Supporting Information

Photoredox Radical/Polar Crossover Enables Construction of Saturated Nitrogen Heterocycles

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General Considerations:

General: All chemical transformations requiring inert atmospheric conditions or vacuum distillation used Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using the LED reactor described in our previous report.[1] NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K. ^{1}H NMR spectra were referenced to residual, non-deuterated chloroform (δ 7.26) in $CDCl_3$ or DMSO in DMSO-d_6 (δ 2.50). ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.3). ^{19}F NMR spectra were referenced using hexafluorobenzene (δ –161.64) as an internal standard and run with C-F/C-H decoupling. Reactions were monitored by ^{1}H NMR and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 μm). Flash chromatography was carried out using standard column chromatography on silica gel or by using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). Solvents were purified with drying cartridges through a solvent delivery system.

Chemicals: Na_2SO_4, $MgSO_4$, CH_2Cl_2, benzene, EtOAc, pentane, hexanes, Et_2O, DMSO and toluene were used as purchased. The organic photocatalyst 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN) was prepared in-house by the procedure outlined in our previous publication.[2] Alkylsilicates were prepared by the procedures outlined here. Imines were prepared either through the procedures outlined here, previously reported procedures by our group,[2] or by known procedures (sulfonyl-protected,[2] aryl,[3] Boc,[4] 3*H*-indole,[5] hydrazone,[6] iminoacetate,[7] and imidate[8]).

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[1] For information on this reactor and its construction see the *Photochemical Reactor Design* of the Supporting Information of: Milligan, J. A.; Phelan, J. P.; Polites, V. C.; Kelly, C. B.; Molander, G. A. *Org. Lett.* **2018**, 20, 6840.

[2] Patel, N. P.; Kelly, C. B.; Siegenfeld, A. P.; Molander, G. A. *ACS Catal.* **2017**, *7*, 1766.

[3] Qu B., Samankumara L. P., Ma S., Fandrick K. R., Desrosiers J.-N., Rodriguez S., Li Z., Haddad N., Han Z. S., McKellop K., Pennino S., Grinberg N., Gonnella N. C., Song J. J., Senanayake C. H., *Angew. Chem. Int. Ed.* **2014***, 53*, 14428; Aslam N. A., Babu S. A., Rani S., Mahajan S., Solanki J., Yasuda M., Baba A., *Eur. J. Org. Chem.* **2015**, 4168; Liu Y., Yang Q., Hao D., Zhang W., *Aust. J. Chem.* **2012**, *65*, 1390; Li Q., Li Y., Wang J., Lin Y., Wei Z., Duan H., Yang Q., Baib F., Lia Y., *New J. Chem.,* **2018**,*42*, 827; Chu J. C. K., Dalton D. M., Rovis T., *J. Am. Chem. Soc.*, **2015***, 137*, 4445; Bäumler C., Kempe R., *Chem. Eur. J.* **2018***, 24*, 8989; Cao C., Lua B., Chen G., *J. Phys. Org. Chem.* **2011***, 24*, 335; Dibble D. J., Kurakake R., Wardrip A. G., Bartlett A., Lopez R., Linares J. A., Firstman M., Schmidt A. M., Umerani M. J., Gorodetsky A. A., *Org. Lett.*, **2018***, 20*, 502; Schwob T., Kempe R., *Angew. Chem. Int. Ed.* **2016***, 55*, 15175; Lawson J. R., Wilkins L. C., Melen R. L., *Chem. Eur. J.* **2017***, 23*, 10997; Peixoto D., Locati A., Marques C. S., Goth A., Ramalhoab P. J. P., Burke A. J., *RSC Adv.,* **2015***, 5*, 99990; Wang H., Wang C., Huang K., Liu L., Chang W., Li J., *Org. Lett.* **2016***, 18*, 2367; Tan D.-W., Li H.-X., Young D. J., Lang J.-P., *Tetrahedron,* **2016***, 72*, 4169; Cao C.-T., Zhou W., Cao C., *J Phys Org Chem.* **2017***, 30*, 3672; Eakins G. L., Cooper M. W., Gerasimchuk N. N., Phillips T. J., Breyfogle B. E., Stearman C. J., *Can. J. Chem.* **2013***, 91*, 1059; Cuesta, L., Maluenda, I., Soler, T. Navarro, R. Urriolabeltia, E. P. *Inorg. Chem.* **2011**, *50*, 37-45.

[4] Pedrosa R., Andrés J. M., Ávila D. P., Ceballos M, Pindado R., *Green Chem.* **2015***, 17*, 2217.

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[6] Xu X., Zavalij P. Y., Doyle M. P., *Angew. Chem. Int. Ed.* **2012***, 51*, 9829.

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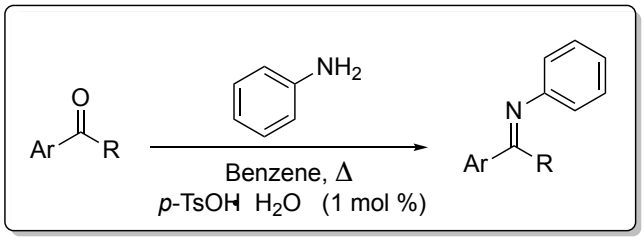
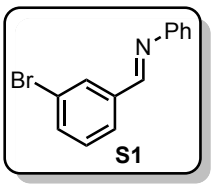
Synthesis of Substrates for RPC Annulation

Synthesis of Imines



Representative Procedure

To an appropriately sized round bottom flask equipped with a stir bar was added either an aldehyde or ketone (1 equiv) followed by benzene. The flask was then charged with the appropriate aniline derivative (1 equiv) and was stirred at rt for 5 min. After this time, p-TsOH • H2O was then added to the mixture in varying proportions (1 mol. % for electron-poor aldehydes and/or electron-rich amines, 5 mol. % for electron-rich aldehydes and/or electron-poor amines and 50 mol. % for ketones) was added in one portion, and the flask was equipped with a Dean-Stark trap with a reflux condenser. The reaction mixture was heated to reflux overnight or until ~1 equiv of H_2O was collected in the trap. The reaction was cooled to rt and the solvent was removed *in vacuo* by rotary evaporation. The resulting crude material was purified differently depending on whether an aldimine or ketimine was produced. For aldimines, the crude material was re-dissolved in a minimum amount of hexane and filtered to remove the *p*-TsOH, giving the pure imine. For ketimines, the mixture was flushed through a small silica plug with hexane/EtOAc (9:1), and the resulting filtrate was concentrated and recrystallized from hexane/CH_2Cl_2. Below is data for imines not previously reported by us and/or unknown in the literature.



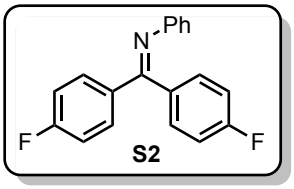
***N*-(3-Bromobenzylidene)aniline S1**[9] (2.50 g, 96%) was prepared according to the representative procedure for imine synthesis from 3-bromobenzaldehyde (1.86 g, 10.1 mmol, 1.01 equiv), aniline (0.930 g, 9.99 mmol, 1.00 equiv) and *p*-TsOH (20 mg, 0.11 mmol, 1 mol %) in benzene (50 mL). Imine **S1** was obtained as an orange-tinted oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.41 (s, 1 H), 8.12 (s, 1 H), 7.81 (d, 1 H, *J* = 7.5 Hz), 7.62 (d, 1 H, *J* = 8.0 Hz), 7.46-7.40 (m, 2 H), 7.36 (t, 1 H), 7.30-7.26 (m, 1 H), 7.25-7.22 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.4, 151.4, 138.1, 134.1, 131.2, 130.2, 129.1, 127.5, 126.3, 123.0, 120.8

FT-IR (ATR) 3075, 1625, 1186, 782, 760, 692, 679 cm^{-1}

[9]Tong, S.; Piemontesi, S.; Wang, Q.; Wang, M.; Zhu, J. *Angew Chem., Int. Ed.* **2017***, 56*, 7958-7962.



S2

***N*-(Bis(4-fluorophenyl)methylene)aniline S2** (0.925 g, 63%) was prepared by treating bis(4-fluorophenyl)methanone (1.09 g, 5.00 mmol, 1 equiv), Et_3N (3.5 mL, 25 mmol, 5.0 equiv), and aniline (0.699 g, 7.50 mmol, 1.50 equiv) with $TiCl_4$ (1.1 mL, 9.9 mmol, 2.0 equiv) in CH_2Cl_2 (50 mL) at 0 °C. The reaction was warmed to rt and stirred for 16 h. The reaction mixture was carefully quenched with H_2O (10 mL) and extracted with CH_2Cl_2 (50 mL). The organic layers were washed with brine (50 mL), then were dried (Na_2SO_4) and concentrated. Purification by chromatography on SiO_2 afforded **S2** as a colorless solid (mp = 109-111 °C).

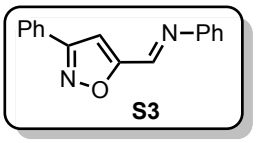
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79-7.72 (m, 2 H), 7.21-7.15 (m, 2 H), 7.14-7.08 (m, 4 H), 7.00-6.93 (m, 3 H), 6.74-6.68 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.8, 164.4 ($^1J_{CF}$ = 245 Hz), 162.5 ($^1J_{CF}$ = 242 Hz), 150.8, 135.7 ($^4J_{CF}$ = 4 Hz), ($^4J_{CF}$ = 4 Hz),131.8 ($^4J_{CF}$ = 4 Hz), 131.4 ($^3J_{CF}$ = 9 Hz), 131.3 ($^3J_{CF}$ = 9 Hz), 128.5, 123.3, 120.7, 115.2 ($^2J_{CF}$ = 21 Hz), 115.1 ($^2J_{CF}$ = 21 Hz).

^{19}F NMR ($CDCl_3$, 476 MHz) δ –109.5 (s, 1 F), –111.3 (s, 1 F)

FT-IR (ATR) 1589, 1502, 1218, 843, 769 cm^{-1}

HRMS (EI$^+$) calcd for $C_{19}H_{14}NF_2$ $[M+H]^+$ 294.1094, found 294.1086



S3

***N*-((3-Phenylisoxazol-5-yl)methylene)aniline S3** (1.02 g, 95%) was prepared according to the representative procedure for imine synthesis from 3-phenylisoxazole-5-carbaldehyde (0.748 g, 4.32 mmol, 1.00 equiv) and aniline (0.422 g, 4.54 mmol, 1.00 equiv) using *p*-TsOH • H_2O (8 mg, 0.043 mmol, 1 mol %) in benzene (25 mL). The desired imine **S3** was obtained as a colorless solid (mp = 124–125 °C).

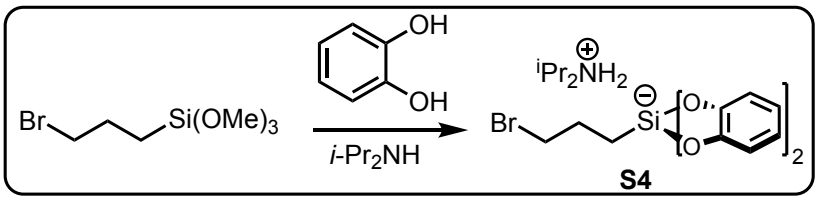
^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.55 (s, 1 H), 7.92 (m, 2 H), 7.54-7.42 (m, 5 H), 7.38-7.30 (m, 3 H), 7.21 (s, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.0, 163.1, 150.3, 146.3, 130.5, 129.5, 129.2, 128.6, 127.9, 127.0, 121.3, 103.2

FT-IR (ATR) 3026, 1566, 1438, 1174, 768, 753, 687, 681 cm^{-1}

HRMS (EI$^+$) calcd for $C_{16}H_{13}N_2O$ $[M+H]^+$ 249.1028, found 249.1025

Synthesis of Haloalkylsilicates[10]



Representative Procedure: Diisopropylammonium Bis(catecholato)(3-bromopropyl)silicate (S4)

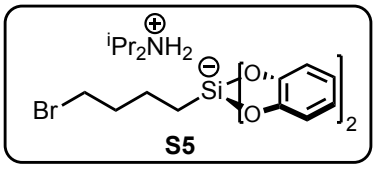
To a flame-dried 50 mL round bottom flask equipped with a stir bar was added anhydrous *i*-Pr_2NH (8.66 g, 12 mL, 85.6 mmol, 4.28 equiv) under argon. The flask was heated to 40 °C and, once at temperature, catechol[11] (4.30 g, 39 mmol, 1.95 equiv) was added followed by (3-bromopropyl)trimethoxysilane (4.85 g, 20 mmol, 1 equiv). The solution quickly became heterogeneous and produced a white precipitate. The solution was vigorously stirred at this temp for 60 min. After this time, a 1:1 mixture by volume of pentane/Et_2O (20 mL) was added. The resulting solution was filtered, and the solid was washed with a 1:1 mixture by volume of pentane/Et_2O (~50 mL) followed by pentane (3 × 50 mL). The solid was then dried under high vacuum at 50 °C to give the desired bromosilicate **S4** (9.35 g, 97%) as a powdery white solid (mp = 145-147 °C)

^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.11 (br s, 2 H), 6.56-6.50 (m, 4 H), 6.47-6.41 (m, 4 H), 3.39-3.29 (m, 4 H), 1.75-1.64 (m, 2 H), 1.20 (d, 12 H, *J* = 6.5 Hz), 0.61-0.54 (m, 2 H)

^{13}C NMR (DMSO-d_6, 125 MHz) δ 150.4, 117.2, 109.6, 46.4, 38.6, 28.8, 18.8, 17.1

FT-IR (ATR): 3075, 1485, 1466, 1237, 812, 744 cm^{-1}

HRMS (EI^+) calcd for $C_{15}H_{14}O_4BrSi^-$ [M] 364.9845, found 364.9867



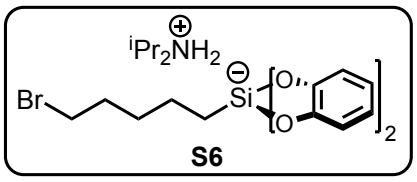
Diisopropylammonium Bis(catecholato)(4-bromobutyl)silicate S5 (8.09 g, 82%) was prepared according to the representative procedure for silicate synthesis from (4-bromobutyl)trimethoxysilane (5.12 g, 19.9 mmol, 1.00 equiv), catechol (4.28 g, 38.9 mmol, 1.95 equiv), and *i*-Pr_2NH (8.6 g, 4.3 equiv). The desired imine **S5** was obtained as a colorless solid (mp = 161-162 °C)

^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.96 (br s, 2 H), 6.53-6.48 (m, 4 H), 6.44-6.39 (m, 4 H), 3.41-3.34 (m, 4 H), 1.70-1.60 (m, 2 H), 1.35-1.25 (m, 2 H), 1.18 (d, 12 H, *J* = 6.5 Hz), 0.51-0.48 (m, 2 H)

[10] This protocol is general for all haloalkyltrimethoxysilanes except for 2-bromoethyltrimethoxysilane, which undergoes degradation as soon as the silane is added. Due to the strong effervescence observed, the compound likely undergoes β-elimination, releasing ethylene gas.
[11] Recrystallized from hexane or heptane prior to use

^{13}C NMR (DMSO-d_6, 125 MHz) δ 150.5, 117.1, 109.5, 46.4, 35.8, 35.2, 23.0, 18.9, 17.2

FT-IR (ATR): 3045, 1484, 1449, 1237, 812, 736 cm^{-1}



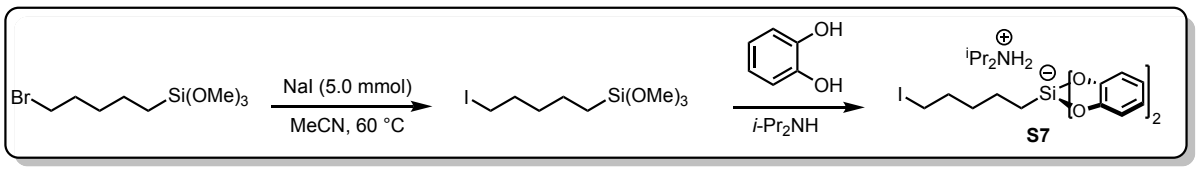
S6

Diisopropylammonium Bis(catecholato)(4-bromopentyl)silicate S6 (4.39 g, 86%) was prepared according to the representative procedure for silicate synthesis from (5-bromopentyl)trimethoxysilane (2.71 g, 9.99 mmol, 1.00 equiv), catechol (2.14 g, 19.4 mmol, 1.95 equiv), and *i*-Pr_2NH (4.0 g, 40 mmol, 4.0 equiv) The desired imine **S6** was obtained as a colorless solid (mp = 169-171°C)

^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.67 (br s, 2 H), 6.54-6.48 (m, 4 H), 6.45-6.39 (m, 4 H), 3.35 (t, 2 H, *J* = 7.0 Hz), 3.29-3.25 (m, 2 H), 1.68-1.60 (m, 2 H), 1.16-1.18 (m, 4 H), 1.17 (d, 12 H, *J* = 6.5 Hz), 0.51-0.44 (m, 2 H)

^{13}C NMR (DMSO-d_6, 125 MHz) δ 150.5, 117.1, 109.5, 46.4, 35.2, 32.3, 31.2, 23.5, 19.2, 18.1

FT-IR (ATR): 3046, 1484, 1467, 1238, 811, 741 cm^{-1}



S7

To an oven-dried 100 mL round bottom flask equipped with stir bar was charged with flame-dried sodium iodide (15.0 g, 100 mmol, 5.00 equiv). The flask was backfilled with N_2, cooled, and sealed with a rubber septum. The flask was backfilled with Ar and anhydous MeCN (15 mL) and 5-bromopropylltrimethoxysilane (5.42 g, 20 mmol, 1.0 equiv). After stirring for 5 min, the flask was heated to 60 °C in an oil bath. The reaction mixture was stirred at this temperature for 48 h. After this time, the reaction mixture was cooled to rt, and diluted with a 1:1 mixture of Et_2O/pentane (~80 mL). The heterogeneous solution washed with water (3 x 40 mL), and brine (40 mL). The solvent was removed in vacuo by careful rotary evaporation in a rt water bath (~23 o C). Purification by vacuum distillation (bp 83 °C @ 1 mmHg) afforded (5-iodopentyl)trimethoxysilane (5.20 g, 16.3 mmol, 82%) as a yellow-tinted oil.

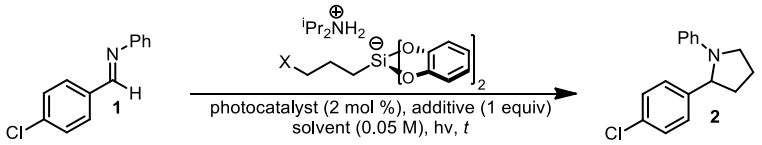
Diisopropylammonium Bis(catecholato)(4-bromopentyl)silicate S7 (7.67 g, 86%) was prepared according to the representative procedure for silicate synthesis from (5-iodopentyl)trimethoxysilane (5.20 g, 16.3 mmol, 1.00 equiv), catechol (3.51 g, 31.9 mmol, 1.95 equiv), and *i*-Pr_2NH (7.1 g, 70 mmol, 4.3 equiv) The desired imine **S7** was obtained as a colorless solid (mp = 168-170 °C)

^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.03 (br s, 2 H), 6.54-6.48 (m, 4 H), 6.45-6.40 (m, 4 H), 3.41-3.29 (m, 2 H), 3.11 (t, 2 H, *J* = 7.0 Hz), 1.66-1.55 (m, 2 H), 1.25-1.14 (m, 4 H), 1.17 (d, 12 H, *J* = 6.5 Hz), 0.51-0.44 (m, 2 H)

^{13}C NMR (DMSO-d_6, 125 MHz) δ 150.5, 117.0, 109.5, 46.4, 35.5, 33.0, 23.3, 18.8, 18.1, 9.1

Optimization of RPC Annulation

Table S1. Optimization of RPC Annulation



Entry	X	Imine:Silicate ratio	Photocatalyst[a]	Light Source	Additive	Time (h)	Solvent	Yield (%)[b]
1	I	1 : 5	$Ru(bpy)_3(PF_6)_2$	CFL	–	16	DMF	10
2	Br	1 : 5	$Ru(bpy)_3(PF_6)_2$	CFL	–	16	DMF	20
3	Cl	1 : 5	$Ru(bpy)_3(PF_6)_2$	CFL	–	16	DMF	8
4	Br	1 : 2	$Ru(bpy)_3(PF_6)_2$	CFL	–	16	DMF	20
5	Br	1 : 2	$Ru(bpy)_3(PF_6)_2$	CFL	Cs_2CO_3	16	DMF	traces
6	Br	1 : 2	$Ru(bpy)_3(PF_6)_2$	CFL	$AlCl_3$	16	DMF	traces
7	Br	1 : 2	$Ru(bpy)_3(PF_6)_2$	CFL	CSA	16	DMF	traces
9	Br	1 : 2	$Ru(bpy)_3(PF_6)_2$	CFL	Pyridine	16	DMF	20
10	Br	1 : 2	$Ru(bpy)_3(PF_6)_2$	CFL	Lutidine	16	DMF	18
11	Br	1 : 2	$Ru(bpy)_3(PF_6)_2$	CFL	–	16	DMF	46
12	Br	2 : 1	$Ru(bpy)_3(PF_6)_2$	Blue LED	–	16	DMSO	46
13	Br	2 : 1	$Ru(bpy)_3(PF_6)_2$	Blue LED	$PhCO_2H$	16	DMSO	57
14	Br	2 : 1	$Ru(bpy)_3(PF_6)_2$	Blue LED	$MeCO_2H$	16	DMSO	47
15	Br	2 : 1	$Ru(bpy)_3(PF_6)_2$	Blue LED	HCO_2H	16	DMSO	48
16[c]	Br	2 : 1	$Ru(bpy)_3(PF_6)_2$	Blue LED	$PhCO_2H$	16	DMSO	49
17[d]	Br	2 : 1	$Ru(bpy)_3(PF_6)_2$	Blue LED	$PhCO_2H$	16	DMSO	55
18	Br	2 : 1	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	Blue LED	–	16	DMSO	54
19	I	2 : 1	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	Blue LED	–	16	DMSO	16
20	Br	2 : 1	$Ir(ppy)_2(bpy)PF_6$	Blue LED	$MeCO_2H$	16	DMSO	50
21	Br	2 : 1	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	Blue LED	Lutidine	16	DMSO	42
22	Br	2 : 1	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	Blue LED	HCO_2H	16	DMSO	52
23	Br	2 : 1	4CzIPN	Blue LED		16	DMSO	35
24	Br	2 : 1	4CzIPN	Blue LED	Lutidine	16	DMSO	34
25	Br	2 : 1	$Ru(bpy)_3(PF_6)_2$	Kessil Bay	$PhCO_2H$	16	DMSO	48
26	Br	2 : 1	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	Kessil Bay		16	DMSO	60
27	Br	2 : 1	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	Kessil Bay		0.5	DMSO	59
28	Br	2 : 1	*none*	Kessil Bay		16	DMSO	17[e]
29	Br	2 : 1	$Ir(dF(CF_3)ppy)_2(bpy)PF_6$	*none*		16	DMSO	n.r.

[a]Unless otherwise noted, 2 mol % photocatalyst was used; [b]Unless otherwise noted, isolated yield after purification; [c]1 mol % photocatalyst used; [d]5 mol % photocatalyst used; [e]^{1}H NMR yield of crude.

General High-throughtput Experimentation (HTE) Information

High Throughput Experimentation (HTE) was performed at the Penn/Merck Center for High Throughput Experimentation at the University of Pennsylvania. Screens were conducted on a 0.01 mmol scale and analyzed by UPLC with addition of 4,4′-di-tert-butylbiphenyl as internal standard (IS). The ratios corresponding to the areas of the product to internal standard (P/IS) are outlined below. Each screen was carried out independently, and the ratios from one screen should not be quantitatively compared to those from a different screen.

General Procedure for HTE Screens

The reactions were carried out in a 24 or 96-well plate reactor block containing 1 mL glass vials equipped with a Teflon-coated magnetic stir bar. The plate was placed in a glovebox, and stock solutions of the appropriate reagents (silicate, imine, potential additives and photocatalysts) were added using micropipettes. A centrifugal evaporator was used to remove excess solvents. To these vials was then added 100 µL of an appropriate solvent. The vials were sealed and stirred over blue LED lights at rt (~24°C). After 24 hr, the reactions were exposed to air and diluted with 500 µL of a 0.002 µM solution of internal standard in MeCN. The vials were stirred for 5 min. Aliquots (25 µL) were transferred into a 96-well UPLC block, diluted with MeCN (700 µL) and then analyzed by UPLC.

Table S2. Optimization of Solvent, Alkylsilicate Structure, and Photocatalyst using HTE[a,b]

		iodosilicate	bromosilicate
$Ru(bpy)_3(PF_6)_2$	MeCN	15	8
	DMF	41	39
	MeOH	13	10
	HFIP	43	18
4CzIPn	MeCN	12	9
	DMF	16	12
	MeOH	2	10
	HFIP	19	6

[a] Values indicate ratio of P (pyrrolidine **2**) to IS (4,4′-di-*tert*-butylbiphenyl) by UPLC analysis [b] Structures of iridium photocatalysts given at end of this section.

Table S3. Optimization of Solvent, Reagent Ratio, Additive, and Photocatalyst using HTE[a,b]

Imine : Silicate Ratio 1 : 2

Additives		none	Lutidine	DIPEA	CSA	$Cu(Otf)_2$	$PhCO_2H$
DMSO	MesAc	2.47	1.87	0	3.19	0.2	3.7
	[Ir] 1	1.57	2.09	1.37	3.39	0.18	0.85
	4CzIPn	1.63	2.23	1	3.27	0.18	2.67
	$Ru(bpy)_3(PF_6)_2$	2.67	3.31	0.51	3.28	2	1.97
DMF	MesAc	1.02	0.74	0	1.88	0.31	0.57
	[Ir] 1	1.09	1.2	0.25	2.48	0	0.75
	4CzIPn	1.01	1.86	0.27	2.17	0.24	1.16
	$Ru(bpy)_3(PF_6)_2$	1.92	5.6	0.28	3.22	0.23	2.77

Imine : Silicate Ratio 2 : 1

Additives		none	Lutidine	DIPEA	CSA	$Cu(Otf)_2$	$PhCO_2H$
DMSO	MesAc	2.96	2.32	0	0.37	0.54	2.8
	[Ir] 1	4.6	4.7	2.29	0.81	0.27	4.33
	4CzIPn	3.88	4.72	0.26	1.12	0.28	0.38
	$Ru(bpy)_3(PF_6)_2$	4.52	4.26	0.76	2.62	1.23	4.54
DMF	MesAc	1.99	0	0	0.54	0.35	1.98
	[Ir] 1	3.23	2.45	0	1.49	0.9	3.91
	4CzIPn	2.96	2.54	0.47	0.41	0.36	3.46
	$Ru(bpy)_3(PF_6)_2$	2.77	2.35	0.49	2.05	0.39	3.86

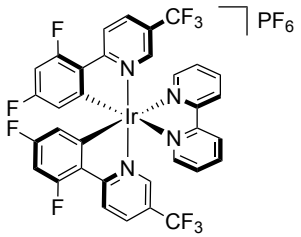
[a] Values indicate ratio of P (pyrrolidine **2**) to IS (4,4′-di-*tert*-butylbiphenyl) by UPLC analysis [b] Structures of iridium photocatalysts given at end of this section.

Table S3. Investigation of Additives and Photocatalysts using HTE[a,b]

		Acid Additive				
		none	acetic	benzoic	formic	2-bromobenzoic
DMSO	$Ru(bpy)_3(PF6)_2$	4.05	4.33	3.83	4.08	4.1
	$Ru(bpy)_2(bpm)(PF_6)_2$	4.32	4.56	4.12	4.25	3.89
	[Ir] 1	3.86	4.21	3.79	4.99	2.78
	[Ir] 2	1.87	2.42	3.91	4.4	2.84
	[Ir] 3	4.3	5.08	4.43	0.59	4.55

[a] Values indicate ratio of P (pyrrolidine **2**) to IS (4,4′-di-*tert*-butylbiphenyl) by UPLC analysis [b] Structures of iridium photocatalysts given below

[Ir] **1**



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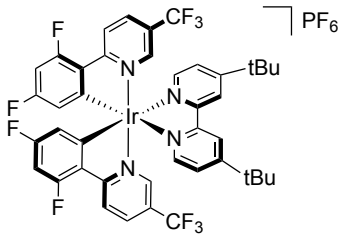

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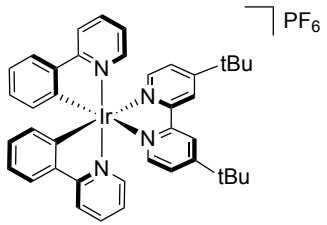
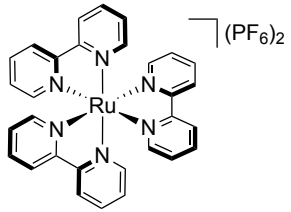
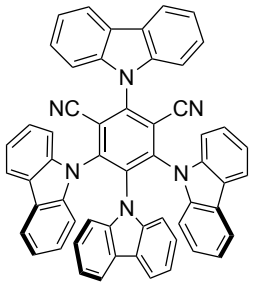
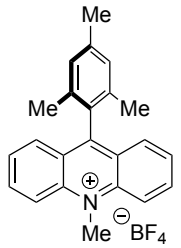




$Ru(bpy)_3(PF_6)_2$

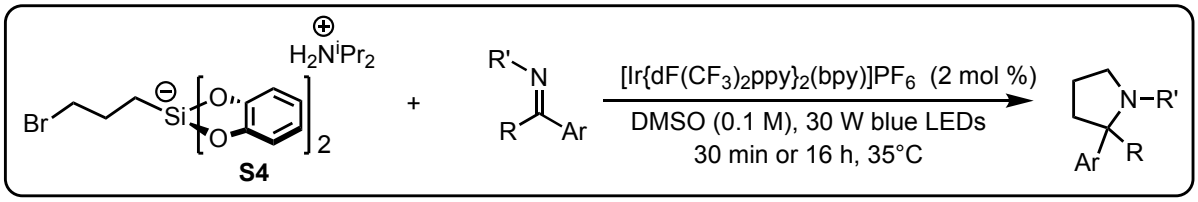


4CzIPN

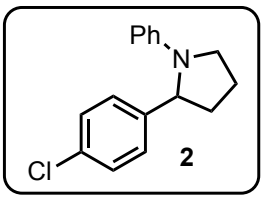


MesAcr

General Procedure for RPC Annulation



Bromoalkyl bis(cathecolato)silicate (0.3 mmol, 1 equiv) was added to an 8 mL vial, followed by the imine (2 equiv) and the photocatalyst (2 mol %). Dry DMSO (0.1 M) was added to the vial and the solution was purged with argon for 5 min. The vial was then further sealed with Parafilm and irradiated using two 30W blue LED lamps (see "Photochemical Reactor Setup" from our previous publications) for (A) 30 min or (B) 16 h. After the adequate amount of time, the vial was removed from the chamber, and H_2O and EtOAc were added. The phases were separated, and the aqueous phase was extracted with EtOAc. The organic phases were combined, washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo* by rotary evaporation. The crude mixture was then purified my column chromatography on silica gel in either hexane or hexane/EtOAc (100:0 to 90:10), depending on the polarity of the product. In a few cases, separation between product and starting material was still not total, and the mix was further subjected to preparatory TLC in either hexane or hexane:EtOAc (95:5) to yield the pure product, all of which were obtained as oils of various hues.



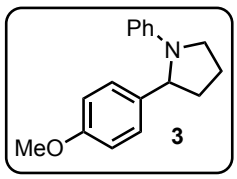
2-(4-Chlorophenyl)-1-phenylpyrrolidine, 2 (46 mg, 60%) was prepared using the general procedure with ethyl 4-((4-chlorobenzylidene)amino)benzoate (0.129 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **2** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27-7.25 (m, 2 H), 7.17-7.14 (m, 4 H), 6.66 (t, 1 H, *J* = 7.0 Hz), 6.47 (d, 2 H, *J* = 8.0 Hz), 4.69 (dd, 1 H, *J* = 8.5 Hz, 1.5 Hz), 3.72-3.69 (m, 1 H), 3.40 (dd, 1 H, *J* = 16.5 Hz, 8.0 Hz), 2.42-2.35 (m, 1 H), 2.03-1.97 (m, 2 H), 1.91-1.88 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.3, 143.5, 132.5, 129.3, 128.9, 127.6, 116.4, 112.7, 62.7, 49.4, 36.3, 23.4

FT-IR (ATR) 2969, 2871, 1597, 1503, 1360 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{16}NCl$ $[M]^+$ 257.0971, found 257.0960



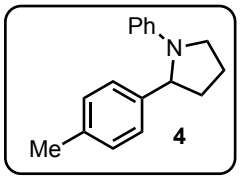
2-(4-Methoxyphenyl)-1-phenylpyrrolidine, 3 (55 mg, 72%) was prepared using the general procedure with *N*-(4-methoxybenzylidene)aniline (0.127 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **3** was obtained as a red-tinted oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.17-7.14 (m, 4 H), 6.85 (d, 2 H, *J* = 8.5 Hz), 6.64 (t, 1 H, *J* = 7.0 Hz), 6.51 (d, 2 H, *J* = 8.1 Hz), 4.69 (d, 1 H, *J* = 8.0 Hz), 3.79 (s, 3 H), 3.70 (t, 1 H, *J* = 8.0 Hz), 3.40 (dd, 1 H, *J* = 16.0 Hz, 9.0 Hz), 2.40-2.32 (m, 1 H), 2.06-1.90 (m, 3 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.6, 147.5, 136.9, 129.2, 127.2, 116.0, 114.1, 112.6, 62.6, 55.5, 49.3, 36.5, 23.4

FT-IR (ATR) 2966, 2833, 1597, 1504, 1245 cm^{-1}

HRMS (EI^+) calcd for $C_{17}H_{19}NO$ $[M]^+$ 253.1467, found 253.1461



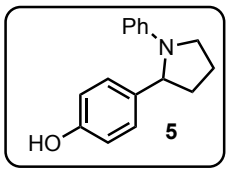
1-Phenyl-2-(*p*-tolyl)pyrrolidine, **4** (40 mg, 56%) was prepared using the general procedure with *N*-(4-methylbenzylidene)aniline (0.117 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **4** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.18-7.11 (m, 6 H), 6.65 (t, 1 H, *J* = 7.0 Hz), 6.52 (d, 2 H, *J* = 8.0 Hz), 4.72 (dd, 1 H, J = 8.0 Hz, 1.5 Hz), 3.73-3.69 (m, 1 H), 3.44-3.39 (m, 1 H), 2.43-2.34 (m, 1 H), 2.32 (s, 3 H), 2.10-1.92 (m, 3 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.5, 141.9, 136.4, 129.4, 129.2, 126.1, 115.9, 112.6, 62.9, 49.3, 36.4, 23.4, 21.3

FT-IR (ATR) 2968, 2871, 1598, 1504, 1362 cm-1

HRMS (EI^+) calcd for $C_{17}H_{19}N$ [M]+ 237.1517, found 237.1517



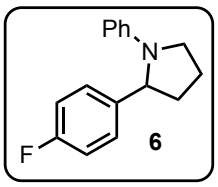
4-(1-Phenylpyrrolidin-2-yl)phenol, 5 (45 mg, 63%) was prepared using the general procedure with 4-((phenylimino)methyl)phenol (0.118 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidne **5** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.14 (t, 2 H, *J* = 7.5 Hz), 7.09 (d, 2 H, *J* = 7.9 Hz), 6.75 (d, 2 H, *J* = 7.9 Hz), 6.63 (t, 1 H, *J* = 7.0 Hz), 6.49 (d, 2 H, *J* = 8.0 Hz), 4.67 (d, 1 H, *J* = 7.5 Hz), 4.56 (s, 1 H), 3.68 (t, 1 H, *J* = 7.0 Hz), 3.38 (dd, 1 H, *J* = 15.5 Hz, 8.0 Hz), 2.38-2.31 (m, 1 H), 2.05-1.88 (m, 3 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.5, 147.5, 137.2, 129.3, 127.4, 116.0, 115.6, 112.6, 62.6, 49.3, 36.5, 23.4

FT-IR (ATR) 3402, 2966, 2871, 1597, 1505, 1363 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1388, found 240.1390



2-(4-Fluorophenyl)-1-phenylpyrrolidine, 6 (50 mg, 69%) was prepared using the general procedure with *N*-(4-fluorobenzylidene)aniline (0.119 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **6** was obtained as a yellow oil.

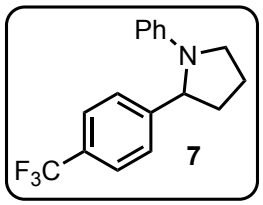
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.20-7.14 (m, 4 H), 6.98 (t, 2 H, *J* = 8.5 Hz), 6.66 (t, 1 H, *J* = 7.0 Hz), 6.49 (d, 2 H, *J* = 8.0 Hz), 4.70 (d, 1 H, *J* = 7.1 Hz), 3.72-3.69 (m, 1 H), 3.41 (dd, 1 H, *J* = 16.3 Hz, 8.8 Hz), 2.38 (tt, 1 H, *J* = 10.8 Hz, 8.0 Hz), 2.04-1.98 (m, 2 H), 1.93-1.90 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.0 (d, $^1J_{CF}$ = 244.1 Hz), 147.3, 140.5, 129.3, 127.6 (d, $^3J_{CF}$ = 8.0 Hz), 116.3, 115.5 (d, $^2J_{CF}$ = 21.3 Hz), 112.7, 62.6, 49.4, 36.4, 23.3

^{19}F NMR ($CDCl_3$, 476 MHz) δ –116.6 (s, 1 F)

FT-IR (ATR) 2969, 2872, 1597, 1504, 1361 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{16}NF$ $[M]^+$ 241.1267, found 241.1281



1-Phenyl-2-(4-(trifluoromethyl)phenyl)pyrrolidine, 7 (64 mg, 73%) was prepared using the general procedure with *N*-(4-(trifluoromethyl)benzylidene)aniline (0.150 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **7** was obtained as a yellow oil.

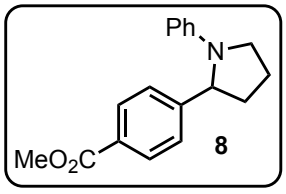
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (d, 2 H, *J* = 8.0 Hz), 7.36 (d, 2 H, *J* = 8.0 Hz), 7.18 (t, 2 H, *J* = 7.5 Hz), 6.69 (t, 1 H, *J* = 7.0 Hz), 6.49 (d, 2 H, *J* = 8.0 Hz), 4.78 (d, 1 H, *J* = 7.9 Hz), 3.77-3.73 (m, 1 H), 3.45 (dd, 1 H, *J* = 16.5 Hz, 8.2 Hz), 2.48-2.41 (m, 1 H), 2.04-2.02 (m, 2 H), 1.96-1.94 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.2, 147.2, 129.4, 129.3 (q, $^2J_{CF}$ = 32.3 Hz), 126.6, 125.8 (q, $^3J_{CF}$ = 3.6 Hz), 124.6 (q, $^1J_{CF}$ = 272.0 Hz), 116.6, 112.7, 62.9, 49.5, 36.2, 23.4

^{19}F NMR ($CDCl_3$, 476 MHz) δ –62.2 (s, 3 F)

FT-IR (ATR) 2973, 2874, 1599, 1505, 1322, 1120 cm^{-1}

HRMS (EI^+) calcd for $C_{17}H_{16}NF_3$ $[M]^+$ 291.1235, found 291.1248



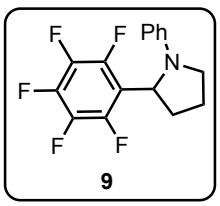
Methyl 4-(1-phenylpyrrolidin-2-yl)benzoate, 8 (46 mg, 55%) was prepared using the general procedure with methyl 4-((phenylimino)methyl)benzoate (0.148 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **8** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97 (d, 2 H, *J* = 7.5 Hz), 7.30 (d, 2 H, *J* = 7.5 Hz), 7.14 (t, 2 H, *J* = 7.0 Hz), 6.65 (t, 1 H, *J* = 7.0 Hz), 6.46 (d, 2 H, *J* = 7.5 Hz), 4.75 (d, 1 H, *J* = 7.5 Hz), 3.89 (s, 3 H), 3.75-3.71 (m, 1 H), 3.43 (dd, 1 H, *J* = 15.9 Hz, 7.5 Hz), 2.46-2.39 (m, 1 H), 2.04-2.00 (m, 2 H), 1.95-1.93 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.3, 150.5, 147.2, 130.2, 129.3, 129.0, 126.2, 116.4, 112.7, 63.2, 52.3, 49.5, 36.2, 23.4

FT-IR (ATR) 2949, 2844, 1721, 1505, 1277 cm^{-1}

HRMS (EI^+) calcd for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.1494, found 282.1495



2-(Perfluorophenyl)-1-phenylpyrrolidine, 9 (55 mg, 58%) was prepared using the general procedure with *N*-((perfluorophenyl)methylene)aniline (0.165 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **9** was obtained as a yellow oil.

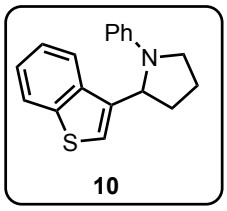
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.19 (t, 2 H, *J* = 7.0 Hz), 6.69 (t, 1 H, *J* = 7.0 Hz), 6.48 (d, 2 H, *J* = 7.5 Hz), 5.22 (d, 1 H, *J* = 4.5 Hz), 3.65-3.62 (m, 1 H), 3.50-3.46 (m, 1 H), 2.57-2.54 (m, 1 H), 2.22-2.17 (m, 1 H), 2.12-2.08 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.0, 146.0-143.8 (m), 141.4-139.2 (m), 139.0-136.7 (m), 129.5, 117.8-117.6 (m), 116.8, 112.1, 53.5, 48.7, 34.5, 24.7

^{19}F NMR ($CDCl_3$, 476 MHz) δ –144.7 (dd, 2 F, *J* = 22.0 Hz, 8.0 Hz), –156.1 (t, 1 F, *J* = 22.0 Hz), –161.9 (td, 2 F, *J* = 22.0 Hz, 8.0 Hz)

FT-IR (ATR) 2975, 2854, 1599, 1497, 1369 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{12}NF_5$ $[M]^+$ 313.0890, found 313.0905



10

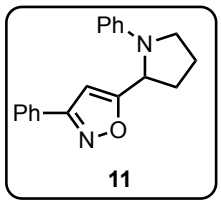
2-(Benzo[β]thiophen-3-yl)-1-phenylpyrrolidine, 10 (20 mg, 24%) was prepared using the general procedure with *N*-(benzo[β]thiophen-3-ylmethylene)aniline (0.141 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **10** was obtained as a brown oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76 (d, 1 H, *J* = 8.0 Hz), 7.66 (d, 1 H, *J* = 8.0 Hz), 7.31 (t, 2 H, *J* = 7.5 Hz), 7.26 (t, 2 H, *J* = 7.5 Hz), 7.13 (s, 1 H), 6.70 (t, 1 H, *J* = 7.5 Hz), 6.66 (d, 2 H, *J* = 8.0 Hz), 5.02 (d, 1 H, *J* = 7.9 Hz), 3.73 (t, 1 H, *J* = 7.5 Hz), 3.39-3.34 (m, 1 H), 2.44-2.36 (m, 1 H), 2.27-2.14 (m, 2 H), 2.10-2.05 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.2, 147.3, 140.4, 139.5, 129.4, 124.4, 123.9, 123.4, 122.7, 119.7, 116.9, 112.7, 59.8, 49.0, 36.2, 23.8

FT-IR (ATR) 2969, 2851, 1598, 1503, 1341 cm^{-1}

HRMS (EI^+) calcd for $C_{18}H_{17}NS$ $[M]^+$ 279.1082, found 279.1084



11

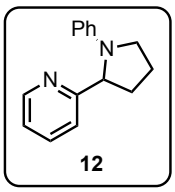
3-Phenyl-5-(1-phenylpyrrolidin-2-yl)isoxazole, 11 (55 mg, 63%) was prepared using the general procedure with *N-((*3-phenylisoxazol-5-yl)methylene) **S3** (0.149 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **11** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76 (dd, 2 H, *J* = 6.5 Hz, 3.0 Hz), 7.42-7.41 (m, 3 H), 7.23 (t, 2 H, *J* = 8.0 Hz), 6.74 (t, 1 H, *J* = 7.3 Hz), 6.61 (d, 2 H, *J* = 8.0 Hz), 6.32 (s, 1 H), 4.93 (d, 1 H, *J* = 7.5 Hz), 3.68-3.65 (m, 1 H), 3.36 (q, 1 H, *J* = 9.0 Hz), 2.39-2.28 (m, 2 H), 2.15-2.09 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.4, 162.6, 146.9, 130.2, 129.5, 129.3, 129.1, 127.1, 117.2, 112.6, 100.0, 56.6, 48.5, 32.6, 23.9

FT-IR (ATR) 2974, 2849, 1596, 1504, 1363 cm^{-1}

HRMS (EI^+) calcd for $C_{19}H_{18}N_2O$ $[M]^+$ 290.1419, found 290.1433



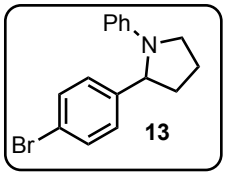
2-(1-Phenylpyrrolidin-2-yl)pyridine, 12 (47 mg, 70%) was prepared using the general procedure with *N*-(pyridin-2-ylmethylene)aniline (0.109 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **12** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.62 (d, 1 H, *J* = 4.0 Hz), 7.55 (t, 1 H, *J* = 7.5 Hz), 7.18-7.14 (m, 4 H), 6.67 (t, 1 H, *J* = 7.0 Hz), 6.51 (d, 2 H, *J* = 8.0 Hz), 4.84 (d, 1 H, *J* = 8.5 Hz), 3.77-3.73 (m, 1 H), 3.45 (dd, 1 H, *J* = 16.5 Hz, 8.5 Hz), 2.51-2.43 (m, 1 H), 2.16-2.13 (m, 1 H), 2.04-1.98 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.2, 149.8, 147.3, 136.9, 129.3, 122.0, 120.4, 116.4, 112.7, 65.0, 49.5, 34.6, 23.5

FT-IR (ATR) 2970, 2871, 1597, 1503, 1360 cm^{-1}

HRMS (EI^+) calcd for $C_{15}H_{17}N_2$ $[M+H]^+$ 225.1392, found 225.1376



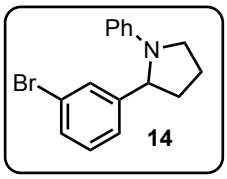
2-(4-Bromophenyl)-1-phenylpyrrolidine, 13 (76 mg, 84%) was prepared using the general procedure with *N*-(4-bromobenzylidene)aniline (0.155 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **13** was obtained as a yellow-tinted oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (d, 2 H, *J* = 8.0 Hz), 7.18 (d, 2 H, *J* = 8.0 Hz), 7.13 (d, 2 H, *J* = 8.0 Hz), 6.68 (t, 1 H, *J* = 7.2 Hz), 6.50 (d, 2 H, *J* = 8.0 Hz), 4.69 (d, 1 H, *J* = 7.0 Hz), 3.74-3.71 (m, 1 H), 3.42 (dd, 1 H, *J* = 16.5 Hz, 8.5 Hz), 2.44-2.37 (m, 1 H), 2.05-1.99 (m, 2 H), 1.93-1.91 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.2, 144.0, 131.8, 129.3, 128.0, 120.6, 116.4, 112.7, 62.7, 49.4, 36.3, 23.3

FT-IR (ATR) 2968, 2870, 1597, 1503, 1359 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{16}N^{81}Br$ $[M]^+$ 303.0446, found 303.0445



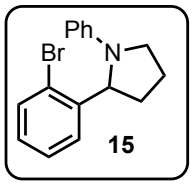
2-(3-Bromophenyl)-1-phenylpyrrolidine, 14 (52 mg, 57%) was prepared using the general procedure with *N*-(3-bromobenzylidene)aniline **S1** (0.155 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **14** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.41 (s, 1 H), 7.37-7.35 (m, 1 H), 7.19-7.16 (m, 4 H), 6.68 (t, 1 H, *J* = 7.5 Hz), 6.50 (d, 2 H, *J* = 8.0 Hz), 4.68 (dd, 1 H, *J* = 8.5 Hz, 2.0 Hz), 3.75-3.71 (m, 1 H), 3.41 (td, 1 H, *J* = 9.0 Hz, 7.0 Hz), 2.43-2.36 (m, 1 H), 2.09-1.97 (m, 2 H), 1.95-1.91 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.7, 147.3, 130.4, 130.1, 129.3, 129.2, 124.9, 123.1, 116.5, 112.7, 62.9, 49.5, 36.3, 23.3

FT-IR (ATR) 2969, 2870, 1598, 1504, 1360 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{16}N^{81}Br$ $[M]^+$ 303.0446, found 303.0470



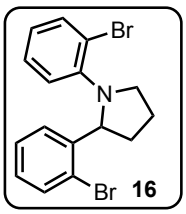
2-(2-Bromophenyl)-1-phenylpyrrolidine, 15 (61 mg, 67%) was prepared using the general procedure with *N*-(2-bromobenzylidene)aniline (0.155 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **15** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, 1 H, *J* = 7.5 Hz), 7.19-7.08 (m, 5 H), 6.66 (t, 1 H, *J* = 7.0 Hz), 6.43 (d, 2 H, *J* = 8.0 Hz), 4.99 (d, 1 H, *J* = 8.5 Hz), 3.76-3.75 (m, 1 H), 3.44 (dd, 1 H, *J* = 16.0 Hz, 8.0 Hz), 2.48-2.41 (m, 1 H), 2.02-1.97 (m, 3 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.0, 142.9, 133.3, 129.4, 128.6, 128.0, 127.7, 122.5, 116.4, 112.6, 63.1, 49.6, 34.3, 23.2

FT-IR (ATR) 2971, 2834, 1598, 1504, 1362 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{16}N^{79}Br$ $[M]^+$ 301.0466, found 301.0462



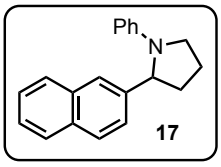
1,2-Bis(2-bromophenyl)pyrrolidine, 16 (244 mg, 64%) was prepared using the general procedure with 2-bromo-*N*-(2-bromobenzylidene)aniline (0.678 g, 2.00 mmol), 3-bromopropyl bis(catecholato)-silicate (0.466 g, 1.00 mmol), and iridium photocatalyst (10 mg, 0.01 mmol, 1 mol %) in DMSO (10 mL) for 16 h. Pyrrolidine **16** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51-7.48 (m, 3 H), 7.17 (t, 1 H, *J* = 7.5 Hz), 7.07 (t, 1 H, *J* = 7.5 Hz), 7.01 (t, 1 H, *J* = 7.5 Hz), 6.81 (d, 1 H, *J* = 8.0 Hz), 6.73 (t, 1 H, *J* = 7.5 Hz), 5.08 (t, 1 H, *J* = 7.5 Hz), 4.37 (dd, 1 H, *J* = 16.0 Hz, 7.5 Hz), 3.07-3.03 (m, 1 H), 2.63-2.62 (m, 1 H), 2.09-2.08 (m, 1 H), 2.02-1.93 (m, 1 H), 1.73-1.65 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.8, 142.1, 134.4, 132.7, 128.5, 128.3, 128.1, 128.0, 123.4, 122.8, 120.3, 117.0, 63.5, 54.4, 34.6, 24.9

FT-IR (ATR) 2971, 2876, 1586, 1474, 1312, 1022 cm^{-1}

HRMS (EI^+) calcd for $C_{16}H_{15}NBr_2$ $[M]^+$ 378.9571, found 378.9556



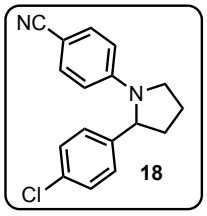
2-(Naphthalen-2-yl)-1-phenylpyrrolidine, 17 (43 mg, 52%) was prepared using the general procedure with *N*-(naphthalen-2-ylmethylene)aniline (0.140 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **17** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82-7.81 (m, 2 H), 7.77-7.76 (m, 1 H), 7.66 (s, 1 H), 7.46-7.41 (m, 2 H), 7.39 (dd, 1 H, *J* = 8.5 Hz, 1.5 Hz), 7.14 (dd, 2 H, *J* = 8.5 Hz, 7.5 Hz), 6.64 (t, 1 H, *J* = 7.5 Hz), 6.55 (d, 2 H, *J* = 8.3 Hz), 4.88 (d, 1 H, *J* = 8.3 Hz), 3.82-3.79 (m, 1 H), 3.47 (td, 1 H, *J* = 9.0 Hz, 7.0 Hz), 2.49-2.41 (m, 1 H), 2.14-2.06 (m, 1 H), 2.04-1.99 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 147.6, 142.4, 133.7, 132.9, 129.3, 128.6, 128.1, 127.9, 126.3, 125.7, 124.9, 124.6, 116.2, 112.7, 63.5, 49.5, 36.2, 23.4

FT-IR (ATR) 2968, 2870, 1598, 1504, 1371 cm^{-1}

HRMS (EI^+) calcd for $C_{20}H_{19}N$ $[M]^+$ 273.1517, found 273.1518



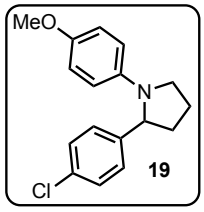
4-(2-(4-Chlorophenyl)pyrrolidin-1-yl)benzonitrile, 18 (50 mg, 59%) was prepared using the general procedure with 4-((4-chlorobenzylidene)amino)benzonitrile (0.143 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **18** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (d, 2 H, *J* = 9.0 Hz), 7.30-7.26 (m, 2 H), 7.07 (d, 2 H, *J* = 8.5 Hz), 6.43 (d, 2 H, *J* = 9.0 Hz), 4.77 (dd, 1 H, *J* = 8.5 Hz, 2.0 Hz), 3.73-3.69 (m, 1 H), 3.47 (dd, 1 H, *J* = 16.5 Hz, 9.0 Hz), 2.47-2.39 (m, 1 H), 2.06-2.00 (m, 2 H), 1.97-1.93 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.6, 141.5, 133.6, 133.1, 129.2, 127.3, 120.9, 112.7, 98.1, 77.6, 77.3, 77.1, 62.6, 49.3, 36.1, 23.1

FT-IR (ATR) 2972, 2854, 2211, 1603, 1517, 1378, 1175 cm^{-1}

HRMS (EI^+) calcd for $C_{17}H_{15}N_2Cl$ $[M]^+$ 283.1002, found 283.1004



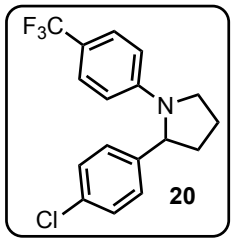
2-(4-Chlorophenyl)-1-(4-methoxyphenyl)pyrrolidine, 19 (48 mg, 55%) was prepared using the general procedure with *N*-(4-chlorobenzylidene)-4-methoxyaniline (0.150 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **19** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27-7.25 (m, 2 H), 7.17 (d, 2 H, *J* = 8.5 Hz), 6.76 (d, 2 H, *J* = 9.0 Hz), 6.41 (d, 2 H, *J* = 9.0 Hz), 4.59 (dd, 1 H, *J* = 8.5 Hz, 2.5 Hz), 3.71 (s, 3 H), 3.71-3.67 (m, 1 H), 3.34 (dd, 1 H, *J* = 16.0 Hz, 9.0 Hz), 2.42-2.36 (m, 1 H), 2.03-1.95 (m, 2 H), 1.89-1.84 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.3, 144.0, 142.2, 132.4, 128.9, 127.6, 115.1, 113.4, 63.1, 56.2, 50.0, 36.5, 23.6

FT-IR (ATR) 2944, 2830, 1509, 1236, 1039 cm^{-1}

HRMS (EI^+) calcd for $C_{17}H_{18}NOCl$ $[M]^+$ 287.1077, found 287.1070



2-(4-Chlorophenyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidine, 20 (50 mg, 51%) was prepared using the general procedure with *N*-(4-chlorobenzylidene)-4-(trifluoromethyl)aniline (0.170 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **20** was obtained as a yellow oil.

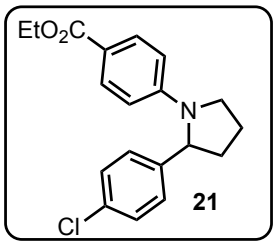
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (d, 2 H, *J* = 8.5 Hz), 7.28 (d, 2 H, *J* = 8.5 Hz), 7.11 (d, 2 H, *J* = 8.5 Hz), 6.47 (d, 2 H, *J* = 8.5 Hz), 4.75 (dd, 1 H, *J* = 8.5 Hz, 2.0 Hz), 3.74-3.70 (m, 1 H), 3.46 (q, 1 H, *J* = 8.5 Hz), 2.46-2.38 (m, 1 H), 2.06-2.00 (m, 2 H), 1.97-1.92 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.2, 142.2, 132.9, 129.1, 127.5, 126.6 (q, $^3J_{CF}$ = 4 Hz), 125.4 (q, $^1J_{CF}$ = 270 Hz), 118.0 (q, $^2J_{CF}$ = 33 Hz), 112.1, 62.6, 49.4, 36.2, 23.2

^{19}F NMR ($CDCl_3$, 476 MHz) δ –60.7 (s, 3 F)

FT-IR (ATR) 2975, 2874, 1615, 1321, 1104 cm^{-1}

HRMS (EI$^+$) calcd for $C_{17}H_{15}NF_3Cl$ $[M]^+$ 325.0845, found 325.0830



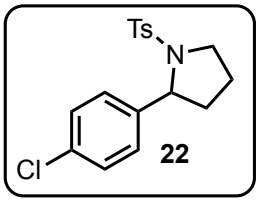
Ethyl 4-(2-(4-chlorophenyl)pyrrolidin-1-yl)benzoate, **21** (50 mg, 51%) was prepared using the general procedure with ethyl 4-((4-chlorobenzylidene)amino)benzoate (0.171 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Pyrrolidine **21** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (d, 2 H, *J* = 8.5 Hz), 7.27 (d, 2 H, *J* = 8.5 Hz), 7.10 (d, 2 H, *J* = 8.5 Hz), 6.43 (d, 2 H, *J* = 8.5 Hz), 4.80 (d, 1 H, *J* = 8.0 Hz), 4.32-4.28 (m, 2 H), 3.76-3.72 (m, 1 H), 3.49 (dd, 1 H, *J* = 17.0 Hz, 8.5 Hz), 2.46-2.38 (m, 1 H), 2.05-1.99 (m, 2 H), 1.96-1.93 (m, 1 H), 1.34 (t, 3 H, *J* = 7.0 Hz)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.2, 150.2, 142.1, 132.8, 131.4, 129.0, 127.4, 117.9, 111.9, 62.5, 60.3, 49.3, 36.1, 23.1, 14.7

FT-IR (ATR) 2976, 2872, 1698, 1605, 1365, 1274 cm^{-1}

HRMS (EI$^+$) calcd for $C_{19}H_{20}NO_2Cl$ $[M]^+$ 330.1261, found 330.1274



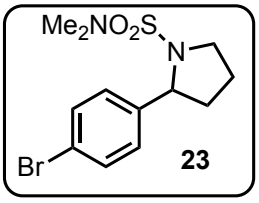
2-(4-Chlorophenyl)-1-tosylpyrrolidine, 22 (30 mg, 30%) was prepared using the general procedure with *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (0.175 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **22** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.66 (d, 2 H, *J* = 8.0 Hz), 7.30-7.23 (m, 6 H), 4.73 (dd, 1 H, *J* = 8.0 Hz, 4.0 Hz), 3.63-3.58 (m, 1 H), 3.44-3.39 (m, 1 H), 2.43 (s, 3 H), 2.03-1.96 (m, 1 H), 1.88-1.74 (m, 2 H), 1.70-1.64 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.8, 141.9, 135.3, 133.1, 129.9, 128.8, 127.9, 127.8, 63.0, 49.7, 36.1, 24.3, 21.8

FT-IR (ATR) 2976, 2880, 1492, 1346, 1159 cm^{-1}

HRMS (EI$^+$) calcd for $C_{17}H_{18}NO_2SCl$ $[M]^+$ 335.0747, found 335.0757



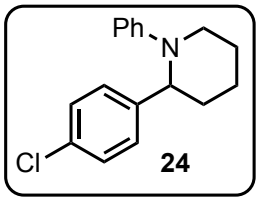
2-(4-Bromophenyl)-*N,N*-dimethylpyrrolidine-1-sulfonamide, 23 (38 mg, 38%) was prepared using the general procedure with *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (0.175 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **23** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45 (d, 2 H, *J* = 8.5 Hz), 7.19 (d, 2 H, *J* = 8.5 Hz), 4.77 (dd, 1 H, *J* = 8.5 Hz, 5.0 Hz), 3.63 (dt, 1 H, *J* = 10.0 Hz, 7.5 Hz), 3.48 (dt, 1 H, *J* = 10.0 Hz, 6.0 Hz), 2.62 (s, 6 H), 2.36 (dq, 1 H, *J* = 13.0 Hz, 7.5 Hz), 2.01-1.94 (m, 2 H), 1.82 (td, 1 H, *J* = 12.0 Hz, 6.0 Hz)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.1, 131.8, 128.4, 121.2, 63.4, 50.5, 37.9, 36.4, 24.9

FT-IR (ATR) 2972, 2884, 1487, 1333, 1145 cm^{-1}

HRMS (EI^+) calcd for $C_{12}H_{17}N_2O_2SBr$ $[M]^+$ 333.0272, found 333.0286



24

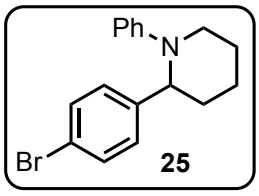
2-(4-Chlorophenyl)-1-phenylpiperidine, **24** (51 mg, 63%) was prepared using the general procedure with *N*-(4-chlorobenzylidene)aniline (0.129 g, 0.600 mmol), 4-bromobutyl bis(catecholato)silicate (0.144 g, 0.300 mmol), and iridium photocatalyst (0.006 g, 0.002 mmol, 2 mol %) in DMSO (3 mL) for 30 min. Piperidine **24** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21-7.13 (m, 6 H), 6.88 (d, 2 H, *J* = 8.0 Hz), 6.79 (t, 1 H, *J* = 7.5 Hz), 4.40 (dd, 1 H, *J* = 7.5 Hz, 4.0 Hz), 3.39 (dt, 1 H, *J* = 12.0 Hz, 5.5 Hz), 3.20-3.15 (m, 1 H), 2.00-1.94 (m, 1 H), 1.88-1.81 (m, 1 H), 1.80-1.75 (m, 2 H), 1.73-1.66 (m, 1 H), 1.58-1.51 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.0, 142.7, 132.0, 129.1, 128.9, 128.7, 120.6, 119.8, 61.2, 51.9, 34.3, 26.0, 22.6

FT-IR (ATR) 2935, 2856, 1597, 1490, 1241 cm^{-1}

HRMS (EI^+) calcd for $C_{17}H_{18}NCl$ $[M]^+$ 271.1128, found 271.1113



25

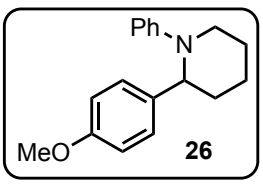
2-(4-Bromophenyl)-1-phenylpiperidine, **25** (38 mg, 30%) was prepared using the general procedure with *N*-(4-bromobenzylidene)aniline (0.205 g, 0.789 mmol), 4-bromobutyl bis(catecholato)silicate (0.150 g, 0.394 mmol), and iridium photocatalyst (8 mg, 2 mol %) in DMSO (4 mL) for 30 min. Piperidine **25** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2 H), 7.18-7.12 (m, 4 H), 7.78 (d, 2 H, *J* = 7.5 Hz), 6.80 (t, 1 H, *J* = 7.5 Hz), 4.39 (dd, 1 H, 7.5 Hz, 4.0 Hz), 3.43-3.35 (m, 1 H), 3.22-3.13 (m, 1 H), 2.02-1.92 (m, 1 H), 1.89-1.80 (m, 1 H), 1.81-1.74 (m, 2 H), 1.74-1.65 (m, 1 H), 1.60-1.48 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 143.1, 131.5, 129.1, 129.0, 120.4, 120.0, 119.7, 61.2, 51.8, 34.1, 25.8, 22.5.

FT-IR (ATR) 2933 (m), 1596 (s), 1501 (vs), 1258 (s), 1239 (s), 1103 (s), 1072 (vs), 1028 (s), 1008 (vs), 817 (vs), 801 (s), 766 (vs), 747 (vs), 696 (vs)

HRMS (EI^+) *m/z* calcd for $C_{17}H_{18}BrN$ $[M]^+$ 315.0623, found 315.01623



26

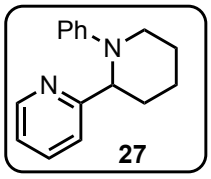
2-(4-Methoxyphenyl)-1-phenylpiperidine, **26** (23 mg, 55%) was prepared using the general procedure with *N*-(4-methoxybenzylidene)aniline (0.083 g, 0.39 mmol), 4-bromobutyl bis(catecholato)silicate (0.075 g, 0.16 mmol), and iridium photocatalyst (4 mg, 2 mol %) in DMSO (2 mL) for 30 min. Piperidine **26** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.10 (m, 4 H), 6.89 (d, 2 H, *J* = 8.0 Hz), 6.79-6.73 (m, 3 H), 4.46 (dd, 1 H, *J* = 7.0 Hz, 5.0 Hz), 3.75 (s, 3 H), 3.44-3.36 (m, 1 H), 3.28-3.21 (m, 1 H), 2.02-1.86 (m, 2 H), 1.79-1.63 (m, 3 H), 1.60-1.50 (m, 1 H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 152.0, 135.6, 128.9, 128.4, 119.7, 118.9, 113.7, 60.5, 55.3, 50.6, 33.6, 25.8, 22.2

FT-IR (ATR) 2932 (m), 1726 (w), 1597 (m), 1509 (s), 1244 (vs)

HRMS (EI^+) *m/z* calcd for $C_{18}H_{21}NO$ $[M]^+$ 267.1623, found 267.1620



27

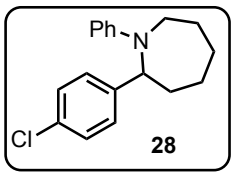
2-(1-Phenylpiperidin-2-yl)pyridine, 27 (24 mg, 66%) was prepared using the general procedure with *N*-(pyridin-2-ylmethylene)aniline (0.071 g, 0.39 mmol), 4-bromobutyl bis(catecholato)silicate (0.075 g, 0.16 mmol), and iridium photocatalyst (4 mg, 2 mol %) in DMSO (2 mL) for 16 h. Piperidine **27** was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, 1 H, J = 5.0 Hz), 7.47 (td, 1 H, J = 7.5 Hz, 2.0 Hz), 7.19 (d, 1 H, J = 8.0 Hz), 7.17-7.11 (m, 2 H), 7.05-7.01 (m, 1 H), 6.91 (d, 2 H, J = 8.0 Hz), 6.76 (t, 1 H, J = 7.5 Hz), 4.63 (dd, 1 H, J = 7.0 Hz, 5.5 Hz), 3.46 (ddd, 1 H, J = 12.0 Hz, 7.5 Hz, 4.5 Hz), 3.27 (ddd, 1 H, J = 12.5 Hz, 7.5 Hz, 4.0 Hz), 2.14-2.01 (m, 2 H), 1.86-1.69 (m, 2 H), 1.68-1.52 (m, 2 H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 151.8, 149.2, 136.4, 129.0, 122.0, 121.4, 119.9, 118.7, 62.8, 50.9, 32.5, 25.9, 22.1

FT-IR (ATR) 2932 (m), 1589 (s), 1501 (s), 1432 (m), 1259 (w), 748 (vs)

HRMS (EI^+) *m/z* calcd for $C_{16}H_{18}N_2$ $[M]^+$ 238.1470, found 238.1469



28

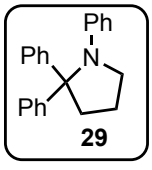
2-(4-Chlorophenyl)-1-phenylazepane, 28 (21 mg, 24%) was prepared using the general procedure with *N*-(4-chlorobenzylidene)aniline (0.129 g, 0.600 mmol), 5-bromopentyl bis(catecholato)silicate (0.152 g, 0.300 mmol), and iridium photocatalyst (0.006 g, 0.002 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Azepane **28** was obtained as a colorless oil. The linear byproduct (silicate addition to imine, but no cyclization onto the alkyl halide) was also obtained in 51% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27-7.25 (m, 2 H), 7.17-7.12 (m, 4 H), 6.63 (t, 1 H, *J* = 7.0 Hz), 6.59 (d, 2 H, *J* = 8.0 Hz), 4.57 (dd, 1 H, *J* = 12.0 Hz, 6.0 Hz), 3.83 (d, 1 H, *J* = 16.0 Hz), 3.49 (ddd, 1 H, *J* = 16.0 Hz, 10.5 Hz, 2.0 Hz), 2.43 (ddd, 1 H, *J* = 14.5 Hz, 8.0 Hz, 6.0 Hz), 1.95-1.87 (m, 2 H), 1.82-1.69 (m, 3 H), 1.50-1.43 (m, 1 H), 1.39-1.31 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.1, 143.0, 132.4, 129.5, 129.1, 127.5, 116.0, 111.6, 62.7, 45.5, 38.9, 29.9, 28.6, 26.8

FT-IR (ATR) 2926, 2855, 1597, 1504, 1384 cm^{-1}

HRMS (EI^+) calcd for $C_{18}H_{20}NCl$ $[M]^+$ 285.1284, found 285.1287



29

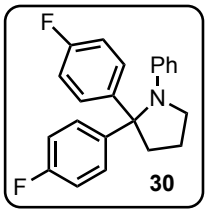
1,2,2-Triphenylpyrrolidine, 29 (41 mg, 45%) was prepared using the general procedure with *N*-(diphenylmethylene)aniline (0.156 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **29** was obtained as a colorless oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40 (d, 4 H, *J* = 7.5 Hz), 7.30 (t, 4 H, *J* = 7.5 Hz), 7.24 (dd, 2 H, *J* = 13.0 Hz, 6.0 Hz), 6.95 (t, 2 H, *J* = 7.5 Hz), 6.53 (t, 1 H, *J* = 7.0 Hz), 6.36 (d, 2 H, *J* = 8.0 Hz), 3.82 (t, 2 H, *J* = 6.5 Hz), 2.70 (t, 2 H, *J* = 6.5 Hz), 1.90-1.87 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.2, 143.6, 129.0, 128.3, 128.1, 126.9, 115.7, 114.4, 74.6, 50.8, 50.7, 23.1

FT-IR (ATR) 3058, 2978, 1597, 1504, 1343 cm^{-1}

HRMS (EI^+) calcd for $C_{22}H_{21}N$ $[M]^+$ 299.1674, found 299.1687



2,2-Bis(4-fluorophenyl)-1-phenylpyrrolidine, 30 (55 mg, 55%) was prepared using the general procedure with *N*-(bis(4-fluorophenyl)methylene) (0.175 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **30** was obtained as a colorless oil.

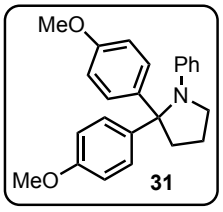
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (dd, 4 H, *J* = 8.0 Hz, 5.5 Hz), 6.98-6.96 (m, 6 H), 6.54 (t, 1 H, *J* = 7.0 Hz), 6.30 (d, 2 H, *J* = 8.0 Hz), 3.78 (t, 2 H, *J* = 6.4 Hz), 2.62 (t, 2 H, *J* = 6.5 Hz), 1.89-1.84 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.8 (d, $^{1}J_{CF}$ = 246.0 Hz), 145.8, 139.1 (d, $^{3}J_{CF}$ = 3.0 Hz), 130.5 (d, $^{3}J_{CF}$ = 7.8 Hz), 128.5, 116.2, 115.0 (d, $^{2}J_{CF}$ = 21.1 Hz), 114.5, 73.8, 50.7, 22.9

^{19}F NMR ($CDCl_3$, 476 MHz) δ –116.2 (s, 2 F)

FT-IR (ATR) 2978, 2833, 1597, 1504, 1342, 1225, 1160 cm^{-1}

HRMS (EI^+) calcd for $C_{22}H_{19}NF_2$ $[M]^+$ 335.1486, found 335.1492



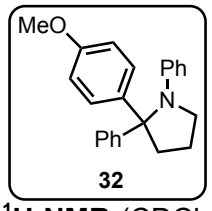
2,2-Bis(4-methoxyphenyl)-1-phenylpyrrolidine, 31 (70 mg, 65%) was prepared using the general procedure with *N*-(bis(4-methoxyphenyl)methylene)aniline (0.189 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **31** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (d, 4 H, *J* = 8.5 Hz), 6.98 (t, 2 H, *J* = 8.0 Hz), 6.84 (d, 4 H, *J* = 8.5 Hz), 6.54 (t, 1 H, *J* = 7.0 Hz), 6.38 (d, 2 H, *J* = 8.0 Hz), 3.81 (s, 6 H), 3.79 (t, 2 H, *J* = 6.5 Hz), 2.63 (t, 2 H, *J* = 6.5 Hz), 1.91-1.86 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.3, 146.2, 135.7, 130.0, 128.3, 115.5, 114.4, 113.4, 73.6, 55.4, 50.6, 50.4, 22.9

FT-IR (ATR) 2951, 2834, 1596, 1502, 1342, 1246, 1175 cm^{-1}

HRMS (EI^+) calcd for $C_{24}H_{26}NO_2$ $[M+H]^+$ 360.1964, found 360.1959



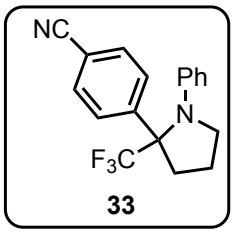
2-(4-Methoxyphenyl)-1,2-diphenylpyrrolidine, 32 (65 mg, 66%) was prepared using the general procedure with *N*-((4-methoxyphenyl)(phenyl)methylene) (0.171 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **32** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (d, 2 H, *J* = 7.5 Hz), 7.30-7.27 (m, 4 H), 7.22 (t, 1 H, *J* = 7.0 Hz), 6.95 (t, 2 H, *J* = 8.0 Hz), 6.82 (d, 2 H, *J* = 9.0 Hz), 6.52 (t, 1 H, *J* = 7.0 Hz), 6.35 (d, 2 H, *J* = 8.0 Hz), 3.80-3.77 (m, 5 H), 2.66-2.64 (t, 2 H, *J* = 6.5 Hz), 1.89-1.84 (m, 2 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.4, 146.2, 143.9, 135.5, 130.1, 128.9, 128.3, 128.1, 126.8, 115.6, 114.4, 113.4, 74.1, 55.5, 50.7, 50.5, 23.0

FT-IR (ATR) 2951, 2835, 1597, 1503, 1343, 1251, 1178 cm^{-1}

HRMS (EI^+) calcd for $C_{23}H_{24}NO$ $[M+H]^+$ 330.1858, found 330.1865



33

4-(1-Phenyl-2-(trifluoromethyl)pyrrolidin-2-yl)benzonitrile, 33 (35 mg, 37%) was prepared using the general procedure with 4-(2,2,2-trifluoro-1-(phenylimino)ethyl)benzonitrile (0.164 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **33** was obtained as a colorless oil.

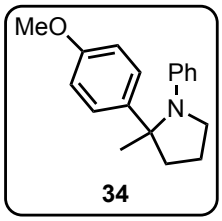
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.66 (d, 2 H, *J* = 8.5 Hz), 7.56 (d, 2 H, *J* = 8.5 Hz), 7.08 (dd, 2 H, *J* = 8.5, 7.5 Hz), 6.74 (t, 1 H, *J* = 7.5 Hz), 6.49 (d, 2 H, *J* = 8.5 Hz), 3.80-3.77 (m, 2 H), 2.85-2.79 (m, 1 H), 2.18-2.10 (m, 2 H), 2.07-2.00 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.2, 144.3, 132.9, 128.7, 127.6 (q, $^{1}J_{CF}$ = 291 Hz), 127.4 (q, $^{3}J_{CF}$ = 3 Hz), 118.7, 115.8 (d, $^{4}J_{CF}$ = 2 Hz), 112.1, 73.0 (q, $^{2}J_{CF}$ = 27 Hz), 52.2, 42.6, 22.2

^{19}F NMR ($CDCl_3$, 476 MHz) δ –64.8 (s, 3 F)

FT-IR (ATR) 2981, 2855, 2230, 1599, 1504, 1325, 1146 cm^{-1}

HRMS (EI^+) calcd for $C_{18}H_{15}N_2F_3$ $[M]^+$ 316.1187, found 316.1199



34

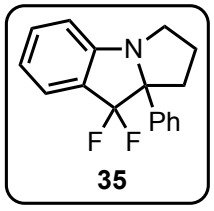
2-(4-Methoxyphenyl)-2-methyl-1-phenylpyrrolidine, 34 (20 mg, 25%) was prepared using the general procedure with *N*-(1-(4-methoxyphenyl)ethylidene)aniline (0.134 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **34** was obtained as a yellow oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 (d, 2 H, *J* = 8.5 Hz), 7.07 (t, 2 H, *J* = 8.0 Hz), 6.83 (d, 2 H, *J* = 8.5 Hz), 6.58 (t, 1 H, *J* = 7.0 Hz), 6.43 (d, 2 H, *J* = 8.5 Hz), 3.79 (s, 3 H), 3.65-3.56 (m, 2 H), 2.16-2.11 (m, 1 H), 2.09-2.04 (m, 1 H), 1.96-1.91 (m, 2 H), 1.76 (s, 3 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.2, 146.0, 140.0, 128.7, 127.1, 115.6, 114.5, 113.9, 65.6, 55.5, 50.5, 47.5, 24.0, 22.4

FT-IR (ATR) 2965, 2833, 1597, 1504, 1344 cm^{-1}

HRMS (EI^+) calcd for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1701, found 268.1702



35

9,9-Difluoro-9a-phenyl-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indole, 35 (35 mg, 43%) was prepared using the general procedure with 3,3-difluoro-2-phenyl-3H-indole (0.138 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **35** was obtained as a colorless oil.

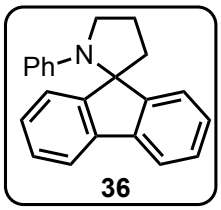
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.61 (d, 2 H, *J* = 7.5 Hz), 7.42 (d, 2 H, *J* = 7.0 Hz), 7.40 (d, 2 H, *J* = 7.5 Hz), 7.34 (t, 1 H, *J* = 7.0 Hz), 6.94 (t, 1 H, *J* = 7.5 Hz), 6.83 (d, 1 H, *J* = 8.0 Hz), 3.56 (t, 1 H, *J* = 9.5 Hz), 3.39-3.34 (m, 1 H), 2.28 (dd, 1 H, *J* = 12.0, 6.5 Hz), 2.13-2.02 (m, 2 H), 1.78-1.68 (m, 1 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 155.1 (dd, $^3J_{CF}$ = 9 Hz, 5 Hz), 138.4 (d, $^3J_{CF}$ = 6 Hz), 133.2, 128.5, 128.0, 126.9, 126.1 (dd, $^1J_{CF}$ = 250 Hz, 244 Hz), 124.6, 122.5 (dd, J_{CF} = 28 Hz, 25 Hz), 120.7, 112.6, 82.3 (dd, $^2J_{CF}$ = 27 Hz, 22 Hz), 51.6 (d, $^4J_{CF}$ = 3 Hz), 33.9 (dd, $^3J_{CF}$ = 8 Hz, 2 Hz), 26.4

^{19}F NMR ($CDCl_3$, 476 MHz) δ –83.3 (d, 1 F, $^2J_{FF}$ = 257 Hz), –96.6 (d, 1 F, $^2J_{FF}$ = 257 Hz)

FT-IR (ATR) 2954, 2887, 1617, 1469, 1307, 1257 cm^{-1}

HRMS (EI^+) calcd for $C_{17}H_{15}NF_2$ $[M]^+$ 271.1173, found 271.1181



36

1'-Phenylspiro[fluorene-9,2'-pyrrolidine], 36 (18 mg, 20%) was prepared using the general procedure with *N*-(9H-fluoren-9-ylidene)aniline (0.154 g, 0.600 mmol), 3-bromopropyl bis(catecholato)silicate (0.140 g, 0.300 mmol), and iridium photocatalyst (6 mg, 0.006 mmol, 2 mol %) in DMSO (3 mL) for 16 h. Pyrrolidine **36** was obtained as a yellow oil.

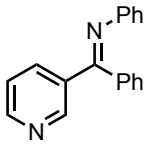
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.76 (d, 2 H, *J* = 7.5 Hz), 7.35 (t, 2 H, *J* = 7.5 Hz), 7.29 (d, 2 H, *J* = 7.5 Hz), 7.21 (t, 2 H, *J* = 7.5 Hz), 6.86 (t, 2 H, *J* = 8.0 Hz), 6.45 (t, 1 H, *J* = 7.0 Hz), 6.02 (d, 2 H, *J* = 8.5 Hz), 3.95 (t, 2 H, *J* = 6.5 Hz), 2.41-2.31 (m, 4 H)

^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.2, 145.7, 139.1, 128.7, 128.2, 128.1, 123.4, 120.5, 116.1, 113.3, 74.3, 51.2, 44.2, 23.7

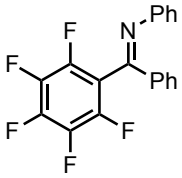
FT-IR (ATR) 2966, 2860, 1597, 1504, 1342 cm^{-1}

HRMS (EI^+) calcd for $C_{22}H_{19}N$ $[M]^+$ 297.1517, found 297.1509

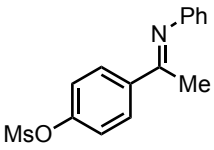
No product isolated from reactions with the following starting materials:



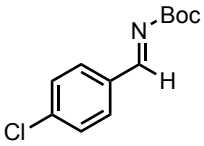
30% [a]



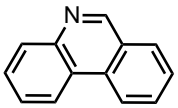
13% [a]



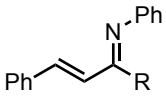
15% [a]



(b)

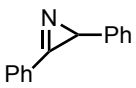


(b)

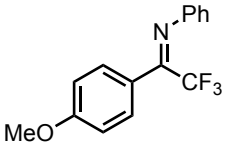


R = H or Ph

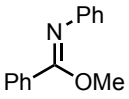
(b)



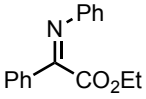
(b)



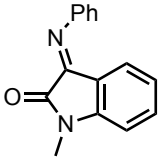
(b)



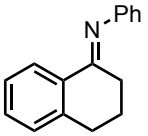
(b)



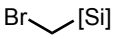
(b)



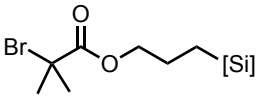
(c)



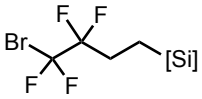
(c)



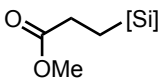
(c)



(c)



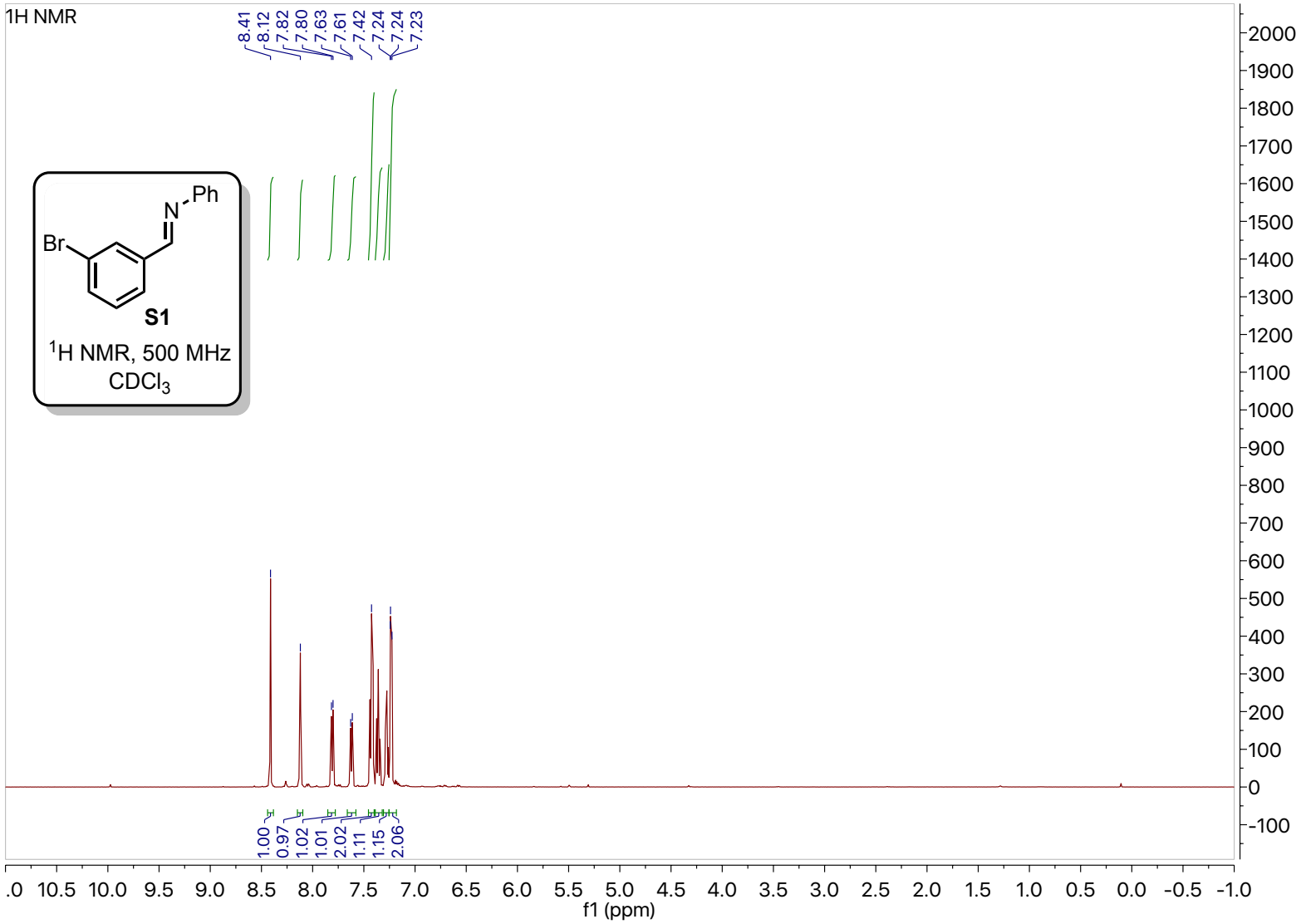
(d)

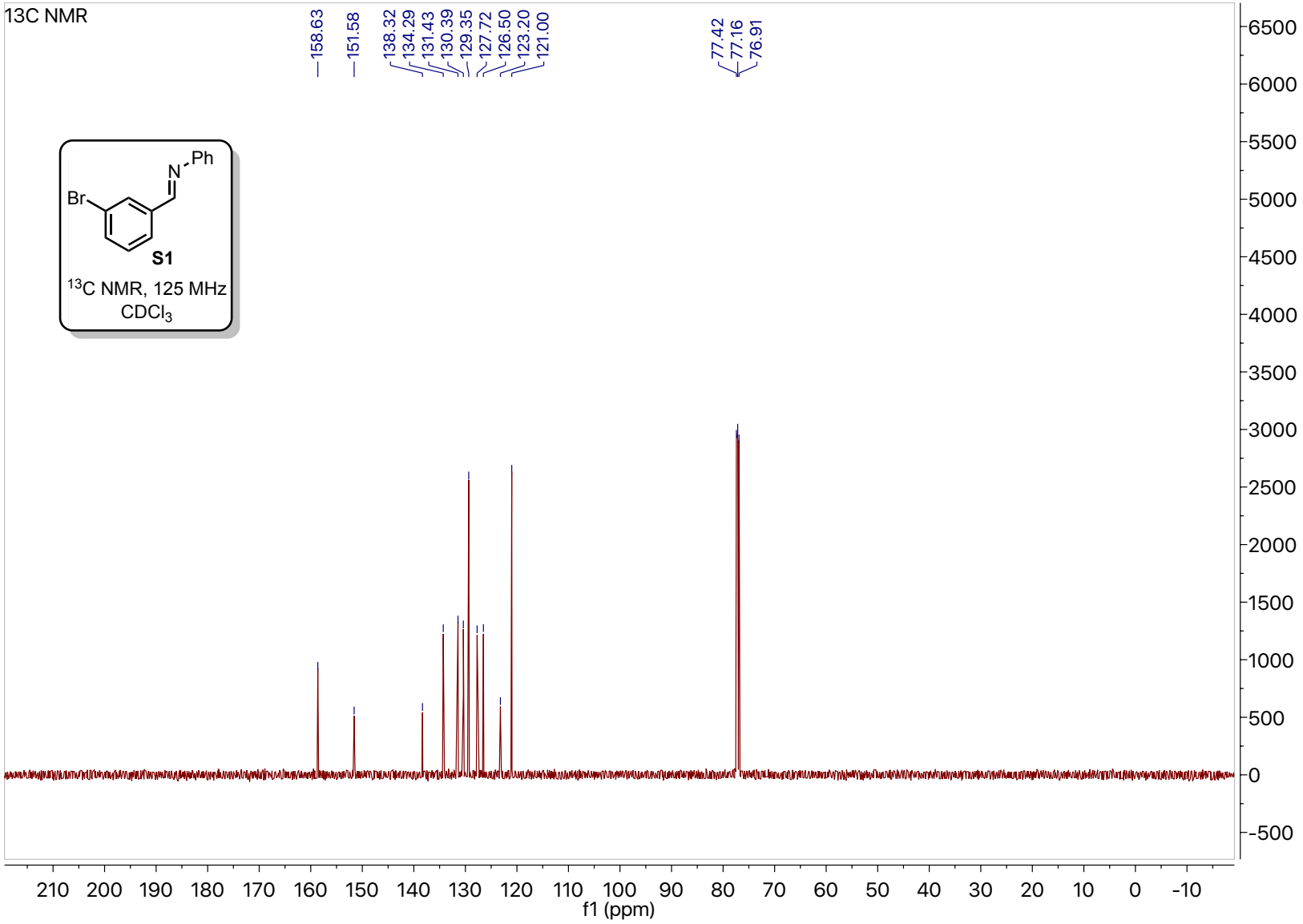


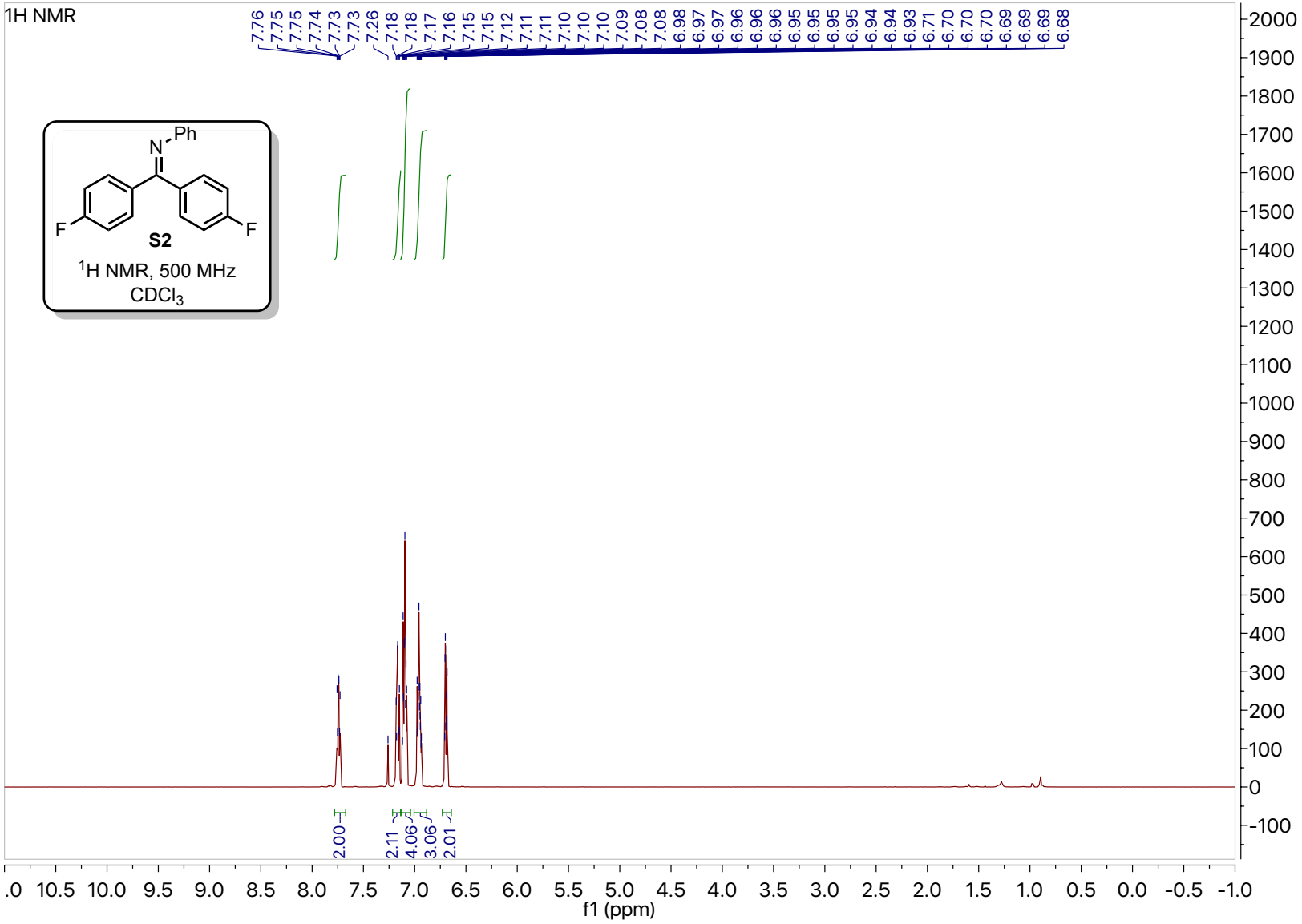
(c,d)

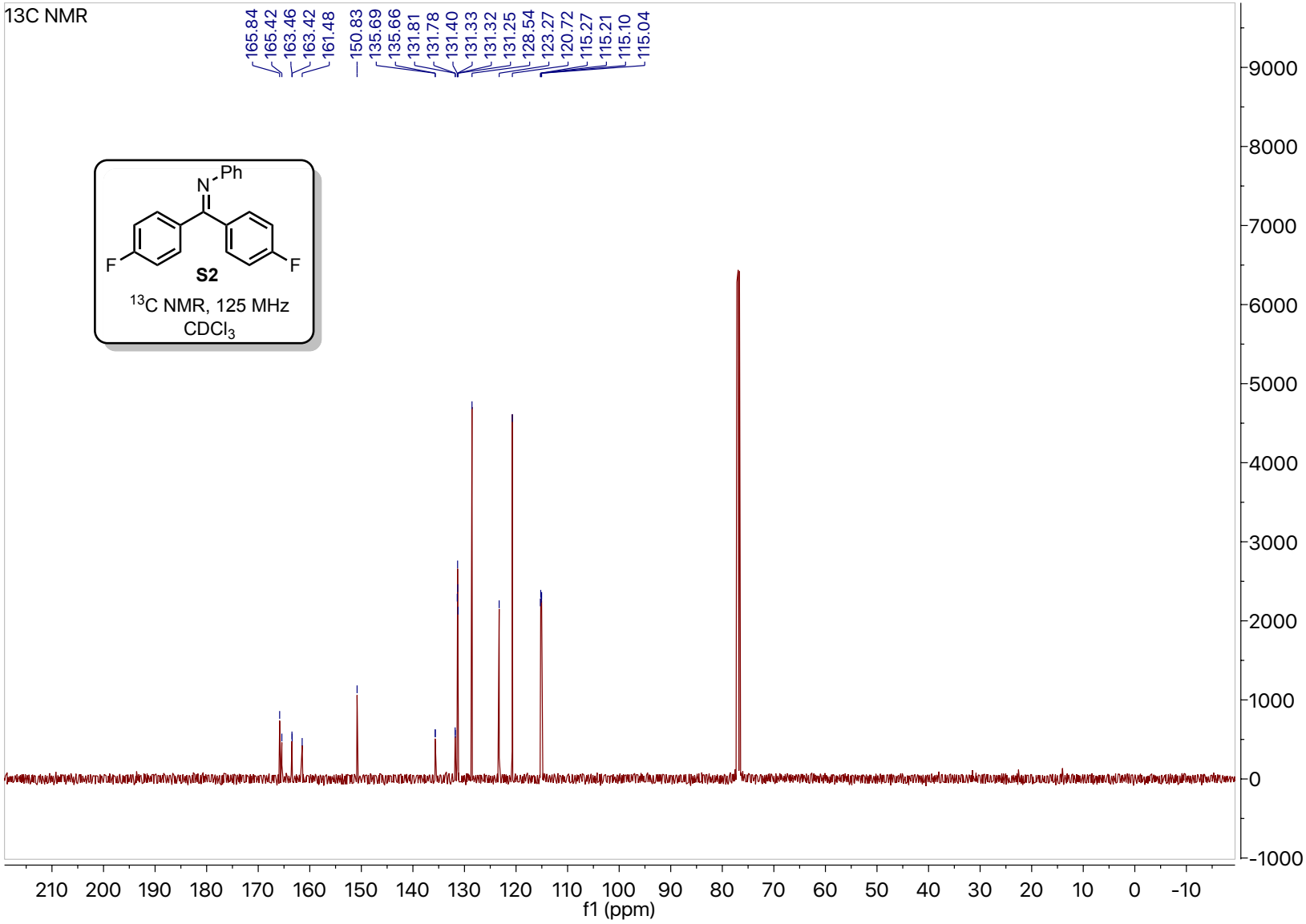
[a] Product inseparable from imine starting material, yield obtained by ^{1}H NMR of the purified product/reagent mix;
[b] Reaction does not occur; [c] Traces of product found; [d] Linear intermediate byproduct observed as major product

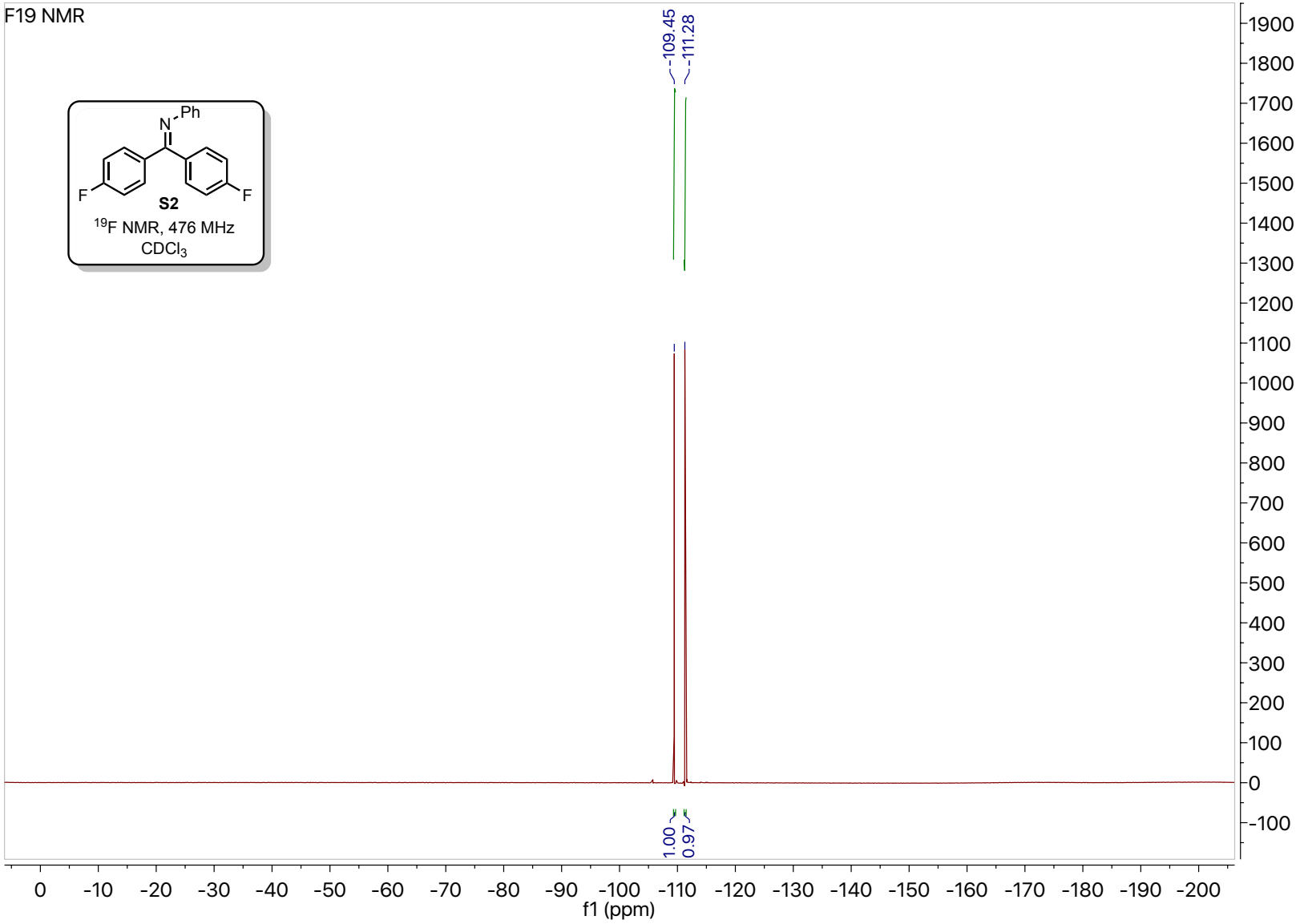
NMR Spectra of Synthesized Compounds

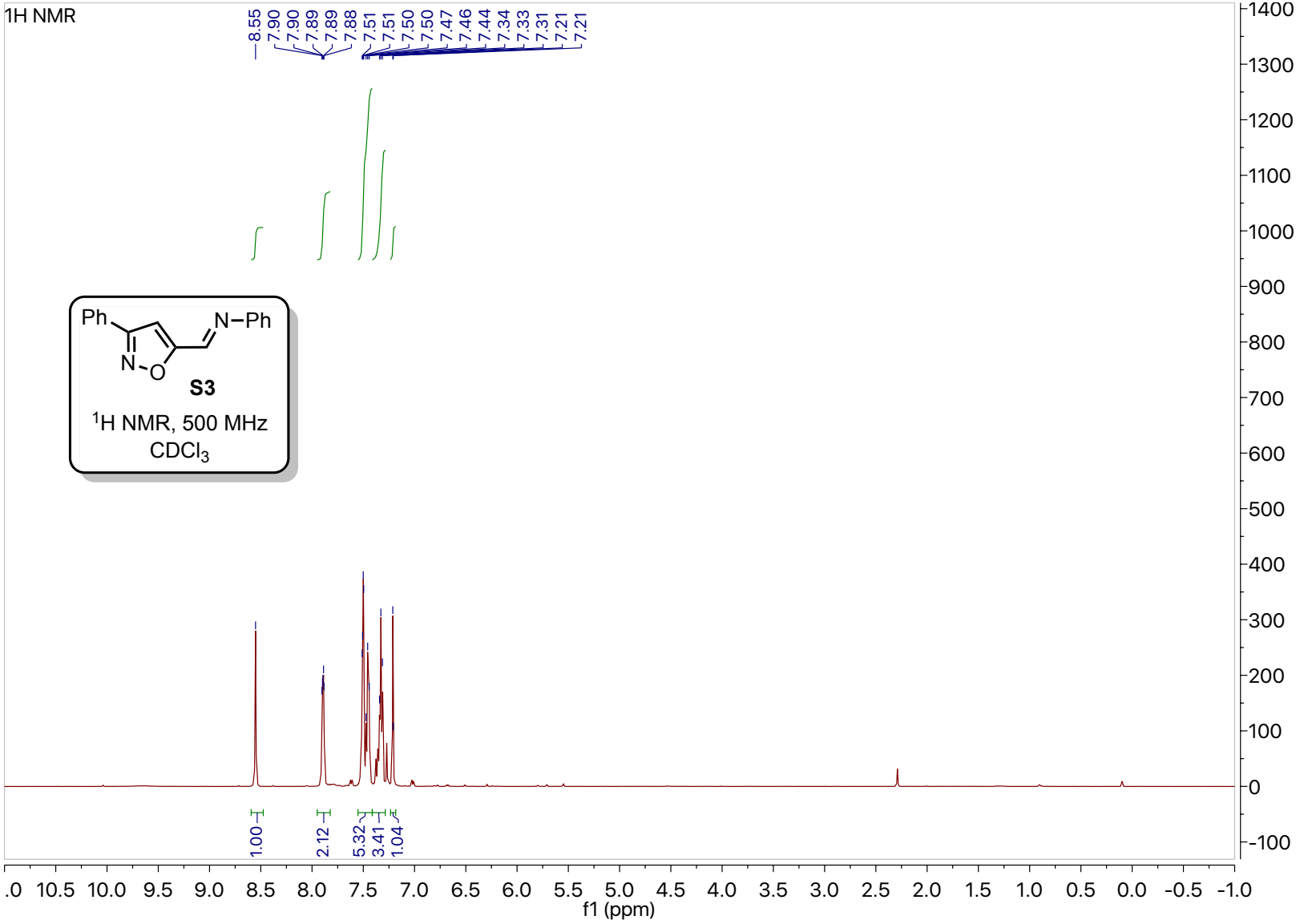


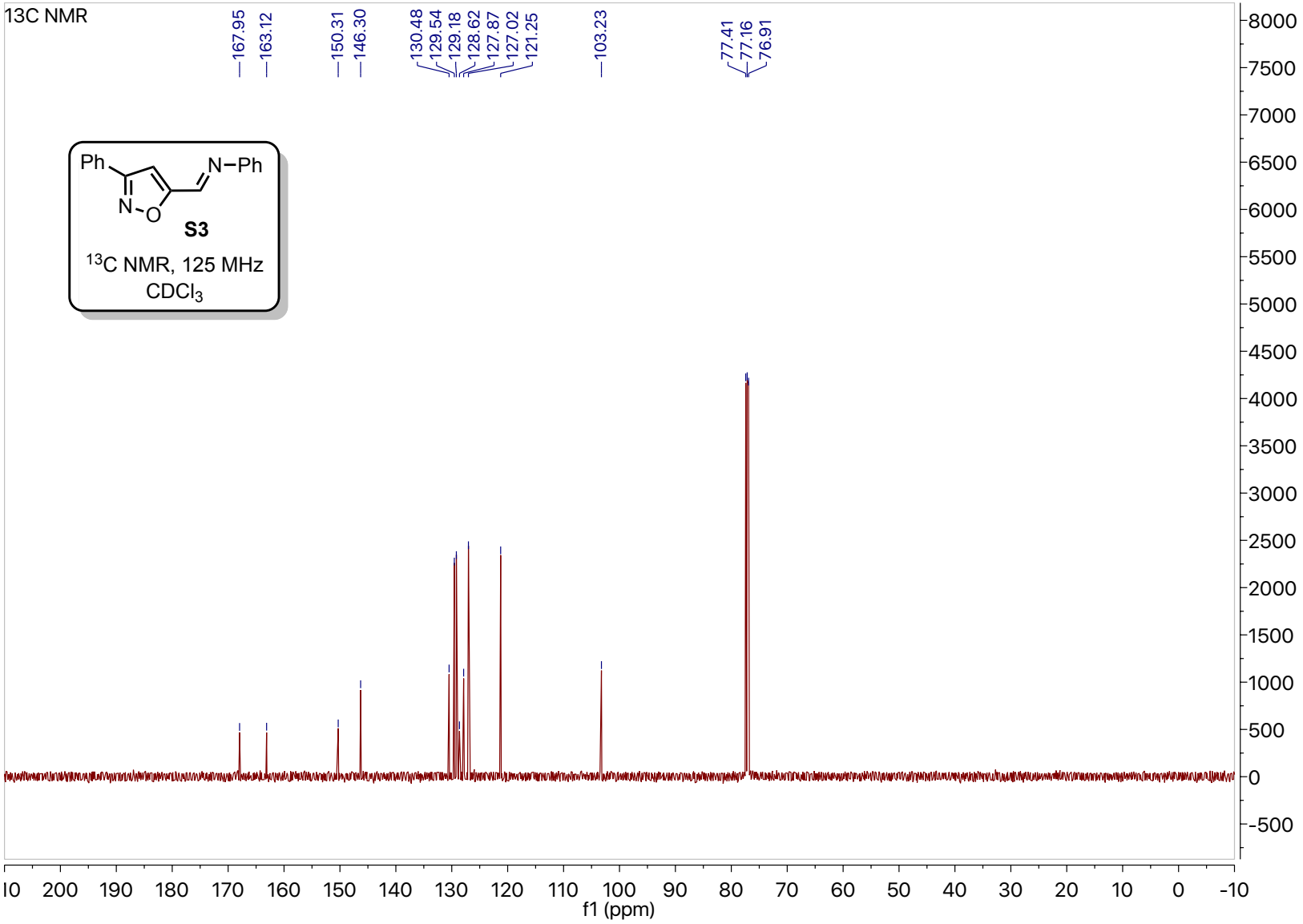

13C NMR
158.63
151.58
138.32
134.29
131.43
130.39
129.35
127.72
126.50
123.20
121.00
77.42
77.16
76.91
Br
N
Ph
S1
13C NMR, 125 MHz
CDCl3
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

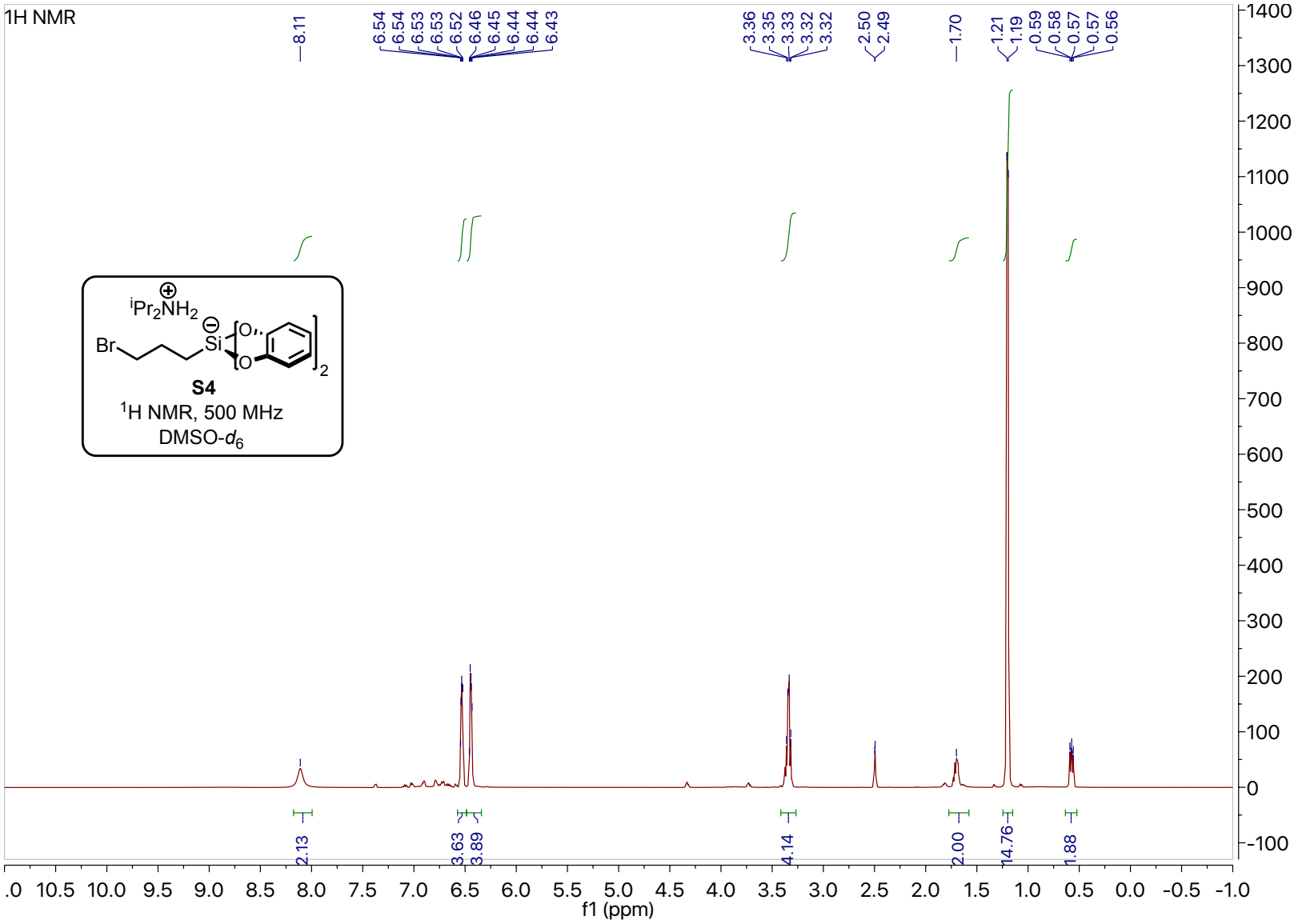

1H NMR
7.76
7.75
7.75
7.74
7.73
7.73
7.26
7.18
7.18
7.17
7.16
7.15
7.15
7.12
7.11
7.11
7.10
7.10
7.10
7.09
7.08
7.08
6.98
6.97
6.97
6.96
6.96
6.96
6.95
6.95
6.95
6.95
6.94
6.94
6.93
6.71
6.70
6.70
6.70
6.69
6.69
6.69
6.68
N
Ph
F
F
S2
1H NMR, 500 MHz
CDCl3
2.00
2.11
4.06
3.06
2.01
f1 (ppm)

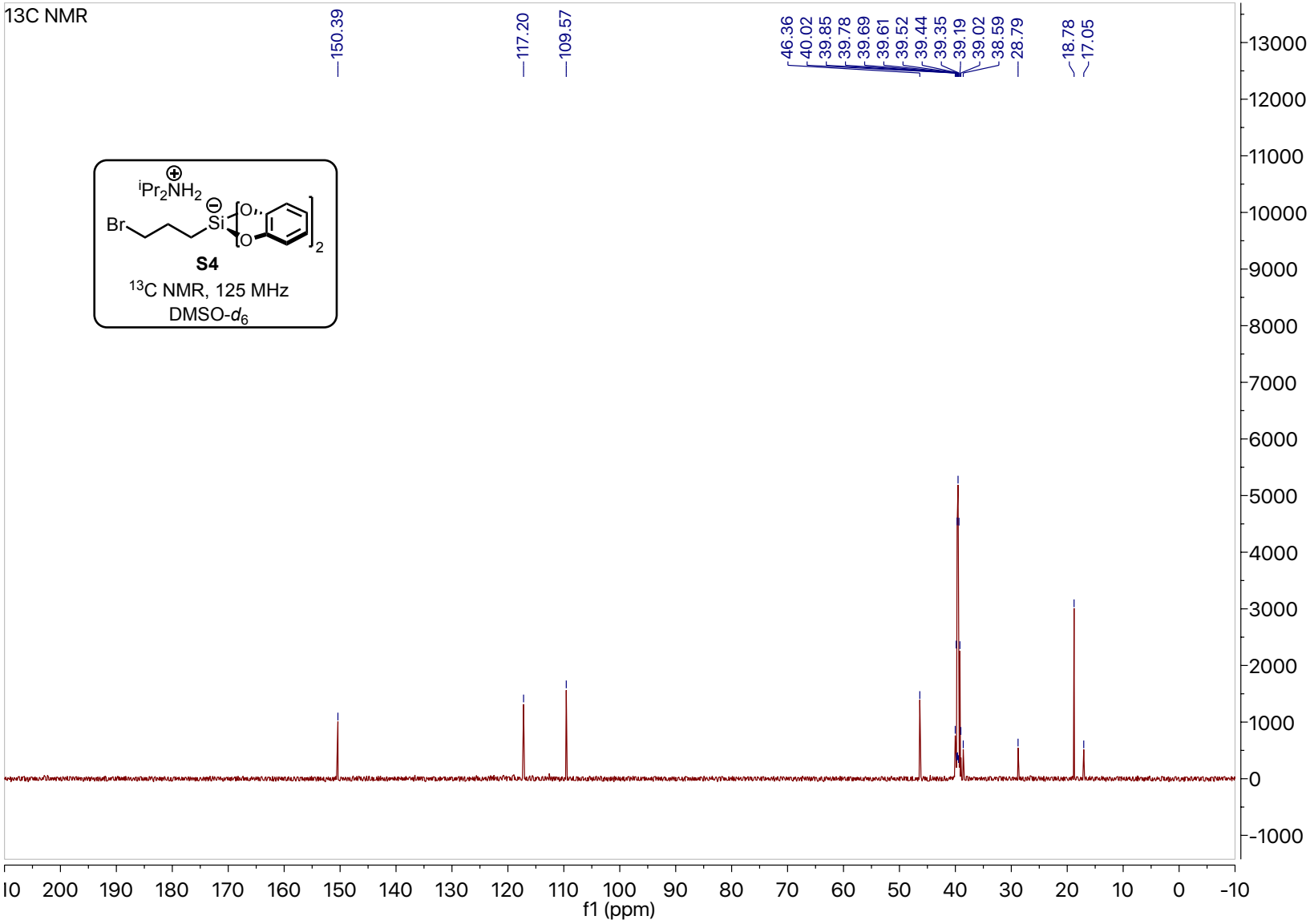

13C NMR
165.84
165.42
163.46
163.42
161.48
150.83
135.69
135.66
131.81
131.78
131.40
131.33
131.32
131.25
128.54
123.27
120.72
115.27
115.21
115.10
115.04
N
Ph
F
F
S2
13C NMR, 125 MHz
CDCl3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

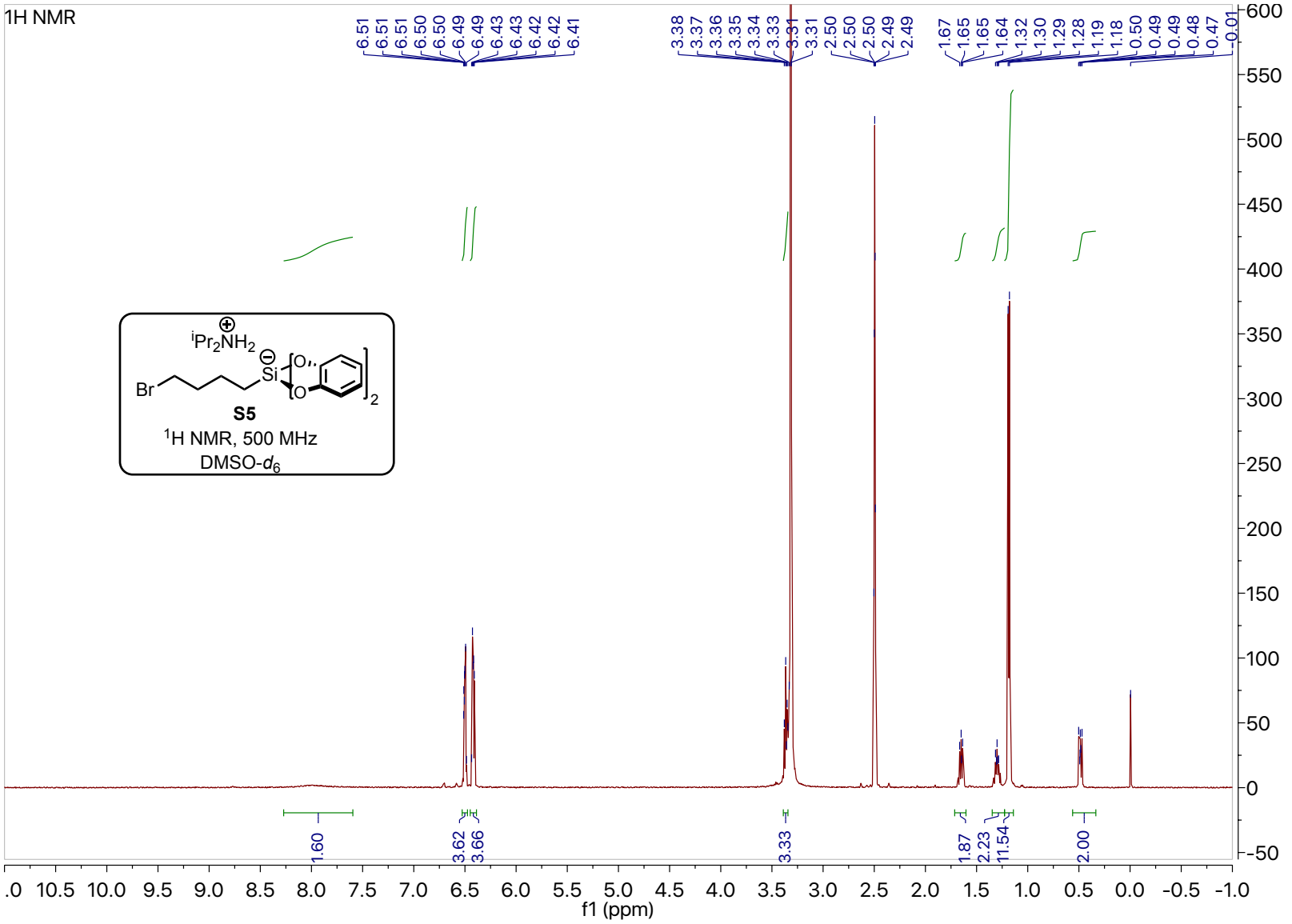

F19 NMR
-109.45
-111.28
N
Ph
F
F
S2
19F NMR, 476 MHz
CDCl3
1.00
0.97
f1 (ppm)

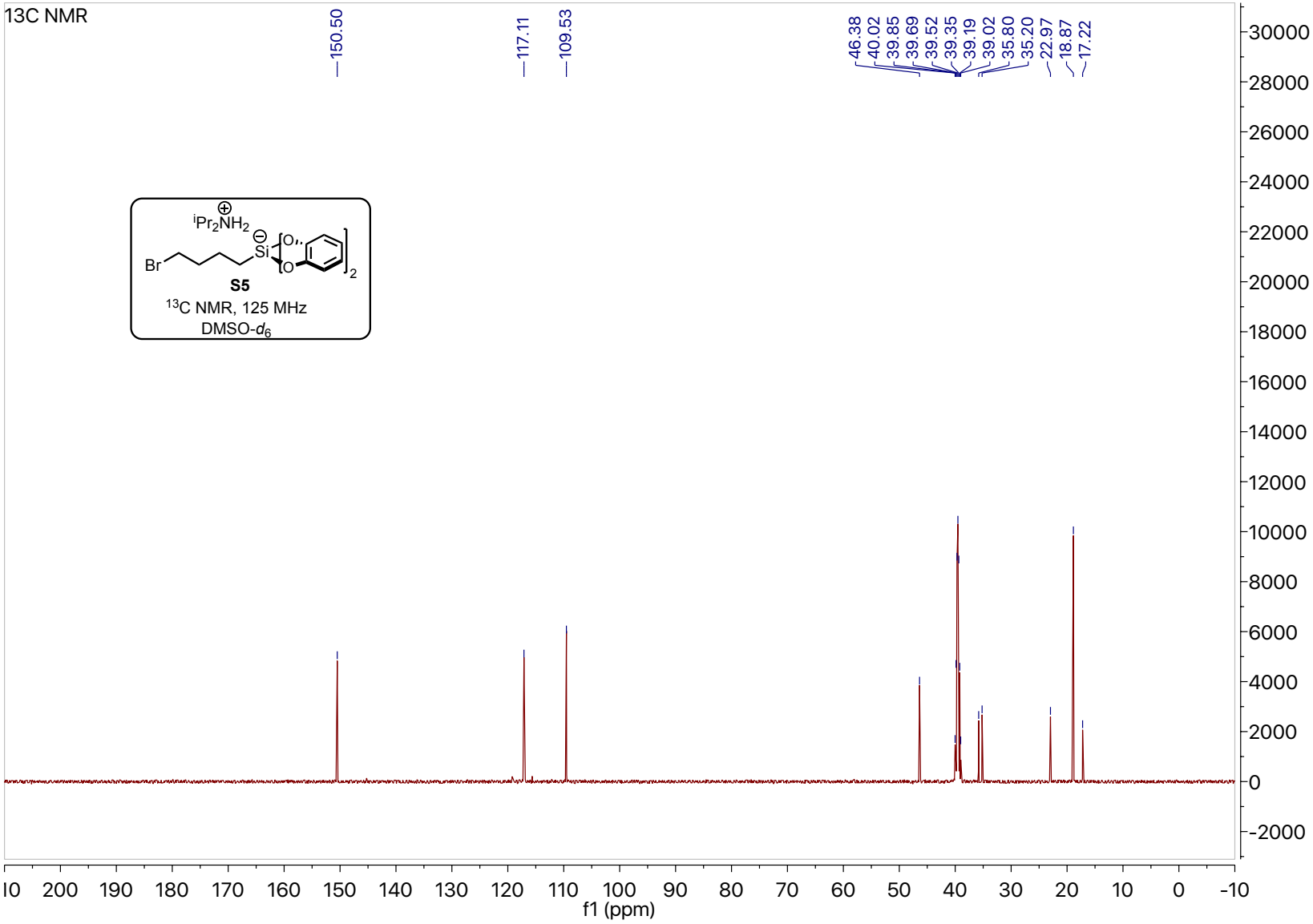

1H NMR
8.55
7.90
7.90
7.89
7.89
7.88
7.51
7.51
7.50
7.50
7.47
7.46
7.44
7.34
7.33
7.31
7.21
7.21
Ph
N–Ph
N
O
S3
1H NMR, 500 MHz
CDCl3
1.00
2.12
5.32
3.41
1.04
f1 (ppm)

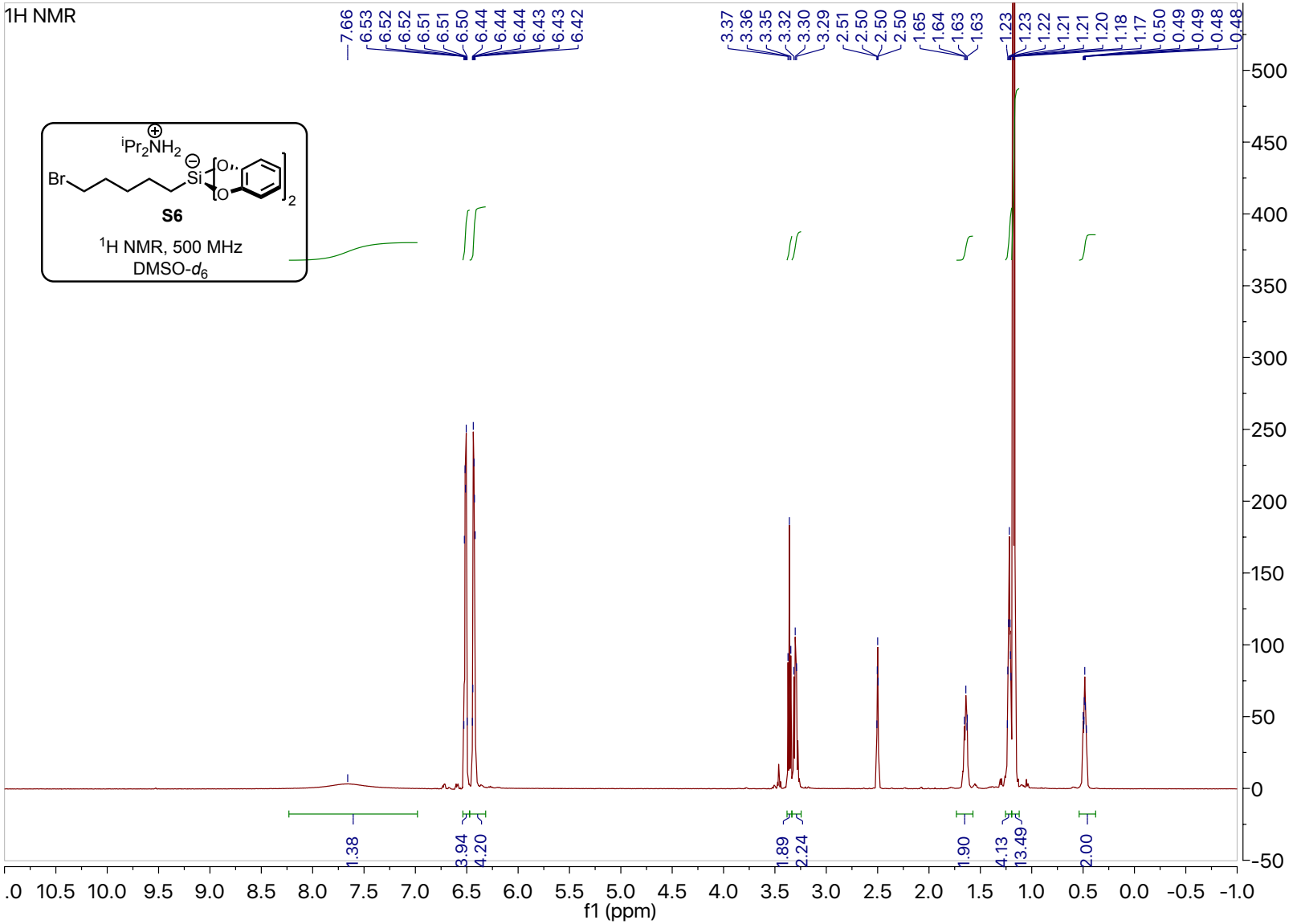

13C NMR
167.95
163.12
150.31
146.30
130.48
129.54
129.18
128.62
127.87
127.02
121.25
103.23
77.41
77.16
76.91
Ph
N–Ph
N
O
S3
13C NMR, 125 MHz
CDCl3
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
f1 (ppm)

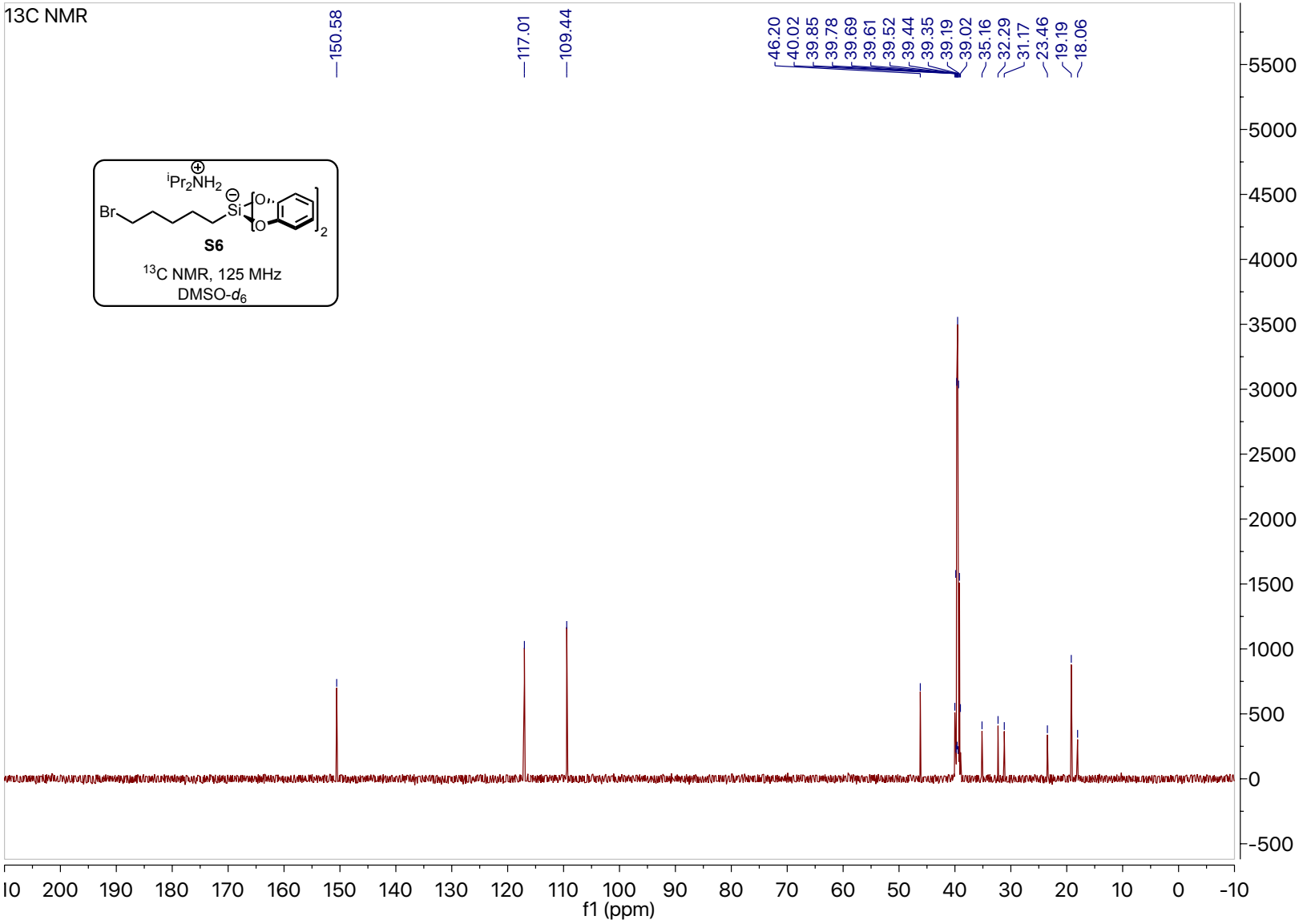

1H NMR
8.11
6.54
6.54
6.53
6.53
6.52
6.46
6.45
6.44
6.44
6.43
3.36
3.35
3.33
3.32
3.32
2.50
2.49
1.70
1.21
1.19
0.59
0.58
0.57
0.57
0.56
iPr2NH2
Br
Si
O
O
2
S4
1H NMR, 500 MHz
DMSO-d6
2.13
3.63
3.89
4.14
2.00
14.76
1.88
f1 (ppm)

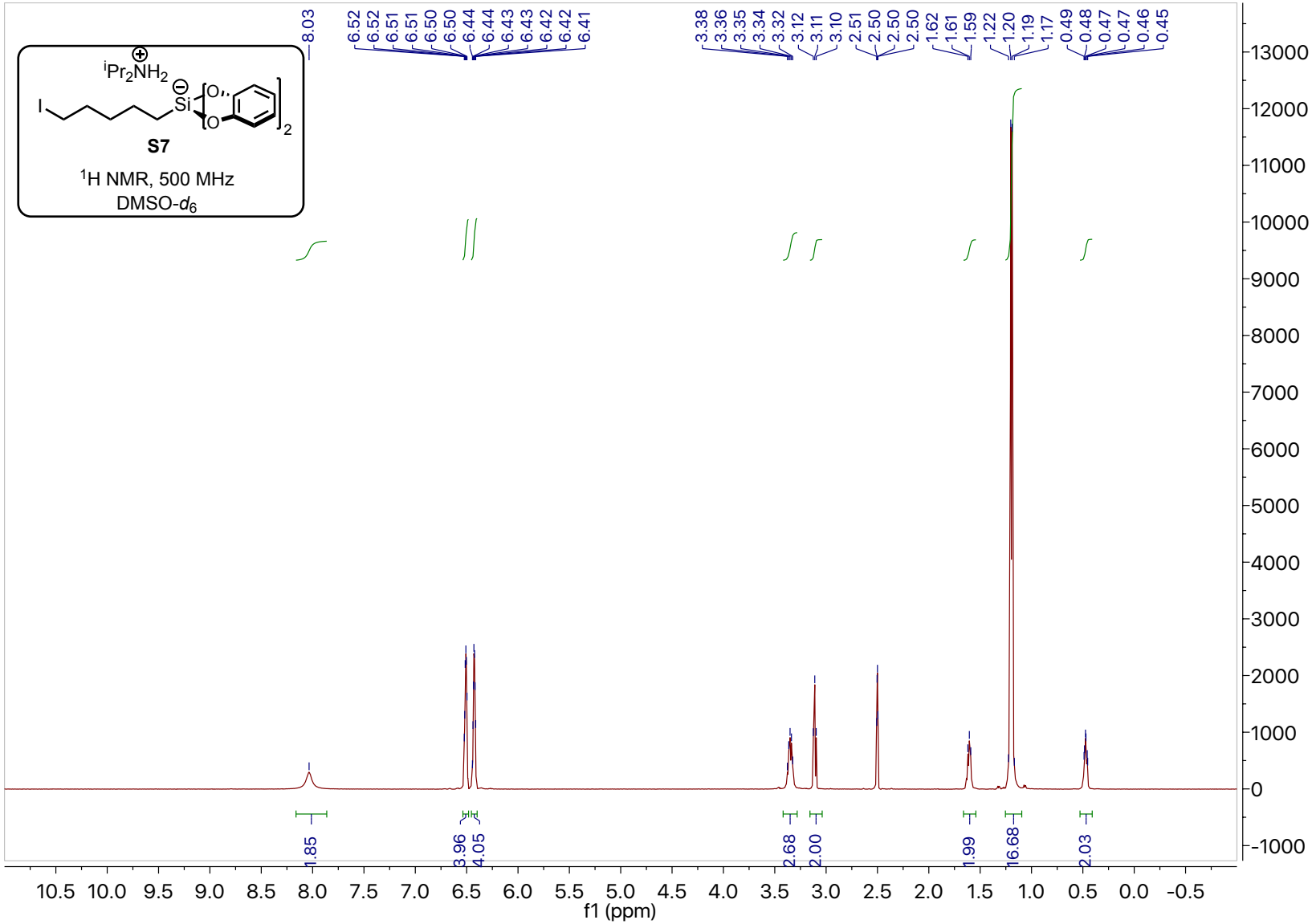

13C NMR
150.39
117.20
109.57
46.36
40.02
39.85
39.78
39.69
39.61
39.52
39.44
39.35
39.19
39.02
38.59
28.79
18.78
17.05
iPr2NH2
Br
Si
O
O
2
S4
13C NMR, 125 MHz
DMSO-d6
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
f1 (ppm)

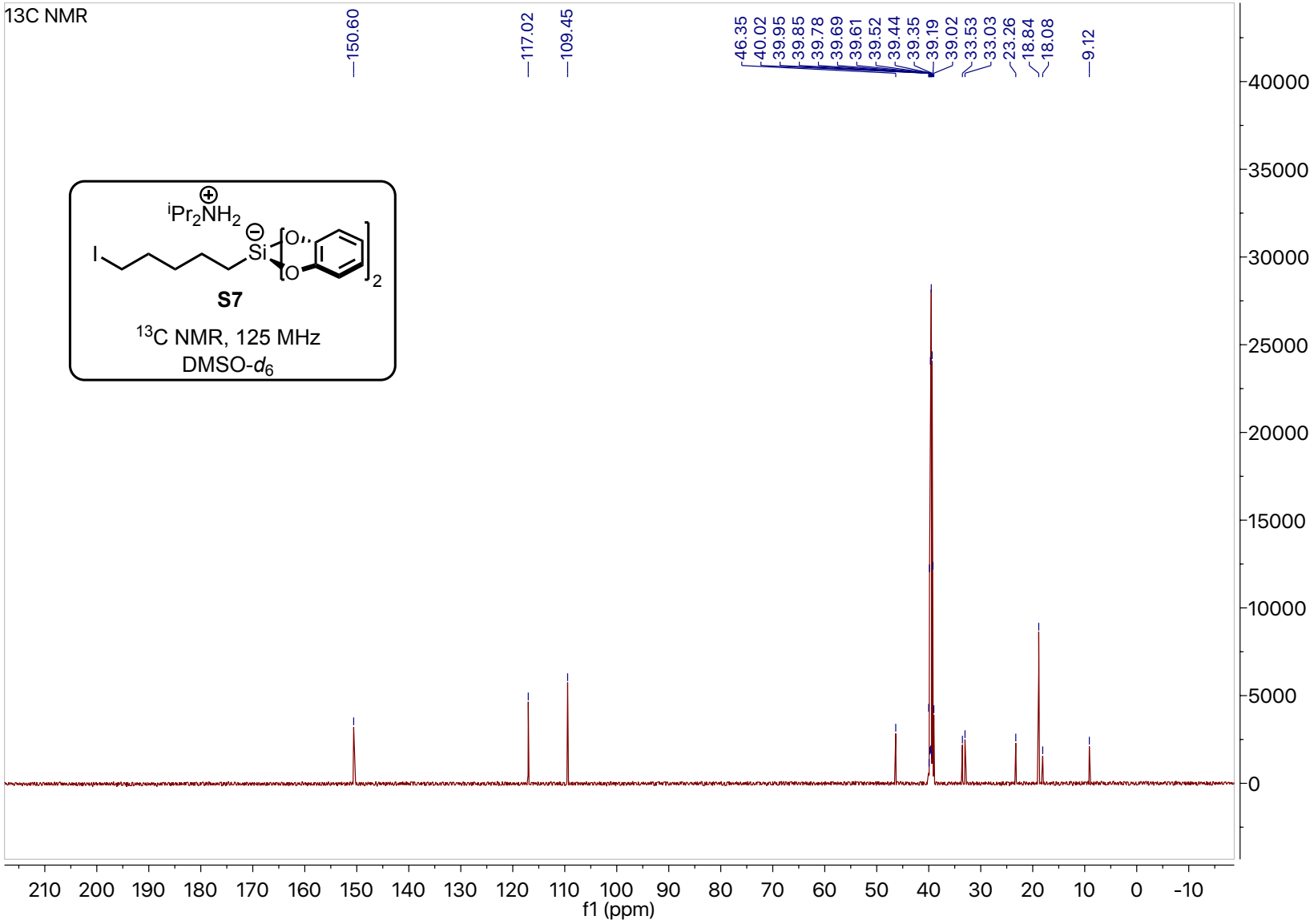

1H NMR
6.51 6.51 6.51 6.50 6.50 6.49 6.49 6.43 6.43 6.42 6.42 6.41
3.38 3.37 3.36 3.35 3.34 3.33 3.31 3.31 2.50 2.50 2.50 2.49 2.49
1.67 1.65 1.65 1.64 1.32 1.30 1.29 1.28 1.19 1.18 0.50 0.49 0.49 0.48 0.47 0.01
iPr2NH2
Br
Si
O
O
2
S5
1H NMR, 500 MHz
DMSO-d6
1.60
3.62
3.66
3.33
1.87
2.23
11.54
2.00
f1 (ppm)

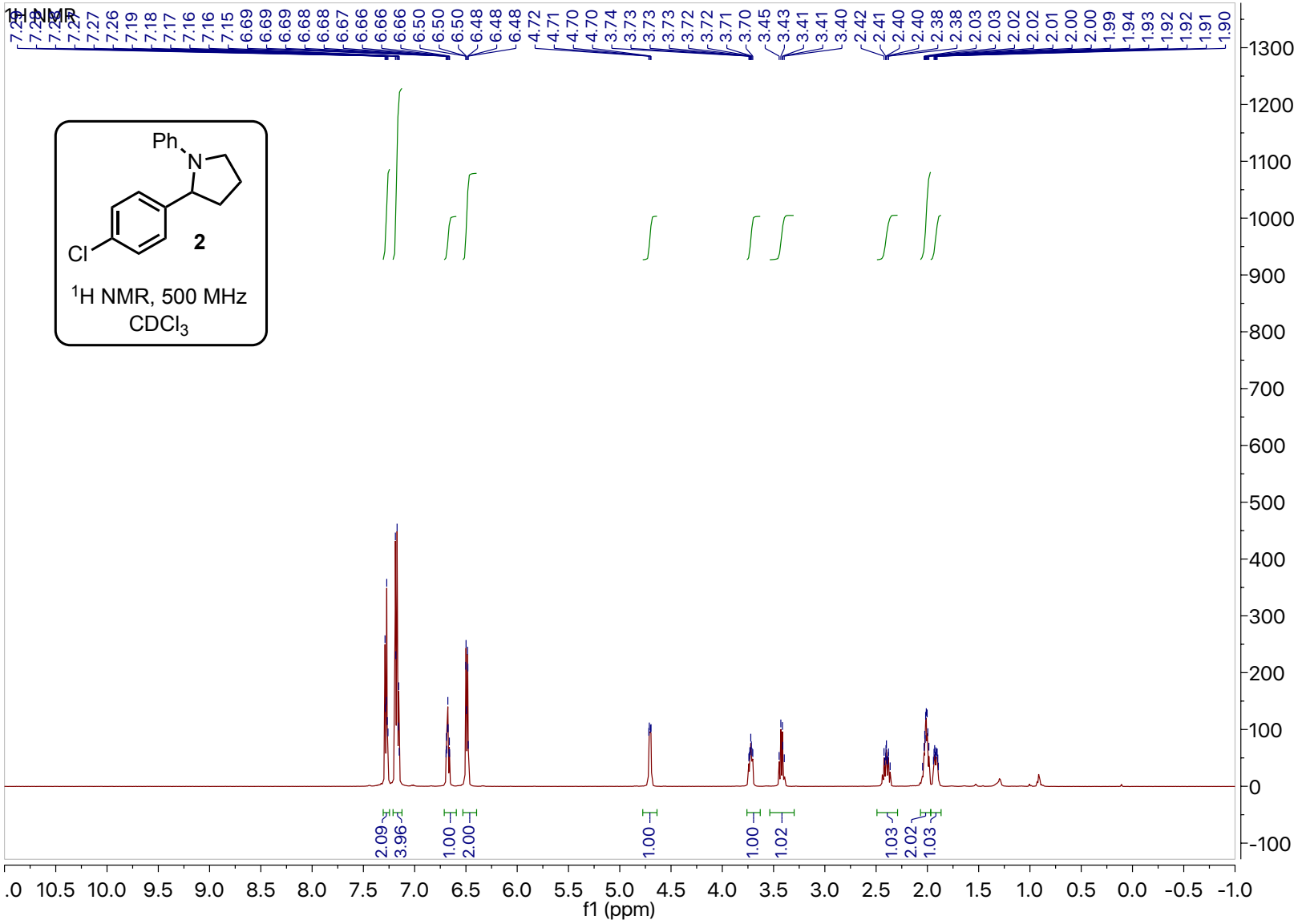

13C NMR
150.50
117.11
109.53
46.38
40.02
39.85
39.69
39.52
39.35
39.19
39.02
35.80
35.20
22.97
18.87
17.22
$^{i}Pr_2NH_2$
Br
Si
O
O
2
S5
^{13}C NMR, 125 MHz
DMSO-d_6
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

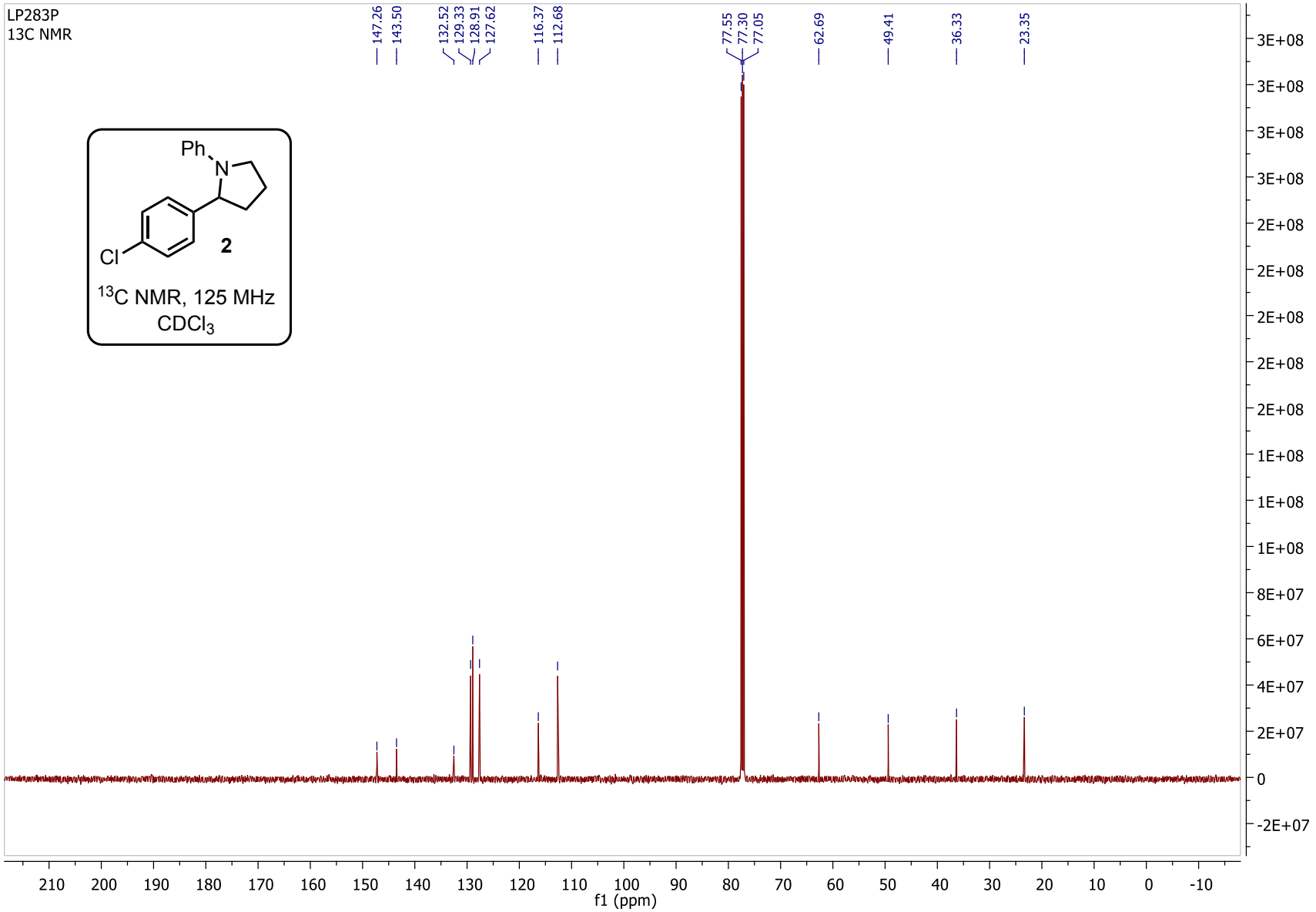

1H NMR
S6
1H NMR, 500 MHz
DMSO-d6
f1 (ppm)

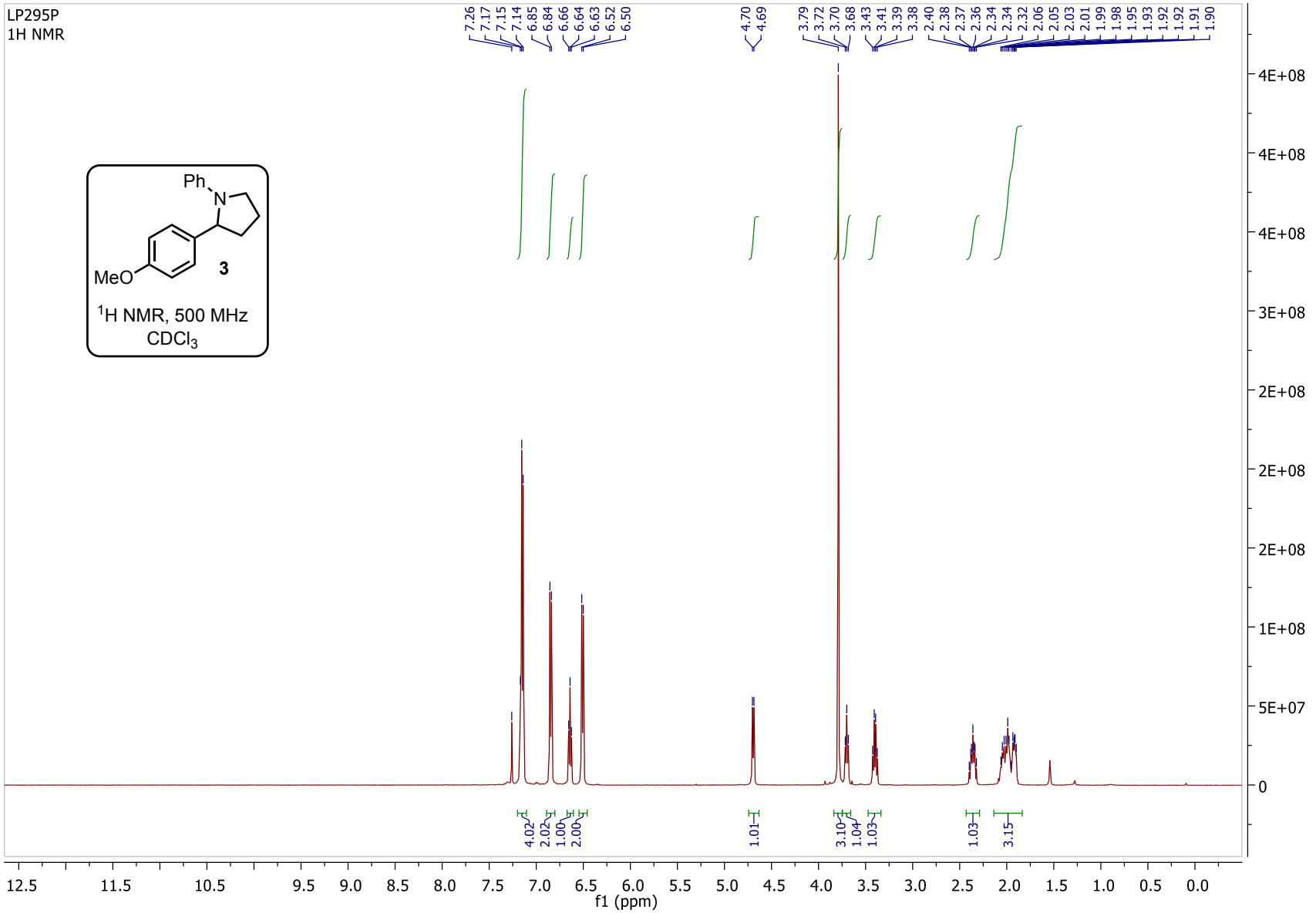

13C NMR
150.58
117.01
109.44
46.20
40.02
39.85
39.78
39.69
39.61
39.52
39.44
39.35
39.19
39.02
35.16
32.29
31.17
23.46
19.19
18.06
S6
13C NMR, 125 MHz
DMSO-d6
f1 (ppm)

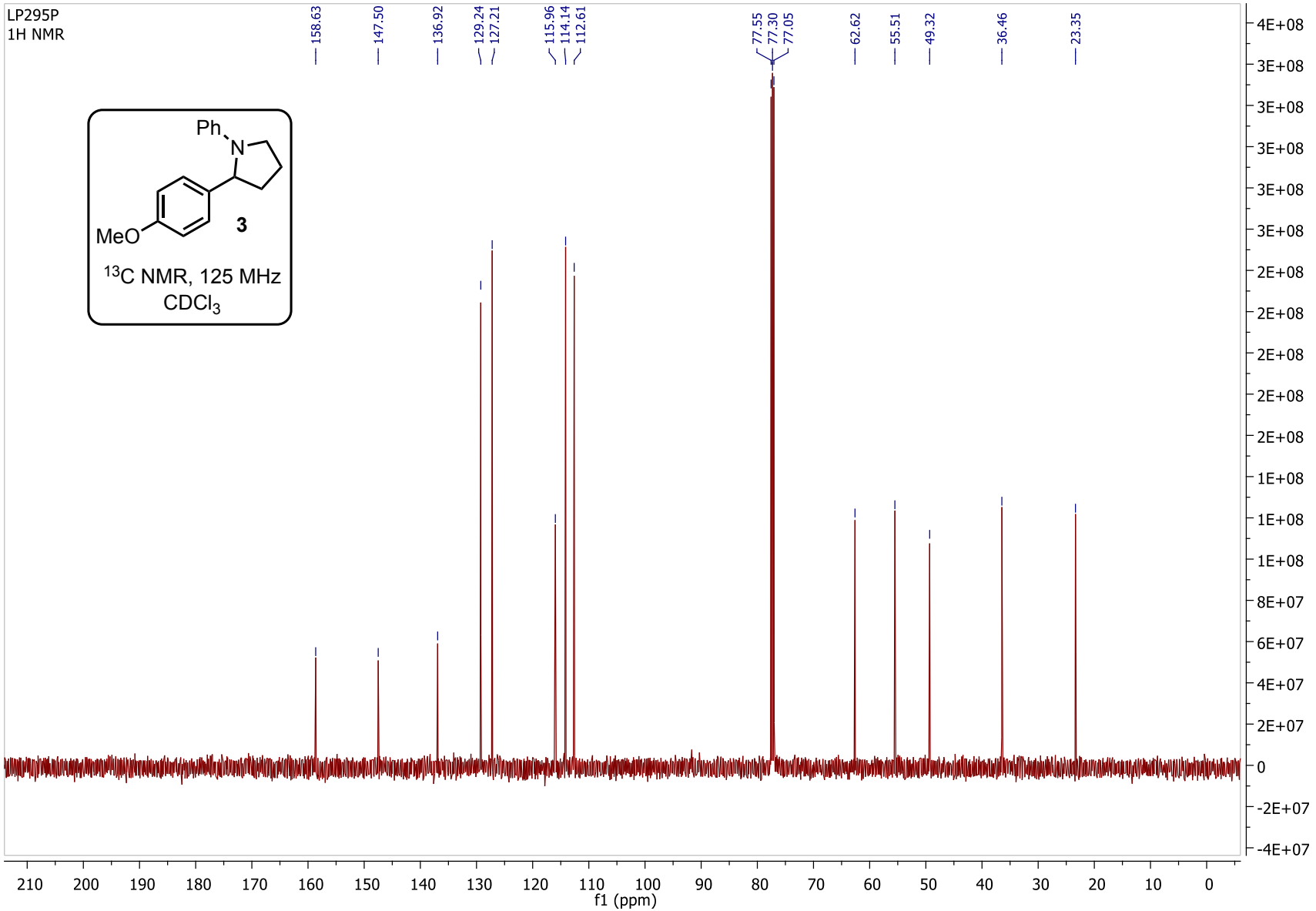

S7
1H NMR, 500 MHz
DMSO-d6
f1 (ppm)

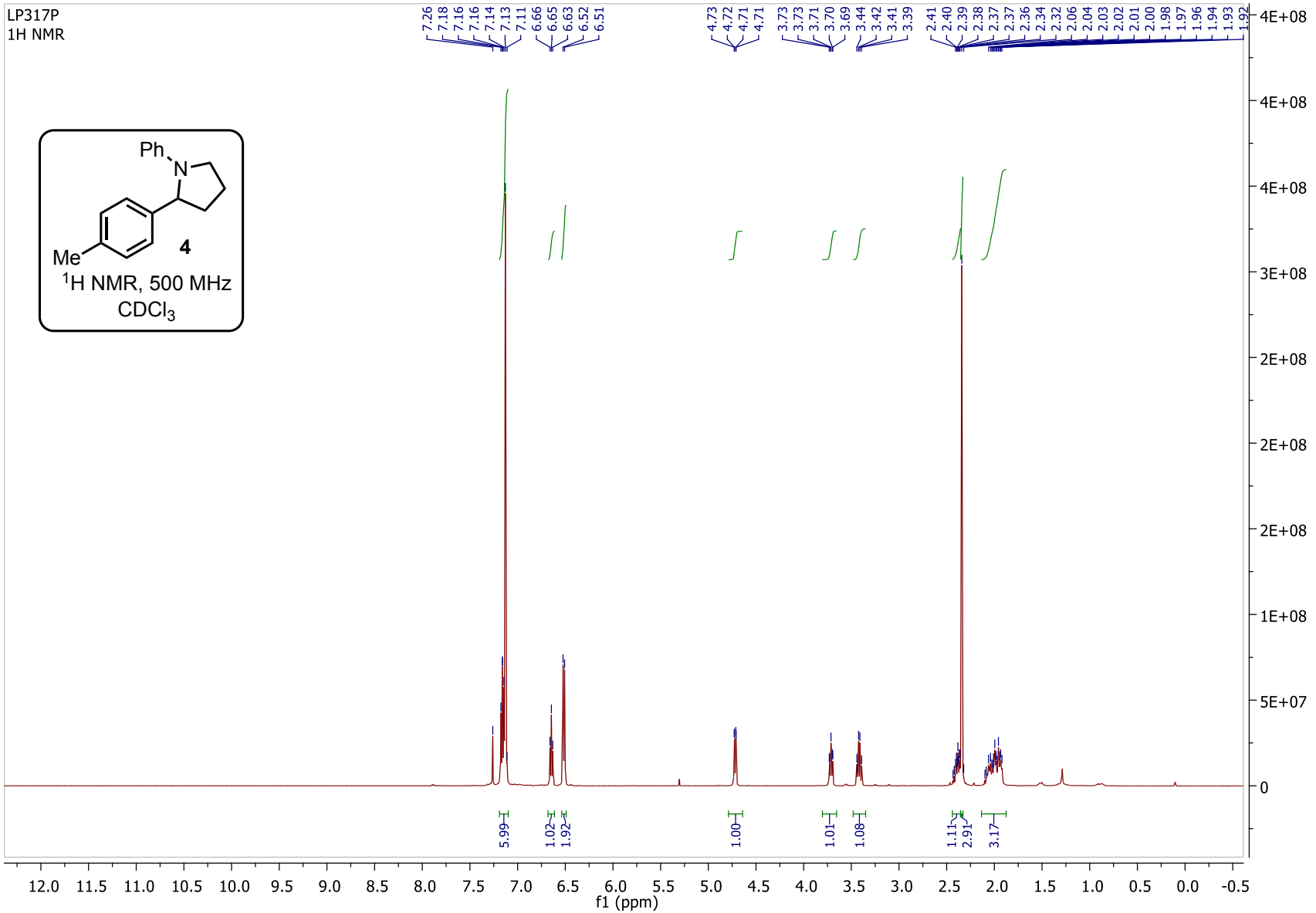

13C NMR
150.60
117.02
109.45
46.35
40.02
39.95
39.85
39.78
39.69
39.61
39.52
39.44
39.35
39.19
39.02
33.53
33.03
23.26
18.84
18.08
9.12
S7
13C NMR, 125 MHz
DMSO-d6
f1 (ppm)

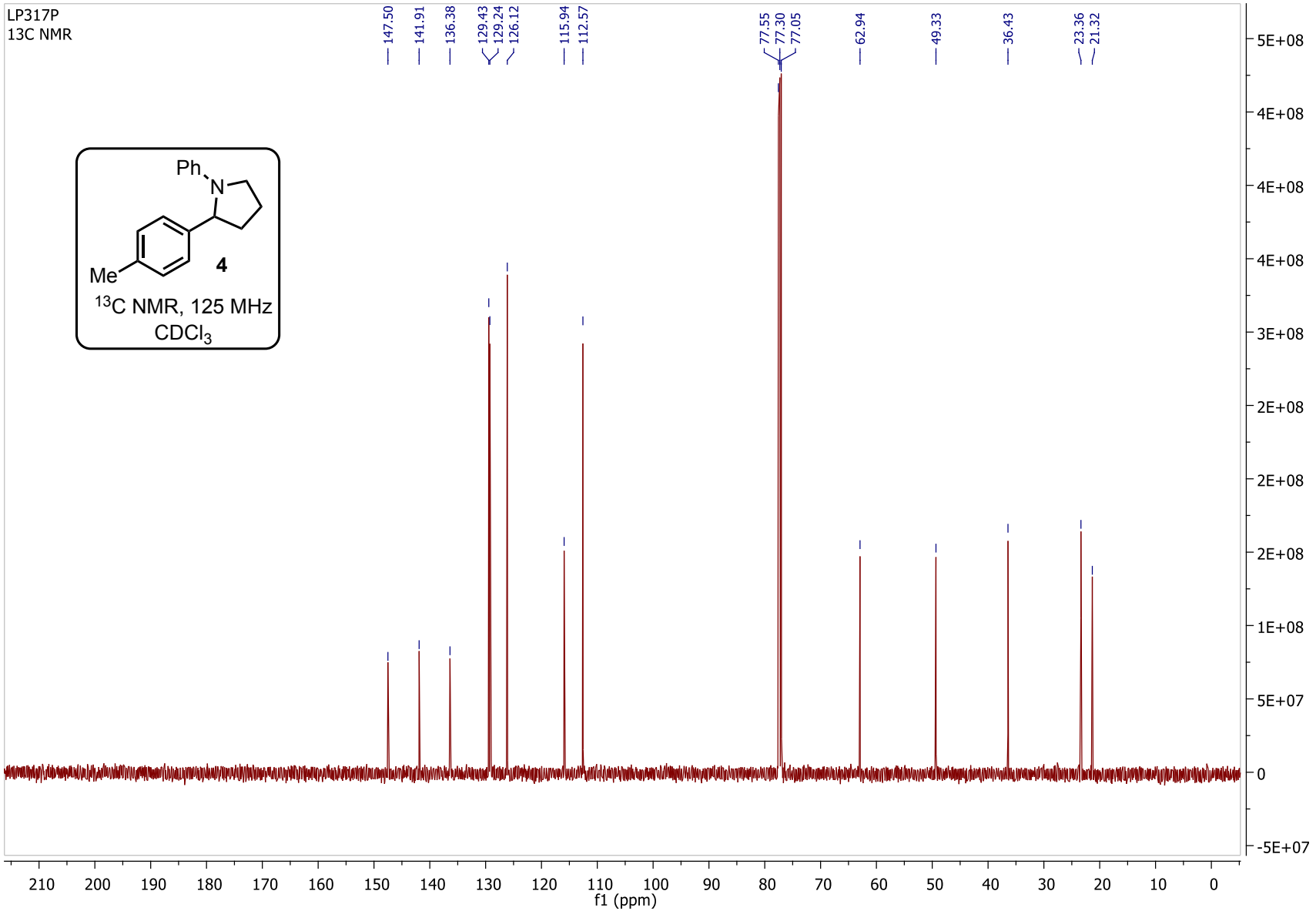

1H NMR
Ph
N
Cl
2
1H NMR, 500 MHz
CDCl3
f1 (ppm)

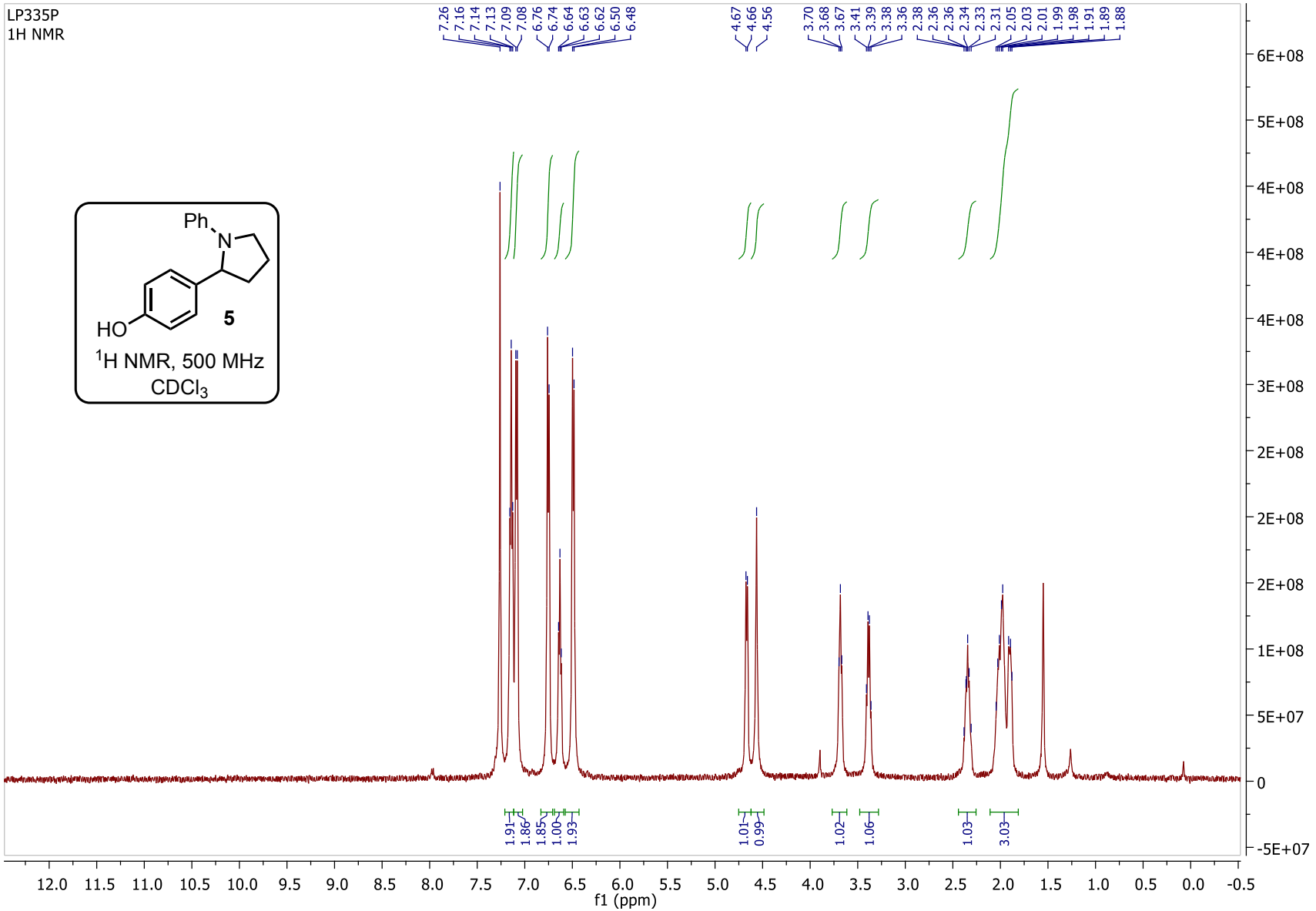

LP283P
13C NMR
147.26
143.50
132.52
129.33
128.91
127.62
116.37
112.68
77.55
77.30
77.05
62.69
49.41
36.33
23.35
Ph
N
Cl
2
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

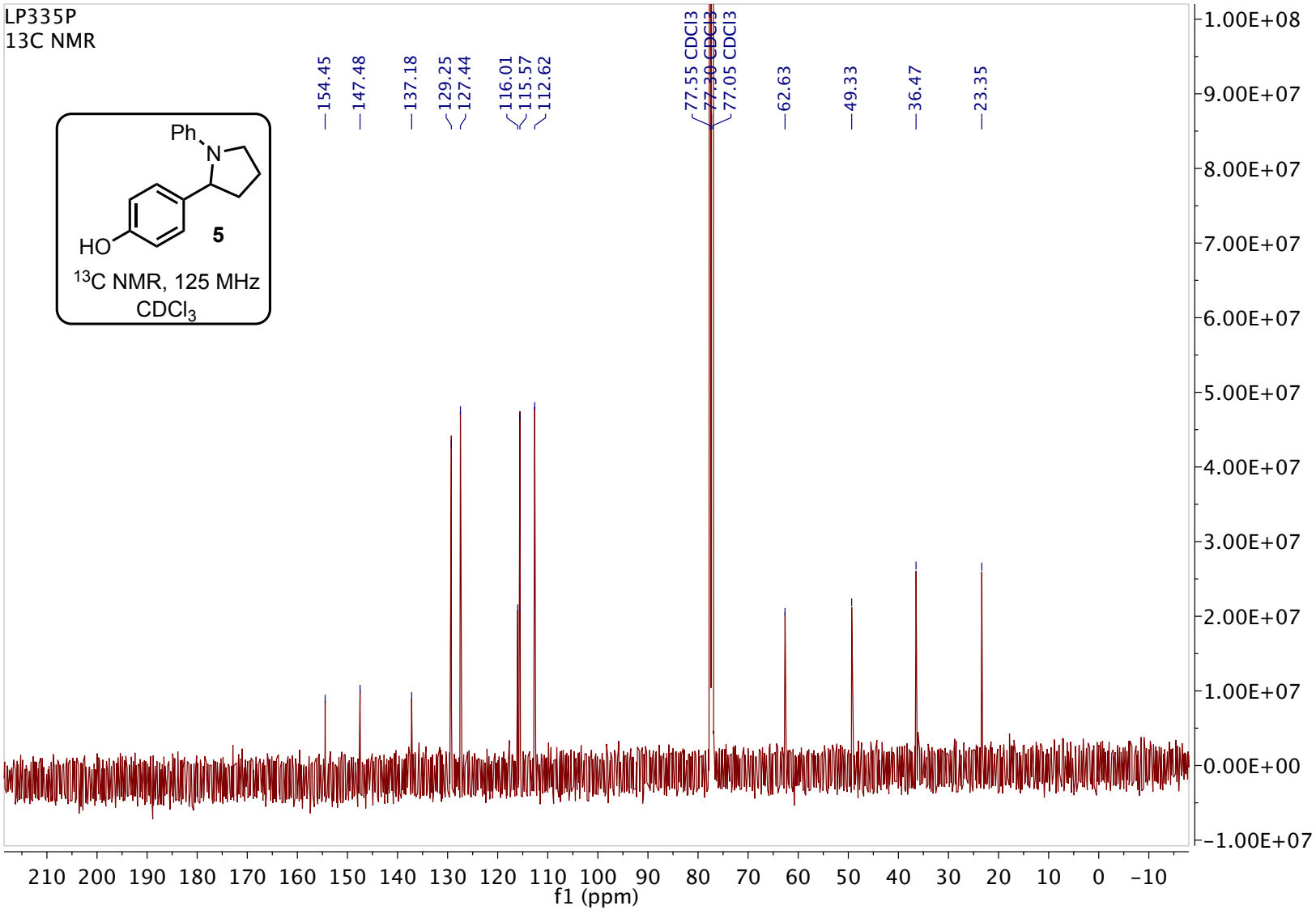

LP295P
1H NMR
Ph
N
MeO
3
1H NMR, 500 MHz
CDCl3
7.26 7.17 7.15 7.14 6.85 6.84 6.66 6.64 6.63 6.52 6.50
4.70 4.69
3.79 3.72 3.70 3.68 3.43 3.41 3.39 3.38
2.40 2.38 2.37 2.36 2.34 2.34 2.32 2.06 2.05 2.03 2.01 1.99 1.98 1.95 1.93 1.92 1.92 1.91 1.90
4.02 2.02 1.00 2.00 1.01 3.10 1.04 1.03 1.03 3.15
4E+08 4E+08 4E+08 3E+08 2E+08 2E+08 2E+08 1E+08 5E+07 0
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

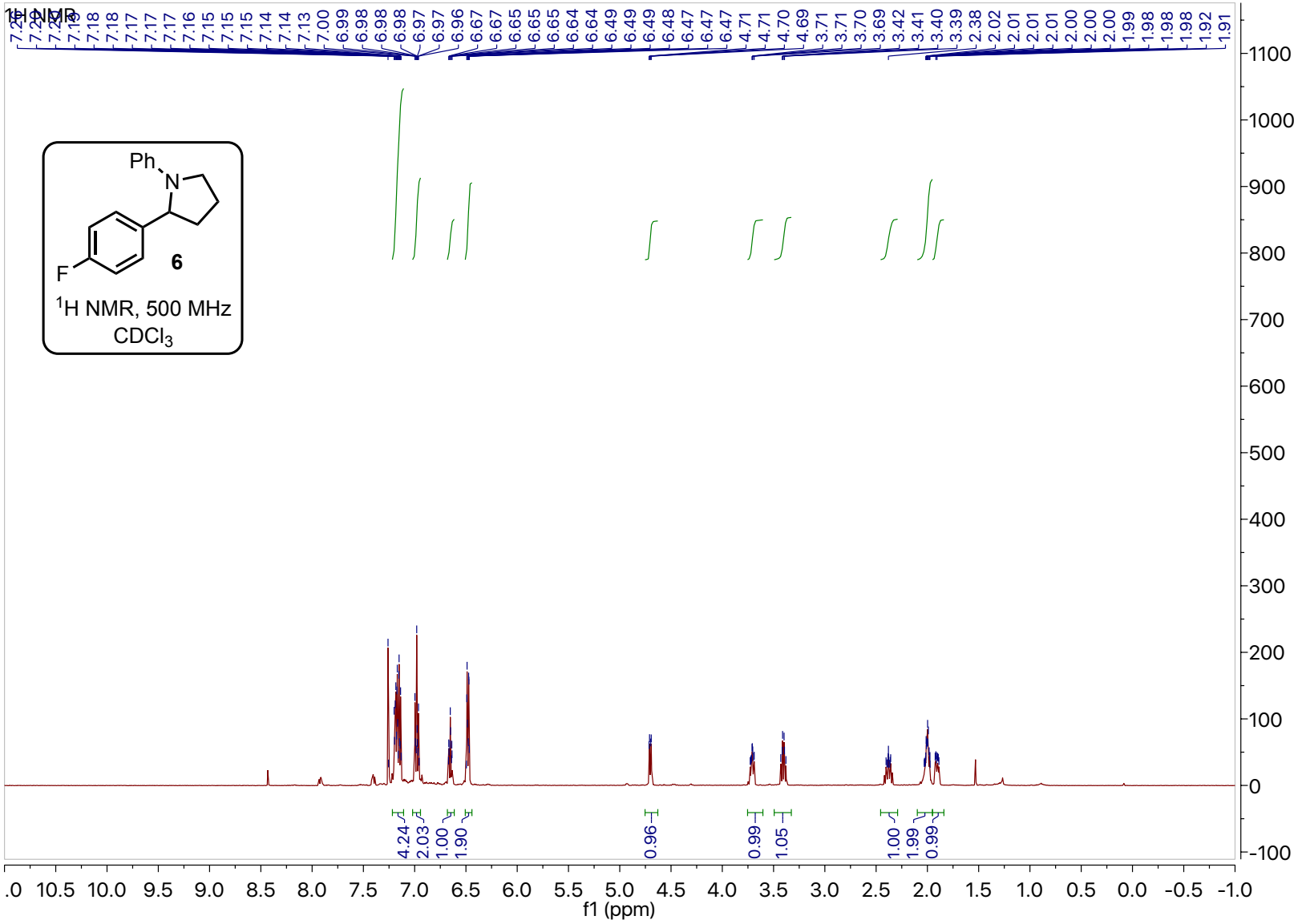

LP295P
1H NMR
158.63
147.50
136.92
129.24
127.21
115.96
114.14
112.61
77.55
77.30
77.05
62.62
55.51
49.32
36.46
23.35
Ph
N
MeO
3
13C NMR, 125 MHz
CDCl3
4E+08
3E+08
3E+08
3E+08
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
-4E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

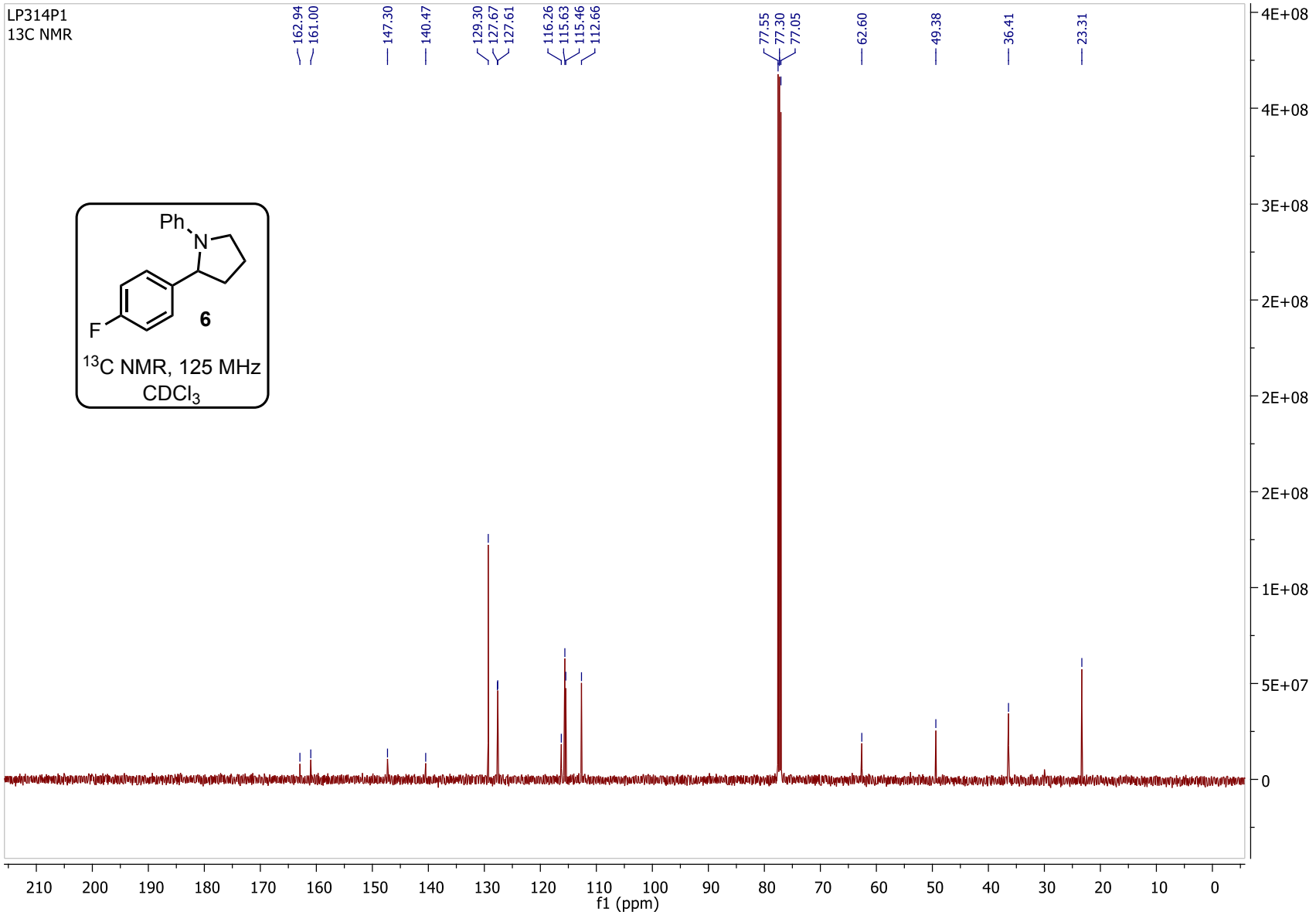

LP317P
1H NMR
Ph
N
Me
4
1H NMR, 500 MHz
CDCl3
7.26 7.18 7.16 7.16 7.14 7.13 7.11 6.66 6.65 6.63 6.52 6.51
4.73 4.72 4.71 4.71 3.73 3.73 3.71 3.70 3.69 3.44 3.42 3.41 3.39
2.41 2.40 2.39 2.38 2.37 2.37 2.36 2.34 2.32 2.06 2.04 2.03 2.02 2.01 2.00 1.98 1.97 1.96 1.94 1.93 1.92
5.99 1.02 1.92 1.00 1.01 1.08 1.11 2.91 3.17
f1 (ppm)

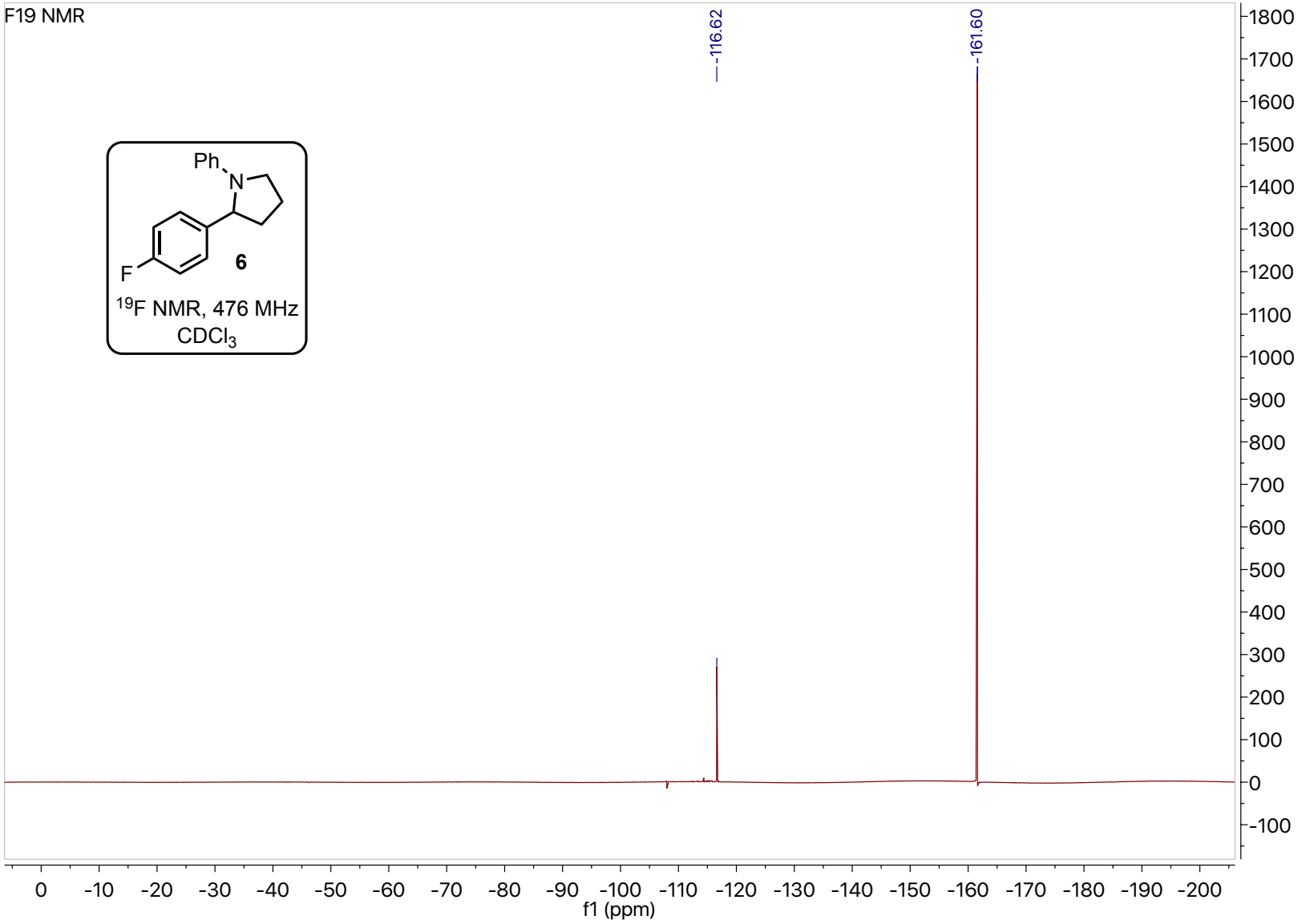

LP317P
13C NMR
147.50
141.91
136.38
129.43
129.24
126.12
115.94
112.57
77.55
77.30
77.05
62.94
49.33
36.43
23.36
21.32
Ph
N
Me
4
13C NMR, 125 MHz
CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

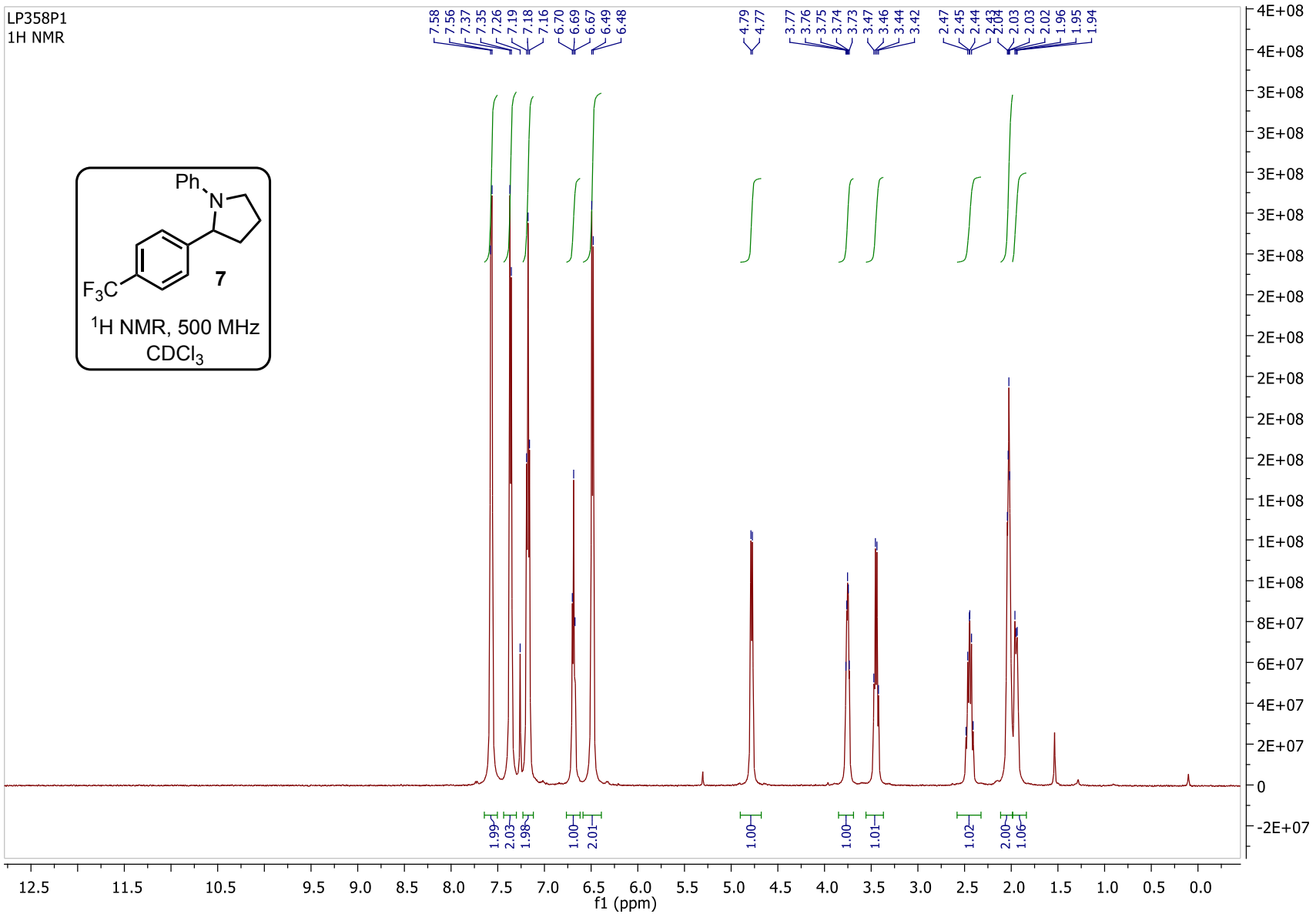

LP335P
1H NMR
7.26
7.16
7.14
7.13
7.09
7.08
6.76
6.74
6.64
6.63
6.62
6.50
6.48
4.67
4.66
4.56
3.70
3.68
3.67
3.41
3.39
3.38
3.36
2.38
2.36
2.36
2.34
2.33
2.31
2.05
2.03
2.01
1.99
1.98
1.91
1.89
1.88
Ph
N
HO
5
1H NMR, 500 MHz
CDCl3
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
1.91
1.86
1.85
1.00
1.93
1.01
0.99
1.02
1.06
1.03
3.03
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

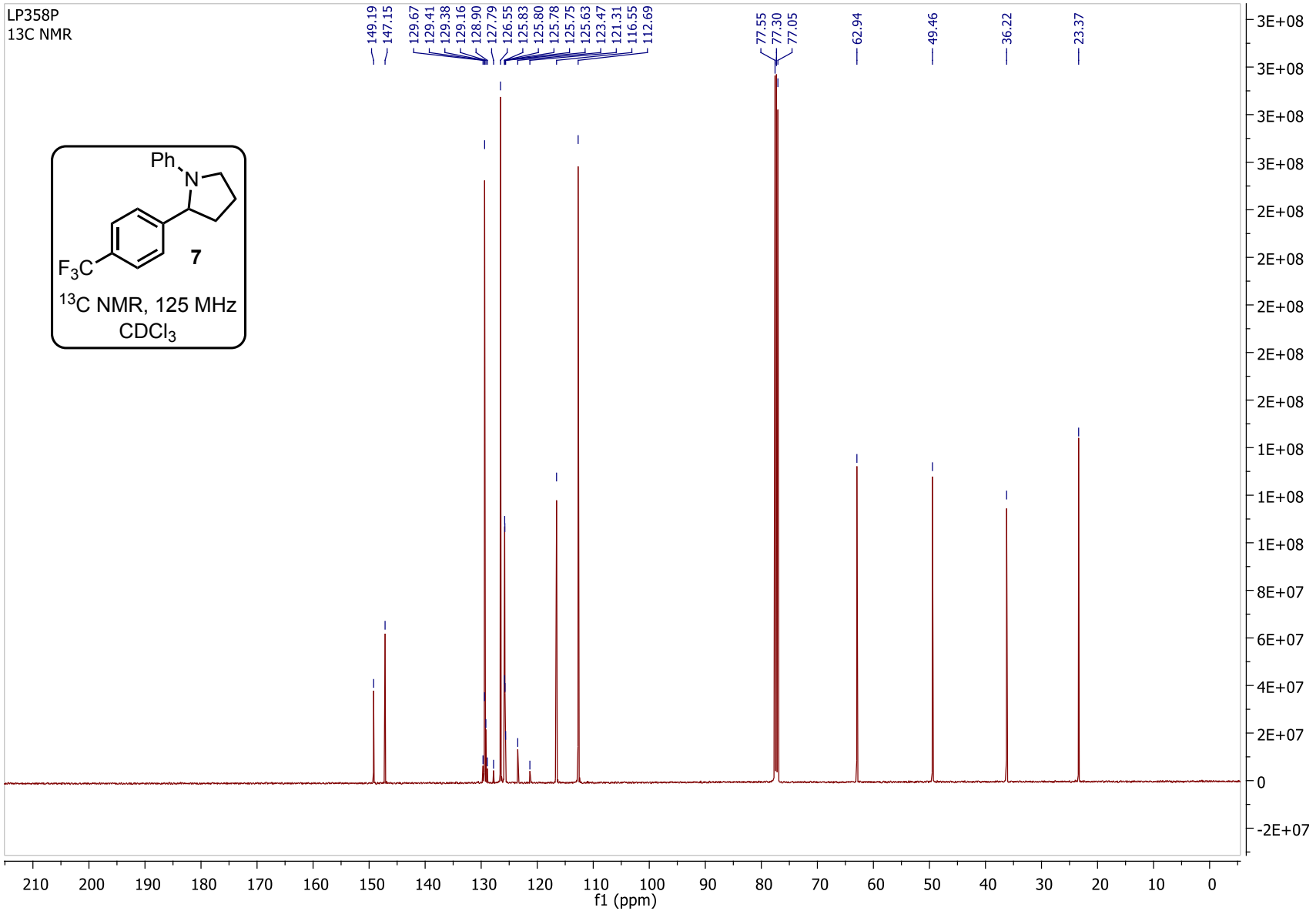

LP335P
13C NMR
154.45
147.48
137.18
129.25
127.44
116.01
115.57
112.62
77.55 CDCl3
77.30 CDCl3
77.05 CDCl3
62.63
49.33
36.47
23.35
Ph
N
HO
5
13C NMR, 125 MHz
CDCl3
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

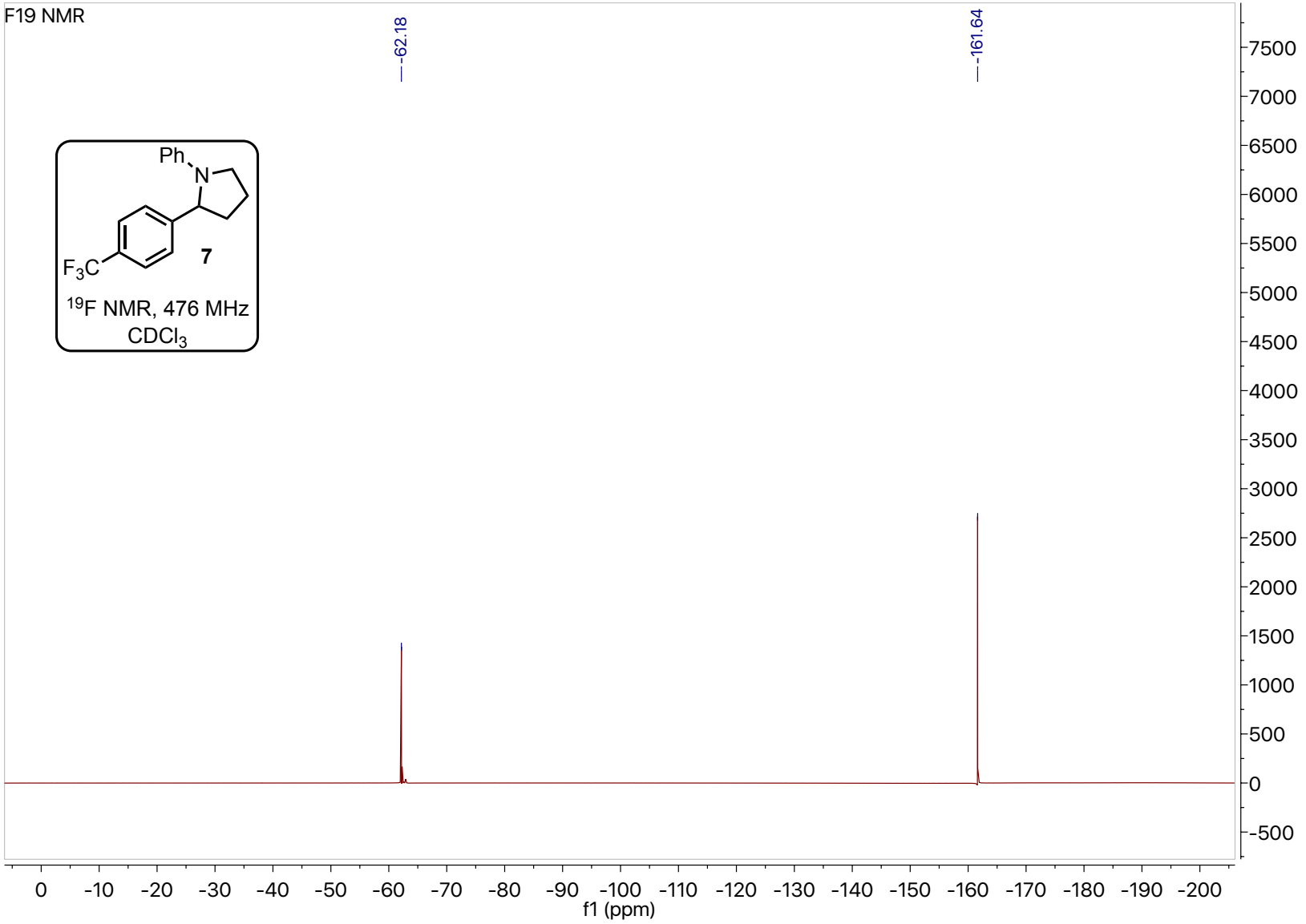

1H NMR
Ph
N
F
6
1H NMR, 500 MHz
CDCl3
4.24
2.03
1.00
1.90
0.96
0.99
1.05
1.00
1.99
0.99
f1 (ppm)

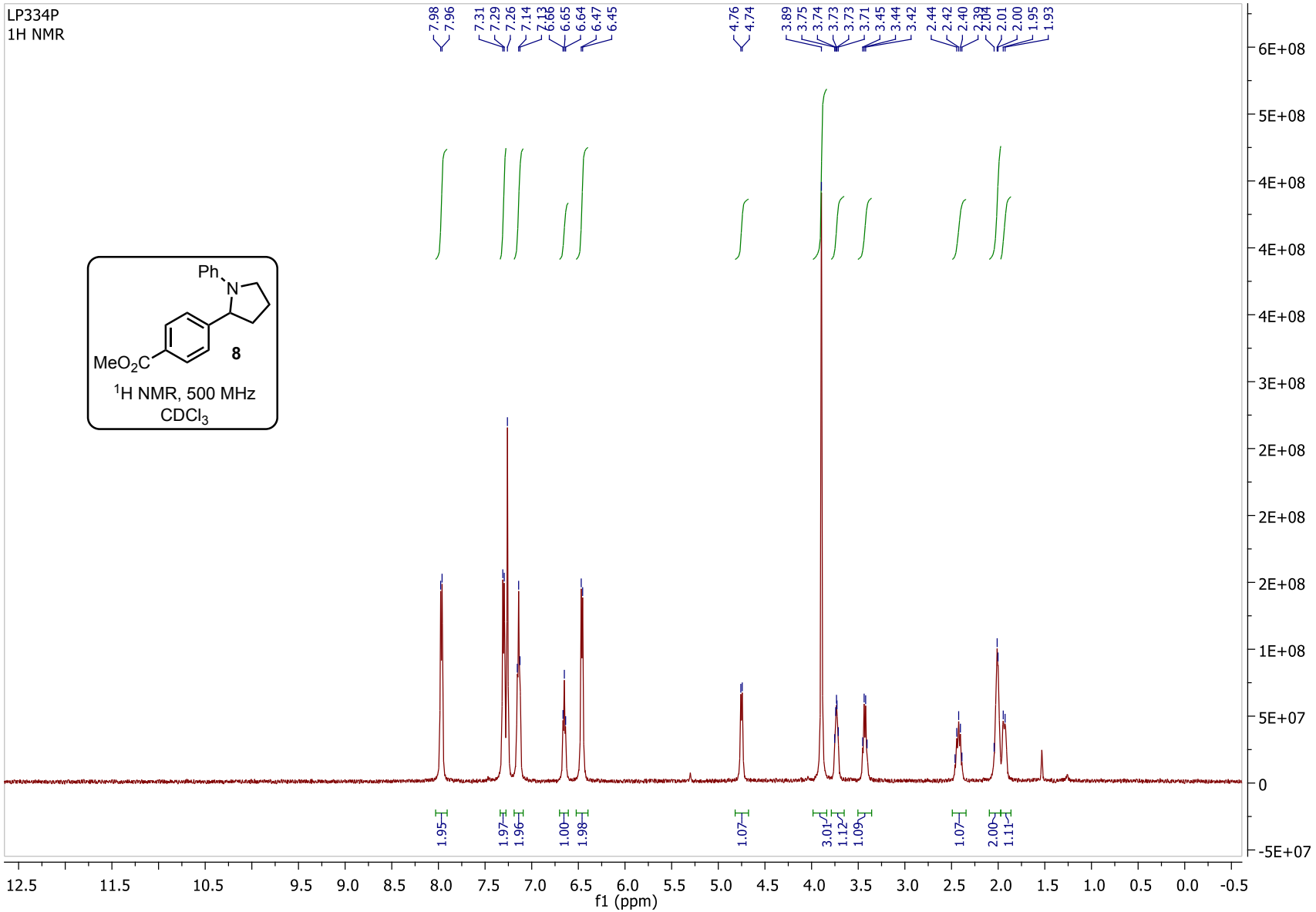

LP314P1
13C NMR
162.94
161.00
147.30
140.47
129.30
127.67
127.61
116.26
115.63
115.46
112.66
77.55
77.30
77.05
62.60
49.38
36.41
23.31
Ph
N
F
6
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

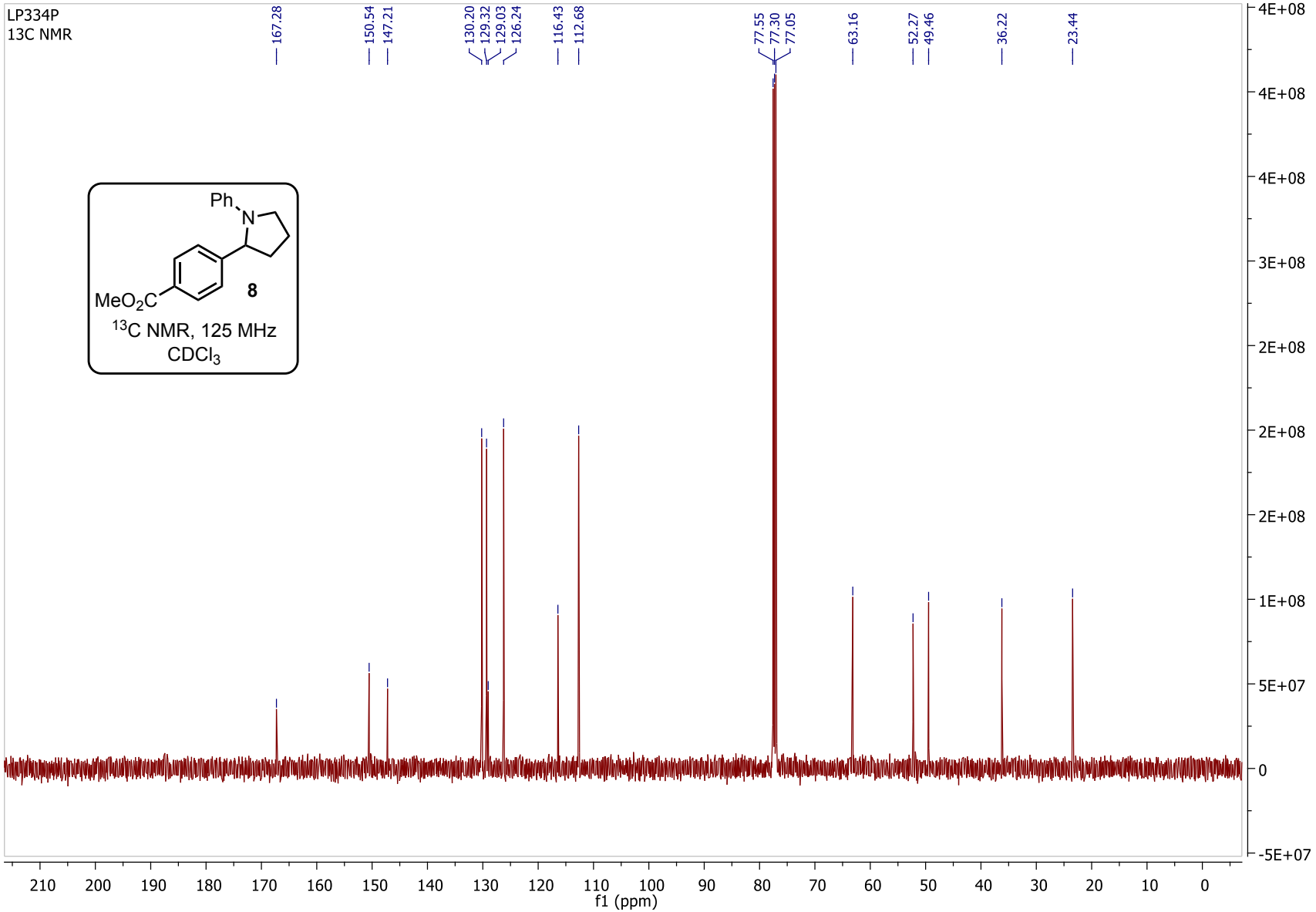

F19 NMR
-116.62
-161.60
Ph
N
F
6
19F NMR, 476 MHz
CDCl3
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

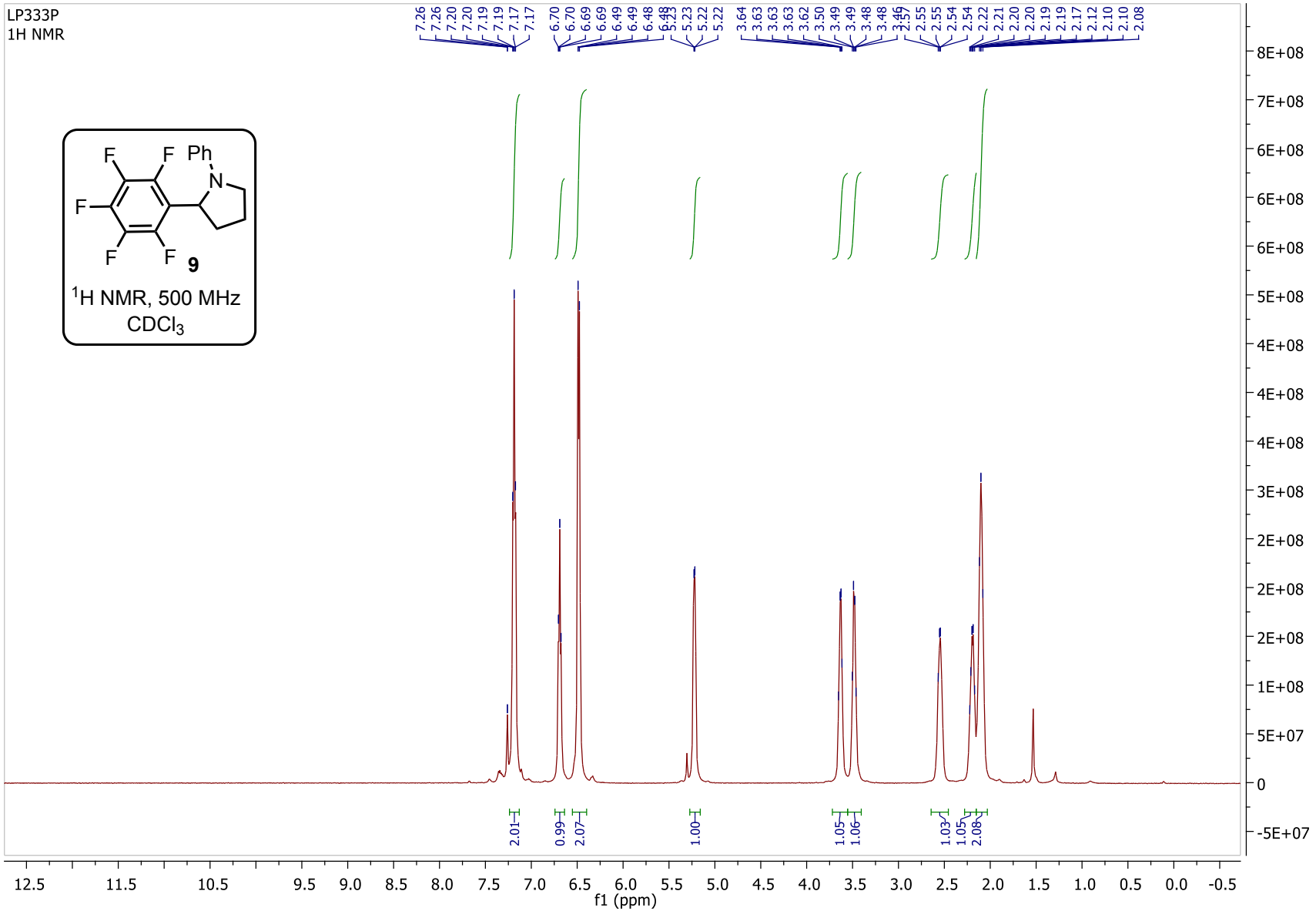

LP358P1
1H NMR
Ph
N
F3C
7
1H NMR, 500 MHz
CDCl3
7.58
7.56
7.37
7.35
7.26
7.19
7.18
7.16
6.70
6.69
6.67
6.49
6.48
4.79
4.77
3.77
3.76
3.75
3.74
3.73
3.47
3.46
3.44
3.42
2.47
2.45
2.44
2.03
2.02
1.96
1.95
1.94
1.99
2.03
1.98
1.00
2.01
1.00
1.00
1.01
1.02
2.00
1.06
f1 (ppm)

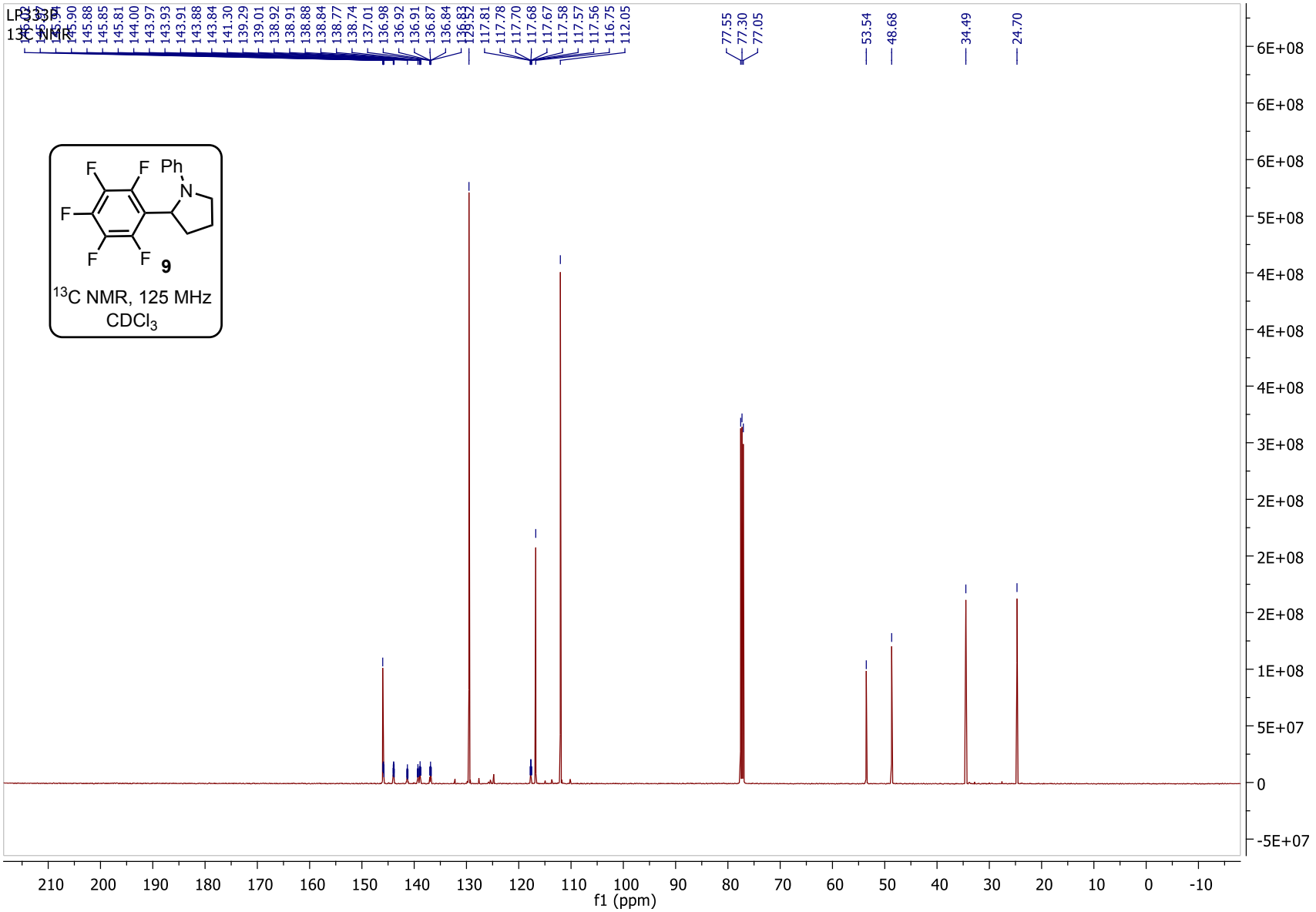

LP358P
13C NMR
149.19
147.15
129.67
129.41
129.38
129.16
128.90
127.79
126.55
125.83
125.80
125.78
125.75
125.63
123.47
121.31
116.55
112.69
77.55
77.30
77.05
62.94
49.46
36.22
23.37
Ph
N
F3C
7
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

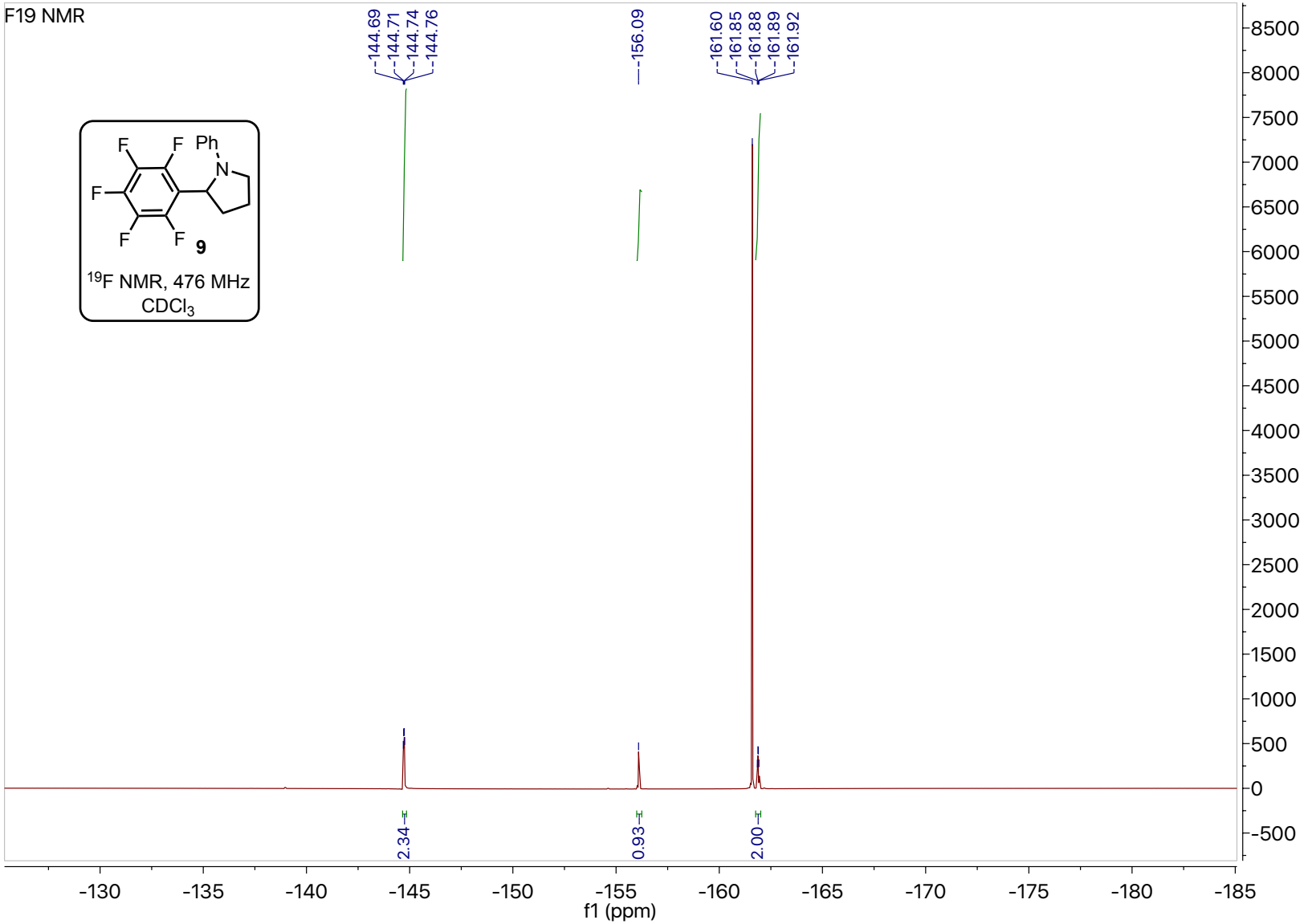

F19 NMR
-62.18
-161.64
Ph
N
F3C
7
19F NMR, 476 MHz
CDCl3
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

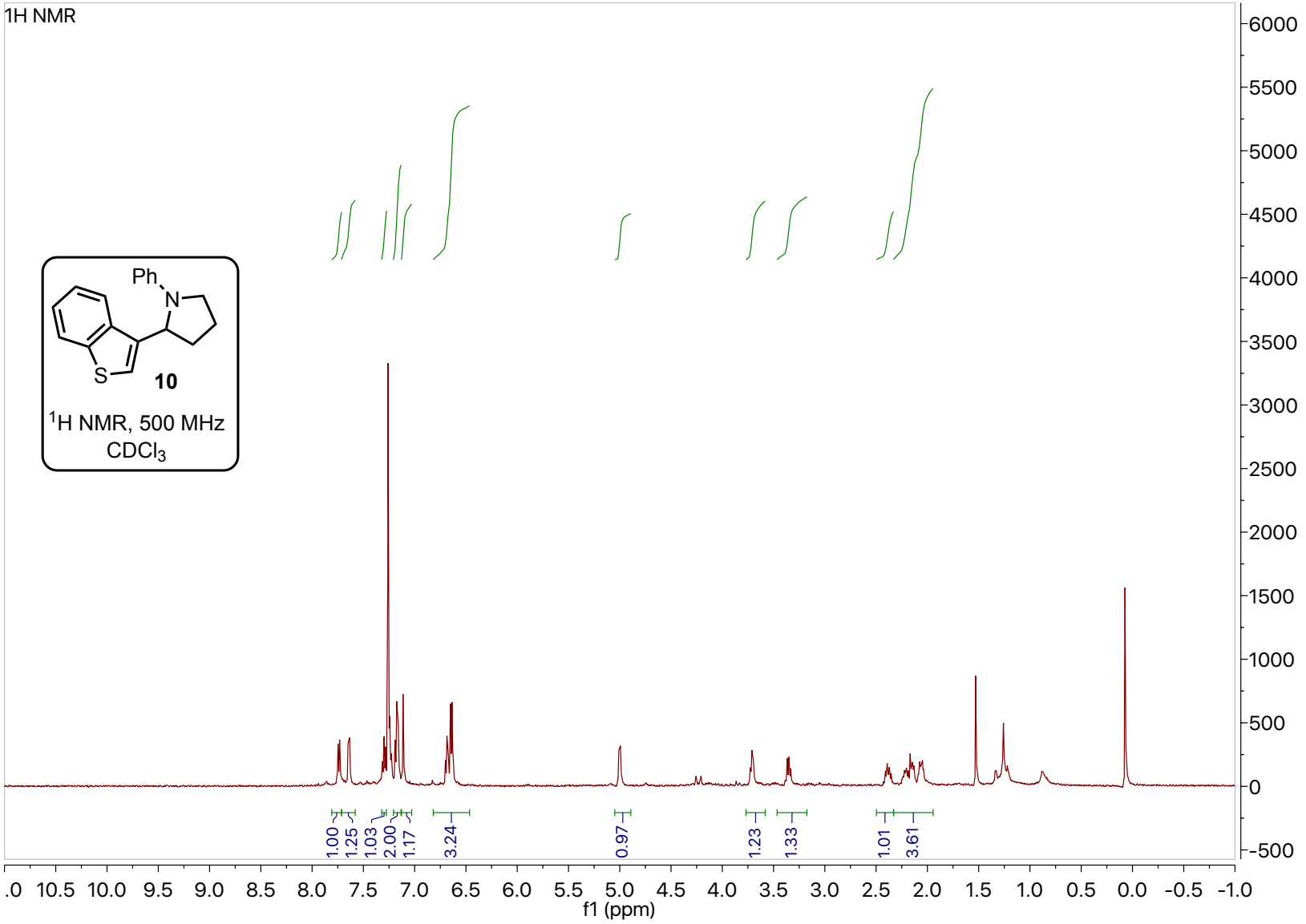

LP334P
1H NMR
7.98
7.96
7.31
7.29
7.26
7.14
7.13
6.66
6.65
6.64
6.47
6.45
4.76
4.74
3.89
3.75
3.74
3.73
3.73
3.71
3.45
3.44
3.42
2.44
2.42
2.40
2.39
2.04
2.01
2.00
1.95
1.93
Ph
N
MeO2C
8
1H NMR, 500 MHz
CDCl3
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
1.95
1.97
1.96
1.00
1.98
1.07
3.01
1.12
1.09
1.07
2.00
1.11
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

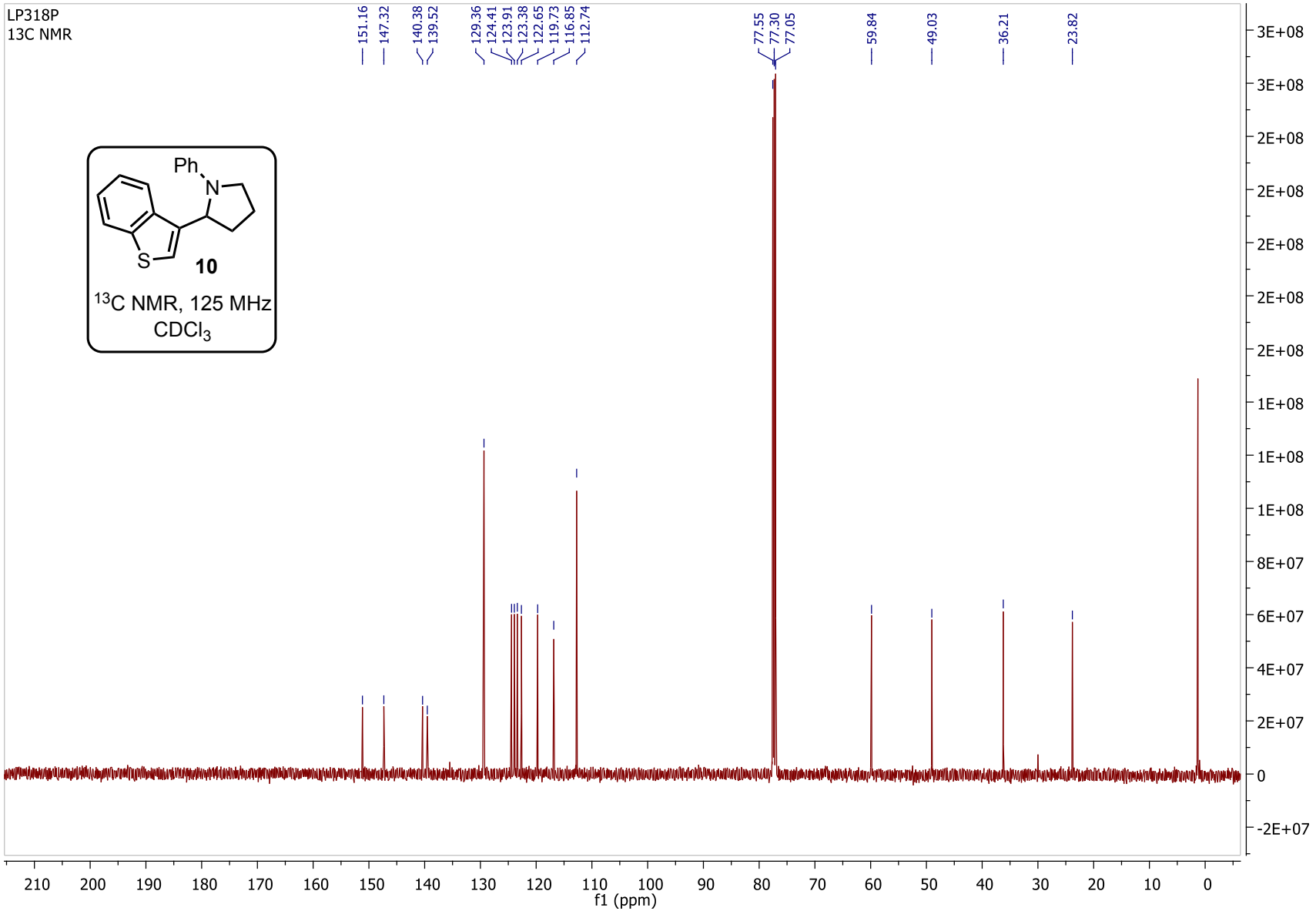

LP334P
13C NMR
167.28
150.54
147.21
130.20
129.32
129.03
126.24
116.43
112.68
77.55
77.30
77.05
63.16
52.27
49.46
36.22
23.44
Ph
N
MeO2C
8
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

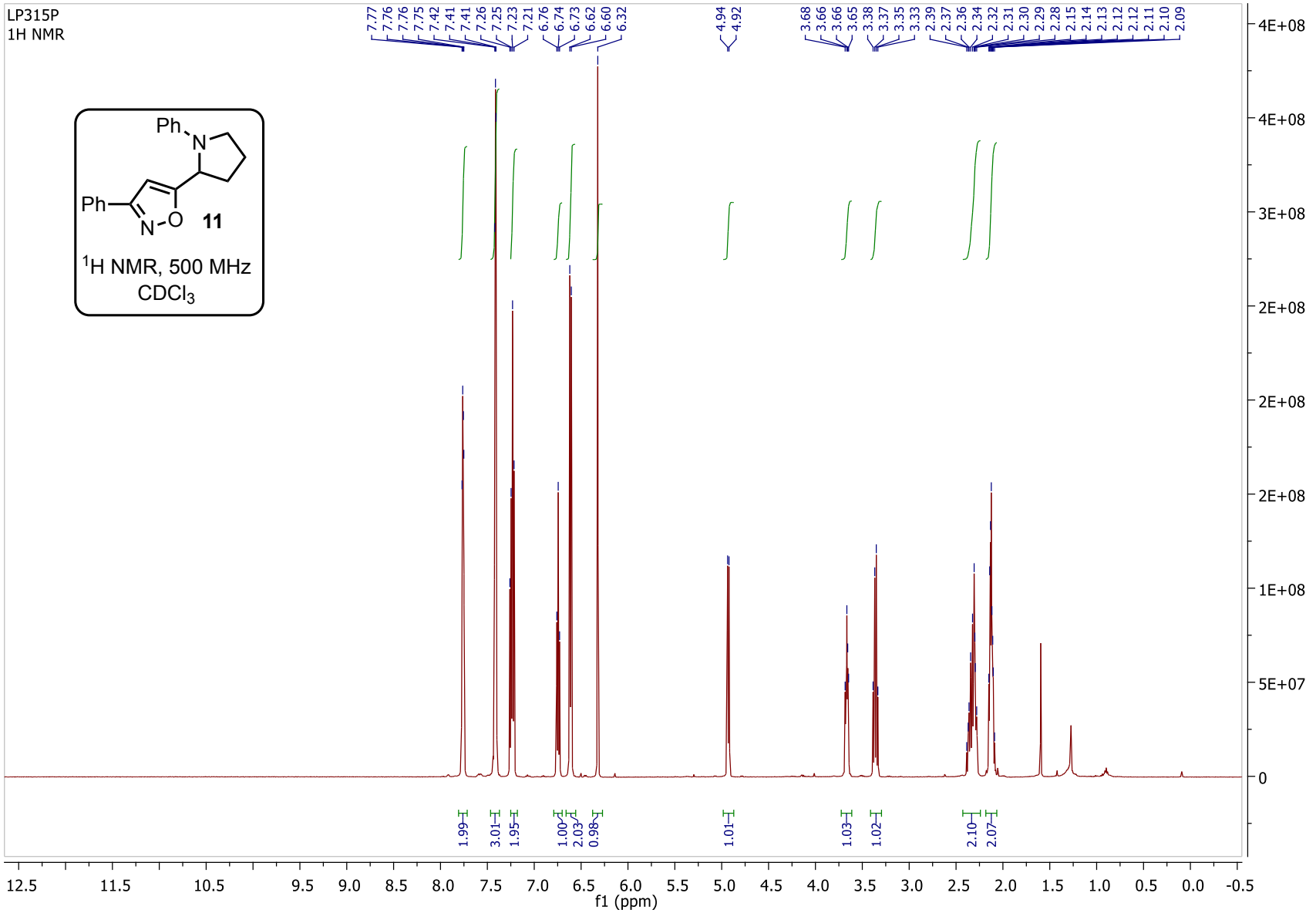

LP333P
1H NMR
F
F
Ph
N
F
F
F
9
1H NMR, 500 MHz
CDCl3
f1 (ppm)

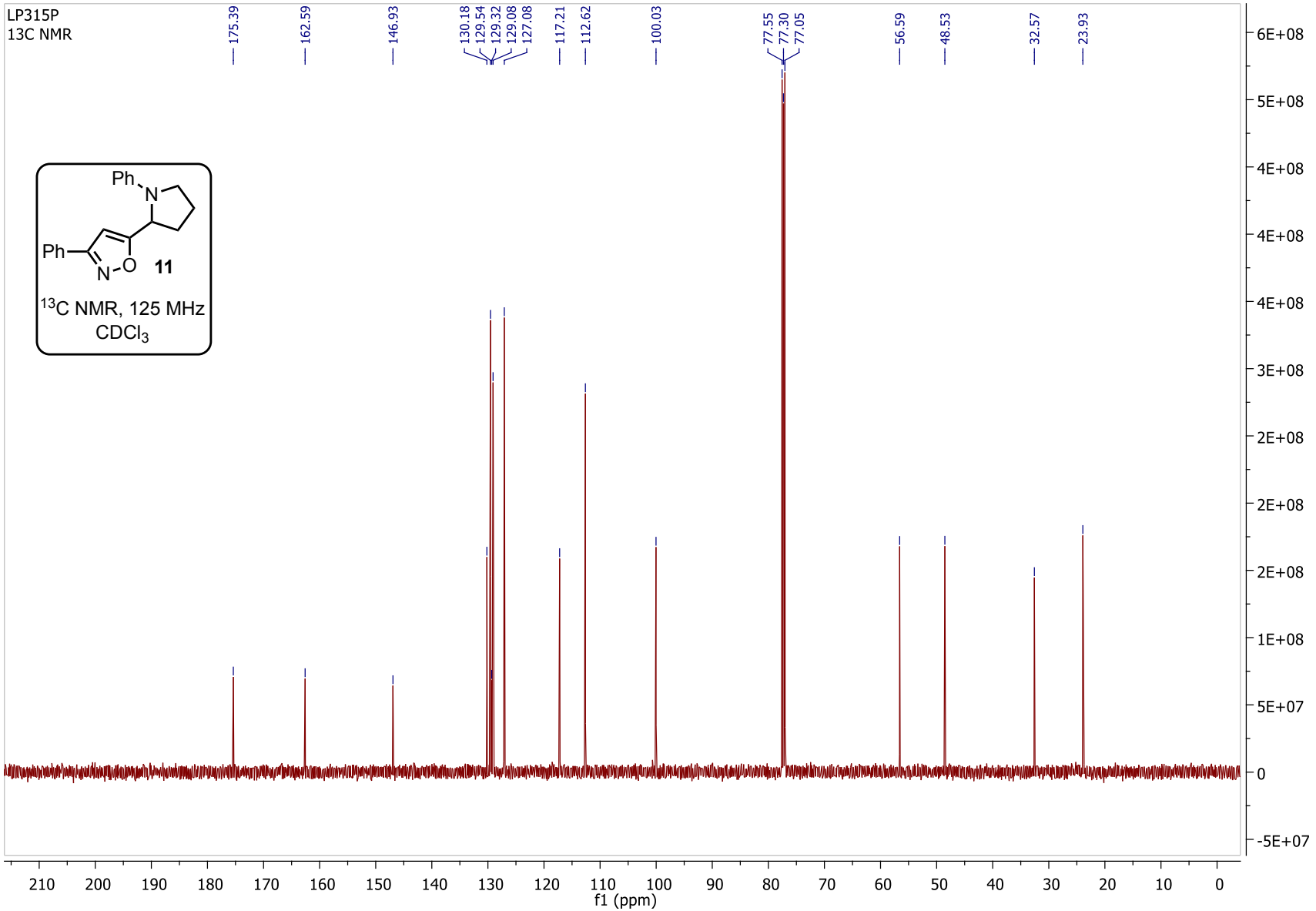

LP-Q33F
13C NMR
145.90
145.88
145.85
145.81
144.00
143.97
143.93
143.91
143.88
143.84
141.30
139.29
139.01
138.92
138.91
138.88
138.84
138.77
138.74
137.01
136.98
136.92
136.91
136.87
136.84
117.81
117.78
117.70
117.68
117.67
117.58
117.57
117.56
116.75
112.05
77.55
77.30
77.05
53.54
48.68
34.49
24.70
F
F
Ph
N
F
F
F
9
13C NMR, 125 MHz
CDCl3
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
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)

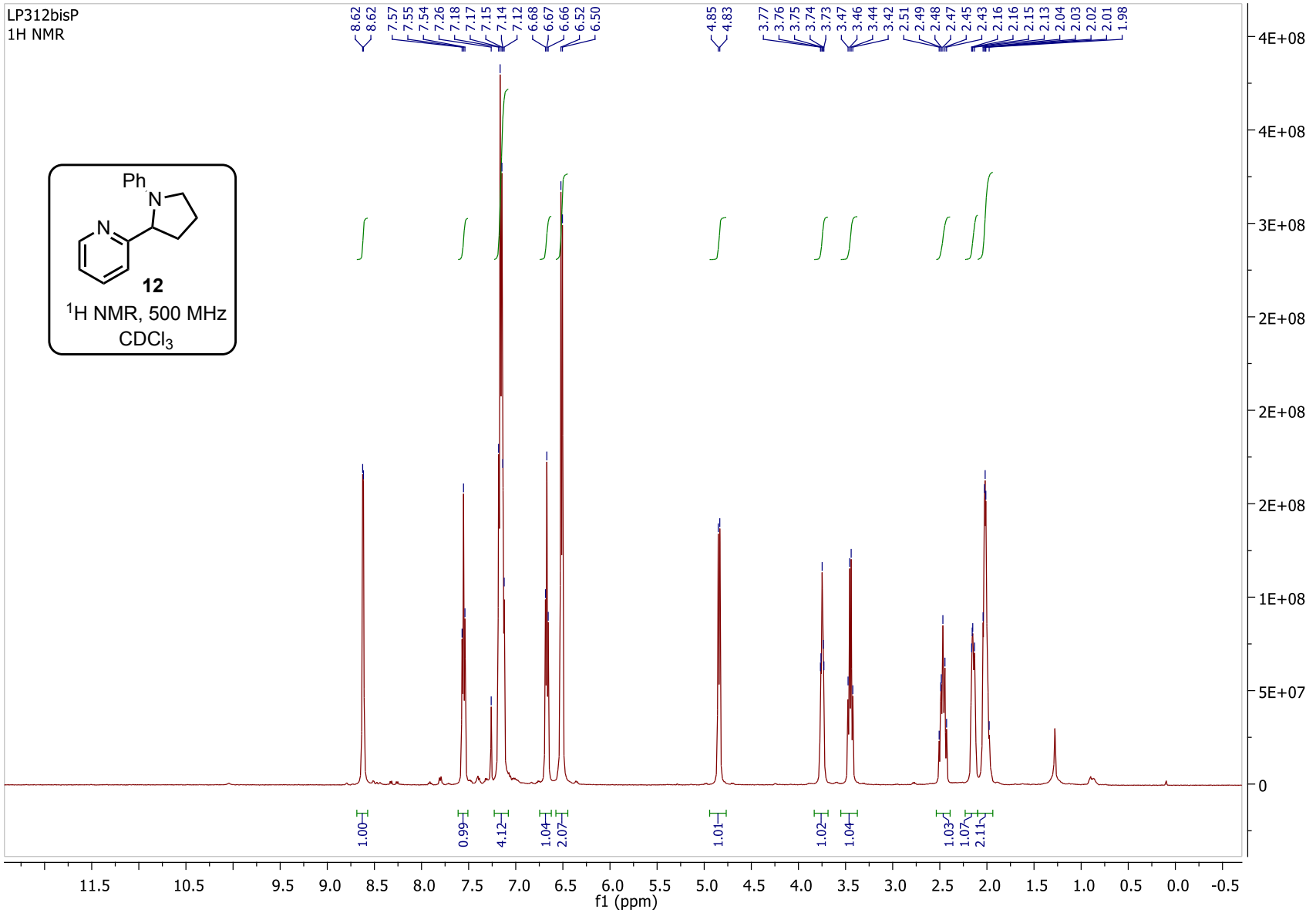

F19 NMR
144.69
144.71
144.74
144.76
156.09
161.60
161.85
161.88
161.89
161.92
F
F
Ph
N
F
F
F
9
19F NMR, 476 MHz
CDCl3
2.34
0.93
2.00
f1 (ppm)

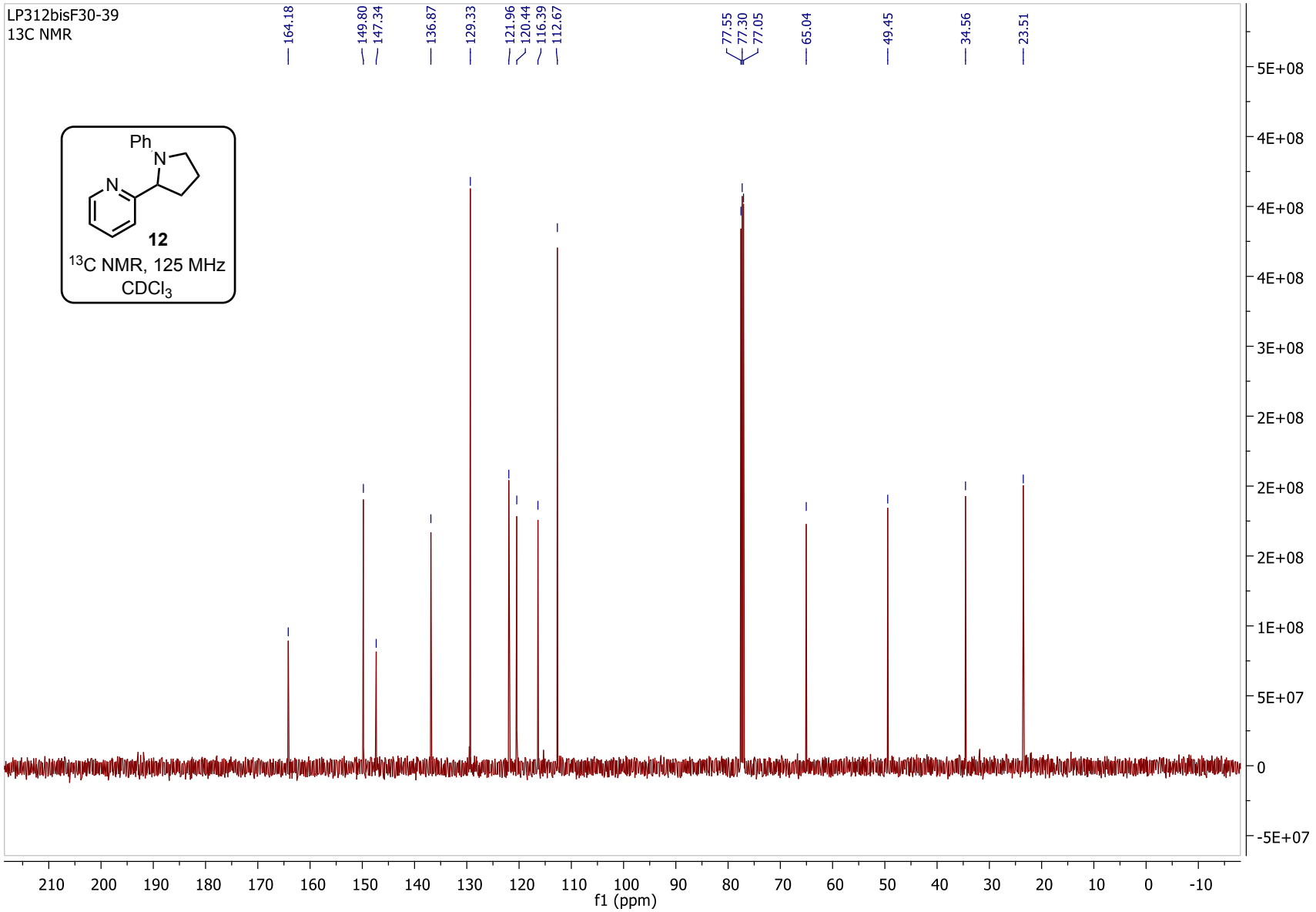

1H NMR
Ph
N
S
10
1H NMR, 500 MHz
CDCl3
1.00
1.25
1.03
2.00
1.17
3.24
0.97
1.23
1.33
1.01
3.61
f1 (ppm)

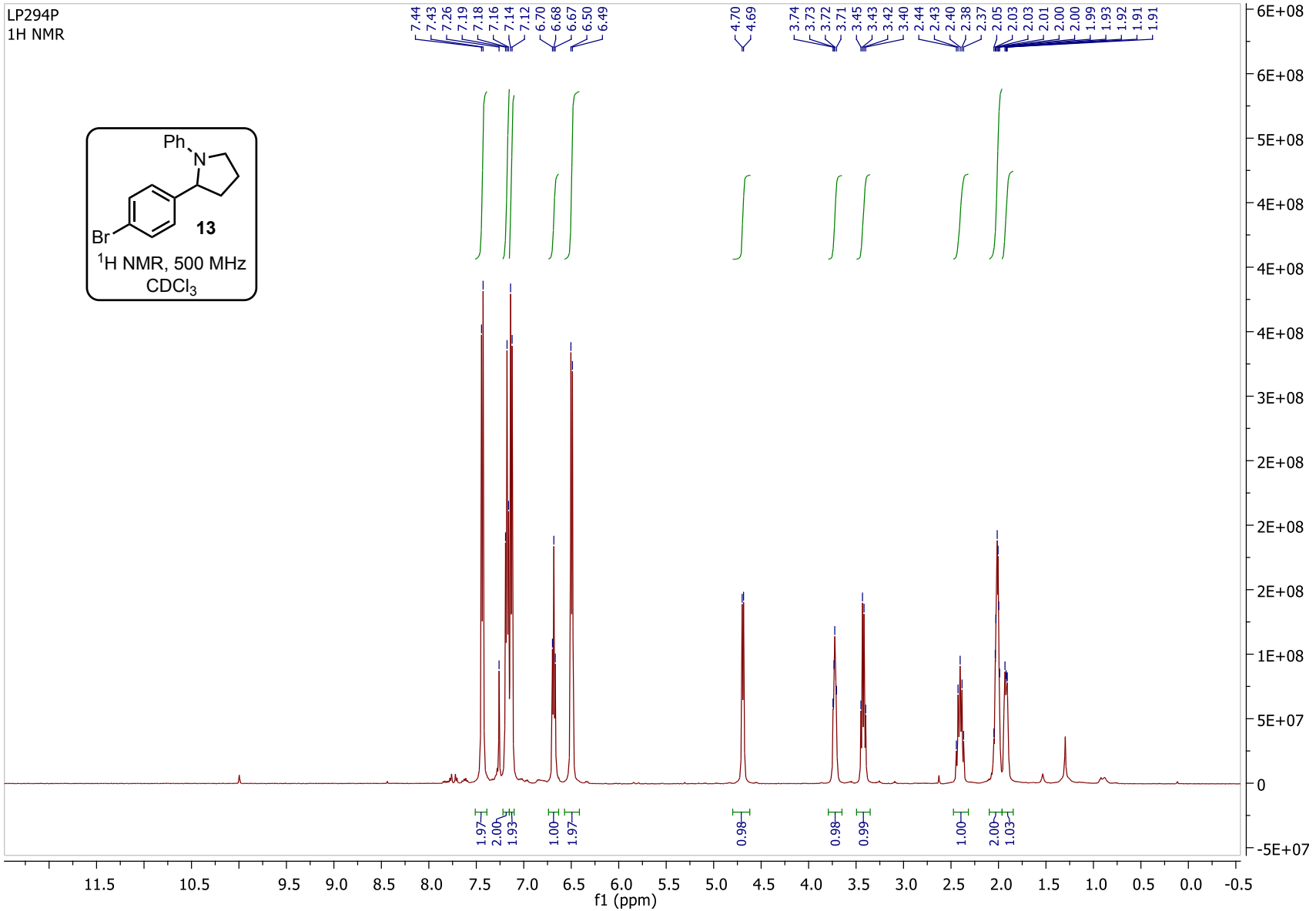

LP318P
13C NMR
151.16
147.32
140.38
139.52
129.36
124.41
123.91
123.38
122.65
119.73
116.85
112.74
77.55
77.30
77.05
59.84
49.03
36.21
23.82
Ph
N
S
10
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

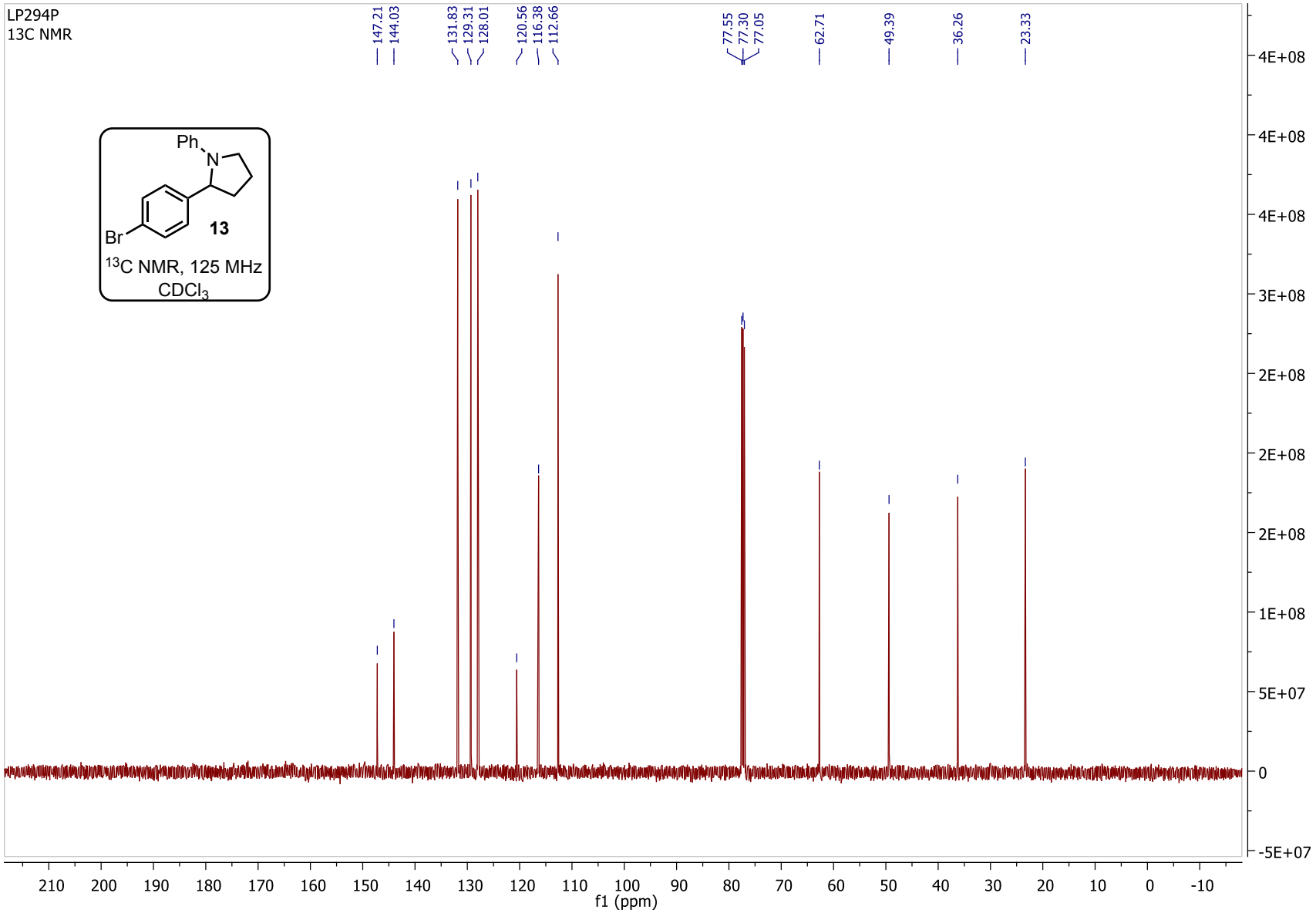

LP315P
1H NMR
Ph
N
Ph
N
O
11
1H NMR, 500 MHz
CDCl3
7.77
7.76
7.76
7.75
7.42
7.41
7.41
7.26
7.25
7.23
7.21
6.76
6.74
6.73
6.62
6.60
6.32
4.94
4.92
3.68
3.66
3.66
3.65
3.38
3.37
3.35
3.33
2.39
2.37
2.36
2.34
2.32
2.31
2.30
2.29
2.28
2.15
2.14
2.13
2.12
2.12
2.11
2.10
2.09
1.99
3.01
1.95
1.00
2.03
0.98
1.01
1.03
1.02
2.10
2.07
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

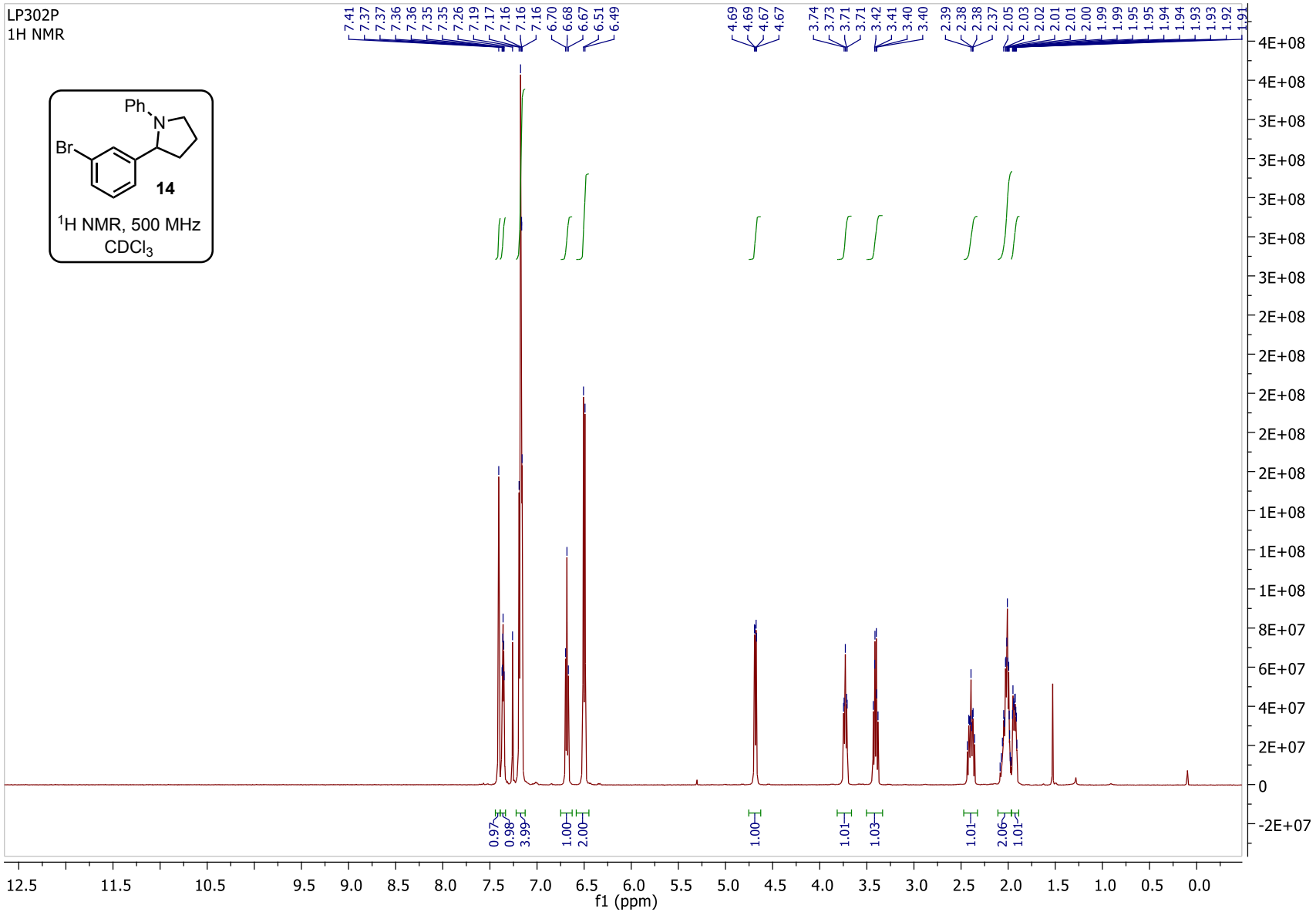

LP315P
13C NMR
175.39
162.59
146.93
130.18
129.54
129.32
129.08
127.08
117.21
112.62
100.03
77.55
77.30
77.05
56.59
48.53
32.57
23.93
Ph
N
Ph
N
O
11
13C NMR, 125 MHz
CDCl3
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

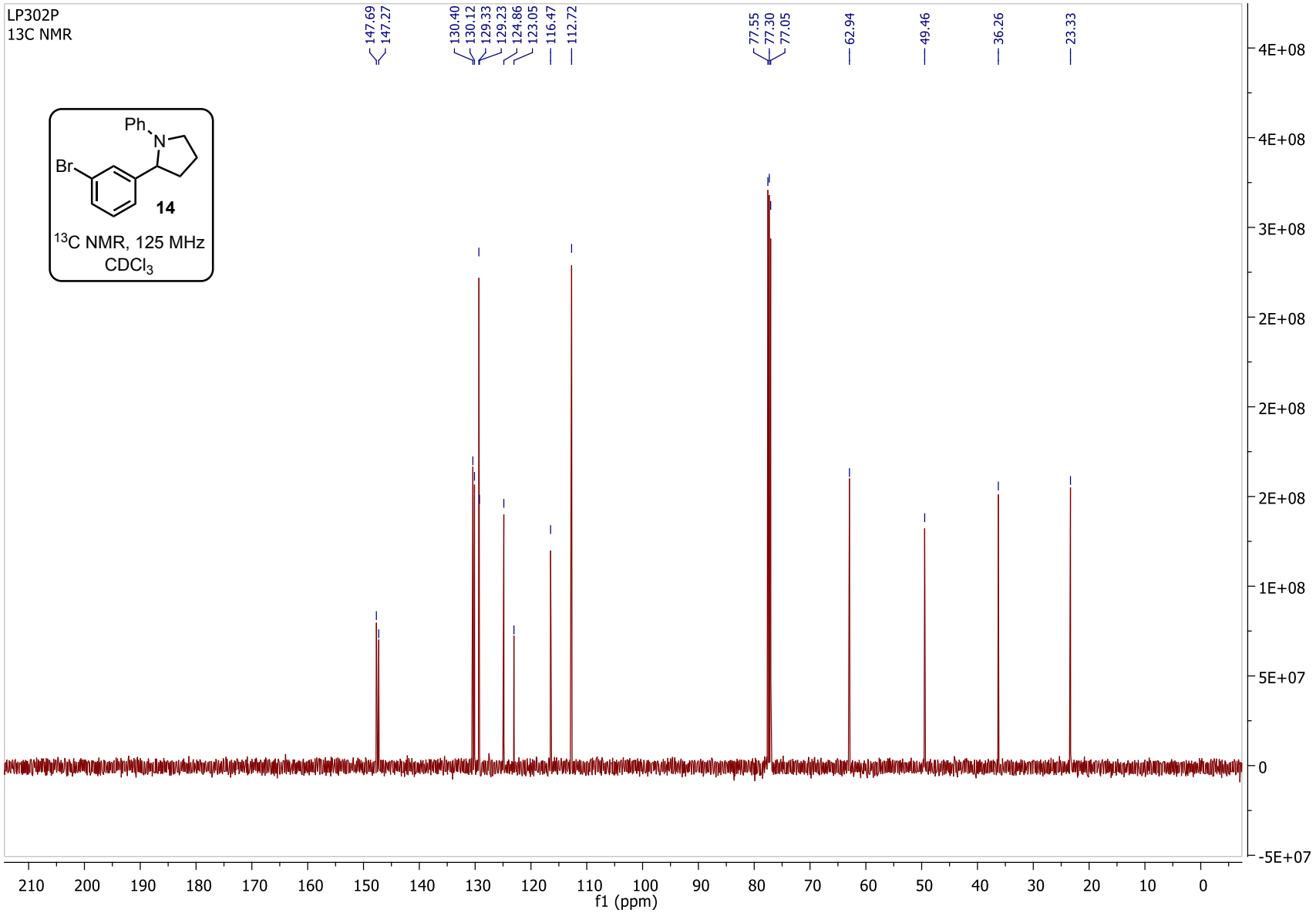

LP312bisP
1H NMR
Ph
N
N
12
1H NMR, 500 MHz
CDCl3
8.62
8.62
7.57
7.55
7.54
7.26
7.18
7.17
7.15
7.14
7.12
6.68
6.67
6.66
6.52
6.50
4.85
4.83
3.77
3.76
3.75
3.74
3.73
3.47
3.46
3.44
3.42
2.51
2.49
2.48
2.47
2.45
2.43
2.16
2.15
2.13
2.04
2.03
2.02
2.01
1.98
1.00
0.99
4.12
1.04
2.07
1.01
1.02
1.04
1.03
1.07
2.11
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

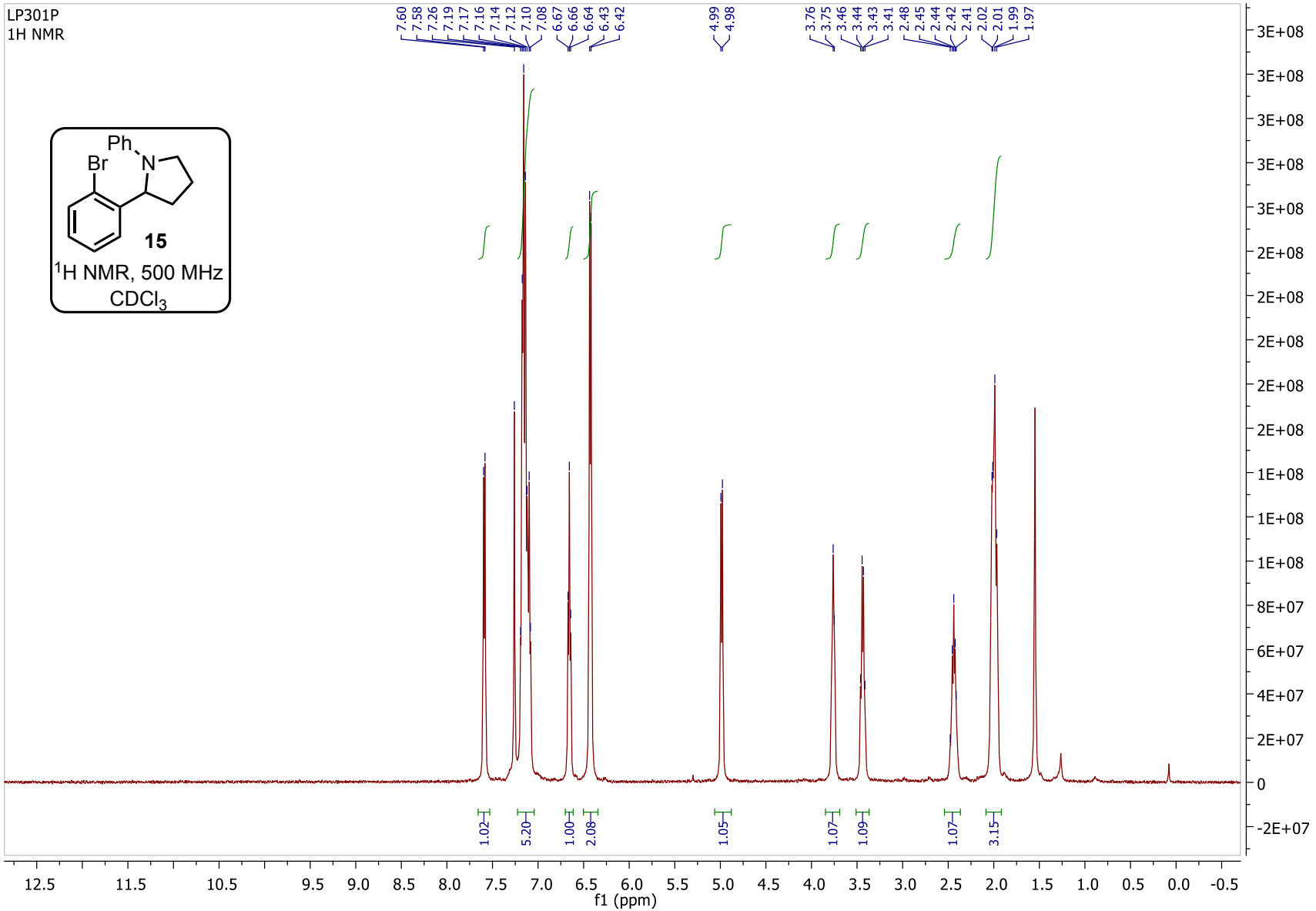

LP312bisF30-39
13C NMR
164.18
149.80
147.34
136.87
129.33
121.96
120.44
116.39
112.67
77.55
77.30
77.05
65.04
49.45
34.56
23.51
Ph
N
N
12
13C NMR, 125 MHz
CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

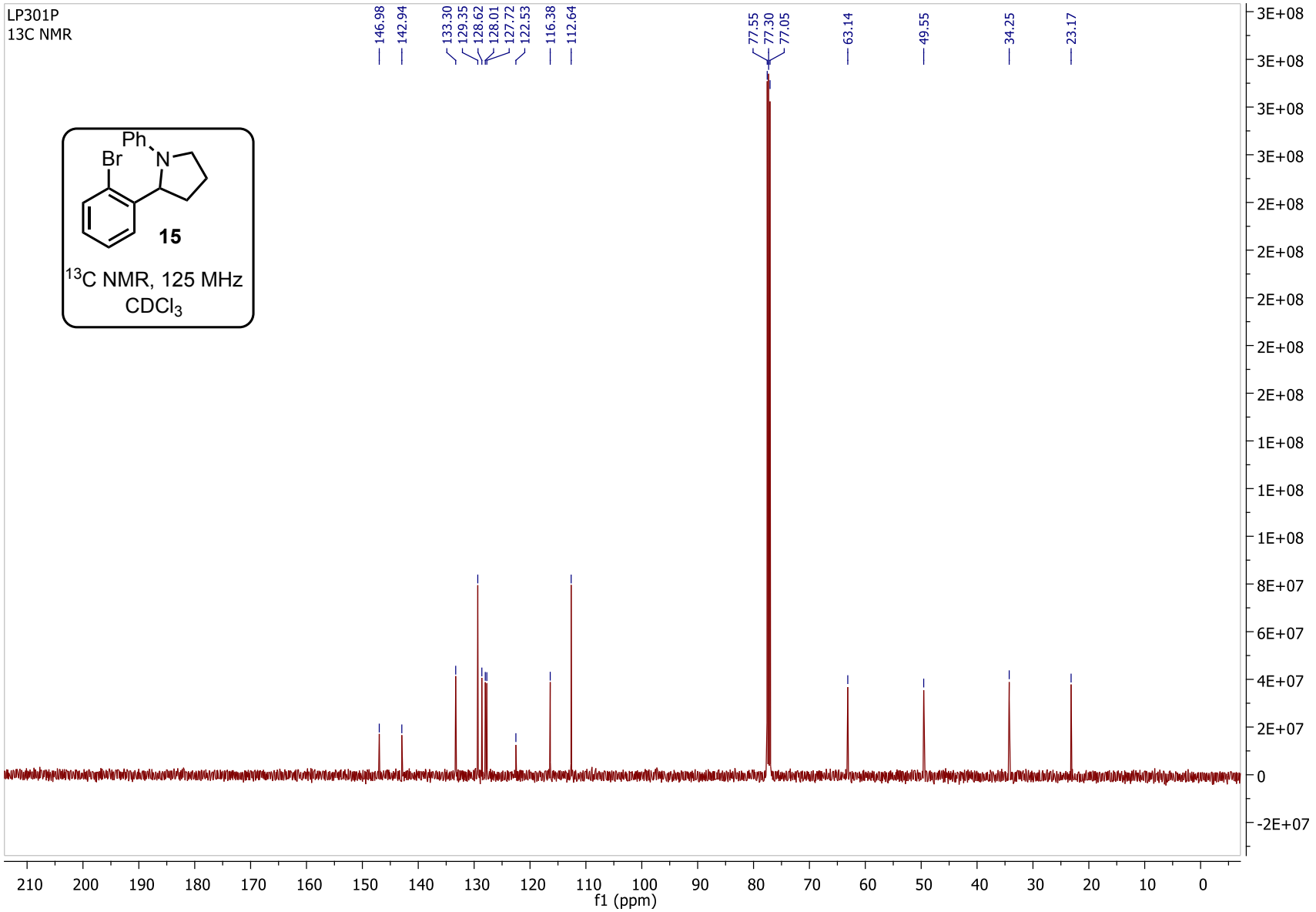

LP294P
1H NMR
7.44
7.43
7.26
7.19
7.18
7.16
7.14
7.12
6.70
6.68
6.67
6.50
6.49
4.70
4.69
3.74
3.73
3.72
3.71
3.45
3.43
3.42
3.40
2.44
2.43
2.40
2.38
2.37
2.05
2.03
2.03
2.01
2.00
2.00
1.99
1.93
1.92
1.91
1.91
Ph
N
Br
13
1H NMR, 500 MHz
CDCl3
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
1.97
2.00
1.93
1.00
1.97
0.98
0.98
0.99
1.00
2.00
1.03
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

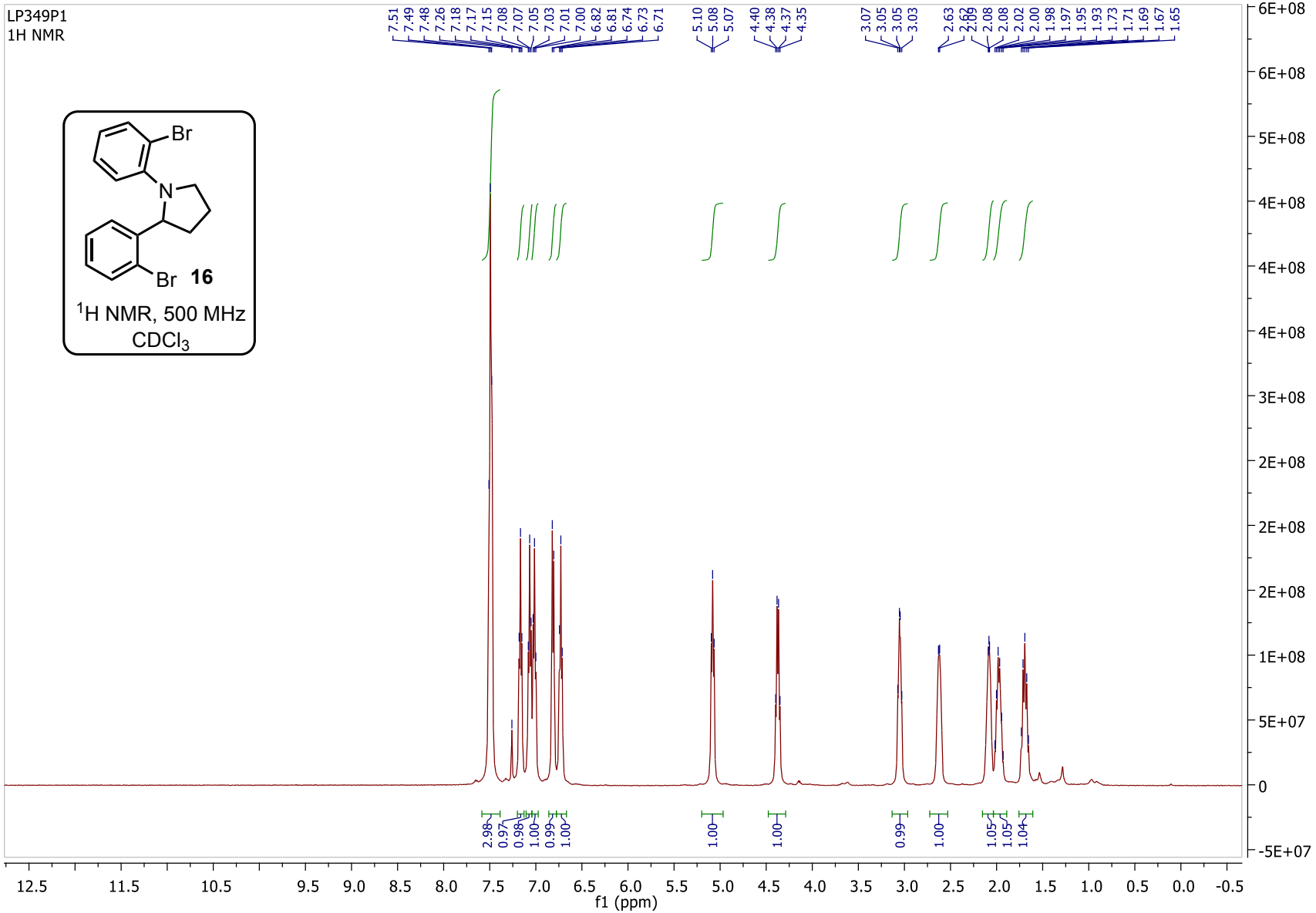

LP294P
13C NMR
147.21
144.03
131.83
129.31
128.01
120.56
116.38
112.66
77.55
77.30
77.05
62.71
49.39
36.26
23.33
Ph
N
Br
13
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

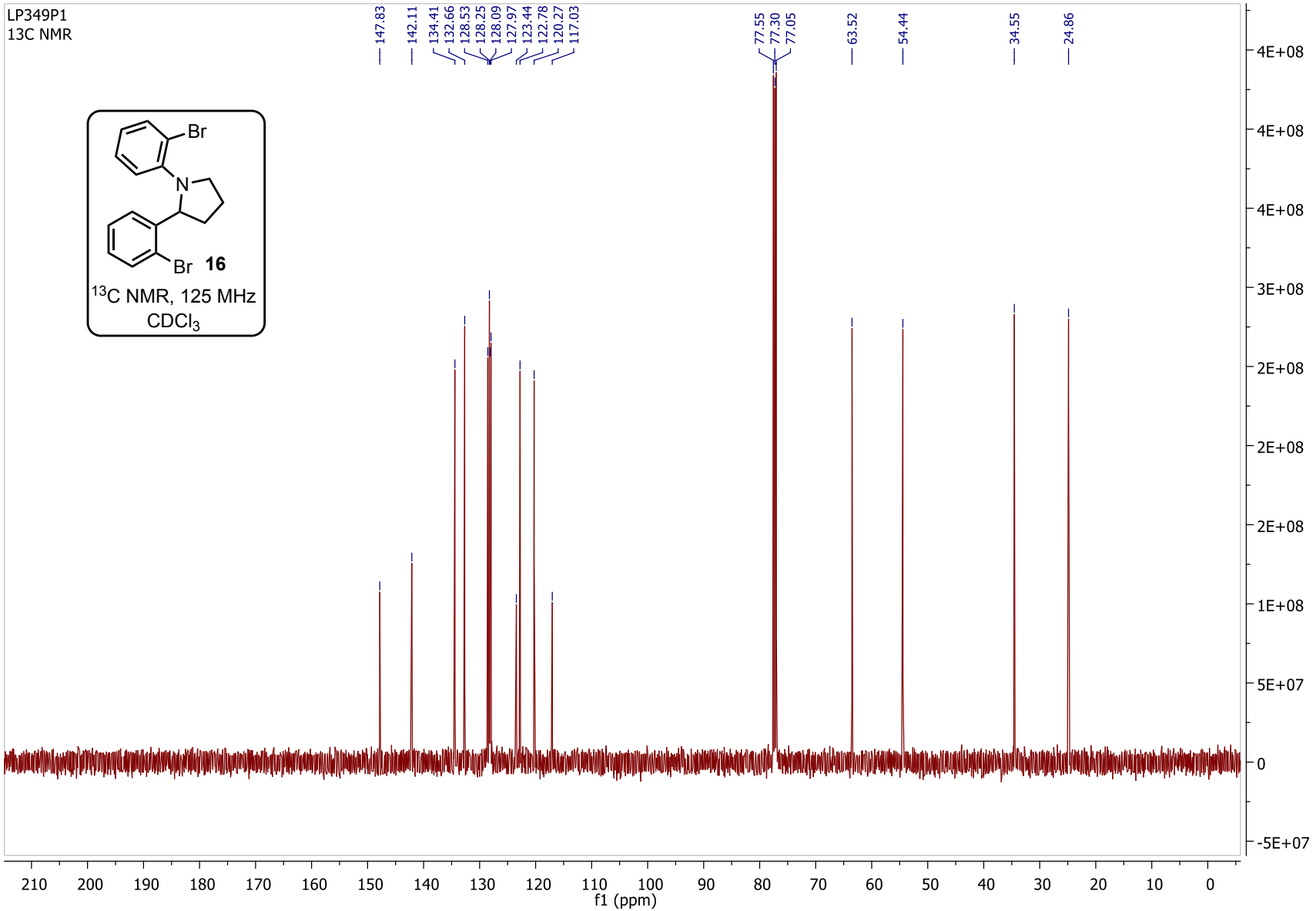

LP302P
1H NMR
Ph
N
Br
14
1H NMR, 500 MHz
CDCl3
f1 (ppm)

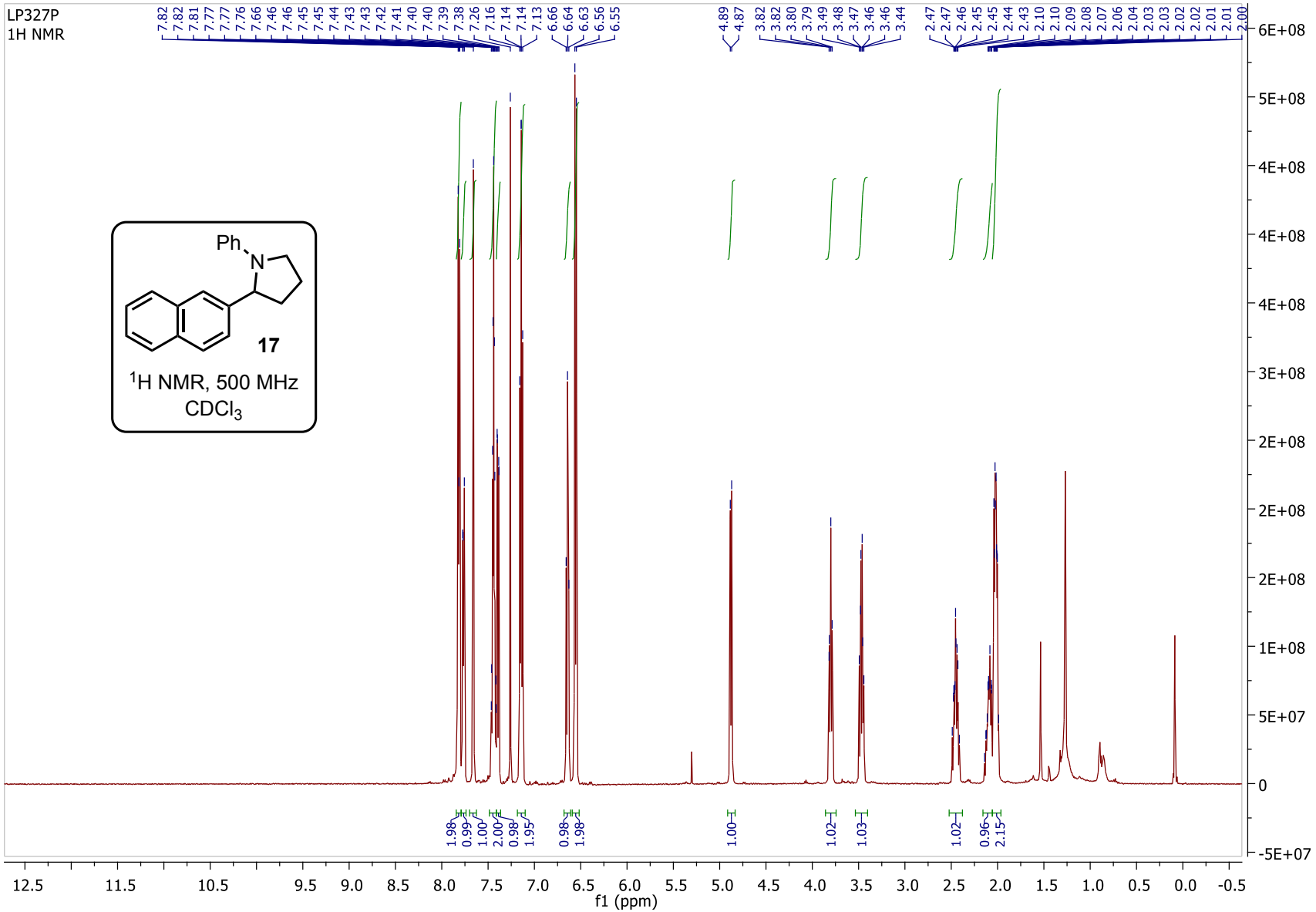

LP302P
13C NMR
147.69
147.27
130.40
130.12
129.33
129.23
124.86
123.05
116.47
112.72
77.55
77.30
77.05
62.94
49.46
36.26
23.33
Ph
N
Br
14
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

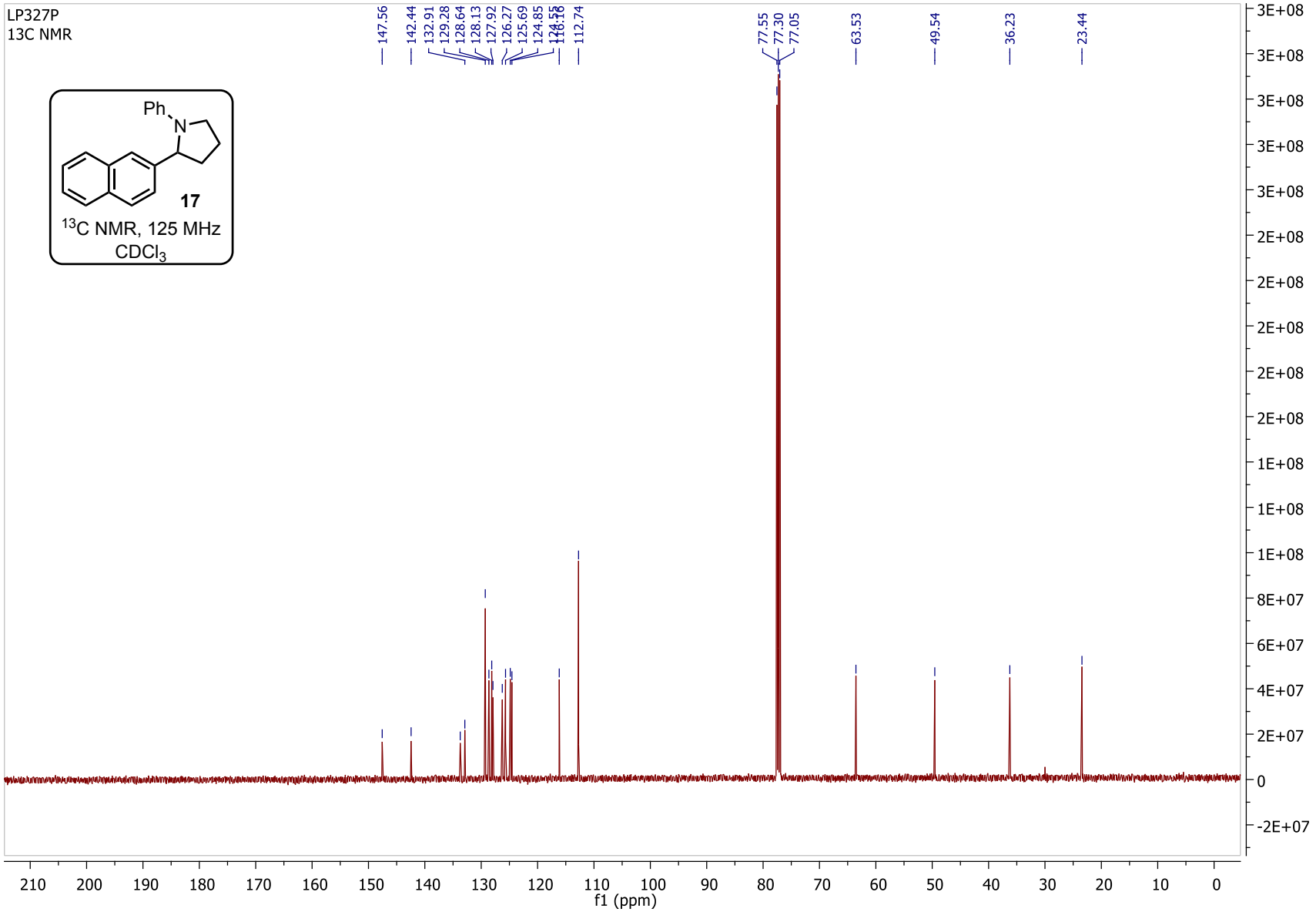

LP301P
1H NMR
Ph
Br
N
15
1H NMR, 500 MHz
CDCl3
7.60
7.58
7.26
7.19
7.17
7.16
7.14
7.12
7.10
7.08
6.67
6.66
6.64
6.43
6.42
4.99
4.98
3.76
3.75
3.46
3.44
3.43
3.41
2.48
2.45
2.44
2.42
2.41
2.02
2.01
1.99
1.97
1.02
5.20
1.00
2.08
1.05
1.07
1.09
1.07
3.15
f1 (ppm)

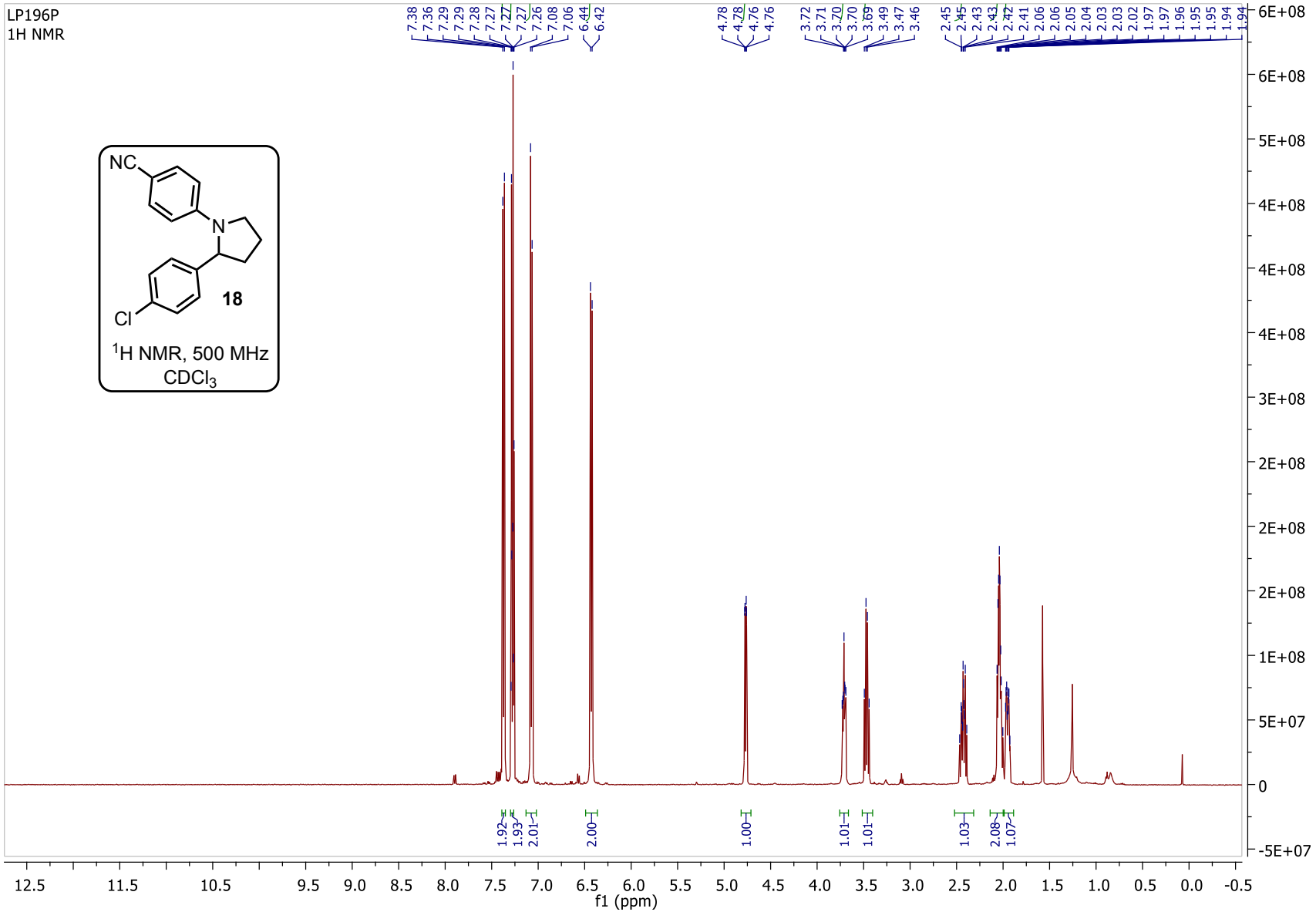

LP301P
13C NMR
146.98
142.94
133.30
129.35
128.62
128.01
127.72
122.53
116.38
112.64
77.55
77.30
77.05
63.14
49.55
34.25
23.17
Ph
Br
N
15
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

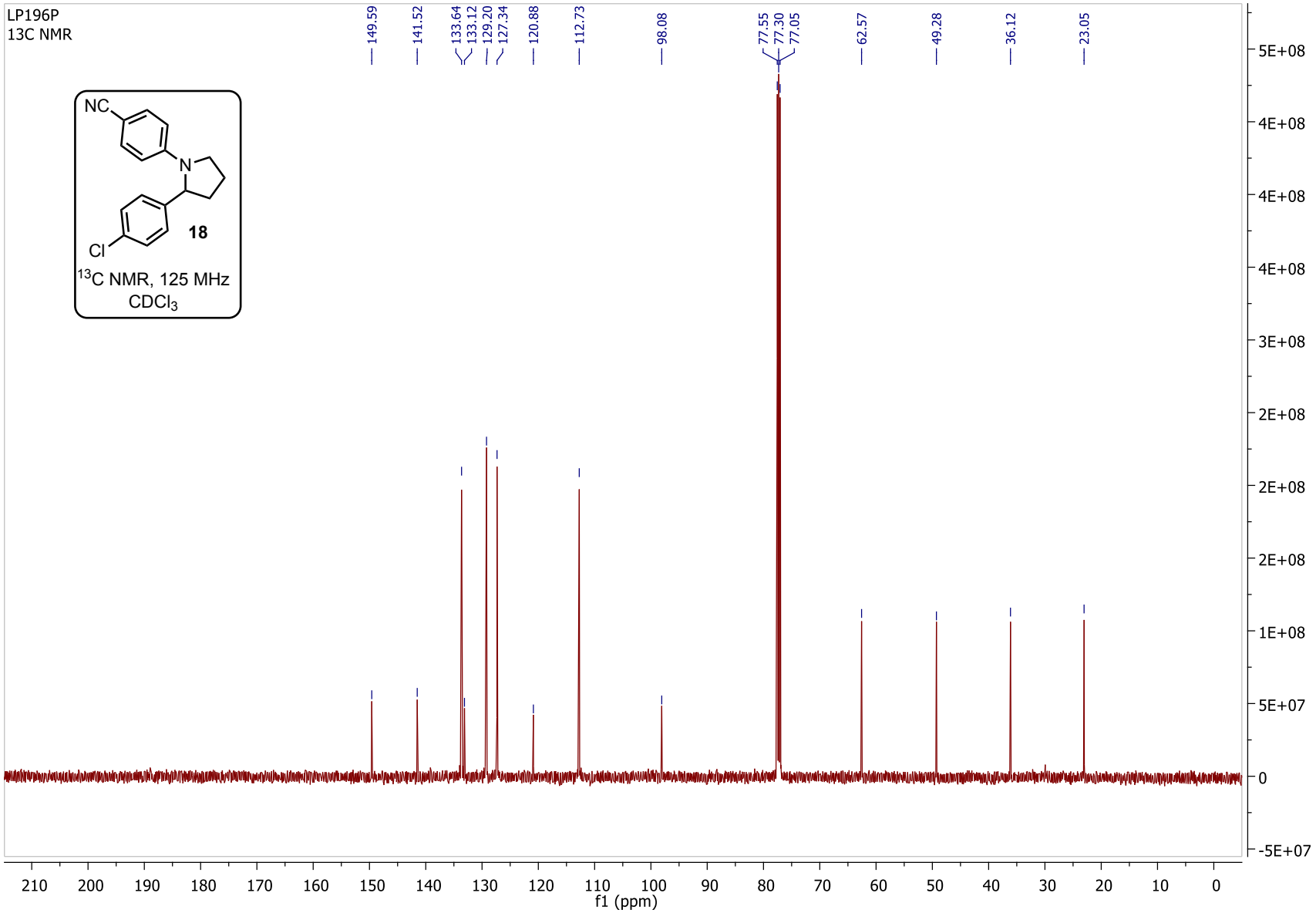

LP349P1
1H NMR
Br
N
Br 16
1H NMR, 500 MHz
CDCl3
f1 (ppm)

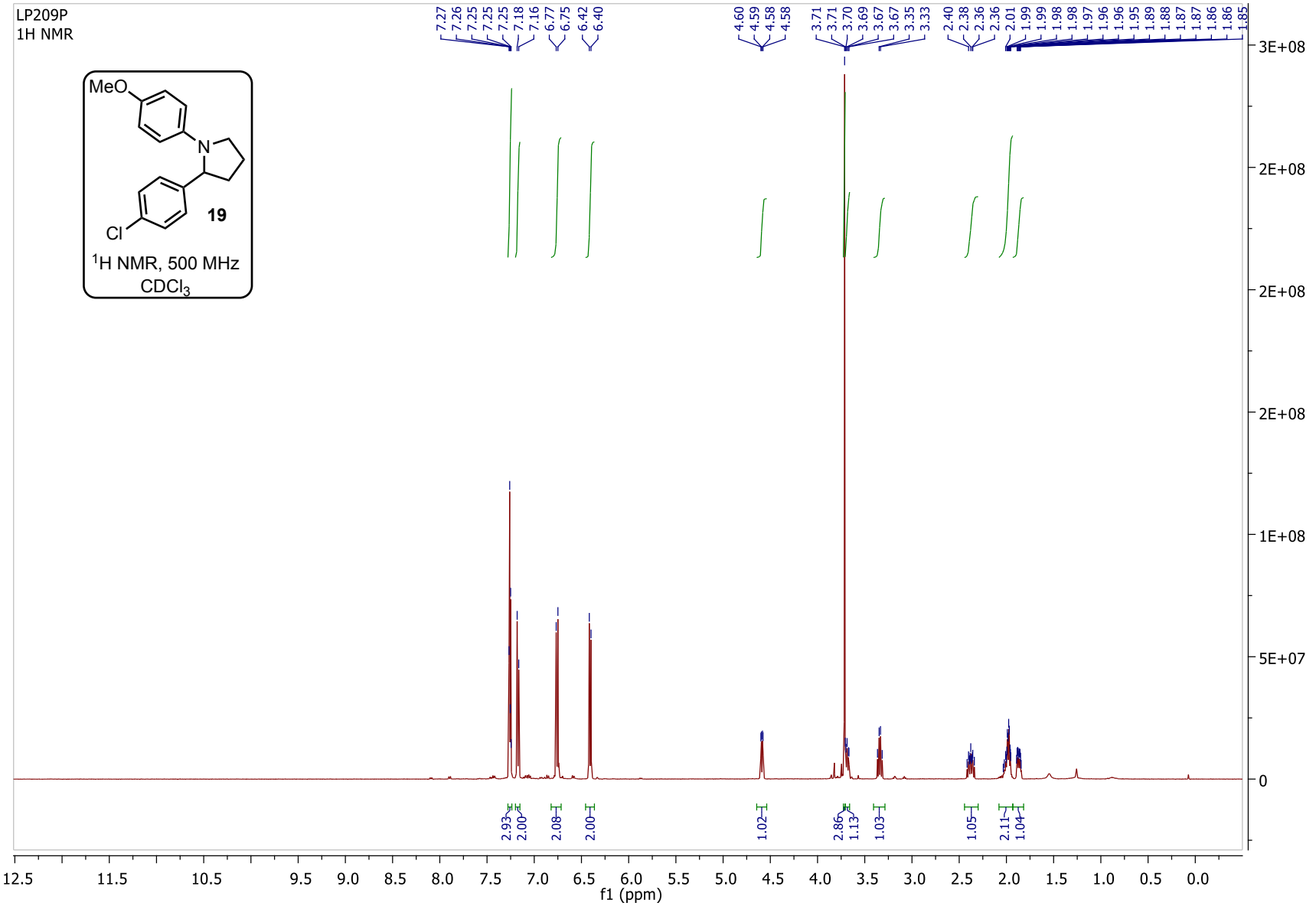

LP349P1
13C NMR
147.83
142.11
134.41
132.66
128.53
128.25
128.09
127.97
123.44
122.78
120.27
117.03
77.55
77.30
77.05
63.52
54.44
34.55
24.86
Br
N
Br
16
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

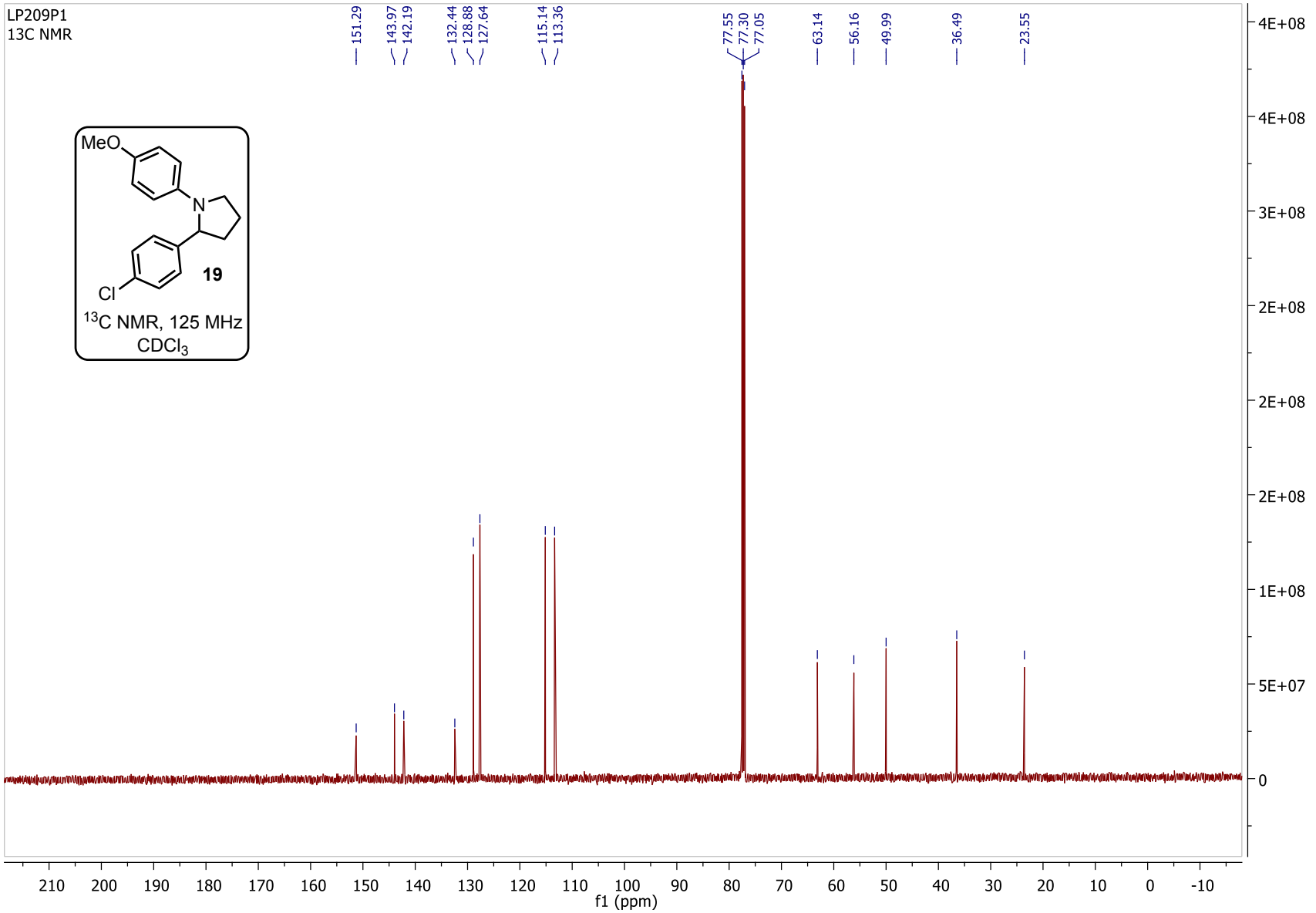

LP327P
1H NMR
Ph
N
17
^{1}H NMR, 500 MHz
$CDCl_3$
f1 (ppm)

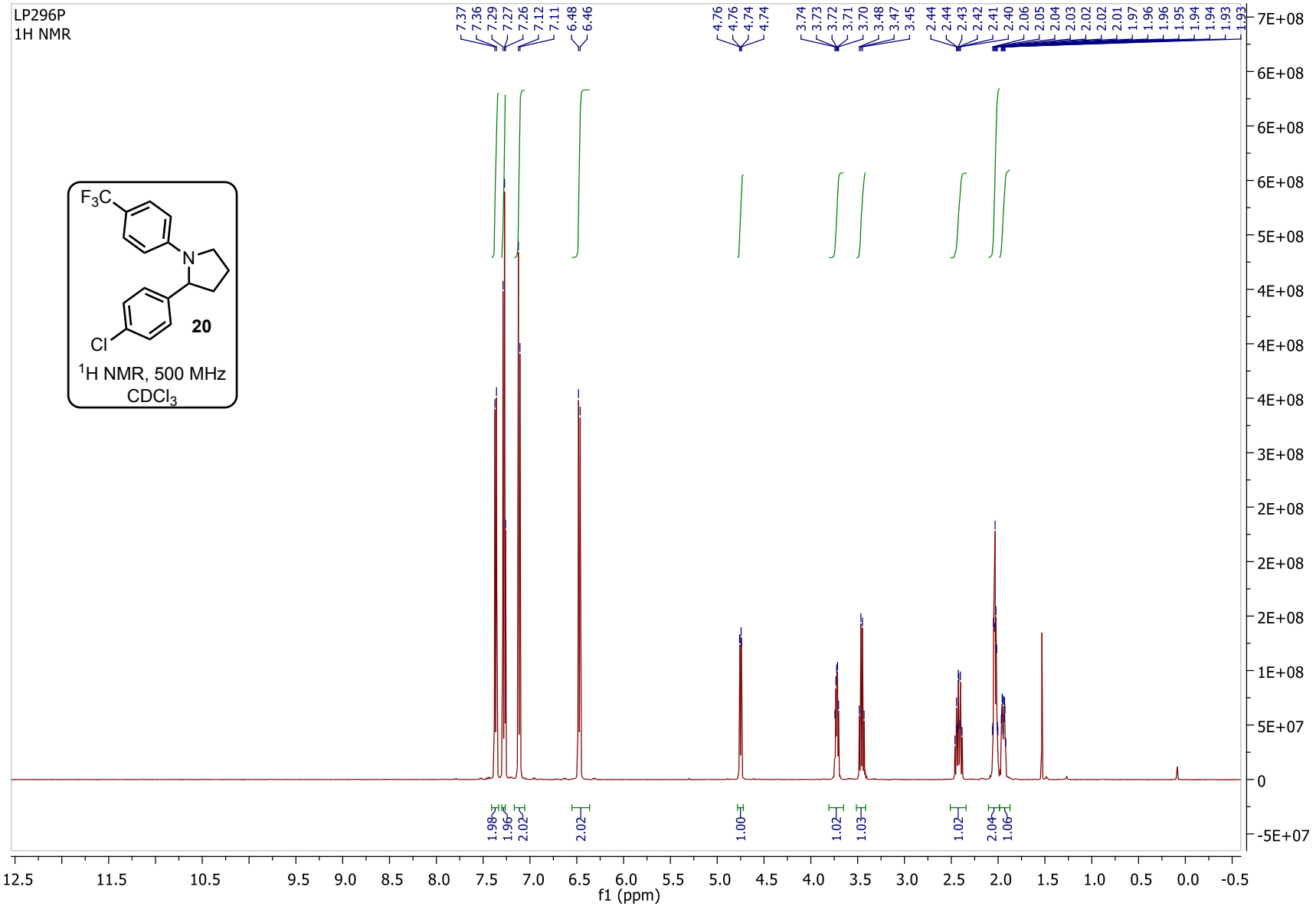

LP327P
13C NMR
147.56
142.44
132.91
129.28
128.64
128.13
127.92
126.27
125.69
124.85
112.74
77.55
77.30
77.05
63.53
49.54
36.23
23.44
Ph
N
17
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

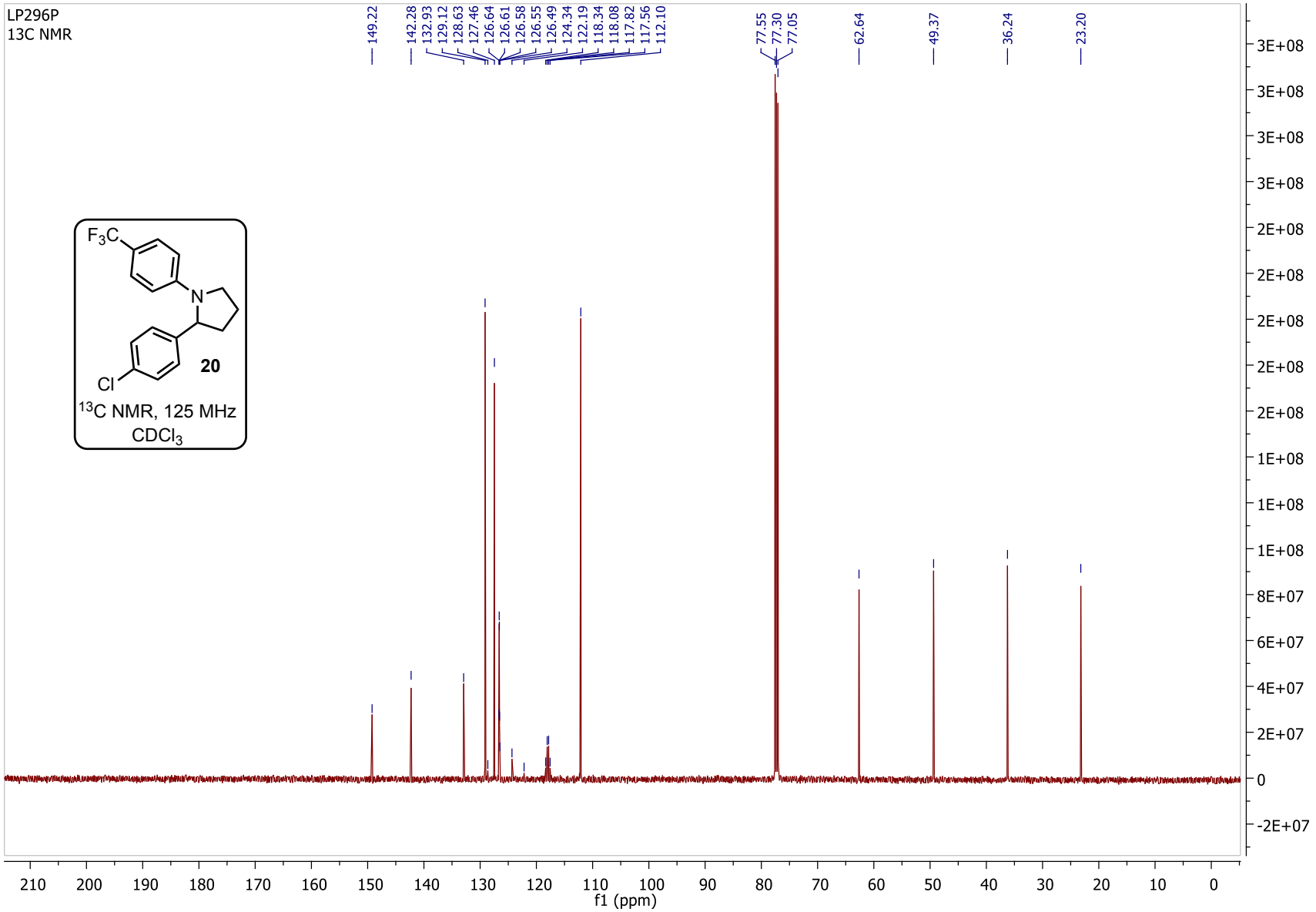

LP196P
1H NMR
NC
N
Cl
18
1H NMR, 500 MHz
CDCl3
f1 (ppm)

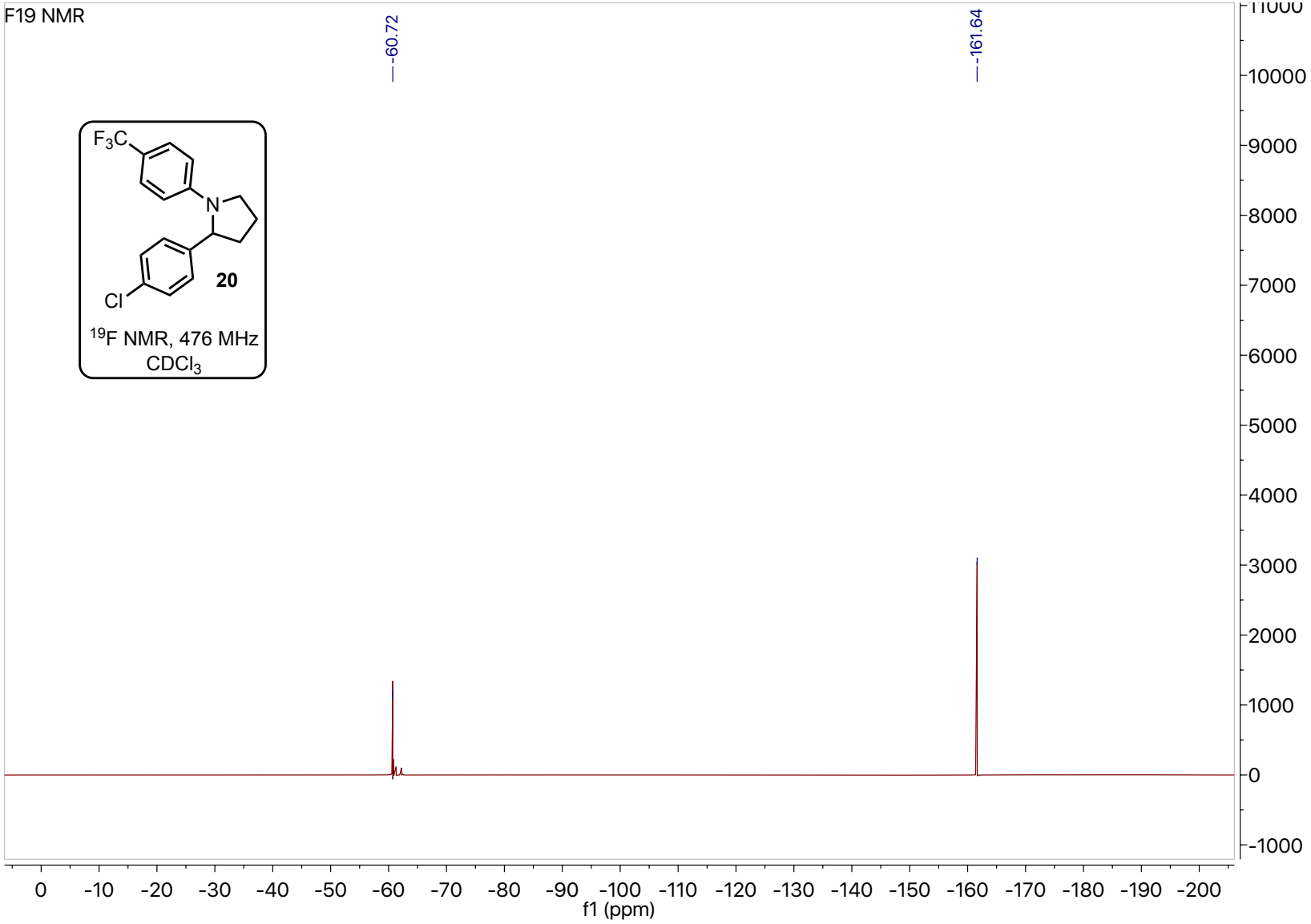

LP196P
13C NMR
149.59
141.52
133.64
133.12
129.20
127.34
120.88
112.73
98.08
77.55
77.30
77.05
62.57
49.28
36.12
23.05
NC
N
Cl
18
13C NMR, 125 MHz
CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

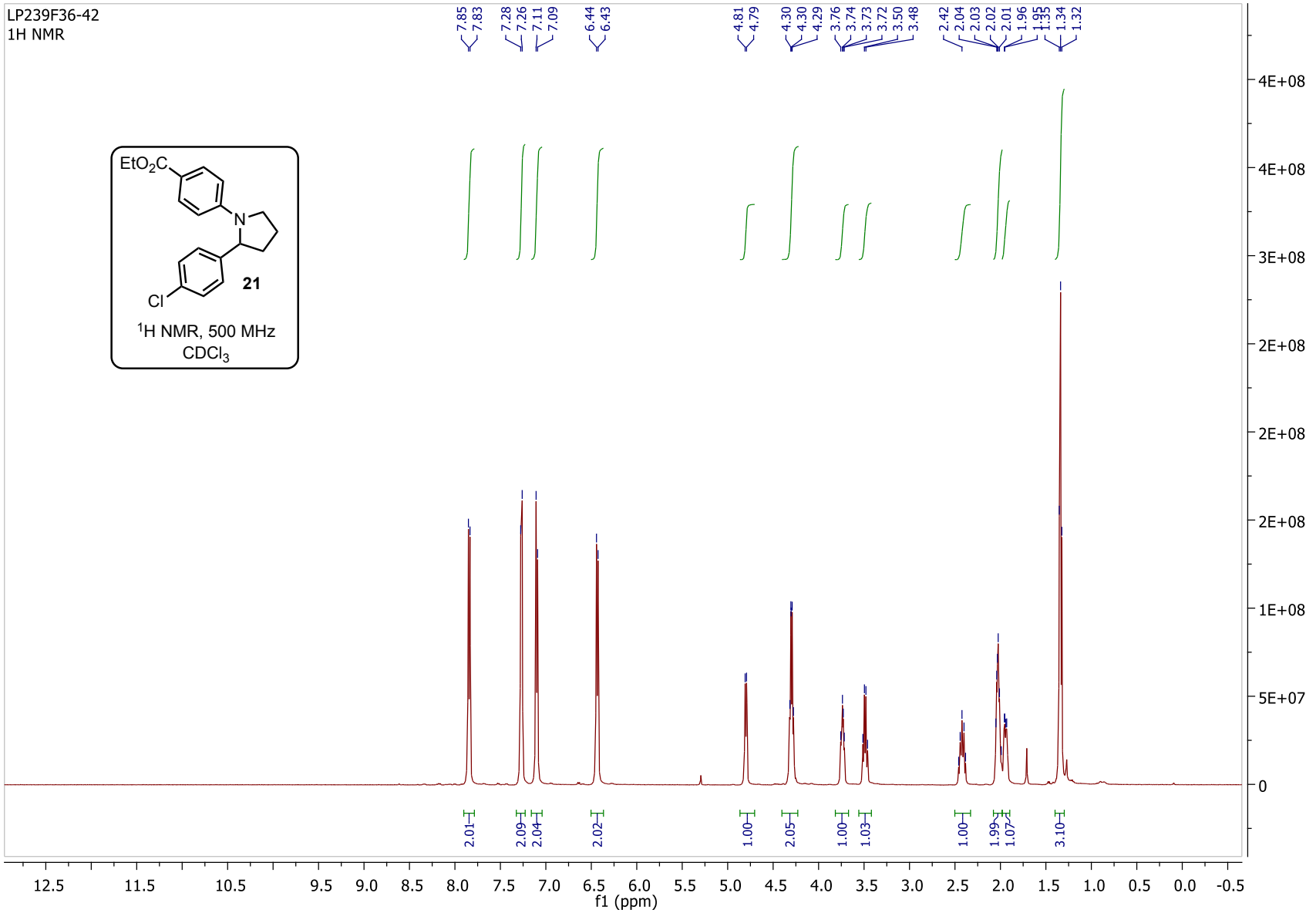

LP209P
1H NMR
MeO
N
Cl
19
1H NMR, 500 MHz
CDCl3
7.27 7.26 7.25 7.25 7.25 7.18 7.16 6.77 6.75 6.42 6.40
4.60 4.59 4.58 4.58
3.71 3.71 3.70 3.69 3.67 3.67 3.35 3.33
2.40 2.38 2.36 2.36 2.01 1.99 1.99 1.98 1.98 1.97 1.96 1.96 1.95 1.89 1.88 1.87 1.87 1.86 1.86 1.85
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
2.93 2.00 2.08 2.00 1.02 2.86 1.13 1.03 1.05 2.11 1.04
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

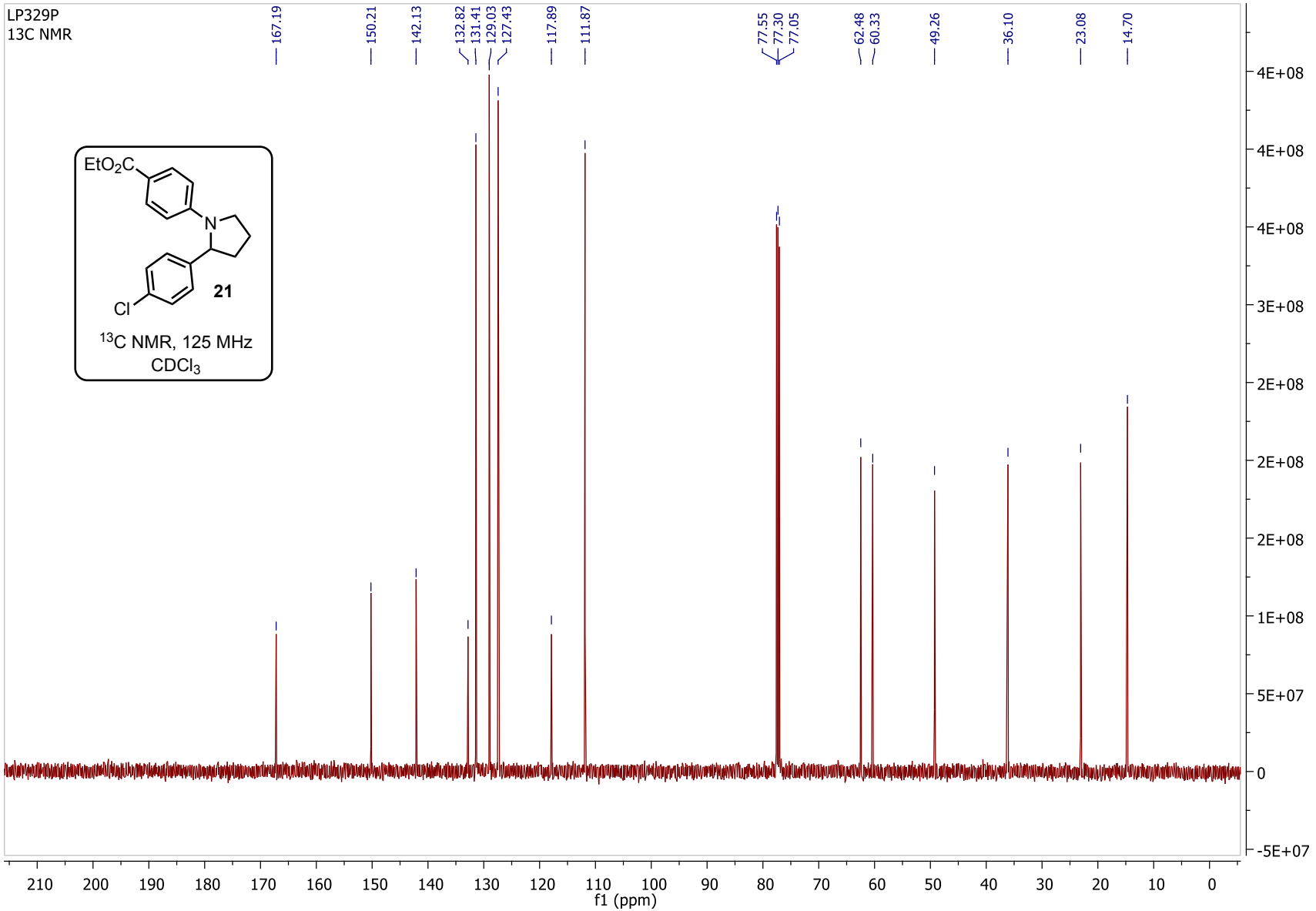

LP209P1
13C NMR
151.29
143.97
142.19
132.44
128.88
127.64
115.14
113.36
77.55
77.30
77.05
63.14
56.16
49.99
36.49
23.55
MeO
N
Cl
19
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

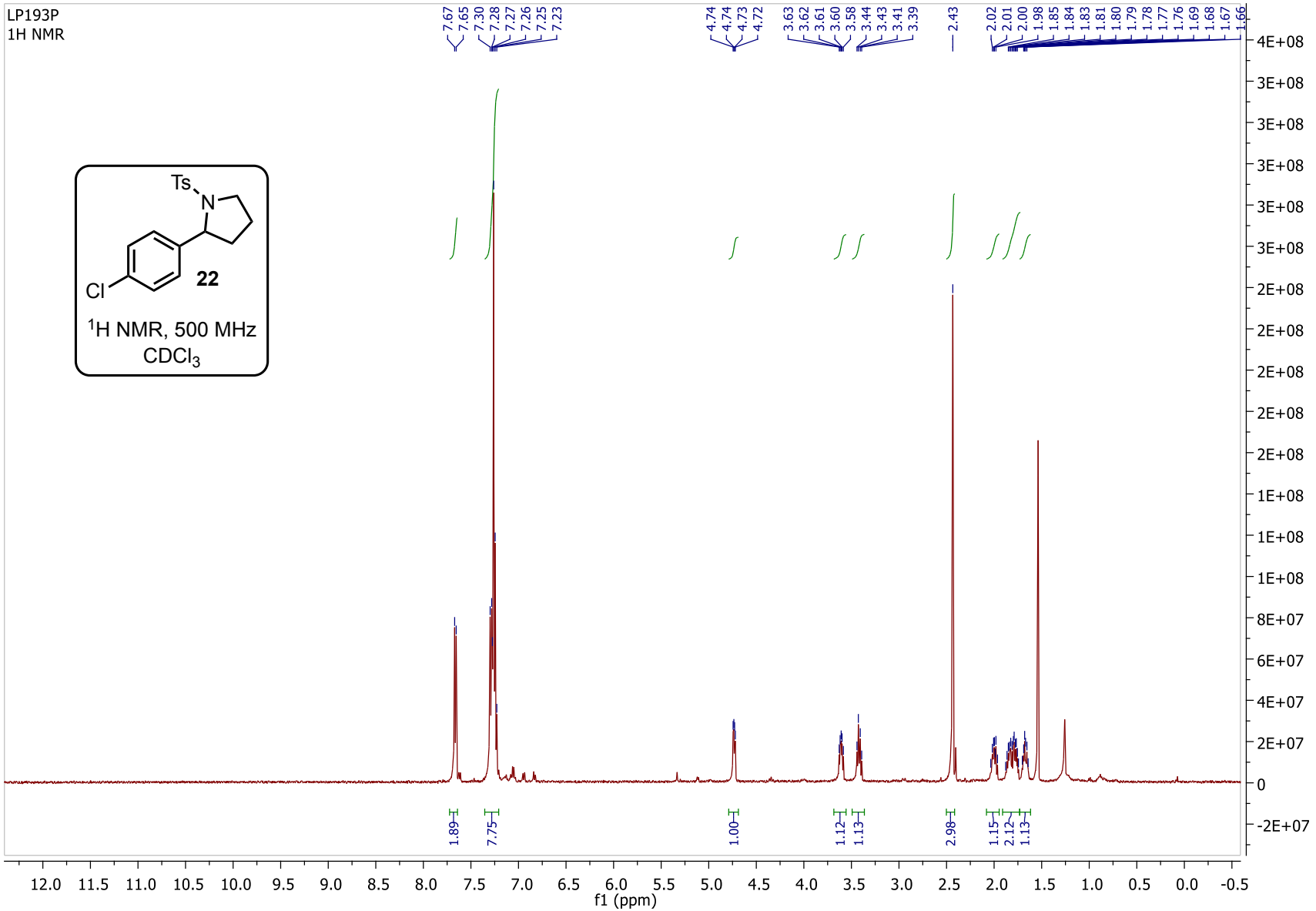

LP296P
1H NMR
F3C
N
Cl
20
1H NMR, 500 MHz
CDCl3
f1 (ppm)

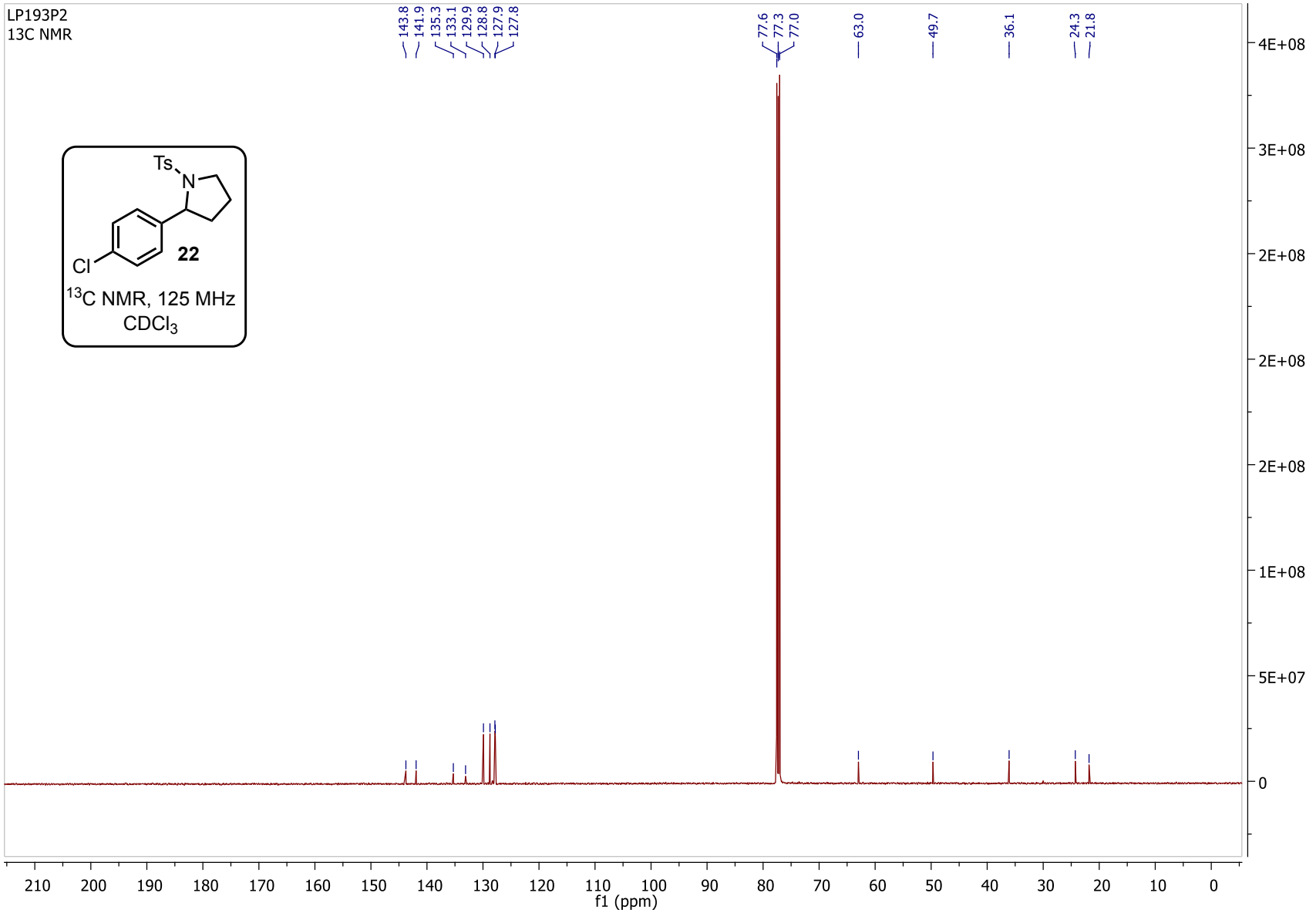

LP296P
13C NMR
149.22
142.28
132.93
129.12
128.63
127.46
126.64
126.61
126.58
126.55
126.49
124.34
122.19
118.34
118.08
117.82
117.56
112.10
77.55
77.30
77.05
62.64
49.37
36.24
23.20
F3C
N
Cl
20
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

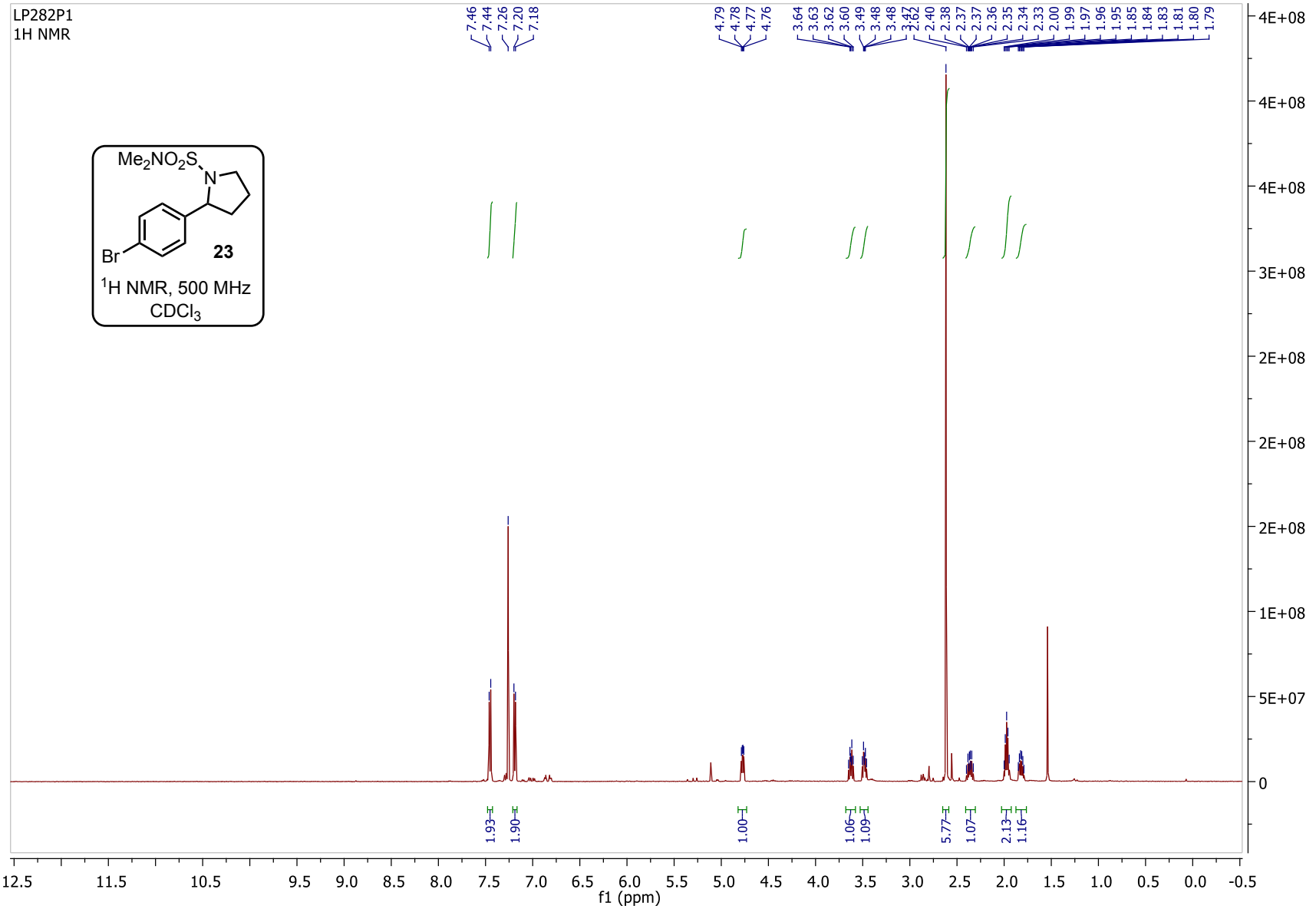

F19 NMR
-60.72
-161.64
F3C
N
Cl
20
19F NMR, 476 MHz
CDCl3
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

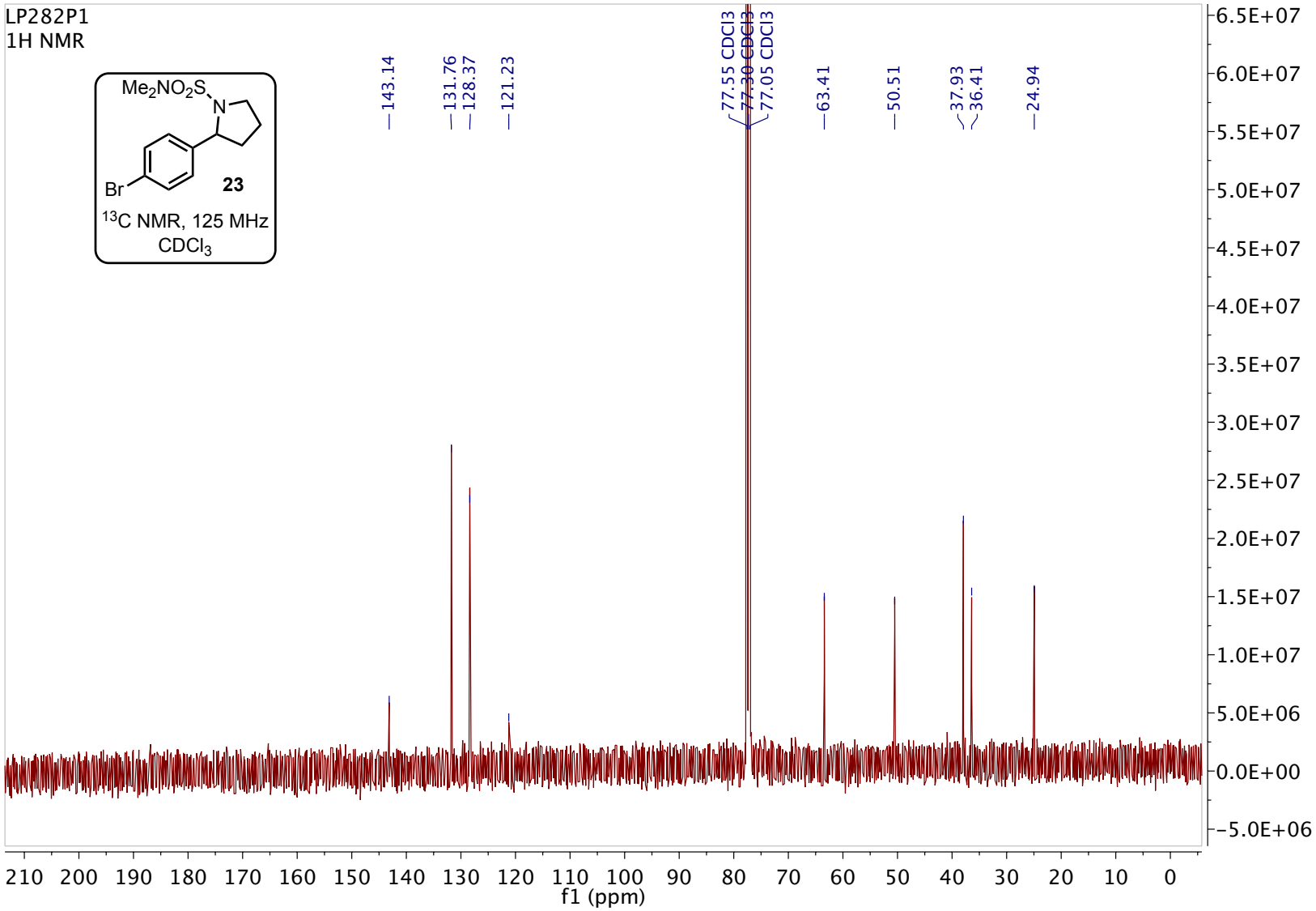

LP239F36-42
1H NMR
7.85
7.83
7.28
7.26
7.11
7.09
6.44
6.43
4.81
4.79
4.30
4.30
4.29
3.76
3.74
3.73
3.72
3.50
3.48
2.42
2.04
2.03
2.02
2.01
1.96
1.95
1.34
1.32
EtO2C
N
Cl
21
1H NMR, 500 MHz
CDCl3
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
2.01
2.09
2.04
2.02
1.00
2.05
1.00
1.03
1.00
1.99
1.07
3.10
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

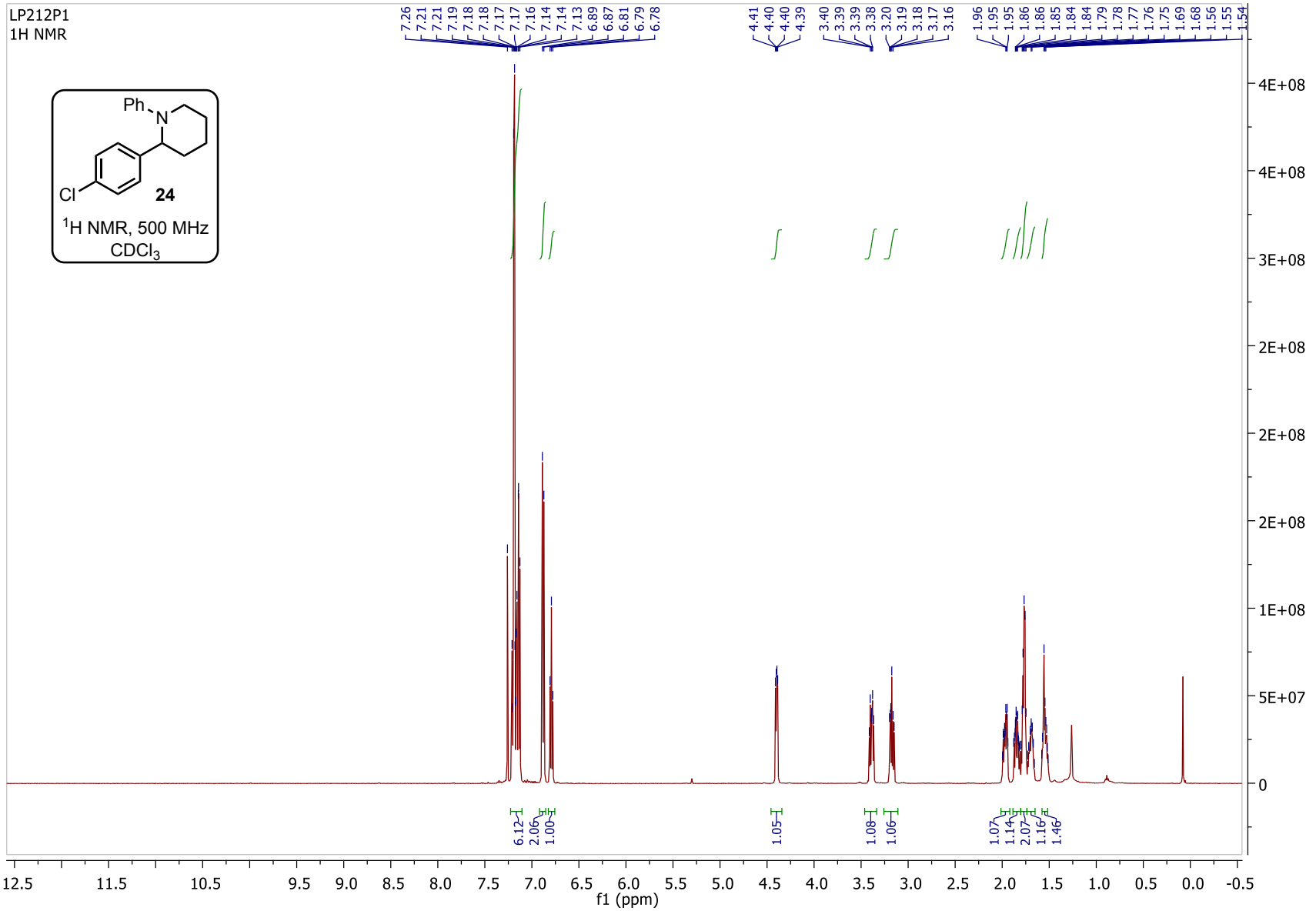

LP329P
13C NMR
167.19
150.21
142.13
132.82
131.41
129.03
127.43
117.89
111.87
77.55
77.30
77.05
62.48
60.33
49.26
36.10
23.08
14.70
EtO2C
N
Cl
21
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

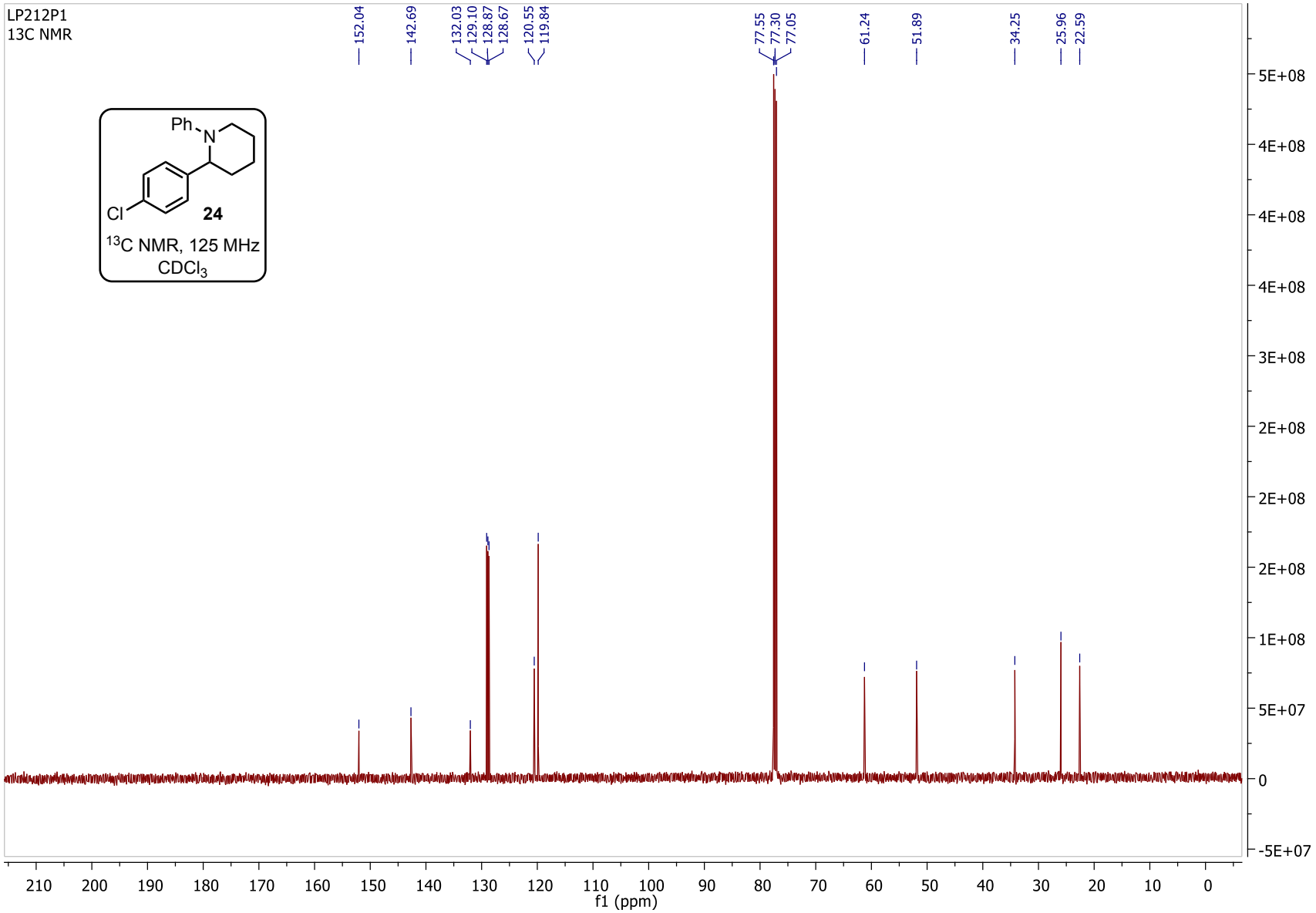

LP193P
1H NMR
Ts
N
Cl
22
^{1}H NMR, 500 MHz
$CDCl_3$
f1 (ppm)

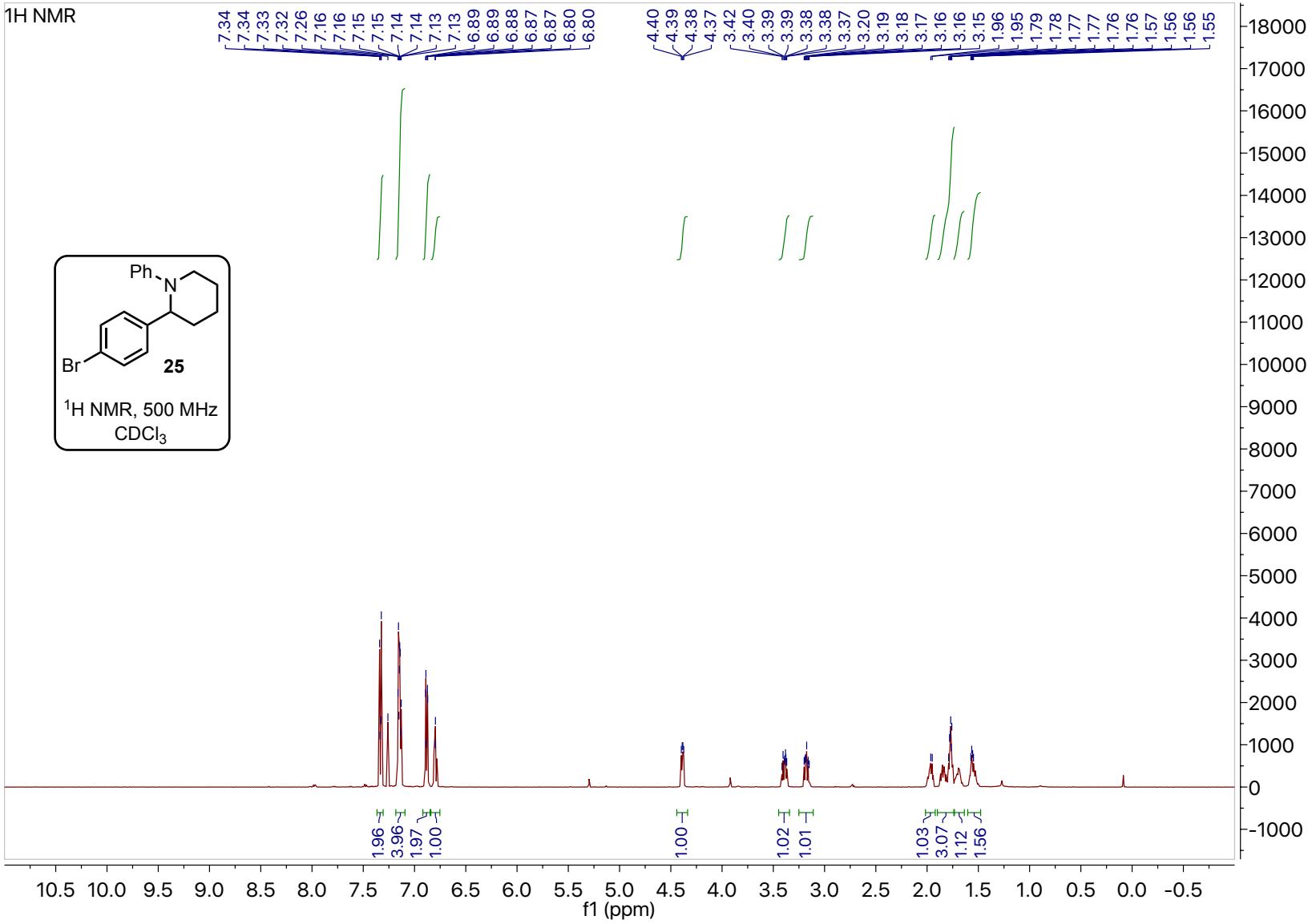

LP193P2
13C NMR
143.8
141.9
135.3
133.1
129.9
128.8
127.9
127.8
77.6
77.3
77.0
63.0
49.7
36.1
24.3
21.8
Ts
N
Cl
22
13C NMR, 125 MHz
CDCl3
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

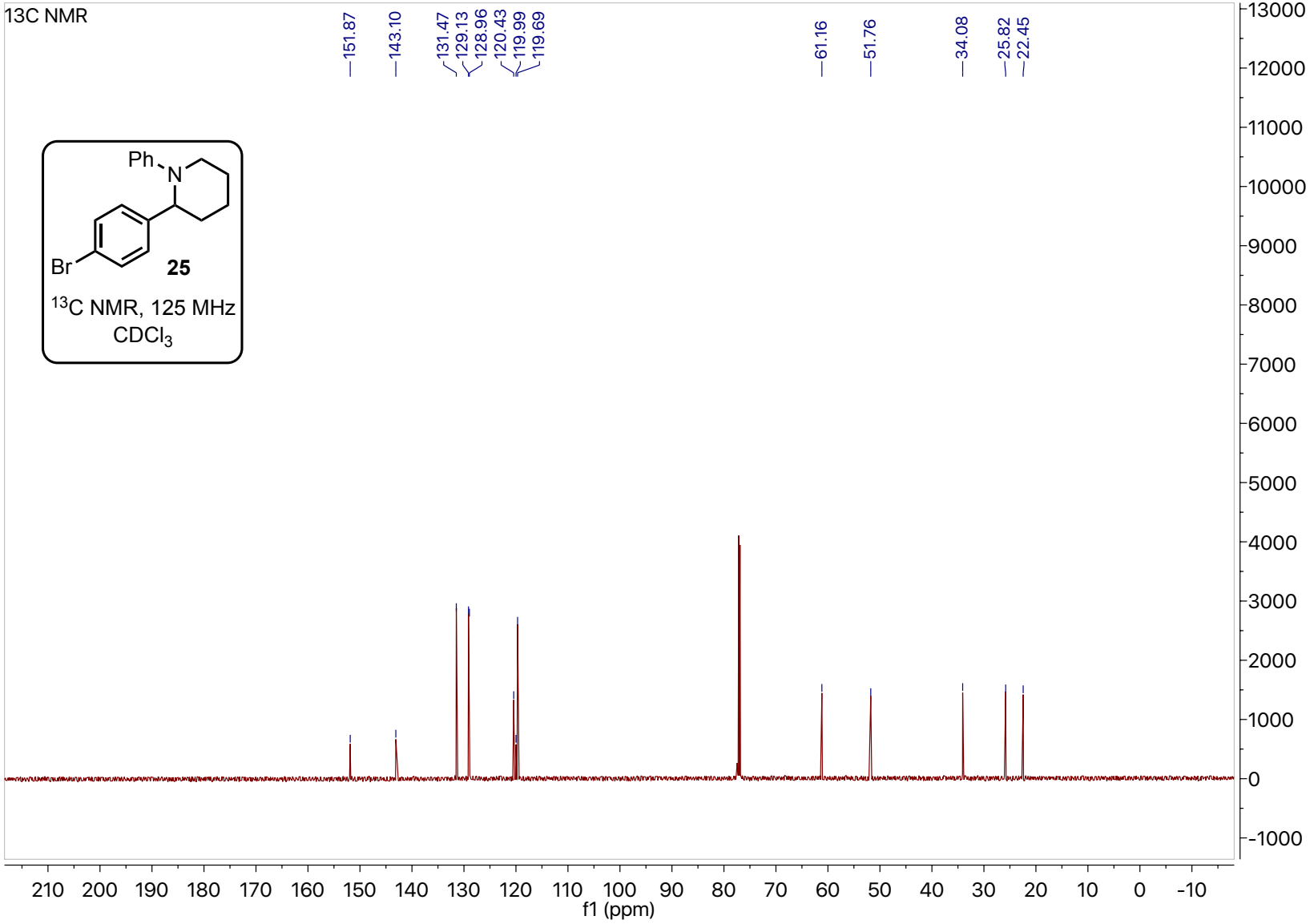

LP282P1
1H NMR
Me2NO2S
N
Br
23
1H NMR, 500 MHz
CDCl3
f1 (ppm)

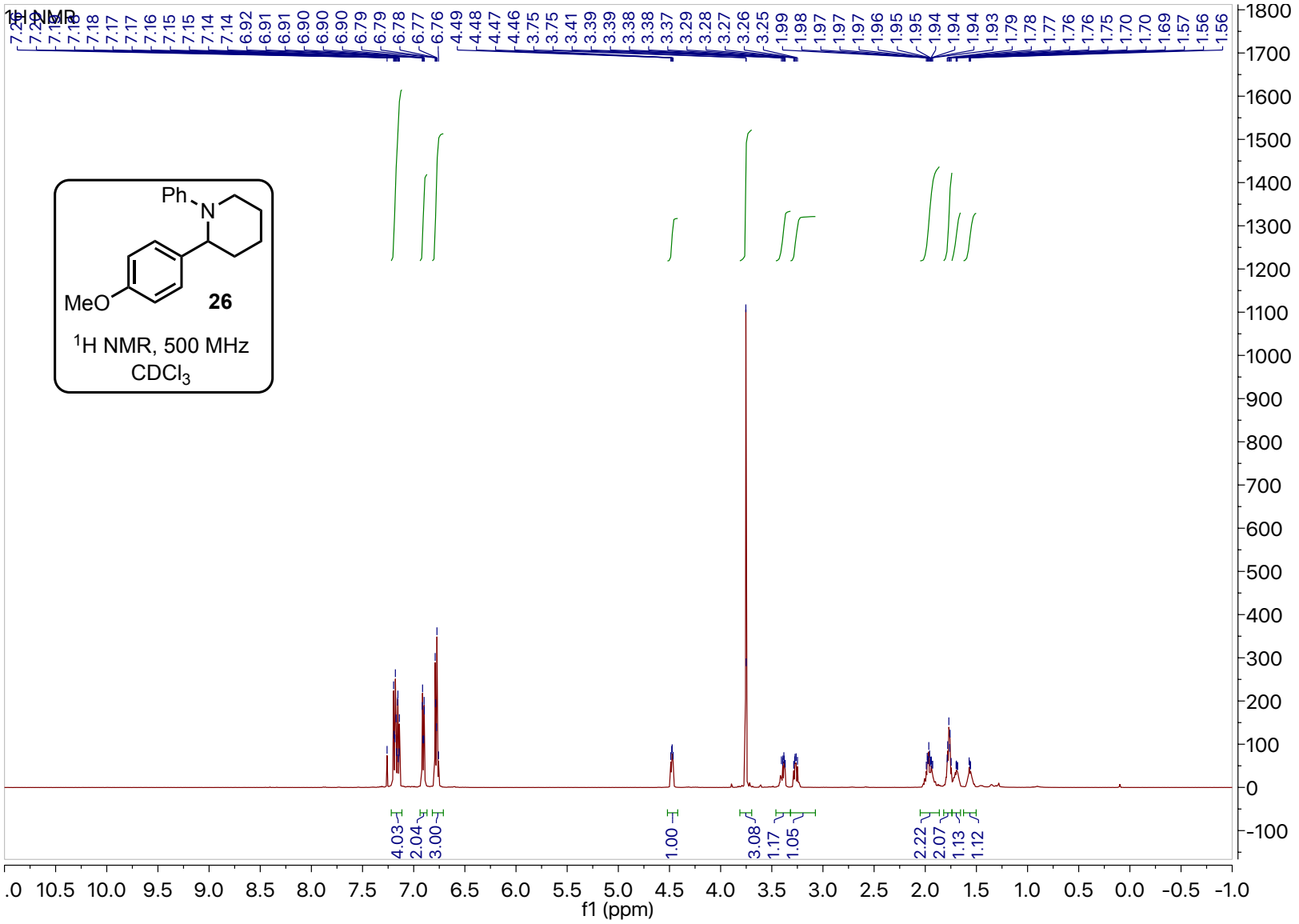

LP282P1
1H NMR
Me2NO2S
N
Br
23
13C NMR, 125 MHz
CDCl3
143.14
131.76
128.37
121.23
77.55 CDCl3
77.30 CDCl3
77.05 CDCl3
63.41
50.51
37.93
36.41
24.94
6.5E+07
6.0E+07
5.5E+07
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
-5.0E+06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

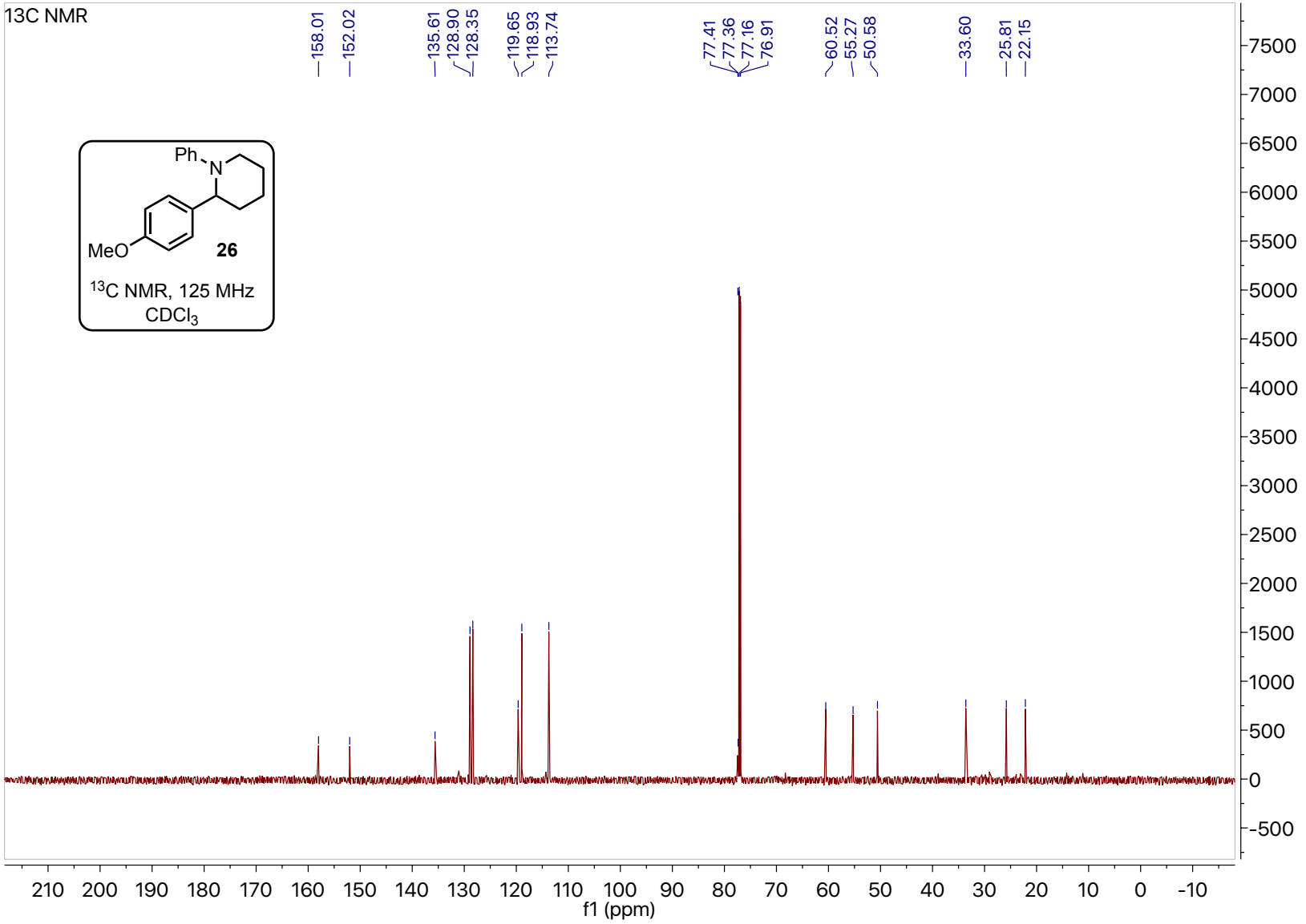

LP212P1
1H NMR
Ph
N
Cl
24
1H NMR, 500 MHz
CDCl3
7.26 7.21 7.21 7.19 7.18 7.18 7.17 7.17 7.16 7.14 7.14 7.13 6.89 6.87 6.81 6.79 6.78
4.41 4.40 4.40 4.39
3.40 3.39 3.39 3.38 3.20 3.19 3.18 3.17 3.16
1.96 1.95 1.95 1.86 1.86 1.85 1.84 1.84 1.79 1.78 1.77 1.76 1.75 1.69 1.68 1.56 1.55 1.54
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
6.12 2.06 1.00 1.05 1.08 1.06 1.07 1.14 2.07 1.16 1.46
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

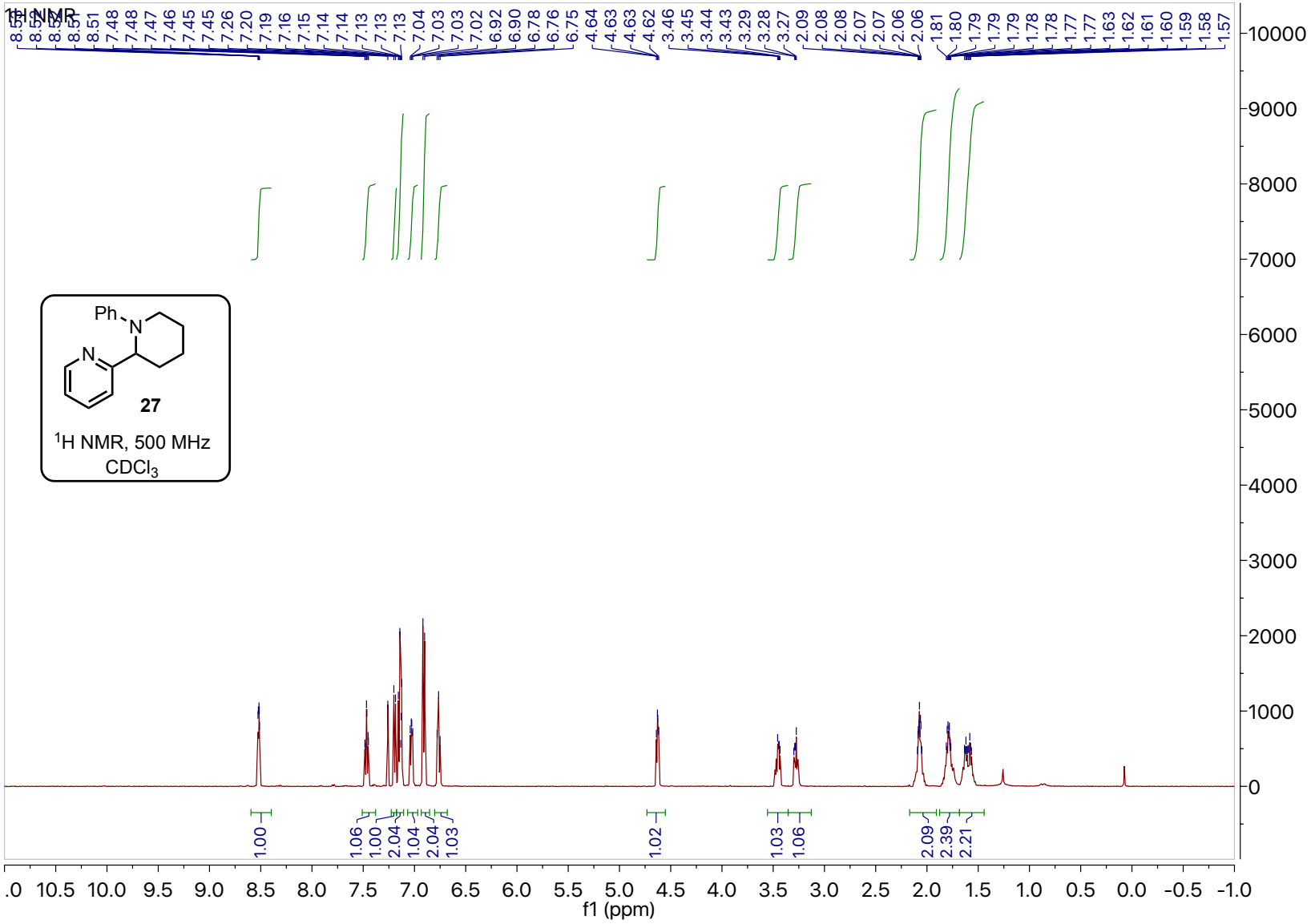

LP212P1
13C NMR
152.04
142.69
132.03
129.10
128.87
128.67
120.55
119.84
77.55
77.30
77.05
61.24
51.89
34.25
25.96
22.59
Ph
N
Cl
24
13C NMR, 125 MHz
CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

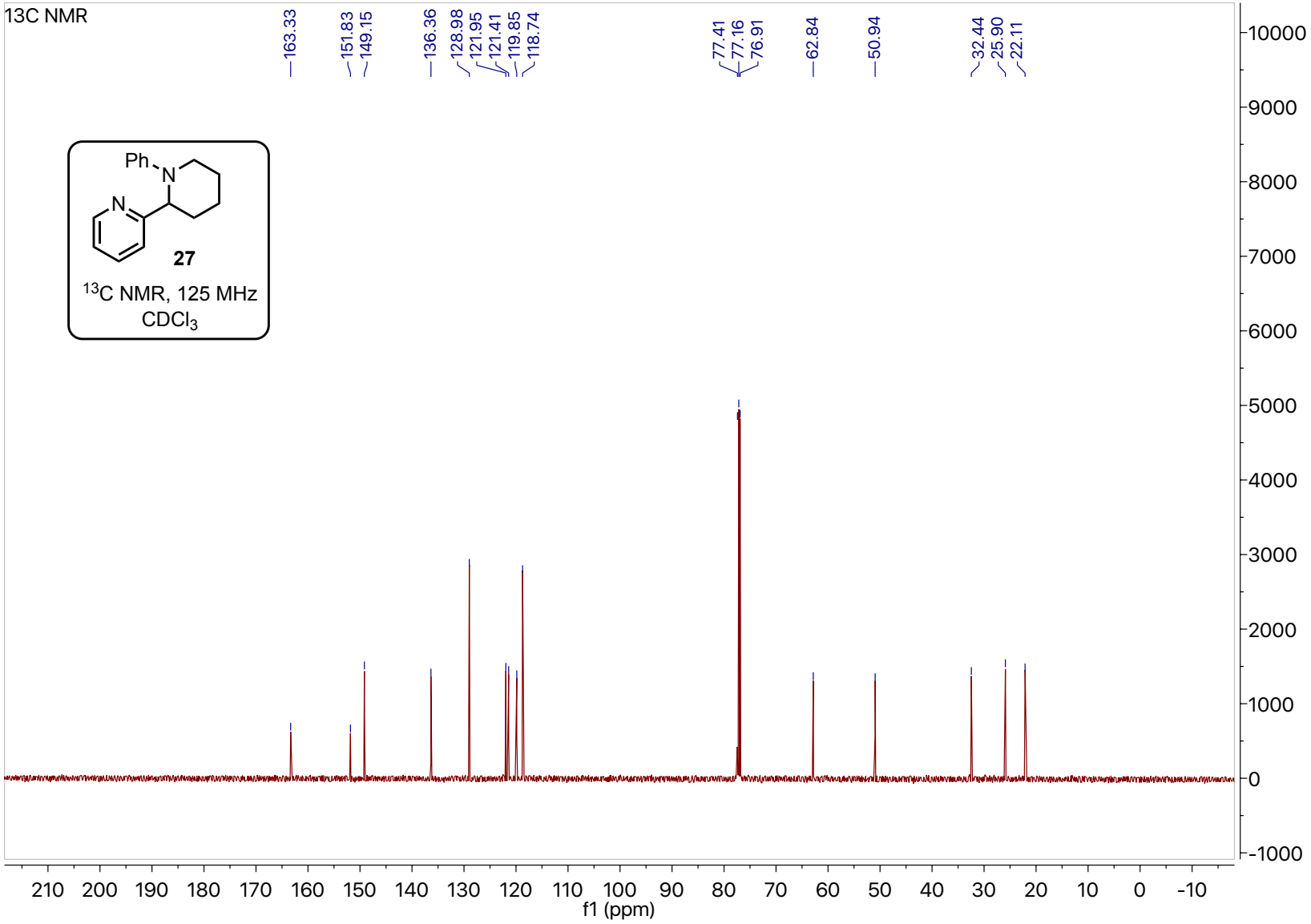

1H NMR
7.34 7.34 7.33 7.32 7.26 7.16 7.16 7.15 7.15 7.14 7.14 7.13 7.13 6.89 6.89 6.88 6.87 6.87 6.80 6.80
4.40 4.39 4.38 4.37 3.42 3.40 3.39 3.39 3.38 3.38 3.37 3.20 3.19 3.18 3.17 3.16 3.16 3.15 1.96 1.95 1.79 1.78 1.77 1.77 1.76 1.76 1.57 1.56 1.56 1.55
Ph
N
Br
25
1H NMR, 500 MHz
CDCl3
1.96 3.96 1.97 1.00 1.00 1.02 1.01 1.03 3.07 1.12 1.56
18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

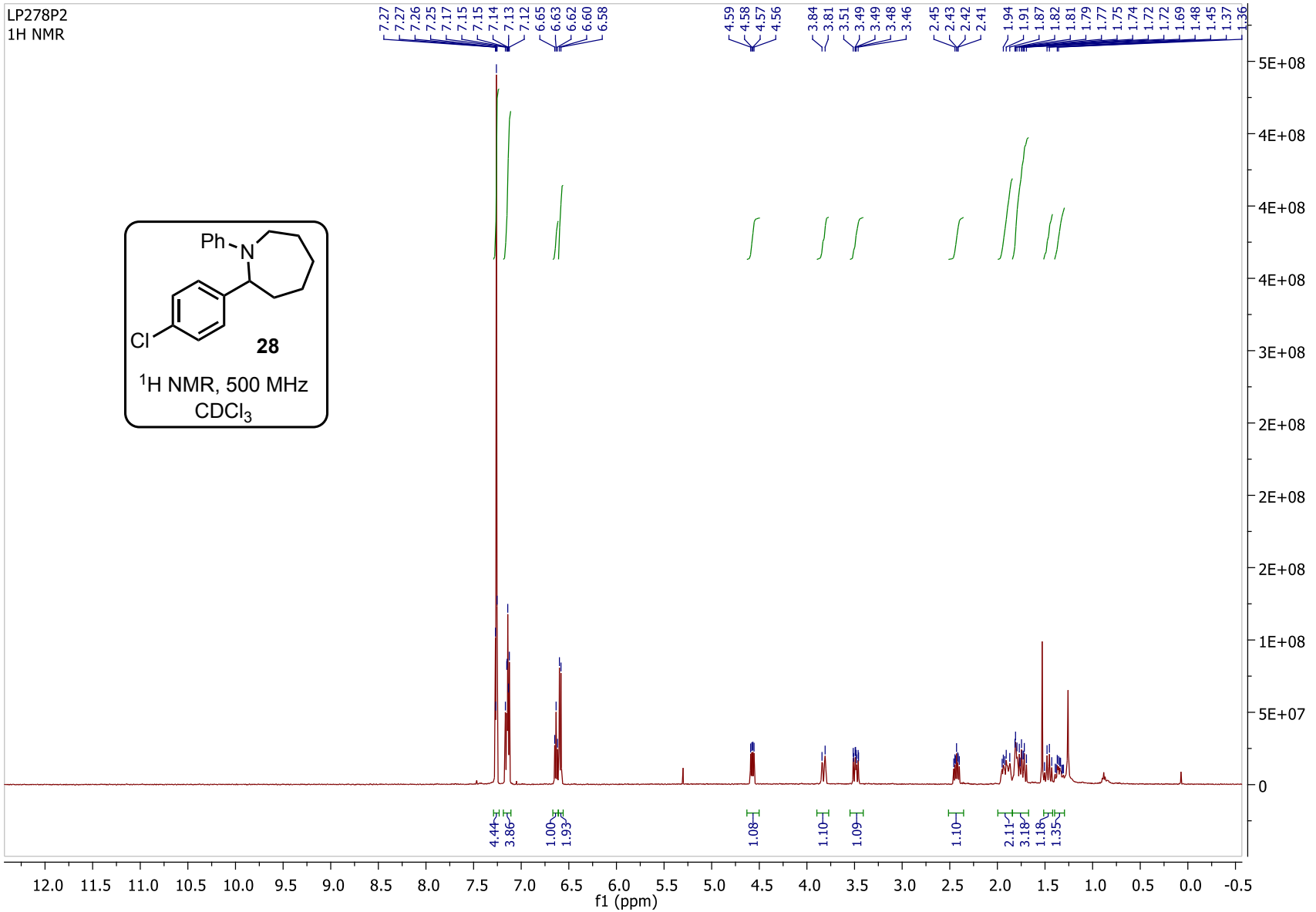

13C NMR
151.87
143.10
131.47
129.13
128.96
120.43
119.99
119.69
61.16
51.76
34.08
25.82
22.45
Ph
N
Br
25
13C NMR, 125 MHz
CDCl3
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

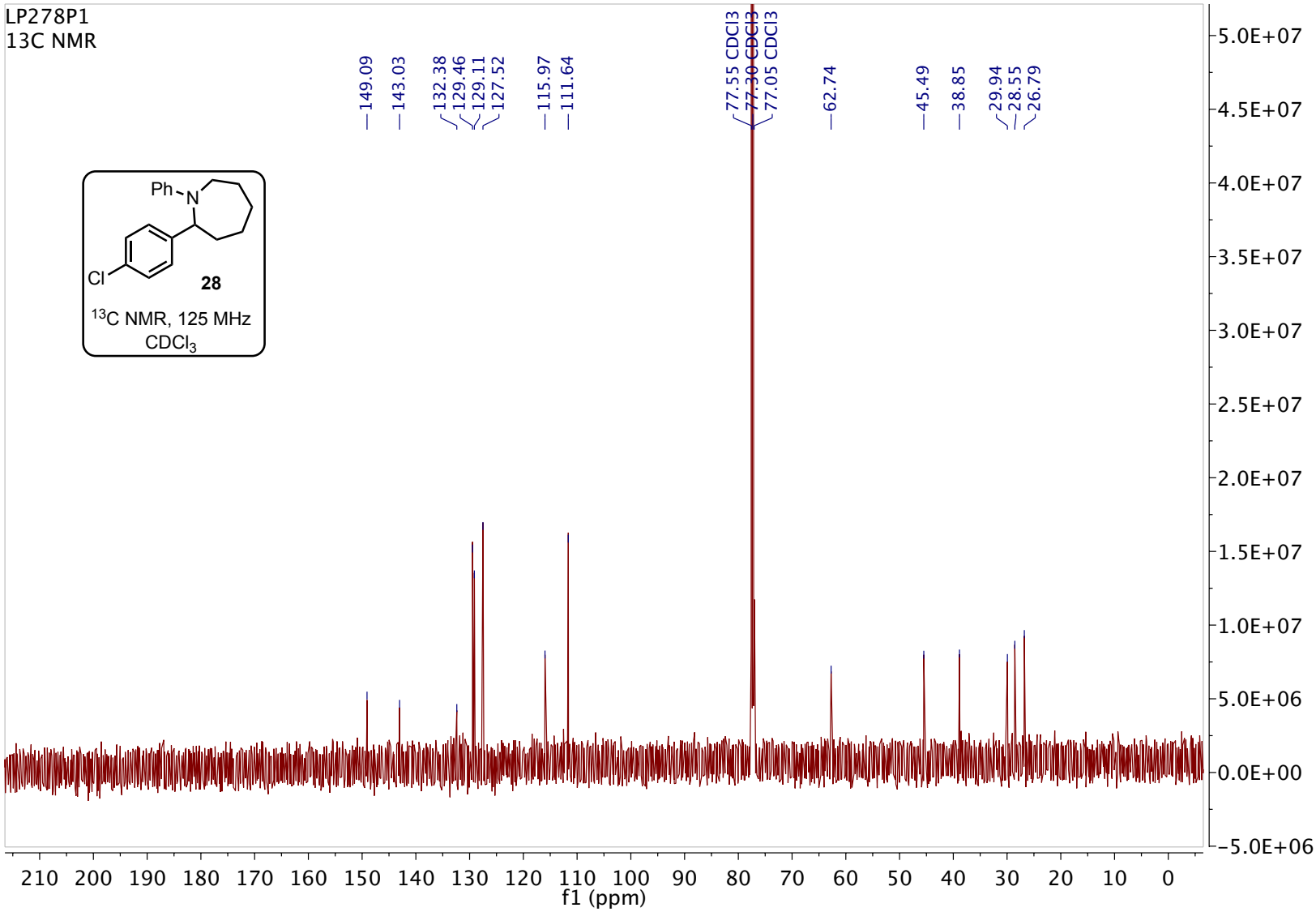

1H NMR
Ph
N
MeO
26
1H NMR, 500 MHz
CDCl3
f1 (ppm)

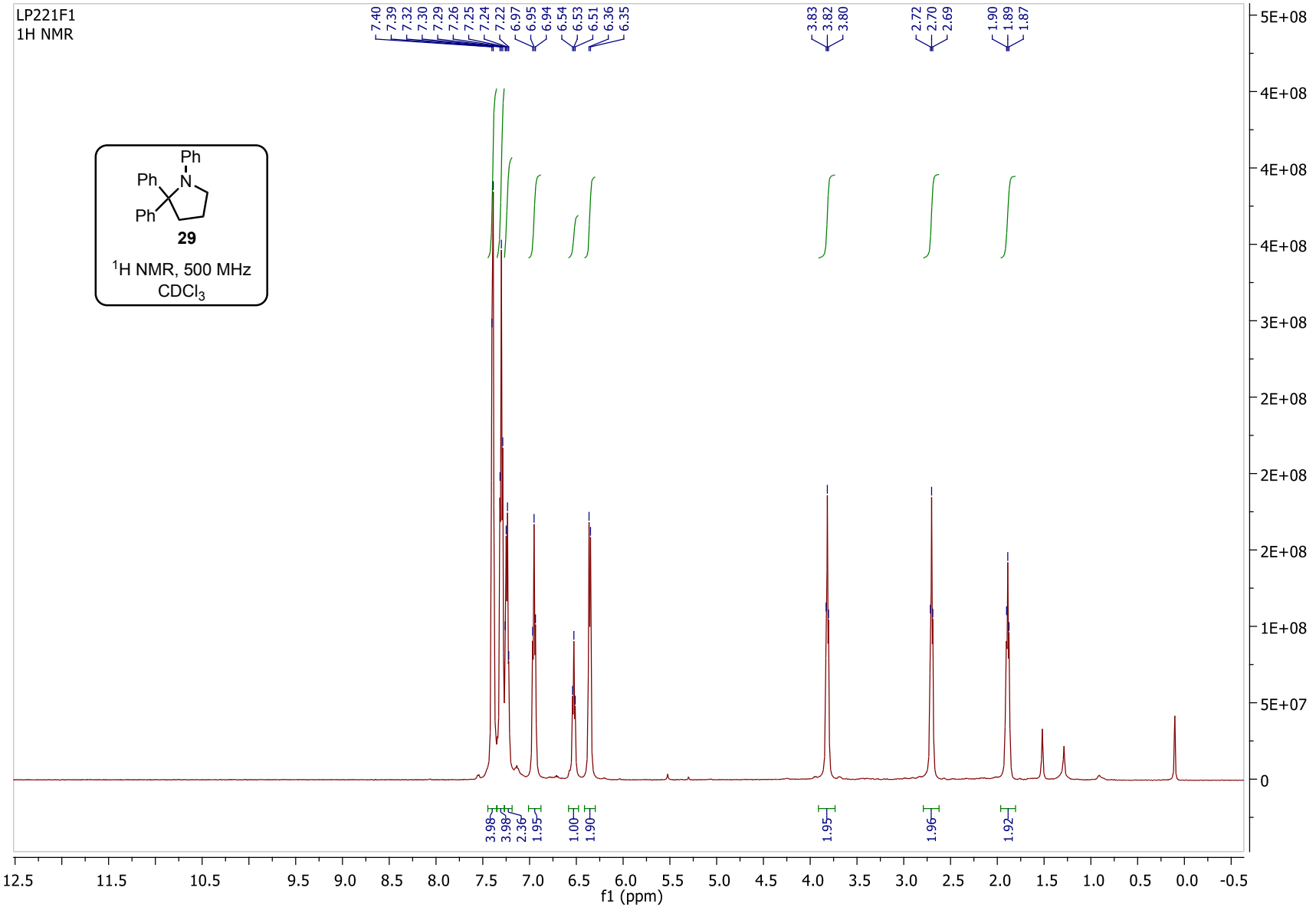

13C NMR
158.01
152.02
135.61
128.90
128.35
119.65
118.93
113.74
77.41
77.36
77.16
76.91
60.52
55.27
50.58
33.60
25.81
22.15
Ph
N
MeO
26
13C NMR, 125 MHz
CDCl3
f1 (ppm)

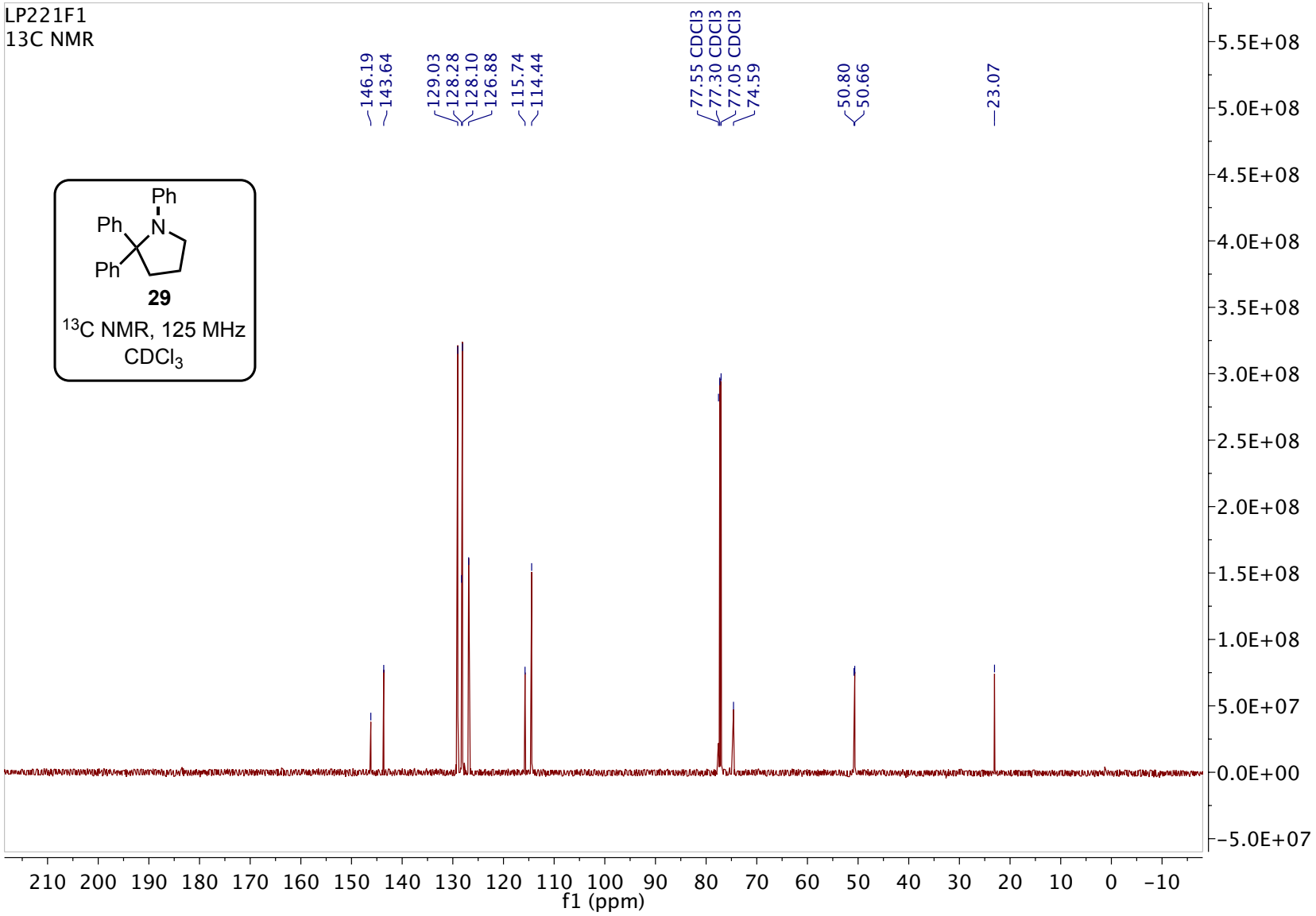

1H NMR
8.57 8.57 8.57 8.57 8.51 7.48 7.48 7.47 7.46 7.45 7.45 7.26 7.20 7.19 7.16 7.15 7.14 7.14 7.13 7.13 7.13 7.04 7.03 7.03 7.02 6.92 6.90 6.78 6.76 6.75 4.64 4.63 4.63 4.62 3.46 3.45 3.44 3.43 3.29 3.28 3.27 2.09 2.08 2.08 2.07 2.07 2.06 2.06 1.81 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.63 1.62 1.61 1.60 1.59 1.58 1.57
Ph
N
N
27
1H NMR, 500 MHz
CDCl3
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.00
1.06
1.00
2.04
1.04
2.04
1.03
1.02
1.03
1.06
2.09
2.39
2.21
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

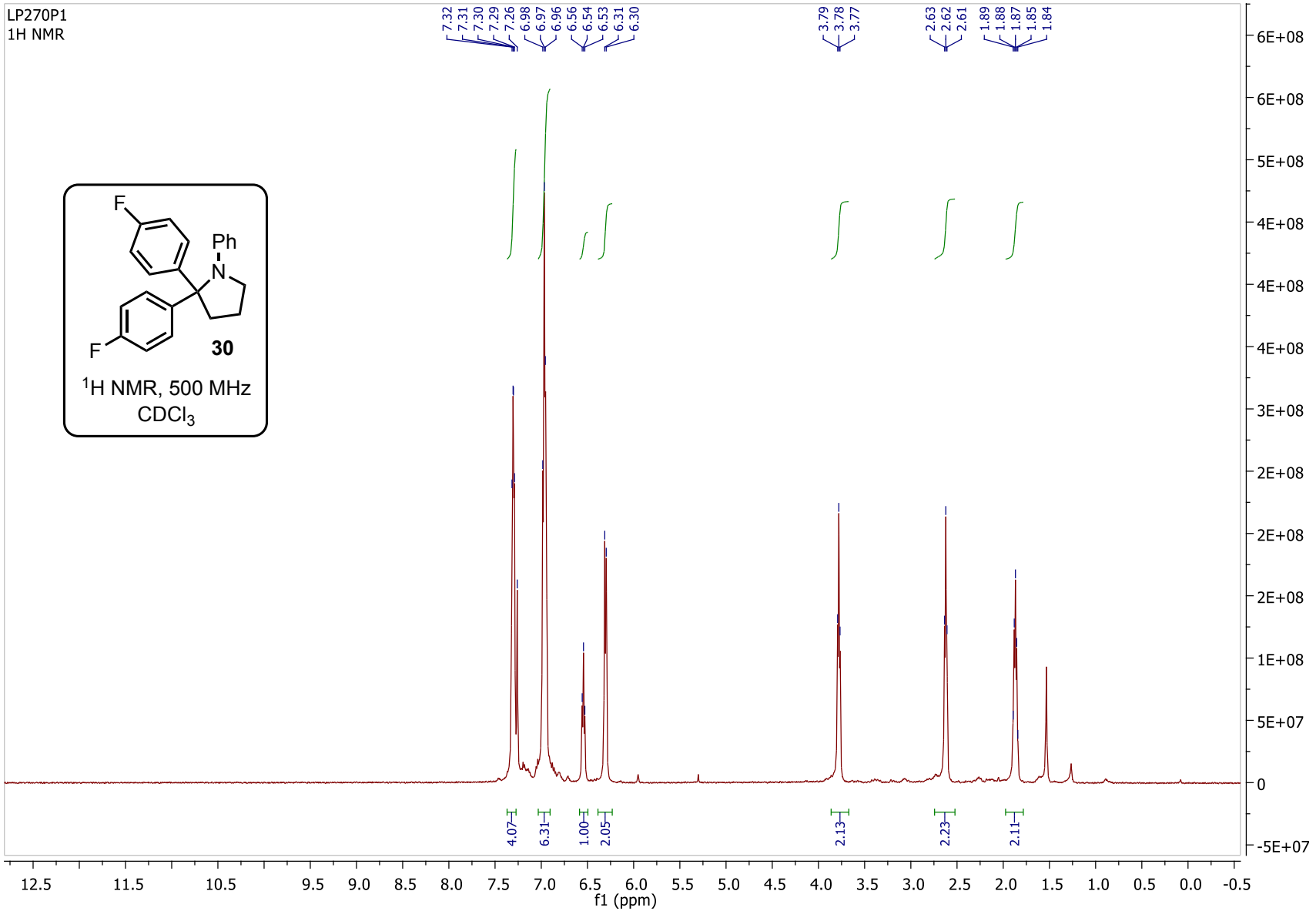

13C NMR
163.33
151.83
149.15
136.36
128.98
121.95
121.41
119.85
118.74
77.41
77.16
76.91
62.84
50.94
32.44
25.90
22.11
Ph
N
N
27
13C NMR, 125 MHz
CDCl3
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

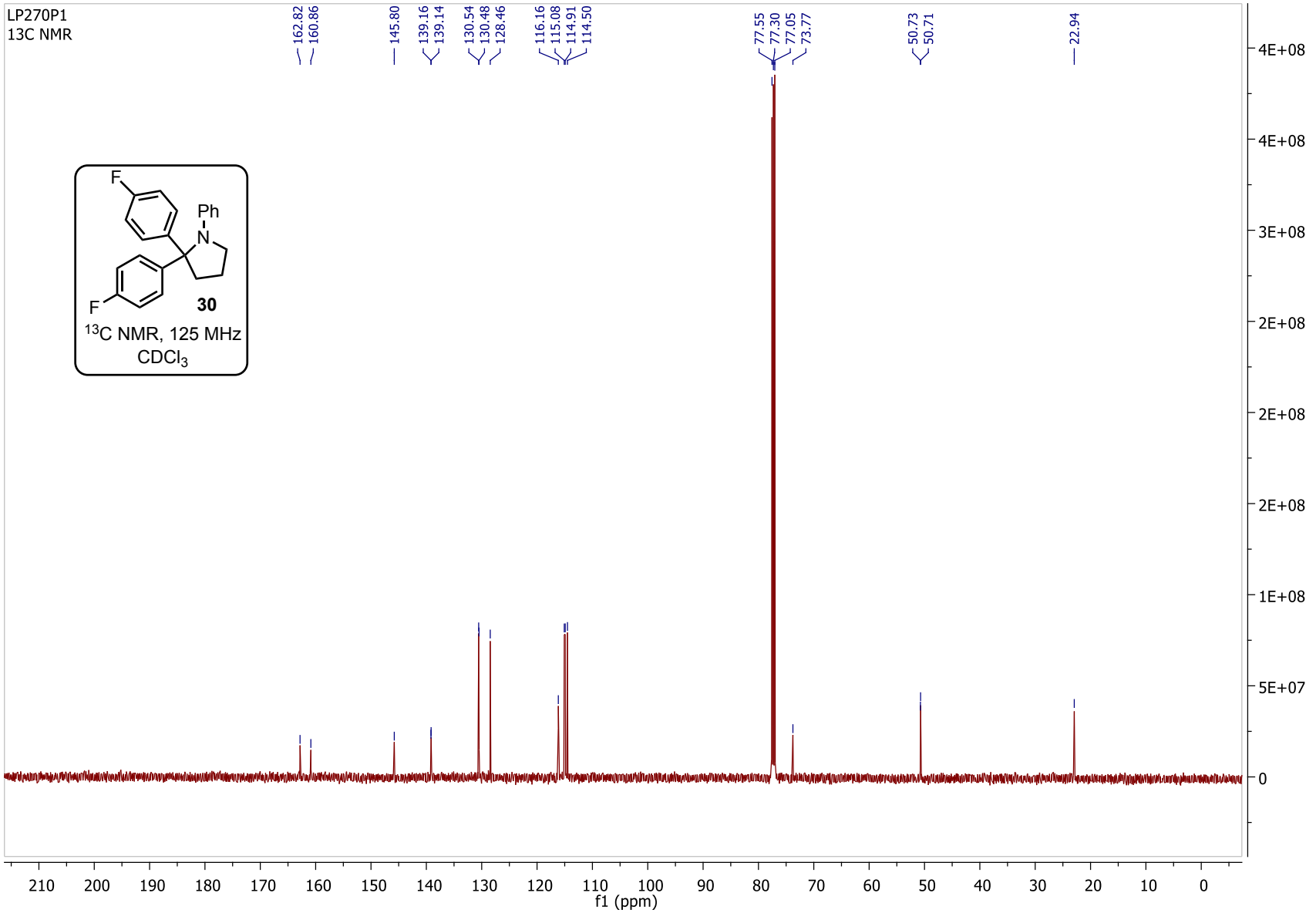

LP278P2
1H NMR
Ph
N
Cl
28
^{1}H NMR, 500 MHz
$CDCl_3$
f1 (ppm)

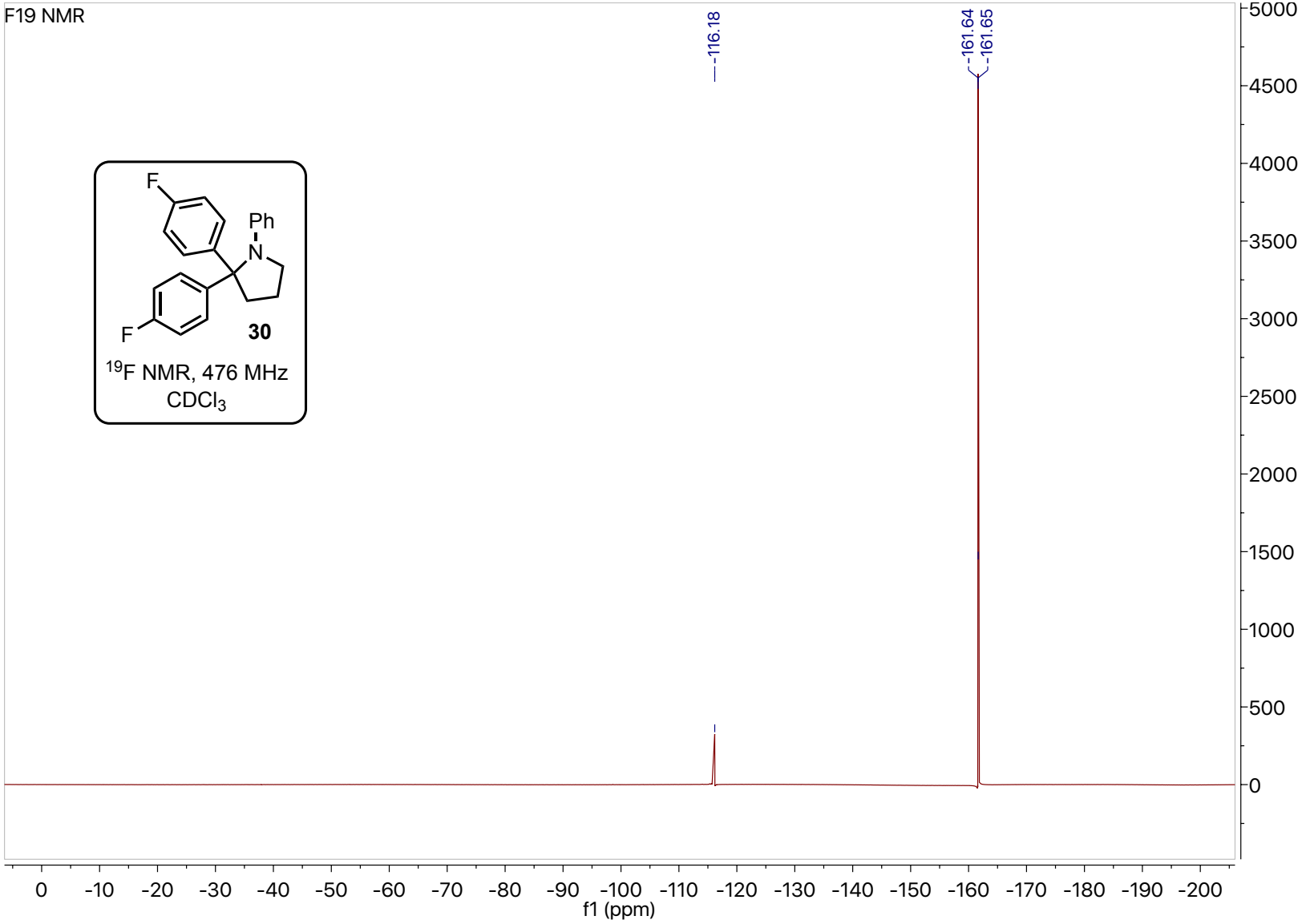

LP278P1
13C NMR
149.09
143.03
132.38
129.46
129.11
127.52
115.97
111.64
77.55 CDCl3
77.30 CDCl3
77.05 CDCl3
62.74
45.49
38.85
29.94
28.55
26.79
Ph
N
Cl
28
13C NMR, 125 MHz
CDCl3
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
-5.0E+06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

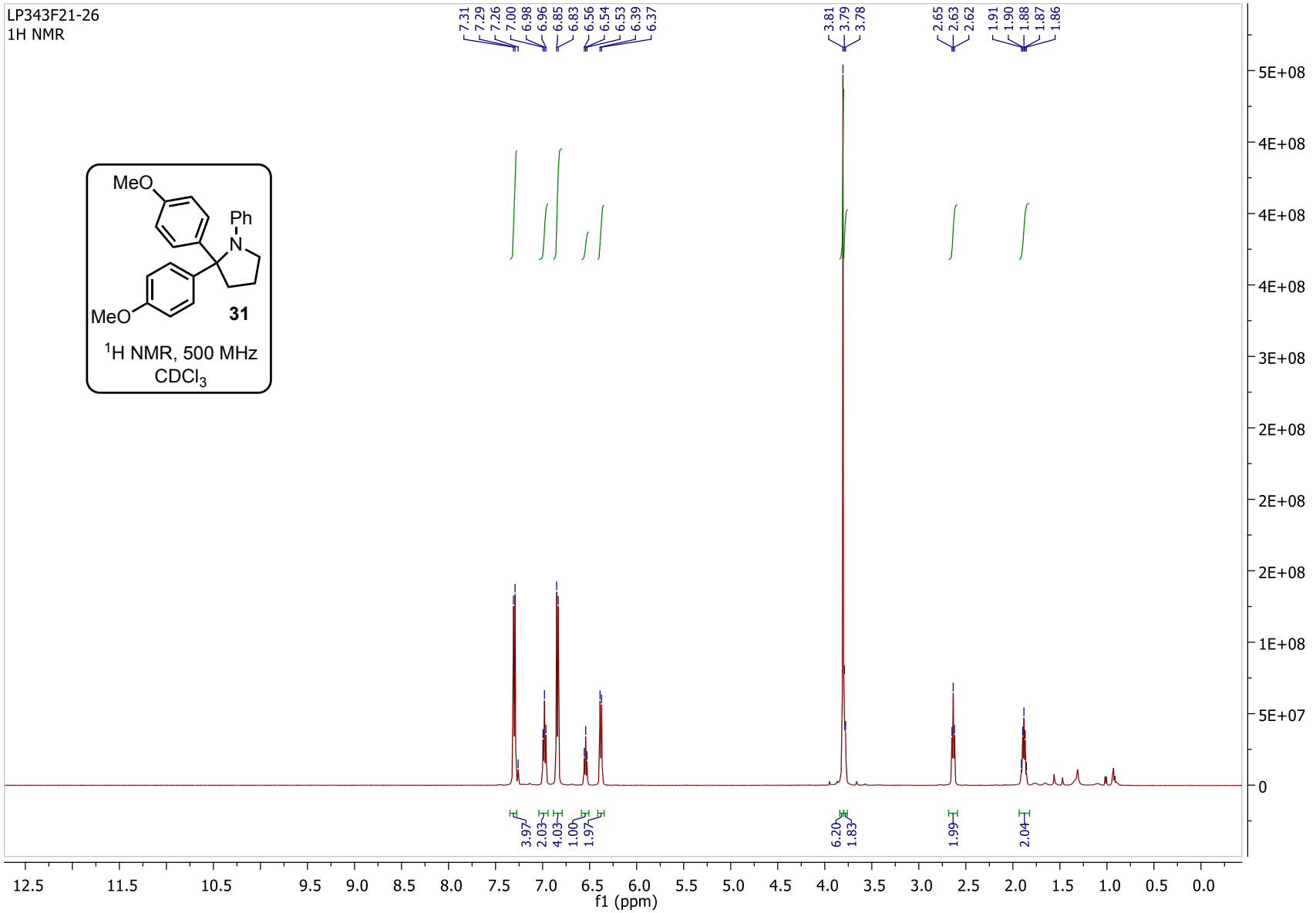

LP221F1
1H NMR
7.40
7.39
7.32
7.30
7.29
7.26
7.25
7.24
7.22
6.97
6.95
6.94
6.54
6.53
6.51
6.36
6.35
3.83
3.82
3.80
2.72
2.70
2.69
1.90
1.89
1.87
Ph
Ph
N
Ph
29
1H NMR, 500 MHz
CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
3.98
3.98
2.36
1.95
1.00
1.90
1.95
1.96
1.92
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

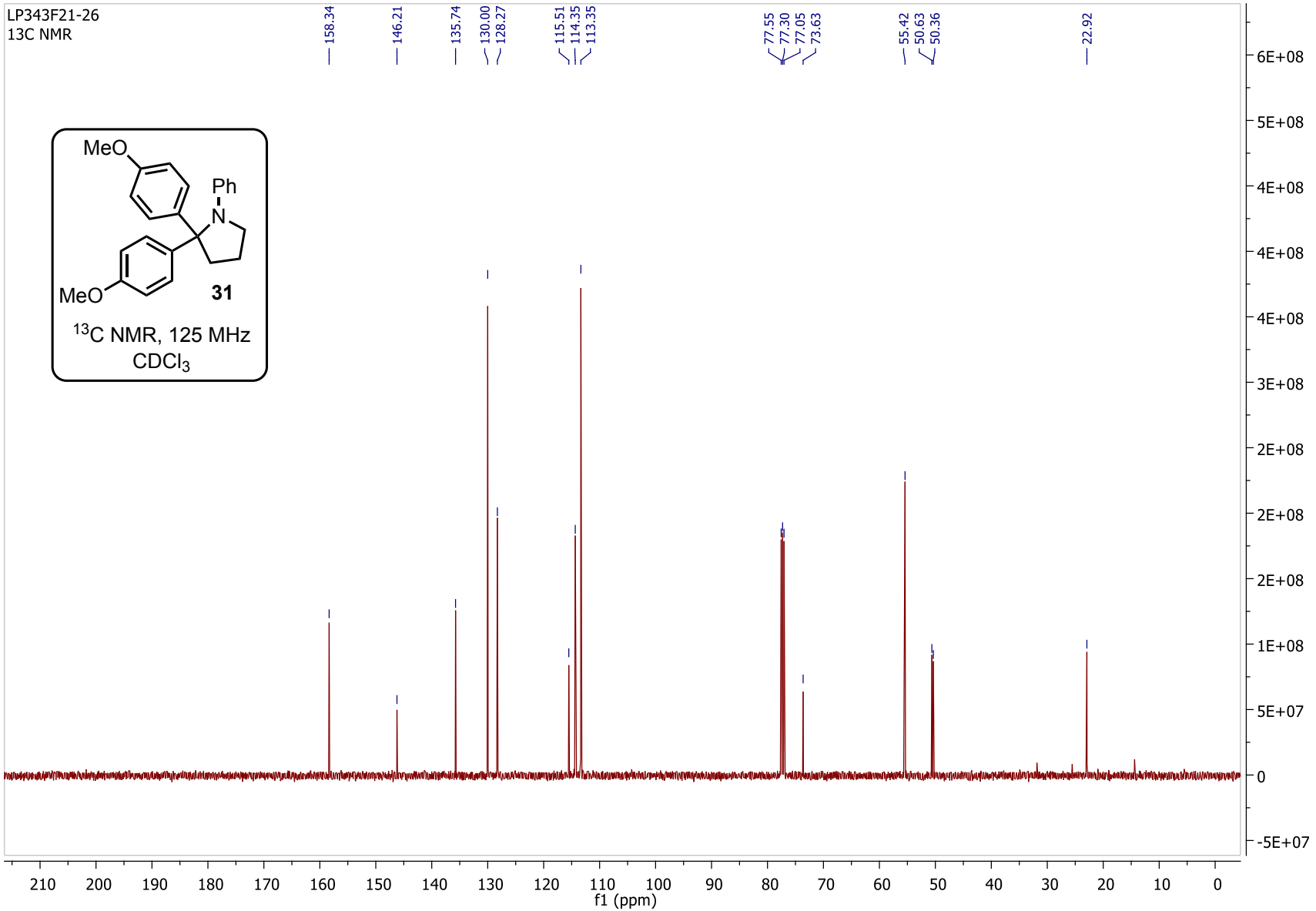

LP221F1
13C NMR
146.19
143.64
129.03
128.28
128.10
126.88
115.74
114.44
77.55 CDCl3
77.30 CDCl3
77.05 CDCl3
74.59
50.80
50.66
23.07
Ph
Ph
N
Ph
29
13C NMR, 125 MHz
CDCl3
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

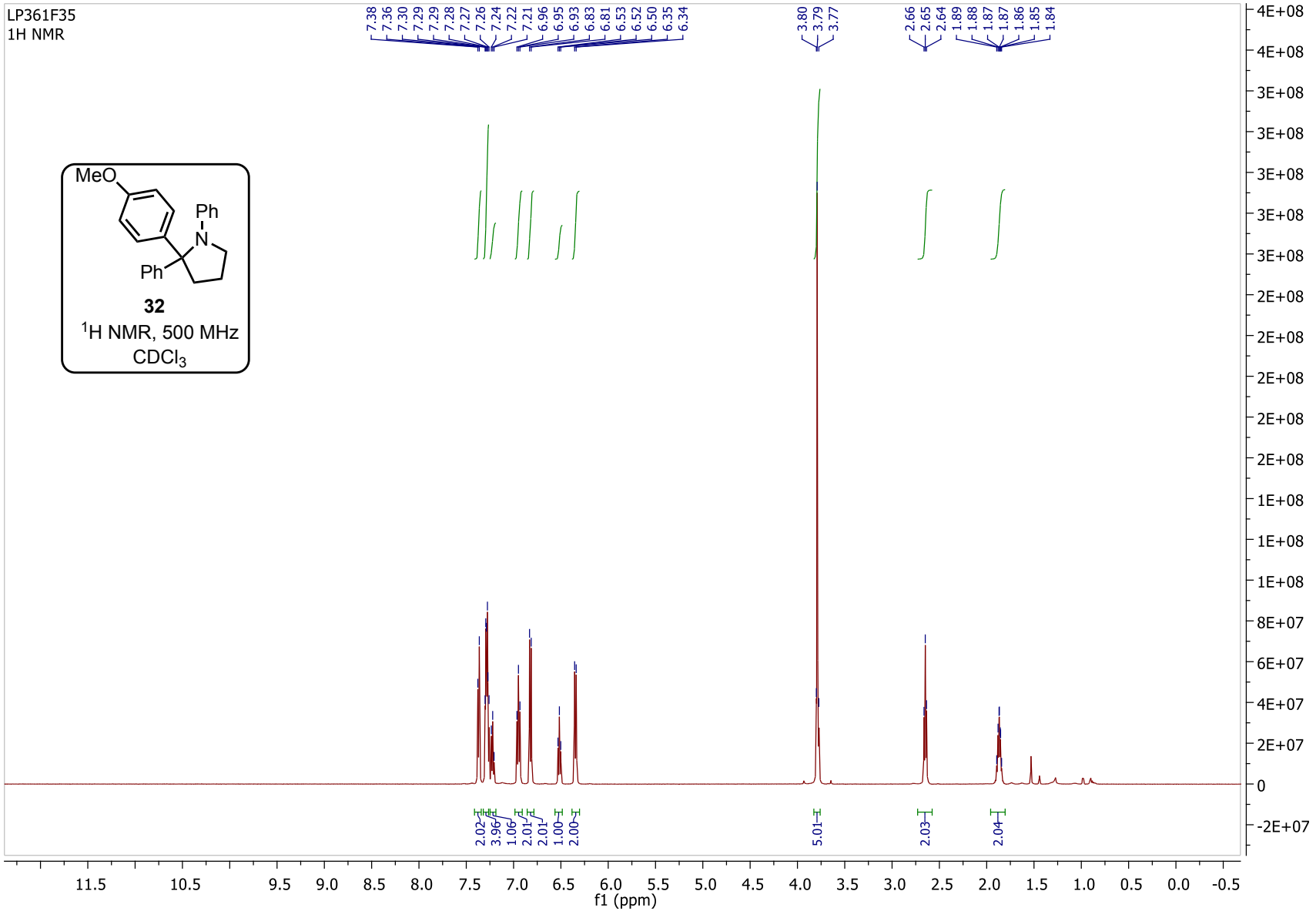

LP270P1
1H NMR
7.32
7.31
7.30
7.29
7.26
6.98
6.97
6.96
6.56
6.54
6.53
6.31
6.30
3.79
3.78
3.77
2.63
2.62
2.61
1.89
1.88
1.87
1.85
1.84
F
Ph
N
F
30
1H NMR, 500 MHz
CDCl3
4.07
6.31
1.00
2.05
2.13
2.23
2.11
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

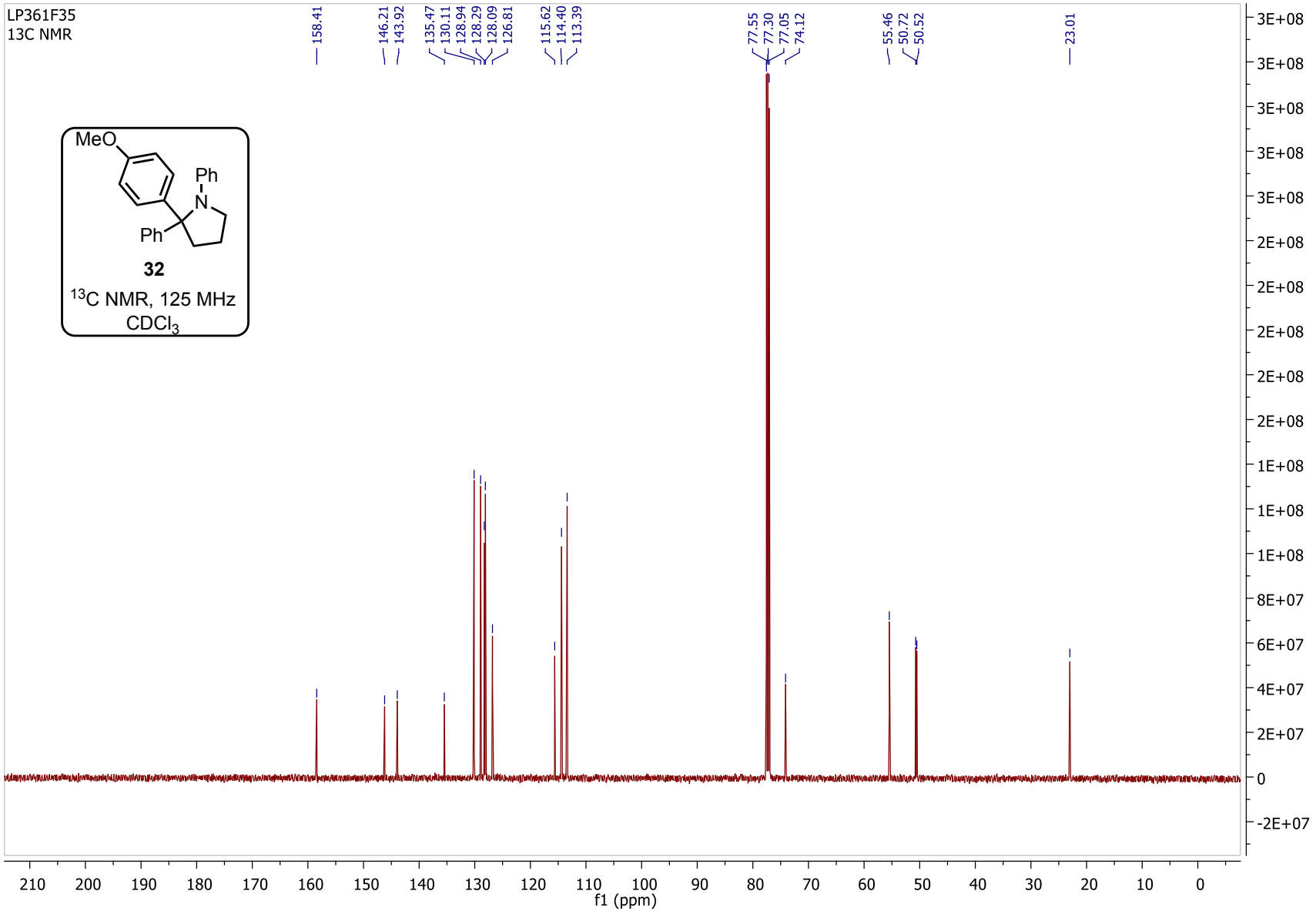

LP270P1
13C NMR
162.82
160.86
145.80
139.16
139.14
130.54
130.48
128.46
116.16
115.08
114.91
114.50
77.55
77.30
77.05
73.77
50.73
50.71
22.94
F
Ph
N
F
30
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

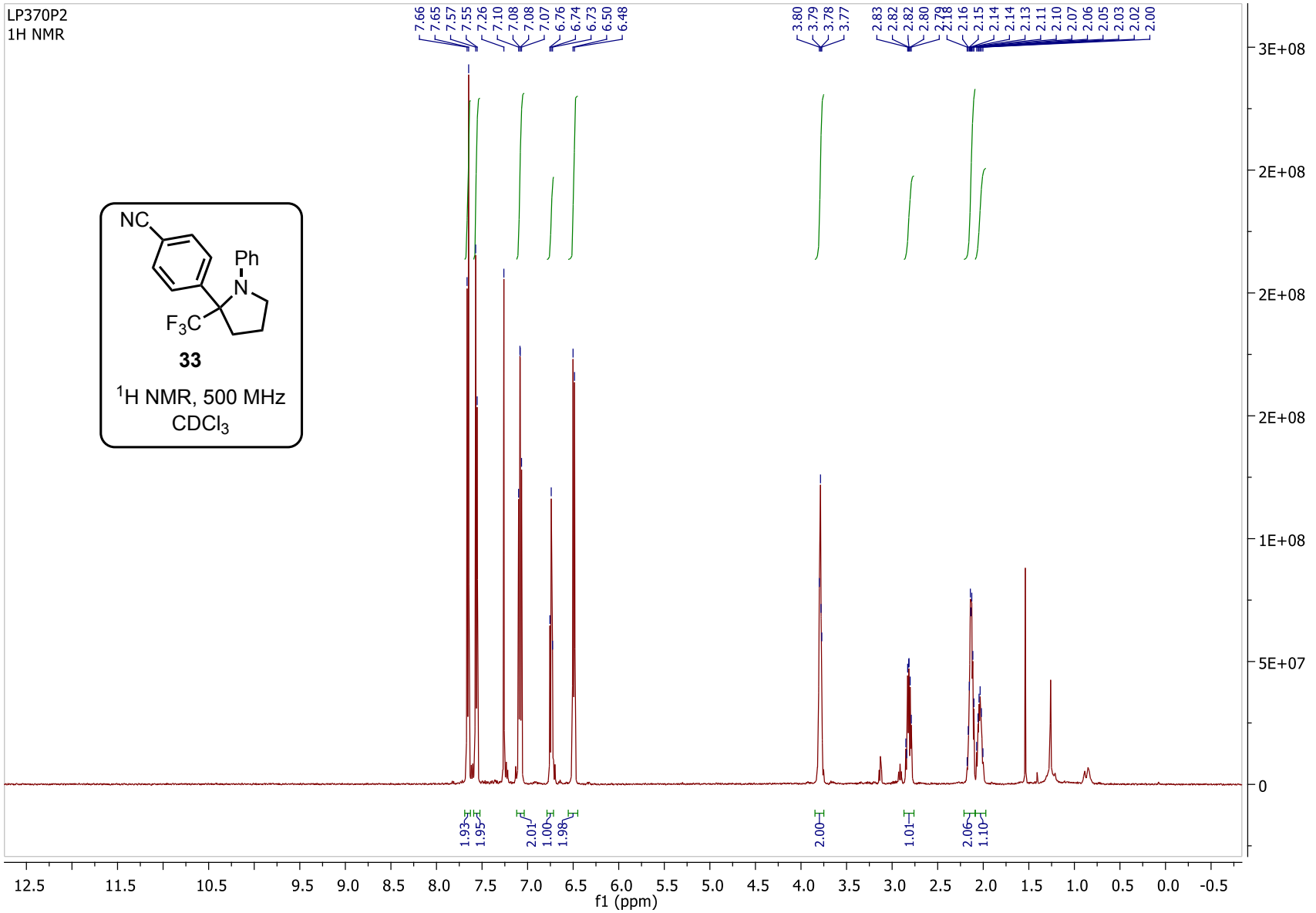

F19 NMR
-116.18
-161.64
-161.65
F
Ph
N
F
30
^{19}F NMR, 476 MHz
$CDCl_3$
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

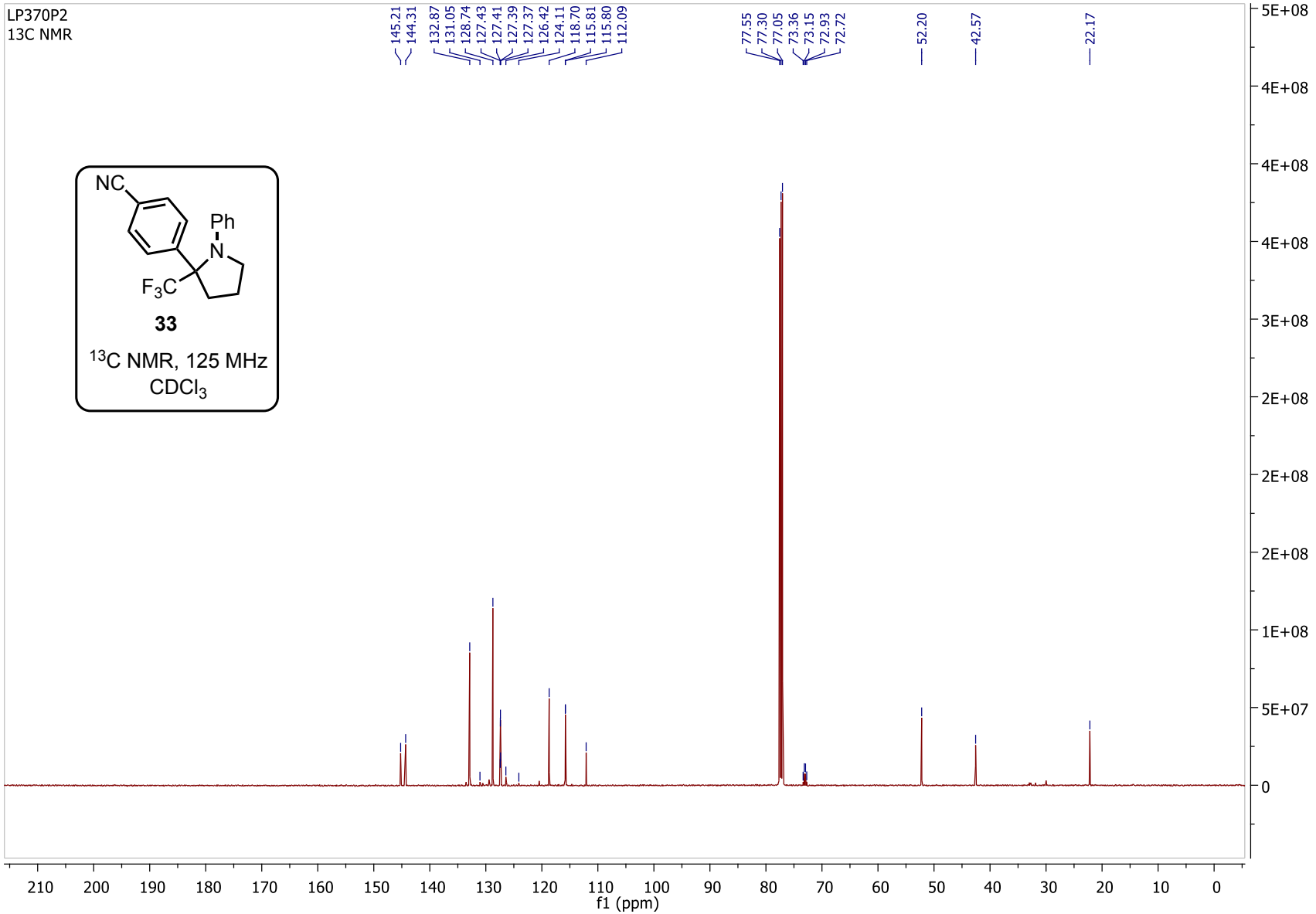

LP343F21-26
1H NMR
7.31
7.29
7.26
7.00
6.98
6.96
6.85
6.83
6.56
6.54
6.53
6.39
6.37
3.81
3.79
3.78
2.65
2.63
2.62
1.91
1.90
1.88
1.87
1.86
MeO
Ph
N
MeO
31
1H NMR, 500 MHz
CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
3.97
2.03
4.03
1.00
1.97
6.20
1.83
1.99
2.04
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

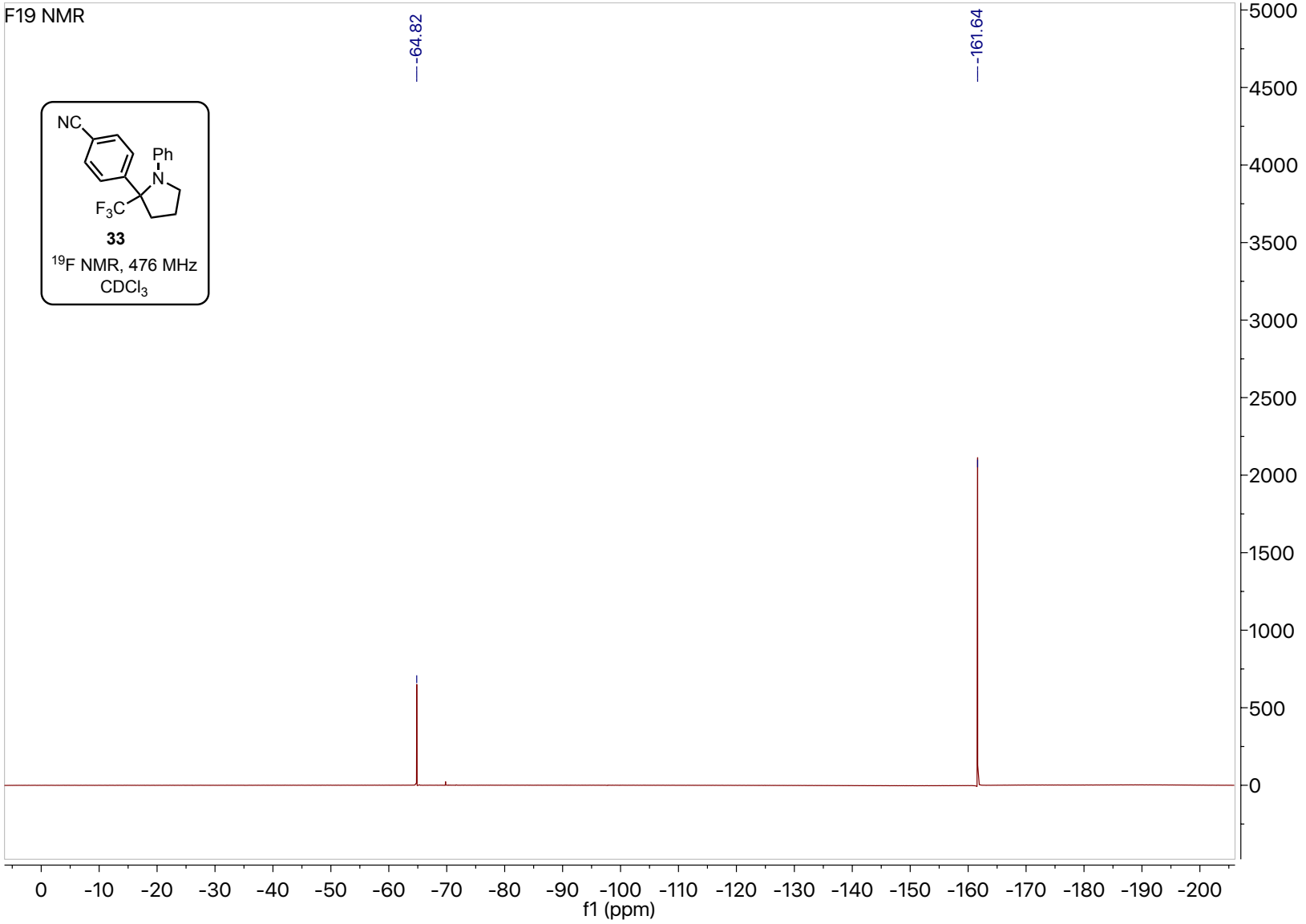

LP343F21-26
13C NMR
158.34
146.21
135.74
130.00
128.27
115.51
114.35
113.35
77.55
77.30
77.05
73.63
55.42
50.63
50.36
22.92
MeO
Ph
N
MeO
31
13C NMR, 125 MHz
CDCl3
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

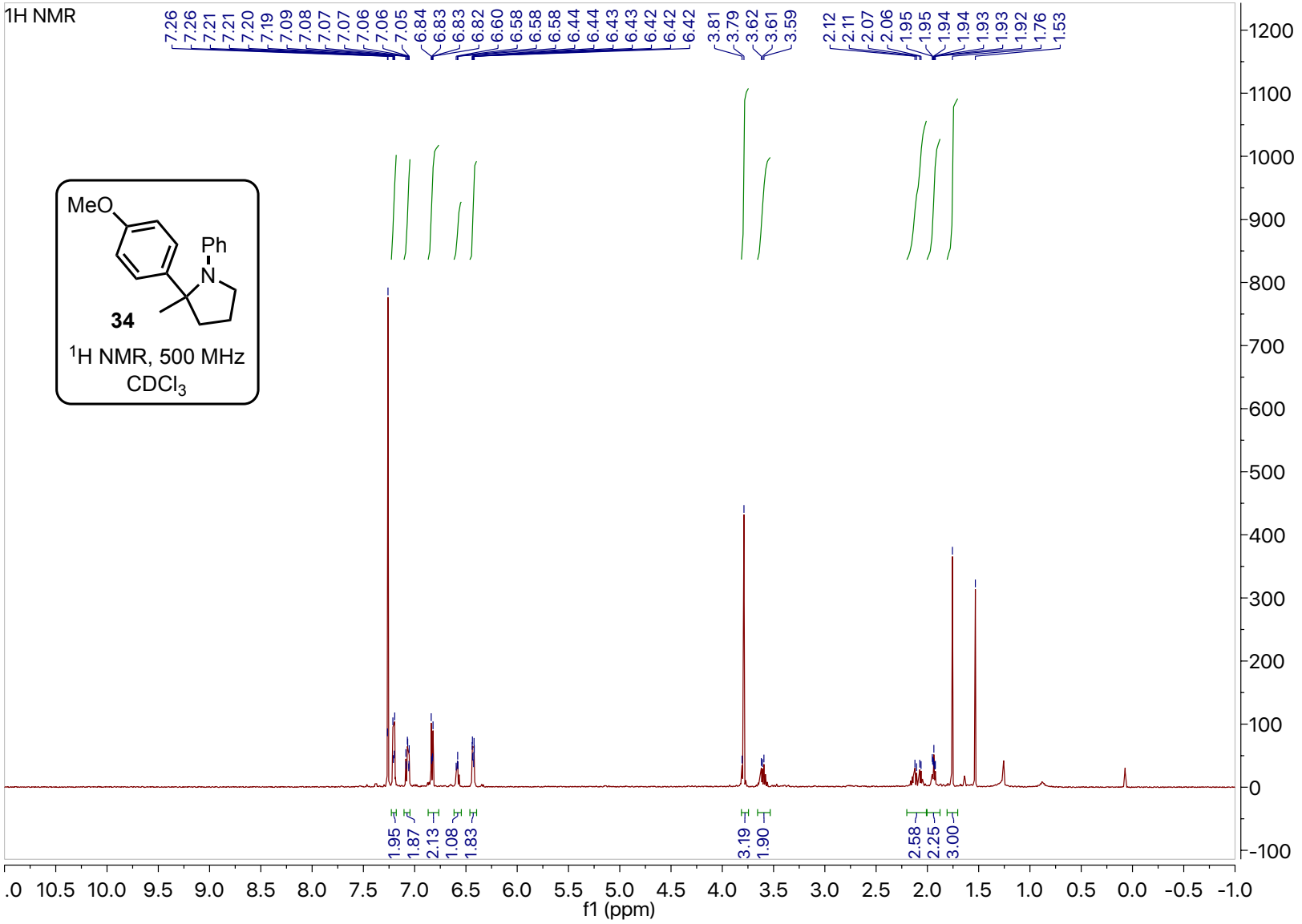

LP361F35
1H NMR
MeO
Ph
N
Ph
32
1H NMR, 500 MHz
CDCl3
f1 (ppm)

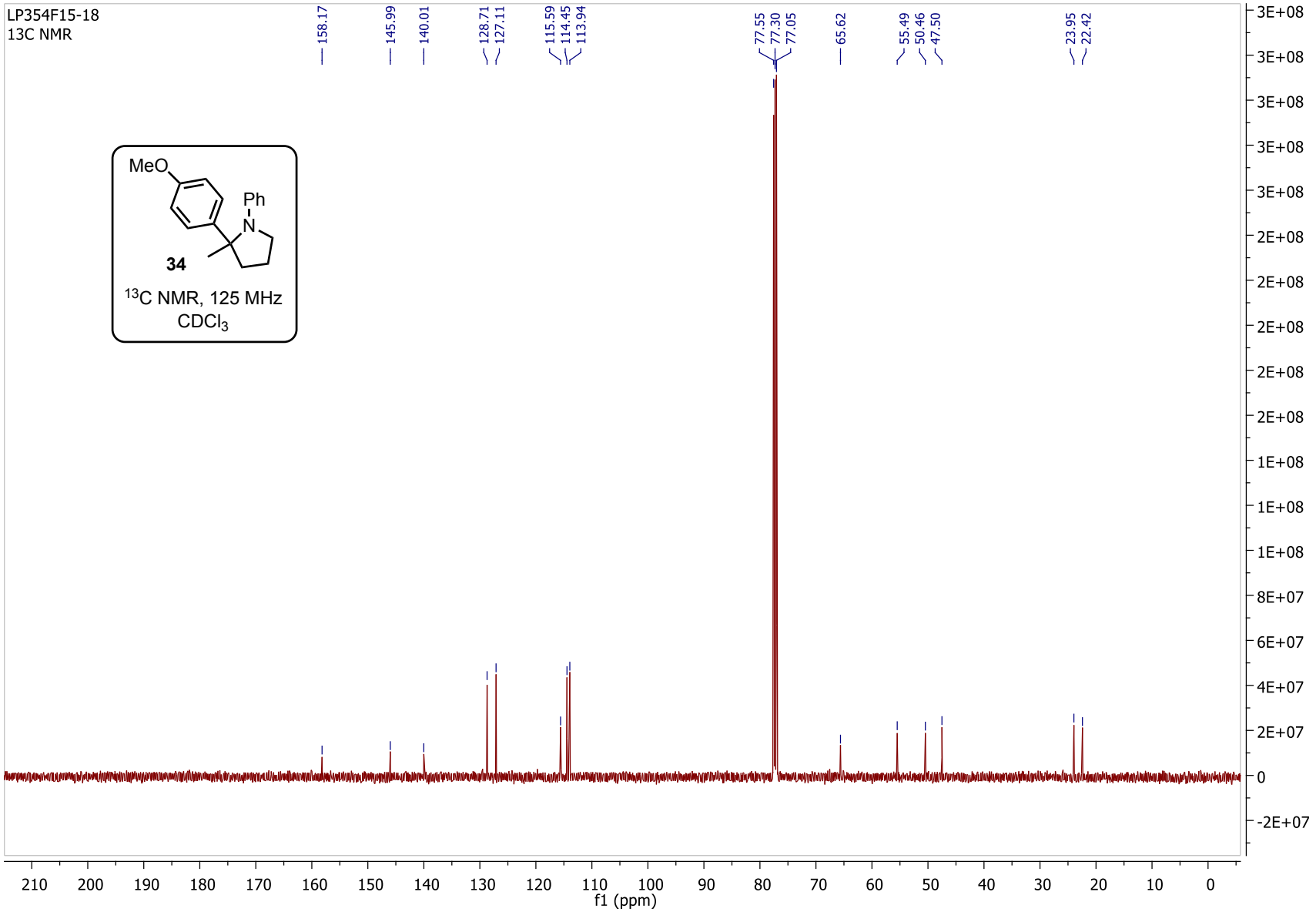

LP361F35
13C NMR
158.41
146.21
143.92
135.47
130.11
128.94
128.29
128.09
126.81
115.62
114.40
113.39
77.55
77.30
77.05
74.12
55.46
50.72
50.52
23.01
MeO
Ph
N
Ph
32
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

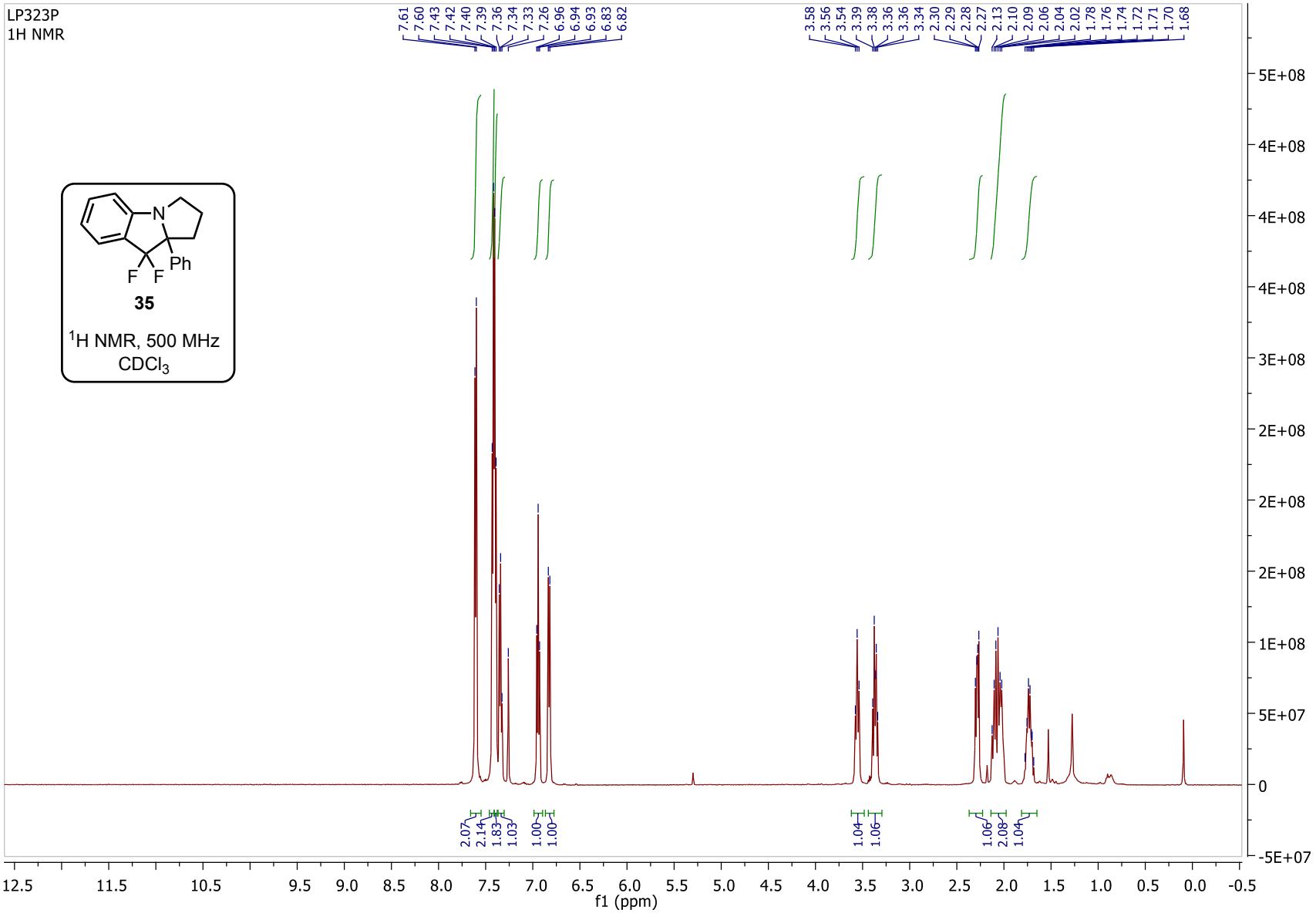

LP370P2
1H NMR
NC
Ph
N
F3C
33
1H NMR, 500 MHz
CDCl3
7.66 7.65 7.57 7.55 7.26 7.10 7.08 7.08 7.07 6.76 6.74 6.73 6.50 6.48
3.80 3.79 3.78 3.77
2.83 2.82 2.82 2.80 2.79 2.18 2.16 2.15 2.14 2.14 2.13 2.11 2.10 2.07 2.06 2.05 2.03 2.02 2.00
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
1.93 1.95 2.01 1.00 1.98 2.00 1.01 2.06 1.10
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

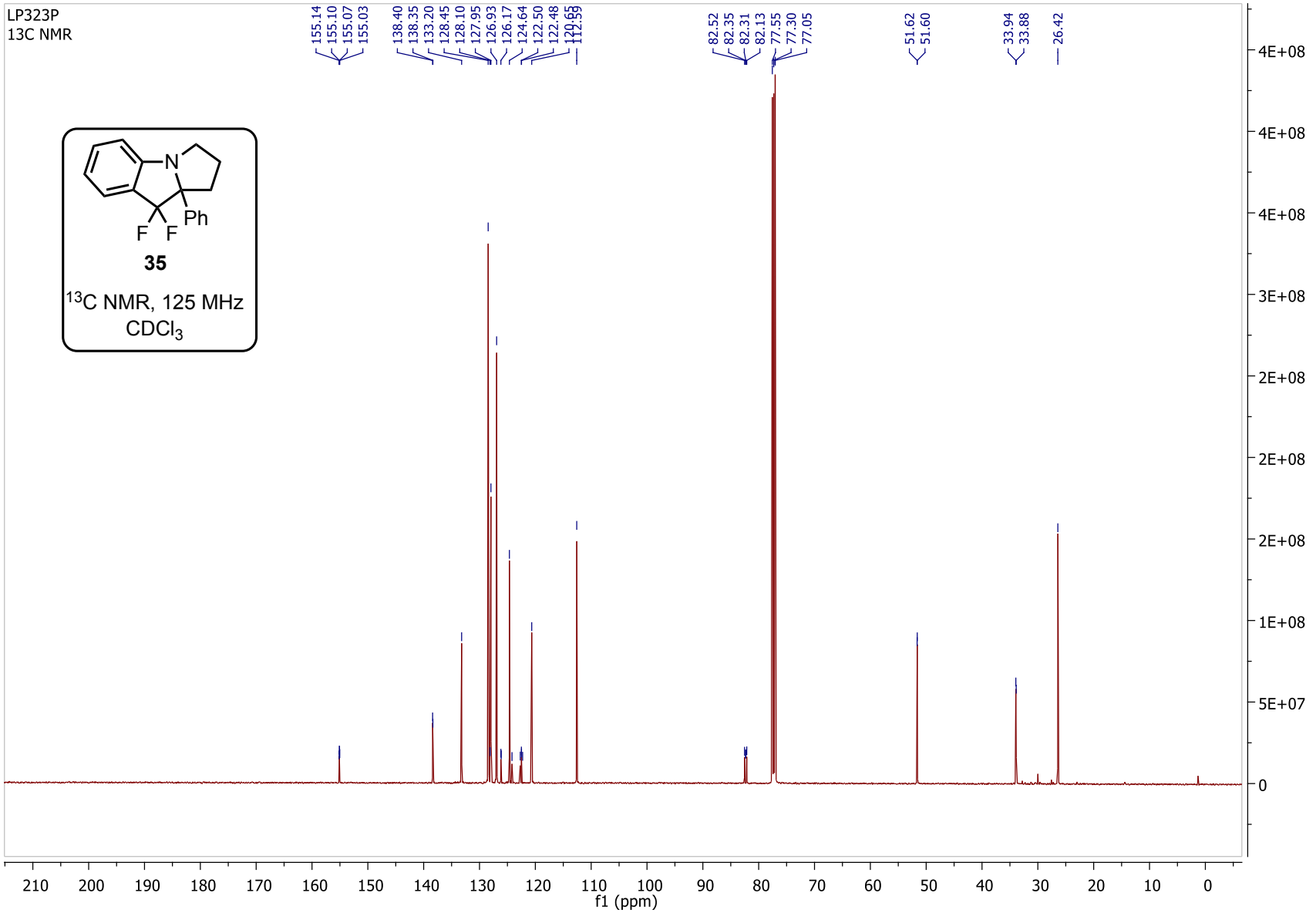

LP370P2
13C NMR
145.21
144.31
132.87
131.05
128.74
127.43
127.41
127.39
127.37
126.42
124.11
118.70
115.81
115.80
112.09
77.55
77.30
77.05
73.36
73.15
72.93
72.72
52.20
42.57
22.17
NC
Ph
N
F3C
33
13C NMR, 125 MHz
CDCl3
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

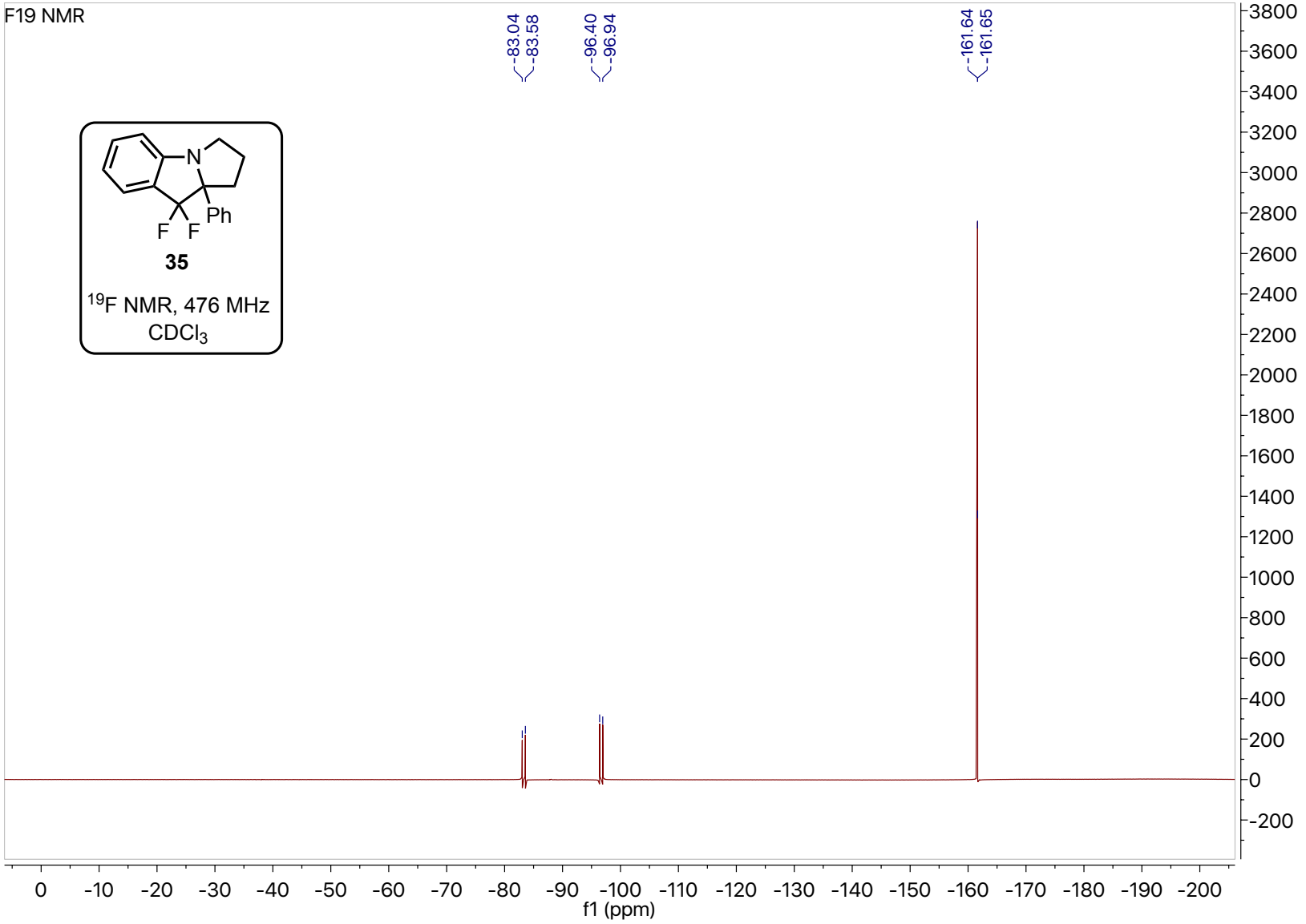

F19 NMR
-64.82
-161.64
NC
Ph
N
F3C
33
19F NMR, 476 MHz
CDCl3
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

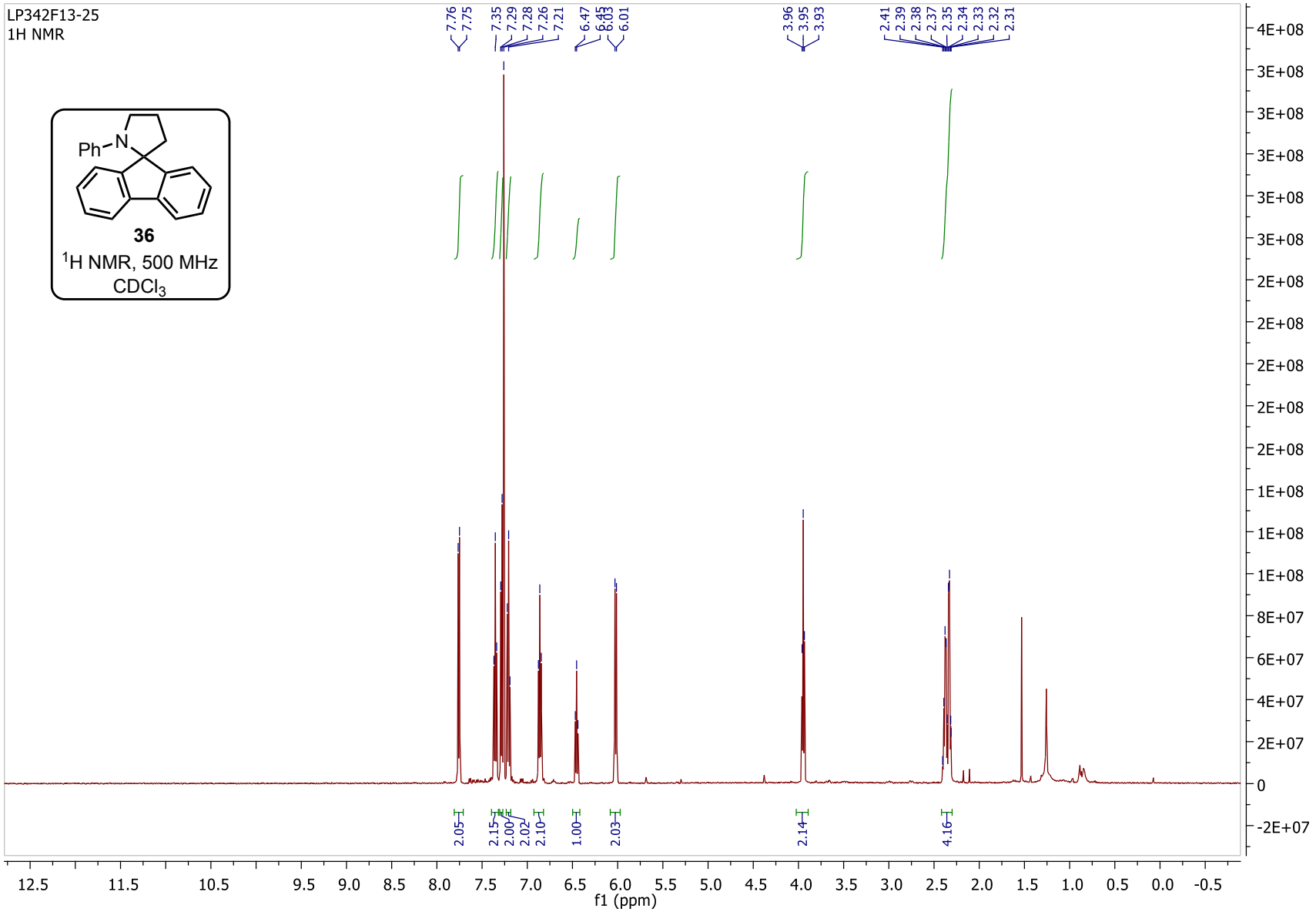

1H NMR
MeO
Ph
N
34
1H NMR, 500 MHz
CDCl3
f1 (ppm)

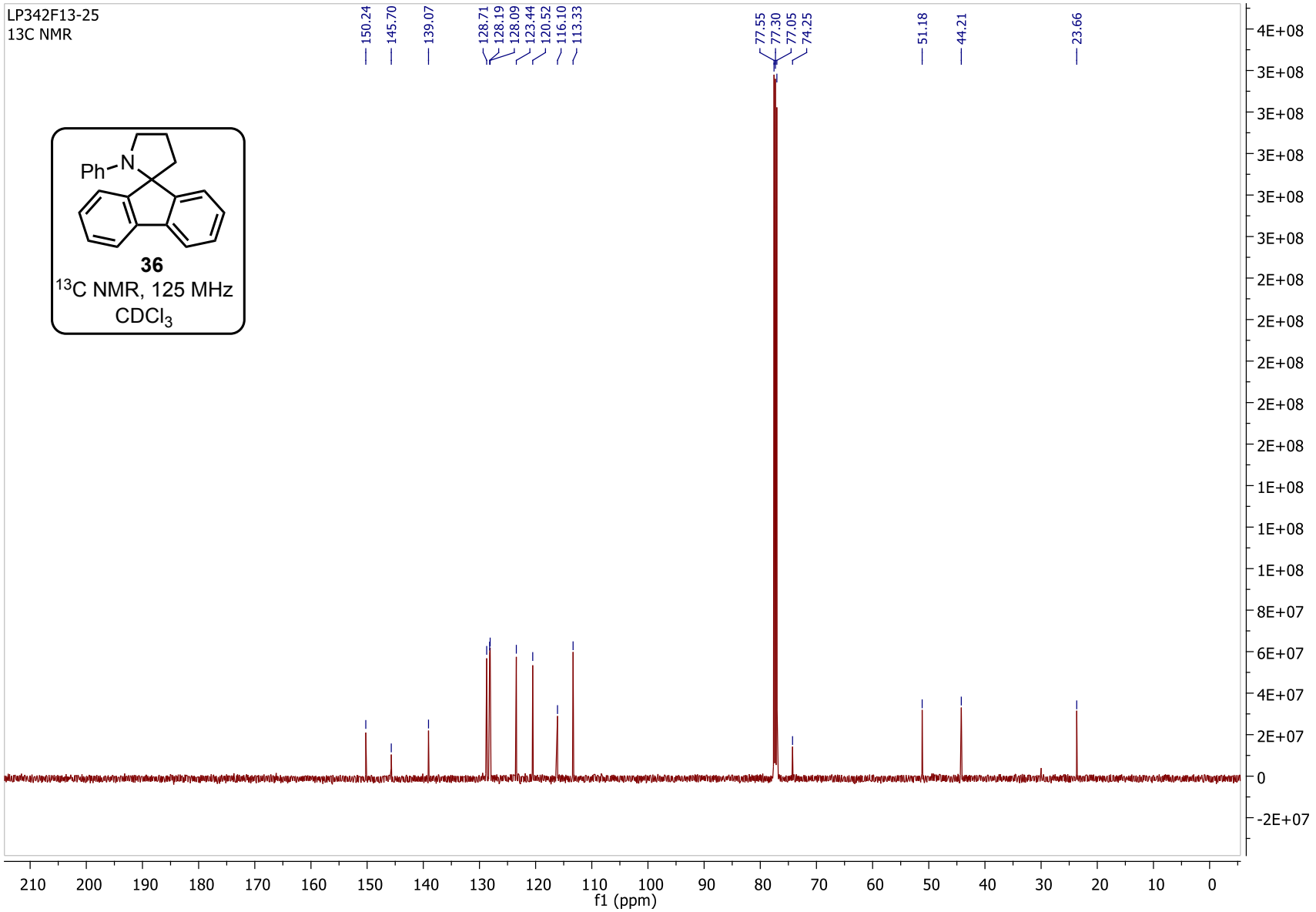

LP354F15-18
13C NMR
158.17
145.99
140.01
128.71
127.11
115.59
114.45
113.94
77.55
77.30
77.05
65.62
55.49
50.46
47.50
23.95
22.42
MeO
Ph
N
34
13C NMR, 125 MHz
CDCl3
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


LP323P
1H NMR
7.61 7.60 7.43 7.42 7.40 7.39 7.36 7.34 7.33 7.26 6.96 6.94 6.93 6.83 6.82
3.58 3.56 3.54 3.39 3.38 3.36 3.36 3.34 2.30 2.29 2.28 2.27 2.13 2.10 2.09 2.06 2.04 2.02 1.78 1.76 1.74 1.72 1.71 1.70 1.68
N
F F Ph
35
1H NMR, 500 MHz
CDCl3
2.07 2.14 1.83 1.03 1.00 1.00 1.04 1.06 1.06 2.08 1.04
5E+08 4E+08 4E+08 4E+08 3E+08 2E+08 2E+08 2E+08 1E+08 5E+07 0 -5E+07
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


LP323P
13C NMR
155.14
155.10
155.07
155.03
138.40
138.35
133.20
128.45
128.10
127.95
126.93
126.17
124.64
122.50
122.48
120.65
112.59
82.52
82.35
82.31
82.13
77.55
77.30
77.05
51.62
51.60
33.94
33.88
26.42
N
Ph
F F
35
13C NMR, 125 MHz
CDCl3
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F19 NMR
-83.04
-83.58
-96.40
-96.94
-161.64
-161.65
N
Ph
F F
35
19F NMR, 476 MHz
CDCl3
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


LP342F13-25
1H NMR
Ph
N
36
1H NMR, 500 MHz
CDCl3
7.76
7.75
7.35
7.29
7.28
7.26
7.21
6.47
6.45
6.03
6.01
3.96
3.95
3.93
2.41
2.39
2.38
2.37
2.35
2.34
2.33
2.32
2.31
2.05
2.15
2.00
2.02
2.10
1.00
2.03
2.14
4.16
f1 (ppm)


LP342F13-25
13C NMR
150.24
145.70
139.07
128.71
128.19
128.09
123.44
120.52
116.10
113.33
77.55
77.30
77.05
74.25
51.18
44.21
23.66
Ph
N
36
13C NMR, 125 MHz
CDCl3
f1 (ppm)