Electronic Supplementary Information

Electrophilic Glycoluril-Based Reagents for Atom-Economic Thiocyanation and Selenocyanation of (Hetero)arenes

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1. Stability studies of reagents 5a and 5b

1.1. DSC

Differential scanning calorimetry (DSC) was performed using a Mettler DSC3+ Star system thermal analyzer under a nitrogen purge gas (50 mL/min) with heating rates of 2 ºC/min and cooling rates of 30 ºC/min in a temperature range of 25 ºC to 200 ºC. Calibration was conducted using indium standards for both heat flow and temperature. Samples weighing 2 mg were enclosed in perforated aluminum pans.

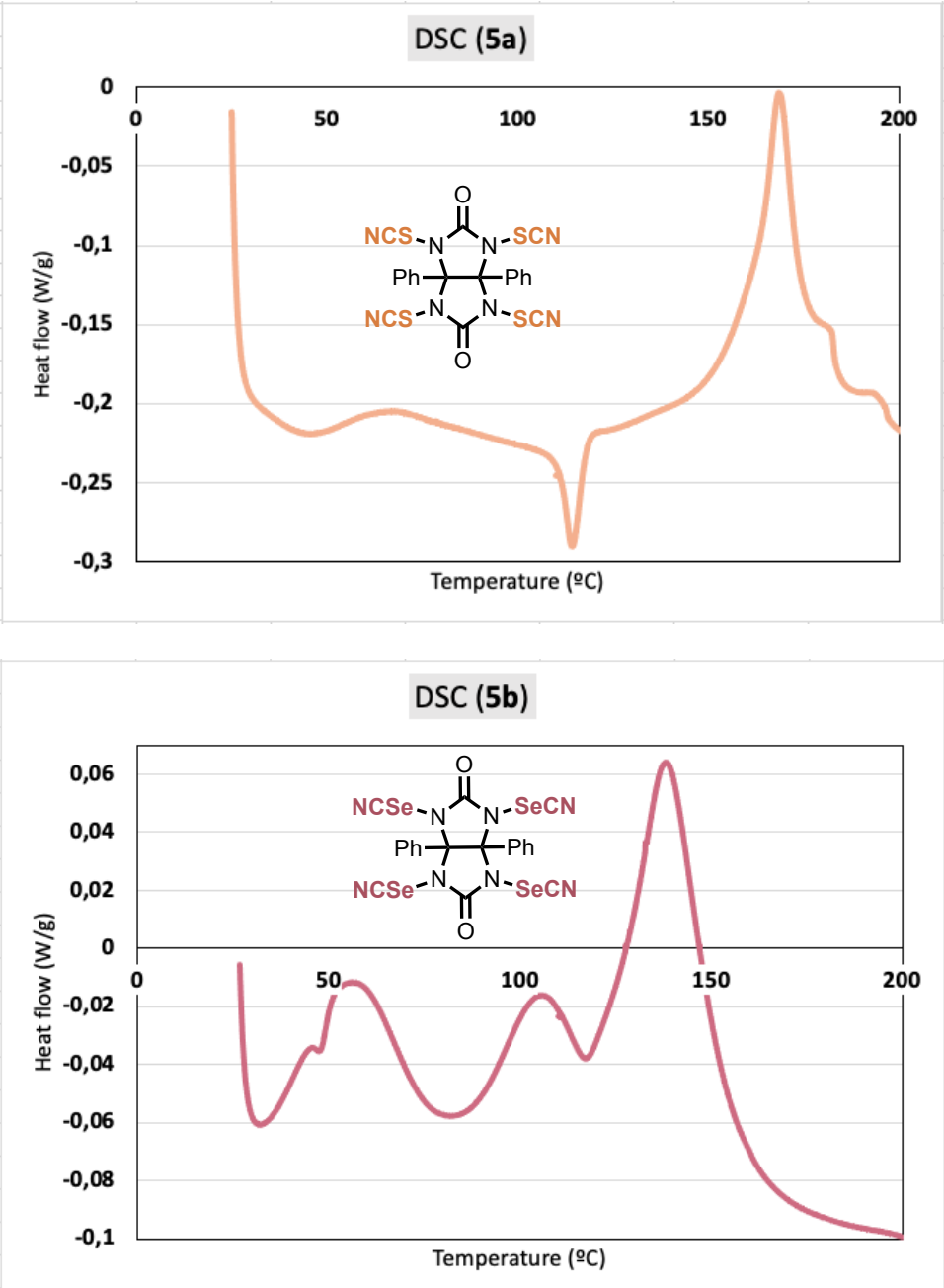


Figure S1. DSC analysis of reagents **5a** and **5b**

1.2. TGA

A Mettler TGA/SDTA851e/LF/1100 equipment was utilized to conduct thermogravimetric analysis (TGA) on samples weighing 2 mg in ceramic crucibles. N_2 was used as the purge gas (50 mL/min) and the analysis was performed at a scanning rate of 10 ºC/min within a temperature range of 30 ºC to 600 ºC.

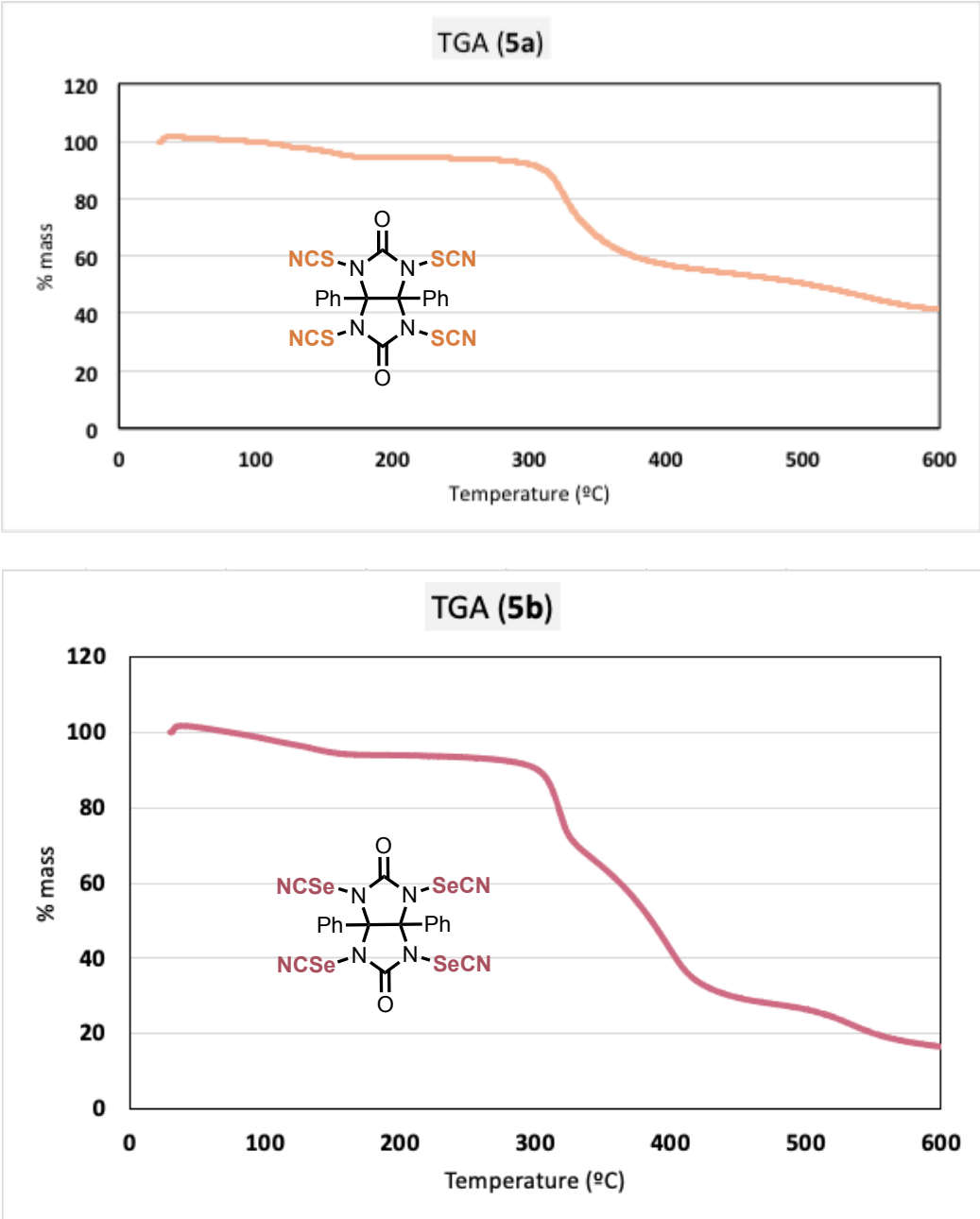
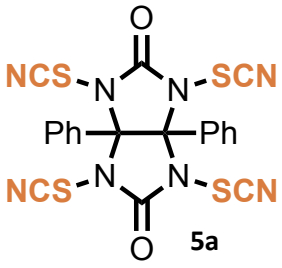
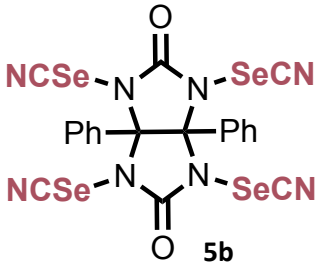


Figure S2. TGA analysis of reagents **5a** and **5b**. 5% weight decomposition (**5a**) = 167 ºC; 5% weight decomposition (**5b**) = 143 ºC

2. Solubility studies of reagents 5a and 5b

Procedure. A 10 mL round-bottom flask, equipped with a magnetic stir bar, was charged with 20 mg of reagent (**5a** or **5b**) and 1.5 mL of the corresponding solvent. The solution was stirred 30 min at room temperature. Then, the mixture was filtered under vacuum and the filtrate was concentrated under pressure. The resulting solid was then dried under vacuum and weighted (Table S1).

Table S1. Solubility studies of reagents **5a,b** in selected solvents

REAGENT	SOLVENT	SOLUBILITY (mg/mL)
 **5a**	CH_3CN	5.67 mg/mL
	CH_2Cl_2	1.27 mg/mL
	$CHCl_3$	1.30 mg/mL
	$CH_3COO(CH_2)_3CH_3$ (*n*-butyl acetate, *n*BuOAc)	1.21 mg/mL
 **5b**	CH_3CN	1.03 mg/mL
	CH_2Cl_2	0.87 mg/mL
	$CHCl_3$	1.01 mg/mL
	$CH_3COO(CH_2)_3CH_3$ (*n*-butyl acetate, *n*BuOAc)	0.83 mg/mL

3. Green metrics calculations

The following formulas were used for calculating Atom Economy (AE), Reaction Mass Efficiency (RME), simple E Factor (sEF), E factor (EF), and solvent contribution.[1]

$$\text{AE} = \frac{\text{molecular weight desired product}}{\sum \text{molecular weight reagents}} \text{ x } 100$$

$$\text{sEF} = \frac{\sum \text{m(raw materials)} + \sum \text{m(reagents)} - \text{m(desired product)}}{\text{m (desired product)}}$$

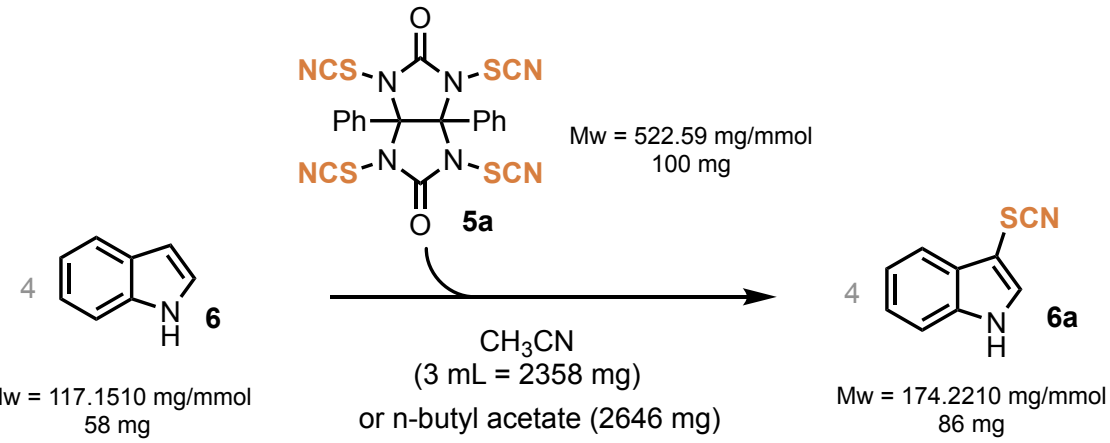
$$\text{EF} = \frac{\sum \text{m(raw materials)} + \sum \text{m(reagents)} + \sum \text{m(solvents)} - \text{m(desired product)}}{\text{m (desired product)}}$$

$$\text{Solvent contribution} = \frac{\text{EF} - \text{sEF}}{\text{EF}} \text{x} 100$$

$$\text{RME} = \frac{\text{m (desired product)}}{\sum \text{m(reagents)}} \text{x } 100$$

Protocol 1 (5a). *This work*

The calculations of the green metrics for the electrophilic aromatic substitution reaction are as follows:



$$\text{AE} = \frac{(4 \text{ x } 174.2210 \text{ mg/mmol } \mathbf{6a})}{522.594 \text{ mg/mmol } \mathbf{5a} + (4 \text{ x } 117.1510 \text{ mg/mmol } \mathbf{6})} \text{ x } 100 = 70\%$$

$$\text{RME} = \frac{86 \text{ mg } \mathbf{6a}}{86 \text{ mg } \mathbf{5a} + 58 \text{ mg } \mathbf{6}} \text{x} 100 = 60\%$$

$$\text{sEF} = \frac{58 \text{ mg } \mathbf{6} + 86 \text{ mg } \mathbf{5a} - 86 \text{ mg } \mathbf{6a}}{86 \text{ mg } \mathbf{6a}} = 0.67$$

$$\text{EF} = \frac{58\ \text{mg}\ \mathbf{6} + 86\ \text{mg}\ \mathbf{5a} + 2358\ \text{mg}\ \text{CH}_3\text{CN} - 86\ \text{mg}\ \mathbf{6a}}{86\ \text{mg}\ \mathbf{6a}} = 28.1$$

$$\text{Solvent contribution} = \frac{28.1\ \text{EF} - 0.67\ \text{sEF}}{28.1\ \text{EF}} \text{x} 100 = 97\%$$

Within solvent recovery (71% of CH_3CN recovery):

$$\text{EF} = \frac{58\ \text{mg}\ \mathbf{6} + 86\ \text{mg}\ \mathbf{5a} + 2358\ \text{mg}\ \text{CH}_3\text{CN} - 86\ \text{mg}\ \mathbf{6a} - 1674\ \text{mg}\ \text{CH}_3\text{CN}}{86\ \text{mg}\ \mathbf{6a} + \ 1674\ \text{mg}\ \text{CH}_3\text{CN}} = 0.47$$

$$\text{EF} = \frac{58\ \text{mg}\ \mathbf{6} + 86\ \text{mg}\ \mathbf{5a} + 2646\ \text{mg}\ n\text{BuOAc} - 86\ \text{mg}\ \mathbf{6a}}{86\ \text{mg}\ \mathbf{6a}} = 31.4$$

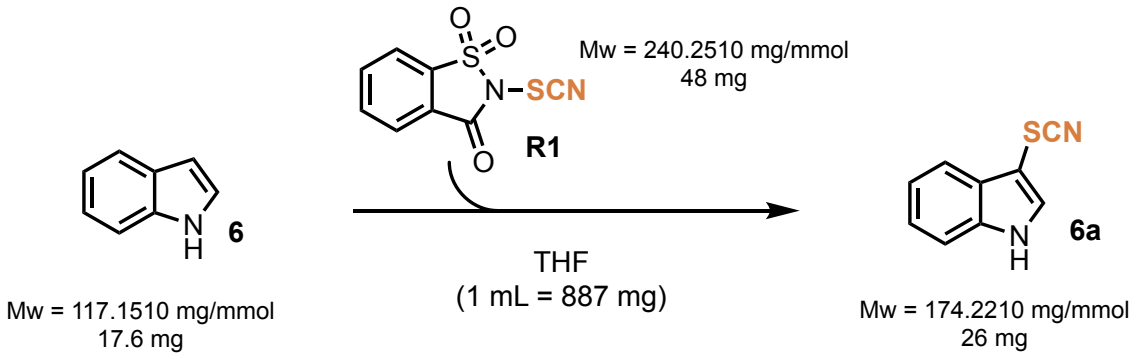
$$\text{Solvent contribution} = \frac{31.4\ \text{EF} - 0.67\ \text{sEF}}{31.4\ \text{EF}} \text{x} 100 = 97\%$$

Within solvent recovery (80% of *n*-butyl acetate (*n*BuOAc) recovery):

$$\text{EF} = \frac{58\ \text{mg}\ \mathbf{6} + 86\ \text{mg}\ \mathbf{5a} + 2358\ \text{mg}\ n\text{BuOAc} - 86\ \text{mg}\ \mathbf{6a} - 2116\ \text{mg}\ n\text{BuOAc}}{86\ \text{mg}\ \mathbf{6a} + \ 2116\ \text{mg}\ n\text{BuOAc}} = 0.14$$

Protocol 2 (R1)

J. Org. Chem., 2018, **83**, 1576–1583.



$$\text{AE} = \frac{174.2210\ \text{mg/mmol}\ \mathbf{6a}}{240.2510\ \text{mg/mmol}\ \mathbf{R1} + 117.1510\ \text{mg/mmol}\ \mathbf{6}} \text{ x } 100 = 49\%$$

$$\text{RME} = \frac{26\ \text{mg}\ \mathbf{6a}}{48\ \text{mg}\ \mathbf{R1} + 17.6\ \text{mg}\ \mathbf{6}} \text{x} 100 = 40\%$$

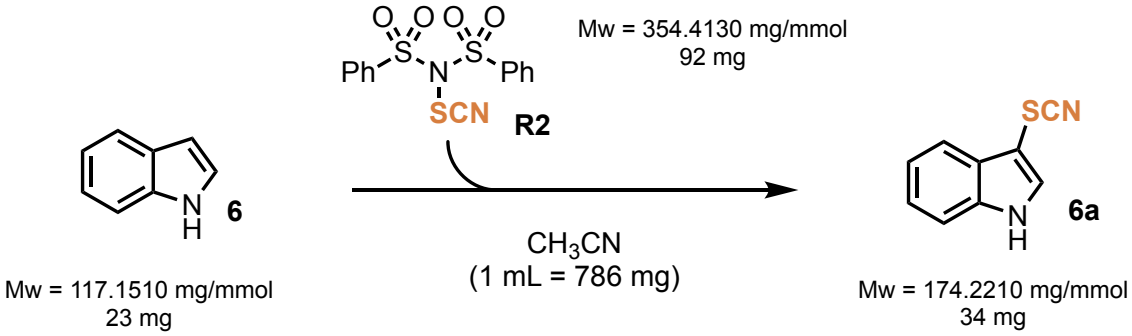
$$\text{sEF} = \frac{17.6\ \text{mg}\ \mathbf{6} + 48\ \text{mg}\ \mathbf{R1} - 26\ \text{mg}\ \mathbf{6a}}{26\ \text{mg}\ \mathbf{6a}} = 1.52$$

$$\text{EF} = \frac{17.6\ \text{mg}\ \mathbf{6} + 48\ \text{mg}\ \mathbf{5a} + 887\ \text{mg}\ \text{CH}_3\text{CN} - 26\ \text{mg}\ \mathbf{6a}}{26\ \text{mg}\ \mathbf{6a}} = 35.6$$

$$\text{Solvent contribution} = \frac{35.6\ \text{EF} - 1.52\ \text{sEF}}{35.6\ \text{EF}} \text{x} 100 = 95\%$$

Protocol 3 (R2)

Org. Biomol. Chem., 2019, **17**, 7131–7134.



$$\text{AE} = \frac{174.2210\ \text{mg/mmol}\ \mathbf{6a}}{354.4130\ \text{mg/mmol}\ \mathbf{R2} + 117.1510\ \text{mg/mmol}\ \mathbf{6}} \text{ x } 100 = 37\%$$

$$\text{RME} = \frac{34\ \text{mg}\ \mathbf{6a}}{92\ \text{mg}\ \mathbf{R2} + 23\ \text{mg}\ \mathbf{6}} \text{x} 100 = 30\%$$

$$\text{sEF} = \frac{23\ \text{mg}\ \mathbf{6} + 92\ \text{mg}\ \mathbf{R2} - 34\ \text{mg}\ \mathbf{6a}}{34\ \text{mg}\ \mathbf{6a}} = 2.38$$

$$\text{EF} = \frac{23\ \text{mg}\ \mathbf{6} + 92\ \text{mg}\ \mathbf{5a} + 786\ \text{mg}\ \text{CH}_3\text{CN} - 34\ \text{mg}\ \mathbf{6a}}{34\ \text{mg}\ \mathbf{6a}} = 25.5$$

$$\text{Solvent contribution} = \frac{25.5\ \text{EF} - 2.38\ \text{sEF}}{25.5\ \text{EF}} \text{x} 100 = 90\%$$

4. ECOSCALE Calculation

The Ecoscale values for the different protocols were calculated using the *Ecoscale calculator* website https://ecoscale.cheminfo.org/.

Protocol 1 (5a). *This work*

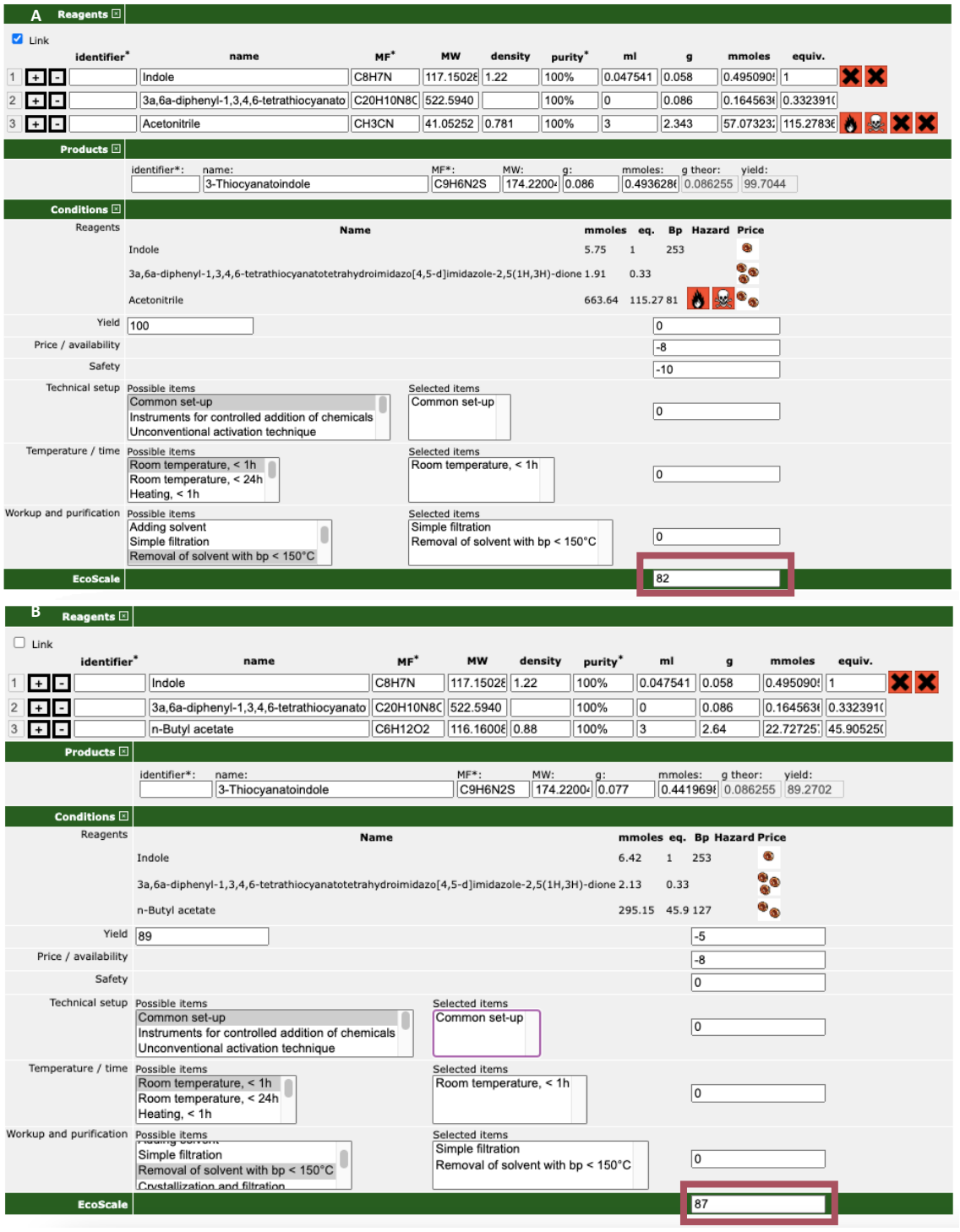


Figure S3. Ecoscale calculation for Protocol 1 with reagent **5a**. (A) Using acetonitrile as a solvent and (B) using n-butyl acetate as a solvent

Protocol 2 (R1)

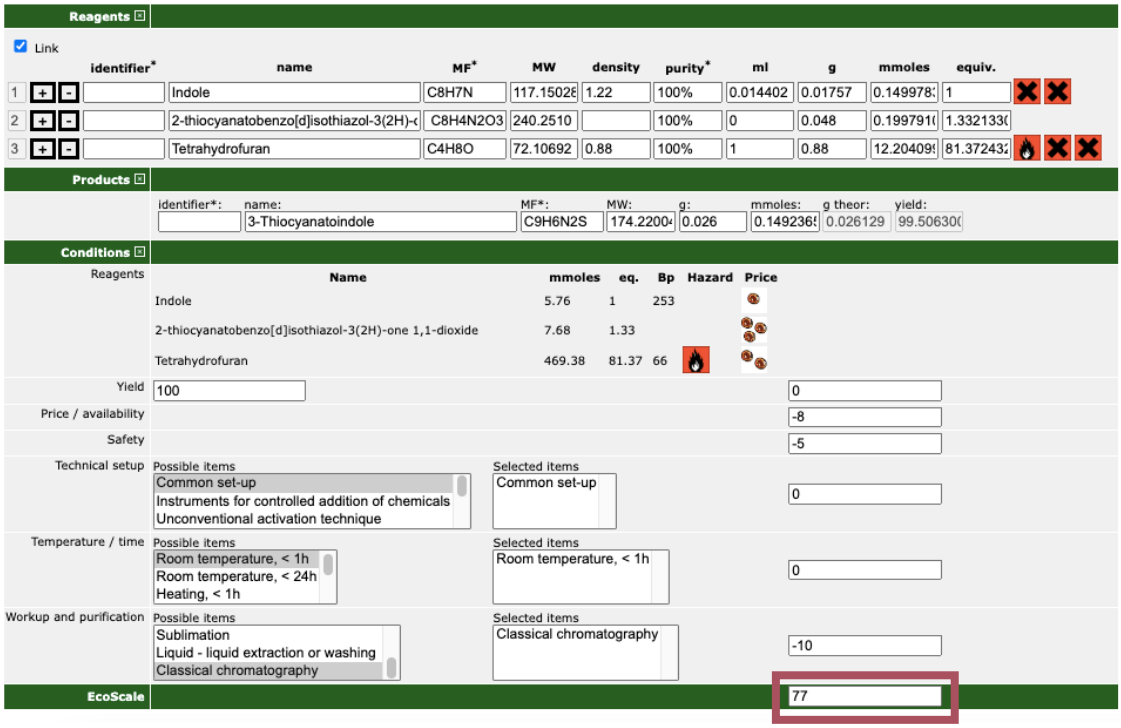


Figure S4. Ecoscale calculation for Protocol 2 with **R1** reagent. *J. Org. Chem*., 2018, **83**, 1576–1583

Protocol 3 (R2)

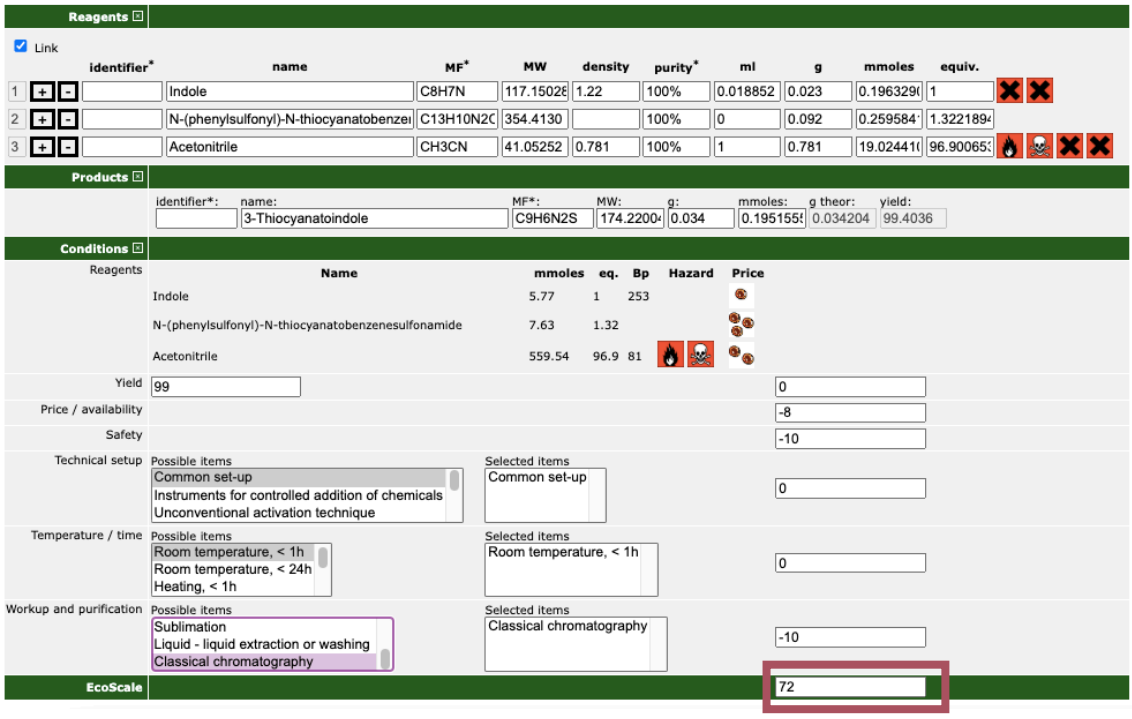


Figure S5. Ecoscale calculation for Protocol 3 with **R2** reagent. *Org. Biomol. Chem*., 2019, **17**, 7131–7134

5. Experimental procedures for flow chemistry

5.1 Packed bed reactor preparation

To perform flow chemistry experiments, a packed bed was selected as the appropriate module for reagent **5a**. The reactor consisted of an empty polypropylene (PP) cartridge from an automated flash chromatography column, which was filled with a mixture of **5a** and glass beads (425–600 µL) in a weight ratio of 1:1. Importantly, this mixture was grinded in an agate mortar and dried 30 min under vacuum before filling up the cartridge. In our system, the cartridge could be filled with a mixture of ~6 g of **5a** and glass beads. The empty volume of the reactor was determined to be ~4 mL by weighting the filled cartridge before and after flushing it with the solvent of choice. (Figure S6).[2]

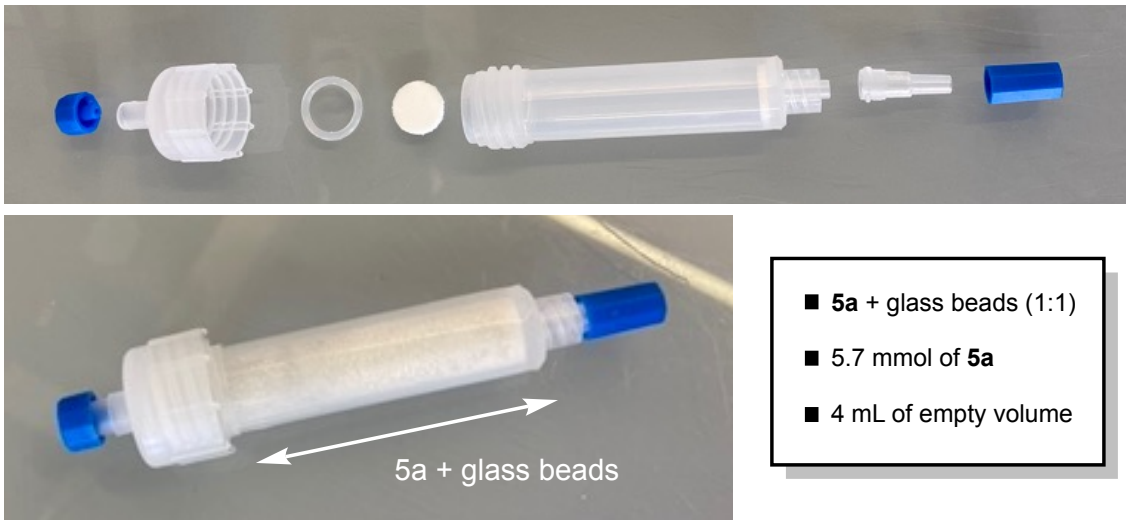


Figure S6. Packed bed reactor used in this study

5.2 Flow chemistry set-up

The set-up consists of a syringe pump where a syringe is inserted, which is connected to the cartridge via PFA tubing using Luer adapters. From the reactor, another tube will be attached ending with a needle in order to release the liquid drop by drop in a controlled manner (Figure S7A).

Once the set-up is complete, a solution of the desired substrate was prepared in the solvent of choice. This solution will be loaded into the syringe of the syringe pump, which will push the corresponding solution through the system. As it passes through the reactor, the reaction will occur, retaining the solid byproducts formed during the reaction and allowing the corresponding solution containing the product to pass through. The product will be collected at the end of the system (Figure S7B).

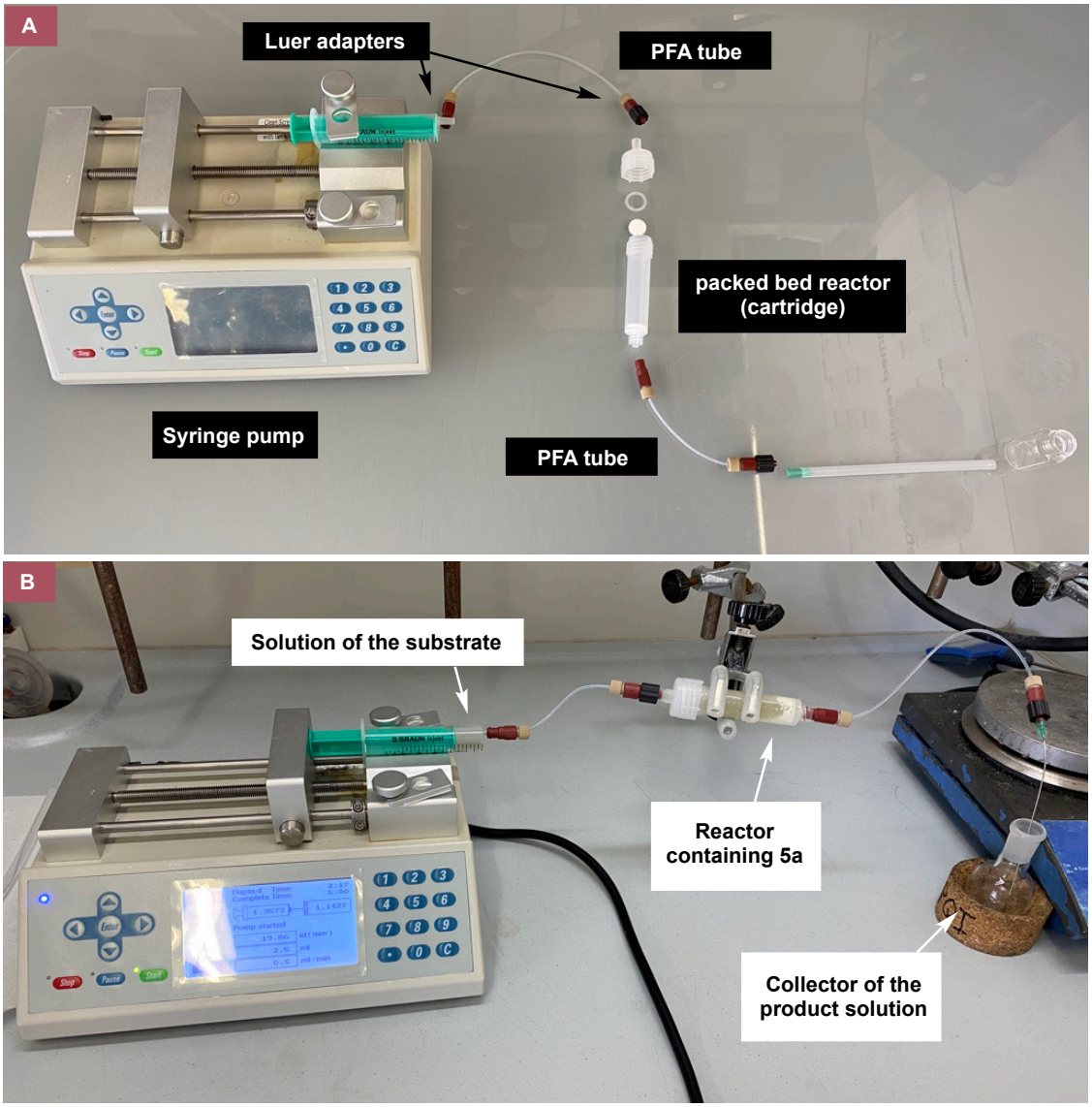
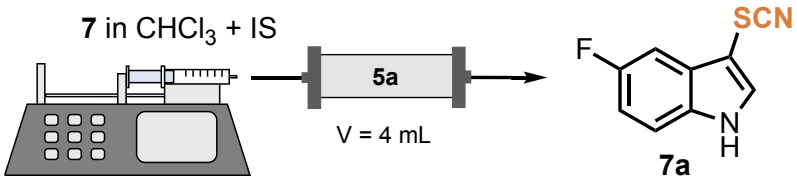


Figure S7. (A) Set-up description. (B) Schematic representation of the reaction procedure using a flow chemistry setup

5.3 Flow chemistry optimization

A 0.2 M solution of 5-fluoroindole **7** (810 mg 6 mmol) in $CHCl_3$ (30 mL) was prepared by adding 1,3-bis(trifluoromethyl)benzene (155 µL, 1 mmol) as an internal standard (IS). This solution is loaded into the syringe pump to pass through the reactor, which was charged with reagent **5a** (2.3 g, 4.4 mmol), in 5 mL increments at different flow rates (Table S2).

Table S2. Flow chemistry optimization with 5-fluoroindole



Entry	Flow rate (mL/min)	Residence time (min)	7 (%)[a]	7a (%)[a]
1	8	0.5	80	0
2	4	1	78	7
3	2	2	73	8
4	1	4	60	22
5	0.67	6	30	50
6	0.5	8	0	91

[a]The yield was determined by ^{19}F NMR by directing the flow into an NMR tube and collecting approximately 0.6 mL using 1,3-bis(trifluoromethyl)benzene (BTB) as an internal standard.

When the optimal conditions were repeated using *n*-butyl as a solvent, the product **7a** was obtained in 87% yield.

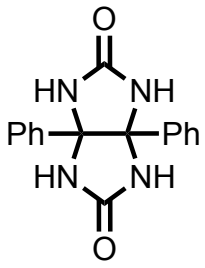
5.4 Sequential flow chemistry procedure for multiple consecutive experiments

Three 0.5 M solutions of the substrate 5-fluoroindole **7** (135 mg, 1 mmol), aniline **20** (91 µL, 1 mmol), and phenol **21** (94 mg, 1 mmol) were prepared in $CHCl_3$ (5 mL) each. Considering that the cartridge has a capacity of 4 mL, it was begun by passing the first solution through the reactor, which was charged with reagent **5a** (3.0 g, 5.7 mmol). Once the solution was fully consumed, an additional 4 mL of pure solvent was passed through to wash the reactor, pushing any potential product that might remain inside the cartridge, which was collected in the same flask obtaining **7a** in 91% of yield. Using the same cartridge, the next syringe was loaded with the solution of the subsequent substrate, and the process was repeated, with the new product being collected in a new flask obtaining **21a** in quantitative yield. The same procedure was followed for the third substrate yielding **20a** in 90%. The same procedure was repeated replacing the solvent with the greener n-butyl acetate. Although the yields slightly decreased (**7a**: 82%, **21a**: 88% , and **20a**: 79%), the corresponding products were still obtained in a pure clean form.

6. Synthesis

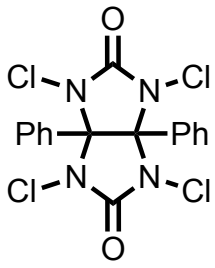
General Remarks. Proton (^{1}H NMR), carbon (^{13}C NMR), selenium (^{77}Se NMR), and fluorine (^{19}F NMR) nuclear magnetic resonance spectra were recorded on a Varian Mercury or a Bruker Avance Ultrashield spectrometer operating at 400 MHz for ^{1}H, 100.6 MHZ for ^{13}C, 76.5 MHz for ^{77}Se, and 376.5 MHz for ^{19}F. For insoluble samples, carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^{1}H, using a 5 mm BBO gradient probe with enhanced proton sensitivity, and 125.77 MHZ for ^{13}C. All chemical shifts are quoted on the δ scale in parts per million (ppm) using the residual solvent as internal standard (^{1}H NMR: $CDCl_3$ = 7.26, CD_3CN = 1.94, CD_3OD = 3.31, CD_2Cl_2 = 5.32 and ^{13}C RMN; $CDCl_3$ = 77.16, CD_3CN = 118.26, CD_3OD = 49.00, CD_2Cl_2 = 53.84). Coupling constants (*J*) are reported in Hz with the following splitting abbreviations: s = singlet, bs = broad singlet, d = doublet, t =triplet, q = quartet, dd = doublet of doublet, tt = triplet of triplet, td = triplet of doublet, dt = doublet of triplet, ddt = doublet of doublet of triplet. High–resolution mass spectra (HRMS) were recorded on an Agilent 1100 Series LC/MSD mass spectrometer with electrospray ionization (ESI). For GC−HRMS mass determination the compounds were directly analyzed by gas chromatography coupled to high-resolution mass spectrometry (Thermo Scientific™ TRACETM 1310 GC system/Exactive GC Orbitrap mass spectrometer). The chromatographic column was a HP−5MS and carried gas was He. Ionization was done by electronic impact (EI), with electron energy of 70 eV. The instrument operated in high-resolution MS scan mode between 40−400 *m/z*. Nominal and exact *m/z* values are reported in Daltons. Thin layer chromatography (TLC) was carried out using commercial backed sheets coated with 60 Å F_{254} silica gel. Visualization of the silica plates was achieved using UV lamp (λ_{max} = 254 nm), 6% H_2SO_4 in EtOH, cerium molybdate and/or potassium permanganate staining solutions. Flash column chromatography was carried out using silica gel 60 Å CC (230–400 mesh). Mobile phases are reported in relative composition (*e.g.*, 1:1 EtOAc/hexane v/v). All reactions using anhydrous conditions were performed using oven–dried apparatus under an atmosphere of argon. Brine refers to a saturated solution of sodium chloride. Anhydrous sodium sulfate (Na_2SO_4) was used as drying agent after reaction work–up, as indicated. All reagents were purchased from Sigma Aldrich, Cymit, Carbosynth, Apollo Scientific, Fluorochem, and Manchester Organics chemical companies.

6.1. Reagent preparation

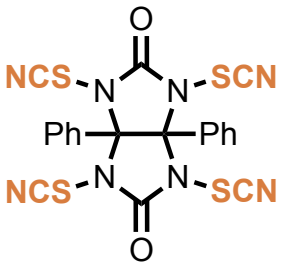


3a,6a-diphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (3). Following a reported procedure,[3] a 2000 mL round-bottom flask, equipped with a magnetic stir bar, was charged with urea (20 g, 333 mmol, 1 equiv.), benzil (35 g, 166 mmol, 0.5 equiv.), and toluene (666 mL, 0.5 M). Then, trifluoroacetic acid (33.3 mL, 434 mmol, 1.3 equiv.) was added and the mixture was refluxed for 20 h. Once the reaction was completed, the mixture was cooled to room temperature. The resulting precipitate was filtered, washed with 9:1 EtOH/MeOH, and dried under reduced pressure to afford diphenylglycoluril **3** (36 g, 74%) as a white solid. **^{1}H NMR (DMSO-d_6, 400 MHz):** δ 7.73 (s, 4H), 7.10–6.93 (m, 10H). **FT–IR (neat) *v* in cm^{-1}:** 3212.8, 3062.4, 1669.1, 1483.9, 1448.3, 1313.3,

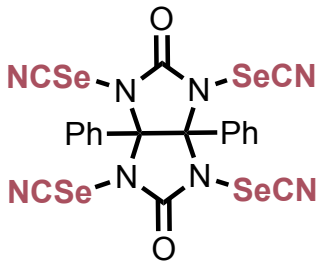
1224.6, 1138.8, 1076.1, 1030.8. Spectroscopic data are consistent with those previously reported.[4]



1,3,4,6-tetrachloro-3a,6a-diphenyltetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (4). Following a reported procedure,[4] a 2000 mL round-bottom flask, equipped with a magnetic stir bar, was charged with diphenylglycoluril **3** (20 g, 68 mmol, 1 equiv.) and H_2O (884 mL, 0.08 M). The solution was cooled down to 0 ºC with an ice-water bath and sodium acetate (NaOAc) (40 g, 487 mmol, 7 equiv.) was added followed by trichloroisocyanuric acid (TCCA). The mixture was stirred at room temperature for 20 h. Once the reaction was completed, the resulting precipitate was filtered, washed with H_2O (500 mL), and dried under reduced pressure to afford **4** (26 g, 89%) as a white solid. **^{1}H NMR (Acetone-d_6, 400 MHz):** δ 5.81 (m, 10H). **FT–IR (neat) *v* in cm^{-1}:** 1762.6, 1491.7, 1449.2, 1321.9, 1237.1, 1138.8, 1078.9, 1031.7, 1001.8. Spectroscopic data are consistent with those previously reported.[4]



3a,6a-diphenyl-1,3,4,6-tetrathiocyanatotetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (5a). A 500 mL round-bottom flask was charged with ammonium thiocyanate (3 g, 40.5 mmol, 5 equiv.). The flask was then evacuated and backfilled with argon three times. Subsequently, anhydrous CH_3CN (32 mL, 0.04 M) was added. The mixture was then cooled down to –10 ºC and **4** (3.5 g, 8.1 mmol, 1 equiv.) was added. The mixture was stirred 15 min at room temperature. Once the reaction was completed, the solution was filtered and concentrated under reduced pressure to afford **5a** (4 g, 95%) as a white solid. **^{1}H NMR (CD_3CN, 400 MHz):** δ 7.37–6.90 (m, 10H). **^{13}C NMR (CD_3CN, 125.8 MHz):** δ 156.30, 133.35, 130.91, 129.51, 128.66, 112.52, 87.32. **FT–IR (neat) *v* in cm^{-1}:** 2154.1, 1749.1, 1449.2, 1402.0, 1320.0, 1226.5, 1079.9, 1032.6, 1000.9, 931.5, 880.3, 852.4, 819.6. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{20}H_{11}N_8O_2S_4^+$ (*m/z*): calc. 522.9883; found 522.9861.



3a,6a-diphenyl-1,3,4,6-tetraselenocyanatotetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione (5b). A 500 mL round-bottom flask was charged with potassium selenocyanate (2.6 g, 18.4 mmol, 4 equiv.). The flask was then evacuated and backfilled with argon three times. Subsequently, anhydrous CH_3CN (12.5 mL, 0.09 M) was added. The mixture was then cooled down to –30 ºC and **4** (2 g, 4.6 mmol, 1 equiv.) was added. The mixture was stirred 20 min at room temperature. Once the reaction was completed, the solution was filtered and concentrated under reduced pressure to afford **5b** (2.5 g, 80%) as a red solid. **^{1}H NMR (CD_3CN, 400 MHz):** δ 7.13–6.94 (m, 10H). **FT–IR (neat) *v* in cm^{-1}:** 2247.63, 2121.6, 2091.4, 1672.9, 1407.8, 1316.2, 1219.8, 1142.6, 1108.9, 1076.1, 1030.8, 998.9, 956.5, 935.3.

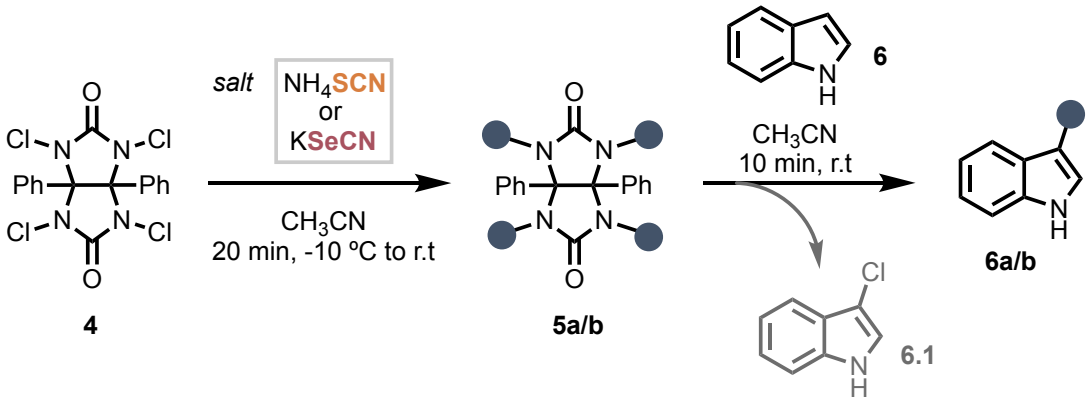
6.2. Additional characterization data and reactivity experiments

Reagents **5a** and **5b** were difficult to characterize by NMR due to their low solubility and high reactivity in solution.

N–Cl substitution

To rule out the presence of N–Cl substitution in the reagent, a series of experiments were conducted by preparing reagent **5a/b** using different equivalents of NH_4SCN/KSeCN (Table S3). When no source of XCN (X = S or Se) was used in the preparation of reagent **5**, only 3-chloroindole **6.1** was observed in the subsequent reaction (Table S3, entry 1). In contrast, using a substoichiometric amount of the XCN salts resulted in a mixture of both 3-chloroindole **6.1** and the XCN product (**6a** or **6b**, respectively). Finally, when an excess of the inorganic salt was added, only the XCN products were observed.

Table S3. One-pot consecutive reactions. Identification of reaction products and confirmation of N–Cl absence in the reagent structure



Entry	4 (equiv.)	Salt (equiv.)	6 (equiv.)	6a/b conv. (%)	6.1 conv. (%)
1	0.33	0	1	0	100
2	0.33	0.66	1	45	55
3	0.33	1.65	1	100	0

Throughout the investigation of nucleophiles, no chlorinated products were observed, indicating that N–Cl substitution is highly unlikely to be present in the reagent's structure.

Number of reactive S/SeCN groups in the glycoluril core

To estimate the number of reactive XCN groups (X = S or Se), a 1:10 equivalent reaction between 5-fluoroindole **7** and reagent **5a** or **5b** was carried out. In both cases, the ratio of starting material **7** to product **7a** or **7b** was 6:4, indicating the presence of four units of SCN or SeCN per glycoluril core (Figure S8).

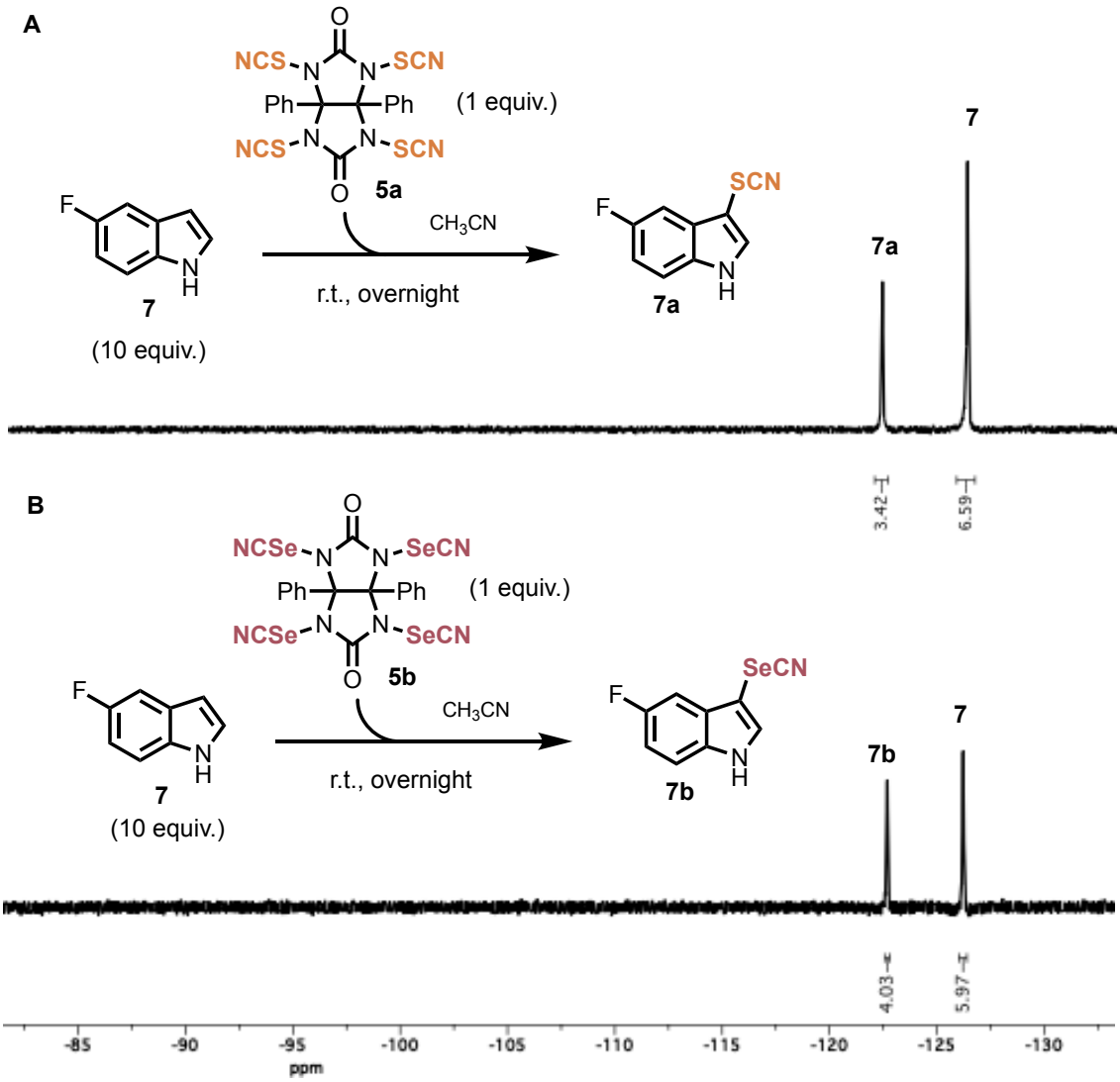


Figure S8. ^{19}F NMR demonstrates the ratio **7**/**7a,b**

HRMS and GC–MS analysis

The HRMS peak for **5a** was determined by HPLC–MS (ESI$^+$). However, obtaining an HRMS peak for **5b** proved difficult, likely due to its previously mentioned low solubility and high reactivity in solution (see Section 2). Nevertheless, the GC–MS (EI) chromatogram showed a single peak (t_R: 11.71 min) and *m/z* peaks in the mass spectrum with the characteristic selenium isotopic pattern (Figure S9).

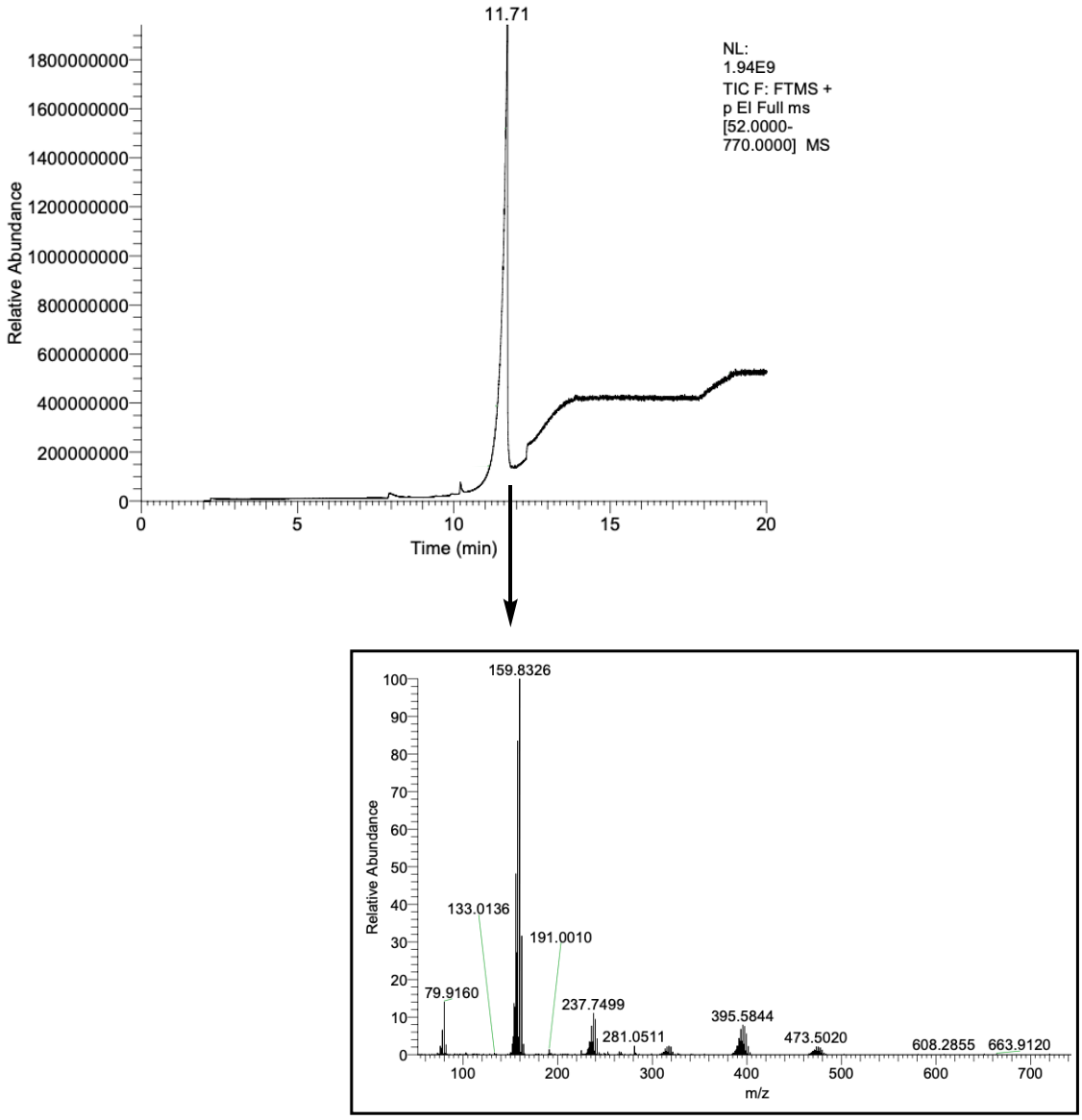
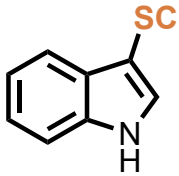


Figure S9. GC–MS (EI) chromatogram of **5b**

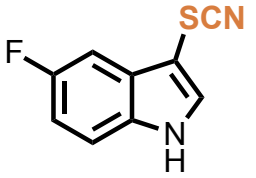
6.3. Substrate scope

General procedure A for thiocyanation (6a,b–30a). A 25 mL round-bottom flask, equipped with a magnetic stir bar, was charged with the substrate (1 equiv.), CH_3CN (or CH_2Cl_2) (0.16 M) and reagent **5a,b** (0.33 equiv.). Certain substrates required the addition of trifluoromethanesulfonic acid (TfOH) (1.5 equiv.). The mixture was stirred at room temperature, monitoring the progress of the reaction by TLC. Once the reaction was completed, the solution was filtered, concentrated under reduced pressure, and purified by flash column chromatography.

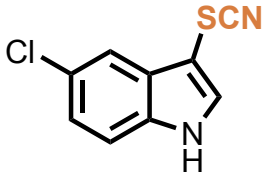


3-Thiocyanato-1*H*-indole (6a). This compound was prepared following the general procedure A, starting from 1*H*-indole **6** (58 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room

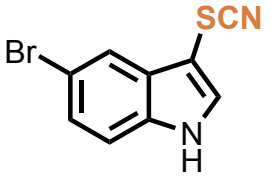
temperature for 10 min and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane) to afford **6a** (86 mg, 99%) as a yellow solid. ***R*$_f$**: (3:7 EtOAc/hexane): 0.39. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.67 (bs, 1H), 7.85–7.78 (m, 1H), 7.51 (d, *J* = 2.8 Hz, 1H), 7.47–7.41 (m, 1H), 7.36–7.29 (m, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 136.12, 131.06, 127.81, 124.05, 122.06, 118.92, 112.19, 111.98, 92.51. Spectroscopic data are consistent with those previously reported.[5]



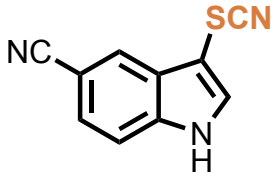
5-Fluoro-3-thiocyanato-1*H*-indole (7a). This compound was prepared following the general procedure A, starting from 5-fluoroindole **7** (67 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **7a** (93 mg, 97%) as a brown solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.13. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.84 (bs, 1H), 7.52 (d, *J* = 2.9 Hz, 1H), 7.42 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.34 (dd, *J* = 8.9, 4.2 Hz, 1H), 7.04 (td, *J* = 9.0, 2.5 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 159.11 (d, *J* = 238.8 Hz), 132.79, 132.54, 128.56 (d, *J* = 10.5 Hz), 113.32 (d, *J* = 9.6 Hz), 112.68 (d, *J* = 26.5 Hz), 112.02, 104.01 (d, *J* = 24.8 Hz), 92.15 (d, *J* = 3.9 Hz). **^{19}F NMR ($CDCl_3$, 376 MHz)**: δ –120.73 (td, *J* = 9.0, 4.2 Hz). Spectroscopic data are consistent with those previously reported.[6]



5-Chloro-3-thiocyanato-1*H*-indole (8a). This compound was prepared following the general procedure A, starting from 5-chloroindole **8** (76 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **8a** (103 mg, 99%) as a brown solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.14. **^{1}H NMR (CD_3OD, 400 MHz):** δ 12.50 (bs, 1H), 9.22 (d, *J* = 2.2 Hz, 1H), 8.99 (d, *J* = 2.0 Hz, 1H), 8.87–8.81 (m, 1H), 8.54 (dd, *J* = 8.7, 2.0 Hz, 1H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 135.02, 134.02, 128.86, 126.67, 123.31, 117.22, 114.09, 110.92, 90.58. Spectroscopic data are consistent with those previously reported.[5]

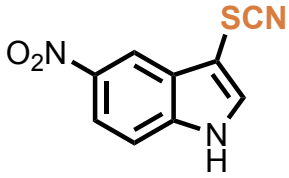


5-Bromo-3-thiocyanato-1*H*-indole (9a). This compound was prepared following the general procedure A, starting from 5-bromoindole **9** (98 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 22 h and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane) to afford **7a** (124 mg, 98%) as a white solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.28. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.74 (bs, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 2.9 Hz, 1H), 7.40 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.30 (dd, *J* = 8.7, 0.6 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 134.68, 132.06, 129.41, 127.10, 121.51, 115.49, 113.57, 111.46, 92.26. Spectroscopic data are consistent with those previously reported.[5]

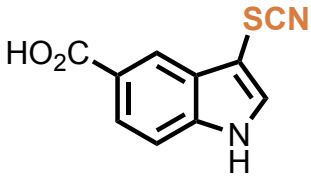


3-Thiocyanato-1*H*-indole-5-carbonitrile (10a). This compound was prepared following the general procedure A, starting from 5-cianoindole **10** (71 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 18 h

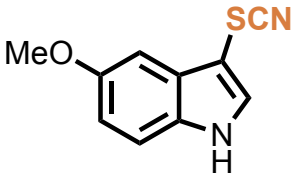
and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane) to afford **10a** (99 mg, 99%) as a white solid. ***R*$_f$**: (3:7 EtOAc/hexane): 0.15. **^{1}H NMR (CD_3OD), 400 MHz):** δ 13.31 (bs, 1H), 9.02 (s,1H), 9.00–8.94 (m, 1H), 8.58–8.46 (m, 1H), 8.43 (dd, *J* = 8.5, 1.5 Hz, 1H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 138.20, 135.93, 127.30, 125.71, 123.37, 119.91, 114.24, 112.01, 103.47, 91.50. Spectroscopic data are consistent with those previously reported.[7]



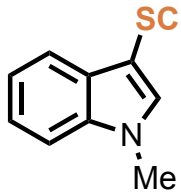
5-Nitro-3-thiocyanato-1*H*-indole (11a). This compound was prepared following the general procedure A, starting from 5-nitroindole **11** (81 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 22 h and purified by flash column chromatography (SiO_2, 1:1 EtOAc/hexane) to afford **11a** (108 mg, 99%) as an orange solid. ***R*$_f$**: (1:1 EtOAc/hexane): 0.32. **^{1}H NMR (CD_3CN, 400 MHz):** δ 10.38 (bs, 1H), 8.66 (dd, *J* = 2.2, 0.7 Hz, 1H), 8.18 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.93 (d, *J* = 2.9 Hz, 1H), 7.70 (dd, *J* = 9.0, 0.6 Hz, 1H). **^{13}C NMR (CD_3CN, 100.6 MHz):** δ 143.79, 140.03, 136.61, 127.77, 119.16, 115.47, 113.92, 111.93, 94.80. Spectroscopic data are consistent with those previously reported.[7]



3-thiocyanato-1*H*-indole-5-carboxylic acid (12a). This compound was prepared following the general procedure A, starting from 1*H*-indole-5-carboxylic acid **12** (81 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 18 h and purified by flash column chromatography (SiO_2, 1:9 MeOH/CH_2Cl_2) to afford **12a** (88 mg, 80%) as a yellow solid. ***R*$_f$**: (1:9 MeOH/CH_2Cl_2): 0.22. **^{1}H NMR (CD_3OD, 400 MHz):** δ 8.46 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.96 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.83 (s, 1H), 7.54 (dd, *J* = 8.6, 0.7 Hz, 1H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 139.41, 133.69, 127.28, 124.24, 123.62, 120.62, 111.98, 111.39, 92.26. Spectroscopic data are consistent with those previously reported.[8]

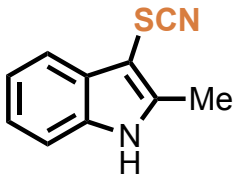


5-Methoxy-3-thiocyanato-1*H*-indole (13a). This compound was prepared following the general procedure A, starting from 5-methoxyindole **13** (74 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 10 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **11a** (101 mg, 99%) as an orange solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.20. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.79 (bs, 1H), 7.42 (d, *J* = 2.9 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 155.76, 131.62, 130.95, 128.56, 114.50, 113.19, 112.32, 99.85, 91.24, 55.94. Spectroscopic data are consistent with those previously reported.[5]

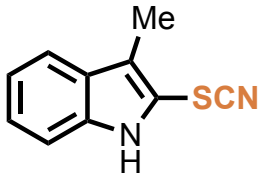


1-Methyl-3-thiocyanato-1*H*-indole (14a). This compound was prepared following the general procedure A, starting from 1-methyl-1*H*-indole **14** (66 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 22 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **14a** (89 mg, 94%) as a yellow solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.42. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.80 (dd, *J* = 7.2, 1.0 Hz,

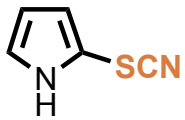
1H), 7.41–7.28 (m, 4H), 3.71 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 137.17, 135.17, 128.44, 123.42, 121.59, 118.85, 112.03, 110.32, 89.61, 33.37. Spectroscopic data are consistent with those previously reported.[5]



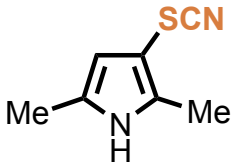
2-Methyl-3-thiocyanato-1*H*-indole (15a). This compound was prepared following the general procedure A, starting from 2-methyl-1*H*-indole **15** (66 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 3 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **15a** (90 mg, 96%) as a pink solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.23. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.65 (bs, 1H), 7.67 (ddd, *J* = 7.6, 1.5, 0.8 Hz, 1H), 7.34–7.16 (m, 3H), 2.44 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 141.10, 132.88, 127.44, 123.63, 120.47, 119.93, 118.92, 110.73, 109.57, 8.28. Spectroscopic data are consistent with those previously reported.[6]



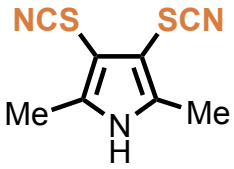
3-Methyl-2-thiocyanato-1*H*-indole (16a). This compound was prepared following the general procedure A, starting from 3-methyl-1*H*-indole **16** (66 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 22 h and purified by flash column chromatography (SiO_2, 1:9 EtOAc/hexane) to afford **16a** (61 mg, 64%) as a yellow solid. ***R*$_f$**: (1:9 EtOAc/hexane): 0.20. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.74 (bs, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.34–7.17 (m, 3H), 2.37 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 136.3, 130.4, 129.0, 123.1, 121.0, 119.0, 115.9 (t, *J* = 242.5 Hz), 111.8, 103.9, 39.1 (t, *J* = 23.2 Hz). Spectroscopic data are consistent with those previously reported.[9]



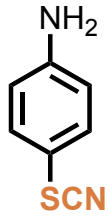
2-Thiocyanato-1*H*-pyrrole (17a). This compound was prepared following the general procedure A, starting from 1*H*-pyrrole **17** (34 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 24 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **17a** (64 mg, 99%) as a brown liquid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.27. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ 8.86 (bs, 1H), 6.94–6.86 (m, 1H), 6.61–6.48 (m, 1H), 6.19 (q, *J* = 3.0 Hz, 1H). **^{13}C NMR (CD_2Cl_2, 100.6 MHz):** δ 124.52, 121.14, 119.99, 111.14, 103.24. Spectroscopic data are consistent with those previously reported.[5]



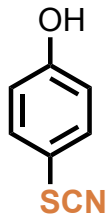
2,5-Dimethyl-3-thiocyanato-1*H*-pyrrole (18a). This compound was prepared following the general procedure A, starting from 2,5-dimethyl-1*H*-pyrrole **18** (47 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 10 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **18a** (54 mg, 72%) as a brown solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.25. **m.p.**: 145.3–148.6 ºC; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.20 (bs, 1H), 5.94 (s, 1H), 2.30 (s, 3H), 2.19 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 132.92, 127.60, 113.14, 110.48, 94.51, 12.83, 11.21. **FT–IR (neat) *v* in cm^{-1}:** 3325.6, 3181.0, 2921.6, 2151.2, 1592.9, 1522.5, 1408.75, 1393.3, 1286.3, 1240.9. Spectroscopic data are consistent with those previously reported.[6]



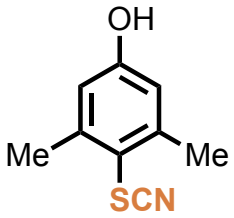
2,5-Dimethyl-3,4-dithiocyanato-1*H*-pyrrole (19a). This compound was prepared following the general procedure A, starting from 2,5-dimethyl-1*H*-pyrrole **18** (47 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 2 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **19a** (21 mg, 20%) as a brown solid. ***R_f***: (1:4 EtOAc/hexane): 0.13. **m.p.**: 80.9–83.1 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.93 (bs, 1H), 2.29 (s, 6H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 135.62, 111.16, 99.90, 11.89. **FT–IR (neat) *ν* in cm^{-1}:** 3350.7, 2921.63, 2852.2, 2155.1, 1730.8, 1577.5, 1534.1, 1439.6, 1389.5, 1366.3. **HRMS (EI)** for $(M)^{+\cdot}$ $C_8H_7N_3S_2^{+\cdot}$ (*m/z*): calc. 209.0081; found 209.0076.



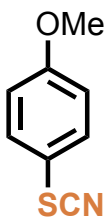
4-Thiocyanatoaniline (20a). This compound was prepared following the general procedure A, starting from aniline **20** (46 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 10 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **20a** (74 mg, 99%) as an orange solid. ***R_f***: (1:4 EtOAc/hexane): 0.15. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.6 Hz, 2H), 3.92 (bs, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 148.99, 134.54, 116.10, 112.57, 109.33. Spectroscopic data are consistent with those previously reported.[8]



4-Thiocyanatophenol (21a). This compound was prepared following the general procedure A, starting from phenol **21** (47 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 10 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **21a** (75 mg, 99%) as a yellow oil. ***R_f***: (1:4 EtOAc/hexane): 0.20. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.42 (dd, *J* = 8.6, 1.4 Hz, 2H), 6.87 (dd, *J* = 8.6, 1.5 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 158.26, 134.33, 117.57, 112.92, 112.49. Spectroscopic data are consistent with those previously reported.[8]

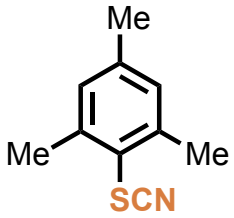


3,5-Dimethyl-4-thiocyanatophenol (22a). This compound was prepared following the general procedure A, starting from 3,5-dimethylphenol **22** (61 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 10 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **22a** (89 mg, 99%) as a yellow solid. ***R_f***: (1:4 EtOAc/hexane): 0.32. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.65 (d, *J* = 0.7 Hz, 2H), 5.76 (bs, 1H), 2.52 (s, 6H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 158.03, 145.05, 116.23, 112.54, 111.64, 22.07. Spectroscopic data are consistent with those previously reported.[8]

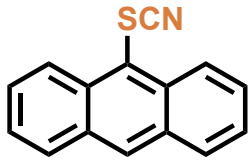


1-Methoxy-4-thiocyanatobenzene (23a). This compound was prepared following the general procedure A, starting from anisole **23** (54 mg, 0.5 mmol), **5a** (86 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 30 min and purified by flash column chromatography (SiO_2, 1:9 EtOAc/hexane) to afford **23a** (62 mg, 75%) as a yellow oil. ***R_f***: (1:9 EtOAc/hexane): 0.30. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.50 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J*

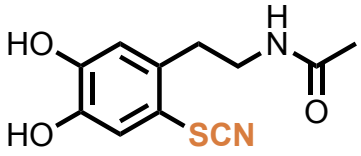
= 8.9 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 161.34, 133.82, 115.87, 113.82, 111.62, 55.56. Spectroscopic data are consistent with those previously reported.[8]



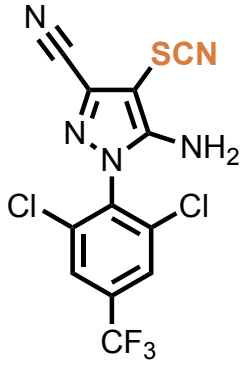
1,3,5-Trimethyl-2-thiocyanatobenzene (24a). This compound was prepared following the general procedure A, starting from mesitylene **24** (60 mg, 0.5 mmol), **5a** (86 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 18 h and purified by flash column chromatography (SiO_2, 100% hexane) to afford **24a** (77 mg, 86%) as a white solid. ***R*$_f$**: (100% hexane): 0.18. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.01 (d, *J* = 0.5 Hz, 2H), 2.55 (s, 6H), 2.30 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 142.71, 141.49, 130.06, 119.12, 110.88, 21.88, 21.08. Spectroscopic data are consistent with those previously reported.[7]



9-Thiocyanatoanthracene (25b). This compound was prepared following the general procedure A, starting from anthracene **25** (89 mg, 0.5 mmol), **5a** (86 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 18 h and purified by flash column chromatography (SiO_2, 100% hexane) to afford **25a** (86 mg, 73%) as an orange solid. ***R*$_f$**: (100% hexane): 0.13. **m.p.**: 174.6–176.0 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.57 (dd, *J* = 8.9, 1.0 Hz, 2H), 8.50 (s, 1H), 7.99–7.88 (m, 2H), 7.62 (ddd, *J* = 8.9, 6.6, 1.3 Hz, 2H), 7.46 (ddd, *J* = 8.1, 6.6, 1.1 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 133.91, 132.51, 131.86, 129.28, 128.69, 126.93, 125.31, 114.91, 110.88. **FT–IR (neat) *ν* in cm^{-1}:** 3050.83, 2920.7, 2851.2, 2148.3, 1731.8, 1621.8, 1521.6, 1438.6, 1377.9, 1306.5. **HRMS (EI)** for $(M)^{+\cdot}$ $C_{15}H_9NS^{+\cdot}$ (*m/z*): calc. 235.0456; found 235.0452.

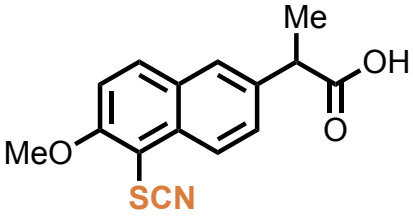


***N*-(4,5-Dihydroxy-2-thiocyanatophenethyl)acetamide (26a).** This compound was prepared following the general procedure A, starting from *N*-(3,4-dihydroxyphenethyl)acetamide **26** (54 mg, 0.28 mmol) and **5a** (48 mg, 0.092 mmol) in CH_3CN (2.5 mL). The mixture was stirred at room temperature for 18 h and purified by flash column chromatography (SiO_2, 0.5:9.5 MeOH/CH_2Cl_2 + 2% Et_3N) to afford **26a** (42 mg, 58%) as a brown oil. ***R*$_f$**: (0.5:9.5 MeOH/CH_2Cl_2 + 2% Et_3N): 0.18. **^{1}H NMR (CD_3OD, 400 MHz):** δ 7.08 (s, 1H), 6.80 (s, 1H), 3.39 (t, *J* = 7.3 Hz, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 1.92 (s, 3H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 171.98, 148.44, 145.15, 133.78, 120.46, 117.42, 111.75, 110.86, 39.90, 32.78, 21.14. **FT–IR (neat) *ν* in cm^{-1}:** 2920.7, 2159.9, 1558.2, 1507.1, 1434.8, 1362.5, 1036.6. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{11}H_{13}N_2O_3S^+$ (*m/z*): calc. 253.0641; found 253.0640.

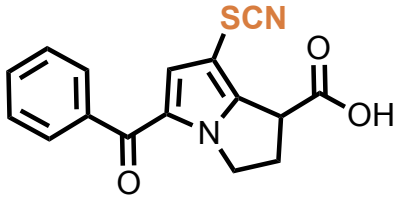


5-Amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-thiocyanato-1*H*-pyrazole-3-carbonitrile (27a). This compound was prepared following the general procedure A, starting from 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1*H*-pyrazole-3-carbonitrile **27** (96 mg, 0.3 mmol), **5a** (52 mg, 0.099 mmol), and TfOH (40 µL, 0.45 mmol) in CH_2Cl_2 (2.5 mL). The mixture was stirred at room temperature for 8 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **27a** (45 mg, 40%) as a yellow oil. ***R*$_f$**: (1:4 EtOAc/hexane): 0.10. **^{1}H**

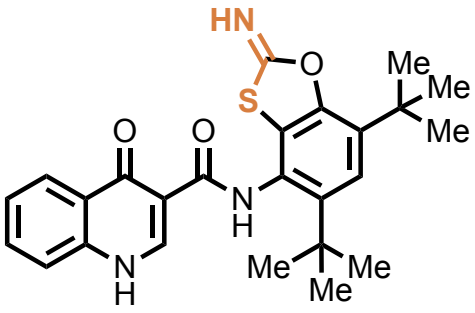
NMR ($CDCl_3$, 400 MHz): δ 7.82 (s, 2H), 4.53 (s, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 149.93, 136.45, 135.32 (q, *J* = 34.6 Hz), 134.35, 131.40, 126.53 (q, *J* = 3.7 Hz), 121.80 (appq, *J* = 274.2 Hz), 110.88, 108.47, 82.34. **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ –63.33 (s, 3F). **FT–IR (neat) *v* in cm^{-1}:** 3316.9, 3195.5, 2247.6, 1647.9, 1571.1, 1507.1, 1459.9, 1394.3, 1319.1, 1210.1. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{12}H_5Cl_2F_3N_5S^+$ (*m/z*): calc. 377.9589; found 377.9590.



2-(6-Methoxy-5-thiocyanatonaphthalen-2-yl)propanoic acid (28a). This compound was prepared following the general procedure A, starting from *rac*-Naproxen **28** (115 mg, 0.5 mmol), **5a** (86 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 1 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane + 1% AcOH) to afford **28a** (115 mg, 80%) as a white solid. ***R*$_f$**: (1:4 EtOAc/hexane + 1% AcOH): 0.15. **m.p.**: 169.1–172.6 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.29 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.75 (s, 1H), 7.64 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.32 (d, *J* = 9.1 Hz, 1H), 4.10 (s, 3H), 3.91 (q, *J* = 7.1 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 179.90, 158.74, 136.06, 133.83, 133.80, 129.42, 128.72, 127.12, 124.61, 113.36, 110.95, 103.63, 59.97, 44.99, 18.06. **FT–IR (neat) *v* in cm^{-1}:** 2941.8, 2152.2, 1704.8, 1594.8, 1495.5, 1479.1, 1456.9, 1418.4, 1374.0, 1354.8. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{15}H_{14}NO_3S^+$ (*m/z*): calc. 288.0688; found 288.0687.



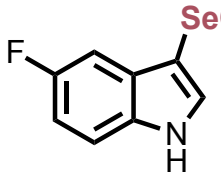
5-Benzoyl-7-thiocyanato-2,3-dihydro-1*H*-pyrrolizine-1-carboxylic acid (29a). This compound was prepared following the general procedure A, starting from Ketorolac **29** (127 mg, 0.5 mmol) and **5a** (86 mg, 0.165 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 24 h and purified by flash column chromatography (SiO_2, 1:10 CH_3CN/CH_2Cl_2 + 1% AcOH) to afford **29a** (150 mg, 96%) as a brown oil. ***R*$_f$**: (1:10 CH_3CN/CH_2Cl_2 + 1% AcOH): 0.16. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 10.11 (bs, 1H), 7.82–7.76 (m, 2H), 7.62–7.53 (m, 1H), 7.48 (dd, *J* = 8.2, 6.8 Hz, 2H), 6.99 (s, 1H), 4.60–4.48 (m, 2H), 4.20 (dd, *J* = 7.9, 5.5 Hz, 1H), 3.00–2.84 (m, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 185.18, 177.73, 175.06, 145.05, 137.83, 132.45, 128.93, 128.55, 128.45, 128.21, 111.24, 94.29, 48.93, 42.21, 31.41, 20.82. **FT–IR (neat) *v* in cm^{-1}:** 2925.5, 2156.0, 1714.4, 1625.7, 1596.8, 1573.6, 1524.5, 1489.7, 1457.9, 1438.6. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{16}H_{13}N_2O_3S^+$ (*m/z*): calc. 313.0641; found 313.0643.



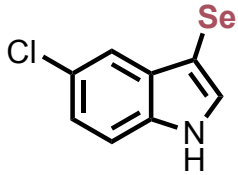
***N*-(5,7-di-*tert*-Butyl-2-iminobenzo[*d*][1,3]oxathiol-4-yl)-4-oxo-1,4-dihydroquinoline-3-carboxamide (30a).** This compound was prepared following the general procedure A, starting from Ivacaftor **30** (117 mg, 0.3 mmol) and **5a** (52 mg, 0.099 mmol) in CH_2Cl_2 (2.5 mL). The mixture was stirred at room temperature for 5 h and purified by flash column chromatography (SiO_2, 1:9 $MeOH/CH_2Cl_2$) to afford **30a** (116 mg, 87%) as a white solid. ***R*$_f$**: (1:9 $MeOH/CH_2Cl_2$): 0.25. **m.p.**: 228.1–230.2 ºC. **^{1}H NMR (CD_3OD, 400 MHz):** δ 8.87 (s, 1H), 8.45–8.39 (m, 1H), 7.87–7.78 (m, 1H), 7.69 (dt, *J* = 8.3, 0.9

Hz, 1H), 7.56 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.38 (s, 1H), 1.46 (s, 9H), 1.44 (s, 9H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 177.44, 166.85, 163.83, 146.58, 144.39, 142.17, 139.36, 133.20, 132.06, 126.76, 126.28, 126.03, 125.56, 125.54, 122.46, 11868, 109.80, 34.92, 34.40, 29.76, 28.53. **FT–IR (neat) *v* in cm^{-1}:** 3178.1, 2957.3, 1634.4, 1560.1, 1538.9, 1512.9, 1473.35, 1417.4, 1399.1, 1382.7. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{25}H_{28}N_3O_3S^+$ (*m/z*): calc. 450.1845; found 450.1845.

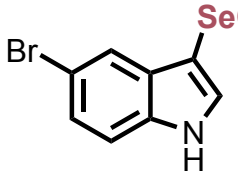
3-Selenocyanato-1*H*-indole (6b). This compound was prepared following the general procedure A, starting from 1*H*-indole **6** (58 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane) to afford **6b** (110 mg, 99%) as a brown solid. ***R$_f$***: (3:7 EtOAc/hexane): 0.34. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.78 (bs, 1H), 7.74–7.65 (m, 1H), 7.41–7.28 (m, 2H), 7.32–7.19 (m, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 136.07, 132.07, 128.70, 123.69, 121.79, 119.43, 112.10, 102.53, 89.01. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 152.97. Spectroscopic data are consistent with those previously reported.[10]



5-Fluoro-3-selenocyanato-1*H*-indole (7b). This compound was prepared following the general procedure A, starting from 5-fluoroindole **7** (67 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **7b** (111 mg, 93%) as a brown solid. ***R$_f$***: (1:4 EtOAc/hexane): 0.11. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.66 (bs, 1H), 77.57 (d, *J* = 2.8 Hz, 1H), 7.44–7.34 (m, 2H), 7.06 (td, *J* = 9.0, 2.5 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 159.07 (d, *J* = 238.6 Hz), 132.42, 132.45, 129.61 (d, *J* = 10.5 Hz), 112.92 (d, *J* = 9.6 Hz), 112.53 (d, *J* = 26.5 Hz), 104.83 (d, *J* = 24.7 Hz), 101.64, 89.55 (d, *J* = 4.8 Hz). **^{19}F NMR ($CDCl_3$, 376 MHz)**: δ –120.92 (td, *J* = 9.0, 4.2 Hz). **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 153.64. **FT–IR (neat) *v* in cm^{-1}:** 3315.0, 2915.8, 2848.4, 2156.0, 1735.6, 1582.3, 1484.9, 1455.0, 1416.5, 1373.1. Spectroscopic data are consistent with those previously reported.[11]

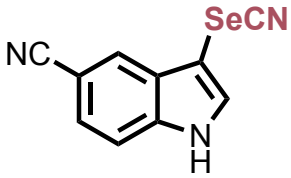


5-Chloro-3-selenocyanato-1*H*-indole (8b). This compound was prepared following the general procedure A, starting from 5-chloroindole **8** (76 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **8b** (128 mg, 99%) as an orange solid. ***R$_f$***: (1:4 EtOAc/hexane): 0.10. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.64 (bs, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 2.8 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.28–7.21 (m, 1H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 134.38, 132.99, 129.97, 127.98, 124.44, 119.32, 112.94, 101.21, 89.59. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 151.89. **FT–IR (neat) *v* in cm^{-1}:** 3330.5, 3125.1, 2154.1, 1860.0, 1700.9, 1617.9, 1568.8, 1495.5, 1460.8, 1446.4. **HRMS (ESI$^-$)** for $[M-H]^-$ $C_9H_4ClN_2Se^-$ (*m/z*): calc. 254.9233; found 254.9222.

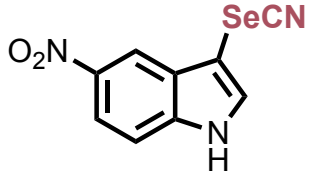


5-Bromo-3-selenocyanato-1*H*-indole (9b). This compound was prepared following the general procedure A, starting from 5-bromoindole **8** (98 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in

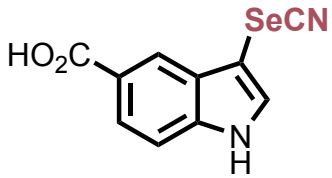
CH_3CN (3 mL). The mixture was stirred at room temperature for 20 h and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane) to afford **9b** (148 mg, 98%) as a brown solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.22; **^{1}H NMR (CD_3OD, 400 MHz):** δ 12.86 (bs, 1H), 8.73 (d, *J* = 2.8 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 8.30 (dd, *J* = 8.6, 0.6 Hz, 1H), 8.17 (dd, *J* = 8.6, 1.9 Hz, 1H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 135.38, 133.78, 130.60, 125.52, 121.13, 113.93, 113.57, 102.19, 88.24. **^{77}Se NMR (CD_3OD, 76.5 MHz)**: δ 151.73. Spectroscopic data are consistent with those previously reported.[12]



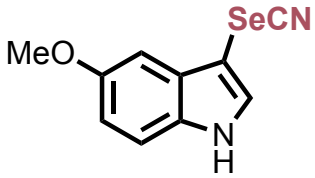
3-Selenocyanato-1*H*-indole-5-carbonitrile (10b). This compound was prepared following the general procedure A, starting from 5-cianoindole **10** (71 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 18 h and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane) to afford **10b** (119 mg, 98%) as a red solid. ***R*$_f$**: (3:7 EtOAc/hexane): 0.13. **^{1}H NMR (CD_3OD, 400 MHz):** δ 13.18 (bs, 1H), 8.92–8.86 (m, 2H), 8.49 (d, *J* = 8.5 Hz, 1H), 8.44–8.37 (m, 1H). **^{13}C NMR (CD_3OD, 100.6 MHz):** δ 138.15, 135.87, 128.61, 125.30, 124.28, 120.10, 113.89, 104.51, 103.00, 91.06. **^{77}Se NMR (CD_3OD, 76.5 MHz)**: δ 151.47. Spectroscopic data are consistent with those previously reported.[12]



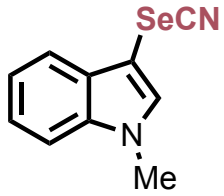
5-Nitro-3-selenocyanato-1H-indole (11b). This compound was prepared following the general procedure A, starting from 5-nitroindole **11** (81 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 h and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane) to afford **11b** (130 mg, 98%) as a yellow solid. ***R*$_f$**: (3:7 EtOAc/hexane): 0.12. **m.p.**: 208.7–210.1 ºC. **^{1}H NMR (CD_3CN, 400 MHz):** δ 10.35 (bs, 1H), 8.55 (d, *J* = 2.2 Hz, 1H), 8.13 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.86 (d, *J* = 2.8 Hz, 1H), 7.65 (dd, *J* = 9.0, 0.6 Hz, 1H). **^{13}C NMR (CD_3CN, 100.6 MHz):** δ 143.57, 140.05, 137.09, 128.95, 118.95, 116.32, 113.64, 102.64, 92.33. **^{77}Se NMR (CD_3CN, 76.5 MHz)**: δ 152.70. **FT–IR (neat) *ν* in cm^{-1}:** 2921.6, 2149.3, 1701.9, 1595.8, 1495.5, 1456.9, 1355.7, 1330.6, 1297.9, 1227.6. **HRMS (ESI$^-$)** for $[M\text{-}H]^-$ $C_9H_4N_3O_2Se^-$ (*m/z*): calc. 265.9474; found 265.9474.



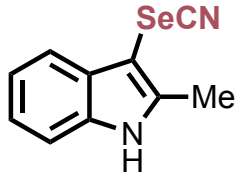
3-Selenocyanato-1*H*-indole-5-carboxylic acid (12b). This compound was prepared following the general procedure A, starting from 1*H*-indole-5-carboxylic acid **12** (81 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 22 h and purified by flash column chromatography (SiO_2, 1:9 $MeOH/CH_2Cl_2$) to afford **12b** (97 mg, 73%) as a yellow solid. ***R*$_f$**: (1:9 $MeOH/CH_2Cl_2$): 0.20. **m.p.**: 212.4–216.1 ºC. **^{1}H NMR (CD_3CN, 400 MHz):** δ 10.19 (bs, 1H), 8.46–8.41 (m, 1H), 8.01–7.94 (m, 1H), 7.84 (d, *J* = 2.9 Hz, 1H), 7.64 (dd, *J* = 8.7, 0.7 Hz, 1H). **^{13}C NMR (CD_3CN, 100.6 MHz):** δ 167.96, 139.68, 134.71, 127.86, 125.15, 123.99, 121.29, 113.29, 112.24, 93.36. **^{77}Se NMR (CD_3CN, 76.5 MHz)**: δ 146.93. **FT–IR (neat) *ν* in cm^{-1}:** 3303.5, 2250.5, 1665.2, 1616.1, 1418.4, 1347.0, 1288.2, 819.6. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{10}H_6N_2O_2Se^+$ (*m/z*): calc. 266.9666; found 266.9669.



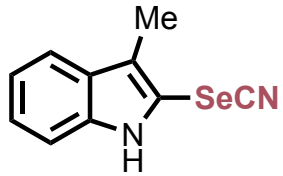
5-Methoxy-3-selenocyanato-1*H*-indole (13b). This compound was prepared following the general procedure A, starting from 5-methoxyindole **13** (74 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 10 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **13b** (124 mg, 99%) as an orange solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.17. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.79 (bs, 1H), 7.42 (d, *J* = 2.9 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 155.78, 132.39, 130.96, 129.60, 114.43, 112.96, 102.24, 100.76, 88.91, 55.97. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 151.51. Spectroscopic data are consistent with those previously reported.[12]



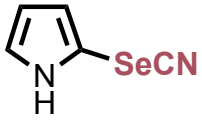
1-Methyl-3-selenocyanato-1*H*-indole (14b). This compound was prepared following the general procedure A, starting from 1-methyl-1*H*-indole **14** (66 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **14b** (107 mg, 91%) as a red solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.26. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.74 (dt, *J* = 7.1, 1.2 Hz, 1H), 7.43–7.22 (m, 4H), 3.73 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 137.17, 136.01, 129.50, 123.29, 121.49, 119.71, 110.12, 102.00, 87.03, 33.32. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 150.07. Spectroscopic data are consistent with those previously reported.[12]



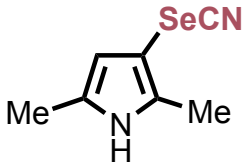
2-Methyl-3-selenocyanato-1*H*-indole (15b). This compound was prepared following the general procedure A, starting from 2-methyl-1*H*-indole **15** (66 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **15b** (110 mg, 94%) as a brown solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.19. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.53 (bs, 1H), 7.64–7.57 (m, 1H), 7.31–7.17 (m, 3H), 2.50 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 142.03, 135.42, 129.80, 122.88, 121.48, 118.92, 111.05, 102.07, 87.85, 13.04. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 128.74. Spectroscopic data are consistent with those previously reported.[12]



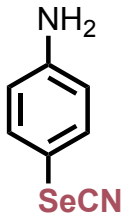
3-Methyl-2-selenocyanato-1*H*-indole (16b). This compound was prepared following the general procedure A, starting from 3-methyl-1*H*-indole **16** (66 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 22 h and purified by flash column chromatography (SiO_2, 1:9 EtOAc/hexane) to afford **16b** (93 mg, 79%) as a red solid. ***R*$_f$**: (1:9 EtOAc/hexane): 0.11. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.33 (bs, 1H), 7.59 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.36–7.25 (m, 2H), 7.22–7.14 (m, 1H), 2.46 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 138.15, 127.62, 124.77, 122.38, 120.34, 119.81, 111.26, 107.76, 100.09, 10.44. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 190.82. **FT–IR (neat) *v* in cm^{-1}:** 3374.8, 2149.3, 1541.8, 1454.1, 1398.1, 1290.1, 1224.6, 1058.7, 1009.5; Spectroscopic data are consistent with those previously reported.[13]



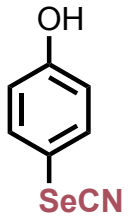
2-Selenocyanato-1*H*-pyrrole (17b). This compound was prepared following the general procedure A, starting from 1*H*-pyrrole **17** (34 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 1 h and purified by flash column chromatography (SiO_2, 1:9 EtOAc/hexane) to afford **17b** (61 mg, 70%) as a brown oil. ***R_f***: (1:9 EtOAc/hexane): 0.25. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ 8.80 (bs, 1H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.69–6.63 (m, 1H), 6.28 (q, *J* = 3.0 Hz, 1H). **^{13}C NMR (CD_2Cl_2, 100.6 MHz):** δ 124.65, 121.35, 111.34, 101.33, 99.63. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 217.72. **FT–IR (neat) *v* in cm^{-1}:** 3325.6, 2922.6, 2157.9, 2049.0, 1701.9, 1570.7, 1462.7, 1372.1. **HRMS (EI)** for $(M)^{+\cdot}$ $C_5H_4N_2Se^{+\cdot}$ (*m/z*): calc. 171.9540; found 171.9534.



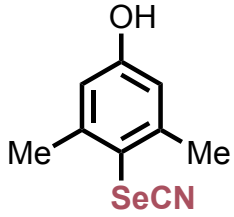
2,5-Dimethyl-3-selenocyanato-1*H*-pyrrole (18b). This compound was prepared following the general procedure A, starting from 2,5-dimethyl-1*H*-pyrrole **18** (47 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 30 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **18b** (55 mg, 55%) as a brown solid. ***R_f***: (1:4 EtOAc/hexane): 0.25. **m.p.**: 117.4–119.3 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.20 (bs, 1H), 5.97 (dd, *J* = 2.8, 1.1 Hz, 1H), 2.33 (s, 3H), 2.20 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 133.15, 127.86, 111.87, 103.15, 92.28, 12.79, 12.16. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 169.48. **FT–IR (neat) *v* in cm^{-1}:** 3331.4, 2921.6, 2853.2, 2144.5, 1587.1, 1403.9, 1391.4, 1369.2, 1233.3. **HRMS (TOF EI)** for $(M)^{+\cdot}$ for $C_7H_8N_2Se^{+\cdot}$ (*m/z*): calc. 199.9853; found 199.9848.



4-Selenocyanatoaniline (20b). This compound was prepared following the general procedure A, starting from aniline **20** (46 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **20b** (82 mg, 84%) as a brown solid. ***R_f***: (1:4 EtOAc/hexane): 0.11. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.44 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 3.94 (bs, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 148.81, 136.50, 116.27, 107.17, 102.71. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 306.37. Spectroscopic data are consistent with those previously reported.[13]

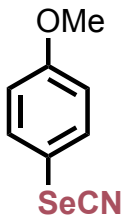


4-Selenocyanatophenol (21b). This compound was prepared following the general procedure A, starting from phenol **21** (47 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 1 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **21b** (84 mg, 85%) as a yellow solid. ***R_f***: (1:4 EtOAc/hexane): 0.18. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.53 (d, J = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 158.06, 136.38, 117.65, 110.63, 102.77. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 308.65. Spectroscopic data are consistent with those previously reported.[11]

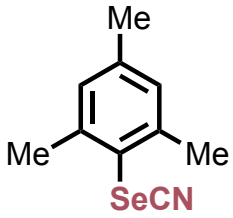


3,5-Dimethyl-4-selenocyanatophenol (22b). This compound was prepared following the general procedure A, starting from 3,5-dimethylphenol **22** (61 mg, 0.5 mmol) and **5b** (117 mg, 0.165 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature for 20 min and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane)

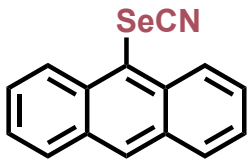
to afford **22b** (91 mg, 81%) as a yellow solid. ***R*$_f$**: (1:4 EtOAc/hexane): 0.26. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.66 (s, 2H), 2.55 (s, 6H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 157.82, 145.27, 115.81, 114.15, 101.75. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 193.10. Spectroscopic data are consistent with those previously reported.[12]



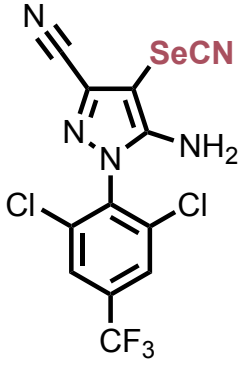
1-Methoxy-4-selenocyanatobenzene (23b). This compound was prepared following the general procedure A, starting from anisole **23** (54 mg, 0.5 mmol), **5b** (117 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 10 min and purified by flash column chromatography (SiO_2, 1:9 EtOAc/hexane) to afford **23b** (73 mg, 69%) as a yellow solid. ***R*$_f$**: (1:9 EtOAc/hexane): 0.27. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 161.38, 136.05, 116.02, 111.09, 102.02, 55.50. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 307.27. Spectroscopic data are consistent with those previously reported.[10]



1,3,5-Trimethyl-2-selenocyanatobenzene (24b). This compound was prepared following the general procedure A, starting from mesitylene **24** (60 mg, 0.5 mmol), **5b** (117 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 5 h and purified by flash column chromatography (SiO_2, 100% hexane) to afford **24b** (78 mg, 70%) as a yellow oil. ***R*$_f$**: (100% hexane): 0.13. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.01 (s, 2H), 2.58 (s, 6H), 2.30 (s, 3H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 142.92, 141.27, 129.66, 120.41, 101.29, 24.36, 21.01. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 195.47. **FT–IR (neat) *v* in cm^{-1}:** 2918.7, 2851.2, 2146.4, 1760.7, 1598.7, 1452.1, 1376.9, 1299.8, 1278.6, 1251.6. **HRMS (EI)** for $(M)^{+\cdot}$ $C_{10}H_{11}NSe^{+\cdot}$ (*m/z*): calc. 225.0057; found 225.0048.

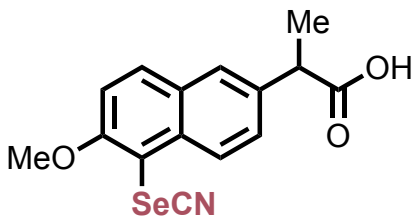


9-Selenocyanatoanthracene (25b). This compound was prepared following the general procedure A, starting from anthracene **25** (89 mg, 0.5 mmol), **5b** (117 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 8 h and purified by flash column chromatography (SiO_2, 100% hexane) to afford **25b** (100 mg, 71%) as a yellow solid. ***R*$_f$**: (100% hexane): 0.10. **m.p.**: 181.1–183.0 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.69–8.61 (m, 3H), 8.08–8.01 (m, 2H), 7.71 (ddd, *J* = 8.9, 6.6, 1.3 Hz, 2H), 7.57 (ddd, *J* = 8.0, 6.6, 1.1 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 134.40, 132.43, 131.95, 129.27, 128.54, 127.93, 125.87, 117.90, 101.11. **^{77}Se NMR ($CDCl_3$, 76.5 MHz)**: δ 161.00. **FT–IR (neat) *v* in cm^{-1}:** 30489, 2920.7, 2851.2, 2146.4, 1931.4, 1803.1, 1728.8, 1623.8, 1520.6, 1438.6. Spectroscopic data are consistent with those previously reported.[14]



5-Amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-selenocyanato-1*H*-pyrazole-3-carbonitrile (27b). This compound was prepared following the general procedure A, starting from 5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1*H*-pyrazole-3-carbonitrile **27** (96 mg, 0.3 mmol), **5b** (70 mg, 0.099 mmol), and TfOH (40 µL, 0.45 mmol) in CH_2Cl_2 (2.5 mL). The mixture was stirred at room temperature for 2 h and purified by flash column chromatography (SiO_2, 3:7 EtOAc/hexane)

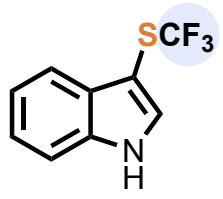
to afford **27b** (44 mg, 35%) as a yellow oil. ***R*$_f$**: (3:7 EtOAc/hexane): 0.15. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ 7.82 (s, 2H), 4.47 (s, 2H). **^{13}C NMR (CDCl$_3$, 100.6 MHz):** δ 150.40, 136.44, 135.29 (appq, *J* = 36.7 Hz), 134.54, 132.32, 126.50 (q, *J* = 3.9 Hz), 121.73 (q, *J* = 276.9 Hz), 111.47, 98.77, 79.02. **^{19}F NMR (CDCl$_3$, 376.5 MHz):** δ –63.31 (s, 3F). **^{77}Se NMR (CDCl$_3$, 76.5 MHz)**: δ 141.92. **FT–IR (neat) *v* in cm^{-1}:** 3417.2, 3332.4, 3243.7, 2251.5, 2161.8, 1742.4, 1636.3, 1567.9, 1509.0, 1455.0. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{12}H_5Cl_2F_3N_5Se^+$ (*m/z*): calc. 425.9033; found 425.9029.



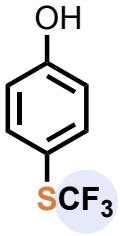
2-(6-Methoxy-5-selenocyanatonaphthalen-2-yl)propanoic acid (28b). This compound was prepared following the general procedure A, starting from *rac*-naproxen **28** (115 mg, 0.5 mmol), **5b** (117 mg, 0.165 mmol), and TfOH (66 µL, 0.75 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 5 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane + 1% AcOH) to afford **28b** (70 mg, 42%) as a yellow solid. ***R*$_f$**: (1:4 EtOAc/hexane + 1% AcOH): 0.13. **m.p.**: 169.3–171.6 ºC. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ 8.23 (d, *J* = 8.9 Hz, 1H), 7.94 (d, *J* = 9.1 Hz, 1H), 7.73 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.31 (d, *J* = 9.1 Hz, 1H), 4.06 (s, 3H), 3.91 (q, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (CDCl$_3$, 100.6 MHz):** δ 180.22, 158.17, 135.98, 134.20, 133.64, 129.66, 128.58, 127.09, 126.81, 113.29, 104.88, 101.33, 57.06, 45.03, 18.05. **^{77}Se NMR (CDCl$_3$, 76.5 MHz)**: δ 159.60. **FT–IR (neat) *v* in cm^{-1}:** 2921.6, 2149.3, 1701.9, 1595.8, 1495.5, 1456.9, 1355.7, 1330.6, 1297.8, 1271.8. **HRMS (ESI$^+$)** for $[M+H]^+$ $C_{15}H_{14}NO_3Se^+$ (*m/z*): calc. 336.0134; found 336.0135.

6.4. Derivatizations

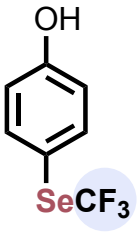
General procedure B for trifluoromethylation (31a–32a,b). A 5 mL round-bottom flask, equipped with a magnetic stir bar, was charged with the substrate (1 equiv.), potassium fluoride (3 equiv.), and DMF (0.2 M). The solution was cooled down to 0 ºC and trimethyl(trifluoromethyl)silane ($TMSCF_3$) was added. The mixture was stirred for 2 h at room temperature, monitoring the progress of the reaction by TLC. Upon completion, Et_2O was added to the reaction mixture, and then extracted with ammonium chloride. The organic layer was dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash column chromatography.



3-((Trifluoromethyl)thio)-1*H*-indole (31a). This compound was prepared following the general procedure B, starting from 3-thiocyanato-1*H*-indole **6a** (35 mg, 0.2 mmol), potassium fluoride (35 mg, 0.6 mmol), and $TMSCF_3$ (90 µL, 0.6 mmol) in DMF (1 mL). The mixture was stirred at room temperature for 2 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **31a** (33 mg, 75%) as a pink solid. ***R*$_f$**: (2:8 EtOAc/hexane): 0.23. **^{1}H NMR (CDCl$_3$, 400 MHz):** δ 8.51 (bs, 1H), 7.84–7.77 (m, 1H), 7.54 (dd, *J* = 2.7, 0.8 Hz, 1H), 7.48–7.37 (m, 1H), 7.34–7.23 (m, 2H). **^{13}C NMR (CDCl$_3$, 100.6 MHz):** δ 136.04, 134.07, 132.78, 129.48, 129.45 (q, *J* = 309.9 Hz), 123.47, 121.67, 119.38, 95.66 (appq, *J* = 2.6 Hz). **^{19}F NMR (CDCl$_3$, 376.5 MHz):** δ –44.64 (s, 3F). **HRMS (EI)** for $(M)^{+\cdot}$ $C_9H_6F_3NS^{+\cdot}$ (*m/z*): calc. 217.0173; found 217.0168.



4-((Trifluoromethyl)thio)phenol (32a). This compound was prepared following the general procedure B, starting from 4-thiocyanatophenol **21** (51 mg, 0.3 mmol), potassium fluoride (60 mg, 1 mmol), and $TMSCF_3$ (150 µL, 1 mmol) in DMF (2 mL). The mixture was stirred at room temperature for 2 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **32a** (46 mg, 70%) as a yellow oil. R_f: (1:4 EtOAc/hexane): 0.25. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.56–7.50 (m, 2H), 6.90–6.83 (m, 2H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 158.05, 138.57, 129.59 (q, *J* = 308.1 Hz), 116.54, 115.19 (appq, *J* = 2.2 Hz). **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ –43.94 (s, 3F). **HRMS (EI)** for $(M)^{+\cdot}$ $C_7H_5F_3OS^{+\cdot}$ (*m/z*): calc. 194.0013; found 194.0008.



4-((Trifluoromethyl)selanyl)phenol (32b). This compound was prepared following the general procedure B, starting from 4-selenocyanatophenol **21** (28 mg, 0.1 mmol), potassium fluoride (24 mg, 0.4 mmol), and $TMSCF_3$ (63 µL, 0.4 mmol) in DMF (0.7 mL). The mixture was stirred at room temperature for 2 h and purified by flash column chromatography (SiO_2, 1:4 EtOAc/hexane) to afford **32b** (25 mg, 72%) as a yellow oil. R_f: (1:4 EtOAc/hexane): 0.24. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.66–7.51 (m, 1H), 6.81–6.70 (m, 1H), 5.05 (bs, 1H). **^{13}C NMR ($CDCl_3$, 100.6 MHz):** δ 157.61, 139.23, 122.47 (q, *J* = 333.2 Hz), 116.70, 113.19. **^{19}F NMR ($CDCl_3$, 376.5 MHz):** δ –37.16 (s, 3F). **HRMS (EI)** for $(M)^{+\cdot}$ $C_7H_5F_3OSe^{+\cdot}$ (*m/z*): calc. 241.9458; found 241.9452.

7. NMR spectra

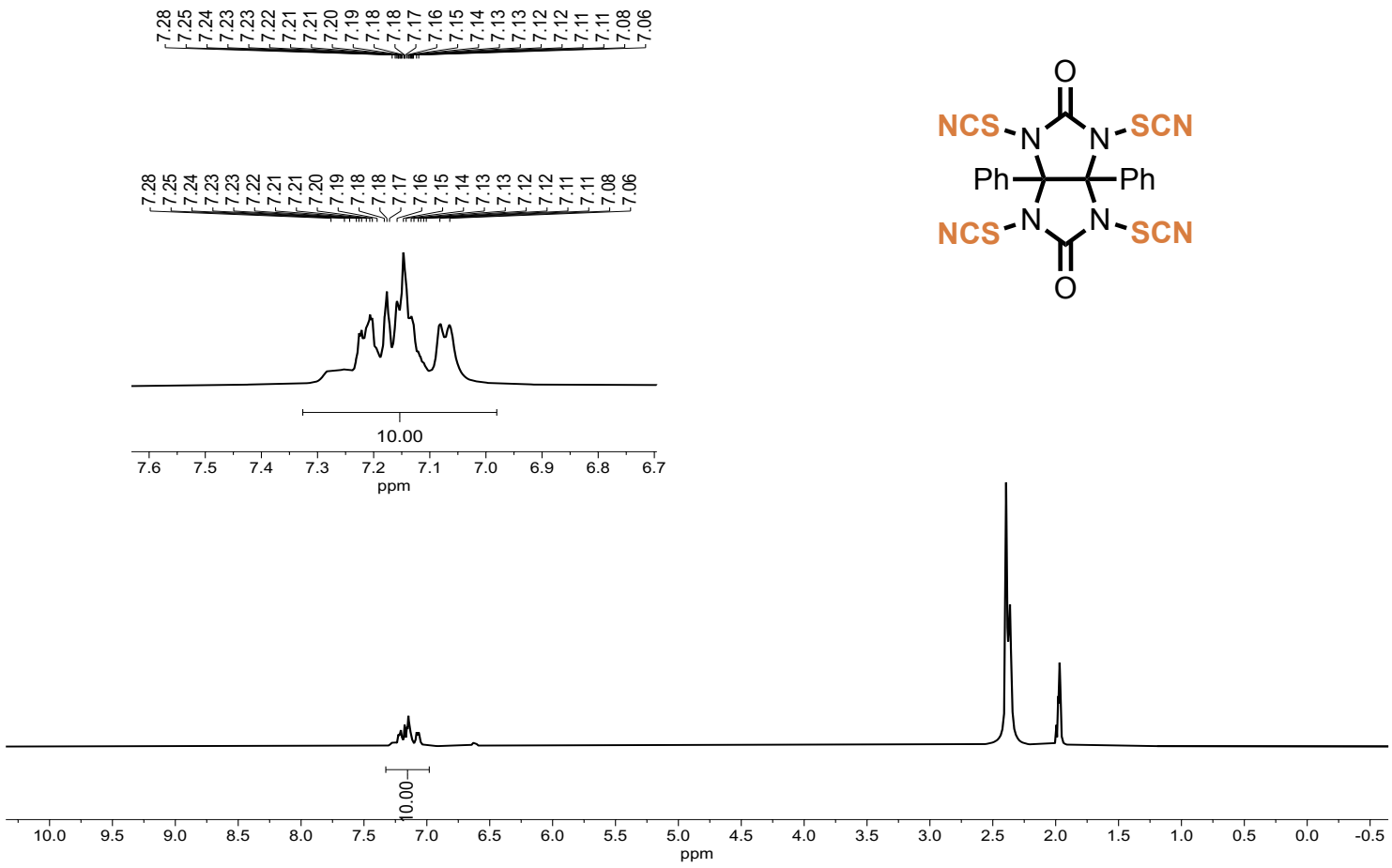


Figure S10. ^{1}H NMR (CD_3CN, 400 MHz) of **5a**

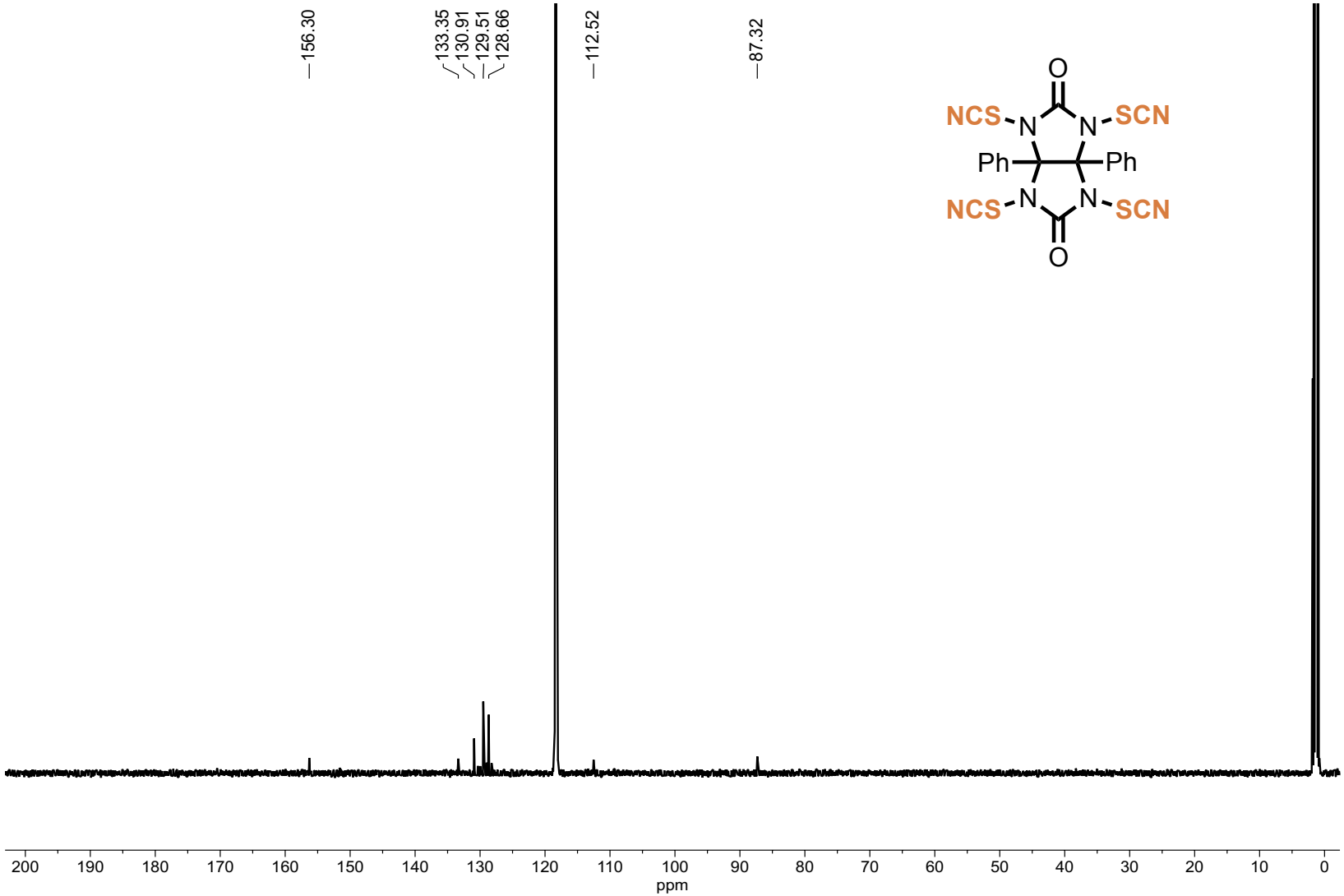


Figure S11. ^{13}C NMR (CD_3CN, 125.8 MHz) of **5a**

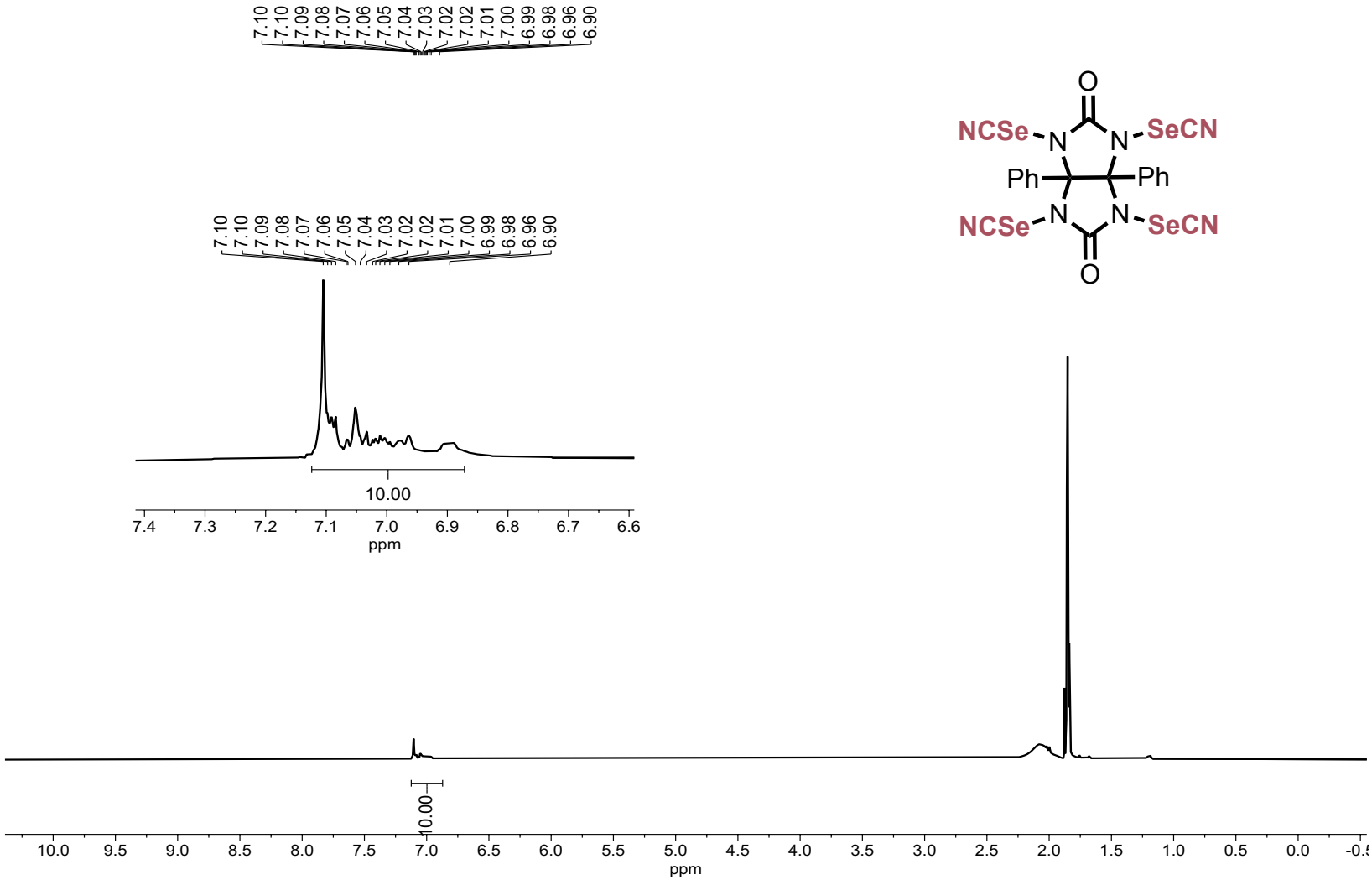


Figure S12. ^{1}H NMR (CD_3CN, 400 MHz) of **5b**

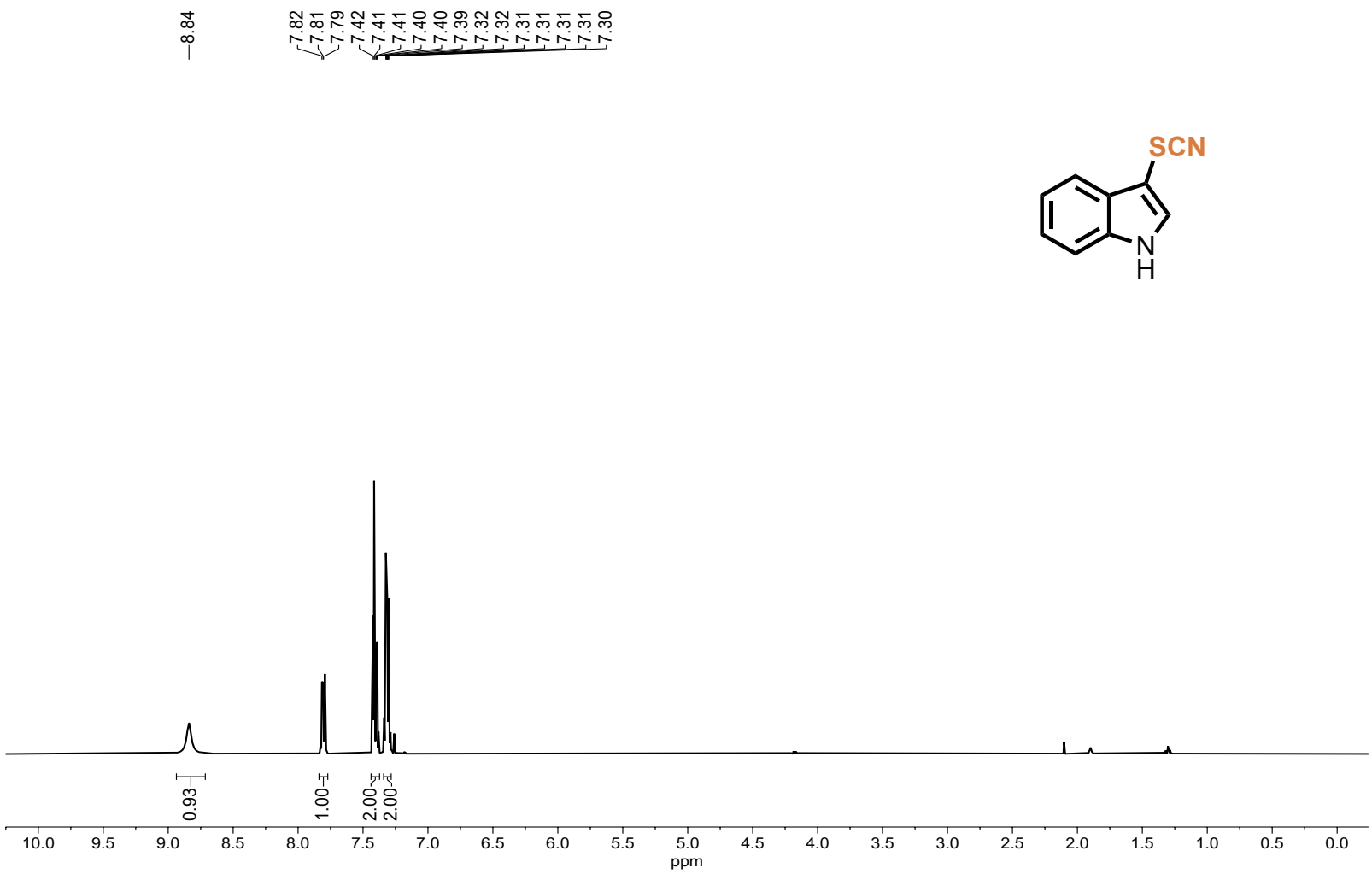


Figure S13. ^{1}H NMR ($CDCl_3$, 400 MHz) of **6a**

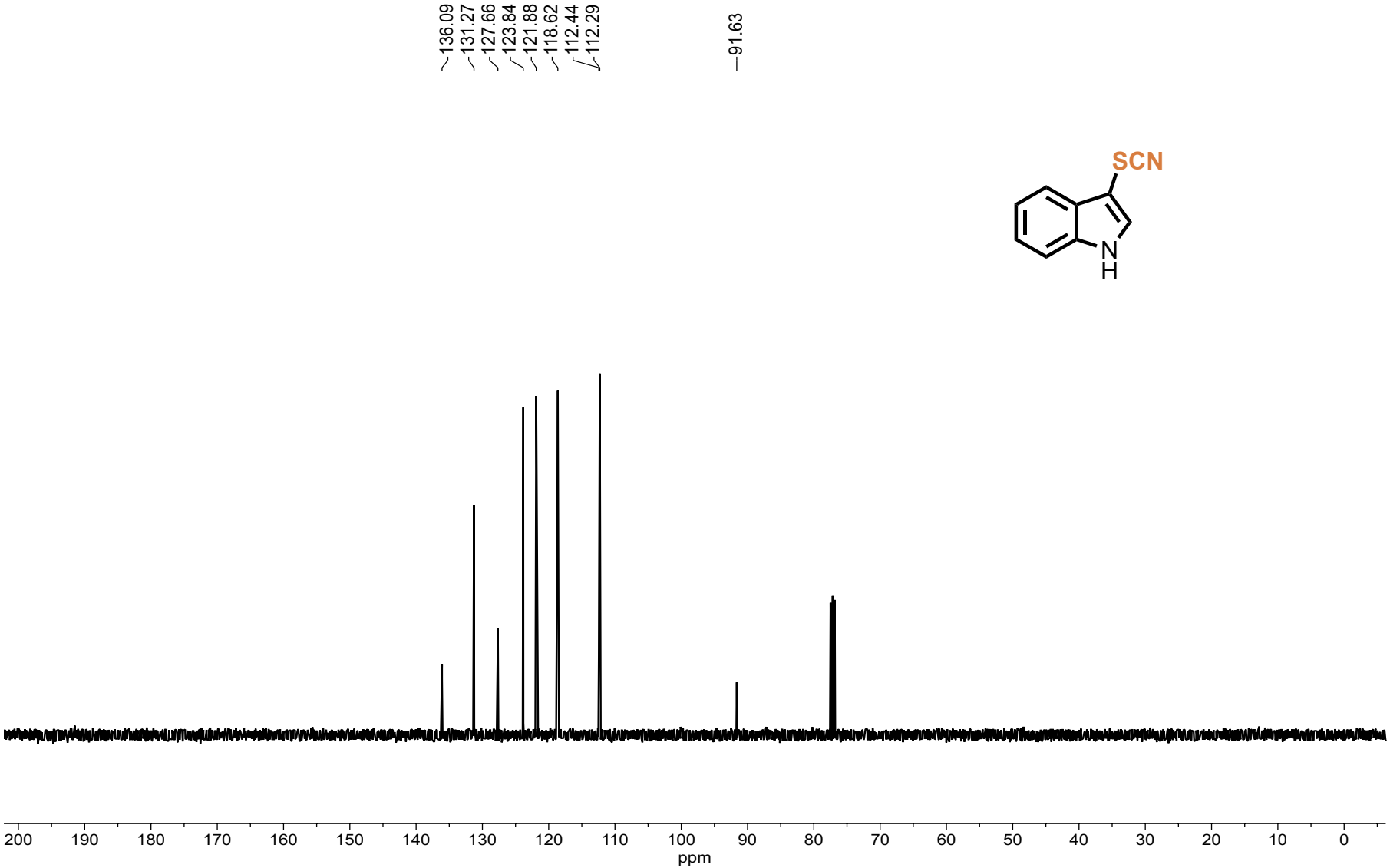


Figure S14. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **6a**

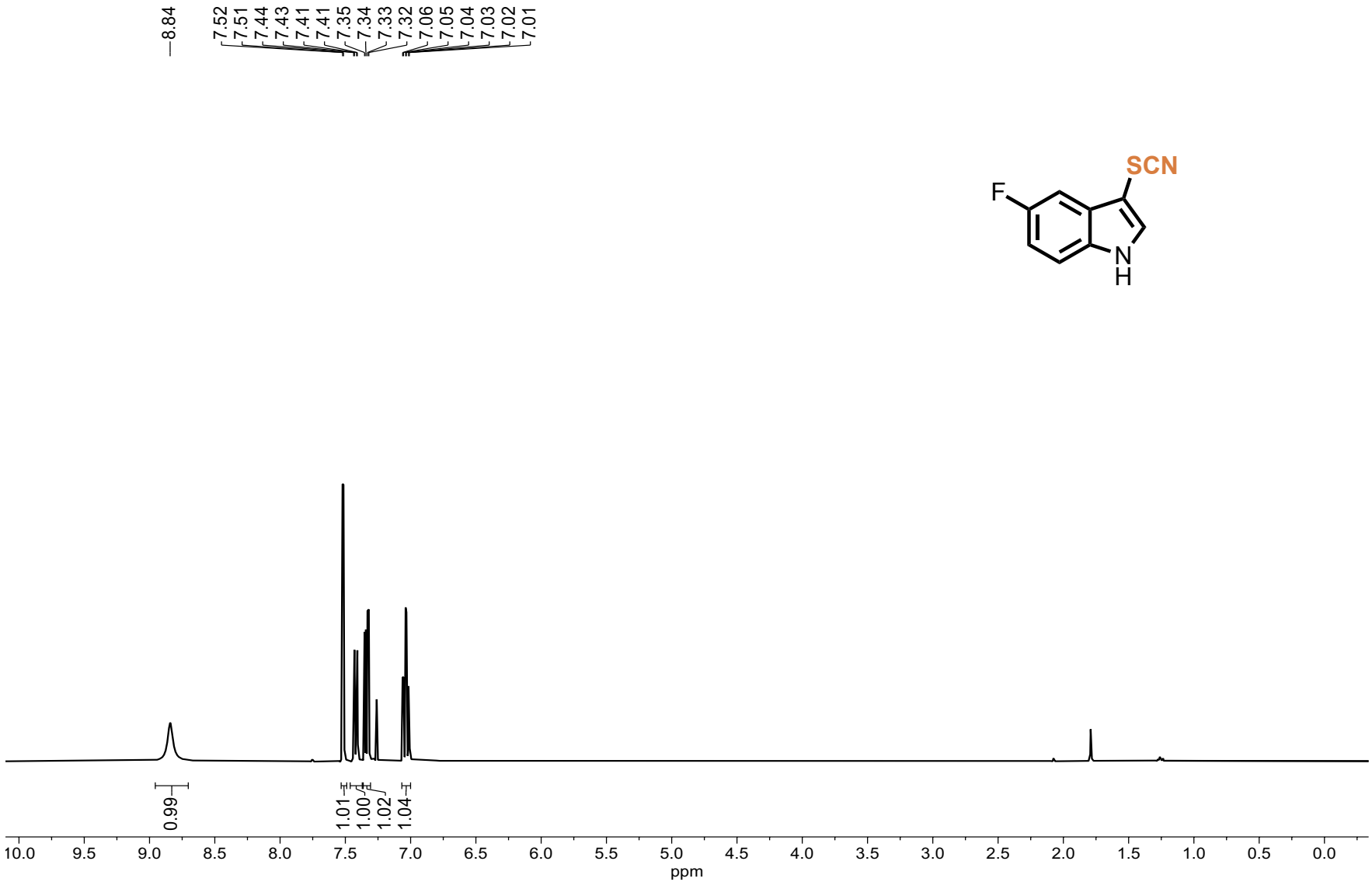


Figure S15. ^{1}H NMR ($CDCl_3$, 400 MHz) of **7a**

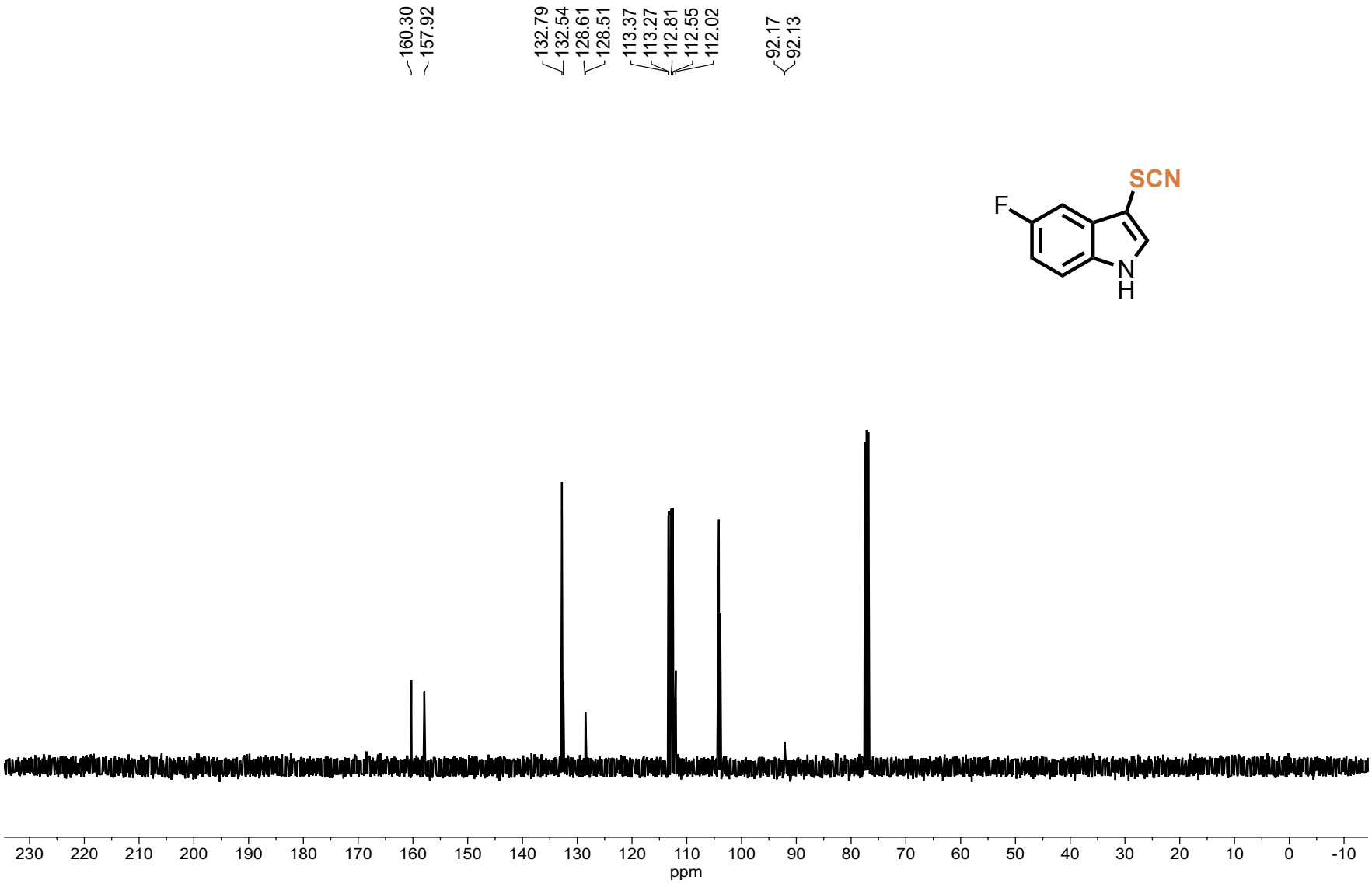


Figure S16. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **7a**

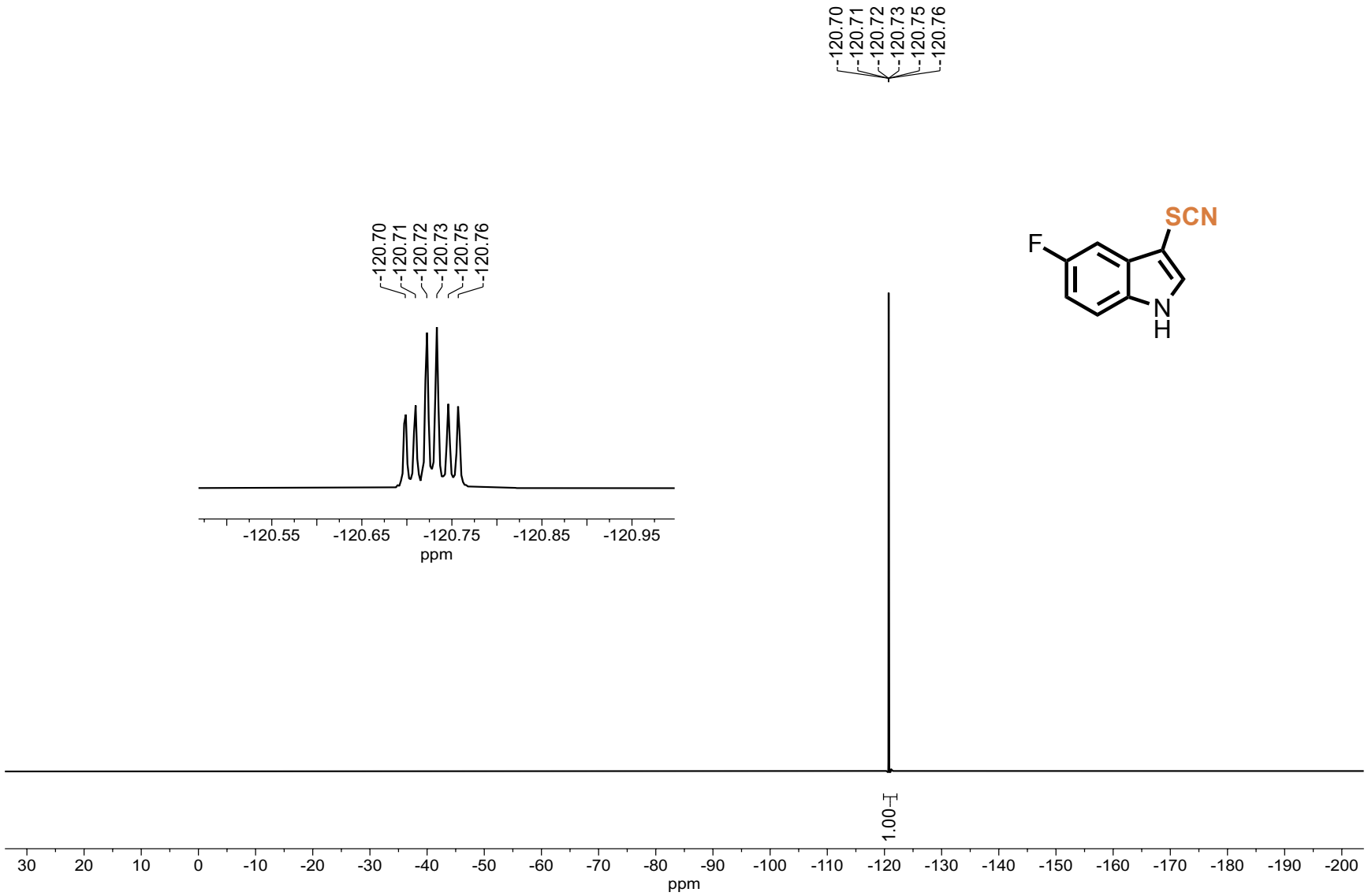


Figure S17. ^{19}F NMR ($CDCl_3$ 376.5 MHz) of **7a**

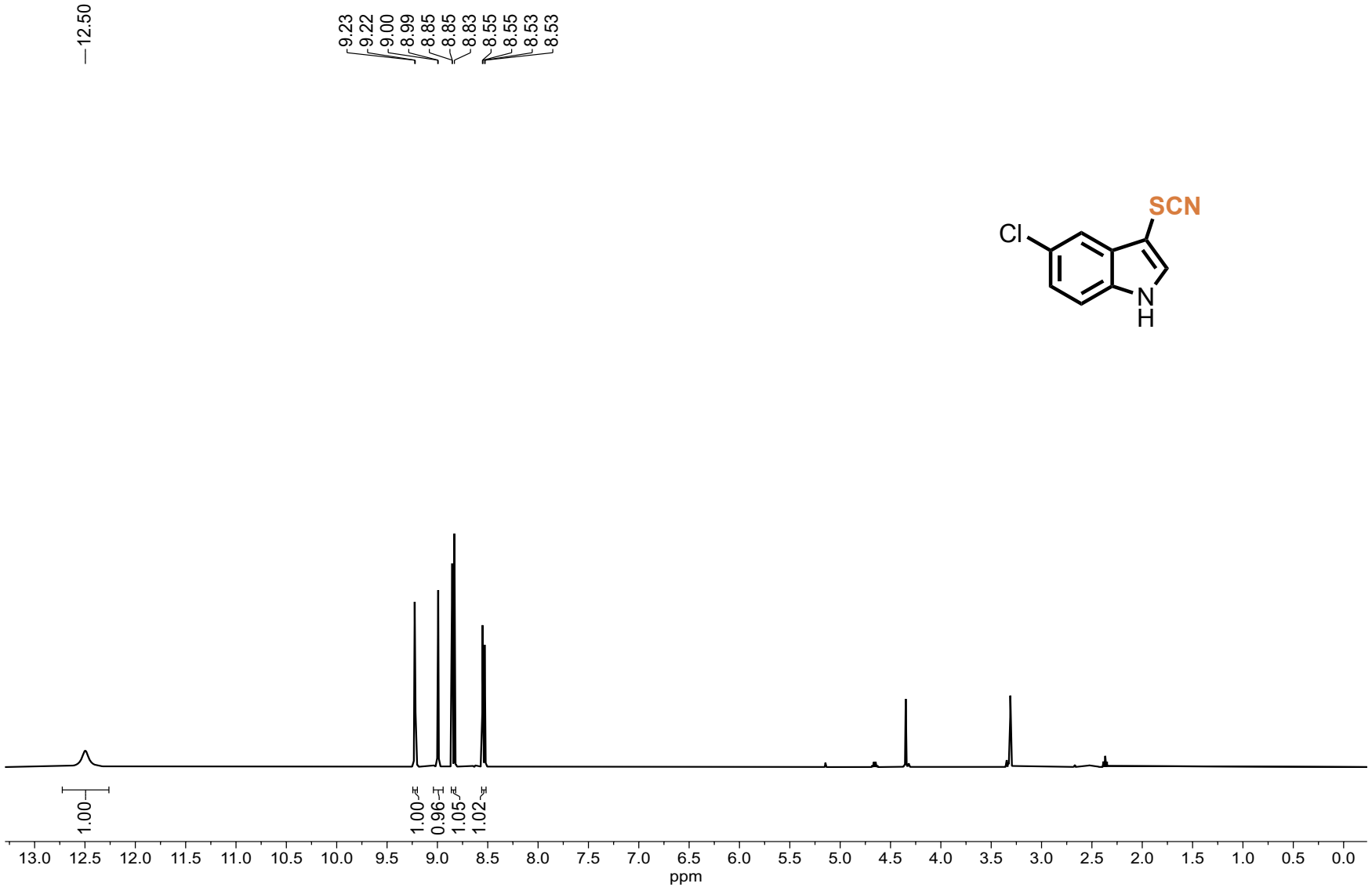


Figure S18. ^{1}H NMR (CD_3OD, 400 MHz) of **8a**

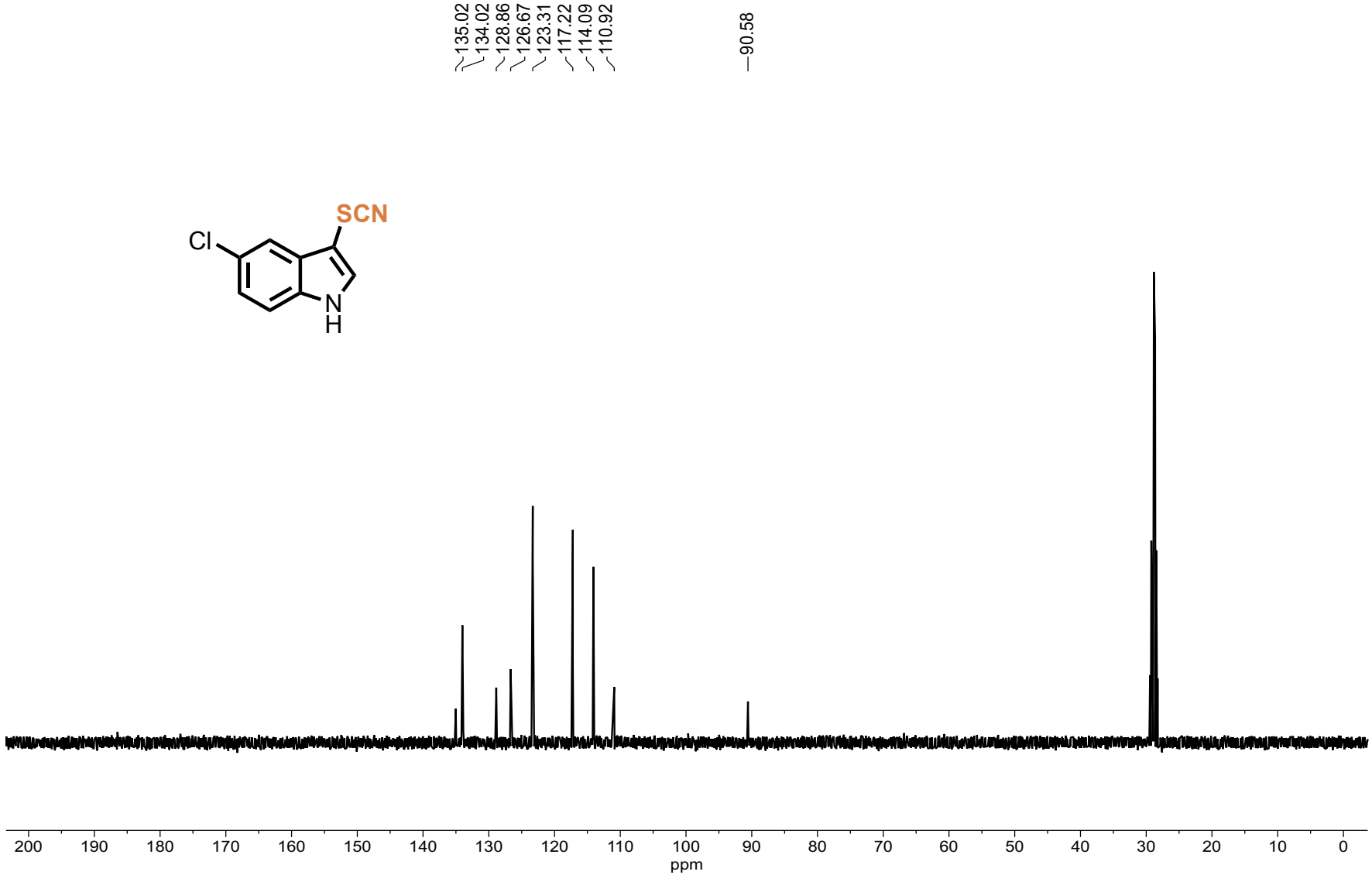


Figure S19. ^{13}C NMR (CD_3OD, 100.6 MHz) of **8a**

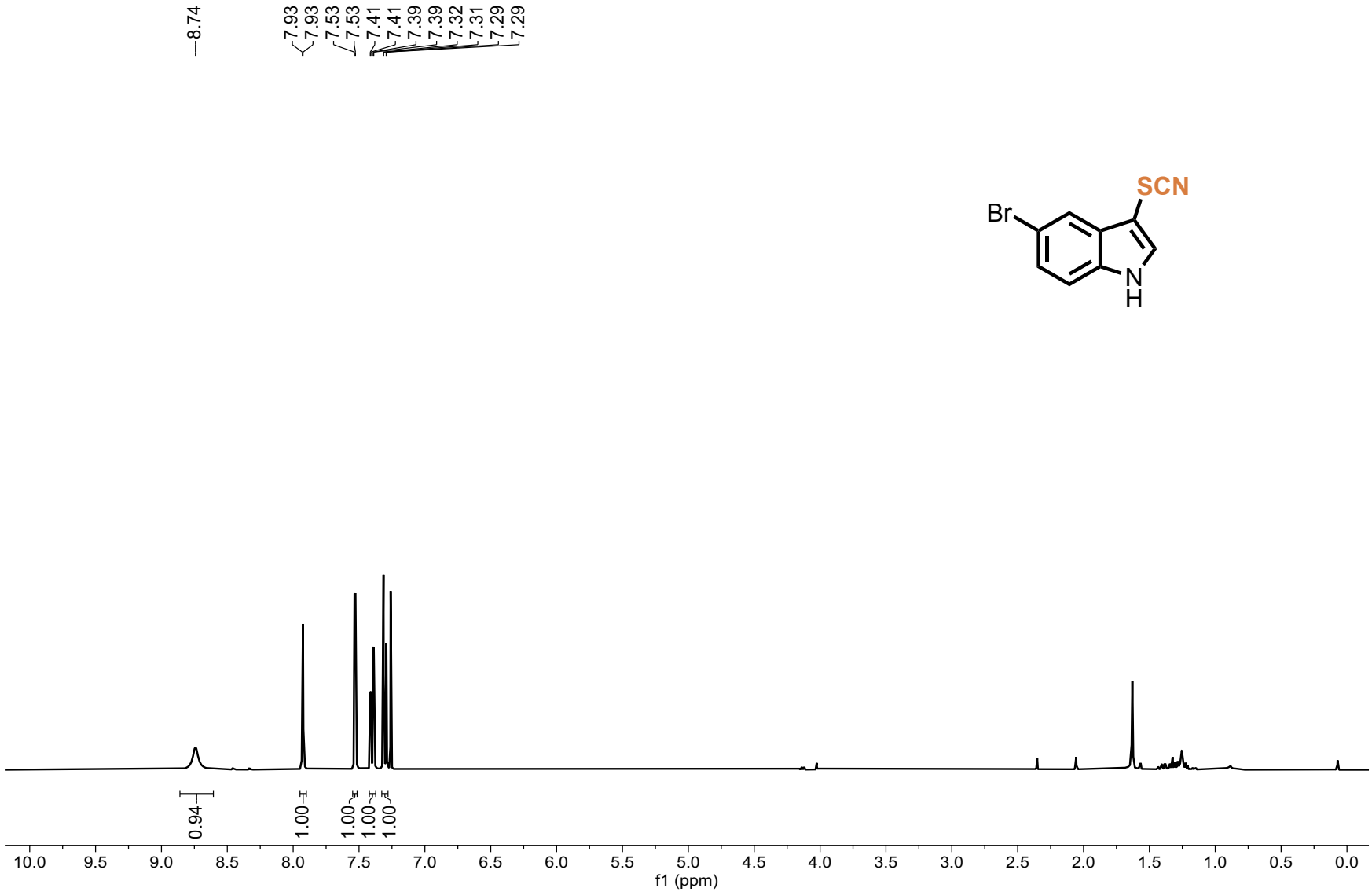


Figure S20. ^{1}H NMR ($CDCl_3$, 400 MHz) of **9a**

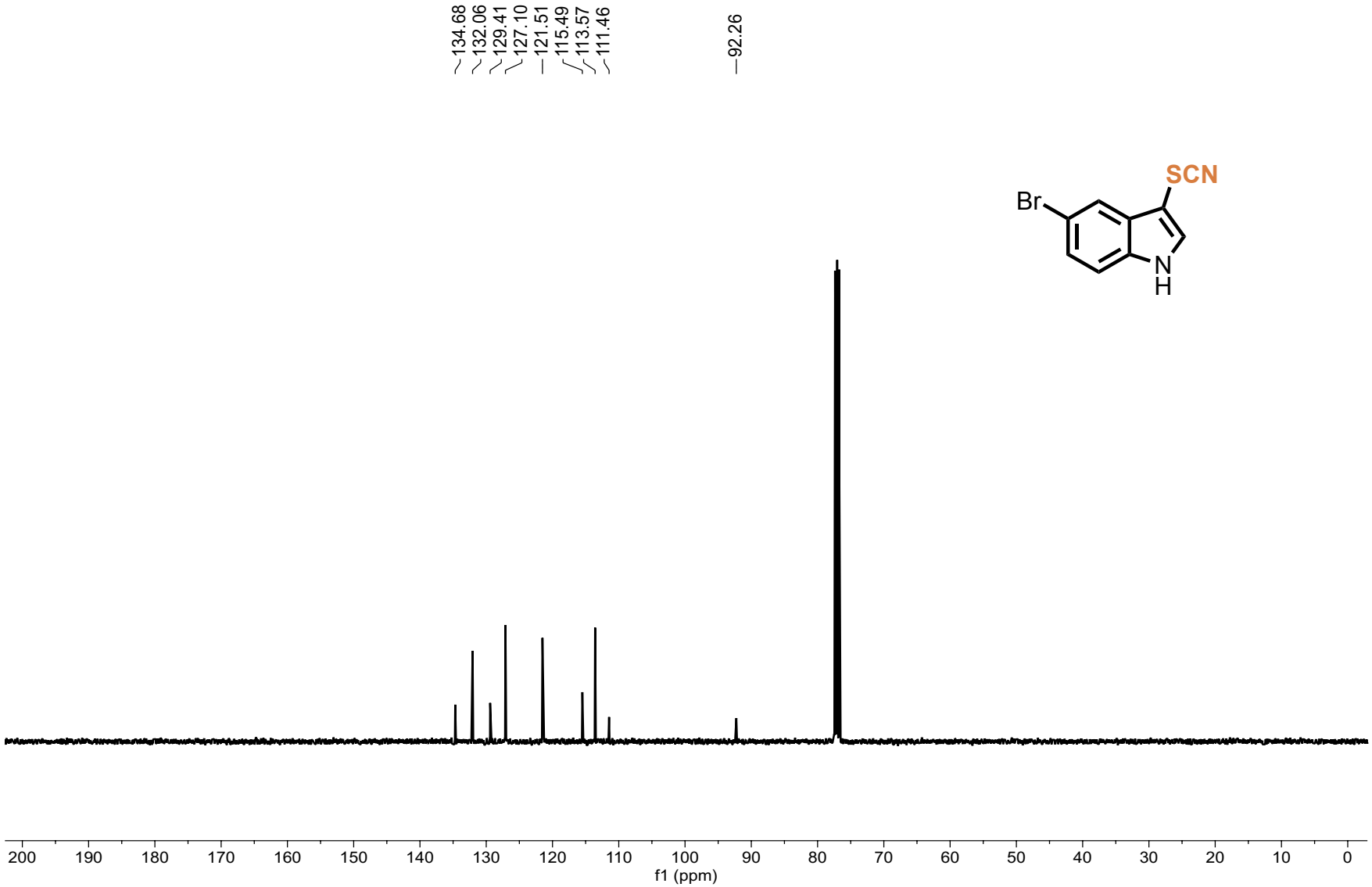


Figure S21. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **9a**

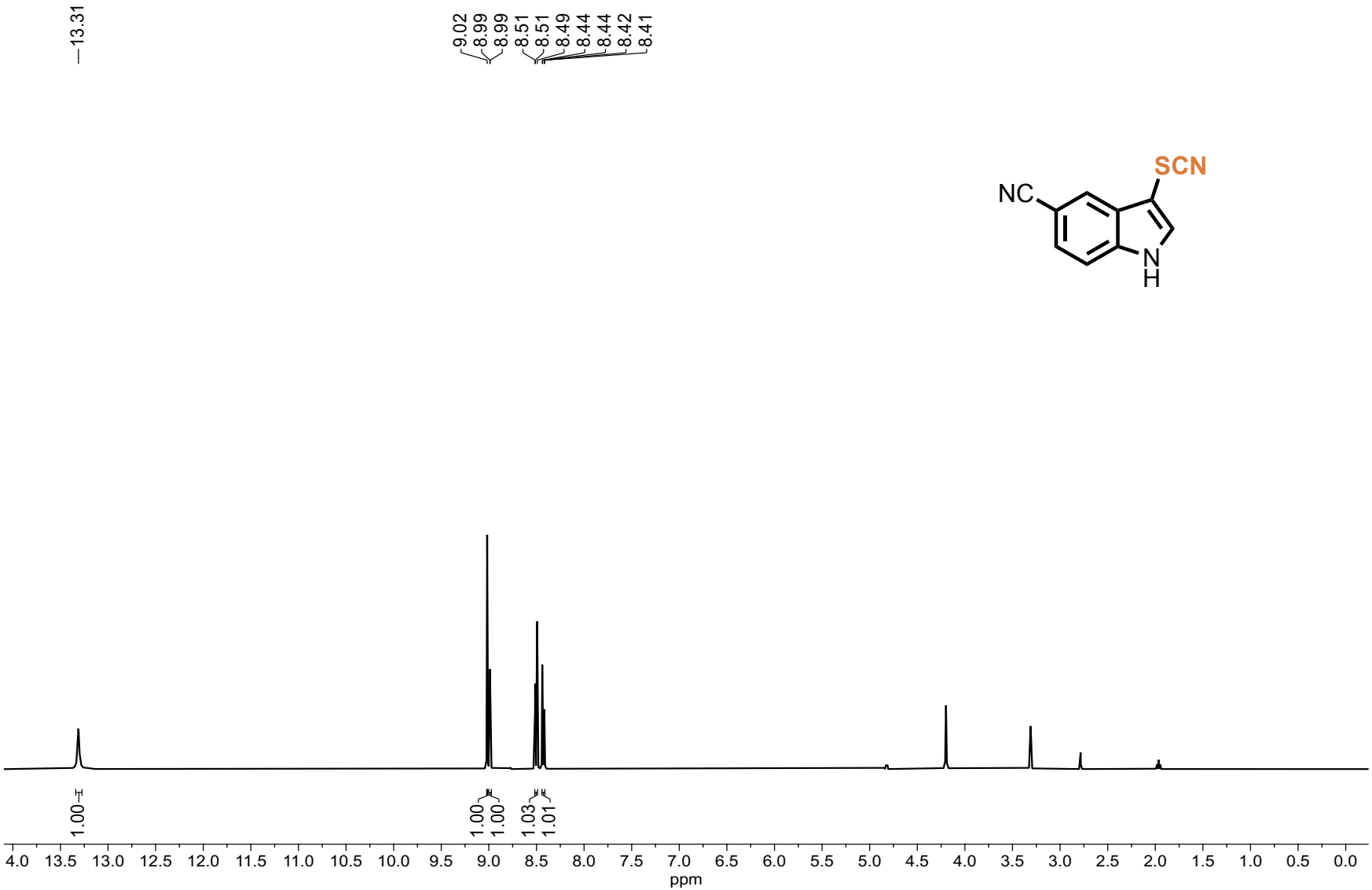


Figure S22. ^{1}H NMR (CD_3OD, 400 MHz) of **10a**

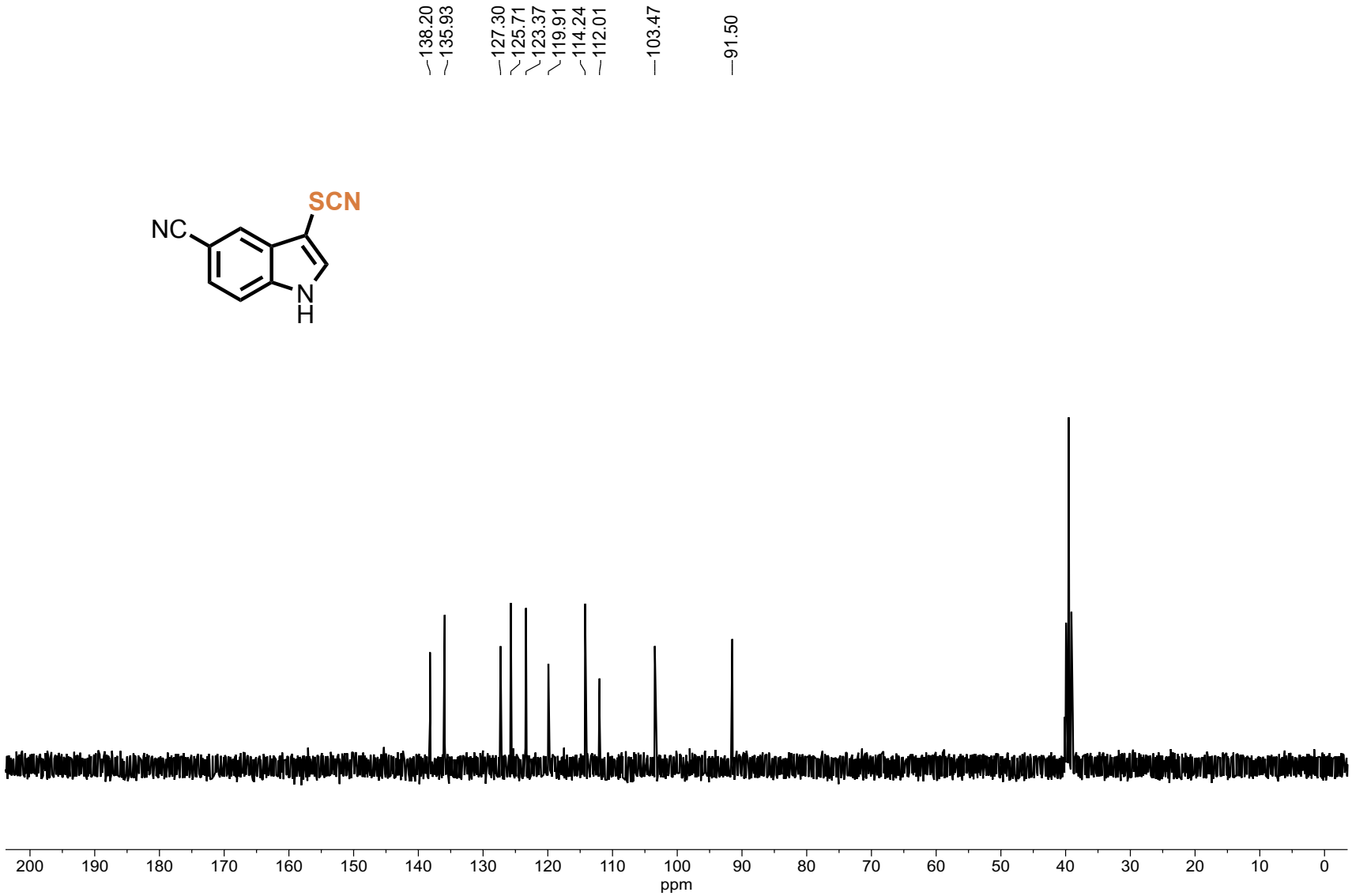


Figure S23. ^{13}C NMR (CD_3OD, 100.6 MHz) of **10a**

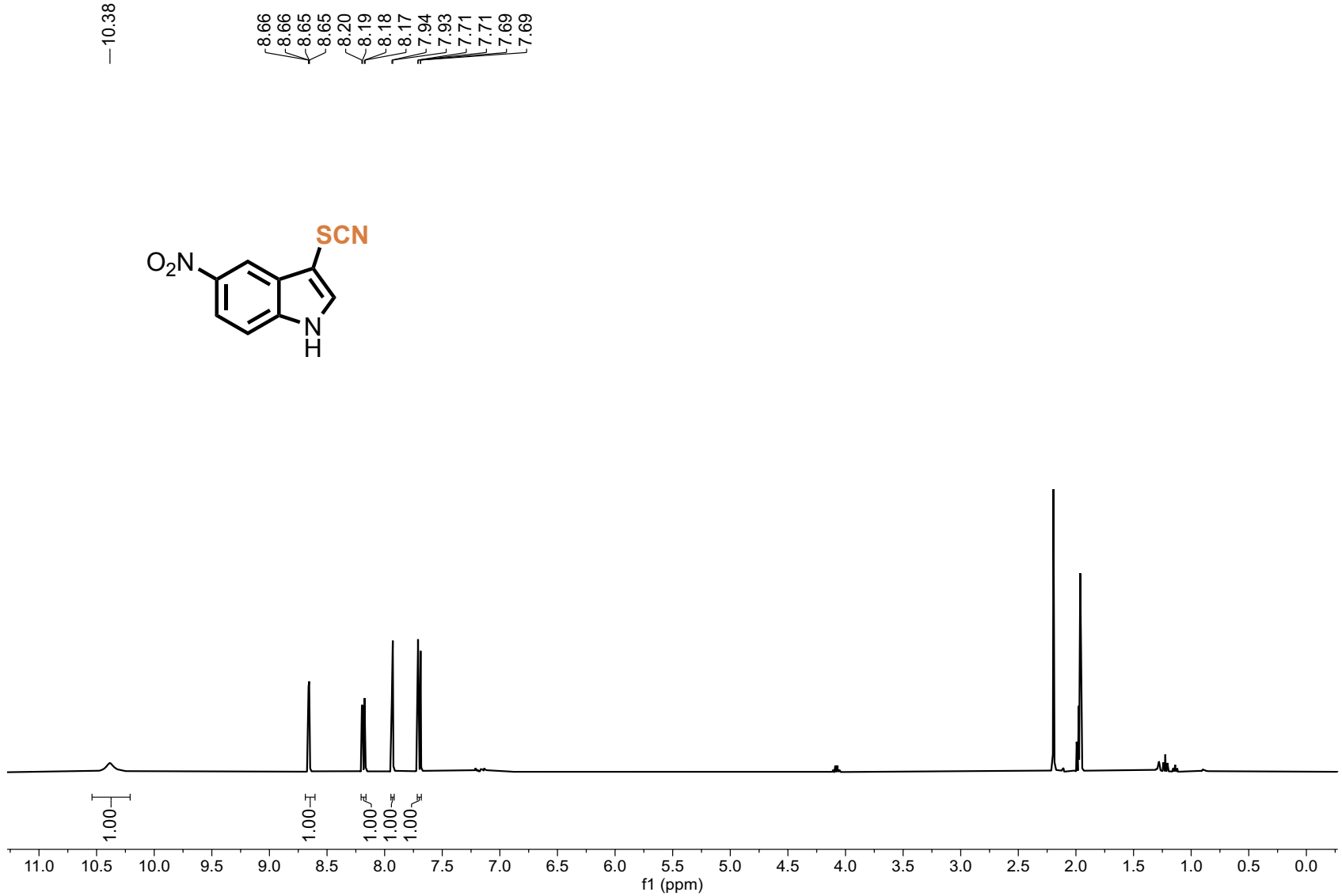


Figure S24. ^{1}H NMR (CD_3CN, 400 MHz) of **11a**

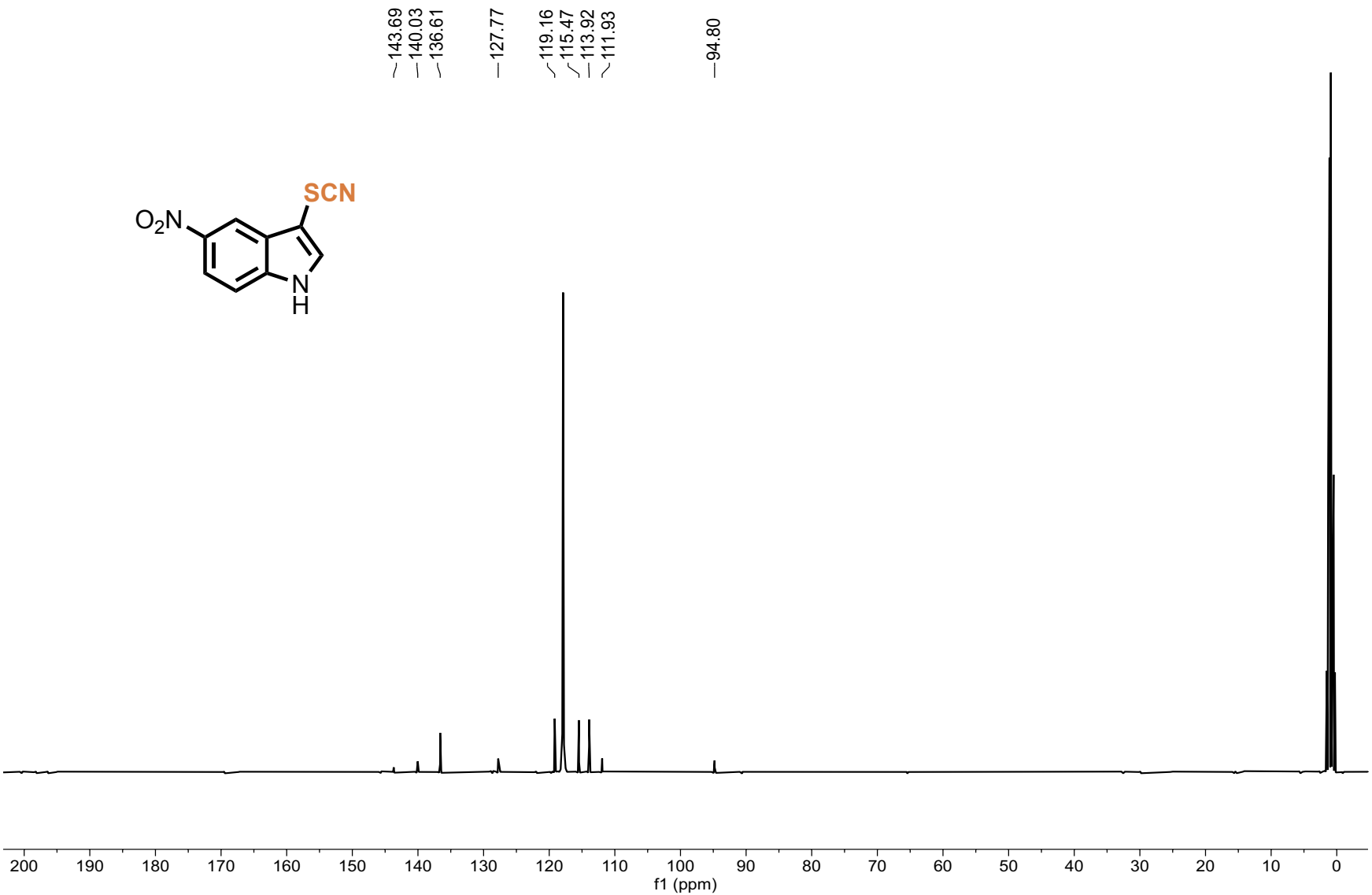


Figure S25. ^{13}C NMR (CD_3CN, 100.6 MHz) of **11a**

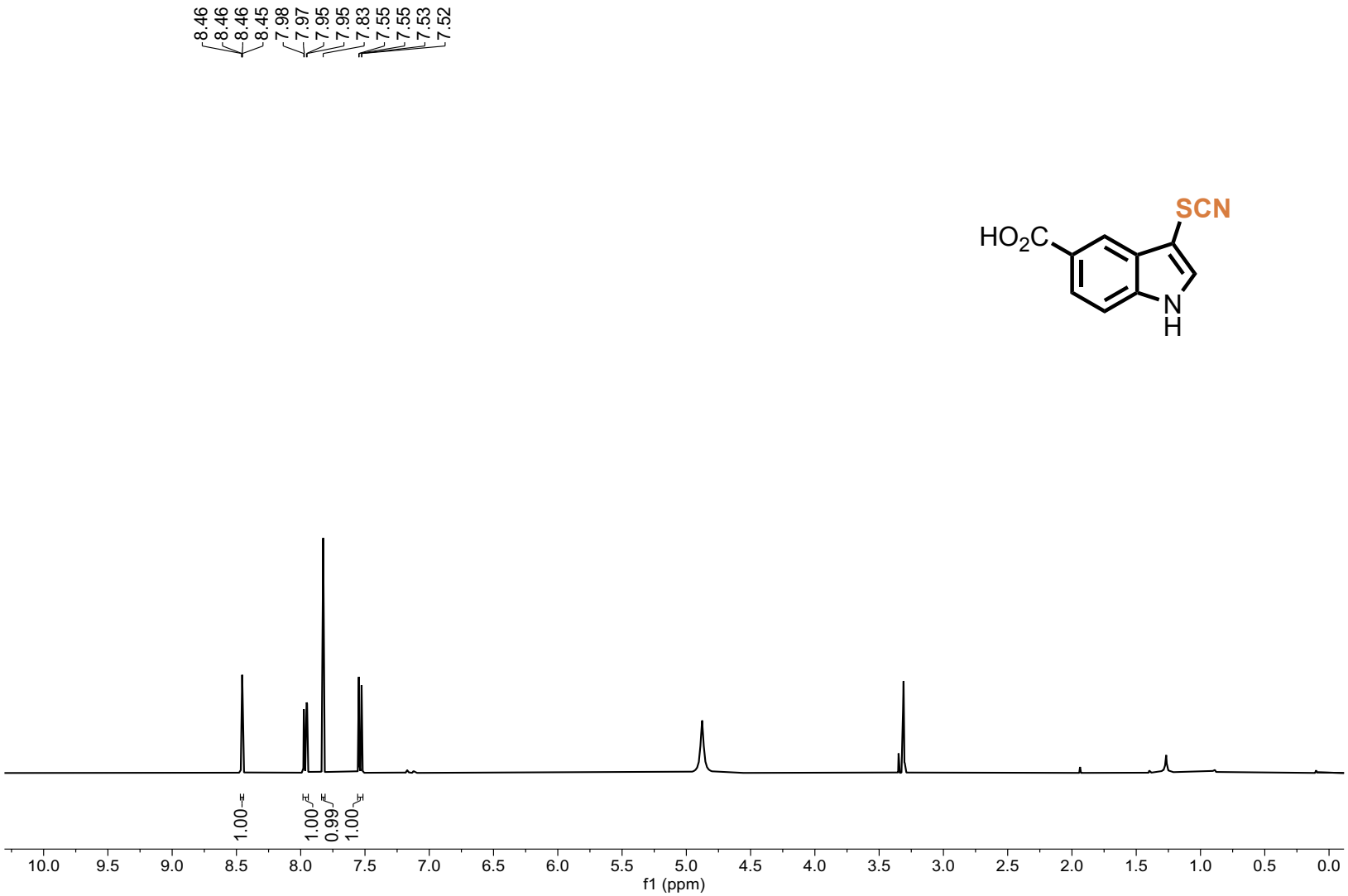


Figure S26. ^{1}H NMR (CD_3OD, 400 MHz) of **12a**

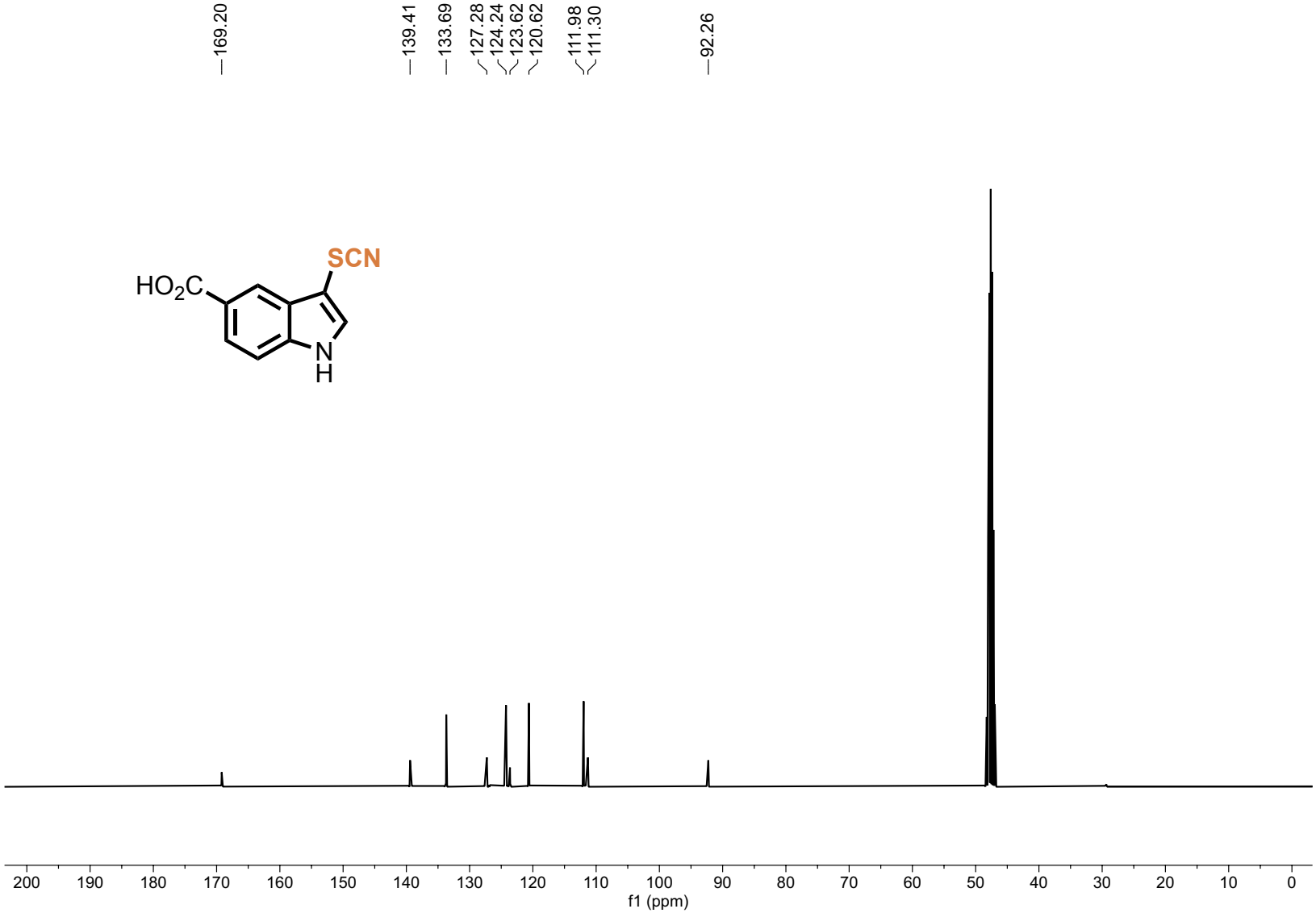


Figure S27. ^{13}C NMR (CD_3OD, 100.6 MHz) of **12a**

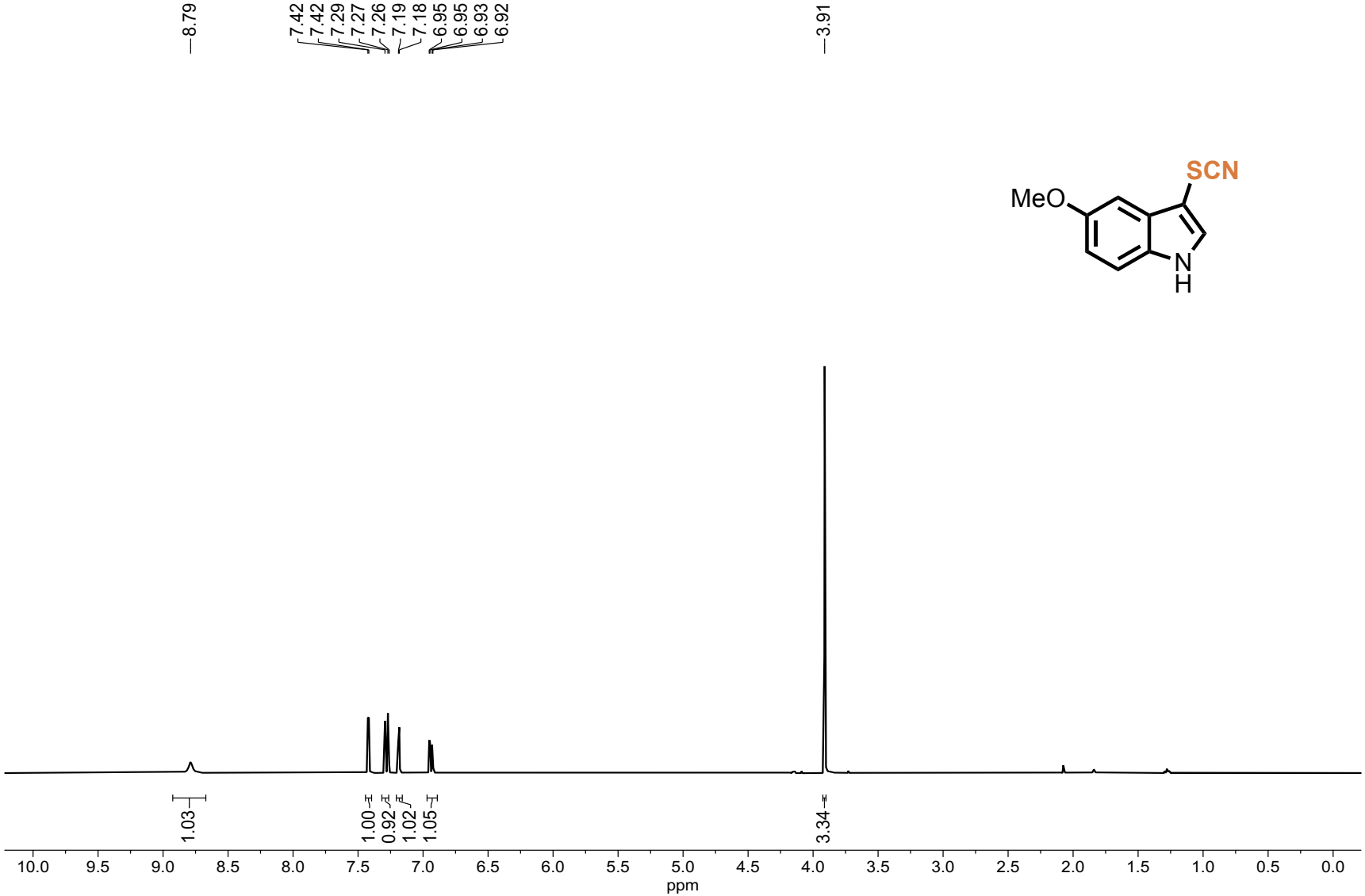


Figure S28. ^{1}H NMR ($CDCl_3$, 400 MHz) of **13a**

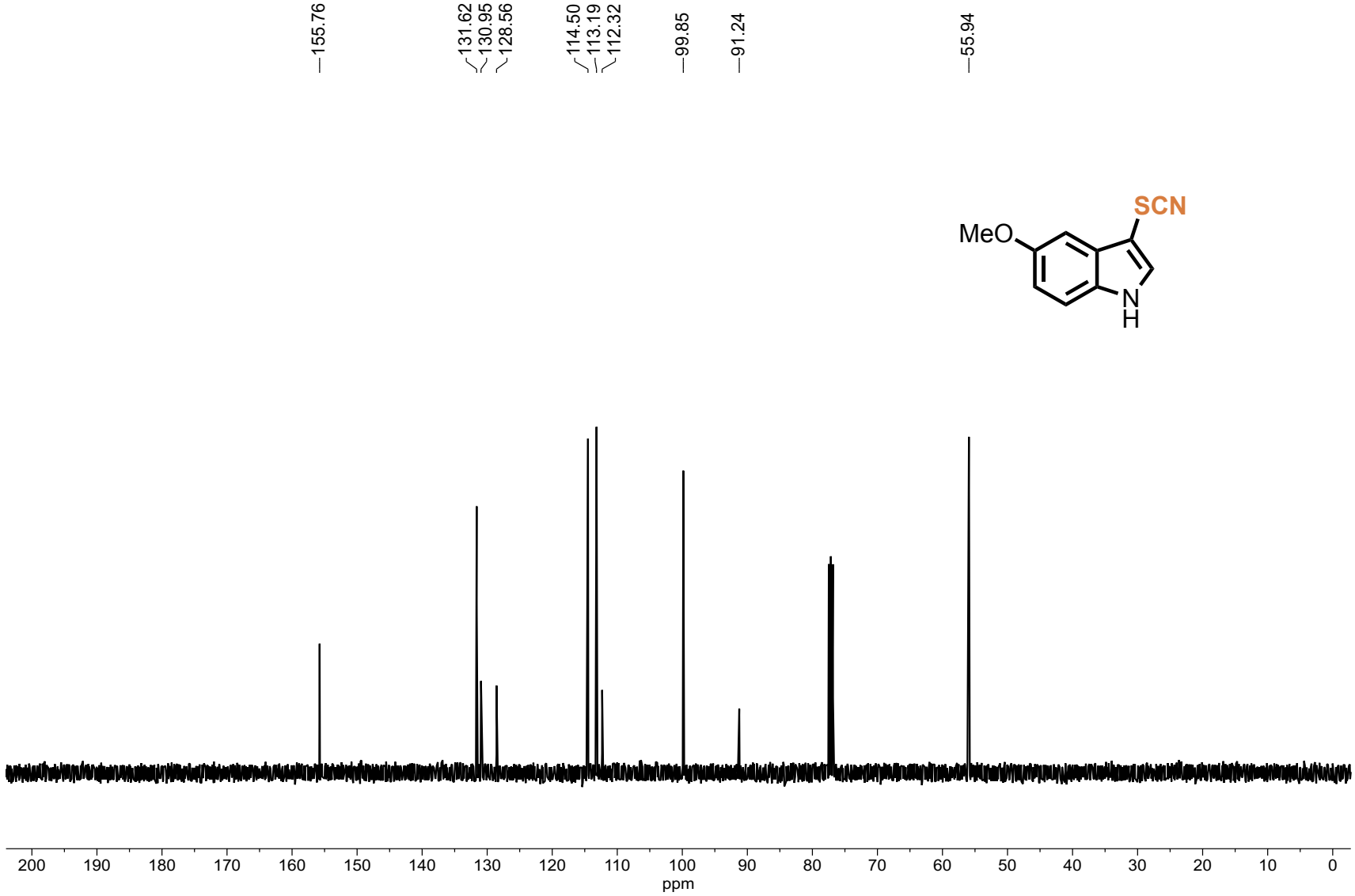


Figure S29. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **13a**

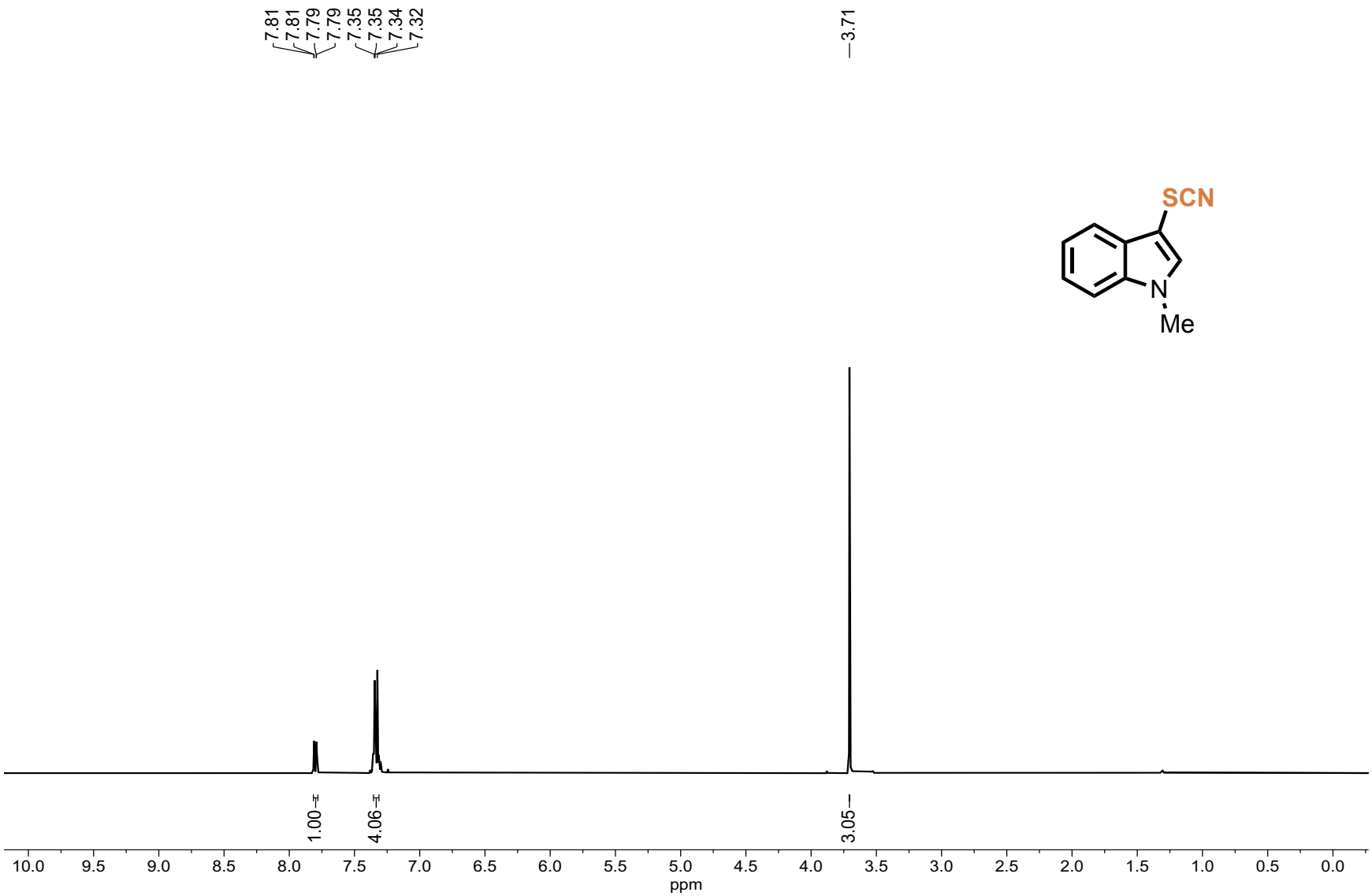


Figure S30. ^{1}H NMR ($CDCl_3$, 400 MHz) of **14a**

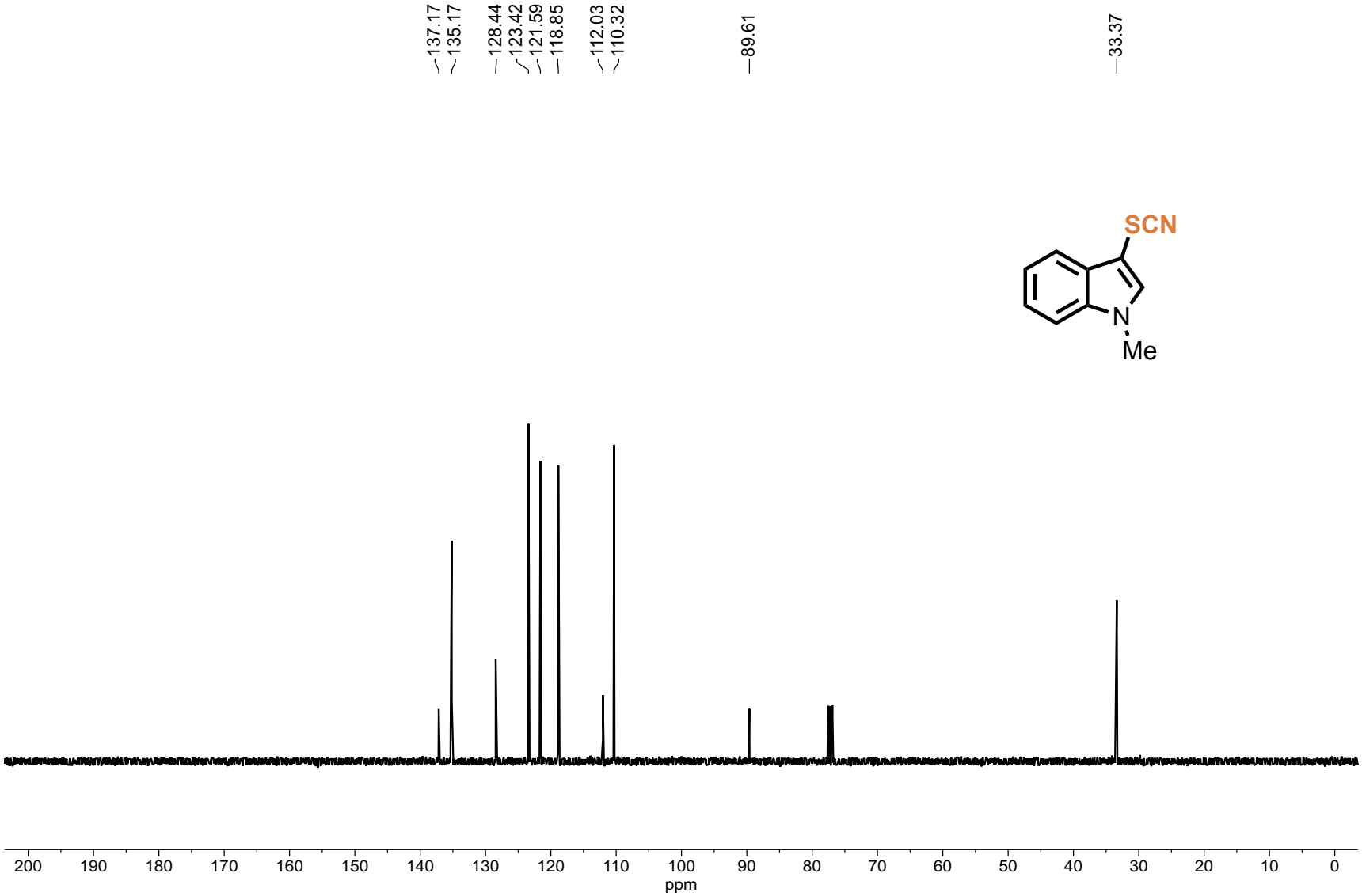


Figure S31. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **14a**

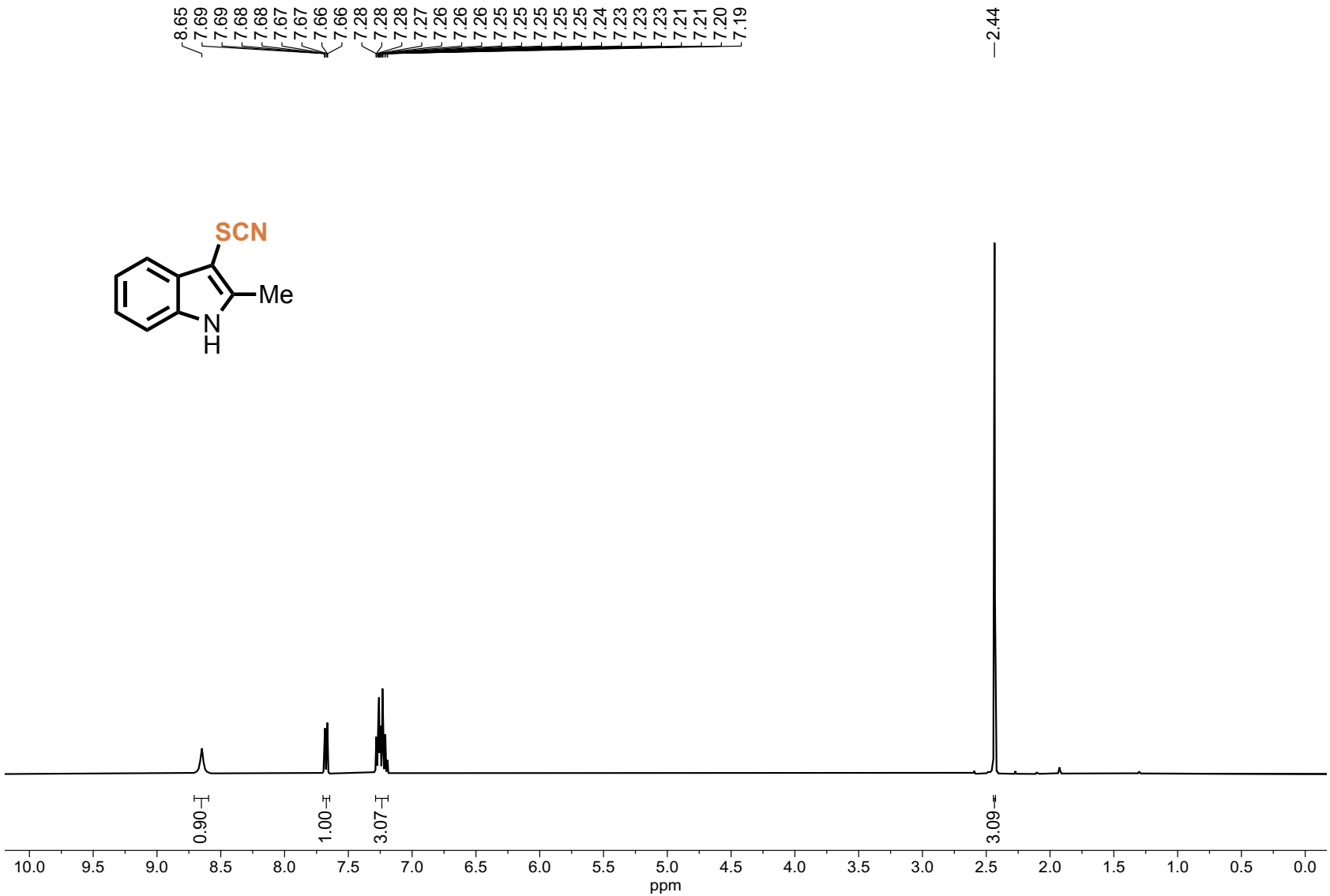


Figure S32. ^{1}H NMR ($CDCl_3$, 400 MHz) of **15a**

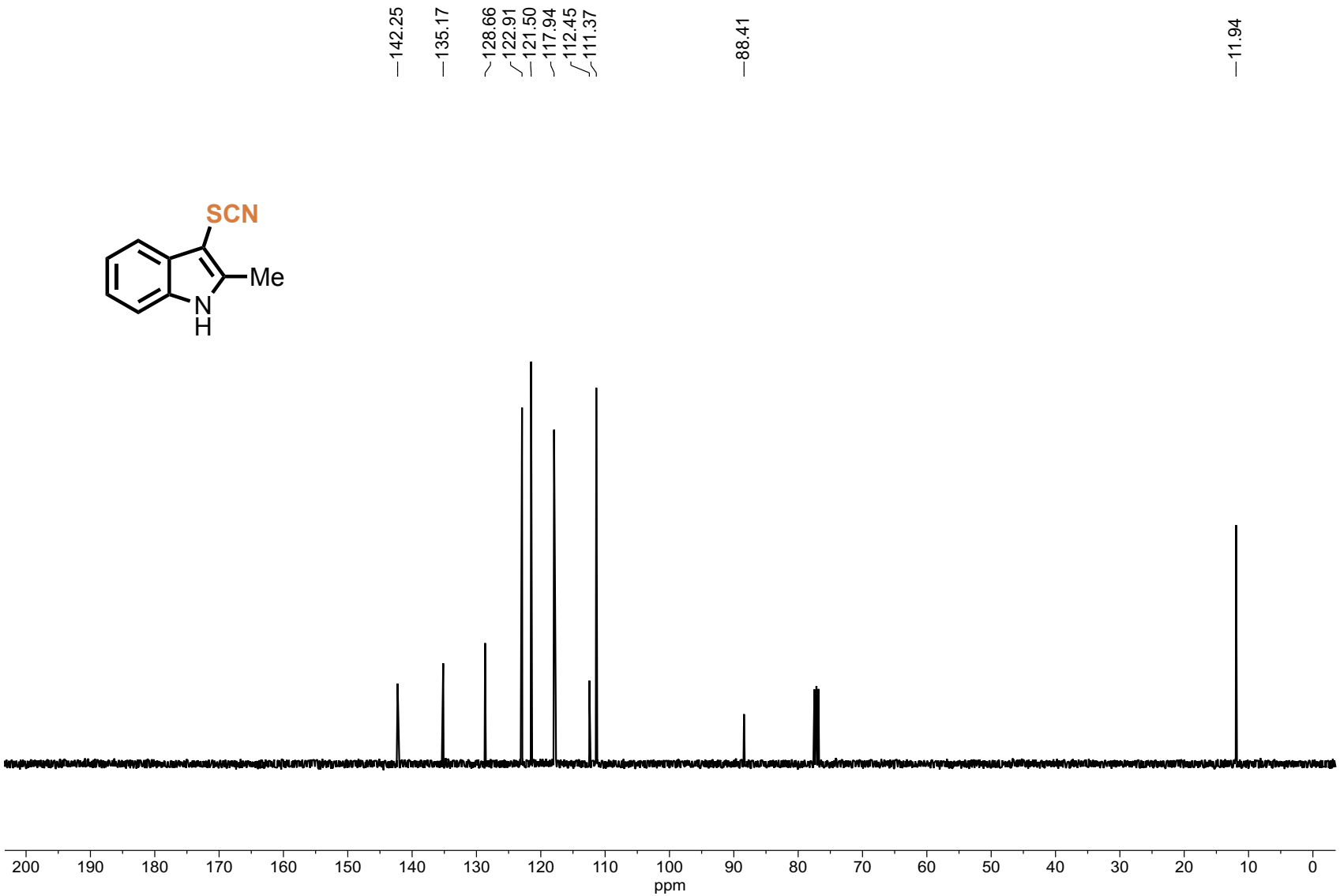


Figure S33. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **15a**

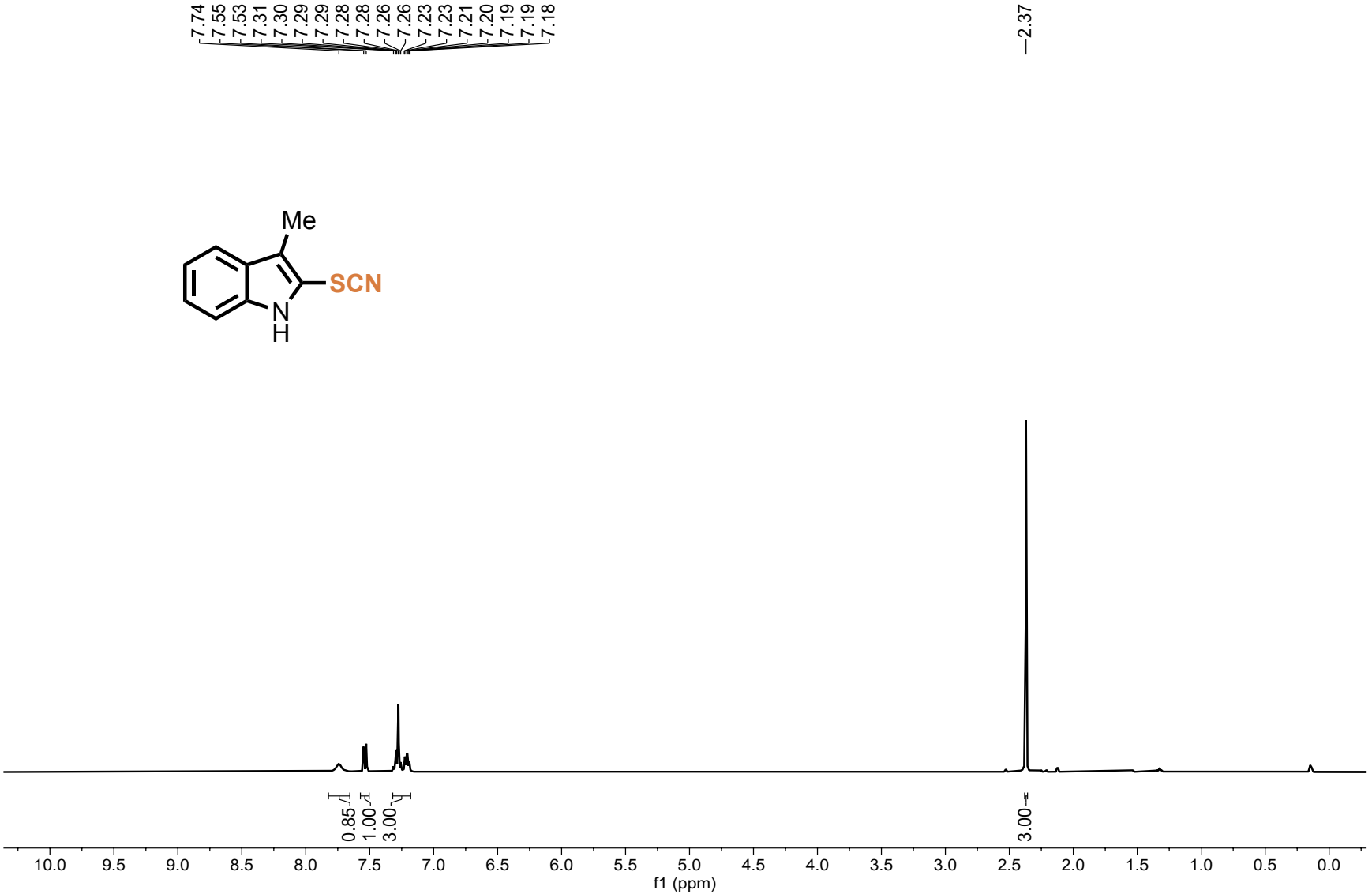


Figure S34. ^{1}H NMR ($CDCl_3$, 400 MHz) of **16a**

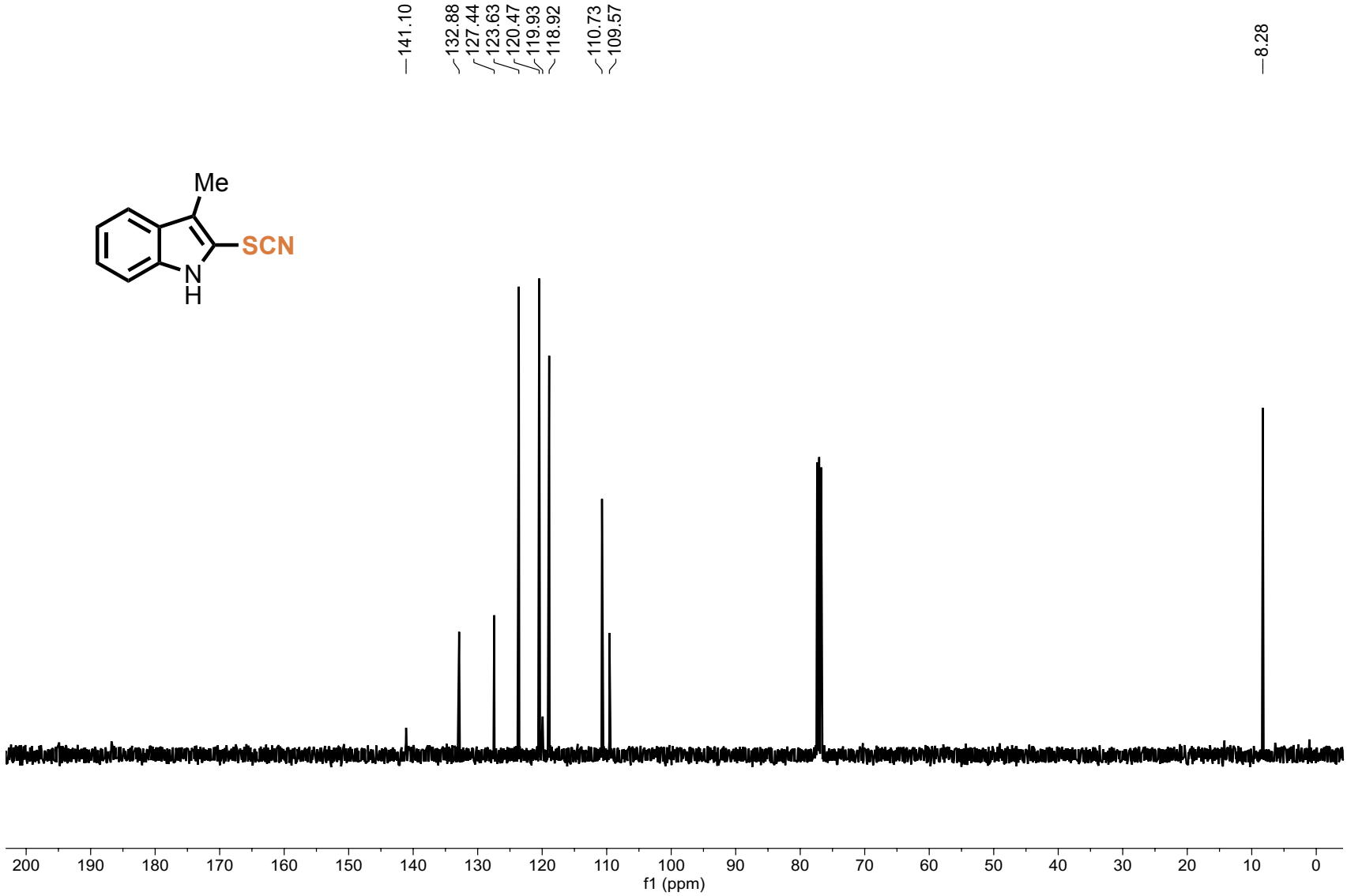


Figure S35. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **16a**

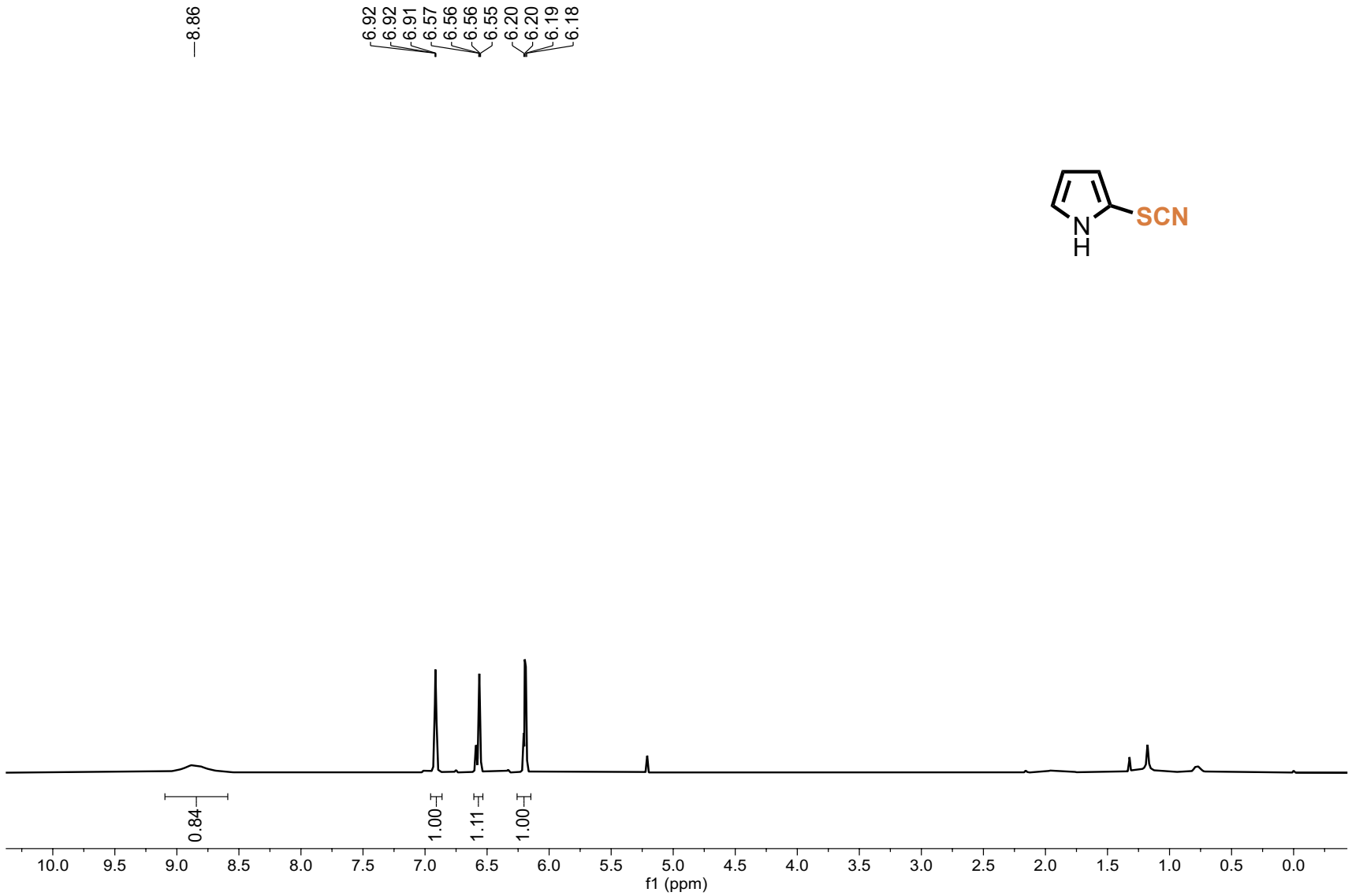


Figure S36. ^{1}H NMR (CD_2Cl_2, 400 MHz) of **17a**

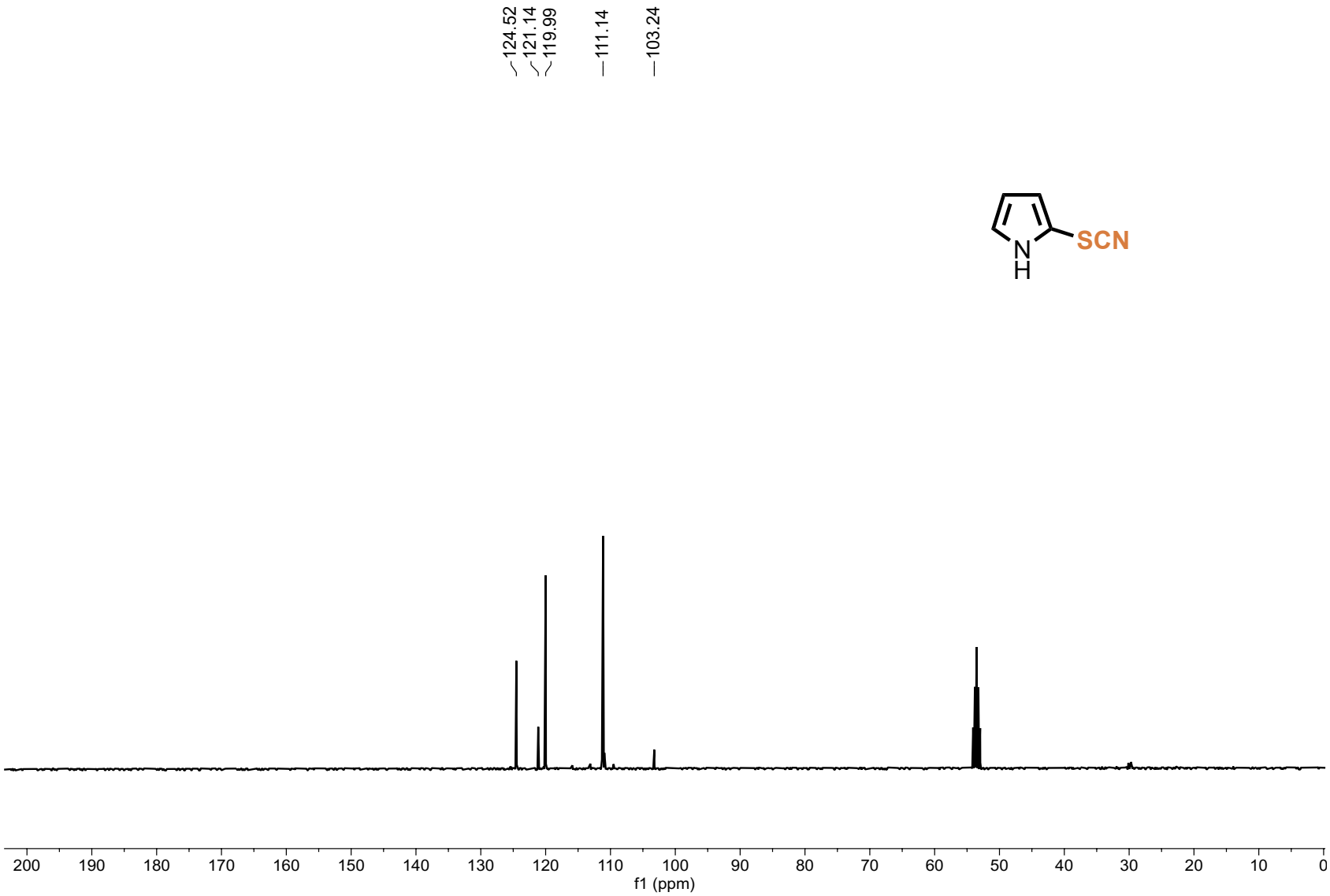


Figure S37. ^{13}C NMR (CD_2Cl_2, 100.6 MHz) of **17b**

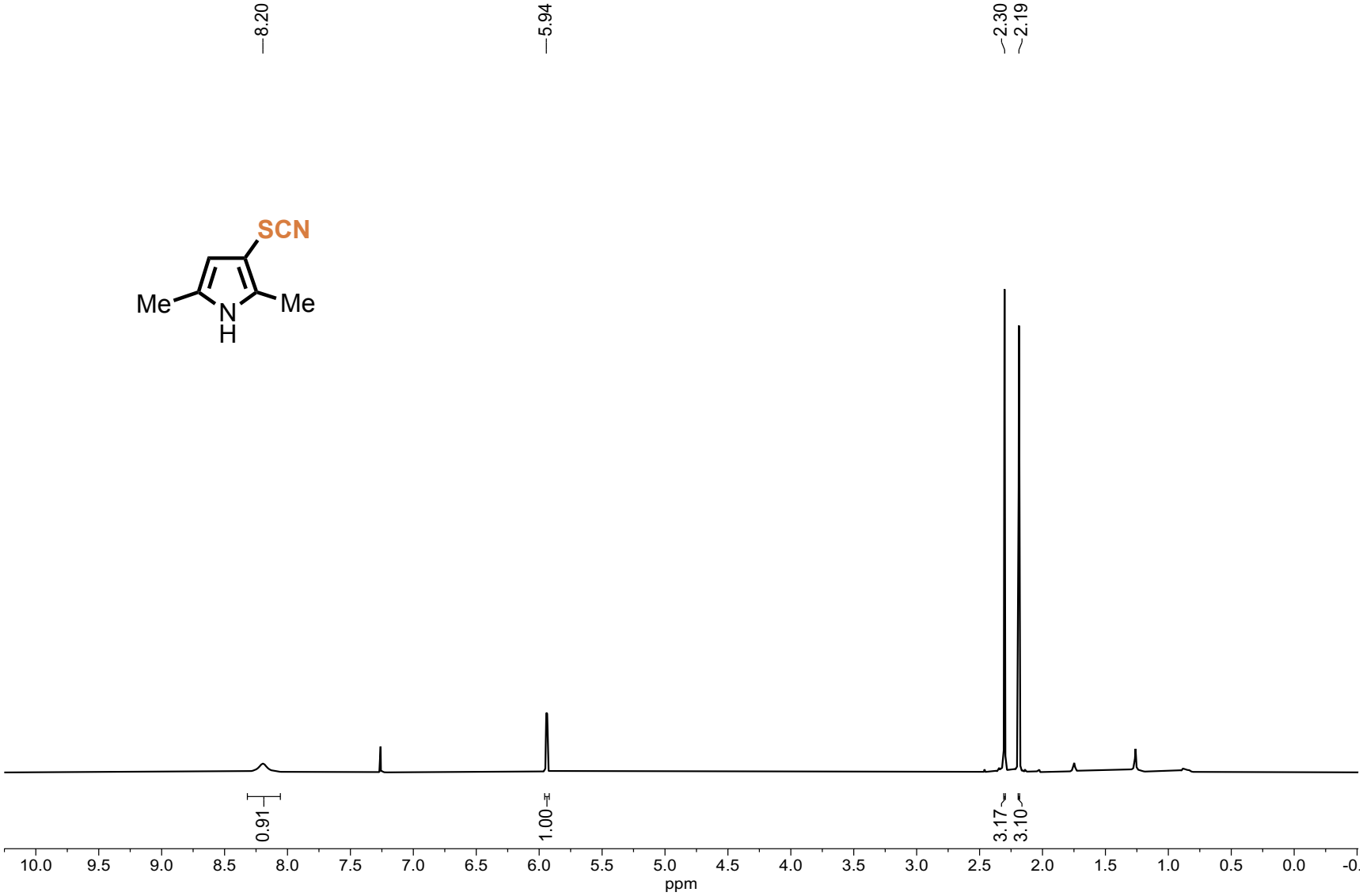


Figure S38. ^{1}H NMR ($CDCl_3$, 400 MHz) of **18a**

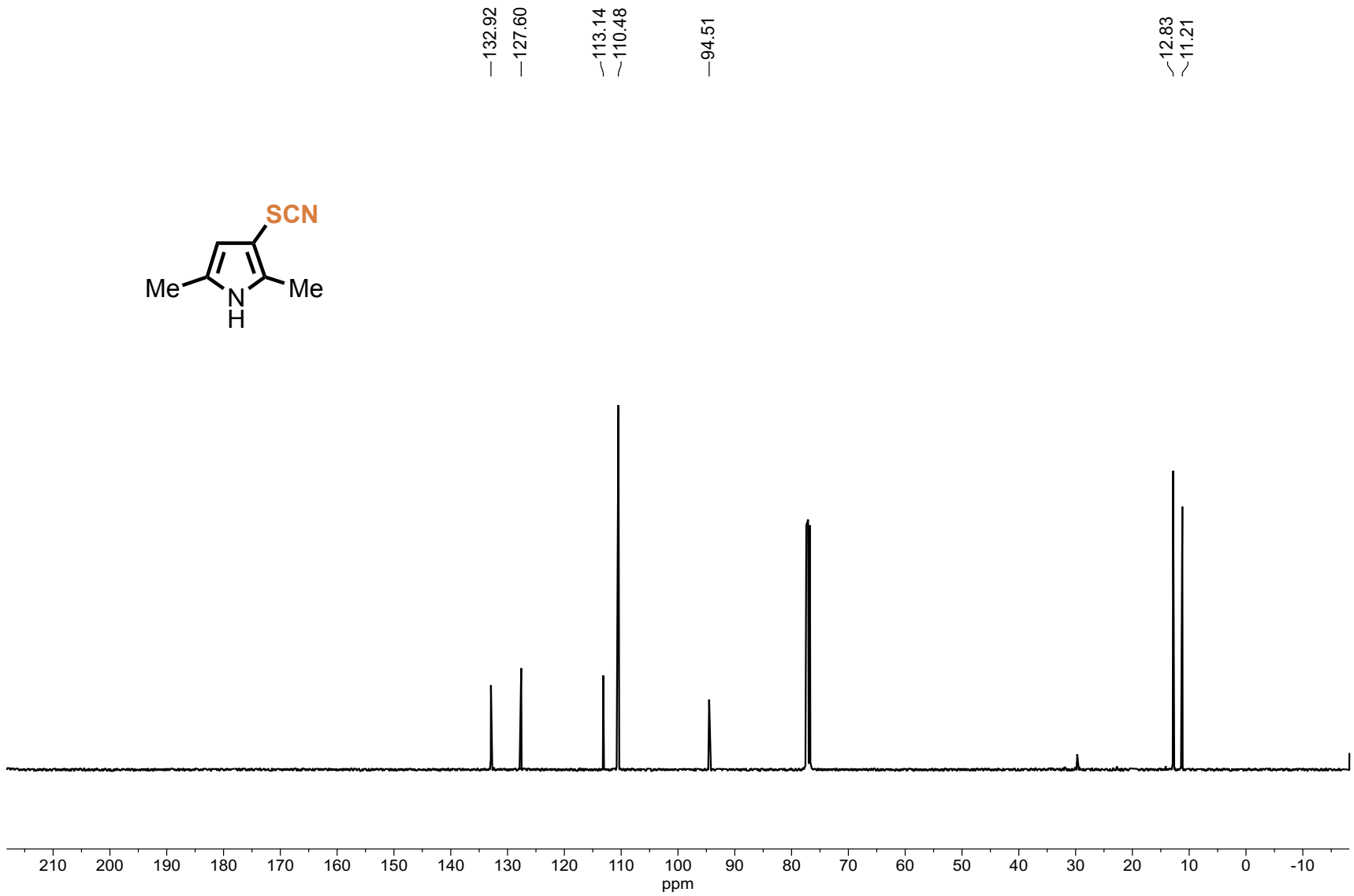


Figure S39. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **18a**

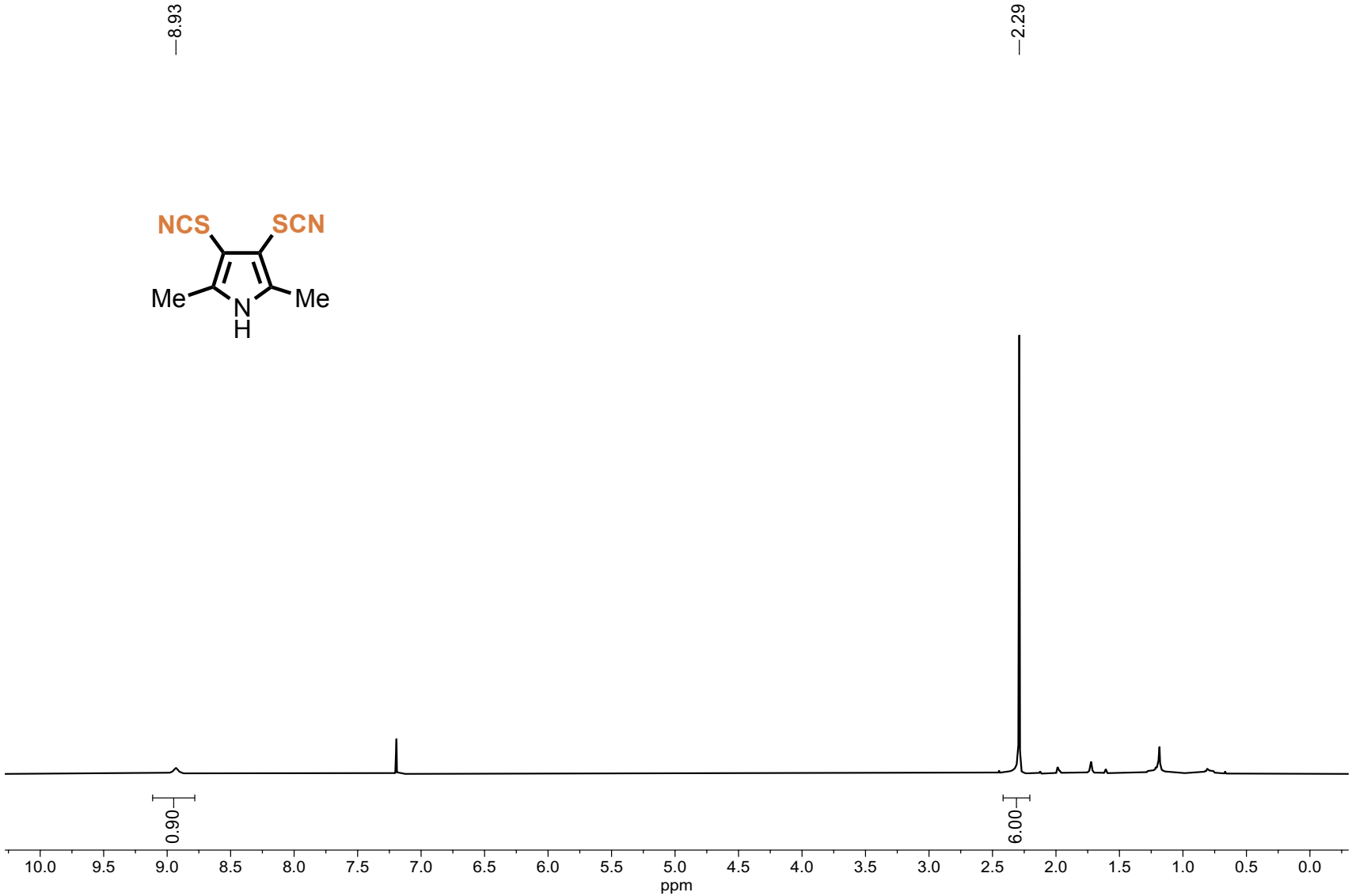


Figure S40. ^{1}H NMR ($CDCl_3$, 400 MHz) of **19a**

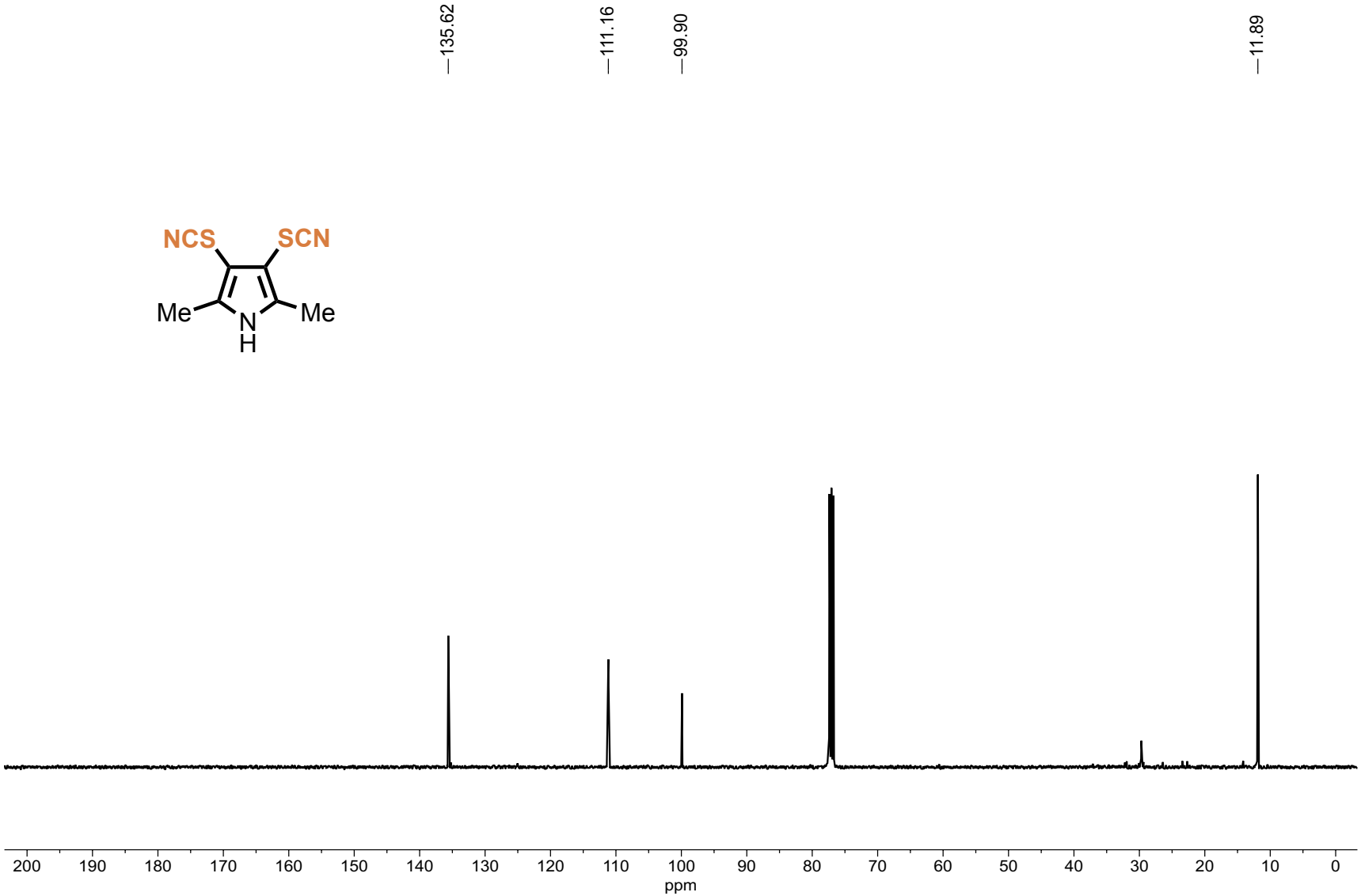


Figure S41. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **19a**

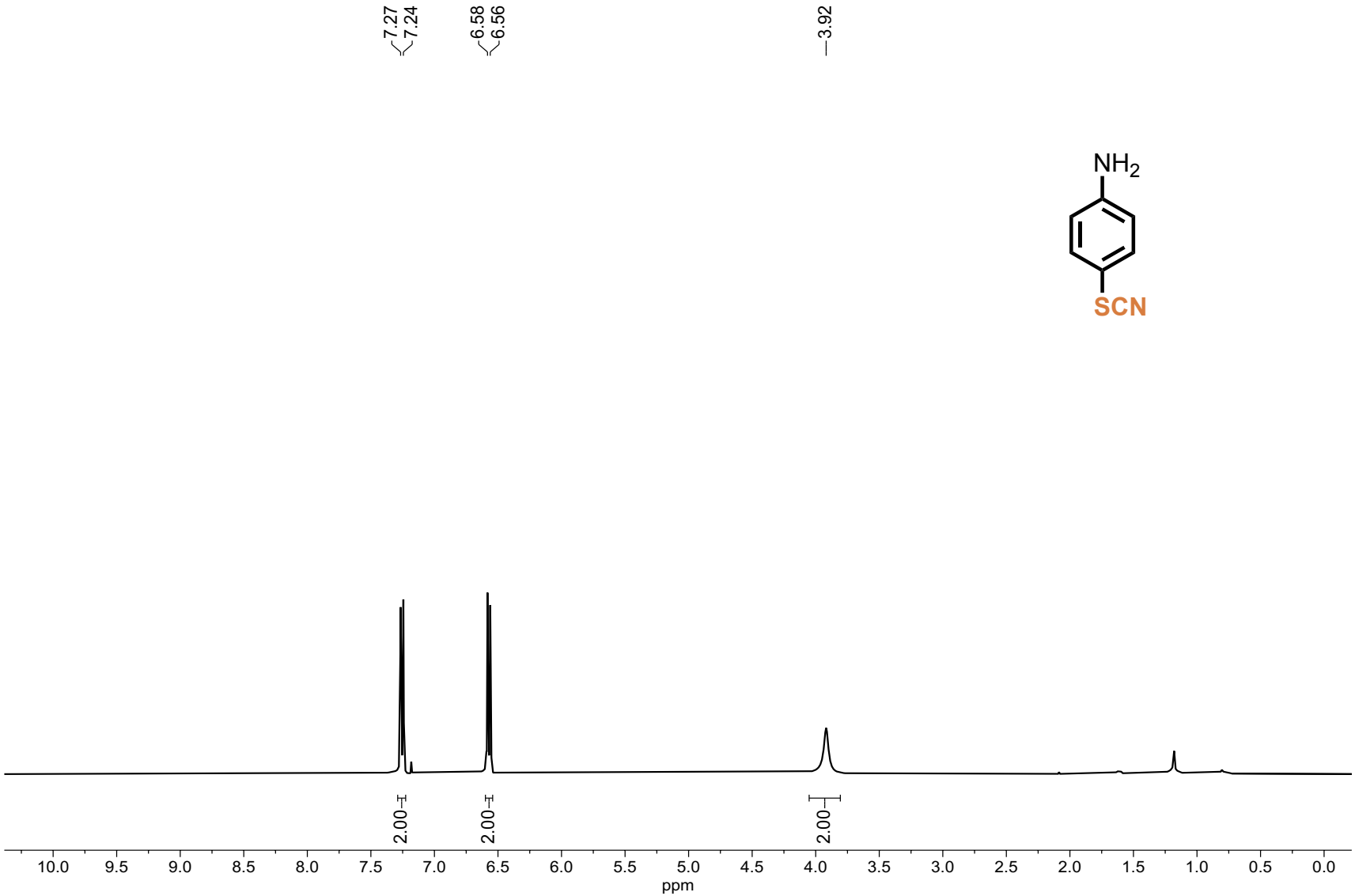


Figure S42. ^{1}H NMR ($CDCl_3$, 400 MHz) of **20a**

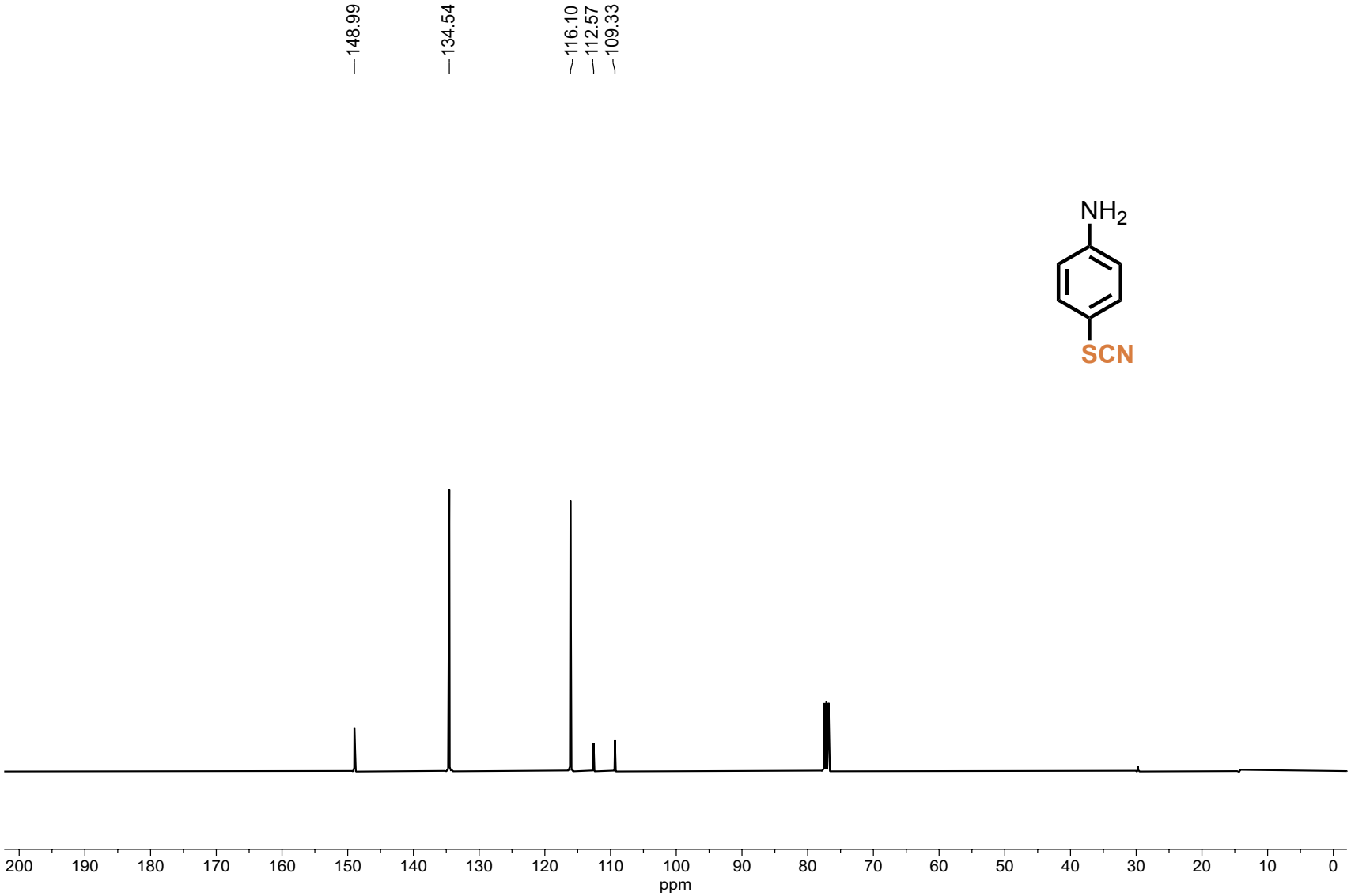


Figure S43. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **20a**

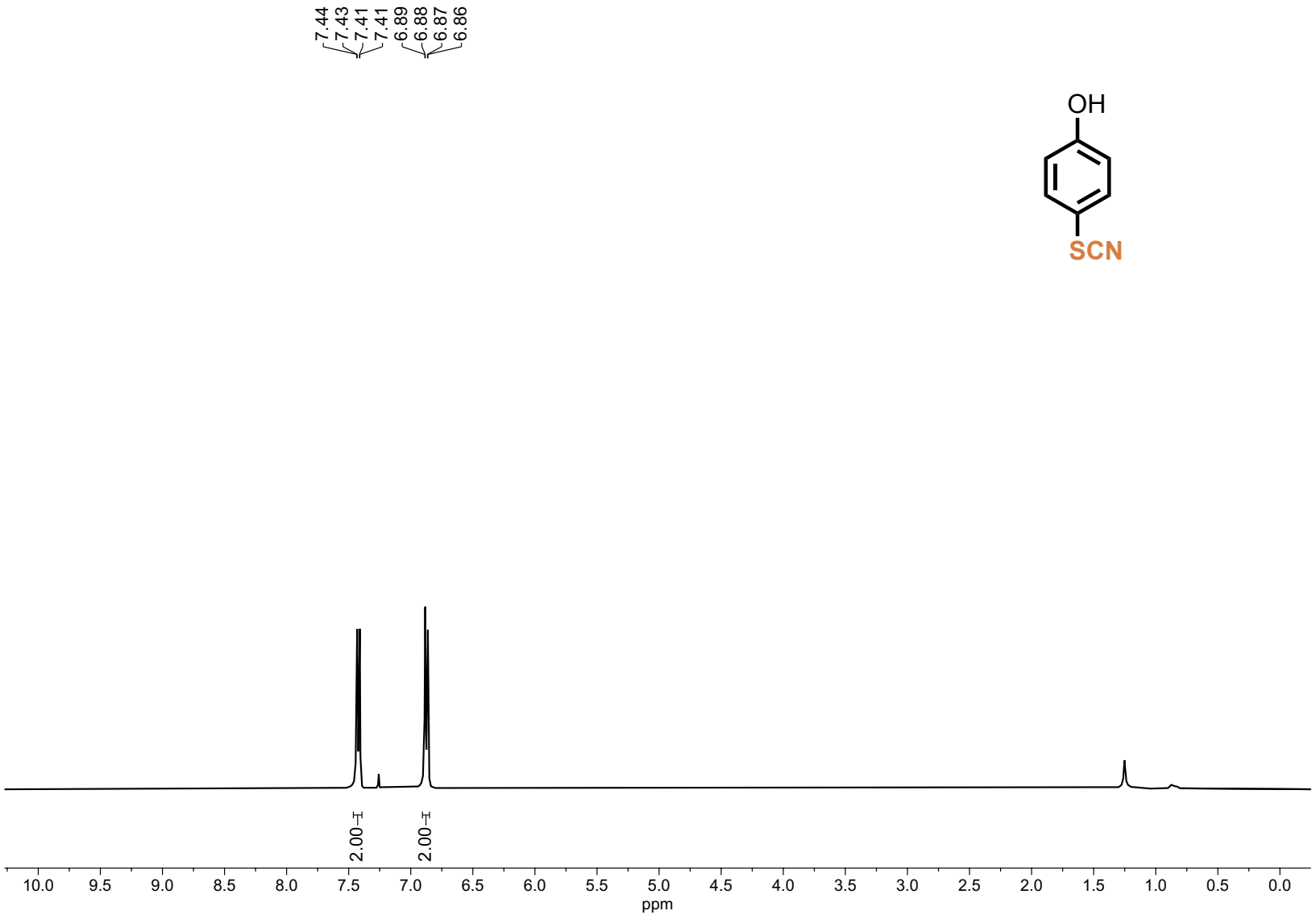


Figure S44. ^{1}H NMR ($CDCl_3$, 400 MHz) of **21a**

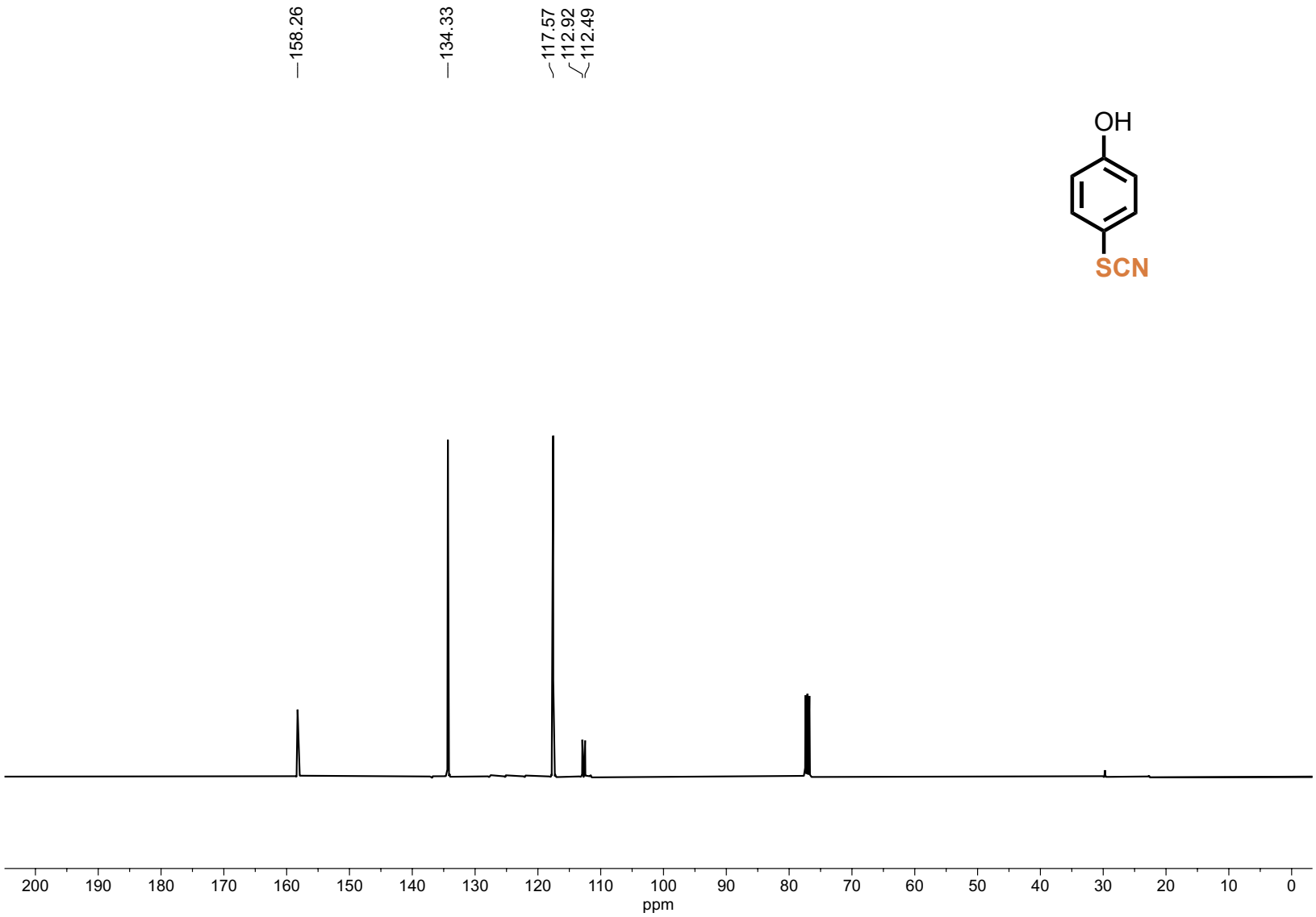


Figure S45. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **21a**

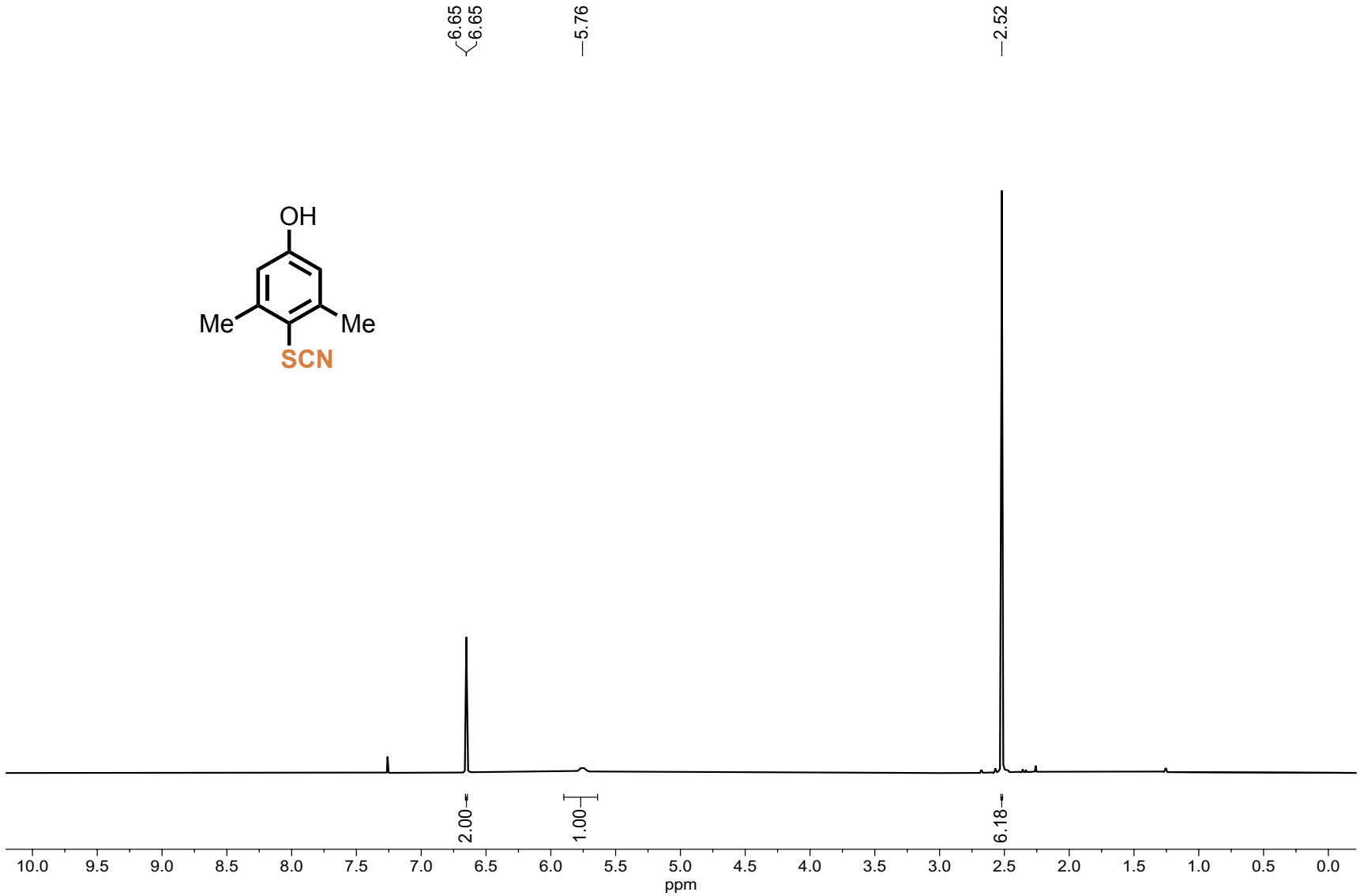


Figure S46. ^{1}H NMR ($CDCl_3$, 400 MHz) of **22a**

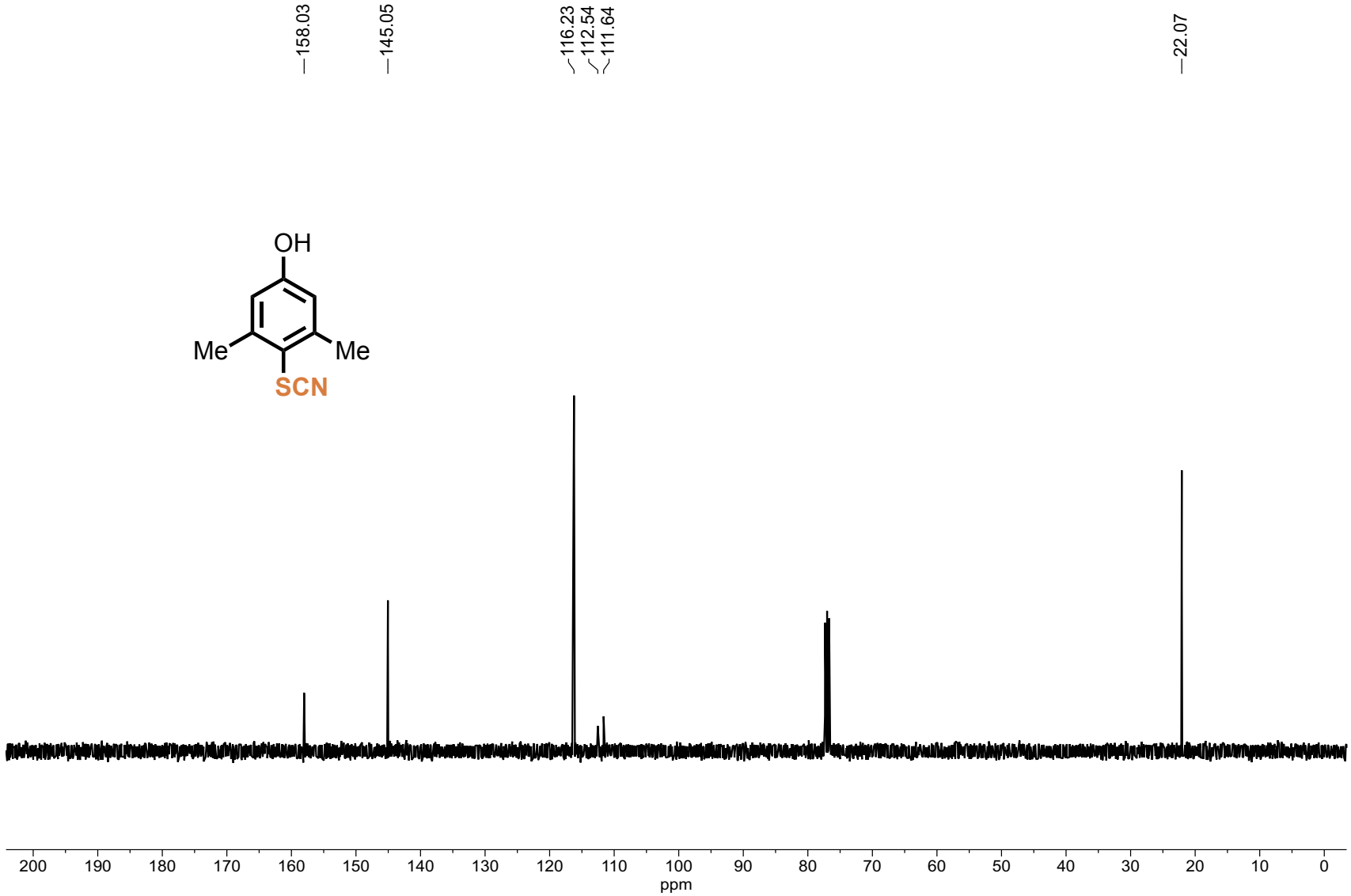


Figure S47. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **22a**

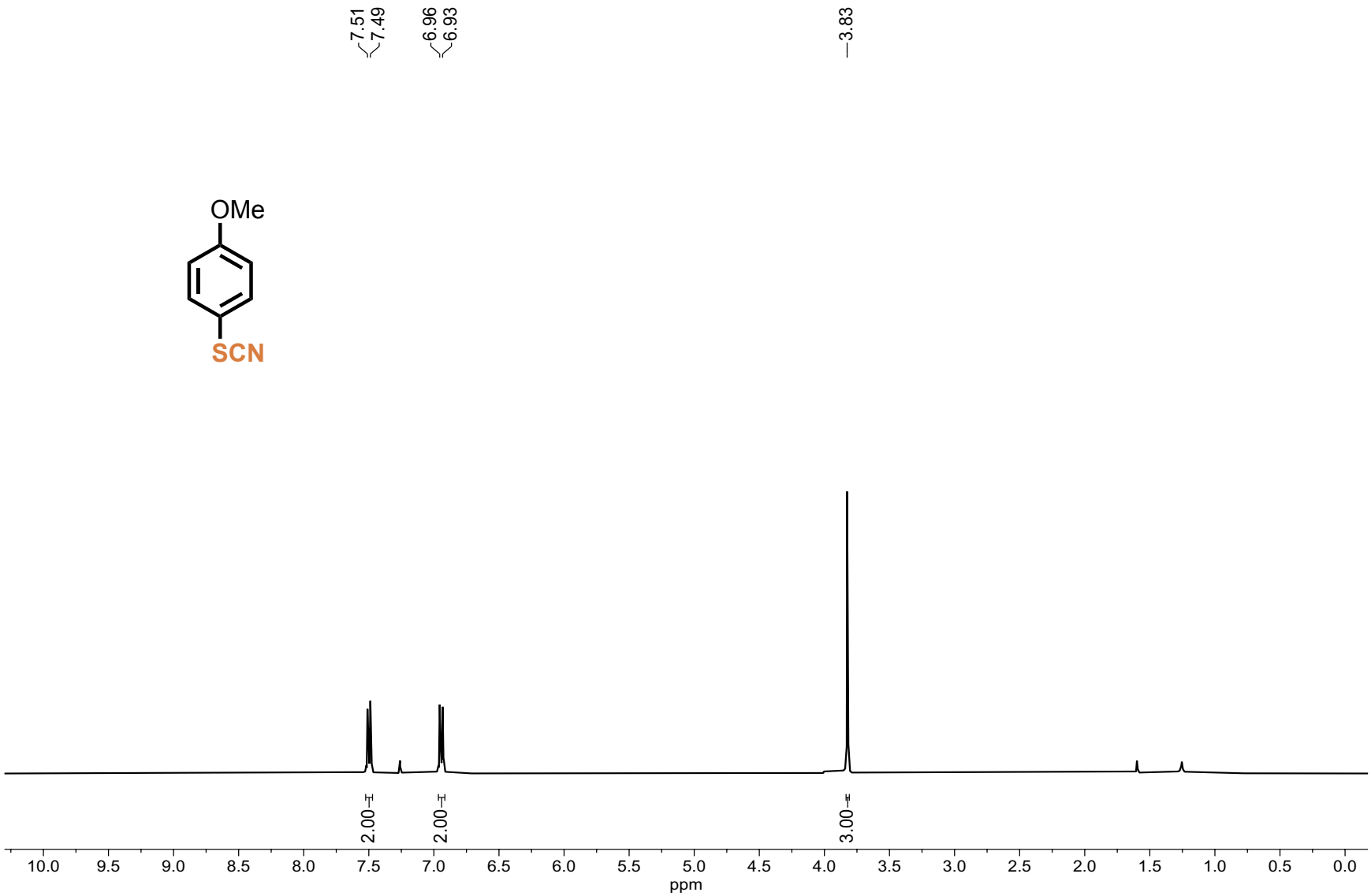


Figure S48. ^{1}H NMR ($CDCl_3$, 400 MHz) of **23a**

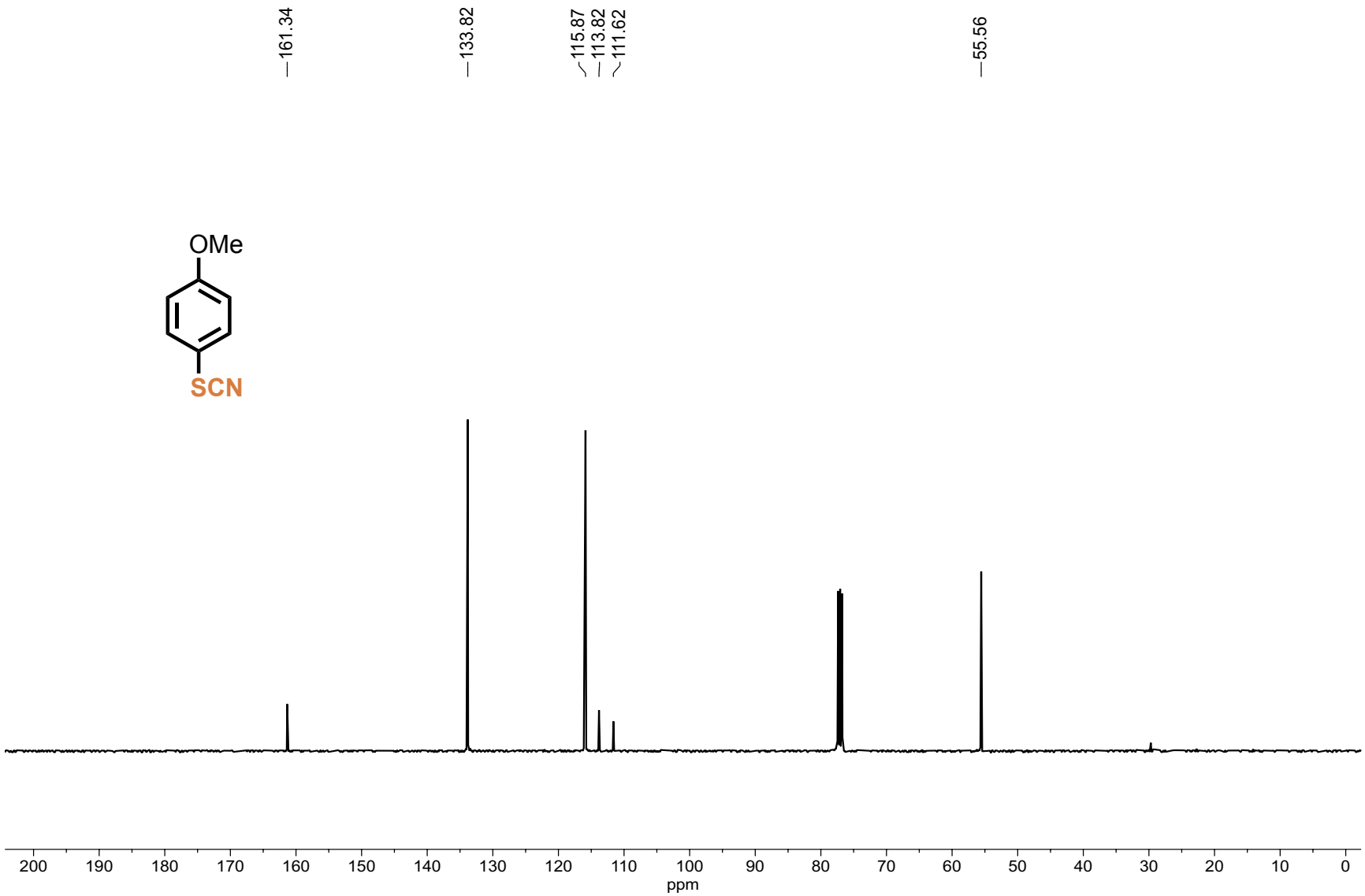


Figure S49. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **23a**

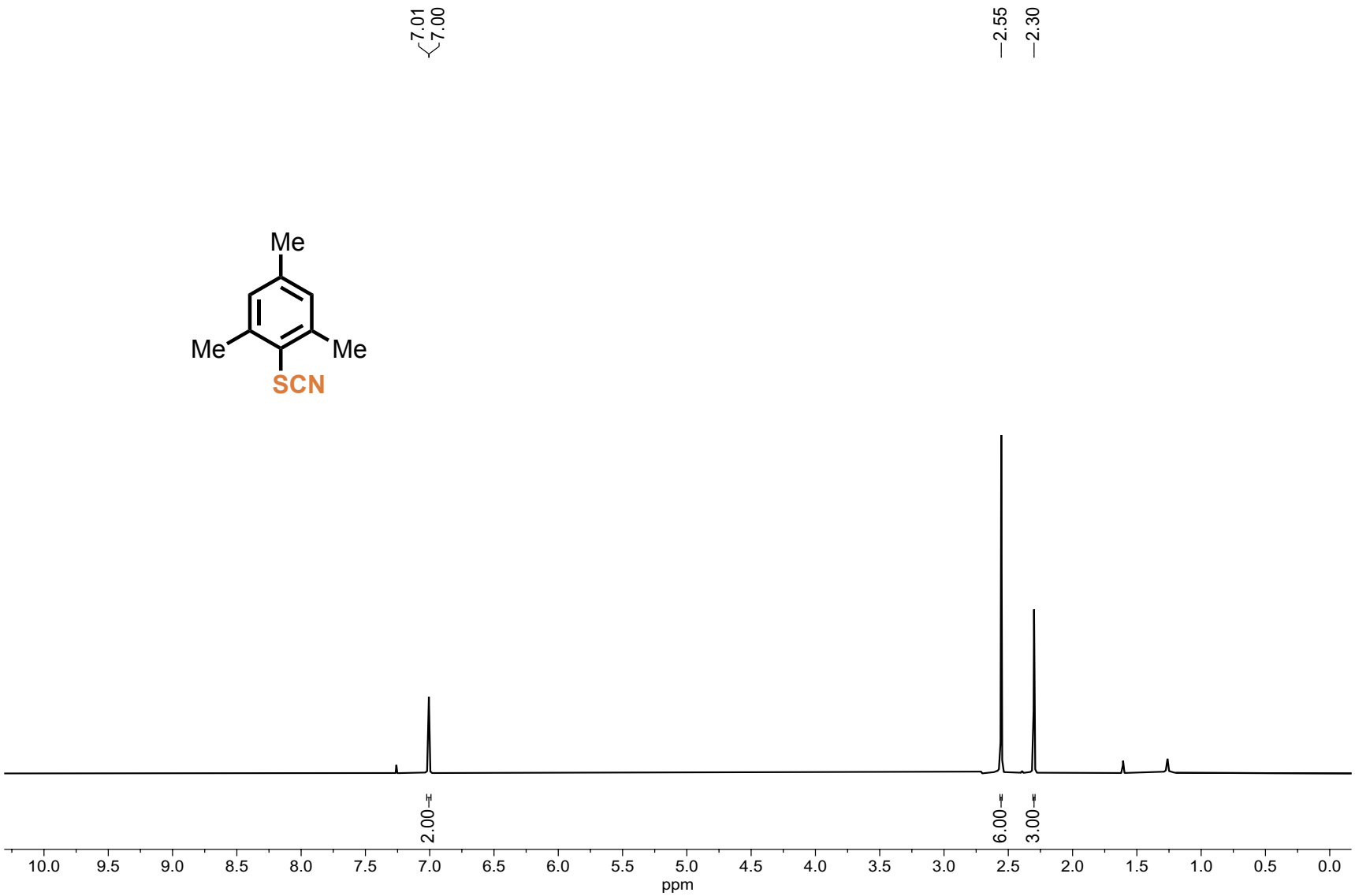


Figure S50. ^{1}H NMR ($CDCl_3$, 400 MHz) of **24a**

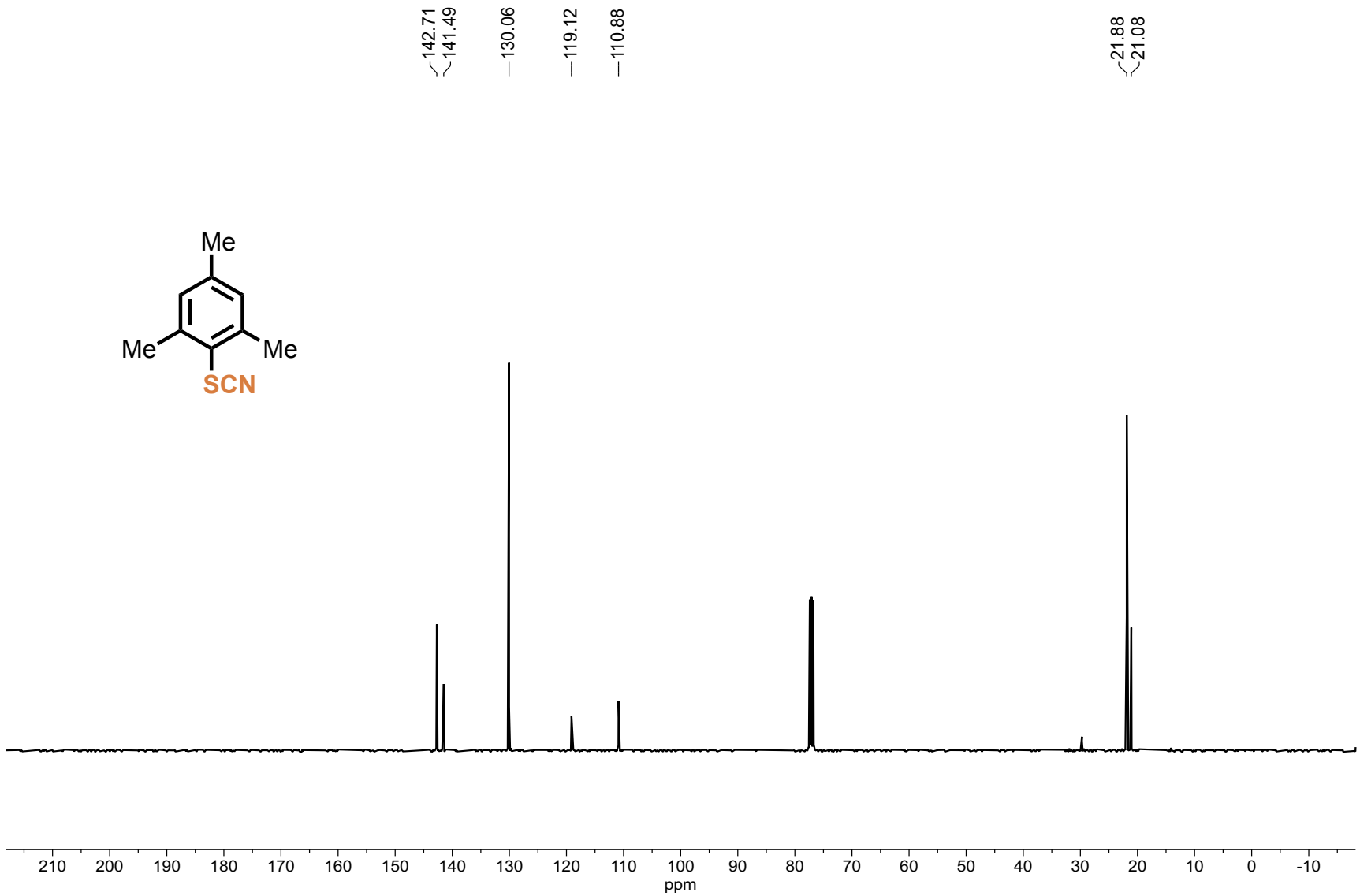


Figure S51. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **24a**

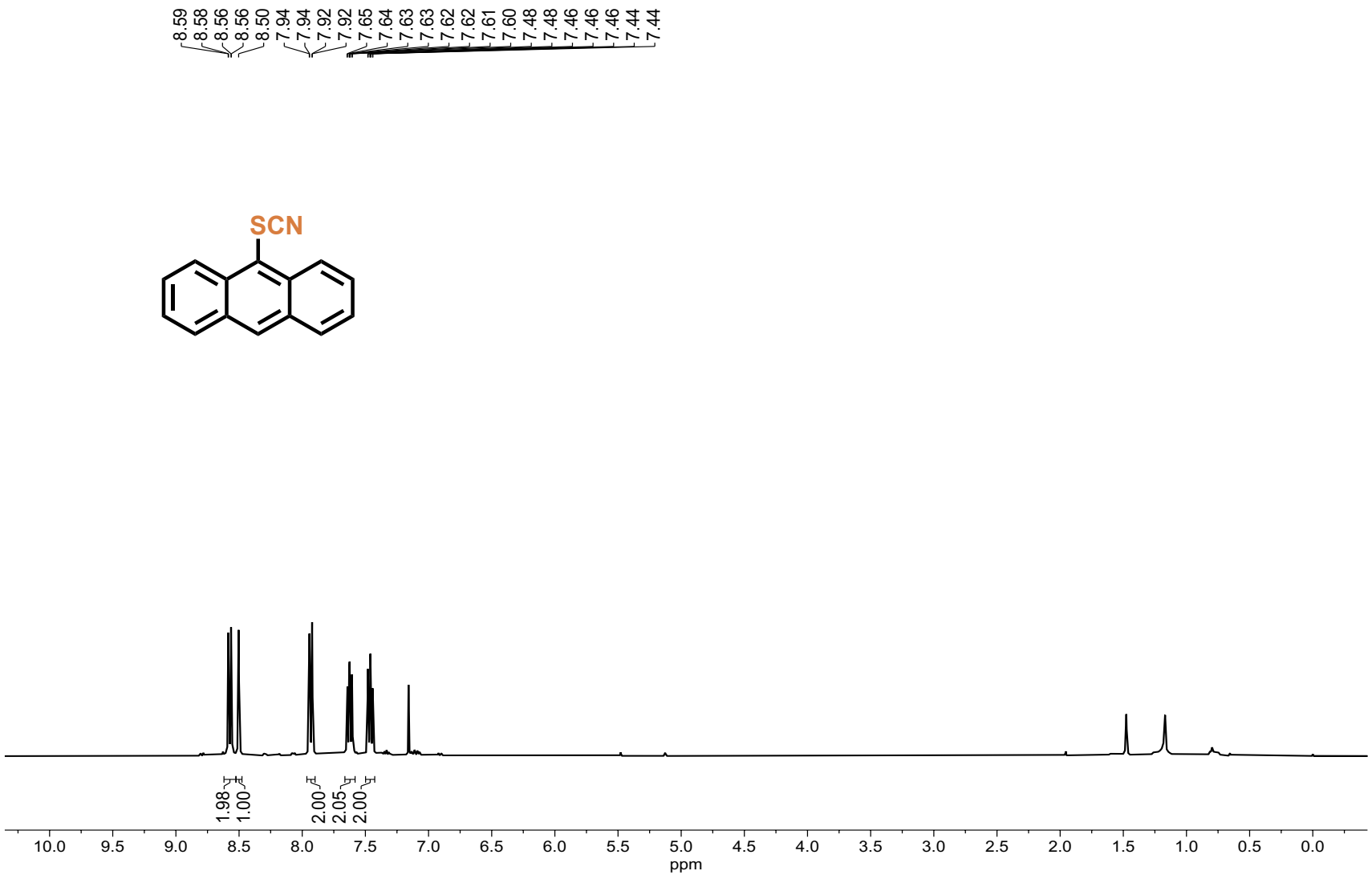


Figure S52. ^{1}H NMR ($CDCl_3$, 400 MHz) of **25a**

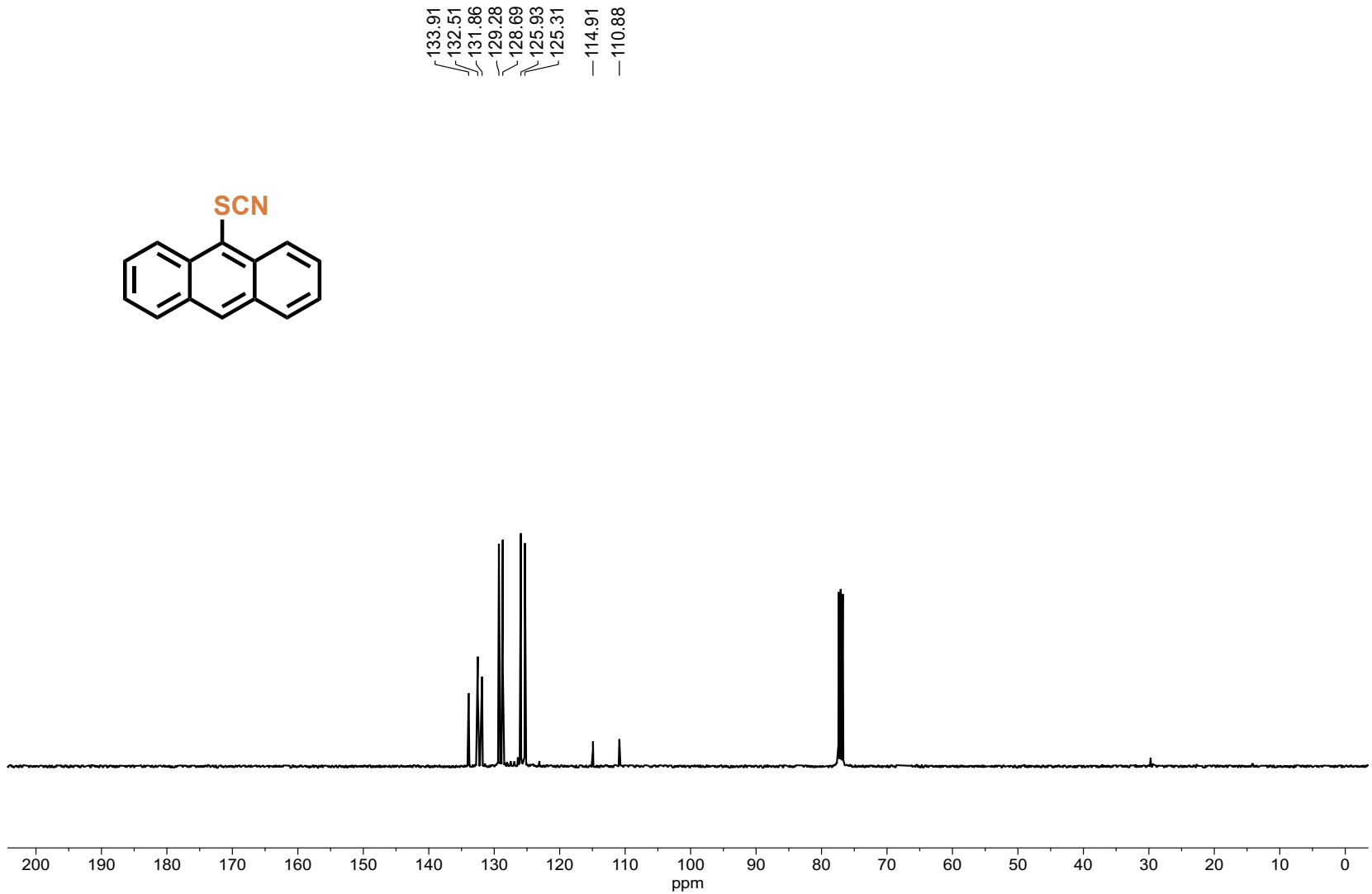


Figure S53. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **25a**

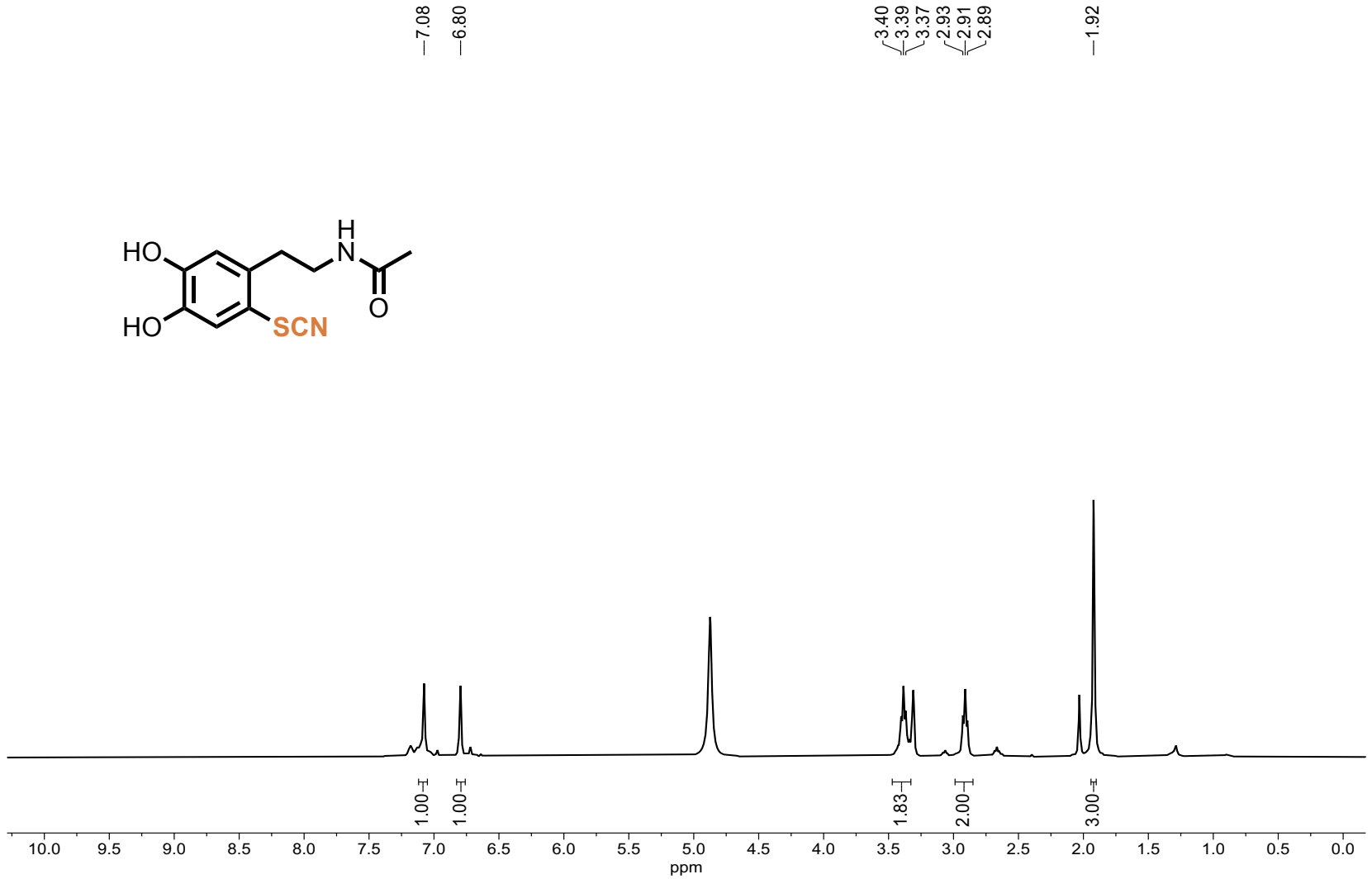


Figure S54. ^{1}H NMR (CD_3OD, 400 MHz) of **26a**

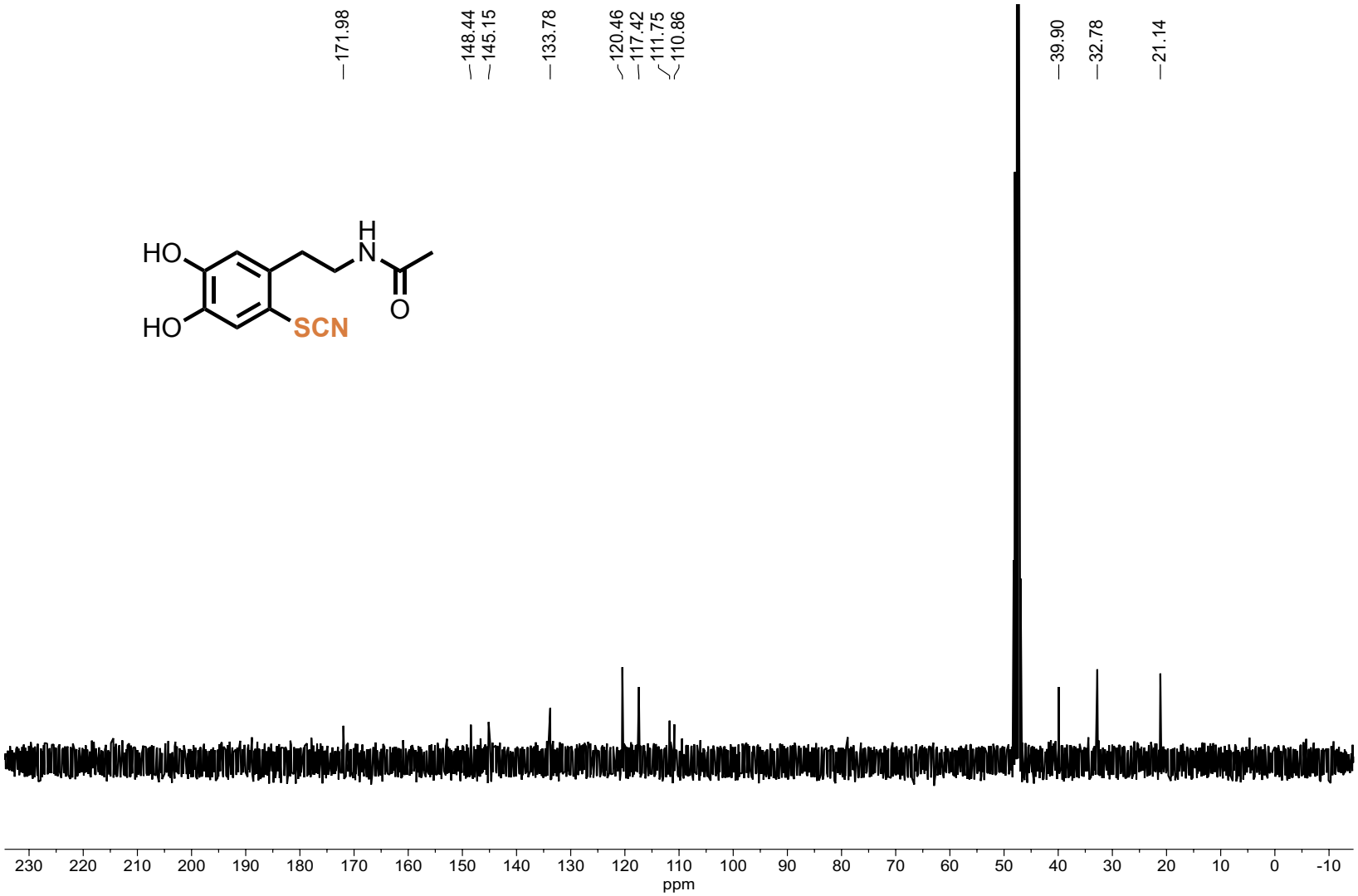


Figure S55. ^{13}C NMR (CD_3OD, 100.6 MHz) of **26a**

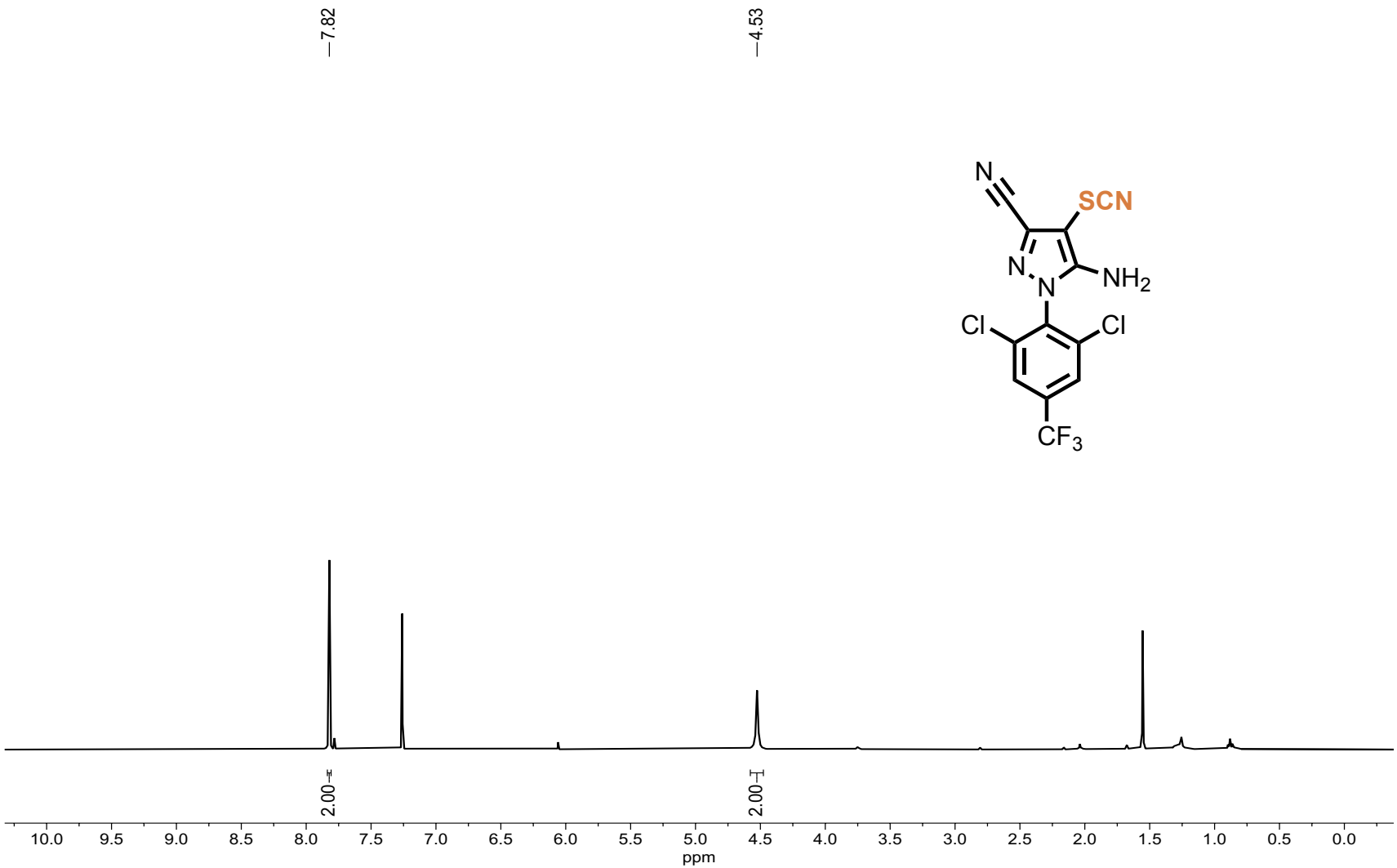


Figure S56. ^{1}H NMR ($CDCl_3$, 400 MHz) of **27a**

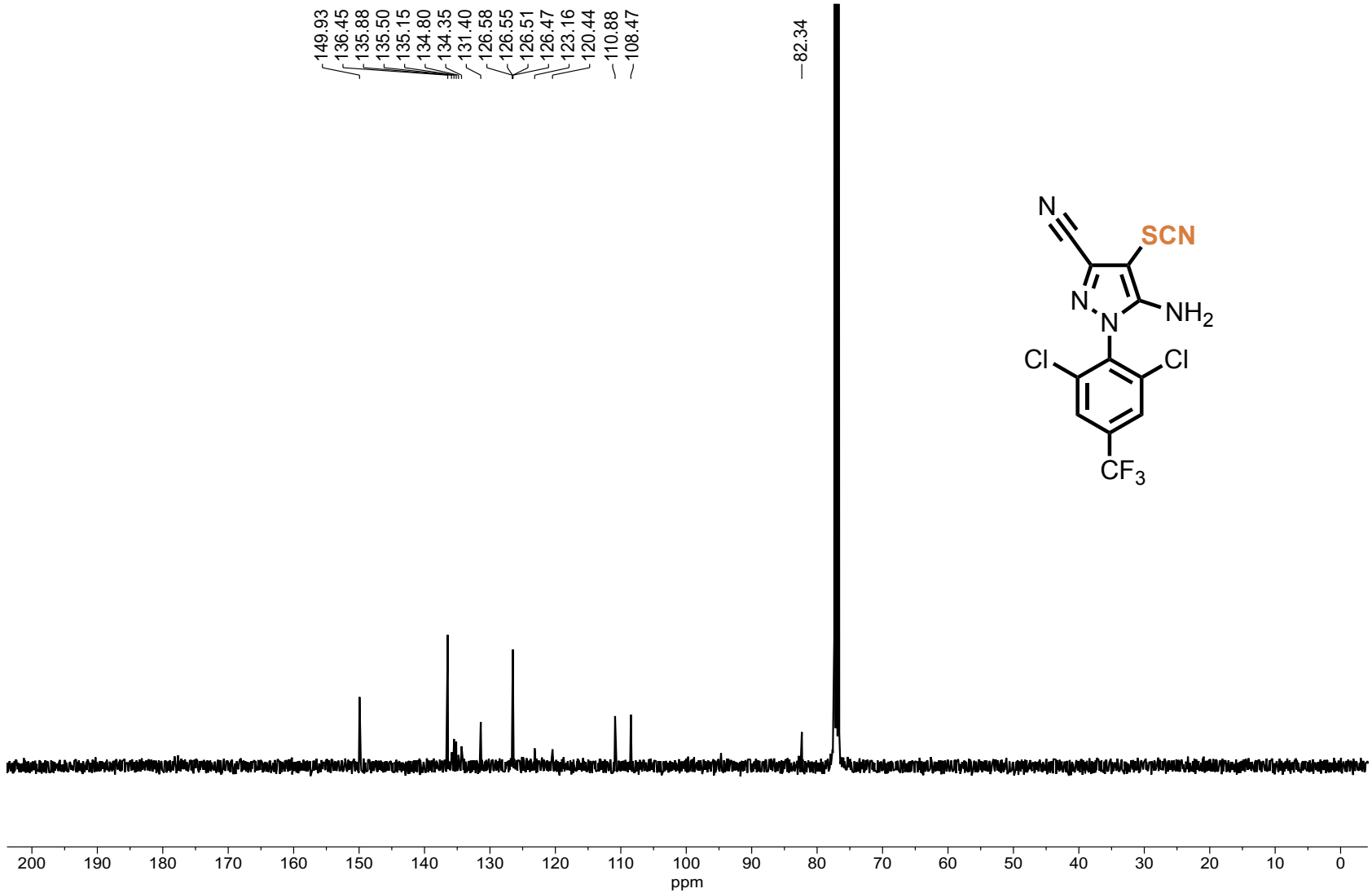


Figure S57. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **27a**

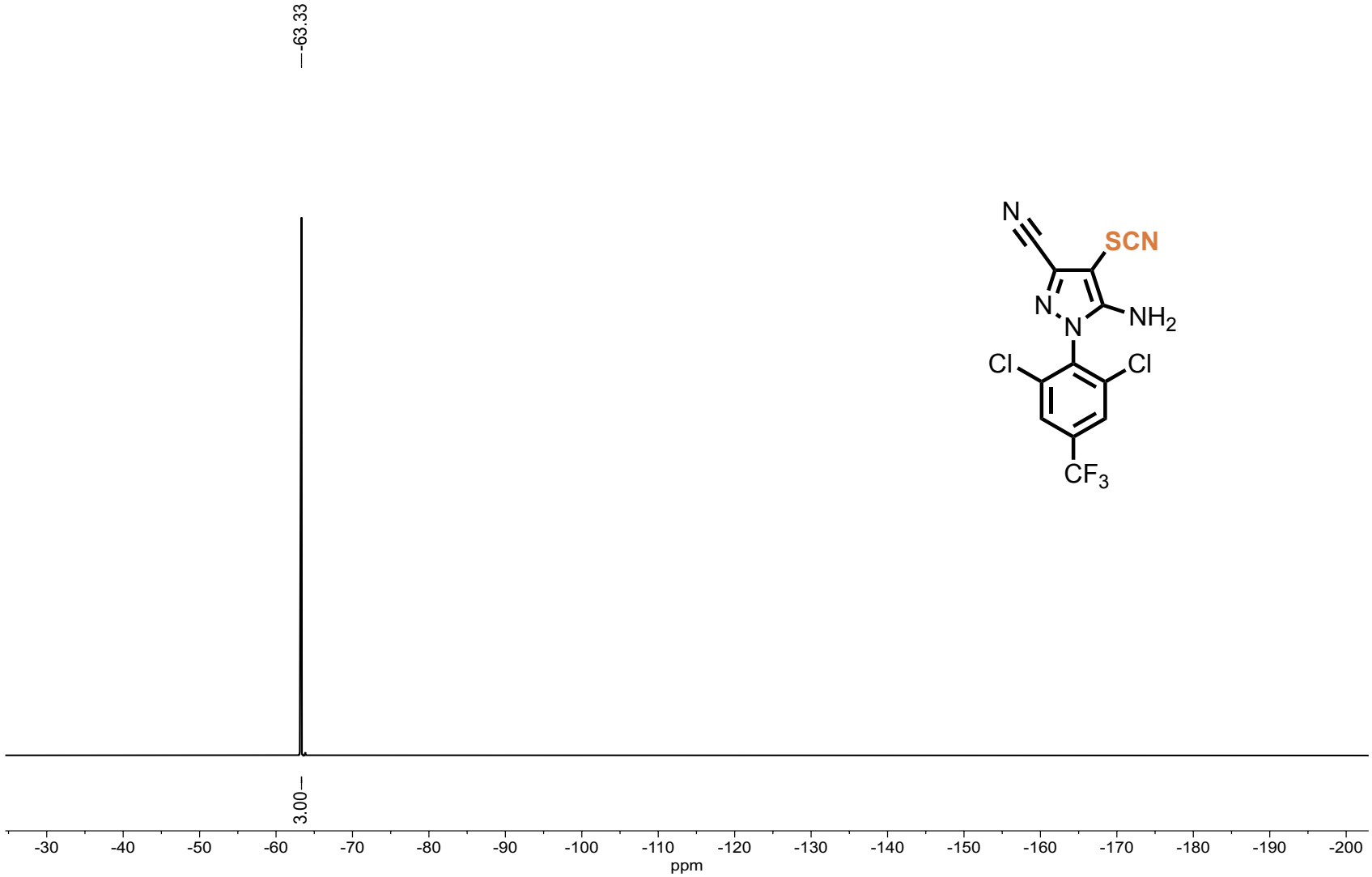


Figure S58. ^{19}F NMR ($CDCl_3$ 376.5 MHz) of **27a**

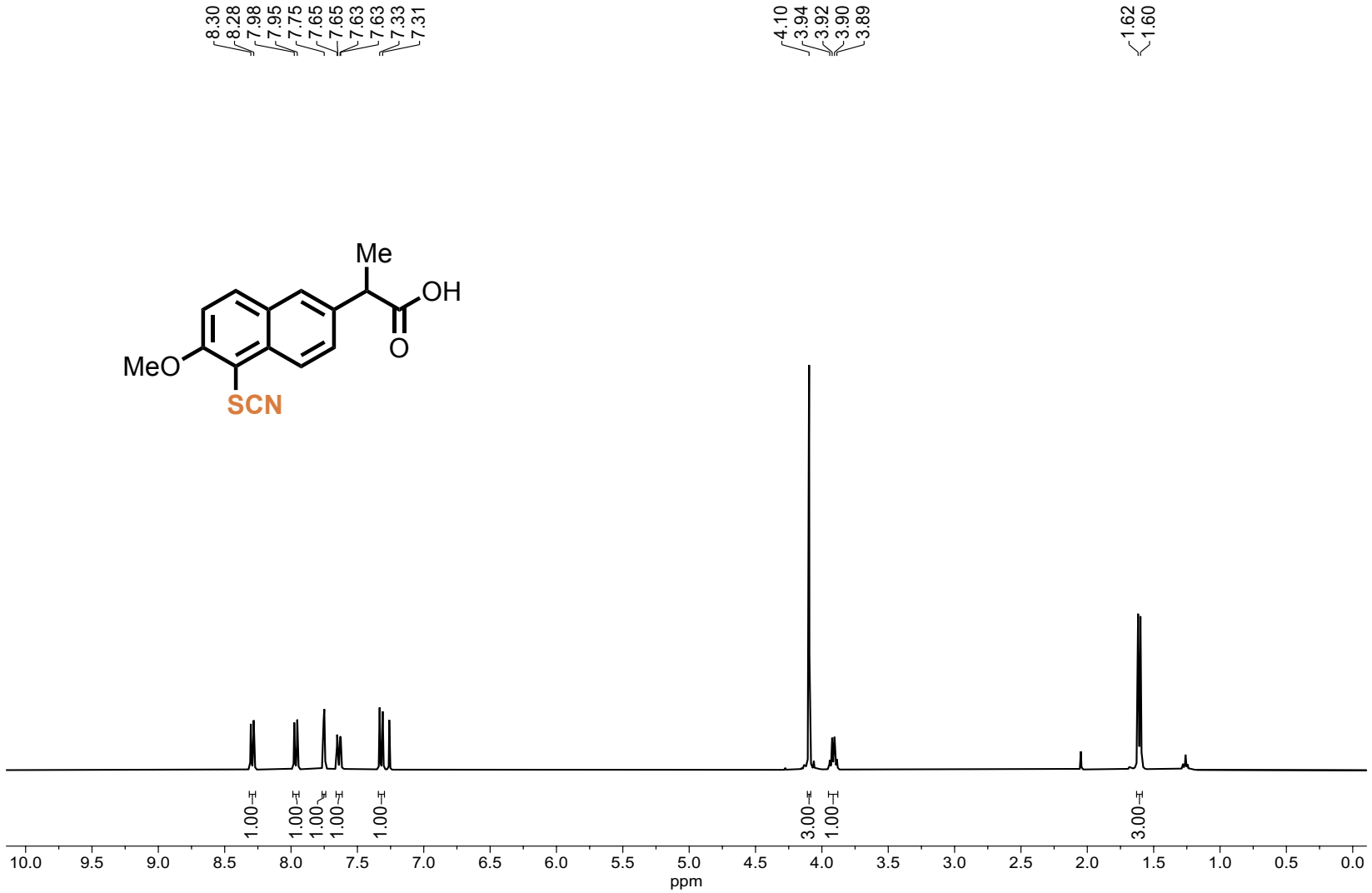


Figure S59. ^{1}H NMR ($CDCl_3$, 400 MHz) of **28a**

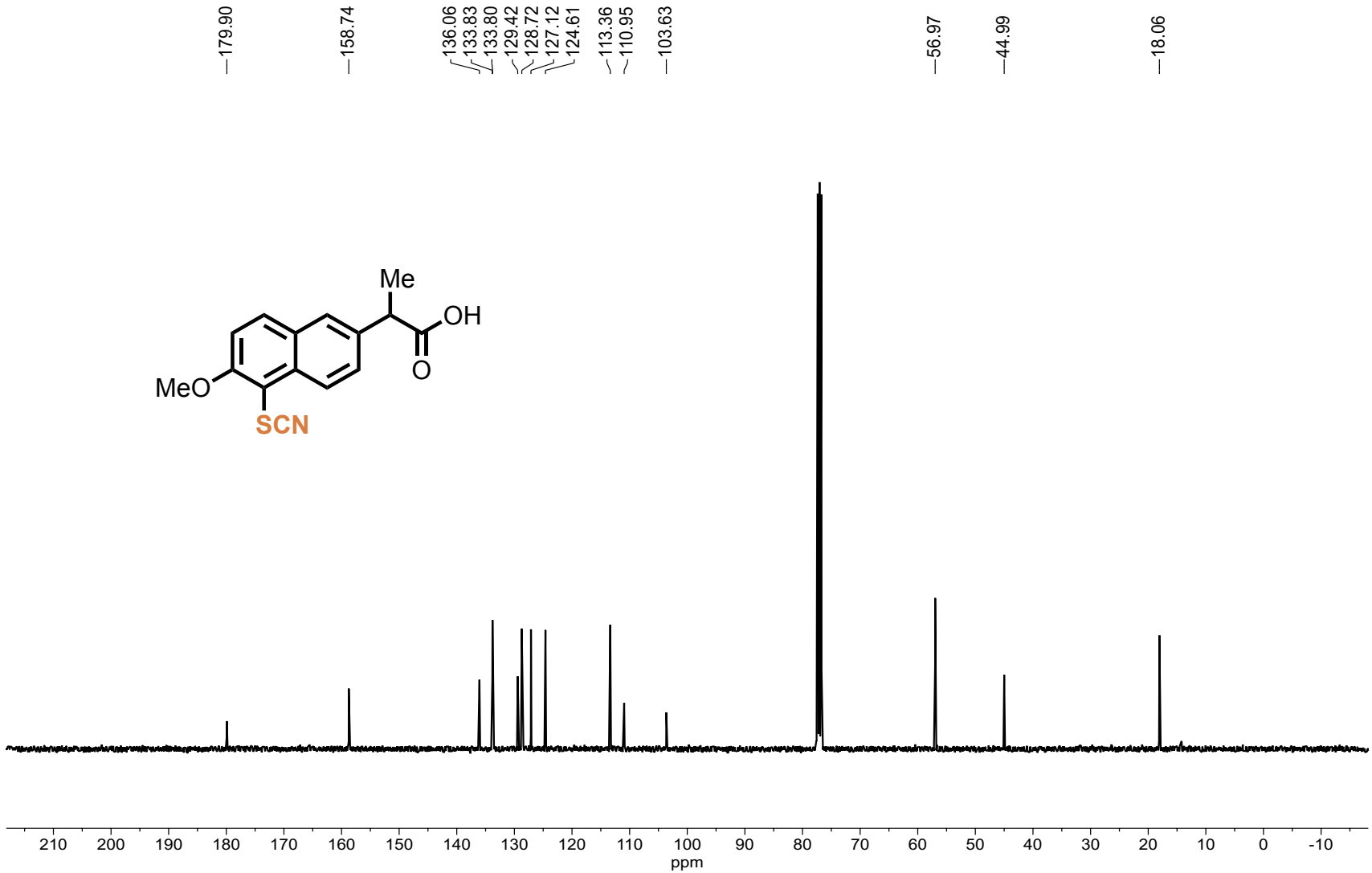


Figure S60. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **28a**

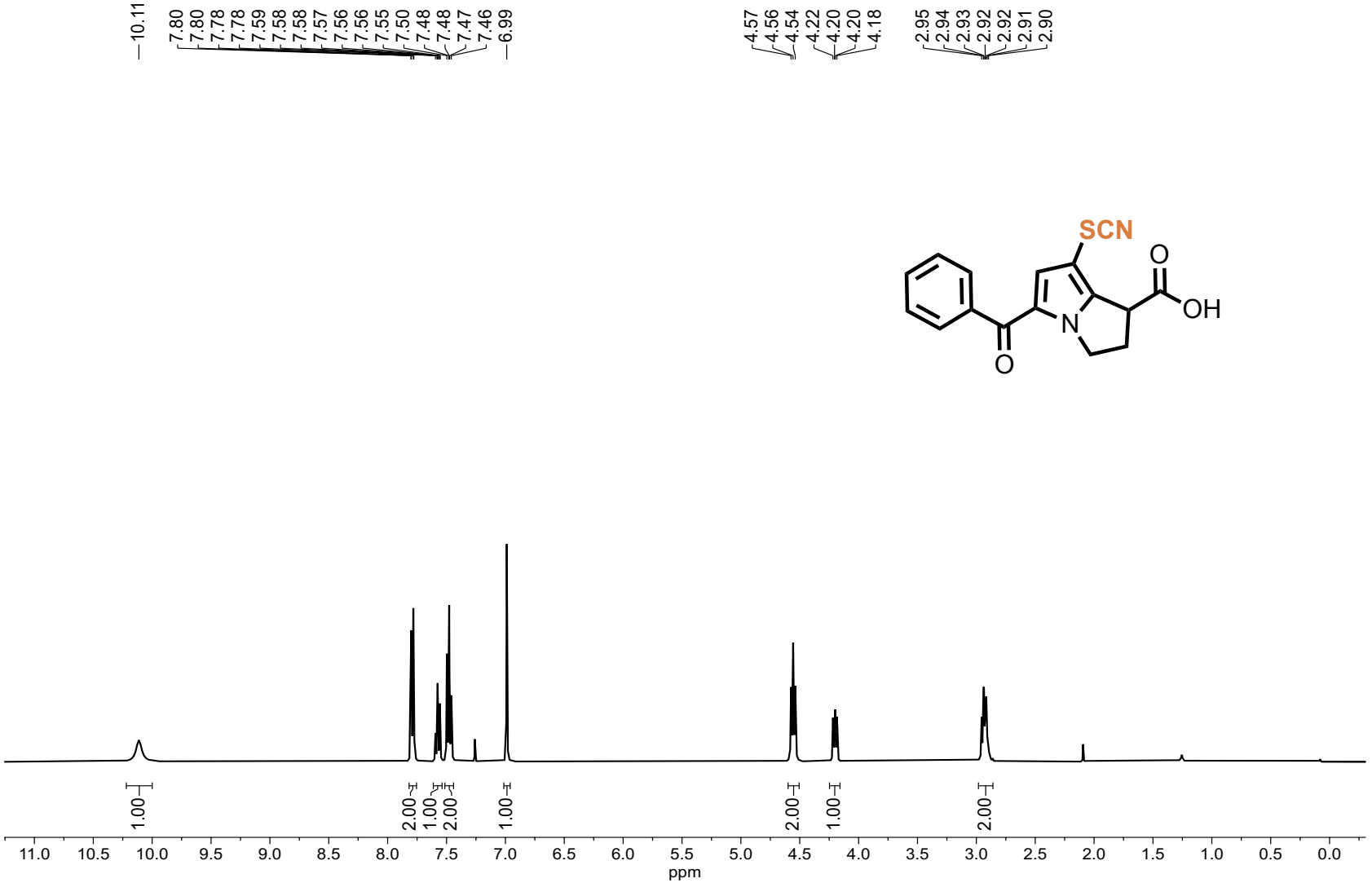


Figure S61. ^{1}H NMR ($CDCl_3$, 400 MHz) of **29a**

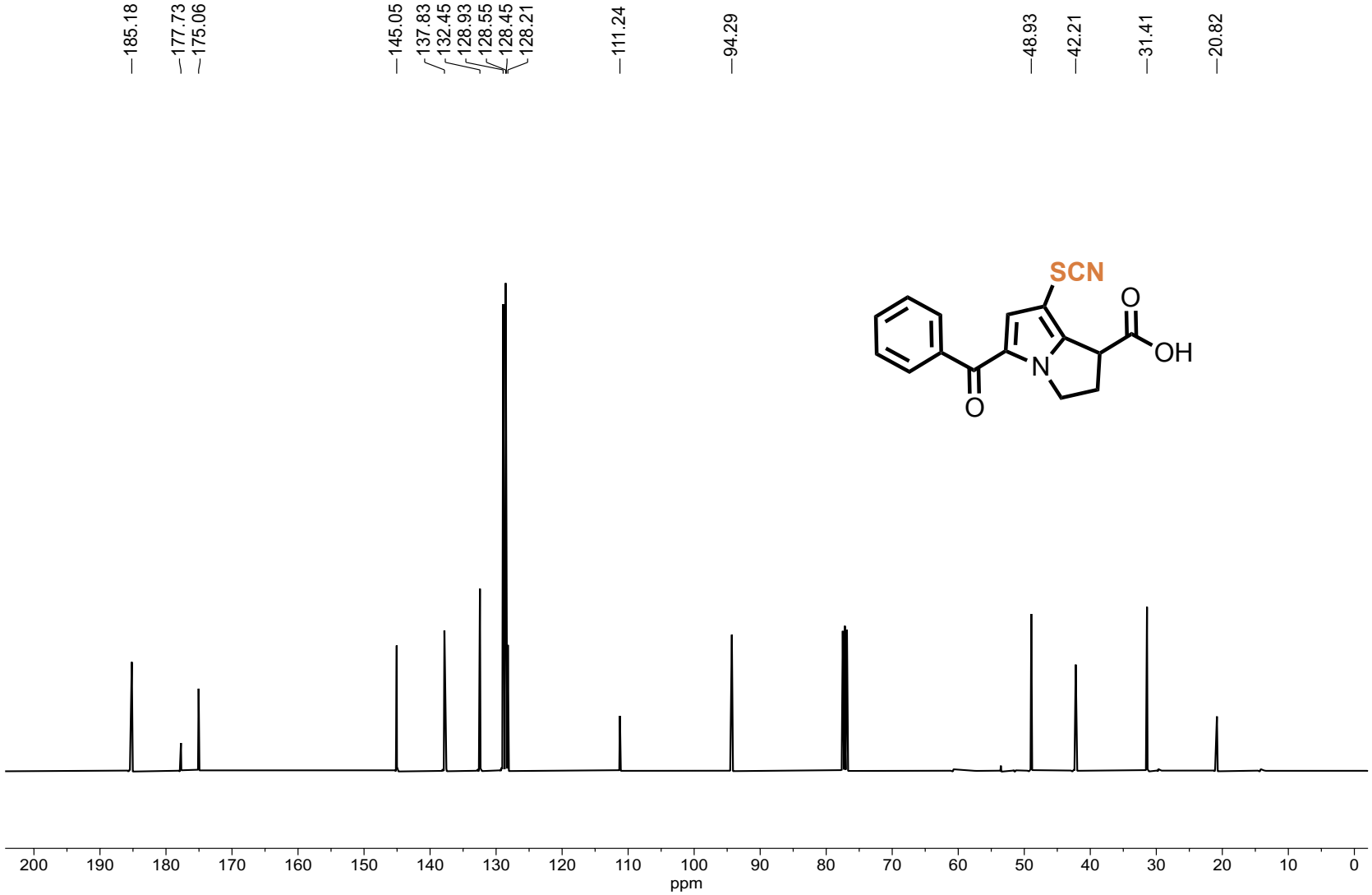


Figure S62. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **29a**

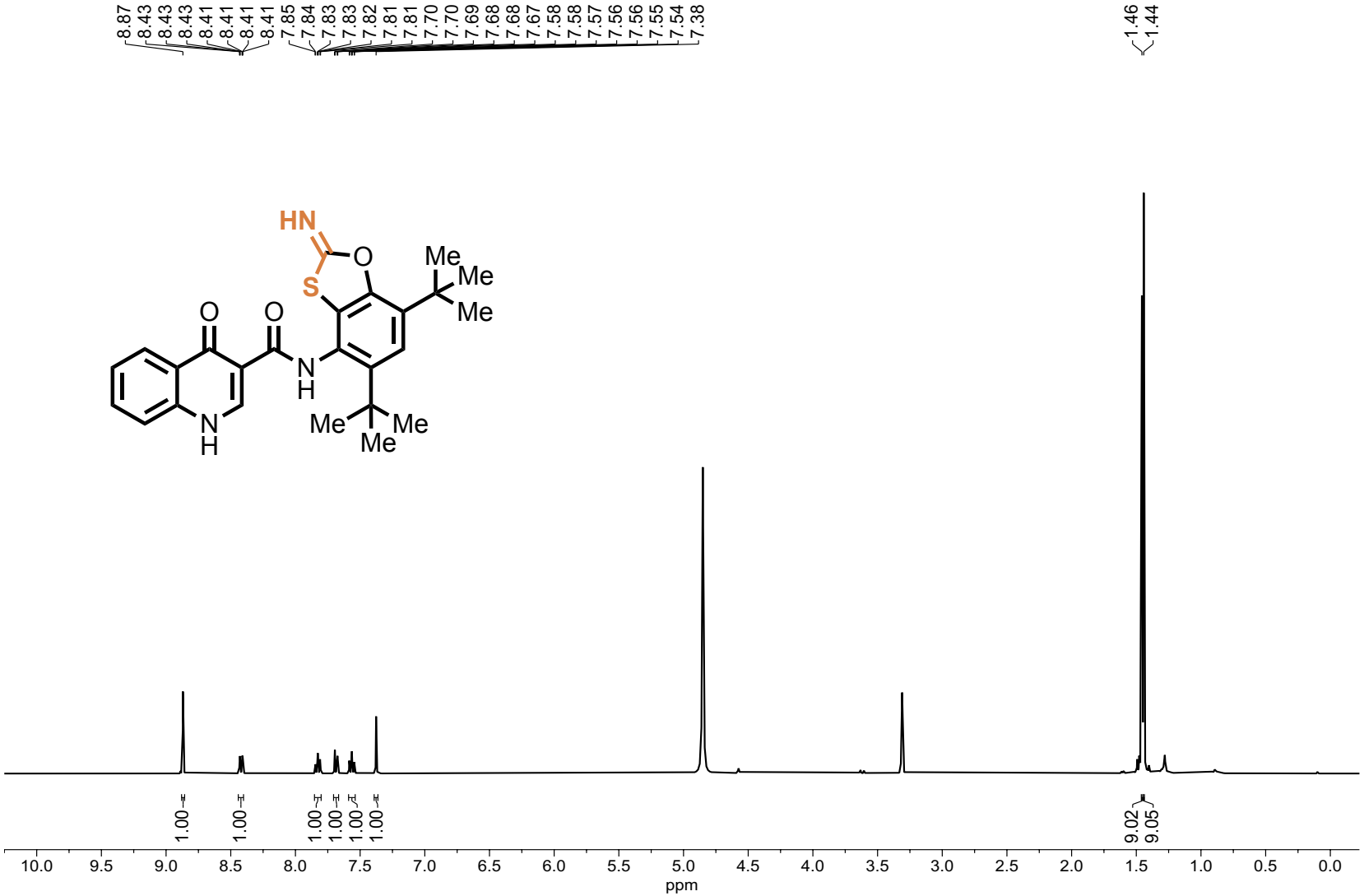


Figure S63. ^{1}H NMR (CD_3OD, 400 MHz) of **30a**

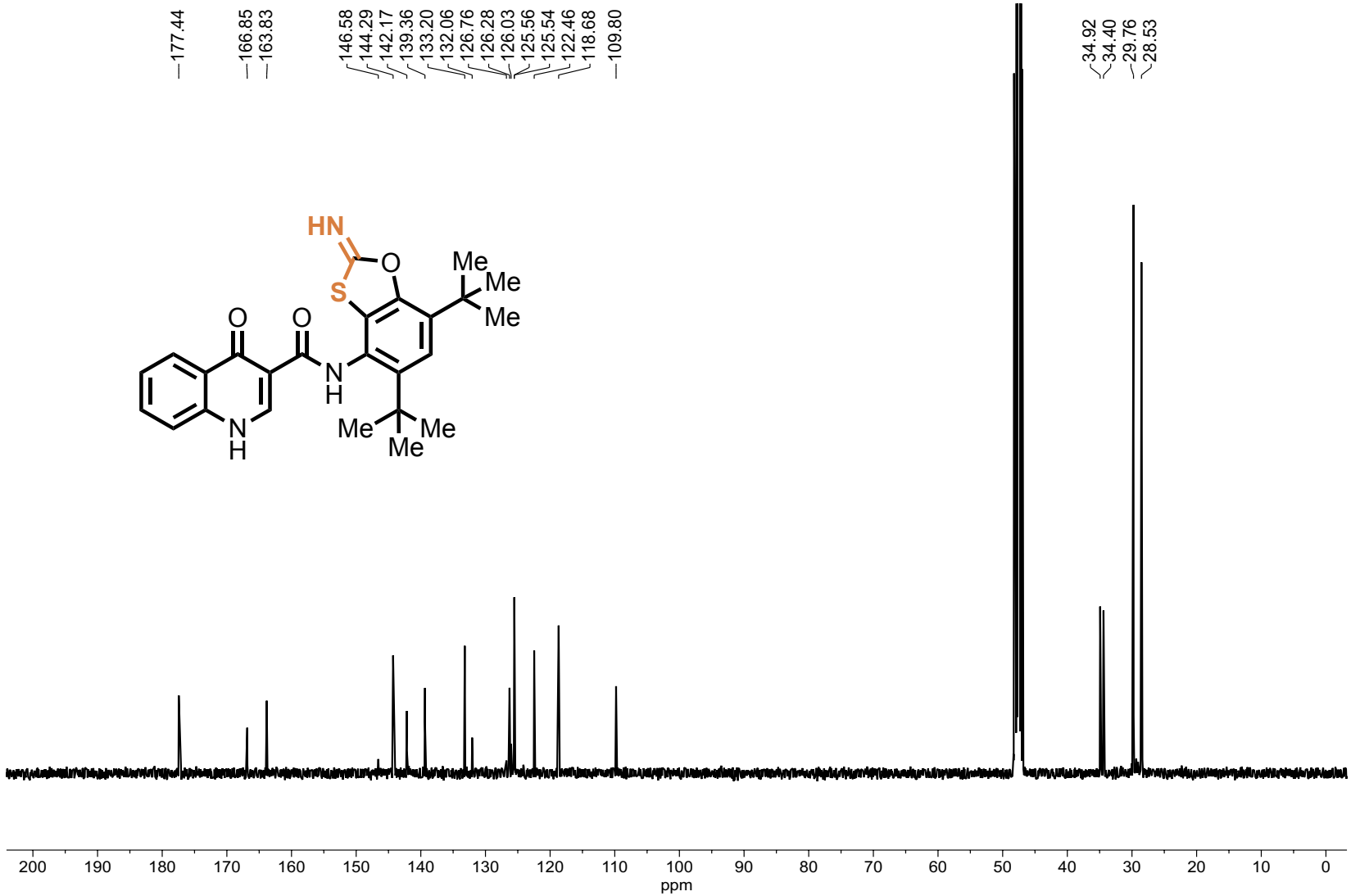


Figure S64. ^{13}C NMR (CD_3OD, 100.6 MHz) of **30a**

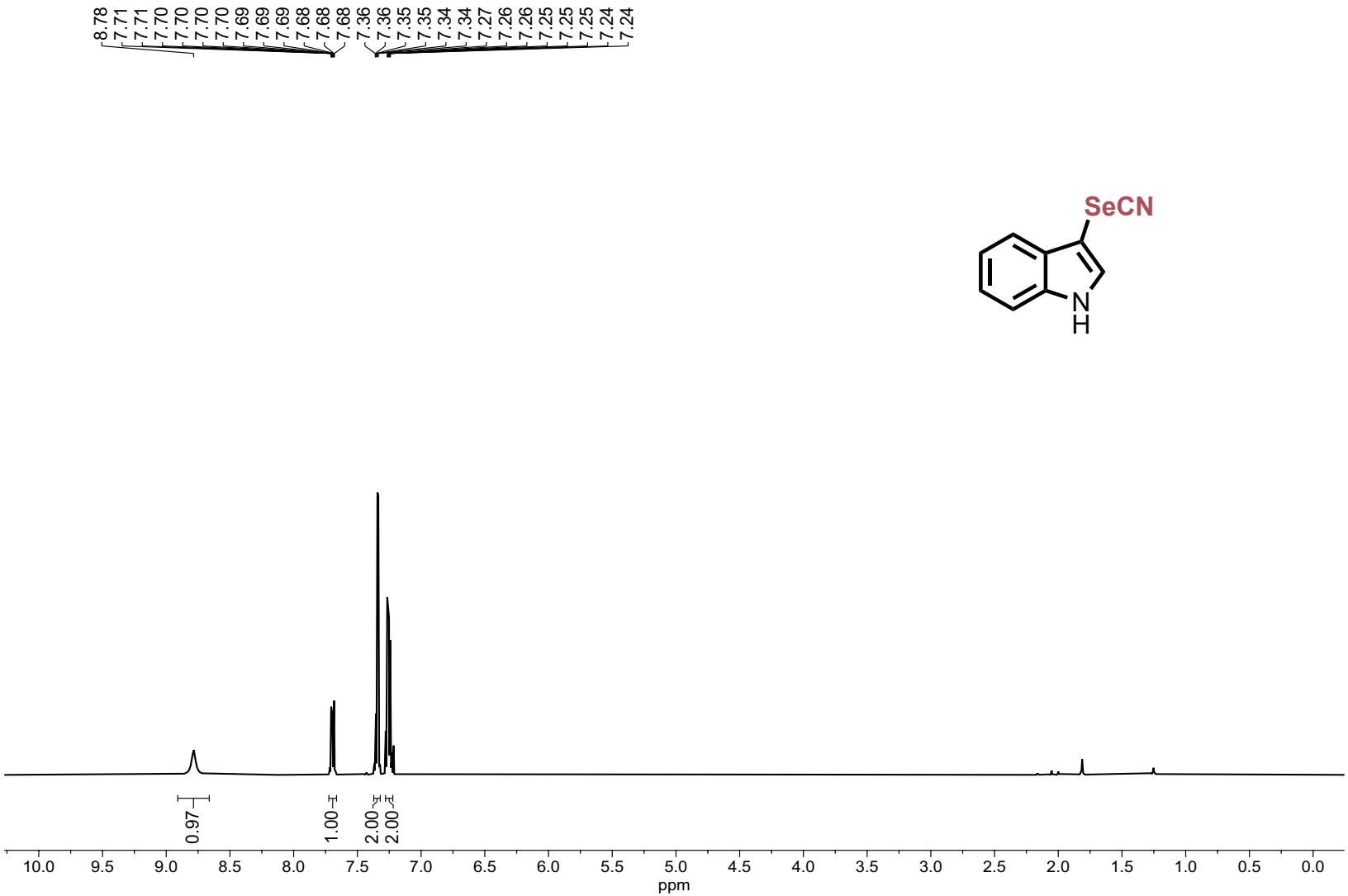


Figure S65. ^{1}H NMR ($CDCl_3$, 400 MHz) of **6b**

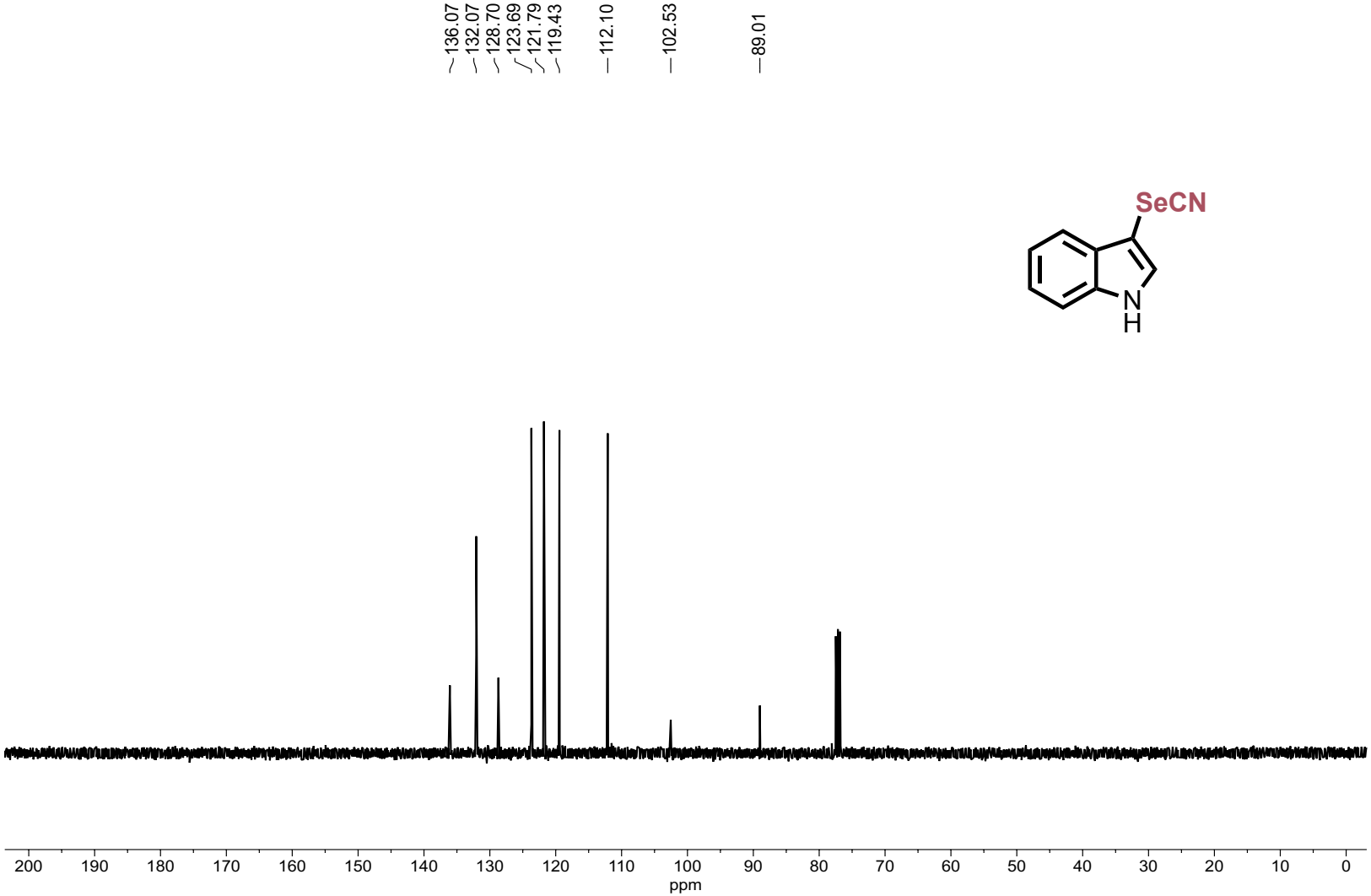


Figure S66. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **6b**

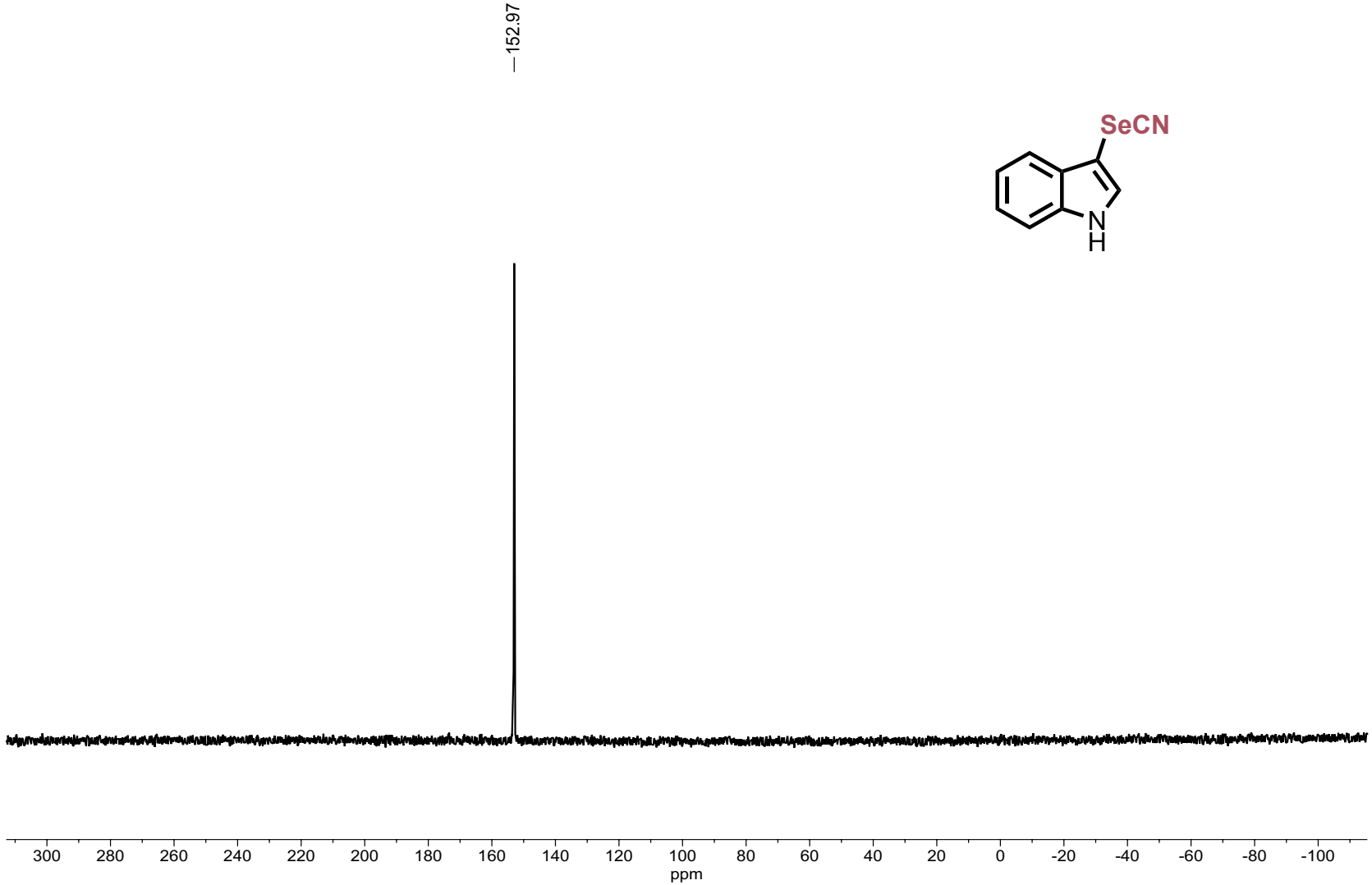


Figure S67. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **6b**

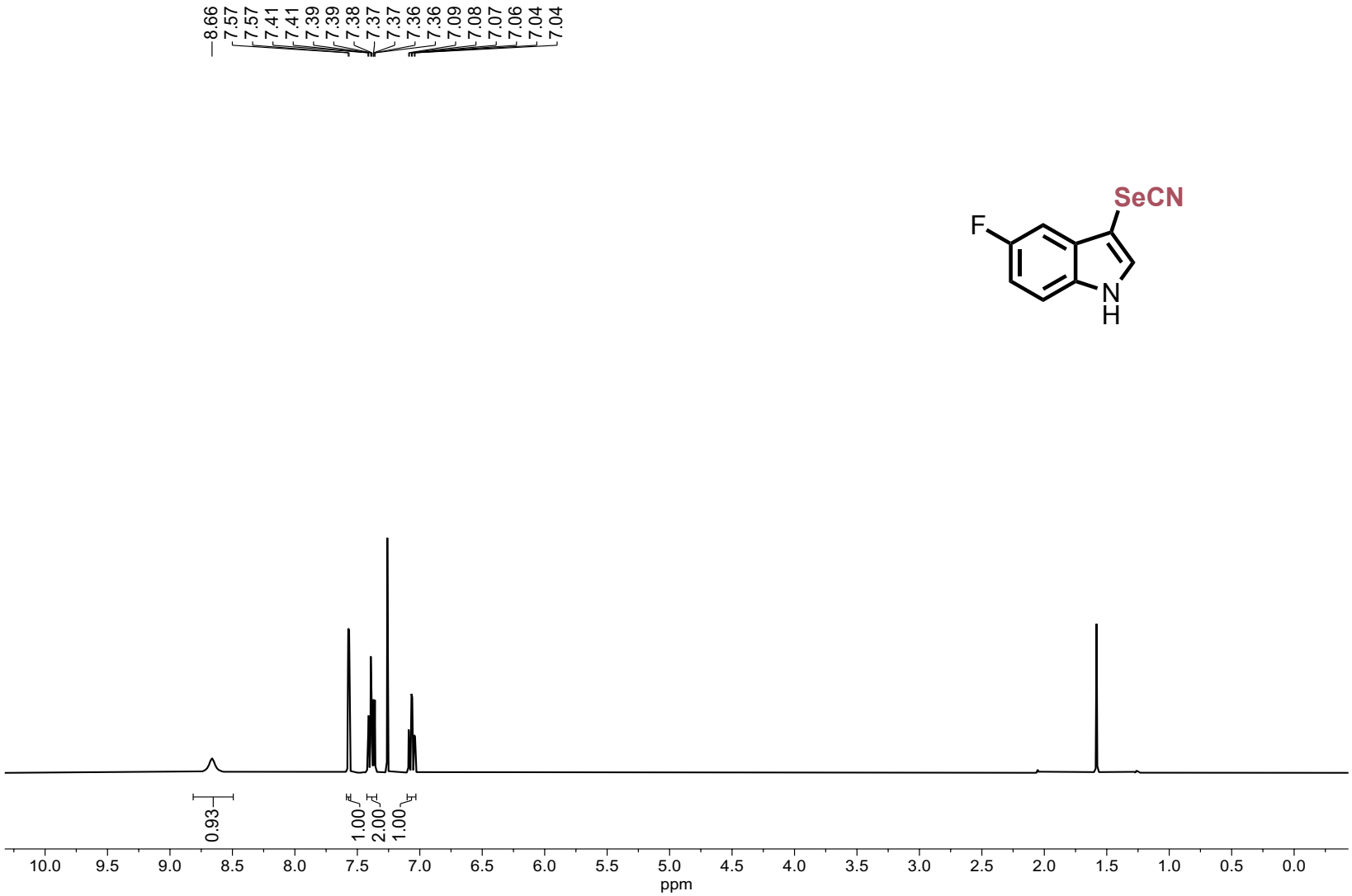


Figure S68. ^{1}H NMR ($CDCl_3$, 400 MHz) of **7b**

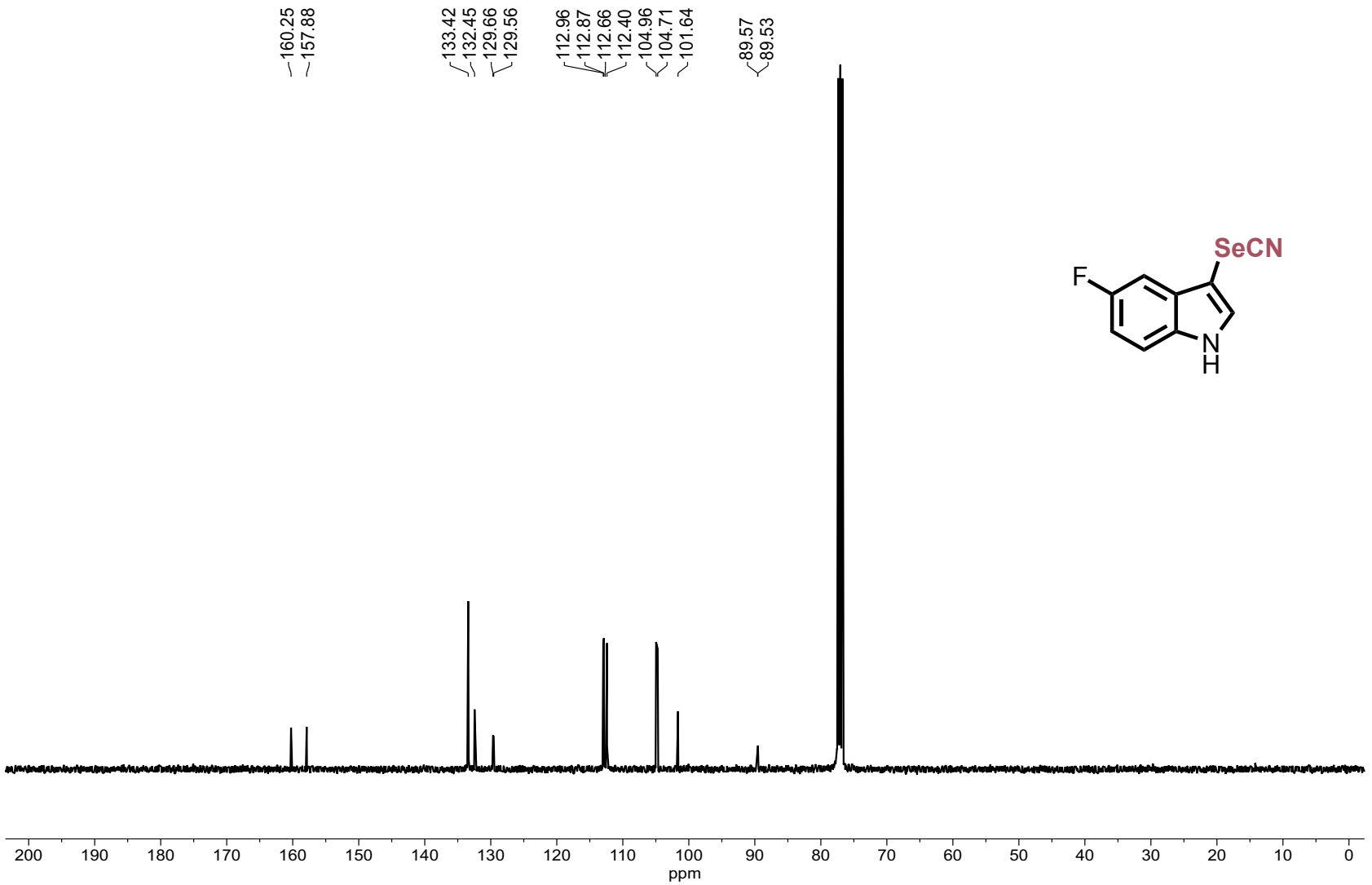


Figure S69. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **7b**

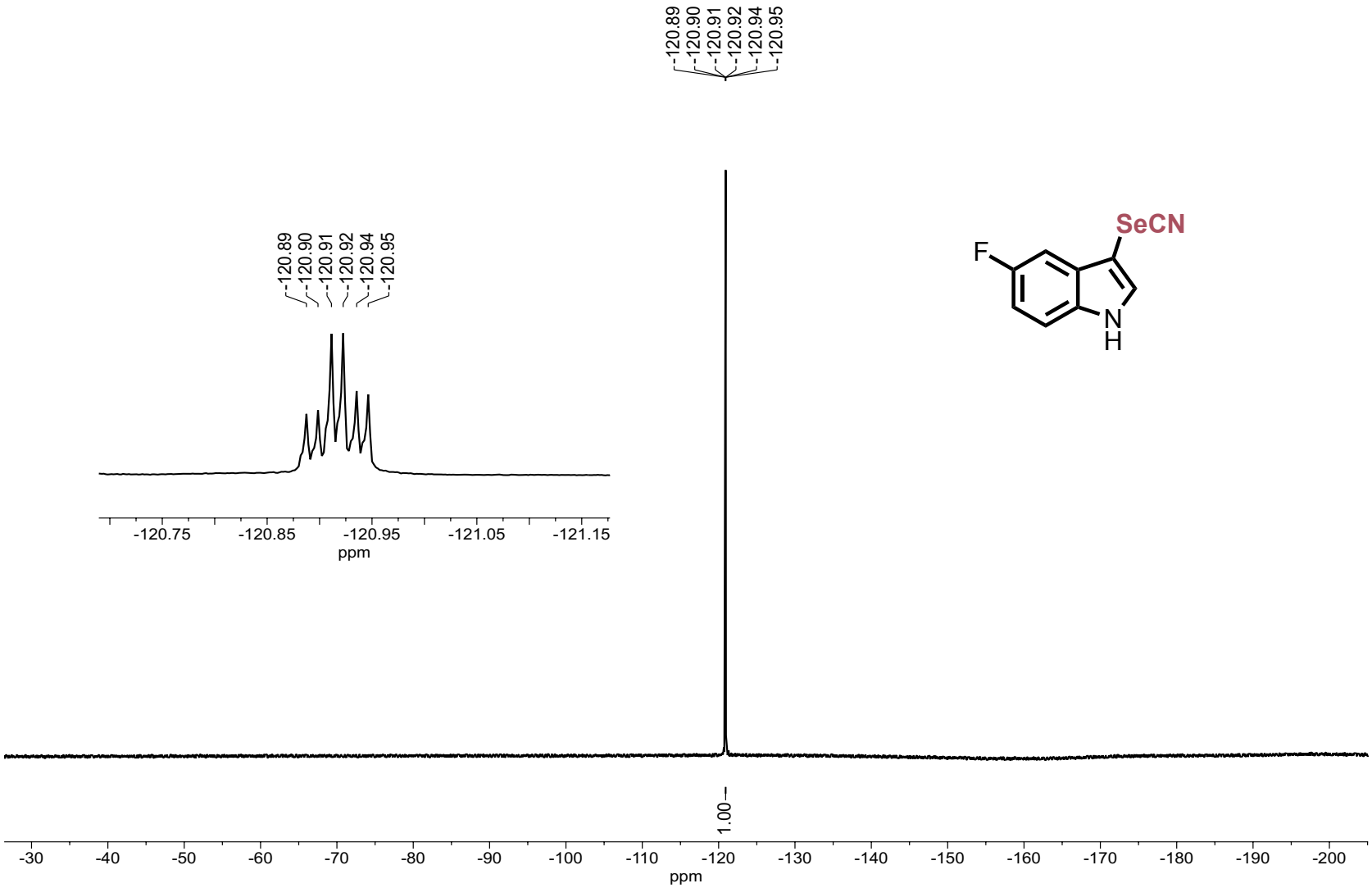


Figure S70. ^{19}F NMR ($CDCl_3$ 376.5 MHz) of **7b**

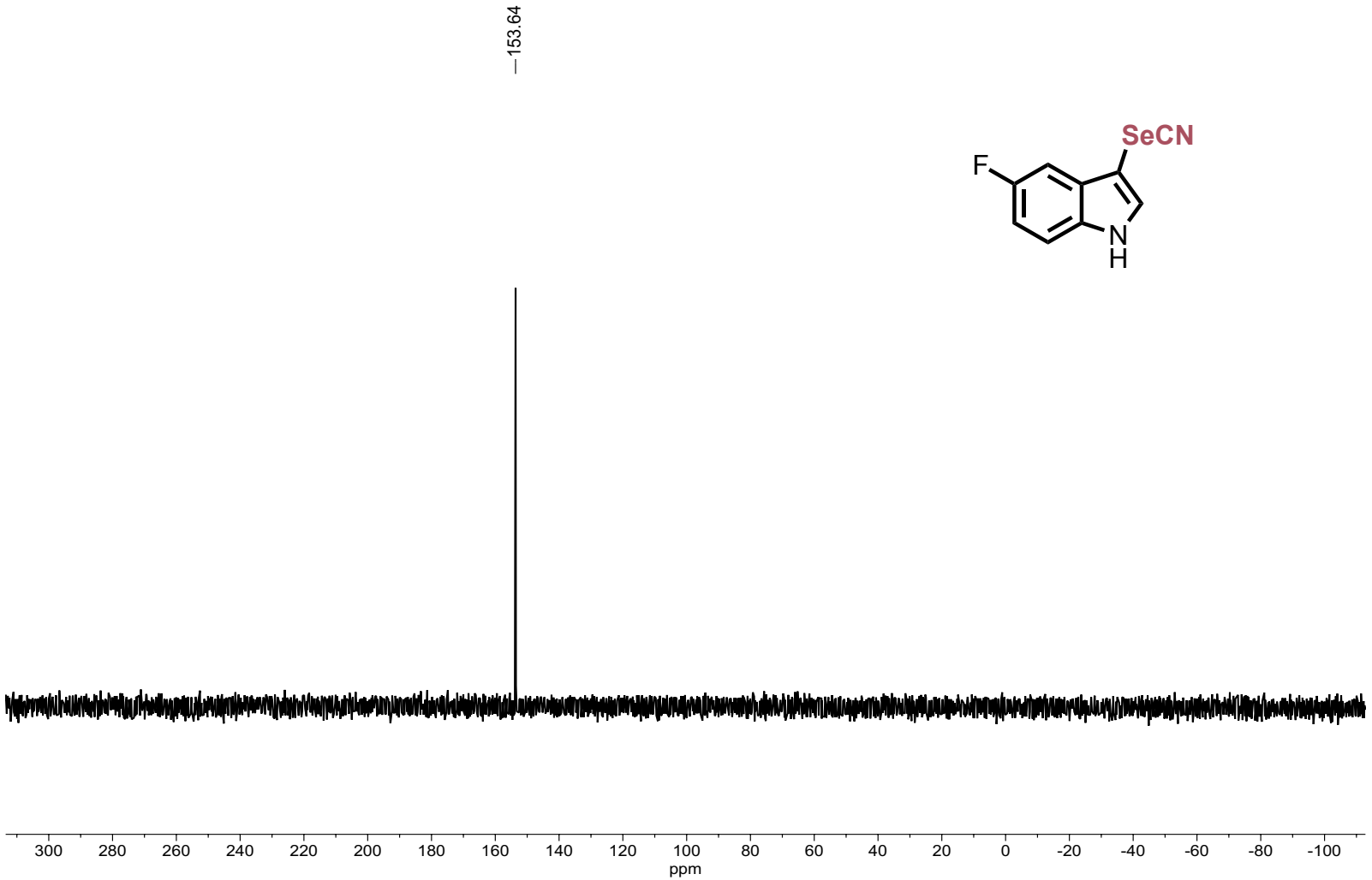


Figure S71. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **7b**

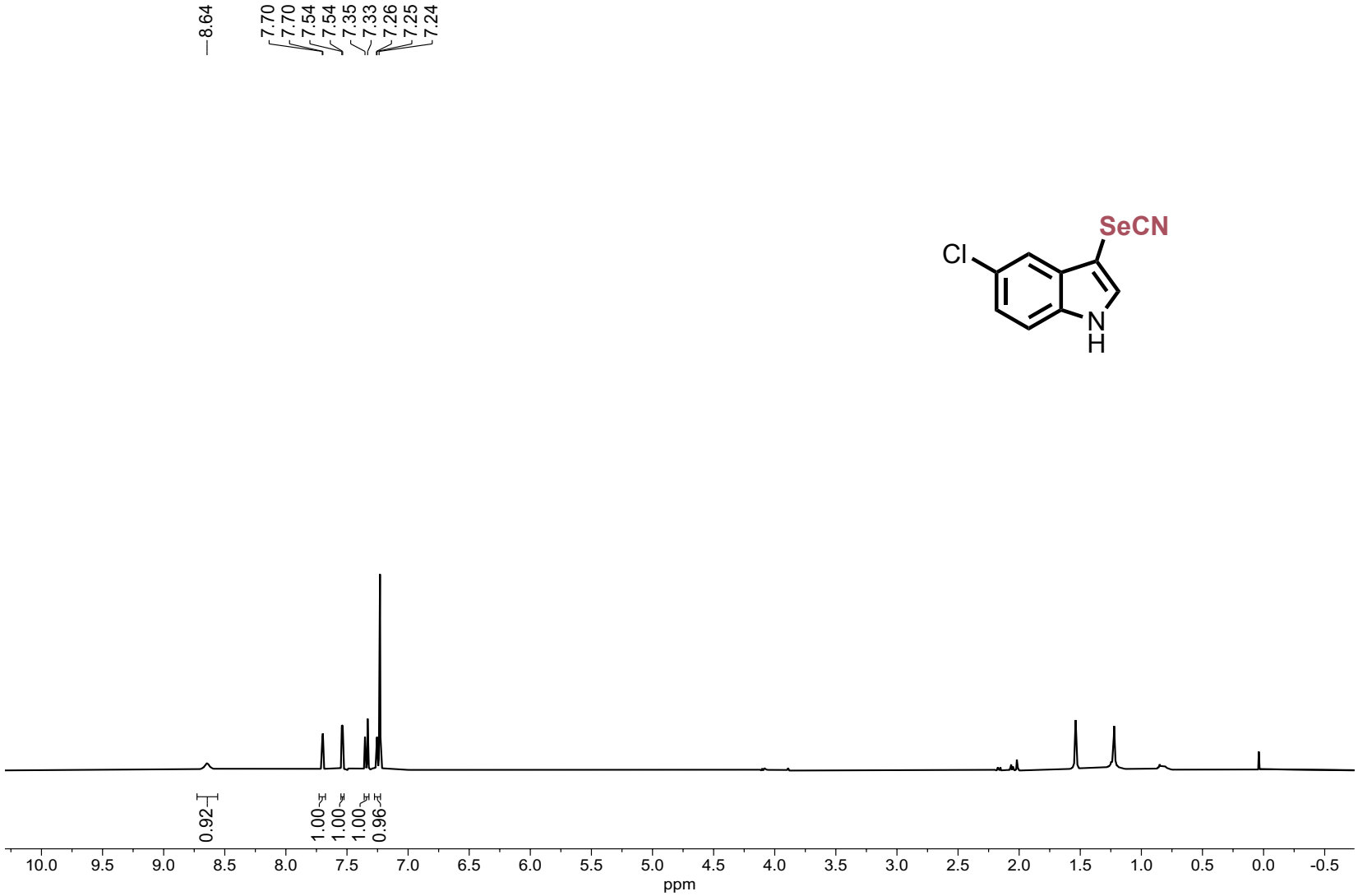


Figure S72. ^{1}H NMR ($CDCl_3$, 400 MHz) of **8b**

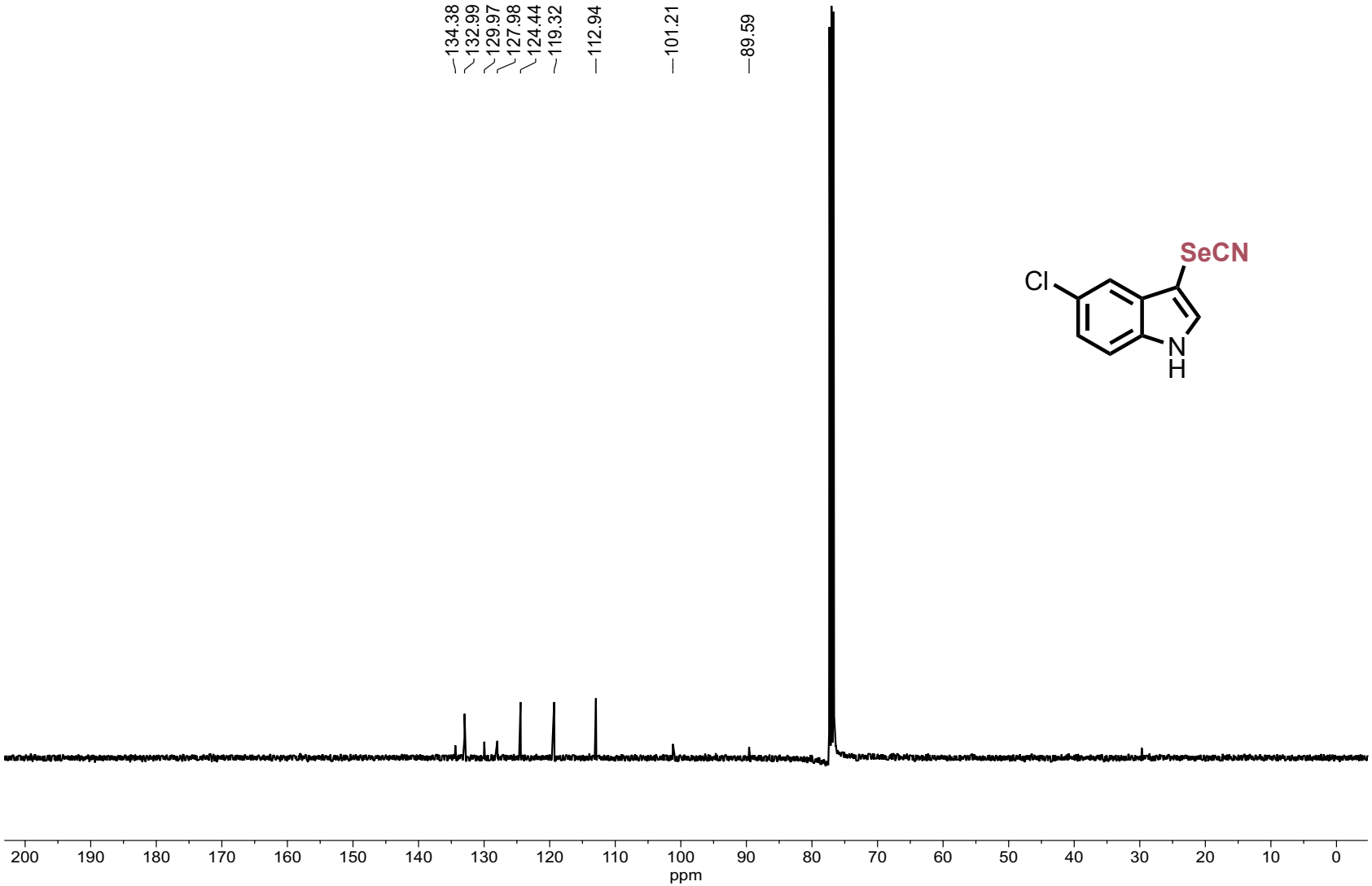


Figure S73. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **8b**

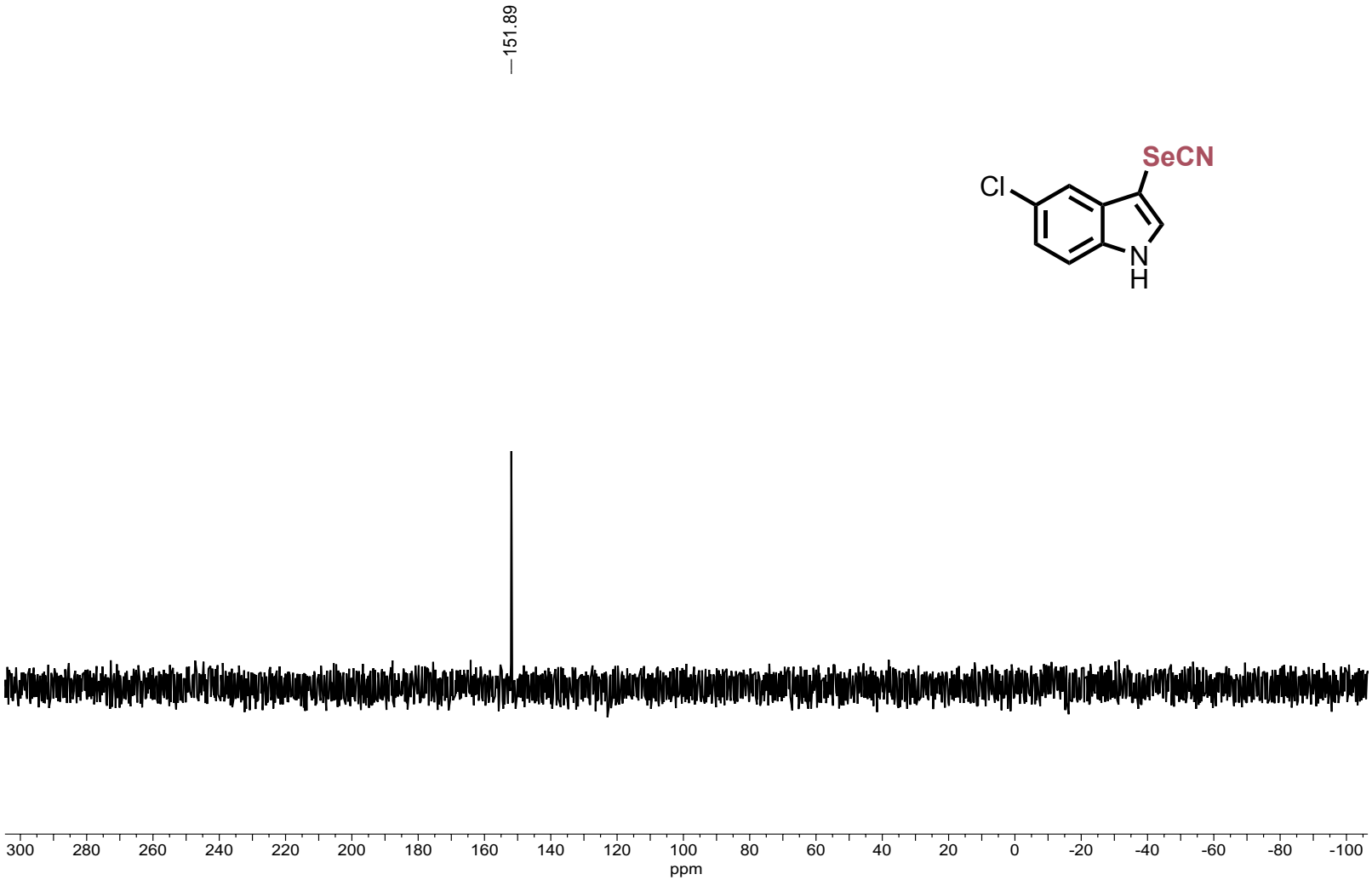


Figure S74. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **8b**

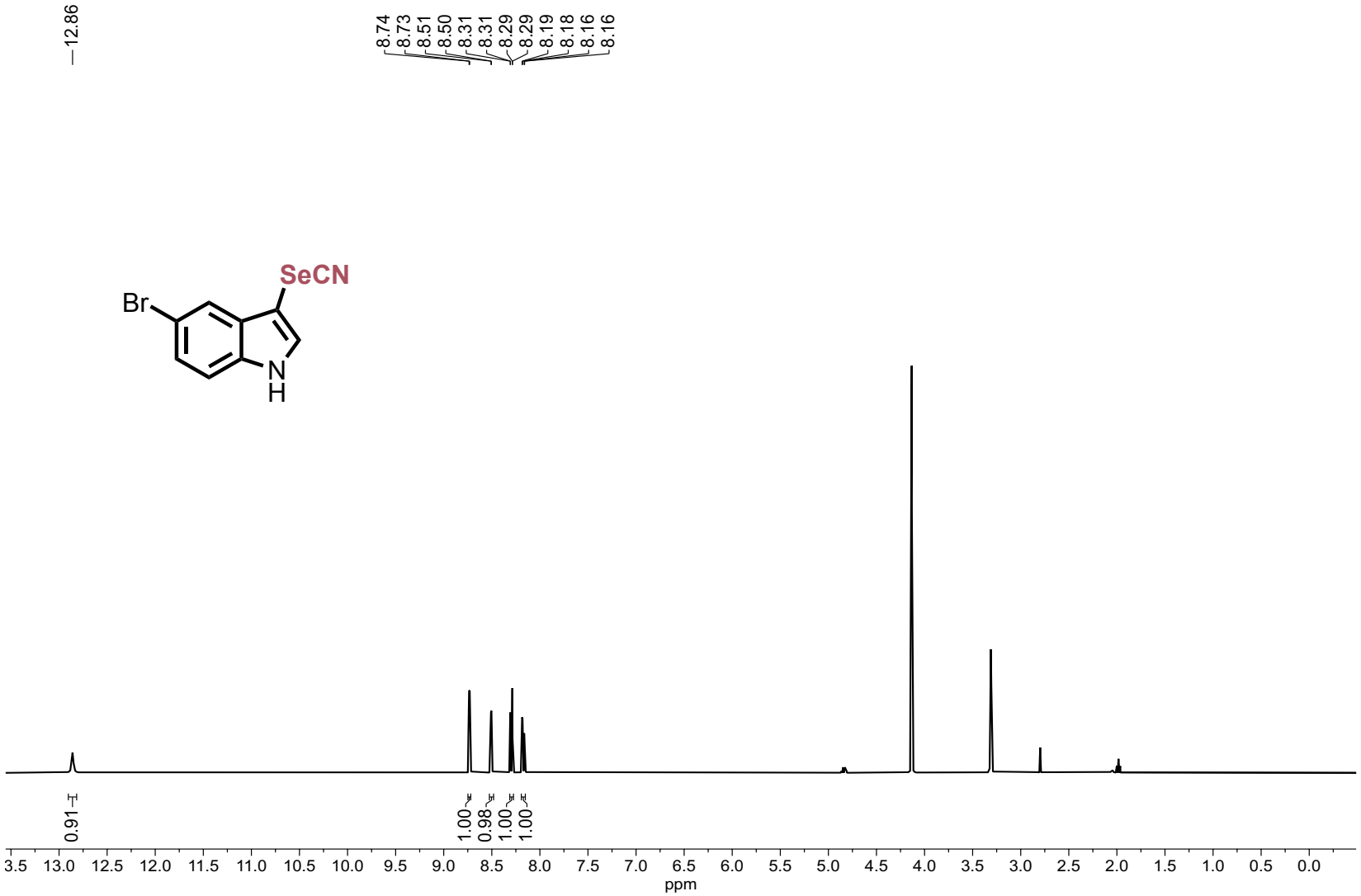


Figure S75. ^{1}H NMR (CD_3OD, 400 MHz) of **9b**

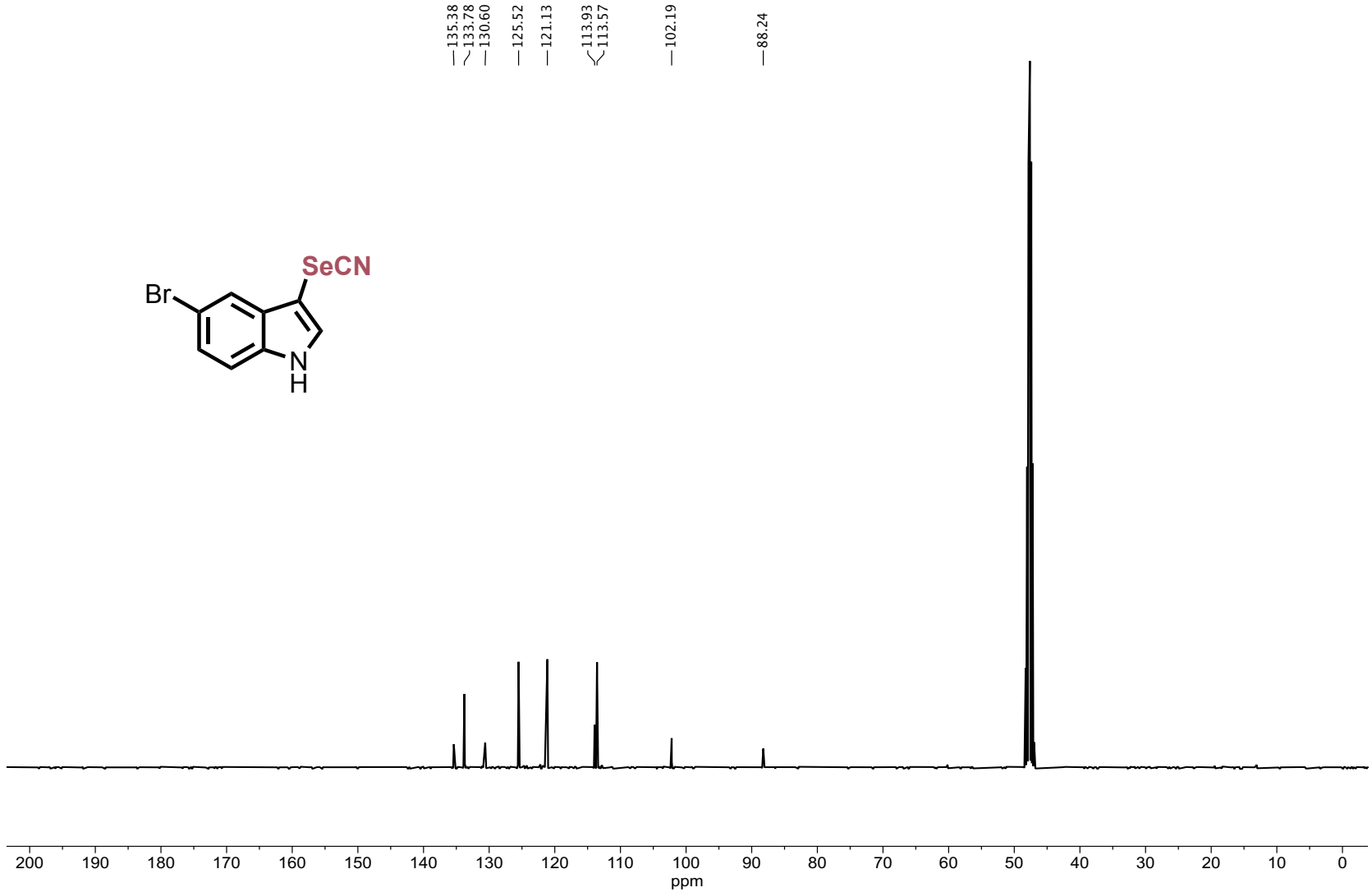


Figure S76. ^{13}C NMR (CD_3OD, 100.6 MHz) of **9b**

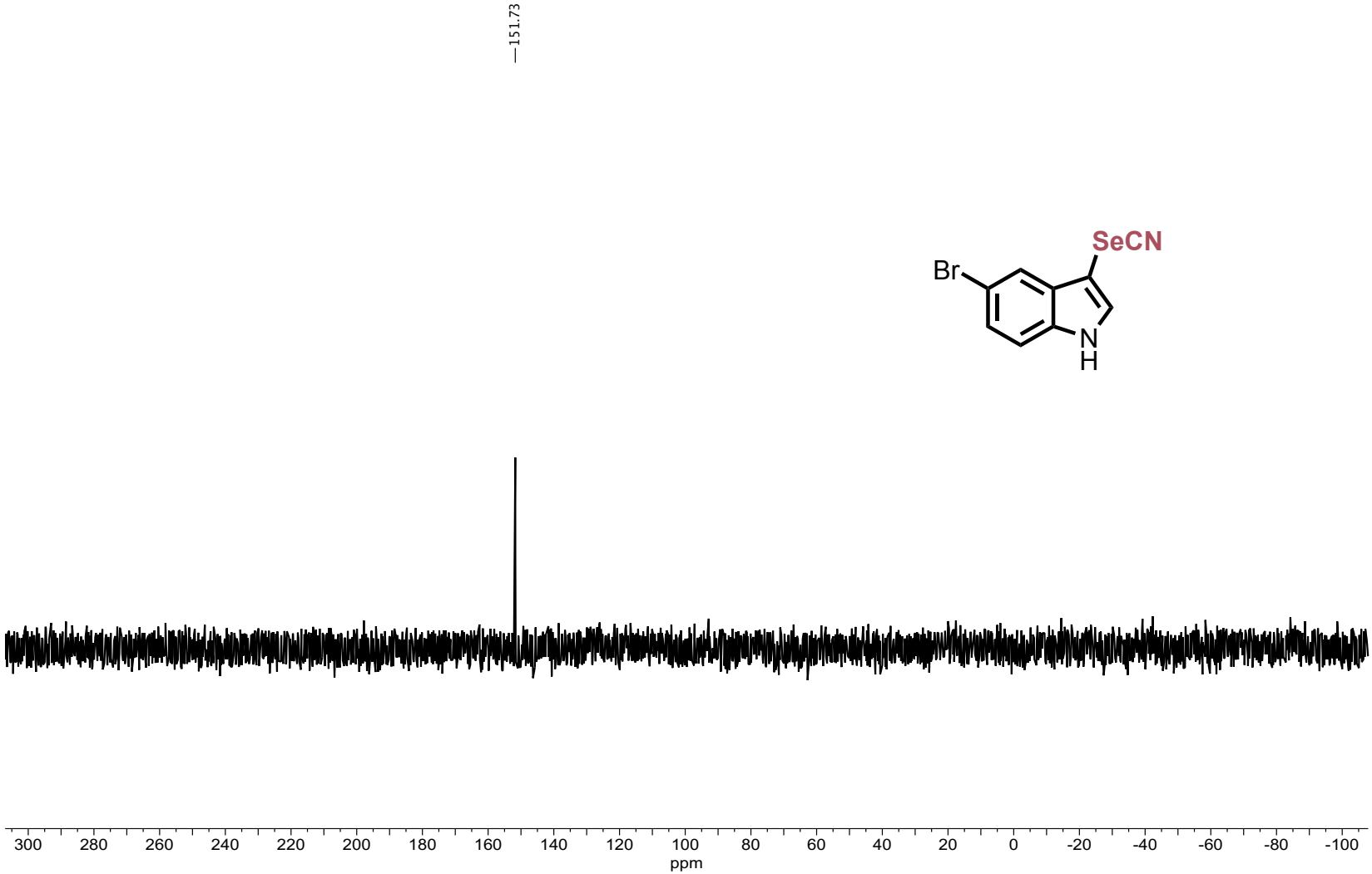


Figure S77. ^{77}Se NMR (CD_3OD, 76 MHz) of **9b**

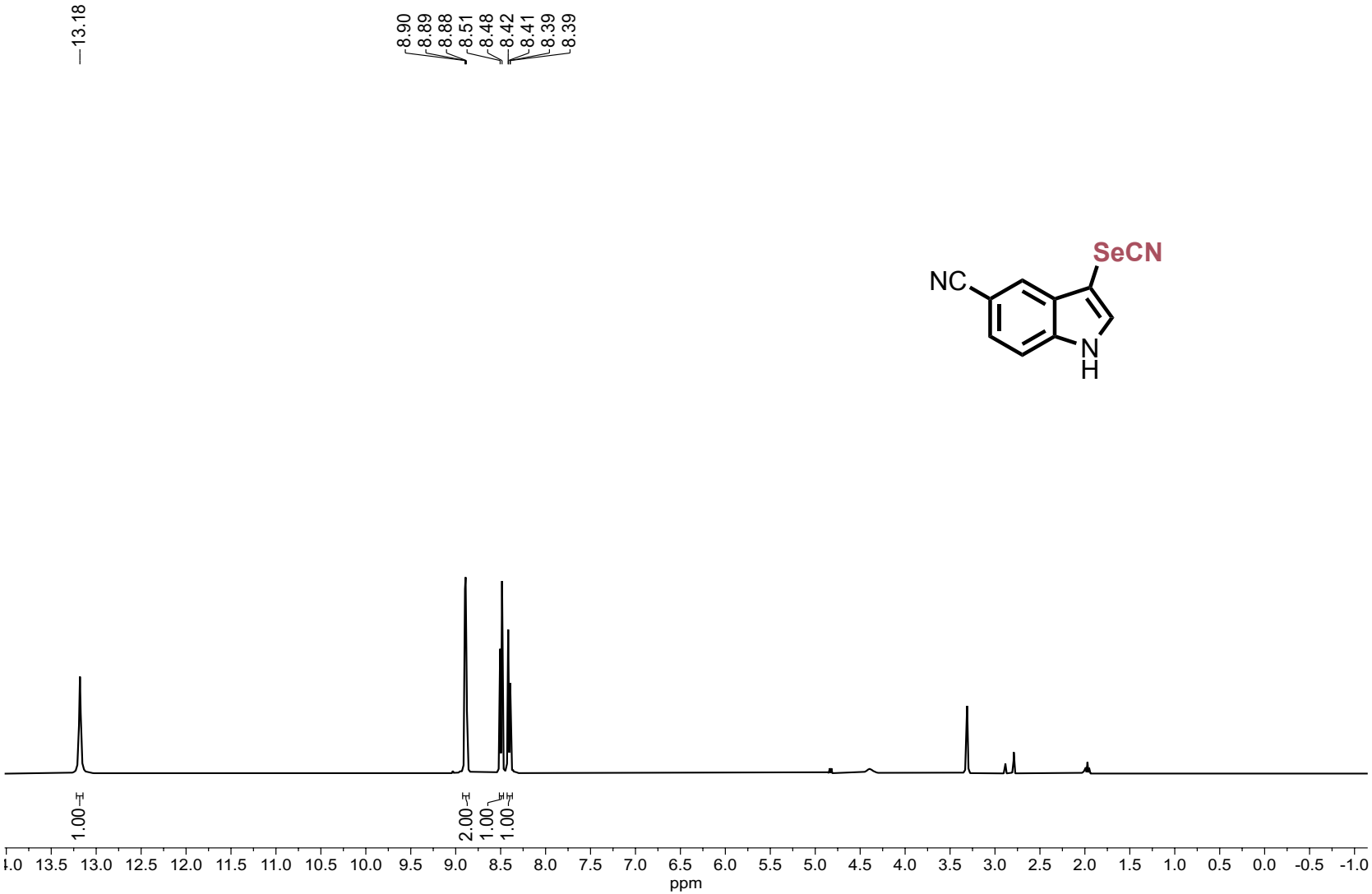


Figure S78. ^{1}H NMR (CD_3OD, 400 MHz) of **10b**

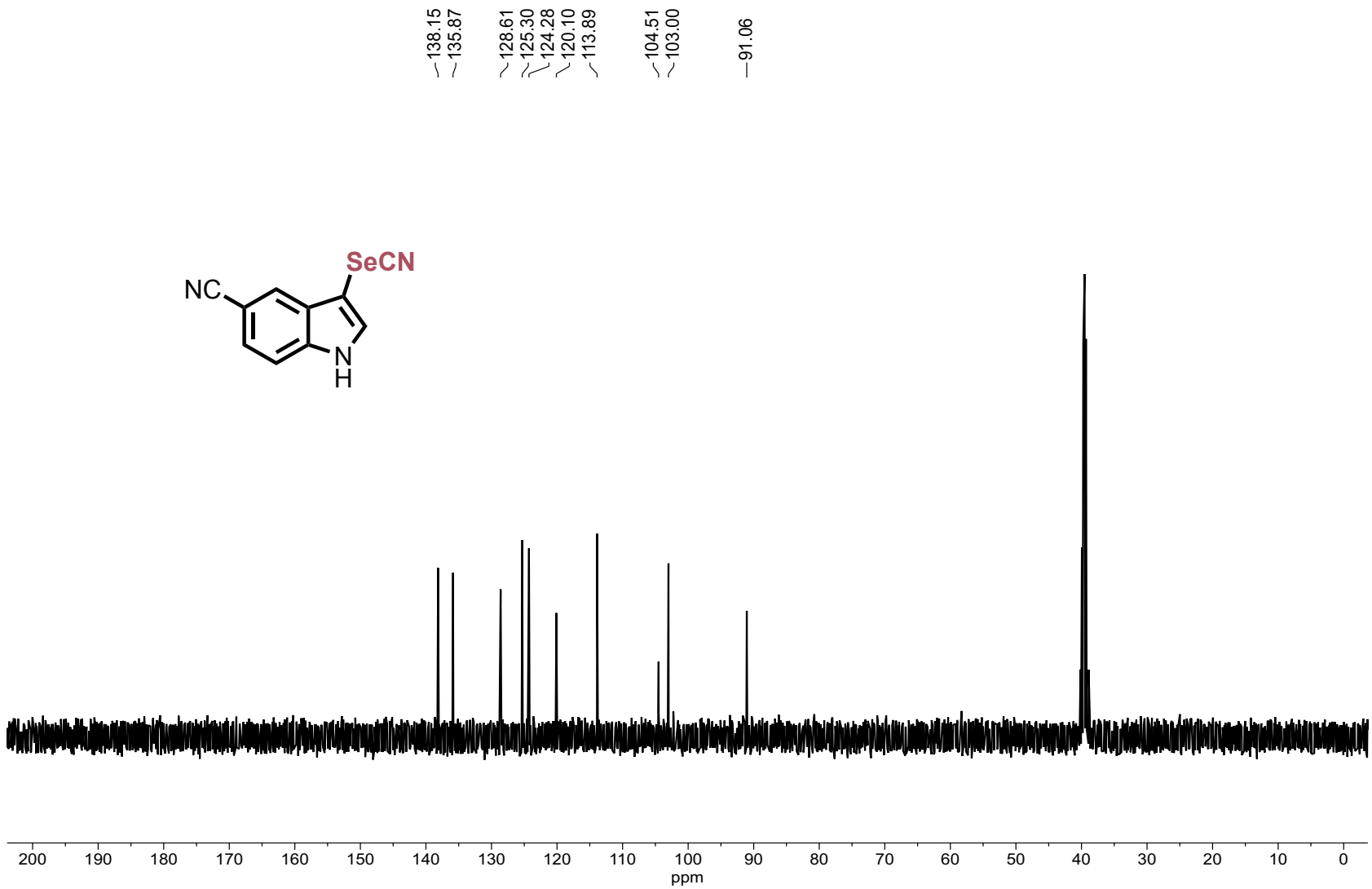


Figure S79. ^{13}C NMR (CD_3OD, 100.6 MHz) of **10b**

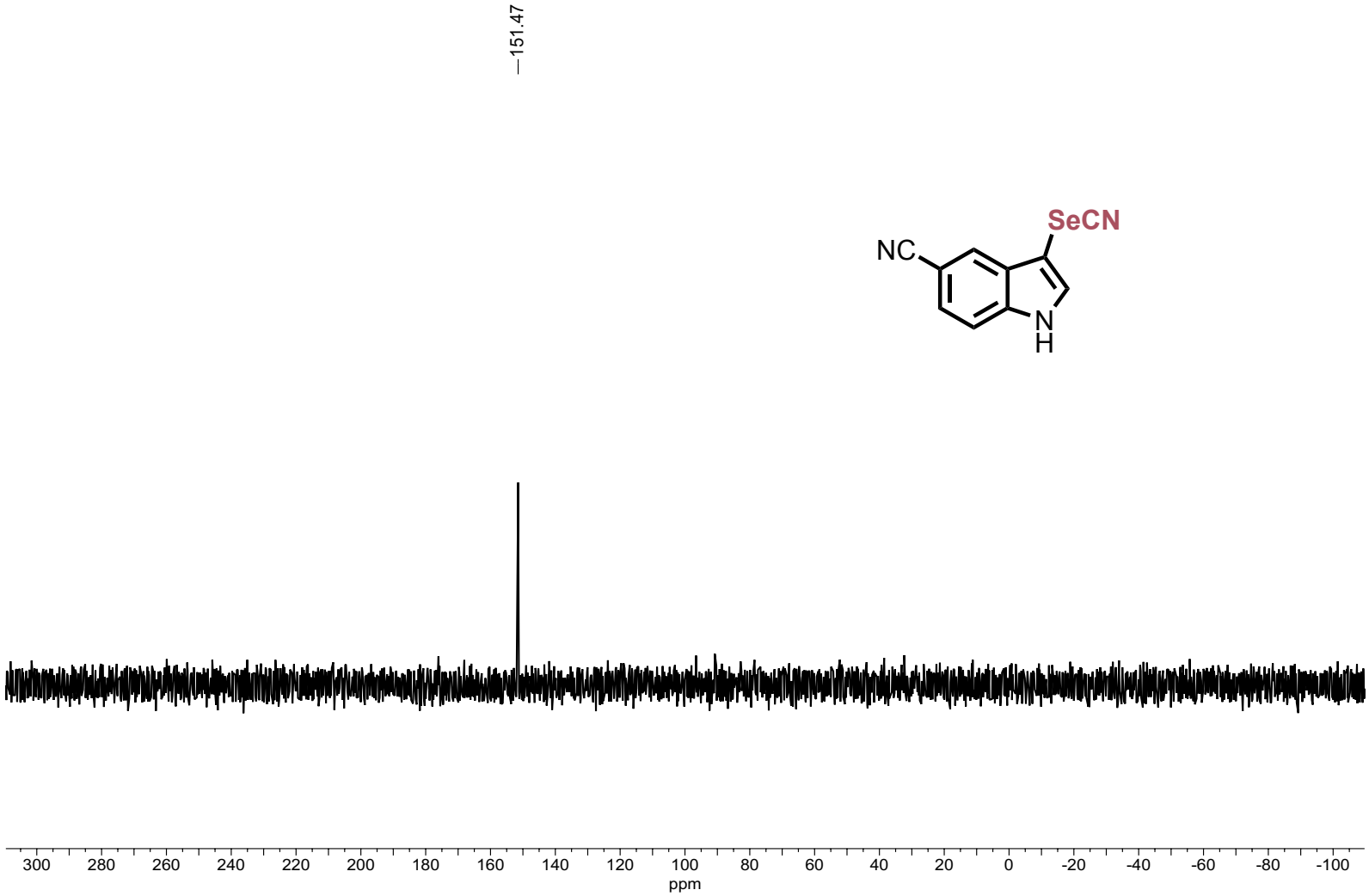


Figure S80. ^{77}Se NMR (CD_3OD, 76 MHz) of **10b**

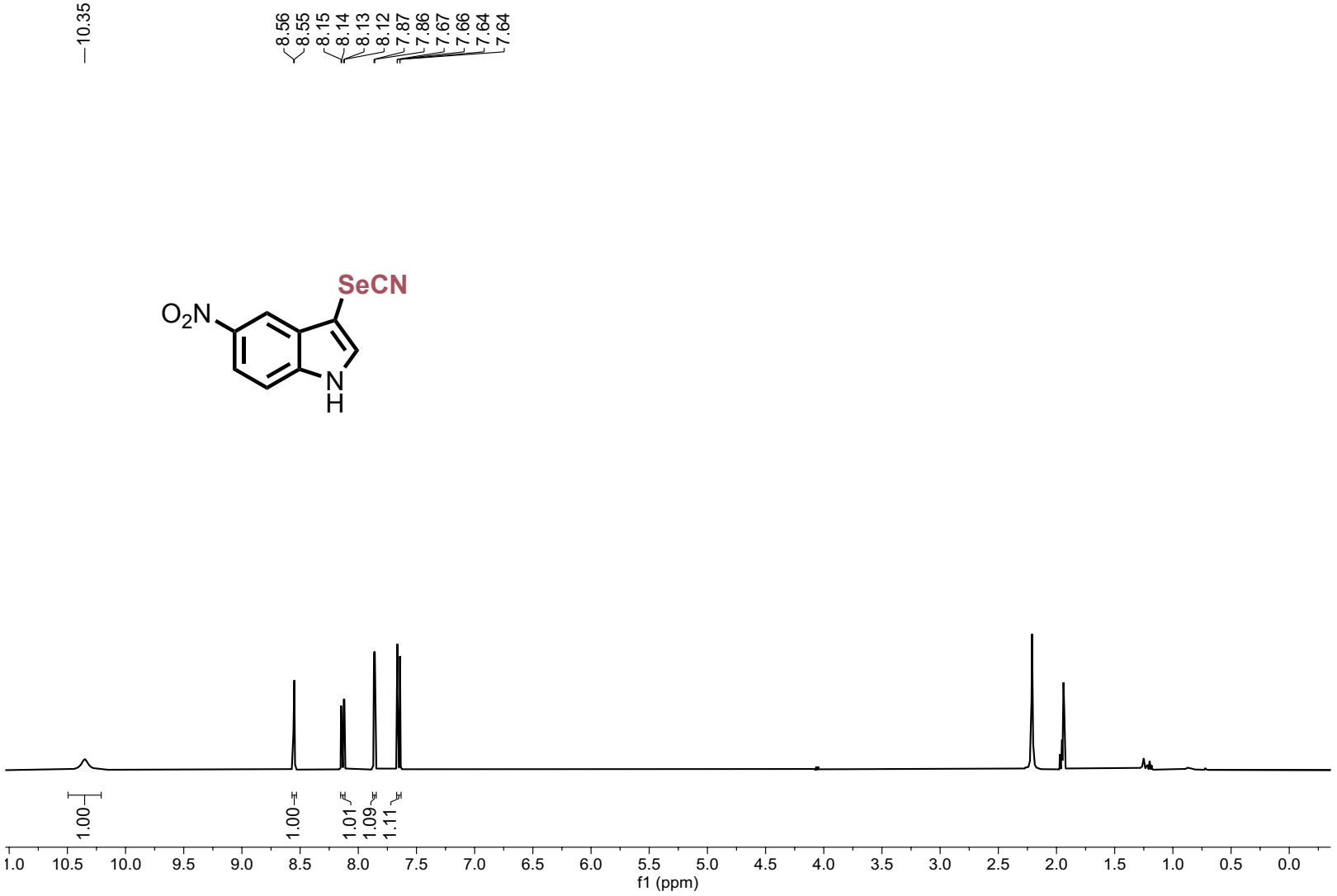


Figure S81. ^{1}H NMR (CD_3CN, 400 MHz) of **11b**

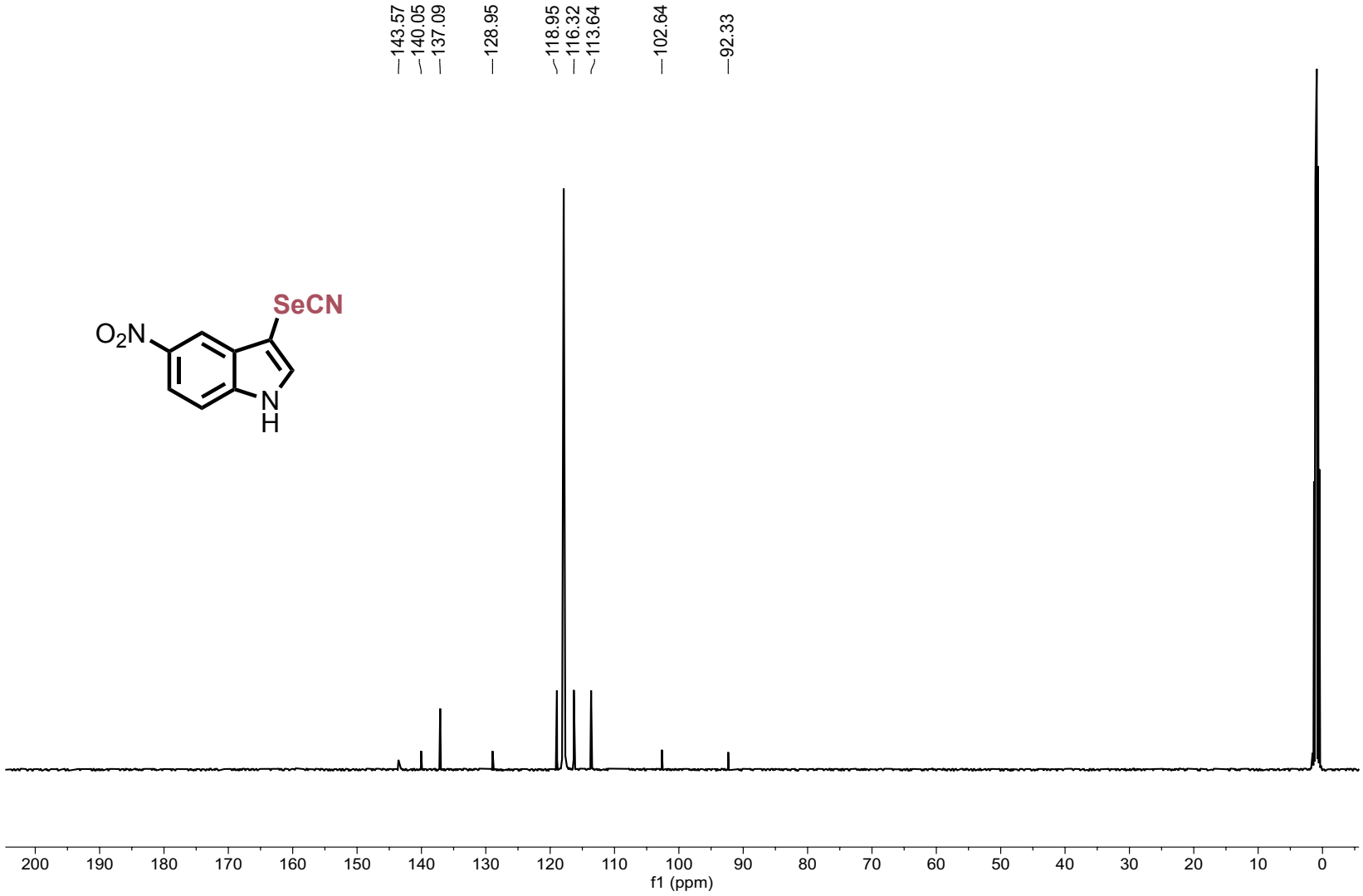


Figure S82. ^{13}C NMR (CD_3CN, 100.6 MHz) of **11b**

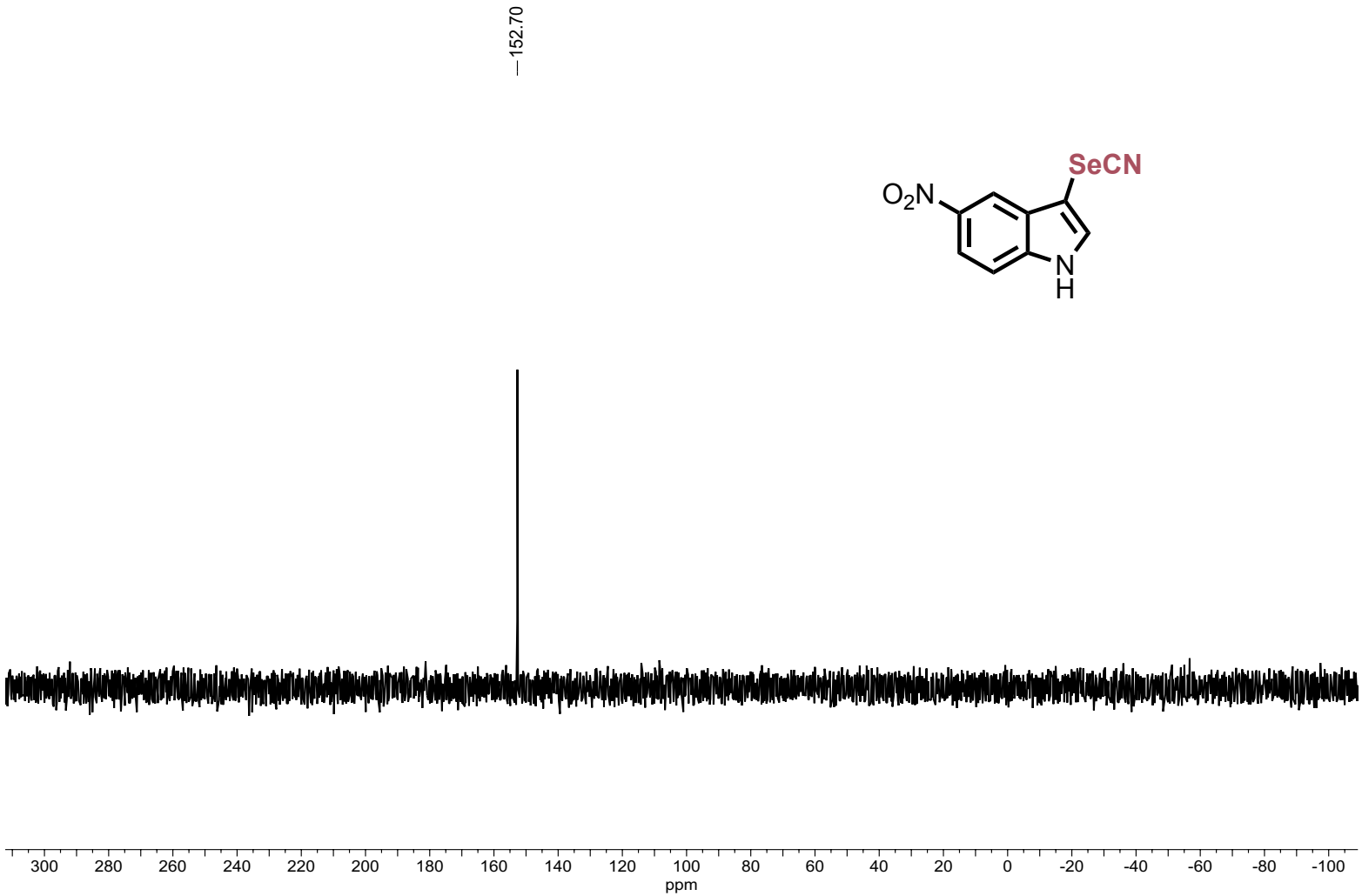


Figure S83. ^{77}Se NMR (CD_3CN, 76 MHz) of **11b**

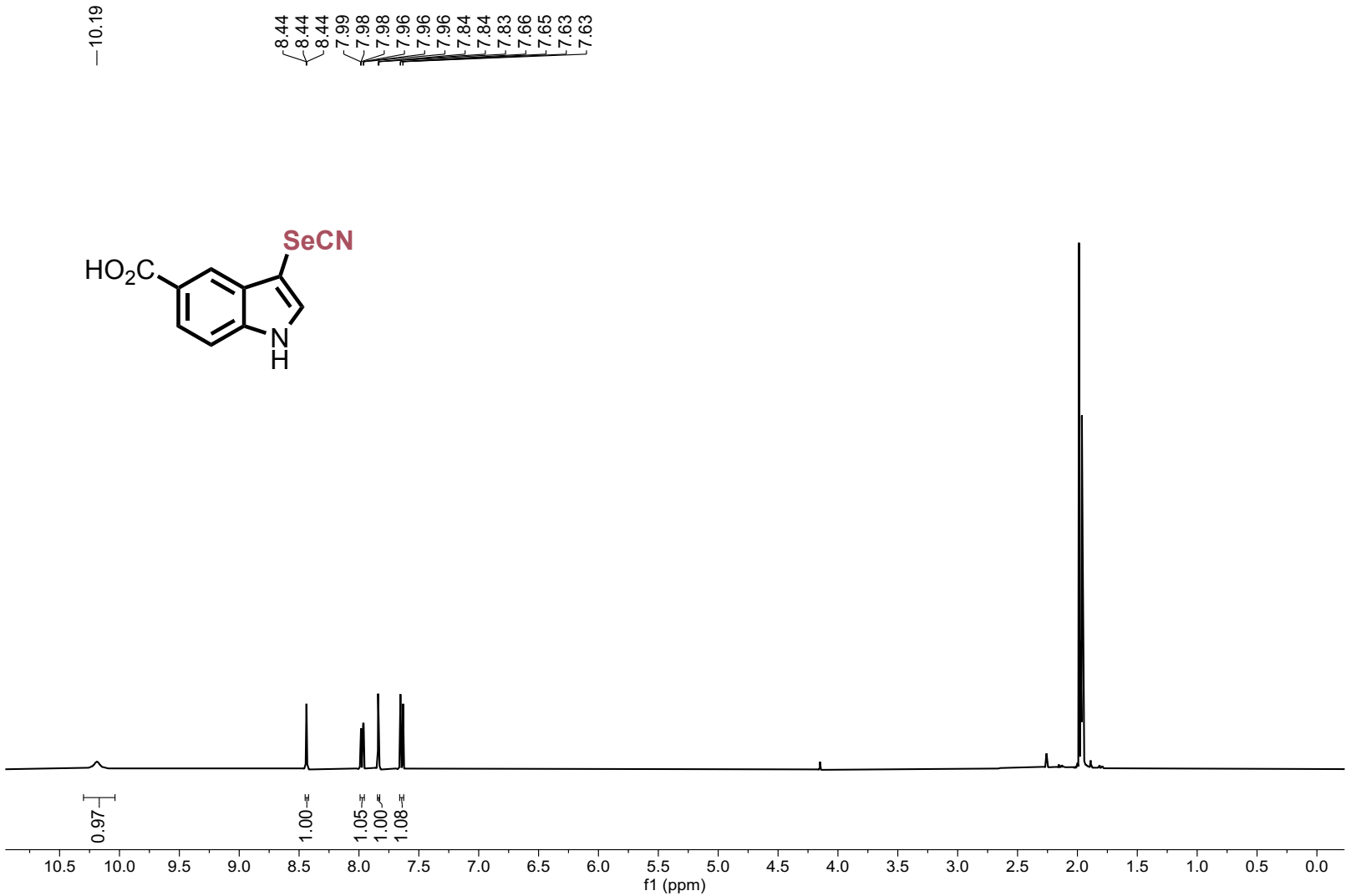


Figure S84. ^{1}H NMR (CD_3CN, 400 MHz) of **12b**

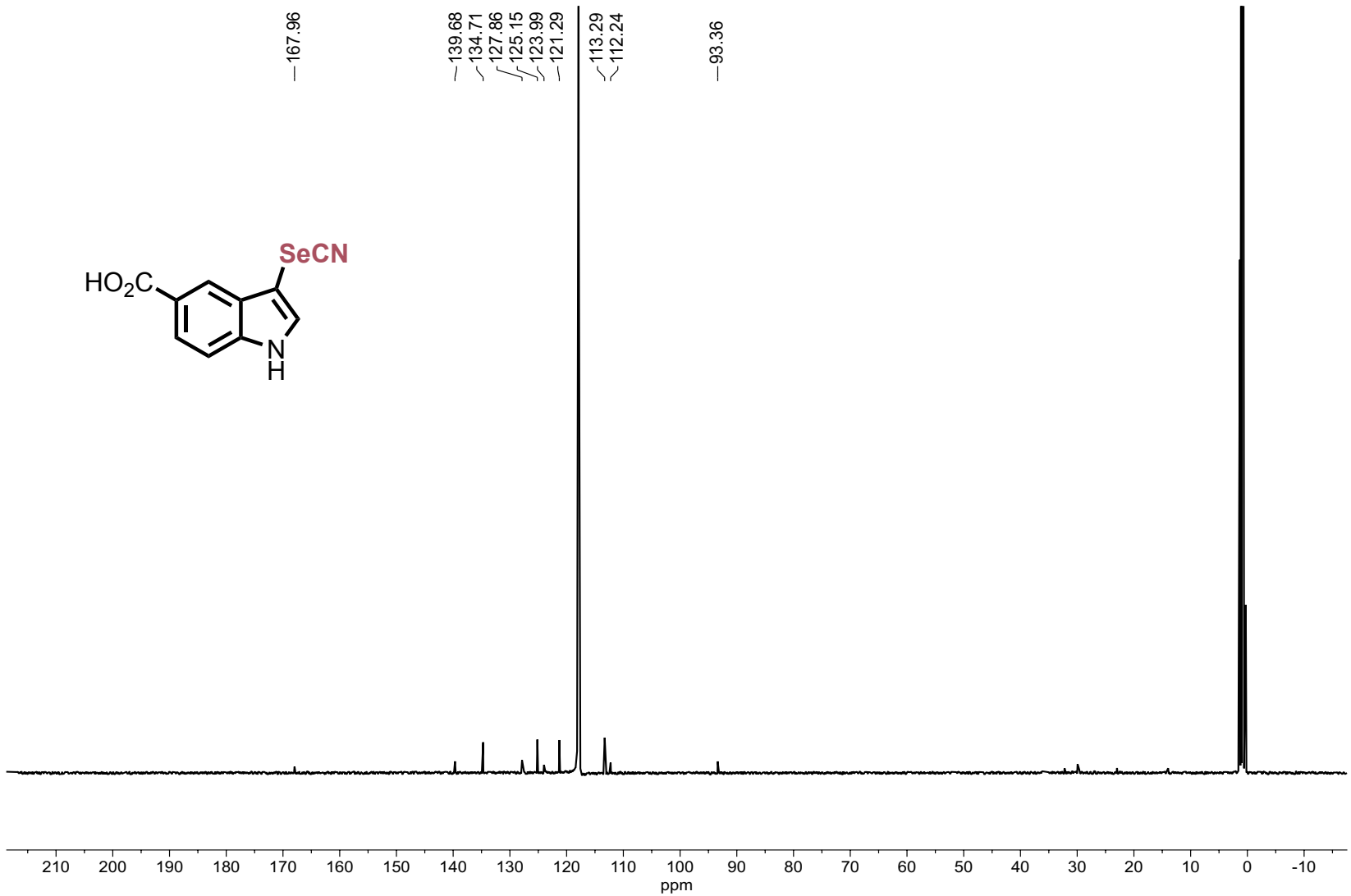


Figure S85. ^{13}C NMR (CD_3CN, 100.6 MHz) of **12b**

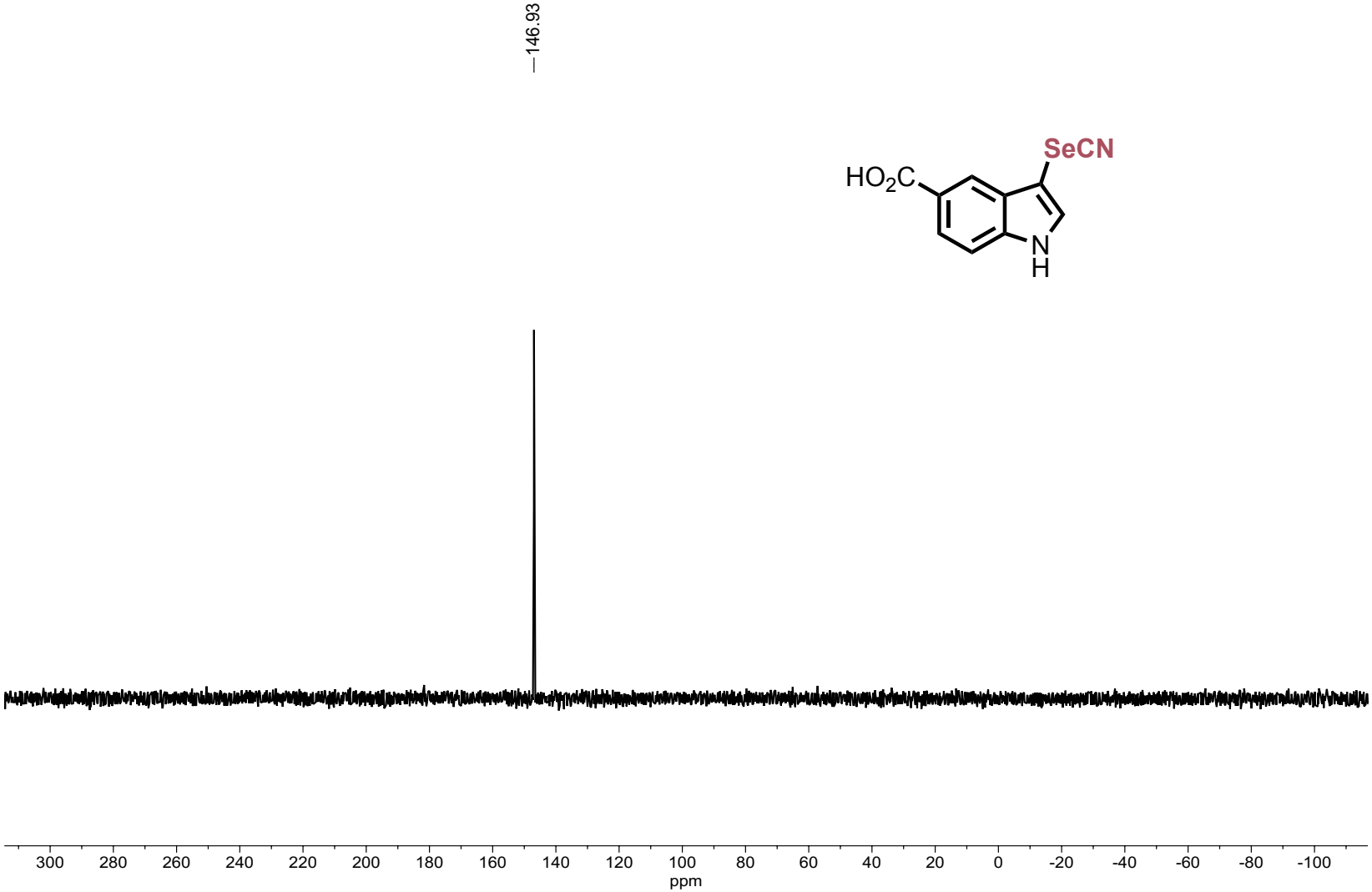


Figure S86. ^{77}Se NMR (CD_3CN, 76 MHz) of **12b**

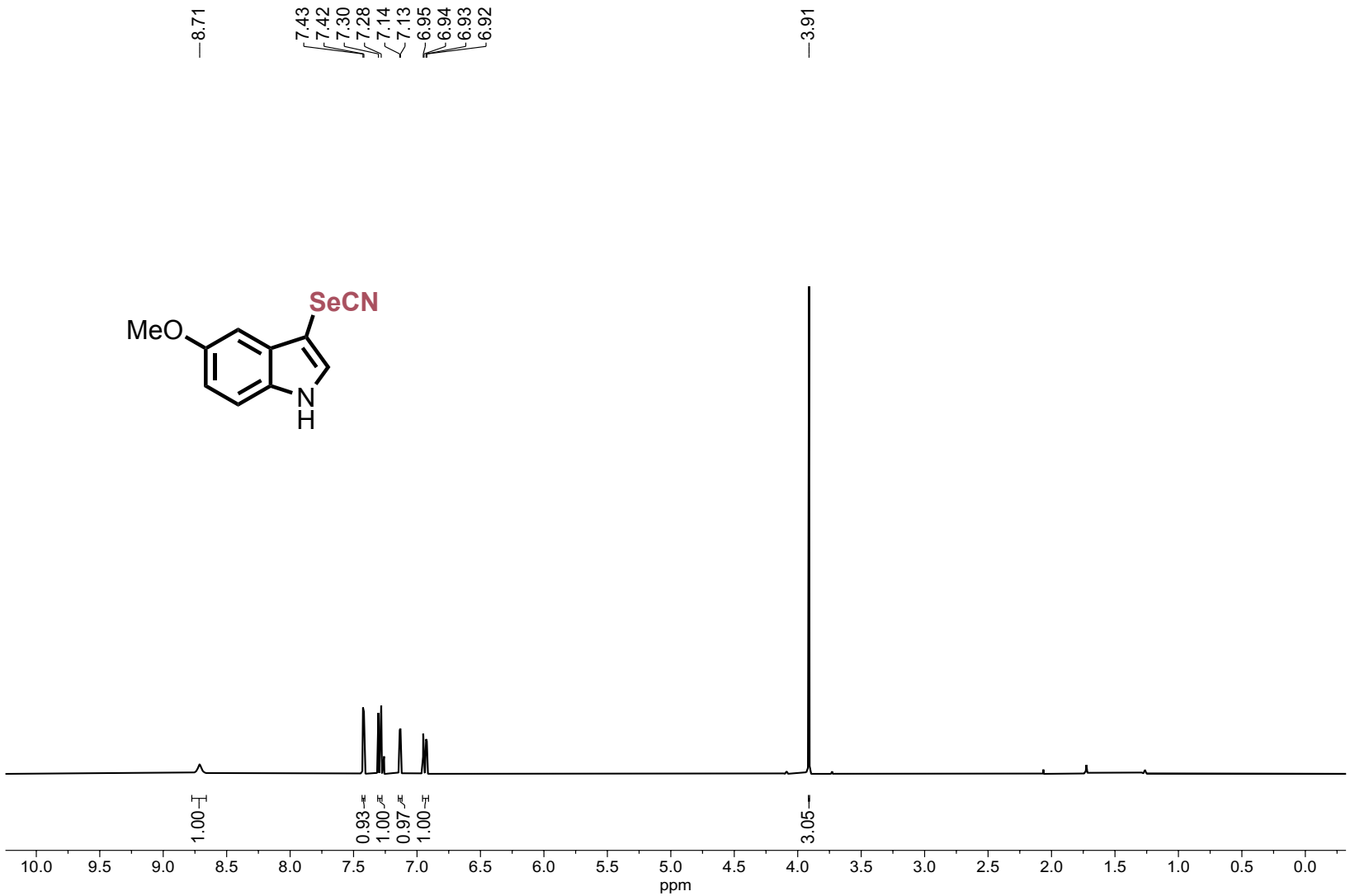


Figure S87. ^{1}H NMR ($CDCl_3$, 400 MHz) of **13b**

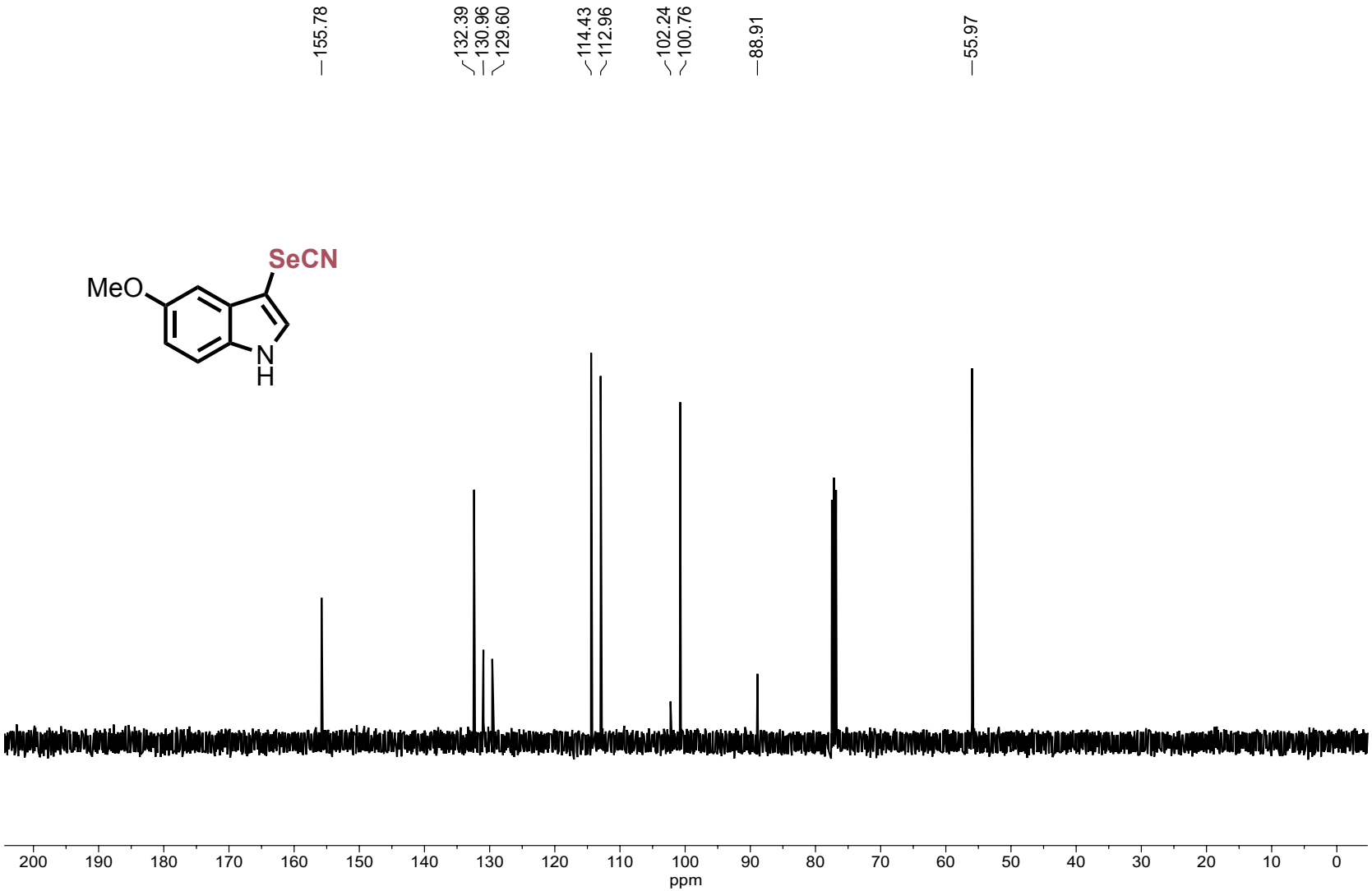


Figure S88. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **13b**

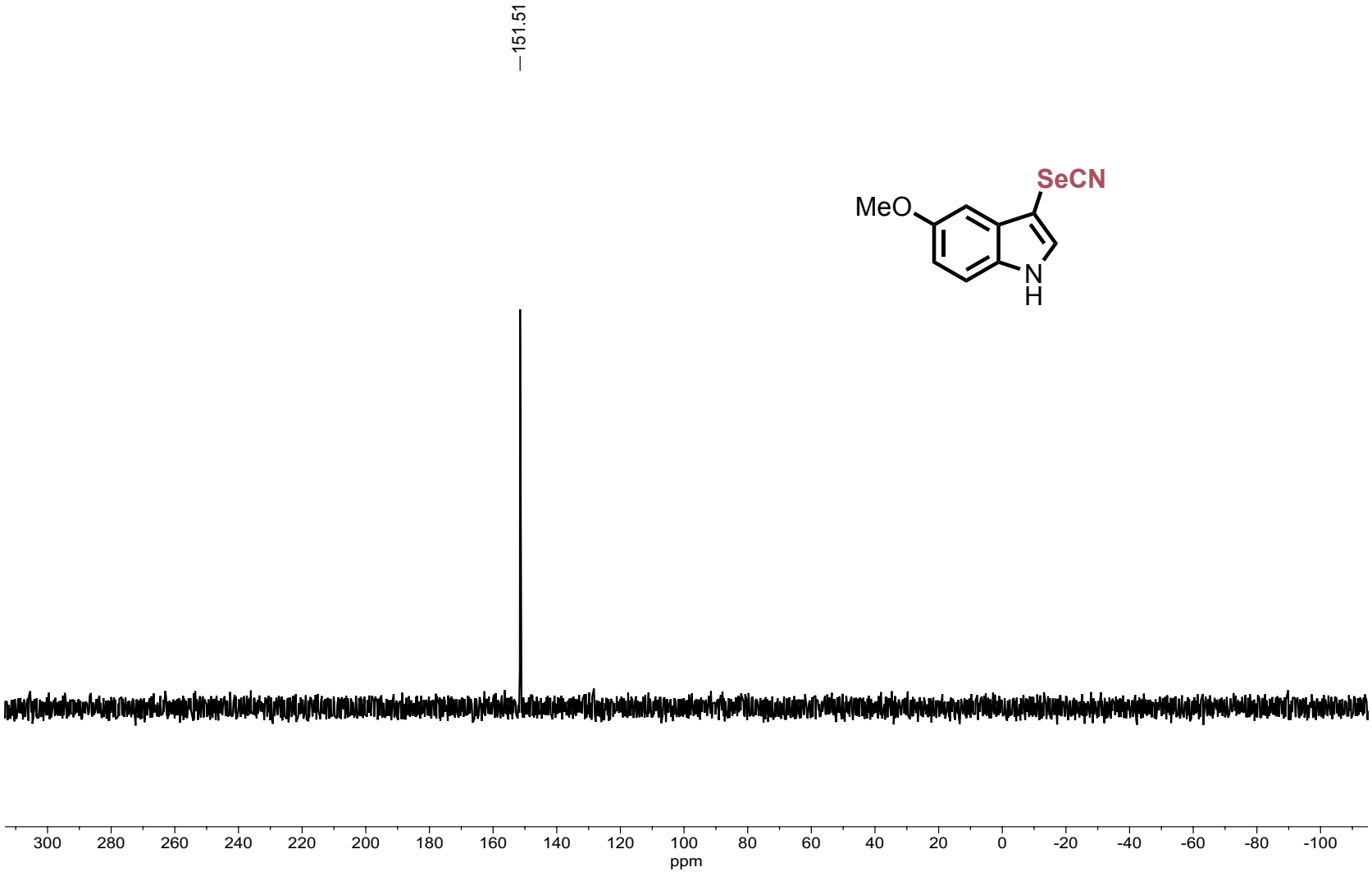


Figure S89. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **13b**

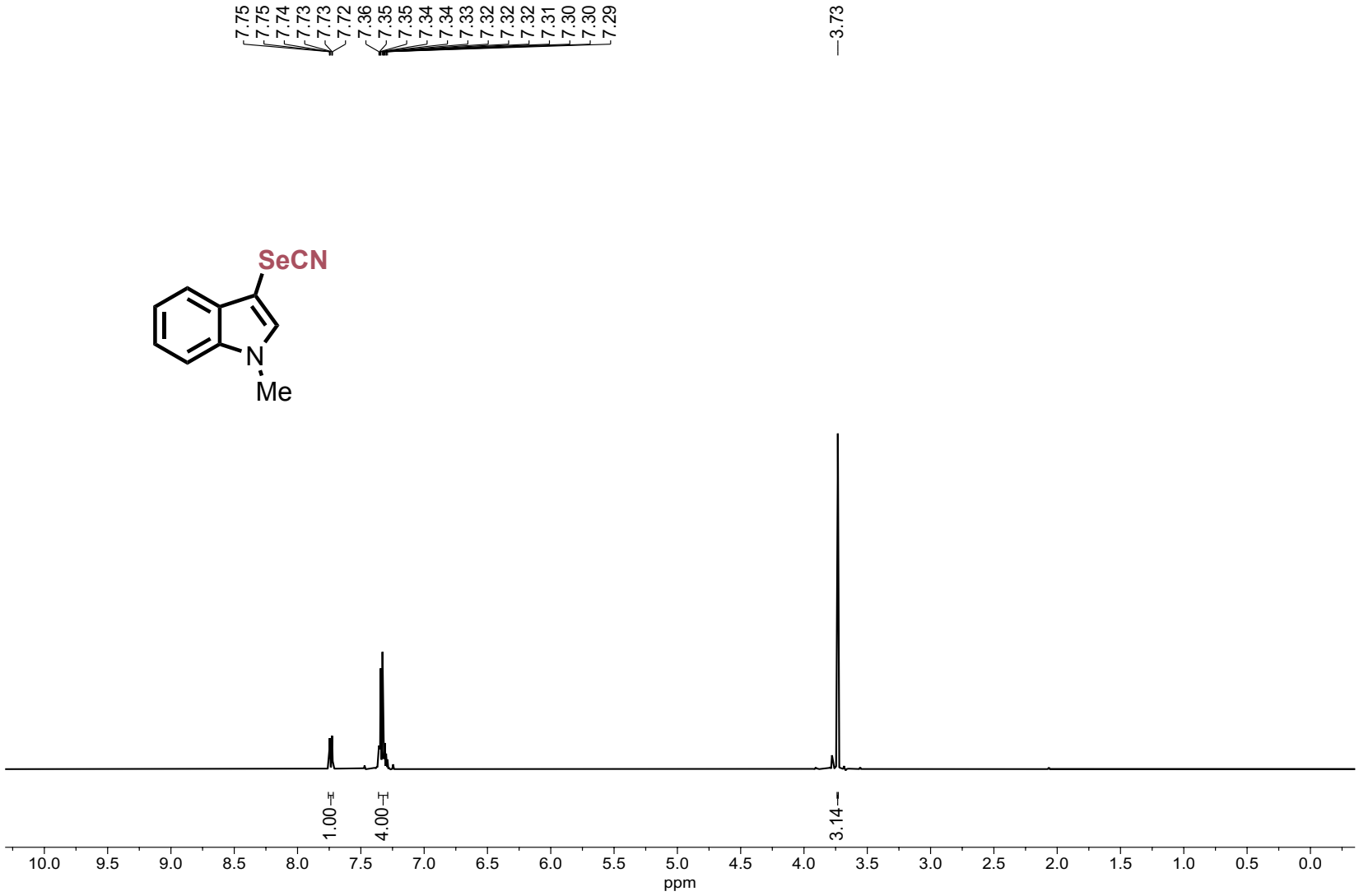


Figure S90. ^{1}H NMR ($CDCl_3$, 400 MHz) of **14b**

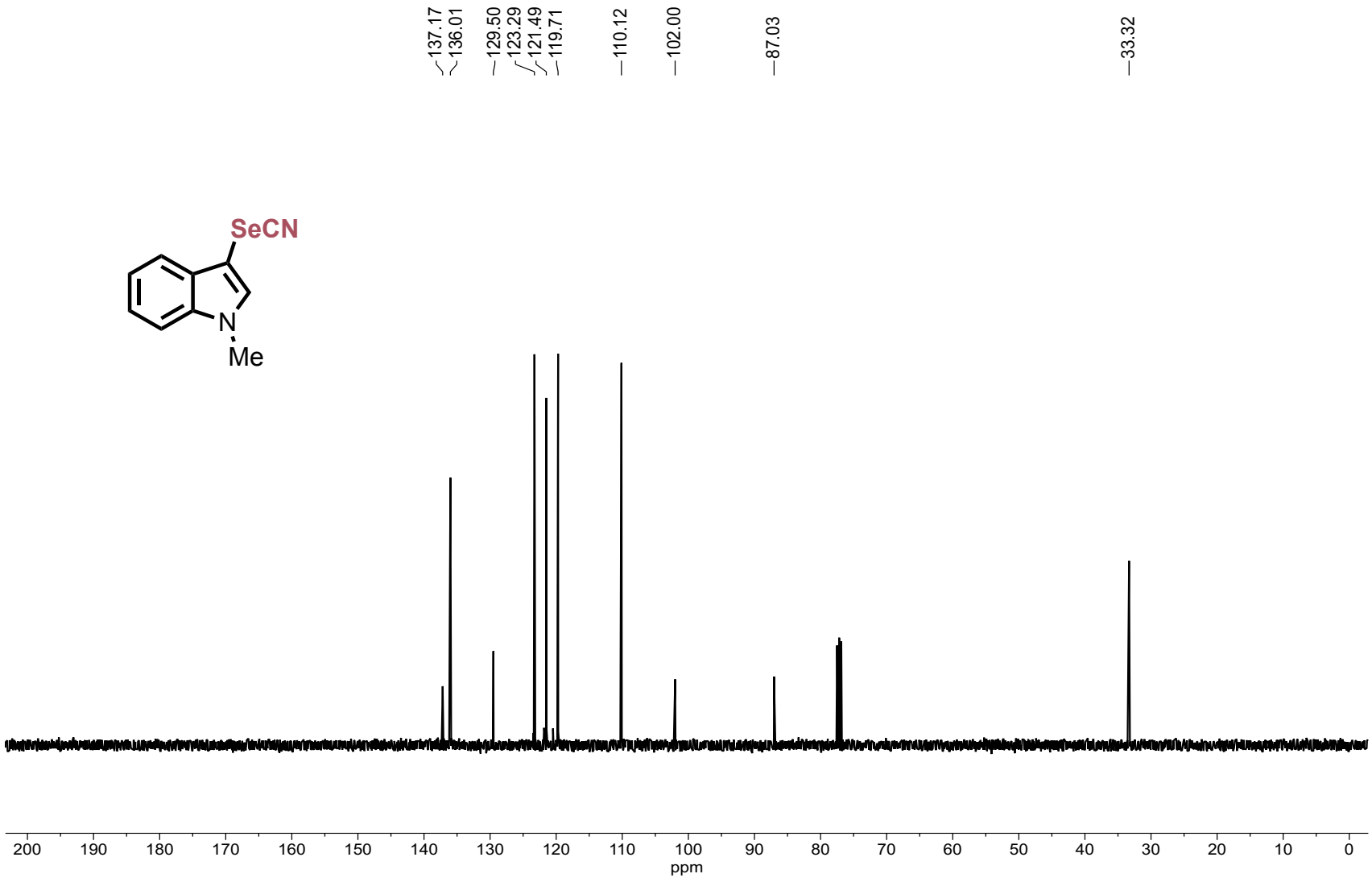


Figure S91. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **14b**

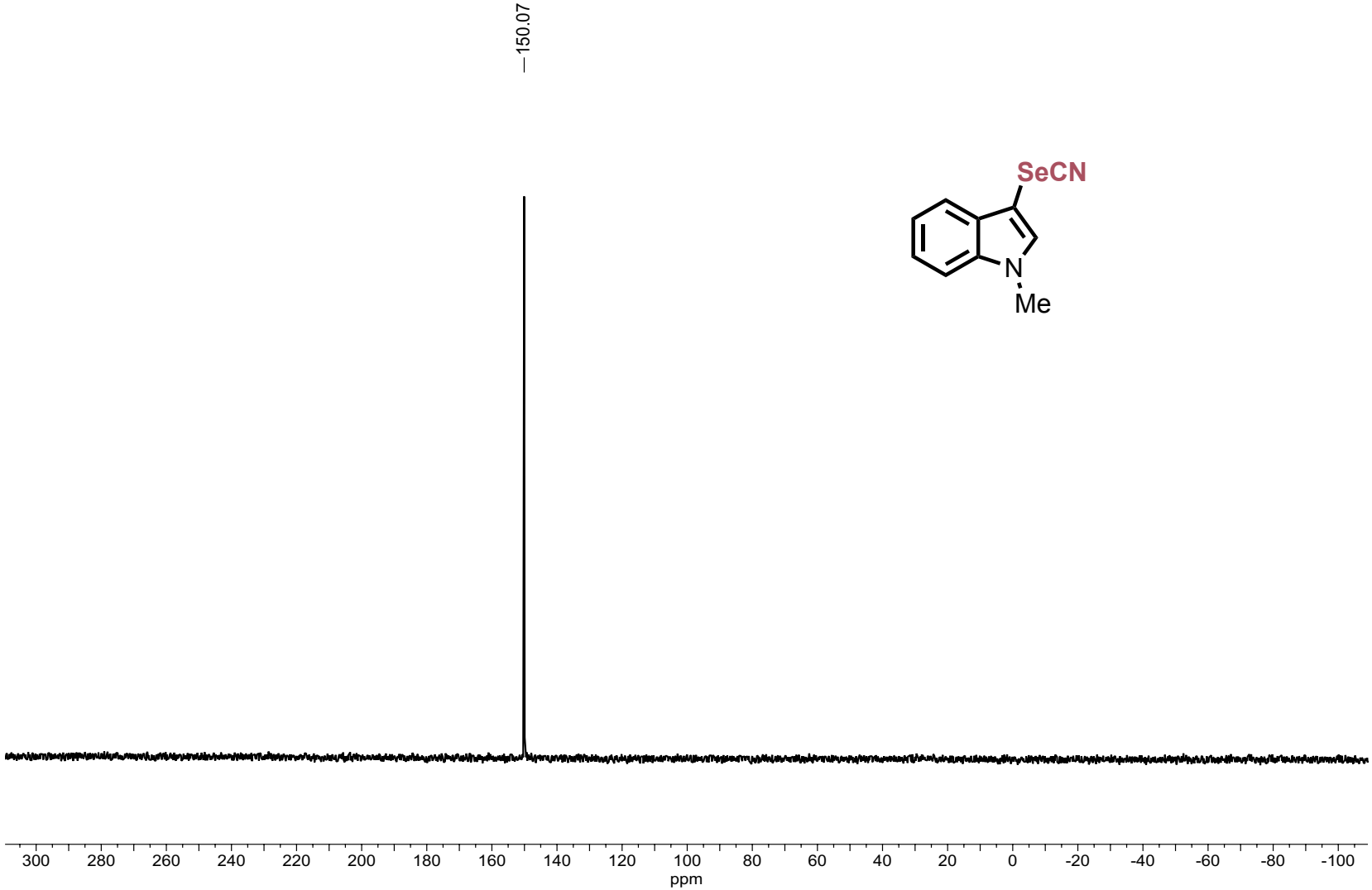


Figure S92. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **14b**

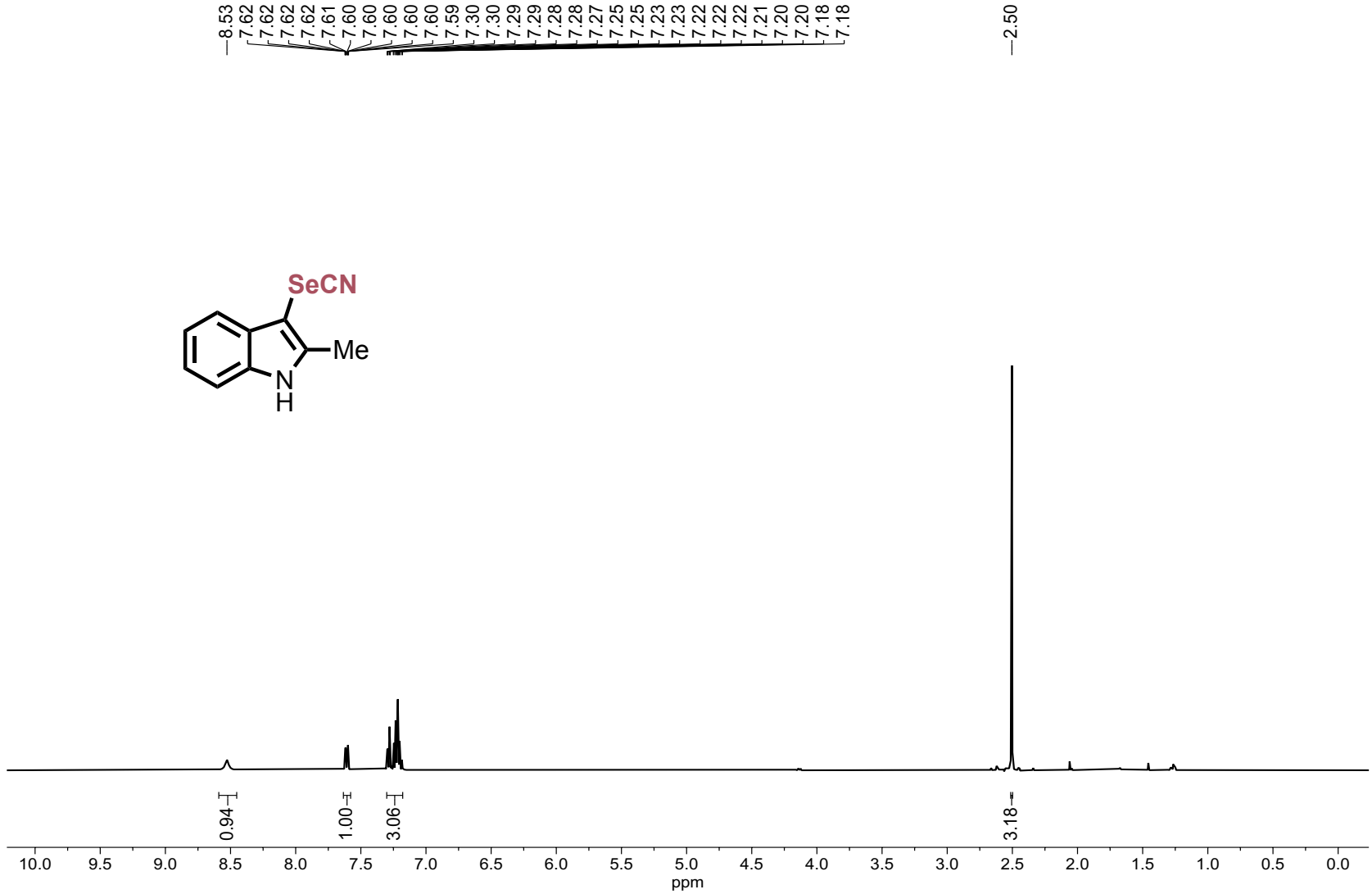


Figure S93. ^{1}H NMR ($CDCl_3$, 400 MHz) of **15b**

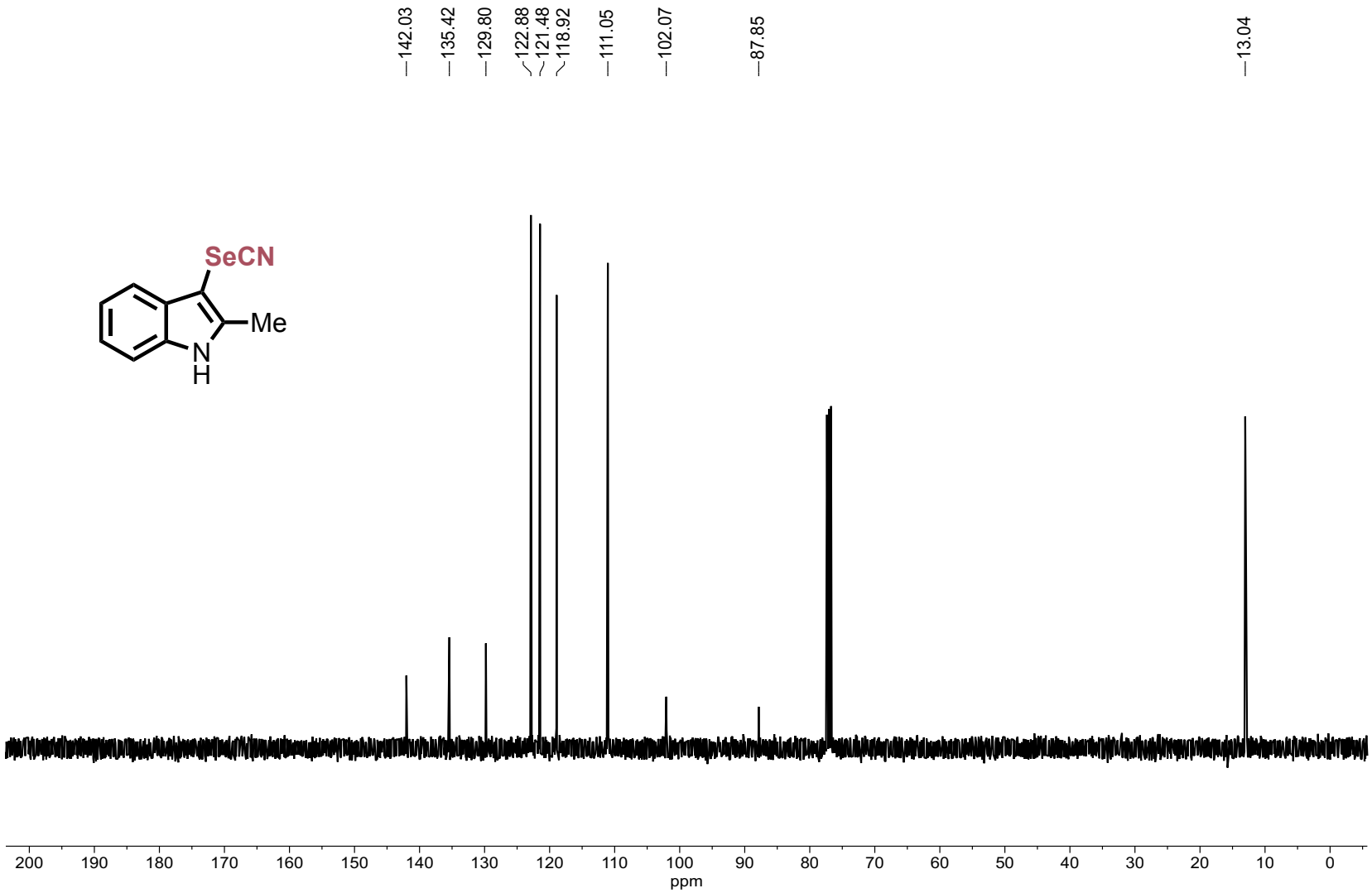


Figure S94. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **15b**

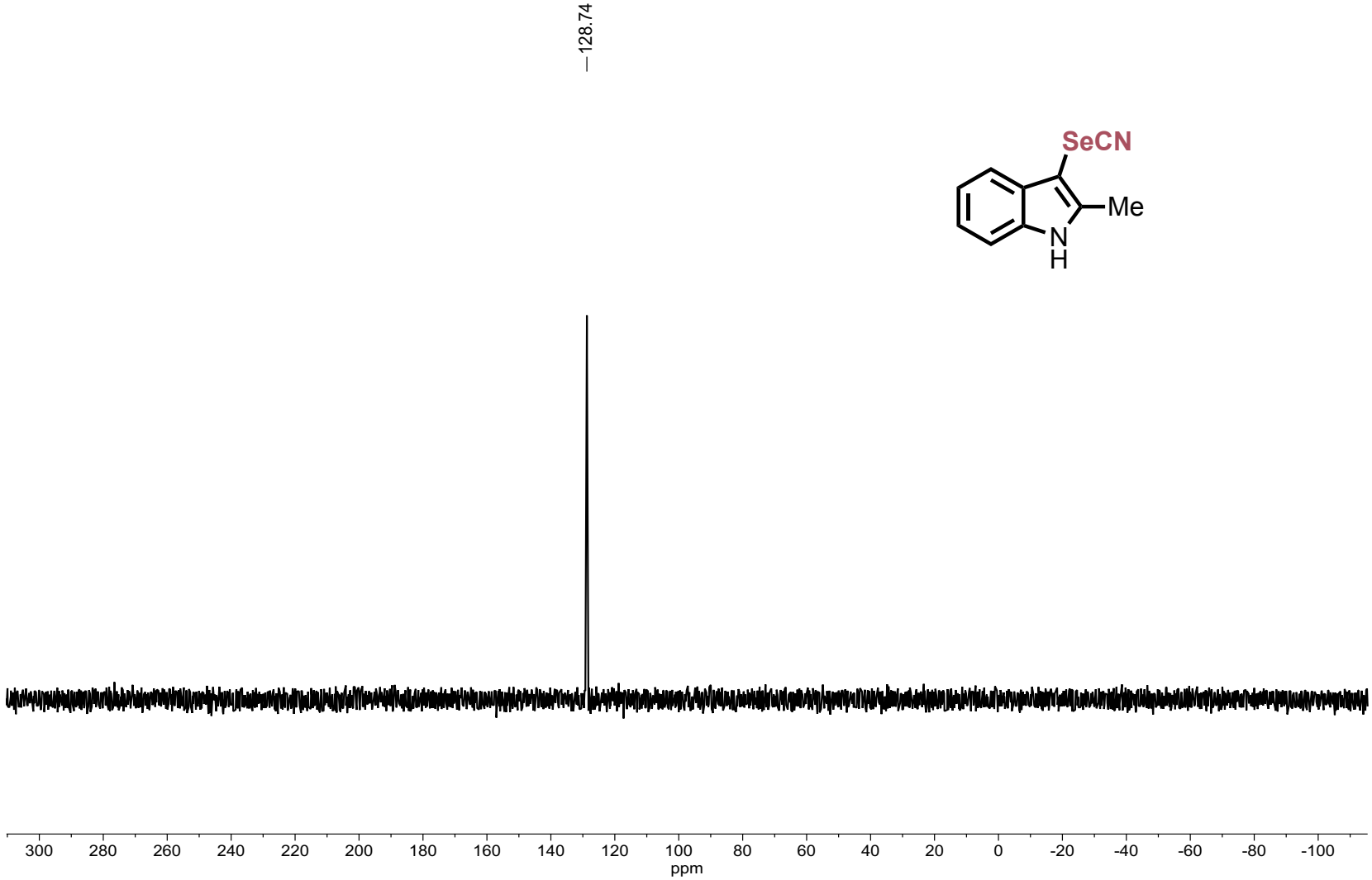


Figure S95. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **15b**

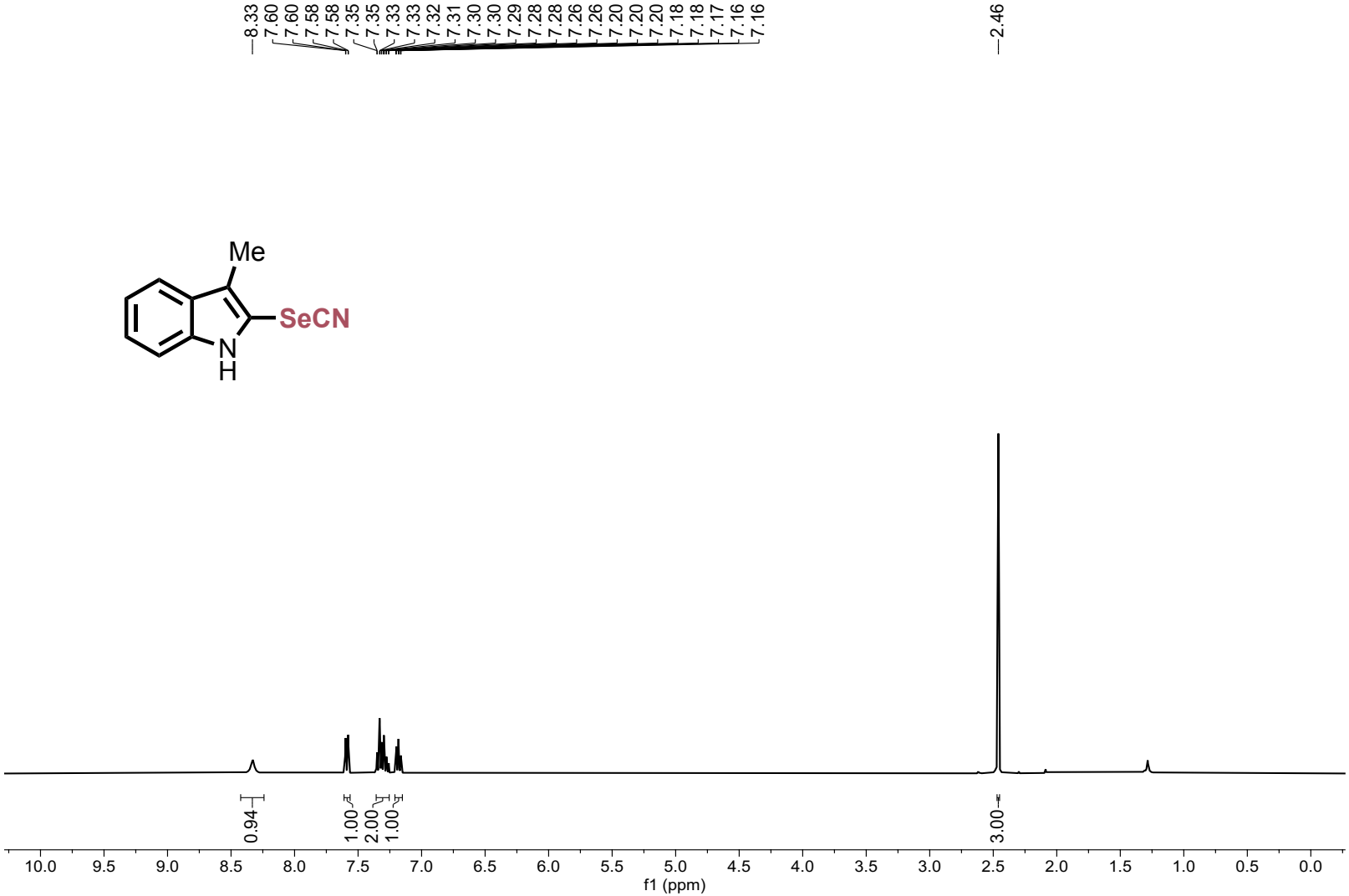


Figure S96. ^{1}H NMR ($CDCl_3$, 400 MHz) of **16b**

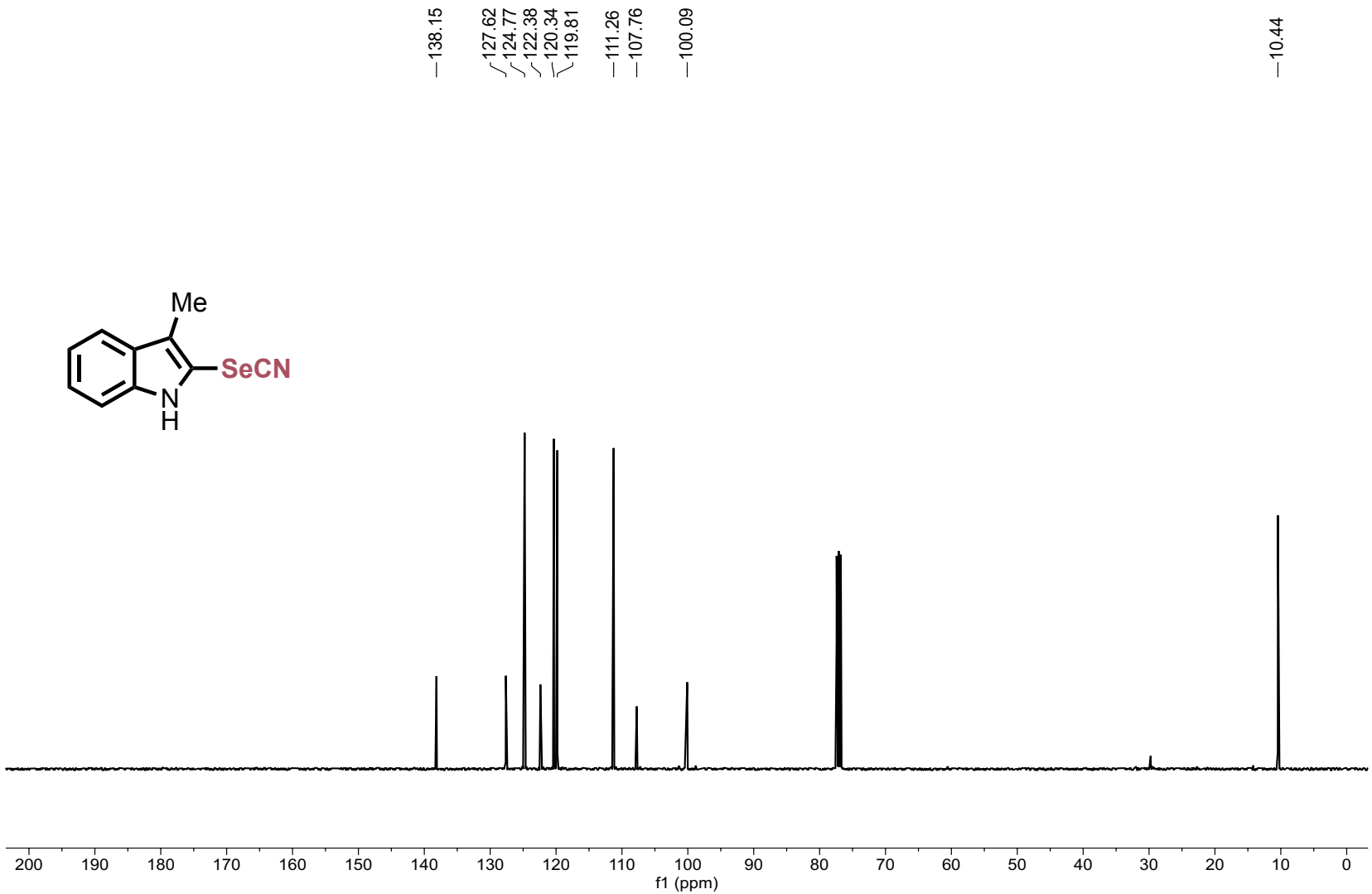


Figure S97. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **16b**

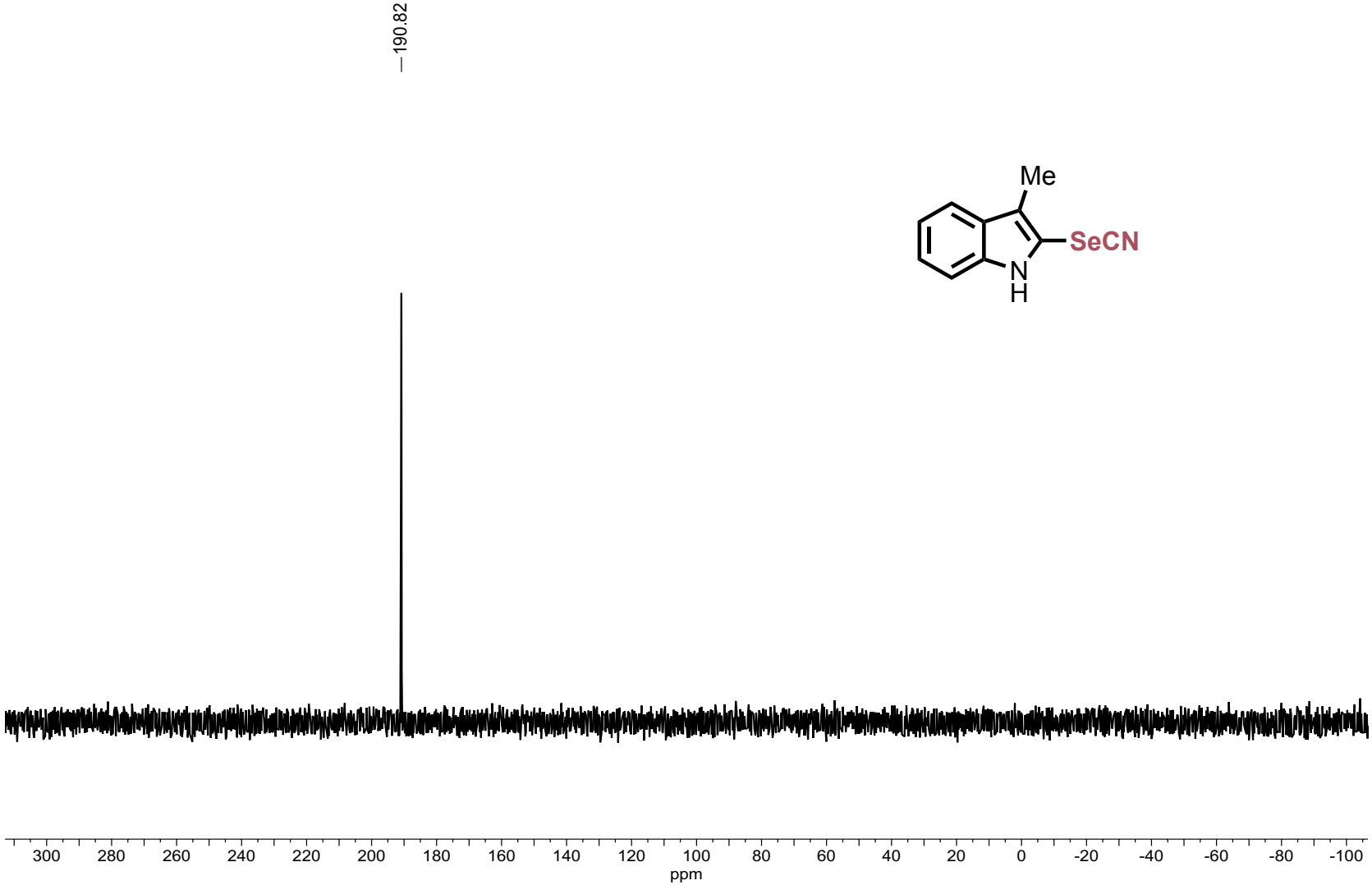


Figure S98. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **16b**

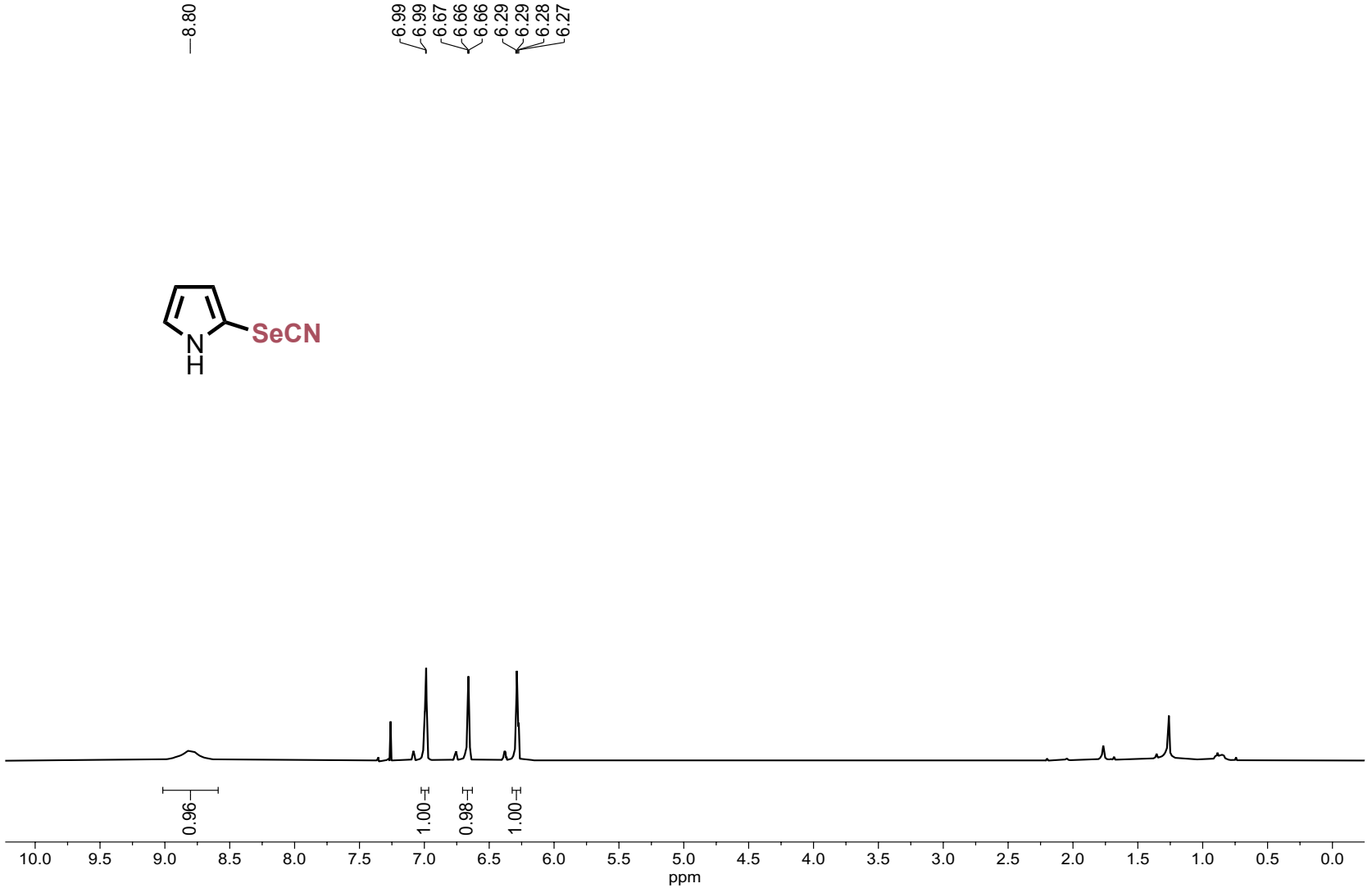


Figure S99. ^{1}H NMR ($CDCl_3$, 400 MHz) of **17b**

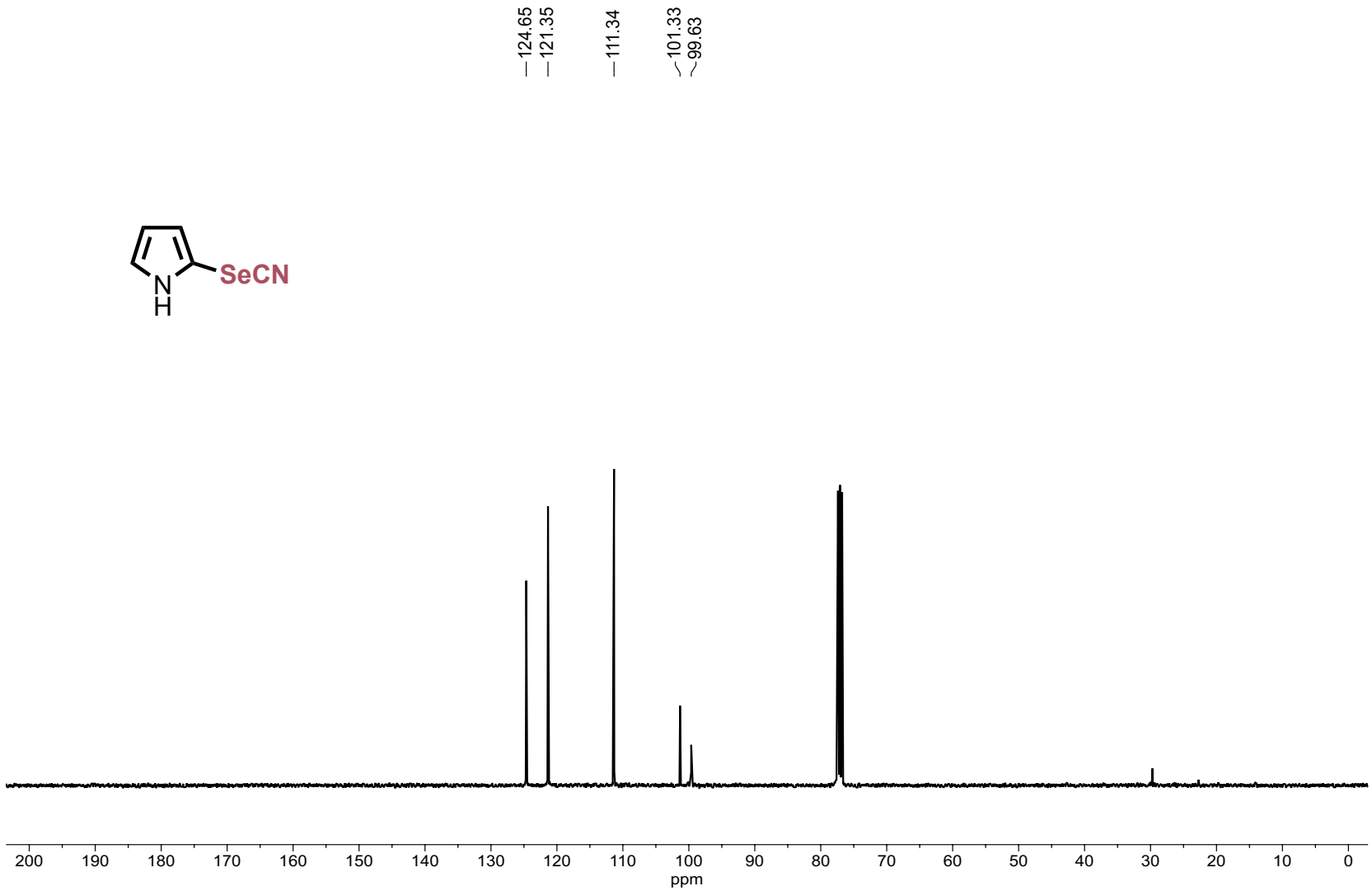


Figure S100. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **17b**

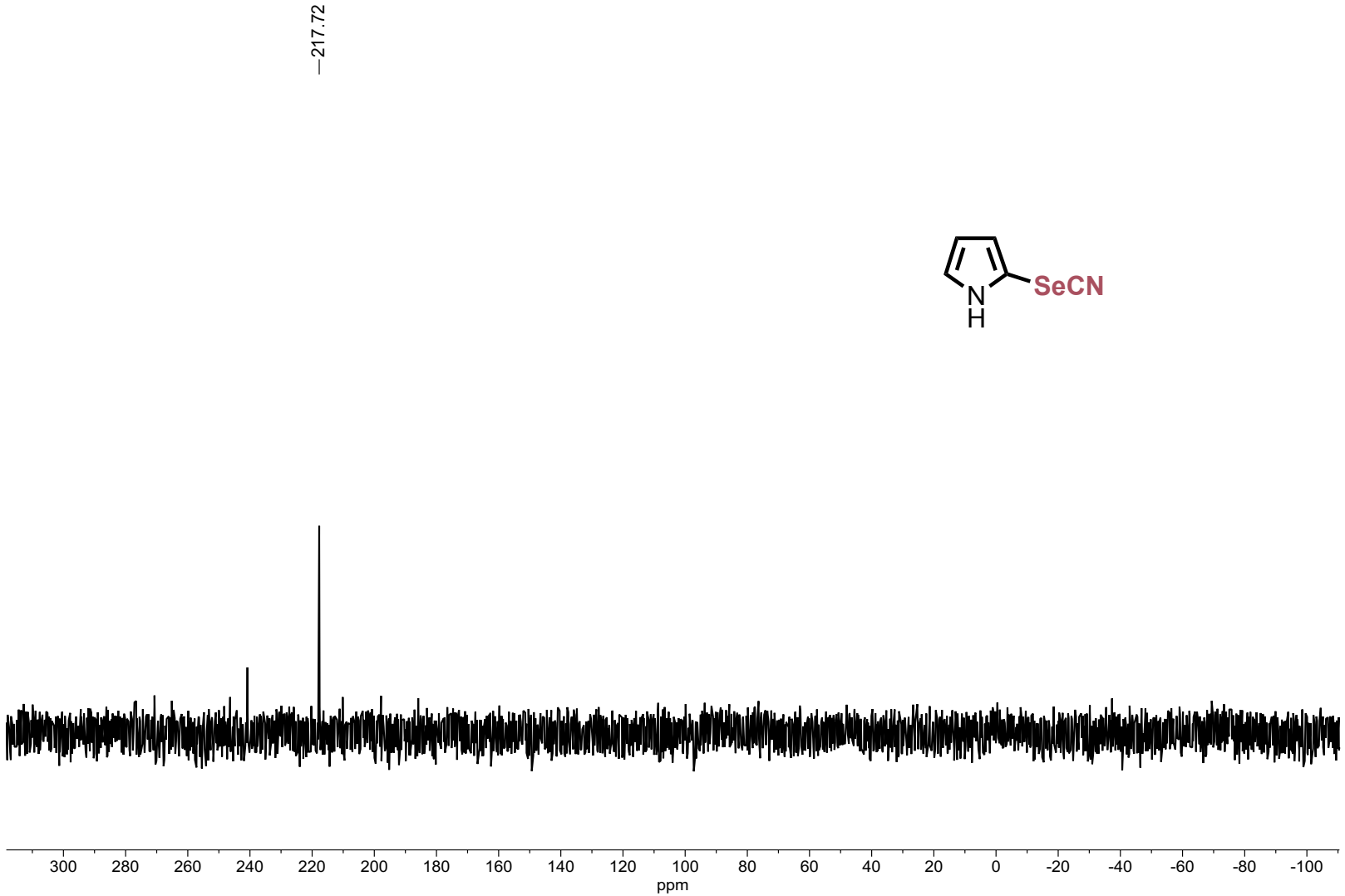


Figure S101. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **17b**

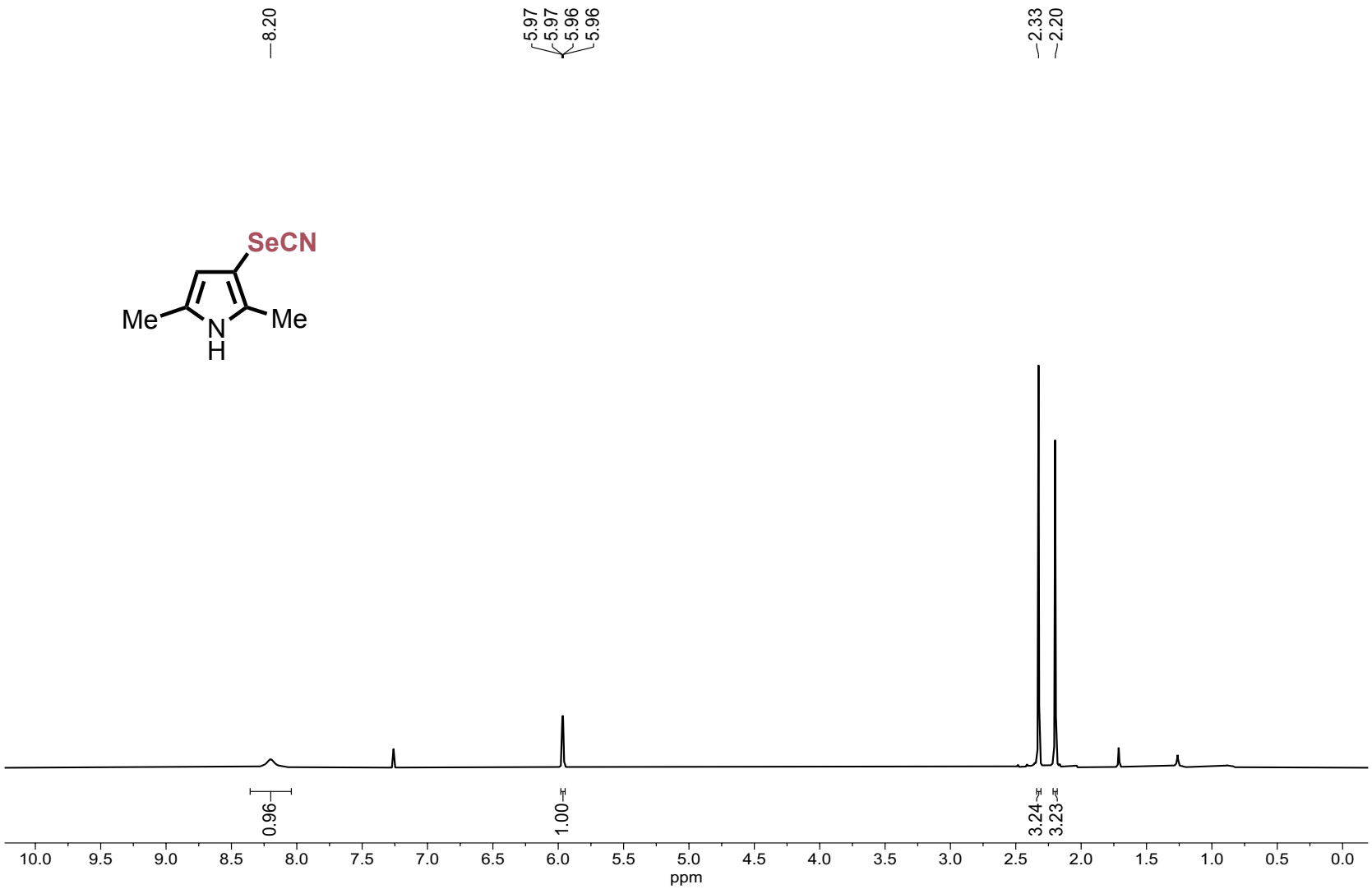


Figure S102. ^{1}H NMR ($CDCl_3$, 400 MHz) of **18b**

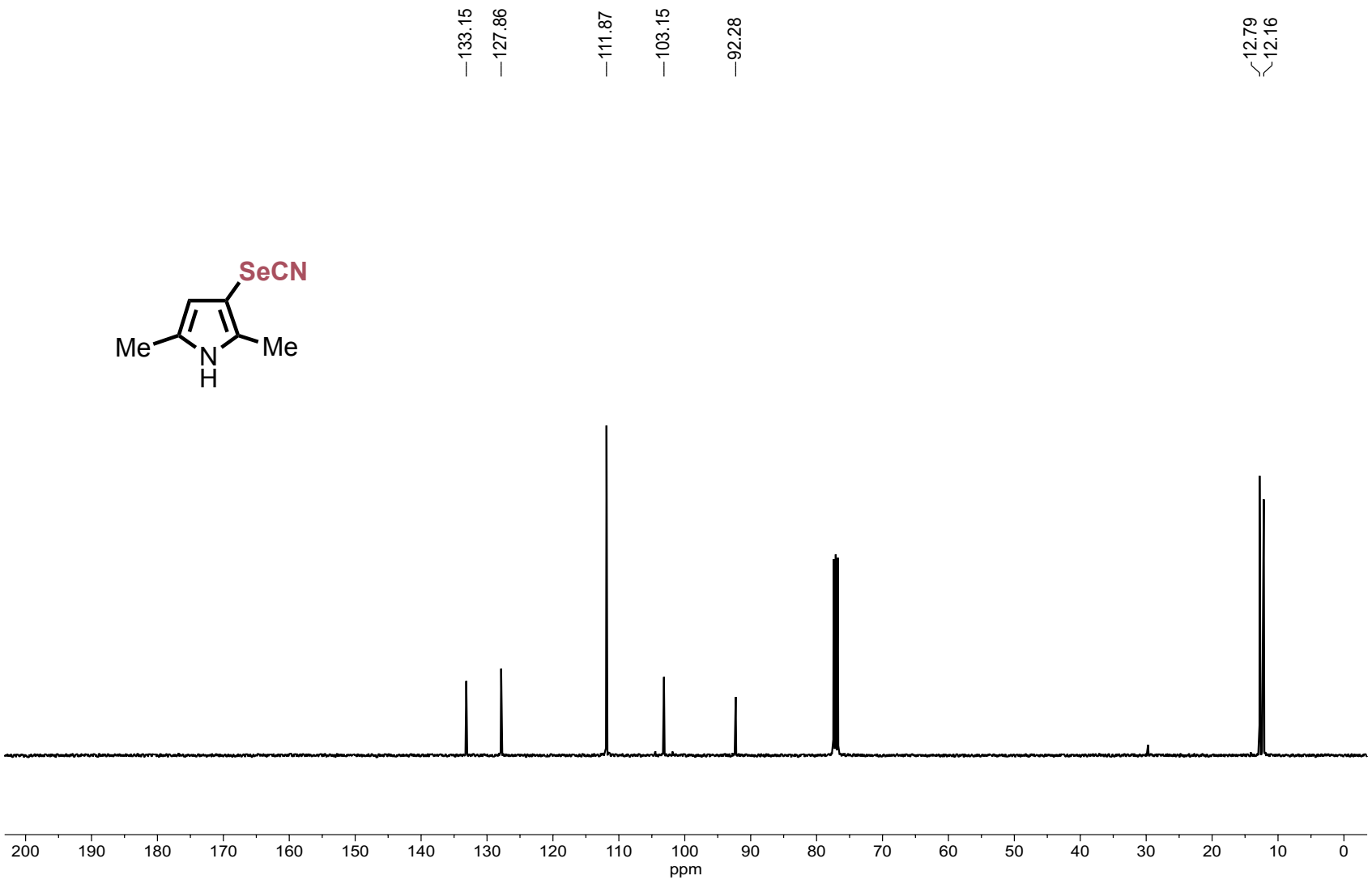


Figure S103. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **18b**

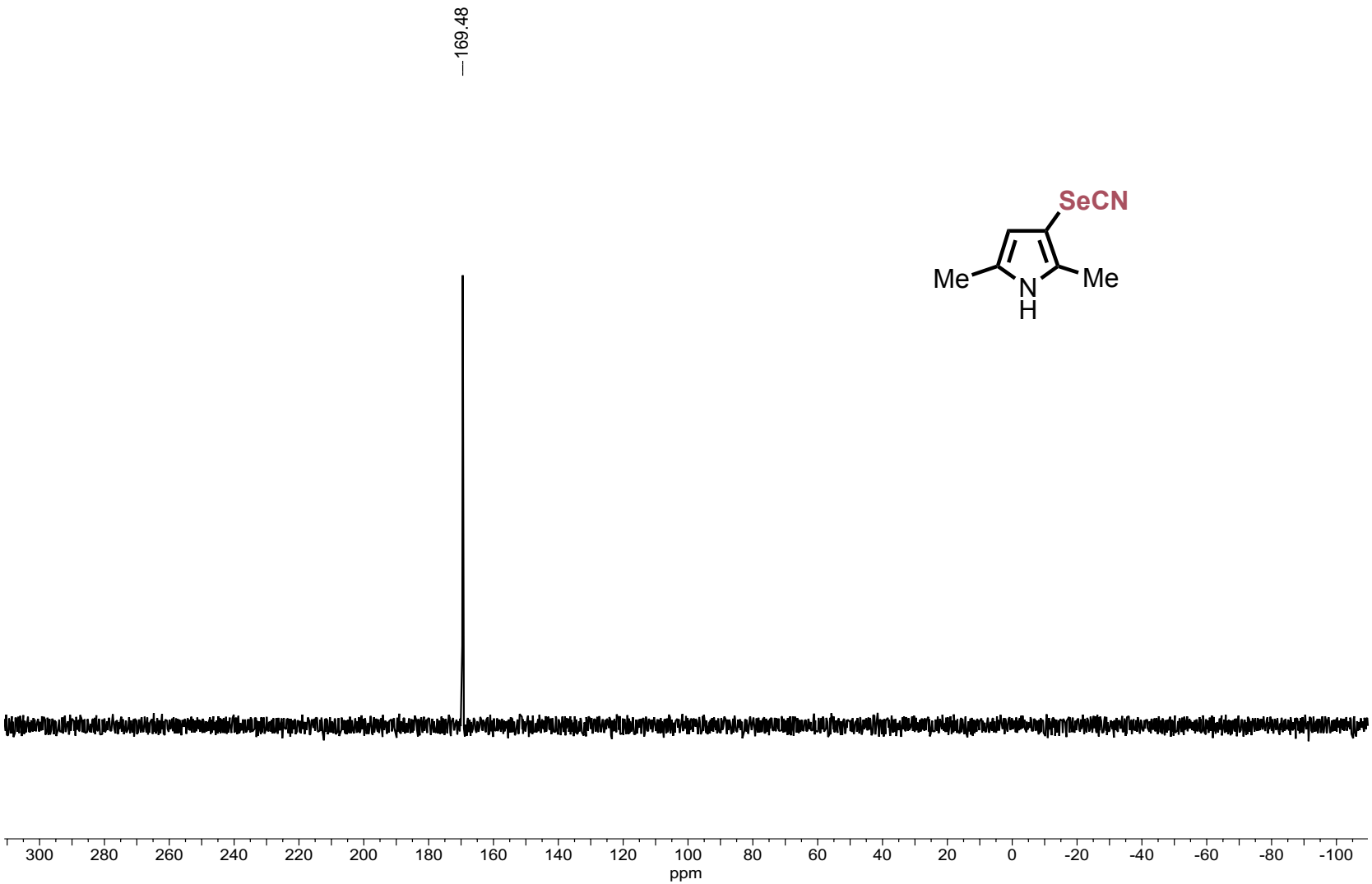


Figure S104. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **18b**

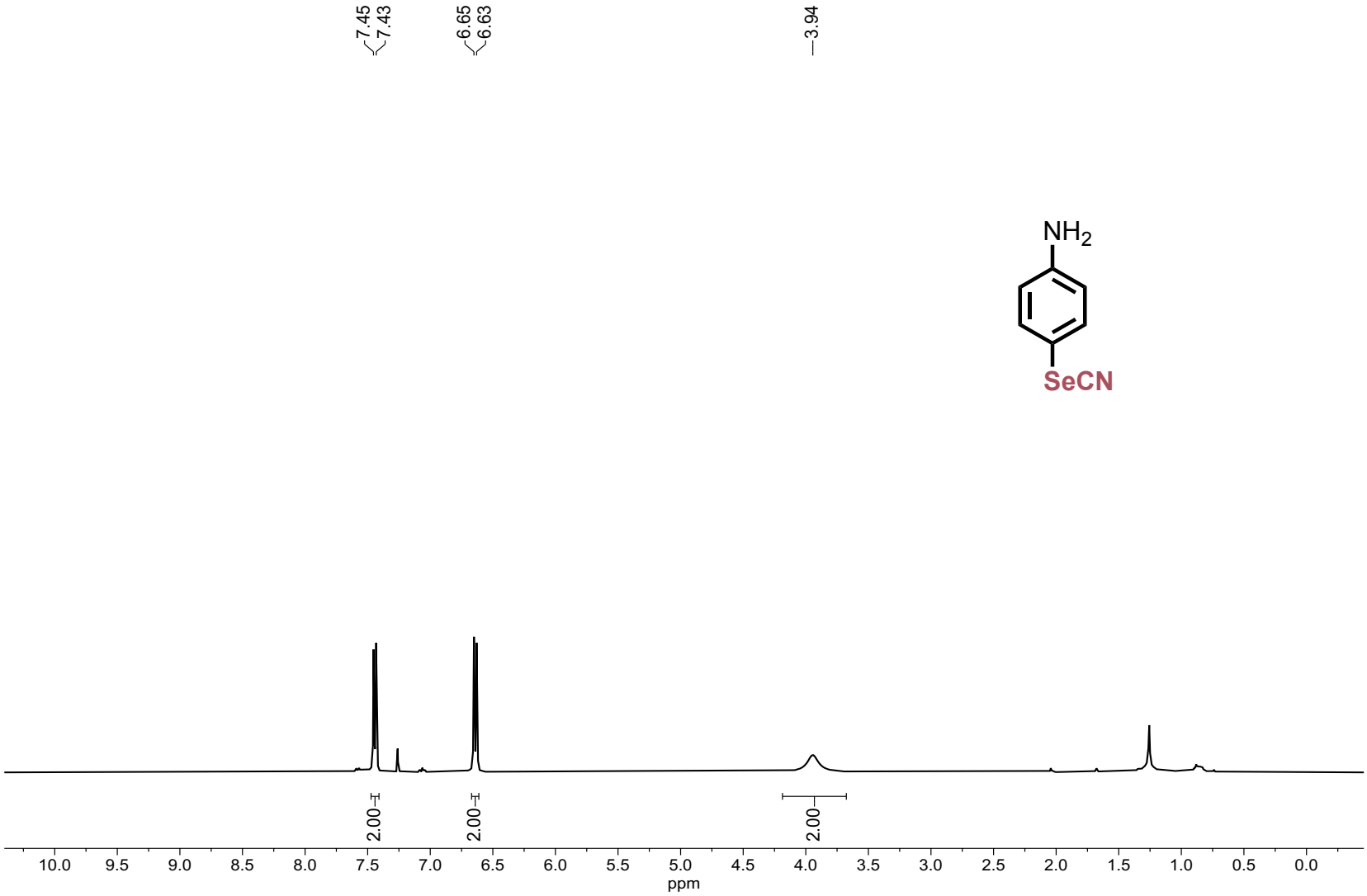


Figure S105. ^{1}H NMR ($CDCl_3$, 400 MHz) of **20b**

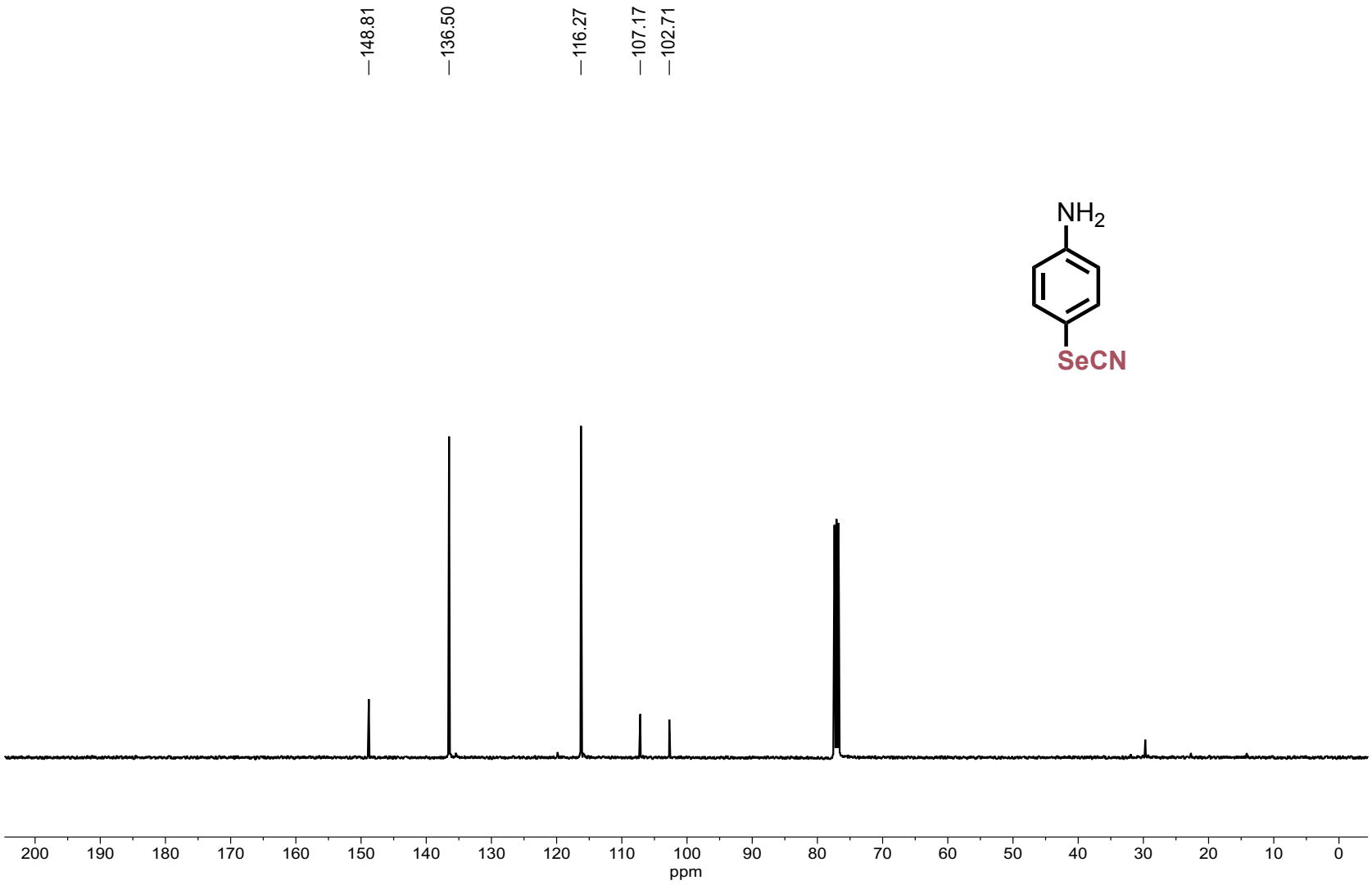


Figure S106. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **20b**

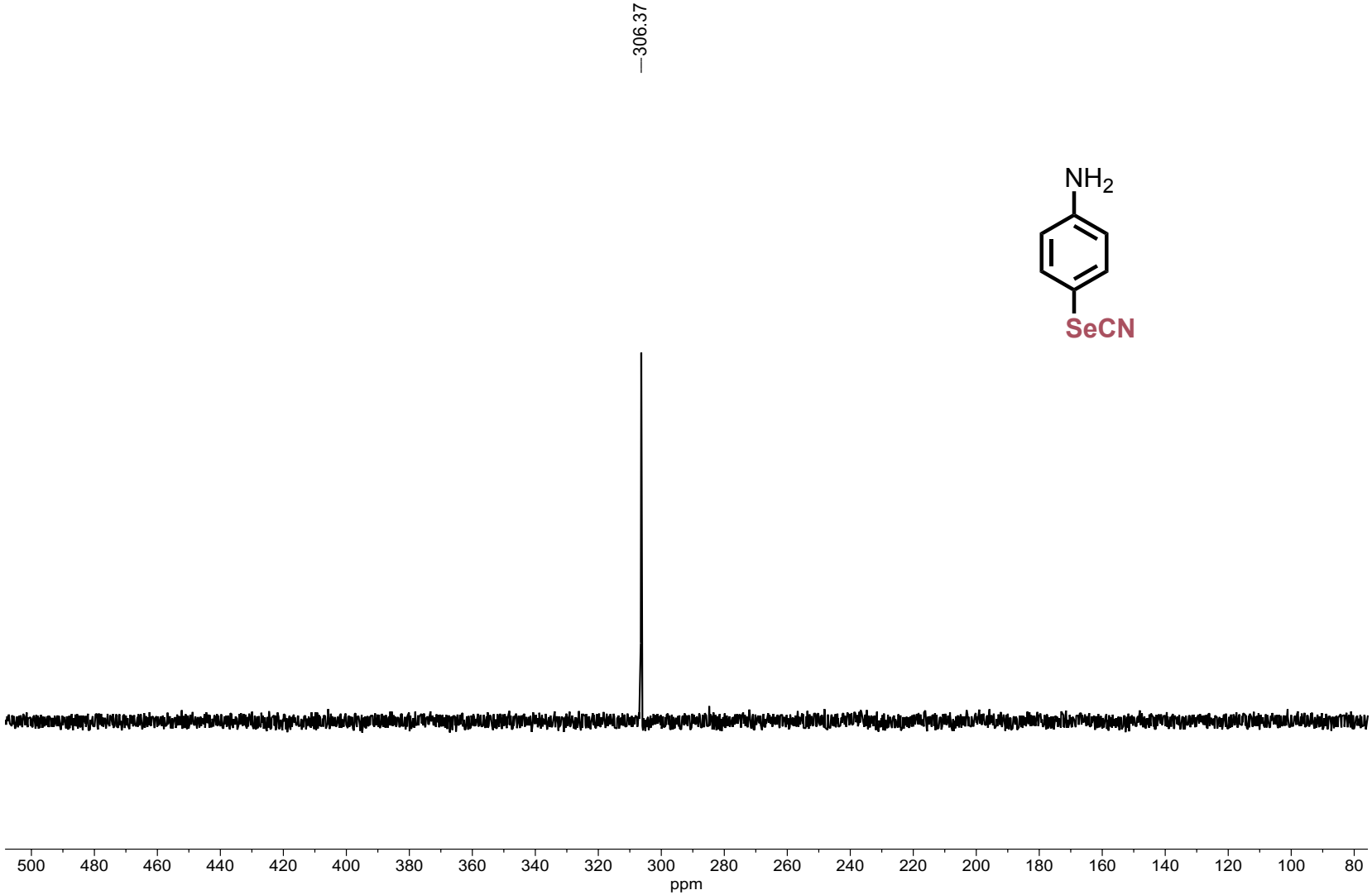


Figure S107. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **20b**

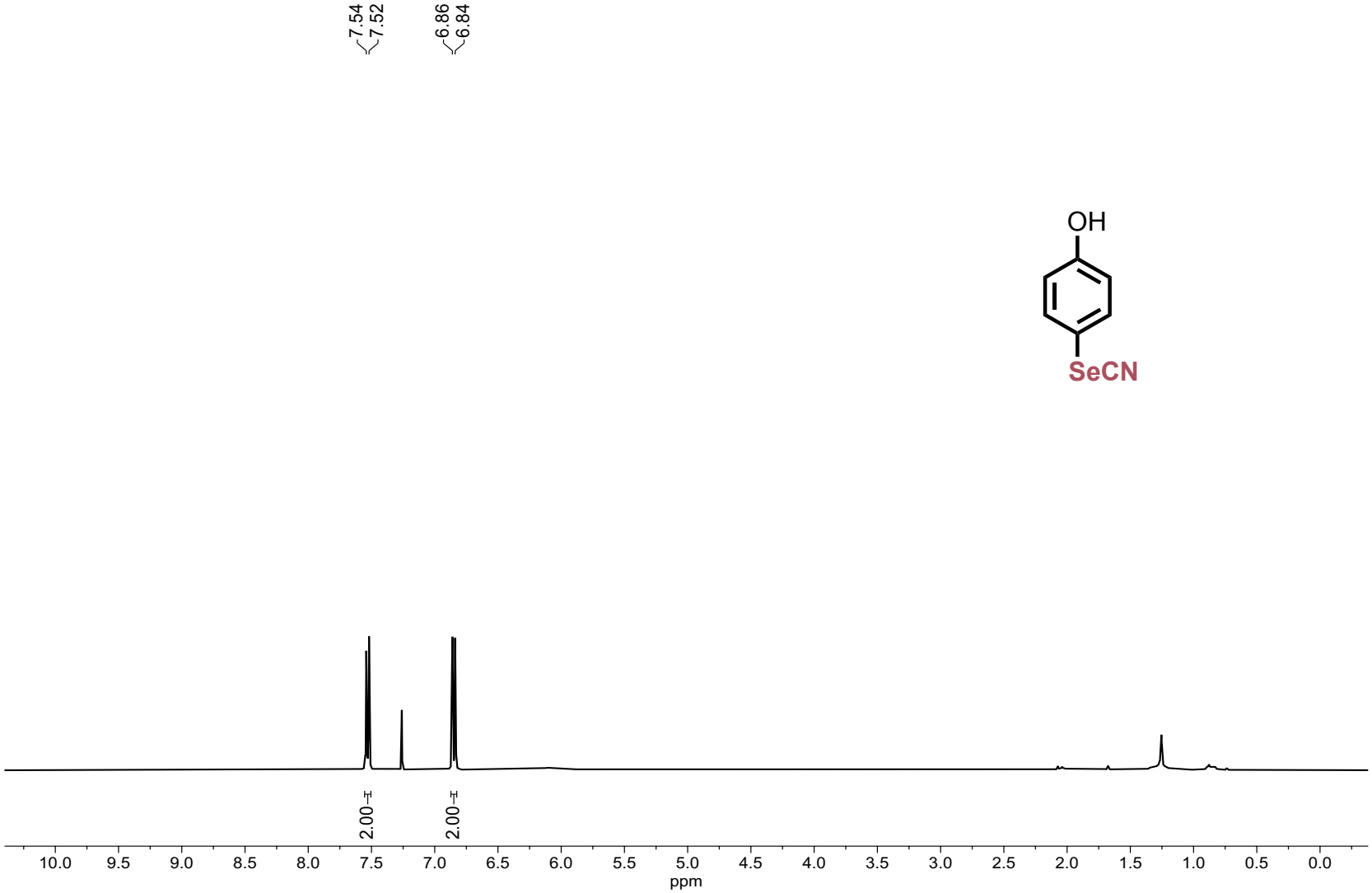


Figure S108. ^{1}H NMR ($CDCl_3$, 400 MHz) of **21b**

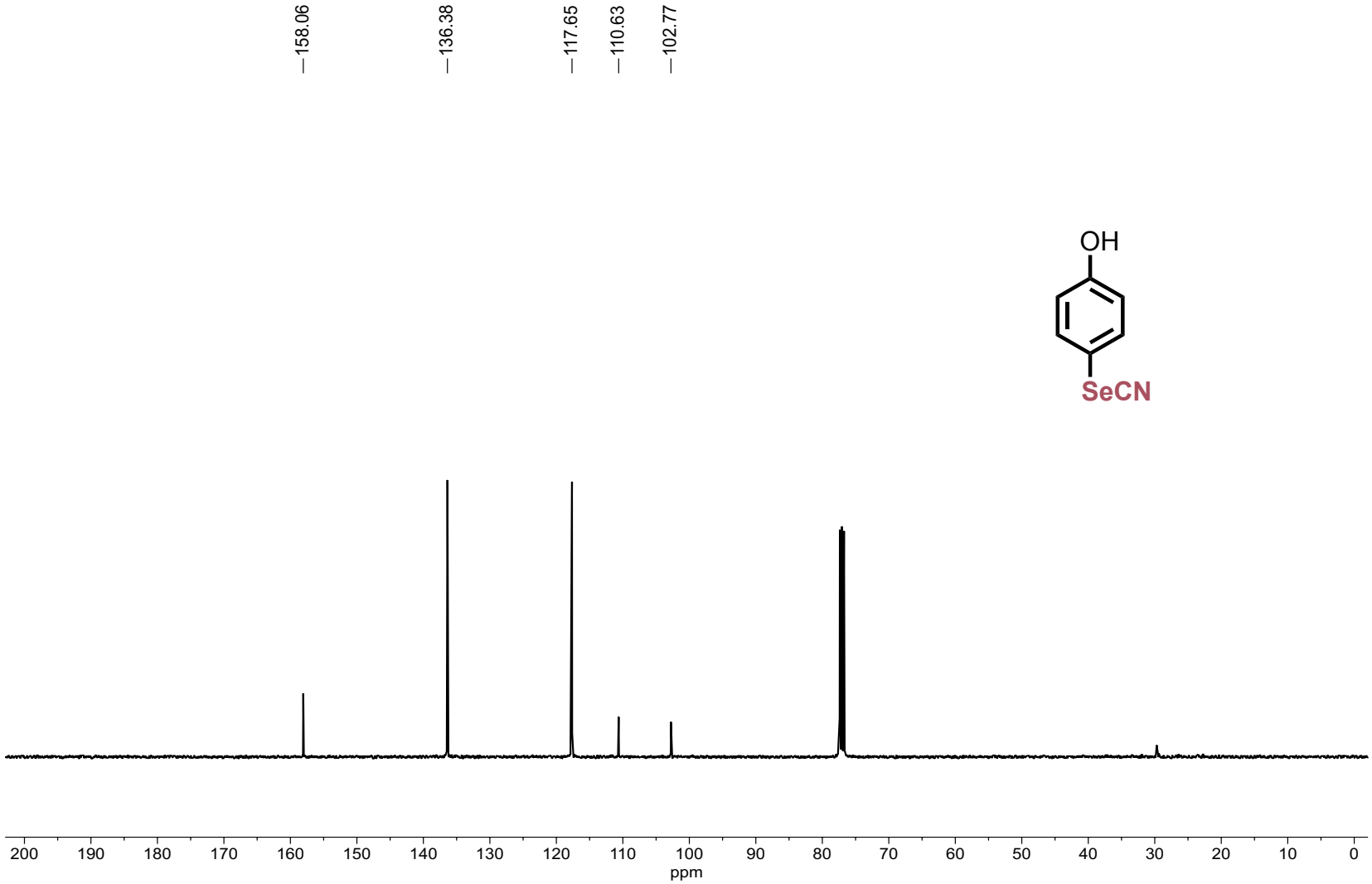


Figure S109. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **21b**

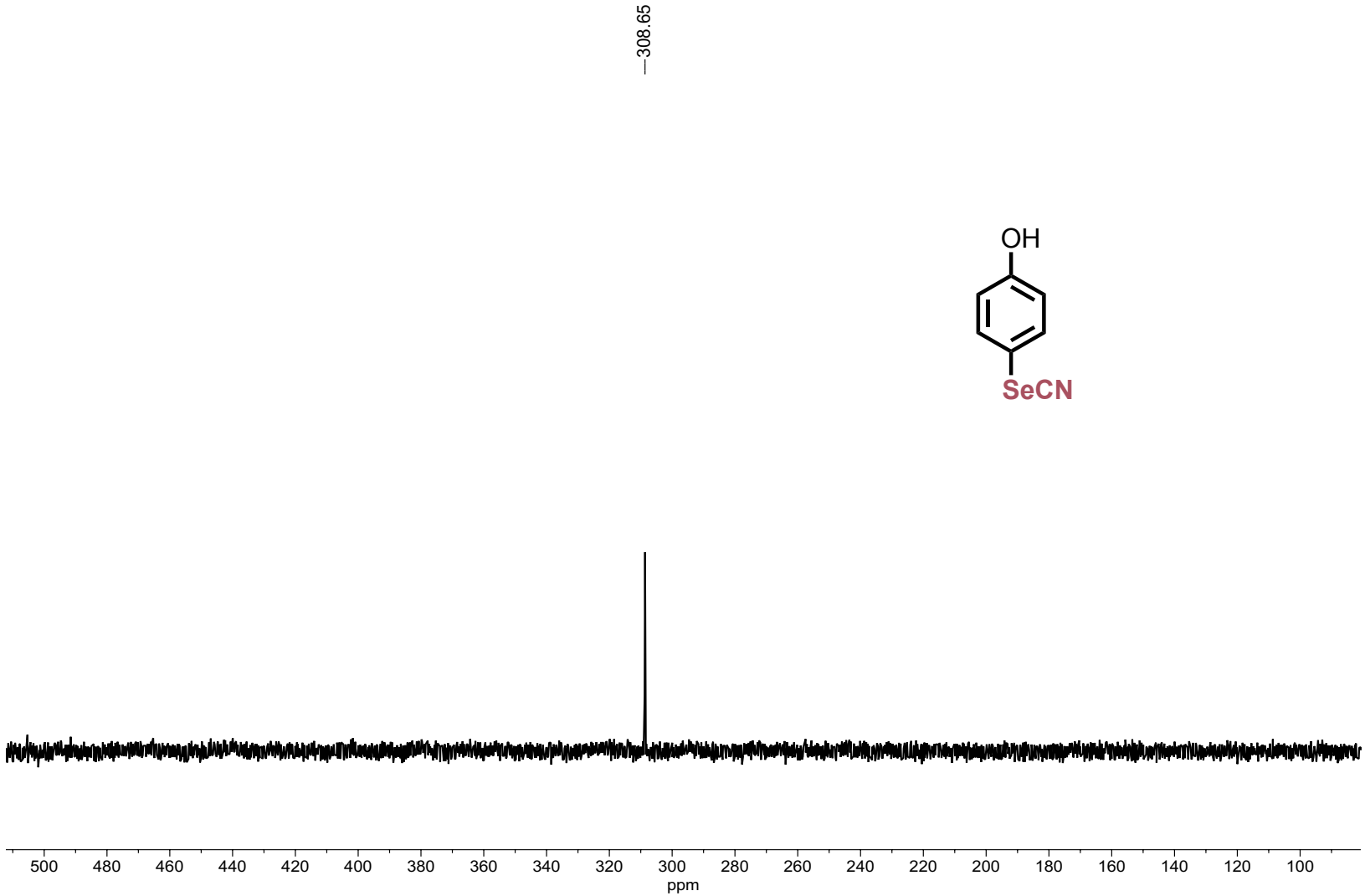


Figure S110. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **21b**

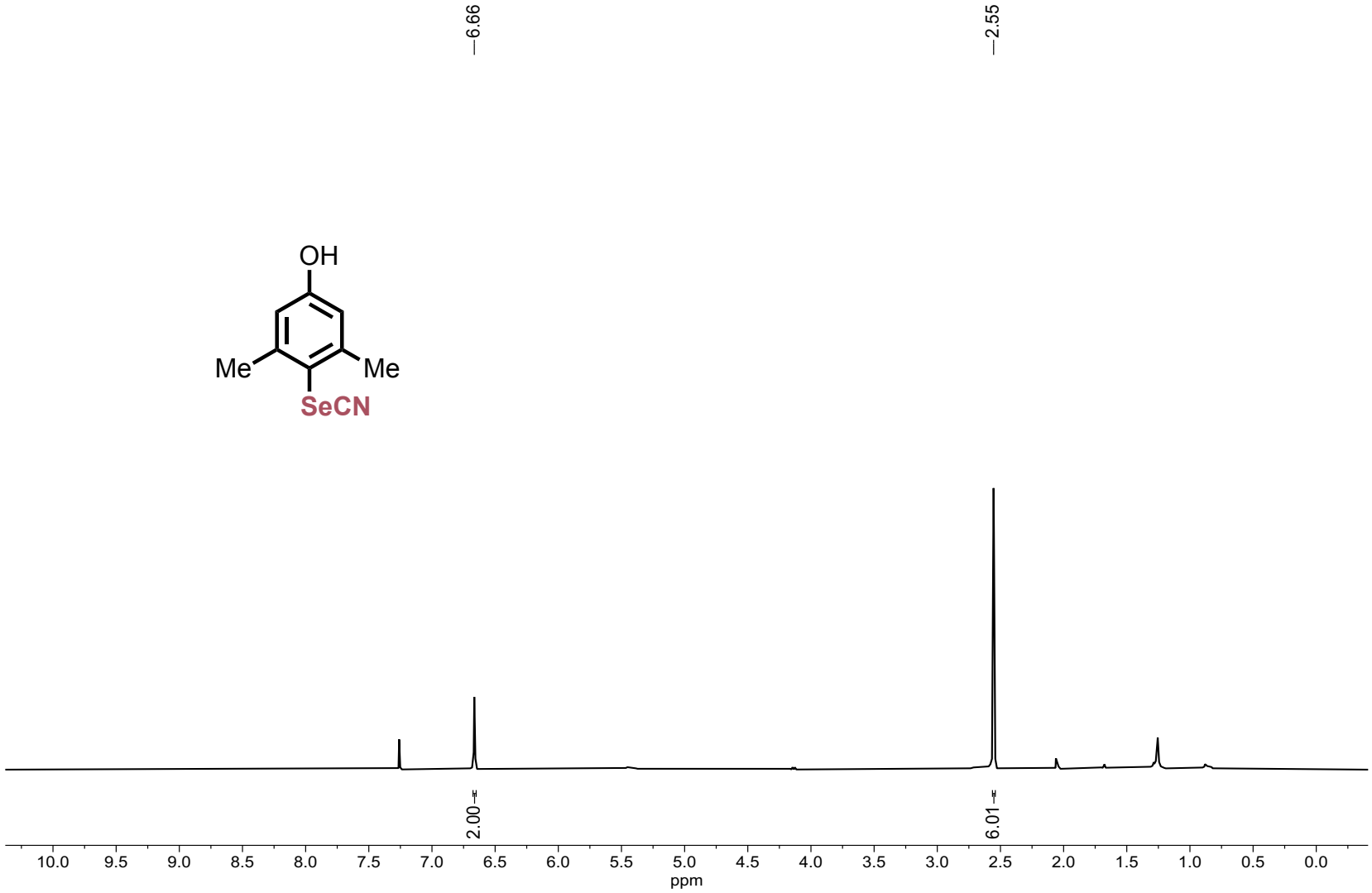


Figure S111. ^{1}H NMR ($CDCl_3$, 400 MHz) of **22b**

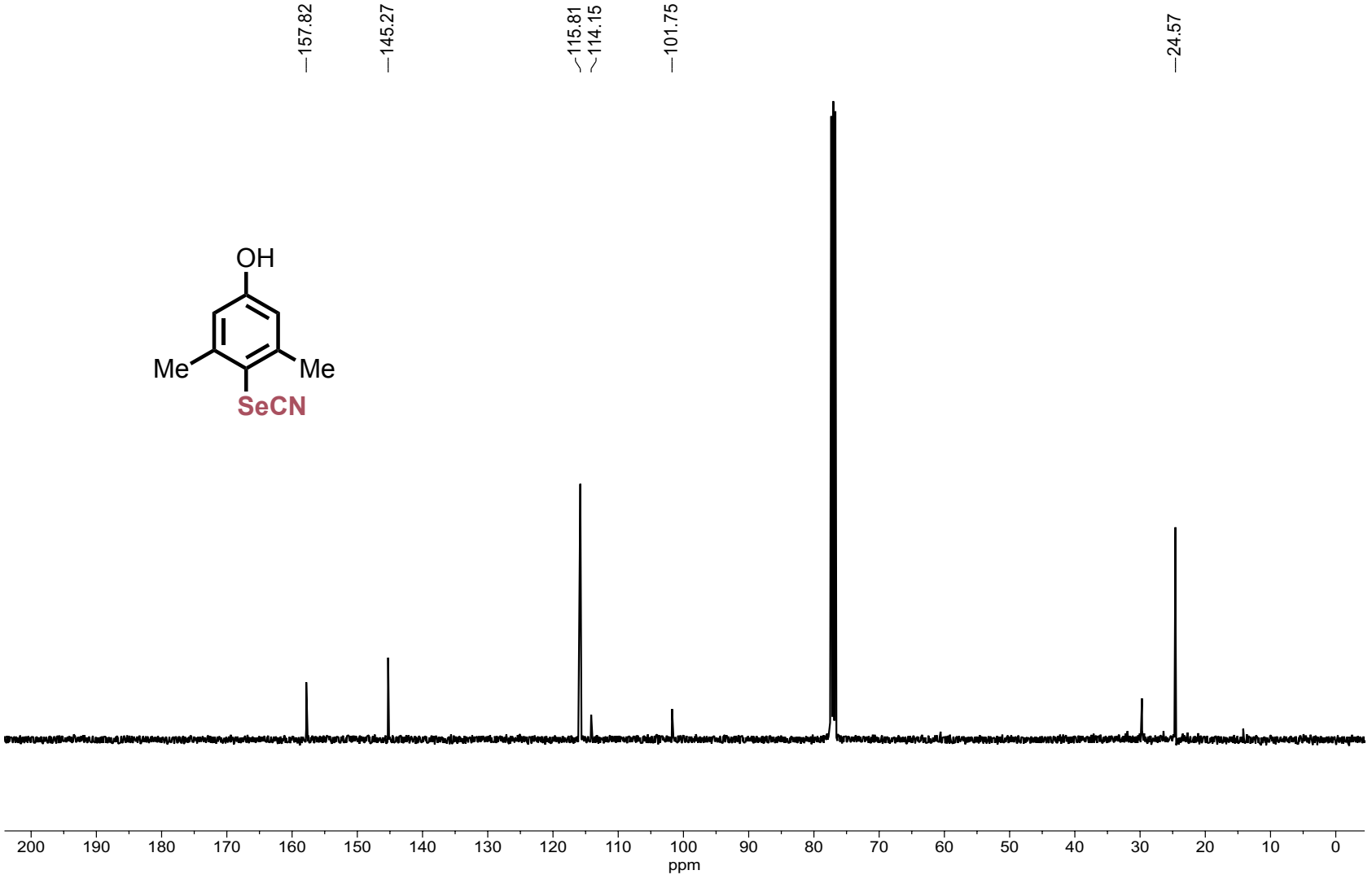


Figure S112. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **22b**

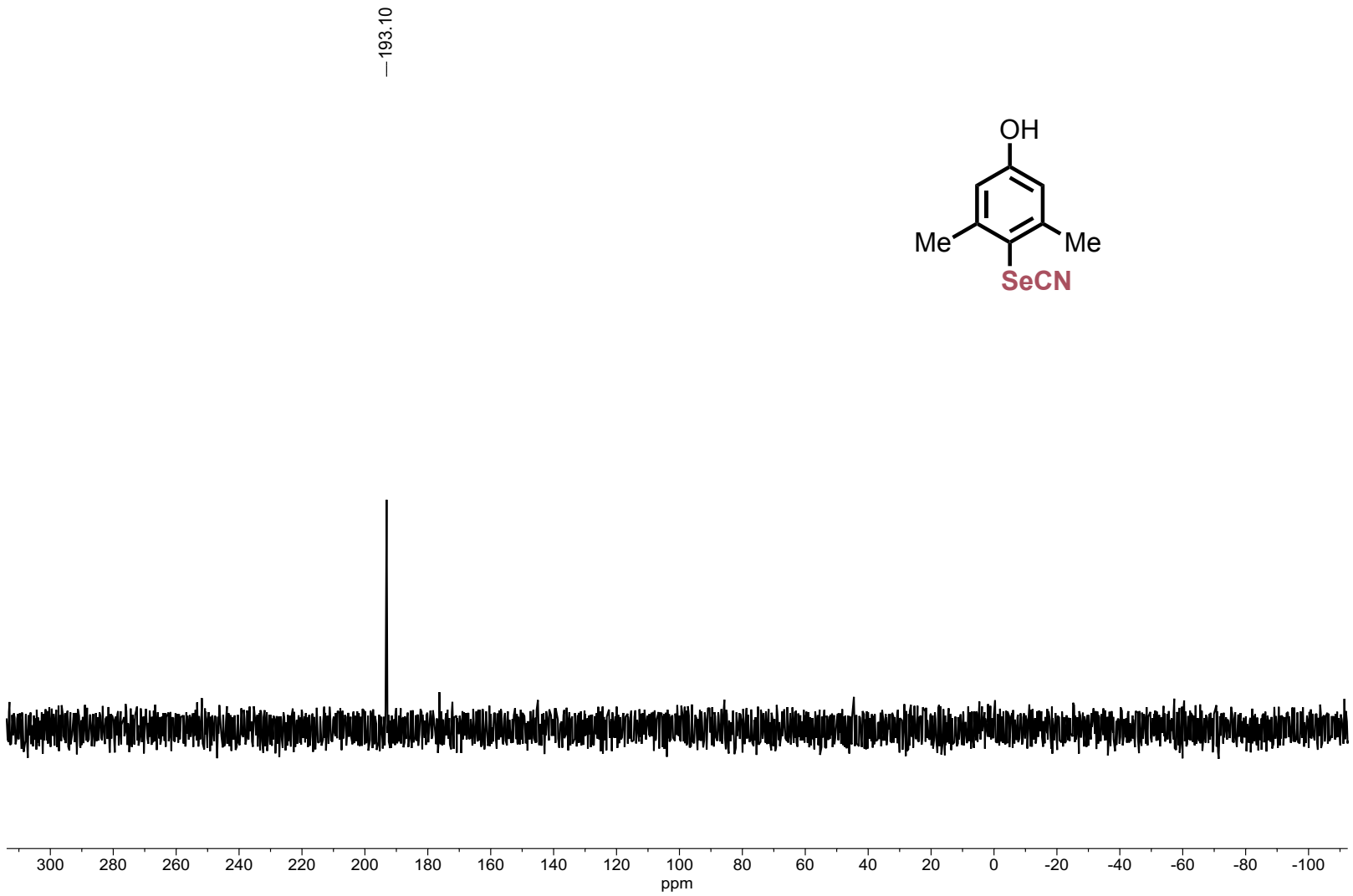


Figure S113. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **22b**

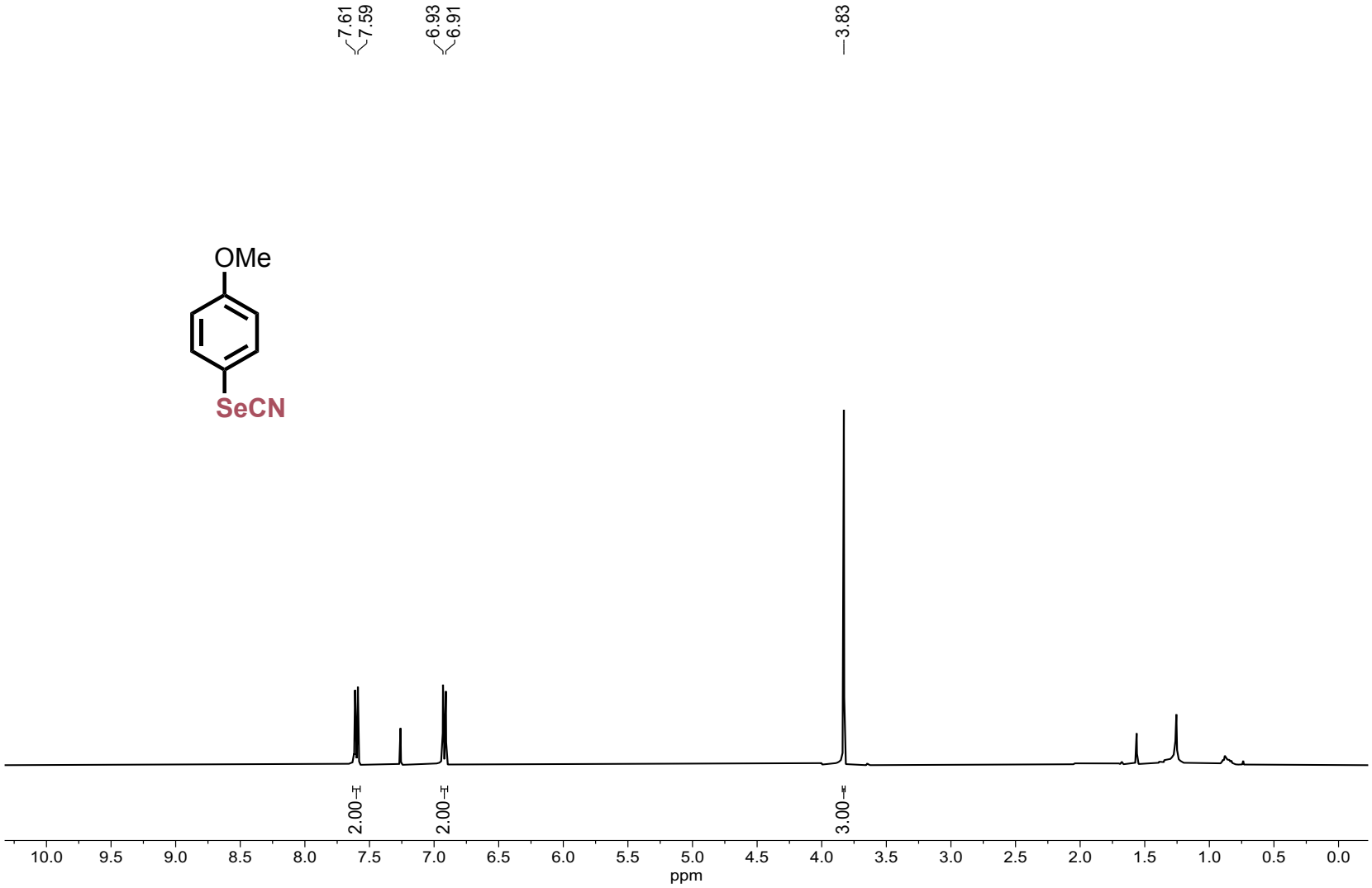


Figure S114. ^{1}H NMR ($CDCl_3$, 400 MHz) of **23b**

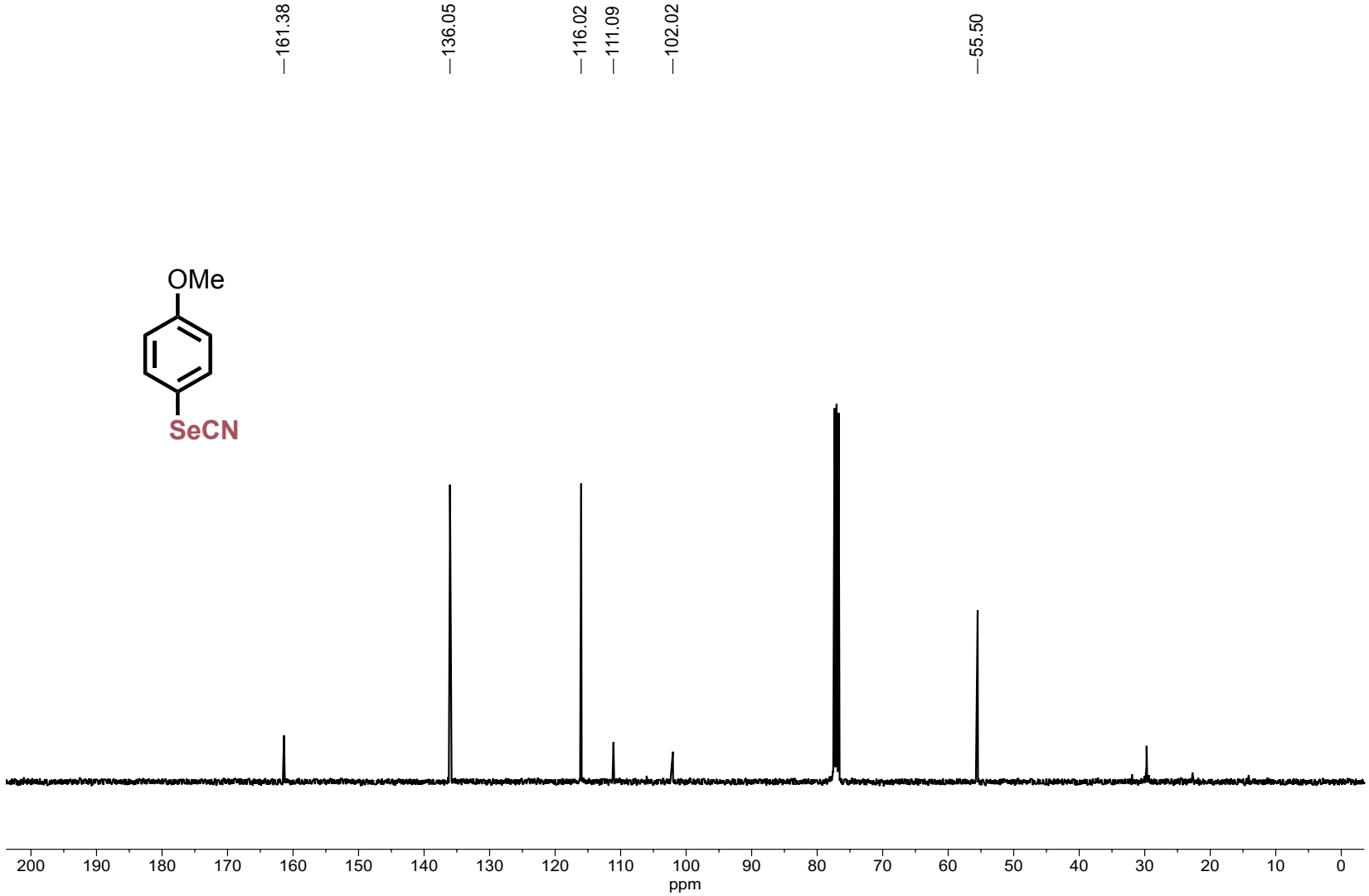


Figure S115. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **23b**

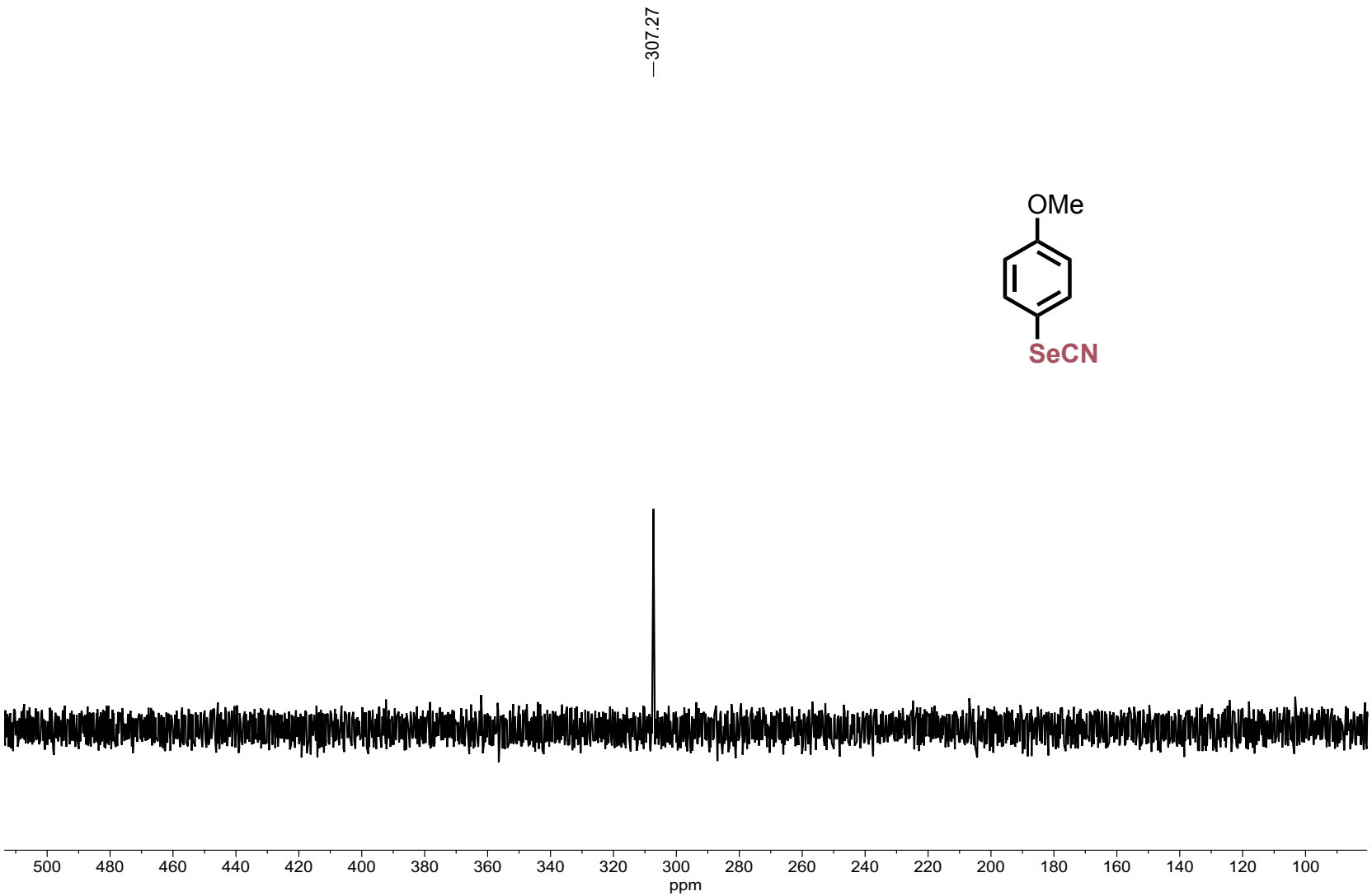


Figure S116. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **23b**

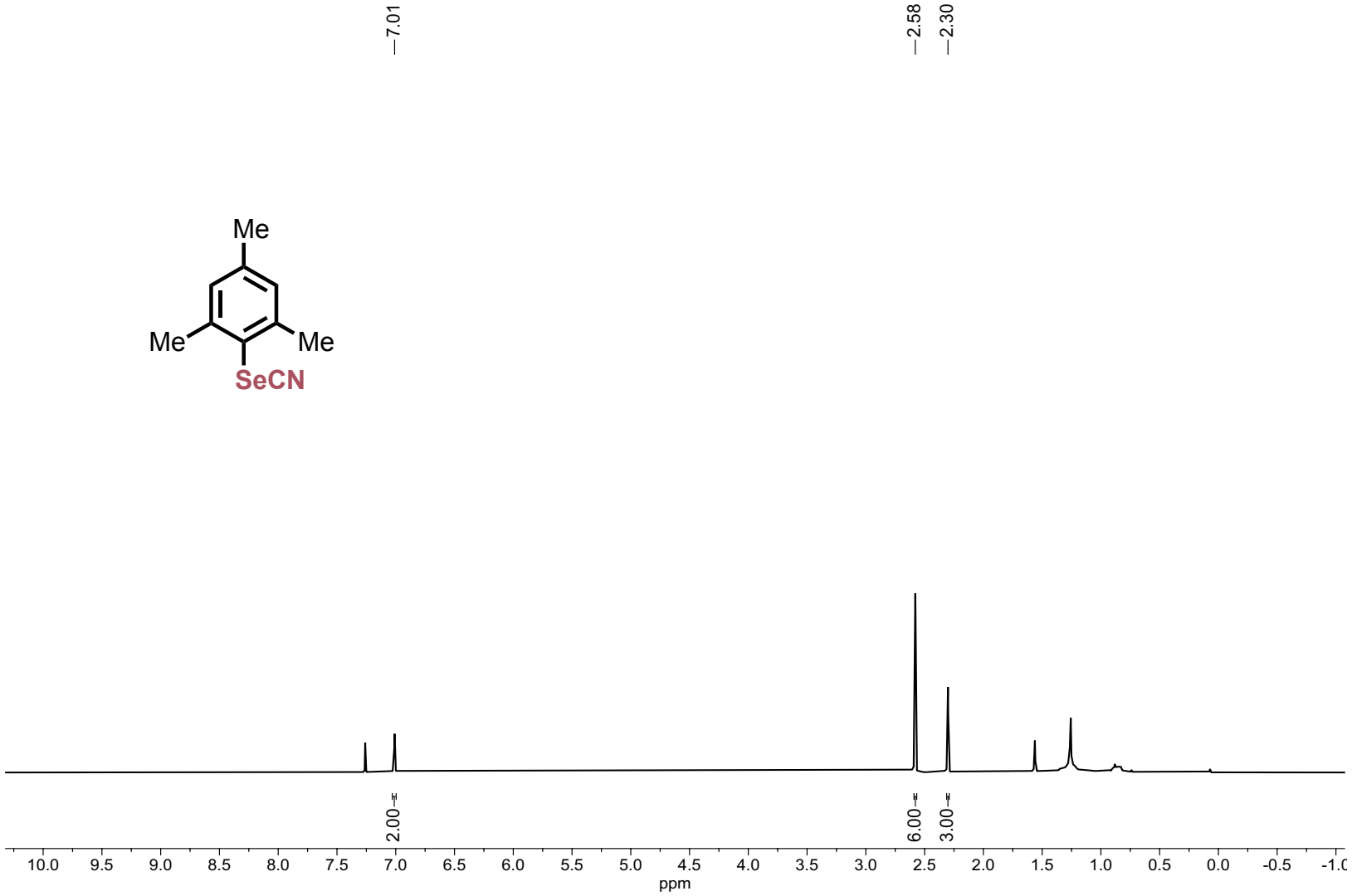


Figure S117. ^{1}H NMR ($CDCl_3$, 400 MHz) of **24b**

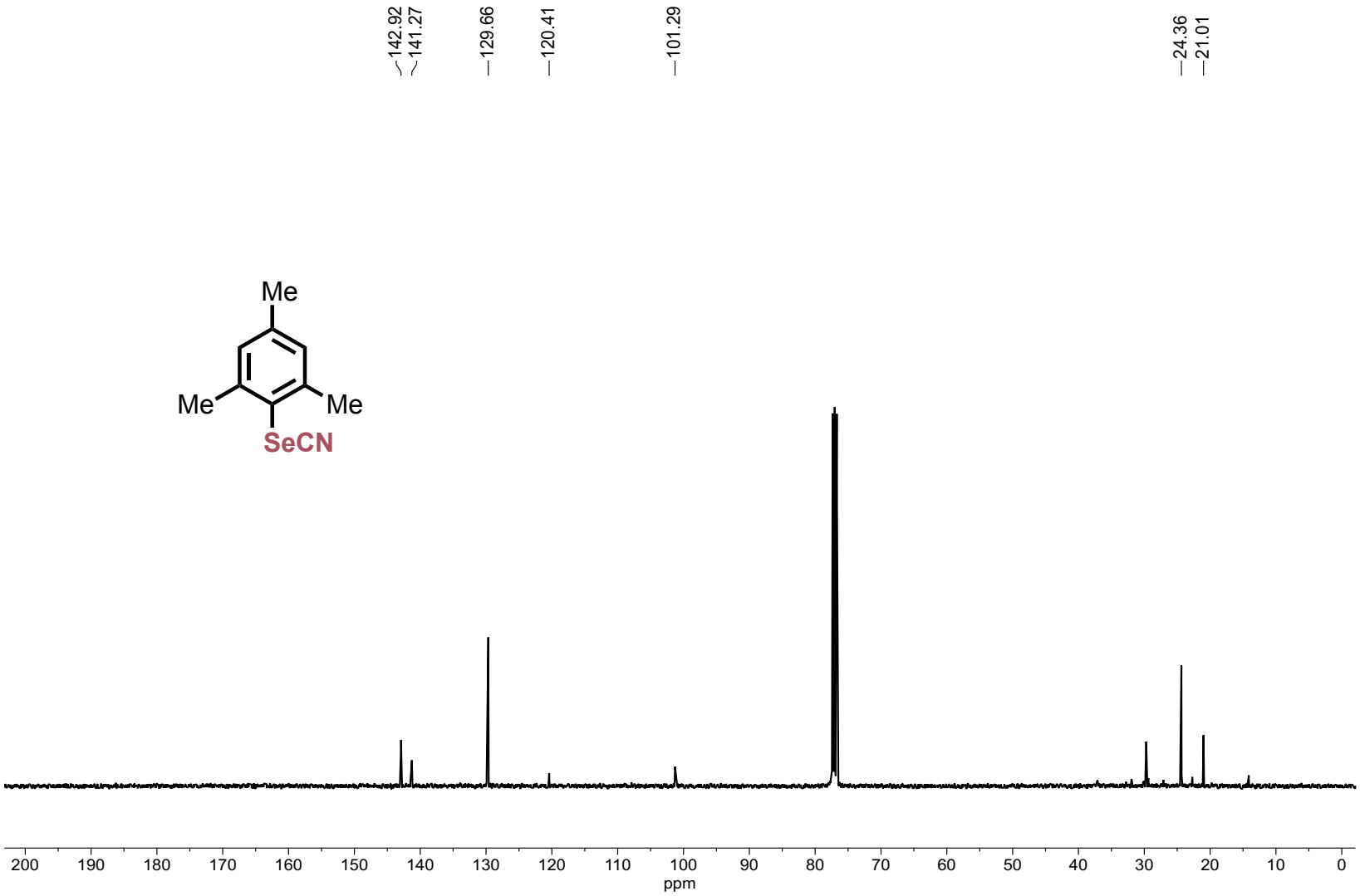


Figure S118. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **24b**

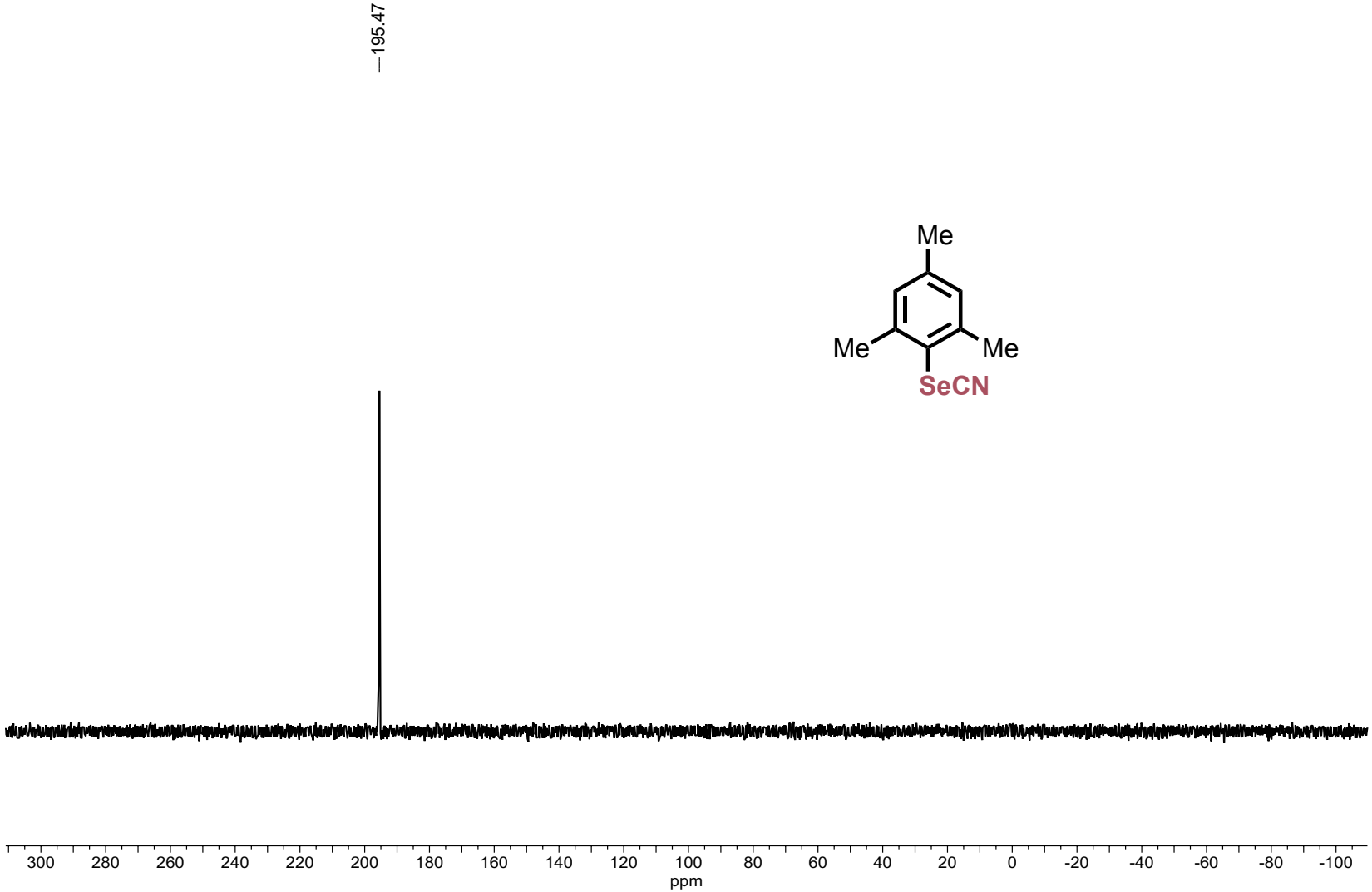


Figure S119. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **24b**

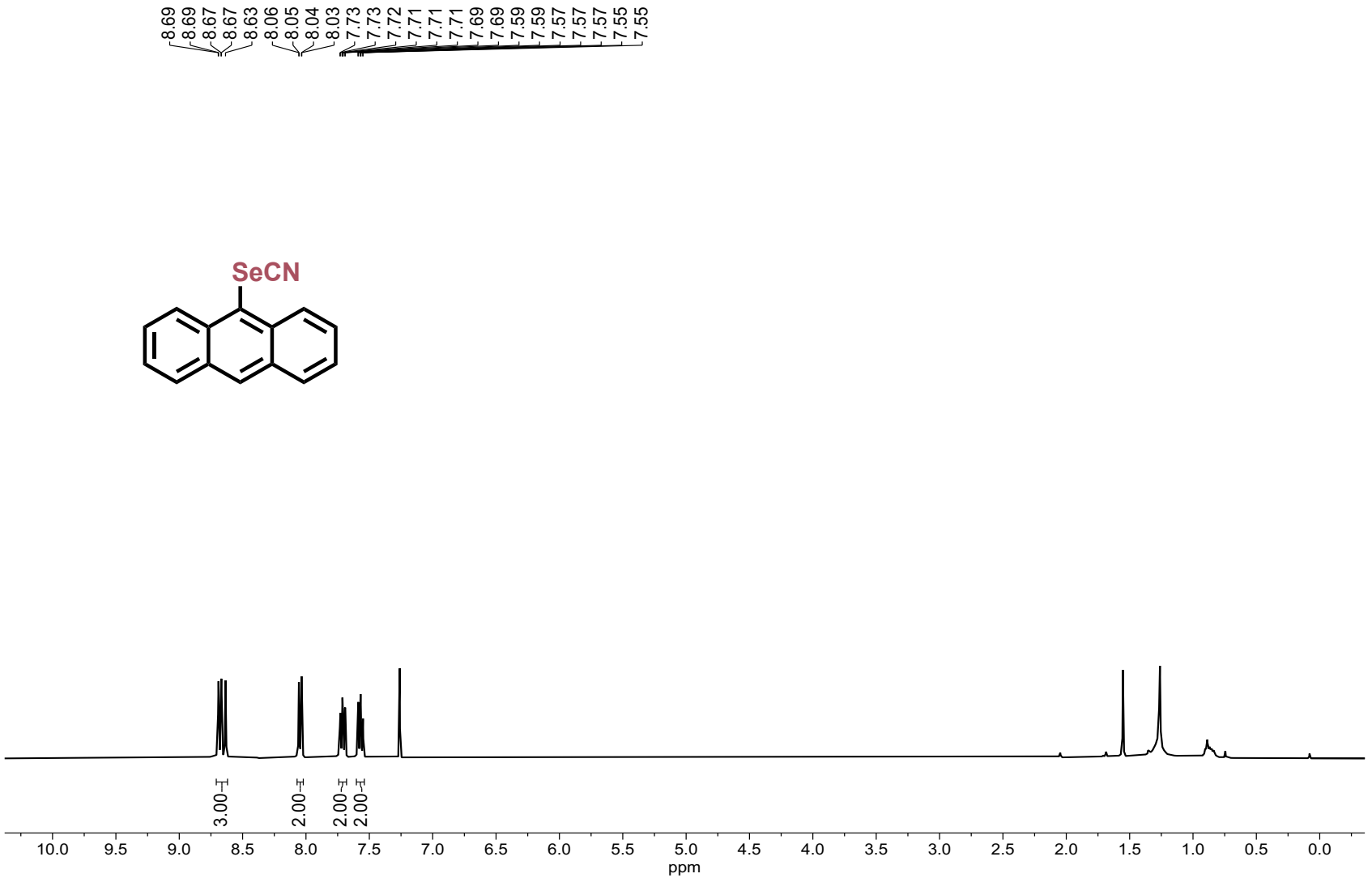


Figure S120. ^{1}H NMR ($CDCl_3$, 400 MHz) of **25b**

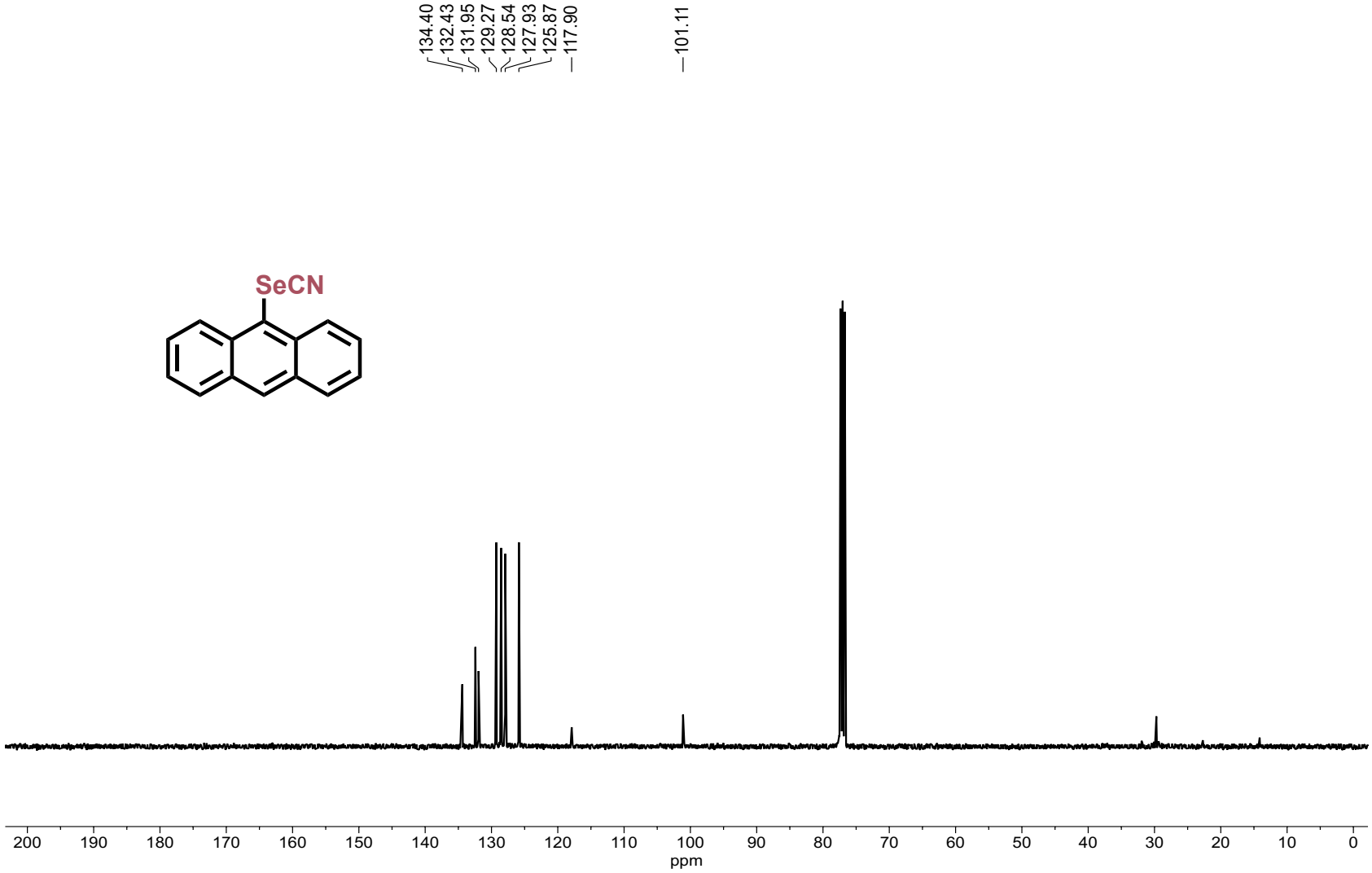


Figure S121. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **25b**

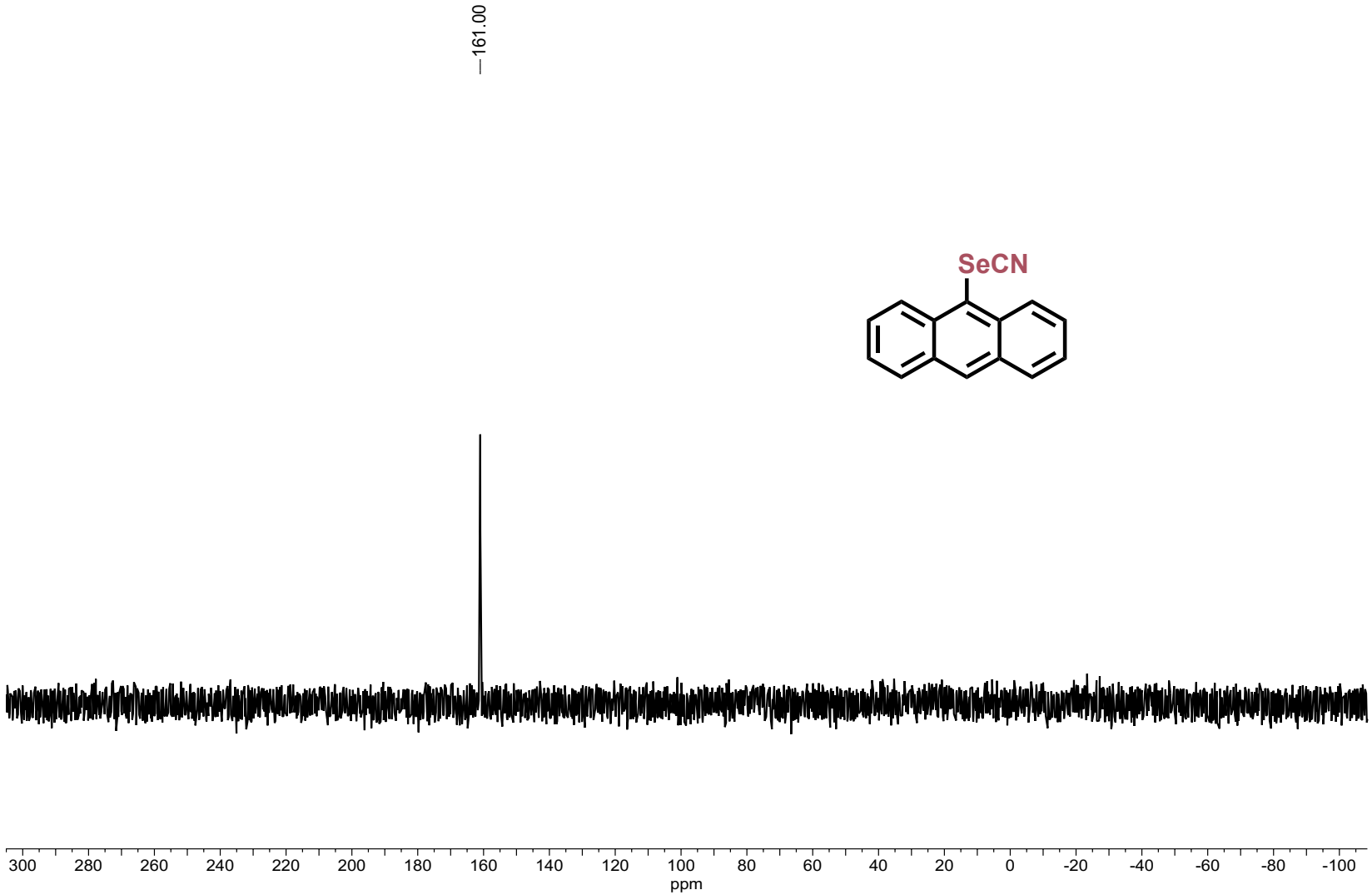


Figure S122. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **25b**

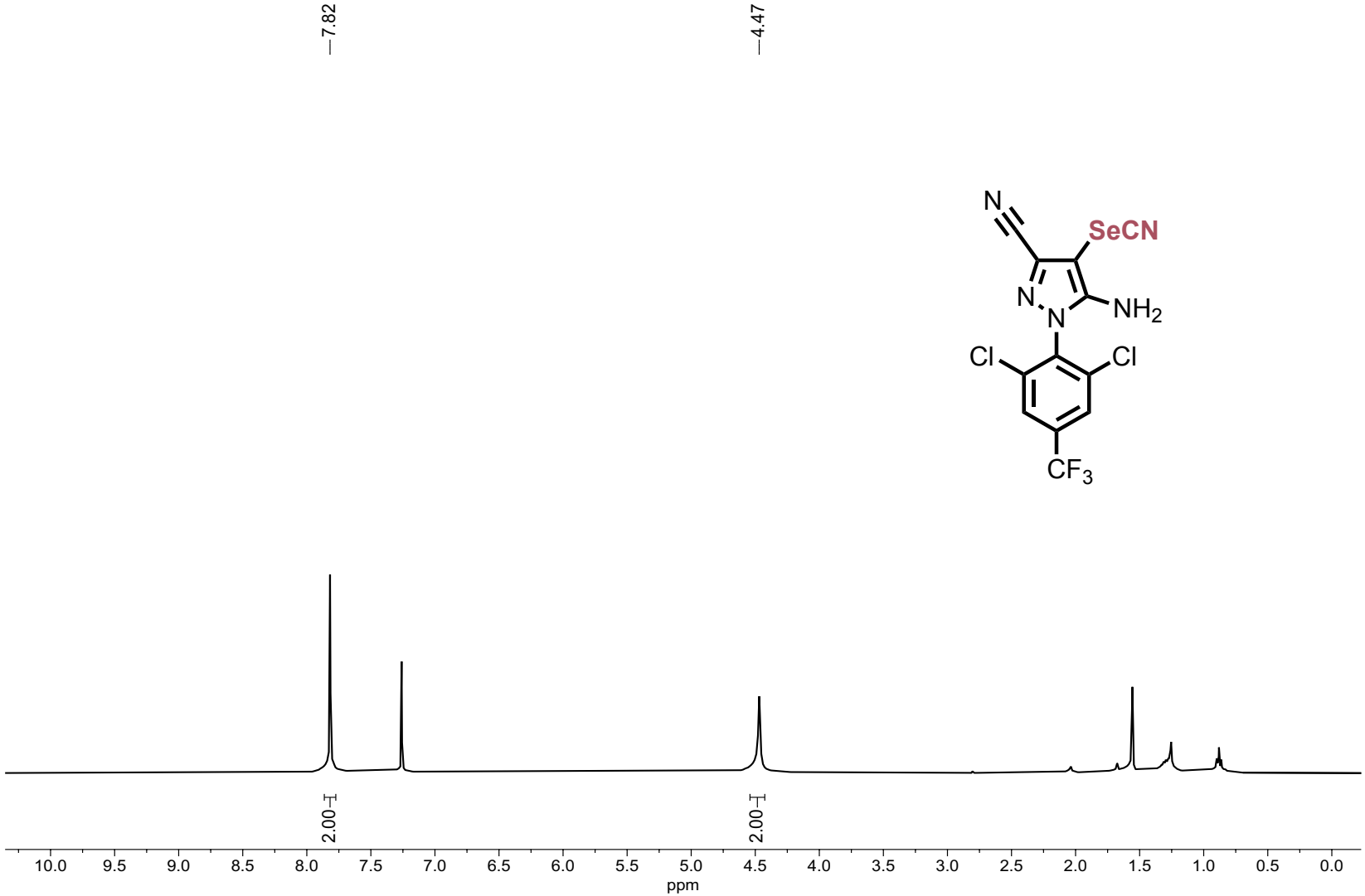


Figure S123. ^{1}H NMR ($CDCl_3$, 400 MHz) of **27b**

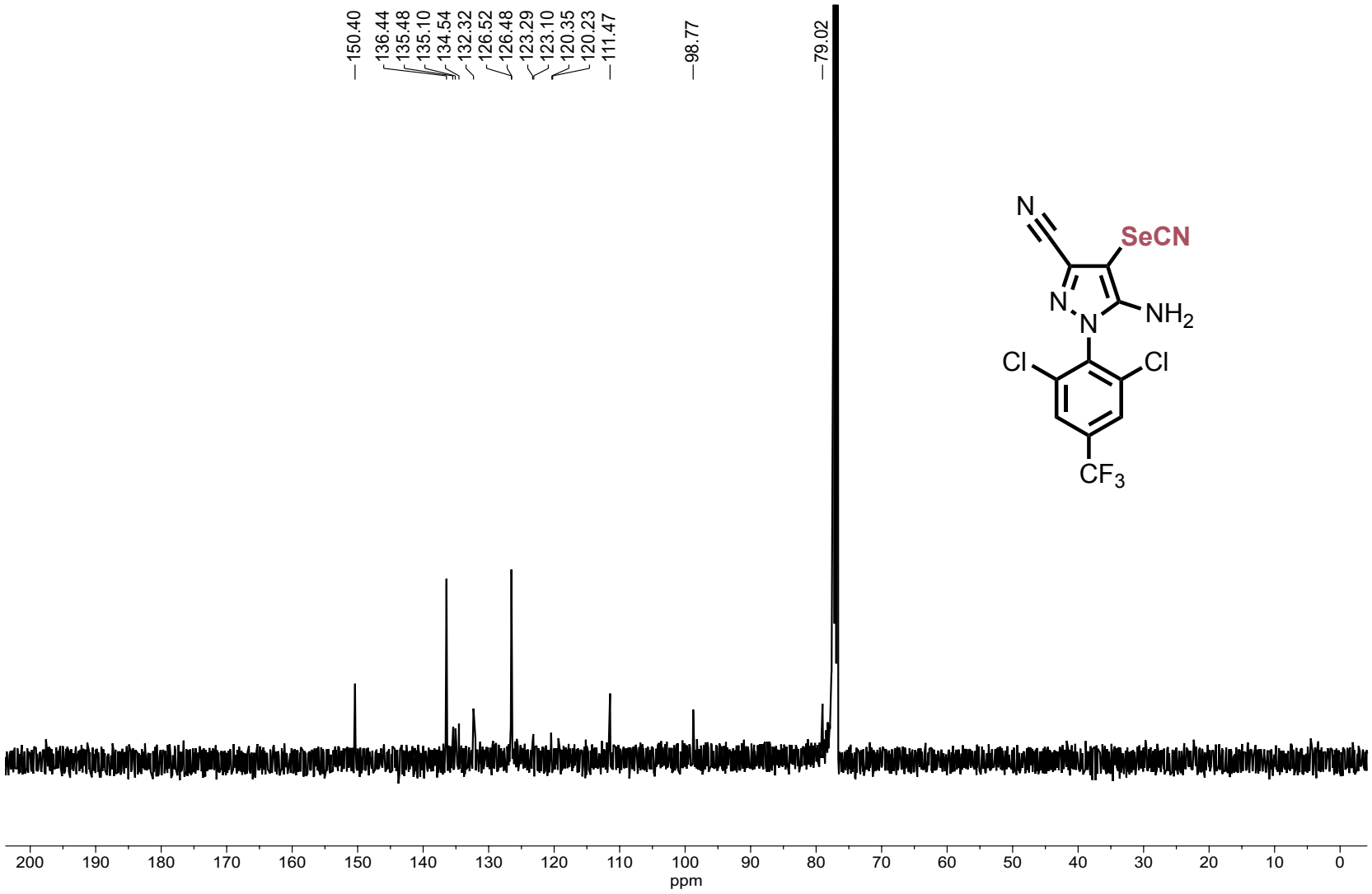


Figure S124. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **27b**

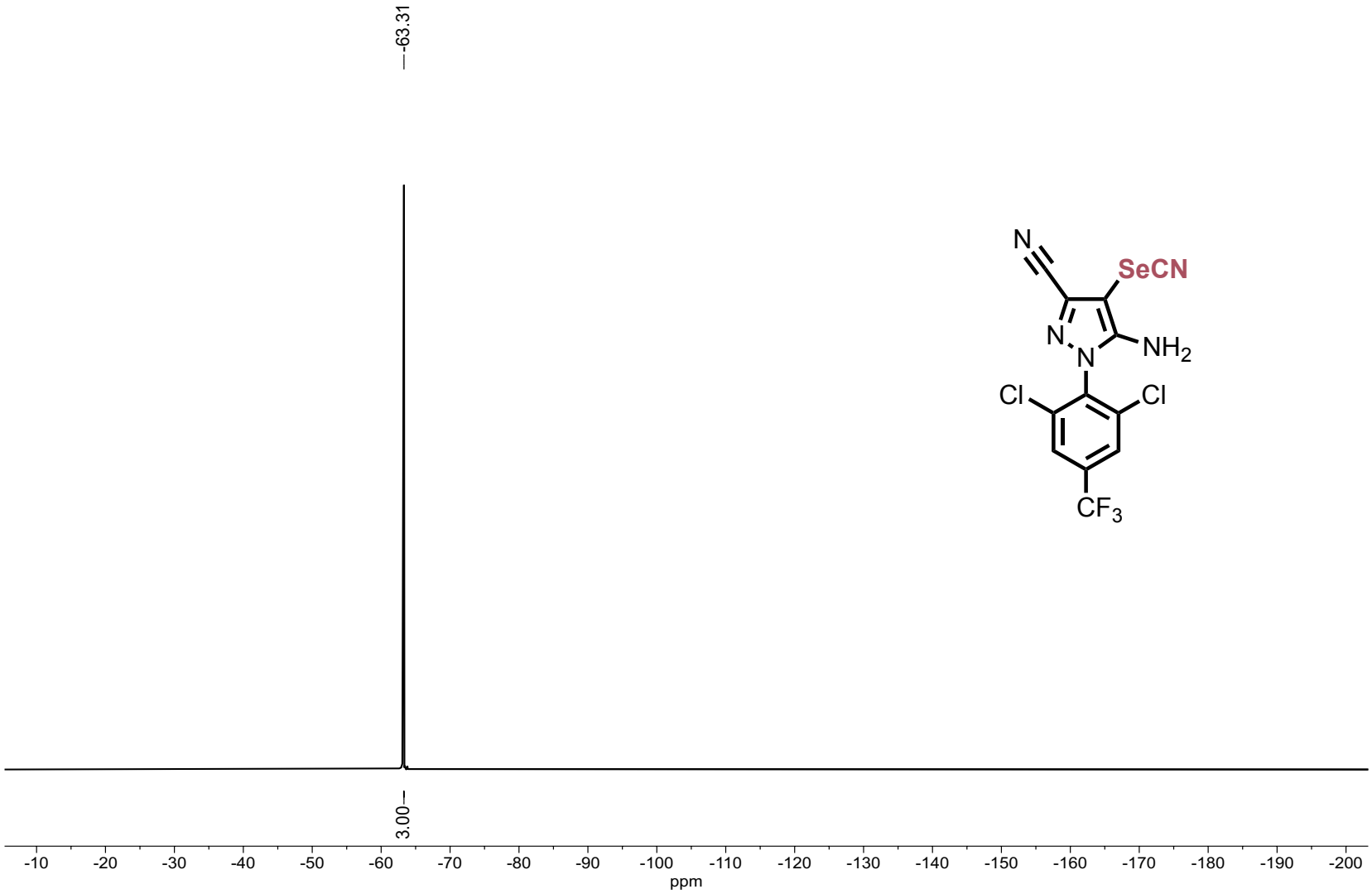


Figure S125. ^{19}F NMR ($CDCl_3$ 376.5 MHz) of **27b**

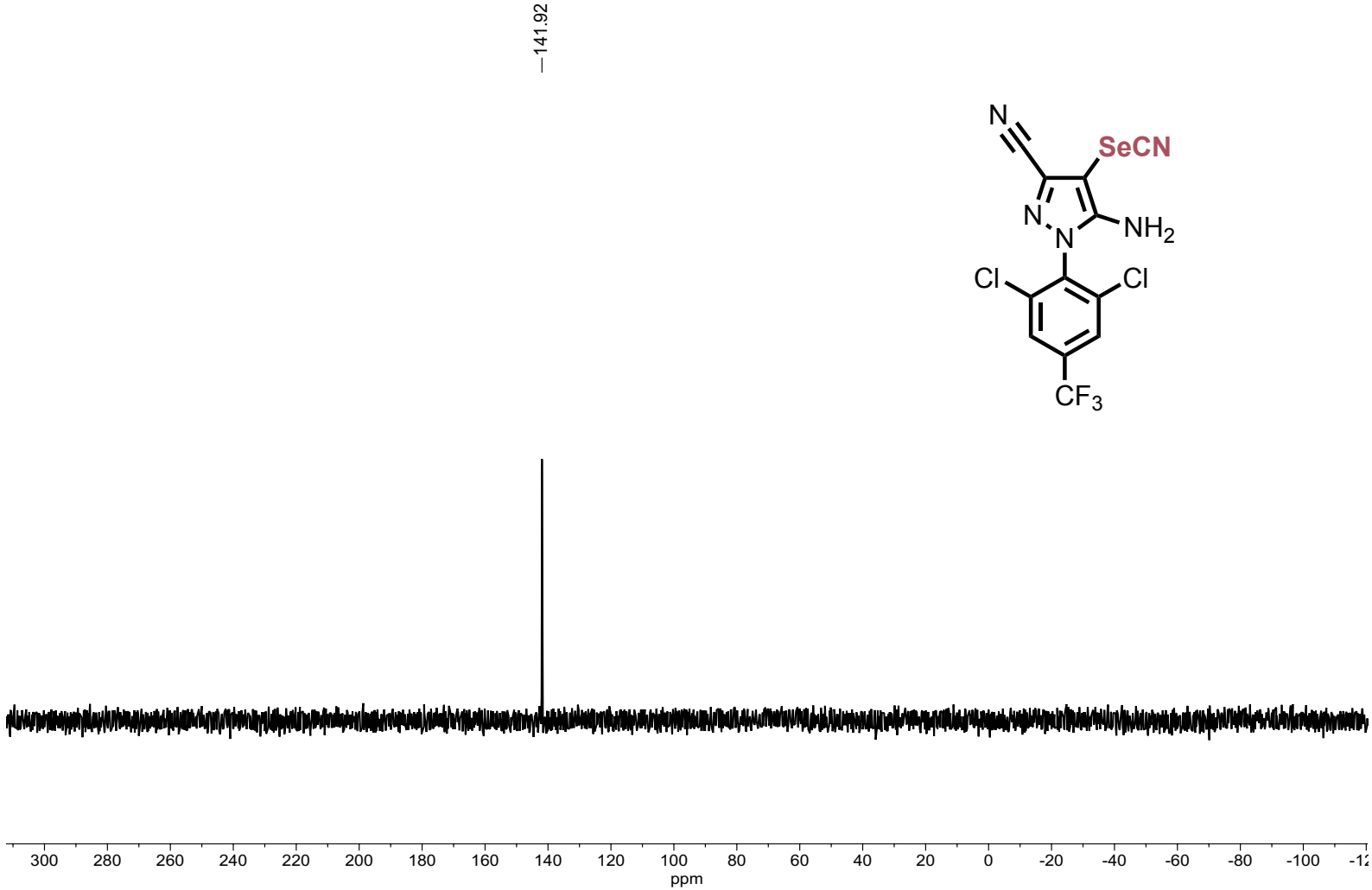


Figure S126. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **27b**

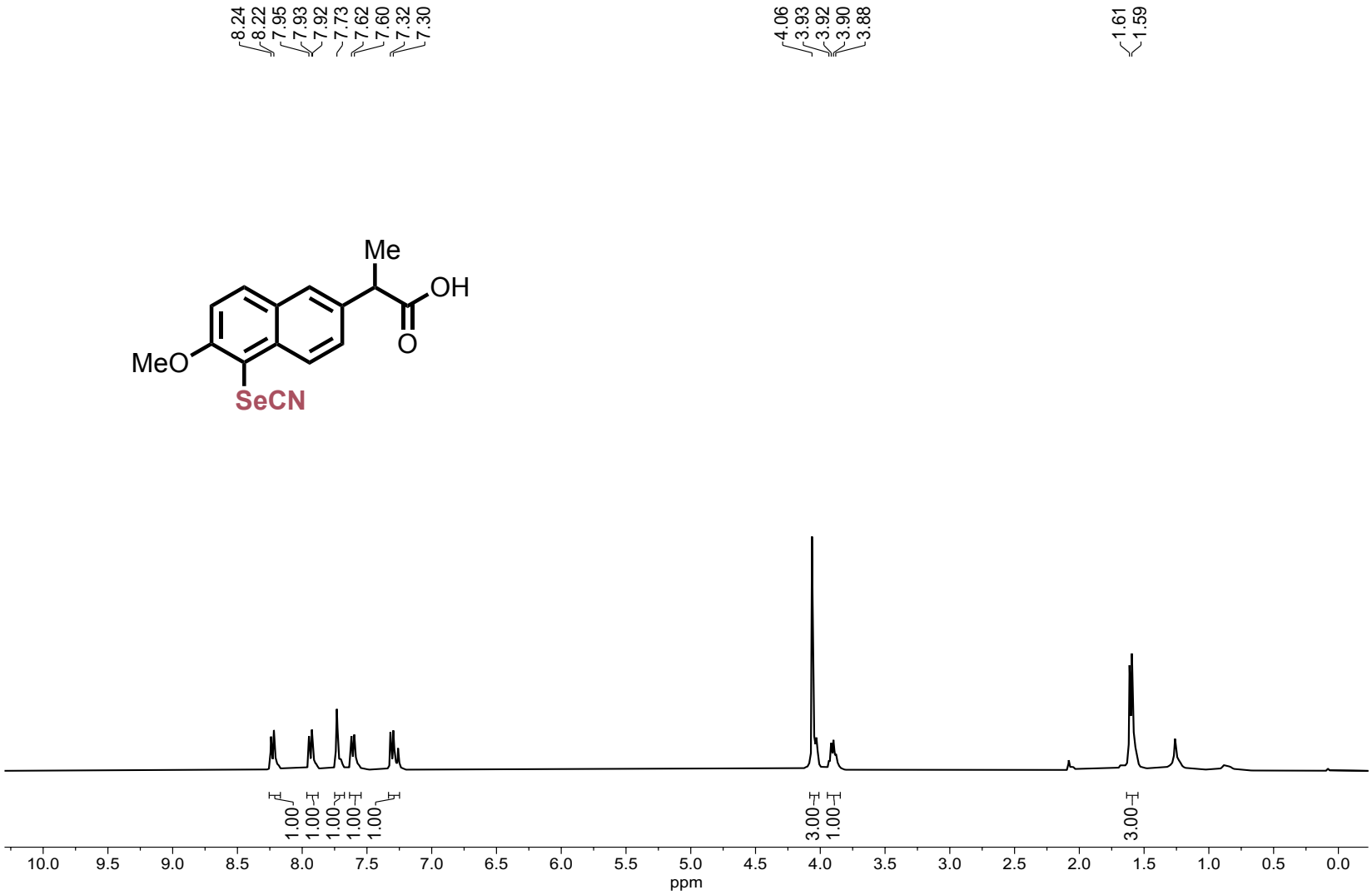


Figure S127. ^{1}H NMR ($CDCl_3$, 400 MHz) of **28b**

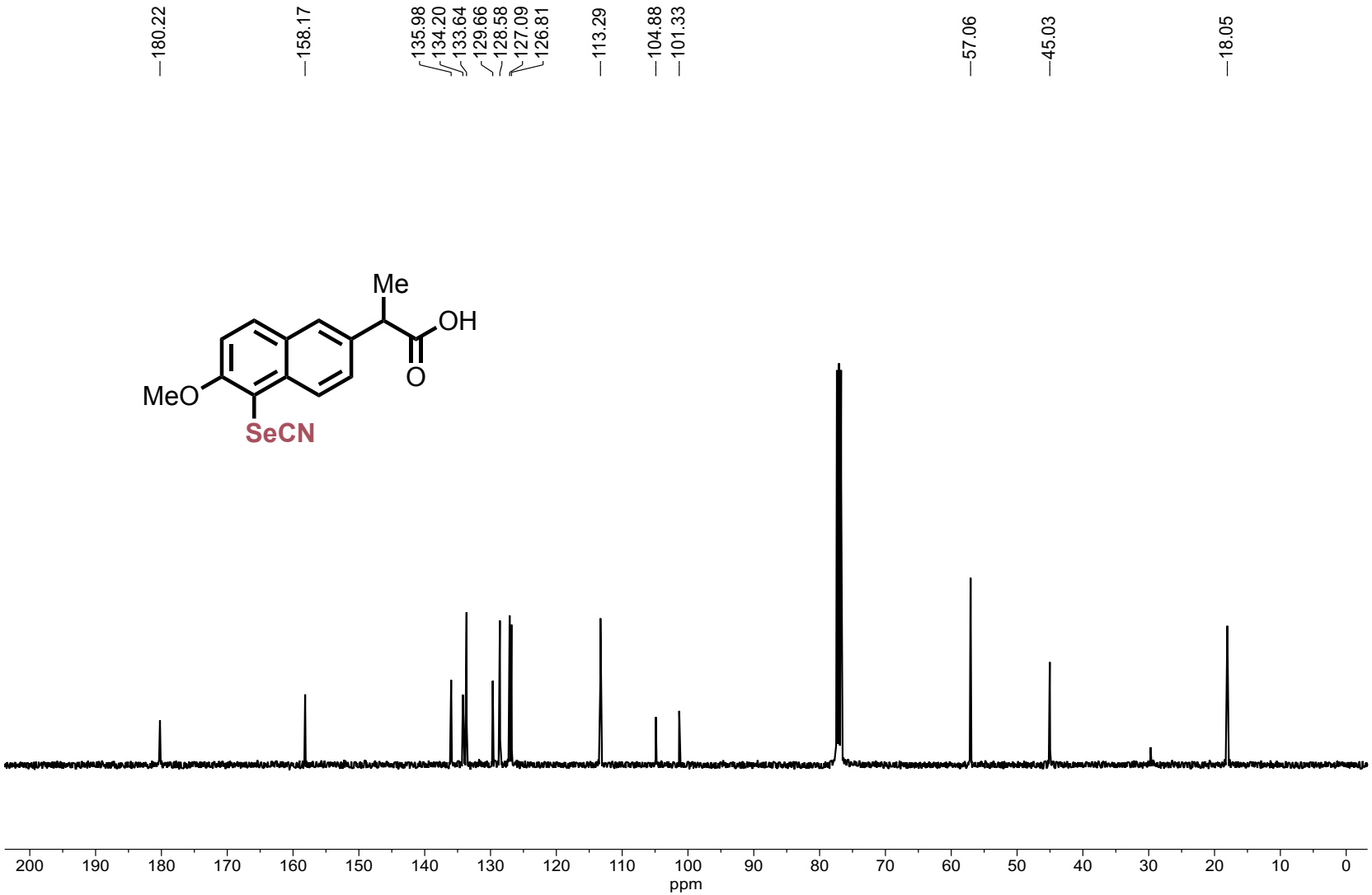


Figure S128. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **28b**

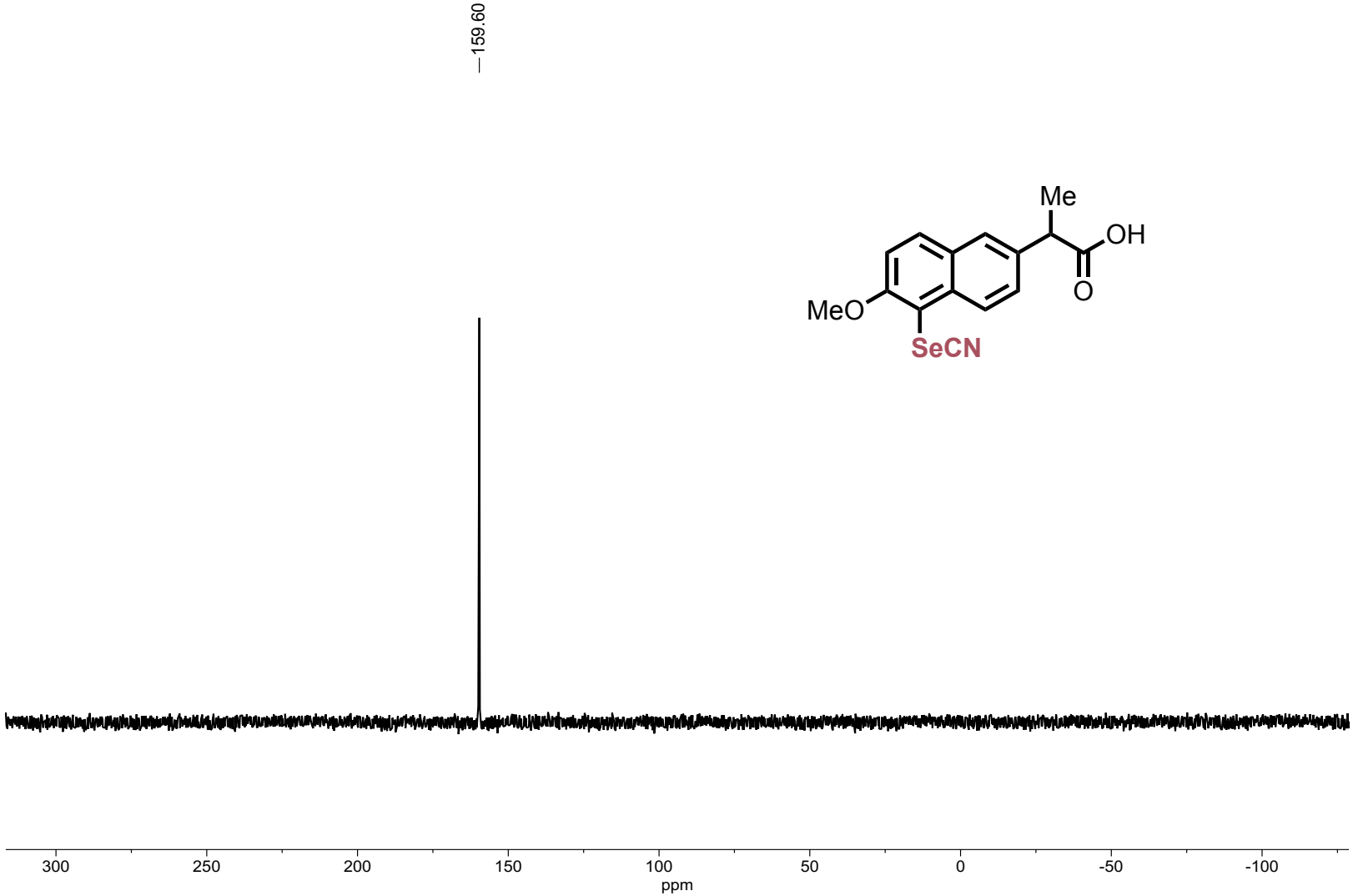


Figure S129. ^{77}Se NMR ($CDCl_3$, 76 MHz) of **28b**

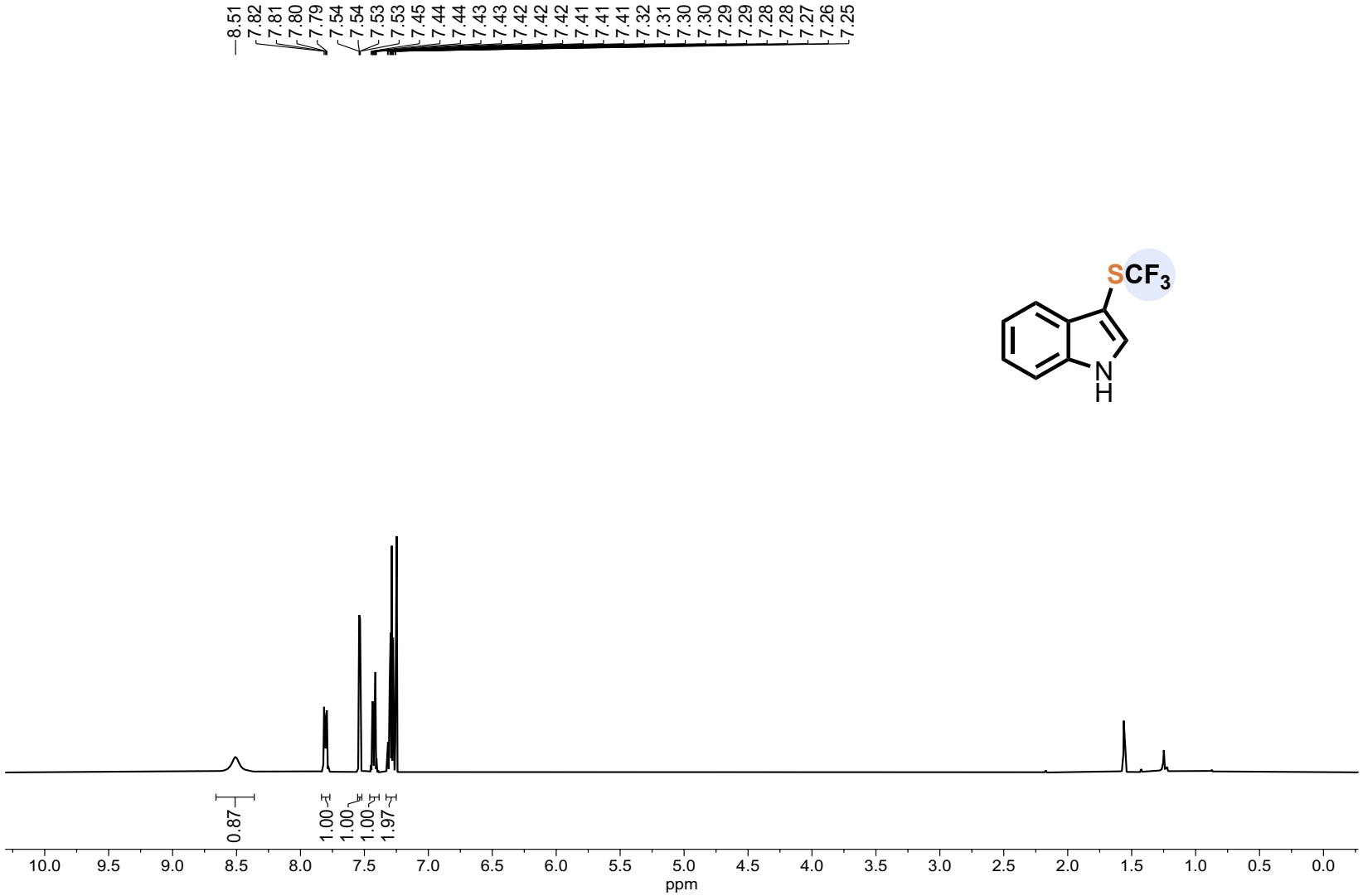


Figure S130. ^{1}H NMR ($CDCl_3$, 400 MHz) of **31a**

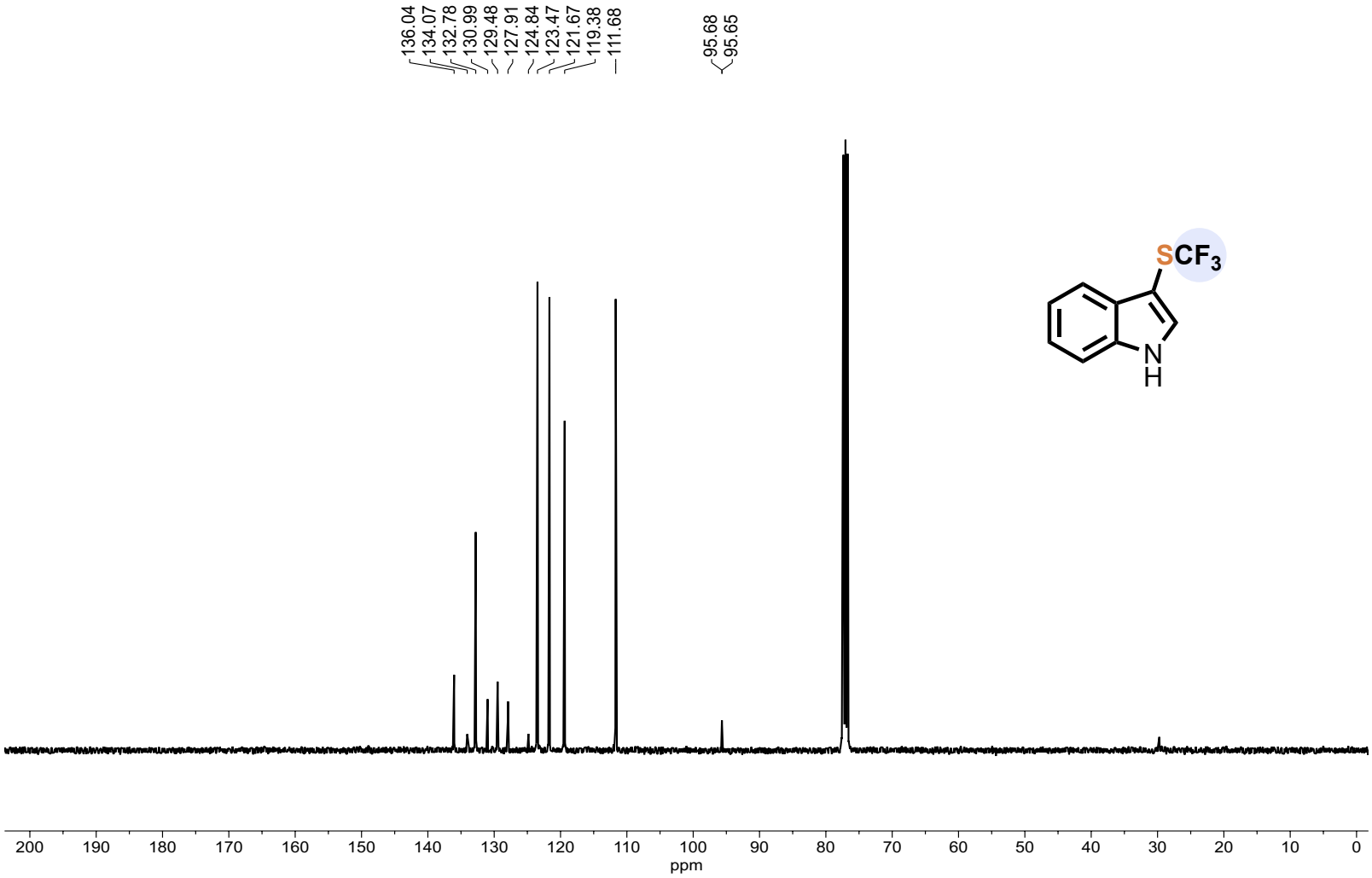


Figure S131. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **31a**

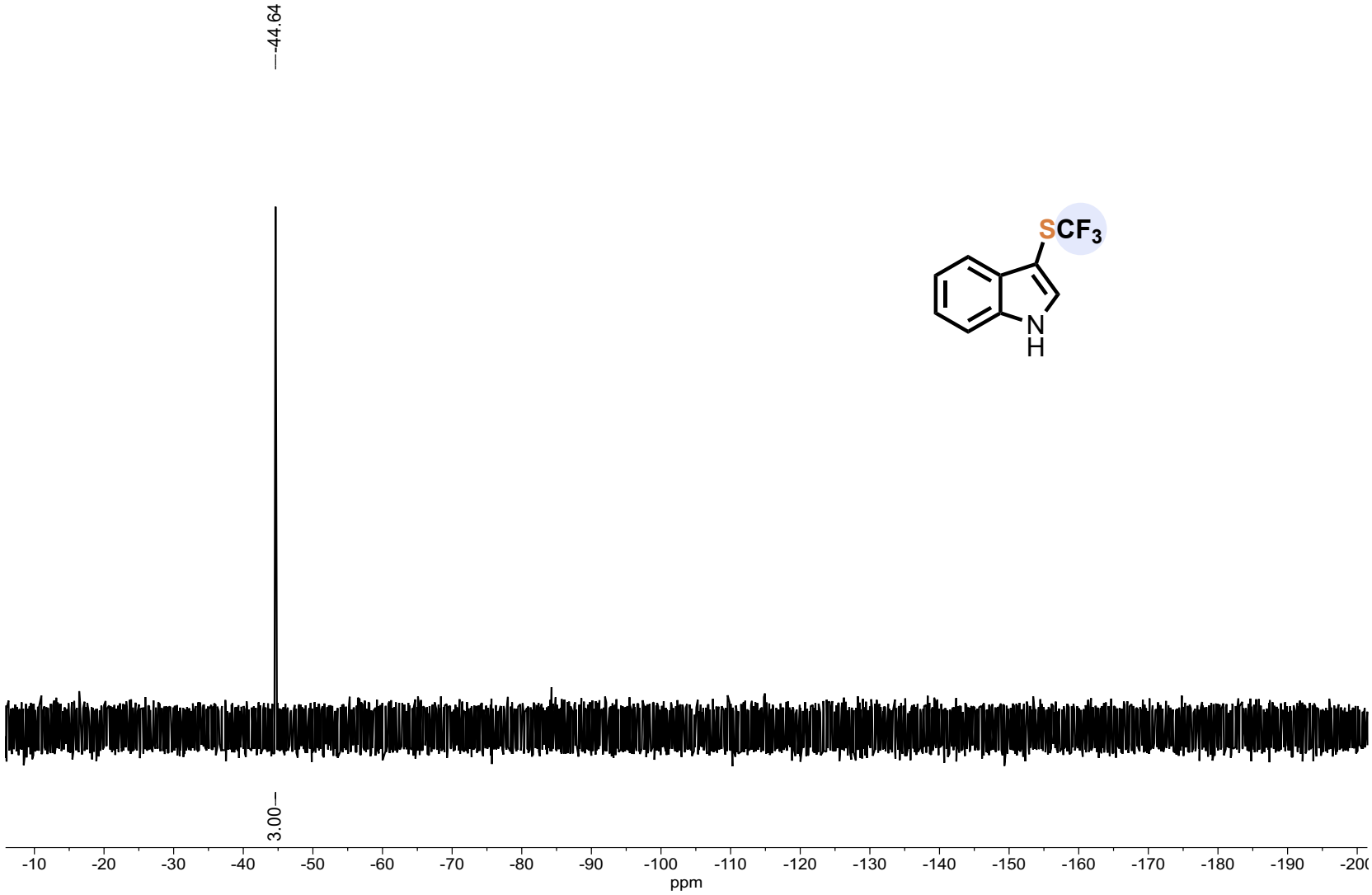


Figure S132. ^{19}F NMR ($CDCl_3$ 376.5 MHz) of **31a**

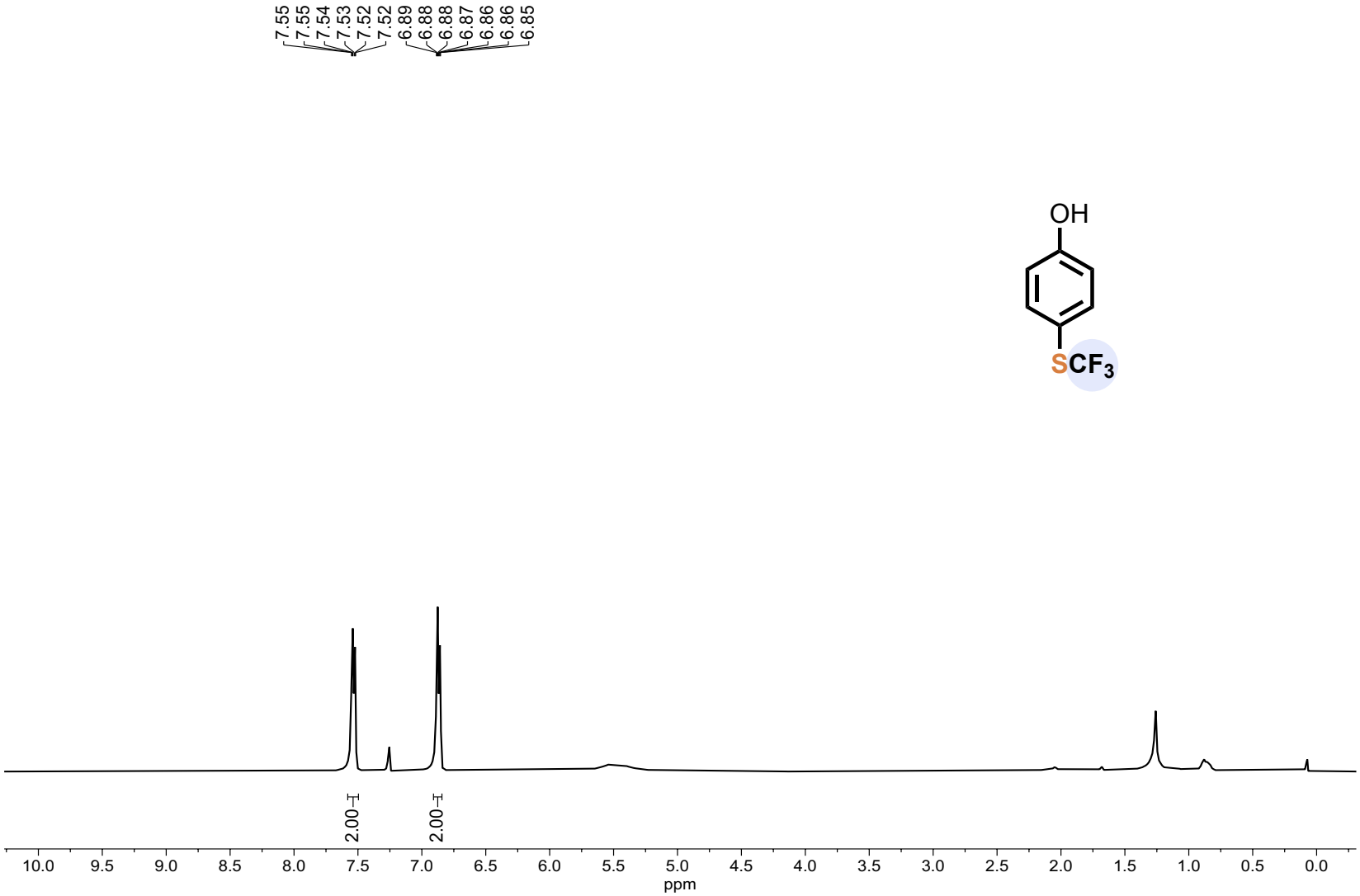


Figure S133. ^{1}H NMR ($CDCl_3$, 400 MHz) of **32a**

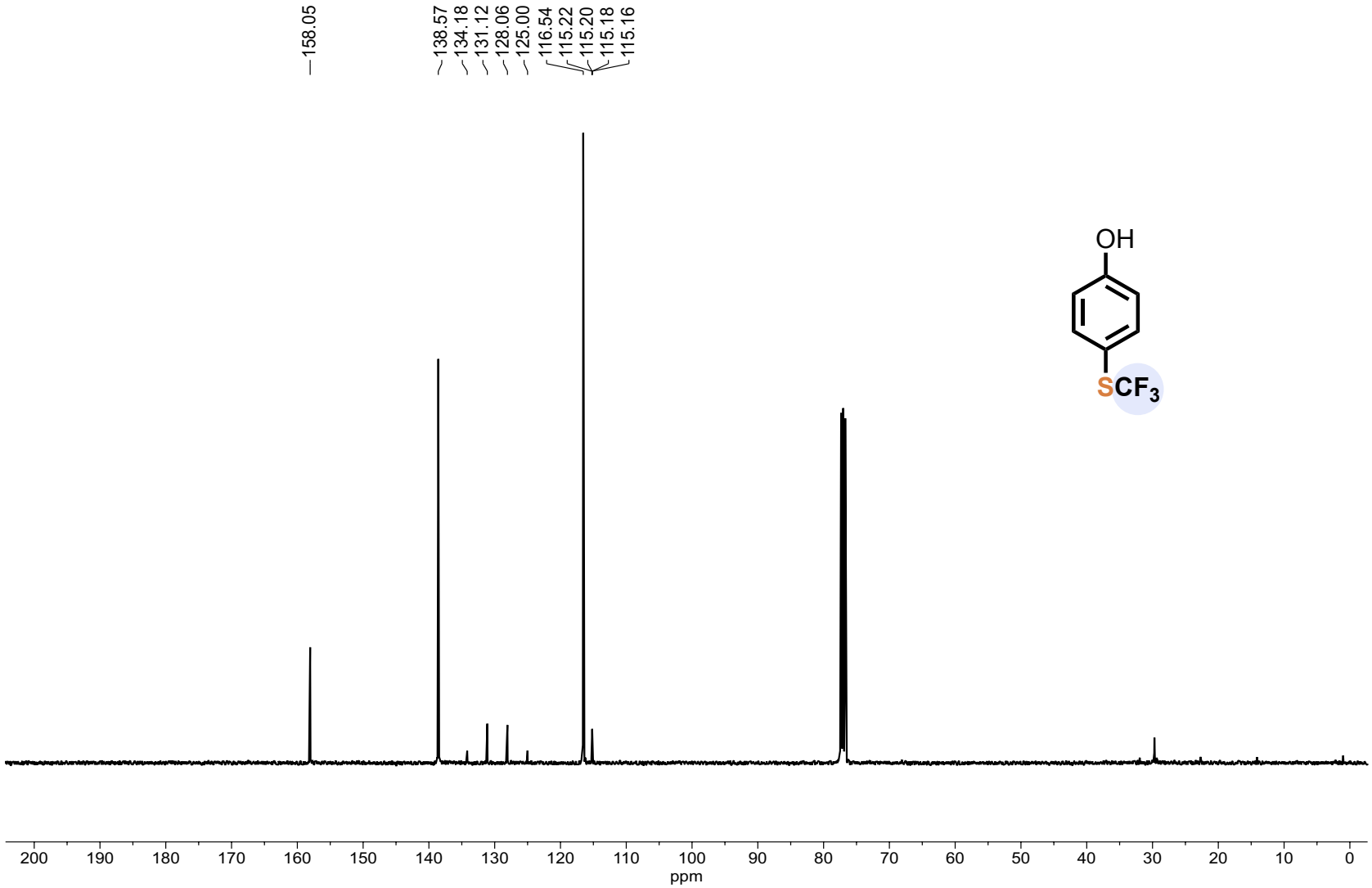


Figure S134. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **32a**

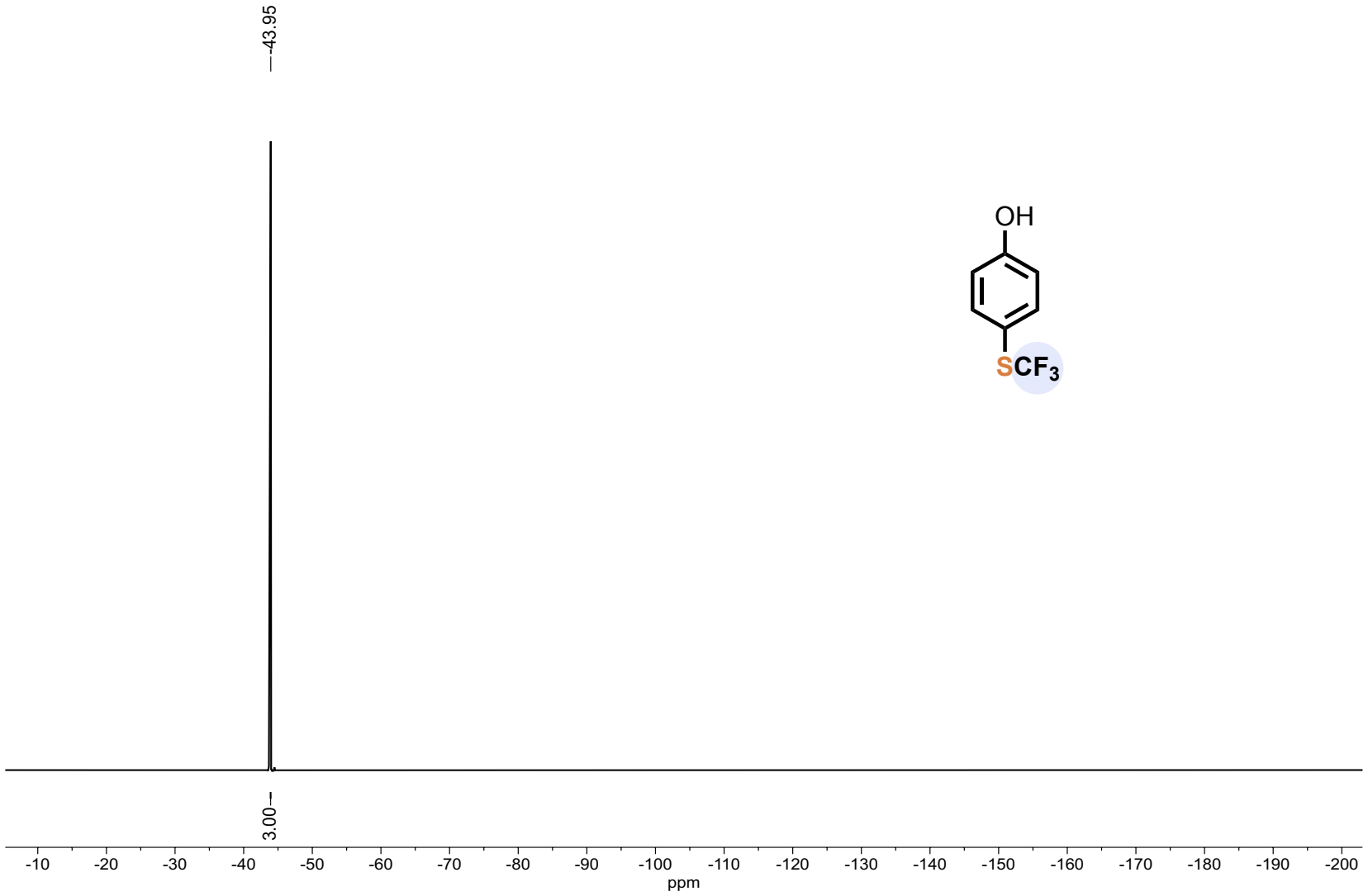


Figure S135. ^{19}F NMR ($CDCl_3$ 376.5 MHz) of **32a**

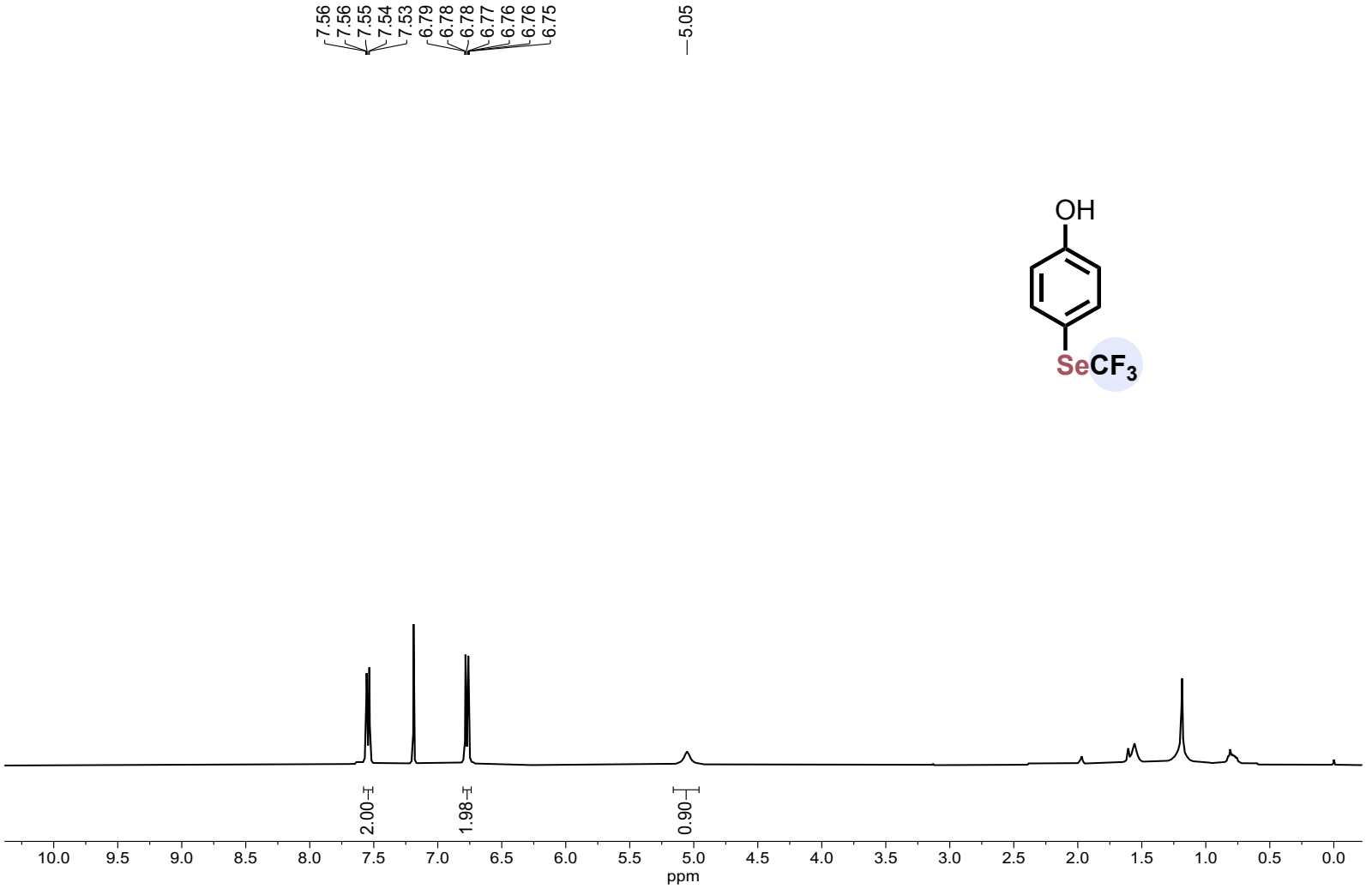


Figure S136. ^{1}H NMR ($CDCl_3$, 400 MHz) of **32b**

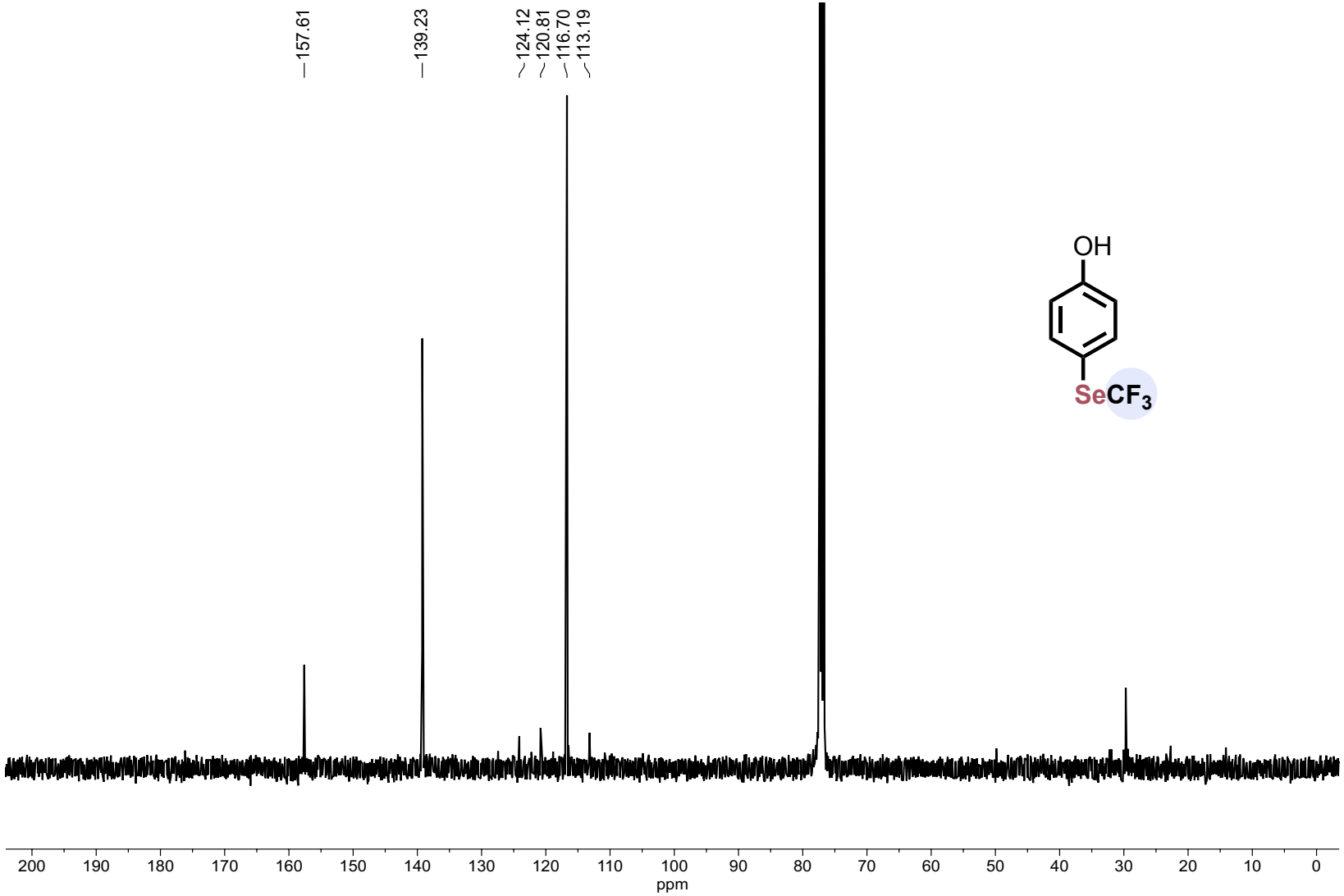


Figure S137. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **32b**

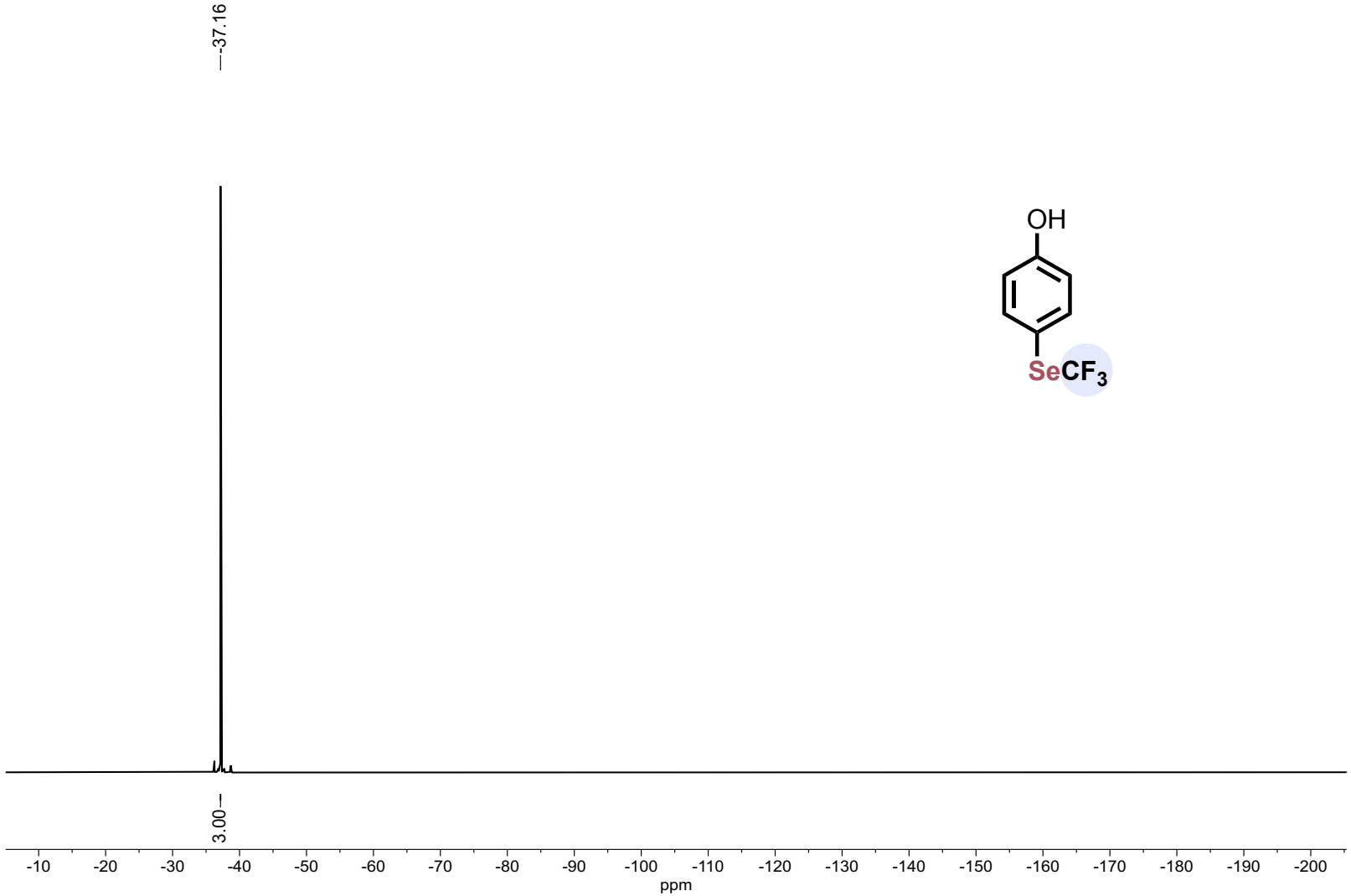


Figure S138. ^{19}F NMR ($CDCl_3$ 376.5 MHz) of **32b**

8. References

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