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Supporting Information

General Reagent Information

Unless otherwise noted, all reactions were set up on the bench top and run under an argon atmosphere. THF and CH_2Cl_2 were purchased from J. T. Baker in CYCLE-TAINER® and vigorously purged with argon for 2 h. The solvents were then passed through two packed columns of alumina (THF) or a column of neutral alumina and a column of copper(II) oxide (CH_2Cl_2) under argon pressure. Anhydrous cyclopentyl methyl ether (CPME), dioxane, and hexane were purchased from Aldrich in Sure-Seal® bottles and used as received. Sodium *tert*-butoxide was purchased from Aldrich Chemical Company and potassium phosphate tribasic was purchased from Alfa Aesar. The bulk of sodium *tert*-butoxide and potassium phosphate tribasic were stored in a nitrogen-filled glovebox and small amounts (1 g) were removed and stored in air for up to a week in a desiccator filled with calcium sulfate. *Cis*-2,6-dimethylpiperidine was distilled before use. (R)-(+)-*N*-benzyl-α-methylbenzylamine (≥97% ee) was purchased from Aldrich Chemical Company. (R)-(–)-phenylglycinol (99% ee) and (±)-phenylglycinol for the preparation of (R)-3-phenylmorpholine and (±)-phenylglycinol, were purchased from Alfa Aesar. All other commercially available reagents were used as received. Flash chromatography was performed using SiliaFlash F60 silica gel from SiliCycle. In some cases, flash chromatography was performed with the aid of a Biotage SP4 instrument using silica-packed cartridges.

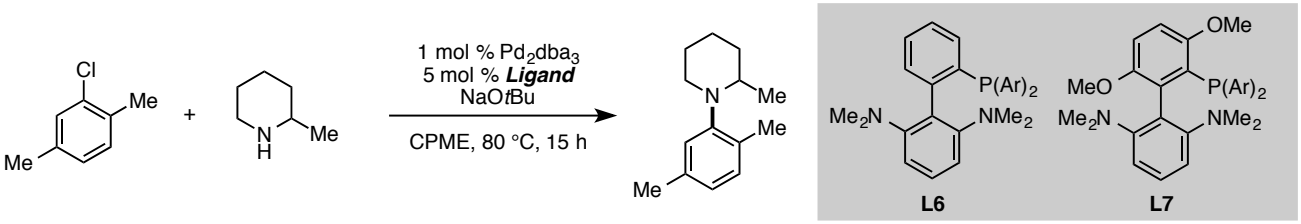
General Analytical Information

All compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and either elemental analysis or high-resolution mass spectrometry (HRMS). Fluorine- and phosphine-containing compounds were further characterized by ^{19}F and ^{31}P NMR spectroscopy. The NMR spectra are available at the end of the Supporting Information. NMR analyses were performed on a Varian 500 MHz, Varian 300 MHz or Bruker 400 MHz instruments. Chemical shifts for ^{1}H NMR were measured relative to the residual solvent signals of C_6D_6 (7.16 ppm), $CDCl_3$ (7.26 ppm), CD_2Cl_2 (5.32 ppm) or CD_3OD (3.31 ppm). Chemical shifts for ^{13}C NMR were measured relative to the residual solvent signals of C_6D_6 (128.0 ppm), $CDCl_3$ (77.2 ppm), CD_2Cl_2 (54.0 ppm) or CD_3OD (49.0 ppm). All ^{19}F chemical shifts are reported in δ (ppm) units relative to an external standard of $CFCl_3$ (0.00 ppm) or α,α,α-trifluorotoluene (–63.90 ppm). All ^{31}P NMR were collected on a Varian Inova-300 spectrometer operating at

220 MHz and are reported in δ (ppm) units relative to H_3PO_4 (0.00 ppm) as an external standard. Yields refer to the isolated yield of compounds with greater than 95% purity as determined by gas chromatography (GC), ^1H and ^{13}C NMR spectroscopy, as well as, in most cases, elemental analysis. The conversion of starting aryl halide and all product yields (C–N and C–O cross-coupled, as well as reduced arene products) in Tables 1, 2, and SI-1 were determined using GC analysis on samples of crude reaction mixtures using dodecane as the internal standard. GC analyses were performed on an Agilent 6890 gas chromatograph using a J&W DB-1 column with an FID detector. Enantiomeric excesses were determined by high-pressure liquid chromatography (HPLC) on a Agilent 1200 Series using columns with chiral stationary phases. A Jasco P-1010 polarimeter was used to determine the optical rotations with the $[\alpha]_D$ values reported in degrees; concentration (*c*) is in g/100 mL. The infrared (IR) data were collected on the neat material and were recorded using a Thermo Scientific instrument – Nicolet iS5 (iD5 ATR – Diamond). Elemental analyses (EA) of samples were performed by Atlantic Microlabs Inc., Norcross, GA.

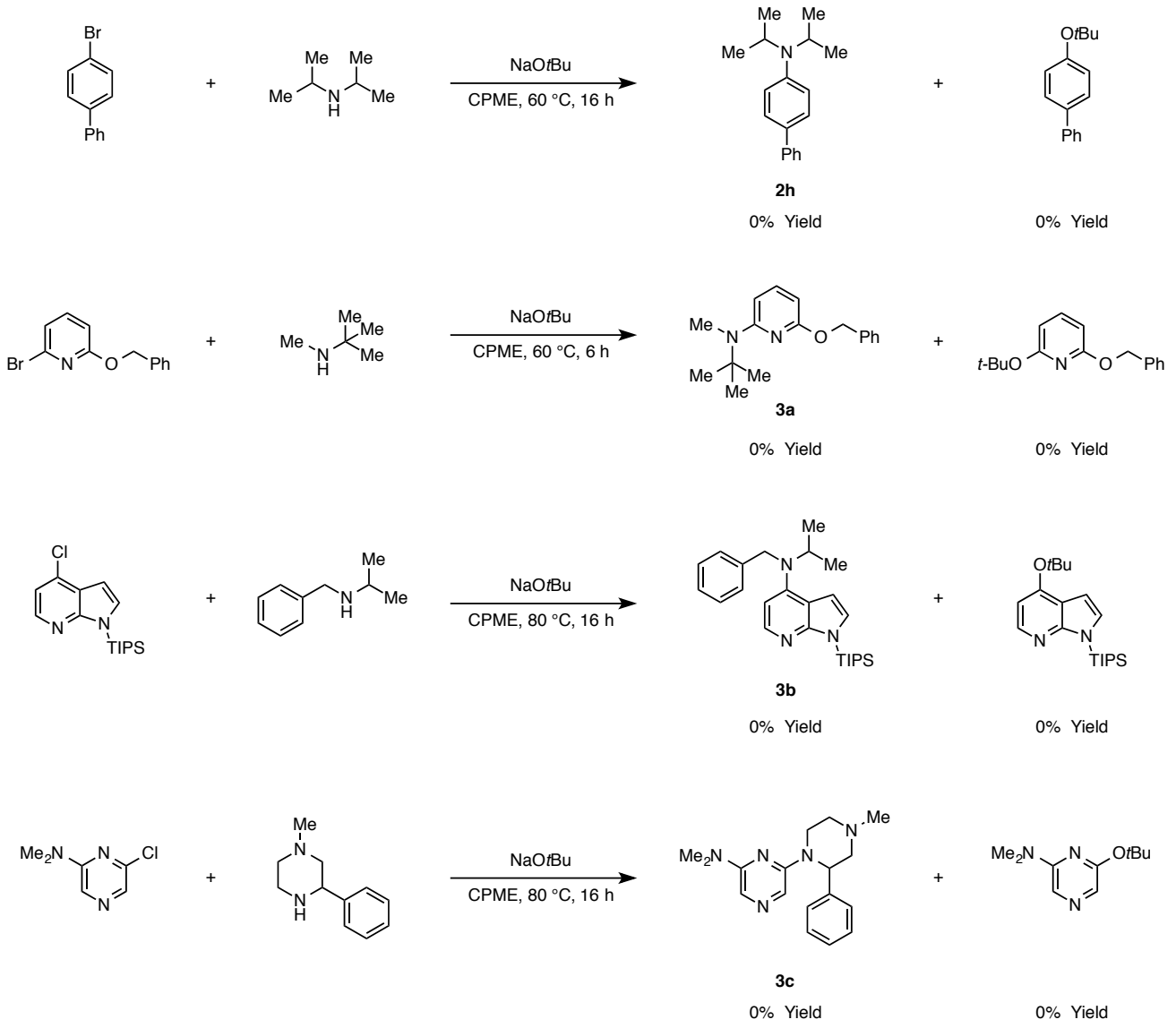
Additional Experiments:

Comparsion of L6 and L7: Scheme SI-1 depicts early results comparing the performance of catalyst systems based on **L6** and **L7**. *Note*: These results were obtained prior to further optimization of the palladium source. Hence, they were performed using Pd_2dba_3 as the palladium source.



Scheme SI-1. Comparison of **L6** and **L7** with an aryl chloride electrophile. Reaction conditions: 2-chloro-*p*-xylene (0.25 mmol), 2-methylpiperdine (0.30mmol), NaO*t*Bu (0.35 mmol), 1 mol % Pd_2dba_3, CPME (0.5 mL), 80 °C, 15 h. Conversion and yield were determined by GC analysis of the crude reaction mixture using dodecane as the internal standard.

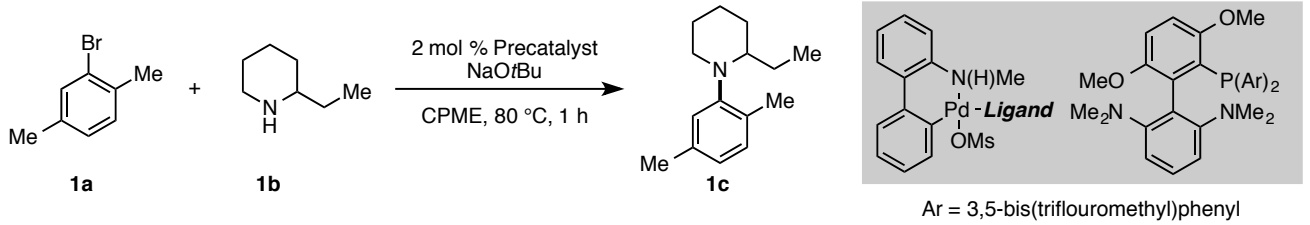
Control Experiments: These experiments were run in the absence of the palladium precatalyst.



Scheme SI-2. Control experiments for substrates. Reaction conditions: aryl halide (0.25 mmol), amine (0.30mmol), NaO*t*Bu (0.35 mmol), CPME (0.5 mL), 60–80 °C, 6–16 h. Yields were determined by GC analysis of the crude reaction mixture using dodecane as the internal standard.

Effect of Excess Amine: Table SI-1 shows the effect of adding excess amine relative to NaO*t*Bu on the conversion and yield of the reaction.

Table SI-1. Effect of excess amine.[a]



Ar = 3,5-bis(triflouromethyl)phenyl

Entry	Amine Equiv.	NaO*t*Bu Equiv.[b]	Conversion[b]	ArO*t*Bu[b]	Yield[b]
1	1.2	1.4	100%	6%	93%
2	1.4	1.4	100%	6%	94%
3	1.6	1.4	53%	—	47%
4	1.8	1.4	53%	—	46%

[a] Reaction conditions: **1a** (0.25 mmol), **1b** (0.30–0.45 mmol), NaO*t*Bu (0.35 mmol), 2 mol % precatalyst, CPME (0.5 mL), 80 °C, 1 h. [b] Conversion, yield, and ArO*t*Bu were measured by GC analysis of the crude reaction mixture using dodecane as the internal standard. Only very trace amounts of reduction were observed in these experiments.

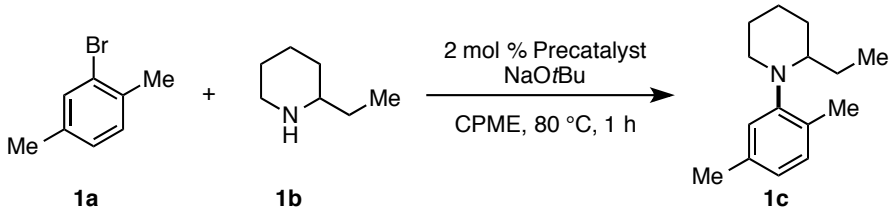
Arylation of Diisopropylamine with 4-bromoanisole:

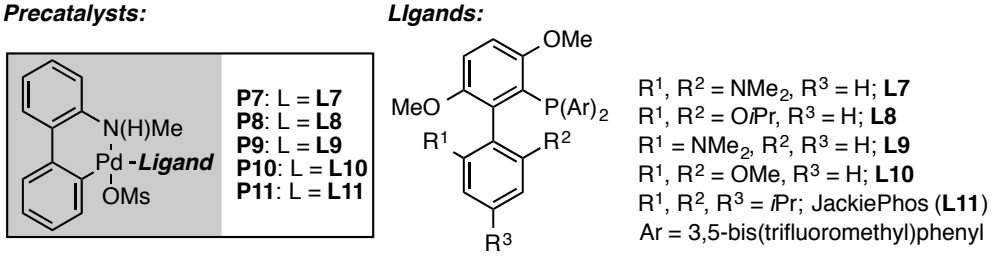
In our hands, we were unable to reproduce the arylation of diisopropylamine with 4-bromoanisole as reported by Herrmann.[1] Instead, our products originated from the arylation of *N*-isopropylpropan-2-imine, which arises from the dehydrogenation of diisopropylamine. Reduction of 3-bromoanisole to anisole was also observed under these conditions.

Ligand Modification:

Table SI-2 shows comparison experiments of precatalysts **P7** to **P11**, which helps illustrate their inherent differences in reactivity with respect to the formation of byproducts.

Table SI-2. Modification of the Supporting Ligand.[a]



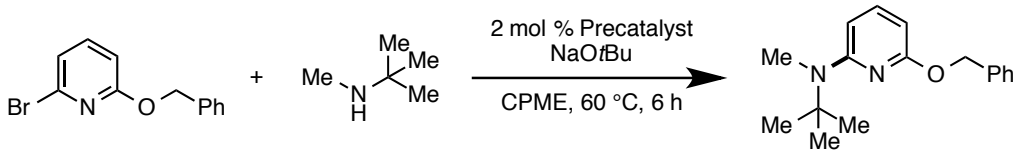


[1] Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23.

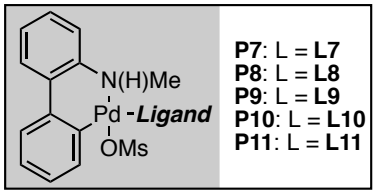
Entry	Ligand Modification	Conversion[b]	ArO*t*Bu[b]	Reduction[b]	Yield[b]
1	None (**P7**)	100%	6%	Trace	93%
2	2',4',6'-*i*Pr– instead of 2',6'-Me_2N– (**P11**)	43%	Trace	9%	16%
3	Removal of 6'-Me_2N– (**P9**)	71%	4%	4%	56%
4	2',6'-MeO– instead of 2', 6'-Me_2N– (**P10**)	73%	Trace	11%	52%
5	2',6'-*i*PrO– instead of 2', 6'-Me_2N– (**P8**)	100%	Trace	4%	91%

[a] Reaction conditions: **1a** (0.25 mmol), **1b** (0.30 mmol), NaO*t*Bu (0.35 mmol), 2 mol % precatalyst, CPME (0.5 mL), 80 °C, 1 h. [b] Conversion, yield, ArO*t*Bu, and reduction were measured by GC analysis of the crude reaction mixture using dodecane as the internal standard.

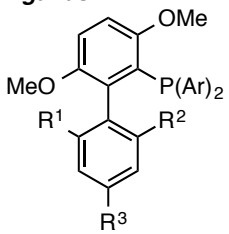
Table SI-3. Modification of the Supporting Ligand.[a]



Precatalysts:



LIgands:

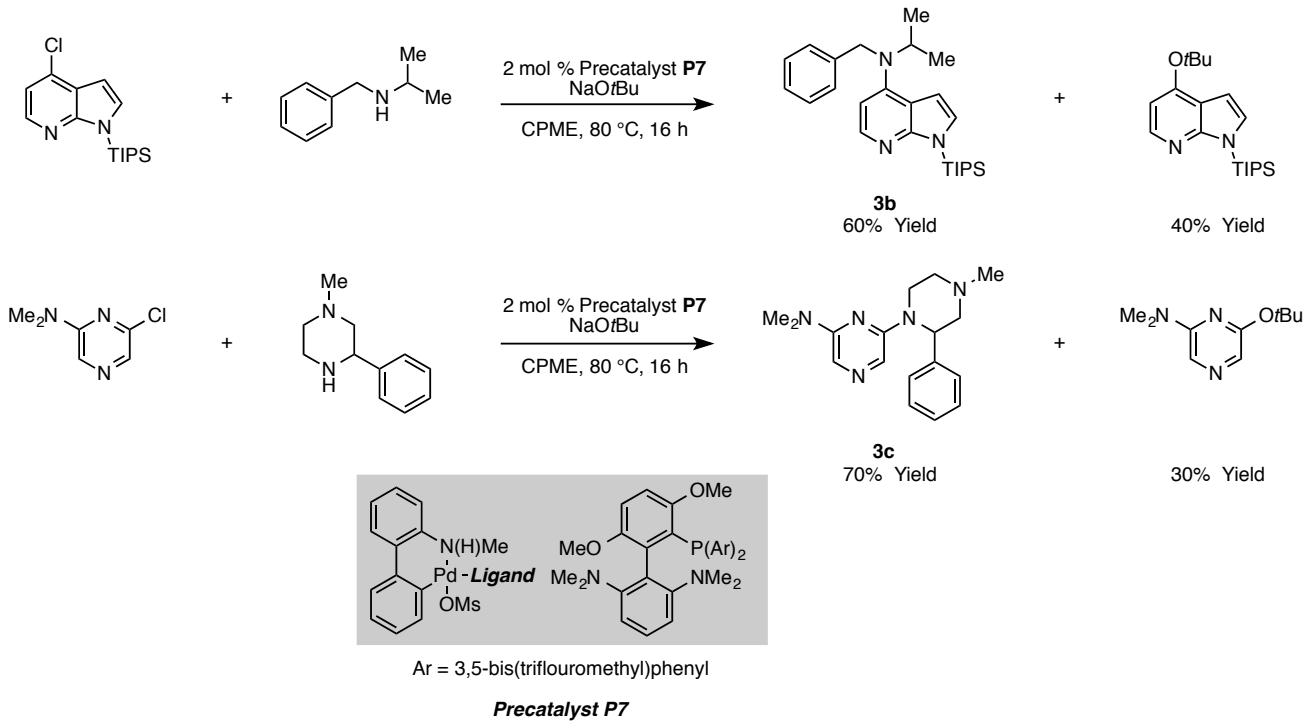


R^1, R^2 = NMe_2, R^3 = H; **L7**
R^1, R^2 = O*i*Pr, R^3 = H; **L8**
R^1 = NMe_2, R^2, R^3 = H; **L9**
R^1, R^2 = OMe, R^3 = H; **L10**
R^1, R^2, R^3 = *i*Pr; JackiePhos (**L11**)
Ar = 3,5-bis(trifluoromethyl)phenyl

Entry	Ligand Modification	Conversion	ArO*t*Bu	Yield
1	None (**P7**)	70%	65%	5%
2	2',4',6'-*i*Pr– instead of 2',6'-Me_2N– (**P11**)	53%	38%	5%
3	Removal of 6'-Me_2N– (**P9**)	100%	11%	86%
4	2',6'-MeO– instead of 2',6'-Me_2N– (**P10**)	31%	Trace	30%
5	2',6'-*i*PrO– instead of 2',6'-Me_2N– (**P8**)	84%	6%	79%
6	2',6'-*i*PrO– with additional equivalents of amine and base (**P8**)	100%	Trace	89%[b],[c]

[a] Reaction conditions: 2-bromo-6-benzyloxypyridine (0.25 mmol), *N*-methyl-*tert*-butylamine (0.30 mmol), NaO*t*Bu (0.35 mmol), 2 mol % precatalyst, CPME (0.5 mL), 60 °C, 6 h. Conversion, C–N cross-coupling, and ArO*t*Bu product yields were measured by GC analysis of the crude reaction mixture using dodecane as the internal standard. [b] Reaction conditions: 2-bromo-6-benzyloxypyridine (0.25 mmol), *N*-methyl-*tert*-butylamine (0.60 mmol), NaO*t*Bu (0.7 mmol), 2 mol % precatalyst, CPME (0.5 mL), 60 °C, 6 h. [c] Isolated yield: 92% (1 mmol scale, average of two runs).

Arylation of heteroaryl electrophiles: The following experiments show the results of the cross-coupling reactions for **3b** and **3c** using precatalyst **P7**.

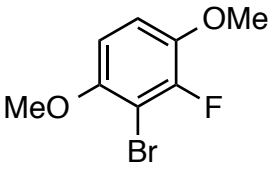


Scheme SI-3. Cross-coupling reactions for **3b** and **3c** using precatalyst **P7**. Reaction conditions: aryl halide (0.25 mmol), amine (0.30mmol), NaO*t*Bu (0.35 mmol), 2 mol % Precatalyst **P7**, CPME (0.5 mL), 80 °C, 16 h. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as the internal standard.

Synthesis of Ligand Precursors.

N^1,N^1,N^3,N^3-tetramethylbenzene-1,3-diamine and 2'-bromo-N^2,N^2,N^6,N^6-tetramethyl-[1,1'-biphenyl]-2,6-diamine were prepared according to literature procedures.[2]

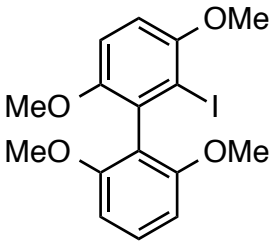
2-bromo-3-fluoro-1,4-dimethoxybenzene. A flame-dried 500 mL round-bottom flask equipped with a magnetic stir-bar and a septum was charged with 2-fluoro-1,4-dimethoxybenzene (7.8 g, 50 mmol) and THF (150 mL). The reaction mixture was cooled to –78 °C in a dry ice/acetone bath and *n*-butyllithium (2.5 M in hexane, 21 mL, 52.5 mmol) was added dropwise via syringe. The reaction mixture was allowed to stir at –78 °C for 1 h, after which time bromine (2.7 mL, 52.5 mmol) was added dropwise via syringe and the



[2] Han, C.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 7532.

reaction mixture was allowed to slowly warm up to room temperature over the course of 6 h. The reaction was then quenched with 100 mL of a saturated solution of Na_2SO_3 in water and the resulting mixture was transferred to a separatory funnel. The aqueous and organic phases were separated and the aqueous phase was extracted with EtOAc (2 x 80 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated with the aid of a rotary evaporator. The crude residue was dissolved in CH_2Cl_2 and filtered through a short plug of silica gel, eluting with 20% CH_2Cl_2 in hexanes. The filtrate was concentrated and the residue was purified via column chromatography on silica gel (5% EtOAc in hexanes). Trituration of the isolated material from pentane provided the title compound as a white solid (5.07 g, 43%), mp = 44–46 °C.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.89 (t, *J* = 9.2 Hz, 1H), 6.64 (dd, *J* = 2.1, 9.2 Hz, 1H), 3.83 (s, 6H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 151.9 (d, *J* = 244.9 Hz), 151.4 (d, *J* = 2.5 Hz), 143.2 (d, *J* = 12.0 Hz), 112.9 (d, *J* = 3.0 Hz), 106.6 (d, *J* = 3.7 Hz), 100.9 (d, *J* = 20.0 Hz), 57.4, 57.2.
^{19}F NMR (282 MHz, CD_2Cl_2) δ –125.74 (d, *J* = 9.0 Hz).
FTIR (neat, cm^{-1}): 2966.9, 2942.9, 2839.7, 1491.5, 1432.9, 1317.5, 1261.4, 1175.5, 1145.9, 1074.7, 1034.4, 828.8, 789.4, 717.9, 645.5, 614.1.
EA: Anal. Calcd. for $C_8H_8BrFO_2$: C, 40.88; H, 3.43. Found: C, 40.91; H, 3.33.

2-iodo-2',3,6,6'-tetramethoxy-1,1'-biphenyl. A flame-dried 500 mL round-bottom flask equipped with a magnetic stir-bar and a septum was charged with 1,3-dimethoxybenzene (2.94 mL, 22.5 mmol) and THF (52 mL). The solution was cooled to 0 °C in an ice/water bath and a solution of *n*-butyllithium (2.5 M in hexanes, 9.4 mL, 23.6 mmol) was added dropwise via syringe. The cold bath was then removed and the reaction mixture was allowed to stir at room temperature for 4 h.



A separate flame-dried 500 mL three-neck round-bottom flask equipped with a magnetic stir-bar and a septum was charged with 2-fluoro-1,4-dimethoxybenzene (2.34 g, 15 mmol) and THF (75 mL) and cooled to –78 °C in a dry ice/acetone bath. Subsequently, a solution of *n*-butyllithium (2.5 M in hexanes, 6.6 mL, 15.8 mmol) was added dropwise via syringe and the reaction mixture was allowed to stir for 1 h at –78 °C, after which the contents of the first flask (lithiated 1,3-dimethoxybenzene) were added to the reaction mixture dropwise via cannula. Once the addition of the lithiated 1,3-dimethoxybenzene was complete, the reaction mixture was stirred at –78 °C for 30 min and then at 0

°C for 1 h. A solution of iodine (9.5 g, 37.5 mmol) in THF (60 mL) was then added dropwise via cannula. The reaction mixture was stirred at rt for 30 min and then quenched with 100 mL of a saturated solution of aqueous Na_2SO_3. The mixture was then transferred to a separatory funnel and the organic and aqueous phases were separated. The aqueous phase was extracted with EtOAc (2 x 100 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. Addition of MeOH (20 mL) to the crude residue resulted in precipitation of a yellow solid, which was collected via vacuum filtration and washed with additional MeOH (40 mL). The solid was then purified via column chromatography on silica gel (20% acetone in hexanes). The isolated solid was recrystallized from EtOAc to provide the title compound as a white solid (2.32 g, 41%), mp = 164–167 °C.

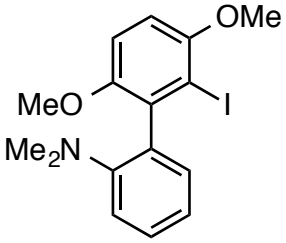
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.38 (t, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H) 3.74 (s, 6H), 3.68 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.1, 153.4, 152.7, 132.1, 129.9, 119.6, 112.2, 110.4, 104.7, 95.7, 57.2, 57.2, 56.5.

FTIR (neat, cm^{-1}): 3008.1, 2958.2, 2927.5, 2828.7, 1584.3, 1463.9, 1427.0, 1405.9, 1281.5, 1246.3, 1101.5, 1081.2, 1014.0, 876.6, 789.3, 720.3, 700.0.

EA: Anal. Calcd. for $C_{16}H_{17}IO_4$: C, 48.02; H, 4.28. Found: C, 47.93; H, 4.18.

2'-iodo-3',6'-dimethoxy-*N*,*N*-dimethyl-[1,1'-biphenyl]-2-amine. A flame-dried



resealable Schlenk tube equipped with a magnetic stir-bar was charged with magnesium turnings (1.72 g, 72 mmol) and fitted with a septum. The vessel was evacuated and backfilled with argon, after which THF (42 mL) was added and the reaction mixture was heated to 70 °C in a pre-heated oil bath. Next, 2-bromo-*N*,*N*-dimethylaniline (0.30 mL, 2.1 mmol) and 1,2-dibromoethane (0.467 mL, 5.4 mmol) were added via syringe. Once the reaction had initiated, the remaining 2-bromo-*N*,*N*-dimethylaniline (4.0 mL, 28.9 mmol) was carefully added dropwise via syringe in three portions over a period of 15 min. ***Warning: vigorous reaction, use caution*!** After the addition was complete, the reaction mixture was stirred at 70 °C for 1.5 h. After this time, the sealed tube was removed from the oil bath and allowed to cool to rt.

A flame-dried 500 mL three-neck round-bottom flask equipped with a magnetic stir-bar and a septum was charged with 2-fluoro-1,4-dimethoxybenzene (2.34 g, 15 mmol) and THF (75 mL). The solution was cooled to –78 °C in a dry ice/acetone bath and *n*-butyllithium (2.5 M in hexanes, 6.6 mL, 15.8 mmol) was

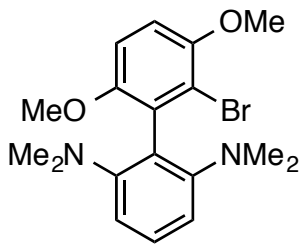
added dropwise via syringe. After the addition of *n*-butyllithium was complete, the reaction mixture was stirred at –78 °C for 1 h. The corresponding Grignard reagent of 2-bromo-*N*,*N*-dimethylaniline (the contents of the Schlenk tube) was then added dropwise via cannula and the reaction mixture was allowed to warm to rt over 12 h. At this time a solution of iodine (11.4 g, 45 mmol) in THF (60 mL) was added dropwise via cannula. The reaction mixture was stirred at rt for 1 h and then quenched with 100 mL of a saturated aqueous Na_2SO_3 solution. The mixture was then transferred to a separatory funnel and the organic and aqueous phases were separated. The aqueous phase was extracted with EtOAc (2 x 100 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (0–10% EtOAc in hexanes). Addition of MeOH (20 mL) to the isolated oil produced a white solid, which was collected via vacuum filtration and washed with additional MeOH (30 mL). The solid was recrystallized by suspending it in MeOH (5 mL) and adding small amounts of EtOAc (1 mL) with heating until it had completely dissolved. The solution was allowed to cool slowly to rt and then cooled further to –25 °C in a freezer. The colorless crystals that formed were isolated via vacuum filtration and washed with additional cold MeOH (10 mL) to give the title compound (2.32 g, 41%). Mp= 99–100 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.37–7.33 (m, 1H), 7.14–7.12 (m, 1H), 7.07–7.03 (m, 1H), 6.99–6.95 (m, 2H), 6.86–6.84 (d, J = 8.9 Hz, 1H), 3.88 (s, 3H) 3.73 (s, 3H), 2.57 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.3, 152.7, 152.1, 137.8, 135.5, 132.1, 129.1, 121.9, 119.2, 111.9, 110.1, 95.6, 57.3, 56.8, 43.9.

FTIR (neat, cm^{-1}): 2943.7, 2839.4, 2795.0, 1588.8, 1565.6, 1468.4, 1426.5, 1323.6, 1247.9, 1178.8, 1134.6, 1084.9, 1054.6, 1015.1, 946.1, 876.3, 845.4, 784.0, 755.6, 731.5, 704.6.

EA: Anal. Calcd. for $C_{16}H_{18}INO_2$: C, 50.15; H, 4.73. Found: C, 50.09; H, 4.64.



2'-bromo-3',6'-dimethoxy-N^2,N^2,N^6,N^6-tetramethyl-[1,1'-biphenyl]-2,6-diamine. To an oven-dried screw-cap test tube (Fisher Scientific, catalog number: 1495937A) equipped with screw-cap septum and a magnetic stir-bar, N^1,N^1,N^3,N^3-tetramethylbenzene-1,3-diamine (492 mg, 3.0 mmol) and hexanes (6 mL) were added followed by *n*-butyllithium (2.5 M in hexane). The screw-cap septum was exchanged for an unpunctured screw-cap septum under a continuous flow of argon and the tube

was heated to 80 °C in a pre-heated oil bath for 1 h. After cooling to rt, a solution of 2-bromo-3-fluoro-1,4-dimethoxybenzene (1.06 g, 4.5 mmol) in Et_2O (6 mL) was then added dropwise via cannula. The reaction mixture was stirred at rt for 1 h and then diluted with Et_2O and extracted with 2M HCl (4 x 30 mL). The combined aqueous layers were cooled to 0 °C in an ice/water bath and basified with KOH until pH = 14 was reached. The resulting mixture was extracted with CH_2Cl_2 (4 x 40 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The residue was purified via column chromatography (8% acetone in hexanes) to provide the title compound as an off-white solid (643 mg, 57%). Mp = 86–89 °C.

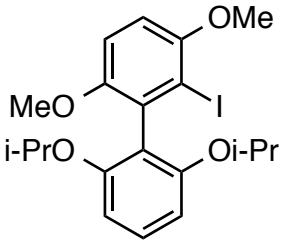
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.34 (t, *J* = 8.0 Hz, 1H), 6.98–6.96 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H) 3.75 (s, 3H), 2.46 (s, 12H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 154.5, 153.0, 151.0, 132.3, 129.9, 129.5, 116.3, 115.5, 110.5, 110.5, 57.0, 56.6, 44.7.

FTIR (neat, cm^{-1}): 2936.1, 2820.4, 2769.4, 1575.4, 1460.2, 1428.4, 1296.7, 1251.1, 1168.6, 1092.9, 1039.3, 1008.7, 815.1, 789.0, 752.2, 722.8.

EA: Anal. Calcd. for $C_{18}H_{23}BrN_2O_2$: C, 57.00; H, 6.11. Found: C, 57.14; H, 6.05.

2-iodo-2',6'-diisopropoxy-3,6-dimethoxy-1,1'-biphenyl. An oven-dried resealable Schlenk tube equipped with a septum was charged with 1,3-diisopropoxybenzene (3.50 g, 18.0 mmol) and subsequently evacuated and backfilled with argon. Hexane (36 mL) was introduced into the flask followed by *n*-butyllithium (2.4 M in hexane, 7.90 mL, 18.9 mmol). The septum was exchanged with a Teflon® stopcock under a continuous flow of argon. The resealable Schlenk tube was then sealed and heated to 80 °C for 5 h.



An oven-dried 200 mL round-bottom flask fitted with a septum was charged with 1-fluoro-2,4-dimethoxybenzene (2.34 g, 15.0 mmol) and THF (75 mL). The solution was cooled to –78 °C in a dry ice/acetone bath, and *n*-butyllithium (2.4 M in hexane; 6.60 mL, 15.8 mmol) was added dropwise via syringe. The reaction mixture was stirred at –78 °C for 1 h.

The sealed Schlenk tube was cooled to rt and the Teflon® stopcock was exchanged for a septum under a continuous flow of argon. Its contents were then added dropwise via cannula to the round-bottom flask containing the lithiated 1-fluoro-2,4-dimethoxybenzene at –78 °C. Additional THF (20 mL) was added to the Schlenk tube to dissolve any residual lithiated 1,3-diisopropoxybenzene and

the solution was transferred dropwise via cannula to the reaction mixture at –78 °C. The reaction mixture was stirred at –78 °C for 1 h and then warmed to 0 °C in an ice/water bath. After stirring for 1 h at 0 °C, the reaction mixture was quenched with a solution of iodine (4.6 g, 18 mmol) in THF (20 mL). The reaction mixture was then poured into a saturated aqueous Na_2SO_3 solution (100 mL) and extracted with EtOAc (3 x 80 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude residue was dissolved in CH_2Cl_2 and filtered through a short silica gel plug eluting with 10% EtOAc in hexanes. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (0–7.5% EtOAc in hexanes). Trituration of the isolated oil from MeOH afforded the title compound as a white solid (1.86 g, 27%). Mp = 79–81 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.27 (t, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.43 (sp, *J* = 6.1 Hz, 2H), 3.86 (s, 3H) 3.66 (s, 3H), 1.20 (d, *J* = 6.1 Hz, 6H), 1.14 (d, *J* = 6.1 Hz, 6H).

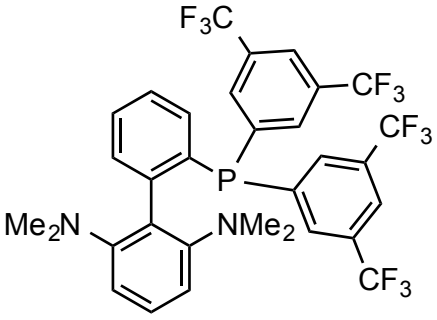
^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.0, 153.2, 152.9, 132.9, 129.4, 122.2, 111.8, 110.1, 107.0, 95.8, 71.1, 57.3, 57.1, 22.7, 22.5.

FTIR (neat, cm^{-1}): 2973.6, 2928.9, 2835.1, 1586.2, 1457.7, 1431.6, 1382.5, 1243.7, 1111.1, 1058.5, 1029.3, 1017.2, 792.8, 721.5, 647.0, 607.1.

EA: Anal. Calcd. for $C_{20}H_{25}IO_4$: C, 52.64; H, 5.52. Found: C, 52.52; H, 5.57.

Synthesis of the Ligands.

2'-(bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)-*N*^{2},*N*^{2},*N*^{6},*N*^{6}-tetramethyl-[1,1'-biphenyl]-2,6-diamine (L6). An oven-dried resealable Schlenk tube fitted with a septum was charged with 2'-bromo-*N*^{2},*N*^{2},*N*^{6},*N*^{6}-tetramethyl-[1,1'-biphenyl]-2,6-diamine (1.20 g, 3.7 mmol) and subsequently evacuated and backfilled with argon. THF (15 mL) was added and the reaction mixture was cooled to –78 °C in a dry ice/acetone bath. Next, *tert*-butyllithium (1.5 M in pentane; 4.50 mL, 7.6 mmol) was added dropwise via syringe and the reaction mixture was stirred at –78 °C for 1 h. After this time, the septum was removed and copper(I) chloride (366 mg, 3.70 mmol) was added as a solid under a continuous flow of argon. The tube was then resealed with the septum, removed from the cold bath, and allowed to warm to rt. Once at rt, bis(3,5-di(trifluoromethyl)phenyl)chlorophosphine (2.20 g, 4.1 mmol) was added via



syringe and the septum was exchanged for a Teflon® stopcock under a continuous flow of argon. The Schlenk tube was then sealed and the reaction mixture was stirred at 80 °C in a pre-heated oil bath for 20 h. After this time, the reaction mixture was cooled to rt, diluted with 200 mL of EtOAc, and washed with a 1:1 solution of brine and 30% aqueous NH_4OH (4 x 100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude brown residue was dissolved in 30 mL of MeOH and concentrated again. This process was repeated a total of three times. The resulting crude solid was recrystallized from MeOH to provide the desired product as off-white needles (1.08 g, 42%). Mp = 105–107 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.86 (s, 2H), 7.71 (s, 2H), 7.70 (s, 2H), 7.56–7.55 (m, 2H), 7.40–7.31 (m, 3H), 6.92 (d, J = 8.1 Hz 2H), 2.21 (s, 12H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.5, 147.0, 146.6, 143.6, 143.3, 136.2, 136.1, 133.8, 133.7, 133.6, 133.4, 133.1, 132.5, 132.5, 132.2, 132.2, 131.9, 131.8, 131.5, 131.5, 131.3, 129.9, 129.9, 129.7, 128.1, 128.0, 125.2, 122.8, 122.5, 119.8, 114.5, 43.9 (observed complexity due to C–F and C–P splitting).

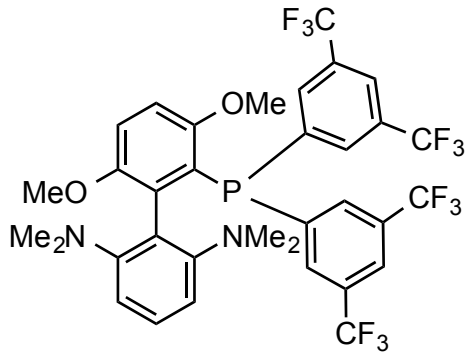
^{31}P NMR (121 MHz, CD_2Cl_2) δ –11.25.

^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.74.

FTIR (neat, cm^{-1}): 2862.6, 2828.5, 2784.9, 1575.4, 1476.5, 1351.2, 1274.0, 1172.4, 1116.7, 1106.5, 1092.2, 1006.3, 898.8, 843.2, 805.0, 746.9, 734.2, 702.4, 681.6.

EA: Anal. Calcd. for $C_{32}H_{25}F_{12}N_2P$: C, 55.18; H, 3.62. Found: C, 55.44; H, 3.81.

2'-(bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)-3',6'-dimethoxy-*N*^{2},*N*^{2},*N*^{6},*N*^{6}-tetramethyl-[1,1'-biphenyl]-2,6-diamine (L7). An oven-dried resealable Schlenk tube fitted with a septum was charged with 2'-bromo-3',6'-dimethoxy-*N*^{2},*N*^{2},*N*^{6},*N*^{6}-tetramethyl-[1,1'-biphenyl]-2,6-diamine (1.84 g, 4.86 mmol) and subsequently evacuated and backfilled with argon. THF (7.5 mL) was added, after which the reaction mixture was cooled to –78 °C in a dry ice/acetone bath and *tert*-butyllithium (1.7 M in pentane, 1.30 mL, 2.2 mmol) was introduced dropwise via syringe. The reaction mixture was stirred at –78 °C for 1 h. After this time, the septum was removed and copper(I) chloride (366 mg, 3.70 mmol) was added as a solid under a continuous flow of argon. The tube was then resealed with the septum, removed from the cold bath, and allowed to warm to rt. Once at rt, bis(3,5-di(trifluoromethyl)phenyl)chlorophosphine (3.83 g, 7.78



mmol) was added via syringe and the septum was exchanged for a Teflon® stopcock under a continuous flow of argon. The Schlenk tube was then sealed and the reaction mixture was stirred at 80 °C in a pre-heated oil-bath for 24 h. After this time, the reaction mixture was cooled to rt, diluted with 200 mL of EtOAc, and washed with a 1:1 solution of brine and 30% aqueous NH_4OH (4 x 100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude brown residue was dissolved in 30 mL of MeOH and concentrated again. This process was repeated a total of three times. The resulting crude solid was recrystallized from MeOH to provide the desired product as off-white needles (2.21 g, 58%, two recrystallization crops). Mp = 159–160 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.80 (s, 2H), 7.75–7.74 (m, 4H), 7.33 (t, 7.9 Hz 1H), 7.23 (d, *J* = 9.00 Hz, 1H), 6.92 (m, 3H), 3.79 (s, 3H), 3.37 (s, 3H), 2.28 (s, 12H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.1, 156.1, 154.5, 153.0, 152.8, 142.1, 141.9, 138.3, 137.9, 133.3, 133.0, 131.6, 131.6, 131.3, 131.3, 131.0, 130.9, 130.7, 130.6, 129.6, 129.1, 129.0, 128.2, 125.5, 122.8, 121.9, 121.0, 120.8, 120.1, 116.1, 115.0, 111.2, 56.5, 55.0, 44.2 (observed complexity due to C–F and C–P splitting).

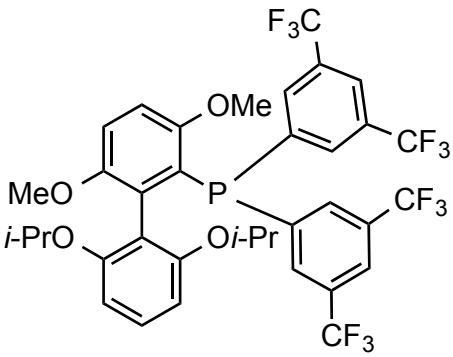
^{31}P NMR (121 MHz, CD_2Cl_2) δ –10.61.

^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.67.

FTIR (neat, cm^{-1}): 2944.7, 2827.6, 2785.5, 1575.4, 1460.9, 1426.3, 1353.0, 1272.4, 1249.6, 1173.5, 1118.5, 1047.5, 1010.9, 894.0, 842.7, 803.3, 680.3.

EA: Anal. Calcd. for $C_{34}H_{29}F_{12}N_2O_2P$: C, 53.98; H, 3.86. Found: C, 53.90; H, 3.79.

Bis(3,5-bis(trifluoromethyl)phenyl)(2',6'-diisopropoxy-3,6-dimethoxy-[1,1'-biphenyl]-2-yl)phosphane (L8). An oven-dried screw-cap test tube (Fisher Scientific, catalog number: 1495937A) equipped with a screw-cap septum and a magnetic stir-bar was charged with 2-iodo-2',6'-diisopropoxy-3,6-dimethoxy-1,1'-biphenyl (349 mg, 0.76 mmol) and subsequently evacuated and backfilled with argon. THF (7.5 mL) was added, after which the reaction mixture was cooled to –78 °C and *tert*-butyllithium (1.7 M in pentane, 1.30 mL, 2.2 mmol) was introduced dropwise via syringe. The reaction mixture was stirred at –78 °C for 1 h. After this time, the screw-cap septum was



removed and copper(I) chloride (366 mg, 3.70 mmol) was added as a solid under a continuous flow of argon. The tube was then resealed with the screw-cap septum, removed from the cold bath, and allowed to warm to rt. Once at rt, bis(3,5-di(trifluoromethyl)phenyl)chlorophosphine (524 mg, 1.06 mmol) was then added via syringe and the screw-cap septum was exchanged for an unpunctured screw-cap septum under a continuous flow of argon. The resulting mixture was stirred at 80 °C in a pre-heated oil bath for 24 h. After this time, the reaction mixture was cooled to rt, diluted with 100 mL of EtOAc, and washed with a 1:1 solution of brine and 30% aqueous NH_4OH (4 x 60 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was dissolved in 30 mL of MeOH and concentrated. This process was repeated a total of three times. The resulting crude solid was recrystallized from MeOH to provide the desired product as a white solid (353 mg, 45%). Mp = 147–149 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.81 (s, 2H), 7.77–7.76 (m, 4H), 7.28 (t, *J* = 8.3 Hz, 1H), 7.15 (d, *J* = 8.9 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 2H), 4.42 (sept, *J* = 6.1 Hz, 2H), 3.71 (s, 3H), 3.35 (s, 3H), 1.05 (d, *J* = 6.1 Hz, 6H), 0.98 (d, *J* = 6.1 Hz, 6H).

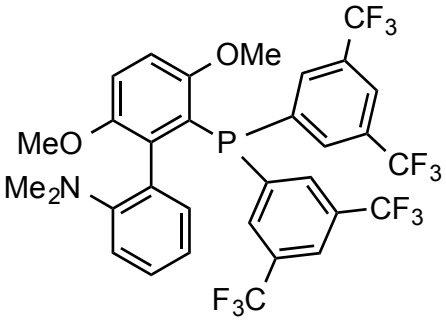
^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.5, 157.5, 155.5, 155.5, 152.7, 152.6, 141.6, 141.4, 135.9, 135.5, 133.2, 133.2, 133.0, 133.0, 131.8, 131.7, 131.5, 131.4, 131.1, 131.1, 130.8, 130.7, 129.5, 128.2, 125.5, 122.8, 122.2, 122.2, 122.2, 122.1, 122.1, 122.1, 120.0, 119.4, 119.2, 115.7, 115.7, 111.2, 106.9, 71.3, 56.7, 55.0, 22.3, 22.2 (observed complexity due to C–P and C–F splitting).

^{31}P NMR (121 MHz, CD_2Cl_2) δ –11.75.

^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.57.

FTIR (neat, cm^{-1}): 2986.3, 1592.8, 1459.6, 1351.3, 1273.1, 1246.5, 1168.2, 1116.8, 1051.6, 1016.8, 891.3, 842.7, 802.7, 728.5, 702.6, 679.8.

EA: Anal. Calcd. for $C_{36}H_{31}F_{12}O_4P$: C, 54.97; H, 3.97. Found: C, 54.82; H, 4.13.



2'-(bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)-3',6'-dimethoxy-*N*,*N*-dimethyl-[1,1'-biphenyl]-2-amine (L9). A flame-dried screw-cap test tube (Fisher Scientific, catalog number: 1495937A) equipped with a screw-cap septum and a magnetic stir-bar was charged with 2'-iodo-3',6'-dimethoxy-*N*,*N*-dimethyl-[1,1'-biphenyl]-2-amine (400 mg, 1.0 mmol) and subsequently evacuated and backfilled with argon. THF (7.5 mL) was added, after which the reaction mixture was cooled to –78 °C in a dry ice/acetone bath and *tert*-butyllithium (1.7 M in pentane, 1.30 mL, 2.2 mmol) was introduced dropwise via syringe. The reaction mixture was stirred at –78 °C for 1 h. After this time, the screw-cap septum was removed and copper(I) chloride (366 mg, 3.70 mmol) was added as a solid under a continuous flow of argon. The tube was then resealed with the screw-cap septum, removed from the cold bath, and allowed to warm to rt. Once at rt, bis(3,5-bis(trifluoromethyl)phenyl)chlorophosphine (591 mg, 1.2 mmol) was added via syringe and the screw-cap septum was exchanged for an unpunctured screw-cap septum under a continuous flow of argon. The reaction mixture was then stirred at 80 °C in a pre-heated oil bath for 16 h. After this time, the reaction mixture was cooled to rt and diluted with EtOAc (100 mL). The resulting solution was washed with a 1:1 solution of 30% aqueous NH_4OH and brine (5 x 40 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude solid was recrystallized from MeOH to give the title compound as a white solid (125 mg, 19% yield). Mp = 107–108 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.86 (s, 1H), 7.78–7.76 (m, 3H), 7.65–7.76 (m, 2H), 7.38–7.34 (m, 1H), 7.26–7.21 (m, 2H), 7.14–7.10 (m, 1H), 7.04–7.02 (m, 1H), 6.91–6.89 (m, 1H), 3.81 (s, 3H), 3.35 (s, 3H), 2.20 (s, 6H).

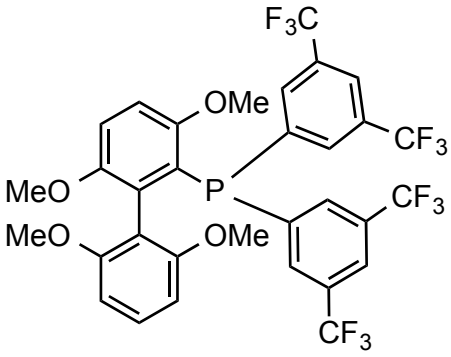
^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.8, 155.8, 153.1, 153.0, 152.1, 152.0, 142.7, 142.4, 141.3, 141.1, 139.6, 139.2, 133.2, 133.0, 132.7, 132.3, 132.2, 132.1, 132.1, 132.0, 131.9, 131.8, 131.7, 131.7, 131.5, 131.5, 131.4, 131.3, 131.2, 131.2, 131.1, 131.0, 130.9, 130.8, 130.7, 130.7, 129.2, 128.3, 128.1, 125.6, 125.4, 122.9, 122.7, 122.4, 122.3, 122.3, 122.2, 122.2, 121.7, 121.7, 121.5, 120.1, 120.0, 118.3, 116.6, 116.6, 111.7, 56.7, 55.1, 42.9 (observed complexity due to C–P and C–F splitting).

^{31}P NMR (121 MHz, CD_2Cl_2) δ –11.13.

^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.61, –63.68.

FTIR (neat, cm^{-1}): 2949.5 2831.3, 2783.7, 1581.0, 1464.3, 1351.7, 1272.4, 1249.7, 1186.1, 1167.5, 1117.0, 1047.1, 1016.5, 946.8, 892.3, 843.0, 805.1, 753.4, 731.7, 702.9, 680.6

EA: Anal. Calcd. for $C_{32}H_{24}F_{12}NO_2P$: C, 53.87; H, 3.89. Found: C, 53.94; H, 3.49.



Bis(3,5-bis(trifluoromethyl)phenyl)(2',3,6,6'-tetramethoxy-[1,1'-biphenyl]-2-yl)phosphane (L10). A flame-dried screw-cap test tube (Fisher Scientific, catalog number: 1495937A) equipped with a screw-cap septum and a magnetic stir-bar was charged with 2-iodo-2',6'-methoxy-3,6-dimethoxy-1,1'-biphenyl (400 mg, 1.0 mmol) and subsequently evacuated and backfilled with argon. THF (7.5 mL) was added, after which the reaction mixture was cooled to –78 °C in a dry ice/acetone bath and *tert*-butyllithium (1.7 M in pentane, 1.30 mL, 2.2 mmol) was introduced dropwise via syringe. The reaction mixture was stirred at –78 °C for 1 h. After this time, the screw-cap septum was removed and copper(I) chloride (366 mg, 3.70 mmol) was added as a solid under a continuous flow of argon. The tube was then resealed with the screw-cap septum, removed from the cold bath, and allowed to warm to rt. Once at rt, bis(3,5-bis(trifluoromethyl)phenyl)chlorophosphine (591 mg, 1.2 mmol) was added via syringe and the screw-cap septum was exchanged for an unpunctured screw-cap septum under a continuous flow of argon. The reaction mixture was then stirred at 80 °C for 16 h in a pre-heated oil bath. After this time, the reaction mixture was cooled to rt and diluted with EtOAc (100 mL). The resulting solution was washed with a 1:1 solution of 30% aqueous NH_4OH and brine (5 x 40 mL) until the blue color was no longer visible. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The solid was recrystallized by suspending it in MeOH (5 mL) and adding small amounts of EtOAc (1 mL) with heating until it had completely dissolved. The solution was allowed to cool slowly to rt and then cooled further to –25 °C in a freezer. The white crystals were isolated via vacuum filtration and washed with additional cold MeOH (5 mL) to give the title compound (433 mg, 55%). Mp = 163–165 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83–7.79 (m, 6H), 7.38 (t, J = 8.3 Hz, 1H), 7.18–7.16 (d, J = 9.0 Hz, 1H), 6.87–6.85 (d, J = 9.0 Hz, 1H), 6.69 (d, J = 8.3 Hz, 2H), 3.72 (s, 3H), 3.65 (s, 6H), 3.37 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.6, 158.6, 155.8, 155.7, 152.8, 152.6, 141.1, 140.9, 134.8, 134.4, 132.9, 132.9, 132.7, 132.7, 131.9, 131.9, 131.6, 131.5, 131.3, 131.2, 130.9, 130.9, 130.0, 128.2, 125.5, 122.7, 122.5, 122.4, 122.3, 122.2, 122.2, 122.2, 122.1, 120.0, 116.7, 116.7, 116.5, 116.3, 111.6, 104.1, 57.1, 56.0, 55.1 (observed complexity due to C–P and C–F splitting).
^{31}P NMR (121 MHz, CD_2Cl_2) δ –11.17.
^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.72.
FTIR (neat, cm^{-1}): 3070.3, 2946.4, 2842.6, 1590.5, 1463.3, 1432.8, 1353.0, 1273.5, 1250.4, 1181.5, 1121.8, 1107.7, 1018.3, 893.5, 841.6, 803.5, 775.7, 680.3, 629.5.
EA: Anal. Calcd. for $C_{32}H_{23}F_{12}O_4P$: C, 52.62; H, 3.17. Found: C, 52.35; H, 3.27.

Preparation of *N*-methyl-2-aminobiphenyl Palladium Methanesulfonate Precatalysts.

N-methyl-2-aminobiphenyl palladium methanesulfonate dimer, RuPhos (**P1**), XPhos (**P2**), and BrettPhos (**P3**) precatalysts were prepared according to literature procedures.[3]

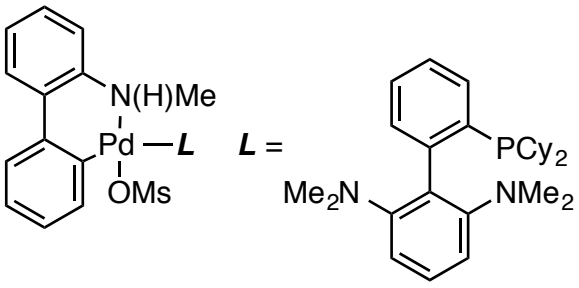
General Procedure for the Synthesis of Precatalysts

An oven-dried screw-cap test tube (Fisher Scientific, catalog number: 1495925C) equipped with a screw-cap septum and a magnetic stir bar was cooled under vacuum, filled with argon and charged with *N*-methyl-2-aminobiphenyl palladium methanesulfonate dimer (**A**) and the corresponding ligand. The reaction vessel was then evacuated and backfilled with argon. The solvent (CH_2Cl_2 or THF) was subsequently added via syringe and the reaction was stirred at rt for 2 h. After this time, the reaction mixture was diluted with Et_2O (5 mL) and filtered through a Whatman GF/F glass fiber filter. The filtrate was concentrated with the aid of a rotary evaporator and the residue was triturated from pentane to produce the title compound.

Note: *Several of the precatalysts retained small amounts of solvent (THF or pentane) after drying under high vacuum (<100 mTorr) for extended time periods (>24 h).*

***Note**: Characterization of the following N-methyl palladium methanesulfonate precatalysts via elemental analysis was unsuccessful. This was consistent with previous observations for this class of precatalysts.*[3]

[3] Bruno, N. C.; Niljianskul, N.; Buchwald, S. L. *J. Org. Chem.* **2014**, *79*, 4161.



CPhos Precatalyst (P4). Following the general procedure, a solution of **A** (96 mg, 0.25 mmol) and CPhos (**L4**) (109 mg, 0.25 mmol), in CH_2Cl_2 (1.3 mL) was stirred at rt for 2 h. After performing the workup as described in the general procedure, pentane was added to the residue and mixture was concentrated with the aid of a rotary evaporator to afford the title compound as an orange solid (107 mg, 51%).

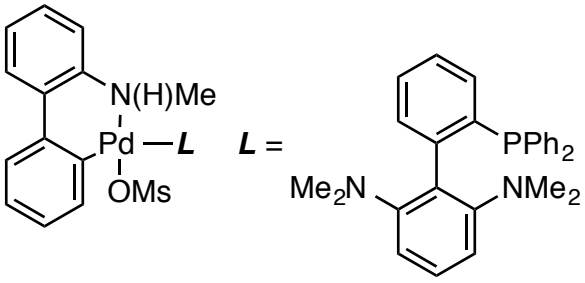
^{1}H NMR (400 MHz, CD_3OD) δ 7.91–7.82 (m, 2H), 7.57 (m, 2H), 7.46, (m, 2H), 7.32–7.18 (m, 8H), 7.10 (m, 1H), 2.72 (s, 3H), 2.57 (s, 6H), 2.41 (s, 6H), 2.17–1.78 (m, 10H), 1.53–1.42 (m, 10H), 1.15–0.90 (m, 4H), 0.36 (m, 1H).

^{13}C NMR (101 MHz, CD_3OD) δ 160.9, 156.9, 146.9, 146.7, 145.8, 145.8, 142.9, 142.9, 142.6, 140.2, 137.4, 137.3, 135.7, 135.3, 134.8, 134.8, 134.7, 133.3, 133.2, 129.8, 129.1, 128.9, 128.8, 128.8 128.5, 128.2, 128.1, 128.0, 122.6, 122.6, 113.7, 113.6, 113.2, 45.2, 44.1, 40.2, 40.2, 39.5, 38.4, 38.2, 38.1, 37.9, 31.9, 31.8, 31.3, 31.3, 31.1, 30.8, 30.7, 29.1, 29.0, 29.0, 28.9, 28.2, 28.1, 27.9, 27.8, 27.1, 26.8 (observed complexity due to C–P splitting).

^{31}P NMR (121 MHz, CD_3OD) δ 40.65.

FTIR (neat, cm^{-1}): 3233.2, 2924.9, 2849.1, 1568.5, 1421.4, 1195.0, 1037.4, 742.7.

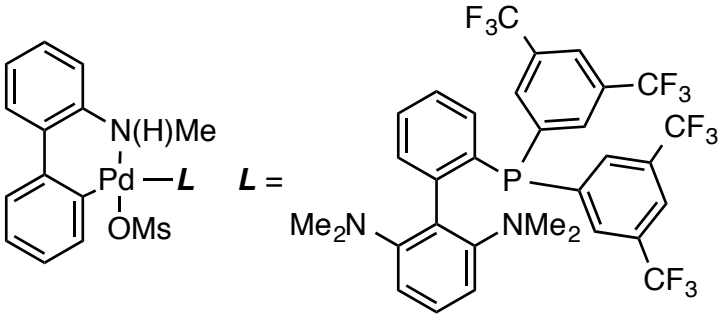
Precatalyst P5. Following the general procedure, a solution of **A** (327 mg, 0.85 mmol) and **L5** (360 mg, 0.85 mmol) in THF (3.3 mL) was stirred at rt for 1 h. Performing the workup and purification as described in the general procedure afforded the title compound as a yellow solid (653 mg, 94%).



^{1}H NMR (400 MHz, CD_3OD) δ 8.00–7.96 (m, 1H), 7.74–7.62 (m, 4H), 7.55–7.31 (m, 8H), 7.33–7.31 (m, 1H), 7.26–7.09 (m, 9H) 6.77–6.73 (m, 1H), 6.43–6.42 (m, 1H), 2.75 (s, 6H), 2.71 (s, 3H), 2.16 (m, 3H), 2.05 (s, 6H).

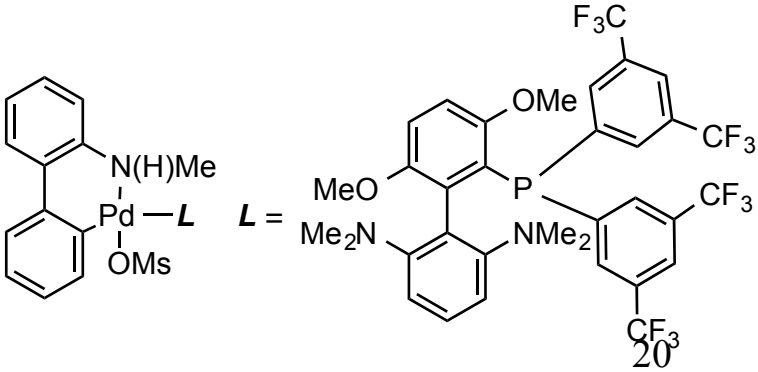
^{13}C NMR (101 MHz, CD_3OD) δ 159.0, 156.9, 148.6, 146.5, 146.3, 143.1, 143.1, 142.4, 139.7, 137.3, 137.1, 136.3, 136.0, 135.9, 135.5, 135.4, 135.3, 134.1, 134.0, 133.3, 133.1, 132.8, 132.7, 132.6, 132.6, 130.9, 130.1, 123.0, 123.0, 129.9, 129.8, 129.6, 129.6, 129.5, 129.4, 129.1, 129.1, 128.8, 128.3, 128.1,

122.8, 122.7, 114.1, 114.0, 113.9, 113.6, 45.0, 43.6, 40.9, 40.9, 39.5 (observed complexity due to C–P splitting).
^{31}P NMR (121 MHz, CD_2Cl_2) δ 39.26.
FTIR (neat, cm^{-1}): 3231.6, 3049.2, 2941.8, 2823.2, 2787.8, 1568.4, 1422.4, 1300.9, 1204.4, 1095.6, 1037.8, 1015.7, 977.9, 789.4, 763.6, 739.0, 692.7.



Precatalyst P6. Following the general procedure, a solution of **A** (51 mg, 0.13 mmol) and **L6** (93 mg, 0.13 mmol) in CH_2Cl_2 (0.6 mL) was stirred at rt for 2 h. After performing the workup as described in the general procedure, pentane was added to the residue and mixture was concentrated with the aid of a rotary evaporator to afford the title compound as a yellow-orange solid (142 mg, 99%).
^{1}H NMR (400 MHz, CD_3OD) δ 8.48 (s, 1H), 8.16 (s, 1H), 8.11–8.07 (m, 1H), 7.91–7.86 (m, 3H), 7.82–7.77 (m, 2H) 7.74–7.71 (m, 2H), 7.65–7.61 (m, 1H) 7.49–7.43 (m, 3H), 7.38–7.34 (m, 2H), 7.27–7.25 (m, 3H), 6.91–6.87 (m, 1H), 6.45–6.42 (m, 1H), 2.71 (s, 3H), 2.67 (s, 6H), 2.22 (s, 9H).
^{13}C NMR (101 MHz, CD_3OD) δ 157.8, 155.3, 145.8, 145.5, 145.1, 140.9, 140.9, 139.3, 137.3, 135.3, 134.6, 134.4, 133.9, 133.9, 133.8, 133.7, 133.7, 133.6, 133.6, 132.8, 132.7, 132.6, 132.4, 132.3, 132.3, 132.1, 132.0, 131.9, 131.7, 131.5, 131.0, 129.3, 129.2, 129.1, 128.8, 128.4, 128.3, 128.2, 127.9, 127.6, 125.8, 124.2, 123.8, 121.5, 121.2, 121.1, 113.4, 112.7, 111.8, 43.6, 42.4, 40.4, 40.3, 38.1 (observed complexity due to C–P and C–F splitting).
^{31}P NMR (121 MHz, CD_3OD) δ 38.59.
^{19}F NMR (282 MHz, CD_3OD) δ –63.60, –63.96.
FTIR (neat, cm^{-1}): 1572.5, 1460.2, 1353.2, 1275.3, 1122.0, 1010.1, 894.5, 843.6, 762.8, 739.3, 698.5, 681.5.

Precatalyst P7. Following the general procedure, a solution of **A** (403 mg, 1.05 mmol) and **L7** (800 mg, 1.05 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 2 h. After performing the workup as described in the general procedure, pentane was added



to the residue and mixture was concentrated with the aid of a rotary evaporator to afford the title compound as a yellow solid (1.13 g, 94%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.17 (s, 1H), 8.11–8.07 (m, 1H), 7.89 (s, 1H), 7.72–7.69 (m, 2H), 7.62–7.59 (m, 2H) 7.52–7.50 (m, 1H), 7.34–7.30 (m, 4H) 7.21–7.04 (m, 5H), 6.85–6.81 (m, 1H), 6.33–6.29 (m, 1H), 3.66 (s, 3H), 3.40 (s, 3H), 2.64 (s, 6H), 2.58 (s, 3H), 2.20 (s, 6H), 2.14 (s, 3H).

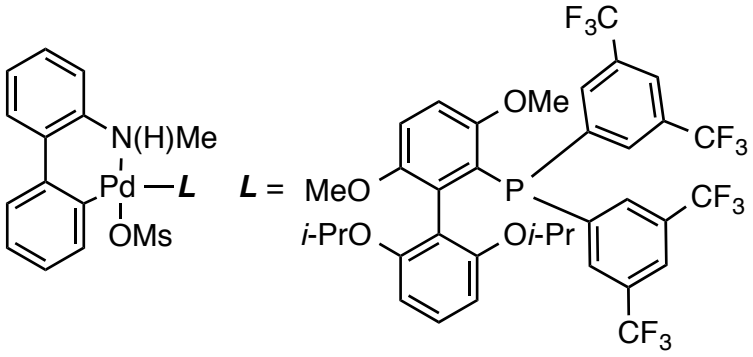
^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.5, 158.0, 154.8, 152.6, 147.1, 141.5, 140.2, 138.0, 136.7, 134.9, 133.0, 129.50, 128.9, 128.5, 128.3, 125.9, 125.4, 122.0, 121.8, 119.6, 114.1, 113.0, 112.4, 57.1, 55.8, 44.9, 43.7, 41.8, 39.9 (observed complexity due to C–P and C–F splitting).

^{31}P NMR (121 MHz, CD_2Cl_2) δ 35.55.

^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.50, –63.63.

FTIR (neat, cm^{-1}): 3743.5, 3214.8, 2938.2, 2834.8, 1616.1, 1571.2, 1553.7, 1498.1, 1464.2, 1423.2, 1353.5, 1275.7, 1175.5, 1122.9, 1038.6, 1012.5, 893.4, 807.1, 763.4, 741.4, 681.7.

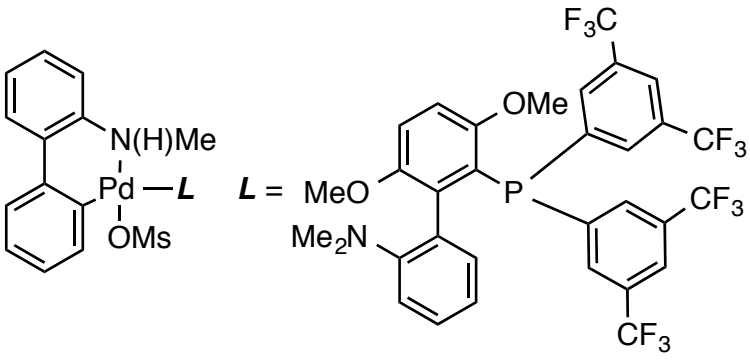
Precatalyst P8. Following the general procedure, a solution of **A** (103 mg, 0.27 mmol) and **L8** (210 mg, 0.27 mmol) in CH_2Cl_2 (1.2 mL) was stirred at rt for 2 h. After performing the workup as described in the general procedure, pentane was added to the residue and mixture was concentrated with the aid of a rotary evaporator to afford the title compound as an off-white solid (305 mg, 97%).



^{1}H NMR (400 MHz, CD_3OD) δ 8.39 (s, 1H), 8.26 (m, 1H), 8.19 (s, 1H), 7.88–7.85 (m, 2H), 7.48–7.45 (m, 1H) 7.42–7.40 (m, 2H), 7.34–7.24 (m, 6H) 7.22–7.20 (m, 1H), 7.16–7.14 (m, 1H), 6.96–6.94 (m, 1H), 6.78–6.74 (m, 1H), 6.21–6.18 (m, 1H), 5.00–4.94 (sept, J = 6.1Hz, 1H), 4.41–4.32 (sept, J = 6.0 Hz, 1H), 3.66 (s, 3H), 3.36 (s, 3H), 2.72 (s, 3H), 2.25 (s, 3H), 1.58 (d, J = 6.0 Hz, 3H), 1.28 (d, J = 6.0 Hz, 3H), 0.89 (d, J = 6.1 Hz, 3H), 0.20 (d, J = 5.6 Hz, 3H).

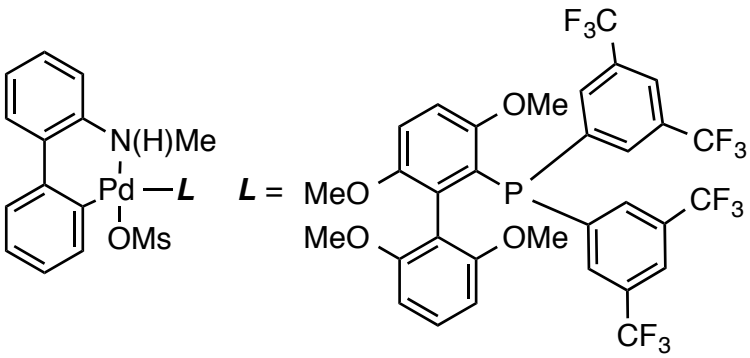
^{13}C NMR (101 MHz, CD_3OD) δ 164.6, 155.0, 152.8, 152.6, 146.7, 142.1, 141.0, 138.8, 138.3, 136.5, 136.4, 134.3, 134.1, 133.7, 133.6, 133.3, 133.2, 131.0, 130.5, 130.4, 129.1, 128.8, 128.3, 126.7, 126.4, 125.6, 125.3, 123.0, 122.9, 122.6, 120.0, 114.7, 106.6, 106.5, 74.4, 73.1, 56.9, 56.0, 41.6, 39.5, 23.4, 22.9, 22.0, 21.6 (observed complexity due to C–P and C–F splitting).

^{31}P NMR (121 MHz, CD_3OD) δ 30.36.
^{19}F NMR (282 MHz, CD_3OD) δ –63.50, –63.59.
FTIR (neat, cm^{-1}): 2979.1, 2935.9, 1582.8, 1458.8, 1426.0, 1353.7, 1276.1, 1182.4, 1122.0, 1058.6, 1016.1, 889.7, 844.0, 808.9, 771.9, 740.6, 709.6.



Precatalyst P9. Following the general procedure a solution of **A** (37 mg, 0.096 mmol) and **L9** (69 mg, 0.096 mmol) in CH_2Cl_2 (0.5 mL) was stirred at rt for 2 h. After performing the workup as described in the general procedure, pentane was added to the residue and mixture was concentrated with the aid of a rotary evaporator to afford the title compound as an orange solid (103 mg, 97%).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99–7.96 (m, 2H), 7.85 (m, 1H), 7.66–7.59 (m, 3H), 7.41–7.18 (m, 7H), 7.06–6.96 (m, 2H), 6.88–6.83 (m, 2H), 6.65–6.52 (m, 2H), 6.29 (m, 1H), 3.67–3.22 (m, 6H), 2.41–2.23 (m, 12H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 142.54, 142.51, 135.86, 134.97, 131.10, 130.18, 129.04, 128.87, 128.69, 127.84, 127.77, 127.30, 126.59, 124.60, 122.22, 121.71, 117.12, 111.90, 56.74, 42.70, 40.84, 40.31, 39.43, 32.16, 23.23 (observed complexity due to C–P and C–F splitting).
^{31}P NMR (121 MHz, CD_2Cl_2) δ 28.69.
^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.07, –63.45, –63.67.
FTIR (neat, cm^{-1}): 3060.5, 2937.3, 2838.1, 2798.5, 1457.9, 1426.1, 1353.5, 1275.7, 1175.5, 1122.4, 1094.8, 1015.7, 896.9, 844.0, 761.8, 739.6, 699.2, 681.4.

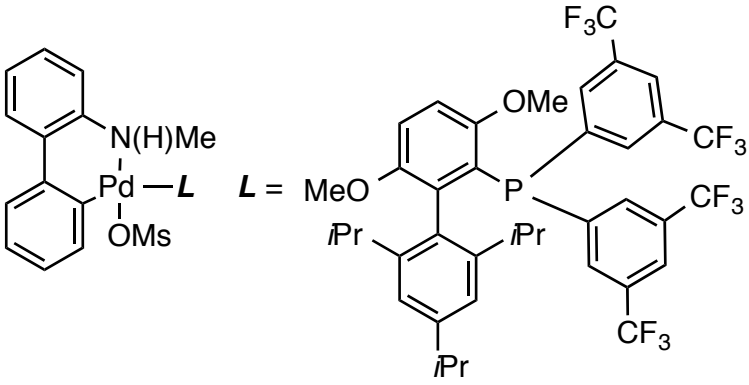
Precatalyst P10. Following the general procedure, a solution of **A** (81 mg, 0.21 mmol) and **L10** (130 mg, 0.25 mmol) in CH_2Cl_2 (1.3 mL) was stirred at rt for 2 h. Performing the workup and purification as described in the general procedure afforded the title compound as a yellow solid (182 mg, 77%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.84–7.80 (m, 4H), 7.70 (m, 2H), 7.52 (m, 1H), 7.27 (m, 4H), 7.16–7.14 (m, 1H)

6.99 (m, 1H), 6.89 (m, 1H) 6.58 (m, 3H), 6.16–6.11 (m, 2H), 4.00–3.00 (m, 12H), 2.49 (s, 3H), 2.26 (s, 3H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 158.2, 152.9, 152.8, 142.4, 141.5, 138.1, 136.9, 135.0, 131.3, 131.1, 128.9, 128.8, 127.6, 127.5, 127.2, 126.7, 125.9, 124.9, 124.8, 122.2, 121.8, 117.7, 111.1, 104.1, 104.1, 57.5, 55.8, 55.5, 40.8, 39.3 (observed complexity due to C–P and C–F splitting).
^{31}P NMR (121 MHz, CD_2Cl_2) δ 27.99
^{19}F NMR (282 MHz, CD_2Cl_2) δ –63.32, –63.45.
FTIR (neat, cm^{-1}): 2938.8, 2838.6, 1618.0, 1591.0, 1473.0, 1458.8, 1426.2, 1353.9, 1276.0, 1249.9, 1182.7, 1123.0, 1107.4, 1094.8, 1015.2, 897.3, 843.9, 810.5, 771.5, 740.7, 725.9, 715.4, 704.4, 681.5.

JackiePhos Precatalyst (P11). Following the general procedure, a solution of **A** (144 mg, 0.38 mmol) and JackiePhos (**L11**) (299 mg, 0.38 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 2 h. After performing the workup as described in the general procedure, pentane was added to the residue and mixture was concentrated with the aid of a rotary evaporator to afford the title compound as a white solid (252 mg, 51%).

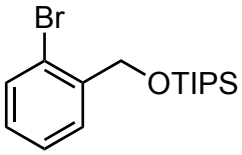


^{1}H NMR (400 MHz, CD_3OD) δ 8.46 (s, 1H), 8.25 (s, 1H), 7.84–7.81 (m, 3H), 7.48–7.43 (m, 2H), 7.58–7.56 (m, 2H), 7.40–7.36 (m, 1H), 7.31–7.28 (m, 5H) 6.99–6.97 (m, 1H), 6.78–6.74 (m, 1H), 6.20–6.17 (m, 1H), 3.65 (s, 3H), 3.55–3.48 (m, 1H), 3.42 (s, 3H), 3.07–3.00 (m, 1H), 2.71 (s, 3H), 2.16–2.11 (m, 4H), 1.99 (d, J = 6.9 Hz, 3H), 1.66 (d, J = 6.9 Hz, 3H), 1.58 (d, J = 7.0 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.7 Hz, 3H), 0.08 (d, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, CD_3OD) δ 157.9, 157.9, 156.6, 155.3, 155.2, 154.2, 153.8, 153.6, 146.0, 146.0, 141.6, 141.6, 141.5, 140.6, 140.6, 138.3, 136.4, 136.1, 136.1, 136.0, 134.5, 134.4, 134.3, 134.2, 134.1, 134.0, 134.9, 133.9, 133.7, 133.7, 133.5, 133.5, 133.4, 133.3, 133.2, 132.9, 132.8, 132.7, 132.6, 130.8, 130.7, 129.9, 129.4, 129.4, 129.3, 129.2, 129.2, 128.2, 128.0, 127.0, 126.9, 126.2, 125.5, 125.3, 124.5, 122.9, 122.9, 122.8, 122.5, 122.3, 121.7, 121.2, 121.1, 121.1, 121.0, 120.8, 120.7, 120.1, 119.8, 116.1, 116.1, 56.3, 56.2, 41.8, 41.7, 39.5, 35.8, 34.8, 33.2, 25.8, 25.5, 24.5, 23.8, 23.8, 23.2 (observed complexity due to C–P and C–F splitting).

^{31}P NMR (121 MHz, CD_2Cl_2) δ 29.58.
^{19}F NMR (282 MHz, CD_2Cl_2) δ –64.02, –64.09.
FTIR (neat, cm^{-1}): 3176.4, 3070.8, 2967.9, 2935.9, 2872.5, 1463.7, 1423.1, 1385.0, 1351.9, 1274.4, 1239.8, 1183.4, 1132.8, 1022.5, 897.5, 821.8, 773.0, 740.1, 702.9, 681.6.

Substrate Synthesis.
4-chloro-1-(triisopropylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine[4], (±)-3-phenylmorpoline, and (R)-3-phenylmorpholine[5] were prepared according to literature procedures.

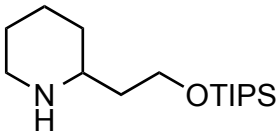
((2-bromobenzyl)oxy)triisopropylsilane. To an oven-dried 300 mL round-bottom flask equipped with a magnetic stir-bar and a septum, 2-bromobenzyl alcohol (3.05 g, 16.3 mmol), imidazole (2.22 g, 32.6 mmol), and DMF (10 mL) were added. The reaction flask was cooled to 0 °C in an ice/water bath and chlorotriisopropylsilane (4.15 mL, 19.6 mmol) was added. The reaction mixture was stirred at 0 °C for 5 min and was then allowed to warm to rt. After stirring for 13 h at rt, the reaction mixture was poured into 100 mL of water and extracted with Et_2O (3 x 60 mL). The combined organic layers were washed with water (60 mL) and brine (60 mL), dried over anhydrous $MgSO_4$, filtered and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (hexanes) to provide the title compound as a colorless oil (2.55 g, 45%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72–7.70 (m, 1H), 7.55 (dd, J = 1.2, 7.94 Hz, 1H), 7.41–7.38 (m, 1H), 7.18–7.15 (m, 1H), 4.90 (s, 2H), 1.33–1.23 (m, 3H), 1.19–1.17 (m, 18H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 141.3, 132.6, 128.8, 128.2, 128.0, 121.5, 65.6, 18.6, 12.8.
FTIR (neat, cm^{-1}): 2942.1, 2864.9, 1569.7, 1462.8, 1374.6, 1264.7, 1202.8, 1120.5, 1098.3, 1042.7, 1025.1, 880.7, 801.7, 745.3, 681.6.
EA: Anal. Calcd. for $C_{16}H_{27}BrOSi$: C, 55.97; H, 7.81. Found: C, 56.23; H, 7.81.

2-(2-((triisopropylsilyl)oxy)ethyl)piperidine. An oven-dried 300 mL round-bottom flask equipped with a magnetic stir-bar was charged with 2-

[4] Heinrich, T.; Seenisamy, J.; Emmanuvel, L.; Kulkarni, S. S.; Bomke, J.; Rohdich, F.; Greiner, H.; Esdar, C.; Krier, M.; Grädler, U.; Musil, D. *J. Med. Chem.* **2013**, *56*, 1160.
[5] Hu, P.; Hu, J.; Jiao, J.; Tong, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 5319.



piperdineethanol (2.15 g, 15 mmol), DMAP (183 mg, 1.5 mmol) and imidazole (1.43 g, 21 mmol). The flask was fitted with a septum and evacuated and backfilled with argon. DMF (30 mL) was then added and the reaction mixture was cooled to 0 °C in an ice/water bath. Chlorotriisopropylsilane (3.34 mL, 15.75 mmol) was added dropwise via syringe and the reaction was stirred at 0 °C for 15 min, warmed to rt and stirred for 5 h. After this time, the reaction mixture was poured into 100 mL of water and extracted with Et_2O (4 x 50 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (10% acetone in hexanes with 1% triethylamine) to provide the title product as a light yellow oil (3.21 g, 75% yield).

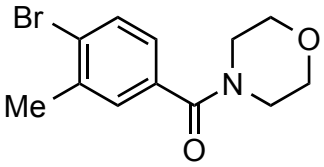
^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.82–3.73 (m, 2H), 2.99–2.95 (m, 1H), 2.62–2.54 (m, 2H), 1.75–1.73 (m, 1H), 1.63–1.48 (m, 5H), 1.39–1.28 (m, 2H), 1.13–1.01 (m, 21H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 62.2, 55.9, 47.8, 40.9, 34.2, 27.5, 25.9, 18.5, 12.7.

FTIR (neat, cm^{-1}): 2929.5, 2864.7, 1462.6, 1382.0, 1329.5, 1256.8, 1200.1, 1101.6, 1068.8, 996.2, 881.1, 726.6, 678.5, 657.4.

EA: Anal. Calcd. for $C_{16}H_{35}NOSi$: C, 67.30; H, 12.36. Found: C, 67.23; H, 12.47.

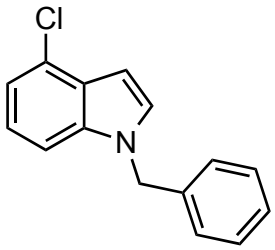
(4-bromo-3-methylphenyl)(morpholino)methanone. An oven-dried 100 mL round-bottom flask fitted with a septum was charged with 4-bromo-3-methylbenzoyl chloride (2.34 g, 10.0 mmol), CH_2Cl_2 (20 mL), and triethylamine (1.95 mL, 14 mmol). Morpholine (0.95 mL, 11 mmol) was then added and the reaction mixture was allowed to stir at rt for 12 h. The reaction mixture was then poured into 60 mL of water and extracted with CH_2Cl_2 (3 x 60 mL). The combined organic layers were washed with water and brine (60 mL each) and then dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The resulting residue was purified via column chromatography on silica gel (40% EtOAc in hexanes) to provide the title product as a light yellow solid (2.11 g, 74%). Mp = 72–74 °C.



^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.58 (d, *J* = 8.1 Hz, 1H), 7.28 (s, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 3.65–3.42 (m, 8H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 139.0, 135.4, 132.8, 130.0, 126.7, 126.5, 67.3, 48.7, 43.0, 23.2.
FTIR (neat, cm^{-1}): 2959.9, 2847.6, 1627.2, 1386.4, 1366.1, 1301.4, 1289.4, 1254.0, 1205.9, 1148.7, 1109.9, 1025.7, 947.0, 884.1, 855.9, 847.8, 818.1, 754.1, 695.9.
EA: Anal. Calcd. for $C_{12}H_{14}BrNO_2$: C, 50.72; H, 4.97. Found: C, 51.02; H, 4.94.

1-benzyl-4-chloro-1*H*-indole. An oven-dried 100 mL round-bottom flask equipped with a magnetic stir-bar and a septum was charged with 4-chloroindole (0.96 mL, 8.0 mmol) and DMF (20 mL). The reaction mixture was cooled to 0 °C in an ice/water bath and sodium hydride (60% dispersion in mineral oil; 576 mg, 14.4 mmol) was added with venting to release the liberated hydrogen gas. After stirring at 0 °C for 30 min, benzyl chloride (1.0 mL, 8.8 mmol) was added, the reaction mixture was allowed to warm to rt and was stirred for 15 h. The reaction mixture was then poured into 100 mL of water and extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated with the aid of a rotary evaporator. The resulting residue was purified via Biotage (50 g silica gel column, 8–10% CH_2Cl_2 in hexanes) to provide the title compound as a white solid (1.76 g, 91%). Mp = 60–62 °C.



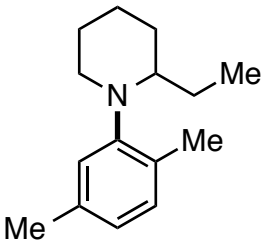
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.37–7.29 (m, 3H), 7.25–7.24 (m, 2H), 7.17–7.10 (m, 4H), 6.71 (dd, J = 0.8, 3.5 Hz, 1H), 5.33 (s, 2H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 137.8, 137.6, 129.7, 129.3, 128.3, 128.0, 127.3, 126.5, 122.8, 119.8, 109.2, 100.6, 51.0.
FTIR (neat, cm^{-1}): 3124.6, 3101.7, 3062.5, 3029.7, 2933.8, 2159.6, 1604.9, 1557.0, 1479.7, 1453.6, 1435.7, 1362.9, 1354.1, 1343.0, 1313.6, 1290.0, 1274.1, 1165.5, 1147.4, 1105.1, 1078.6, 945.6, 896.6, 817.5, 771.9, 711.8, 617.4.
EA: Anal. Calcd. for $C_{15}H_{12}ClN$: C, 74.54; H, 5.00. Found: C, 74.79; H, 5.15.

General Procedure for the Tables 1, 2, SI-1, SI-2, and SI-3
An oven-dried screw-cap test tube (Fisher Scientific, catalog number: 1495925C) equipped with a screw-cap septum and a magnetic stir bar was cooled under vacuum, filled with argon and then charged with the precatalyst (0.005 mmol) and NaO*t*Bu (34 mg, 0.35 mmol). If solid, the aryl halide (0.25 mmol) was also added at this point. The reaction vessel was then evacuated and backfilled with argon. This sequence was repeated a total of three times. If liquid, the aryl halide (0.25 mmol), were added at this point followed by the amine (0.30 mmol) and

CPME (2 mL). The screw-cap septum was exchanged for an unpunctured screw-cap septum under a continuous flow of argon. The reaction mixture was then heated in a pre-heated oil bath at the specified temperature for the specified time. After cooling to rt, dodecane (0.057 mL, 0.25 mmol) was added and the reaction mixture was then diluted with ethyl acetate. A small aliquot was filtered through a short silica gel plug and analyzed by GC.

General Procedure for the Arylation of α-Branched Amines (General Procedure A).

An oven-dried screw-cap test tube (Fisher Scientific, catalog number: 1495937A) equipped with a screw-cap septum and a magnetic stir bar was cooled under vacuum, filled with argon and then charged with **P7** (22.8 mg, 0.02 mmol) and NaO*t*Bu (135 mg, 1.4 mmol). If solid, the aryl halide (1.0 mmol) and the amine (1.2 mmol) were also added at this point as well as any additional ligand (0.02 mmol) that was required. The reaction vessel was then evacuated and backfilled with argon. This sequence was repeated a total of three times. If liquid, the aryl halide (1.0 mmol) and amine (1.2 mmol), were added at this point, followed by CPME (2 mL). The screw-cap septum was exchanged for an unpunctured screw-cap septum under a continuous flow of argon. The reaction mixture was then heated in a pre-heated oil bath at the specified temperature for the specified time for each substrate. Upon completion of the reaction, the reaction mixture was cooled to rt and diluted with CH_2Cl_2. This mixture was then poured into water (40 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was then purified via column chromatography.

1-(2,5-dimethylphenyl)-2-ethylpiperidine (1c). 

Following general procedure A, a mixture of 2-bromo-1,4-dimethylbenzene (0.138 mL, 1.0 mmol), 2-ethylpiperidine (0.160 mL, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.05 mmol) in CPME (2 mL) was heated to 80 °C for 1 h. After cooling to rt, the reaction mixture was then diluted with Et_2O (30 mL) and extracted with 2M HCl (3 x 15 mL). The combined aqueous layers were cooled to 0 °C, basified with KOH until pH = 14, and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (the column was pre-

packed with 3% triethylamine in hexanes, 1% Et_2O in hexanes was used as the eluent) to provide the title compound as a light yellow oil (Run 1: 193 mg (89%); Run 2: 193 mg (89%); Average Yield: 89%).

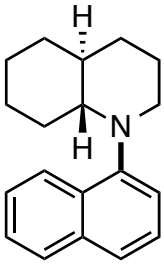
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.14 (m, 1H), 7.01 (s, 1H), 6.89 (m, 1H), 2.98–2.93 (m, 2H), 2.59 (m, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 1.91–1.98 (m, 2H), 1.72 (m, 2H), 1.51 (m, 2H), 1.39 (m, 2H), 0.89–0.77 (m, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 151.9, 136.1, 132.7, 131.1, 125.0, 123.9, 60.6, 55.2, 31.0, 27.6, 25.2, 24.6, 21.5, 17.6, 10.1.

FTIR (neat, cm^{-1}): 2931.4, 2855.7, 2789.1, 1504.9, 1440.2, 1373.4, 1246.6, 1220.2, 1125.8, 1112.1, 1061.1, 1033.4, 983.1, 877.7, 804.3.

EA: Anal. Calcd. for $C_{15}H_{23}N$: C, 82.89; H, 10.67. Found: C, 83.03; H, 10.56.

1-(naphthalen-1-yl)decahydroquinoline (2a). Following general procedure A, a mixture of 1-bromonaphthalene (0.140 mL, 1.0 mmol), *trans*-decahydroquinoline (167 mg, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 15 h. After cooling to rt, the reaction mixture was then diluted with Et_2O (60 mL) and extracted with 5M HCl (3 x 50 mL). The combined aqueous layers were cooled to 0 °C, basified with KOH until pH = 14, and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (4% CH_2Cl_2 in hexanes) to provide the title compound as a light yellow oil (Run 1: 223 mg (84%); Run 2: 220 mg (83%); Average Yield: 84%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.65–8.63 (m, 1H), 7.91–7.89 (m, 1H), 7.72–7.70 (m, 1H), 7.58–7.50 (m, 3H), 7.38–7.37 (m, 1H), 3.19–3.16 (m, 1H) 2.81–2.67 (m, 2H), 2.06–1.97 (m, 1H), 1.89–1.56 (m, 7H), 1.43–1.22 (m, 4H), 1.07–0.97 (m, 1H).

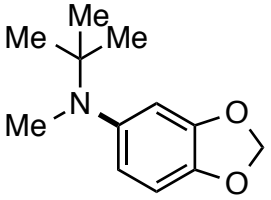
^{13}C NMR (101 MHz, C_6D_6) δ 150.0, 135.3, 133.29, 128.4, 126.4, 126.3, 126.0, 124.9, 124.6, 120.3, 66.4, 58.2, 43.7, 33.7, 33.4, 31.4, 27.6, 27.1, 26.2.

FTIR (neat, cm^{-1}): 3041.9, 2919.0, 2849.3, 2789.9, 1591.7, 1575.1, 1505.0, 1446.0, 1391.9, 1362.5, 1282.0, 1254.0, 1223.7, 1137.4, 1126.2, 1086.4, 1012.8, 798.8, 775.5 625.7.

EA: Anal. Calcd. for $C_{19}H_{23}N$: C, 85.99; H, 8.74. Found: C, 86.01; H, 8.72.

The 1:49 *cis*:*trans* ratio of the product isomers was determined by GC analysis of the crude reaction mixture.

***N*-(*tert*-butyl)-*N*-methylbenzo[*d*][1,3]dioxol-5-amine (2b).** Following general procedure A, a mixture of 5-chloro-1,3-benzodioxole (0.117 mL, 1.0 mmol), N-methyl-*tert*-butylamine (0.144 mL, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 6 h. After cooling to rt and performing the workup described in general procedure A, the crude material was purified via column chromatography on silica gel (5–10% Et_2O in hexanes with 1% triethylamine). The title compound was isolated as a light yellow oil (Run 1: 156 mg (75%); Run 2: 158 mg (76%); Average Yield: 76%).



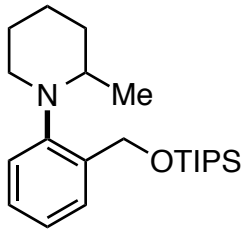
^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.70–6.68 (m, 2H), 6.63 (dd, *J* = 2.2, 8.3 Hz, 1H), 5.91 (s, 2H), 2.67 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 147.6, 146.3, 144.9, 121.8, 109.9, 107.5, 101.7, 55.4, 37.7, 27.7.

FTIR (neat, cm^{-1}): 2971.5, 2872.3, 2792.5, 1502.1, 1479.9, 1386.8, 1358.6, 1336.8 1284.0, 1234.9, 1209.0, 1151.0, 1128.7, 1037.3, 931.1, 865.1, 810.8, 773.0, 730.8, 650.3.

EA: Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27. Found: C, 69.59; H, 8.09.

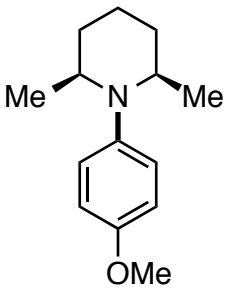
2-methyl-1-(2-(((triisopropylsilyl)oxy)methyl)phenyl)piperidine (2c). Following general procedure A, a mixture of ((2-bromobenzyl)oxy)triisopropylsilane (342 mg, 1.0 mmol), 2-methylpiperidine (0.141 mL, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 60 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude residue was dissolved in hexanes and passed through a short silica gel plug (0.5% acetone in hexanes with 3% triethylamine). The filtrate was concentrated and the crude residue was purified via column chromatography on silica gel (2–30% CH_2Cl_2 in hexanes with 1% triethylamine) to provide the title compound as a light yellow oil (Run 1: 241 mg (67%); Run 2: 240 mg (66%); Average Yield: 67%). Contains <5% of the corresponding aryl *tert*-butyl ether as determined by GC analysis.



^{1}H NMR (500 MHz, C_6D_6) δ 7.66–7.64 (m, 1H), 7.28–7.24 (m, 1H), 7.21–7.17 (m, 2H), 5.12 (d, *J* = 14.0 Hz, 1H), 4.93 (d, *J* = 14.0 Hz, 1H), 3.04–2.96 (m, 1H), 2.93–2.90 (m, 1H), 2.63–2.56 (m, 1H), 1.84–1.82 (m, 2H), 1.71–1.65 (m, 2H), 1.54–1.37 (m, 2H) 1.31–1.24 (m, 3H), 1.19–1.17 (m, 18 H), 0.85 (d, *J* = 6.2**,** 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 150.4, 139.8, 127.6, 127.5, 125.0, 123.0, 62.0, 56.1, 55.8, 35.8, 27.8, 25.1, 20.3, 18.6, 12.9.
FTIR (neat, cm^{-1}): 2931.3, 2864.5, 1486.7, 1451.4, 1368.0, 1241.2, 1111.4, 1065.5, 1012.9, 995.2, 881.0, 795.8, 762.6, 725.4, 679.0, 657.0.
DART–MS: calcd. For $C_{22}H_{39}NOSi$ [M+H]: 362.2874. Found: 362.2888.

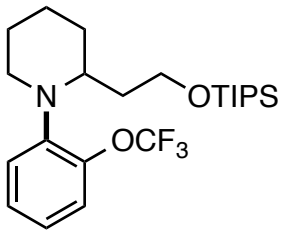
(2*R*,6*S*)-1-(4-methoxyphenyl)-2,6-dimethylpiperidine (2d). Following general procedure A, a mixture of 4-chloroanisole (0.123 mL, 1.0 mmol), *cis*-2,6-dimethylpiperidine (0.162 mL, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 1 h. After cooling to rt, the reaction mixture was then diluted with Et_2O (30 mL) and extracted with 2M HCl (3 x 15 mL). The combined aqueous layers were cooled to 0 °C, basified with KOH until pH = 14, and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (the column was pre-packed with 3% triethylamine in hexanes, 2% acetone in hexanes was used as the eluent) to provide the title compound as a light yellow oil (Run 1: 178 mg (81%); Run 2: 178 mg (81%); Average Yield: 81%).



^{1}H NMR (500 MHz, C_6D_6) δ 7.08 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H), 2.80–2.73 (m, 2H), 1.77–1.71 (m, 3H), 1.54–1.47 (m, 1H), 1.36–1.29 (m, 2H), 0.71 (d, *J* = 6.2 Hz 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 157.7, 144.7, 128.8, 114.2, 58.7, 55.8, 36.1, 25.3, 22.6.
FTIR (neat, cm^{-1}): 2960.9, 2926.2, 2833.2, 2787.2, 1506.3, 1451.5, 1369.9, 1310.4, 1290.4, 1232.1, 1179.5, 1089.6, 1038.5, 956.2, 930.0, 895.4, 850.2, 820.3, 788.6, 699.9.
The 22:1 *cis*:*trans* ratio of the product isomers was determined by GC analysis of the crude reaction mixture.
Characterization data are in accordance with those previously reported in the literature.[6]

1-(2-(trifluoromethoxy)phenyl)-2-(2-((triisopropylsilyl)oxy)ethyl)piperidine (2e). Following general procedure A, a mixture of 1-bromo-2-(trifluoromethoxy)benzene (0.149 mL, 1.0 mmol), 2-(2-((triisopropylsilyl)oxy)ethyl)piperidine (342 mg, 1.2 mmol), NaO*t*Bu (135 mg,

[6] Boga, C.; Manescalchi, F.; Savoia, D. *Tetrahedron* **1994**, *50*, 4709.



1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt and following the workup described in general procedure A, the crude residue was dissolved in hexanes and passed through a short silica gel plug (pre-packed with hexanes containing 3% triethylamine, hexanes used as the eluent). The filtrate was concentrated and the crude residue was purified via column chromatography on silica gel (2–10% CH_2Cl_2 in hexanes with 1% triethylamine) to provide the title compound as a light yellow oil (Run 1: 282 mg (63%); Run 2: 281 mg (63%) Average Yield: 63%).

^{1}H NMR (500 MHz, C_6D_6) δ 7.08–7.07 (m, 1H), 6.96–6.91 (m, 2H), 6.86–6.64 (m, 1H), 3.67–3.64 (m, 1H), 3.50–3.47 (m, 2H), 2.99–2.94 (m, 1H), 2.66–2.63 (m, 1H), 1.34 (m, 1H), 1.91–1.87 (m, 1H), 1.76–1.71 (m, 1H), 1.60–1.57 (m, 1H), 1.50 (m, 4H), 1.04–0.97 (m, 21H).

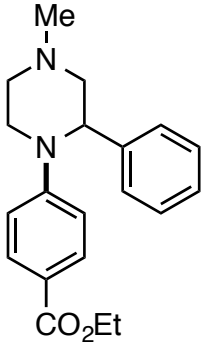
^{13}C NMR (101 MHz, C_6D_6) δ 145.9, 143.9, 127.6, 123.5, 122.8, 122.7 (q, J = 256.3 Hz), 122.7, 61.3, 54.9, 49.4, 32.9, 29.9, 26.6, 21.4, 18.3, 12.3.

^{19}F NMR (282 MHz, C_6D_6) δ –57.27.

FTIR (neat, cm^{-1}): 2940.7, 2865.1, 1602.3, 1495.6, 1462.7, 1389.2, 1240.9, 1221.9, 1160.3, 1098.5, 1012.8, 939.5, 917.0, 881.5, 750.1, 677.1.

EA: Anal. Calcd. for $C_{23}H_{38}F_3NO_2Si$: C, 61.99; H, 8.59. Found: C, 62.20; H, 8.47.

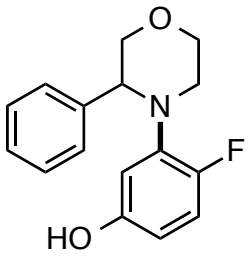
Ethyl 4-(4-methyl-2-phenylpiperazin-1-yl)benzoate (2f). Following general procedure A, a mixture of ethyl 4-chlorobenzoate (0.156 mL, 1.0 mmol), 1-methyl-3-phenylpiperazine (212 mg, 1.2 mmol), K_3PO_4 (1.27 g, 6.0 mmol), and **P7** (22.8 mg, 0.05 mmol) in CPME (3 mL) was heated to 110 °C for 16 h. After this time, the reaction was cooled to room temperature and diluted with EtOAc. The solids were removed via filtration and the filtrate was concentrated with the aid of a rotary evaporator. Purification of the crude residue via column chromatography on silica gel (10% acetone in hexanes with 1.5% triethylamine) provided the title compound as a light yellow oil (Run 1: 280 mg (87%); Run 2: 291 mg (91%); Average Yield: 89%).



^{1}H NMR (500 MHz, C_6D_6) δ 8.14 (d, J = 8.70 Hz, 2H), 7.23–7.22 (m, 2H), 7.09–7.06 (m, 2H), 7.00–6.97 (m, 1H), 6.65 (d, J = 8.7 Hz, 2H), 4.53 (t, J = 4.0 Hz, 1H), 4.20–4.16 (m, 2H), 3.20–3.15 (m, 1H), 3.07–3.03 (m, 1H), 2.65 (dd, J =

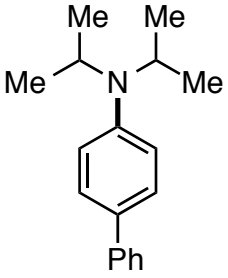
4.0, 11.4 Hz 1H), 2.34 (m, 1H), 2.34 (dd, *J* = 4.0, 11.4 Hz, 1H), 2.04–1.98 (m, 1H), 1.98 (s, 3H), 1.05 (t, *J* = 7.0 Hz).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 166.8, 154.2, 141.6, 131.4, 128.8, 128.0, 127.3, 120.5, 115.3, 61.6, 60.7, 58.5, 55.6, 46.7, 46.6, 14.8.
FTIR (neat, cm^{-1}): 2974.7, 2936.9, 2843.2, 2793.2, 1699.4 1600.6, 1515.8, 1449.4, 1383.7, 1364.9, 1262.7, 1215.2, 1184.1, 1102.7, 1021.3, 963.9, 925.4, 873.3, 829.9, 768.8, 695.9.
EA: Anal. Calcd. for $C_{20}H_{24}N_2O_2$: C, 74.05; H, 7.46. Found: C, 73.84; H, 7.25.

4-fluoro-3-(3-phenylmorpholino)phenol (2g). Following general procedure A, a mixture of 3-bromo-4-fluorophenol (191 mg, 1.0 mmol), (±)-3-phenylmorpholine (195 mg, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), **P7** (22.8 mg, 0.02 mmol), and **L7** (15.1 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt, the reaction mixture was diluted with CH_2Cl_2 and poured into 40 mL of water. The aqueous layer was acidified with 2 M HCl until pH = 6 and then extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (20% acetone in hexanes) to provide the title compound as a beige solid (Run 1: 181 mg (66%); Run 2: 172 mg (63%); Average Yield: 64%). Mp = 144–145 °C.



^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.34–7.33 (m, 2H), 7.24–7.16 (m, 3H), 6.87 (dd, *J* = 8.7, 11.3 Hz, 1H), 6.42–6.33 (m, 2H), 5.91 (s, 1H), 4.33–4.30 (m, 1H), 3.97–3.90 (m, 3H), 3.60–3.55 (m, 1H), 3.36–3.33 (m, 1H), 3.01–2.95 (m, 1H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.7 (d, *J* = 238.2 Hz), 152.4 (d, *J* = 1.9 Hz), 139.8 (d, *J* = 11.2 Hz), 139.1, 128.9, 128.4, 128.1, 116.9 (d, *J* = 22.5 Hz), 111.8 (d, *J* = 2.3 Hz), 111.0 (d, *J* = 7.8 Hz), 74.0, 68.0, 62.9, 53.6 (d, *J* = 2.9 Hz).
^{19}F NMR (282 MHz, CD_2Cl_2) δ –134.46.
FTIR (neat, cm^{-1}): 3236.5, 2957.4, 2825.9, 1621.7, 1592.7, 1502.8, 1491.7, 1478.7, 1393.8, 1326.8, 1303.1, 1295.2, 1259.9, 1208.3 1187.5, 1099.9, 979.1, 972.4, 928.2, 895.3, 849.2, 759.6, 696.2, 654.5.
EA: Anal. Calcd. for $C_{16}H_{16}FNO_2$: C, 70.31; H, 5.90. Found: C, 70.36; H, 6.04.

***N*,*N*-diisopropyl-[1,1'-biphenyl]-4-amine (2h).** Following general procedure A, a mixture of 4-bromobiphenyl (233 mg, 1.0 mmol), diisopropylamine (1.35 mL, 9.6 mmol), NaO*t*Bu (1.04 g, 10.8 mmol), **P7** (22.8 mg, 0.02 mmol), **L7** (15.1 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 1 h. After



cooling to rt, the reaction mixture was diluted with Et_2O (30 mL) and extracted with 2M HCl (3 x 15 mL). The combined aqueous layers were cooled to 0 °C, basified with KOH until pH = 14, and then extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (5% acetone in hexanes) to provide the title compound as a white solid (Run 1: 159 mg (63%); Run 2: 164 mg (65%); Average Yield: 64%). Mp = 63–64 °C.

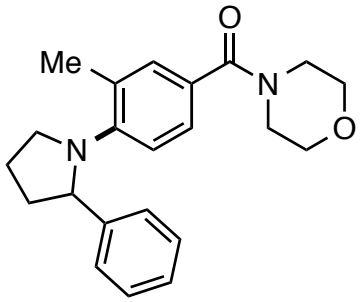
^{1}H NMR (500 MHz, C_6D_6) δ 7.63–7.61 (m, 2H), 7.52–7.51 (m, 2H), 7.30–7.27 (m, 2H), 7.16–7.13 (m, 1H), 6.92–6.91 (m, 2H), 3.58 (sept, *J* = 6.8 Hz, 2H), 1.07–1.06 (d, *J* = 6.8 Hz, 12H).

^{13}C NMR (101 MHz, C_6D_6) δ 147.9, 141.9, 131.5, 129.1, 127.5, 126.8, 126.4, 119.8, 47.8, 21.5.

FTIR (neat, cm^{-1}): 3028.0, 2984.4, 2965.2, 2929.1, 2868.7, 1608.6, 1599.7, 1550.6, 1522.2, 1485.7, 1411.6, 1381.5, 1365.7, 1330.6, 1314.7, 1279.1, 1187.4, 1154.4, 1120.2, 1023.7, 943.6, 851.1, 826.5, 764.9, 726.8, 699.1.

EA: Anal. Calcd. for $C_{18}H_{23}N$: C, 85.32; H, 9.15. Found: C, 85.46; H, 9.26.

(3-methyl-4-(2-phenylpyrrolidin-1-yl)phenyl)(morpholino)methanone (2i).



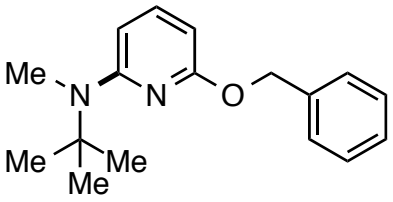
Following general procedure A, a mixture of (4-bromo-3-methylphenyl)(morpholino)methanone (283 mg, 1.0 mmol), 2-phenylpyrrolidine (177 mg, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 1 h. After cooling to rt and performing the workup described in general procedure A, the crude material was purified via column chromatography on silica gel (15% acetone in hexanes with 1% triethylamine) to provide the title compound as a light yellow solid (Run 1: 192 mg (54%); Run 2: 195 mg (56%); Average Yield: 55%), mp = 49–52 °C.

^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (s, 1H), 7.24–7.23 (m, 2H), 7.09–7.06 (m, 3H), 6.98–6.95 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 4.46–4.43 (m, 1H), 3.62–3.57 (m, 1H), 3.18 (m, 8H), 2.75–2.71 (m, 1H), 2.24 (s, 3H) 2.06–2.01 (m, 1H), 1.61–1.50 (m, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.9, 150.7, 144.1, 131.6, 129.8, 128.9, 127.3, 127.0, 125.9, 117.0, 67.4, 64.9, 54.7, 46.3, 37.9, 25.4, 21.0.

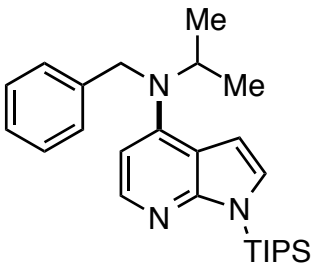
FTIR (neat, cm^{-1}): 2959.2, 2852.5, 1626.9, 1603.0, 1501.5, 1451.3, 1418.8, 1297.9, 1271.2, 1252.1, 1192.8, 1112.1, 1027.2, 995.4, 945.3, 901.7, 811.1, 757.3, 699.5.
EA: Anal. Calcd. for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48. Found: C, 75.61; H, 7.31.

6-(benzyloxy)-*N*-(*tert*-butyl)-*N*-methylpyridin-2-amine (3a). Following general procedure A, a mixture of 2-bromo-6-benzyloxypyridine (264 mg, 1 mmol), *N*-methyl-*tert*-butylamine (0.238 mL, 2.4 mmol), NaO*t*Bu (269 mg, 2.8 mmol), and **P11** (23.4 mg, 0.02 mmol) in CPME (2 mL) was heated to 60 °C for 6 h. After cooling to rt, the reaction mixture was diluted with Et_2O (40 mL) and extracted with 3M HCl (3 x 30 mL). The combined aqueous layers were cooled to 0 °C, basified with KOH until pH = 14, and then extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (2% Et_2O in hexanes with 1% triethylamine) to provide the title compound as a colorless oil (Run 1: 247 mg (91%); Run 2: 249 mg (92%); Average yield: 92%).



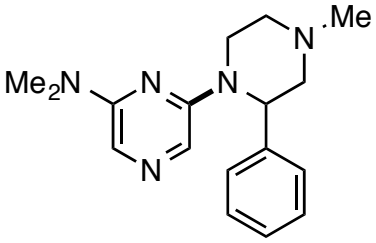
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.52–7.47 (m, 2H), 7.47–7.43 (m, 3H), 7.39–7.36 (m, 1H), 6.30 (d, *J* = 8.1 Hz, 1H), 6.24 (d, *J* = 7.8 Hz, 1H), 5.43 (s, 2H), 3.03 (s, 3H), 1.56 (s, 9H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 161.9, 160.5, 139.8, 138.9, 128.9, 128.2, 128.1, 104.2, 98.7, 67.9, 56.4, 35.3, 29.3.
FTIR (neat, cm^{-1}): 2972.9, 2920.6, 1589.9, 1570.9, 1495.7, 1445.7, 1423.3, 1348.2, 1253.8, 1211.3, 1149.4, 1079.2, 1038.2, 1025.5, 1014.3, 981.5, 958.5, 777.6, 726.9, 695.3.
EA: Anal. Calcd. for $C_{17}H_{22}N_2O$: C, 75.52; H, 8.20. Found: C, 75.50; H, 8.19.

***N*-benzyl-*N*-isopropyl-1-(triisopropylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridin-4-amine (3b).** Following general procedure A, a mixture of 4-chloro-1-(triisopropylsilyl)-1*H*-pyrrolo[2,3-*b*]pyridine (308 mg, 1 mmol), *N*-benzylisopropylamine (0.186 mL, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P11** (23.4 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude residue was dissolved in hexanes and passed through a short silica gel plug (eluting



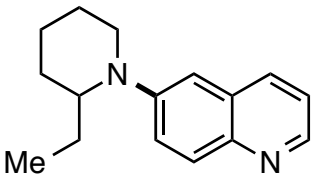
with 2% acetone in hexanes). The filtrate was concentrated with the aid of a rotary evaporator and the resulting oil was purified via column chromatography on silica gel (1–1.5% Et_2O in hexanes). The title compound was isolated as a yellow oil (Run 1: 337 mg (80%); Run 2: 356 mg (85%); Average Yield: 83%).
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.95 (d, *J* = 5.6 Hz, 1H), 7.47–7.45 (m, 2H), 7.40 –7.38 (m, 2H), 7.31–7.27 (m, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 6.64 (d, *J* = 3.7 Hz, 1H), 6.35 (d, *J* = 5.7, 1H), 4.84–4.76 (sept, *J* = 6.6 Hz, 1H), 4.73 (s, 2H), 2.00–1.89 (sept, *J* = 7.6 Hz, 3H), 1.40 (d, *J* = 6.6 Hz**,** 6H), 1.24 (d, *J* = 7.6 Hz, 18H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.5, 150.5, 143.8, 141.2, 129.0, 127.3, 127.3, 127.2, 111.1, 104.0, 102.0, 51.1, 48.9, 20.9, 18.8, 13.0.
FTIR (neat, cm^{-1}): 2944.0, 2864.7, 1568.0, 1485.0, 1390.5, 1336.2, 1291.9, 1256.7, 1156.3, 1052.8, 1021.1, 882.1, 795.6, 778.4, 728.4, 663.4.
EA: Anal. Calcd. for $C_{26}H_{39}N_3Si$: C, 74.05; H, 9.32. Found: C, 74.33; H, 9.19.

***N*,*N*-dimethyl-6-(4-methyl-2-phenylpiperazin-1-yl)pyrazin-2-amine (3c).**



Following general procedure A, a mixture of 2-chloro-6-(dimethylamino)-pyrazine (157 mg, 1 mmol), 1-methyl-3-phenylpiperazine (212 mg, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P11** (29.2 mg, 0.025 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude residue was purified via column chromatography on silica gel (12% acetone in hexanes with 1% triethylamine). The title compound was isolated as a brown solid (Run 1: 279 mg (94%); Run 2: 278 mg (94%); Average Yield: 94%). Mp = 87–89 °C.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44–7.41 (m, 3H), 7.37 (s, 1H), 7.33–7.31 (m, 2H), 7.26–7.23 (m, 1H), 5.58 (m, 1H), 4.15–4.12 (m, 1H), 3.48–3.41 (td, *J* = 3.5, 12.3 Hz, 1H), 3.29–3.26, (m, 1H), 3.04 (s, 6H), 2.90–2.87 (m, 1H), 2.57 (dd, *J* = 4.35, 11.7 Hz, 1H), 2.31 (s, 3H), 2.27–2.21 (td, *J* = 3.7, 11.3 Hz, 1H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.8, 153.1, 142.2, 128.7, 128.0, 126.9, 117.6, 117.0, 59.8, 55.5, 54.4, 46.8, 41.6, 37.7.
FTIR (neat, cm^{-1}): 2933.0, 2798.5, 1563.4, 1523.9, 1493.6, 1455.9, 1427.6, 1400.8, 1359.2, 1346.9, 1294.4, 1261.6, 1235.1, 1177.5, 1063.1, 1017.3, 960.7, 833.3, 795.7, 739.3, 726.4, 698.9, 667.3, 596.4.
EA: Anal. Calcd. for $C_{17}H_{23}N_5$: C, 68.66; H, 7.80. Found: C, 68.54; H, 7.68.

6-(2-ethylpiperidin-1-yl)quinolone (3d). Following general procedure A, a mixture of 6-chloroquinoline (163 mg, 1 mmol), 2-ethylpiperidine (0.160 mL,



1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), **P7** (22.8 mg, 0.02 mmol), and **L7** (15 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude material was purified via column chromatography on silica gel (45–50% Et_2O in hexanes). The title compound was isolated as an orange oil (Run 1: 174 mg (72%), Run 2: 183 mg (74%); Average Yield: 73%).

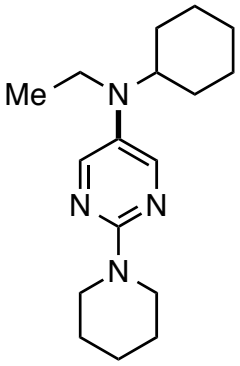
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.62–8.61 (d, J = 1.5, 4.2 Hz, 1H), 7.93–7.90 (m, 2H), 7.51 (dd, J = 2.7, 9.3 Hz, 1H), 7.27 (dd, J = 4.3, 8.2 Hz, 1H), 6.97 (d, J = 2.7 Hz, 1H), 3.95–3.94 (m, 1H), 3.53–3.50 (m, 1H), 3.11–3.04 (m, 1H), 1.81–1.53 (m, 8H), 0.88 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 149.9, 147.1, 143.7, 134.4, 130.3, 130.3, 122.7, 121.7, 108.9, 57.8, 43.6, 27.6, 26.0, 20.8, 19.4, 11.8.

FTIR (neat, cm^{-1}): 2929.7, 2863.2, 1615.6, 1587.1, 1498.4, 1456.0, 1435.8, 1376.4, 1248.5, 1176.6, 1132.8, 1118.6, 955.5, 934.7, 821.0, 768.7, 620.1.

DART–MS: calcd. for $C_{16}H_{20}N_2$ [M + H]: 241.1699. Found: 241.1707.

***N*-cyclohexyl-*N*-ethyl-2-(piperidin-1-yl)pyrimidin-5-amine (3e).** Following



general procedure A, a mixture of 5-bromo-2-(piperidin-1-yl)pyrimidine (242 mg, 1 mmol), *N*-ethylcyclohexylamine (0.181 mL, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), **P7** (34.2 mg, 0.03 mmol), and **L7** (22.6 mg, 0.03 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude material was purified via column chromatography on silica gel (2–10% Et_2O in hexanes). The title compound was isolated as a red–brown oil (Run 1: 171 mg (60%); Run 2: 176 mg (61%); Average Yield: 61%).

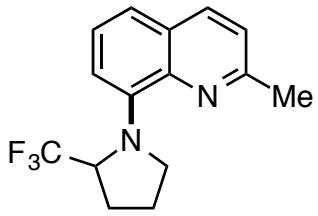
^{1}H NMR (400 MHz, C_6D_6) δ 8.22 (s, 2H), 3.93–3.90 (m, 4H), 2.84–2.78 (q, J = 7.1 Hz, 2H), 2.77–2.74 (m, 1H), 1.68–1.66 (m, 2H), 1.57–1.38 (m, 9H), 1.07–0.93 (m, 4H), 0.88–0.84 (t, J = 7.0 Hz, 3H), 0.82–0.78 (m, 1H).

^{13}C NMR (101 MHz, C_6D_6) δ 159.1, 153.1, 132.9, 61.3, 45.5, 43.0, 30.9, 26.3, 26.1, 26.1, 25.3, 14.4.

FTIR (neat, cm^{-1}): 2926.63, 2850.92, 1595.97, 1482.98, 1442.44, 1360.14, 1267.92, 1253.34, 1150.82, 1011.2, 944.93, 891.13, 852.5, 795.92.

EA: Anal. Calcd. for $C_{17}H_{28}N_4$: C, 70.79; H, 9.79. Found: C, 70.67; H, 9.85.

2-methyl-8-(2-(trifluoromethyl)pyrrolidin-1-yl)quinolone (3f). Following



general procedure A, a mixture of 8-chloro-2-methylquinoline (178 mg, 1.0 mmol), 2-trifluoromethylpyrrolidine (0.139 mL, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude residue was dissolved in hexanes and passed through a short silica gel plug (2% acetone in hexanes). The filtrate was concentrated and the crude residue was purified via column chromatography (2% acetone in hexanes) to provide the title compound as a light yellow solid (Run 1: 266 mg (95%); Run 2: 270 mg (97%); Average Yield: 96%). Mp = 41–43 °C.

^{1}H NMR (500 MHz, C_6D_6) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.67–6.60 (m, 1H), 3.62–3.58 (m, 1H), 3.19–3.15 (m, 1H), 2.43 (s, 3H), 2.15–2.08 (m, 1H), 2.03–2.00 (m, 1H), 1.84–1.77 (m, 1H), 1.62–1.55 (m, 1H).

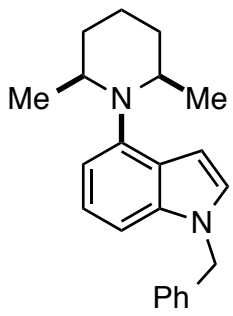
^{13}C NMR (101 MHz, C_6D_6) δ 155.3, 144.5, 142.0, 136.7, 129.9 (q, *J* = 287.6 Hz), 128.2, 126.2, 121.4, 120.1, 117.4, 60.6 (q, *J* = 28 Hz), 51.6, 26.2, 25.3, 22.8.

^{19}F NMR (282 MHz, C_6D_6) δ –73.79 (d, *J* = 7.4 Hz).

FTIR (neat, cm^{-1}): 2987.6, 2915.1, 2852.4, 1611.1, 1598.3, 1562.2, 1505.0, 1461.8, 1433.9, 1358.1, 1342.5, 1263.7, 1187.8, 1148.4, 1116.1, 1078.2, 1063.5, 950.0, 919.7, 826.7, 794.7, 746.4, 708.2, 647.8, 613.6.

EA: Anal. Calcd. for $C_{15}H_{15}F_3N_2$: C, 64.28; H, 5.39. Found: C, 64.53; H, 5.36.

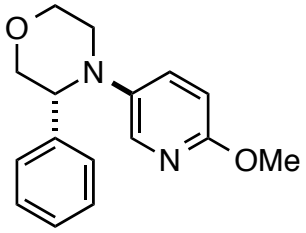
1-benzyl-4-((2*R*,6*S*)-2,6-dimethylpiperidin-1-yl)-1*H*-indole (3g). Following



general procedure A, a mixture of 1-benzyl-4-chloro-1*H*-indole (241 mg, 1 mmol), *cis*-2,6-dimethylpiperidine (0.484 mL, 3.6 mmol), NaO*t*Bu (404 mg, 4.2 mmol), **P7** (22.8 mg, 0.02 mmol), and **L7** (15 mg, 0.02 mmol) in CPME (2 mL) was heated to 60 °C for 16 h. After cooling to rt, the reaction mixture was then diluted with Et_2O (40 mL) and extracted with 2M HCl (3 x 30 mL). The combined aqueous layers were cooled to 0 °C, basified with KOH until pH = 14, and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated with the aid of a rotary evaporator. The crude residue was purified via column chromatography on silica gel (0–1% EtOAc in hexanes with 1% triethylamine) to provide the title compound as a white solid (Run 1: 242 mg (76%); Run 2: 252 mg (79%); Average yield: 78%). Mp = 66–68˚C.

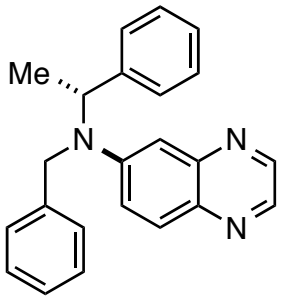
^{1}H NMR (500 MHz, C_6D_6) δ 7.14–7.11 (m, 2H), 6.95–6.91 (m, 5H), 6.78 (m, 2H), 6.66 (d, *J* = 3.11 Hz, 1H), 4.64 (s, 2H), 3.09 (m, 2H), 1.72–1.64 (m, 3H), 1.54–1.48 (m, 3H), 0.88–0.86 (d, *J* = 6 Hz, 6H).
^{13}C NMR (101 MHz, C_6D_6) δ 145.3, 138.1, 137.9, 130.8, 128.8, 127.6, 127.4, 127.1, 122.5, 116.8, 107.4, 101.7, 58.4, 50.1, 36.3, 25.5, 22.5.
FTIR (neat, cm^{-1}): 2961.0, 2930.7, 2788.5, 1603.5, 1575.3, 1489.2, 1454.4, 1440.8, 1430.5, 1370.8, 1358.1, 1332.9, 1289.3, 1241.6, 1216.9, 1095.0, 1011.8, 957.6, 907.4, 840.5, 799.5, 742.1, 727.3, 716.8, 690.8.
EA: Anal. Calcd. for $C_{22}H_{26}N_2$: C, 82.97; H, 8.23. Found: C, 83.10; H, 8.23.
The 19:1 *cis*:*trans* ratio of the product isomers was determined by GC analysis of the crude reaction mixture.

4-(6-methoxypyridin-3-yl)-3-phenylmorpholine (3h). Following general procedure A, a mixture of 5-bromo-2-methoxypyridine (0.120 mL, 1.0 mmol), (R)-3-phenylmorpholine (99% ee) (195 mg, 1.2 mmol), NaO*t*Bu (135 mg, 1.4 mmol), and **P7** (22.8 mg, 0.02 mmol) in CPME (2 mL) was heated to 80 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude material was purified via column chromatography on silica gel (7% acetone in hexanes). The title compound was isolated as a light yellow oil (Run 1: 253 mg (94%); Run 2: 264 mg (98%); Average Yield: 96%).



^{1}H NMR (500 MHz, C_6D_6) δ 7.95 (d, *J* = 2.7 Hz, 1H), 7.12–7.11 (m, 2H), 6.98–6.95 (m, 2H), 6.93–6.87 (m, 2H), 6.46 (d, *J* = 8.8 Hz, 1H), 3.95 (dd, *J* = 3.4, 9.3 Hz, 1H), 3.86 (dd, *J* = 3.4, 11.3 Hz, 1H), 3.68 (s, 3H), 3.65–3.63 (m, 2H), 3.49 (dd, *J* = 9.3, 11.3 Hz, 1H), 2.80–2.72 (m, 2H).
^{13}C NMR (101 MHz, C_6D_6) δ 160.7, 142.4, 141.7, 139.2, 134.0, 128.6, 128.4, 127.7, 110.8, 73.8, 67.6, 63.7, 55.6, 53.1.
FTIR (neat, cm^{-1}): 2958.9, 2848.5, 1604.3, 1564.7, 1488.5, 1453.2, 1381.7, 1278.0, 1253.8, 1114.3, 1025.3, 941.1, 822.2, 755.9, 699.5.
EA: Anal. Calcd. for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71. Found: C, 70.98; H, 6.60.
Optical Rotation: $[\alpha]_D^{24}$ = 32.3 (*c* = 1.0, $CHCl_3$).
HPLC Analysis: (OJ, 10% isopropanol/hexanes, 0.8 mL/min, 230 nm) indicates 98% ee: t_R (major) = 9.3 min, t_R (minor) = 10.9 min.

***N*-benzyl-*N*-(1-phenylethyl)quinoxalin-6-amine (3i).** Following general procedure A, a mixture of 6-chloroquinoxazoline (165 mg, 1 mmol), (R)-(+)-*N*-benzyl-α-methylbenzylamine (≥97% ee) (0.502 mL, 2.4 mmol), NaO*t*Bu (269



mg, 2.8 mmol), **P7** (22.8 mg, 0.02 mmol), and **L7** (15 mg, 0.02 mmol) in dioxane (2 mL) was heated to 60 °C for 16 h. After cooling to rt and performing the workup described in general procedure A, the crude material was purified via column chromatography on silica gel (20% EtOAc in hexanes with 1.5% triethylamine) The title compound was isolated as an orange oil (Run 1: 243 mg (72%); Run 2: 230 mg (68%); Average Yield: 70%).

^{1}H NMR (500 MHz, C_6D_6) δ 8.24 (s, 1H), 8.17 (s, 1H), 7.94 (d, J = 9.4, 1H), 7.50 (d, J = 2.5 Hz, 1H), 7.12–6.99 (m, 11H), 5.10–5.06 (q, J = 6.9 Hz, 1H), 4.24 (s, 2H), 1.25 (d, J = 6.9 Hz, 3H).

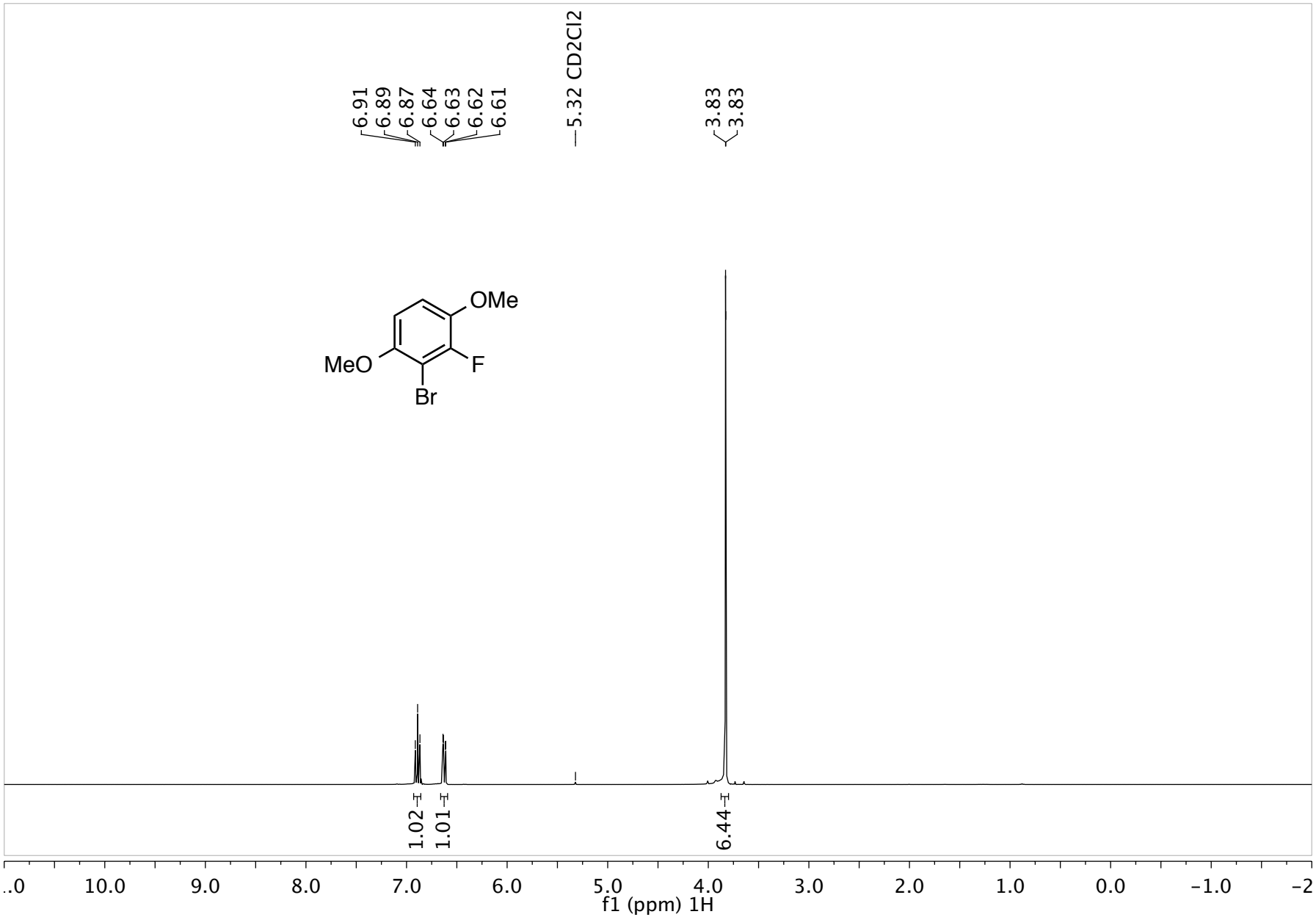
^{13}C NMR (101 MHz, C_6D_6) δ 150.2, 145.7, 145.6, 142.2, 141.5, 139.4, 138.2, 130.6, 128.9, 128.8, 127.4, 127.1, 127.0, 126.6, 120.8, 108.9, 57.4, 50.2, 18.4.

FTIR (neat, cm^{-1}): 3027.3, 2977.1, 2932.5, 2872.9, 2278.2, 1609.3, 1559.2, 1541.4, 1499.9, 1494.4, 1435.8, 1377.5, 1354.6, 1329.6, 1297.1, 1240.5, 1200.1, 1144.4, 1096.5, 1047.4, 1026.0, 1001.9, 948.3, 860.2, 812.5, 778.1, 732.3, 696.0.

DART–MS: calcd. for $C_{23}H_{21}N_3$ [M+H]: 340.1808. Found: 340.1800.

Optical Rotation: $[\alpha]_D^{24}$ = 144.0 (c = 1.0, $CHCl_3$).

HPLC Analysis: (IC, 10% isopropanol/hexanes, 0.8 mL/min, 230 nm) indicates 83% ee: t_R (minor) = 27.3 min, t_R (major) = 31.0 min.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6.64
6.63
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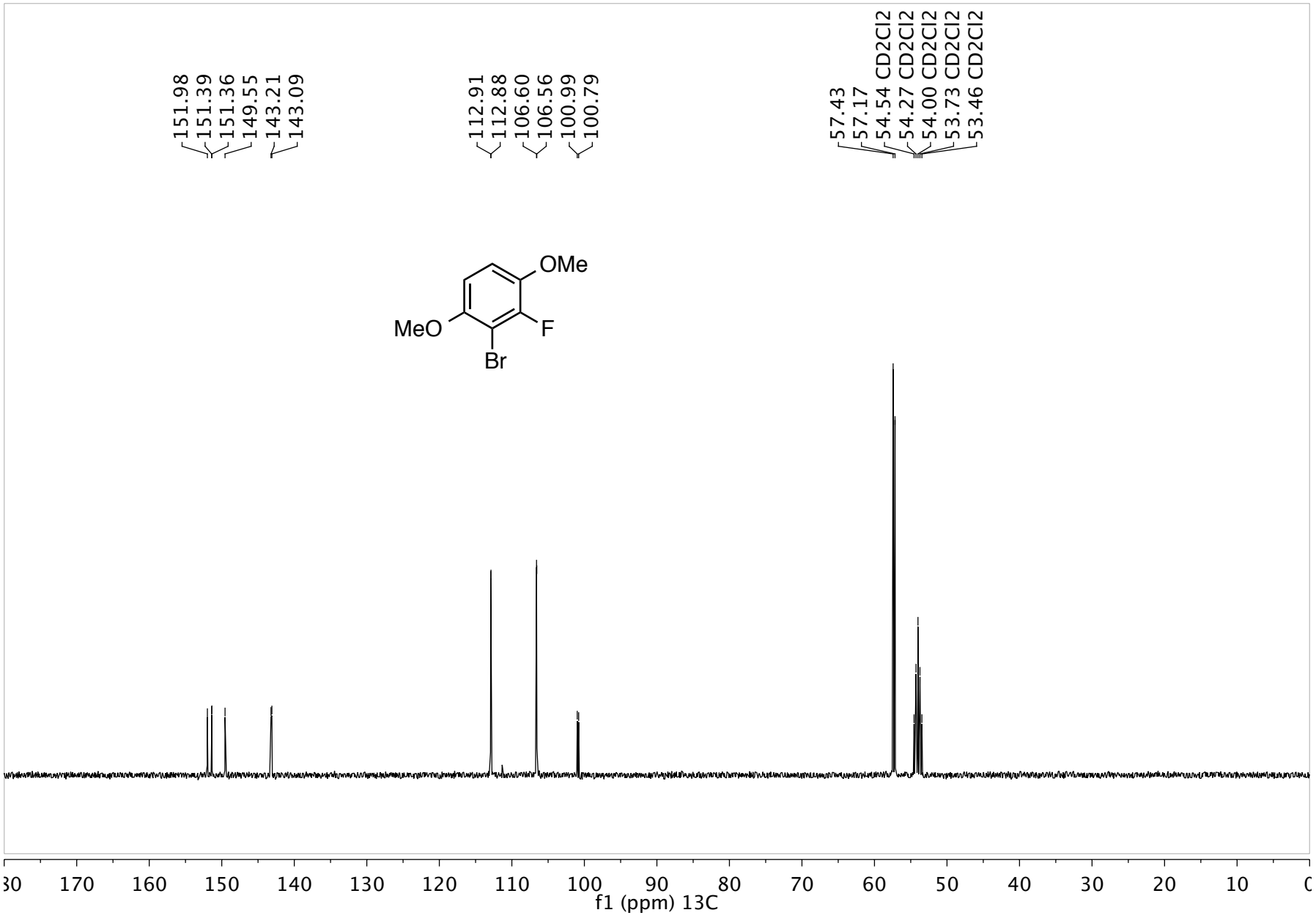
MeO
F
Br
1.02
1.01
6.44
f1 (ppm) 1H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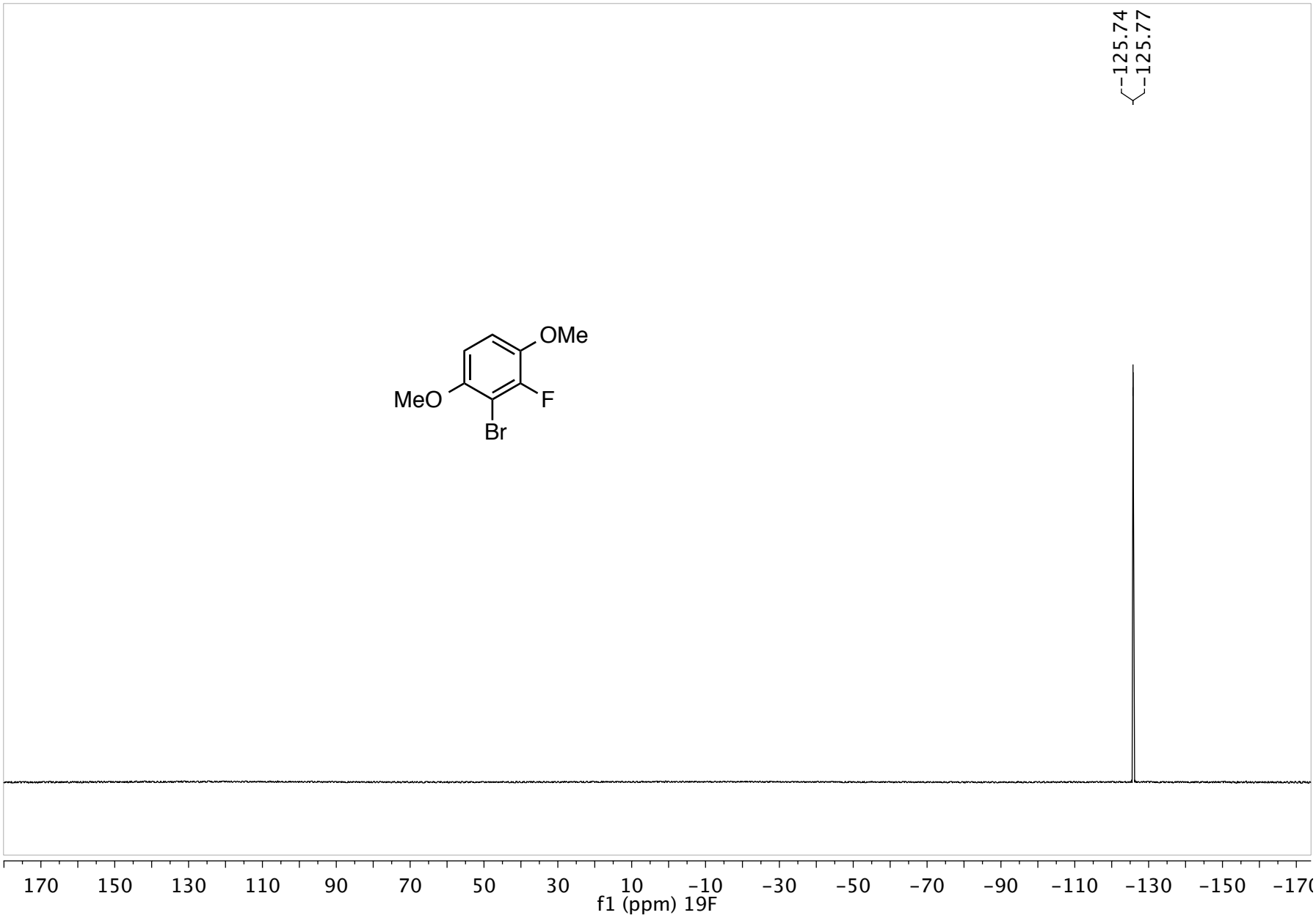
57.17
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
OMe
MeO
F
Br
f1 (ppm) 13C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F
Br
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150
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110
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10
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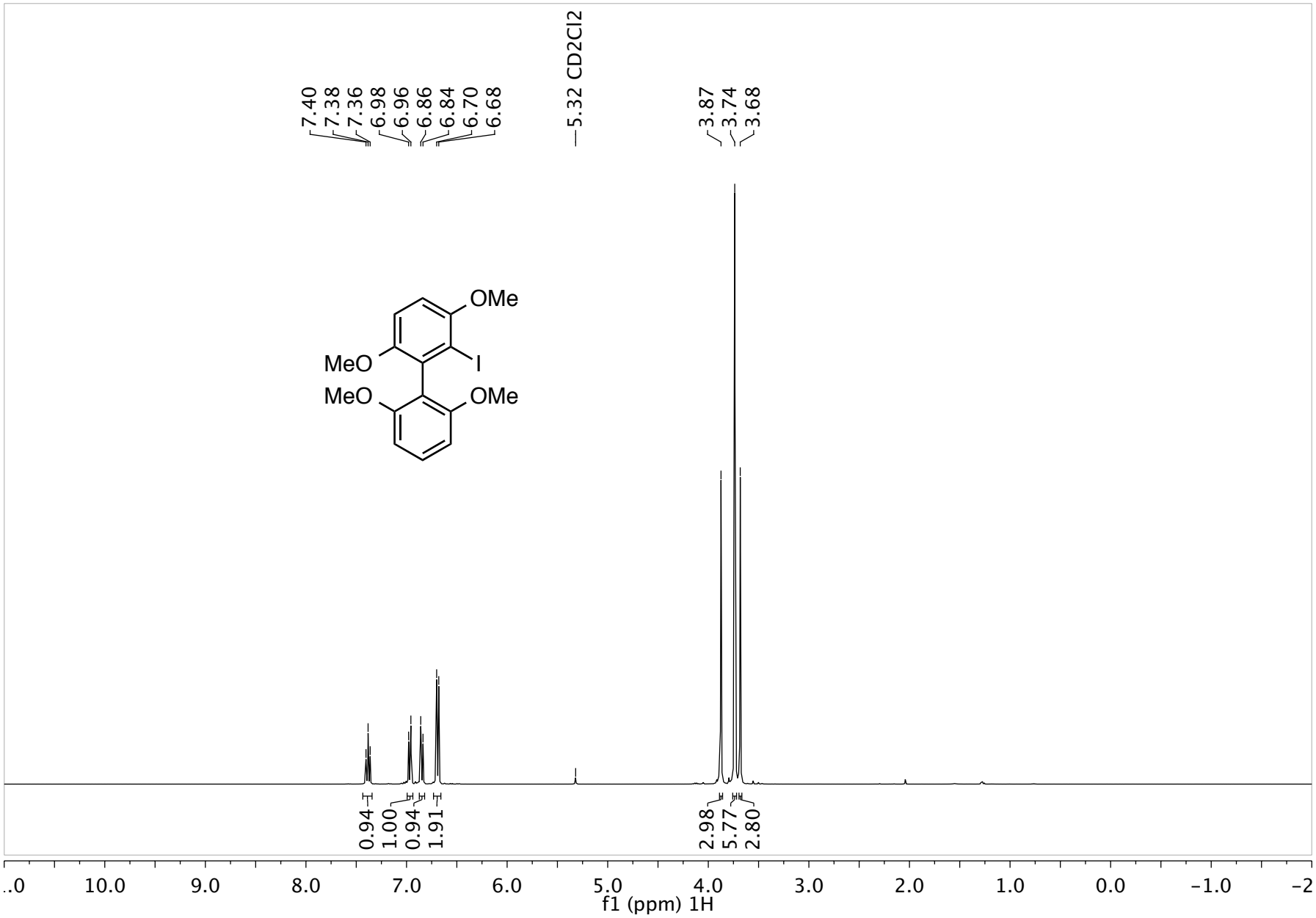
-90
-110
-130
-150
f1 (ppm) 19F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6.70
6.68
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3.74
3.68
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MeO
OMe
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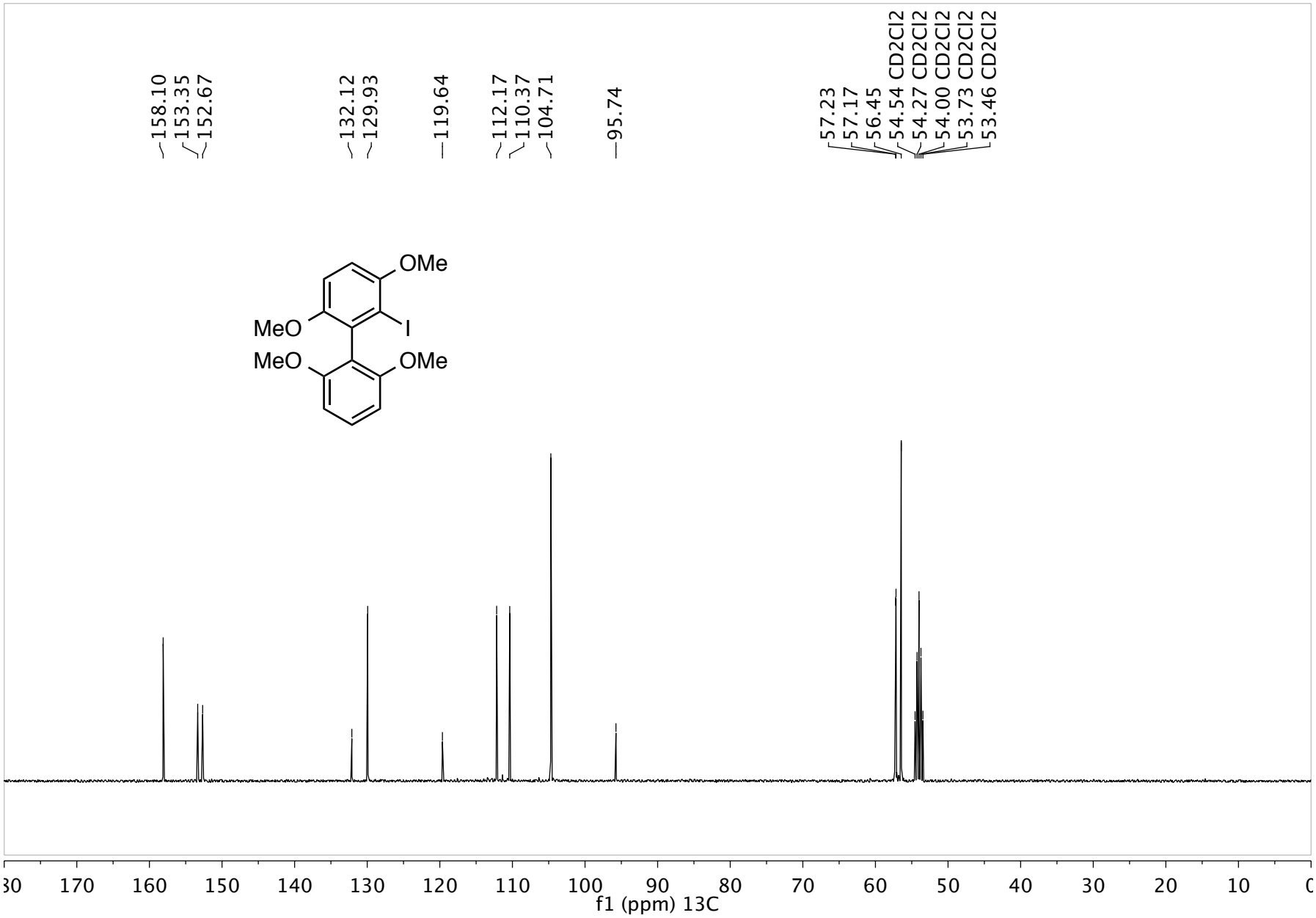
f1 (ppm) 1H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95.74
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57.17
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54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
OMe
MeO
I
MeO
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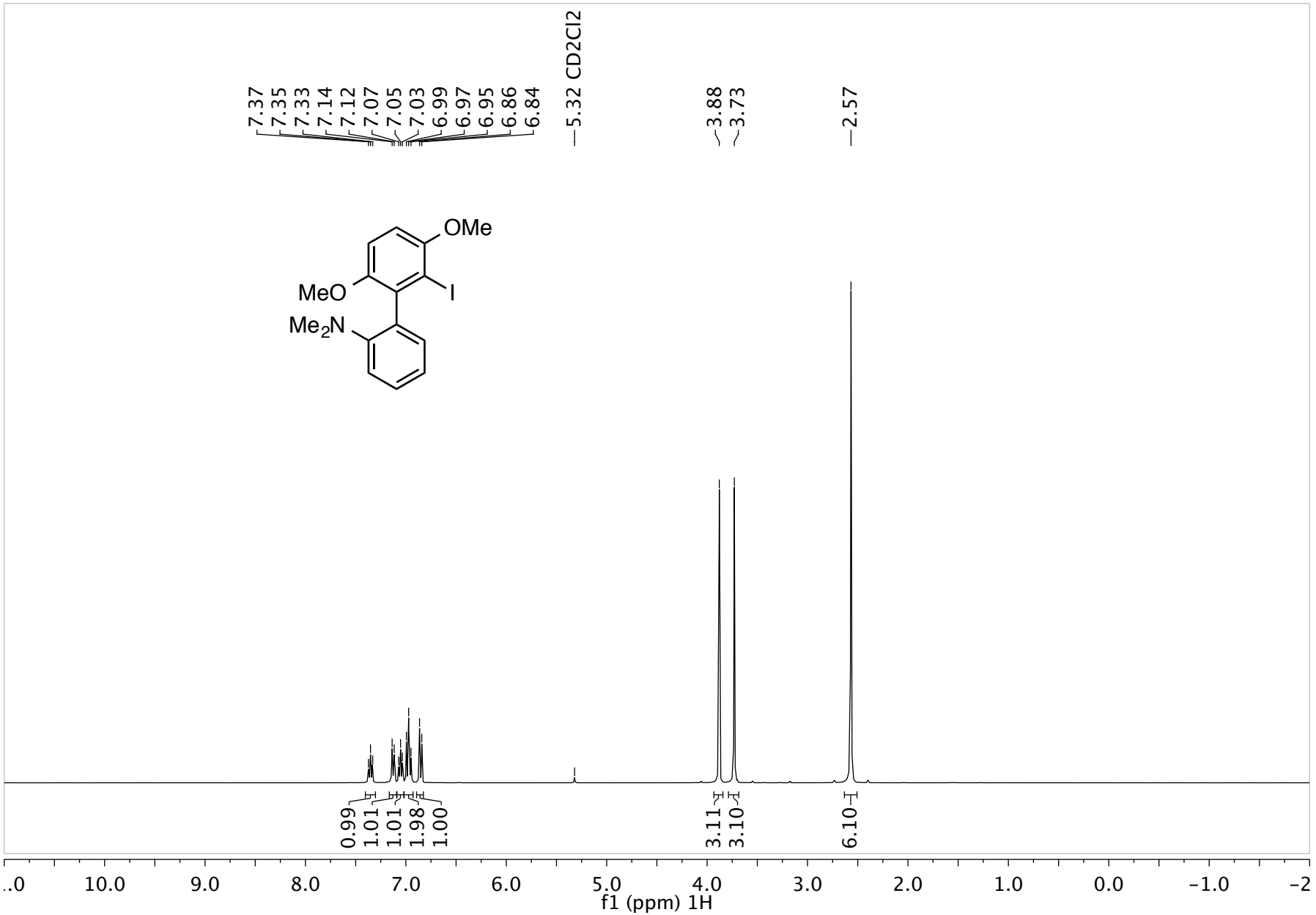
50
40
30
20
10
f1 (ppm) 13C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7.03
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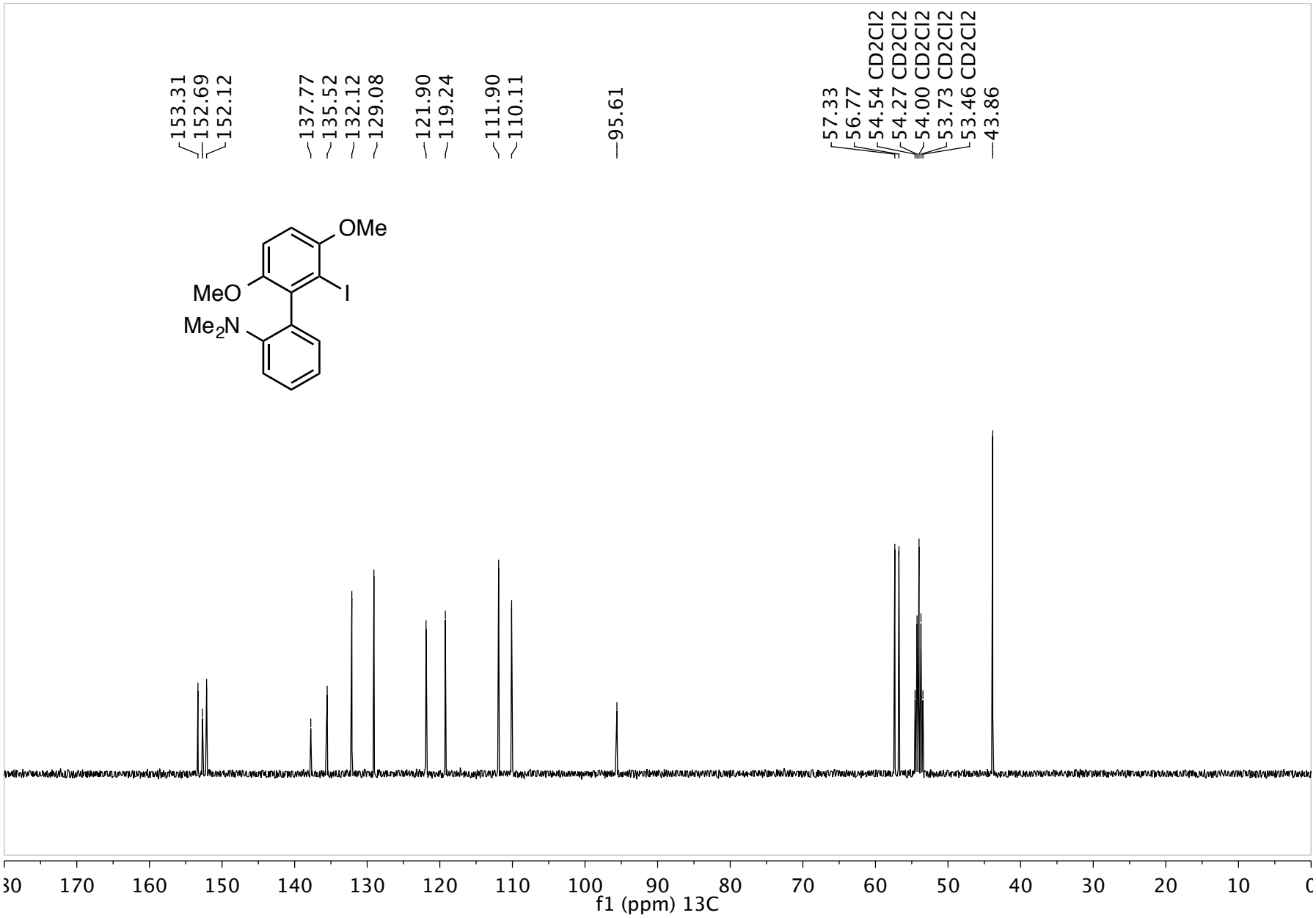
6.97
6.95
6.86
6.84
5.32 CD2Cl2
3.88
3.73
2.57
OMe
MeO
I
Me2N
0.99
1.01
1.01
1.98
1.00
3.11
3.10
6.10
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H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121.90
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111.90
110.11
95.61
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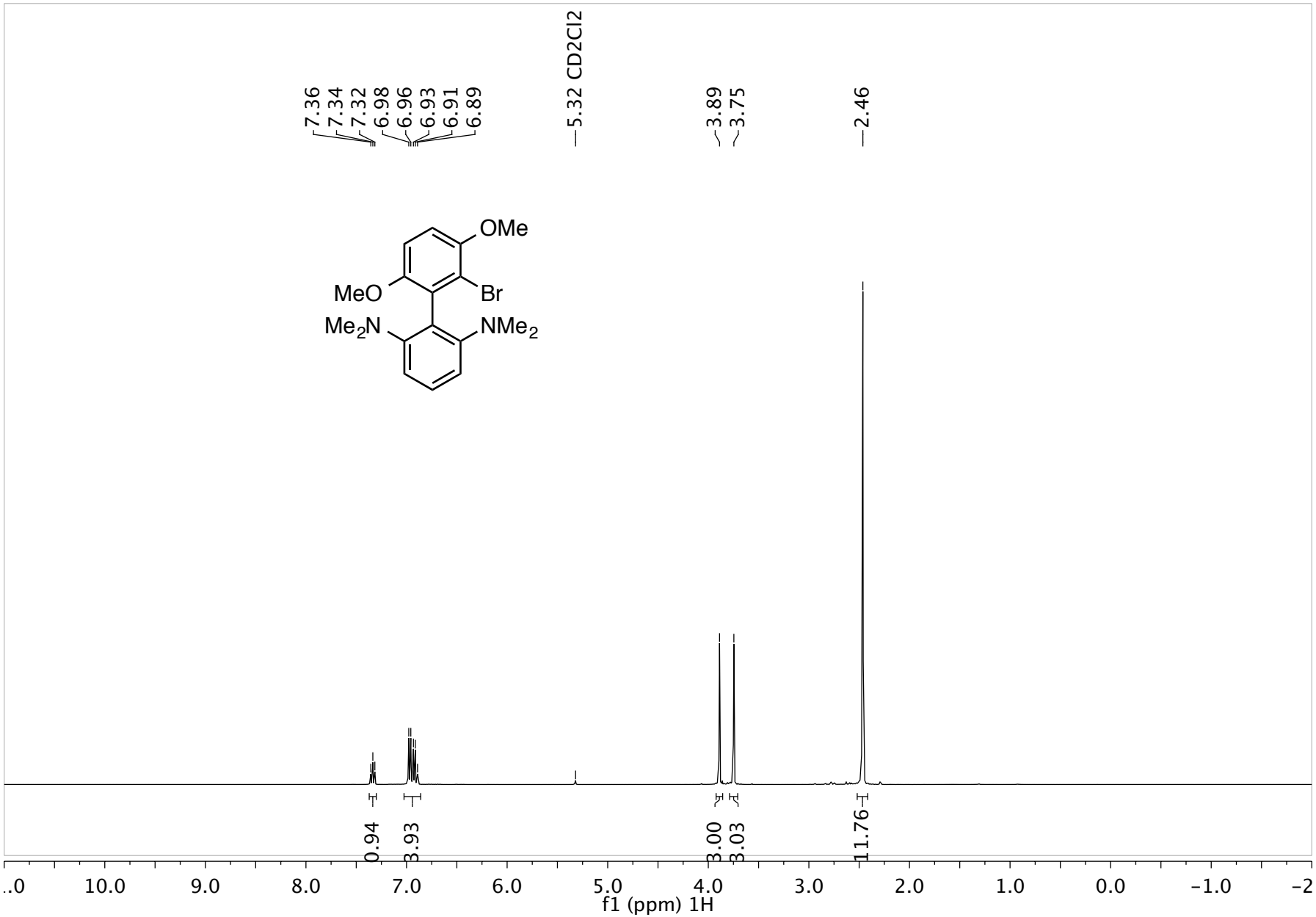
56.77
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
43.86
OMe
MeO
I
Me2N
f1 (ppm) 13C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6.89
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3.75
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Br
Me2N
NMe2
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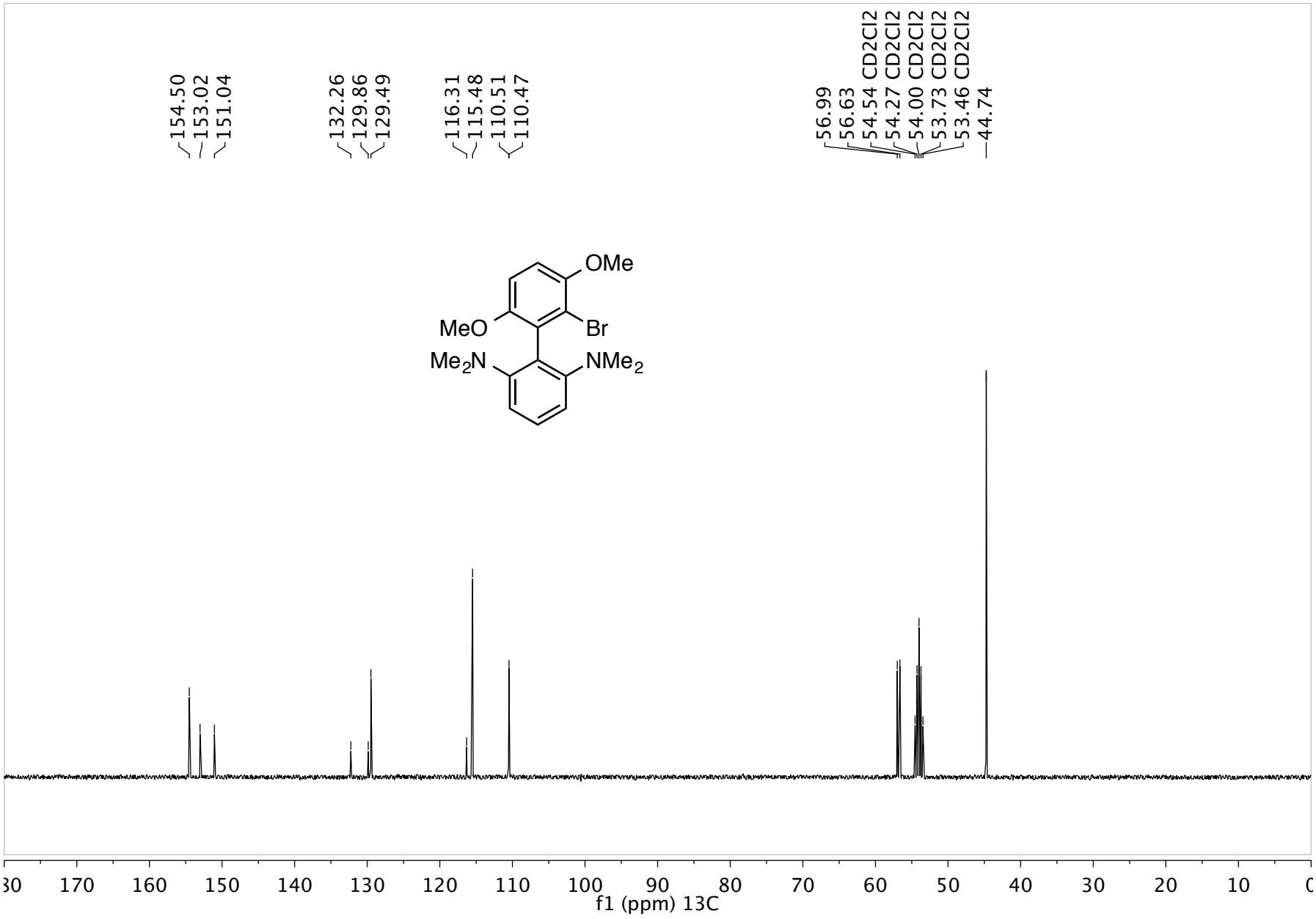
3.00
3.03
11.76
f1 (ppm) 1H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115.48
110.51
110.47
56.99
56.63
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
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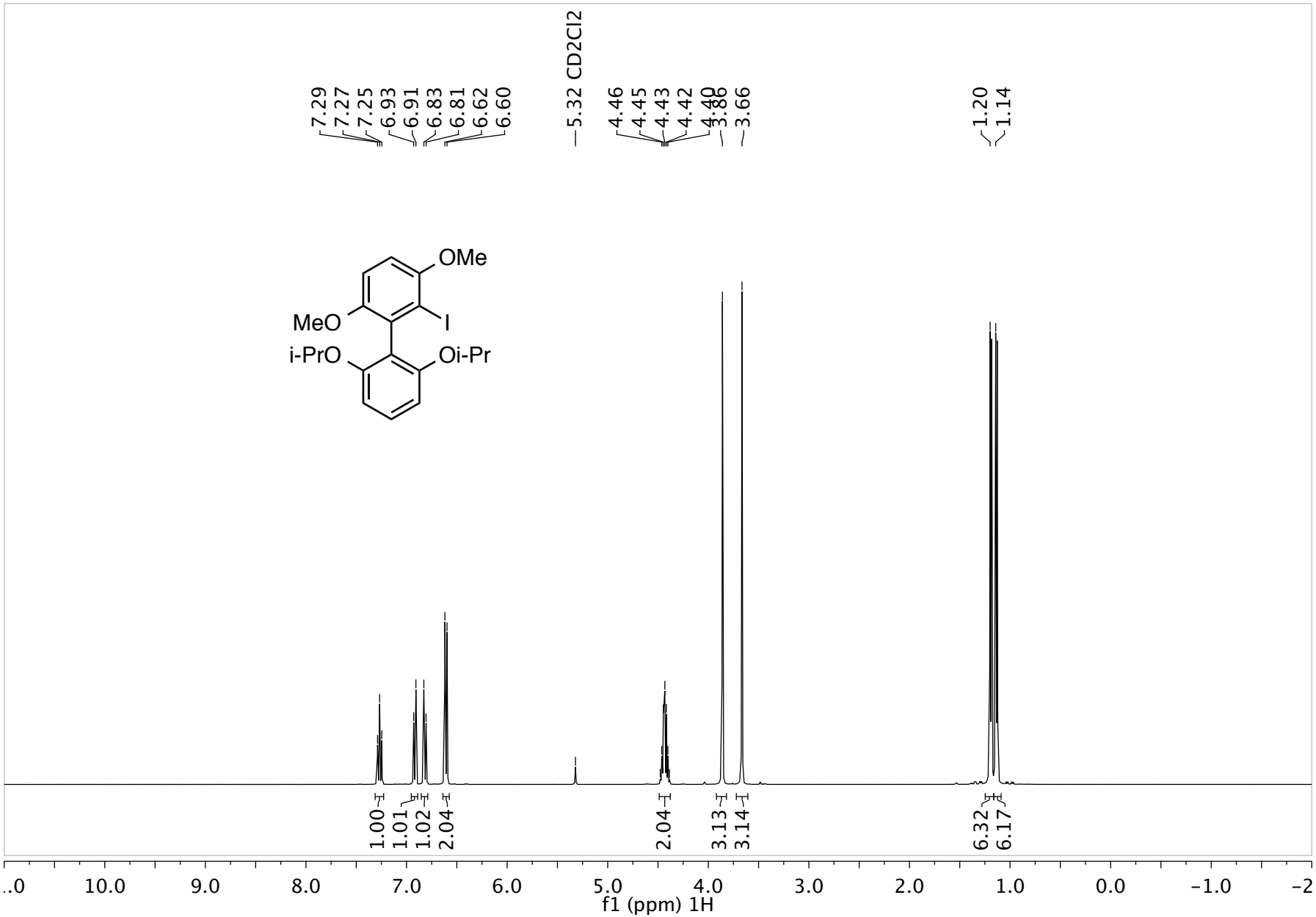
53.46 CD2Cl2
44.74
OMe
MeO
Br
Me2N
NMe2
f1 (ppm) 13C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4.45
4.43
4.42
4.40
3.86
3.66
1.20
1.14
OMe
MeO
I
i-PrO
Oi-Pr
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1.01
1.02
2.04
2.04
3.13
3.14
6.32
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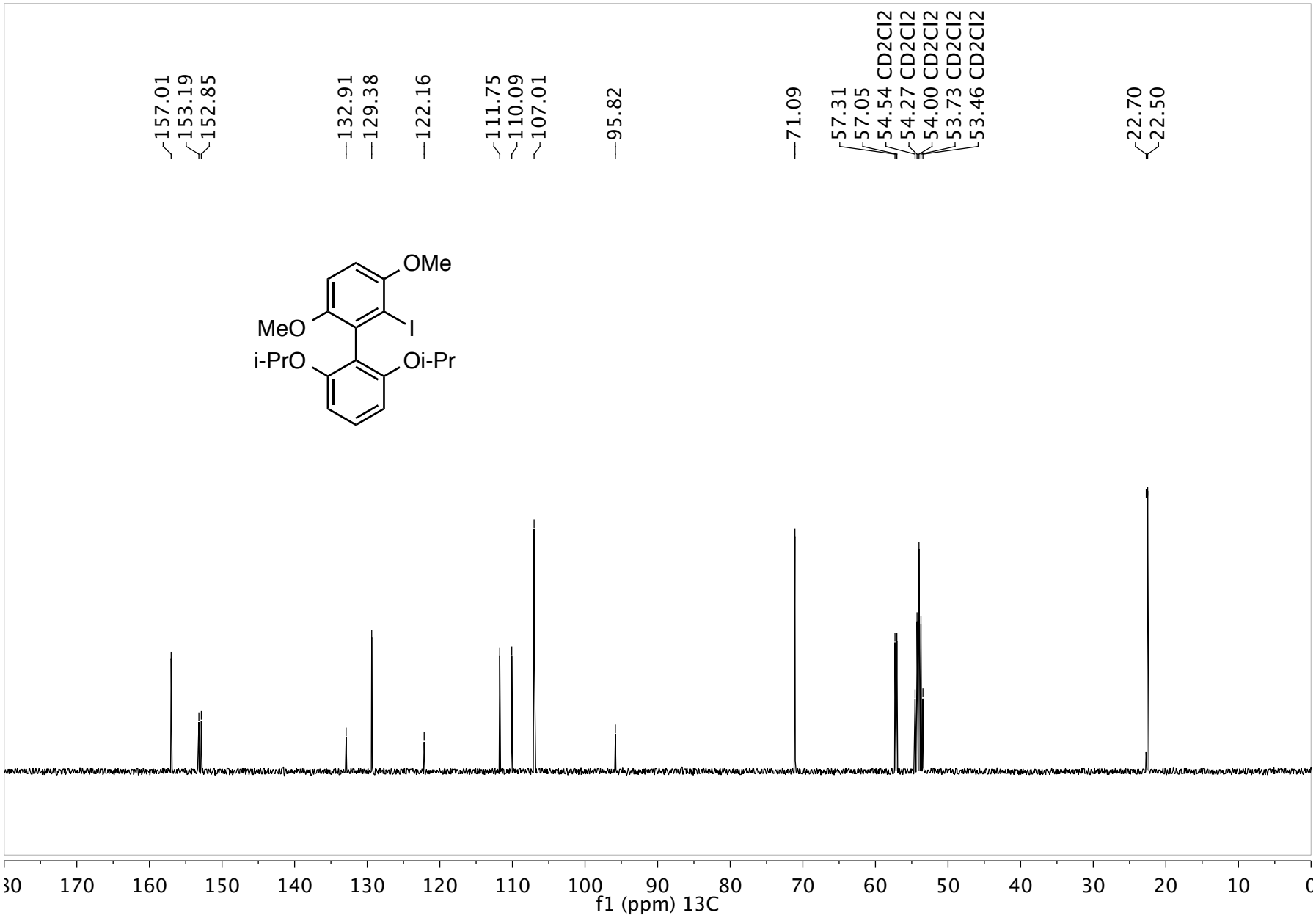
f1 (ppm) 1H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95.82
71.09
57.31
57.05
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
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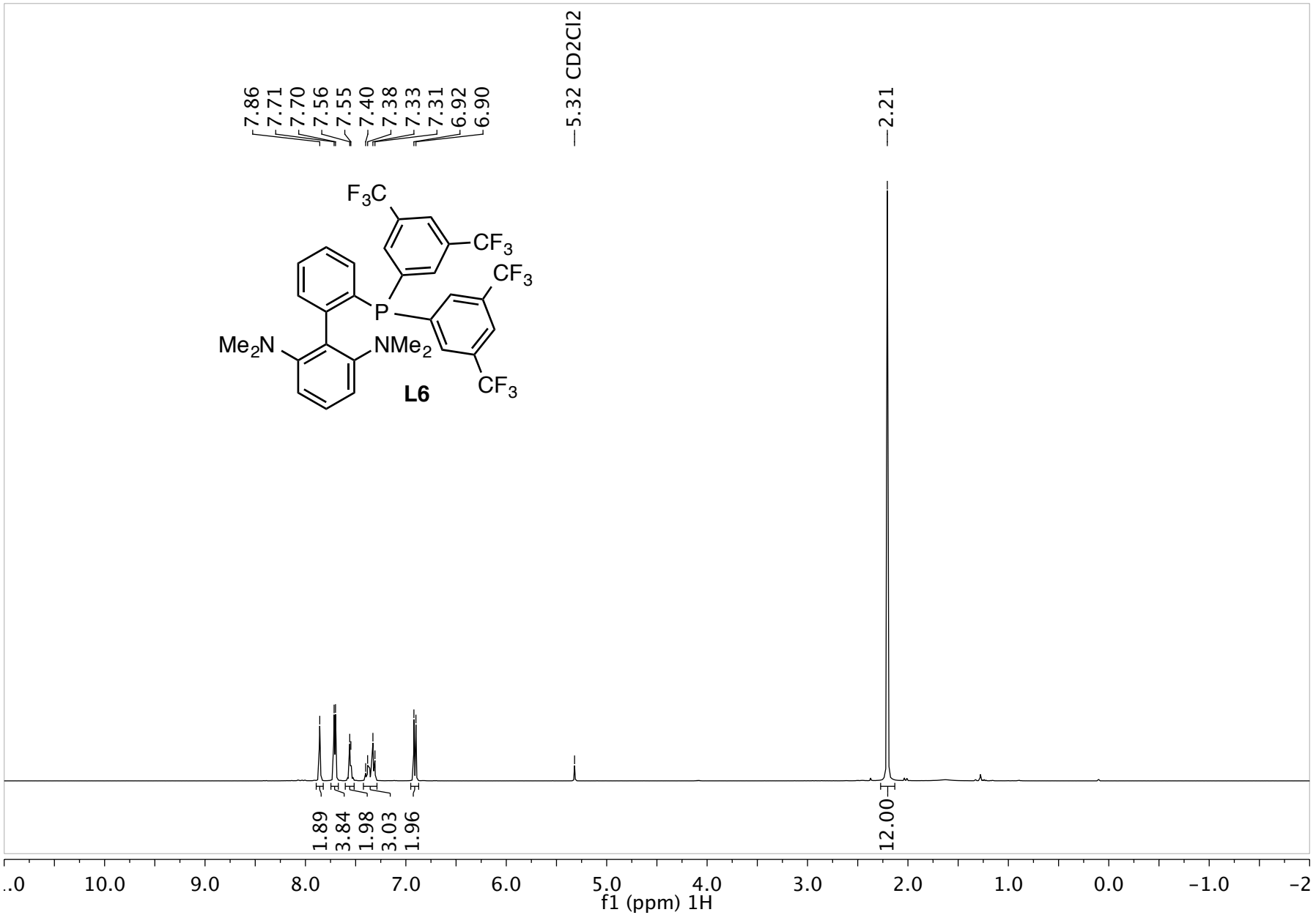
22.70
22.50
OMe
MeO
I
i-PrO
Oi-Pr
f1 (ppm) 13C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7.55
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7.33
7.31
6.92
6.90
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2.21
F3C
CF3
CF3
P
Me2N
NMe2
CF3
L6
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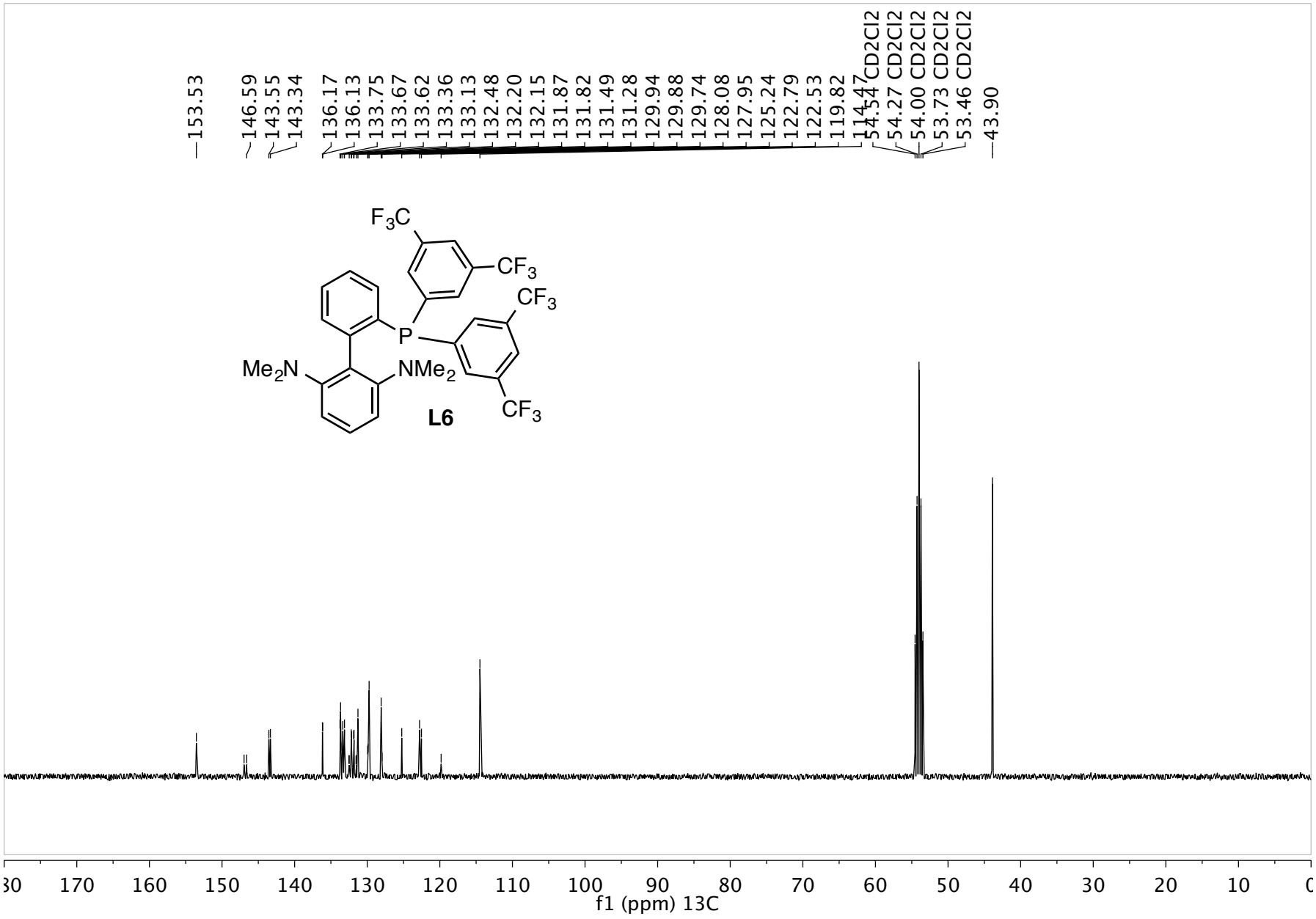
1.98
3.03
1.96
12.00
f1 (ppm) 1H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131.87
131.82
131.49
131.28
129.94
129.88
129.74
128.08
127.95
125.24
122.79
122.53
119.82
114.47
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
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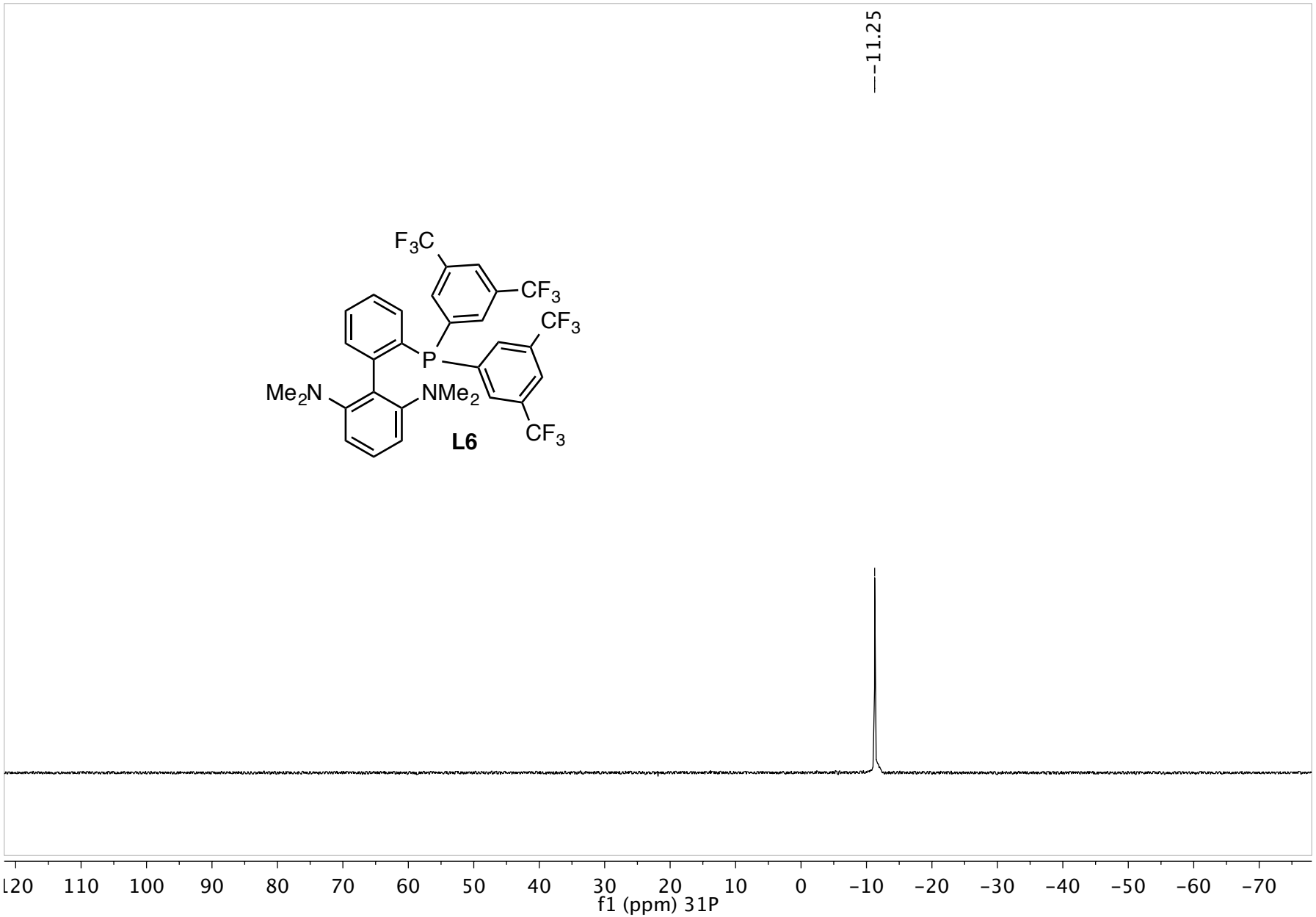
CF3
CF3
P
Me2N
NMe2
CF3
L6
f1 (ppm) 13C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CF3
L6
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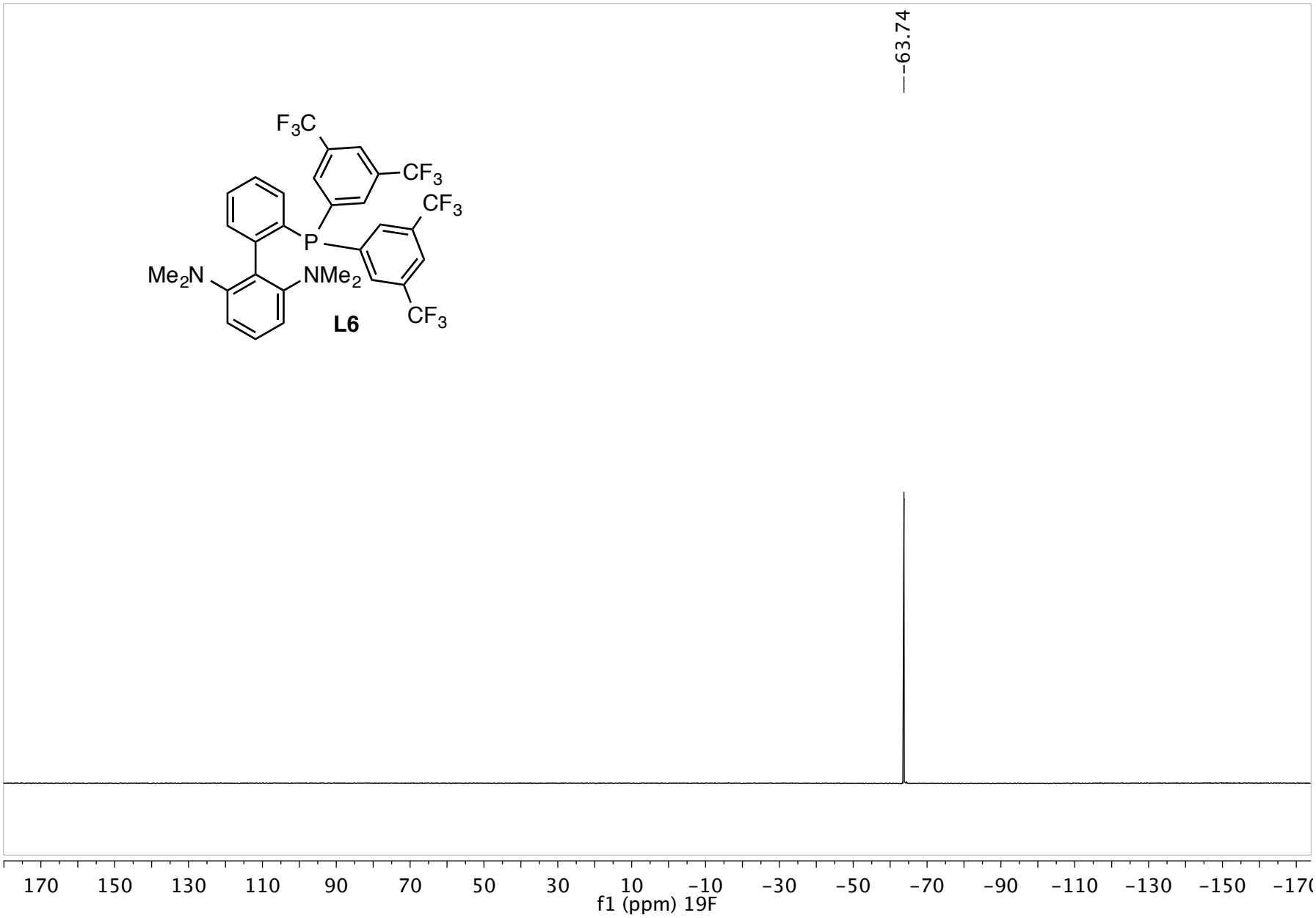
−40
−50
−60
−70
f1 (ppm) 31P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CF3
P
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L6
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110
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30
10
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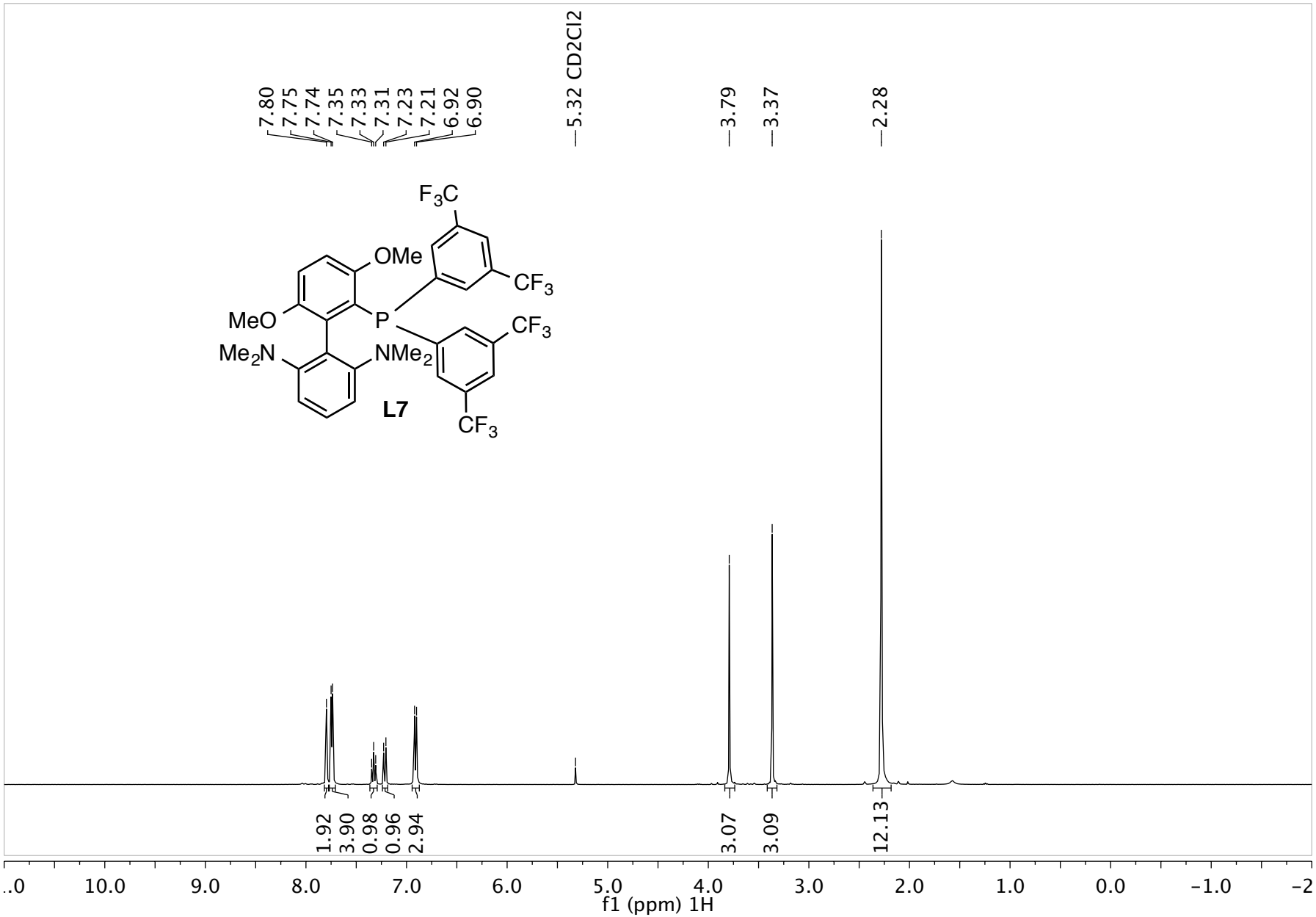
−30
−50
−70
−90
−110
−130
−150
f1 (ppm) 19F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6.90
5.32 CD2Cl2
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3.37
2.28
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CF3
OMe
MeO
P
CF3
Me2N
NMe2
CF3
L7
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0.96
2.94
3.07
3.09
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9.0
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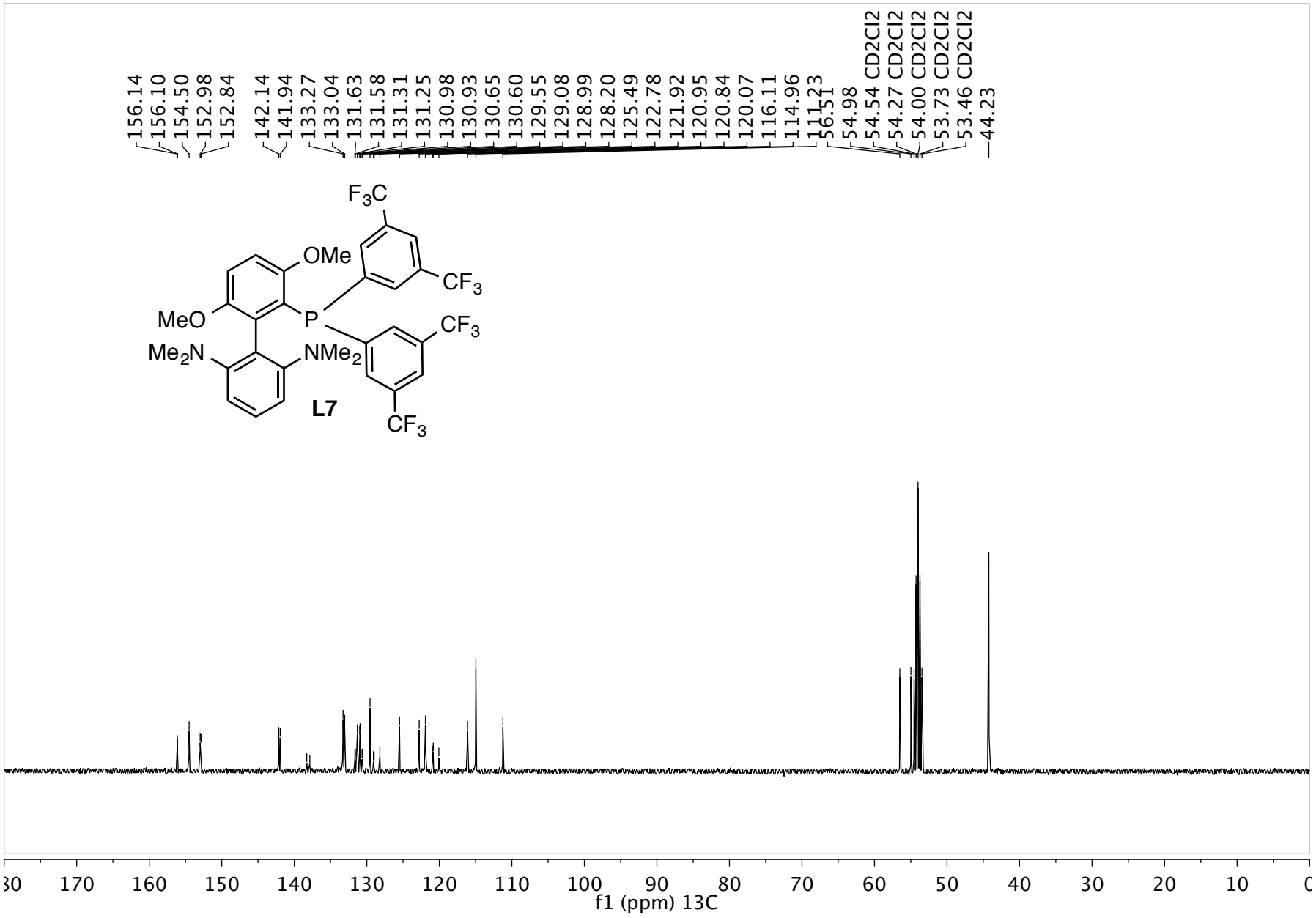
f1 (ppm) 1H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120.95
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116.11
114.96
111.23
56.51
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54.54 CD2Cl2
54.27 CD2Cl2
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53.73 CD2Cl2
53.46 CD2Cl2
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MeO
P
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NMe2
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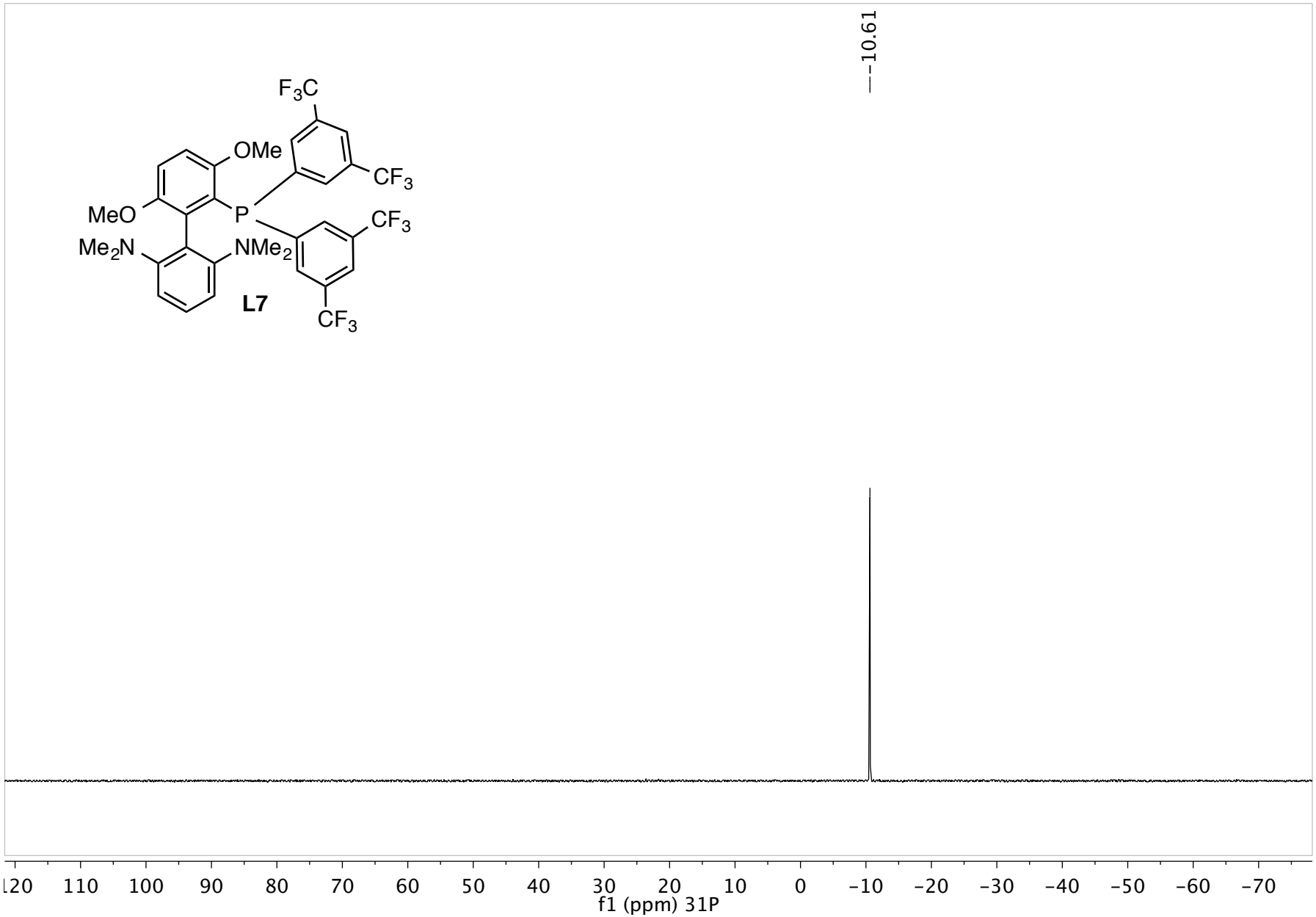
CF3
f1 (ppm) 13C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L7
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80
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-40
-50
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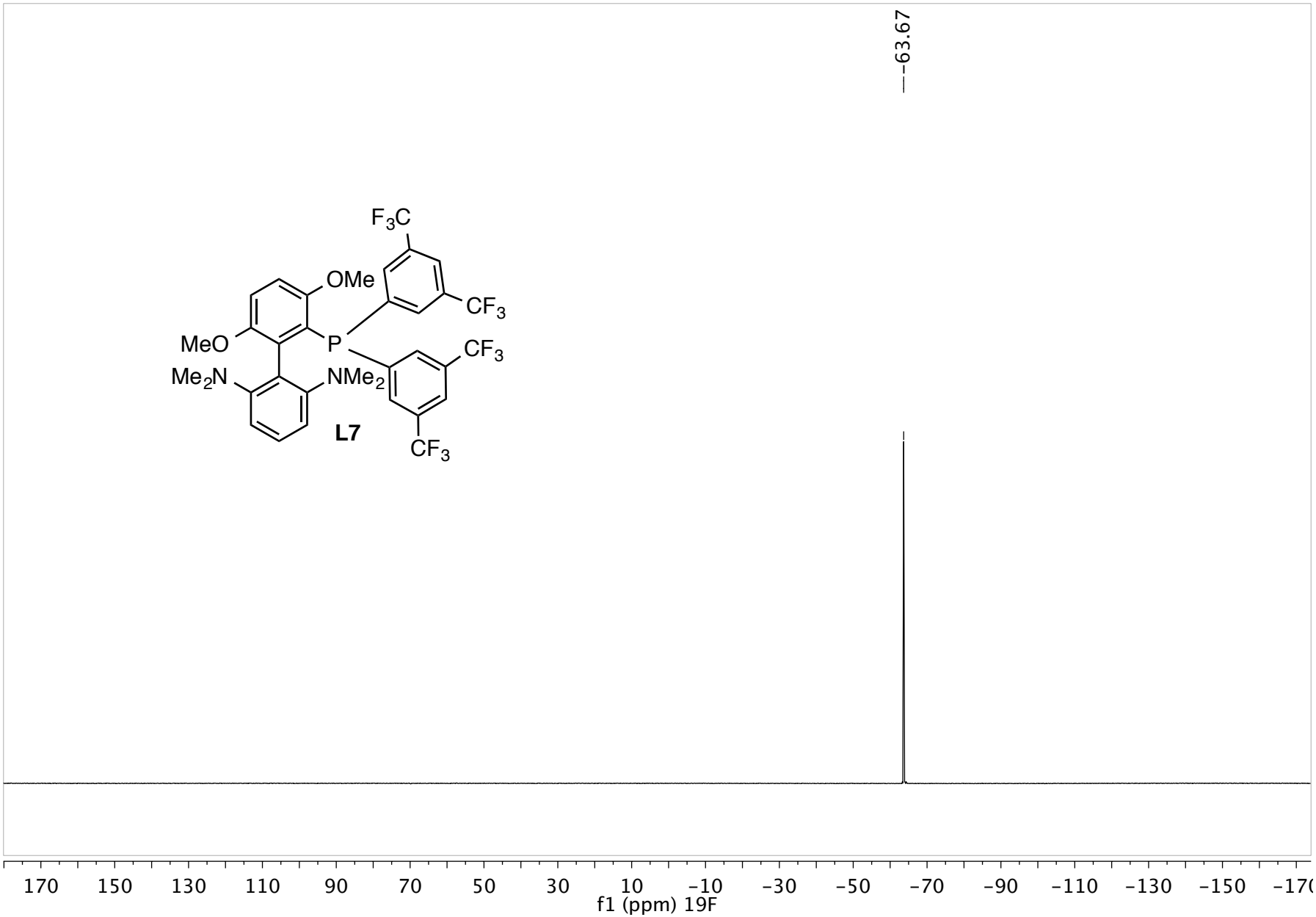
-70
f1 (ppm) 31P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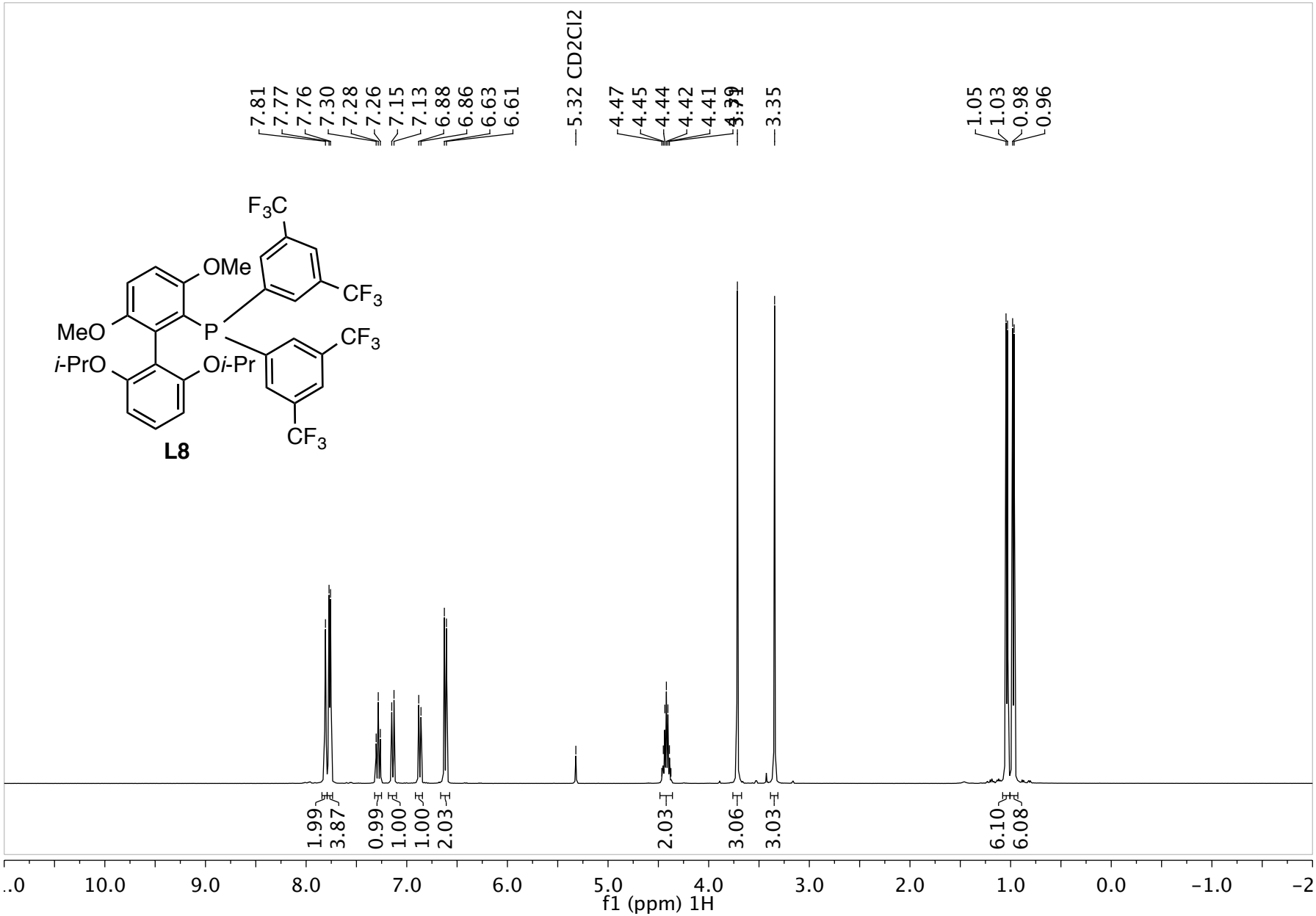
-90
-110
-130
-150
f1 (ppm) 19F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5.32 CD2Cl2
4.47
4.45
4.44
4.42
4.41
3.35
1.05
1.03
0.98
0.96
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OMe
CF3
MeO
P
CF3
i-PrO
Oi-Pr
CF3
L8
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1.00
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3.03
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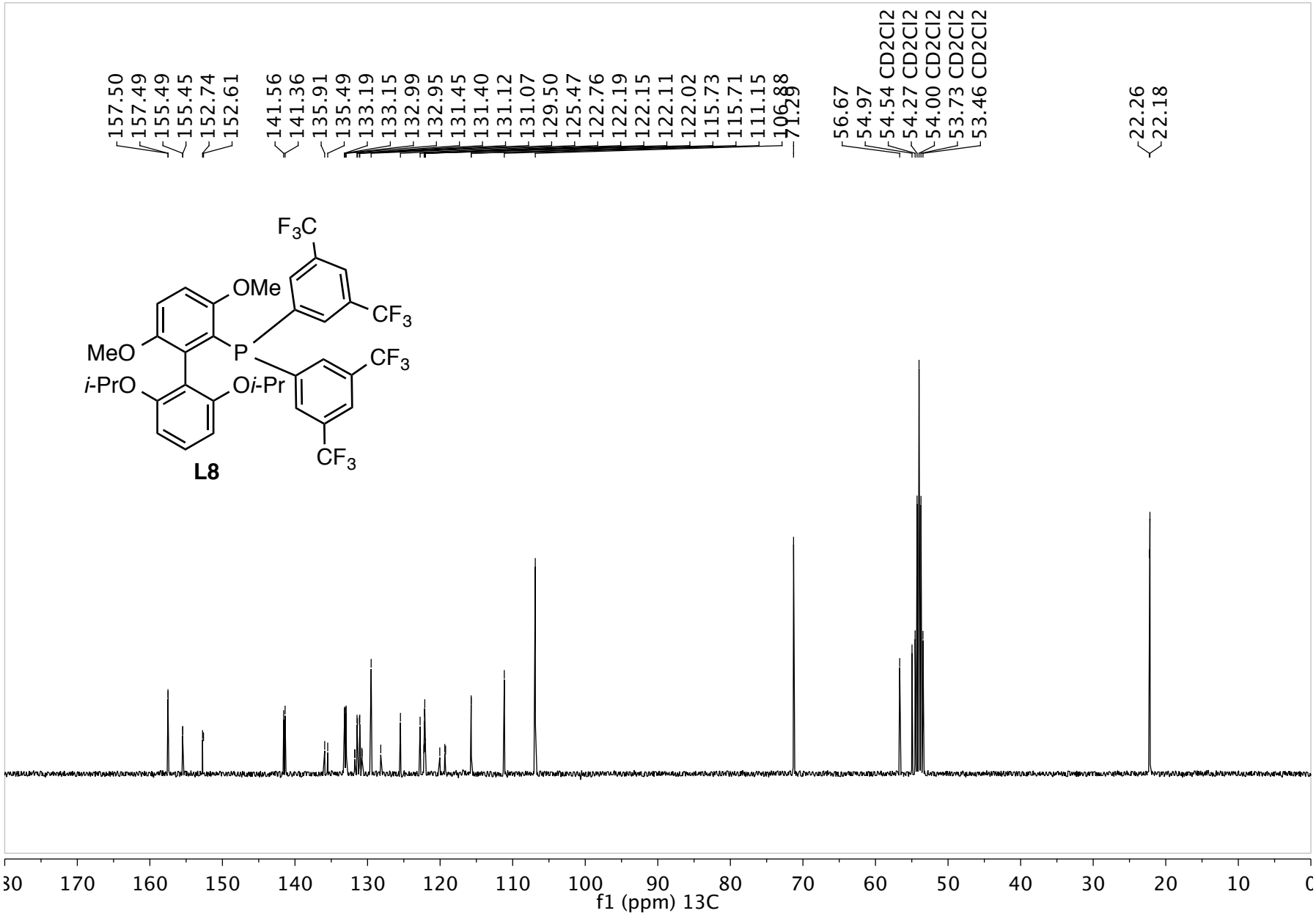
f1 (ppm) 1H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54.54 CD2Cl2
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54.00 CD2Cl2
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53.46 CD2Cl2
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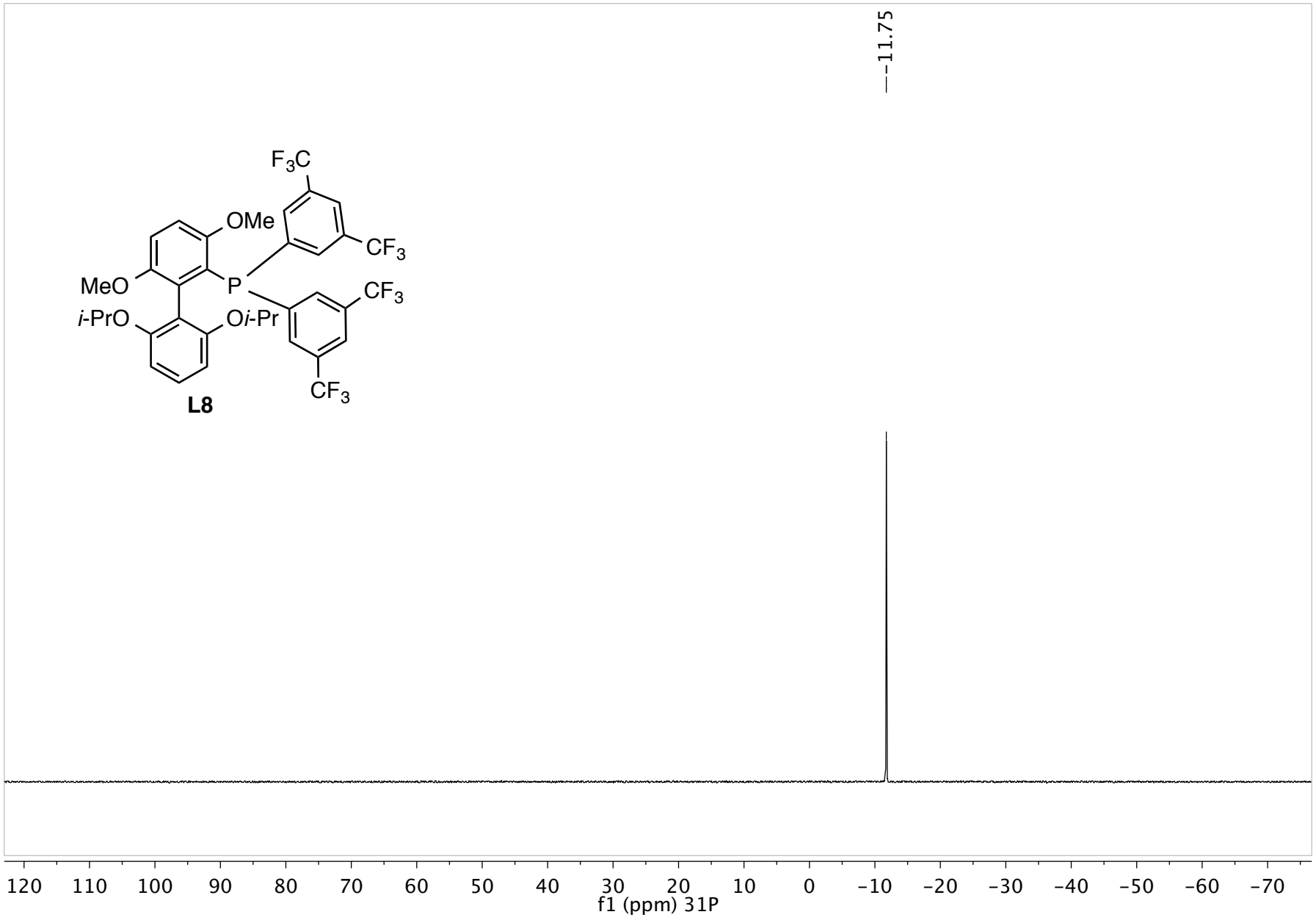
Oi-Pr
CF3
L8
f1 (ppm) 13C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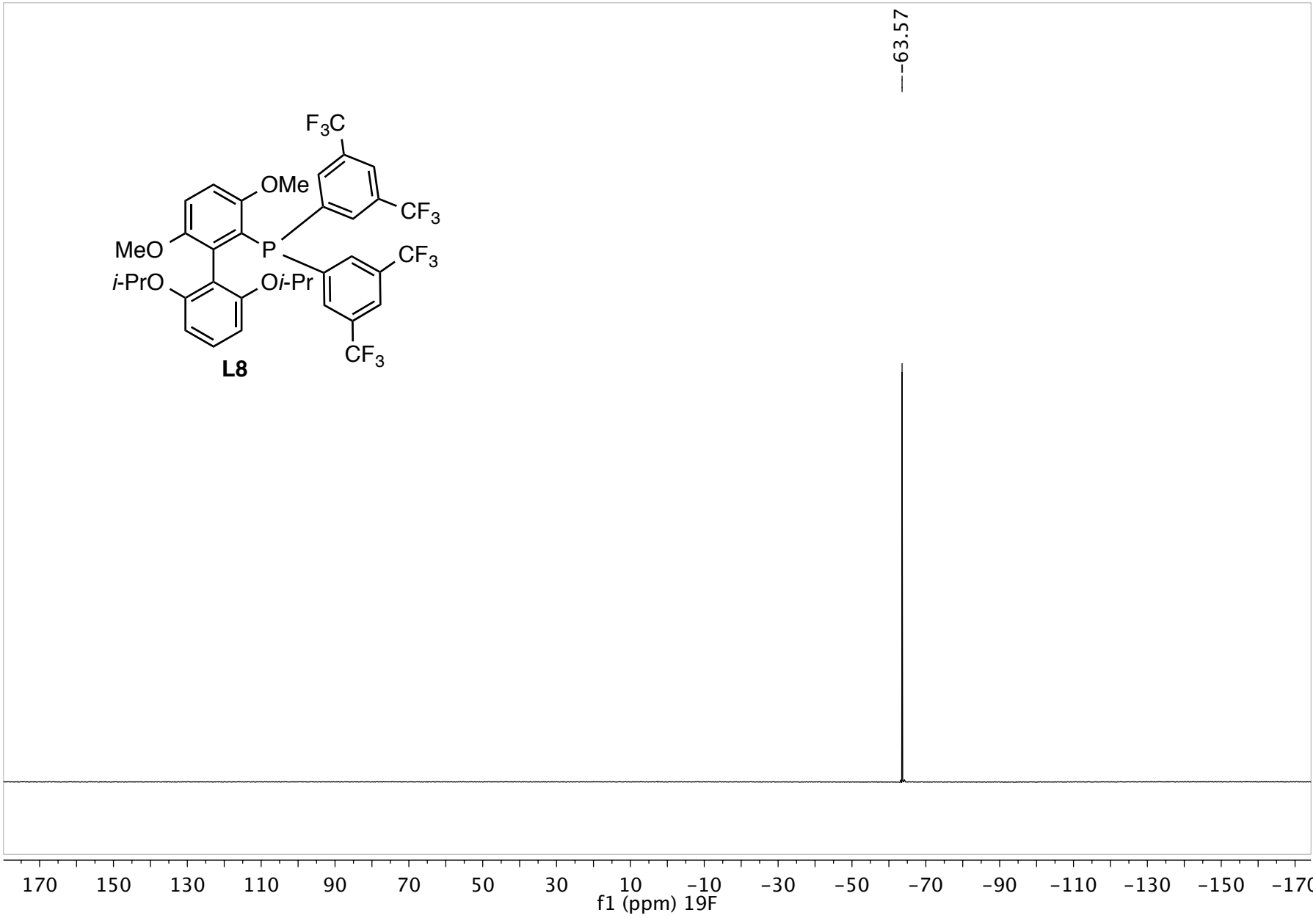
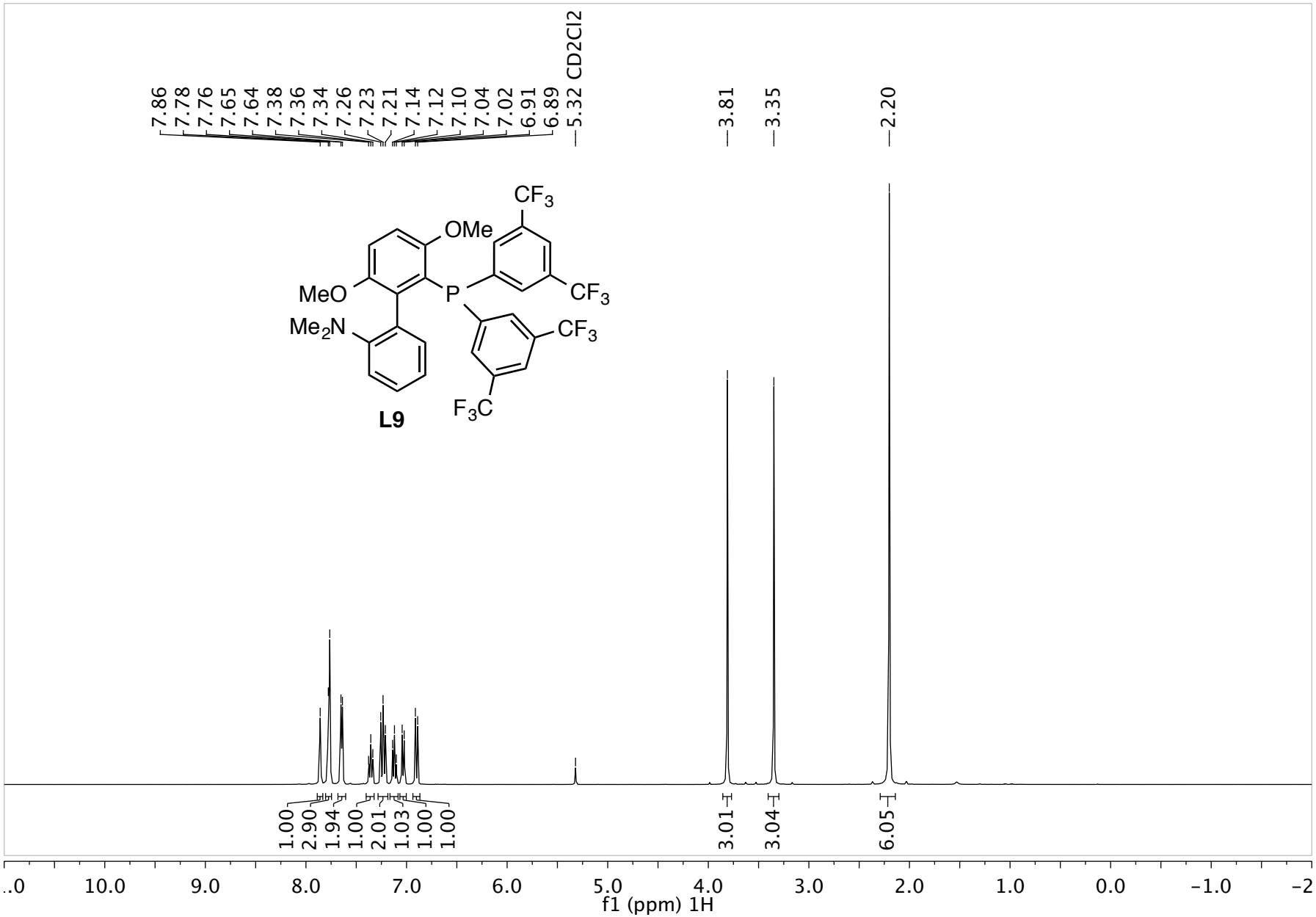
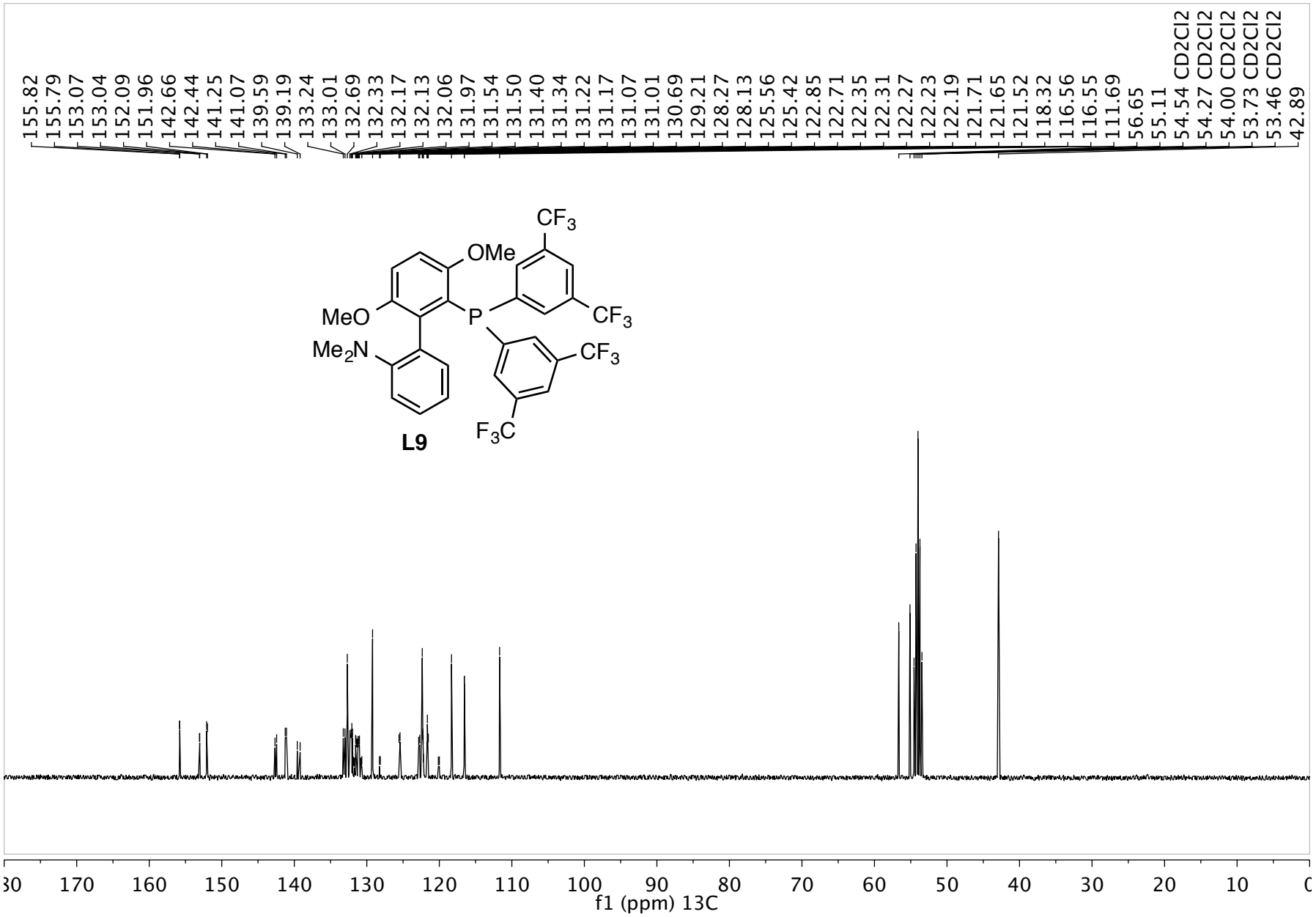
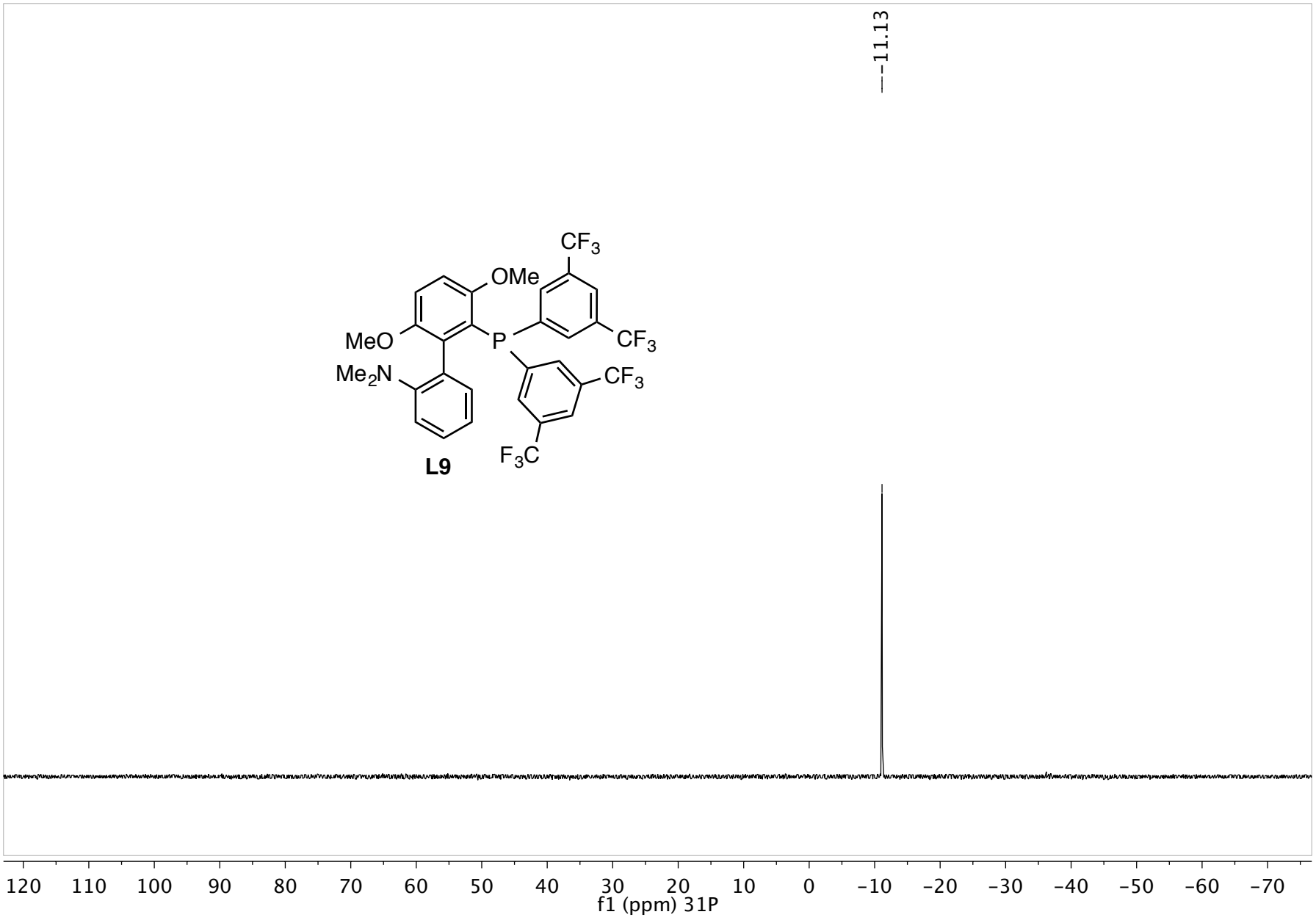
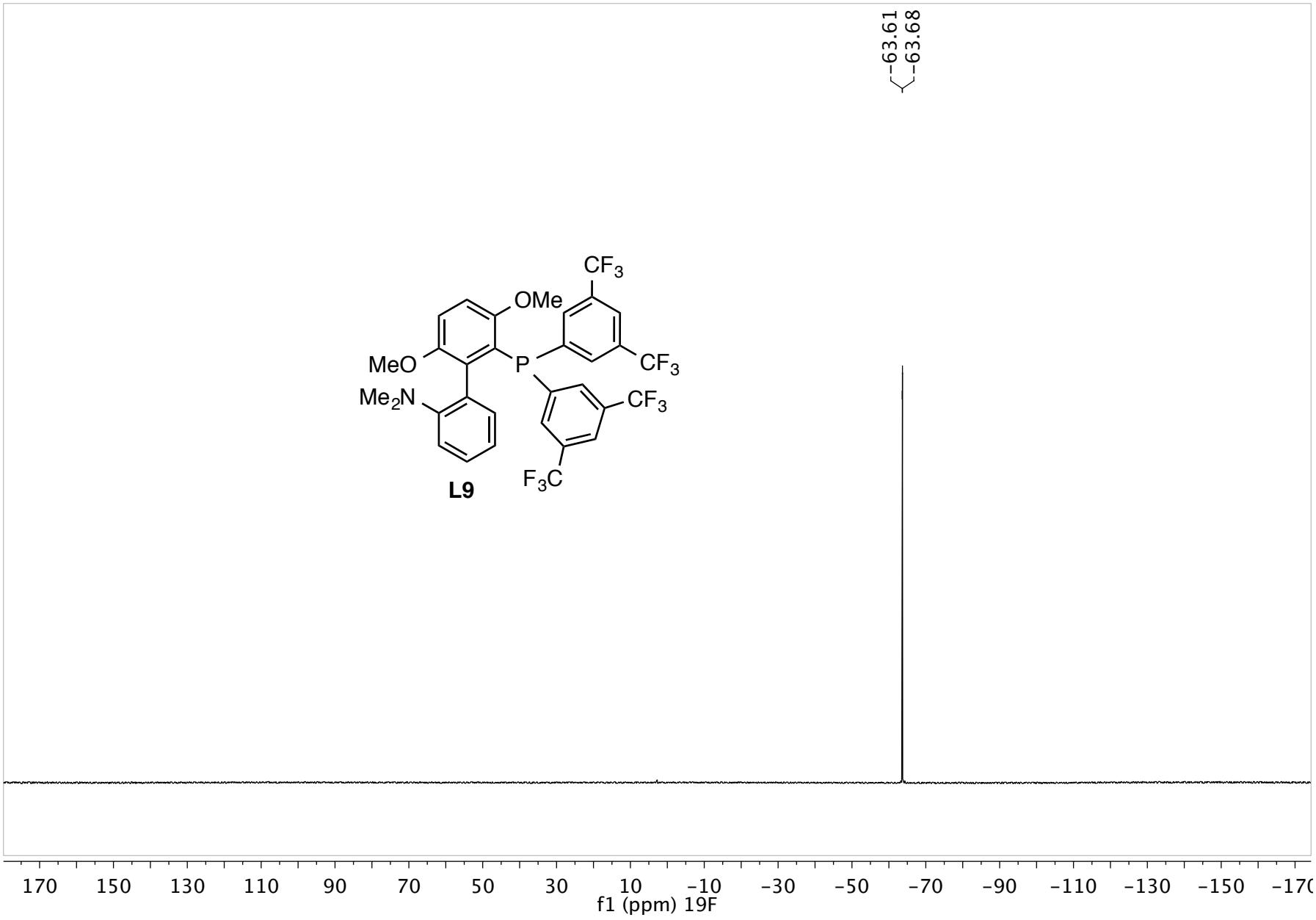
MeO
P
CF3
i-PrO
Oi-Pr
CF3
L8
120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70
f1 (ppm) 31P

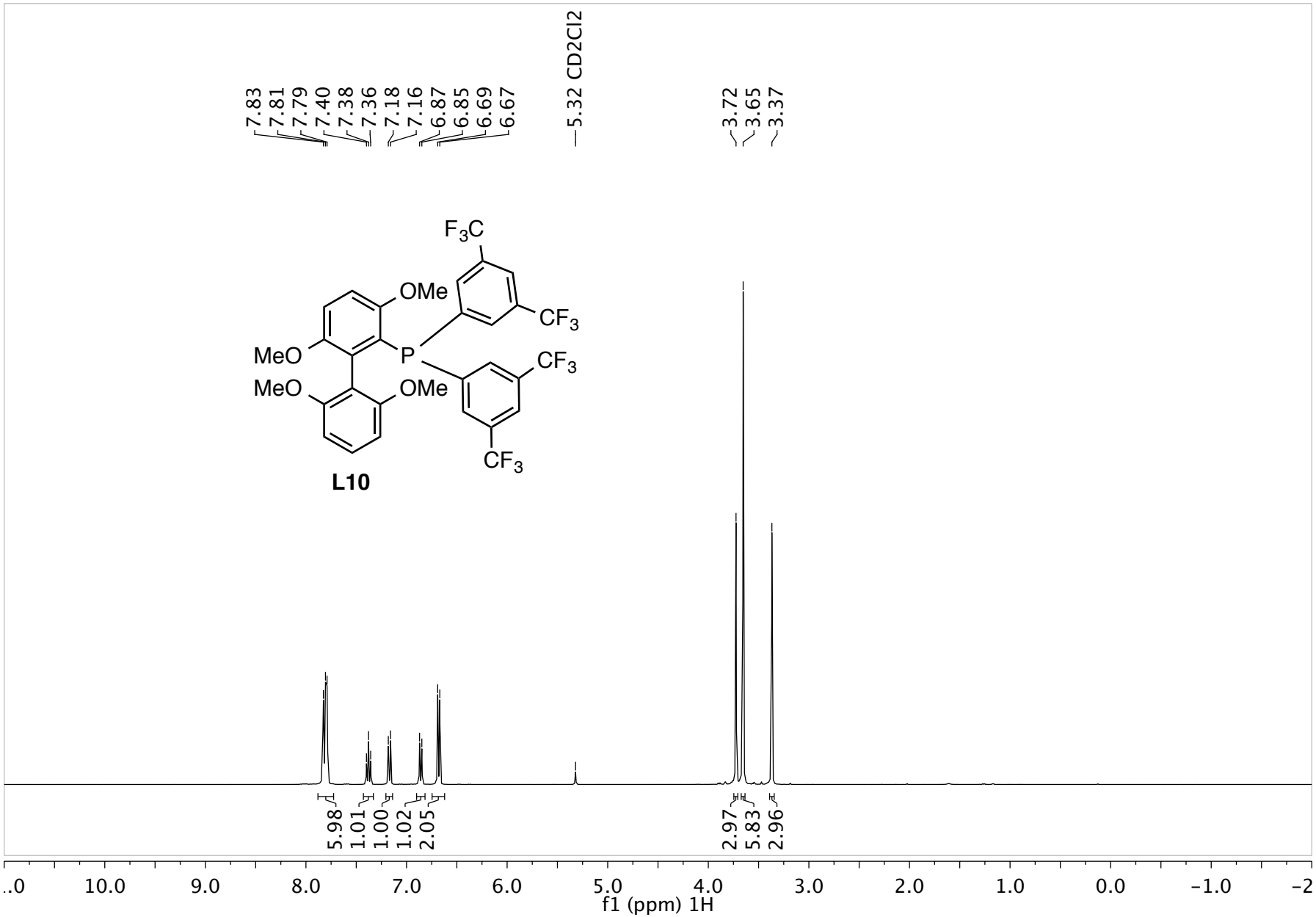

−63.57
F3C
OMe
CF3
MeO
P
CF3
i-PrO
Oi-Pr
CF3
L8
170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm) 19F

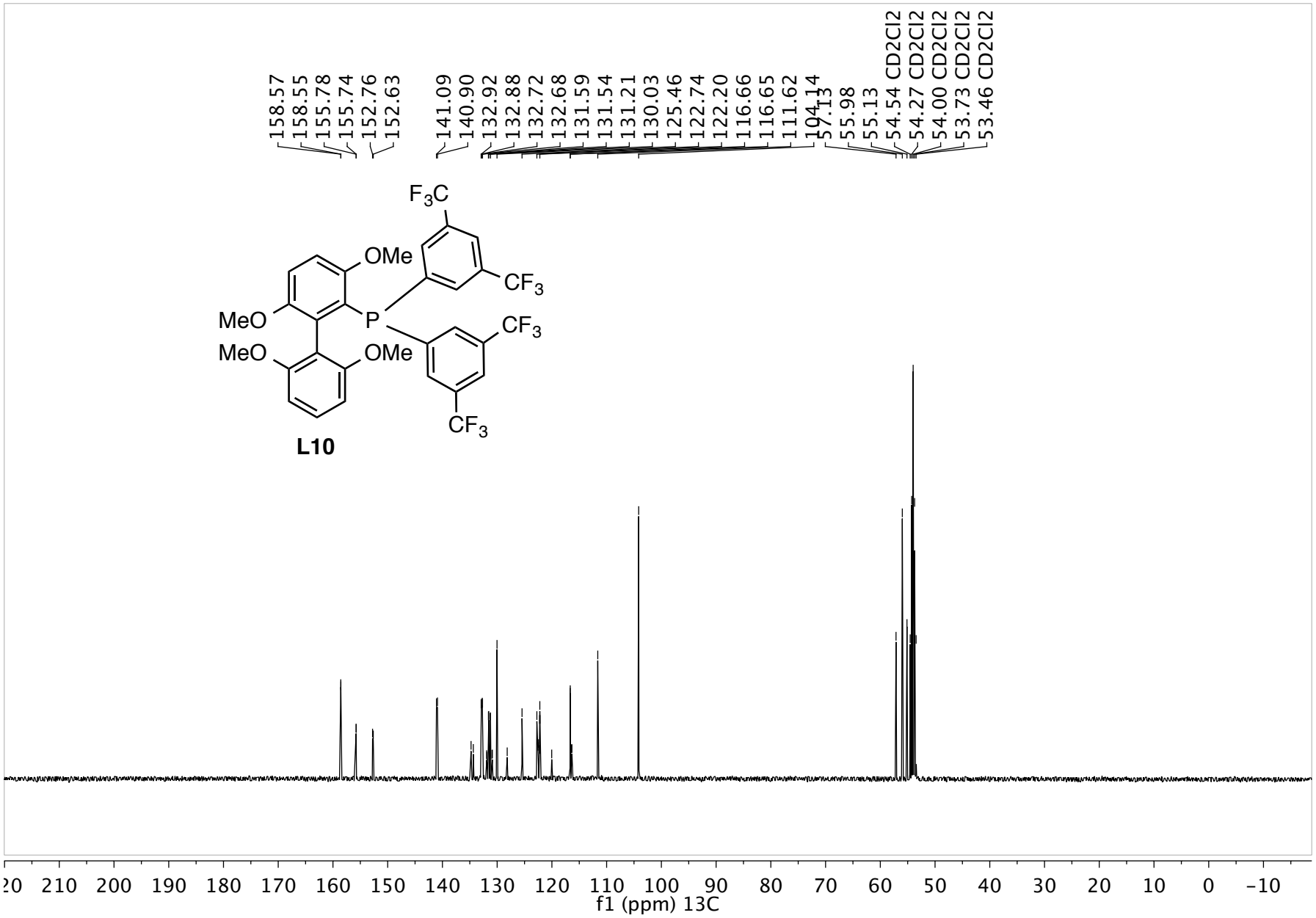

7.86
7.78
7.76
7.65
7.64
7.38
7.36
7.34
7.26
7.23
7.21
7.14
7.12
7.10
7.04
7.02
6.91
6.89
5.32 CD2Cl2
3.81
3.35
2.20
CF3
OMe
MeO
P
CF3
Me2N
CF3
F3C
L9
1.00
2.90
1.94
1.00
2.01
1.03
1.00
1.00
3.01
3.04
6.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

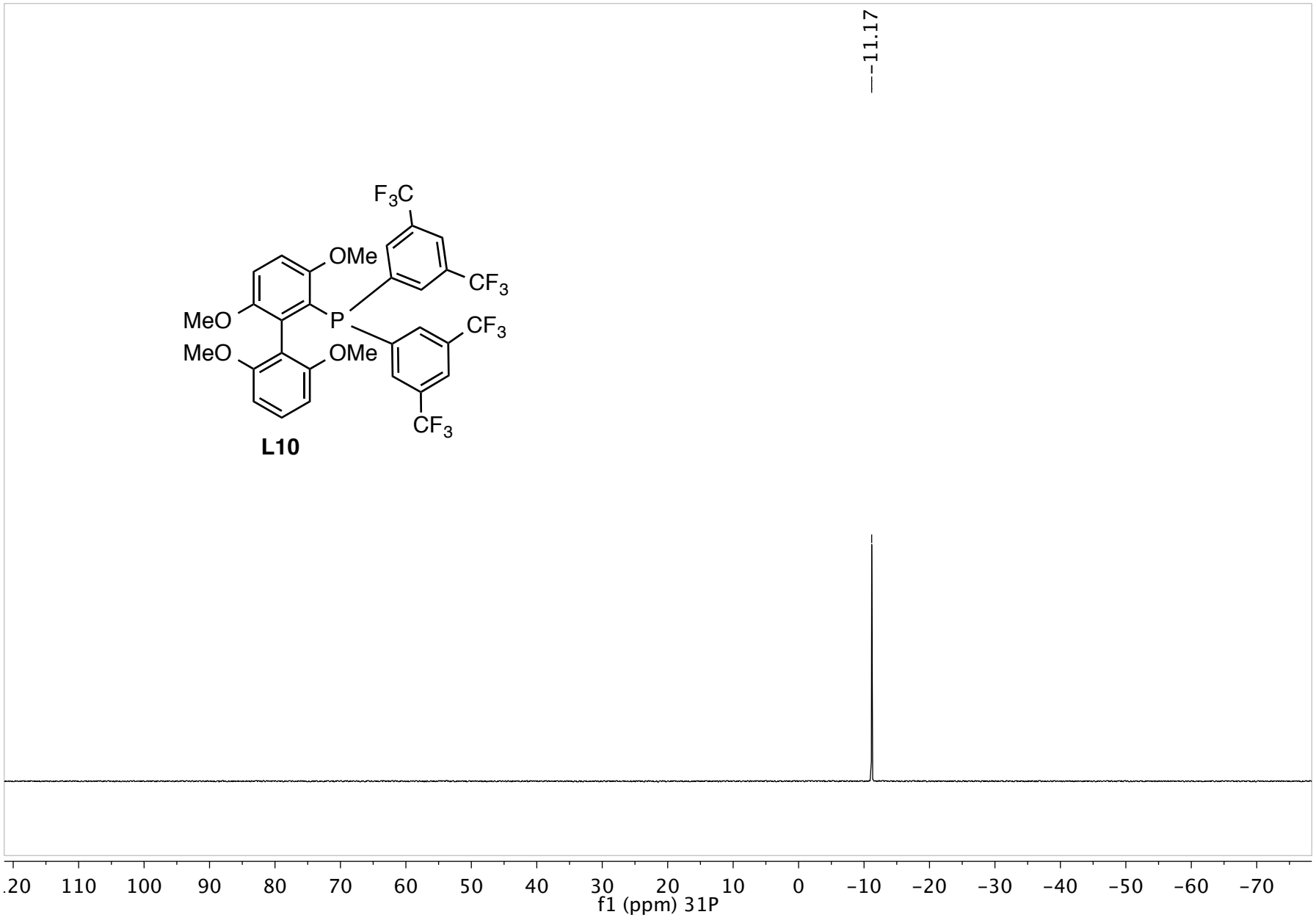

155.82
155.79
153.07
153.04
152.09
151.96
142.66
142.44
141.25
141.07
139.59
139.19
133.24
133.01
132.69
132.33
132.17
132.13
132.06
131.97
131.54
131.50
131.40
131.34
131.22
131.17
131.07
131.01
130.69
129.21
128.27
128.13
125.56
125.42
122.85
122.71
122.35
122.31
122.27
122.23
122.19
121.71
121.65
121.52
118.32
116.56
116.55
111.69
56.65
55.11
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
42.89
CF3
OMe
MeO
P
CF3
Me2N
CF3
F3C
L9
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C

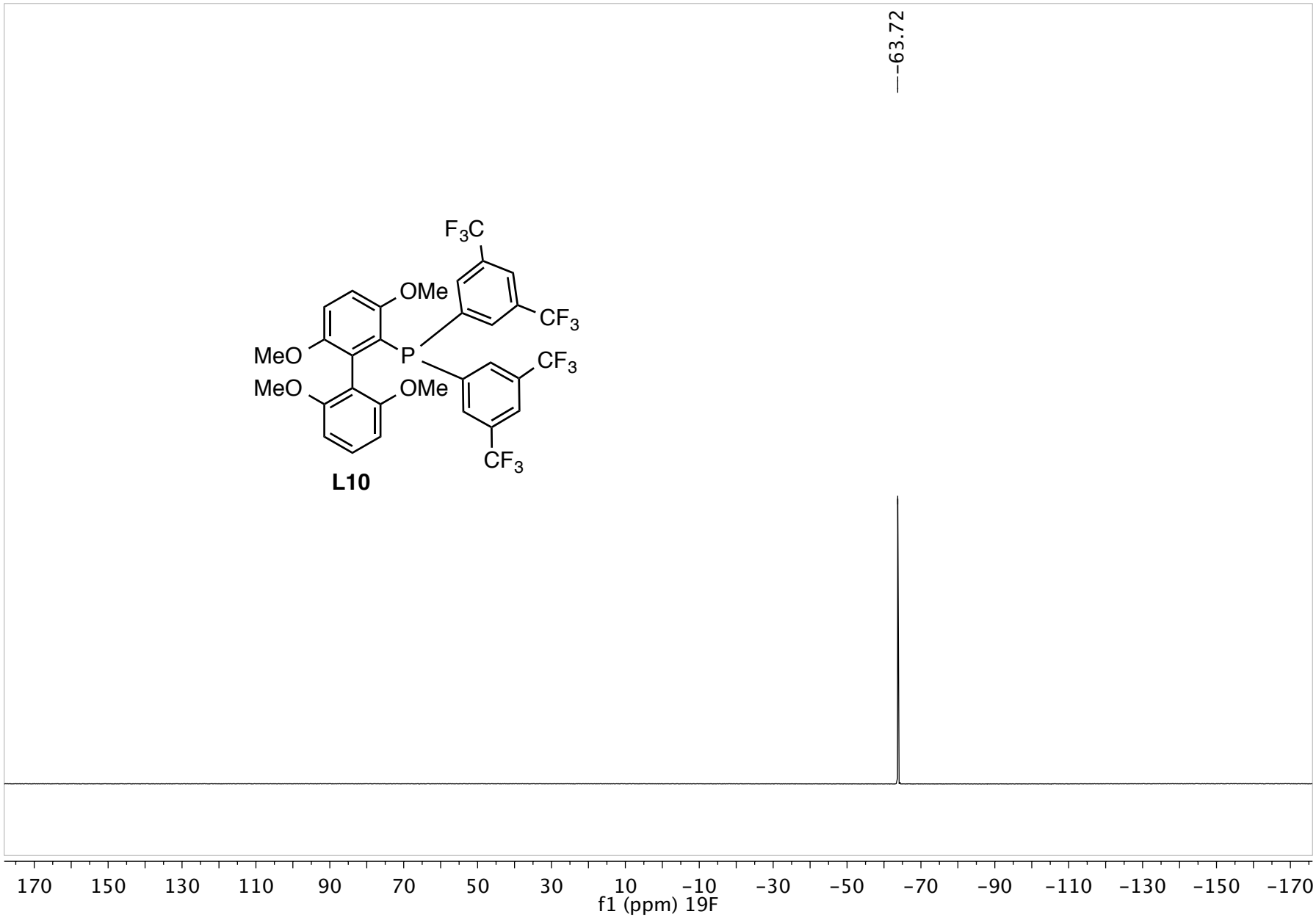

-11.13
CF3
OMe
MeO
P
CF3
Me2N
CF3
F3C
L9
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

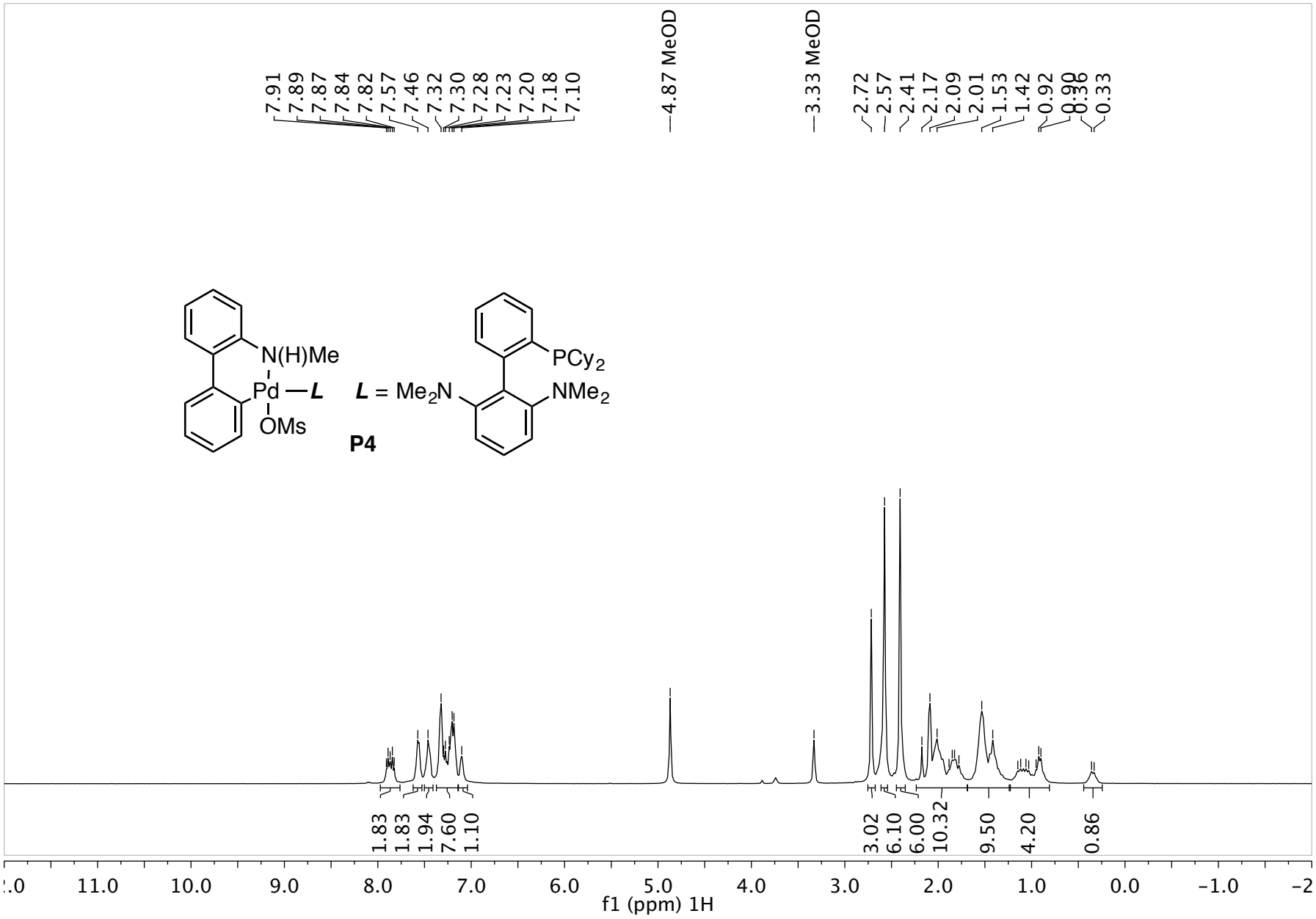

-63.61
-63.68
CF3
OMe
MeO
P
CF3
Me2N
CF3
F3C
L9
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm) 19F

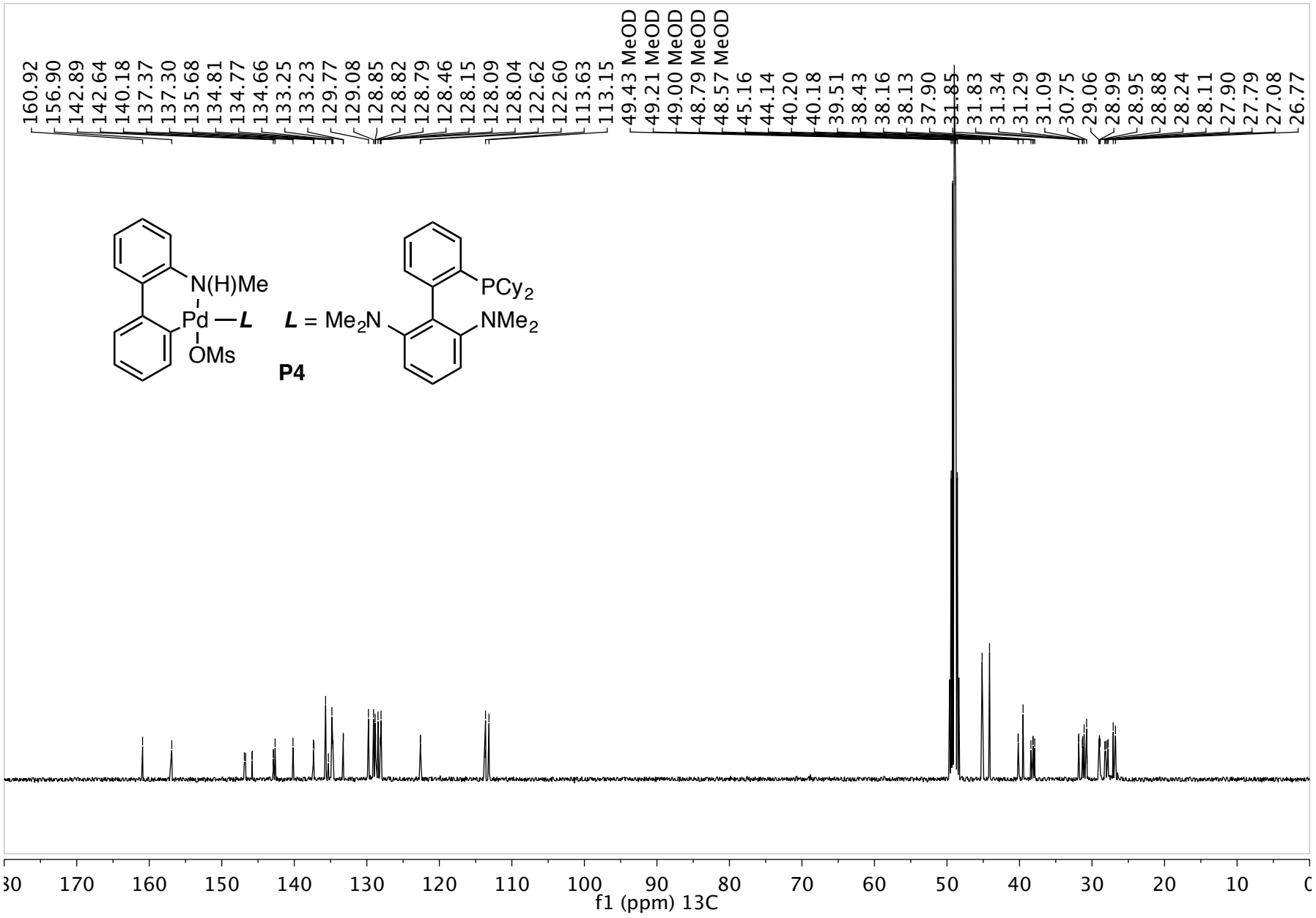

7.83
7.81
7.79
7.40
7.38
7.36
7.18
7.16
6.87
6.85
6.69
6.67
5.32 CD2Cl2
3.72
3.65
3.37
F3C
OMe
CF3
MeO
P
CF3
MeO
OMe
CF3
L10
5.98
1.01
1.00
1.02
2.05
2.97
5.83
2.96
f1 (ppm) 1H

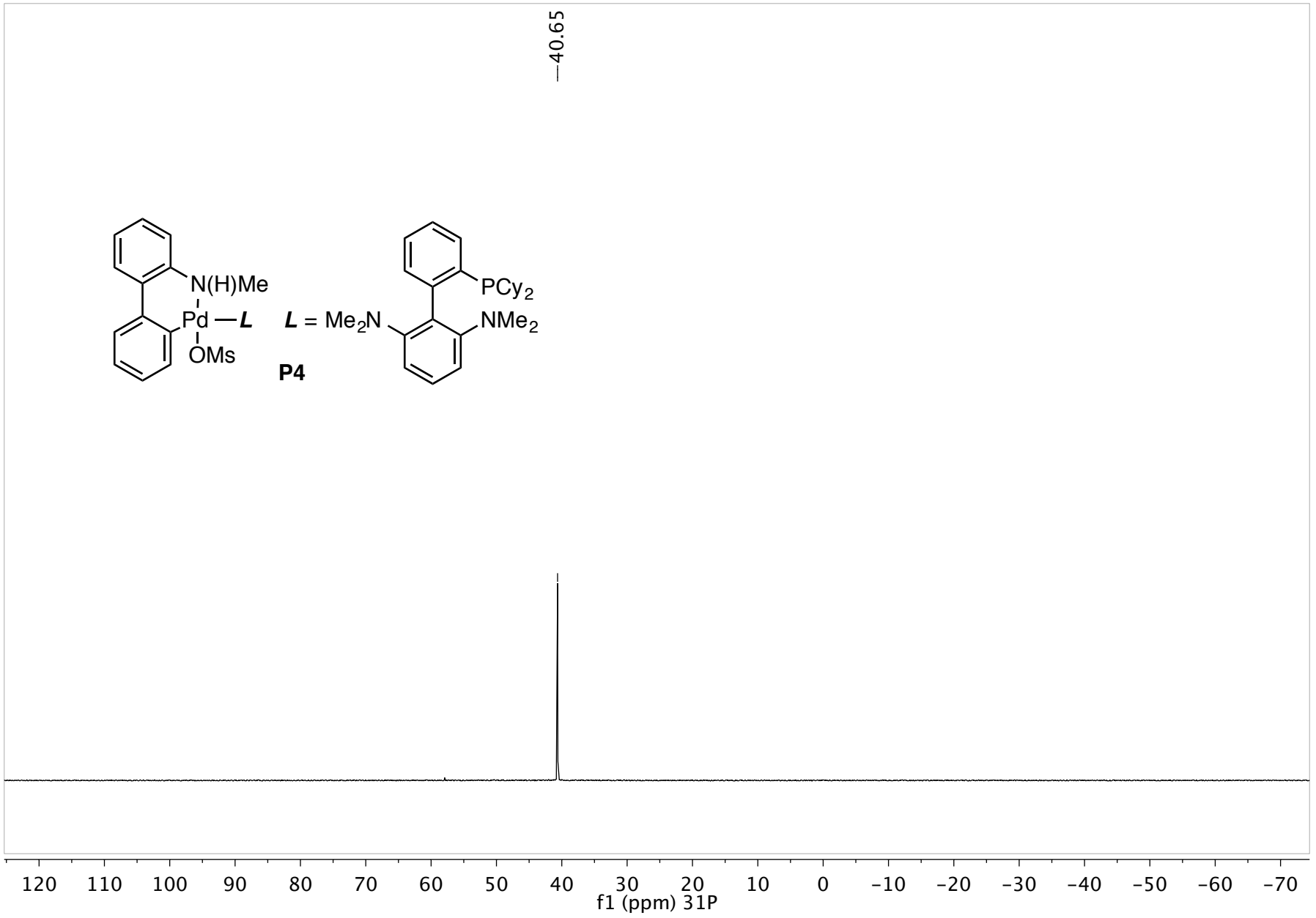

158.57
158.55
155.78
155.74
152.76
152.63
141.09
140.90
132.92
132.88
132.72
132.68
131.59
131.54
131.21
130.03
125.46
122.74
122.20
116.66
116.65
111.62
104.14
57.13
55.98
55.13
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
F3C
OMe
CF3
MeO
P
CF3
MeO
OMe
CF3
L10
f1 (ppm) 13C

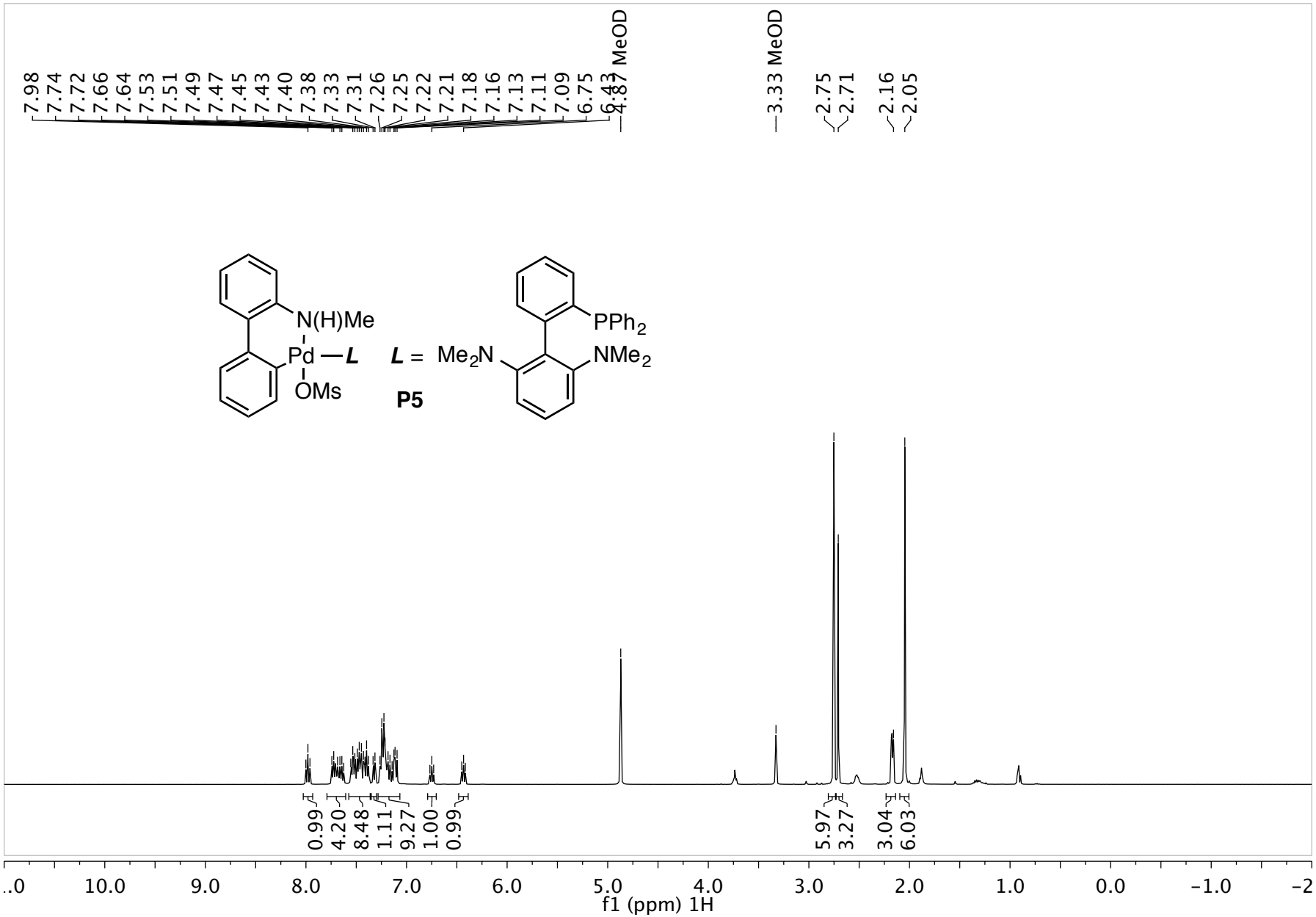

−11.17
F3C
OMe
CF3
MeO
P
CF3
MeO
OMe
CF3
L10
.20
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
f1 (ppm) 31P

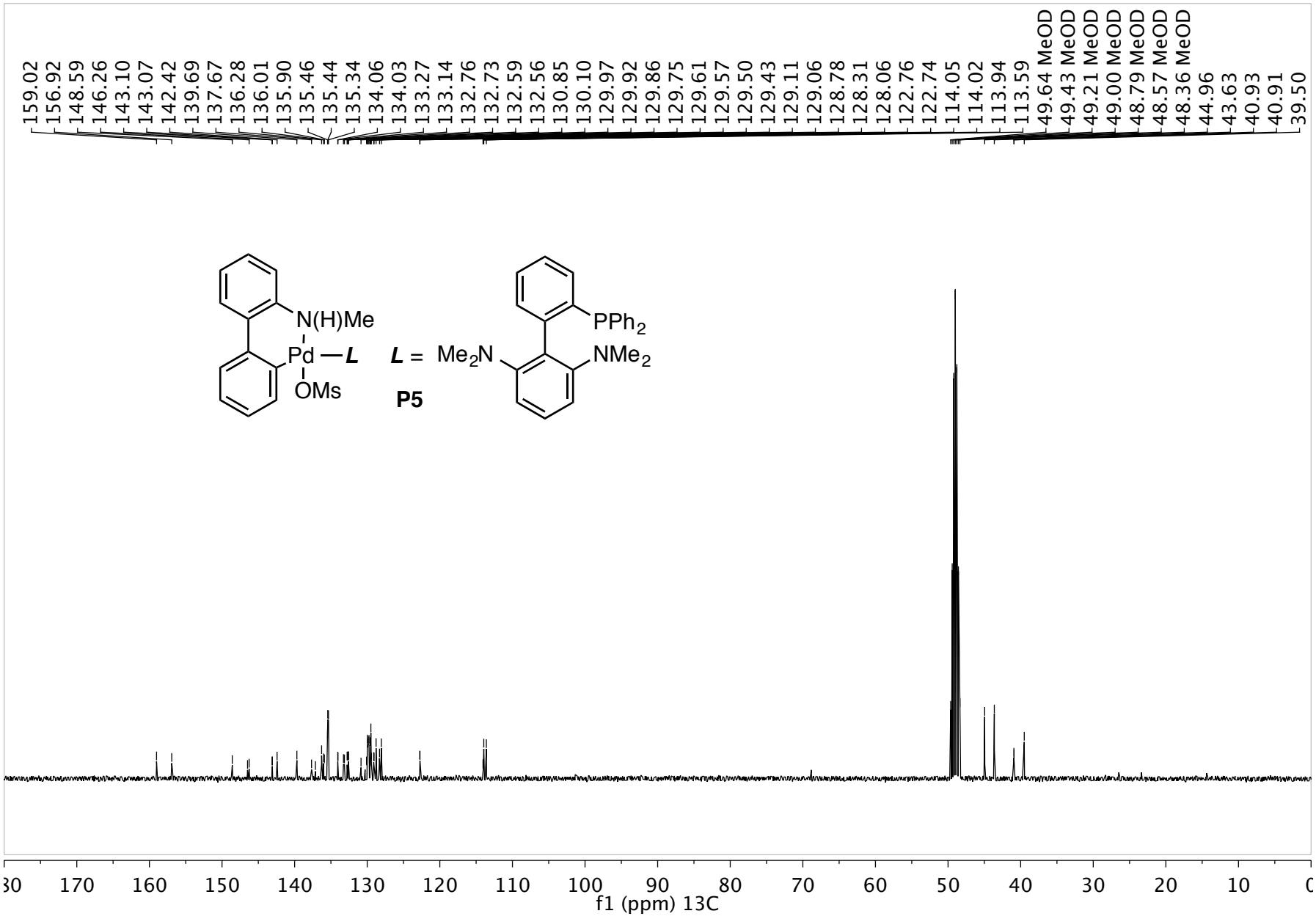

−63.72
F3C
OMe
CF3
MeO
P
CF3
MeO
OMe
CF3
L10
170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170
f1 (ppm) 19F

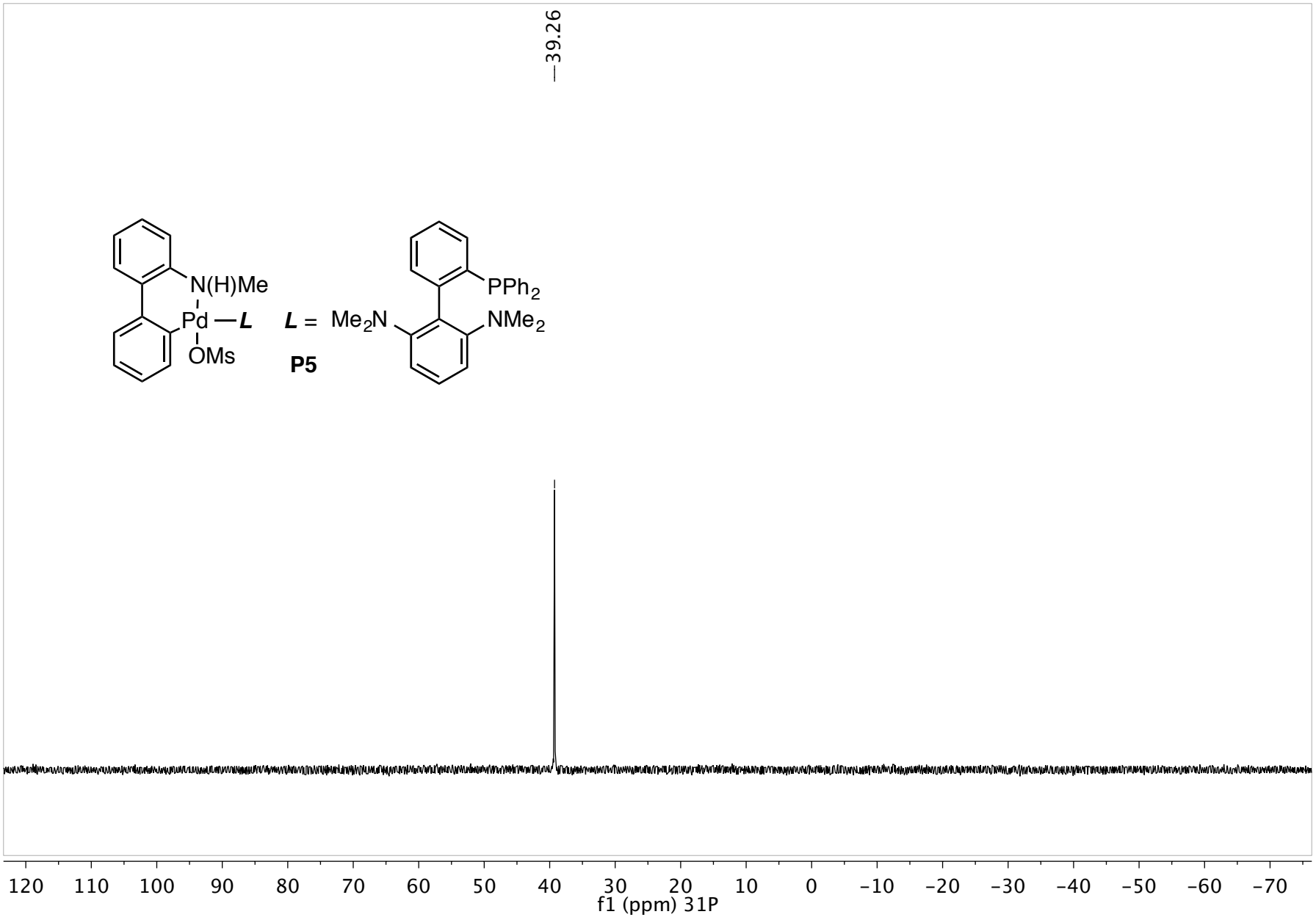

7.91
7.89
7.87
7.84
7.82
7.57
7.46
7.32
7.30
7.28
7.23
7.20
7.18
7.10
4.87 MeOD
3.33 MeOD
2.72
2.57
2.41
2.17
2.09
2.01
1.53
1.42
0.92
0.90
0.38
0.33
N(H)Me
Pd — L
OMs
L = Me2N
PCy2
NMe2
P4
1.83
1.83
1.94
7.60
1.10
3.02
6.10
6.00
10.32
9.50
4.20
0.86
f1 (ppm) 1H

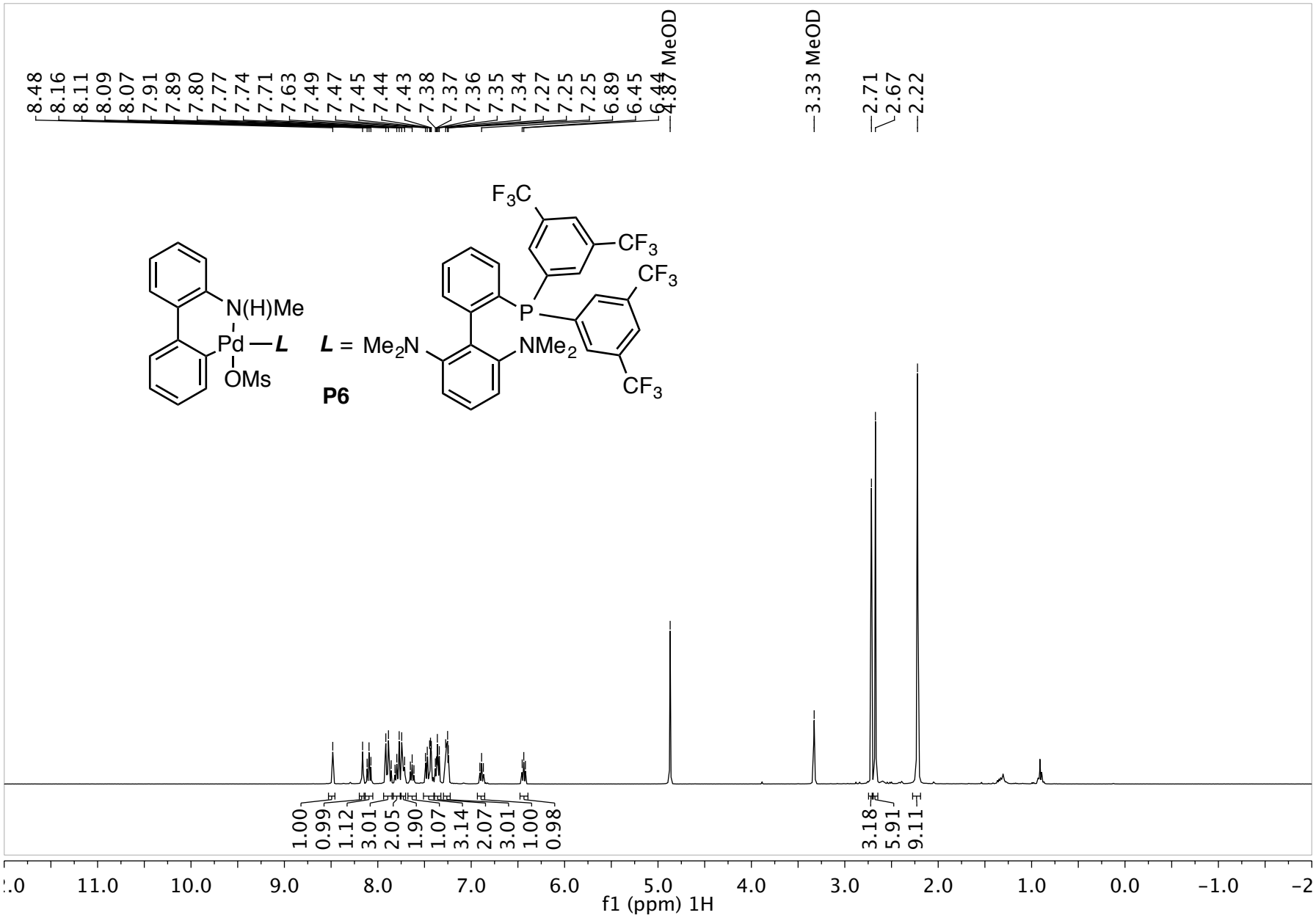

160.92
156.90
142.89
142.64
140.18
137.37
137.30
135.68
134.81
134.77
134.66
133.25
133.23
129.77
129.08
128.85
128.82
128.79
128.46
128.15
128.09
128.04
122.62
122.60
113.63
113.15
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.57 MeOD
45.16
44.14
40.20
40.18
39.51
38.43
38.16
38.13
37.90
31.85
31.83
31.34
31.29
31.09
30.75
29.06
28.99
28.95
28.88
28.24
28.11
27.90
27.79
27.08
26.77
N(H)Me
Pd — L
OMs
L = Me2N
PCy2
NMe2
P4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C

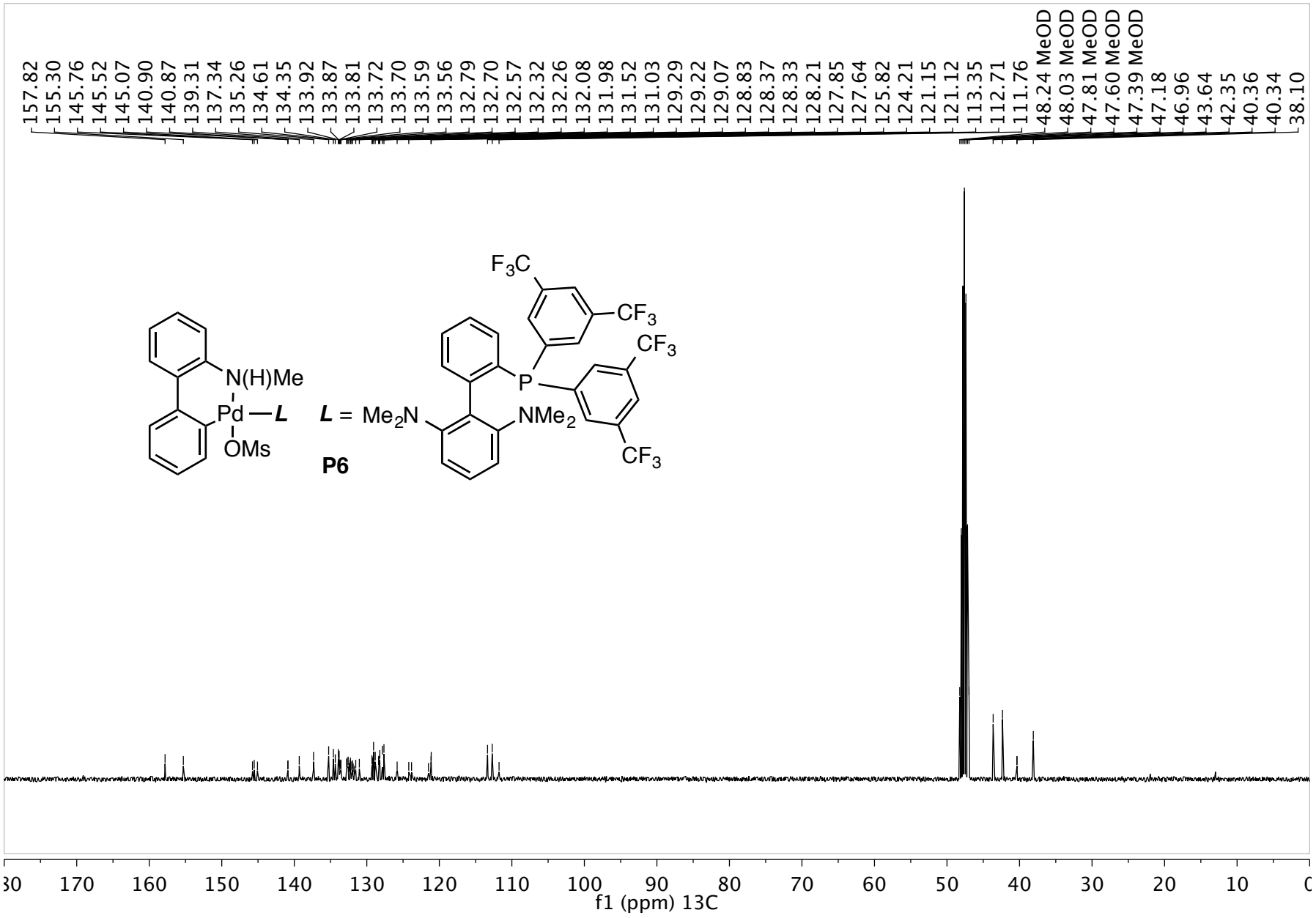

—40.65
N(H)Me
Pd —L
OMs
L = Me2N
PCy2
NMe2
P4
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

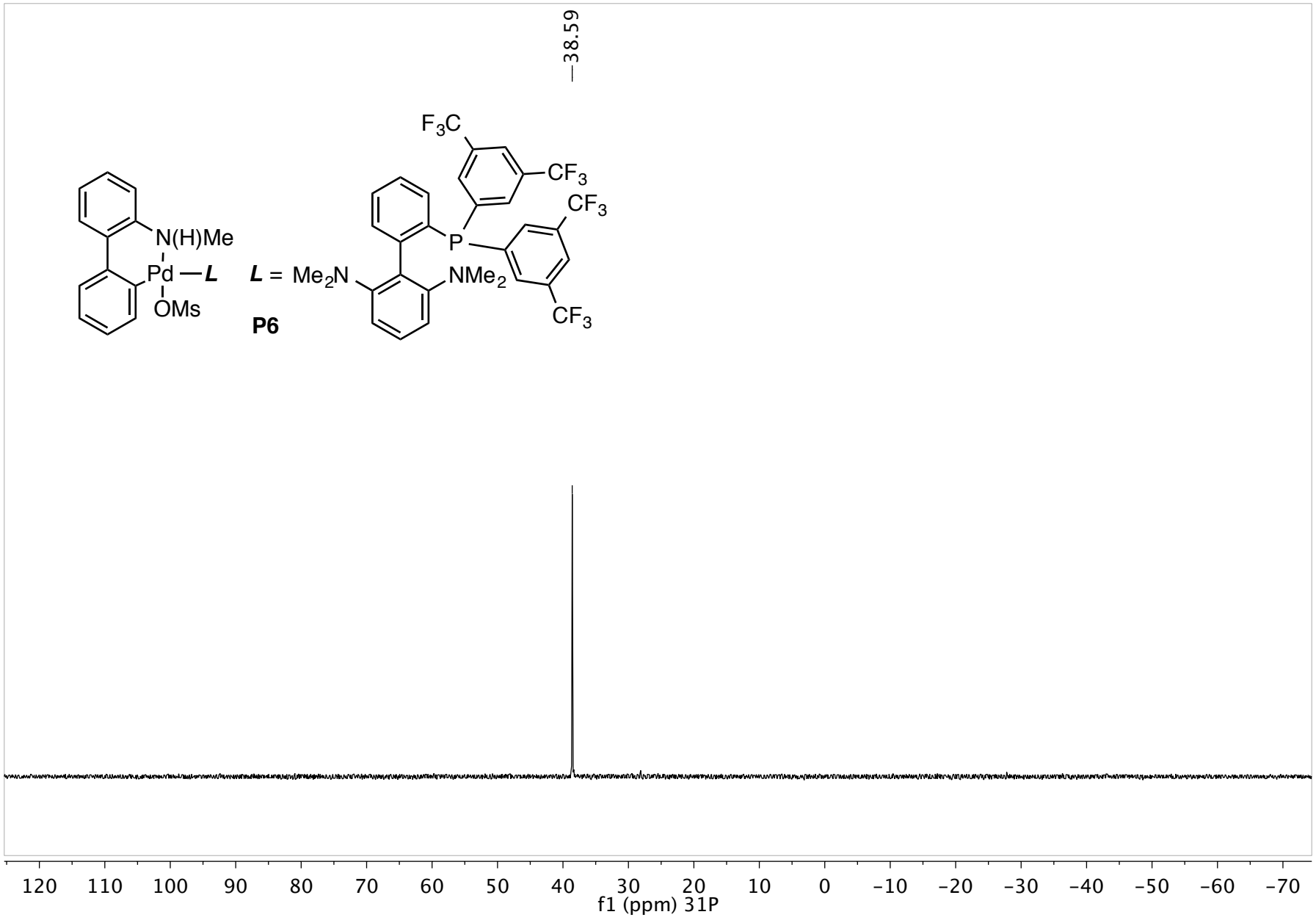

7.98
7.74
7.72
7.66
7.64
7.53
7.51
7.49
7.47
7.45
7.43
7.40
7.38
7.33
7.31
7.26
7.25
7.22
7.21
7.18
7.16
7.13
7.11
7.09
6.75
6.43
4.87 MeOD
3.33 MeOD
2.75
2.71
2.16
2.05
N(H)Me
Pd—L
OMs
L = Me2N
PPh2
NMe2
P5
0.99
4.20
8.48
1.11
9.27
1.00
0.99
5.97
3.27
3.04
6.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

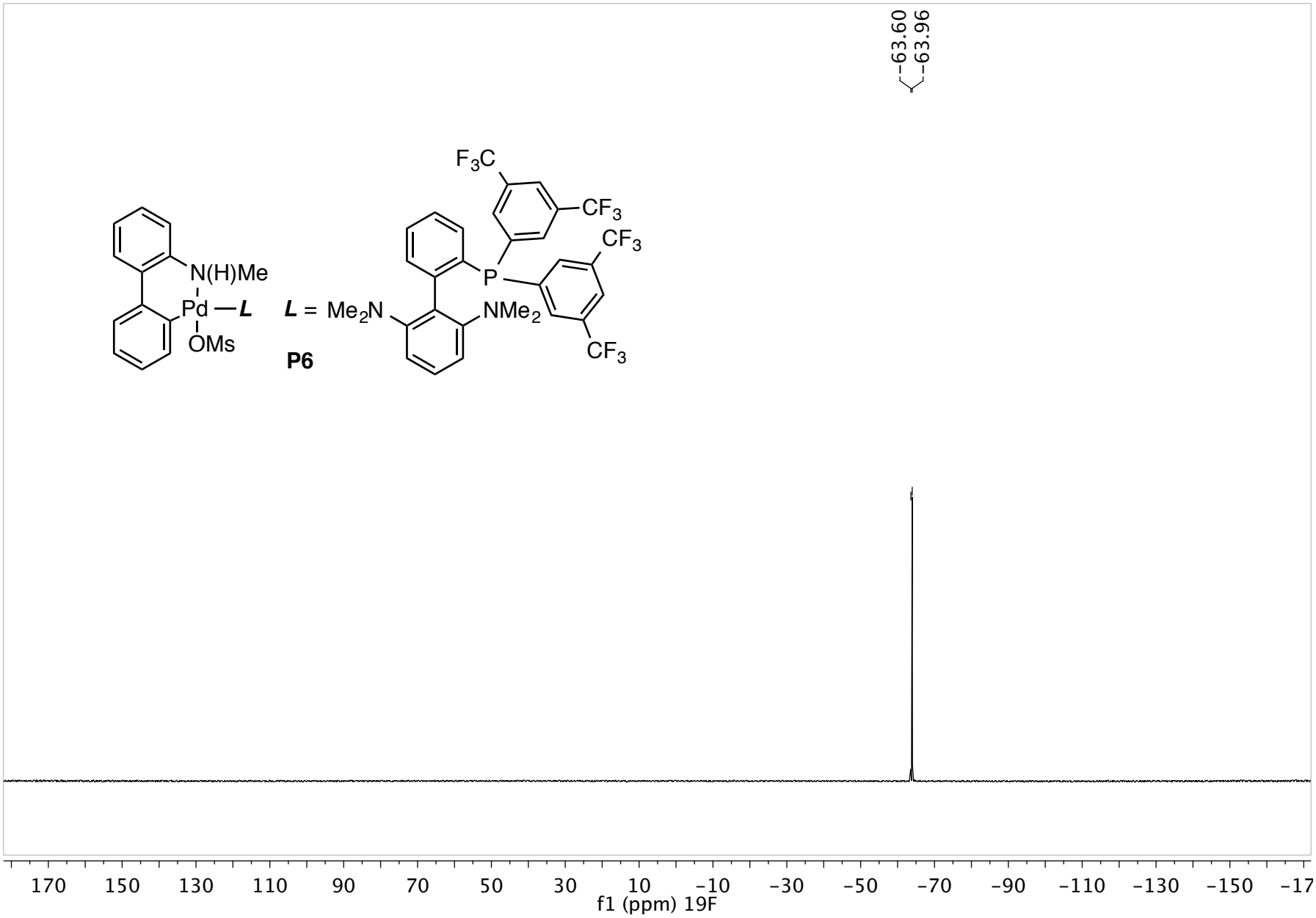

159.02
156.92
148.59
146.26
143.10
143.07
142.42
139.69
137.67
136.28
136.01
135.90
135.46
135.44
135.34
134.06
134.03
133.27
133.14
132.76
132.73
132.59
132.56
130.85
130.10
129.97
129.92
129.86
129.75
129.61
129.57
129.50
129.43
129.11
129.06
128.78
128.31
128.06
122.76
122.74
114.05
114.02
113.94
113.59
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.57 MeOD
48.36 MeOD
44.96
43.63
40.93
40.91
39.50
N(H)Me
Pd —L
OMs
L = Me2N
PPh2
NMe2
P5
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C

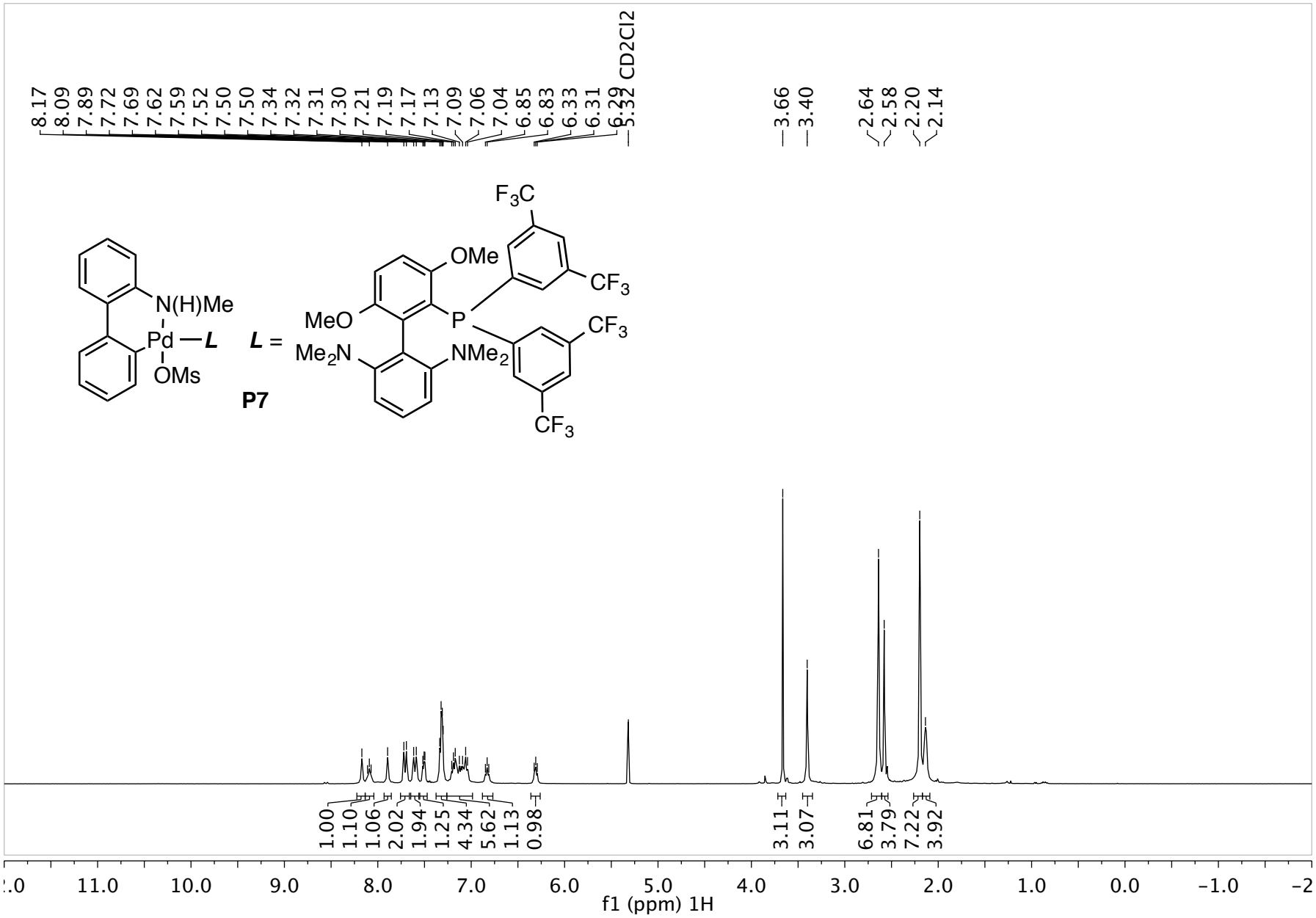

39.26
N(H)Me
Pd — L
OMs
L =
Me2N
PPh2
NMe2
P5
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

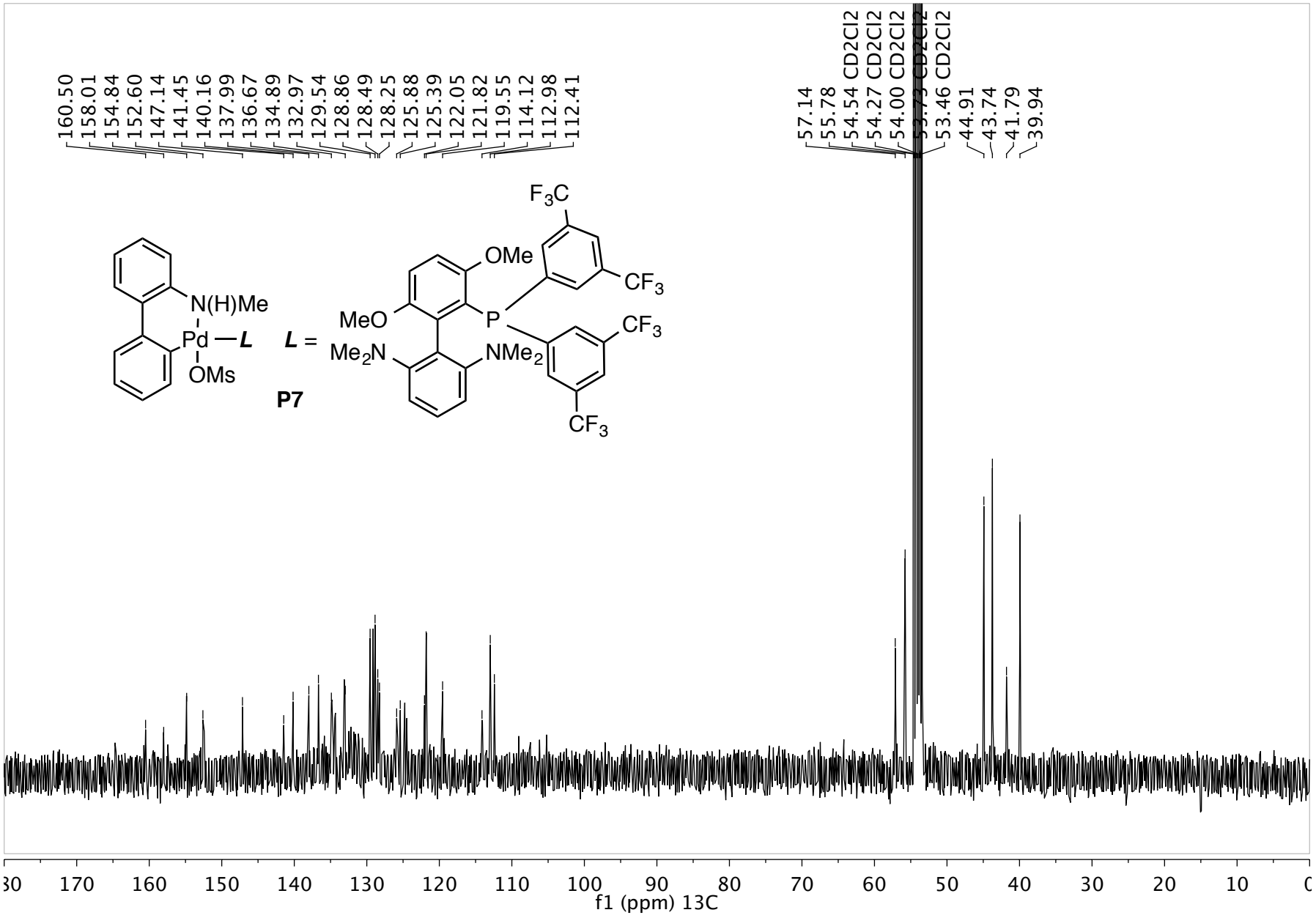

8.48
8.16
8.11
8.09
8.07
7.91
7.89
7.80
7.77
7.74
7.71
7.63
7.49
7.47
7.45
7.44
7.43
7.38
7.37
7.36
7.35
7.34
7.27
7.25
7.25
6.89
6.45
6.44
4.87 MeOD
3.33 MeOD
2.71
2.67
2.22
N(H)Me
Pd—L
OMs
L = Me2N
NMe2
P
F3C
CF3
CF3
CF3
P6
1.00
0.99
1.12
3.01
2.05
1.90
1.07
3.14
2.07
3.01
1.00
0.98
3.18
5.91
9.11
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

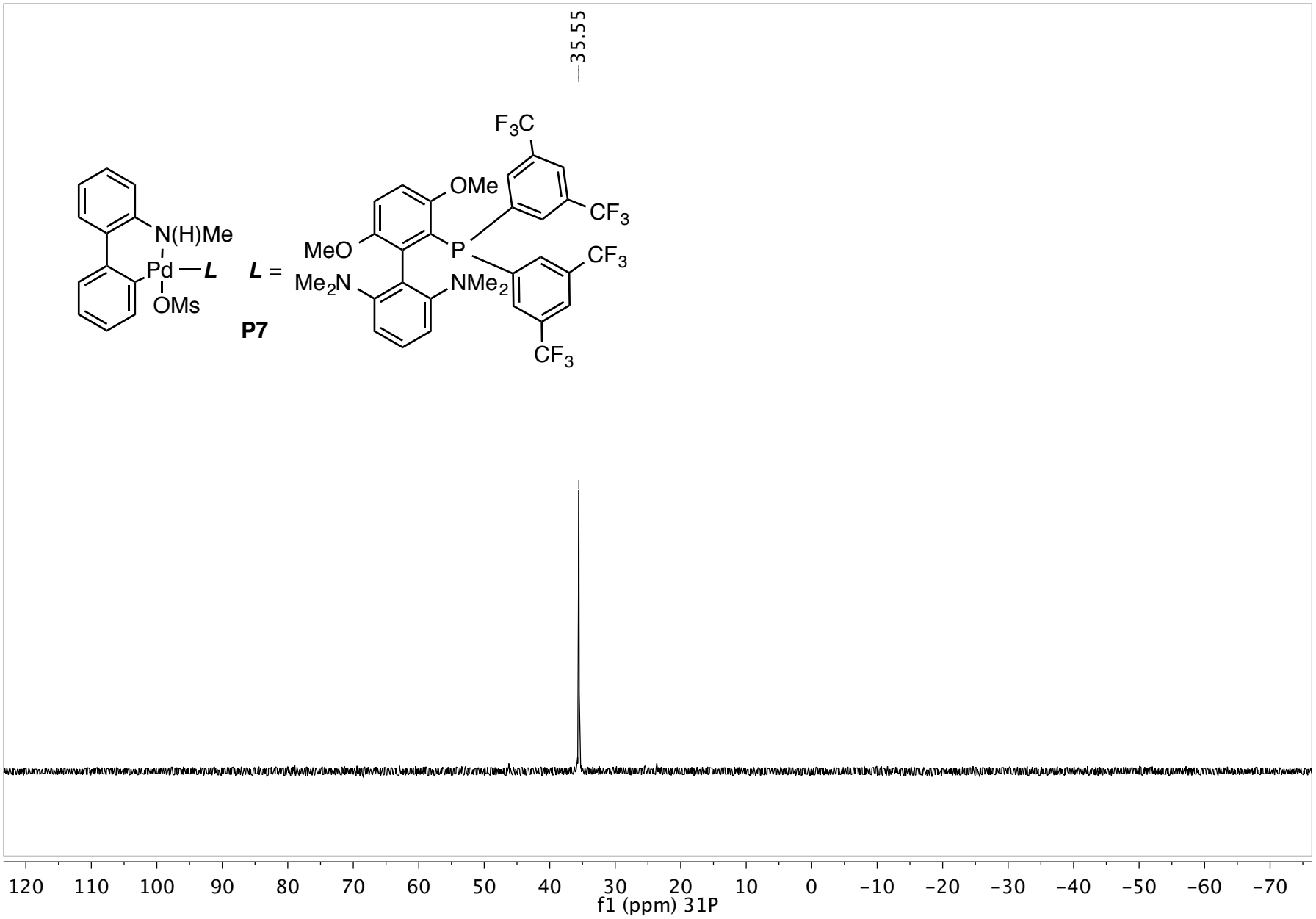

157.82
155.30
145.76
145.52
145.07
140.90
140.87
139.31
137.34
135.26
134.61
134.35
133.92
133.87
133.81
133.72
133.70
133.59
133.56
132.79
132.70
132.57
132.32
132.26
132.08
131.98
131.52
131.03
129.29
129.22
129.07
128.83
128.37
128.33
128.21
127.85
127.64
125.82
124.21
121.15
121.12
113.35
112.71
111.76
48.24 MeOD
48.03 MeOD
47.81 MeOD
47.60 MeOD
47.39 MeOD
47.18
46.96
43.64
42.35
40.36
40.34
38.10
N(H)Me
Pd — L
OMs
L = Me2N
NMe2
P
F3C
CF3
CF3
CF3
P6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C

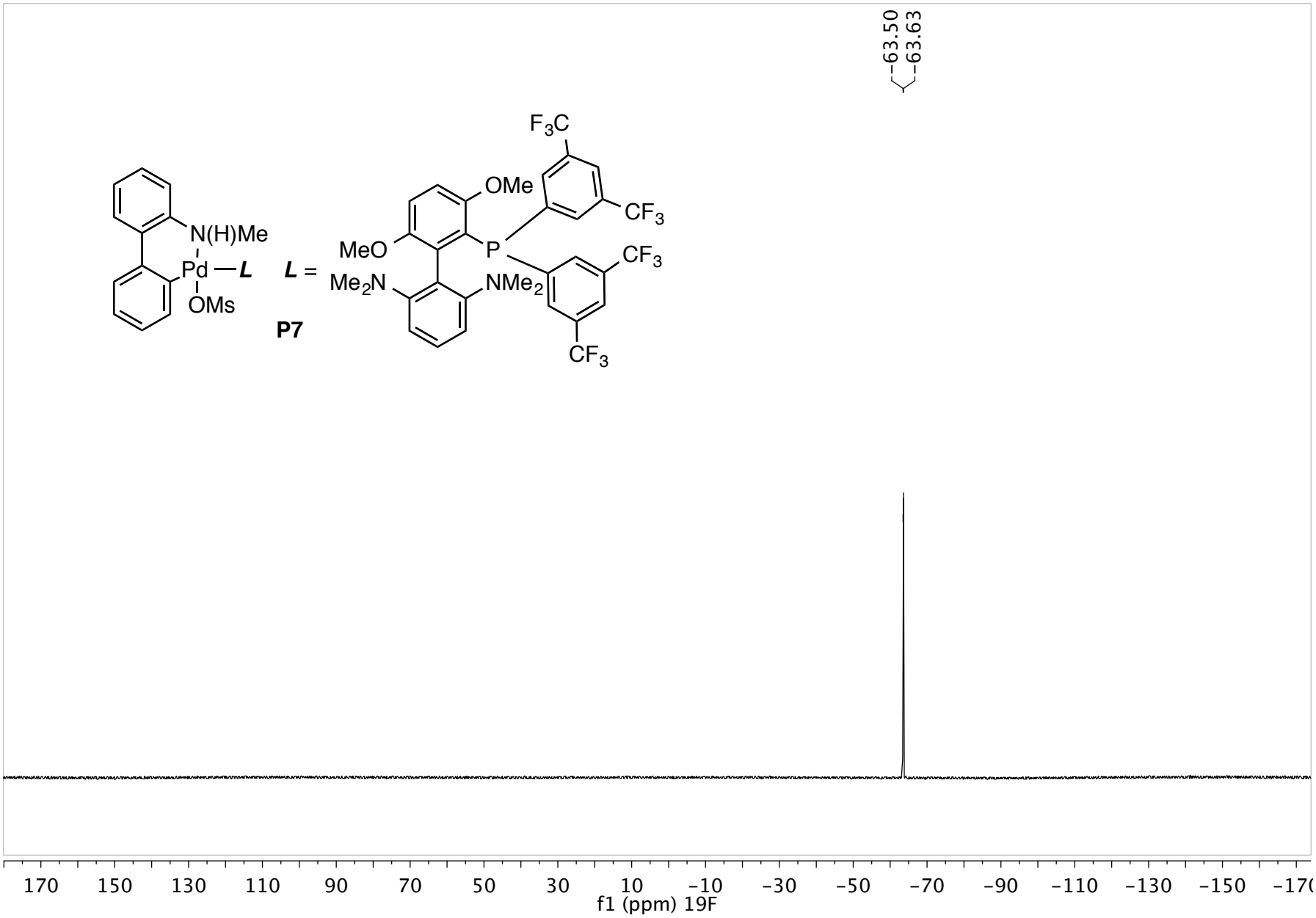

38.59
N(H)Me
Pd —L
OMs
L = Me2N
NMe2
P
F3C
CF3
CF3
CF3
P6
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

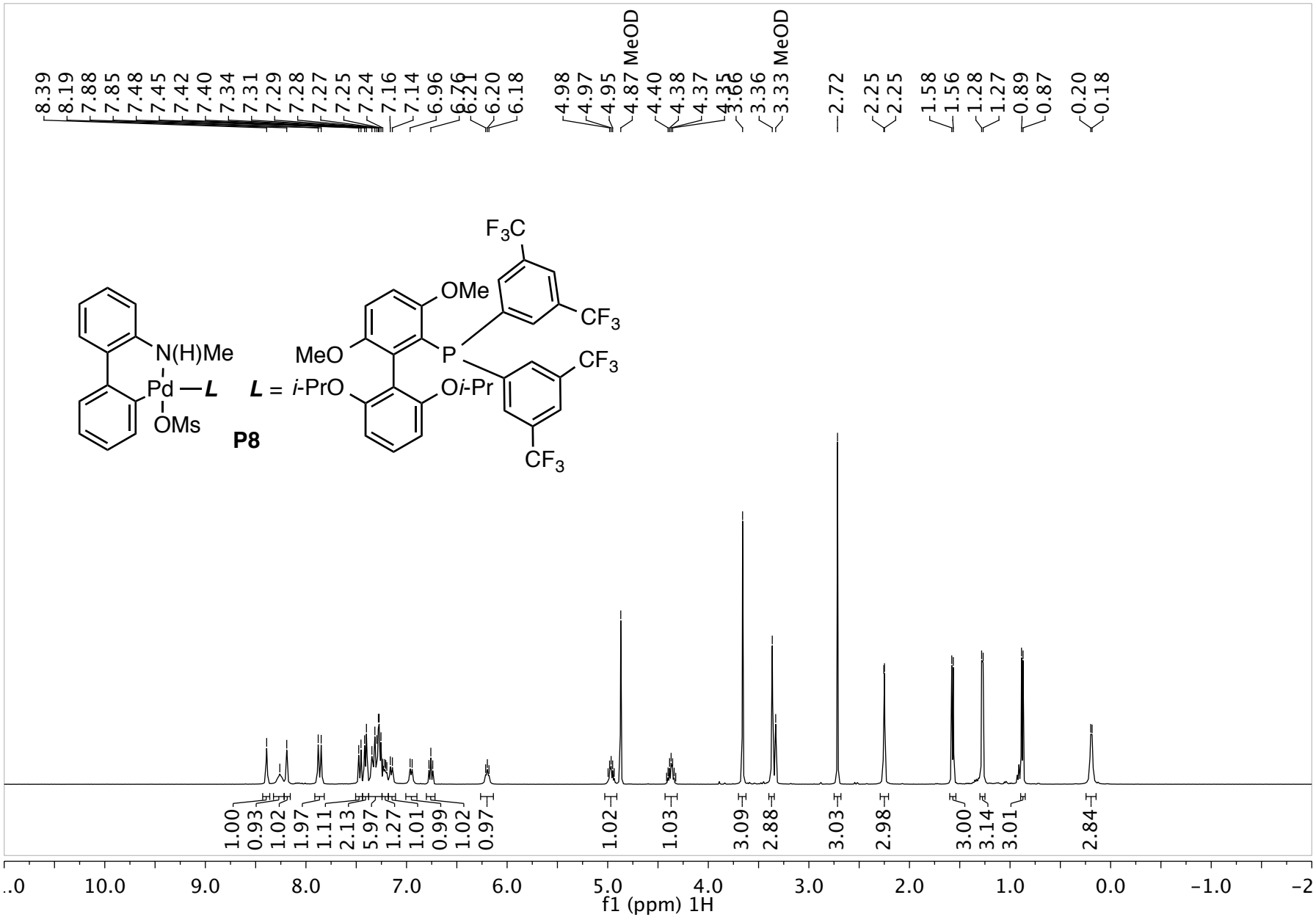

-63.60
-63.96
N(H)Me
Pd —L
OMs
L = Me2N
NMe2
P
F3C
CF3
CF3
CF3
P6
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-17
f1 (ppm) 19F

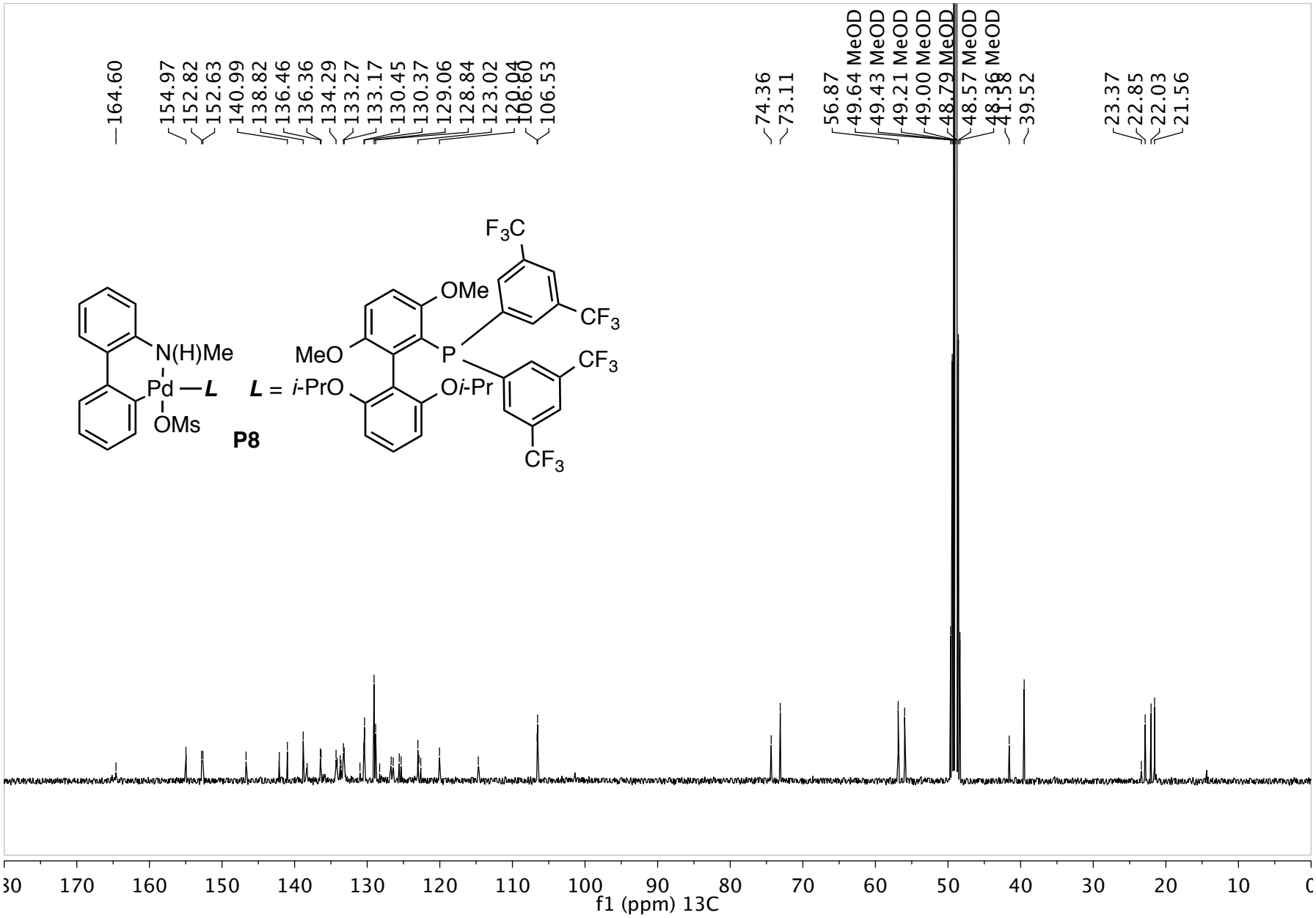

8.17
8.09
7.89
7.72
7.69
7.62
7.59
7.52
7.50
7.50
7.34
7.32
7.31
7.30
7.21
7.19
7.17
7.13
7.09
7.06
7.04
6.85
6.83
6.33
6.31
6.29
5.32
CD2Cl2
3.66
3.40
2.64
2.58
2.20
2.14
N(H)Me
Pd
L
OMs
L =
P7
F3C
CF3
CF3
CF3
OMe
MeO
Me2N
NMe2
1.00
1.10
1.06
2.02
1.94
1.25
4.34
5.62
1.13
0.98
3.11
3.07
6.81
3.79
7.22
3.92
f1 (ppm) 1H

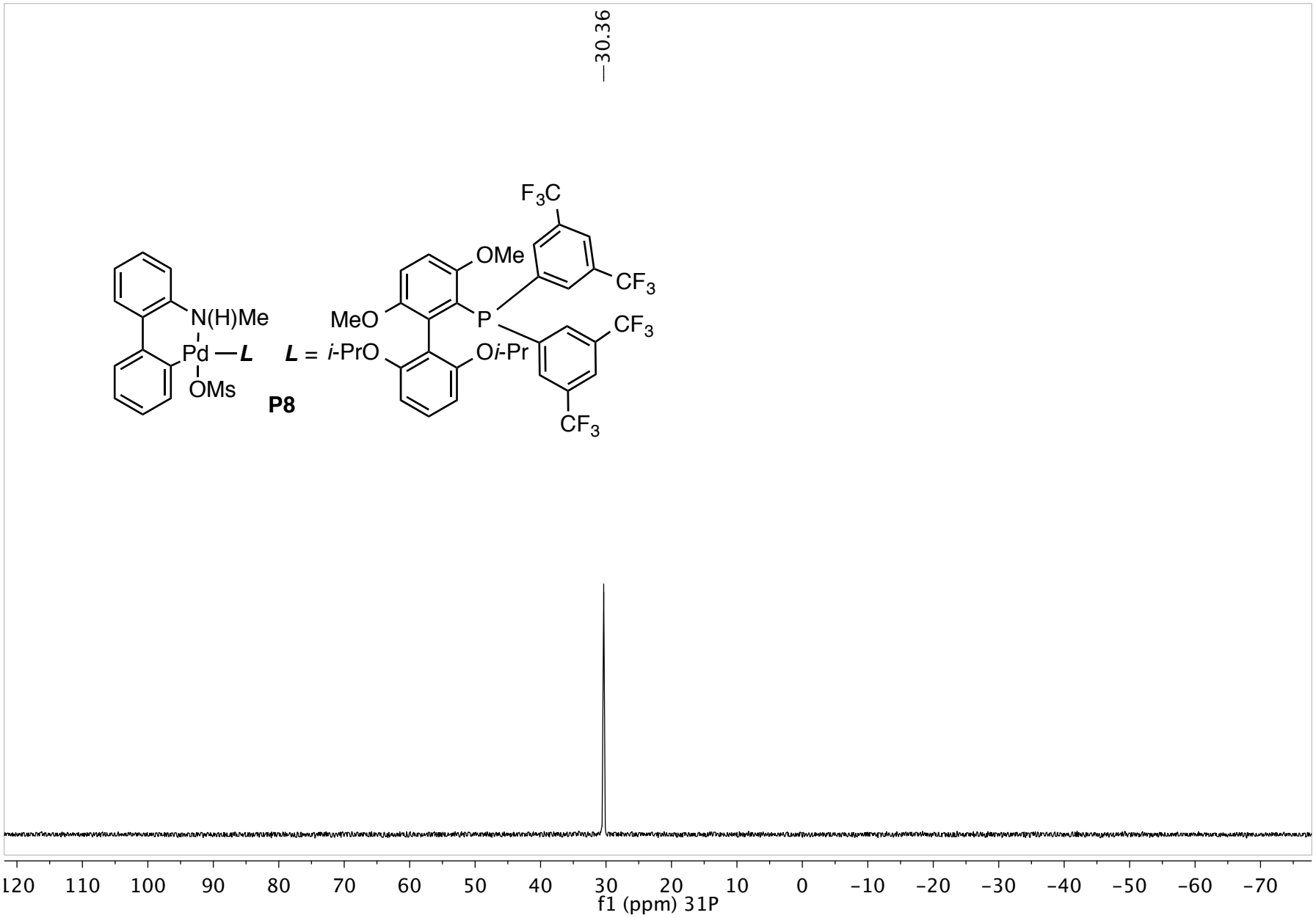

160.50
158.01
154.84
152.60
147.14
141.45
140.16
137.99
136.67
134.89
132.97
129.54
128.86
128.49
128.25
125.88
125.39
122.05
121.82
119.55
114.12
112.98
112.41
57.14
55.78
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.46 CD2Cl2
44.91
43.74
41.79
39.94
N(H)Me
Pd — L
OMs
L =
P7
F3C
CF3
OMe
MeO
P
CF3
Me2N
NMe2
CF3
f1 (ppm) 13C

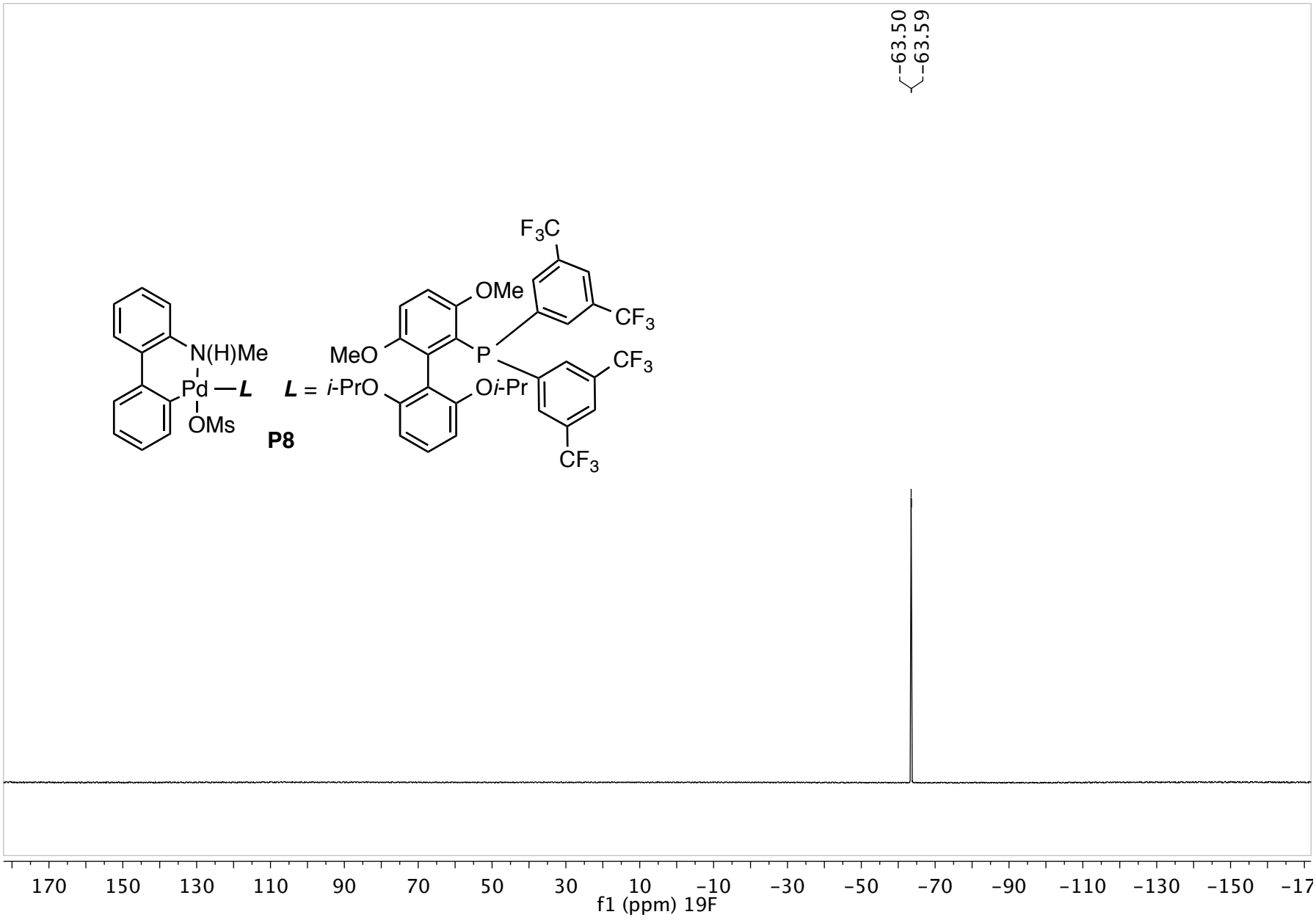

35.55
N(H)Me
Pd — L
OMs
L =
P7
F3C
CF3
CF3
CF3
OMe
MeO
Me2N
NMe2
P
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

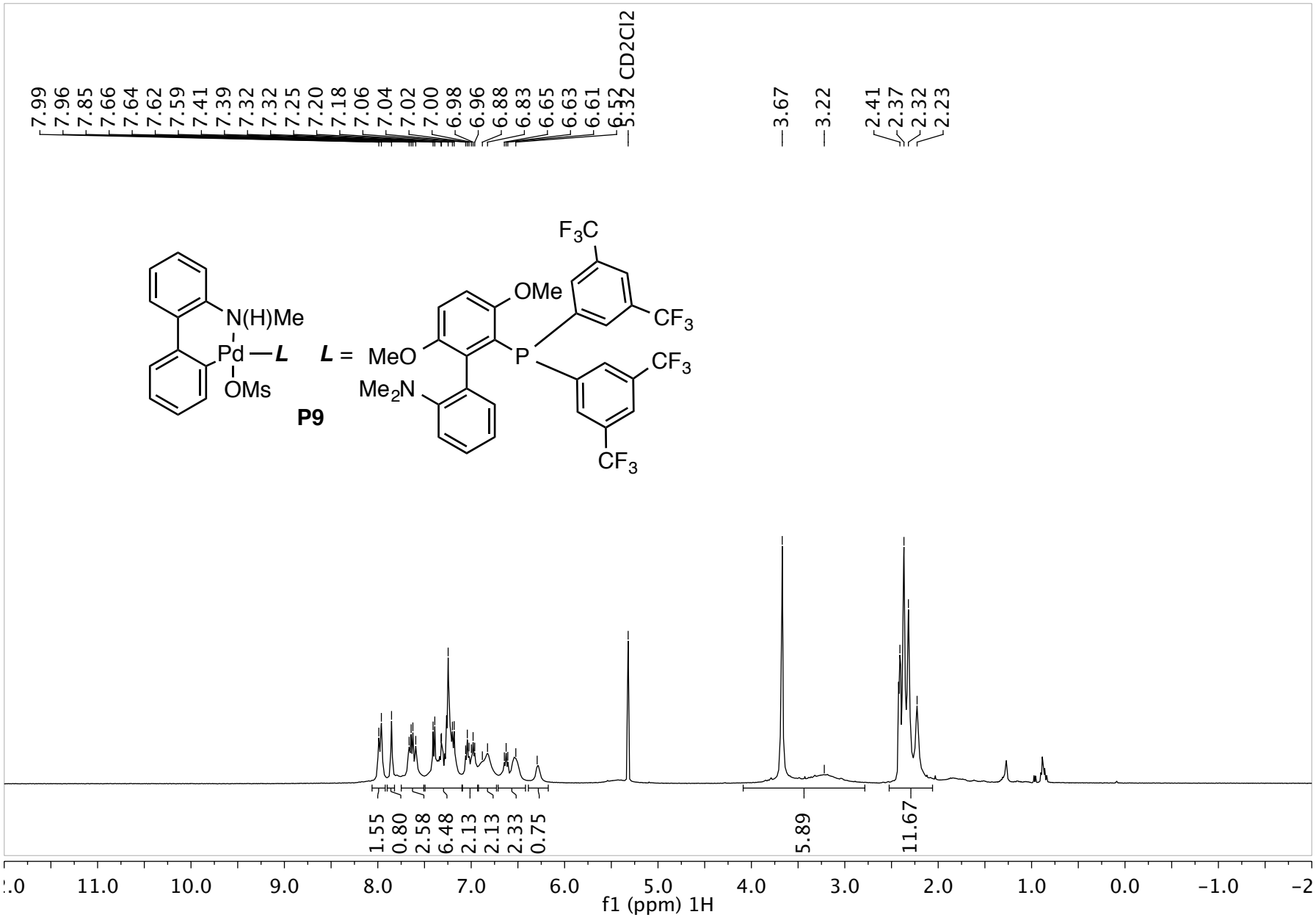

−63.50
−63.63
N(H)Me
Pd —L
OMs
L =
P7
F3C
OMe
CF3
MeO
P
CF3
Me2N
NMe2
CF3
170 150 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −17(
f1 (ppm) 19F

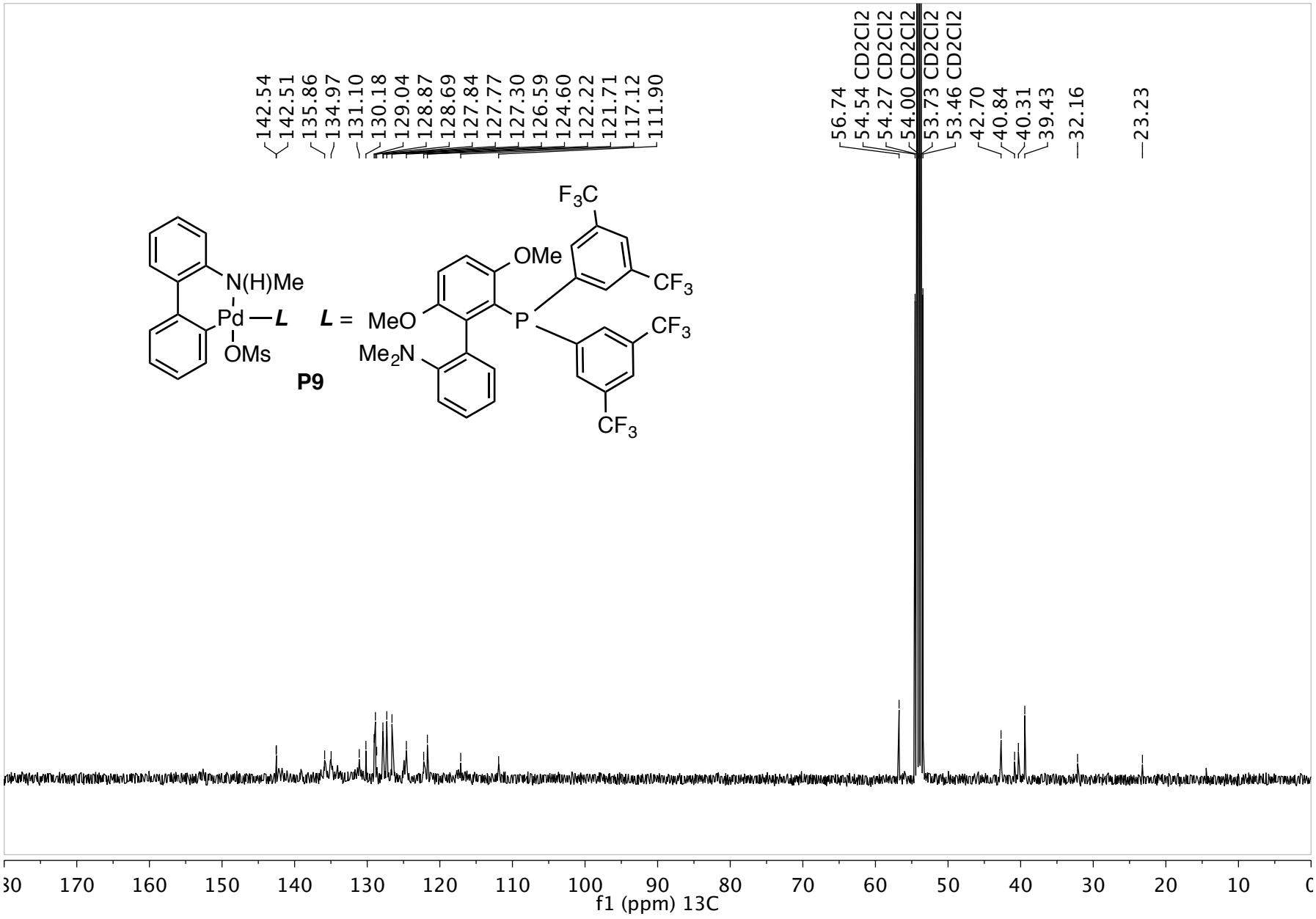

8.39
8.19
7.88
7.85
7.48
7.45
7.42
7.40
7.34
7.31
7.29
7.28
7.27
7.25
7.24
7.16
7.14
6.96
6.76
6.21
6.20
6.18
4.98
4.97
4.95
4.87 MeOD
4.40
4.38
4.37
4.35
3.66
3.36
3.33 MeOD
2.72
2.25
2.25
1.58
1.56
1.28
1.27
0.89
0.87
0.20
0.18
N(H)Me
Pd —L
OMs
P8
L = i-PrO
MeO
OMe
P
F3C
CF3
CF3
CF3
O i-Pr
1.00
0.93
1.02
1.97
1.11
2.13
5.97
1.27
1.01
0.99
1.02
0.97
1.02
1.03
3.09
2.88
3.03
2.98
3.00
3.14
3.01
2.84
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

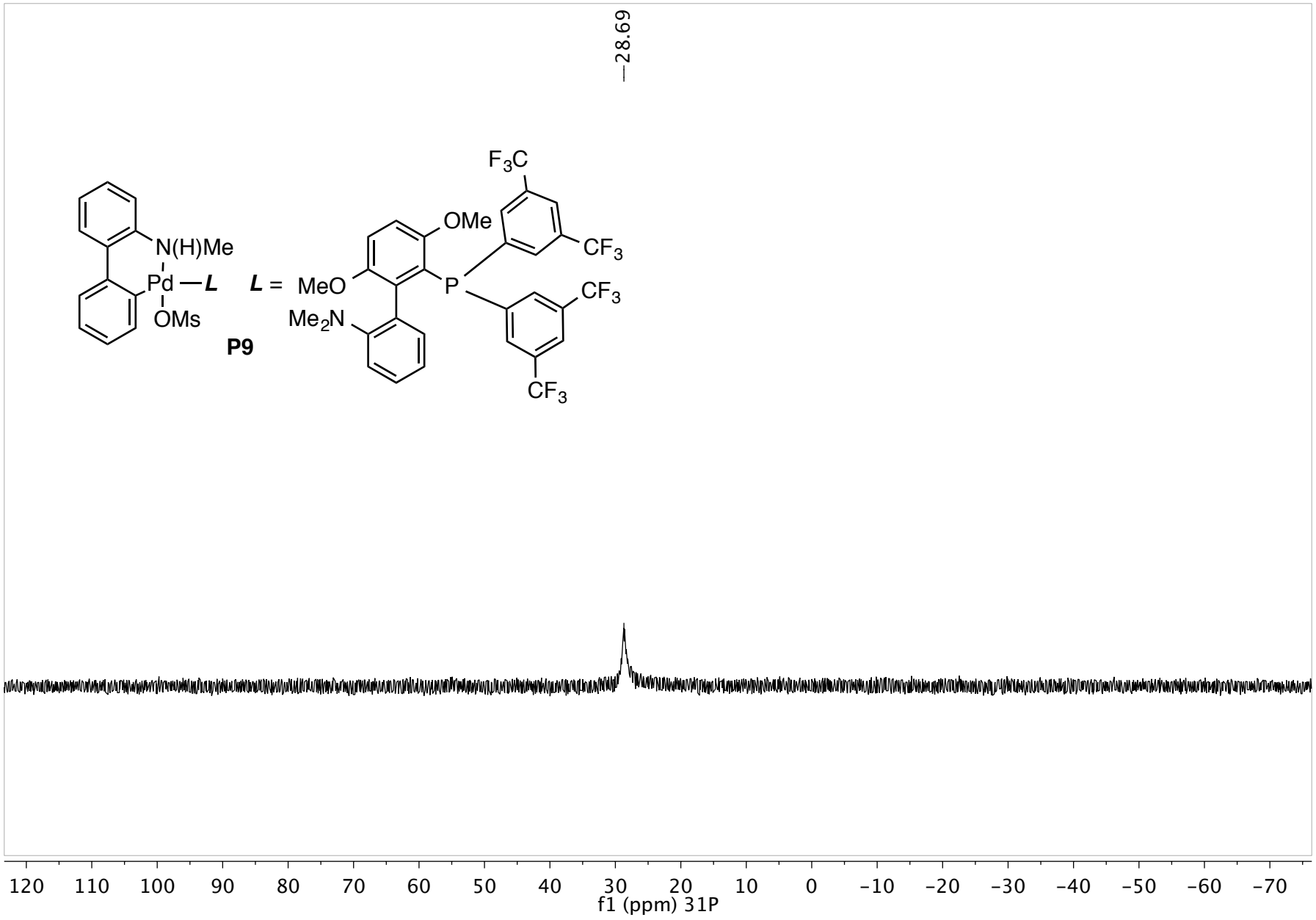

164.60
154.97
152.82
152.63
140.99
138.82
136.46
136.36
134.29
133.27
133.17
130.45
130.37
129.06
128.84
123.02
120.04
106.80
106.53
74.36
73.11
56.87
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.57 MeOD
48.36 MeOD
41.58
39.52
23.37
22.85
22.03
21.56
N(H)Me
Pd—L
OMs
L = i-PrO
P8
F3C
OMe
CF3
MeO
P
CF3
O i-Pr
CF3
f1 (ppm) 13C

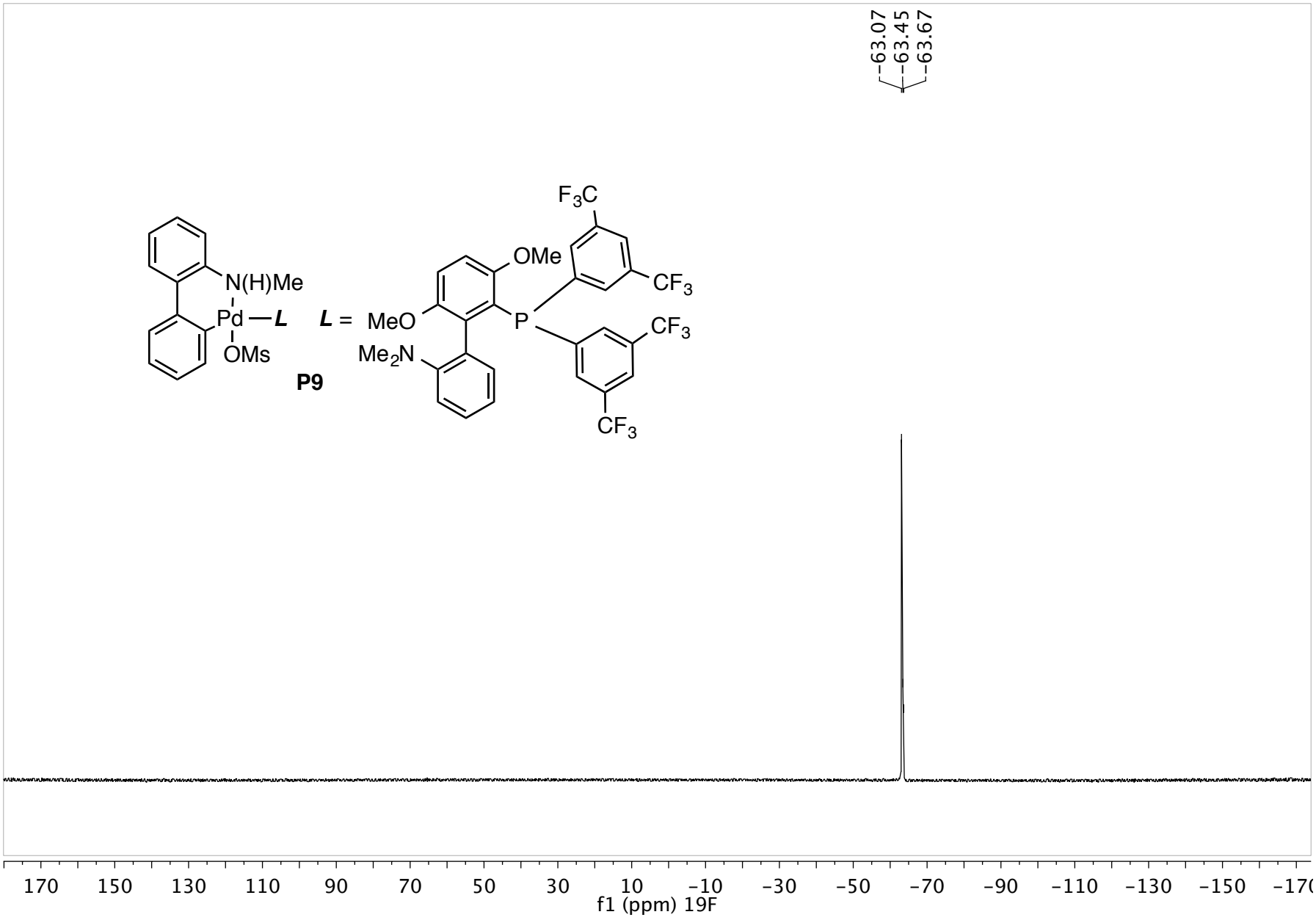

30.36
N(H)Me
Pd —L
OMs
L = i-PrO
MeO
OMe
P
F3C
CF3
CF3
CF3
O i-Pr
P8
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

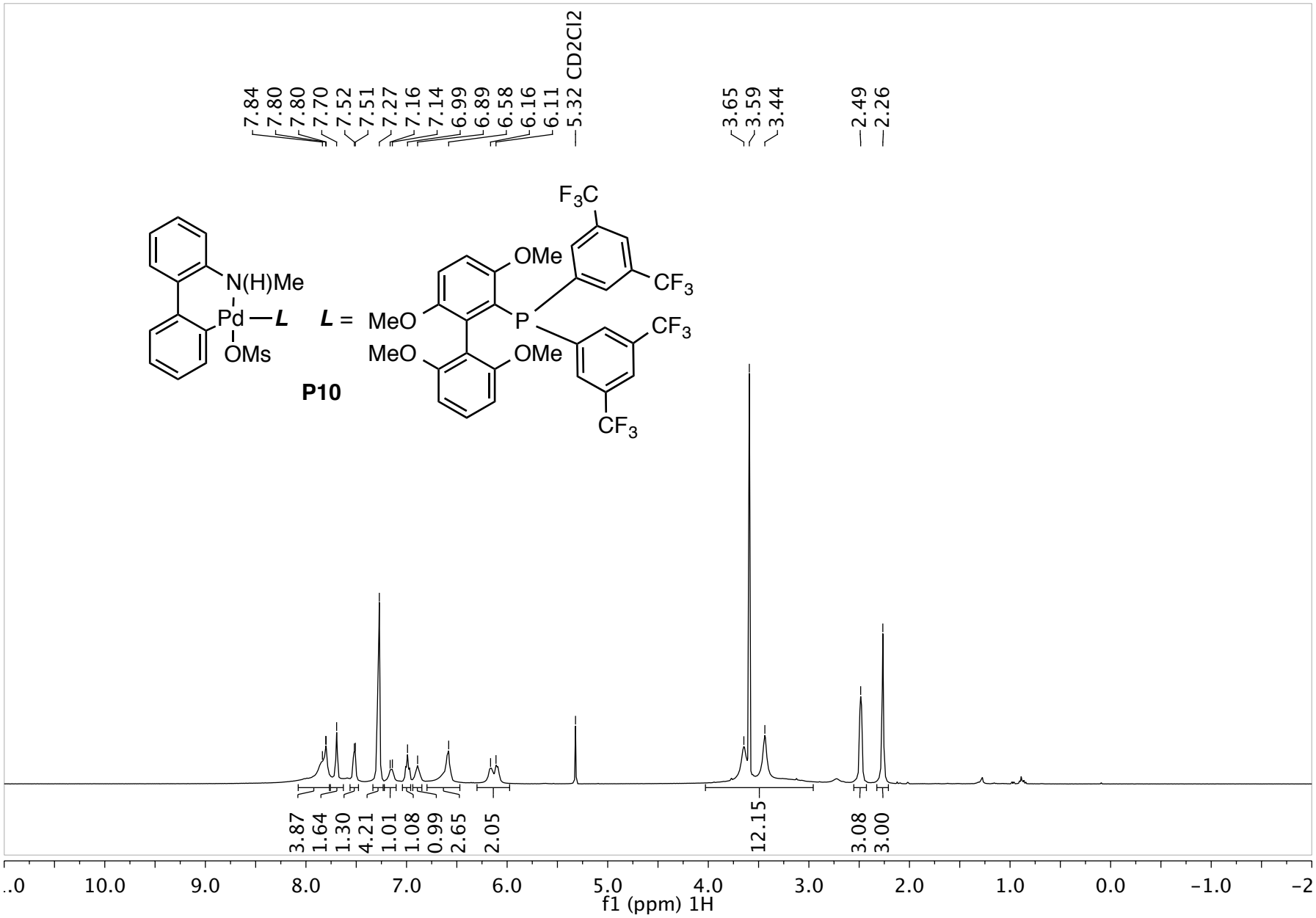

-63.50
-63.59
N(H)Me
Pd —L
OMs
P8
L = i-PrO
MeO
OMe
P
F3C
CF3
CF3
CF3
O i-Pr
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -17
f1 (ppm) 19F

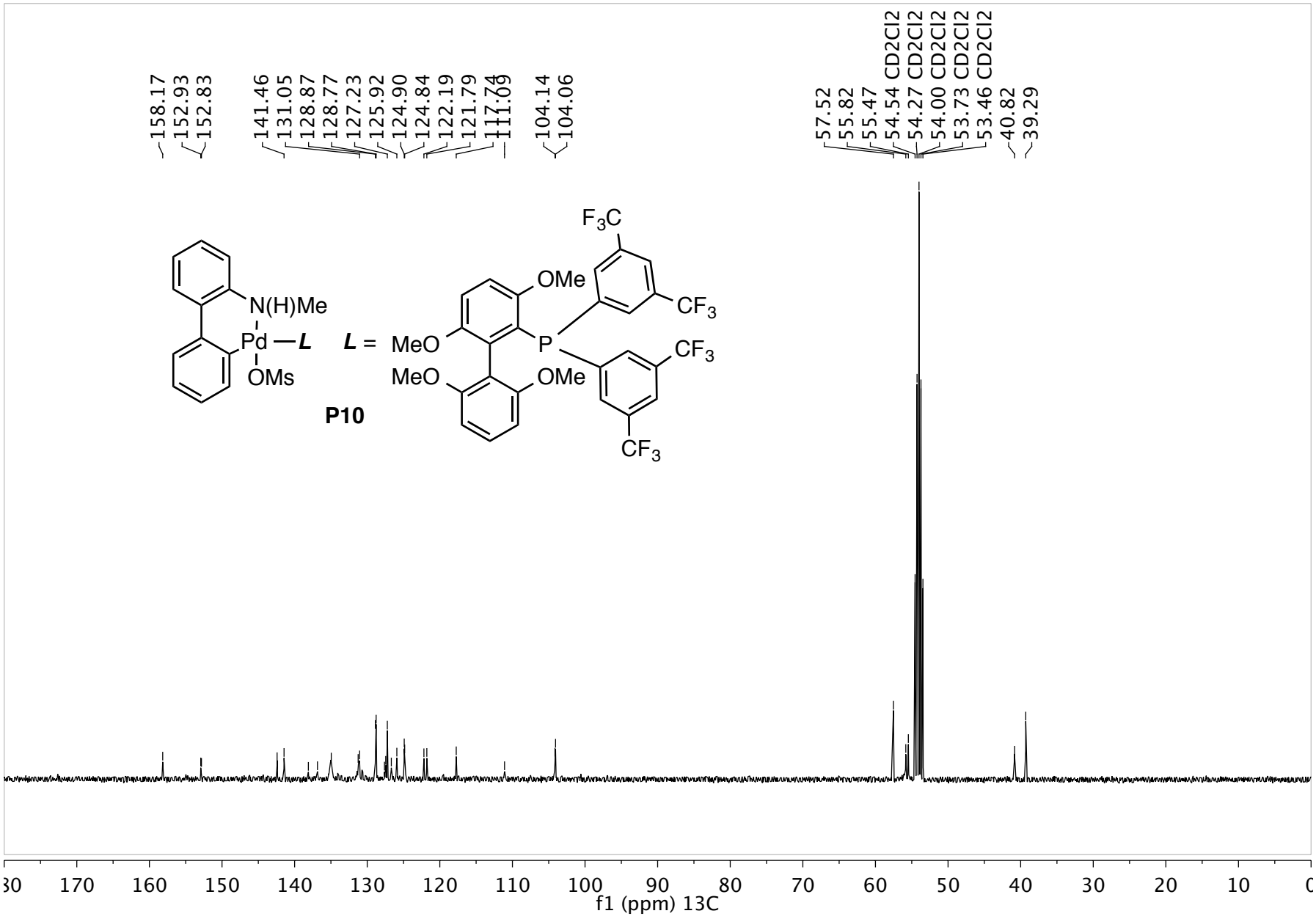

7.99
7.96
7.85
7.66
7.64
7.62
7.59
7.41
7.39
7.32
7.32
7.25
7.20
7.18
7.06
7.04
7.02
7.00
6.98
6.96
6.88
6.83
6.65
6.63
6.61
6.52
5.32 CD2Cl2
3.67
3.22
2.41
2.37
2.32
2.23
N(H)Me
Pd—L
OMs
L =
MeO
Me2N
OMe
P
F3C
CF3
CF3
CF3
P9
1.55
0.80
2.58
6.48
2.13
2.13
2.33
0.75
5.89
11.67
f1 (ppm) 1H

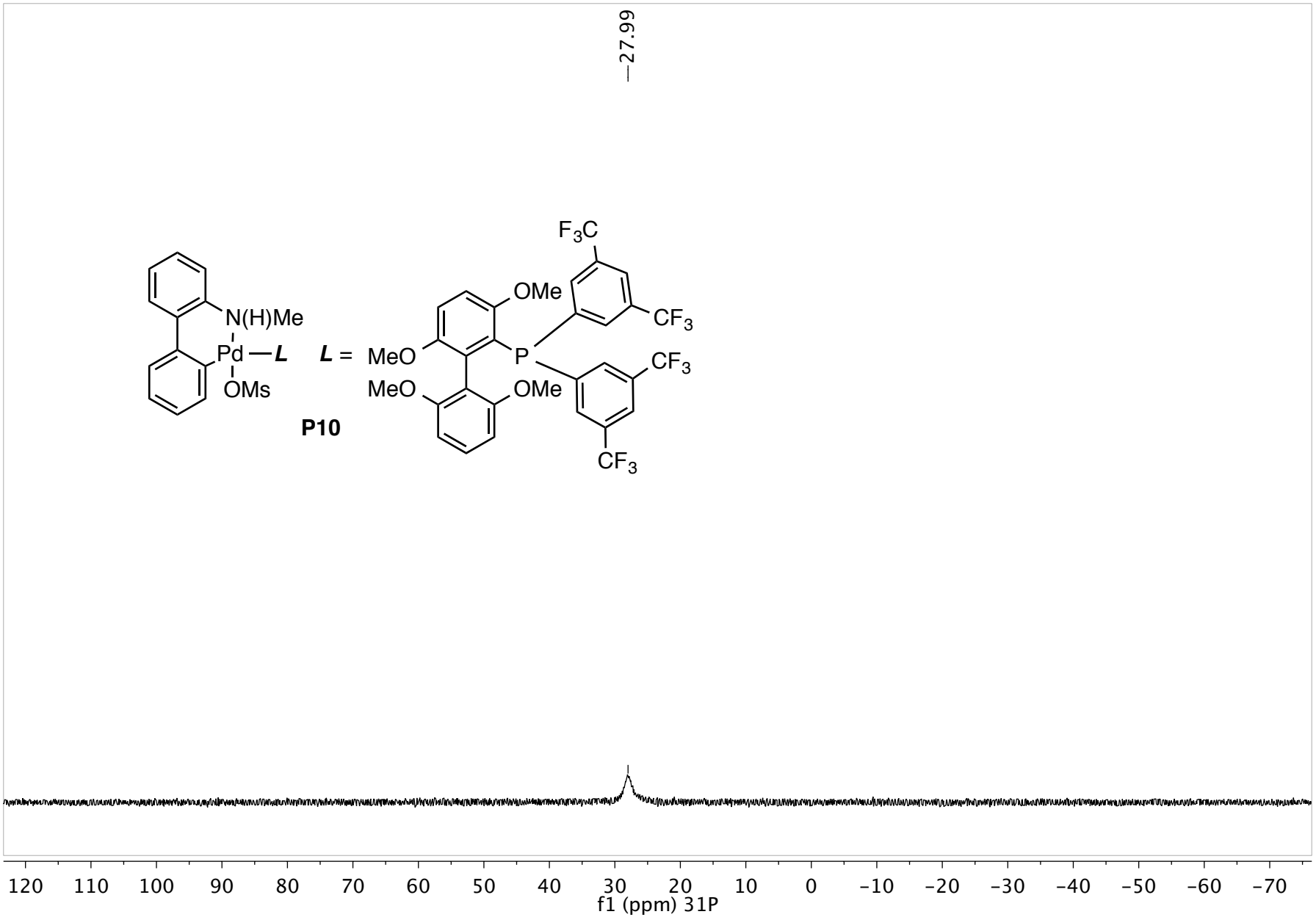

142.54
142.51
135.86
134.97
131.10
130.18
129.04
128.87
128.69
127.84
127.77
127.30
126.59
124.60
122.22
121.71
117.12
111.90
56.74
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
42.70
40.84
40.31
39.43
32.16
23.23
N(H)Me
Pd
L
OMs
L =
MeO
Me2N
OMe
P
F3C
CF3
CF3
CF3
P9
f1 (ppm) 13C

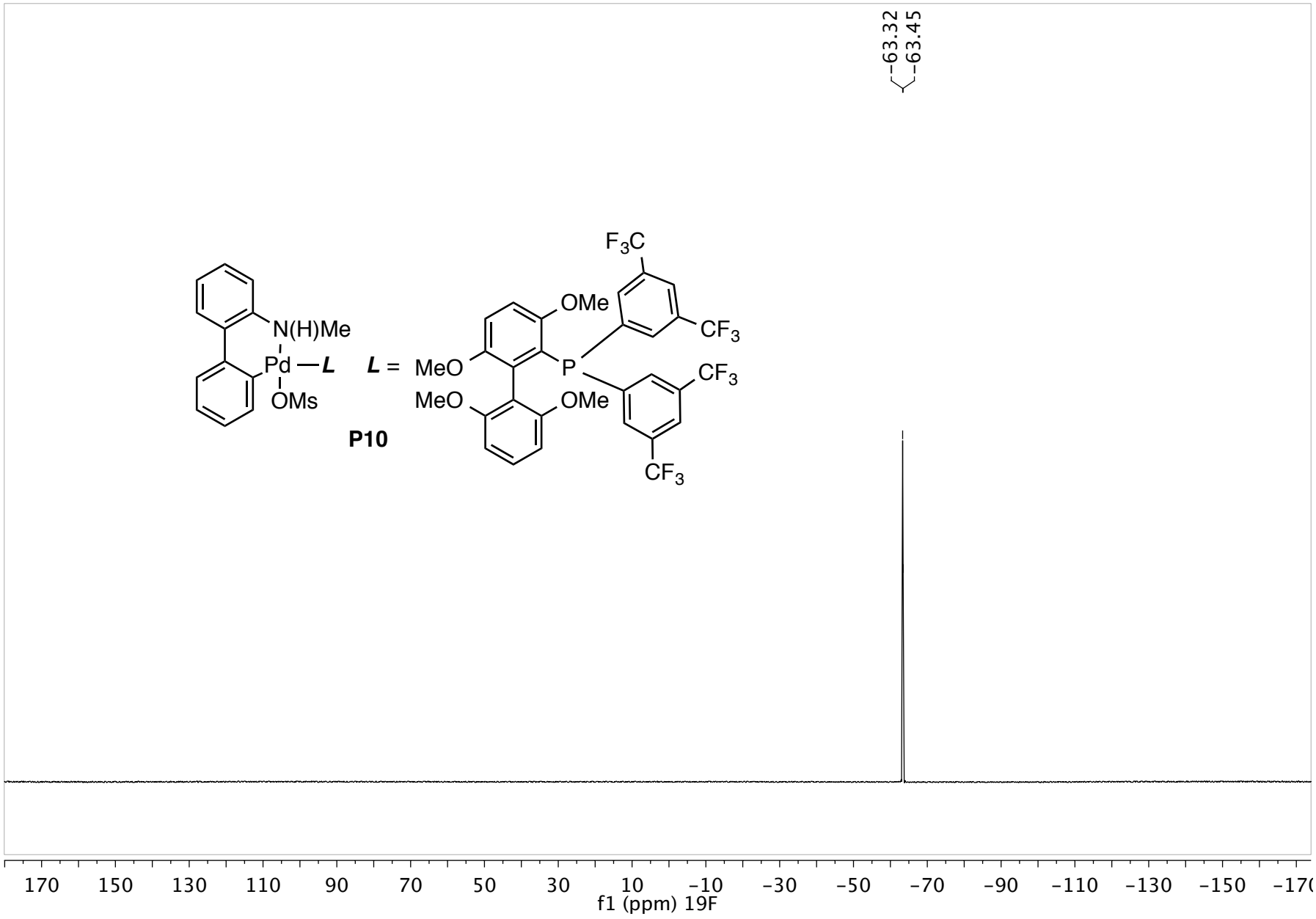

28.69
N(H)Me
Pd —L
OMs
P9
L =
MeO
Me2N
OMe
P
F3C
CF3
CF3
CF3
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

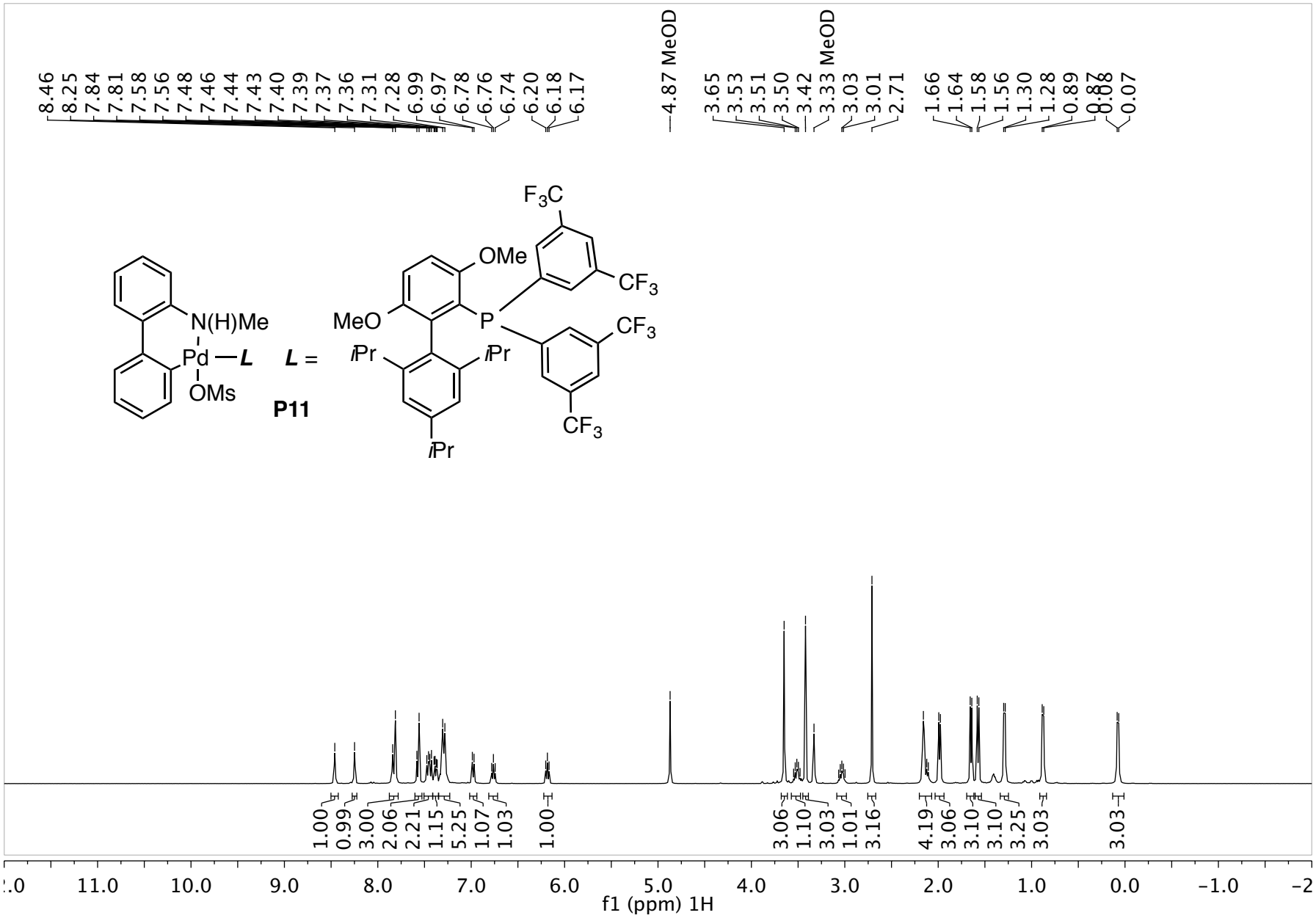

-63.07
-63.45
-63.67
N(H)Me
Pd—L
OMs
P9
L =
MeO
Me2N
OMe
P
F3C
CF3
CF3
CF3
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
f1 (ppm) 19F

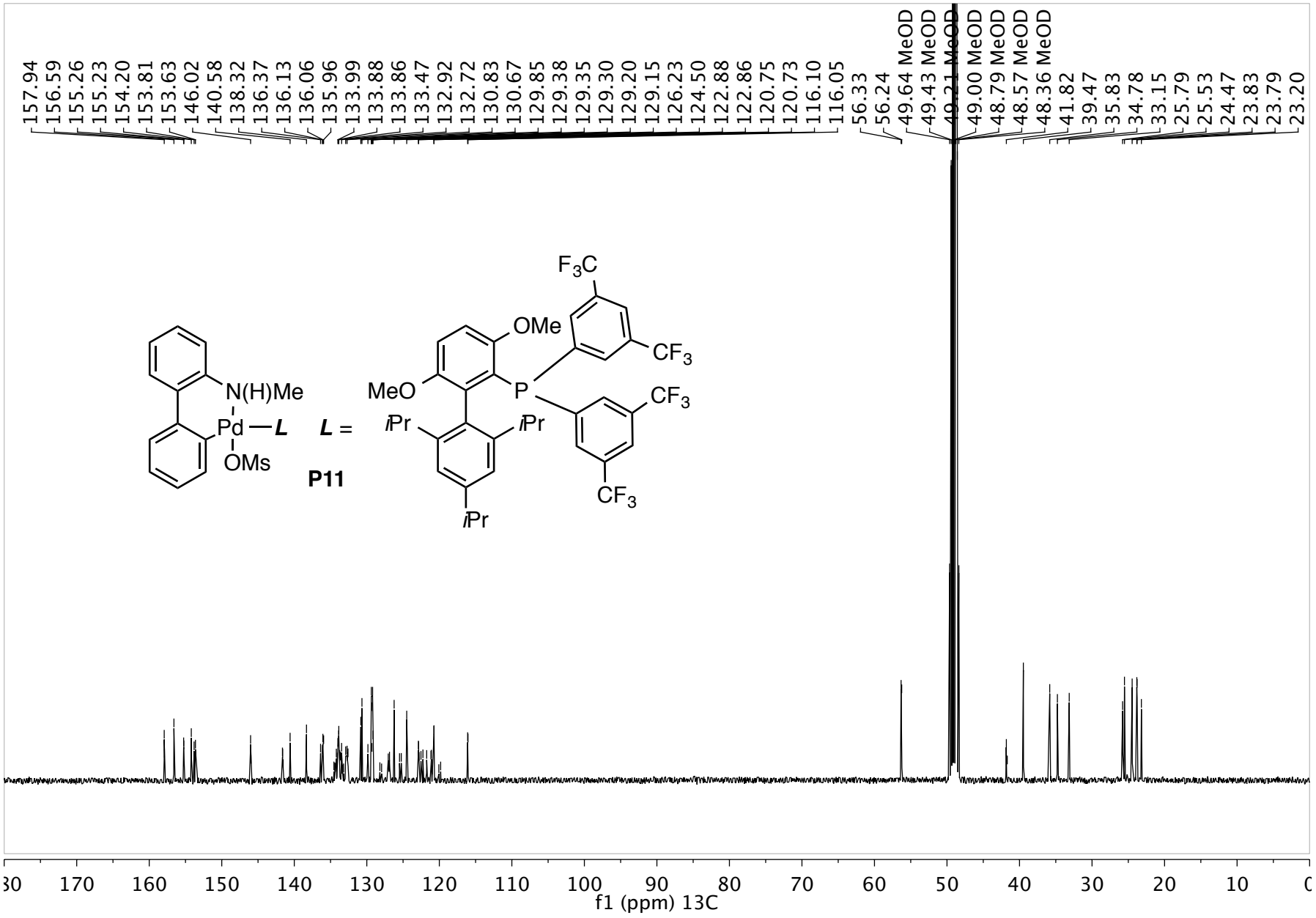

7.84
7.80
7.80
7.70
7.52
7.51
7.27
7.16
7.14
6.99
6.89
6.58
6.16
6.11
5.32 CD2Cl2
3.65
3.59
3.44
2.49
2.26
N(H)Me
Pd—L
OMs
L =
MeO
MeO
OMe
OMe
P
F3C
CF3
CF3
CF3
P10
3.87
1.64
1.30
4.21
1.01
1.08
0.99
2.65
2.05
12.15
3.08
3.00
f1 (ppm) 1H

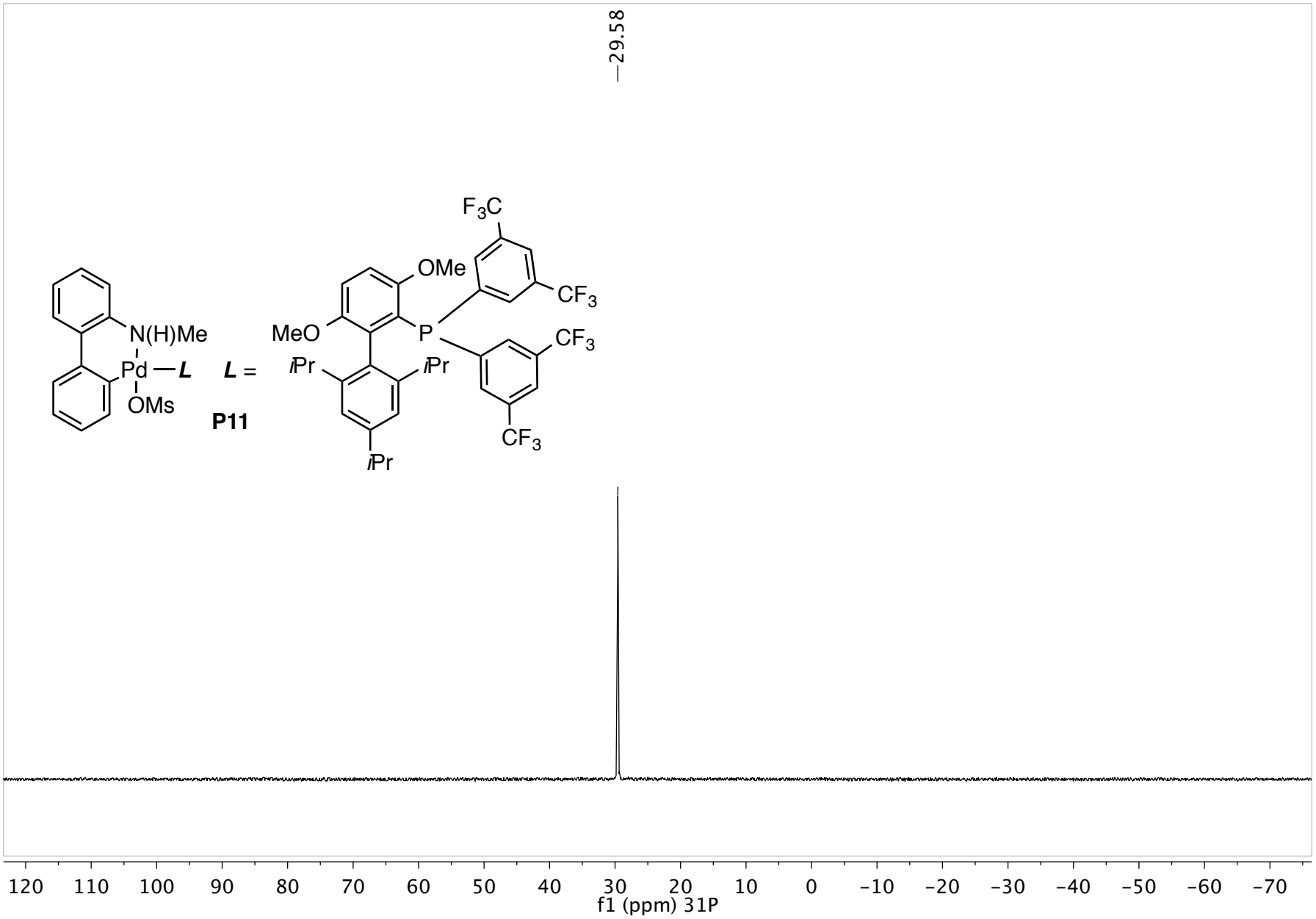

158.17
152.93
152.83
141.46
131.05
128.87
128.77
127.23
125.92
124.90
124.84
122.19
121.79
117.74
111.09
104.14
104.06
57.52
55.82
55.47
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
40.82
39.29
N(H)Me
Pd — L
OMs
L =
MeO
MeO
P
OMe
OMe
F3C
CF3
CF3
CF3
P10
f1 (ppm) 13C

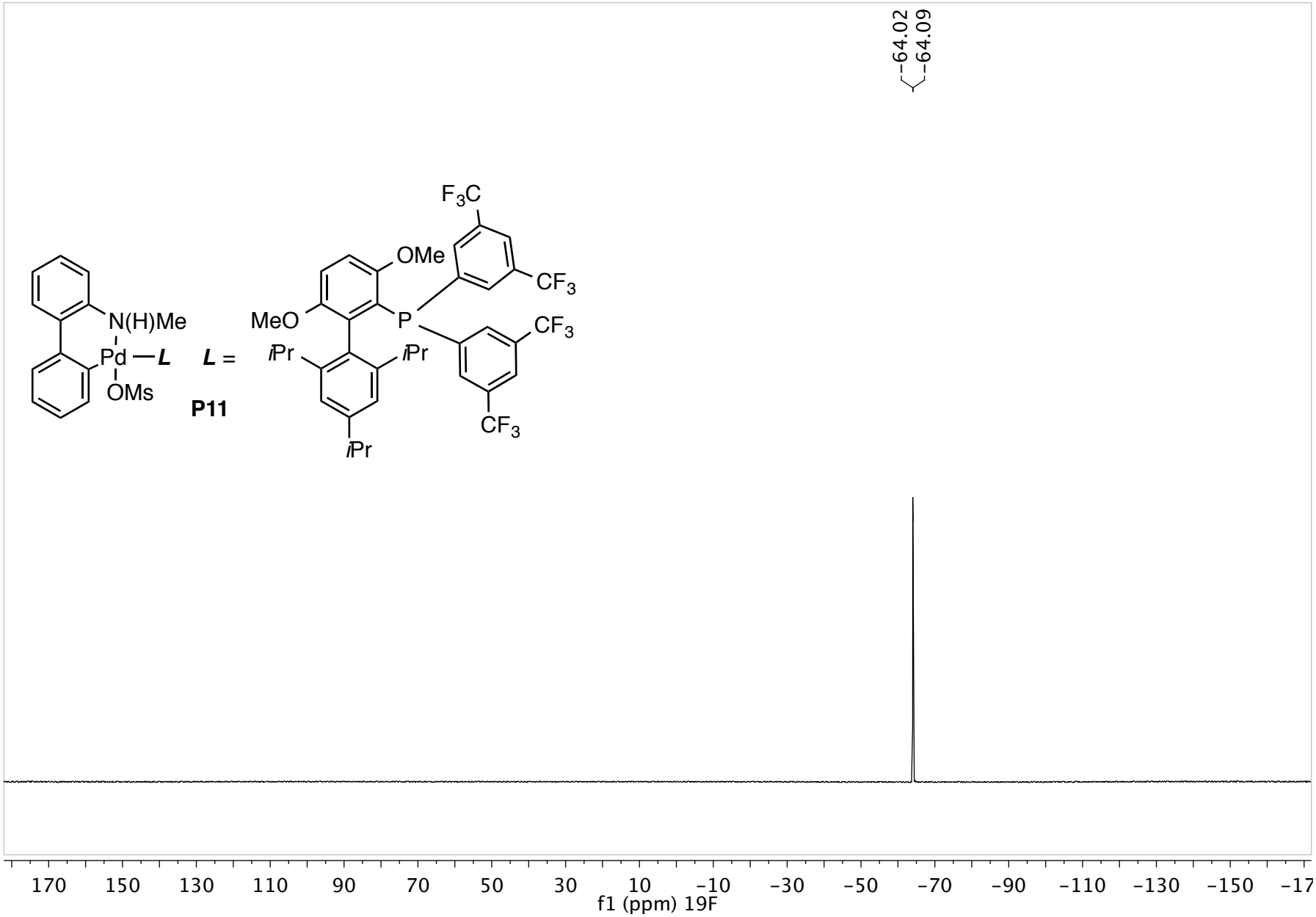

27.99
N(H)Me
Pd—L
OMs
L =
MeO
MeO
P
OMe
OMe
F3C
CF3
CF3
CF3
P10
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

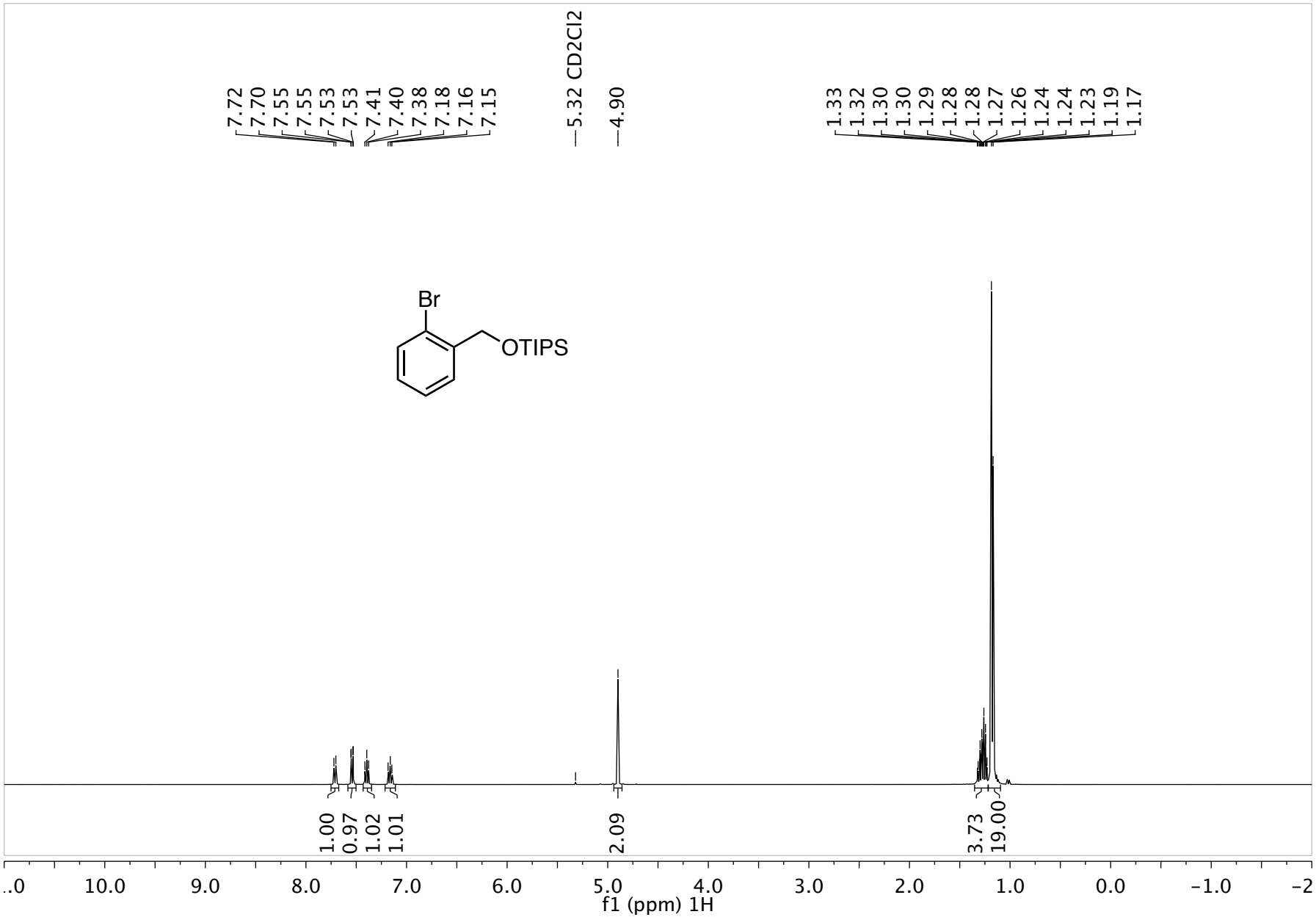

-63.32
-63.45
N(H)Me
Pd —L
OMs
L =
MeO
MeO
OMe
OMe
P
F3C
CF3
CF3
CF3
P10
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
f1 (ppm) 19F

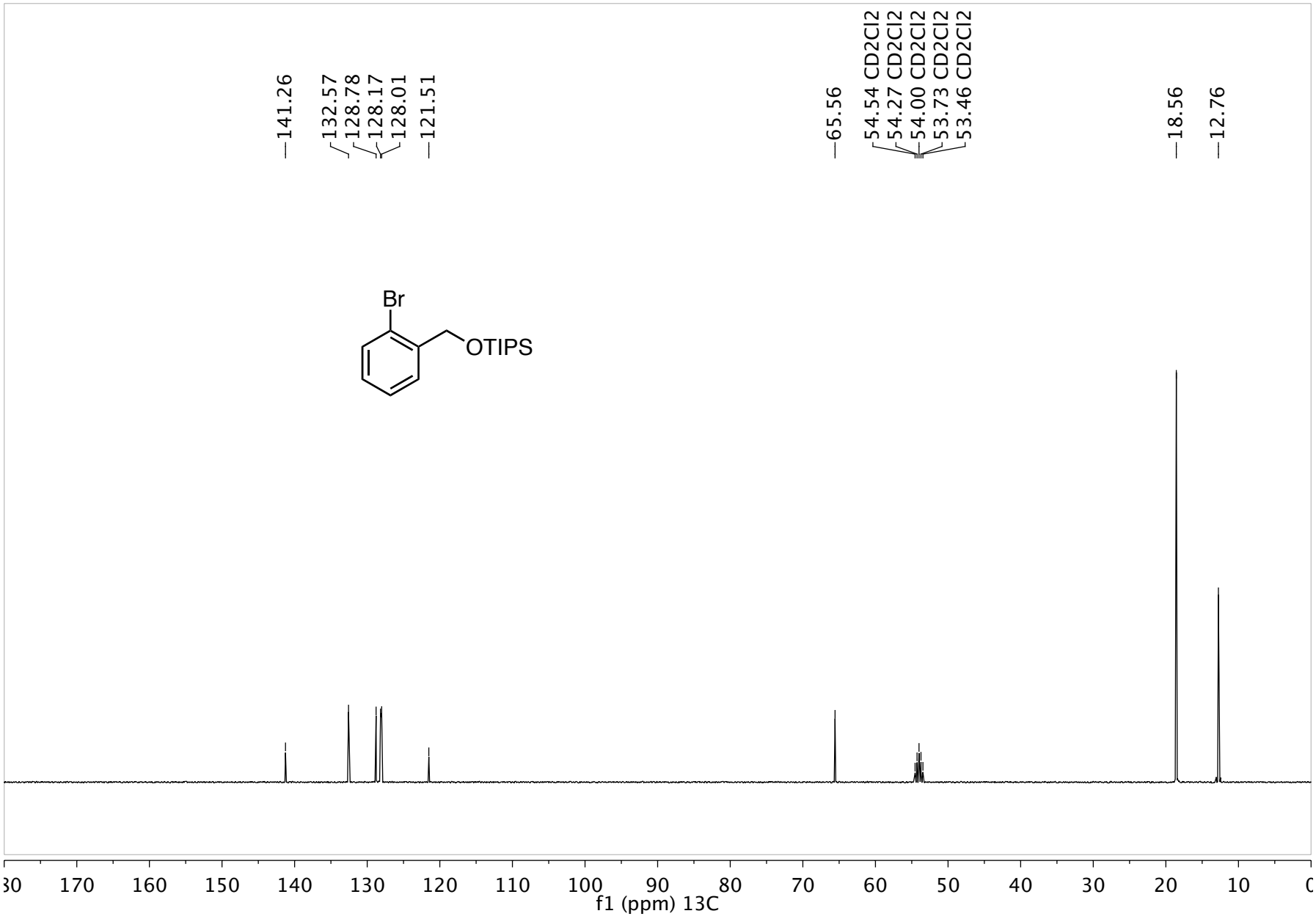

8.46
8.25
7.84
7.81
7.58
7.56
7.48
7.46
7.44
7.43
7.40
7.39
7.37
7.36
7.31
7.28
6.99
6.97
6.78
6.76
6.74
6.20
6.18
6.17
4.87 MeOD
3.65
3.53
3.51
3.50
3.42
3.33 MeOD
3.03
3.01
2.71
1.66
1.64
1.58
1.56
1.30
1.28
0.89
0.88
0.07
N(H)Me
Pd
L
OMs
L =
P11
F3C
OMe
CF3
MeO
P
CF3
iPr
iPr
CF3
iPr
1.00
0.99
3.00
2.06
2.21
1.15
5.25
1.07
1.03
1.00
3.06
1.10
3.03
1.01
3.16
4.19
3.06
3.10
3.10
3.25
3.03
3.03
f1 (ppm) 1H

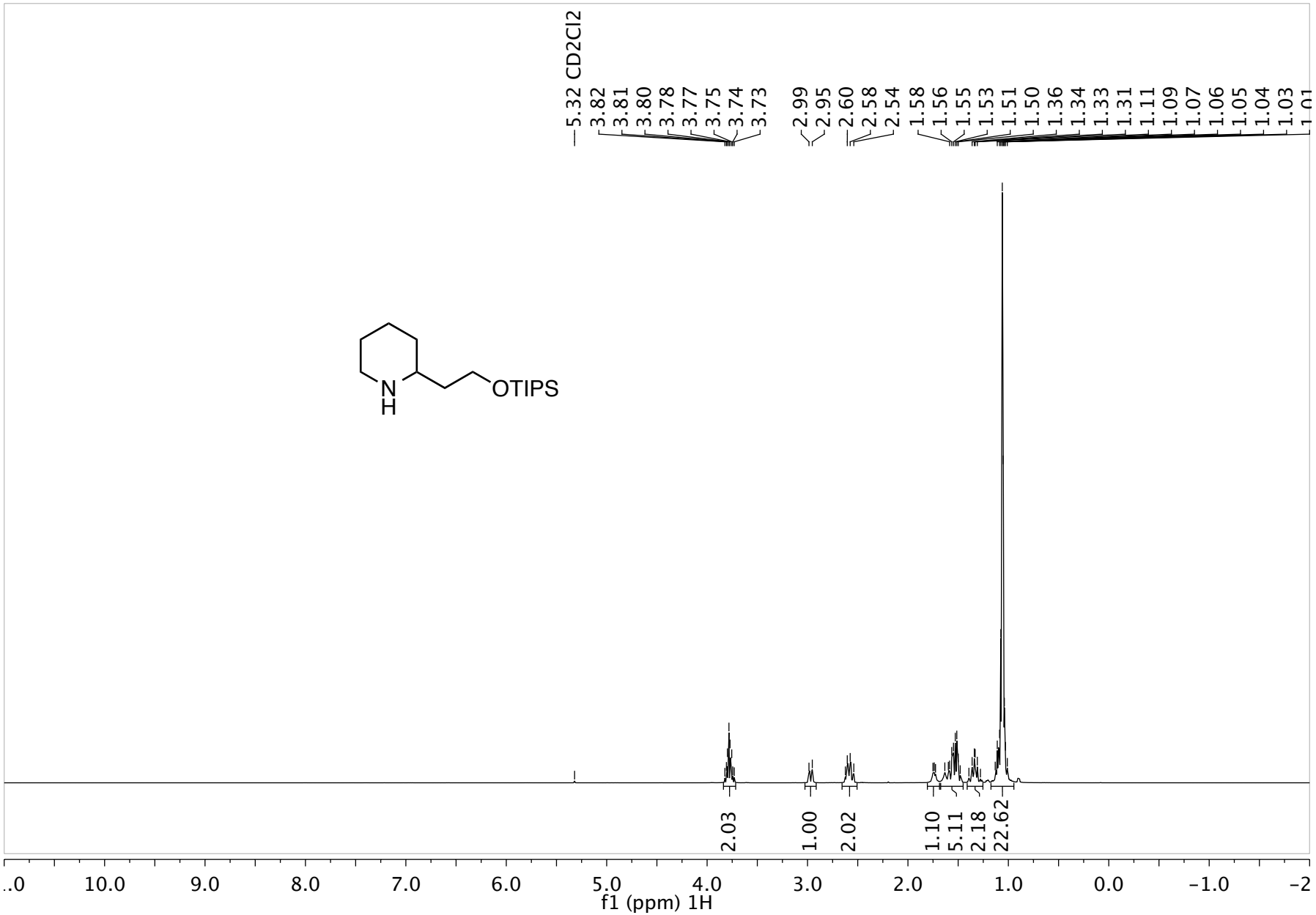

157.94
156.59
155.26
155.23
154.20
153.81
153.63
146.02
140.58
138.32
136.37
136.13
136.06
135.96
133.99
133.88
133.86
133.47
132.92
132.72
130.83
130.67
129.85
129.38
129.35
129.30
129.20
129.15
126.23
124.50
122.88
122.86
120.75
120.73
116.10
116.05
56.33
56.24
49.64 MeOD
49.43 MeOD
49.21 MeOD
49.00 MeOD
48.79 MeOD
48.57 MeOD
48.36 MeOD
41.82
39.47
35.83
34.78
33.15
25.79
25.53
24.47
23.83
23.79
23.20
N(H)Me
Pd
L
OMs
L =
P11
F3C
OMe
CF3
MeO
P
CF3
iPr
iPr
CF3
iPr
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C

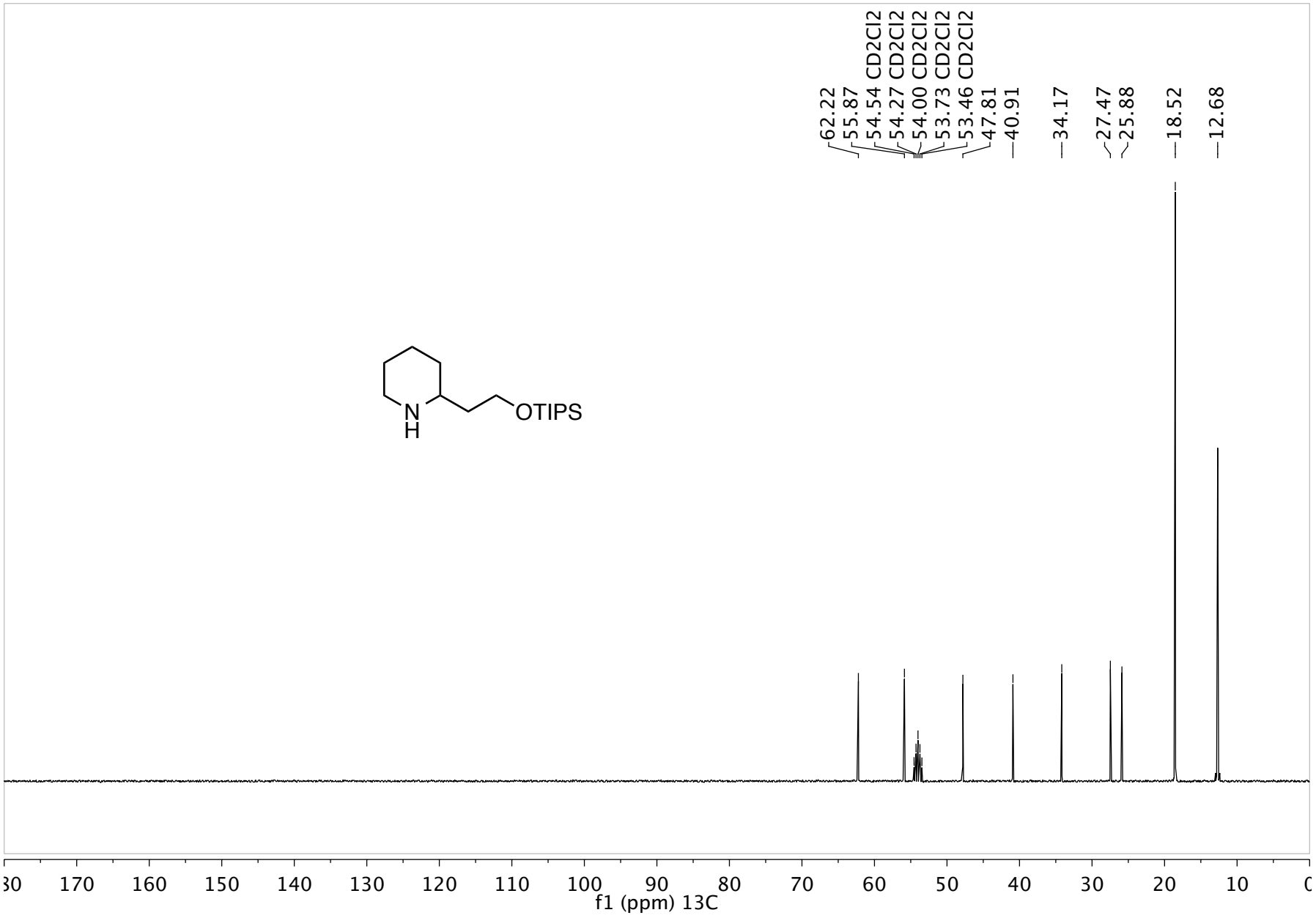

29.58
N(H)Me
Pd
L
OMs
L =
P11
F3C
OMe
CF3
MeO
P
CF3
iPr
iPr
CF3
iPr
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm) 31P

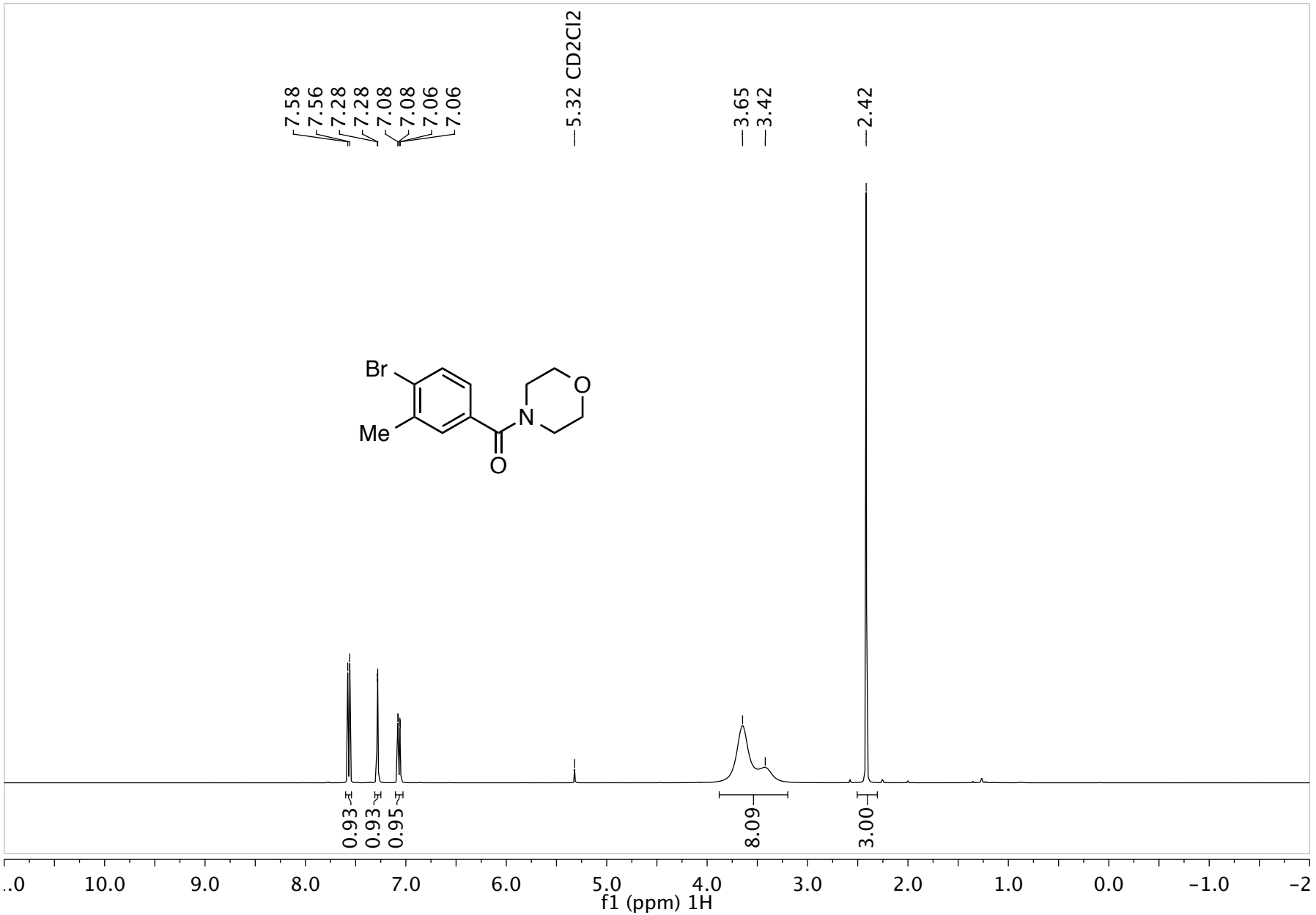

-64.02
-64.09
N(H)Me
Pd — L
OMs
L =
P11
MeO
OMe
P
F3C
CF3
CF3
CF3
iPr
iPr
iPr
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -17
f1 (ppm) 19F

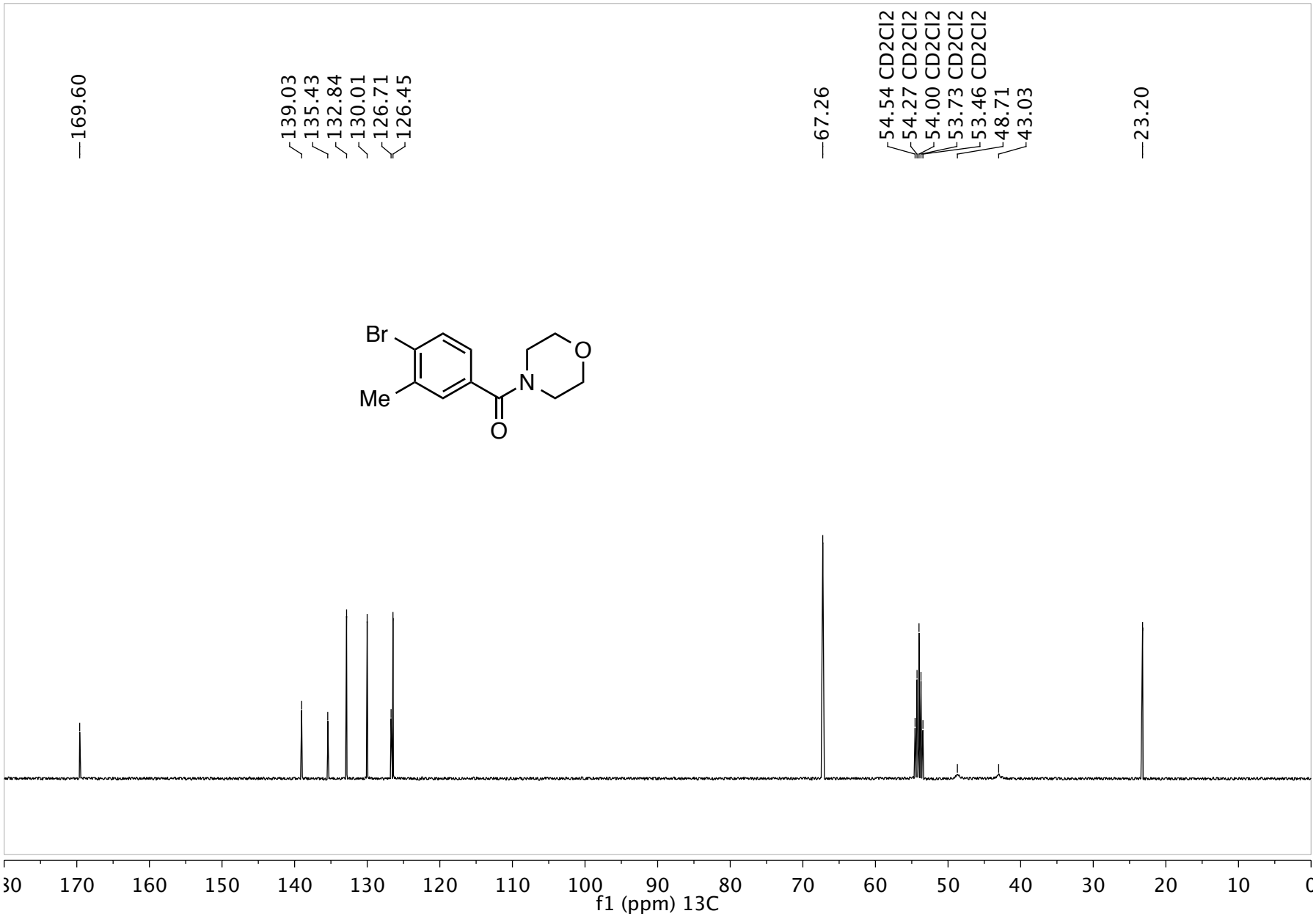

7.72
7.70
7.55
7.55
7.53
7.53
7.41
7.40
7.38
7.18
7.16
7.15
5.32 CD2Cl2
4.90
1.33
1.32
1.30
1.30
1.29
1.28
1.28
1.27
1.26
1.24
1.24
1.23
1.19
1.17
Br
OTIPS
1.00
0.97
1.02
1.01
2.09
3.73
19.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

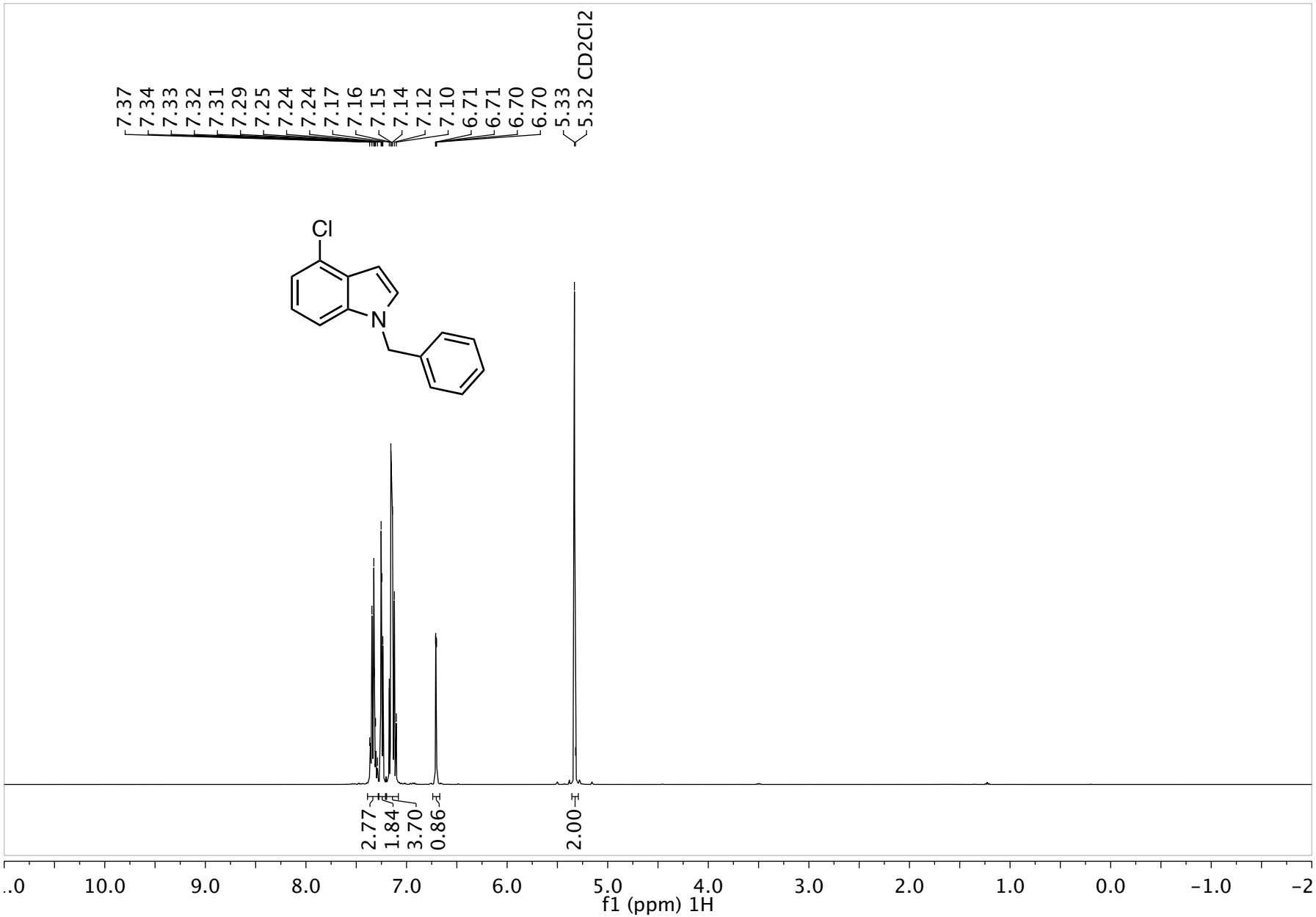

141.26
132.57
128.78
128.17
128.01
121.51
65.56
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
18.56
12.76
Br
OTIPS
f1 (ppm) 13C

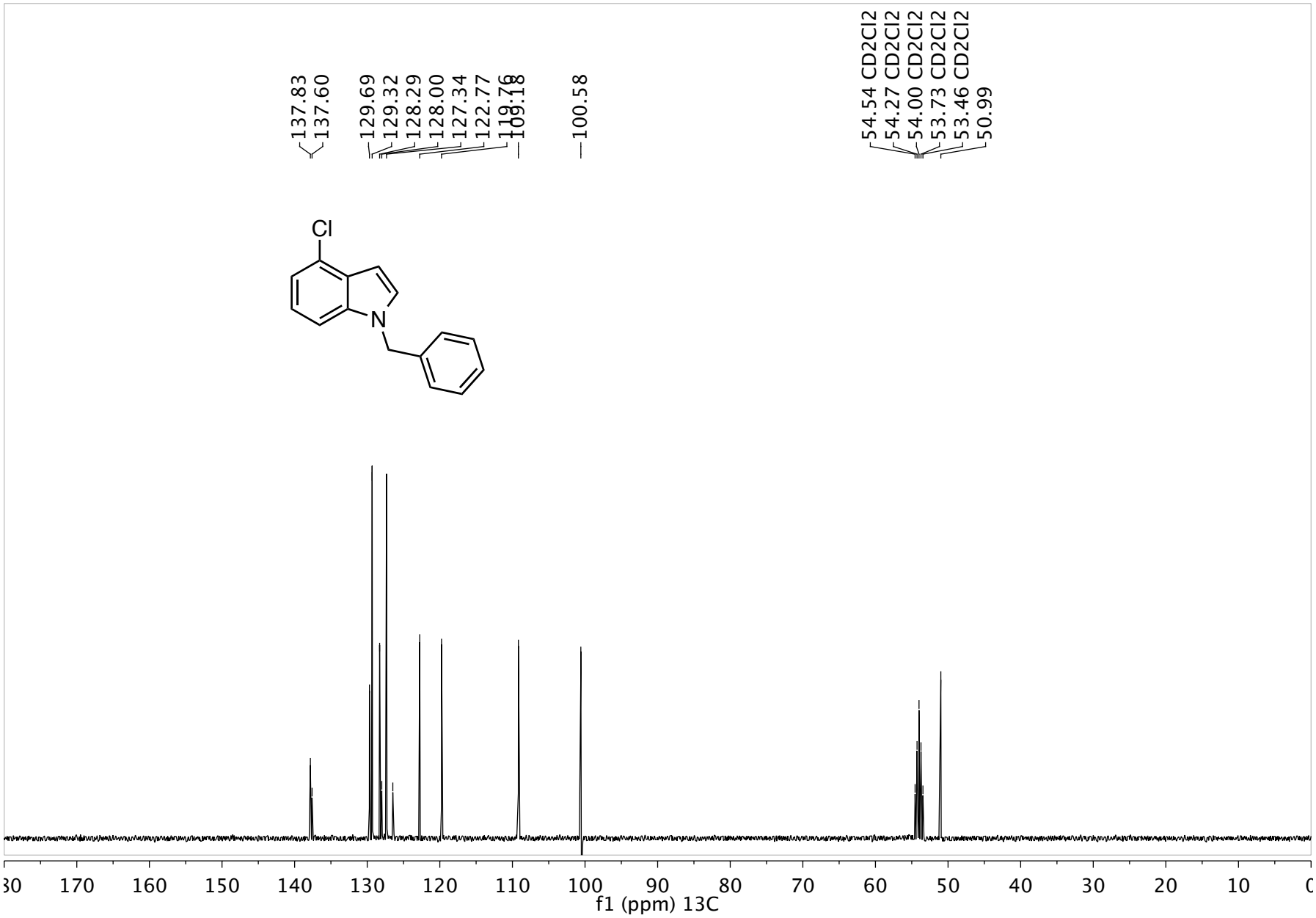

5.32 CD2Cl2
3.82
3.81
3.80
3.78
3.77
3.75
3.74
3.73
2.99
2.95
2.60
2.58
2.54
1.58
1.56
1.55
1.53
1.51
1.50
1.36
1.34
1.33
1.31
1.11
1.09
1.07
1.06
1.05
1.04
1.03
N
H
OTIPS
2.03
1.00
2.02
1.10
5.11
2.18
22.62
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

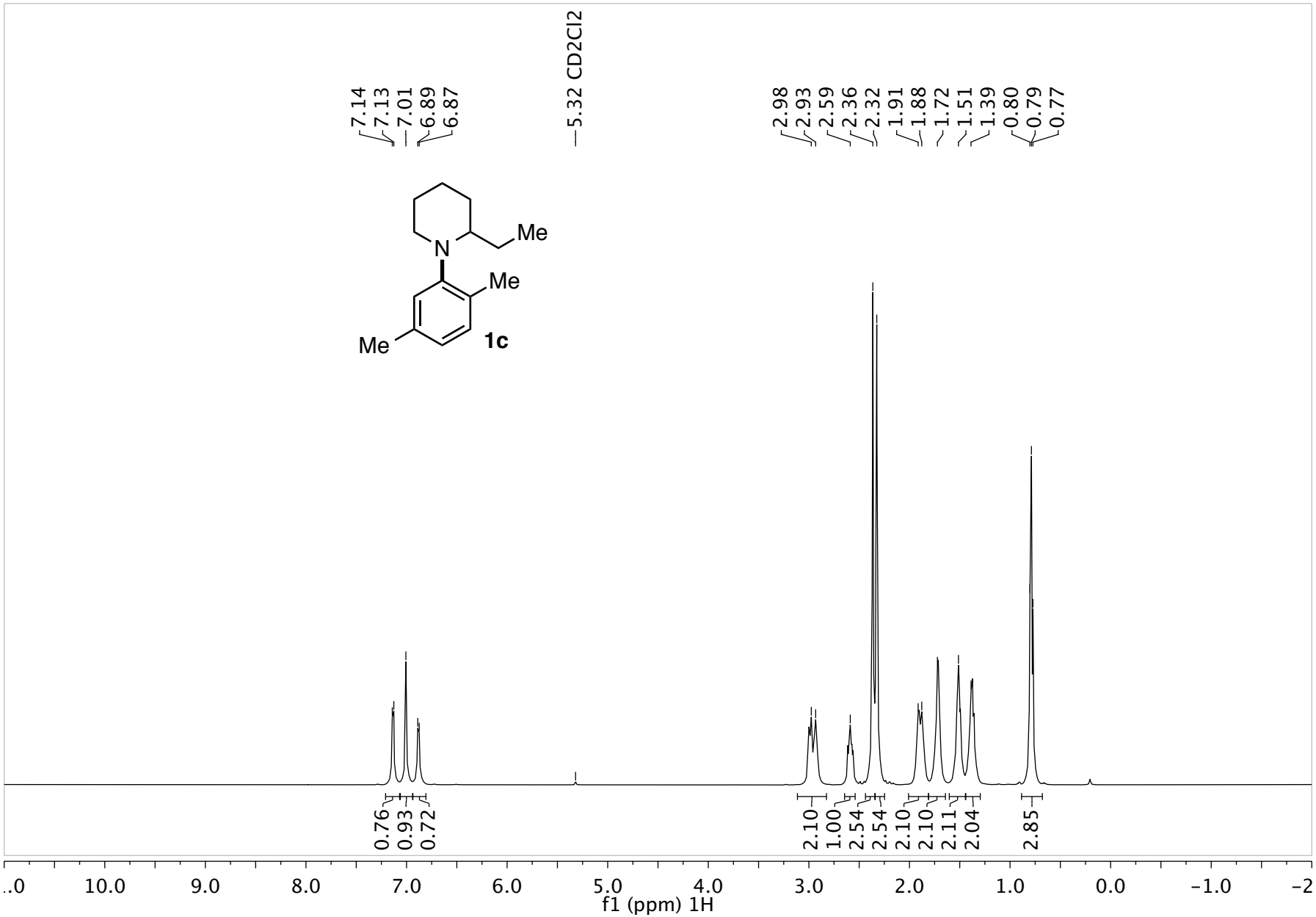

62.22
55.87
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
47.81
40.91
34.17
27.47
25.88
18.52
12.68
N
H
OTIPS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C


7.58
7.56
7.28
7.28
7.08
7.08
7.06
7.06
5.32 CD2Cl2
3.65
3.42
2.42
Br
Me
N
O
O
0.93
0.93
0.95
8.09
3.00
f1 (ppm) 1H

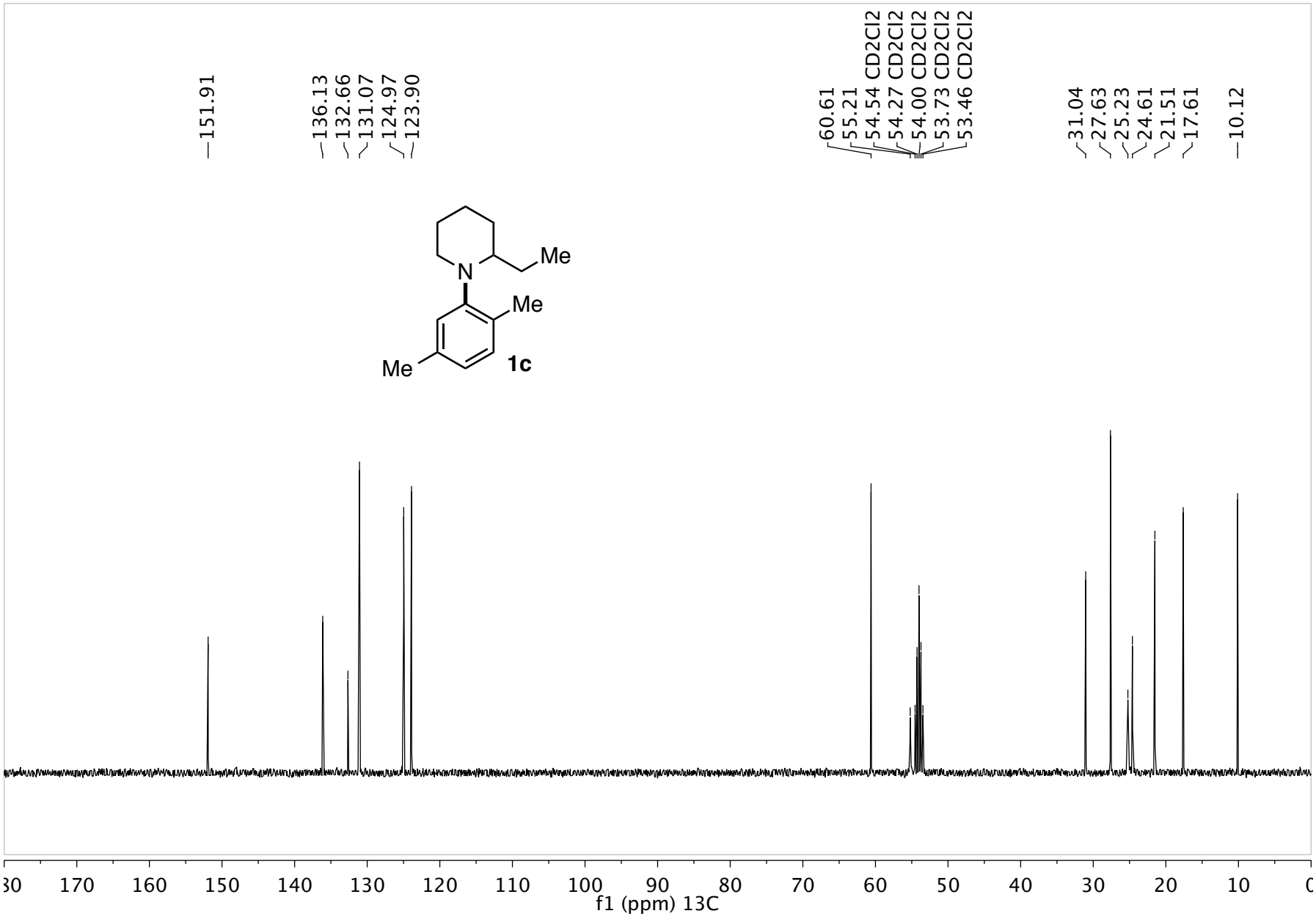

169.60
139.03
135.43
132.84
130.01
126.71
126.45
67.26
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
48.71
43.03
23.20
Br
Me
O
N
O
f1 (ppm) 13C


7.37
7.34
7.33
7.32
7.31
7.29
7.25
7.24
7.24
7.17
7.16
7.15
7.14
7.12
7.10
6.71
6.71
6.70
6.70
5.33
5.32 CD2Cl2
Cl
N
2.77
1.84
3.70
0.86
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H


137.83
137.60
129.69
129.32
128.29
128.00
127.34
122.77
119.76
109.18
100.58
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
50.99
Cl
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C


7.14
7.13
7.01
6.89
6.87
5.32 CD2Cl2
2.98
2.93
2.59
2.36
2.32
1.91
1.88
1.72
1.51
1.39
0.80
0.79
0.77
Me
N
Me
Me
1c
0.76
0.93
0.72
2.10
1.00
2.54
2.54
2.10
2.10
2.11
2.04
2.85
f1 (ppm) 1H

ZZ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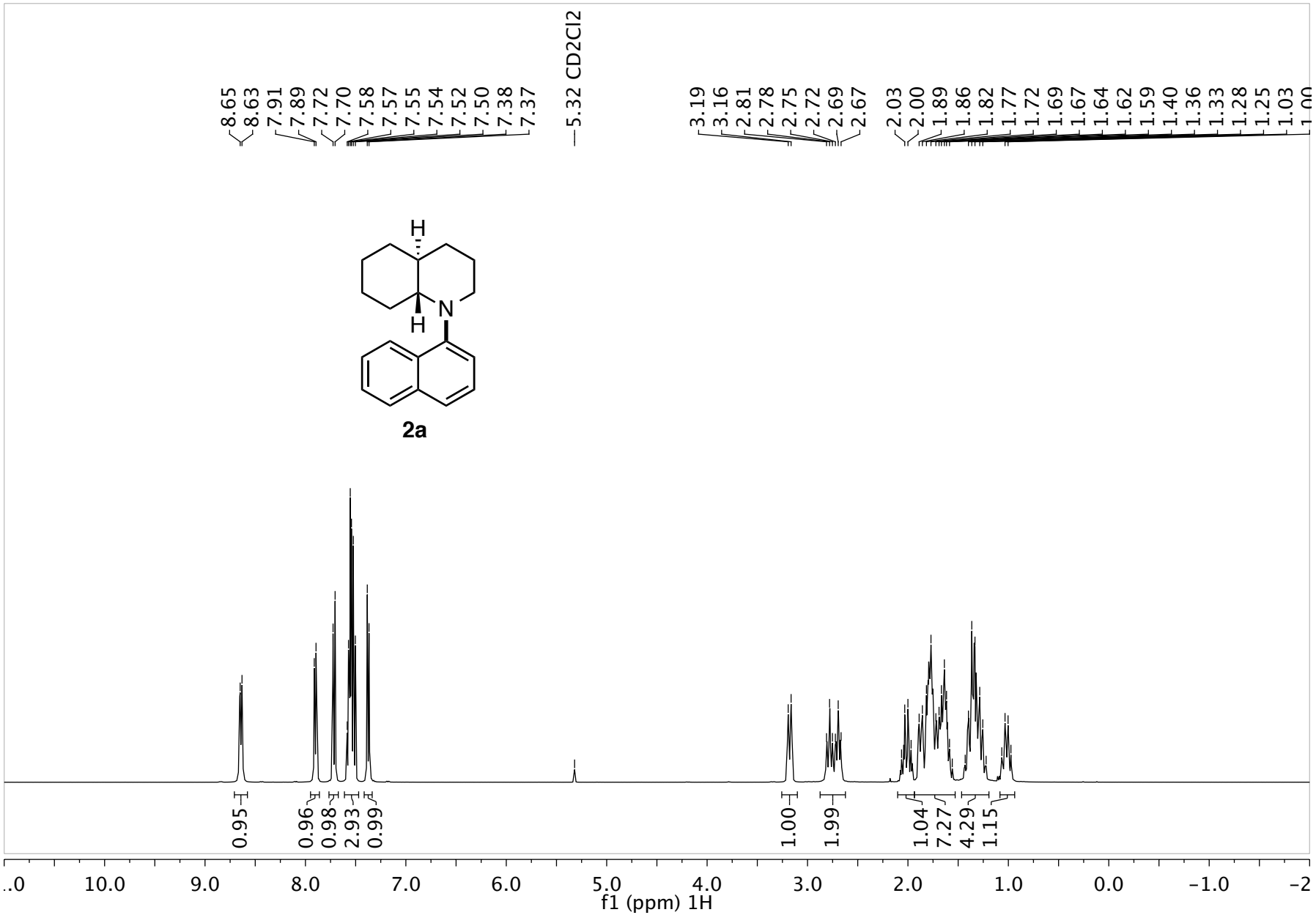
136.13
132.66
131.07
124.97
123.90
60.61
55.21
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
31.04
27.63
25.23
24.61
21.51
17.61
10.12
N
Me
Me
Me
1c
f1 (ppm) 13C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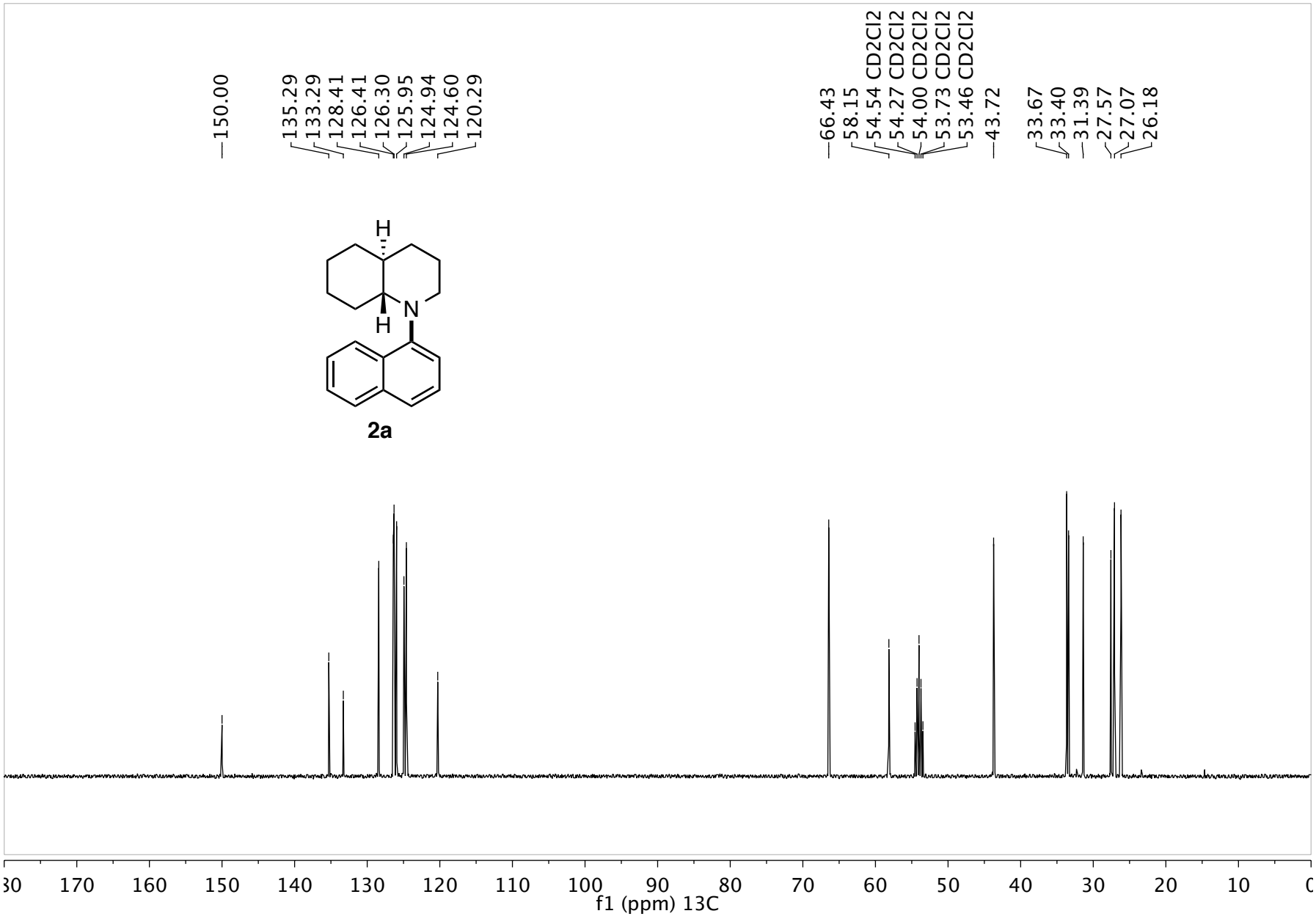
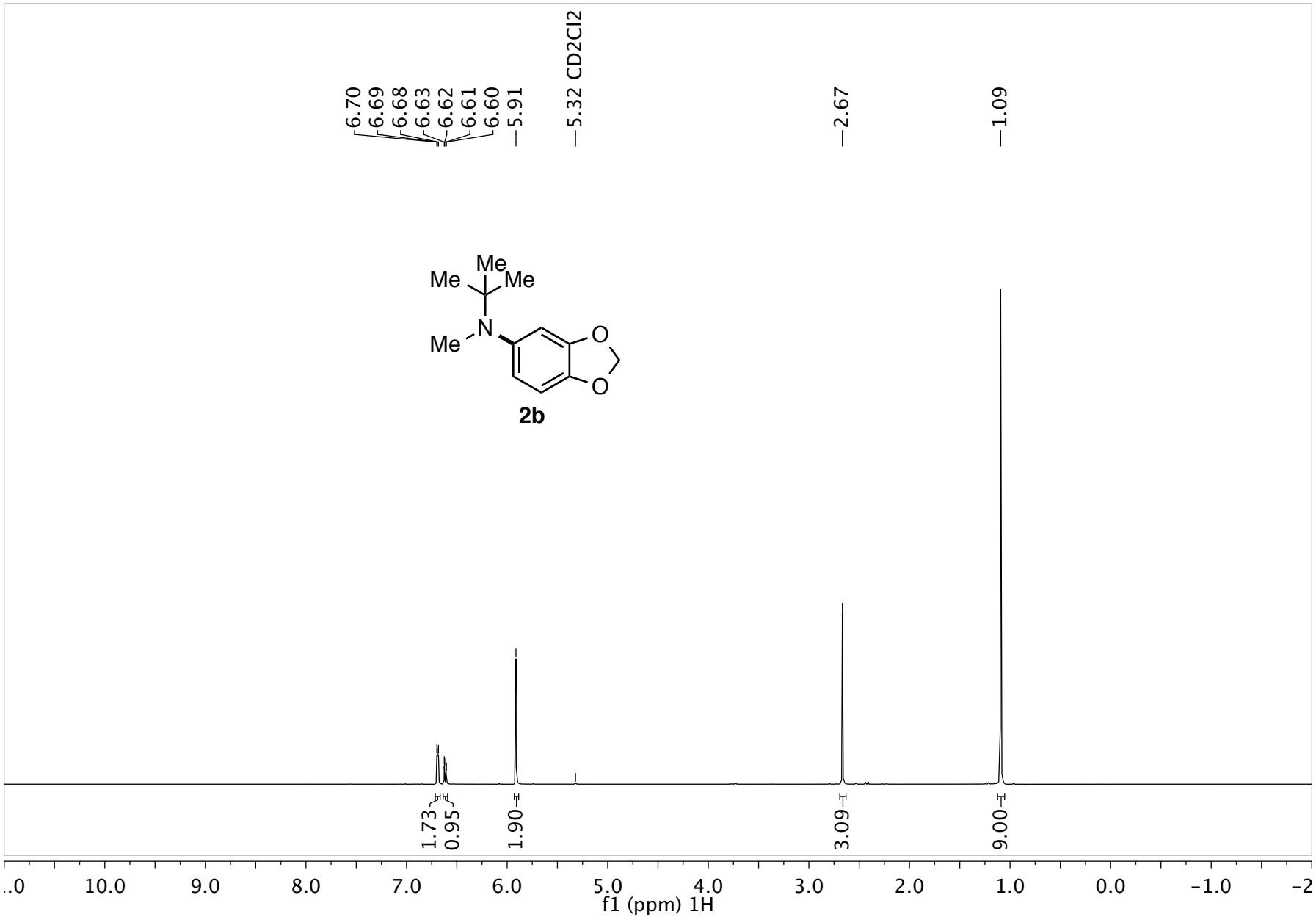
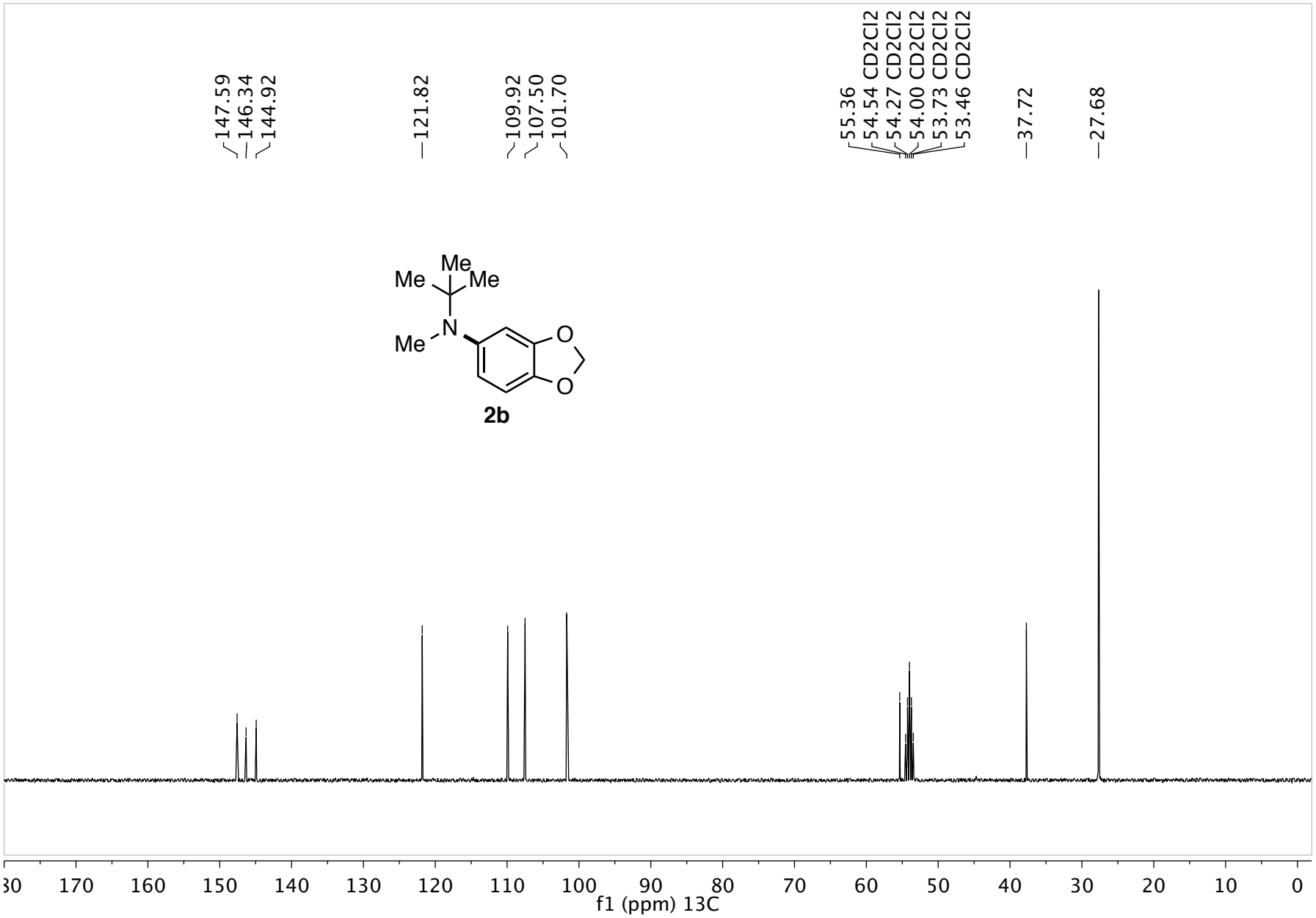
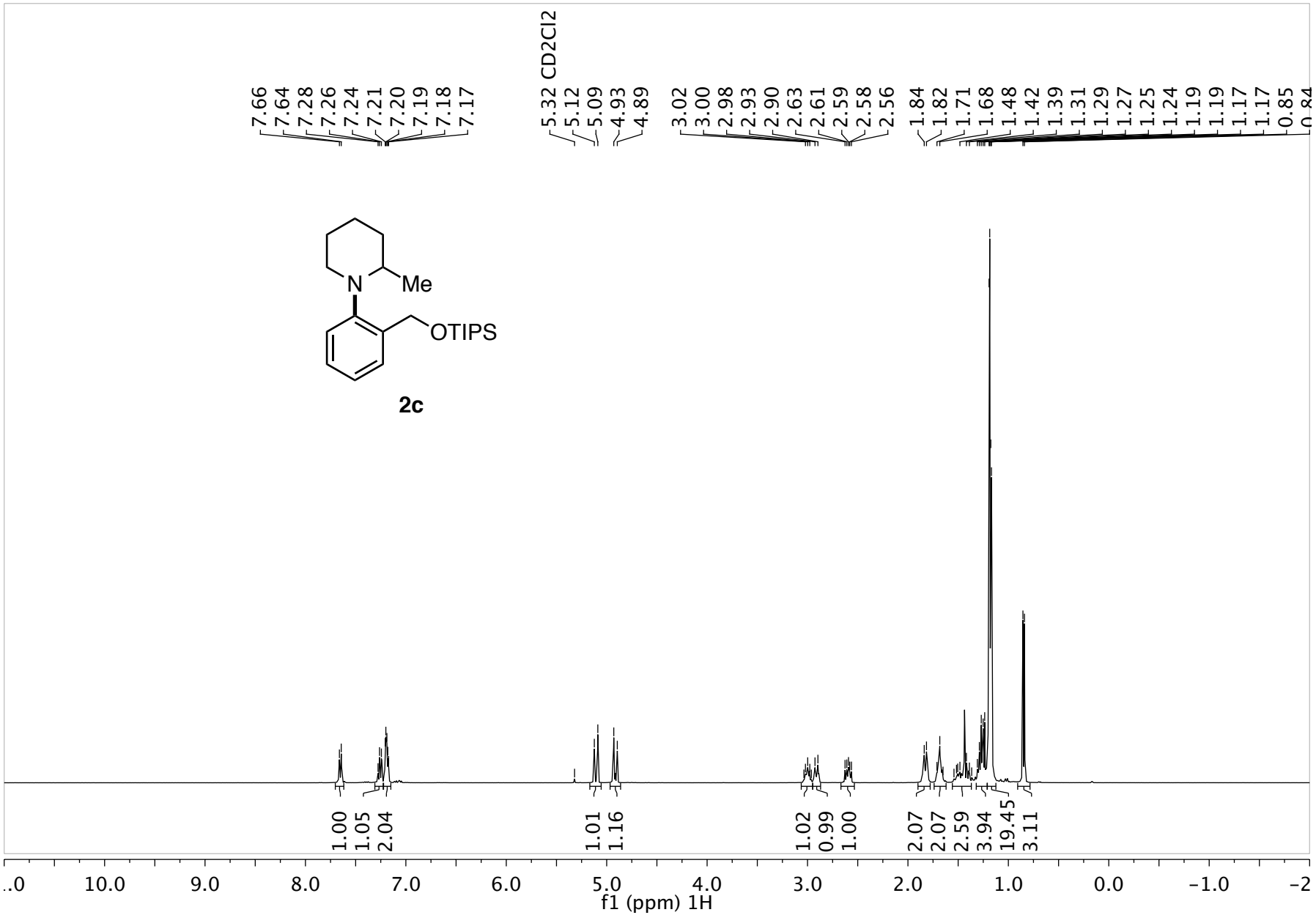
8.63
7.91
7.89
7.72
7.70
7.58
7.57
7.55
7.54
7.52
7.50
7.38
7.37
5.32 CD2Cl2
3.19
3.16
2.81
2.78
2.75
2.72
2.69
2.67
2.03
2.00
1.89
1.86
1.82
1.77
1.72
1.69
1.67
1.64
1.62
1.59
1.40
1.36
1.33
1.28
1.25
1.03
H
N
H
2a
0.95
0.96
0.98
2.93
0.99
1.00
1.99
1.04
7.27
4.29
1.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H


150.00
135.29
133.29
128.41
126.41
126.30
125.95
124.94
124.60
120.29
66.43
58.15
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
43.72
33.67
33.40
31.39
27.57
27.07
26.18
H
N
H
2a
f1 (ppm) 13C


6.70
6.69
6.68
6.63
6.62
6.61
6.60
5.91
5.32 CD2Cl2
2.67
1.09
Me
Me
Me
N
Me
O
O
2b
1.73
0.95
1.90
3.09
9.00
f1 (ppm) 1H


147.59
146.34
144.92
121.82
109.92
107.50
101.70
55.36
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
37.72
27.68
Me
Me
Me
N
O
O
2b
f1 (ppm) 13C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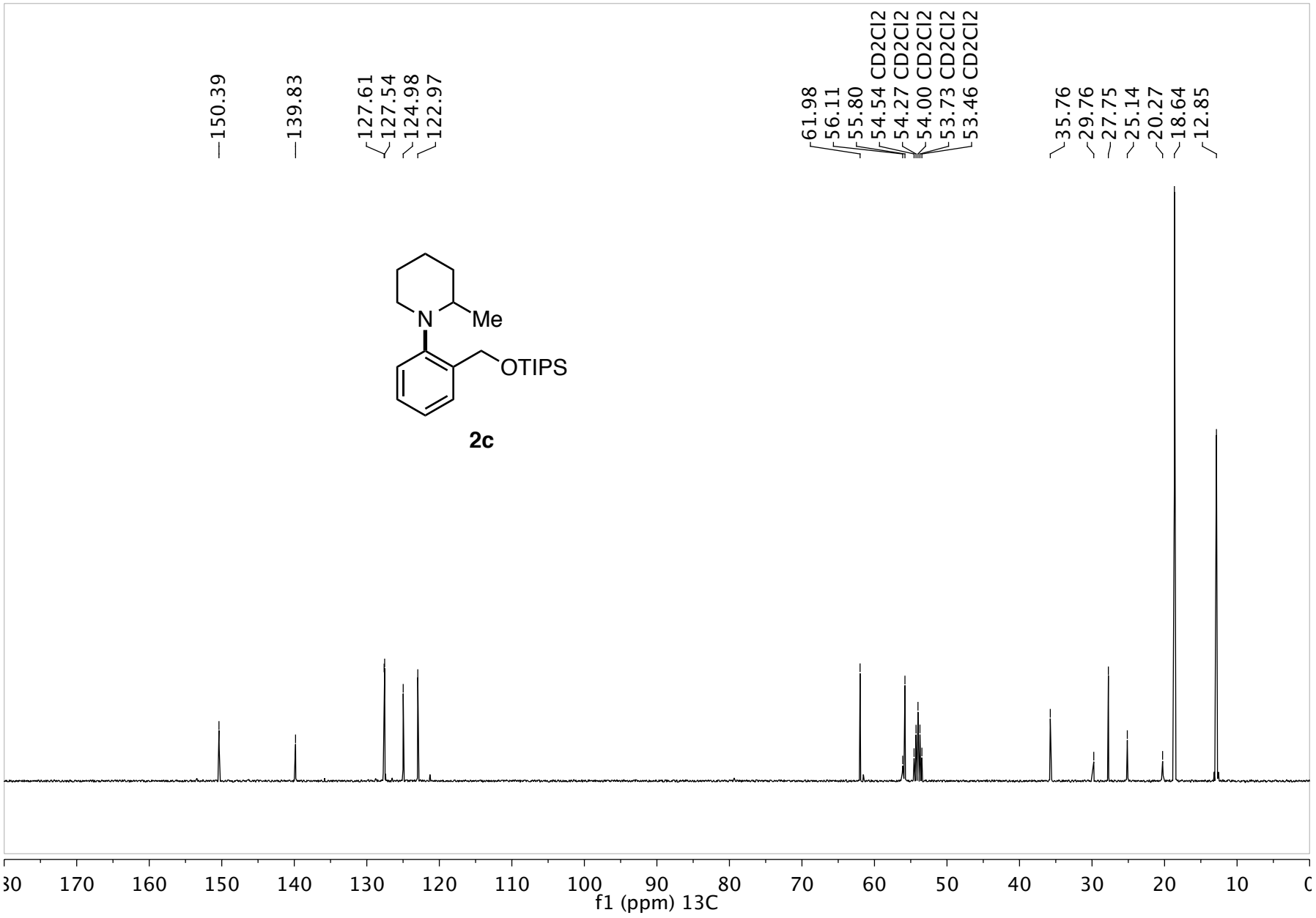
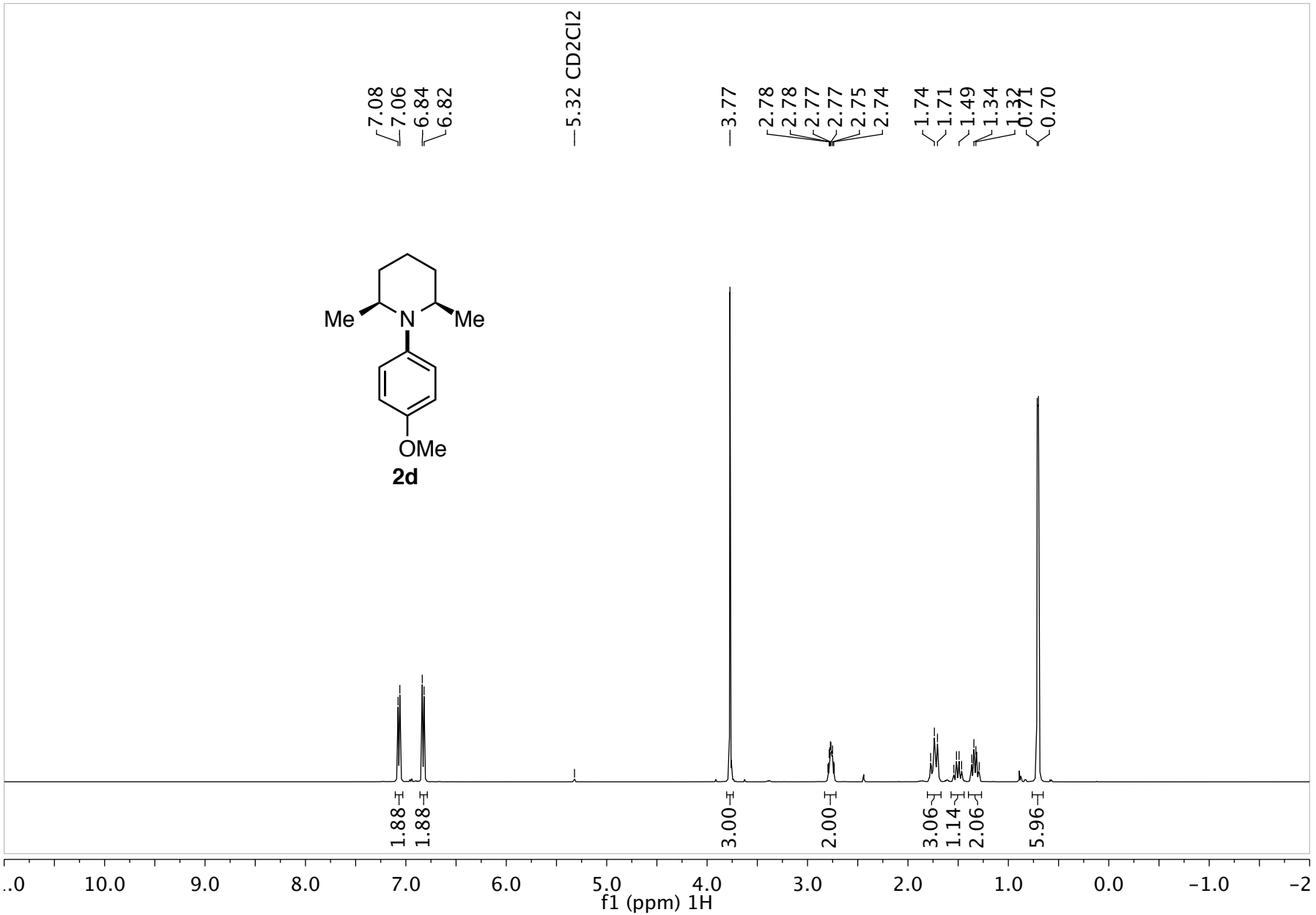
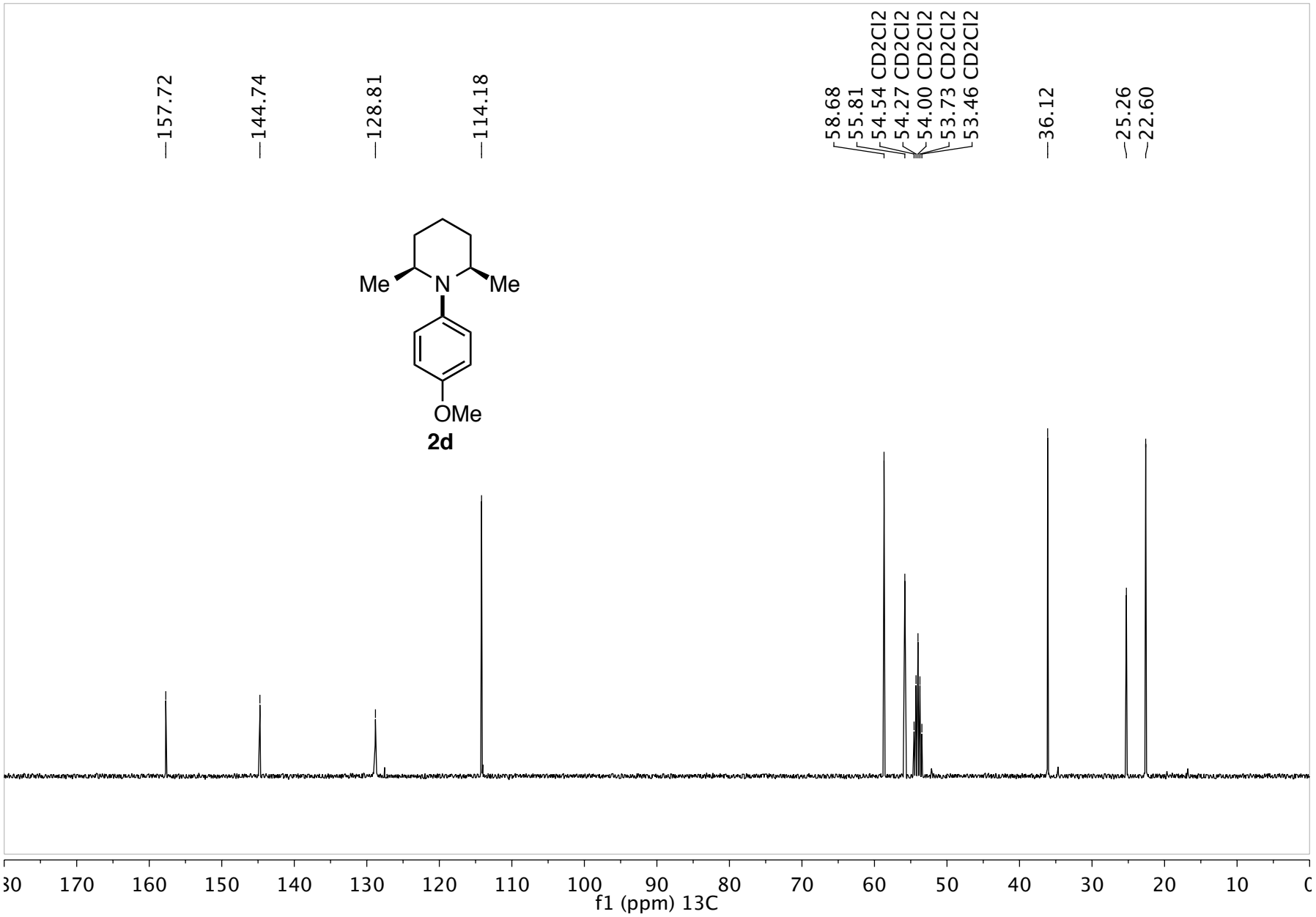
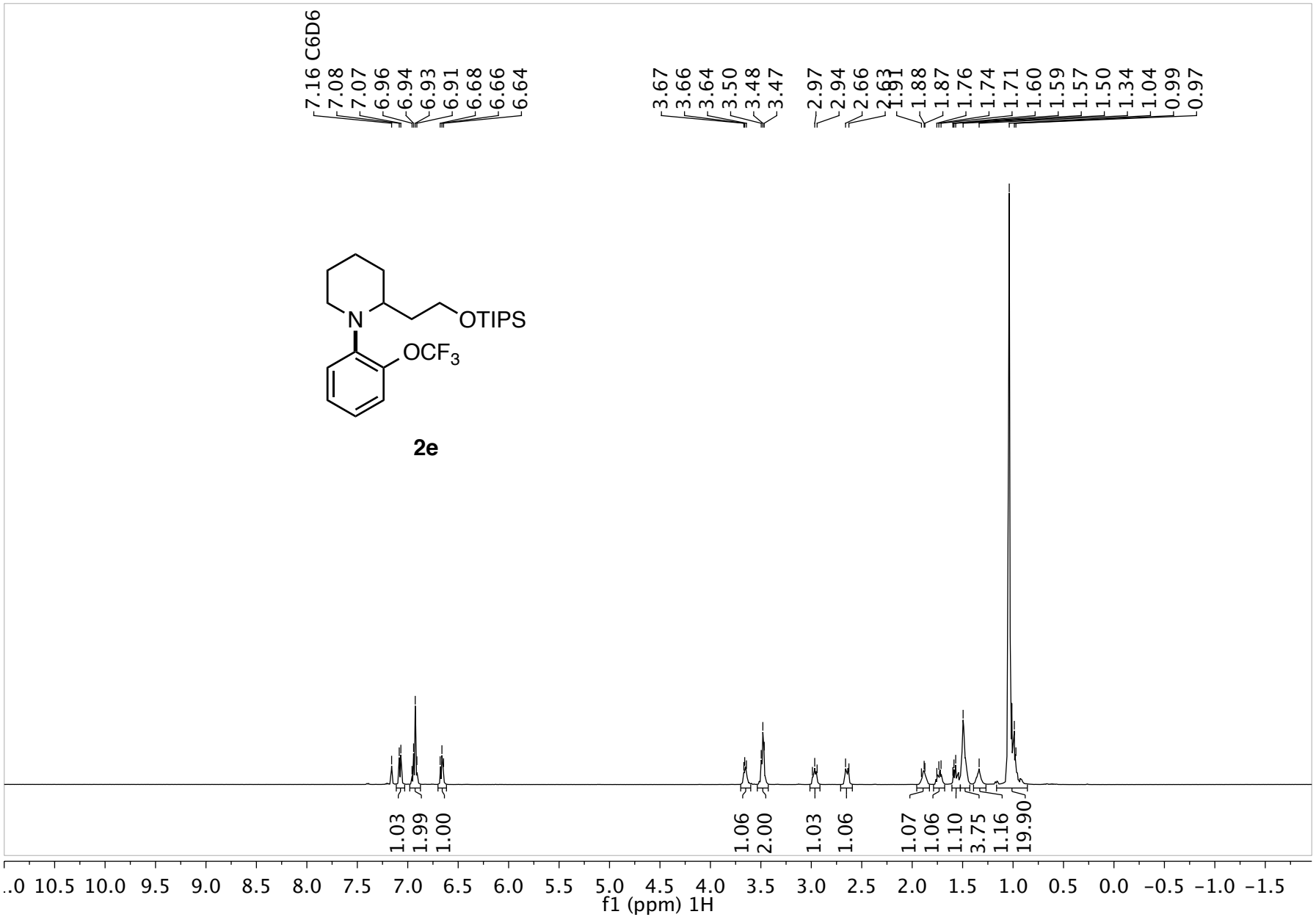
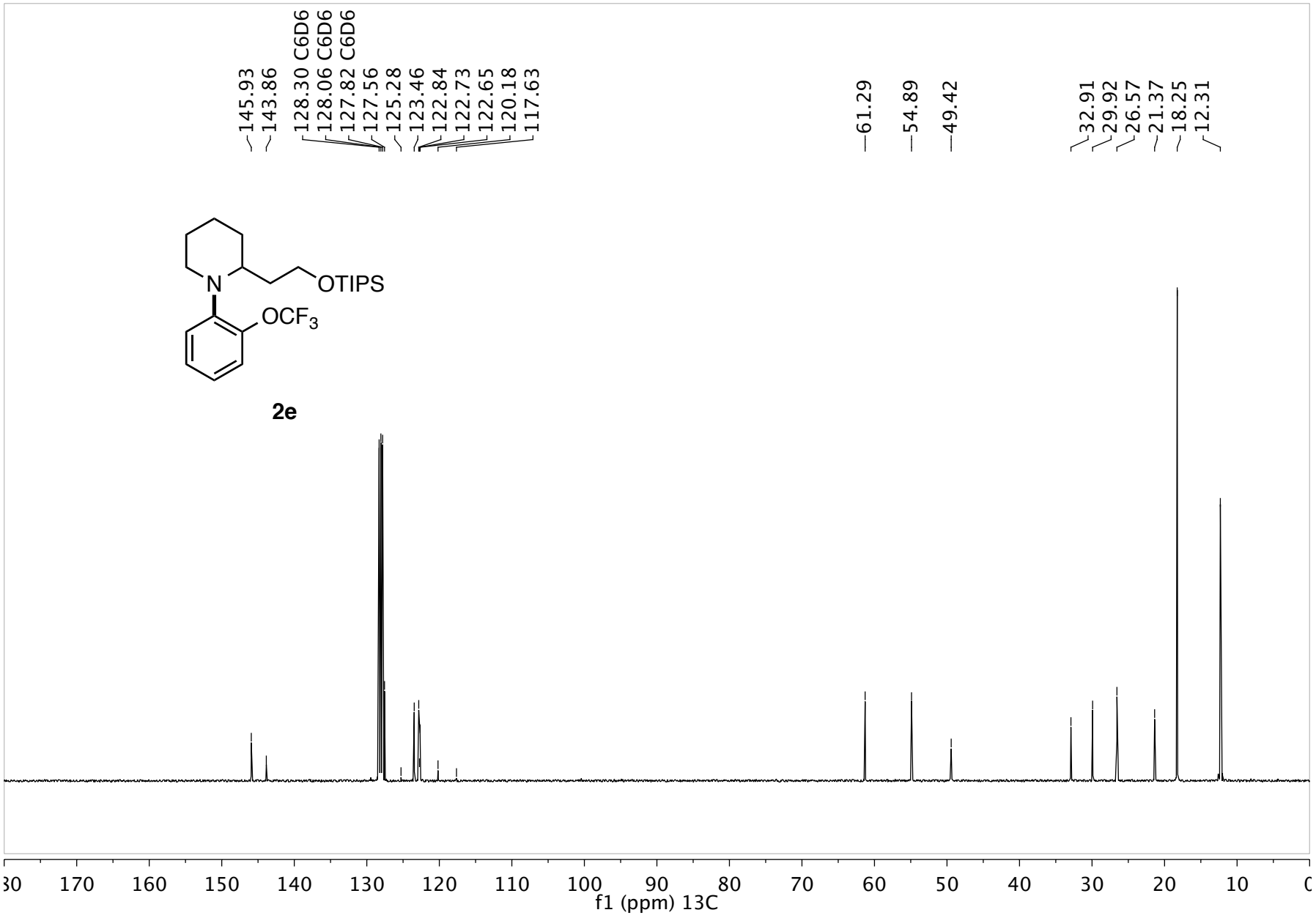
7.64
7.28
7.26
7.24
7.21
7.20
7.19
7.18
7.17
5.32 CD2Cl2
5.12
5.09
4.93
4.89
3.02
3.00
2.98
2.93
2.90
2.63
2.61
2.59
2.58
2.56
1.84
1.82
1.71
1.68
1.48
1.42
1.39
1.31
1.29
1.27
1.25
1.24
1.19
1.19
1.17
1.17
0.85
N
Me
OTIPS
2c
1.00
1.05
2.04
1.01
1.16
1.02
0.99
1.00
2.07
2.07
2.59
3.94
19.45
3.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

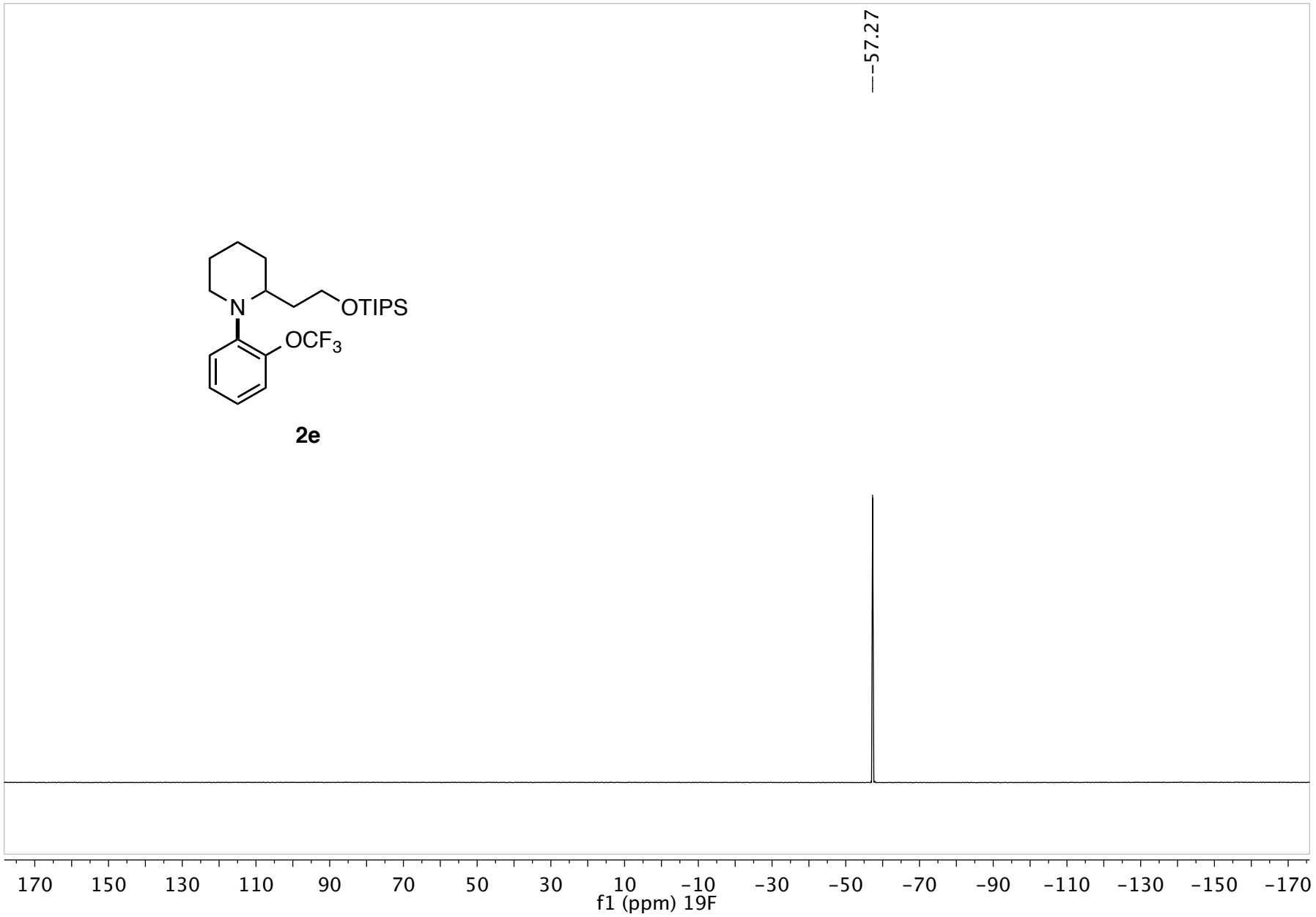

150.39
139.83
127.61
127.54
124.98
122.97
61.98
56.11
55.80
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
35.76
29.76
27.75
25.14
20.27
18.64
12.85
N
Me
OTIPS
2c
f1 (ppm) 13C


7.08
7.06
6.84
6.82
5.32 CD2Cl2
3.77
2.78
2.78
2.77
2.77
2.75
2.74
1.74
1.71
1.49
1.34
1.32
0.71
0.70
Me
N
Me
OMe
2d
1.88
1.88
3.00
2.00
3.06
1.14
2.06
5.96
f1 (ppm) 1H


157.72
144.74
128.81
114.18
58.68
55.81
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
36.12
25.26
22.60
Me
N
Me
OMe
2d
f1 (ppm) 13C


7.16 C6D6
7.08
7.07
6.96
6.94
6.93
6.91
6.68
6.66
6.64
3.67
3.66
3.64
3.50
3.48
3.47
2.97
2.94
2.66
2.63
1.91
1.88
1.87
1.76
1.74
1.71
1.60
1.59
1.57
1.50
1.34
1.04
0.99
0.97
N
OTIPS
OCF3
2e
1.03
1.99
1.00
1.06
2.00
1.03
1.06
1.07
1.06
1.10
3.75
1.16
19.90
f1 (ppm) 1H


145.93
143.86
128.30 C6D6
128.06 C6D6
127.82 C6D6
127.56
125.28
123.46
122.84
122.73
122.65
120.18
117.63
61.29
54.89
49.42
32.91
29.92
26.57
21.37
18.25
12.31
N
OTIPS
OCF3
2e
f1 (ppm) 13C


-57.27
N
OTIPS
OCF3
2e
170
150
130
110
90
70
50
30
10
-10
-30
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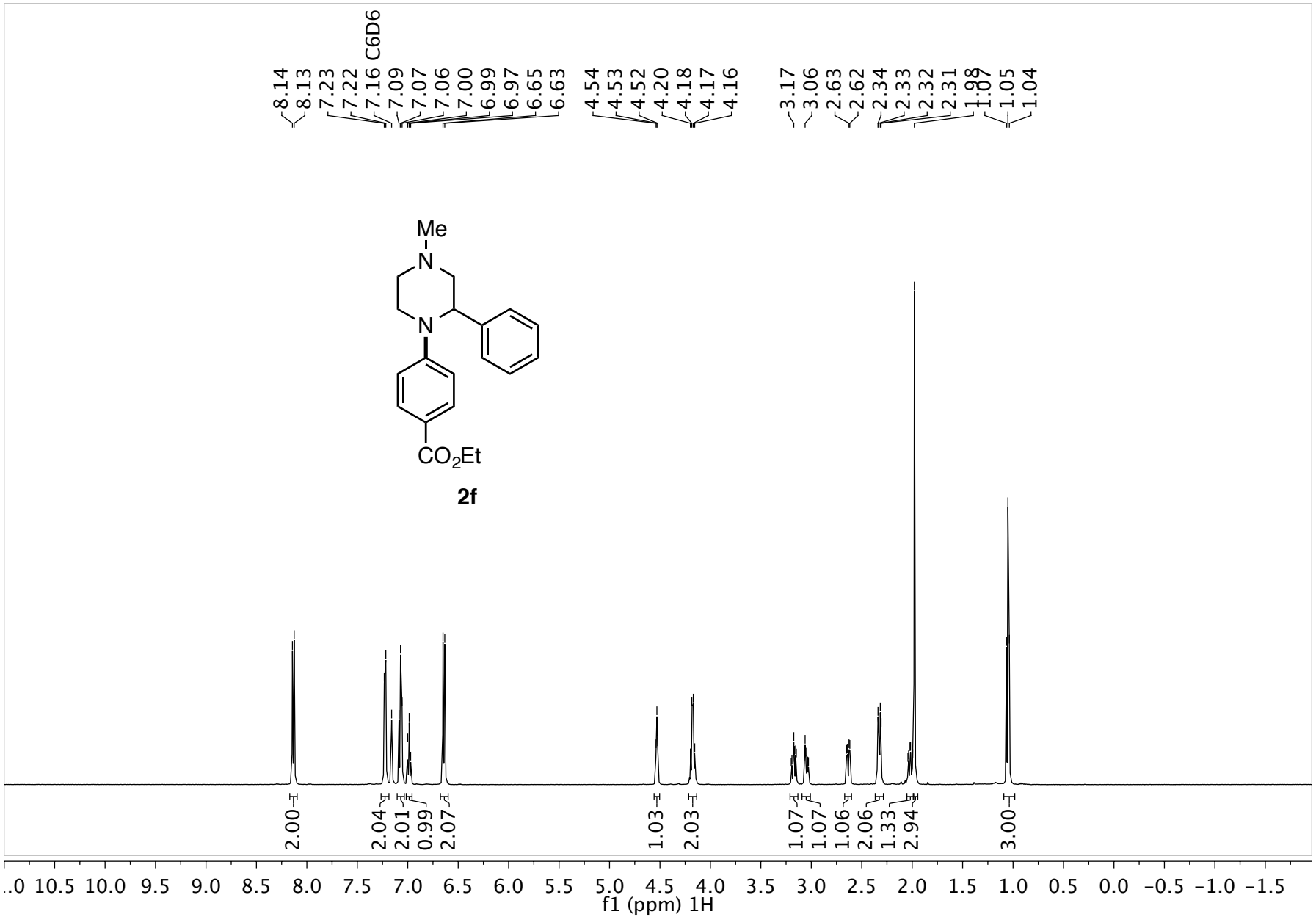
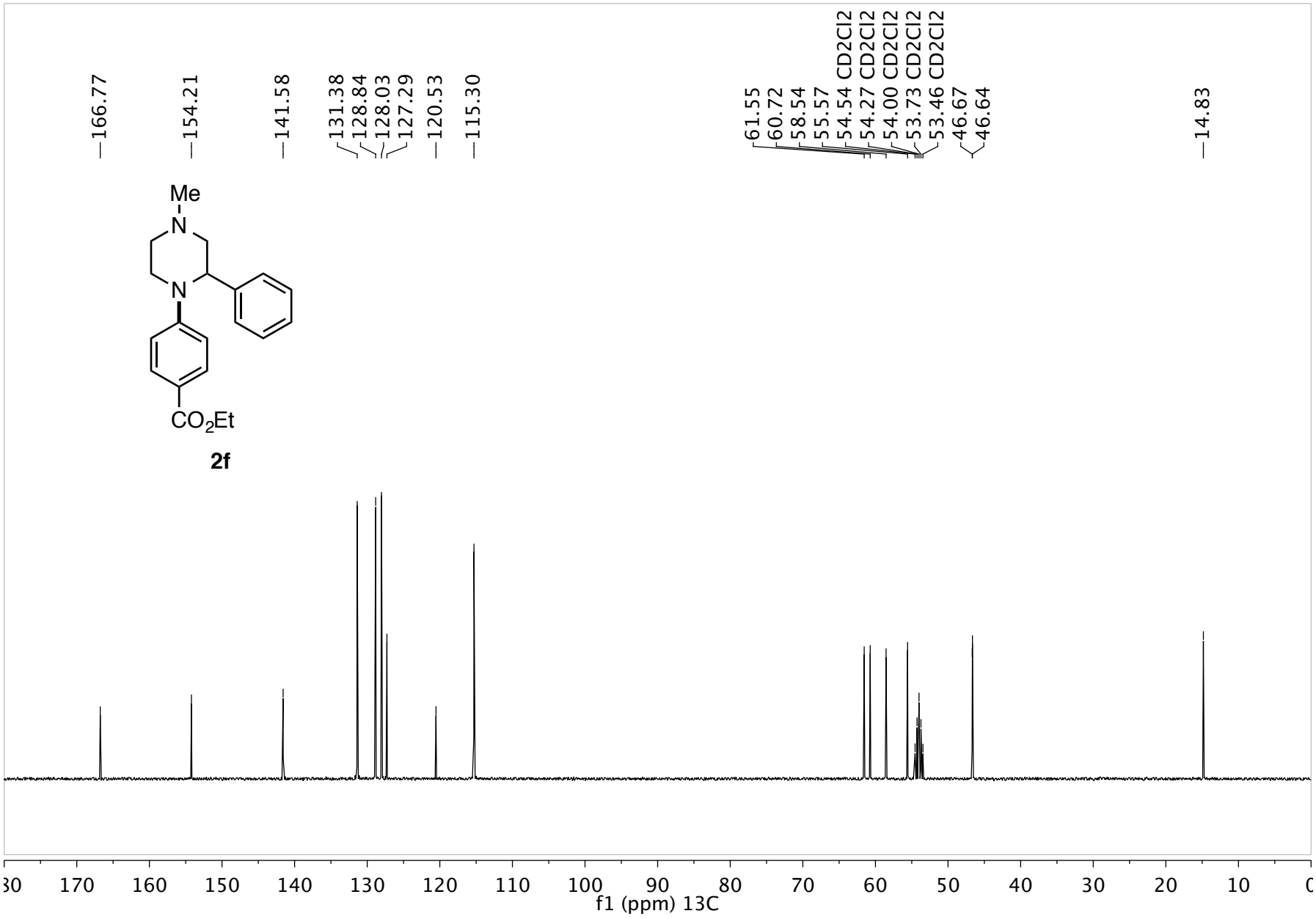
-90
-110
-130
-150
-170
f1 (ppm) 19F


8.14
8.13
7.23
7.22
7.16 C6D6
7.09
7.07
7.06
7.00
6.99
6.97
6.65
6.63
4.54
4.53
4.52
4.20
4.18
4.17
4.16
3.17
3.06
2.63
2.62
2.34
2.33
2.32
2.31
1.98
1.07
1.05
1.04
Me
N
N
CO2Et
2f
2.00
2.04
2.01
0.99
2.07
1.03
2.03
1.07
1.07
1.06
2.06
1.33
2.94
3.00
f1 (ppm) 1H


166.77
154.21
141.58
131.38
128.84
128.03
127.29
120.53
115.30
61.55
60.72
58.54
55.57
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
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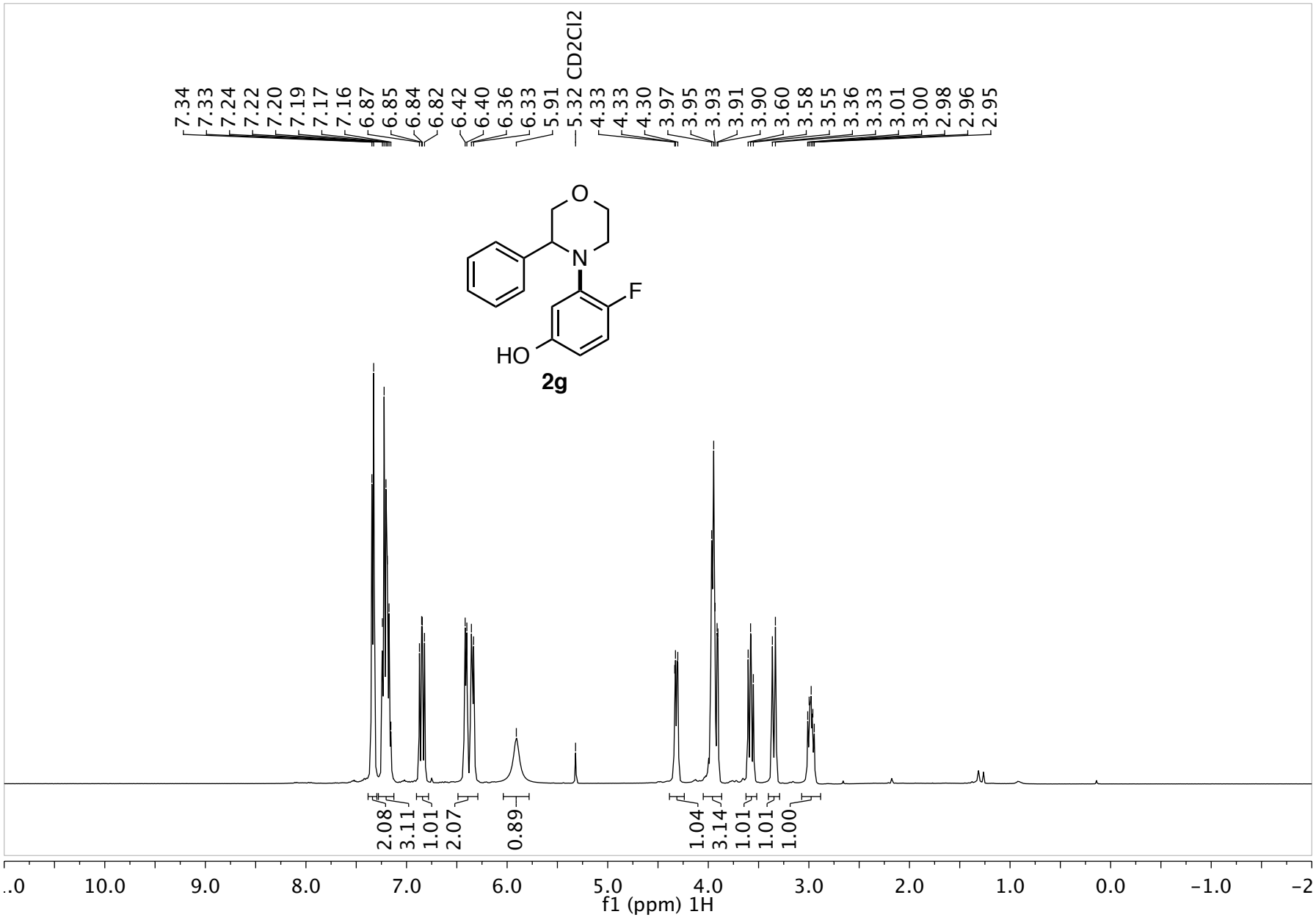
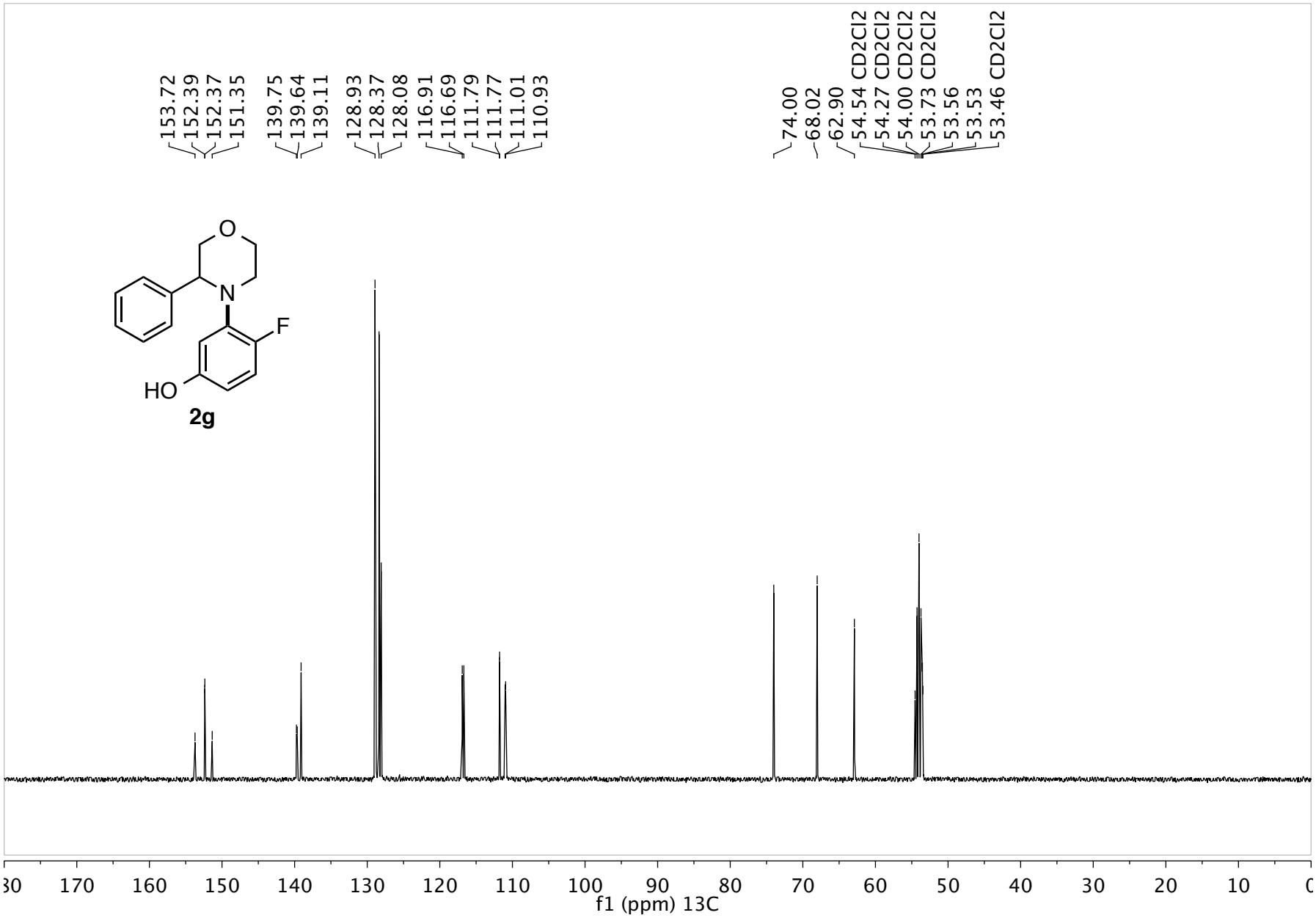
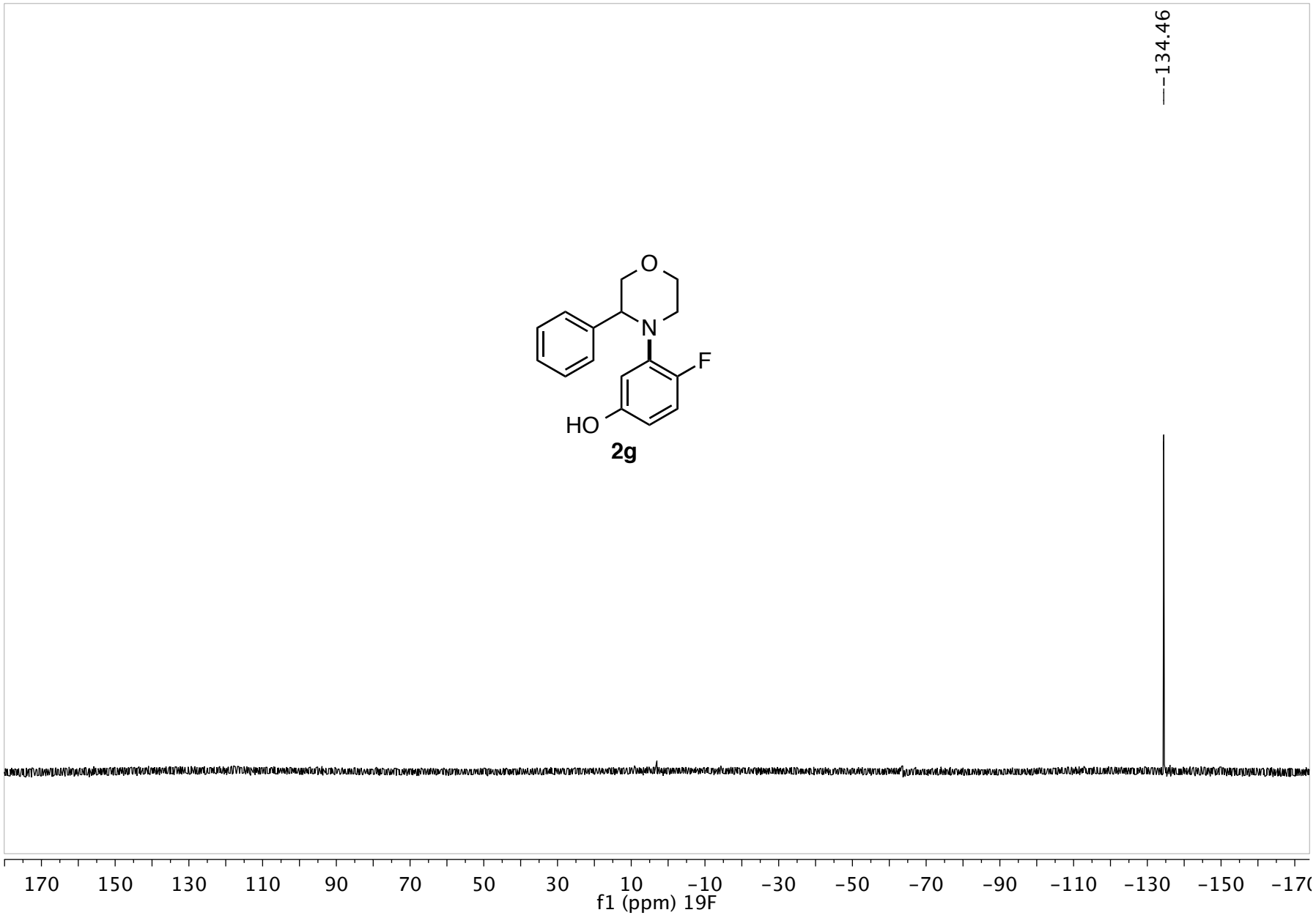
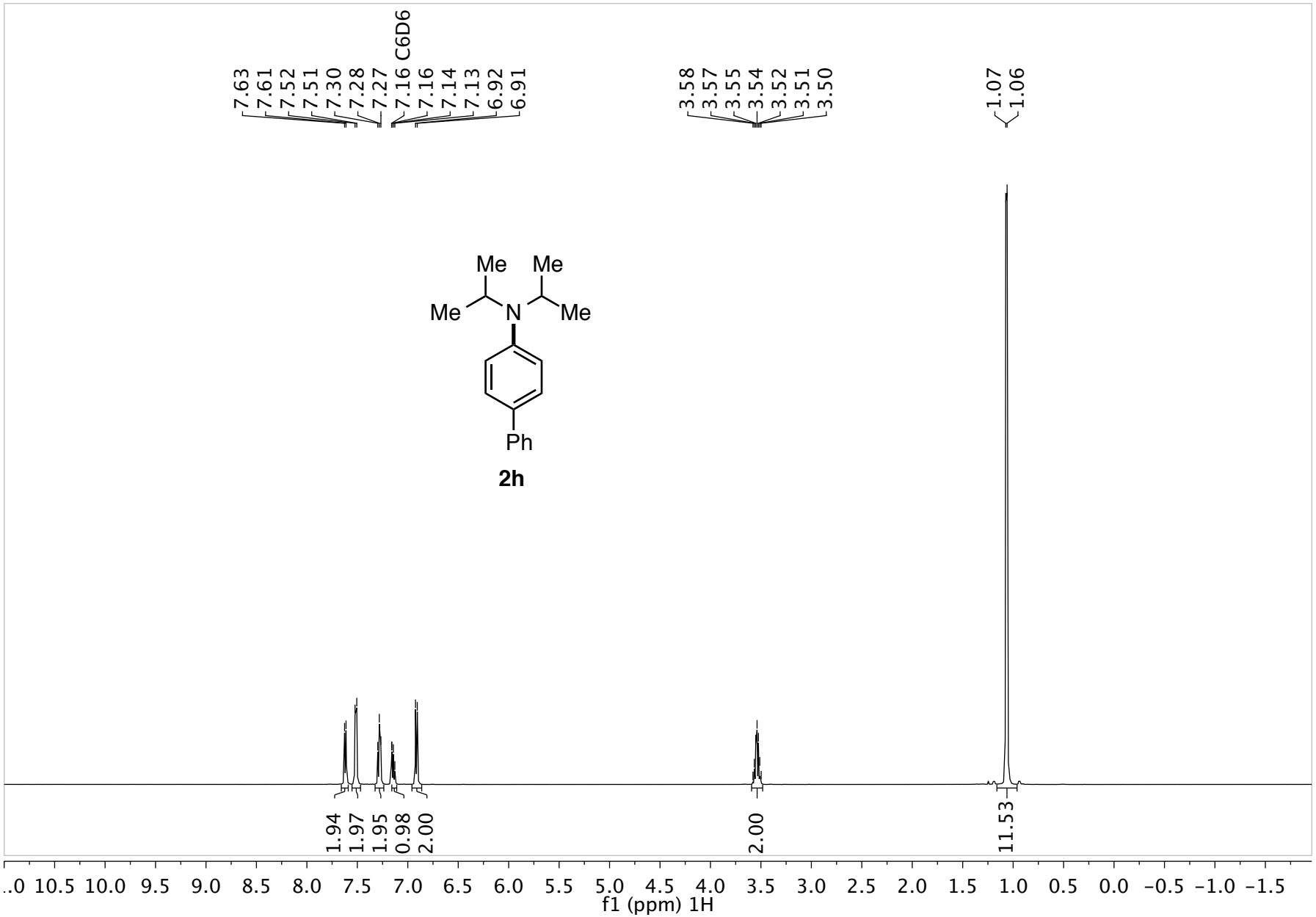
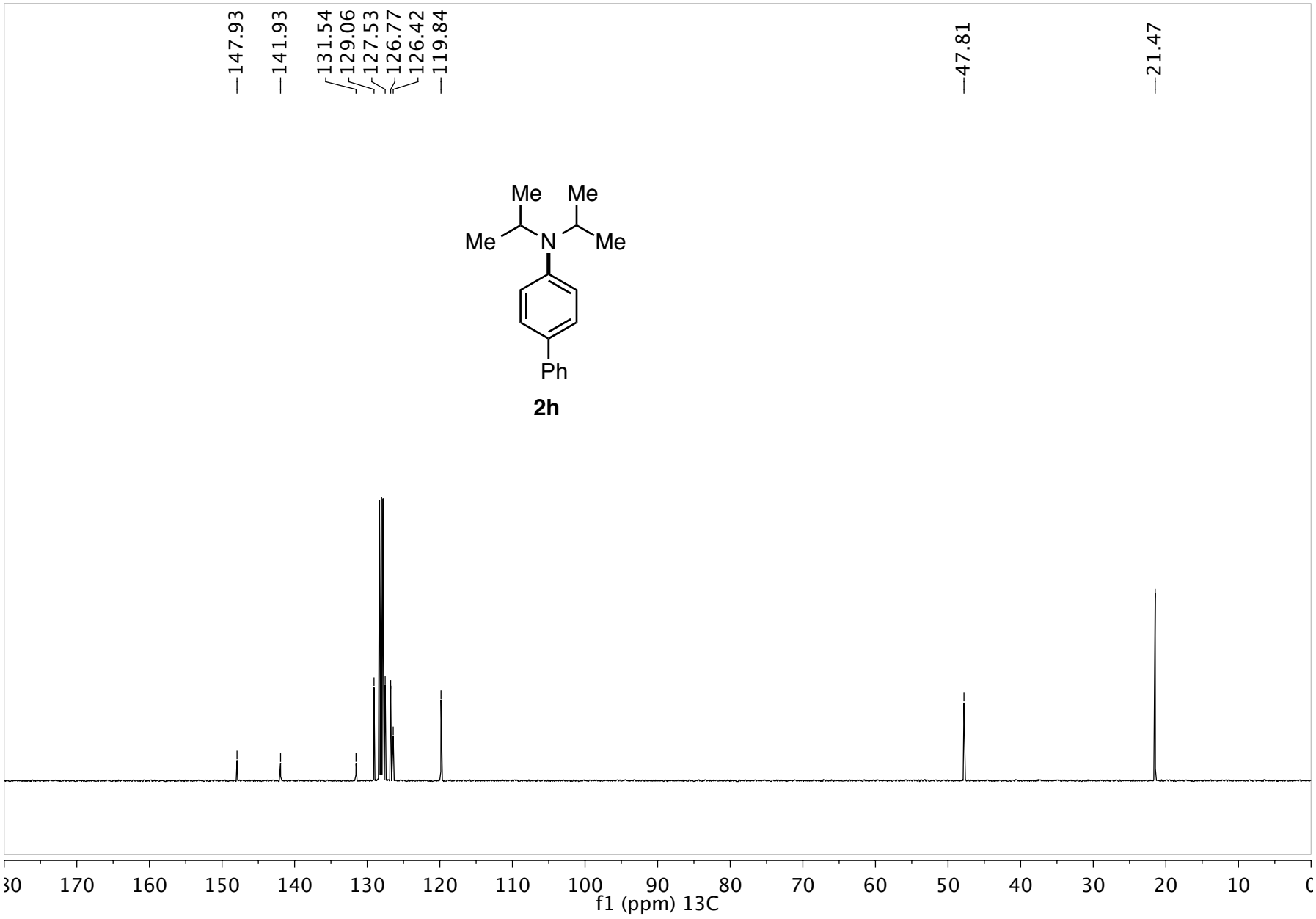
Me
N
N
CO2Et
2f
f1 (ppm) 13C

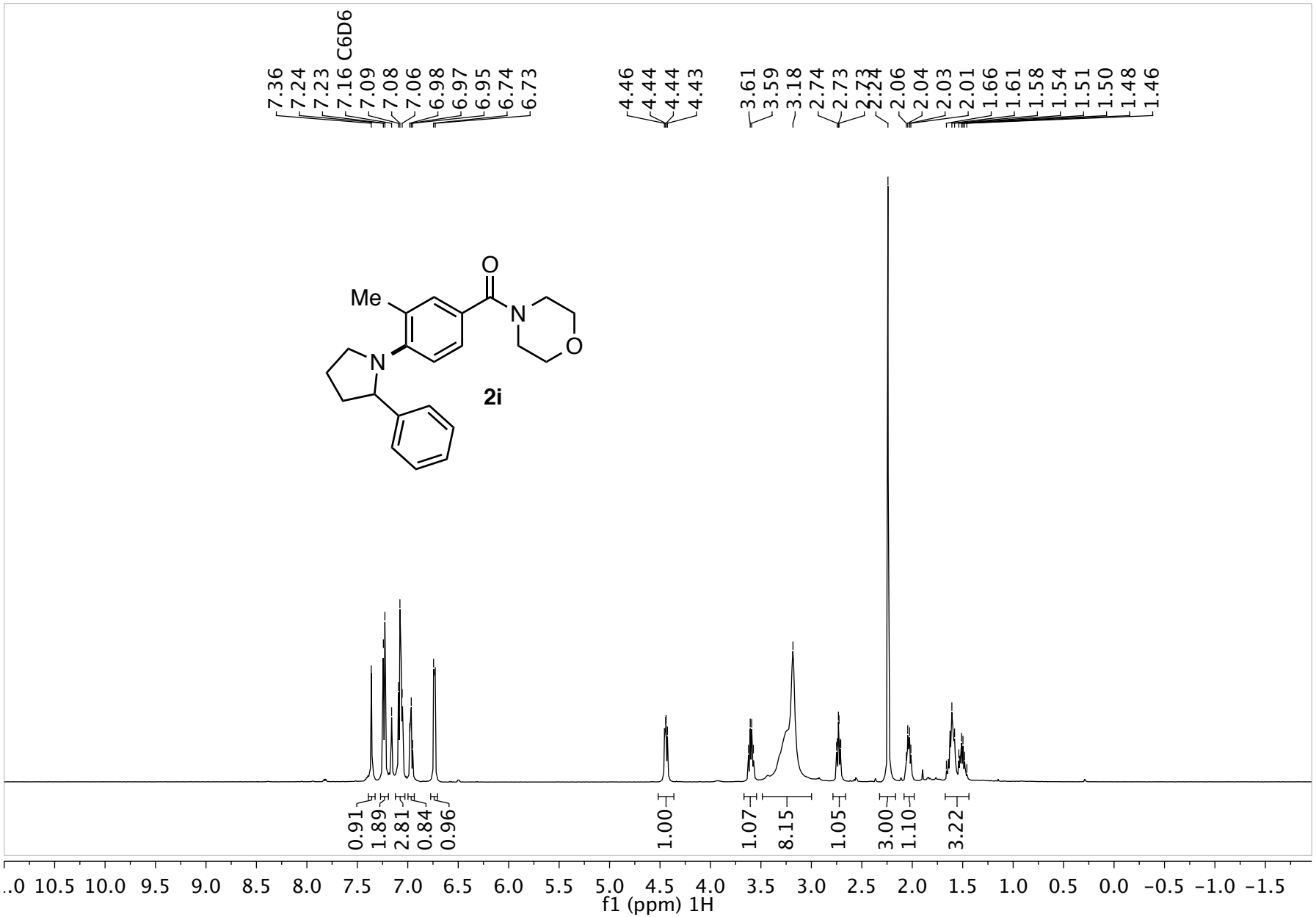

7.34
7.33
7.24
7.22
7.20
7.19
7.17
7.16
6.87
6.85
6.84
6.82
6.42
6.40
6.36
6.33
5.91
5.32 CD2Cl2
4.33
4.33
4.30
3.97
3.95
3.93
3.91
3.90
3.60
3.58
3.55
3.36
3.33
3.01
3.00
2.98
2.96
2.95
O
N
F
HO
2g
2.08
3.11
1.01
2.07
0.89
1.04
3.14
1.01
1.01
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

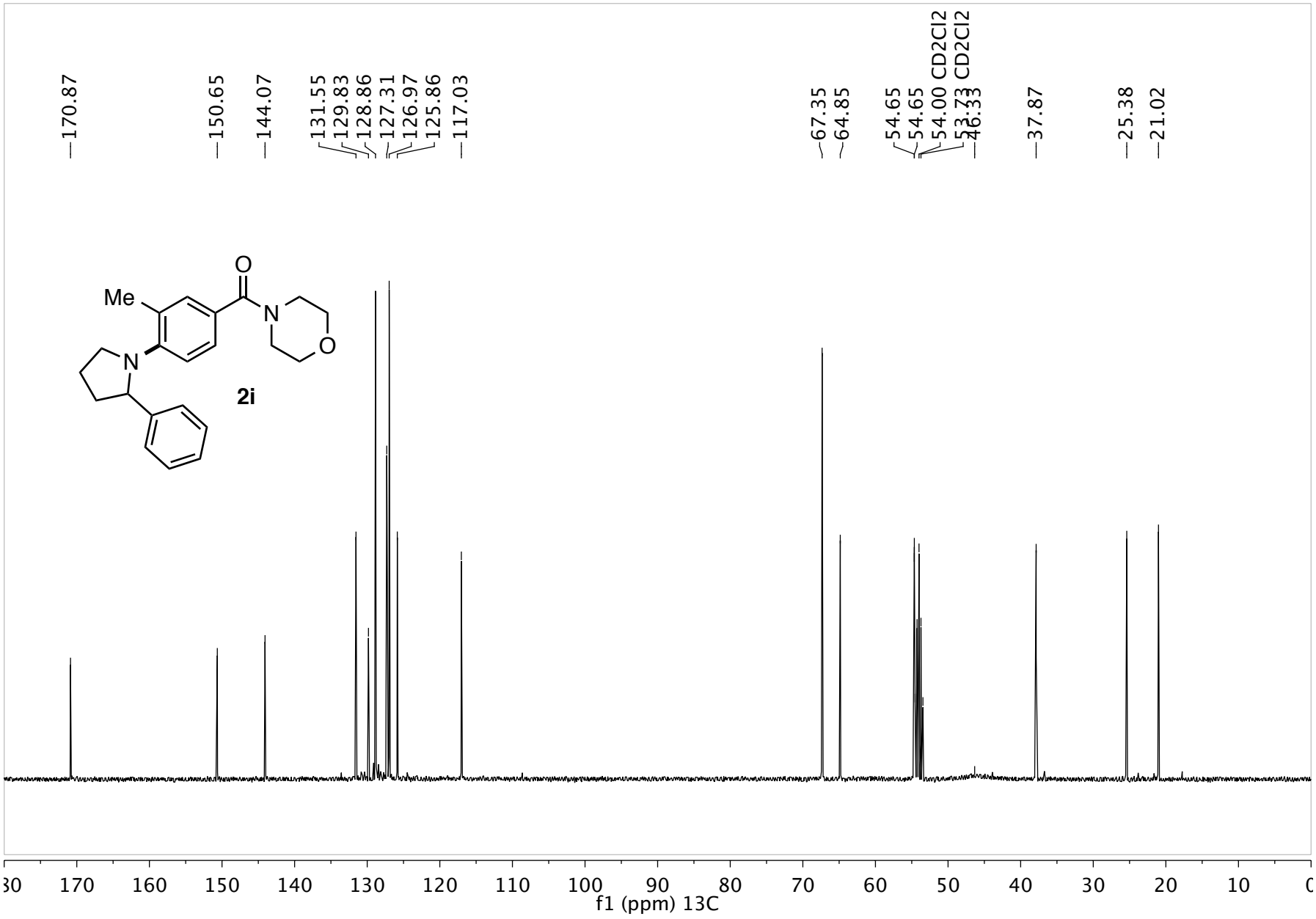

153.72
152.39
152.37
151.35
139.75
139.64
139.11
128.93
128.37
128.08
116.91
116.69
111.79
111.77
111.01
110.93
74.00
68.02
62.90
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.56
53.53
53.46 CD2Cl2
O
N
F
HO
2g
f1 (ppm) 13C

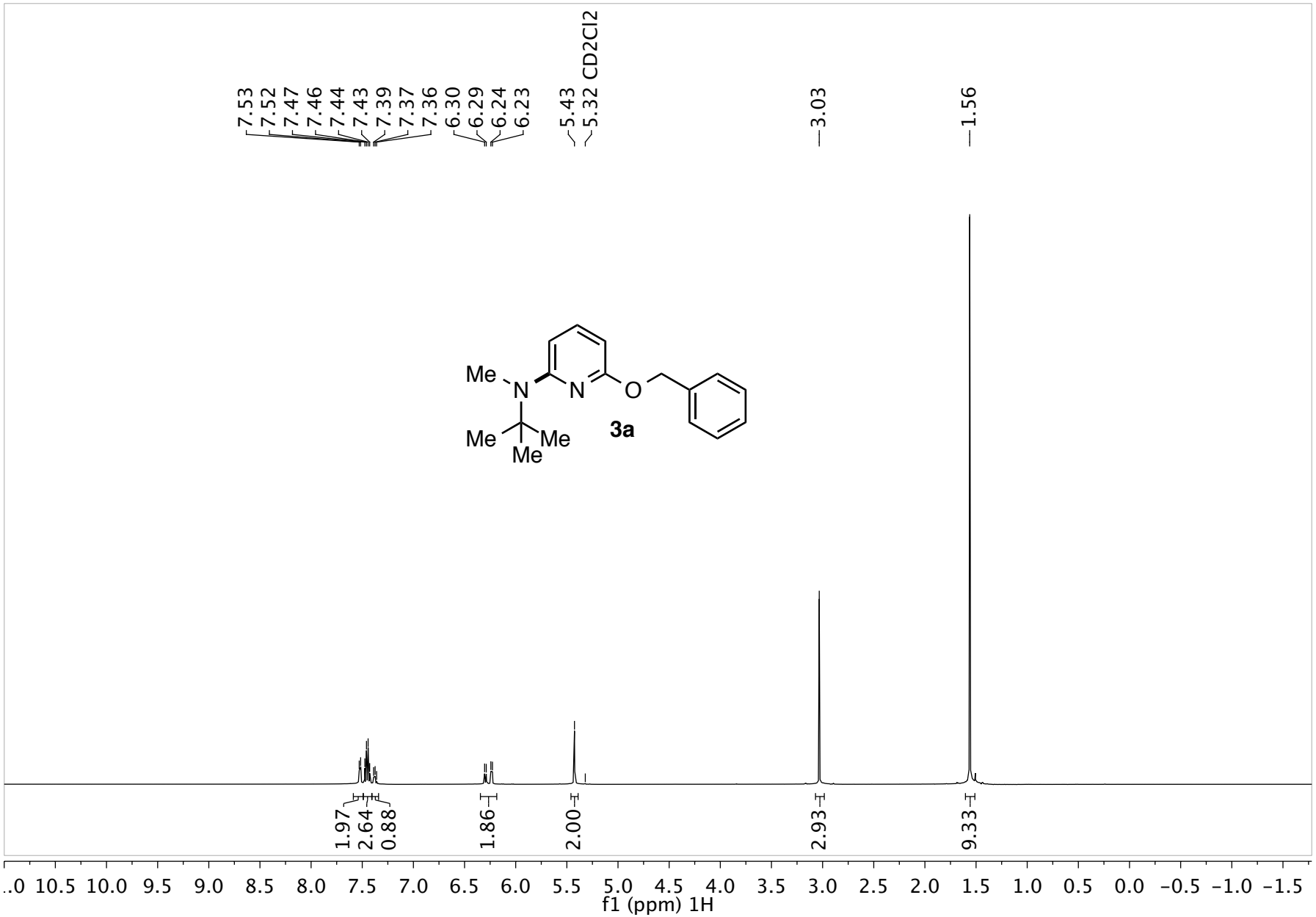

-134.46
O
N
F
HO
2g
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
f1 (ppm) 19F

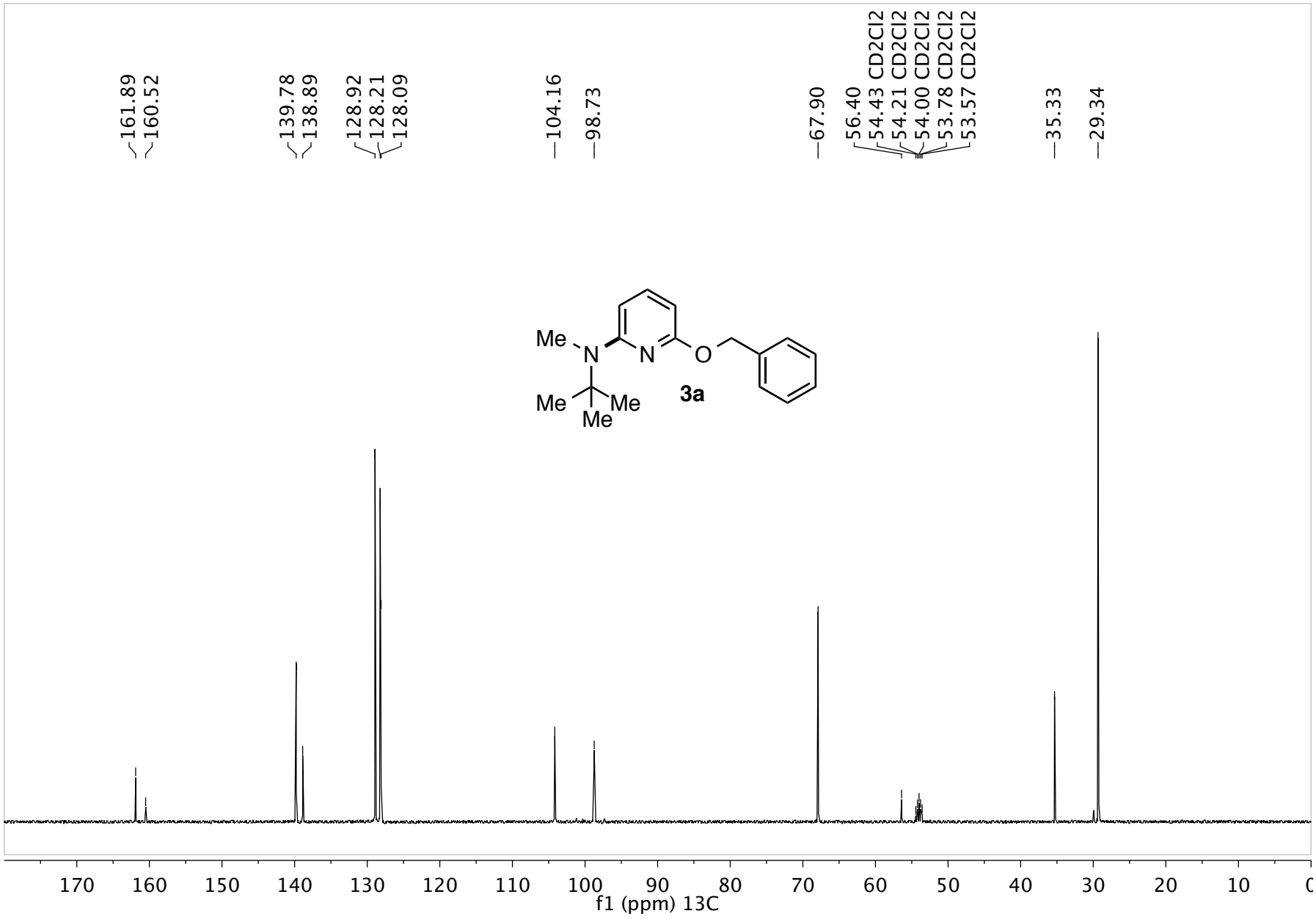

7.63
7.61
7.52
7.51
7.30
7.28
7.27
7.16 C6D6
7.16
7.14
7.13
6.92
6.91
3.58
3.57
3.55
3.54
3.52
3.51
3.50
1.07
1.06
Me
Me
Me
N
Me
Ph
2h
1.94
1.97
1.95
0.98
2.00
2.00
11.53
f1 (ppm) 1H

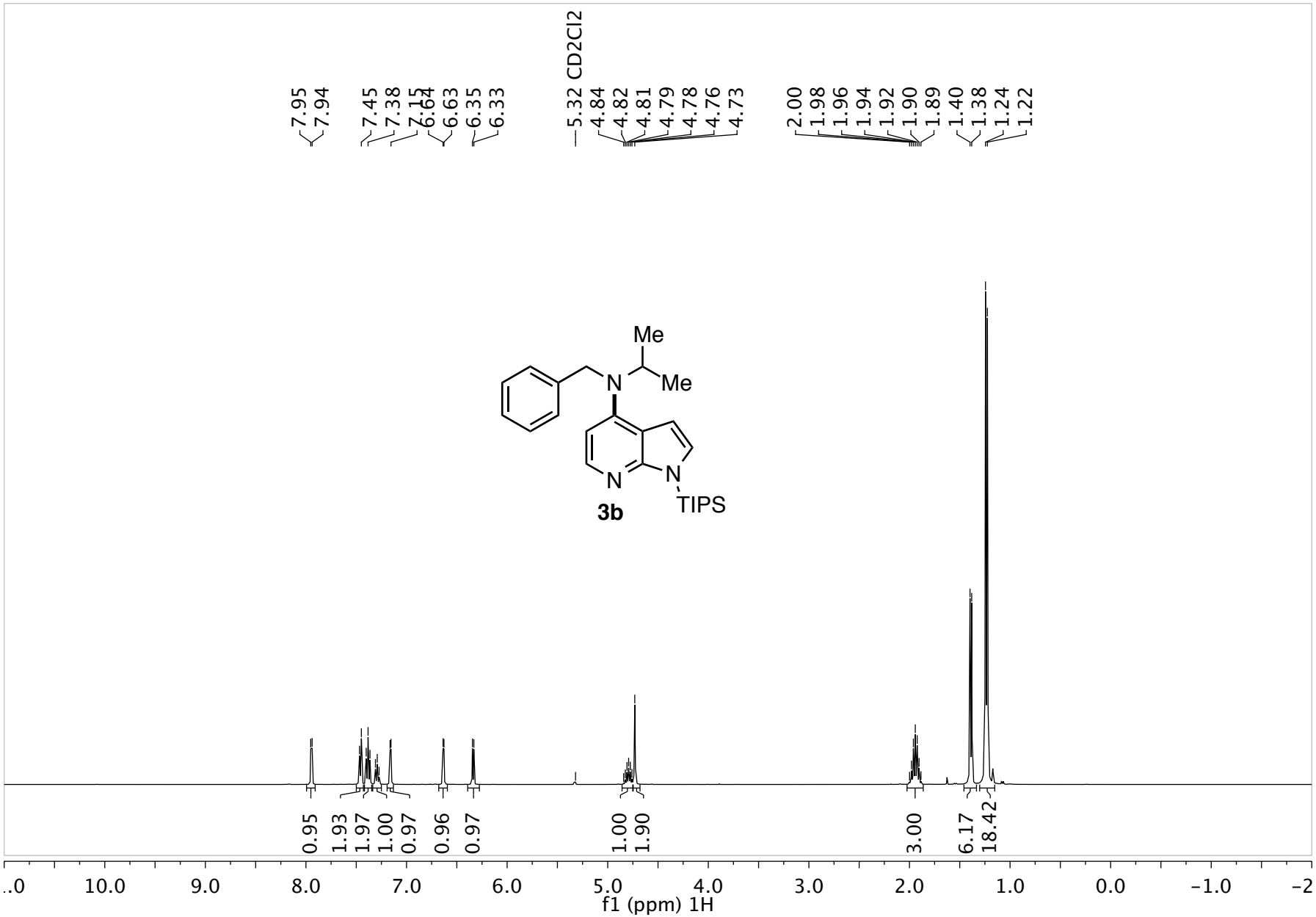

147.93
141.93
131.54
129.06
127.53
126.77
126.42
119.84
47.81
21.47
Me
Me
Me
N
Me
Ph
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C

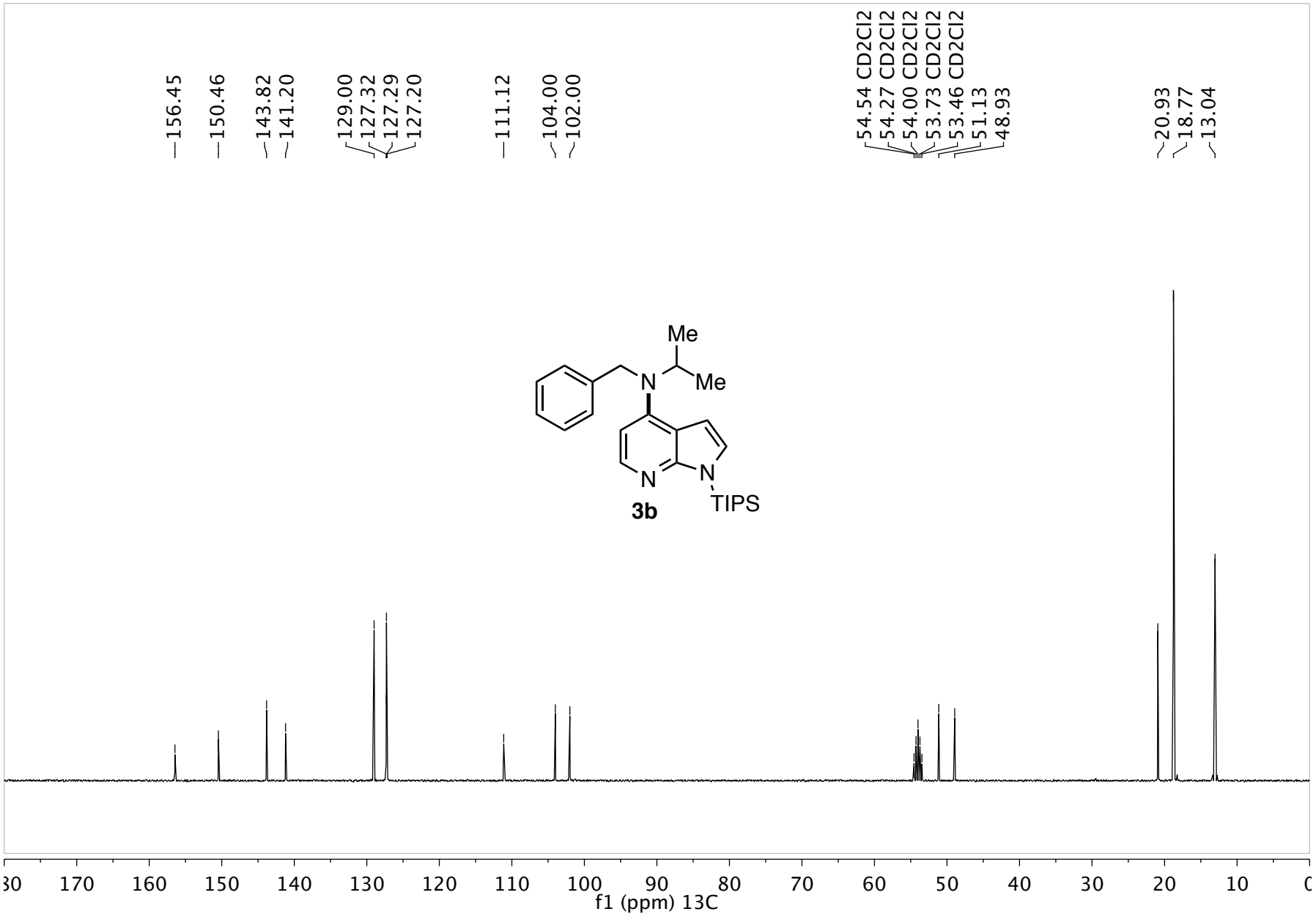

7.36
7.24
7.23
7.16 C6D6
7.09
7.08
7.06
6.98
6.97
6.95
6.74
6.73
4.46
4.44
4.44
4.43
3.61
3.59
3.18
2.74
2.73
2.06
2.04
2.03
2.01
1.66
1.61
1.58
1.54
1.51
1.50
1.48
1.46
Me
O
N
O
N
2i
0.91
1.89
2.81
0.84
0.96
1.00
1.07
8.15
1.05
3.00
1.10
3.22
f1 (ppm) 1H

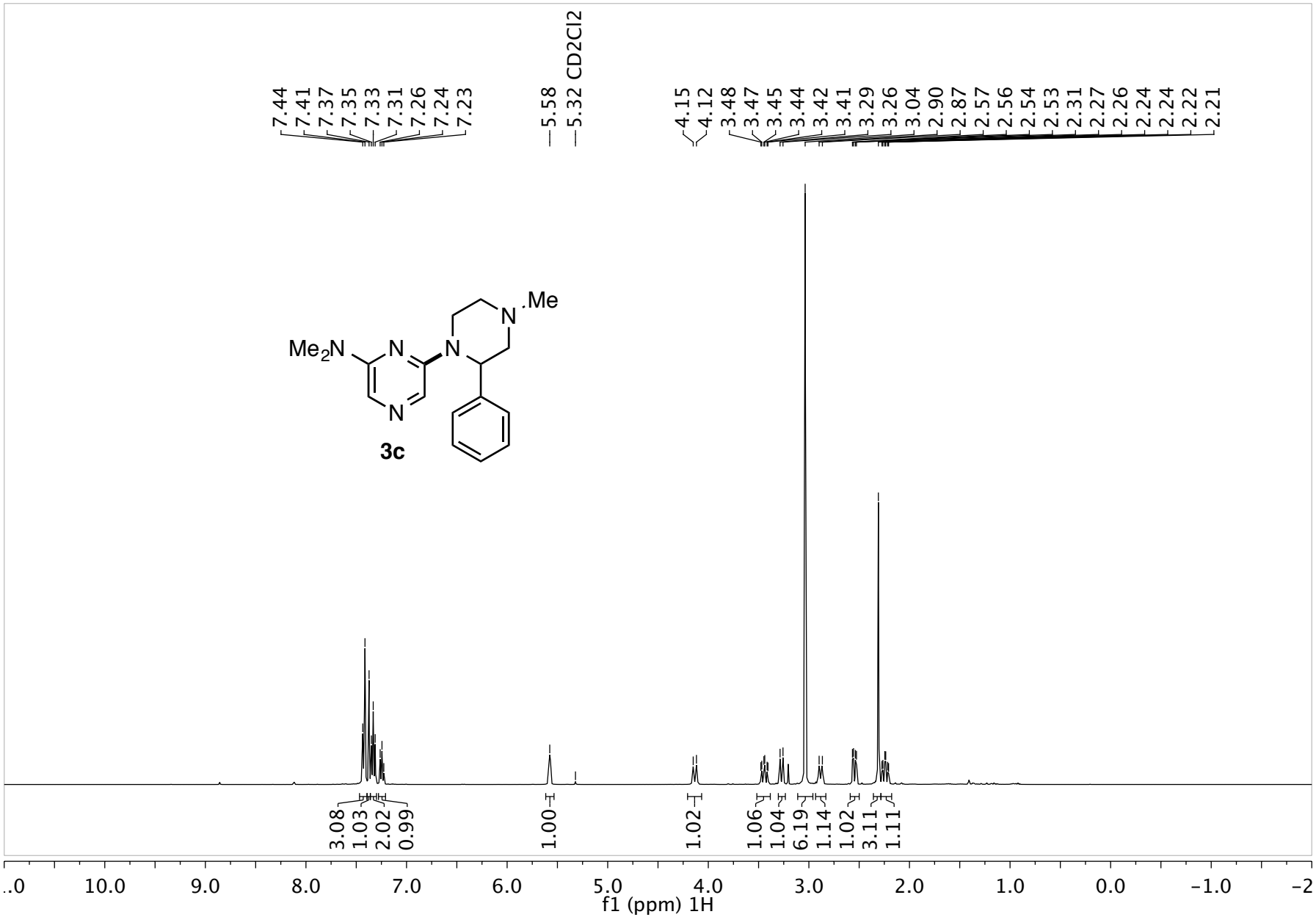

170.87
150.65
144.07
131.55
129.83
128.86
127.31
126.97
125.86
117.03
67.35
64.85
54.65
54.65
54.00 CD2Cl2
53.73 CD2Cl2
46.33
37.87
25.38
21.02
Me
O
N
N
O
2i
f1 (ppm) 13C

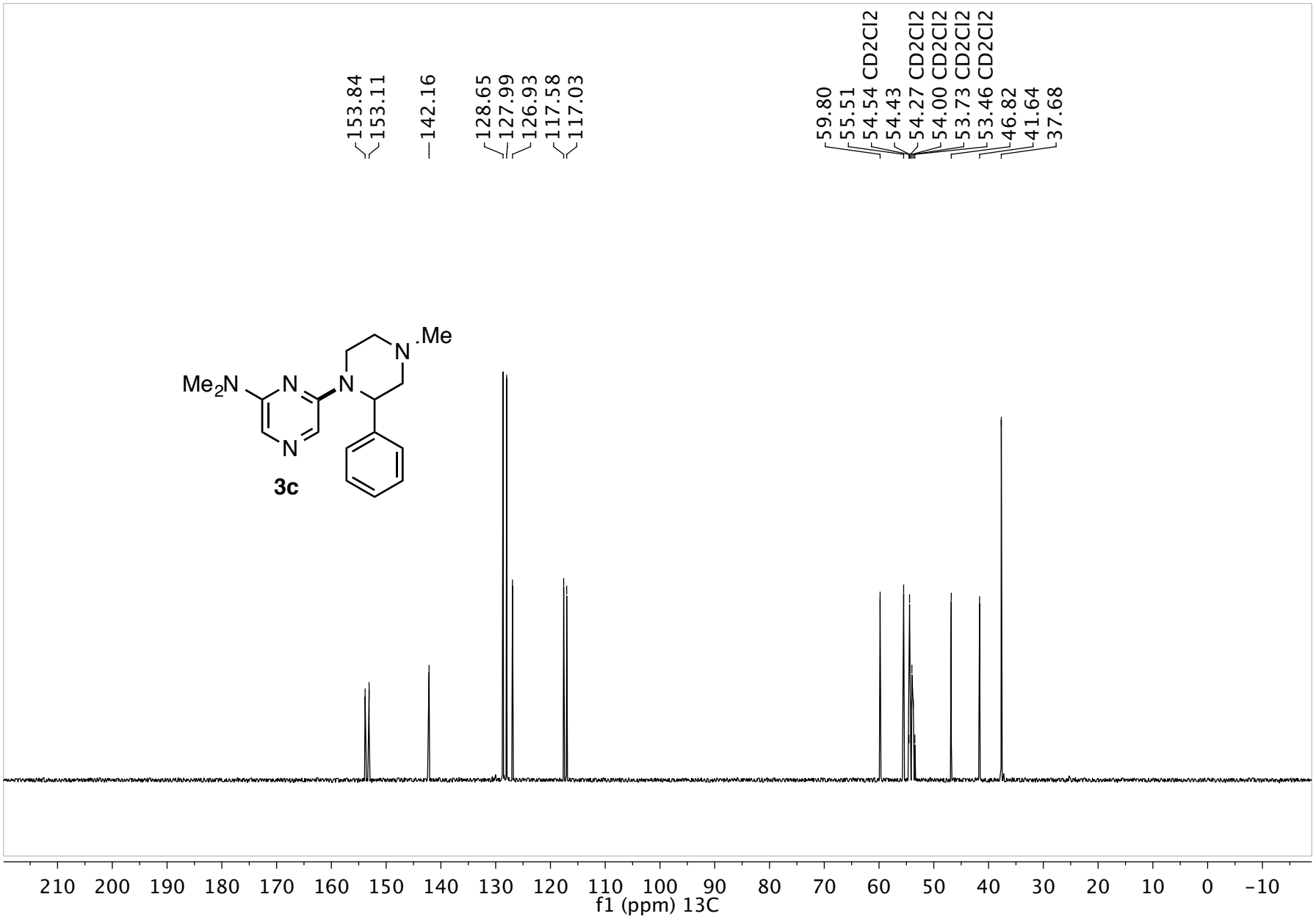

7.53
7.52
7.47
7.46
7.44
7.43
7.39
7.37
7.36
6.30
6.29
6.24
6.23
5.43
5.32 CD2Cl2
3.03
1.56
Me
N
N
O
Me
Me
Me
3a
1.97
2.64
0.88
1.86
2.00
2.93
9.33
f1 (ppm) 1H

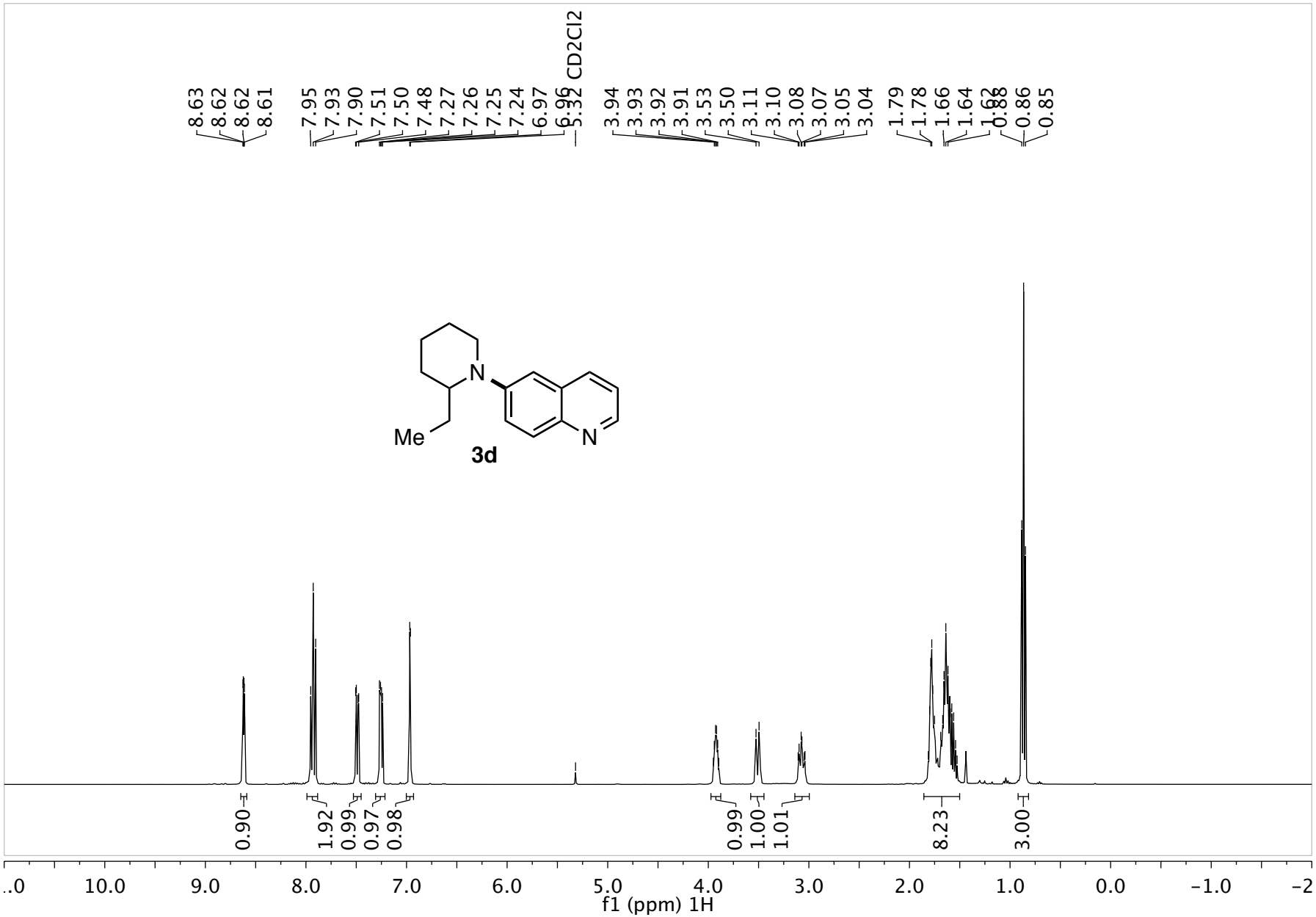

161.89
160.52
139.78
138.89
128.92
128.21
128.09
104.16
98.73
67.90
56.40
54.43 CD2Cl2
54.21 CD2Cl2
54.00 CD2Cl2
53.78 CD2Cl2
53.57 CD2Cl2
35.33
29.34
Me
N
N
O
Me
Me
Me
3a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C

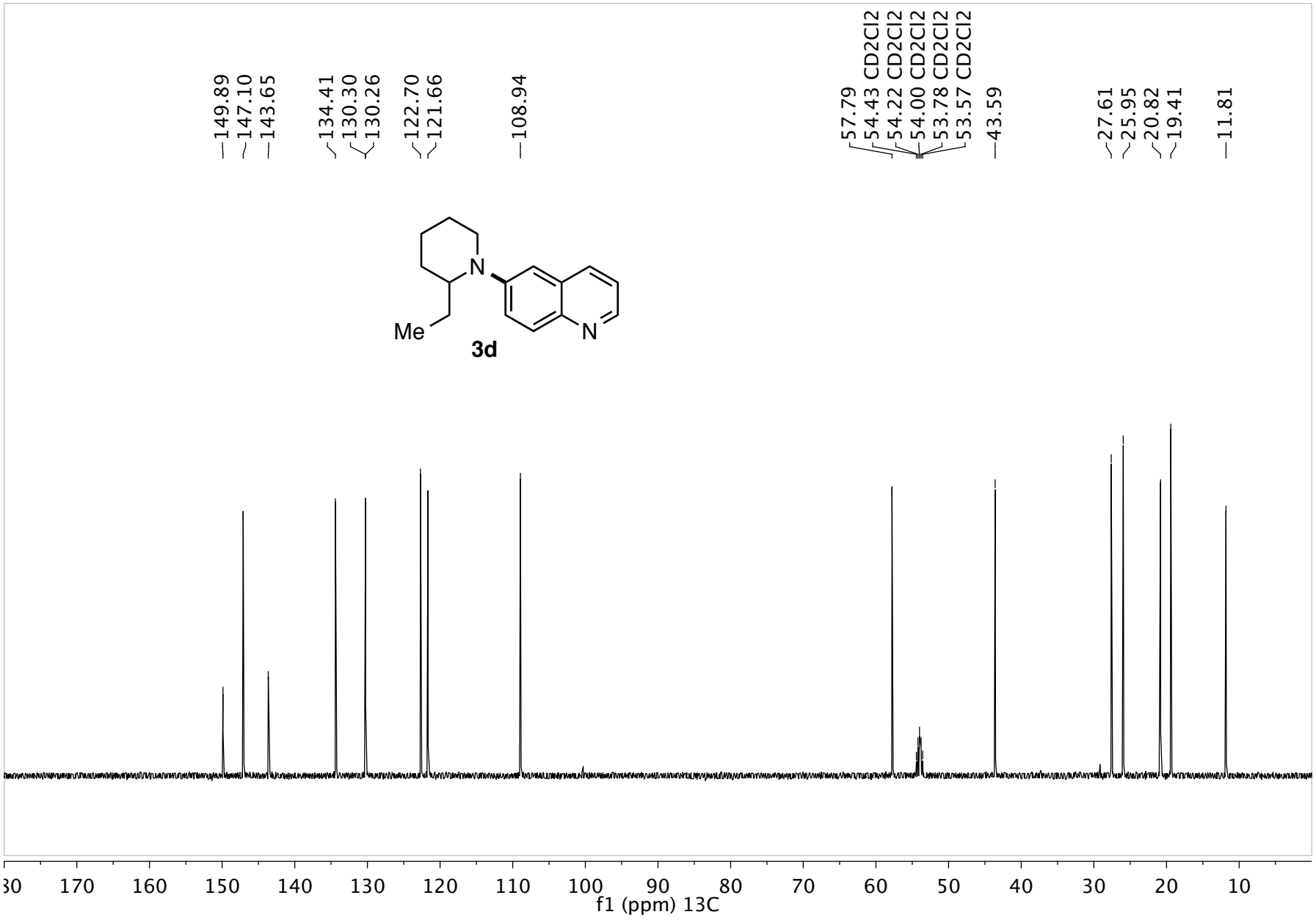

7.95
7.94
7.45
7.38
7.15
6.64
6.63
6.35
6.33
5.32 CD2Cl2
4.84
4.82
4.81
4.79
4.78
4.76
4.73
2.00
1.98
1.96
1.94
1.92
1.90
1.89
1.40
1.38
1.24
1.22
Me
N
Me
N
N
TIPS
3b
0.95
1.93
1.97
1.00
0.97
0.96
0.97
1.00
1.90
3.00
6.17
18.42
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

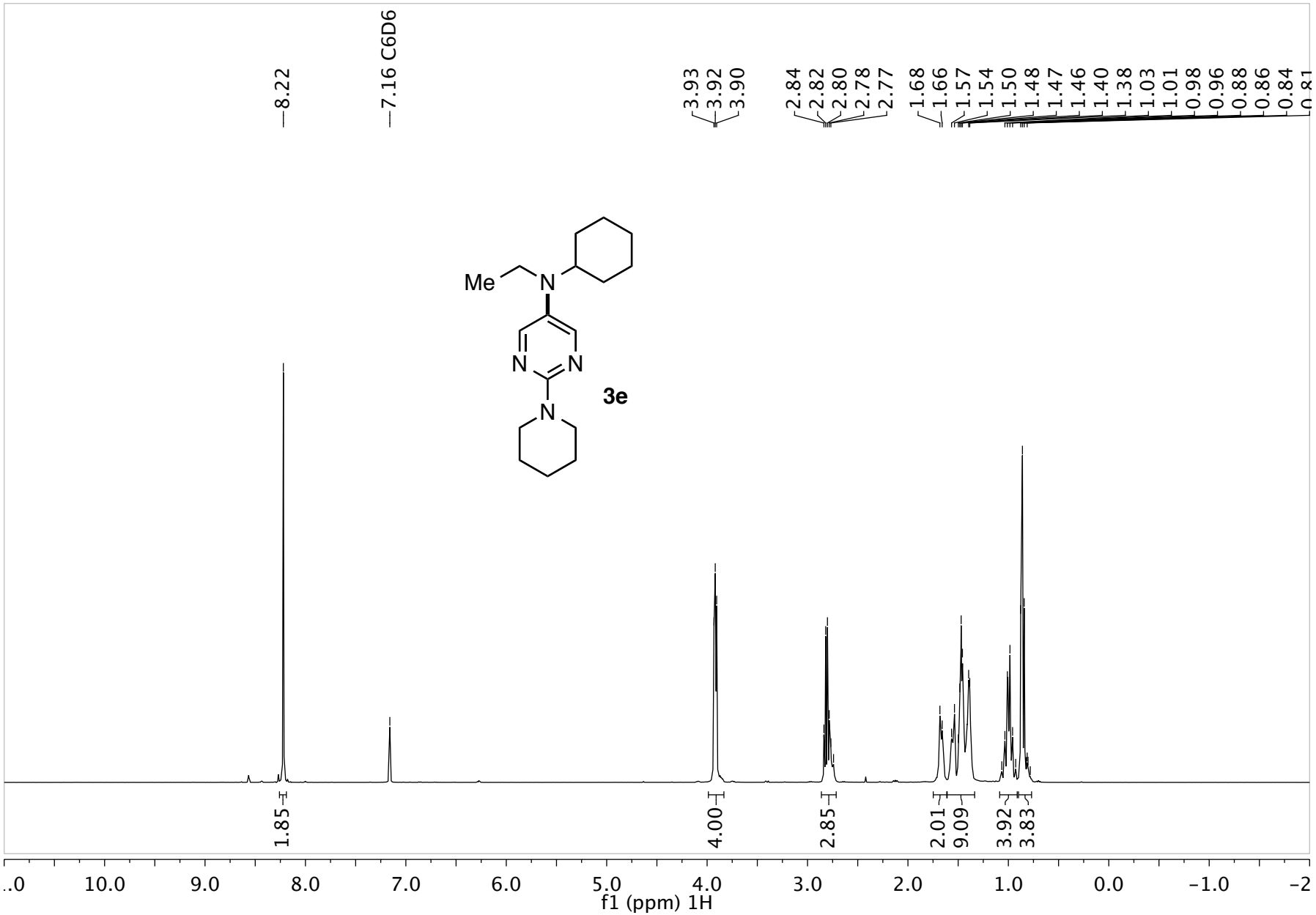

156.45
150.46
143.82
141.20
129.00
127.32
127.29
127.20
111.12
104.00
102.00
54.54 CD2Cl2
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
51.13
48.93
20.93
18.77
13.04
Me
N
Me
N
N
TIPS
3b
f1 (ppm) 13C

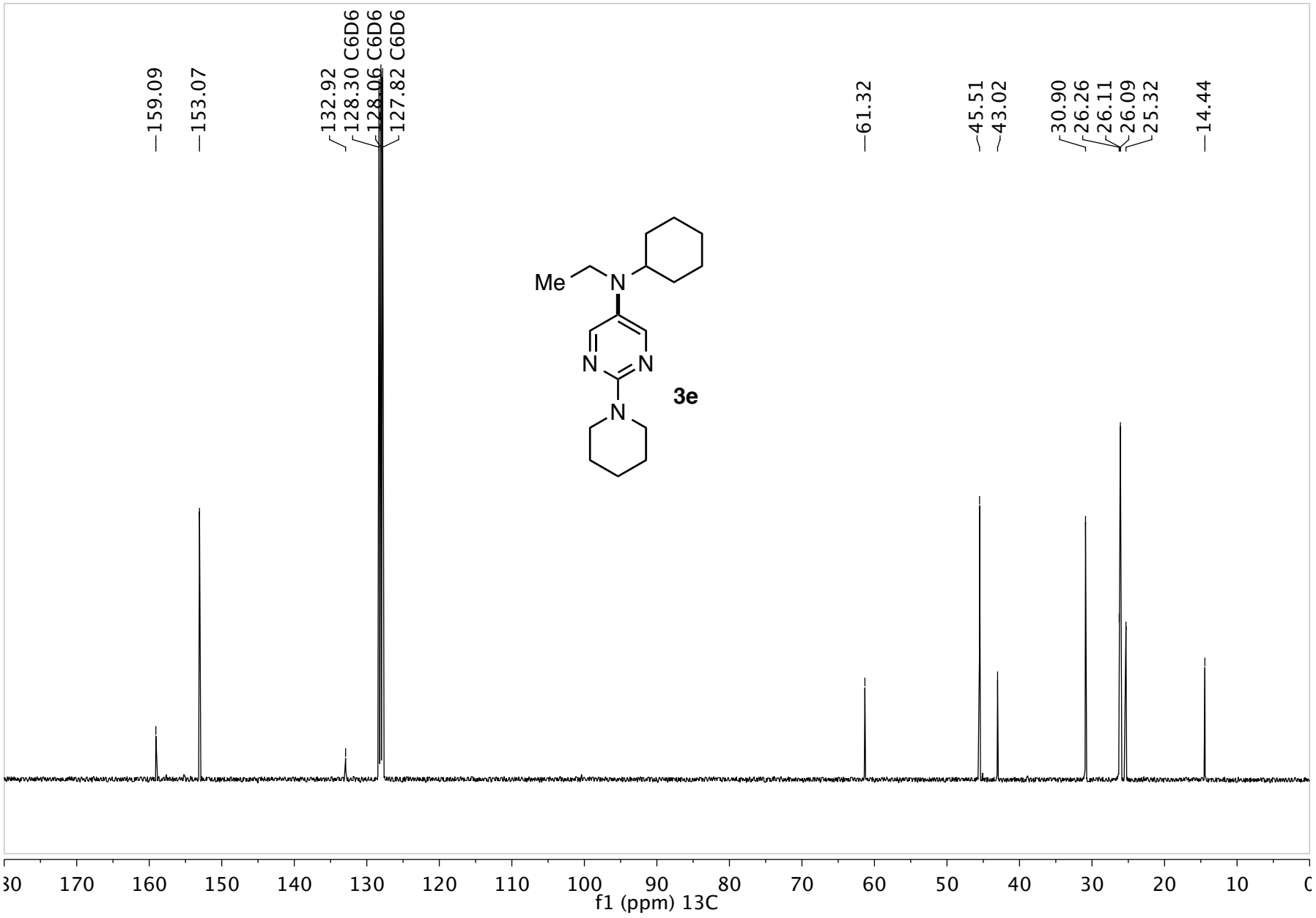

7.44
7.41
7.37
7.35
7.33
7.31
7.26
7.24
7.23
5.58
5.32 CD2Cl2
4.15
4.12
3.48
3.47
3.45
3.44
3.42
3.41
3.29
3.26
3.04
2.90
2.87
2.57
2.56
2.54
2.53
2.31
2.27
2.26
2.24
2.24
2.22
2.21
Me2N
N
N
N
N
Me
3c
3.08
1.03
2.02
0.99
1.00
1.02
1.06
1.04
6.19
1.14
1.02
3.11
1.11
f1 (ppm) 1H

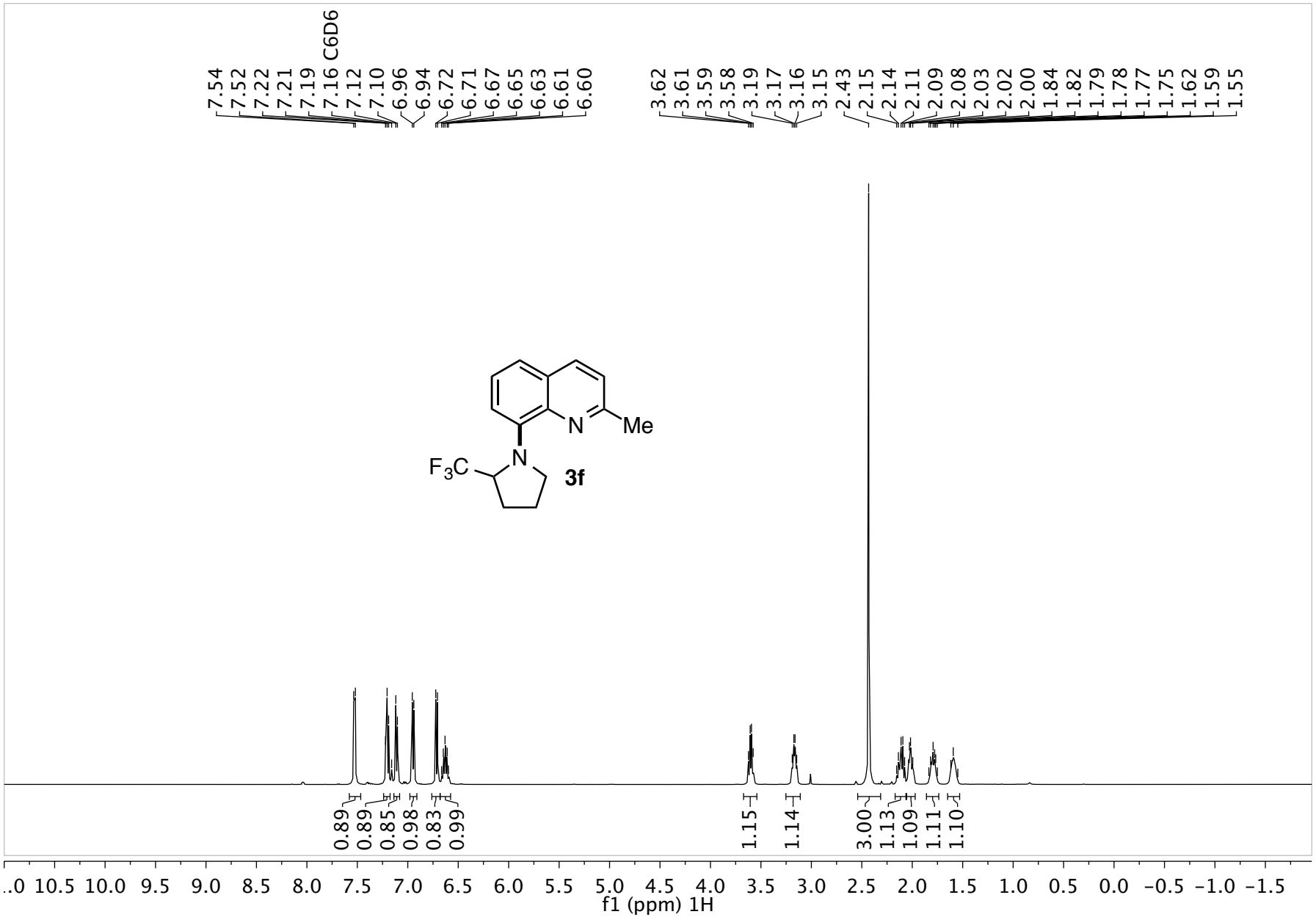

153.84
153.11
142.16
128.65
127.99
126.93
117.58
117.03
59.80
55.51
54.54 CD2Cl2
54.43
54.27 CD2Cl2
54.00 CD2Cl2
53.73 CD2Cl2
53.46 CD2Cl2
46.82
41.64
37.68
Me2N
N
N
N
N
Me
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm) 13C

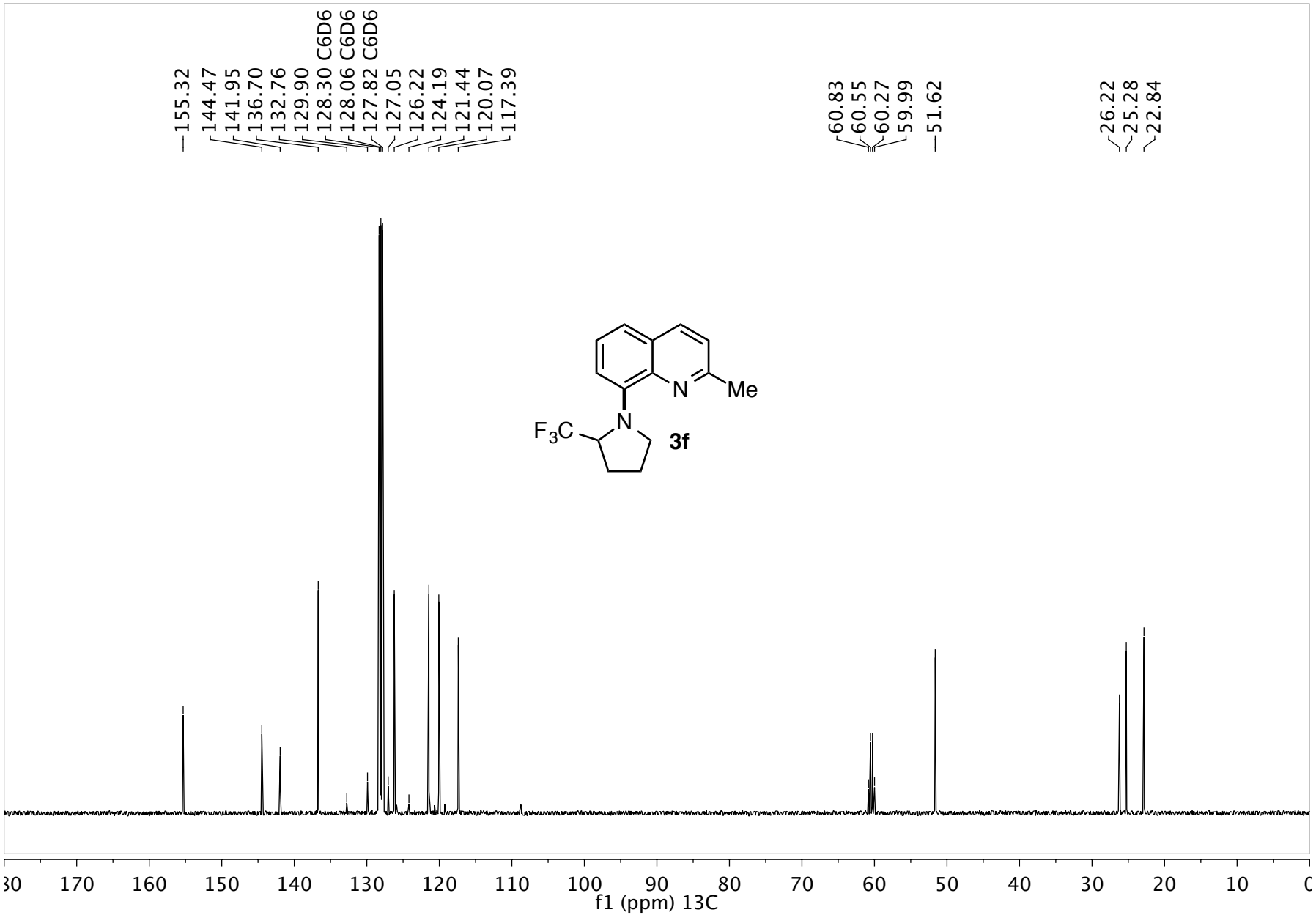

8.63
8.62
8.62
8.61
7.95
7.93
7.90
7.51
7.50
7.48
7.27
7.26
7.25
7.24
6.97
6.96
5.32 CD2Cl2
3.94
3.93
3.92
3.91
3.53
3.50
3.11
3.10
3.08
3.07
3.05
3.04
1.79
1.78
1.66
1.64
1.62
0.88
0.86
0.85
N
Me
N
3d
0.90
1.92
0.99
0.97
0.98
0.99
1.00
1.01
8.23
3.00
f1 (ppm) 1H

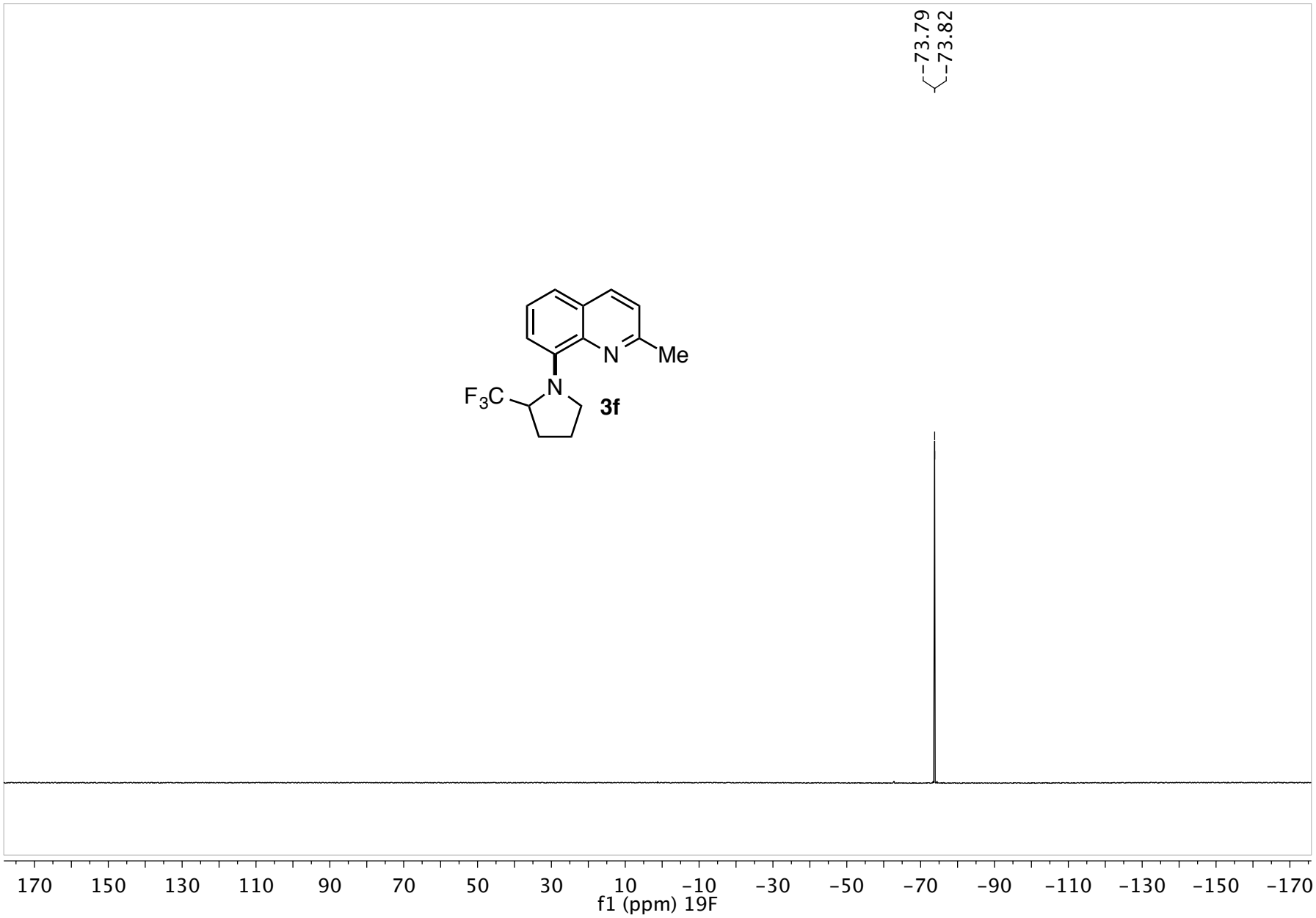

149.89
147.10
143.65
134.41
130.30
130.26
122.70
121.66
108.94
57.79
54.43 CD2Cl2
54.22 CD2Cl2
54.00 CD2Cl2
53.78 CD2Cl2
53.57 CD2Cl2
43.59
27.61
25.95
20.82
19.41
11.81
N
N
Me
3d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C

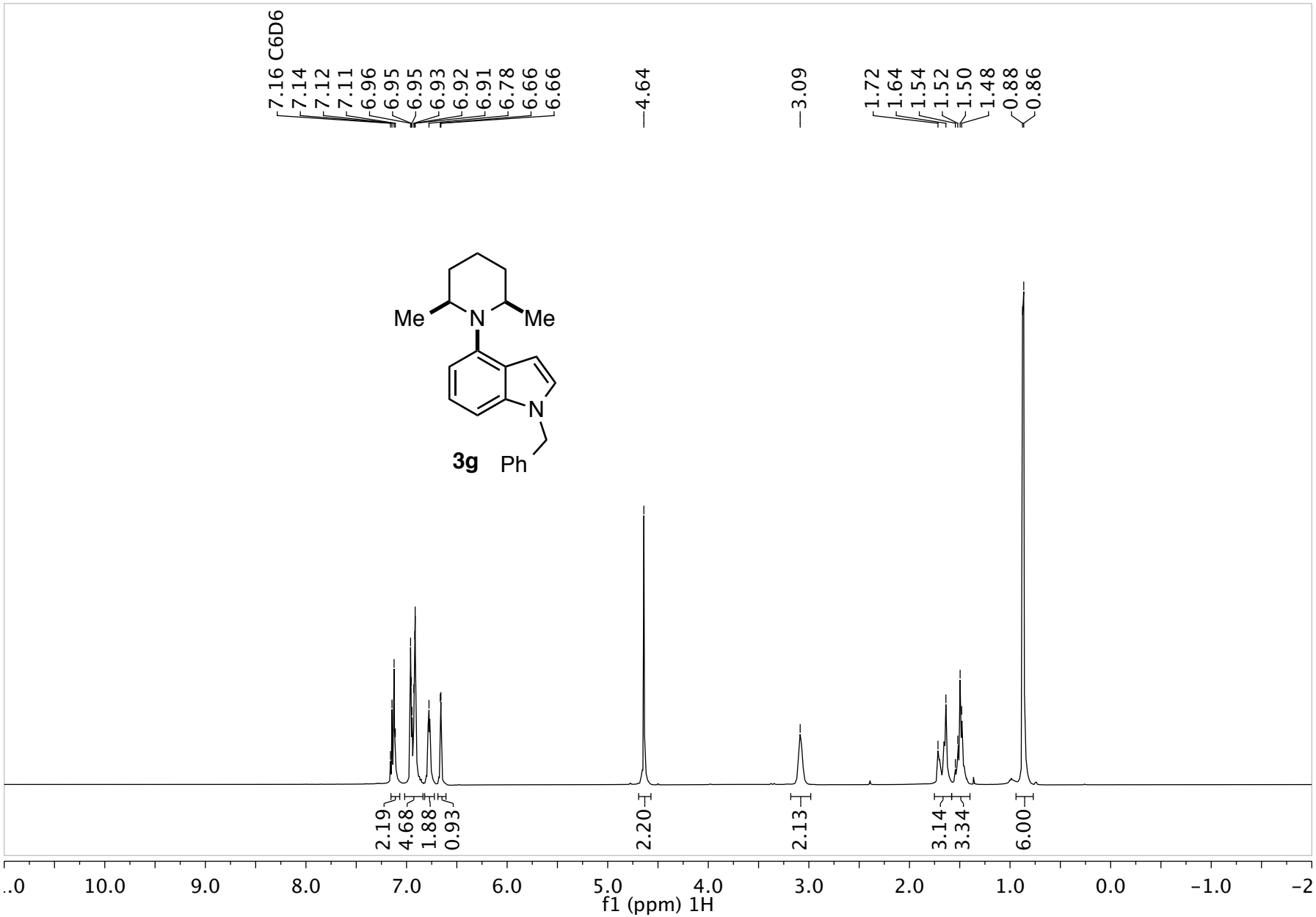

8.22
7.16 C6D6
3.93
3.92
3.90
2.84
2.82
2.80
2.78
2.77
1.68
1.66
1.57
1.54
1.50
1.48
1.47
1.46
1.40
1.38
1.03
1.01
0.98
0.96
0.88
0.86
0.84
Me
N
N
N
N
3e
1.85
4.00
2.85
2.01
9.09
3.92
3.83
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm) 1H

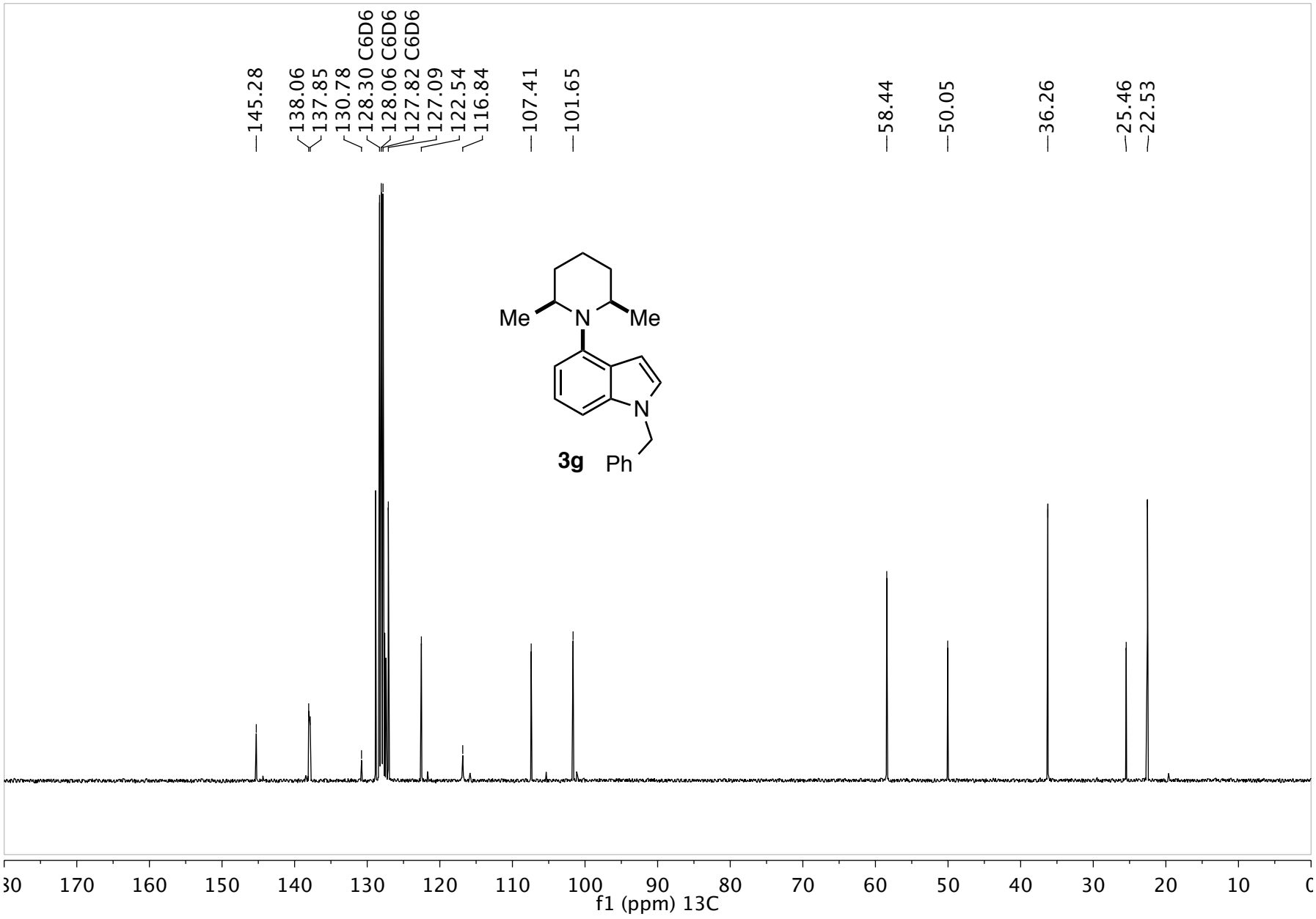

159.09
153.07
132.92
128.30 C6D6
128.06 C6D6
127.82 C6D6
61.32
45.51
43.02
30.90
26.26
26.11
26.09
25.32
14.44
Me
N
N
N
N
3e
f1 (ppm) 13C

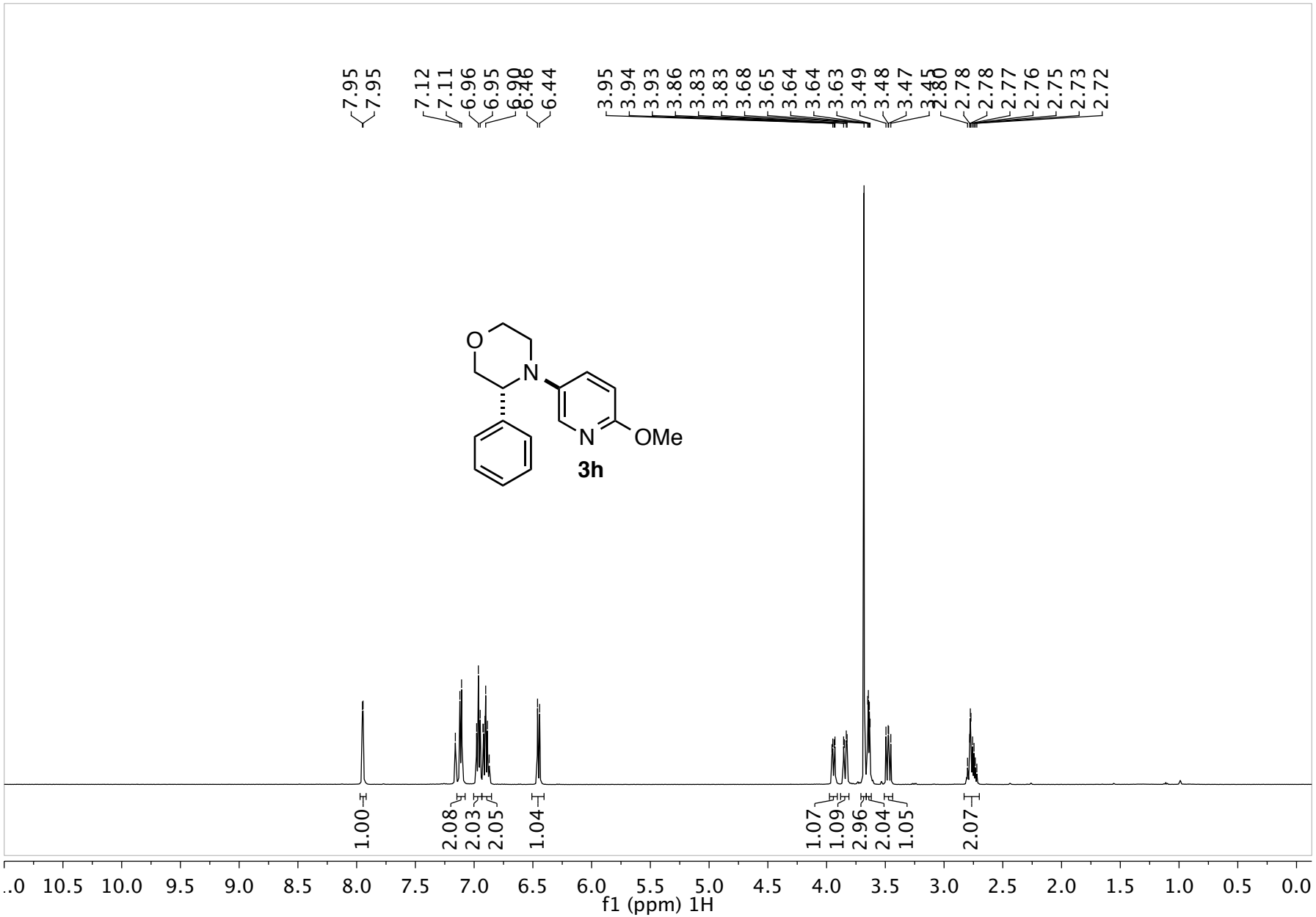

7.54
7.52
7.22
7.21
7.19
C6D6
7.16
7.12
7.10
6.96
6.94
6.72
6.71
6.67
6.65
6.63
6.61
6.60
3.62
3.61
3.59
3.58
3.19
3.17
3.16
3.15
2.43
2.15
2.14
2.11
2.09
2.08
2.03
2.02
2.00
1.84
1.82
1.79
1.78
1.77
1.75
1.62
1.59
1.55
N
Me
N
F3C
3f
0.89
0.89
0.85
0.98
0.83
0.99
1.15
1.14
3.00
1.13
1.09
1.11
1.10
f1 (ppm) 1H

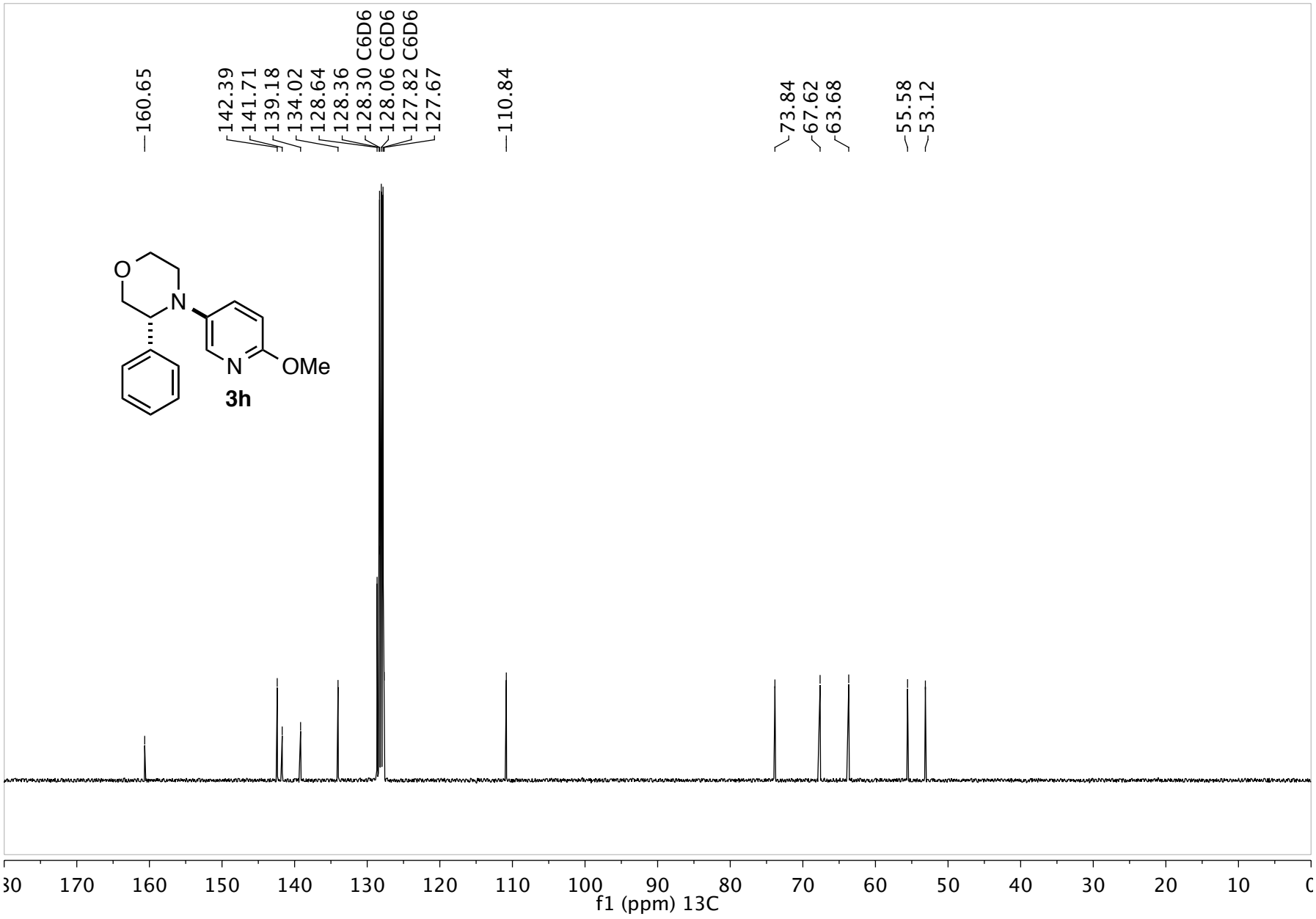

155.32
144.47
141.95
136.70
132.76
129.90
128.30 C6D6
128.06 C6D6
127.82 C6D6
127.05
126.22
124.19
121.44
120.07
117.39
60.83
60.55
60.27
59.99
51.62
26.22
25.28
22.84
N
Me
N
F3C
3f
f1 (ppm) 13C


-73.79
-73.82
N
Me
N
F3C
3f
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
f1 (ppm) 19F


7.16 C6D6
7.14
7.12
7.11
6.96
6.95
6.95
6.93
6.92
6.91
6.78
6.66
6.66
4.64
3.09
1.72
1.64
1.54
1.52
1.50
1.48
0.88
0.86
Me
N
Me
N
Ph
3g
2.19
4.68
1.88
0.93
2.20
2.13
3.14
3.34
6.00
f1 (ppm) 1H


145.28
138.06
137.85
130.78
128.30 C6D6
128.06 C6D6
127.82 C6D6
127.09
122.54
116.84
107.41
101.65
58.44
50.05
36.26
25.46
22.53
Me
N
Me
N
Ph
3g
f1 (ppm) 13C


7.95
7.95
7.12
7.11
6.96
6.95
6.90
6.46
6.44
3.95
3.94
3.93
3.86
3.83
3.83
3.68
3.65
3.64
3.64
3.63
3.49
3.48
3.47
3.45
2.80
2.78
2.78
2.77
2.76
2.75
2.73
2.72
O
N
N
OMe
3h
1.00
2.08
2.03
2.05
1.04
1.07
1.09
2.96
2.04
1.05
2.07
f1 (ppm) 1H


160.65
142.39
141.71
139.18
134.02
128.64
128.36
128.30 C6D6
128.06 C6D6
127.82 C6D6
127.67
110.84
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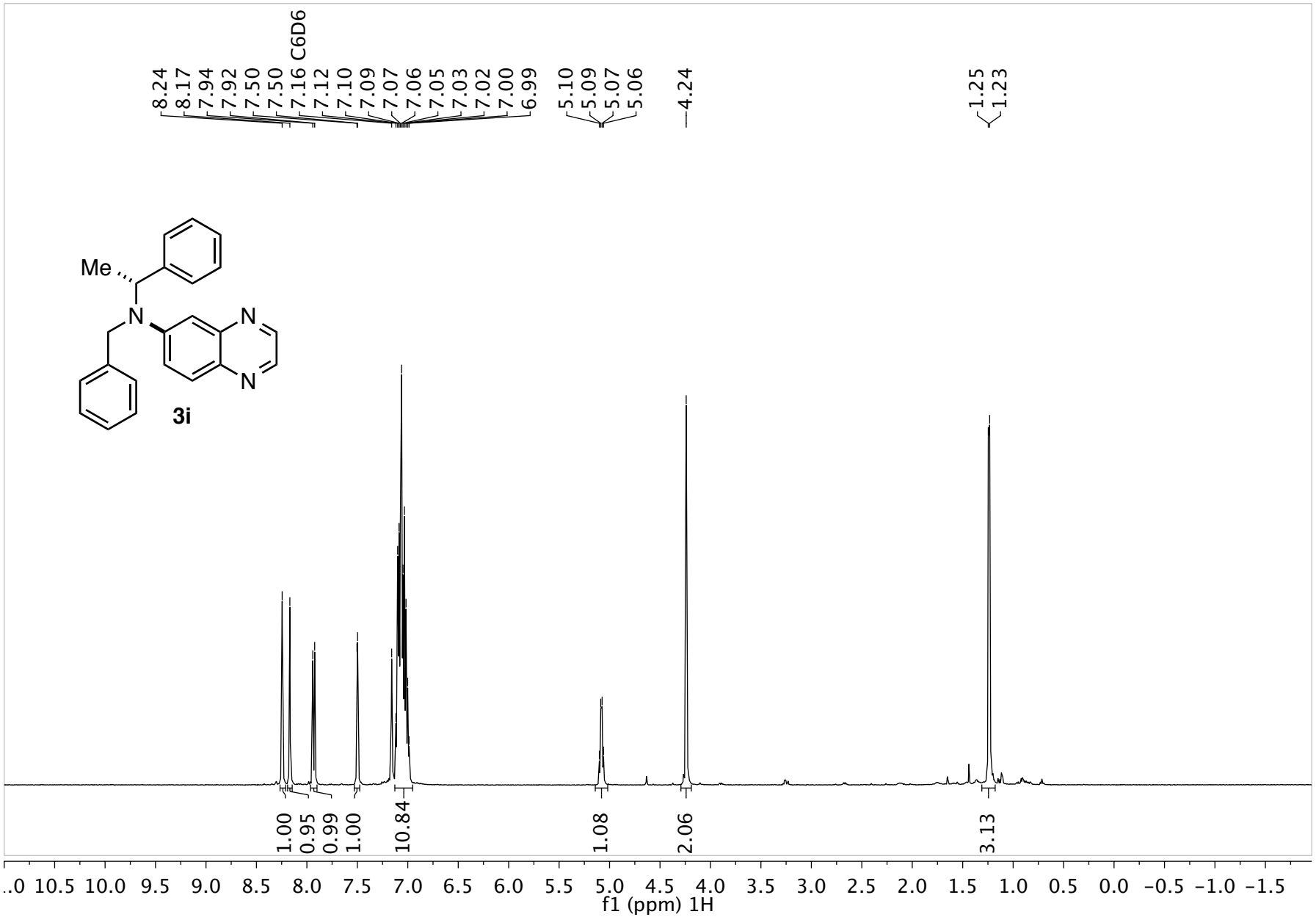
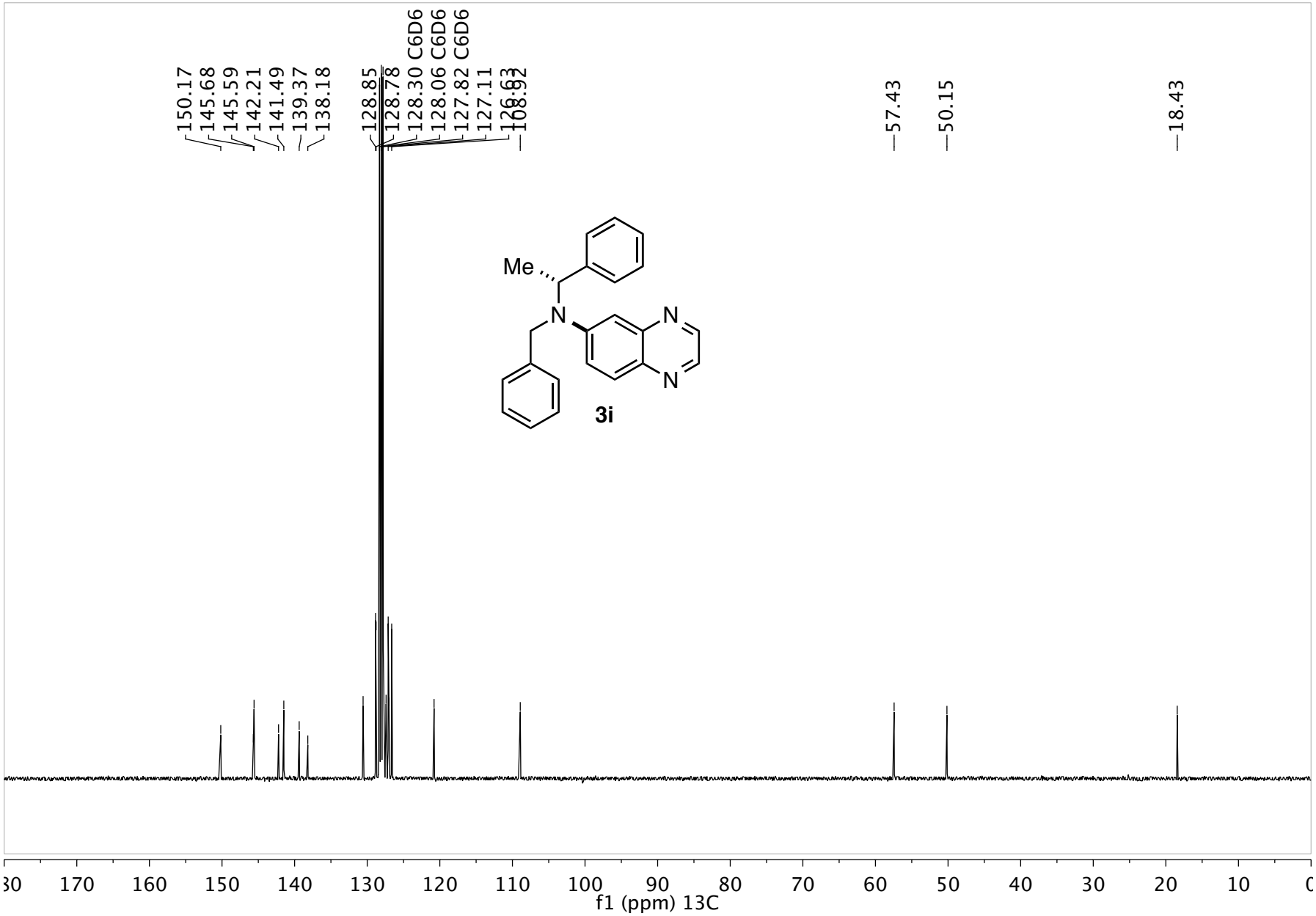
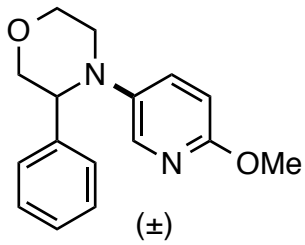
67.62
63.68
55.58
53.12
O
N
N
OMe
3h
f1 (ppm) 13C


8.24
8.17
7.94
7.92
7.50
7.50
7.16 C6D6
7.12
7.10
7.09
7.07
7.06
7.05
7.03
7.02
7.00
6.99
5.10
5.09
5.07
5.06
4.24
1.25
1.23
Me
N
N
N
3i
1.00
0.95
0.99
1.00
10.84
1.08
2.06
3.13
f1 (ppm) 1H


150.17
145.68
145.59
142.21
141.49
139.37
138.18
128.85
128.78
128.30 C6D6
128.06 C6D6
127.82 C6D6
127.11
126.63
108.92
57.43
50.15
18.43
Me
N
N
N
3i
f1 (ppm) 13C

Chiral HPLC Traces

Data File C:\CHEM32\2\DATA\JEFF\HPLC 2014-10-01 15-01-17\NHP-VIII-203-OJ.D
Sample Name: NHP-VIII-203-OJ



(±)

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======================================================================
Acq. Operator    : JSB                          Seq. Line :   1
Acq. Instrument : Instrument 2                   Location : Vial 1
Injection Date  : 10/1/2014 3:02:28 PM               Inj :   1
                                               Inj Volume : 3 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\2\DATA\JEFF\HPLC 2014-10-01 15-01-17\NHP-OJ-10.M
Last changed    : 10/1/2014 3:00:06 PM by JSB
Analysis Method : C:\CHEM32\2\METHODS\NN-3MIX-97HEX-08ML-MIL-60MIN.M
Last changed    : 10/4/2014 3:55:58 PM by NN
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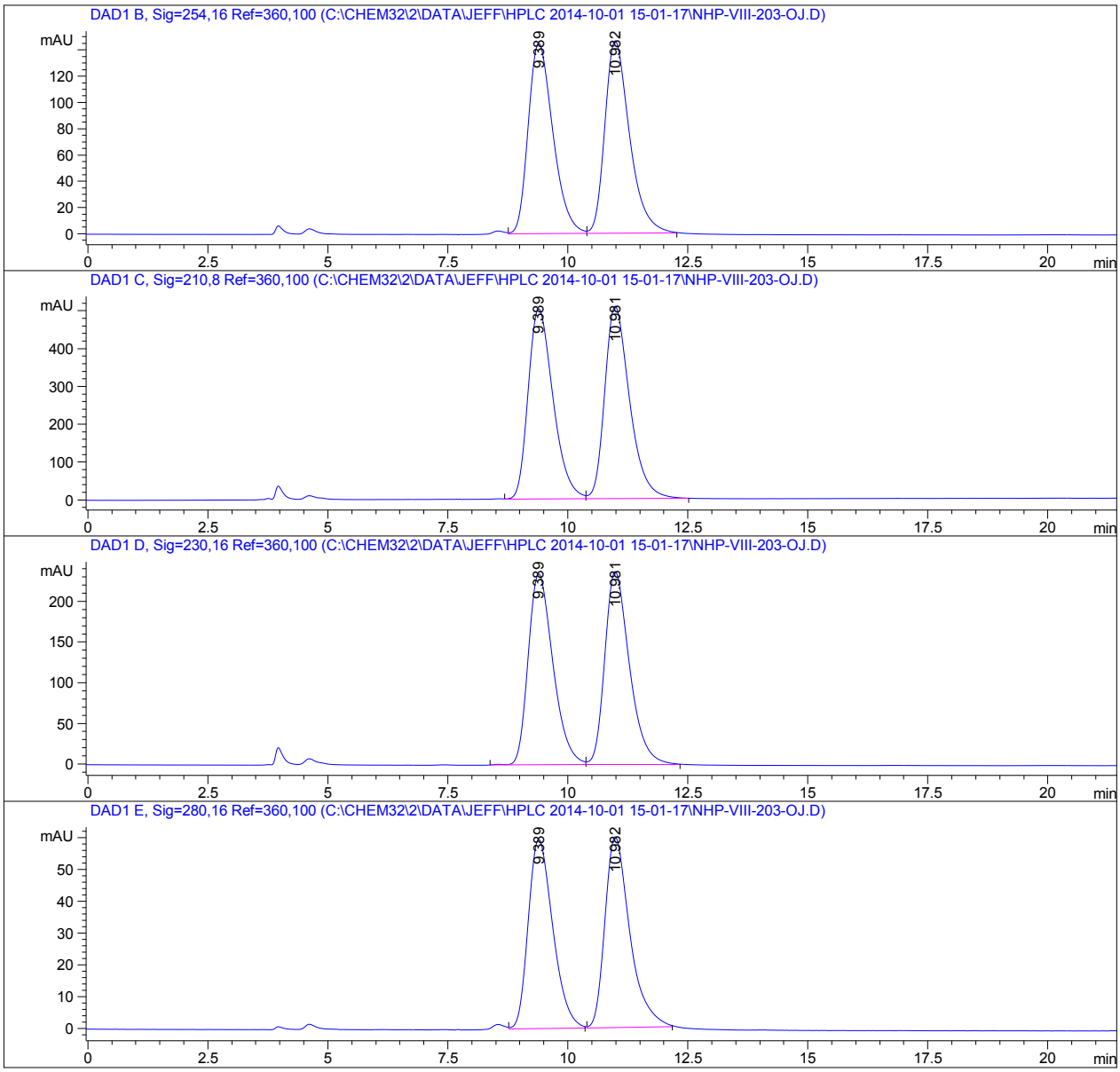
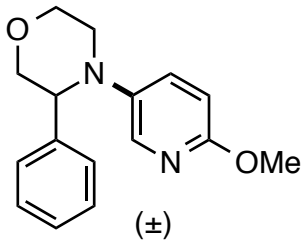




(±)

Data File C:\CHEM32\2\DATA\JEFF\HPLC 2014-10-01 15-01-17\NHP-VIII-203-OJ.D
Sample Name: NHP-VIII-203-OJ

==========

Area Percent Report

==========

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.389	VB	0.5540	5203.33691	145.22722	49.7037
2	10.982	BB	0.5467	5265.37109	146.71877	50.2963
Totals :				1.04687e4	291.94598	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.389	VV	0.5569	1.81416e4	502.86679	49.7409
2	10.981	VB	0.5503	1.83306e4	508.77103	50.2591
Totals :				3.64722e4	1011.63782	

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

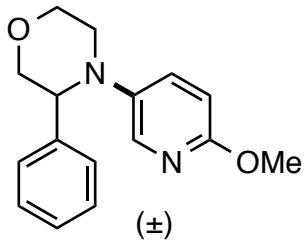
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.389	BV	0.5555	8444.08594	234.82710	49.8733
2	10.981	VB	0.5470	8486.97852	237.45679	50.1267
Totals :				1.69311e4	472.28389	

Signal 4: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.389	VB	0.5513	2120.94385	59.57853	49.3597
2	10.982	BB	0.5468	2175.96582	60.04803	50.6403

Instrument 2 11/11/2014 10:46:24 AM SSL

Data File C:\CHEM32\2\DATA\JEFF\HPLC 2014-10-01 15-01-17\NHP-VIII-203-OJ.D
Sample Name: NHP-VIII-203-OJ



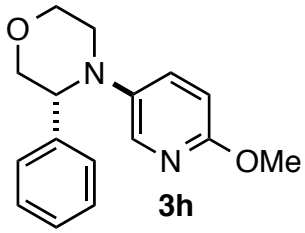
(±)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
Totals :				4296.90967	119.62656	

*** End of Report ***

Instrument 2 11/11/2014 10:46:24 AM SSL

Data File C:\CHEM32\2\DATA\PARK\HPLC 2014-10-01 15-31-05\NHP-VIII-087.D
Sample Name: NHP-VIII-087



3h

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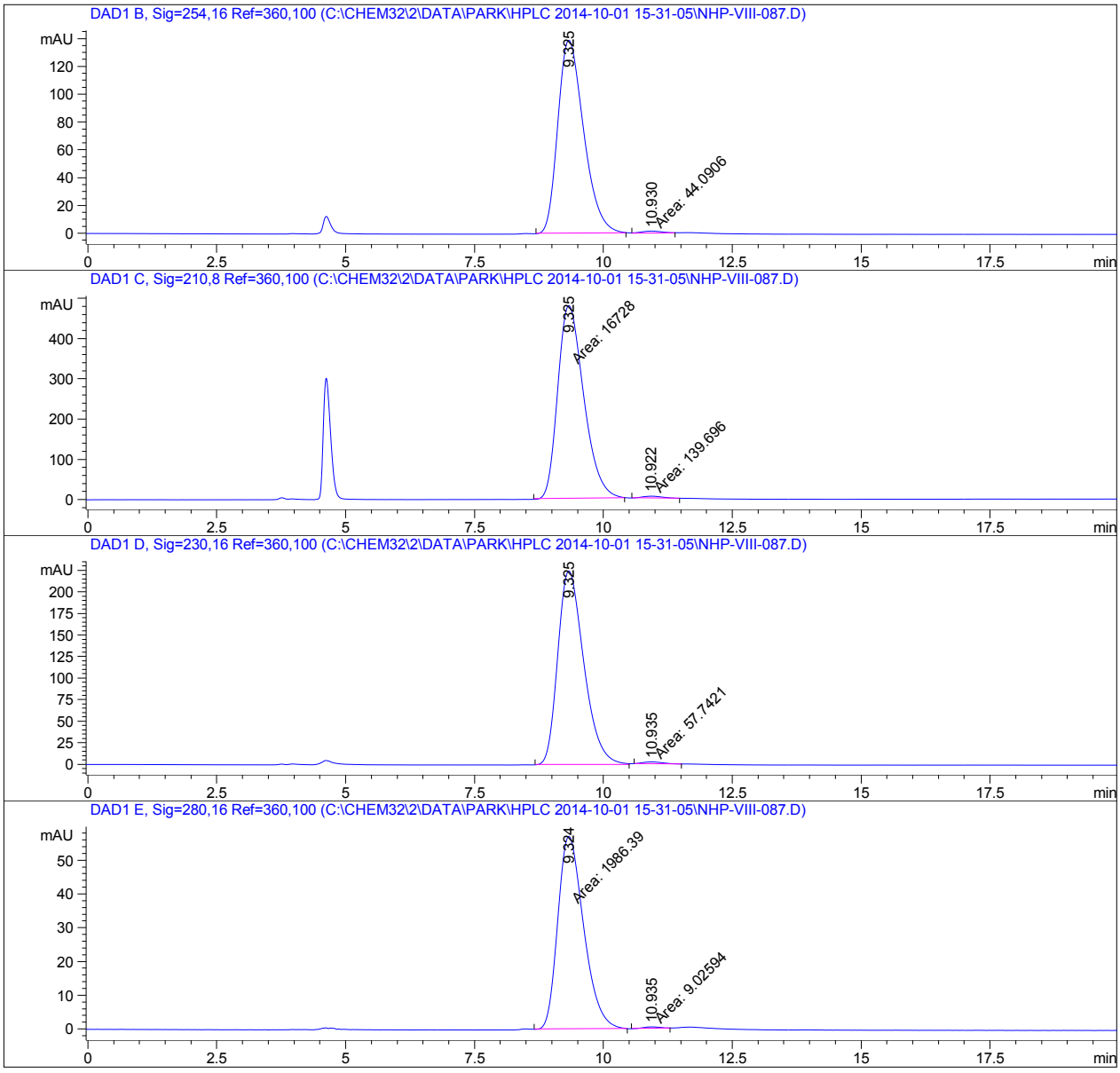
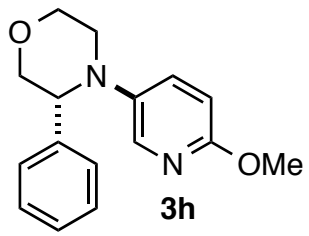
Acq. Operator : JSB Seq. Line : 1
Acq. Instrument : Instrument 2 Location : Vial 1
Injection Date : 10/1/2014 3:32:13 PM Inj : 1
Inj Volume : 3 µl
Acq. Method : C:\CHEM32\2\DATA\PARK\HPLC 2014-10-01 15-31-05\NHP-OJ-10.M
Last changed : 10/1/2014 3:24:23 PM by JSB
Analysis Method : C:\CHEM32\2\METHODS\NN-3MIX-97HEX-08ML-MIL-60MIN.M
Last changed : 10/4/2014 3:55:58 PM by NN



Data File C:\CHEM32\2\DATA\PARK\HPLC 2014-10-01 15-31-05\NHP-VIII-087.D
Sample Name: NHP-VIII-087



3h

```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=254,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.325 BB    0.5370 4843.59668  138.83755  99.0979
       2  10.930 MM    0.4860   44.09058    1.51189   0.9021

    Totals :                  4887.68726  140.34945



    Signal 2: DAD1 C, Sig=210,8 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.325 MM    0.5821 1.67280e4   478.96866  99.1718
       2  10.922 MM    0.4613  139.69585    5.04726   0.8282

    Totals :                  1.68677e4   484.01592



    Signal 3: DAD1 D, Sig=230,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.325 BB    0.5419 7893.34912  224.63597  99.2738
       2  10.935 MM    0.4499   57.74208    2.13917   0.7262

    Totals :                  7951.09120  226.77514



    Signal 4: DAD1 E, Sig=280,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.324 MM    0.5801 1986.39307   57.07454  99.5477
       2  10.935 MM    0.3542    9.02594 4.24727e-1   0.4523

Instrument 2 11/11/2014 11:08:16 AM SSL
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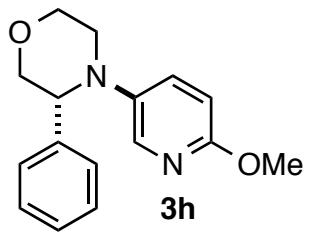
Data File C:\CHEM32\2\DATA\PARK\HPLC 2014-10-01 15-31-05\NHP-VIII-087.D
Sample Name: NHP-VIII-087



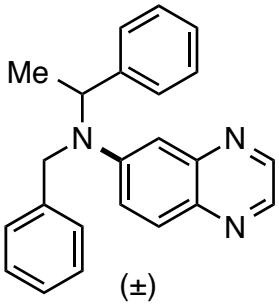
3h

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
Totals :				1995.41901	57.49927	

*** End of Report ***

Instrument 2 11/11/2014 11:08:16 AM SSL

Data File C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 18-50-59\NHP-VIII-204.D
Sample Name: NHP-VIII-204

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==========================================================================
Acq. Operator    : EA                                Seq. Line :   1
Acq. Instrument : Instrument 1                        Location : Vial 71
Injection Date  : 9/28/2014 6:53:19 PM                    Inj :   1
                                                    Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 18-50-59\NHP-IC.M
Last changed    : 9/28/2014 6:50:57 PM by EA
Analysis Method : C:\CHEM32\2\METHODS\NN-3MIX-97HEX-08ML-MIL-60MIN.M
Last changed    : 10/4/2014 3:55:58 PM by NN
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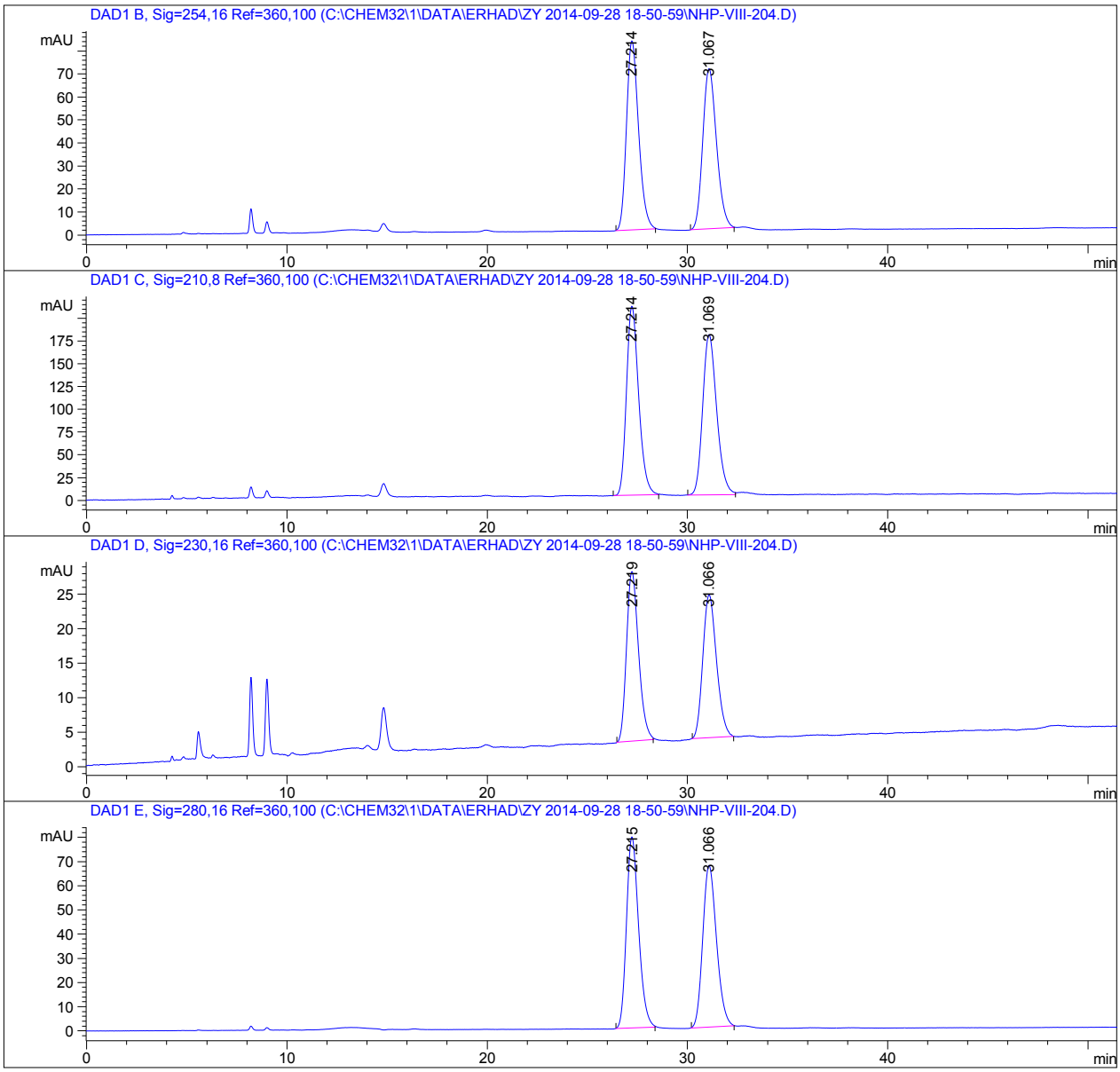
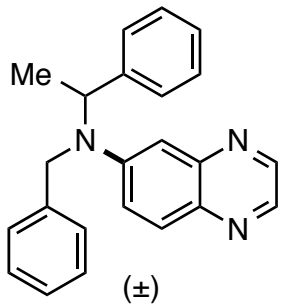


Data File C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 18-50-59\NHP-VIII-204.D
Sample Name: NHP-VIII-204




```
    ========================================================================
                            Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=254,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.214 BB    0.6411 3464.16089   82.30141  51.0010
       2  31.067 BB    0.7270 3328.17749   69.70670  48.9990

    Totals :                  6792.33838  152.00812



    Signal 2: DAD1 C, Sig=210,8 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.214 BV    0.6472 8829.55371  208.00008  50.7664
       2  31.069 BB    0.7113 8562.95020  176.10077  49.2336

    Totals :                  1.73925e4   384.10085



    Signal 3: DAD1 D, Sig=230,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.219 BB    0.5958 1030.51343   24.64864  50.9885
       2  31.066 BB    0.6381  990.55566   20.78127  49.0115

    Totals :                  2021.06909   45.42991



    Signal 4: DAD1 E, Sig=280,16 Ref=360,100

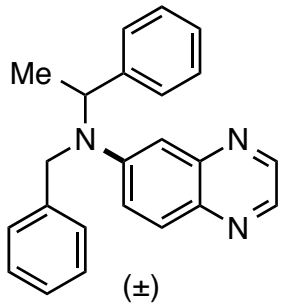
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.215 BB    0.6389 3326.35132   79.05402  50.9811
       2  31.066 BB    0.7217 3198.32642   66.90871  49.0189

Instrument 2 11/11/2014 11:19:22 AM SSL
```

Data File C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 18-50-59\NHP-VIII-204.D
Sample Name: NHP-VIII-204

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
Totals :				6524.67773	145.96274	

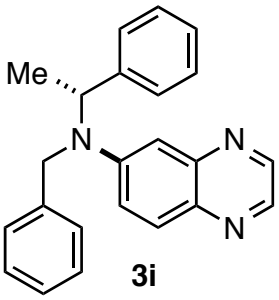
*** End of Report ***



(±)

Instrument 2 11/11/2014 11:19:22 AM SSL

Data File C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 19-49-39\NHP-VIII-139.D
Sample Name: NHP-VIII-139



3i

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======================================================================
Acq. Operator   : EA                                 Seq. Line :   1
Acq. Instrument : Instrument 1                       Location : Vial 71
Injection Date  : 9/28/2014 7:51:58 PM                    Inj :   1
                                                   Inj Volume : 5 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 19-49-39\NHP-IC.M
Last changed    : 9/28/2014 7:49:38 PM by EA
Analysis Method : C:\CHEM32\2\METHODS\NN-3MIX-97HEX-08ML-MIL-60MIN.M
Last changed    : 10/4/2014 3:55:58 PM by NN
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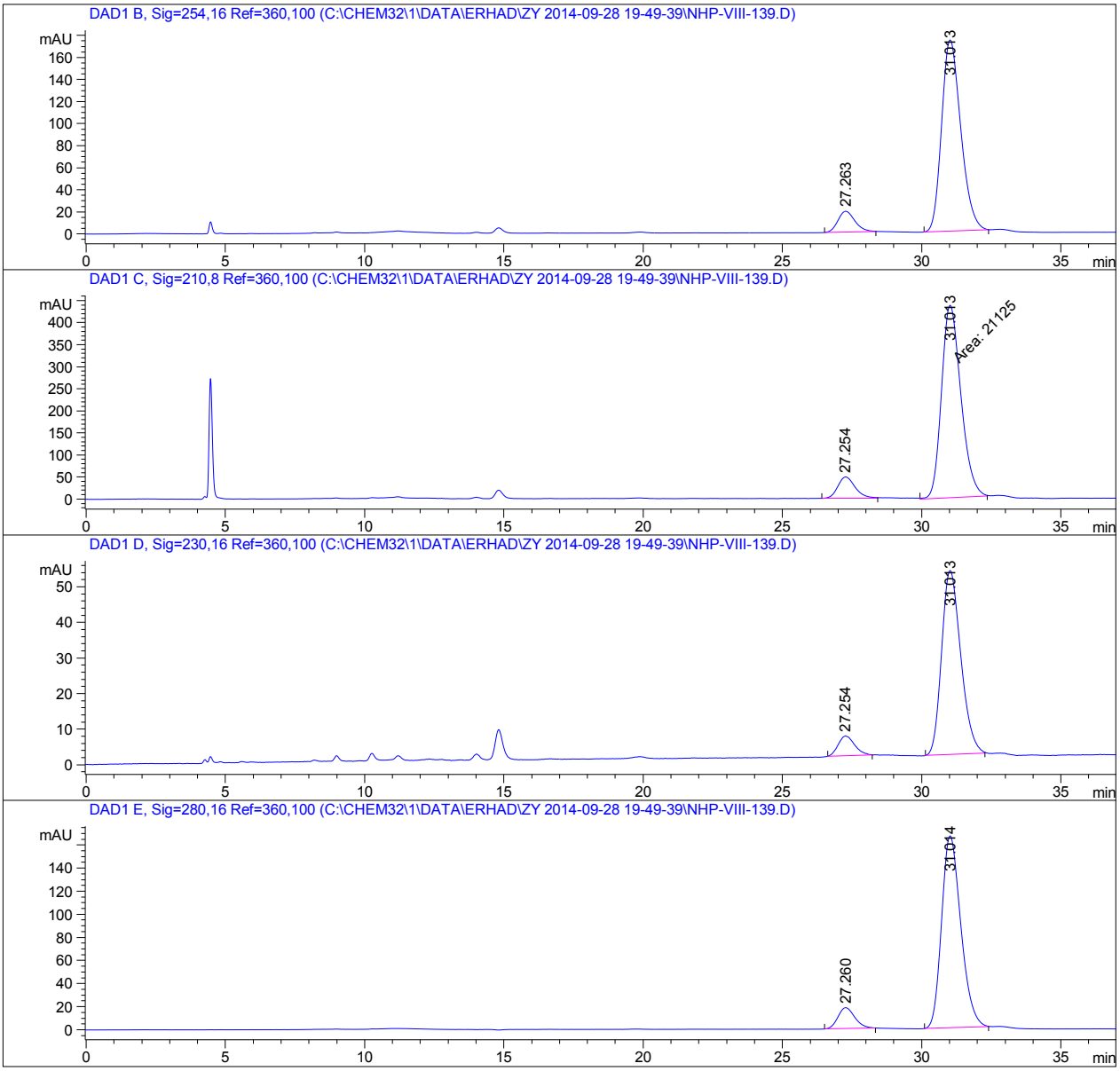
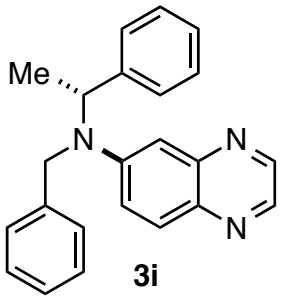


Data File C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 19-49-39\NHP-VIII-139.D
Sample Name: NHP-VIII-139



3i

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Area Percent Report

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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.263	BB	0.5915	804.43768	18.94236	8.8385
2	31.013	BB	0.7445	8297.08398	173.33557	91.1615
Totals :				9101.52167	192.27793	

Signal 2: DAD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.254	VB	0.5260	2135.22852	48.65247	9.1798
2	31.013	MM	0.8065	2.11250e4	436.53473	90.8202
Totals :				2.32602e4	485.18719	

Signal 3: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.254	BB	0.4905	228.77698	5.57756	8.4506
2	31.013	BB	0.7231	2478.45264	51.71788	91.5494
Totals :				2707.22961	57.29544	

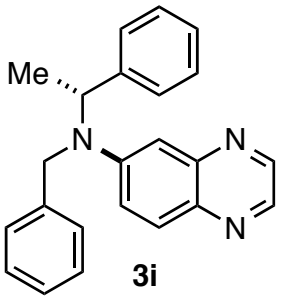
Signal 4: DAD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.260	BB	0.5849	771.57318	18.19035	8.8165
2	31.014	BB	0.7421	7979.89063	166.21817	91.1835

Instrument 2 11/11/2014 11:15:46 AM SSL

Data File C:\CHEM32\1\DATA\ERHAD\ZY 2014-09-28 19-49-39\NHP-VIII-139.D
Sample Name: NHP-VIII-139

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
Totals :				8751.46381	184.40852	



3i

*** End of Report ***