Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Stereodivergent Asymmetric Synthesis of P-Atropisomeric Si-Stereogenic Monohydrosilanes

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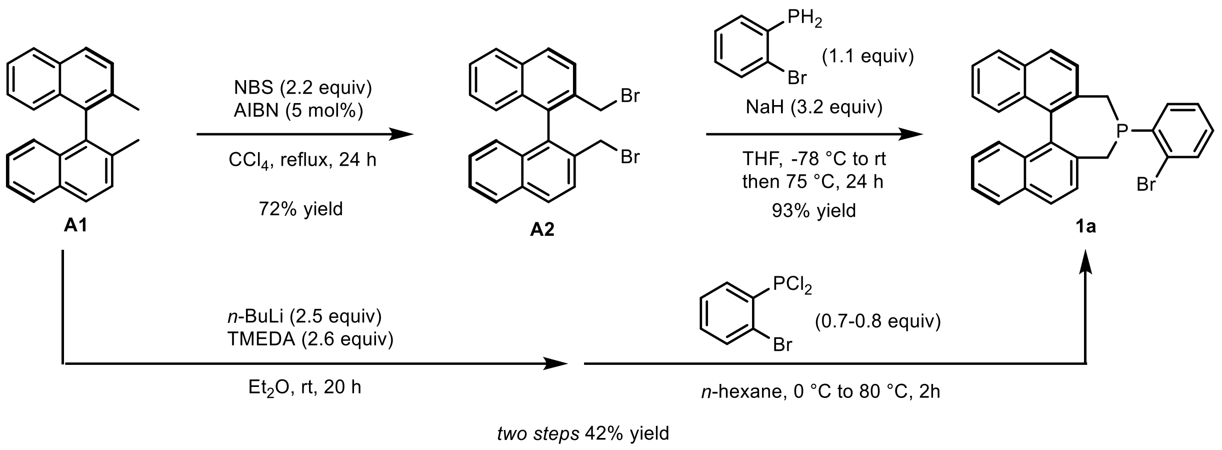
1. General Information

Regular reactions were carried out under argon atmosphere with magnetic stirring. Catalysis reactions were performed in colourless 5 mL microwave reaction tube under an inert atmosphere of argon. Anhydrous solvents were obtained from Inert Pure Solv solvent purification system (Et_2O, CH_2Cl_2, THF and toluene). TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λmax = 254 nm). Column chromatography was performed using GENERAL-REAGENT silica gel (200-300 mesh). Unless otherwise specified, all reagents were purchased from commercial suppliers (Bide Pharmatech, Energy Chemical, TCI, Aldrich, Alfa and J&K) and directly used without further purification. -84 °C is obtained using ethyl acetate/N_2(l) bath and -116 °C is obtained using ethanol/N_2(l) bath.

NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ^{1}H NMR, 100 or 151 MHz for ^{13}C NMR and 376 MHz or 565 MHz for ^{19}F NMR, respectively, at ambient temperature. Chemical shifts (δ) were reported in ppm and coupling constants (J) were quoted in Hertz (Hz). NMR standards were used as follows: (^{1}H NMR) $CDCl_3$ = 7.26 ppm; (^{13}C NMR) $CDCl_3$ = 77.16 ppm. ^{1}H NMR data were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; dd = doublet of doublets, t = triplet; q = quarter; m = multiplet; br = broad), coupling constant (Hz), integration. ^{13}C NMR data were reported in terms of chemical shift (δ, ppm). Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectrometry (HRMS) was performed on Waters Premier GC-TOF MS, Agilent Technologies 7250 GCQTOF, Agilent Technologies 6230 TOF LC/MS, Thermo Fisher Scientific LTQ FT Ultra under the conditions of electron impact ionization (EI), electrospray ionization (ESI) or direct analysis real time (DART) in a positive mode. Optical rotations were measured on Rudolph Autopol-I Automatic Polarimeter at concentrations of 1.0 g/100 mL, 0.1 g/100 mL or 0.5 g/100 mL in CH_2Cl_2.

2. Synthesis of P-Atropisomeric Compounds



Synthesis of (*R*)-4-(2-bromophenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (1a)

Experimental procedure A:

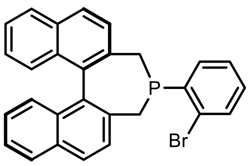
According to a modified procedure.[1-3] A mixture of (*R*)-2,2'-dimethyl-1,1'-binaphthalene (**A1**) (4.24 g, 15.0 mmol, 1.0 equiv), *N*-bromosuccinimide (NBS) (5.87 g, 33.0 mmol, 2.2 equiv), and 2,2′-Azobis(2-methylpropionitrile) (AIBN) (123.2 mg, 0.75 mmol, 0.05 equiv) in degassed CCl_4 (150 mL) was refluxed for 24 h under Ar atmosphere. After being cooled to room temperature, filtered through a celite pad, and washed with CH_2Cl_2. The organic layer was neutralized with saturated $NaHCO_3$, washed with brine, dried over Na_2SO_4 and the solvent was removed in vacuo. The resultant residue was filtered through the pad of silica gel. The solvent was removed in vacuo and the crude material was recrystallized in DCM/petroleum ether to afford (*R*)-2,2'-bis(bromomethyl)-1,1'-binaphthalene (**A2**) as a colourless solid (4.74 g, 72% yield). The product was characterized by ^1H and ^{13}C NMR spectroscopy and the data is in agreement with that reported in the literature.[1]

To a solution of **A2** (4.74 g, 10.8 mmol, 1.0 equiv) and NaH (60% in mineral oil, 1.38 g, 34.6 mmol, 3.2 equiv) in anhydrous THF (0.12 M) was added (2-bromophenyl)phosphane[4,5] (2.04 g, 10.8 mmol, 1 equiv) dropwise at °C under Ar atmosphere. The mixture was warmed to room temperature spontaneously and stirred at room temperature for 24 h. After additional (2-bromophenyl)phosphane (204 mg, 1.08 mmol, 0.1 equiv) was added, the mixture was heated to refluxing for 24 h. The solvent was removed under vacuum after the reaction was completed (monitored by TLC). The residue was purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (100/1) as elute to afford **1a** as white solid (4.67 g, 93% yield).

Experimental procedure B:

According to a modified procedure from Oestreich.[6] *n*-BuLi (2.5M in *n*-hexane, 20 mL, 50 mmol, 2.5 equiv) was placed in a 250 mL Schlenk tube, and the solvent was evaporated in high vacuum. The residue was dissolved in Et_2O (60 mL), and the mixture was cooled to 0 °C. A solution of (*R*)-2,2'-dimethyl-1,1'-binaphthalene (**A1**) (5.65 g, 20 mmol, 1 equiv) in Et_2O (60 mL) was added dropwise, followed by freshly distilled TMEDA (7.8 mL, 52 mmol, 2.6 equiv). The resulting suspension was stirred for 20 h at room temperature. The mixture was filtered under Ar atmosphere, and the resulting solid was washed with dry *n*-hexane (60 mL). Drying in high vacuum afforded dilithiated (*R*)-2,2'-dimethyl-1,1'-binaphthalene·2TMEDA (5.4 g, 51%) as a red solid.

A suspension of dilithiated (*R*)-2,2'-dimethyl-1,1'-binaphthalene·2TMEDA (5.4 g, 10.26 mmol, 1equiv) in *n*-hexane (60 mL) was cooled to 0 °C, (2-bromophenyl)dichlorophosphane[4] (2.91 g, 11.29 mmol, 1.1 equiv) was added, and the resulting mixture was heated at 80 °C for 2 h. The reaction was quenched by the addition of water and extracted with CH_2Cl_2, the solvent was removed in vacuo. The residue was purified by a flash column chromatography on silica gel with petroleum ether/ethyl acetate (100/0 to 100/1) as elute to afford the **1a** as white solid (3.87 g, 42% yield over 2 steps).



1a

$[\alpha]_D^{25}$ = +439.00 (c = 0.1, CH_2Cl_2);

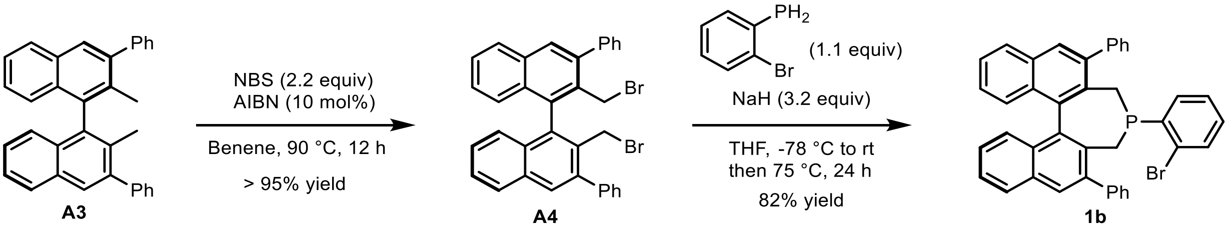
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.88 – 7.80 (m, 1H), 7.73 – 7.58 (m, 3H), 7.47 – 7.36 (m, 2H), 7.30 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.16 (td, *J* = 7.6, 1.7 Hz, 1H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 6.79 (dt, *J* = 7.6, 1.7 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.11 (dd, *J* = 14.3, 3.7 Hz, 1H), 2.89 (dd, *J* = 16.6, 11.3 Hz, 1H), 2.84 – 2.70 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.61 (d, *J* = 25.8 Hz), 134.09 (d, *J* = 4.6 Hz), 133.85 (d, *J* = 2.1 Hz), 133.82, 133.26, 133.24, 133.06, 133.03 (d, *J* = 1.8 Hz), 132.43, 132.26 (d, *J* = 2.1 Hz), 131.95, 131.90, 130.23, 128.98 (d, *J* = 29.1 Hz), 128.50 (d, *J* = 1.8 Hz), 128.44, 128.32, 127.74, 127.63 (d, *J* = 2.5 Hz), 127.15, 126.85, 126.75, 126.12, 126.02, 125.31, 125.02, 30.36 (d, *J* = 22.7 Hz), 29.43 (d, *J* = 17.7 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ 3.07.

HRMS (ESI) m/z calcd for $C_{28}H_{21}BrP$ $[M + H]^+$ 467.0559, found 467.0561.

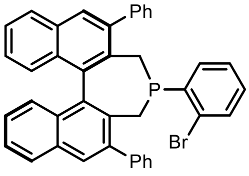
Synthesis of (*R*)-4-(2-bromophenyl)-2,6-diphenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (1b)



A mixture of (*R*)-2,2'-dimethyl-3,3'-diphenyl-1,1'-binaphthalene[7] (**A3**) (3.04 g, 7.0 mmol, 1.0 equiv), *N*-bromosuccinimide (NBS) (2.74 g, 15.4 mmol, 2.2 equiv), and 2,2′-Azobis(2-methylpropionitrile) (AIBN) (114.9 mg, 0.7 mmol, 0.1 equiv) in degassed benzene (35 mL) was refluxed for 12 h under Ar atmosphere. After being cooled to room temperature, filtered through a celite pad, and washed with CH_2Cl_2. The organic layer was neutralized with saturated $NaHCO_3$, washed with brine, dried over Na_2SO_4 and the solvent was removed in vacuo. The resultant residue was filtered through the pad of silica gel. The solvent was removed in vacuo and the crude material was recrystallized in DCM/petroleum ether to afford (*R*)-2,2'-

bis(bromomethyl)-3,3'-diphenyl-1,1'-binaphthalene (**A4**) as a colourless solid (3.95 g, 95% yield).

To a solution of **A4** (3.95 g, 6.7 mmol, 1.0 equiv) and NaH (60% in mineral oil, 0.86 g, 21.3 mmol, 3.2 equiv) in anhydrous THF (0.12 M) was added (2-bromophenyl)phosphane[4,5] (1.27 g, 6.7 mmol, 1.0 equiv) dropwise at °C under Ar atmosphere. The mixture was warmed to room temperature spontaneously and stirred at room temperature for 24 h. After additional (2-bromophenyl)phosphane (127 mg, 0.67 mmol, 0.1 equiv) was added, the mixture was heated to refluxing for 24 h. The solvent was removed under vacuum after the reaction was completed (monitored by TLC). The residue was purified by a flash column chromatography on silica gel with petroleum ether/dichloromethane (100/1) as elute to afford the product as white solid (3.38 g, 82% yield).



1b

$[\alpha]_D^{25}$ = +266.00 (c = 0.1, CH_2Cl_2);

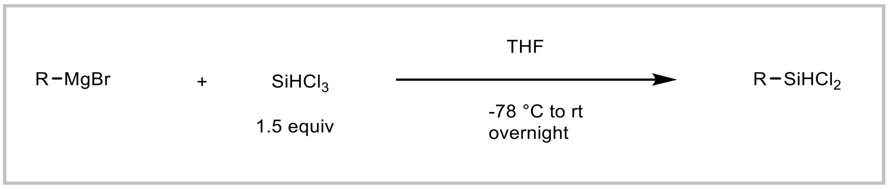
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.60 (s, 1H), 7.47 (dt, *J* = 8.1, 3.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 3H), 7.38 – 7.18 (m, 9H), 7.18 – 7.02 (m, 4H), 6.64 (d, *J* = 7.4 Hz, 1H), 3.76 (dd, *J* = 14.7, 3.1 Hz, 1H), 2.89 (dd, *J* = 14.6, 11.3 Hz, 1H), 2.71 – 2.62 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.56, 141.12, 140.41 (d, *J* = 2.9 Hz), 140.27, 137.64 (d, *J* = 217.4 Hz), 136.75, 135.14 (d, *J* = 4.5 Hz), 134.40, 133.41, 133.40, 132.40, 131.87, 131.76, 131.71 (d, *J* = 1.7 Hz), 131.38, 131.28, 130.07, 130.05 (d, *J* = 28.8 Hz), 130.04, 129.65, 129.46, 128.90, 128.33 (2), 128.28, 127.34, 126.92, 126.90, 126.77, 126.63, 126.12, 125.96, 125.77, 125.44, 26.02 (d, *J* = 18.4 Hz), 25.03 (d, *J* = 25.2 Hz).

^{31}P NMR (243 MHz, $CDCl_3$) δ 1.18.

HRMS (ESI) m/z calcd for $C_{40}H_{29}BrP$ $[M + H]^+$ 619.1185, found 619.1186.

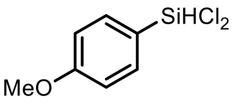
3. Synthesis of Dichlorosilane Compounds



Experimental procedure C:

To the solution of $SiHCl_3$ (4.6 mL, 45.0 mmol, 1.5 equiv) in THF (50 mL) at -78 °C was added freshly prepared grignard reagent (30.0 mmol, 1.0 equiv) dropwise. The reaction was stirred at -78 °C for 1 h, then warmed to room temperature overnight. Next, the reaction mixture was evaporated to dryness in vacuo to yield colourless oil with much solid inorganic salts. *n*-hexane (50 mL) was added to the crude mixture and the resulting slurry was sonicated and filtered to remove any unwanted inorganic salts, which was washed with *n*-hexane (2 × 50 mL). The clear and colourless filtrate was evaporated to dryness in vacuo to yield a translucent brown oil, the crude oil was distilled to yield pure dichlorosilane compound.

Dichloro(4-methoxyphenyl)silane (2b).



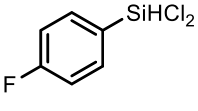
According to experimental procedure C, To the solution of $SiHCl_3$ (4.6 mL, 45.0 mmol, 1.5 equiv) in THF (50 mL) at -78 °C was added freshly prepared *p*-MeO-C_6H_4MgBr (30.0 mmol, 1.0 equiv) dropwise. The reaction was stirred at -78 °C for 1 h, then warmed to room temperature overnight. Next, the reaction mixture was evaporated to dryness in vacuo to yield colourless oil with much solid inorganic salts. *n*-hexane (50 mL) was added to the crude mixture and the resulting slurry was sonicated and filtered to remove any unwanted inorganic salts, which was washed with *n*-hexane (2 × 50 mL). The clear and colourless filtrate was evaporated to dryness in vacuo to yield a translucent brown oil, the crude oil was distilled to yield pure **2b** (4.24 g, 68% yield) as colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.39 (m, 2H), 6.97 – 6.77 (m, 2H), 5.96 – 5.68 (m, 1H), 3.81 – 3.62 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.97, 135.31, 122.14, 114.41, 55.31;

^{29}Si NMR (79 MHz, $CDCl_3$) δ -2.39.

Dichloro(4-fluorophenyl)silane (2c).



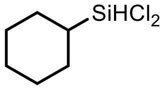
According to experimental procedure C, To the solution of $SiHCl_3$ (4.6 mL, 45.0 mmol, 1.5 equiv) in THF (50 mL) at -78 °C was added freshly prepared *p*-F-C_6H_4MgBr (30.0 mmol, 1.0 equiv) dropwise. The reaction was stirred at -78 °C for 1 h, then warmed to room temperature overnight. Next, the reaction mixture was evaporated to dryness in vacuo to yield colourless oil with much solid inorganic salts. *n*-hexane (50 mL) was added to the crude mixture and the resulting slurry was sonicated and filtered to remove any unwanted inorganic salts, which was washed with *n*-hexane (2 × 50 mL). The clear and colourless filtrate was evaporated to dryness in vacuo to yield a translucent brown oil, the crude oil was distilled to yield pure **2c** (3.62 g, 62% yield) as colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.66 (m, 2H), 7.25 – 7.15 (m, 2H), 5.98 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.60 (d, *J* = 253.6 Hz), 136.01 (d, *J* = 8.4 Hz), 127.06 (d, *J* = 3.7 Hz), 116.17 (d, *J* = 20.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -105.69.

Dichloro(cyclohexyl)silane (2d).

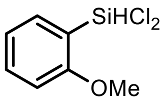


According to experimental procedure C, To the solution of $SiHCl_3$ (4.6 mL, 45.0 mmol, 1.5 equiv) in THF (50 mL) at -78 °C was added freshly prepared CyMgBr (30.0 mmol, 1.0 equiv) dropwise. The reaction was stirred at -78 °C for 1 h, then warmed to room temperature overnight. Next, the reaction mixture was evaporated to dryness in vacuo to yield colourless oil with much solid inorganic salts. *n*-hexane (50 mL) was added to the crude mixture and the resulting slurry was sonicated and filtered to remove any unwanted inorganic salts, which was washed with *n*-hexane (2 × 50 mL). The clear and colourless filtrate was evaporated to dryness in vacuo to yield a translucent brown oil, the crude oil was distilled to yield pure **2d** (3.19 g, 58% yield) as colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.34 (s, 1H), 1.91 – 1.77 (m, 4H), 1.76 – 1.69 (m, 1H), 1.36 – 1.24 (m, 5H), 1.25 – 1.14 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 29.51, 26.99, 26.36, 25.29.

Dichloro(2-methoxyphenyl)silane (2e).

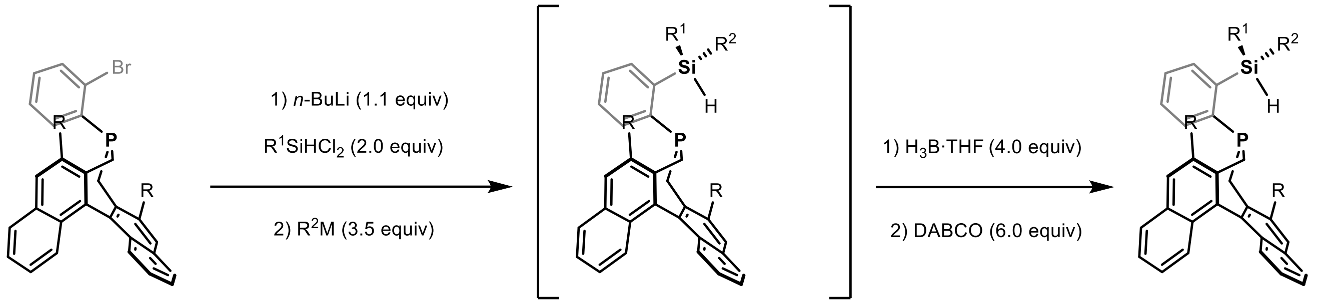


According to experimental procedure C, To the solution of $SiHCl_3$ (4.6 mL, 45.0 mmol, 1.5 equiv) in THF (50 mL) at -78 °C was added freshly prepared *o*-MeO-C_6H_4MgBr (30.0 mmol, 1.0 equiv) dropwise. The reaction was stirred at -78 °C for 1 h, then warmed to room temperature overnight. Next, the reaction mixture was evaporated to dryness in vacuo to yield colourless oil with much solid inorganic salts. *n*-hexane (50 mL) was added to the crude mixture and the resulting slurry was sonicated and filtered to remove any unwanted inorganic salts, which was washed with *n*-hexane (2 × 50 mL). The clear and colourless filtrate was evaporated to dryness in vacuo to yield a translucent brown oil, the crude oil was distilled to yield pure **2e** (4.03 g, 65% yield) as colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.53 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.07 (td, *J* = 7.4, 0.9 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 5.98 (s, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.27, 135.49, 134.55, 121.33, 119.36, 110.47, 55.90.

4. Synthesis of P-Atropisomeric Si-Stereogenic Monohydrosilanes

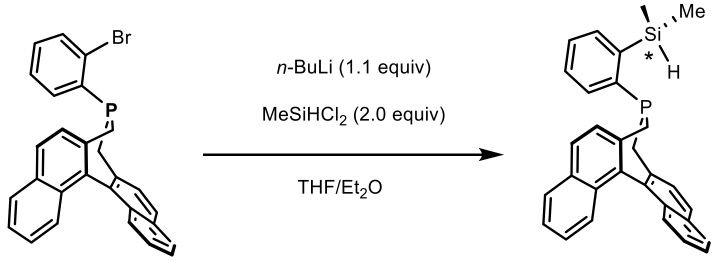


1a/1b **crude 5** **5**

Experimental procedure D:

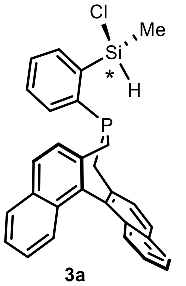
To a Schlenk flask with P-atropisomeric **1a/1b** (1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. R^1SiHCl_2 (2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared R^2MgBr/ R^2Li (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. Crude P-atropisomeric Si-stereogenic monohydrosilanes **5** were characterized by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5**$\cdot BH_3$, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography to afford P-atropisomeric Si-stereogenic monohydrosilanes **5.**

Synthesis of (4*S*,11b*R*)-4-(2-((*R*)-chloro(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (3a)



1a **3a**, 92% NMR yield, dr > 99:1

To a Schlenk flask with chiral phosphorus compound **1a** (467.3 mg, 1 mmol, 1 equiv) was added THF (5 mL) at room temperature. The reaction mixture was cooled to -84 °C (using ethyl acetate / liquid nitrogen bath) before the drop-wise addition of *n*-BuLi (0.44 mL, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. $MeSiHCl_2$ (210 μL, 2 mmol, 2 equiv) was added **quickly** and the solution was stirred at -84 °C for another 1 h. Then the solution was warmed to room temperature. The solvent was removed in vacuo. 95% yield and > 99:1 dr were determined by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard.

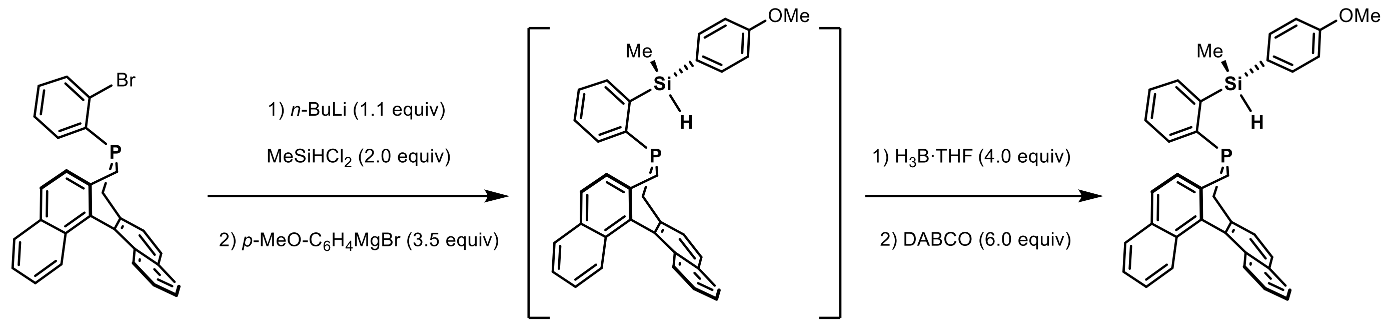


3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.84 (m, 4H), 7.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.63 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.48 – 7.37 (m, 3H), 7.32 – 7.17 (m, 5H), 6.96 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.80 (dd, *J* = 7.3, 3.3 Hz, 1H), 5.70 (ddt, *J* = 8.3, 5.4, 2.9 Hz, 1H), 3.14 – 2.99 (m, 1H), 2.98 – 2.76 (m, 2H), 2.64 (dt, *J* = 14.2, 3.4 Hz, 1H), 0.89 (d, *J* = 3.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.69 (d, *J* = 18.8 Hz), 140.85 (d, *J* = 47.3 Hz), 135.47 (d, *J* = 16.5 Hz), 133.83, 133.29, 133.09, 133.00, 132.58, 132.35, 132.19, 131.55, 130.22, 129.73, 129.03, 128.74, 128.40, 128.36, 127.77, 127.60, 126.85, 126.79, 126.16, 126.03, 125.32, 125.23, 125.11 (d, *J* = 9.7 Hz), 31.71 (d, *J* = 20.0 Hz), 30.34 (d, *J* = 14.9 Hz), 2.94 (d, *J* = 10.7 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -5.27.



1a **crude 5a**, 83% NMR yield, dr = 11:1 **5a**, 58% isolated yield, > 99% de

(4*R*, 11b*S*)-4-(2-((*R*)-(4-Methoxyphenyl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5a). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *p*-MeO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 83% yield and 11:1 dr were determined by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5a**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5a** (313.5 mg, 58% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +278.40 (c = 1.0, CH_2Cl_2);

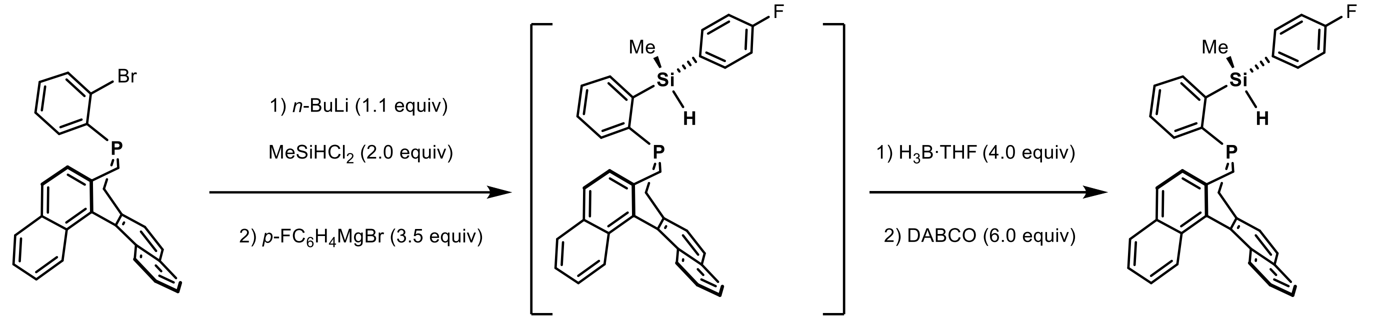
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 3H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.64 (dt, *J* = 7.4, 1.9 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.40 (m, 2H), 7.31 (m, 1H), 7.27 – 7.19 (m, 2H), 7.21 – 7.11 (m, 3H), 6.90 – 6.86 (m, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.79 – 6.76 (m, 1H), 5.20 (dt, *J* = 7.4, 3.7 Hz, 1H), 3.77 (s, 3H), 2.98 (dd, *J* = 11.9, 2.1 Hz, 1H), 2.71 (dd, *J* = 17.3, 11.9 Hz, 1H), 2.63 (dd, *J* = 14.4, 12.1 Hz, 1H), 2.22 (dd, *J* = 14.4, 3.7 Hz, 1H), 0.76 (dd, *J* = 3.8, 1.7 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.68, 143.70 (d, *J* = 30.6 Hz), 143.47 (d, *J* = 5.5 Hz), 136.81, 136.80, 136.66 (d, *J* = 15.0 Hz), 134.56, 133.75, 133.70 (d, *J* = 4.8 Hz), 133.09, 132.87, 132.44, 132.32 (d, *J* = 1.9 Hz), 132.16, 131.66 (d, *J* = 2.1 Hz), 129.15, 129.09, 128.98, 128.46, 128.35, 128.31, 127.80 (d, *J* = 2.3 Hz), 127.50, 126.82, 126.80, 126.00, 125.98, 125.12, 125.00, 113.77, 55.15, 31.69 (d, *J* = 22.4 Hz), 30.77 (d, *J* = 16.9 Hz), -3.01 (d, *J* = 12.5 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -3.07;

HRMS (ESI) m/z calcd for $C_{36}H_{32}OPSi$ $[M + H]^+$ 539.1955, found 539.1953.

Melting point: 97.6-99.3 °C.



1a

crude 5b, 87% NMR yield, dr = 12:1

5b, 65% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-(4-Fluorophenyl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5b). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *p*-F-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 87% yield and 12:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5b**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5b** (342.9 mg, 65% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +239.00 (c = 1.0, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 3H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.13 (m, 5H), 7.03 (t, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.79 (dd, *J* = 7.7, 2.7 Hz, 1H), 5.21 (m, 1H), 2.98 (dd, *J* = 11.9, 2.4 Hz, 1H), 2.74 – 2.60 (m, 2H), 2.20 (dd, *J* = 14.4, 3.7 Hz, 1H), 0.77 (dd, *J* = 3.8, 1.5 Hz, 3H);

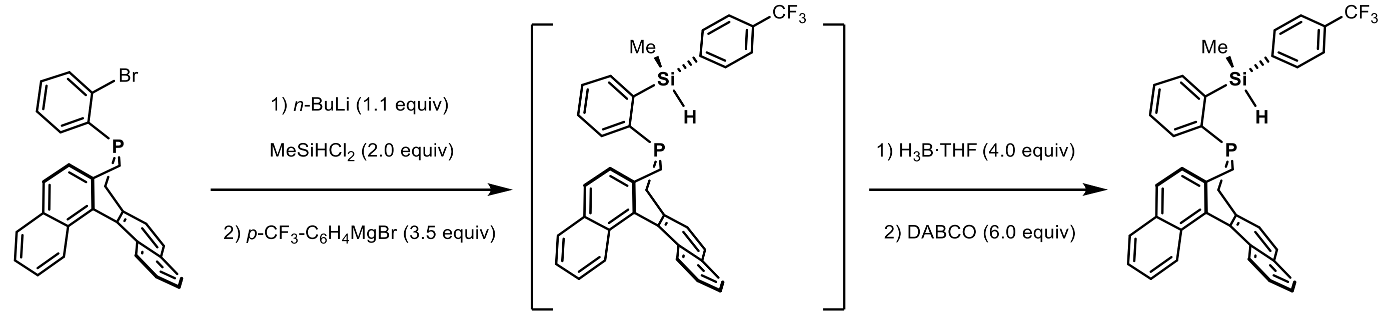
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.89 (d, *J* = 248.5 Hz), 143.59 (d, *J* = 21.8 Hz), 142.94 (d, *J* = 47.4 Hz), 137.29 (d, *J* = 2.6 Hz), 137.24 (d, *J* = 2.6 Hz), 136.61 (d, *J* = 15.2 Hz), 134.38, 133.70 (d, *J* = 4.7 Hz), 133.57, 133.14, 132.90 (d, *J* = 1.3 Hz), 132.48, 132.37 (d, *J* = 3.8 Hz), 132.33 (d, *J* = 2.3 Hz), 132.17, 131.82 (d, *J* = 2.2 Hz), 129.40, 129.13, 129.05, 128.53, 128.36, 128.32, 127.71 (d, *J* = 2.4 Hz), 127.56, 126.84, 126.79, 126.06, 126.03, 125.18, 125.07, 115.22, 115.09, 31.59, 30.76 (d, *J* = 16.5 Hz), -3.08 (d, *J* = 12.5 Hz);

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.56;

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.30;

HRMS (ESI) m/z calcd for $C_{35}H_{29}FPSi$ $[M + H]^+$ 527.1755, found 527.1755.

Melting point: 118.8-119.9 °C.



1a **crude 5c**, 82% NMR yield, dr > 20:1 **5c**, 62% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-Methyl(4-(trifluoromethyl)phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5c). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *p*-CF_3-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 82% yield and 20:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5c**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5c** (356.4 mg, 62% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +207.40 (c = 1.0, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.1 Hz, 1H), 7.90 (dd, J = 8.4, 3.8 Hz, 2H), 7.80 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 7.7 Hz, 2H), 7.62 (m, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 8.3 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 6.2 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.15 (d, J = 8.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.82 (dd, J = 7.7, 2.6 Hz, 1H), 5.29 – 5.24 (m, 1H), 2.97 (dd, J = 11.9, 2.7 Hz, 1H), 2.68 (dt, J = 17.2, 11.7 Hz, 2H), 2.29 (dd, J = 14.4, 3.6 Hz, 1H), 0.79 (dd, J = 3.8, 1.6 Hz, 3H);

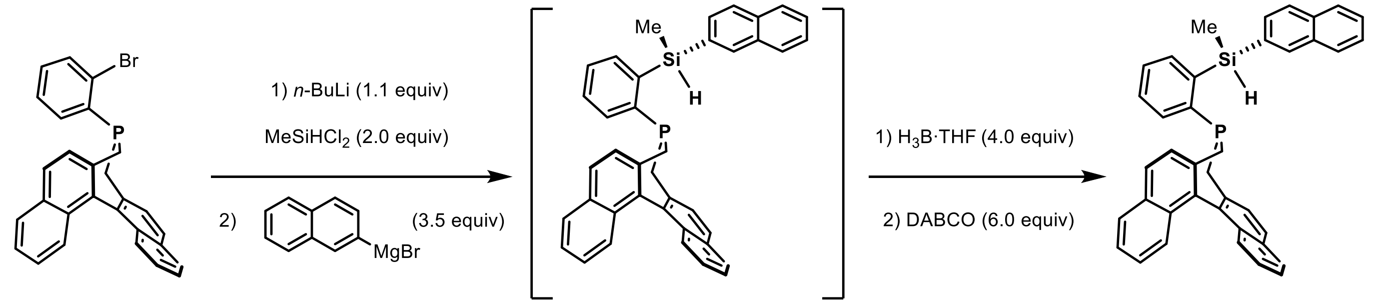
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.82 (d, J = 21.5 Hz), 142.22 (d, J = 4.5 Hz), 142.01 (d, J = 48.1 Hz), 136.56 (d, J = 15.2 Hz), 135.54, 135.52, 134.21, 133.67 (d, J = 4.8 Hz), 133.46, 133.21, 132.92 (d, J = 1.5 Hz), 132.51, 132.33 (d, J = 2.1 Hz), 131.99 (d, J = 2.1 Hz), 131.99, 131.19 (q, J = 32.1 Hz), 129.68, 129.30, 129.05, 128.59, 128.37, 128.33, 127.63, 126.85, 126.80, 126.09, 126.07, 125.22, 125.13, 124.43 (q, J = 3.7 Hz), 31.66 (d, J = 21.9 Hz), 30.91 (d, J = 16.3 Hz), -3.30 (d, J = 12.2 Hz);

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.83;

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.36;

HRMS (ESI) m/z calcd for $C_{36}H_{29}F_3PSi$ $[M + H]^+$ 577.1723, found 577.1722.

Melting point: 119.6-120.1 °C.



1a

crude 5d, 81% NMR yield, dr = 9:1

5d, 62% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*R*)-Methyl(naphthalen-2-yl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5d). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared naphthalen-2-ylmagnesium bromide

(3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 81% yield and 9:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5d**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5d** (346.9 mg, 62% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +269.90 (c = 1.0, CH_2Cl_2);

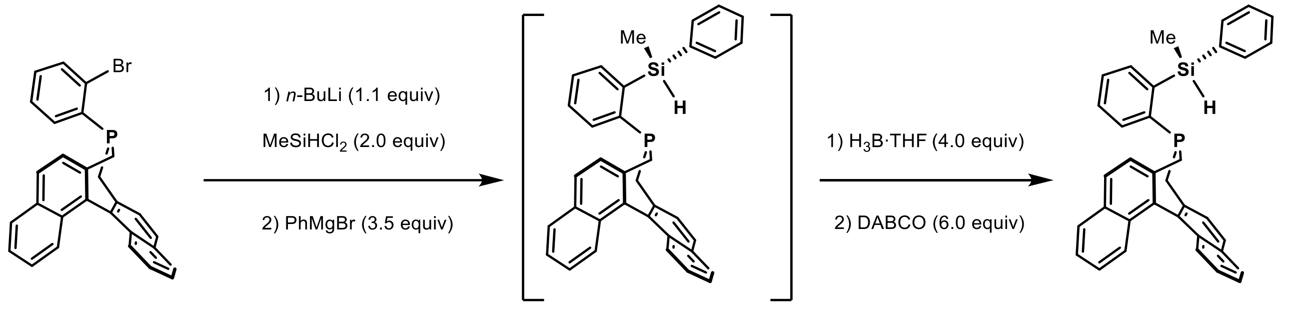
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.76 (m, 4H), 7.70 – 7.63 (m, 2H), 7.48 – 7.32 (m, 6H), 7.22 (d, *J* = 3.8 Hz, 2H), 7.20 – 7.14 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 7.7, 2.7 Hz, 1H), 5.36 (dq, *J* = 7.3, 3.7 Hz, 1H), 2.95 (dd, *J* = 11.8, 2.5 Hz, 1H), 2.71 – 2.58 (m, 2H), 2.27 (dd, *J* = 14.3, 3.7 Hz, 1H), 0.85 (dd, *J* = 3.8, 1.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.85 (d, *J* = 21.9 Hz), 143.13 (d, *J* = 47.7 Hz), 136.71 (d, *J* = 15.2 Hz), 136.16, 136.14, 134.43 (d, *J* = 4.0 Hz), 134.41, 133.91, 133.69, 133.62 (d, *J* = 4.9 Hz), 133.14, 133.12, 132.86, 132.45, 132.29 (d, *J* = 2.0 Hz), 132.18, 131.86 (d, *J* = 1.8 Hz), 131.35, 131.32, 129.36, 129.12, 128.47 (d, *J* = 1.3 Hz), 128.33, 128.30, 128.23, 127.89, 127.71 (d, *J* = 2.1 Hz), 127.54, 127.15, 126.83, 126.77, 126.60, 126.07, 125.98, 125.10, 125.03, 31.67 (d, *J* = 22.6 Hz), 30.98 (d, *J* = 16.8 Hz), -3.06 (d, *J* = 12.2 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -3.10;

HRMS (ESI) m/z calcd for $C_{39}H_{32}PSi$ $[M + H]^+$ 559.2005, found 559.2004.

Melting point: 128.6-129.8 °C.



1a **crude 5e**, 77% NMR yield, dr = 8:1 **5e**, 55% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-Methyl(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5e). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared PhMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 77% yield and 8:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5e**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5e** (278.8 mg, 55% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +273.60 (c = 1.0, CH_2Cl_2);

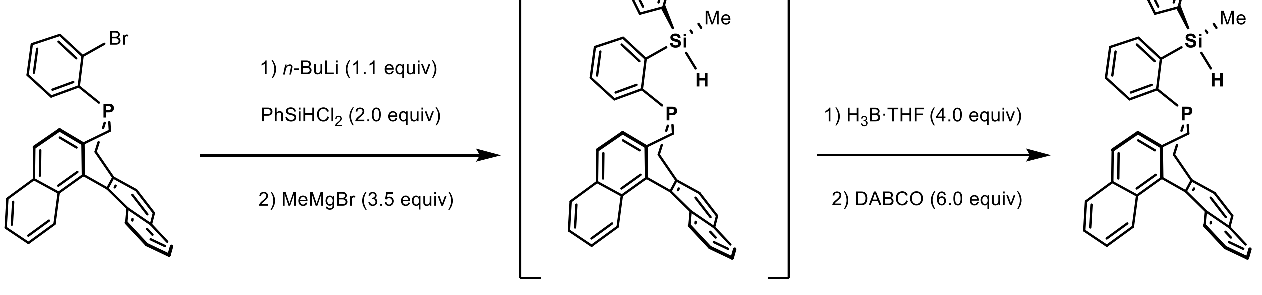
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.85 (m, 3H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.65 (dt, *J* = 7.4, 1.9 Hz, 1H), 7.58 (m, 2H), 7.51 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.20 (m, 2H), 7.20 – 7.11 (m, 3H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.79 (dd, *J* = 7.8, 2.8 Hz, 1H), 5.22 (m, 1H), 2.97 (dd, *J* = 11.8, 2.3 Hz, 1H), 2.75 – 2.57 (m, 2H), 2.20 (dd, *J* = 14.3, 3.8 Hz, 1H), 0.78 (dd, *J* = 3.8, 1.7 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.67 (d, *J* = 21.9 Hz), 143.24 (d, *J* = 47.7 Hz), 136.90 (d, *J* = 4.2 Hz), 136.71 (d, *J* = 15.0 Hz), 135.32, 135.31, 134.50, 133.73, 133.68 (d, *J* = 4.6 Hz), 133.13, 132.88, 132.46, 132.32 (d, *J* = 2.0 Hz), 132.18, 131.76 (d, *J* = 2.2 Hz), 129.31, 129.27, 129.09, 129.05, 128.49(d, *J* = 1.5 Hz), 128.36, 128.32, 127.97, 127.77 (d, *J* = 2.2 Hz), 127.53, 126.84, 126.79, 125.99, 125.12, 125.02, 31.59 (d, *J* = 22.4 Hz), 30.86 (d, *J* = 16.8 Hz), -3.22 (d, *J* = 12.6 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -3.03;

HRMS (ESI) m/z calcd for $C_{35}H_{30}PSi$ $[M + H]^+$ 509.1849, found 509.1848.

Melting point: 117.1-118.6 °C.

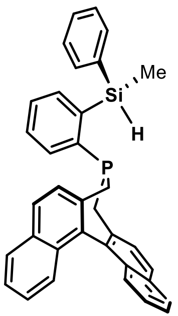


1a

crude 5f, 78% NMR yield, dr = 1:1

5f, 32% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*S*)-Methyl(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5f). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared MeMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 78% yield and 1:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5f**·BH_3 and **5e**·BH_3 respectively, that was then respectively removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was respectively concentrated and purified respectively by flash silica gel column chromatography (PE/EA = 100:1) to afford **5f** (161.3 mg, 32% yield, > 99% de) as white foam and **5e** (142.1 mg, 28% yield, > 99% de) as white foam:



5f

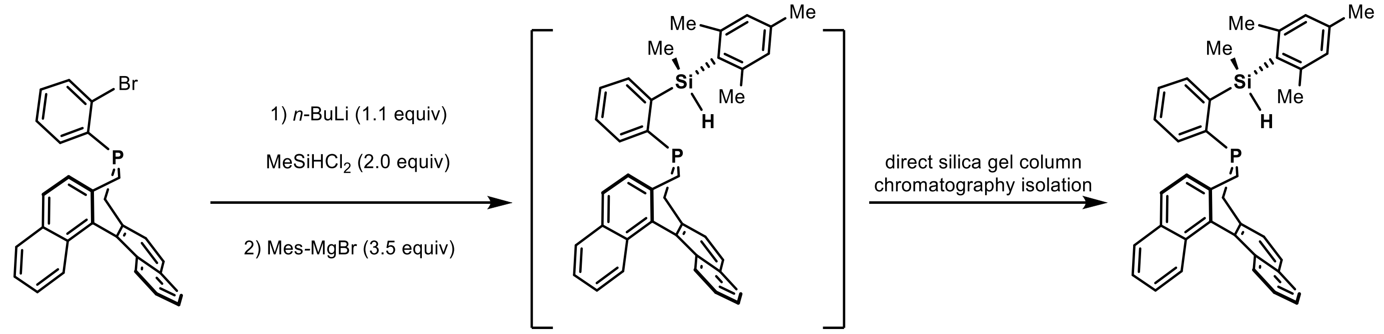
$[\alpha]_D^{25}$ = +26.00 (c = 0.5, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 3H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.64 – 7.56 (m, 3H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.34 (m, 5H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 9.1 Hz, 2H), 7.17 (dt, *J* = 18.7, 8.1 Hz, 3H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.81 (dd, *J* = 7.7, 2.8 Hz, 1H), 5.30 (dt, *J* = 7.2, 3.8 Hz, 1H), 2.95 (dd, *J* = 11.8, 2.3 Hz, 1H), 2.67 (dd, *J* = 16.2, 12.2 Hz, 2H), 2.30 (dd, *J* = 14.4, 3.7 Hz, 1H), 0.73 (d, *J* = 3.7 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.73 (d, *J* = 22.0 Hz), 142.98 (d, *J* = 46.8 Hz), 136.93 (d, *J* = 3.9 Hz), 136.40, 136.31, 135.36, 134.45, 133.75, 133.67 (d, *J* = 4.9 Hz), 133.13, 132.88, 132.45, 132.31, 132.16, 131.66, 129.37, 129.26, 129.01, 128.97, 128.48, 128.35, 128.31, 128.03, 127.75 (d, *J* = 1.6 Hz), 127.54, 126.83, 126.78, 125.99, 125.12, 125.02, 31.60 (d, *J* = 22.4 Hz), 30.77 (d, *J* = 16.9 Hz), -3.01 (d, *J* = 11.6 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.34;

HRMS (ESI) m/z calcd for $C_{35}H_{30}PSi$ $[M + H]^+$ 509.1849, found 509.1850.



1a

crude 5g, 72% NMR yield, dr > 99:1

5g, 65% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-Mesityl(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5g). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. MeSiHCl$_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared mesitylmagnesium bromide (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 72% yield and >99:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using CHCl$_2$CHCl$_2$ as internal standard. Then the crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5g** (359.6 mg, 65% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +0.5 (c = 1.0, CH$_2$Cl$_2$);

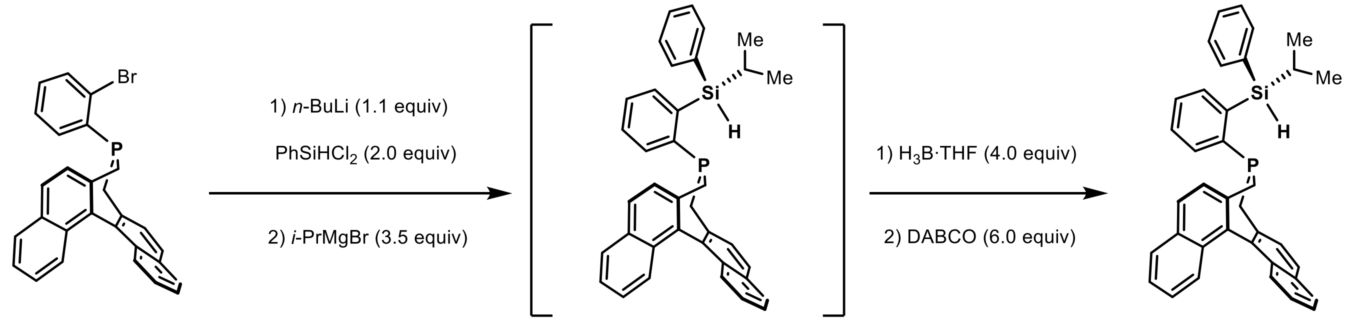
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (m, 4H), 7.64 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.32 (td, *J* = 7.4, 1.3 Hz, 1H), 7.26 – 7.07 (m, 7H), 7.01 (dd, *J* = 7.7, 2.5 Hz, 1H), 6.86 (s, 2H), 5.45 (dq, *J* = 8.4, 4.2 Hz, 1H), 2.78 (ddd, *J* = 13.0, 9.2, 6.2 Hz, 2H), 2.56 (dd, *J* = 14.5, 3.2 Hz, 1H), 2.32 (m, 10H), 0.69 (d, *J* = 4.1 Hz, 3H);

^{13}C NMR (151 MHz, CDCl$_3$) δ 144.82, 144.80 (d, *J* = 22.3 Hz), 144.52 (d, *J* = 47.9 Hz), 139.34, 135.68, 135.58, 134.68, 134.14, 133.38, 133.36, 132.78, 132.43, 132.32, 131.59, 131.57, 131.49 (d, *J* = 4.7 Hz), 129.27, 129.07, 128.84, 128.30, 128.26, 127.69, 127.67, 127.66, 126.89, 126.83, 125.99, 125.90, 125.04, 125.03, 31.84 (d, *J* = 16.5 Hz), 31.47 (d, *J* = 23.3 Hz), 24.03, 24.01, 21.33, -2.33 (d, *J* = 9.1 Hz).

^{31}P NMR (162 MHz, CDCl$_3$) δ -2.44;

HRMS (ESI) m/z calcd for C$_{38}$H$_{36}$PSi [M + H]$^+$ 551.2318, found 551.2317.

Melting point: 184.8-185.2 °C.



1a

crude 5h, 75% NMR yield, dr = 4:1

5h, 41% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*S*)-Isopropyl(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5h). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et$_2$O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. PhSiHCl$_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *i*-PrMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 75% yield and 4:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using

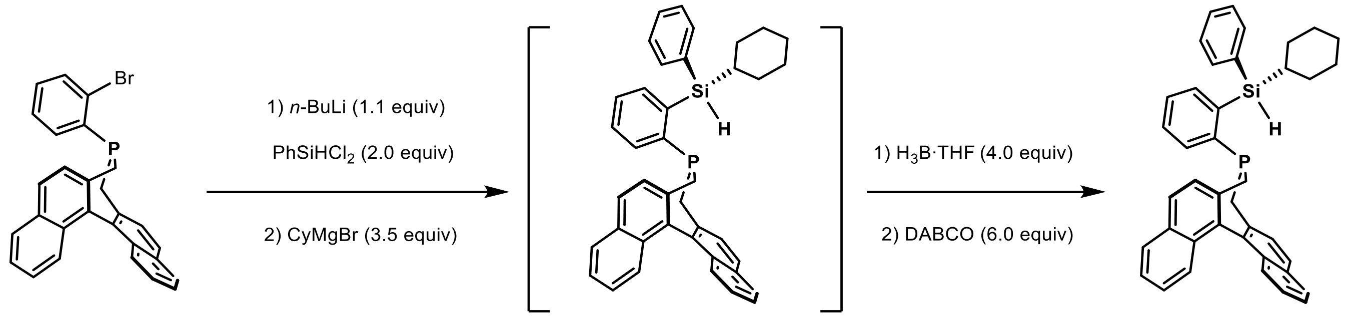
$CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5h**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5h** (218.9 mg, 41% yield, > 99% de) as white foam: $[\alpha]_D^{25}$ = +252.30 (c = 1.0, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.2, 3.1 Hz, 3H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.72 (dt, *J* = 7.4, 1.9 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.50 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.44 – 7.31 (m, 6H), 7.24 – 7.11 (m, 5H), 6.86 – 6.79 (m, 2H), 5.01 (dd, *J* = 7.3, 4.5 Hz, 1H), 2.91 (dd, *J* = 11.8, 2.2 Hz, 1H), 2.69 – 2.58 (m, 2H), 2.25 (dd, *J* = 14.3, 3.7 Hz, 1H), 1.72 (m, 1H), 1.12 (dd, *J* = 7.4, 3.8 Hz, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.03 (d, *J* = 22.0 Hz), 141.96 (d, *J* = 47.8 Hz), 136.78, 136.68, 136.00, 135.99, 135.76 (d, *J* = 3.2 Hz), 134.50, 133.82, 133.67 (d, *J* = 4.5 Hz), 133.11, 132.88, 132.44, 132.32, 132.16, 131.73, 129.31, 129.18, 128.94, 128.84, 128.47, 128.36, 128.30, 127.95, 127.74 (d, *J* = 1.5 Hz), 127.55, 126.83, 126.78, 126.00, 125.97, 125.12, 125.00, 31.56 (d, *J* = 22.1 Hz), 30.96 (d, *J* = 17.3 Hz), 19.24, 19.02, 12.58 (d, *J* = 9.8 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.46;

HRMS (ESI) m/z calcd for $C_{37}H_{34}PSi$ $[M + H]^+$ 537.2162, found 537.2162.



1a **crude 5i**, 75% NMR yield, dr = 12:1 **5i**, 56% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-Cyclohexyl(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5i). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared CyMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 75% yield and 12:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of

BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5i**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5i** (324.7 mg, 56% yield, > 99% de) as white foam: $[\alpha]_D^{25}$ = +205.80 (c = 1.0, CH_2Cl_2);

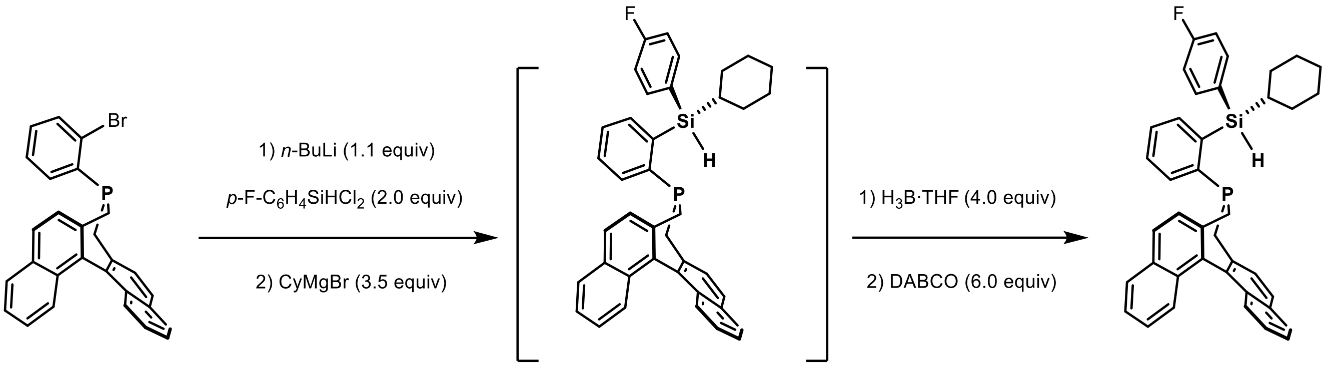
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.3, 3.0 Hz, 3H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.62 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.41 (m, 2H), 7.35 (m, 4H), 7.27 – 7.21 (m, 2H), 7.21 – 7.11 (m, 3H), 6.83 (dd, *J* = 8.4, 3.5 Hz, 2H), 5.00 (dd, *J* = 6.9, 4.7 Hz, 1H), 2.90 (dd, *J* = 11.9, 2.3 Hz, 1H), 2.65 (ddd, *J* = 19.5, 15.6, 12.1 Hz, 2H), 2.28 (dd, *J* = 14.4, 3.7 Hz, 1H), 1.78 (dd, *J* = 24.3, 12.1 Hz, 2H), 1.74 – 1.65 (m, 3H), 1.62 – 1.53 (m, 1H), 1.37 – 1.19 (m, 5H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.11 (d, *J* = 22.3 Hz), 141.75 (d, *J* = 47.0 Hz), 136.87 (d, *J* = 14.6 Hz), 136.06 (d, *J* = 2.6 Hz), 135.65 (d, *J* = 3.3 Hz), 134.52, 133.85, 133.67 (d, *J* = 4.8 Hz), 133.11, 132.88, 132.44, 132.33, 132.16, 131.72, 129.28, 129.16, 128.94, 128.83, 128.48, 128.36, 128.31, 127.93, 127.75 (d, *J* = 2.3 Hz), 127.57, 126.84, 126.78, 126.01, 125.97, 125.12, 125.00, 31.60 (d, *J* = 22.8 Hz), 31.04 (d, *J* = 17.2 Hz), 29.17, 28.99, 28.09, 28.00, 26.97, 24.29 (d, *J* = 9.6 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -2.27;

HRMS (ESI) m/z calcd for $C_{40}H_{38}PSi$ $[M + H]^+$ 577.2475, found 577.2472.

Melting point: 135.5-136.9 °C.



1a **crude 5j**, 78% NMR yield, dr = 22:1 **5j**, 57% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-Cyclohexyl(4-fluorophenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5j). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. *p*-F-$C_6H_4SiHCl_2$ (390.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared CyMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 78% yield and 22:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5j**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5j** (340.8 mg, 57% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +164.20 (c = 1.0, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.2, 2.6 Hz, 3H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.69 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.61 (dd, *J* = 8.4, 6.2 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.12 (m, 5H), 7.06 (dd, *J* = 10.0, 7.7 Hz, 2H), 6.89 – 6.79 (m, 2H), 4.97 (dd, *J* = 7.1, 4.6 Hz, 1H), 2.92 (dd, *J* = 11.7, 2.3 Hz, 1H), 2.66 (ddd, *J* = 24.5, 15.6, 12.1 Hz, 2H), 2.27 (dd, *J* = 14.3, 3.7 Hz, 1H), 1.73 (m, 5H), 1.57 (m, 1H), 1.43 – 1.19 (m, 5H);

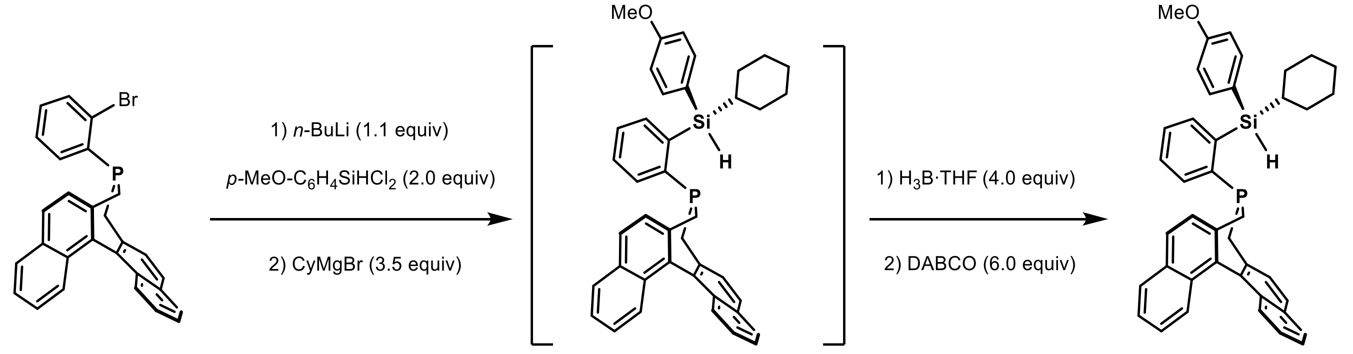
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.89 (d, *J* = 248.8 Hz), 143.99 (d, *J* = 21.9 Hz), 141.61 (d, *J* = 47.9 Hz), 138.02 (d, *J* = 3.0 Hz), 137.97 (d, *J* = 2.9 Hz), 136.84 (d, *J* = 14.8 Hz), 134.38, 133.67 (d, *J* = 5.0 Hz), 133.65, 133.14, 132.89 (d, *J* = 1.5 Hz), 132.46, 132.33 (d, *J* = 2.1 Hz), 132.17, 131.87, 131.09 (t, *J* = 3.5 Hz), 129.29, 128.98, 128.94, 128.54, 128.37, 128.31, 127.65 (d, *J* = 2.3 Hz), 127.60, 126.83, 126.77, 126.07, 126.02, 125.18, 125.06, 115.17, 115.04, 31.63 (d, *J* = 22.6 Hz), 31.06 (d, *J* = 16.8 Hz), 29.12, 28.92, 28.03, 27.95, 26.93, 24.42 (d, *J* = 9.8 Hz);

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.54;

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.68;

HRMS (ESI) m/z calcd for $C_{40}H_{37}FPSi$ $[M + H]^+$ 595.2381, found 595.2376.

Melting point: 125.2-126.2 °C.



1a **crude 5k**, 72% NMR yield, dr = 17:1 **5k**, 61% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-Cyclohexyl(4-methoxyphenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5k). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. *p*-MeO-$C_6H_4SiHCl_2$ (414.3 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared CyMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 72% yield and 17:1 dr were determined by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5k**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5k** (368.9 mg, 61% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +201.00 (c = 1.0, CH_2Cl_2);

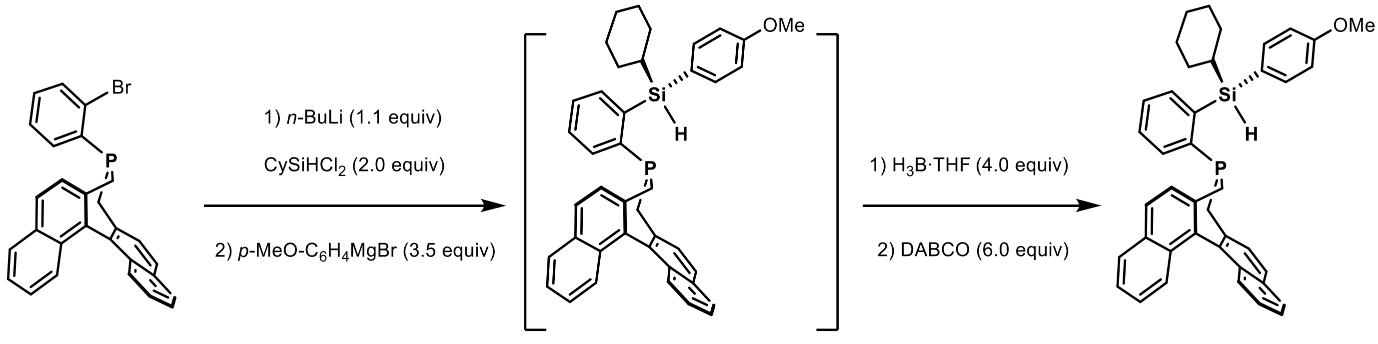
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 3H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.70 (dt, *J* = 7.5, 1.9 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.46 – 7.37 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.09 (m, 5H), 6.91 (d, *J* = 6.7 Hz, 2H), 6.86 – 6.76 (m, 2H), 4.99 (dd, *J* = 6.9, 4.5 Hz, 1H), 3.80 (s, 3H), 2.91 (dd, *J* = 11.7, 2.0 Hz, 1H), 2.76 – 2.59 (m, 2H), 2.30 (dd, *J* = 14.3, 3.8 Hz, 1H), 1.85 – 1.64 (m, 5H), 1.53 (m, 1H), 1.35 – 1.20 (m, 5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.66, 144.01 (d, *J* = 22.2 Hz), 142.05 (d, *J* = 46.5 Hz), 137.55, 137.52, 136.76 (d, *J* = 14.4 Hz), 134.58, 133.89, 133.71 (d, *J* = 4.9 Hz), 133.09, 132.88 (d, *J* = 1.0 Hz), 132.44, 132.33 (d, *J* = 1.8 Hz), 132.15, 131.63 (d, *J* = 1.0 Hz), 129.04, 128.95, 128.76, 128.46, 128.36, 128.31, 127.77 (d, *J* = 1.0 Hz), 127.54, 126.81 (d, *J* = 3.3 Hz), 126.18 (d, *J* = 3.0 Hz), 126.01, 125.97, 125.12, 124.99, 113.74, 55.15, 31.68 (d, *J* = 22.8 Hz), 30.98 (d, *J* = 17.2 Hz), 29.18, 28.94, 28.10, 28.03, 26.99, 24.50 (d, *J* = 9.0 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.41;

HRMS (ESI) m/z calcd for $C_{41}H_{40}OPSi$ $[M + H]^+$ 607.2581, found 607.2575.

Melting point: 128.0-128.7 °C.



1a

crude 5l, 89% NMR yield, dr = 5:1

5l, 43% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-Cyclohexyl(4-methoxyphenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5l). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $CySiHCl_2$ (366.3 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *p*-MeO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 89% yield and 5:1 dr were determined by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5l**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5l** (262.1 mg, 43% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +247.50 (c = 1.0, CH_2Cl_2);

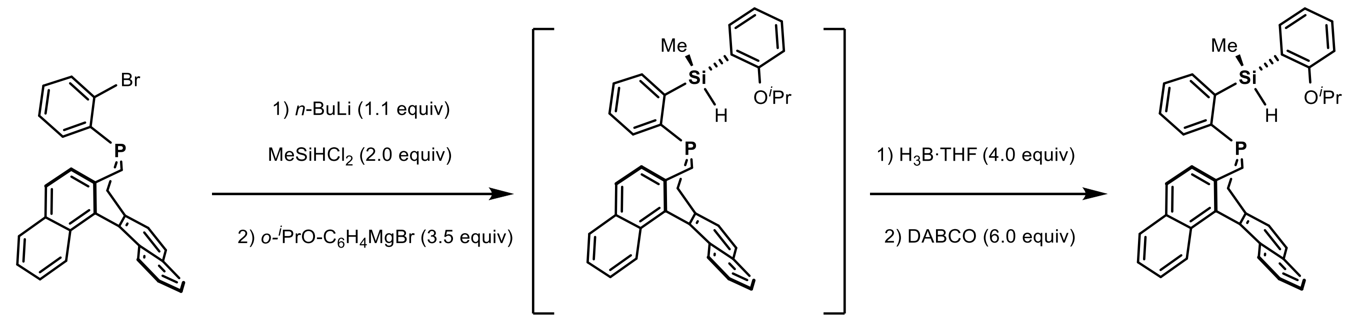
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 3H), 7.79 – 7.70 (m, 2H), 7.58 – 7.50 (m, 3H), 7.46 – 7.38 (m, 2H), 7.33 (m, 1H), 7.25 – 7.21 (m, 2H), 7.21 – 7.10 (m, 3H), 6.87 – 6.79 (m, 3H), 6.76 (m, 1H), 4.86 (dd, *J* = 6.5, 4.4 Hz, 1H), 3.75 (s, 3H), 2.96 (dd, *J* = 11.8, 2.0 Hz, 1H), 2.64 (ddd, *J* = 26.2, 15.7, 11.8 Hz, 2H), 2.14 (dd, *J* = 14.3, 3.6 Hz, 1H), 1.86 (d, *J* = 8.5 Hz, 1H), 1.73 (m, 5H), 1.41 – 1.21 (m, 6H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.56, 143.47 (d, *J* = 21.4 Hz), 142.72 (d, *J* = 49.0 Hz), 137.47, 137.45, 137.28 (d, *J* = 15.2 Hz), 134.64, 133.84, 133.73 (d, *J* = 4.5 Hz), 133.05, 132.88 (d, *J* = 1.5 Hz), 132.44, 132.35 (d, *J* = 2.3 Hz), 132.16, 131.57, 129.09, 129.01, 128.91, 128.47, 128.36, 128.32, 127.81 (d, *J* = 2.3 Hz), 127.50, 126.83, 126.12 (d, *J* = 3.4 Hz), 126.01, 125.96, 125.13, 124.98, 113.69, 54.43, 31.74 (d, *J* = 22.5 Hz), 31.03 (d, *J* = 16.9 Hz), 29.20, 29.17, 28.21, 28.02, 27.04, 24.15 (d, *J* = 10.5 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -1.51;

HRMS (ESI) m/z calcd for $C_{41}H_{40}OPSi$ $[M + H]^+$ 607.2581, found 607.2578.

Melting point: 141.1-142.8 °C.



1a

crude 5m, 90% NMR yield, dr = 26:1

5m, 70% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*R*)-(2-Isopropoxyphenyl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-

***e*]phosphepine (5m).** According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *o*-^{i}PrO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 90% yield and 26:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5m**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5m** (397.9 mg, 70% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +109.00 (c = 1.0, CH_2Cl_2);

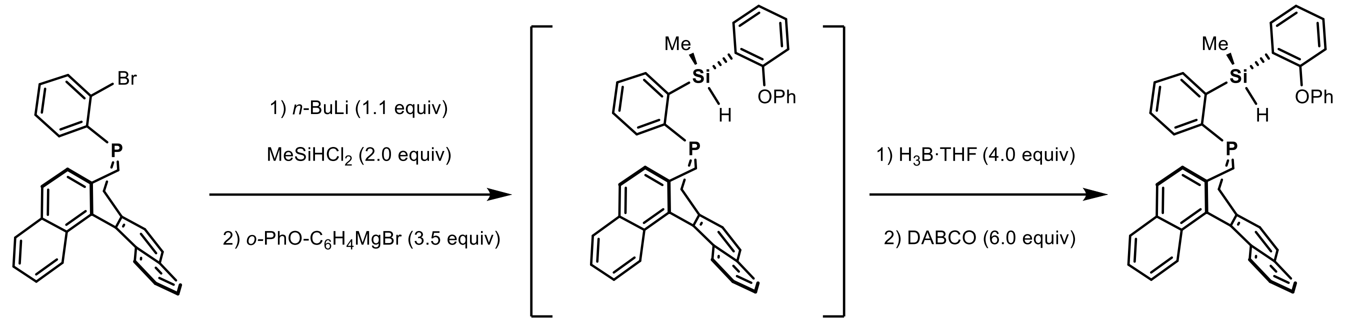
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 3H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.72 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.30 (td, *J* = 7.6, 2.1 Hz, 2H), 7.26 – 7.08 (m, 5H), 6.91 (dd, *J* = 7.9, 5.9 Hz, 2H), 6.82 (dd, *J* = 7.6, 2.5 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 5.20 (dq, *J* = 7.4, 3.8 Hz, 1H), 4.50 (h, *J* = 6.0 Hz, 1H), 2.90 (dd, *J* = 11.8, 1.9 Hz, 1H), 2.60 (ddd, *J* = 40.2, 15.6, 12.1 Hz, 2H), 2.31 (dd, *J* = 14.4, 3.5 Hz, 1H), 1.10 (dd, *J* = 12.2, 6.0 Hz, 6H), 0.74 (d, *J* = 3.7 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.45, 143.90 (d, *J* = 45.9 Hz), 143.61 (d, *J* = 22.8 Hz), 137.63 (d, *J* = 3.6 Hz), 136.74 (d, *J* = 14.5 Hz), 134.72, 134.08, 133.56 (d, *J* = 4.6 Hz), 133.14, 132.81, 132.39, 132.30, 132.19, 131.21, 131.17, 129.11, 128.75, 128.55, 128.37, 128.33, 128.28, 127.84, 127.49, 126.84, 126.78, 125.92, 125.91, 125.62 (d, *J* = 3.5 Hz), 125.02, 124.95, 120.31, 110.98, 69.00, 31.68 (d, *J* = 22.9 Hz), 31.10 (d, *J* = 17.0 Hz), 21.98, 21.83, -3.39 (d, *J* = 11.0 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.16;

HRMS (ESI) m/z calcd for $C_{38}H_{36}OPSi$ $[M + H]^+$ 567.2268, found 567.2265.

Melting point: 175.4-177.2 °C.



1a

crude 5n, 47% NMR yield, dr = 7:1

5n, 33% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*R*)-Methyl(2-phenoxyphenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5n). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 µL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *o*-PhO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 47% yield and 7:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5n**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5n** (197.1 mg, 33% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +160.00 (c = 0.1, CH_2Cl_2);

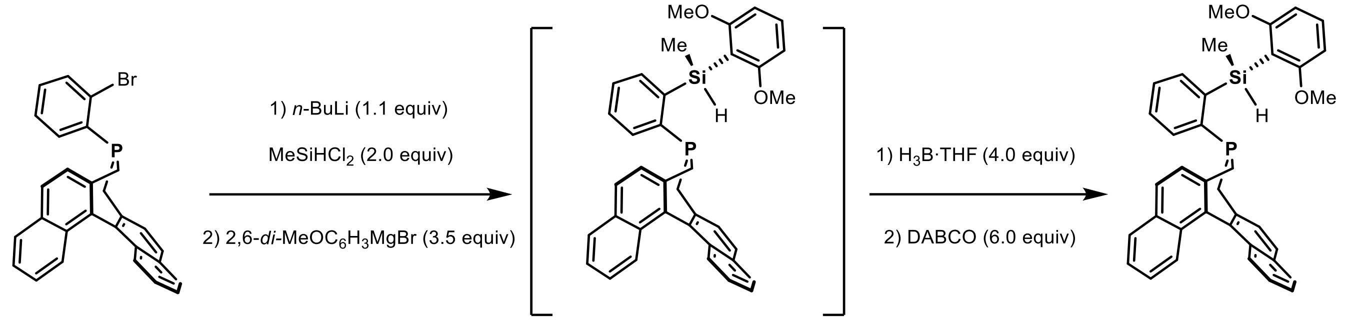
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 3H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.56 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.29 (td, *J* = 7.8, 1.7 Hz, 1H), 7.20 (ddd, *J* = 30.9, 22.3, 7.2 Hz, 7H), 7.08 (dt, *J* = 14.1, 7.4 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.88 – 6.68 (m, 4H), 5.29 (dq, *J* = 7.5, 3.8 Hz, 1H), 2.94 (dd, *J* = 11.9, 2.0 Hz, 1H), 2.65 (ddd, *J* = 37.1, 15.7, 12.0 Hz, 2H), 2.36 (dd, *J* = 14.4, 3.5 Hz, 1H), 0.75 (d, *J* = 3.7 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.05, 157.25, 143.50 (d, *J* = 22.5 Hz), 142.77 (d, *J* = 46.1 Hz), 137.59 (d, *J* = 3.1 Hz), 136.61, 136.51, 134.60, 133.87, 133.64 (d, *J* = 5.1 Hz), 133.12, 132.84, 132.43, 132.31 (d, *J* = 1.5 Hz), 132.18, 131.39, 131.31, 129.63, 129.12, 129.00, 128.83, 128.42, 128.33, 128.30, 127.97 (d, *J* = 3.9 Hz), 127.76, 127.53, 126.82, 126.79, 125.97, 125.08, 125.00, 123.29, 123.05, 118.94, 117.47, 31.77 (d, *J* = 22.8 Hz), 30.94 (d, *J* = 16.9 Hz), -3.32 (d, *J* = 11.0 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.48;

HRMS (ESI) m/z calcd for $C_{41}H_{34}OPSi$ $[M + H]^+$ 601.2111, found 601.2109.

Melting point: 108.8-109.8 °C.



1a **crude 5o**, 91% NMR yield, dr = 12:1 **5o**, 55% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*R*)-(2,6-Dimethoxyphenyl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5o). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared 2,6-*di*-MeO-C_6H_3PhMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 91% yield and 12:1 dr were determined by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5o**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5o** (314.5 mg, 55% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +132.10 (c = 1.0, CH_2Cl_2);

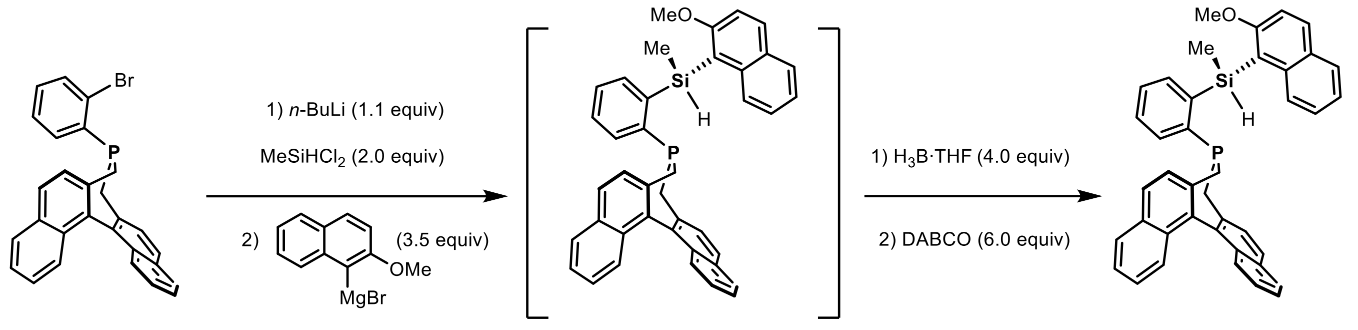
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 3H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.58 (dt, *J* = 7.5, 1.9 Hz, 1H), 7.44 – 7.33 (m, 3H), 7.31 (t, *J* = 8.2 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.21 – 7.11 (m, 3H), 7.07 (td, *J* = 7.5, 1.5 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.85 (dd, *J* = 7.7, 2.5 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 2H), 5.40 (dq, *J* = 7.6, 3.9 Hz, 1H), 3.59 (s, 6H), 2.88 (dd, *J* = 11.7, 1.9 Hz, 1H), 2.76 (dd, *J* = 14.5, 12.6 Hz, 1H), 2.59 – 2.46 (m, 2H), 0.71 (d, *J* = 3.9 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.47, 145.06 (d, *J* = 46.8 Hz), 143.38 (d, *J* = 22.1 Hz), 135.80, 135.70, 134.87, 134.20, 133.51 (d, *J* = 5.1 Hz), 133.16, 132.76, 132.37, 132.29, 132.28, 132.21, 131.03, 129.23, 128.44, 128.32, 128.29, 128.25, 127.79, 127.78, 127.50, 126.79, 125.90, 125.88, 124.97, 124.92, 112.59 (d, *J* = 4.9 Hz), 104.12, 55.67, 31.73 (d, *J* = 23.8 Hz), 31.46 (d, *J* = 17.4 Hz), -1.98, -2.01 (d, *J* = 9.8 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.10;

HRMS (ESI) m/z calcd for $C_{37}H_{34}O_2PSi$ $[M + H]^+$ 569.2060, found 569.2058.

Melting point: 123.4-124.5 °C.



1a **crude 5p**, 93% NMR yield, dr = 28:1 **5p**, 73% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*R*)-(2-Methoxynaphthalen-1-yl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5p). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared (2-methoxynaphthalen-1-yl)magnesium bromide (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 93% yield and 28:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5p**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5p** (431.5 mg, 73% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = -161.30 (c = 1.0, CH_2Cl_2);

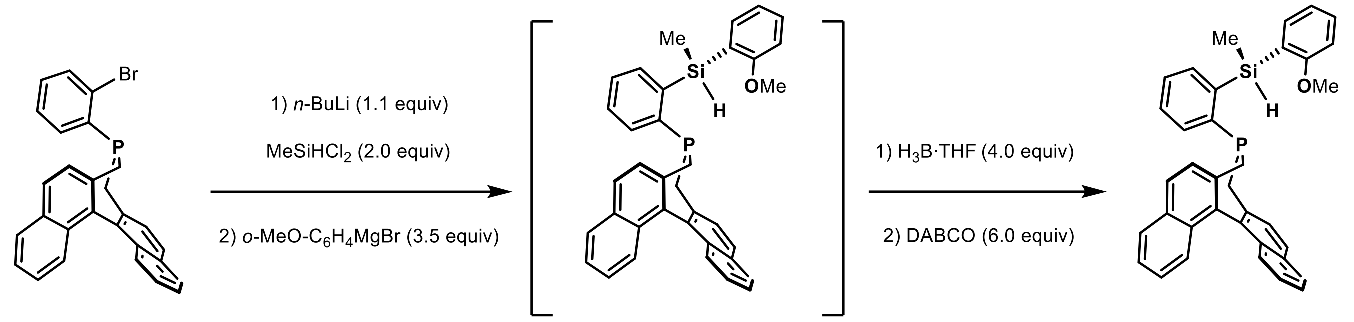
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.37 (m, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.81 (dd, *J* = 10.5, 8.2 Hz, 2H), 7.71 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.27 (m, 5H), 7.20 – 6.98 (m, 8H), 6.39 (dt, *J* = 8.4, 1.3 Hz, 1H), 5.89 (dq, *J* = 7.6, 3.8, 2.9 Hz, 1H), 3.48 (d, *J* = 1.0 Hz, 3H), 2.79 (dd, *J* = 14.4, 12.7 Hz, 1H), 2.74 – 2.53 (m, 2H), 1.92 (dd, *J* = 15.7, 11.5 Hz, 1H), 0.77 (dd, *J* = 3.9, 1.5 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42, 144.70 (d, *J* = 25.4 Hz), 144.35, 138.05, 135.77, 135.62, 134.48, 134.20, 133.34, 133.08 (d, *J* = 5.1 Hz), 132.65 (d, *J* = 1.3 Hz), 132.55, 132.36, 132.26, 132.14 (d, *J* = 2.2 Hz), 131.30 (d, *J* = 2.5 Hz), 129.76, 129.28, 128.75, 128.66, 128.54, 128.20, 128.12, 128.11, 127.63, 127.39 (d, *J* = 2.4 Hz), 126.83, 126.77, 126.73, 125.91, 125.77, 124.98, 124.89, 123.70, 119.60 (d, *J* = 4.3 Hz), 113.64, 56.25, 31.96 (d, *J* = 16.8 Hz), 31.53 (d, *J* = 23.7 Hz), -2.91, -3.01;

^{31}P NMR (162 MHz, $CDCl_3$) δ -3.26;

HRMS (ESI) m/z calcd for $C_{40}H_{34}OPSi$ $[M + H]^+$ 589.2111, found 589.2108.

Melting point: 147.5-148.7 °C.



1a **crude 5q**, 81% NMR yield, dr = 21:1 **5q**, 58% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-(2-Methoxyphenyl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5q). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *o*-MeO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 81% yield and 21:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5q**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5q** (314.1 mg, 58% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = 223.10 (c = 1.0, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.88 (t, *J* = 9.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.33 (m, 4H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.10 (m, 5H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 8.4 Hz, 2H), 5.26 (dq, *J* = 7.4, 3.8 Hz, 1H), 3.71 (s, 3H), 2.95 (dd, *J* = 11.9, 2.0 Hz, 1H), 2.68 (ddd, *J* = 17.7, 12.1, 4.7 Hz, 2H), 2.37 (dd, *J* = 14.4, 3.6 Hz, 1H), 0.73 (d, *J* = 2.5 Hz, 2H);

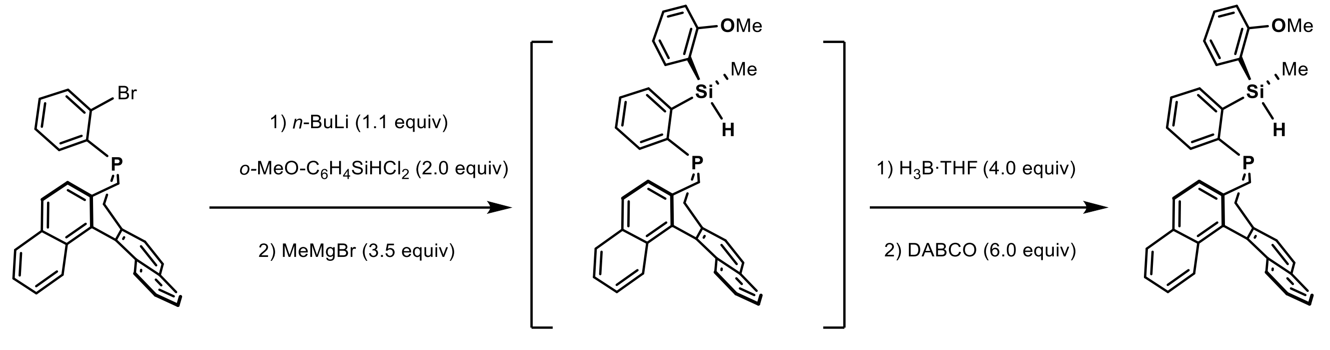
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.40, 143.52 (d, *J* = 13.6 Hz), 143.29 (d, *J* = 36.7 Hz), 137.21, 137.19, 136.53, 136.43, 134.67, 133.95, 133.64 (d, *J* = 4.8 Hz), 133.14, 132.86 (d, *J* = 1.5 Hz), 132.43, 132.31 (d, *J* = 2.0 Hz), 132.19, 131.47, 131.27 (d, *J* = 1.5 Hz), 129.10, 128.83, 128.74, 128.41, 128.35, 128.31, 127.85 (d, *J*

= 2.3 Hz), 127.51, 126.85, 126.79, 125.95, 125.06, 124.98, 120.88, 109.91, 55.40, 31.85 (d, *J* = 22.8 Hz), 30.85 (d, *J* = 17.0 Hz), -3.29 (d, *J* = 11.0 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.43;

HRMS (ESI) m/z calcd for $C_{36}H_{32}OPSi$ $[M + H]^+$ 539.1955, found 539.1954.

Melting point: 117.9-119.1 °C.

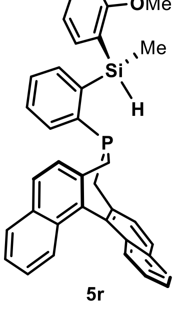


1a

crude 5r, 80% NMR yield, dr = 1.66:1

5r, 44% isolated yield, > 99% de
5q, 28% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*S*)-(2-Methoxyphenyl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5r). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. *o*-MeO-$C_6H_4SiHCl_2$ (345.4 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that MeMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 80% yield and 1.66:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5r**·BH_3 and **5q**·BH_3 respectively, that was then respectively removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5r** (235.9 mg, 44% yield, > 99% de) as white foam and **5q** (151.4 mg, 28% yield, > 99% de) as white foam respectively:

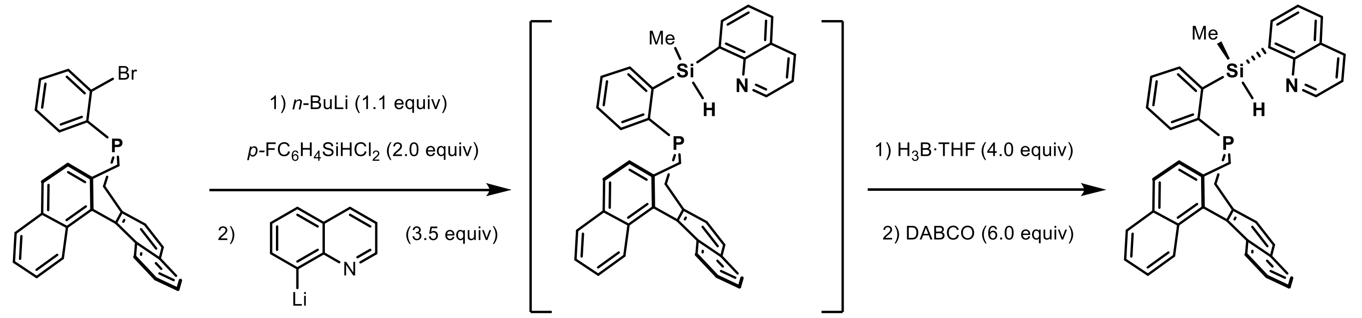


5r

$[\alpha]_D^{25}$ = +202.10 (c = 1.0, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4, 3.4 Hz, 3H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.53 (m, 2H), 7.48 (dt, *J* = 7.2, 1.4 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.33 – 7.07 (m, 6H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.82 – 6.70 (m, 2H), 5.34 (m, 1H), 3.72 (s, 3H), 2.98 (d, *J* = 11.4 Hz, 1H), 2.82 – 2.57 (m, 2H), 2.38 (dd, *J* = 14.2, 3.8 Hz, 1H), 0.70 (d, *J* = 3.8 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.40, 143.28 (d, J = 8.6 Hz), 143.06 (d, J = 30.5 Hz), 137.30, 136.19, 136.09, 134.66, 134.01, 133.75 (d, J = 4.6 Hz), 133.07, 132.89, 132.42, 132.32, 132.14, 131.57, 130.90, 128.85, 128.76, 128.58, 128.41, 128.37, 128.32, 127.89 (d, J = 2.2 Hz), 127.47, 126.83, 126.80, 125.96, 125.09, 124.95, 124.82 (d, J = 3.4 Hz), 120.94, 110.01, 55.43, 31.86 (d, J = 22.4 Hz), 30.38 (d, J = 17.4 Hz), -3.44 (d, J = 9.3 Hz);
^{31}P NMR (162 MHz, $CDCl_3$) δ -3.16;
HRMS (ESI) m/z calcd for $C_{36}H_{32}OPSi$ $[M + H]^+$ 539.1955, found 539.1954.
Melting point: 116.2-117.0 °C.



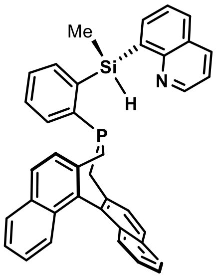
1a

crude 5s and 5s', 70% NMR yield, dr = 1:1

5s, 35% isolated yield, > 99% de;
5s', 28% isolated yield, > 99% de

8-((R)-(2-((4R,11bS)-3,5-dihydro-4H-dinaphtho[2,1-c:1',2'-e]phosphepin-4-yl)phenyl)(methyl)silyl)quinoline (5s). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared quinolin-8-yllithium (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 70% yield and 1:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5s**·BH_3 (**upper dot of TLC**) and **5s'**·BH_3 (**nether dot of TLC**) respectively, that was then respectively removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was respectively concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5s** (196.5 mg, 35% yield, > 99% de) as white solid and **5s'** (158.4 mg, 28% yield, > 99% de) as white solid.

The presumptive characterization data of 5s are as follows:



$[\alpha]_D^{25}$ = +211.70 (c = 1.0, CH_2Cl_2);

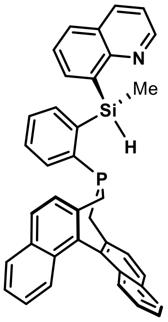
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.96 (dd, *J* = 6.7, 1.5 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.7 Hz, 3H), 7.81 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.58 (td, *J* = 8.1, 3.4 Hz, 2H), 7.51 (dd, *J* = 8.1, 6.7 Hz, 1H), 7.37 (tdd, *J* = 8.1, 6.2, 1.7 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.26 – 7.11 (m, 4H), 7.08 (td, *J* = 7.5, 1.5 Hz, 1H), 6.78 (dd, *J* = 7.7, 2.8 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.79 (dq, *J* = 7.4, 3.7 Hz, 1H), 2.98 (dd, *J* = 11.7, 1.7 Hz, 1H), 2.78 (dd, *J* = 17.1, 11.7 Hz, 1H), 2.63 (d, *J* = 8.0 Hz, 2H), 0.85 (dd, *J* = 3.8, 0.9 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.46, 149.55, 143.48 (d, *J* = 43.3 Hz), 143.11 (d, *J* = 22.4 Hz), 138.41 (d, *J* = 3.4 Hz), 138.23, 138.21, 136.38 (d, *J* = 13.3 Hz), 136.21, 134.67, 134.19, 134.17, 133.78 (d, *J* = 4.5 Hz), 132.97, 132.84 (d, *J* = 1.7 Hz), 132.37, 132.27 (d, *J* = 2.1 Hz), 132.07, 130.63, 129.79, 128.81, 128.61, 128.45, 128.34, 128.29, 127.87 (d, *J* = 2.4 Hz), 127.77, 127.41, 126.77, 126.31, 125.92, 125.89, 125.04, 124.87, 121.03, 31.78 (d, *J* = 22.6 Hz), 30.21 (d, *J* = 17.5 Hz), -2.79 (d, *J* = 8.1 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.69;

HRMS (ESI) m/z calcd for $C_{38}H_{31}NPSi$ $[M + H]^+$ 560.1958, found 560.1956.

The presumptive characterization data of 5s' are as follows:



$[\alpha]_D^{25}$ = +215.00 (c = 1.0, CH_2Cl_2);

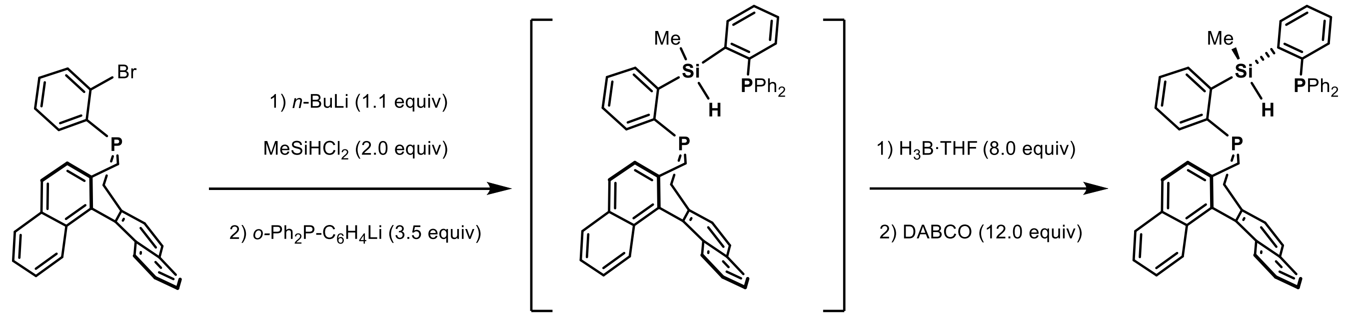
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.93 – 7.78 (m, 5H), 7.79 – 7.69 (m, 2H), 7.47 (dd, *J* = 8.1, 6.7 Hz, 1H), 7.44 – 7.26 (m, 5H), 7.26 – 7.10 (m, 5H), 6.89 – 6.77 (m, 2H), 5.71 (dq, *J* = 7.4, 3.7 Hz, 1H), 2.96 (dd, *J* = 11.8, 1.9 Hz, 1H), 2.72 – 2.60 (m, 2H), 2.37 (dd, *J* = 14.2, 3.8 Hz, 1H), 0.90 (dd, *J* = 3.8, 1.2 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.54, 149.56, 143.65 (d, *J* = 10.0 Hz), 143.31 (d, *J* = 12.8 Hz), 138.54 (d, *J* = 3.8 Hz), 138.21, 138.19, 136.87 (d, *J* = 14.2 Hz), 136.23, 134.61, 133.93, 133.63 (d, *J* = 4.7 Hz), 133.04, 132.80 (d, *J* = 1.7 Hz), 132.40, 132.25 (d, *J* = 2.1 Hz), 132.13, 131.18, 131.16, 129.66, 129.07, 128.79, 128.72, 128.34, 128.30, 127.79 (d, *J* = 2.4 Hz), 127.75, 127.48, 126.80, 126.76, 126.32, 125.91, 125.03, 124.94, 120.96, 31.96 (d, *J* = 22.8 Hz), 30.66 (d, *J* = 17.5 Hz), -2.63 (d, *J* = 10.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ -3.53;

HRMS (ESI) m/z calcd for $C_{38}H_{31}NPSi$ $[M + H]^+$ 560.1958, found 560.1955.

Melting point: 136.3-137.6 ℃.



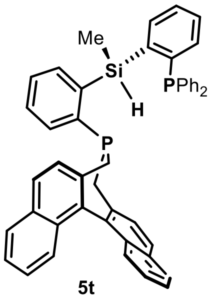
1a

crude 5t and 5t', 90% NMR yield, dr = 2.1:1

5t, 34% isolated yield, > 99% de
5t', 18% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-(2-(Diphenylphosphaneyl)phenyl)(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5t). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et$_2$O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. MeSiHCl$_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *o*-Ph$_2$P-C$_6$H$_4$Li (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 90% yield and 2.1:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using CHCl$_2$CHCl$_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH$_3$ solution (8.0 mL, 1.0 M in THF, 4.0 mmol, 8.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 1:1) to afford **5t**·BH$_3$ and **5t'**·BH$_3$ respectively, that was then respectively removed BH$_3$ using DABCO (12.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was respectively concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5t** (236.9 mg, 34% yield, > 99% de) as white solid and **5t'** (126.1 mg, 18% yield, > 99% de) as white solid:

The presumptive characterization data of 5t are as follows:



5t

$[\alpha]_D^{25}$ = +229.40 (c = 1.0, CH$_2$Cl$_2$);

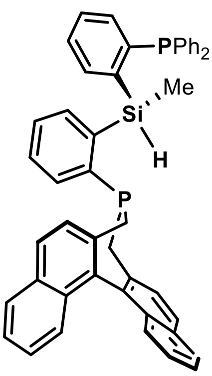
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 – 7.87 (m, 3H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.49 – 7.35 (m, 4H), 7.32 – 7.17 (m, 13H), 7.17 – 7.06 (m, 4H), 6.80 – 6.66 (m, 2H), 5.86 – 5.69 (m, 1H), 3.00 (d, *J* = 11.7 Hz, 1H), 2.74 (dd, *J* = 17.3, 11.6 Hz, 1H), 2.56 (d, *J* = 8.1 Hz, 2H), 0.78 (d, *J* = 3.8 Hz, 3H);

^{13}C NMR (101 MHz, CDCl$_3$) δ 144.89 (d, *J* = 3.8 Hz), 144.43 (d, *J* = 4.0 Hz), 143.96 (d, *J* = 4.0 Hz), 143.93 (d, *J* = 10.1 Hz), 143.52 (d, *J* = 3.3 Hz), 142.71 (d, *J* = 22.1 Hz), 137.84 (d, *J* = 11.7 Hz), 137.65 (d, *J* = 11.4 Hz), 136.83 (d, *J* = 1.0 Hz), 136.68 (d, *J* = 2.2 Hz), 136.58 (d, *J* = 1.8 Hz), 136.44 (d, *J* = 2.5 Hz), 134.67, 134.64, 134.12, 133.84 (d, *J* = 4.6 Hz), 133.71, 133.51, 133.32, 132.94, 132.88 (d, *J* = 1.8 Hz), 132.36, 132.29 (d, *J* = 2.1 Hz), 132.04, 130.63, 129.88, 129.09, 128.77, 128.65, 128.55, 128.54, 128.49, 128.37, 128.34, 128.31, 128.27, 127.92 (d, *J* = 2.3 Hz), 127.26, 126.83, 126.77, 125.94, 125.84, 125.08, 124.85, 31.01 (d, *J* = 22.0 Hz), 29.81 (d, *J* = 17.4 Hz), -2.95 (t, *J* = 7.6 Hz);

^{31}P NMR (162 MHz, CDCl$_3$) δ -2.91 (d, *J* = 3.6 Hz), -11.97 (d, *J* = 2.9 Hz);

HRMS (ESI) m/z calcd for C$_{47}$H$_{39}$P$_2$Si [M + H]$^+$ 693.2291, found 693.2286.

The presumptive characterization data of 5t' are as follows:



5t'

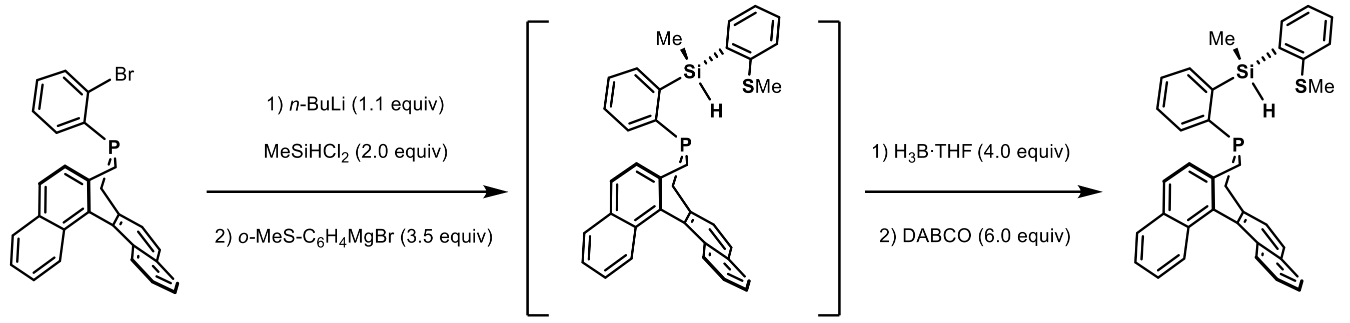
$[\alpha]_D^{25}$ = +64.30 (c = 1.0, CH$_2$Cl$_2$);

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.61 – 7.53 (m, 1H), 7.40 (m, 2H), 7.37 – 7.26 (m, 4H), 7.26 – 7.19 (m, 6H), 7.19 – 7.06 (m, 10H), 6.80 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.75 (dd, *J* = 7.6, 2.4 Hz, 1H), 5.62 – 5.51 (m, 1H), 2.80 (dt, *J* = 11.8, 2.1 Hz, 1H), 2.57 – 2.40 (m, 2H), 2.24 (dt, *J* = 14.3, 2.7 Hz, 1H), 0.76 (t, *J* = 3.0 Hz, 3H);

^{13}C NMR (101 MHz, CDCl$_3$) δ 145.53 (d, *J* = 4.5 Hz), 145.08 (d, *J* = 4.4 Hz), 143.84 (d, *J* = 3.7 Hz), 143.74, 143.79 (d, *J* = 34.6 Hz), 143.37 (d, *J* = 3.8 Hz), 137.94 (d, *J* = 11.6 Hz), 137.37 (d, *J* = 11.6 Hz), 137.09 (d, *J* = 2.7 Hz), 136.94 (d, *J* = 2.8 Hz), 136.66 (d, *J* = 3.3 Hz), 136.52 (d, *J* = 3.2 Hz), 134.64, 134.09, 134.01, 133.86, 133.73, 133.68, 133.59 (d, *J* = 4.9 Hz), 133.54, 133.03, 132.79 (d, *J* = 1.7 Hz), 132.36, 132.30 (d, *J* = 2.1 Hz), 132.14, 131.28 (d, *J* = 2.1 Hz), 129.57, 129.15, 129.02, 128.81, 128.45, 128.43, 128.37, 128.35, 128.33, 128.28, 128.26, 127.75 (d, *J* = 2.4 Hz), 127.46, 126.80, 125.95, 125.90, 125.06, 124.94, 31.51 (d, *J* = 23.4 Hz), 30.86 (d, *J* = 17.7 Hz), -2.50 (dd, *J* = 10.3, 7.0 Hz);

^{31}P NMR (162 MHz, CDCl$_3$) δ -3.54, -11.21;

HRMS (ESI) m/z calcd for C$_{47}$H$_{39}$P$_2$Si [M + H]$^+$ 693.2291, found 693.2285.



1a **crude 5u**, 76% NMR yield, dr = 7:1 **5u**, 54% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-Methyl(2-(methylthio)phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5u). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et$_2$O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. MeSiHCl$_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *o*-MeS-C$_6$H$_4$MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 76% yield and 7:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5u**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5u** (300.7 mg, 54% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +186.20 (c = 1.0, CH_2Cl_2);

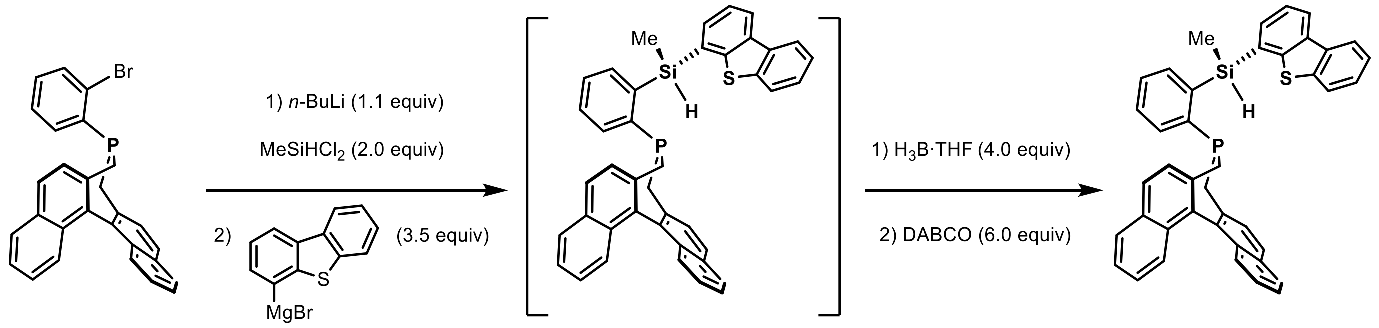
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.83 (m, 3H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.41 (m, 2H), 7.33 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.21 – 7.08 (m, 4H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 5.35 (m, 1H), 2.94 (d, *J* = 11.9 Hz, 1H), 2.64 (dd, *J* = 17.1, 11.8 Hz, 1H), 2.55 (t, *J* = 13.2 Hz, 1H), 2.33 (s, 3H), 2.24 (dd, *J* = 14.6, 3.7 Hz, 1H), 0.80 (d, *J* = 3.8 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.18, 143.58 (d, *J* = 22.5 Hz), 143.19 (d, *J* = 46.5 Hz), 138.02 (d, *J* = 4.4 Hz), 137.12, 137.02, 136.75, 136.73, 134.64, 133.92, 133.67 (d, *J* = 4.4 Hz), 133.06, 132.85, 132.43, 132.32, 132.16, 131.27, 130.43, 129.13, 129.07, 128.90, 128.39, 128.34, 128.32, 127.83 (d, *J* = 2.4 Hz), 127.58, 127.52, 126.82, 125.95, 125.42, 125.08, 124.97, 31.63 (d, *J* = 22.8 Hz), 30.72 (d, *J* = 17.3 Hz), 17.89, -2.99 (d, *J* = 11.3 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -2.72;

HRMS (ESI) m/z calcd for $C_{36}H_{32}PSSi$ $[M + H]^+$ 555.1726, found 555.1725.

Melting point: 202.9-203.1 °C.



1a **crude 5v**, 78% NMR yield, dr = 15:1 **5v**, 61% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-Dibenzo[*b*,*d*]thiophen-4-yl(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5v). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly**

and the solution was stirred at -116 °C for another 1 h. After that fresh prepared dibenzo[*b*,*d*]thiophen-4-ylmagnesium bromide (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 78% yield and 15:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5v**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5v** (373.8 mg, 61% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = 68.00 (c = 1.0, CH_2Cl_2);

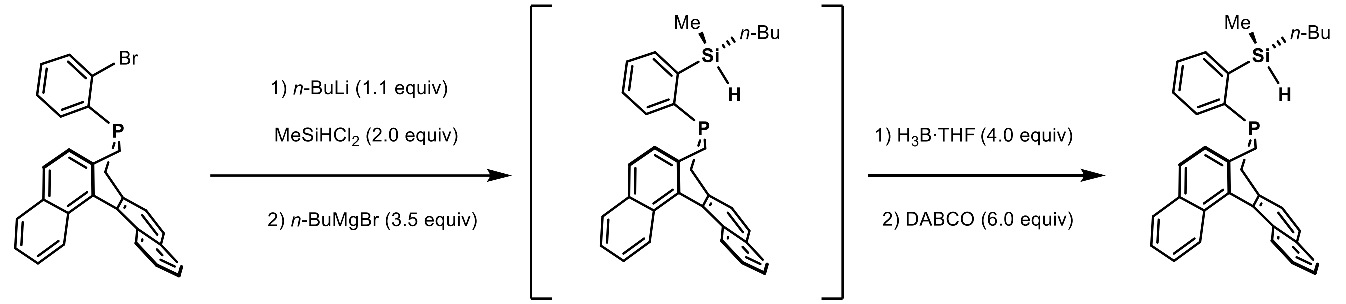
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.98 (m, 2H), 7.81 (dd, *J* = 9.5, 8.0 Hz, 3H), 7.73 (dd, *J* = 8.5, 4.8 Hz, 2H), 7.71 – 7.63 (m, 2H), 7.43 – 7.26 (m, 7H), 7.20 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.10 – 7.03 (m, 2H), 6.78 (dd, *J* = 7.6, 2.7 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 5.48 (dq, *J* = 7.5, 3.8 Hz, 1H), 2.90 (dd, *J* = 11.8, 2.6 Hz, 1H), 2.63 – 2.43 (m, 2H), 2.04 (dd, *J* = 14.3, 3.7 Hz, 1H), 0.91 (dd, *J* = 3.9, 1.6 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.23, 144.19 (d, *J* = 21.8 Hz), 141.78 (d, *J* = 48.1 Hz), 139.72, 137.22 (d, *J* = 15.2 Hz), 135.40, 134.74, 134.36, 134.23 (d, *J* = 3.2 Hz), 133.59, 133.57 (d, *J* = 5.6 Hz), 133.00, 132.77 (d, *J* = 1.8 Hz), 132.36, 132.21 (d, *J* = 2.1 Hz), 132.06, 131.63 (d, *J* = 2.1 Hz), 131.30 (d, *J* = 4.7 Hz), 129.61, 129.18, 129.09, 128.37, 128.36, 128.28, 128.25, 127.68, 127.66, 127.46, 126.73, 126.71, 126.66, 125.93, 125.05, 124.96, 124.31, 124.22, 122.73, 121.62, 31.45 (d, *J* = 22.3 Hz), 30.72 (d, *J* = 16.8 Hz), -3.51 (d, *J* = 12.8 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.77;

HRMS (ESI) m/z calcd for $C_{41}H_{32}PSSi$ $[M + H]^{+}$ 615.1726, found 615.1722.

Melting point: 185.9-186.5 °C.



1a

crude 5w, 72% NMR yield, dr = 2:1

5w, 36% isolated yield, > 99% de

(4*S*,11b*R*)-4-(2-((*R*)-Butyl(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5w). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et$_2$O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. MeSiHCl$_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that *n*-BuMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 72% yield and 2:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using CHCl$_2$CHCl$_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH$_3$ solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5w**·BH$_3$, that was then removed BH$_3$ using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5w** (177.4 mg, 36% yield, > 99% de) as white foam:

$[\alpha]_D^{25}$ = +179.30 (c = 1.0, CH$_2$Cl$_2$);

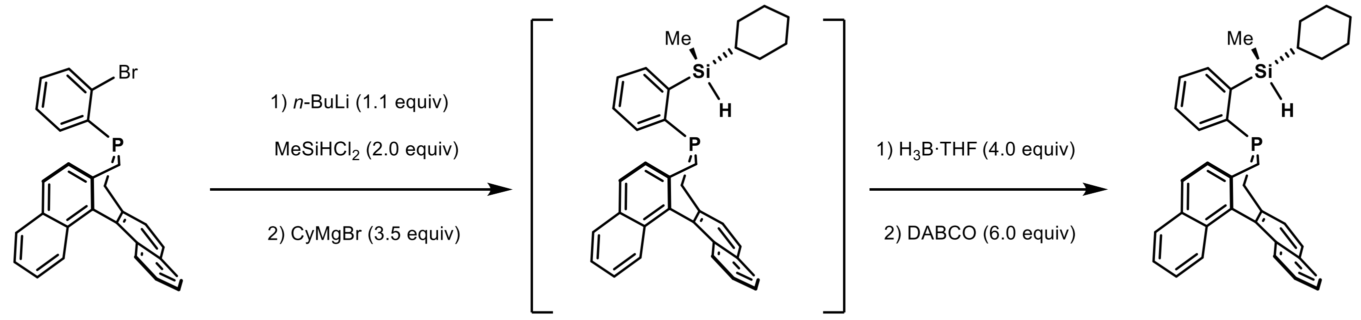
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (dd, *J* = 8.1, 5.0 Hz, 3H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.65 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.61 (dt, *J* = 7.5, 1.9 Hz, 1H), 7.43 (m, 2H), 7.34 – 7.19 (m, 5H), 7.13 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.80 (dd, *J* = 7.7, 2.8 Hz, 1H), 4.65 (m, 1H), 3.04 (dd, *J* = 11.8, 2.0 Hz, 1H), 2.94 – 2.78 (m, 2H), 2.60 (dd, *J* = 14.2, 3.9 Hz, 1H), 1.35 (m, 4H), 1.08 – 0.91 (m, 2H), 0.90 – 0.84 (m, 3H), 0.45 (dd, *J* = 3.8, 1.2 Hz, 3H);

^{13}C NMR (151 MHz, CDCl$_3$) δ 144.02 (d, *J* = 46.8 Hz), 143.31 (d, *J* = 21.9 Hz), 135.89 (d, *J* = 14.7 Hz), 134.57, 133.76 (d, *J* = 4.8 Hz), 133.71, 133.19, 132.95 (d, *J* = 1.5 Hz), 132.51, 132.38 (d, *J* = 2.3 Hz), 132.19, 131.35 (d, *J* = 2.0 Hz), 129.07, 128.84, 128.78, 128.56 (d, *J* = 1.5 Hz), 128.40, 128.35, 127.77 (d, *J* = 2.3 Hz), 127.58, 126.86, 126.82, 126.06, 126.02, 125.16, 125.05, 32.37 (d, *J* = 22.3 Hz), 30.72 (d, *J* = 16.8 Hz), 27.16, 26.34, 14.79 (d, *J* = 9.3 Hz), 13.97, -3.79 (d, *J* = 9.7 Hz);

^{31}P NMR (162 MHz, CDCl$_3$) δ -4.08;

HRMS (ESI) m/z calcd for C$_{33}$H$_{34}$PSi [M + H]$^+$ 489.2162, found 489.2161.

Melting point: 94.0-95.9 °C.



1a

crude 5x, 66% NMR yield, dr = 3:1

5x, 37% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-Cyclohexyl(methyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5x). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $MeSiHCl_2$ (210 μL, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared CyMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 66% yield and 3:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5x**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5x** (191.5 mg, 37% yield, > 99% de) as white foam: $[\alpha]_D^{25}$ = +203.60 (c = 1.0, CH_2Cl_2);

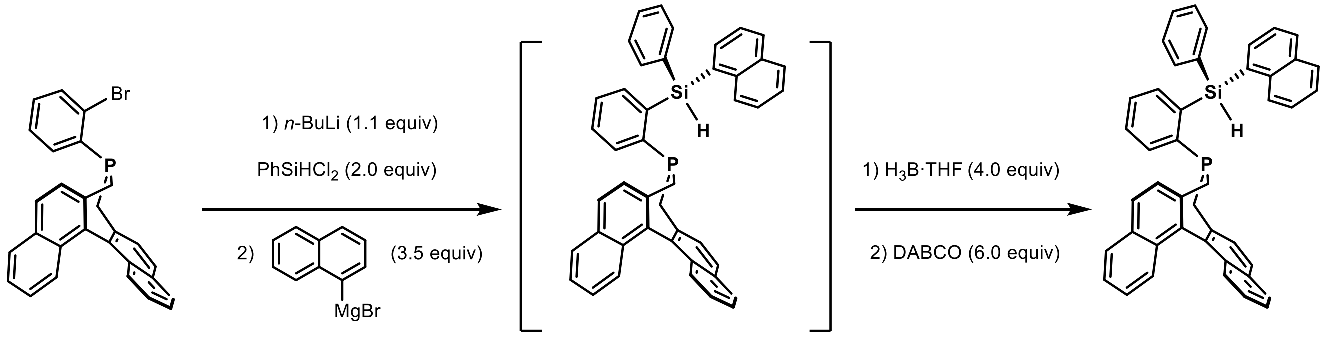
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (m, 3H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.30 (t, *J* = 8.4 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 4.49 (d, *J* = 4.5 Hz, 1H), 3.03 (d, *J* = 11.7 Hz, 1H), 2.94 – 2.74 (m, 2H), 2.60 (dt, *J* = 14.4, 3.2 Hz, 1H), 1.69 (m, 5H), 1.21 (m, 6H), 0.43 (d, *J* = 6.0 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.41 (d, *J* = 12.3 Hz), 143.18 (d, *J* = 36.8 Hz), 136.36 (d, *J* = 14.6 Hz), 134.60, 133.77 (d, *J* = 5.5 Hz), 133.76, 133.16, 132.94, 132.50, 132.37 (d, *J* = 2.1 Hz), 132.17, 131.28, 129.03, 128.72, 128.67, 128.55, 128.40, 128.34, 127.78 (d, *J* = 2.3 Hz), 127.57, 126.85, 126.82, 126.06, 126.01, 125.16, 125.03, 32.38 (d, *J* = 22.6 Hz), 30.78 (d, *J* = 17.0 Hz), 29.16, 28.17, 28.10, 28.04, 27.00, 25.21 (d, *J* = 8.0 Hz), -5.77 (d, *J* = 10.4 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -3.48;

HRMS (ESI) m/z calcd for $C_{35}H_{36}PSi$ $[M + H]^+$ 515.2318, found 515.2315.

Melting point: 111.5-113.2 °C.



1a

crude 5y, 90% NMR yield, dr = 45:1

5y, 73% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-Naphthalen-1-yl(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5y). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared naphthalen-1-ylmagnesium bromide (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 90% yield and 45:1 dr were determined by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5y**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5y** (451.9 mg, 73% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +267.90 (c = 1.0, CH_2Cl_2);

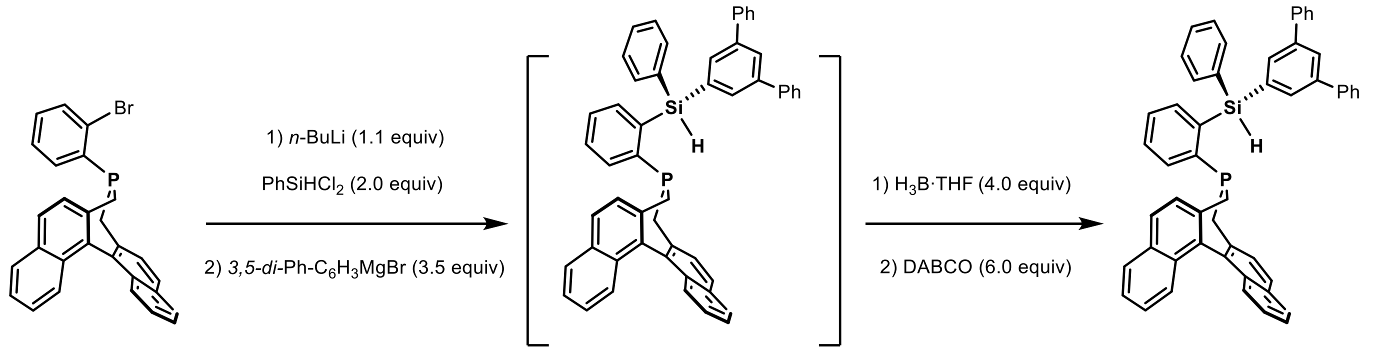
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.95 – 7.87 (m, 3H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 8.1 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.51 (dt, *J* = 6.9, 1.3 Hz, 1H), 7.47 (m, 1H), 7.39 (m, 8H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.07 (m, 6H), 6.91 – 6.82 (m, 2H), 6.36 (dd, *J* = 8.0, 1.2 Hz, 1H), 2.93 (dd, *J* = 11.8, 2.3 Hz, 1H), 2.55 (ddd, *J* = 36.7, 15.7, 11.9 Hz, 2H), 2.16 (dd, *J* = 14.3, 3.8 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.31 (d, *J* = 22.8 Hz), 141.08 (d, *J* = 46.4 Hz), 137.60 (d, *J* = 14.1 Hz), 137.41, 136.96, 136.52, 134.59 (d, *J* = 4.4 Hz), 134.39, 133.83, 133.58 (d, *J* = 4.6 Hz), 133.39, 133.12, 133.01 (d, *J* = 5.8 Hz), 132.82 (d, *J* = 1.3 Hz), 132.43, 132.23 (d, *J* = 2.0 Hz), 132.17, 131.90, 130.58, 129.80, 129.59, 129.09, 129.00, 128.93, 128.51, 128.39, 128.38, 128.31, 128.26, 127.74 (d, *J* = 2.5 Hz), 127.54, 126.83, 126.72, 126.27, 125.98, 125.93, 125.83, 125.40, 125.06, 125.01, 31.20 (d, *J* = 22.6 Hz), 30.88 (d, *J* = 17.3 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.98;

HRMS (ESI) m/z calcd for $C_{44}H_{34}PSi$ $[M + H]^+$ 621.2162, found 621.2158.

Melting point: 167.2-168.4 °C.



1a

crude 5z, 88% NMR yield, dr = 10:1

5z, 69% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-[1,1':3',1''-Terphenyl]-5'-yl(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5z). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared 3,5-*di*-Ph-C_6H_3MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 88% yield and 10:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5z**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5z** (497.4 mg, 69% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +226.40 (c = 1.0, CH_2Cl_2);

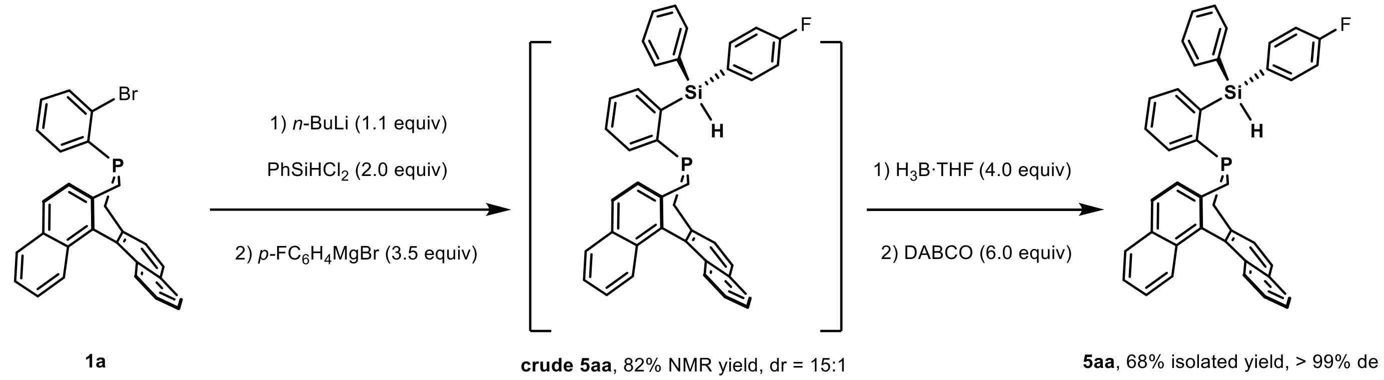
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.84 – 7.76 (m, 4H), 7.68 (dt, *J* = 7.3, 2.5 Hz, 2H), 7.62 – 7.57 (m, 4H), 7.55 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.46 – 7.28 (m, 13H), 7.25 – 7.08 (m, 5H), 7.00 – 6.88 (m, 2H), 5.99 (dd, *J* = 8.7, 3.4 Hz, 1H), 2.92 (dt, *J* = 12.0, 2.8 Hz, 1H), 2.67 – 2.53 (m, 2H), 2.30 (dt, *J* = 14.6, 3.2 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.52 (d, *J* = 22.2 Hz), 141.34, 141.10 (d, *J* = 48.5 Hz), 137.59, 137.44, 136.23, 136.15 (d, *J* = 4.9 Hz), 134.63 (d, *J* = 5.2 Hz), 134.30, 133.98, 133.97, 133.79, 133.53 (d, *J* = 4.9 Hz), 133.24, 132.85 (d, *J* = 1.0 Hz), 132.46, 132.25 (d, *J* = 1.8 Hz), 132.21, 132.09, 129.81, 129.21, 129.06, 128.93, 128.48, 128.34, 128.30, 128.27, 127.73, 127.64, 127.57, 127.53, 127.47, 126.86, 126.74, 126.02, 125.97, 125.08, 125.07, 31.33 (d, *J* = 12.3 Hz), 31.14 (d, *J* = 6.4 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -3.13;

HRMS (ESI) m/z calcd for $C_{52}H_{40}PSi$ $[M + H]^+$ 723.2631, found 723.2626.

Melting point: 158.3-159.5 °C.



(4*R*,11b*S*)-4-(2-((*R*)-(4-Fluorophenyl)(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5aa). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *p*-F-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 82% yield and 15:1 dr were determined by ^1H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5aa**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5aa** (401.5 mg, 68% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +263.50 (c = 1.0, CH_2Cl_2);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 1H), 7.87 (t, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.57 (m, 4H), 7.47 – 7.34 (m, 7H), 7.30 (m, 1H), 7.25 – 7.03 (m, 7H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.85 (m, 1H), 5.87 (d, *J* = 8.4 Hz, 1H), 2.95 (dd, *J* = 11.8, 2.7 Hz, 1H), 2.69 – 2.52 (m, 2H), 2.21 (dd, *J* = 14.4, 3.7 Hz, 1H);

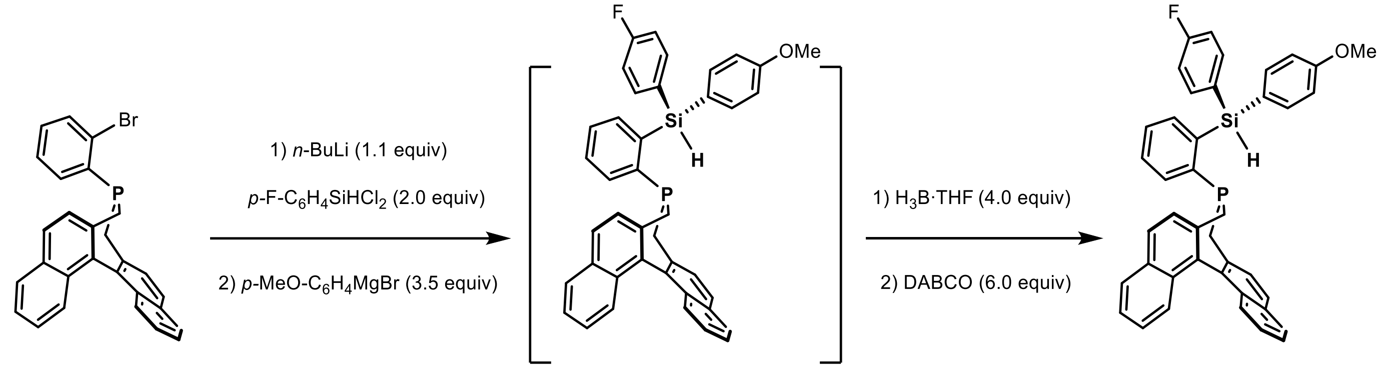
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.16 (d, *J* = 248.9 Hz), 144.21 (d, *J* = 22.1 Hz), 140.98 (d, *J* = 47.2 Hz), 138.18 (d, *J* = 1.0 Hz), 138.10 (d, *J* = 2.0 Hz), 137.47 (d, *J* = 14.6 Hz), 136.12, 136.10, 134.65 (d, *J* = 4.8 Hz), 134.28, 133.66, 133.64 (d, *J* = 5.2 Hz), 133.16, 132.87 (d, *J* = 2.0 Hz), 132.47, 132.28 (d, *J* = 2.1 Hz), 132.19, 132.01 (d, *J* = 2.0 Hz), 130.29 (dd, *J* = 5.5, 3.8 Hz), 129.83, 129.75, 129.15, 129.00, 128.51 (d, *J* = 1.0 Hz), 128.35, 128.32, 128.23, 127.71 (d, *J* = 2.2 Hz), 127.59, 126.85, 126.75, 126.03, 125.15, 125.07, 115.44, 115.24, 31.29 (d, *J* = 22.4 Hz), 30.91 (d, *J* = 16.8 Hz);

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.03;

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.83;

HRMS (ESI) m/z calcd for $C_{40}H_{31}FPSi$ $[M + H]^+$ 589.1911, found 589.1908.

Melting point: 136.6-138.1 °C.



1a **crude 5ab**, 69% NMR yield, dr = 5:1 **5ab**, 36% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-(4-Fluorophenyl)(4-methoxyphenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5ab). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. *p*-F-$C_6H_4SiHCl_2$ (390.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *p*-MeO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 69% yield and 5:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5ab**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5ab** (224.1 mg, 36% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +248.50 (c = 1.0, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.87 (dd, *J* = 11.3, 8.3 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.59 (t, *J* = 7.1 Hz, 2H), 7.48 (t, *J* = 8.5 Hz, 3H), 7.45 – 7.37 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 5.1 Hz, 2H), 7.18 (q, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.83 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 2.94 (d, *J* = 11.9 Hz, 1H), 2.68 – 2.53 (m, 2H), 2.20 (dd, *J* = 14.3, 3.5 Hz, 1H);

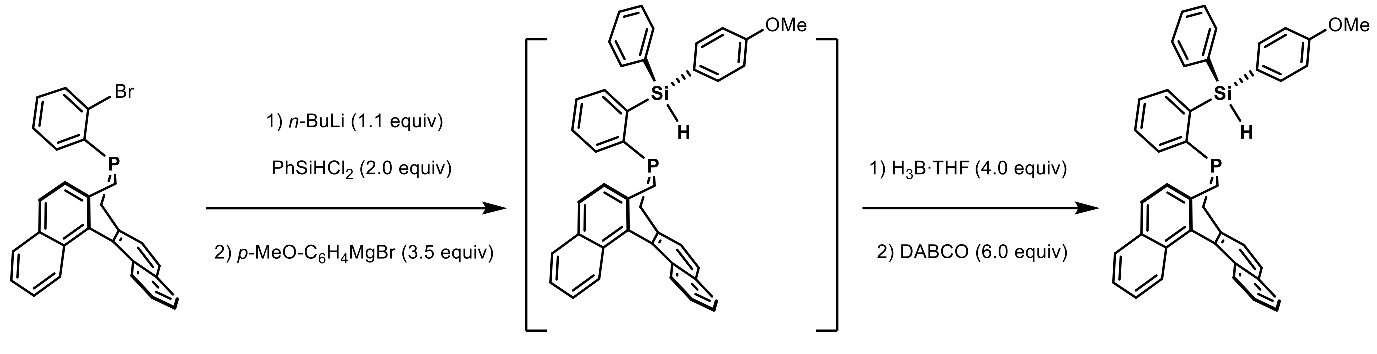
^{13}C NMR (151 MHz, $CDCl_3$) δ 164.12 (d, *J* = 249.0 Hz), 161.05, 144.18 (d, *J* = 22.2 Hz), 141.41 (d, *J* = 47.2 Hz), 138.14, 138.09, 137.62, 137.45 (d, *J* = 14.7 Hz), 134.33, 133.69, 133.64 (d, *J* = 5.3 Hz), 133.17, 132.87, 132.47, 132.29 (d, *J* = 1.5 Hz), 132.20, 131.99, 130.82 (t, *J* = 4.1 Hz), 129.66, 129.11, 129.02, 128.49, 128.34, 128.32, 127.73 (d, $J = 1.5$ Hz), 127.59, 126.85, 126.76, 126.02, 125.14, 125.06, 115.43, 115.29, 113.99, 55.21, 31.35 (d, $J = 22.6$ Hz), 31.00 (d, $J = 17.1$ Hz);

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.07;

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.95;

HRMS (ESI) m/z calcd for $C_{41}H_{33}FOPSi$ $[M + H]^+$ 619.2017, found 619.2012.

Melting point: 137.7-138.9 °C.



1a **crude 5ac**, 87% NMR yield, dr = 12:1 **5ac**, 70% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-(4-Methoxyphenyl)(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5ac). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *p*-MeO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 87% yield and 12:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5ac**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5ac** (419.4 mg, 70% yield, > 99% de) as white solid:

$[\alpha]_D^{25} = 239.50$ (c = 1.0, CH_2Cl_2);

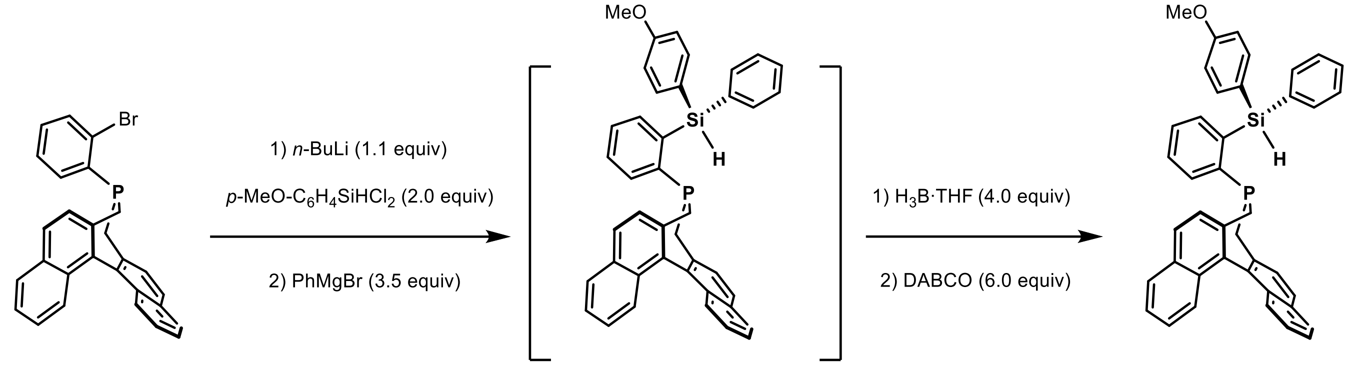
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $J = 8.2$ Hz, 1H), 7.86 (t, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.63 – 7.57 (m, 2H), 7.50 (m, 3H), 7.45 – 7.33 (m, 6H), 7.29 (m, 1H), 7.24 – 7.21 (m, 2H), 7.17 (m, 2H), 7.12 (d, $J = 8.4$ Hz, 1H), 6.95 – 6.90 (m, 2H), 6.88 (d, $J = 8.3$ Hz, 1H), 6.86 – 6.82 (m, 1H), 5.86 (dd, $J = 8.1$, 1.9 Hz, 1H), 3.81 (s, 3H), 2.94 (dd, $J = 11.8$, 2.4 Hz, 1H), 2.60 (ddd, $J = 34.0$, 15.4, 11.7 Hz, 2H), 2.21 (dd, $J = 14.4$, 3.6 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.97, 144.18 (d, J = 22.4 Hz), 141.61 (d, J = 46.8 Hz), 137.71, 137.70, 137.50 (d, J = 14.5 Hz), 136.13, 135.29 (d, J = 4.6 Hz), 134.45, 133.84, 133.63 (d, J = 4.5 Hz), 133.12, 132.84, 132.44, 132.28 (d, J = 2.0 Hz), 132.18, 131.86 (d, J = 1.0 Hz), 129.61, 129.52, 129.03, 128.99, 128.43, 128.33, 128.31, 128.12, 127.79 (d, J = 1.9 Hz), 127.54, 126.84, 126.75, 125.97, 125.31 (d, J = 5.5 Hz), 125.09, 125.01, 113.92, 55.20, 31.31 (d, J = 22.8 Hz), 30.95 (d, J = 17.3 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.69;

HRMS (ESI) m/z calcd for $C_{41}H_{34}OPSi$ $[M + H]^+$ 601.2111, found 601.2108.

Melting point: 135.7-136.8 °C.



1a **crude 5ad**, 83% NMR yield, dr = 8:1 **5ad**, 51% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*S*)-(4-Methoxyphenyl)(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5ad). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. *p*-MeO-$C_6H_4SiHCl_2$ (414.3 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared PhMgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 83% yield and 8:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5ad**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5ad** (307.6 mg, 51% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = 287.10 (c = 1.0, CH_2Cl_2);

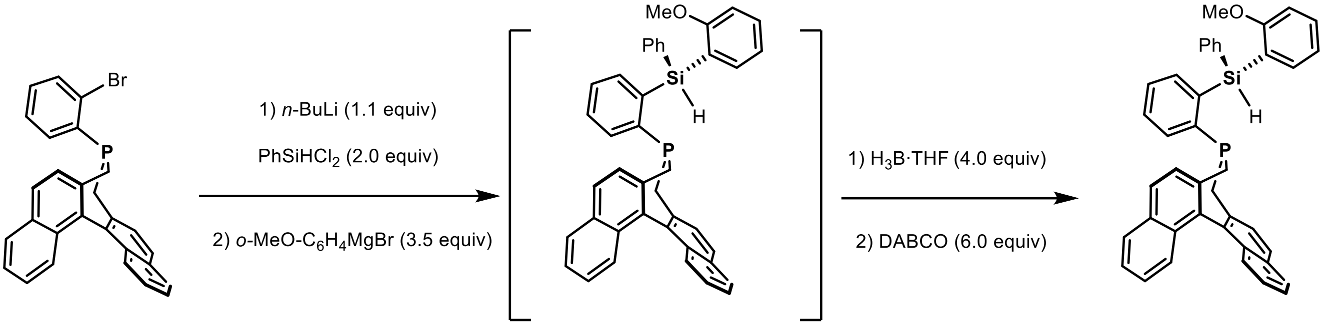
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.83 (m, 3H), 7.79 (d, J = 8.4 Hz, 1H), 7.60 – 7.52 (m, 4H), 7.49 – 7.33 (m, 7H), 7.29 (m, 1H), 7.26 – 7.21 (m, 2H), 7.21 – 7.15 (m, 2H), 7.12 (d, J = 8.4 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.89 (d, J = 8.3 Hz, 1H), 6.87 – 6.82 (m, 1H), 5.86 (d, J = 8.1 Hz, 1H), 3.80 (s, 3H), 2.94 (dd, J = 11.8, 2.4 Hz, 1H), 2.60 (ddd, J = 31.1, 15.6, 11.9 Hz, 2H), 2.22 (dd, J = 14.4, 3.7 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.00, 144.21 (d, J = 22.3 Hz), 141.60 (d, J = 46.8 Hz), 137.74, 137.48 (d, J = 14.4 Hz), 136.09, 135.28 (d, J = 5.4 Hz), 134.46, 133.86, 133.63 (d, J = 4.6 Hz), 133.14, 132.86, 132.44, 132.28, 132.19, 131.88, 129.54, 129.52, 129.05, 128.99, 128.44, 128.34, 128.31, 128.07, 127.79, 127.55, 126.85, 126.76, 125.98, 125.97, 125.37 (d, J = 4.6 Hz), 125.09, 125.02, 113.99, 55.18, 31.30 (d, J = 22.7 Hz), 30.97 (d, J = 17.1 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.85;

HRMS (ESI) m/z calcd for $C_{41}H_{34}OPSi$ $[M + H]^+$ 601.2111, found 601.2107.

Melting point: 137.3-138.2 °C.



1a **crude 5ae**, 80% NMR yield, dr = 11.5:1 **5ae**, 53% isolated yield, 88% de

(4*S*,11b*R*)-4-(2-((*R*)-(2-Methoxyphenyl)(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5ae). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *o*-MeO-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 80% yield and 11.5:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5ae**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5ae** (320.2 mg, 53% yield, 88% de) as white solid:

$[\alpha]_D^{25}$ = +253.30 (c = 1.0, CH_2Cl_2);

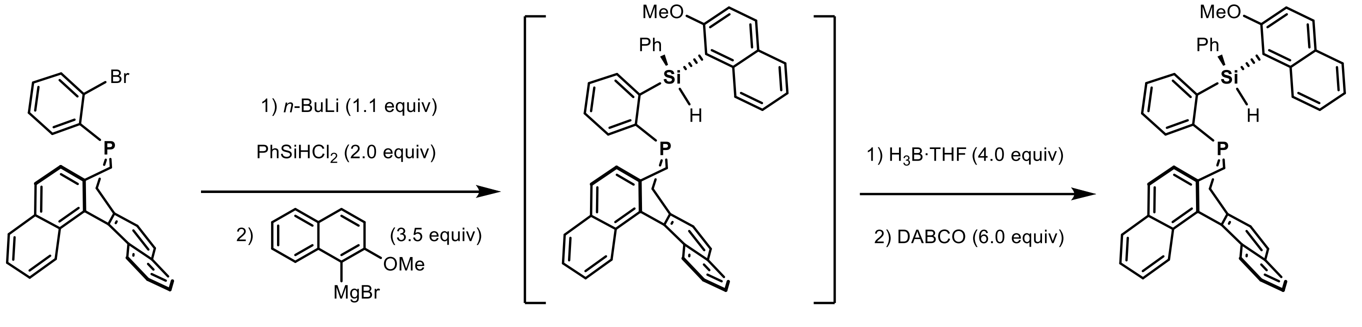
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 1H), 7.84 (dd, J = 14.0, 8.3 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.41 (dddd, J = 12.6, 8.1, 4.5, 1.7 Hz, 4H), 7.37 – 7.31 (m, 4H), 7.28 – 7.19 (m, 4H), 7.16 – 7.10 (m, 3H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.87 (dd, *J* = 8.2, 2.8 Hz, 2H), 6.81 (dd, *J* = 7.7, 2.5 Hz, 1H), 5.92 (d, *J* = 8.2 Hz, 1H), 3.65 (s, 3H), 2.93 (dd, *J* = 11.8, 2.1 Hz, 1H), 2.64 (dd, *J* = 17.0, 11.8 Hz, 1H), 2.49 (dd, *J* = 14.4, 12.1 Hz, 1H), 2.15 (dd, *J* = 14.5, 3.7 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.48, 143.76 (d, *J* = 22.9 Hz), 141.57 (d, *J* = 45.9 Hz), 138.13, 137.13 (d, *J* = 14.1 Hz), 136.25, 135.40 (d, *J* = 4.3 Hz), 134.59, 133.98, 133.60 (d, *J* = 5.0 Hz), 133.08, 132.81, 132.39, 132.25, 132.16, 131.86, 131.54, 129.36, 129.15, 129.07, 128.71, 128.35, 128.31, 128.29, 127.94, 127.85, 127.47, 126.82, 126.73, 125.93, 125.90, 125.02, 124.94, 123.17 (d, *J* = 5.5 Hz), 120.95, 110.11, 55.44, 31.13 (d, *J* = 23.0 Hz), 30.93 (d, *J* = 17.4 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -2.46 (minor), -2.81 (major);

HRMS (ESI) m/z calcd for $C_{41}H_{34}OPSi$ $[M + H]^+$ 601.2111, found 601.2107.

Melting point: 157.0-157.7 °C.



1a

crude 5af, 94% NMR yield, dr = 40:1

5af, 82% isolated yield, 95% de

(4*S*,11b*R*)-4-(2-((*R*)-(2-Methoxynaphthalen-1-yl)(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5af). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared (2-methoxynaphthalen-1-yl)magnesium bromide (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 94% yield and 40:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5af**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5af** (534.3 mg, 82% yield, 95% de) as white solid:

$[\alpha]_D^{25}$ = -137.90 (c = 1.0, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.37 (m, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.52 (dt, *J* = 7.4, 1.8 Hz, 1H), 7.45 – 7.29 (m, 7H), 7.25 (dd, *J* = 8.1, 5.3 Hz, 2H), 7.21 – 7.12 (m, 4H), 7.12 – 7.07 (m, 2H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.45 (d, *J* = 8.5 Hz, 1H), 6.30 (d, *J* = 8.3 Hz, 1H), 3.29 (s, 3H), 2.79 – 2.67 (m, 2H), 2.63 (dd, *J* = 11.6, 3.0 Hz, 1H), 1.84 (dd, *J* = 15.4, 11.7 Hz, 1H);

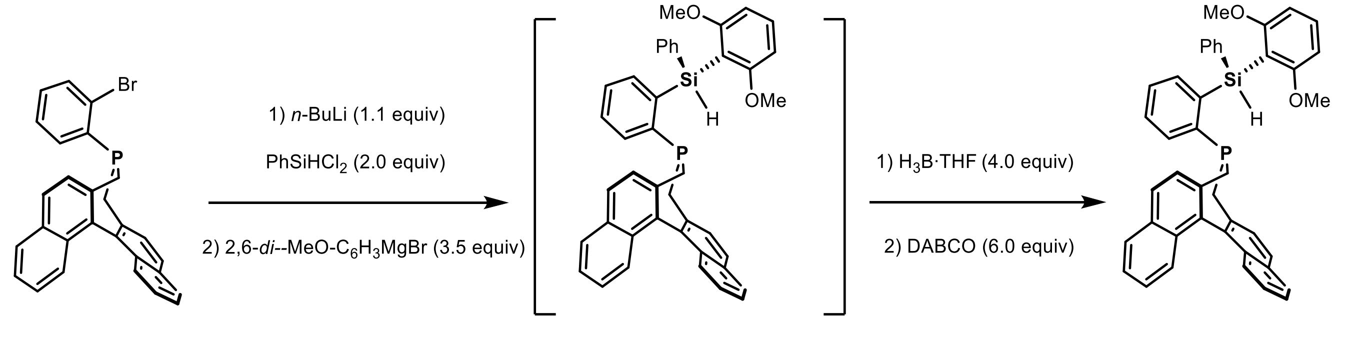
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.43, 144.81 (d, *J* = 22.6 Hz), 143.44 (d, *J* = 47.3 Hz), 138.31, 136.90 (d, *J* = 15.4 Hz), 136.34, 135.34 (d, *J* = 7.5 Hz), 134.35, 134.26, 133.37, 133.05, 132.61, 132.35, 132.26, 132.09, 131.47, 129.94, 129.30, 129.26, 128.98, 128.64, 128.58, 128.56, 128.19, 128.10, 127.99, 127.87, 127.85, 127.70, 127.29, 127.02, 126.81, 126.67, 125.93, 125.77, 125.00, 124.88, 123.87, 118.05 (d, *J* = 5.0 Hz), 113.88, 56.06, 32.22 (d, *J* = 17.1 Hz), 31.28 (d, *J* = 23.1 Hz);

^{29}Si NMR (80 MHz, $CDCl_3$) -34.1 [d, $J(^{31}P\text{-}^{29}Si)$ = 25.1 Hz] ppm

^{31}P NMR (243 MHz, $CDCl_3$) δ -2.15 (minor) -3.12 (major);

HRMS (ESI) m/z calcd for $C_{45}H_{36}OPSi$ $[M + H]^+$ 651.2268, found 651.2267.

Melting point: 160.1-160.9 °C.



1a **crude 5ag**, 92% NMR yield, dr = 6:1 **5ag**, 86% isolated yield, 71% de

(4*S*,11b*R*)-4-(2-((*R*)-(2,6-Dimethoxyphenyl)(phenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5ag). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared 2,6-*di*-MeO-C_6H_3MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 92% yield and 6:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5ag**$\cdot BH_3$, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5ag** (540.6 mg, 86% yield, 71% de) as white solid:

$[\alpha]_D^{25}$ = +124.60 (c = 1.0, CH_2Cl_2);

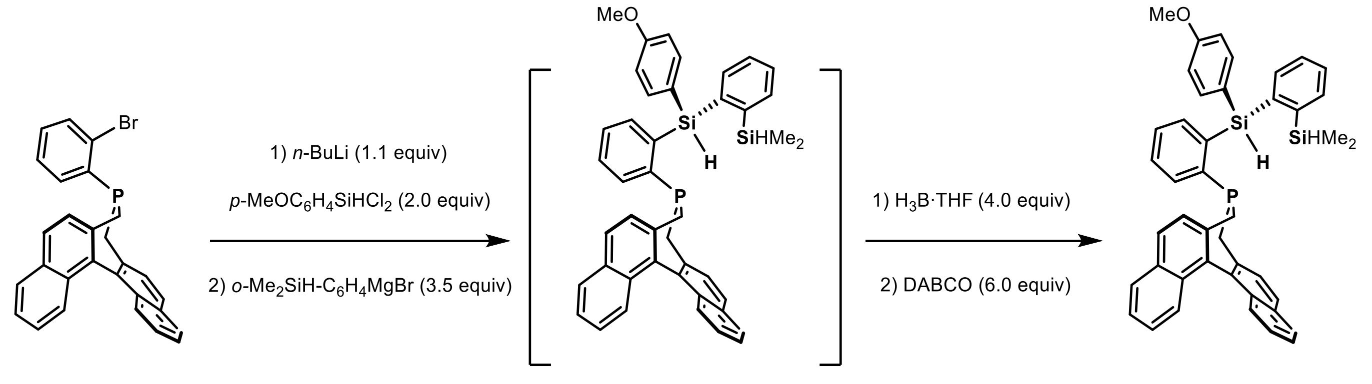
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.76 (m, 4H), 7.73 – 7.60 (m, 2H), 7.53 – 7.29 (m, 7H), 7.28 – 7.17 (m, 4H), 7.17 – 7.04 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.52 (dd, *J* = 60.3, 8.2 Hz, 2H), 6.05 – 5.93 (m, 1H), 3.54 (s, 6H), 2.99 – 2.78 (m, 1H), 2.78 – 2.63 (m, 1H), 2.53 (dd, *J* = 14.6, 3.1 Hz, 1H), 2.34 (dd, *J* = 16.0, 11.7 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.55, 144.15 (d, *J* = 22.1 Hz), 143.54 (d, *J* = 46.5 Hz), 136.75, 136.65, 136.34, 136.32 (d, *J* = 6.3 Hz), 136.23 (d, *J* = 6.7 Hz), 134.77, 134.42, 133.43 (d, *J* = 5.1 Hz), 133.23, 132.73, 132.66, 132.38, 132.26, 131.38, 129.32, 129.00, 128.66, 128.42, 128.25, 128.18, 127.80, 127.67, 127.62, 127.60, 126.83, 126.78, 125.91, 125.86, 124.94, 111.57 (d, *J* = 5.4 Hz), 104.38, 55.66, 32.09 (d, *J* = 17.2 Hz), 31.29 (d, *J* = 23.9 Hz);

^{31}P NMR (243 MHz, $CDCl_3$) δ -2.16 (minor), -3.23 (major);

HRMS (ESI) m/z calcd for $C_{42}H_{36}O_2PSi$ $[M + H]^+$ 631.2217, found 631.2212.

Melting point: 221.4-222.7 °C.



1a

crude 5ah, 76% NMR yield, dr = 33:1

5ah, 67% isolated yield, > 99% de

(4*R*,11b*S*)-4-(2-((*R*)-(2-(dimethylsilyl)phenyl)(4-methoxyphenyl)silyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5ah). According to experimental procedure D, to a Schlenk flask with **1a** (467.3 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. *p*-MeO-$C_6H_4SiHCl_2$ (414.3 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared *o*-Me_2SiH-C_6H_4MgBr (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 76% yield and 33:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5ah**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5ah** (440.1 mg, 67% yield, > 99% de) as white solid:

$[\alpha]_D^{25}$ = +158.00 (c = 0.1, CH_2Cl_2);

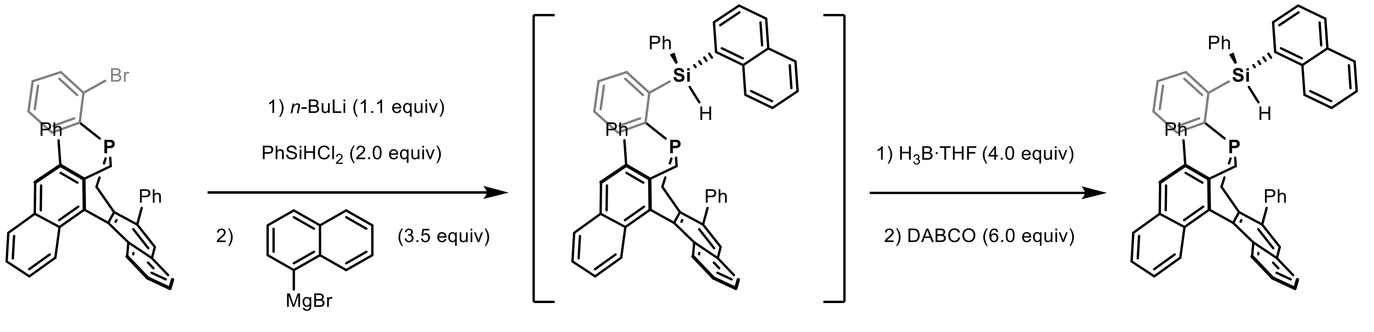
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.65 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.42 – 7.30 (m, 6H), 7.23 (m, 4H), 7.18 – 7.09 (m, 3H), 6.90 (m, 4H), 6.16 (d, *J* = 7.6 Hz, 1H), 4.60 (p, *J* = 3.7 Hz, 1H), 3.77 (s, 3H), 2.89 (dd, *J* = 11.8, 2.2 Hz, 1H), 2.63 – 2.49 (m, 2H), 2.32 (dd, *J* = 14.4, 3.7 Hz, 1H), 0.24 (d, *J* = 3.7 Hz, 3H), 0.17 (d, *J* = 3.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.88, 145.44, 144.17 (d, *J* = 23.1 Hz), 142.24 (d, *J* = 37.2 Hz), 141.99 (d, *J* = 3.3 Hz), 137.87, 137.60 (d, *J* = 13.9 Hz), 137.08, 137.06, 134.60, 134.56, 134.01, 133.54 (d, *J* = 4.7 Hz), 133.11, 132.80 (d, *J* = 1.5 Hz), 132.39, 132.24 (d, *J* = 2.1 Hz), 132.16, 131.67 (d, *J* = 1.8 Hz), 129.33, 128.97, 128.72, 128.70, 128.32, 128.28, 127.82, 127.79, 127.55, 126.82, 126.76, 125.94, 125.91, 125.82 (d, *J* = 4.8 Hz), 125.03, 124.97, 113.95, 55.10, 31.24 (d, *J* = 20.7 Hz), 31.03 (d, *J* = 15.0 Hz), -2.61, -2.78.

^{31}P NMR (162 MHz, $CDCl_3$) δ -2.80.

HRMS (ESI) m/z calcd for $C_{43}H_{40}OPSi_2$ $[M + H]^+$ 659.2350, found 659.2349.

Melting point: 185.3-185.8 °C.



1b **crude 5ai**, 65% NMR yield, dr = 49:1 **5ai**, 43% isolated yield, 96% de

(4*S*,11b*R*)-4-(2-((*R*)-Naphthalen-1-yl(phenyl)silyl)phenyl)-2,6-diphenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine (5ai). According to experimental procedure D, to a Schlenk flask with **1b** (619.5 mg, 1.0 mmol, 1.0 equiv) was added THF (5.0 mL) at room temperature. The reaction mixture was cooled to -84 °C before the drop-wise addition of *n*-BuLi (0.44 mL, 2.5 M in *n*-hexane, 1.1 mmol, 1.1 equiv) under Ar atmosphere. The brown solution was stirred for 1 h at -84 °C. Then Et_2O (5.0 mL) was added dropwise to the mixture and the solution was cooled to -116 °C. $PhSiHCl_2$ (354.2 mg, 2.0 mmol, 2.0 equiv) was added **quickly** and the solution was stirred at -116 °C for another 1 h. After that fresh prepared naphthalen-1-ylmagnesium bromide (3.5 mmol, 3.5 equiv) was added to the flask and the solution was gradually warmed to room temperature. The mixture was concentrated. 65% yield and 49:1 dr were determined by ^{1}H NMR and ^{31}P NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard. Then the crude reaction mixture was cooled to 0 °C before the addition of BH_3 solution (4.0 mL, 1.0 M in THF, 4.0 mmol, 4.0 equiv) under Ar atmosphere. The yellow solution was stirred for 12 h at room temperature. The reaction was concentrated and purified by silica gel column chromatography (PE/DCM = 100:1 to 3:1) to afford **5ai**·BH_3, that was then removed BH_3 using DABCO (6.0 equiv) in toluene (5.0 mL) at 50 °C for 6 h. The crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford **5ai** (333.9 mg, 43% yield, 96% de) as white solid:

$[\alpha]_D^{25}$ = +252.00 (c = 0.1, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 3H), 7.85 (dd, *J* = 8.2, 3.8 Hz, 2H), 7.79 (s, 1H), 7.71 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.02 (m, 26H), 6.65 (dd, *J* = 6.3, 2.6 Hz, 1H), 6.04 (d, *J* = 9.2 Hz, 1H), 3.05 (dd, *J* = 14.5, 4.2 Hz, 1H), 2.90 (d, *J* = 11.9 Hz, 1H), 2.71 (dd, *J* = 16.0, 11.8 Hz, 1H), 2.55 (dd, *J* = 14.6, 11.3 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.00 (d, *J* = 21.9 Hz), 141.36, 141.34, 140.95, 140.67 (d, *J* = 45.9 Hz), 140.32 (d, *J* = 1.9 Hz), 137.85, 137.75, 137.44, 136.80, 136.20, 134.74 (d, *J* = 4.5 Hz), 134.37 (d, *J* = 5.3 Hz), 134.18, 133.30, 132.62 (d, *J* = 4.5 Hz), 132.52, 132.28, 132.08, 131.85, 131.73 (d, *J* = 1.3 Hz), 131.56, 130.81, 130.26, 130.03, 129.99, 129.75, 129.61, 129.37, 129.33, 128.83, 128.80, 128.70, 128.58, 128.35, 128.26, 128.01, 128.00, 127.89, 127.07, 126.76, 126.68, 126.45, 126.07, 125.97, 125.64, 125.53, 125.38, 27.16 (d, *J* = 25.4 Hz), 26.63 (d, *J* = 18.2 Hz);

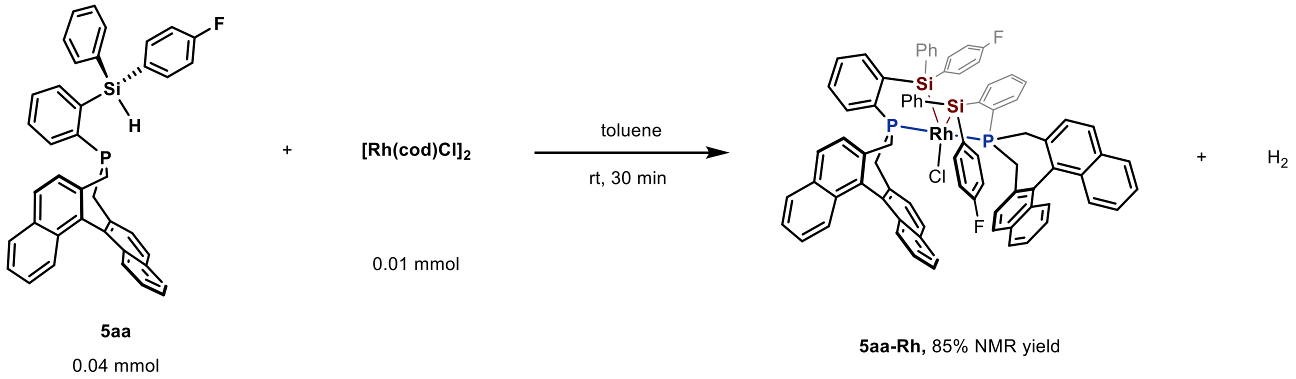
^{31}P NMR (243 MHz, $CDCl_3$) δ -1.83;

HRMS (ESI) m/z calcd for $C_{56}H_{42}PSi$ $[M + H]^+$ 773.2788, found 773.2782.

Melting point: 185.3-186.7 °C.

5. Synthetic Application of P-Atropisomeric Si-Stereogenic Monohydrosilanes

➢ Synthesis of chiral silyl Rhodium(III) complex



In a glove box under argon atmosphere, [Rh(cod)Cl]$_2$ (4.9 mg, 0.01 mmol) was solved in toluene (1 mL), and then **5aa** (23.5 mg, 0.04 mmol) was added, and the reaction was stirred for 30 min. After that, the solvent was removed under vacuum, the resulting solid was washed with 2 mL of *n*-hexane and 1 mL of methanol and dried under vacuum, then the desired complex **5aa-Rh** was obtained as a pale-yellow solid. 85% yield was determined by ^{1}H NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.2 Hz, 4H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.83 – 7.69 (m, 6H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.23 (m, 12H), 7.19 – 7.08 (m, 6H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.96 (t, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.65 (q, *J* = 7.6 Hz, 2H), 6.36 (t, *J* = 8.7 Hz, 4H), 5.79 (d, *J* = 8.3 Hz, 2H), 5.57 (d, *J* = 7.6 Hz, 2H), 3.63 – 3.53 (m, 2H), 3.29 (d, *J* = 13.7 Hz, 2H), 3.19 – 3.08 (m, 2H), 1.74 (d, *J* = 14.0 Hz, 2H).

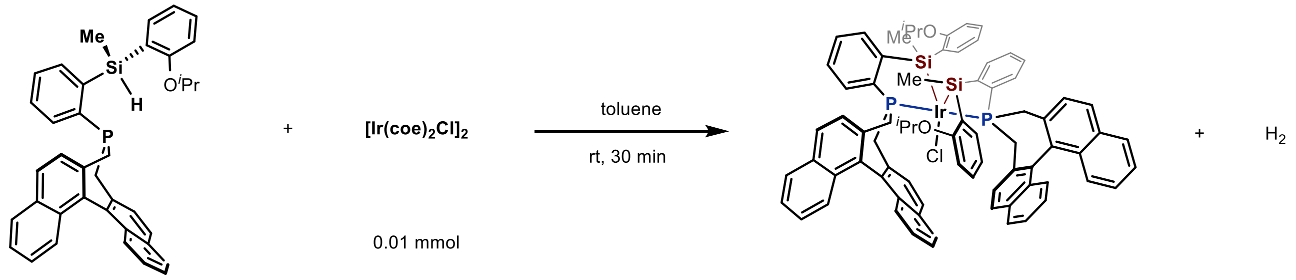
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.03, 161.55, 150.62 – 149.80 (m), 139.49, 138.65, 138.57, 136.71, 134.34, 133.40, 133.20 (t, *J* = 4.6 Hz), 132.58, 132.41, 132.09 (t, *J* = 3.0 Hz), 131.97, 131.80 (d, *J* = 3.5 Hz), 131.07 (t, *J* = 2.6 Hz), 130.01, 129.92, 129.46, 129.33, 129.31, 128.44, 128.29, 128.09, 127.49, 127.16, 126.95, 126.84, 126.11, 125.99, 125.52, 125.42, 114.11, 113.91, 33.12 (t, *J* = 10.7 Hz), 28.97 (t, *J* = 10.9 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 71.06 (d, *J* = 114.4 Hz).

^{19}F NMR (377 MHz, Chloroform-*d*) δ -111.77 (t, *J* = 7.7 Hz).

HRMS (ESI) m/z calcd for $C_{80}H_{58}F_2P_2RhSi_2$ $[M-Cl]^+$ 1277.2575, found 1277.2570.

➢ Synthesis of chiral silyl Iridium(III) complex



5m
0.04 mmol

5m-Ir, 93% NMR yield

In a glove box under argon atmosphere, [Ir(coe)$_2$Cl]$_2$ (8.9 mg, 0.01 mmol) was solved in toluene (1 mL), and then **5m** (22.7 mg, 0.04 mmol) was added, and the reaction was stirred for 30 min. After that, the solvent was removed under vacuum, the resulting solid was washed with 2 mL of *n*-hexane and 1 mL of methanol and dried under vacuum, then the desired complex **5m-Ir** was obtained as a pale-yellow solid. 93% yield was determined by ^{1}H NMR analysis of crude reaction mixture using $CHCl_2CHCl_2$ as internal standard.

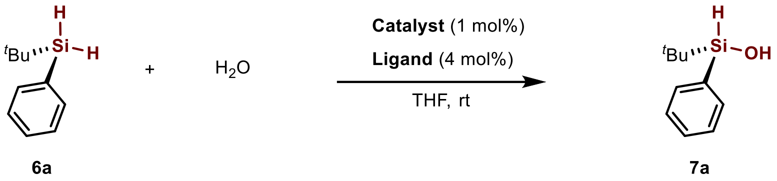
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.4 Hz, 2H), 8.00 (dd, *J* = 14.0, 8.2 Hz, 4H), 7.85 (dd, *J* = 8.3, 4.7 Hz, 4H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.35 (dt, *J* = 8.4, 5.8 Hz, 4H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.11 (t, 4H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 2H), 6.97 – 6.84 (m, 8H), 6.36 (d, *J* = 8.2 Hz, 2H), 6.30 (t, *J* = 7.2 Hz, 2H), 4.17 (hept, *J* = 6.0 Hz, 2H), 3.86 – 3.64 (m, 4H), 3.17 (dt, *J* = 13.0, 4.8 Hz, 2H), 2.69 (d, *J* = 14.9 Hz, 2H), 0.88 – 0.79 (m, 6H), 0.75 (d, *J* = 6.0 Hz, 6H), 0.44 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.71, 155.86 (t, *J* = 25.2 Hz), 138.27, 134.52, 134.09, 134.01, 133.95, 133.39 (t, *J* = 3.7 Hz), 133.08, 132.75, 132.72, 132.68, 132.64, 132.45, 130.91, 130.68, 130.21, 129.58, 129.45, 129.10, 128.37, 128.17, 127.78, 127.51, 127.42, 127.14, 126.09, 125.56, 125.49, 125.21, 118.97, 110.94, 68.02, 21.71, 21.61, 3.17, 1.17.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 70.05.

HRMS (ESI) m/z calcd for $C_{76}H_{68}IrO_2P_2Si_2$ [M-Cl]$^+$ 1323.3862, found 1323.3867.

- **Chiral silyl metal complexes or silyl ligands enabled asymmetric hydrolytic oxidation of dihydrosilane**[a]



Entry	Catalyst	Ligand	Yield (%)	*ee* (%)
1	$[Ir(cod)Cl]_2$	**5c**	84	10
2	$[Ir(cod)Cl]_2$	**5g**	79	10
3	$[Ir(cod)Cl]_2$	**5m**	98	17
4[b]	$[Ir(cod)Cl]_2$	**5o**	99	10
5	$[Ir(cod)Cl]_2$	**5u**	7	-30
6	$[Ir(cod)Cl]_2$	**5x**	99	16
7	$[Ir(cod)Cl]_2$	**5y**	23	14
8[b]	$[Ir(cod)Cl]_2$	**5ae**	99	8
9	$[Ir(cod)Cl]_2$	**5af**	trace	
10	$[Rh(cod)Cl]_2$	**5c**	5	-14
11[b]	$[Rh(cod)Cl]_2$	**5g**	99	-35
12	$[Rh(cod)Cl]_2$	**5m**	59	-31
13	$[Rh(cod)Cl]_2$	**5o**	99	-52
14	$[Rh(cod)Cl]_2$	**5s**	99	3
15	$[Rh(cod)Cl]_2$	**5u**	99	-66
16	$[Rh(cod)Cl]_2$	**5v**	84	0
17	$[Rh(cod)Cl]_2$	**5ae**	17	-75
18[b]	$[Rh(cod)_2]BF_4$	**5u**	99	-72
19[b]	$[Rh(cod)_2]BF_4$	**5q**	99	22
20[b]	$[Rh(cod)_2]BF_4$	**5r**	99	-2
21[b]	**5aa-Rh**		99	-19
22	**5m-Ir**		98	-17

[a] Conditions: **6a** (0.1 mmol), H_2O (0.2 mmol), Catalyst (1 mol%), ligand (4 mol%), in 1.0 mL THF under argon atmosphere at room temperature for 12 h. Isolated yields after chromatography purification. The *ee* values were determined by chiral HPLC. [b] The reaction time was 2 h.

Experimental procedure E:

Inside an argon-filled glovebox, an oven-dried 5 mL microwave reaction tube was charged with catalyst (1 mol%), chiral silyl ligand (4 mol%) and anhydrous THF (1.0 mL). After being stirred at room temperature for 5 min, **6a** (0.10 mmol) and H_2O (0.20 mmol) were added respectively. The tube was capped and taken outside of the glovebox. The resulting mixture was stirred at room temperature (approximately 25-28 °C). After the solvent was removed under vacuum, the residues were purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 10/1) to afford the target product silanol. The *ee* values were determined by chiral HPLC. note: $ee = \frac{\text{(former peak area)}-\text{(latter peak area)}}{\text{(former peak area)}+\text{(latter peak area)}}*100\%$.

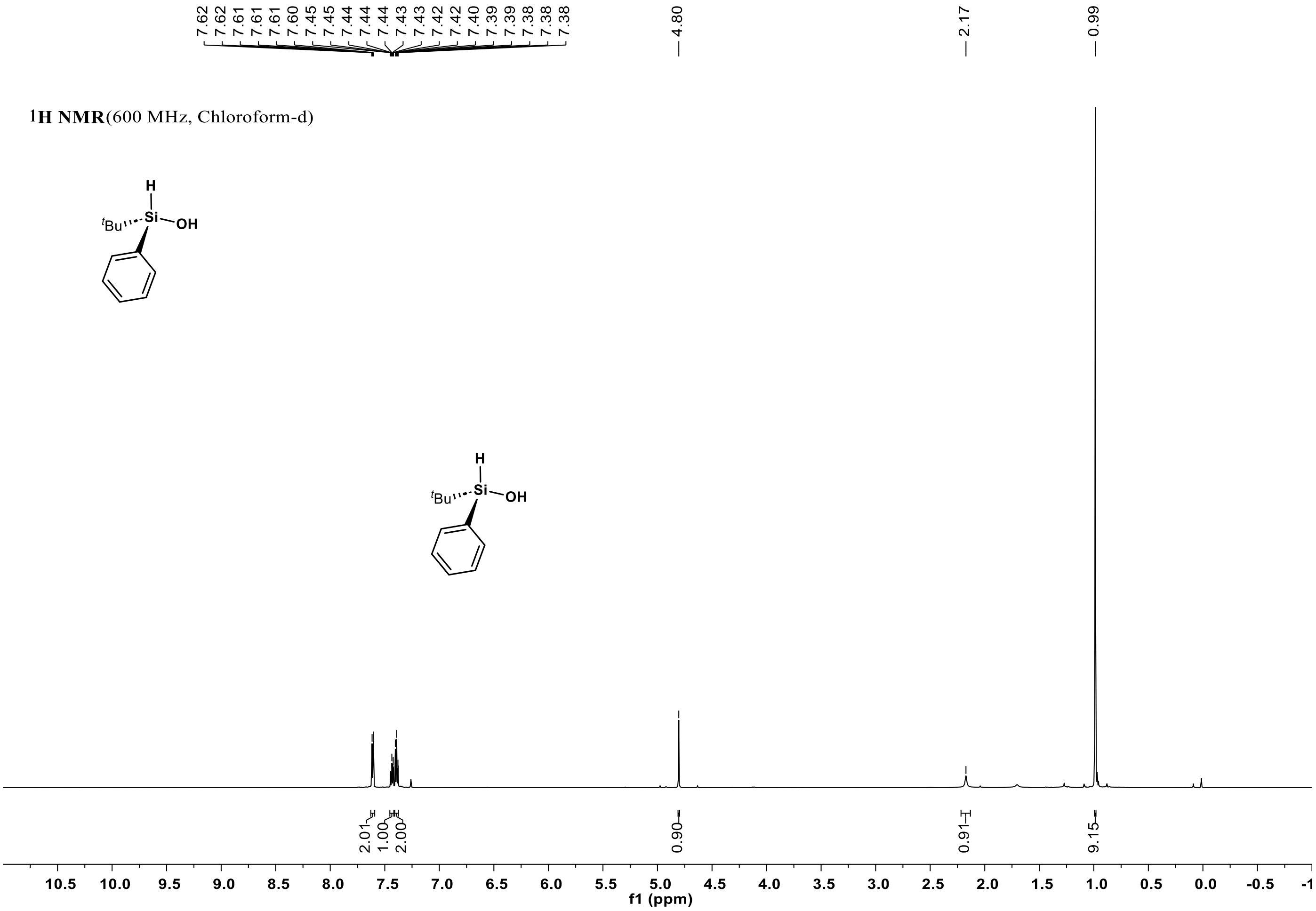
Experimental procedure F:

Inside an argon-filled glovebox, an oven-dried 5 mL microwave reaction tube was charged with chiral silyl metal complex (1 mol%) and anhydrous THF (1.0 mL). After being stirred at room temperature for 5 min, dihydrosilane (0.10 mmol) and H_2O (0.20 mmol) were added respectively. The tube was capped and taken outside of the glovebox. The resulting mixture was stirred at room temperature (approximately 25-28 °C). After the solvent was removed under vacuum, the residues were purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 10/1) to afford the target product silanol. The *ee* values were determined by chiral HPLC. note: $ee = \frac{\text{(former peak area)}-\text{(latter peak area)}}{\text{(former peak area)}+\text{(latter peak area)}}*100\%$.

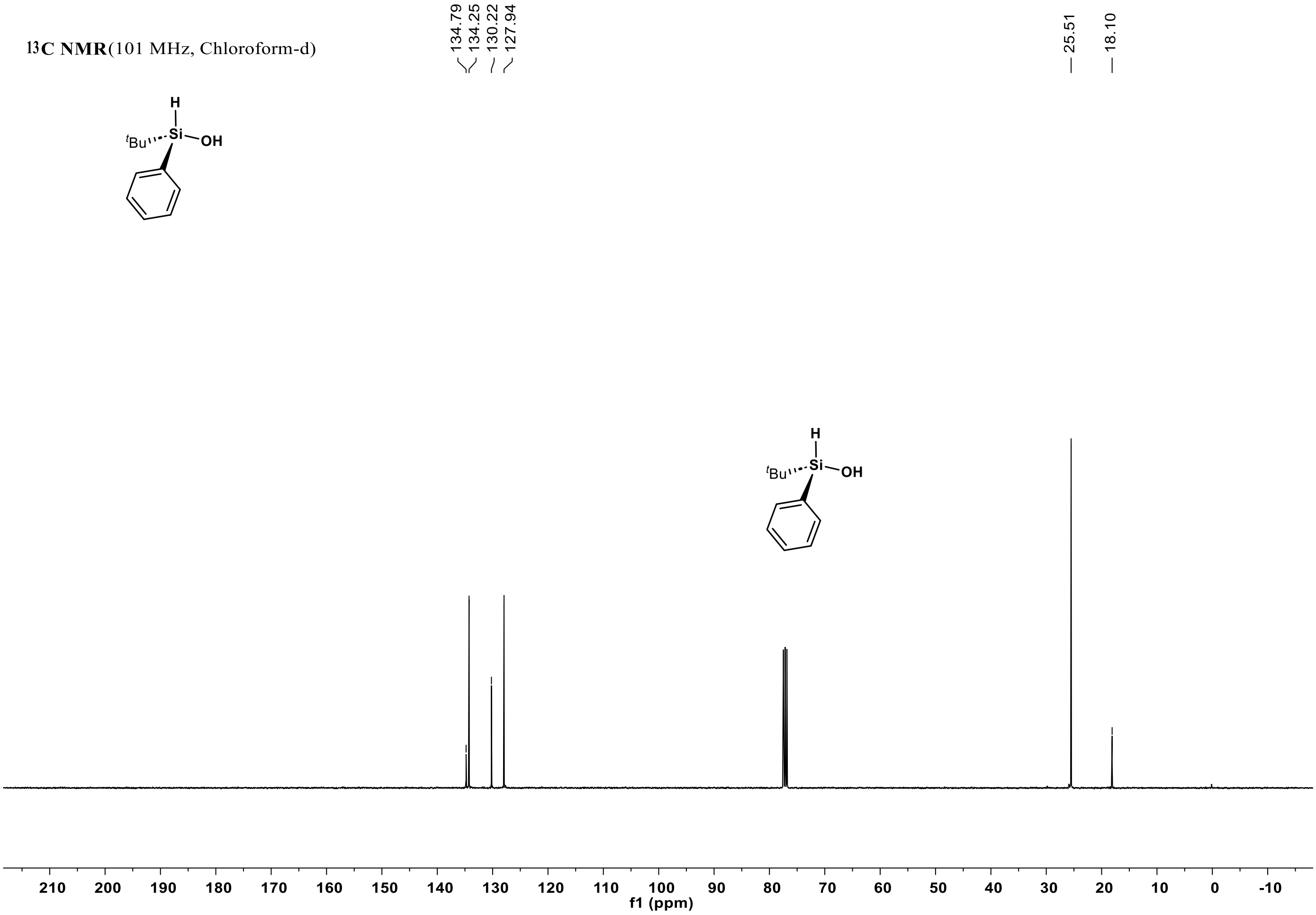
According to **experimental procedure E**, Inside an argon-filled glovebox, an oven-dried 5 mL microwave reaction tube was charged with $[Rh(cod)_2]BF_4$ (1 mol%), chiral silyl ligand **5u** (4 mol%) and anhydrous THF (1.0 mL). After being stirred at room temperature for 5 min, **6a** (0.10 mmol) and H_2O (0.20 mmol) were added respectively. The tube was capped and taken outside of the glovebox. The resulting mixture was stirred at room temperature (approximately 25-28 °C) for 2 h. After the solvent was removed under vacuum, the residues were purified by flash chromatography on silica gel (petroleum ether/ ethyl acetate = 10/1) to afford the target product silanol as a colorless oil 17.9 mg with 99% yield. Enantiomeric excess was established as -72% *ee* by HPLC analysis using a Chiralpak AD-3 column. (HPLC conditions: AD-3, wavelength = 220 nm, eluents: *n*-hexane/isopropanol = 95:5, flow rate = 1.0 mL/min, temperature = 28 °C, t_r (minor) = 5.9 min, t_r (major) = 6.7 min). $[\alpha]_D^{22.3}$ = -7.8 (c = 1.0, $CHCl_3$). Corresponding racemic samples were obtained as references by carrying out the reactions at the identical conditions with (±)-BINAP ligand.

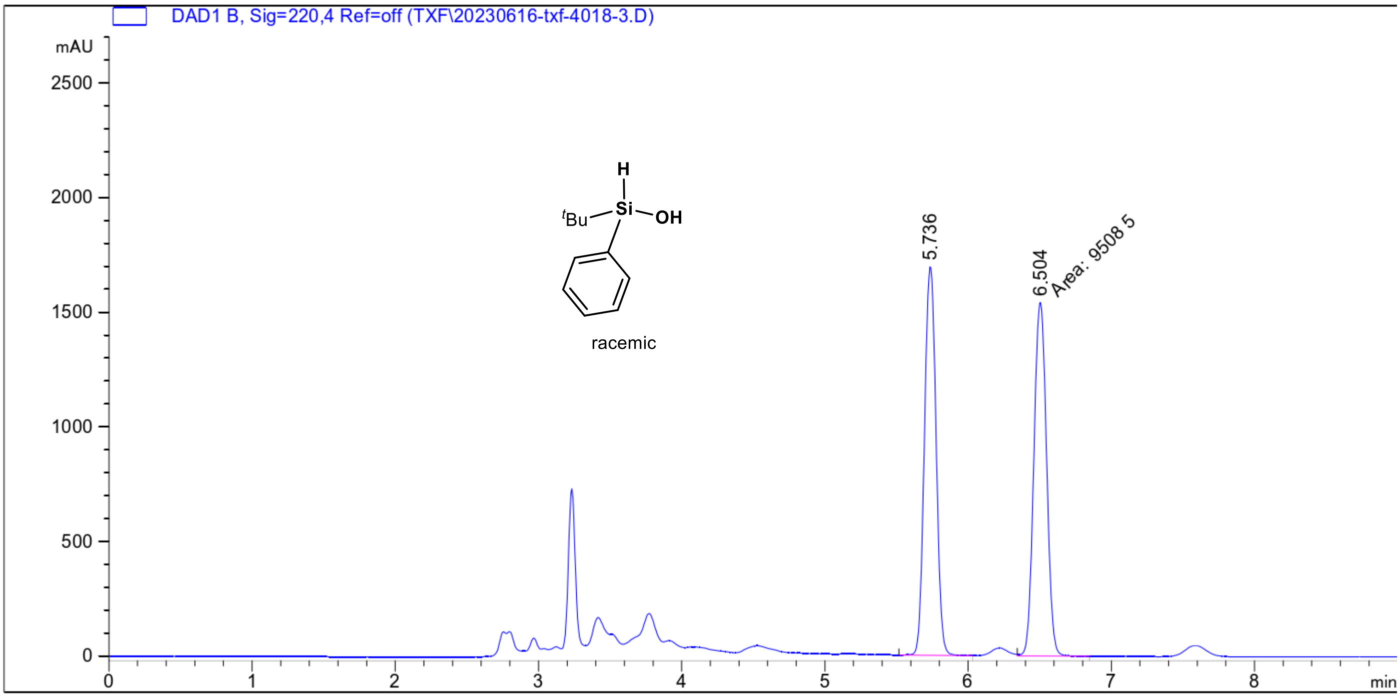
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 – 7.59 (m, 2H), 7.46 – 7.41 (m, 1H), 7.39 (dd, *J* = 7.9, 6.5 Hz, 2H), 4.80 (s, 1H), 2.17 (s, 1H), 0.99 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 134.79, 134.25, 130.22, 127.94, 25.51, 18.10.

1H NMR(600 MHz, Chloroform-d)



13C NMR(101 MHz, Chloroform-d)





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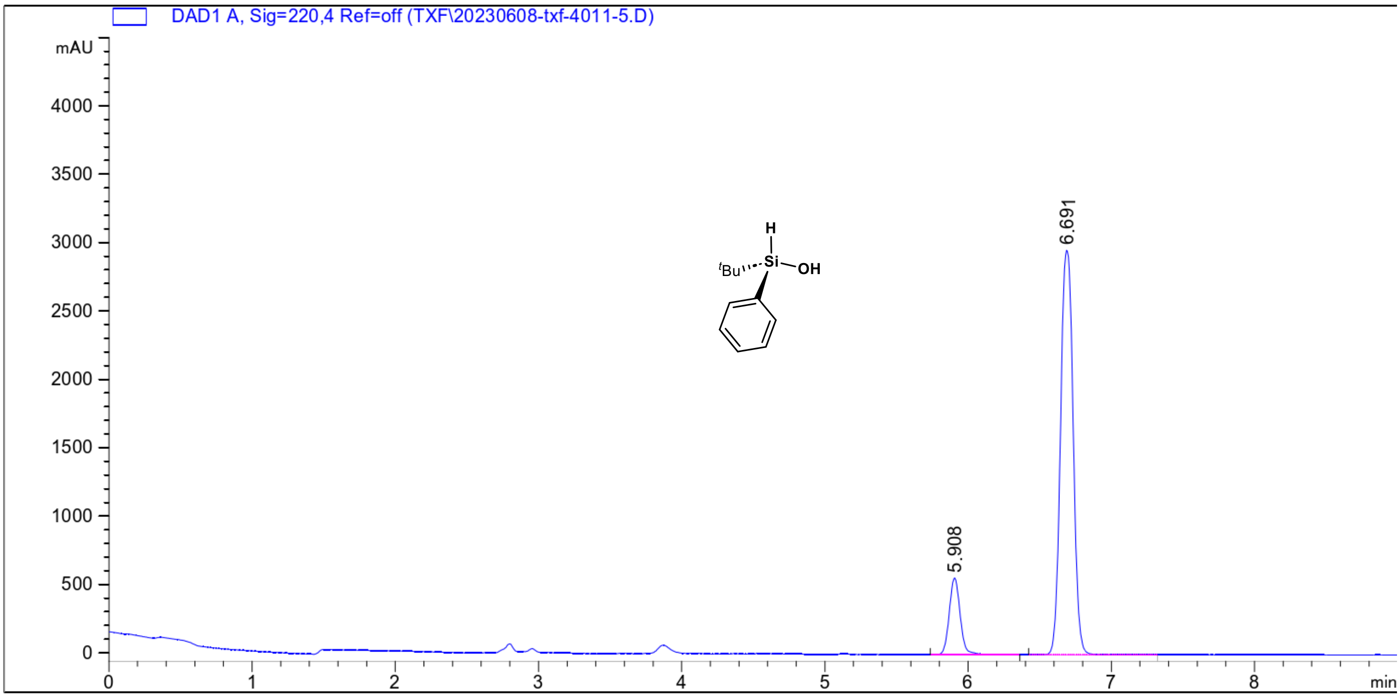

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   2   6.691 BB     0.0971 1.80544e4 2961.22217  85.9201
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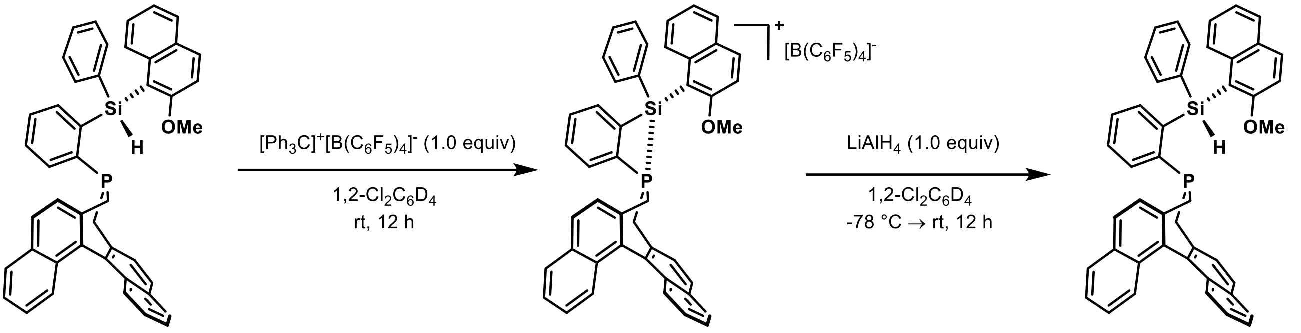
➢ Synthesis of chiral silylium ions and preliminary chiral memory study



(^{Si}*R*)-5af
dr = 97:3

δ (**^{29}Si**) -34.1 [d, *J*(^{31}P-^{29}Si) = 25.1 Hz] ppm
δ (**^{31}P**) -2.6 (minor), -3.3 (major) ppm

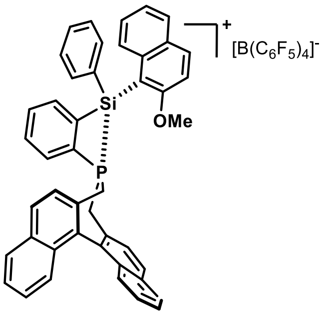
(^{Si}*R*)-9
dr = 90:10

δ (**^{29}Si**) 8.5 [d, *J*(^{31}P-^{29}Si) = 48.7 Hz] ppm
δ (**^{31}P**) 35.7 (minor), 29.1 (major) ppm

(^{Si}*R*)-5af
dr = 86:14

δ (**^{29}Si**) -34.3 [d, *J*(^{31}P-^{29}Si) = 24.2 Hz] ppm
δ (**^{31}P**) -2.6 (minor), -3.3 (major) ppm

In a glove box under argon atmosphere, a dry J. Young NMR tube was charged with trityl tetrakis(pentafluorophenyl)borate (36.8 mg, 0.04 mmol, 1.0 equiv), silane (^{Si}*R*)-**5af** (26.0 mg, 0.04 mmol, 1.0 equiv) and 1,2-$Cl_2C_6D_4$ (0.2 mL). After being stirred at room temperature for 12 h, the sample was subjected to ^{1}H NMR, ^{29}Si NMR and ^{31}P NMR spectroscopy analysis. (^{Si}*R*)-**9** was obtained in 95% NMR yield with 90:10 dr (the yield was determined using triphenylmethane as internal standard and the dr was determined by ^{31}P NMR analysis). Then, a solution of $LiAlH_4$ (0.016 mL, 2.5 M in THF, 0.04 mmol, 1.0 equiv) was added to the solution at °C, and the solution was gradually warmed to room temperature and stirred for 12 h. After the presence of the returned silane (^{Si}*R*)-**5af** (86:14 dr) was confirmed by ^{31}P NMR analysis of crude reaction mixture, then the crude mixture was concentrated and purified by flash silica gel column chromatography (PE/EA = 100:1) to afford (^{Si}*R*)-**5af** as white solid (17.7 mg, 68% yield, 86:14 dr).



(^{Si}*R*)-9
dr = 90:10

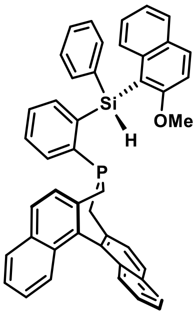
^{1}H NMR (400 MHz, 1,2-$Cl_2C_6D_4$) δ 8.01 – 7.82 (m, 4H), 7.75 (m, 1H), 7.57 (m, 4H), 7.48 – 7.25 (m, 7H), 7.24 – 7.00 (m, 26H), 6.96 (d, *J* = 2.7 Hz, 1H), 6.89 (s, 1H), 6.66 – 6.55 (m, 1H), 4.10 – 4.03 (m, 0.33H), 3.55 (s, 3H), 3.36 (q, *J* = 7.1 Hz, 0.53H), 3.29 – 3.07 (m, 2.54H), 2.80 (dd, *J* = 14.9, 4.3 Hz, 1H).

^{11}B NMR (128 MHz, 1,2-$Cl_2C_6D_4$) δ -16.24.

^{19}F NMR (377 MHz, 1,2-$Cl_2C_6D_4$) δ -131.59, -162.17, -166.01.

^{29}Si NMR (80 MHz, 1,2-$Cl_2C_6D_4$) δ 8.48 [d, *J*(^{31}P-^{29}Si) = 48.7 Hz].

^{31}P NMR (162 MHz, 1,2-$Cl_2C_6D_4$) δ 35.66 (minor), 29.13 (major).

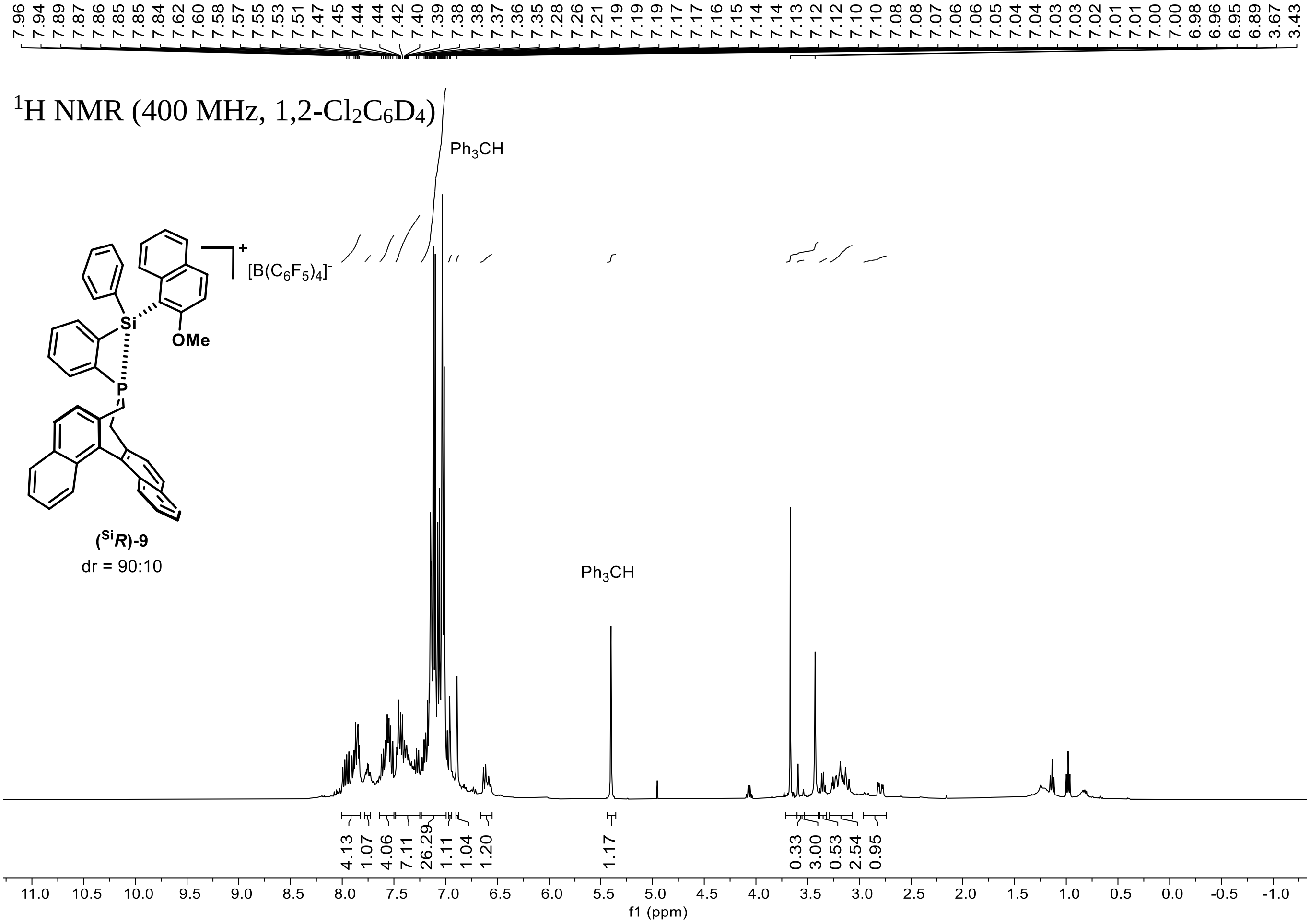


(^{Si}*R*)-5af
dr = 86:14

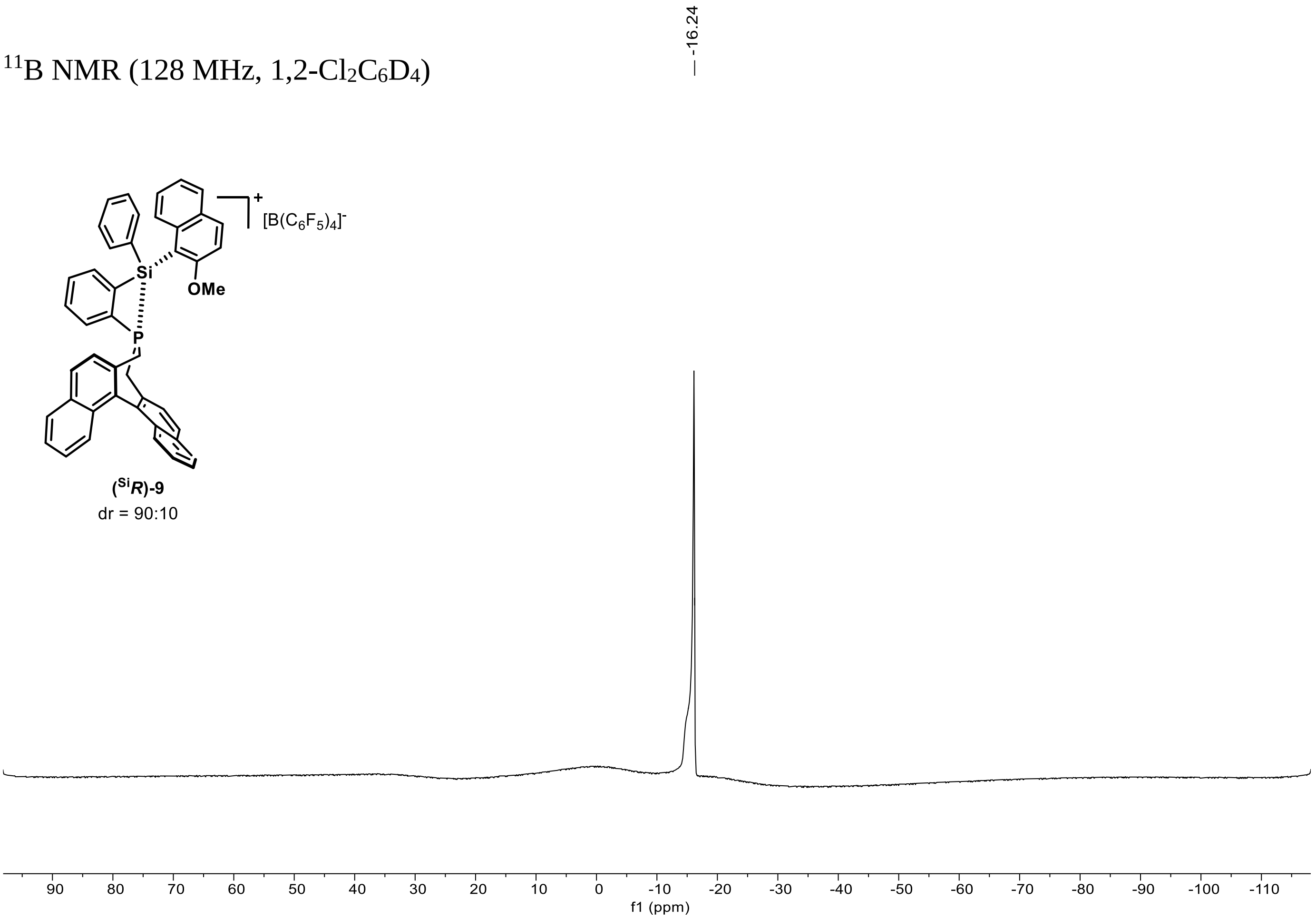
^{1}H NMR (600 MHz, DMSO-d_6) δ 8.28 (d, *J* = 7.4 Hz, 0.81H), 8.17 (d, *J* = 9.2 Hz, 1H), 8.03 (dd, *J* = 7.3, 2.4 Hz, 0.85H), 8.01 – 7.86 (m, 3.17H), 7.82 – 7.75 (m, 0.38H), 7.69 – 7.63 (m, 2.33H), 7.62 – 7.59 (m, 0.35H), 7.52 (d, *J* = 8.3 Hz, 0.22H), 7.47 – 7.34 (m, 8.65H), 7.34 – 7.28 (m, 2H), 7.26 – 7.11 (m, 3.32H), 7.03 (dt, *J* = 7.4, 1.9 Hz, 0.82H), 7.00 (d, *J* = 8.6 Hz, 0.17H), 6.96 – 6.91 (m, 0.81H), 6.86 (dd, *J* = 8.5, 3.3 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 0.16H), 6.36 (d, *J* = 8.3 Hz, 0.78H), 6.34 (d, *J* = 7.7 Hz, 0.77H), 6.30 (d, *J* = 6.8 Hz, 0.15H), 3.59 (s, 0.42H), 3.32 (s, 2.54H), 2.86 – 2.76 (m, 1H), 2.48 – 2.45 (m, 1H), 1.94 (dd, *J* = 15.2, 11.5 Hz, 0.87H), 1.72 (dd, *J* = 14.2, 11.9 Hz, 0.15H).

^{31}P NMR (243 MHz, DMSO-d_6) δ -2.56 (minor), -3.32 (major).

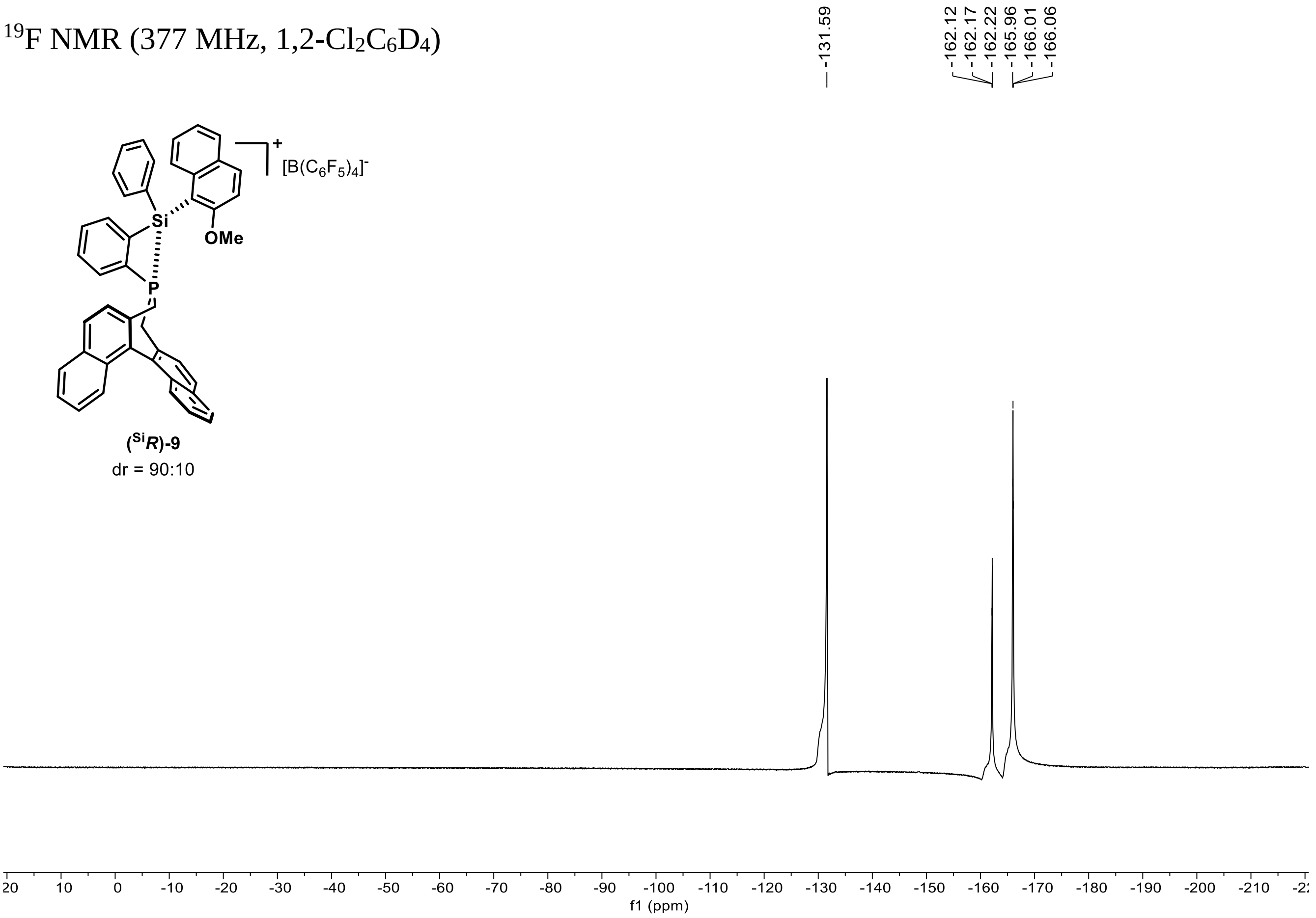
^{29}Si NMR (80 MHz, DMSO-d_6) δ -34.3 [d, J(^{31}P-^{29}Si) = 24.2 Hz] ppm.



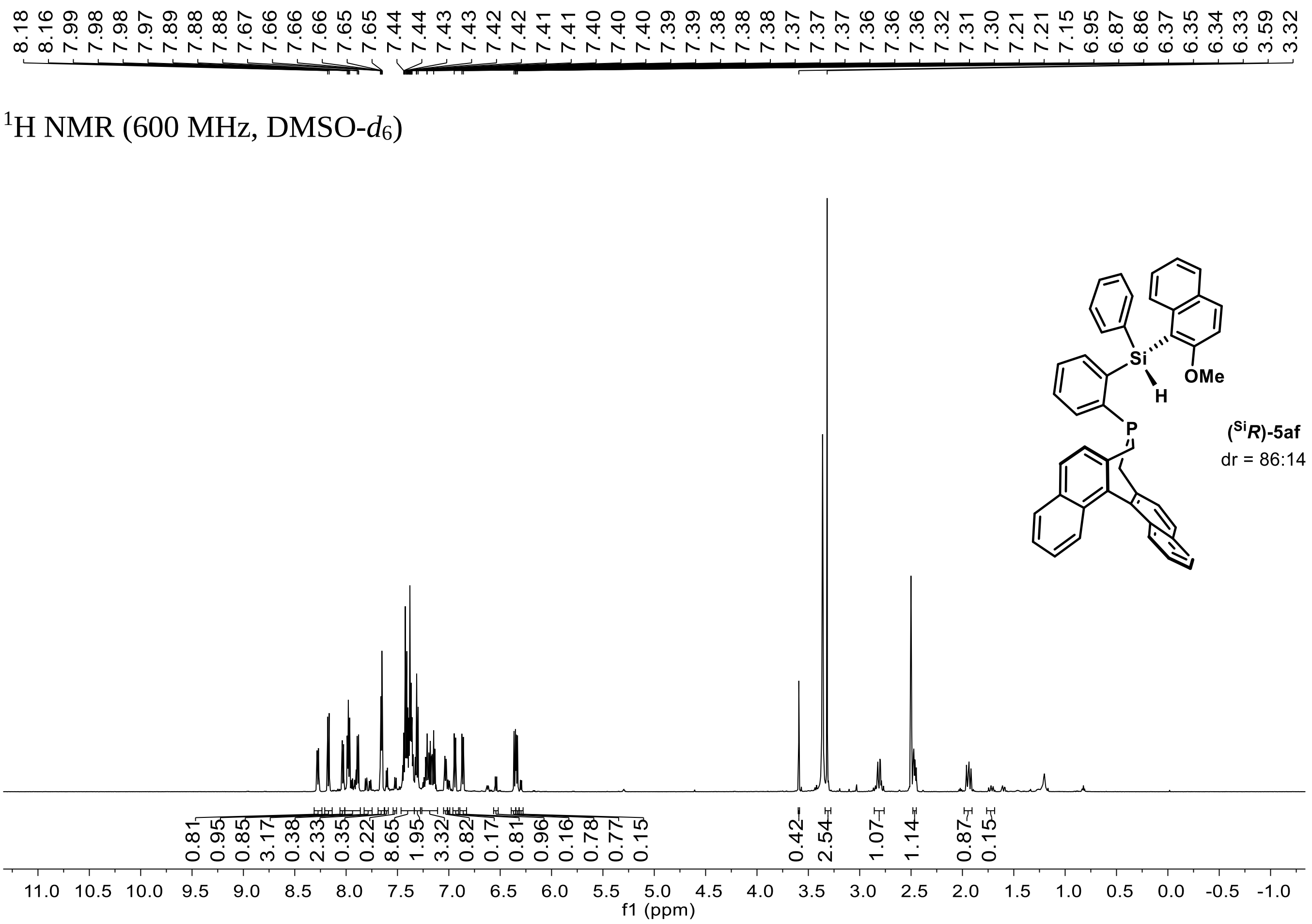
^{11}B NMR (128 MHz, 1,2-$Cl_2C_6D_4$)



^{19}F NMR (377 MHz, 1,2-$Cl_2C_6D_4$)

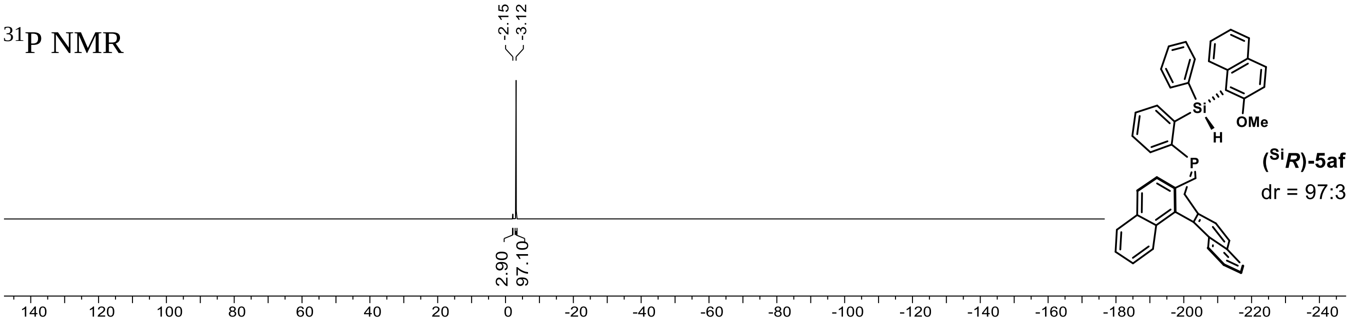


^{1}H NMR (600 MHz, DMSO-d_6)

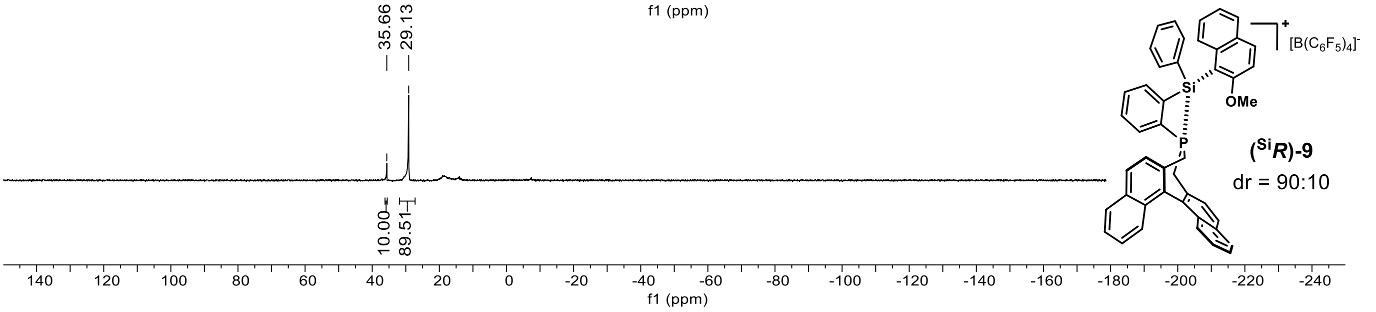


(^{Si}*R*)-5af
dr = 86:14

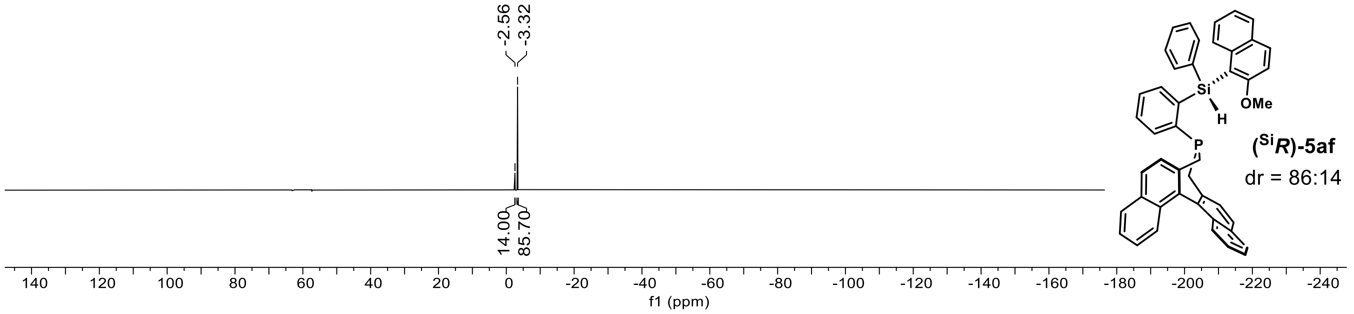
^{31}P NMR



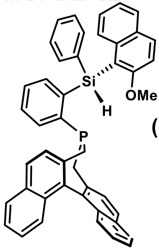
(^{Si}*R*)-5af
dr = 97:3



(^{Si}*R*)-9
dr = 90:10

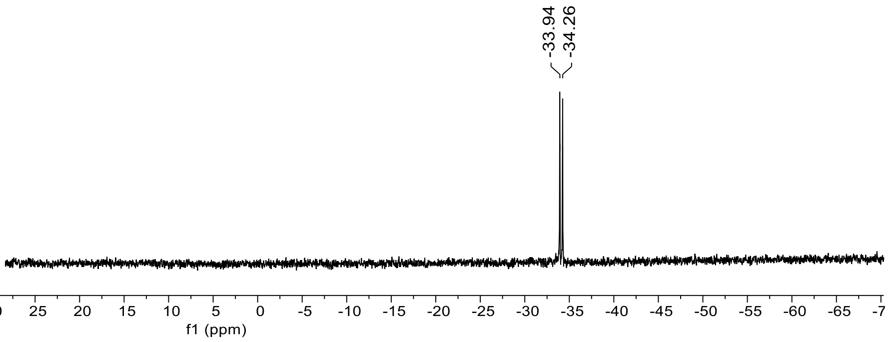


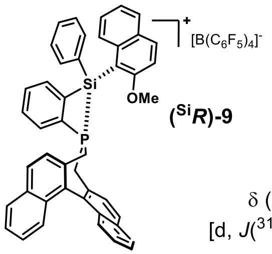
(^{Si}*R*)-5af
dr = 86:14



(^{Si}*R*)-5af

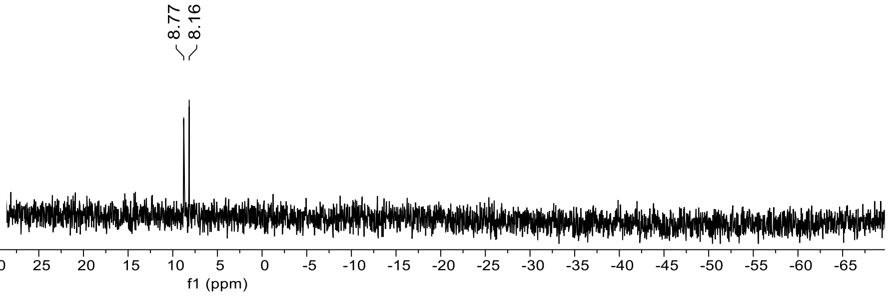
δ (^{29}Si): -34.1 ppm,
[d, *J*(^{31}P-^{29}Si) = 25.1 Hz]

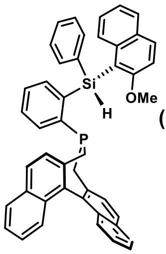




(^{Si}*R*)-9

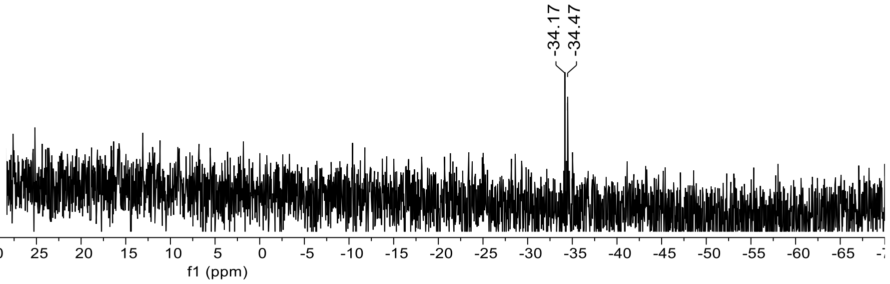
δ (^{29}Si): 8.5 ppm
[d, *J*(^{31}P-^{29}Si) = 48.7 Hz]





(^{Si}*R*)-5af

δ (^{29}Si): -34.3 ppm
[(d, *J*(^{31}P-^{29}Si)= 24.2 Hz)]



6. Single Crystal X-Ray Diffraction

Single crystal suitable for X-ray diffraction of compound **5ah** was obtained from a solution of the compound **5ah** (> 99% *de*) in dichloromethane and ethyl acetate layered with *n*-hexane. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre under reference number CCDC 2220118. Diffraction Data were collected on a BrukerD8 venture employing Cu-Kα radiation (λ = 1.54178 Å). The crystal structure was shown in **Figure S1**. The detailed information was listed in the **Tables S1**. The chiral compound of **5ah** was prepared according to general procedure D.

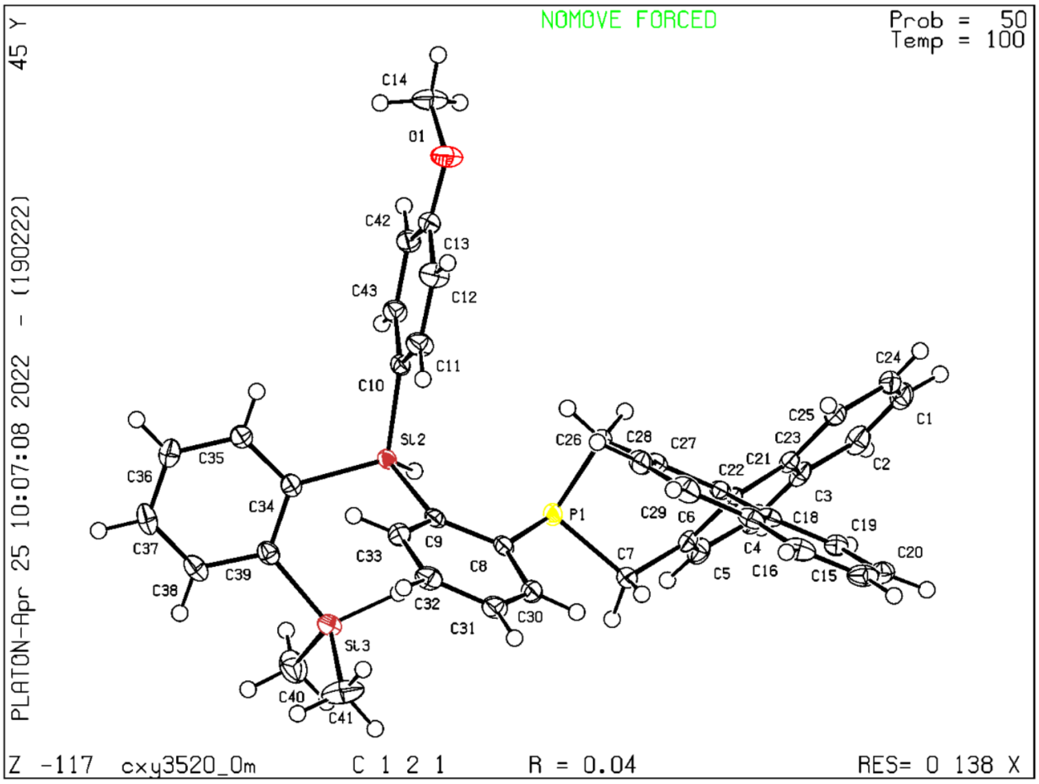


Figure S1. Crystal structure of **5ah** (CCDC 2220118).

Tables S1. Crystallographic Data and Structure Refinement for Compound 5ah

Compound	**Compound 5ah**
CCDC deposition No.	2220118
Empirical formula	$C_{43}H_{39}OPSi_2$
Formula weight	658.89
Temperature	100.0 K
Crystal system, space group	monoclinic, *C2*
Unit cell dimensions	*a* = 18.5232(6) Å alpha = 90° *b* = 8.0913(3) Å beta = 93.7850(10)° *c* = 23.4502(8) Å gamma = 90°
Volume	3507.0(2) Å^3

Z; Calculated density	4; 1.248 g/cm^3
Absorption coefficient	1.599 mm^{-1}
F(000)	1392.0
Crystal size	0.35 × 0.06 × 0.05 mm^3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	3.776 to 136.964°
Index ranges	$-22 \le h \le 20$, $-9 \le k \le 9$, $-28 \le l \le 27$
Reflections collected	26040
Independent reflections	6446 [R_{int} = 0.0408, R_{sigma} = 0.0272]
Data / restraints / parameters	6446 /1 / 427
Goodness-of-fit on F^2	1.030
Final R indices [I>=2sigma(I)]	R_1 = 0.0356, wR_2 = 0.0920
R indices (all data)	R_1 = 0.0359, wR_2 = 0.0924
Largest diff. peak/hole	0.34 and -0.28 e Å^{-3}
Flack parameter	0.017 (19)

Single crystal suitable for X-ray diffraction of compound **5aa-Rh** was obtained from a solution of the compound **5aa-Rh** (> 99% *de*) in 1 mL *n*-hexane and 0.3 mL *tert*-butyl methyl ether with a few drops of dichloromethane and isopropyl alcohol. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre under reference number CCDC 2276631. Diffraction Data were collected on a BrukerD8 venture employing Cu-Kα radiation (λ = 1.54178 Å). The crystal structure was shown in **Figure S2**. The detailed information was listed in the **Tables S2**.

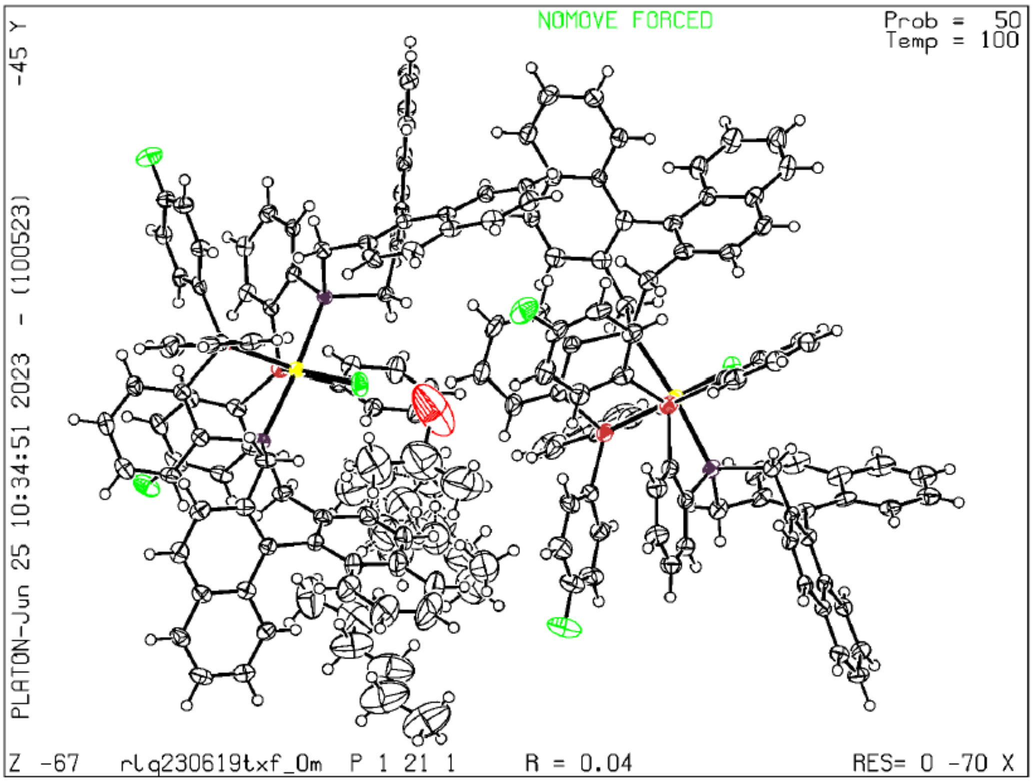


Figure S2. Crystal structure of **5aa-Rh** (CCDC 2276631).

Tables S2. Crystallographic Data and Structure Refinement for Compound 5aa-Rh

Compound	**Compound 5aa-Rh**
CCDC deposition No.	2276631
Empirical formula	$C_{175}H_{152}Cl_2F_4OP_4Rh_2Si_4$ [+ solvent]
Formula weight	2859.93
Temperature	100.0 K
Crystal system, space group	monoclinic, $P2_1$
Unit cell dimensions	a = 14.5095(9) Å alpha = 90° b = 26.0433(14) Å beta = 105.980(3)° c = 20.4814(12) Å gamma = 90°
Volume	7440.3(8) Å^3
Z; Calculated density	2; 1.277 g/cm^3
Absorption coefficient	3.296 mm^{-1}
F(000)	2972.0
Crystal size	0.36 × 0.2 × 0.03 mm^3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	0.573 to 0.753°
Index ranges	$-17 \leq h \leq 15$, $-31 \leq k \leq 31$, $-24 \leq l \leq 24$
Reflections collected	23879

Independent reflections	27045 [R_{int} = 0.0828, R_{sigma} = 0.1140]
Data / restraints / parameters	27045 / 187 / 1756
Goodness-of-fit on F^2	0.975
Final R indices [I>=2sigma(I)]	R_1 = 0.0483, wR_2 = 0.0911
R indices (all data)	R_1 = 0.0409, wR_2 = 0.0941
Largest diff. peak/hole	0.703 and - 0.485 e Å^{-3}
Flack parameter	0.016(3)

Single crystal suitable for X-ray diffraction of compound **5m-Ir** was obtained from a solution of the compound **5m-Ir** (> 99% *de*) in 1 mL *n*-hexane and 0.3 mL *tert*-butyl methyl ether with a few drops of dichloromethane. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre under reference number CCDC 2276694. Diffraction Data were collected on a BrukerD8 venture employing Cu-Kα radiation (λ = 1.54178 Å). The crystal structure was shown in **Figure S3**. The detailed information was listed in the **Tables S3**.

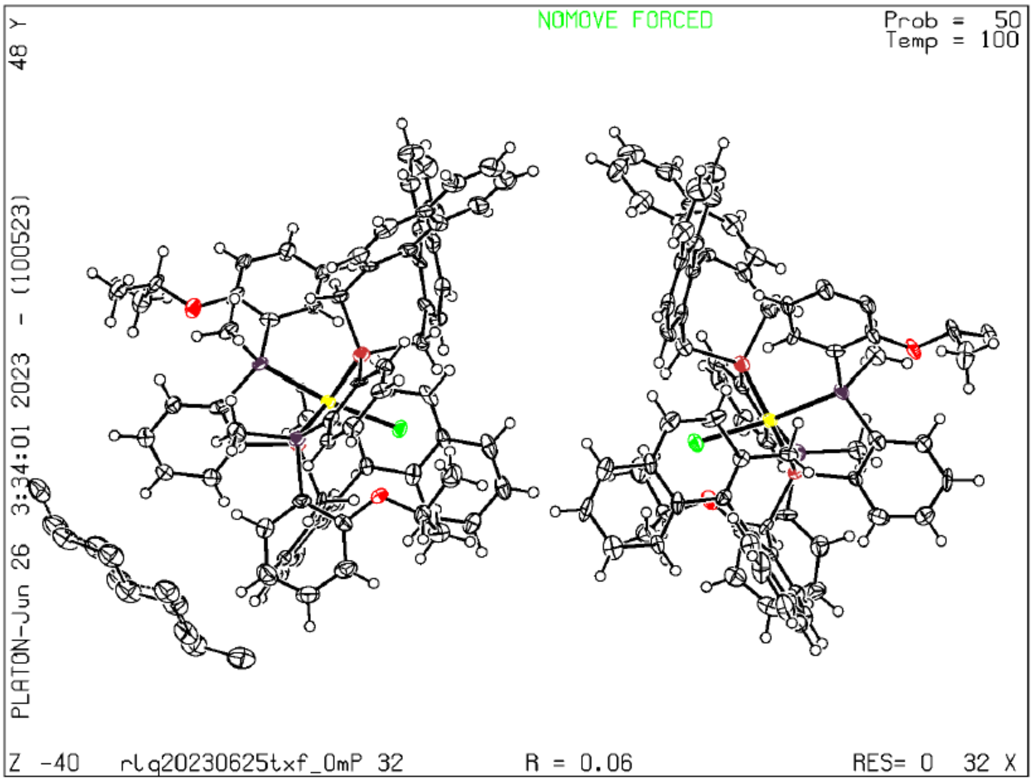


Figure S3. Crystal structure of **5m-Ir** (CCDC 2276694).

Tables S3. Crystallographic Data and Structure Refinement for Compound 5m-Ir

Compound	**Compound 5m-Ir**
CCDC deposition No.	2276694
Empirical formula	$C_{158}H_{130}Cl_2Ir_2O_4P_4Si_4$ [+ solvent]
Formula weight	2784.21

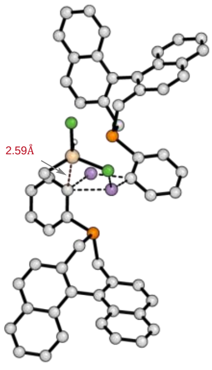
Temperature	100.0 K
Crystal system, space group	monoclinic, $P3_2$
Unit cell dimensions	a = 13.7047(5) Å alpha = 90° b = 13.7047(5) Å beta = 90° c = 62.729(3) Å gamma = 120°
Volume	10203.3(9) $Å^3$
Z; Calculated density	6; 1.359 g/cm^3
Absorption coefficient	5.298 mm^{-1}
F(000)	4242.0
Crystal size	0.12 × 0.06 × 0.04 mm^3
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	0.576 to 0.753°
Index ranges	$-15 \leq h \leq 16$, $-16 \leq k \leq 16$, $-75 \leq l \leq 75$
Reflections collected	23810
Independent reflections	24923 [R_{int} = 0.0750, R_{sigma} = 0.1013]
Data / restraints / parameters	24923 / 255 / 1634
Goodness-of-fit on F^2	1.065
Final R indices [I>=2sigma(I)]	R_1 = 0.0633, wR_2 = 0.1363
R indices (all data)	R_1 = 0.0669, wR_2 = 0.1379
Largest diff. peak/hole	1.448 and -1.602 e $Å^{-3}$
Flack parameter	0.000 (7)

7. Computational Details

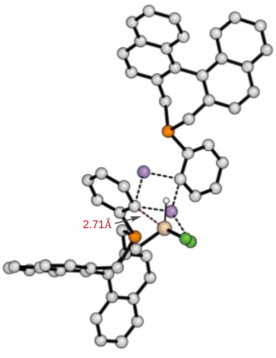
7.1 Computational methods

Density functional theory (DFT) calculations were performed with Gaussian 16 Revision C.01[8]. All geometry optimizations were performed in the gas phase using the dispersion-corrected B3LYP[9,10] functional with a basis set 6-31G(d,p)[11,12]. A manual conformational search was performed to generate by rotate key bonds and dihedral angles, the key conformational transition states were shown in below. The M06[13] functional was used with a 6-311+G(d,p)[14] basis set to calculate the single-point energies in tetrahydrofuran. Solvation effects were modeled using the SMD[15] in tetrahydrofuran solvent implicit solvation model. Automated thermochemistry for heterogeneous computational chemistry data were collected at 189.15 K (-84 °C) by GoodVibes 3.0.2.[16] PyMol[17] was employed to render the molecular graphics using our display settings.

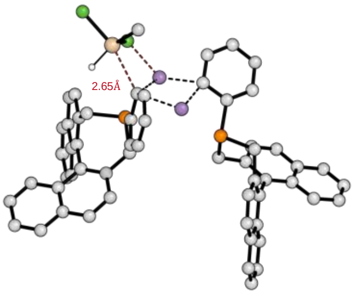
7.2 Conformational transition states of desymmetric substitution



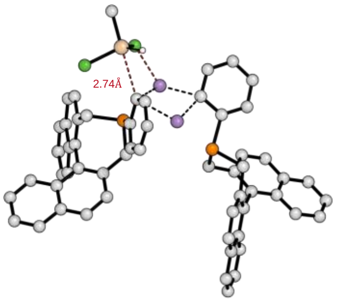
TS1_R_{si}_favored_1
$\Delta\Delta G^{\ddagger}$ = 0.0 kcal/mol



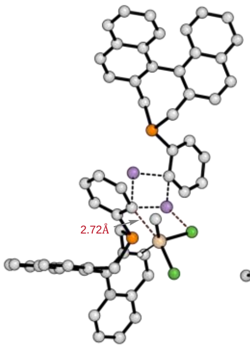
TS1_R_{si}_favored_2
$\Delta\Delta G^{\ddagger}$ = 1.0 kcal/mol



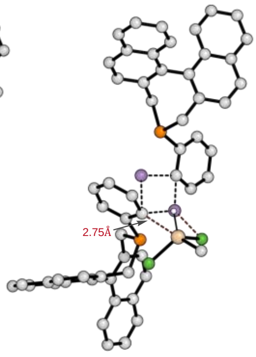
TS1_R_{si}_favored_3
$\Delta\Delta G^{\ddagger}$ = 2.7 kcal/mol



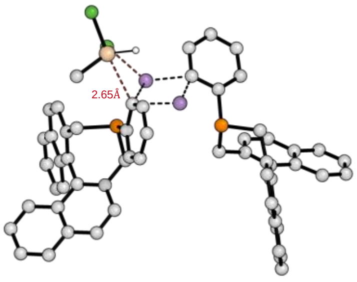
TS1_R_{si}_favored_4
$\Delta\Delta G^{\ddagger}$ = 8.7 kcal/mol



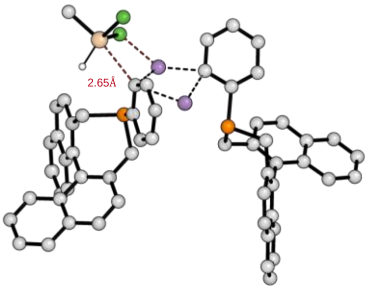
TS1_S_{si}_disfavored_1
$\Delta\Delta G^{\ddagger}$ = 2.4 kcal/mol



TS1_S_{si}_disfavored_2
$\Delta\Delta G^{\ddagger}$ = 7.8 kcal/mol



TS1_S_{si}_disfavored_3
$\Delta\Delta G^{\ddagger}$ = 2.0 kcal/mol

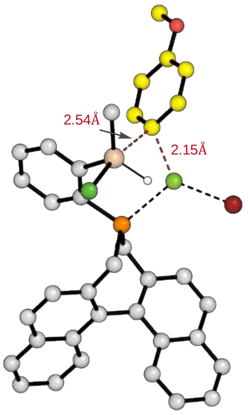


TS1_S_{si}_disfavored_4
$\Delta\Delta G^{\ddagger}$ = 10.4 kcal/mol

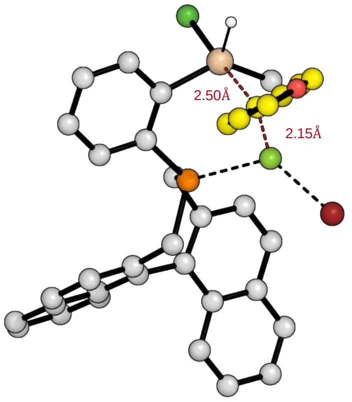
Selectivity[8]	Excess (%)	Ratio (%)	Ratio	Major Iso	ddG
	98.76	99:1	161:1	R	1.91

1. The values for stereoisomer excess (in%), ratio, major isomer present, and ddG were calculated by GoodVibes (-t 189.15 --ee *R*:*S*).

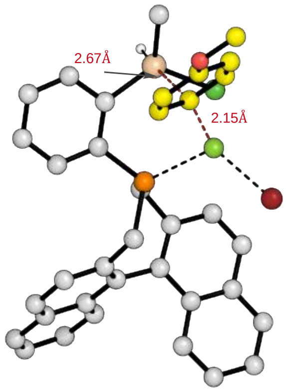
7.3 Conformational transition states of stereospecific transformation



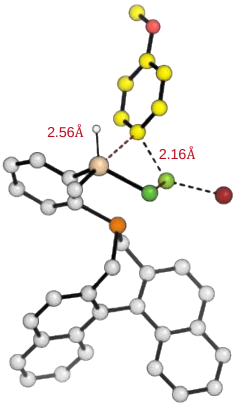
TS2_R_{si}_favored_1
ΔΔG‡ = 0.0 kcal/mol



TS2_R_{si}_favored_2
ΔΔG‡ = 4.6 kcal/mol



TS2_S_{si}_disfavored_1
ΔΔG‡ = 6.7 kcal/mol



TS2_S_{si}_disfavored_2
ΔΔG‡ = 7.4 kcal/mol

Selectivity[2]	Excess (%)	Ratio (%)	Ratio	Major Iso	ddG
	99.99	100:0	44113238:1	R	3.72

2. The values for stereoisomer excess (in%), ratio, major isomer present, and ddG were calculated by GoodVibes (-t 189.15 --ee *R*:*S*).

7.4 Absolute energies, zero-point energies

Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and Gibbs free energy (at 189.15 K) for optimized structures with THF solvent in single-point energy calculations are given below.

Structure	**E_SPC**	**E**	**ZPE**	**H_SPC**	**T.qh-S**	**G(T)_SPC**	**im freq**
TS1_R_favored_1	-4105.258	-4106.4928	0.837062	-4104.3967	0.07235	-4104.4691	-98.51
TS1_R_favored_2	-4105.2562	-4106.4926	0.836861	-4104.395	0.072532	-4104.4675	-72.3
TS1_R_favored_3	-4105.2544	-4106.4888	0.836999	-4104.3932	0.071473	-4104.4647	-96.32
TS1_R_favored_4	-4105.2447	-4106.482	0.836541	-4104.384	0.071071	-4104.4551	-108.98
TS1_S_disfavored_1	-4105.2545	-4106.4907	0.836913	-4104.3934	0.071897	-4104.4653	-86.36
TS1_S_disfavored_2	-4105.2462	-4106.4852	0.836796	-4104.3853	0.071309	-4104.4566	-103.86
TS1_S_disfavored_3	-4105.2554	-4106.4909	0.836999	-4104.3942	0.071676	-4104.4659	-90.37
TS1_S_disfavored_4	-4105.242	-4106.4785	0.83639	-4104.3814	0.071119	-4104.4525	-124.98
TS2_R_favored_1	-5330.2982	-5328.7924	0.566864	-5329.7138	0.055081	-5329.7689	-103.98
TS2_R_favored_2	-5330.2902	-5328.7813	0.566335	-5329.7064	0.055136	-5329.7615	-82.95
TS2_S_disfavored_1	-5330.2872	-5328.7843	0.56639	-5329.7034	0.054891	-5329.7583	-132.49
TS2_S_disfavored_2	-5330.2857	-5328.7834	0.565993	-5329.7023	0.054867	-5329.7571	-131.89

7.5 Cartesian coordinates of the computed structures

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TS1_R_favored_1 Eopt -4106.492787

C	-9.393228	-3.601240	0.012406
C	-9.379895	-2.405105	0.768451
C	-8.461452	-1.415373	0.500117
C	-7.500837	-1.564451	-0.540377
C	-7.501345	-2.790593	-1.285498
C	-8.470426	-3.786836	-0.990059
C	-6.523949	-0.555919	-0.843658
C	-5.554618	-0.804273	-1.814464
C	-5.568753	-2.027545	-2.534625
C	-6.520873	-2.986272	-2.291355
H	-10.126068	-4.371904	0.232140
H	-10.099048	-2.268667	1.570743
H	-8.459087	-0.507398	1.091636
H	-8.461679	-4.706513	-1.569403
H	-4.813593	-2.192963	-3.298639
H	-6.526944	-3.913033	-2.858980
C	-6.495848	0.746843	-0.100911
C	-7.554304	1.706648	-0.251657
C	-5.398786	1.047281	0.707132
C	-8.658422	1.504287	-1.128238
C	-7.495635	2.939006	0.480746
C	-5.357914	2.277780	1.415547
C	-9.652614	2.448499	-1.252033
H	-8.708211	0.591067	-1.709553
C	-8.543848	3.887561	0.337426
C	-6.379863	3.189223	1.319759
H	-4.499604	2.487365	2.047249
C	-9.602852	3.650699	-0.507213
H	-10.482249	2.270505	-1.930042
H	-8.486980	4.812084	0.906223
H	-6.339350	4.120968	1.877695
H	-10.396312	4.384855	-0.610843
C	-4.450445	0.193447	-2.065451
H	-4.842193	1.214171	-2.073835
H	-3.965556	0.012229	-3.029086
C	-4.231655	0.101157	0.806906
H	-4.567197	-0.928620	0.962035
H	-3.577824	0.359220	1.644653
C	-2.180546	1.627333	-0.768571
C	-2.759619	2.874795	-1.057457
C	-0.788965	1.462895	-0.500287
C	-1.968690	4.022192	-1.080742
H	-3.824945	2.964389	-1.251780
C	-0.040919	2.665680	-0.544306
C	-0.601536	3.916294	-0.821881
H	-2.414973	4.988588	-1.299130
H	1.038782	2.642676	-0.366977
H	0.025541	4.804859	-0.845064
P	-3.132569	0.047570	-0.730801
Li	0.685565	0.622143	0.792372

C	9.268857	3.809147	1.074092
C	9.452276	2.417195	1.251406
C	8.519722	1.520740	0.780411
C	7.347644	1.964588	0.104524
C	7.153753	3.377953	-0.049044
C	8.141415	4.275076	0.439516
C	6.350140	1.059660	-0.393970
C	5.184454	1.565167	-0.967735
C	5.008951	2.967017	-1.103080
C	5.969481	3.848217	-0.671763
H	10.014531	4.504786	1.447235
H	10.335962	2.053325	1.767342
H	8.670847	0.457908	0.928829
H	7.982501	5.342300	0.308613
H	4.098656	3.338039	-1.566364
H	5.827363	4.918935	-0.791239
C	6.511865	-0.425956	-0.265797
C	7.526786	-1.127248	-1.001906
C	5.624271	-1.139058	0.540967
C	8.408243	-0.474489	-1.910413
C	7.650215	-2.548745	-0.850564
C	5.759697	-2.547114	0.667876
C	9.366244	-1.179059	-2.603921
H	8.314416	0.595008	-2.057737
C	8.656784	-3.243726	-1.573707
C	6.749832	-3.230797	0.006978
H	5.067698	-3.082793	1.311623
C	9.500631	-2.577152	-2.430743
H	10.024112	-0.657495	-3.292935
H	8.741441	-4.319164	-1.440498
H	6.848096	-4.306707	0.124778
H	10.264015	-3.119580	-2.980495
C	4.078695	0.629661	-1.395299
H	4.495678	-0.246959	-1.897084
H	3.390282	1.121625	-2.088493
C	4.493093	-0.438821	1.246006
H	4.835169	0.478172	1.734731
H	4.050110	-1.069281	2.021207
C	2.189626	-1.440357	-0.388475
C	2.638247	-2.277818	-1.422464
C	0.955166	-1.675012	0.298121
C	1.865197	-3.359441	-1.851929
H	3.591589	-2.095668	-1.909319
C	0.220972	-2.786568	-0.178889
C	0.641562	-3.607837	-1.236379
H	2.218900	-3.996016	-2.657999
H	-0.725846	-3.046674	0.302890
H	0.022699	-4.440644	-1.561803
P	3.081603	0.106705	0.110994
Li	-0.749116	-0.674073	-0.746768
Si	0.137378	-1.684795	2.751938
Cl	0.761580	0.332876	3.132505
H	-1.090418	-1.765680	1.947193
Cl	-0.878891	-2.023261	4.640391
C	1.515766	-2.947239	2.965194
H	2.354606	-2.786007	2.289861

H	1.850890	-2.926886	4.005424
H	1.099848	-3.941059	2.766834

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C	-9.355757	-2.911032	-1.897383
C	-9.484845	-1.668050	-1.233302
C	-8.382607	-0.874383	-1.009061
C	-7.085440	-1.278136	-1.435736
C	-6.956337	-2.551254	-2.084891
C	-8.116281	-3.340497	-2.309974
C	-5.912335	-0.480312	-1.213658
C	-4.661200	-0.975132	-1.579044
C	-4.554511	-2.240802	-2.212390
C	-5.668149	-3.000720	-2.472268
H	-10.234276	-3.525192	-2.071214
H	-10.462860	-1.339159	-0.894403
H	-8.495950	0.072360	-0.493910
H	-8.001964	-4.299040	-2.809484
H	-3.569964	-2.600463	-2.498780
H	-5.573831	-3.963555	-2.967251
C	-5.995395	0.860509	-0.546762
C	-6.636861	1.972076	-1.192224
C	-5.388356	1.038558	0.697061
C	-7.198922	1.883864	-2.497898
C	-6.694802	3.238569	-0.520255
C	-5.449718	2.304153	1.338881
C	-7.802154	2.971122	-3.088806
H	-7.142963	0.942654	-3.032036
C	-7.333910	4.337723	-1.154709
C	-6.095113	3.367765	0.758428
H	-4.981923	2.419296	2.312646
C	-7.879757	4.210698	-2.410444
H	-8.220716	2.877768	-4.086632
H	-7.376252	5.287333	-0.627474
H	-6.144491	4.326199	1.268465
H	-8.363042	5.058701	-2.886430
C	-3.409285	-0.195745	-1.254163
H	-3.561609	0.866716	-1.460283
H	-2.562644	-0.542993	-1.853583
C	-4.626802	-0.084260	1.349295
H	-5.182482	-1.025067	1.297755
H	-4.439579	0.120077	2.406429
C	-1.859881	0.973270	1.006562
C	-1.862791	2.194447	0.303724
C	-0.931111	0.701017	2.065053
C	-0.935303	3.194438	0.613601
H	-2.581599	2.378562	-0.488914
C	-0.032020	1.757749	2.339151
C	-0.014547	2.974022	1.638958
H	-0.936436	4.129976	0.061595
H	0.713988	1.628761	3.124779
H	0.721390	3.735959	1.883693
P	-2.950565	-0.462445	0.552261
Li	0.465612	0.530422	0.269574
C	8.890720	4.036658	0.401583
C	9.101519	2.674508	0.721945

C	8.209161	1.710414	0.310282
C	7.051860	2.052414	-0.445678
C	6.829004	3.438054	-0.744043
C	7.775905	4.406125	-0.313771
C	6.096360	1.074185	-0.885645
C	4.938518	1.487577	-1.543221
C	4.734392	2.864624	-1.821723
C	5.656512	3.811179	-1.449431
H	9.605223	4.786168	0.728668
H	9.974406	2.387724	1.301028
H	8.380791	0.671885	0.567926
H	7.595906	5.450495	-0.555507
H	3.832534	3.162432	-2.350187
H	5.492895	4.860451	-1.680541
C	6.295750	-0.386334	-0.608718
C	7.357792	-1.120325	-1.239267
C	5.402361	-1.047983	0.234417
C	8.250430	-0.529434	-2.178665
C	7.520129	-2.515095	-0.944545
C	5.576804	-2.431735	0.503617
C	9.254511	-1.264545	-2.767478
H	8.128325	0.516506	-2.434553
C	8.573266	-3.241931	-1.562288
C	6.611133	-3.141316	-0.054029
H	4.875182	-2.926116	1.169243
C	9.426357	-2.633475	-2.452792
H	9.919843	-0.790186	-3.482995
H	8.686192	-4.295757	-1.321092
H	6.737775	-4.196917	0.171228
H	10.225479	-3.200324	-2.921143
C	3.866981	0.489072	-1.906631
H	4.307249	-0.428251	-2.306666
H	3.189561	0.894490	-2.663777
C	4.225672	-0.323513	0.832937
H	4.527385	0.639974	1.254796
H	3.768237	-0.904523	1.638877
C	1.979310	-1.515537	-0.761742
C	2.566580	-2.549588	-1.510978
C	0.652831	-1.589494	-0.240737
C	1.853789	-3.719903	-1.765463
H	3.581117	-2.457480	-1.889234
C	-0.017798	-2.802265	-0.541535
C	0.553487	-3.846448	-1.275936
H	2.307727	-4.522555	-2.340302
H	-1.049790	-2.953550	-0.208475
H	-0.015922	-4.752028	-1.473388
P	2.835757	0.073734	-0.388451
Li	-0.689733	-1.421135	1.431406
Si	-0.790361	-0.639611	4.410741
Cl	-1.253347	-2.505805	3.475734
Cl	-0.321970	-1.366372	6.383384
C	-2.288903	0.414122	4.819483
H	-1.933585	1.348953	5.267190
H	-2.888214	0.657562	3.944601
H	-2.895666	-0.104623	5.566428
H	0.563031	-0.186841	4.071232

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C	5.231502	-3.978597	4.613697
C	4.593530	-4.645344	3.541351
C	4.282146	-3.971780	2.381528
C	4.589431	-2.590124	2.225835
C	5.210457	-1.912618	3.327483
C	5.528833	-2.640260	4.505468
C	4.273085	-1.851169	1.033546
C	4.516704	-0.480206	0.988526
C	5.124463	0.172870	2.093659
C	5.477363	-0.523281	3.222253
H	5.476132	-4.522950	5.520945
H	4.344348	-5.698308	3.635253
H	3.788276	-4.496328	1.572134
H	6.006697	-2.112392	5.326671
H	5.313798	1.240637	2.029396
H	5.953085	-0.013987	4.056010
C	3.645275	-2.531703	-0.145930
C	4.374130	-3.522770	-0.891134
C	2.350634	-2.188810	-0.536406
C	5.735922	-3.837872	-0.619403
C	3.730505	-4.209121	-1.973481
C	1.728646	-2.896433	-1.600901
C	6.408747	-4.786082	-1.356656
H	6.248666	-3.311909	0.177154
C	4.449518	-5.190837	-2.706920
C	2.387574	-3.883678	-2.290286
H	0.698373	-2.659126	-1.853746
C	5.760298	-5.478082	-2.406820
H	7.449030	-5.002840	-1.132455
H	3.942556	-5.706117	-3.518664
H	1.889253	-4.421601	-3.092398
H	6.301838	-6.227046	-2.976891
C	4.070826	0.337359	-0.196208
H	4.245950	-0.185582	-1.140656
H	4.589951	1.297673	-0.233517
C	1.588444	-1.084547	0.157324
H	1.594306	-1.242152	1.241042
H	0.538256	-1.079915	-0.150935
C	1.757350	1.328589	-1.703751
C	1.315304	0.498634	-2.752599
C	1.779334	2.758044	-1.808531
C	0.832906	1.051798	-3.939971
H	1.341322	-0.580703	-2.648074
C	1.285694	3.255917	-3.041413
C	0.808203	2.440504	-4.080260
H	0.480379	0.407672	-4.740264
H	1.255700	4.330259	-3.211040
H	0.427158	2.889922	-4.994395
P	2.228764	0.688557	-0.028253
Li	-0.478359	2.605705	-1.557575
C	-6.096473	-4.638264	-2.263613
C	-6.011105	-4.425931	-0.867073
C	-5.708882	-3.180738	-0.363673
C	-5.473043	-2.074018	-1.228206

C	-5.534606	-2.301225	-2.643604
C	-5.860023	-3.596298	-3.129355
C	-5.148863	-0.763286	-0.738453
C	-4.841902	0.254556	-1.640710
C	-4.901958	0.006019	-3.037121
C	-5.252400	-1.227907	-3.526709
H	-6.340851	-5.624491	-2.646885
H	-6.183316	-5.254405	-0.186264
H	-5.642322	-3.033977	0.708002
H	-5.911033	-3.749050	-4.204349
H	-4.674818	0.818286	-3.722564
H	-5.306559	-1.400031	-4.598429
C	-5.084810	-0.475272	0.731954
C	-6.270317	-0.494840	1.543083
C	-3.860192	-0.129013	1.303841
C	-7.564963	-0.753589	1.008875
C	-6.166801	-0.212954	2.946120
C	-3.783707	0.158163	2.692683
C	-8.680497	-0.759550	1.815575
H	-7.668010	-0.942646	-0.053210
C	-7.336969	-0.237207	3.751830
C	-4.897184	0.102932	3.493575
H	-2.819858	0.420761	3.119087
C	-8.568815	-0.507163	3.203521
H	-9.656712	-0.956746	1.382298
H	-7.238838	-0.028862	4.814097
H	-4.820454	0.314594	4.556753
H	-9.456486	-0.519261	3.828919

C	-4.385899	1.604915	-1.144004
H	-4.983910	1.925251	-0.286726
H	-4.482251	2.365631	-1.924093
C	-2.621200	-0.009366	0.456793
H	-2.520929	-0.863486	-0.219946
H	-1.719785	0.031539	1.074997
C	-2.265125	2.959061	0.471085
C	-3.241505	3.517357	1.313364
C	-0.938098	3.471792	0.372811
C	-2.927033	4.618695	2.107788
H	-4.242625	3.097880	1.365687
C	-0.685704	4.593155	1.201691
C	-1.641840	5.159801	2.050469
H	-3.678216	5.051738	2.762744
H	0.296111	5.076108	1.188415
H	-1.389883	6.026414	2.657526
P	-2.572144	1.527771	-0.647809
Li	1.173836	3.068159	0.316775
Si	3.663237	4.445446	-1.003228
Cl	3.240828	4.066679	1.063054
H	4.258410	3.321510	-1.733680
Cl	5.519136	5.528137	-0.744026
C	2.579576	5.854965	-1.605554
H	1.513318	5.648325	-1.505342
H	2.836297	6.734760	-1.009570
H	2.808299	6.089148	-2.649887

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C	4.925712	-4.136334	4.647618
C	4.271222	-4.742131	3.549379
C	4.017298	-4.025864	2.401188
C	4.402109	-2.659914	2.283390
C	5.039562	-2.043171	3.411060
C	5.297193	-2.814127	4.576256
C	4.147323	-1.877549	1.104114
C	4.465675	-0.521194	1.094826
C	5.088107	0.071150	2.225821
C	5.382821	-0.668343	3.343449
H	5.124384	-4.714023	5.545462
H	3.963314	-5.781695	3.613940
H	3.509688	-4.503619	1.571591
H	5.788491	-2.332275	5.417643
H	5.336002	1.128233	2.189626
H	5.870085	-0.205120	4.197276
C	3.501536	-2.494153	-0.100361
C	4.184281	-3.507687	-0.858541
C	2.234817	-2.068068	-0.500728
C	5.521394	-3.906926	-0.574959
C	3.519755	-4.130376	-1.966440
C	1.590324	-2.714299	-1.590548
C	6.150571	-4.874747	-1.325143
H	6.050702	-3.429839	0.241330
C	4.193110	-5.134296	-2.713048
C	2.202623	-3.721266	-2.294220
H	0.578554	-2.414124	-1.851189
C	5.480403	-5.503500	-2.401146
H	7.173130	-5.156141	-1.091255
H	3.670419	-5.600267	-3.544405
H	1.686889	-4.211017	-3.115956
H	5.987226	-6.268757	-2.981457
C	4.089358	0.346831	-0.077527
H	4.247722	-0.165813	-1.030366
H	4.660378	1.276573	-0.091816
C	1.527019	-0.938112	0.208584
H	1.511001	-1.119019	1.288542
H	0.482649	-0.868452	-0.110813
C	1.847901	1.500845	-1.595835
C	1.310021	0.734123	-2.650581
C	1.974985	2.923748	-1.674554
C	0.831392	1.358374	-3.805365
H	1.249919	-0.345926	-2.573553
C	1.498716	3.493525	-2.875629
C	0.915887	2.750601	-3.914033
H	0.395998	0.766830	-4.605344
H	1.556124	4.575299	-3.008391
H	0.535890	3.251467	-4.801488
P	2.269036	0.800668	0.069412
Li	-0.336414	2.601793	-1.613523
C	-5.868138	-4.779541	-2.084475
C	-5.857467	-4.475765	-0.702340
C	-5.592069	-3.197024	-0.266832
C	-5.320458	-2.146175	-1.188717
C	-5.305848	-2.465883	-2.587422
C	-5.595072	-3.793463	-3.003287

C	-5.033308	-0.802663	-0.769925
C	-4.687146	0.157833	-1.719696
C	-4.671360	-0.182223	-3.097963
C	-4.985921	-1.449255	-3.523174
H	-6.084094	-5.791396	-2.414342
H	-6.058019	-5.260130	0.021615
H	-5.582369	-2.980070	0.794920
H	-5.588392	-4.016462	-4.067162
H	-4.414572	0.586229	-3.822391
H	-4.982221	-1.691468	-4.582674
C	-5.049875	-0.417767	0.679466
C	-6.276644	-0.398132	1.426776
C	-3.860400	-0.018636	1.290028
C	-7.538693	-0.708583	0.844245
C	-6.250574	-0.021848	2.811126
C	-3.860990	0.362001	2.658426
C	-8.695445	-0.675171	1.589938
H	-7.583256	-0.969501	-0.206612
C	-7.461613	-0.007437	3.554216
C	-5.014887	0.346445	3.401729
H	-2.923633	0.665008	3.115937
C	-8.660062	-0.329336	2.961690
H	-9.645351	-0.913507	1.120330
H	-7.421936	0.272641	4.603737
H	-4.996844	0.629960	4.450723
H	-9.579542	-0.311188	3.539191
C	-4.268235	1.542247	-1.289496
H	-4.911987	1.909955	-0.486109

H	-4.331414	2.249826	-2.121342
C	-2.578934	0.058317	0.503753
H	-2.436190	-0.839571	-0.105333
H	-1.712810	0.150578	1.165274
C	-2.245980	3.024054	0.332439
C	-3.271536	3.620501	1.085574
C	-0.924735	3.555170	0.259115
C	-3.016412	4.783142	1.810960
H	-4.266455	3.184782	1.121434
C	-0.735465	4.741569	1.011163
C	-1.741039	5.348085	1.770734
H	-3.806006	5.245664	2.397072
H	0.234969	5.246717	1.003195
H	-1.535073	6.263813	2.320587
P	-2.479002	1.517466	-0.701853
Li	1.201648	3.193677	0.373630
Si	3.678478	4.866461	-0.777577
Cl	3.145317	4.331450	1.242079
H	2.596644	5.483476	-1.568034
C	4.813772	6.318496	-0.359765
H	5.207715	6.752179	-1.285925
H	4.250331	7.096327	0.167737
H	5.661801	6.025207	0.265233
Cl	5.045610	3.593439	-1.744784

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C	-9.222265	-0.462242	-3.413849
C	-9.316155	0.164858	-2.148702

C	-8.180994	0.507403	-1.449314
C	-6.884296	0.242025	-1.974544
C	-6.794979	-0.417976	-3.245530
C	-7.986683	-0.748017	-3.945480
C	-5.678401	0.579034	-1.271716
C	-4.443144	0.211763	-1.803471
C	-4.377218	-0.448305	-3.058250
C	-5.516210	-0.741479	-3.766694
H	-10.125921	-0.723637	-3.956352
H	-10.293642	0.374216	-1.724163
H	-8.268484	0.981400	-0.478636
H	-7.901252	-1.241445	-4.910177
H	-3.402273	-0.713801	-3.457876
H	-5.451708	-1.237973	-4.731229
C	-5.717370	1.278208	0.054523
C	-6.170285	2.637156	0.163561
C	-5.252087	0.610406	1.188097
C	-6.573338	3.406600	-0.965208
C	-6.194304	3.270325	1.451031
C	-5.276999	1.260606	2.450941
C	-6.997281	4.708848	-0.825247
H	-6.538447	2.954303	-1.949331
C	-6.647604	4.612530	1.561390
C	-5.747047	2.543729	2.583945
H	-4.924701	0.718210	3.323873
C	-7.044196	5.319486	0.450570
H	-7.296736	5.274410	-1.702778
H	-6.667764	5.073355	2.545677
H	-5.772356	3.022020	3.559578
H	-7.385968	6.345722	0.547092
C	-3.174168	0.463225	-1.025469
H	-3.201595	1.455650	-0.568585
H	-2.295527	0.408876	-1.674730
C	-4.682897	-0.779302	1.086142
H	-5.314681	-1.424113	0.468462
H	-4.603577	-1.250804	2.068640
C	-1.808111	-0.130040	1.544747
C	-1.681058	1.260990	1.735204
C	-0.960100	-1.075744	2.210544
C	-0.695146	1.775265	2.585730
H	-2.339854	1.955162	1.222767
C	0.008492	-0.492850	3.063862
C	0.154439	0.890802	3.253793
H	-0.593915	2.848450	2.718935
H	0.710223	-1.134418	3.592008
H	0.938805	1.274594	3.901245
P	-2.964391	-0.873305	0.287302
Li	0.448362	0.096573	0.739577
C	8.949188	2.676861	2.919007
C	9.146956	1.448941	2.243967
C	8.228904	0.999048	1.321988
C	7.057516	1.750958	1.021436
C	6.848803	2.981817	1.728630
C	7.821837	3.422486	2.665633
C	6.075570	1.309193	0.070692
C	4.907772	2.049233	-0.109859

C	4.718338	3.260718	0.605577
C	5.664485	3.723561	1.486251
H	9.683925	3.022168	3.640244
H	10.030512	0.854672	2.457765
H	8.391145	0.054285	0.816497
H	7.652180	4.361417	3.186363
H	3.808297	3.830340	0.436260
H	5.511614	4.659317	2.017428
C	6.258061	0.036531	-0.701610
C	7.290492	-0.085665	-1.693196
C	5.375178	-1.022408	-0.487025
C	8.169319	0.984533	-2.026080
C	7.435392	-1.320687	-2.408999
C	5.531020	-2.231660	-1.215685
C	9.144879	0.833414	-2.985603
H	8.059408	1.934008	-1.515409
C	8.459429	-1.446150	-3.386070
C	6.537869	-2.384345	-2.136156
H	4.837169	-3.046231	-1.029074
C	9.300298	-0.395662	-3.669537
H	9.800092	1.666591	-3.222543
H	8.559580	-2.391590	-3.912939
H	6.650628	-3.320033	-2.677313
H	10.076976	-0.502477	-4.420943
C	3.812187	1.540937	-1.014823
H	4.229594	1.126128	-1.936186
H	3.123105	2.344593	-1.290270
C	4.227537	-0.885641	0.477977
H	4.556597	-0.445461	1.424197
H	3.780955	-1.857820	0.705849
C	1.930759	-0.737921	-1.436770
C	2.465392	-0.971586	-2.715329
C	0.641943	-1.200329	-1.036457
C	1.735423	-1.695123	-3.656892
H	3.452704	-0.605072	-2.983206
C	-0.047020	-1.926787	-2.041180
C	0.471654	-2.177495	-3.315816
H	2.148707	-1.879939	-4.644697
H	-1.053187	-2.312507	-1.845814
H	-0.110282	-2.739845	-4.042715
P	2.811933	0.215830	-0.128507
Li	-0.602510	-2.226746	0.377339
Si	-1.839025	-3.545322	2.951767
Cl	-1.100793	-4.397313	1.129643
Cl	-2.970516	-5.246061	3.647388
C	-0.484527	-3.464383	4.245250
H	0.480113	-3.222336	3.796516
H	-0.722524	-2.701970	4.992958
H	-0.415088	-4.433480	4.743713
H	-2.986433	-2.648623	2.802384

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C	-9.469113	-3.017546	-1.437087
C	-9.540553	-1.709114	-0.902587
C	-8.410925	-0.928435	-0.804818
C	-7.142468	-1.411235	-1.235726

C	-7.071064	-2.748256	-1.751677
C	-8.258302	-3.522973	-1.848753
C	-5.942745	-0.627698	-1.143228
C	-4.719672	-1.194026	-1.500459
C	-4.669636	-2.521344	-2.000302
C	-5.810930	-3.272303	-2.137436
H	-10.368823	-3.621034	-1.512226
H	-10.495565	-1.318931	-0.563035
H	-8.479313	0.069485	-0.387691
H	-8.187935	-4.531209	-2.248776
H	-3.706560	-2.937144	-2.283872
H	-5.760081	-4.283771	-2.531643
C	-5.964928	0.777815	-0.620242
C	-6.604130	1.833811	-1.355264
C	-5.299116	1.067899	0.571215
C	-7.226127	1.625655	-2.619509
C	-6.596402	3.165913	-0.821942
C	-5.293827	2.396520	1.074009
C	-7.825220	2.662602	-3.298695
H	-7.220023	0.631681	-3.051274
C	-7.232835	4.211025	-1.544210
C	-5.934789	3.411753	0.408435
H	-4.776368	2.597367	2.007645
C	-7.838108	3.969086	-2.755153
H	-8.290507	2.476948	-4.262416
H	-7.224829	5.212289	-1.121071
H	-5.932961	4.420919	0.812039
H	-8.318679	4.776930	-3.299043

C	-3.437794	-0.418750	-1.308604
H	-3.582281	0.620273	-1.615751
H	-2.626063	-0.844534	-1.905670
C	-4.543589	-0.000886	1.314123
H	-5.125015	-0.924619	1.385781
H	-4.296095	0.312191	2.330148
C	-1.779219	0.940064	0.765129
C	-1.645990	1.992227	-0.163400
C	-0.937615	0.833331	1.920011
C	-0.670181	2.980208	0.015717
H	-2.288682	2.050691	-1.036162
C	0.003668	1.875711	2.060662
C	0.155929	2.924530	1.140600
H	-0.563369	3.779791	-0.711572
H	0.681139	1.866306	2.915938
H	0.926389	3.676924	1.288437
P	-2.915537	-0.506986	0.498086
Li	0.515097	0.539698	0.098967
C	8.939762	4.096800	0.103265
C	9.139962	2.793255	0.616345
C	8.270379	1.773620	0.300959
C	7.147829	1.998045	-0.546020
C	6.934695	3.327683	-1.041313
C	7.857743	4.354373	-0.705435
C	6.216745	0.959913	-0.890511
C	5.089108	1.268157	-1.650461
C	4.894276	2.592145	-2.124474
C	5.795035	3.589546	-1.843882

H	9.636211	4.890694	0.356214
H	9.986530	2.596467	1.267632
H	8.433385	0.781570	0.705541
H	7.685783	5.354092	-1.096012
H	4.017193	2.806106	-2.729621
H	5.639032	4.595660	-2.224106
C	6.407194	-0.447231	-0.407640
C	7.499045	-1.251044	-0.883043
C	5.476422	-0.995718	0.475478
C	8.433798	-0.785388	-1.851508
C	7.650018	-2.591847	-0.395075
C	5.640344	-2.329317	0.936275
C	9.465897	-1.585007	-2.288139
H	8.321775	0.215194	-2.252304
C	8.732415	-3.386822	-0.859230
C	6.700836	-3.099516	0.528358
H	4.908231	-2.735421	1.628302
C	9.625370	-2.897372	-1.783378
H	10.163139	-1.206270	-3.029807
H	8.835656	-4.397554	-0.472841
H	6.817955	-4.114424	0.899019
H	10.446615	-3.515800	-2.133221
C	4.038966	0.219175	-1.921899
H	4.501239	-0.739877	-2.170518
H	3.397632	0.509875	-2.758985
C	4.271962	-0.206520	0.914866
H	4.551942	0.808015	1.214489
H	3.778989	-0.676406	1.770813

C	2.107223	-1.626128	-0.598196
C	2.724748	-2.740770	-1.190998
C	0.766518	-1.646892	-0.110803
C	2.028755	-3.942024	-1.315343
H	3.749526	-2.686656	-1.548577
C	0.114534	-2.895963	-0.274418
C	0.714828	-4.019034	-0.853182
H	2.505832	-4.806051	-1.769985
H	-0.926908	-3.015148	0.042471
H	0.157029	-4.947718	-0.952239
P	2.936119	0.009245	-0.410567
Li	-0.628776	-1.309684	1.486319
Si	-1.004033	-0.196170	4.465927
Cl	-1.196931	-2.168666	3.620626
H	0.297497	0.453063	4.221550
Cl	-2.738643	0.998953	4.521094
C	-0.915139	-0.714288	6.281238
H	-0.045301	-1.360330	6.444591
H	-0.802555	0.175389	6.911098
H	-1.808817	-1.251917	6.609948

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C	5.570375	-3.900616	4.501946
C	4.931290	-4.586243	3.442207
C	4.562928	-3.919257	2.295389
C	4.811101	-2.525623	2.140899
C	5.433743	-1.830146	3.230402
C	5.811575	-2.550964	4.394936

C	4.434245	-1.793551	0.962167
C	4.623072	-0.413880	0.918958
C	5.233306	0.256477	2.012278
C	5.642513	-0.430789	3.127314
H	5.860022	-4.439859	5.398906
H	4.726586	-5.648764	3.535704
H	4.069054	-4.458489	1.495725
H	6.289437	-2.009126	5.206974
H	5.379075	1.331299	1.949958
H	6.118789	0.092588	3.951982
C	3.799608	-2.490753	-0.203805
C	4.543687	-3.447872	-0.977589
C	2.482584	-2.193525	-0.554613
C	5.922955	-3.715213	-0.745762
C	3.895998	-4.148026	-2.048642
C	1.858246	-2.912513	-1.610110
C	6.609357	-4.631998	-1.509812
H	6.437734	-3.178008	0.041974
C	4.629935	-5.096446	-2.810536
C	2.534183	-3.868428	-2.326799
H	0.815081	-2.706814	-1.835676
C	5.958009	-5.338202	-2.548660
H	7.662450	-4.812902	-1.315564
H	4.120048	-5.623035	-3.613122
H	2.034791	-4.415997	-3.121687
H	6.510522	-6.062131	-3.140120
C	4.114365	0.392624	-0.248291
H	4.288860	-0.116497	-1.200683
H	4.591521	1.374798	-0.286295
C	1.700244	-1.124118	0.170165
H	1.746098	-1.286332	1.252180
H	0.642172	-1.157464	-0.107503
C	1.704063	1.296960	-1.684741
C	1.367520	0.463281	-2.766205
C	1.560721	2.719544	-1.742044
C	0.820510	1.003057	-3.932250
H	1.525672	-0.608805	-2.706620
C	1.005530	3.204778	-2.950337
C	0.622815	2.380525	-4.020313
H	0.551277	0.352849	-4.759767
H	0.873144	4.282701	-3.078600
H	0.189600	2.814190	-4.918710
P	2.265215	0.672089	-0.032691
Li	-0.628187	2.843630	-1.236947
C	-6.314494	-4.159045	-2.936717
C	-6.128319	-4.222809	-1.535309
C	-5.781108	-3.097950	-0.821540
C	-5.598629	-1.842327	-1.468063
C	-5.762240	-1.789419	-2.892532
C	-6.131738	-2.966735	-3.597125
C	-5.230243	-0.650294	-0.756388
C	-4.979878	0.525764	-1.462392
C	-5.140496	0.553893	-2.872631
C	-5.534698	-0.562824	-3.567222
H	-6.593537	-5.052919	-3.486633
H	-6.258497	-5.169200	-1.018623

H	-5.637455	-3.162744	0.250670
H	-6.260142	-2.907033	-4.674848
H	-4.955507	1.485447	-3.400965
H	-5.665713	-0.522951	-4.645347
C	-5.060496	-0.654475	0.733711
C	-6.186103	-0.840363	1.606881
C	-3.796255	-0.418399	1.274651
C	-7.516978	-0.998270	1.124960
C	-5.982132	-0.837759	3.027115
C	-3.620318	-0.407922	2.683969
C	-8.572957	-1.169526	1.991441
H	-7.695906	-0.976429	0.056380
C	-7.092792	-1.027045	3.892928
C	-4.674946	-0.626399	3.535017
H	-2.627164	-0.226718	3.084763
C	-8.362071	-1.192847	3.390560
H	-9.578649	-1.284567	1.597799
H	-6.918626	-1.029710	4.965826
H	-4.522119	-0.626062	4.610975
H	-9.203611	-1.332925	4.062437
C	-4.478673	1.756182	-0.746256
H	-5.011153	1.901230	0.197449
H	-4.623348	2.653475	-1.354877
C	-2.618755	-0.127751	0.382371
H	-2.570995	-0.833790	-0.452314
H	-1.676393	-0.200403	0.932951
C	-2.236572	2.789443	0.939231
C	-3.140103	3.150291	1.953562
C	-0.926856	3.345012	0.830990
C	-2.766049	4.084931	2.917075
H	-4.129327	2.703636	2.007391
C	-0.612119	4.293121	1.836577
C	-1.495575	4.659832	2.856366
H	-3.460323	4.364733	3.704826
H	0.358684	4.795092	1.831018
H	-1.199229	5.400785	3.595356
P	-2.635334	1.593855	-0.404880
Li	1.167348	2.952262	0.490600
Si	3.031070	4.824730	-1.097109
Cl	3.174340	4.212436	0.952304
Cl	3.982774	6.753885	-0.913370
H	1.699073	5.341520	-1.434802
C	4.279450	3.981668	-2.219924
H	4.208363	2.895376	-2.206611
H	4.099835	4.325206	-3.244604
H	5.284214	4.301858	-1.931765

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C	4.782725	-4.377917	4.497187
C	4.235548	-4.928875	3.314611
C	4.027576	-4.141891	2.204109
C	4.353810	-2.755848	2.210812
C	4.881254	-2.196812	3.422247
C	5.094407	-3.039387	4.546097
C	4.144496	-1.900514	1.073846
C	4.397999	-0.535289	1.183563

C	4.909403	-0.000745	2.395840
C	5.160958	-0.807127	3.477075
H	4.946087	-5.010944	5.364271
H	3.973940	-5.982536	3.283656
H	3.602010	-4.578816	1.308554
H	5.502302	-2.599977	5.452709
H	5.104467	1.066368	2.454552
H	5.563185	-0.387098	4.395064
C	3.611802	-2.453661	-0.213653
C	4.390318	-3.382145	-0.988296
C	2.356142	-2.053425	-0.671970
C	5.723380	-3.742127	-0.640364
C	3.830331	-3.954785	-2.177852
C	1.814825	-2.653328	-1.841560
C	6.446120	-4.627106	-1.408339
H	6.174378	-3.300938	0.240622
C	4.598516	-4.874165	-2.941603
C	2.518621	-3.582796	-2.565844
H	0.807379	-2.384157	-2.148522
C	5.878906	-5.207770	-2.567388
H	7.463317	-4.879817	-1.123832
H	4.154308	-5.303731	-3.835801
H	2.080359	-4.038519	-3.449734
H	6.458771	-5.908135	-3.161056
C	4.063944	0.397557	0.048534
H	4.312017	-0.039629	-0.922607
H	4.600835	1.343509	0.143877
C	1.551897	-1.004336	0.059373
H	1.474551	-1.259165	1.121547
H	0.527357	-0.957491	-0.322242
C	1.890808	1.561243	-1.554388
C	1.365724	0.830401	-2.641794
C	2.028831	2.987949	-1.592380
C	0.917403	1.484791	-3.791783
H	1.289526	-0.249284	-2.592853
C	1.571551	3.592688	-2.788029
C	1.010854	2.878506	-3.858628
H	0.495773	0.915603	-4.615006
H	1.622254	4.672845	-2.881184
H	0.649850	3.408098	-4.737072
P	2.217220	0.771523	0.096070
Li	-0.327157	2.584975	-1.702509
C	-5.586674	-5.067529	-1.845077
C	-5.607901	-4.682898	-0.483331
C	-5.400549	-3.370962	-0.121312
C	-5.158496	-2.365795	-1.100596
C	-5.111259	-2.766209	-2.477662
C	-5.340715	-4.126722	-2.817454
C	-4.931697	-0.989428	-0.758698
C	-4.611412	-0.072699	-1.759500
C	-4.562631	-0.492137	-3.114933
C	-4.819573	-1.793865	-3.468101
H	-5.756955	-6.105037	-2.116909
H	-5.786992	-5.430953	0.283422
H	-5.414780	-3.091676	0.925714
H	-5.310140	-4.411374	-3.866103

H	-4.327225	0.242561	-3.880481
H	-4.791389	-2.097396	-4.511334
C	-4.982528	-0.521489	0.665248
C	-6.218421	-0.507899	1.397341
C	-3.817560	-0.039661	1.263343
C	-7.459625	-0.902856	0.821191
C	-6.224890	-0.050204	2.757186
C	-3.850603	0.420201	2.606768
C	-8.626158	-0.872628	1.551626
H	-7.480478	-1.226401	-0.212874
C	-7.444907	-0.041169	3.485527
C	-5.012370	0.401746	3.337640
H	-2.931847	0.786774	3.055415
C	-8.621983	-0.445613	2.900773
H	-9.559804	-1.176351	1.087162
H	-7.429760	0.301563	4.516944
H	-5.018929	0.747020	4.368097
H	-9.548723	-0.430724	3.466653
C	-4.256210	1.350901	-1.407022
H	-4.926582	1.736584	-0.634406
H	-4.337504	2.005191	-2.279917
C	-2.531095	0.043795	0.486340
H	-2.346936	-0.879904	-0.070821
H	-1.676242	0.206748	1.148944
C	-2.326561	3.003293	0.163292
C	-3.392232	3.617242	0.842140
C	-1.016149	3.559982	0.112459
C	-3.187107	4.823378	1.511174
H	-4.379642	3.163902	0.864137
C	-0.875775	4.788636	0.803991
C	-1.922625	5.413521	1.489799
H	-4.008251	5.300415	2.039480
H	0.084054	5.314814	0.797916
H	-1.757671	6.362921	1.994256
P	-2.475833	1.438208	-0.796934
Li	1.076713	3.237096	0.380158
Si	3.959877	4.408219	-0.464824
Cl	3.034159	4.046592	1.464490
H	4.523205	3.302110	-1.270108
C	5.538599	5.200380	0.226179
H	6.102885	4.468883	0.816921
H	6.174577	5.517510	-0.608671
H	5.341014	6.071238	0.856838
Cl	3.128161	6.089278	-1.423560

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P	-0.076248	-0.272787	-0.042984
C	-0.873917	-1.908121	-0.301855
C	-2.029640	-2.207225	0.462235
C	-2.661968	-3.442606	0.241481
H	-3.544450	-3.705904	0.817753
C	-2.186859	-4.351506	-0.703142
H	-2.704472	-5.294341	-0.853880
C	-1.048995	-4.047770	-1.447460
H	-0.666301	-4.750331	-2.181581
C	-0.396942	-2.832884	-1.243212

H	0.490250	-2.614008	-1.826861
C	1.233564	-0.503304	1.285624
H	1.483981	0.507343	1.622051
H	0.748895	-1.020319	2.118800
C	2.445987	-1.248485	0.789553
C	3.357869	-0.636106	-0.070638
C	3.145353	0.795543	-0.465389
C	2.007682	1.138751	-1.193922
C	0.981954	0.083096	-1.542235
H	1.476745	-0.838563	-1.857499
H	0.326487	0.413265	-2.352804
C	1.775788	2.486227	-1.570566
H	0.880192	2.730460	-2.134703
C	2.662111	3.476775	-1.228039
H	2.475417	4.505224	-1.523345
C	3.817832	3.179364	-0.462277
C	4.063106	1.823605	-0.061698
C	5.200359	1.562039	0.754086
H	5.387053	0.548473	1.089000
C	6.054829	2.574469	1.127748
H	6.913044	2.350443	1.754358
C	5.822741	3.906071	0.708684
H	6.506431	4.694251	1.009343
C	4.725590	4.198428	-0.066693
H	4.527680	5.219365	-0.381932
C	4.453625	-1.398022	-0.602021
C	4.623583	-2.763001	-0.193451
C	3.691446	-3.334746	0.709866
H	3.825678	-4.367166	1.021187
C	2.626012	-2.603606	1.173455
H	1.907553	-3.054201	1.851935
C	5.709201	-3.517256	-0.714878
H	5.828703	-4.547026	-0.388433
C	6.585744	-2.964369	-1.618688
H	7.409852	-3.551800	-2.012299
C	6.407394	-1.626563	-2.044434
H	7.093149	-1.197498	-2.769066
C	5.372160	-0.865135	-1.550932
H	5.246177	0.156751	-1.888999
Si	-2.799025	-1.145477	1.834940
C	-3.848341	0.304198	0.027383
C	-4.941581	1.084106	0.493196
C	-6.105491	1.279003	-0.239449
C	-6.233040	0.693839	-1.508727
C	-5.180828	-0.074375	-2.023485
C	-4.022545	-0.247642	-1.259998
H	-4.890911	1.553281	1.476866
H	-6.928395	1.876156	0.140975
H	-5.254347	-0.534597	-3.002427
H	-3.233009	-0.861436	-1.690203
Mg	-2.034915	1.345196	0.540492
Br	-1.501460	3.623374	0.913068
O	-7.409437	0.929430	-2.152722
C	-7.594822	0.376724	-3.447774
H	-7.553567	-0.719594	-3.429694
H	-8.587800	0.693228	-3.769538

H	-6.848074	0.752335	-4.158363
H	-2.185621	0.169021	2.229239
Cl	-1.721143	-2.091751	3.531655
C	-4.563712	-1.549670	2.349750
H	-4.950536	-0.740792	2.976777
H	-5.225657	-1.654199	1.489119
H	-4.570563	-2.464526	2.947590

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P	-0.130913	-0.441528	-0.150350
C	-1.046096	-2.022432	-0.274889
C	-2.229583	-2.048324	-1.051522
C	-2.939207	-3.263400	-1.108287
H	-3.841945	-3.325613	-1.709321
C	-2.515110	-4.398659	-0.422548
H	-3.097499	-5.313481	-0.482319
C	-1.338120	-4.361802	0.324959
H	-0.988511	-5.246576	0.848626
C	-0.605973	-3.180242	0.390097
H	0.318296	-3.161596	0.956321
C	0.894565	-0.396307	1.427232
H	1.049789	0.673030	1.606518
H	0.253366	-0.762749	2.234725
C	2.213406	-1.134661	1.399310
C	3.263519	-0.709444	0.586534
C	3.127052	0.545776	-0.223149
C	2.175746	0.616259	-1.238424
C	1.207198	-0.519072	-1.457899
H	1.688475	-1.497586	-1.371846
H	0.726535	-0.467446	-2.438514
C	2.057949	1.790297	-2.027517
H	1.322043	1.816193	-2.826432
C	2.861922	2.878848	-1.802126
H	2.765111	3.769734	-2.415978
C	3.813324	2.867816	-0.750635
C	3.948155	1.691530	0.059285
C	4.875541	1.727758	1.138910
H	4.974129	0.859868	1.780078
C	5.637498	2.847580	1.385250
H	6.333770	2.851479	2.218664
C	5.518817	3.995737	0.567270
H	6.128020	4.870948	0.771739
C	4.622733	4.002359	-0.475555
H	4.510283	4.882963	-1.102161
C	4.468563	-1.492182	0.518478
C	4.606073	-2.652203	1.350472
C	3.541001	-3.007637	2.216067
H	3.654014	-3.872077	2.864662
C	2.378292	-2.278412	2.226399
H	1.567946	-2.564099	2.891935
C	5.797393	-3.423611	1.285390
H	5.887078	-4.294949	1.928692
C	6.811811	-3.084625	0.421358
H	7.716203	-3.683785	0.376112
C	6.671562	-1.955596	-0.419849
H	7.467794	-1.699891	-1.112549

C	5.534724	-1.180674	-0.372180
H	5.440430	-0.322718	-1.027089
Si	-3.033522	-0.676135	-2.114399
C	-4.028508	-0.450866	1.151395
C	-4.937534	1.244619	-0.258933
C	-5.168001	-0.415395	1.961048
H	-3.253826	-1.167689	1.419679
C	-6.084352	1.303243	0.520195
H	-4.895492	1.902419	-1.127879
C	-6.206391	0.468080	1.642580
H	-5.238721	-1.072623	2.820298
H	-6.900501	1.980211	0.287839
C	-3.857211	0.361211	0.008526
O	-7.365011	0.590286	2.345638
C	-7.546887	-0.220695	3.497674
H	-8.525810	0.044205	3.899101
H	-7.536483	-1.288510	3.245951
H	-6.779501	-0.022497	4.256207
Mg	-1.973140	1.388596	-0.098113
Br	-1.204565	3.548657	0.513890
Cl	-2.441279	-1.629995	-4.048134
C	-2.344643	1.029326	-2.670476
H	-2.739355	1.919418	-2.158816
H	-1.250737	1.071564	-2.689994
H	-2.654593	1.142142	-3.713009
H	-4.483377	-0.855190	-2.276653

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P	-0.064474	0.560114	0.205754
C	-0.873099	2.202381	0.401335
C	-2.070302	2.298859	1.152849
C	-2.669293	3.568961	1.264784
H	-3.583644	3.686226	1.841486
C	-2.131014	4.699258	0.652319
H	-2.632308	5.657725	0.750791
C	-0.949138	4.592081	-0.077108
H	-0.510597	5.465756	-0.549947
C	-0.325244	3.352353	-0.191978
H	0.604249	3.282734	-0.744828
C	0.988065	0.551136	-1.356042
H	1.089086	-0.515540	-1.583729
H	0.380510	0.986588	-2.155102
C	2.344086	1.214686	-1.275477
C	3.357308	0.699533	-0.467148
C	3.143840	-0.584896	0.277210
C	2.167028	-0.658856	1.267240
C	1.256405	0.514285	1.532754
H	1.792263	1.467636	1.513162
H	0.752116	0.420723	2.497980
C	1.963176	-1.866670	1.984233
H	1.195298	-1.898221	2.751835
C	2.715756	-2.982143	1.717729
H	2.551793	-3.900614	2.273960
C	3.696312	-2.964124	0.693489
C	3.912166	-1.755627	-0.048630
C	4.863336	-1.784478	-1.107639

H	5.021686	-0.891301	-1.700244
C	5.573690	-2.928017	-1.395847
H	6.289439	-2.924822	-2.212671
C	5.375964	-4.109377	-0.643147
H	5.944483	-5.003602	-0.880223
C	4.453809	-4.123339	0.376626
H	4.279287	-5.028667	0.951722
C	4.599244	1.415218	-0.345206
C	4.812536	2.601127	-1.122893
C	3.784040	3.047630	-1.990477
H	3.954378	3.930318	-2.600978
C	2.585453	2.381462	-2.050624
H	1.804179	2.736133	-2.717906
C	6.040887	3.305207	-1.004145
H	6.188015	4.197121	-1.607564
C	7.020003	2.876546	-0.139157
H	7.953513	3.424504	-0.053155
C	6.805552	1.721167	0.649068
H	7.574562	1.393792	1.342443
C	5.631119	1.009999	0.548257
H	5.479805	0.129969	1.161943
C	-4.876776	1.258896	2.382211
H	-5.340064	0.316036	2.685735
H	-5.070231	1.996140	3.169125
H	-5.343498	1.573312	1.447831
Si	-3.013727	1.019763	2.213018
C	-3.939775	0.783404	-1.138052
C	-4.844302	-1.026698	0.121465
C	-5.086602	0.828205	-1.921348
H	-3.157000	1.508496	-1.354977
C	-6.009778	-1.016400	-0.652407
H	-4.796505	-1.761904	0.926285
C	-6.132681	-0.077848	-1.683183
H	-5.201351	1.546733	-2.727606
H	-6.799834	-1.730166	-0.448090
C	-3.763884	-0.136226	-0.072744
O	-7.216174	0.040574	-2.502067
C	-8.294987	-0.866047	-2.326858
H	-9.034495	-0.603124	-3.084531
H	-7.977867	-1.905547	-2.476481
H	-8.748001	-0.769495	-1.332010
Mg	-1.945041	-1.263429	0.179072
Br	-1.151278	-3.336350	-0.691063
Cl	-2.256116	-1.032454	2.662883
H	-2.518779	1.445346	3.564324

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P	0.124443	0.314907	0.032700
C	0.857502	1.991177	-0.202577
C	1.979793	2.361727	0.580403
C	2.543306	3.632462	0.356596
H	3.404588	3.949883	0.940529
C	2.045286	4.504600	-0.610301
H	2.518695	5.469885	-0.764473
C	0.940290	4.130776	-1.370735
H	0.533877	4.801167	-2.122011

C	0.352036	2.885293	-1.160698
H	-0.511058	2.615786	-1.758133
C	-1.205167	0.513643	1.351803
H	-1.456480	-0.505107	1.661278
H	-0.737208	1.007668	2.207040
C	-2.414666	1.266965	0.862232
C	-3.322093	0.664660	-0.009530
C	-3.109327	-0.763840	-0.412960
C	-1.962883	-1.104956	-1.129043
C	-0.934830	-0.047121	-1.468792
H	-1.432797	0.868339	-1.795709
H	-0.273260	-0.383315	-2.271669
C	-1.731424	-2.450389	-1.513242
H	-0.827647	-2.695595	-2.061581
C	-2.626787	-3.439015	-1.189086
H	-2.438741	-4.465928	-1.488821
C	-3.790700	-3.144041	-0.435260
C	-4.035805	-1.790771	-0.026673
C	-5.181540	-1.531958	0.778368
H	-5.369071	-0.520552	1.119488
C	-6.043996	-2.544109	1.134142
H	-6.908734	-2.321852	1.752476
C	-5.811834	-3.873155	0.706940
H	-6.501833	-4.661315	0.993046
C	-4.706750	-4.162867	-0.058110
H	-4.508620	-5.181849	-0.379556
C	-4.412739	1.433806	-0.541040
C	-4.585402	2.794479	-0.119720
C	-3.659577	3.355690	0.796384
H	-3.795085	4.384872	1.117808
C	-2.598066	2.617971	1.258344
H	-1.884556	3.063637	1.945553
C	-5.666641	3.554920	-0.641195
H	-5.788234	4.581347	-0.305022
C	-6.536270	3.011923	-1.557569
H	-7.357012	3.603861	-1.951475
C	-6.354957	1.678637	-1.996164
H	-7.034971	1.257748	-2.730901
C	-5.324035	0.911417	-1.502669
H	-5.195306	-0.106840	-1.850317
Si	2.888209	1.450321	1.993943
C	2.278750	2.447080	3.509559
H	2.759014	2.096846	4.429466
H	2.537908	3.504688	3.378123
H	1.194913	2.388119	3.655960
C	3.869646	-0.092761	0.202293
C	5.005803	-0.774599	0.715021
C	6.195506	-0.906135	0.011357
C	6.307699	-0.353705	-1.274325
C	5.215919	0.321611	-1.832775
C	4.031934	0.434454	-1.096176
H	4.966719	-1.201988	1.717593
H	7.052183	-1.427804	0.427013
H	5.276692	0.755534	-2.824591
H	3.211413	0.979251	-1.560924
Mg	2.127366	-1.318630	0.559946

Br	1.600903	-3.599164	0.114993
O	7.512455	-0.524161	-1.888187
C	7.681940	-0.005048	-3.198431
H	7.562978	1.085687	-3.220857
H	8.700553	-0.260739	-3.493508
H	6.976566	-0.456905	-3.907064
Cl	2.192820	-0.477623	2.914686
H	4.345864	1.681613	2.049012

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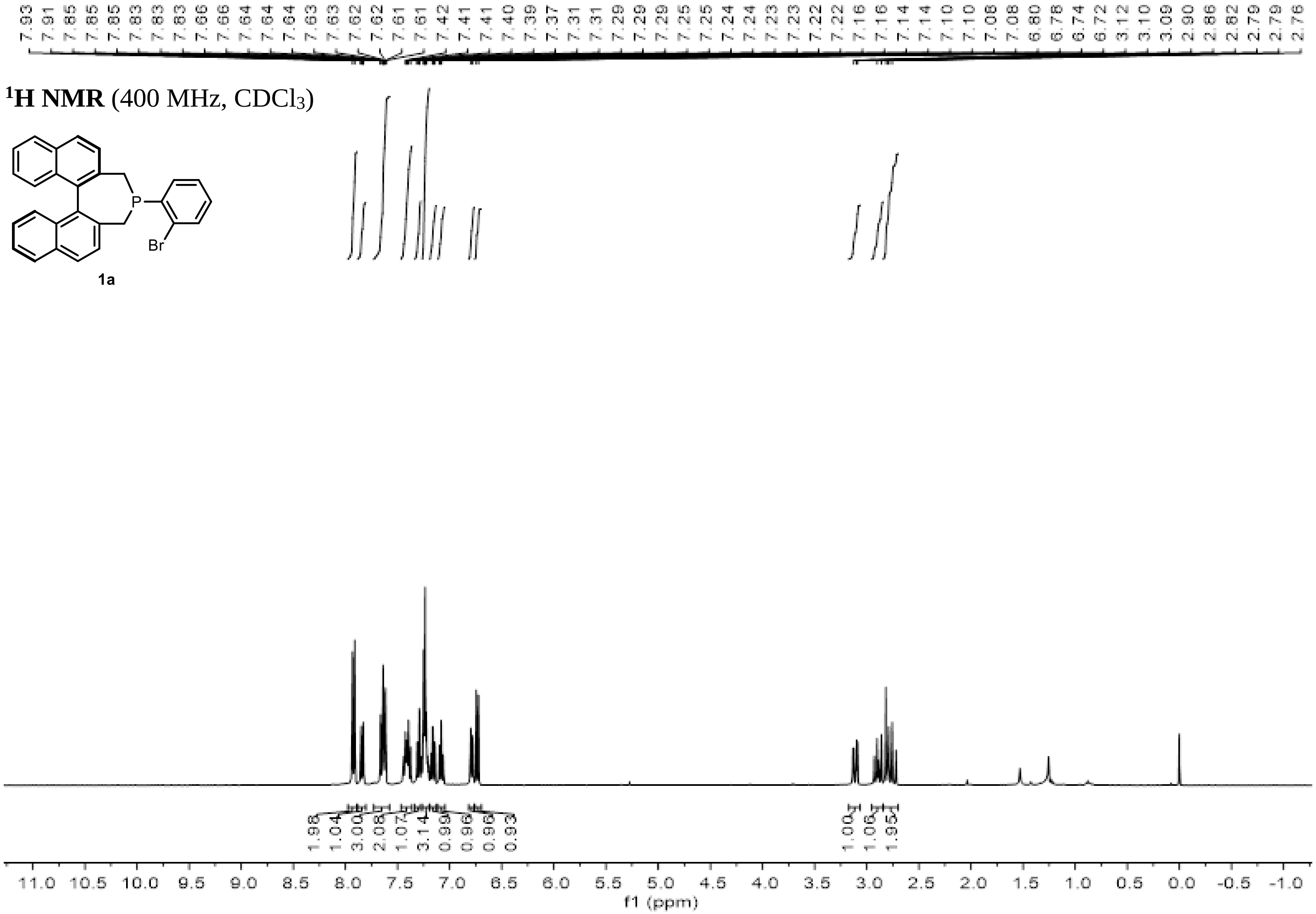
9. NMR Spectra

^{1}H NMR (400 MHz, $CDCl_3$)



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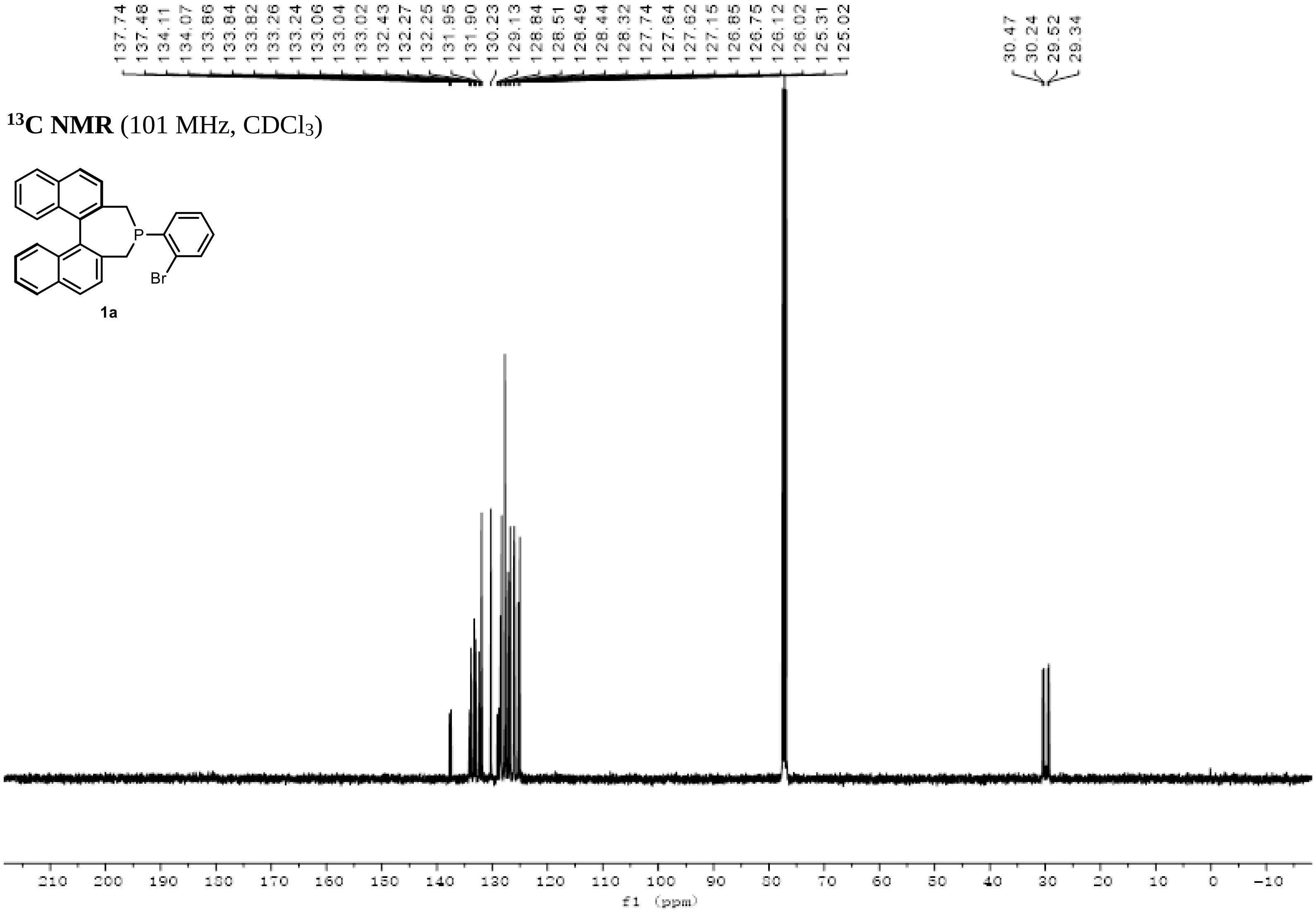
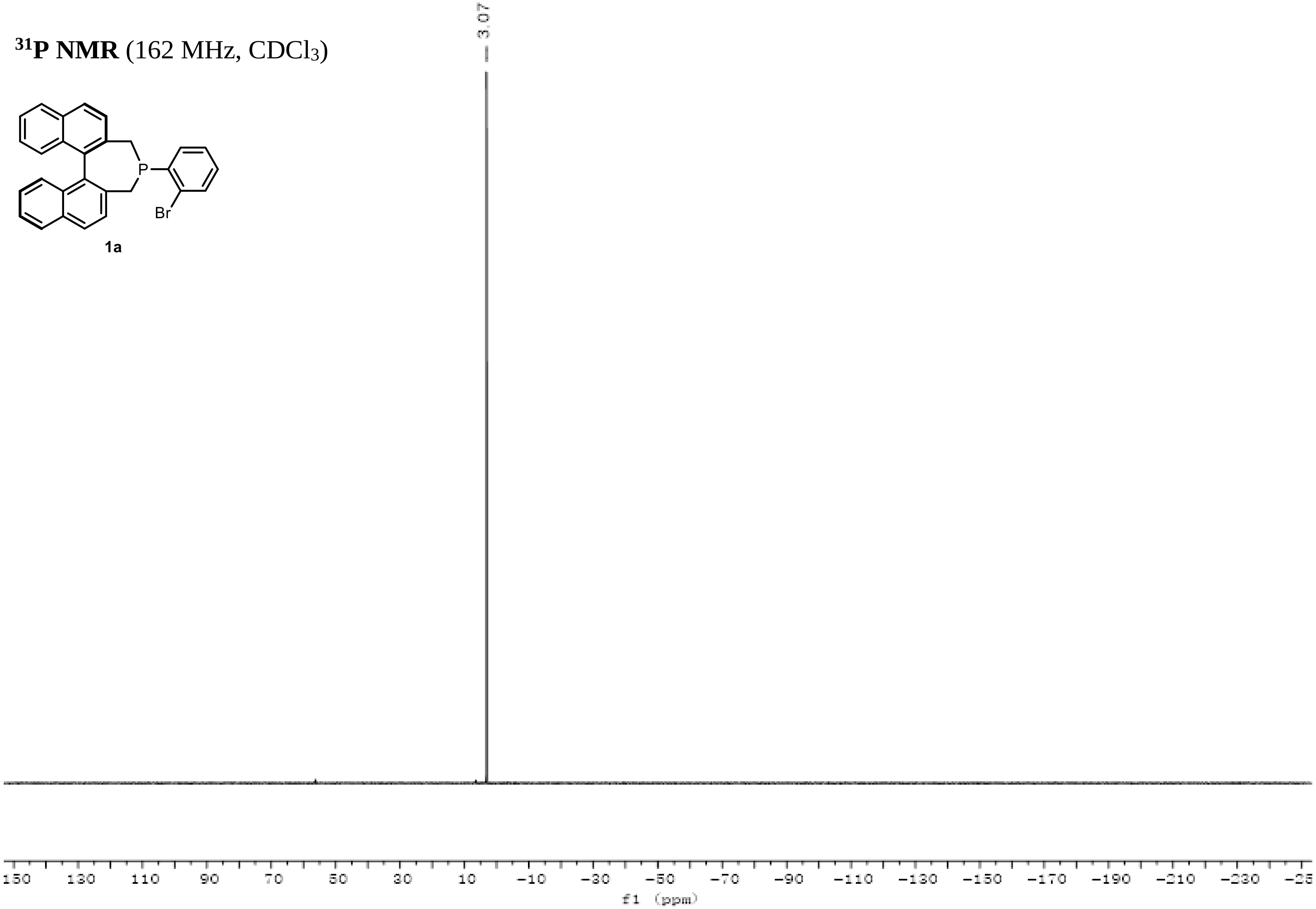
^{13}C NMR (101 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)

1a



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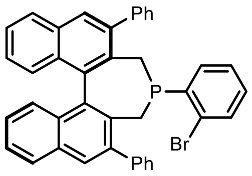

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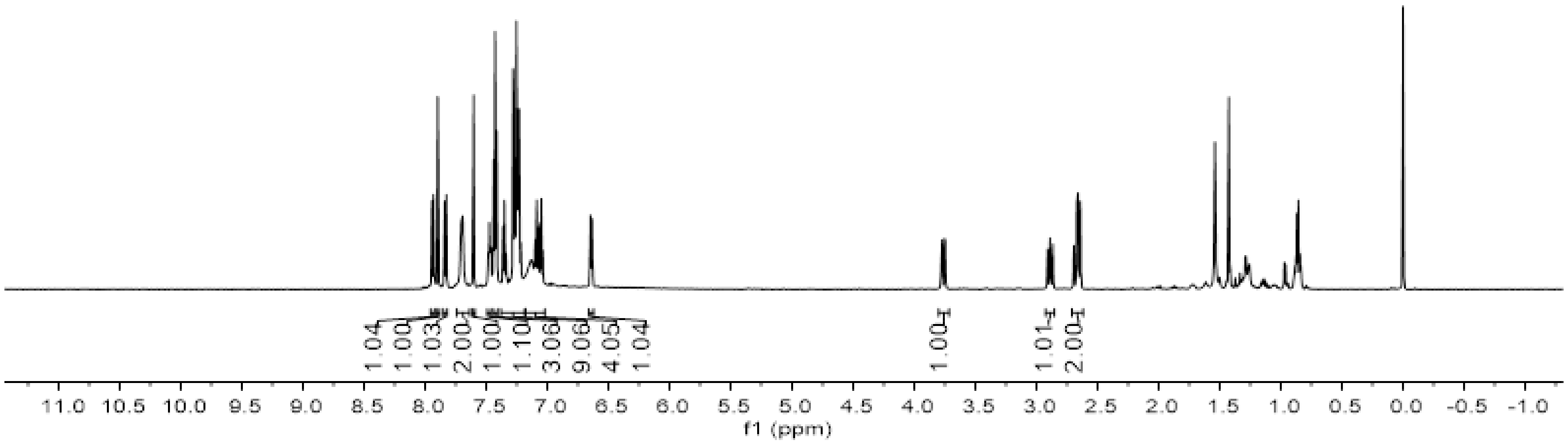
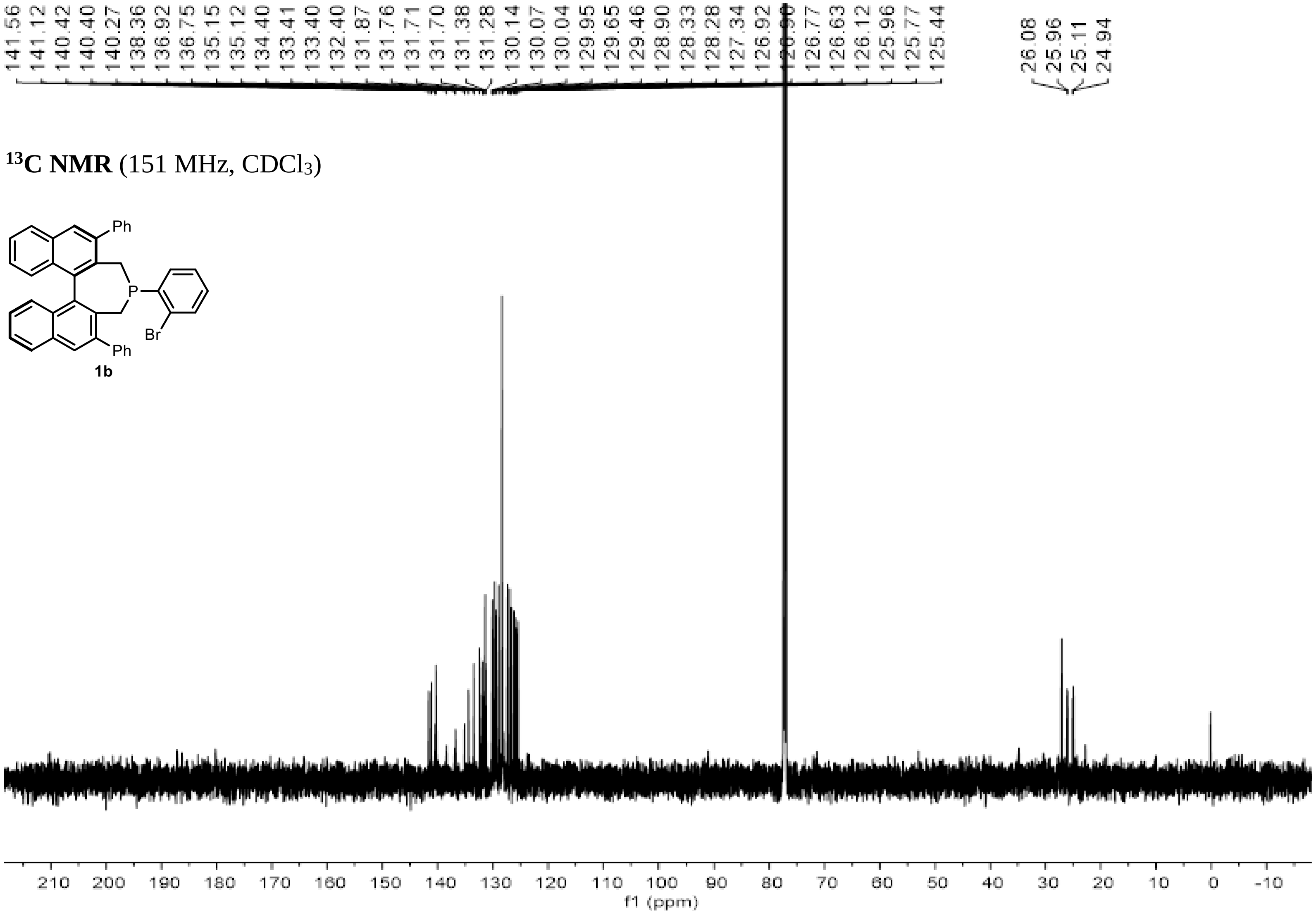
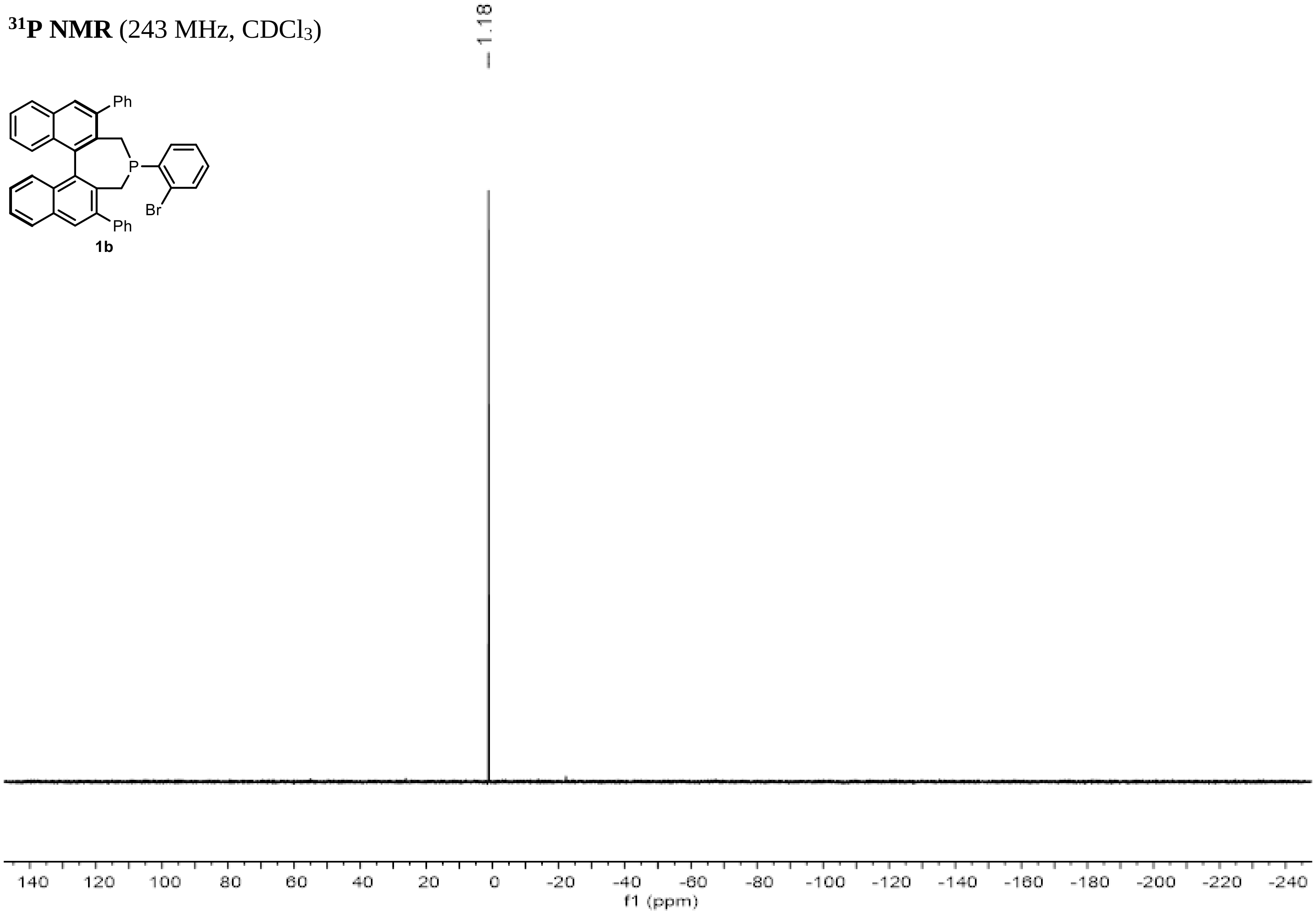




^{13}C NMR (151 MHz, $CDCl_3$)

1b

^{31}P NMR (243 MHz, $CDCl_3$)



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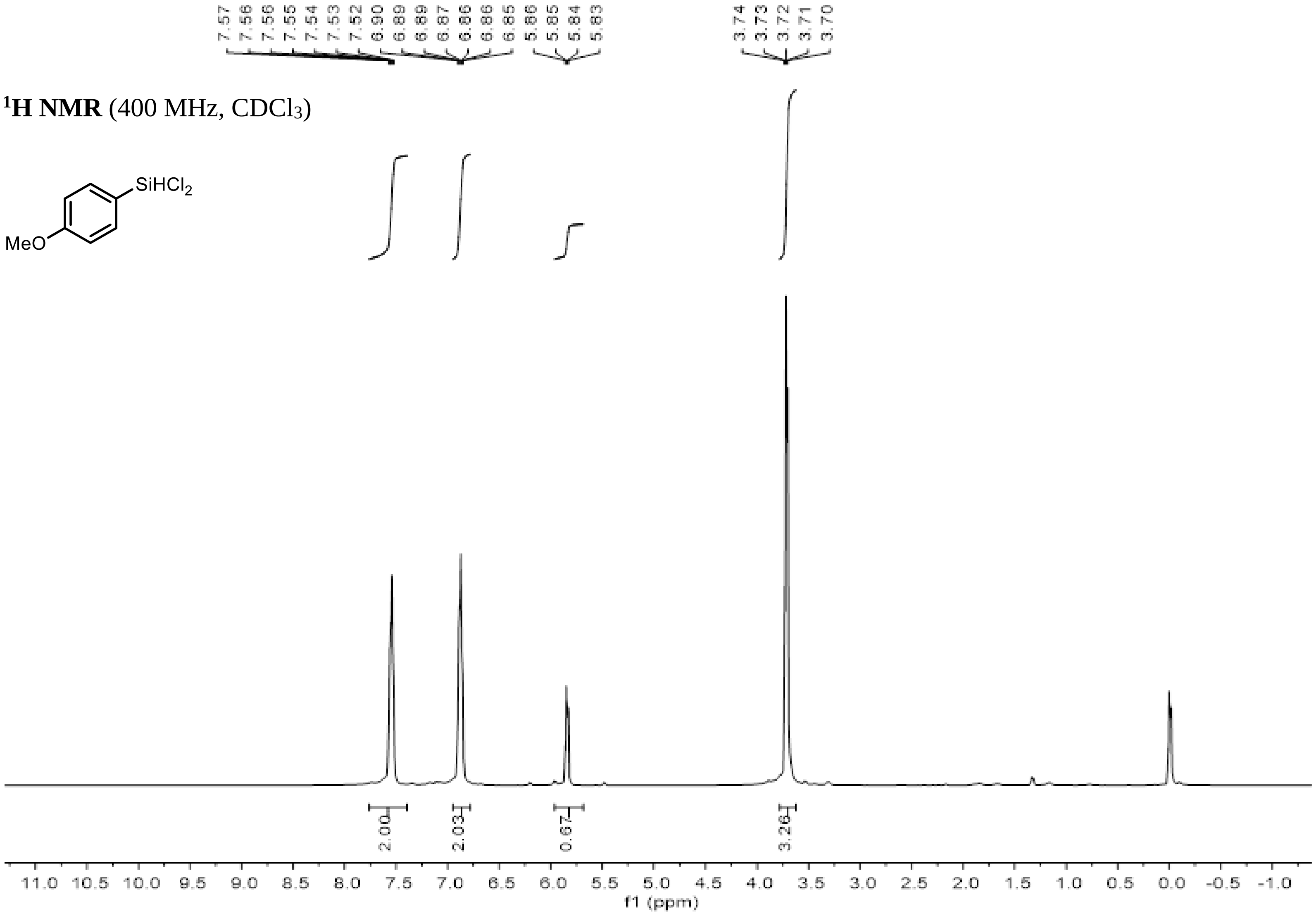

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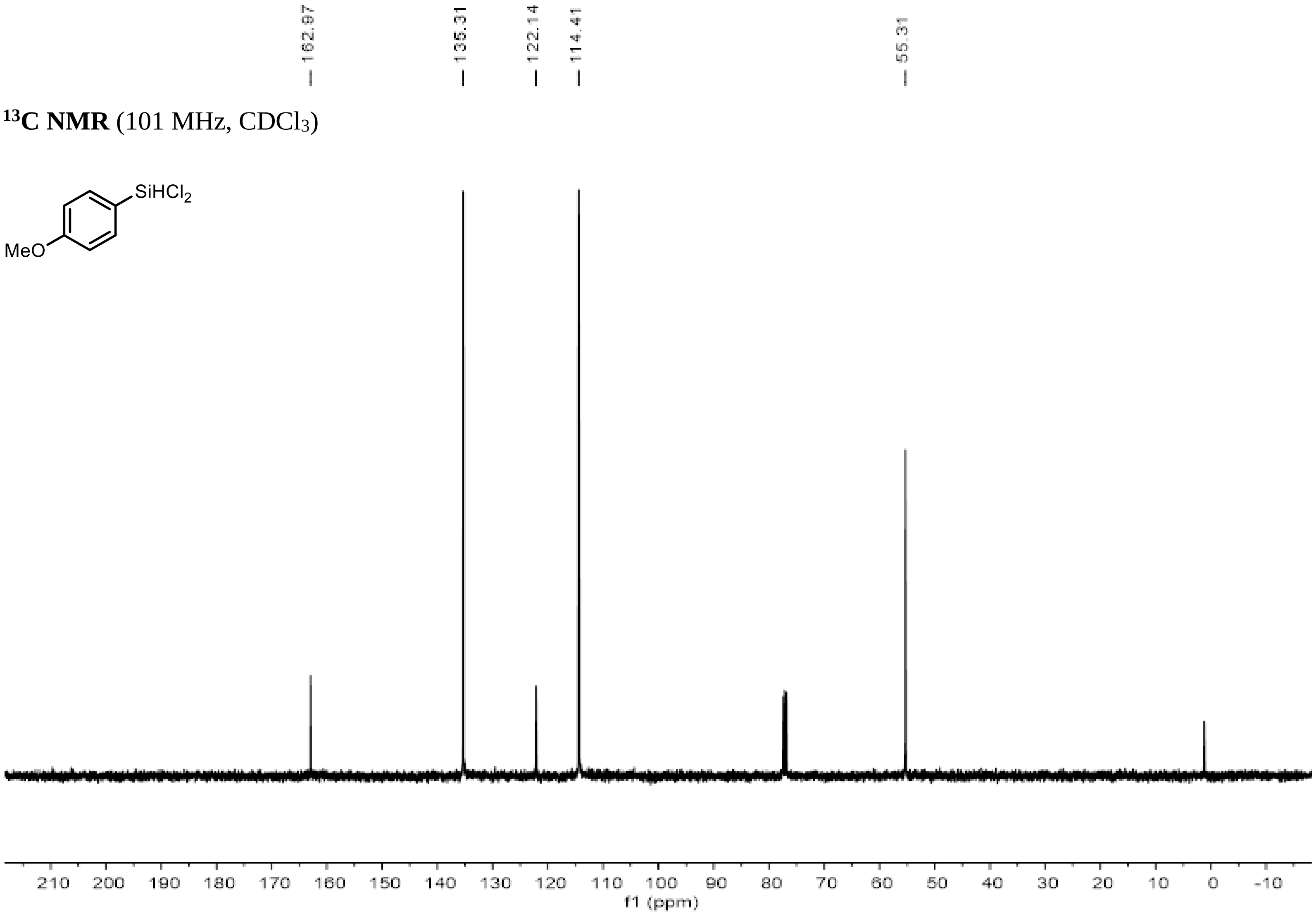
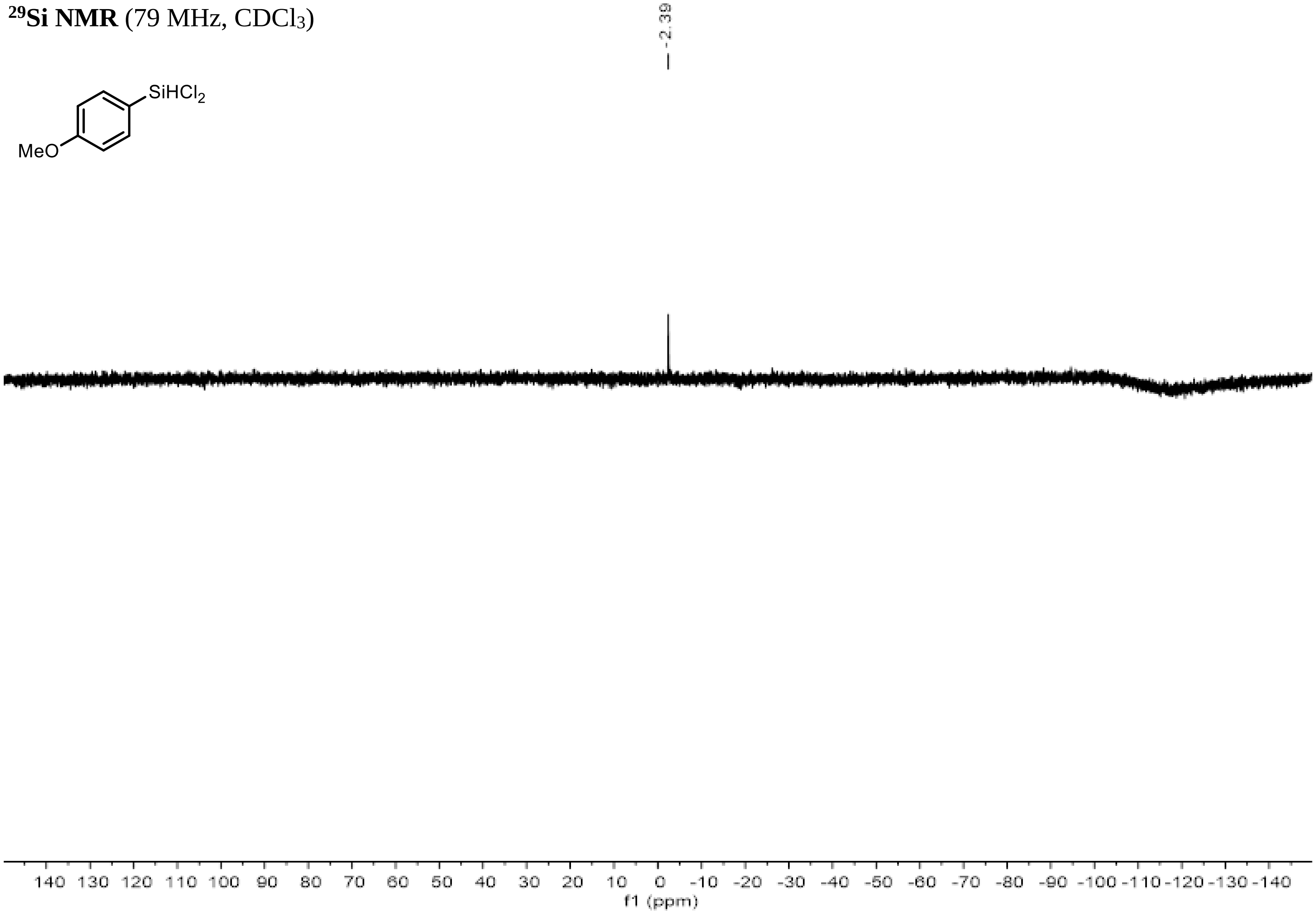


^{29}Si NMR (79 MHz, $CDCl_3$)



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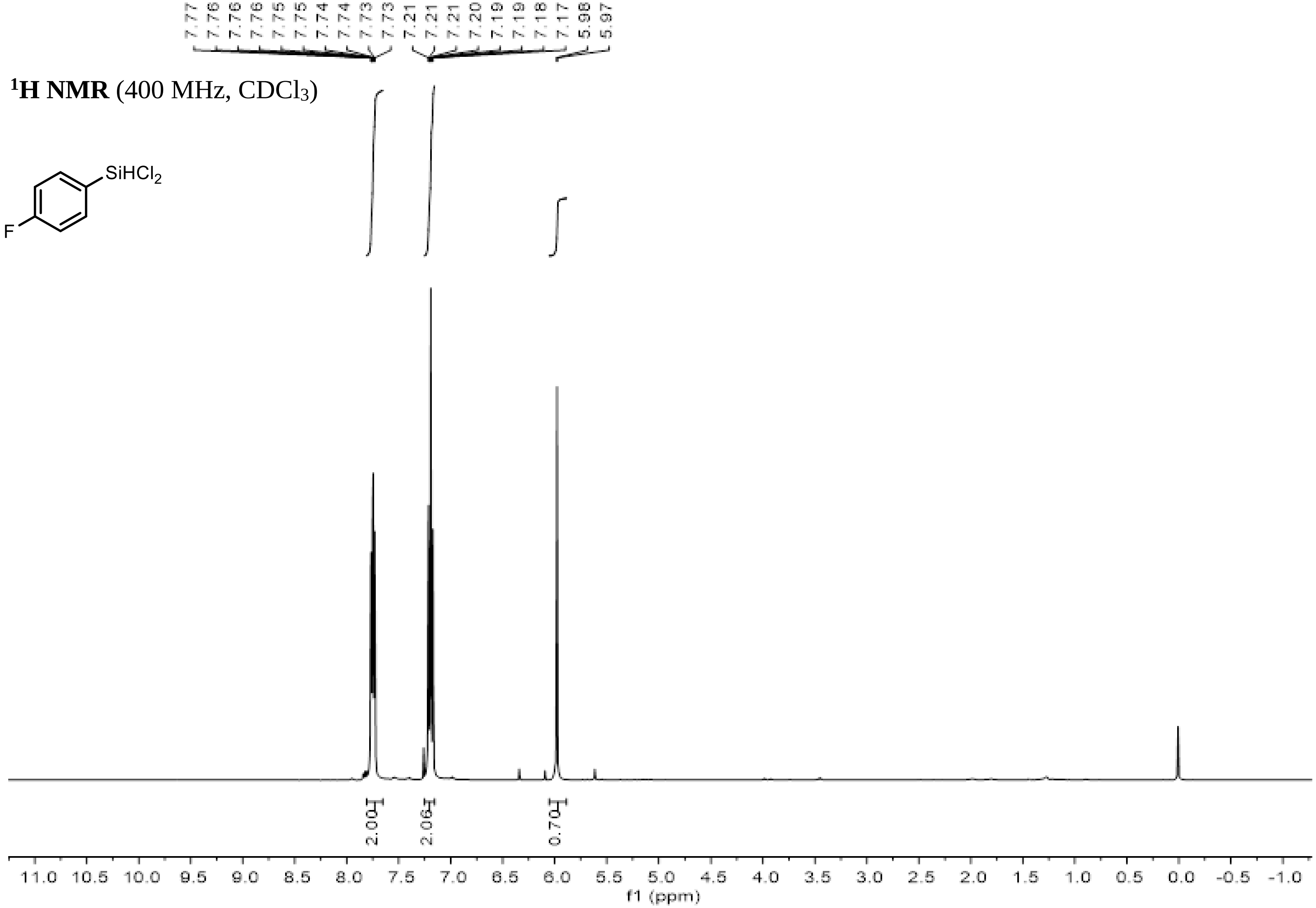

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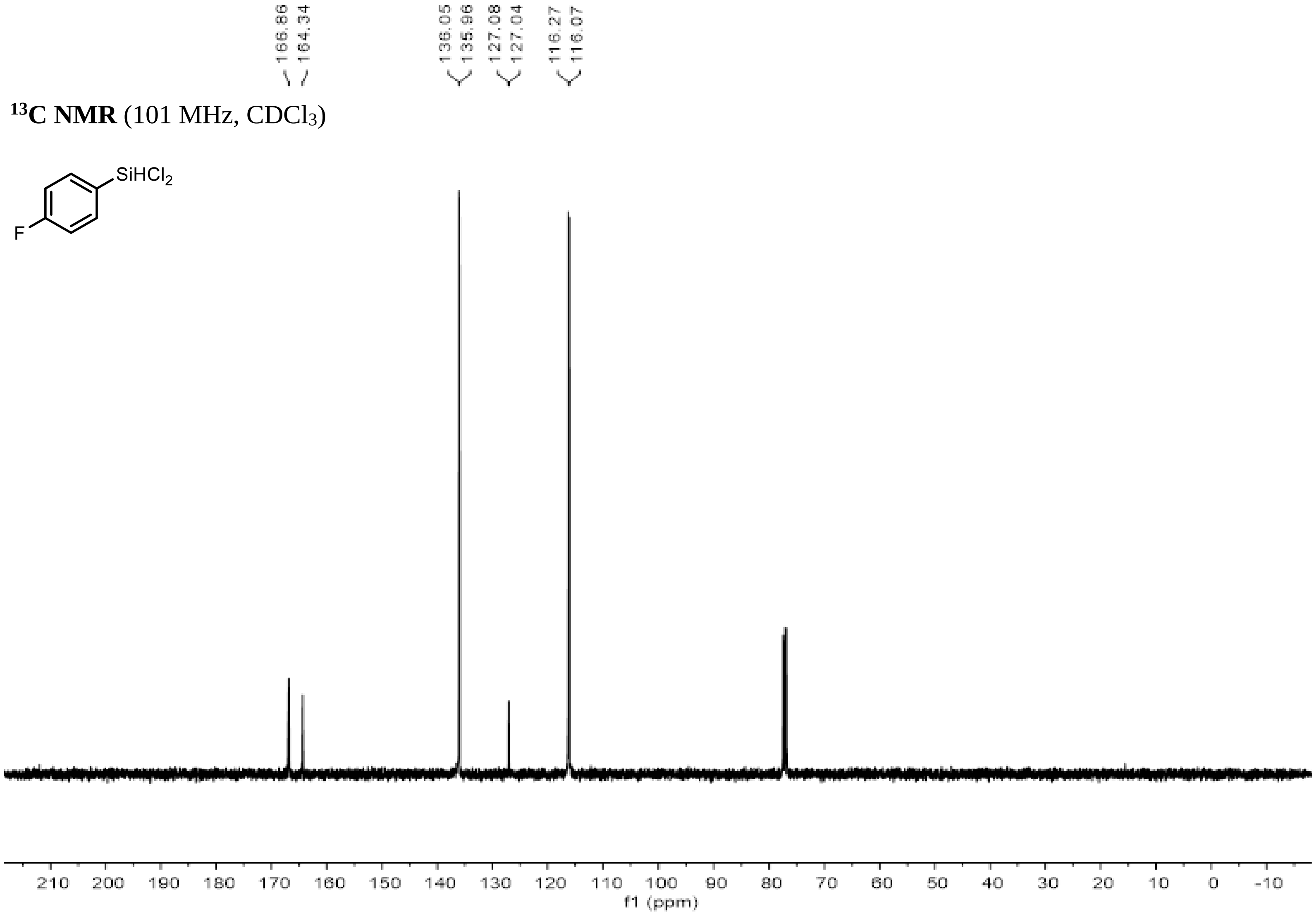
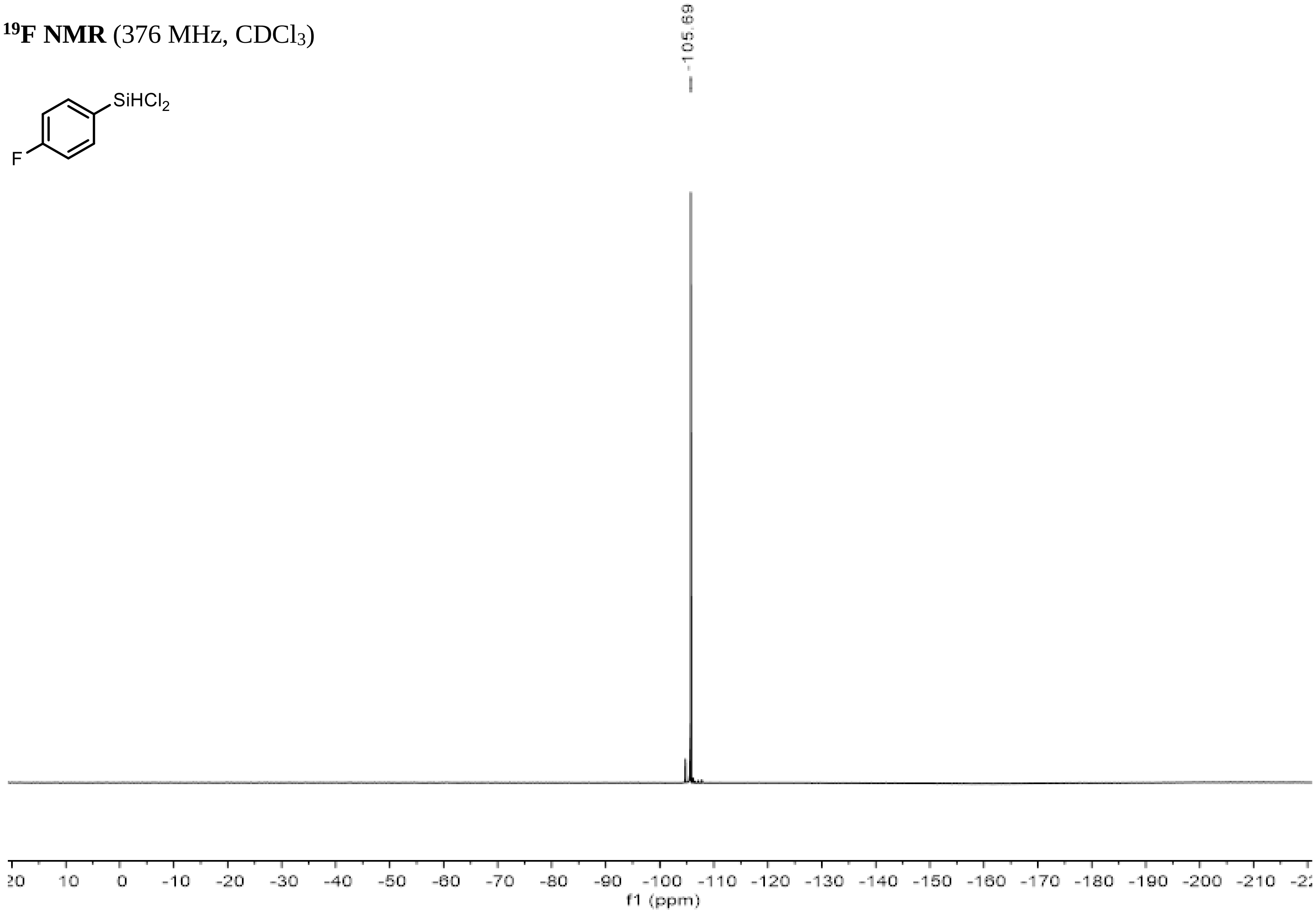
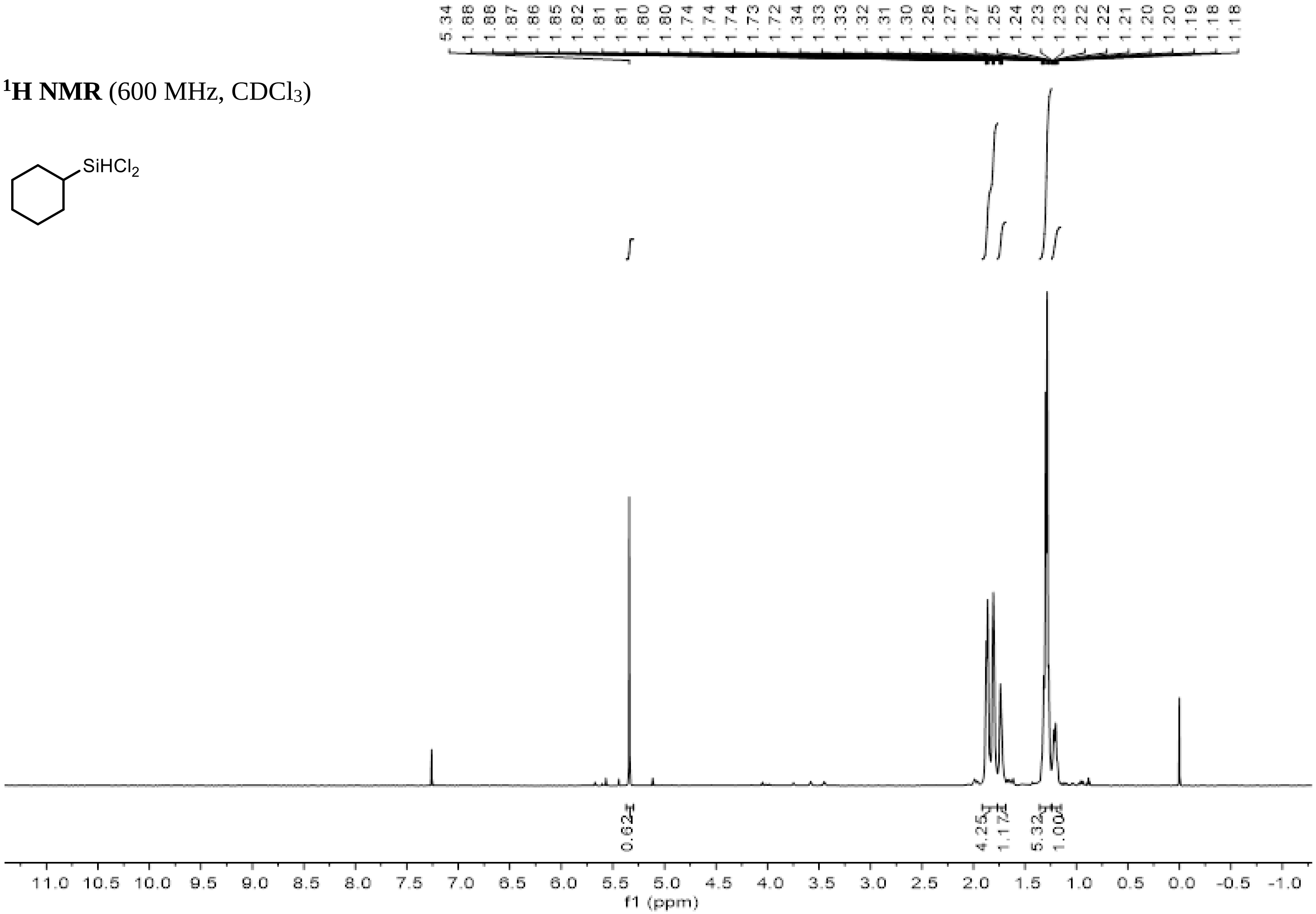


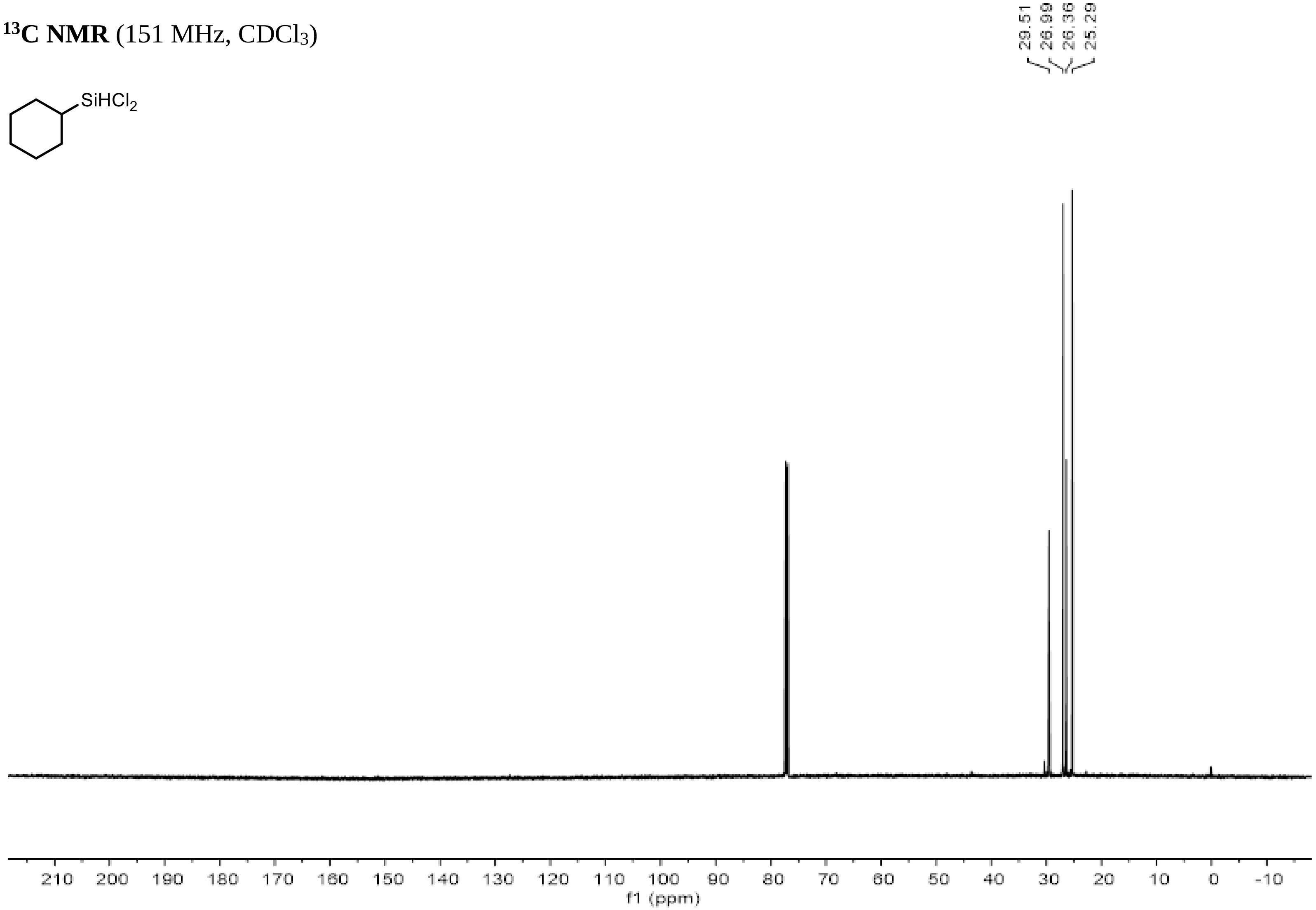
^{19}F NMR (376 MHz, $CDCl_3$)

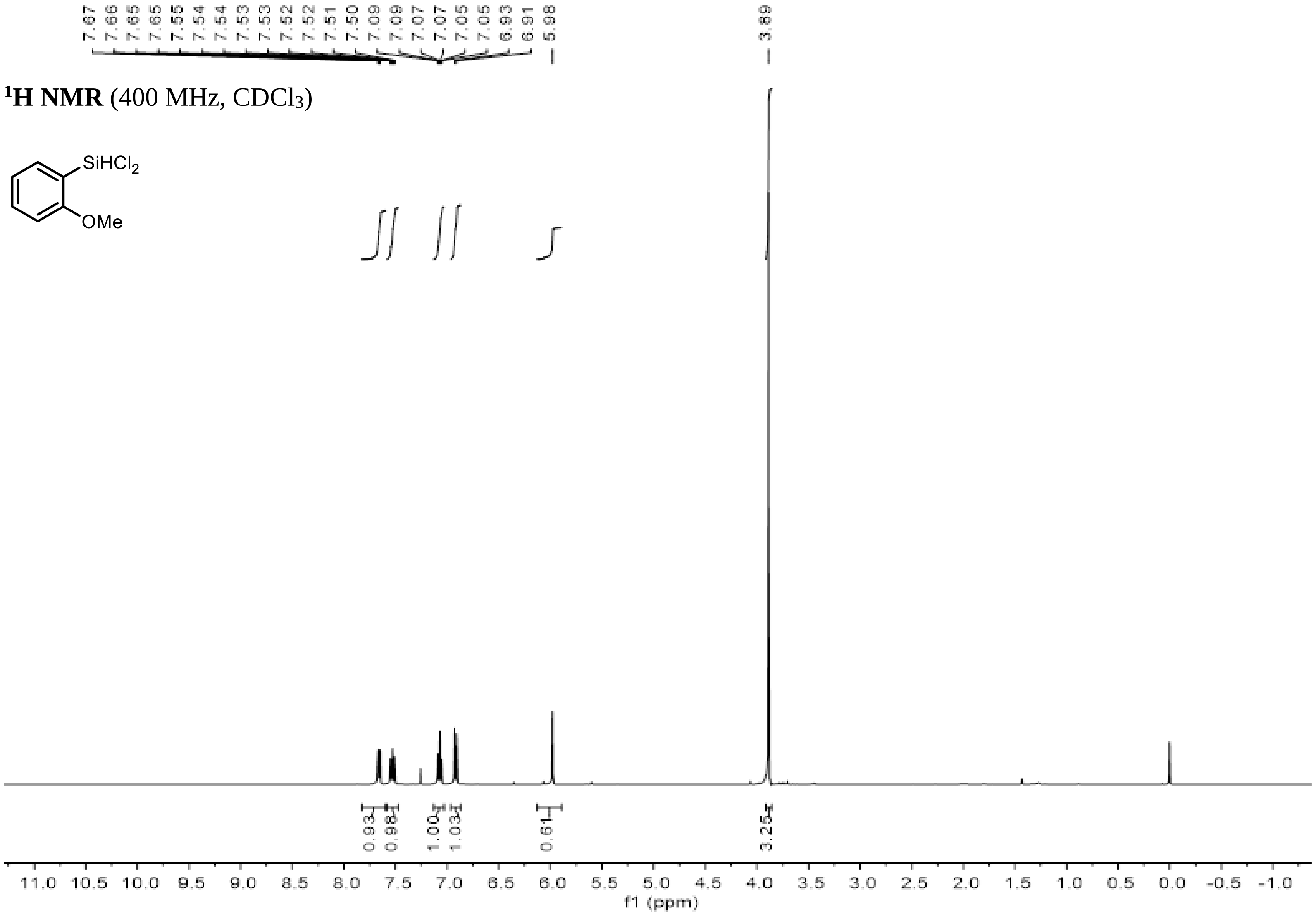


^{1}H NMR (600 MHz, $CDCl_3$)



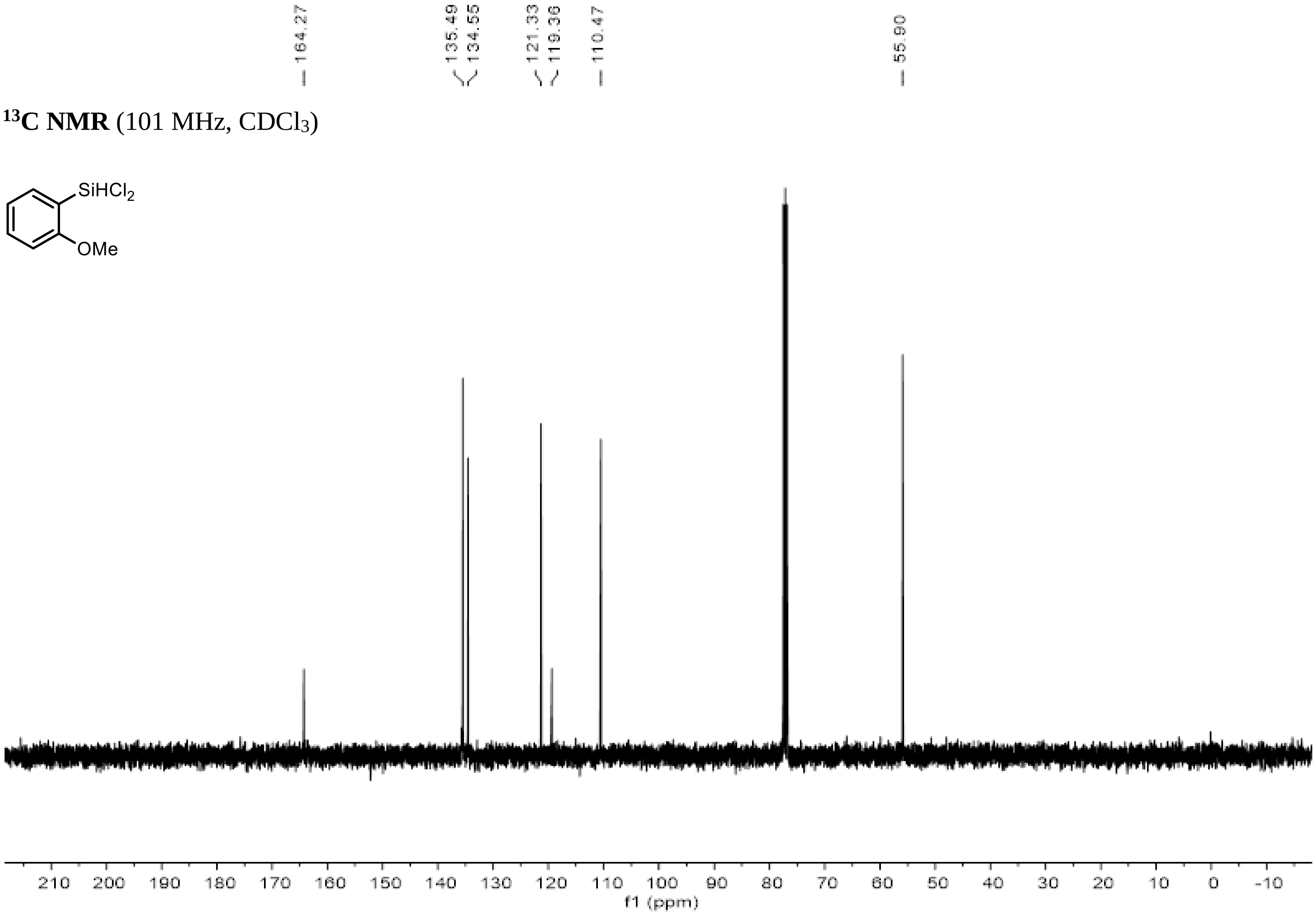
^{13}C NMR (151 MHz, $CDCl_3$)





^{1}H NMR (400 MHz, $CDCl_3$)

^{13}**C NMR** (101 MHz, $CDCl_3$)



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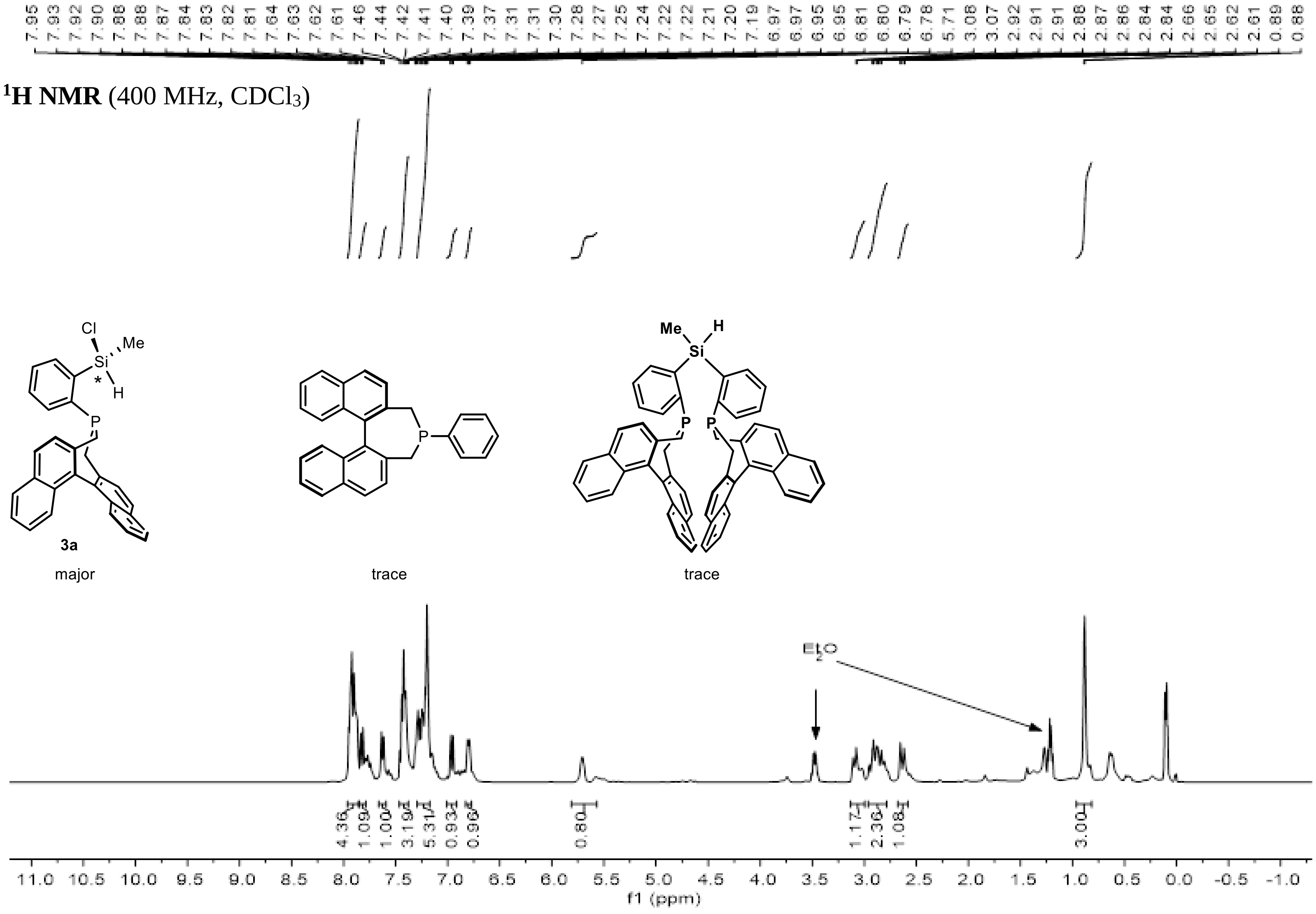

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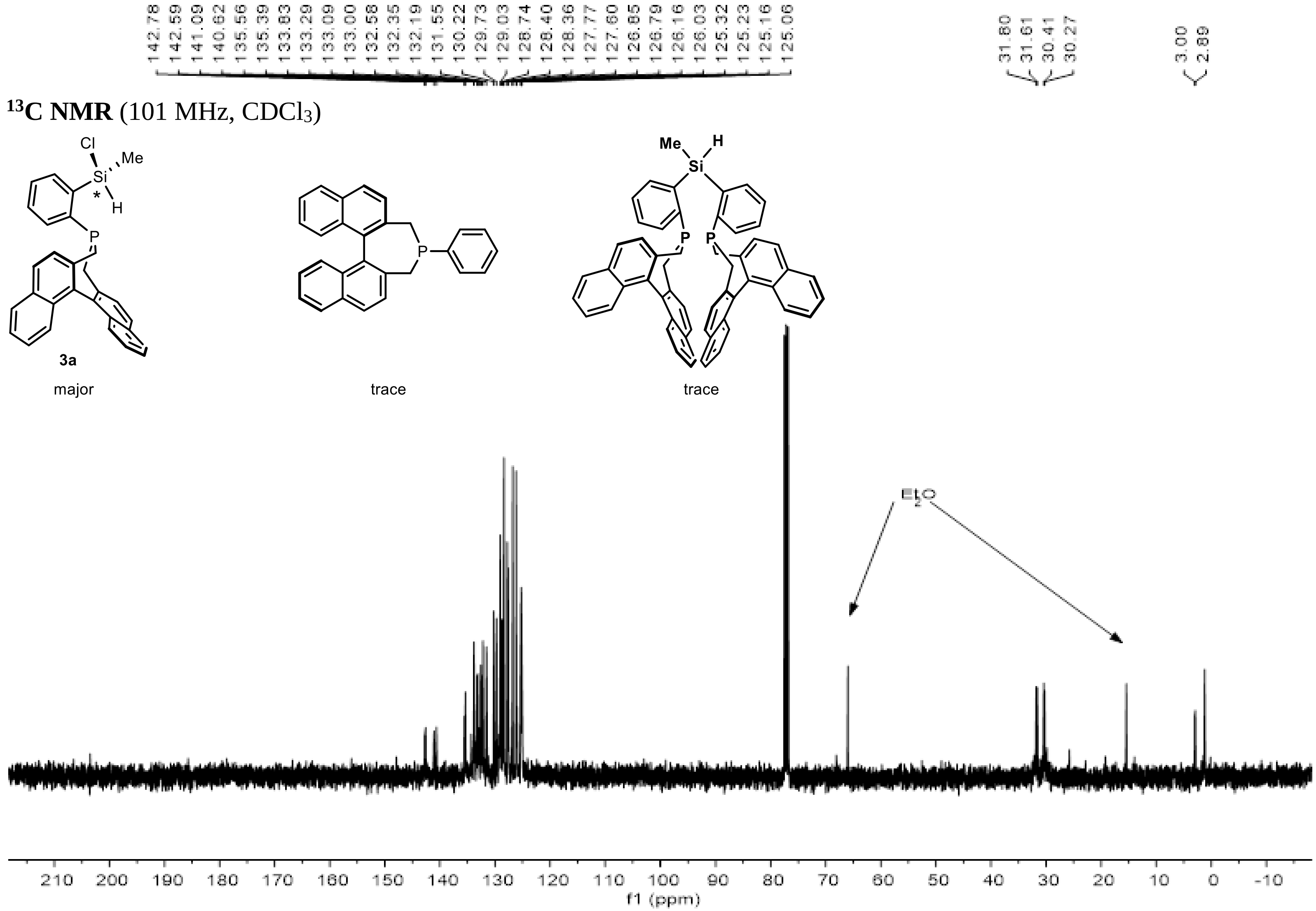


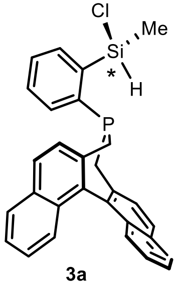
3a

major

trace

trace

^{31}P NMR (162 MHz, $CDCl_3$)



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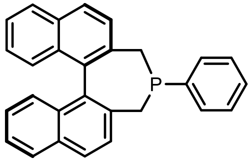
major



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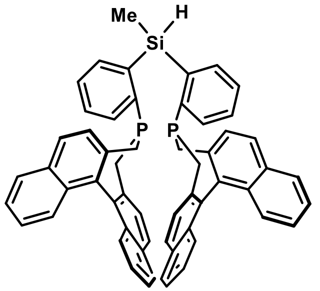

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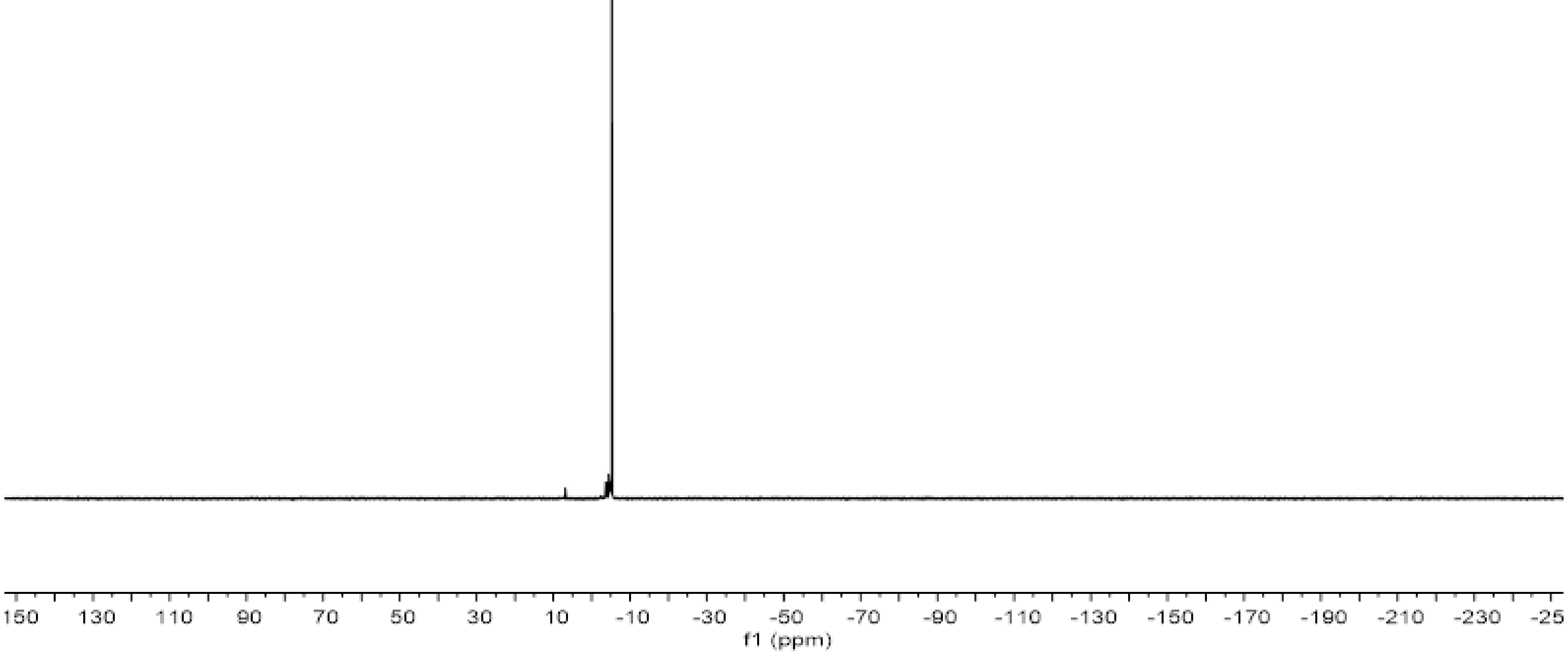

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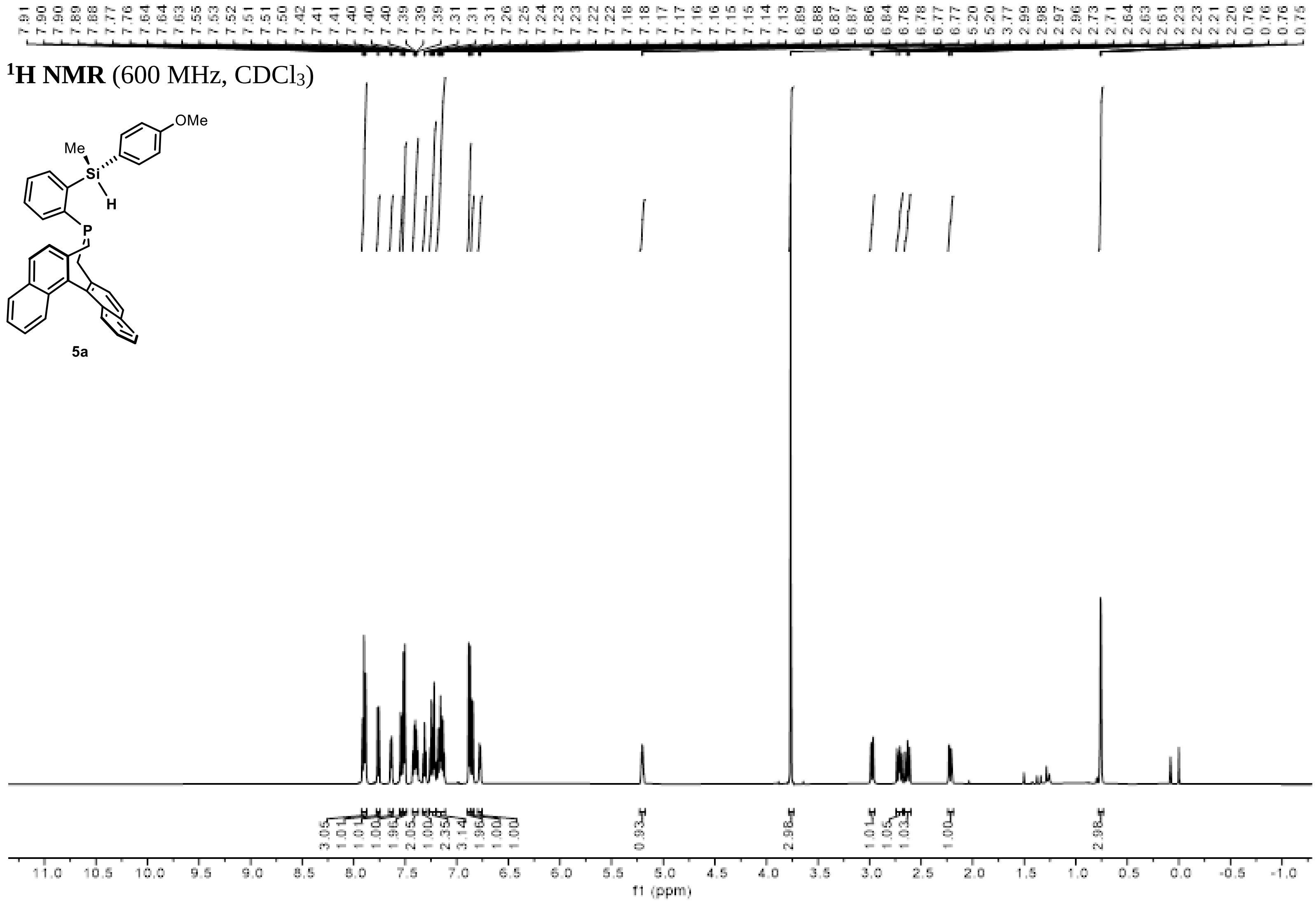

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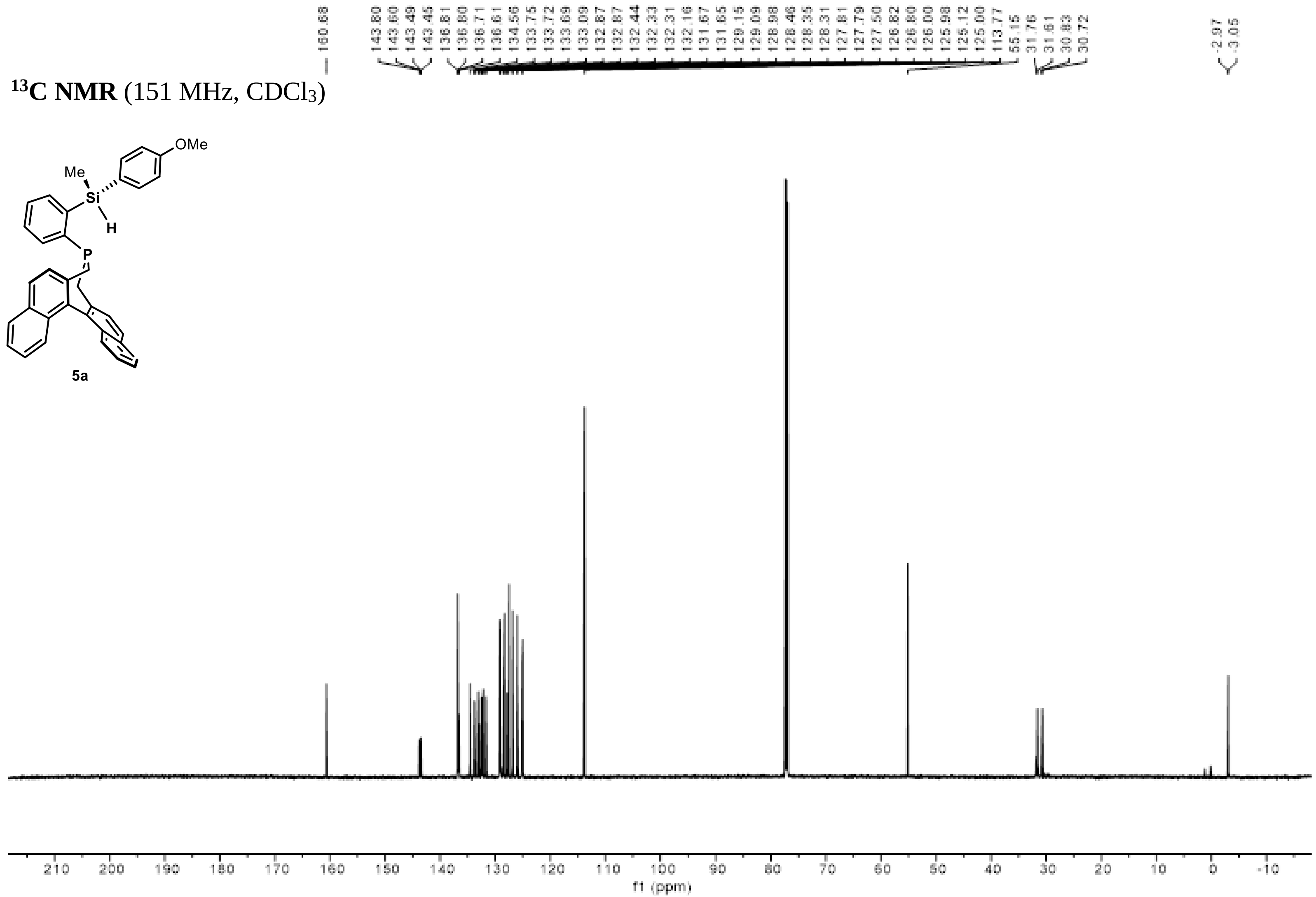
^{13}C NMR (151 MHz, $CDCl_3$)



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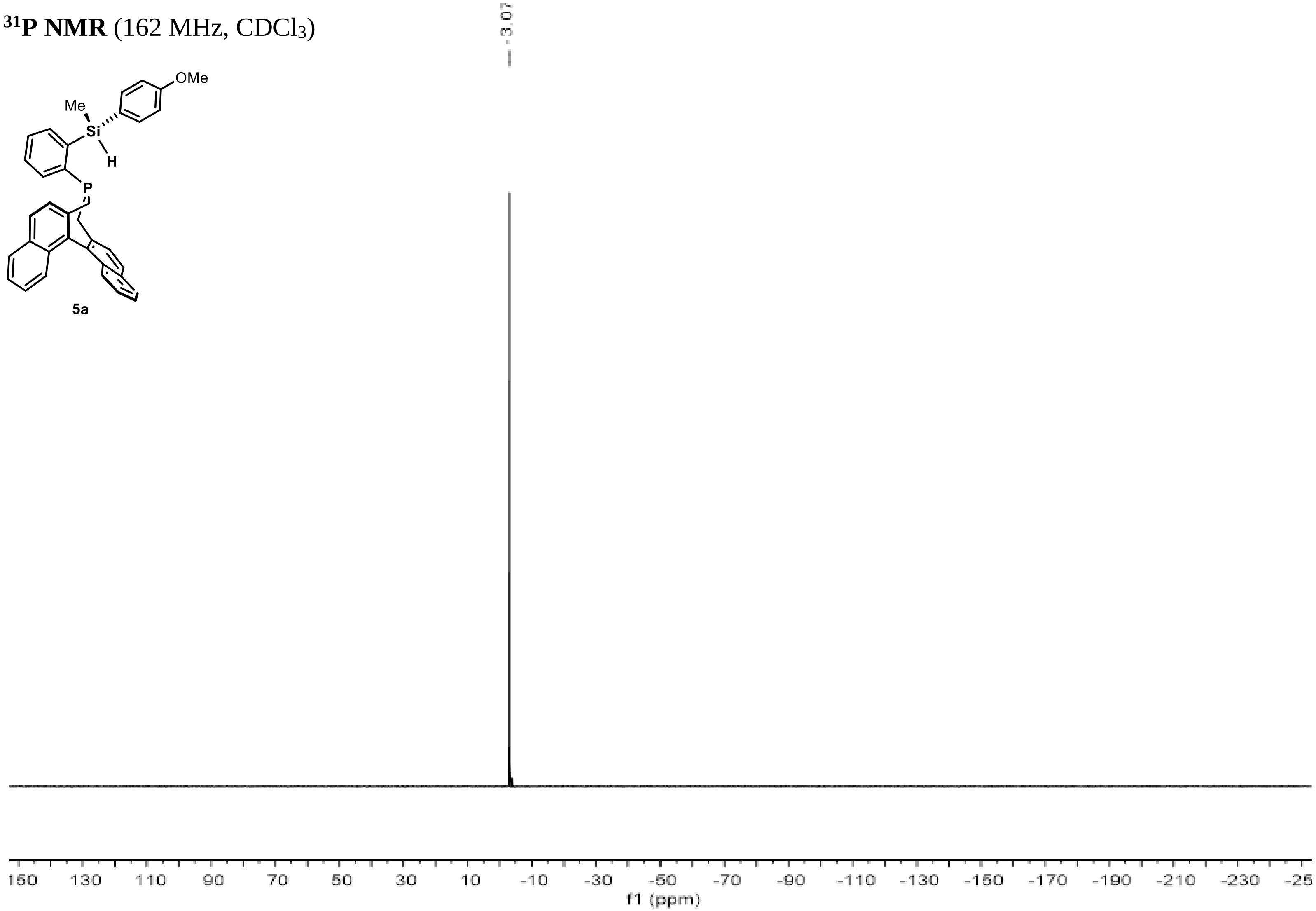

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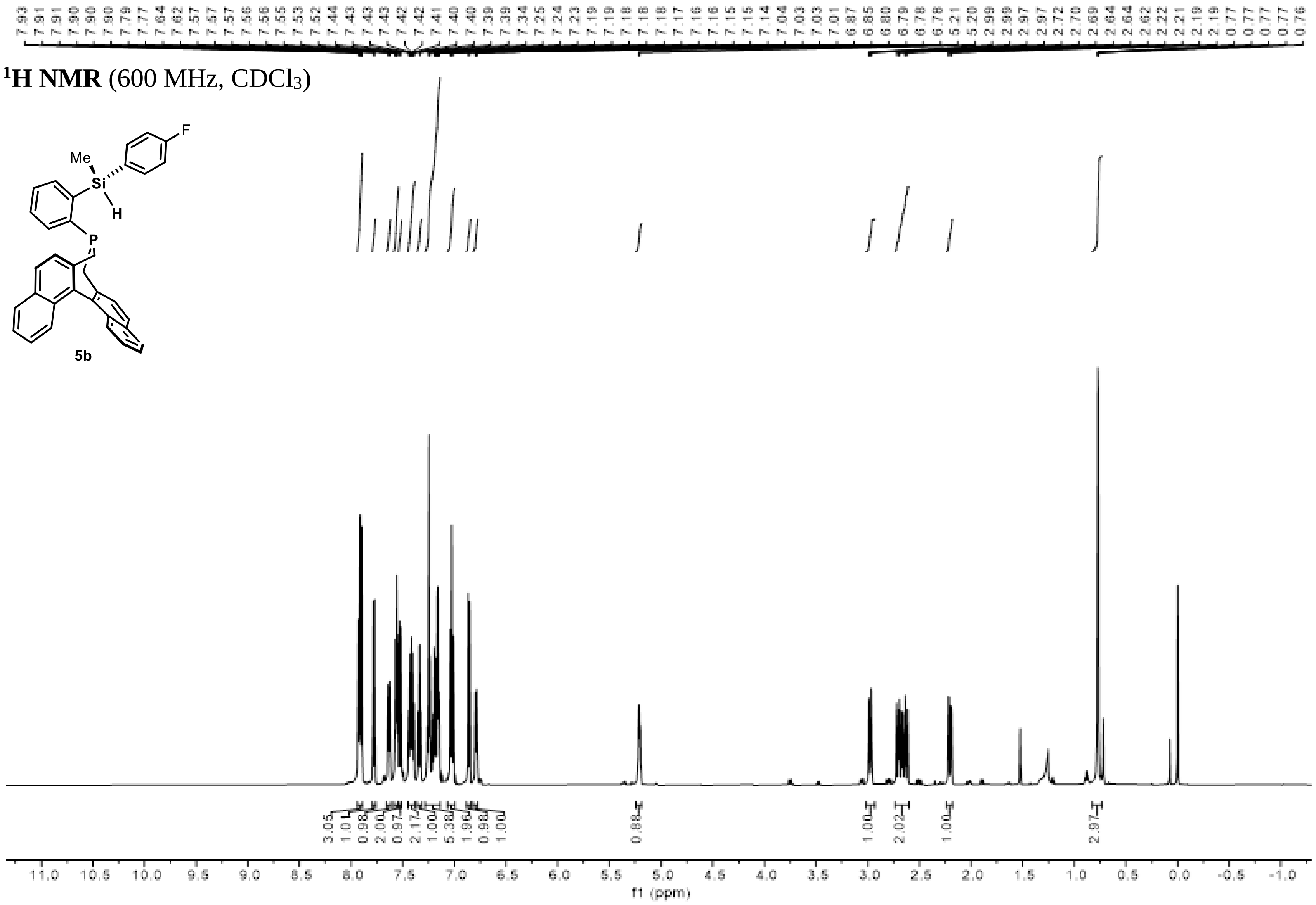

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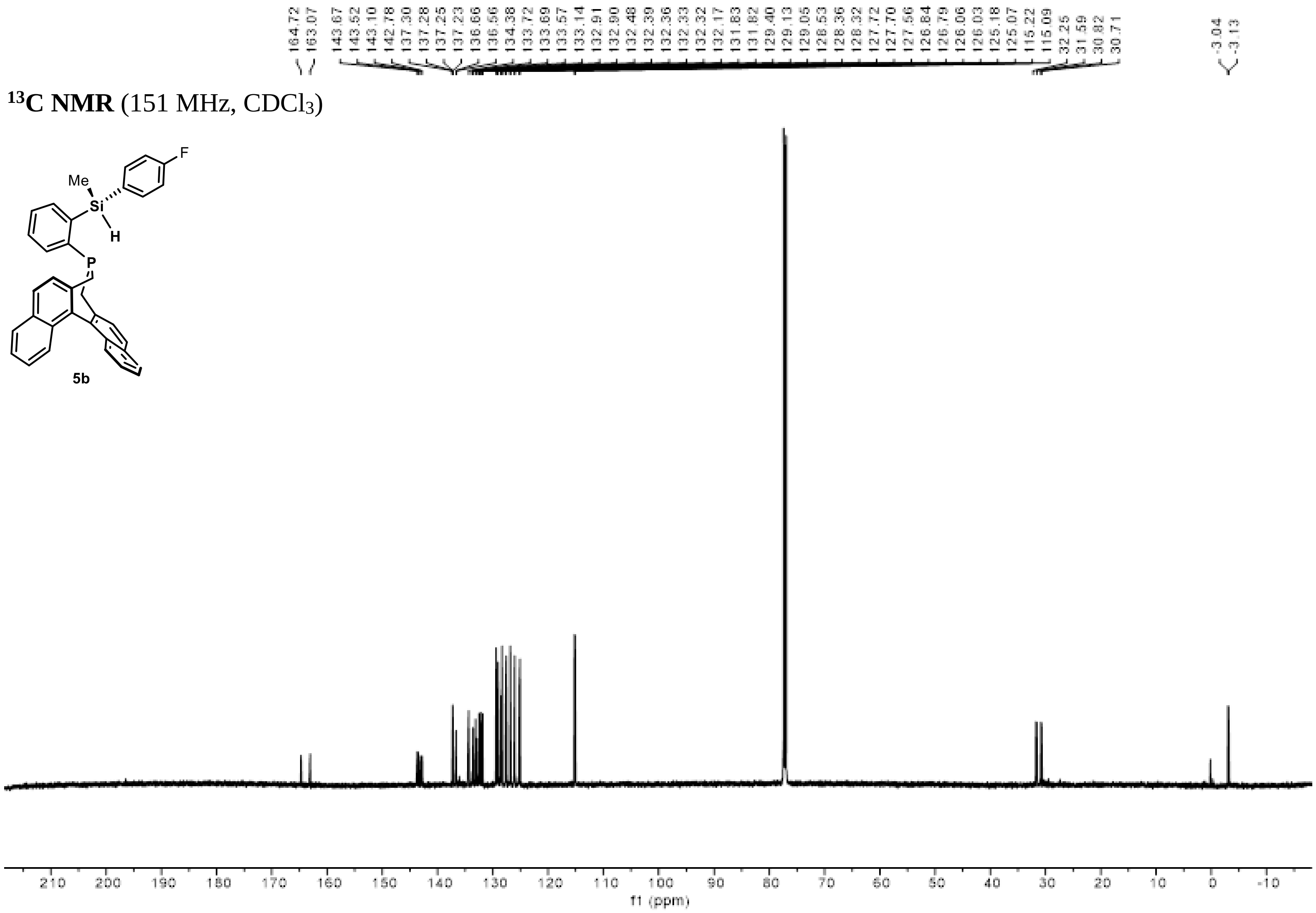
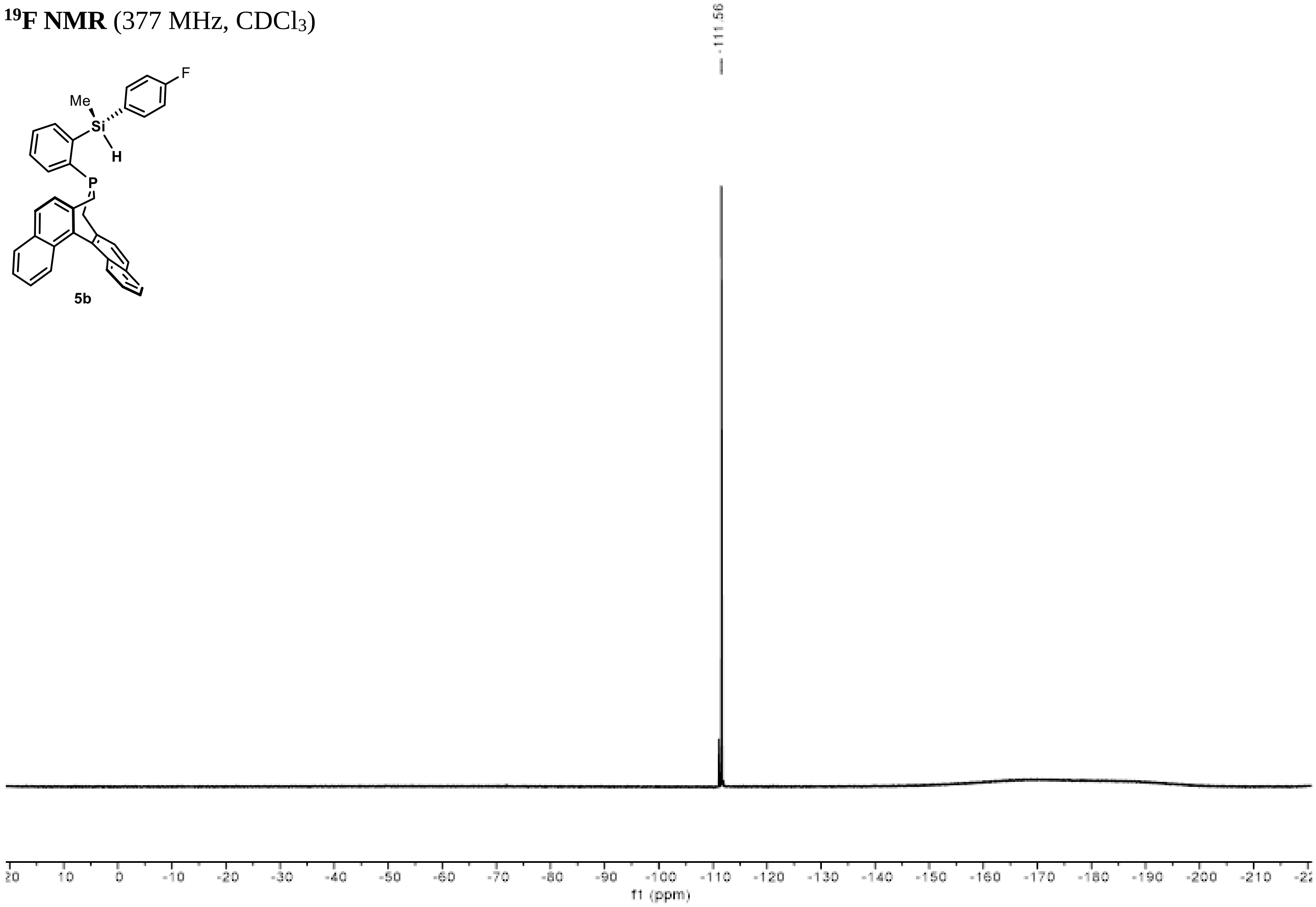


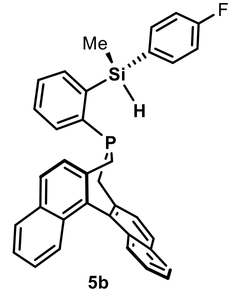
5b

^{19}F NMR (377 MHz, $CDCl_3$)



5b

^{31}P NMR (243 MHz, CDCl$_3$)



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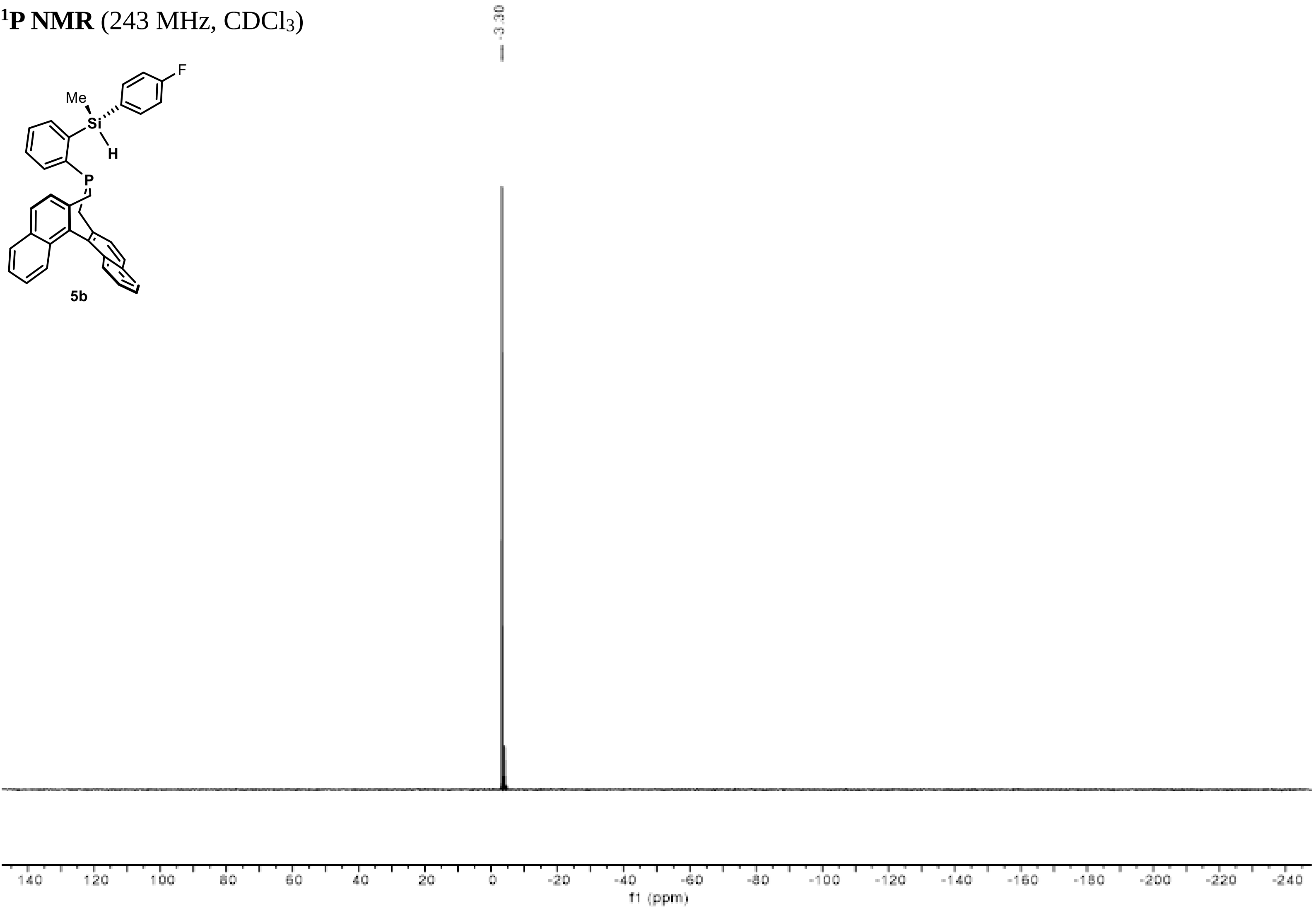

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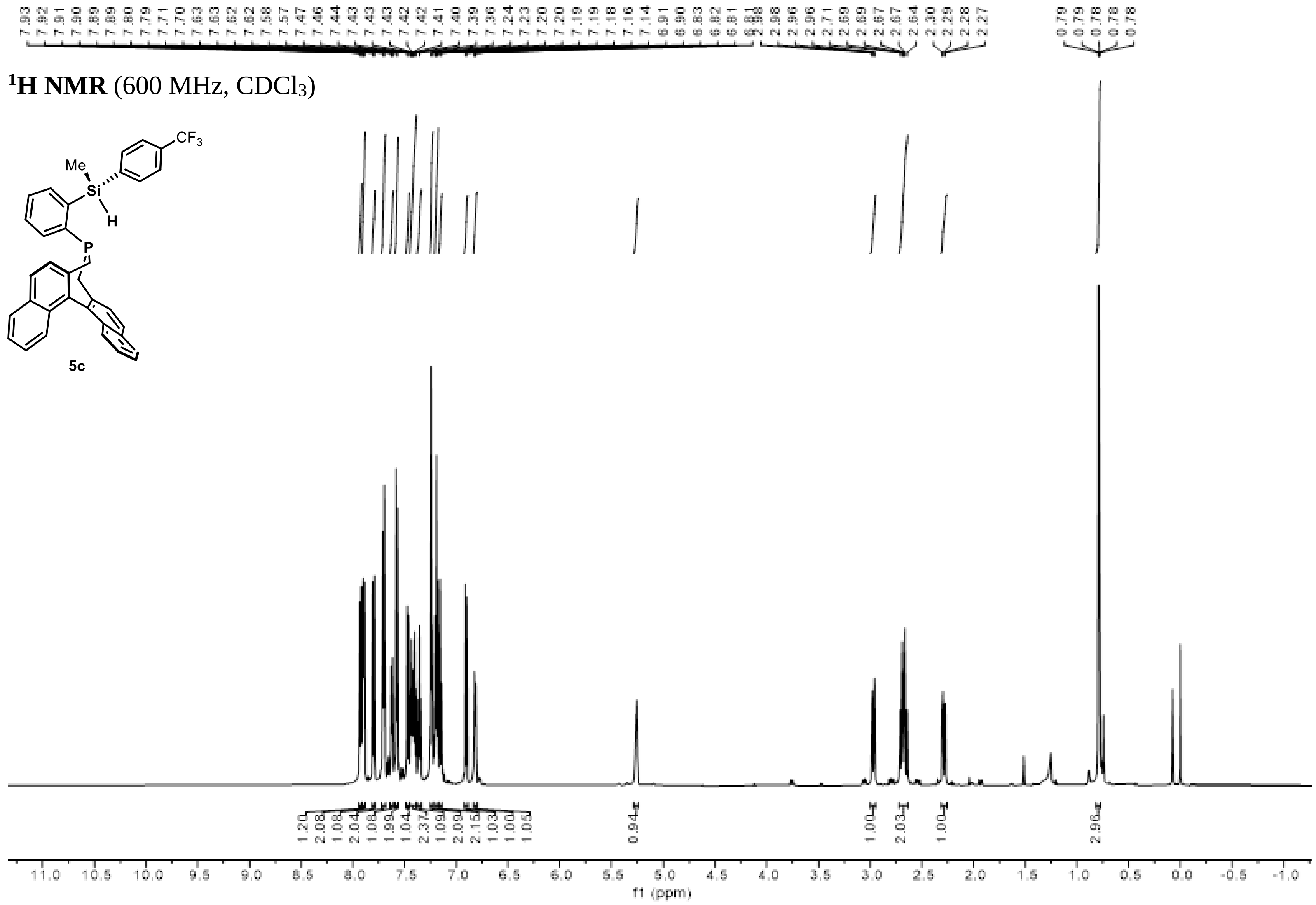

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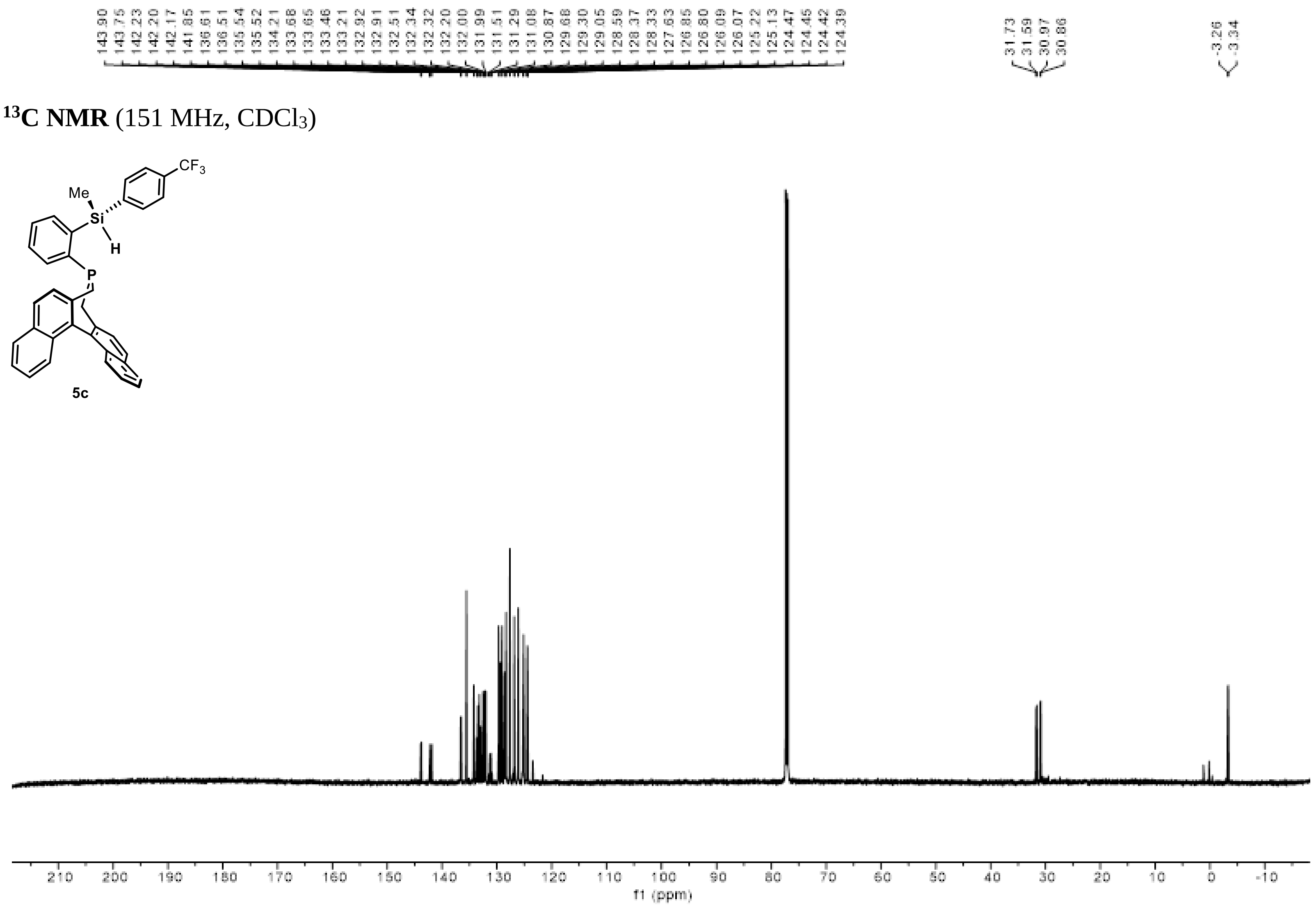

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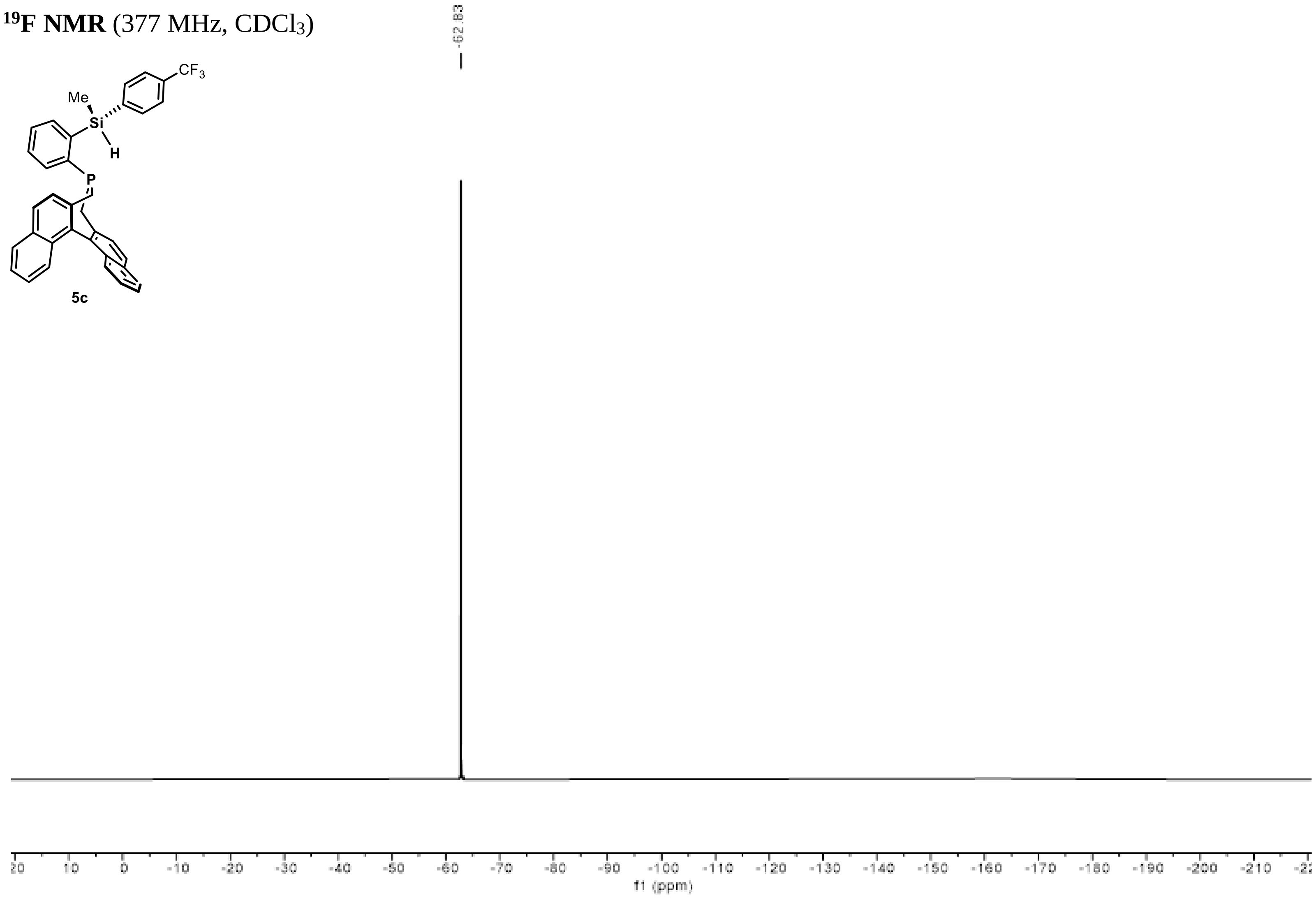

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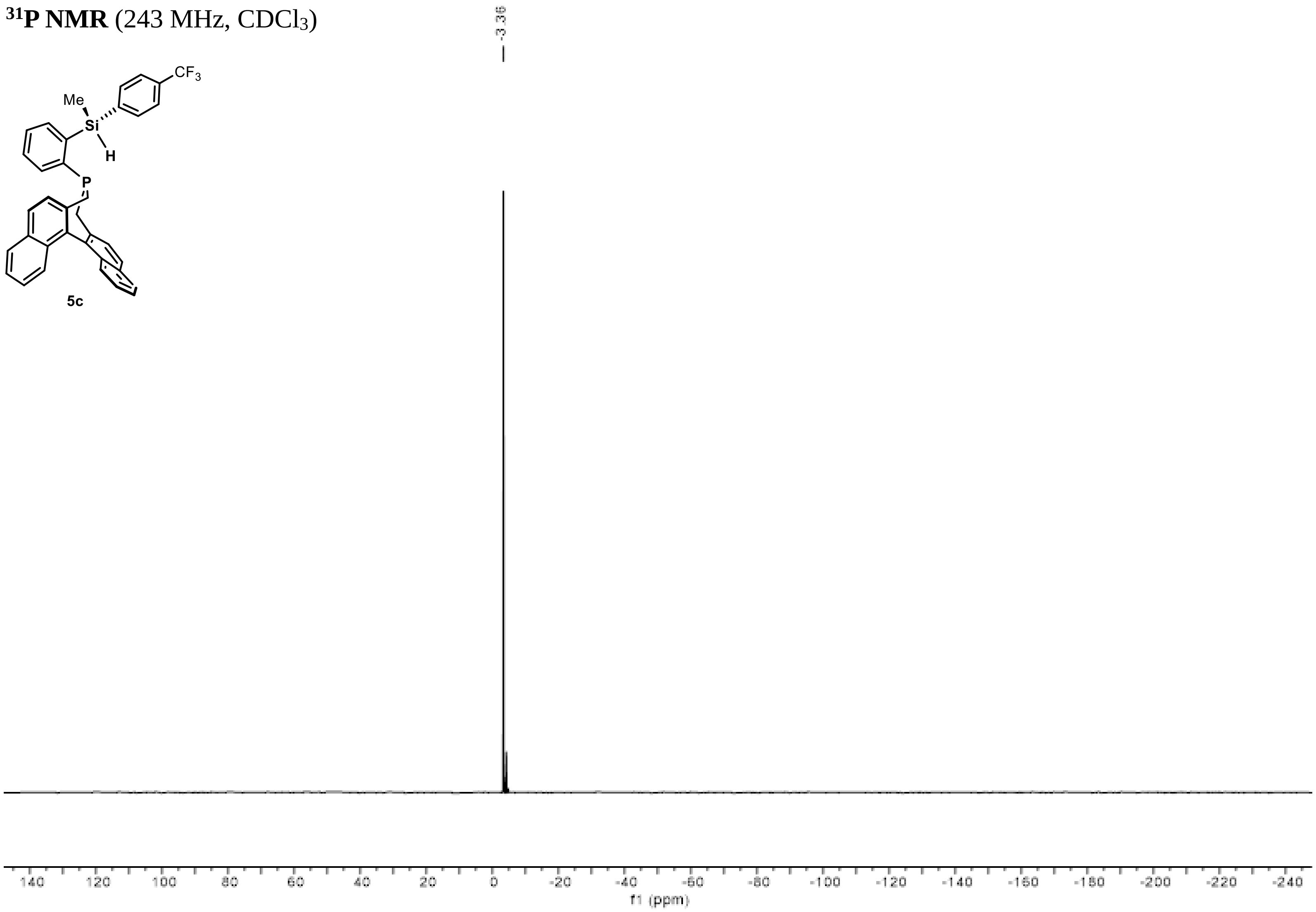

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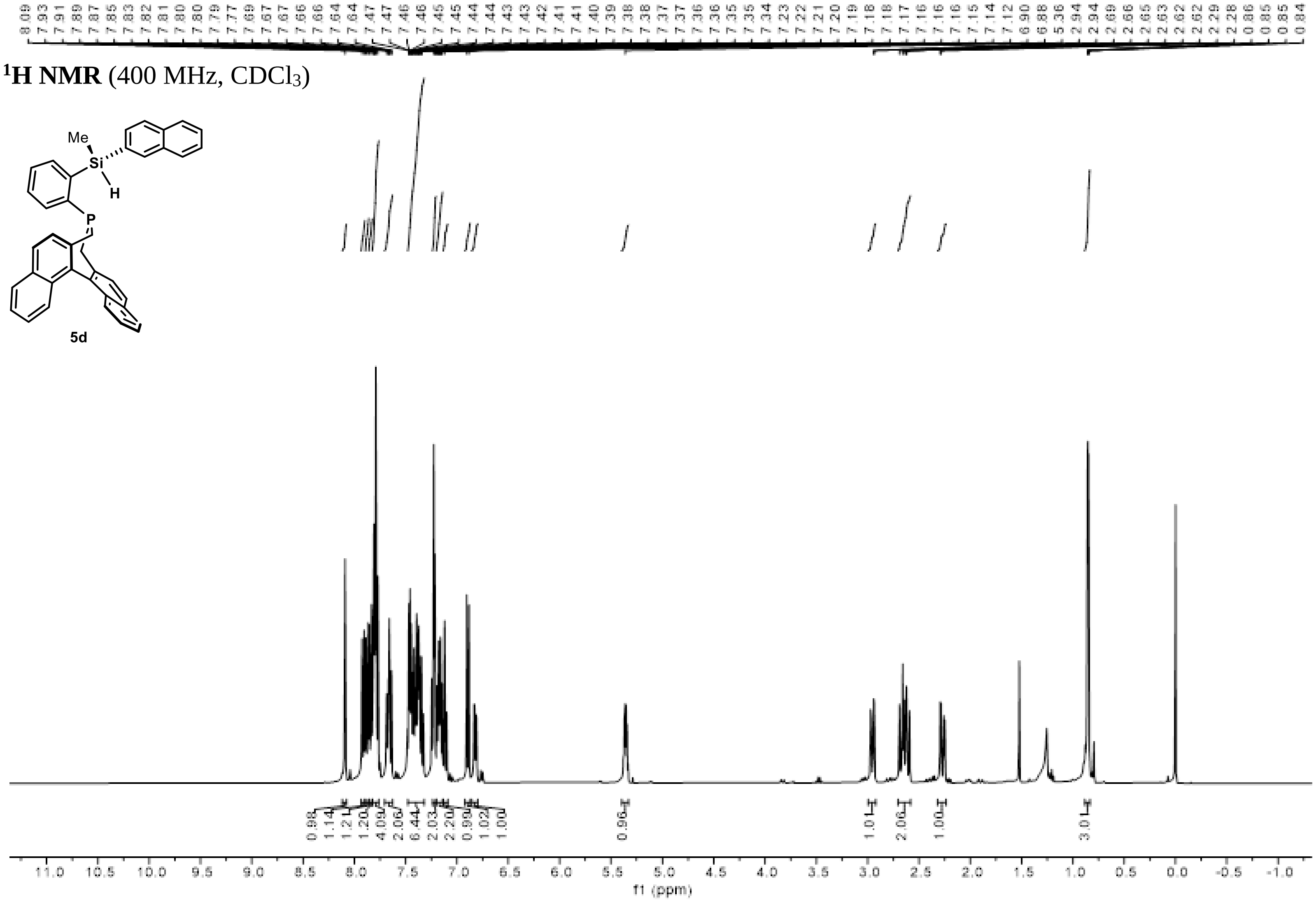

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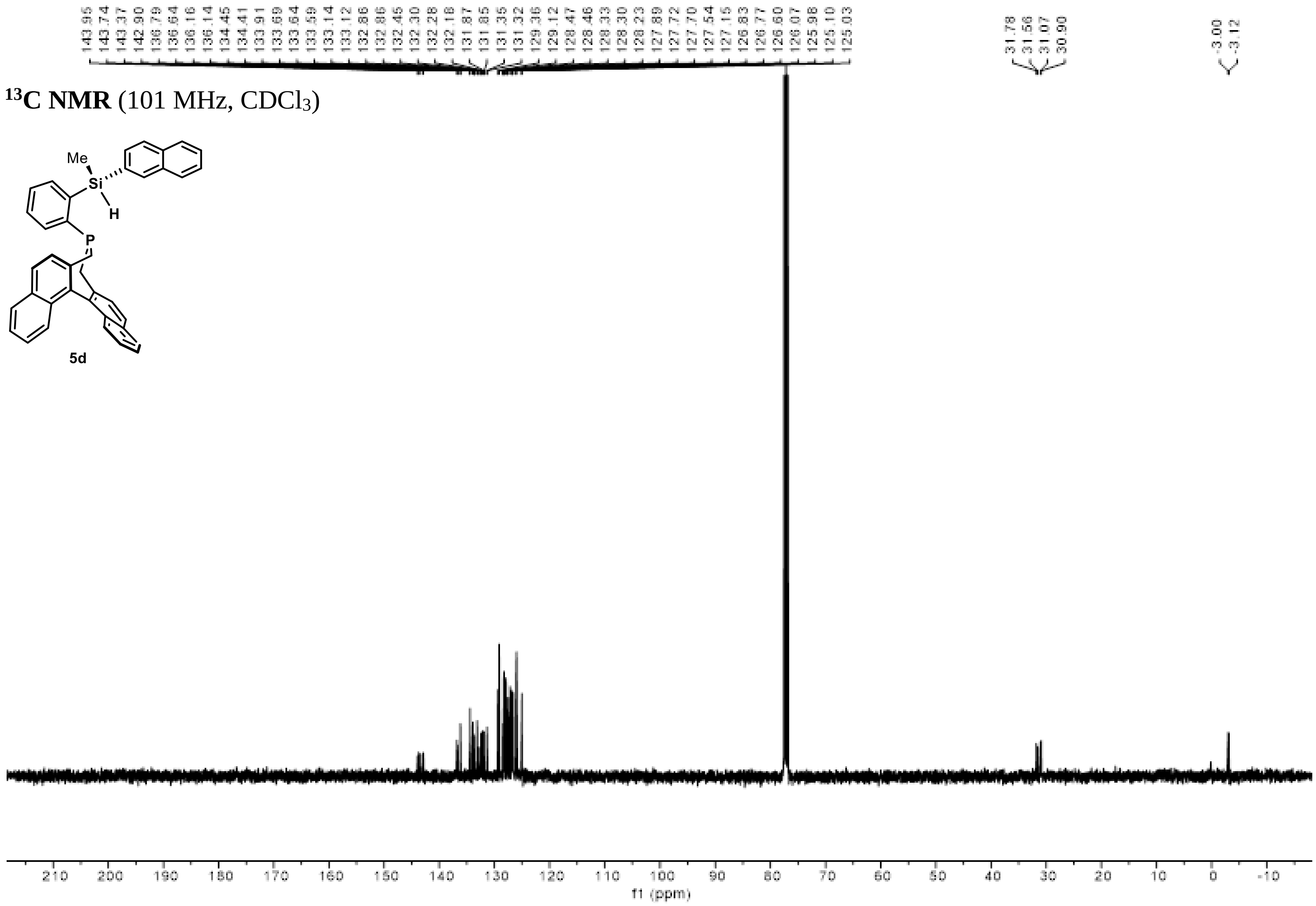
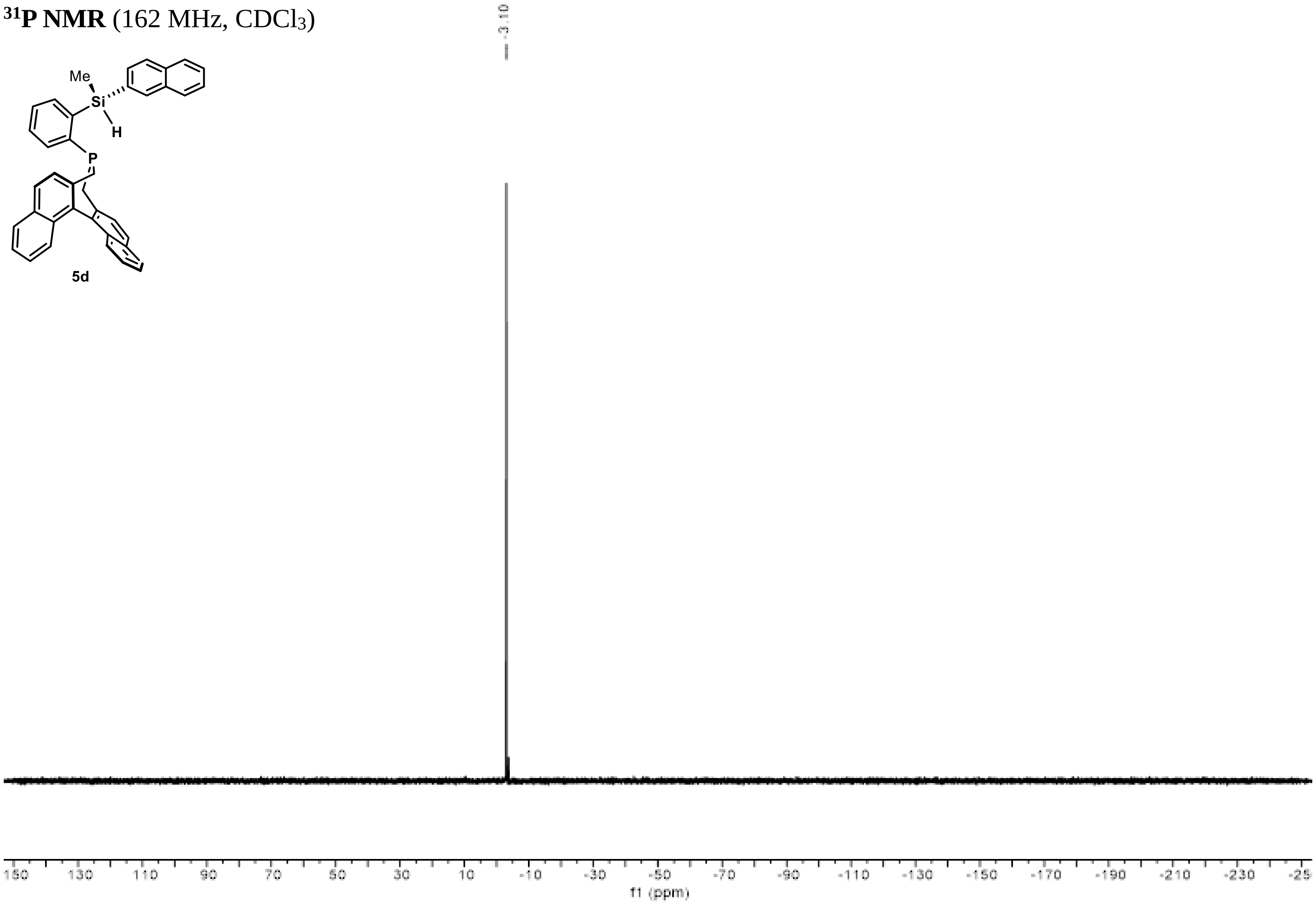
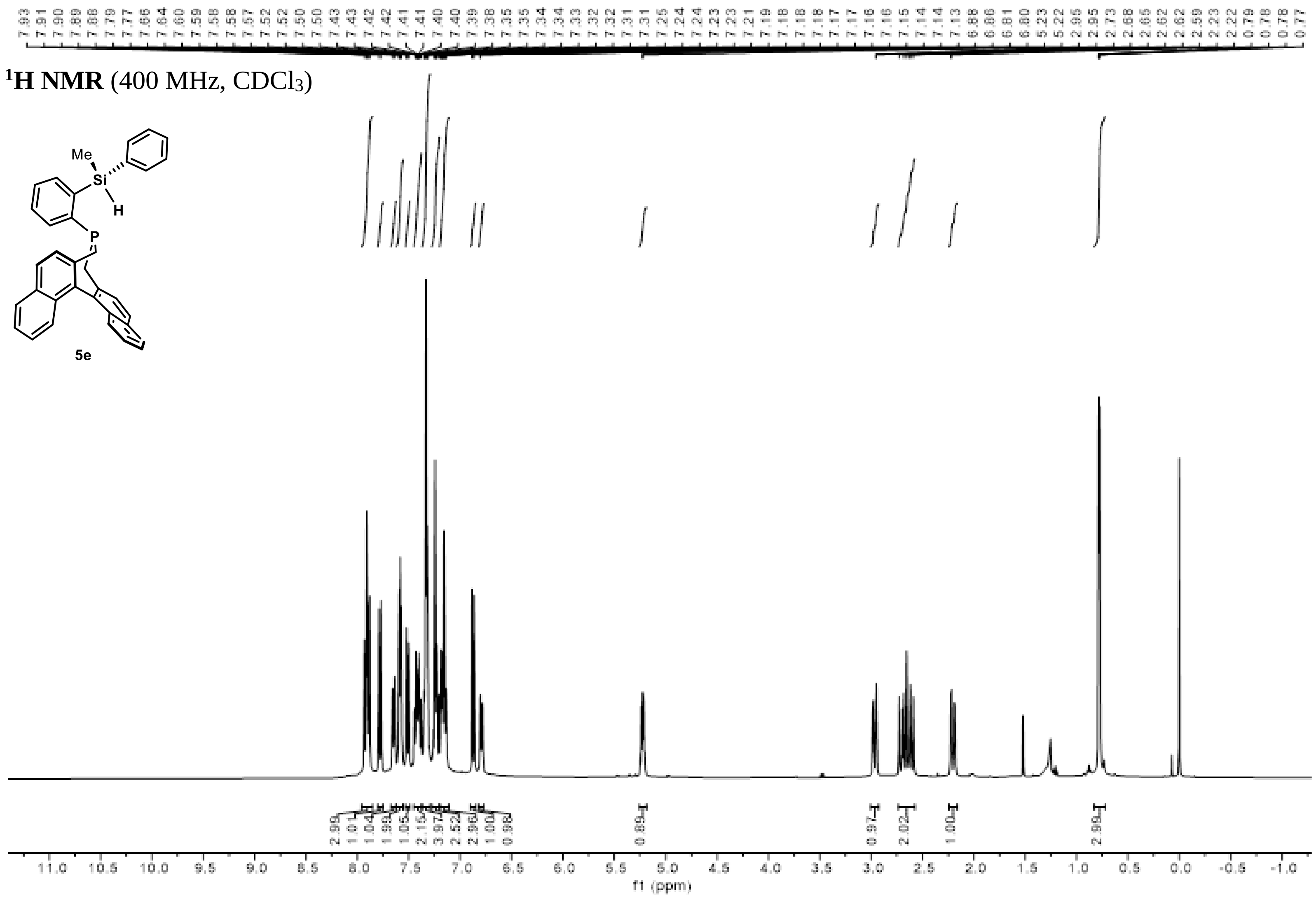


5d

^{31}**P NMR** (162 MHz, $CDCl_3$)

5d





^{1}H NMR (400 MHz, $CDCl_3$)

5e

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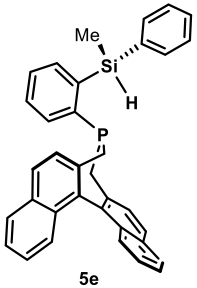

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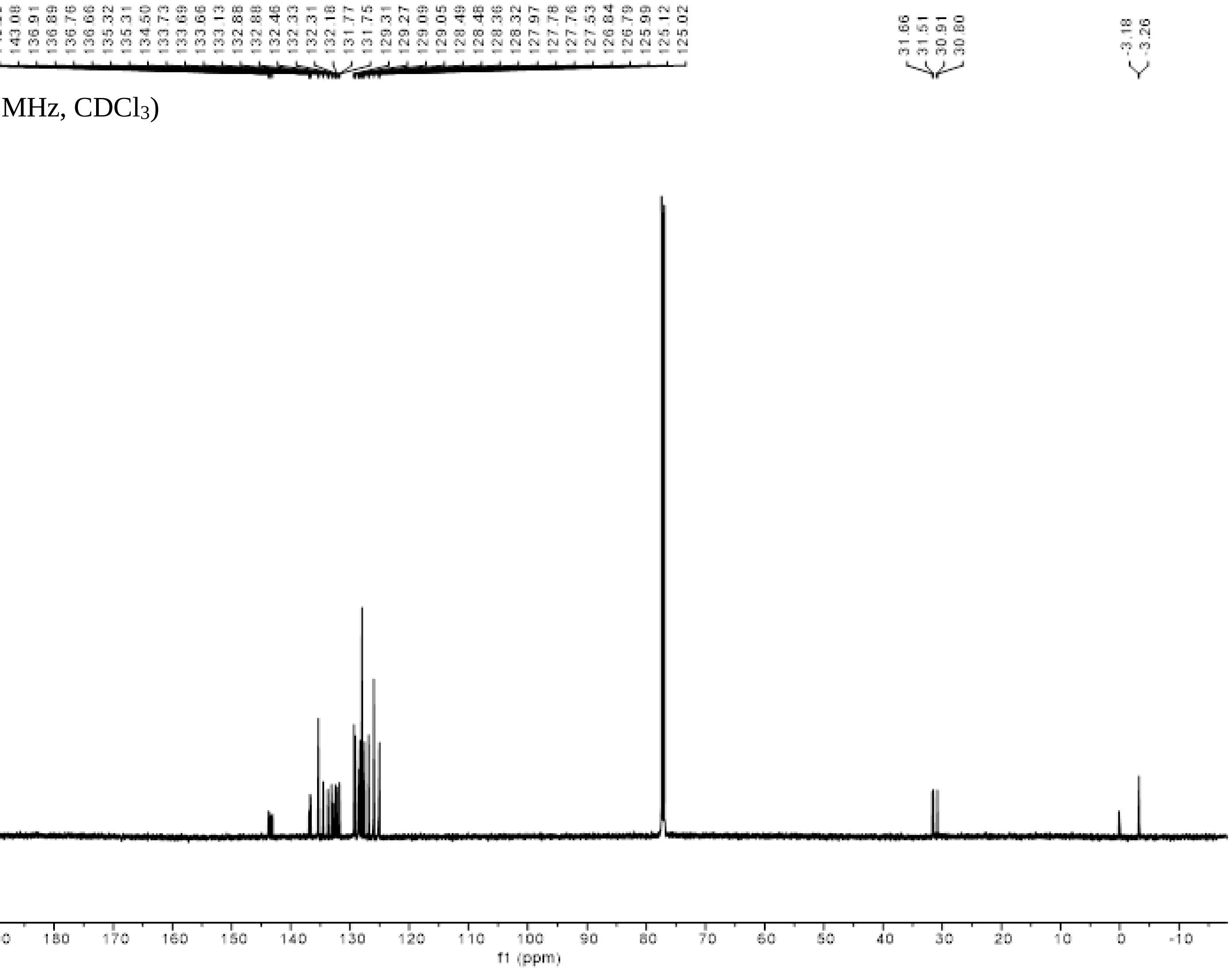

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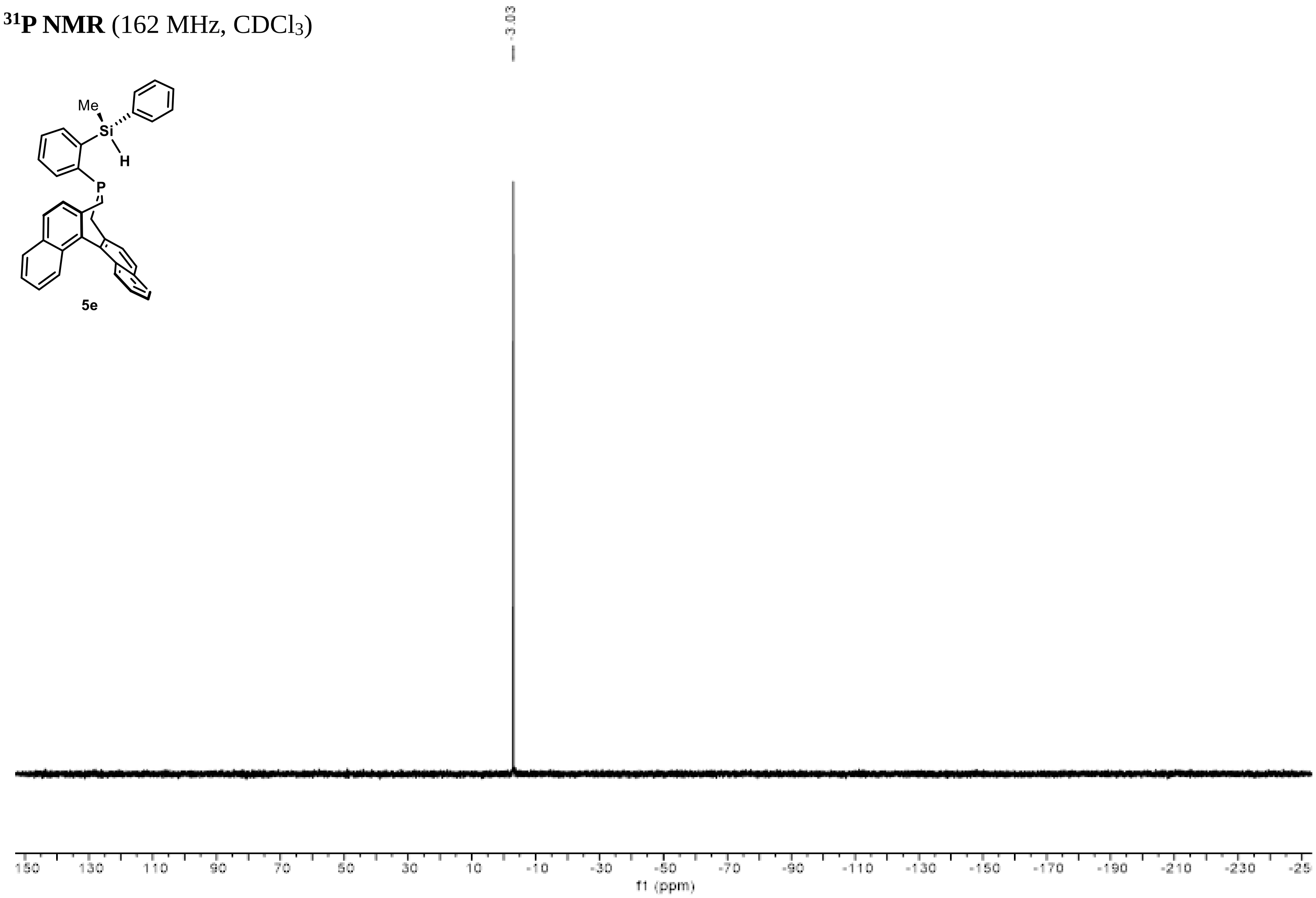

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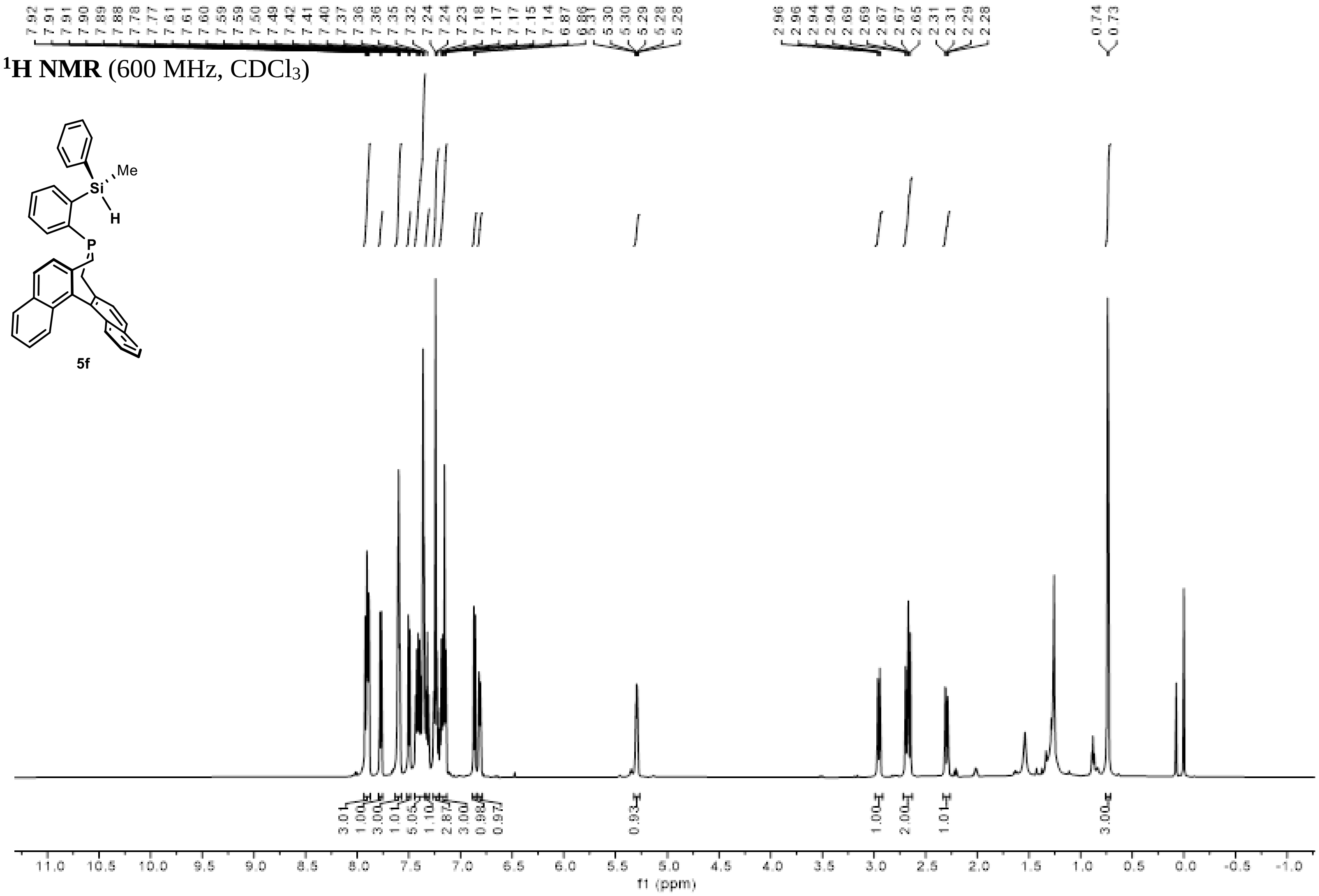

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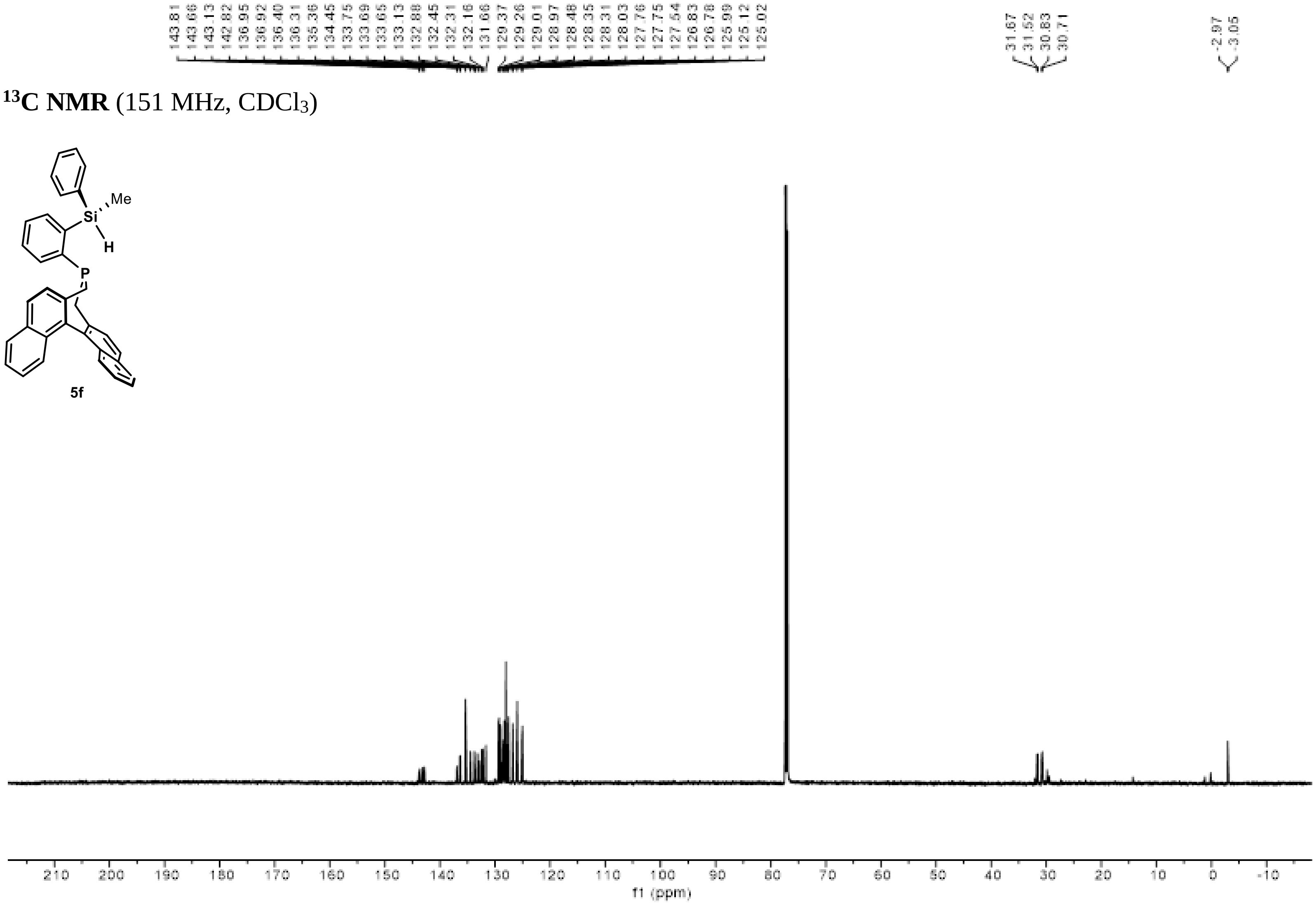
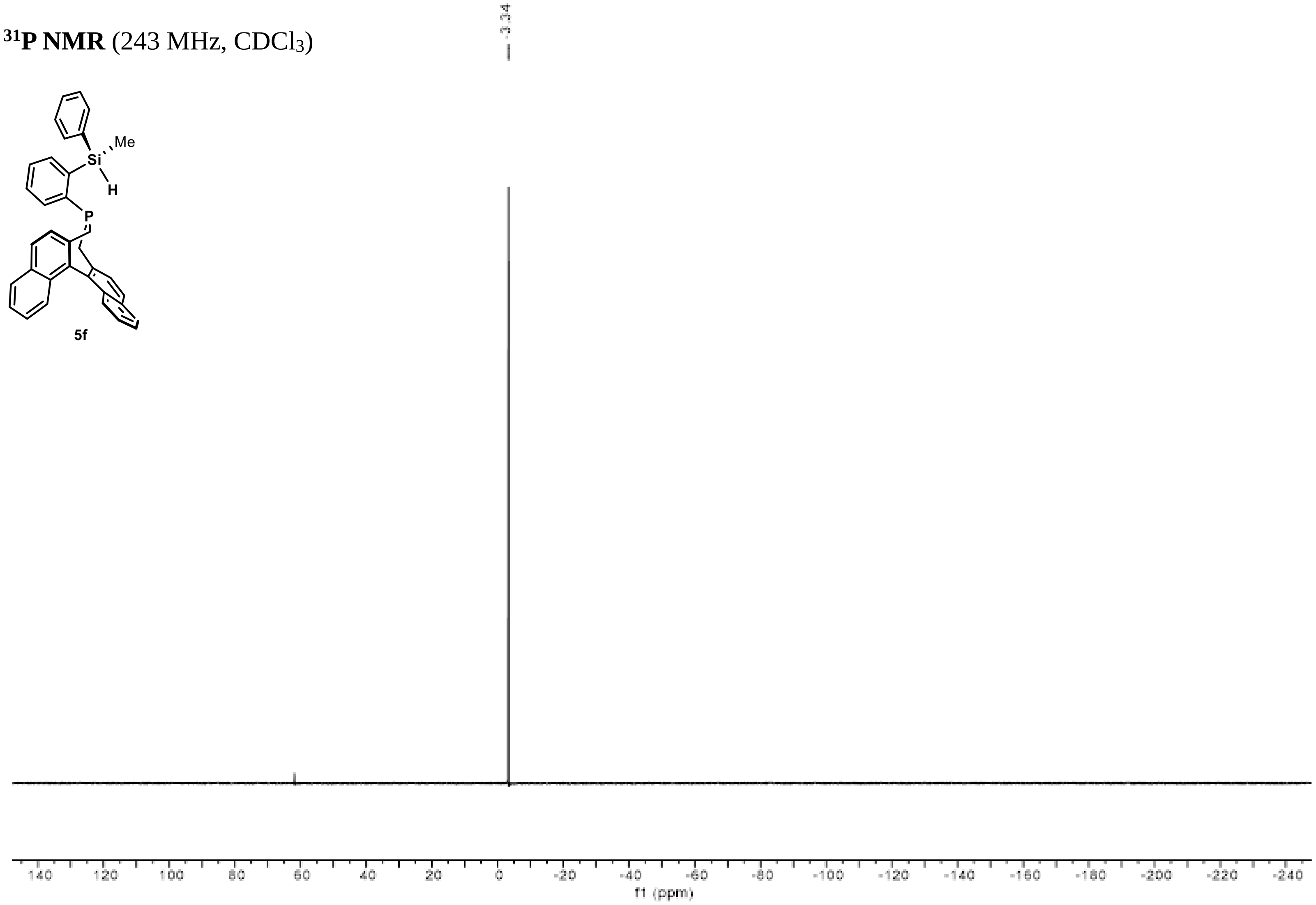


^{31}**P NMR** (243 MHz, $CDCl_3$)



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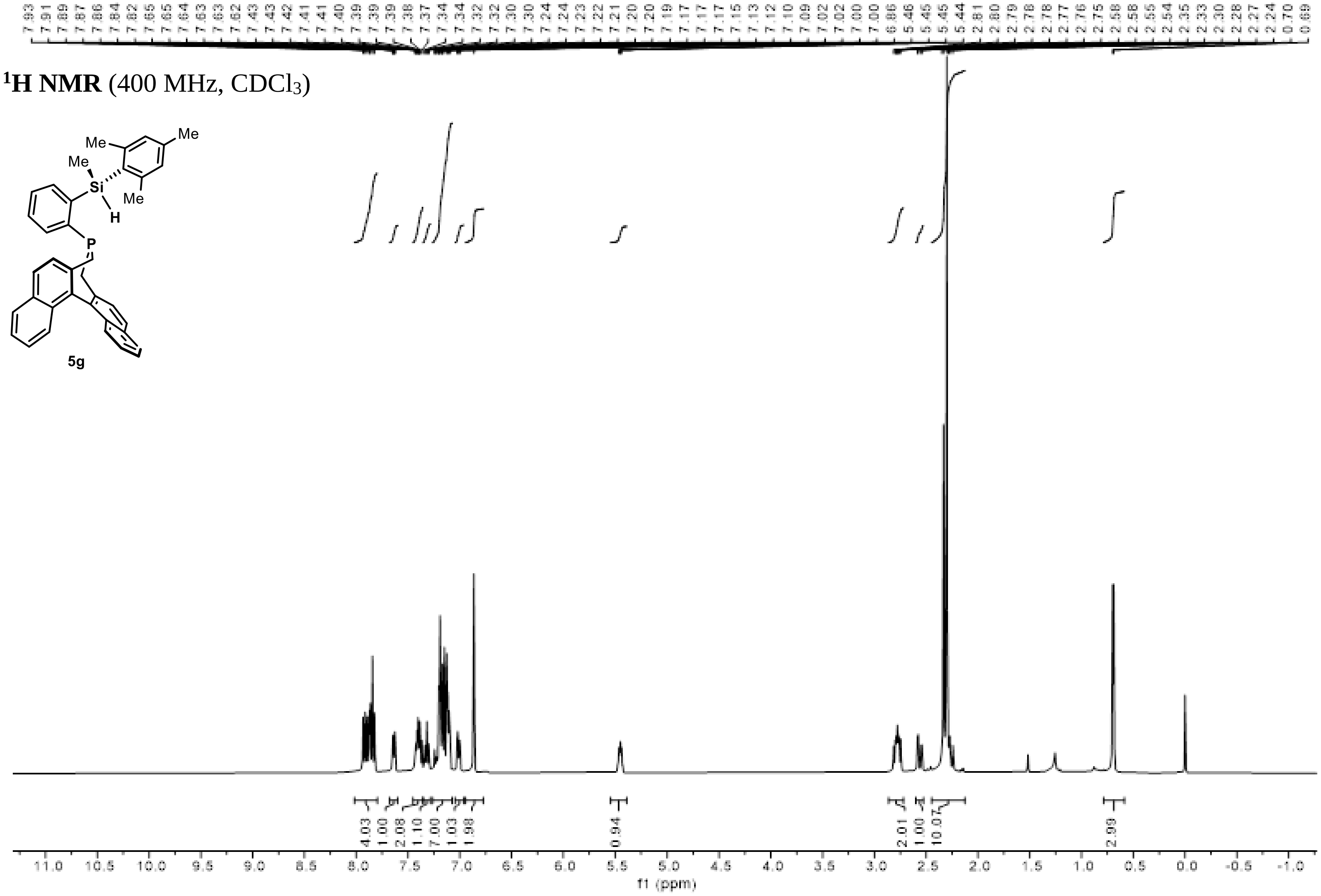

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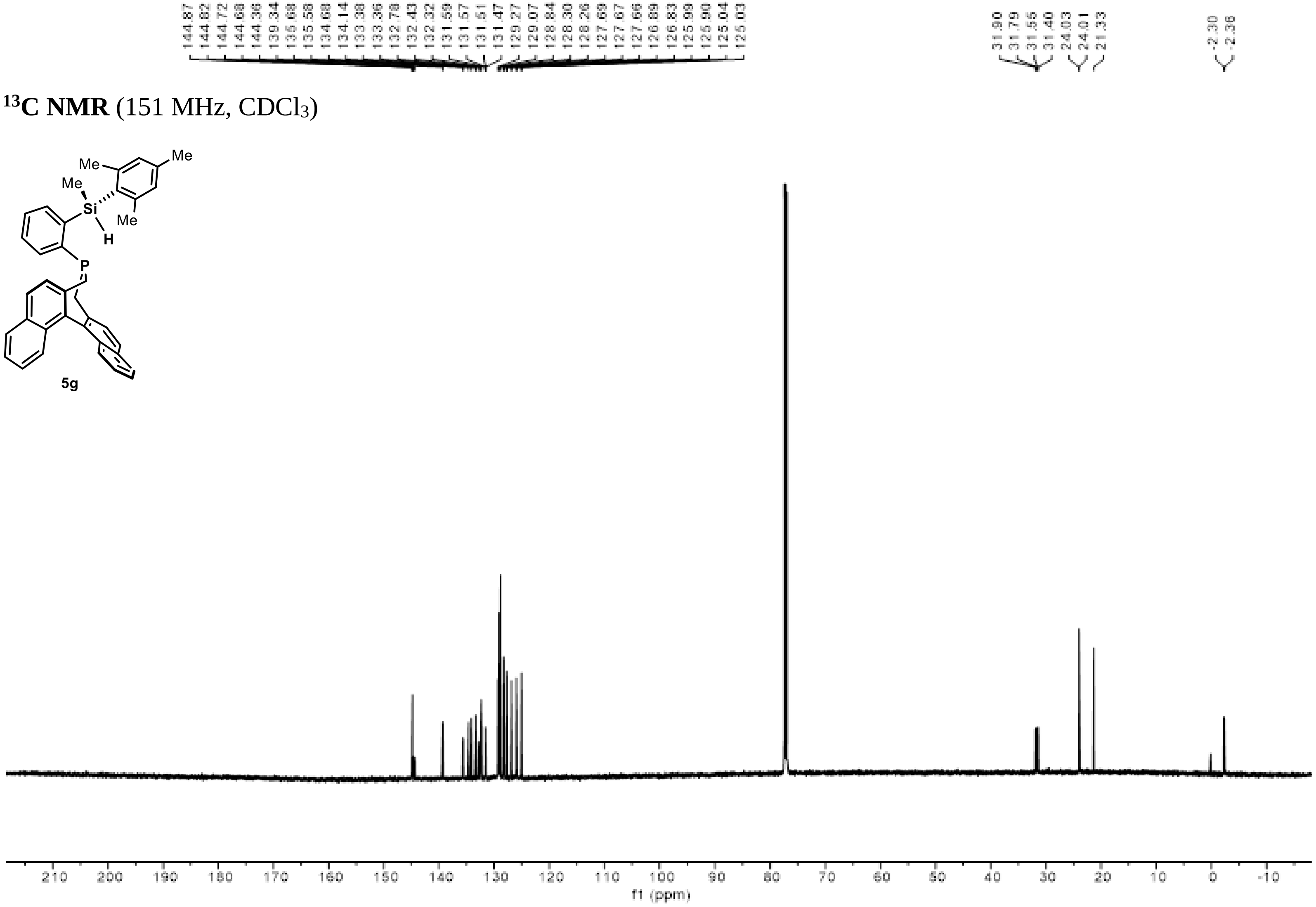

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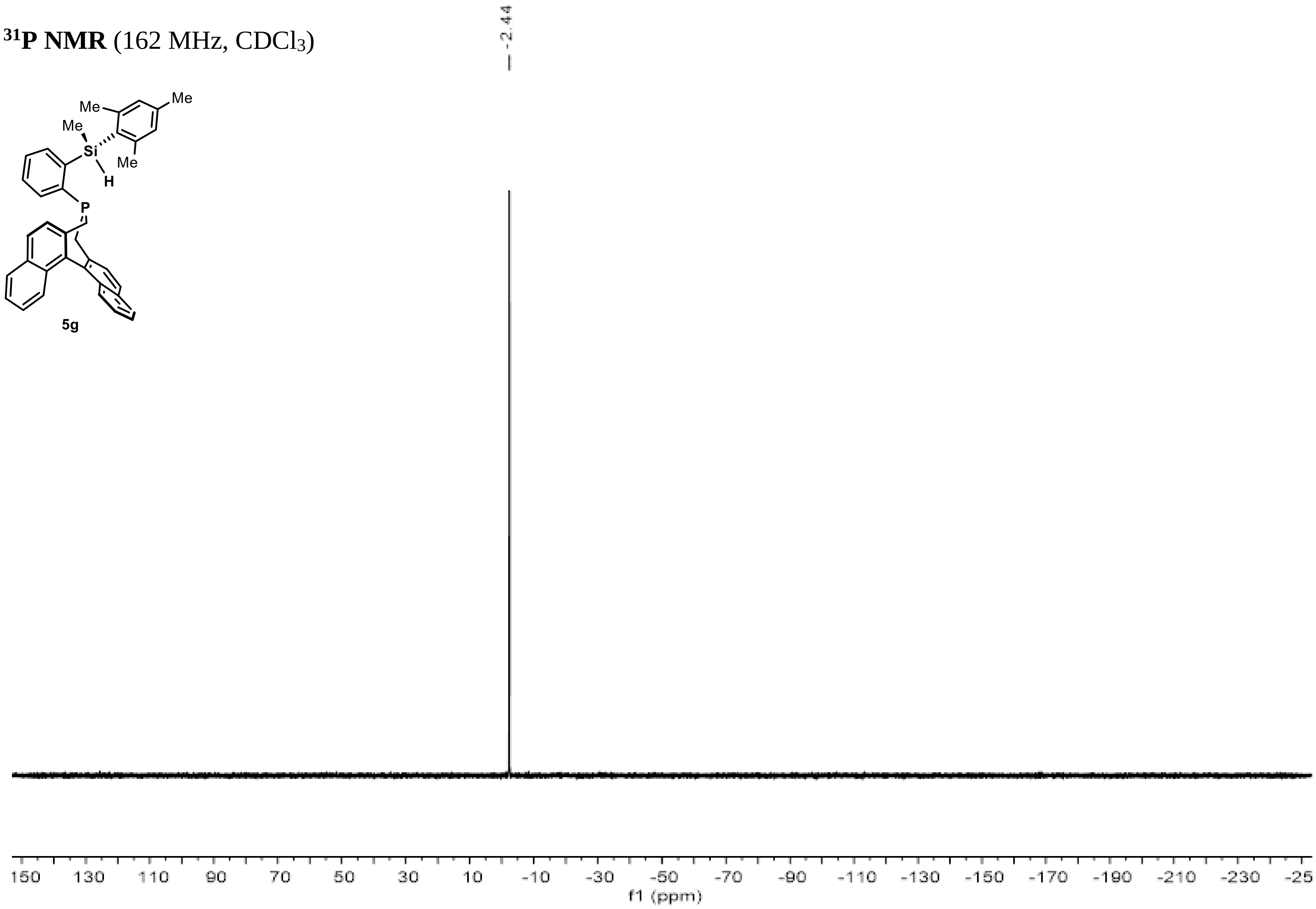

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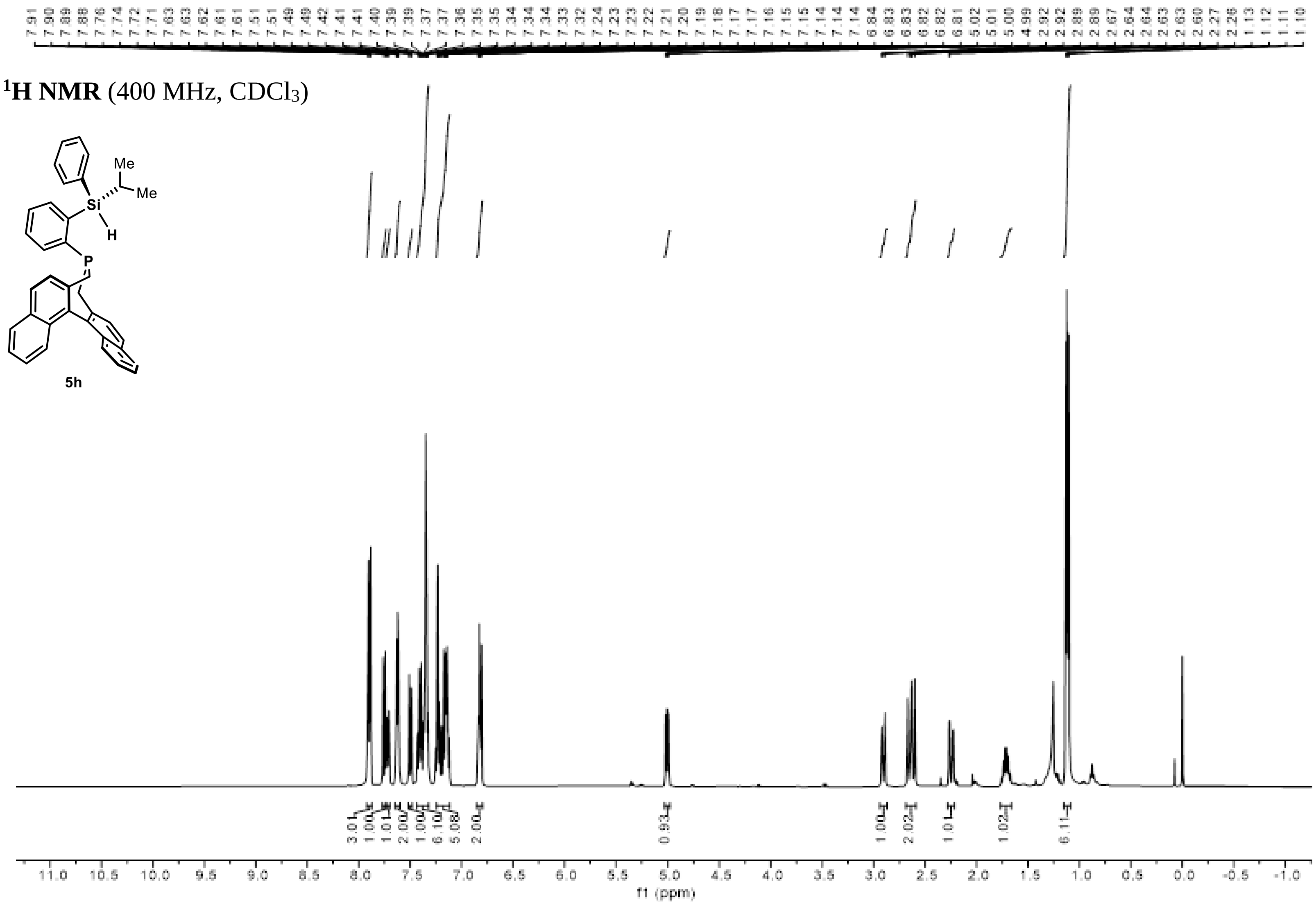

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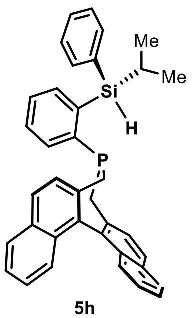

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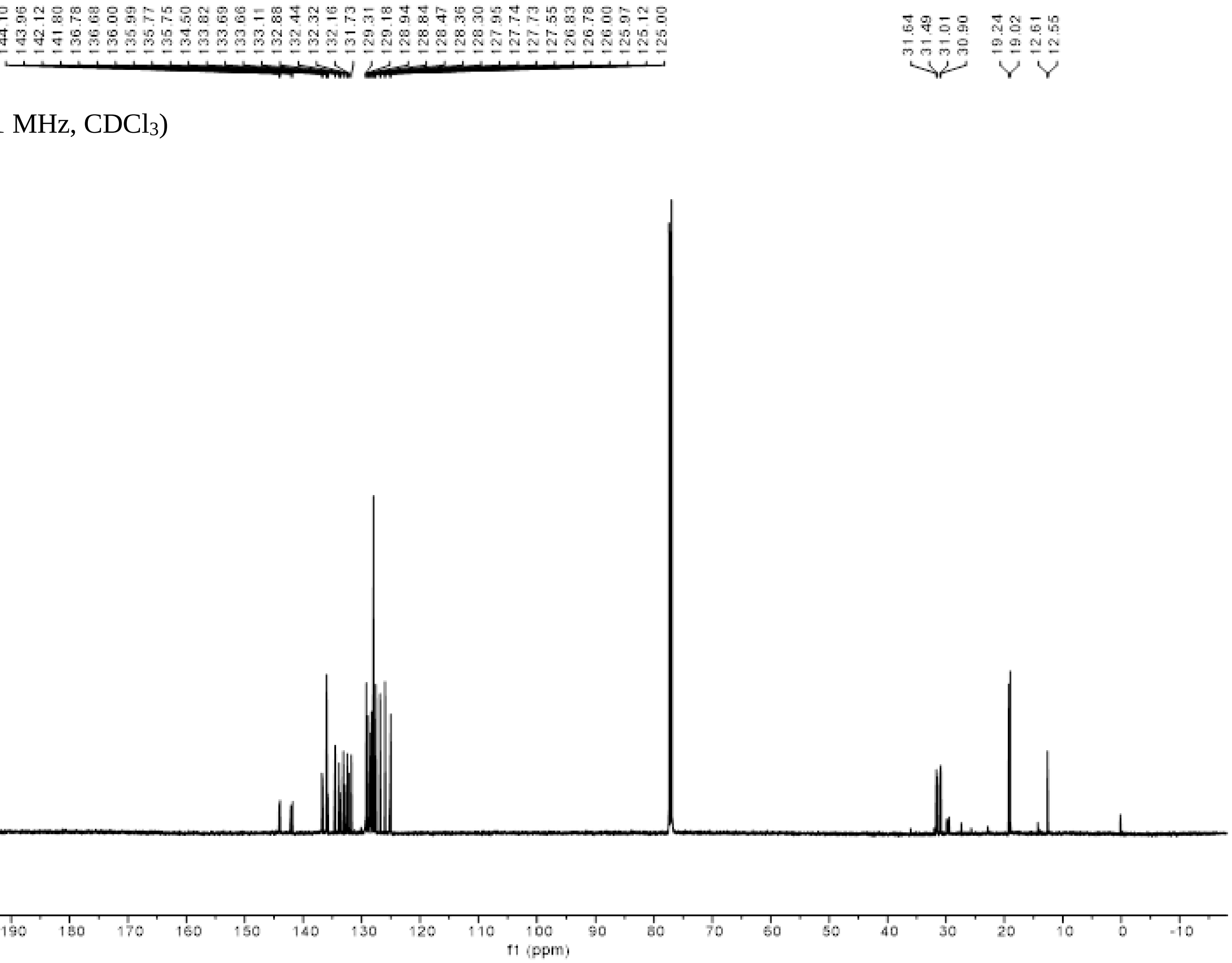

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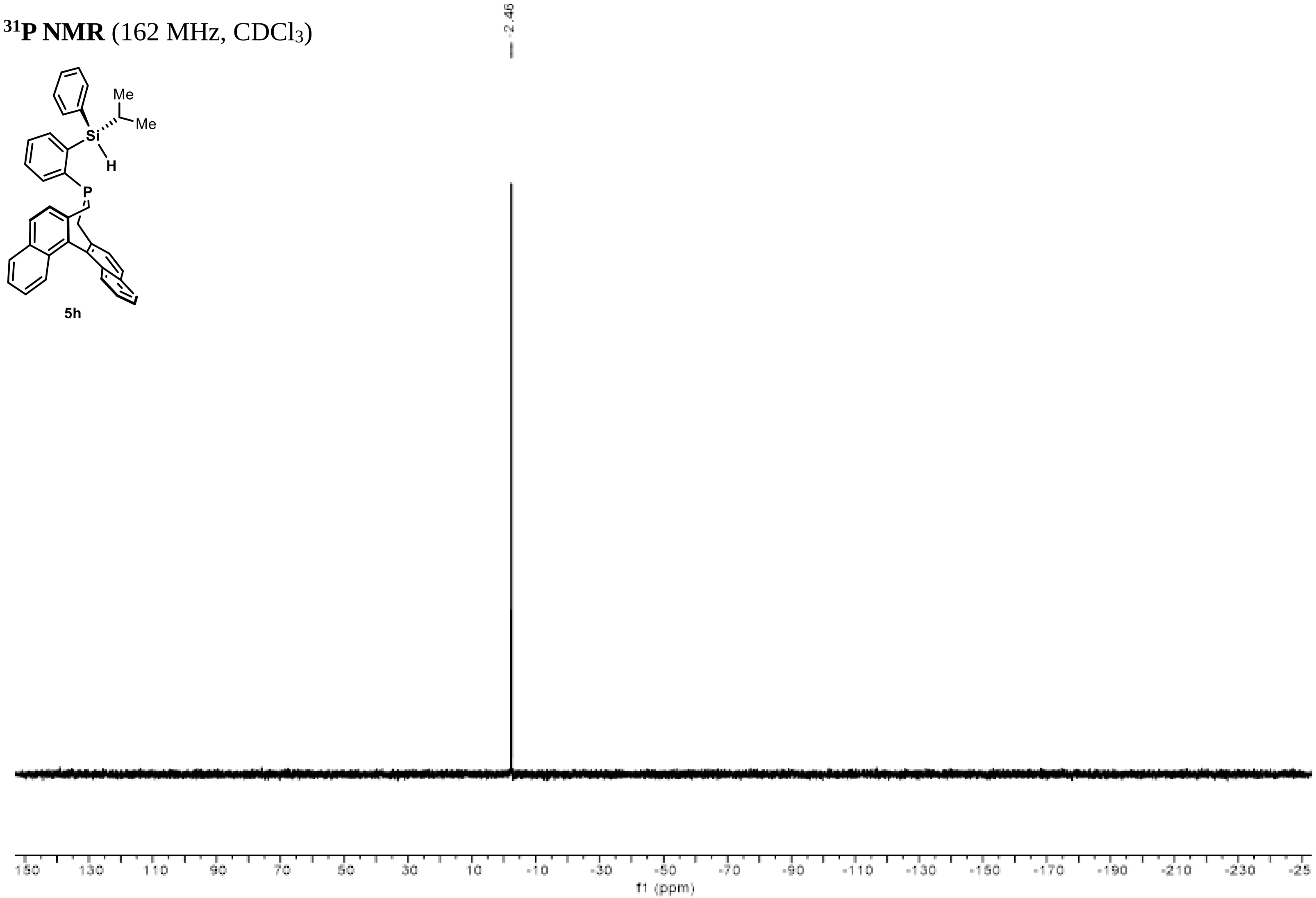

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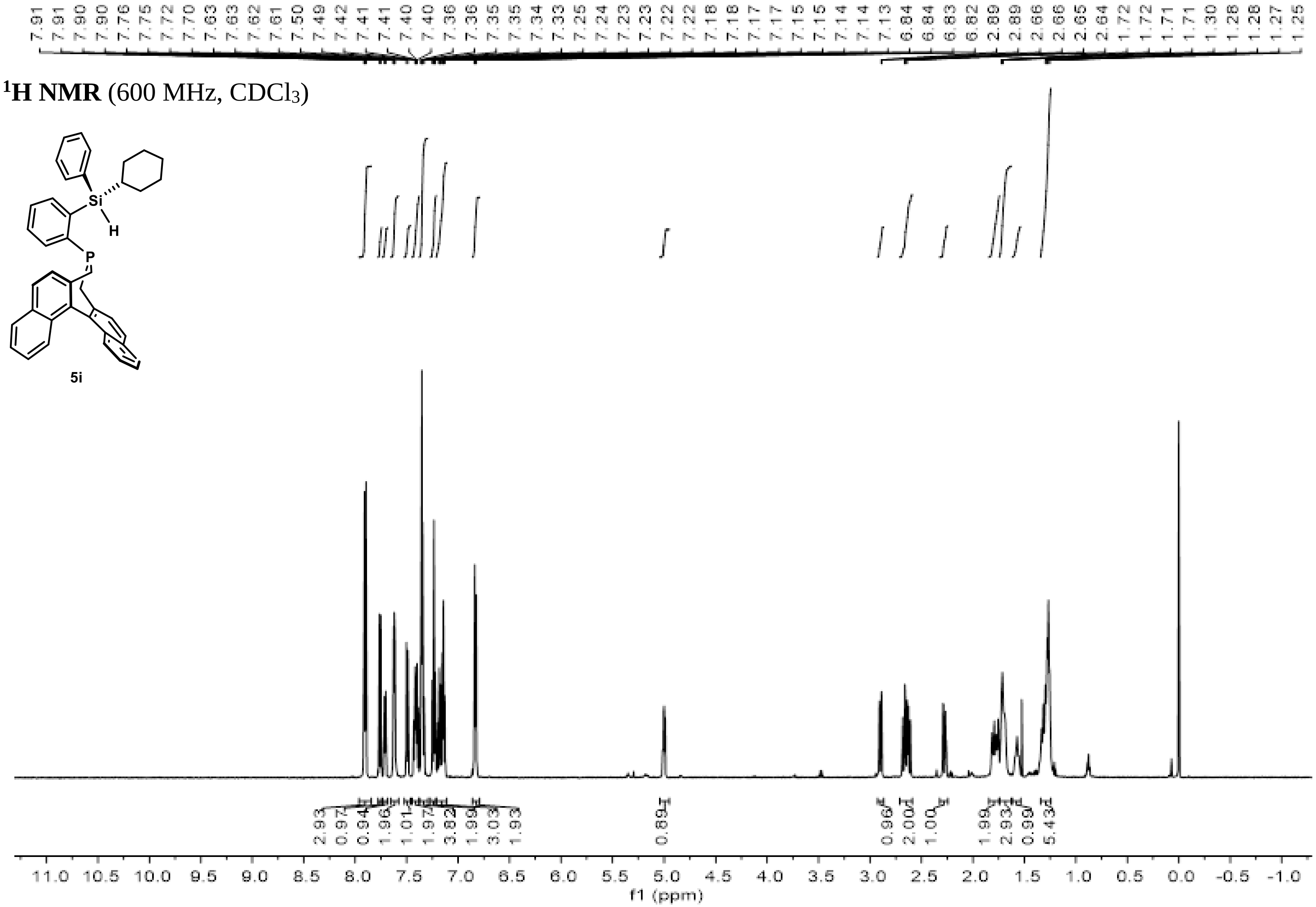

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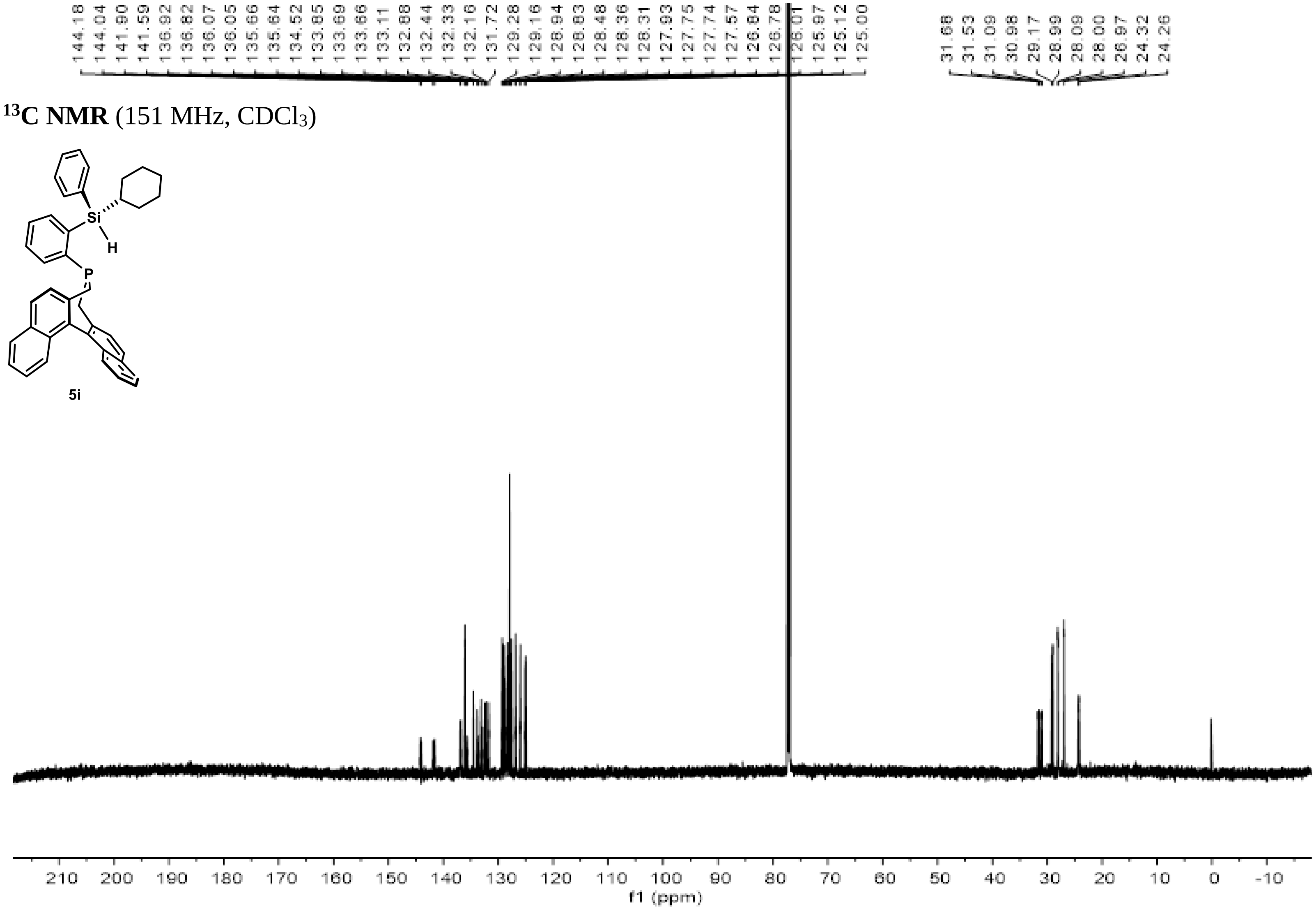
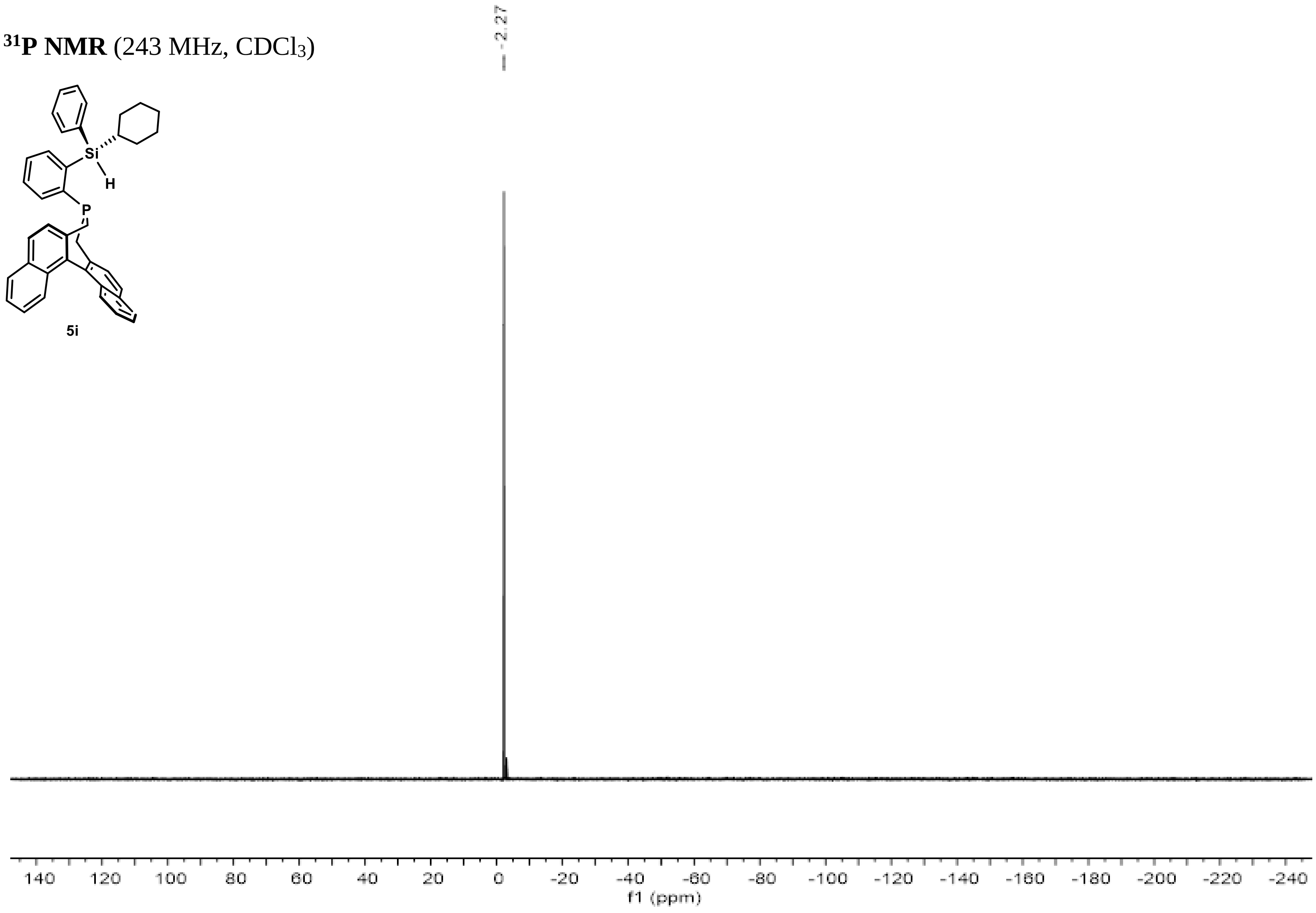
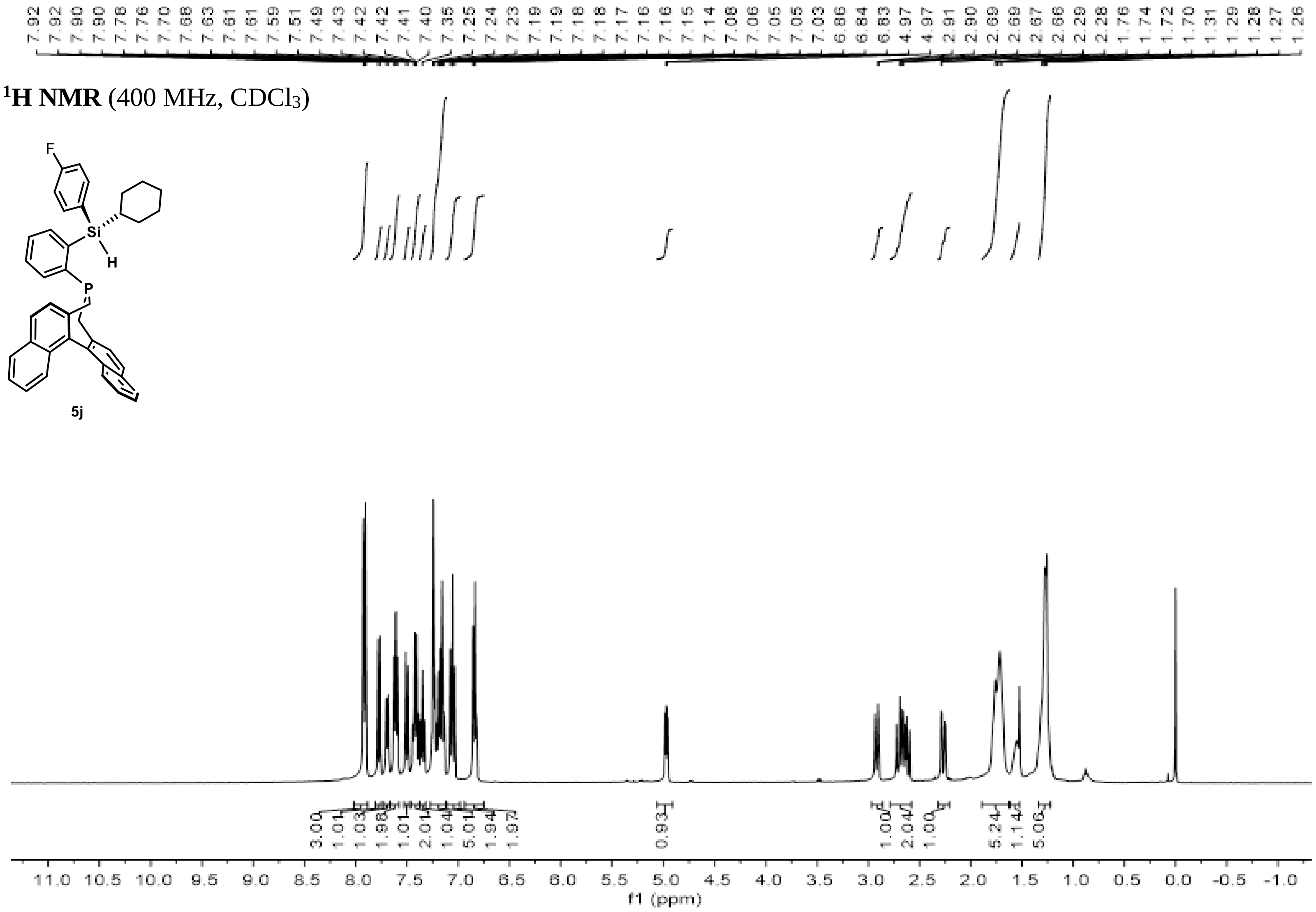


^{31}**P NMR** (243 MHz, $CDCl_3$)

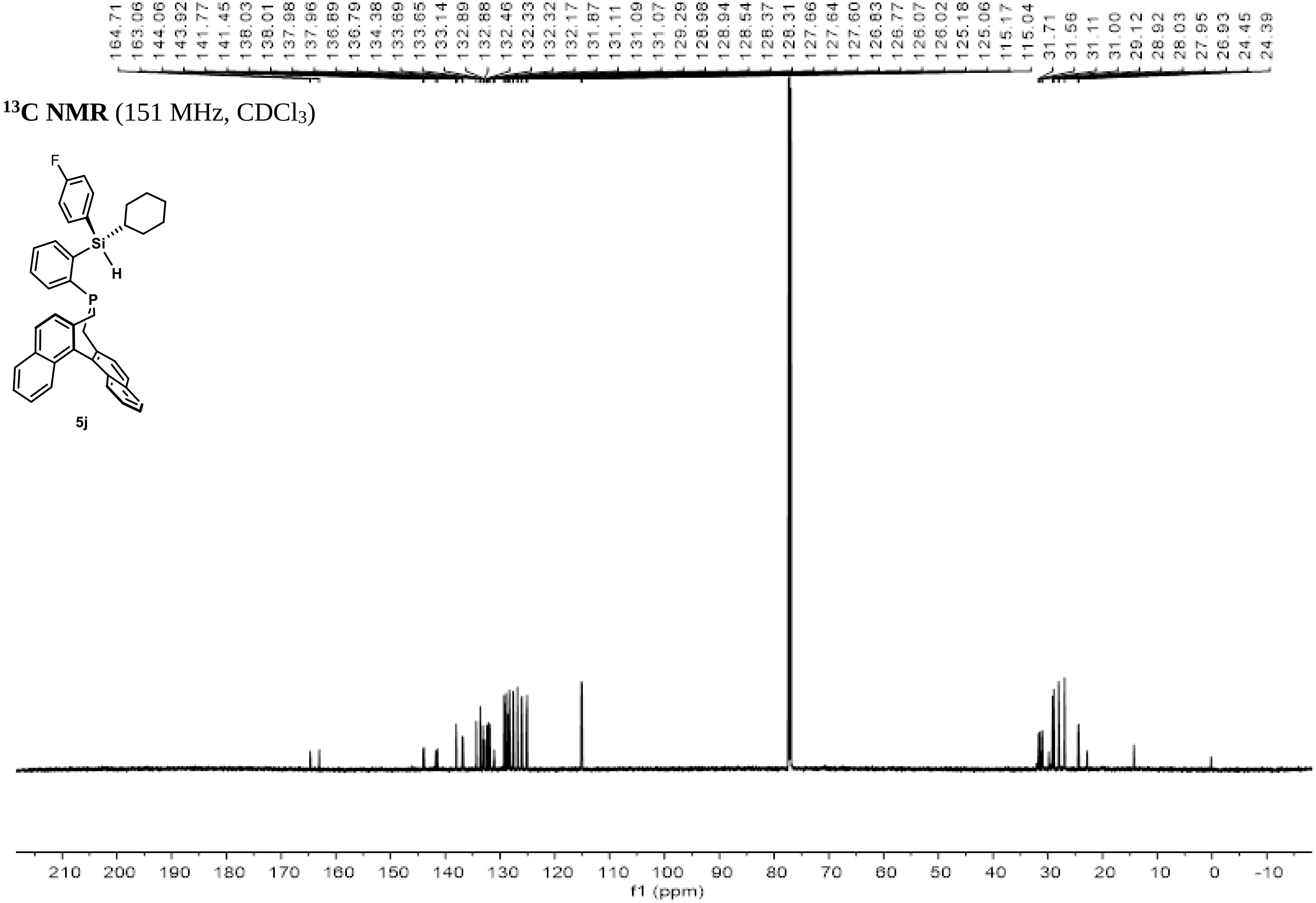


^{1}H NMR (400 MHz, $CDCl_3$)

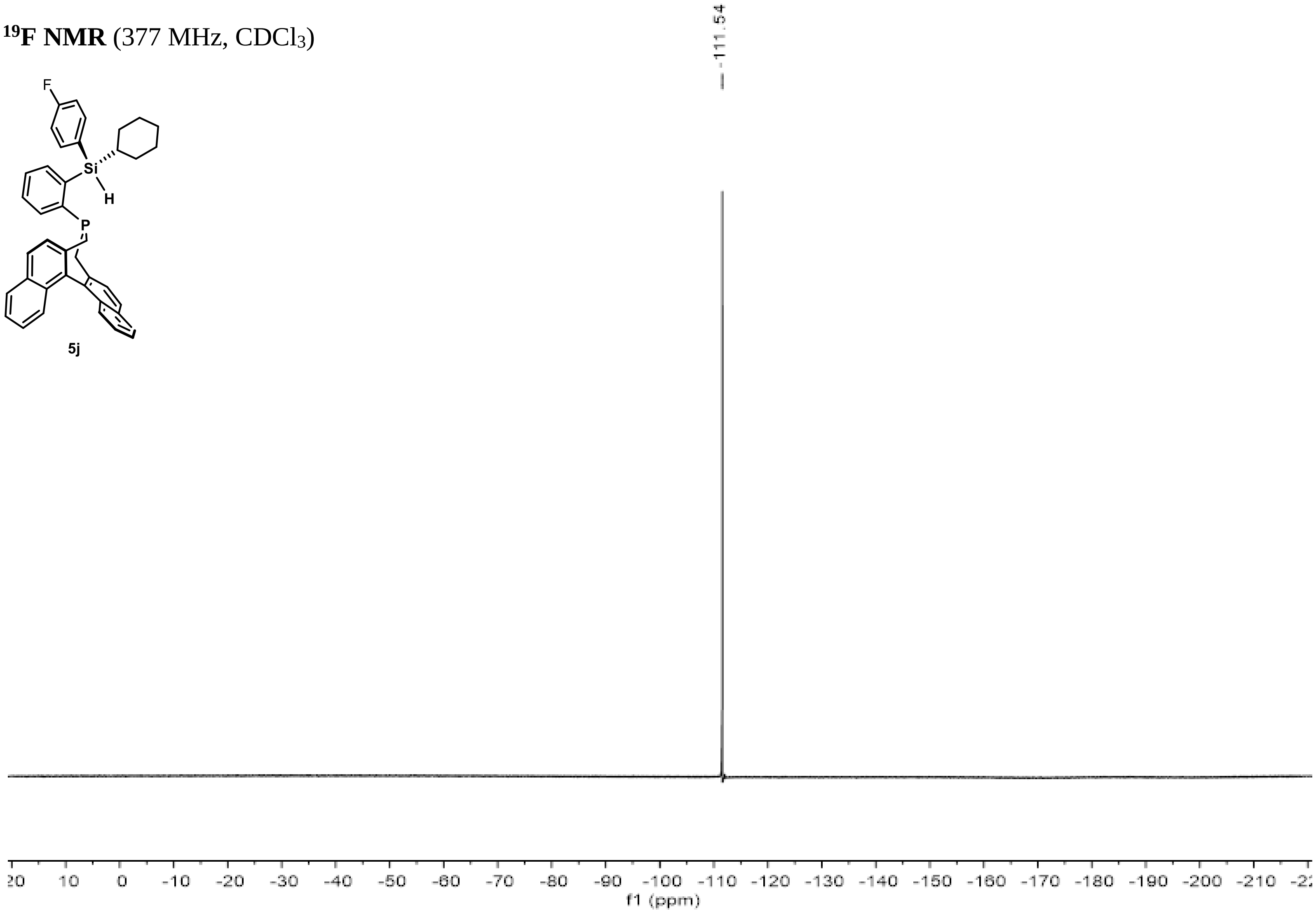


5j

^{13}C NMR (151 MHz, $CDCl_3$)

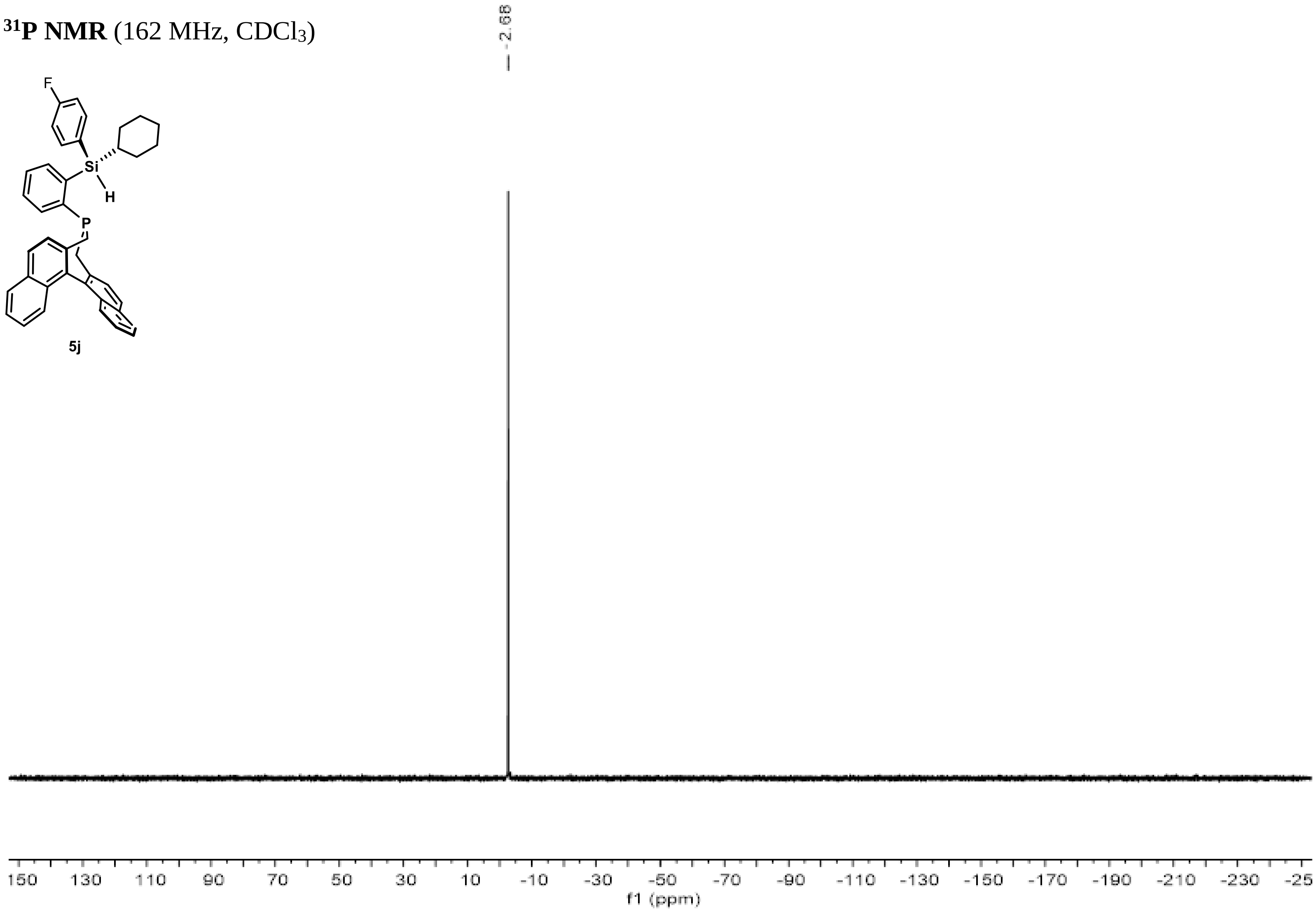


^{19}F NMR (377 MHz, $CDCl_3$)

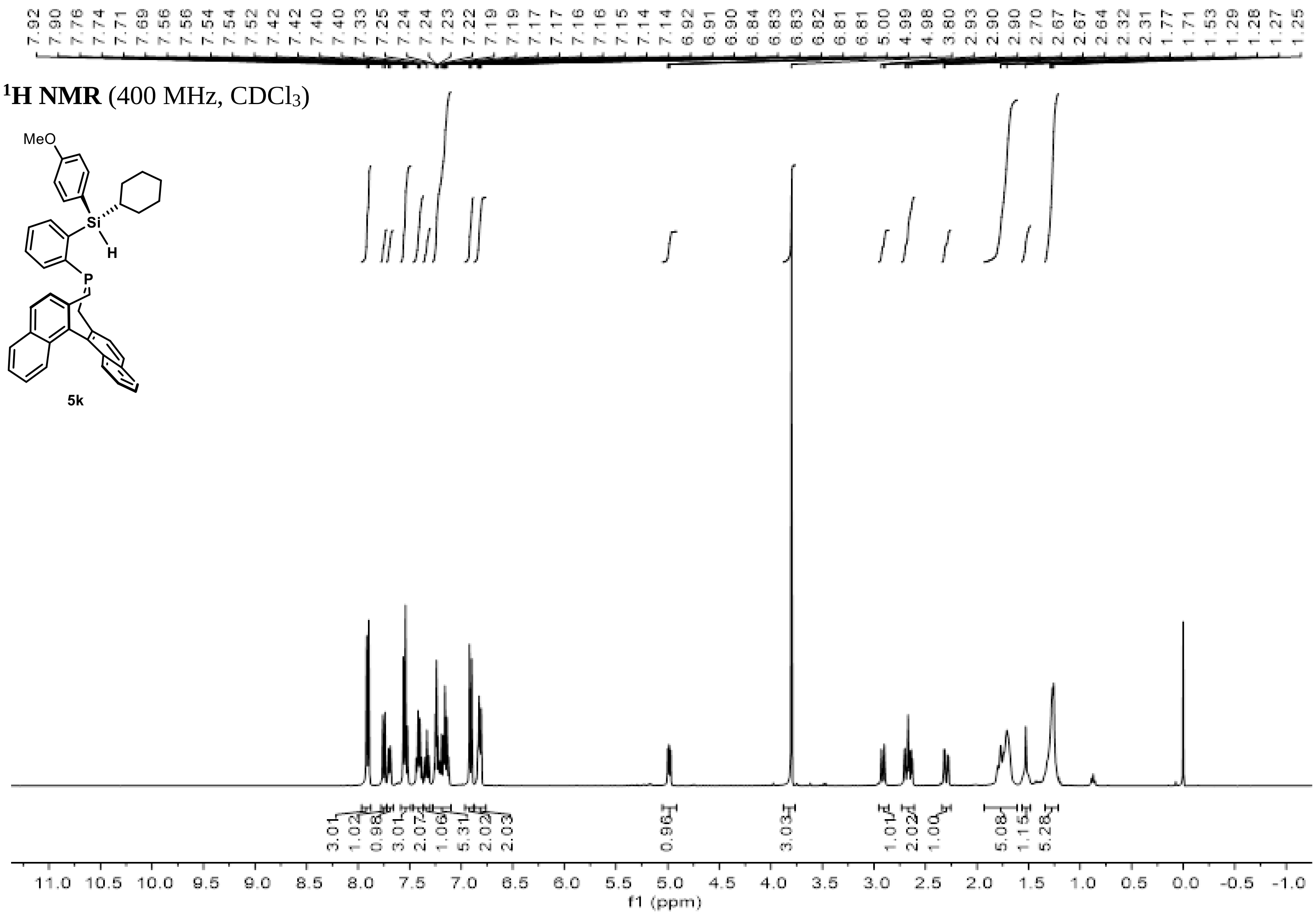


5j

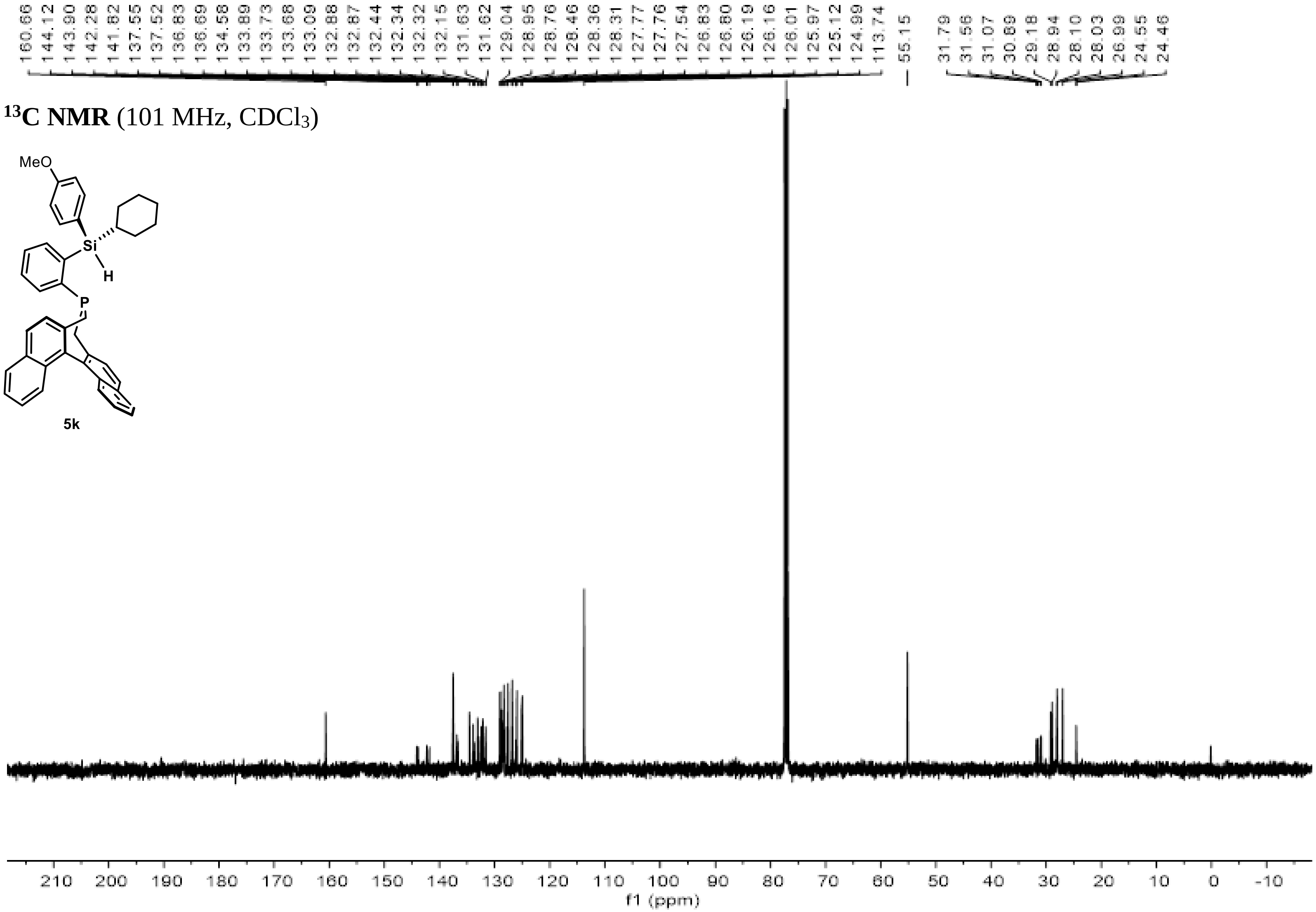
^{31}P NMR (162 MHz, CDCl$_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

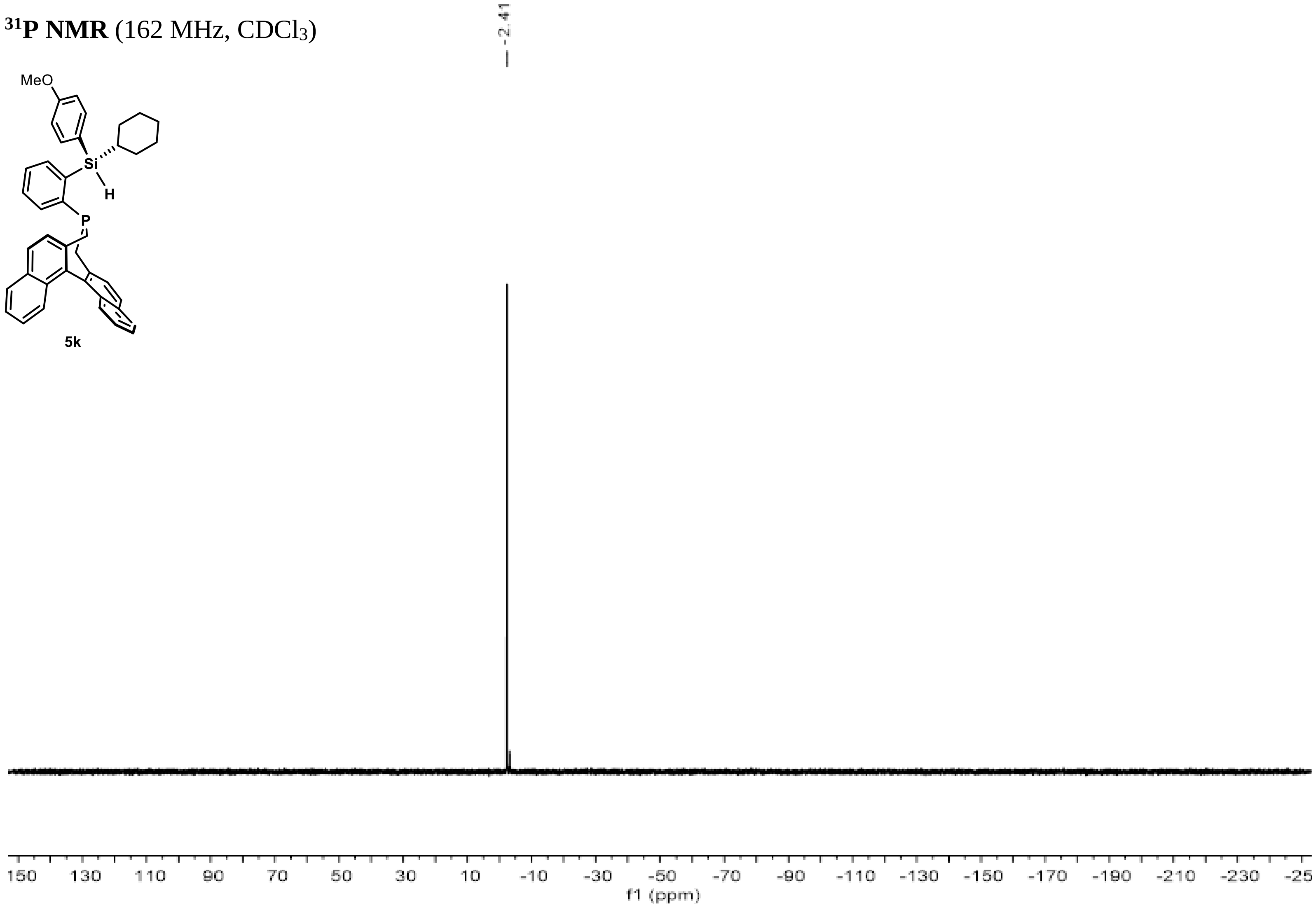


^{13}C NMR (101 MHz, $CDCl_3$)

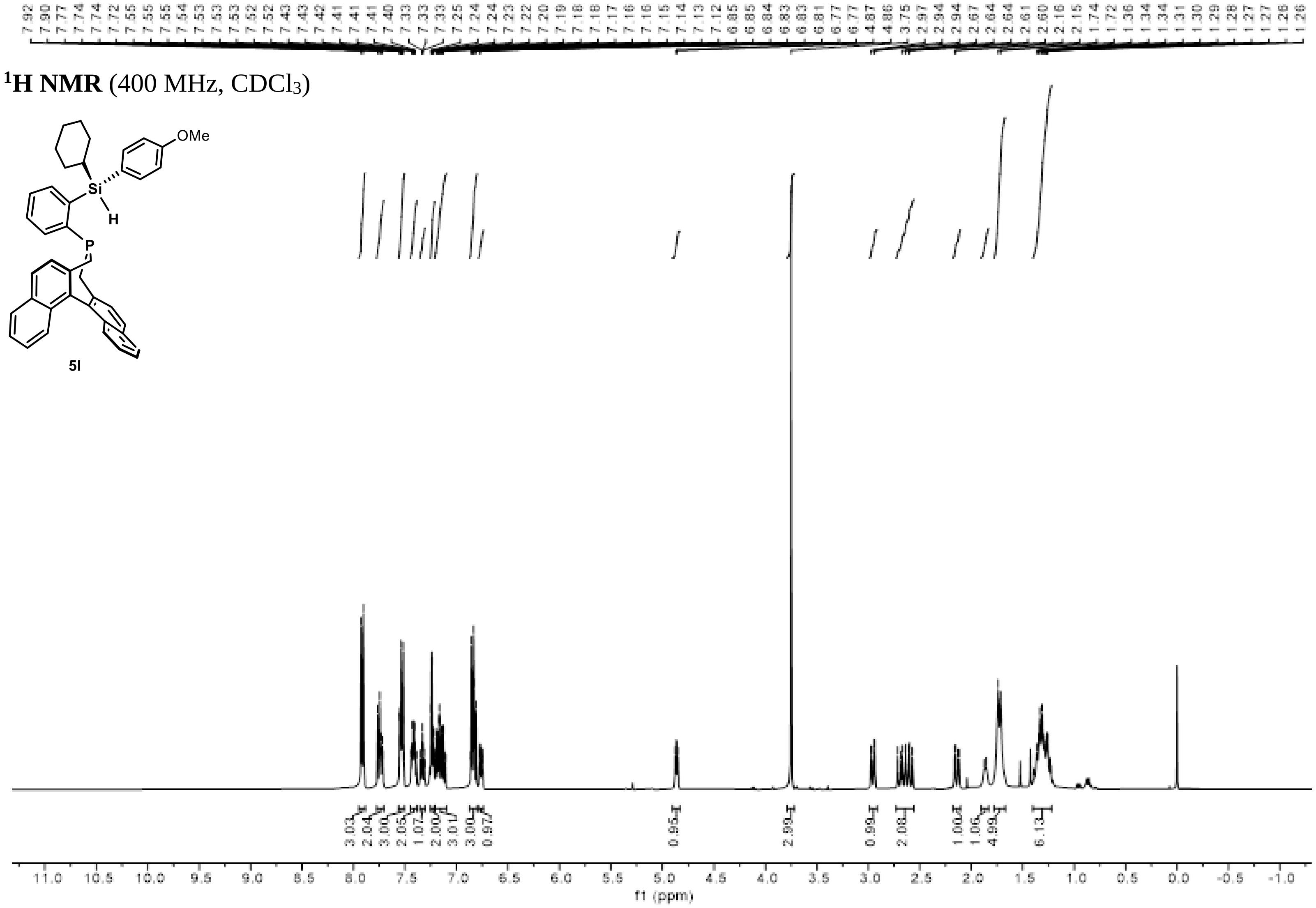


5k

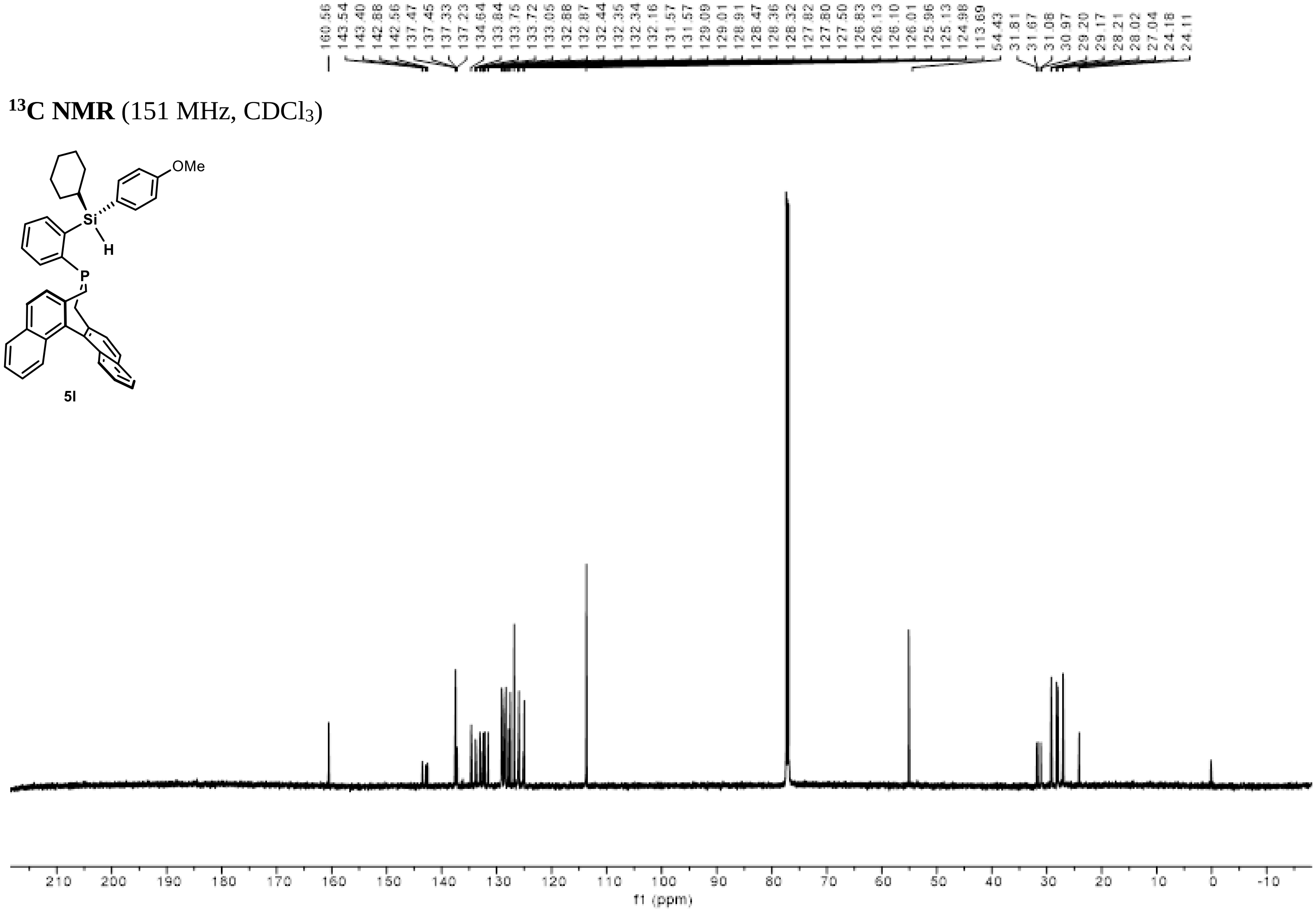
^{31}P NMR (162 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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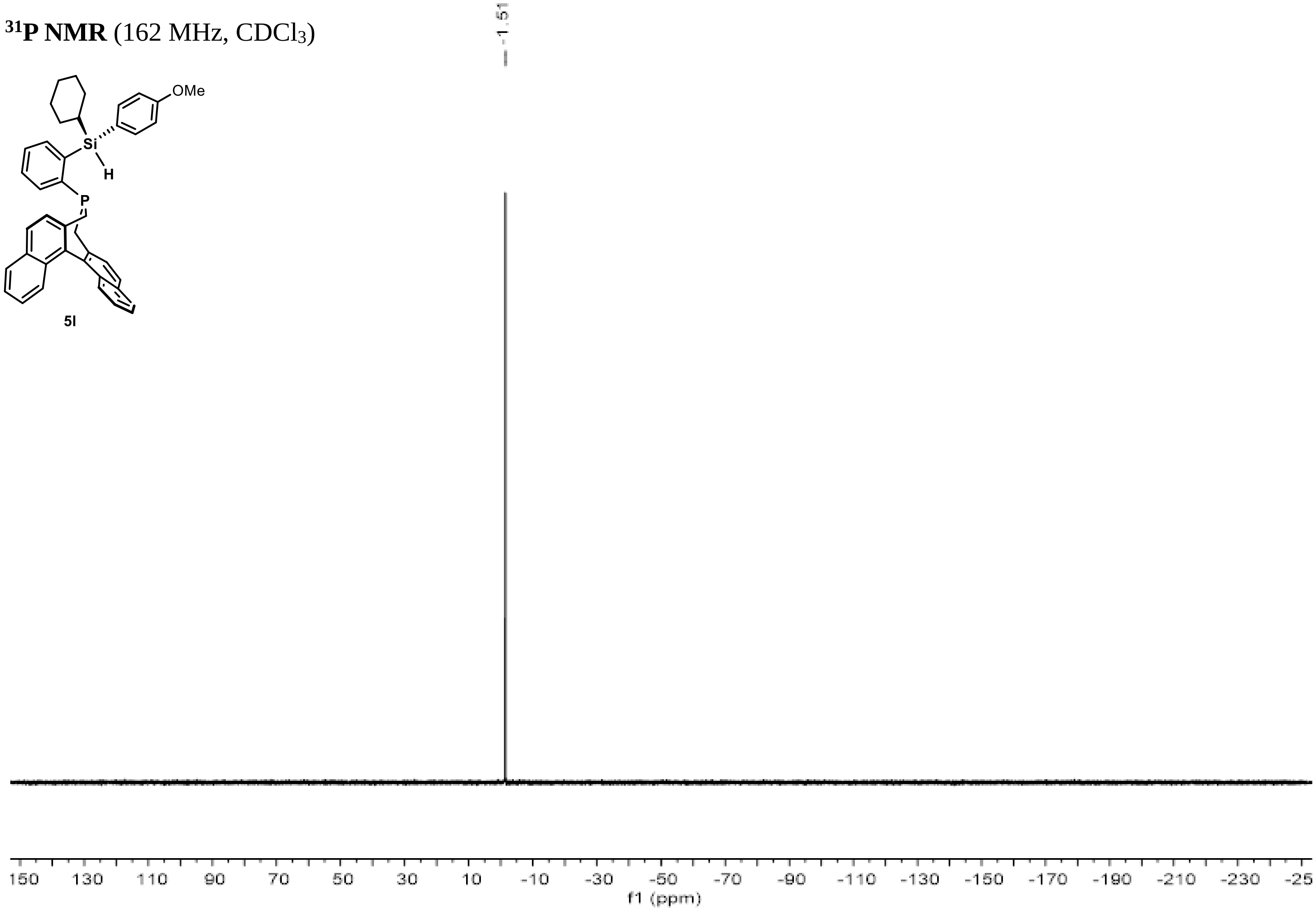
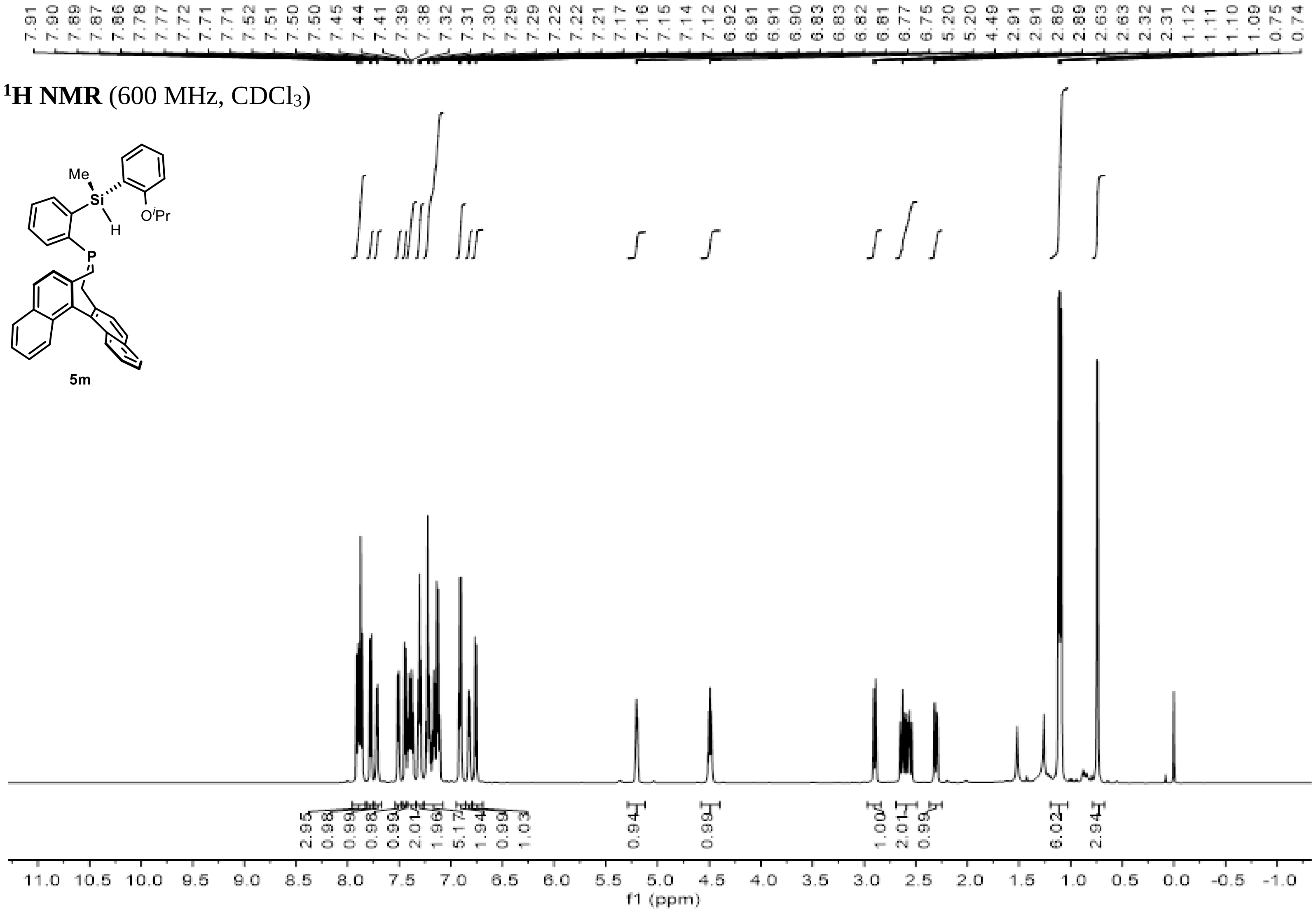
^{31}P NMR (162 MHz, $CDCl_3$)

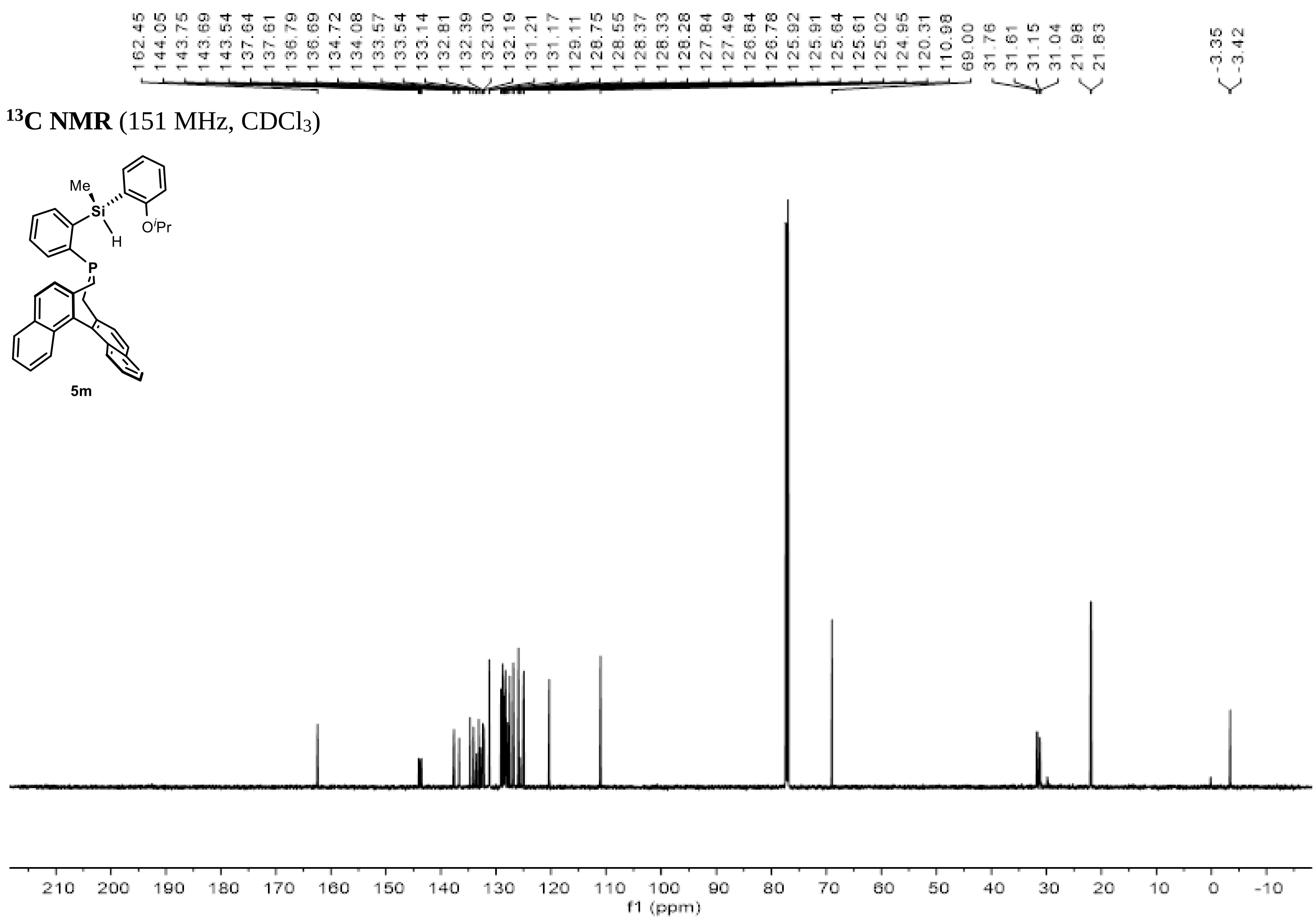


^{1}H NMR (600 MHz, $CDCl_3$)



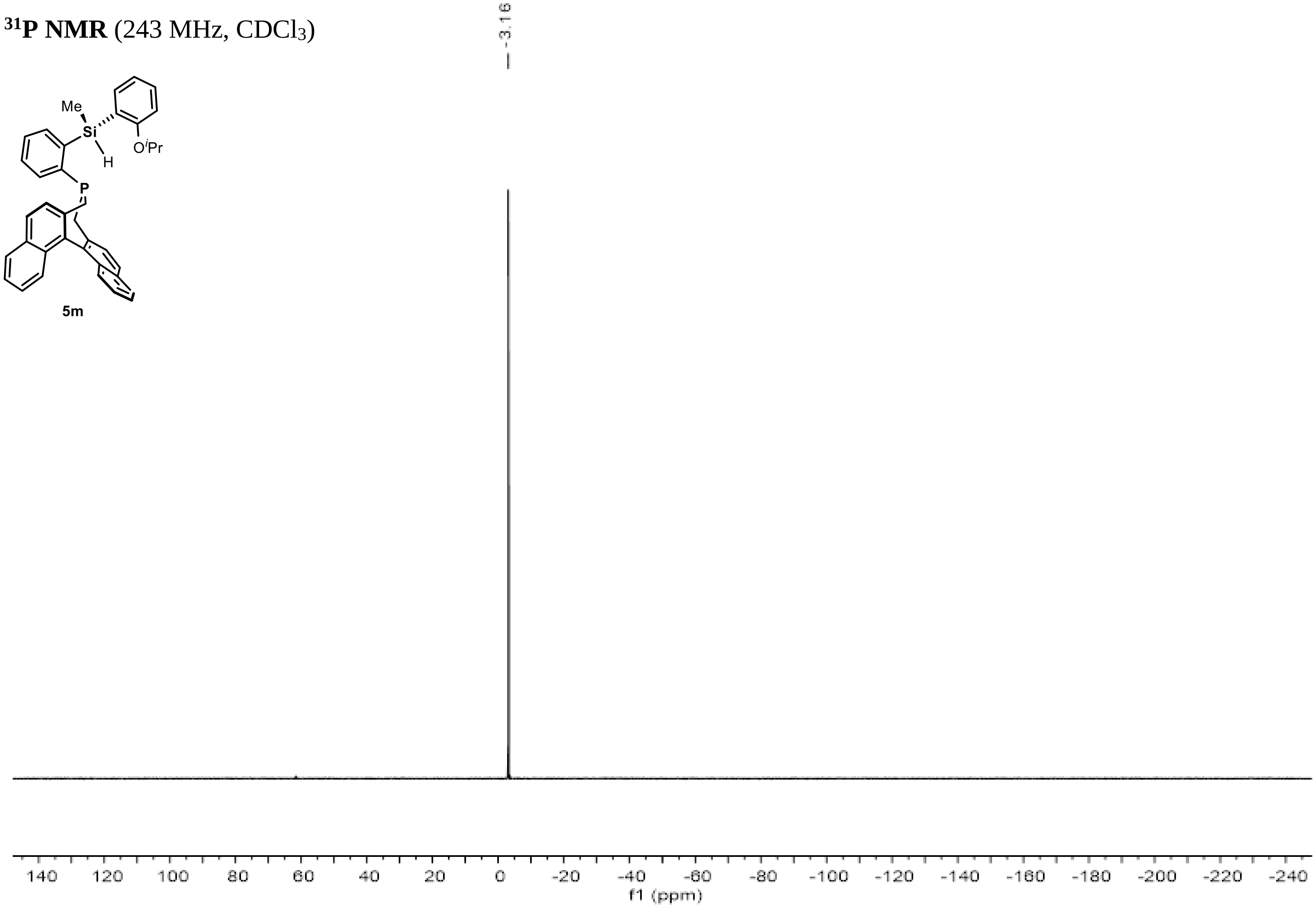
5m

^{13}C NMR (151 MHz, CDCl$_3$)



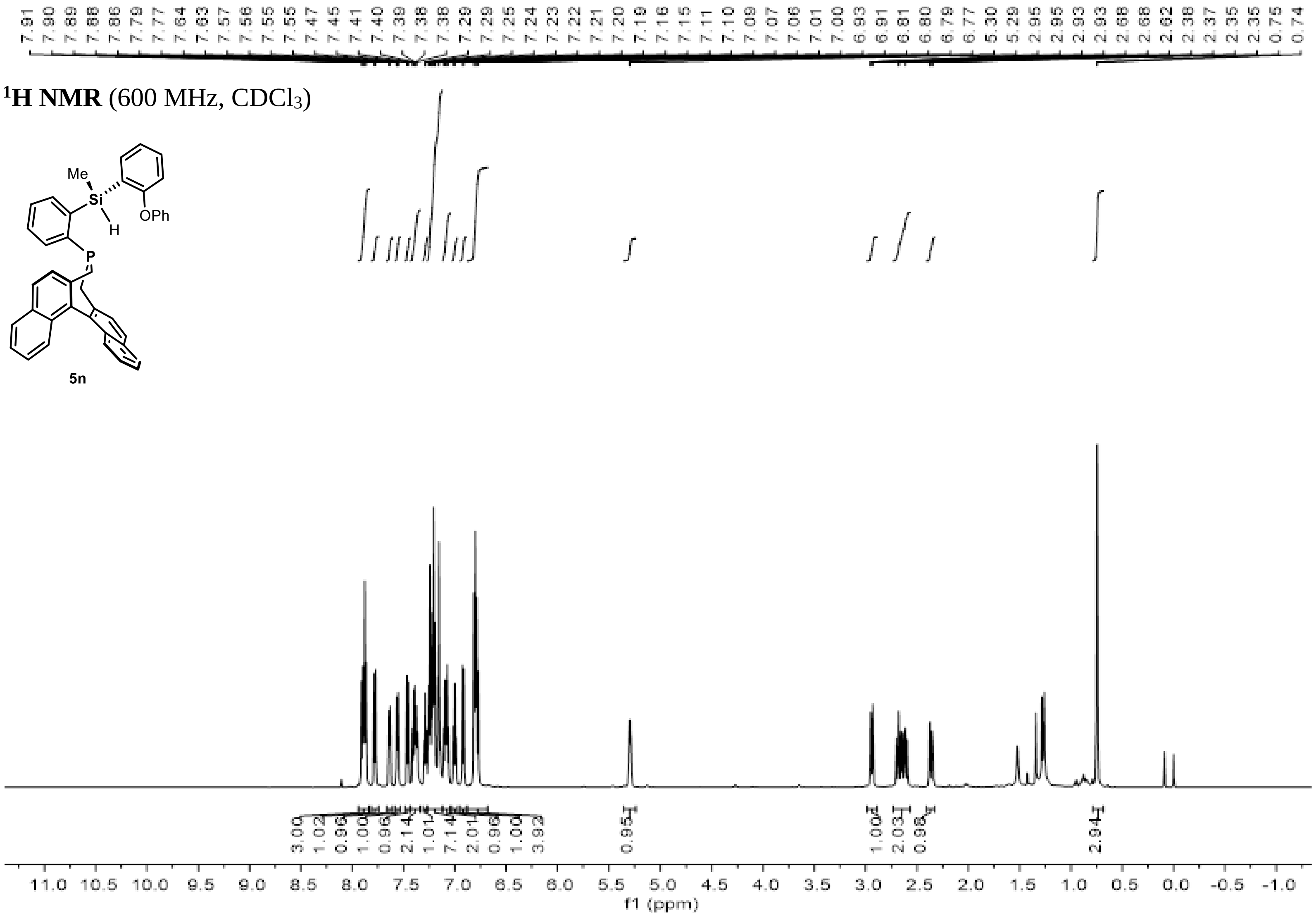
5m

^{31}P NMR (243 MHz, $CDCl_3$)

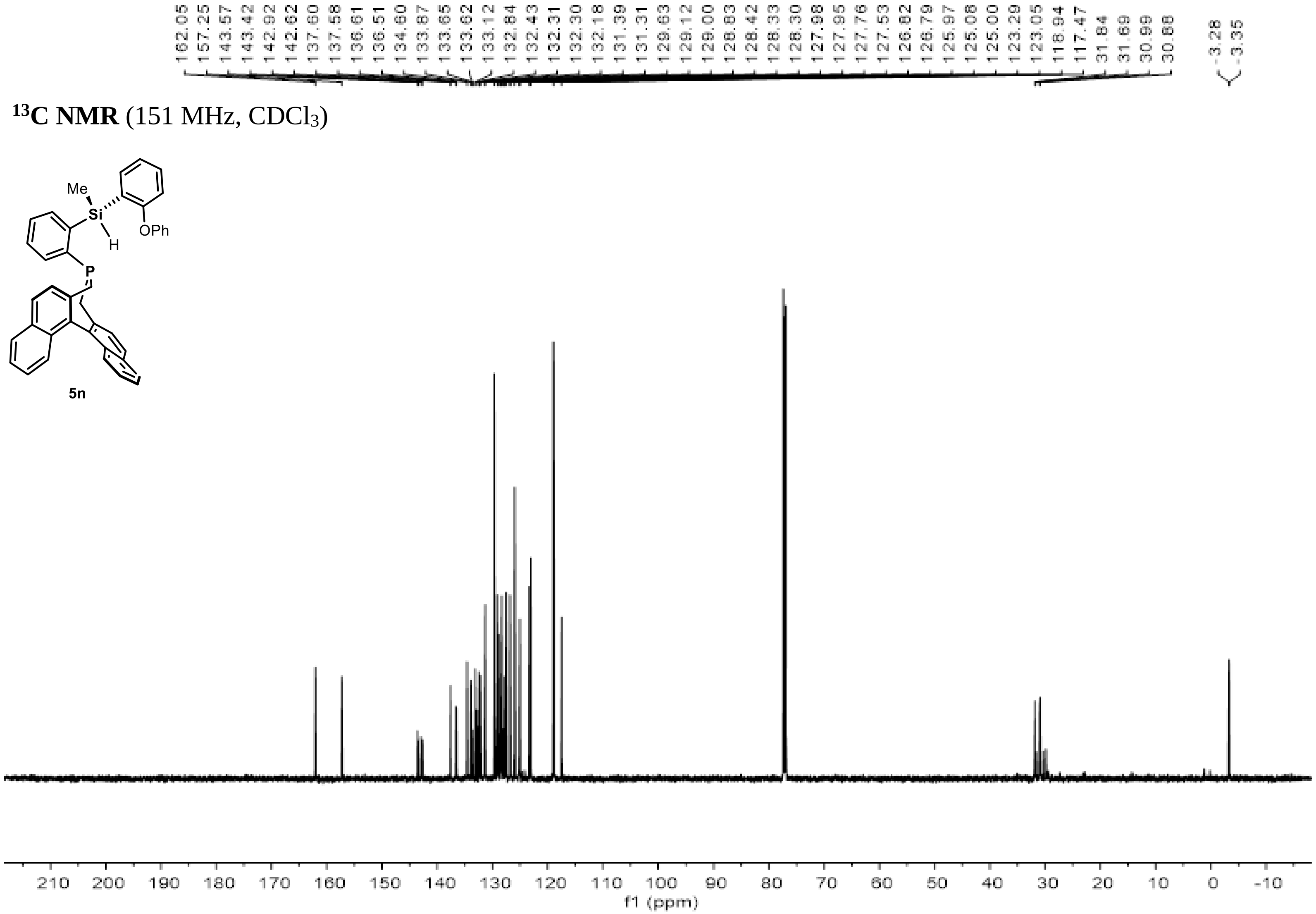


5m

^{1}H NMR (600 MHz, $CDCl_3$)

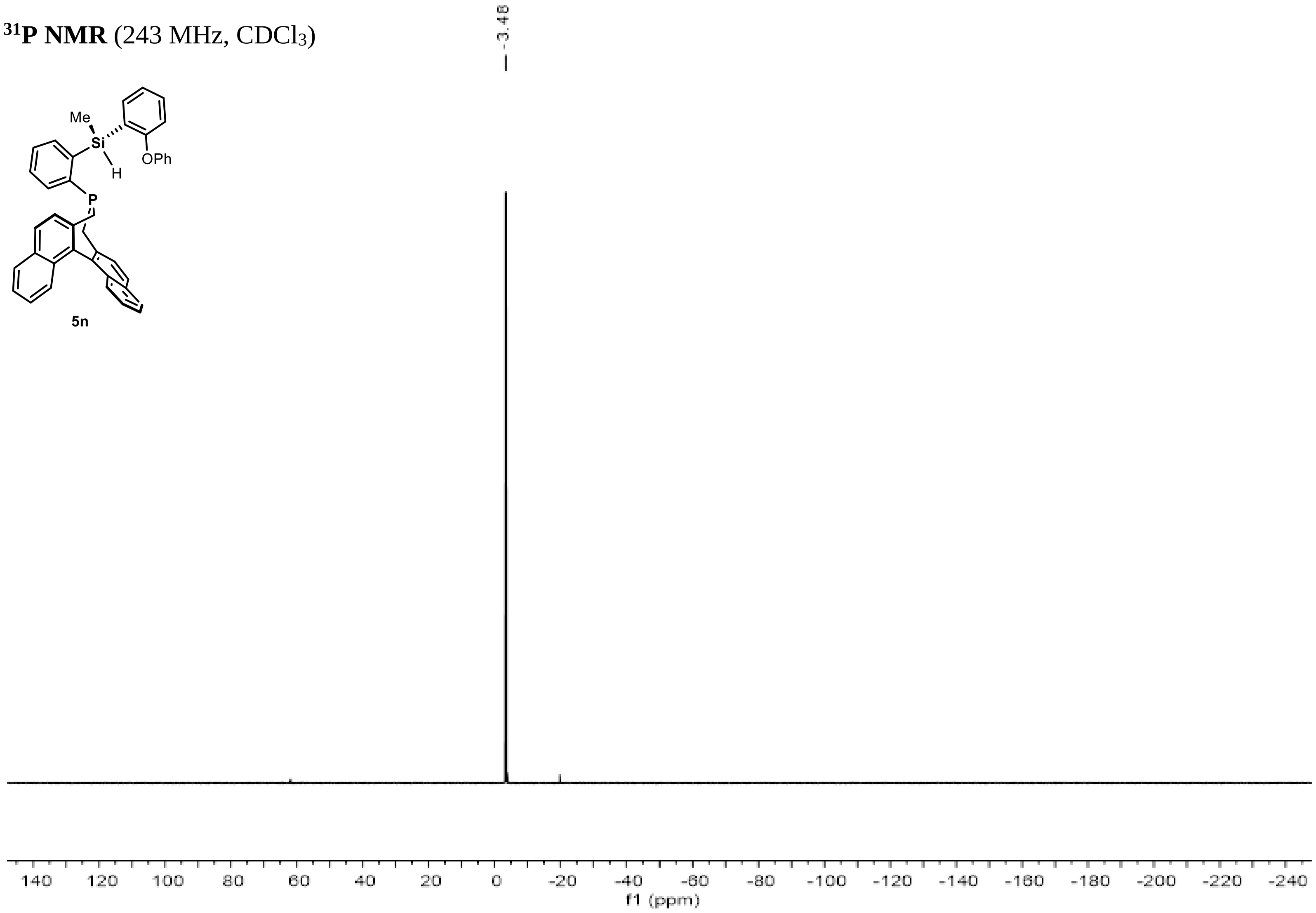


^{13}C NMR (151 MHz, $CDCl_3$)



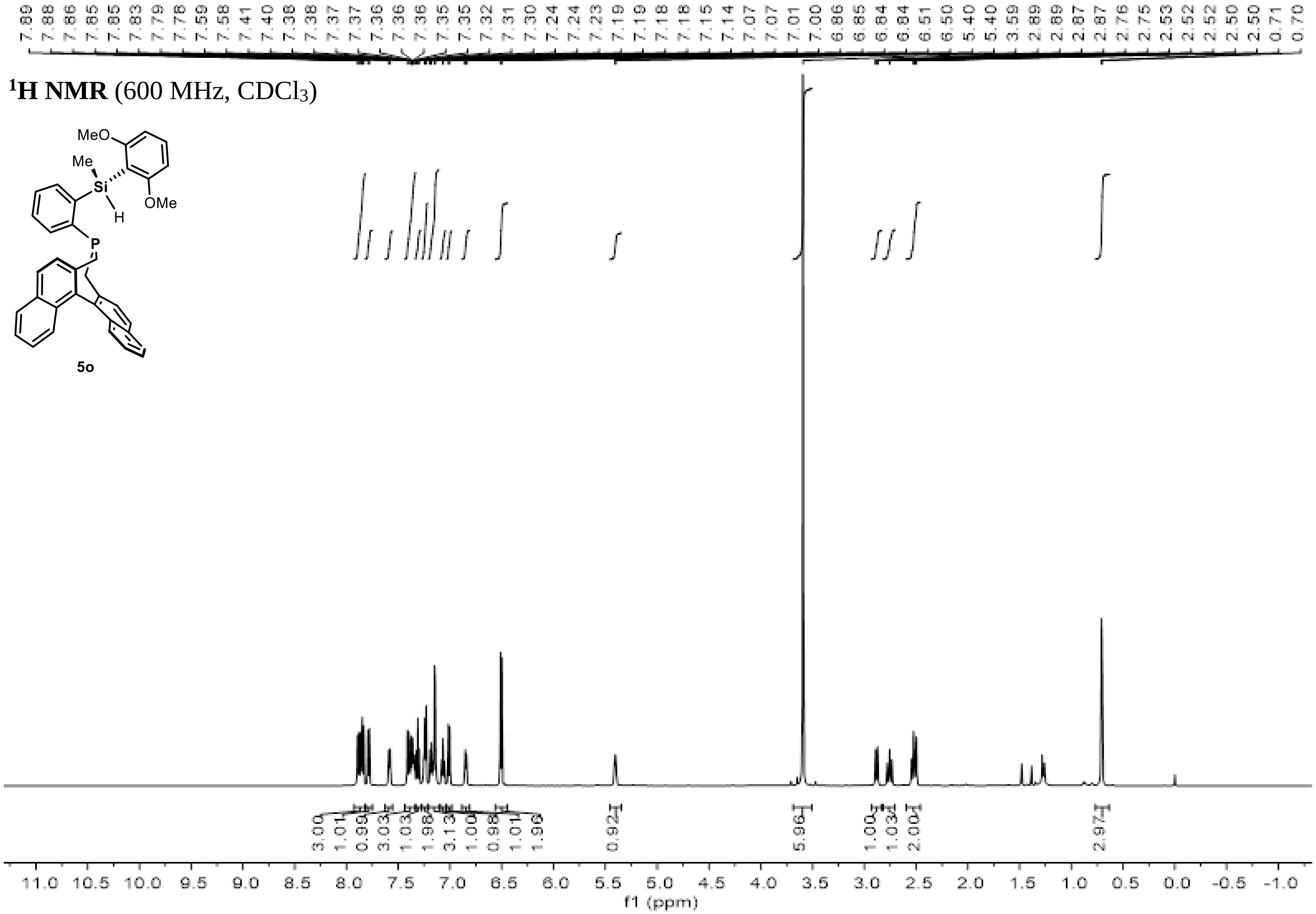
5n

^{31}P NMR (243 MHz, $CDCl_3$)

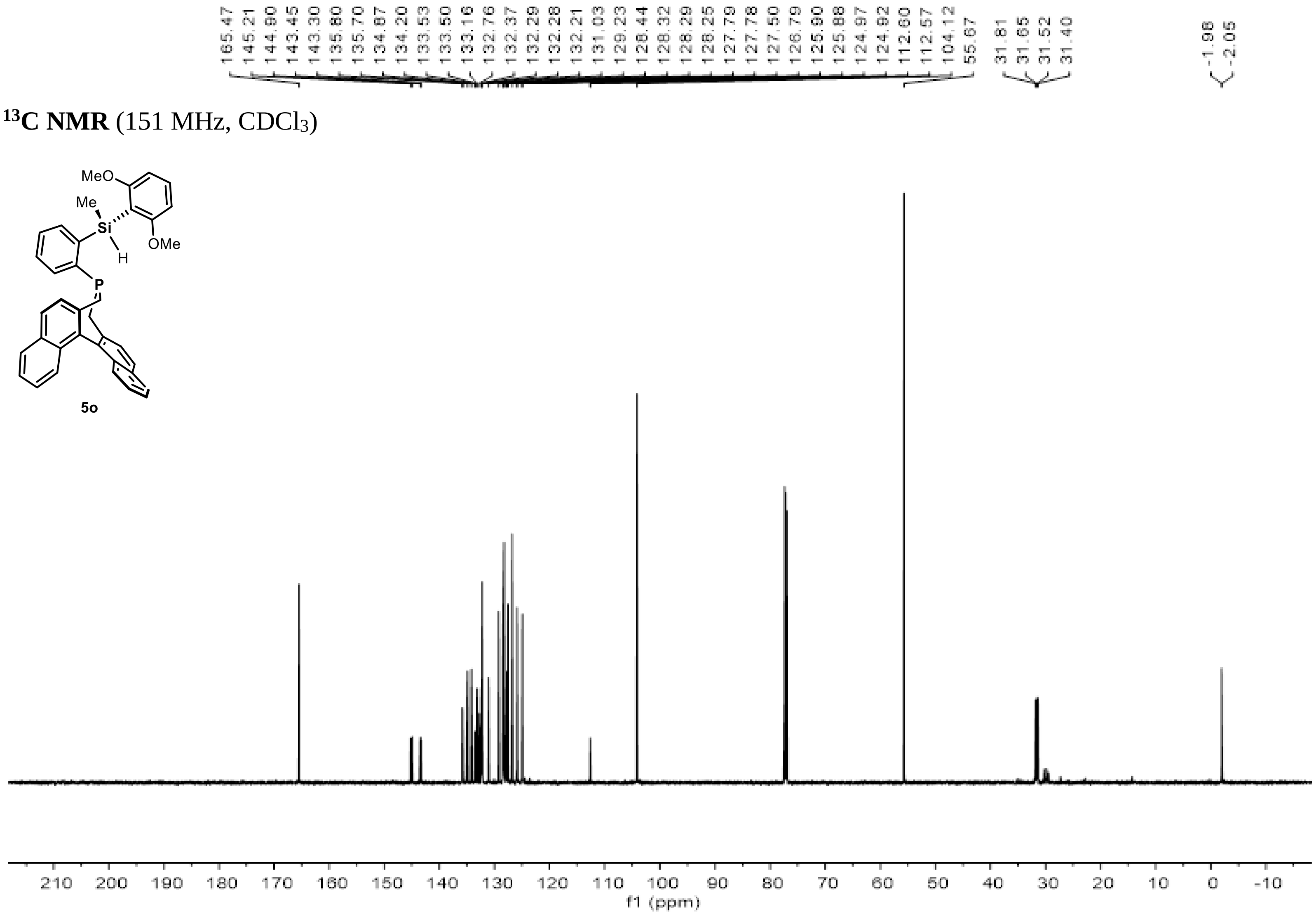


5n

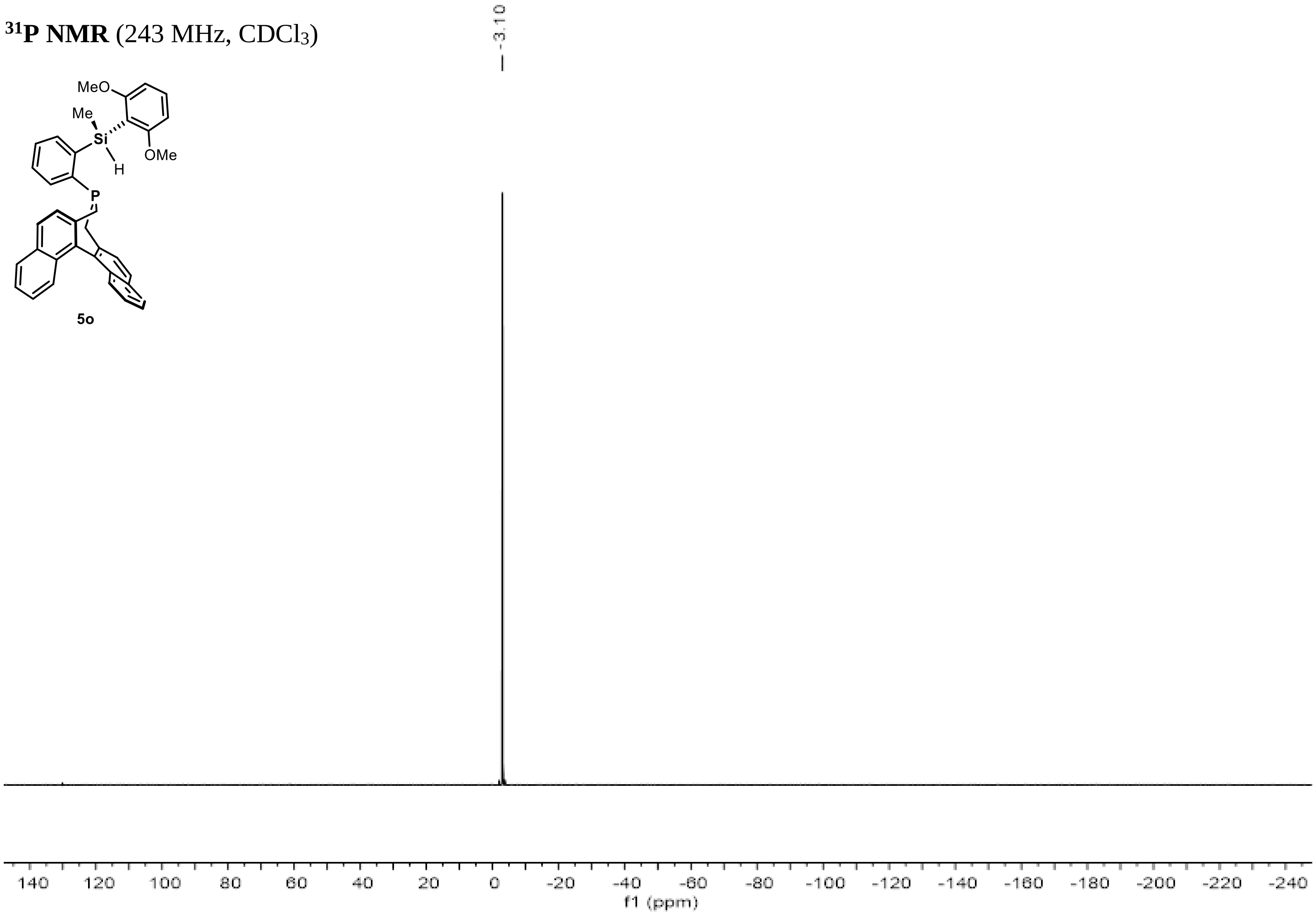
^{1}H NMR (600 MHz, $CDCl_3$)



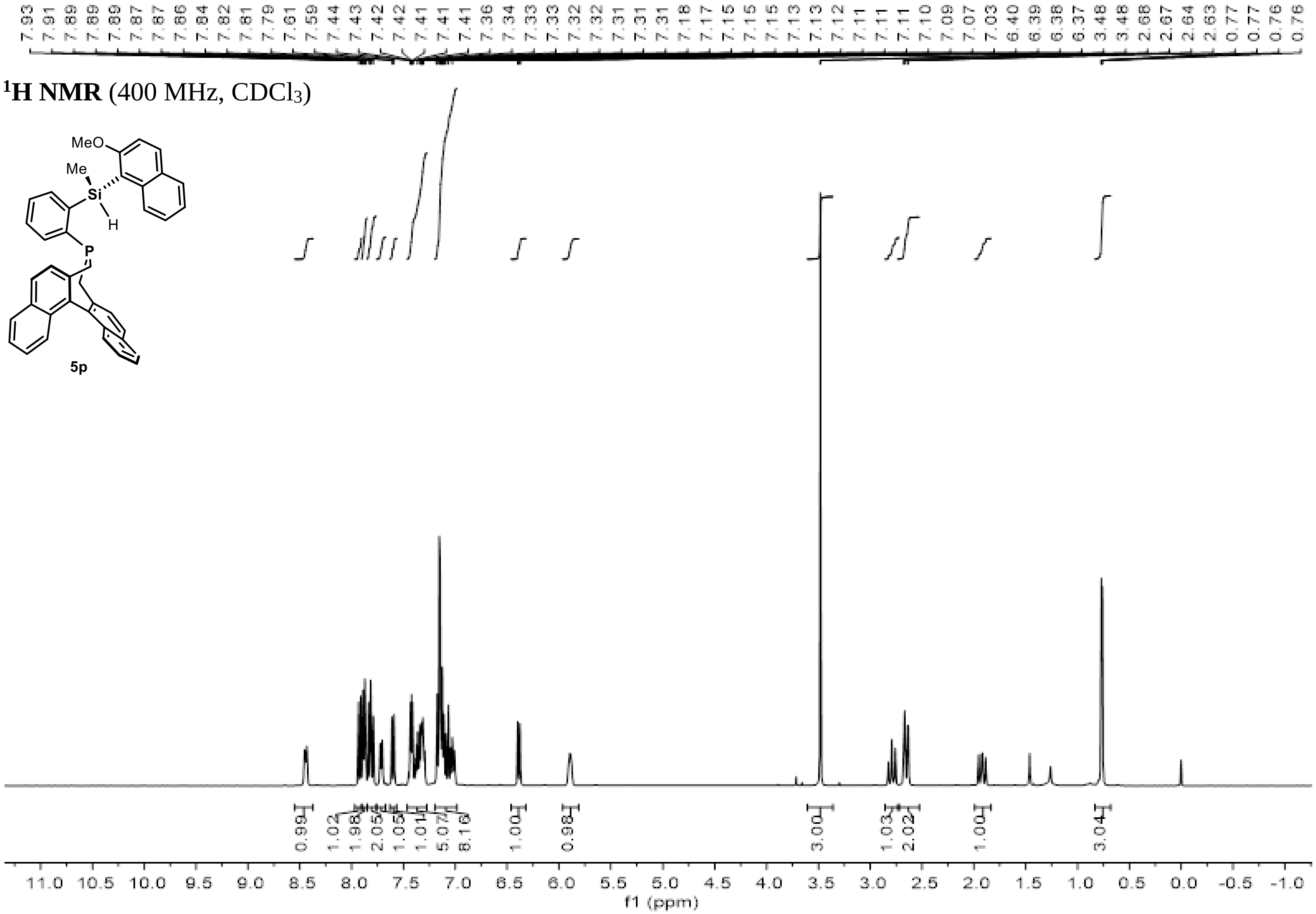
^{13}C NMR (151 MHz, $CDCl_3$)



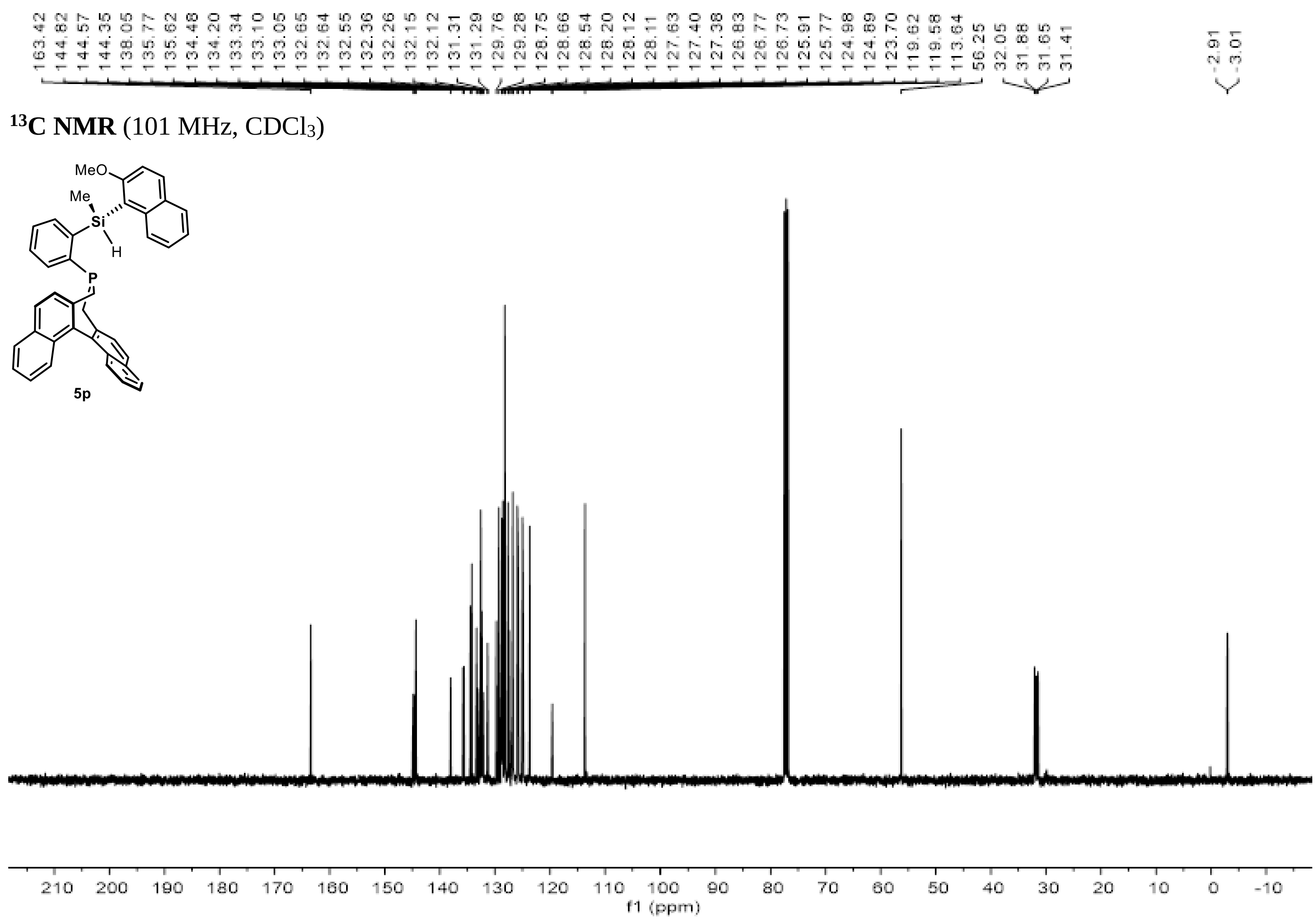
^{31}**P NMR** (243 MHz, $CDCl_3$)


5o

^{1}H NMR (400 MHz, $CDCl_3$)

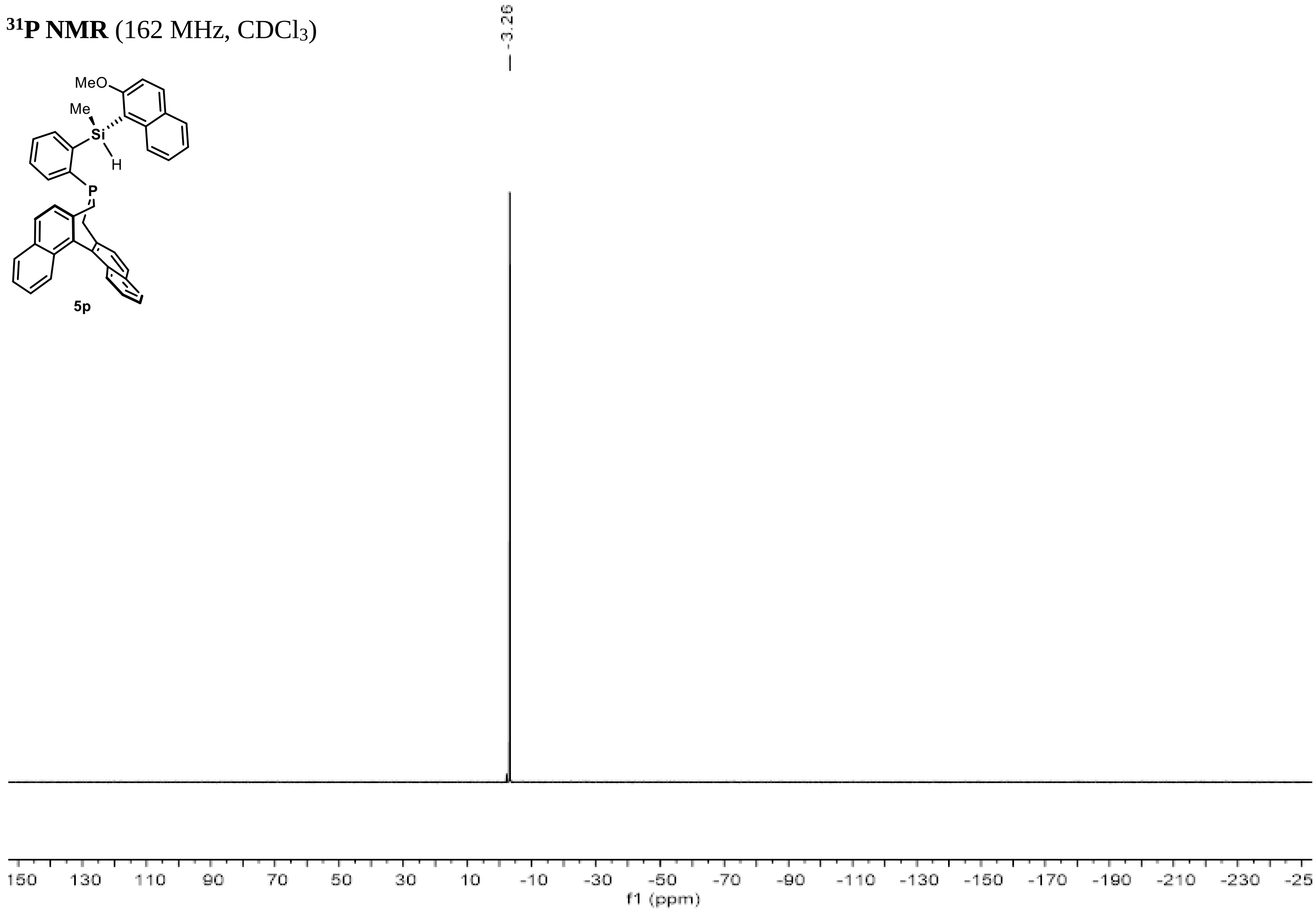


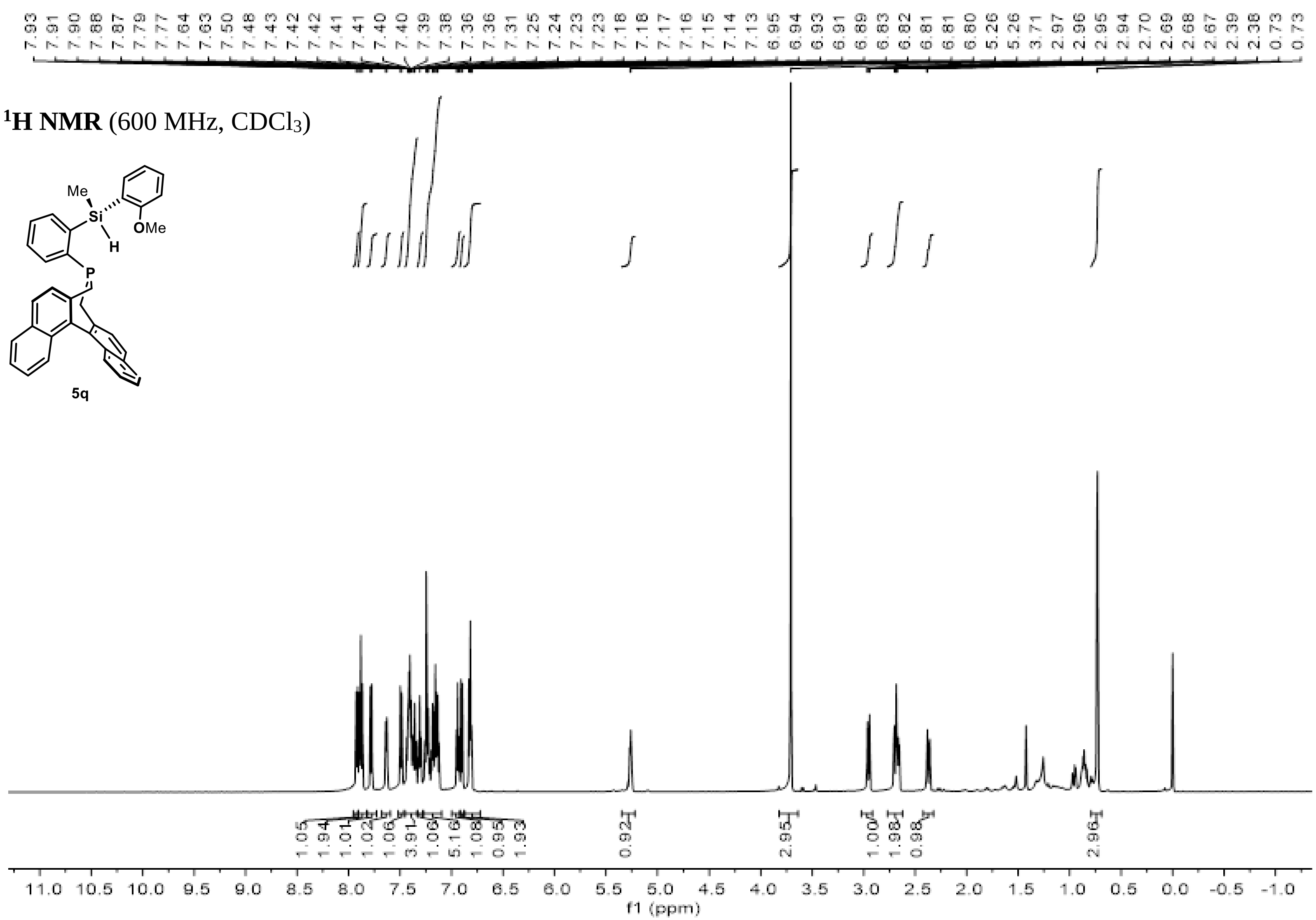
^{13}**C NMR** (101 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)

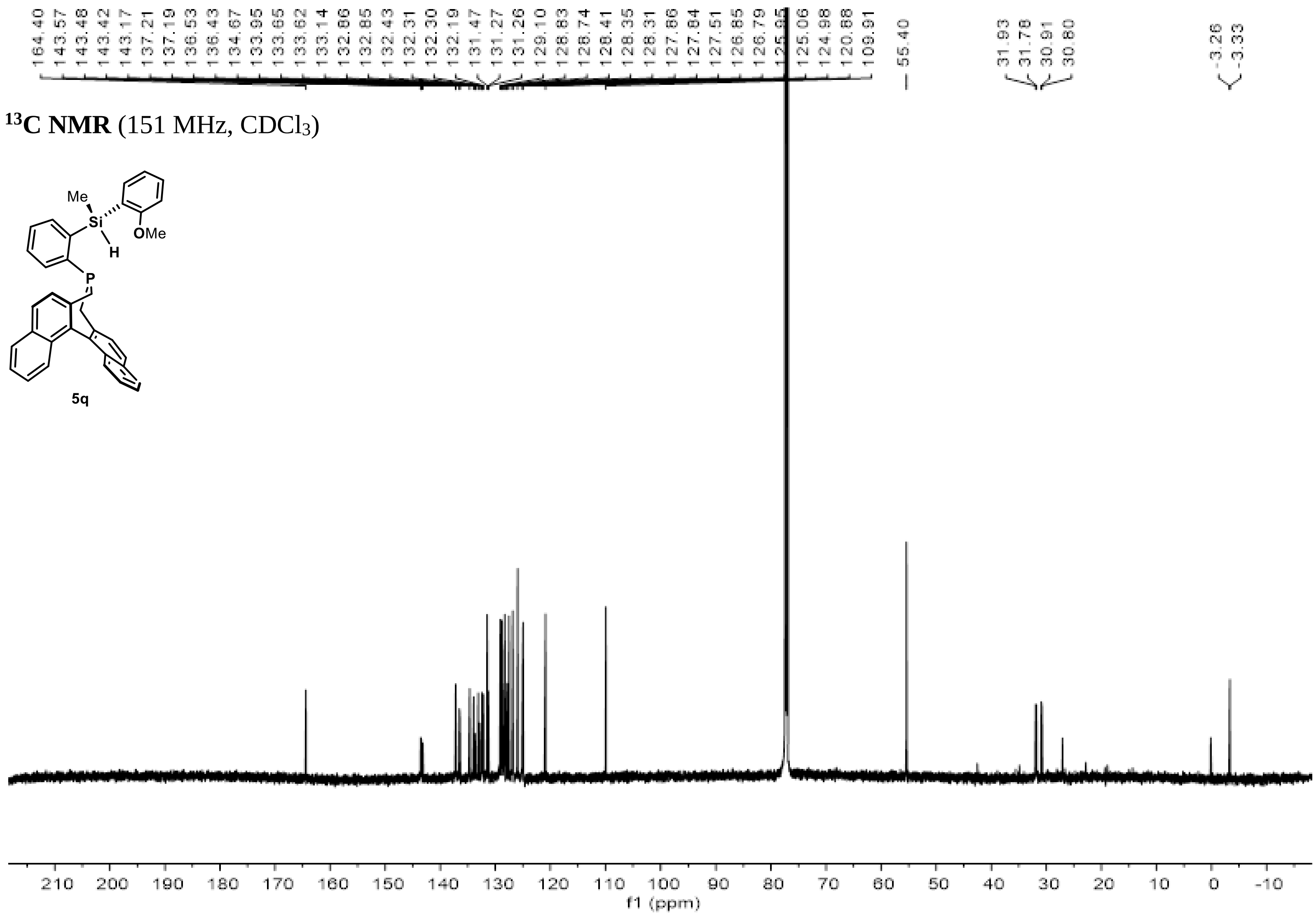
5p





^{1}H NMR (600 MHz, $CDCl_3$)

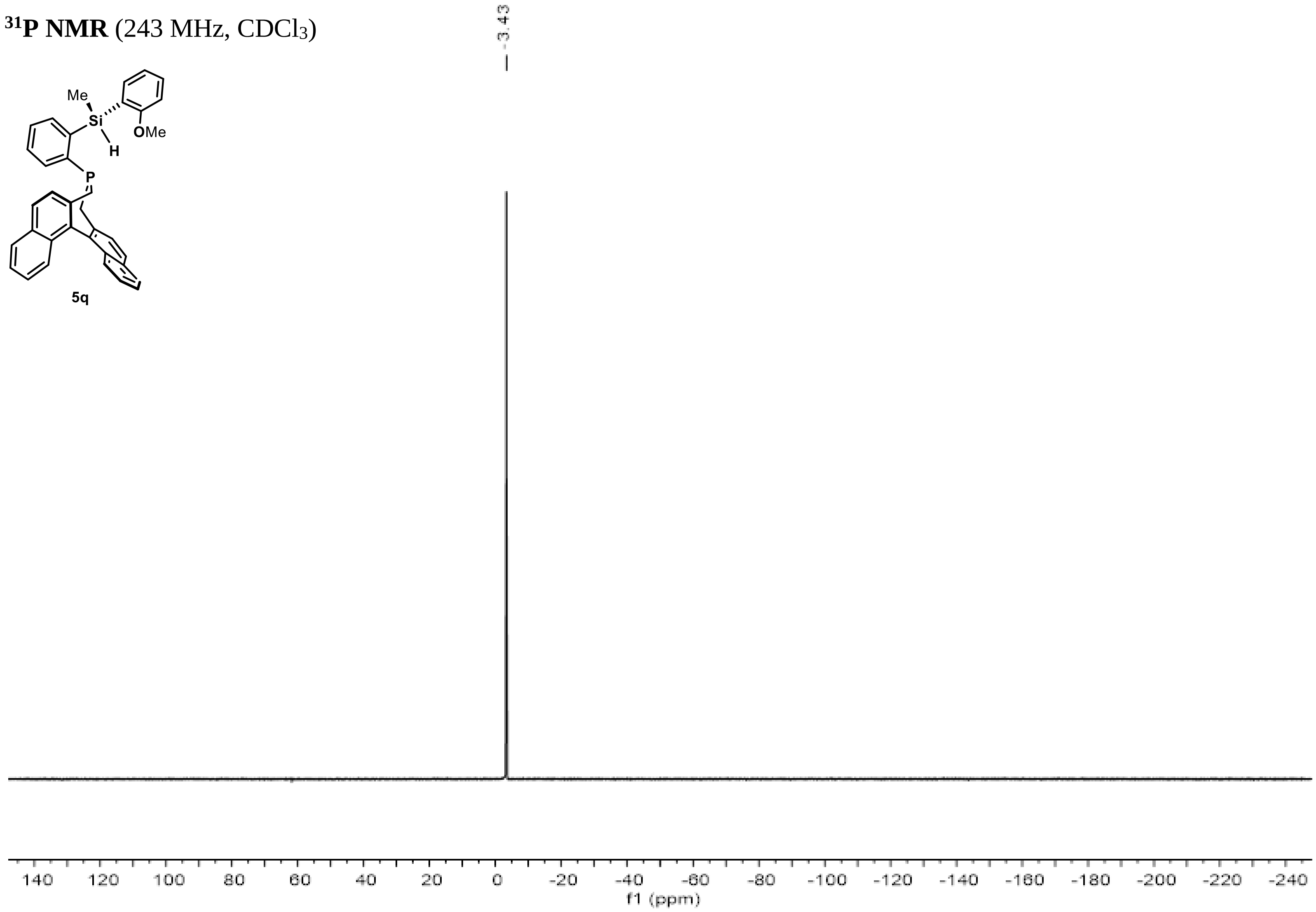
5q



^{13}**C NMR** (151 MHz, $CDCl_3$)

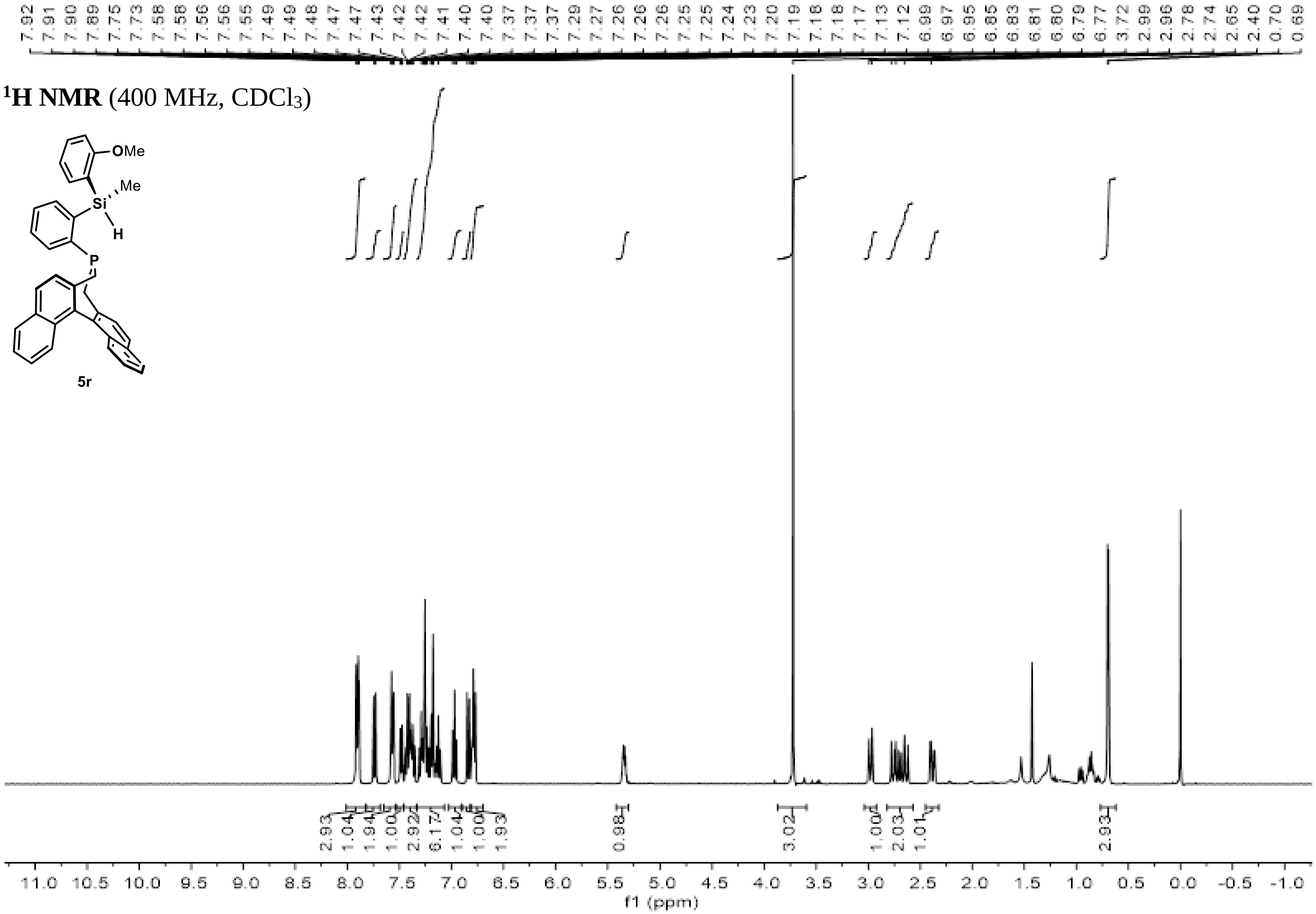
5q

^{31}P NMR (243 MHz, $CDCl_3$)

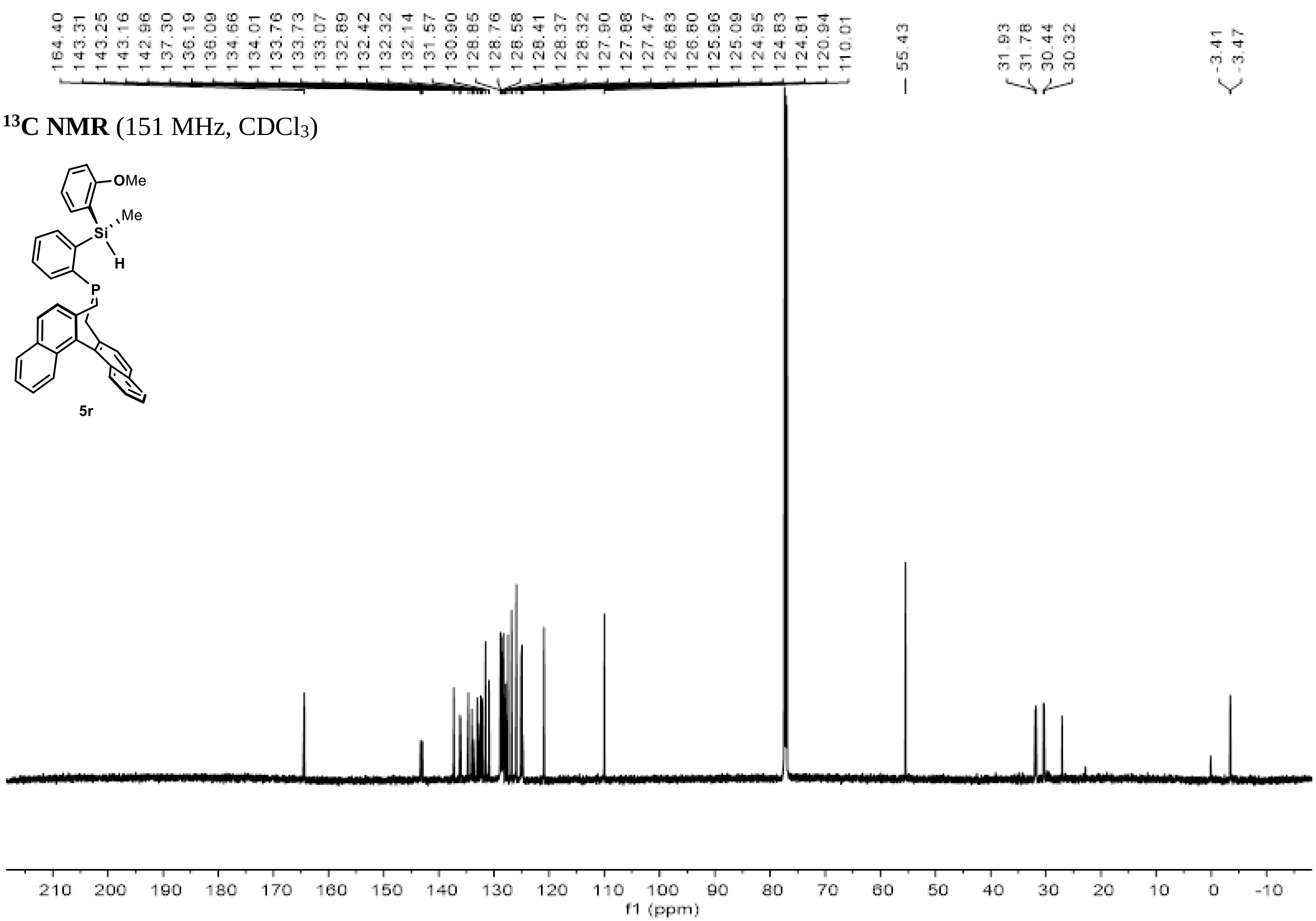


5q

^{1}H NMR (400 MHz, CDCl$_3$)



5r

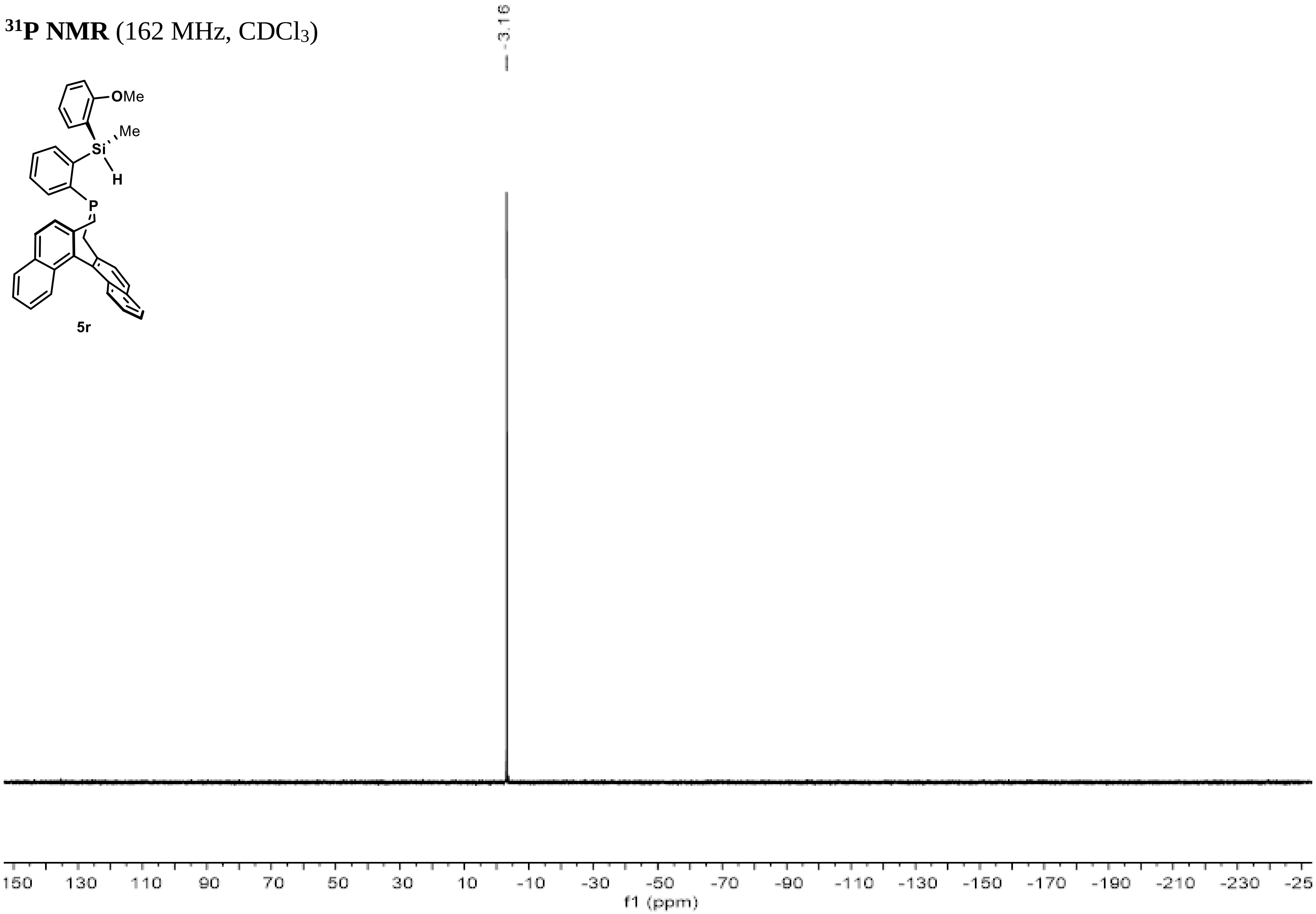


^{13}C NMR (151 MHz, CDCl$_3$)

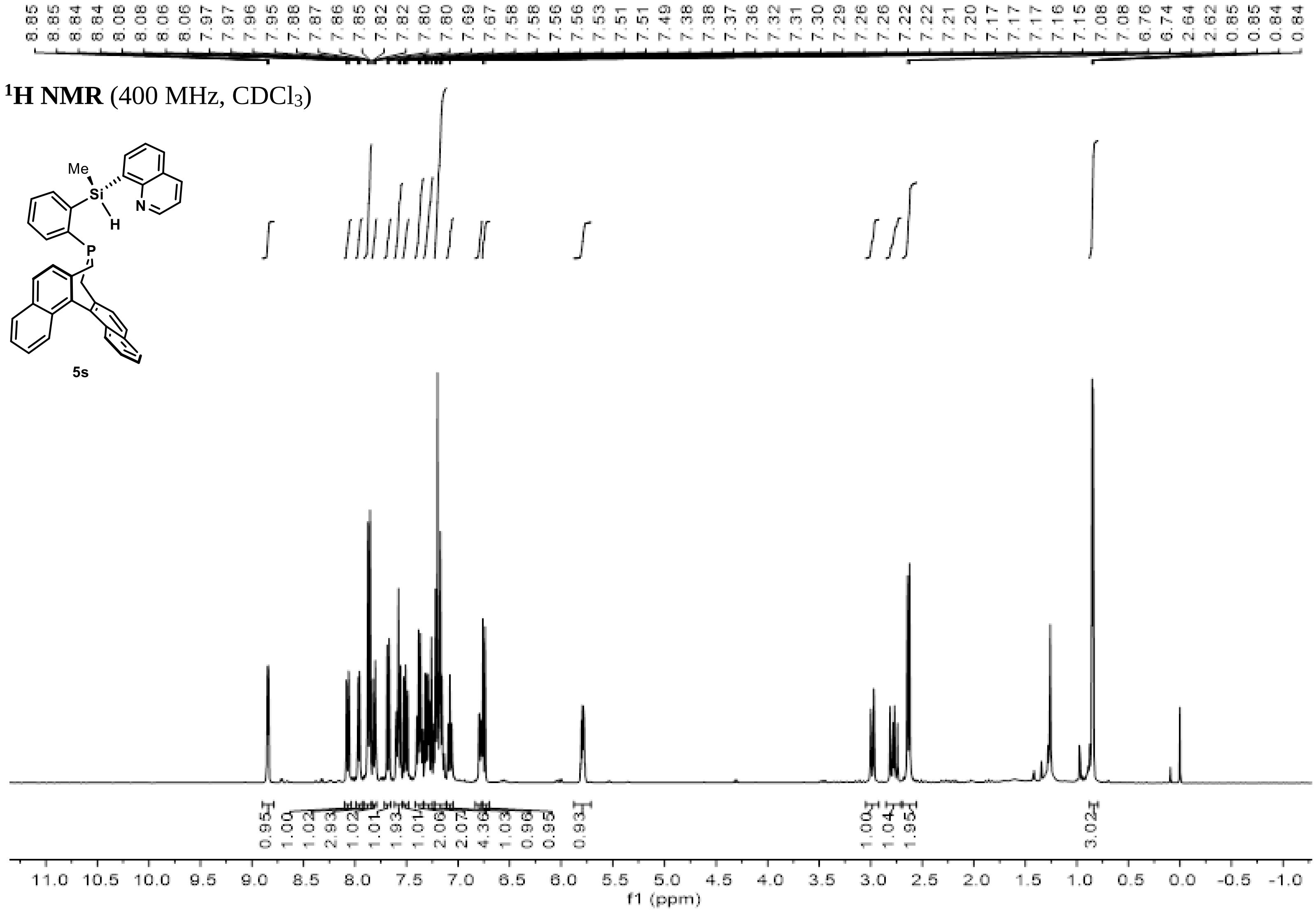
5r

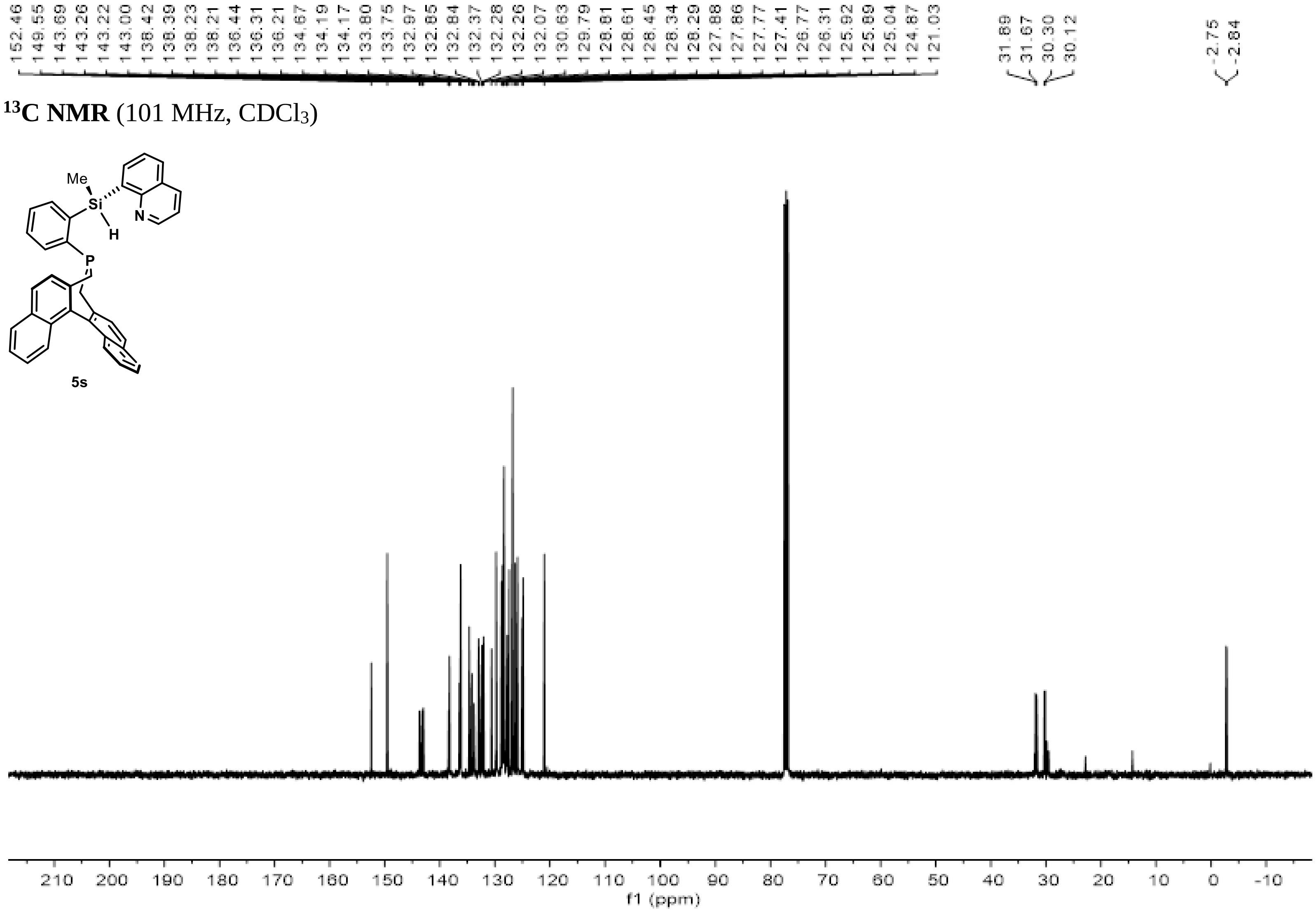
^{31}P NMR (162 MHz, CDCl$_3$)

5r



^{1}H NMR (400 MHz, $CDCl_3$)

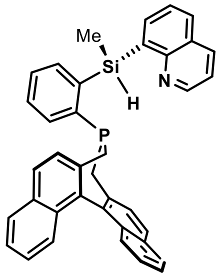




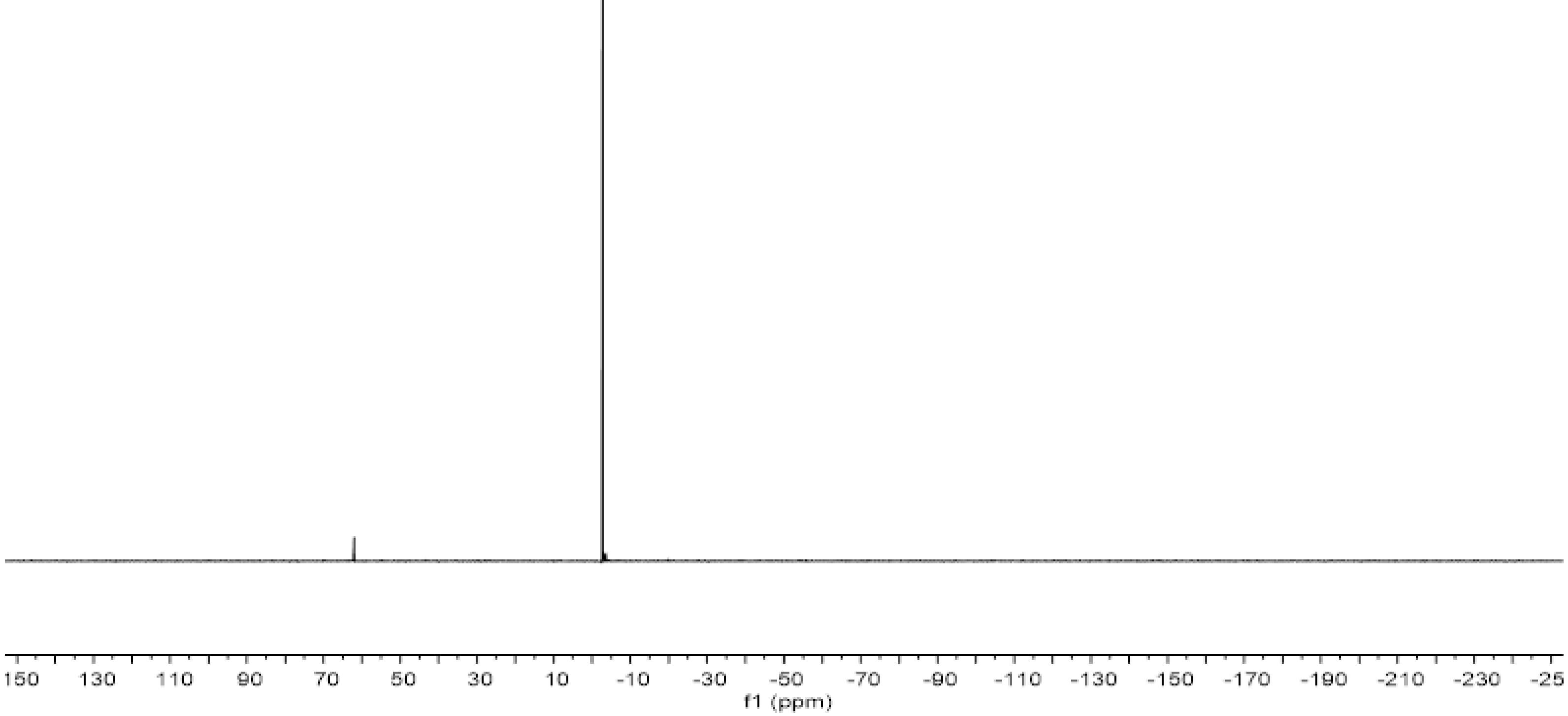
^{13}C NMR (101 MHz, $CDCl_3$)

5s

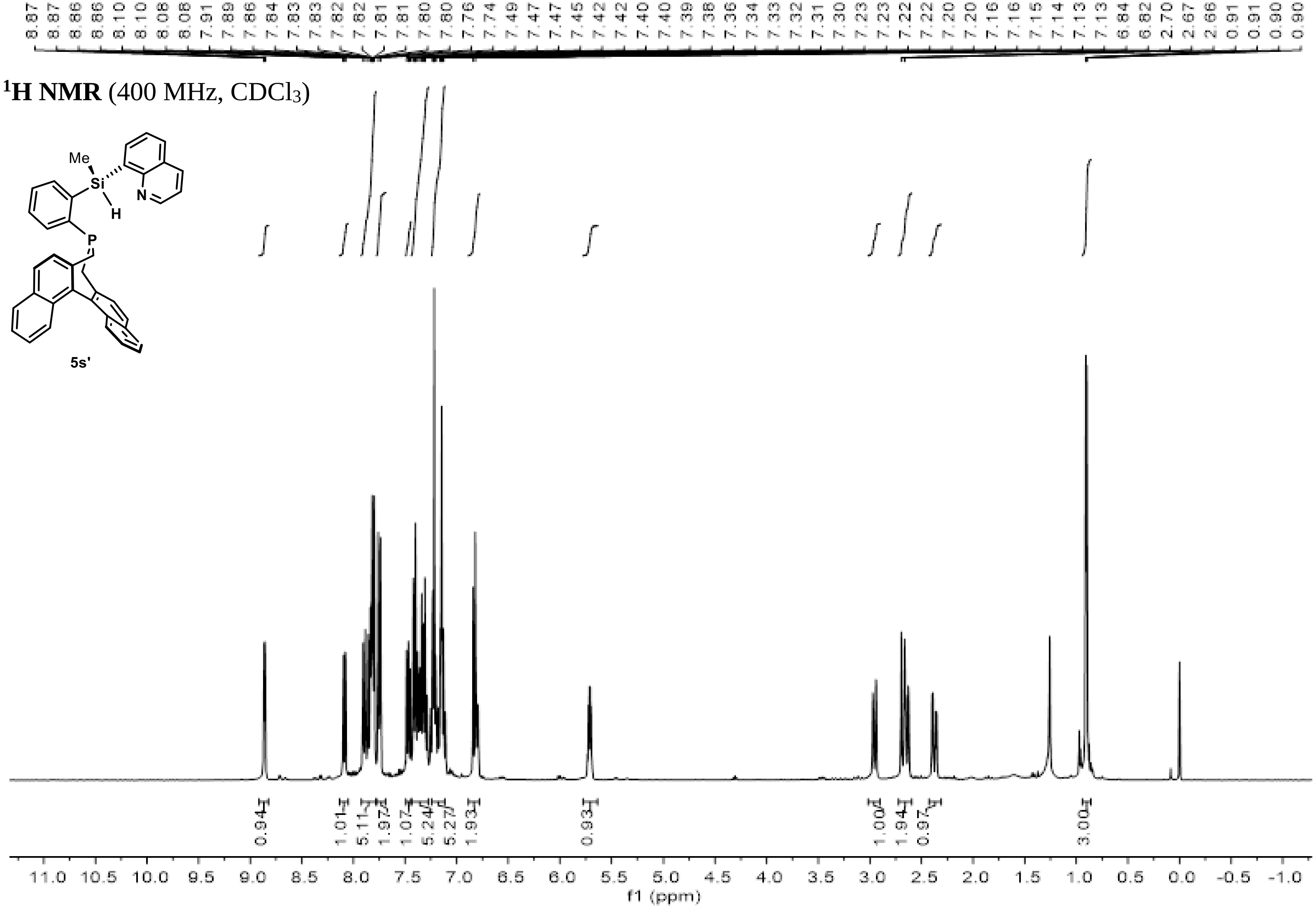
^{31}P NMR (162 MHz, CDCl$_3$)

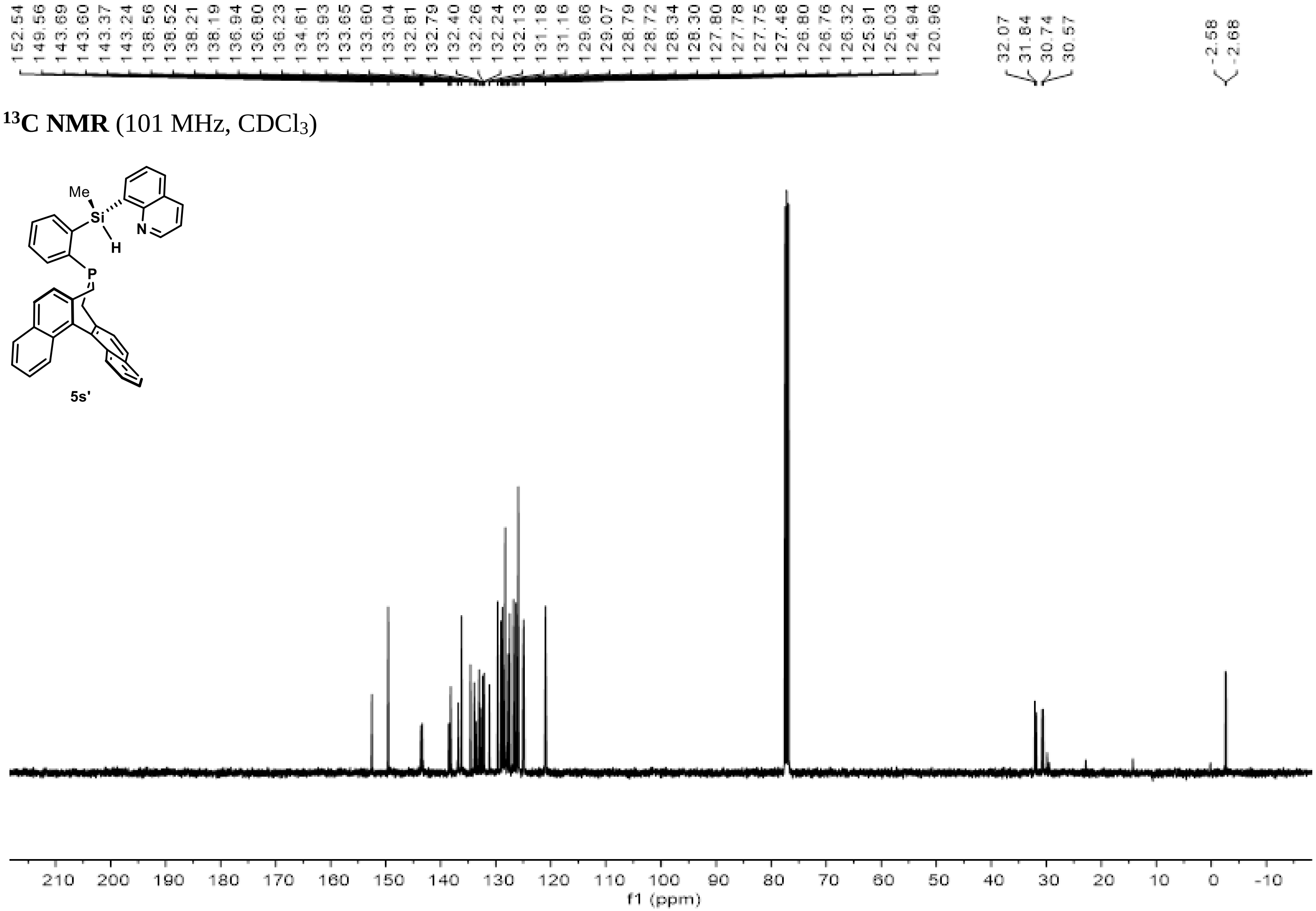


5s



^{1}H NMR (400 MHz, $CDCl_3$)

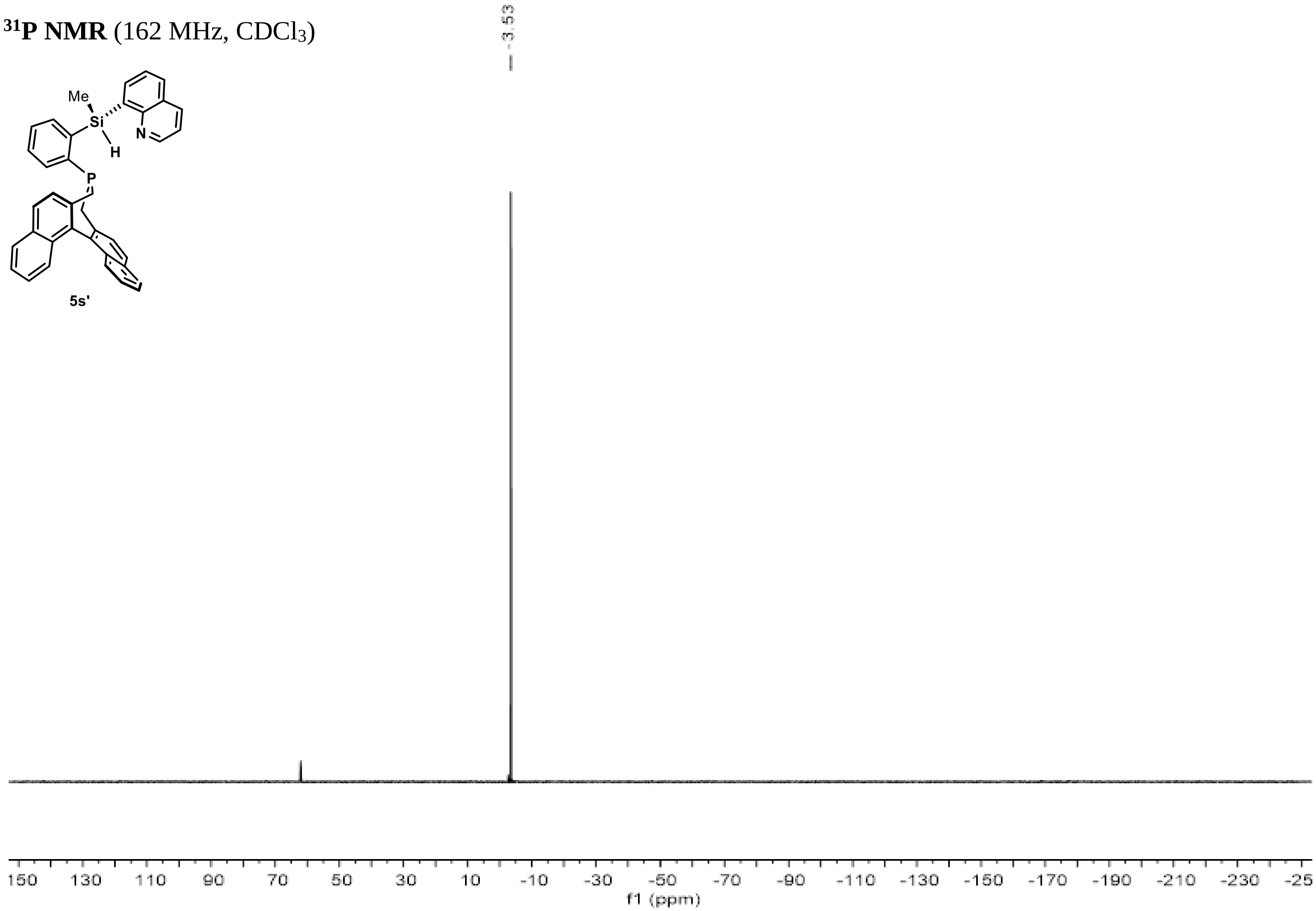




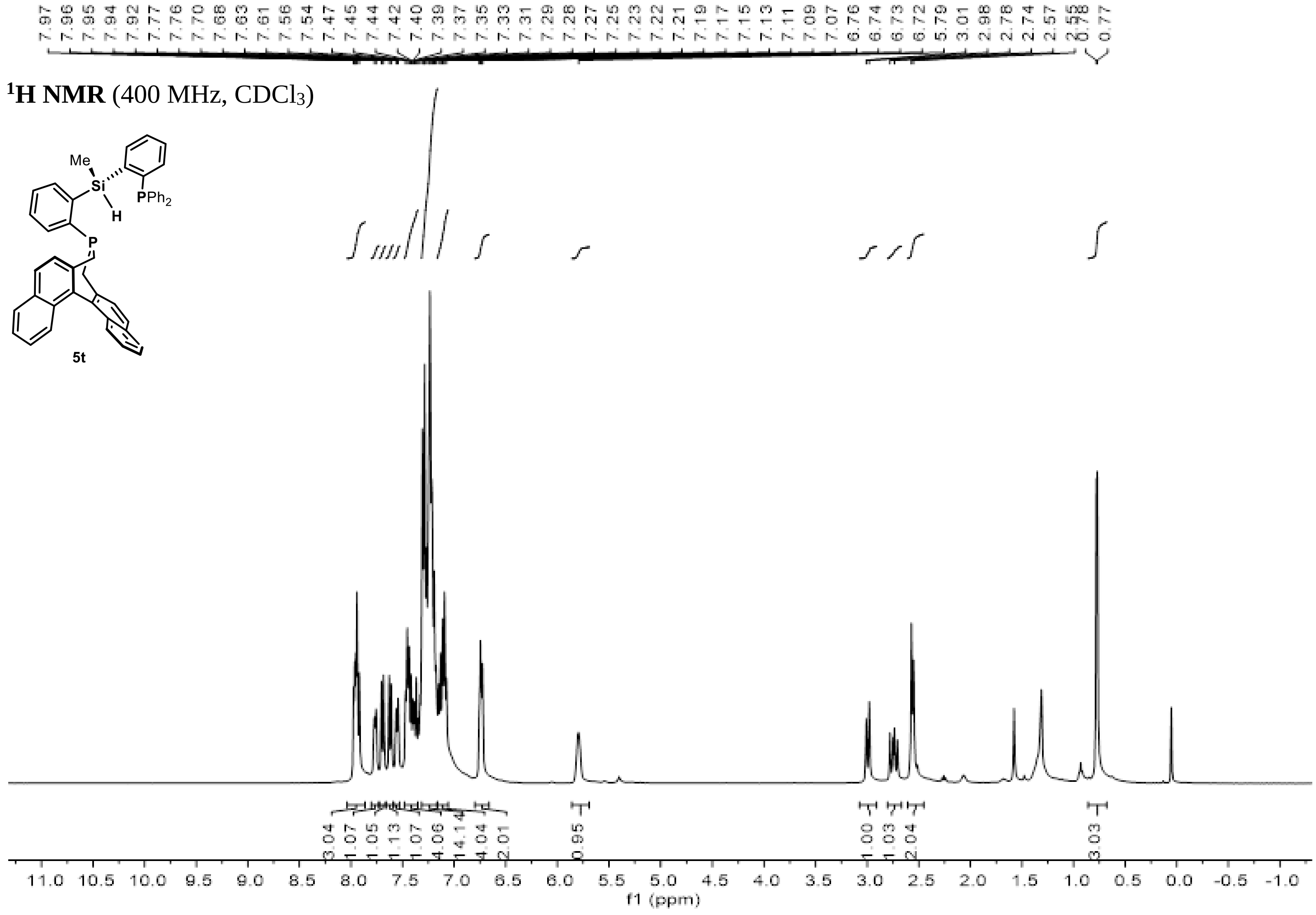
¹³C NMR (101 MHz, $CDCl_3$)

5s'

^{31}P NMR (162 MHz, $CDCl_3$)

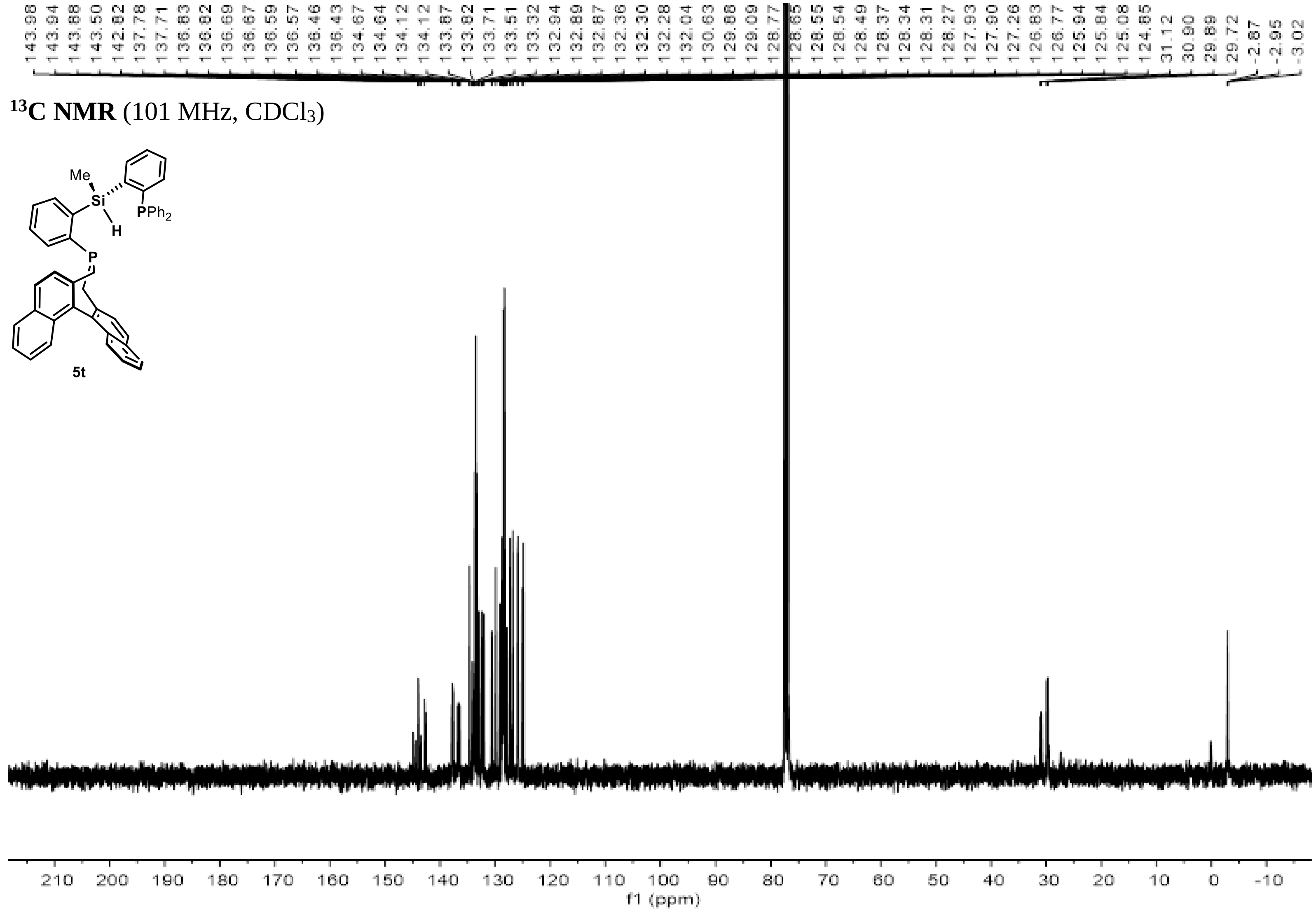


^{1}H NMR (400 MHz, $CDCl_3$)



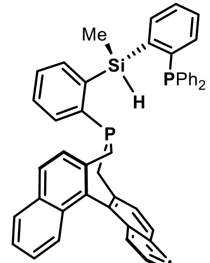
5t

^{13}C NMR (101 MHz, $CDCl_3$)

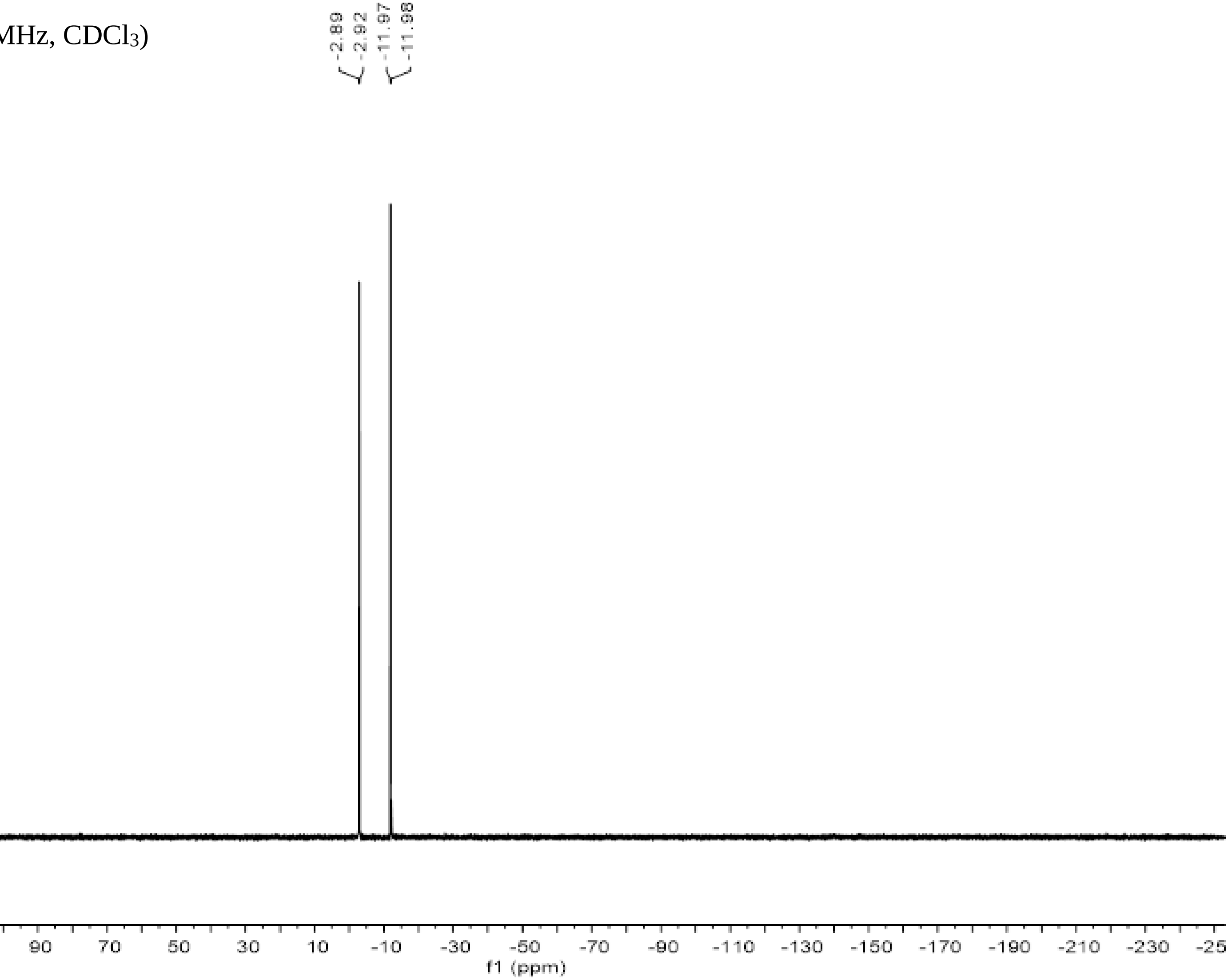


5t

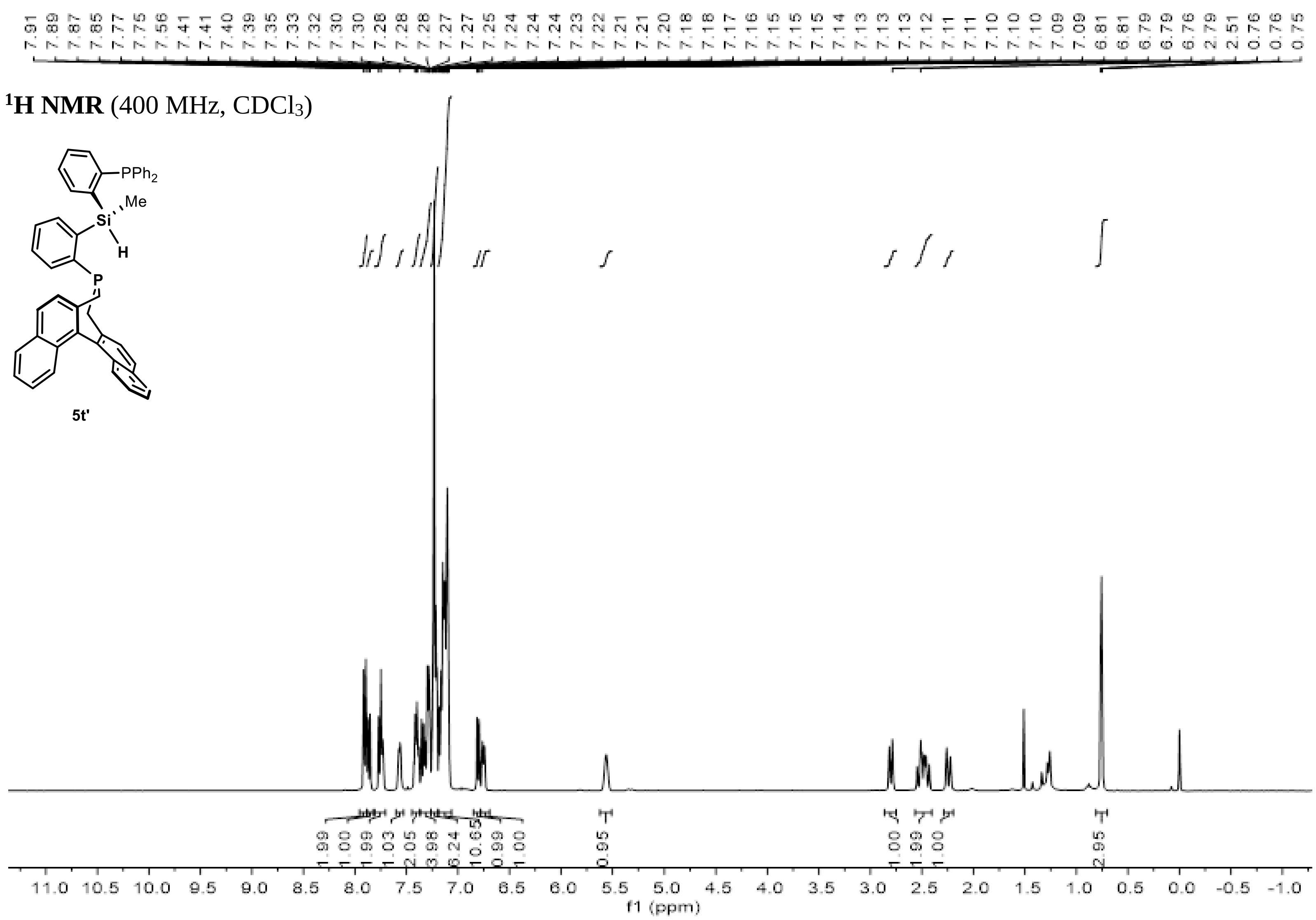
^{31}P NMR (162 MHz, $CDCl_3$)



5t

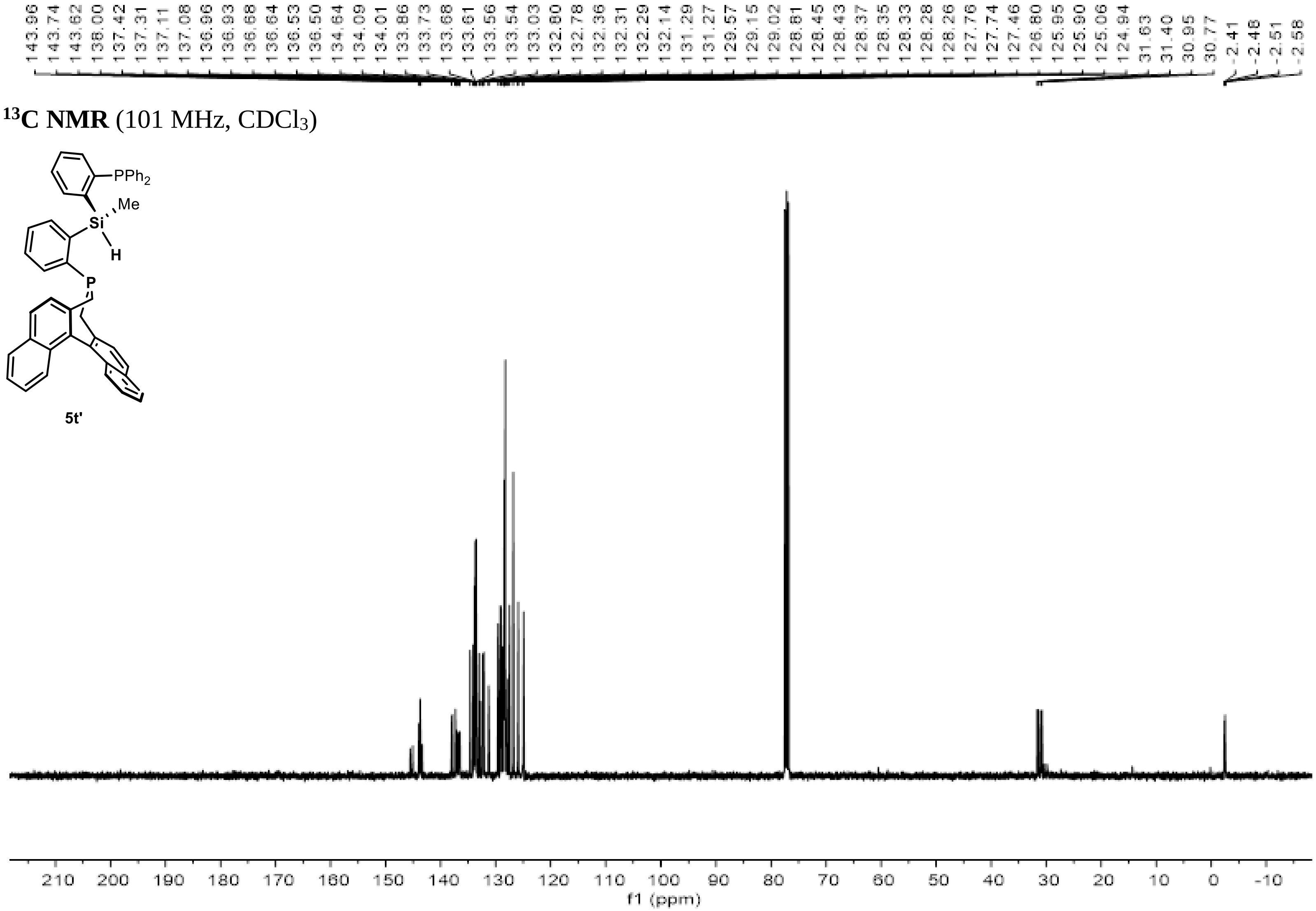


^{1}**H NMR** (400 MHz, CDCl$_3$)



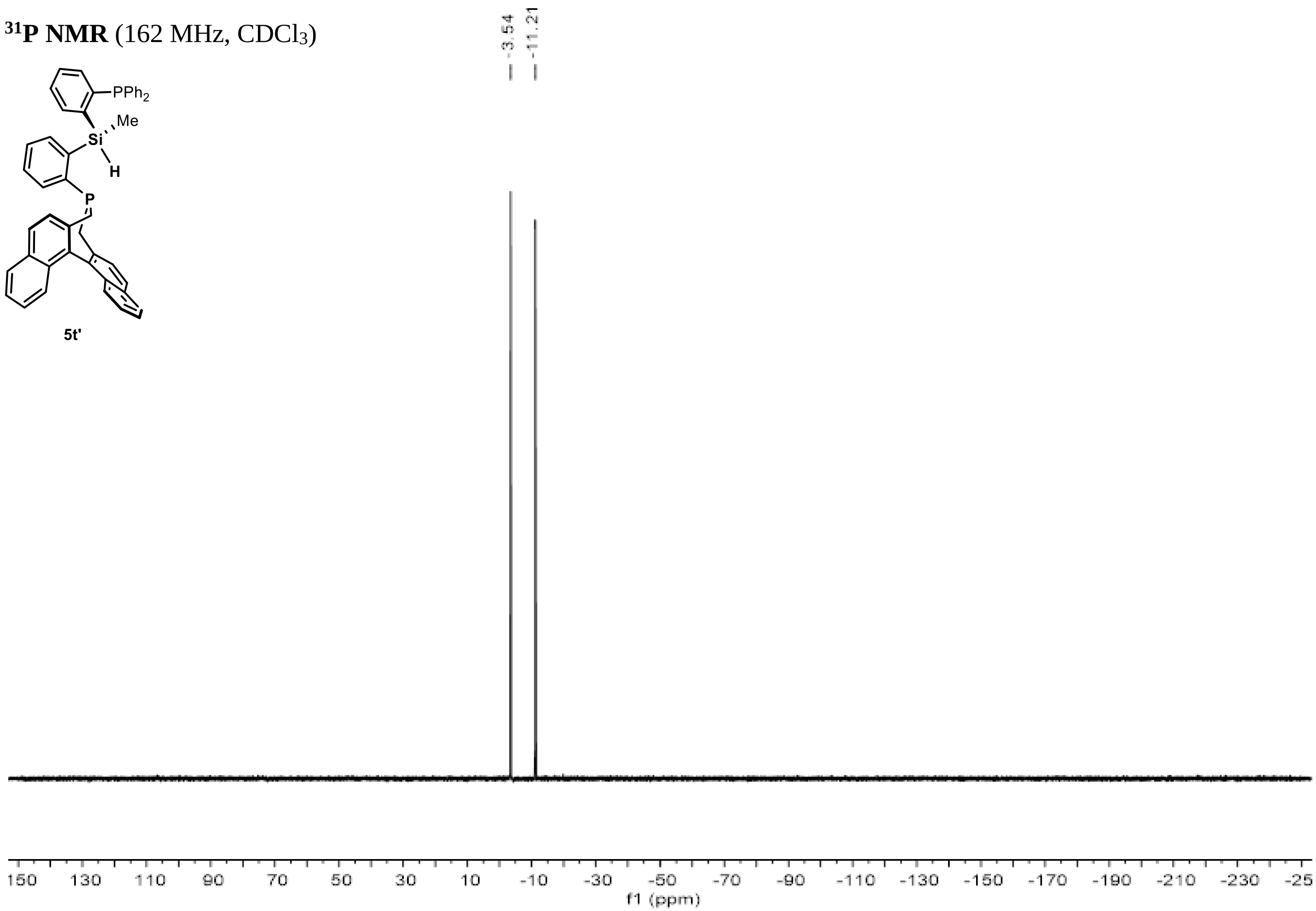
5t'

^{13}C NMR (101 MHz, $CDCl_3$)



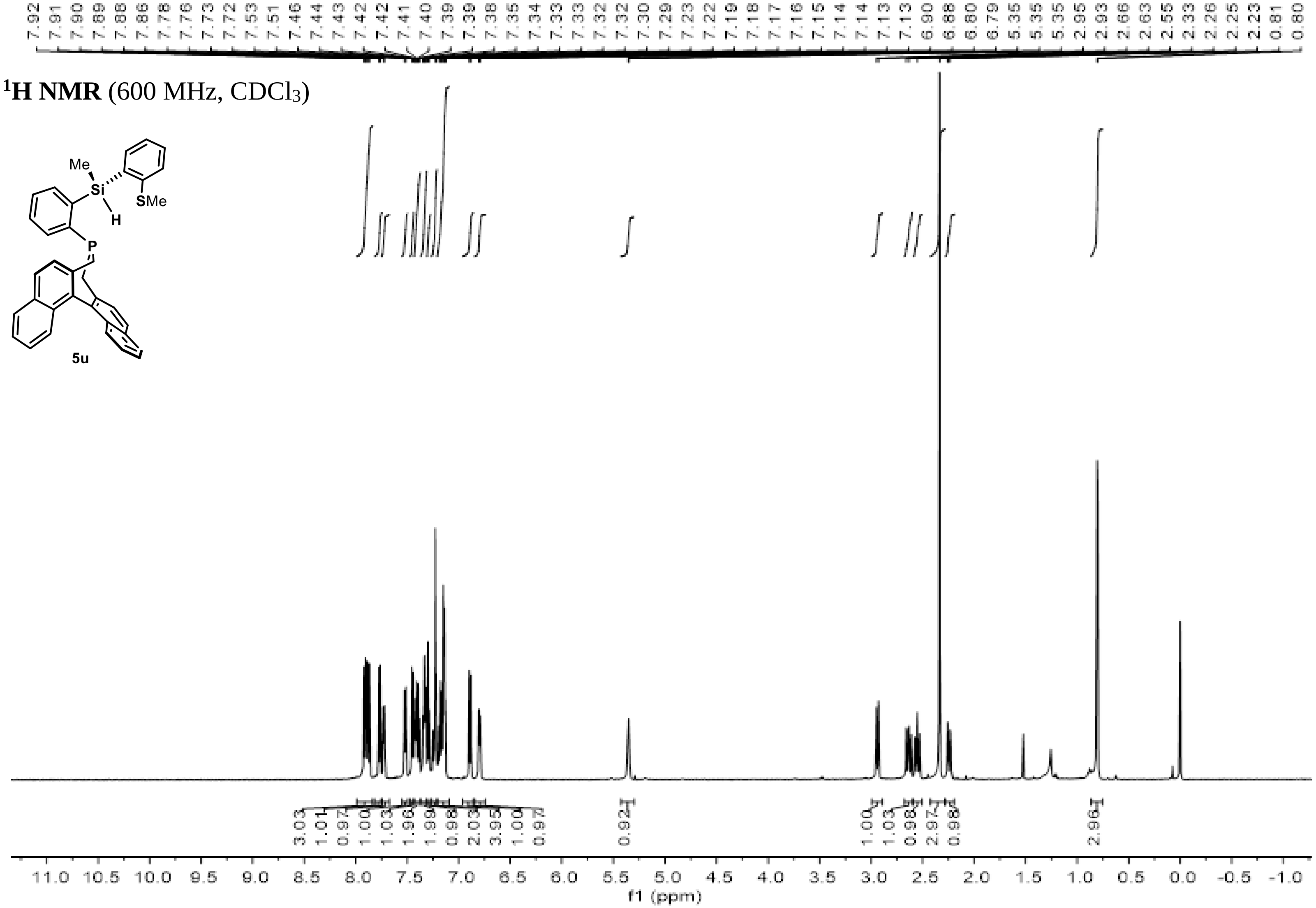
5t'

^{31}P NMR (162 MHz, $CDCl_3$)

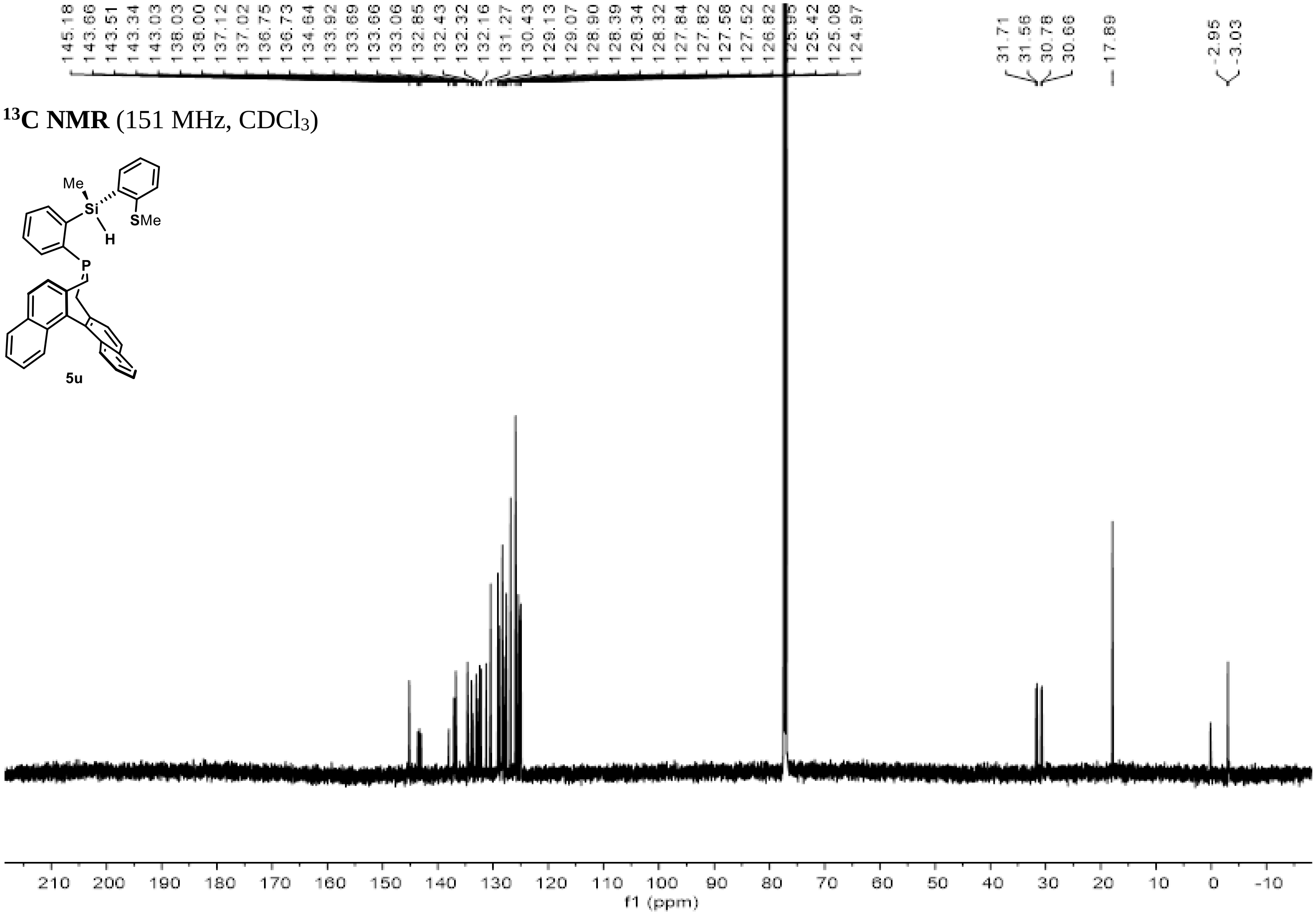


5t'

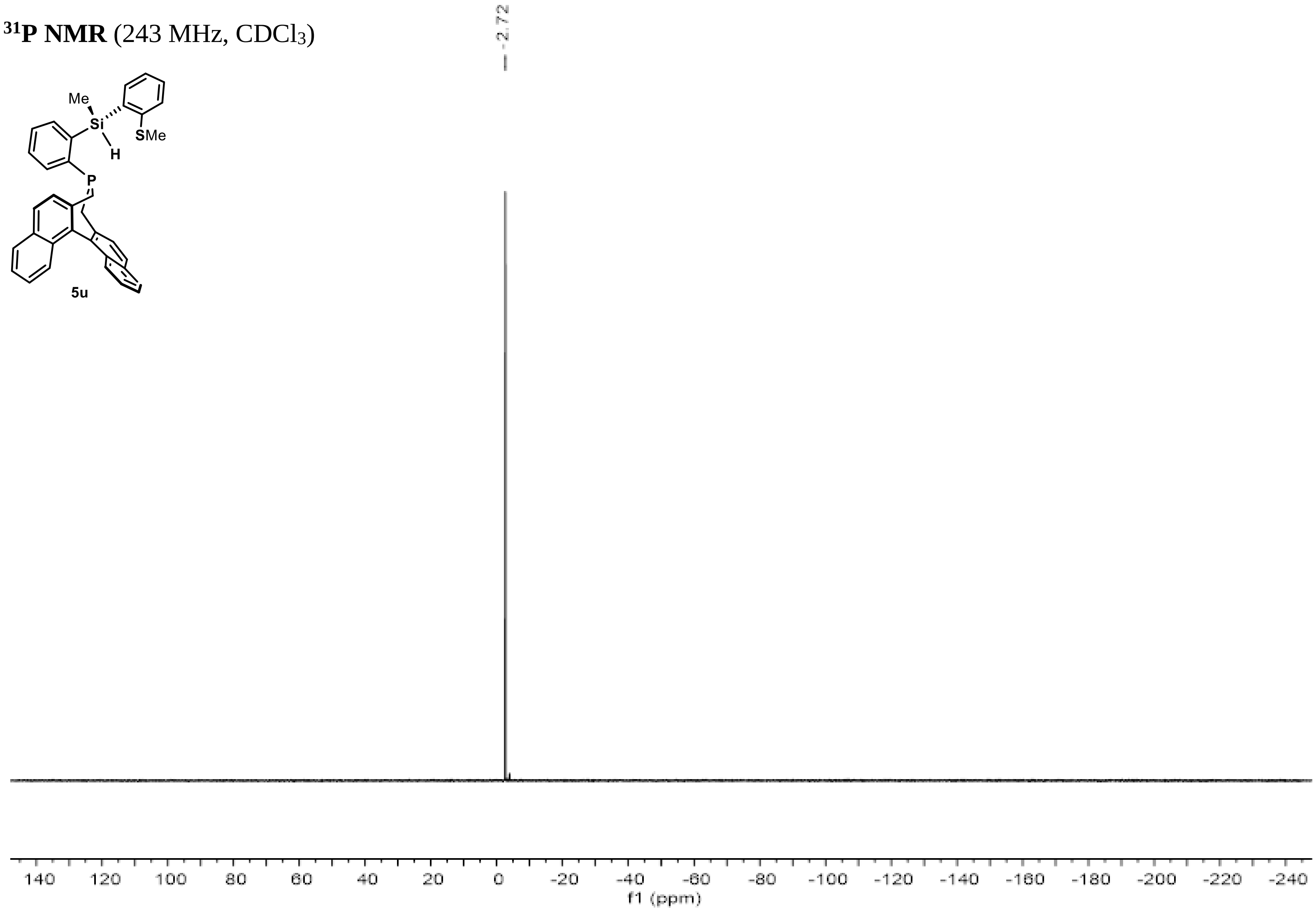
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

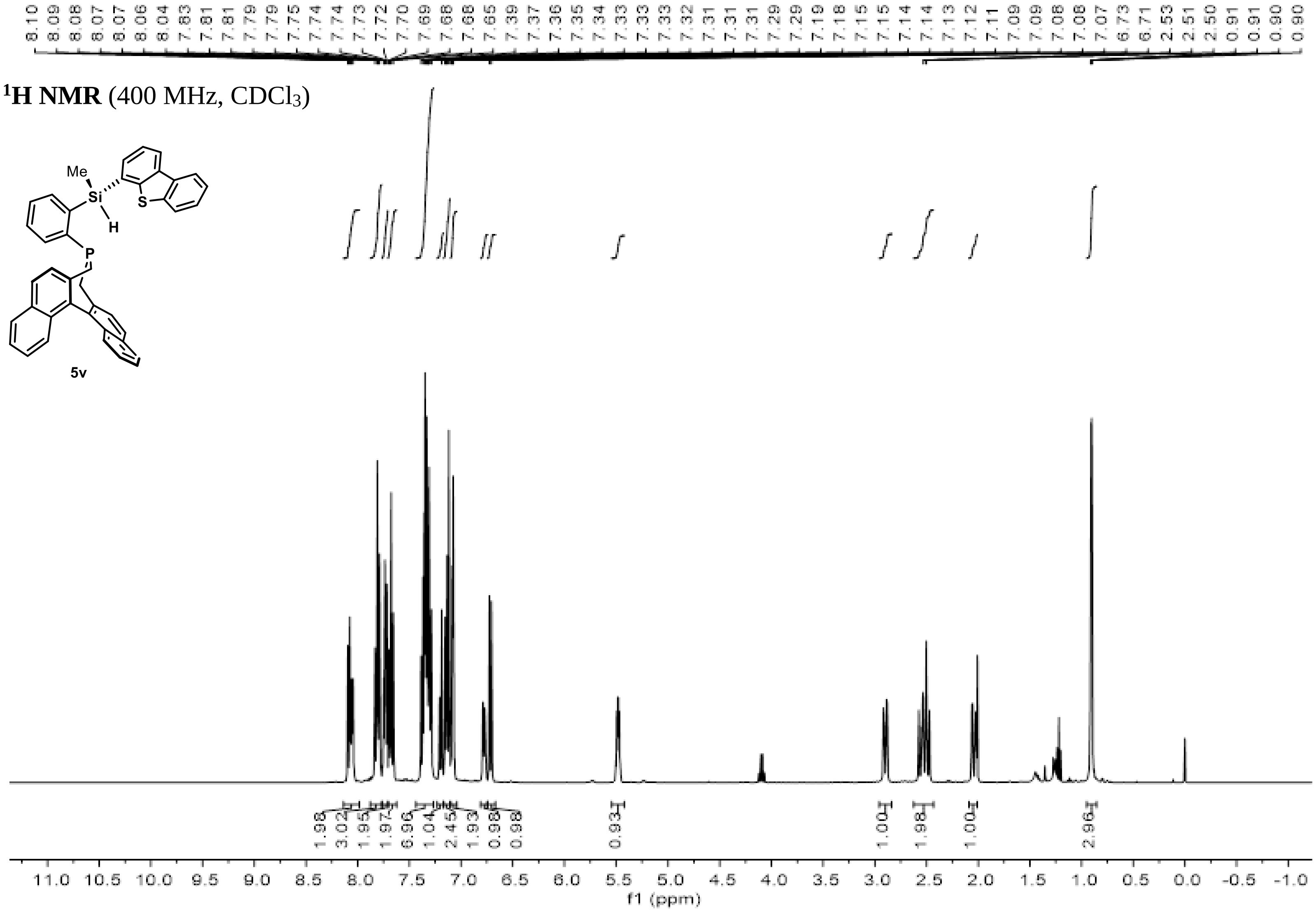


^{31}P NMR (243 MHz, CDCl$_3$)

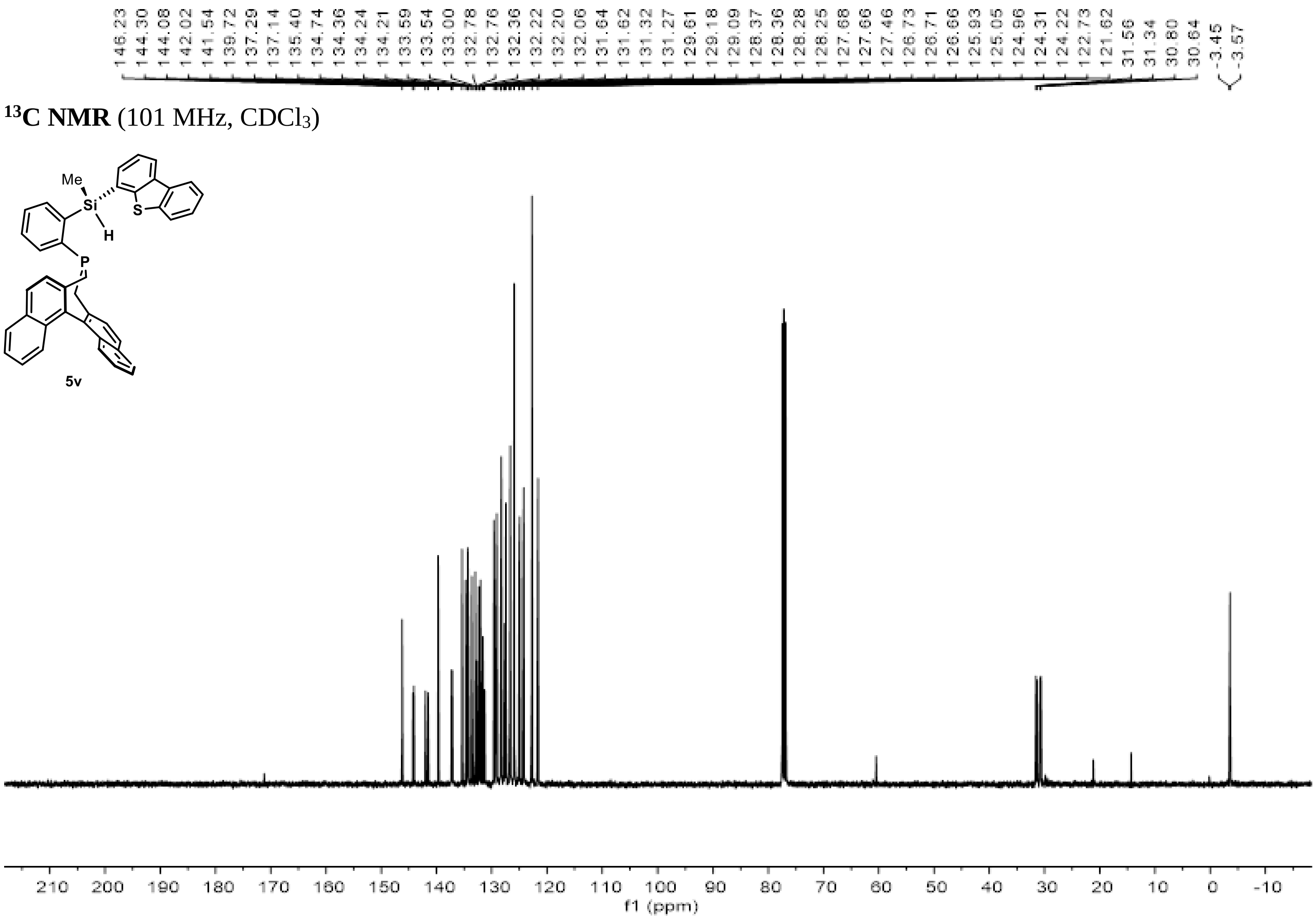


5u

^{1}H NMR (400 MHz, $CDCl_3$)

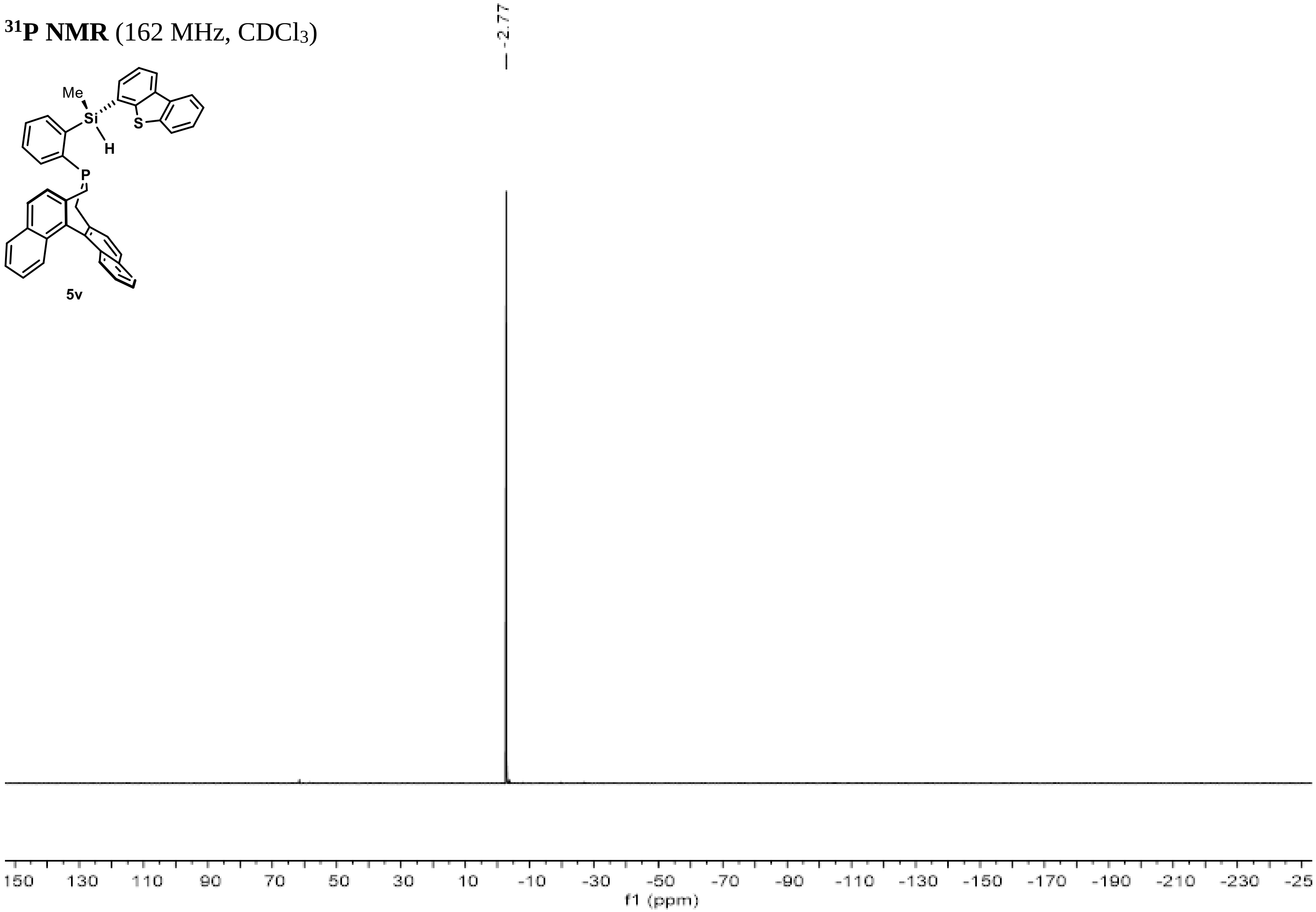


^{13}C NMR (101 MHz, $CDCl_3$)



5v

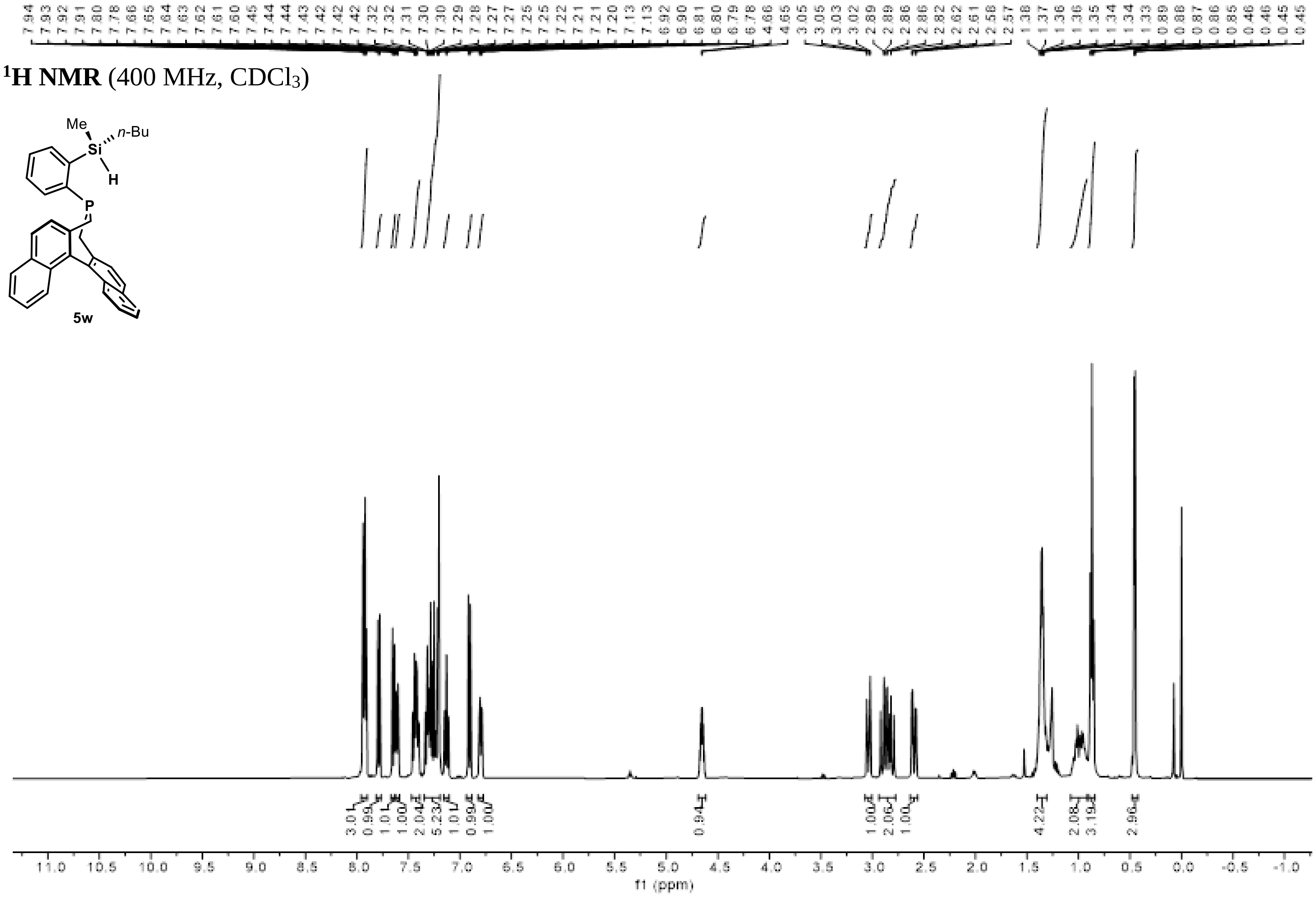
^{31}P NMR (162 MHz, $CDCl_3$)



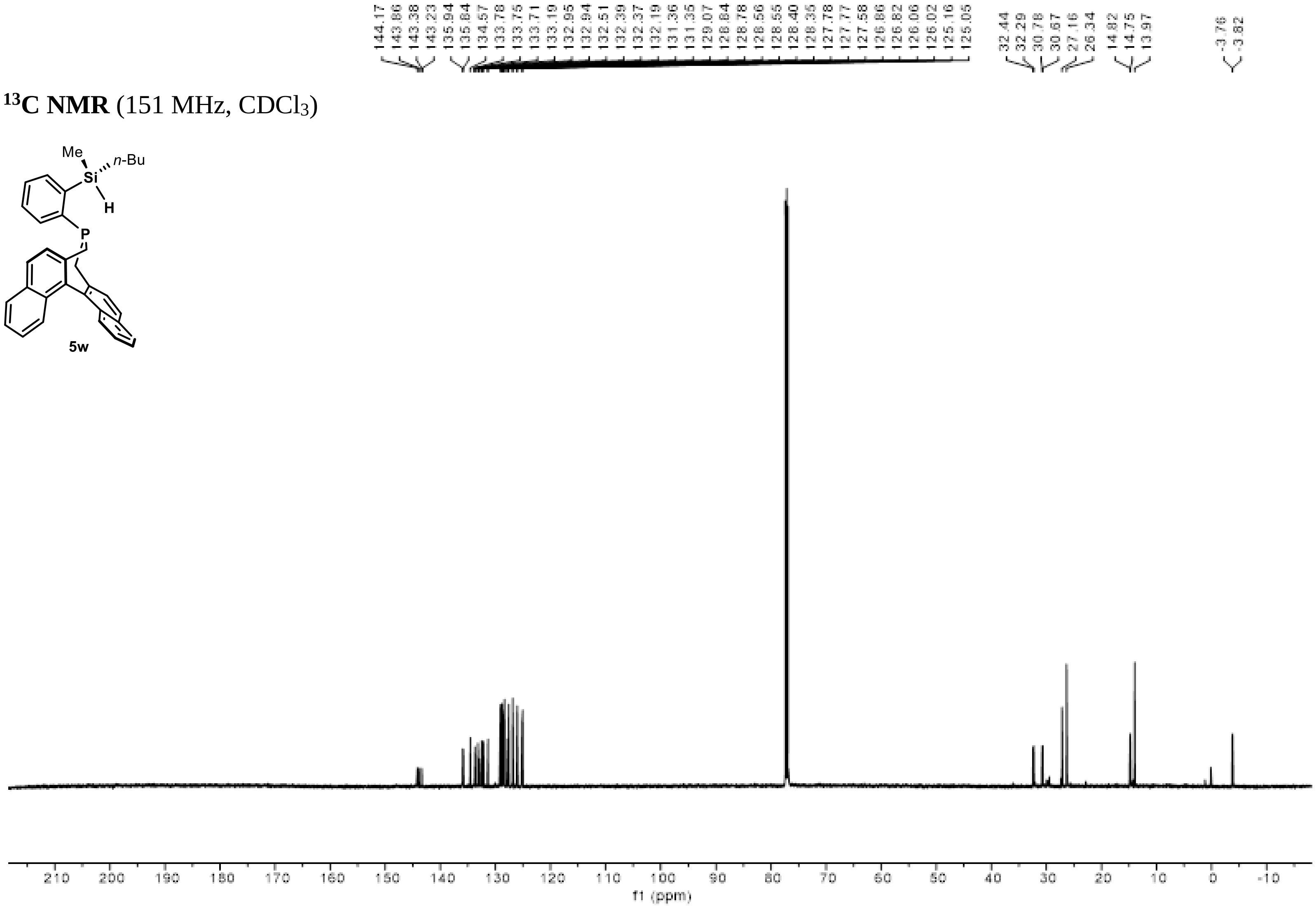
5v

^{1}H NMR (400 MHz, $CDCl_3$)

5w

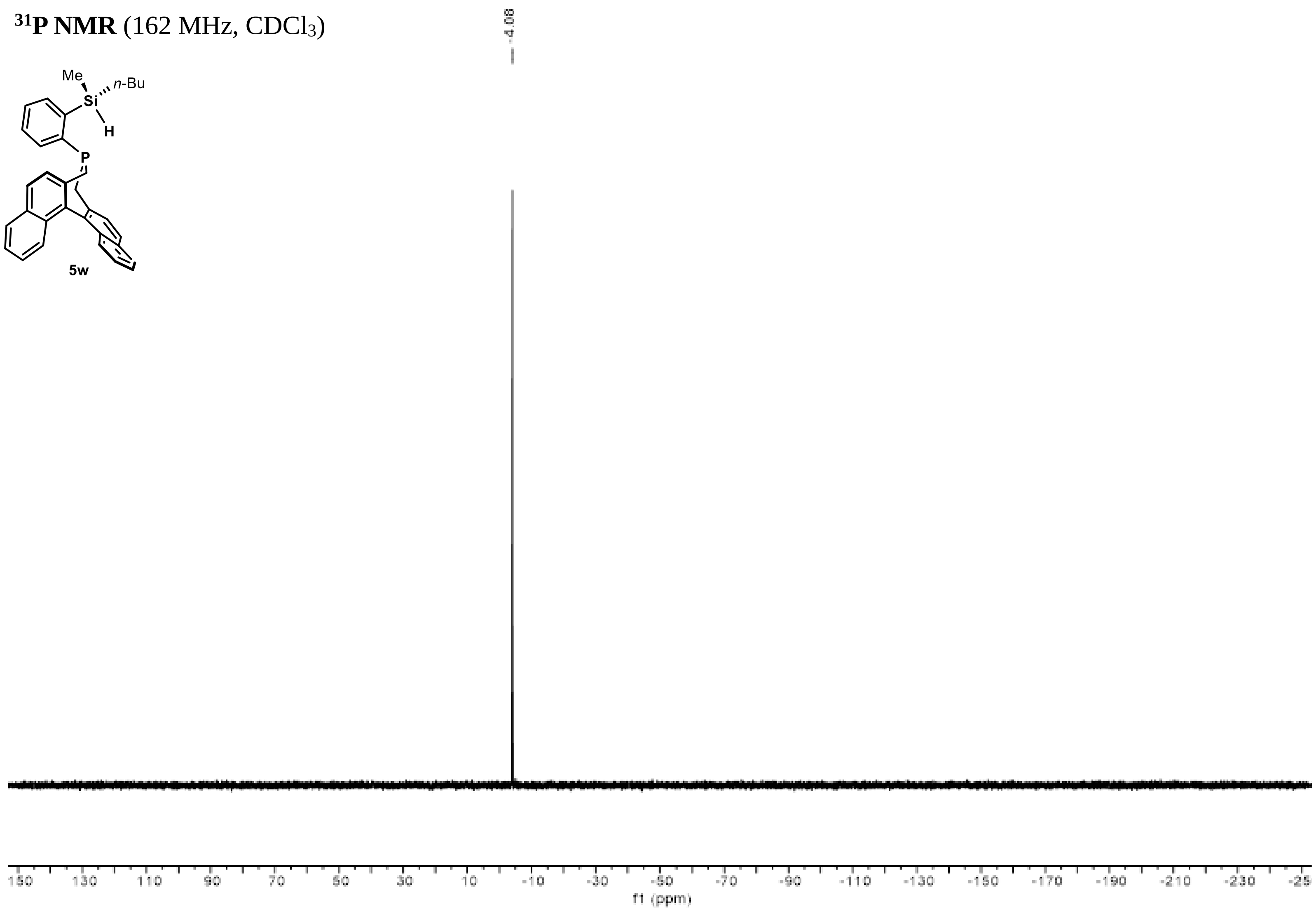


^{13}**C NMR** (151 MHz, $CDCl_3$)



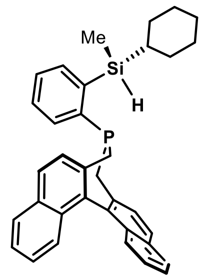
5w

^{31}P NMR (162 MHz, $CDCl_3$)

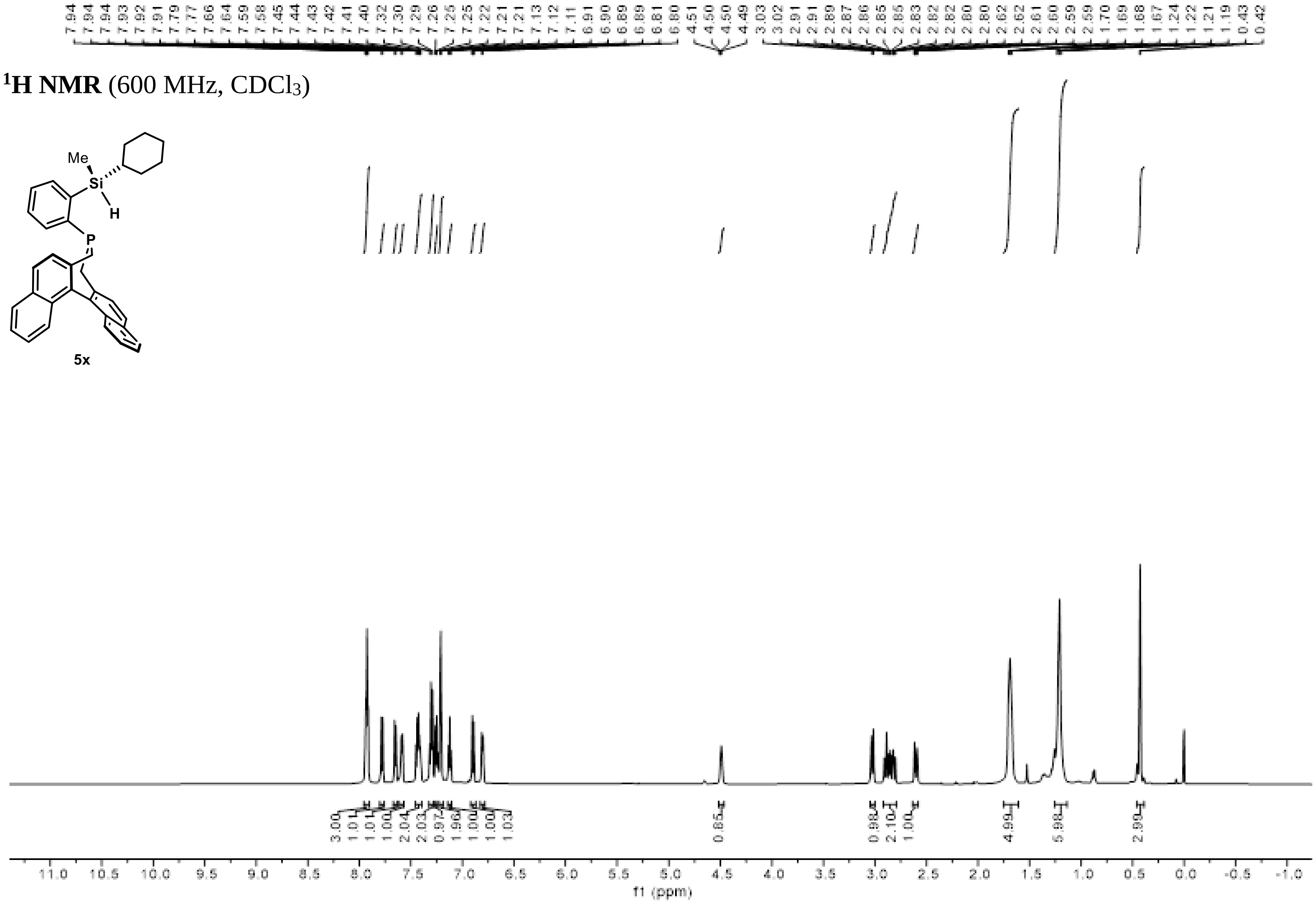


5w

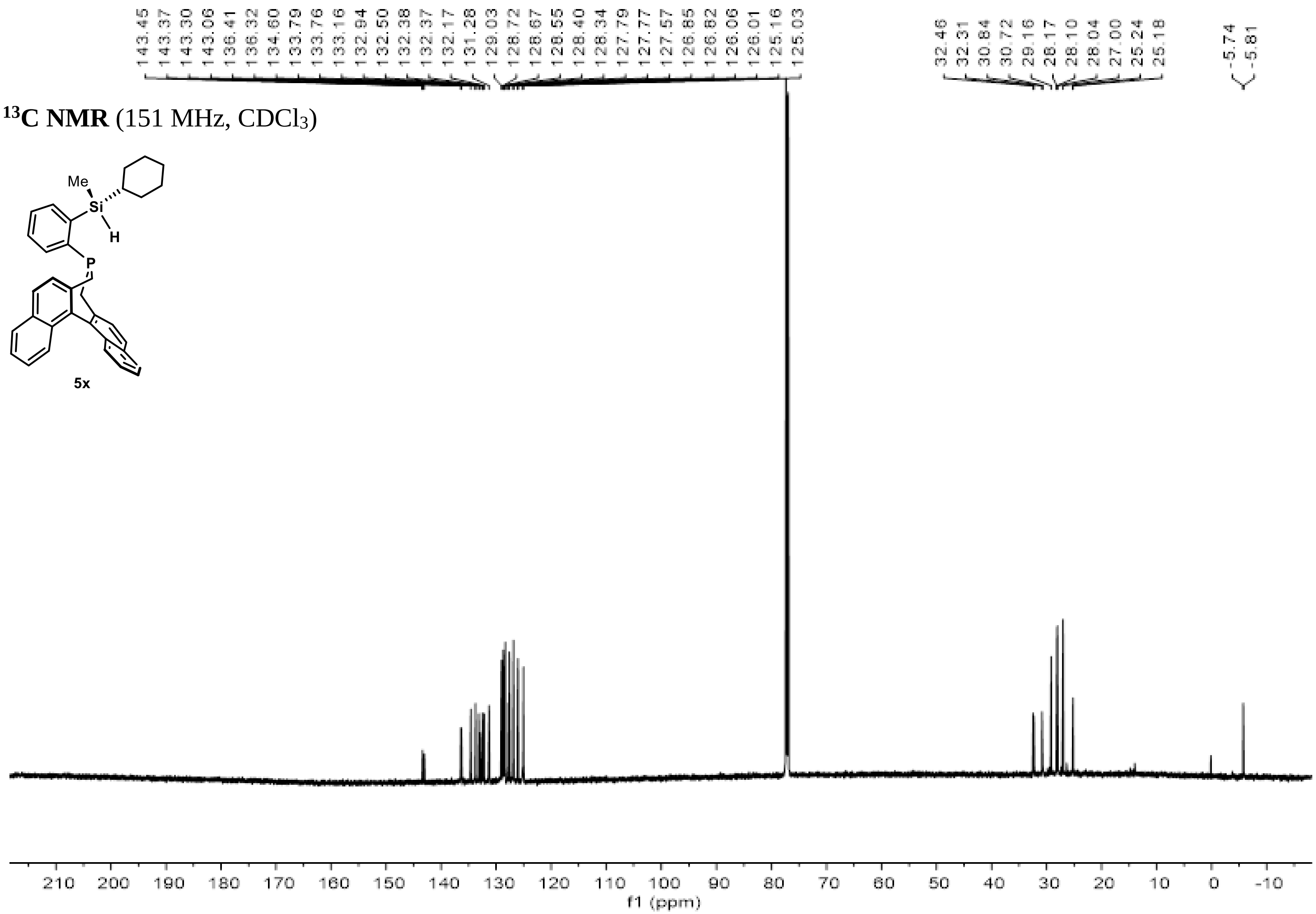
^{1}H NMR (600 MHz, $CDCl_3$)



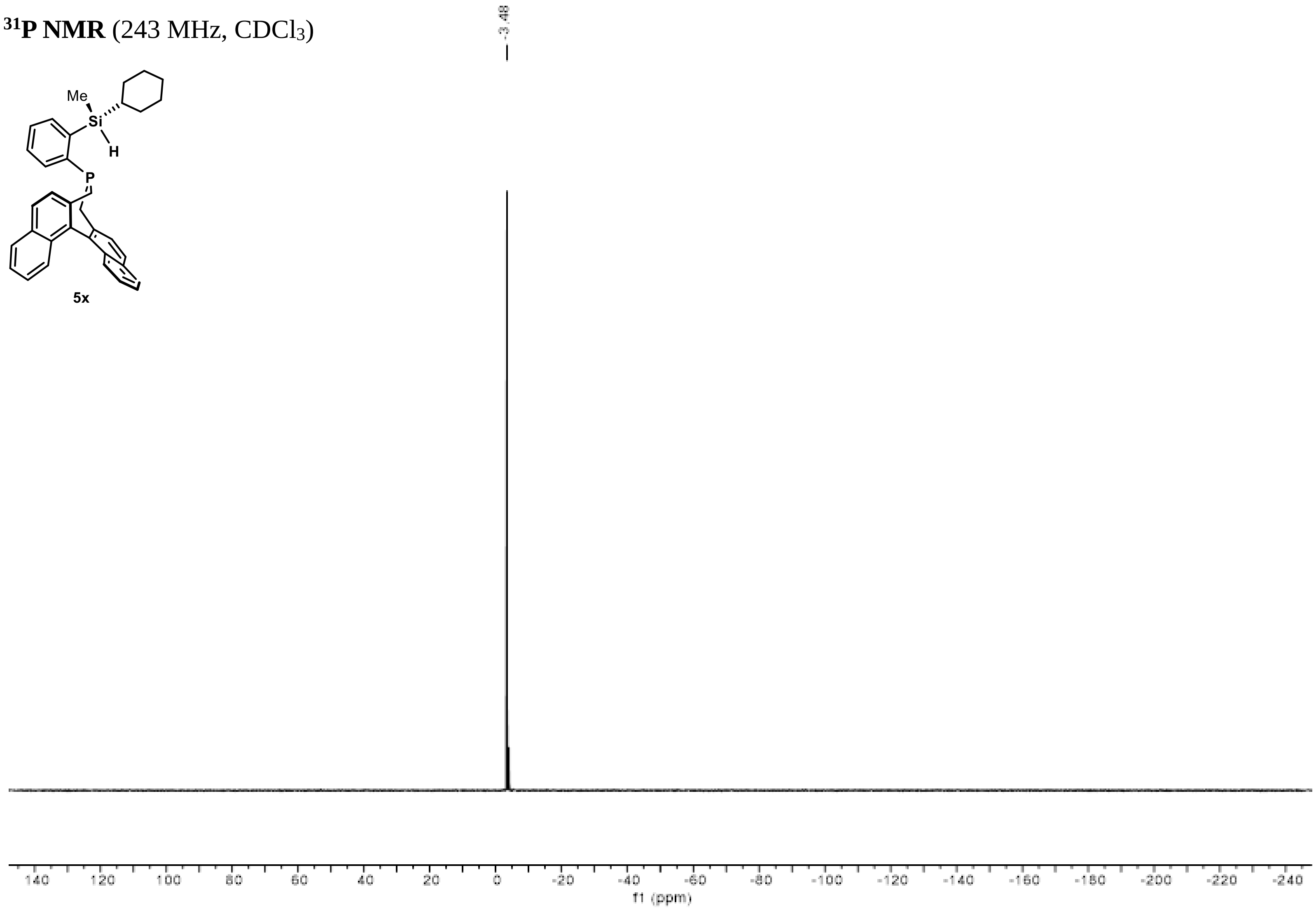
5x



^{13}C NMR (151 MHz, CDCl$_3$)

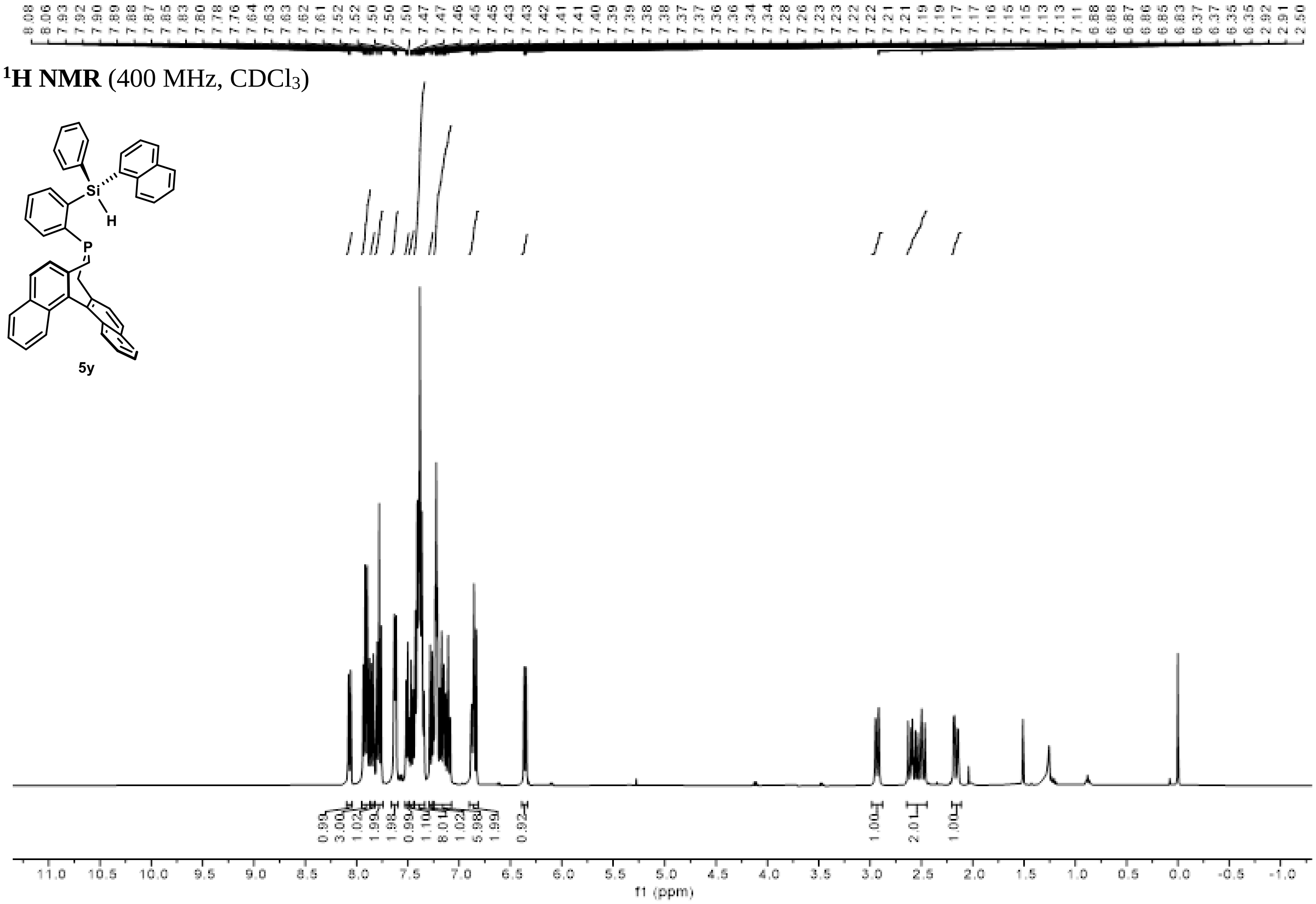


^{31}P NMR (243 MHz, CDCl$_3$)

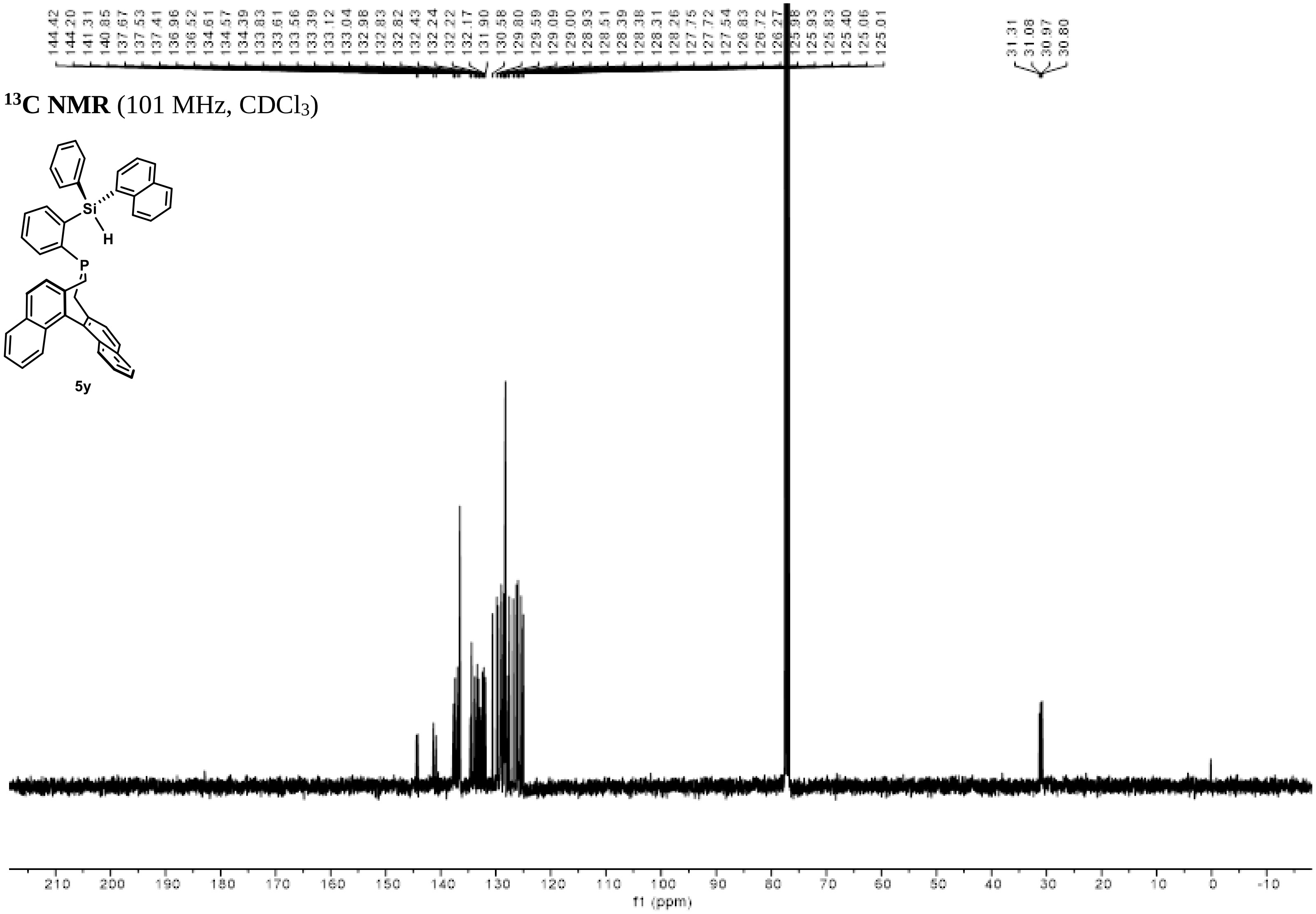


5x

^{1}H NMR (400 MHz, $CDCl_3$)

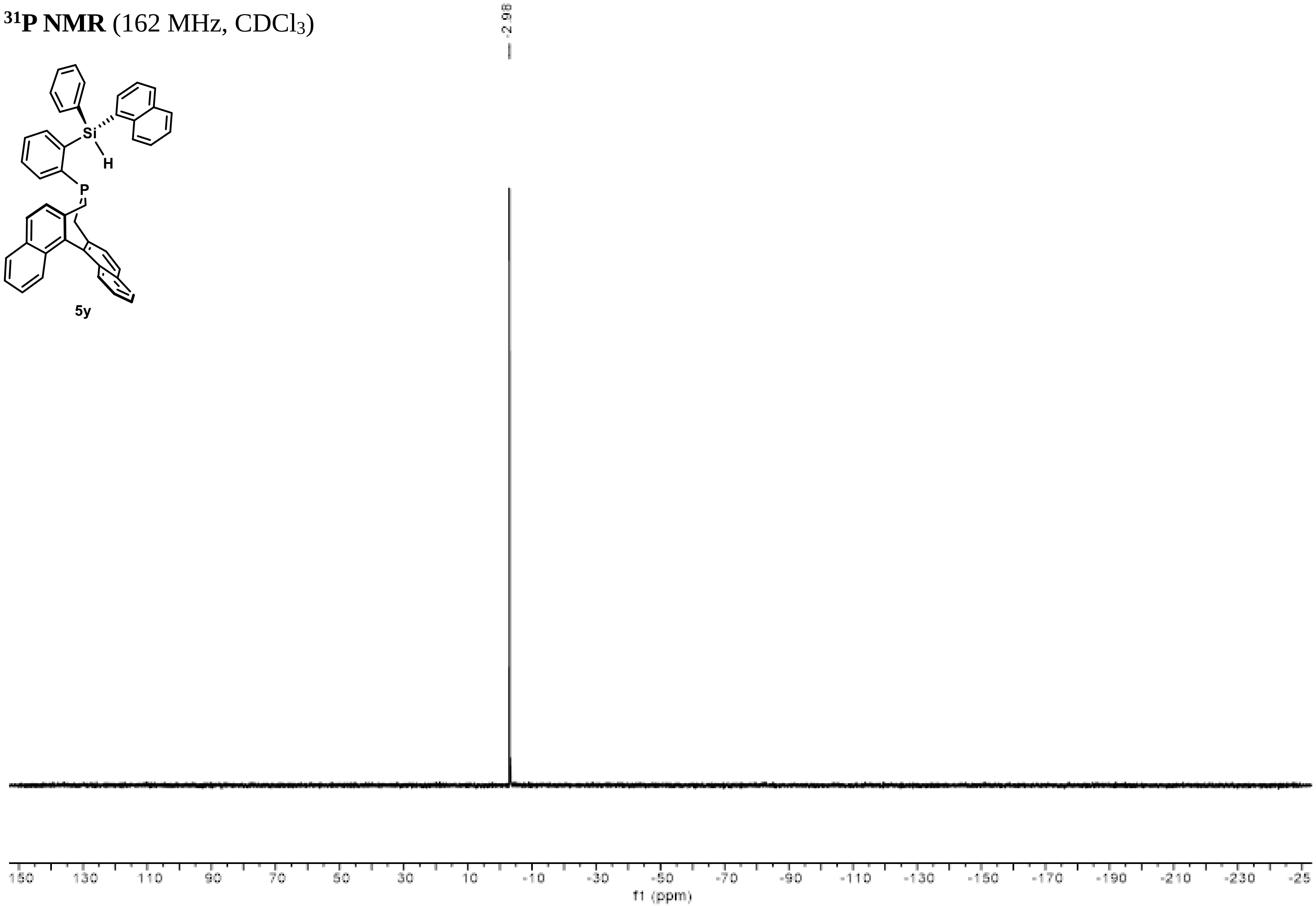

5y

^{13}C NMR (101 MHz, $CDCl_3$)



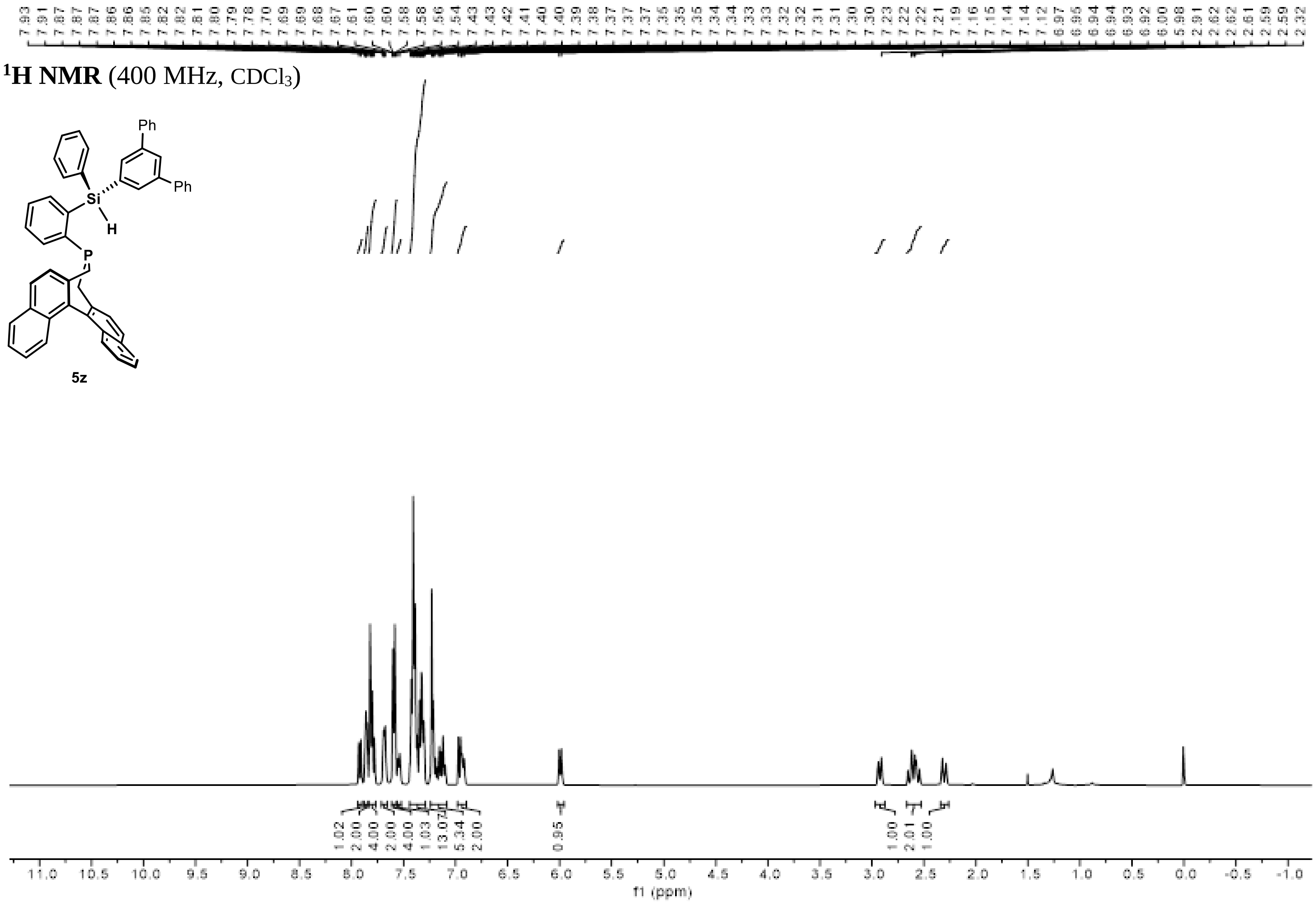
5y

^{31}P NMR (162 MHz, CDCl$_3$)



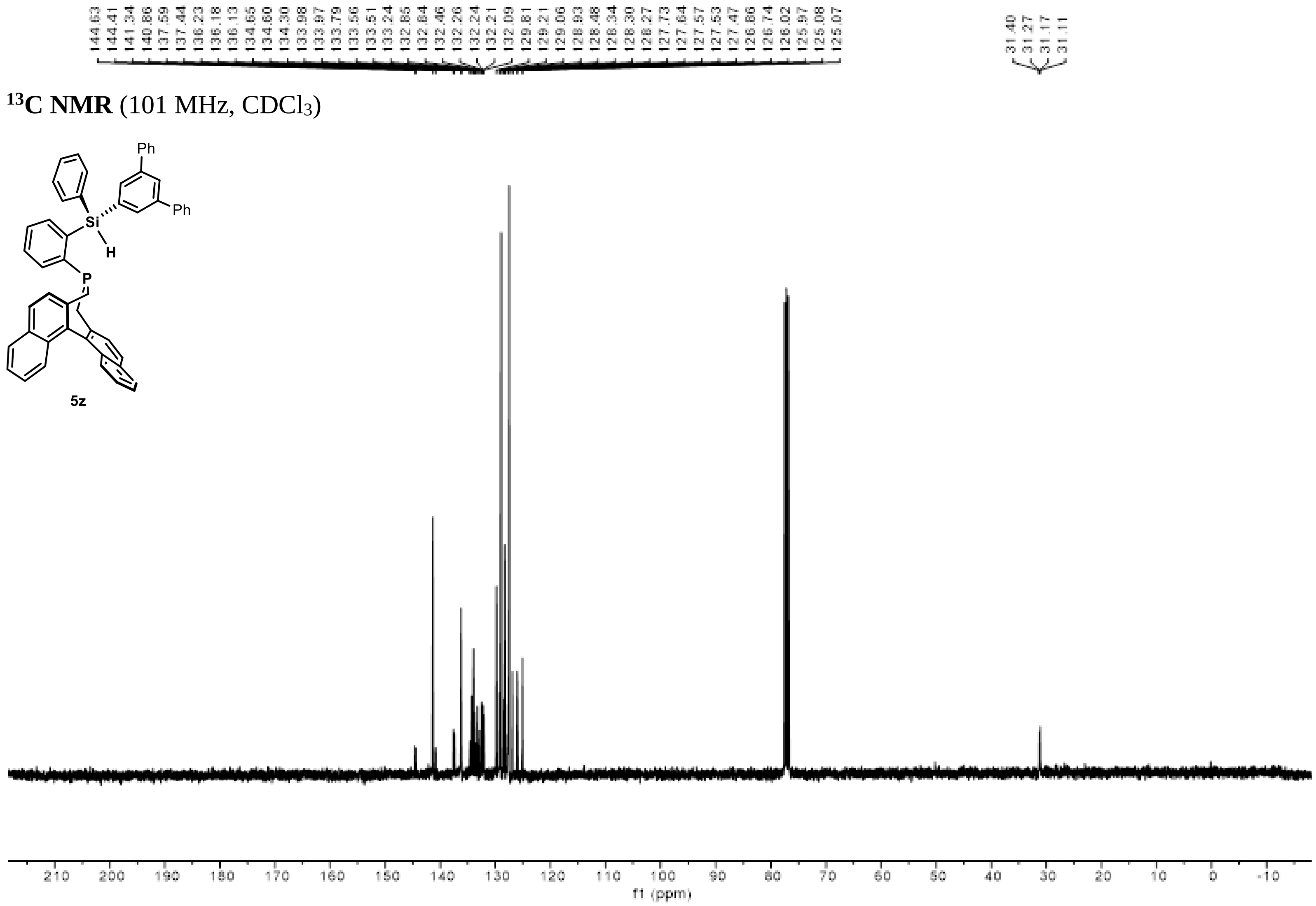
5y

^{1}H NMR (400 MHz, $CDCl_3$)

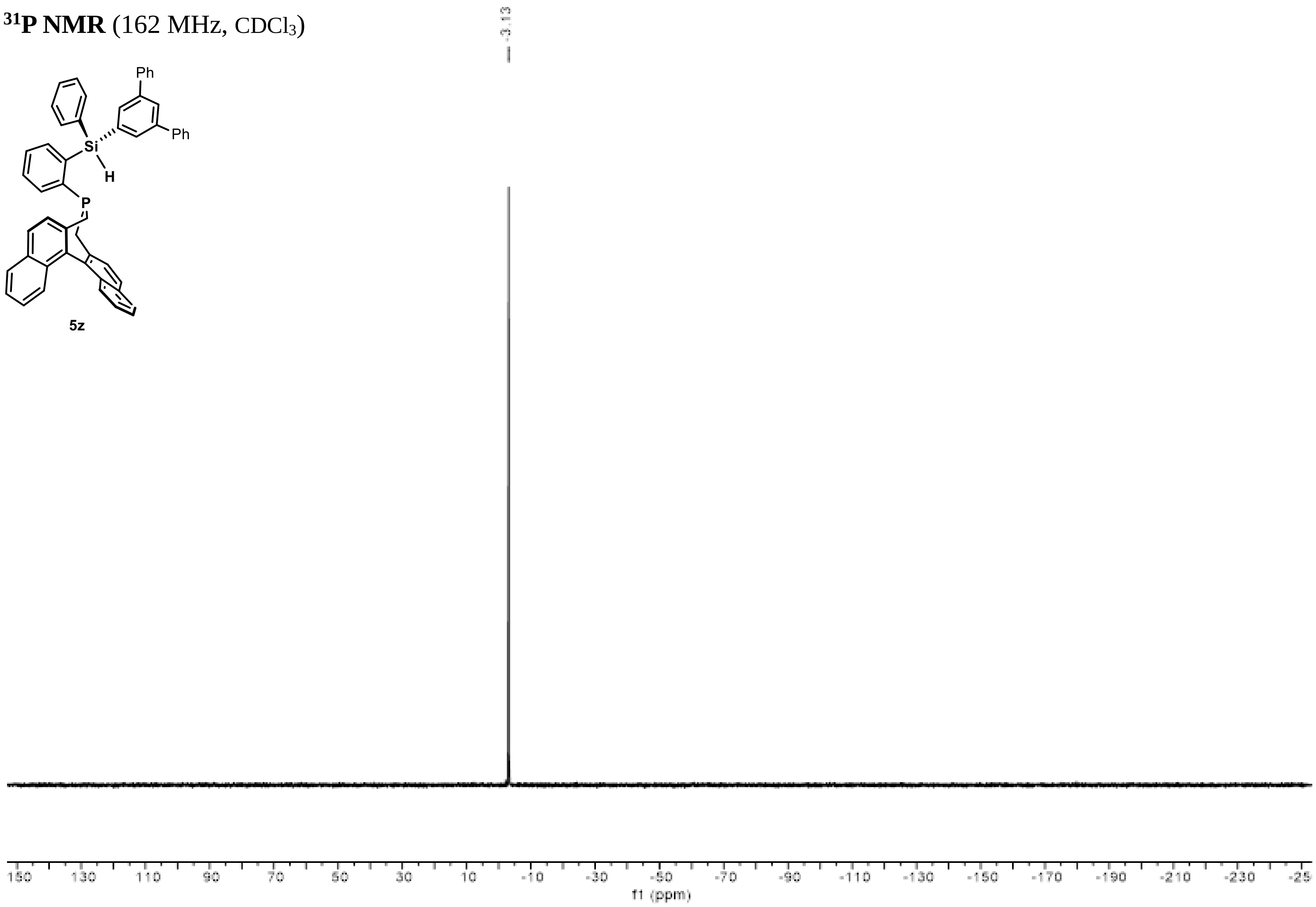


5z

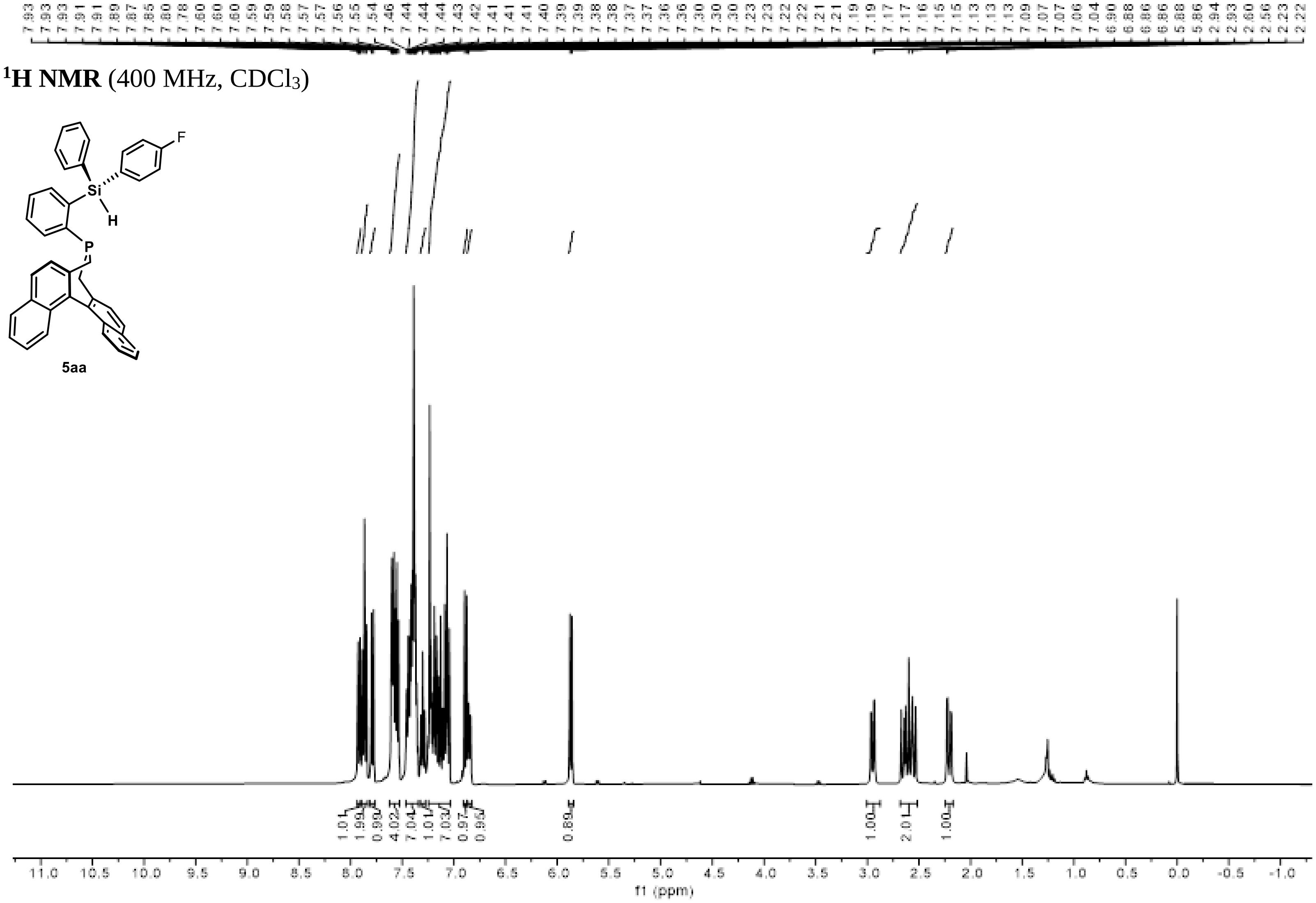
^{13}C NMR (101 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, CDCl$_3$)

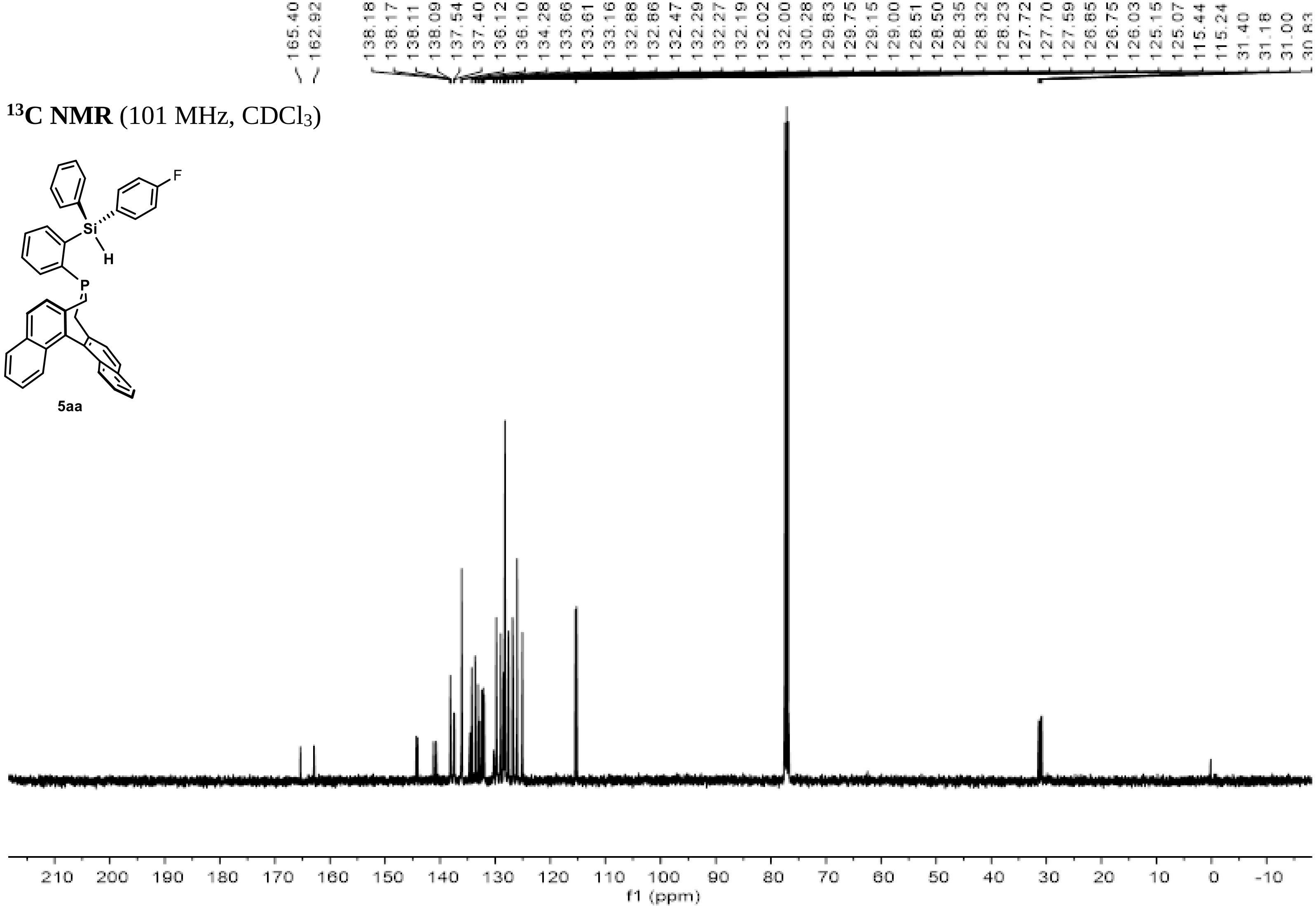


^{1}H NMR (400 MHz, CDCl$_3$)

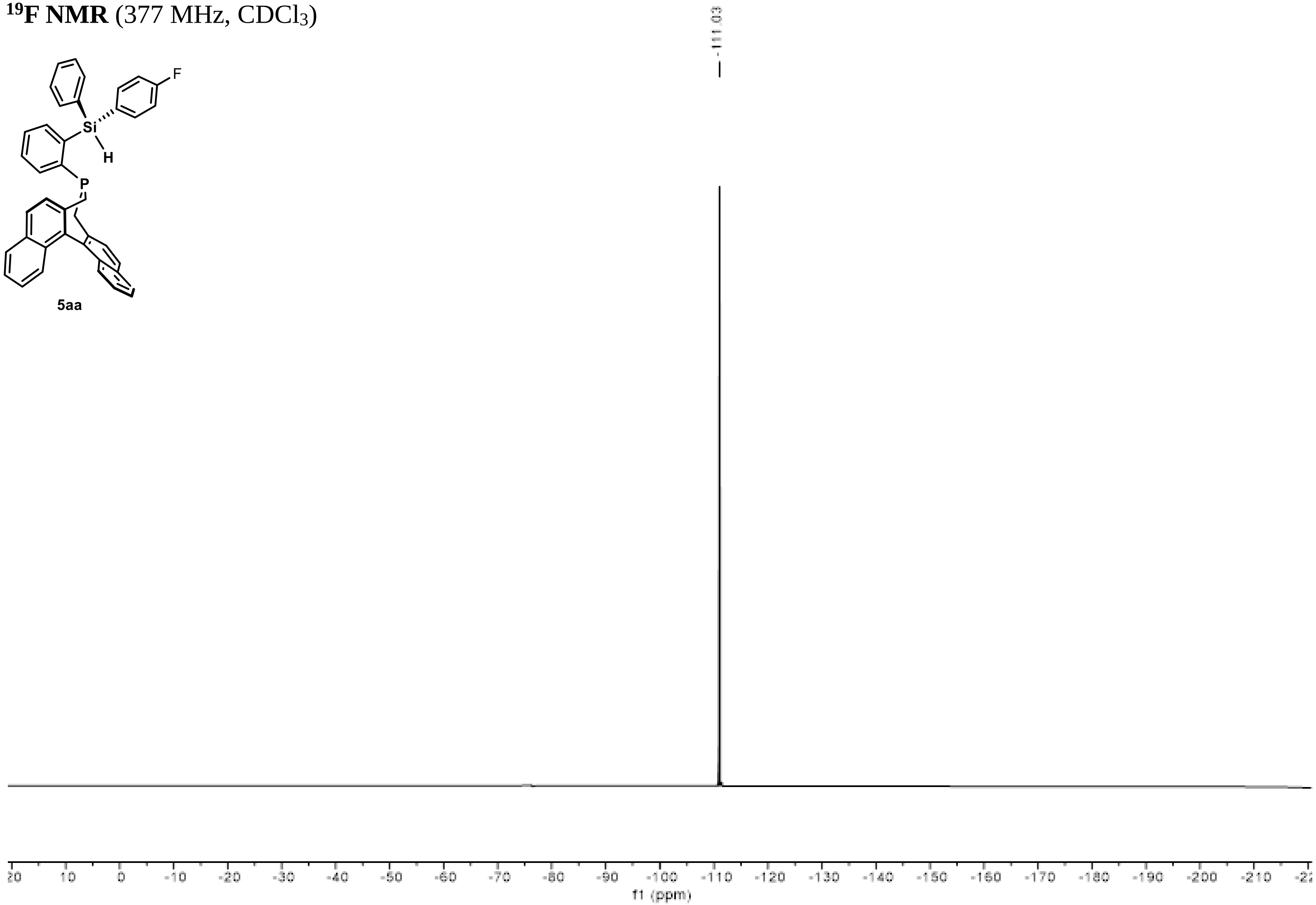


5aa

¹³C NMR (101 MHz, CDCl$_3$)

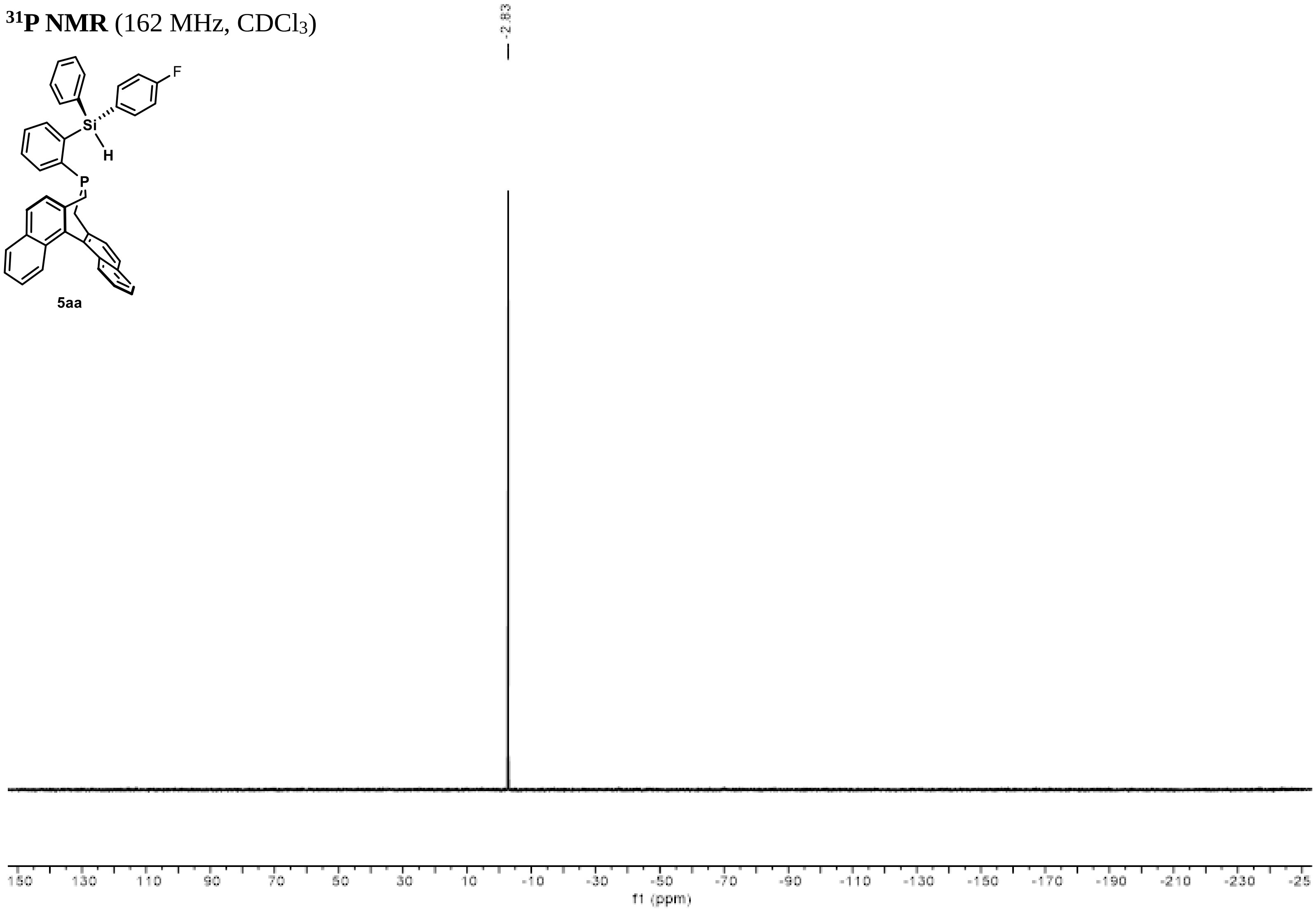


^{19}F NMR (377 MHz, $CDCl_3$)

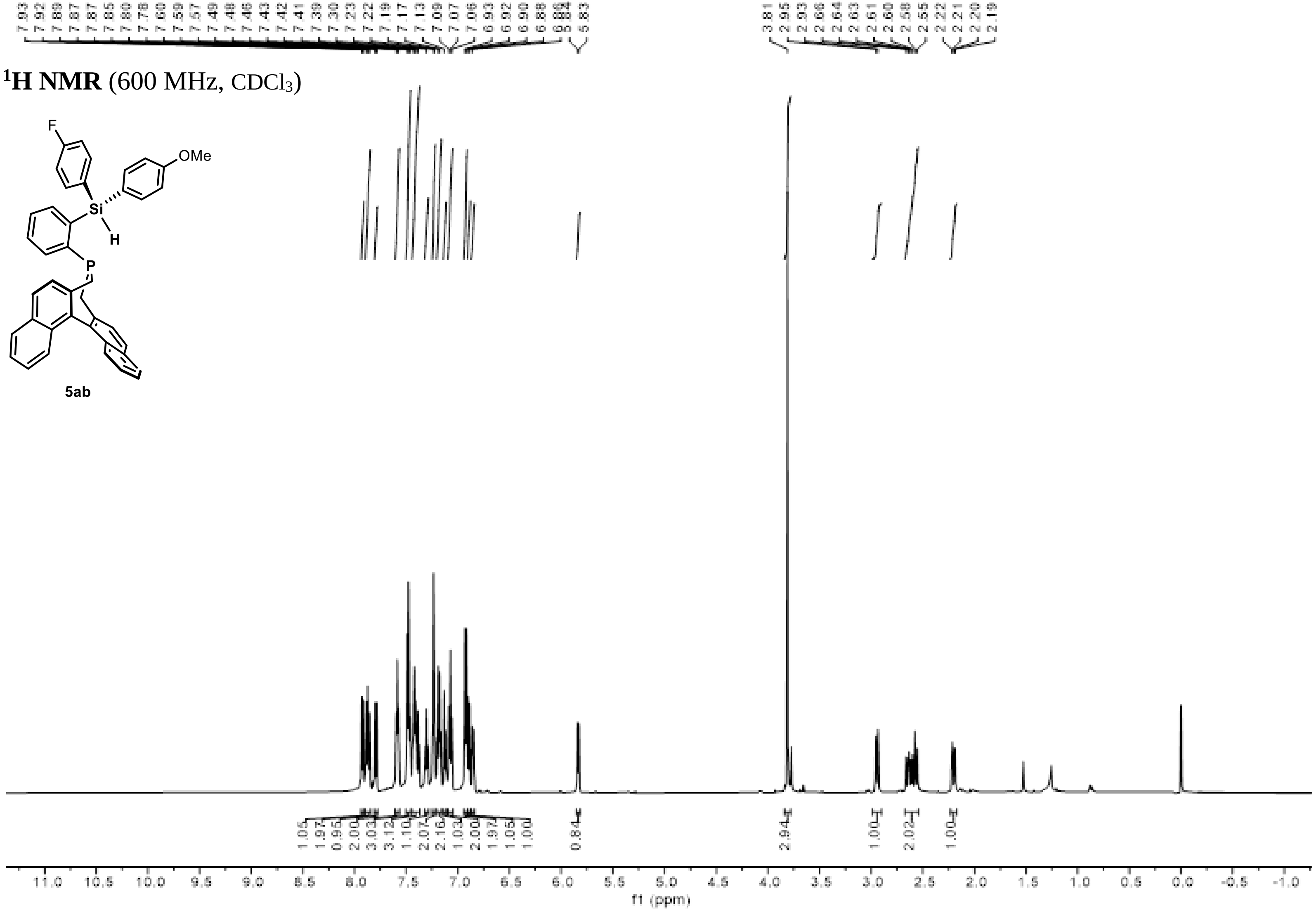


^{31}P NMR (162 MHz, CDCl$_3$)

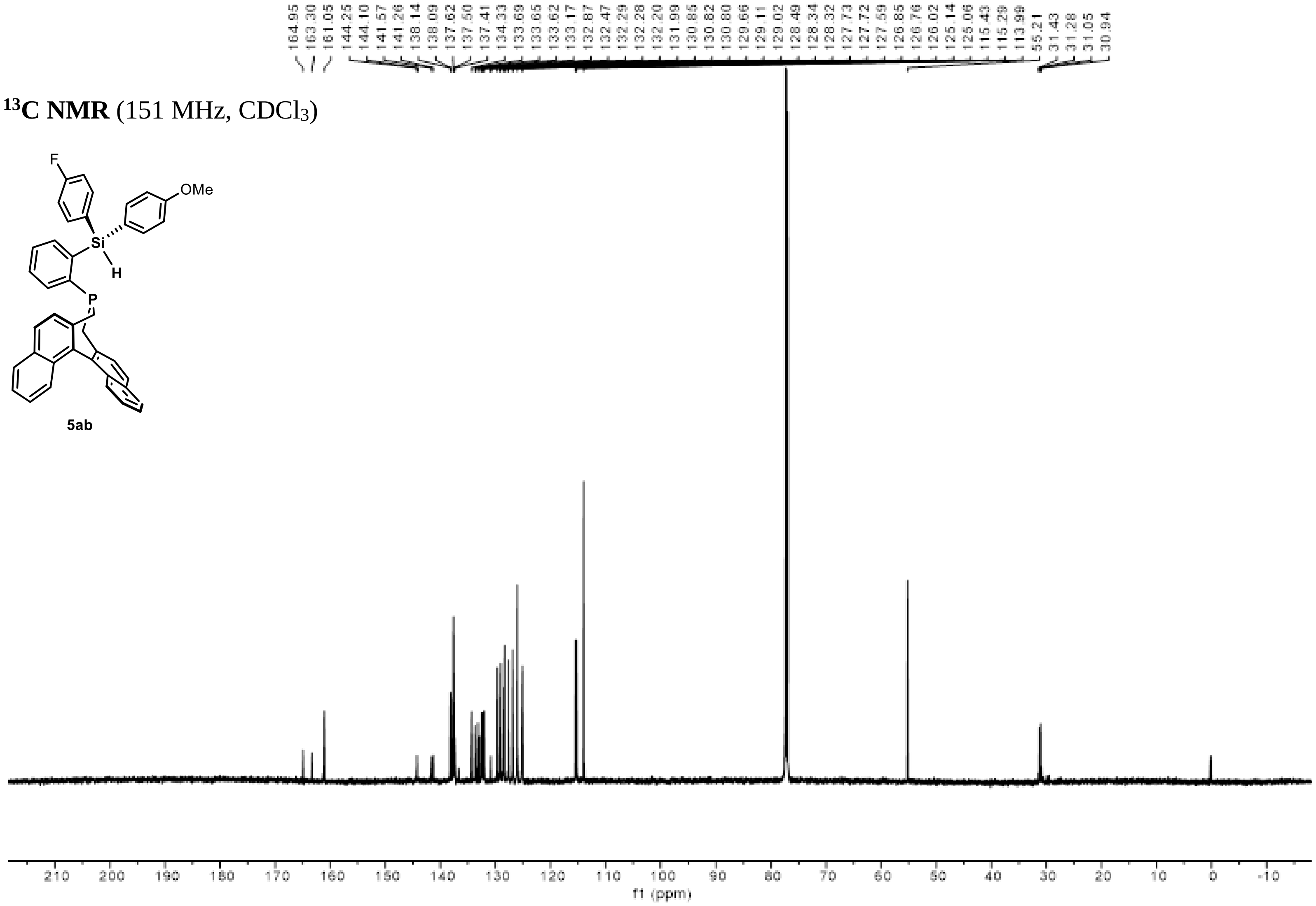
5aa



^{1}H NMR (600 MHz, $CDCl_3$)

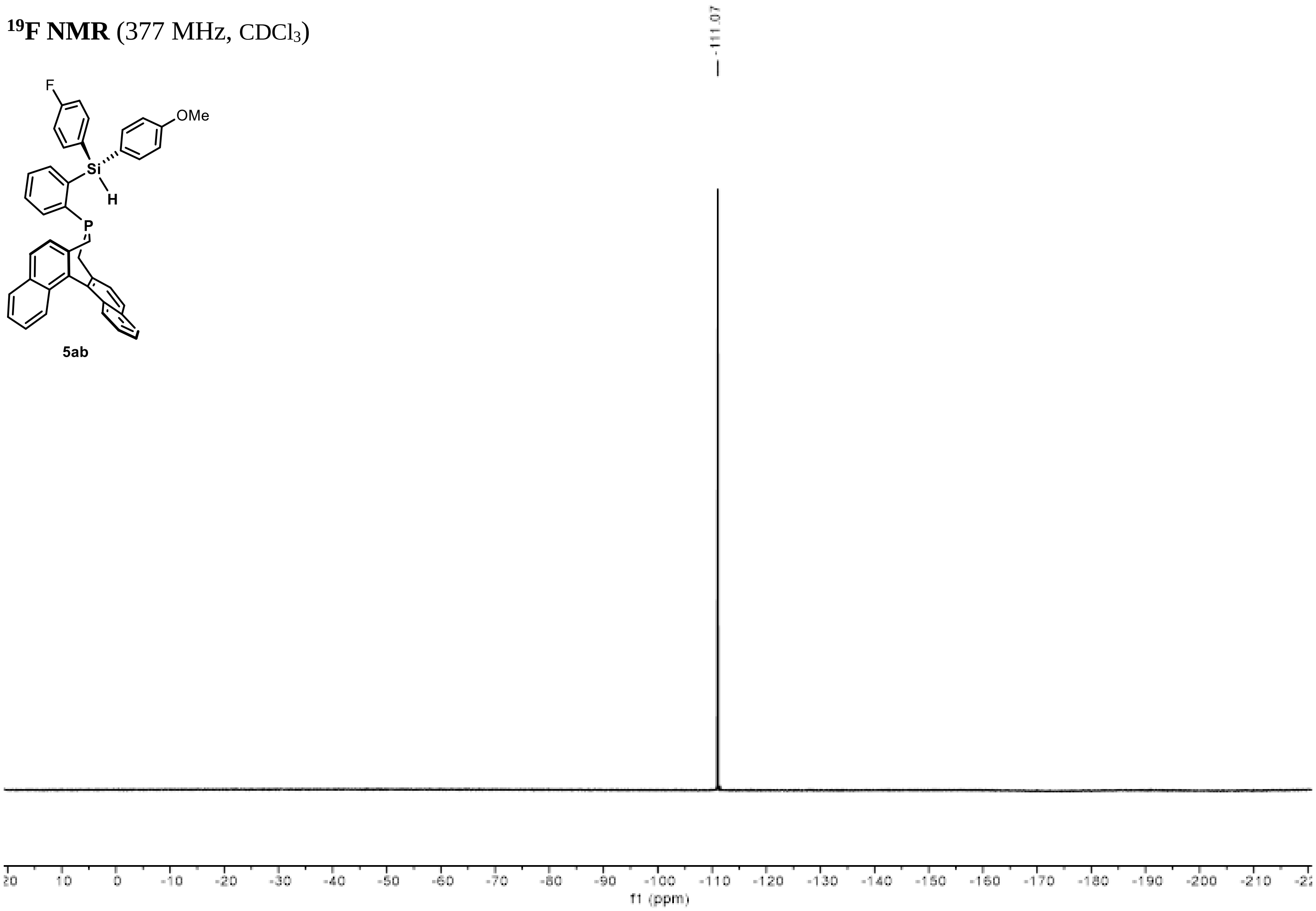


^{13}C NMR (151 MHz, $CDCl_3$)



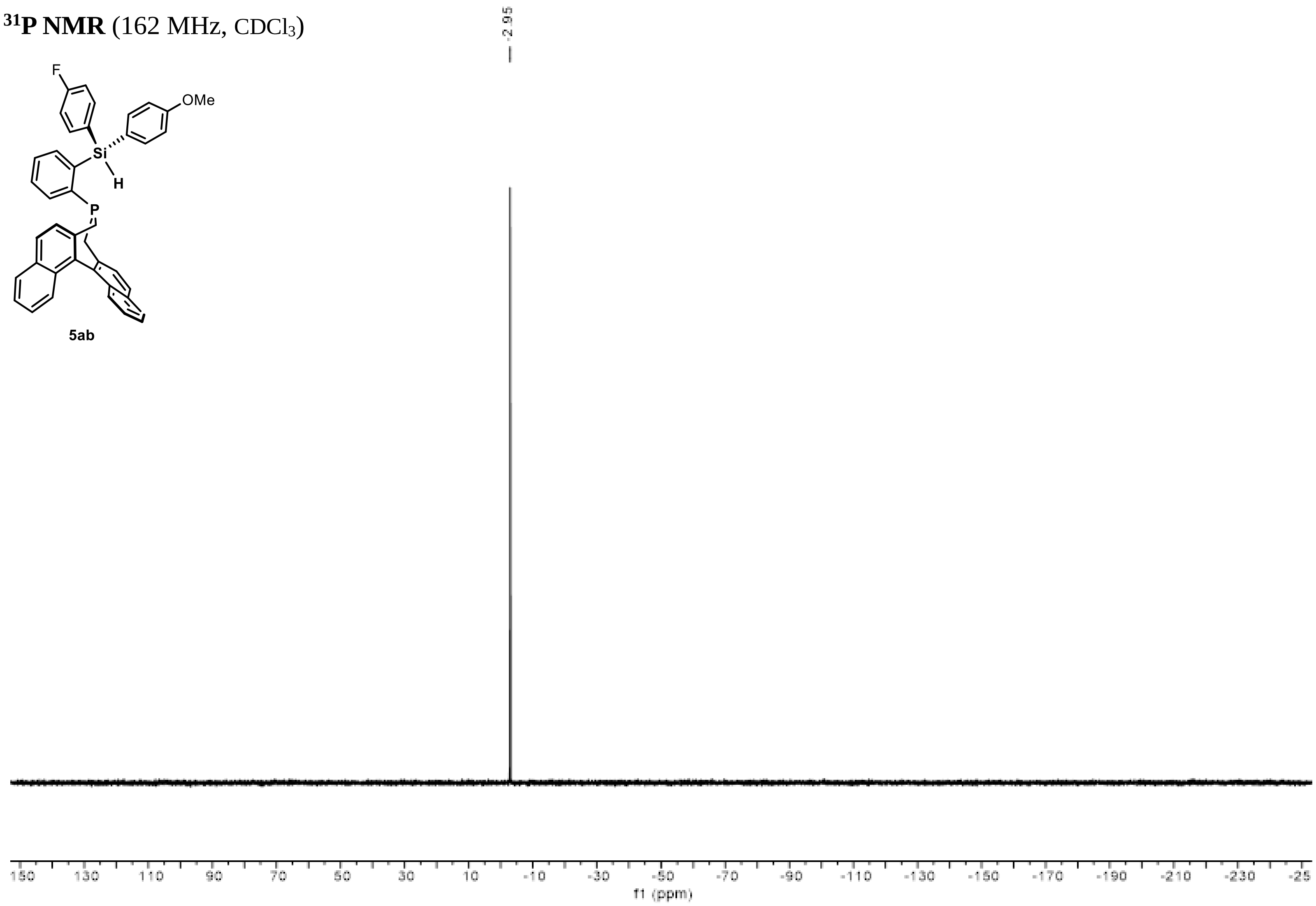
5ab

^{19}F NMR (377 MHz, $CDCl_3$)

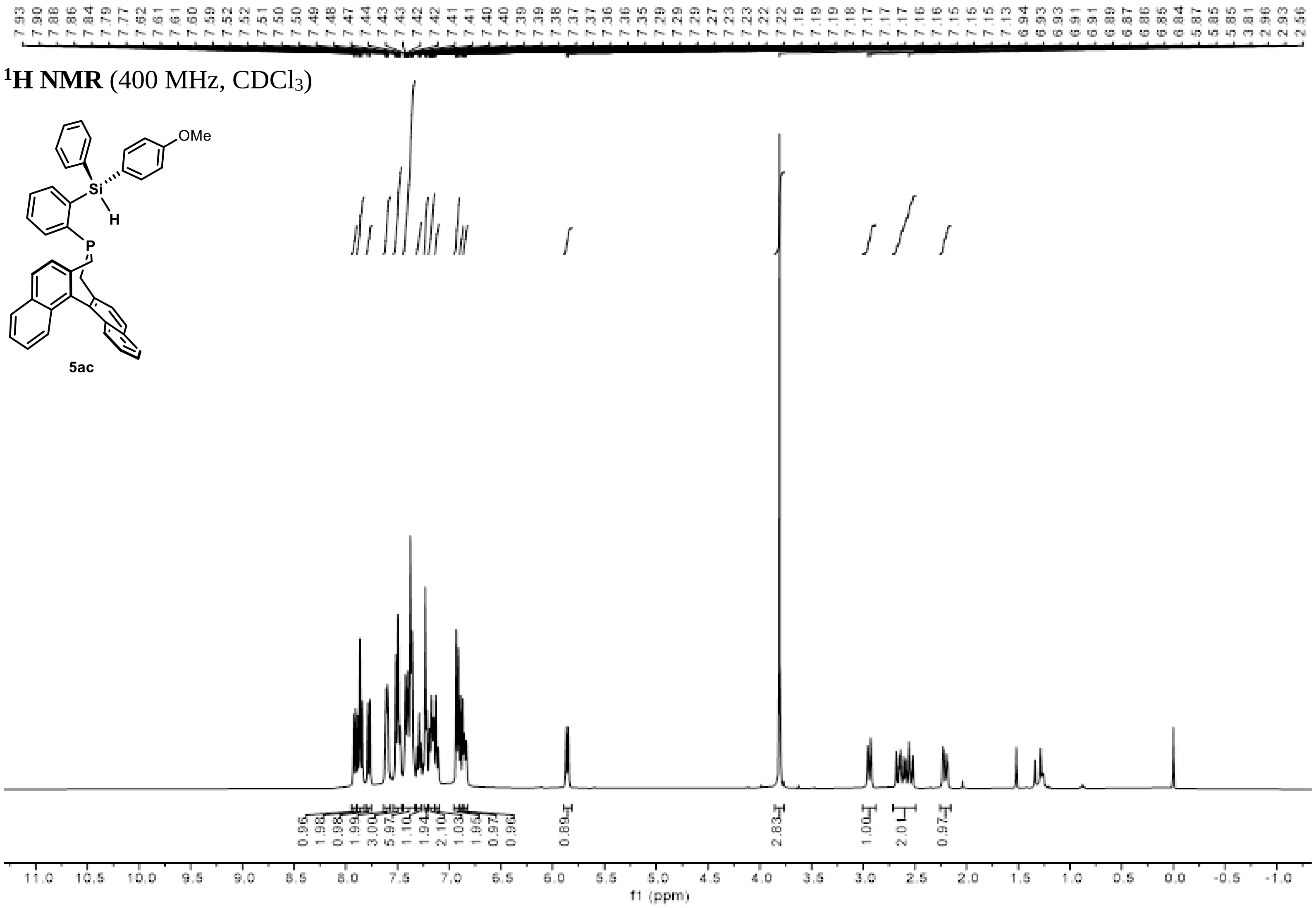


5ab

^{31}P NMR (162 MHz, $CDCl_3$)

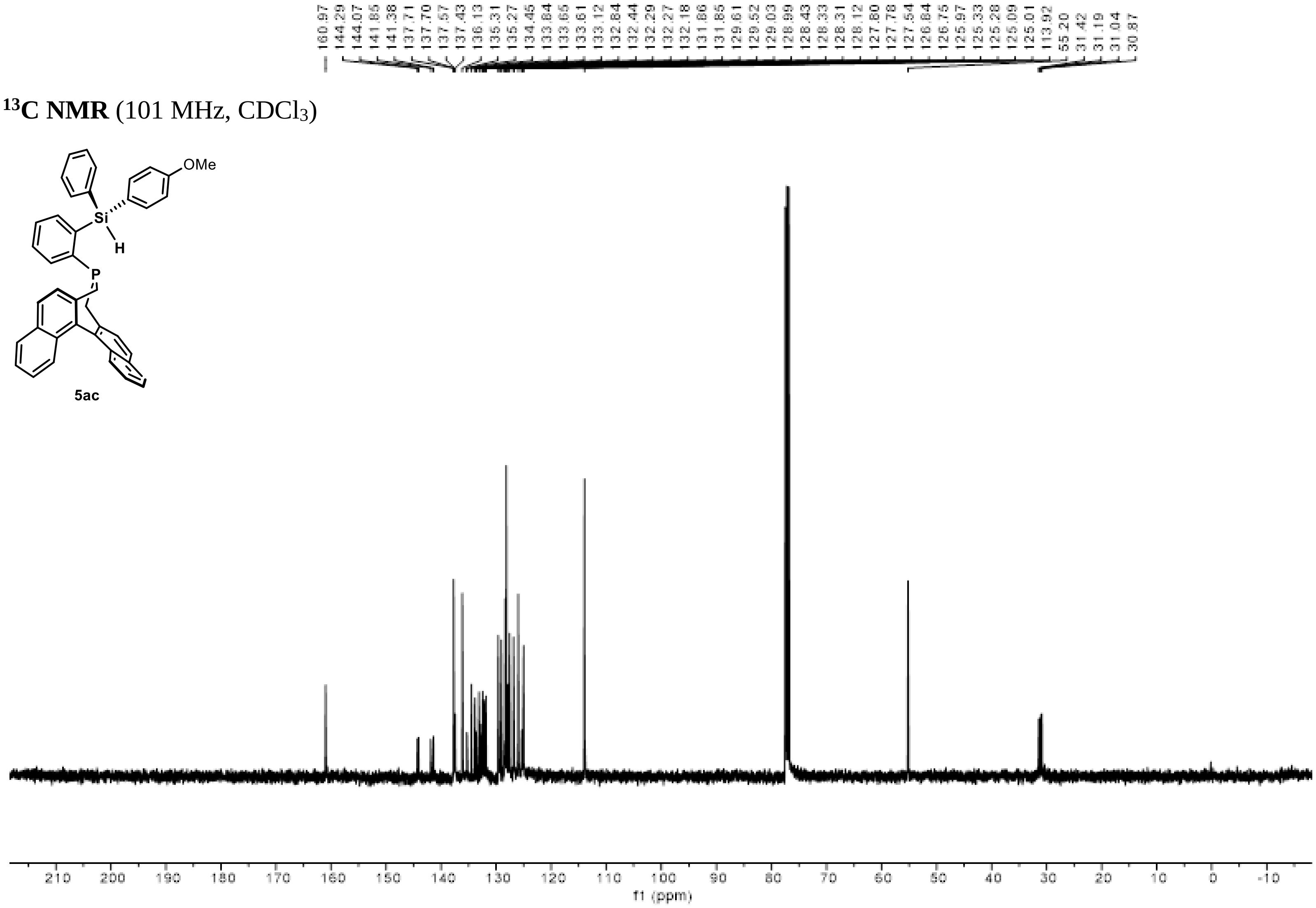


^{1}H NMR (400 MHz, $CDCl_3$)



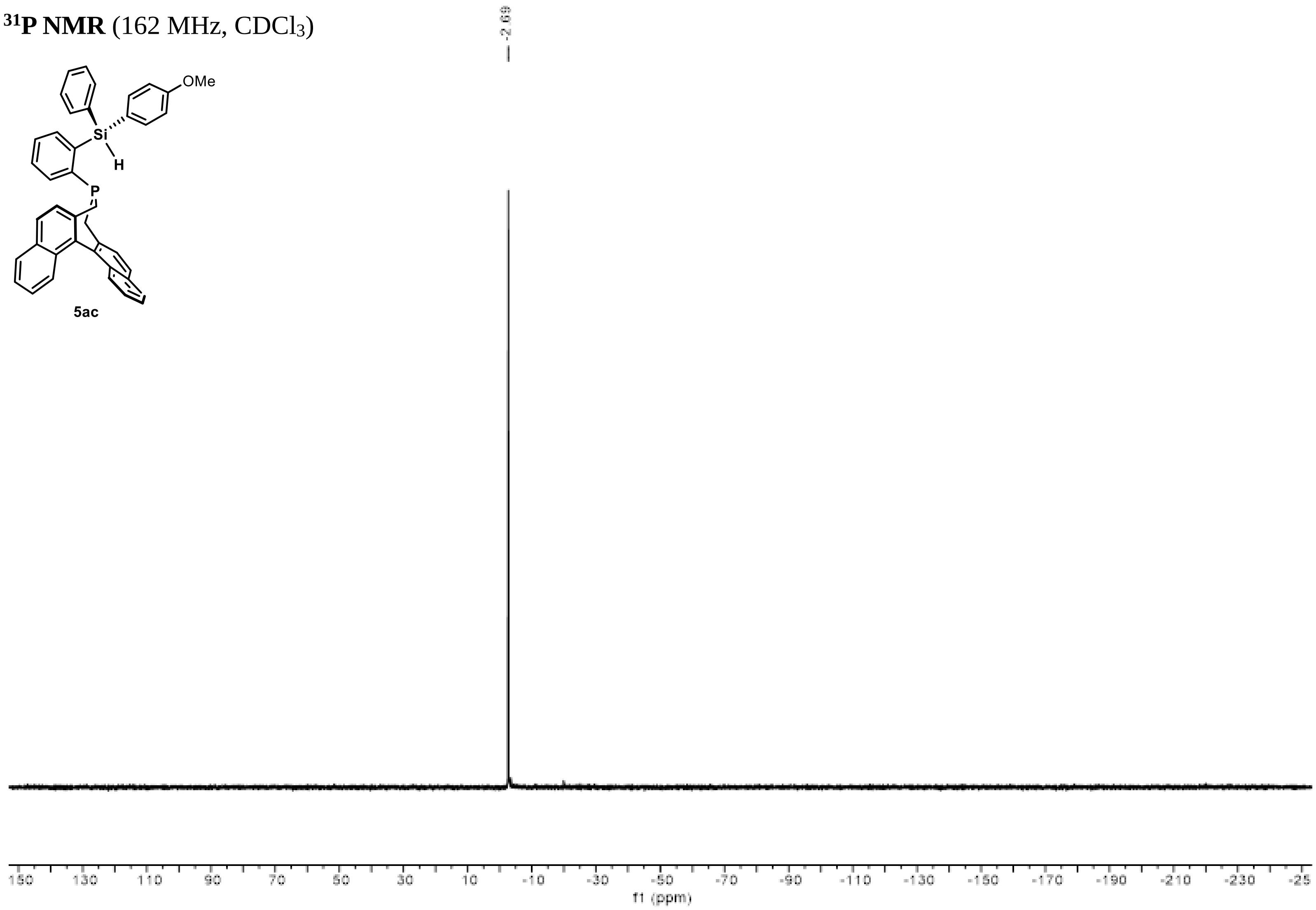
5ac

^{13}C NMR (101 MHz, CDCl$_3$)

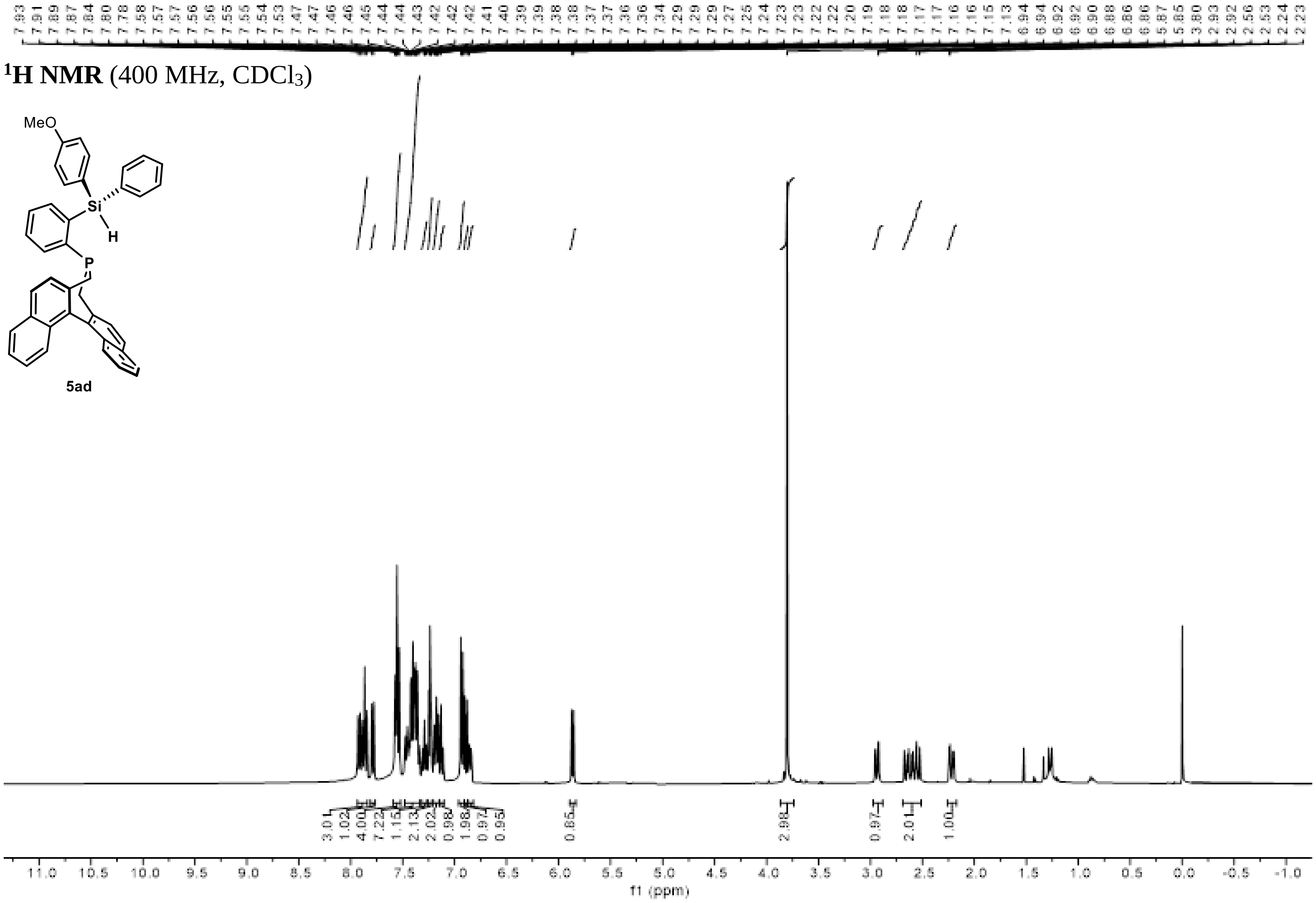


5ac

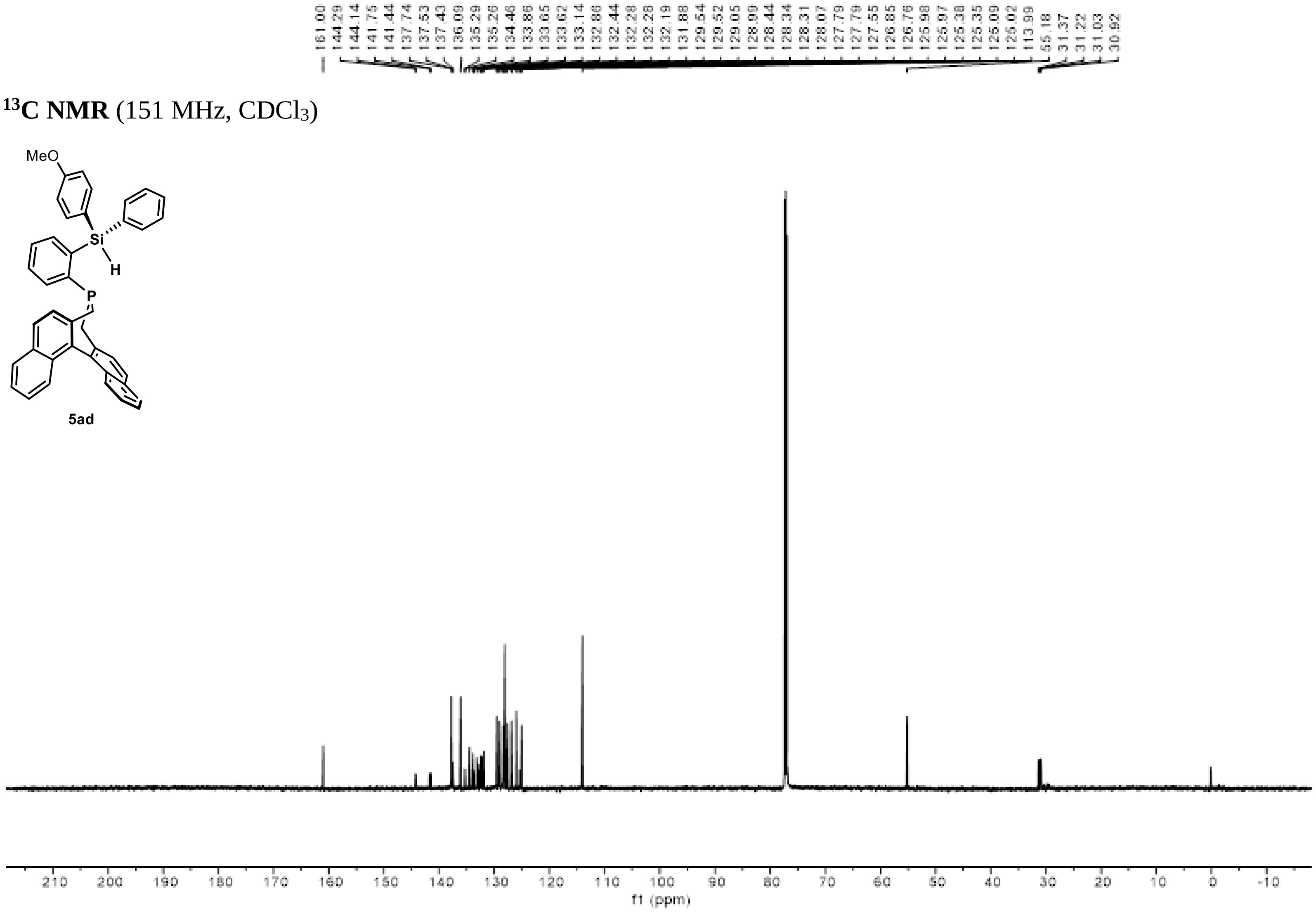
^{31}P NMR (162 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

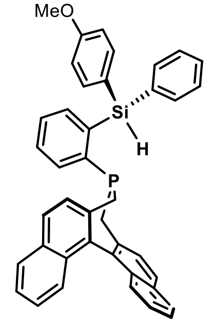


^{13}C NMR (151 MHz, $CDCl_3$)



5ad

^{31}P NMR (162 MHz, CDCl$_3$)



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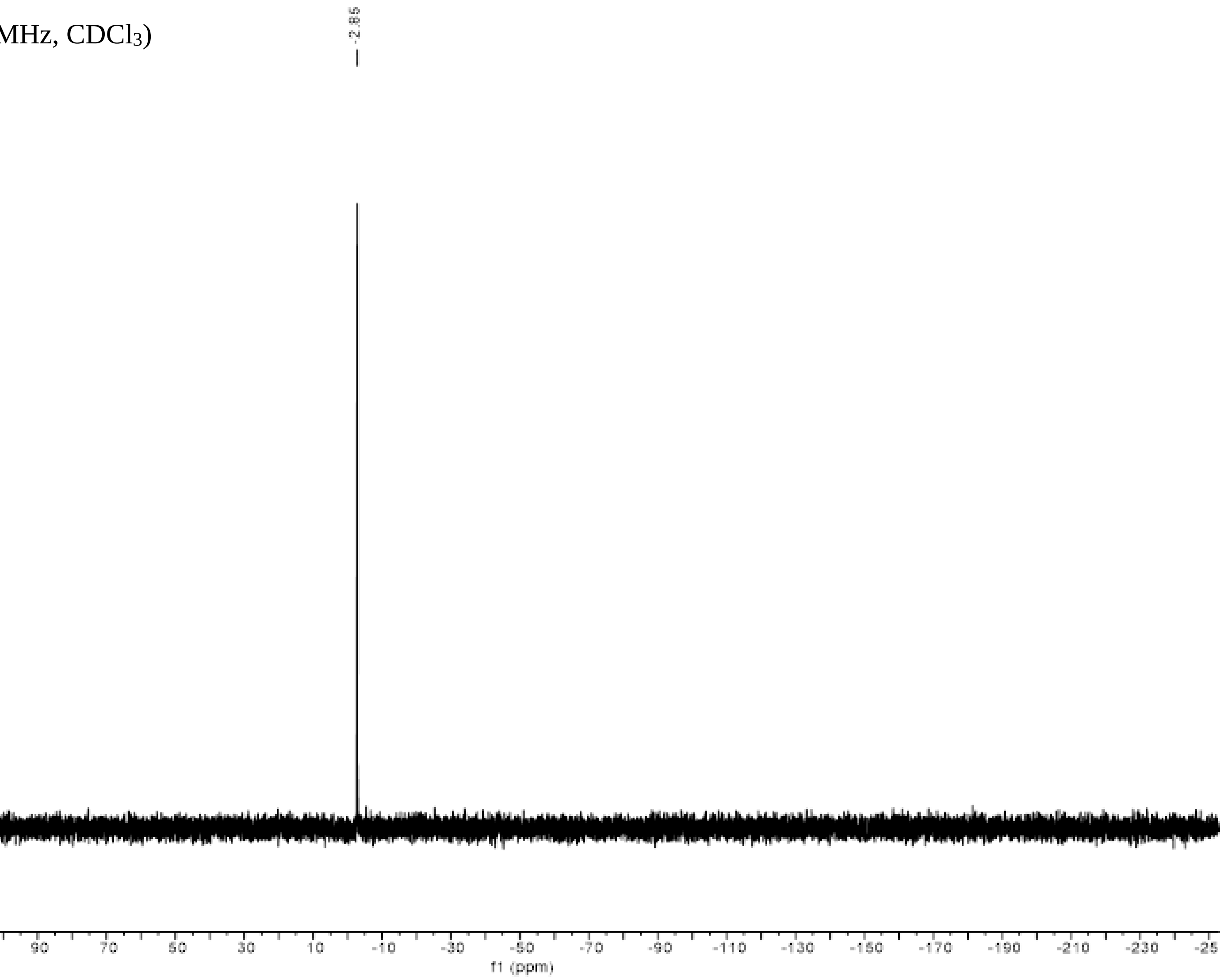
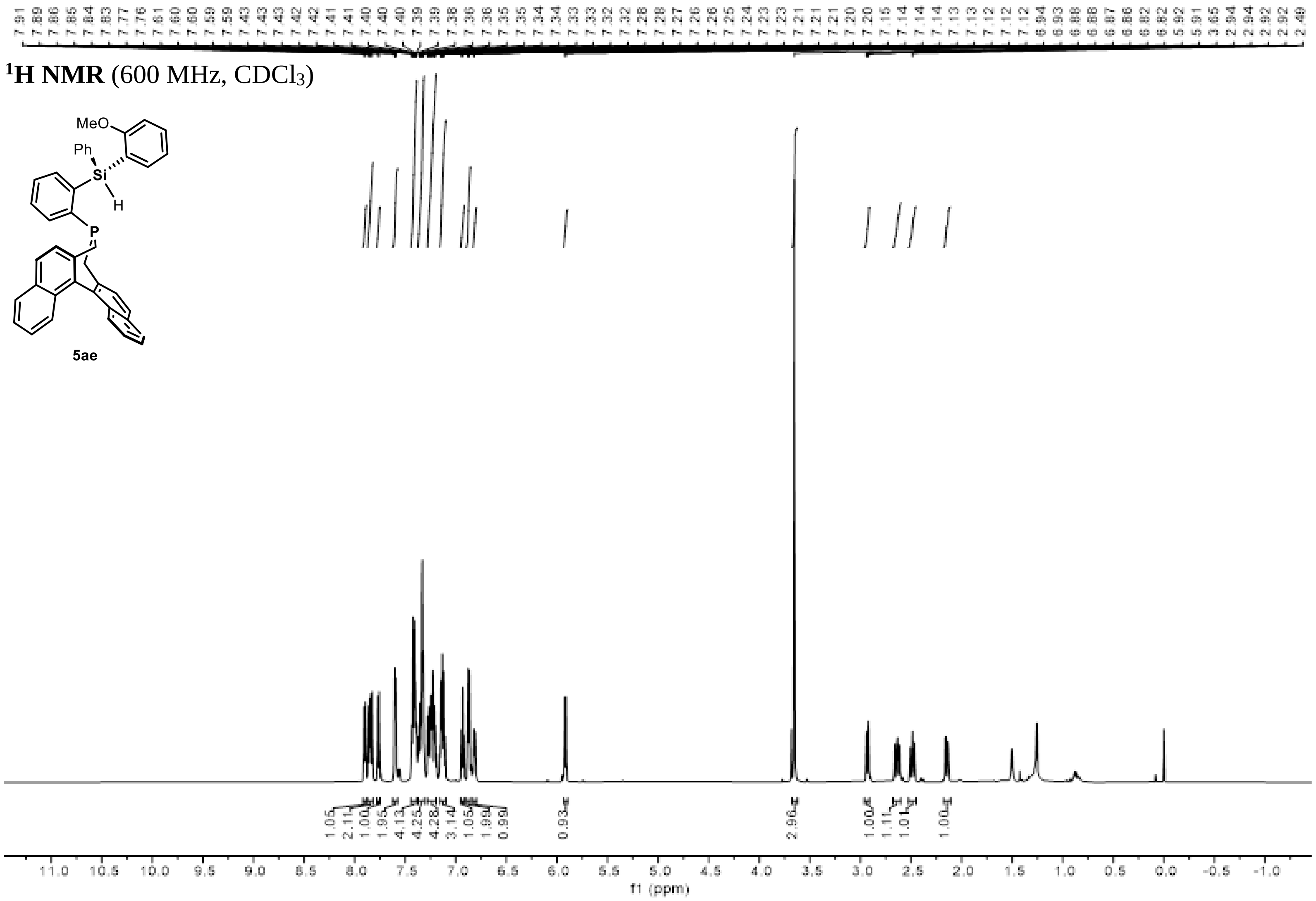
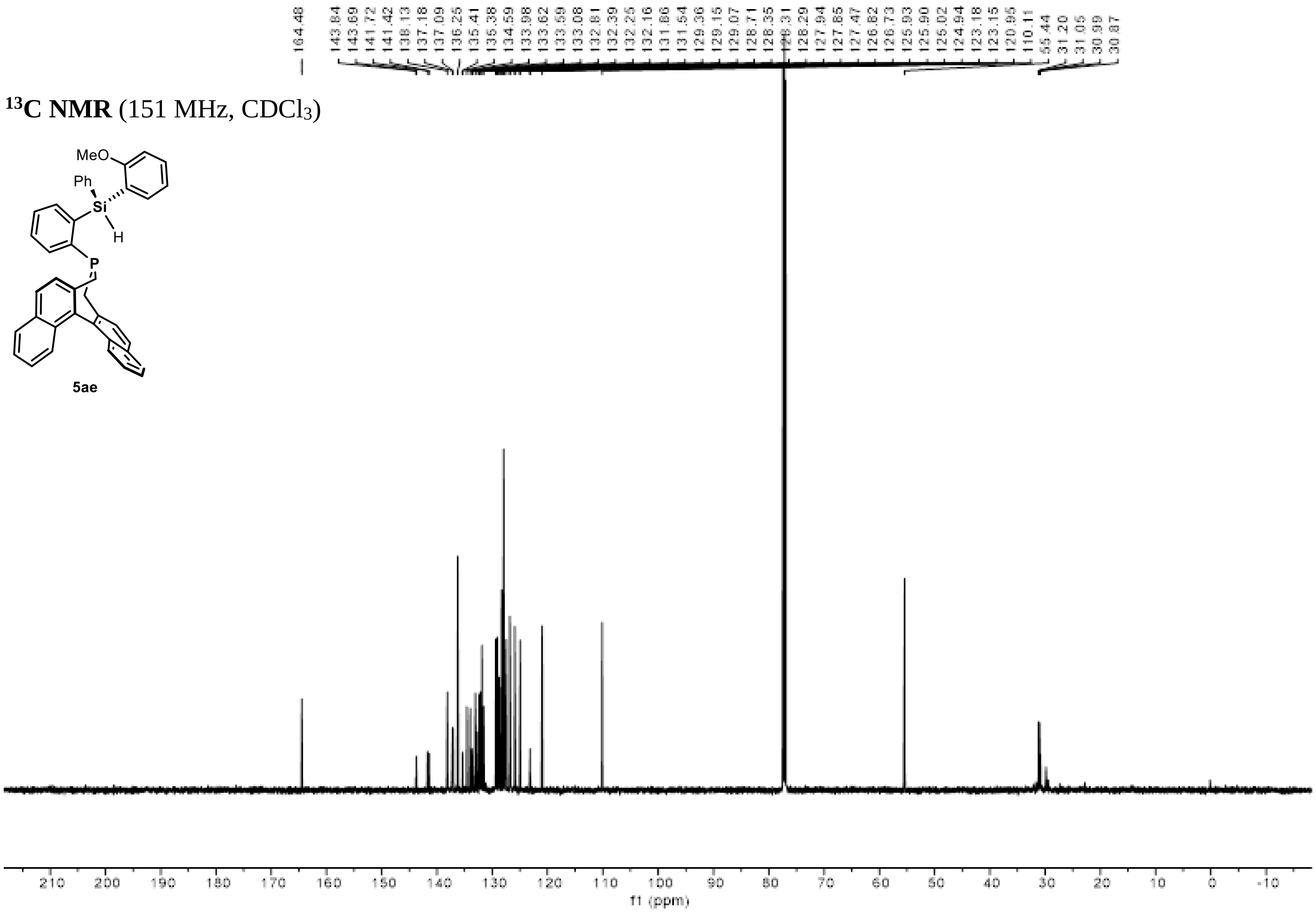


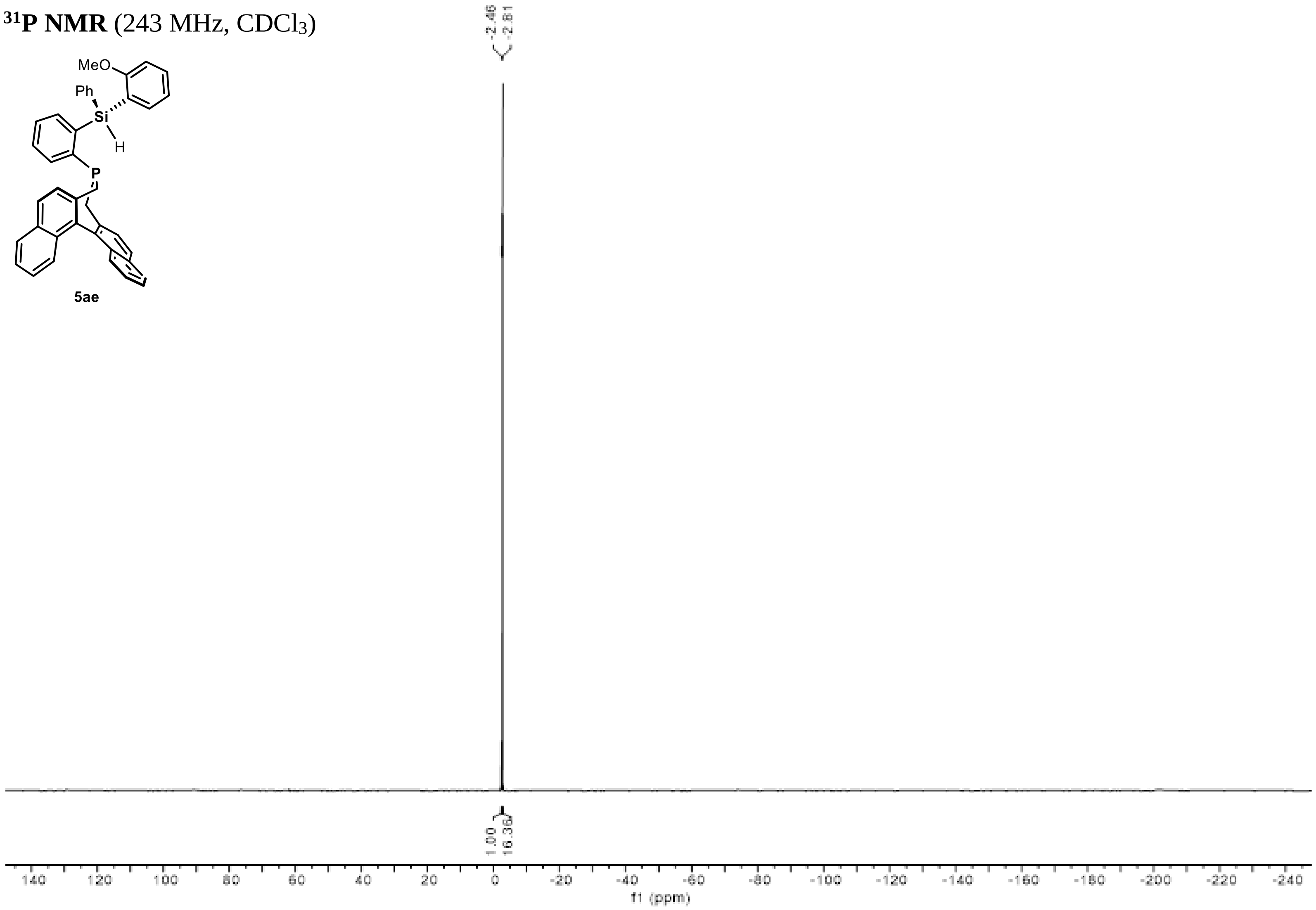
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

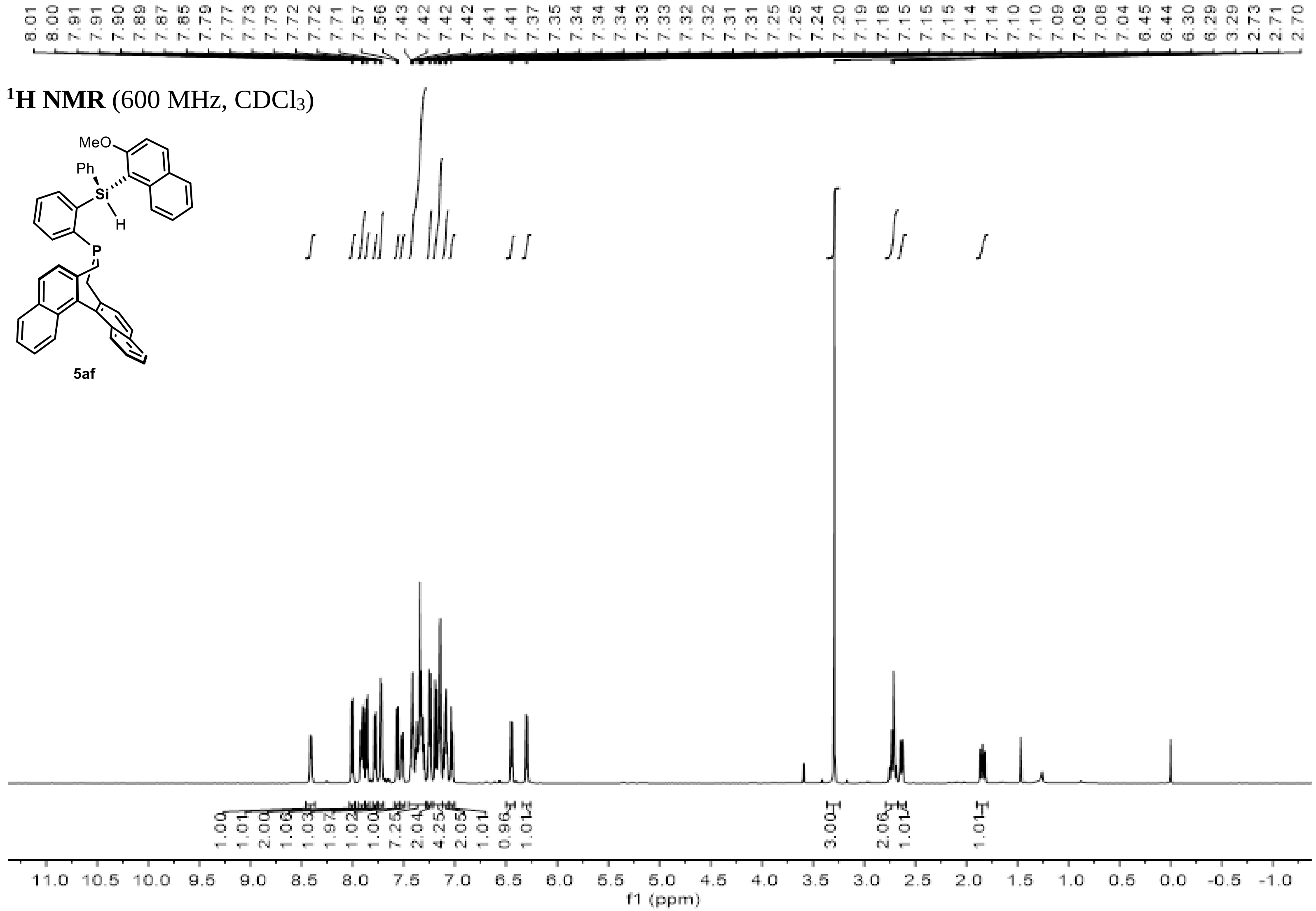


^{31}P NMR (243 MHz, CDCl$_3$)

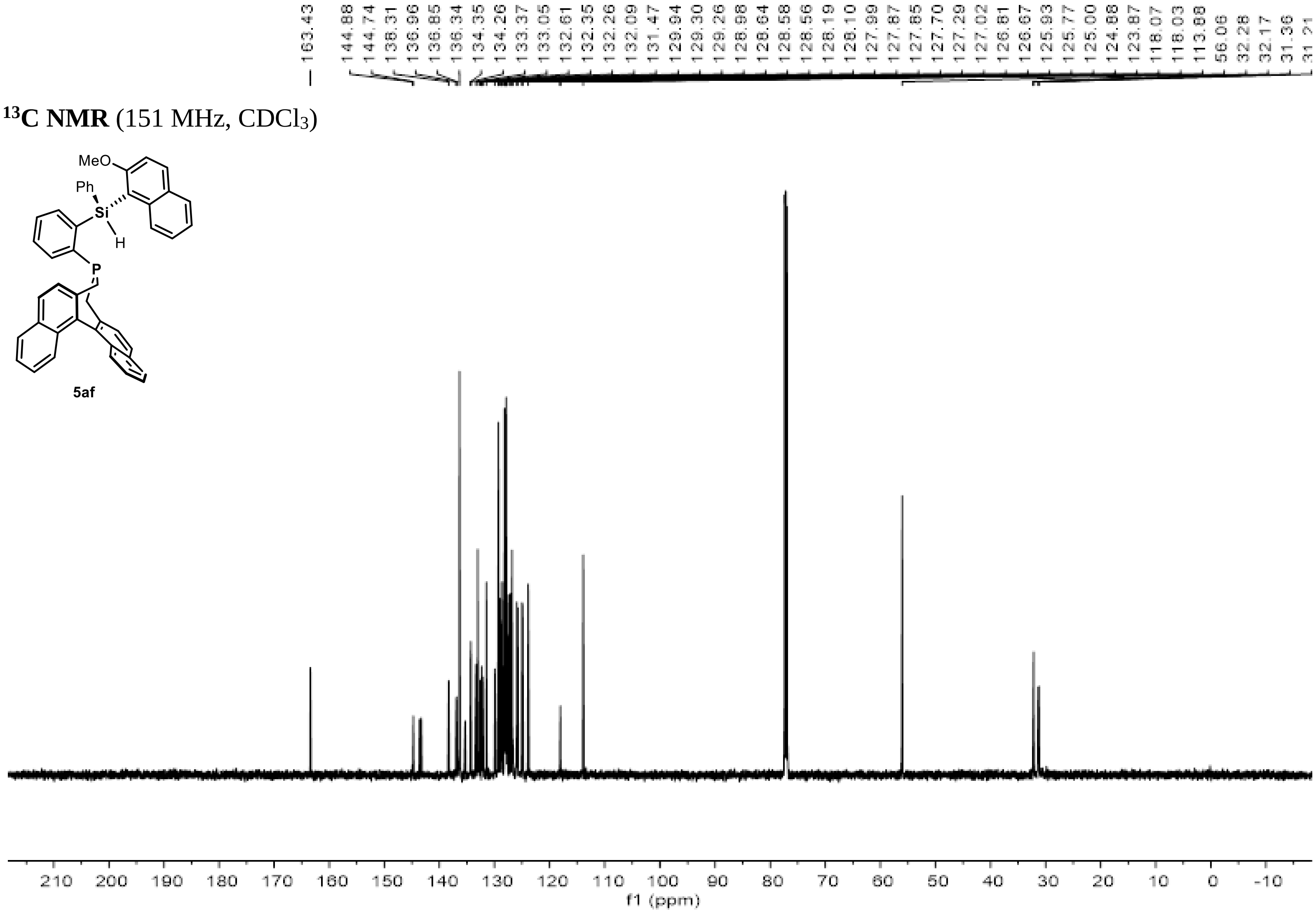


5ae

^{1}H NMR (600 MHz, $CDCl_3$)

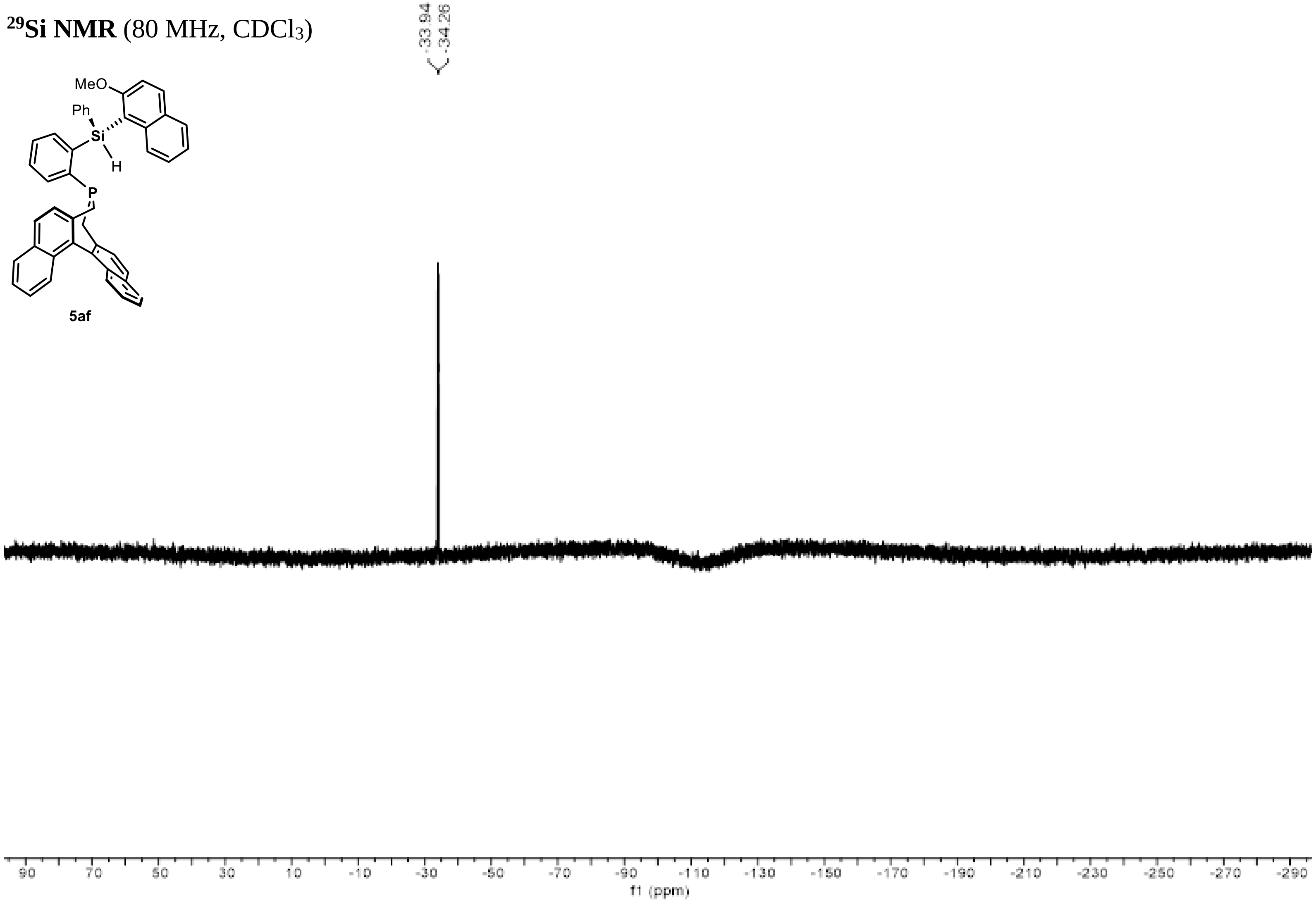


^{13}C NMR (151 MHz, CDCl$_3$)



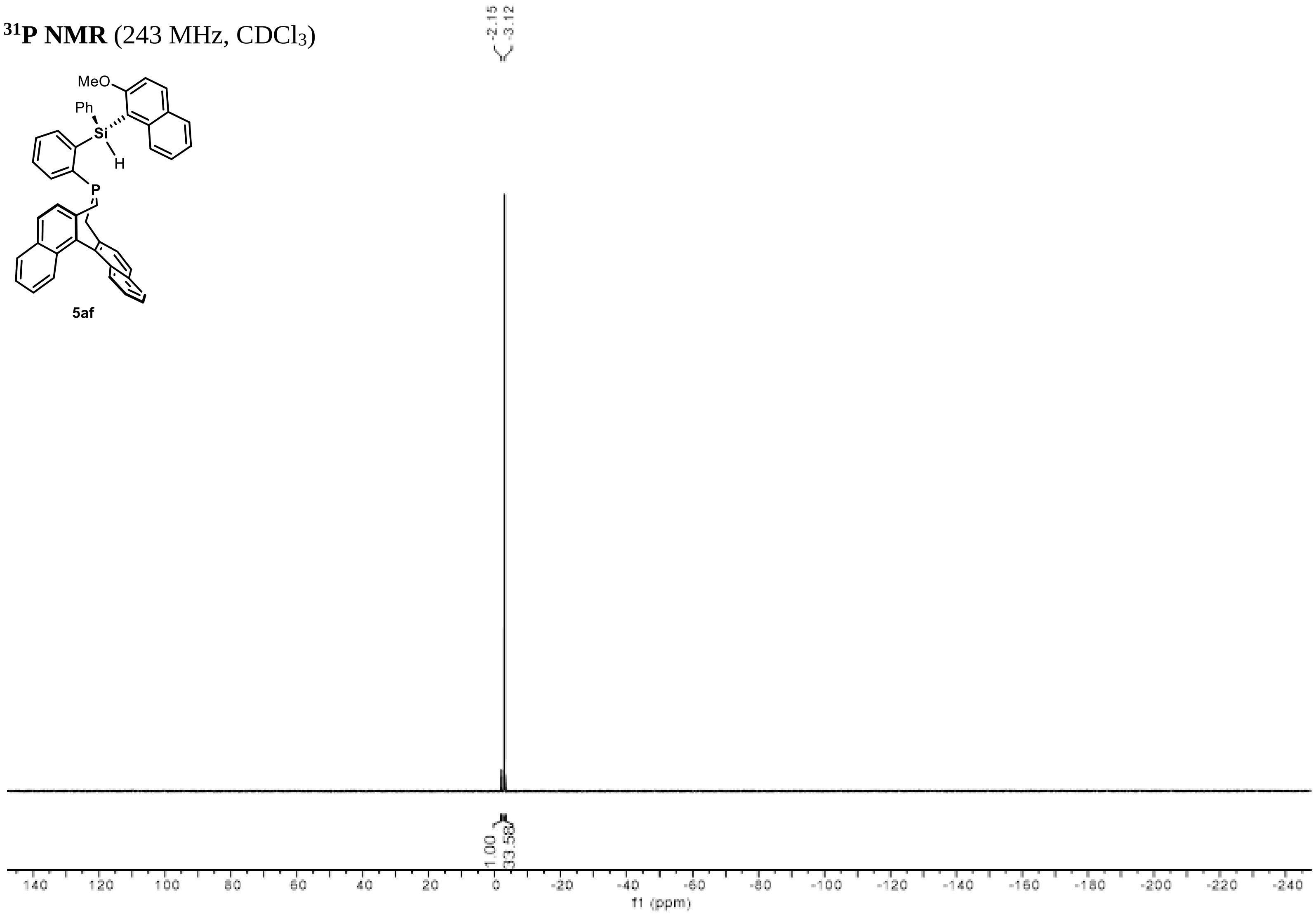
5af

^{29}Si NMR (80 MHz, CDCl$_3$)

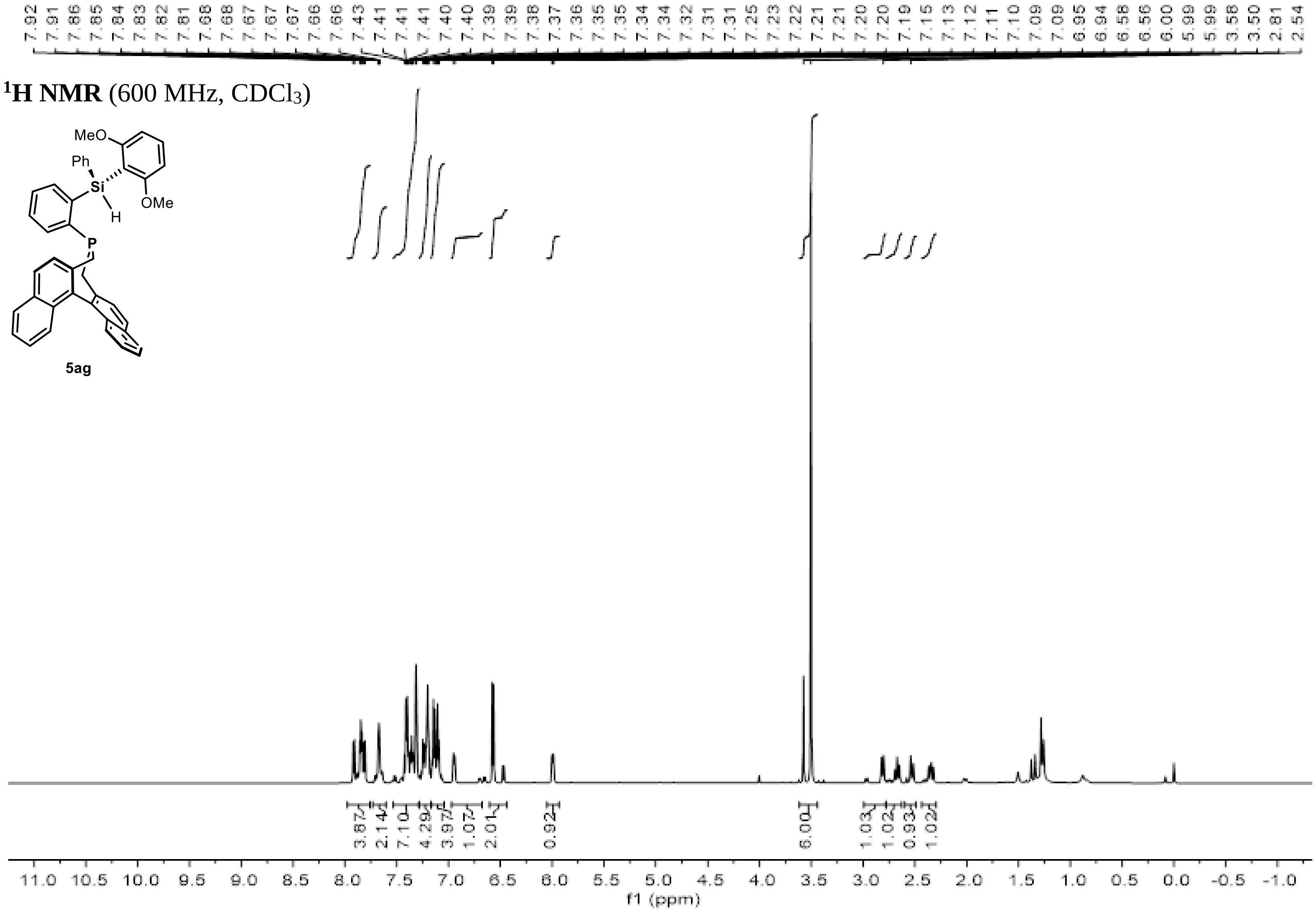


5af

^{31}P NMR (243 MHz, CDCl$_3$)

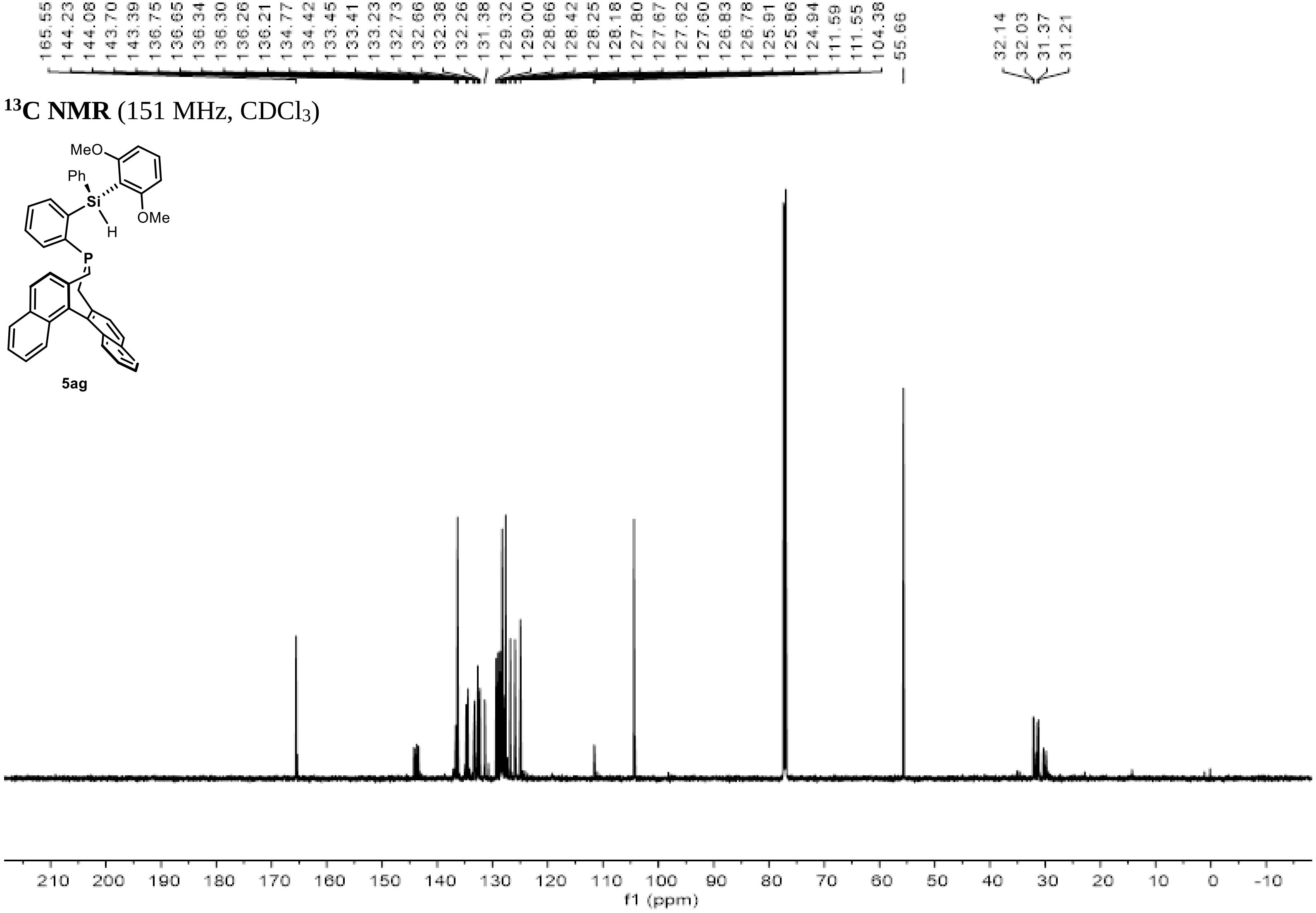


^{1}H NMR (600 MHz, $CDCl_3$)



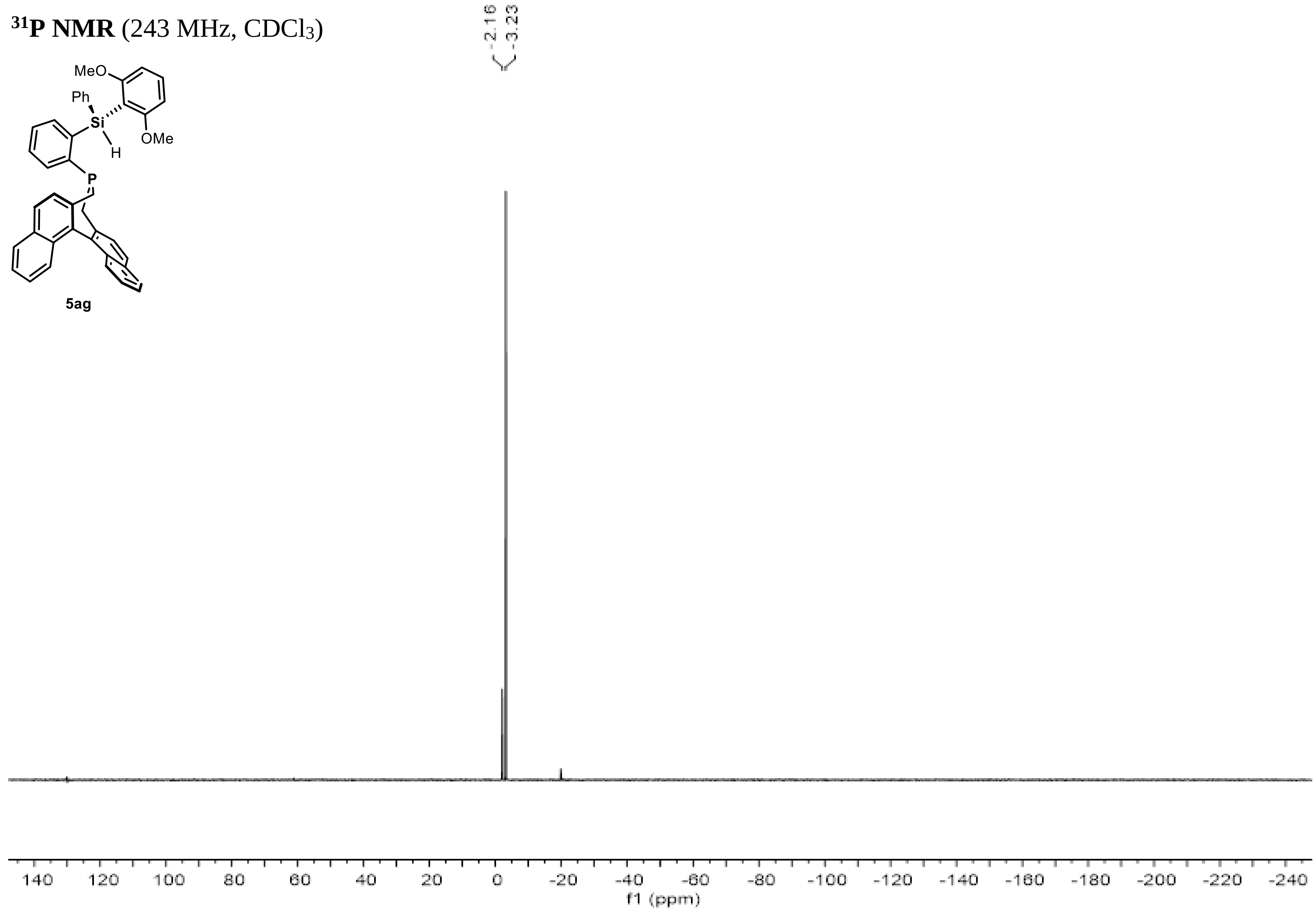
5ag

^{13}C NMR (151 MHz, $CDCl_3$)

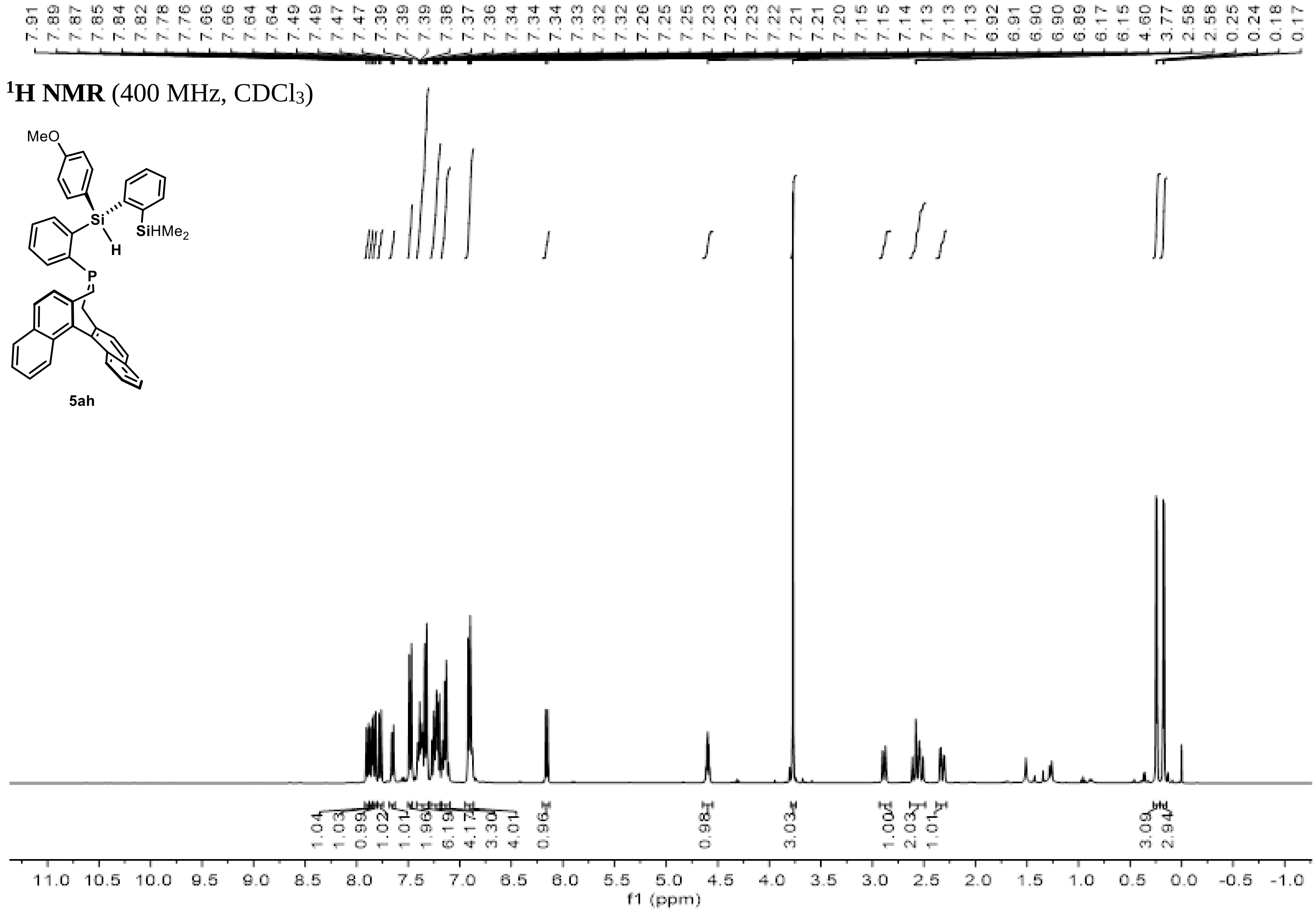


5ag

^{31}P NMR (243 MHz, $CDCl_3$)

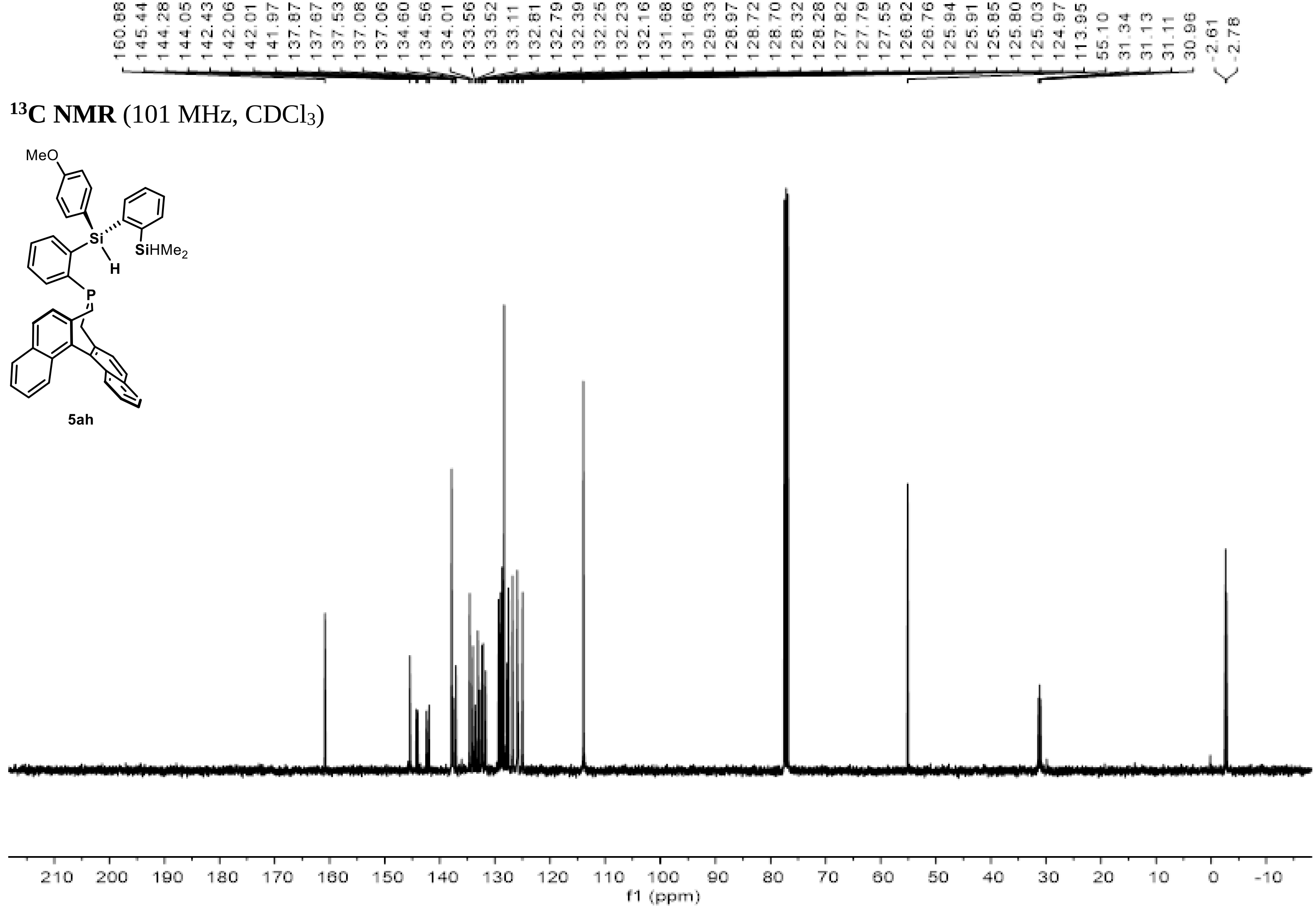

5ag

^{1}H NMR (400 MHz, CDCl$_3$)



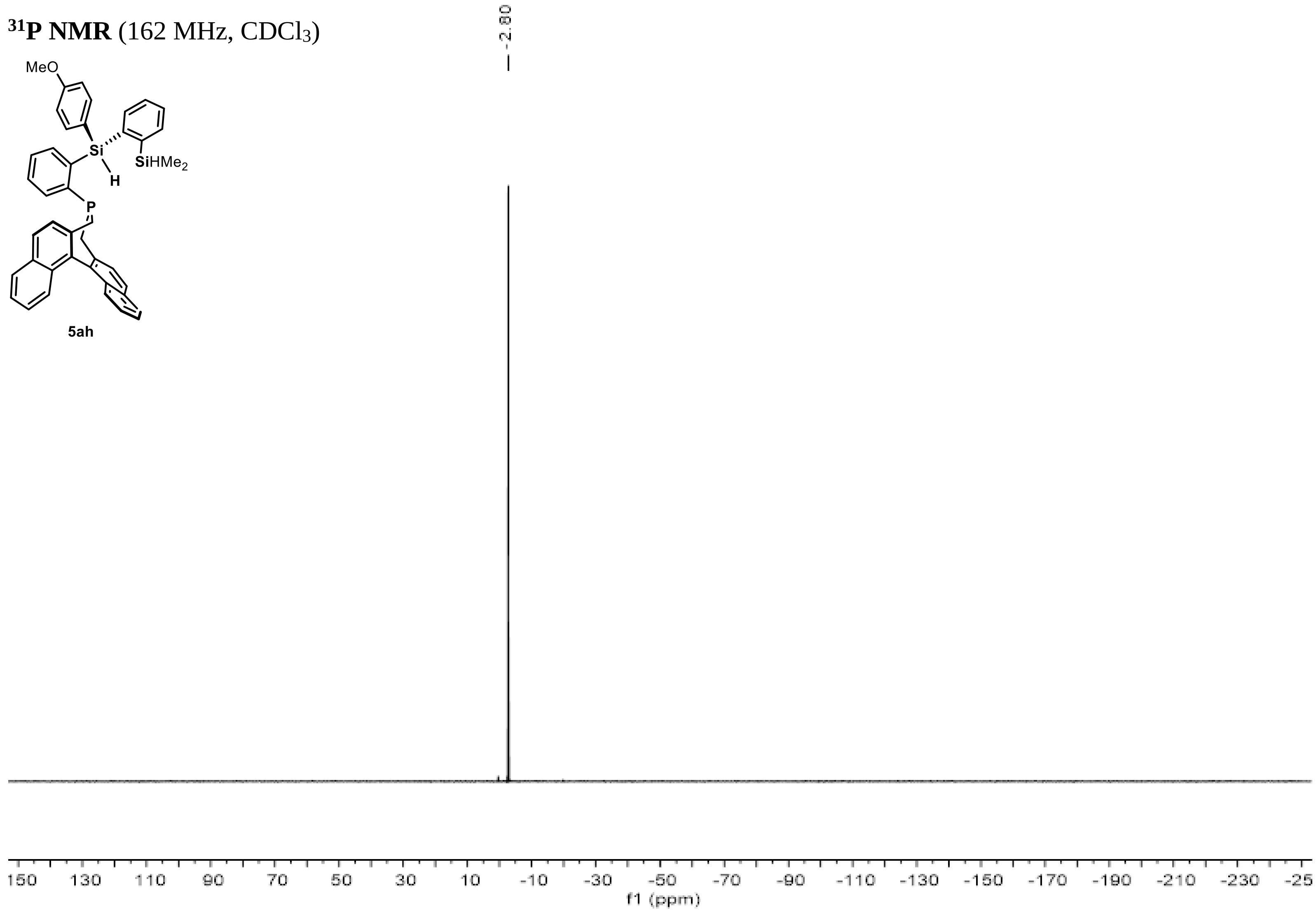
5ah

^{13}C NMR (101 MHz, $CDCl_3$)



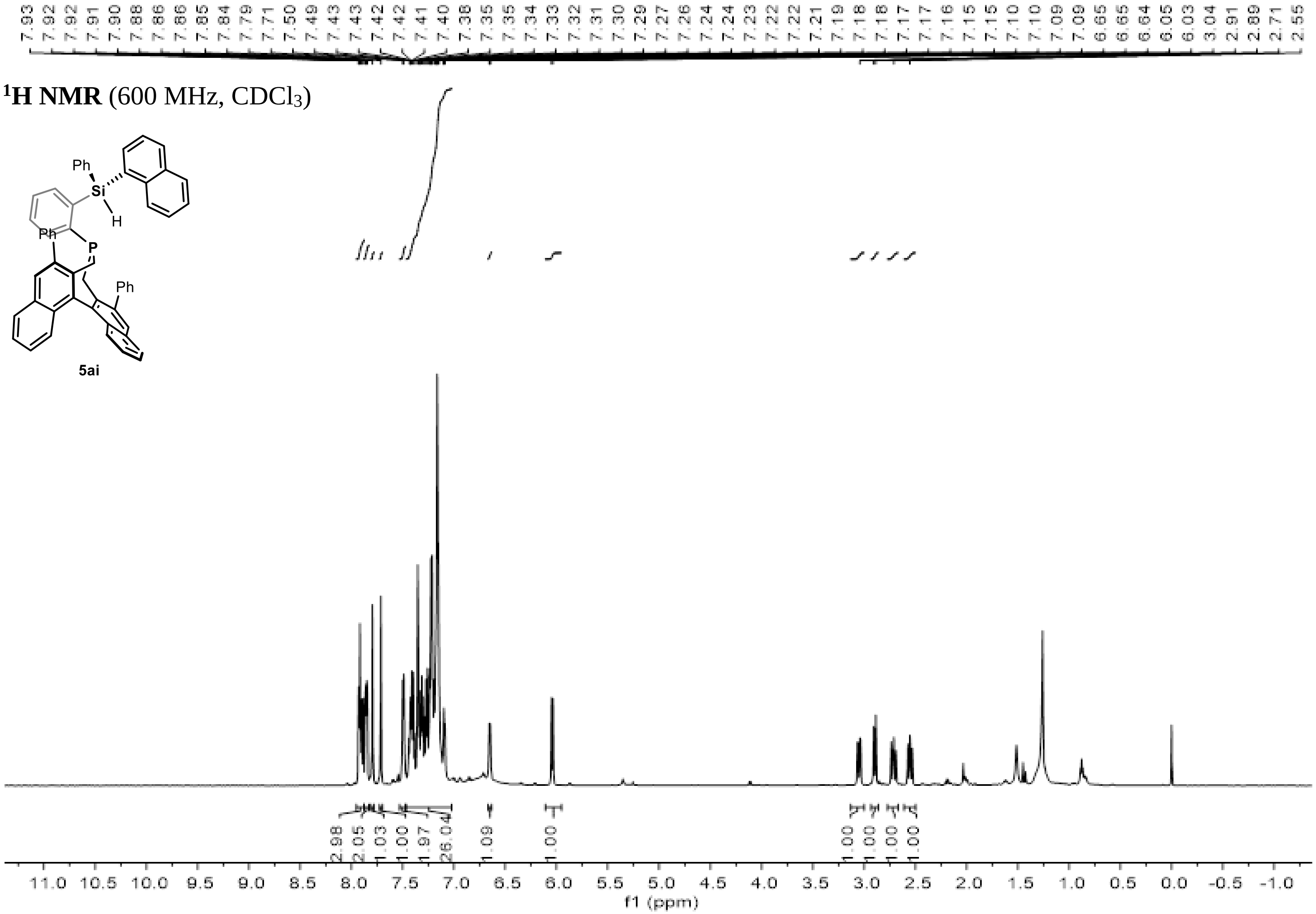
5ah

^{31}**P NMR** (162 MHz, CDCl$_3$)



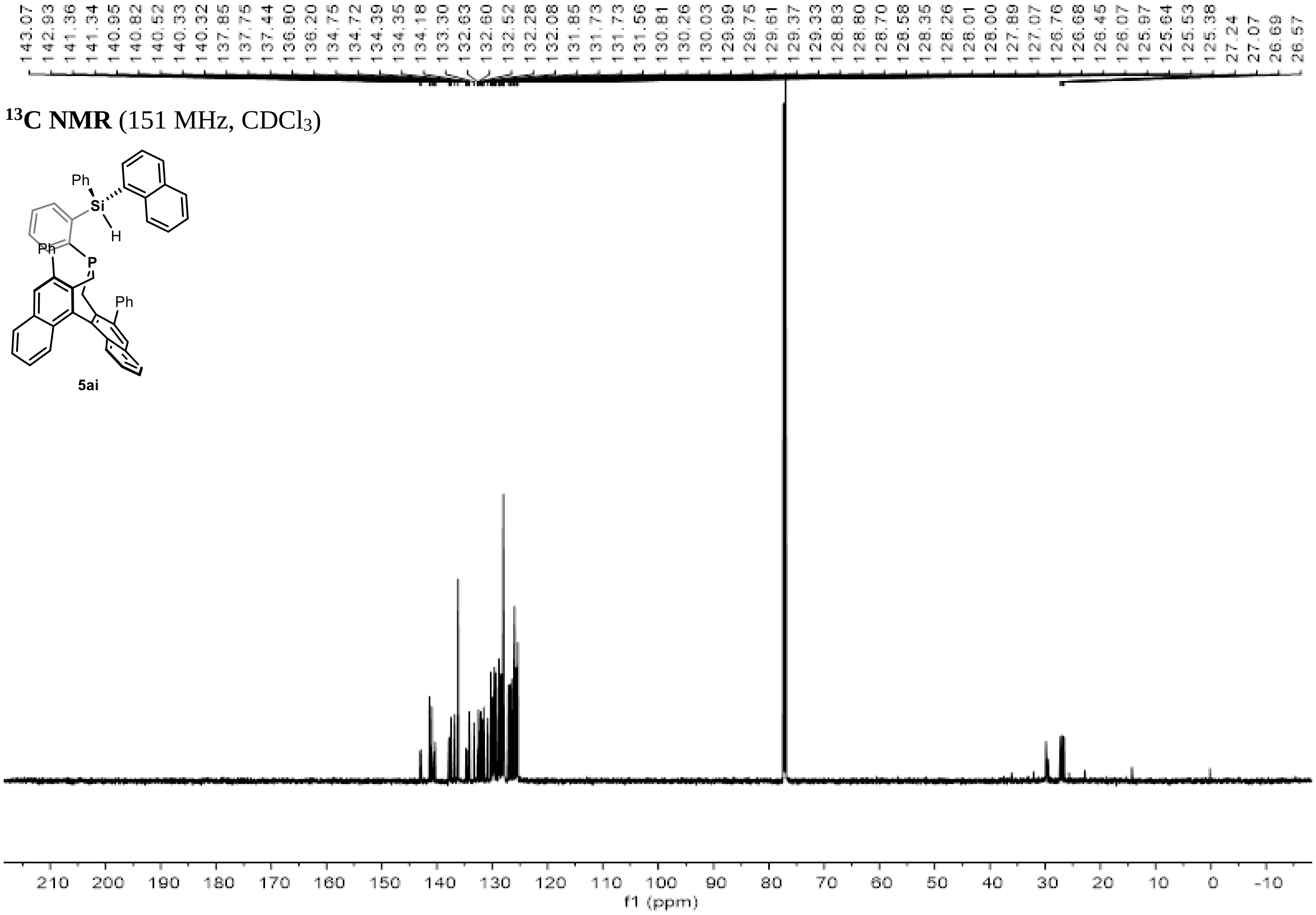
5ah

^{1}H NMR (600 MHz, $CDCl_3$)



5ai

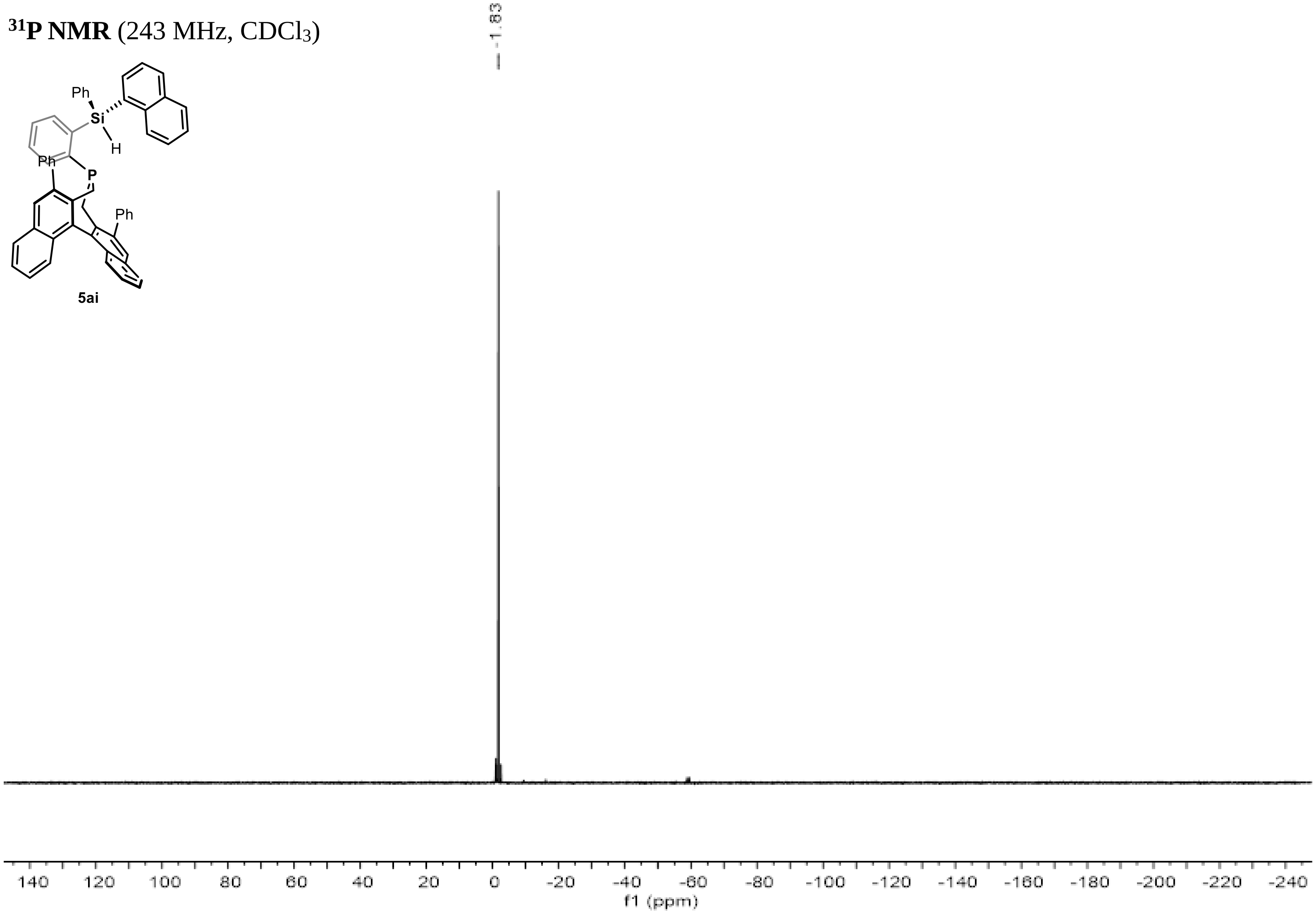
^{13}**C NMR** (151 MHz, $CDCl_3$)



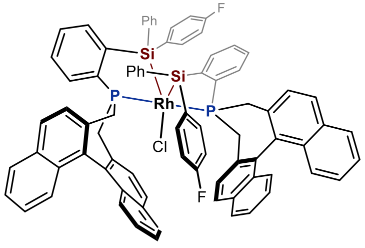
5ai

^{31}P NMR (243 MHz, CDCl$_3$)

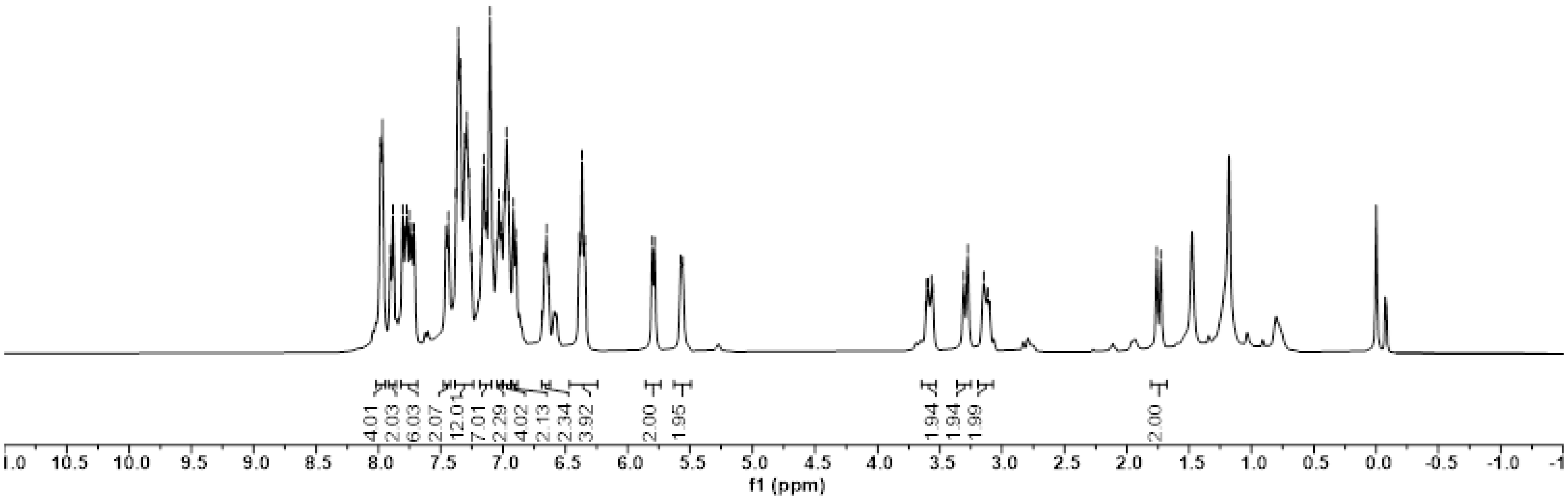
5ai



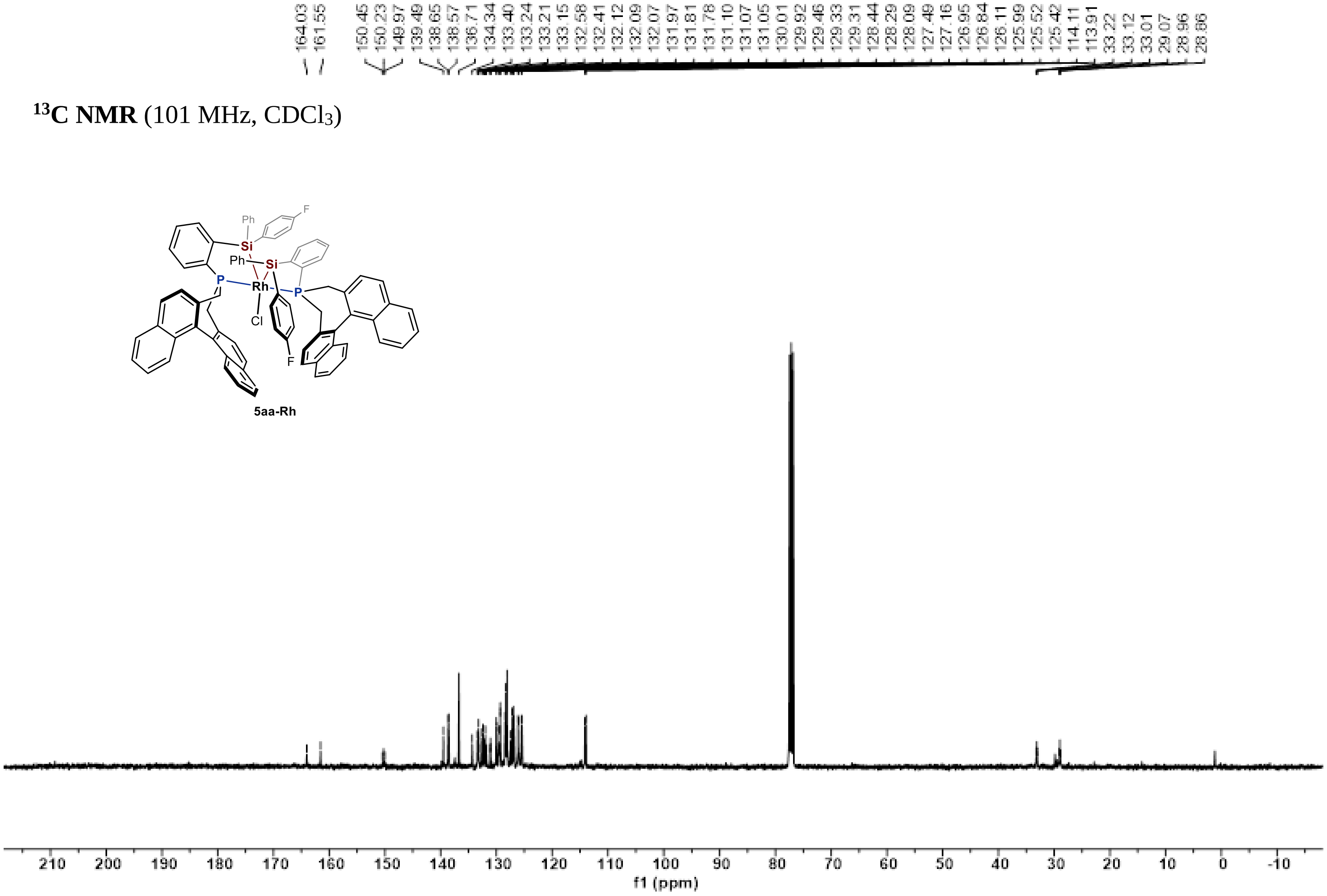
^{1}H NMR (400 MHz, $CDCl_3$)



5aa-Rh

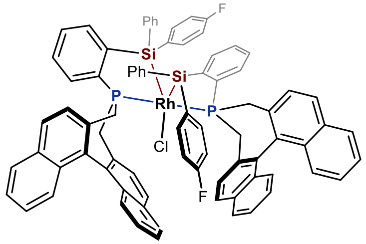


^{13}C NMR (101 MHz, $CDCl_3$)

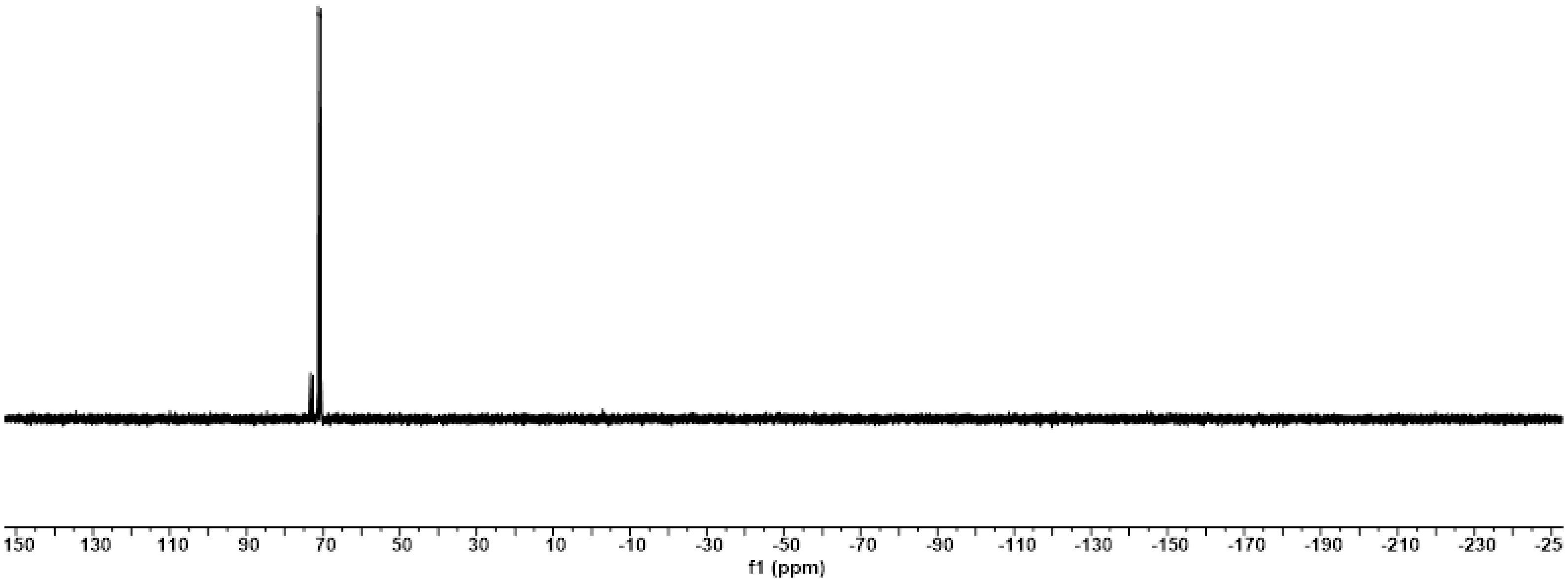


5aa-Rh

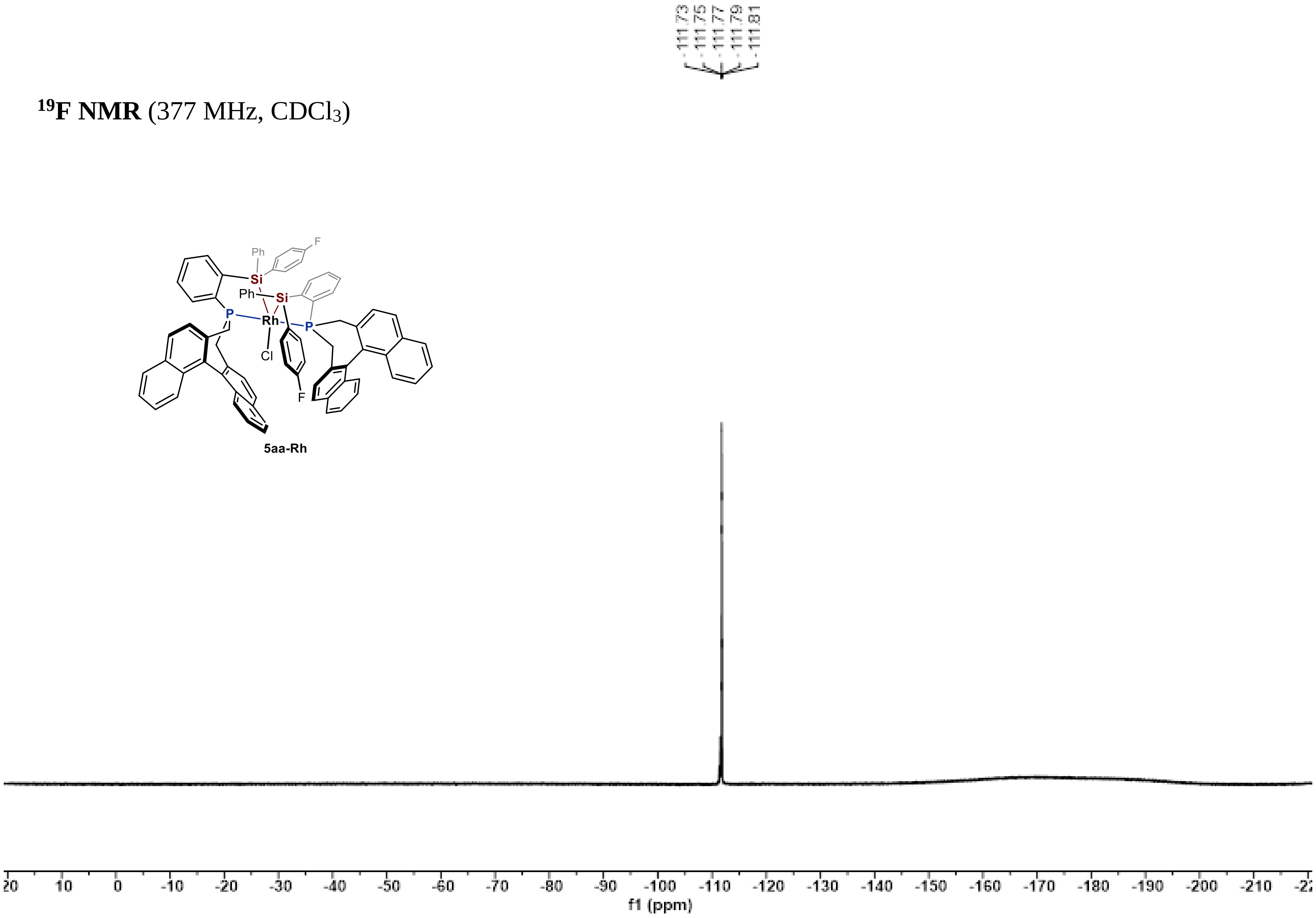
^{31}P NMR (162 MHz, $CDCl_3$)



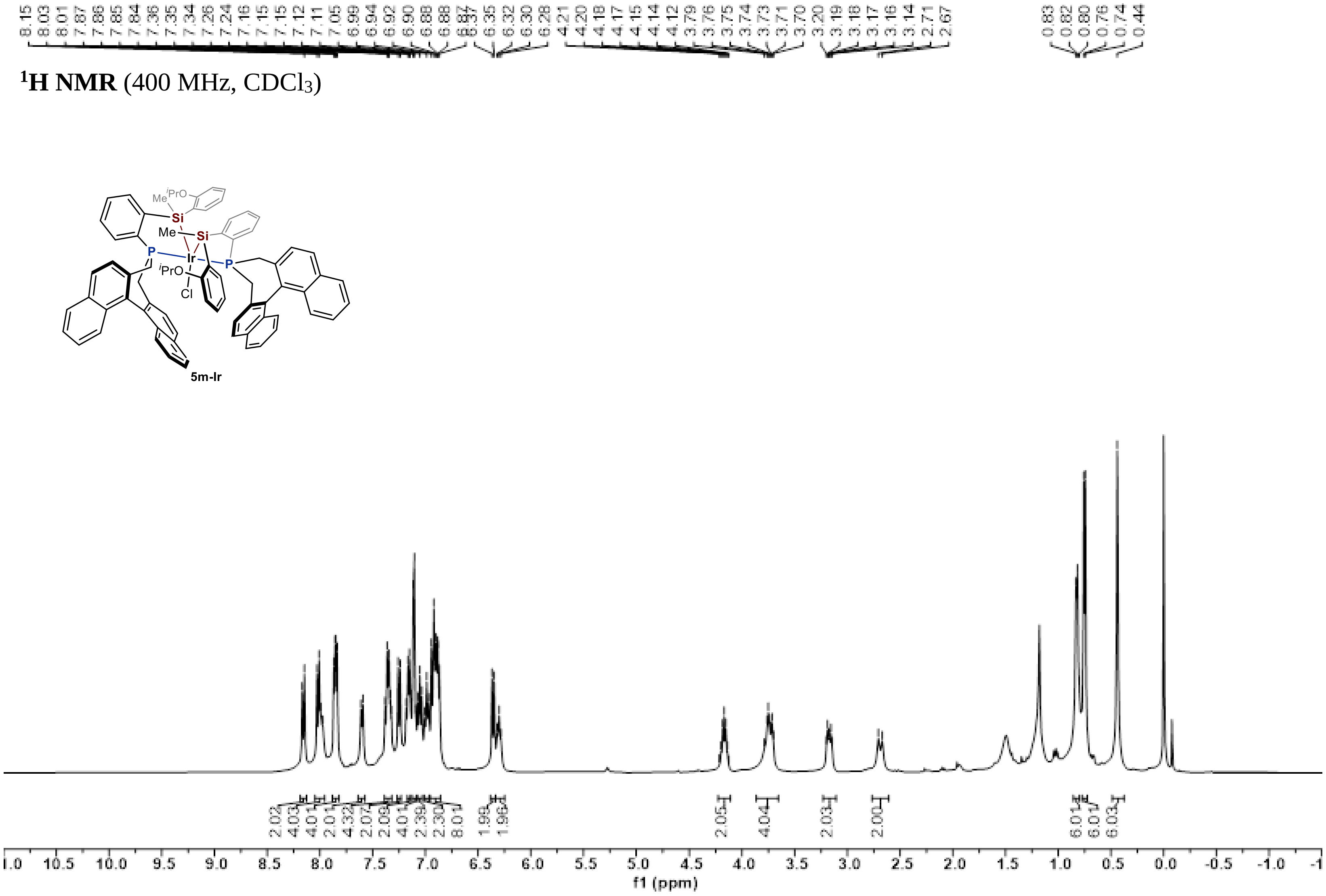
5aa-Rh



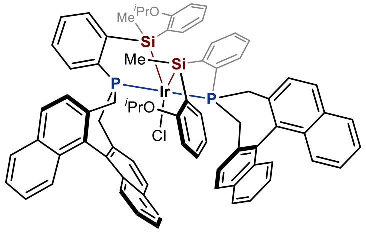
^{19}**F NMR** (377 MHz, $CDCl_3$)



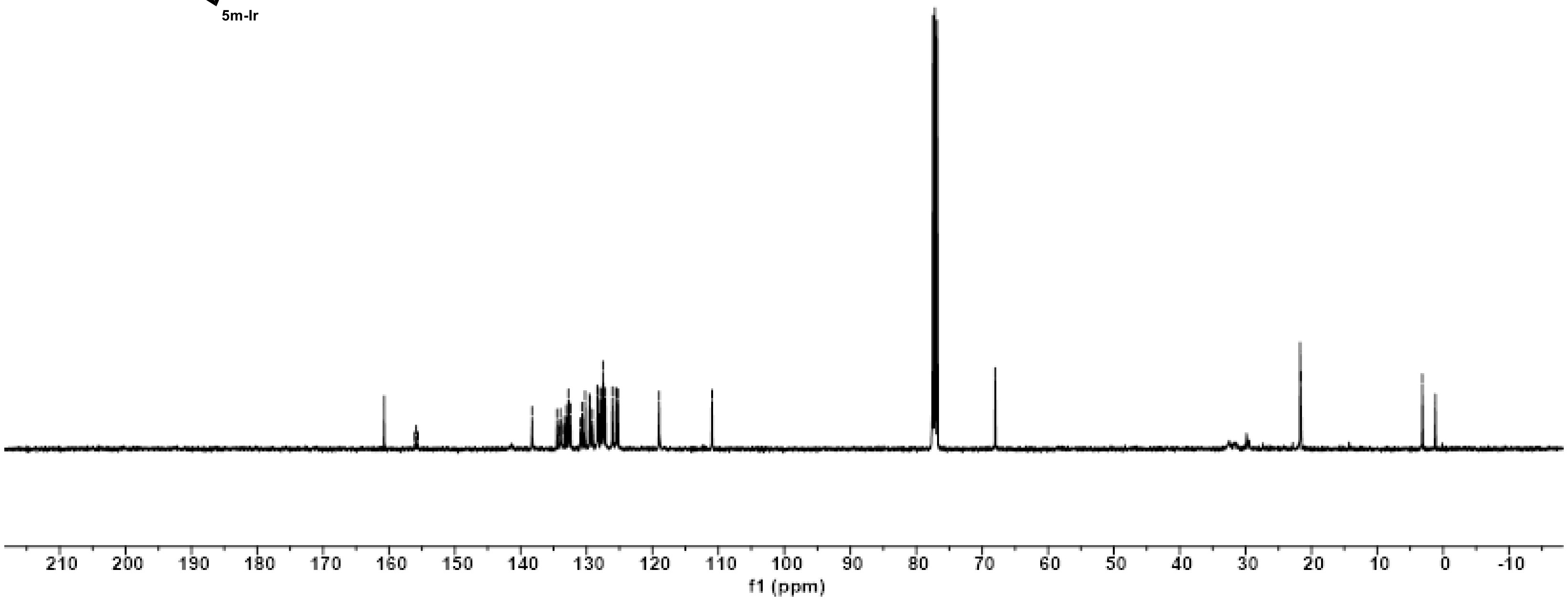
^{1}H NMR (400 MHz, CDCl$_3$)



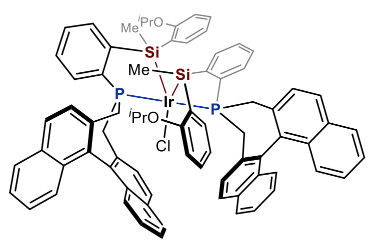
^{13}C NMR (101 MHz, $CDCl_3$)



5m-Ir



^{31}P NMR (162 MHz, $CDCl_3$)



5m-Ir