Supporting Online Material for

Pyridyl Phosphonium Salts as Alternatives to Cyanopyridines in Radical-Radical Coupling Reactions

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1. General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on either a Bruker Ultrashield–400 (400 MHz) spectrometer, a Varian 400 MR (400 MHz) spectrometer or an Agilent Inova 400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (7.26 ppm), C_6D_6 (7.16 ppm), $(CD_3)_2SO$ (2.50 ppm), CD_3OD (3.31 ppm) or CD_3CN (1.94 ppm) and coupling constants (*J*) are quoted in Hertz (Hz). Data are reported as follows: Chemical shift (number of protons, multiplicity, coupling constants). Coupling constants were quoted to the nearest 0.1 Hz and multiplicity reported according to the following convention: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextet, sp = septet, m = multiplet, br = broad. Where coincident coupling constants have been observed, the apparent (app) multiplicity of the proton resonance has been reported. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at ambient temperature on either a Bruker Ultrashield–400 (100 MHz) spectrometer, a Varian 400 MR spectrometer (100 MHz) or an Agilent Inova 400 (100 MHz) spectrometer. Chemical shift (δ) was measured in ppm and quoted to the nearest 0.1 ppm relative to the residual solvent peaks in $CDCl_3$ (77.16 ppm), C_6D_6 (128.06 ppm), $(CD_3)_2SO$ (39.51 ppm), CD_3OD (49.00 ppm) or CD_3CN (1.32 ppm). DEPT135, NOE experiments and 2–dimensional experiments (COSY, HMBC, and HSQC) were used to support assignments where appropriate.

Absorption spectra were obtained with a Hewlett-Packard 8453 spectrometer in quartz cuvettes with a 1 cm path length. Emission spectroscopy was performed on an Edinburgh Instruments FS5 spectrometer using a sealed quartz cuvette.

Low–resolution mass spectra (LRMS) were measured on an Agilent 6310 Quadrupole Mass Spectrometer. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT–IR spectrometer as either solids or neat films, either through direct application or deposited in $CHCl_3$, with absorptions reported in wavenumbers (cm^{-1}).

Analytical thin layer chromatography (TLC) was performed using pre–coated glass backed silica gel plates (Silicagel 60 F254). Flash column chromatography was undertaken on Silicycle silica gel (230–400 mesh) under a positive pressure of air. Visualization was achieved using ultraviolet light (254 nm) and chemical staining with ceric ammonium molybdate or basic potassium permanganate solutions as appropriate.

Tetrahydrofuran (THF), toluene, hexane, diethyl ether and dichloromethane were dried and distilled using standard methods.[1] Ethyl acetate (EtOAc), 1,2–Dichloroethane (DCE), 1,4–dioxane, chloroform, chlorobenzene and acetone were purchased anhydrous from Sigma Aldrich chemical company. All reagents were purchased at the highest commercial quality and used without further purification unless stated otherwise. Reactions were carried out under an atmosphere of nitrogen unless otherwise stated. All reactions were monitored by TLC, ^{1}H NMR spectra taken from reaction samples, and/or liquid chromatography mass spectrometry (LCMS) using an Agilent 6310 Quadrupole Mass Spectrometer. Melting points (mp) were recorded using a Büchi B–450 melting point apparatus and are reported uncorrected.

PPh_3 (99%) was purchased from Oakwood Chemical and is most effective when crushed to a powder before use. Tf_2O (99%) was purchased from Oakwood Chemical and used without further purification and was routinely stored in a –20 ºC fridge. NEt_3 and DBU were distilled before use. 2,6-lutidine was distilled then sparged with a stream of N_2 for 20 mins before use. Sparged, distilled 2,6-lutidine was stored in the glovebox to prevent exposure to oxygen or moisture.

All photoredox reactions were conducted under a nitrogen atmosphere while subject to irradiation from a

455 nm kessil lamp (Kessil PR160 set at 100% intensity or Kessil H150-Blue) at room temperature (see photoredox setup below). Irradiation of the reaction mixture with UV light was done with realUV^{TM} LED Lights (365 nm) which can be purchased from waveformlighting.com. These LEDs were wrapped around the inside of a Pyrex crystallization dish and reaction vials were placed inside the dish as close to the lights as possible. 3DPAFIPN (2,4,6-Tris(diphenylamino)-5-fluoroisophthalonitrile), 5CzBn (2,3,4,5,6-Penta(9H-carbazol-9-yl)benzonitrile), and 3DPA2FBN (2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile) photocatalysts were prepared according to a previously reported procedure.[2]

2. Photoredox Setup

All reactions were conducted under nitrogen at room temperature. Ambient temperature was maintained by using a compressed air line. Shown below is a photograph of the reaction setup, where the LED array was positioned approximately 6 inches away from the vials containing reaction mixture. If using the Kessil PR160 lamps, the intensity dial was set at 100%. **Be sure to wear proper protective eyewear that blocks harmful wavelengths of light when lights are in use until the light has been properly covered or blocked.** An example of appropriate protective goggles from HepatoChem is provided: Skyper eyewear protective goggles, product number HCK1015-01-001. Note: the reactions shown below were covered fully with cardboard after the lights were turned on.

Figure S1. Photoredox setup with lights off

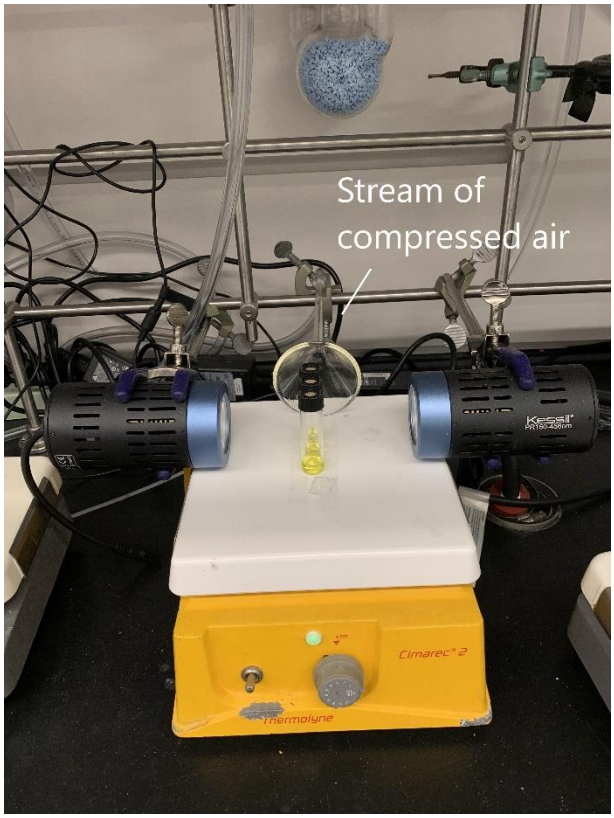
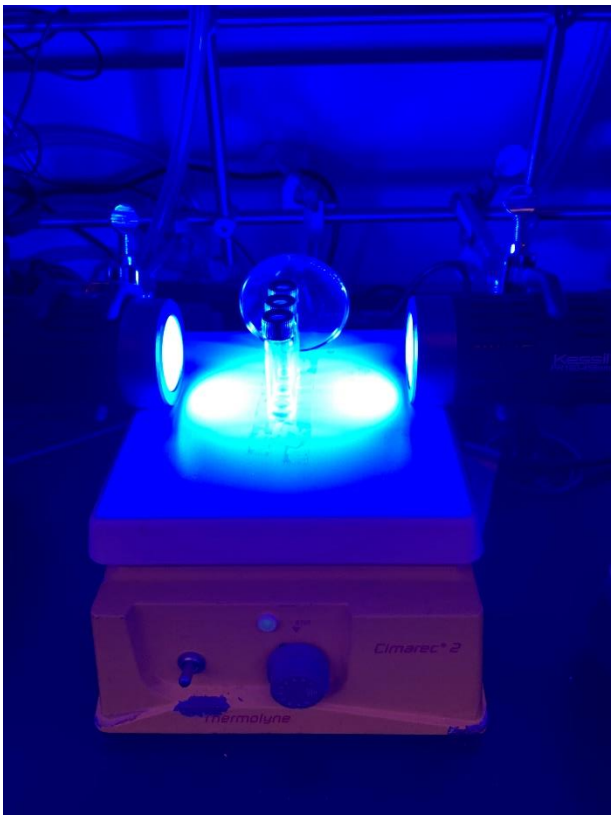


Figure S2. Photoredox setup with lights on

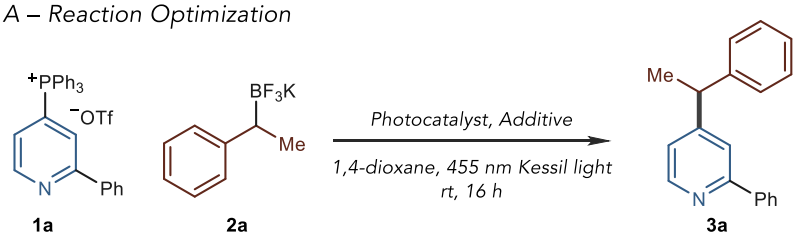


3. Optimization Studies

For optimization studies, an oven dried 8 mL vial equipped with a magnetic stir bar was charged with the triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (56.6 mg, 0.10 mmol, 1.0 equiv), potassium trifluoro(1-phenylethyl)borate (42.4 mg, 0.20 mmol, 2.0 equiv) and photocatalyst (2 mol%). The vial was pumped into a glovebox and then dioxane (333 μL, 0.3 M) and 2,6-lutidine (35 μL, 3.0 equiv) were added via a microliter syringe. The vial was sealed and removed from the glovebox and pre-stirred for ten minutes before irradiation with a 455 nm kessil lamp (5 cm away, with stream of air blowing over vials to keep reaction at 25 °C) for 16 hours. The reaction was quenched with water and the aqueous layer was extracted with CH_2Cl_2 (4x). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. $CDCl_3$ and trimethoxybenzene (16.8 mg, 0.10 mmols) was added, and the sample was analyzed by ^1H NMR. The integral values were used to calculate the data given in **Table S1**. Examples of substrates that worked better with the inclusion of the 2,6-lutidine additive are summarized in **Tables S2 and S3**. Redox potentials and triplet energies of pertinent photocatalysts are included below in **Table 4** that were compiled from previous literature reports.[2-5]

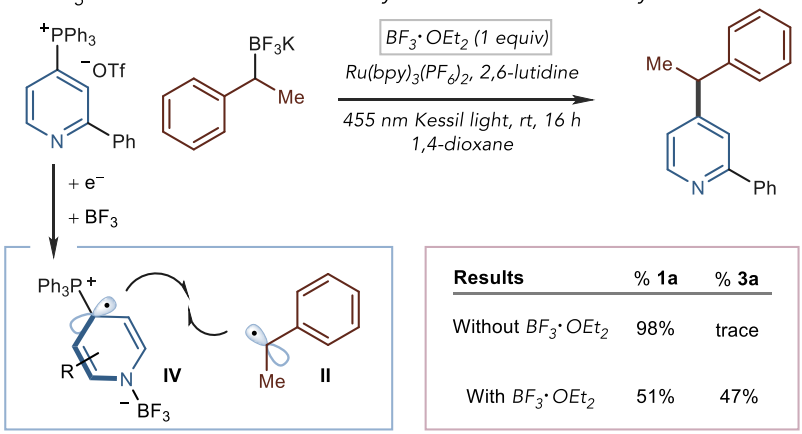
Table S1. Optimization of Pyridine Alkylation[a]

A – Reaction Optimization



Entry	Photocatalyst (2 mol%)	Additive (3 equiv)	Concentration	% **3a**[b]
1	$Ir(ppy)_3$	none	0.1 M	60
2	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	none	0.1 M	66
3	3DPAFIPN	none	0.1 M	77
4	3DPAFIPN	none	0.3 M	82
5	3DPAFIPN	2,6–lutidine	0.3 M	82 (74)[c]
6	4CzIPN	2,6–lutidine	0.3 M	40
7	5CzBn	2,6–lutidine	0.3 M	71
8	3DPA2FBN	2,6–lutidine	0.3 M	73
9	$[Ir(ppy)_2(dtbbpy)]PF_6$	2,6–lutidine	0.3 M	74
10	$[Mes\text{-}Acr]BF_4$	2,6–lutidine	0.3 M	41
11	none	2,6–lutidine	0.3 M	trace
12[d]	none	2,6–lutidine	0.3 M	66

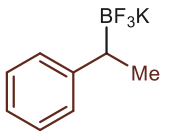
B – BF_3 Additive Enables Previously Ineffective Photocatalyst



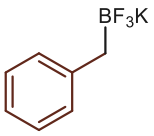
Results	% 1a	% 3a
Without $BF_3{\cdot}OEt_2$	98%	trace
With $BF_3{\cdot}OEt_2$	51%	47%

[a]Conditions: **1a** (1.0 equiv), **2a** (2.0 equiv), photocatalyst (2 mol%), additive (3.0 equiv), rt. [b]Yields determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c]Isolated yield on 0.50 mmol scale. [d]Used 365 nm LEDs instead of 455 nm Kessil light for 89 h.

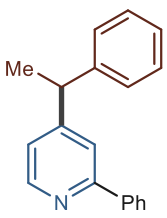
Table S2. Example of BF_3K Salt that Requires 2,6-lutidine Additive[a,b]



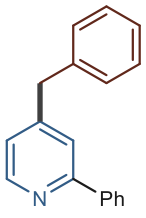
vs.



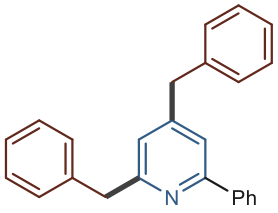
	Yield of Product **3a**	Yield of Product **3aa**
With 2,6-lutidine[c]	82%	50%
Without 2,6-lutidine[d]	82%	29%



3a



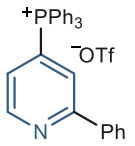
3aa



3aa'

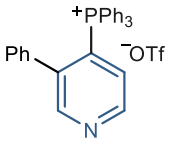
[a]Conditions: **1a** (1.0 equiv), **BF_3K Salt** (2.0 equiv) photocatalyst (2 mol%), additive (3.0 equiv), rt. [b]Yields detemined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c]Ratio of desired product **3aa** to bis-addition **3aa'** = 5.7:1. [d]Ratio of desired product **3aa** to bis-addition **3aa'** = 1.6:1.

Table S3. Example of Phosphonium Salt that Requires 2,6-lutidine Additive[a,b]



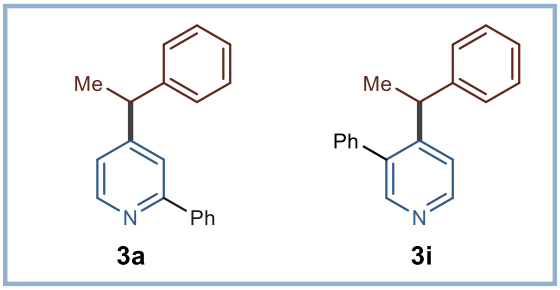
1a

vs.



1i

	Yield of Product **3a**	Yield of Product **3i**
With 2,6-lutidine	82%	60%
Without 2,6-lutidine	82%	20%[c]



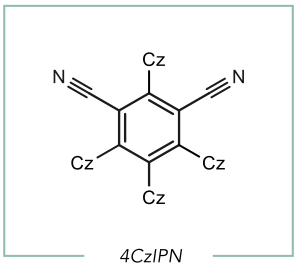
3a **3i**

[a]Conditions: **Phosphonium Salt** (1.0 equiv), **2a** (2.0 equiv) photocatalyst (2 mol%), additive (3.0 equiv), rt. [b]Yields detemined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c]Reaction provided complex mixture of byproducts

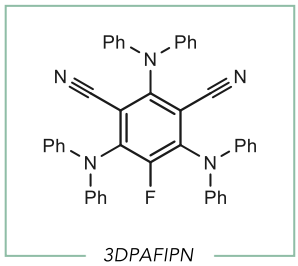
Table S4: Pertinent Photocatalyst Redox Properties and Triplet Energies

Photocatalyst	$E_{1/2}(M^+/M^*)$	$E_{1/2}(M^*/M^-)$	$E_{1/2}(M^+/M)$	$E_{1/2}(M/M^-)$	$E^{T_1}_{0,0}$(kcal/mol)
$Ir(ppy)_3$	*−1.73 V*	*+0.31 V*	*+0.77 V*	*−2.19 V*	*58.1*
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	*−0.89 V*	*+1.21 V*	*+1.69 V*	*−1.37 V*	*61.8*
3DPAFIPN	*−1.38 V*	*+1.09 V*	*+1.30 V*	*−1.59 V*	*61.8*
4CzIPN	*−1.18 V*	*+1.43 V*	*+1.49 V*	*−1.24 V*	*61.6*
5CzBn	*−1.42 V*	*+1.31 V*	*+1.41 V*	*−1.52 V*	*65.2*
3DPA2FBN	*−1.60 V*	*0.92 V*	*+1.24 V*	*−1.92 V*	*65.5*
$[Ir(ppy)_2(dtbbpy)]PF_6$	*−0.96 V*	*+0.66 V*	*+1.21 V*	*−1.57 V*	*49.2*
$[Mes\text{-}Acr]BF_4$		*+2.18 V*		*−0.49 V*	*44.7*
$[Ru(bpy)_3]PF_6$	*−0.81 V*	*+0.77 V*	*+1.29 V*	*−1.33 V*	*49.0*

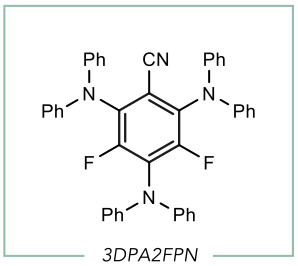
All redox potentials are reported vs SCE. All values are compiled from previous literature reports.



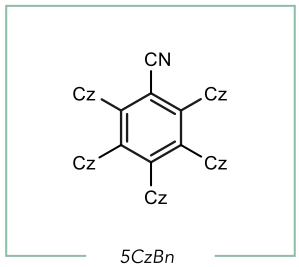
4CzIPN



3DPAFIPN

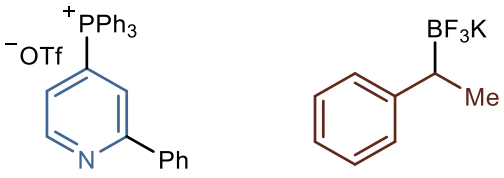


3DPA2FPN



5CzBn

4. UV-Vis Spectroscopy Studies



1a **2a**

Procedure: An oven dried 8 mL vial was charged with either triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate, (5.7 mg, 0.01 mmol), potassium trifluoro(1-phenylethyl)borate (2.1 mg, 0.01 mmol), or both (1:1 mixture, 0.01 mmol each). 1,4-dioxane (1.0 mL, 0.01 M) was added to each of the three vials, and a series of dilutions were made to achieve an absorbance between 0 and 1 a.u. (0.001 M – 0.0001 M). The solutions were transferred to a quartz cuvette with 1 cm pathlength and analyzed via UV-Vis spectroscopy. Results are shown below.

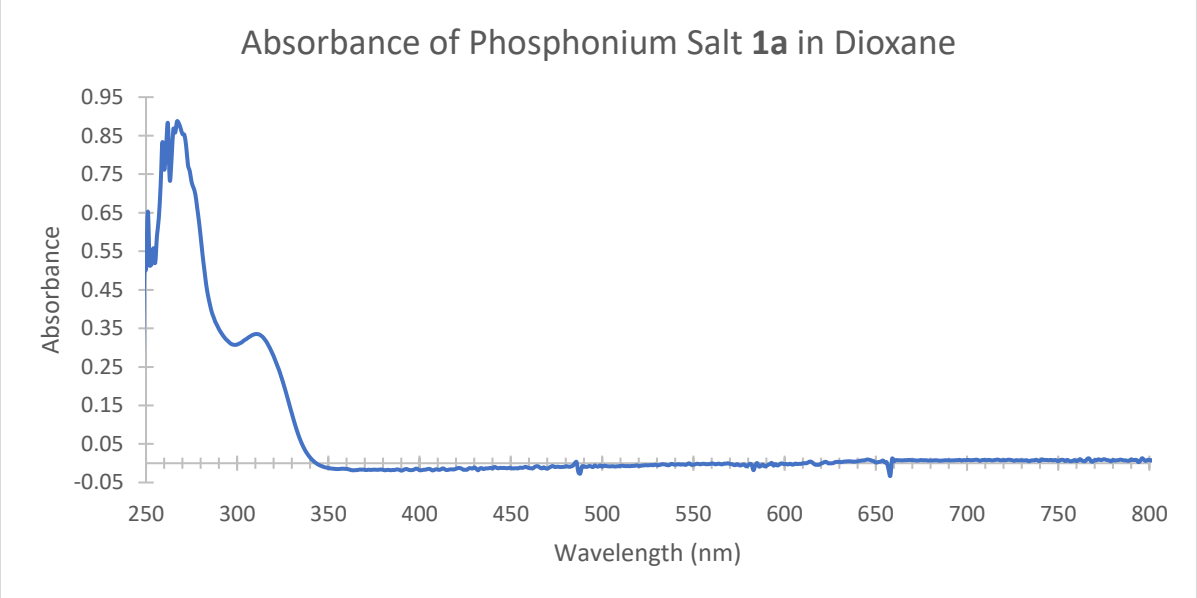


Figure S3: **1a** (5.7 mg, 0.01 mmol) in 1,4-dioxane (1 mL) were added to an 8 mL vial. The sample was then diluted with 1,4-dioxane to 0.0001 M with respect to **1a** and transferred to a cuvette with a 1 cm path length.

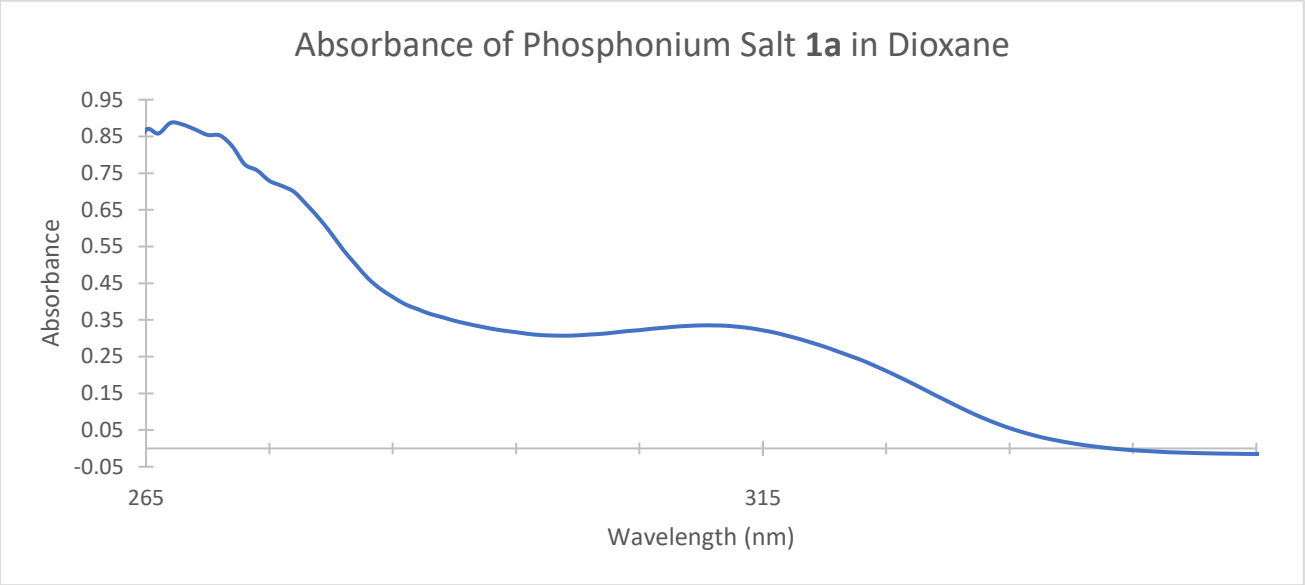


Figure S4: Zoomed in spectra from **Figure S3.**

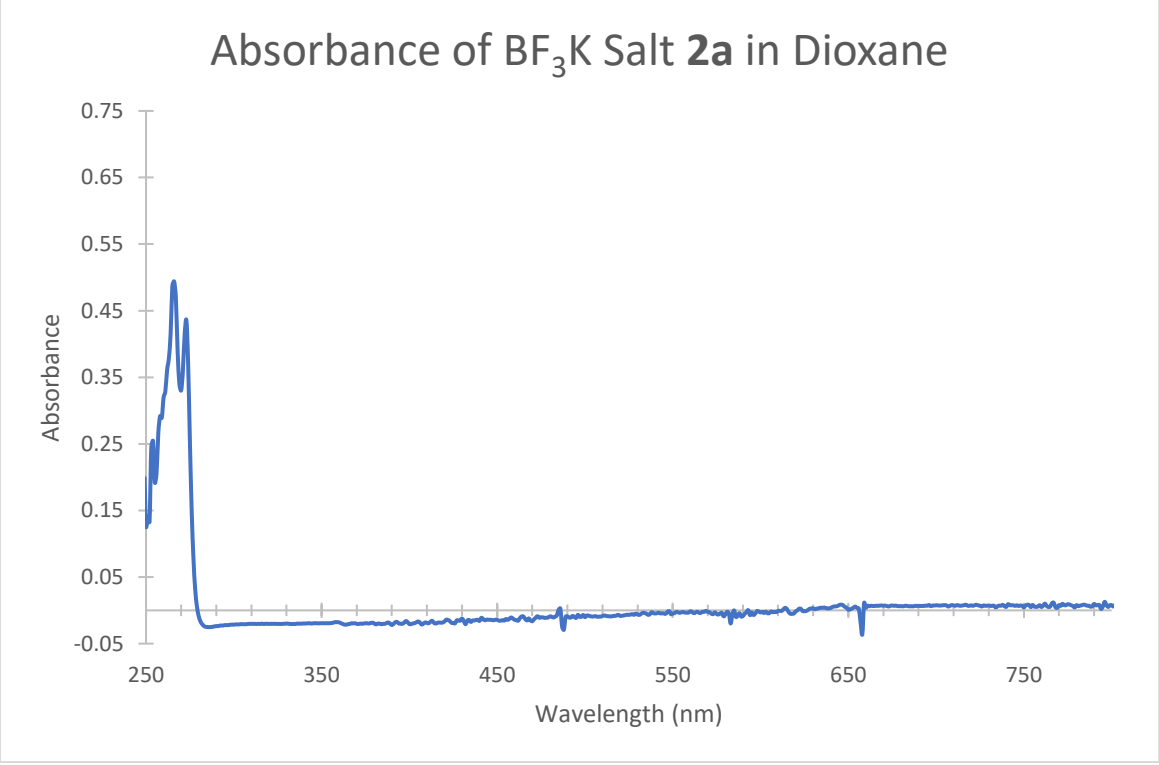


Figure S5: **2a** (2.1 mg, 0.01 mmol) in 1,4-dioxane (1 mL) were added to an 8 mL vial. The sample was then diluted with 1,4-dioxane to 0.001 M with respect to **2a** and transferred to a cuvette with a 1 cm path length.

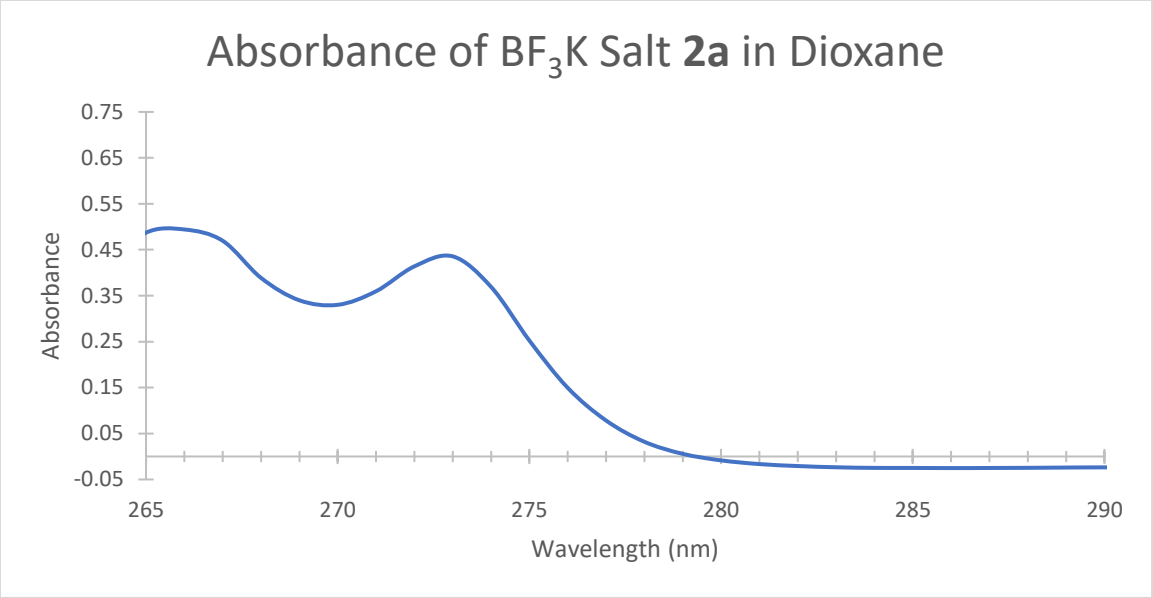


Figure S6: Zoomed in spectra from **Figure S5**.

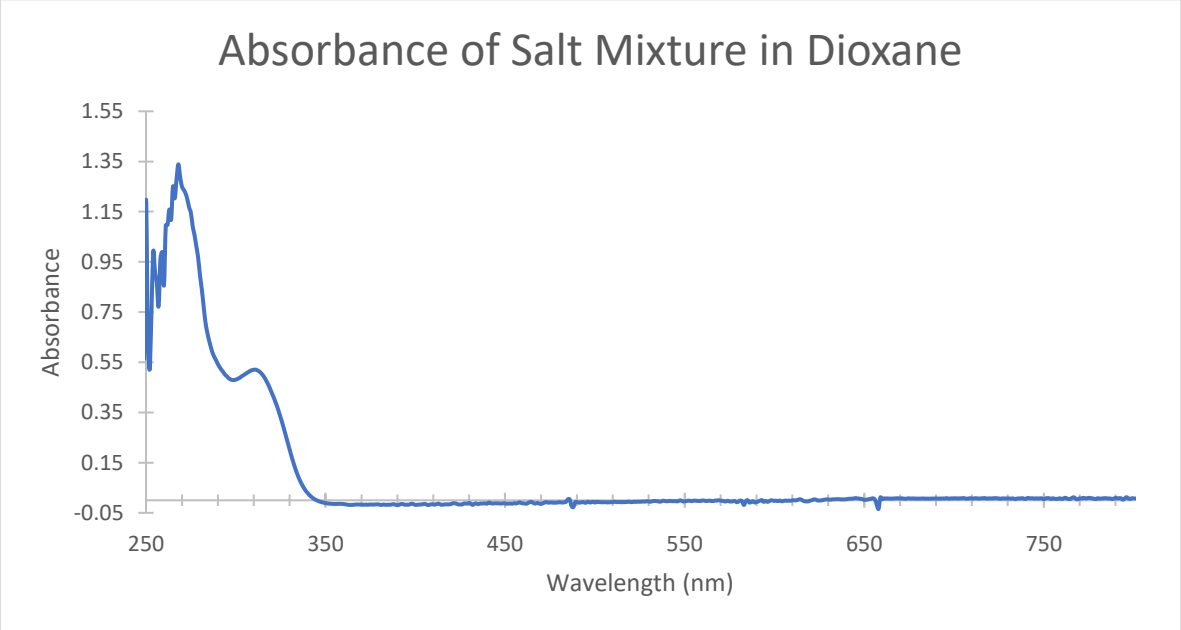


Figure S7: **1a** (5.7 mg, 0.01 mmol) and **2a** (2.1 mg, 0.01 mmol) in 1,4-dioxane (1 mL) were added to an 8 mL vial. The sample was then diluted with 1,4-dioxane to 0.0001 M with respect to both **1a** and **2a** (1:1 mixture) and transferred to a cuvette with a 1 cm path length.

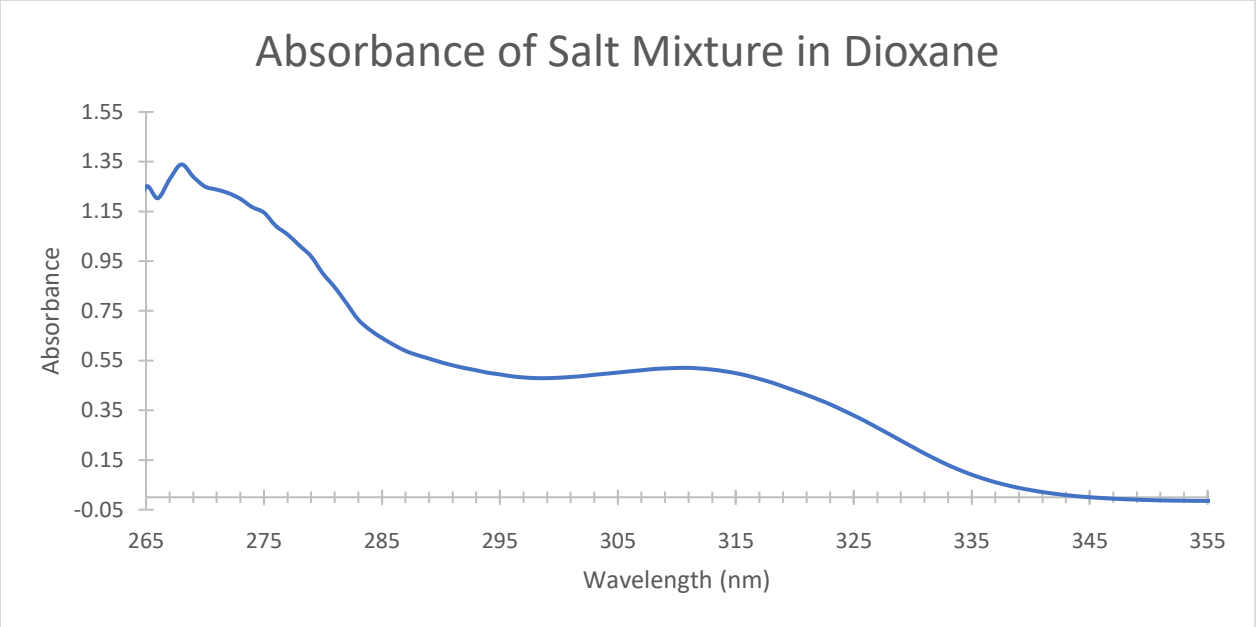


Figure S8: Zoomed in spectra from **Figure S7**.

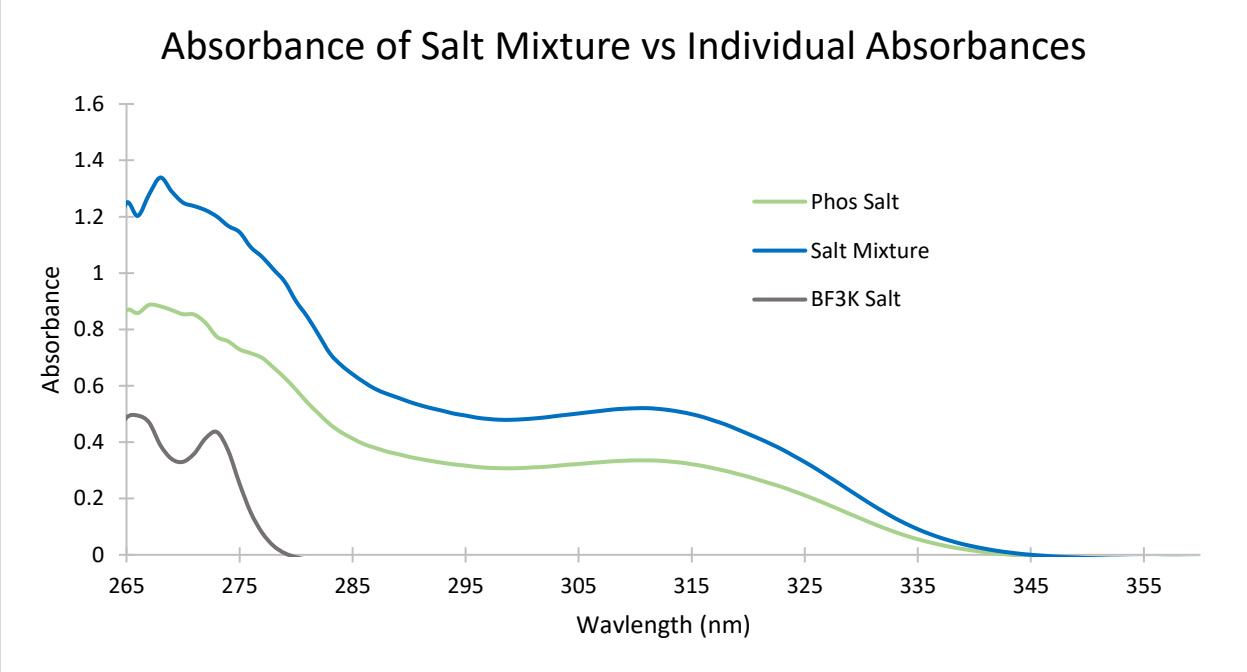


Figure S9. Overlaid UV-Vis spectra for each salt and a 1:1 mixture of both salts.

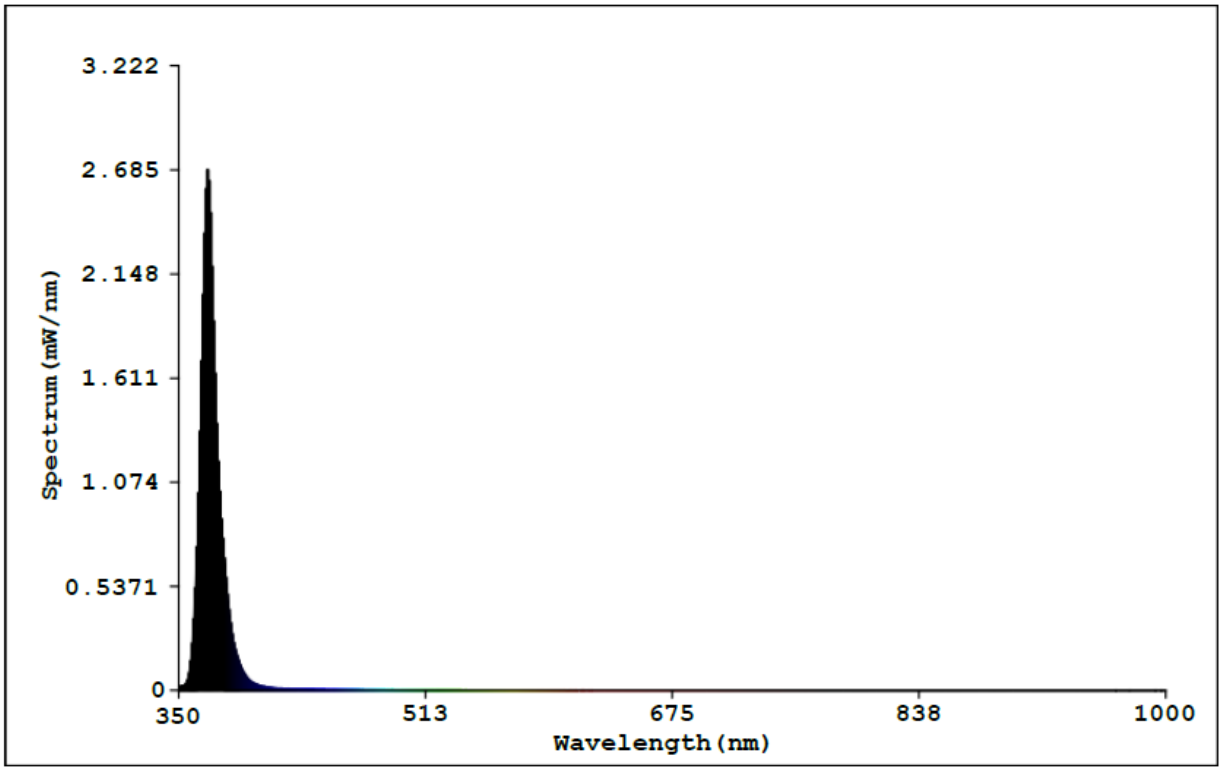


Figure S10. 365 nm LEDs emission spectrum provided by manufacturer.

Analysis: The investigation into whether an electron donor-acceptor (EDA) complex could be observed by UV-Visible spectroscopy between the phosphonium salt **1a** and BF_3K salt **2a** demonstrated that the two salts do not form an EDA complex. No bathochromic-shifted absorption was observed in comparison to the UV-Vis spectra for the two salts on their own. Phosphonium salt **1a** displays a minor absorbance of light approaching 345 nm at low concentration while the emission spectrum of the 365 nm LEDs shows minor emission tailing off past 350 nms. We attribute the success of the reaction irradiated with 365 nm LEDs in the absence of photocatalyst to the overlap of this absorbance and emission, and this minor overlap is consistent with the prolonged reaction time needed.

5. Stern-Volmer Quenching Studies

Fluorescence measurements were acquired at room temperature using an Edinburgh Instruments FS5 spectrometer. Emission quenching of the different samples were done using a screw-top 1.0 cm quartz cuvette with the corresponding solvent (1,4-dioxane or 1,2-dichloroethane) with a photocatalyst concentration of 9 μM. All the prepared solutions were transferred to the cuvette and degassed for 5 minutes with a stream of argon. The solution was excited at a wavelength of 400 nm and the emission spectra was recorded from 420 to 700 nm. Raw fluorescence intensity was measured at the emission λ_{max} (525 nm in 1,2-dichloroethane and 510 nm in 1,4-dioxane). Quenching of the excited state of 3DPAFIPN with phosphonium salt **1a** was carried out in 1,2-dichloroethane the solution of salt **1a** 1,4-dioxane was heterogeneous without the BF_3K salt. Quenching of the excited state of 3DPAFIPN with BF_3K salt **2a** was carried out in 1,4-dioxane.

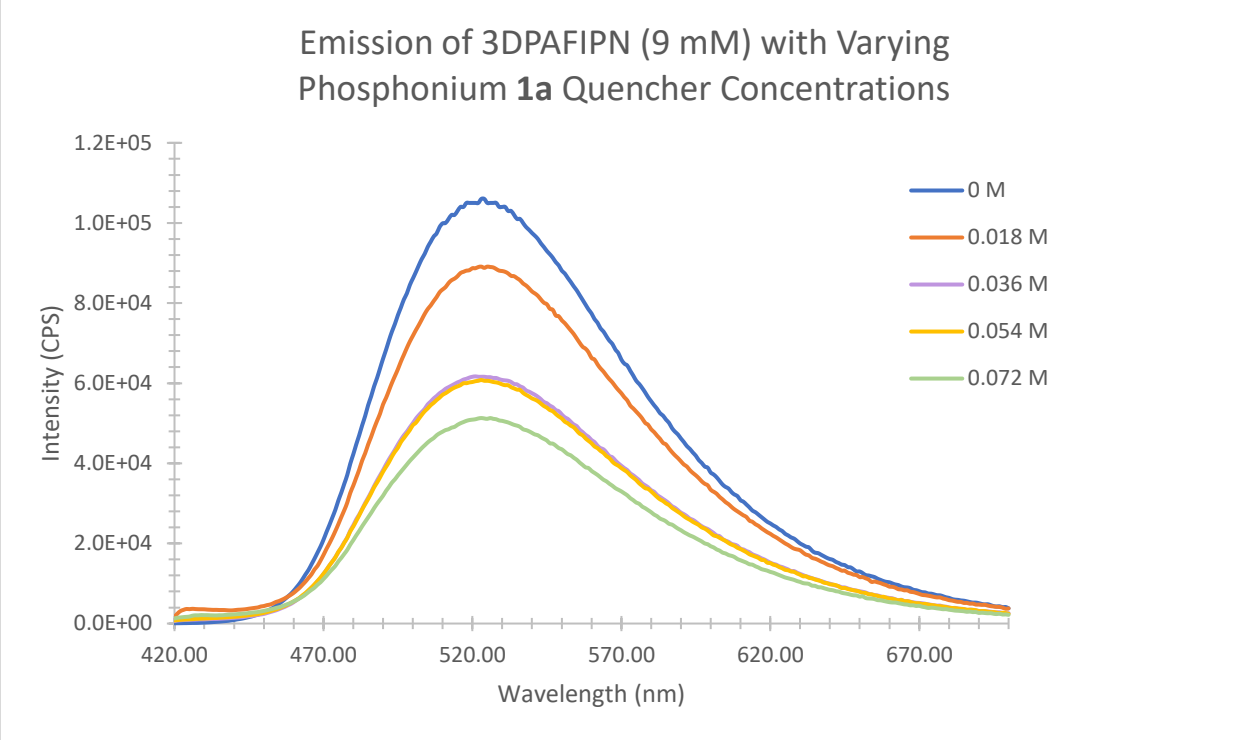


Figure S11. Emission spectra of 9 mM 3DPAFIPN with varying concentrations of phosphonium salt **1a** in 1,2-dichloroethane with excitation slit open at 4 nm and emission slit open at 0.5 nm.

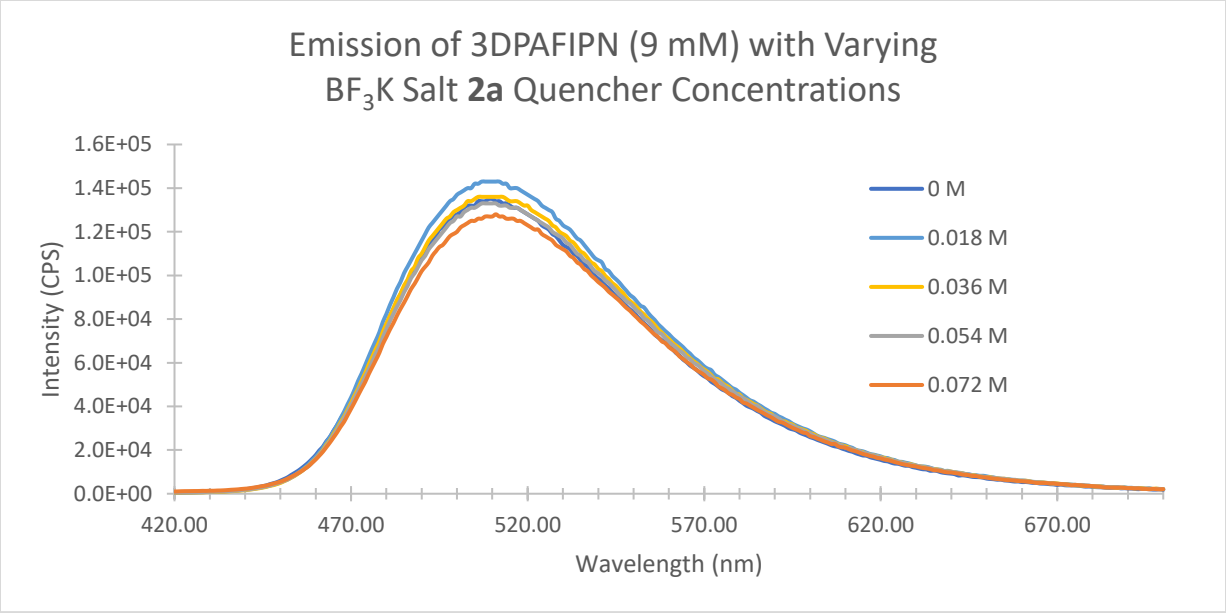


Figure S12. Emission spectra of 9 mM 3DPAFIPN with varying concentrations of BF_3K salt **2a** in 1,4-dioxane with excitation slit open at 2.5 nm and emission slit open at 0.5 nm.

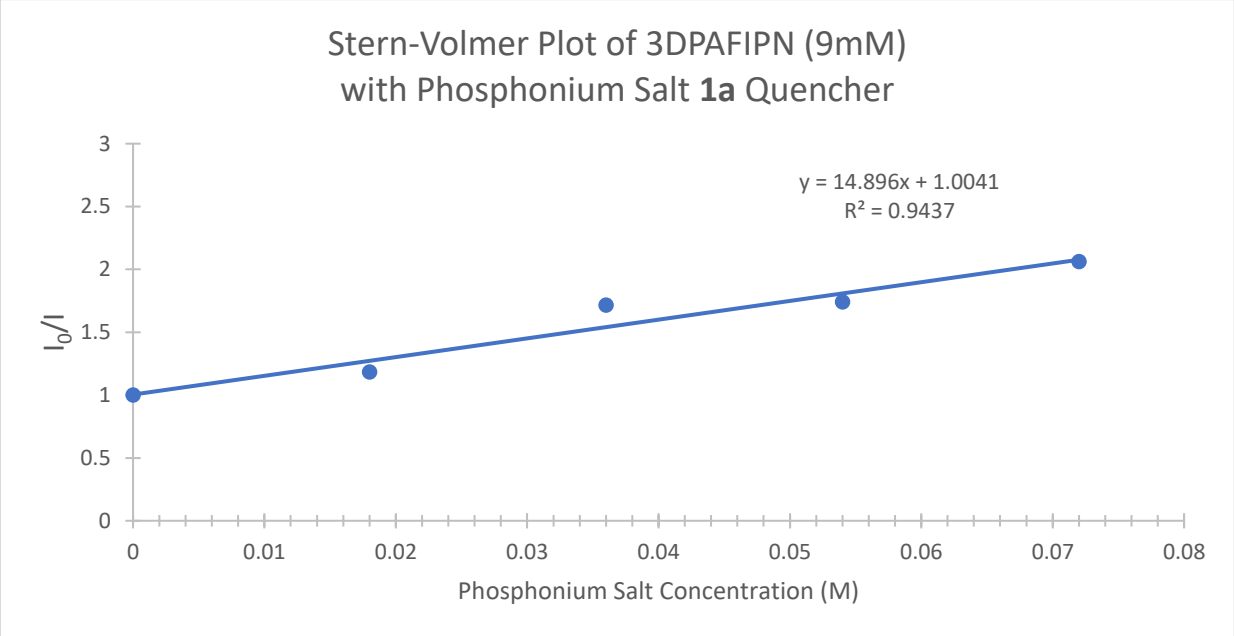


Figure S13. Stern-Volmer plot analysis derived from the data extracted from Figure **S7**. The Kq was determined from Stern-Volmer equation [Ksv = Kq τ] using a lifetime of τ = 4.2 ns for 3DPAFIPN[2]. K_{SV} = 14.9 M^{-1} and the resulting Kq for phosphonium salt **1a** is 3.55 x 10^9 L mol^{-1} s^{-1}.

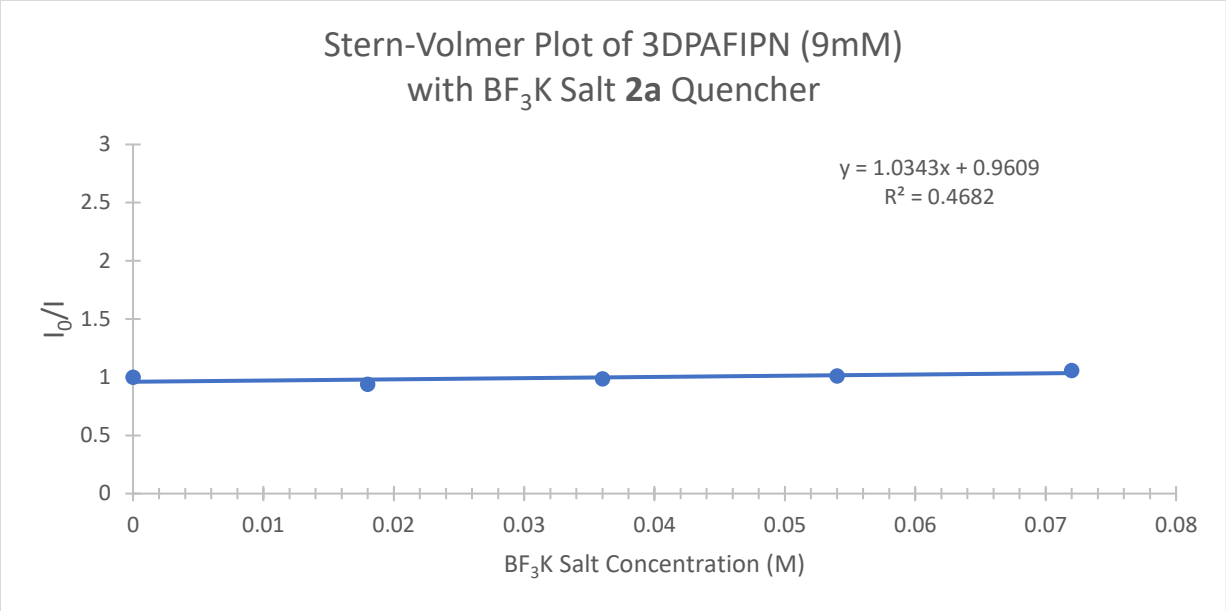


Figure S14. Stern-Volmer plot analysis derived from the data extracted from Figure **S8**. The Kq was determined from Stern-Volmer equation [Ksv = Kq τ] using a lifetime of τ = 4.2 ns for 3DPAFIPN[2]. K_{SV} = 1.0 M^{-1} and the resulting Kq for BF_3K salt **2a** is 2.4 x 10^8 L mol^{-1} s^{-1}. No significant quenching of 3DPAFIPN excited state was observed.

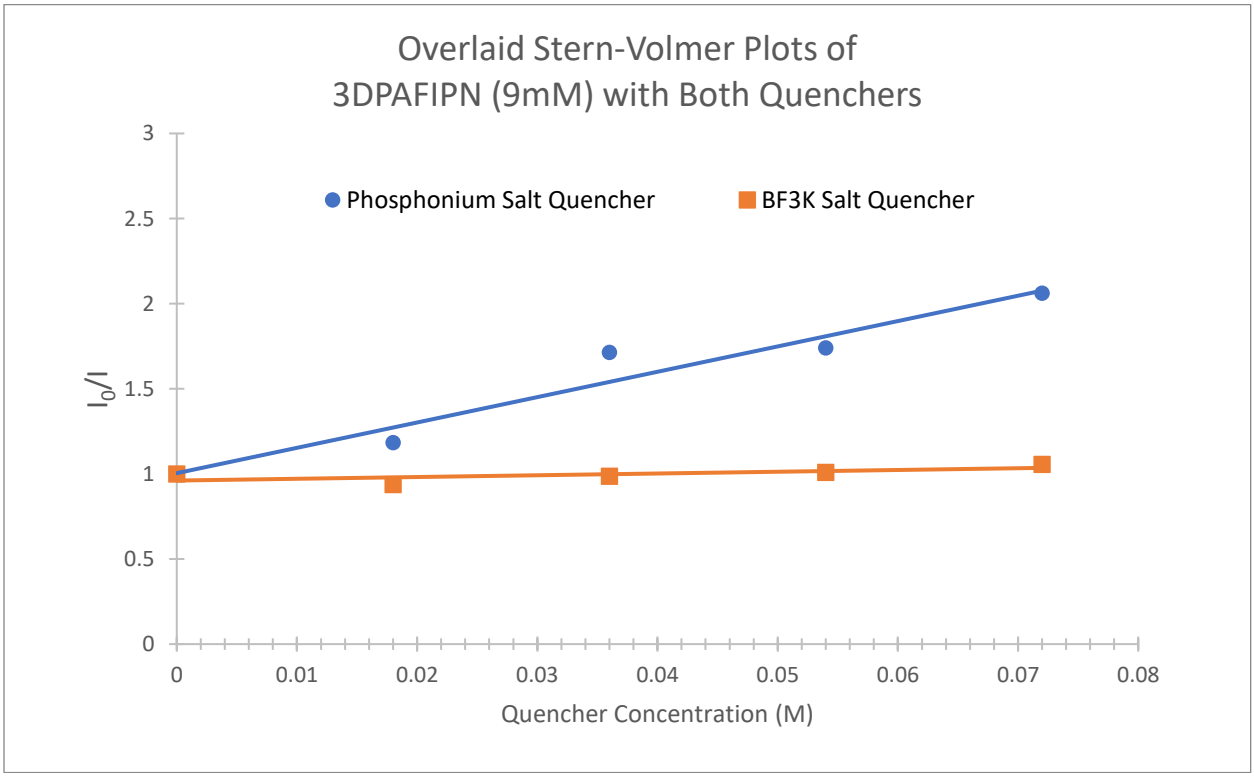
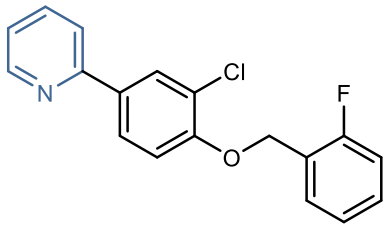


Figure S15. Stern-Volmer plots of both phosphonium salt **1a** and BF3K salt **2a**.

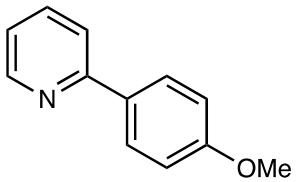
6. Preparation of Heteroaryl Precursors

2-(3-Chloro-4-((2-fluorobenzyl)oxy)phenyl)pyridine



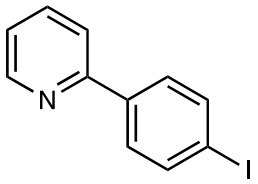
An oven dried 50 mL pressure tube was charged with (3-chloro-4-((2-fluorobenzyl)oxy)phenyl)boronic acid (843.0 mg, 3.00 mmol), K_2CO_3 (828.0 mg, 6 mmol), $Pd(OAc)_2$ (33.8 mg, 0.15 mmol), triphenylphosphine (157.2 mg, 0.60 mmol) and subjected to three cycles of vacuum/nitrogen backfill. Degassed H_2O (9.4 mL), degassed dimethoxyethane (9.4 mL), and 2-bromopyridine (0.29 mL, 3.00 mmol) was charged to the tube and the mixture was heated at 90℃ for 16 hours, then cooled to room temperature and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted 2x with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered over a frit, and concentrated *in vacuo*. Flash column chromatography (silica gel: 10% EtOAc in hexanes) afforded the title compound as a white crystalline solid (835.6 mg, 2.67 mmol, 89% yield). m.p. 74-76 ºC; IR ν_{max}/cm^{-1} (film): 3072, 3053, 2955, 2886, 1623, 1601, 1588, 1494, 1455, 1434, 1306, 1253, 1230, 1011, 772, 749, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 4.8 Hz, 1H), 7.91 (d, *J* = 2.3 Hz, 1H), 7.60 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.48 – 7.29 (m, 3H), 7.15 – 6.73 (m, 5H), 4.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0 (d, *J* = 246.7 Hz), 155.3, 154.4, 149.4, 136.6, 133.1, 129.6 (d, *J* = 8.0 Hz), 129.2 (d, *J* = 3.8 Hz), 128.7, 126.0, 124.3 (d, *J* = 3.5 Hz), 123.5 (d, *J* = 1.9 Hz), 123.3, 121.8, 119.6, 115.1 (d, *J* = 20.9 Hz), 113.4, 64.4 (d, *J* = 4.7 Hz); ^{19}F NMR (365 MHz, CDCl3) δ: –118.46; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 314.1, $C_{18}H_{14}ClFNO^+$ requires 314.1.

2-(4-Methoxyphenyl)pyridine



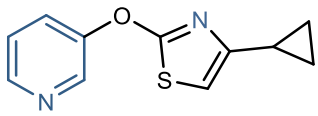
Prepared according to our previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 4.8 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.68–7.62 (m, 2H), 7.15–7.11 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.6, 157.2, 149.6, 136.7, 132.1, 128.2, 121.5, 119.9, 114.2, 55.4.

2-(4-Iodophenyl)pyridine



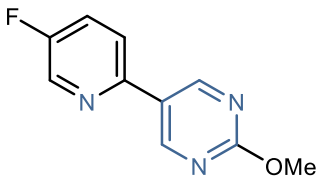
Prepared according to our previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (m, 1H), 7.82-7.66 (m. 6H), 7.27-7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 149.7, 138.7, 137.8, 136.8, 128.6, 122.4, 120.1, 95.4.

4-Cyclopropyl-2-(pyridin-3-yloxy)thiazole



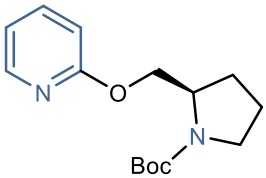
An oven dried mL round-bottom flask was charged with pyridin-3-ol (414.3 mg, 4.36 mmol), 2-bromo-4-cyclopropylthiazole (807.5 mg, 3.96 mmol), K_2CO_3 (658.7 mg, 4.25 mmol), and subjected to three cycles of vacuum/nitrogen backfill. The flask was charged with DMF (10 mL) and heated to 135℃ for four hours. The brown suspension was cooled to room temperature and poured into H_2O (100 mL). The aqueous phase was extracted with EtOAc (3x) and the combined organic layer was washed with brine, dried (Na_2SO_4), filtered through a frit, and concentrated *in vacuo*. Flash column chromatography (silica gel, gradient elution: 33% EtOAc in hexanes) afforded the title compound as a yellow oil (337.1 mg, 1.64 mmol, 41% yield); IR ν_{max}/cm^{-1} (film): 3025, 2955, 2923, 2852, 1604, 1559, 1478, 1422, 1231, 837, 799, 734; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (s, 1H), 8.51 (s, 1H), 7.80 – 7.62 (m, 1H), 7.35 (s, 1H), 6.40 (s, 1H), 1.95 – 1.81 (m, 1H), 1.30 – 1.20 (m, 2H), 0.88 – 0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.2, 153.7, 146.4, 142.1, 127.2, 124.3, 104.9, 12.8, 7.8 *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 219.1, $C_{11}H_{11}N_2OS^+$ requires 219.1.

5-(5-Fluoropyridin-2-yl)-2-methoxypyrimidine



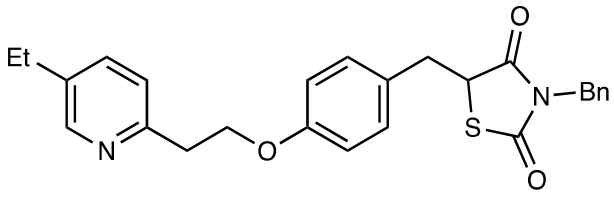
An oven dried 50 mL pressure tube was charged with 2-bromo-5-fluoropyridine (415.4 mg, 2.36 mmol), (2-methoxypyrimidin-5-yl)boronic acid (436.2 mg, 2.8 mmol), K_2CO_3 (651.4 mg, 4.72 mmol), $Pd(OAc)_2$ (79.7 mg, 0.35 mmol), triphenylphosphine (123.7 mg, 0.47 mmol) and subjected to three cycles of vacuum/nitrogen backfill. Degassed H_2O (9.4 mL) and degassed dimethoxyethane (9.4 mL) was charged to the tube and the mixture was heated at 90℃ for 16 hours, then cooled to room temperature and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted 2x with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered over a frit, and concentrated *in vacuo*. Flash column chromatography (silica gel: 35% EtOAc in hexanes) afforded the title compound as a white crystalline solid (201.1 mg, 0.99 mmol, 42% yield). m.p. 132-134 °C; IR ν_{max}/cm^{-1} (film): 3088, 3064, 3008, 2924, 2852, 1576, 1538, 1504, 1474, 1425, 1322, 1227, 1022, 908, 730, 703; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (s, 2H), 8.48 (d, *J* = 2.9 Hz, 1H), 7.60 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.44 (td, *J* = 8.3, 2.9 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.9, 159.2 (d, *J* = 257.5 Hz), 157.7, 148.8 (d, *J* = 4.0 Hz), 138.7 (d, *J* = 23.8 Hz), 126.0, 124.1 (d, *J* = 18.9 Hz), 120.6 (d, *J* = 4.4 Hz), 55.4; ^{19}F NMR (365 MHz, CDCl3) δ: –78.17; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 206.1, $C_{10}H_9FN_3O^+$ requires 206.1.

(R)-Tert-butyl 2-((pyridin-2-yloxy)methyl)pyrrolidine-1-carboxylate



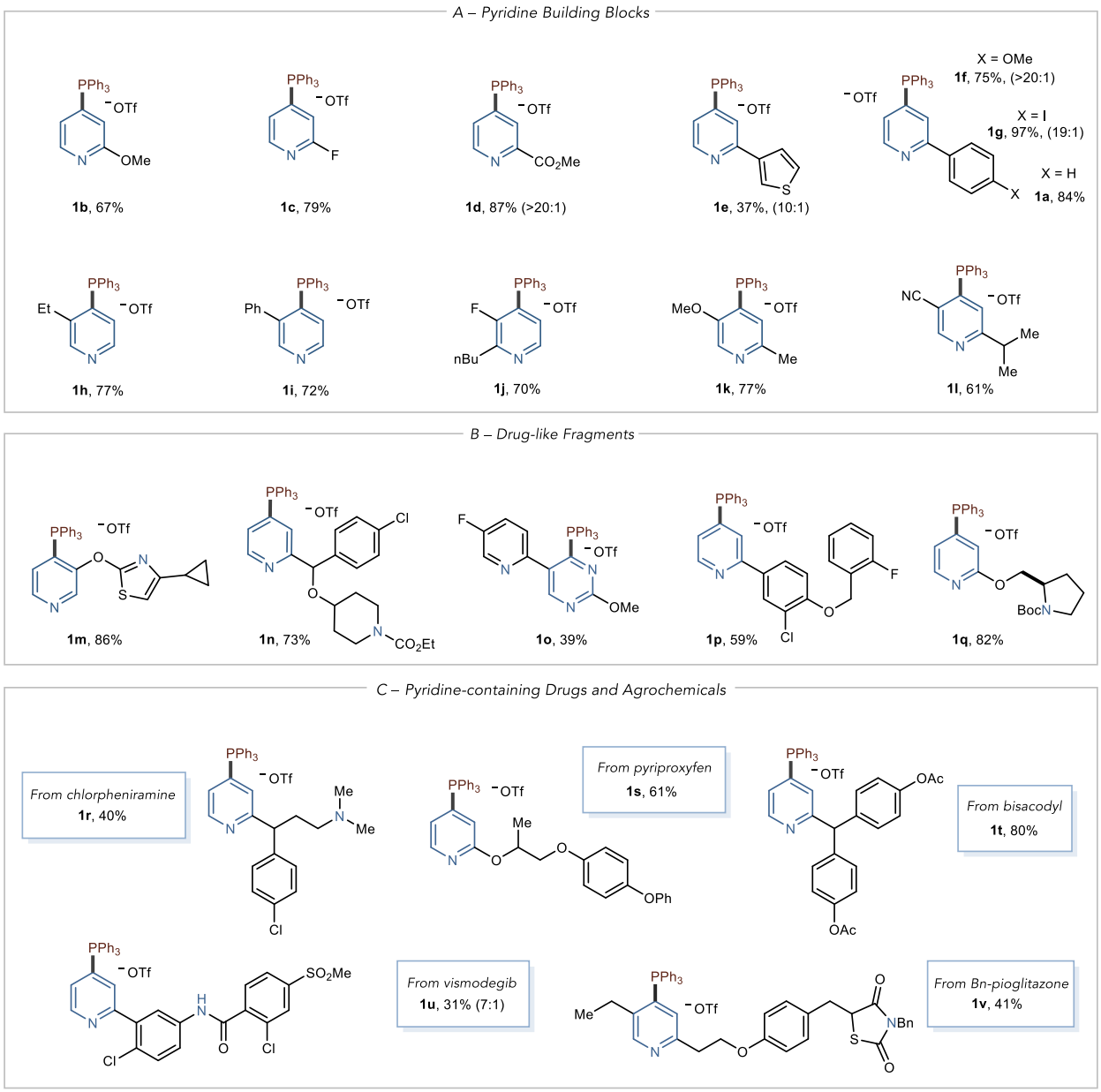
Prepared according to our previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (dd, J = 5.0, 1.5 Hz, 1H), 7.52 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.82 (t, *J* = 5.7 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 4.37-4.35 (m, 1H), 4.21-4.11 (m, 2H), 3.37 (br s, 2H), 1.98-1.90 (m, 3H), 1.83-1.77 (m, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.70, 154.48, 146.81, 138.44, 116.67, 110.89, 79.32, 66.05, 56.00, 46.36, 28.74, 28.45, 22.91; m/z LRMS (ESI + APCI) found $[M + H]^+$ 279.2, $C_{15}H_{23}N_2O_3^+$ requires 279.2.

3-Benzyl-5-(4-(2-(5-ethylpyridin-2-yl)ethoxy)benzyl)thiazolidine-2,4-dione



To a mixture of 5-(4-(2-(5-ethylpyridin-2-yl)ethoxy)benzyl)thiazolidine-2,4-dione (535 mg, 1.5 mmol) in DMF (15 mL) was added NaH (60% dispersion in oil) (66 mg, 1.65 mmol) at 0 °C. The reaction was warmed to rt over 15 minutes, then benzyl bromide (196 μL, 1.65 mmol) was added. The reaction was stirred at rt for 25 hours and then concentrated in vacuo. The crude material was purified by flash chromatography (silica gel: 100 % hexanes to 25 % EtOAc in hexanes) to provide the title compound as a light yellow solid (625 mg, 1.40 mmol, 93 % yield). m.p. 94-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 2.2 Hz, 1H), 7.48 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.32 – 7.23 (m, 5H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 4.79 – 4.59 (m, 2H), 4.43 (dd, *J* = 8.7, 4.0 Hz, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.38 (dd, *J* = 14.1, 4.0 Hz, 1H), 3.24 (t, *J* = 6.6 Hz, 2H), 3.09 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.78, 171.03, 158.32, 155.73, 149.02, 137.24, 136.01, 135.09, 130.49, 128.72, 128.16, 127.45, 123.47, 115.98, 114.83, 67.32, 51.73, 45.22, 37.64, 37.62, 25.82, 15.44. IR υ_{max}/cm^{-1} (film): 3033, 2966, 2931, 2874, 2360, 2342, 1749, 1680, 1611, 1512, 1490, 1430, 1382, 1330, 1247, 1179, 1146, 1029, 908, 730, 700. *m/z* HRMS (DART): $[M+H]^+$ calculated for $C_{26}H_{27}N_2O_3S^+$ = 447.1737, found 447.1748.

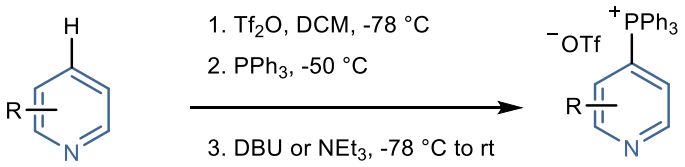
7. Preparation of Heterocyclic Phosphonium Salts



All yields are isolated yields of phosphonium salt as single regioisomers unless stated otherwise. Ratio in parenthesis denotes the ratio of 4-position regioisomer to 2-position regioisomer if any minor regioisomer was detected

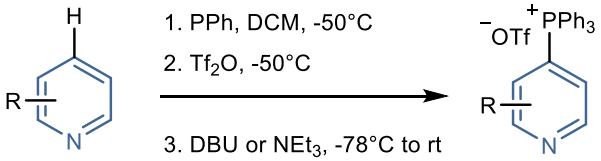
Table S5. Yields and Regioselectivities for Phosphonium Salt Formation Reaction of Salts Used in this Study

General Procedure A



An oven dried 8 mL vial (≤ 0.5 mmol scale) or a round bottom flask (> 0.5 mmol scale) equipped with a stir bar was charged with the heterocycle (1.0 equiv) and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) was added, the reaction vessel cooled to –78 °C, and Tf_2O (1.0 equiv) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes then warmed to –50 °C before PPh_3 (1.1 equiv) was added in one portion. The reaction was subjected to three rapid cycles of vacuum/nitrogen backfill and was stirred for a further 30 minutes at –78 °C. The stated organic base (NEt_3 or DBU, 1.0 equiv) was added dropwise via syringe, the cooling bath was removed, and the reaction was allowed to warm to room temperature while stirring (approximately 15-30 minutes). When the reaction mixture reached room temperature, it was then quenched with H_2O (approximately the same volume as CH_2Cl_2) and the mixture was transferred to a separatory funnel. The mixture was diluted with CH_2Cl_2 and the resulting organic layer was washed three times with H_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Approximately 2-10 mL (depending on the scale of the reaction) of CH_2Cl_2 was added to reaction mixture and was then added dropwise to an excess of Et_2O at room temperature. The flask was then placed in a –20 °C refrigerator for until the solid has settled to the bottom of the flask. The resulting suspension was filtered on a frit, washed with Et_2O, and dried *in vacuo* to provide the pure phosphonium salt.

General Procedure B

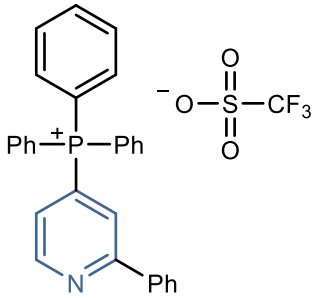


An oven dried round bottom flask equipped with a stir bar was charged with the heterocycle (1.0 equiv), PPh_3 (1.0 equiv), and placed under a nitrogen atmosphere. CH_2Cl_2 (0.1 M) was added, the reaction vessel cooled to –50 °C and Tf_2O (1.0 equiv) was added dropwise. After stirring for 1 hour, the reaction was cooled to –78 °C and DBU or NEt_3 (1.0 equiv) was added dropwise via syringe. The cooling bath was removed, and the reaction was allowed to warm to room temperature while stirring (approximately 20-30 minutes). The reaction mixture was diluted with CH_2Cl_2 and washed with H_2O (3x). The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo to approximately 2-5 mL (depending on the scale of the reaction). Approximately 2-10 mL (depending on the scale of the reaction) of CH_2Cl_2 was added to reaction mixture and was then added dropwise to an excess of Et_2O at room temperature which was then placed in a –20 °C refrigerator until the solid has settled to the bottom of the flask. The suspension was filtered on a frit, washed with Et_2O, and dried in vacuo to provide the pure product.

Notes.

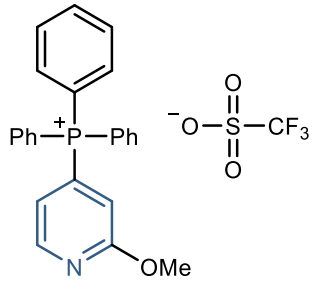
1) PPh_3 was crushed into a powder prior to use.
2) If the product forms an oil rather than a solid during the crash-out purification, allow the oil to settle to the bottom of the flask overnight at -20 °C. Decant the Et_2O away from the oil, and dissolve the oil in CH_2Cl_2. Transfer the solution to an appropriately sized round bottom flask (typically 250 mL round bottom flask for a 1-3 mmol scale salt reaction), concentrate *in vacuo*, and place the flask on high vac to solidify the residue.

Triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (1a)



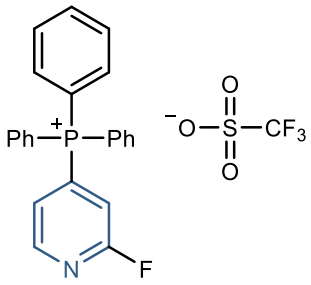
Prepared according to our previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.01 (app t, *J* = 5.1 Hz, 1H), 7.93-7.54 (m, 18H), 7.50 (ddd, *J* = 17.8, 5.1, 1.1 Hz, 1H), 7.42-7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1 (d, *J* = 9.9 Hz), 151.6 (d, *J* = 10.7 Hz), 136.7 (d, *J* = 1.5 Hz), 136.1 (d, *J* = 3.2 Hz), 134.3 (d, *J* = 9.8 Hz), 130.9 (d, *J* = 13.0 Hz), 130.3, 129.2 (d, *J* = 84.1 Hz), 129.0, 127.0, 125.2 (d, *J* = 7.8 Hz), 123.1, (d, *J* = 8.4 Hz), 120.7 (q, *J* = 321.1 Hz), 115.5 (d, *J* = 89.1 Hz).

Triphenyl(2-methoxypyridin-4-yl)phosphonium trifluoromethanesulfonate (1b)



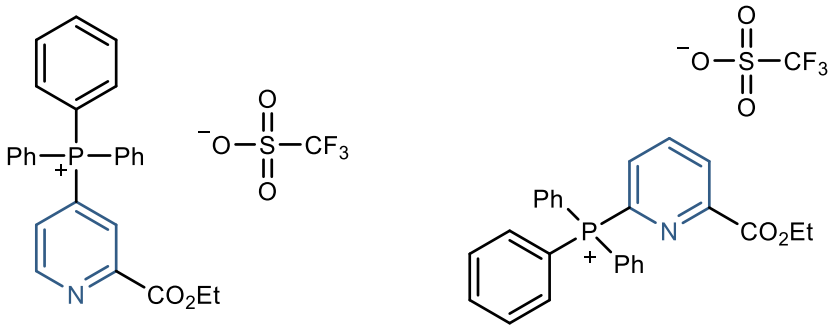
Prepared according to our previous report.[9] ^{1}H NMR (400 MHz, CDCl3) δ: 8.57 (t, *J* = 5.3 Hz, 1H), 7.97- 7.87 (m, 3H), 7.85-7.74 (m, 6H), 7.71-7.59 (m, 6H), 7.12 (dd, *J* = 11.5 Hz, 5.0 Hz, 1H), 6.84 (d, *J* = 15.0 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ: 164.5 (d, *J* = 15.7 Hz), 149.8 (d, *J* = 10.5 Hz), 136.1 (d, *J* = 2.9 Hz), 134.2 (d, *J* = 10.5 Hz), 130.9 (d, *J* = 13.5 Hz), 130.5 (d, *J* = 85.2 Hz), 120.7 (q, *J* = 321.2 Hz), 118.8 (d, *J* = 8.3 Hz), 116.2 (d, *J* = 10.0 Hz), 115.6 (d, *J* = 89.6 Hz), 54.3; ^{19}F NMR (365 MHz, CDCl3) δ: –78.17; ^{31}P NMR (162 MHz, CDCl3) δ: 22.37.

(2-Fluoropyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1c)



Prepared according to our previous report.[8] ^{1}H NMR (400 MHz, CDCl3) δ: 8.67 (app t, *J* = 5.3 Hz, 1H), 7.99-7.88 (m, 3H), 7.87-7.75 (m, 6H), 7.74-7.60 (m, 7H), 7.10 (d, *J* = 13.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ: 163.28 (dd, *J* = 245.4, 16.9 Hz), 150.63 (dd, *J* = 13.7, 12.7 Hz), 136.09 (d, *J* = 3.2 Hz), 134. 21 (d, *J* = 10.7 Hz), 133.95 (dd, *J* = 84.4, 6.6 Hz), 130.81 (d, *J* = 13.8 Hz), 125.18 (dd, *J* = 8.2, 5.1 Hz), 122.44 (q, *J* = 321.6 Hz), 114.81 (d, *J* = 90.1 Hz), 114.19 (dd, *J* = 40.3, 10.2 Hz).

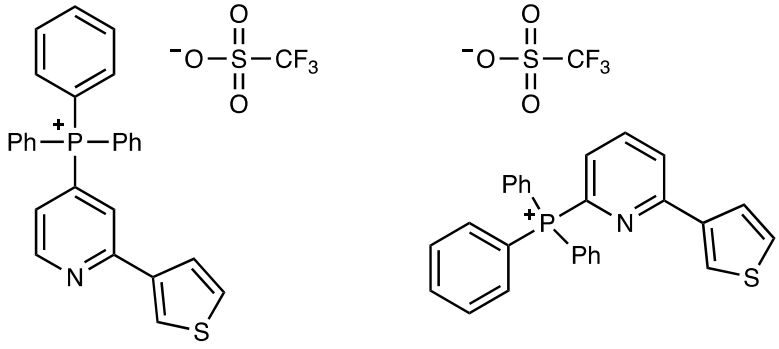
(2-(Ethoxycarbonyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1d)



>20:1 Mixture of Regioisomers

Prepared according to general procedure A using ethyl picolinate (130 μL, 1.00 mmol), Tf_2O (170 μL, 1.00 mmol), PPh_3 (288.2 mg, 1.10 mmol), NEt_3 (140 μL, 1.00 mmol) and CH_2Cl_2 (10 mL). After the purification procedure, the title compound was isolated as a white solid (359.9 mg, 0.87 mmol, 87% yield). m.p. 52–56 °C; IR ν_{max}/cm^{-1} (film): 3062, 1720, 1578, 1485, 1439, 1304, 1260, 1223, 1145, 1107, 1029, 997, 753, 726, 689; major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.18 (t, *J* = 4.8 Hz, 1H), 8.21 (dd, *J* = 13.1, 1.7 Hz, 1H), 8.06 – 7.88 (m, 4H), 7.81 (td, *J* = 7.8, 3.7 Hz, 6H), 7.71 – 7.63 (m, 6H), 4.47 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.9 (d, *J* = 2.7 Hz) 152.5 (d, *J* = 10.0 Hz), 149.9 (d, *J* = 10.2 Hz), 136.6 (d, *J* = 3.2 Hz), 134.8 (d, *J* = 10.6 Hz), 131.3 (d, *J* = 13.1 Hz), 130.2, 127.7 (d, *J* = 9.1 Hz), 120.9 (q, *J* = 321.0 Hz), 115.4 (d, *J* = 89.7 Hz), 63.1, 14.3; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.21; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.55. *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 412.2, $C_{26}H_{23}NO_2P^+$ requires 412.1.

Triphenyl(2-(thiophen-3-yl)pyridin-4-yl)phosphonium trifluoromethanesulfonate (1e)

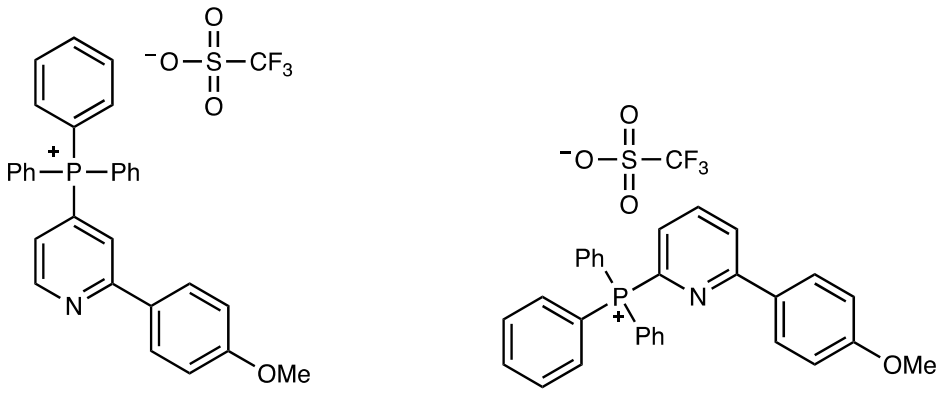


Major Minor

13:1 mixture of regioisomers

Prepared according to our previous report.[6] Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (td, *J* = 5.1, 0.9 Hz, 1H), 8.00 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.90-7.96 (m, 3H), 7.66-7.86 (m, 13H), 7.55 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.44 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.38-7.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1 (d, *J* = 10.9 Hz), 151.7 (d, *J* = 10.6 Hz), 139.8 (d, *J* = 1.6 Hz), 136.3 (d, *J* = 3.1 Hz), 134.4 (d, *J* = 10.3 Hz), 131.0 (d, *J* = 12.8 Hz), 129.3 (d, *J* = 84.2 Hz), 127.3, 126.4, 125.9, 124.8 (d, *J* = 8.2 Hz), 123.0 (d, *J* = 8.7 Hz), 120.8 (q, *J* = 321.1 Hz), 115.6 (d, *J* = 89.4 Hz); ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.15; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.69; m/z LRMS (ESI + APCI) found $[M–OTf]^+$ 422.2, $C_{27}H_{21}NPS^+$ requires 422.1.

(2-(4-Methoxyphenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1f)



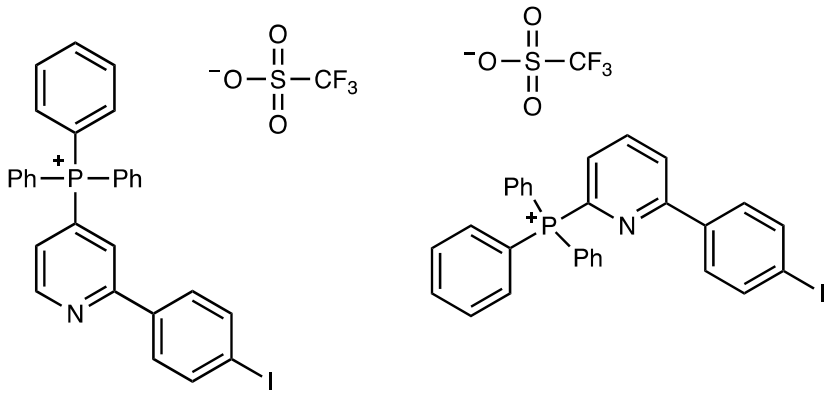
Major Minor

>20:1 mixture of regioisomers

Prepared according to our previous report.[6] Major Isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (app t, *J* = 5.1 Hz, 1H), 7.99-7.62 (m, 18H), 7.41 (dd, *J* = 12.7, 4.9 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.5, 158.8 (d, *J* = 10.5 Hz), 151.5 (d, *J* = 10.8 Hz), 136.2 (d, *J* = 2.9 Hz), 134.3 (d, *J* = 10.5 Hz), 130.9 (d, *J* = 13.0 Hz), 129.2 (d, *J* = 1.3 Hz), 129.0 (d, *J* = 84.0 Hz), 128.5, 124.6 (d, *J* = 8.1 Hz), 122.4 (m), 120.7 (q, *J* = 323.7 Hz), 115.6 (d, *J* = 89.5 Hz), 114.4, 55.4; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.12; ^{31}P NMR (162

MHz, $CDCl_3$) δ: 22.77 (major), 15.16 (minor); m/z LRMS (ESI + APCI) found $[M–OTf]^+$ 446.2, $C_{30}H_{25}NOP^+$ requires 446.2.

(2-(4-Iodophenyl) pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1g)

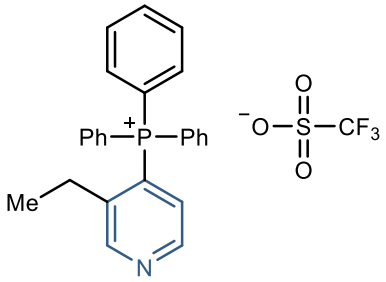


Major Minor

19:1 Mixture of Regioisomers

Prepared according to our previous report.[6] Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.05 (td, *J* = 5.1, 0.7 Hz, 1H), 7.96-7.63 (m, 20H), 7.54 (ddd, *J* = 12.7, 5.0, 1.6 Hz, 1H); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4 (d, *J* = 10.6 Hz), 151.8 (d, *J* = 10.7 Hz), 138.3, 136.5 (d, *J* = 1.5 Hz), 136.3 (d, *J* = 3.0 Hz), 135.6 (d, *J* = 10.6 Hz), 131.1 (d, *J* = 13.1 Hz), 129.7 (d, *J* = 83.9 Hz), 129.0, 125.8 (d, *J* = 8.0 Hz), 123.2 (d, *J* = 8.6 Hz), 121.1 (q, *J* = 321.2 Hz), 115.7 (d, *J* = 89.4 Hz), 97.4; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.14; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.78, 15.72; m/z LRMS (ESI + APCI) found $[M–OTf]^+$ 542.1, $C_{29}H_{22}INP^+$ requires 542.1.

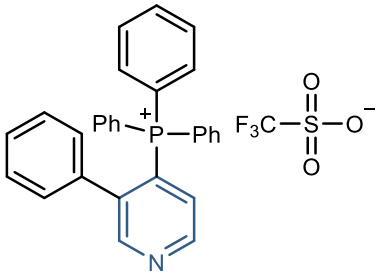
(3-Ethylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1h)



Prepared according to general procedure A using 3-ethylpyridine (110 μL, 1.00 mmol), Tf_2O (170 μL, 1.00 mmol), PPh_3 (288.2 mg, 1.10 mmol), DBU (150 μL, 1.00 mmol) and CH_2Cl_2 (10 mL). After the purification procedure, the title compound was isolated as a tan solid (282.0 mg, 0.77 mmol, 77% yield). m.p. 155–157 °C; IR ν_{max}/cm^{-1} (film): 2976, 1586, 1569, 1437, 1399, 1266, 1257, 1223, 1166, 1106, 1027, 752, 724, 708, 691; major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.92 (d, *J* = 6.8 Hz, 1H), 8.76 (t, *J* = 4.7 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.85 – 7.77 (m, 6H), 7.72 – 7.63 (m, 6H), 7.09 (dd, *J* = 15.2, 5.1 Hz, 1H), 2.44 (q, *J* = 7.4 Hz, 2H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2 (d, *J* = 8.1 Hz), 149.4 (d, *J* = 10.5 Hz), 142.4 (d, *J* = 7.0

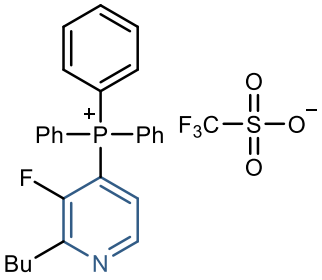
Hz), 136.2 (d, *J* = 3.1 Hz), 134.4 (d, *J* = 10.5 Hz), 131.3 (d, *J* = 13.1 Hz), 128.1 (d, *J* = 10.1 Hz), 126.4 (d, *J* = 83.4 Hz), 121.0 (q, *J* = 321.3 Hz), 116.7 (d, *J* = 88.7 Hz), 27.3 (d, *J* = 5.2 Hz), 13.7; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.13; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.33. *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 368.2, $C_{25}H_{23}NP^+$ requires 368.2.

Triphenyl(3-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (1i)



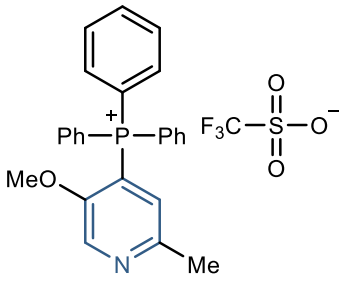
Prepared according to our previous report.[8] ^{1}H NMR (400 MHz, CDCl3) δ: 8.95 (app t, *J* = 4.7 Hz, 1H), 8.74 (d, *J* = 6.8 Hz, 1H), 7.85-7.73 (m, 3H), 7.73-7.40 (m, 13H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.91 (app t, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ: 153.6 (d, *J* = 8.0 Hz), 150.0 (d, *J* = 10.4 Hz), 141.7 (d, *J* = 7.3 Hz), 135.4 (d, *J* = 3.0 Hz), 134.4 (d, *J* = 4.5 Hz), 134.2 (d, *J* = 10.3 Hz), 130.6 (d, *J* = 13.0 Hz), 129.2, 128.9, 128.3, 128.2, 126.4 (d, *J* = 83.4 Hz), 120.8 (q, *J* = 321.2 Hz), 116.9 (d, *J* = 89.2 Hz).

(2-Butyl-3-fluoropyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1j)



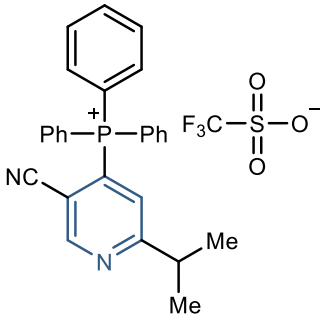
Prepared according to our previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (t, *J* = 4.0 Hz, 1H), 7.94–7.90 (m, 3H), 7.82–7.78 (m, 6H), 7.69–7.64 (m, 6H), 7.12 (dt, *J* = 14.0, 4.7 Hz, 1H), 2.95 (td, *J* = 7.6, 2.5 Hz, 2H), 1.73 (qn, *J* = 7.5 Hz, 2H), 1.37 (sext, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.80 (d, *J* = 263.2 Hz), 153.64 (dd, *J* = 16.0, 4.0 Hz), 147.23 (dd, *J* = 10.7, 6.6 Hz), 136.16 (d, *J* = 3.1 Hz), 133.98 (d, *J* = 10.7 Hz), 130.96 (d, *J* = 13.4 Hz), 125.87 (dd, *J* = 6.0, 2.3 Hz), 120.75 (q, *J* = 319.5 Hz), 115.64 (dd, *J* = 83.5, 15.0 Hz), 115.30 (d, *J* = 90.6 Hz), 31.07, 30.01, 22.18, 13.61.

(5-Methoxy-2-methylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1k)



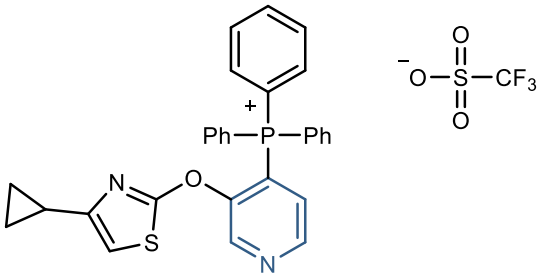
Prepared according to our previous report.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 6.9 Hz, 1H), 7.95–7.40 (m, 15H), 6.79 (d, *J* = 15.0 Hz, 1H), 3.62 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.72, 153.05 (d, *J* = 10.7 Hz), 135.62 (d, *J* = 4.6 Hz), 135.46 (d, *J* = 3.1 Hz), 133.71 (d, *J* = 10.7 Hz), 130.51 (d, *J* = 13.0 Hz), 127.12 (d, *J* = 6.9 Hz), 120.72 (q, *J* = 321.2 Hz), 116.46 (d, *J* = 91.6 Hz), 115.62 (d, *J* = 87.0 Hz), 57.01, 23.55.

(5-Cyano-2-isopropylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1l)



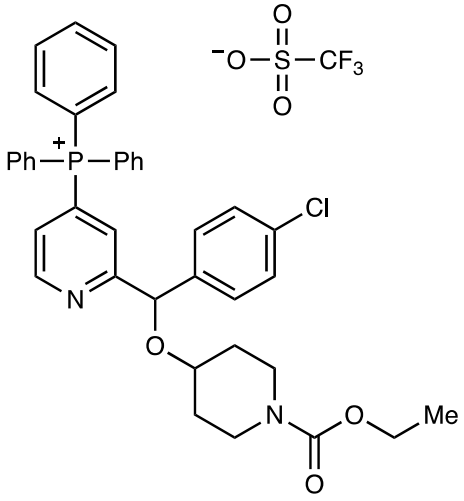
Prepared according to our previous report.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10 (d, *J* = 5.8 Hz, 1H), 7.96-7.90 (m, 3H), 7.86-7.73 (m, 12H), 7.34 (d, *J* = 15.3 Hz, 1H), 3.20 (sp, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5 (d, *J* = 8.9 Hz), 154.8 (d, *J* = 6.1 Hz), 136.3 (d, *J* = 3.0 Hz), 134.6 (d, *J* = 10.8 Hz), 131.0 (d, *J* = 82.5 Hz), 131.0 (d, *J* = 13.4 Hz), 127.6 (d, *J* = 7.5 Hz), 120.6 (q, *J* = 321.2 Hz), 114.4 (d, *J* = 89.8 Hz), 113.9 (d, *J* = 5.2 Hz), 108.9 (d, *J* = 3.7 Hz), 36.9, 21.5.

(3-((4-Cyclopropylthiazol-2-yl)oxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1m)



Prepared according to general procedure A using 4-cyclopropyl-2-(pyridin-3-yloxy)thiazole (382 mg, 1.75 mmol), Tf_2O (295 μL, 1.75 mmol), PPh_3 (506.1 mg, 1.83 mmol), DBU (263 μL, 1.75 mmol) and CH_2Cl_2 (17.5 mL). After the purification procedure, the title compound was isolated as a white solid (947 mg, 1.51 mmol, 86% yield). mp 160–164 °C; IR ν_{max}/cm^{-1} (film): 3112, 3063, 3002, 1533, 1438, 1406, 1287, 1266, 1219, 1107, 1029, 736, 710; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.12 (d, *J* = 6.2 Hz, 1H), 8.81 (t, *J* = 4.4 Hz, 1H), 7.87 (td, *J* = 7.2, 1.9 Hz, 3H), 7.80 – 7.60 (m, 12H), 7.35 (dd, *J* = 14.4, 4.9 Hz, 1H), 6.33 (s, 1H), 1.79 (tt, *J* = 8.5, 4.9 Hz, 1H), 0.93 – 0.80 (m, 2H), 0.72 – 0.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.3, 153.3, 152.0, 148.0 (d, *J* = 10.5 Hz), 144.4 (d, *J* = 4.3 Hz), 136.1 (d, *J* = 3.2 Hz), 134.2 (d, *J* = 10.9 Hz), 131.1 (d, *J* = 13.4 Hz), 128.5 (d, *J* = 6.6 Hz), 120.9 (q, *J* = 321.2 Hz), 119.2 (d, *J* = 85.5 Hz), 115.8 (d, *J* = 91.1 Hz), 106.7, 12.6, 8.0. ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.11; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 21.12. *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 479.2, $C_{29}H_{24}N_2OPS^+$ requires 479.1.

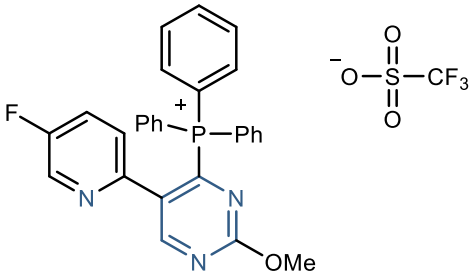
(2-((4-Chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl) triphenylphosphonium trifluoromethanesulfonate (1n)



Prepared according to our previous report.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (t, *J* = 5.1 Hz,

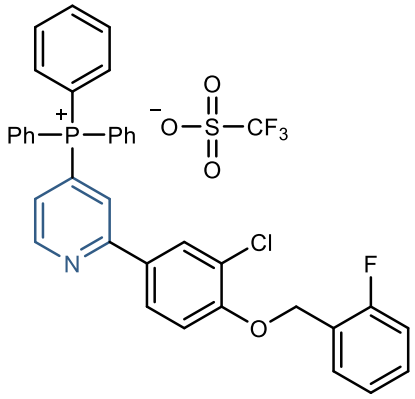
1H), 7.94-7.86 (m, 3H), 7.82-7.73 (m, 6H), 7.71-7.59 (m, 7H), 7.49 (ddd, *J* = 12.6, 5.0, 1.1 Hz, 1H), 7.34-7.25 (m, 4H), 5.71 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.70-3.60 (m, 1H), 3.55-3.42 (m, 2H), 3.25-3.12 (m, 2H), 1.79-1.56 (m, 2H), 1.54-1.37 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.4 (d, *J* = 9.6 Hz), 155.4, 151.1 (d, *J* =10.5 Hz), 138.7, 136.2 (d, *J* = 3.1 Hz), 134.5 (d, *J* = 10.5 Hz), 134.0, 130.9 (d, *J* = 13.1 Hz), 129.3 (d, *J* = 84.1 Hz), 128.8, 128.5, 125.9 (d, *J* = 8.4 Hz), 123.9 (d, *J* = 9.1 Hz), 120.8 (q, *J* = 321.2 Hz), 115.8 (d, *J* = 89.4 Hz), 79.9, 72.8, 61.3, 40.7 (rot), 40.7, 31.3, 30.3 (rot), 14.7.

((Trifluoromethyl)sulfonyl)-l1-oxidane, (5-(5-fluoropyridin-2-yl)-2-methoxypyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1o)



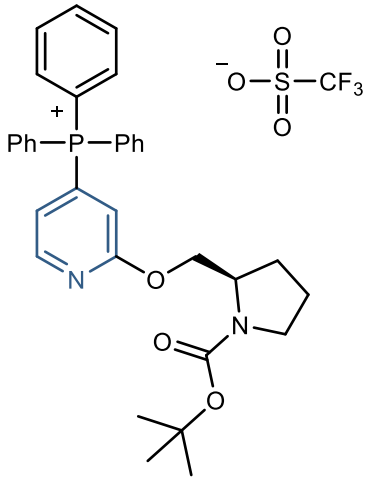
Prepared according to general procedure B using 5-(5-fluoropyridin-2-yl)-2-methoxypyrimidine (201.1 mg, 0.98 mmol), Tf_2O (170 μL, 0.98 mmol), PPh_3 (256.8 mg, 0.98 mmol), DBU (150 μL, 0.98 mmol) and CH_2Cl_2 (9.8 mL). After the purification procedure, the title compound was isolated as a white solid (237.1 mg, 0.38 mmol, 39% yield). mp 238–240 °C; IR ν_{max}/cm^{-1} (film): 3098, 3060, 1585, 1566, 1474, 1412, 1381, 1276, 1257, 1226, 1160, 1136, 1112, 1028, 709; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.32 (d, *J* = 9.3 Hz, 1H), 8.17 – 8.08 (m, 1H), 7.87 – 7.38 (m, 17H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0 (d, *J* = 20.9 Hz), 162.7 (d, *J* = 5.4 Hz), 159.4 (d, *J* = 261.0 Hz), 151.5 (d, *J* = 118.5 Hz), 145.5 (d, *J* = 4.1 Hz), 136.2 (d, *J* = 25.3 Hz), 134.8 (d, *J* = 3.1 Hz), 134.5 (d, *J* = 9.9 Hz), 132.0 (d, *J* = 15.4 Hz), 130.0 (d, *J* = 13.2 Hz), 125.3 (d, *J* = 18.9 Hz), 124.7 (d, *J* = 5.3 Hz), 121.0 (q, *J* = 320.2 Hz), 119.4 (d, *J* = 92.2 Hz), 56.2; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.20, –124.03; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 25.76. *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 466.2, $C_{28}H_{22}FN_3OP^+$ requires 466.1.

(2-(3-Chloro-4-((2-fluorobenzyl)oxy)phenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1p)



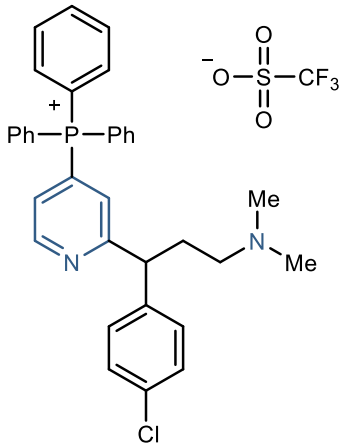
Prepared according to general procedure A using 2-(3-chloro-4-((2-fluorobenzyl)oxy)phenyl)pyridine (800.0 mg, 2.55 mmol), Tf_2O (430 μL, 2.55 mmol), PPh_3 (734 mg, 2.80 mmol), NEt_3 (360 μL, 2.55 mmol) and CH_2Cl_2 (25.5 mL). After the purification procedure, the title compound was isolated as a white solid (1.085 g, 1.50 mmol, 59% yield). mp 76–82 °C; IR ν_{max}/cm^{-1} (film): 3493, 3063, 2963, 2872, 2288, 1599, 1586, 1503, 1459, 1438, 1259, 1223, 1147, 1108, 1029, 997, 753, 725, 689; ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ: 9.03 (t, *J* = 5.1 Hz, 1H), 8.29 (d, *J* = 13.8 Hz, 1H), 8.20 (d, *J* = 2.3 Hz, 1H), 8.09 – 7.95 (m, 4H), 7.90 – 7.79 (m, 12H), 7.64 – 7.54 (m, 2H), 7.48 – 7.41(m, 2H), 7.31 – 7.23 (m, 2H), 5.33 (s, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ: 160.4 (d, *J* = 246.5 Hz), 155.8 (d, *J* = 10.7 Hz), 155.1, 151.2 (d, *J* = 10.9 Hz), 135.7 (d, *J* = 3.1 Hz), 134.9 (d, *J* = 10.7 Hz), 130.9 (d, *J* = 1.8 Hz), 130.8 (d, *J* = 8.4 Hz), 130.6, 130.6 (d, *J* = 4.3 Hz), 130.5, 129.7 (d, *J* = 84.6 Hz), 128.0 (d, *J* = 127.2 Hz), 126.1 (d, *J* = 8.6 Hz), 124.7 (d, *J* = 3.4 Hz), 123.7 (d, *J* = 9.1 Hz), 123.1 (d, *J* = 14.4 Hz), 122.3, 120.7 (q, *J* = 324.2 Hz), 116.5 (d, *J* = 89.3 Hz), 115.6 (d, *J* = 20.8 Hz), 114.5, 64.8 (d, *J* = 3.8 Hz); ^{19}F NMR (365 MHz, $(CD_3)_2SO$) δ: –77.74, -117.95; ^{31}P NMR (162 MHz, $(CD_3)_2SO$) δ: 22.08. *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 574.2, $C_{36}H_{27}ClFNOP^+$ requires 574.2.

(R)-(2-((1-(Tert-butoxycarbonyl)pyrrolidin-2-yl)methoxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1q)



Prepared according to our previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (t, *J* = 5.0 Hz, 1H), 7.94-7.90 (m, 3H), 7.82-7.79 (m, 6H), 7.67-7.62 (m, 6H), 7.10 (br s, 1H), 6.81 (*J* = 14.5 Hz, 1H), 4.48 (dd, *J* = 10.4, 4.1 Hz, 1H), 4.30 (t, *J* = 7.8 Hz, 1H), 4.18-4.12 (m, 1H), 3.48-3.33 (m, 2H), 1.94-1.87 (m, 4H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.19, 164.03, 154.29, 149.71 (d, *J* = 12.3 Hz), 136.07 (d, *J* = 1.0 Hz), 134.22 (d, *J* = 10.3 Hz), 130.85 (d, *J* = 13.0 Hz), 120.69 (q, *J* = 319.5 Hz), 119.00, 116.02 (d, *J* = 11.0 Hz), 115.52 (d, *J* = 89.2 Hz), 79.36, 67.17, 55.38, 46.24, 28.25, 27.78, 23.43-22.74 (rot); ^{19}F NMR (365 MHz, CDCl3) δ: –78.14; ^{31}P NMR (162 MHz, CDCl3) δ: 22.32.

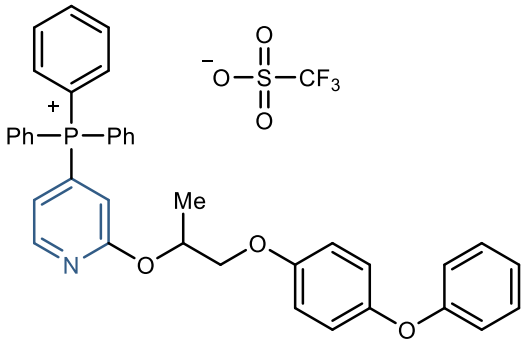
(2-(1-(4-Chlorophenyl)-3-(dimethylamino)propyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1r)



Prepared according to our previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.97 (app t, *J* = 5.1 Hz, 1H), 7.93-7.86 (m, 3H), 7.80-7.70 (m, 6H), 7.61-7.50 (m, 6H), 7.39 (ddd, *J* = 12.8, 5.1, 1.5 Hz, 1H), 7.25-7.16 (m, 5H), 4.28 (app t, *J* = 6.8 Hz, 1H), 2.56-2.43 (m, 1H), 2.32-2.11 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) d: 165.55 (d, *J* = 9.9 Hz), 150.97 (d, *J* = 9.9 Hz), 140.26, 135.82 (d, *J* = 3.1 Hz), 134.02 (d, *J* = 10.7 Hz), 132.25, 130.61 (d, *J* = 13.0 Hz), 128.92 (d, *J* = 85.5 Hz), 128.75, 127.92, 126.26 (d, *J* = 8.4 Hz), 124.42 (d, *J* = 7.6 Hz), 120.46 (q, *J* = 321.2 Hz), 115.31 (d, *J* =

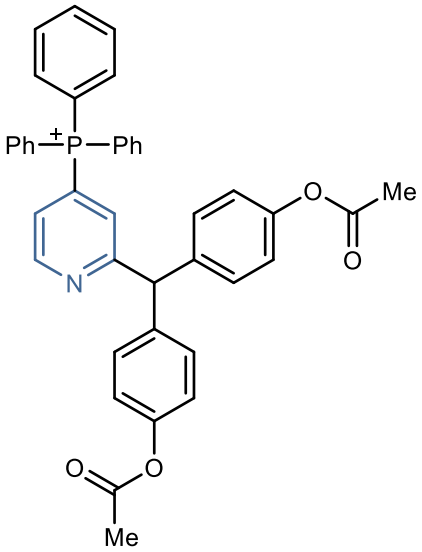
89.3 Hz), 56.73, 49.77, 44.88, 31.99.

(2-((1-(4-Phenoxyphenoxy)propan-2-yl)oxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1s)



Prepared according to our previous report.[12] ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.55 (app t, *J* = 5.3 Hz, 1H), 7.93-7.87 (m, 3H), 7.82-7.74 (m, 6H), 7.67-7.59 (m, 6H), 7.30-7.23 (m, 2H), 7.13 (ddd, *J* = 11.7, 5.3, 1.2 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.94-6.77 (m, 7H), 5.66 (sext, *J* = 5.3 Hz, 1H), 4.18-4.07 (m, 2H), 1.48 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d: 163.72 (d, *J* = 15.9 Hz), 158.13, 154.71, 150.29, 149.77 (d, *J* = 12.1 Hz), 136.11 (d, *J* = 3.0 Hz), 134.32 (d, *J* = 10.6 Hz), 130.91 (d, *J* = 13.0 Hz), 130.78 (d, *J* = 84.2 Hz), 129.50, 122.43, 120.78 (q, *J* = 321.2 Hz), 120.56, 119.08 (d, *J* = 8.1 Hz), 117.47, 116.55 (d, *J* = 10.0 Hz), 115.62 (d, *J* = 89.4 Hz), 115.61, 71.50, 70.49, 16.41.

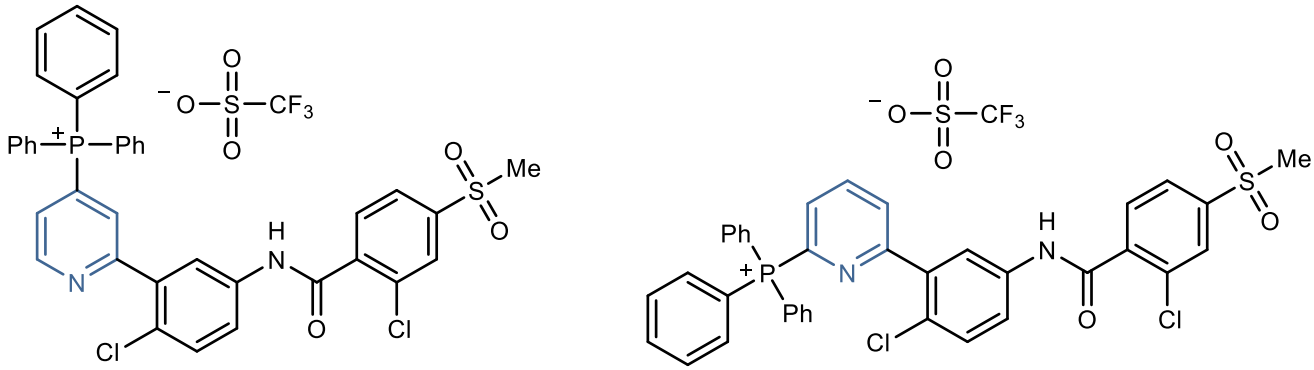
(2-(Bis(4-Acetoxyphenyl)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1t)



Prepared according to our previous report.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.90 (app t, *J* = 5.1 Hz, 1H), 7.86-7.80 (m, 3H), 7.73-7.66 (m, 6H), 7.56-7.39 (m, 7H), 7.18 (d, *J* = 13.7 Hz, 1H), 7.13-

7.08 (m, 4H), 6.97–6.91 (m, 4H), 5.72 (s, 1H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.1, 165.0 (d, *J* = 9.4 Hz), 151.2 (d, *J* = 10.4 Hz), 149.3, 138.4, 135.9 (d, *J* = 3.0 Hz), 134.1 (d, *J* = 10.6 Hz), 130.7 (d, *J* = 13.0 Hz), 129.9, 129.0 (d, *J* = 83.8 Hz), 126.6 (d, *J* = 8.7 Hz), 124.9 (d, *J* = 7.9 Hz), 121.5, 120.6 (q, *J* = 321.2 Hz), 115.3 (d, *J* = 89.4 Hz), 57.4, 20.8; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.05; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.34.

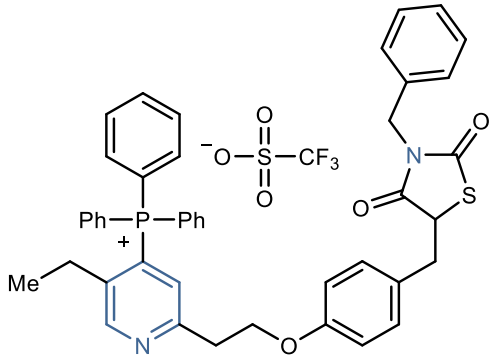
(2-(2-Chloro-5-(2-chloro-4-(methylsulfonyl)benzamido)phenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate and (6-(2-chloro-5-(2-chloro-4-(methylsulfonyl)benzamido)phenyl)pyridin-2-yl)triphenylphosphonium trifluoromethanesulfonate (1u)



7:1 Mixture of Regioisomers

Prepared according to our previous report.[12] Major isomer, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.98 (s, 1H), 8.98 (app t, *J* = 4.9 Hz, 1H), 8.15-7.33 (m, 23H), 3.01 (s, 3H); Major isomer, ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.5, 158.5 (d, *J* = 10.8 Hz), 151.2 (d, *J* = 10.9 Hz), 142.3, 140.4, 137.9, 136.8, 136.2 (d, *J* = 2.9 Hz), 134.4 (d, *J* = 10.5 Hz), 132.5, 130.9 (d, *J* = 13.1 Hz), 130.5, 130.0, 128.7, 128.5 (d, *J* = 84.4 Hz), 128.1 (d, *J* = 8.8 Hz), 126.4, 125.8, 125.4 (d, *J* = 8.4 Hz), 123.2, 122.6, 120.4 (q, *J* = 320.6 Hz), 115.6 (d, *J* = 89.6 Hz), 44.3; Both isomers, ^{19}F NMR (365 MHz, $CDCl_3$) δ: –78.34; Both isomers, ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.60 (major), 17.95 (minor).

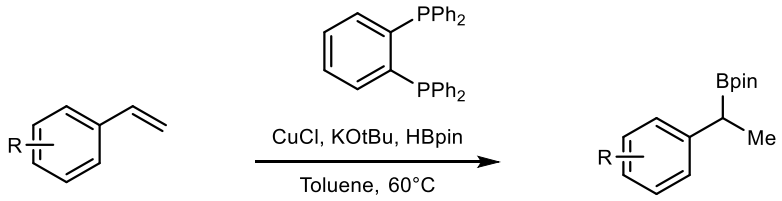
(2-(2-(4-((3-Benzyl-2,4-dioxothiazolidin-5-yl)methyl)phenoxy)ethyl)-5-ethylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (1v)



Prepared according to general procedure B using 3-benzyl-5-(4-(2-(5-ethylpyridin-2-yl)ethoxy)benzyl)thiazolidine-2,4-dione (450.1 mg, 1.01 mmol), Tf_2O (170 μL, 1.01 mmol), PPh_3 (264.6 g, 1.01 mmol), DBU (150 μL, 1.01 mmol) and CH_2Cl_2 (10.1 mL). After the purification procedure, the title compound was isolated as a white solid (355.1 mg, 0.41 mmol, 41% yield). mp 80–85 °C; IR ν_{max}/cm^{-1} (film): 3234, 3135, 3085, 3031, 2959, 2932, 1748, 1676, 1608, 1438, 1264, 1239, 1152, 1052, 1029, 723, 690; ^{1}H NMR (400 MHz, CD_3CN) δ: 8.88 (d, *J* = 7.0 Hz, 1H), 7.97 – 7.81 (m, 3H), 7.78 – 7.60 (m, 12H), 7.26 – 7.18 (m, 3H), 7.07 (ddd, *J* = 12.6, 6.5, 3.2 Hz, 5H), 6.67 – 6.52 (m, 2H), 4.76 – 4.53 (m, 3H), 4.23 (t, *J* = 6.0 Hz, 2H), 3.40 – 3.08 (m, 4H), 2.39 (qd, *J* = 7.4, 1.1 Hz, 2H), 0.70 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ: 174.9, 172.2, 159.5 (d, *J* = 10.8 Hz), 158.7, 153.6 (d, *J* = 8.9 Hz), 141.2 (d, *J* = 7.4 Hz), 136.6 (d, *J* = 3.2 Hz), 136.6, 135.5 (d, *J* = 10.5 Hz), 131.8, 131.6 (d, *J* = 13.0 Hz), 129.5, 129.1, 128.7, 128.7, 127.6, 126.7, 122.2 (q, *J* = 322.2 Hz), 118.0 (d, *J* = 88.9 Hz), 115.3, 66.9, 52.2, 45.7, 38.0, 37.1, 27.4 (d, *J* = 5.2 Hz), 13.9; ^{19}F NMR (365 MHz, CD_3CN) δ: –79.16; ^{31}P NMR (162 MHz, CD_3CN) δ: 21.48; *m/z* LRMS (ESI + APCI) found $[M\text{-}OTf]^+$ 707.3, $C_{28}H_{22}FN_3OP^+$ requires 707.2.

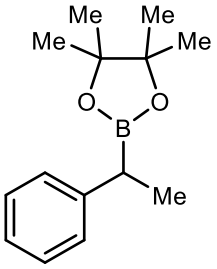
8. Preparation of Pinacol Boronic Esters

General Procedure C



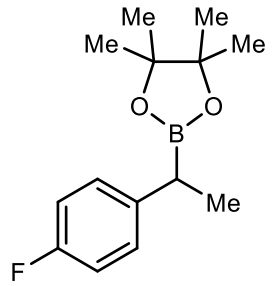
Boronic esters were prepared according to the report of Noh et al.[13] An oven dried pressure tube of appropriate size was equipped with a magnetic stir bar was charged with CuCl (3 mol%), KOtBu (6 mol%), and 1,2-bis(diphenylphosphaneyl)benzene (5 mol%), and the pressure tube was subjected to three rapid cycles of vacuum/nitrogen backfill followed by addition of toluene (2.5 M). The reaction was stirred at room temperature for ten minutes before addition of pinacolborane (1.2 equiv). After stirring for another ten minutes, the reaction mixture was diluted with toluene (1M) and charged with the corresponding styrene (1 equiv). The reaction was sealed with the pressure tube cap and heated to 60 °C overnight. The reaction was filtered through a pad of celite, concentrated *in vacuo*, and purified by flash column chromatography under the stated conditions to provide the benzyl boronic ester.

4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane



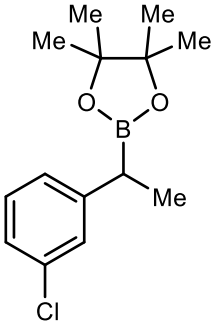
Prepared according to General Procedure C with CuCl (89.1 mg, 0.9 mmol, 3 mol%), KOtBu (201.6 mg, 1.8 mmol, 6 mol%), 1,2-bis(diphenylphosphaneyl)benzene (669.0 mg, 1.5, 5 mol%), and toluene (12 mL, 2.5 M). Then, pinacolborane was added (5.2 mL, 36 mmols, 1.2 equiv) followed by dilution with toluene (18 mL, 1 M) and addition of styrene (3.4 mL, 30 mmol, 1 equiv) to provide the title compound (5.7135 g, 24.6 mmols, 82% yield). The compound was purified via flash column chromatography (silica gel: 5% Et_2O in hexanes) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.3 – 7.2 (m, 4H), 7.2 (t, *J* = 7.1 Hz, 1H), 2.5 (q, *J* = 7.6 Hz, 1H), 1.4 (d, *J* = 7.6 Hz, 3H), 1.2 (d, *J* = 5.7 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.0, 128.3, 127.8, 125.1, 83.3, 24.6, 24.6, 17.1. All characterization data are consistent with previous reports.[10]

2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Prepared according to General Procedure C with CuCl (14.9 mg, 0.15 mmol, 3 mol%), KOtBu (33.6 mg, 1.30 mmol, 6 mol%), 1,2-bis(diphenylphosphaneyl)benzene (111.5 mg, 0.25, 5 mol%), and toluene (2 mL, 2.5 M). Then, pinacolborane was added (0.87 mL, 6 mmols, 1.2 equiv) followed by dilution with toluene (3 mL, 1 M) and addition of 1-fluoro-4-vinylbenzene (0.60 mL, 5 mmol, 1 equiv). The compound was purified via flash column chromatography (silica gel: 5% Et_2O in hexanes) to provide the title compound (1.0505 g, 4.2 mmols, 84% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 – 7.11 (m, 2H), 7.07 – 6.87 (m, 2H), 2.41 (q, *J* = 7.5 Hz, 1H), 1.31 (d, *J* = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.0 (d, *J* = 242.3 Hz), 140.7 (d, *J* = 3.1 Hz), 129.1 (d, *J* = 7.8 Hz), 115.1 (d, *J* = 21.0 Hz), 83.5, 24.8, 24.7, 17.4; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –119.03. All characterization data are consistent with previous reports.[13]

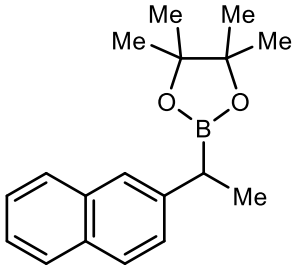
2-(1-(3-Chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Prepared according to General Procedure C with CuCl (14.9 mg, 0.15 mmol, 3 mol%), KOtBu (33.6 mg, 1.30 mmol, 6 mol%), 1,2-bis(diphenylphosphaneyl)benzene (111.5 mg, 0.25, 5 mol%), and toluene (2 mL, 2.5 M). Then, pinacolborane was added (0.87 mL, 6 mmols, 1.2 equiv) followed by dilution with toluene (3 mL, 1 M) and addition of 1-chloro-3-vinylbenzene (0.64 mL, 5 mmol, 1 equiv). The compound was purified via flash column chromatography (silica gel: 3% Et_2O in hexanes) to provide the title compound (1.1366 g, 4.25 mmols, 85% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 – 7.14 (m, 2H), 7.14 – 7.06 (m, 2H), 2.42 (q, *J* = 7.5 Hz,

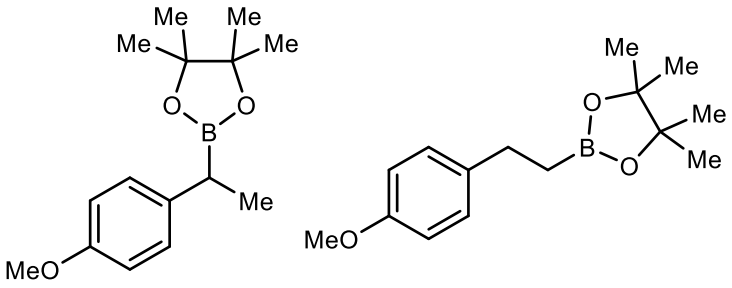
1H), 1.32 (d, J = 7.5 Hz, 3H), 1.22 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 134.1, 129.6, 128.0, 126.2, 125.4, 83.6, 24.7, 24.7, 16.9. All characterization data are consistent with previous reports.[13]

4,4,5,5-Tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane



Prepared according to General Procedure C with CuCl (14.9 mg, 0.15 mmol, 3 mol%), KOtBu (33.6 mg, 1.30 mmol, 6 mol%), 1,2-bis(diphenylphosphaneyl)benzene (111.5 mg, 0.25, 5 mol%), and toluene (2 mL, 2.5 M). Then, pinacolborane was added (0.87 mL, 6 mmols, 1.2 equiv) followed by dilution with toluene (3 mL, 1 M) and addition of 2-vinylnaphthalene (770 mg, 5 mmol, 1 equiv). The compound was purified via flash column chromatography (silica gel: 5% Et_2O in hexanes) to provide the title compound (1.0142 g, 3.6 mmols, 84% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 – 7.73 (m, 3H), 7.67 (d, J = 1.7 Hz, 1H), 7.42 (pd, J = 7.0, 1.5 Hz, 3H), 2.64 (q, J = 7.5 Hz, 1H), 1.45 (d, J = 7.5 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.71, 134.00, 131.86, 127.79, 127.65, 127.60, 127.37, 125.76, 125.39, 124.89, 83.50, 24.77, 24.74, 16.95. All characterization data are consistent with previous reports.[13]

2-(1-(4-Methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



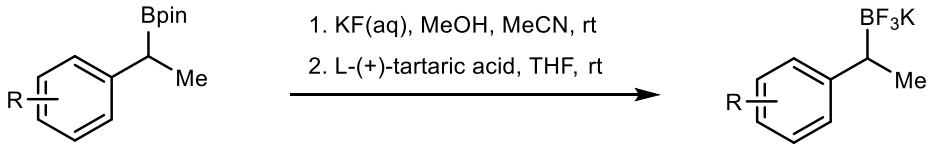
A **B**

3.7 **1**

Prepared according to procedure of Endo et al.[14] To a mixture of [RhCl(cod)]2 (98.6 mg, 0.20 mmol, 5 mol% Rh), DPPB (102.3 mg, 0.24 mmol, 6.0 mol%), and DMAP (29.3 mg, 0.24 mmol, 6.0 mol%) in DCE (4 mL) were added 1-methoxy-4-vinylbenzene (.52 mL, 4.0 mmol) and pinacolborane (0.70 mL, 4.8 mmol, 1.2 equiv) at r.t. The reaction mixture was stirred at r.t. for 10 min and filtered through a pad of silica gel with Et_2O (50 mL) and concentrated *in vacuo*. The crude ^1H NMR analysis shows a mixture of A:B with a ratio of 3.6:1. The compound was purified via flash column chromatography (silica gel: 5% Et_2O in hexanes) to provide the title compound (0.814 g, 3.1 mmols, 78% yield) as a colorless oil. Purified product is a 3.7:1 mixture of regioisomers A:B. ^1H NMR (400 MHz, CD_3CN) δ: 7.16 – 7.05 (m, 2H), 6.82 (d, J = 8.3 Hz, 2H), 3.75 (s, 3H), 2.63 (t, J = 8.0 Hz, regio), 2.32 (q, J = 7.6 Hz, 1H), 1.24 (d, J = 7.5 Hz, 3H), 1.20 (s, 6H), 1.18 (s, 6H), 1.02 (t, J = 7.9 Hz, regio); ^{13}C NMR (100 MHz, CD_3CN) δ: 158.4, 138.3, 129.6, 114.7, 84.1, 55.8, 25.0 (d, J = 2.2 Hz), 17.9. All characterization data are consistent with previous reports.[13]

9. Preparation of Trifluoroborate Salts

General Procedure D



Potassium trifluoroborate salts were prepared according to the report of Lennox and Lloyd-Jones.[15] To the organoboronic acid pinacol ester (1.0 mmol, 1 equiv) was added methanol (2 mL, 0.5M) then acetonitrile (2 mL, 0.5 M), followed by potassium fluoride (4 equiv, 4.0 mmol) in H_2O (0.4 mL, 10 M with respect to KF) at room temperature. The mixture was stirred until complete dissolution of the boronic ester (0.5 - 1 min). L-(+)-tartaric acid (5) (2.05 equiv., 2.05 mmol) was dissolved into THF (1.5 mL, 1.4 M with respect to tartaric acid, gentle heat and agitation is required for rapid dissolution) and added drop-wise to the rapidly (≈ 1000 rpm) stirring biphasic mixture over a period of 5 minutes, as a white precipitate formed. The reaction was stirred for 2 min, diluted with acetonitrile (3 mL) and stirred for a further 2 min before being diluted again with acetonitrile (1 mL) and filtered. The flask and filter cake were rinsed with further portions of acetonitrile (3 x 5 mL) and then the combined filtrates were concentrated *in vacuo* to give a mixture of the corresponding potassium organotrifluoroborate and pinacol. Pinacol was removed by evaporation at 6 mmHg with gentle heating using a heat gun, until there were no visible signs of the condensed pinacol around the flask (5- 10 min). The solid was scrapped off the sides of the flask and subjected to further heating (10 – 15 min) at this low pressure. In most cases this amount was sufficient however in some cases more heating was required.

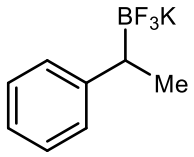
Notes:

1. It is crucial to remove any excess potassium fluoride for the subsequent photoredox catalyzed alkylation, as the fluoride anion can decompose the heterocyclic phosphonium salts, decreasing the yield of alkylated product.

2. To prevent isolation with small amounts of potassium fluoride when the reaction is scaled up, Et_2O was used as an antisolvent to effect precipitation of the pure product after pinacol was removed under vacuum.

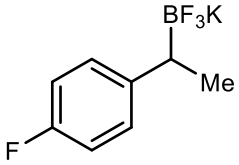
3. As well as the method developed by Lennox and Lloyd-Jones, the procedure reported by Molander that uses KHF_2 is also a viable option for synthesis of the trifluoroborate salts.[16-17]

Potassium trifluoro(1-phenylethyl)borate (2a)



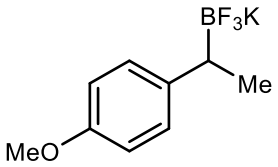
Prepared according to general procedure D using 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (4.1643 g, 18.0 mmol), potassium fluoride (4.164 g, 71.8 mmol), H_2O (7.2 mL, 10 M with respect to KF), MeOH (36.0 mL, 0.5 M with respect to 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane), MeCN (36.0 mL, 0.5 M with respect to 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane), L-(+)-tartaric acid (5.535 g, 36.9 mmol), and THF (26.4 mL, 1.4 M with respect to tartaric acid). Filtration, concentration, and trituration of the crude reaction mixture with Et_2O afforded the title compound as a white crystalline solid (3.0665 g, 14.4 mmol, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 – 7.11 (m, 4H), 6.96 (tt, *J* = 5.7, 2.8 Hz, 1H), 1.72 (s, 1H), 1.12 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.23, 128.64, 128.15, 123.70, 17.28; The carbon attached to boron could not be observed due to quadrupolar relaxation. ^{19}F NMR (365 MHz, CD_3CN) δ: –144.90-–147.40 (m). The data is consistent with those previously reported.[18]

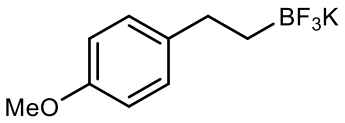
Potassium trifluoro(1-(4-fluorophenyl)ethyl)borate (2b)



Prepared according to general procedure D using 2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0505 g, 4.2 mmol), potassium fluoride (763.8 mg, 71.8 mmol), H_2O (1.3 mL, 10 M with respect to KF), MeOH (6.6 mL, 0.5 M with respect to 2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane), MeCN (6.6 mL, 0.5 M with respect to 2-(1-(4-Fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane), L-(+)-tartaric acid (1.013 g, 36.9 mmol), and THF (26.4 mL, 1.4 M with respect to tartaric acid). Filtration and concentration of the crude reaction mixture afforded the title compound as a white crystalline solid (468.8 g, 1.61 mmol, 49% yield). m.p. 142-145 °C; IR ν_{max}/cm^{-1} (film): 2957, 2931, 2872, 1601, 1505, 1459, 1373, 1241, 1221, 1142, 1087, 1022, 1012, 905, 835, 753; ^{1}H NMR (400 MHz, CD_3CN) δ: 7.17 (dd, *J* = 8.5, 5.8 Hz, 2H), 6.92 (t, *J* = 9.0 Hz, 2H), 1.81 (qn, *J* = 6.3 Hz, 1H), 1.15 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ: 160.8 (d, *J* = 237.5 Hz), 148.1, 129.7 (d, *J* = 7.3 Hz), 114.8 (d, *J* = 20.5 Hz), 31.4, 17.4; ^{19}F NMR (365 MHz, CD_3CN) δ: –123.05, –146.14.

Potassium trifluoro(1-(4-methoxyphenyl)ethyl)borate (2c)



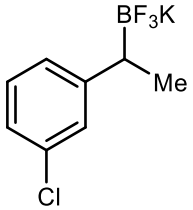


2c **2c'**

1.2 **1**

Prepared according to general procedure D using 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.8:1 mixture of regioisomers) (749.8 mg, 2.9 mmol), potassium fluoride (667 mg, 11.5 mmol), H_2O (1.2 mL, 10 M with respect to KF mg), MeOH (5.7 mL, 0.5 M with respect to 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane), MeCN (5.7 mL, 0.5 M with respect to 2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane), L-(+)-tartaric acid (879 mg, 5.9 mmol), and THF (4.2 mL, 1.4 M with respect to tartaric acid). Filtration, concentration, and trituration of the crude reaction mixture with Et_2O afforded the title compound as a white crystalline solid as a mixture of regioisomers 2c and 2c' (1.2:1) (203 g, 0.83 mmol, 29% yield). m.p. 162-164 °C; IR ν_{max}/cm^{-1} (film): 3008, 2953, 2906, 2837, 1612, 1512, 1247, 1089, 1030, 1018, 934, 860, 838, 812, 757; ^1H NMR (400 MHz, CD_3CN) δ: 7.08 (dd, *J* = 21.0, 8.3 Hz, 2H), 6.88 – 6.66 (m, 2H), 3.73 (s, regio), 3.72 (s, 3H), 2.55 – 2.40 (m, regio), 1.64 (s, 1H), 1.08 (d, *J* = 7.5 Hz, 3H), 0.57 – 0.22 (m, regio); ^{13}C NMR (100 MHz, CD_3CN) δ: 156.94, 141.23, 129.27, 113.73, 55.69, 31.91, 17.67; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –141.26 (regio), –146.06.

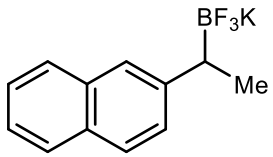
Potassium (1-(3-chlorophenyl)ethyl)trifluoroborate (2d)



Prepared according to general procedure D using 2-(1-(3-Chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0718 g, 4.0 mmol), potassium fluoride (933.8 mg, 16.1 mmol), H_2O (1.6 mL, 10 M with respect to KF), MeOH (8.1 mL, 0.5 M with respect to 2-(1-(3-Chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane), MeCN (8.1 mL, 0.5 M with respect to 2-(1-(3-Chlorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane), L-(+)-tartaric acid (1.239 g, 8.3 mmol), and THF (5.9 mL, 1.4 M with respect to tartaric acid). Filtration, and concentration of the crude reaction mixture afforded the title compound as a tan crystalline solid

(673.3 mg, 2.7 mmol, 68% yield). m.p. 99-105 °C; IR ν_{max}/cm^{-1} (film): 3061, 2960, 2932, 2872, 1591, 1565, 1468, 1426, 1270, 1225, 1111, 1078, 1020, 999, 958, 901, 844, 790, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 – 7.08 (m, 3H), 7.01 (d, *J* = 7.5, 1H), 1.90 – 1.75 (m, 1H), 1.16 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.19, 133.64, 129.82, 128.29, 127.08, 123.90, 32.46, 16.85; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −146.17.

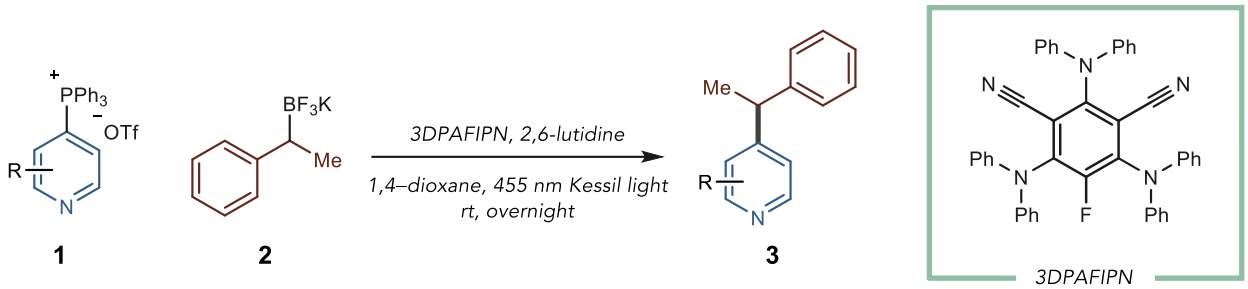
Potassium trifluoro(1-(naphthalen-2-yl)ethyl)borate (2e)



Prepared according to general procedure D using 4,4,5,5-Tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (977.5 mg, 3.5 mmol), potassium fluoride (804.5 mg, 13.9 mmol), H_2O (1.4 mL, 10 M with respect to KF mg), MeOH (6.9 mL, 0.5 M with respect to 4,4,5,5-Tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane), MeCN (6.9 mL, 0.5 M with respect to 4,4,5,5-Tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane), L-(+)-tartaric acid (1.067 g, 7.1 mmol), and THF (5.1 mL, 1.4 M with respect to tartaric acid). Filtration, concentration, and trituration of the crude reaction mixture with Et_2O afforded the title compound as a tan amorphous solid (720.1 mg, 2.7, 79% yield). IR ν_{max}/cm^{-1} (film): 3414, 3054, 2973, 2930, 2870, 1709, 1678, 1629, 1365, 1226, 1093, 1016, 982, 912, 748; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (t, *J* = 7.4 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.52 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.34 – 7.27 (m, 1H), 1.93 (s, 1H), 1.14 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.6, 134.9, 131.8, 129.8, 128.2, 127.8, 126.8, 126.0, 124.7, 124.4, 25.2, 17.2; ^{19}F NMR (365 MHz, $CDCl_3$) δ: −145.66.

10. Preparation of Alkylated Pyridines and Diazines

General Procedure E



An oven dried 8 mL vial equipped with a magnetic stir bar was charged with the heterocyclic phosphonium salt (1.0 equiv), potassium trifluoroborate salt (2.0 equiv) and photocatalyst 3DPAFIPN (2 mol%). The vial was pumped into a glovebox and then dioxane (0.3 M) and 2,6-lutidine (3.0 equiv) were added via a syringe. The vial was sealed and removed from the glovebox and pre-stirred for ten minutes before irradiation with a 455 nm kessil lamp (5 cm away, with stream of air blowing over vials to keep reaction at 25 °C) for 16 hours. The reaction was quenched with water and the aqueous layer was extracted with CH_2Cl_2 (4x). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude residue was put under vacuum for an hour to remove 2,6-lutidine from the crude mixture, then purified by flash column chromatography under the stated conditions to provide the alkylated heteroaryl product.

NOTES:

1. The presence of potassium fluoride leftover from the trifluoroborate salt synthesis has a detrimental effect on the heteroaromatic alkylation reaction, as the fluoride anion can decompose the heterocyclic phosphonium salt back to the heterocycle precursor. To remove excess potassium fluoride (especially when making trifluoroborate salt on large scale) recrystallize the product as described in the notes for Section 7.

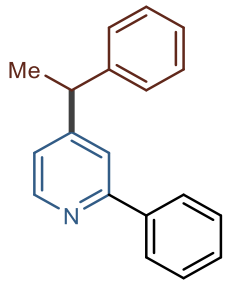
2. The pre-stirring step is important to bring the heterocyclic phosphonium salt into solution before any redox events occur, leading to undesired byproducts. The authors note the observation that heterocyclic phosphonium salts that are difficult to dissolve by themselves, dissolve easier upon stirring with the trifluoroborate salt.

3. Putting the crude residue under vacuum for an hour to remove the 2,6-lutidine before flash column chromatography is not necessary but was done to provide consistent and reproducible column conditions for purification.

4. Protonation of tertiary amines within the substrate with an equivalent of TfOH resulted in slightly higher yields of coupled product.

Heterocyclic Phosphonium Salt Scope for Heteroaromatic Alkylation

2-Phenyl-4-(1-phenylethyl)pyridine (3a)

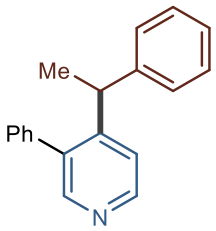


Prepared according to general procedure E using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (283.0 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 7% Et_2O in hexanes) afforded the title compound as a pale yellow oil (85.5 mg, 0.40 mmol, 74% yield).; IR ν_{max}/cm^{-1} (film): 3084, 3028, 2969, 2930, 2874, 1596, 1554, 1474, 1446, 1403, 1265, 1029, 991, 800, 741, 697; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 5.1 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.38 – 7.24 (m, 3H), 7.24 – 7.06 (m, 5H), 6.96 (dd, *J* = 5.1, 1.7 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 155.9, 149.8, 144.5, 139.7, 128.9, 128.7, 128.7, 127.7, 127.1, 126.7, 121.5, 120.0, 44.5, 21.2; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 260.2, $C_{19}H_{18}N^+$ requires 260.1.

Large scale:

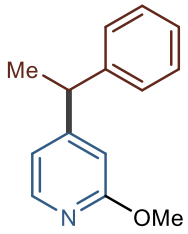
Prepared according to general procedure E except a 16 mL vial was used rather than an 8 mL vial using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (1.132 g, 2.00 mmol), potassium trifluoro(1-phenylethyl)borate (848.0 mg, 4.00 mmol), 3DPAFIPN (26.0 mg, 0.04 mmol), 2,6-lutidine (692 μL, 6.00 mmol), and 1,4-dioxane (6.67 mL, 0.3M). Flash column chromatography (silica gel: 7% Et_2O in hexanes) afforded the title compound as a pale yellow oil (383 mg, 1.48 mmol, 74% yield). Spectra consistent with that obtained upon isolation of small scale reaction.

3-Phenyl-4-(1-phenylethyl)pyridine (3b)



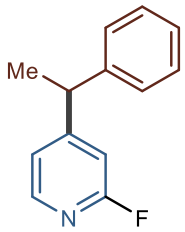
Prepared according to general procedure E using triphenyl(3-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (283.0 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). ^{1}H NMR analysis of the crude reaction mixture gave a mixture of regioisomers with a ratio of 8:1 (4 position:2 position alkylation). Flash column chromatography (silica gel: 5% Et_2O in hexanes) afforded the title compound as a single regioisomer as a yellow oil (54.5 mg, 0.21 mmol, 42% yield). IR ν_{max}/cm^{-1} (film): 3058, 3025, 2968, 1585, 1494, 1444, 1007, 838, 761, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 – 8.43 (m, 2H), 7.59 – 7.46 (m, 3H), 7.42 – 7.26 (m, 6H), 7.14 (dd, *J* = 7.32, 1.78 Hz, 2H), 4.41 (q, *J* = 7.16 Hz, 1H), 1.65 (d, *J* = 7.19 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8, 150.4, 149.0, 144.7, 137.9, 137.5, 129.6, 128.5, 128.5, 127.8, 127.6, 126.4, 122.3, 40.0, 21.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 260.2, $C_{19}H_{18}N^+$ requires 260.1.

2-Methoxy-4-(1-phenylethyl)pyridine (3c)



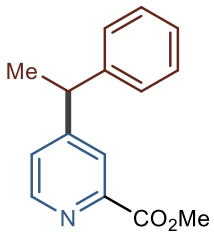
Prepared according to general procedure E using triphenyl(2-methoxypyridin-4-yl)phosphonium trifluoromethanesulfonate (260.0 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 5% Et_2O in hexanes) afforded the title compound as a pale yellow oil (85.5 mg, 0.40 mmol, 80% yield). IR ν_{max}/cm^{-1} (film): 3061, 3025, 2945, 2875, 1607, 1557, 1394, 1317, 1027, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 8.0 Hz 1H), 7.36 – 7.27 (m, 2H), 7.22 (td, *J* = 7.1, 1.2 Hz, 3H), 6.72 (dd, *J* = 5.4, 1.6 Hz, 1H), 6.63 (m, 1H), 4.07 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 1.62 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.7, 158.1, 146.7, 144.6, 128.7, 127.7, 126.7, 116.9, 109.6, 53.4, 44.3, 21.0. *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 214.2, $C_{14}H_{16}NO^+$ requires 214.1.

2-Fluoro-4-(1-phenylethyl)pyridine (3d)



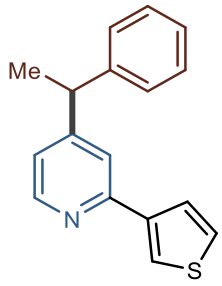
Prepared according to general procedure E using (2-fluoropyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (253.5 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 5% Et_2O in hexanes) afforded the title compound as a yellow oil (55.2 mg, 0.275 mmol, 55% yield). IR ν_{max}/cm^{-1} (film): 3062, 2972, 2933, 1609, 1563, 1480, 1407, 1271, 1148, 919, 699; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 5.3 Hz, 1H), 7.31 – 7.20 (m, 2H), 7.20 – 7.08 (m, 3H), 6.93 (dt, *J* = 5.3, 1.8 Hz, 1H), 6.73 – 6.65 (m, 1H), 4.06 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3 (d, *J* = 238.2 Hz), 161.4 (d, *J* = 7.5 Hz), 147.5 (d, *J* = 15.3 Hz), 143.8, 128.9, 127.7, 127.0, 121.0 (d, *J* = 3.9 Hz), 108.4 (d, *J* = 37.2 Hz), 44.3 (d, *J* = 2.8 Hz), 21.1; ^{19}F (365 MHz, $CDCl_3$) δ: –68.47; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 202.1, $C_{13}H_{13}FN^+$ requires 202.1.

Ethyl 4-(1-phenylethyl)picolinate (3e)



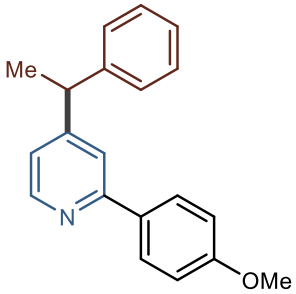
Prepared according to general procedure E using (2-(ethoxycarbonyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (281.0 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 50% Et_2O in hexanes) afforded the title compound as a yellow oil (60.8 mg, 0.24 mmol, 47% yield). IR ν_{max}/cm^{-1} (film): 3059, 2973, 2931, 1738, 1714, 1595, 1451, 1296, 1191, 1097, 1021, 859, 788, 699; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.54 (dd, *J* = 4.9, 0.7 Hz, 1H), 7.94 (d, *J* = 1.8 Hz, 1H), 7.29 – 7.02 (m, 6H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.3 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5, 156.5, 149.9, 148.4, 143.8, 128.8, 127.6, 126.9, 126.1, 124.4, 62.0, 44.3, 21.0, 14.4. *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 256.2, $C_{16}H_{18}NO_2^+$ requires 256.1.

4-(1-Phenylethyl)-2-(thiophen-3-yl)pyridine (3f)



Prepared according to general procedure E using triphenyl(2-(thiophen-3-yl)pyridin-4-yl)phosphonium trifluoromethanesulfonate (286.0 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 20% Et_2O in hexanes), followed by a second column (silica gel, gradient elution: CH_2Cl_2 to 10% Et_2O in CH_2Cl_2) afforded the title compound as a pale yellow oil (64 mg, 0.24 mmol, 48% yield). IR ν_{max}/cm^{-1} (film): 3084, 3060, 2967, 2929, 2873, 1595, 1552, 1451, 1424, 840, 792, 744, 698, 672; ^1H NMR (400 MHz, $CDCl_3$) δ 8.4 (d, *J* = 5.13 Hz, 1H), 7.8 (dd, *J* = 3.09, 1.25 Hz, 1H), 7.5 (dd, *J* = 5.03, 1.29 Hz, 1H), 7.4 (d, *J* = 1.70 Hz, 1H), 7.3 (dd, *J* = 5.04, 3.00 Hz, 1H), 7.3 – 7.2 (m, 2H), 7.2 – 7.1 (m, 3H), 6.9 (dd, *J* = 5.31, 1.73 Hz, 1H), 4.1 (q, *J* = 7.20 Hz, 1H), 1.6 (d, *J* = 7.24 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 153.7, 149.8, 144.5, 142.4, 128.8, 127.7, 126.8, 126.4, 126.3, 123.6, 121.4, 119.8, 44.5, 21.2. *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 266.1, $C_{17}H_{16}NS^+$ requires 266.1.

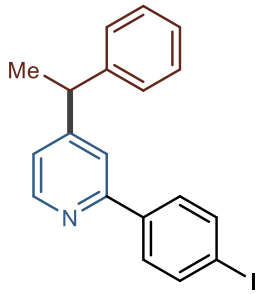
2-(4-Methoxyphenyl)-4-(1-phenylethyl)pyridine (3g)



Prepared according to general procedure E using (2-(4-methoxyphenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (178.8 mg, 0.30 mmol), potassium trifluoro(1-phenylethyl)borate (127.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.9 mmol), and 1,4-dioxane (1.00 mL, 0.3M). Flash column chromatography (silica gel: 10% EtOAc in hexanes) followed by a second column (silica gel: 30% Et_2O in hexanes) afforded the title compound as a yellow amorphous solid (48.1 mg, 0.17 mmol, 55% yield). m.p. 57-60 °C; IR ν_{max}/cm^{-1} (film): 3001, 2966, 2933, 2839, 1597, 1550, 1514, 1245, 1172, 1026, 831,

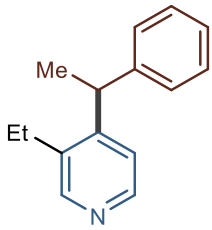
703; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.10 Hz, 1H), 8.14 – 7.78 (m, 2H), 7.52 (s, 1H), 7.39 – 7.20 (m, 5H), 7.04 (dd, *J* = 5.15, 1.64 Hz, 1H), 6.99 (dd, *J* = 8.70, 1.53 Hz, 2H), 4.18 (q, *J* = 7.22 Hz, 1H), 3.86 (s, 3H), 1.69 (d, *J* = 7.26 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.39, 157.24, 155.75, 149.55, 144.53, 132.18, 128.63, 128.24, 127.63, 126.61, 120.84, 119.20, 114.05, 55.34, 44.48, 21.15. *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 290.2, $C_{20}H_{20}NO^+$ requires 290.2.

2-(4-Iodophenyl)-4-(1-phenylethyl)pyridine (3h)



Prepared according to general procedure E using (2-(4-iodophenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (207.6 mg, 0.30 mmol), potassium trifluoro(1-phenylethyl)borate (127.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.9 mmol), and 1,4-dioxane (1.00 mL, 0.3M). Flash column chromatography (silica gel, gradient elution: 5% Et_2O in hexanes to 10% EtOAc in hexanes) afforded the title compound as a yellow oil (71.3 mg, 0.19 mmol, 62% yield). IR ν_{max}/cm^{-1} (film): 3058, 2966, 2927, 1596, 1468, 1411, 1003, 821, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, *J* = 5.10 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.64 – 7.57 (m, 2H), 7.47 – 7.41 (m, 1H), 7.27 – 7.20 (m, 2H), 7.18 – 7.11 (m, 3H), 7.01 (dd, *J* = 5.15, 1.66 Hz, 1H), 4.09 (q, *J* = 7.20 Hz, 1H), 1.59 (d, *J* = 7.20 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.52, 156.11, 149.84, 144.33, 139.05, 137.81, 128.77, 128.73, 127.65, 126.75, 121.89, 119.70, 95.24, 44.48, 21.20; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 386.1, $C_{19}H_{17}IN^+$ requires 386.0.

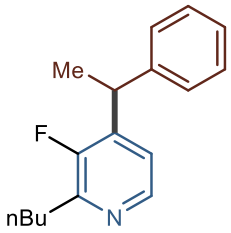
3-Ethyl-4-(1-phenylethyl)pyridine (3i)



Prepared according to general procedure E using (3-ethylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (259.0 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 60% EtOAc in hexanes) followed by a second column (silica gel: 30% EtOAc in hexanes) afforded the title compound as a yellow solid (51.4 mg, 0.25 mmol, 49% yield). m.p. 46-48 °C; IR ν_{max}/cm^{-1} (film): 3062, 2966, 2928, 2871, 1589, 1490, 1449, 843, 764, 725; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (m, 2H), 7.48

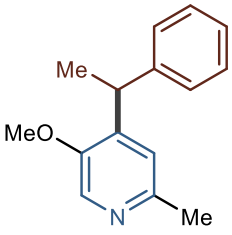
– 6.80 (m, 6H), 4.28 (q, *J* = 7.13 Hz, 1H), 2.56 (ddt, *J* = 27.03, 14.63, 7.33 Hz, 2H), 1.52 (d, *J* = 7.20 Hz, 3H), 1.08 (t, *J* = 7.57 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.27, 150.29, 147.75, 144.77, 137.10, 128.64, 127.64, 126.49, 121.94, 39.83, 23.23, 21.86, 15.29. *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 212.1, $C_{15}H_{18}N^+$ requires 212.1.

2-Butyl-3-fluoro-4-(1-phenylethyl)pyridine (3j)



Prepared according to general procedure E using (2-butyl-3-fluoropyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (225.6 mg, 0.40 mmol), potassium trifluoro(1-phenylethyl)borate (169.6 mg, 0.80 mmol), 3DPAFIPN (2.6 mg, 0.004 mmol), 2,6-lutidine (140 μL, 1.20 mmol), and 1,4-dioxane (1.33 mL, 0.3M). Flash column chromatography (silica gel: 10% EtOAc in hexanes) afforded the title compound as a pale yellow oil (75.2 mg, 0.29 mmol, 73% yield). IR ν_{max}/cm^{-1} (film): 3063, 2958, 2930, 1601, 1496, 1426, 1176, 837, 757, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 5.0 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 6.95 (t, *J* = 5.3 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 1H), 2.86 – 2.75 (m, 2H), 1.68 (qn, *J* = 8.0 Hz, 2H), 1.61 (d, *J* = 7.2 Hz, 3H), 1.38 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.9 (d, *J* = 254.4 Hz), 150.5 (d, *J* = 17.2 Hz), 144.8 (d, *J* = 6.6 Hz), 143.6, 141.2 (d, *J* = 13.4 Hz), 128.7, 127.6, 126.8, 121.0 (d, *J* = 1.4 Hz), 38.0 – 36.6 (m), 31.5 (d, *J* = 1.8 Hz), 30.8 (d, *J* = 1.3 Hz), 22.7, 20.3, 14.0. ^{19}F NMR (365 MHz, $CDCl_3$) δ: –132.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 258.2, $C_{17}H_{21}FN^+$ requires 258.2.

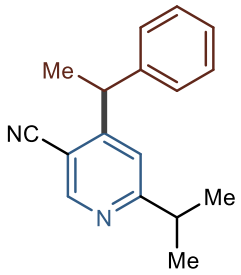
5-Methoxy-2-methyl-4-(1-phenylethyl)pyridine (3k)



Prepared according to general procedure E using (5-methoxy-2-methylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (267.0 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 35% EtOAc in hexanes) afforded the title compound as a pale yellow amorphous solid (96.4 mg, 0.43 mmol, 85% yield). IR ν_{max}/cm^{-1} (film): 3025, 2968, 2930, 2874, 2839, 1597, 1590,

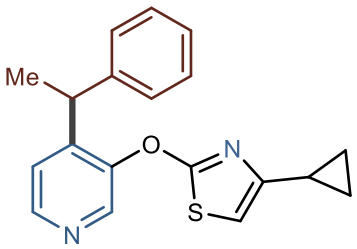
1492, 1450, 1272, 1028, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (s, 1H), 7.23 – 7.02 (m, 5H), 6.80 (s, 1H), 4.40 (q, *J* = 7.25 Hz, 1H), 3.71 (s, 3H), 2.35 (s, 3H), 1.46 (d, *J* = 7.25 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.4, 150.9, 144.5, 143.7, 132.3, 128.3, 127.7, 126.2, 121.7, 56.1, 37.1, 23.7, 20.2.; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 228.2, $C_{15}H_{18}NO^+$ requires 228.1.

6-Isopropyl-4-(1-phenylethyl)nicotinonitrile (3l)



Prepared according to general procedure E using (3-cyano-2-isopropylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (224.0 mg, 0.40 mmol), potassium trifluoro(1-phenylethyl)borate (169.6 mg, 0.80 mmol), 3DPAFIPN (2.6 mg, 0.004 mmol), 2,6-lutidine (140 μL, 1.20 mmol), and 1,4-dioxane (1.33 mL, 0.3M). Flash column chromatography (silica gel: 5% EtOAc in hexanes) afforded the title compound as a pale yellow oil (64.8 mg, 0.26 mmol, 65% yield). IR ν_{max}/cm^{-1} (film): 3062, 2968, 2933, 2225, 1591, 1452, 1064, 916, 762, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (s, 1H), 7.38 – 7.27 (m, 2H), 7.27 – 7.18 (m, 3H), 7.10 (s, 1H), 4.50 (q, *J* = 7.2 Hz, 1H), 3.03 (hept, *J* = 6.9 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.8, 158.6, 152.8 (d, *J* = 1.9 Hz), 142.2, 128.8, 127.6, 127.1, 119.2 (d, *J* = 1.8 Hz), 116.5, 107.4, 42.8 (d, *J* = 2.4 Hz), 36.7, 22.2 (d, *J* = 6.5 Hz), 20.6.; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 251.2, $C_{17}H_{19}N_2^+$ requires 251.2.

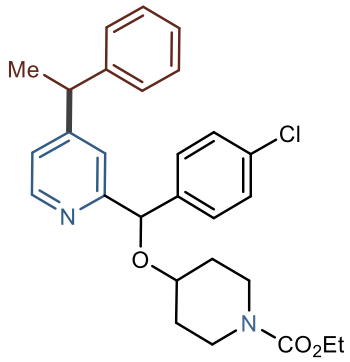
4-Cyclopropyl-2-((4-(1-phenylethyl)pyridin-3-yl)oxy)thiazole (3n)



Prepared according to general procedure E using (3-((4-cyclopropylthiazol-2-yl)oxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (188.7 mg, 0.30 mmol), potassium trifluoro(1-phenylethyl)borate (127.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.90 mmol), and 1,4-dioxane (1.00 mL, 0.3 M). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the title compound as a yellow oil (73.8 mg, 0.23

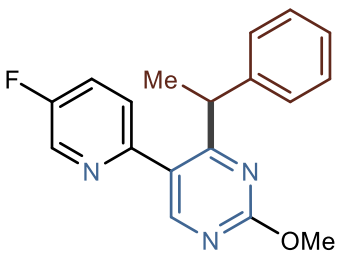
mmol, 76% yield). IR ν_{max}/cm^{-1} (film): 3061, 3007, 2969, 2923, 2859, 1676, 1595, 1538, 1503, 1485, 1409, 1233, 1213, 1194, 967, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (s, 1H), 8.33 (d, *J* = 5.1 Hz, 1H), 7.23 – 7.06 (m, 6H), 6.24 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 1H), 1.88 – 1.67 (m, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 0.87 – 0.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 153.6, 150.0, 147.4, 147.1, 143.2, 128.6, 127.7, 126.7, 123.1, 104.5, 37.8, 20.4, 12.7, 7.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 323.2, $C_{19}H_{19}N_2OS^+$ requires 323.1.

Ethyl 4-((4-chlorophenyl)(4-(1-phenylethyl)pyridin-2-yl)methoxy)piperidine-1-carboxylate (3o)



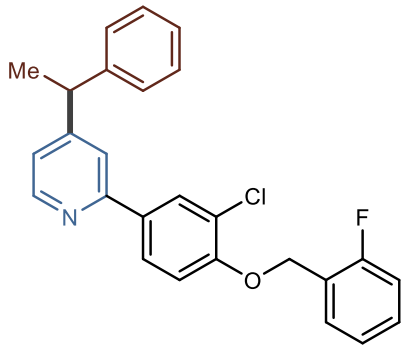
Prepared according to general procedure E using (2-((4-chlorophenyl)((1-(ethoxycarbonyl)piperidin-4-yl)oxy)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (196.0 mg, 0.25 mmol), potassium trifluoro(1-phenylethyl)borate (106.0 mg, 0.50 mmol), 3DPAFIPN (3.2 mg, 0.005 mmol), 2,6-lutidine (87.2 μL, 0.75 mmol), and 1,4-dioxane (833 μL, 0.3M). Flash column chromatography (silica gel: 15% acetone in hexanes) afforded the title compound as a yellow oil as a 1:1 mixture of diastereomers (63.9 mg, 0.13 mmol, 53% yield). IR ν_{max}/cm^{-1} (film): 3059, 2923, 2851, 1693, 1597, 1489, 1471, 1451, 1432, 1273, 1085, 1014, 767, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (dd, *J* = 7.3, 5.1 Hz, 1H), 7.32 – 7.03 (m, 10H), 6.94 (ddd, *J* = 13.9, 5.1, 1.8 Hz, 1H), 5.48 (s, 1H), 4.10 – 3.98 (m, 3H), 3.71 – 3.53 (m, 2H), 3.50 – 3.40 (m, 1H), 3.14 – 2.96 (m, 2H), 1.80 – 1.68 (m, 1H), 1.64 – 1.37 (m, 6H), 1.17 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.9, 156.2, 155.6, 149.2, 144.7, 140.2, 133.4, 128.7, 128.6, 128.3, 127.7, 126.8, 122.1, 120.1, 81.1, 72.8, 61.4, 44.5, 41.1, 31.2, 21.3, 14.8.; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 479.3, $C_{28}H_{32}ClN_2O_3^+$ requires 479.2

5-(5-Fluoropyridin-2-yl)-2-methoxy-4-(1-phenylethyl)pyrimidine (3p)



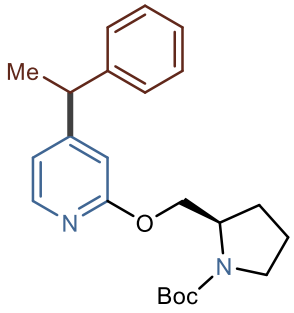
Prepared according to general procedure E using (5-(5-fluoropyridin-2-yl)-2-methoxypyrimidin-4-yl)triphenylphosphonium trifluoromethanesulfonate (154.0 mg, 0.25 mmol), potassium trifluoro(1-phenylethyl)borate (106.0 mg, 0.50 mmol), 3DPAFIPN (3.2 mg, 0.005 mmol), 2,6-lutidine (87.2 μL, 0.75 mmol), and 1,4-dioxane (833 μL, 0.3 M). Flash column chromatography (silica gel: 20% EtOAc in hexanes) afforded the title compound as a pale yellow oil (52.1 mg, 0.17 mmol, 67% yield). IR ν_{max}/cm^{-1} (film): 3070, 2956, 2918, 2849, 1685, 1586, 1461, 1379, 1226, 1013, 845, 772, 748, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.5 (d, *J* = 3.0 Hz, 1H), 8.3 (s, 1H), 7.3 (td, *J* = 8.3, 3.0 Hz, 1H), 7.1 – 6.9 (m, 6H), 4.5 (q, *J* = 7.0 Hz, 1H), 4.0 (s, 3H), 1.6 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.9, 165.1, 159.4, 158.8 (d, *J* = 256.0 Hz), 151.4 (d, *J* = 4.2 Hz), 143.8, 138.0 (d, *J* = 23.6 Hz), 128.4, 127.8, 126.6, 126.5, 125.4 (d, *J* = 4.4 Hz), 123.5 (d, *J* = 18.4 Hz), 55.0, 42.8, 20.8; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –128.14; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 310.2, $C_{18}H_{17}FN_3O^+$ requires 310.1.

2-(3-Chloro-4-((2-fluorobenzyl)oxy)phenyl)-4-(1-phenylethyl)pyridine (3q)



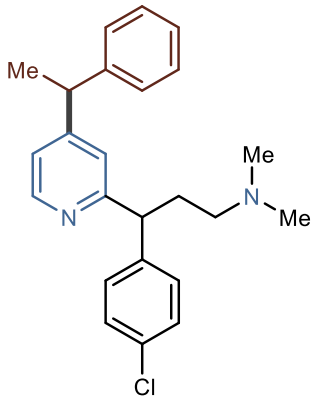
Prepared according to general procedure E using (2-(3-chloro-4-(2-fluorophenoxy)phenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (217.2 mg, 0.30 mmol), potassium trifluoro(1-phenylethyl)borate (127.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.9 mmol), and 1,4-dioxane (1.00 mL, 0.3M). Flash column chromatography (silica gel: 10% Et_2O in hexanes) followed by a second column (silica gel: 100% CH_2Cl_2 to 20% Et_2O in hexanes) afforded the title compound as a yellow oil (84.7 mg, 0.20 mmol, 68% yield). IR ν_{max}/cm^{-1} (film): 2961, 2919, 2850, 1596, 1551, 1451, 1260, 1060, 855, 756, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 5.1 Hz, 1H), 7.94 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.49 (td, *J* = 7.5, 1.8 Hz, 1H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.29 – 6.90 (m, 10H), 5.14 (s, 2H), 4.05 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2 (d, *J* = 246.5 Hz), 156.0, 155.9, 154.5, 149.7, 144.4, 133.6, 129.7 (d, *J* = 8.2 Hz), 129.3 (d, *J* = 3.9 Hz), 129.0, 128.7, 127.6, 126.7, 126.3, 124.4 (d, *J* = 3.6 Hz), 123.7, 123.5, 121.4, 119.3, 115.2 (d, *J* = 21.0 Hz), 113.8, 64.5 (d, *J* = 4.7 Hz), 44.5, 21.1; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –118.69; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 418.2, $C_{26}H_{22}ClFNO^+$ requires 418.1.

Tert-butyl (2R)-2-(((4-(1-phenylethyl)pyridin-2-yl)oxy)methyl)pyrrolidine-1-carboxylate (3r)



Prepared according to general procedure E using (R)-(2-((1-(tert-butoxycarbonyl)pyrrolidin-2-yl)methoxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (344.5 mg, 0.50 mmol), potassium trifluoro(1-phenylethyl)borate (212.0 mg, 1.00 mmol), 3DPAFIPN (6.5 mg, 0.01 mmol), 2,6-lutidine (175 μL, 1.5 mmol), and 1,4-dioxane (1.67 mL, 0.3M). Flash column chromatography (silica gel: 30% Et_2O in hexanes) followed by a second column (silica gel: 20% Et_2O in hexanes) afforded the title compound as a clear oil as a 1:1 mixture of diastereomers (114.5 mg, 0.30 mmol, 60% yield). IR ν_{max}/cm^{-1} (film): 2970, 2917, 2849, 1690, 1608, 1557, 1415, 1390, 1365, 1162, 1105, 1026, 700; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, *J* = 5.4 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 6.70 (d, *J* = 4.9 Hz, 1H), 6.59 (s, 1H), 4.49 – 4.27 (m, 1H), 4.22 – 3.98 (m, 3H), 3.38 (s, 2H), 2.13 – 1.76 (m, 4H), 1.61 (d, *J* = 7.2 Hz, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3, 158.1, 154.7, 146.7, 144.6, 128.7, 127.7, 126.7, 117.0, 109.6, 79.5, 66.3, 56.2, 46.5, 44.3, 28.9, 28.6, 23.1, 21.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 383.3, $C_{23}H_{31}N_2O_3^+$ requires 383.2.

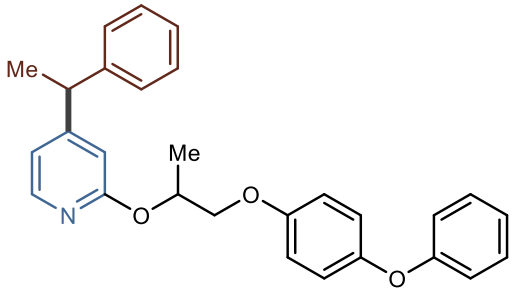
3-(4-Chlorophenyl)-N,N-dimethyl-3-(4-(1-phenylethyl)pyridin-2-yl)propan-1-amine (3s)



Prepared according to general procedure E using (2-(1-(4-chlorophenyl)-3-(dimethylamino)propyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (205.5 mg, 0.30 mmol), potassium trifluoro(1-phenylethyl)borate (127.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.01 mmol), 2,6-lutidine (105 μL, 0.90 mmol), 1,4-dioxane (1.00 mL, 0.3M), and trifluoromethanesulfonic acid (26.5 μL, 0.30) mmol. Flash column chromatography (silica gel: 90% EtOAc in hexanes with 1% NEt_3) afforded the title compound as a brown oil as a 1:1 mixture of diastereomers (52.8 mg, 0.14 mmol, 46% yield). IR ν_{max}/cm^{-1} (film): 3061, 3027, 2923, 2851, 1596, 1456, 1284, 756, 699; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.42 (app t, *J* = 4.0, 1H), 7.31 – 7.18

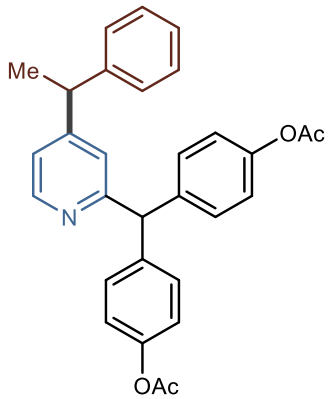
(m, 7H), 7.16 – 7.09 (m, 2H), 6.99 (s, 1H), 6.95 – 6.89 (m, 1H), 4.14 – 3.96 (m, 2H), 2.42 – 2.25 (m, 1H), 2.20 – 2.05 (m, 9H), 1.57 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.1, 155.7, 149.5, 144.7, 142.4, 132.2, 129.5, 128.7, 128.6, 127.7, 126.7, 122.4, 121.0, 57.7, 50.6, 45.5, 44.4, 33.1, 21.2; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 379.3, $C_{24}H_{28}ClN_2^+$ requires 379.2.

2-((1-(4-Phenoxyphenoxy)propan-2-yl)oxy)-4-(1-phenylethyl)pyridine (3t)



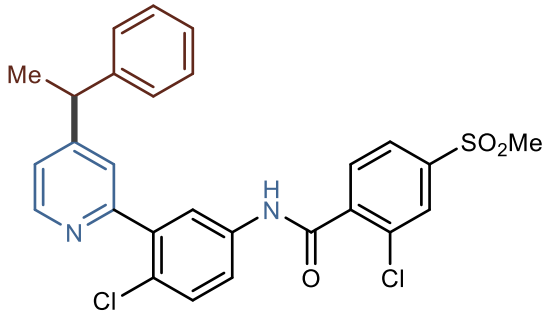
Prepared according to general procedure E using (2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (219.0 mg, 0.30 mmol), potassium trifluoro(1-phenylethyl)borate (127.2 mg,0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.9 mmol), and 1,4-dioxane (1.00 mL, 0.3 M). Flash column chromatography (silica gel: 5% Et_2O in hexanes) afforded the title compound as a brown oil as a 1.3:1 mixture of diastereomers (79.1 mg, 0.19 mmol, 62% yield). IR ν_{max}/cm^{-1} (film): 3027, 2927, 2873, 1607, 1556, 1503, 1488, 1412, 1216, 1157, 829, 699, 691; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 5.3 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.15 – 7.08 (m, 3H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.88 – 6.78 (m, 6H), 6.61 (dd, *J* = 5.4, 1.5 Hz, 1H), 6.53 (s, 1H), 5.47 (q, *J* = 5.7 Hz, 1H), 4.07 (dd, *J* = 9.9, 5.2 Hz, 1H), 4.01 – 3.88 (m, 2H), 1.51 (d, *J* = 7.2 Hz, 3H), 1.37 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7, 158.6, 158.3, 155.3, 150.4, 146.6, 144.6, 129.7, 128.7, 127.7, 126.7, 122.5, 120.9, 117.7, 117.0, 115.9, 110.2, 71.2, 69.4, 44.3, 21.1, 17.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 426.3, $C_{28}H_{28}NO_3^+$ requires 426.2.

((4-(1-Phenylethyl)pyridin-2-yl)methylene)bis(4,1-phenylene) diacetate (3u)



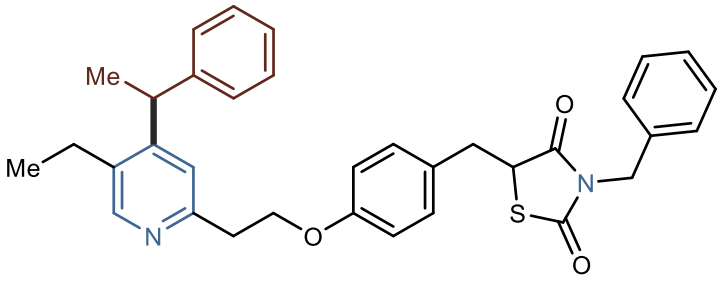
Prepared according to general procedure E using (2-(bis(4-acetoxyphenyl)methyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (231.6 mg, 0.30 mmol), potassium trifluoro(1-phenylethyl)borate (127.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.90 mmol), and 1,4-dioxane (1.00 mL, 0.3 M). Flash column chromatography (silica gel: 30% EtOAc in hexanes) afforded the title compound as a yellow oil (86.7 mg, 0.17 mmol, 56% yield). IR ν_{max}/cm^{-1} (film): 3107, 3030, 2933, 1753, 1595, 1503, 1368, 1195, 1164, 1018, 910, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 5.2, 1H), 7.29 – 7.02 (m, 10H), 6.95 – 6.87 (m, 6H), 3.98 (q, *J* = 7.2 Hz, 1H), 2.19 (s, 6H), 1.50 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 162.5, 156.0, 149.7, 149.4, 144.5, 140.3, 130.3, 128.7, 127.7, 126.7, 123.3, 121.5, 121.0, 58.1, 44.4, 21.3, 21.2; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 466.3 $C_{30}H_{28}NO_4^+$ requires 466.2.

2-Chloro-N-(4-chloro-3-(4-(1-phenylethyl)pyridin-2-yl)phenyl)-4-(methylsulfonyl)benzamide (3v)



Prepared according to general procedure E using (2-(3-(2-chloro-4-(methylsulfonyl)benzamido)phenyl)pyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (166.4 mg, 0.20 mmol), potassium trifluoro(1-phenylethyl)borate (84.8 mg, 0.40 mmol), 3DPAFIPN (2.6 mg, 0.004 mmol), 2,6-lutidine (69.8 μL, 0.60 mmol), and 1,4-dioxane (666 μL, 0.3 M). Flash column chromatography (silica gel: 60% EtOAc in hexanes) afforded the title compound as a tan crystalline solid (57.1 mg, 0.11 mmol, 54% yield). m.p. 81-83 °C; IR ν_{max}/cm^{-1} (film): 3252, 3106, 3059, 3028, 1680, 1540, 1316, 1153, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.37 – 10.17 (m, 1H), 8.13 (dd, *J* = 5.5, 2.7 Hz, 1H), 8.08 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.81 (q, *J* = 1.6 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.51 – 7.41 (m, 3H), 7.34 – 7.28 (m, 2H), 7.25 – 7.14 (m, 3H), 7.02 – 6.97 (m, 1H), 4.13 (q, *J* = 7.2 Hz, 1H), 2.92 (d, *J* = 1.7 Hz, 3H), 1.64 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.1, 156.2, 155.7, 148.5, 144.0, 142.6, 140.9, 138.6, 137.4, 132.4, 131.0, 129.9, 128.9, 128.8, 127.7, 127.2, 126.9, 125.8, 124.9, 122.8, 122.3, 121.8, 44.4, 44.4, 21.0; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 525.2, $C_{27}H_{23}Cl_2N_2O_3S^+$ requires 525.1.

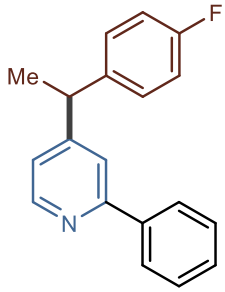
3-Benzyl-5-(4-(2-(5-ethyl-4-((S)-1-phenylethyl)pyridin-2-yl)ethoxy)benzyl)thiazolidine-2,4-dione (3w)



Prepared according to general procedure E using (2-(2-(4-((3-benzyl-2,4-dioxothiazolidin-5-yl)methyl)phenoxy)ethyl)-5-ethylpyridin-4-yl)triphenylphosphonium trifluoromethanesulfonate (169.5 mg, 0.20 mmol), potassium trifluoro(1-phenylethyl)borate (84.0 mg, .40 mmol), 3DPAFIPN (2.6 mg, 0.004 mmol), 2,6-lutidine (69 μL, .59 mmol), and 1,4-dioxane (659 □L, 0.3M). Flash column chromatography (silica gel: 75% Et_2O in hexanes) afforded the title compound as a yellow amorphous solid as a 1:1 mixture of diastereomers (76.2 mg, 0.14 mmol, 72% yield). IR ν_{max}/cm^{-1} (film): 3033, 2968, 2931, 2874, 1749, 1680, 1512, 1381, 1329, 1244, 759, 699; ^1H NMR (400 MHz, CD_3CN) δ: 8.30 (s, 1H), 7.33 – 7.14 (m, 9H), 7.12 – 7.03 (m, 4H), 6.75 – 6.67 (m, 2H), 4.72 – 4.54 (m, 3H), 4.40 (q, *J* = 7.1 Hz, 1H), 4.35 – 4.21 (m, 2H), 3.30 (ddd, *J* = 14.3, 4.4, 2.5 Hz, 1H), 3.23 – 3.06 (m, 3H), 2.76 – 2.52 (m, 2H), 1.57 (dd, *J* = 7.2, 1.9 Hz, 3H), 1.10 (td, *J* = 7.6, 1.7 Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ: 174.9, 172.3, 159.1, 157.3, 153.4, 150.6, 146.2, 136.6, 135.9, 131.8, 129.5, 128.8, 128.7, 128.7, 128.6, 128.5, 127.3, 122.8, 115.3, 68.0, 52.3, 45.7, 40.5, 38.2, 37.2, 23.5, 22.2, 15.7; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 551.3, $C_{34}H_{35}N_2O_3S^+$ requires 551.2.

Potassium Trifluoroborate Scope for Heteroaromatic Alkylation

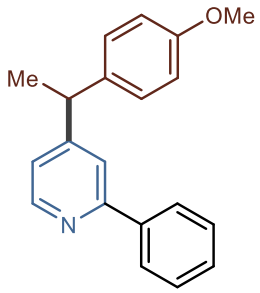
4-(1-(4-Fluorophenyl)ethyl)-2-phenylpyridine (3x)



Prepared according to general procedure E using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (169.8 mg, 0.30 mmol), potassium trifluoro(1-(4-fluorophenyl)ethyl)borate (138.0 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.90 mmol), and 1,4-dioxane (1.00 mL, 0.3 M). Flash column chromatography (silica gel: 10% Et_2O in hexanes) afforded the title compound as a yellow oil (65.9 mg, 0.24 mmol, 79% yield). IR ν_{max}/cm^{-1} (film): 2969, 2930, 1888, 1596, 1553, 1507, 1403, 1221, 1159, 832, 820, 775,

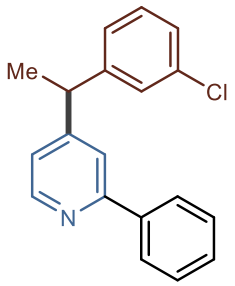
693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 5.1 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.40 – 7.25 (m, 3H), 7.07 (dd, *J* = 8.5, 5.4 Hz, 2H), 6.98 – 6.85 (m, 3H), 4.04 (q, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.6 (d, *J* = 245.1 Hz), 157.8, 155.7, 149.9, 140.2 (d, *J* = 3.2 Hz), 139.6, 129.2 (d, *J* = 7.9 Hz), 129.0, 128.8, 127.1, 121.4, 119.9, 115.5 (d, *J* = 21.3 Hz), 43.8, 21.4; ^{19}F NMR (365 MHz, $CDCl_3$) δ: –116.24; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 278.2, $C_{19}H_{17}FN^+$ requires 278.1.

4-(1-(4-Methoxyphenyl)ethyl)-2-phenylpyridine (3y)



Prepared according to general procedure E using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (226.4 mg, 0.30 mmol), potassium trifluoro(1-(4-methoxyphenyl)ethyl)borate (1.2:1 regiomeric mixture of 2c:2c') (145.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.90 mmol), and 1,4-dioxane (1.00 mL, 0.3 M). Flash column chromatography (silica gel: 100% CH_2Cl_2 to 15% Et_2O in hexanes) afforded the title compound as a clear oil (51.1 mg, 0.15 mmol, 51% yield). IR ν_{max}/cm^{-1} (film): 3030, 3002, 2966, 2931, 2834, 1595, 1580, 1510, 1445, 1402, 1244, 1178, 1033, 829, 776, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59 (dd, *J* = 5.2, 0.8 Hz, 1H), 8.07 – 7.87 (m, 2H), 7.60 – 7.54 (m, 1H), 7.51 – 7.37 (m, 3H), 7.20 – 7.14 (m, 2H), 7.08 (dd, *J* = 5.1, 1.7 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.67 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4, 157.7, 156.4, 149.8, 139.7, 136.7, 128.9, 128.8, 128.7, 127.1, 121.5, 120.0, 114.1, 55.4, 43.7, 21.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 290.2, $C_{20}H_{20}NO^+$ requires 290.2.

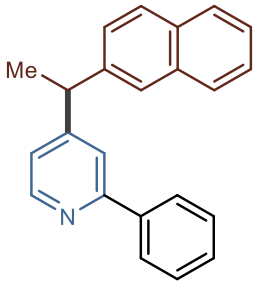
4-(1-(3-Chlorophenyl)ethyl)-2-phenylpyridine (3z)



Prepared according to general procedure E using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (169.8 mg, 0.30 mmol), potassium (1-(3-

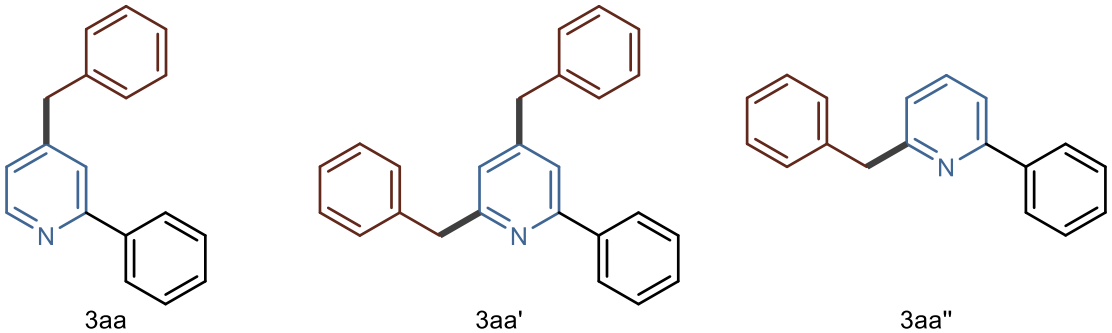
chlorophenyl)ethyl)trifluoroborate (148.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.90 mmol), and 1,4-dioxane (1.00 mL, 0.3 M). Flash column chromatography (silica gel: 100% CH_2Cl_2 to 10% Et_2O in hexanes) afforded the title compound as a yellow oil (87.9 mg, 0.17 mmol, 56% yield). IR ν_{max}/cm^{-1} (film): 3056, 2970, 2932, 2875, 1593, 1579, 1553, 1473, 1403, 1082, 883, 866, 775, 694; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 5.1 Hz, 1H), 8.05 – 7.93 (m, 2H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.32 – 7.22 (m, 3H), 7.19 – 7.11 (m, 1H), 7.09 (dd, *J* = 5.1, 1.7 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 155.1, 150.0, 146.6, 139.5, 134.6, 130.0, 129.1, 128.8, 127.9, 127.1, 127.0, 126.0, 121.4, 119.9, 44.3, 21.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 294.2, $C_{19}H_{17}ClN^+$ requires 294.1.

4-(1-(Naphthalen-2-yl)ethyl)-2-phenylpyridine (3aa)



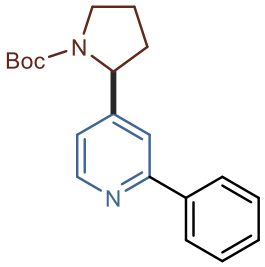
Prepared according to general procedure E using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (169.8 mg, 0.30 mmol), potassium trifluoro(1-(naphthalen-2-yl)ethyl)borate (157.2 mg, 0.60 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), 2,6-lutidine (105 μL, 0.90 mmol), and 1,4-dioxane (1.00 mL, 0.3 M). Flash column chromatography (silica gel: 10% Et_2O in hexanes) afforded the title compound as a yellow oil (70.1 mg, 0.23 mmol, 76% yield). IR ν_{max}/cm^{-1} (film): 3052, 2966, 2917, 2849, 1595, 1580, 1473, 1445, 1403, 907, 891, 818, 751, 693; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 5.1 Hz, 1H), 7.99 (d, *J* = 7.0 Hz, 2H), 7.88 – 7.79 (m, 2H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.65 (s, 1H), 7.57 – 7.39 (m, 6H), 7.33 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.14 (dd, *J* = 5.1, 1.6 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 1H), 1.81 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 155.7, 149.8, 141.9, 139.6, 133.5, 132.3, 128.9, 128.7, 128.4, 127.8, 127.7, 127.0, 126.4, 126.3, 125.8, 125.8, 121.6, 120.1, 44.6, 21.1; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 310.2, $C_{23}H_{20}N^+$ requires 310.2.

4-Benzyl-2-phenylpyridine (3ab)



Prepared according to general procedure E using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (226.4 mg, 0.40 mmol), potassium benzyltrifluoroborate (158.4 mg, 0.80 mmol), 3DPAFIPN (5.2 mg, 0.01 mmol), 2,6-lutidine (140 μL, 1.20 mmol), and 1,4-dioxane (1.33 mL, 0.3 M). The product as well as the bis addition product (3aa') and regioisomer (3aa'') were formed in the crude reaction mixture in a ratio of 5.7:1:<1(3aa:3aa':3aa''). Flash column chromatography (silica gel: 5% Et_2O in hexanes) afforded the title compound (**3aa**) as a yellow oil as a single regioisomer (49.6 mg, 0.20 mmol, 51% yield).; IR ν_{max}/cm^{-1} (film): 3060, 3028, 2922, 2852, 1595, 1555, 1474, 1445, 1402, 774, 762, 731, 693; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, *J* = 5.0 Hz, 1H), 7.86 (dd, *J* = 7.2, 2.8 Hz, 2H), 7.45 (s, 1H), 7.40 – 7.08 (m, 8H), 6.94 (d, *J* = 5.1 Hz, 1H), 3.92 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 150.8, 149.8, 139.6, 139.1, 129.1, 129.0, 128.9, 128.8, 127.1, 126.8, 122.8, 121.2, 41.6.; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 246.2, $C_{18}H_{16}N^+$ requires 246.1.

Tert-butyl 2-(2-phenyl-1l4-pyridin-4-yl)pyrrolidine-1-carboxylate (3ac)

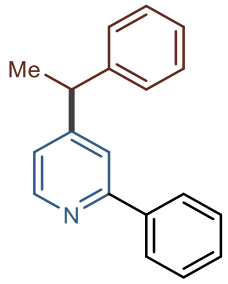


Prepared according to general procedure E using triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (141.5 mg, 0.25 mmol), potassium (1-(tert-butoxycarbonyl)pyrrolidin-2-yl)trifluoroborate (138.5 mg, 0.50 mmol), 3DPAFIPN (3.2 mg, 0.005 mmol), 2,6-lutidine (87.2 μL, 0.75 mmol), and 1,4-dioxane (833 μL, 0.3 M). Flash column chromatography (silica gel: 40% Et_2O in hexanes) afforded the title compound as a yellow oil (59.7 mg, 0.16 mmol, 64% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide.[19] IR ν_{max}/cm^{-1} (film): 3059, 2974, 2930, 2876, 1690, 1598, 1446, 1388 1365, 1156, 1115, 775, 733, 694; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.61 (d, *J* = 5.1 Hz, 1H), 8.01 – 7.91 (m, 2H), 7.66 – 7.36 (m, 4H), 7.05 (dd, *J* = 5.1, 1.6 Hz, 1H), 5.09 – 4.73 (m, 1H), 3.74 – 3.45 (m, 2H), 2.48 – 2.28 (m, 1H), 1.98 – 1.79 (m, 3H), 1.48 (s, 3H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7,

155.1, 154.5, 149.8, 139.5, 129.1, 128.9, 127.0, 119.4, 117.5, 79.9, 60.9, 47.3, 35.7, 28.3, 23.4; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 325.3, $C_{20}H_{25}N_2O_2^+$ requires 325.2.

11. Pyridine Alkylation Using Carboxylic Acid as Alkyl Radical Precursor

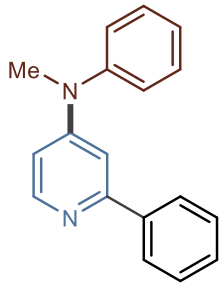
2-Phenyl-4-(1-phenylethyl)pyridine (3a)



An oven dried 8 mL vial equipped with a magnetic stir bar was charged with triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (169.8 mg, 0.30 mmol), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (6.7 mg, 0.006 mmol), and potassium phosphate dibasic (157.0 mg, 0.90 mmol). The reaction vessel was pumped into a glovebox and then 2-phenylpropanoic acid (124.0 μL, 0.90 mmol) and 1,2-dichloroethane (960.0 μL) were added via a syringe. The vial was sealed and removed from the glovebox followed by irradiation with a 455 nm kessil lamp (5 cm away, with stream of air blowing over vials to keep reaction at 25 °C) for 16 hours. Flash column chromatography (silica gel: 7% Et_2O in hexanes) afforded the title compound as a pale yellow oil (16.4 mg, 0.06 mmol, 21% yield).; Spectra match that obtained from **3a** obtained from coupling with BF_3K salt.

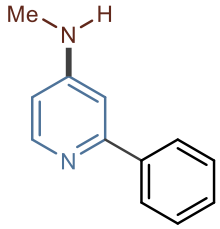
12. Pyridine Amination

N-Methyl-N,2-diphenylpyridin-4-amine (4)



Prepared according to procedure reported by Zhou et al.[20] An oven dried 8 mL vial equipped with a magnetic stir bar was charged with triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethane sulfonate (169.8 mg, 0.30 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), and 1,4-Diazabicyclo[2.2.2]octane (33.6 mg, 0.30 mmol). The reaction vessel was pumped into a glovebox and then *N*-methylaniline (49 μL, 0.45 mmol) and MeCN (3.00 mL) were added via a syringe. The vial was sealed and removed from the glovebox followed by irradiation with a 455 nm kessil lamp (5 cm away, with stream of air blowing over vials to keep reaction at 25 °C) for 16 hours. The reaction was quenched with water and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (neutralized silica gel: 25% EtOAc in hexanes) afforded the title compound as a yellow oil (48.7 mg, 0.19 mmol, 62% yield). IR ν_{max}/cm^{-1} (film): 3056, 3033, 2922, 2852, 2816, 1604, 1586, 1575, 1493, 1480, 1360, 1001, 772, 693; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 5.9 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.41 – 7.08 (m, 8H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.43 (dd, *J* = 5.9, 2.5 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 154.6, 149.9, 146.4, 140.4, 130.0, 128.6, 128.6, 127.0, 126.7, 126.4, 107.3, 105.4, 39.6; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 261.2, $C_{18}H_{17}N_2^+$ requires 261.1.

N-Methyl-2-phenylpyridin-4-amine (5)



Prepared according to procedure reported by Zhou et al.[20] An oven dried 8 mL vial equipped with a magnetic stir bar was charged with triphenyl(2-phenylpyridin-4-yl)phosphonium trifluoromethanesulfonate (169.8 mg, 0.30 mmol), N,O-dimethylhydroxylammonium chloride (75.6 mg, 0.75 mmol), 3DPAFIPN (3.9 mg, 0.006 mmol), and K_3PO_4 (190.8 mg, 0.90 mmol). The reaction vessel was pumped into a glovebox and MeCN (3.00 mL) was added via a syringe. The vial was sealed and removed from the glovebox followed by irradiation with a 455 nm kessil lamp (5 cm away, with stream of air blowing over vials to keep reaction at 25 °C) for 16 hours. The reaction was quenched with water and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (neutralized silica gel: 55% EtOAc in hexanes) afforded the title compound as a yellow solid (35.8 mg, 0.20 mmol, 65% yield). m.p. 89-92 ^oC; IR ν_{max}/cm^{-1} (film): 3231, 3136, 3085, 3032, 2959, 1605, 1598, 1535, 1476, 1355, 1238, 983, 858, 772, 690; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 5.7 Hz, 1H), 7.96 – 7.87 (m, 2H), 7.53 – 7.33 (m, 3H), 6.81 (d, *J* = 2.3 Hz, 1H), 6.37 (dd, *J* = 5.7, 2.3 Hz, 1H), 4.55 (d, *J* = 5.8 Hz, 1H), 2.84 (d, *J* = 4.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 155.2, 149.8, 140.3, 128.6, 128.6, 127.0, 106.1, 104.2, 29.5; *m/z* LRMS (ESI + APCI) found $[M+H]^+$ 185.2, $C_{12}H_{13}N_2^+$ requires 185.1.

12. References

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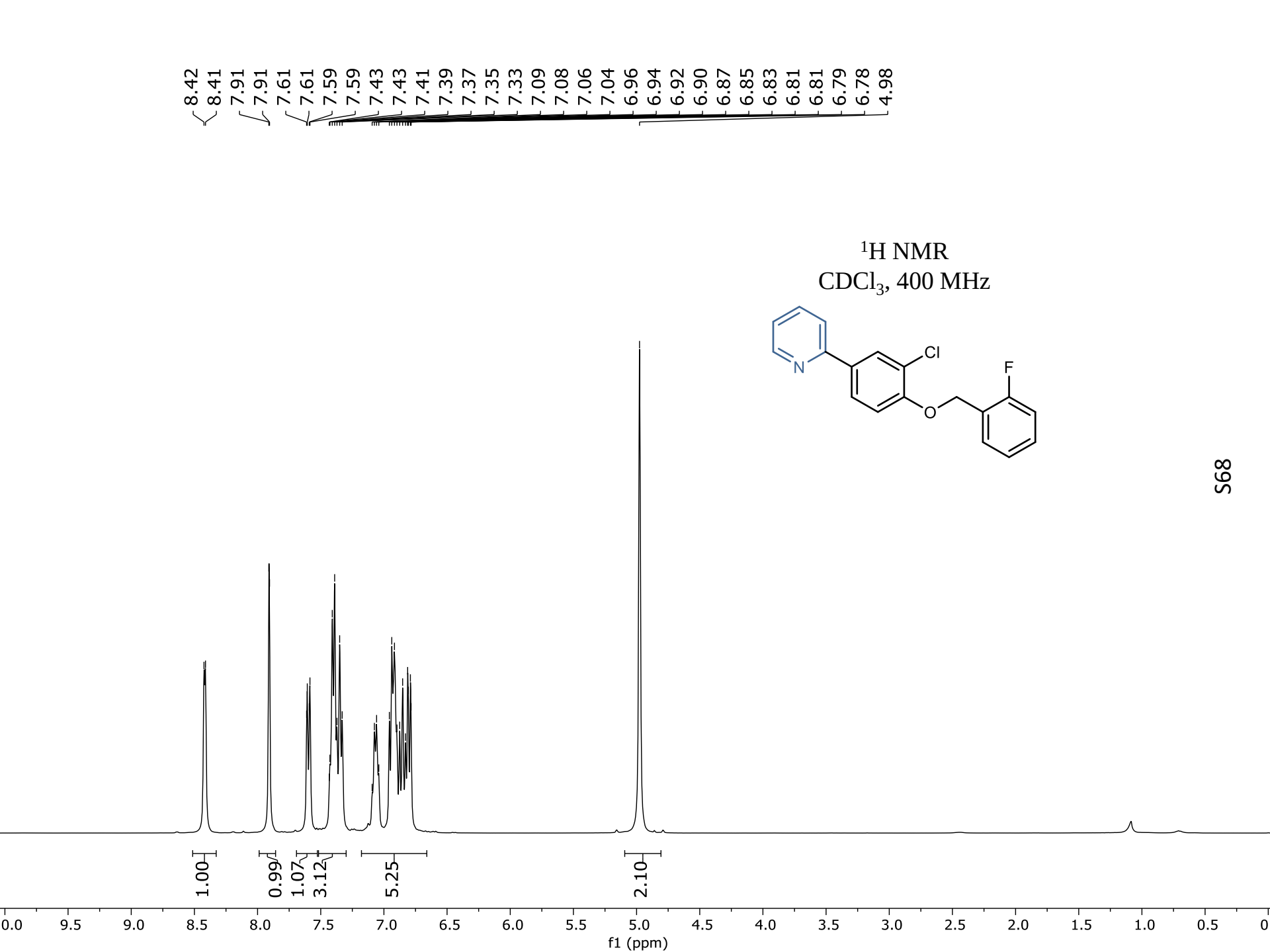
13. ^{1}H, ^{13}C, ^{19}F and ^{31}P Spectra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7.43
7.41
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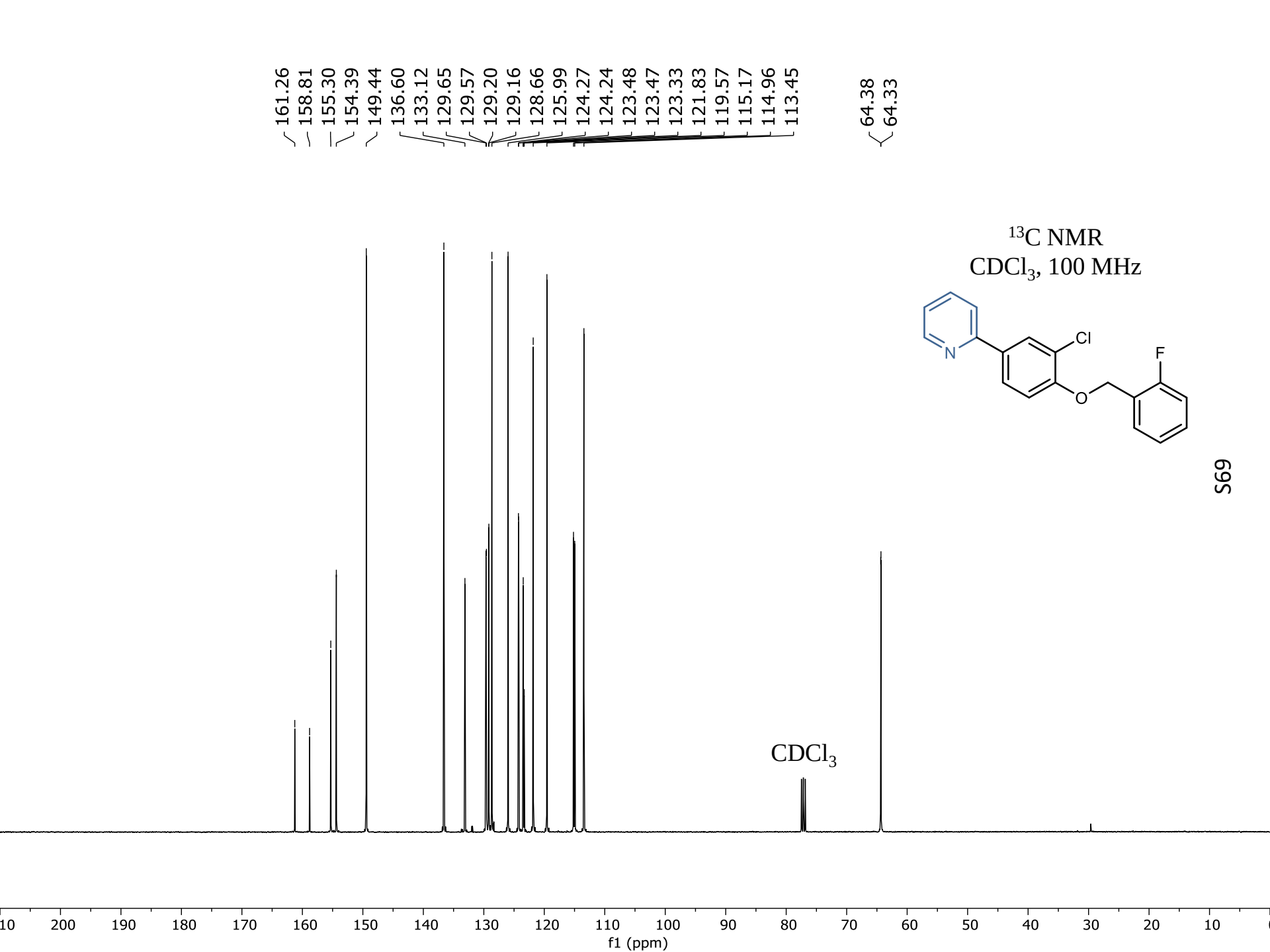
7.37
7.35
7.33
7.09
7.08
7.06
7.04
6.96
6.94
6.92
6.90
6.87
6.85
6.83
6.81
6.81
6.79
6.78
4.98
1H NMR
CDCl3, 400 MHz
N
Cl
F
O
1.00
0.99
1.07
3.12
5.25
2.10
f1 (ppm)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133.12
129.65
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129.20
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125.99
124.27
124.24
123.48
123.47
123.33
121.83
119.57
115.17
114.96
113.45
64.38
64.33
^{13}C NMR
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Cl
F
N
O
$CDCl_3$
f1 (ppm)


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Cl
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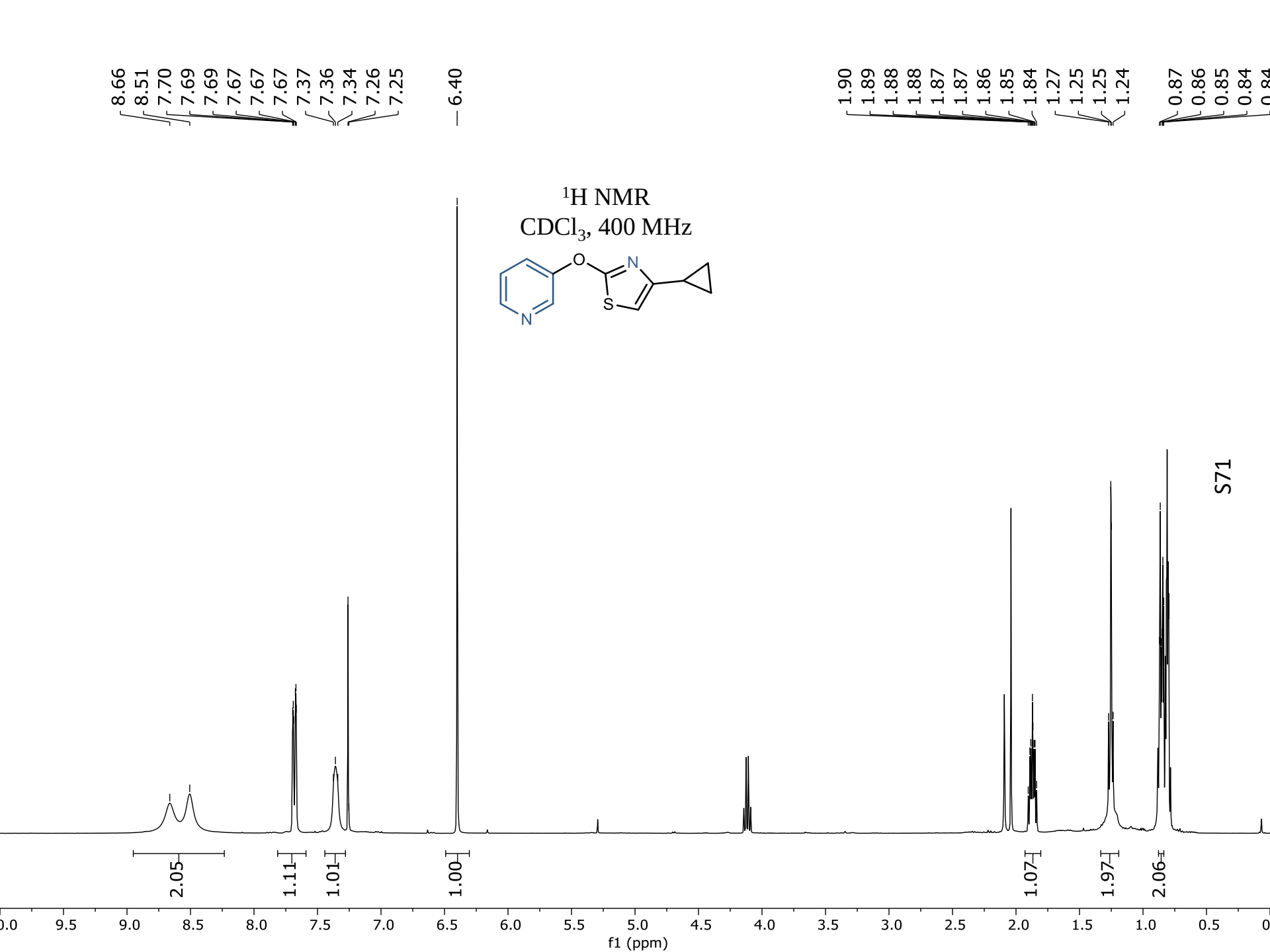
S70
f1 (ppm)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1.88
1.87
1.87
1.86
1.85
1.84
1.27
1.25
1.25
1.24
0.87
0.86
0.85
0.84
1H NMR
CDCl3, 400 MHz
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N
S71
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1.11
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1.00
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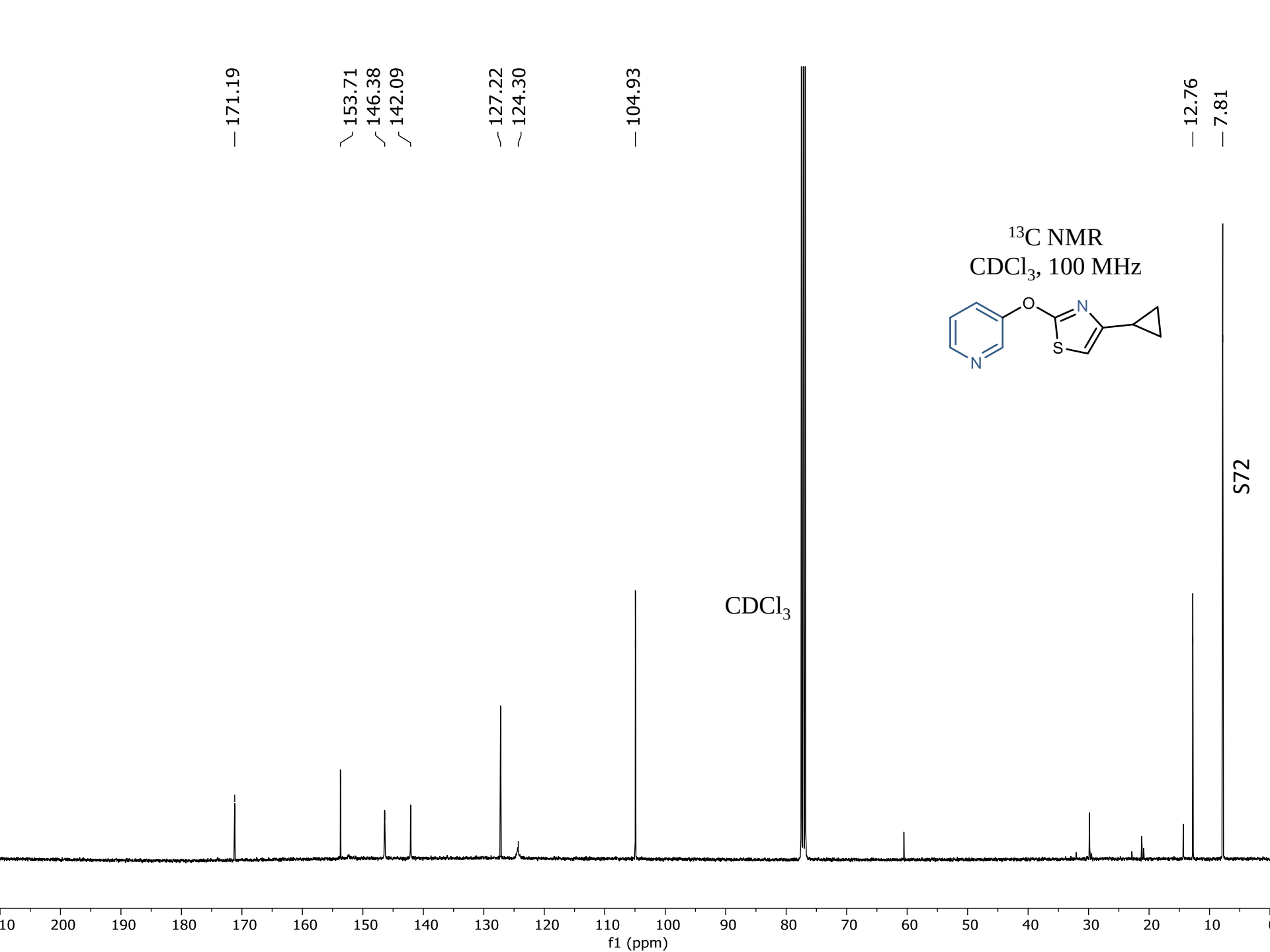
2.06
f1 (ppm)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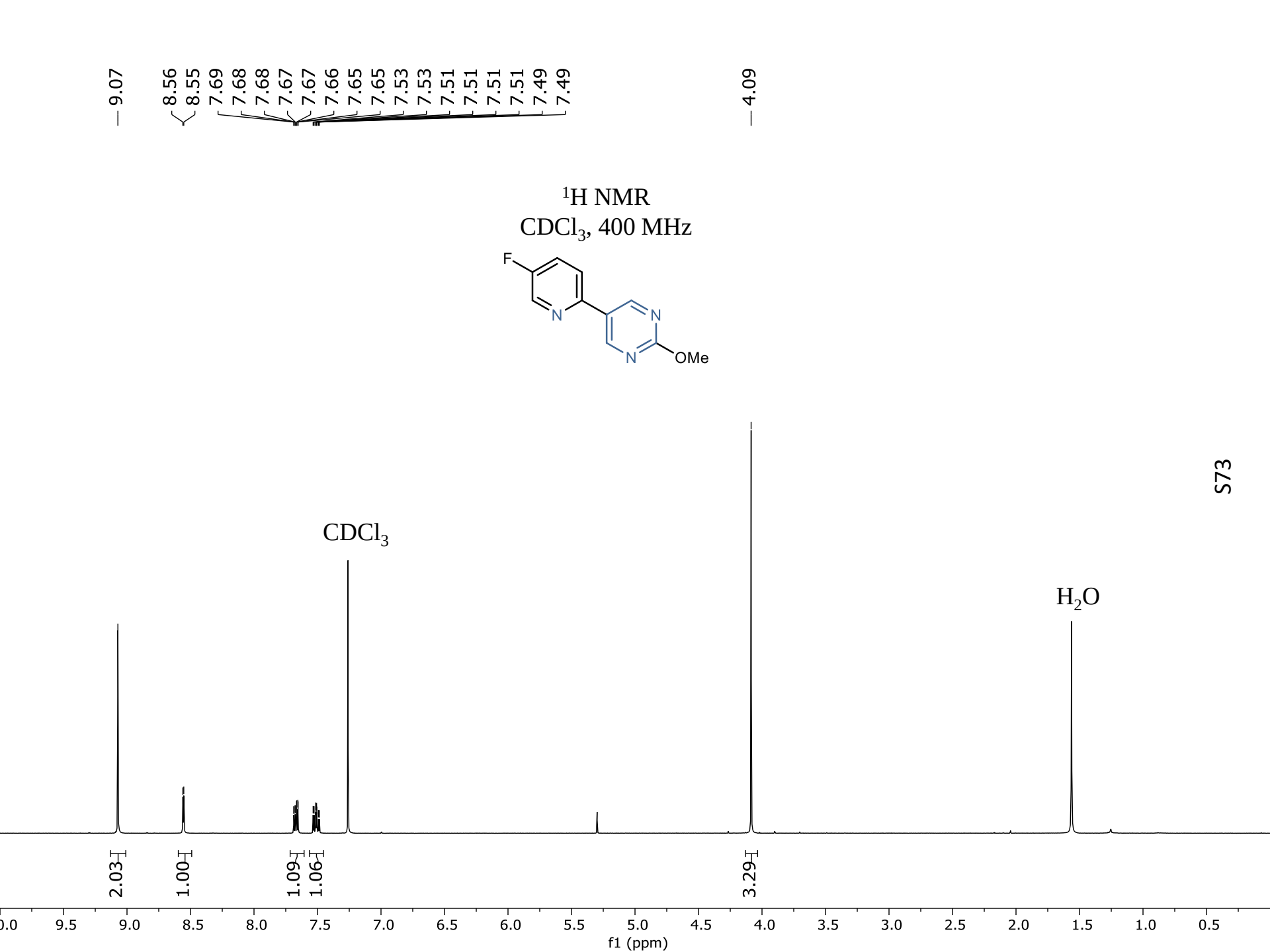
$CDCl_3$, 100 MHz
O
N
S
N
$CDCl_3$
S72
f1 (ppm)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7.53
7.53
7.51
7.51
7.51
7.51
7.49
7.49
4.09
1H NMR
CDCl3, 400 MHz
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N
N
N
OMe
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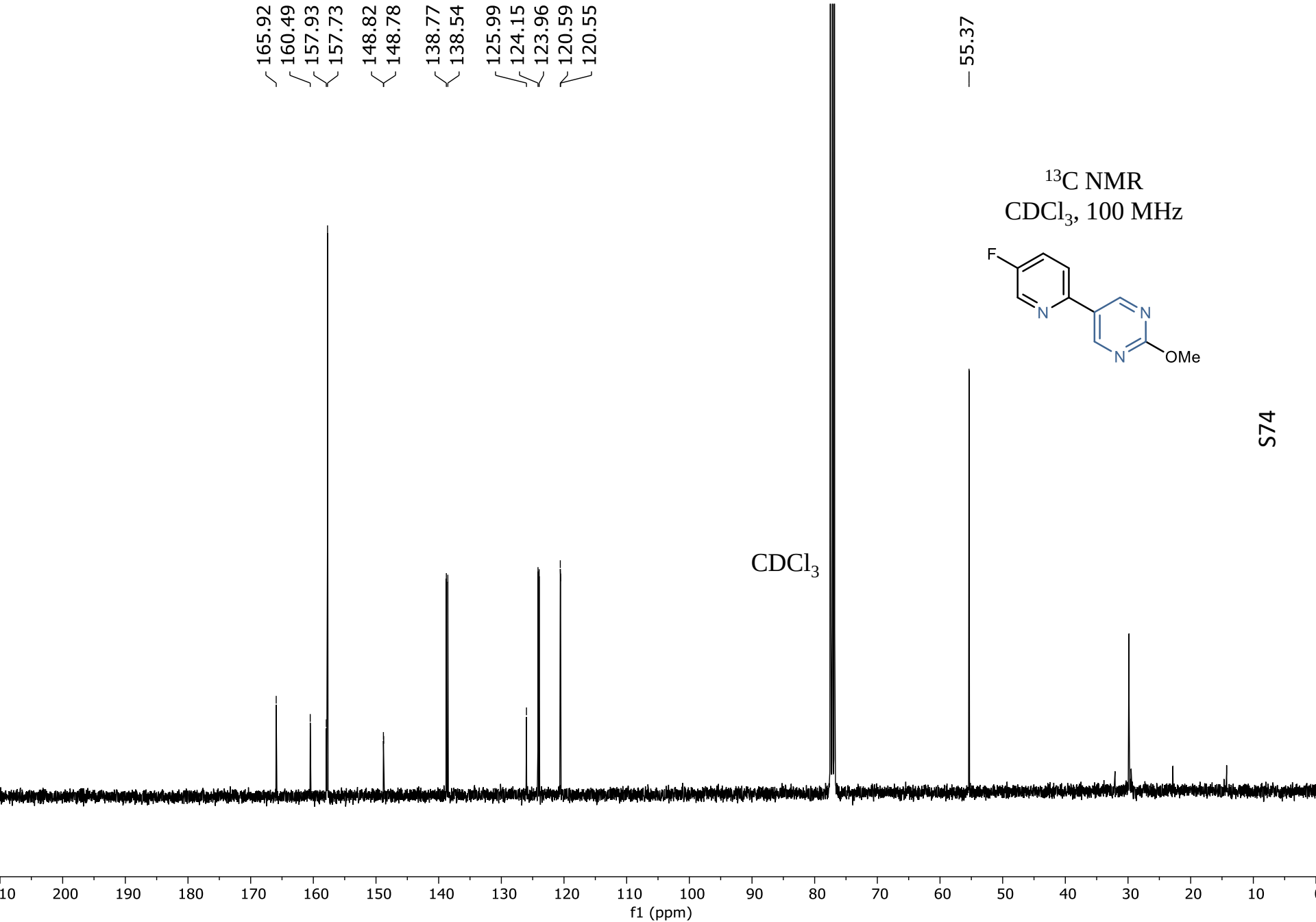
3.29
f1 (ppm)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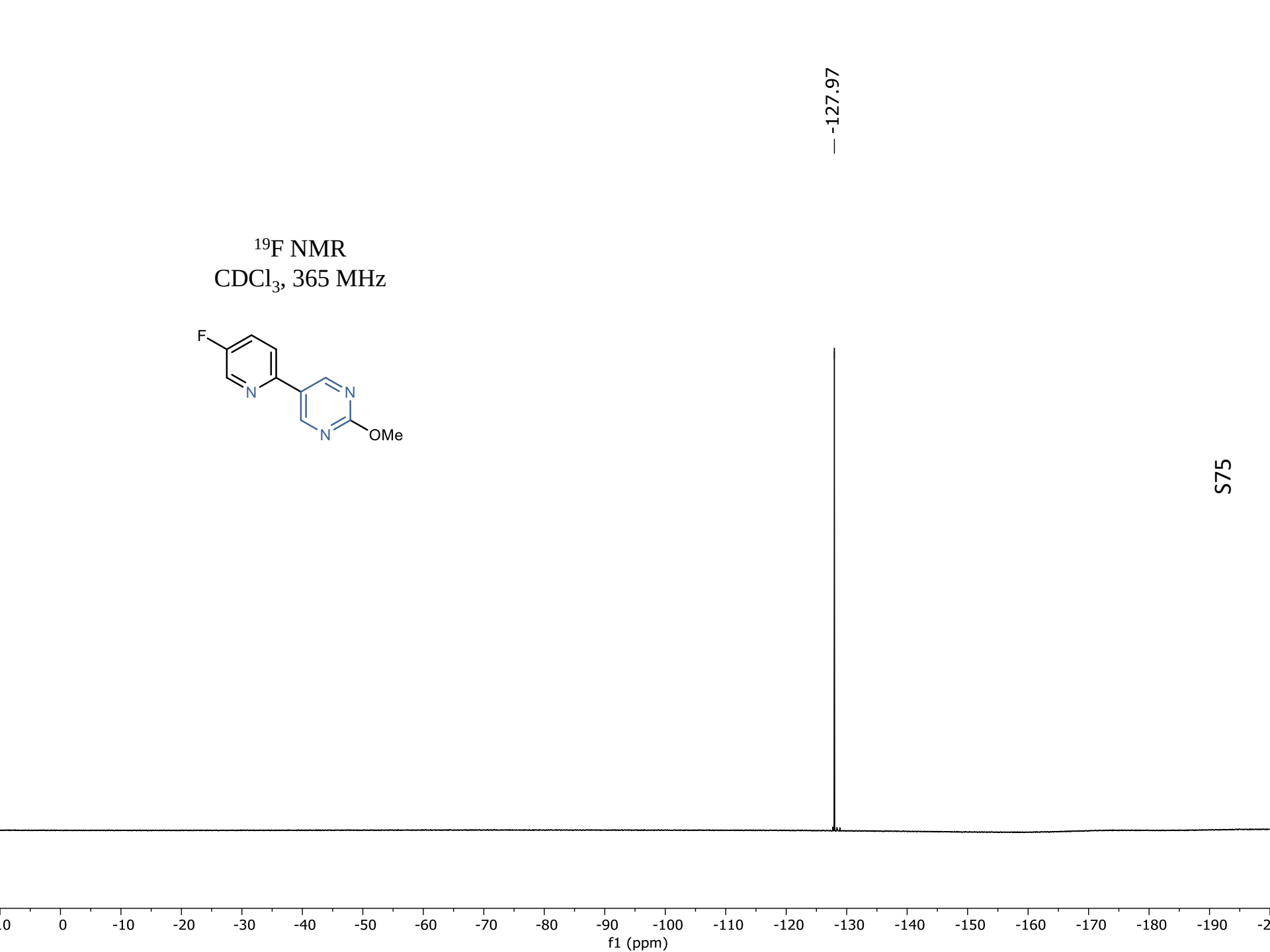
OMe
$CDCl_3$
S74
f1 (ppm)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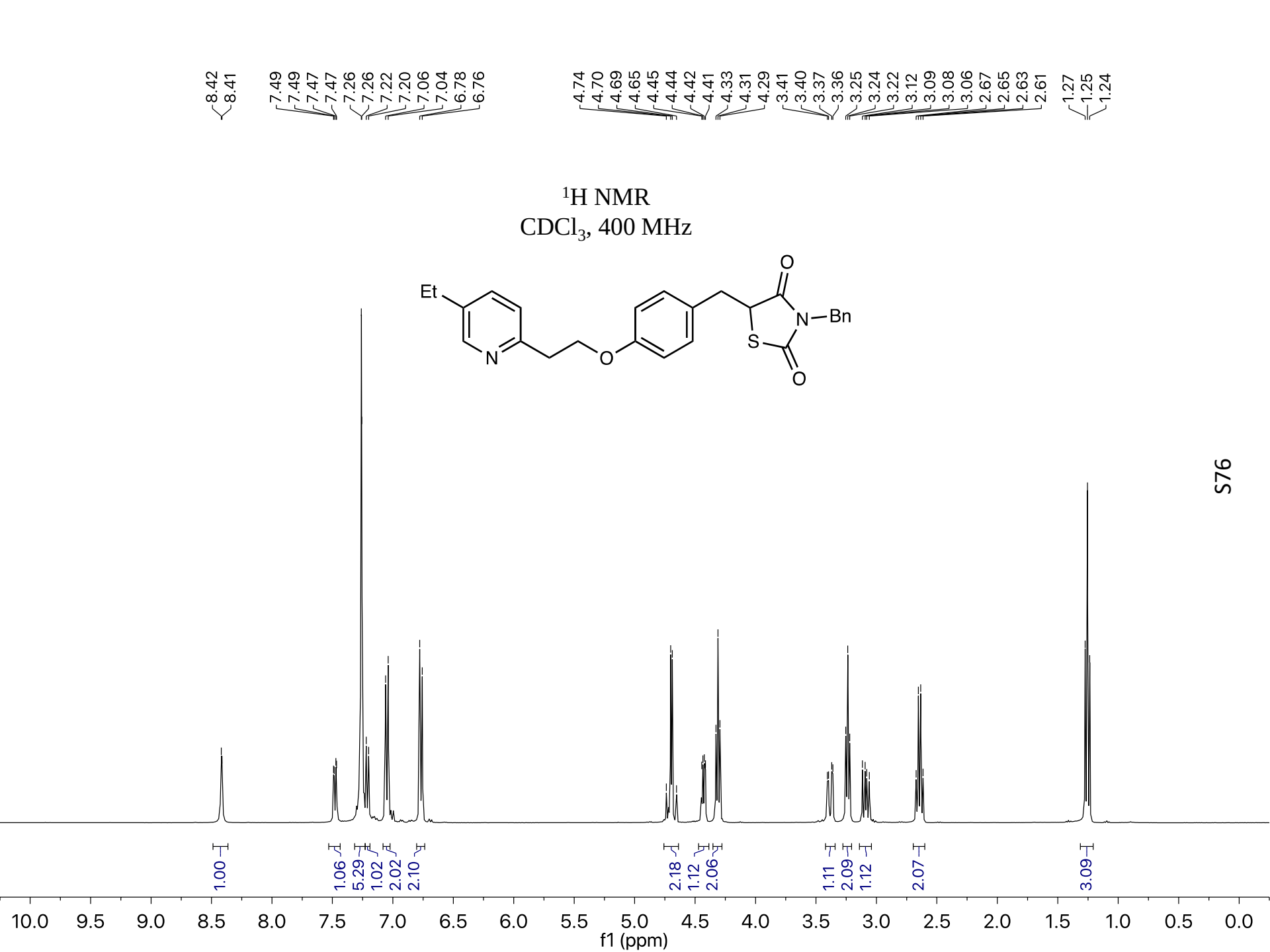
f1 (ppm)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4.33
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3.22
3.12
3.09
3.08
3.06
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1.25
1.24
1H NMR
CDCl3, 400 MHz
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O
O
N
Bn
S
O
S76
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2.18
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2.06
1.11
2.09
1.12
2.07
3.09
10.0
9.5
9.0
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7.0
6.5
6.0
5.5
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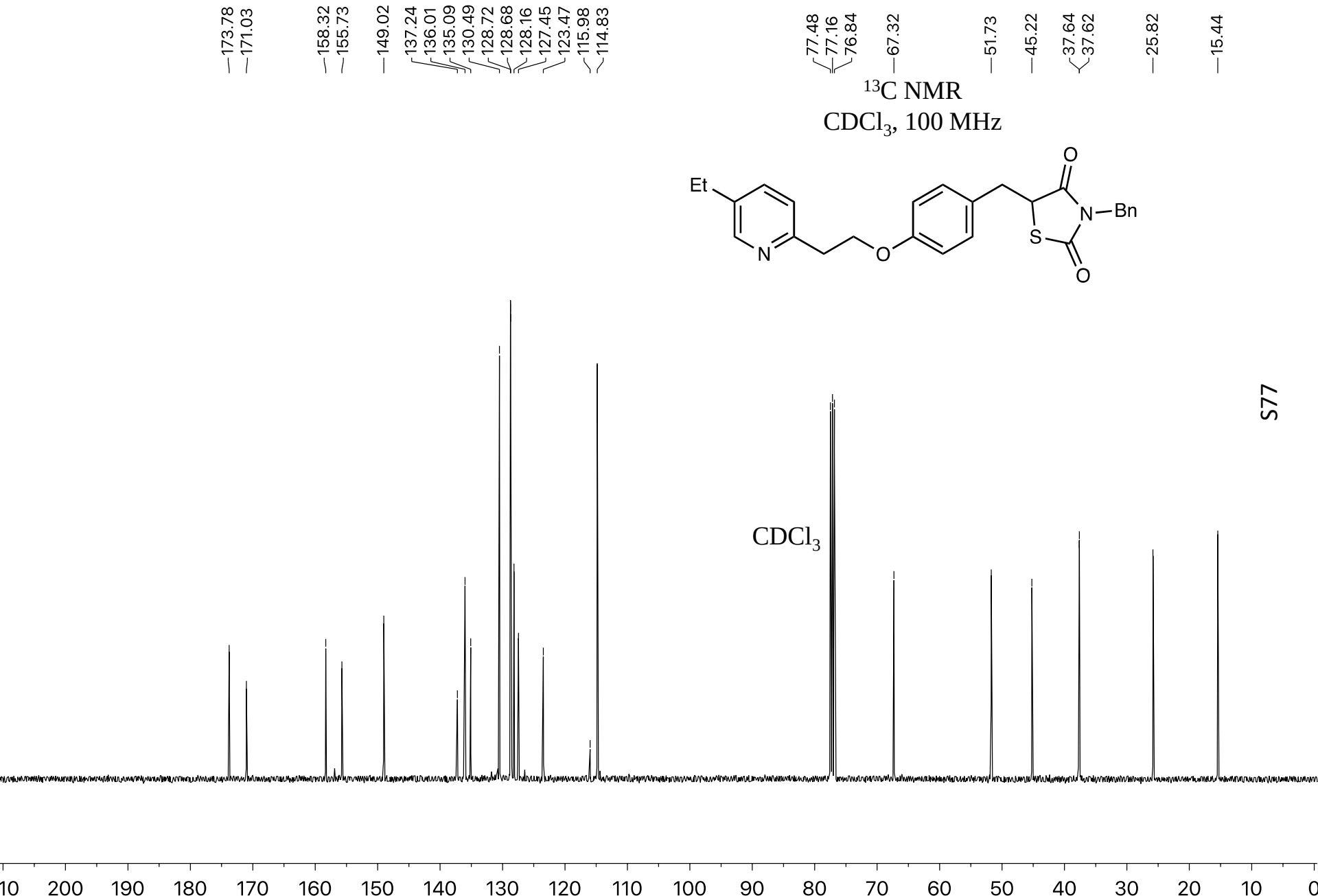
f1 (ppm)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115.98
114.83
77.48
77.16
76.84
67.32
51.73
45.22
37.64
37.62
25.82
15.44
13C NMR
CDCl3, 100 MHz
Et
N
O
O
S
N
Bn
O
CDCl3
S77
210
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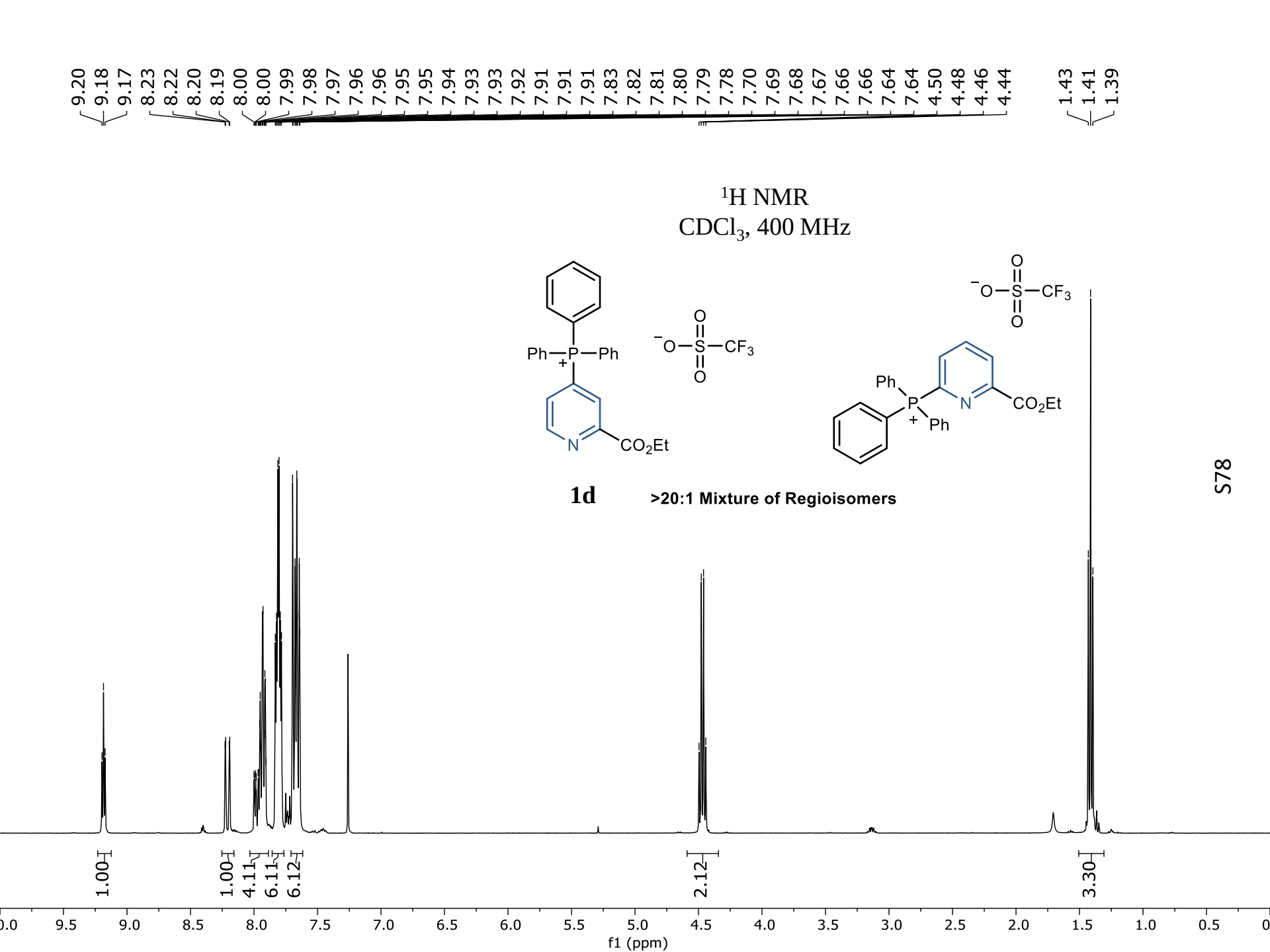
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1.39
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Ph
P
Ph
CO2Et
N
O
S
CF3
1d
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1.00
1.00
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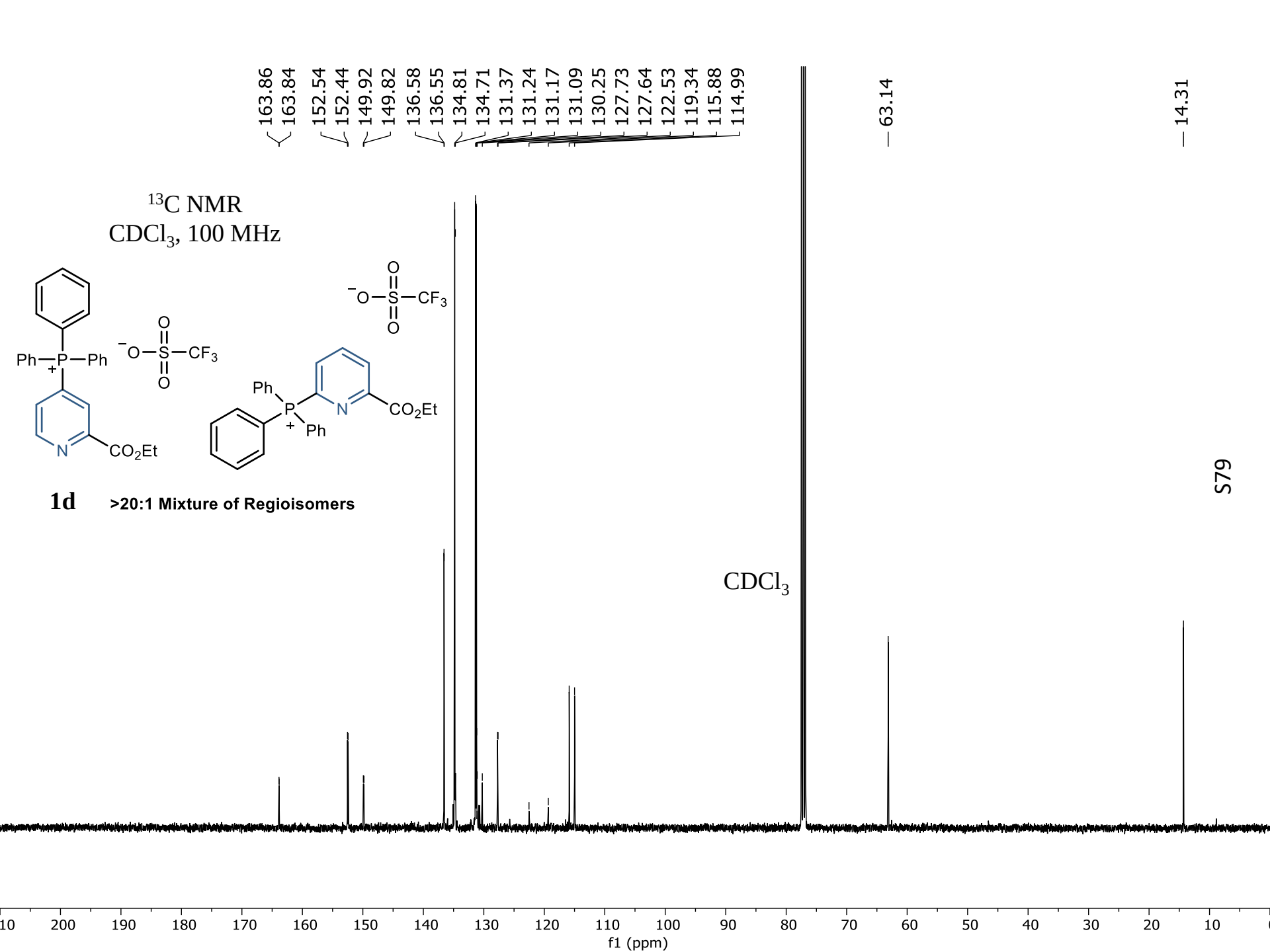
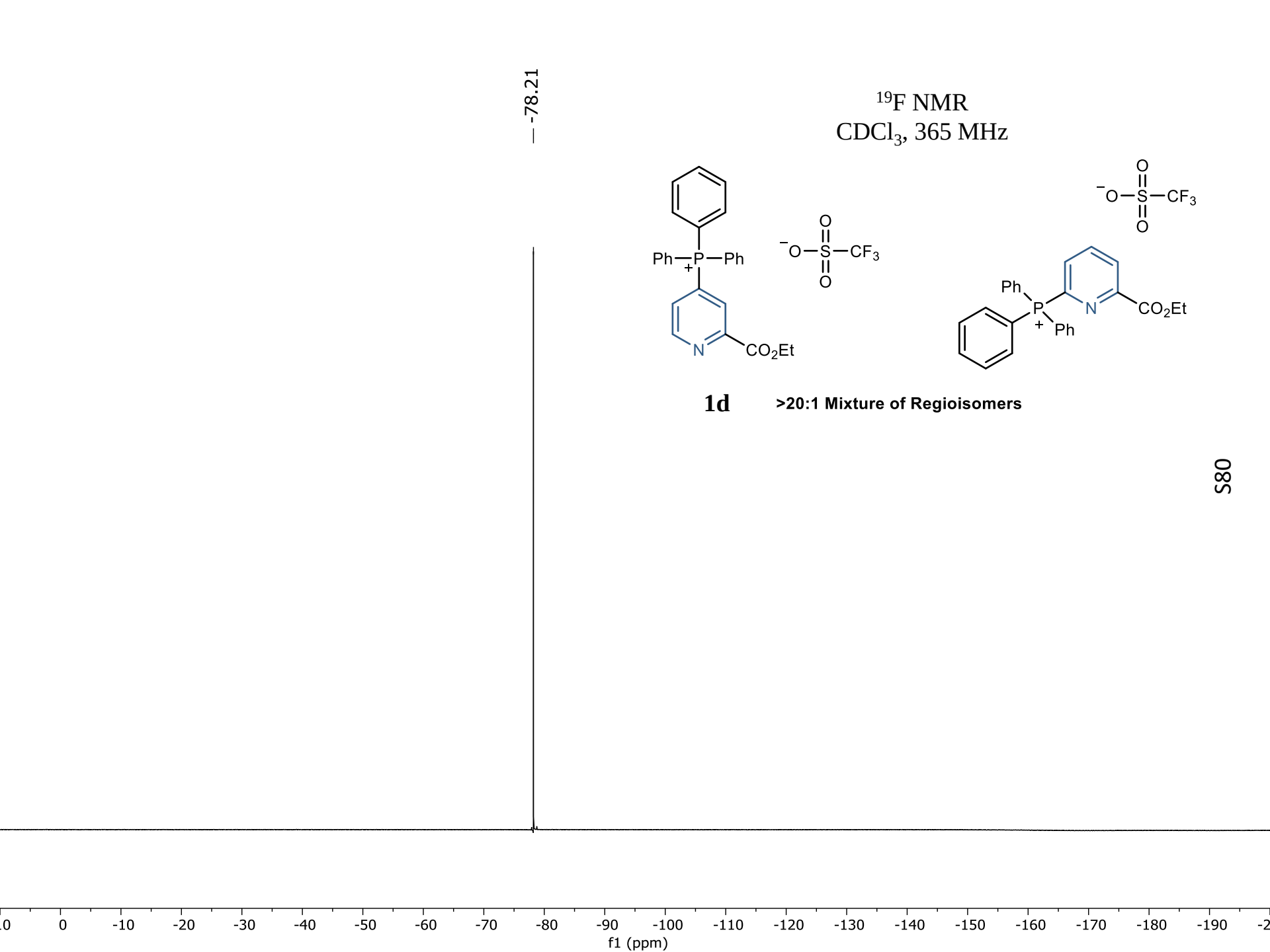
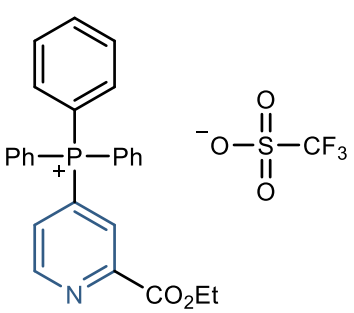
6.11
6.12
2.12
3.30
f1 (ppm)

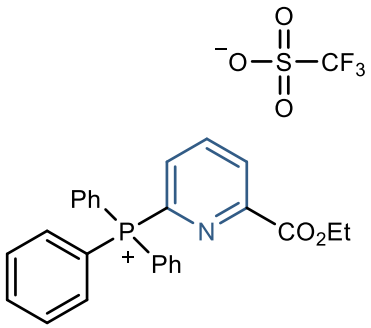


1d **>20:1 Mixture of Regioisomers**


-78.21
19F NMR
CDCl3, 365 MHz
Ph
P
Ph
N
CO2Et
O
S
CF3
1d
>20:1 Mixture of Regioisomers
f1 (ppm)

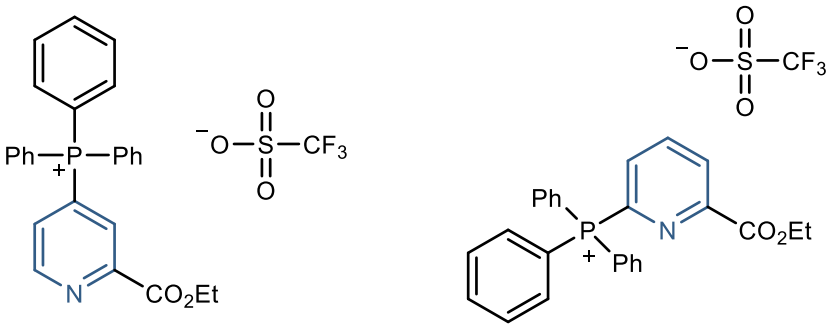
Crude ^{31}P NMR
$CDCl_3$, 162 MHz





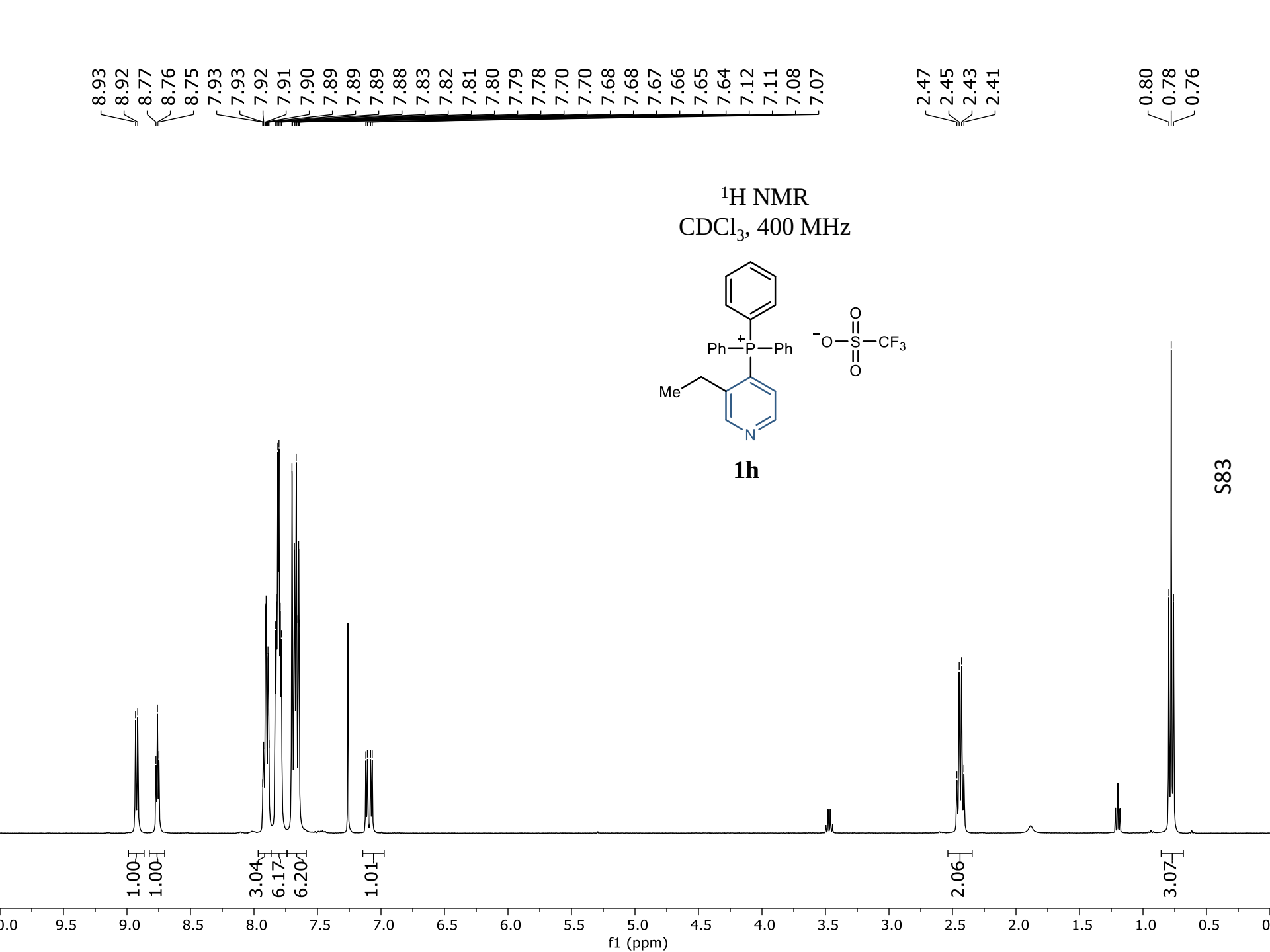
1d **>20:1 Mixture of Regioisomers**

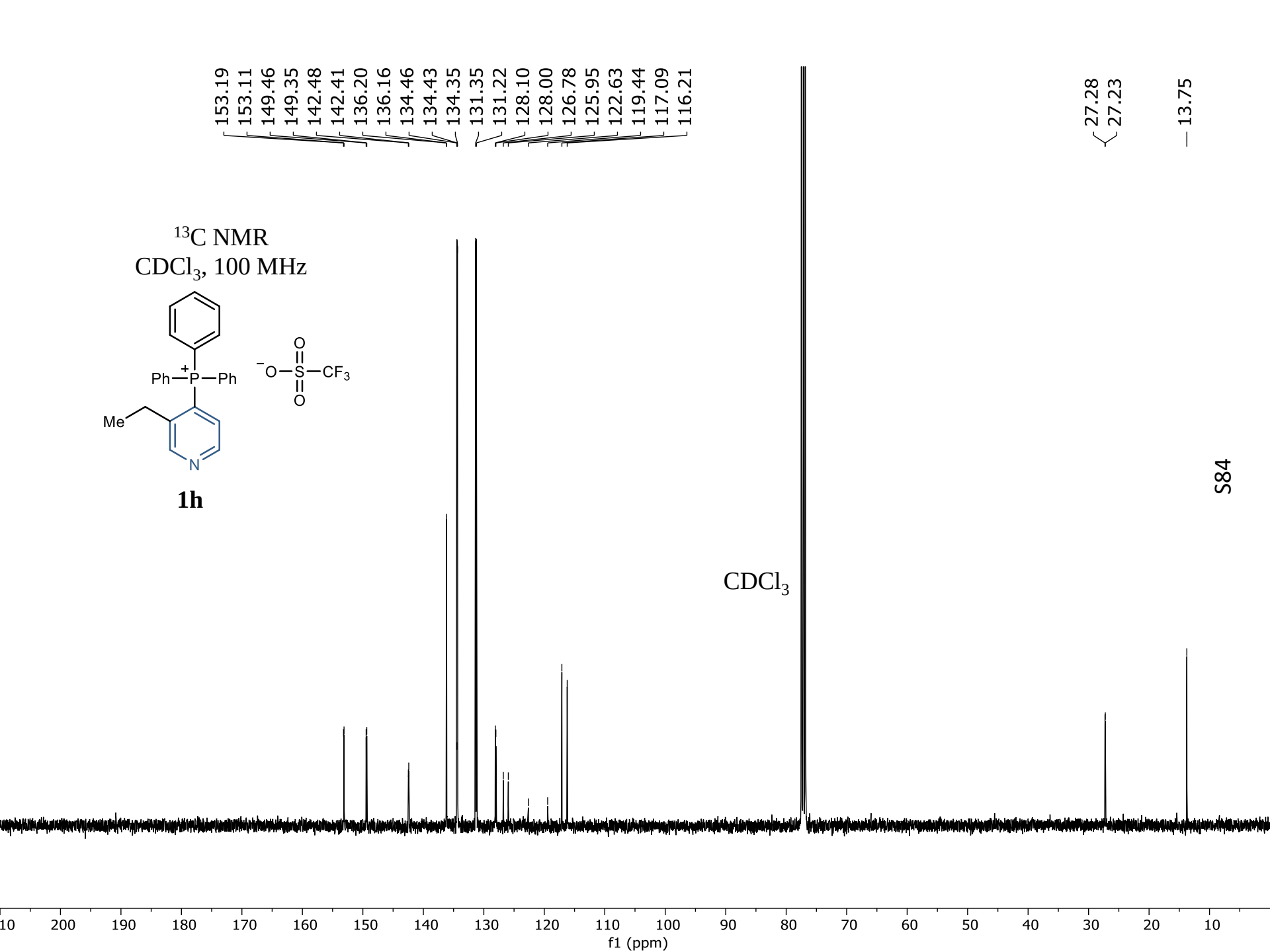
^{31}P NMR
$CDCl_3$, 162 MHz

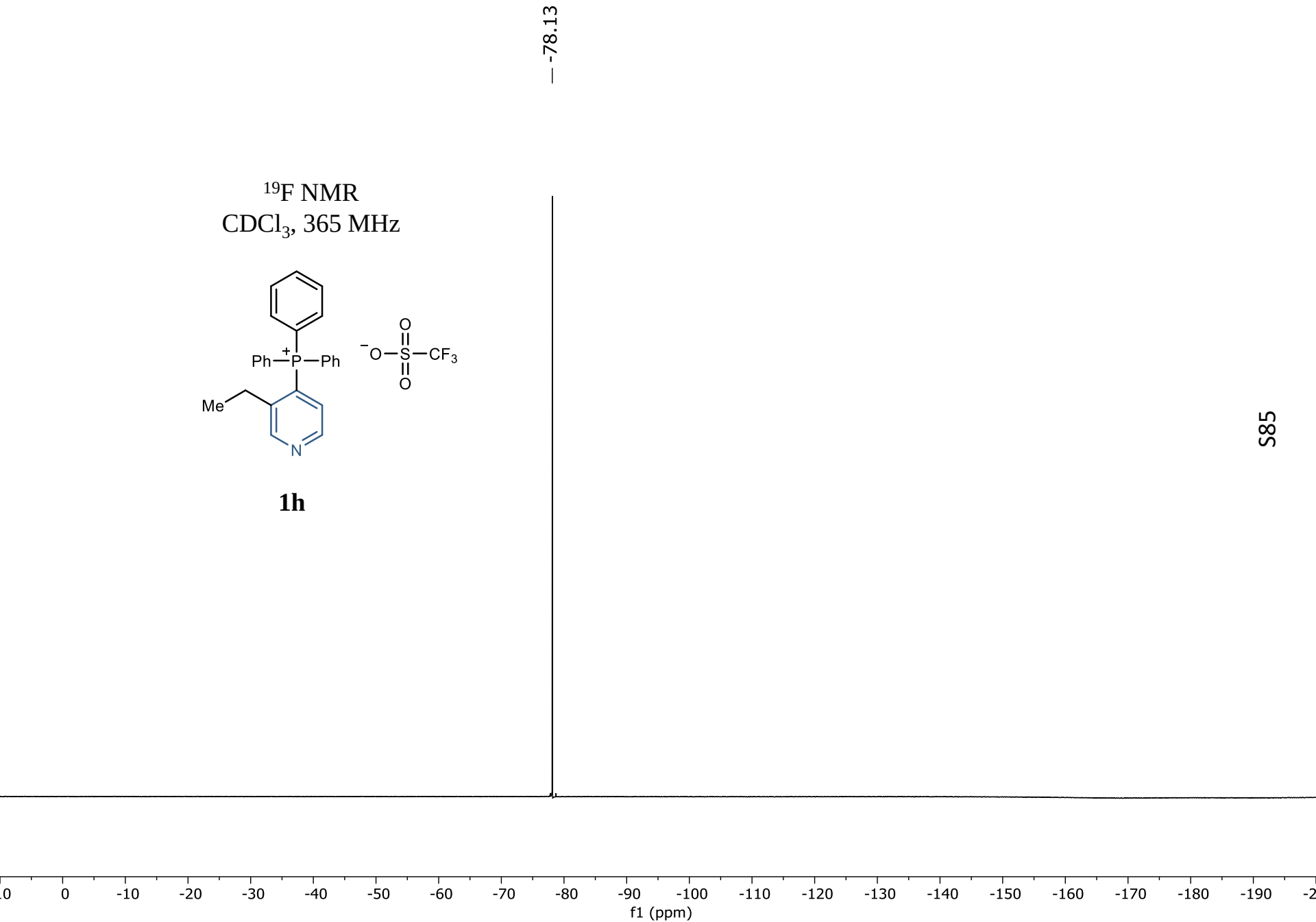


1d

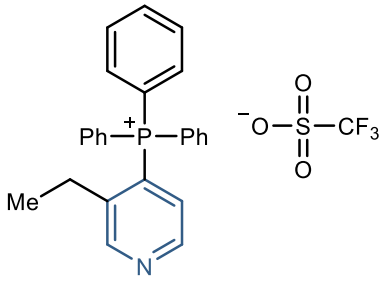
>20:1 Mixture of Regioisomers


8.93
8.92
8.77
8.76
8.75
7.93
7.93
7.92
7.91
7.90
7.89
7.89
7.89
7.88
7.83
7.82
7.81
7.80
7.79
7.78
7.70
7.70
7.68
7.68
7.67
7.66
7.65
7.64
7.12
7.11
7.08
7.07
2.47
2.45
2.43
2.41
0.80
0.78
0.76
1H NMR
CDCl3, 400 MHz
Ph
P
Ph
Me
N
O
S
CF3
1h
S83
1.00
1.00
3.04
6.17
6.20
1.01
2.06
3.07
f1 (ppm)


153.19
153.11
149.46
149.35
142.48
142.41
136.20
136.16
134.46
134.43
134.35
131.35
131.22
128.10
128.00
126.78
125.95
122.63
119.44
117.09
116.21
27.28
27.23
13.75
^{13}C NMR
$CDCl_3$, 100 MHz
Ph
P
Ph
Me
N
O
S
CF_3
1h
$CDCl_3$
S84
f1 (ppm)

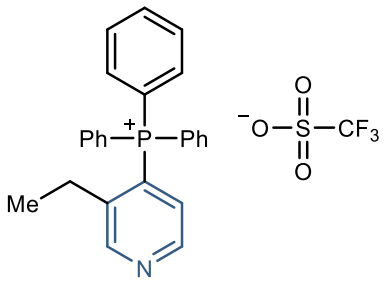

-78.13
^{19}F NMR
$CDCl_3$, 365 MHz
Ph
P
Ph
Me
N
O
S
O
O
CF_3
1h
S85
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

Crude ^{31}P NMR
$CDCl_3$, 162 MHz



1h

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

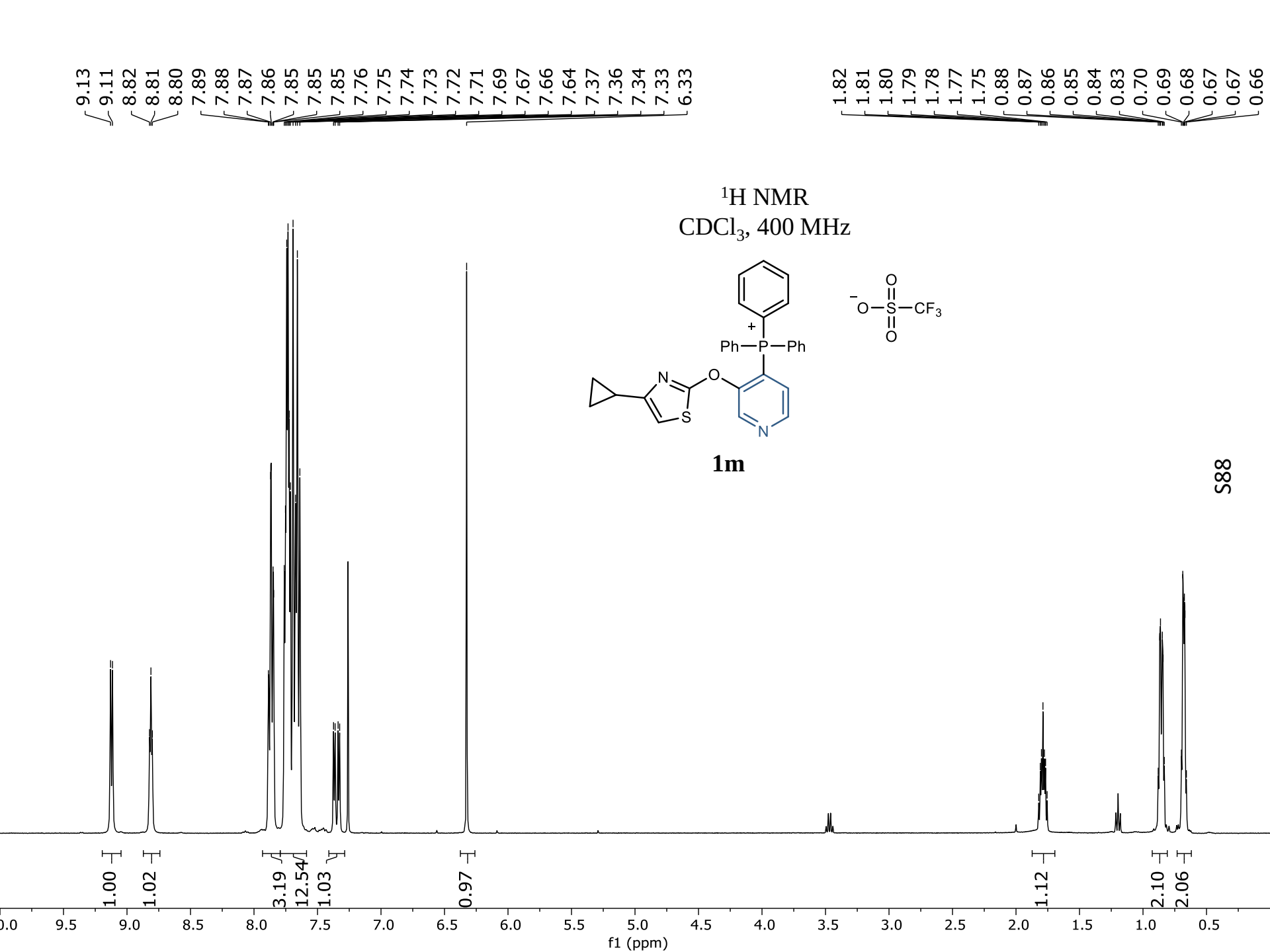


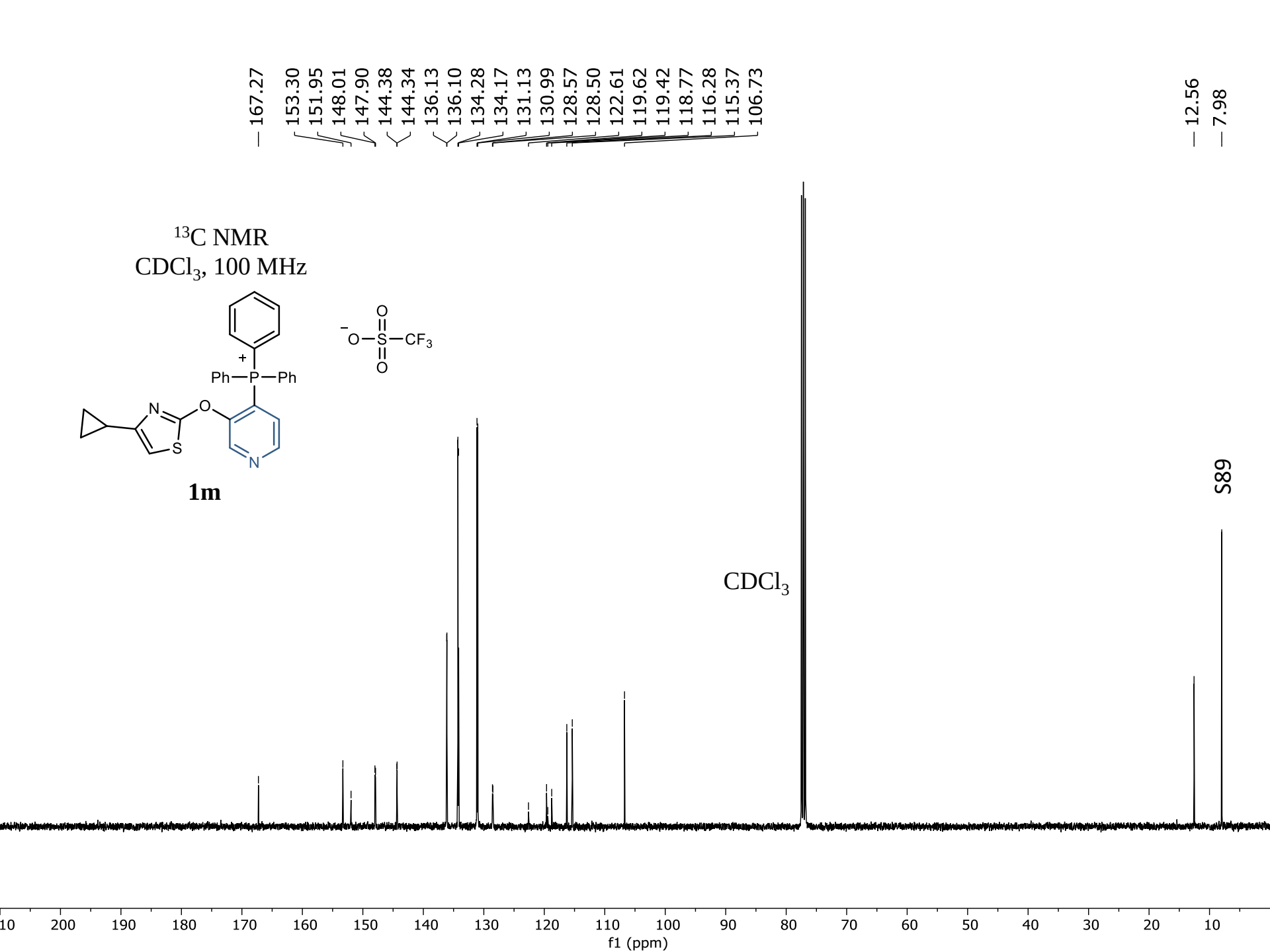
1h

21.33

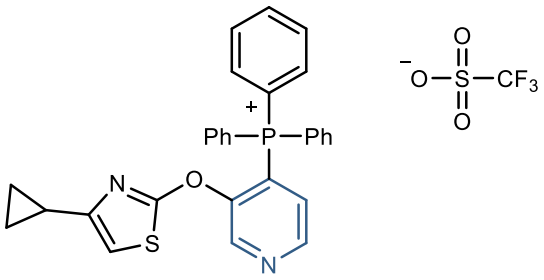
S87

f1 (ppm)


9.13
9.11
8.82
8.81
8.80
7.89
7.88
7.87
7.86
7.85
7.85
7.85
7.76
7.75
7.74
7.73
7.72
7.71
7.69
7.67
7.66
7.64
7.37
7.36
7.34
7.33
6.33
1.82
1.81
1.80
1.79
1.78
1.77
1.75
0.88
0.87
0.86
0.85
0.84
0.83
0.70
0.69
0.68
0.67
0.67
0.66
1H NMR
CDCl3, 400 MHz
Ph—P—Ph
N
O
S
N
O
O
O
O—S—CF3
1m
S88
1.00
1.02
3.19
12.54
1.03
0.97
1.12
2.10
2.06
f1 (ppm)

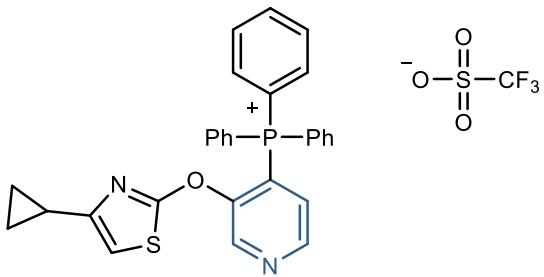

167.27
153.30
151.95
148.01
147.90
144.38
144.34
136.13
136.10
134.28
134.17
131.13
130.99
128.57
128.50
122.61
119.62
119.42
118.77
116.28
115.37
106.73
12.56
7.98
13C NMR
CDCl3, 100 MHz
1m
CDCl3
S89
f1 (ppm)

^{19}F NMR
$CDCl_3$, 365 MHz



1m

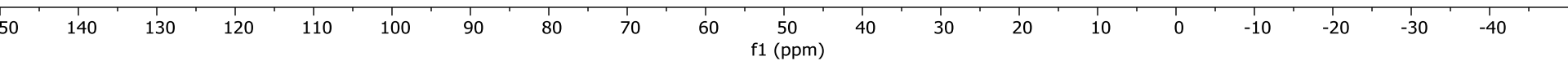
^{31}P NMR
$CDCl_3$, 162 MHz

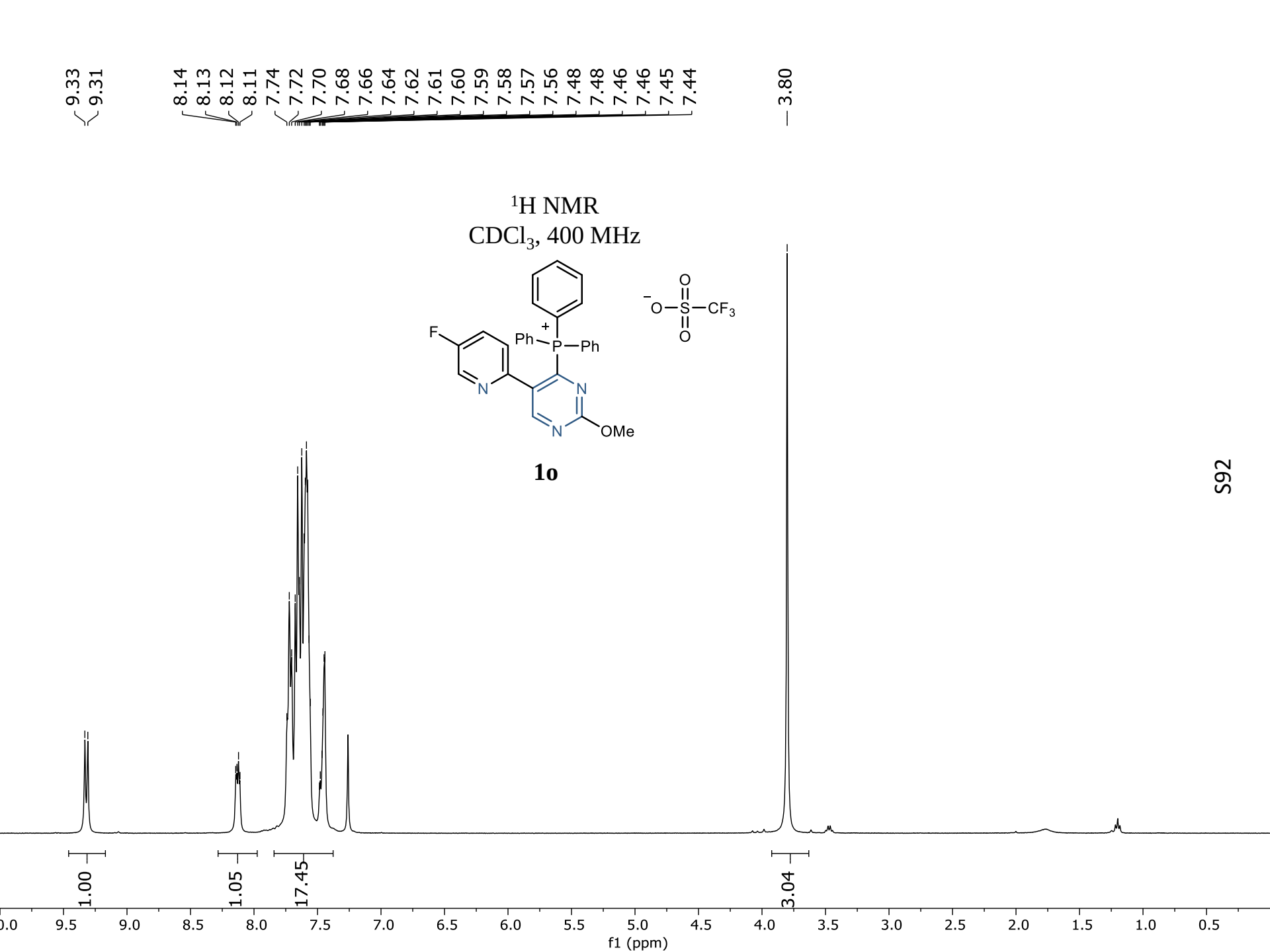


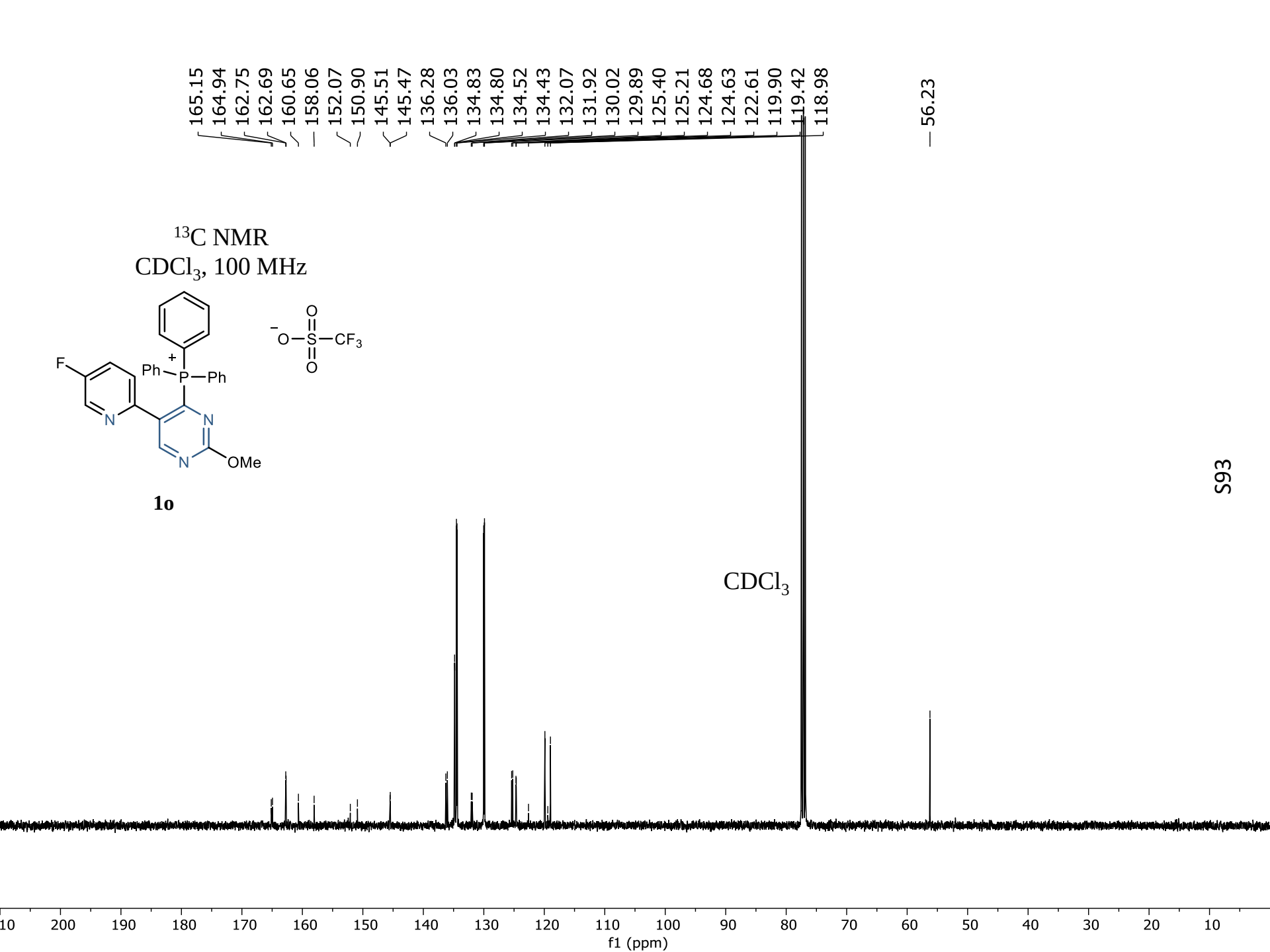
1m

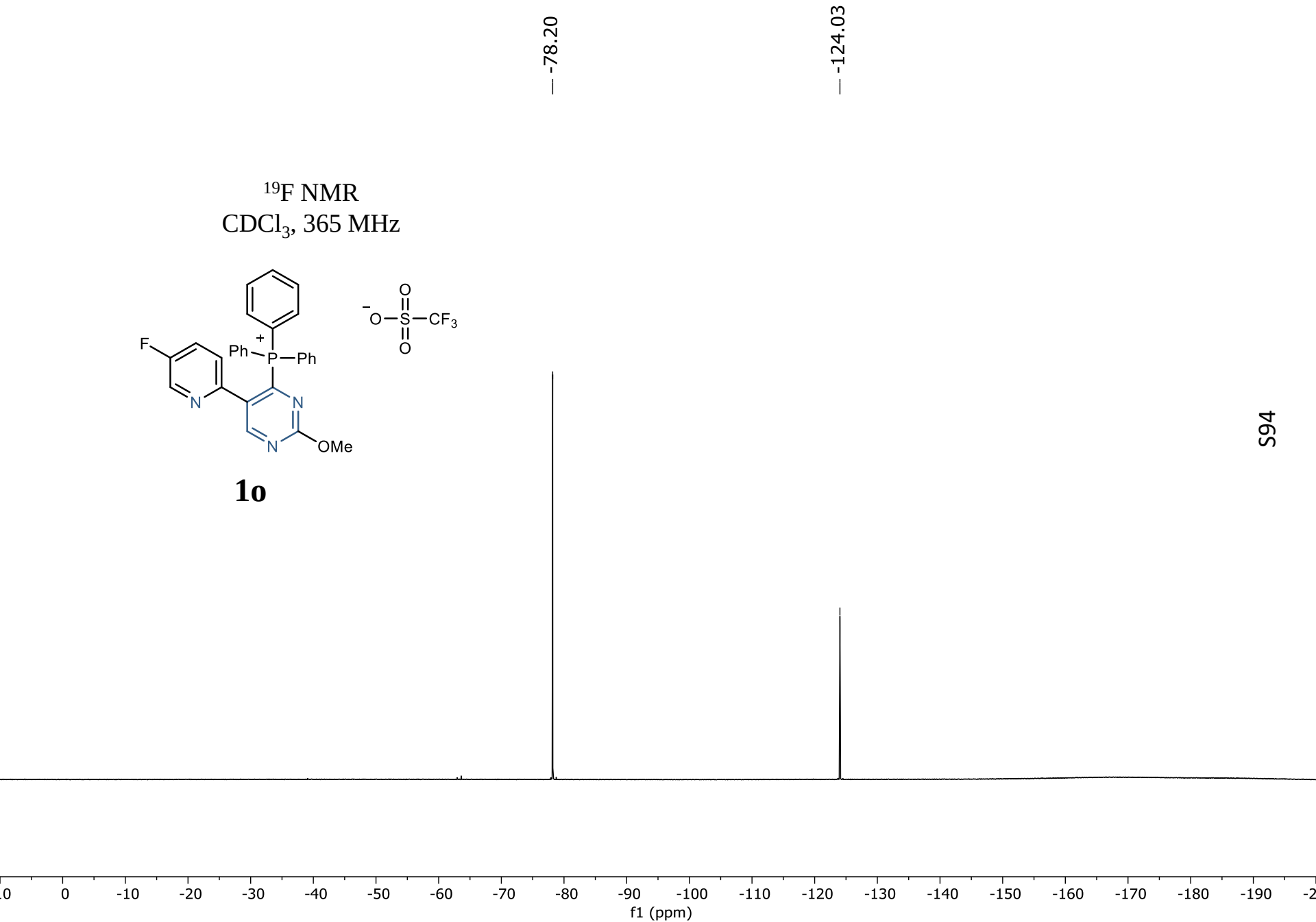
21.12

S91

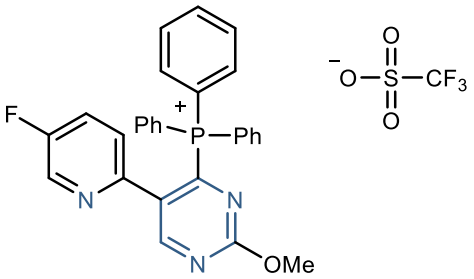



9.33
9.31
8.14
8.13
8.12
8.11
7.74
7.72
7.70
7.68
7.66
7.64
7.62
7.61
7.60
7.59
7.58
7.57
7.56
7.48
7.48
7.46
7.46
7.45
7.44
3.80
1H NMR
CDCl3, 400 MHz
F
Ph
P
Ph
N
N
N
OMe
O
S
CF3
1o
S92
1.00
1.05
17.45
3.04
f1 (ppm)


165.15
164.94
162.75
162.69
160.65
158.06
152.07
150.90
145.51
145.47
136.28
136.03
134.83
134.80
134.52
134.43
132.07
131.92
130.02
129.89
125.40
125.21
124.68
124.63
122.61
119.90
119.42
118.98
56.23
13C NMR
CDCl3, 100 MHz
F
Ph
P
Ph
N
N
N
OMe
O
S
CF3
1o
CDCl3
S93
f1 (ppm)


-78.20
-124.03
19F NMR
CDCl3, 365 MHz
F
Ph
P
Ph
N
N
N
OMe
O
S
CF3
1o
S94
f1 (ppm)

Crude ^{31}P NMR
$CDCl_3$, 162 MHz

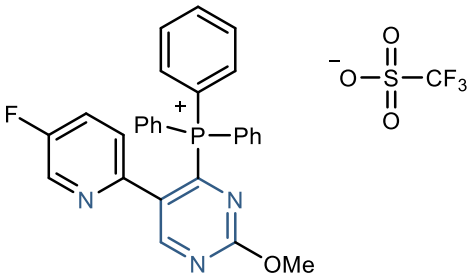


1o

28.93
26.06

f1 (ppm)

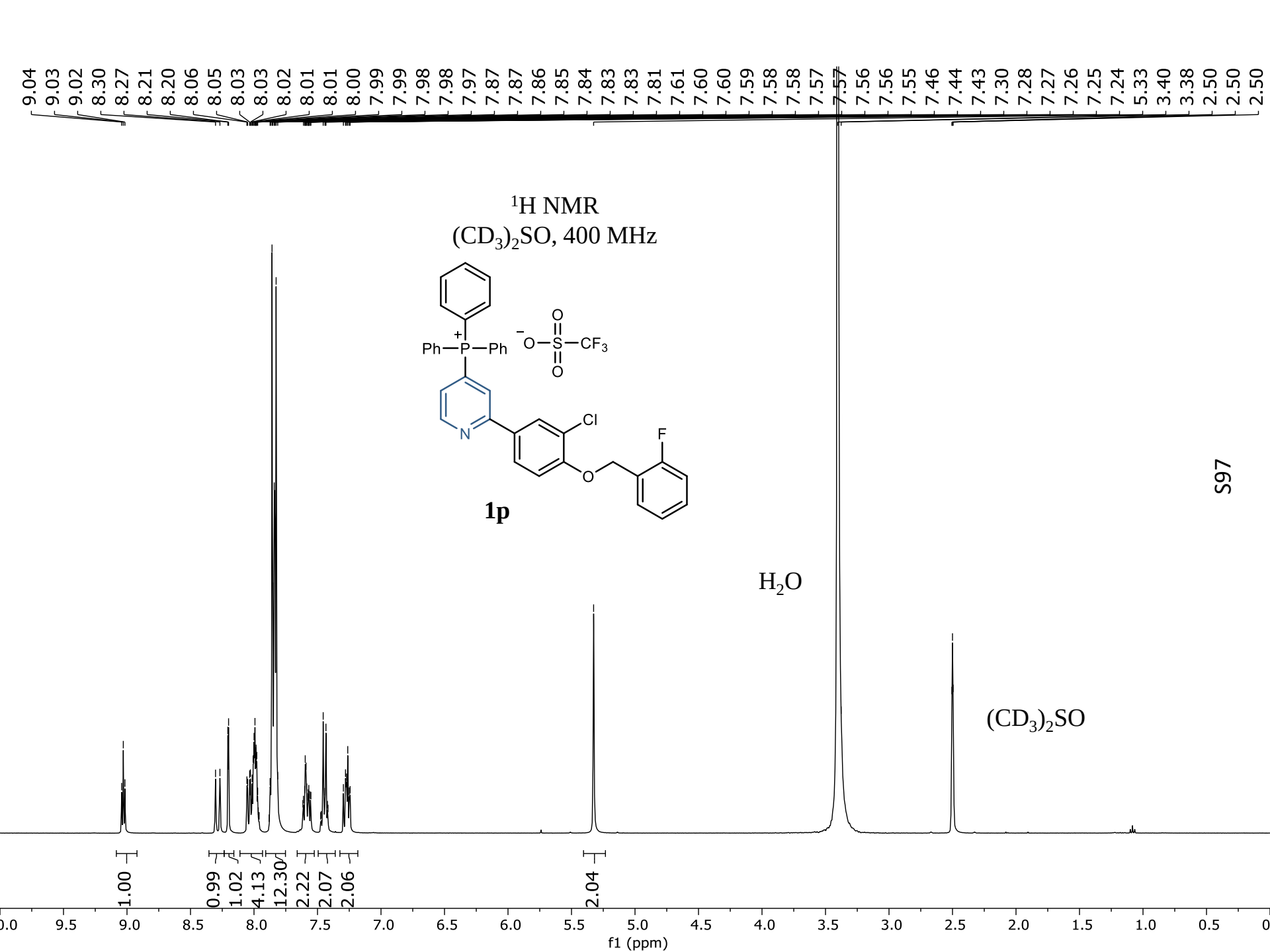
^{31}P NMR
$CDCl_3$, 162 MHz

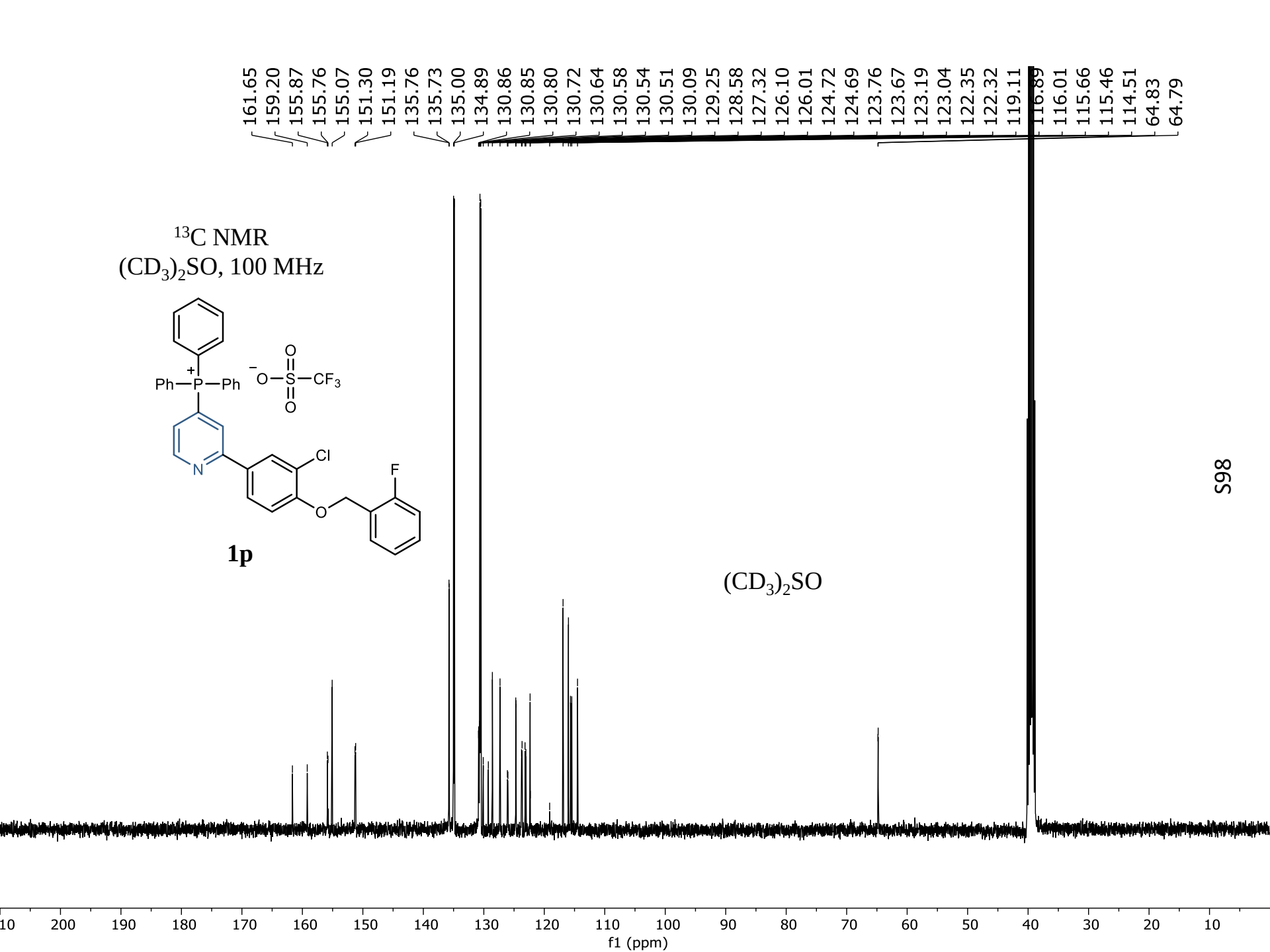


1o

25.76

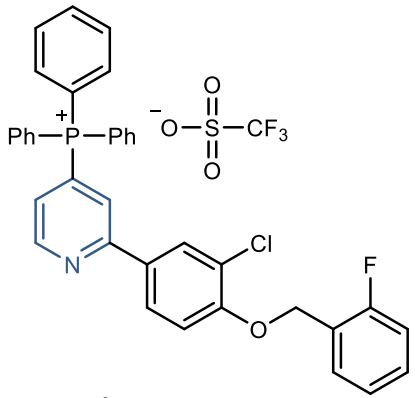
f1 (ppm)


9.04 9.03 9.02 8.30 8.27 8.21 8.20 8.06 8.05 8.03 8.03 8.02 8.01 8.01 8.00 7.99 7.99 7.98 7.98 7.97 7.87 7.87 7.86 7.85 7.84 7.83 7.83 7.81 7.61 7.60 7.60 7.59 7.58 7.58 7.57 7.57 7.56 7.56 7.55 7.46 7.44 7.43 7.30 7.28 7.27 7.26 7.25 7.24 5.33 3.40 3.38 2.50 2.50 2.50
^{1}H NMR
$(CD_3)_2SO$, 400 MHz
Ph—P—Ph
O—S—CF$_3$
Cl
F
N
O
1p
H_2O
$(CD_3)_2SO$
S97
1.00
0.99
1.02
4.13
12.30
2.22
2.07
2.06
2.04
f1 (ppm)


161.65
159.20
155.87
155.76
155.07
151.30
151.19
135.76
135.73
135.00
134.89
130.86
130.85
130.80
130.72
130.64
130.58
130.54
130.51
130.09
129.25
128.58
127.32
126.10
126.01
124.72
124.69
123.76
123.67
123.19
123.04
122.35
122.32
119.11
116.89
116.01
115.66
115.46
114.51
64.83
64.79
^{13}C NMR
$(CD_3)_2SO$, 100 MHz
Ph—P—Ph
O—S—CF3
Cl
F
N
O
1p
$(CD_3)_2SO$
S98
f1 (ppm)


-77.74
-117.95
^{19}F NMR
$(CD_3)_2SO$, 365 MHz
Ph—P—Ph
O—S—CF3
Cl
F
N
O
1p
S99
f1 (ppm)

Crude ^{31}P NMR
$CDCl_3$, 162 MHz



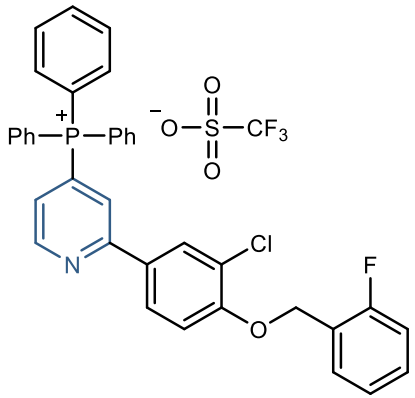
1p

29.01
22.82

S100

f1 (ppm)

^{31}P NMR
$(CD_3)_2SO$, 162 MHz



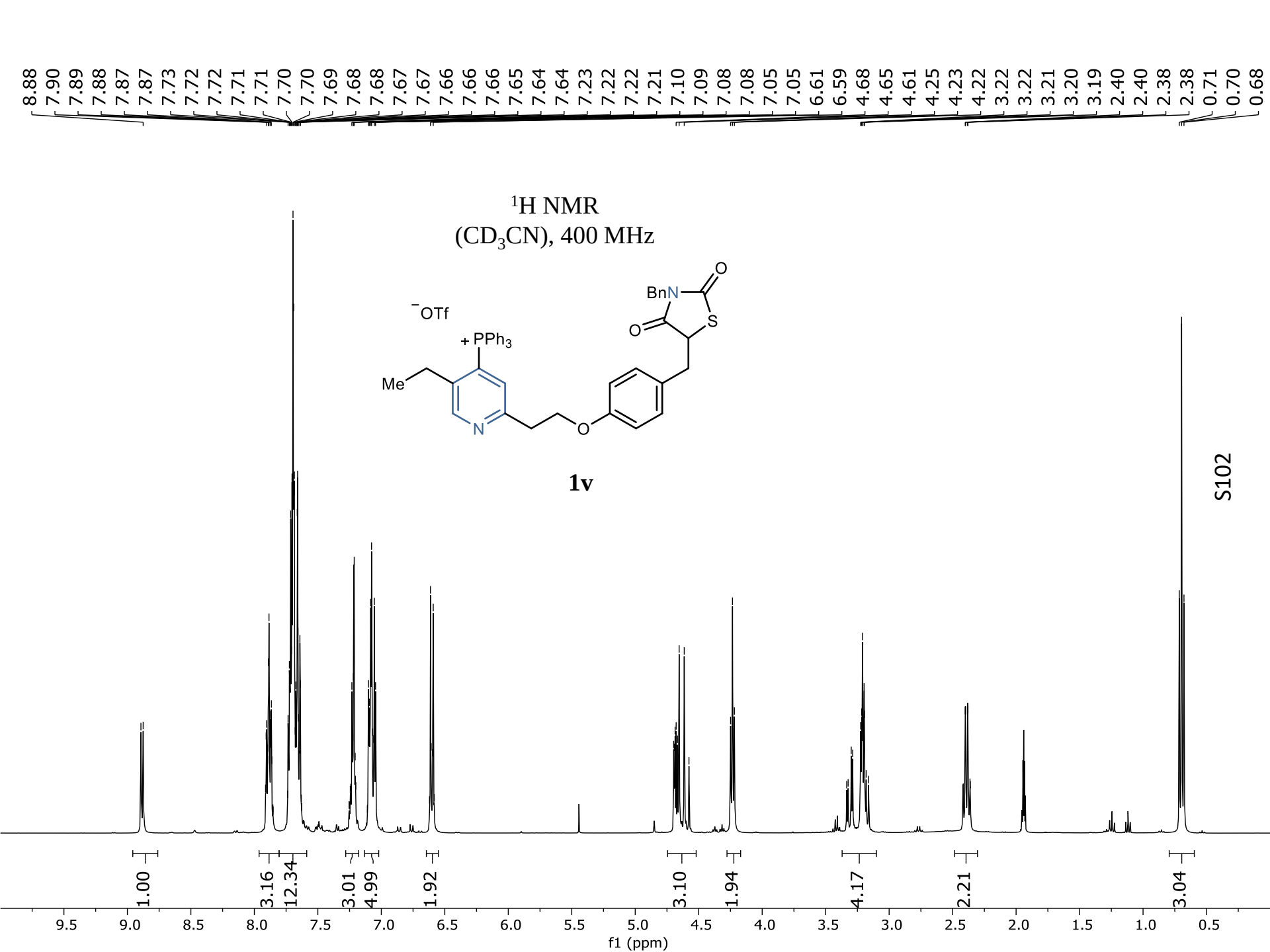
1p

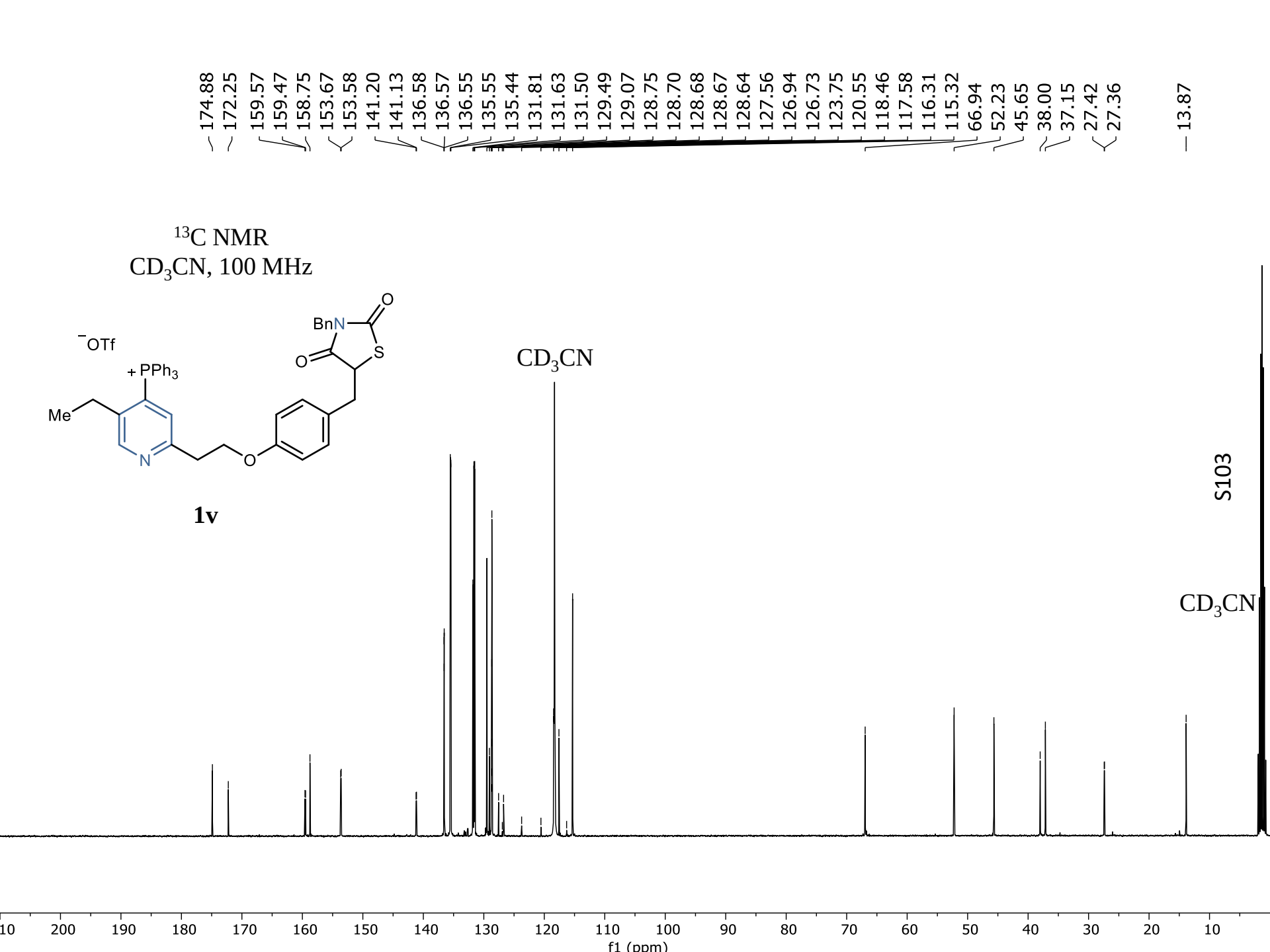
22.08

S101

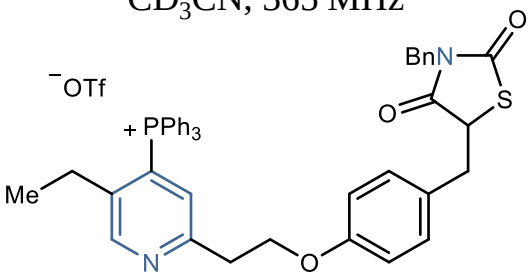
50 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5

f1 (ppm)


8.88 7.90 7.89 7.88 7.87 7.87 7.73 7.72 7.72 7.71 7.71 7.70 7.70 7.69 7.68 7.68 7.67 7.67 7.66 7.66 7.66 7.65 7.64 7.64 7.23 7.22 7.22 7.21 7.10 7.09 7.08 7.08 7.05 7.05 6.61 6.59 4.68 4.65 4.61 4.25 4.23 4.22 3.22 3.22 3.21 3.20 3.19 2.40 2.40 2.38 2.38 0.71 0.70 0.68
1H NMR
(CD3CN), 400 MHz
−OTf
+PPh3
Me
N
O
BnN
O
O
S
1v
S102
1.00 3.16 12.34 3.01 4.99 1.92 3.10 1.94 4.17 2.21 3.04
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
f1 (ppm)


174.88
172.25
159.57
159.47
158.75
153.67
153.58
141.20
141.13
136.58
136.57
136.55
135.55
135.44
131.81
131.63
131.50
129.49
129.07
128.75
128.70
128.68
128.67
128.64
127.56
126.94
126.73
123.75
120.55
118.46
117.58
116.31
115.32
66.94
52.23
45.65
38.00
37.15
27.42
27.36
13.87
13C NMR
CD3CN, 100 MHz
BnN
O
O
S
OTf
+PPh3
Me
N
O
1v
CD3CN
S103
CD3CN
f1 (ppm)

^{19}F NMR
CD_3CN, 365 MHz

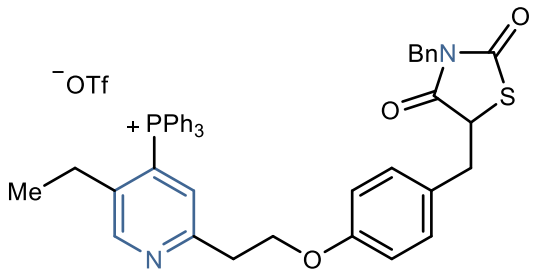


1v

-79.16

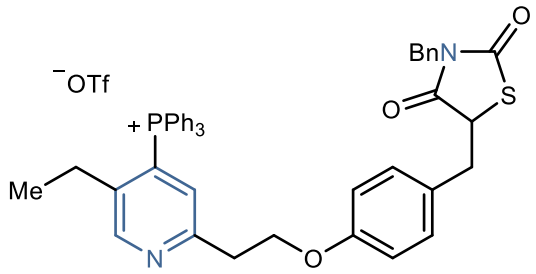
f1 (ppm)

Crude ^{31}P NMR
$CDCl_3$, 162 MHz



1v

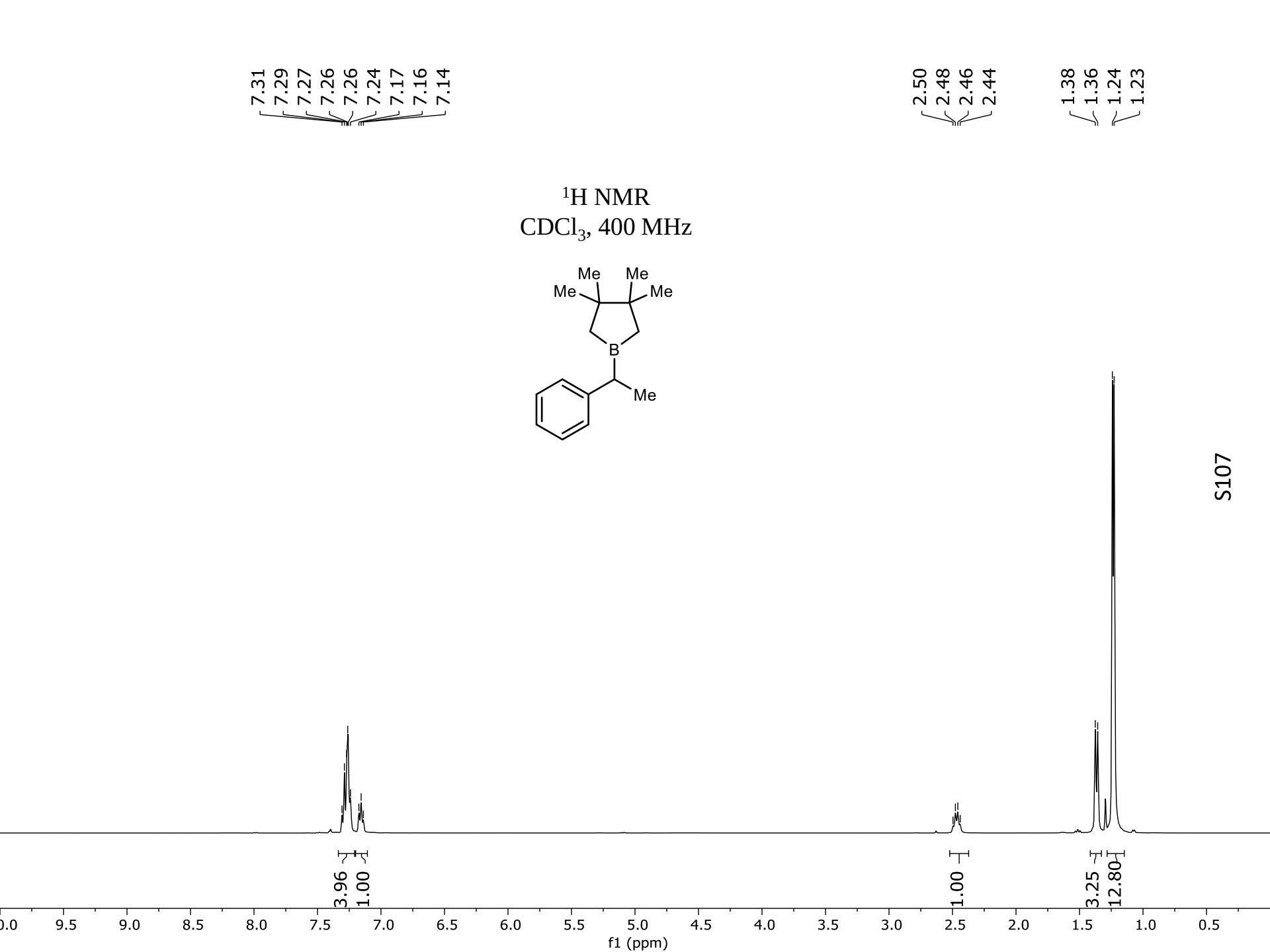
^{31}P NMR
CD_3CN, 162 MHz



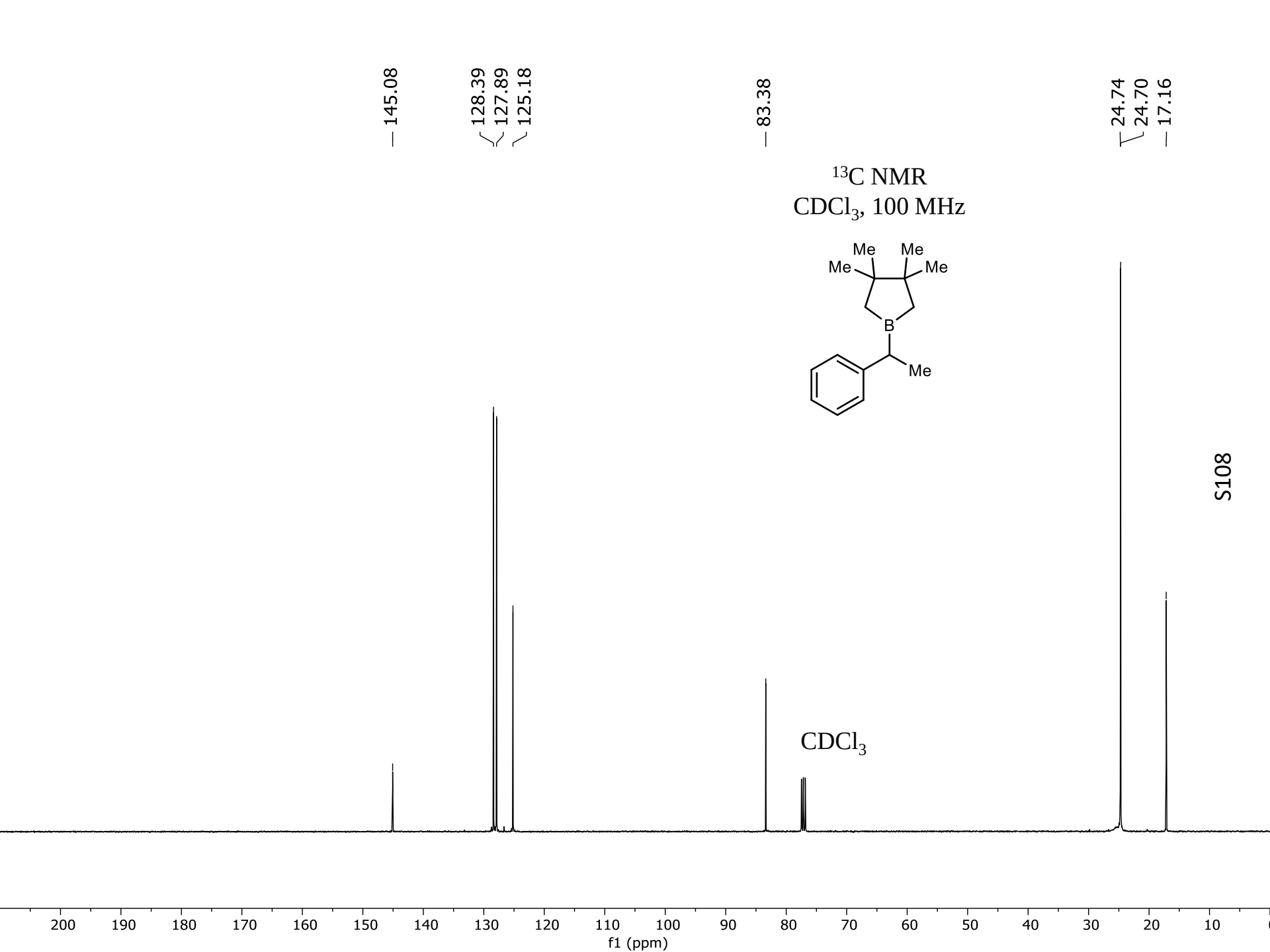
1v

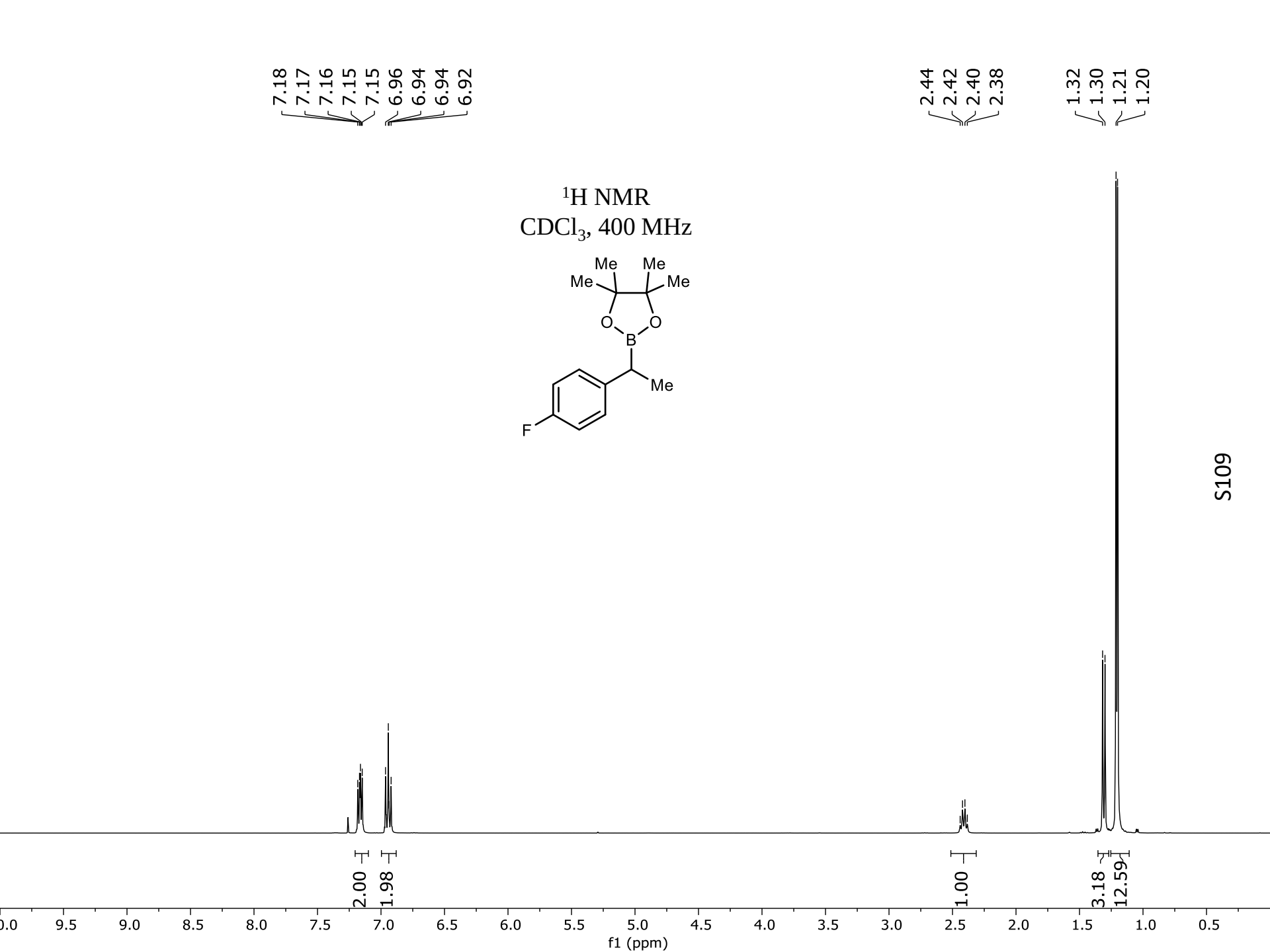
21.48

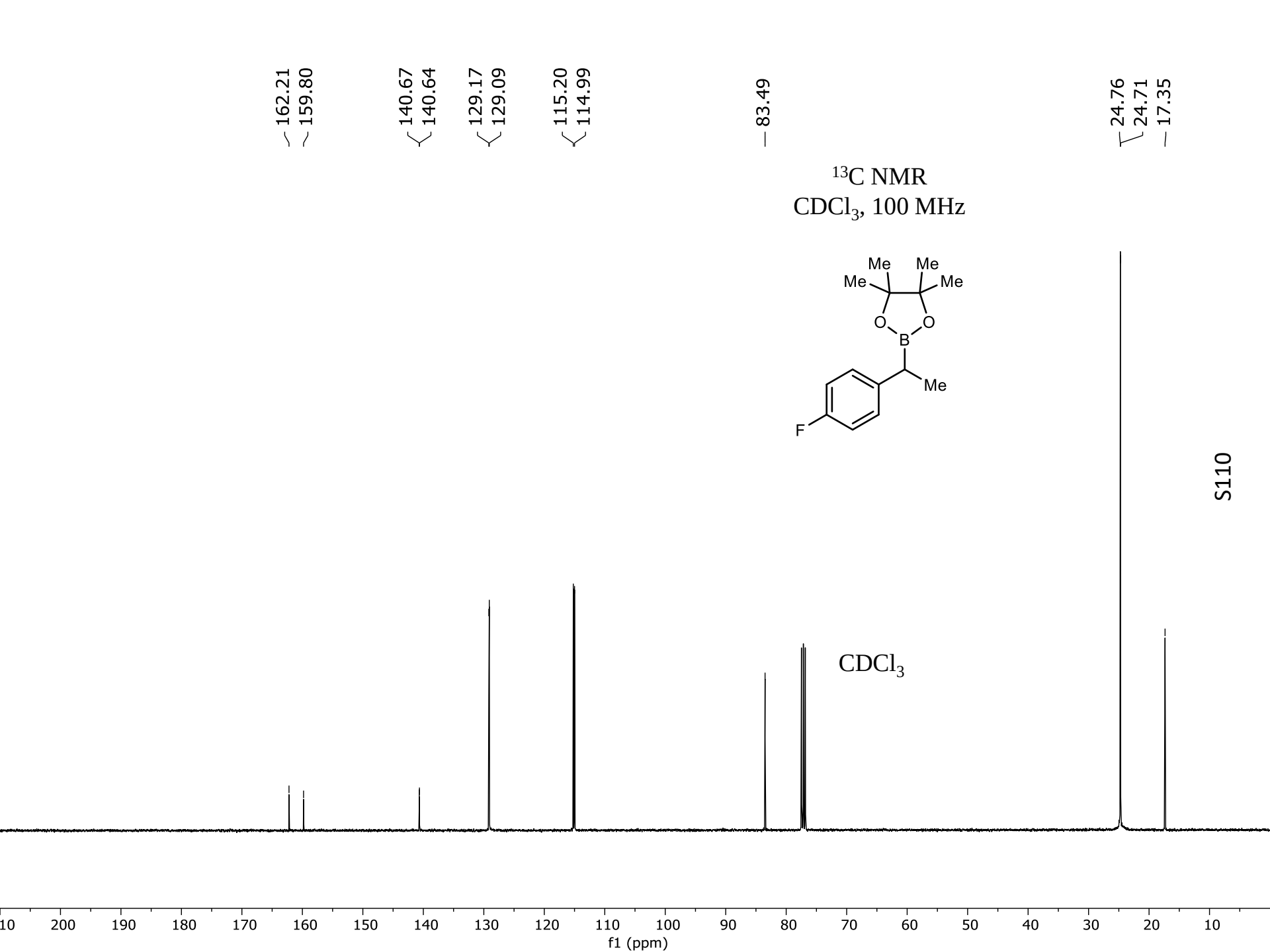
f1 (ppm)

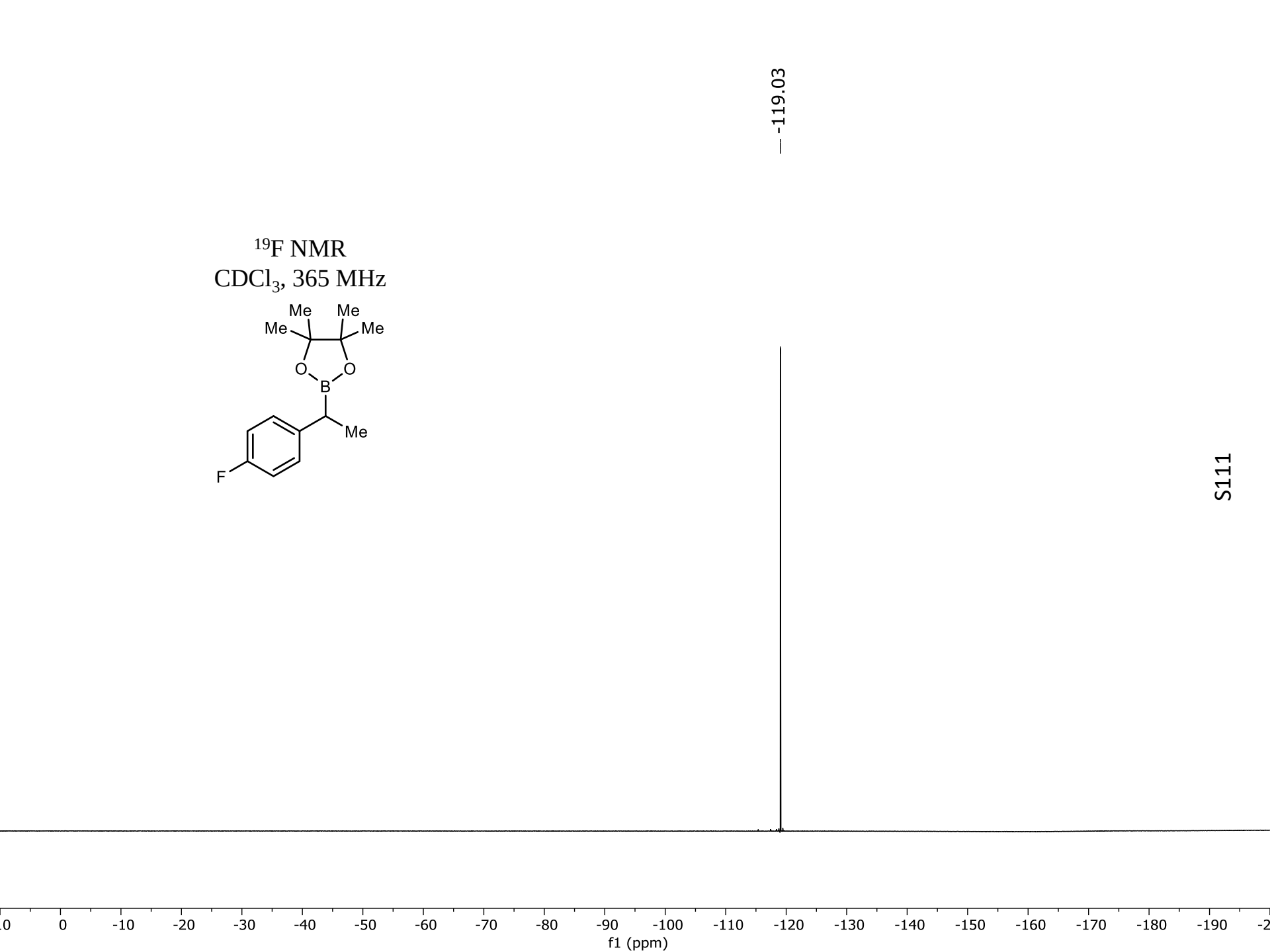


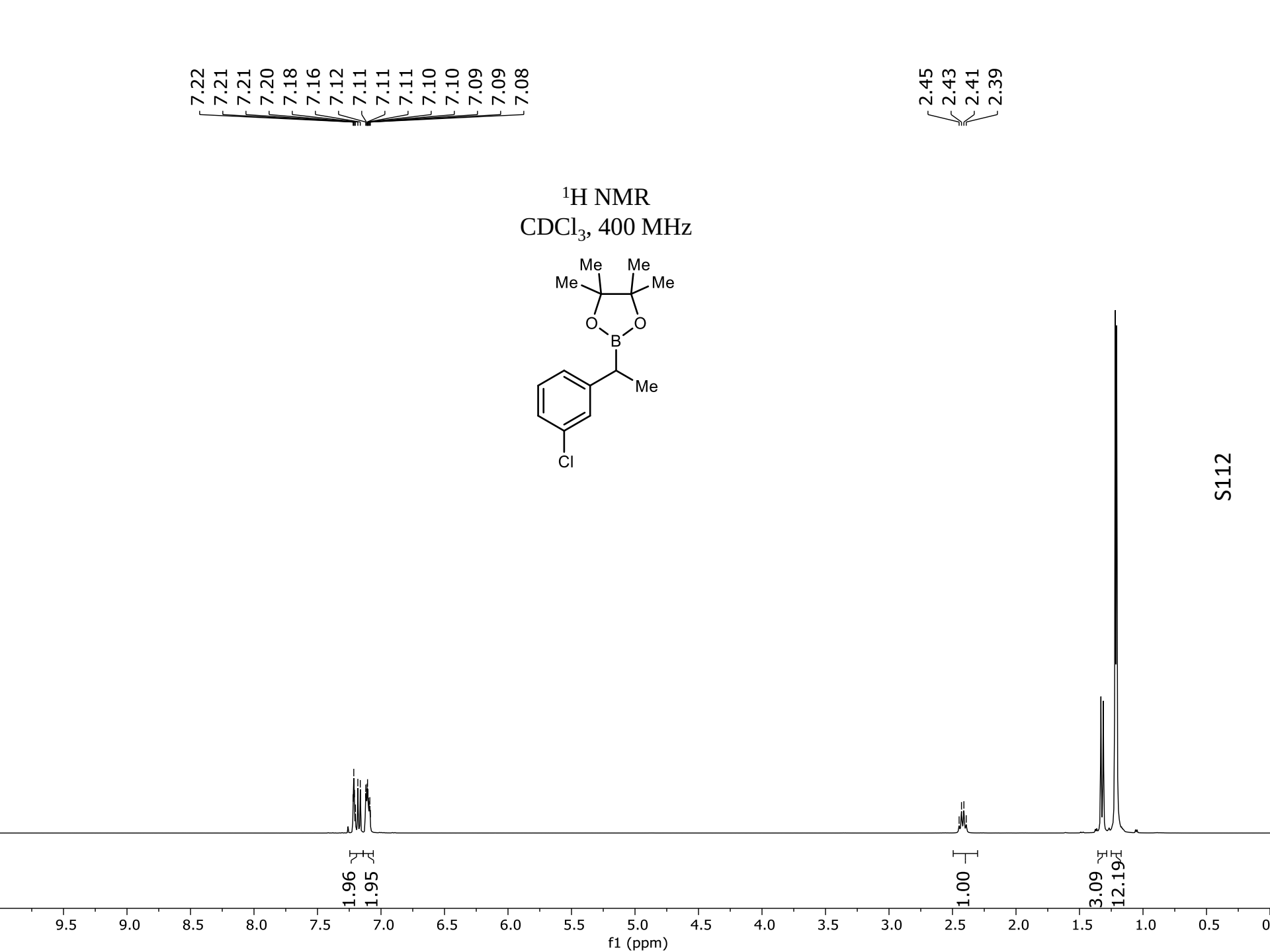
^{1}H NMR
$CDCl_3$, 400 MHz

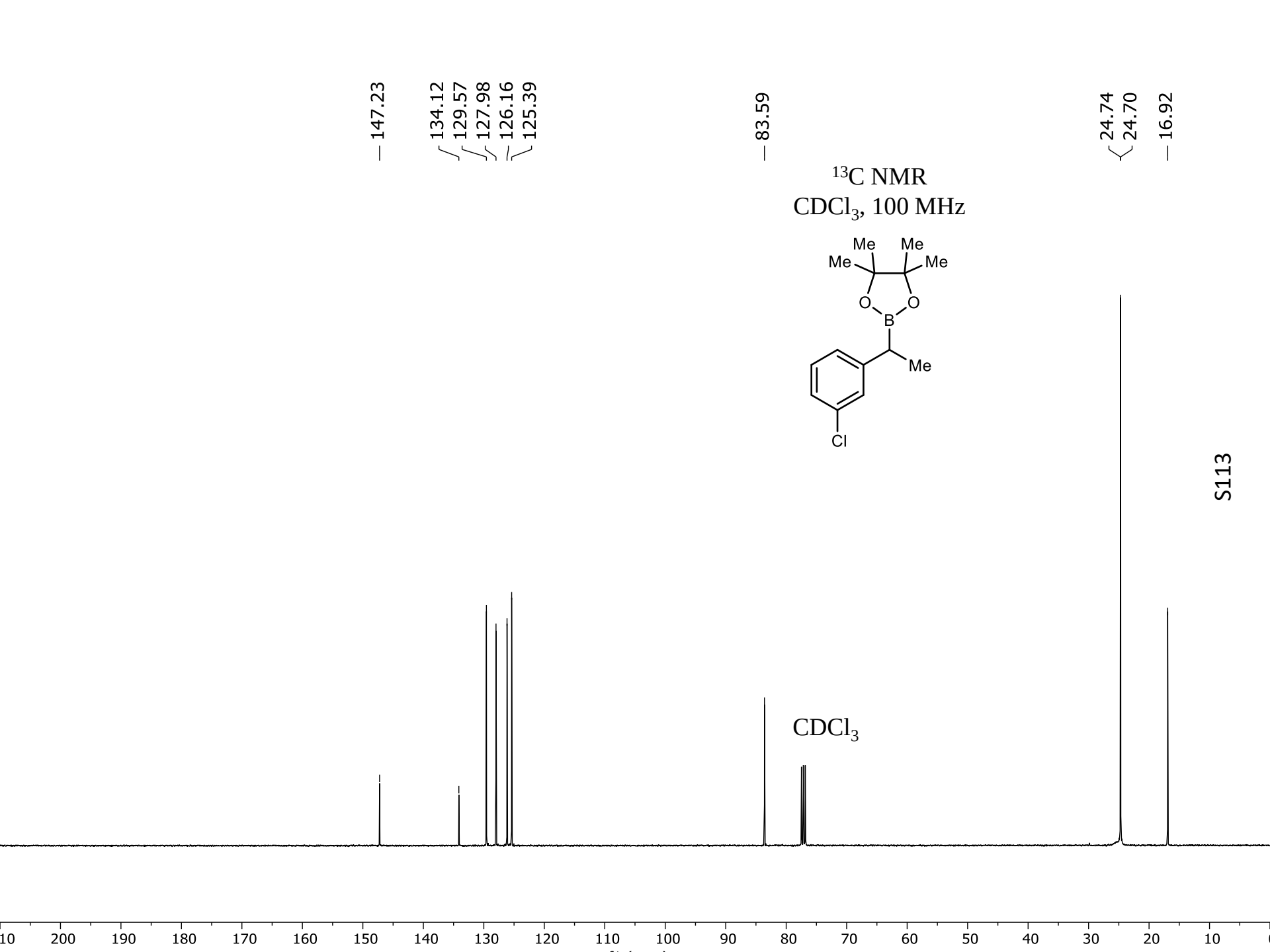

145.08
128.39
127.89
125.18
83.38
24.74
24.70
17.16
^{13}C NMR
$CDCl_3$, 100 MHz
Me
Me
Me
Me
B
Me
$CDCl_3$
S108
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

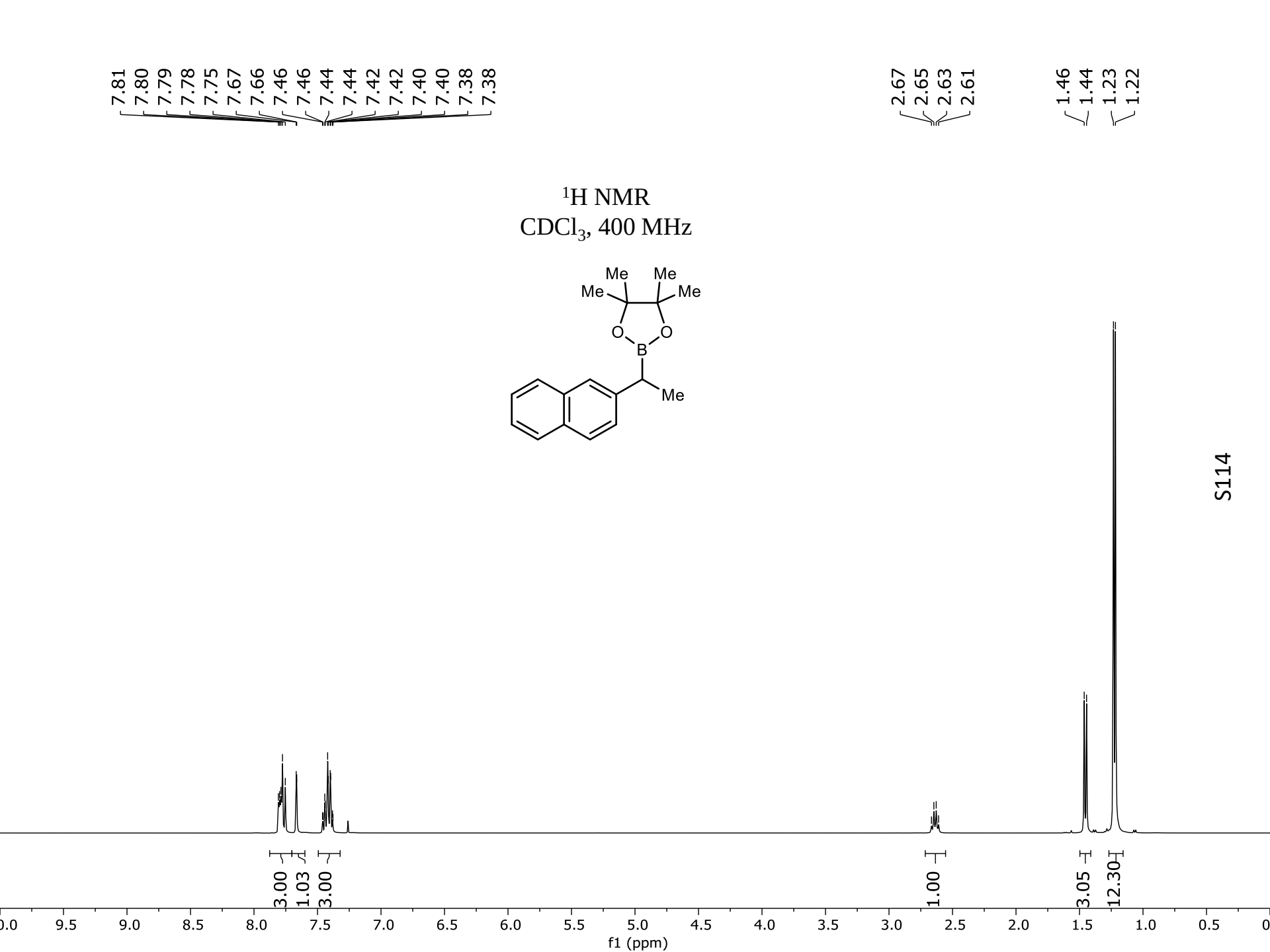

7.18
7.17
7.16
7.15
7.15
6.96
6.94
6.94
6.92
2.44
2.42
2.40
2.38
1.32
1.30
1.21
1.20
1H NMR
CDCl3, 400 MHz
Me
Me
Me
Me
O
O
B
Me
F
S109
2.00
1.98
1.00
3.18
12.59
f1 (ppm)

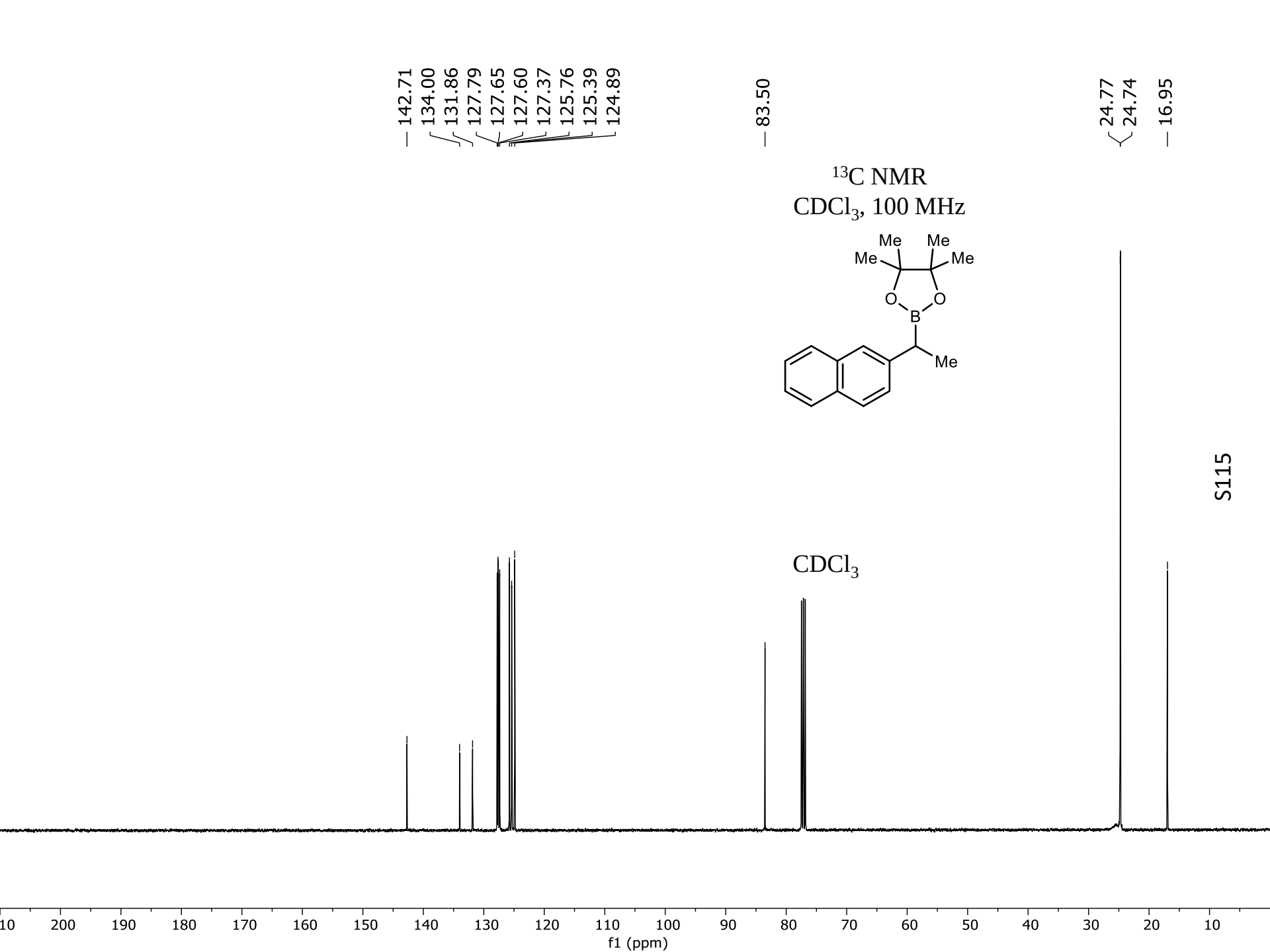

162.21
159.80
140.67
140.64
129.17
129.09
115.20
114.99
83.49
24.76
24.71
17.35
13C NMR
CDCl3, 100 MHz
Me
Me
Me
Me
O
O
B
Me
F
CDCl3
S110
f1 (ppm)

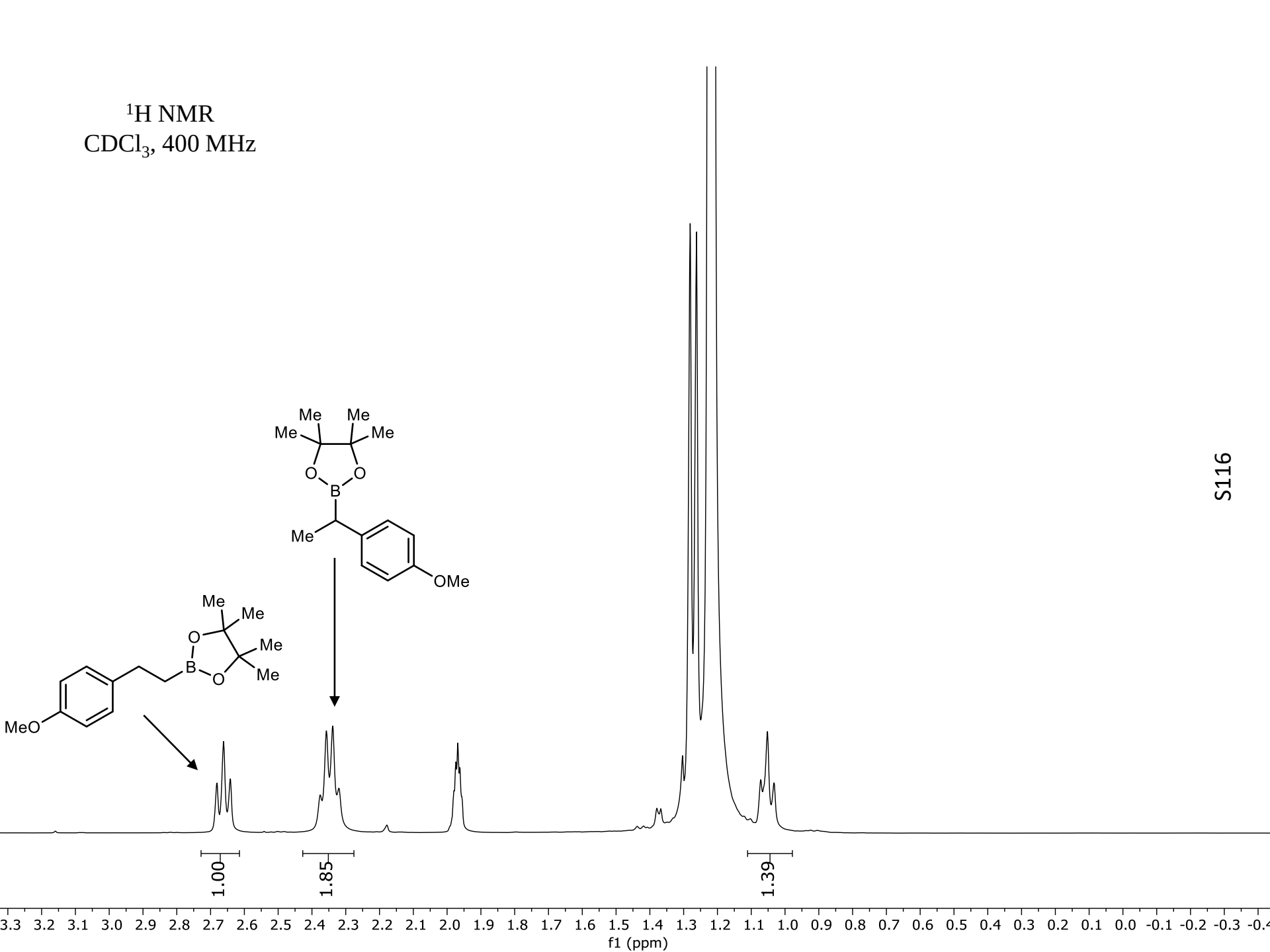

-119.03
^{19}F NMR
$CDCl_3$, 365 MHz
Me
Me
Me
Me
O
O
B
Me
F
S111
f1 (ppm)


7.22
7.21
7.21
7.20
7.18
7.16
7.12
7.11
7.11
7.11
7.10
7.10
7.09
7.09
7.08
2.45
2.43
2.41
2.39
1H NMR
CDCl3, 400 MHz
Me
Me
Me
Me
O
O
B
Me
Cl
S112
1.96
1.95
1.00
3.09
12.19
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
f1 (ppm)

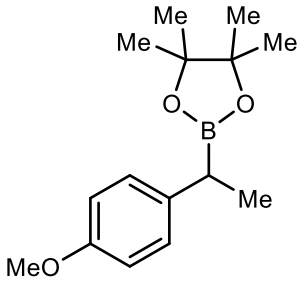

147.23
134.12
129.57
127.98
126.16
125.39
83.59
24.74
24.70
16.92
13C NMR
CDCl3, 100 MHz
Me
Me
Me
Me
O
O
B
Me
Cl
CDCl3
S113
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

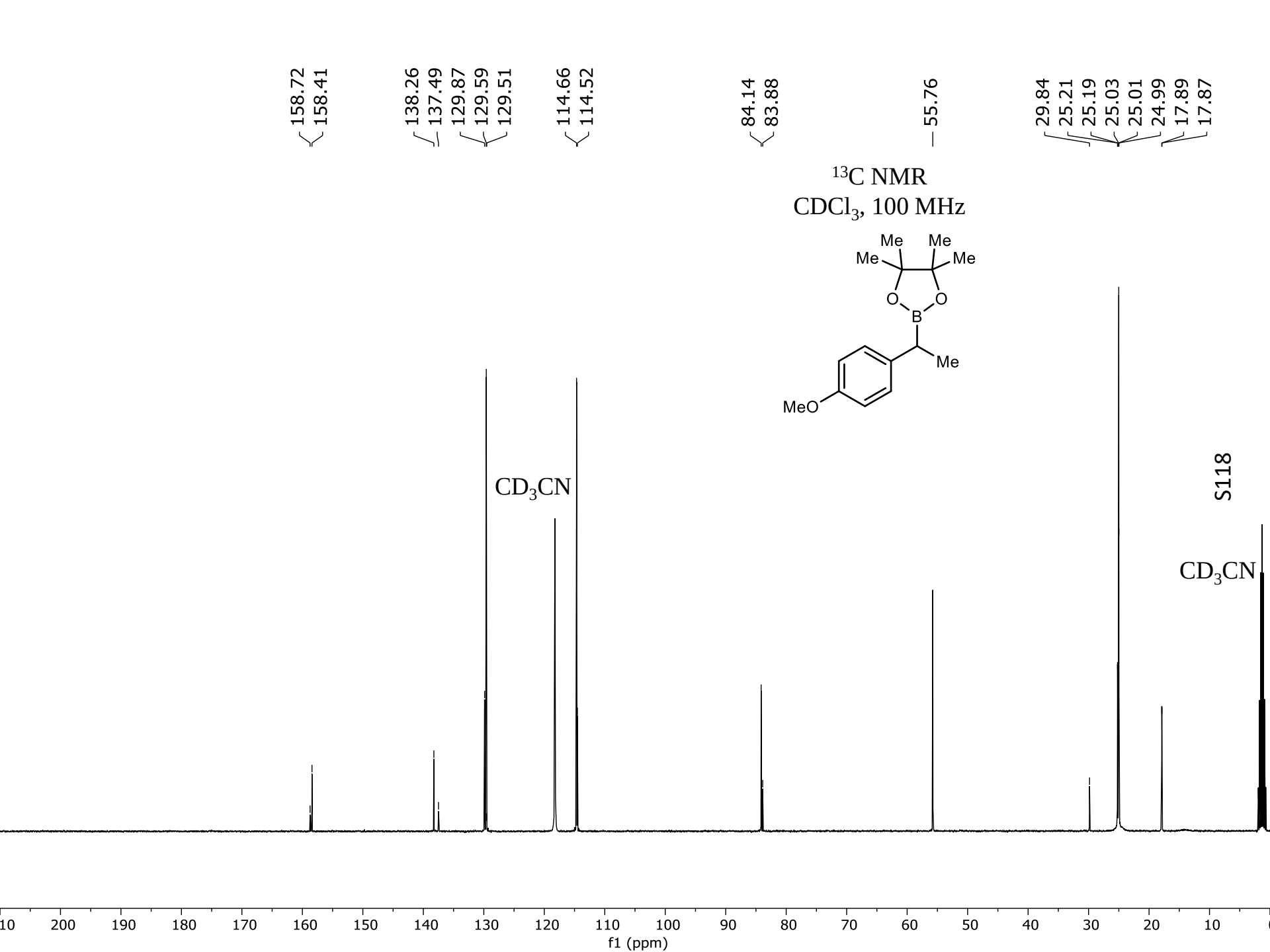

7.81
7.80
7.79
7.78
7.75
7.67
7.66
7.46
7.46
7.44
7.44
7.42
7.42
7.40
7.40
7.38
7.38
2.67
2.65
2.63
2.61
1.46
1.44
1.23
1.22
^{1}H NMR
$CDCl_3$, 400 MHz
Me
Me
Me
Me
O
O
B
Me
S114
3.00
1.03
3.00
1.00
3.05
12.30
f1 (ppm)

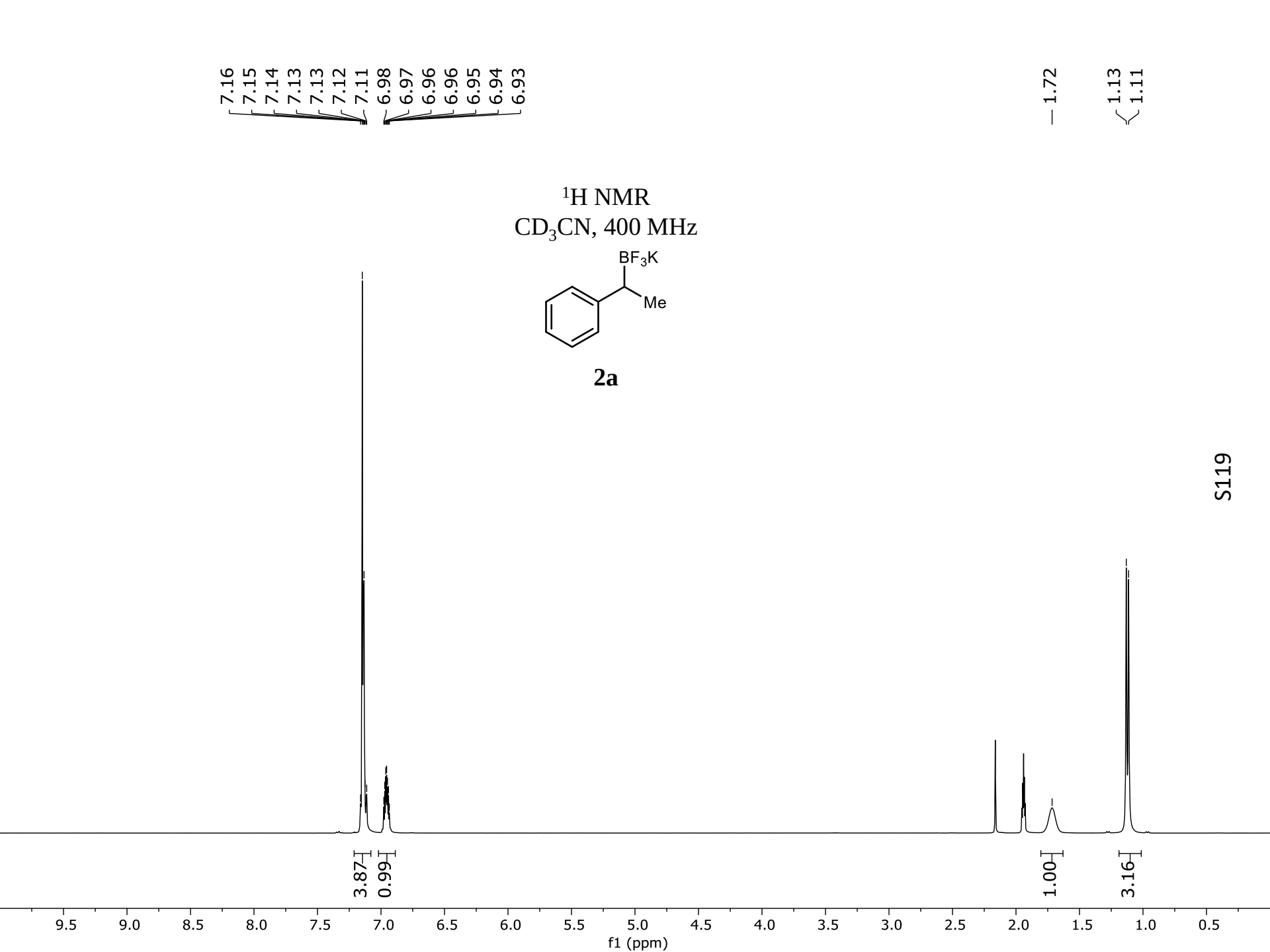

142.71
134.00
131.86
127.79
127.65
127.60
127.37
125.76
125.39
124.89
83.50
24.77
24.74
16.95
13C NMR
CDCl3, 100 MHz
Me
Me
Me
Me
O
O
B
Me
CDCl3
S115
f1 (ppm)

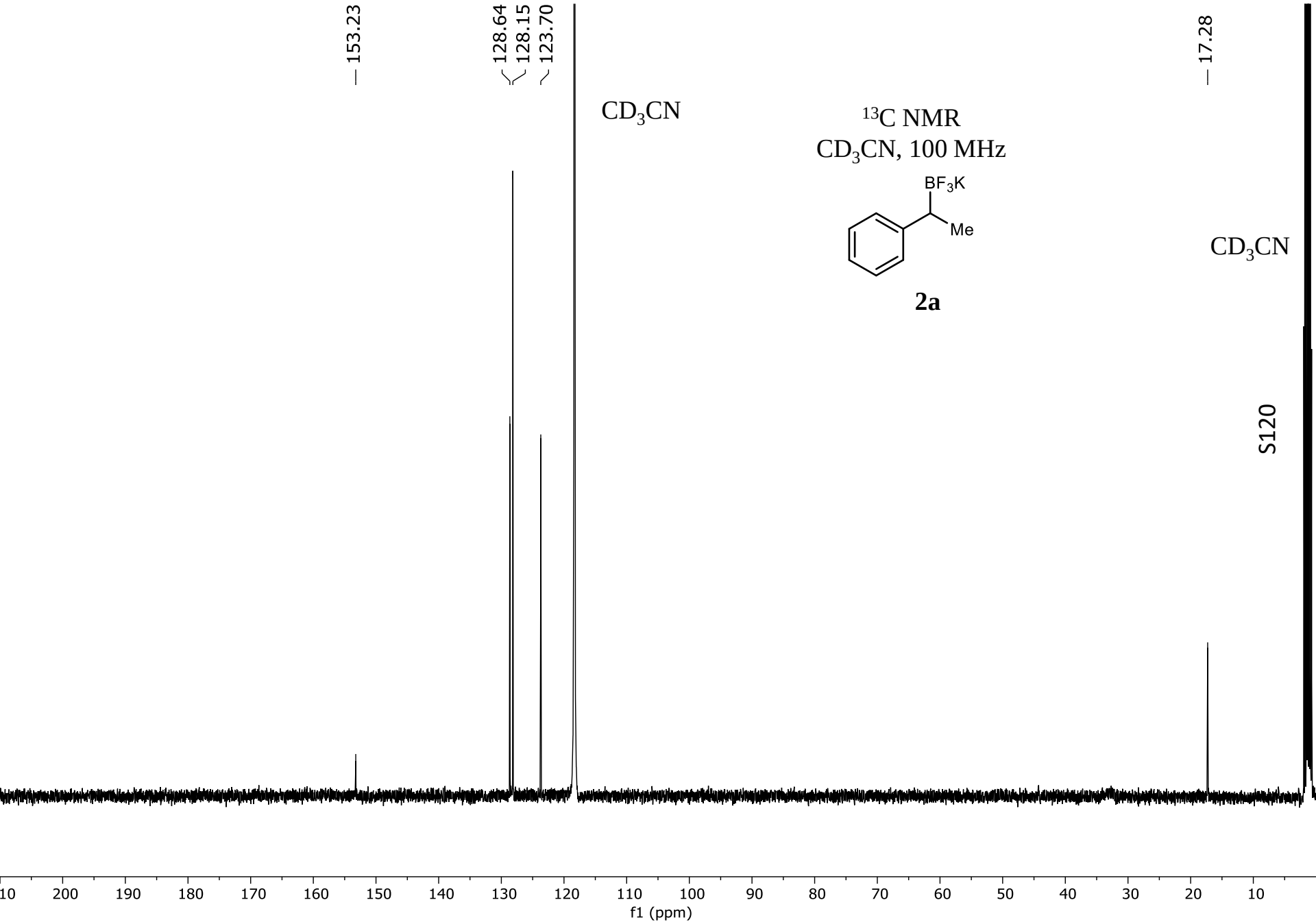

1H NMR
CDCl3, 400 MHz
Me
Me
Me
Me
O
O
B
Me
OMe
Me
Me
Me
Me
O
B
O
MeO
1.00
1.85
1.39
3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1 -0.2 -0.3 -0.4
f1 (ppm)

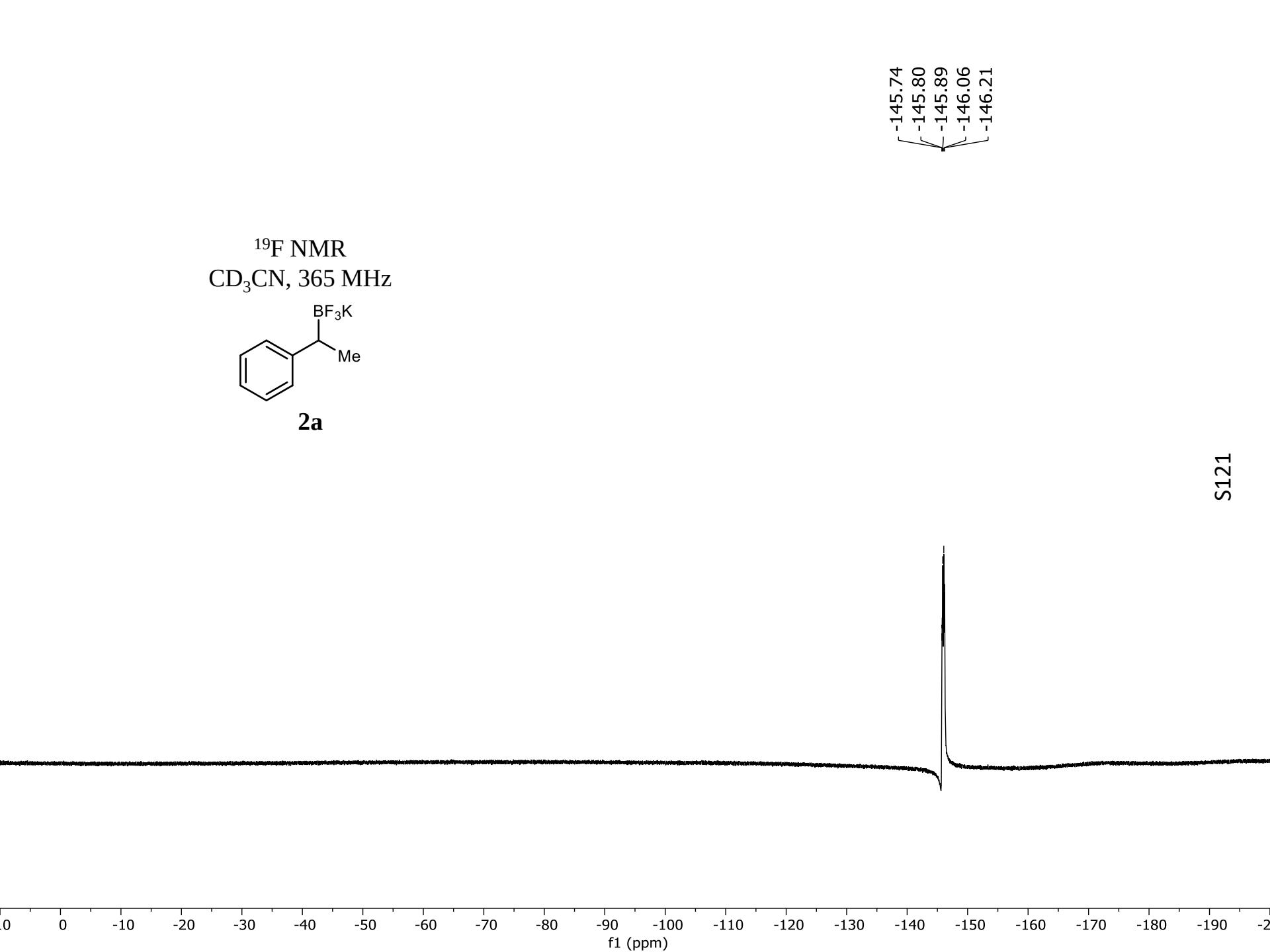
^{1}H NMR
$CDCl_3$, 400 MHz

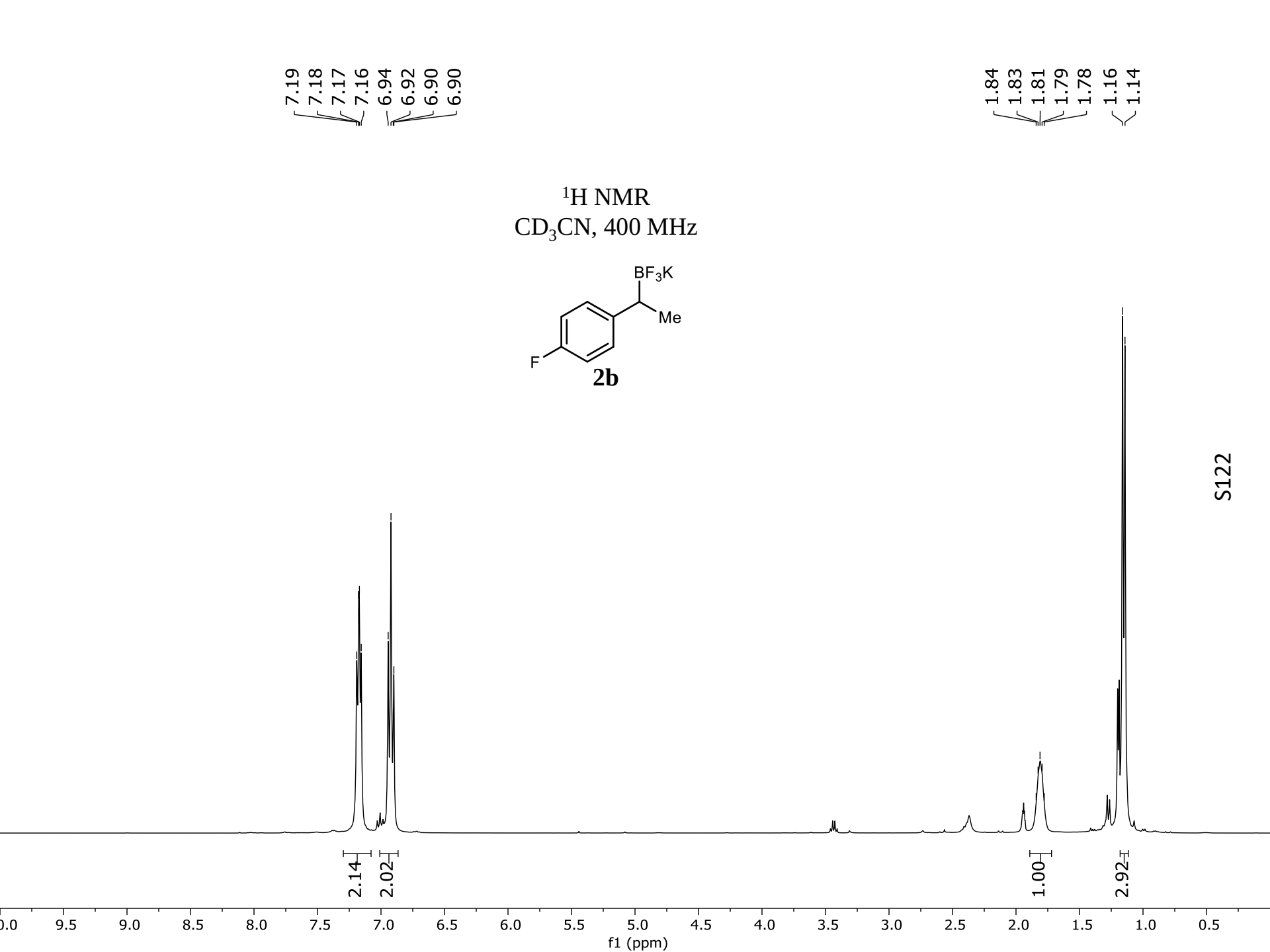


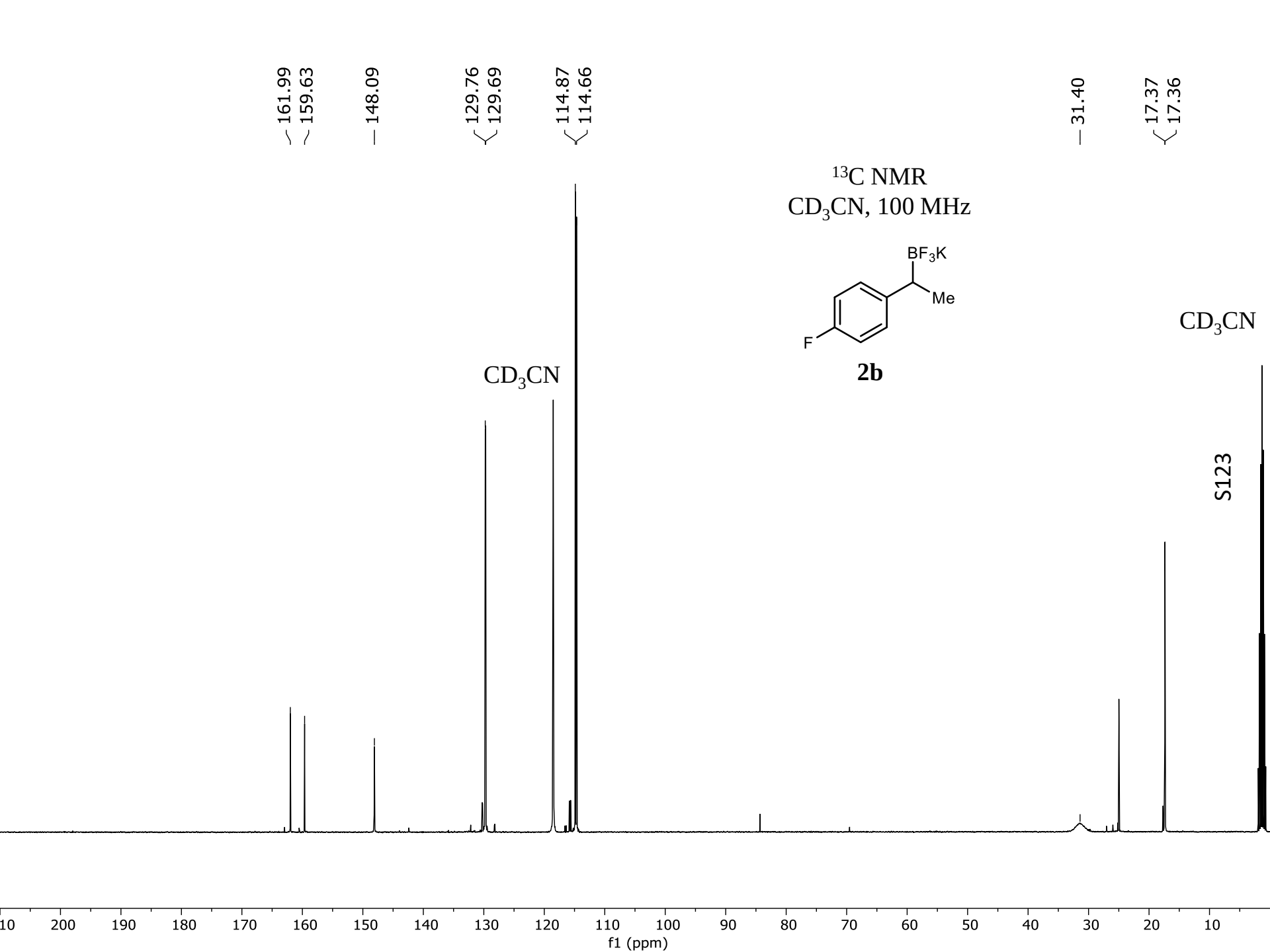

158.72
158.41
138.26
137.49
129.87
129.59
129.51
114.66
114.52
84.14
83.88
55.76
29.84
25.21
25.19
25.03
25.01
24.99
17.89
17.87
13C NMR
CDCl3, 100 MHz
Me
Me
Me
Me
O
O
B
Me
MeO
CD3CN
CD3CN
S118
f1 (ppm)

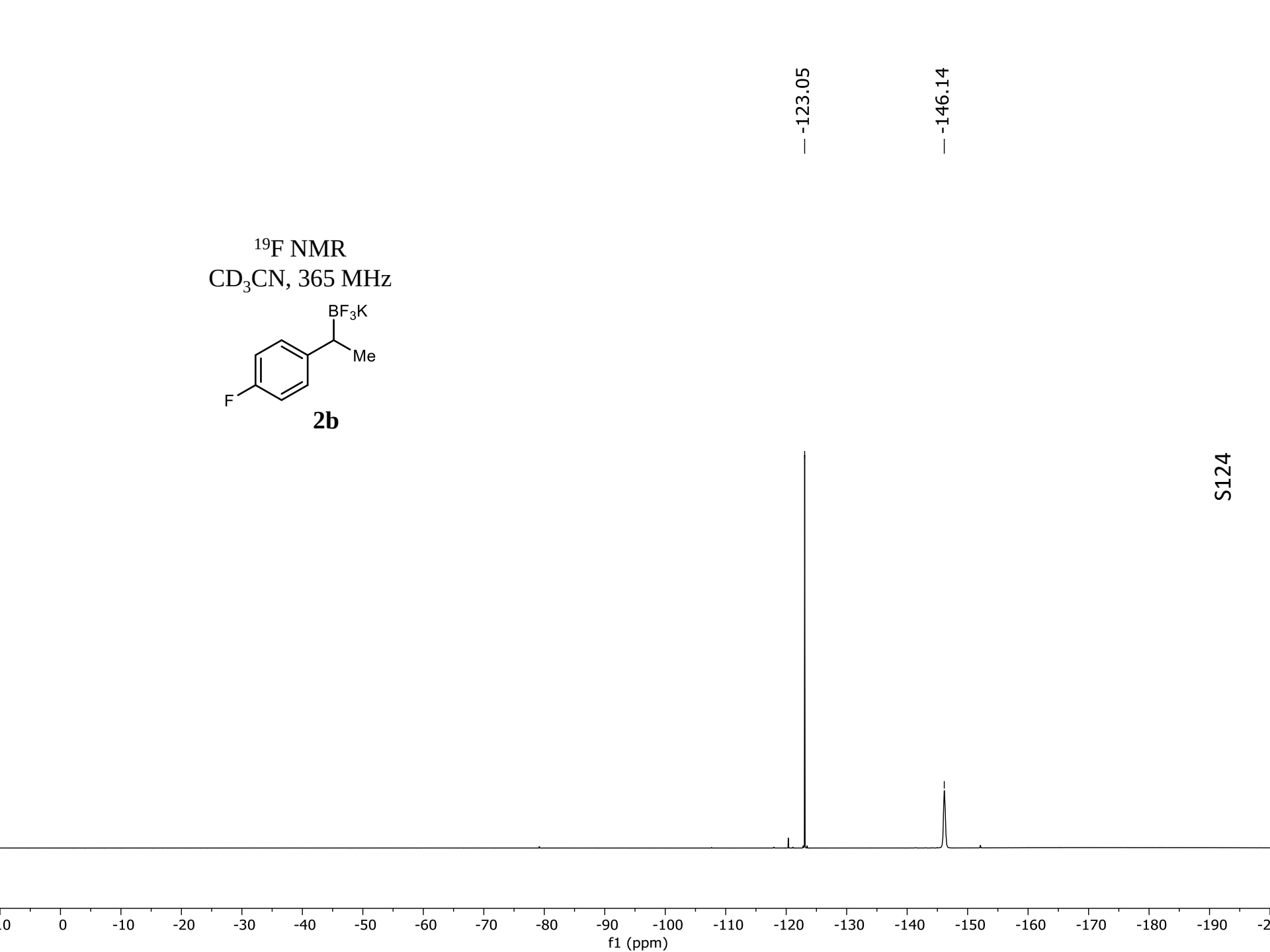

7.16
7.15
7.14
7.13
7.13
7.12
7.11
6.98
6.97
6.96
6.96
6.95
6.94
6.93
1.72
1.13
1.11
^{1}H NMR
CD_3CN, 400 MHz
BF_3K
Me
2a
S119
3.87
0.99
1.00
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

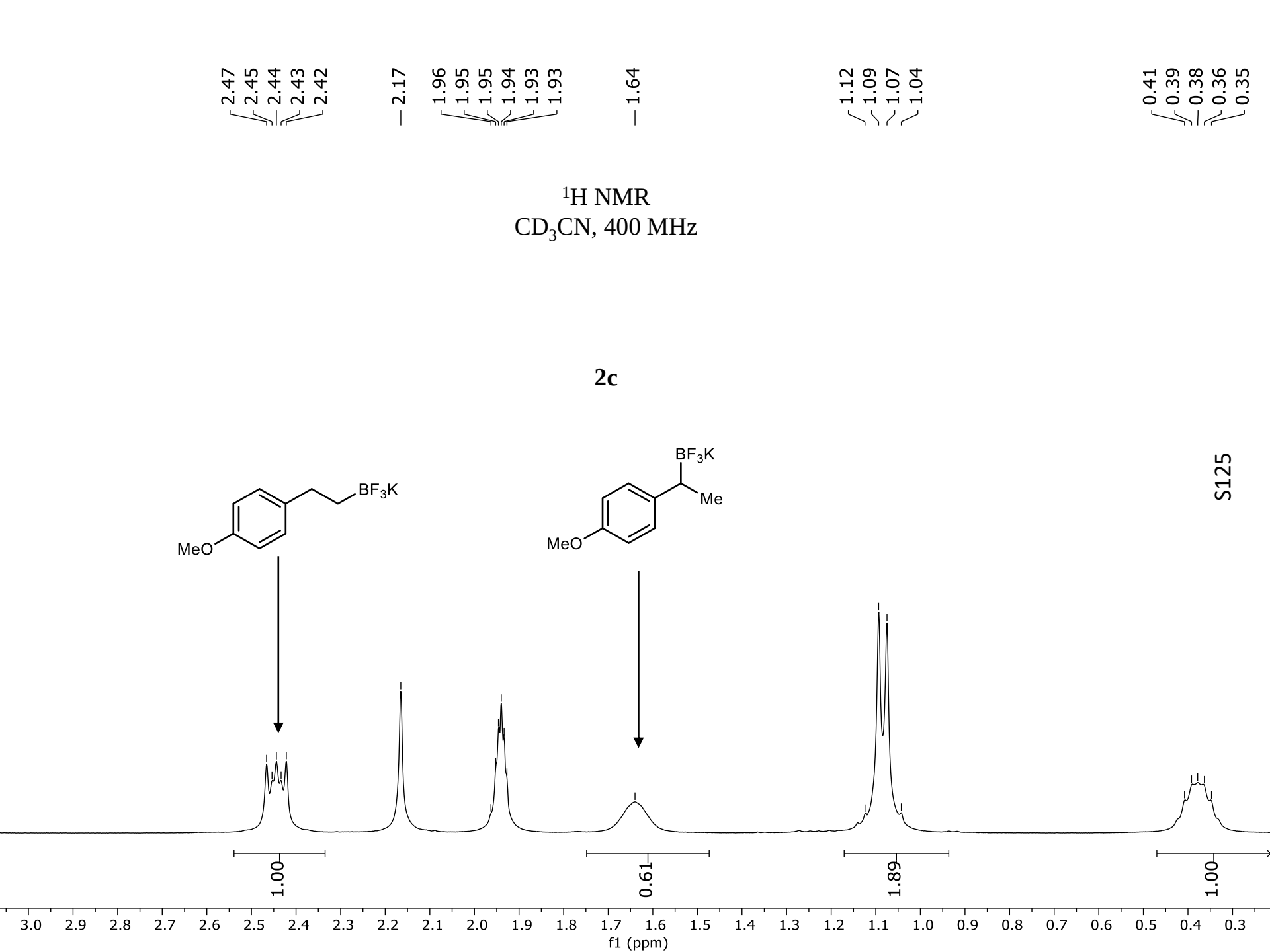

153.23
128.64
128.15
123.70
CD3CN
17.28
13C NMR
CD3CN, 100 MHz
BF3K
Me
2a
CD3CN
S120
f1 (ppm)


-145.74
-145.80
-145.89
-146.06
-146.21
^{19}F NMR
CD_3CN, 365 MHz
BF_3K
Me
2a
S121
f1 (ppm)


7.19
7.18
7.17
7.16
6.94
6.92
6.90
6.90
1.84
1.83
1.81
1.79
1.78
1.16
1.14
^{1}H NMR
CD_3CN, 400 MHz
BF_3K
Me
F
2b
S122
2.14
2.02
1.00
2.92
f1 (ppm)

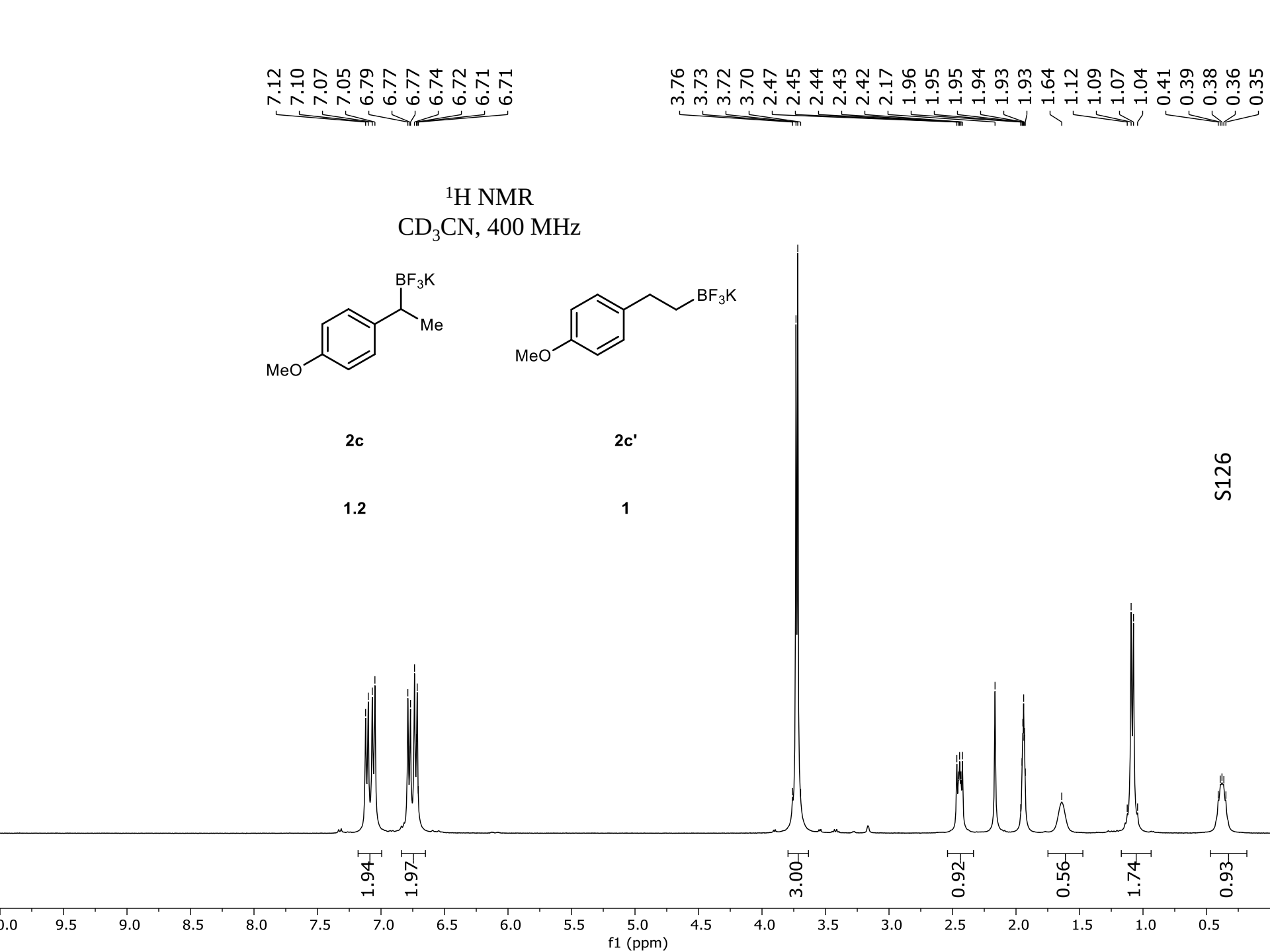

161.99
159.63
148.09
129.76
129.69
114.87
114.66
31.40
17.37
17.36
13C NMR
CD3CN, 100 MHz
BF3K
Me
F
2b
CD3CN
CD3CN
S123
f1 (ppm)

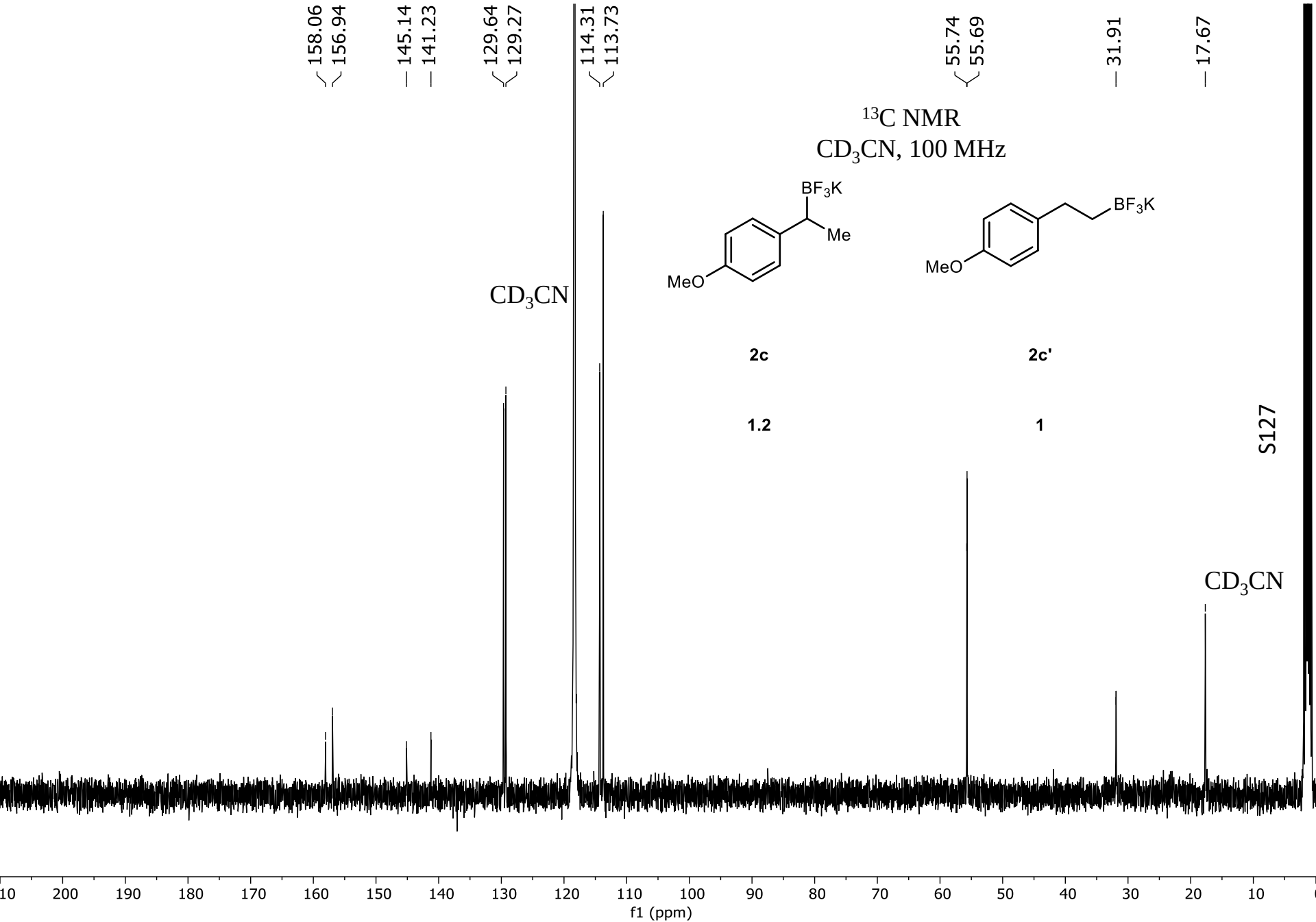

-123.05
-146.14
^{19}F NMR
CD_3CN, 365 MHz
BF_3K
Me
F
2b
S124
f1 (ppm)



^{1}H NMR
CD_3CN, 400 MHz

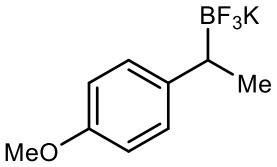
2c


7.12
7.10
7.07
7.05
6.79
6.77
6.77
6.74
6.72
6.71
6.71
3.76
3.73
3.72
3.70
2.47
2.45
2.44
2.43
2.42
2.17
1.96
1.95
1.95
1.94
1.93
1.93
1.64
1.12
1.09
1.07
1.04
0.41
0.39
0.38
0.36
0.35
1H NMR
CD3CN, 400 MHz
BF3K
Me
MeO
BF3K
MeO
2c
2c'
1.2
1
S126
1.94
1.97
3.00
0.92
0.56
1.74
0.93
f1 (ppm)


158.06
156.94
145.14
141.23
129.64
129.27
114.31
113.73
55.74
55.69
31.91
17.67
^{13}C NMR
CD_3CN, 100 MHz
BF_3K
Me
MeO
CD_3CN
2c
1.2
BF_3K
MeO
2c'
1
CD_3CN
S127
f1 (ppm)

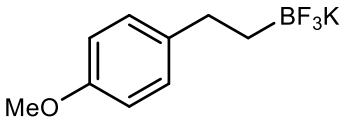
-141.26
-145.87
-146.09
-146.22

^{19}F NMR
CD_3CN, 365 MHz



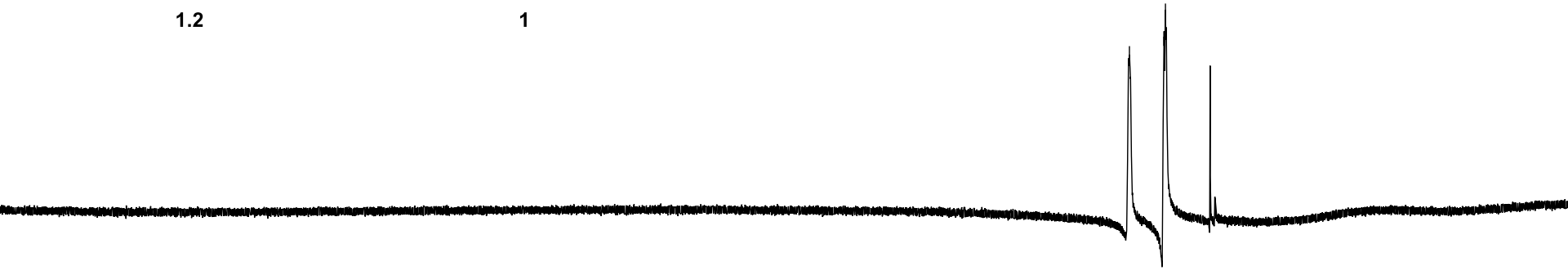
2c

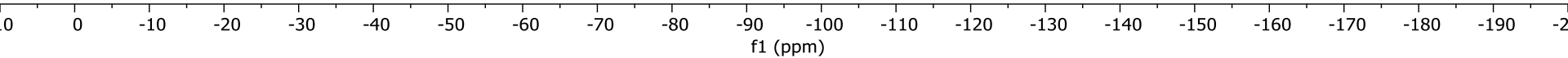
1.2

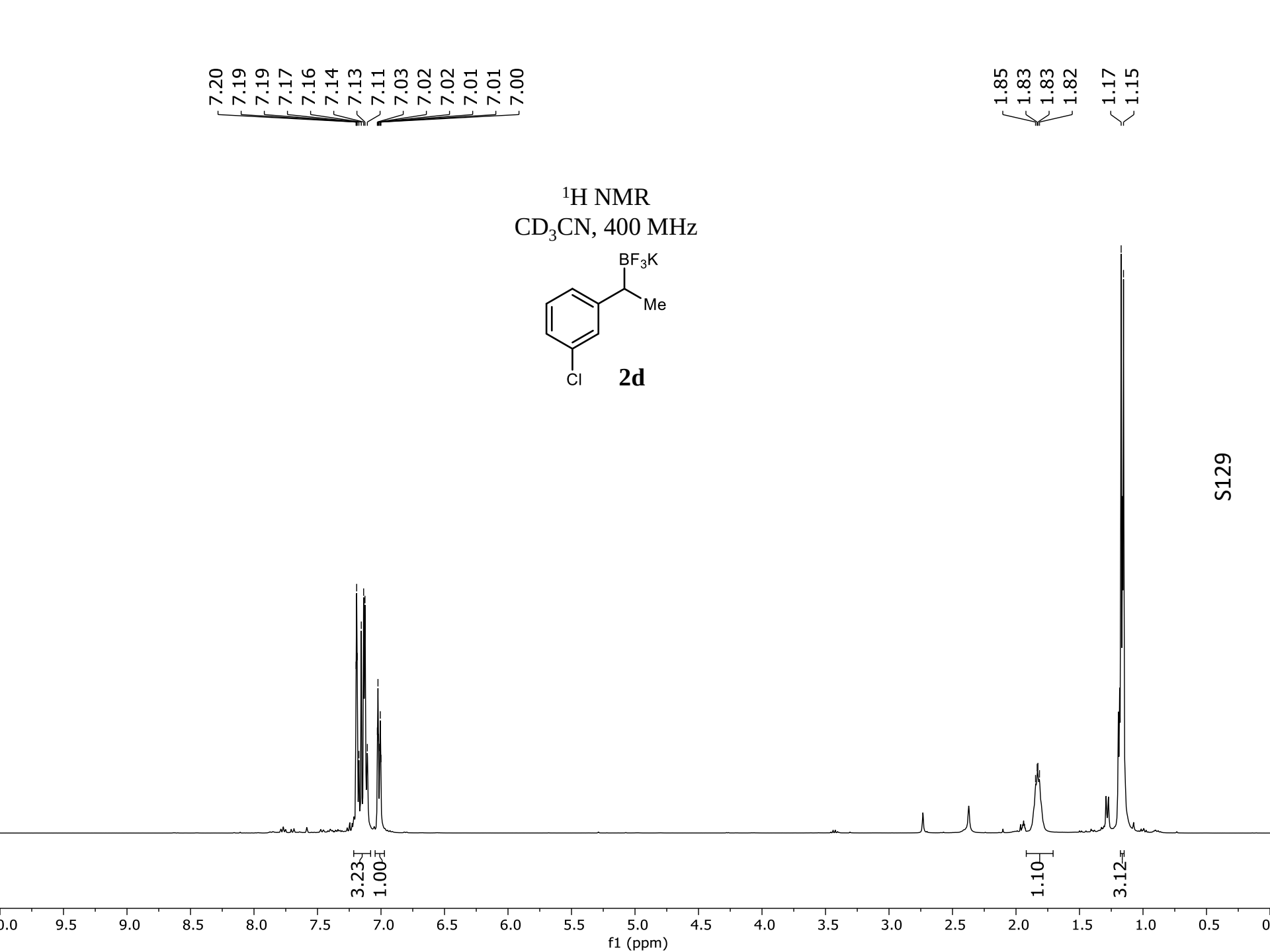


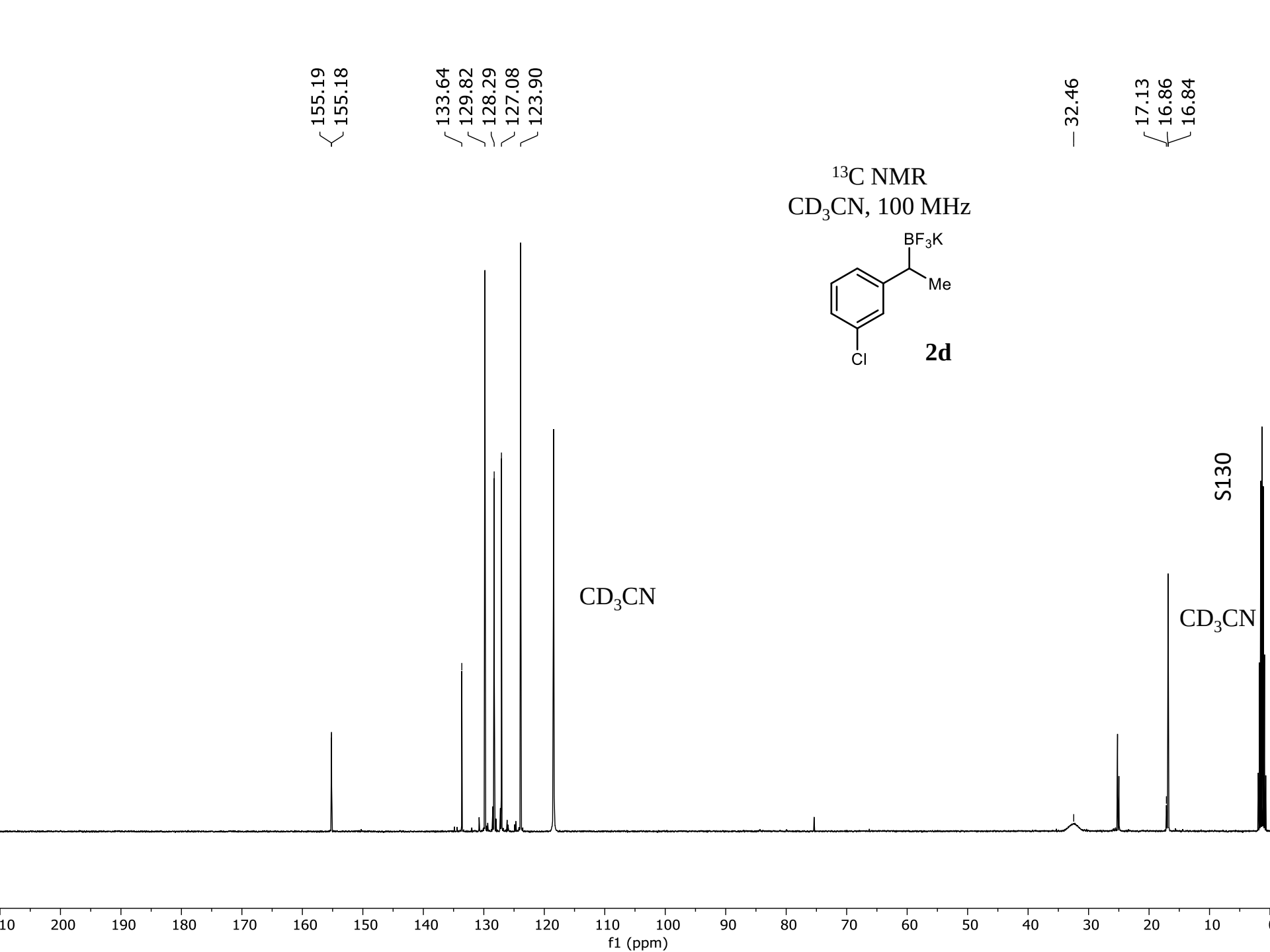
2c'

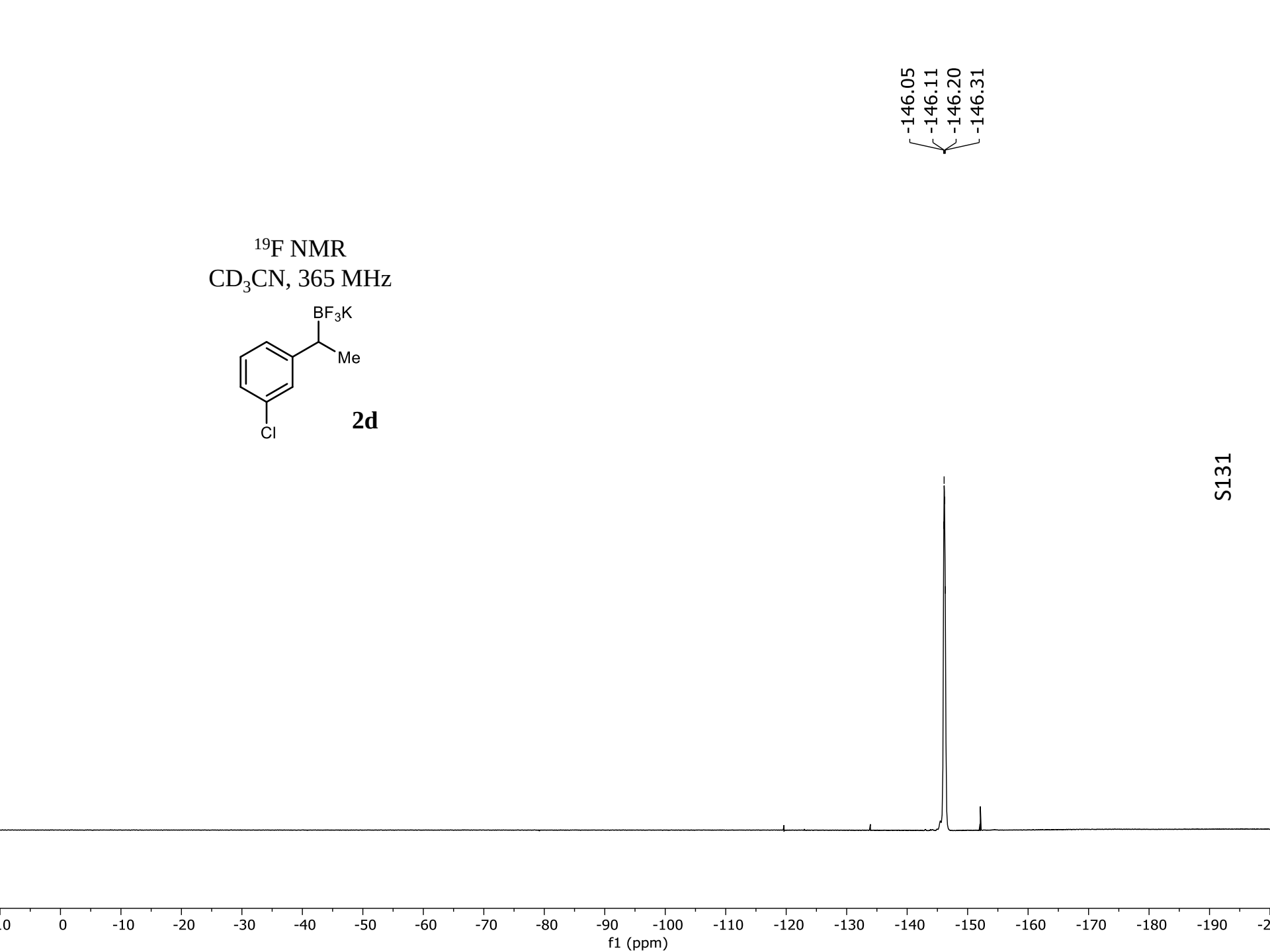
1

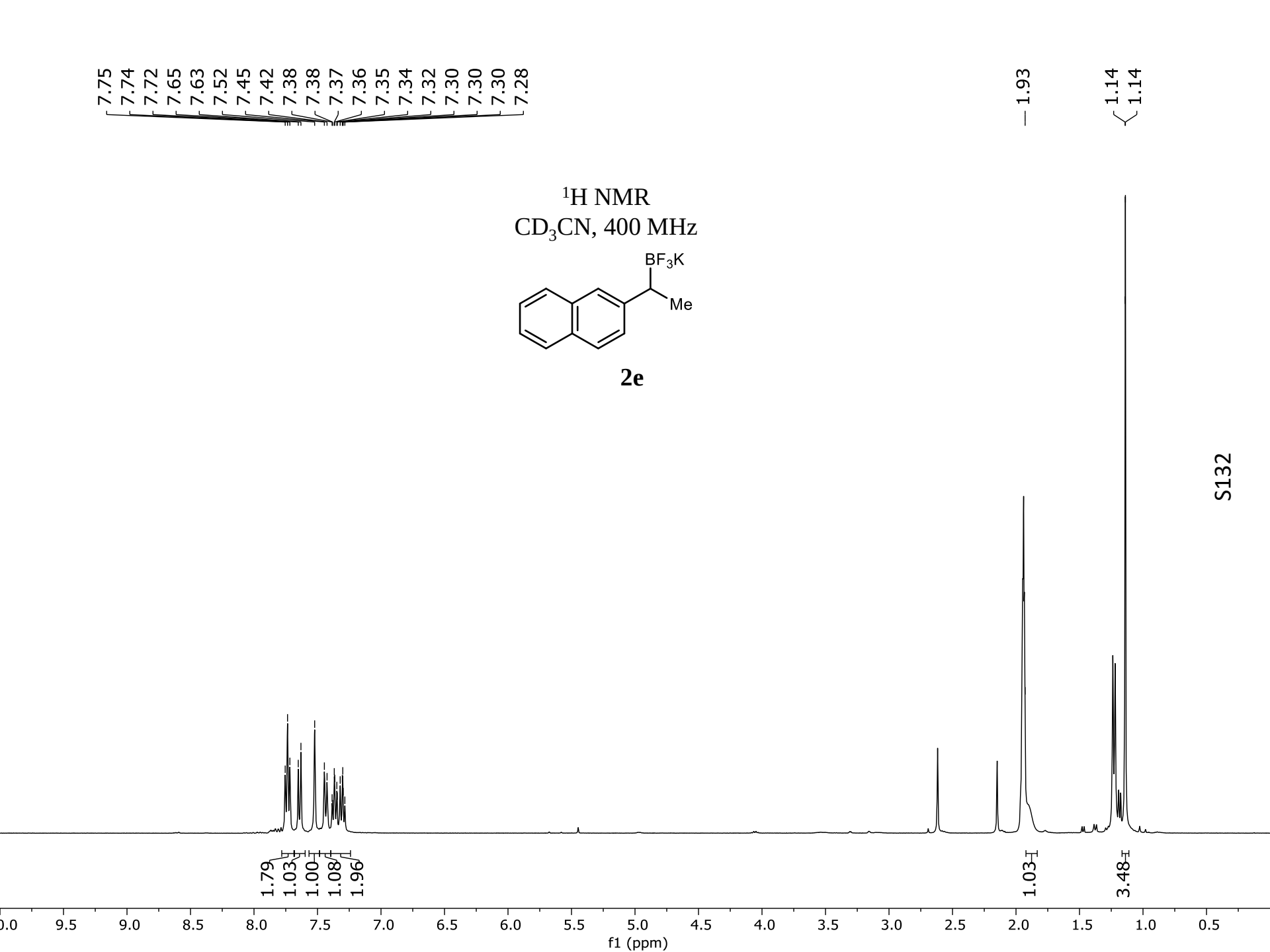


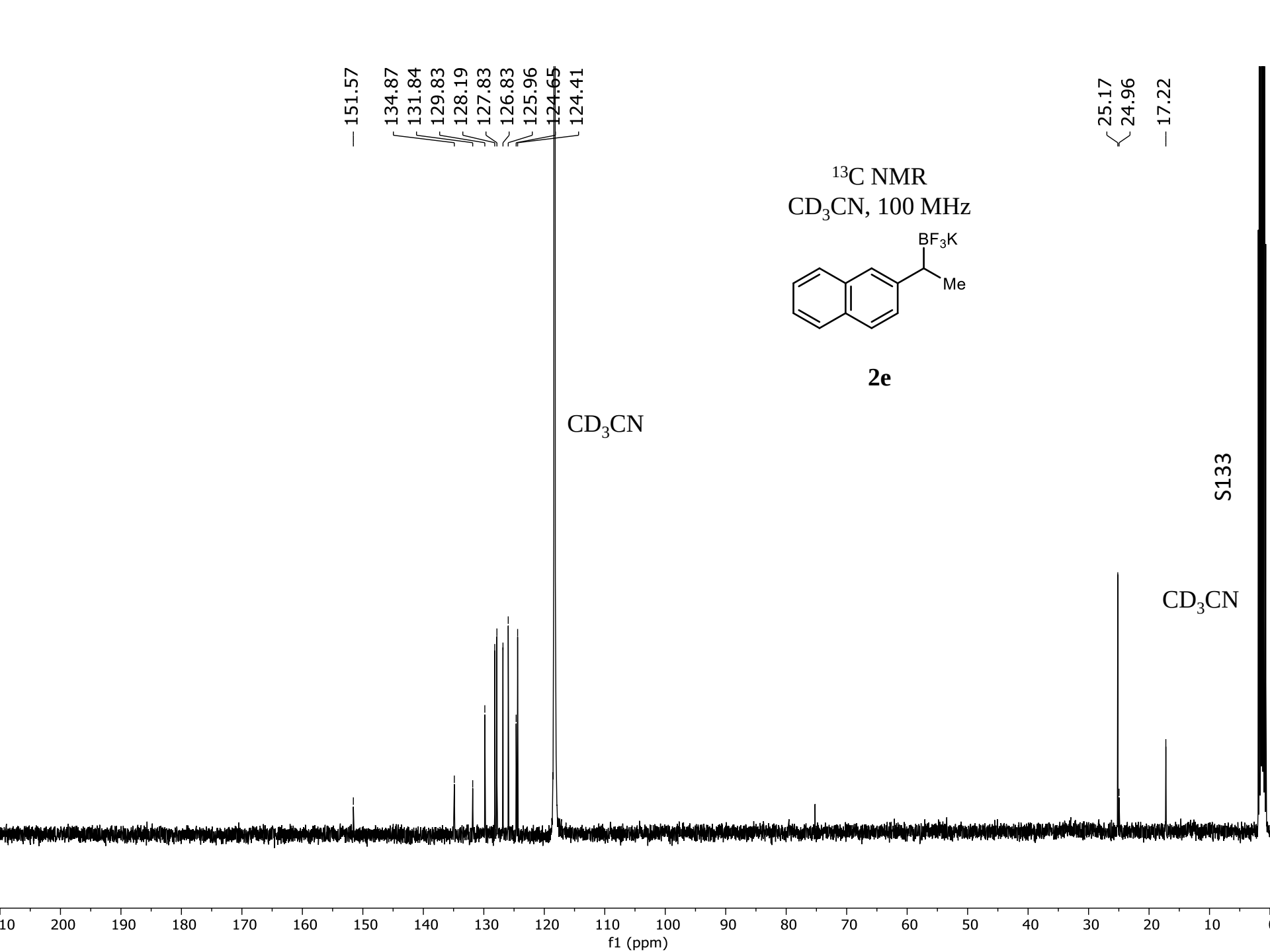



7.20
7.19
7.19
7.17
7.16
7.14
7.13
7.11
7.03
7.02
7.02
7.01
7.01
7.00
1.85
1.83
1.83
1.82
1.17
1.15
1H NMR
CD3CN, 400 MHz
BF3K
Me
Cl
2d
S129
3.23
1.00
1.10
3.12
f1 (ppm)

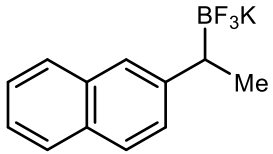

155.19
155.18
133.64
129.82
128.29
127.08
123.90
32.46
17.13
16.86
16.84
13C NMR
CD3CN, 100 MHz
BF3K
Me
Cl
2d
S130
CD3CN
CD3CN
f1 (ppm)


-146.05
-146.11
-146.20
-146.31
^{19}F NMR
CD_3CN, 365 MHz
BF_3K
Me
Cl
2d
S131
f1 (ppm)

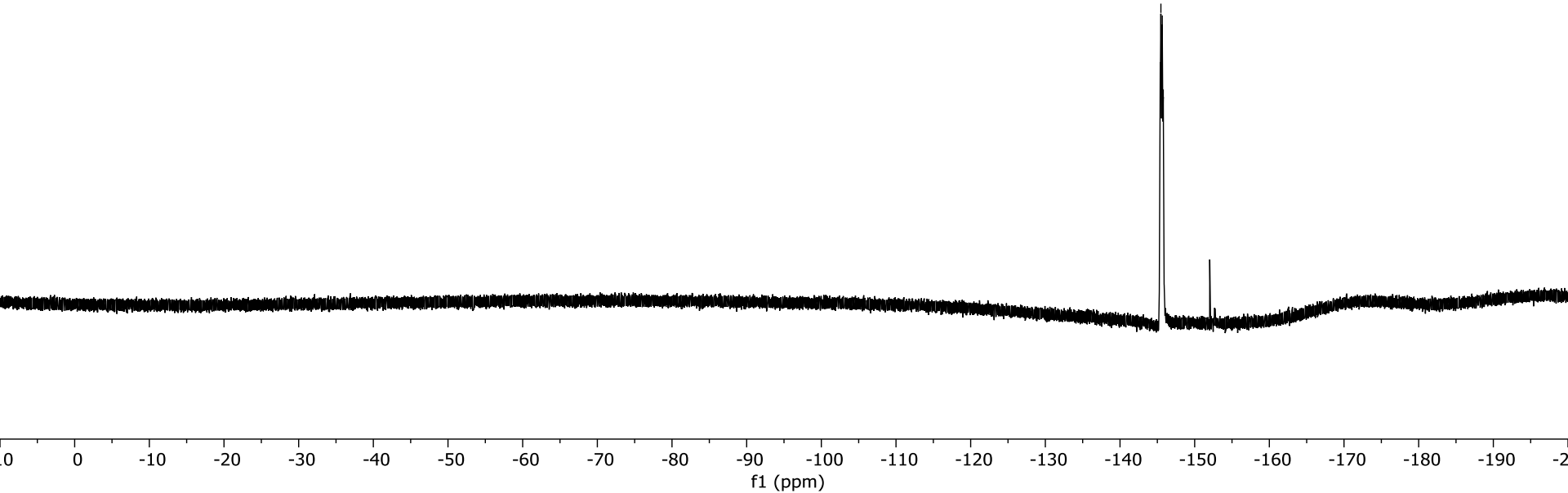

7.75
7.74
7.72
7.65
7.63
7.52
7.45
7.42
7.38
7.38
7.37
7.36
7.35
7.34
7.32
7.30
7.30
7.30
7.28
1.93
1.14
1.14
^{1}H NMR
CD_3CN, 400 MHz
BF_3K
Me
2e
S132
1.79
1.03
1.00
1.08
1.96
1.03
3.48
f1 (ppm)

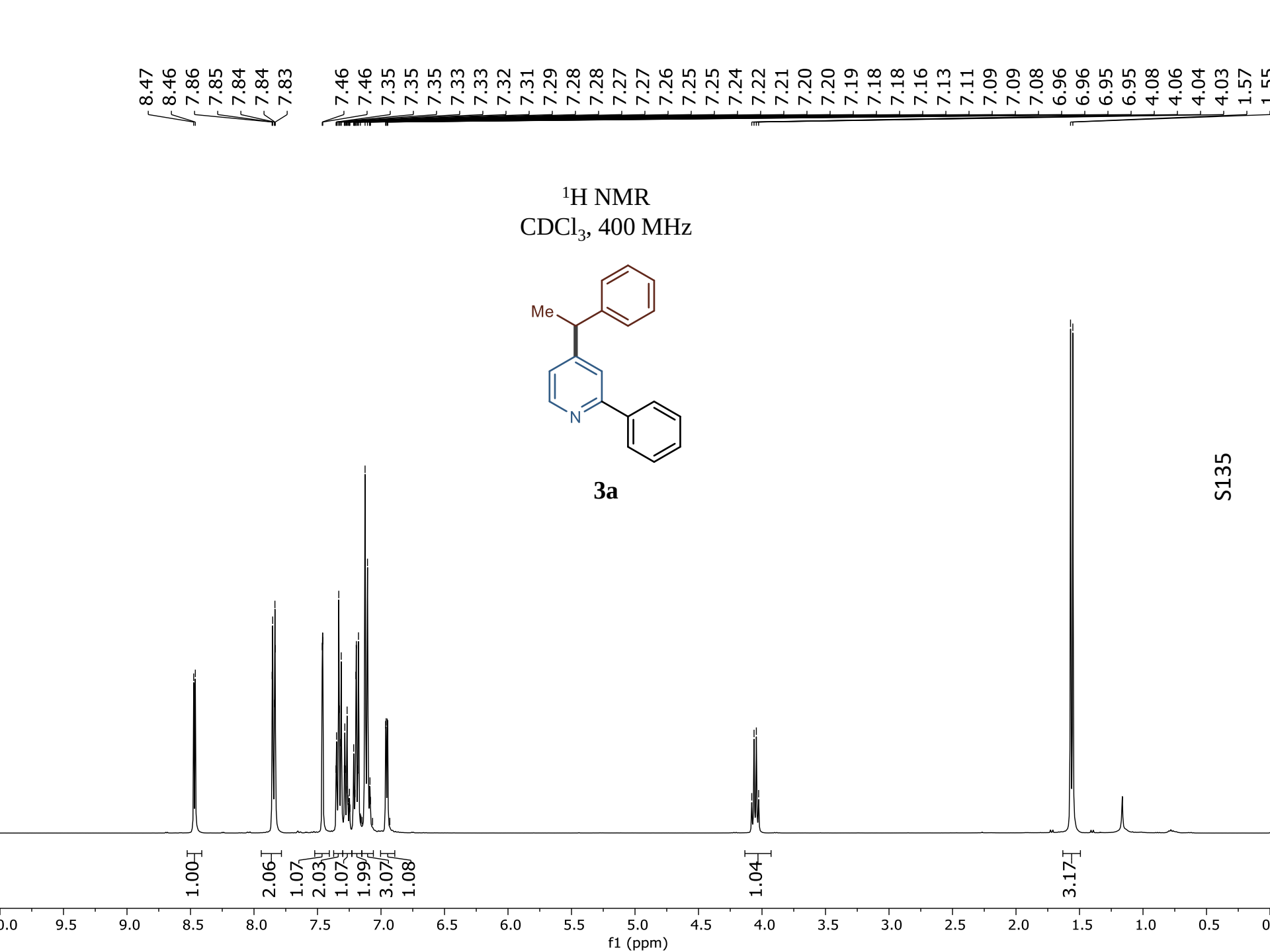

151.57
134.87
131.84
129.83
128.19
127.83
126.83
125.96
124.65
124.41
25.17
24.96
17.22
^{13}C NMR
CD_3CN, 100 MHz
BF_3K
Me
2e
CD_3CN
CD_3CN
S133
f1 (ppm)

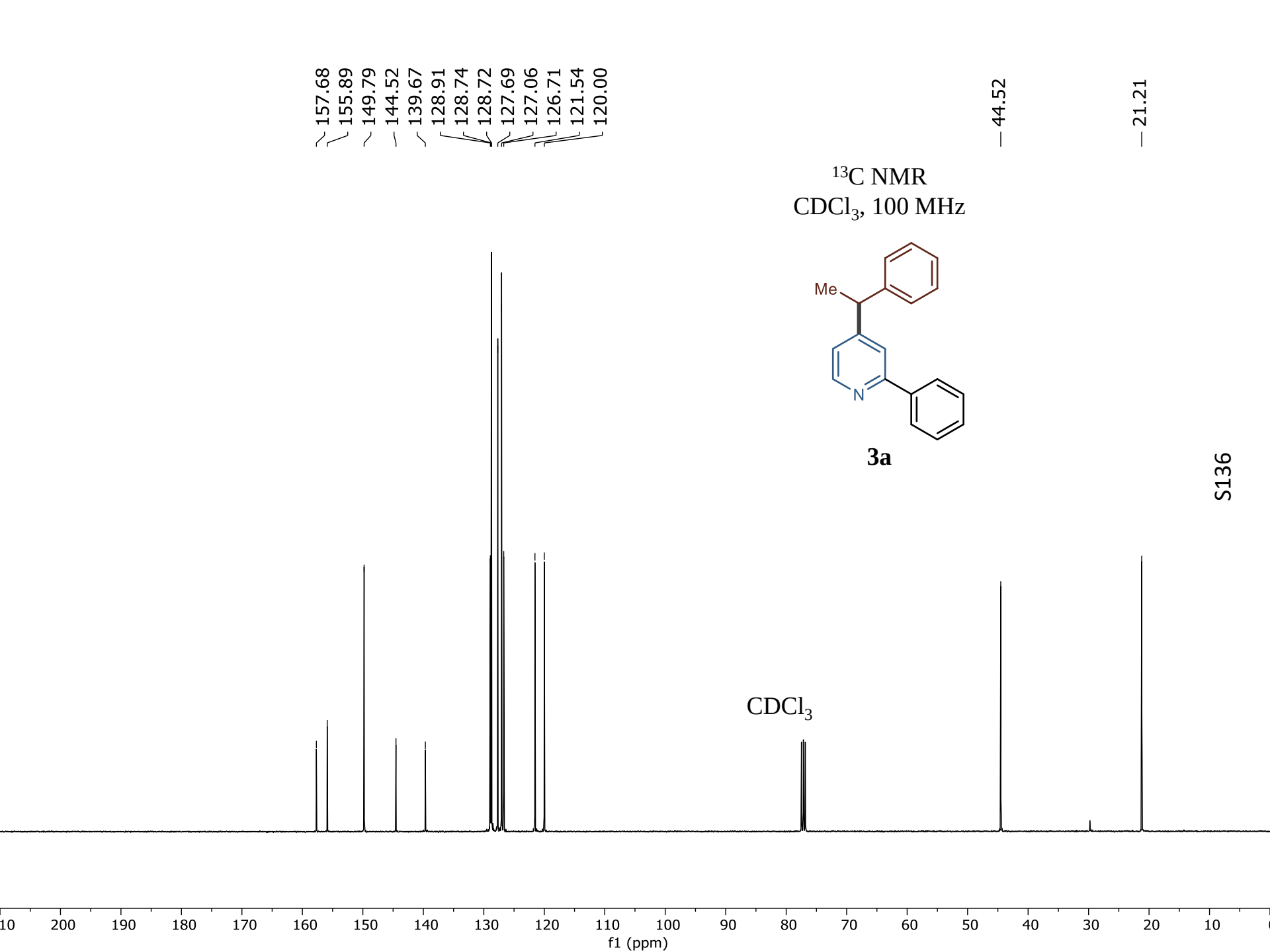
^{19}F NMR
CD_3CN, 365 MHz

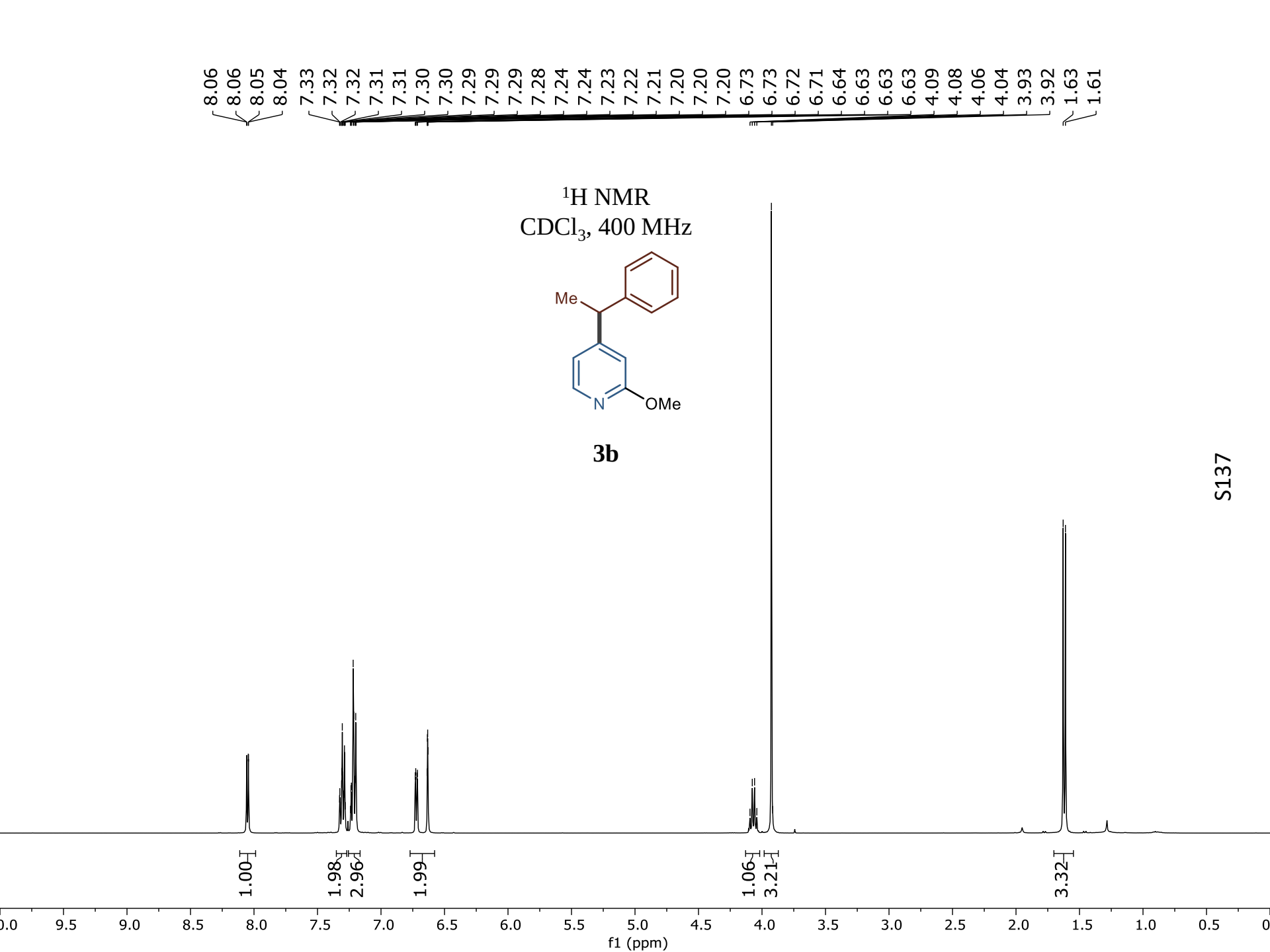


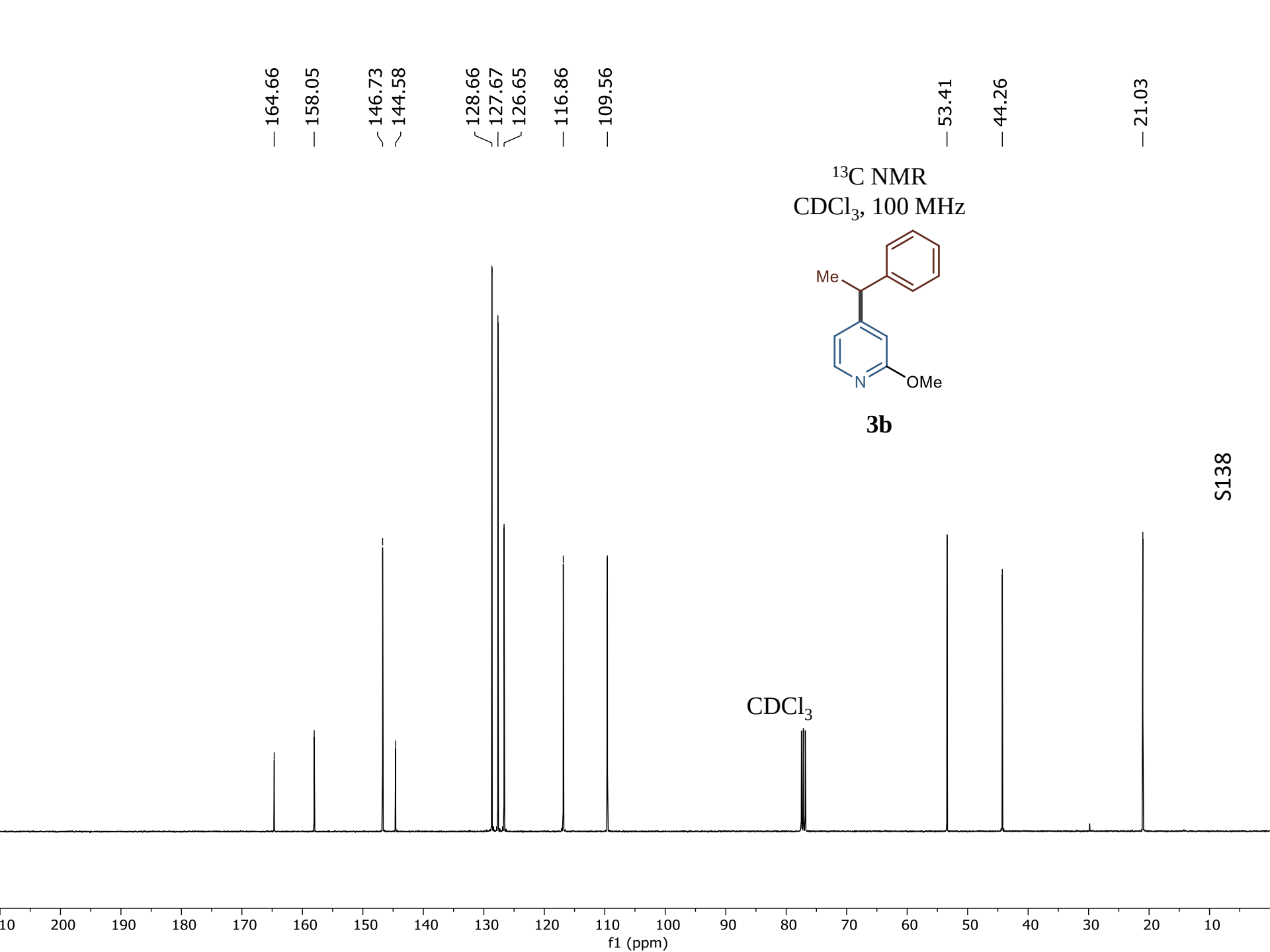
2e

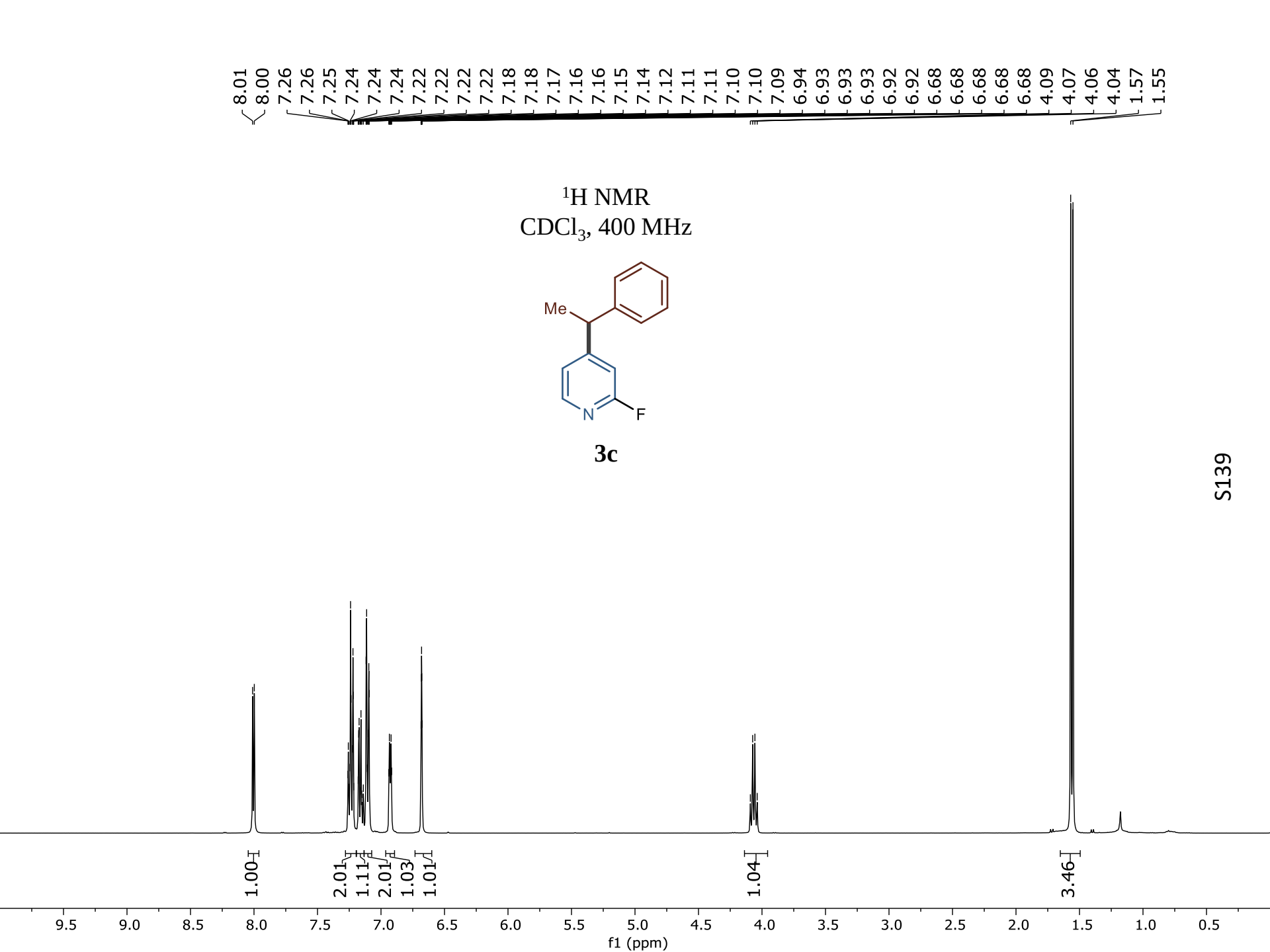


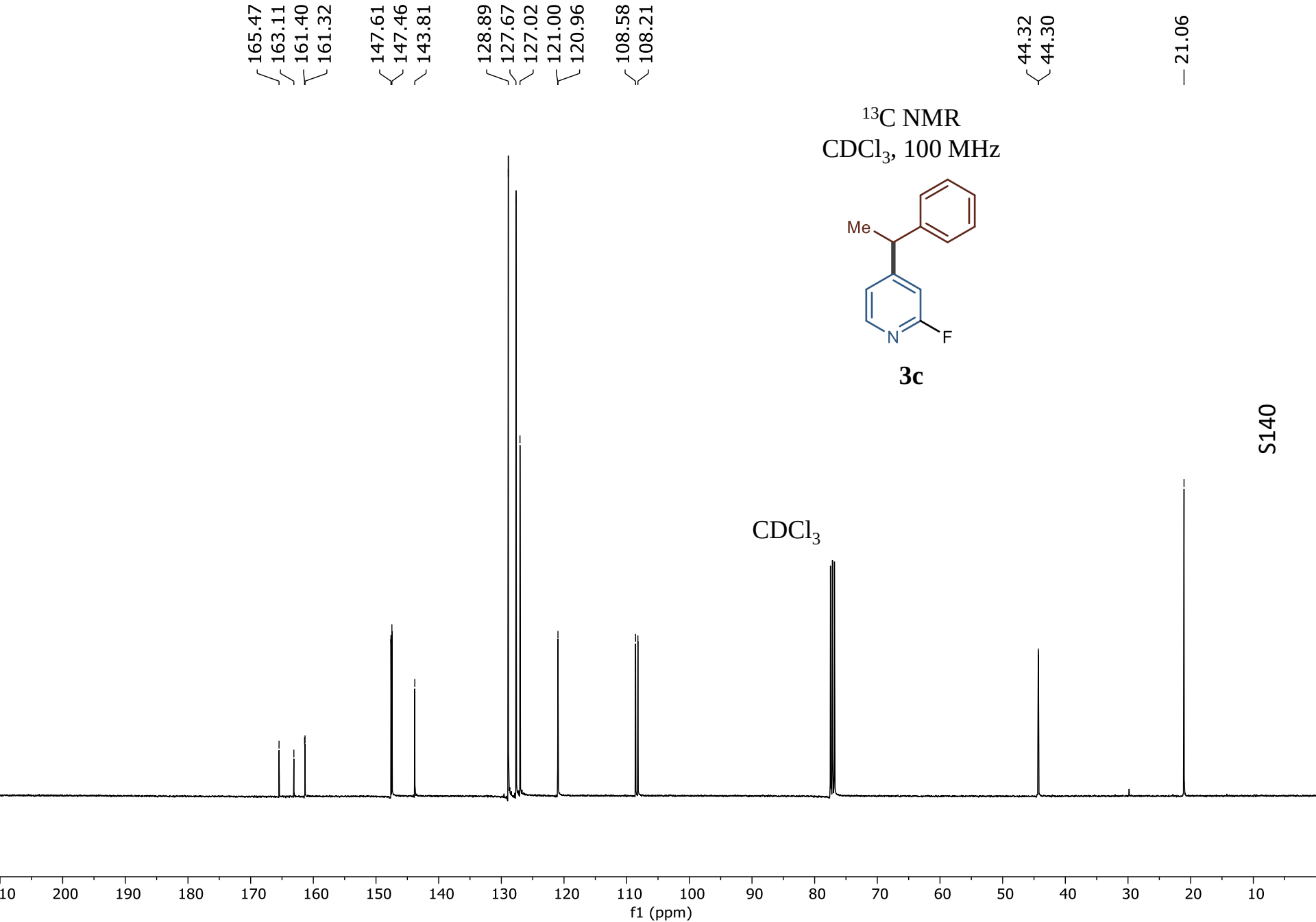

8.47
8.46
7.86
7.85
7.84
7.84
7.83
7.46
7.46
7.35
7.35
7.35
7.33
7.33
7.32
7.31
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.16
7.13
7.11
7.09
7.09
7.08
6.96
6.96
6.95
6.95
4.08
4.06
4.04
4.03
1.57
1H NMR
CDCl3, 400 MHz
Me
N
3a
S135
1.00
2.06
1.07
2.03
1.07
1.99
3.07
1.08
1.04
3.17
f1 (ppm)


157.68
155.89
149.79
144.52
139.67
128.91
128.74
128.72
127.69
127.06
126.71
121.54
120.00
44.52
21.21
^{13}C NMR
$CDCl_3$, 100 MHz
Me
N
3a
S136
$CDCl_3$
f1 (ppm)


8.06
8.06
8.05
8.04
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.20
6.73
6.73
6.72
6.71
6.64
6.63
6.63
6.63
4.09
4.08
4.06
4.04
3.93
3.92
1.63
1.61
1H NMR
CDCl3, 400 MHz
Me
N
OMe
3b
S137
1.00
1.98
2.96
1.99
1.06
3.21
3.32
f1 (ppm)

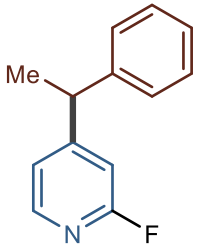

164.66
158.05
146.73
144.58
128.66
127.67
126.65
116.86
109.56
53.41
44.26
21.03
13C NMR
CDCl3, 100 MHz
Me
N
OMe
3b
S138
CDCl3
f1 (ppm)


8.01 8.00 7.26 7.26 7.25 7.24 7.24 7.24 7.22 7.22 7.22 7.22 7.18 7.18 7.17 7.16 7.16 7.15 7.14 7.12 7.11 7.11 7.10 7.10 7.09 6.94 6.93 6.93 6.93 6.92 6.92 6.68 6.68 6.68 6.68 6.68 4.09 4.07 4.06 4.04 1.57 1.55
1H NMR
CDCl3, 400 MHz
Me
N
F
3c
S139
1.00 2.01 1.11 2.01 1.03 1.01 1.04 3.46
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
f1 (ppm)

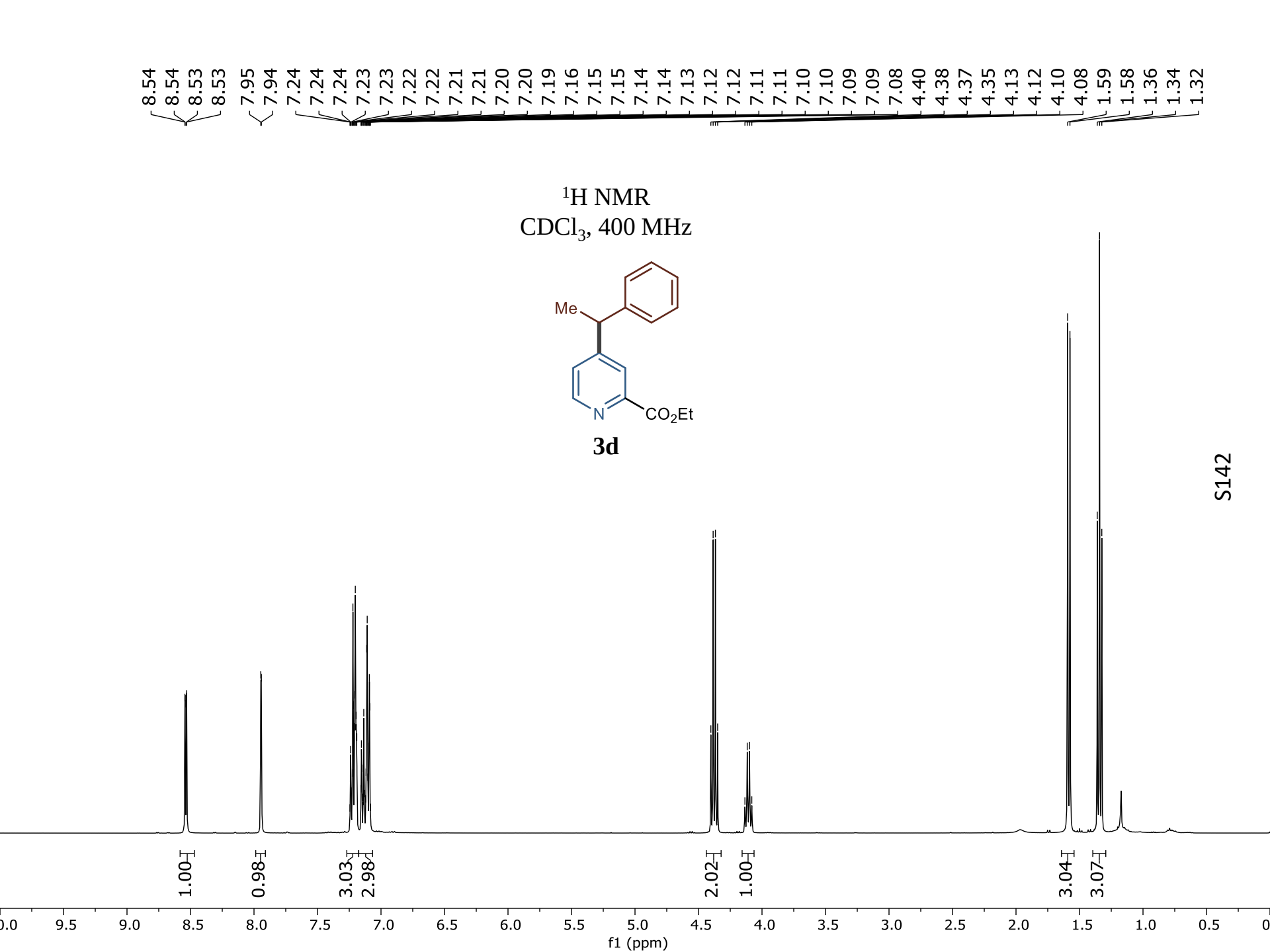

165.47
163.11
161.40
161.32
147.61
147.46
143.81
128.89
127.67
127.02
121.00
120.96
108.58
108.21
44.32
44.30
21.06
13C NMR
CDCl3, 100 MHz
Me
N
F
3c
CDCl3
S140
f1 (ppm)

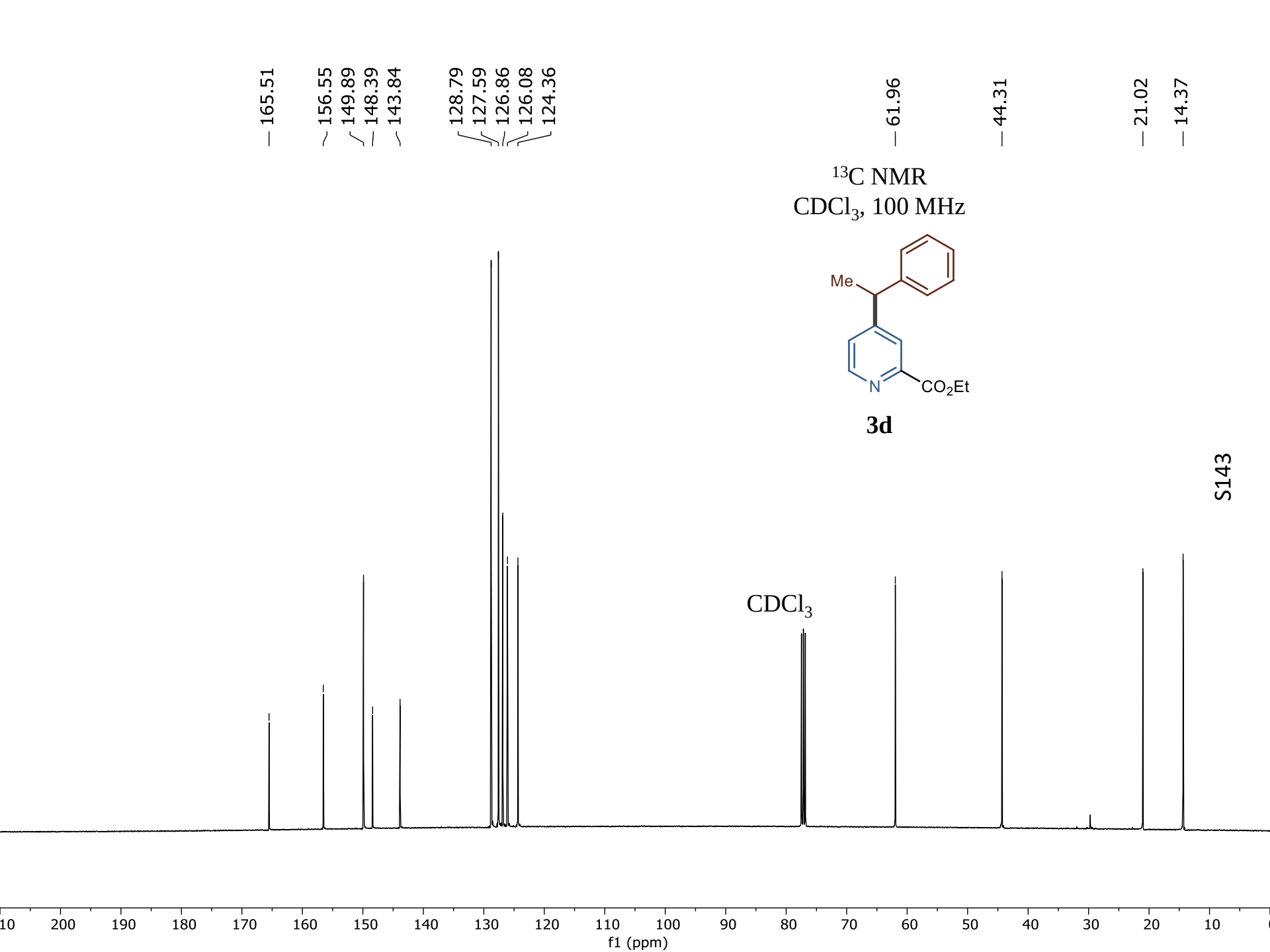
-68.47

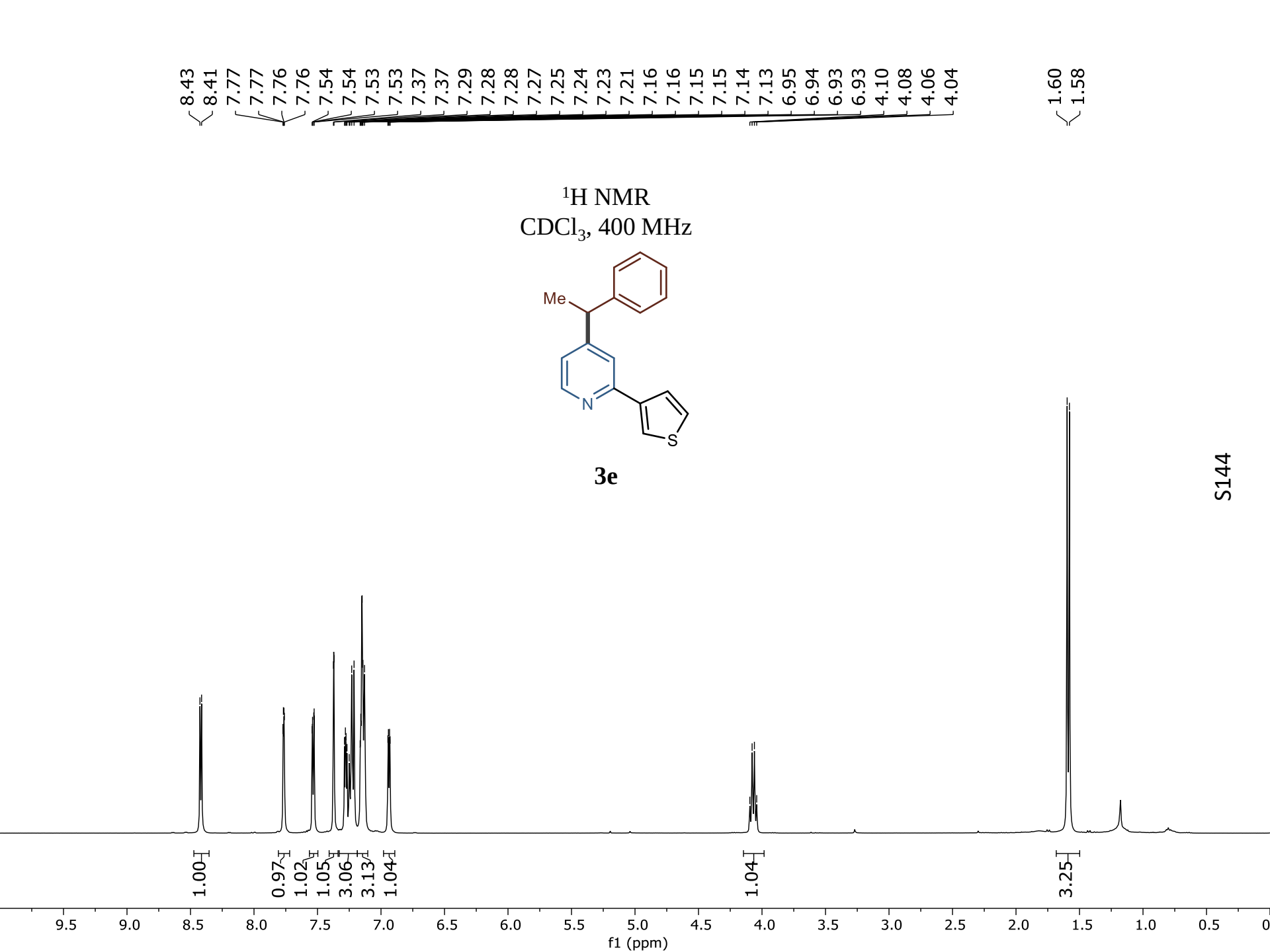
^{19}F NMR
$CDCl_3$, 365 MHz

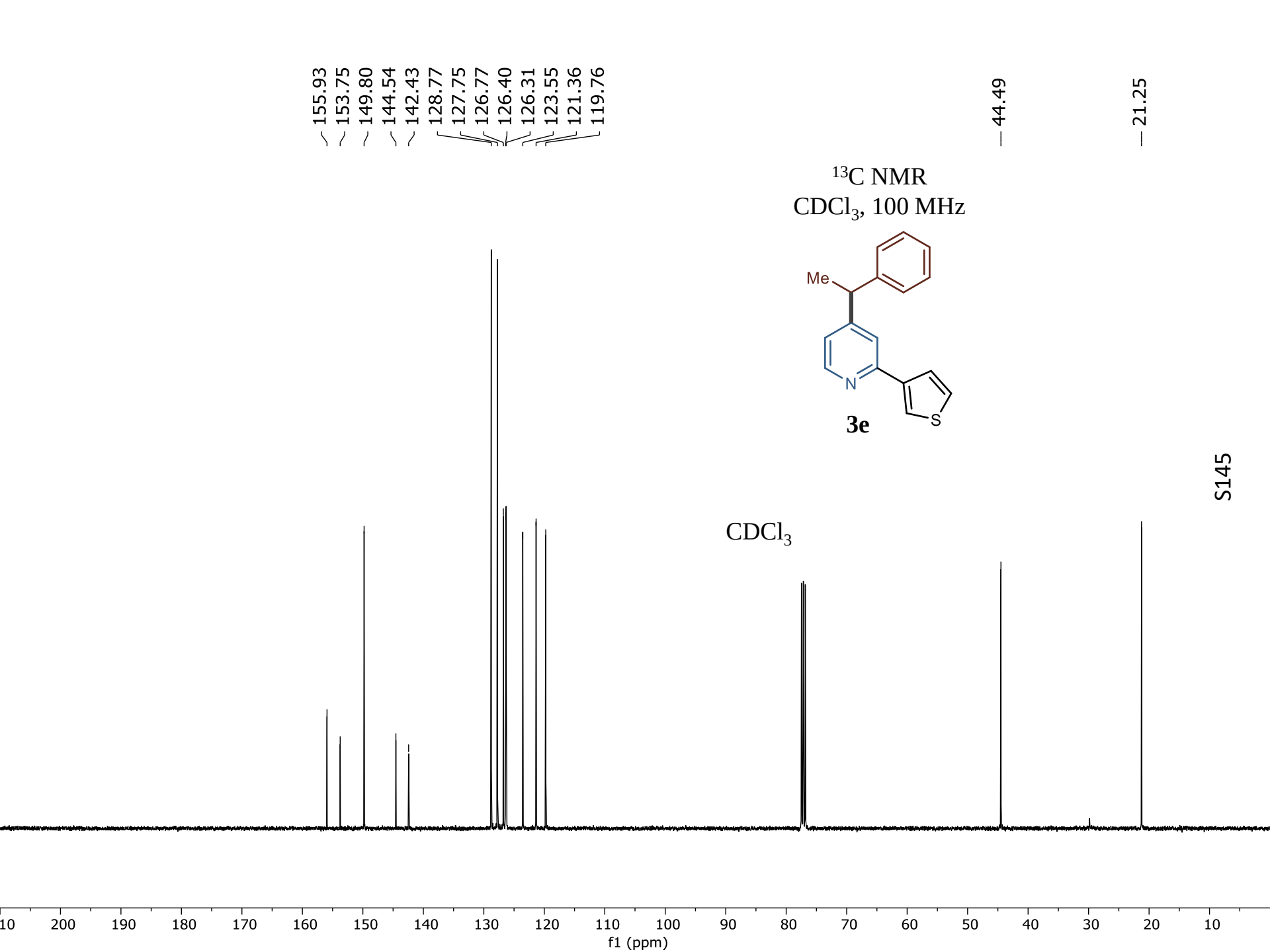


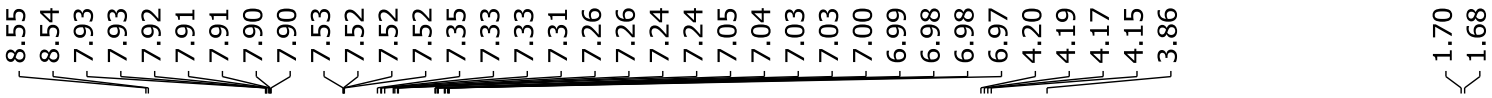
3c


8.54
8.54
8.53
8.53
7.95
7.94
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.16
7.15
7.15
7.14
7.14
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
4.40
4.38
4.37
4.35
4.13
4.12
4.10
4.08
1.59
1.58
1.36
1.34
1.32
1H NMR
CDCl3, 400 MHz
Me
N
CO2Et
3d
S142
1.00
0.98
3.03
2.98
2.02
1.00
3.04
3.07
f1 (ppm)

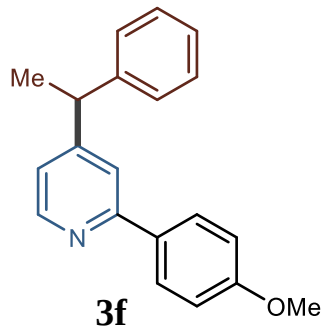

165.51
156.55
149.89
148.39
143.84
128.79
127.59
126.86
126.08
124.36
61.96
44.31
21.02
14.37
13C NMR
CDCl3, 100 MHz
Me
N
CO2Et
3d
S143
CDCl3
f1 (ppm)


8.43
8.41
7.77
7.77
7.76
7.76
7.54
7.54
7.53
7.53
7.37
7.37
7.29
7.28
7.28
7.27
7.25
7.24
7.23
7.21
7.16
7.16
7.15
7.15
7.14
7.13
6.95
6.94
6.93
6.93
4.10
4.08
4.06
4.04
1.60
1.58
1H NMR
CDCl3, 400 MHz
Me
N
S
3e
S144
1.00
0.97
1.02
1.05
3.06
3.13
1.04
1.04
3.25
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
f1 (ppm)

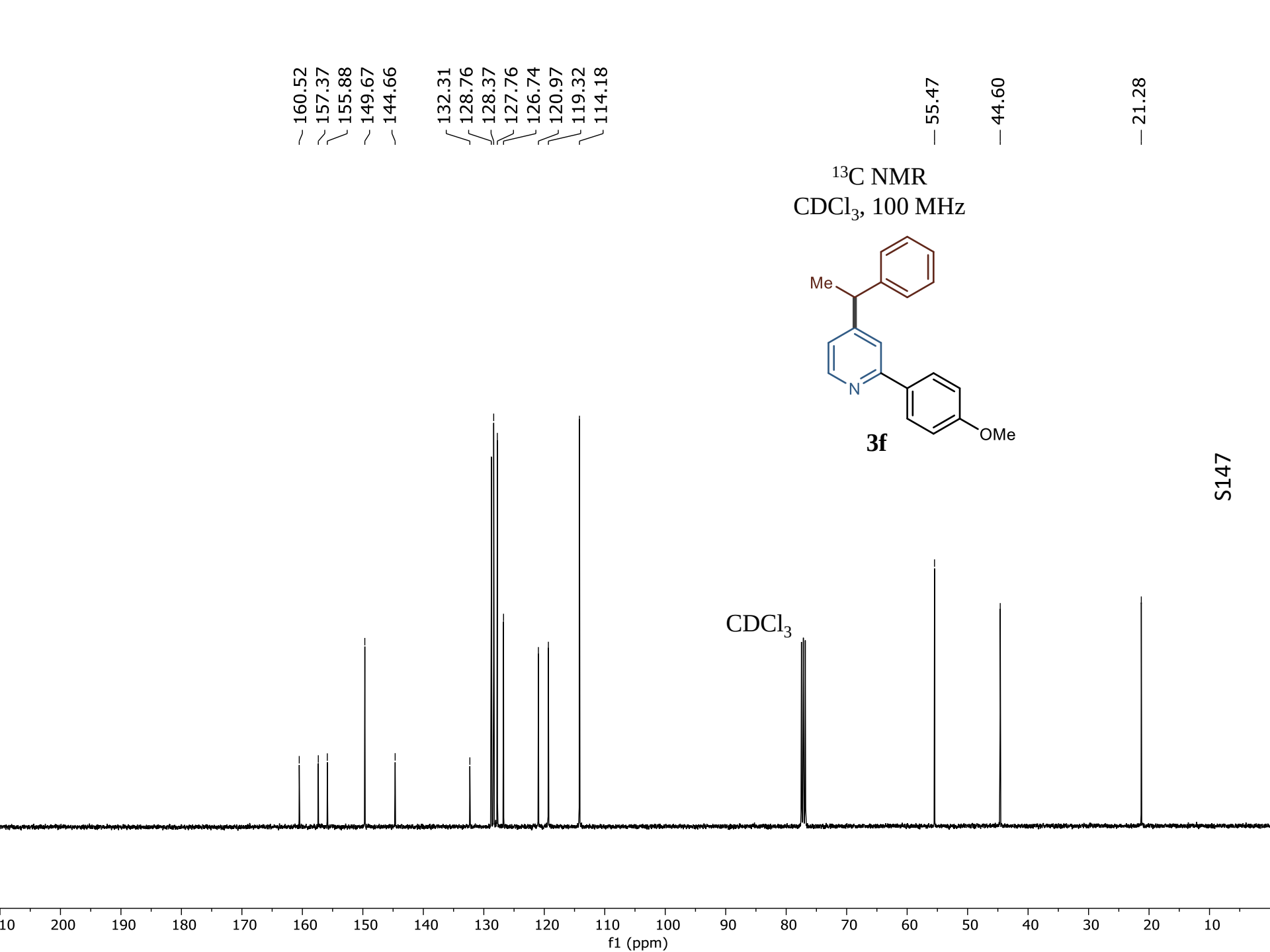

155.93
153.75
149.80
144.54
142.43
128.77
127.75
126.77
126.40
126.31
123.55
121.36
119.76
44.49
21.25
^{13}C NMR
$CDCl_3$, 100 MHz
Me
N
S
3e
S145
$CDCl_3$
f1 (ppm)

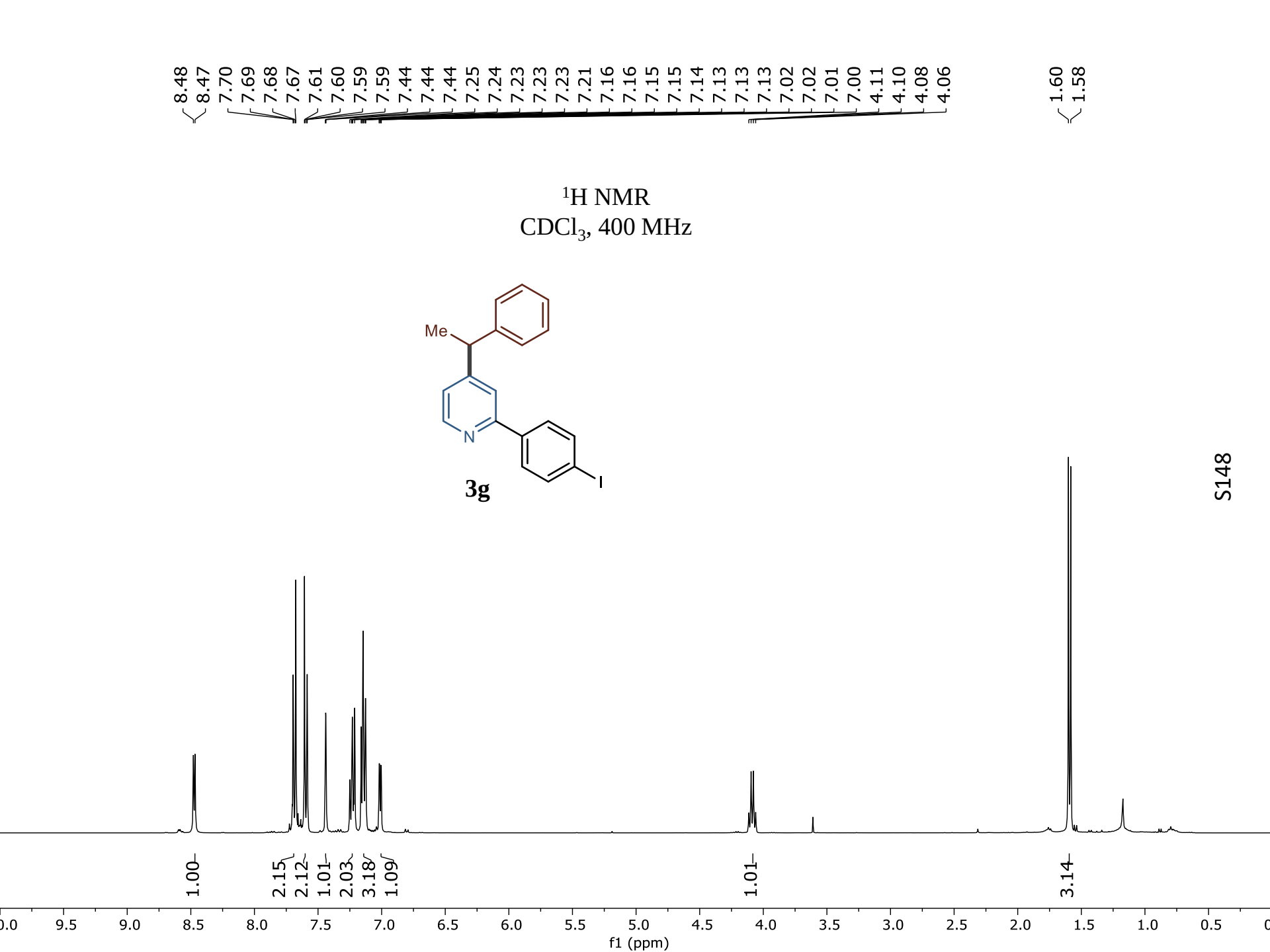


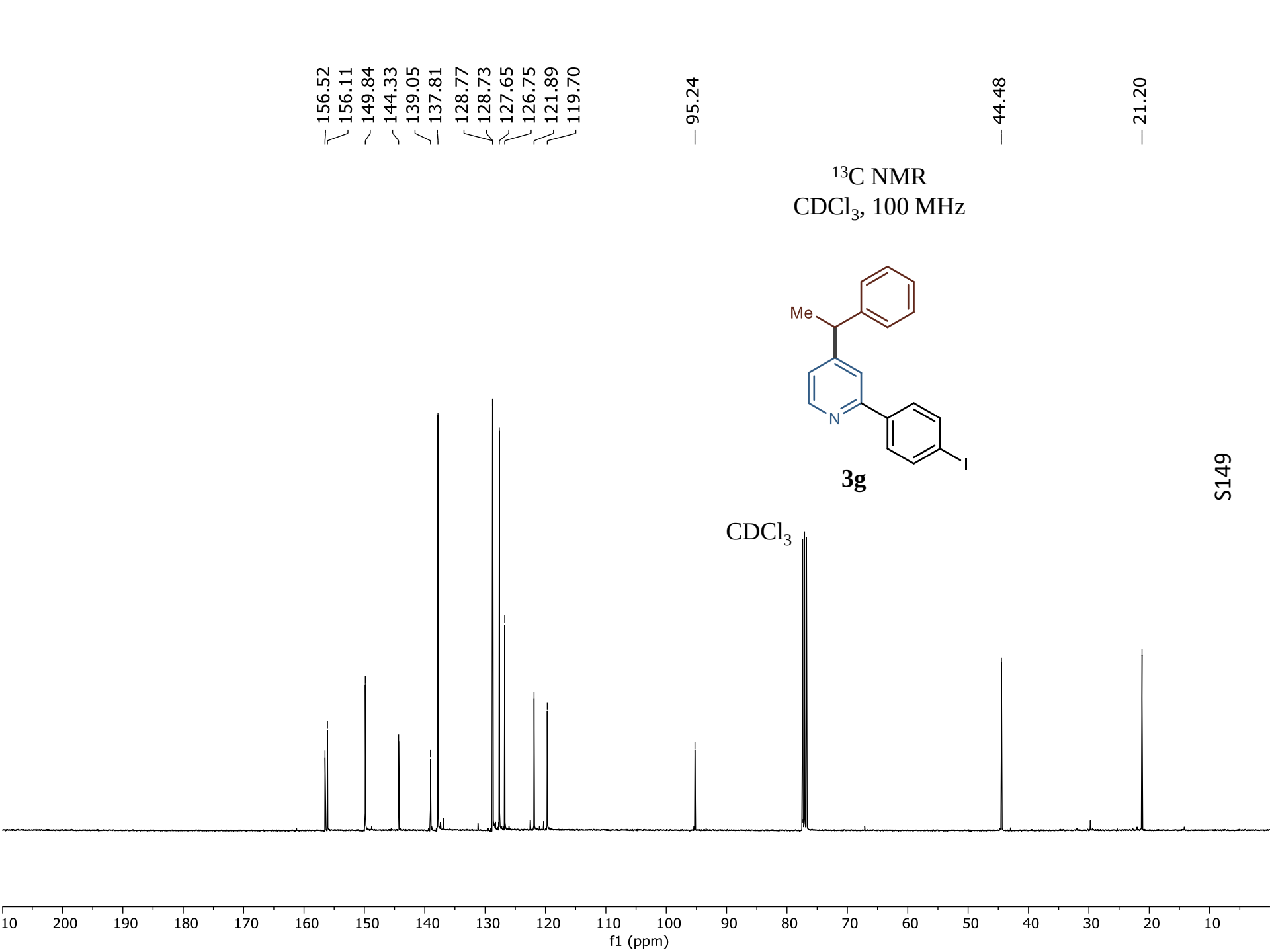
^{1}H NMR
$CDCl_3$, 400 MHz

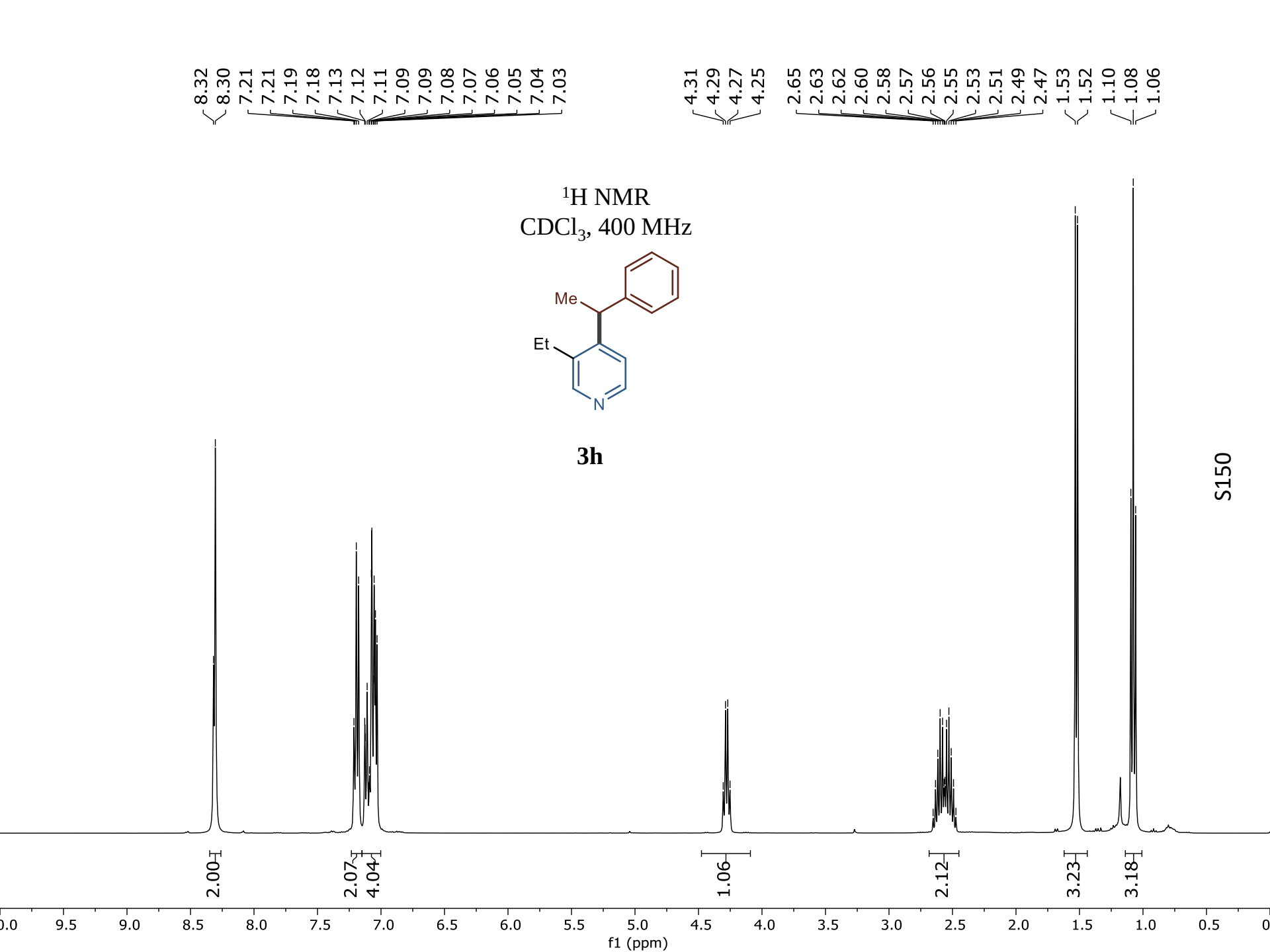


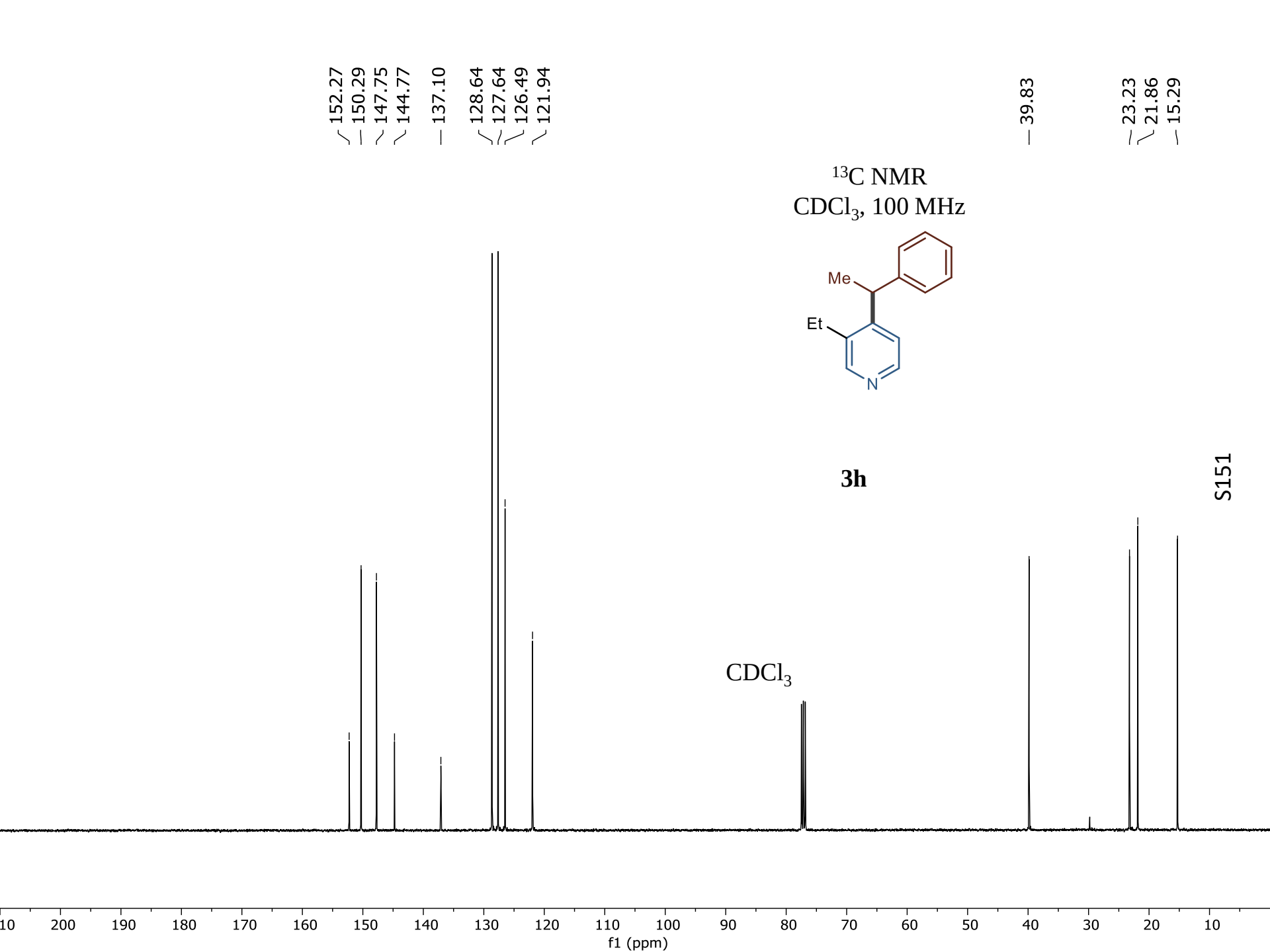
3f

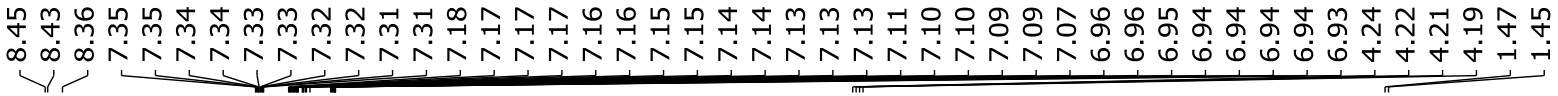

160.52
157.37
155.88
149.67
144.66
132.31
128.76
128.37
127.76
126.74
120.97
119.32
114.18
55.47
44.60
21.28
13C NMR
CDCl3, 100 MHz
Me
N
OMe
3f
S147
CDCl3
f1 (ppm)


8.48
8.47
7.70
7.69
7.68
7.67
7.61
7.60
7.59
7.59
7.44
7.44
7.44
7.25
7.24
7.23
7.23
7.23
7.21
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.13
7.02
7.02
7.01
7.00
4.11
4.10
4.08
4.06
1.60
1.58
^{1}H NMR
$CDCl_3$, 400 MHz
Me
N
I
3g
S148
1.00
2.15
2.12
1.01
2.03
3.18
1.09
1.01
3.14
f1 (ppm)


156.52
156.11
149.84
144.33
139.05
137.81
128.77
128.73
127.65
126.75
121.89
119.70
95.24
44.48
21.20
^{13}C NMR
$CDCl_3$, 100 MHz
Me
N
I
3g
$CDCl_3$
S149
f1 (ppm)

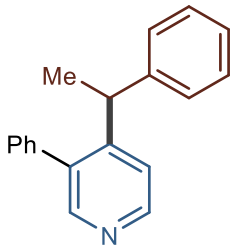

8.32
8.30
7.21
7.21
7.19
7.18
7.13
7.12
7.11
7.09
7.09
7.08
7.07
7.06
7.05
7.04
7.03
4.31
4.29
4.27
4.25
2.65
2.63
2.62
2.60
2.58
2.57
2.56
2.55
2.53
2.51
2.49
2.47
1.53
1.52
1.10
1.08
1.06
^{1}H NMR
$CDCl_3$, 400 MHz
Me
Et
N
3h
S150
2.00
2.07
4.04
1.06
2.12
3.23
3.18
f1 (ppm)


152.27
150.29
147.75
144.77
137.10
128.64
127.64
126.49
121.94
39.83
23.23
21.86
15.29
13C NMR
CDCl3, 100 MHz
Me
Et
N
3h
S151
CDCl3
f1 (ppm)

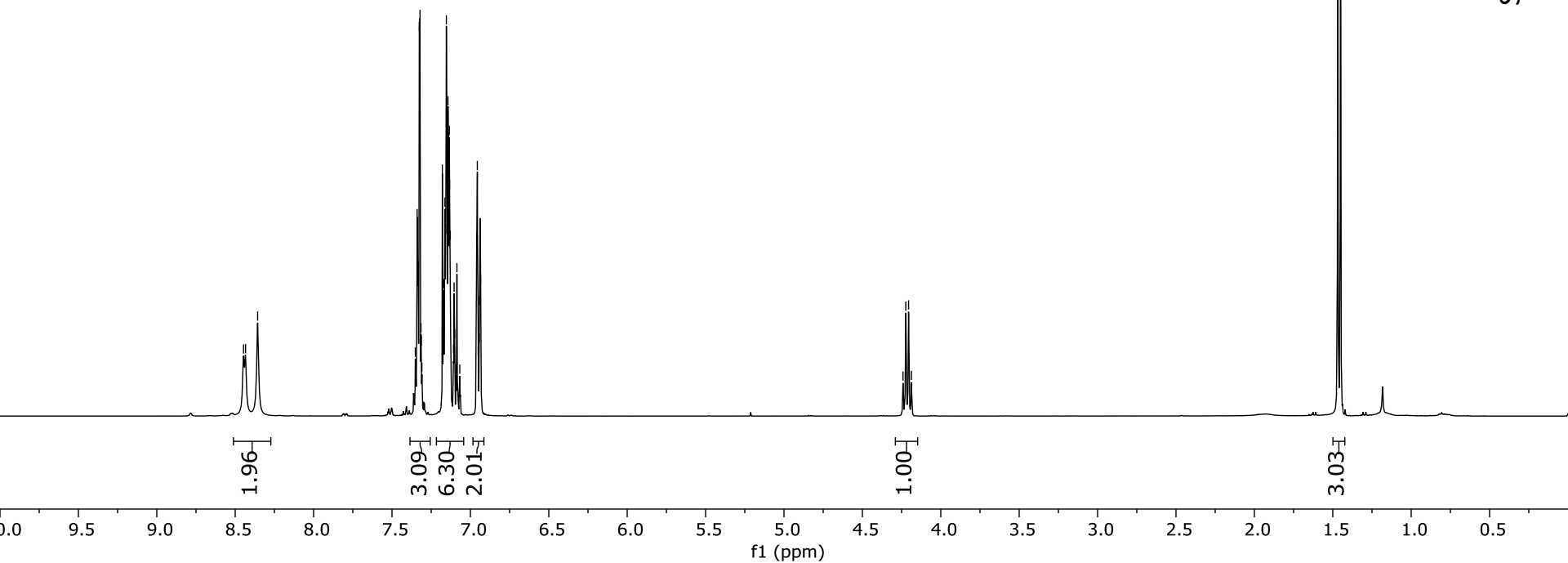


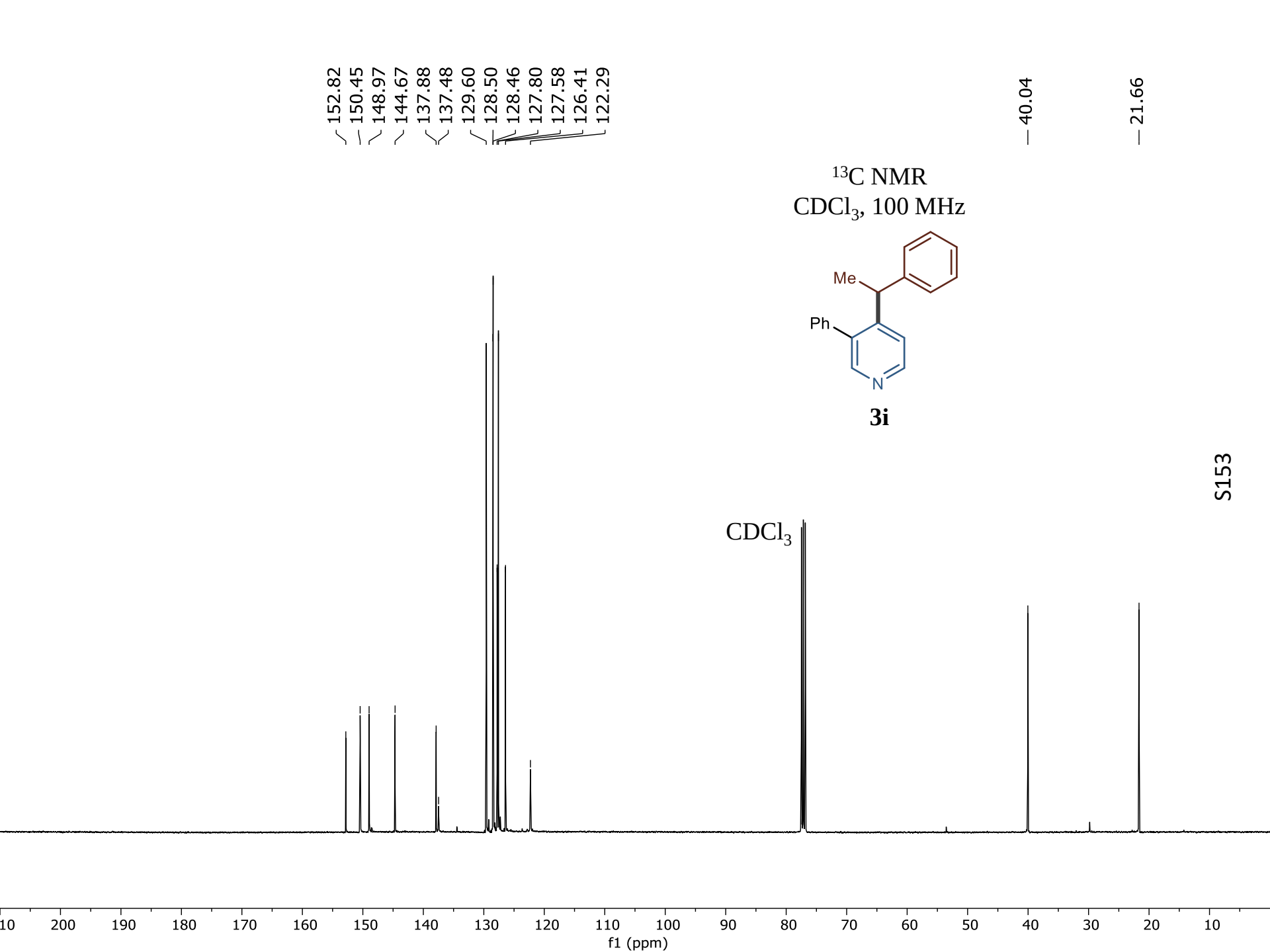
^{1}H NMR

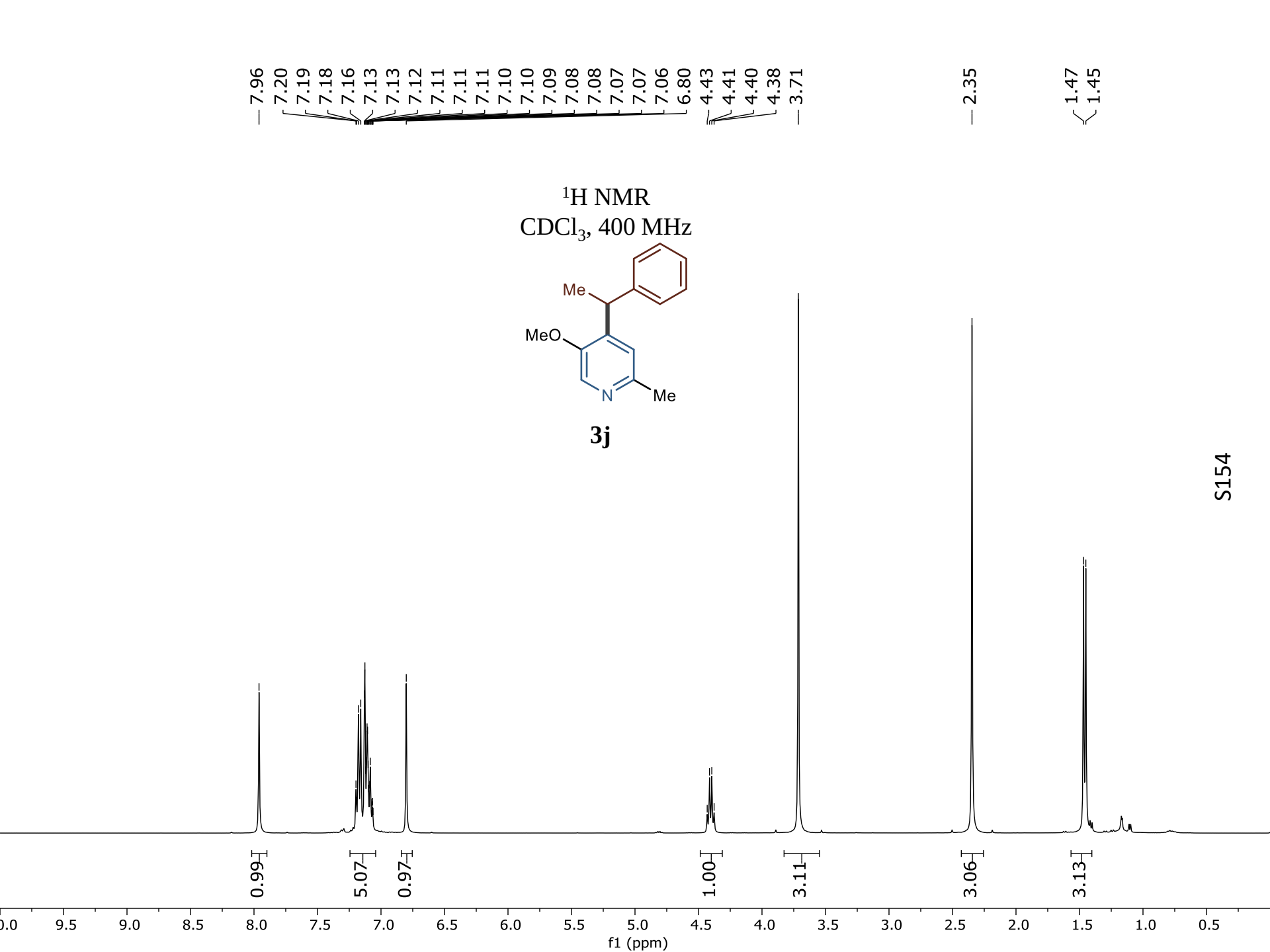
$CDCl_3$, 400 MHz

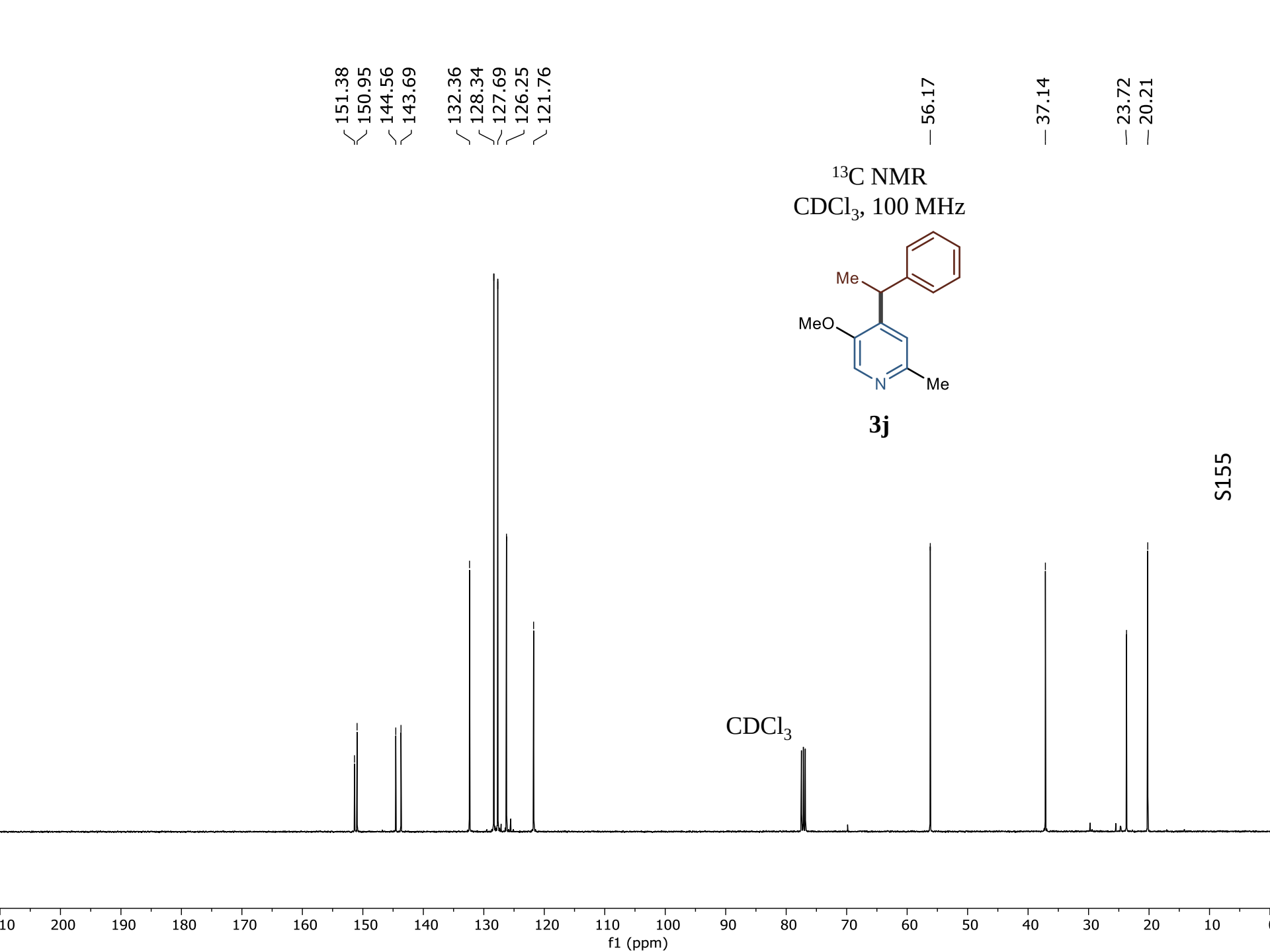


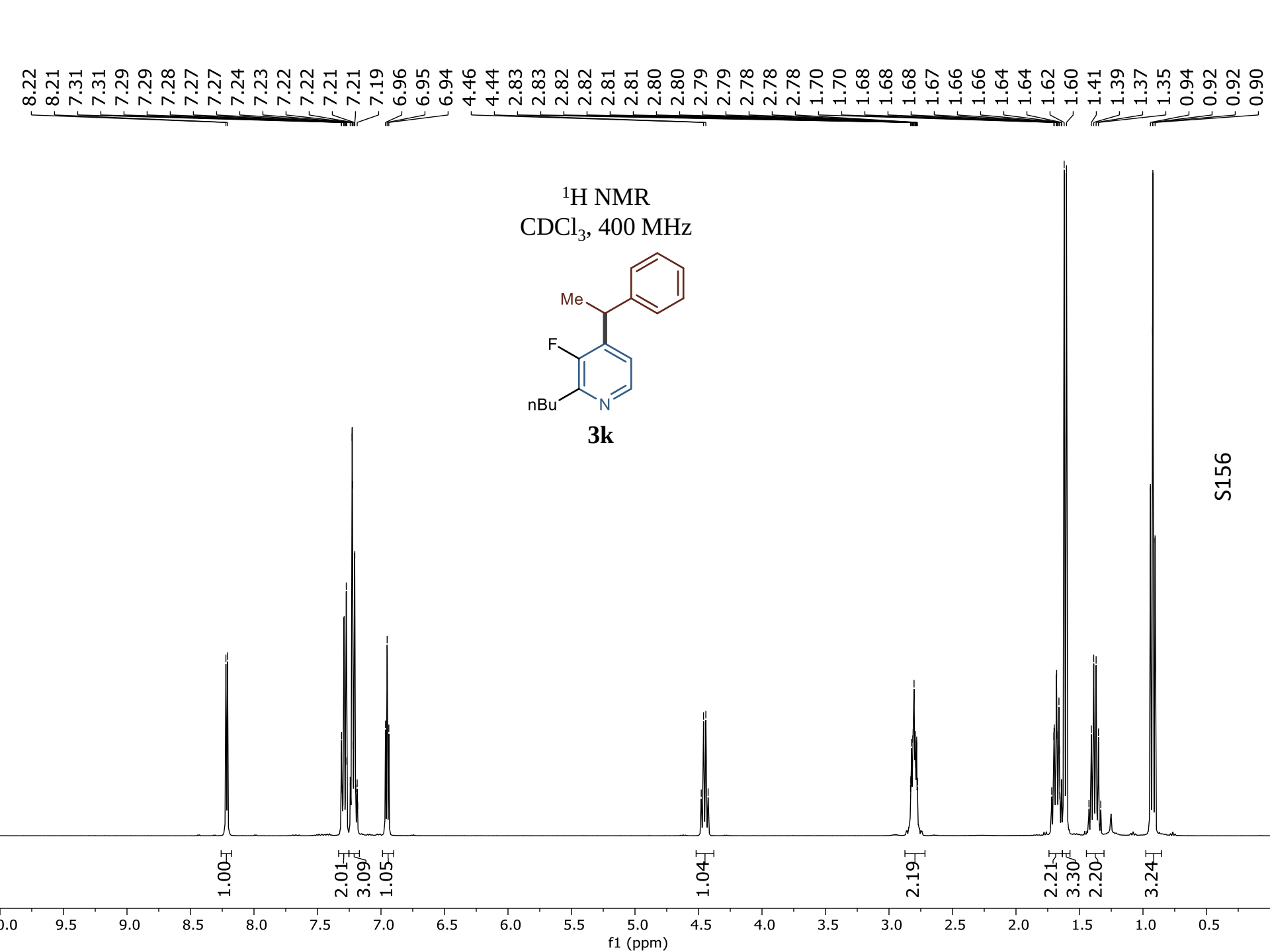
3i

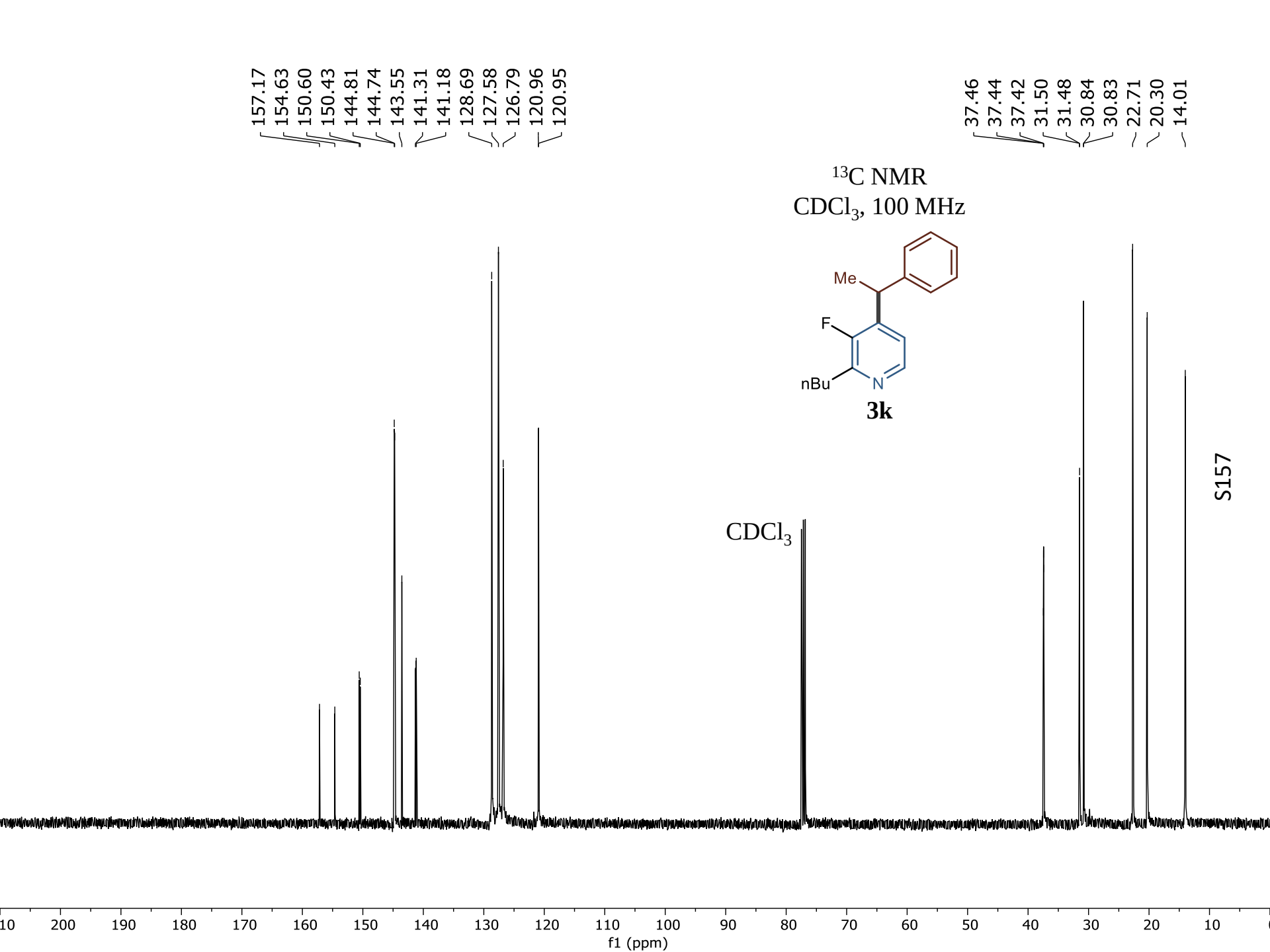



152.82
150.45
148.97
144.67
137.88
137.48
129.60
128.50
128.46
127.80
127.58
126.41
122.29
40.04
21.66
^{13}C NMR
$CDCl_3$, 100 MHz
Me
Ph
N
3i
$CDCl_3$
S153
f1 (ppm)


7.96
7.20
7.19
7.18
7.16
7.13
7.13
7.12
7.11
7.11
7.11
7.10
7.10
7.09
7.08
7.08
7.07
7.07
7.06
6.80
4.43
4.41
4.40
4.38
3.71
2.35
1.47
1.45
1H NMR
CDCl3, 400 MHz
Me
MeO
N
Me
3j
S154
0.99
5.07
0.97
1.00
3.11
3.06
3.13
f1 (ppm)

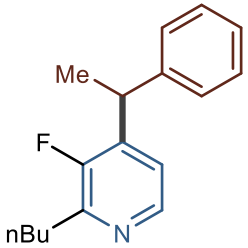

151.38
150.95
144.56
143.69
132.36
128.34
127.69
126.25
121.76
56.17
37.14
23.72
20.21
^{13}C NMR
$CDCl_3$, 100 MHz
Me
MeO
N
Me
3j
S155
$CDCl_3$
f1 (ppm)


8.22 8.21 7.31 7.31 7.29 7.29 7.28 7.27 7.27 7.24 7.23 7.22 7.22 7.21 7.21 7.19 6.96 6.95 6.94 4.46 4.44 2.83 2.83 2.82 2.82 2.81 2.81 2.80 2.80 2.79 2.79 2.78 2.78 2.78 1.70 1.70 1.68 1.68 1.68 1.67 1.66 1.66 1.64 1.64 1.62 1.60 1.41 1.39 1.37 1.35 0.94 0.92 0.92 0.90
^{1}H NMR
$CDCl_3$, 400 MHz
Me
F
nBu
N
3k
S156
1.00 2.01 3.09 1.05 1.04 2.19 2.21 3.30 2.20 3.24
f1 (ppm)


157.17
154.63
150.60
150.43
144.81
144.74
143.55
141.31
141.18
128.69
127.58
126.79
120.96
120.95
37.46
37.44
37.42
31.50
31.48
30.84
30.83
22.71
20.30
14.01
13C NMR
CDCl3, 100 MHz
Me
F
nBu
N
3k
CDCl3
S157
f1 (ppm)

^{19F} NMR

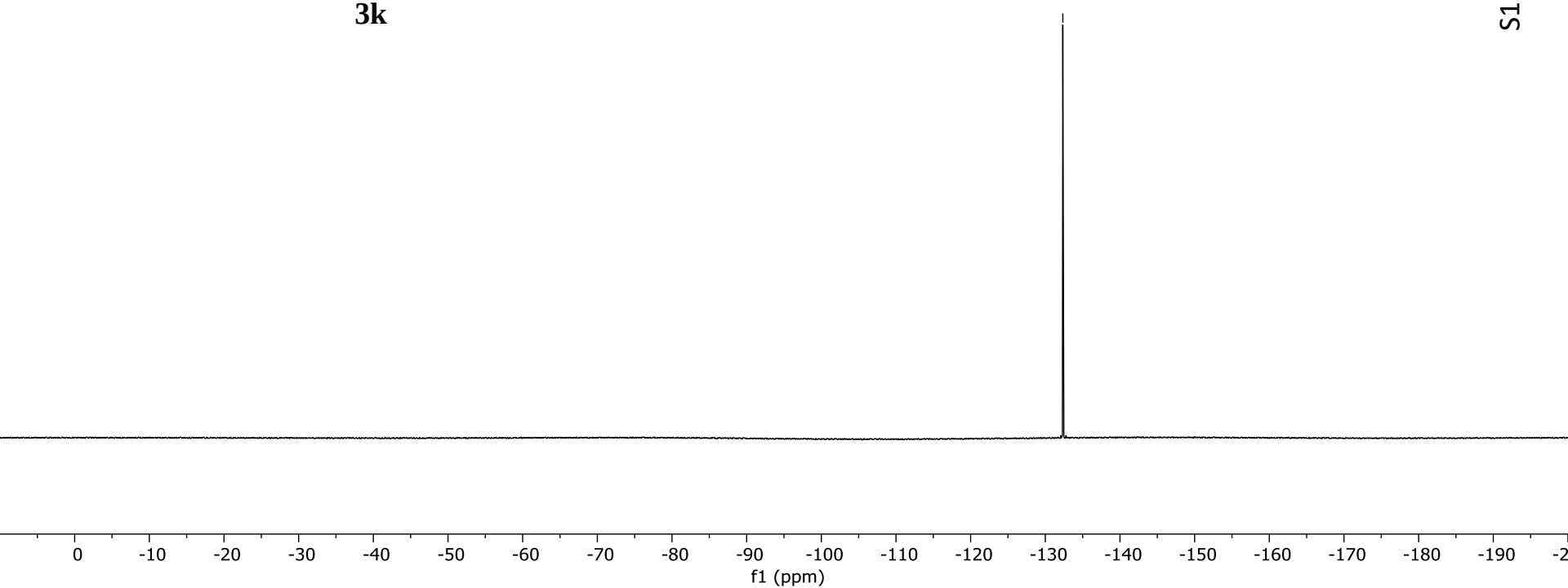
$CDCl_3$, 365 MHz

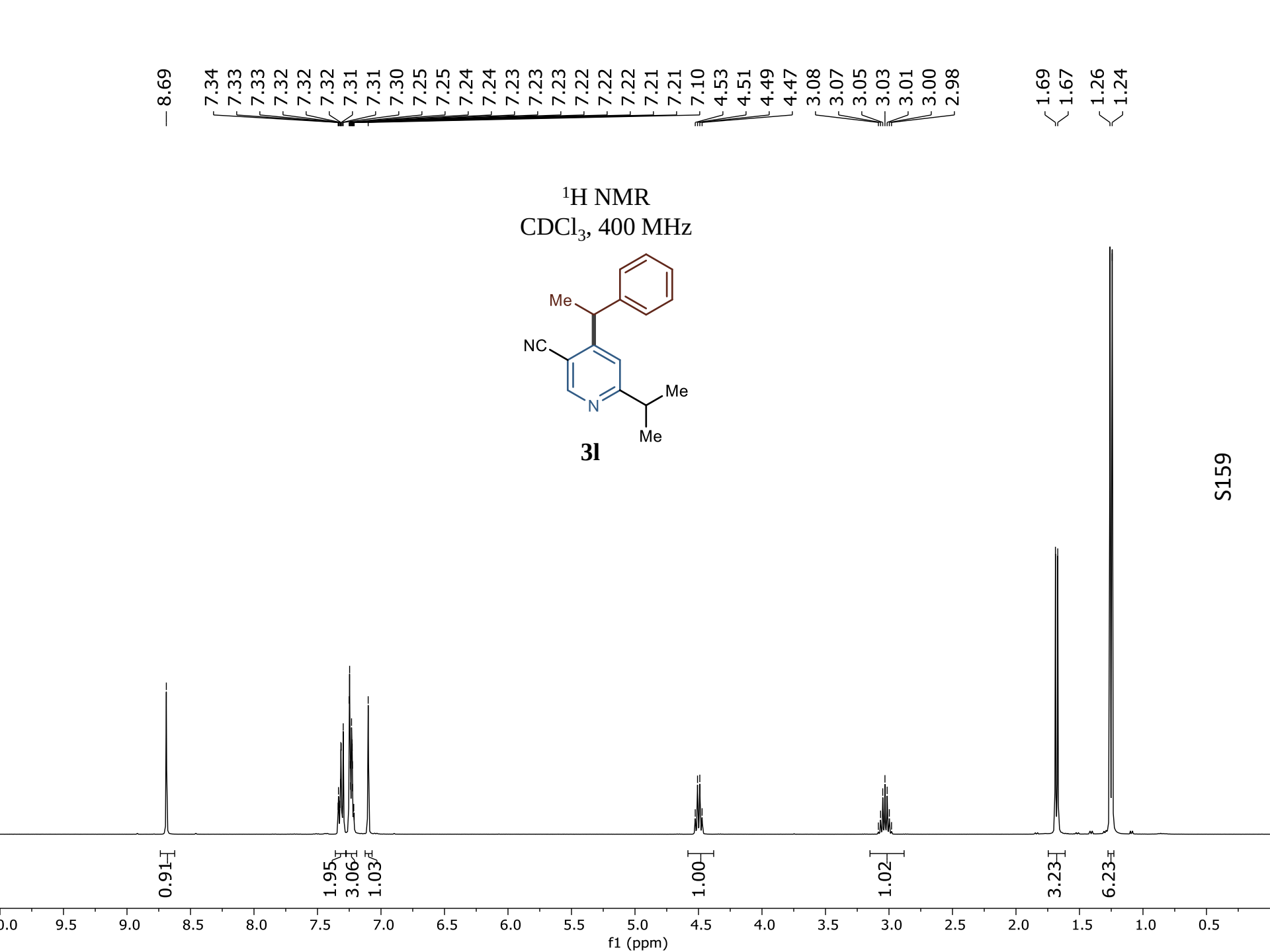


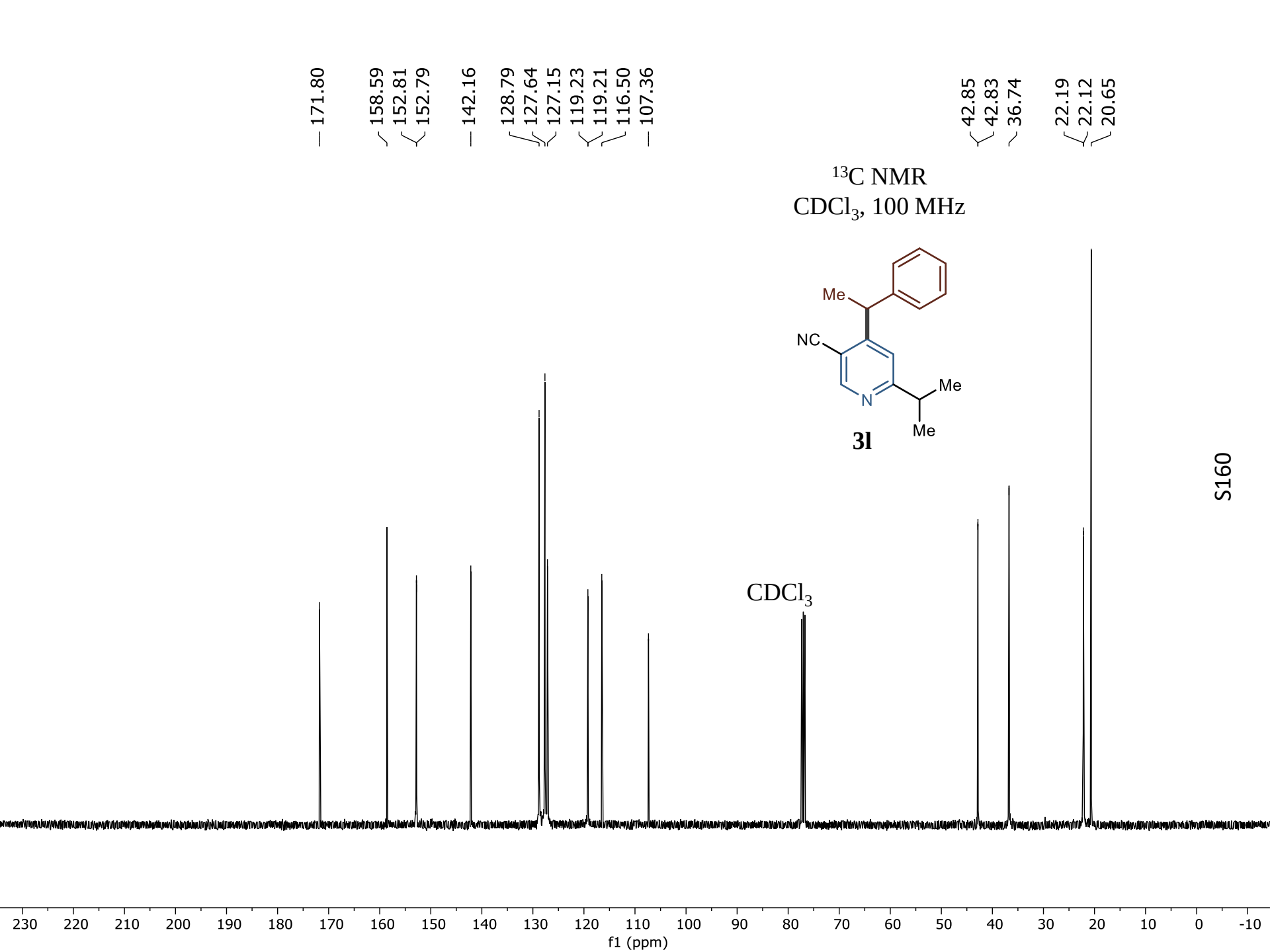
3k

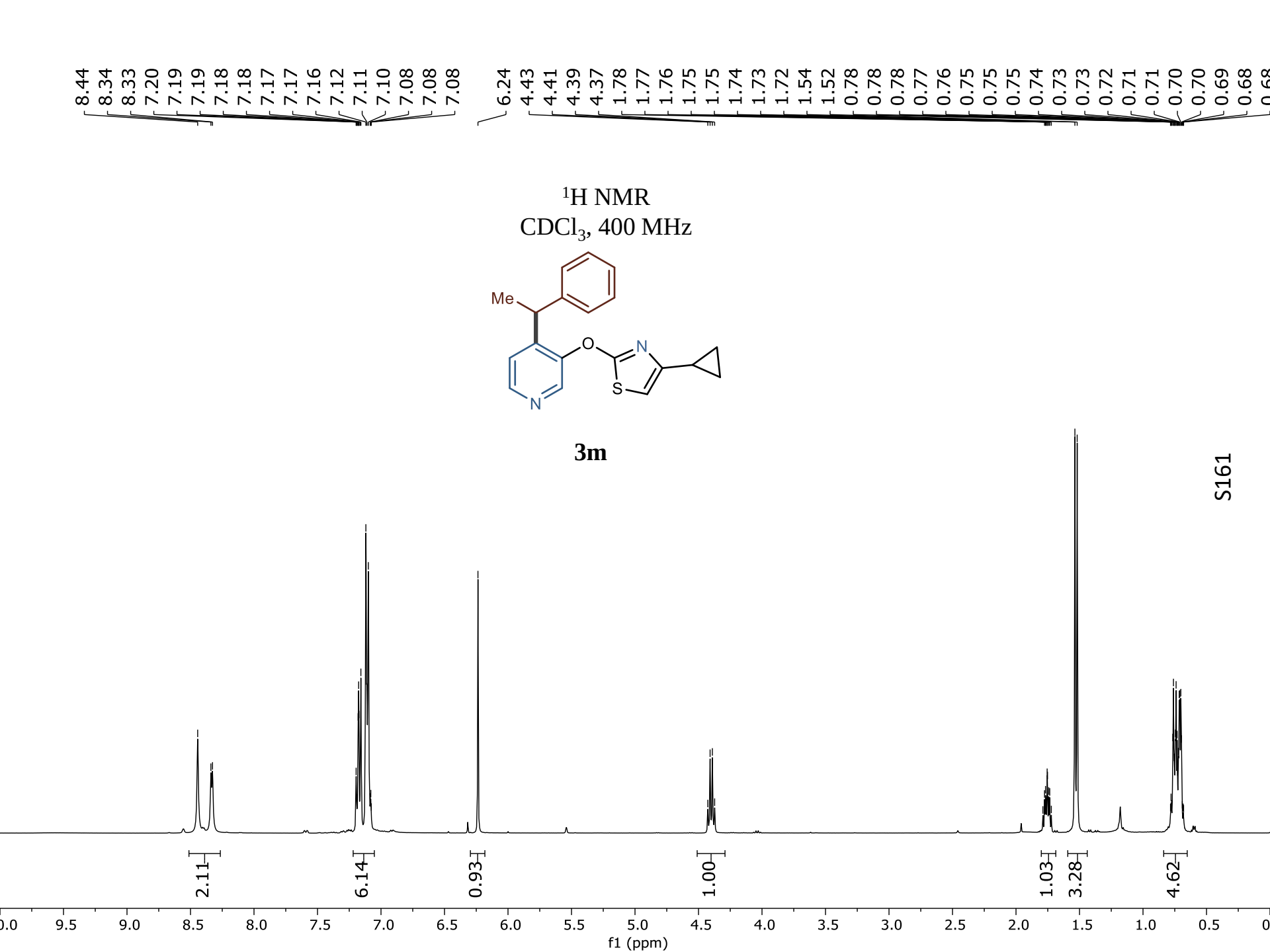
-132.35

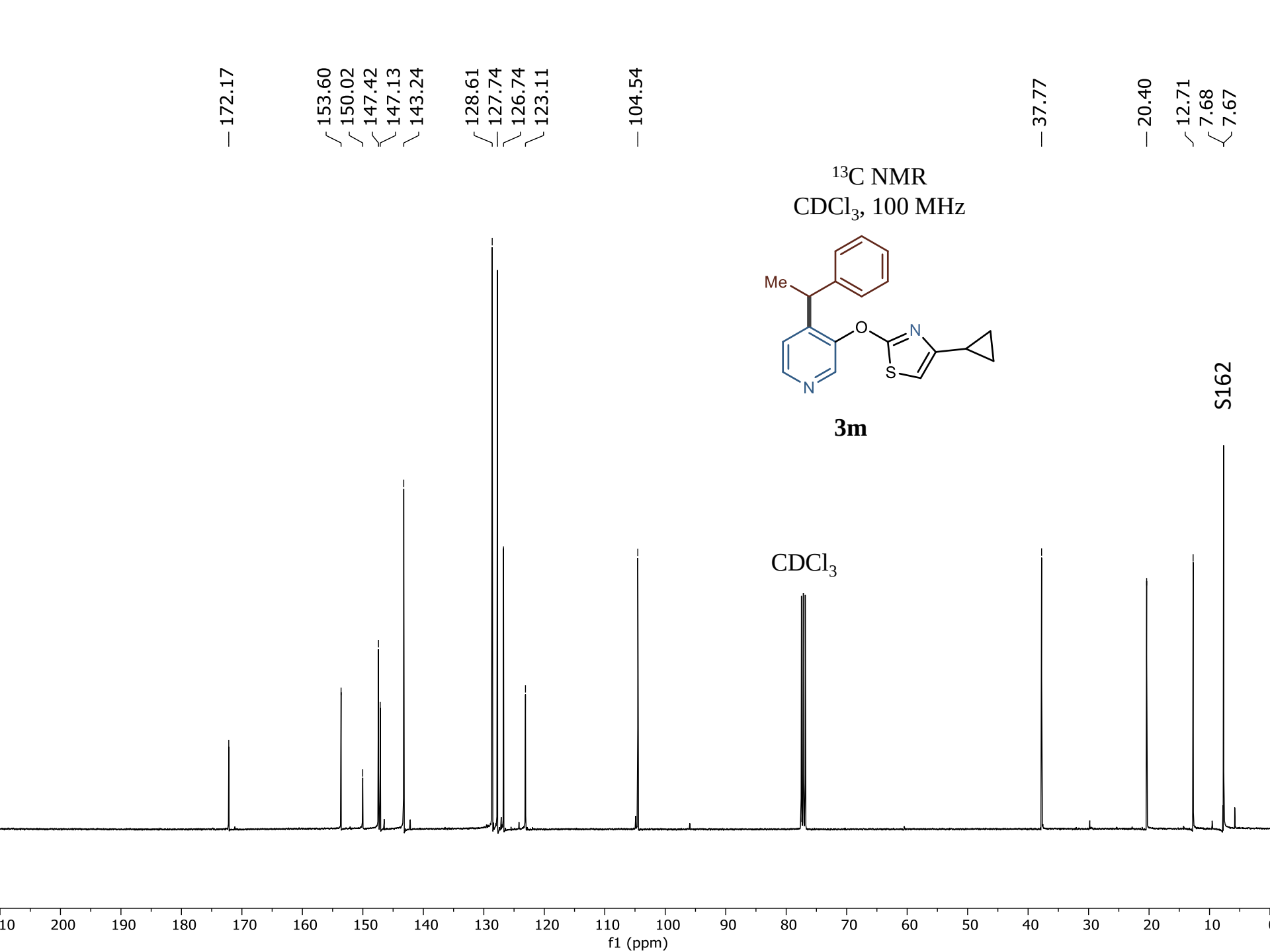
S158




8.69
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.10
4.53
4.51
4.49
4.47
3.08
3.07
3.05
3.03
3.01
3.00
2.98
1.69
1.67
1.26
1.24
1H NMR
CDCl3, 400 MHz
Me
NC
N
Me
Me
3l
S159
0.91
1.95
3.06
1.03
1.00
1.02
3.23
6.23
f1 (ppm)

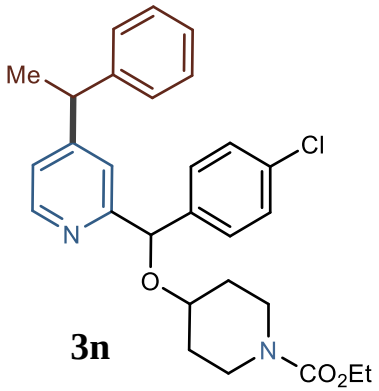

171.80
158.59
152.81
152.79
142.16
128.79
127.64
127.15
119.23
119.21
116.50
107.36
42.85
42.83
36.74
22.19
22.12
20.65
13C NMR
CDCl3, 100 MHz
Me
NC
N
Me
Me
3l
CDCl3
S160
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.44
8.34
8.33
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.12
7.11
7.10
7.08
7.08
7.08
6.24
4.43
4.41
4.39
4.37
1.78
1.77
1.76
1.75
1.75
1.74
1.73
1.72
1.54
1.52
0.78
0.78
0.78
0.77
0.76
0.75
0.75
0.75
0.74
0.73
0.73
0.72
0.71
0.71
0.70
0.70
0.69
0.68
^{1}H NMR
$CDCl_3$, 400 MHz
Me
O
N
S
N
3m
S161
2.11
6.14
0.93
1.00
1.03
3.28
4.62
f1 (ppm)


172.17
153.60
150.02
147.42
147.13
143.24
128.61
127.74
126.74
123.11
104.54
37.77
20.40
12.71
7.68
7.67
S162
^{13}C NMR
$CDCl_3$, 100 MHz
Me
O
N
S
N
3m
$CDCl_3$
f1 (ppm)

8.33 8.31 8.31 8.30 7.28 7.28 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.21 7.20 7.20 7.19 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.13 7.11 7.11 7.09 7.08 7.08 7.06 5.48 5.48 4.07 4.07 4.05 4.05 4.04 4.03 4.03 4.02 4.02 4.01 1.57 1.56 1.54 1.19 1.19 1.18 1.17 1.17 1.16 1.15 1.15

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

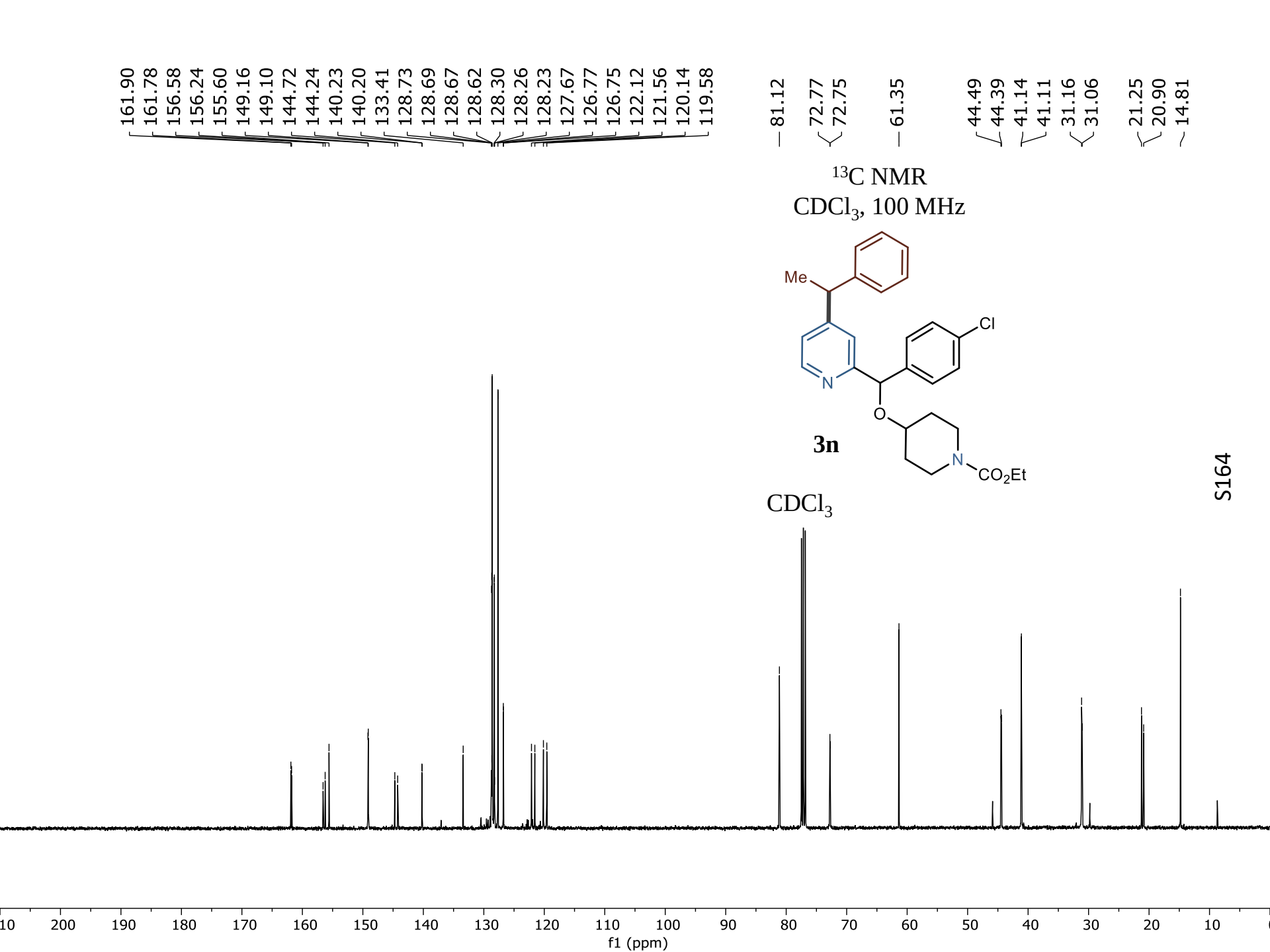


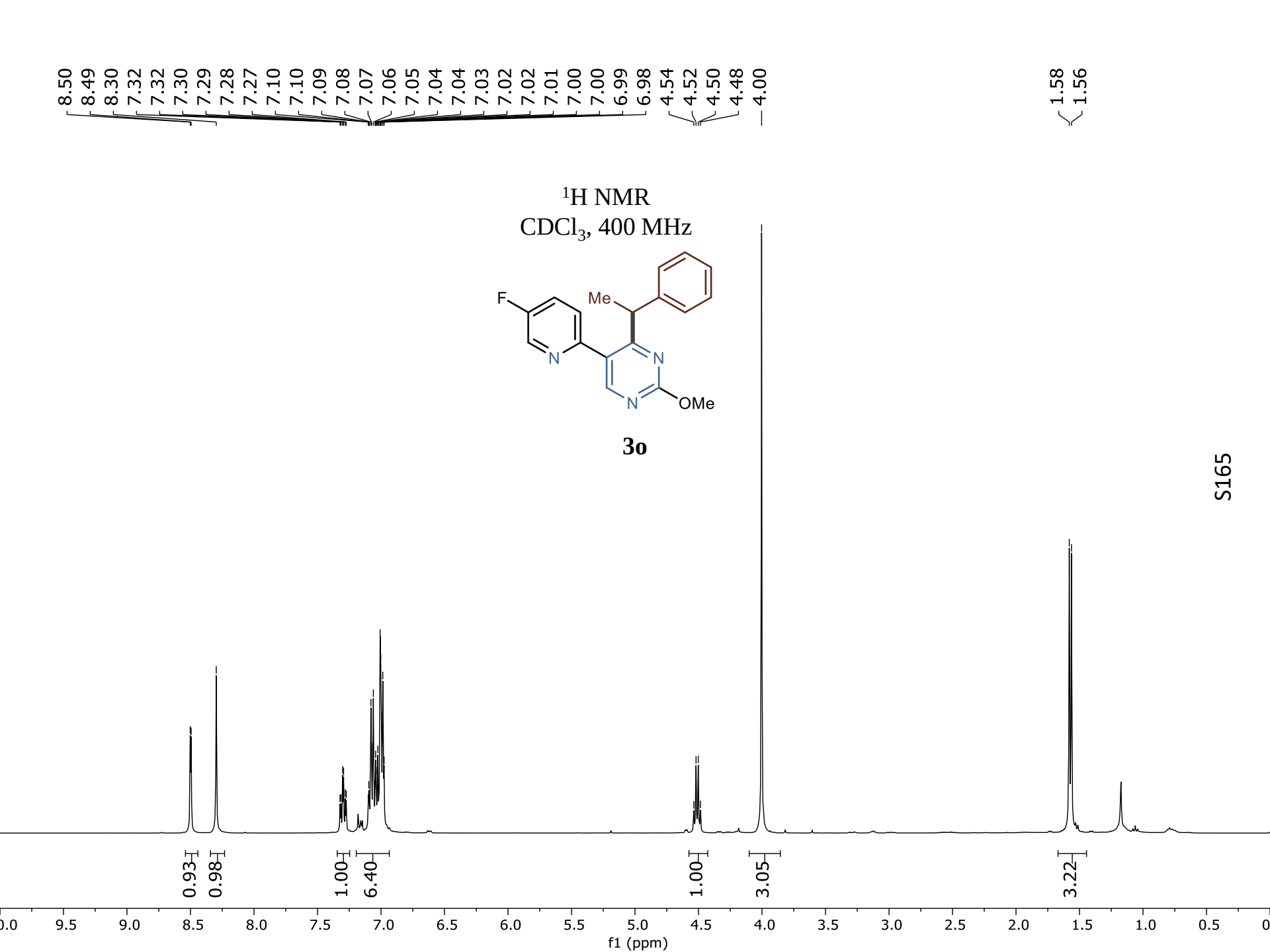
3n

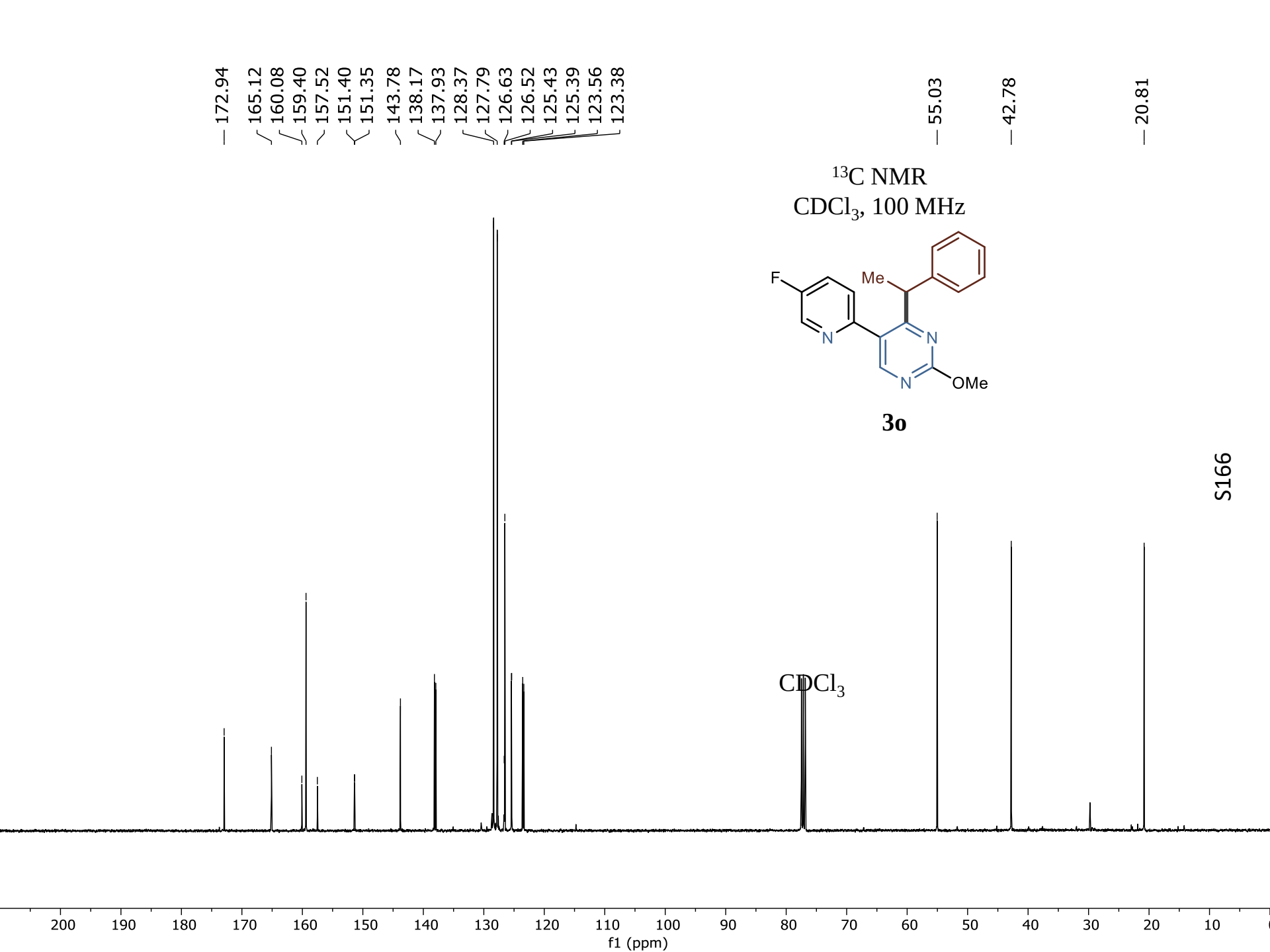
S163

1.00 10.80 1.16 1.02 3.18 2.27 1.08 2.45 1.26 6.41 3.86

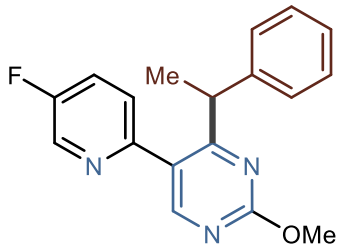
f1 (ppm)


161.90
161.78
156.58
156.24
155.60
149.16
149.10
144.72
144.24
140.23
140.20
133.41
128.73
128.69
128.67
128.62
128.30
128.26
128.23
127.67
126.77
126.75
122.12
121.56
120.14
119.58
81.12
72.77
72.75
61.35
44.49
44.39
41.14
41.11
31.16
31.06
21.25
20.90
14.81
^{13}C NMR
$CDCl_3$, 100 MHz
Me
Cl
N
O
N
CO_2Et
3n
$CDCl_3$
S164
f1 (ppm)


8.50
8.49
8.30
7.32
7.32
7.30
7.29
7.28
7.27
7.10
7.10
7.09
7.08
7.07
7.06
7.05
7.04
7.04
7.03
7.02
7.02
7.01
7.00
7.00
6.99
6.98
4.54
4.52
4.50
4.48
4.00
1.58
1.56
1H NMR
CDCl3, 400 MHz
F
Me
N
N
N
OMe
3o
S165
0.93
0.98
1.00
6.40
1.00
3.05
3.22
f1 (ppm)


172.94
165.12
160.08
159.40
157.52
151.40
151.35
143.78
138.17
137.93
128.37
127.79
126.63
126.52
125.43
125.39
123.56
123.38
55.03
42.78
20.81
13C NMR
CDCl3, 100 MHz
F
Me
N
N
N
OMe
3o
S166
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

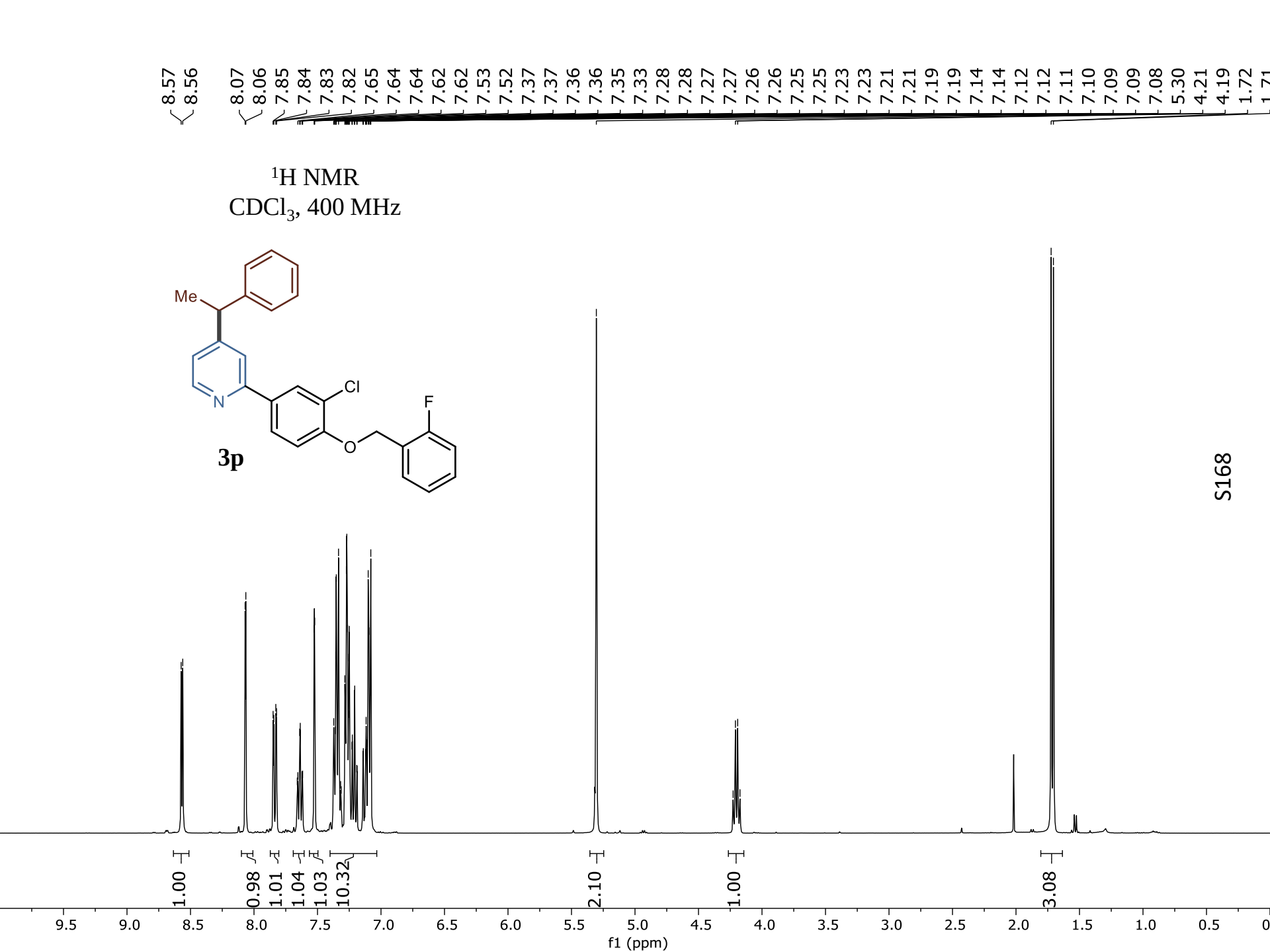
^{19}F NMR
$CDCl_3$, 365 MHz

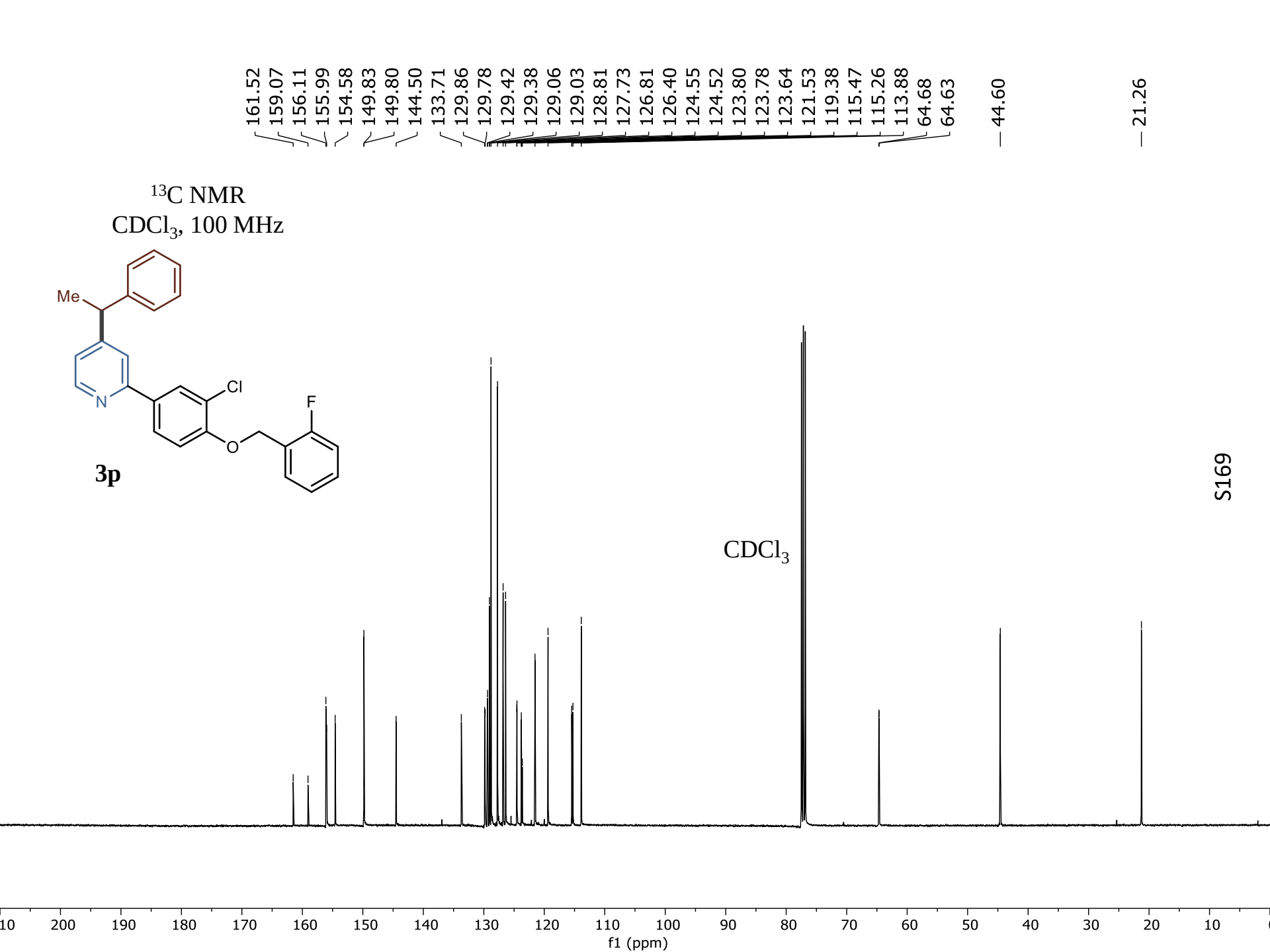


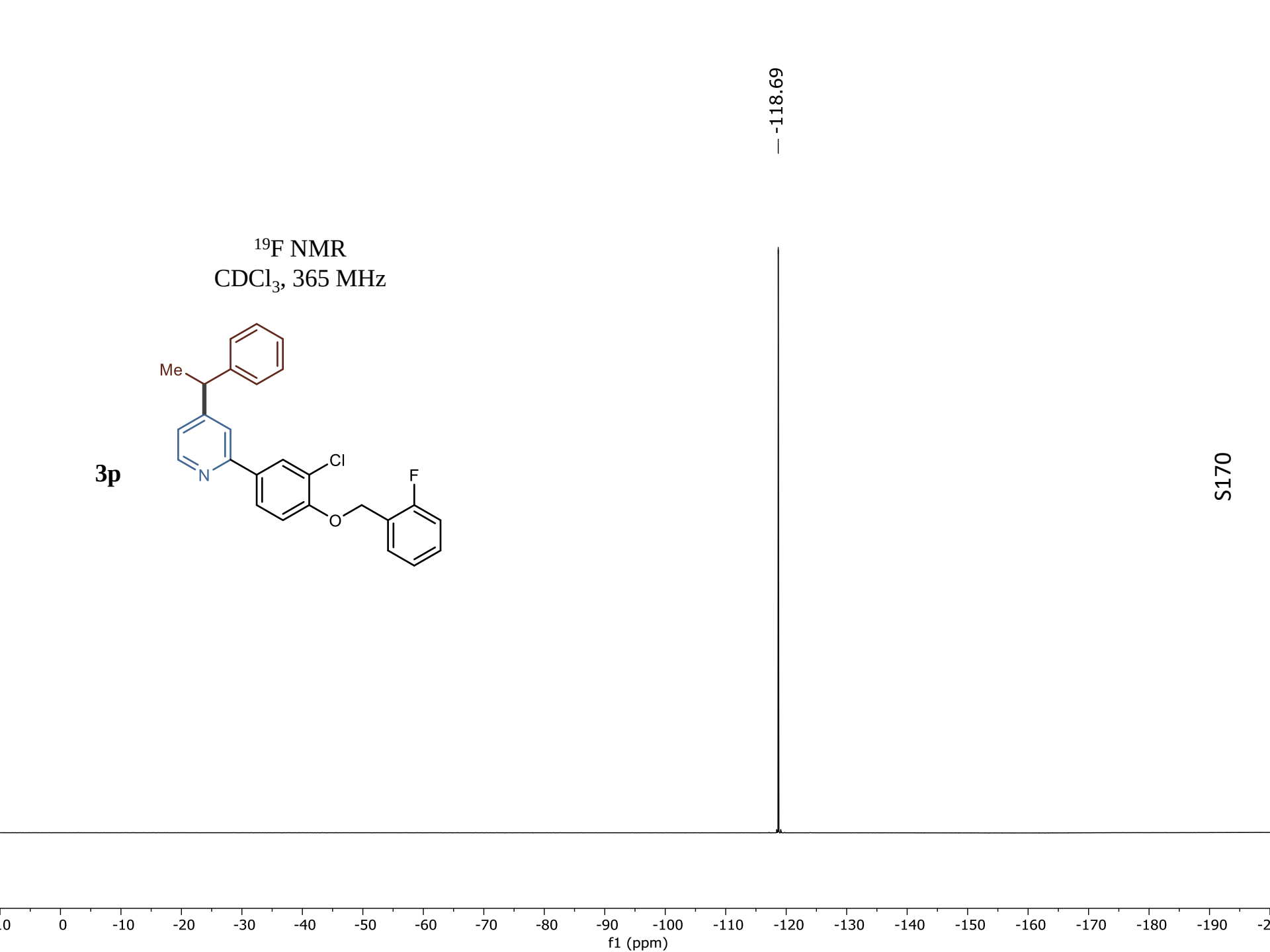
3o

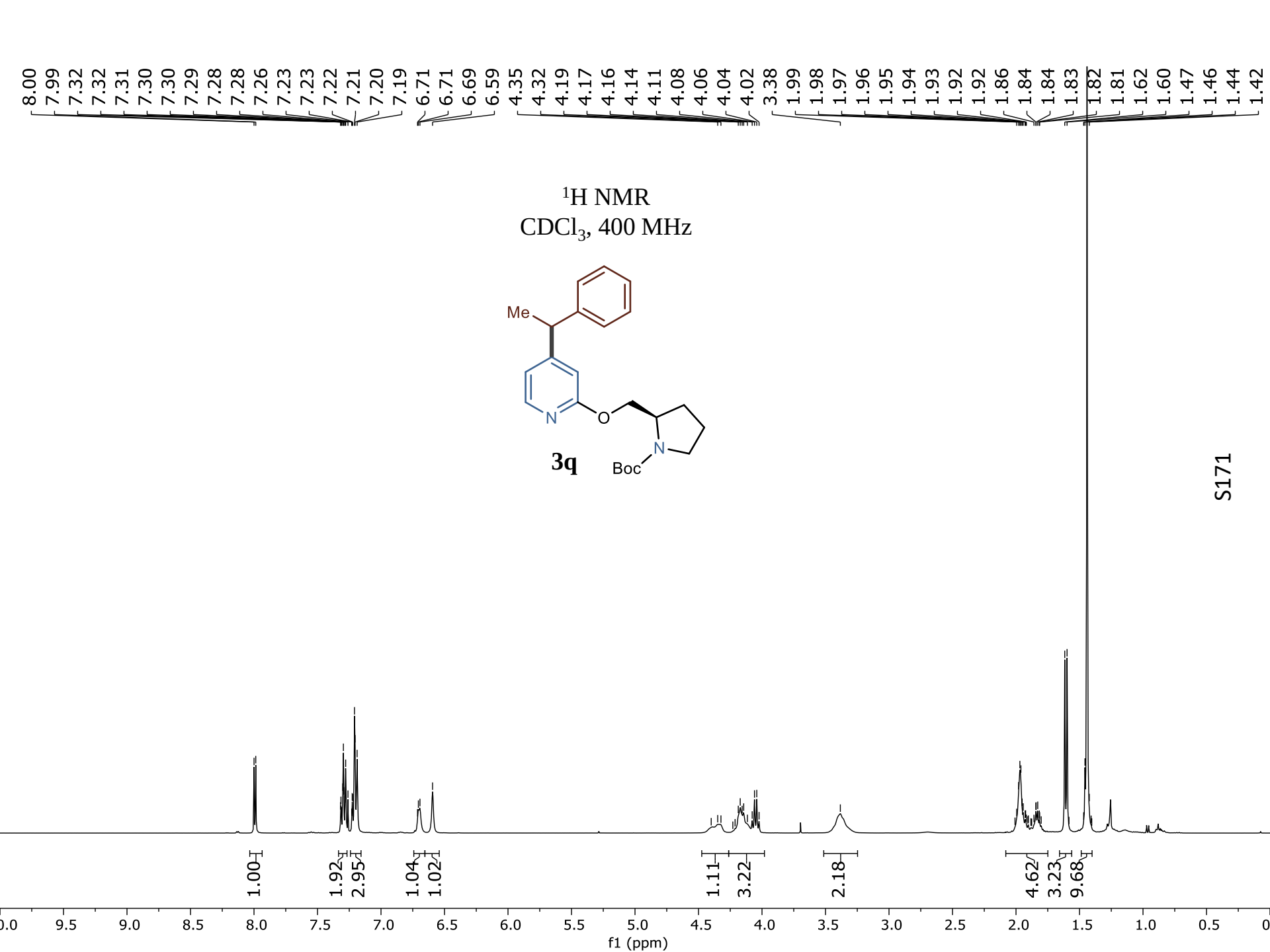
-128.14

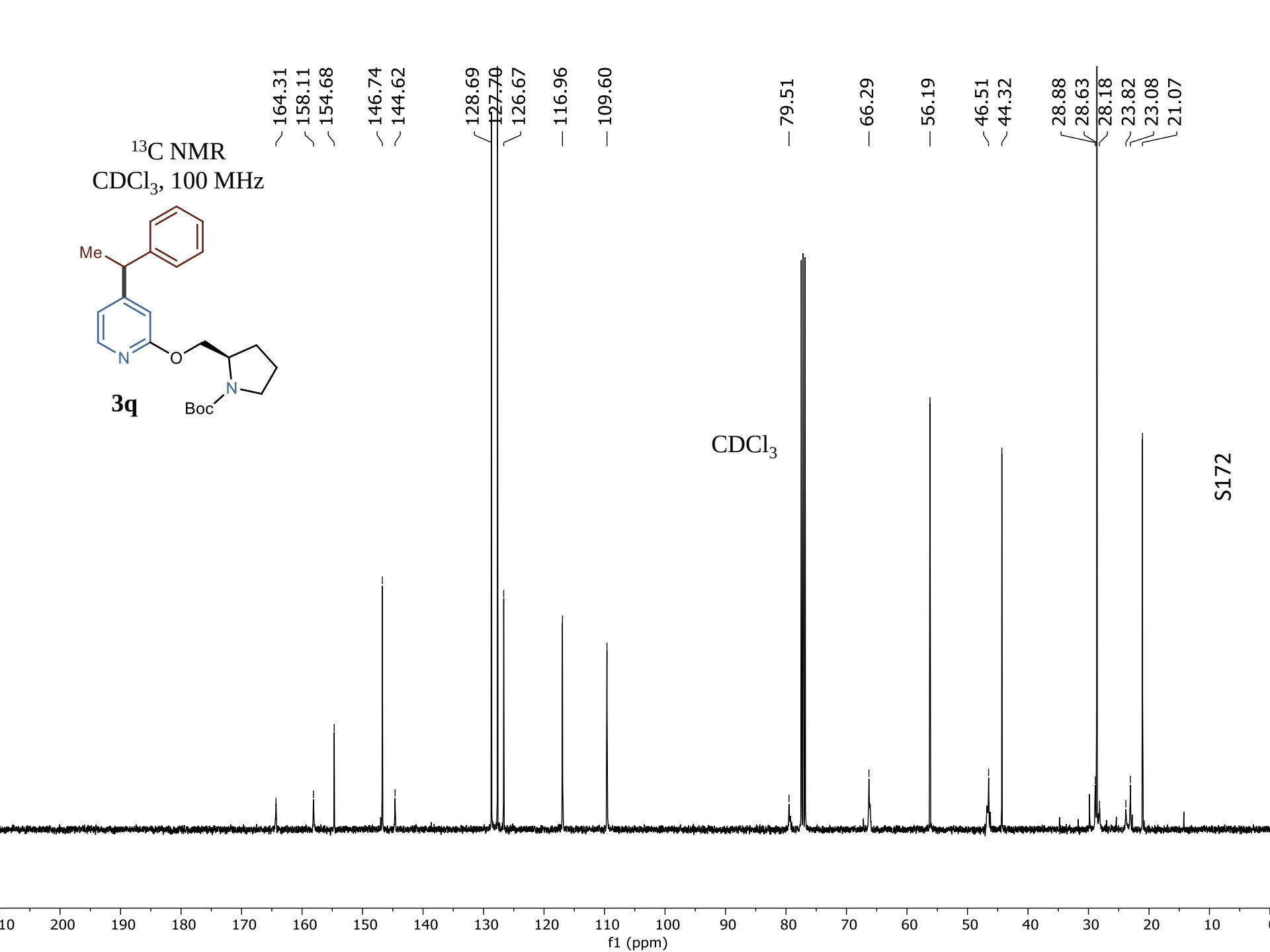
S167

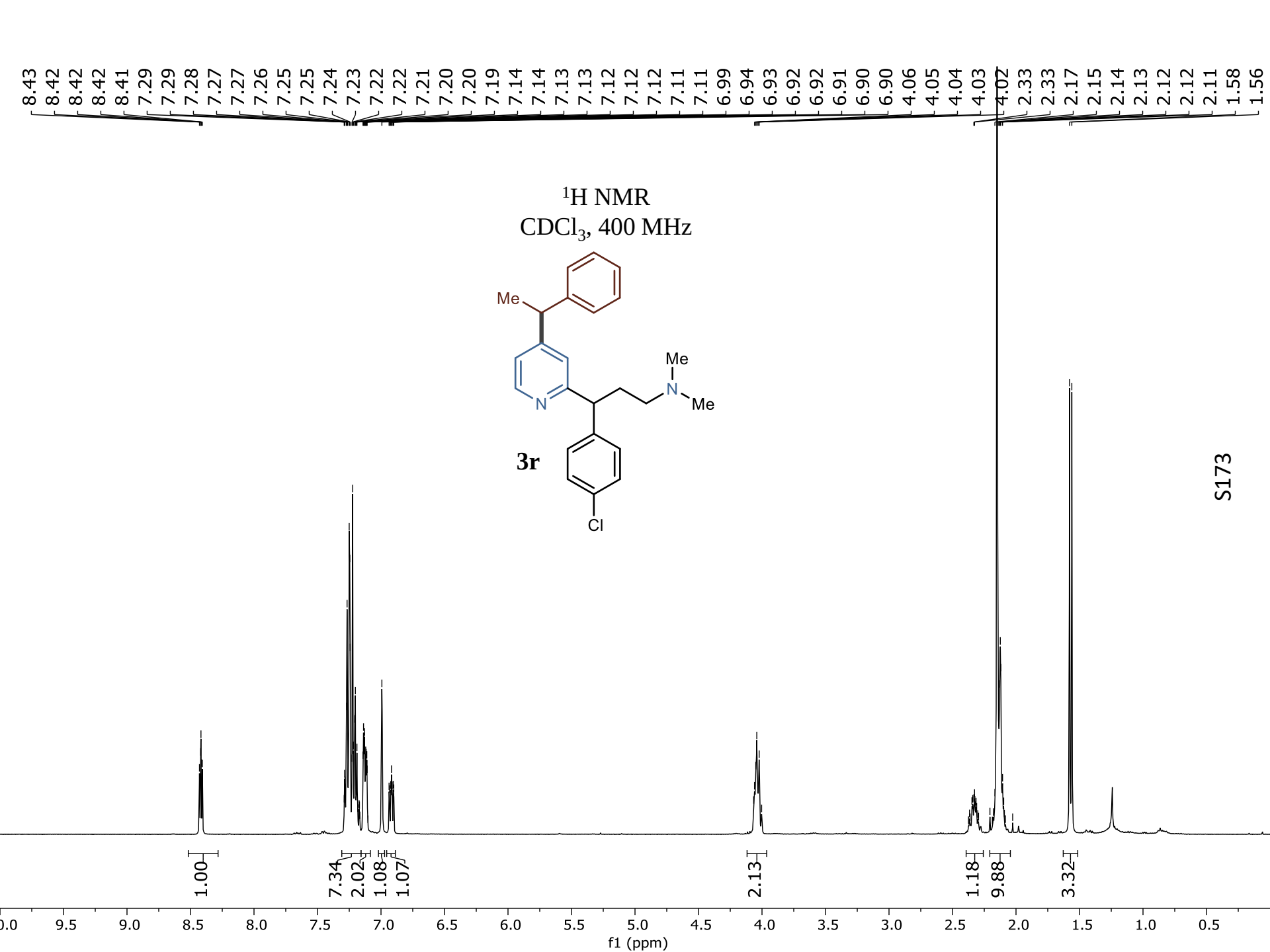

8.57
8.56
8.07
8.06
7.85
7.84
7.83
7.82
7.65
7.64
7.64
7.62
7.62
7.53
7.52
7.37
7.37
7.36
7.36
7.35
7.33
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.23
7.23
7.21
7.21
7.19
7.19
7.14
7.14
7.12
7.12
7.11
7.10
7.09
7.09
7.08
5.30
4.21
4.19
1.72
1H NMR
CDCl3, 400 MHz
Me
N
Cl
F
O
3p
S168
1.00
0.98
1.01
1.04
1.03
10.32
2.10
1.00
3.08
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
f1 (ppm)

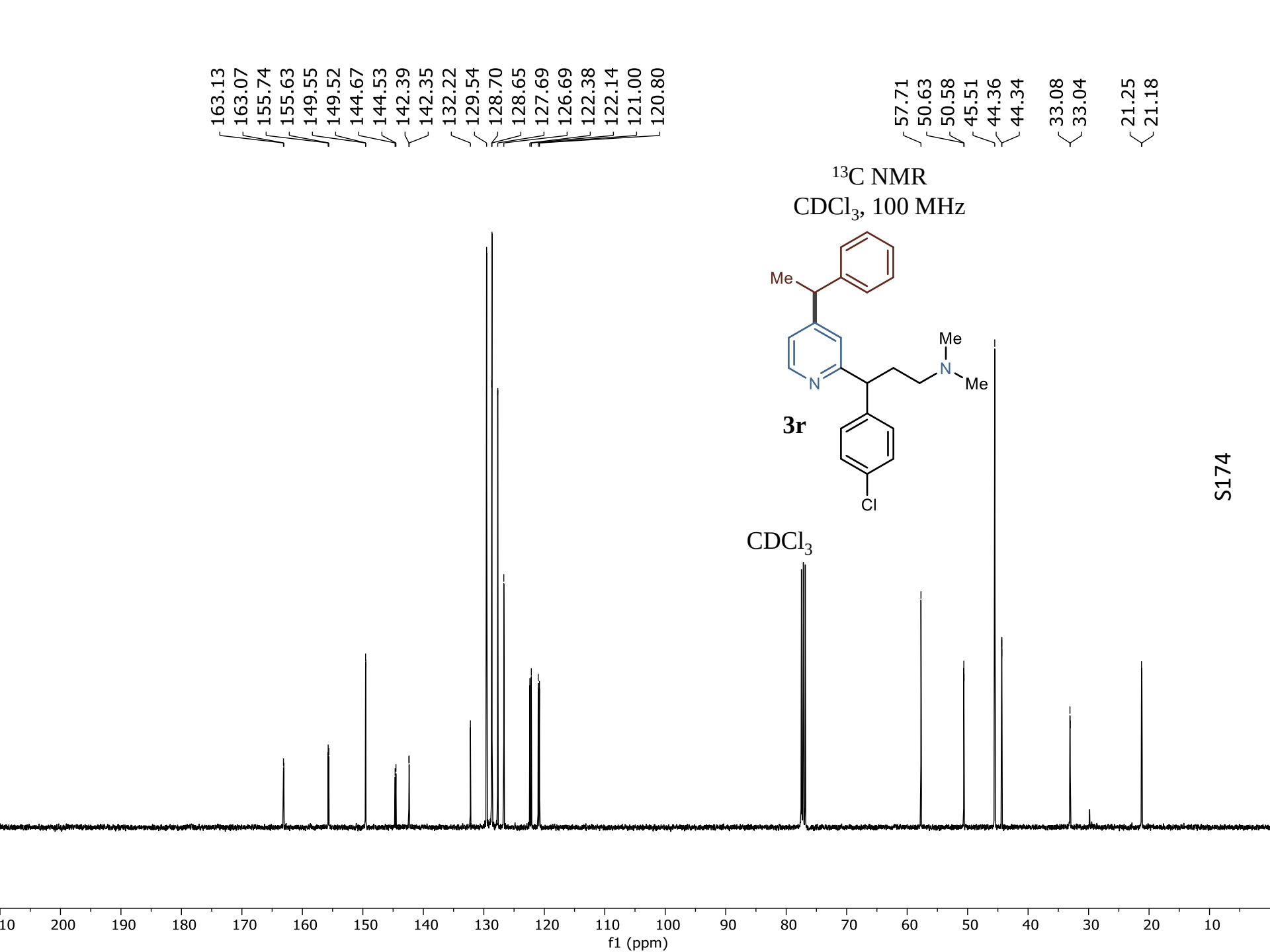

161.52
159.07
156.11
155.99
154.58
149.83
149.80
144.50
133.71
129.86
129.78
129.42
129.38
129.06
129.03
128.81
127.73
126.81
126.40
124.55
124.52
123.80
123.78
123.64
121.53
119.38
115.47
115.26
113.88
64.68
64.63
44.60
21.26
13C NMR
CDCl3, 100 MHz
Me
N
Cl
F
O
3p
CDCl3
S169
f1 (ppm)

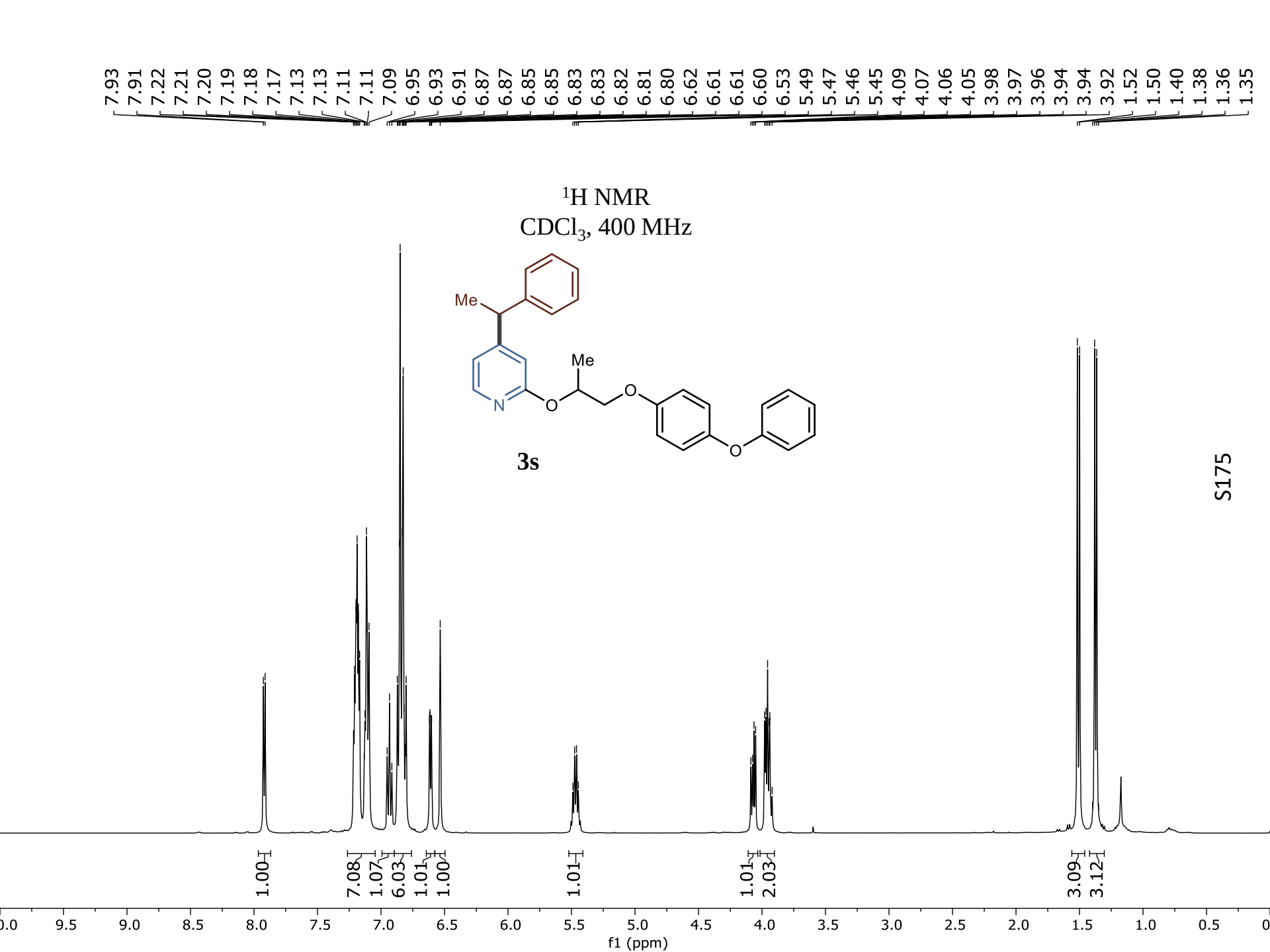

-118.69
^{19}F NMR
$CDCl_3$, 365 MHz
3p
Me
N
Cl
F
O
S170
f1 (ppm)

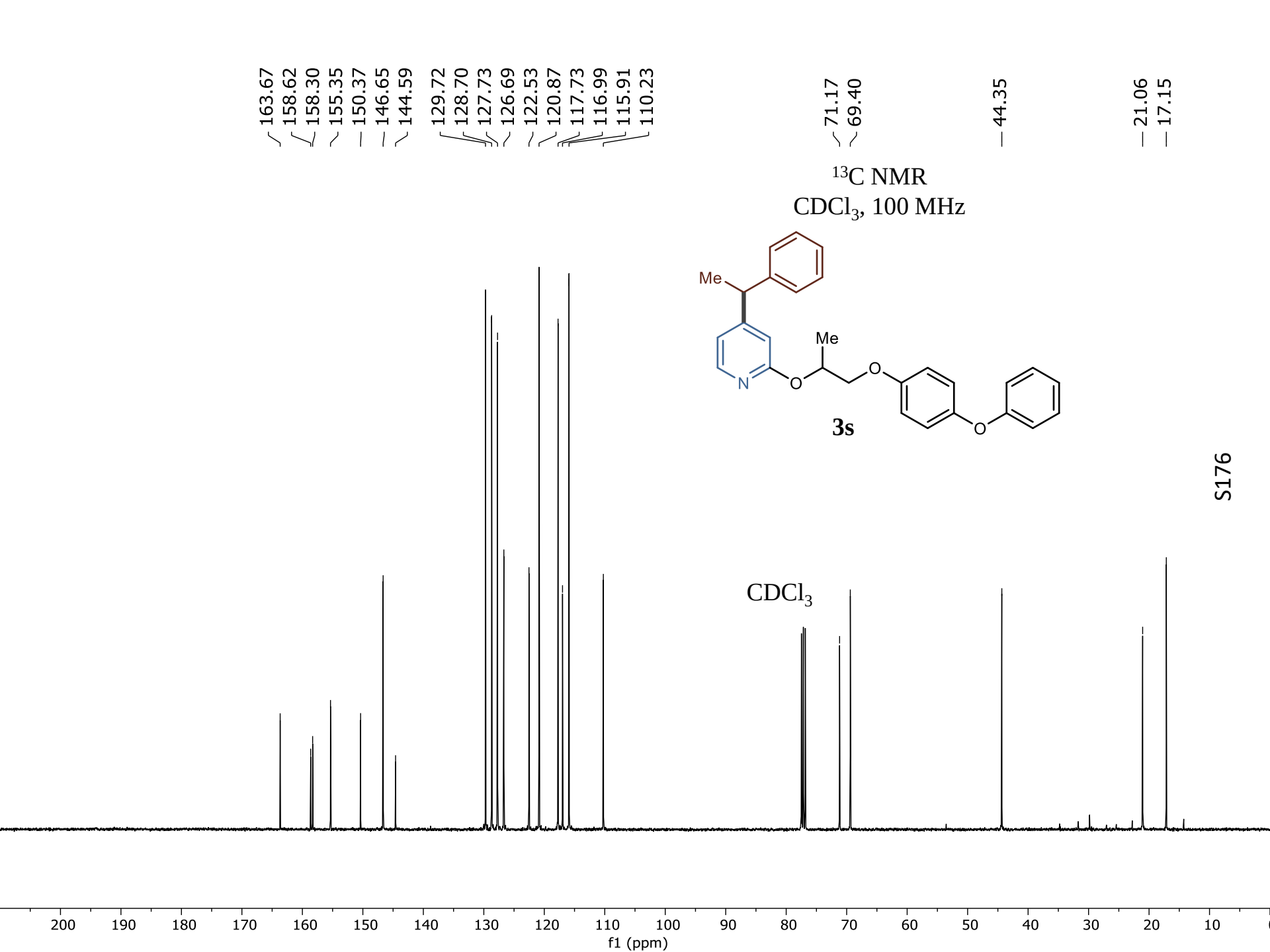

8.00 7.99 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.28 7.26 7.23 7.23 7.22 7.21 7.20 7.19 6.71 6.71 6.69 6.59 4.35 4.32 4.19 4.17 4.16 4.14 4.11 4.08 4.06 4.04 4.02 3.38 1.99 1.98 1.97 1.96 1.95 1.94 1.93 1.92 1.92 1.86 1.84 1.84 1.83 1.82 1.81 1.62 1.60 1.47 1.46 1.44 1.42
1H NMR
CDCl3, 400 MHz
Me
N
O
N
Boc
3q
S171
1.00 1.92 2.95 1.04 1.02 1.11 3.22 2.18 4.62 3.23 9.68
f1 (ppm)


164.31
158.11
154.68
146.74
144.62
128.69
127.70
126.67
116.96
109.60
79.51
66.29
56.19
46.51
44.32
28.88
28.63
28.18
23.82
23.08
21.07
13C NMR
CDCl3, 100 MHz
Me
N
O
N
Boc
3q
CDCl3
S172
f1 (ppm)


8.43 8.42 8.42 8.42 8.41 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.14 7.14 7.13 7.13 7.12 7.12 7.12 7.11 7.11 6.99 6.94 6.93 6.92 6.92 6.91 6.90 6.90 4.06 4.05 4.04 4.03 4.02 2.33 2.33 2.17 2.15 2.14 2.13 2.12 2.12 2.11 1.58 1.56
1H NMR
CDCl3, 400 MHz
Me
Me
N
Me
N
Cl
3r
S173
1.00
7.34
2.02
1.08
1.07
2.13
1.18
9.88
3.32
f1 (ppm)


163.13
163.07
155.74
155.63
149.55
149.52
144.67
144.53
142.39
142.35
132.22
129.54
128.70
128.65
127.69
126.69
122.38
122.14
121.00
120.80
57.71
50.63
50.58
45.51
44.36
44.34
33.08
33.04
21.25
21.18
13C NMR
CDCl3, 100 MHz
Me
N
Me
N
Me
3r
Cl
CDCl3
S174
f1 (ppm)


7.93
7.91
7.22
7.21
7.20
7.19
7.18
7.17
7.13
7.13
7.11
7.11
7.09
6.95
6.93
6.91
6.87
6.87
6.85
6.85
6.83
6.83
6.82
6.81
6.80
6.62
6.61
6.61
6.60
6.53
5.49
5.47
5.46
5.45
4.09
4.07
4.06
4.05
3.98
3.97
3.96
3.94
3.94
3.92
1.52
1.50
1.40
1.38
1.36
1.35
1H NMR
CDCl3, 400 MHz
Me
Me
N
O
O
O
3s
S175
1.00
7.08
1.07
6.03
1.01
1.00
1.01
1.01
2.03
3.09
3.12
f1 (ppm)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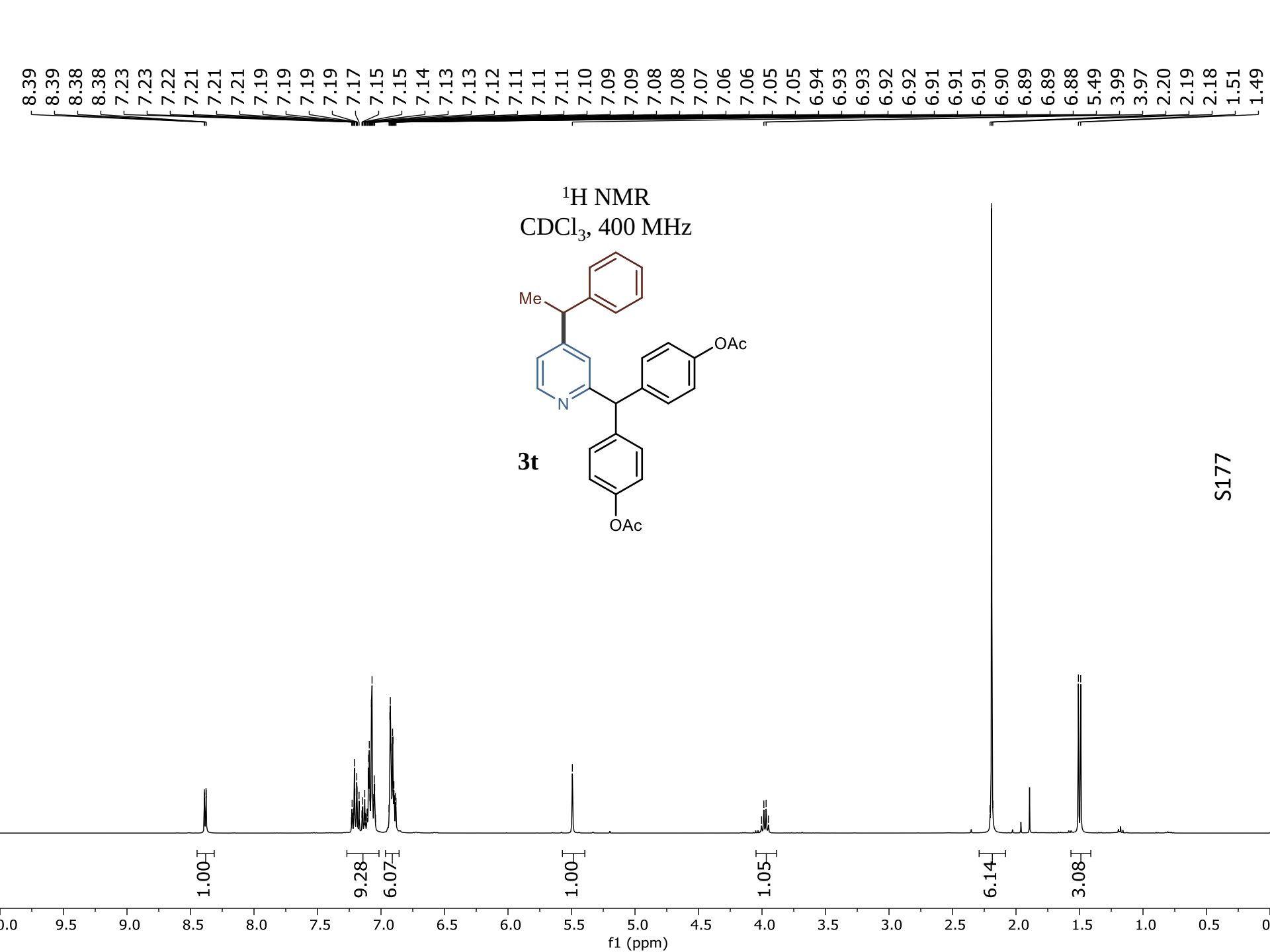
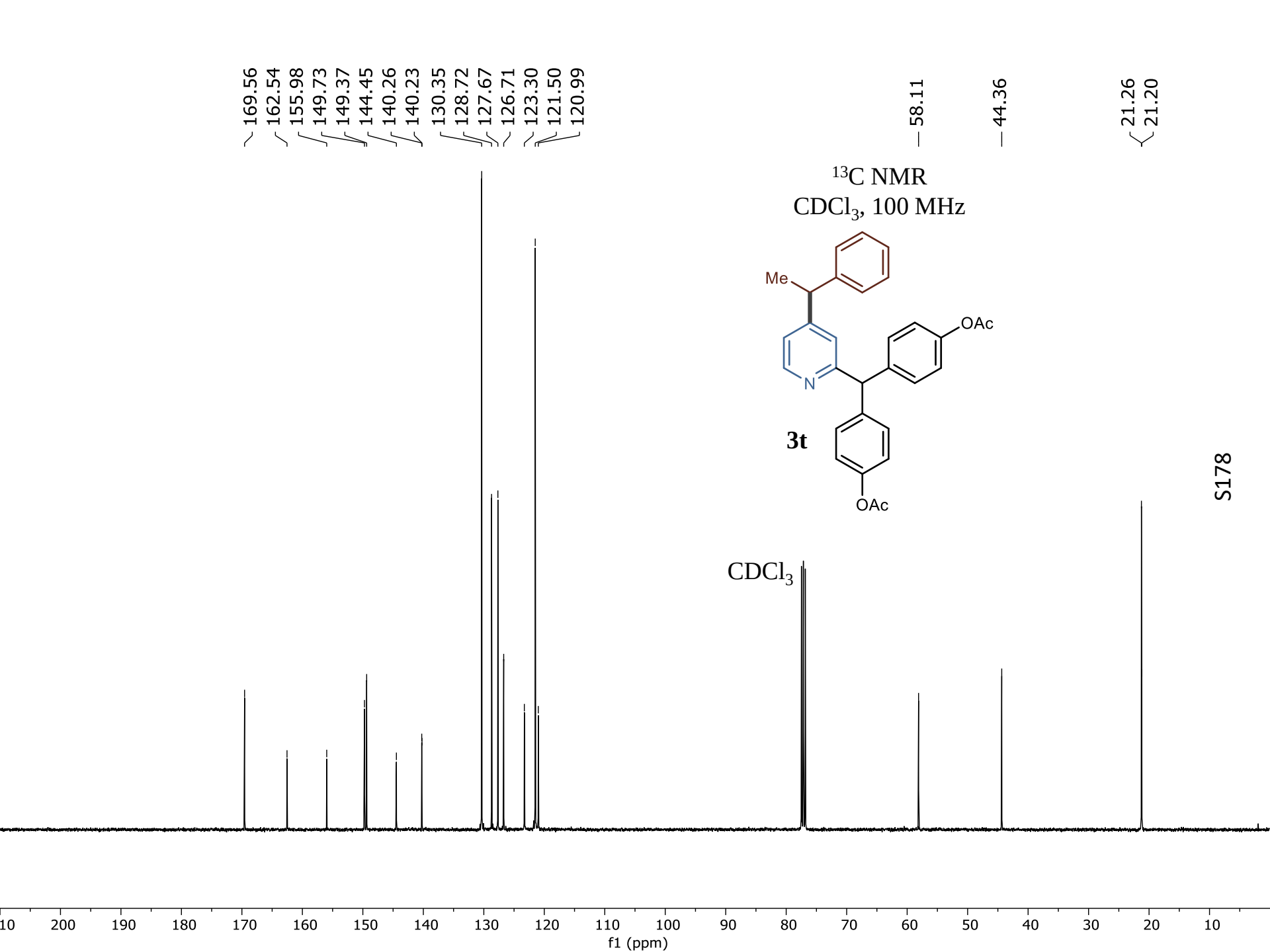
158.62
158.30
155.35
150.37
146.65
144.59
129.72
128.70
127.73
126.69
122.53
120.87
117.73
116.99
115.91
110.23
71.17
69.40
44.35
21.06
17.15
^{13}C NMR
$CDCl_3$, 100 MHz
Me
Me
N
O
O
O
O
3s
S176
$CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.39 8.39 8.38 8.38 7.23 7.23 7.22 7.21 7.21 7.21 7.19 7.19 7.19 7.19 7.17 7.15 7.15 7.14 7.13 7.13 7.12 7.11 7.11 7.11 7.10 7.09 7.09 7.08 7.08 7.07 7.06 7.06 7.05 7.05 6.94 6.93 6.93 6.92 6.92 6.91 6.91 6.91 6.90 6.89 6.89 6.88 5.49 3.99 3.97 2.20 2.19 2.18 1.51 1.49
1H NMR
CDCl3, 400 MHz
Me
OAc
N
OAc
3t
S177
1.00
9.28
6.07
1.00
1.05
6.14
3.08
f1 (ppm)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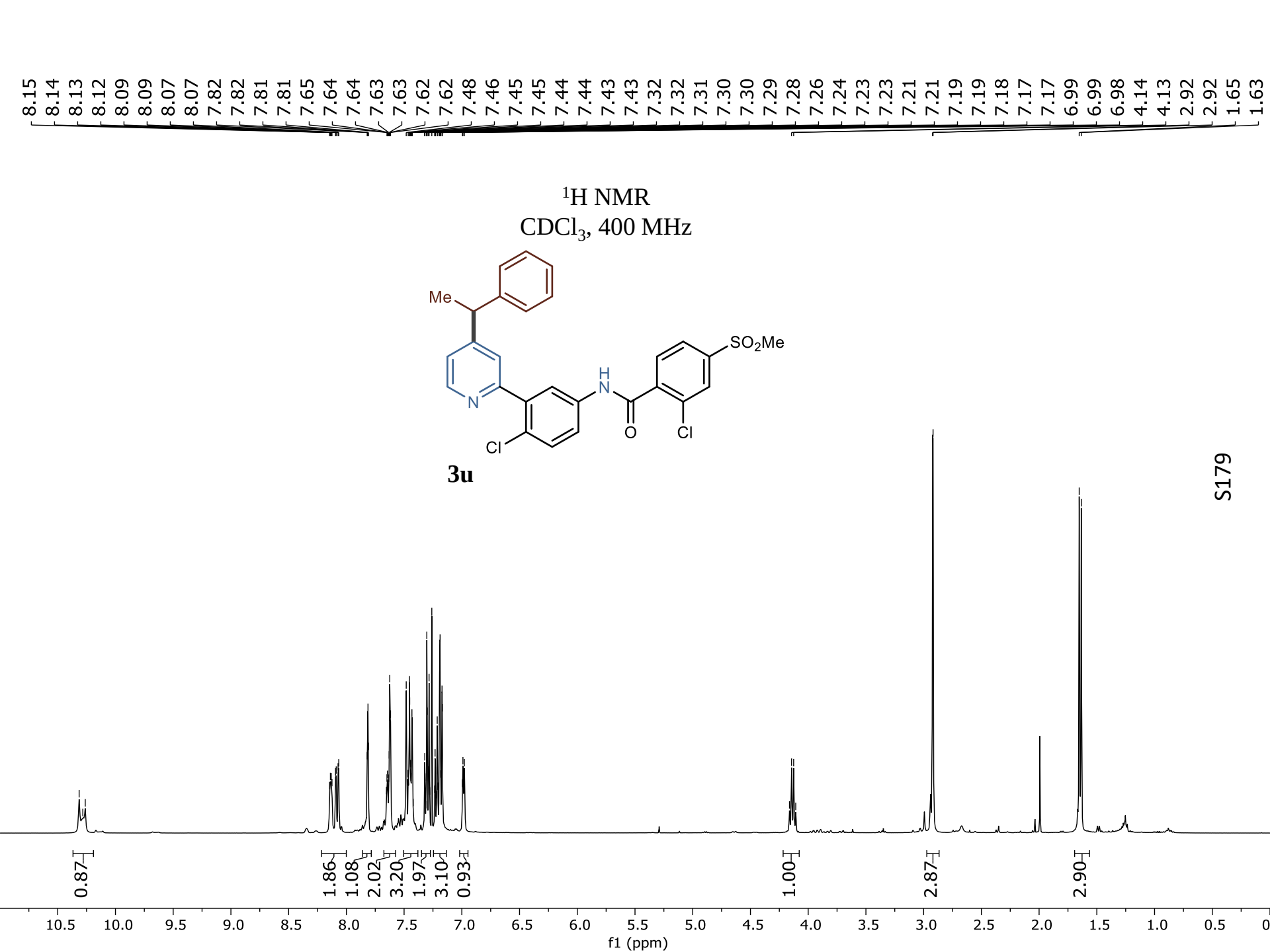
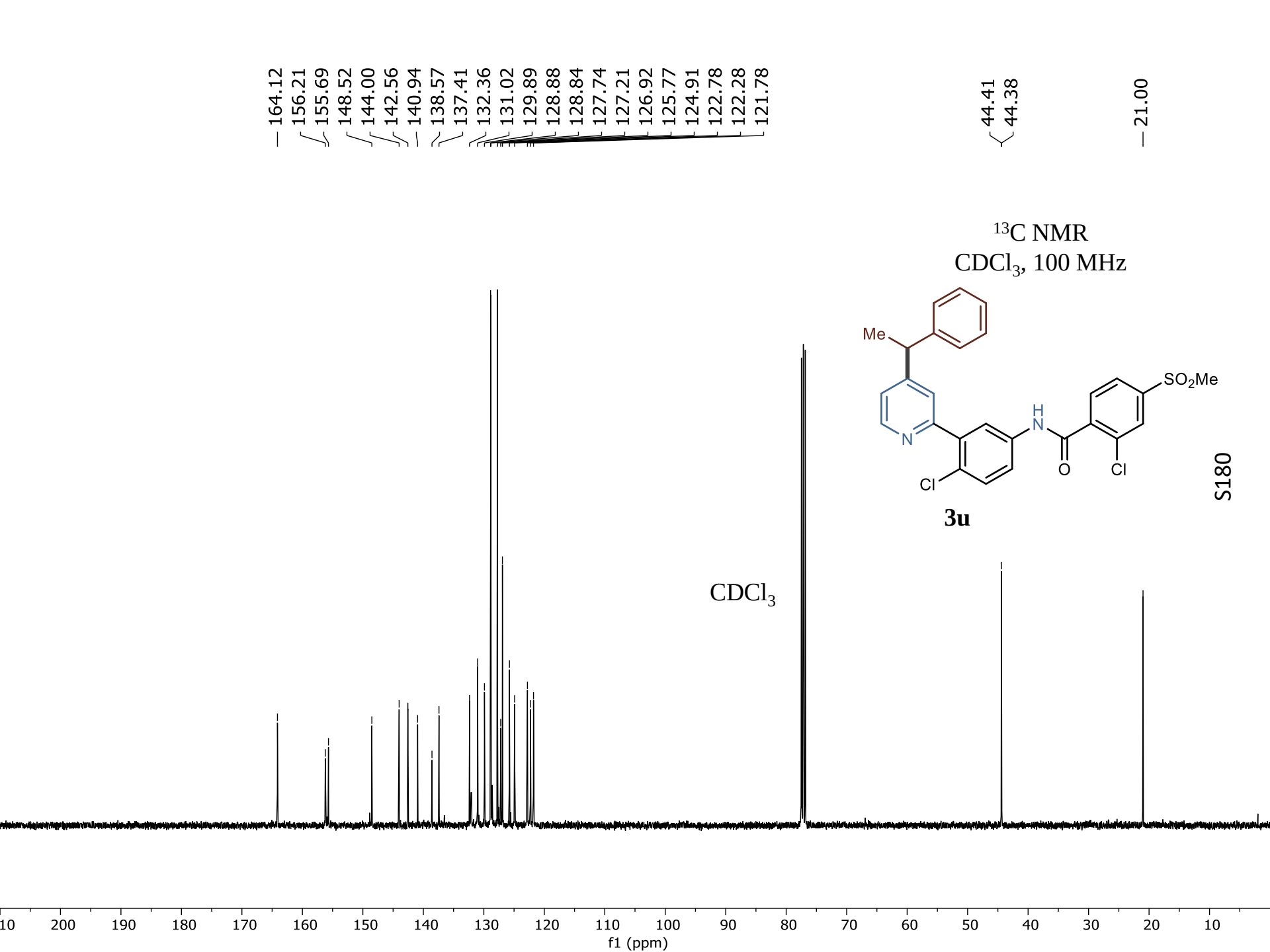
149.73
149.37
144.45
140.26
140.23
130.35
128.72
127.67
126.71
123.30
121.50
120.99
58.11
44.36
21.26
21.20
13C NMR
CDCl3, 100 MHz
Me
OAc
N
OAc
3t
CDCl3
S178
f1 (ppm)


8.15 8.14 8.13 8.12 8.09 8.09 8.07 8.07 7.82 7.82 7.81 7.81 7.65 7.64 7.64 7.63 7.63 7.62 7.62 7.48 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.26 7.24 7.23 7.23 7.21 7.21 7.19 7.19 7.18 7.17 7.17 6.99 6.99 6.98 4.14 4.13 2.92 2.92 1.65 1.63
1H NMR
CDCl3, 400 MHz
Me
SO2Me
H
N
N
O
Cl
Cl
3u
S179
0.87
1.86
1.08
2.02
3.20
1.97
3.10
0.93
1.00
2.87
2.90
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
f1 (ppm)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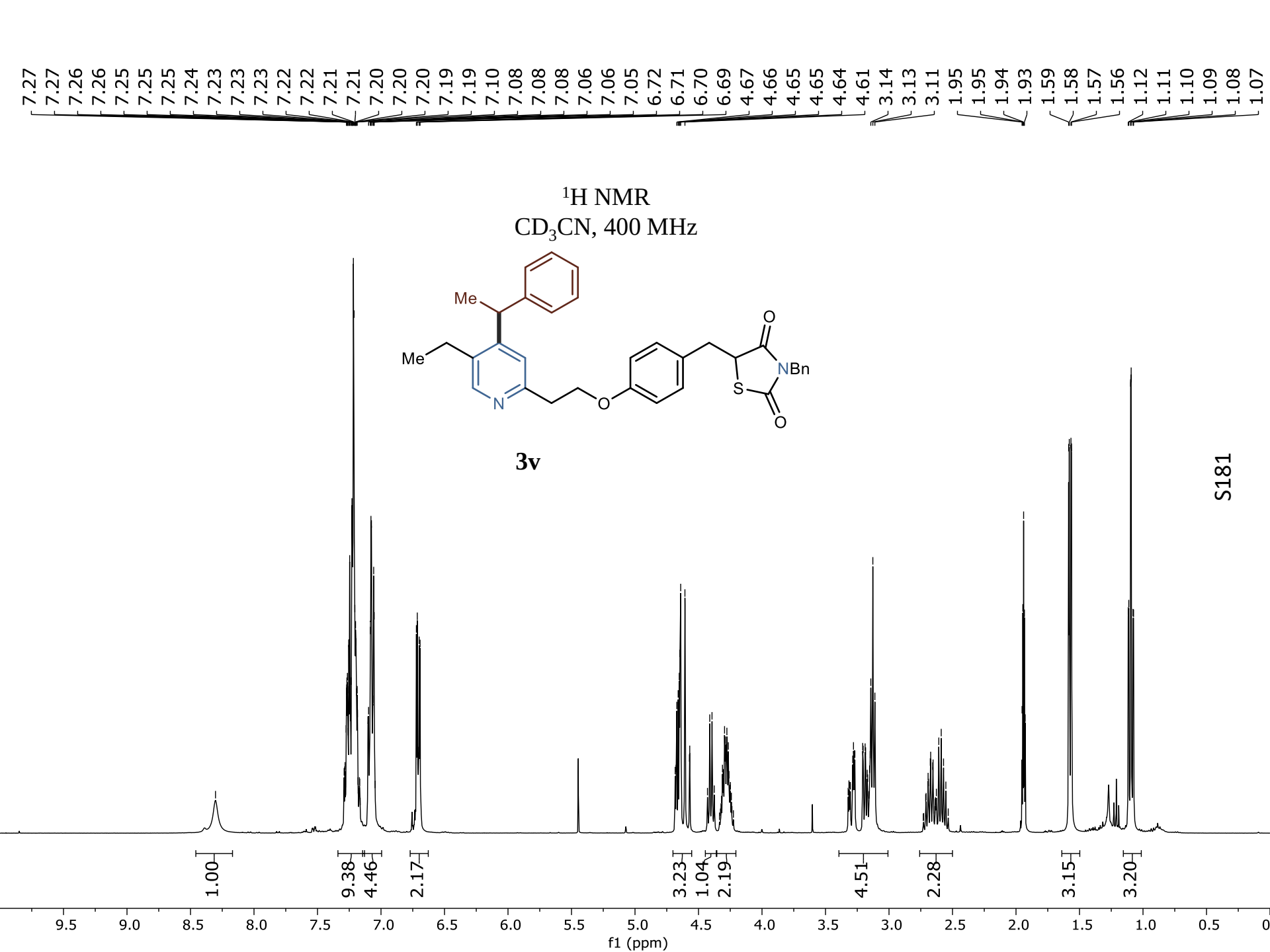
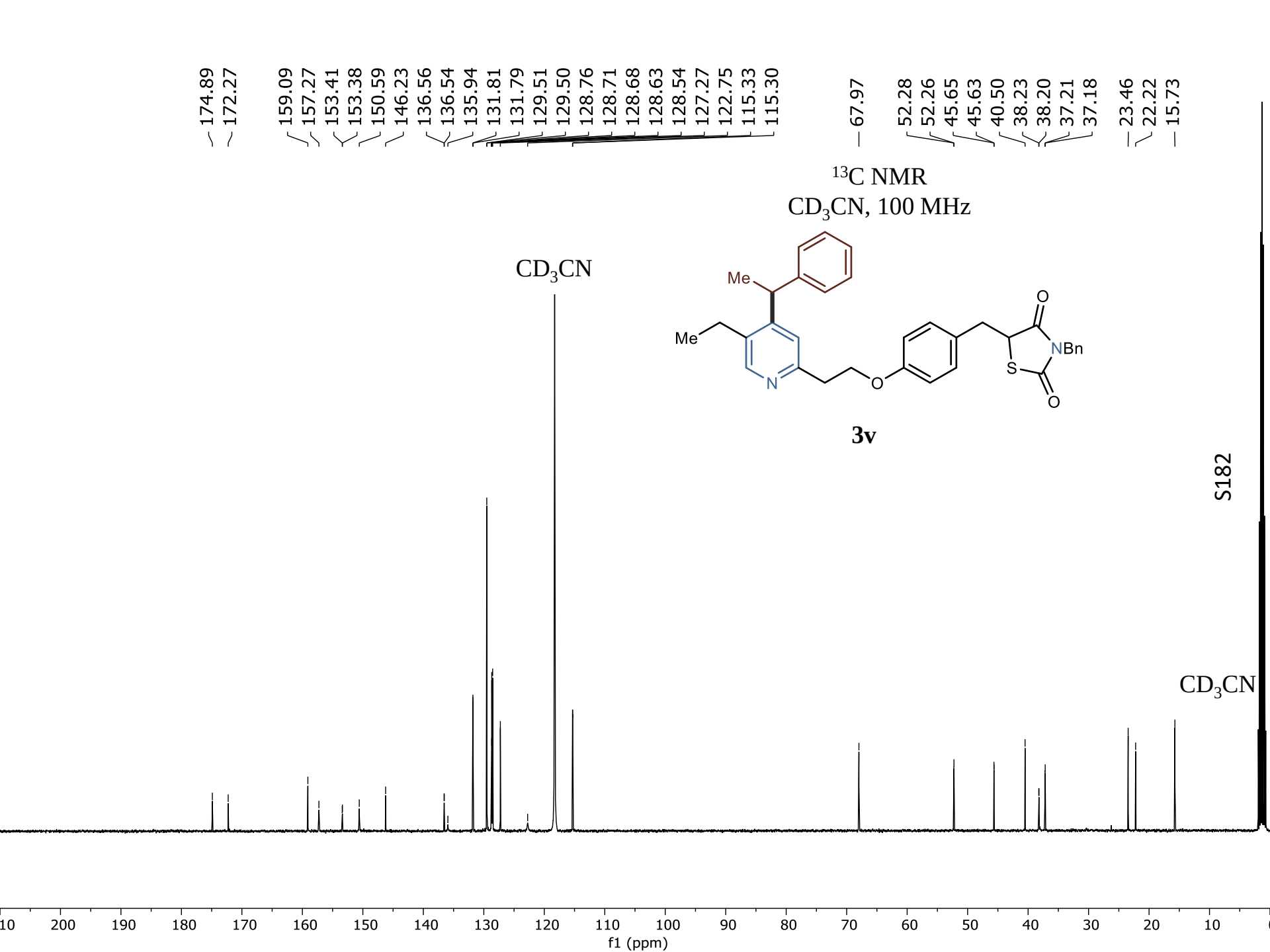
155.69
148.52
144.00
142.56
140.94
138.57
137.41
132.36
131.02
129.89
128.88
128.84
127.74
127.21
126.92
125.77
124.91
122.78
122.28
121.78
44.41
44.38
21.00
13C NMR
CDCl3, 100 MHz
Me
SO2Me
H
N
N
O
Cl
Cl
3u
S180
CDCl3
f1 (ppm)


7.27 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.20 7.19 7.19 7.10 7.08 7.08 7.08 7.06 7.06 7.05 6.72 6.71 6.70 6.69 4.67 4.66 4.65 4.65 4.64 4.61 3.14 3.13 3.11 1.95 1.95 1.94 1.93 1.59 1.58 1.57 1.56 1.12 1.11 1.10 1.09 1.08 1.07
1H NMR
CD3CN, 400 MHz
Me
Me
N
O
O
NBn
S
O
3v
S181
1.00 9.38 4.46 2.17 3.23 1.04 2.19 4.51 2.28 3.15 3.20
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
f1 (ppm)


174.89
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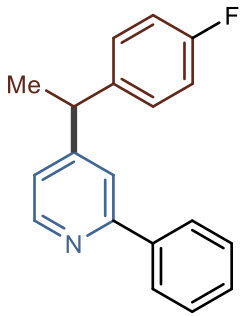
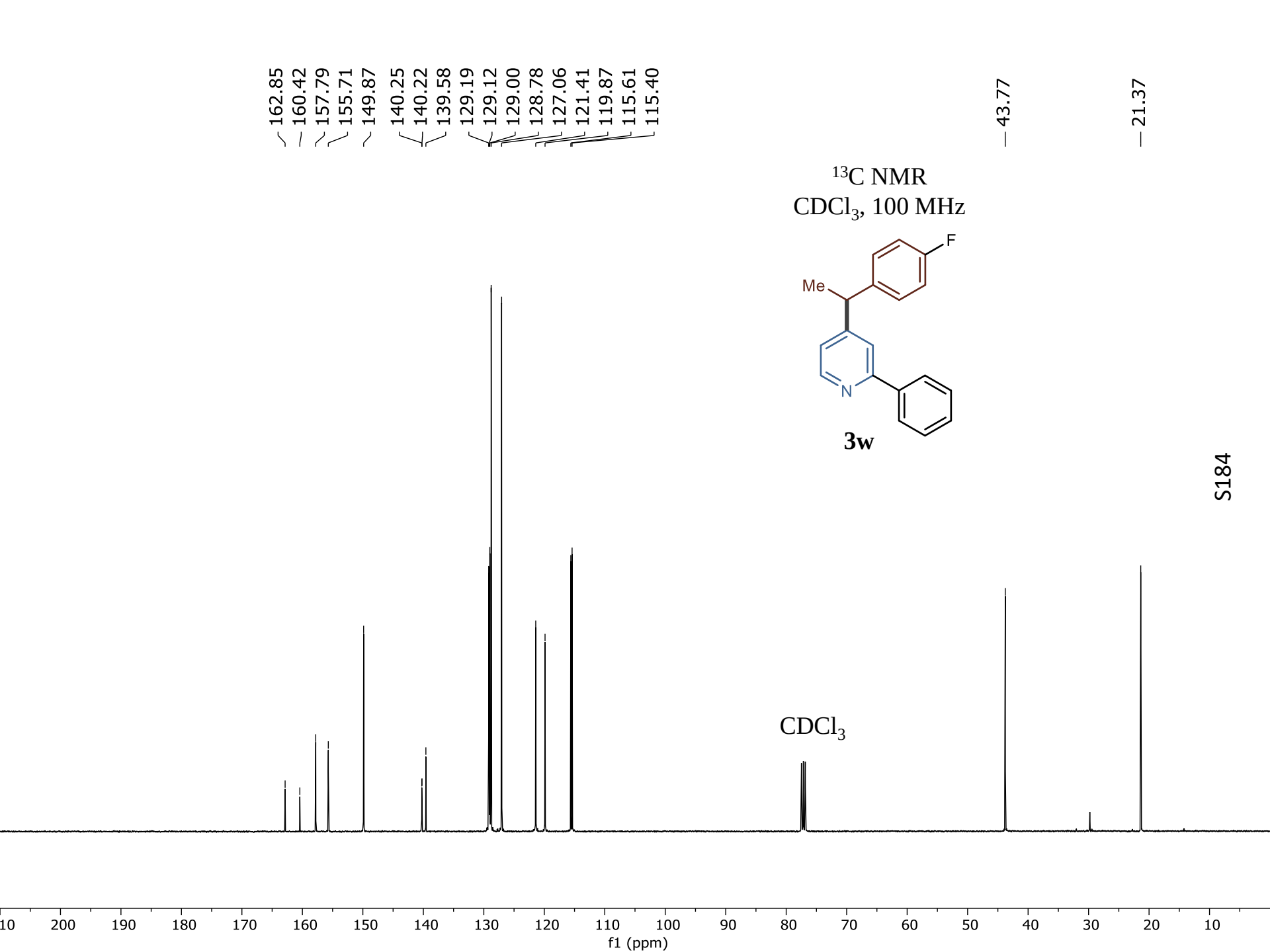
157.27
153.41
153.38
150.59
146.23
136.56
136.54
135.94
131.81
131.79
129.51
129.50
128.76
128.71
128.68
128.63
128.54
127.27
122.75
115.33
115.30
67.97
52.28
52.26
45.65
45.63
40.50
38.23
38.20
37.21
37.18
23.46
22.22
15.73
13C NMR
CD3CN, 100 MHz
CD3CN
Me
Me
N
O
O
NBn
S
O
3v
S182
CD3CN
f1 (ppm)

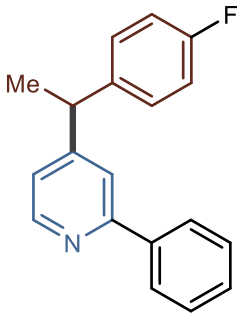
^{1}H NMR
$CDCl_3$, 400 MHz



3w


162.85
160.42
157.79
155.71
149.87
140.25
140.22
139.58
129.19
129.12
129.00
128.78
127.06
121.41
119.87
115.61
115.40
43.77
21.37
13C NMR
CDCl3, 100 MHz
F
Me
N
3w
S184
CDCl3
f1 (ppm)

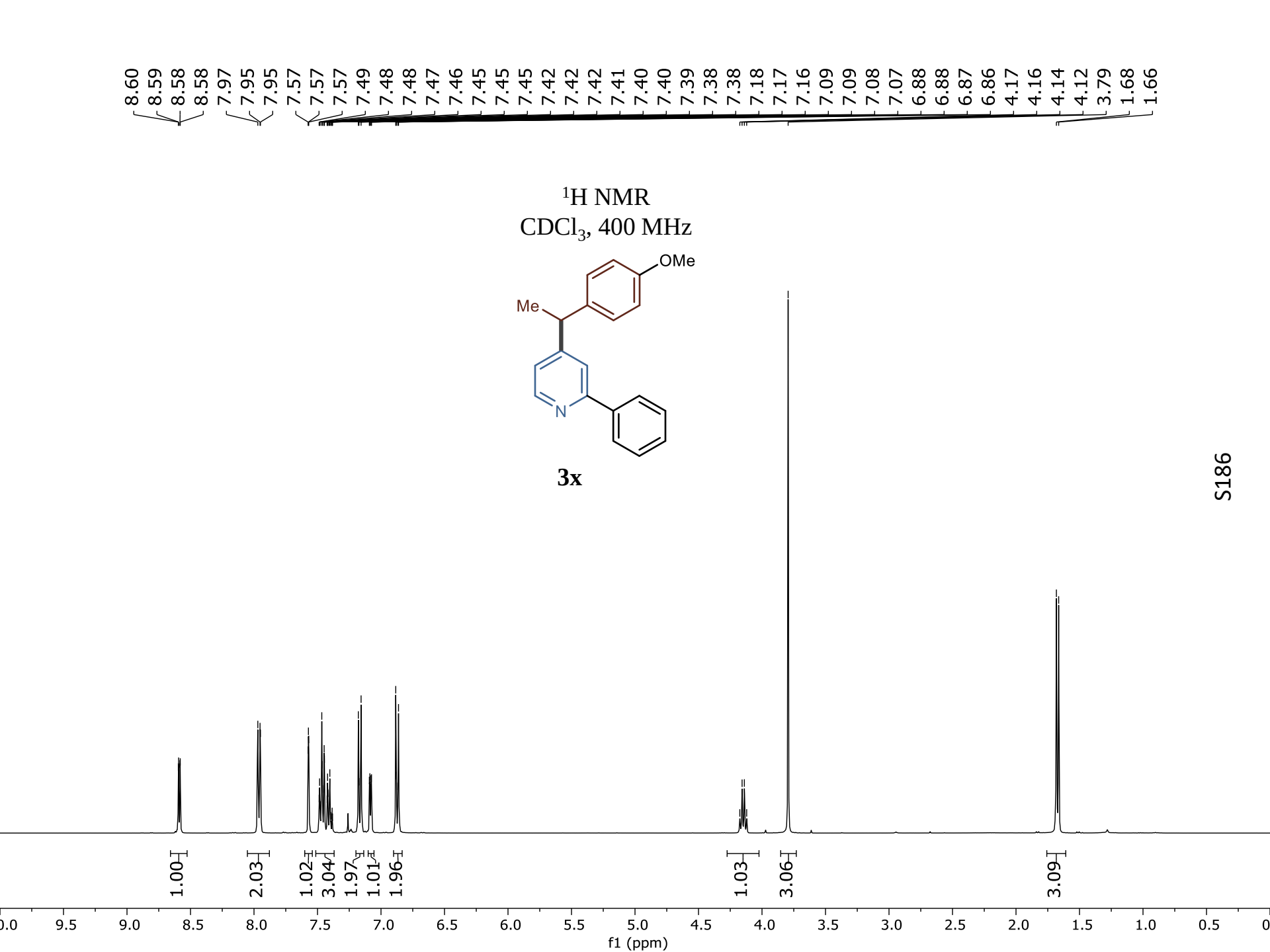
^{19}F NMR
$CDCl_3$, 365 MHz

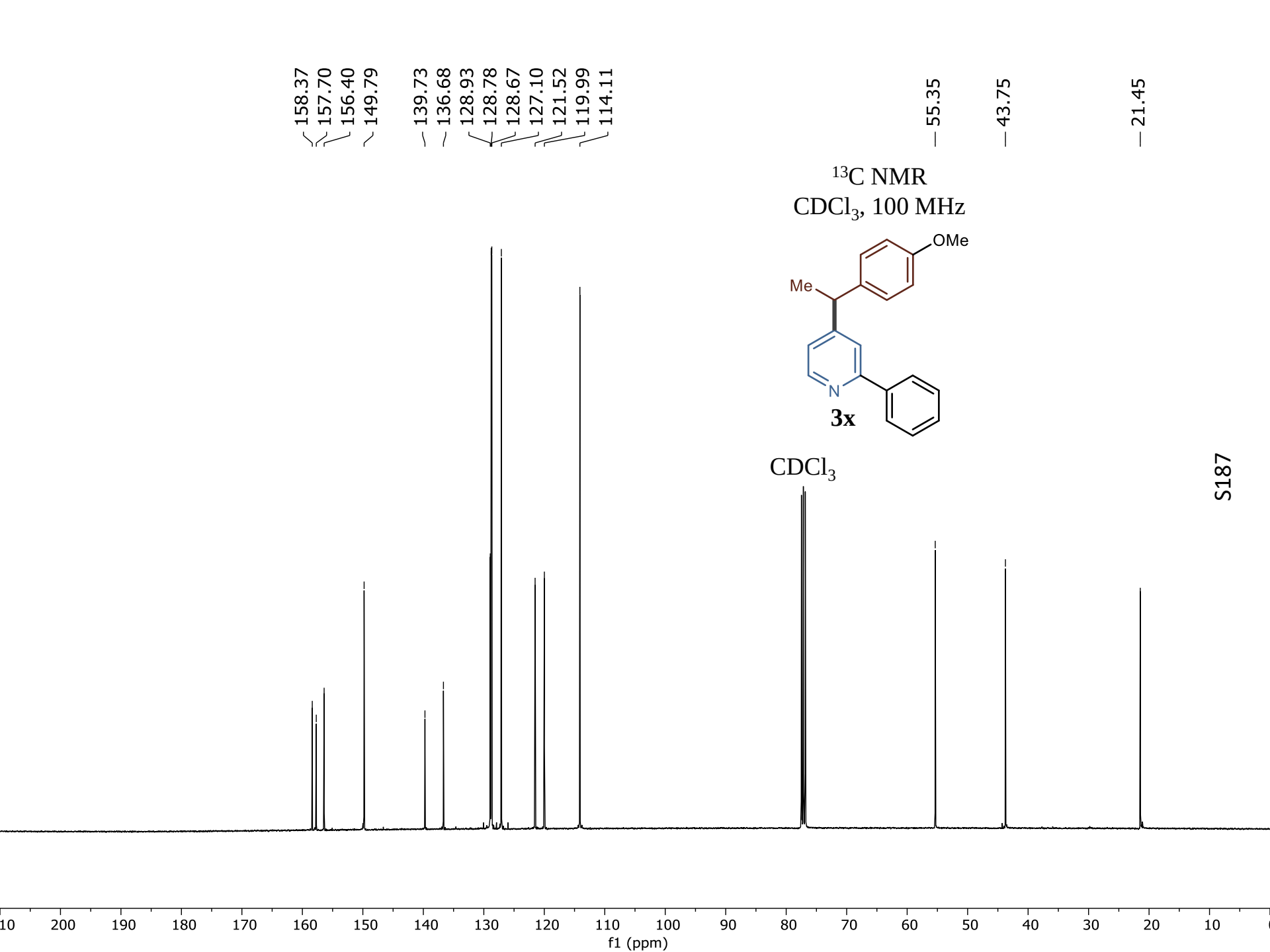


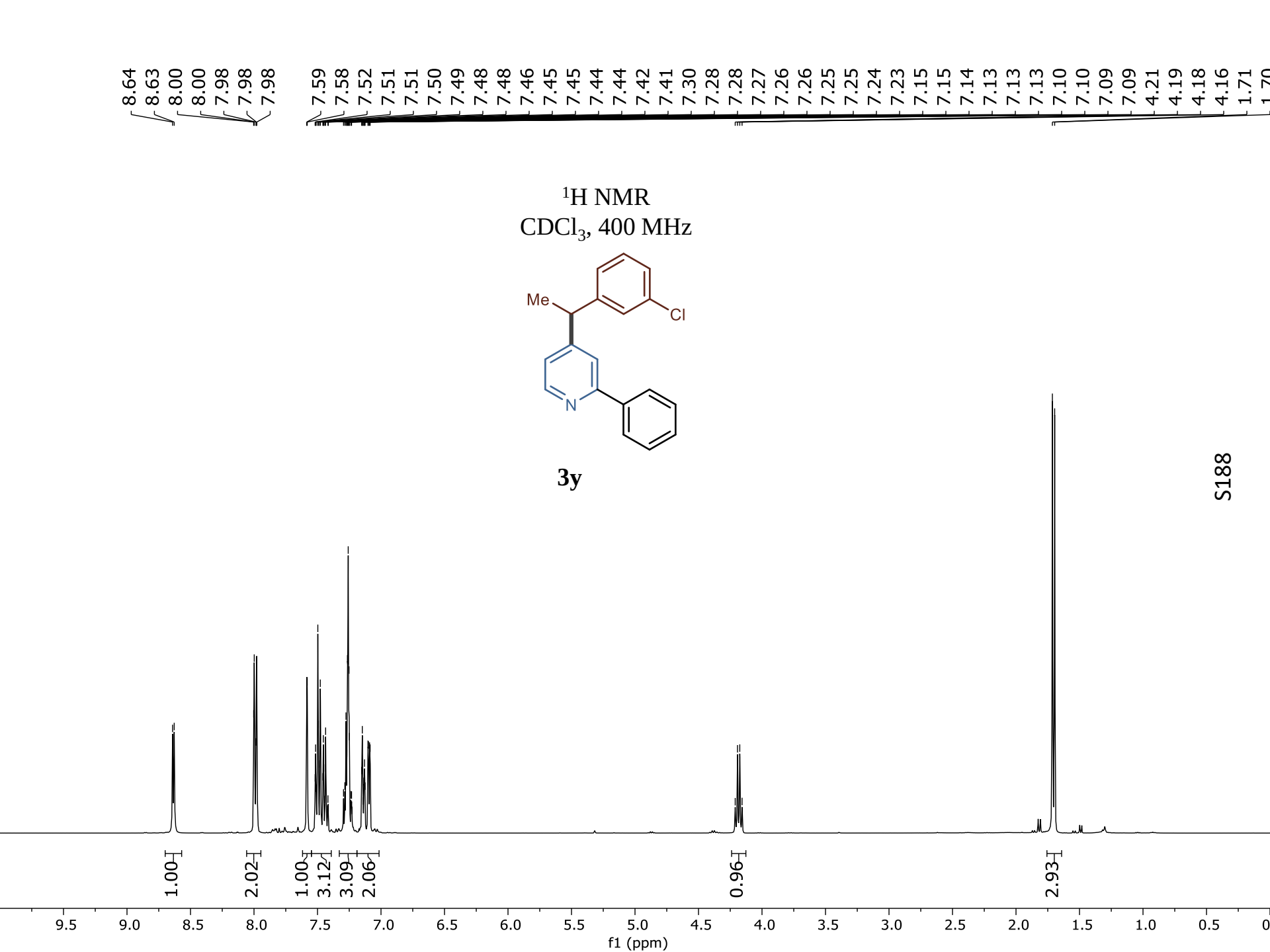
3w

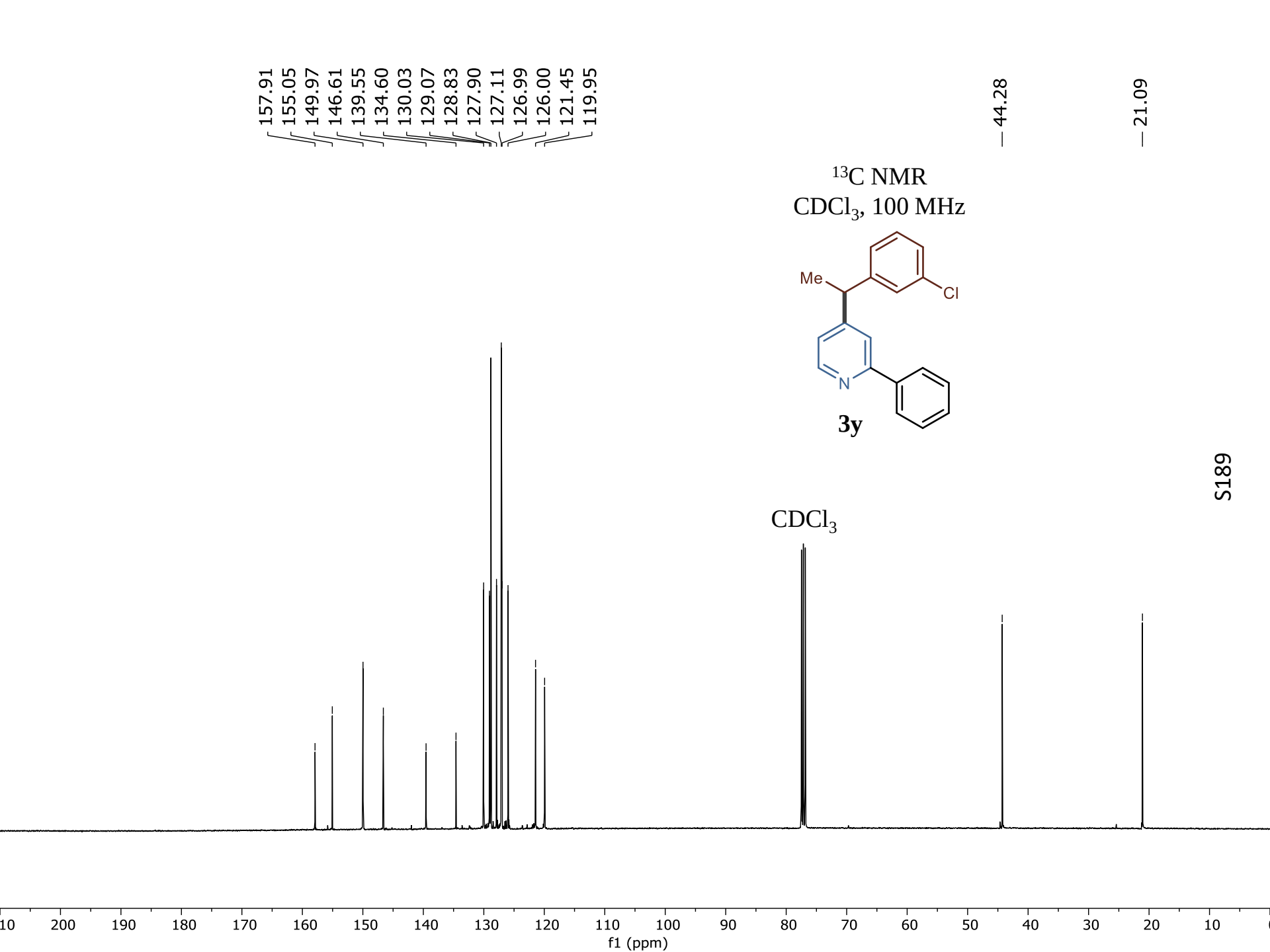
-116.24

S185


8.60
8.59
8.58
8.58
7.97
7.95
7.95
7.57
7.57
7.57
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.45
7.42
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.18
7.17
7.16
7.09
7.09
7.08
7.07
6.88
6.88
6.87
6.86
4.17
4.16
4.14
4.12
3.79
1.68
1.66
1H NMR
CDCl3, 400 MHz
OMe
Me
N
3x
S186
1.00
2.03
1.02
3.04
1.97
1.01
1.96
1.03
3.06
3.09
f1 (ppm)

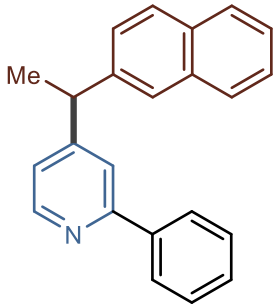

158.37
157.70
156.40
149.79
139.73
136.68
128.93
128.78
128.67
127.10
121.52
119.99
114.11
55.35
43.75
21.45
^{13}C NMR
$CDCl_3$, 100 MHz
OMe
Me
N
3x
$CDCl_3$
S187
f1 (ppm)


8.64
8.63
8.00
8.00
7.98
7.98
7.98
7.59
7.58
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.46
7.45
7.45
7.44
7.44
7.42
7.41
7.30
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.15
7.15
7.14
7.13
7.13
7.13
7.10
7.10
7.09
7.09
4.21
4.19
4.18
4.16
1.71
1H NMR
CDCl3, 400 MHz
Me
Cl
N
3y
S188
1.00
2.02
1.00
3.12
3.09
2.06
0.96
2.93
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
f1 (ppm)

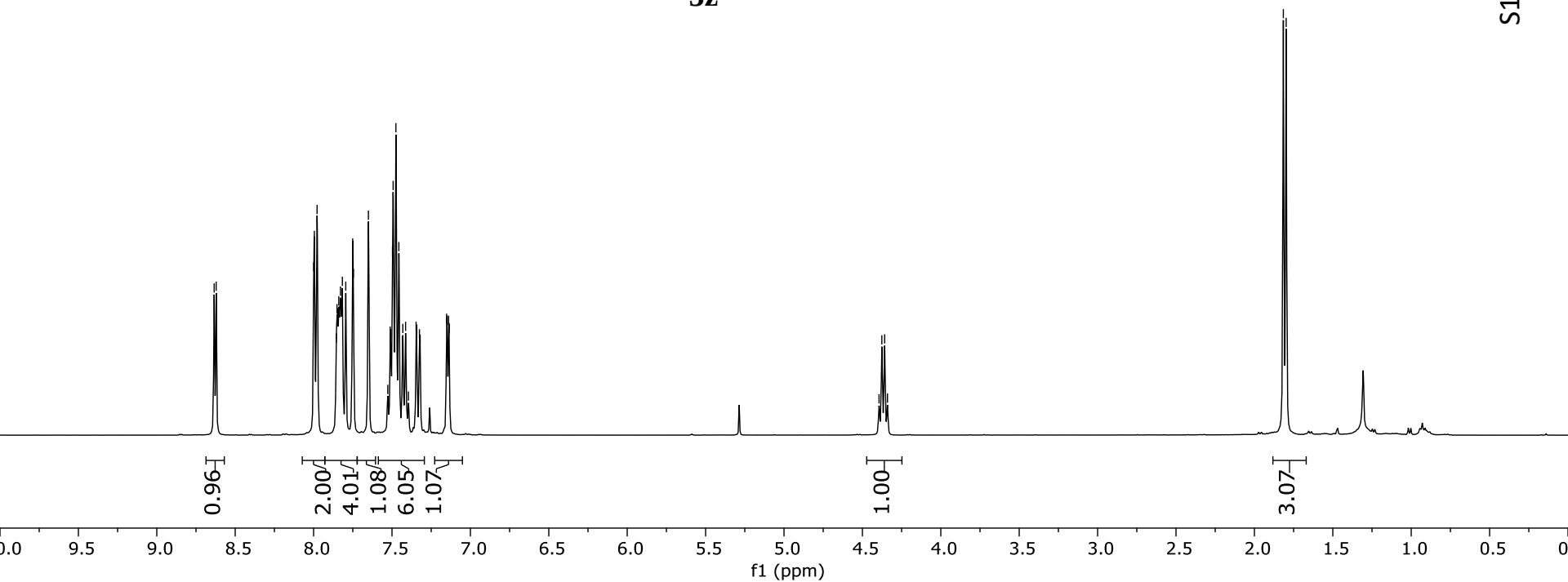

157.91
155.05
149.97
146.61
139.55
134.60
130.03
129.07
128.83
127.90
127.11
126.99
126.00
121.45
119.95
44.28
21.09
13C NMR
CDCl3, 100 MHz
Me
Cl
N
3y
CDCl3
S189
f1 (ppm)

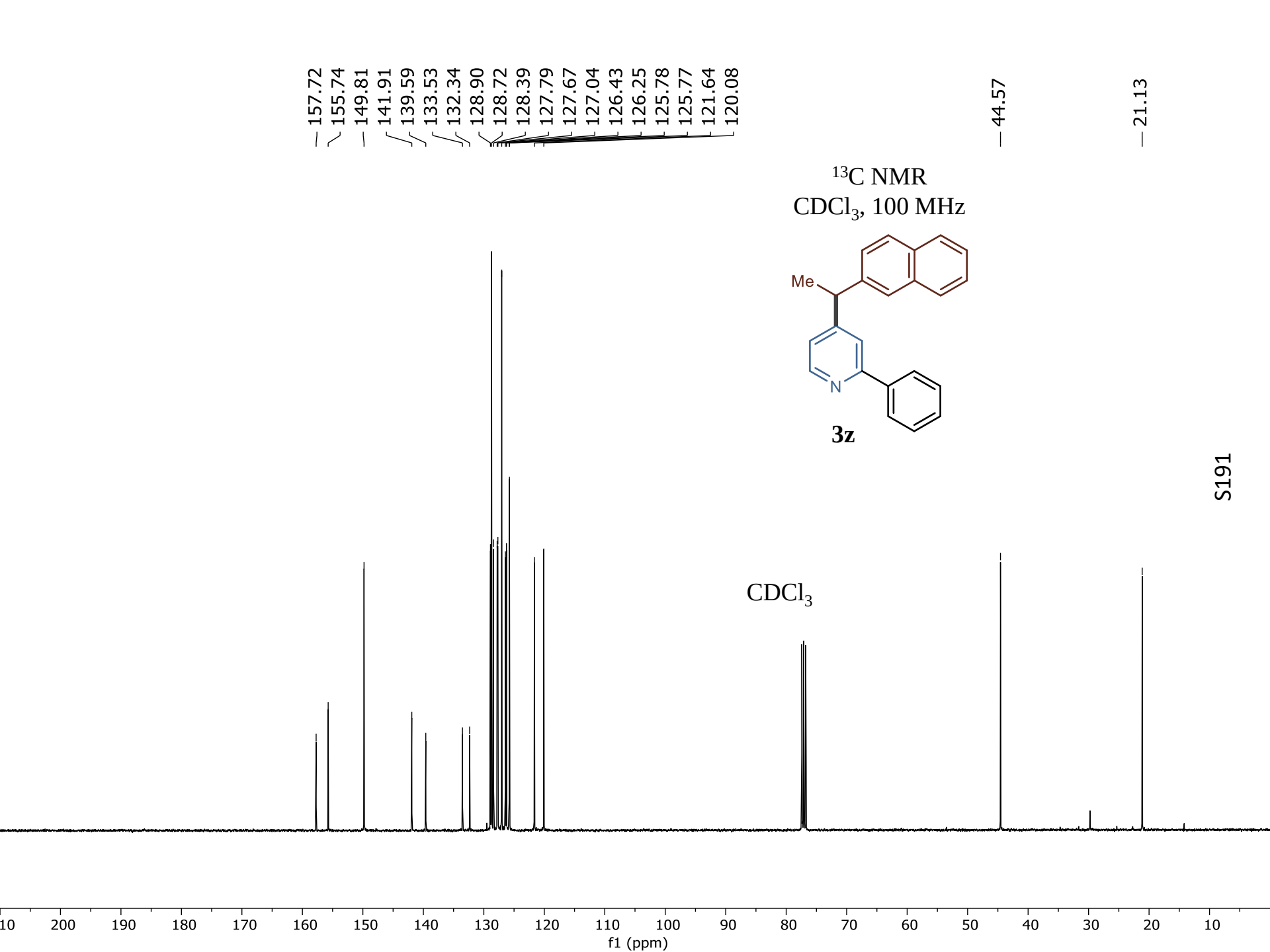
8.63 8.62 8.00 8.00 7.98 7.86 7.85 7.85 7.84 7.83 7.82 7.79 7.75 7.75 7.65 7.53 7.51 7.51 7.50 7.49 7.48 7.46 7.43 7.41 7.40 7.35 7.34 7.32 7.32 7.15 7.15 7.14 7.14 4.39 4.38 4.36 4.34 1.82 1.80

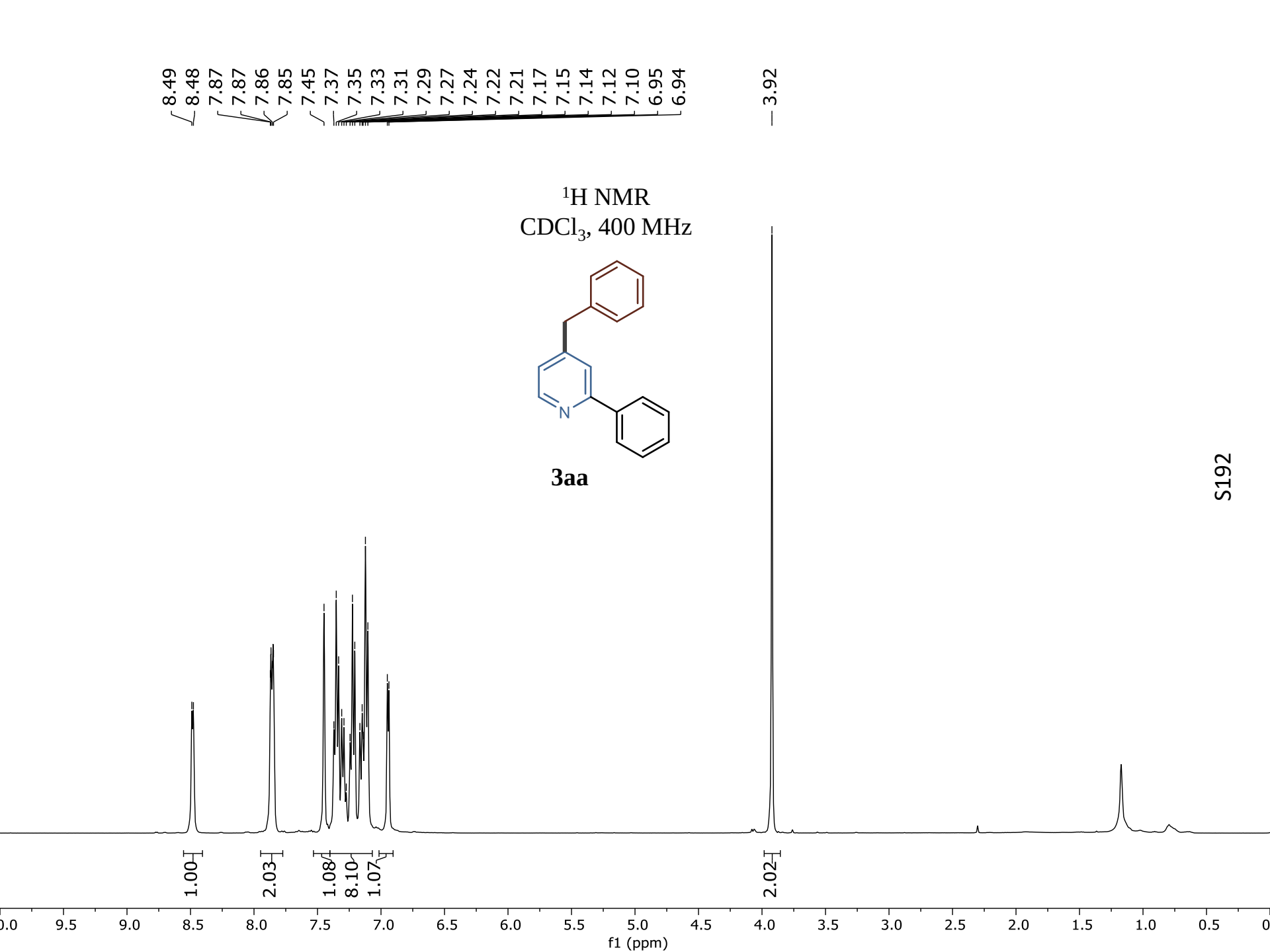
^{1}H NMR
$CDCl_3$, 400 MHz

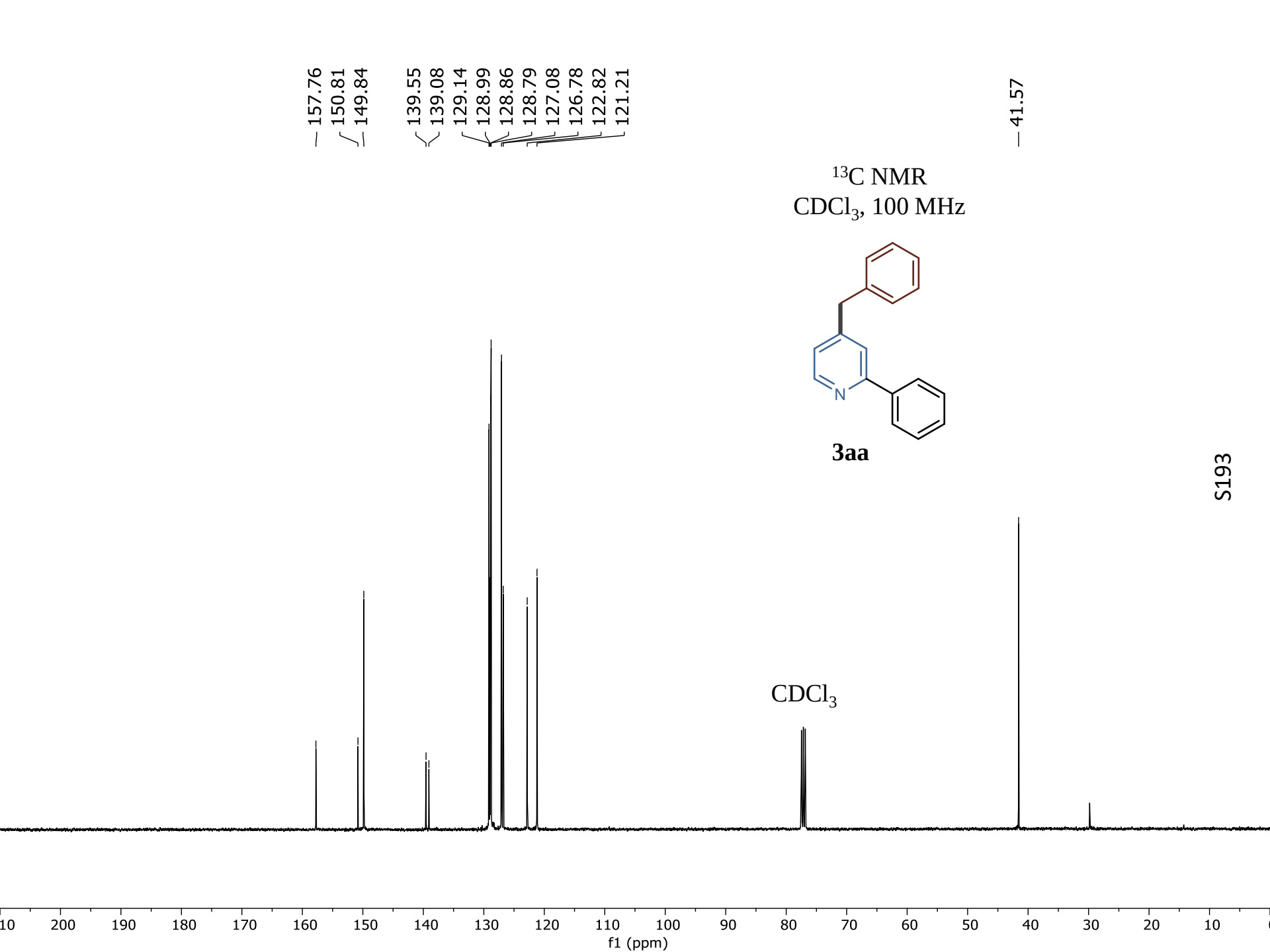


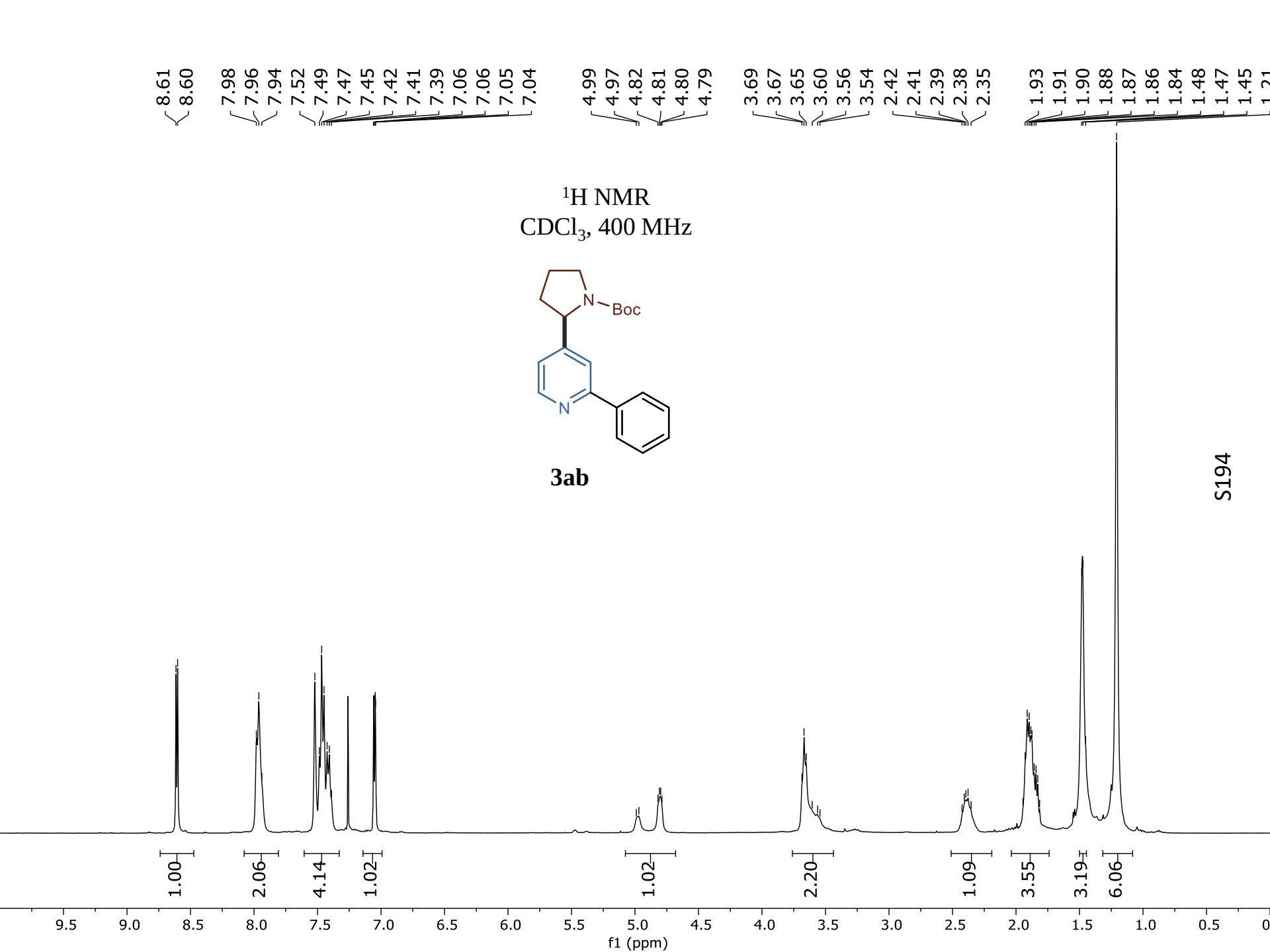
3z

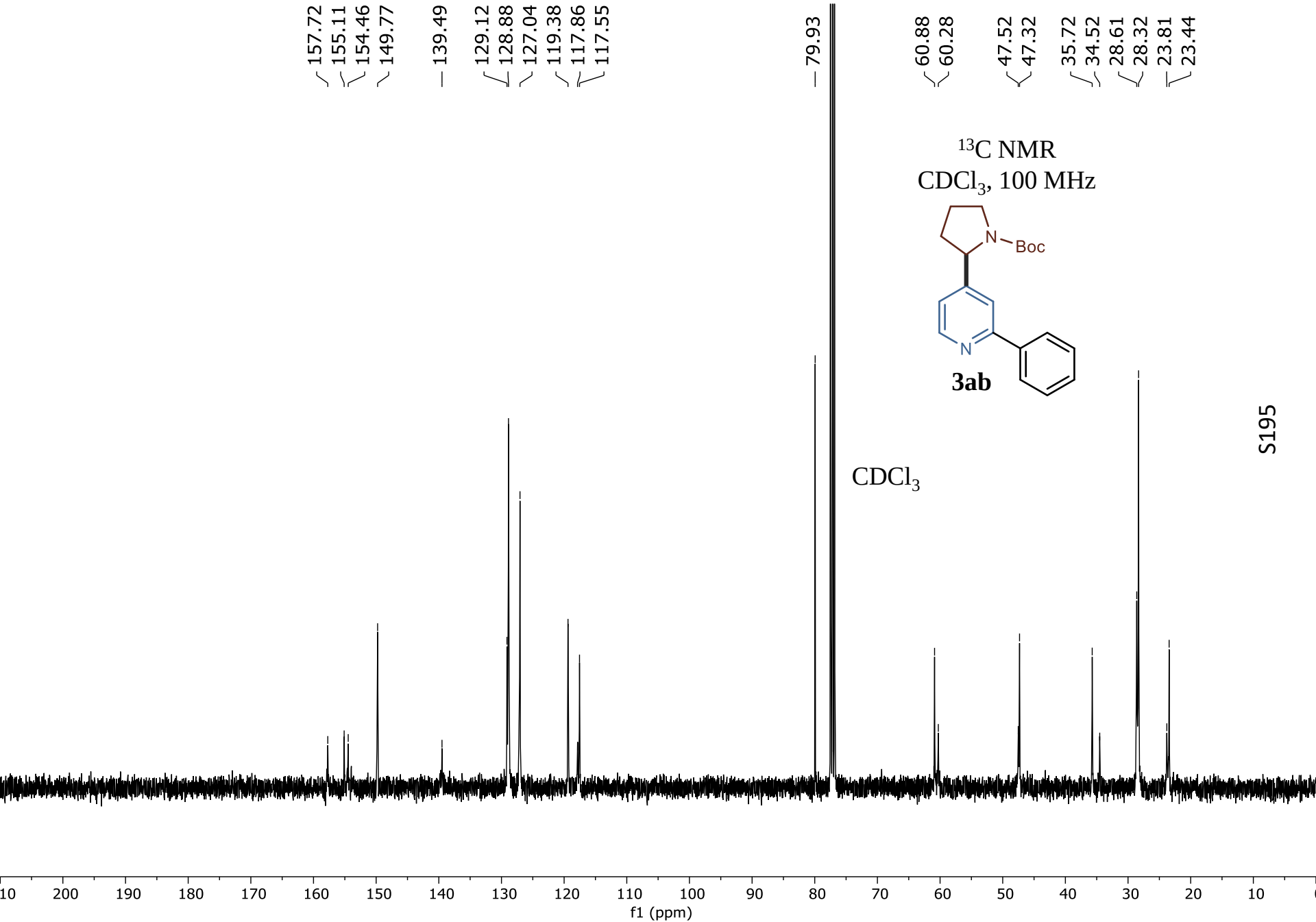


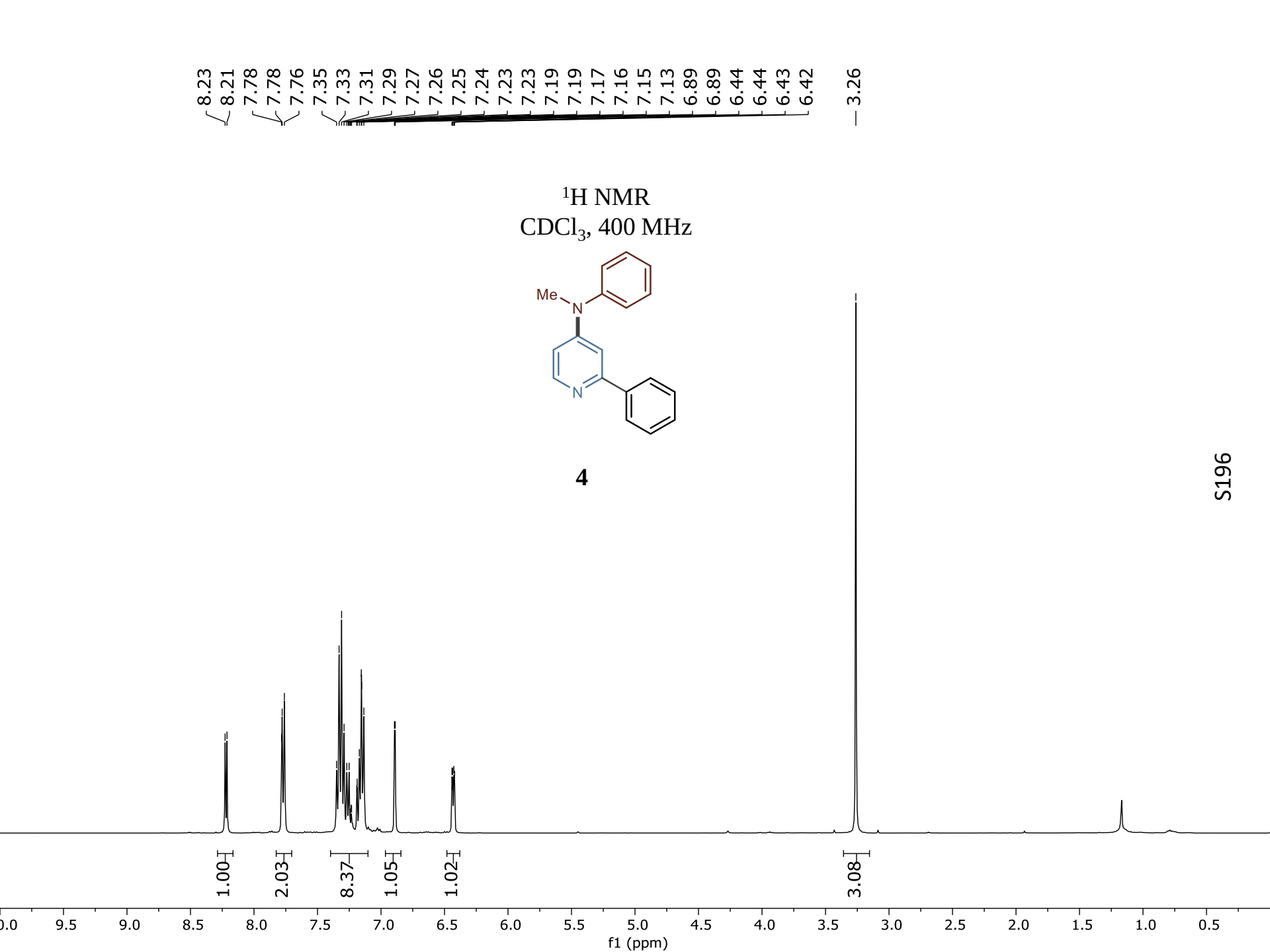

157.72
155.74
149.81
141.91
139.59
133.53
132.34
128.90
128.72
128.39
127.79
127.67
127.04
126.43
126.25
125.78
125.77
121.64
120.08
44.57
21.13
^{13}C NMR
$CDCl_3$, 100 MHz
Me
N
3z
S191
$CDCl_3$
f1 (ppm)

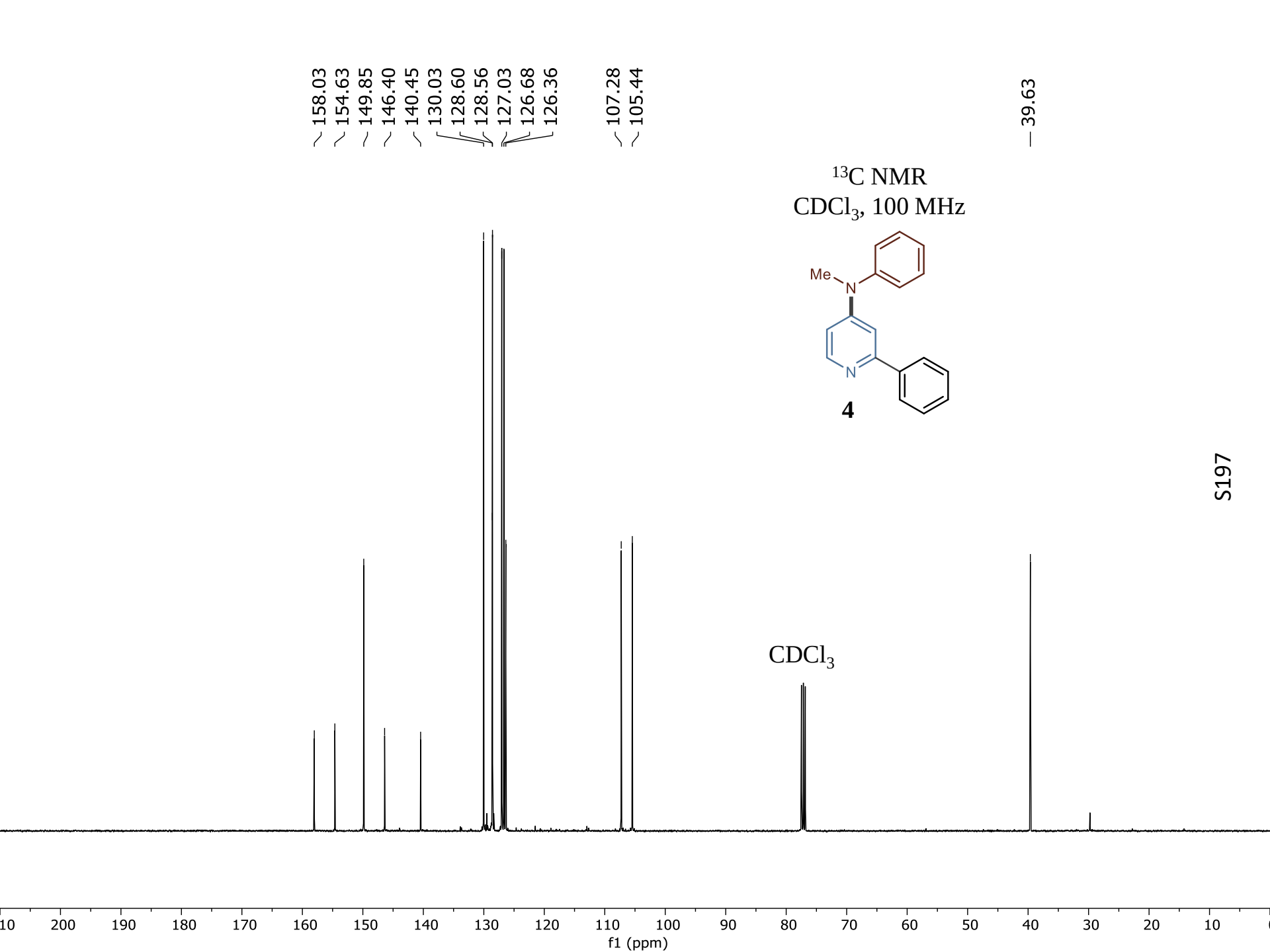

8.49
8.48
7.87
7.87
7.86
7.85
7.45
7.37
7.35
7.33
7.31
7.29
7.27
7.24
7.22
7.21
7.17
7.15
7.14
7.12
7.10
6.95
6.94
3.92
1H NMR
CDCl3, 400 MHz
N
3aa
S192
1.00
2.03
1.08
8.10
1.07
2.02
f1 (ppm)

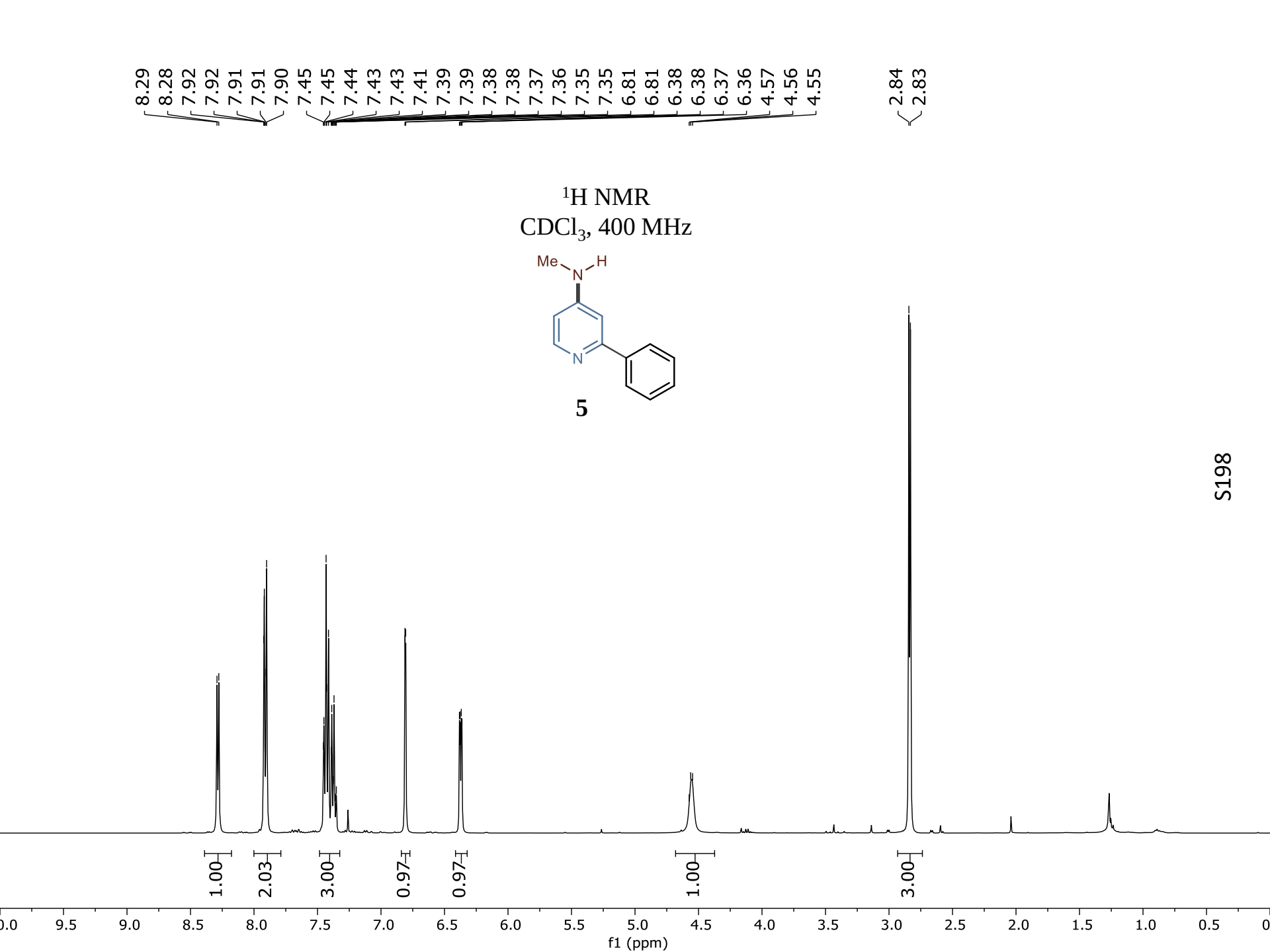

157.76
150.81
149.84
139.55
139.08
129.14
128.99
128.86
128.79
127.08
126.78
122.82
121.21
41.57
^{13}C NMR
$CDCl_3$, 100 MHz
N
3aa
S193
$CDCl_3$
f1 (ppm)

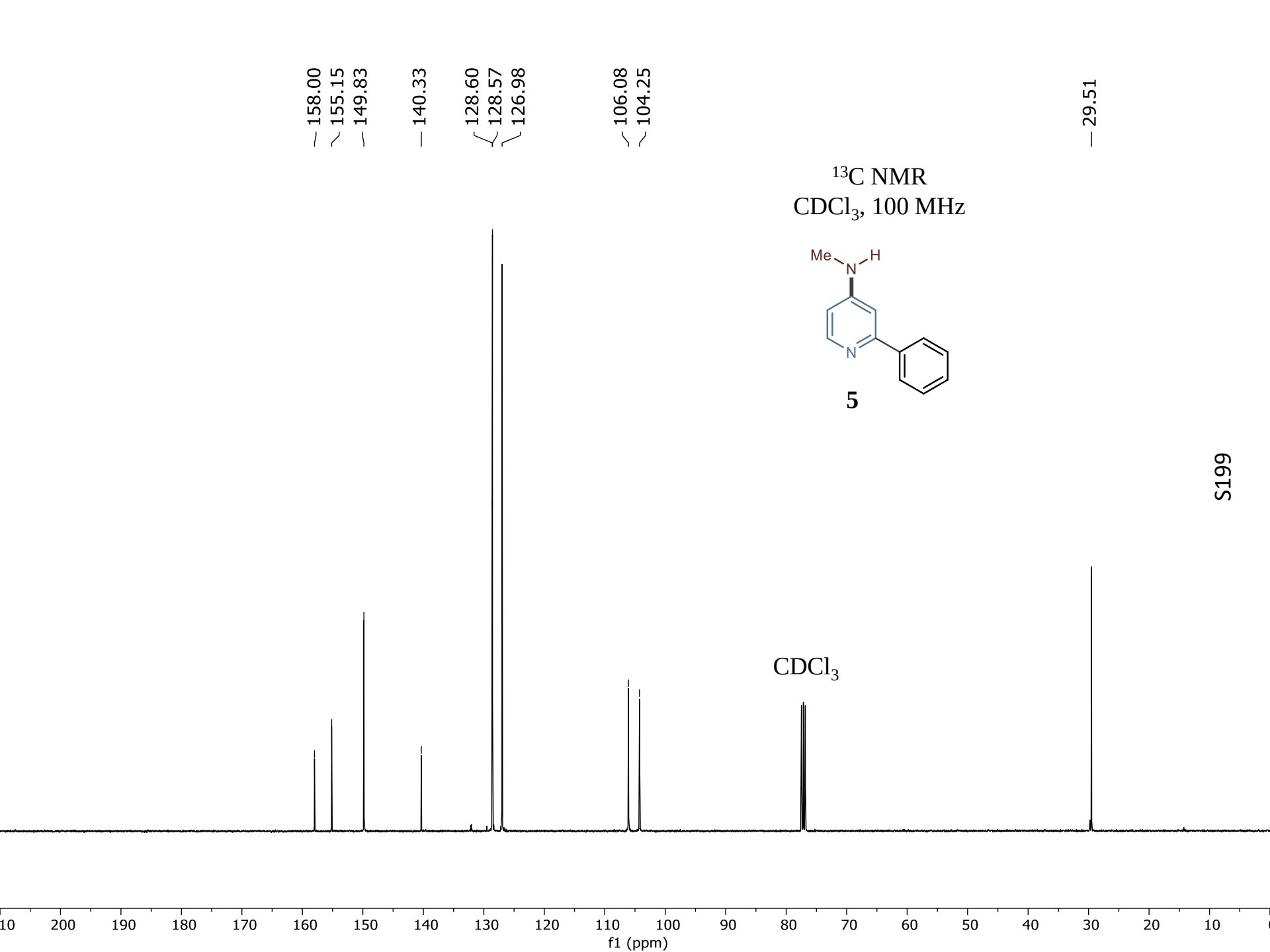

8.61
8.60
7.98
7.96
7.94
7.52
7.49
7.47
7.45
7.42
7.41
7.39
7.06
7.06
7.05
7.04
4.99
4.97
4.82
4.81
4.80
4.79
3.69
3.67
3.65
3.60
3.56
3.54
2.42
2.41
2.39
2.38
2.35
1.93
1.91
1.90
1.88
1.87
1.86
1.84
1.48
1.47
1.45
1H NMR
CDCl3, 400 MHz
N
Boc
N
3ab
S194
1.00
2.06
4.14
1.02
1.02
2.20
1.09
3.55
3.19
6.06
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
f1 (ppm)


157.72
155.11
154.46
149.77
139.49
129.12
128.88
127.04
119.38
117.86
117.55
79.93
60.88
60.28
47.52
47.32
35.72
34.52
28.61
28.32
23.81
23.44
13C NMR
CDCl3, 100 MHz
N
Boc
N
3ab
CDCl3
S195
f1 (ppm)


8.23
8.21
7.78
7.78
7.76
7.35
7.33
7.31
7.29
7.27
7.26
7.25
7.24
7.23
7.23
7.19
7.19
7.17
7.16
7.15
7.13
6.89
6.89
6.44
6.44
6.43
6.42
3.26
1H NMR
CDCl3, 400 MHz
Me
N
N
4
S196
1.00
2.03
8.37
1.05
1.02
3.08
f1 (ppm)


158.03
154.63
149.85
146.40
140.45
130.03
128.60
128.56
127.03
126.68
126.36
107.28
105.44
39.63
13C NMR
CDCl3, 100 MHz
Me
N
N
4
CDCl3
f1 (ppm)


8.29
8.28
7.92
7.92
7.91
7.91
7.90
7.45
7.45
7.44
7.43
7.43
7.41
7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.35
6.81
6.81
6.38
6.38
6.37
6.36
4.57
4.56
4.55
2.84
2.83
1H NMR
CDCl3, 400 MHz
Me
N
H
N
5
S198
1.00
2.03
3.00
0.97
0.97
1.00
3.00
f1 (ppm)


158.00
155.15
149.83
140.33
128.60
128.57
126.98
106.08
104.25
29.51
13C NMR
CDCl3, 100 MHz
Me
N
H
N
5
CDCl3
S199
f1 (ppm)