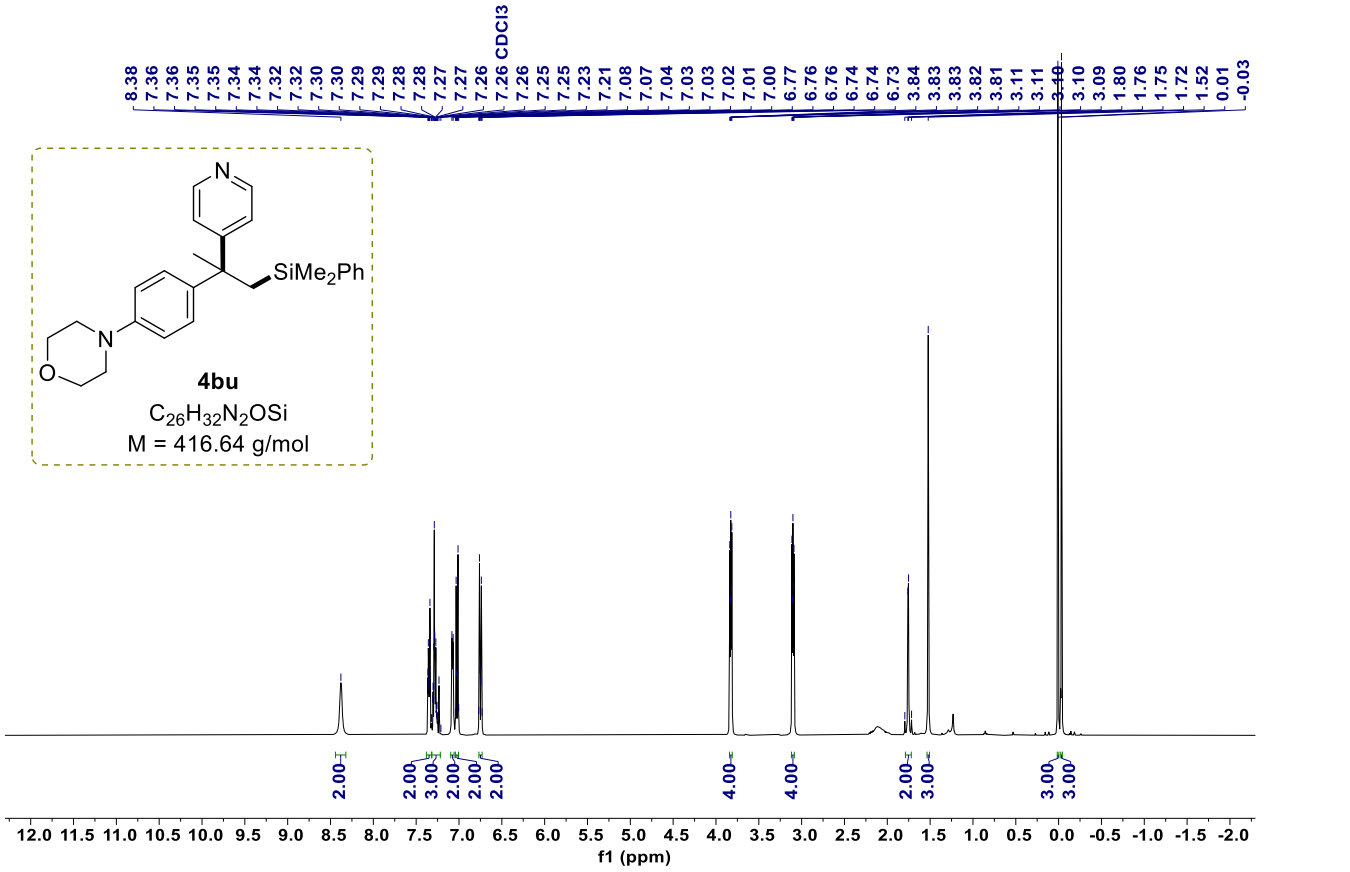
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bs**.



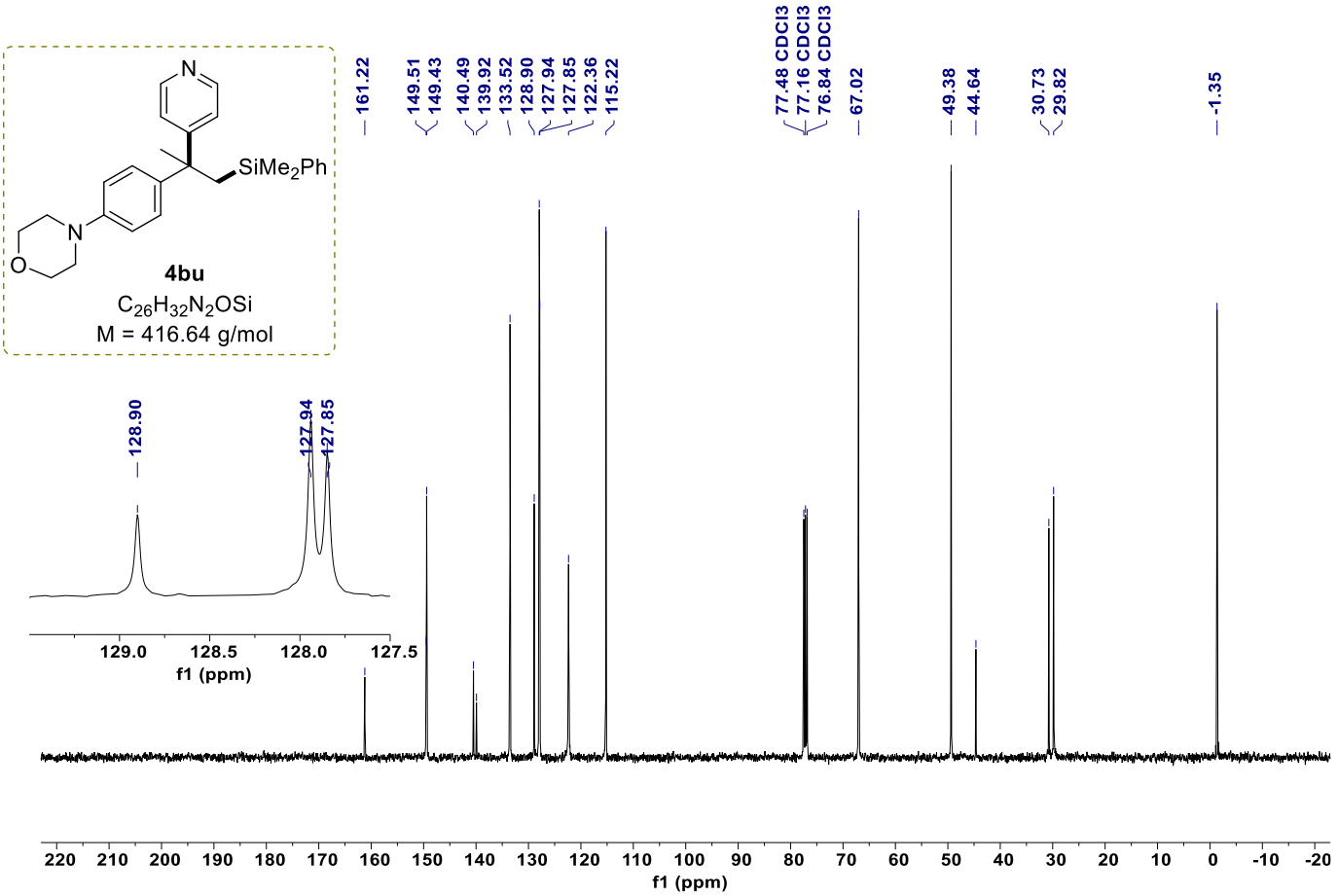
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bt.**



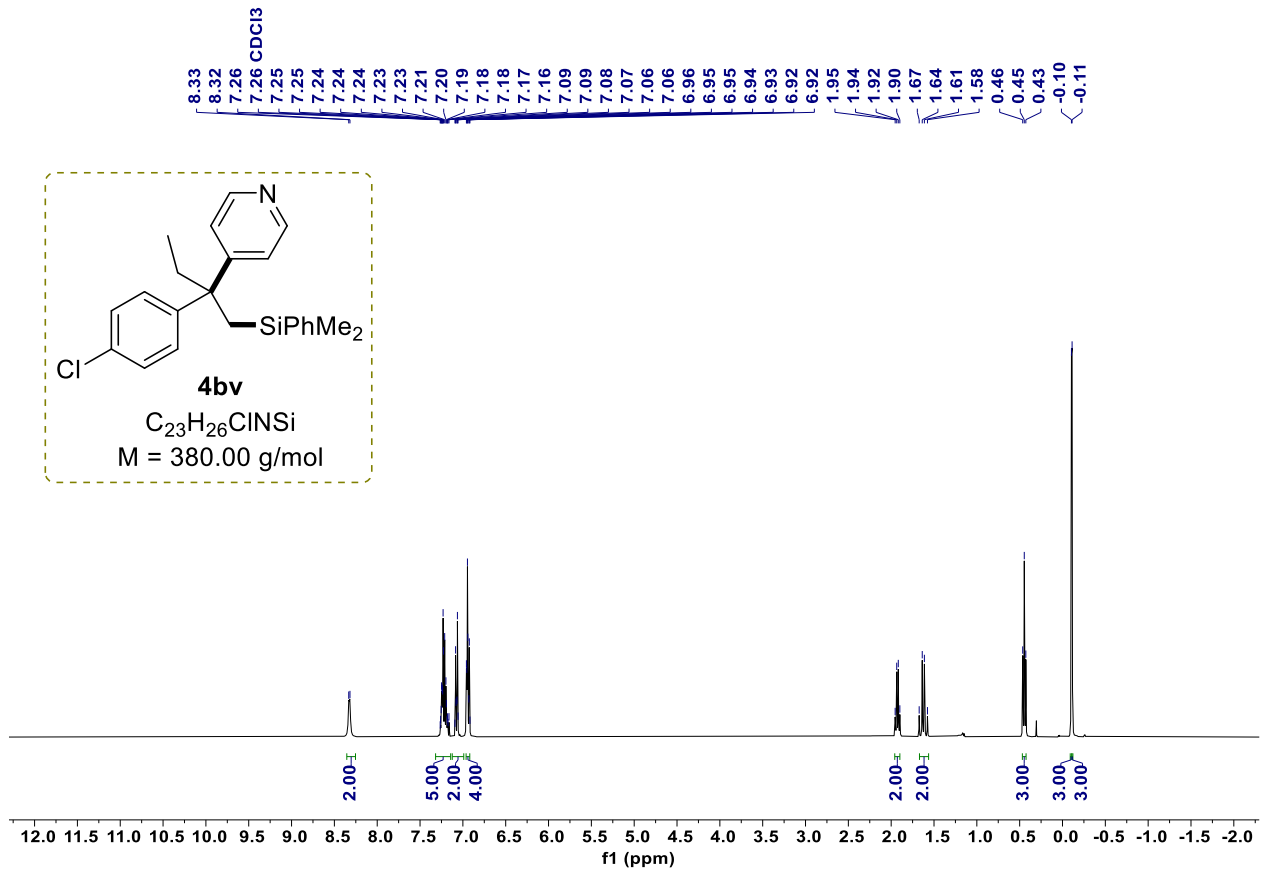
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bt**.



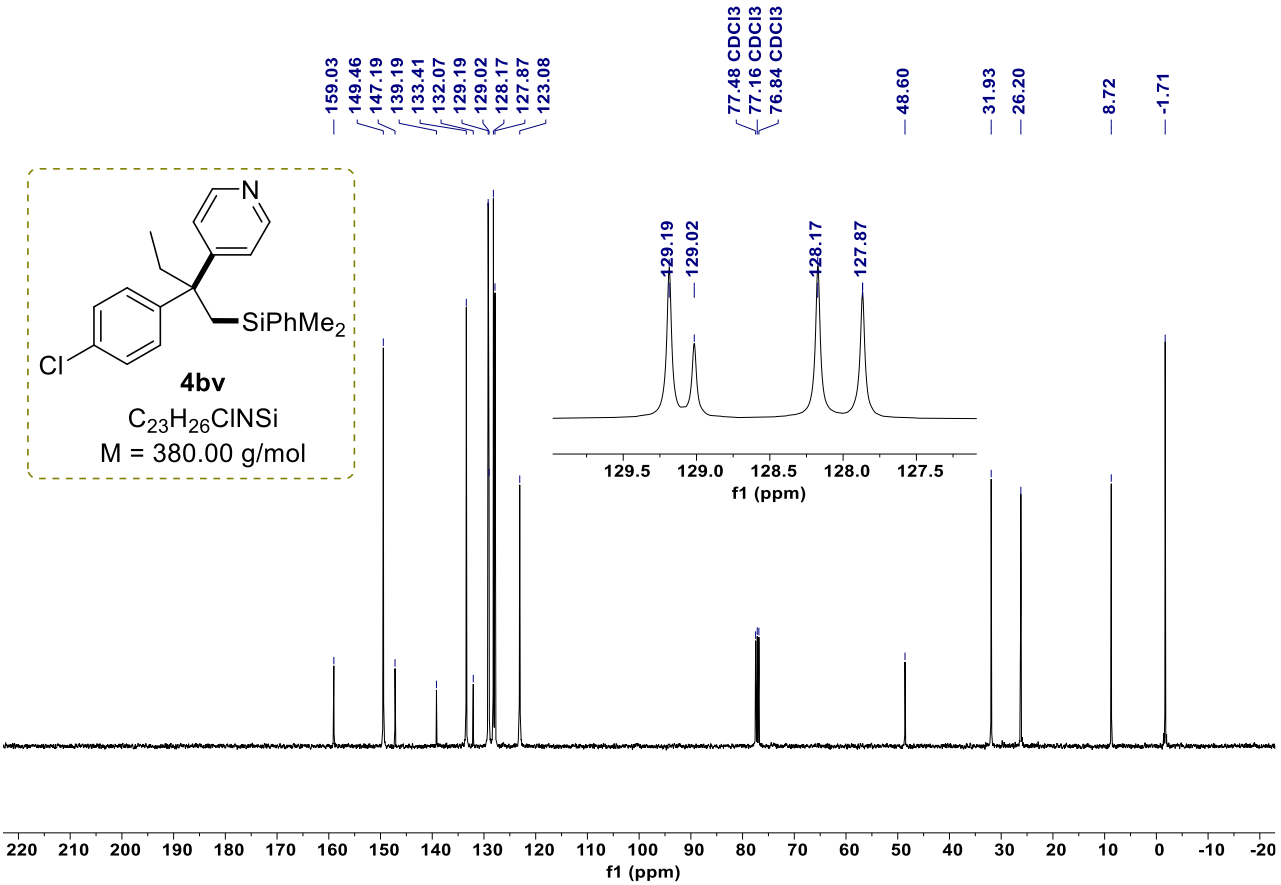
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bu**.



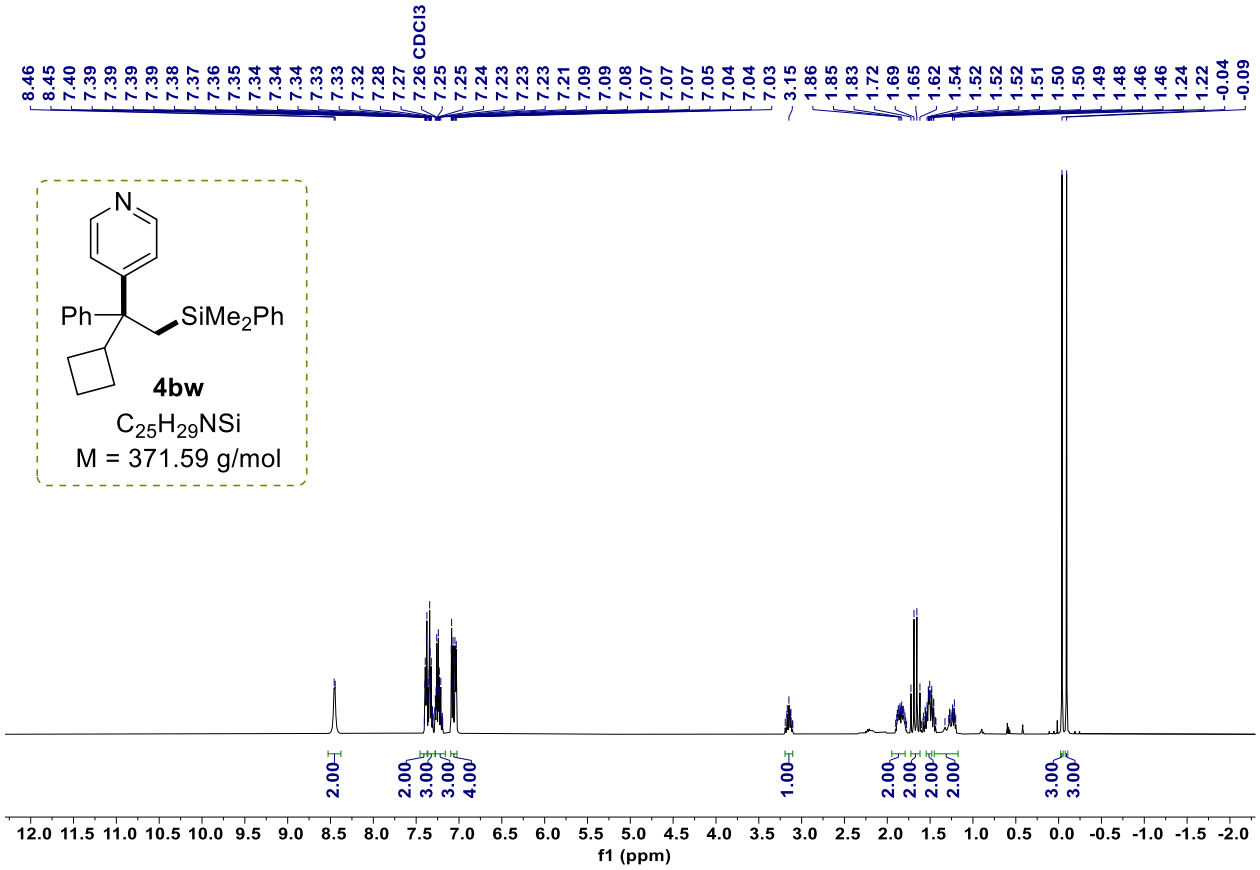
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bu**.



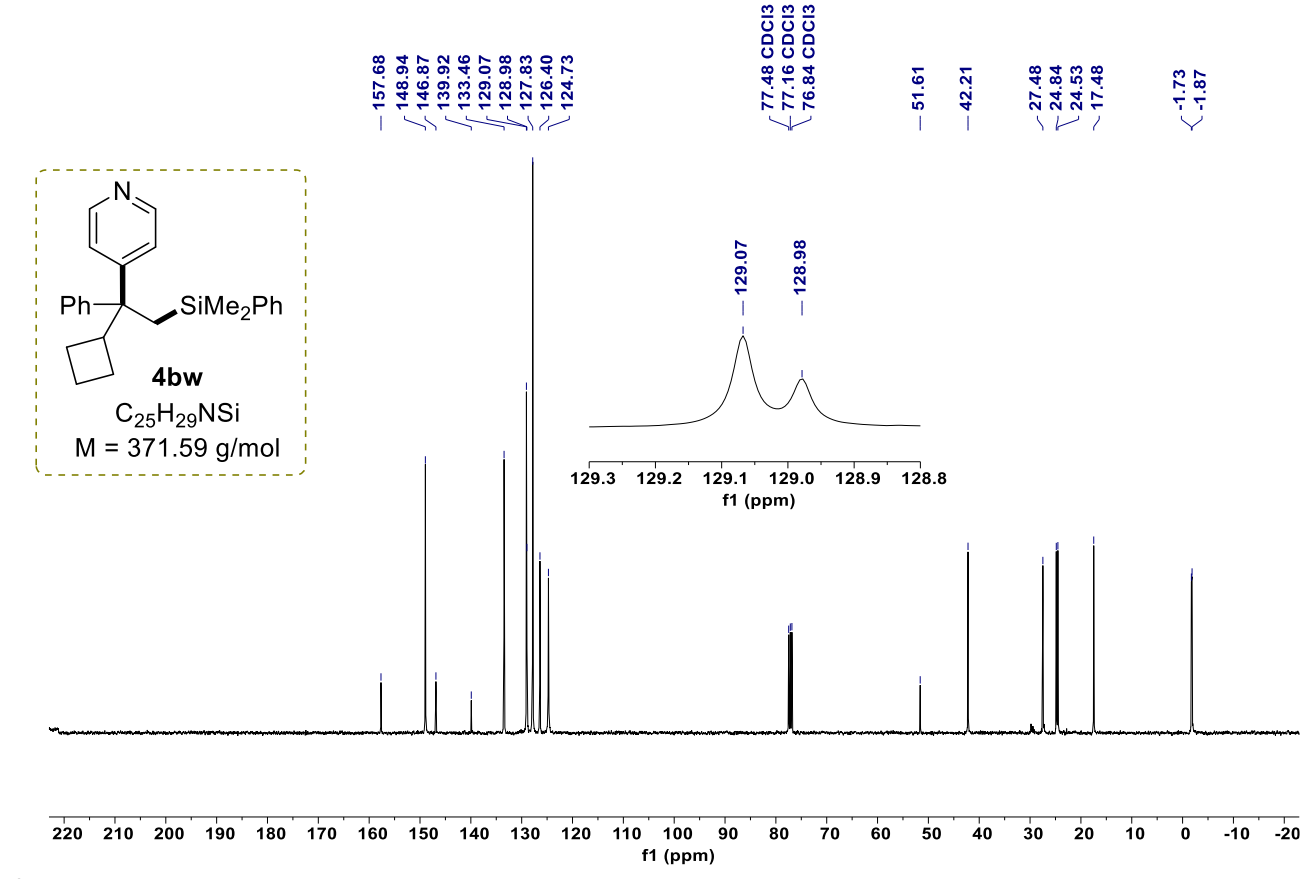
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bv**.



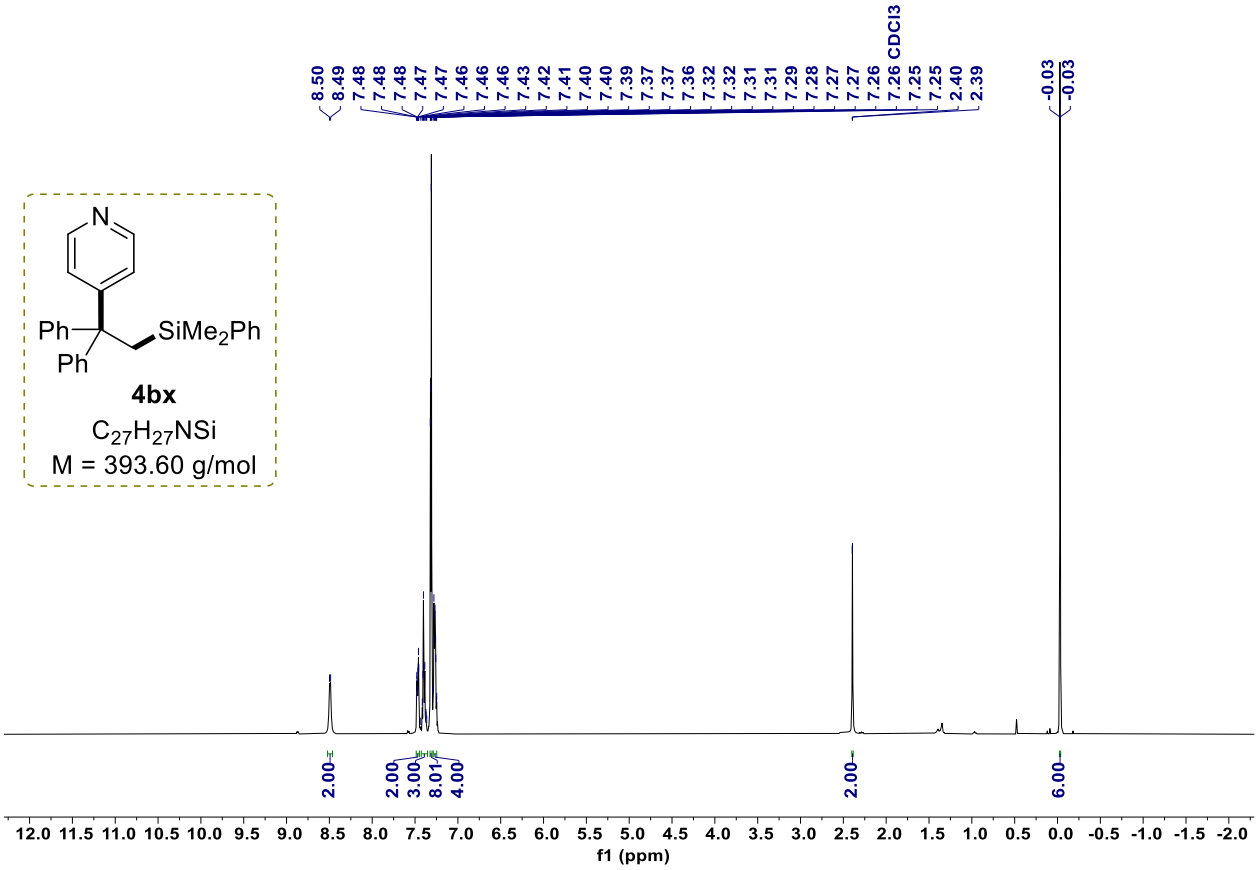
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bv**.



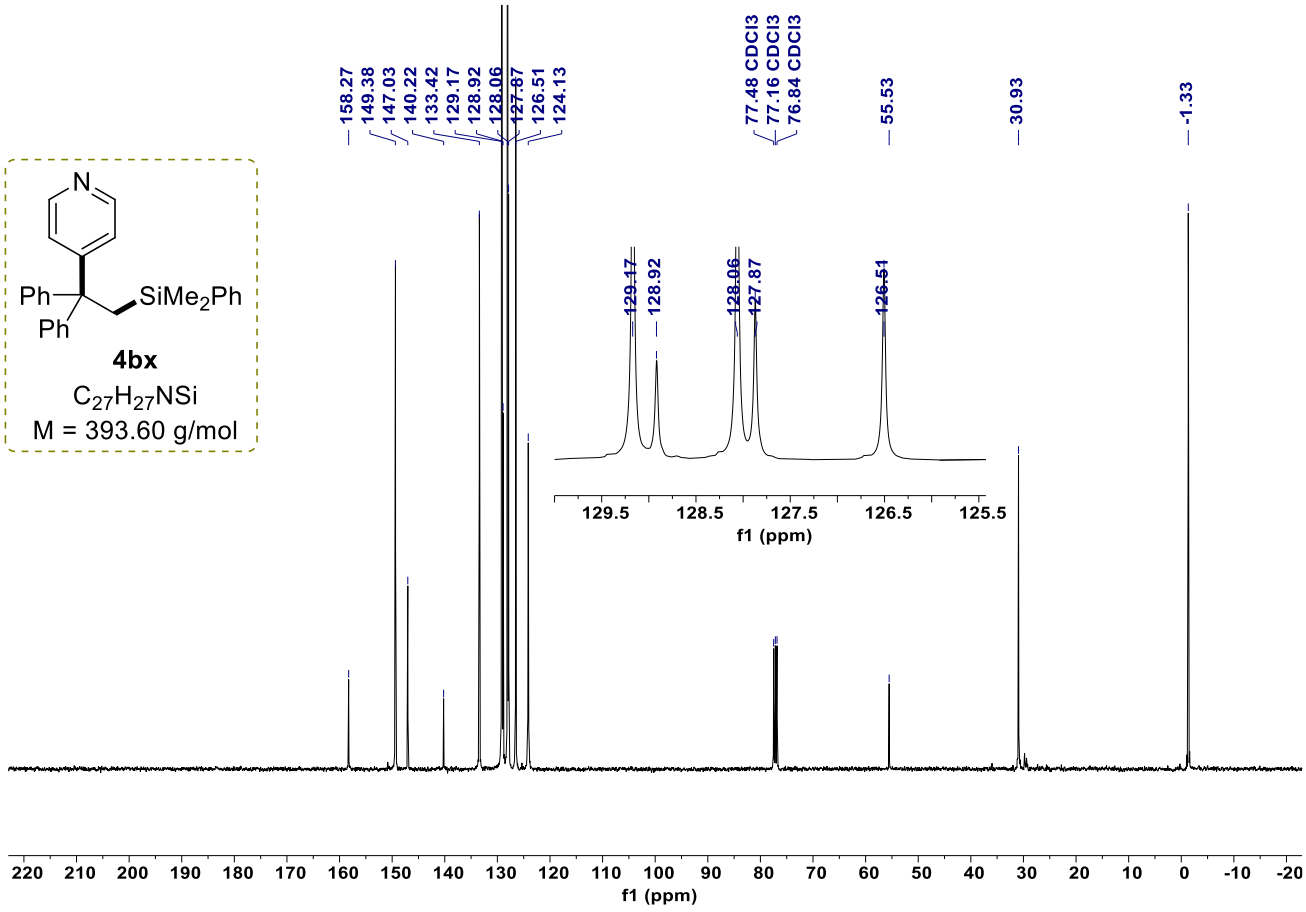
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bw**.



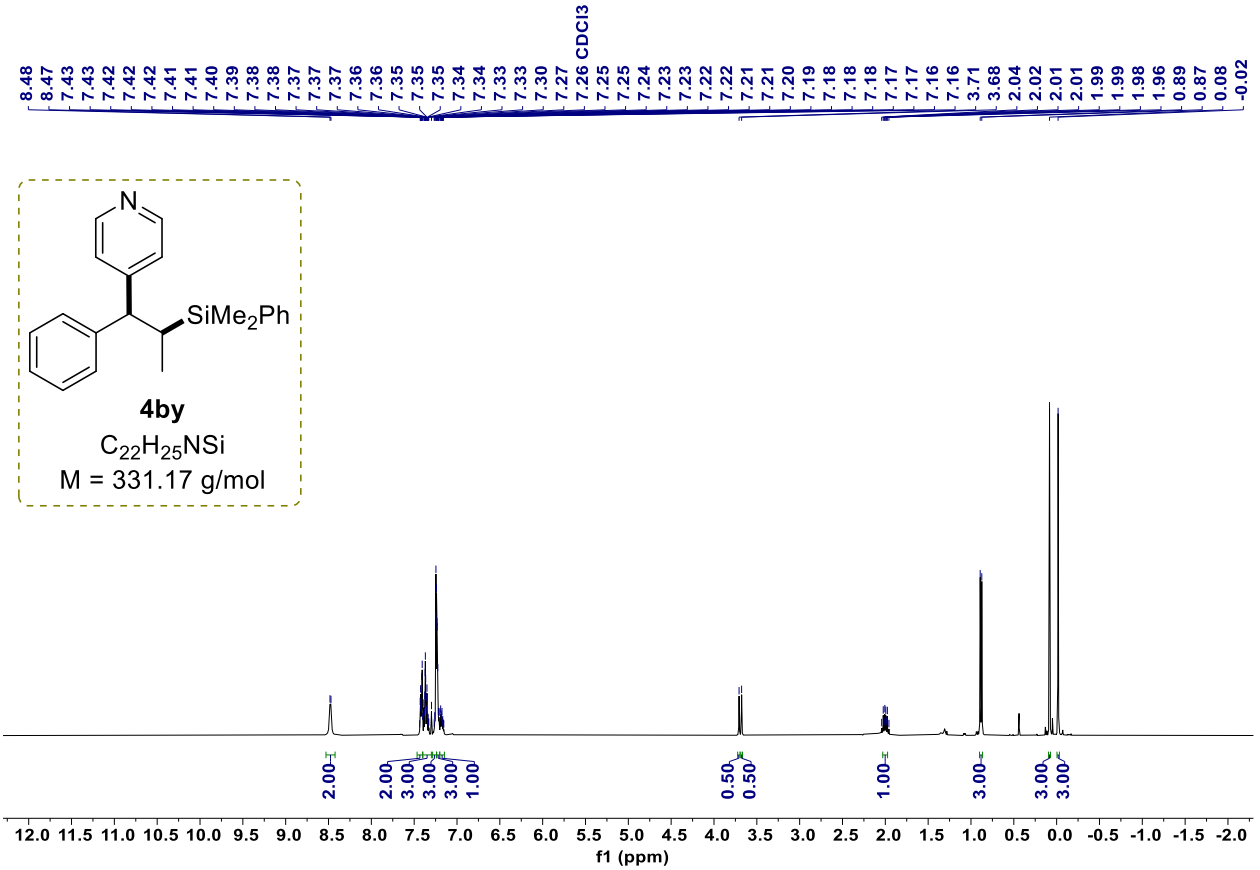
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bw**.



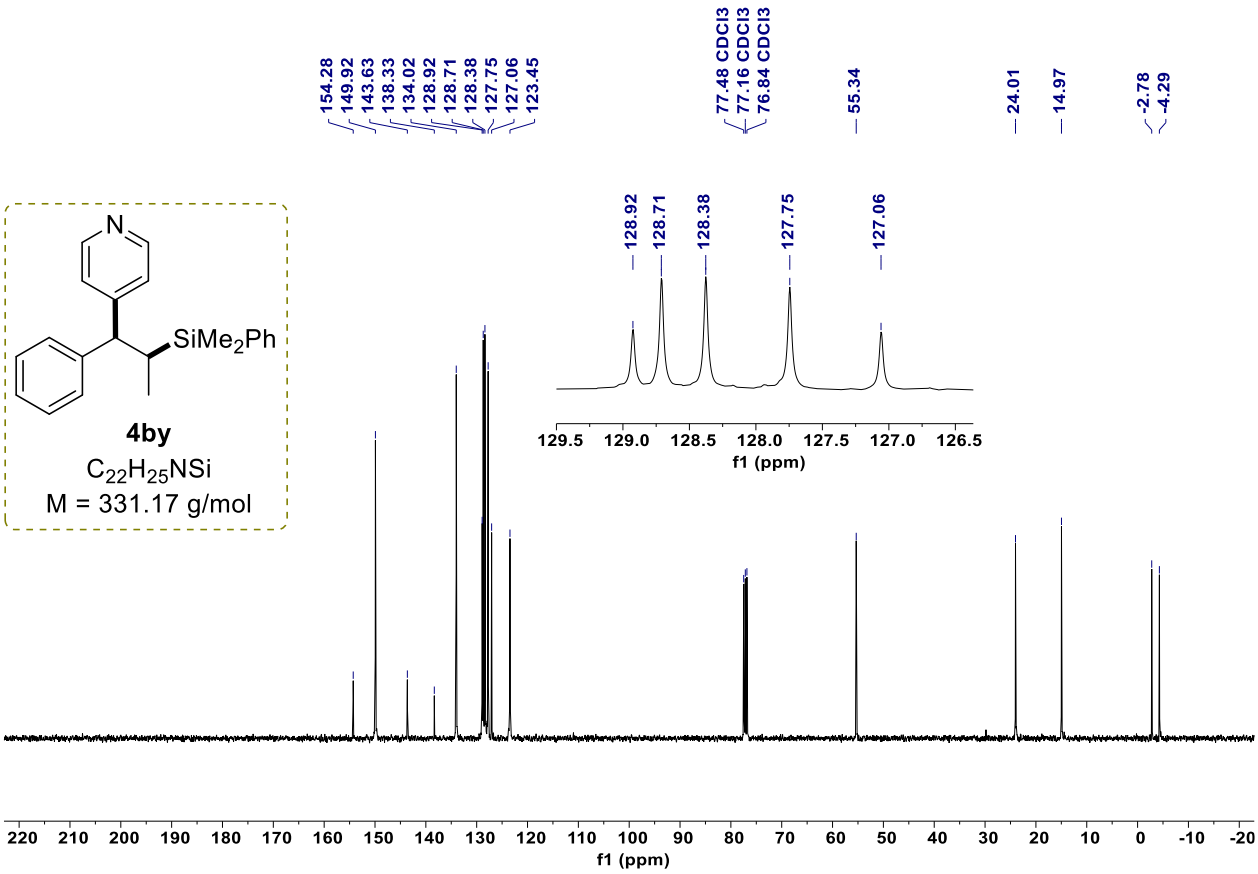
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bx**.



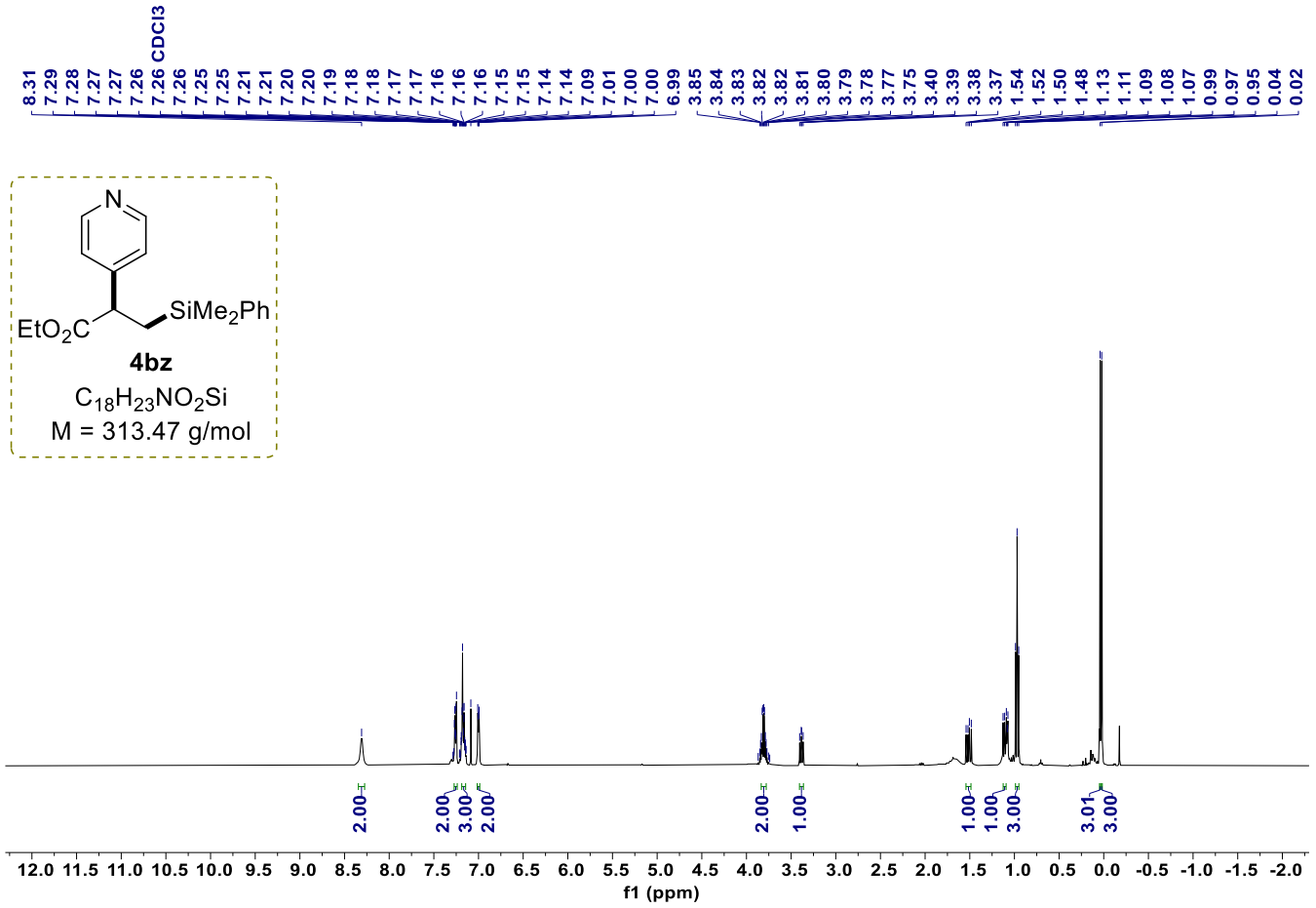
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bx**.



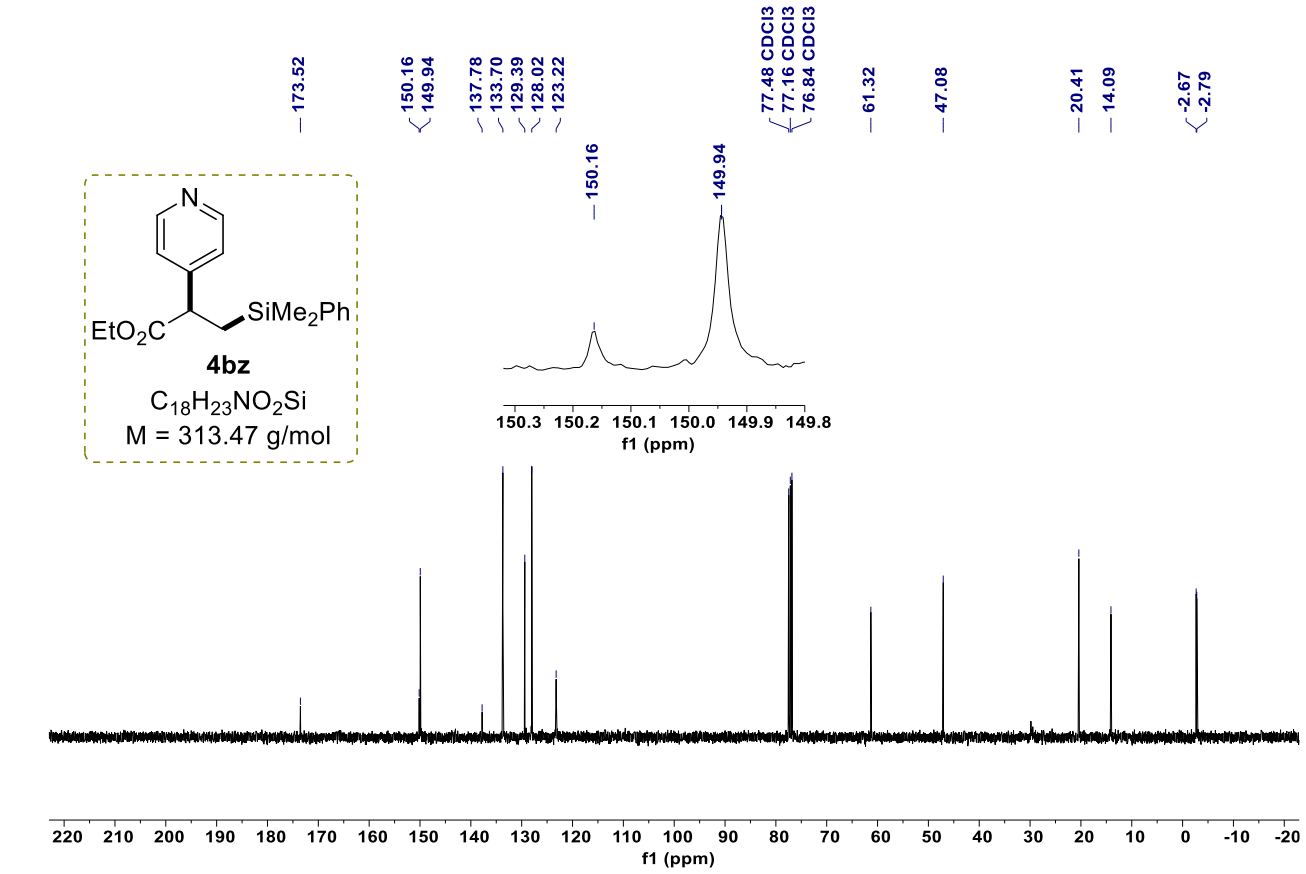
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4by**.



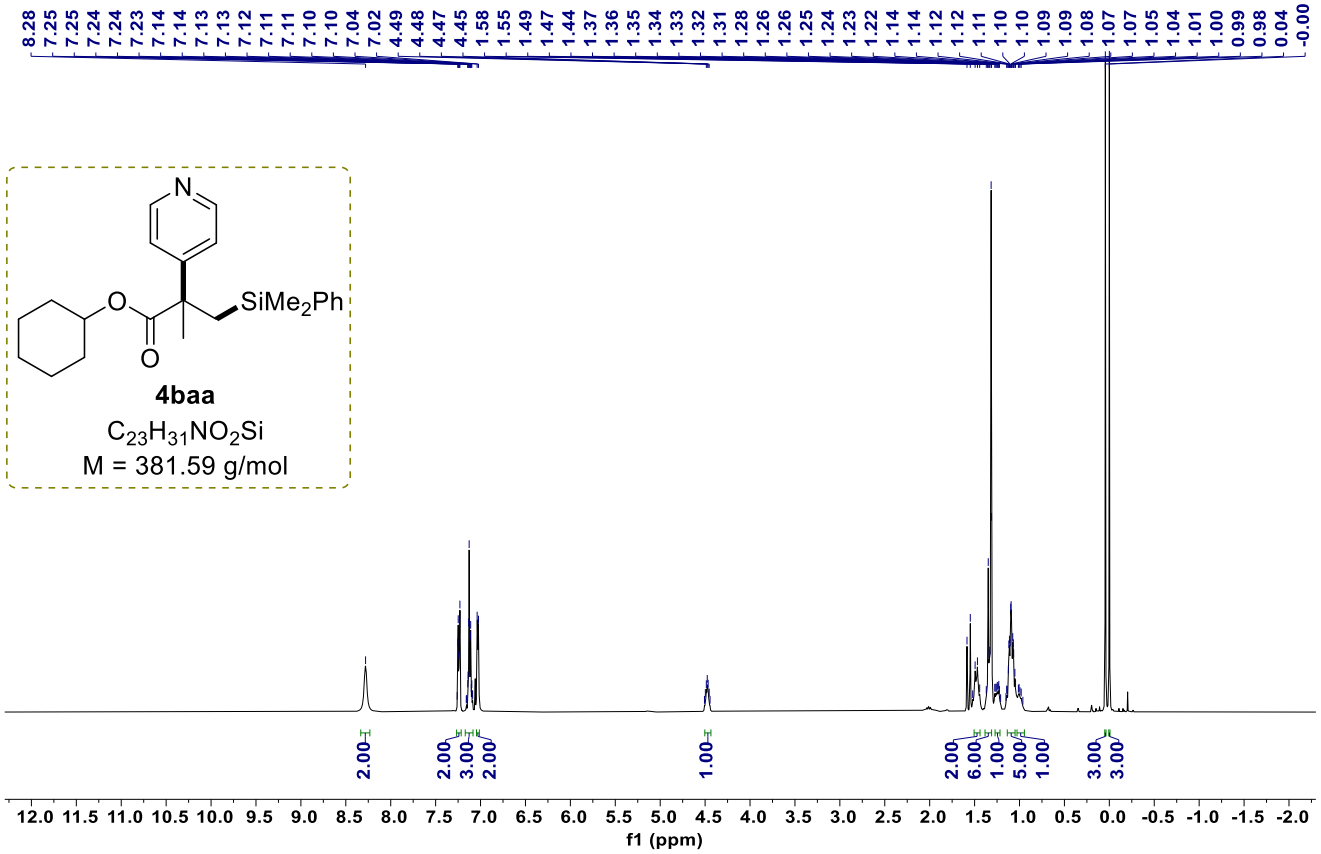
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4by**.



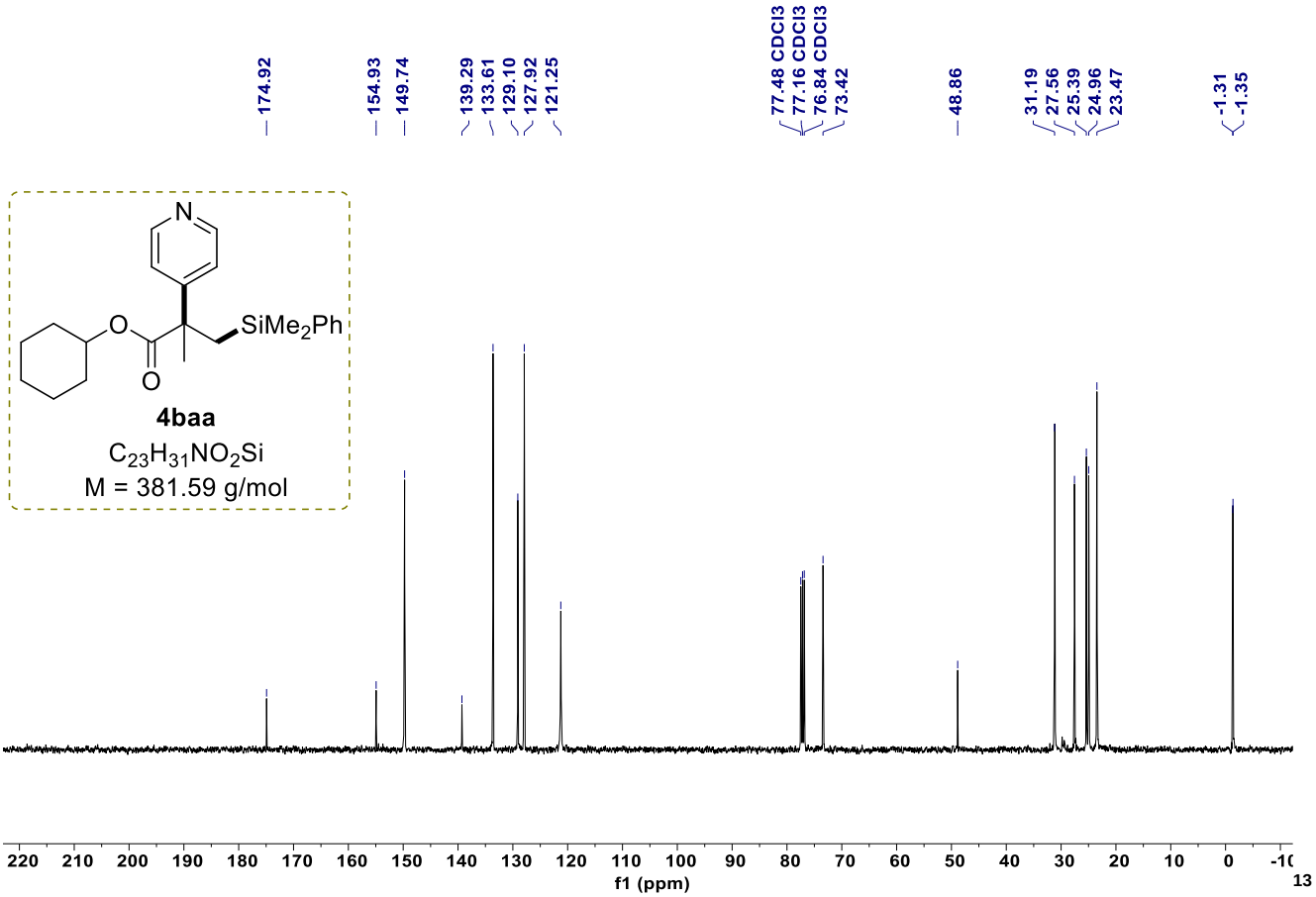
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bz.**



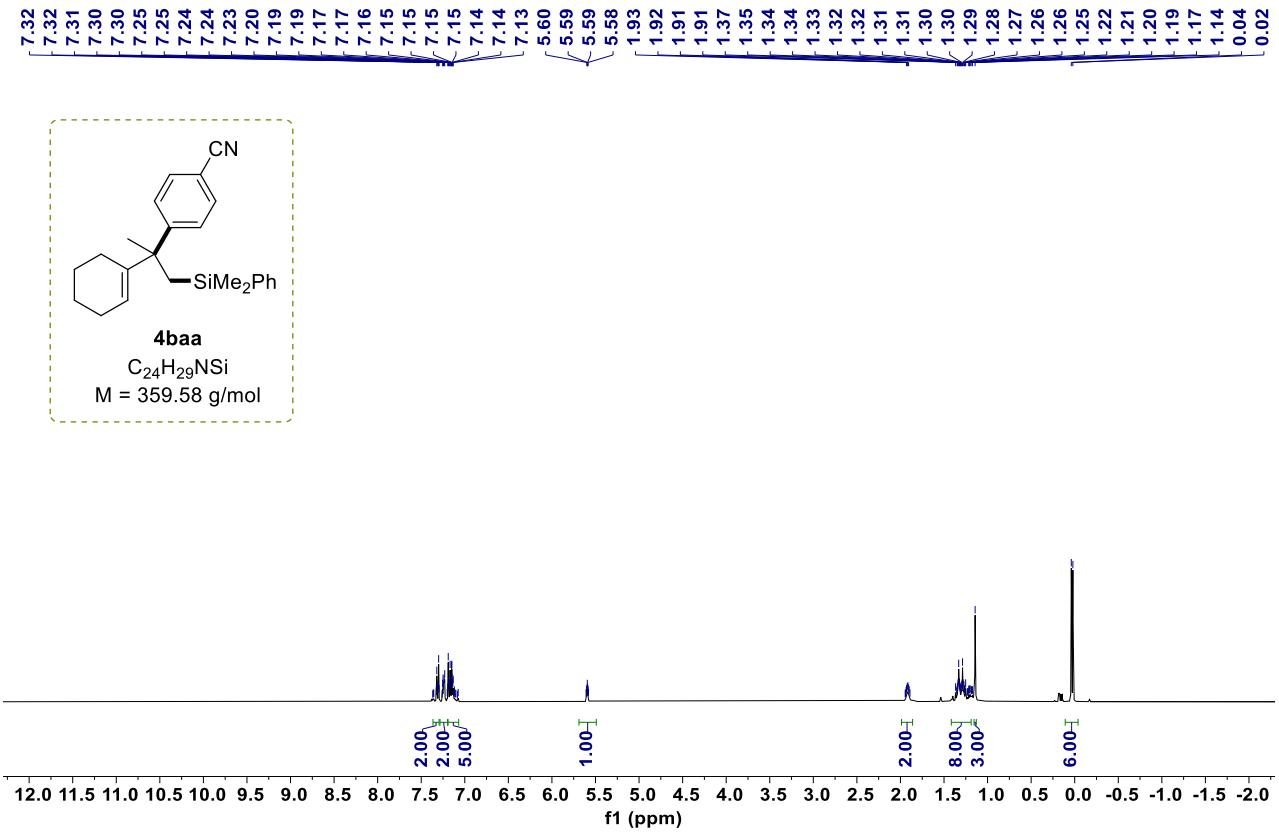
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bz**.



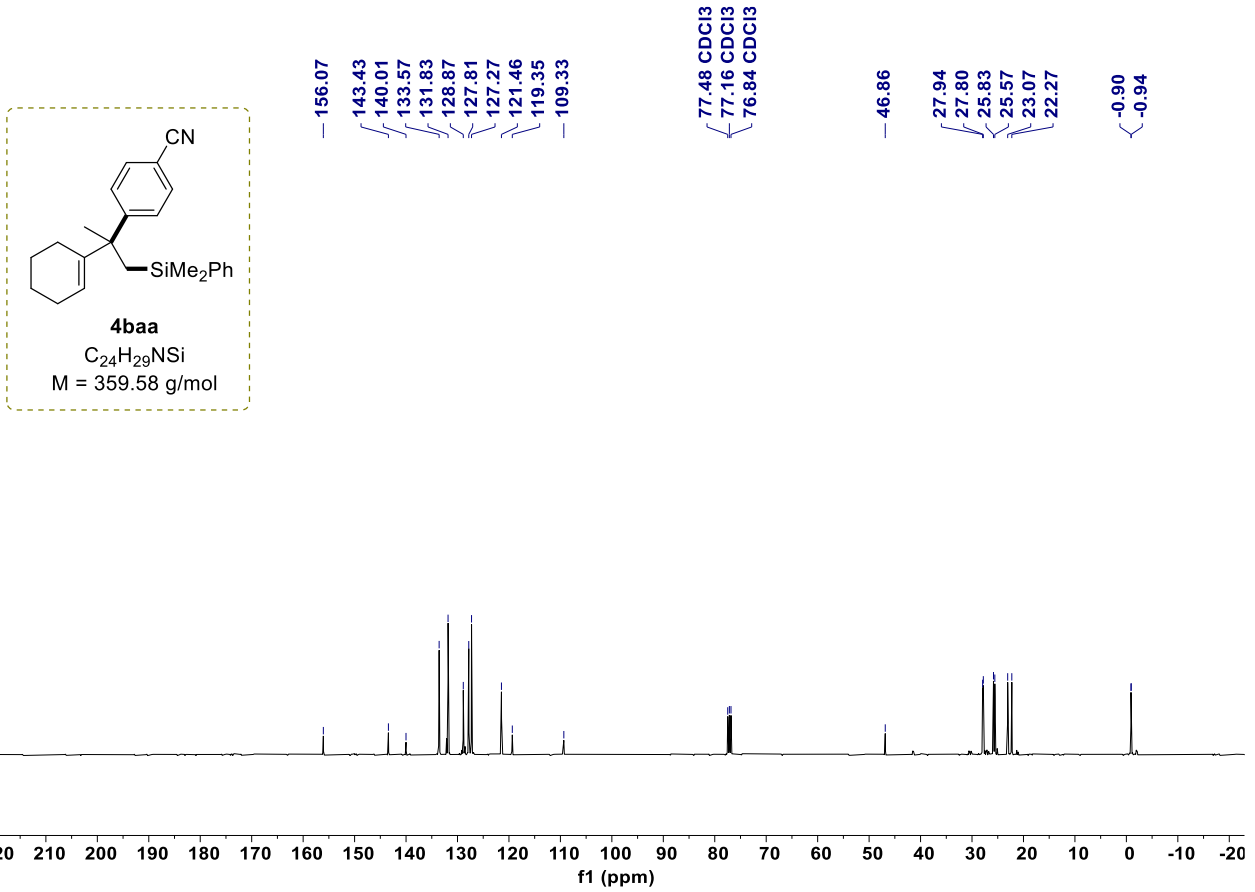
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4baa**.



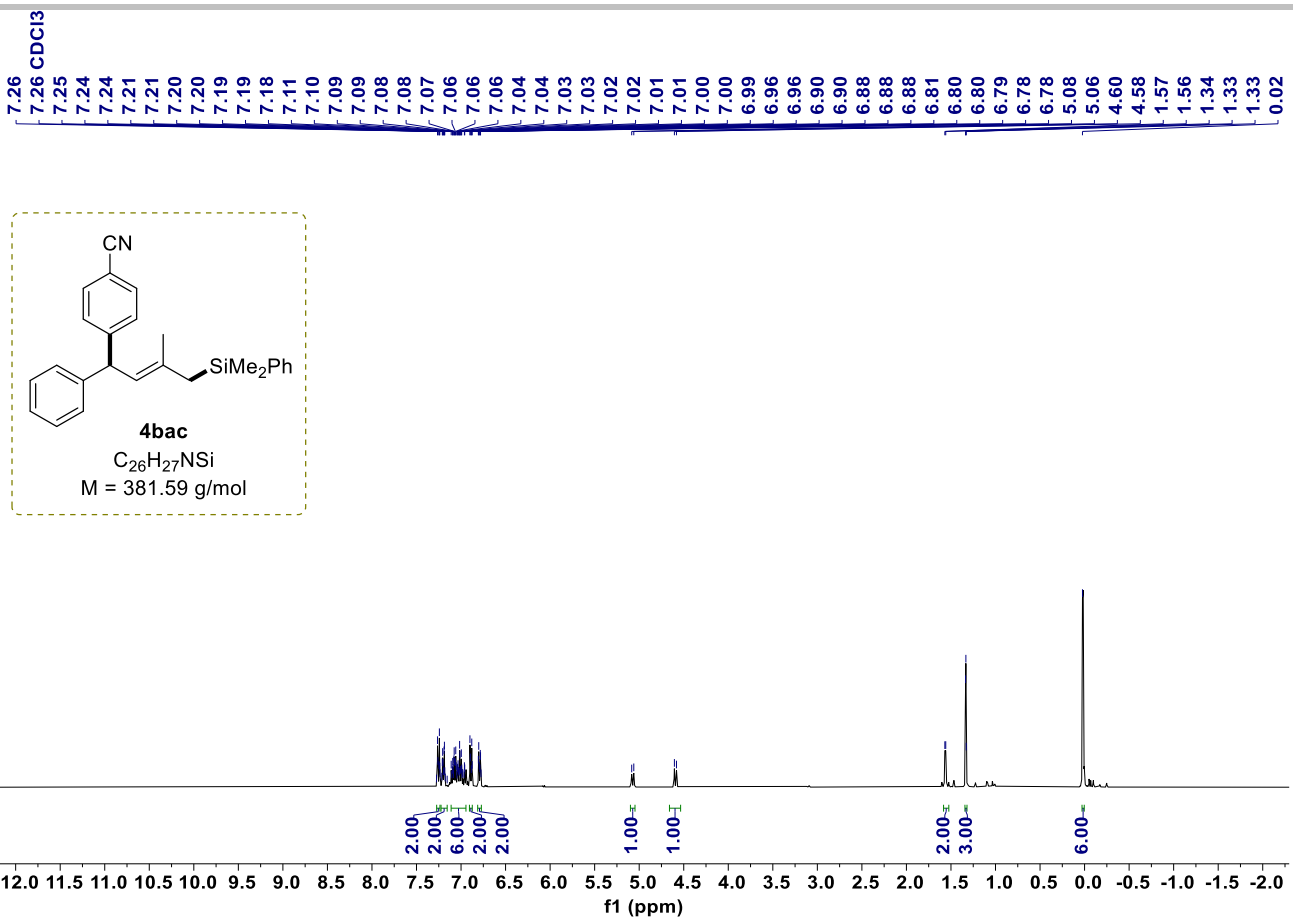
C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4baa**.



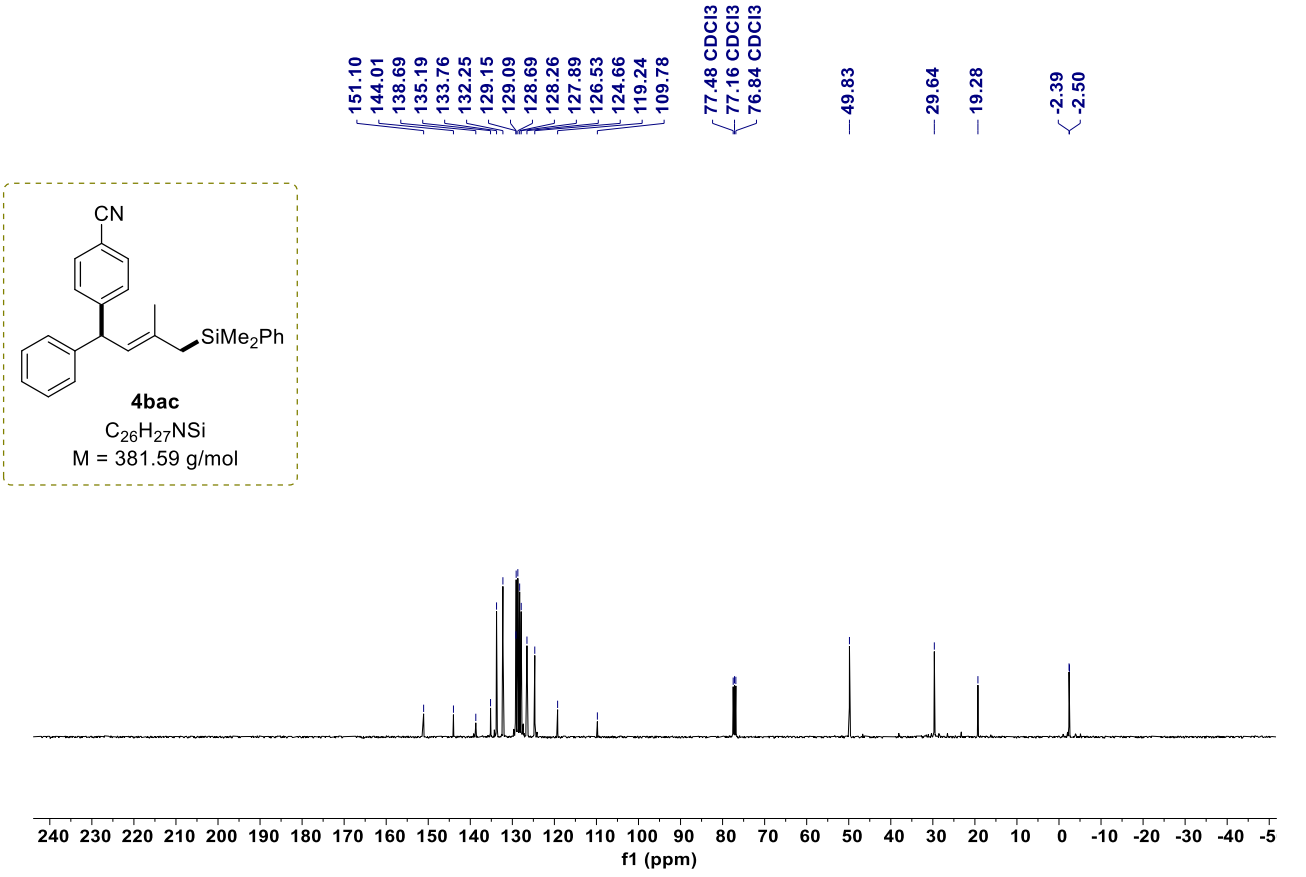
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bab.**



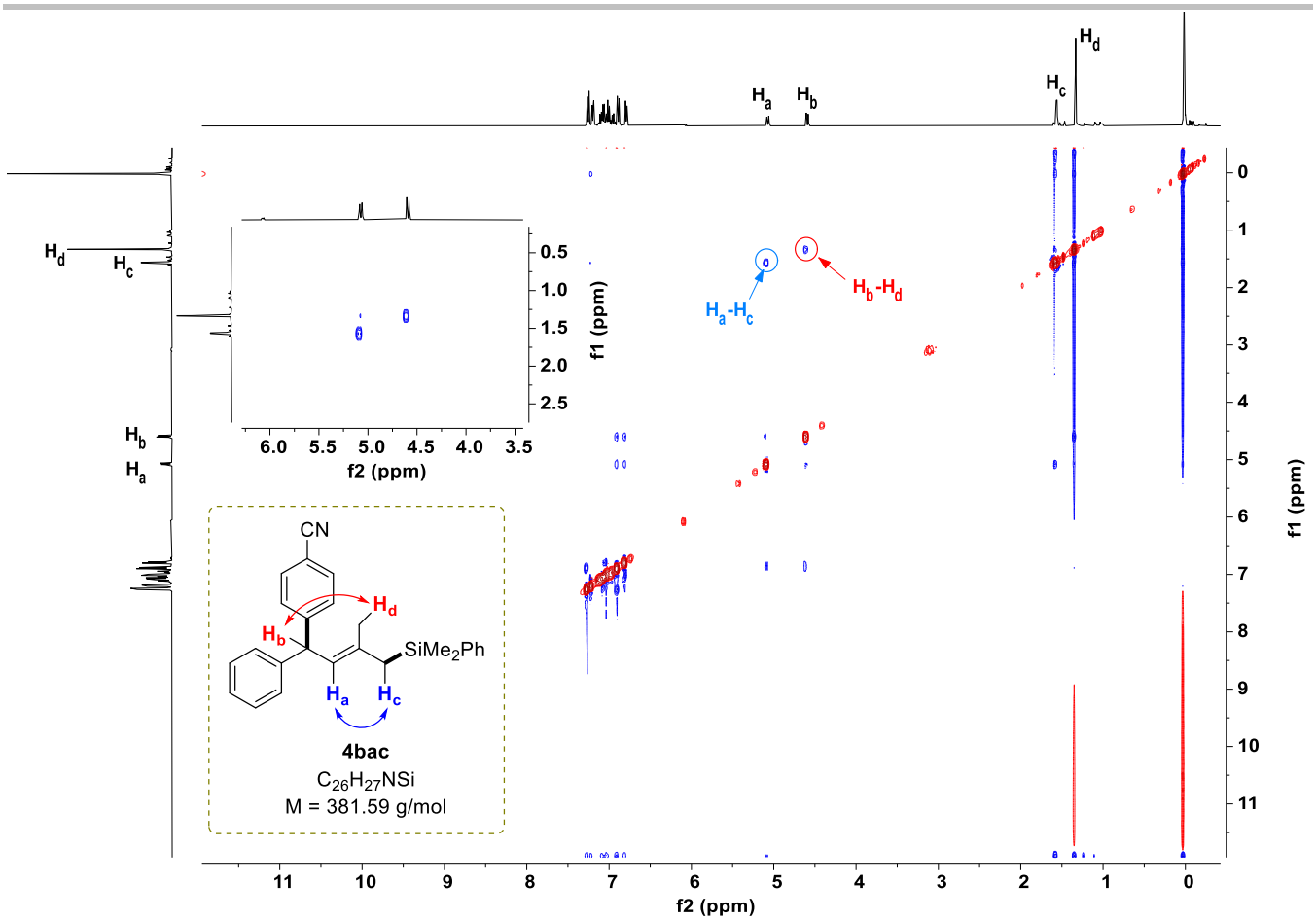
C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bab**.



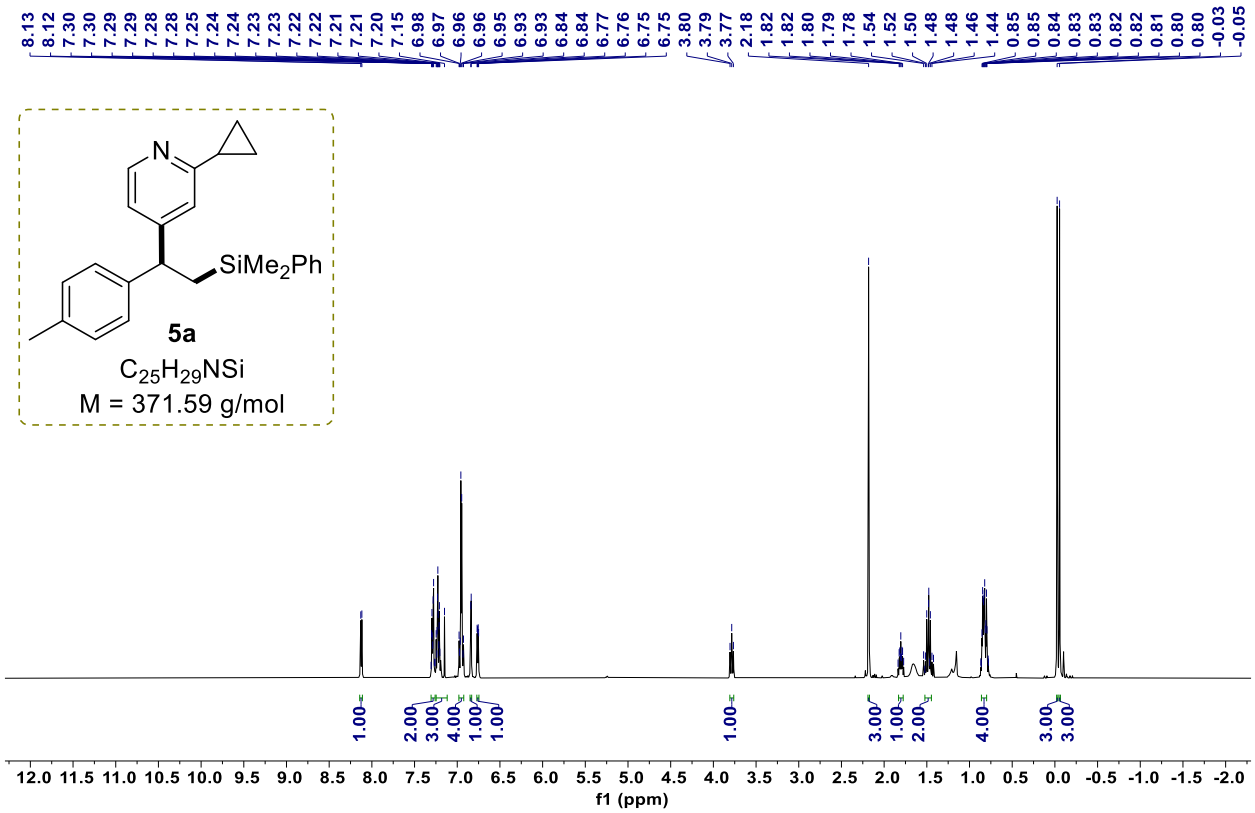
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4bac**.



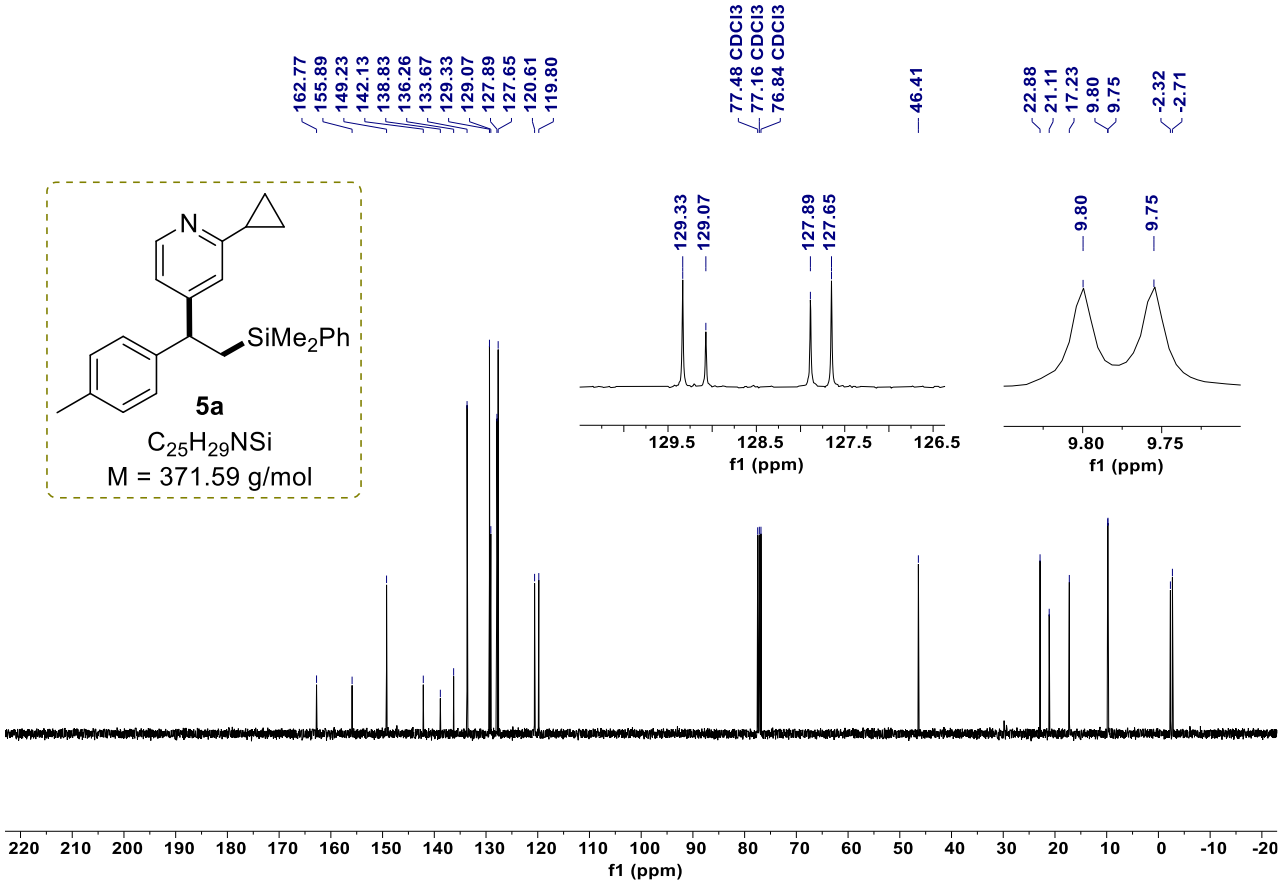
C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4bac**.



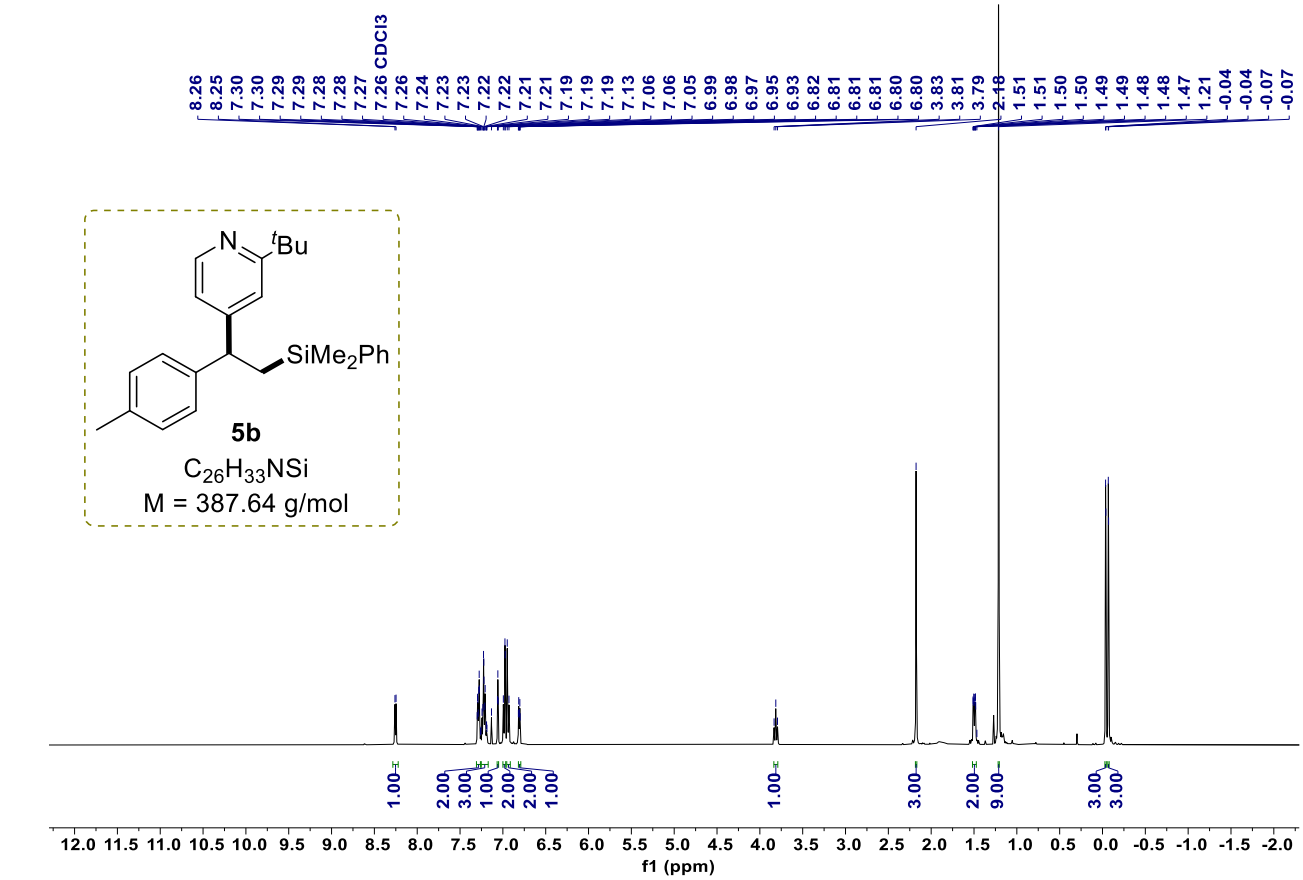
2D NOE spectrum (400 MHz, $CDCl_3$) of compound **4bac**



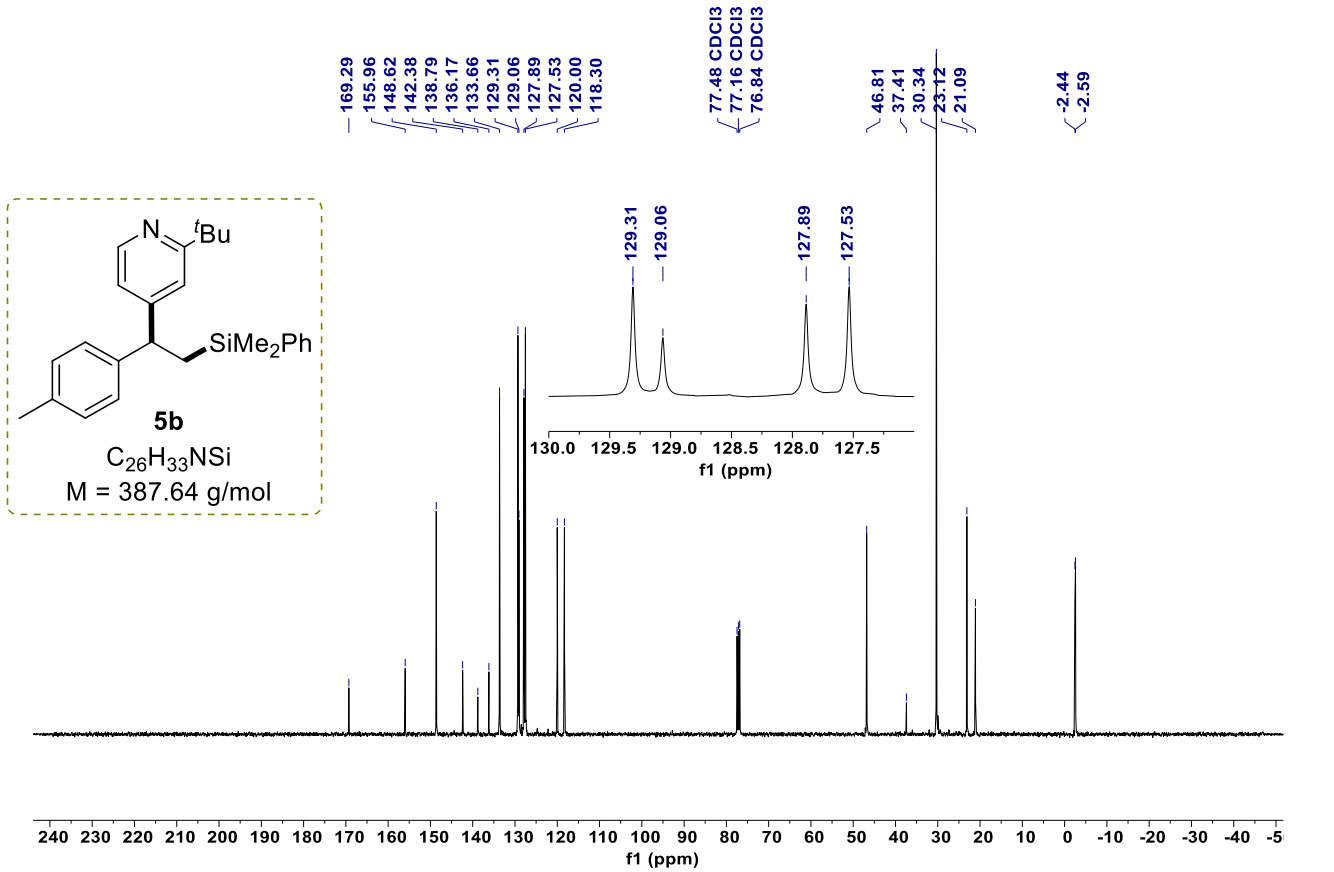
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5a.**



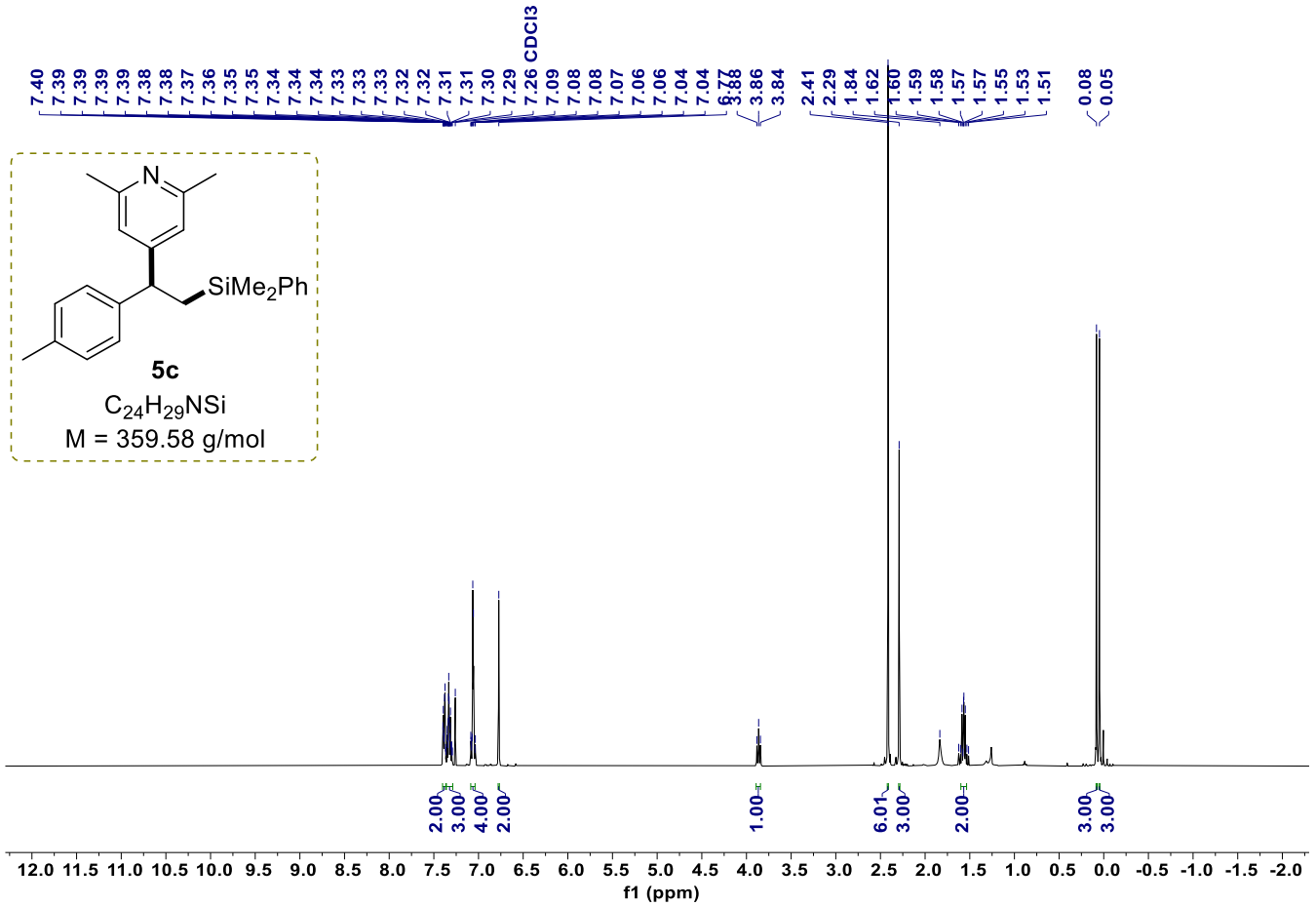
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5a**.



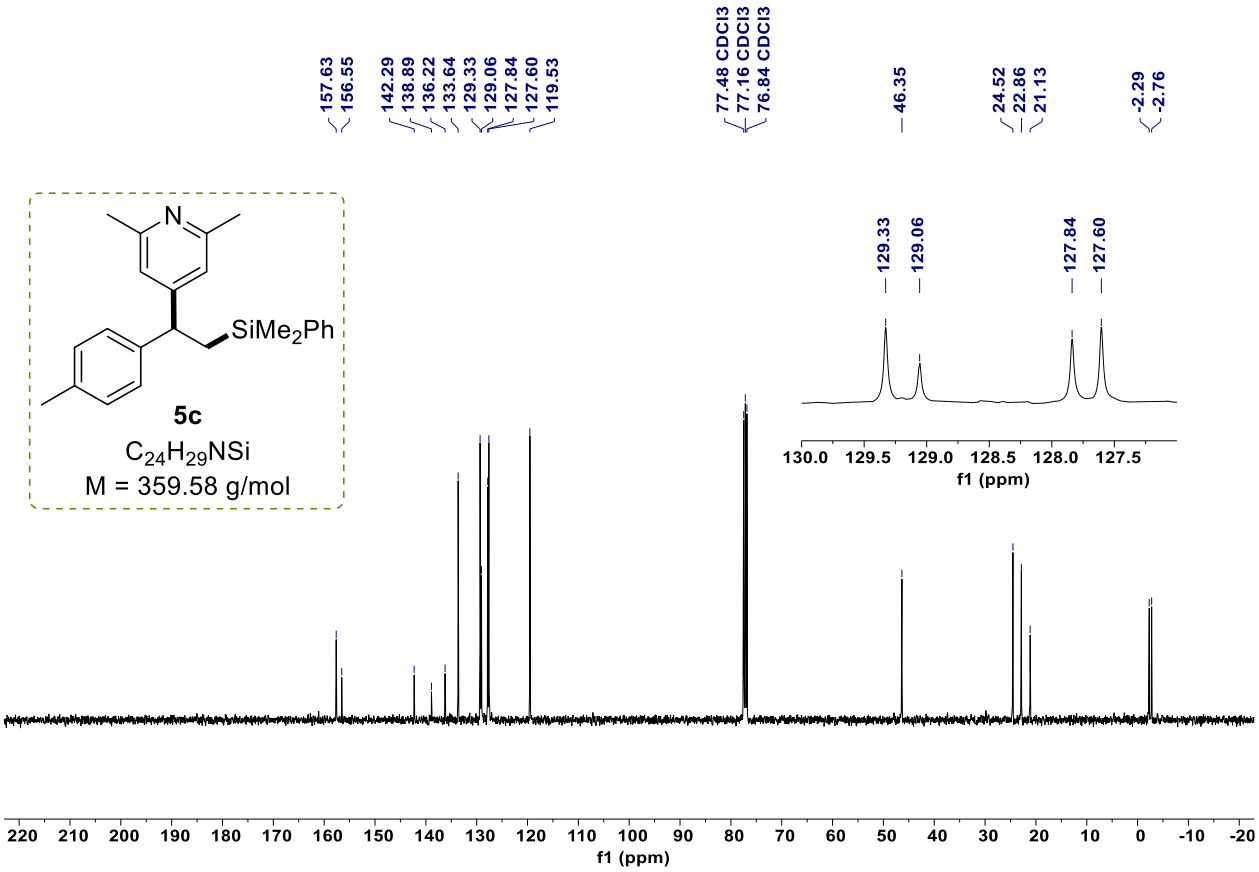
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5b**.



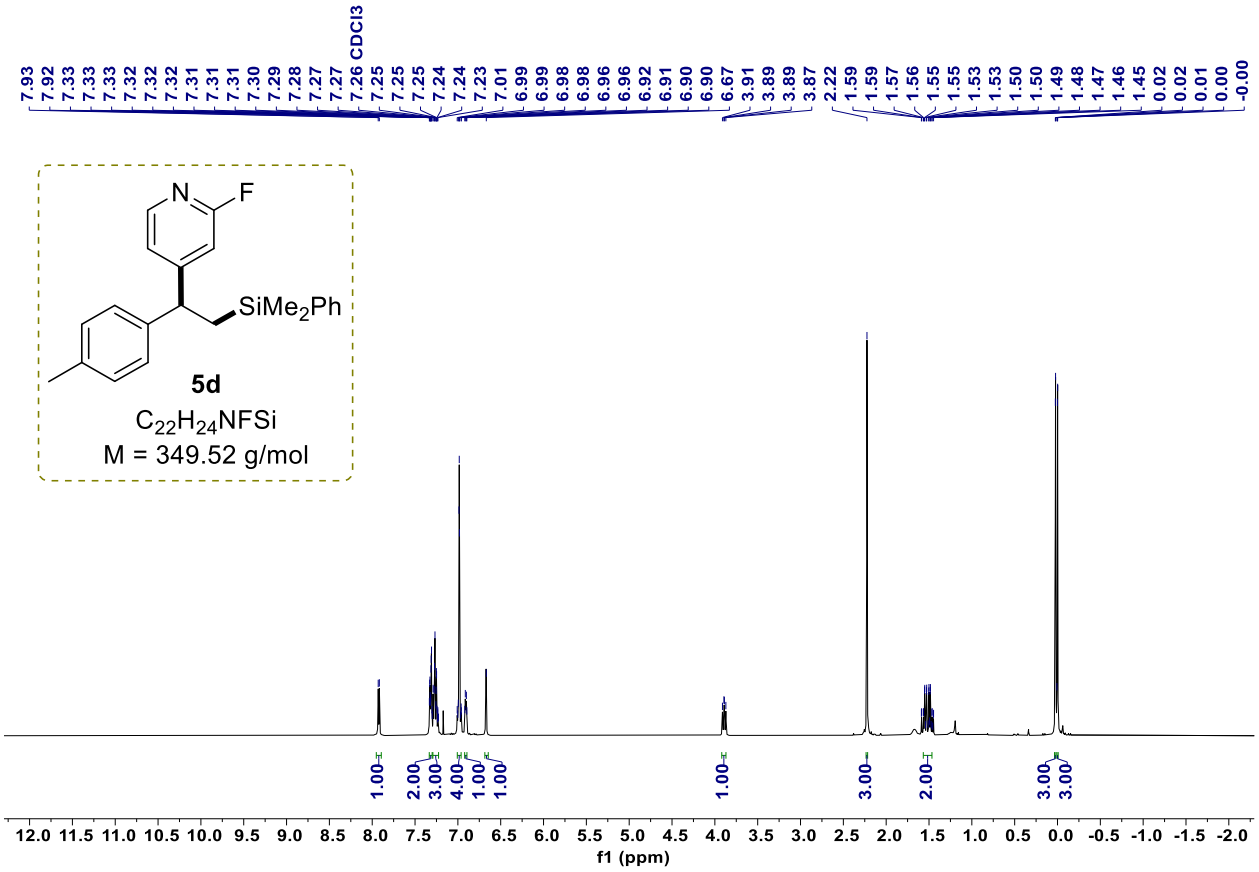
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5b**.



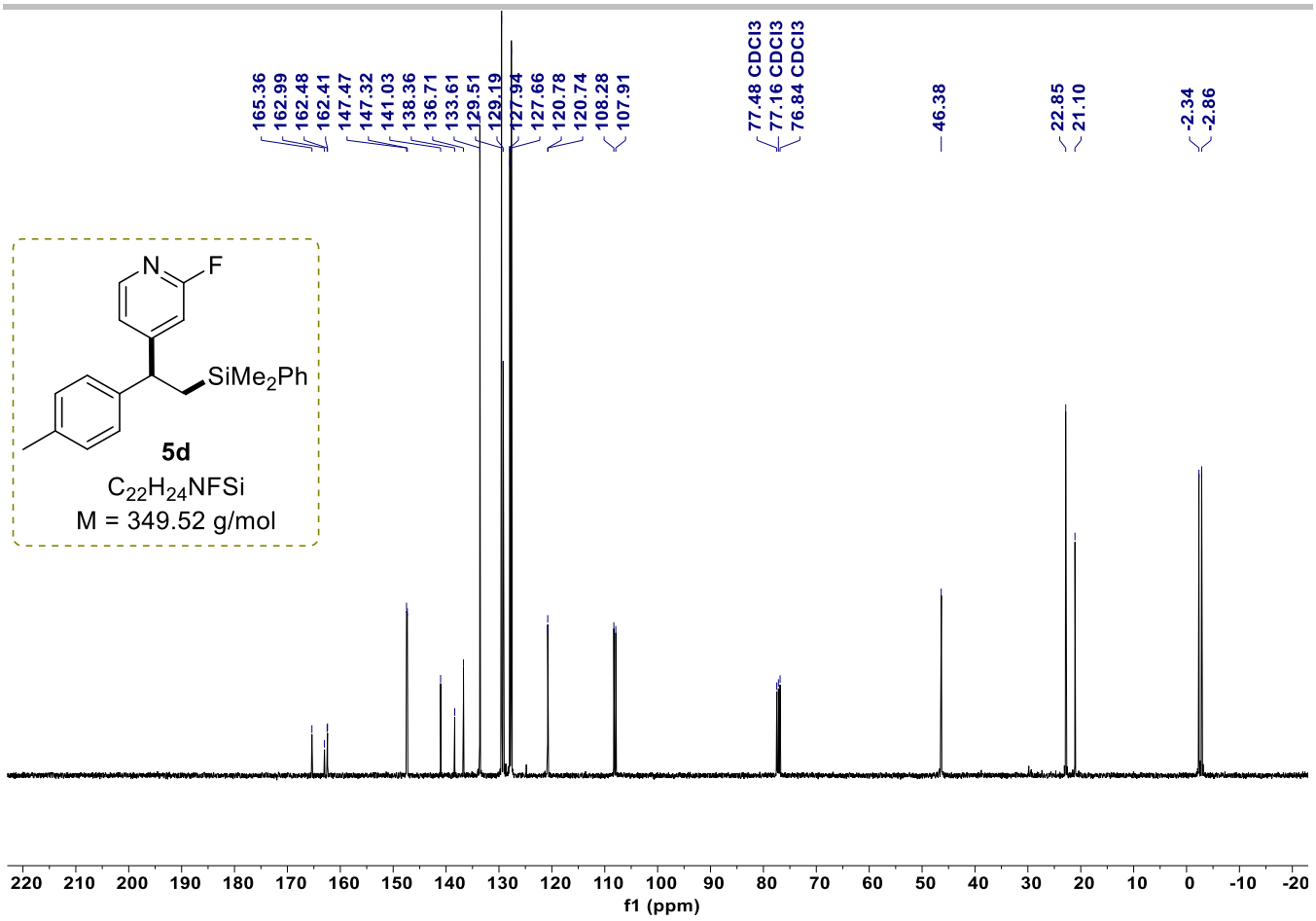
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5c.**



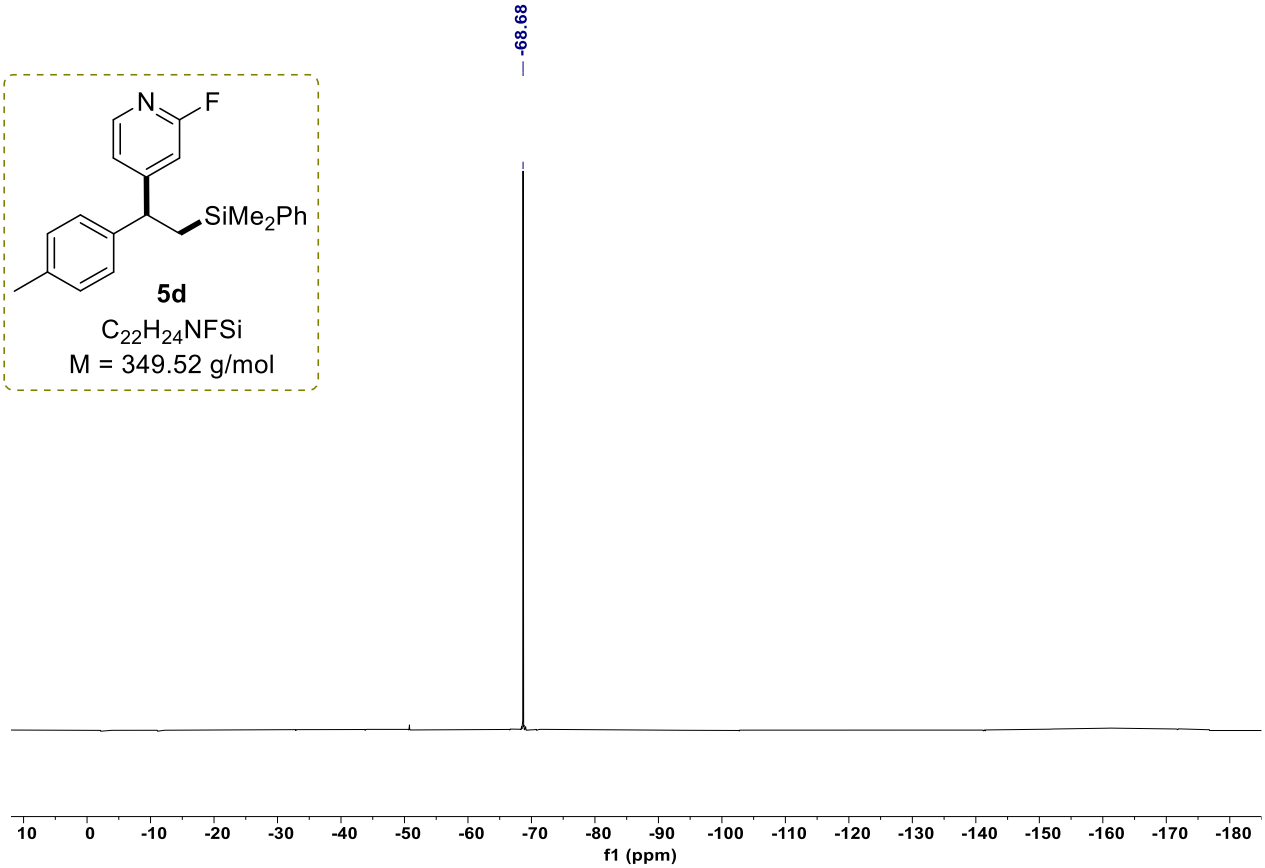
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5c**.



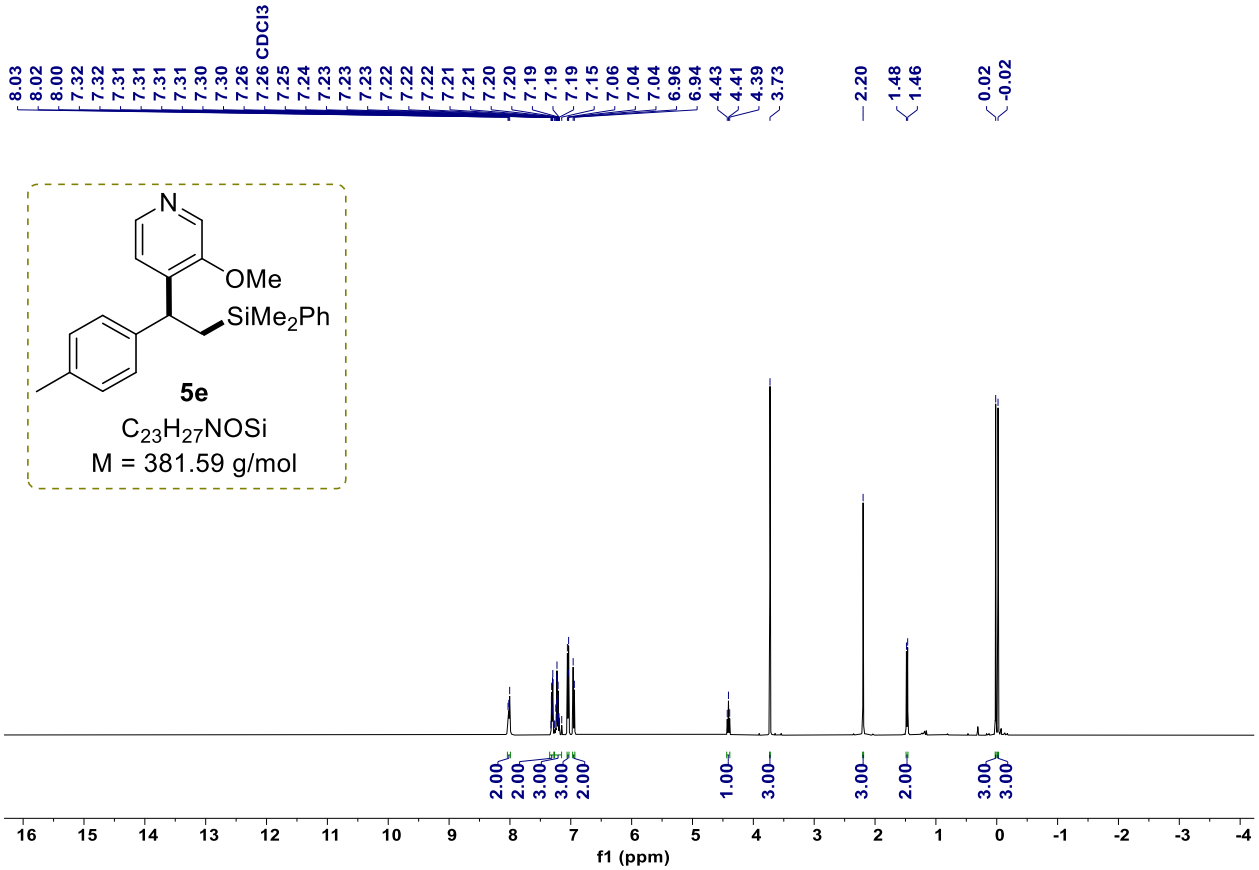
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5d.**



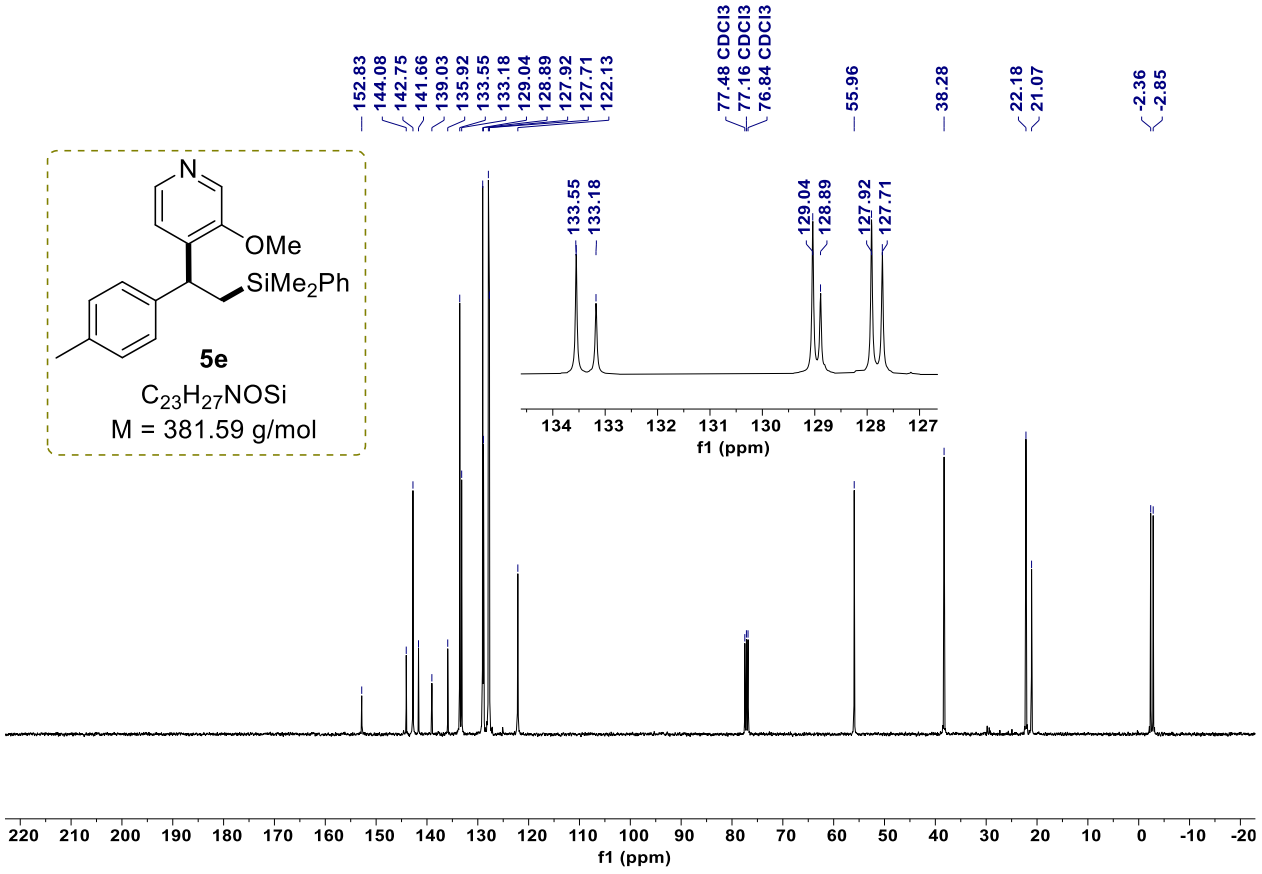
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5d**.



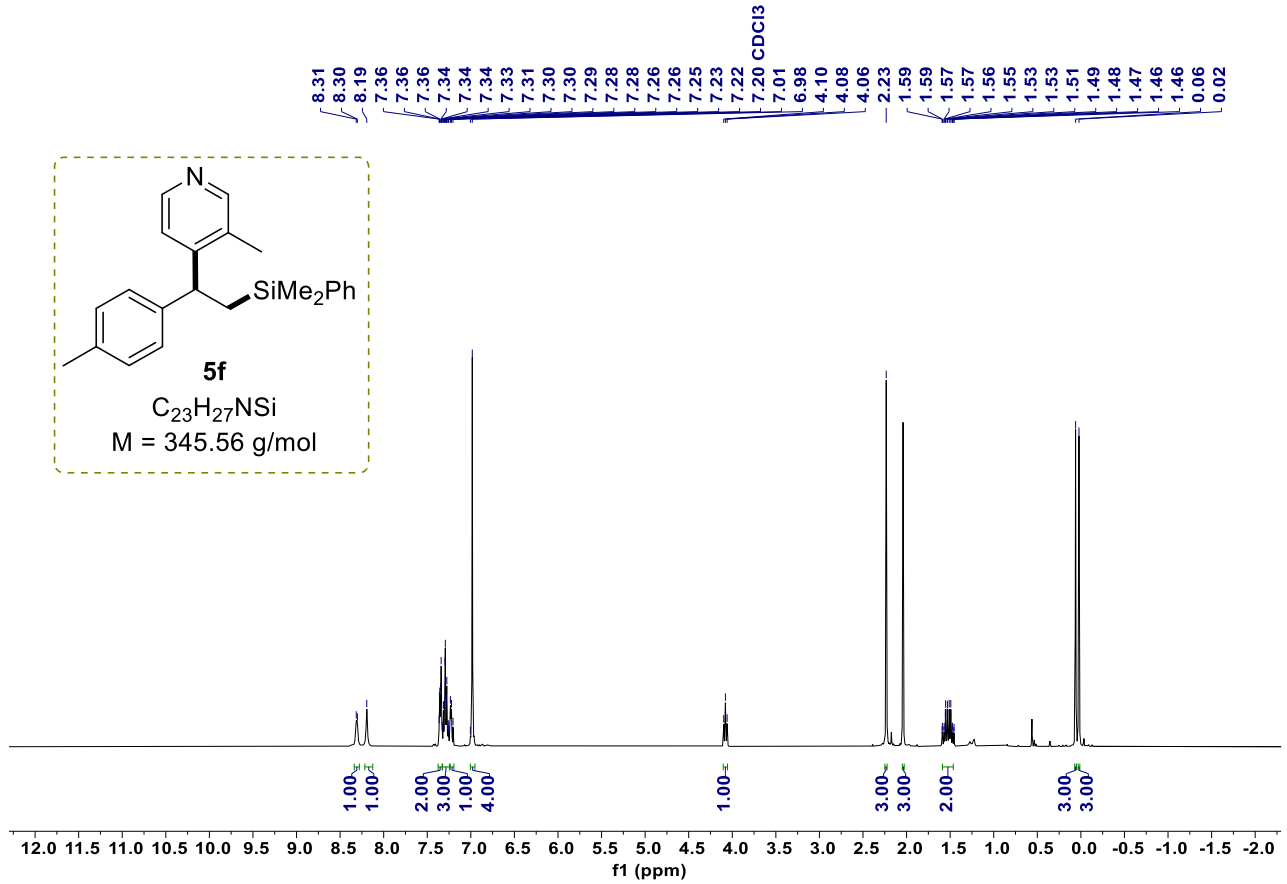
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5e**.



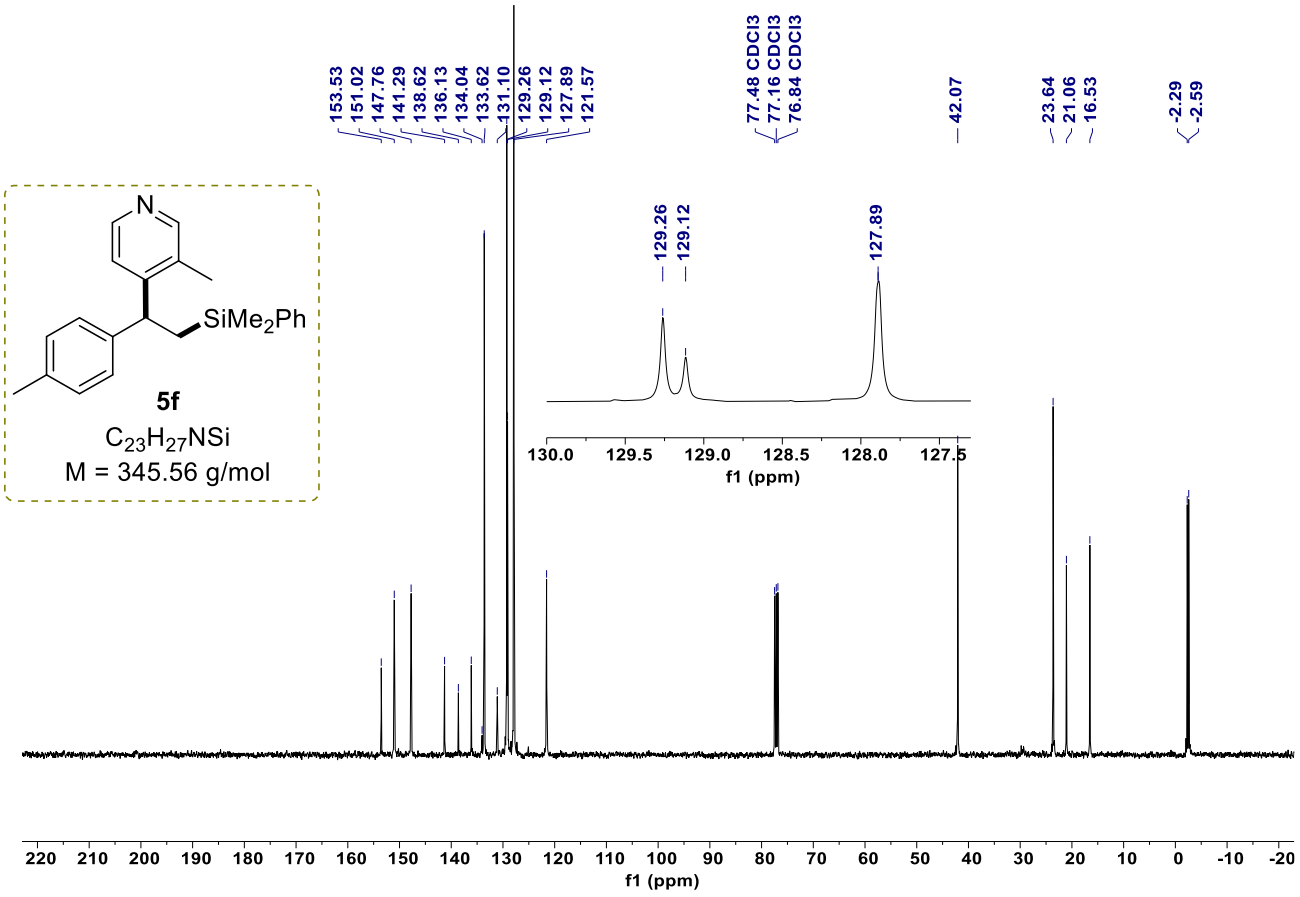
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5e.**



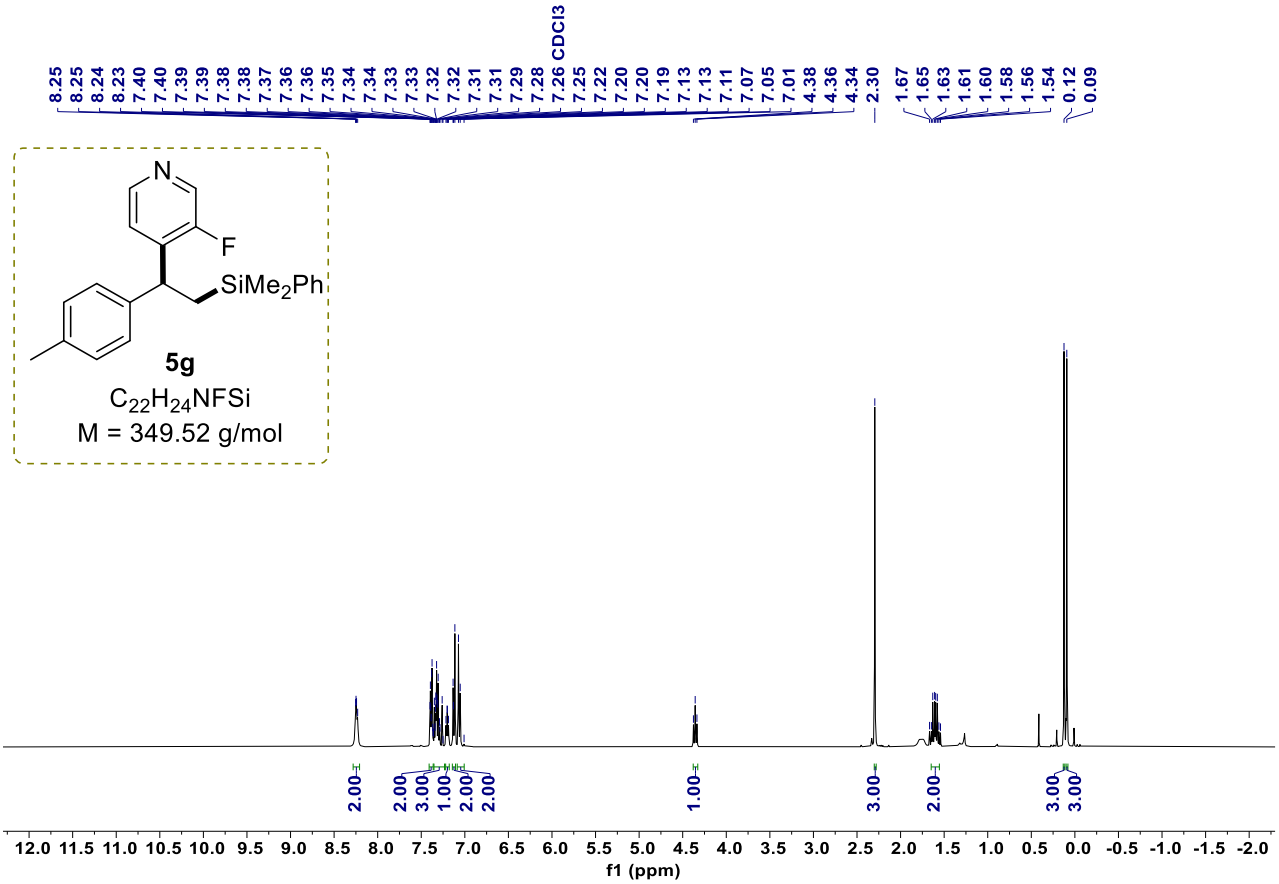
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5e**.



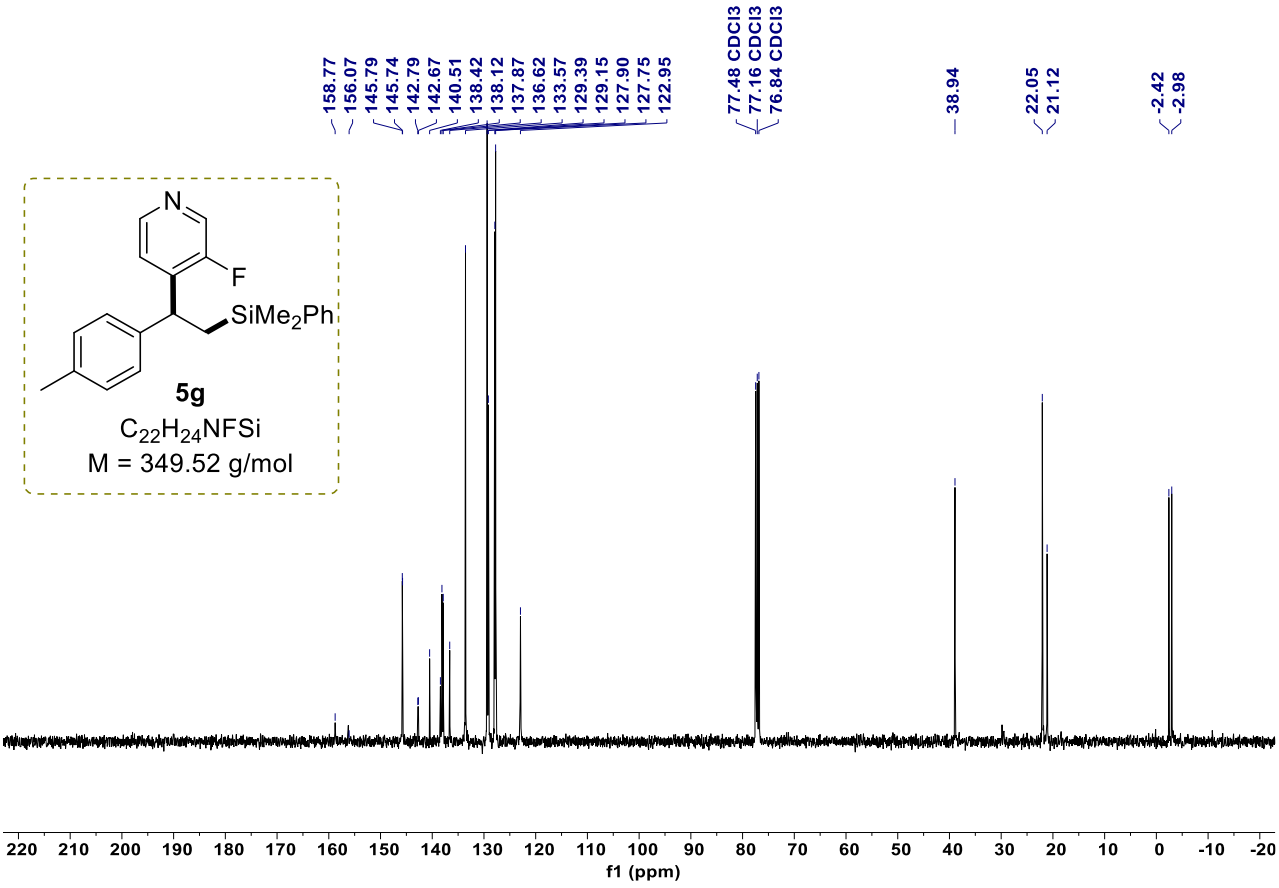
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5f.**



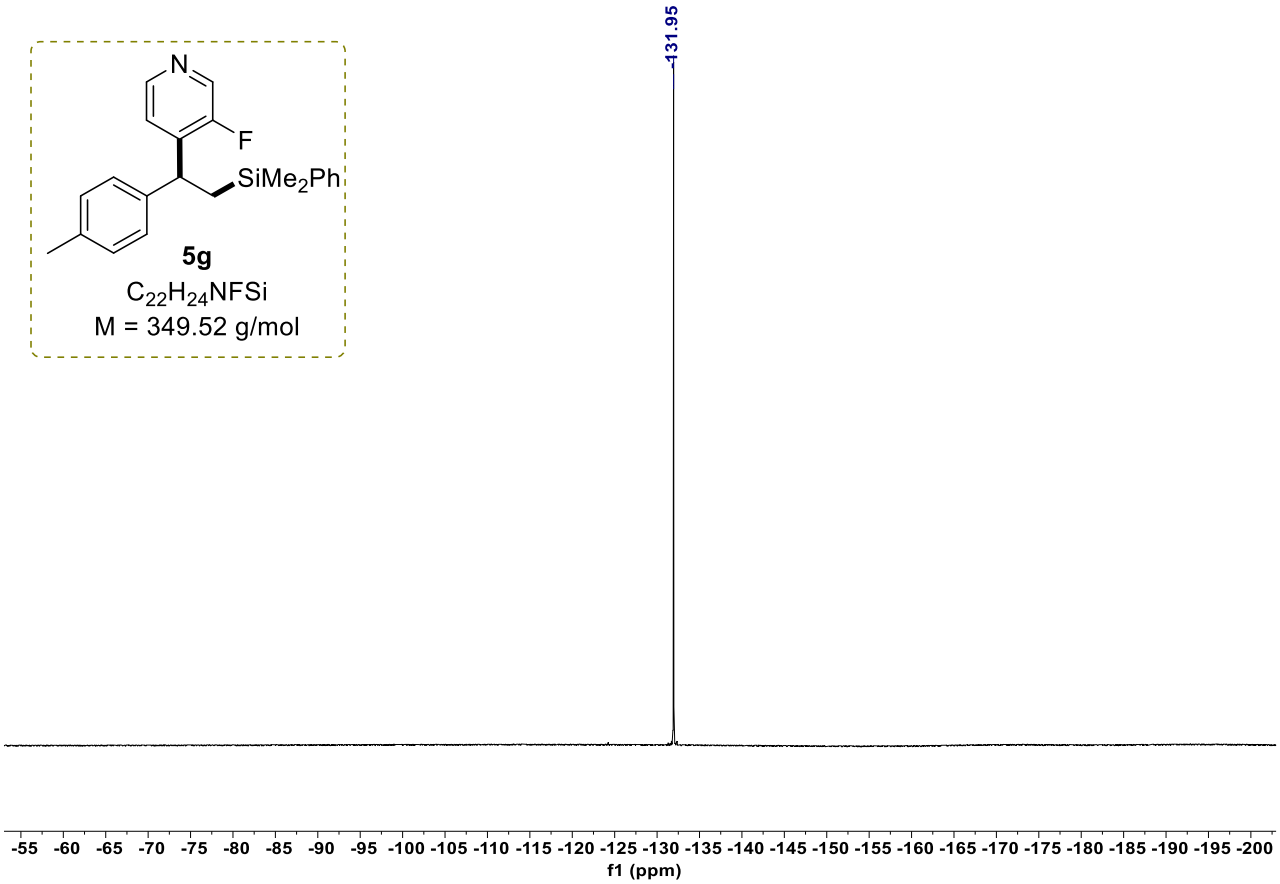
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5f**.



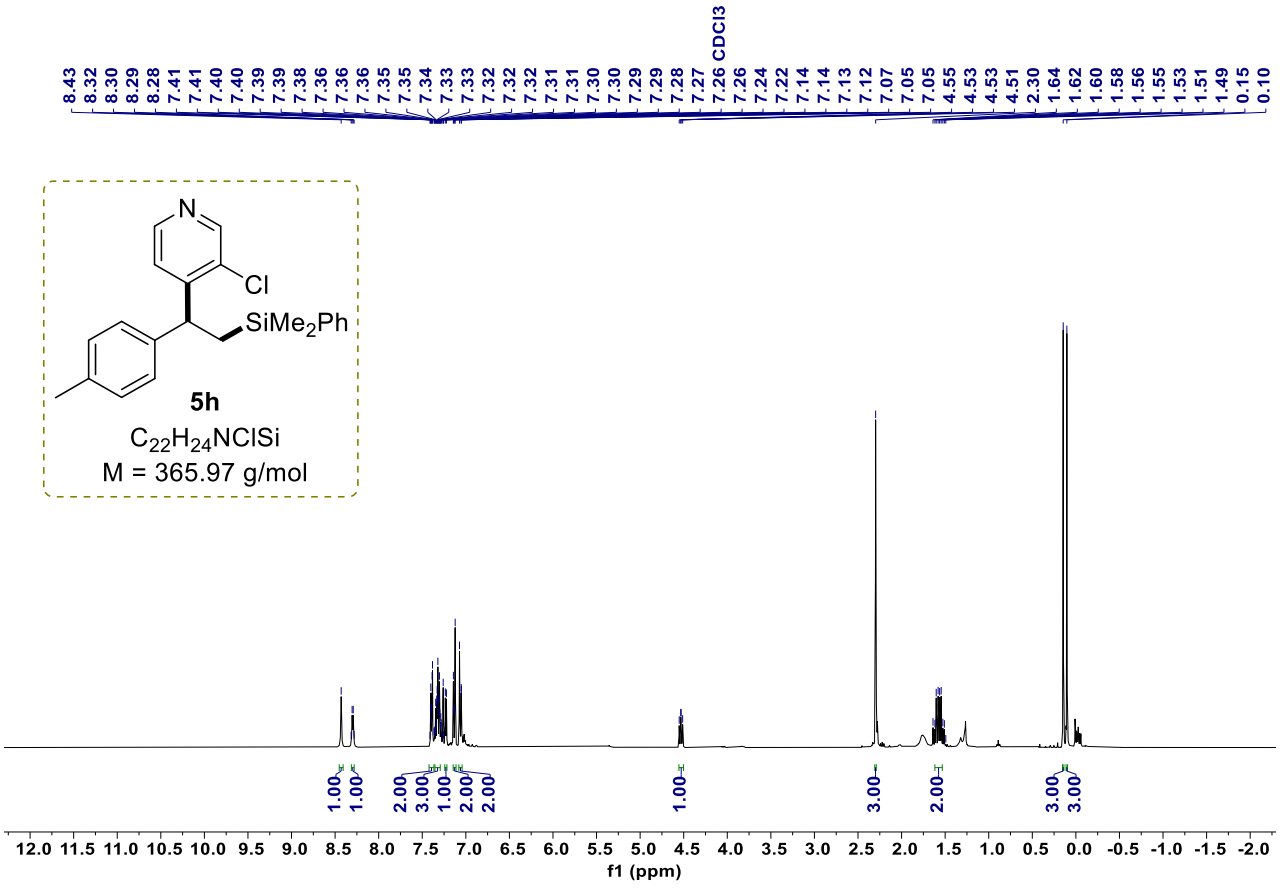
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5g.**



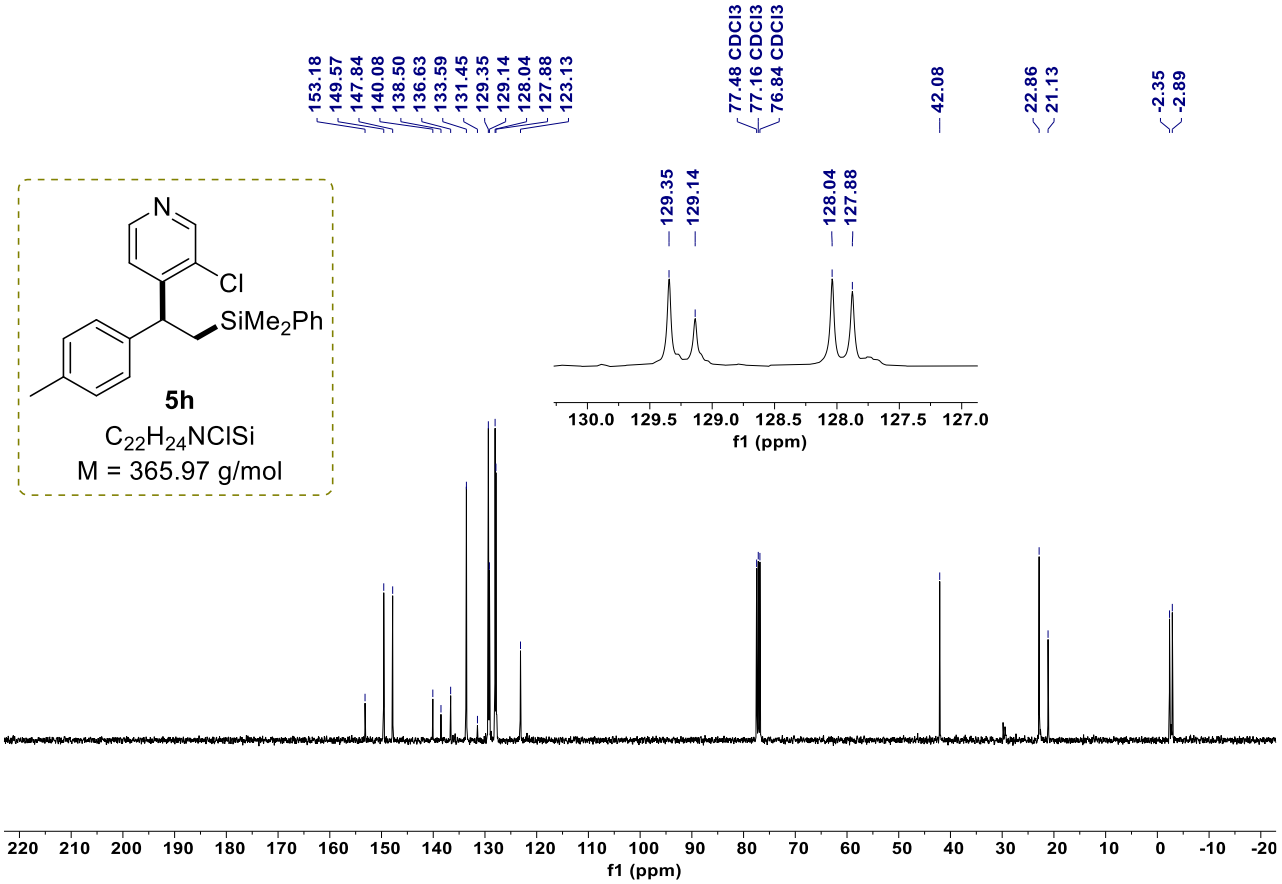
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5g**.



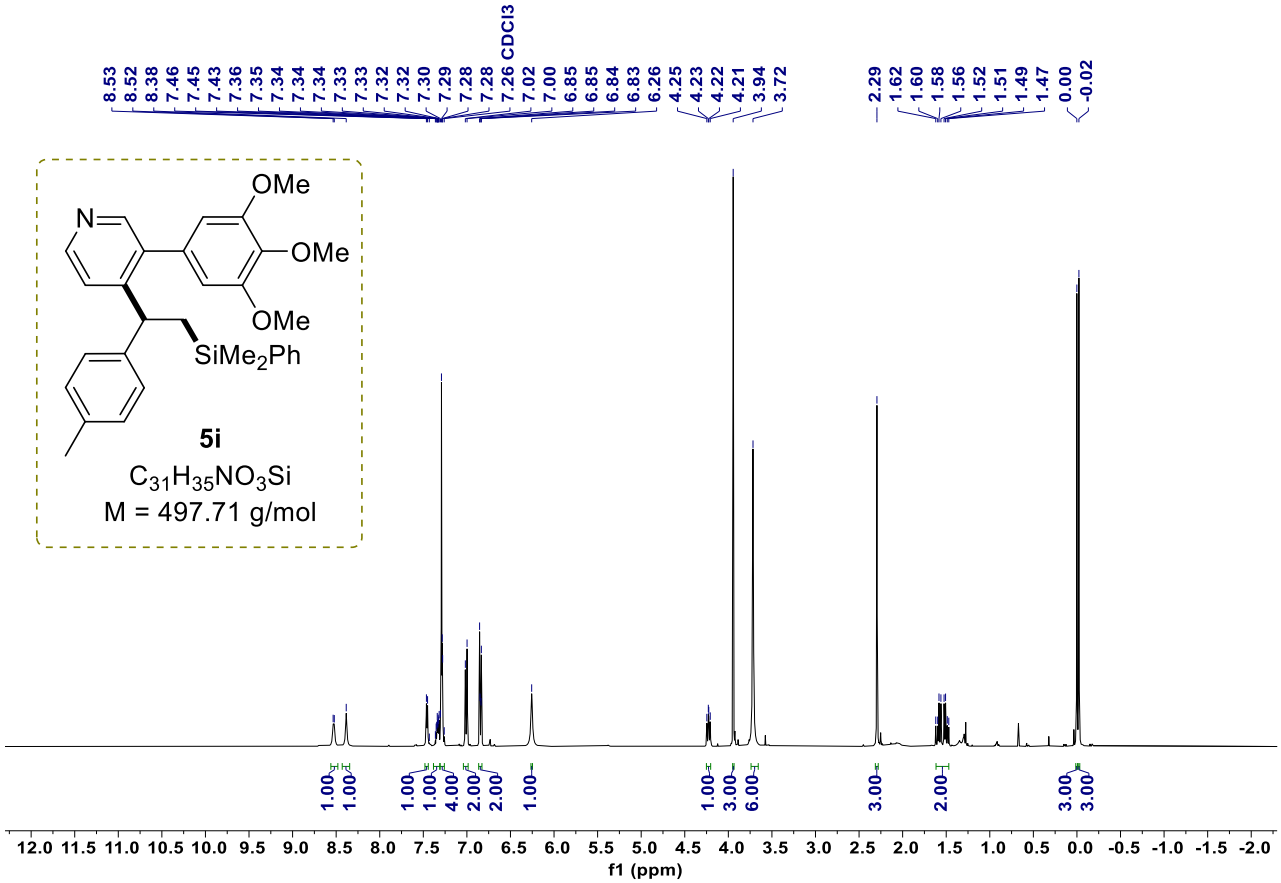
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5g**.



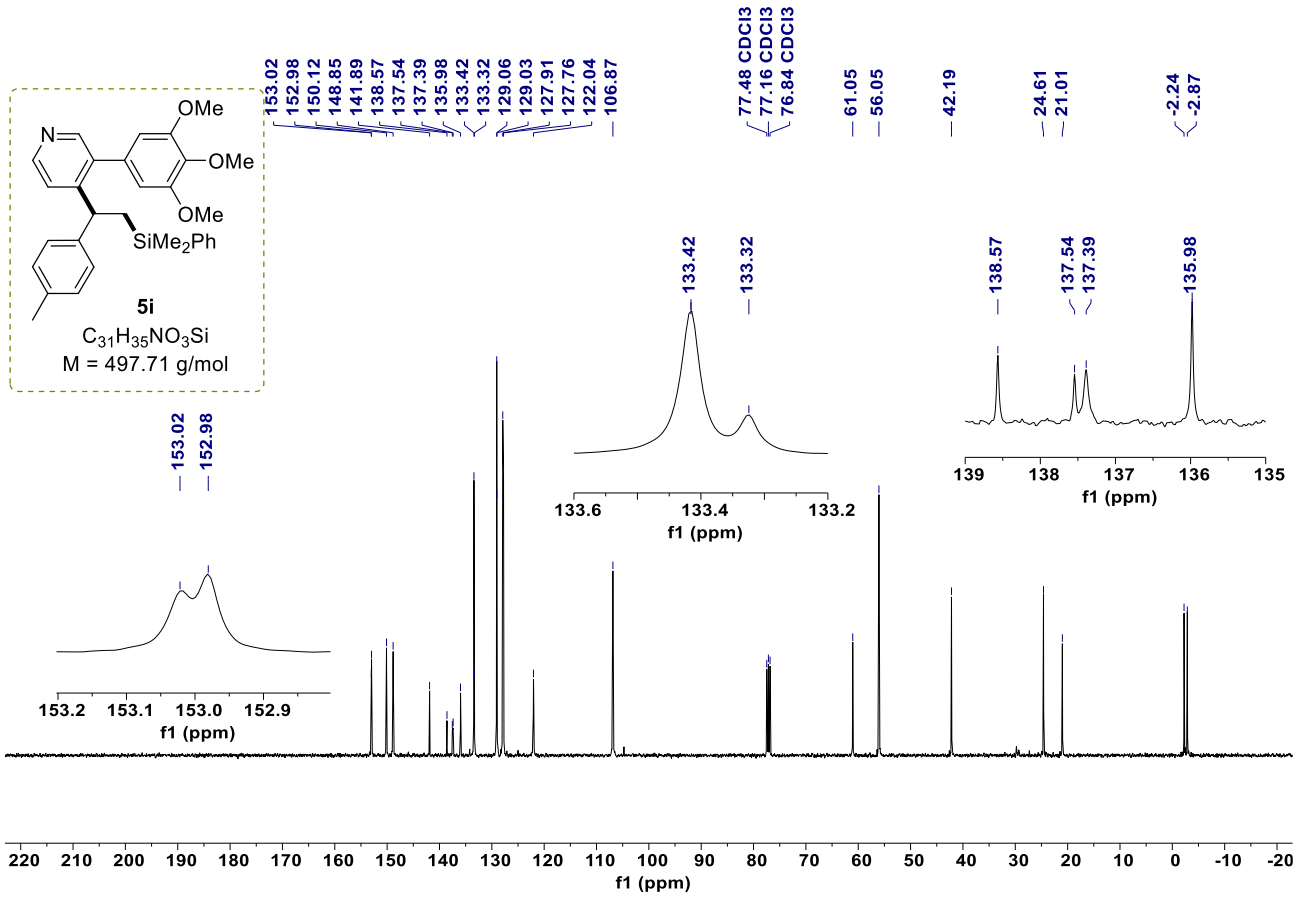
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5h**.



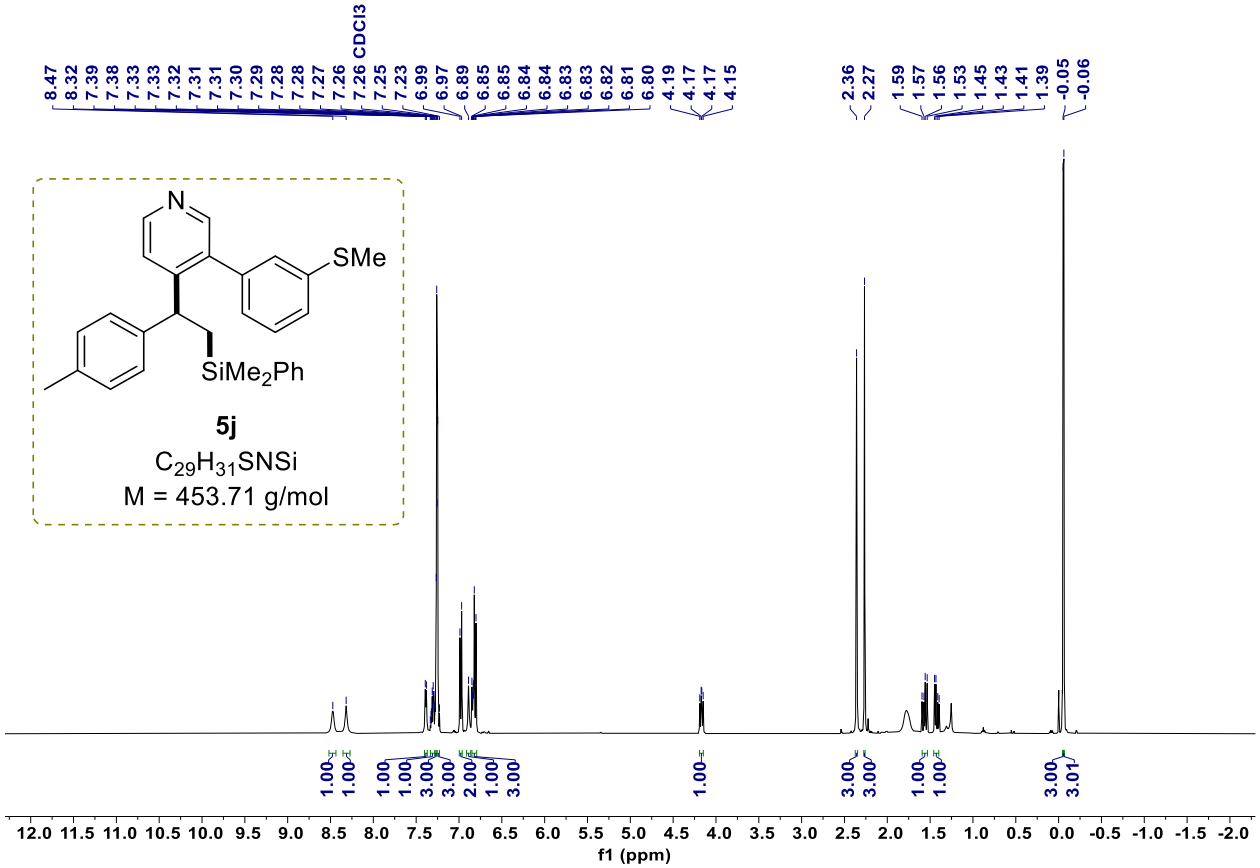
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5h**.



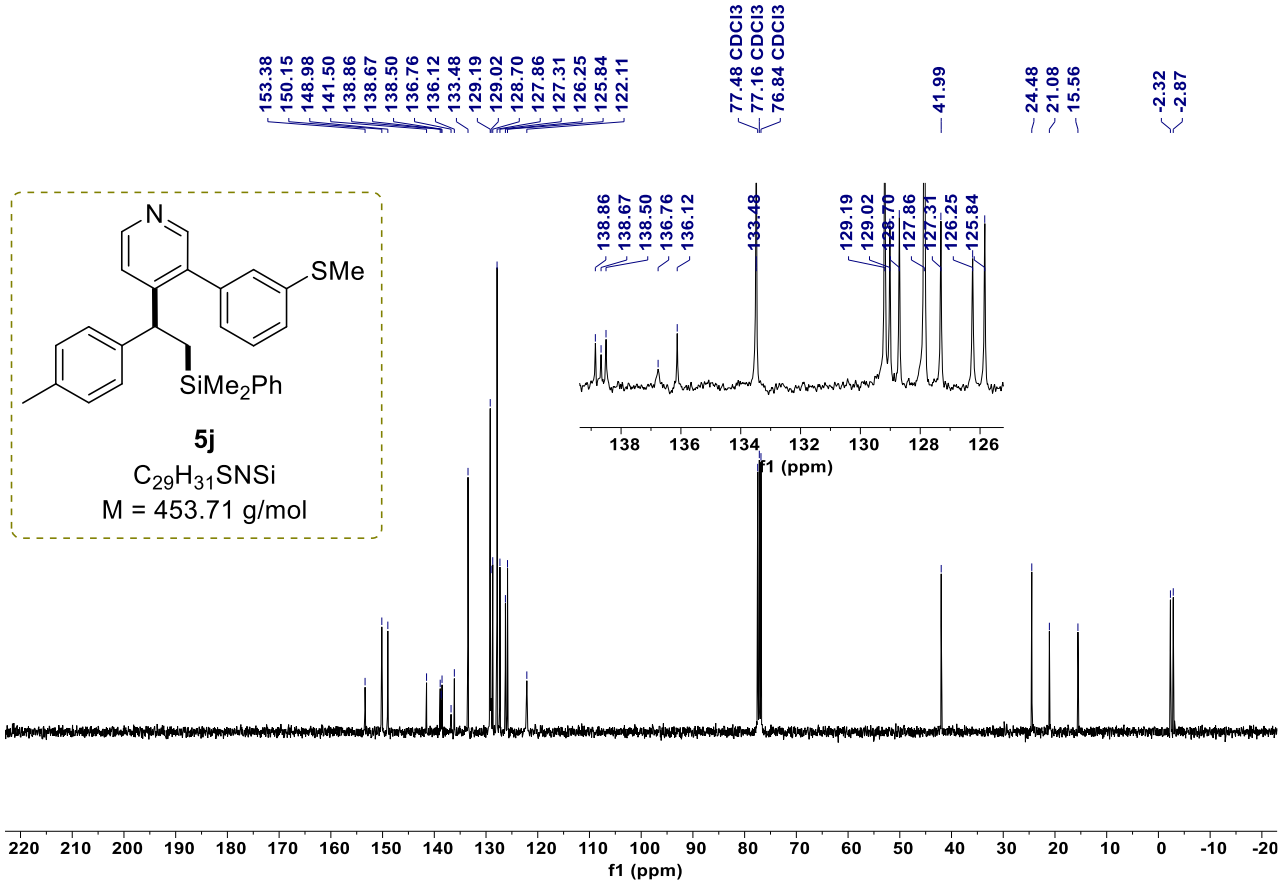
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5i.**



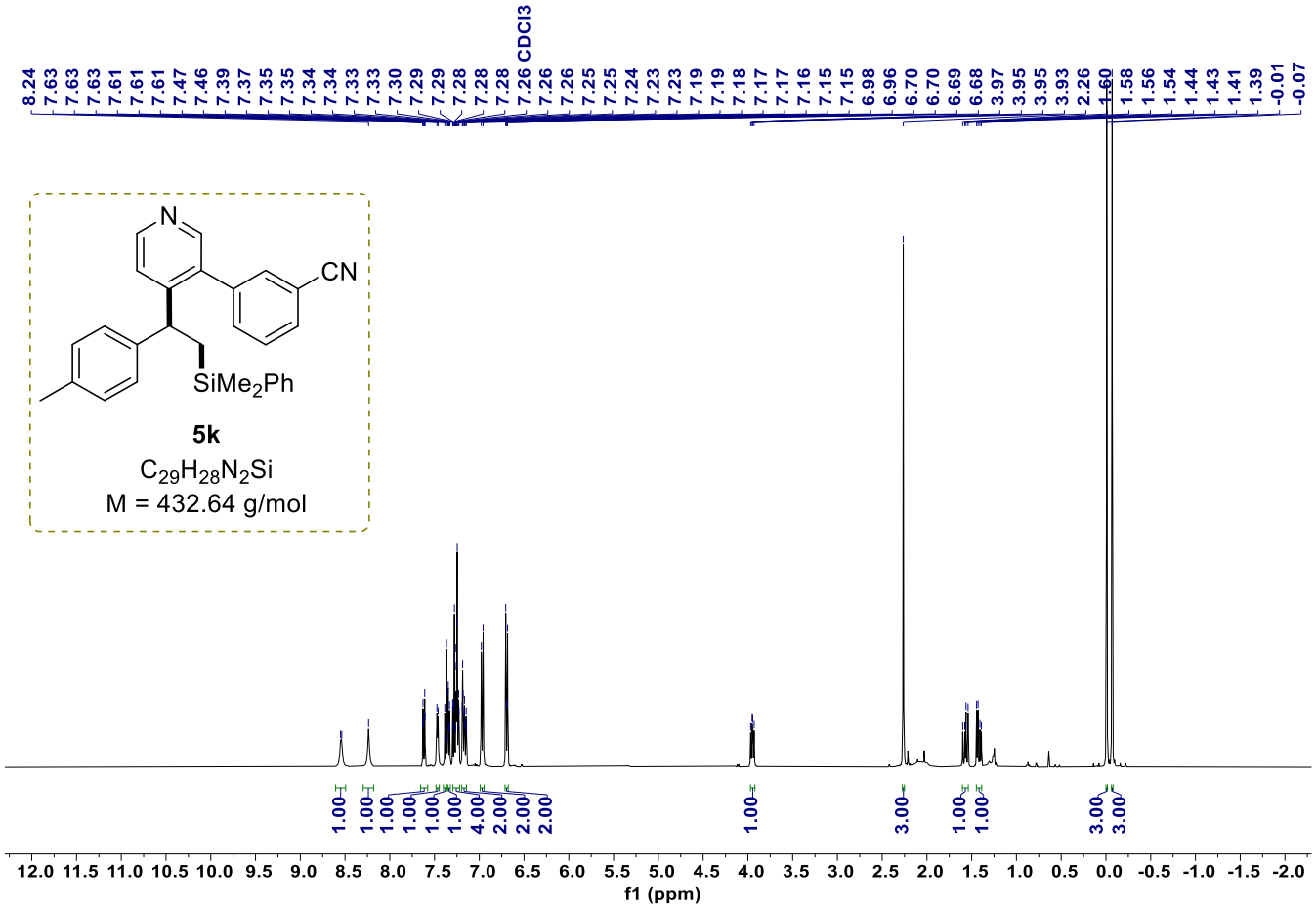
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5i**.



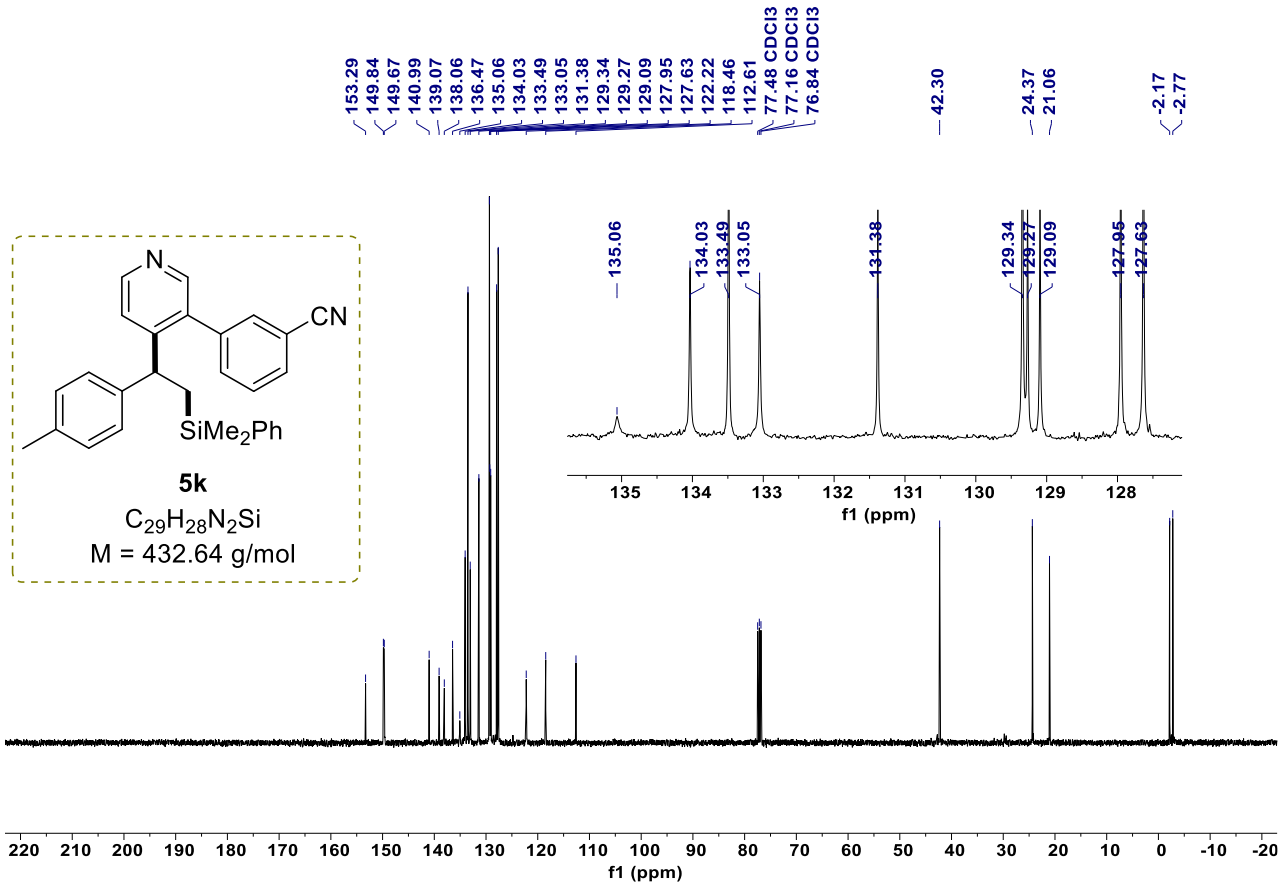
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5j.**



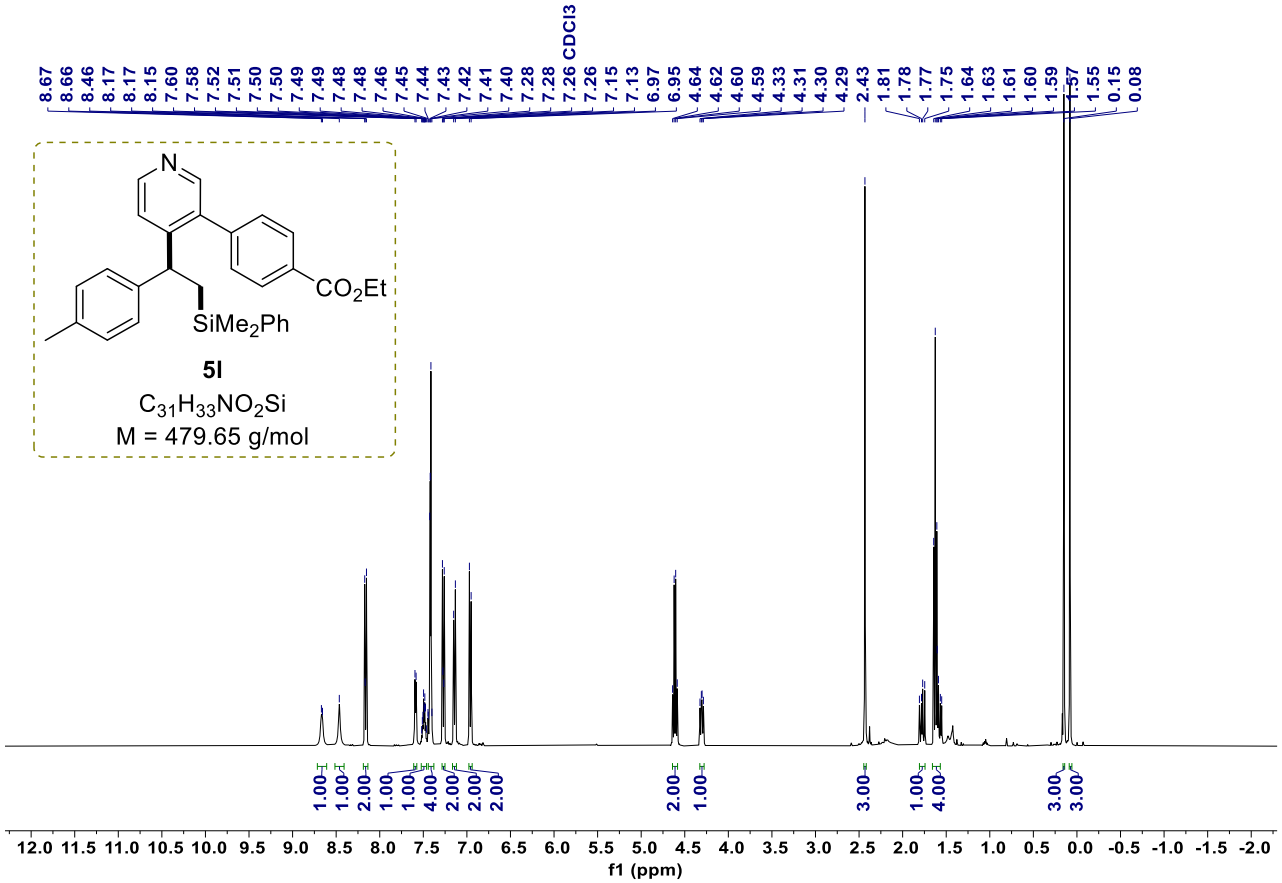
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5j**.



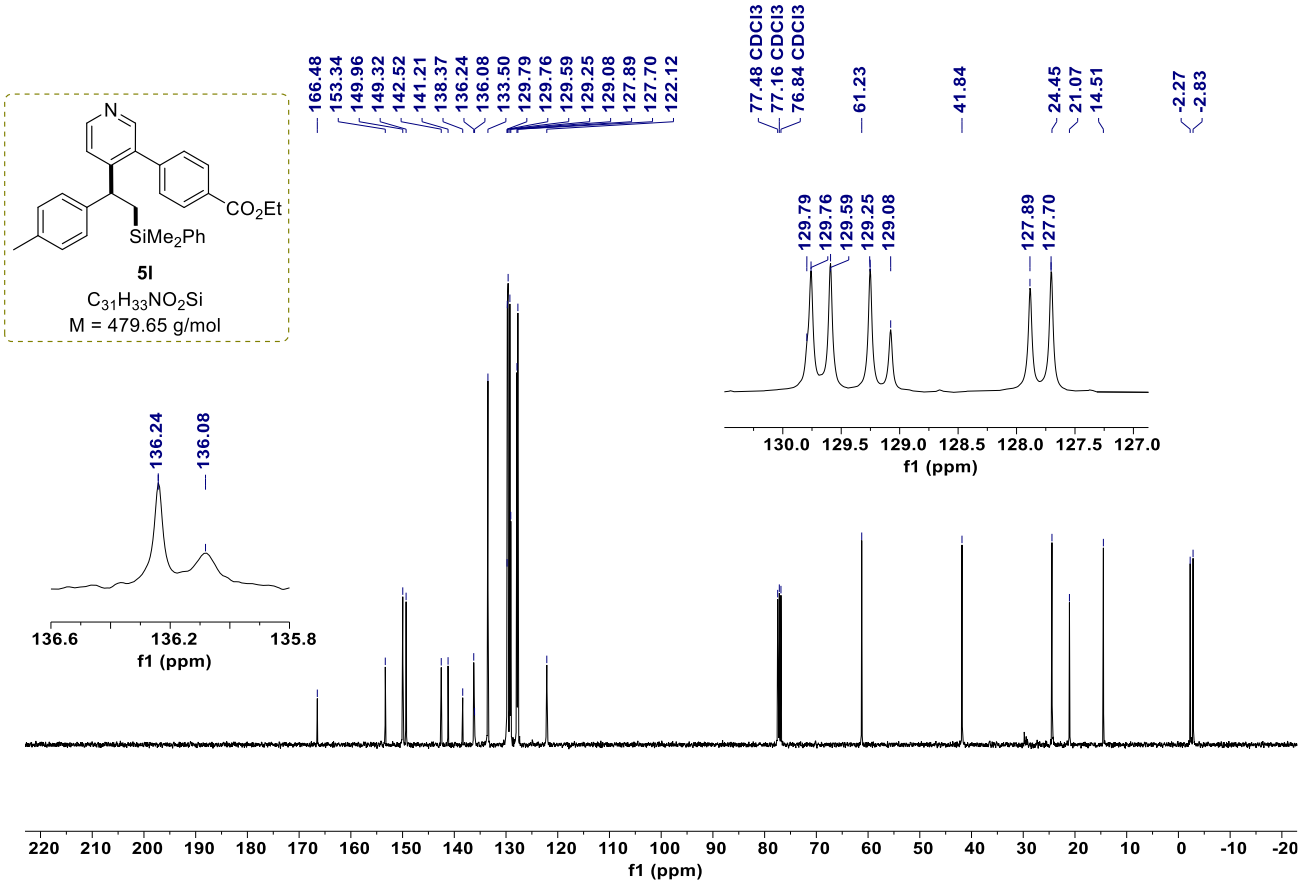
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5k.**



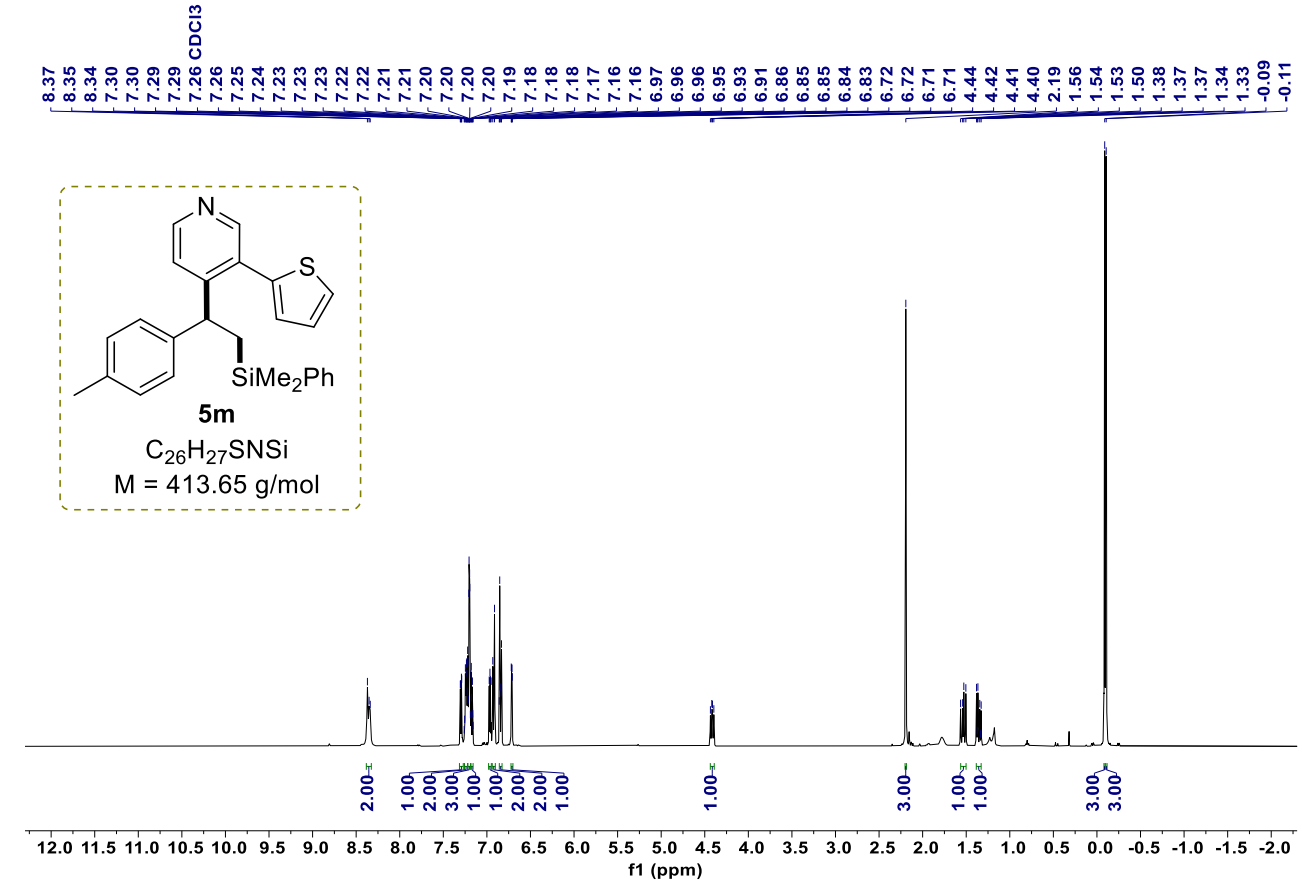
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5k**.



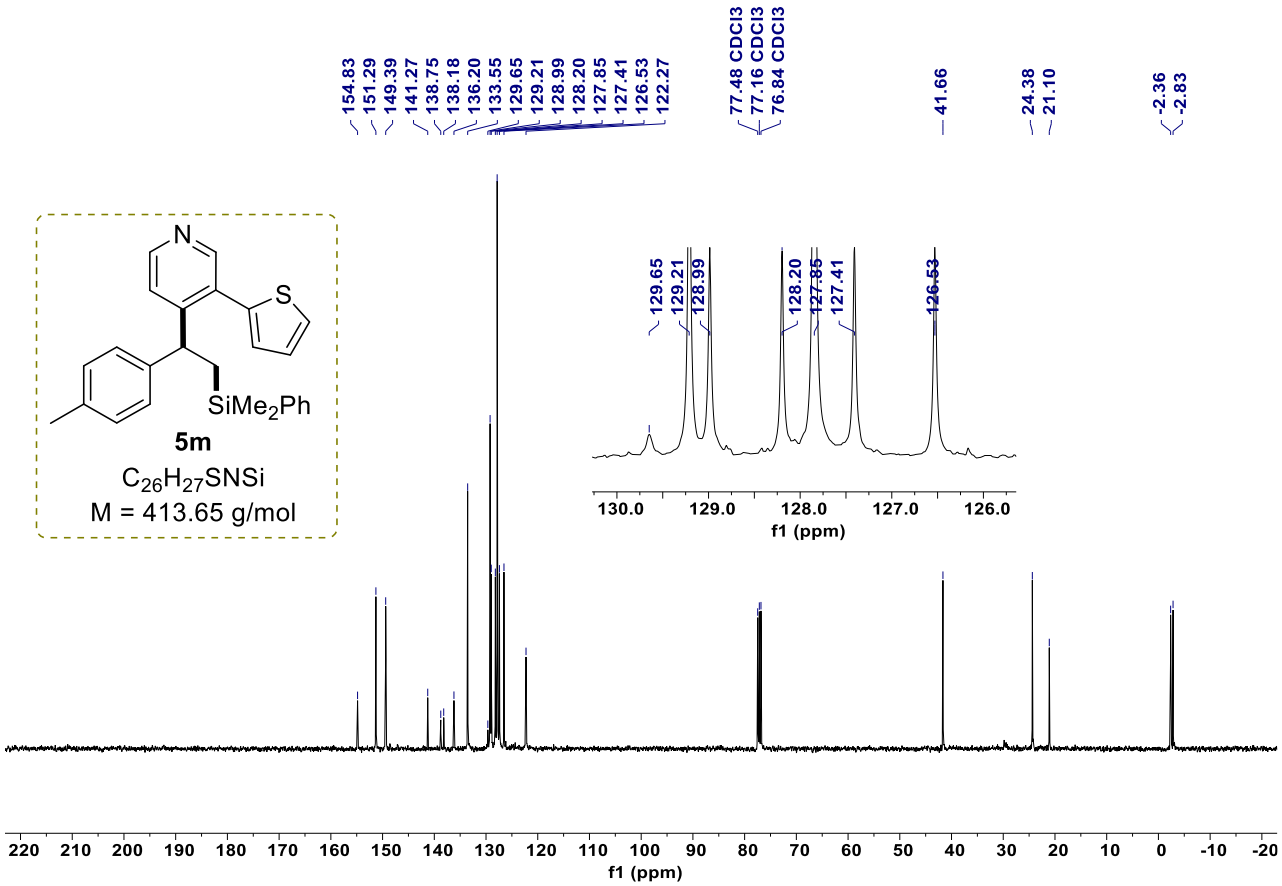
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5l**.



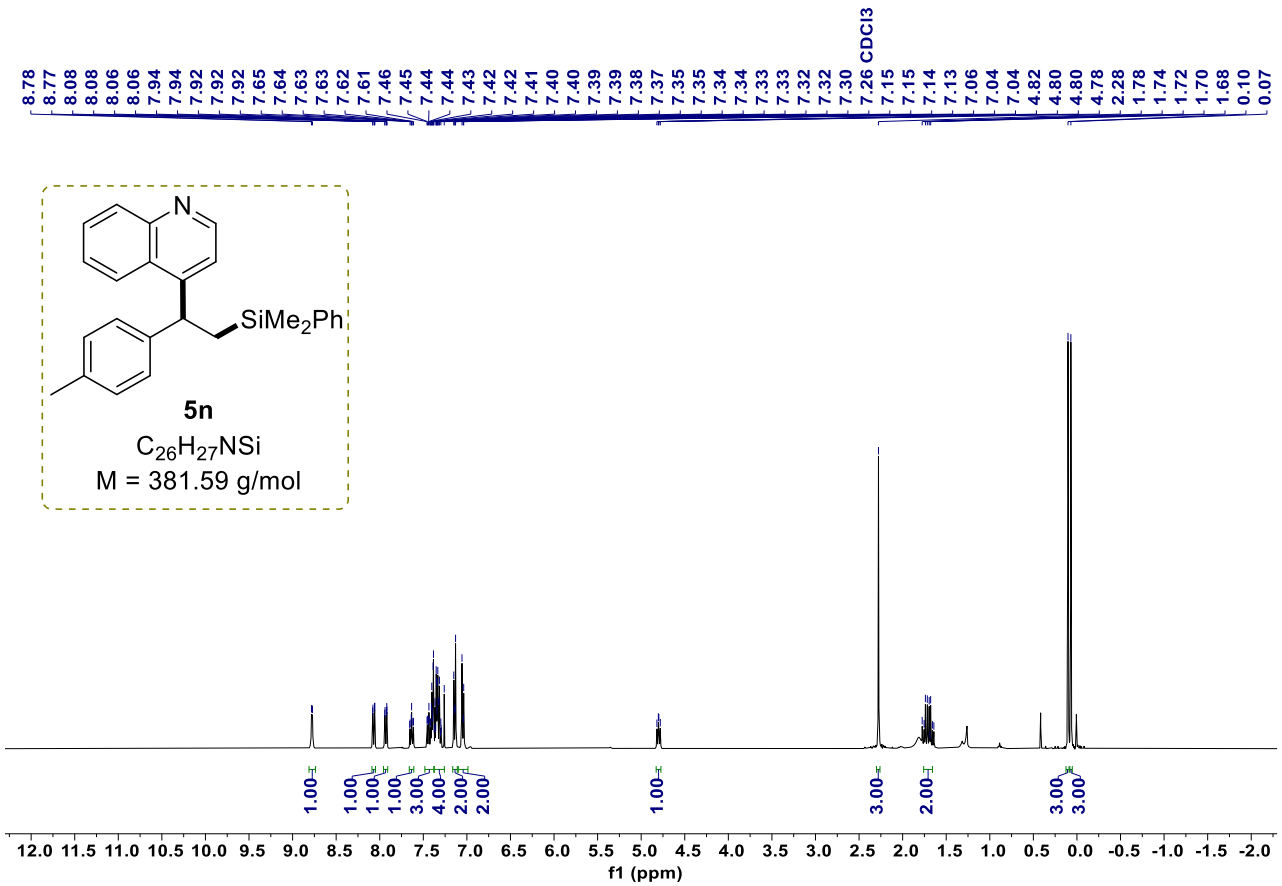
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5l**.



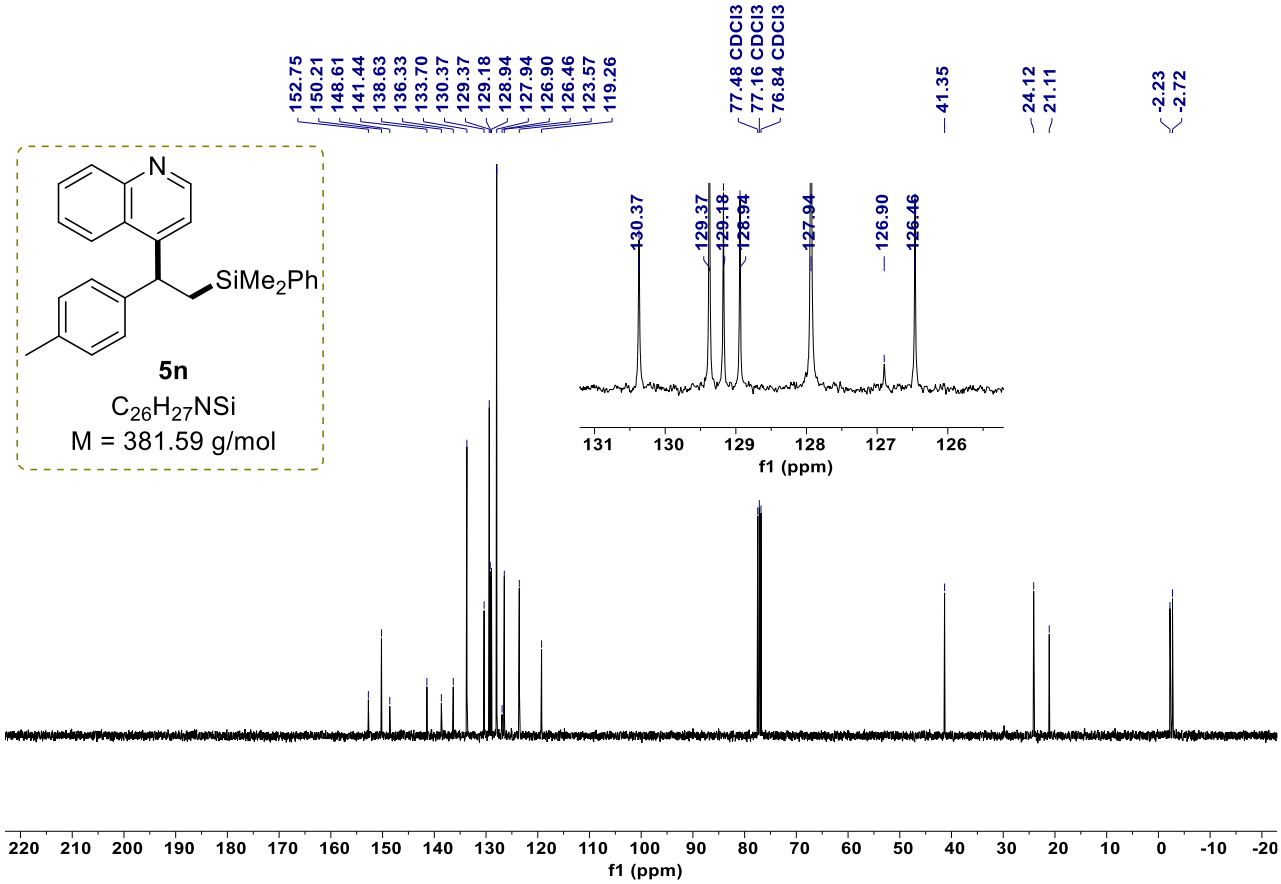
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5m**.



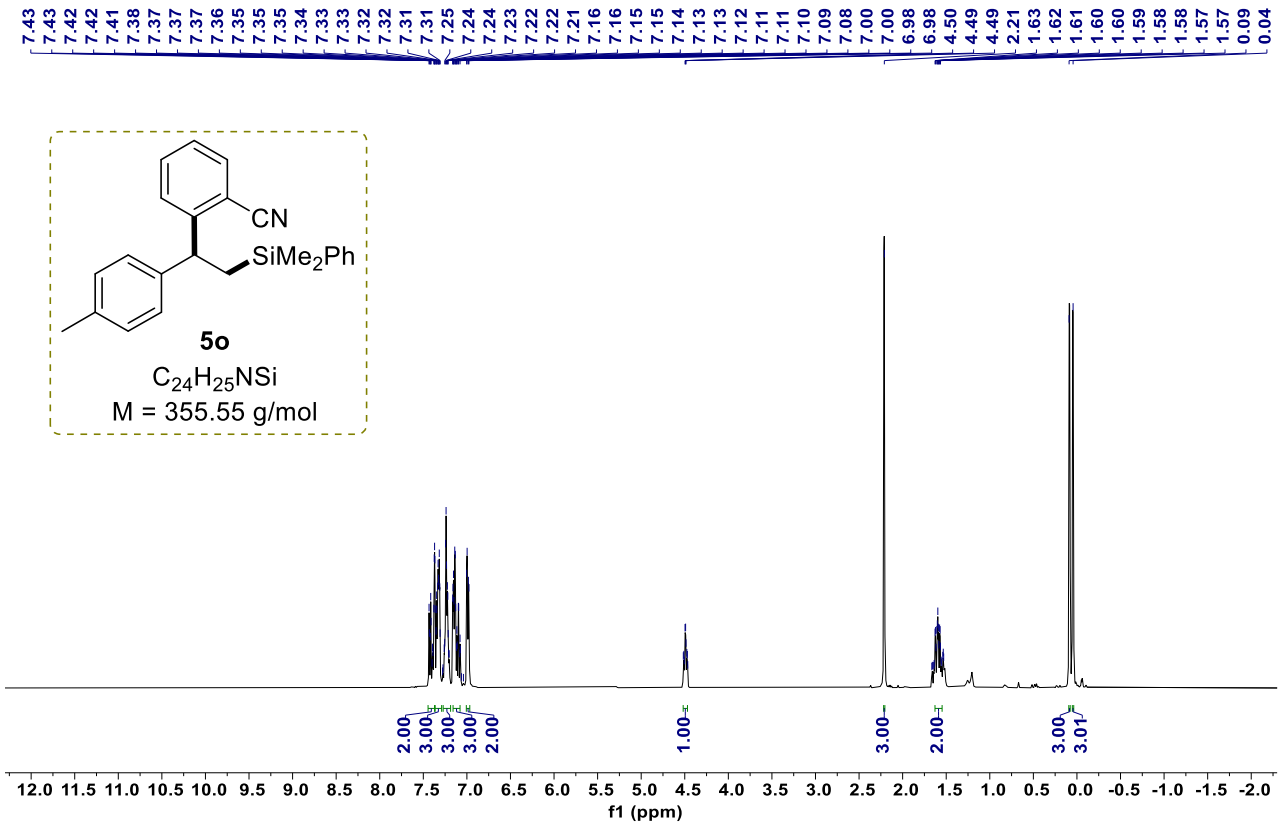
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5m**.



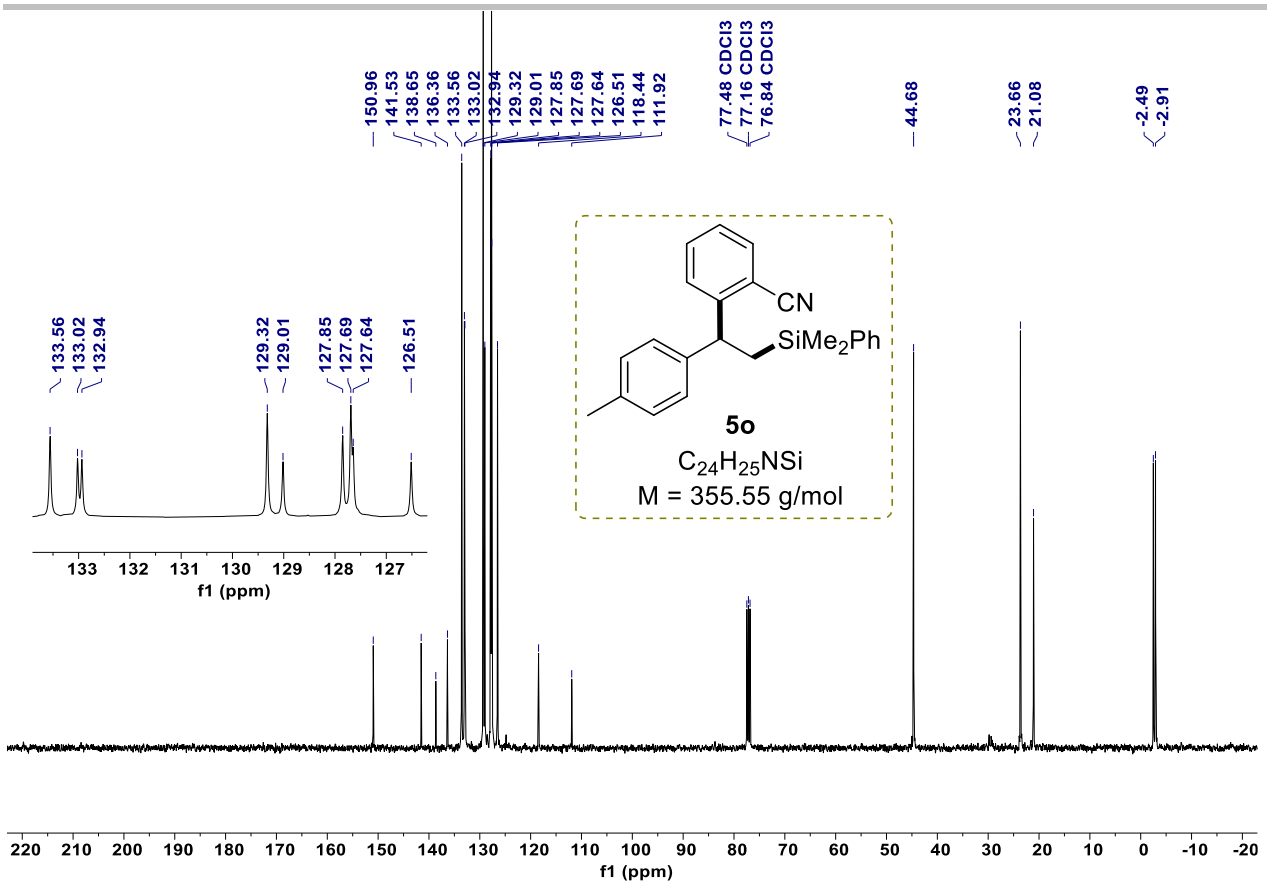
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5n.**



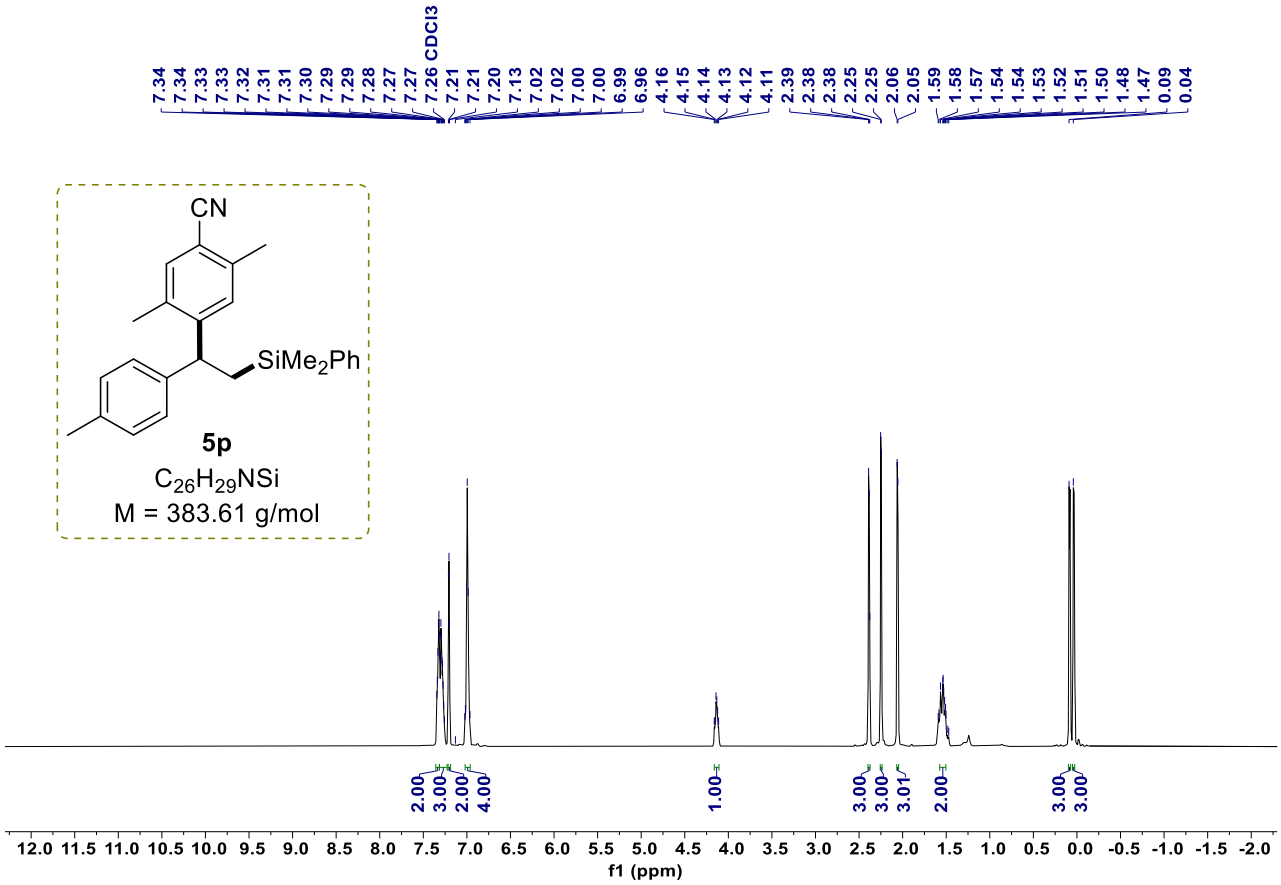
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5n**.



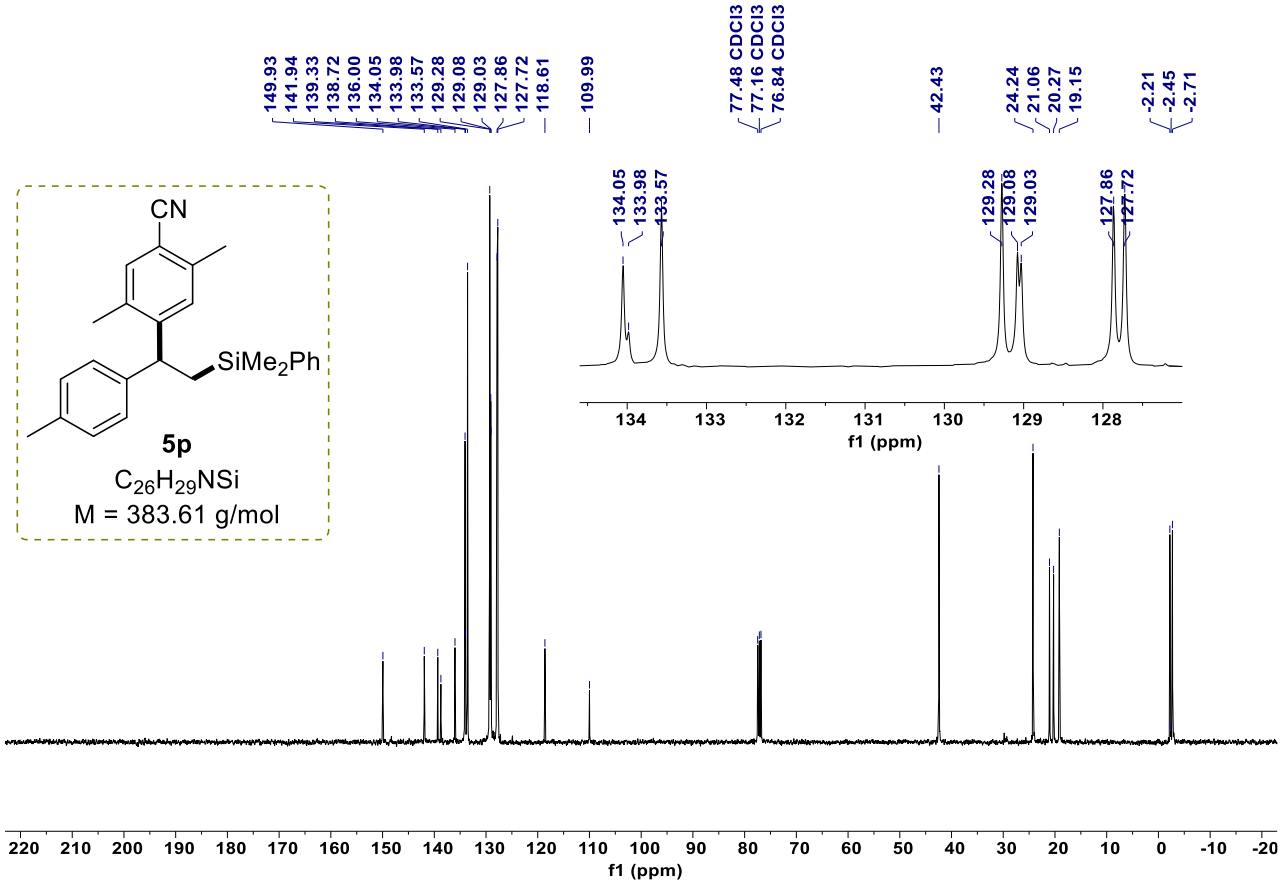
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5o**.



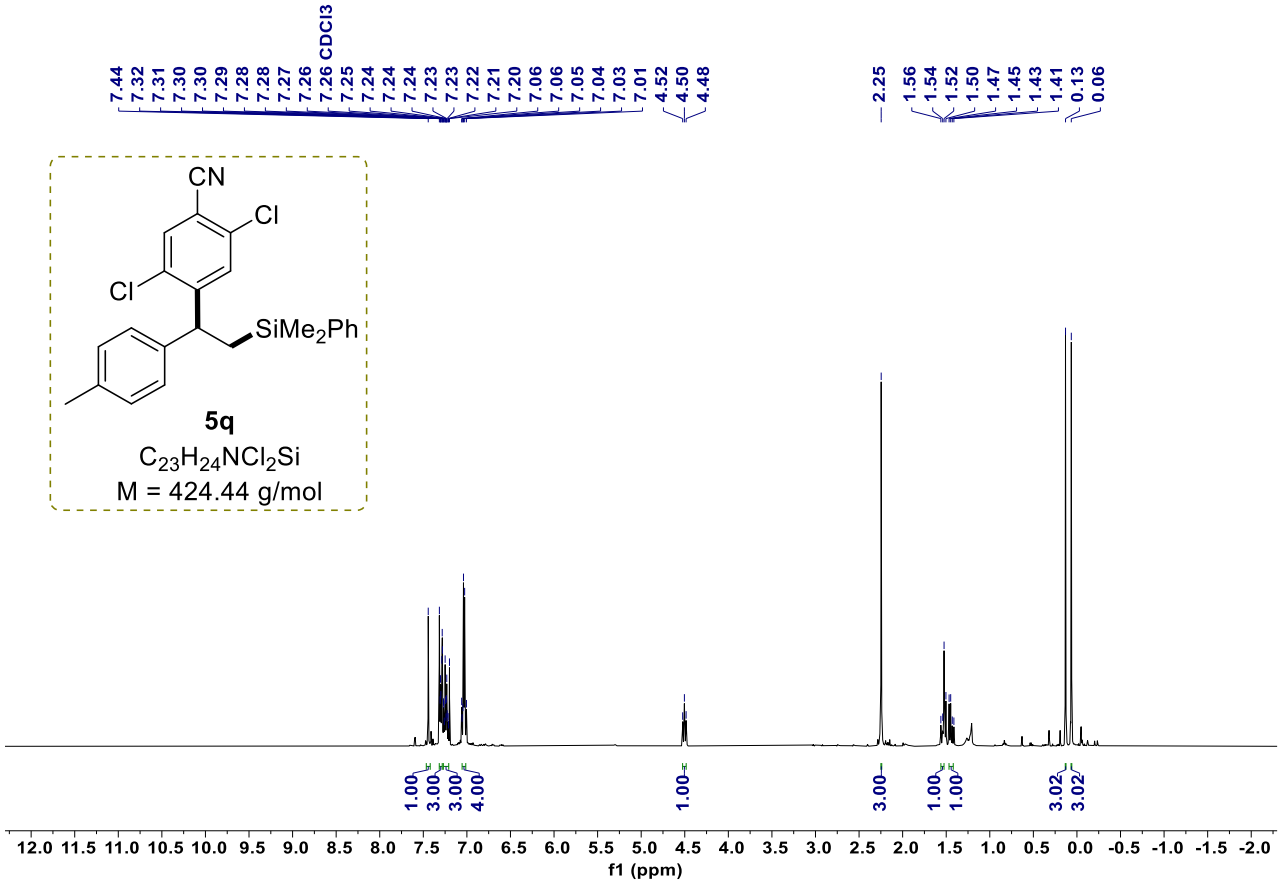
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5o**.



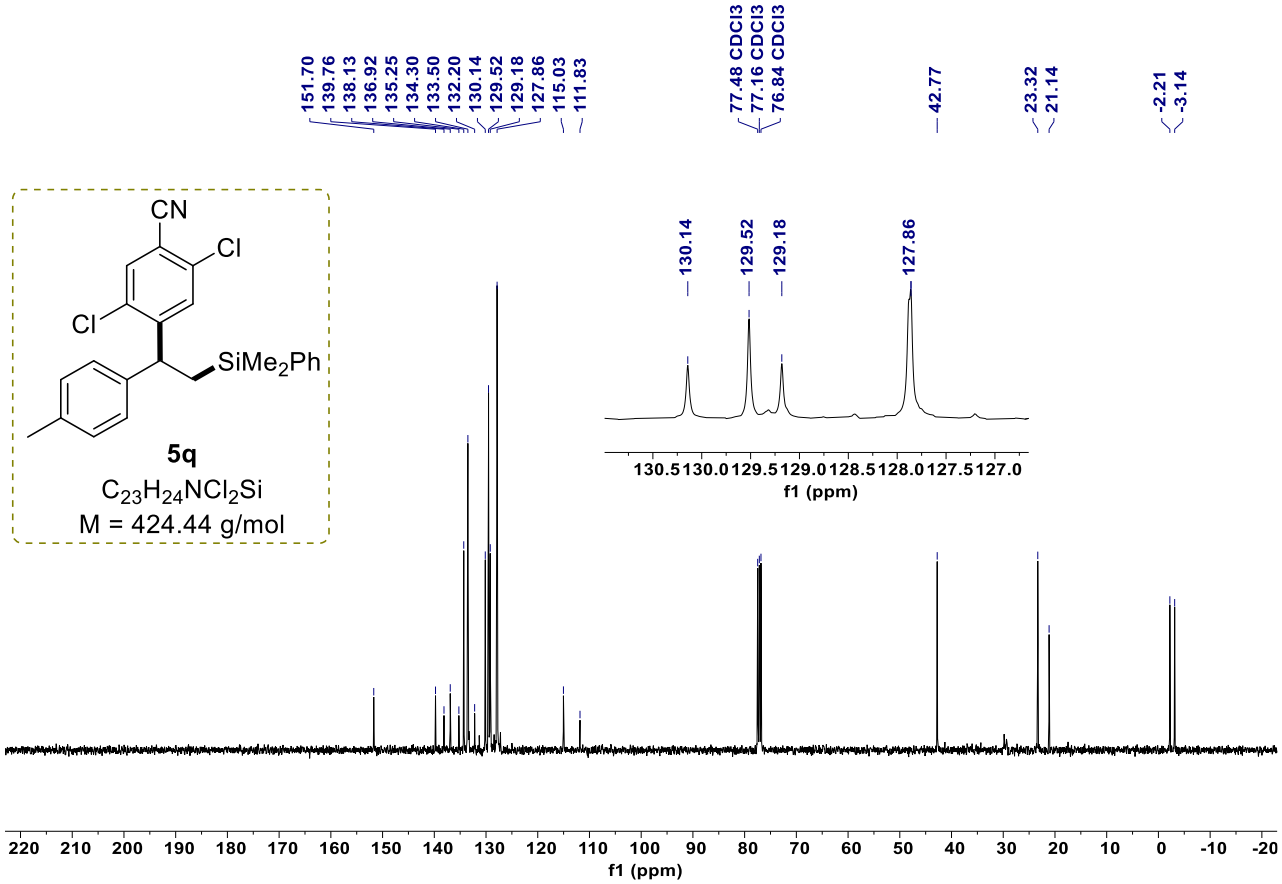
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5p.**



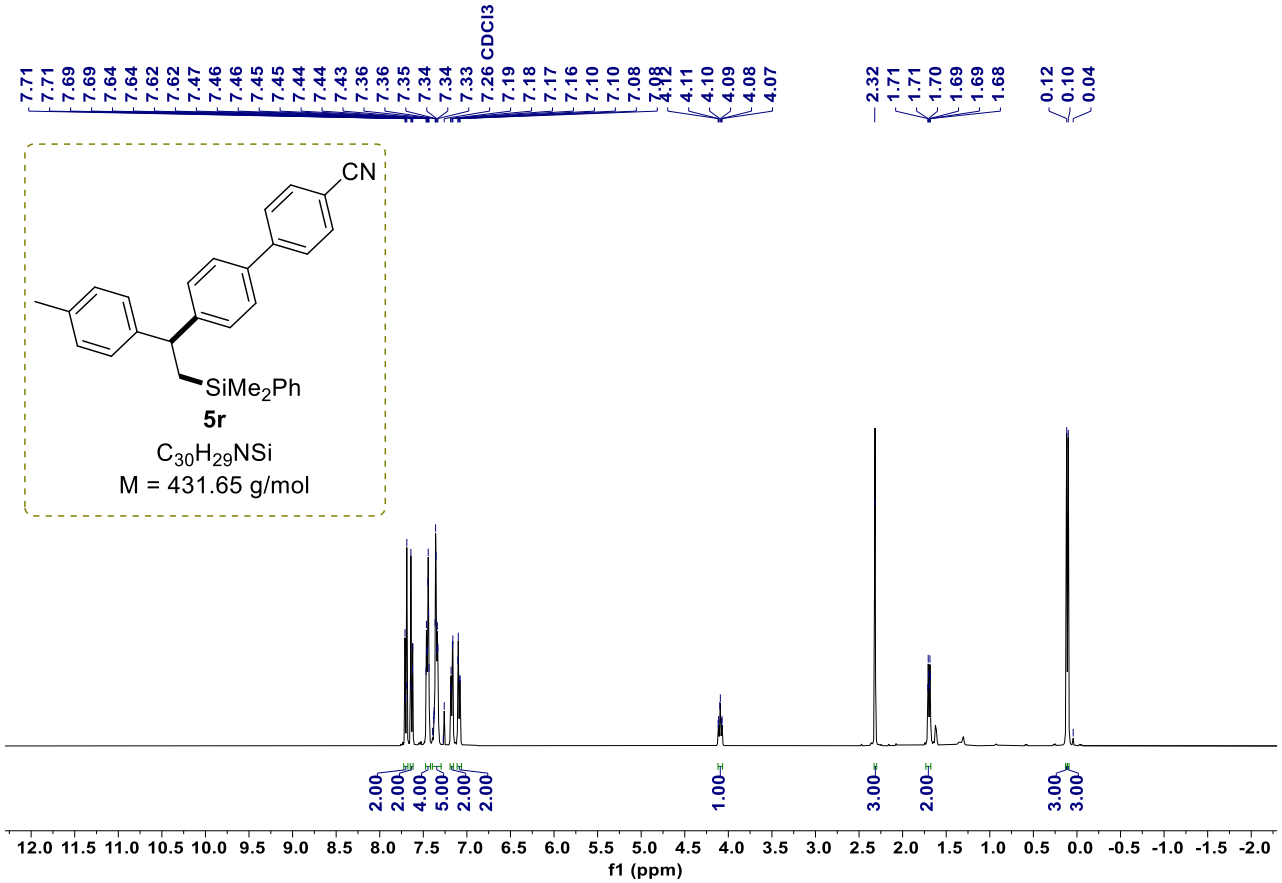
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5p**.



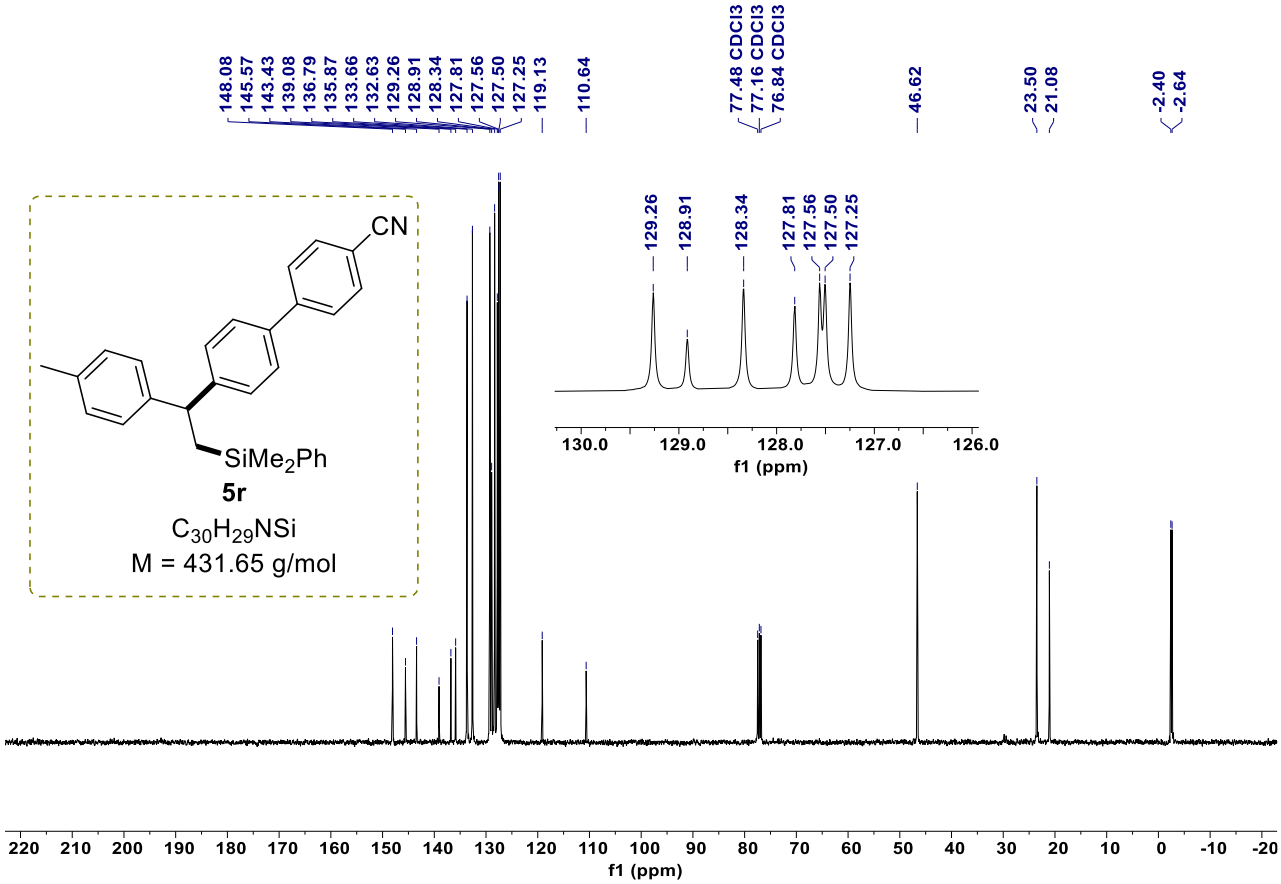
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5q.**



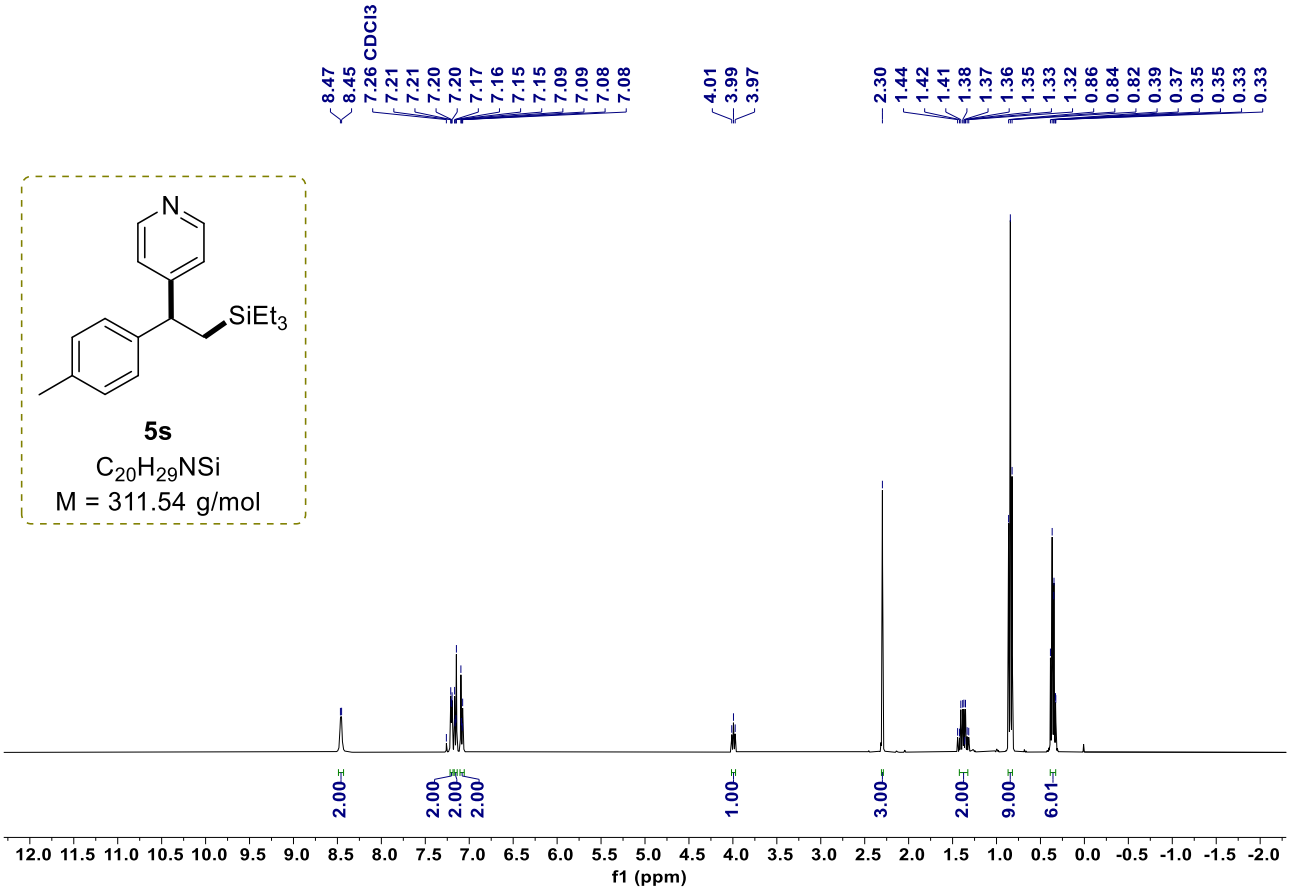
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5q**.



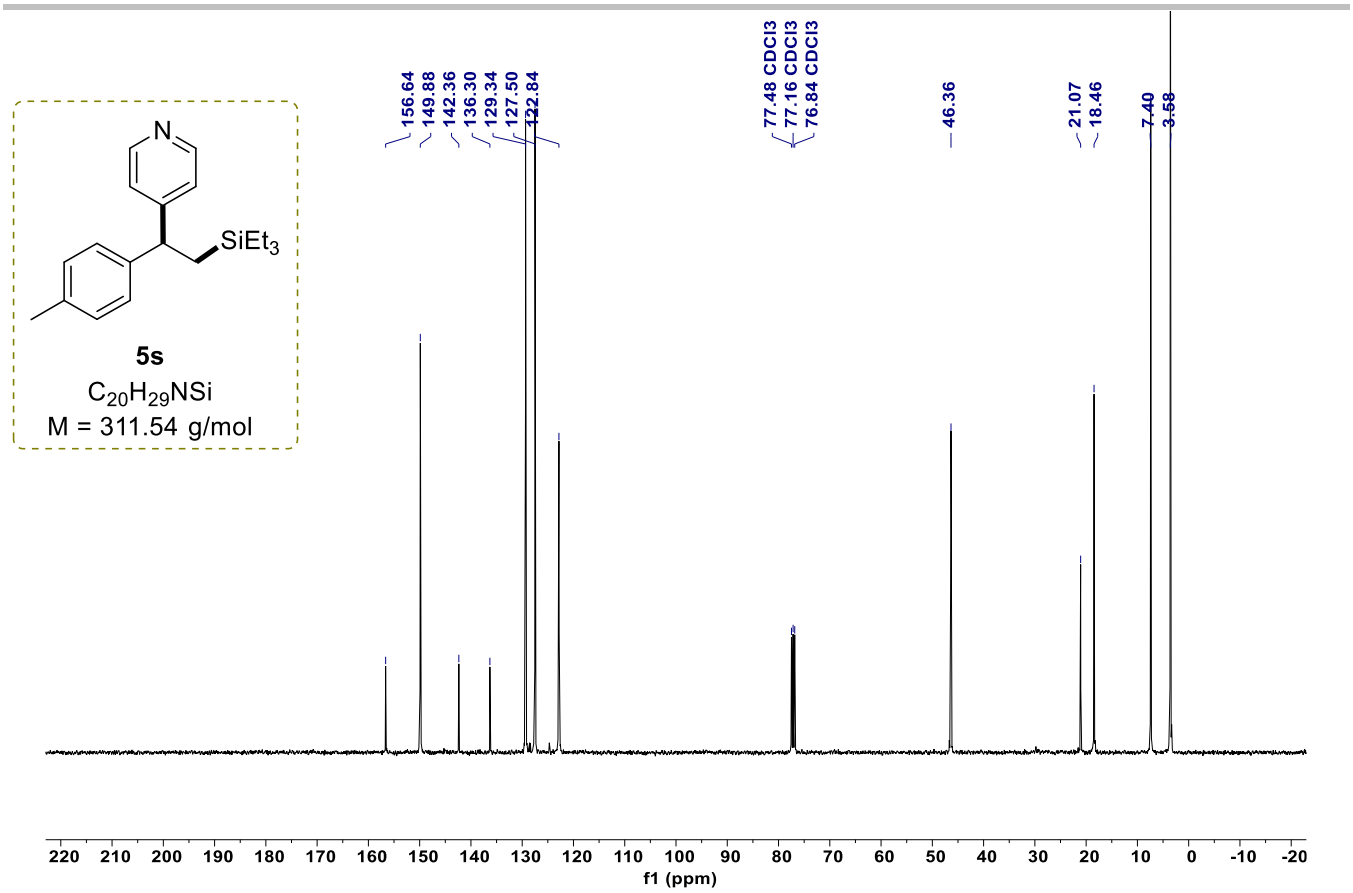
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5r**.



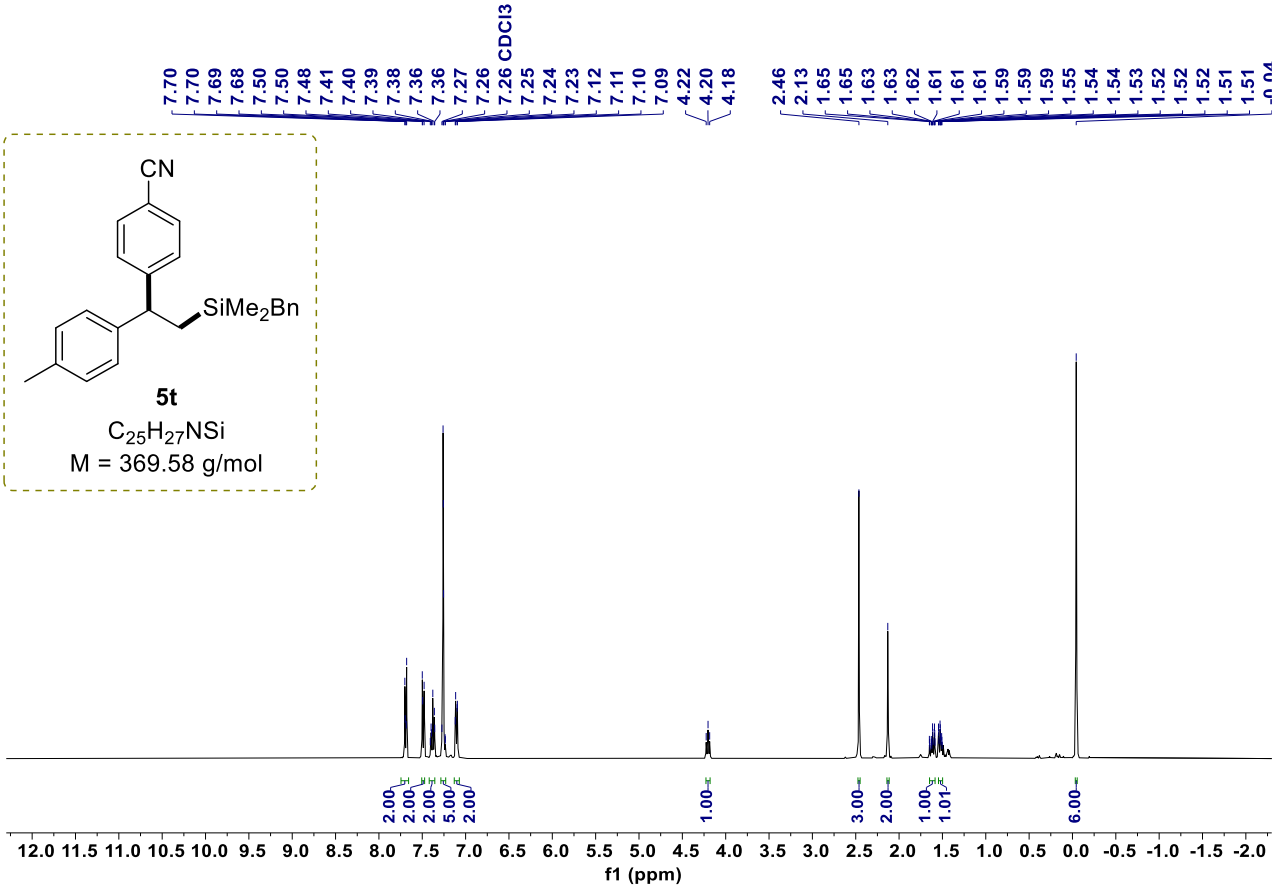
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5r**.



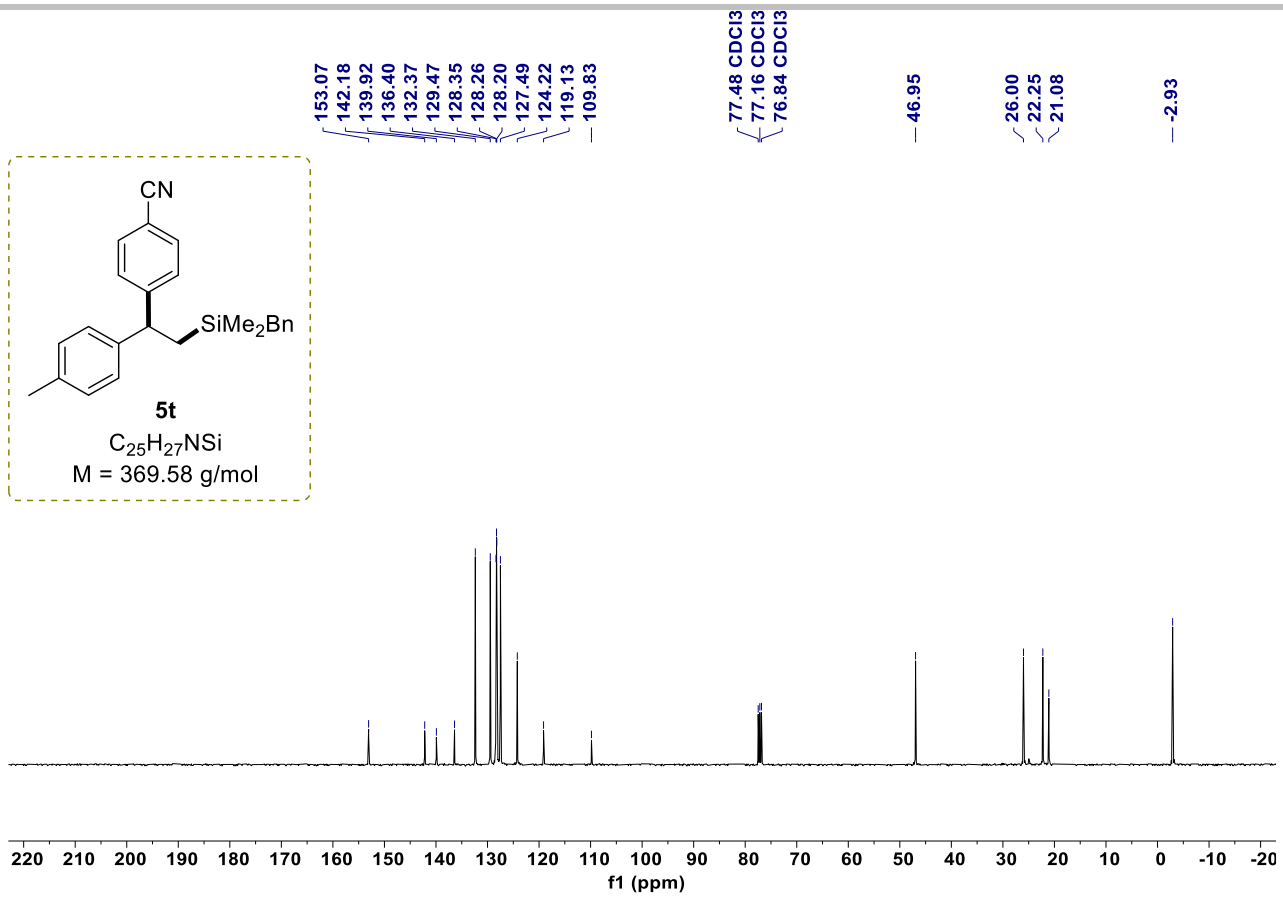
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5s.**



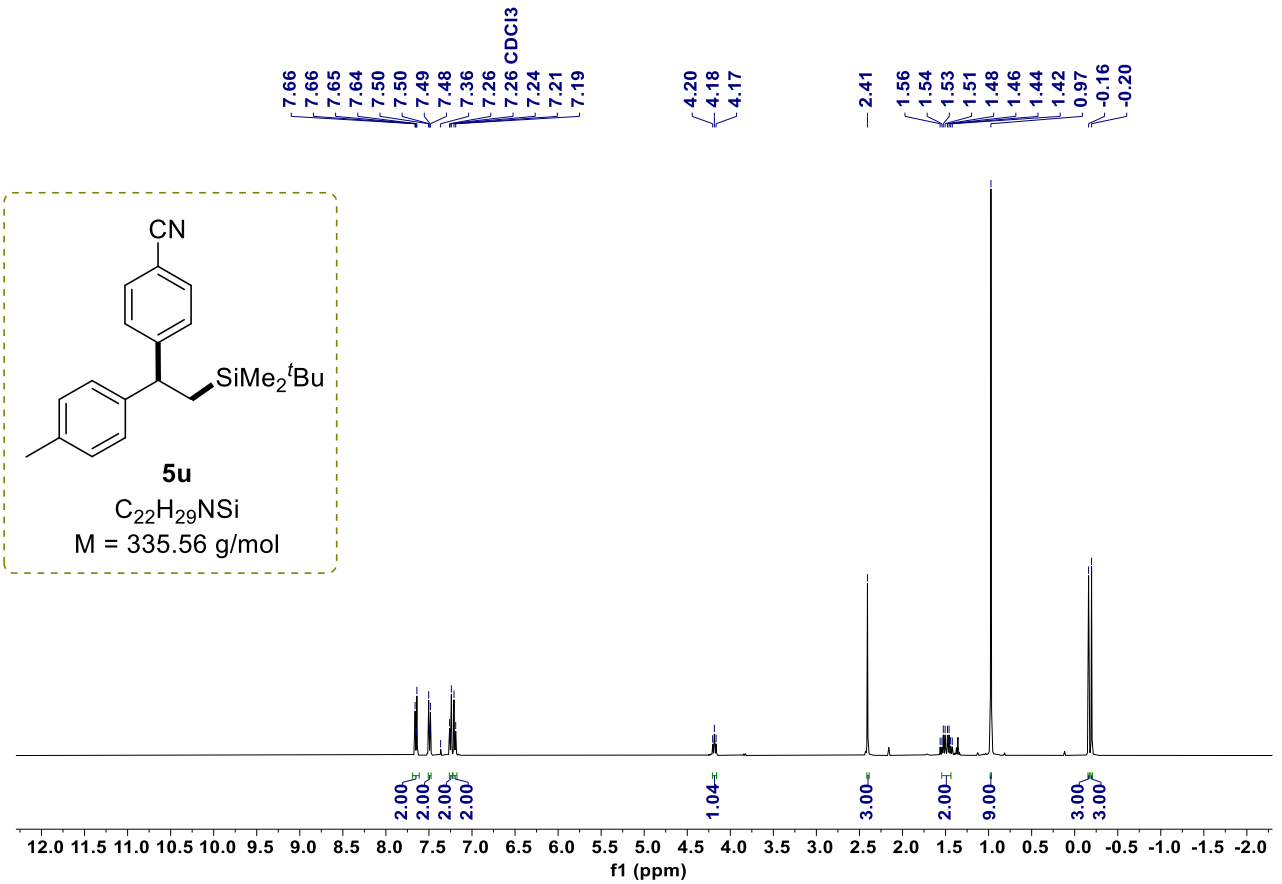
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5s.**



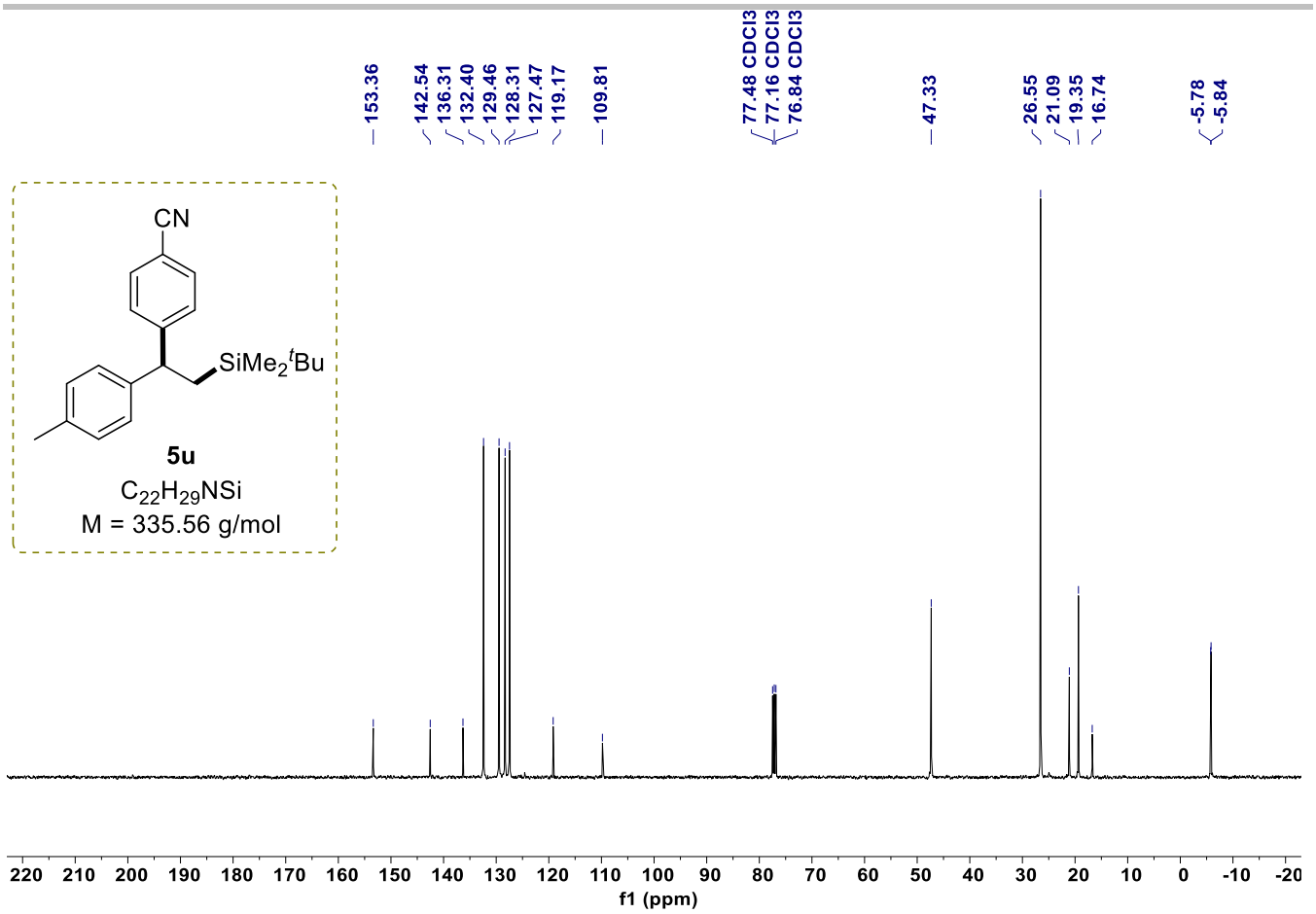
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5t.**



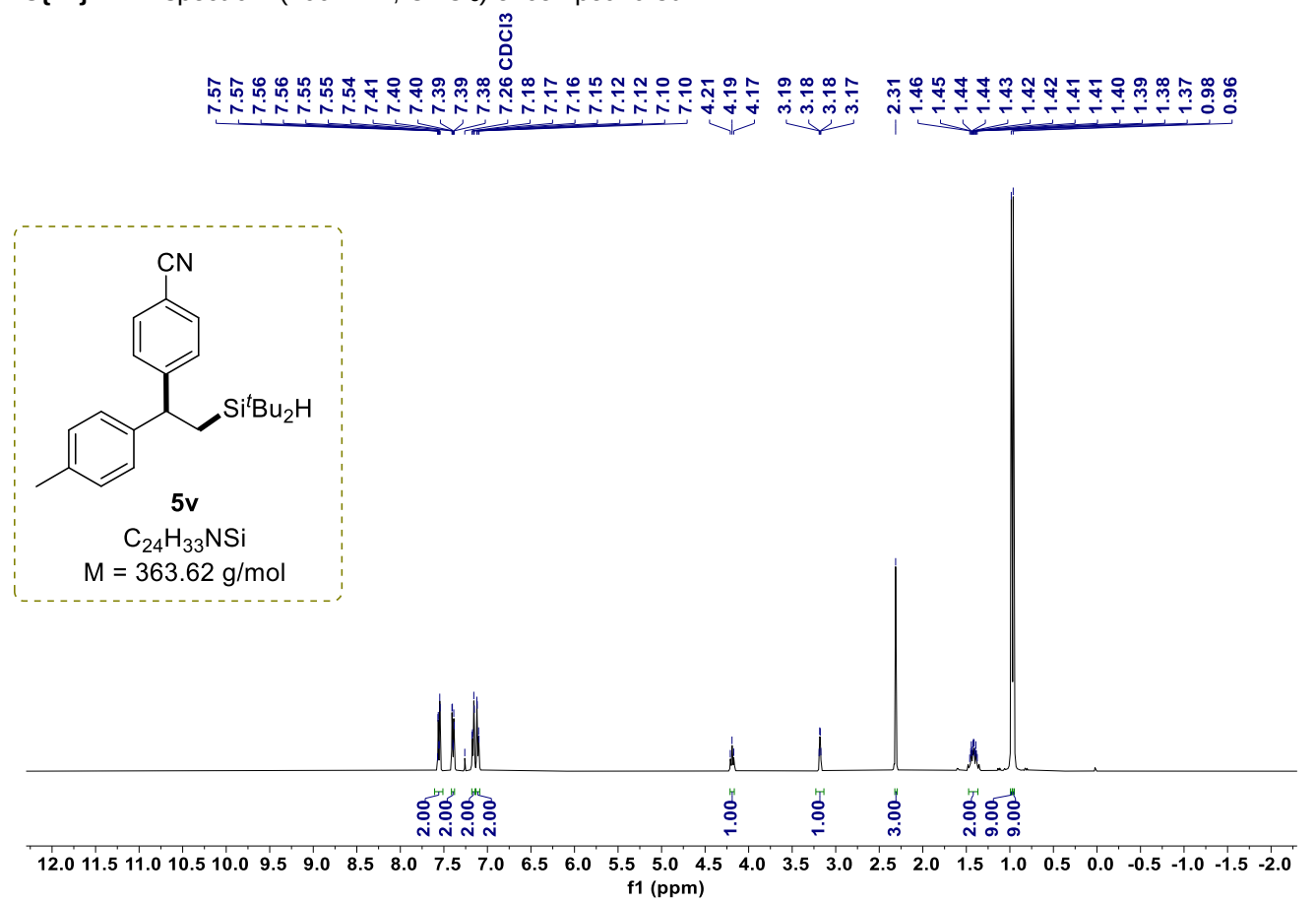
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5t.**



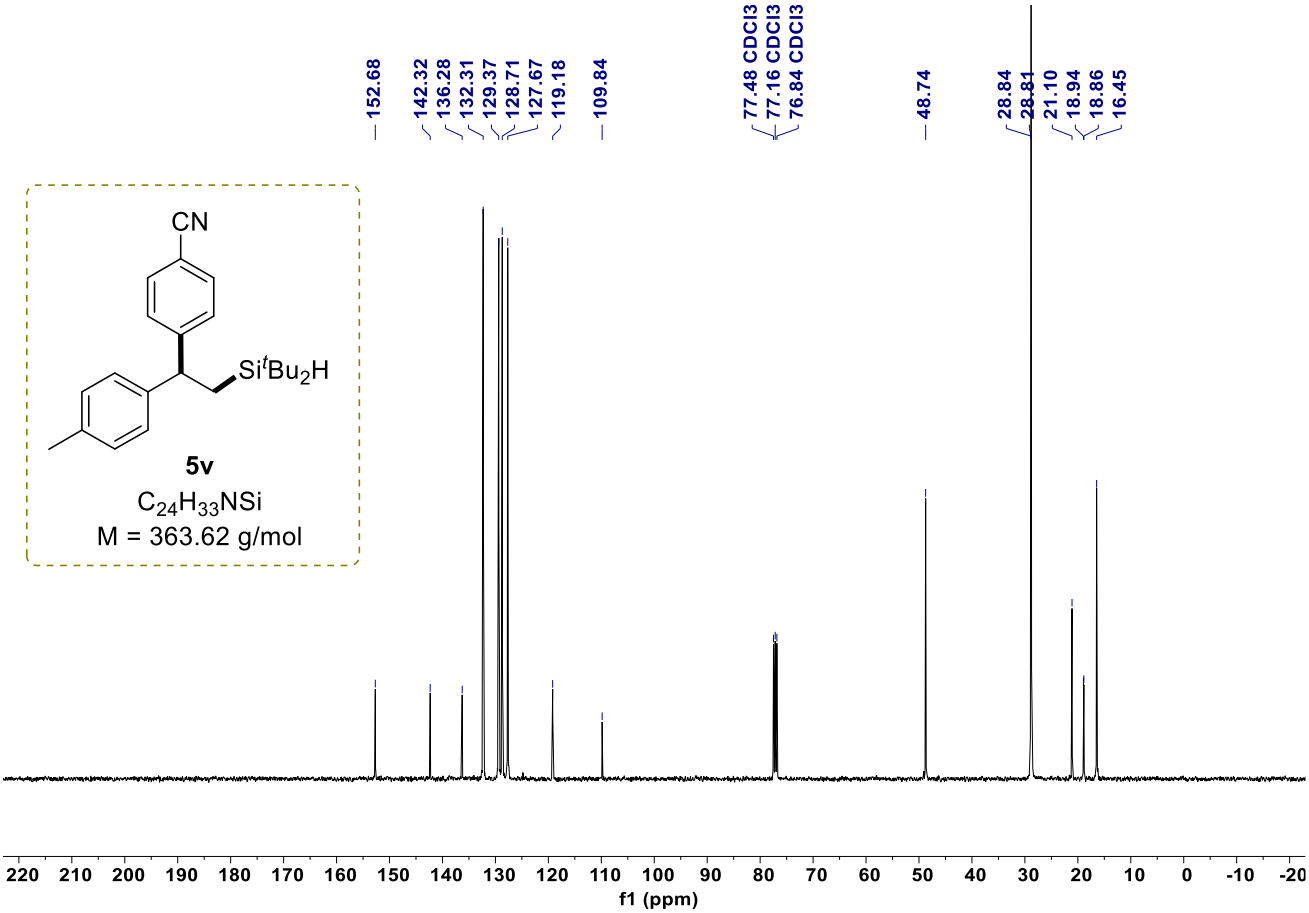
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5u.**



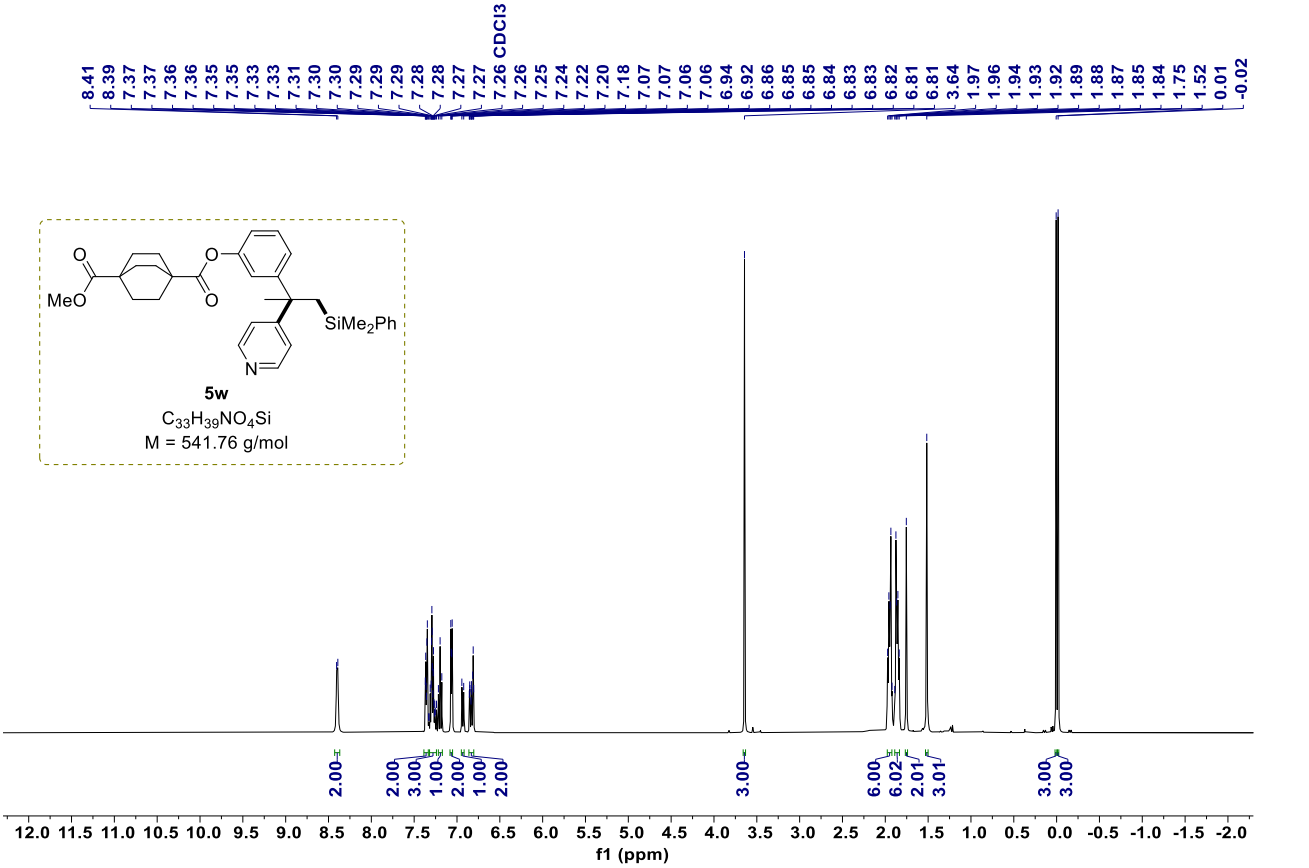
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **5u.**



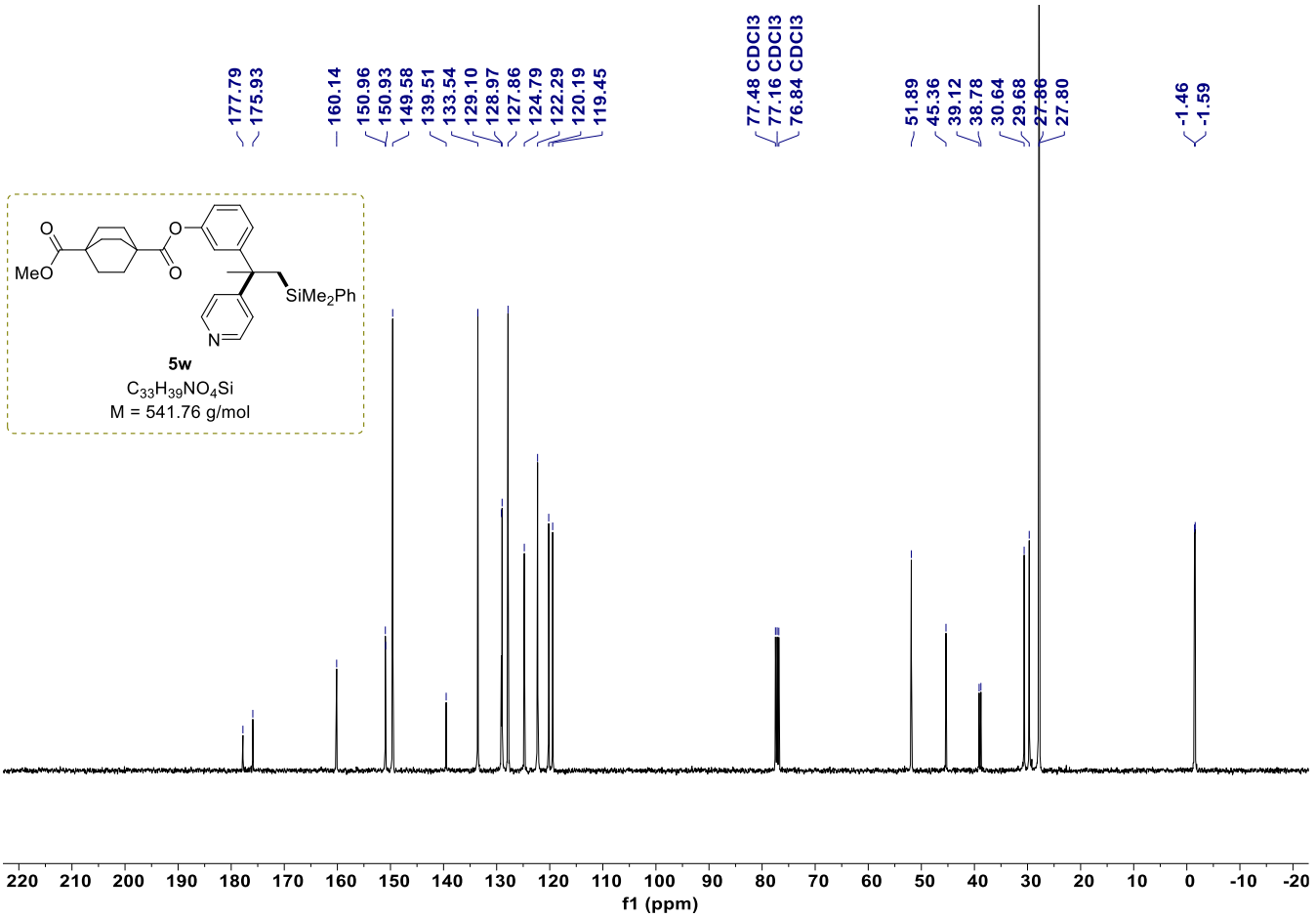
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5v.**



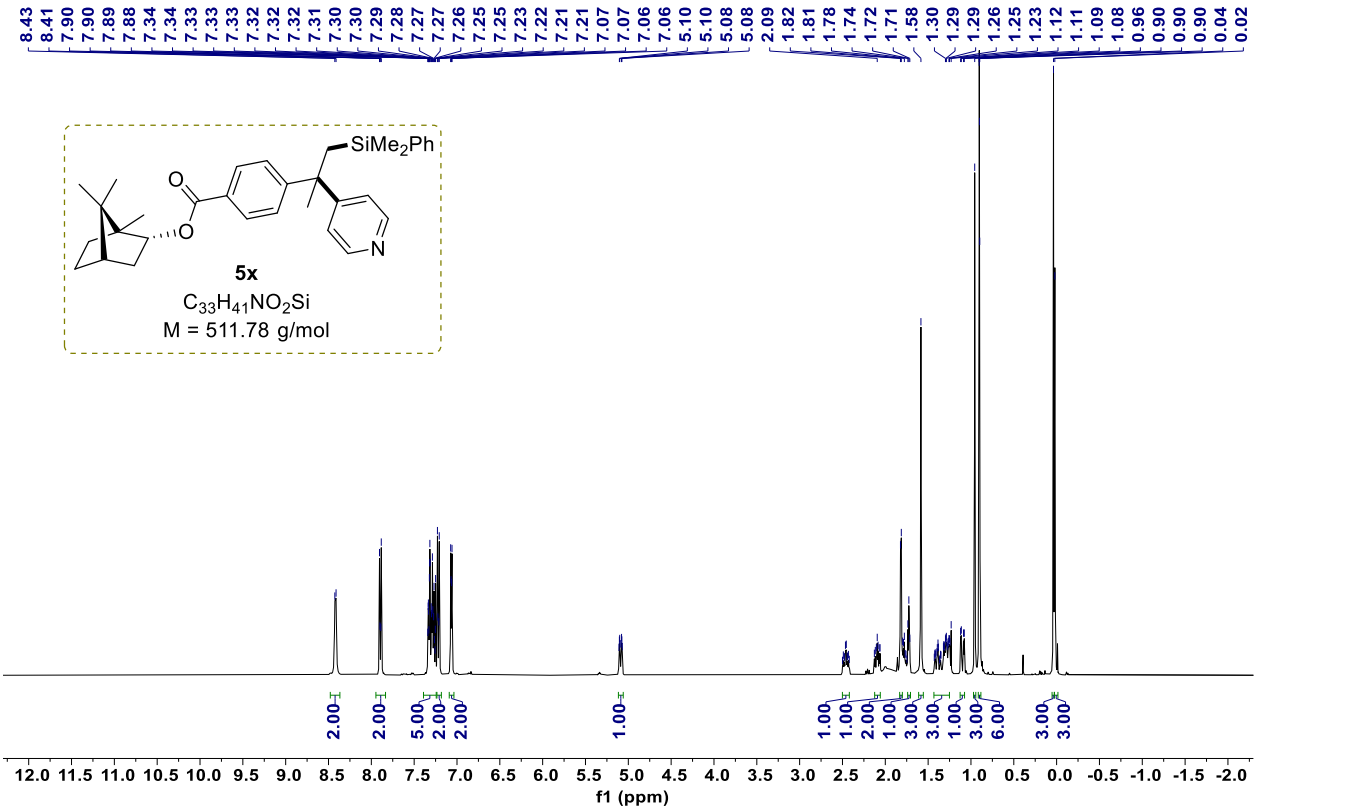
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5v.**



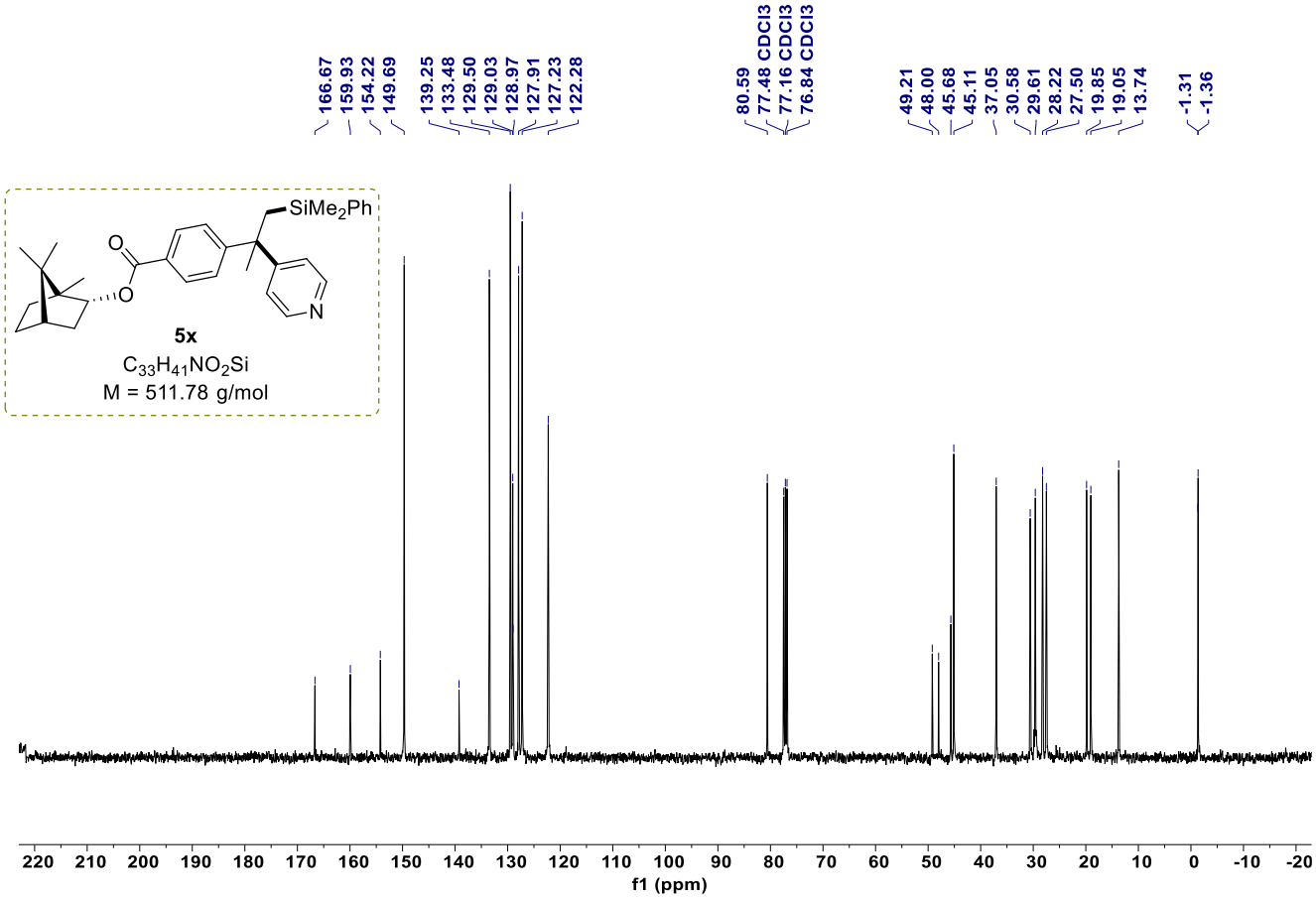
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5w.**



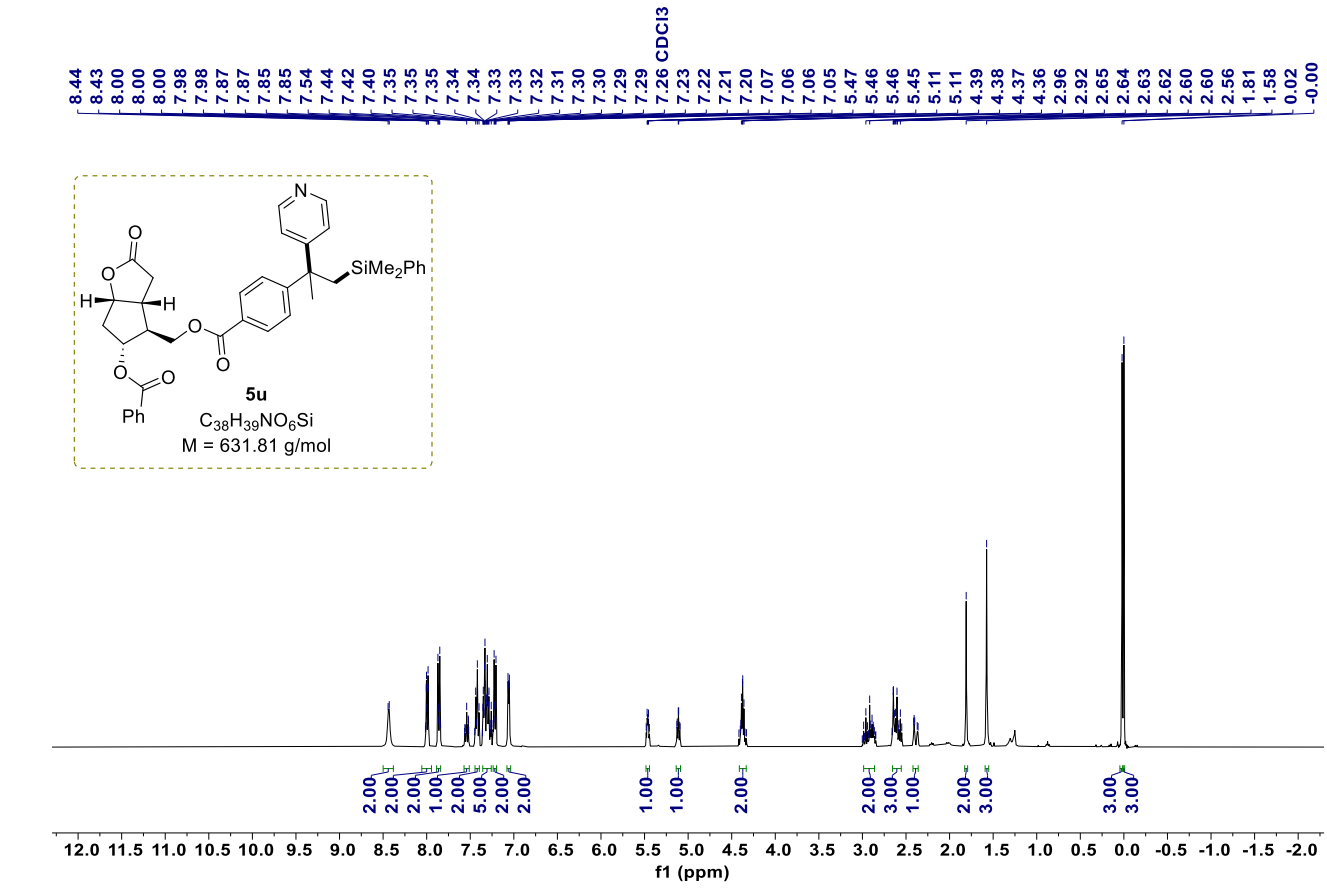
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5w**.



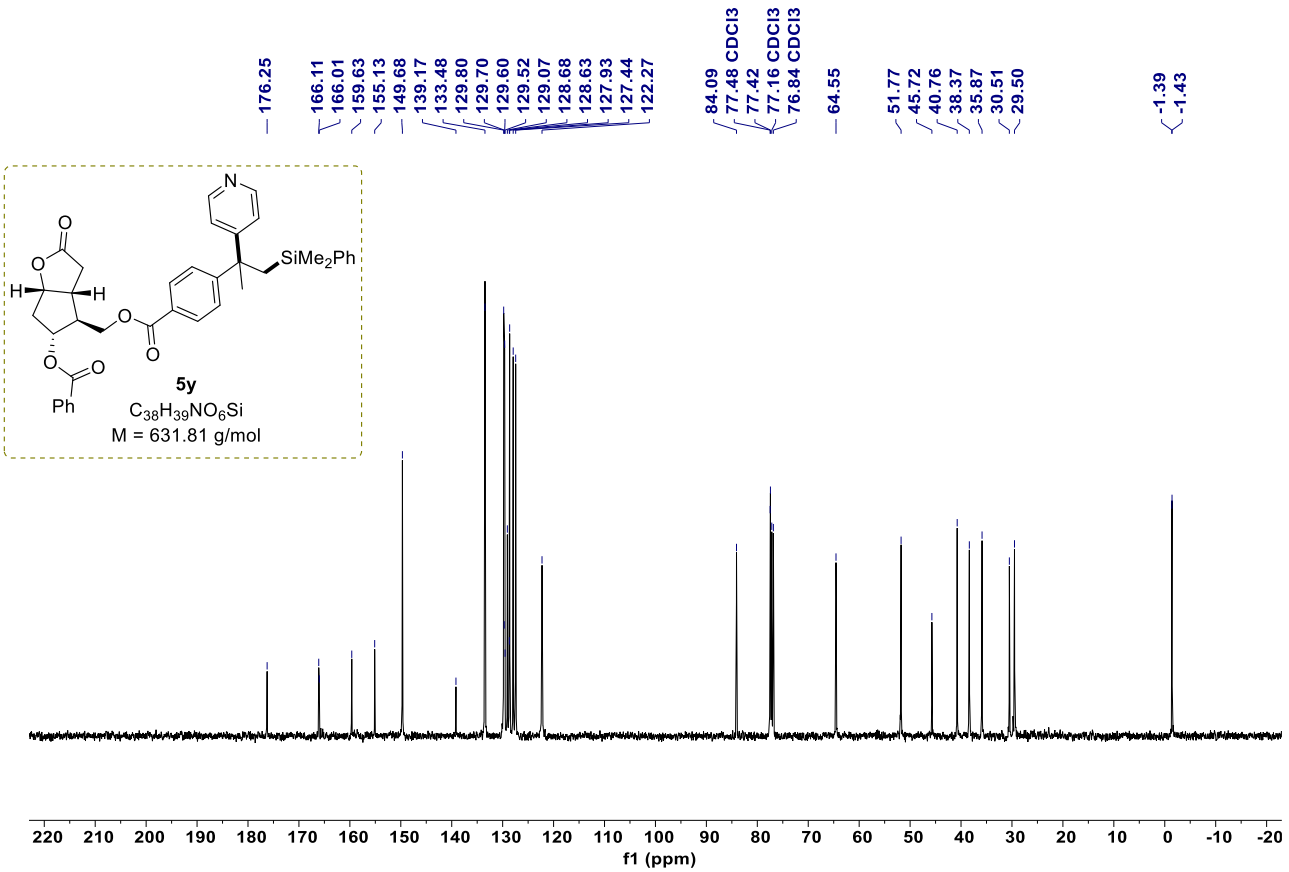
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5x**



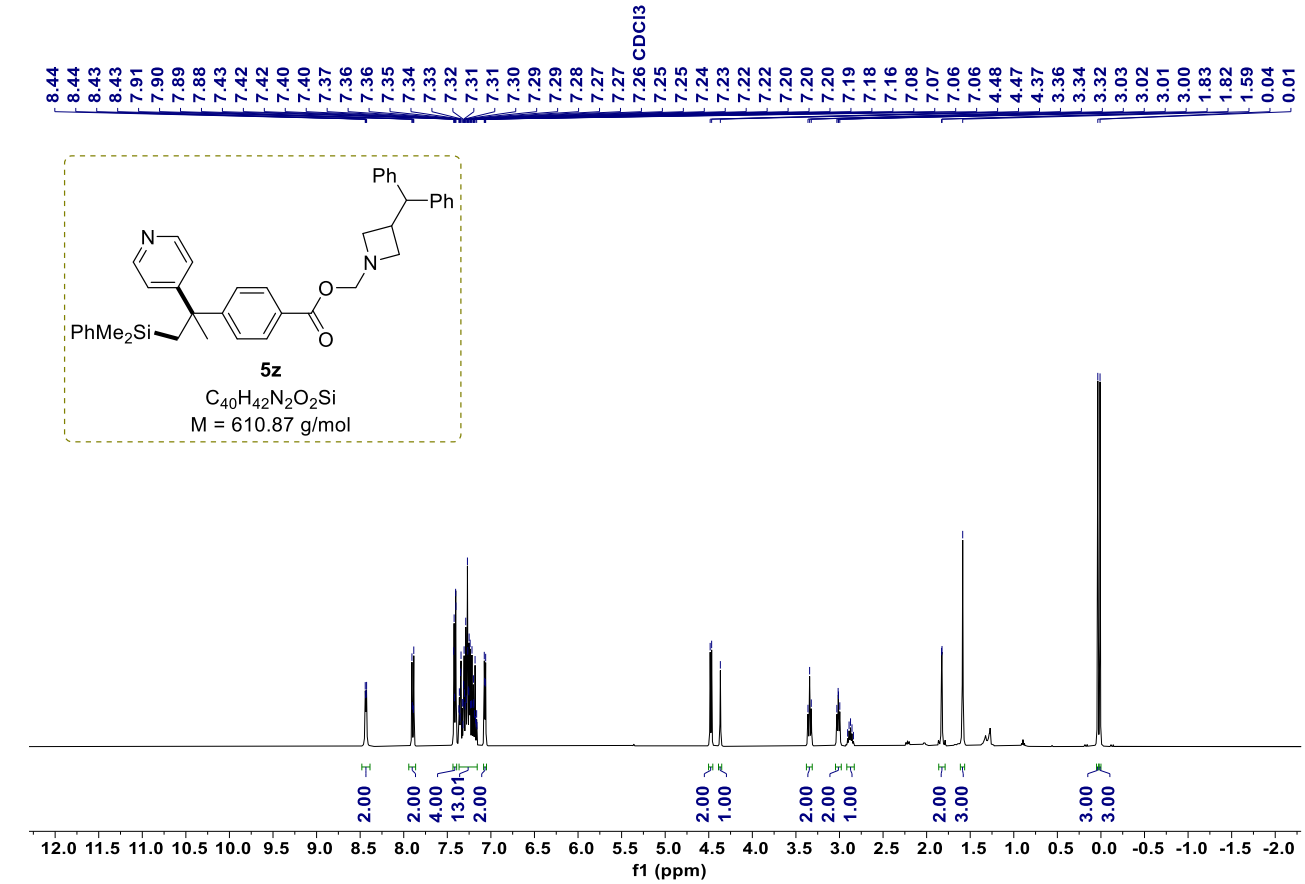
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5x**.



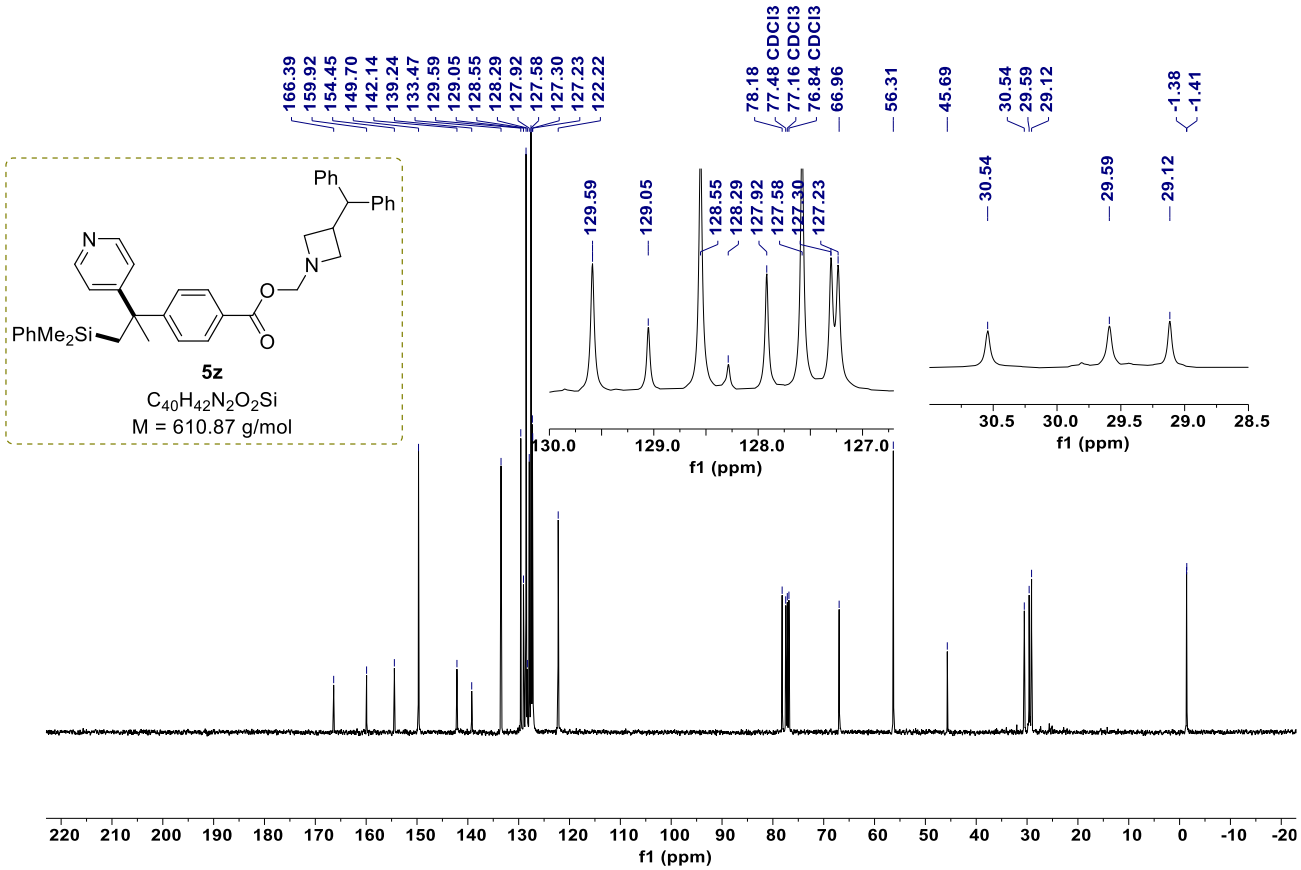
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5y.**



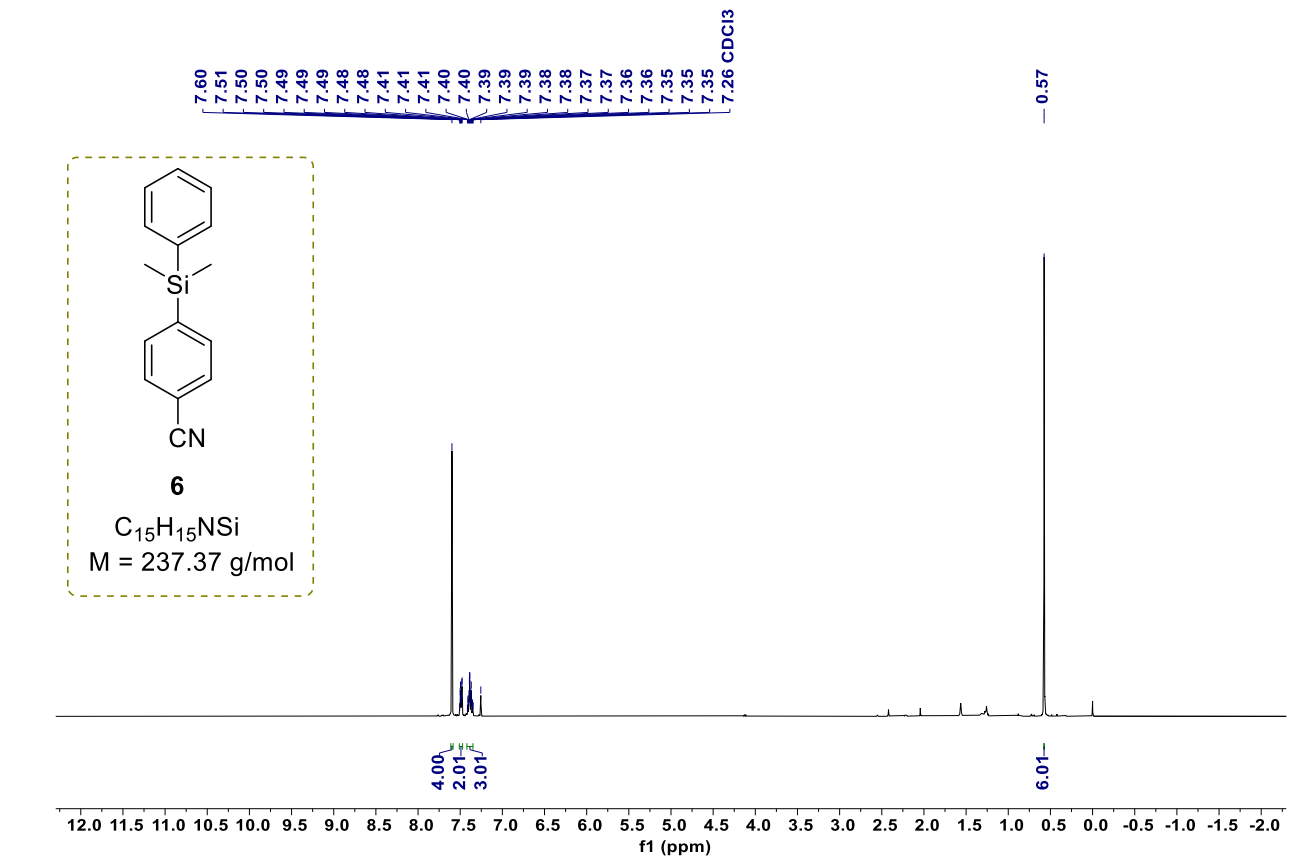
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5y**.



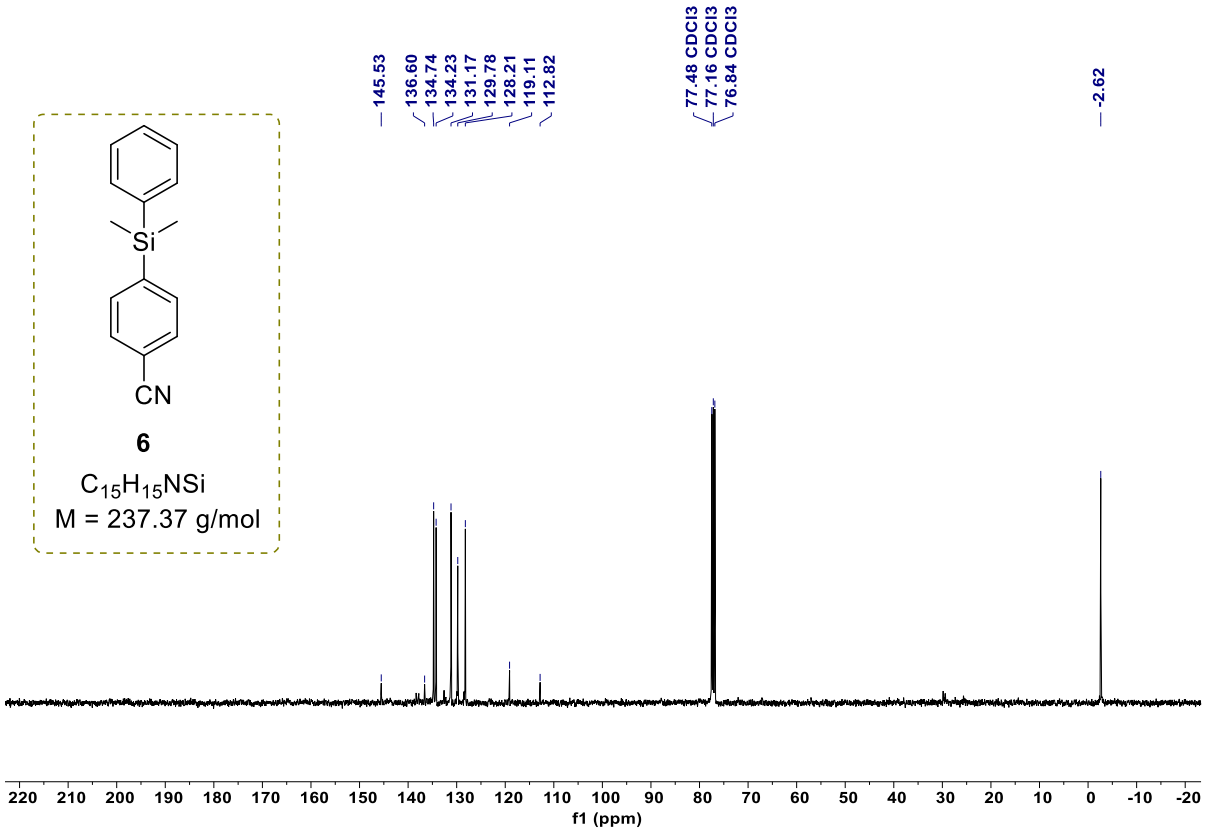
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5z.**



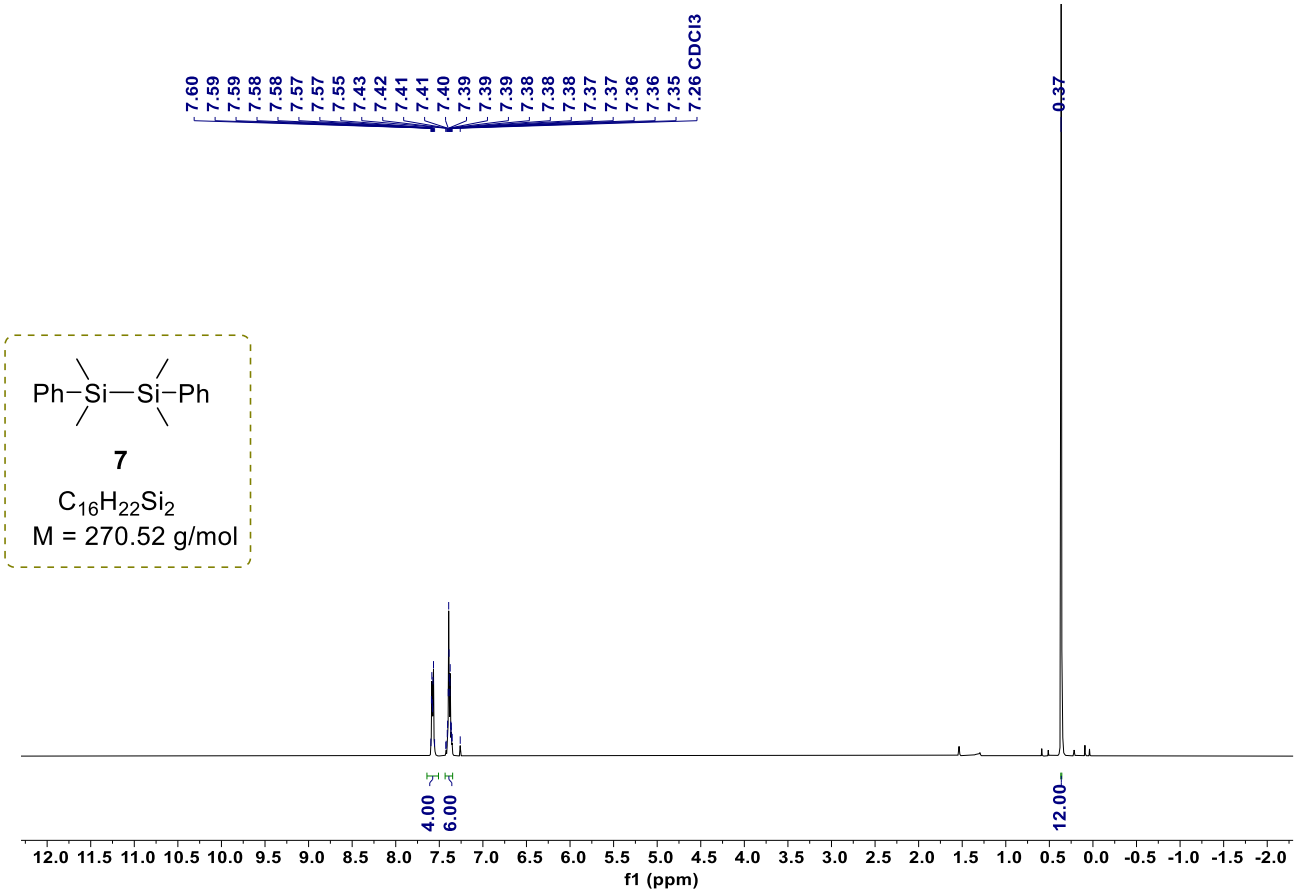
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **5z**.



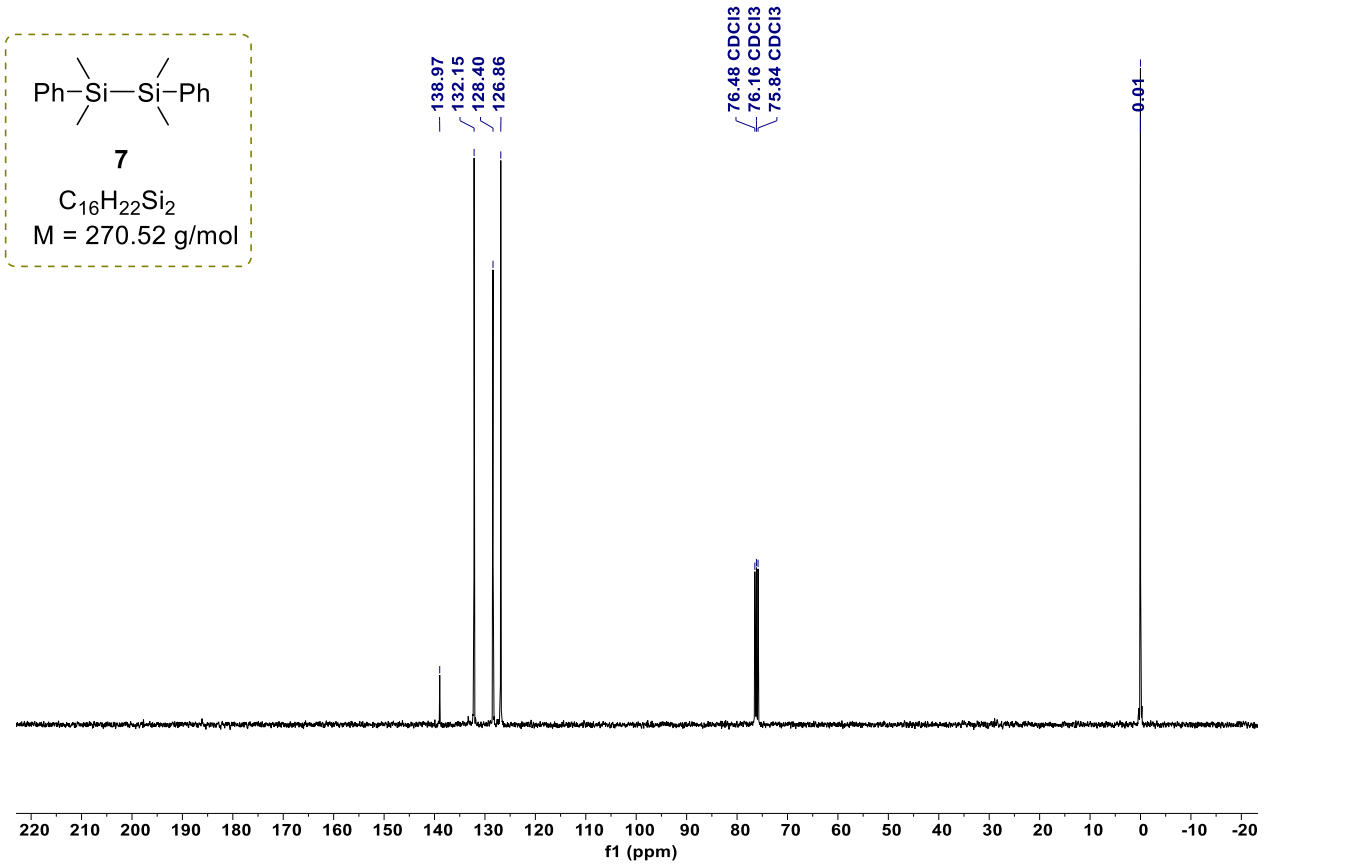
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6.**



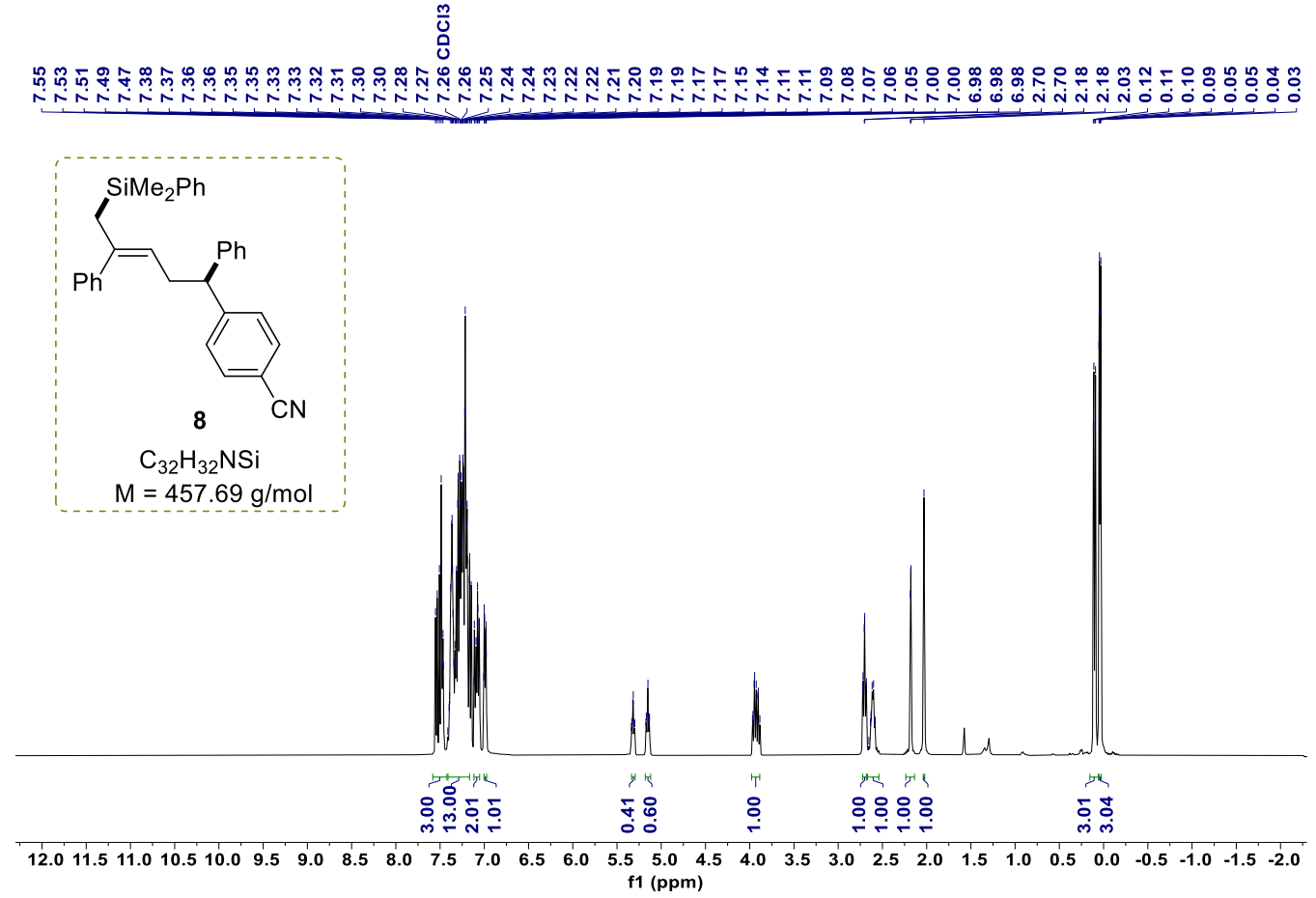
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **6**.



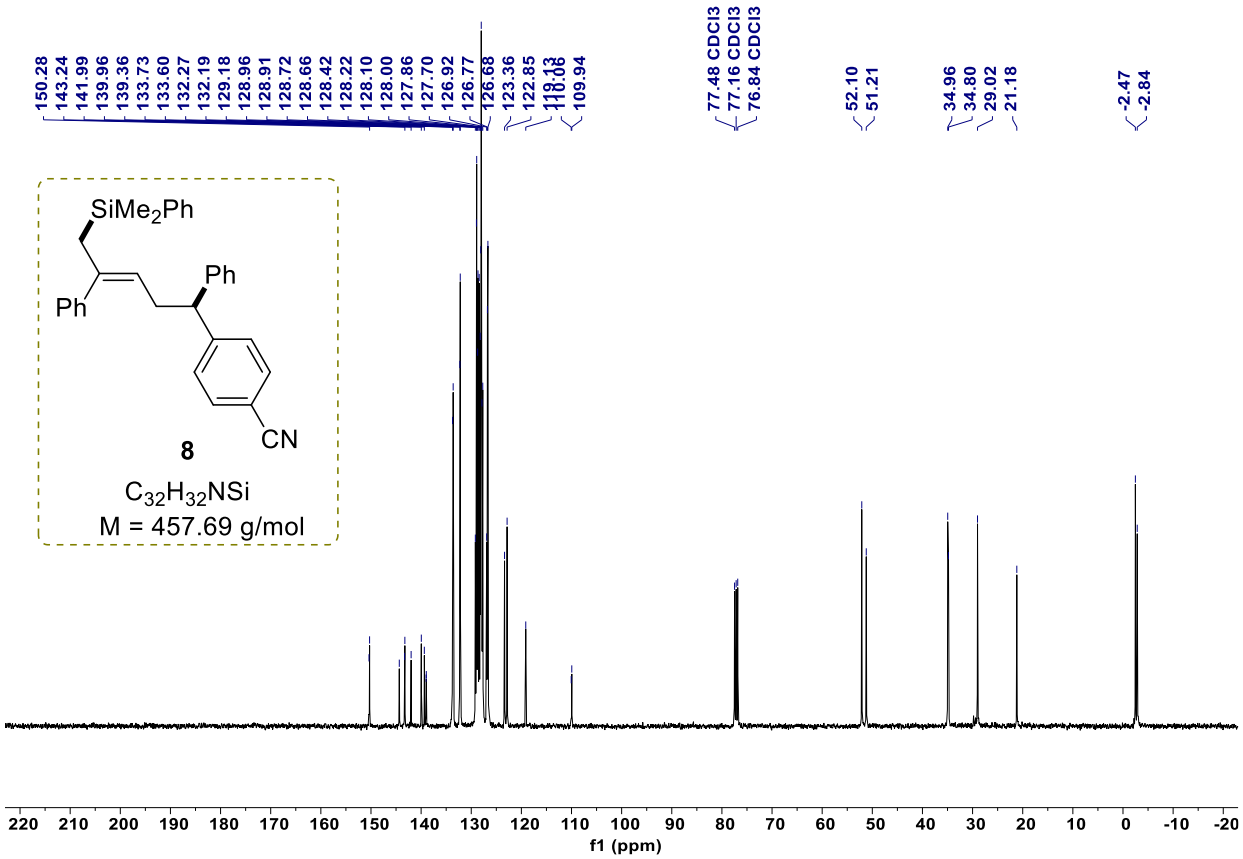
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7.**



$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **7**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8.**



$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **8**.

5. Energies and Cartesian Coordinates of the Optimized Structures

$PhMe_2Si$

M06-2X/6-311G(d,p) Electronic Energy: -600.765986 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -600.637361 a.u.

M06-2X/cc-pVTZ Electronic Energy: -600.9105695 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-2.200526	-3.072465	0.273670
2	6	0	-2.651183	-3.735241	-1.419573
3	6	0	-3.854938	-3.372948	-2.045281
4	6	0	-1.781914	-4.587047	-2.119881
5	6	0	-4.180931	-3.846046	-3.312252
6	1	0	-4.552544	-2.714549	-1.532660
7	6	0	-2.102881	-5.062997	-3.387025
8	1	0	-0.840581	-4.888687	-1.666232
9	6	0	-3.304500	-4.692979	-3.986776
10	1	0	-5.119800	-3.556133	-3.773972
11	1	0	-1.417090	-5.724681	-3.907178
12	1	0	-3.556964	-5.063198	-4.975363
13	6	0	-1.076166	-4.286871	1.183339
14	1	0	-0.856427	-3.920851	2.189723
15	1	0	-1.557669	-5.266564	1.274020
16	1	0	-0.122910	-4.424451	0.666834
17	6	0	-3.756248	-2.712233	1.281798
18	1	0	-4.374587	-3.611596	1.374611
19	1	0	-3.488216	-2.377738	2.287453
20	1	0	-4.365032	-1.928139	0.824650

Styrene

M06-2X/6-311G(d,p) Electronic Energy: -309.5099356 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -309.406730 a.u.

M06-2X/cc-pVTZ Electronic Energy: -309.6244497 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.774676	-2.288413	0.065202
2	6	0	-1.431566	-2.188260	-0.295865
3	6	0	-0.824765	-0.943742	-0.401608
4	6	0	-1.550075	0.229382	-0.154799

5	6	0	-2.893564	0.113327	0.218346
6	6	0	-3.503848	-1.132306	0.324636
7	1	0	-3.245553	-3.262343	0.149971
8	1	0	-0.853229	-3.086371	-0.488246
9	1	0	0.226987	-0.881408	-0.663071
10	1	0	-3.465234	1.015140	0.421077
11	1	0	-4.548348	-1.199232	0.611739
12	6	0	-0.952097	1.572155	-0.269846
13	6	0	0.212476	1.874579	-0.843349
14	1	0	-1.550914	2.378654	0.150886
15	1	0	0.567933	2.898052	-0.876920
16	1	0	0.844919	1.123326	-1.306103

4-canopyridine radical anion

M06-2X/6-311G(d,p) Electronic Energy: -340.3947714 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -340.340466 a.u.

M06-2X/cc-pVTZ Electronic Energy: -340.609116 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.468928	-2.122529	-0.274858
2	6	0	-0.820590	-0.922052	-0.402538
3	6	0	-1.530680	0.306688	-0.155556
4	6	0	-2.910845	0.128535	0.216547
5	6	0	-3.435676	-1.133942	0.307724
6	1	0	-0.909246	-3.040650	-0.467362
7	1	0	0.226951	-0.894494	-0.689132
8	1	0	-3.532317	0.995100	0.424141
9	1	0	-4.484781	-1.243492	0.591693
10	6	0	-0.931409	1.565243	-0.267842
11	7	0	-0.427147	2.624011	-0.362198
12	7	0	-2.774166	-2.304060	0.076348

TS1

M06-2X/6-311G(d,p) Electronic Energy: -910.282174 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -910.031327 a.u.

M06-2X/cc-pVTZ Electronic Energy: -910.5381606 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.217785	0.448948	4.074895
2	6	0	6.750043	0.279440	2.796840
3	6	0	6.084917	0.781268	1.686166
4	6	0	4.863517	1.460382	1.825985

5	6	0	4.346786	1.630205	3.118768
6	6	0	5.013577	1.129438	4.231241
7	1	0	6.741609	0.057360	4.940548
8	1	0	7.693292	-0.241751	2.667273
9	1	0	6.520627	0.653628	0.699743
10	1	0	3.405245	2.159147	3.243515
11	1	0	4.591986	1.270512	5.221322
12	6	0	4.110971	1.984414	0.683083
13	6	0	4.321507	1.691510	-0.617115
14	1	0	3.261961	2.616676	0.937702
15	1	0	3.741508	2.174234	-1.395077
16	1	0	5.172822	1.104197	-0.948857
17	14	0	2.833538	-0.694429	-0.793610
18	6	0	1.909639	-1.517462	-2.202406
19	6	0	0.561903	-1.217670	-2.461216
20	6	0	2.553397	-2.419900	-3.065111
21	6	0	-0.115545	-1.797894	-3.528740
22	1	0	0.030832	-0.524024	-1.812804
23	6	0	1.880611	-3.003504	-4.133661
24	1	0	3.596876	-2.676050	-2.894724
25	6	0	0.542914	-2.693194	-4.368903
26	1	0	-1.159035	-1.554949	-3.705079
27	1	0	2.397978	-3.703265	-4.783004
28	1	0	0.016091	-3.147372	-5.202148
29	6	0	4.217532	-1.812214	-0.163968
30	1	0	4.672291	-1.371911	0.728628
31	1	0	3.830665	-2.802000	0.100666
32	1	0	5.006617	-1.946839	-0.909380
33	6	0	1.644325	-0.244242	0.599946
34	1	0	1.014695	-1.098232	0.869185
35	1	0	2.215503	0.054509	1.484057
36	1	0	0.990055	0.588739	0.326823

IM2

M06-2X/6-311G(d,p) Electronic Energy: -910.331454 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -910.077428 a.u.

M06-2X/cc-pVTZ Electronic Energy: -910.5866586 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.000394	1.003151	3.346469
2	6	0	6.946405	0.508336	2.042238
3	6	0	5.791697	0.629440	1.286262
4	6	0	4.634577	1.257032	1.815237
5	6	0	4.714777	1.750551	3.143615

6	6	0	5.872524	1.626006	3.889191
7	1	0	7.907765	0.905200	3.932574
8	1	0	7.817269	0.022754	1.612563
9	1	0	5.772019	0.234185	0.275607
10	1	0	3.841648	2.235973	3.571596
11	1	0	5.903275	2.014514	4.902456
12	6	0	3.432218	1.406210	1.075876
13	6	0	3.192950	0.898345	-0.296478
14	1	0	2.597326	1.880415	1.585443
15	1	0	2.453104	1.519574	-0.815241
16	1	0	4.100036	0.901063	-0.911247
17	14	0	2.494011	-0.880265	-0.255008
18	6	0	2.058577	-1.386793	-2.015719
19	6	0	1.083267	-0.679267	-2.735235
20	6	0	2.690003	-2.460777	-2.656679
21	6	0	0.751464	-1.027203	-4.040630
22	1	0	0.568984	0.159658	-2.268946
23	6	0	2.363432	-2.816404	-3.963806
24	1	0	3.448676	-3.033658	-2.128645
25	6	0	1.393561	-2.099052	-4.657484
26	1	0	-0.006656	-0.465504	-4.577606
27	1	0	2.865107	-3.653223	-4.439899
28	1	0	1.137227	-2.373685	-5.675923
29	6	0	3.764257	-2.063081	0.461874
30	1	0	4.060187	-1.739909	1.464375
31	1	0	3.353703	-3.074896	0.537105
32	1	0	4.670213	-2.110324	-0.150147
33	6	0	0.942213	-0.869130	0.807296
34	1	0	0.486142	-1.862358	0.841418
35	1	0	1.181874	-0.567646	1.831530
36	1	0	0.194810	-0.171530	0.416557

TS2

M06-2X/6-311G(d,p) Electronic Energy: -1250.7694513 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -1250.436685 a.u.

M06-2X/cc-pVTZ Electronic Energy: -1251.2129727 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.284011	0.443877	3.242522
2	6	0	7.206633	0.175246	1.870813
3	6	0	6.041505	0.389550	1.155555
4	6	0	4.862853	0.900203	1.781452
5	6	0	4.969576	1.163233	3.181354
6	6	0	6.145406	0.941008	3.880736

7	1	0	8.200711	0.263797	3.795151
8	1	0	8.080481	-0.209617	1.349006
9	1	0	6.025571	0.182599	0.089298
10	1	0	4.091357	1.538584	3.700672
11	1	0	6.173920	1.153577	4.947854
12	6	0	3.693898	1.254809	1.073212
13	6	0	3.370032	0.783819	-0.315684
14	1	0	2.842894	1.564545	1.677199
15	1	0	2.599517	1.435270	-0.760174
16	1	0	4.239753	0.853763	-0.984253
17	14	0	2.704918	-0.980450	-0.281636
18	6	0	1.992621	-1.475209	-1.975138
19	6	0	0.946015	-0.730734	-2.542332
20	6	0	2.480817	-2.560018	-2.716072
21	6	0	0.409099	-1.052333	-3.785226
22	1	0	0.542354	0.123123	-2.000412
23	6	0	1.950752	-2.891876	-3.961975
24	1	0	3.293498	-3.159754	-2.312093
25	6	0	0.911800	-2.137993	-4.499858
26	1	0	-0.399729	-0.456753	-4.199336
27	1	0	2.349621	-3.738647	-4.513897
28	1	0	0.497118	-2.392342	-5.471075
29	6	0	4.030837	-2.233406	0.185874
30	1	0	4.475186	-1.951188	1.144795
31	1	0	3.615448	-3.243390	0.272580
32	1	0	4.840569	-2.255367	-0.550333
33	6	0	1.286084	-1.083701	0.958181
34	1	0	0.848527	-2.086210	0.985980
35	1	0	1.655226	-0.831512	1.956409
36	1	0	0.491813	-0.372565	0.708029
37	6	0	3.708383	4.647872	3.077526
38	6	0	4.571738	4.040488	2.183282
39	6	0	4.077574	3.692058	0.898851
40	6	0	2.780143	4.176033	0.572191
41	6	0	2.027061	4.773854	1.559154
42	1	0	4.066637	4.871577	4.082496
43	1	0	5.584361	3.784071	2.468647
44	1	0	2.380435	4.033640	-0.426050
45	1	0	1.015279	5.106241	1.327098
46	6	0	4.981269	3.298310	-0.144087
47	7	0	5.707846	3.006173	-1.003146
48	7	0	2.444595	5.014104	2.817059

IM3

M06-2X/6-311G(d,p) Electronic Energy: -1250.7862207 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -1250.449907 a.u.

M06-2X/cc-pVTZ Electronic Energy: -1251.2389446 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.989643	-0.207683	3.192504
2	6	0	7.156211	0.056748	1.834275
3	6	0	6.141093	0.669353	1.106241
4	6	0	4.932903	1.030030	1.718544
5	6	0	4.791389	0.782270	3.089065
6	6	0	5.803660	0.164191	3.819349
7	1	0	7.780290	-0.692771	3.757551
8	1	0	8.082574	-0.216725	1.337219
9	1	0	6.289723	0.878241	0.051147
10	1	0	3.871943	1.091277	3.579314
11	1	0	5.665914	-0.023353	4.880519
12	6	0	3.817124	1.697986	0.954916
13	6	0	3.491296	0.997787	-0.372070
14	1	0	2.920452	1.681130	1.585694
15	1	0	2.669018	1.552817	-0.844797
16	1	0	4.337989	1.062444	-1.069049
17	14	0	2.938018	-0.791116	-0.175757
18	6	0	2.053471	-1.320403	-1.768394
19	6	0	0.925024	-0.613970	-2.213343
20	6	0	2.480640	-2.406133	-2.543659
21	6	0	0.250369	-0.976333	-3.375336
22	1	0	0.567027	0.240651	-1.641806
23	6	0	1.813380	-2.776283	-3.710360
24	1	0	3.354695	-2.974691	-2.234231
25	6	0	0.694707	-2.061848	-4.127760
26	1	0	-0.619578	-0.411164	-3.696951
27	1	0	2.167877	-3.621173	-4.294130
28	1	0	0.172340	-2.346356	-5.036569
29	6	0	4.340196	-2.010958	0.142469
30	1	0	4.785860	-1.821592	1.123191
31	1	0	3.970166	-3.042033	0.125013
32	1	0	5.137048	-1.918167	-0.602361
33	6	0	1.703178	-0.904069	1.244828
34	1	0	1.267656	-1.905336	1.314181
35	1	0	2.204587	-0.679556	2.192058
36	1	0	0.889412	-0.182664	1.121202
37	6	0	3.275533	4.592260	2.755378
38	6	0	4.289057	3.935454	2.120291
39	6	0	4.050659	3.277694	0.783193
40	6	0	2.846282	3.946953	0.164099
41	6	0	1.943412	4.606879	0.949936

42	1	0	3.470711	4.946298	3.772364
43	1	0	5.248059	3.788499	2.606882
44	1	0	2.684108	3.851419	-0.904873
45	1	0	1.035390	4.976556	0.462689
46	6	0	5.229006	3.426476	-0.110908
47	7	0	6.136990	3.512460	-0.826938
48	7	0	2.049514	4.906870	2.265380

TS4

M06-2X/6-311G(d,p) Electronic Energy: -1250.7681439 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -1250.433287 a.u.

M06-2X/cc-pVTZ Electronic Energy: -1251.2223953 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.837933	-0.377459	3.108373
2	6	0	7.043757	0.155902	1.837252
3	6	0	6.026987	0.843282	1.180759
4	6	0	4.776858	1.017946	1.790240
5	6	0	4.592488	0.497559	3.075196
6	6	0	5.606063	-0.199136	3.730260
7	1	0	7.632550	-0.921195	3.611125
8	1	0	8.005173	0.032362	1.347116
9	1	0	6.201869	1.263383	0.195670
10	1	0	3.633805	0.645597	3.567311
11	1	0	5.432039	-0.598561	4.725416
12	6	0	3.614950	1.694936	1.084549
13	6	0	3.300637	1.002152	-0.252786
14	1	0	2.741434	1.555122	1.738024
15	1	0	2.412259	1.467334	-0.700283
16	1	0	4.117195	1.184616	-0.962231
17	14	0	2.936743	-0.842490	-0.125388
18	6	0	2.111643	-1.376660	-1.747870
19	6	0	0.887118	-0.810315	-2.134138
20	6	0	2.677388	-2.331149	-2.602796
21	6	0	0.253281	-1.179668	-3.316601
22	1	0	0.418843	-0.059962	-1.499248
23	6	0	2.051981	-2.707481	-3.790509
24	1	0	3.628683	-2.788366	-2.340518
25	6	0	0.836697	-2.132604	-4.149076
26	1	0	-0.692860	-0.722899	-3.592069
27	1	0	2.515182	-3.447342	-4.437150
28	1	0	0.347261	-2.421881	-5.074500
29	6	0	4.446875	-1.935479	0.148238
30	1	0	4.852367	-1.779116	1.152601

31	1	0	4.182295	-2.993564	0.043603
32	1	0	5.244563	-1.705531	-0.564922
33	6	0	1.697754	-1.155398	1.265502
34	1	0	1.366699	-2.198284	1.270127
35	1	0	2.156623	-0.937519	2.235035
36	1	0	0.814009	-0.517677	1.161977
37	6	0	3.820420	5.170087	2.519064
38	6	0	4.243700	3.905295	2.179214
39	6	0	3.729988	3.239513	1.007746
40	6	0	2.597752	3.946596	0.459450
41	6	0	2.268958	5.208192	0.900408
42	1	0	4.282039	5.654395	3.382532
43	1	0	5.028689	3.430913	2.760319
44	1	0	2.045000	3.522691	-0.373278
45	1	0	1.438243	5.724262	0.413684
46	6	0	5.152881	3.306810	-0.403029
47	7	0	5.930134	3.563115	-1.237333
48	7	0	2.849067	5.876045	1.913137

P

M06-2X/6-311G(d,p) Electronic Energy: -1157.9739101 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -1157.641293 a.u.

M06-2X/cc-pVTZ Electronic Energy: -1158.3140038 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.930162	-0.169834	2.909111
2	6	0	6.964690	0.587948	1.738439
3	6	0	5.802708	1.173495	1.251285
4	6	0	4.585431	1.004843	1.918874
5	6	0	4.565164	0.265212	3.101031
6	6	0	5.729632	-0.323135	3.594274
7	1	0	7.837152	-0.629704	3.287539
8	1	0	7.901179	0.722176	1.206473
9	1	0	5.834116	1.770921	0.343107
10	1	0	3.627586	0.143944	3.638369
11	1	0	5.695357	-0.900501	4.512687
12	6	0	3.308117	1.583991	1.331477
13	6	0	2.980286	0.933745	-0.022462
14	1	0	2.494724	1.338245	2.028778
15	1	0	2.034122	1.341028	-0.403849
16	1	0	3.745239	1.202811	-0.763763
17	14	0	2.824026	-0.958929	-0.030508
18	6	0	2.001523	-1.405866	-1.667633
19	6	0	0.685487	-0.997568	-1.933637

20	6	0	2.668406	-2.136481	-2.659612
21	6	0	0.060023	-1.303742	-3.137994
22	1	0	0.133693	-0.430335	-1.185470
23	6	0	2.050468	-2.446756	-3.869565
24	1	0	3.688680	-2.471562	-2.488462
25	6	0	0.744701	-2.030553	-4.109950
26	1	0	-0.959504	-0.978077	-3.320029
27	1	0	2.587792	-3.013812	-4.623511
28	1	0	0.260373	-2.271592	-5.051065
29	6	0	4.491823	-1.820865	0.072470
30	1	0	4.946789	-1.684968	1.058020
31	1	0	4.378355	-2.895086	-0.106055
32	1	0	5.191679	-1.425280	-0.670499
33	6	0	1.705957	-1.501987	1.384880
34	1	0	1.493290	-2.572419	1.313780
35	1	0	2.178928	-1.317688	2.354043
36	1	0	0.749607	-0.969700	1.368014
37	6	0	3.701814	5.199209	2.437037
38	6	0	3.629452	3.813792	2.471899
39	6	0	3.391483	3.106599	1.289388
40	6	0	3.246132	3.857017	0.126172
41	6	0	3.341558	5.247460	0.197917
42	1	0	3.883189	5.759513	3.351470
43	1	0	3.766716	3.282569	3.409729
44	1	0	3.057492	3.383238	-0.830409
45	1	0	3.231403	5.843392	-0.705768
46	7	0	3.563022	5.924724	1.322022

CN^-

M06-2X/6-311G(d,p) Electronic Energy: -92.7921816 a.u.

M06-2X/6-311G(d,p) Gibbs free Energy: -92.806220 a.u.

M06-2X/cc-pVTZ Electronic Energy: -92.9592314 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.931923	1.564165	-0.267746
2	7	0	-0.426633	2.625089	-0.362294

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