Direct *N*–Acylation of Sulfoximines with Carboxylic Acids Catalyzed by the B_3NO_2 Heterocycle

Hidetoshi Noda, Yasuko Asada, Masakatsu Shibasaki,* Naoya Kumagai*

Institute of Microbial Chemistry (BIKAKEN), Tokyo, Japan

mshibasa@bikaken.or.jp; nkumagai@bikaken.or.jp

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1. General Methods

1-1. Reactions and purifications

Unless otherwise noted, all reactions were carried out in an oven-dried glassware fitted with a 3-way glass stopcock under an argon atmosphere and were stirred with Teflon-coated magnetically stirred bars. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Thin layer chromatography (TLC) was performed on Merck TLC plates (0.25 mm) pre-coated with silica gel 60 F254 and visualized by UV quenching and staining with ninhydrin, $KMnO_4$, anisaldehyde or ceric ammonium molybdate solution. Flash column chromatography was performed on a Teledyne CombiFlash Rf 200 or a Biotage Isolera Spektra One.

1-2. Chracterizations

Infrared (IR) spectra were recorded on a HORIBA FT210 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ECS-400 or a Bruker AVANCE III HD400. Chemical shifts (δ) are given in ppm relative to residual solvent peaks.[1] Data for ^{1}H NMR are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), q (quartet), m (multiplet), br (broad). For ^{19}F NMR, chemical shifts were reported in the scale relative to $PhCF_3$ (δ –62.7680 ppm in $CDCl_3$) as an external reference. For ^{11}B NMR, chemical shifts were reported in the scale relative to $BF_3 \bullet Et_2O$ (δ 0.00 ppm in $CDCl_3$) as an external reference. High performance liquid chromatography (HPLC) analysis was performed on Jasco analytical instruments with dual pumps, mixer and degasser, a variable wavelength UV detector, and an auto-sampler. A column heater kept analytical HPLC columns 40 °C. The mobile phase were HPLC grade H_2O with 0.1% TFA (Buffer A) and HPLC grade CH_3CN with 0.1% TFA (Buffer B). The eluent was monitored simultaneously at 210 nm, 254 nm, 280 nm and 301 nm. Flow rate for analytical (4.6 x 150 mm) HPLC was 1.0 mL/min. Optical rotation was measured using a 1 mL cell with a 1.0 dm path length on a JASCO polarimeter P-1030. High-resolution mass spectra (ESI TOF (+)) were measured on a Thermo Fisher Scientific LTQ Orbitrap XL.

1-3. Solvents and reagents

Anhydrous diglyme were purchased from commercial suppliers. Toluene was purified by passing through a solvent purification system (Glass Contour). (*S*)-2-Phenylpropionic acid (>98% ee) was purchased from TCI. All other starting materials were used as supplied by commercial vendors or prepared by the method described in the corresponding reference.

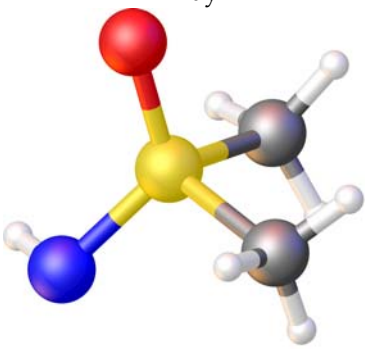
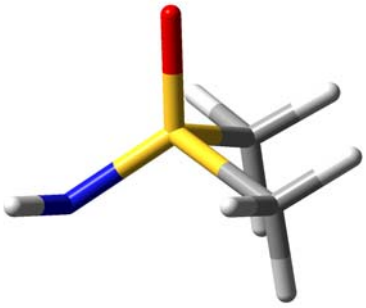
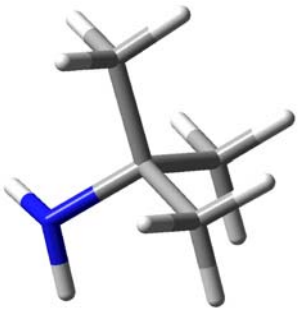
1-4. Computational investigations

All quantum chemical calculations were performed using the Gaussian 09 program.[2] Structural optimizations were conducted with very tight optimization parameters. Frequency calculations confirmed the identity of geometry minima (no imaginary frequencies). NBO calculations were performed using the NBO 3.1 program bundled with the Gaussian 09.

2. Structural and Electronical Comparison of Iminodimethyl-λ^6-sulfanone and *tert*-Butylamine

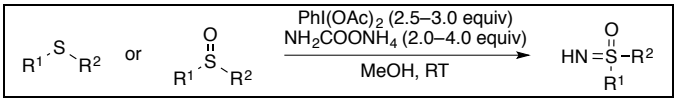
CCSD 1247986 contains the X-ray structure of iminodimethyl-λ^6-sulfanone. The ground state structures of iminodimethyl-λ^6-sulfanone and *tert*-butylamine were calculated by post-Hartree-Fock method. All optimizations were conducted at the MP2/6-311++G(2d,p) level of theory.

Table S1. Structure representation of iminodimethyl-λ^6-sulfanone and *tert*-butylamine

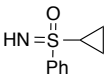
	X-ray	Calculated structure	Calculated structure
Molecular Projection			
N=S or N–C bond (Å)	1.528	1.532	1.473
NBO charge on N	—	–1.245	–0.859

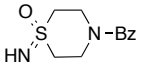
3. Preparation of Sulfoximines

All sulfoximines were prepared according to the known procedure.[3] Sulfoximines **4a**,[4] **4c**,[3a] **4d**,[3a] **4e**,[4] **4f**,[5] **4g**,[6] and **4h**[3a] were previously reported.

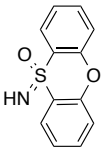


General procedure A: To a round-bottomed flask equipped with a magnetically stirred chip, were added sulfide or sulfoxide (1.0 equiv), $PhI(OAc)_2$ (2.5–3.0 equiv) and ammonium carbamate (2.0–4.0 equiv). MeOH (0.5 M) was added and the resulting suspension was stirred at RT under air for 3–6 h, during which time the gas was evolved vigorously and the mixture became homogeneous. The solvent was removed under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/EtOAc or $CHCl_3$/MeOH).

Cyclopropyl(imino)(phenyl)-λ^6-sulfanone (4b):  Prepared by the general procedure A from (cyclopropylsulfinyl)benzene (2.1 g, 12.4 mmol, 1.0 equiv), $PhI(OAc)_2$ (12.0 g, 37.2 mmol, 3.0 equiv), and ammonium carbamate (3.87 g, 49.5 mmol, 4.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a yellow oil (1.5 g, 67%). **IR** (thin film) 3268, 3061, 1646, 1445, 1304, 1223, 1187, 1096, 983, 884 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.84 (m, 2H), 7.59–7.51 (m, 1H), 7.51–7.42 (m, 2H), 2.70 (s, 1H), 2.48 (tt, *J* = 4.8, 7.9 Hz, 1H), 1.38–1.26 (m, 1H), 1.13 (dddd, *J* = 4.8, 4.9, 6.9, 10.2 Hz, 1H), 0.98 (dddd, *J* = 4.8, 6.9, 8.0, 9.1 Hz, 1H), 0.90–0.79 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.1, 132.7, 129.1, 127.8, 34.2, 6.0, 5.6; **HRMS** (ESI): *m*/*z* calc'd for $C_9H_{12}ONS$ $[M + H]^+$: 182.0634, found: 182.0633.

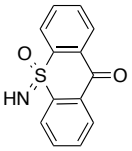
(1-Imino-1-oxido-1λ^6-thiomorpholino)(phenyl)methanone (4i):  Prepared by the general procedure A from (1-oxidothiomorpholino)(phenyl)methanone (2.18 g, 9.76 mmol, 1.0 equiv), $PhI(OAc)_2$ (9.43 g, 29.3 mmol, 3.0 equiv), and ammonium carbamate (3.04 g, 38.9 mmol, 4.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (1.88 g, 81%). **m.p.** 198–199 °C; **IR** (thin film) 3257, 2926, 2854, 1634, 1429, 1313, 1221, 1187, 1131, 1001, 945 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.40 (m, 5H), 4.01 (brs, 4H), 3.10 (brs, 4H), 2.64 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.1, 134.4, 130.7, 129.0, 127.0, 54.3, 46.1, 40.8; **HRMS** (ESI): *m*/*z* calc'd for $C_{11}H_{15}O_2N_2S$ $[M + H]^+$: 239.0849, found: 239.0847.

10-Imino-10*H*-10λ^4-phenoxathiine 10-oxide (4j): Prepared by the general procedure A from phenoxathiine 10-oxide



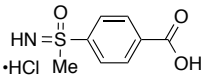
(1.20 g, 5.54 mmol, 1.0 equiv), $PhI(OAc)_2$ (5.36 g, 16.6 mmol, 3.0 equiv), and ammonium carbamate (1.70 g, 21.7 mmol, 4.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (868 mg, 68%).**m.p.** 94–97 °C; **IR** (thin film) 3252, 3072, 1590, 1462, 1439, 1323, 1270, 1223, 1132, 1079, 983, 884 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 1.6, 7.9 Hz, 2H), 7.58 (ddd, *J* = 1.6, 7.4, 8.6 Hz, 2H), 7.40–7.30 (m, 4H), 3.38 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.2, 133.7, 127.5, 124.9, 123.6, 118.8; **HRMS** (ESI): *m*/*z* calc'd for $C_{12}H_{10}O_2NS$ $[M + H]^+$: 232.0427, found: 232.0428.

10-Imino-10λ^4-thioxanthen-9(10*H*)-one 10-oxide (4k): Prepared by the general procedure A from



9*H*-thioxanthen-9-one 10-oxide (2.1 g, 9.05 mmol, 1.0 equiv), $PhI(OAc)_2$ (8.75 g, 27.1 mmol, 3.0 equiv), and ammonium carbamate (2.82 g, 36.1 mmol, 4.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (1.18 g, 54%). **m.p.** 167–168 °C; **IR** (thin film) 3242, 3068, 1664, 1586, 1573, 1442, 1305, 1231, 1132, 988, 923 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 1.2, 7.8 Hz, 2H), 8.22 (dd, *J* = 1.2, 7.9 Hz, 2H), 7.85 (ddd, *J* = 1.2, 7.6, 7.9 Hz, 2H), 7.75 (ddd, *J* = 1.2, 7.6, 7.8 Hz, 2H), 3.54 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 143.6, 134.7, 132.7, 130.1, 129.2, 123.4; **HRMS** (ESI): *m*/*z* calc'd for $C_{13}H_{10}O_2NS$ $[M + H]^+$: 244.0427, found: 244.0425.

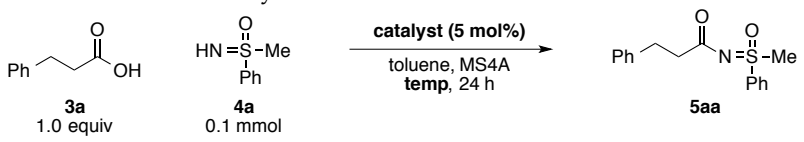
4-(*S*-Methylsulfonimidoyl)benzoic acid hydrochloride (7•HCl): Prepared by the slight modification of the general



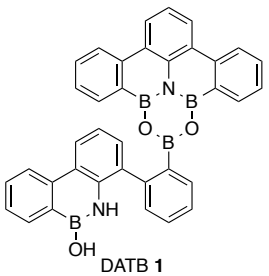
procedure A from 4-(methylthio)benzoic acid (1.92 g, 11.4 mmol, 1.0 equiv), $PhI(OAc)_2$ (9.22 g, 28.6 mmol, 2.5 equiv), and ammonium carbamate (1.78 g, 22.8 mmol, 2.0 equiv). After evaporation of MeOH, the obtained solid was filtered and washed with Et_2O. The material was treated with 4M HCl in dioxane, stirred for 16 h at RT. The suspension was filtered, washed with Et_2O and dried under reduced pressure to give the title compound as a white solid (2.22 g, 82%). Prior to the acylation (Scheme 2b), the compound was treated with 4-methylmorpholine (1 equiv) in THF, filtered and dried. **m.p.** 193–198 °C; **IR** (KBr) 3125, 3012, 2911, 2363, 1716, 1402, 1266, 1228, 1109 cm^{-1}; **^{1}H NMR** (400 MHz, CD_3OD) δ 8.33 (dd, *J* = 1.2, 7.8 Hz, 2H), 8.22 (dd, *J* = 1.2, 7.9 Hz, 2H), 7.85 (ddd, *J* = 1.2, 7.6, 7.9 Hz, 2H), 7.75 (ddd, *J* = 1.2, 7.6, 7.8 Hz, 2H), 3.54 (s, 1H); **^{13}C NMR** (100 MHz, CD_3OD) δ 161.2, 139.4, 138.4, 132.3, 130.3, 42.8; **HRMS** (ESI): *m*/*z* calc'd for $C_8H_{10}O_3NS$ $[M - Cl]^+$: 200.0376, found: 200.0374.

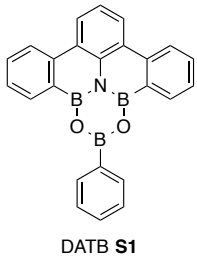
4. Optimization Study for Direct *N*-Acylation of Sulfoximine

Table S2. Optimization Studies for Direct *N*-Acylation of Sulfoximine



Entry	Catalyst	Temp (°C)	Conversion (%)
1	DATB **1**	80	0
2	DATB **1**	reflux	>90
3	DATB **S1**	reflux	40
4	—	reflux	0



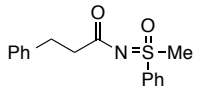


5. Scope and Limitations of Direct *N*-Acylation of Sulfoximines with Carboxylic Acids

General procedure B for Fig. 1 and 2: Prior to the reaction setup, powdered MS4A was activated by a microwave (700W, 1.5 min for 3 times). To a test tube equipped with a magnetically stirred chip was added powdered MS4A (240 mg, 800 mg/mmol), and the tube was flame-dried under reduced pressure. To this acid **3** (0.30 mmol, 1.0 equiv), sulfoximine **4** (0.30 mmol, 1.0 equiv), DATB **1** (8.6 mg, 0.015 mmol, 5 mol%), and toluene (3.0 mL, 0.1M) were added successively. The suspension was stirred under reflux for 14 h. After the addition of H_2O, the aqueous phase was extracted with EtOAc (3x). The combined organic phases were washed with sat aq $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and removed under reduced pressure. The obtained material was purified by flash column chromatography to give a pure *N*-acyl sulfoximine.

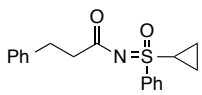
5-1. Scope of sulfoximines (Fig. 1)

***N*-(Methyl(oxo)(phenyl)-λ^6-sulfanylidene)-3-phenylpropanamide (5aa):** Prepared by the general procedure B from



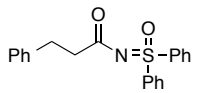
3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and imino(methyl)(phenyl)-λ^6-sulfanone **4a** (46.6 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (80.1 mg, 93%). **m.p.** 82–83 °C; **IR** (thin film) 3060, 3025, 2926, 1637, 1218, 974, 744 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.70–7.62 (m, 1H), 7.59–7.52 (m, 2H), 7.32–7.15 (m, 5H), 3.29 (s, 3H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.75 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.0, 141.5, 138.9, 133.8, 129.7, 128.6, 128.5, 127.2, 126.1, 44.2, 41.0, 31.7; **HRMS** (ESI): *m*/*z* calc'd for $C_{16}H_{18}O_2NS$ $[M + H]^+$: 288.1053, found: 288.1055.

***N*-(Cyclopropyl(oxo)(phenyl)-λ^6-sulfanylidene)-3-phenylpropanamide (5ab):** Prepared by the general procedure B



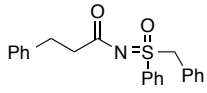
from 3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and cyclopropyl(imino)(phenyl)-λ^6-sulfanone **4b** (54.4 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (85.5 mg, 91%). **m.p.** 101–103 °C; **IR** (thin film) 3059, 3025, 2924, 1642, 1446, 1218, 884, 836 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83–7.76 (m, 2H), 7.69–7.62 (m, 1H), 7.59–7.52 (m, 2H), 7.35–7.28 (m, 2H), 7.28–7.17 (m, 3H), 3.00 (t, *J* = 7.7 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 2H), 2.65 (tt, *J* = 4.8, 7.9 Hz, 1H), 1.64–1.55 (m, 1H), 1.34–1.17 (m, 2H), 1.04–0.96 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.3, 141.6, 139.2, 133.3, 129.6, 128.6, 128.4, 127.2, 126.0, 40.8, 33.2, 31.7, 6.7, 5.3; **HRMS** (ESI): *m*/*z* calc'd for $C_{18}H_{20}O_2NS$ $[M + H]^+$: 314.1209, found: 314.1216.

***N*-(Oxodiphenyl-λ^6-sulfanylidene)-3-phenylpropanamide (5ac):** Prepared by the general procedure B from



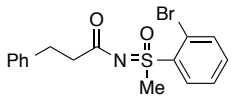
3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and iminodiphenyl-λ^6-sulfanone **5c** (65.2 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a colorless oil (71.2 mg, 68%). **IR** (thin film) 3061, 3025, 2919, 2360, 1646, 1447, 1221, 1094, 995, 837 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 4H), 7.65–7.57 (m, 2H), 7.57–7.48 (m, 4H), 7.40–7.22 (m, 5H), 3.09 (t, *J* = 7.7 Hz, 2H), 2.90 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.6, 141.6, 139.8, 133.3, 129.6, 128.6, 128.5, 127.7, 126.1, 41.0, 31.7; **HRMS** (ESI): *m*/*z* calc'd for $C_{21}H_{20}O_2NS$ $[M + H]^+$: 350.1209, found: 350.1210.

***N*-(Benzyl(oxo)(phenyl)-λ^6-sulfanylidene)-3-phenylpropanamide (5ad):** Prepared by the general procedure B from



3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and benzyl(imino)(phenyl)-λ^6-sulfanone **4d** (69.4 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (76.3 mg, 70%). **m.p.** 147–148 °C; **IR** (thin film) 3061, 2926, 2360, 1640, 1214, 837 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63–7.55 (m, 1H), 7.55–7.49 (m, 2H), 7.43–7.39 (m, 2H), 7.33–7.14 (m, 8H), 6.94–6.87 (m, 2H), 4.74 (s, 2H), 3.02 (t, *J* = 7.3 Hz, 2H), 2.78 (t, *J* = 7.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.2, 141.6, 135.4, 133.8, 131.3, 129.2, 129.1, 128.6, 128.6, 128.6, 128.5, 127.4, 126.0, 62.0, 41.2, 31.7; **HRMS** (ESI): *m*/*z* calc'd for $C_{22}H_{21}O_2NNaS$ $[M + Na]^+$: 386.1185, found: 386.1186.

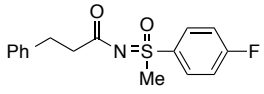
***N*-((2-Bromophenyl)(methyl)(oxo)-λ^6-sulfanylidene)-3-phenylpropanamide (5ae):** Prepared by the general procedure



B from 3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and (2-bromophenyl)(imino)(methyl)-λ^6-sulfanone **4e** (70.2 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a colorless oil (92.3 mg, 84%). **IR** (thin film) 3061, 3025, 2927, 1643, 1220, 755 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 1.7, 8.0 Hz, 1H), 7.76 (dd, *J* = 1.2, 7.9 Hz, 1H), 7.59 (ddd, *J* = 1.2, 7.7, 8.0 Hz, 1H), 7.49 (ddd, *J* = 1.7, 7.7, 8.0 Hz, 1H), 7.32–7.15 (m, 5H), 3.47 (s, 3H), 2.96 (t, *J*

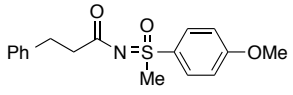
= 7.7 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.3, 141.6, 138.0, 135.8, 134.7, 132.0, 128.6, 128.5, 128.5, 126.0, 119.3, 41.8, 40.7, 31.5; **HRMS** (ESI): *m*/*z* calc'd for $C_{16}H_{17}O_2NBrS$ [M + H]$^+$: 366.0158, found: 366.0158.

***N*-((4-Fluorophenyl)(methyl)(oxo)-λ^6-sulfanylidene)-3-phenylpropanamide (5af):** Prepared by the general procedure



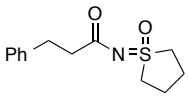
B from 3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and (4-fluorophenyl)(imino)(methyl)-λ^6-sulfanone **4f** (52.0 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (80.6 mg, 88%). **m.p.** 68–69 °C; **IR** (thin film) 3063, 3025, 2927, 1639, 1588, 1493, 1219, 834 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.77 (m, 2H), 7.34–7.25 (m, 2H), 7.25–7.15 (m, 5H), 3.27 (s, 3H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.9, 165.9 (d, *J* = 256.7 Hz), 134.7 (d, *J* = 3.2 Hz), 141.4, 130.1 (d, *J* = 9.6 Hz), 128.6, 128.5, 126.1, 117.1 (d, *J* = 22.9 Hz), 44.4, 40.9, 31.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –103.5; **HRMS** (ESI): *m*/*z* calc'd for $C_{16}H_{16}O_2NFNaS$ [M + Na]$^+$: 328.0778, found: 328.0772.

***N*-((4-Methoxyphenyl)(methyl)(oxo)-λ^6-sulfanylidene)-3-phenylpropanamide (5ag):** Prepared by the general



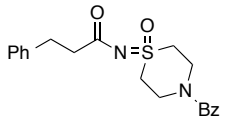
procedure B from 3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and (4-methoxyphenyl)(imino)(methyl)-λ^6-sulfanone **4g** (55.6 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a colorless oil (85.6 mg, 90%). **IR** (thin film) 3024, 2926, 2840, 1635, 1592, 1496, 1260, 1215, 1101, 1023, 831 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80–7.74 (m, 2H), 7.33–7.15 (m, 5H), 7.03–6.97 (m, 2H), 3.88 (s, 3H), 3.27 (s, 3H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.73 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.9, 163.9, 141.6, 129.9, 129.4, 128.6, 128.5, 126.0, 115.0, 55.9, 44.6, 41.1, 31.8; **HRMS** (ESI): *m*/*z* calc'd for $C_{17}H_{19}O_3NNaS$ [M + Na]$^+$: 340.0978, found: 340.0969.

***N*-(1-Oxidotetrahydro-1λ^6-thiophen-1-ylidene)-3-phenylpropanamide (5ah):** Prepared by the general procedure B



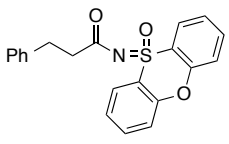
from 3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography ($CHCl_3$/MeOH) and isolated as a colorless oil (70.1 mg, 93%). **IR** (thin film) 3024, 2949, 1626, 1361, 1293, 1207, 1021, 903 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29–7.15 (m, 5H), 3.56–3.42 (m, 2H), 3.27–3.14 (m, 2H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.40–2.24 (m, 2H), 2.22–2.14 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.7, 141.4, 128.5, 128.4, 126.1, 52.6, 40.5, 31.8, 23.7; **HRMS** (ESI): *m*/*z* calc'd for $C_{13}H_{17}O_2NNaS$ [M + Na]$^+$: 274.0872, found: 274.0866.

***N*-(4-Benzoyl-1-oxido-1λ^6-thiomorpholin-1-ylidene)-3-phenylpropanamide (5ai):** Prepared by the general procedure



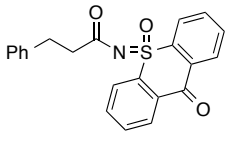
B from 3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and (1-imino-1-oxido-1λ^6-thiomorpholino)(phenyl)methanone **4i** (71.5 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a colorless oil (104 mg, 94%). **IR** (thin film) 3024, 3001, 2931, 1637, 1424, 1312, 1263, 1207, 1024, 949 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55–7.43 (m, 3H), 7.42–7.37 (m, 2H), 7.32–7.16 (m, 5H), 4.13 (brs, 2H), 3.60 (brs, 4H), 3.18 (brs, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.4, 171.1, 141.2, 133.9, 131.0, 129.1, 128.6, 128.5, 127.1, 126.2, 50.7, 44.8, 40.7, 31.7; **HRMS** (ESI): *m*/*z* calc'd for $C_{20}H_{22}O_3N_2NaS$ [M + Na]$^+$: 393.1243, found: 393.1240.

***N*-(10-Oxido-10λ^4-phenoxathiin-10-ylidene)-3-phenylpropanamide (5aj):** Prepared by the general procedure B from



3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and 10-imino-10*H*-10λ^4-phenoxathiine 10-oxide **4j** (69.4 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (79.6 mg, 73%). **m.p.** 104–105 °C; **IR** (thin film) 3062, 3025, 2923, 2359, 1634, 1591, 1465, 1439, 1336, 1272, 1233, 1085, 887, 847 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 1.6, 8.0 Hz, 2H), 7.66 (ddd, *J* = 1.6, 7.2, 8.7 Hz, 2H), 7.43–7.34 (m, 4H), 7.25–7.09 (m, 3H), 7.08–7.01 (m, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.7, 151.8, 141.2, 134.9, 128.4, 128.4, 125.9, 125.0, 124.7, 121.3, 118.6, 40.6, 31.5; **HRMS** (ESI): *m*/*z* calc'd for $C_{21}H_{17}O_3NNaS$ [M + Na]$^+$: 386.0821, found: 386.0811.

***N*-(10-Oxido-9-oxo-9H-10λ^4-thioxanthen-10-ylidene)-3-phenylpropanamide (5ak):** Prepared by the general procedure



B from 3-phenylpropanoic acid **3a** (45.1 mg, 0.30 mmol, 1.0 equiv) and 10-imino-10λ^4-thioxanthen-9(10*H*)-one 10-oxide **4k** (73.0 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (84.4 mg, 75%). **m.p.** 95–96 °C; **IR** (thin film) 3085, 3063, 3025, 2927, 1676, 1634, 1574, 1441, 1298, 1230, 1133, 925 cm^{-1}; **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 8.38–8.34 (m, 2H), 8.18–8.09 (m, 2H), 7.89–7.75 (m, 4H), 7.21–7.08 (m, 3H), 7.08–6.99 (m, 2H), 2.80 (t, *J* = 7.7 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.5, 177.9, 141.0, 138.7, 134.3, 133.8, 131.9, 128.9, 128.4, 128.3, 125.9, 125.0, 40.6, 31.5; **HRMS** (ESI): *m*/*z* calc'd for $C_{22}H_{18}O_3NS$ [M + H]$^+$: 376.1002, found: 376.0999.

5-2. Scope of carboxylic acids (Fig. 2)

***N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)-1-tosylpiperidine-4-carboxamide (5bh):** Prepared by the general procedure B from 1-tosylpiperidine-4-carboxylic acid **4b** (85.0 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (102 mg, 90%). **m.p.** 129–130 °C; **IR** (thin film) 2951, 2927, 2853, 1623, 1335, 1301, 1209, 1160, 929, 905 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.71–3.60 (m, 2H), 3.54–3.39 (m, 2H), 3.27–3.14 (m, 2H), 2.46–2.13 (m, 10H), 2.01–1.90 (m, 2H), 1.82–1.72 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.9, 143.5, 133.4, 129.7, 127.8, 52.6, 45.8, 43.9, 28.2, 23.7, 21.6; **HRMS** (ESI): *m*/*z* calc'd for $C_{17}H_{24}O_4N_2NaS_2$ [M + Na]$^+$: 407.1070, found: 407.1070.

***N*-(1-Oxidotetrahydro-1λ^6-thiophen-1-ylidene)-2-phenylbutanamide (5ch):** Prepared by the general procedure B from 2-phenylbutanoic acid **5c** (49.3 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a colorless oil (69.3 mg, 87%). **IR** (thin film) 3025, 2962, 2873, 1627, 1452, 1269, 1209, 1175, 1080, 903 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.32–7.24 (m, 2H), 7.24–7.17 (m, 1H), 3.55–3.39 (m, 3H), 3.24–3.08 (m, 2H), 2.34–2.21 (m, 2H), 2.21–2.04 (m, 3H), 1.81–1.74 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.9, 140.8, 128.4, 128.2, 126.8, 57.3, 52.5, 52.3, 27.1, 23.8, 23.6, 12.5; **HRMS** (ESI): *m*/*z* calc'd for $C_{14}H_{19}O_2NNaS$ [M + Na]$^+$: 288.1029, found: 288.1031.

(*E*)-2-Methyl-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)-3-phenylacrylamide (5dh): Prepared by the general procedure B from (*E*)-2-methyl-3-phenylacrylic acid **3d** (48.7 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (71.1 mg, 90%). **m.p.** 95–96 °C; **IR** (thin film) 2952, 1596, 1446, 1258, 1208, 1132, 929, 904, 842 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (q, *J* = 1.4 Hz, 1H), 7.45–7.33 (m, 4H), 7.33–7.24 (m, 1H), 3.75–3.59 (m, 2H), 3.38–3.21 (m, 2H), 2.44–2.23 (m, 4H), 2.13 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 137.8, 136.8, 133.7, 129.8, 128.4, 128.0, 52.7, 23.9, 14.1.; **HRMS** (ESI): *m*/*z* calc'd for $C_{14}H_{17}O_2NNaS$ [M + Na]$^+$: 286.0872, found: 286.0870.

***N*-(1-Oxidotetrahydro-1λ^6-thiophen-1-ylidene)furan-2-carboxamide (5eh):** Prepared by the general procedure B from furan-2-carboxylic acid **3e** (33.6 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (51.1 mg, 80%). **m.p.** 92–94 °C; **IR** (thin film) 3132, 3010, 2950, 1624, 1473, 1315, 1209, 1182, 1133, 954, 906 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 0.9, 1.7 Hz, 1H), 7.16 (dd, *J* = 0.9, 3.4 Hz, 1H), 6.47 (dd, *J* = 1.7, 3.4 Hz, 1H), 3.81–3.64 (m, 2H), 3.40–3.27 (m, 2H), 2.44–2.25 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 149.8, 145.7, 116.9, 111.9, 53.1, 23.8; **HRMS** (ESI): *m*/*z* calc'd for $C_9H_{12}O_3NS$ [M + H]$^+$: 214.0532, found: 214.0534.

3-Methyl-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)thiophene-2-carboxamide (5fh): Prepared by the general procedure B from 3-methylthiophene-2-carboxylic acid **3f** (42.7 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (57.6 mg, 79%). **m.p.** 102–105 °C; **IR** (thin film) 3085, 3027, 2966, 1607, 1536, 1410, 1281, 1263, 1196, 1116, 1079, 910 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 5.0 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 3.76–3.64 (m, 2H), 3.36–3.29 (m, 2H), 2.57 (s, 3H), 2.44–2.22 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 144.7, 133.2, 132.1, 129.1, 53.0, 23.9, 16.2; **HRMS** (ESI): *m*/*z* calc'd for $C_{10}H_{13}O_2NNaS_2$ [M + Na]$^+$: 266.0280, found: 266.0282.

2-Methyl-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)quinoline-6-carboxamide (5gh): Prepared by the general procedure B from 2-methylquinoline-6-carboxylic acid **3g** (56.2 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography ($CHCl_3$/MeOH) and isolated as a white solid (66.6 mg, 77%). **m.p.** 177–178 °C; **IR** (thin film) 3007, 2951, 1623, 1609, 1591, 1290, 1270, 1202, 1118, 903, 838 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.9 Hz, 1H), 8.37 (dd, *J* = 1.9, 8.8 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 3.83–3.69 (m, 2H), 3.44–3.31 (m, 2H), 2.76 (s, 3H), 2.47–2.27 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 161.1, 149.7, 137.6, 132.6, 130.2, 129.5, 128.5, 125.8, 122.6, 52.9, 25.7, 23.9; **HRMS** (ESI): *m*/*z* calc'd for $C_{15}H_{17}O_2N_2S$ $[M + H]^+$: 289.1005, found: 289.1004.

***N*-(1-Oxidotetrahydro-1λ^6-thiophen-1-ylidene)-1*H*-indole-2-carboxamide (5hh):** Prepared by the general procedure B from 1*H*-indole-2-carboxylic acid **3h** (48.3 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography ($CHCl_3$/MeOH) and isolated as a brown solid (64.5 mg, 82%). **m.p.** 187–192 °C; **IR** (thin film) 3279, 3056, 3011, 2948, 1590, 1523, 1421, 1382, 1339, 1310, 1254, 1213, 989, 912, 825 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.67 (dt, *J* = 1.0, 8.1 Hz, 1H), 7.41 (ddd, *J* = 1.0, 1.0, 8.3 Hz, 1H), 7.34–7.19 (m, 2H), 7.12 (ddd, *J* = 1.0, 8.1, 8.3 Hz, 1H), 3.78–3.71 (m, 2H), 3.44–3.30 (m, 2H), 2.41–2.29 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 136.8, 133.2, 128.0, 125.0, 122.6, 120.6, 112.0, 107.9, 53.1, 23.9; **HRMS** (ESI): *m*/*z* calc'd for $C_{13}H_{14}O_2N_2NaS$ $[M + Na]^+$: 285.0668, found: 285.0670.

(*E*)-4-((4-(Dimethylamino)phenyl)diazenyl)-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)benzamide (5ih): Prepared by the general procedure B from *p*-methyl red **3i** (80.8 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a red solid (92.2 mg, 83%). **m.p.** 249–251 °C; **IR** (thin film) 2955, 2920, 2852, 1606, 1367, 1292, 1197, 1138, 1079, 938, 902, 813 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27–8.19 (m, 2H), 7.95–7.88 (m, 2H), 7.87–7.81 (m, 2H), 6.80–6.74 (m, 2H), 3.81–3.69 (m, 2H), 3.42–3.31 (m, 2H), 3.11 (s, 6H), 2.46–2.29 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 155.3, 153.1, 143.7, 135.6, 130.5, 125.8, 121.8, 111.8, 52.9, 40.5, 23.9; **HRMS** (ESI): *m*/*z* calc'd for $C_{19}H_{23}O_2N_4S$ $[M + H]^+$: 371.1536, found: 371.1538.

***N*-(1-Oxidotetrahydro-1λ^6-thiophen-1-ylidene)-2-oxo-2*H*-chromene-3-carboxamide (5jh):** Prepared by the general procedure B from coumarin-3-carboxylic acid **3j** (57.0 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (69.0 mg, 79%). **m.p.** 151–153 °C; **IR** (thin film) 3038, 3013, 2950, 1741, 1625, 1608, 1313, 1264, 1251, 1210, 1140, 1031, 1019, 903, 846 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.64–7.52 (m, 2H), 7.37–7.23 (m, 2H), 3.84–3.69 (m, 2H), 3.39–3.19 (m, 2H), 2.45–2.29 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 157.7, 155.1, 147.3, 133.7, 129.4, 124.7, 122.8, 118.5, 116.7, 52.6, 23.9; **HRMS** (ESI): *m*/*z* calc'd for $C_{14}H_{13}O_4NNaS$ $[M + Na]^+$: 314.0457, found: 314.0455.

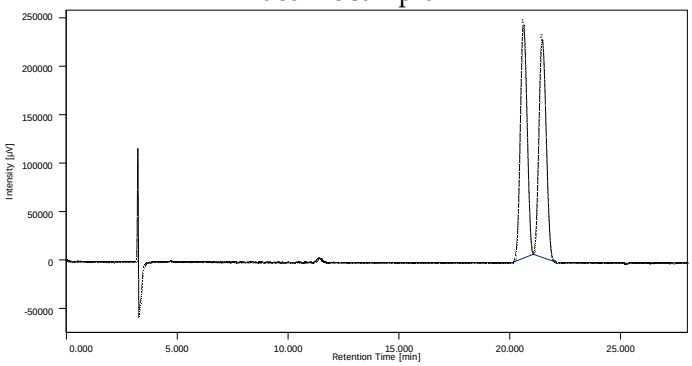
(3-((1-Oxidotetrahydro-1λ^6-thiophen-1-ylidene)carbamoyl)phenyl)boronic acid MIDA ester (5kh): Prepared by the general procedure B from 3-carboxyphenylboronic acid MIDA ester **3k** (83.1 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography ($CHCl_3$/MeOH) and isolated as a white solid (82.8 mg, 73%). **m.p.** 135 °C (decomp); **IR** (thin film) 3012, 2954, 2930, 1766, 1615, 1455, 1411, 1299, 1212, 1037, 1004, 956, 902, 861 cm^{-1}; **^{1}H NMR** (400 MHz, CD_3CN) δ 8.19 (dd, *J* = 1.8, 1.8 Hz, 1H), 8.11 (ddd, *J* = 1.6, 1.8, 7.6 Hz, 1H), 7.66 (ddd, *J* = 1.6, 1.8, 7.4 Hz, 1H), 7.46 (dd, *J* = 7.4, 7.6 Hz, 1H), 4.08 (d, *J* = 17.1 Hz, 2H), 3.91 (d, *J* = 17.1 Hz, 2H), 3.70–3.57 (m, 2H), 3.35–3.28 (m, 2H), 2.51 (s, 3H), 2.40–2.16 (m, 4H); **^{13}C NMR** (100 MHz, CD_3CN) δ 175.5, 169.5, 137.1, 136.4, 133.9, 131.0, 128.8, 62.9, 53.8, 48.6, 24.3: The signal of the boron-bound carbon was not detected due to quadrupolar relaxation of boron; **^{11}B NMR** (128 MHz, CD_3CN) δ 11.5; **HRMS** (ESI): *m*/*z* calc'd for $C_{16}H_{19}O_6N_2BNaS$ $[M + Na]^+$: 401.0949, found: 401.0960.

4-(1,3-Dioxolan-2-yl)-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)benzamide (5lh): Prepared by the general procedure B from 4-(1,3-dioxolan-2-yl)benzoic acid **3l** (58.2 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (73.5 mg, 83%). **m.p.** 114–121 °C; **IR** (thin film) 2952, 2884, 1616, 1574, 1410, 1312, 1291, 1208, 1134, 1081, 1017, 933, 827 cm^{-1}; **^{1}H NMR** (400 MHz, C_6D_6) δ 8.59–8.51 (m, 2H), 7.66–7.58 (m, 2H), 5.73 (s, 1H), 3.62–3.41 (m, 4H), 3.17–2.98 (m, 2H), 2.71–2.54 (m, 2H), 1.36–1.18 (m, 4H); **^{13}C NMR** (100 MHz, C_6D_6) δ 174.2, 142.9, 137.2, 129.9, 126.7, 103.5, 65.2, 52.3, 23.3; **HRMS** (ESI): *m*/*z* calc'd for $C_{14}H_{17}O_4NNaS$ $[M + Na]^+$: 318.0770, found: 318.0771.

4-Formyl-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)benzamide (5mh): Prepared by the general procedure B from 4-formylbenzoic acid **3m** (45.1 mg, 0.30 mmol, 1.0 equiv) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a white solid (60.3 mg, 80%). **m.p.** 86–89 °C; **IR** (thin film) 3013, 2951, 2848, 2736, 1702, 1618, 1272, 1201, 1134, 929, 904, 815 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.27 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 3.81–3.67 (m, 2H), 3.45–3.31 (m, 2H), 2.49–2.27 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.1, 173.9, 140.5, 138.7, 130.0, 129.5, 52.9, 23.9; **HRMS** (ESI): *m*/*z* calc'd for $C_{12}H_{13}O_3NNaS$ $[M + Na]^+$: 274.0508, found: 274.0513.

***(S)*-*N*-(*1*-Oxidotetrahydro-1λ^6-thiophen-1-ylidene)-2-phenylpropanamide (5nh):** Prepared by the general procedure B from (*S*)-2-phenylpropanoic acid **3n** (45.4 mg, 0.30 mmol, 1.0 equiv, >98% ee) and 1-iminotetrahydro-1*H*-1λ^6-thiophene 1-oxide **4h** (35.8 mg, 0.30 mmol, 1.0 equiv), purified by column chromatography (hexane/EtOAc) and isolated as a colorless oil (65.5 mg, 87%). **IR** (thin film) 3545, 3025, 2970, 2933, 1630, 1451, 1327, 1273, 1211, 1176, 1062, 946, 903, 840 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.27 (m, 4H), 7.23–7.17 (m, 1H), 3.75 (q, *J* = 7.2 Hz, 1H), 3.52–3.42 (m, 2H), 3.25–3.09 (m, 2H), 2.35–2.06 (m, 4H), 1.49 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.4, 142.3, 128.5, 127.7, 126.8, 52.5, 52.3, 49.3, 23.8, 23.6, 19.0; **HRMS** (ESI): *m*/*z* calc'd for $C_{13}H_{17}O_2NNaS$ $[M + Na]^+$: 274.0872, found: 274.0879. $[\alpha]_D^{25}$ 46.5 (*c* 0.23, $CHCl_3$, 99% ee sample).

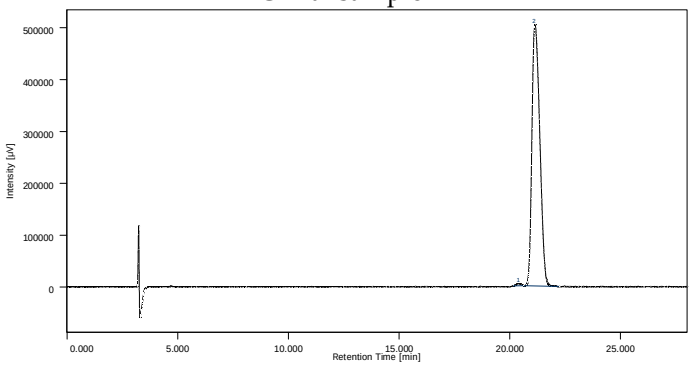
Racemic sample



peak information

#	tR [min]	area%
1	20.615	49.993
2	21.458	50.007

Chiral sample



peak information

#	tR [min]	area%
1	20.420	0.488
2	21.130	99.512

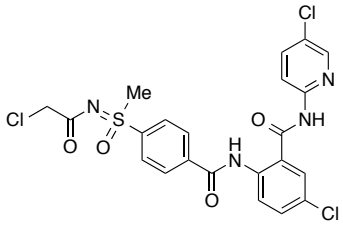
Daicel CHIRALCEL OD-R3. 20% CH_3CN with 0.1% TFA.

5-3. Demonstration of synthetic utility (Scheme 2)

***N*-(4-benzoyl-1-oxido-1λ^6-thiomorpholin-1-ylidene)-1-tosylpiperidine-4-carboxamide (5bi):** To a flame-dried 200 mL flask equipped with a magnetically stirred chip was added 1-tosylpiperidine-4-carboxylic acid **3b** (1.19 g, 4.19 mmol, 1.0 equiv), (1-imino-1-oxido-1λ^6-thiomorpholino)(phenyl)methanone **4i** (1.00 g, 4.19 mmol, 1.0 equiv), DATB **1** (121 mg, 0.210 mmol, 5 mol%), and toluene (42.0 mL, 0.1M) were added successively. A Dean–Stark apparatus was attached with the flask and the solution was stirred under reflux for 14 h. After cooling to an ambient temperature, all volatiles were removed under reduced pressure to give a crude material, which was purified by flash column chromatography, affording **5bi** as an amorphous solid (1.92 g, 91%). **IR** (thin film) 2997, 2926, 2850, 1636, 1424, 1209, 1161, 931, 724 cm^{-1}; **^{1}H NMR** (400 MHz,

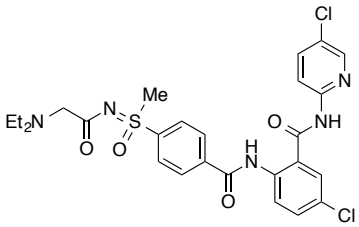
$CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.53–7.36 (m, 5H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.12 (brs, 2H), 3.86 (brs, 2H), 3.74–3.48 (m, 4H), 3.24 (brs, 2H), 2.47–2.30 (m, 5H), 2.19 (tt, *J* = 3.9, 10.9 Hz, 1H), 1.96 (dt, *J* = 3.9, 11.5 Hz, 2H), 1.87–1.68 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.6, 171.1, 143.6, 133.7, 133.3, 131.0, 129.7, 129.1, 127.8, 127.1, 50.7, 45.8, 44.5, 40.5, 28.2, 21.6; **HRMS** (ESI): *m*/*z* calc'd for $C_{24}H_{30}O_5N_3S_2$ [M + H]$^+$: 504.1621, found: 504.1615.

5-Chloro-2-(4-(*N*-(2-chloroacetyl)-*S*-methylsulfonimidoyl)benzamido)-*N*-(5-chloropyridin-2-yl)benzamide (S2): The



title compound was characterized during the optimization study for Scheme 2b. **m.p.** 199 °C (decomp); **IR** (thin film) 3284, 3016, 2927, 2362, 1660, 1511, 1374, 1296, 1227, 1116, 1009, 920, 751 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.88 (s, 1H), 8.80 (d, *J* = 9.0 Hz, 1H), 8.31–8.24 (m, 2H), 8.24–8.17 (m, 2H), 8.17–8.10 (m, 2H), 7.78 (dd, *J* = 2.4, 9.0 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 2.4, 9.0 Hz, 1H), 4.14 (d, *J* = 1.2 Hz, 2H), 3.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.0, 166.4, 163.4, 148.8, 146.9, 141.3, 139.7, 138.5, 138.3, 133.7, 129.0, 128.7, 128.1, 127.8, 127.1, 123.3, 121.0, 115.4, 45.7, 43.9; **HRMS** (ESI): *m*/*z* calc'd for $C_{22}H_{17}O_4N_4Cl_3NaS$ [M + Na]$^+$: 560.9928, found: 560.9912.

5-Chloro-*N*-(5-chloropyridin-2-yl)-2-(4-(*N*-(diethylglycyl)-*S*-methylsulfonimidoyl)benzamido)benzamide (2): Prior



to the reaction setup, powdered MS4A was activated by a microwave (700W, 1.5 min for 3 times). To a test tube equipped with a magnetically stirred chip was added powdered MS4A (240 mg, 800 mg/mmol), and the tube was flame-dried under reduced pressure. To this acid **6** (28.3 mg, 0.30 mmol, 1.0 equiv), sulfoximine **7** (0.30 mmol, 1.0 equiv), aniline **8** (84.6 mg, 0.30 mmol, 1.0 equiv), DATB **1** (8.6 mg, 0.015 mmol, 5 mol%), and 3:1 mesitylene/diglyme (3.0 mL, 0.1M) were added successively. The suspension was stirred at 100 °C for 8 h, then at the reflux temperature (bath temp: 180 °C) for 14 h. After the removal of all volatiles under reduced pressure, the residue was triturated with Et_2O and the suspension was filtered through a pad of Celite. The solvent was removed under reduced pressure to give crude acylated product **S2**, which was dissolved in DMF (300 μL, 1.0M), followed by the addition of NaI (4.5 mg, 0.030 mmol, 10 mol%). To this was added diethylamine (62.1 μL, 0.60 mmol, 2.0 equiv), and the solution was stirred at RT for 2 h. The reaction mixture was directly placed on a silica gel column chromatography, eluted with $CHCl_3$/MeOH (100:0 to 85:15), and the title compound was isolated as an amorphous solid (88 mg, 51% for 3 steps). **IR** (thin film) 3235, 2969, 2929, 2251, 1657, 1512, 1459, 1374, 1296, 1216, 1115, 1095, 919, 731 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.96 (s, 1H), 8.82 (d, *J* = 9.0 Hz, 2H), 8.34–8.24 (m, 2H), 8.19 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.78 (dd, *J* = 2.4, 9.0 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.57 (dd, *J* = 2.4, 9.0 Hz, 1H), 3.40 (s, 2H), 3.38 (s, 3H), 2.70 (q, *J* = 7.2 Hz, 4H), 1.07 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.4, 166.5, 163.7, 149.0, 147.1, 142.4, 139.5, 138.7, 138.4, 133.9, 129.1, 128.8, 128.2, 127.9, 127.1, 123.4, 121.2, 115.5, 58.7, 47.7, 44.2, 12.1; **HRMS** (ESI): *m*/*z* calc'd for $C_{26}H_{28}O_4N_5Cl_2S$ [M + H]$^+$: 576.1234, found: 576.1212.

6. References

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7. Optimized Coordinates

Iminodimethyl-λ⁶-sulfanone MP2/6-311++G(2d,p)

S	-0.01195613	-0.17206764	0.07429442
O	0.23092587	-0.39872017	1.50220770
N	-0.43195839	-1.27668174	-0.90106667
C	1.43090372	0.74012738	-0.49777678
H	1.28095231	1.03610940	-1.53491613
H	1.59513304	1.59887396	0.15216401
H	2.27245567	0.05115776	-0.41815469
C	-1.31365903	1.01920261	-0.12910328
H	-1.39959508	1.28755441	-1.17971656
H	-2.22270691	0.52822258	0.21516741
H	-1.08375853	1.88128773	0.49502552
H	0.22165117	-2.05956997	-0.86719471

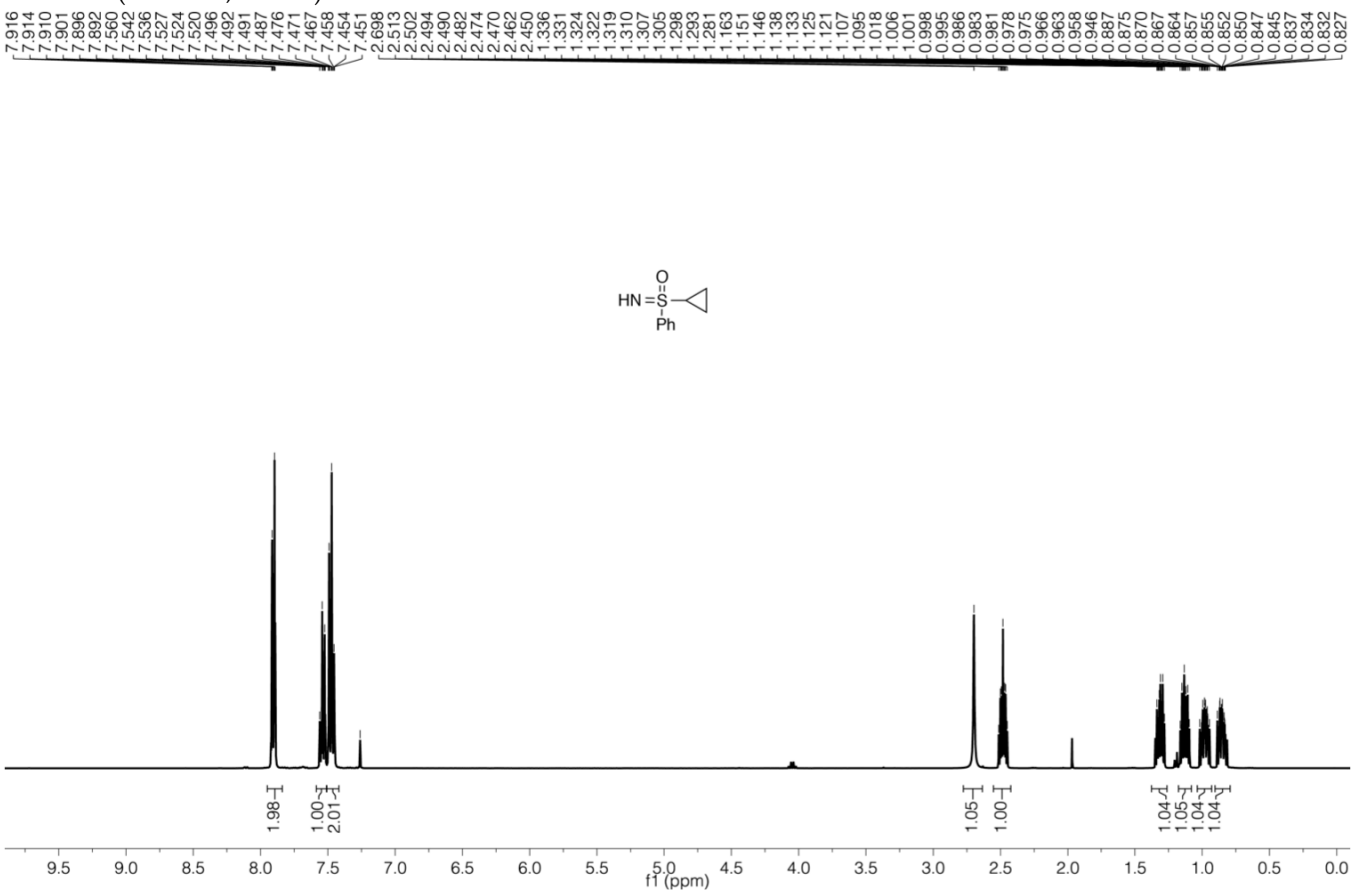
***tert*-Butylamine** MP2/6-311++G(2d,p)

C	-0.00000000	-0.00431767	0.01428690
C	-1.25004835	-0.78812826	-0.37246108
C	1.25004616	-0.78813274	-0.37245914
H	-1.29339180	-0.93979634	-1.45389818
H	-1.25266440	-1.76104147	0.12291611
H	-2.15272646	-0.24747367	-0.07102074
H	1.25265721	-1.76104664	0.12291672
H	1.29339170	-0.93979938	-1.45389635
H	2.15272561	-0.24748215	-0.07101569
N	-0.00000085	0.12034892	1.48211315
H	0.81567781	0.65005805	1.78464393
H	-0.81567997	0.65005794	1.78464289
C	0.00000300	1.35540677	-0.69208322
H	0.00000320	1.23885910	-1.77995241
H	-0.88585671	1.93312858	-0.41191483
H	0.88586486	1.93312501	-0.41191420

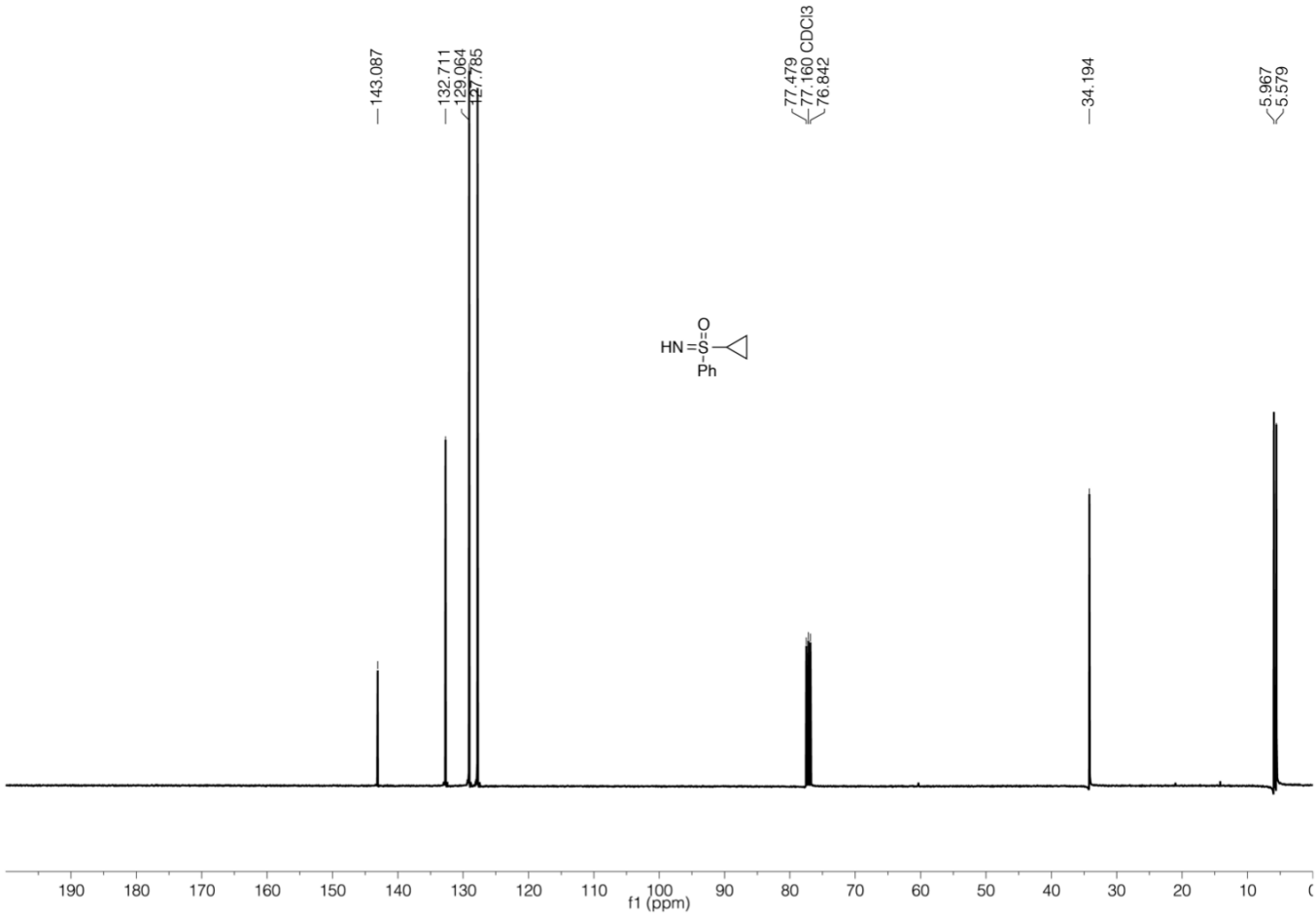
8. Spectra

Cyclopropyl(imino)(phenyl)-λ^6-sulfanone (4b):

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

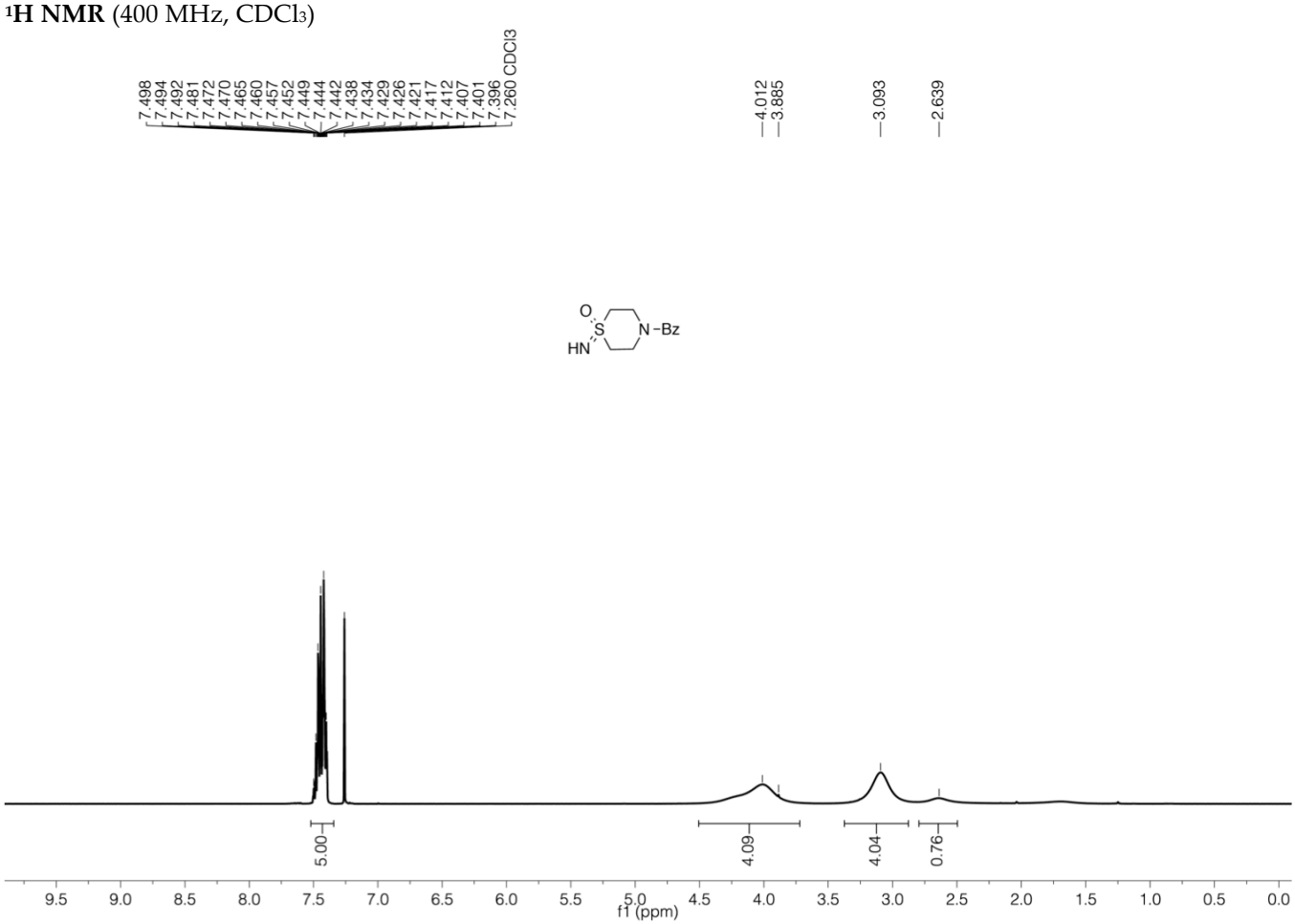


^{13}C NMR (100MHz, $CDCl_3$)

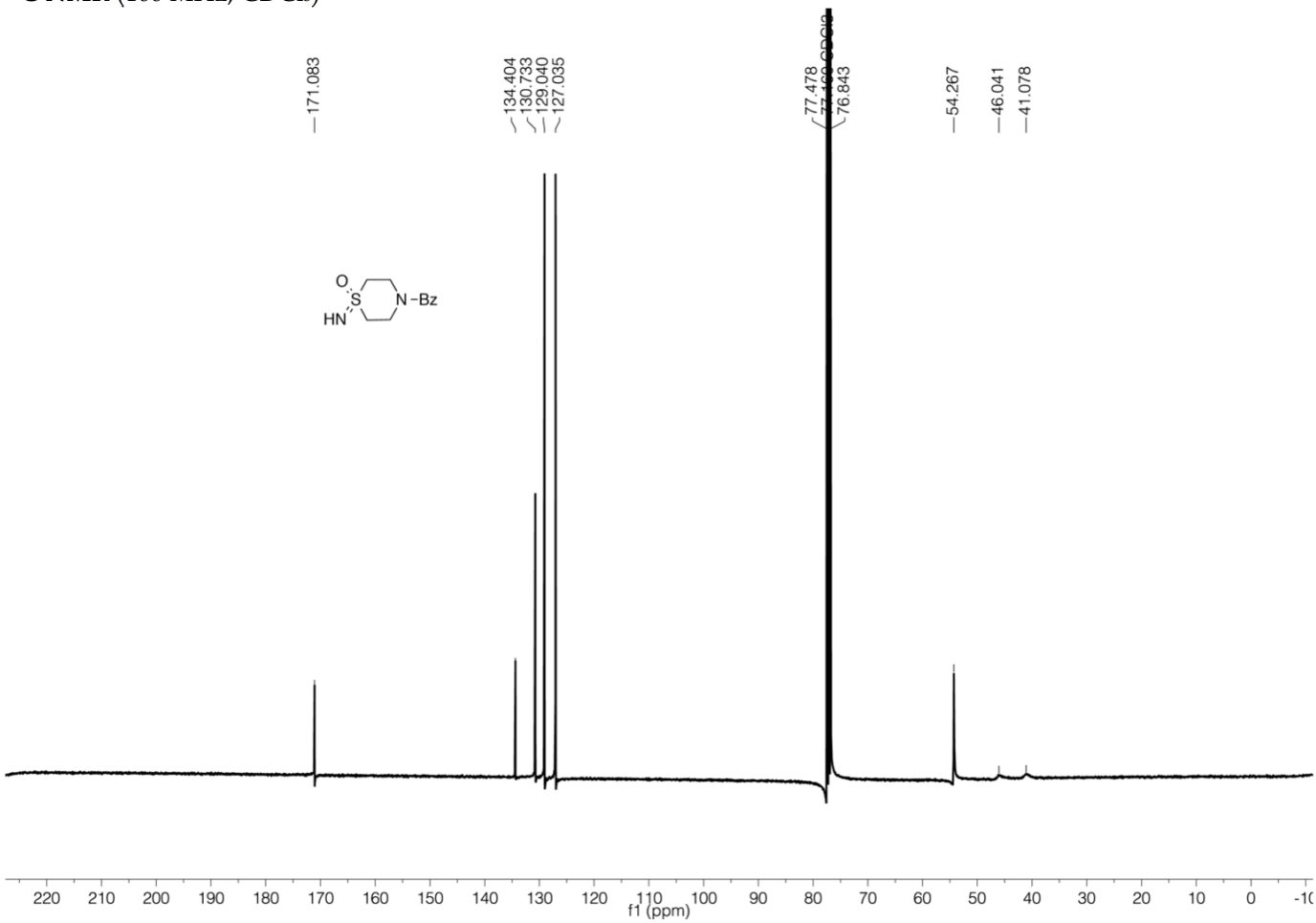


(1-Imino-1-oxido-1λ⁶-thiomorpholino)(phenyl)methanone (4i):

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

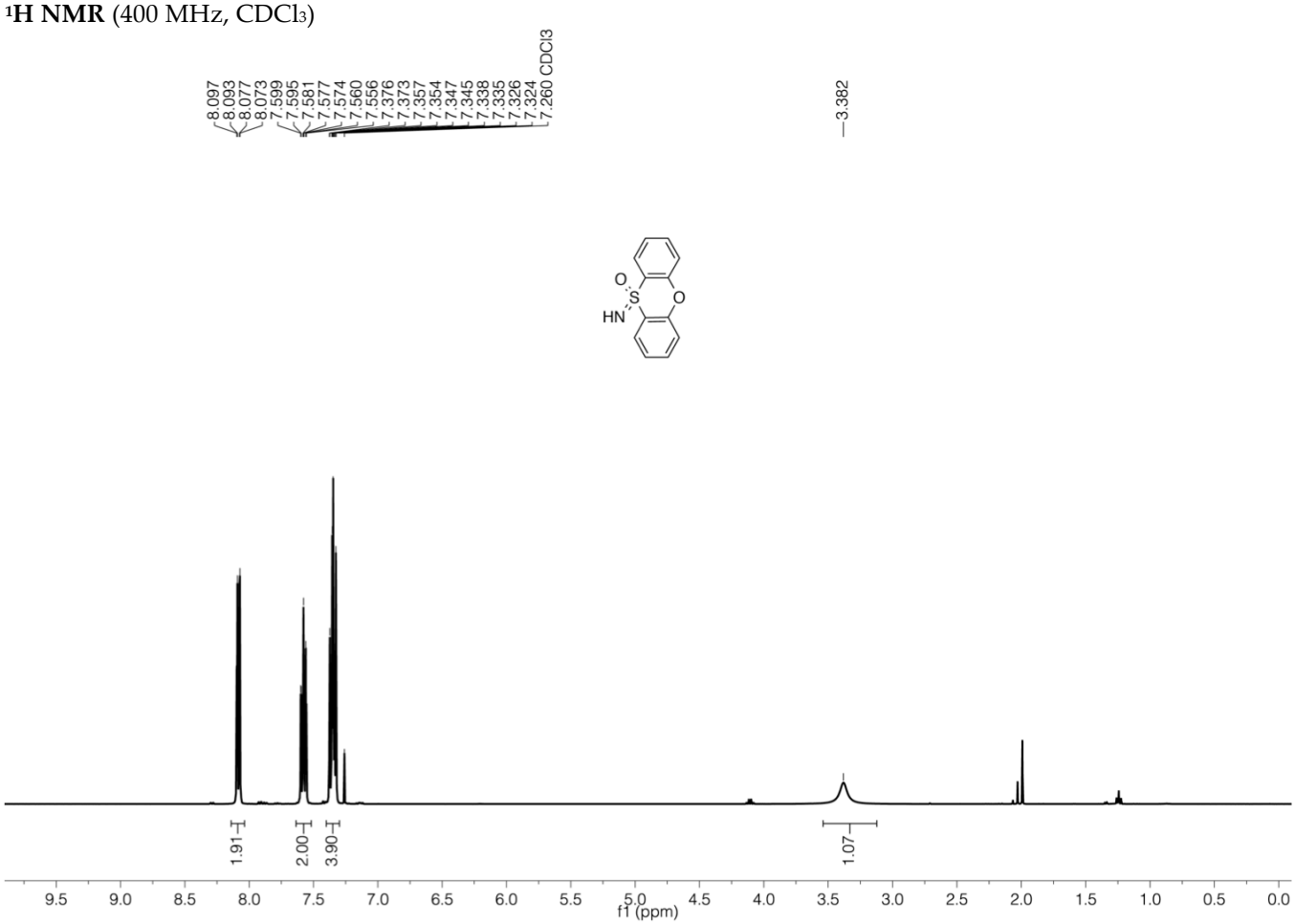


^{13}C NMR (100 MHz, $CDCl_3$)

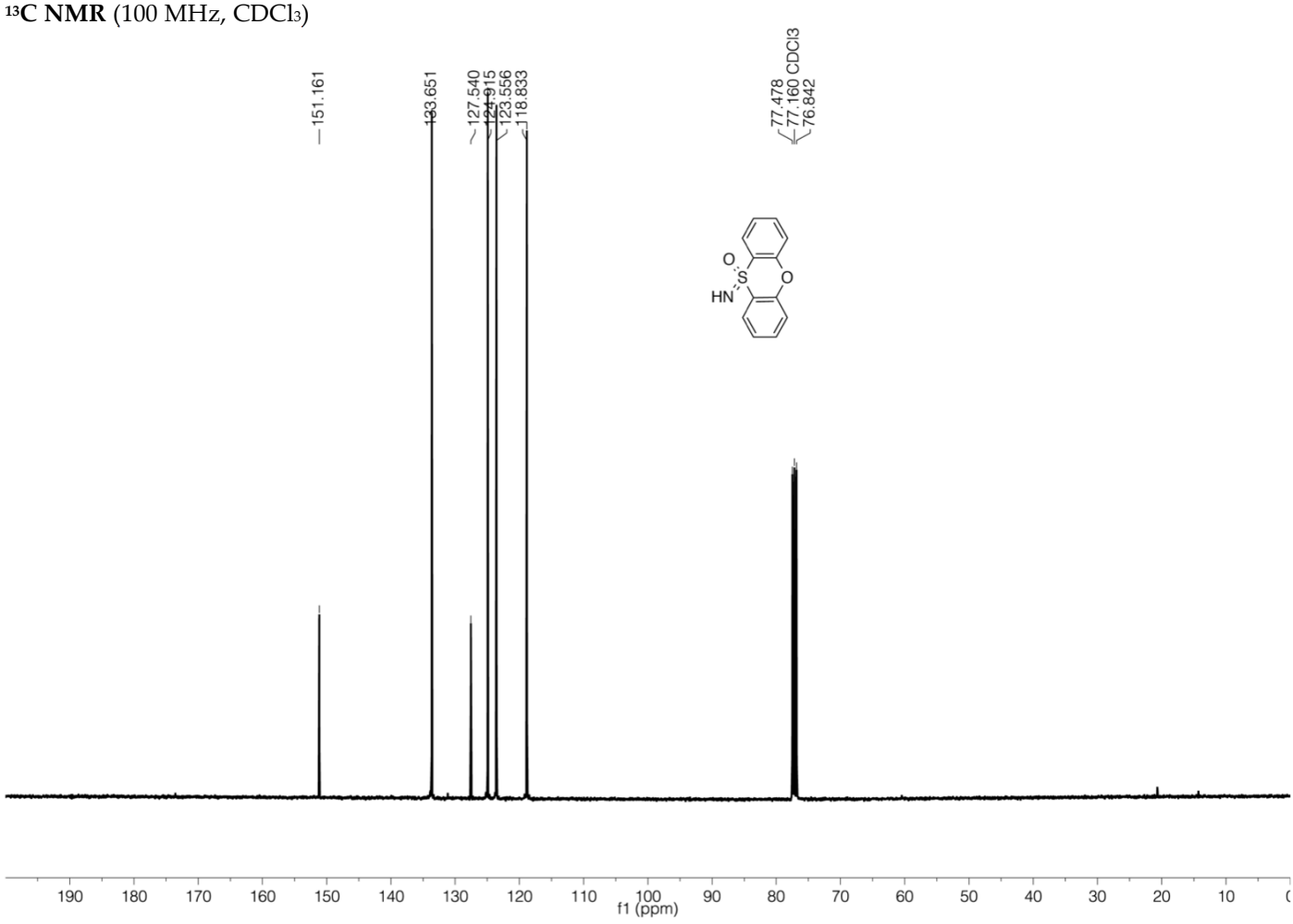


10-Imino-10*H*-10λ^4-phenoxathiine 10-oxide (4j):

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

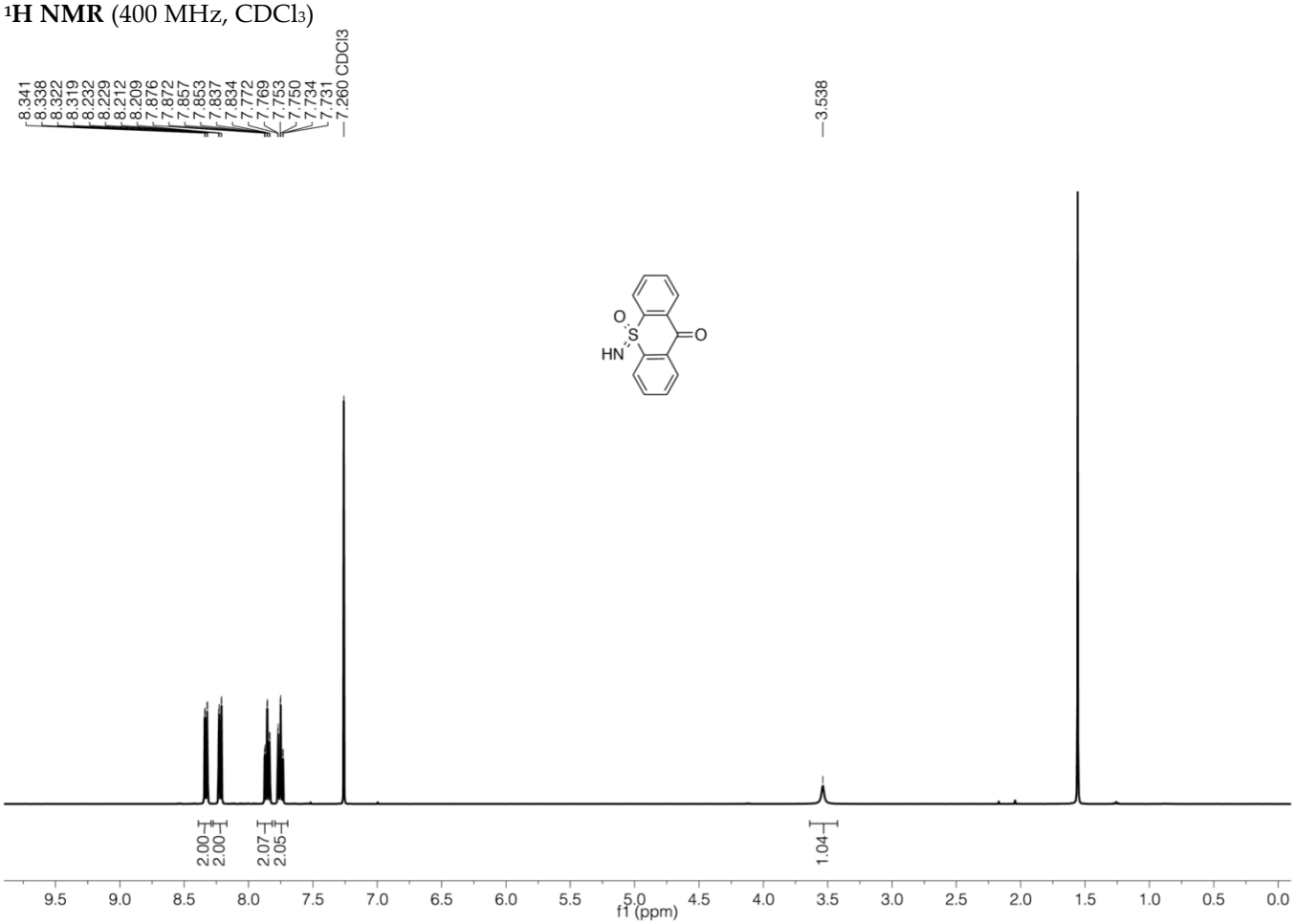


^{13}C NMR (100 MHz, $CDCl_3$)

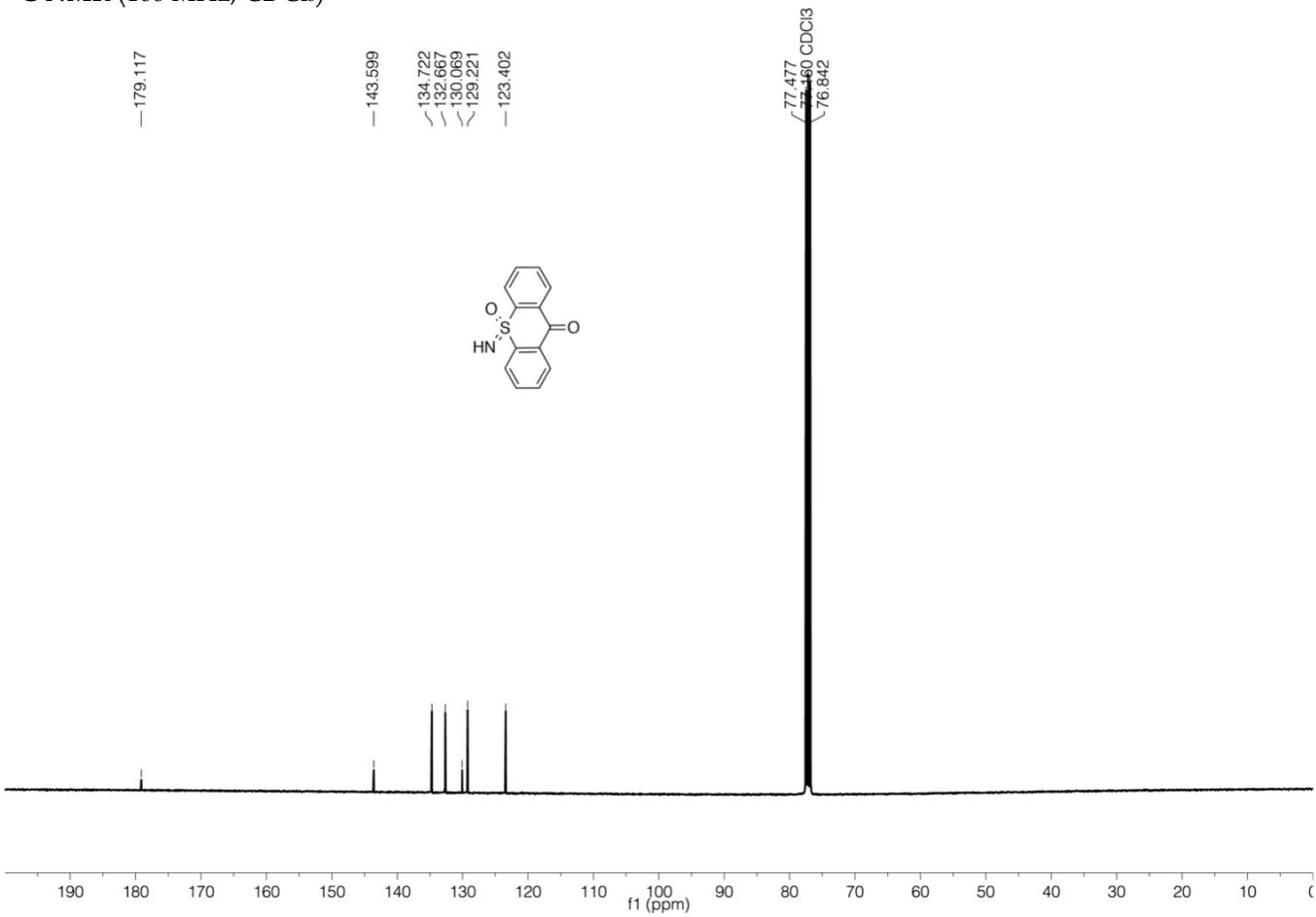


10-Imino-10λ^4-thioxanthen-9(10*H*)-one 10-oxide (4k):

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

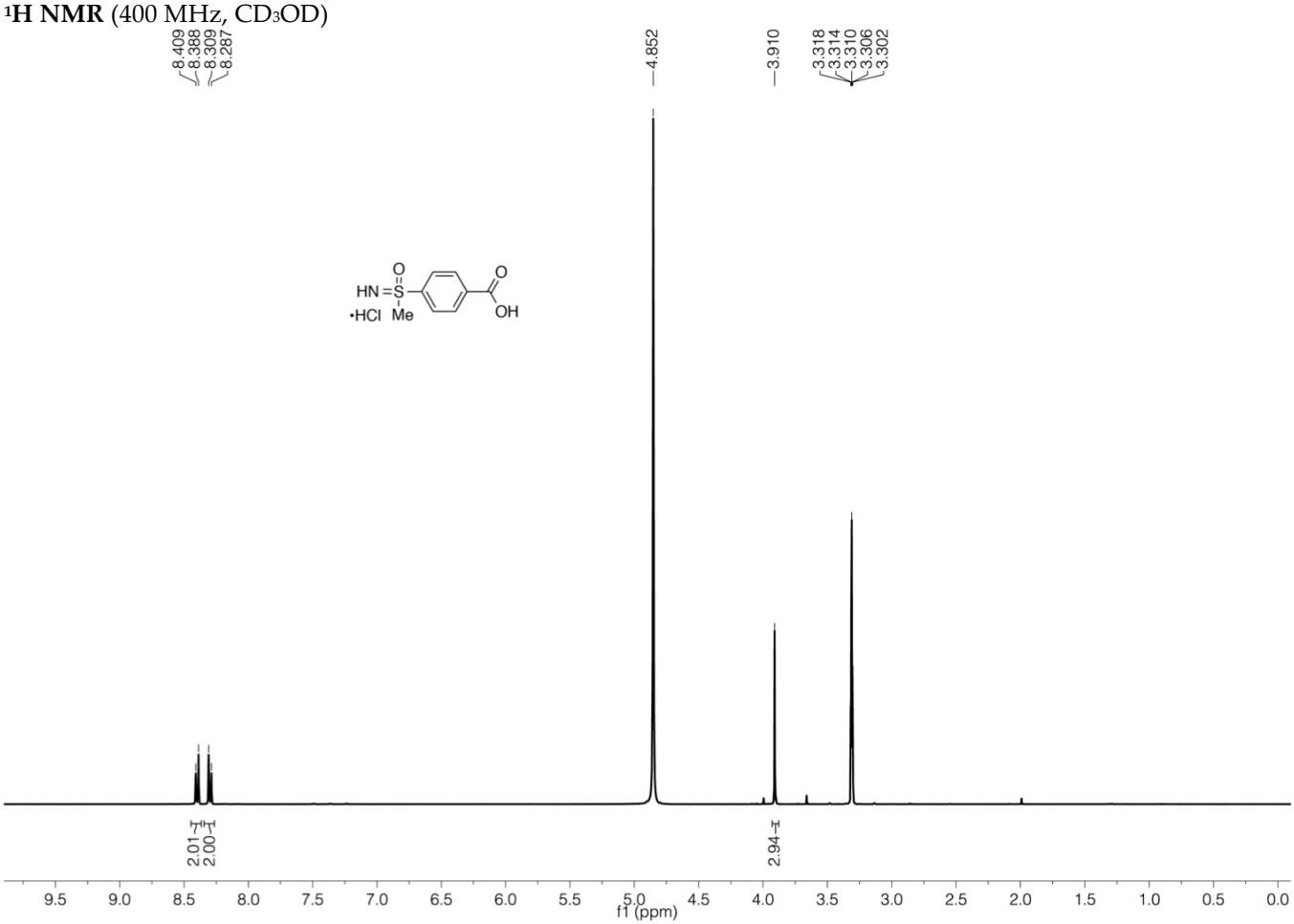


^{13}C NMR (100 MHz, $CDCl_3$)

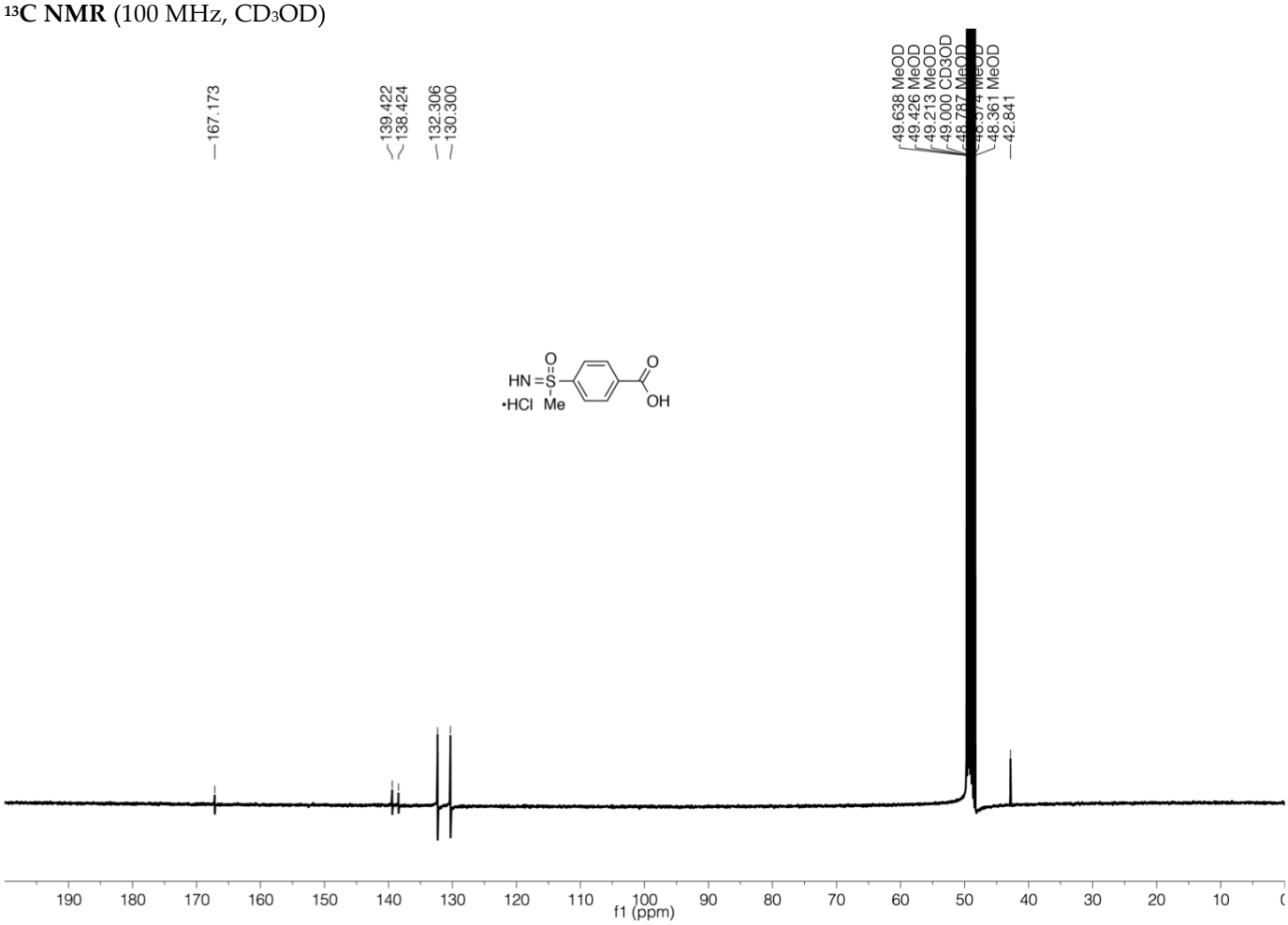


4-(*S*-Methylsulfonimidoyl)benzoic acid hydrochloride (7•HCl):

^{1}H NMR (400 MHz, CD_3OD)

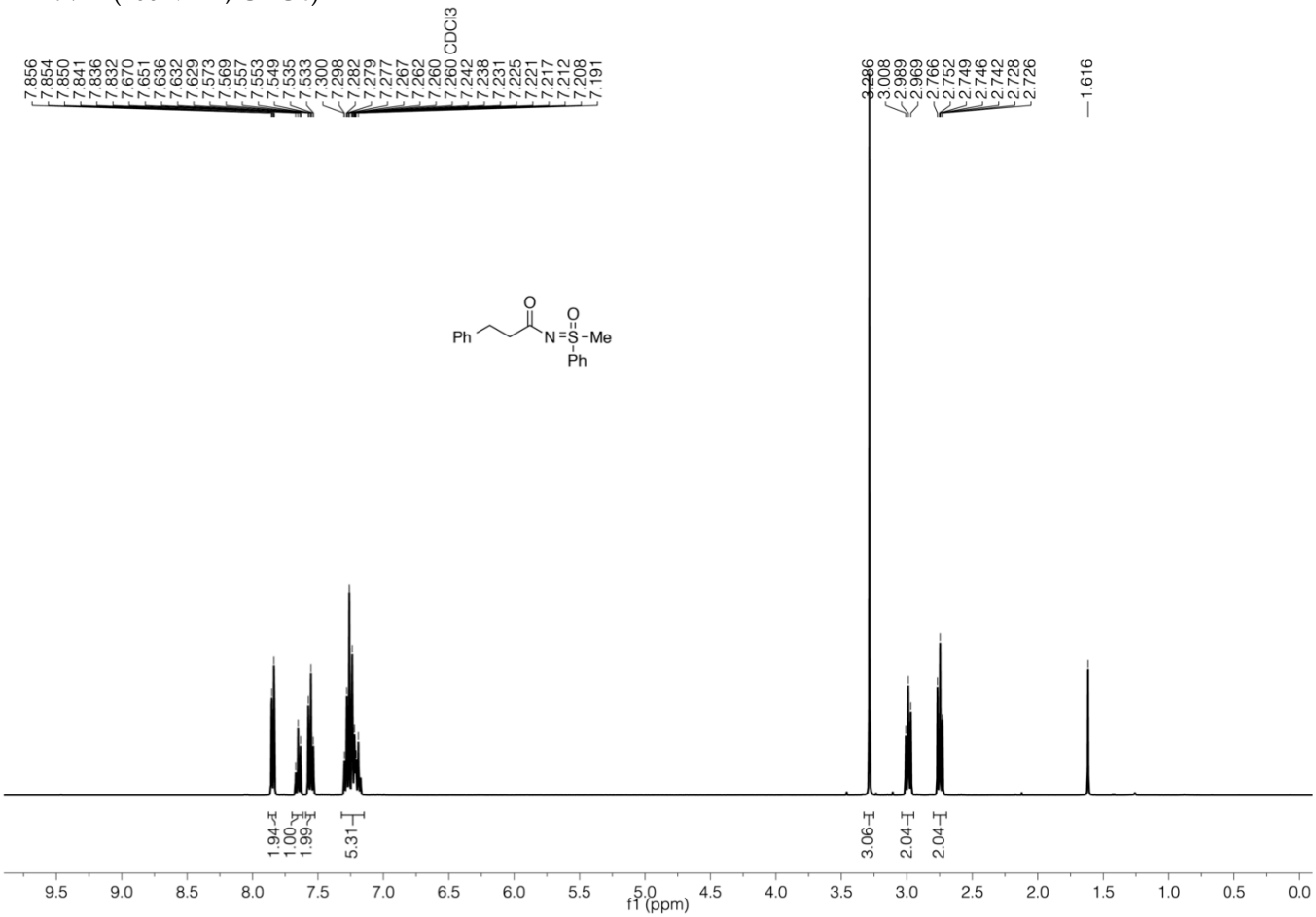


^{13}C NMR (100 MHz, CD_3OD)

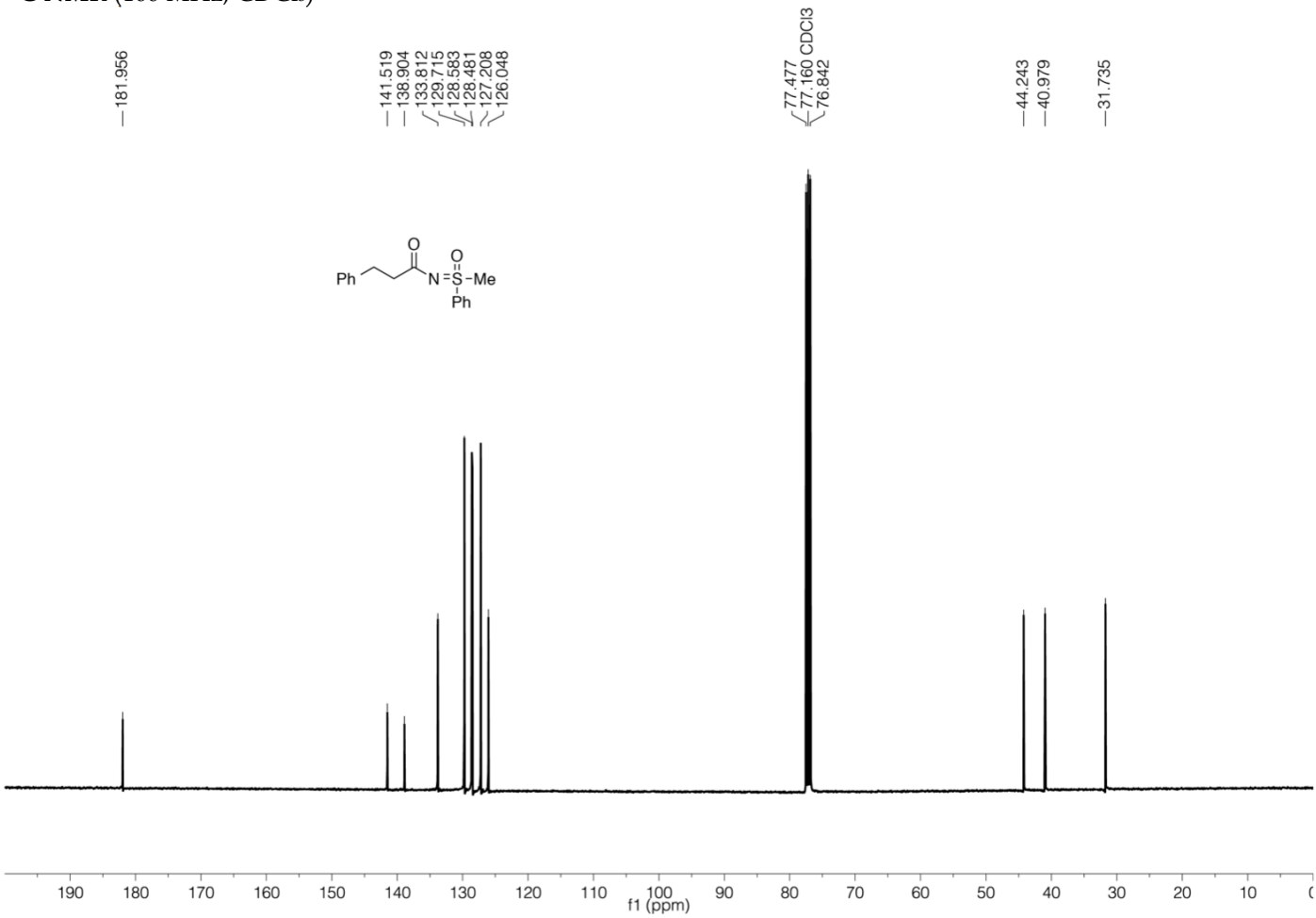


***N*-(Methyl(oxo)(phenyl)-λ⁶-sulfanylidene)-3-phenylpropanamide (5aa):**

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

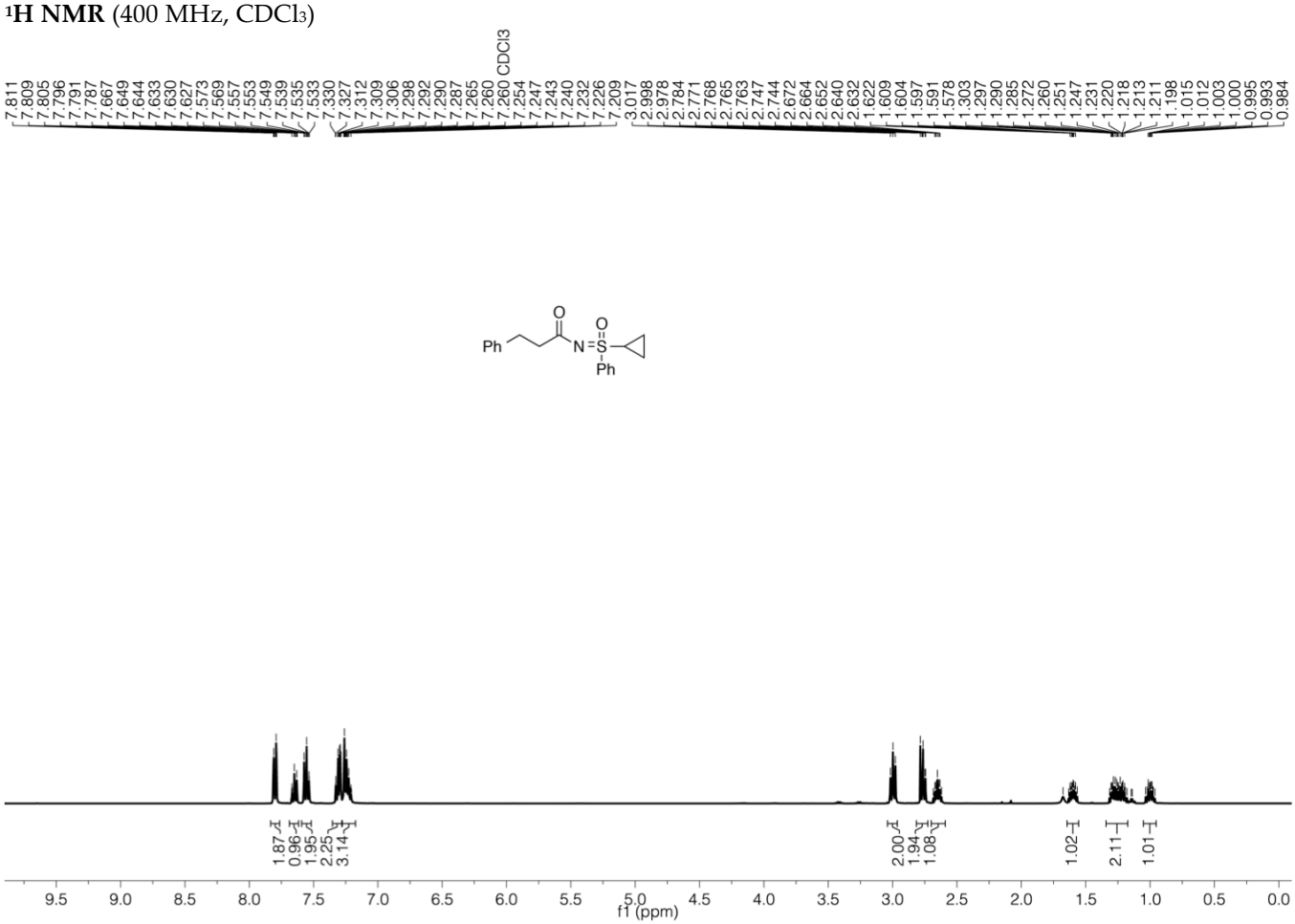


^{13}C NMR (100 MHz, $CDCl_3$)

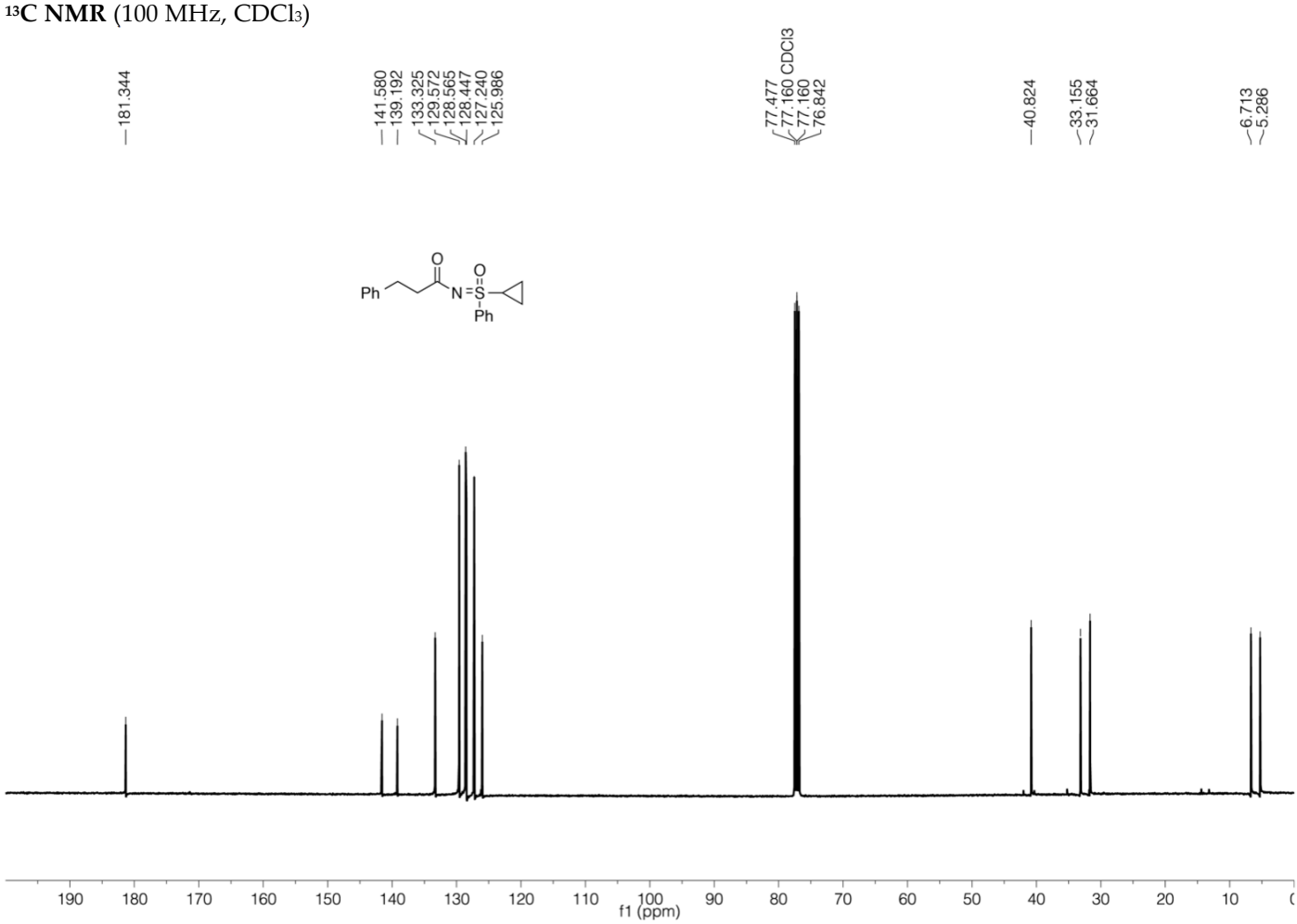


***N*-(Cyclopropyl(oxo)(phenyl)-λ⁶-sulfanylidene)-3-phenylpropanamide (5ab):**

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

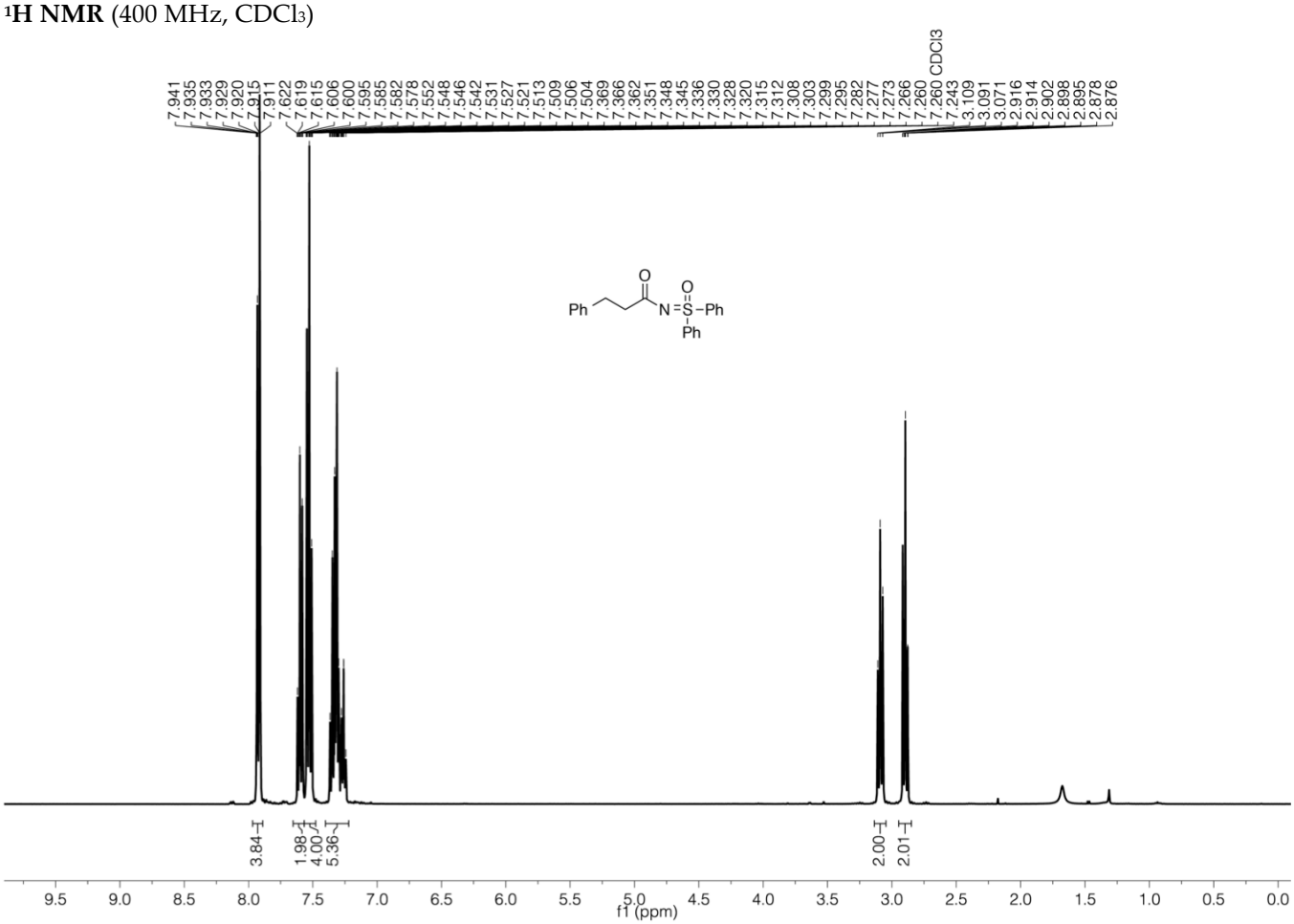


^{13}C NMR (100 MHz, $CDCl_3$)

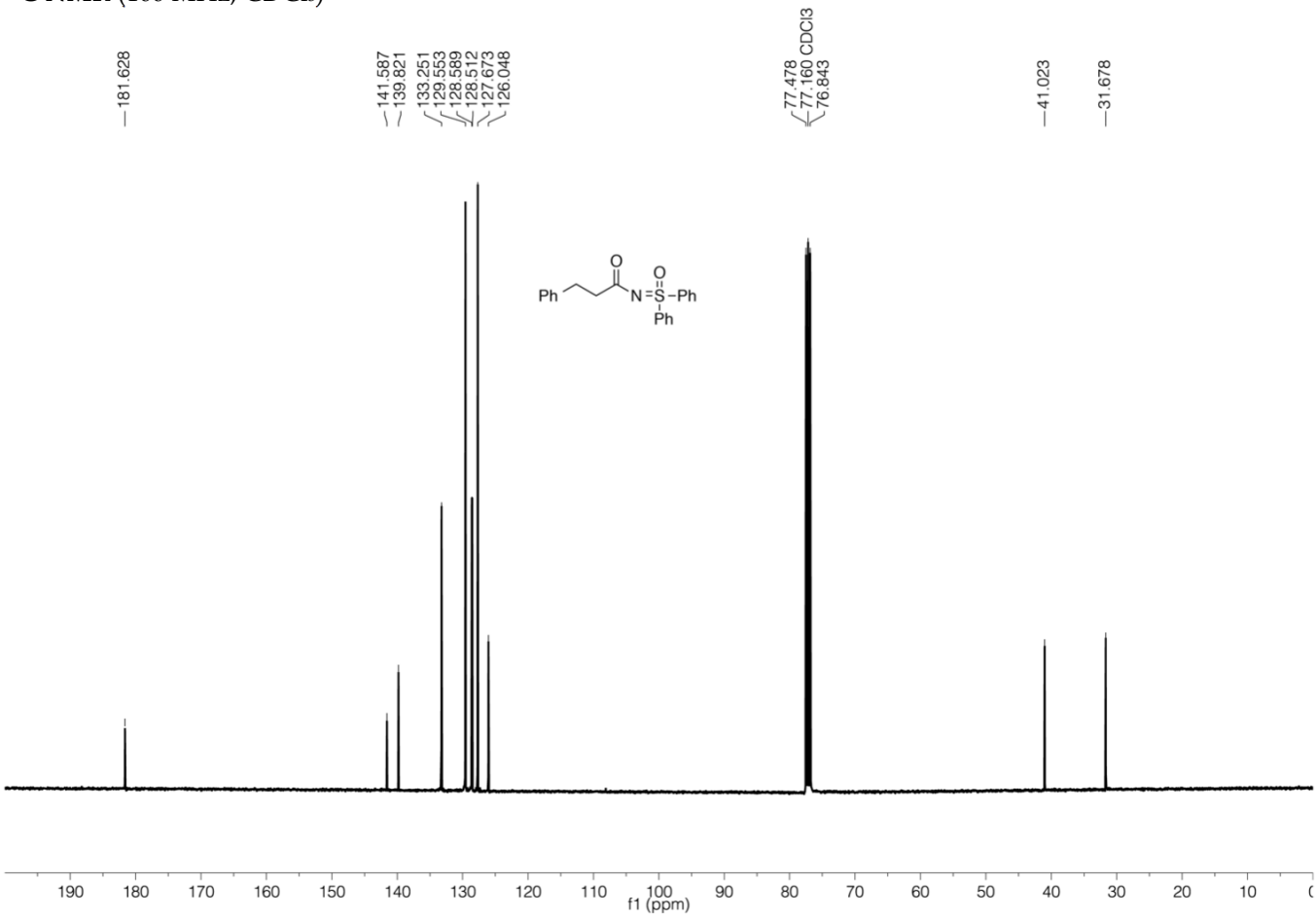


***N*-(Oxodiphenyl-λ⁶-sulfanylidene)-3-phenylpropanamide (5ac):**

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

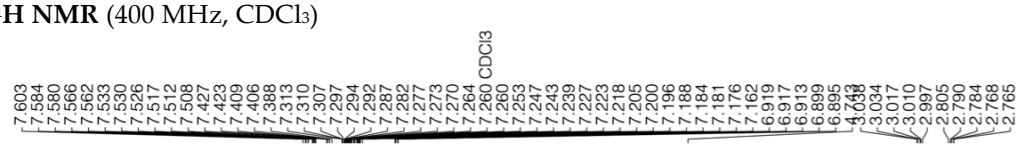


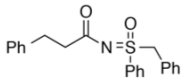
^{13}C NMR (100 MHz, $CDCl_3$)

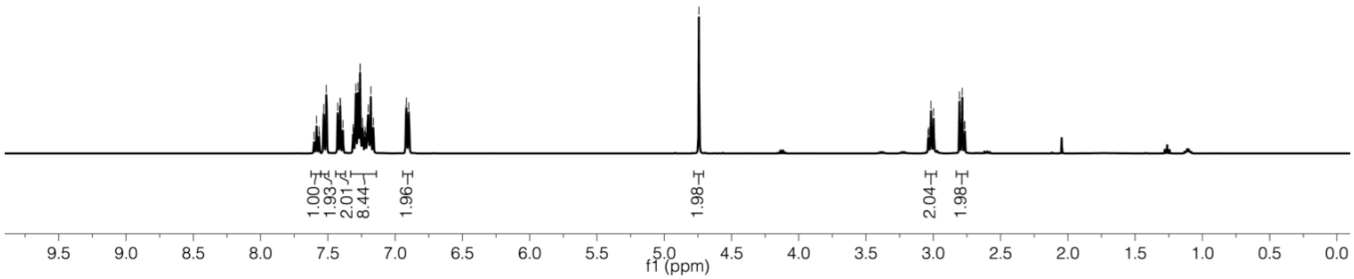


_N_-(Benzyl(oxo)(phenyl)-λ⁶-sulfanylidene)-3-phenylpropanamide (5ad):

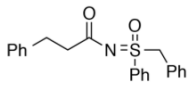
^{1}H NMR (400 MHz, $CDCl_3$)

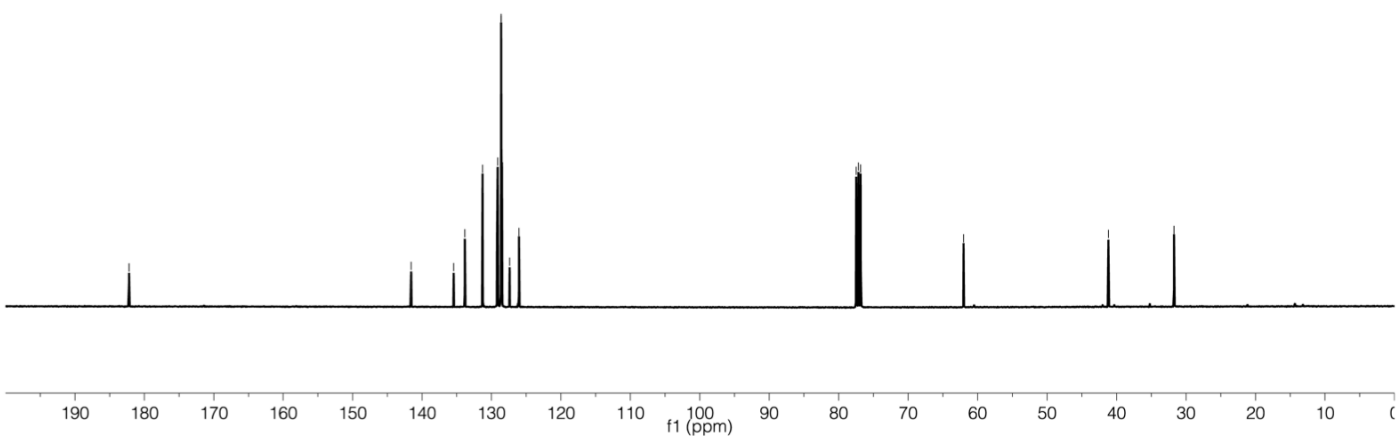






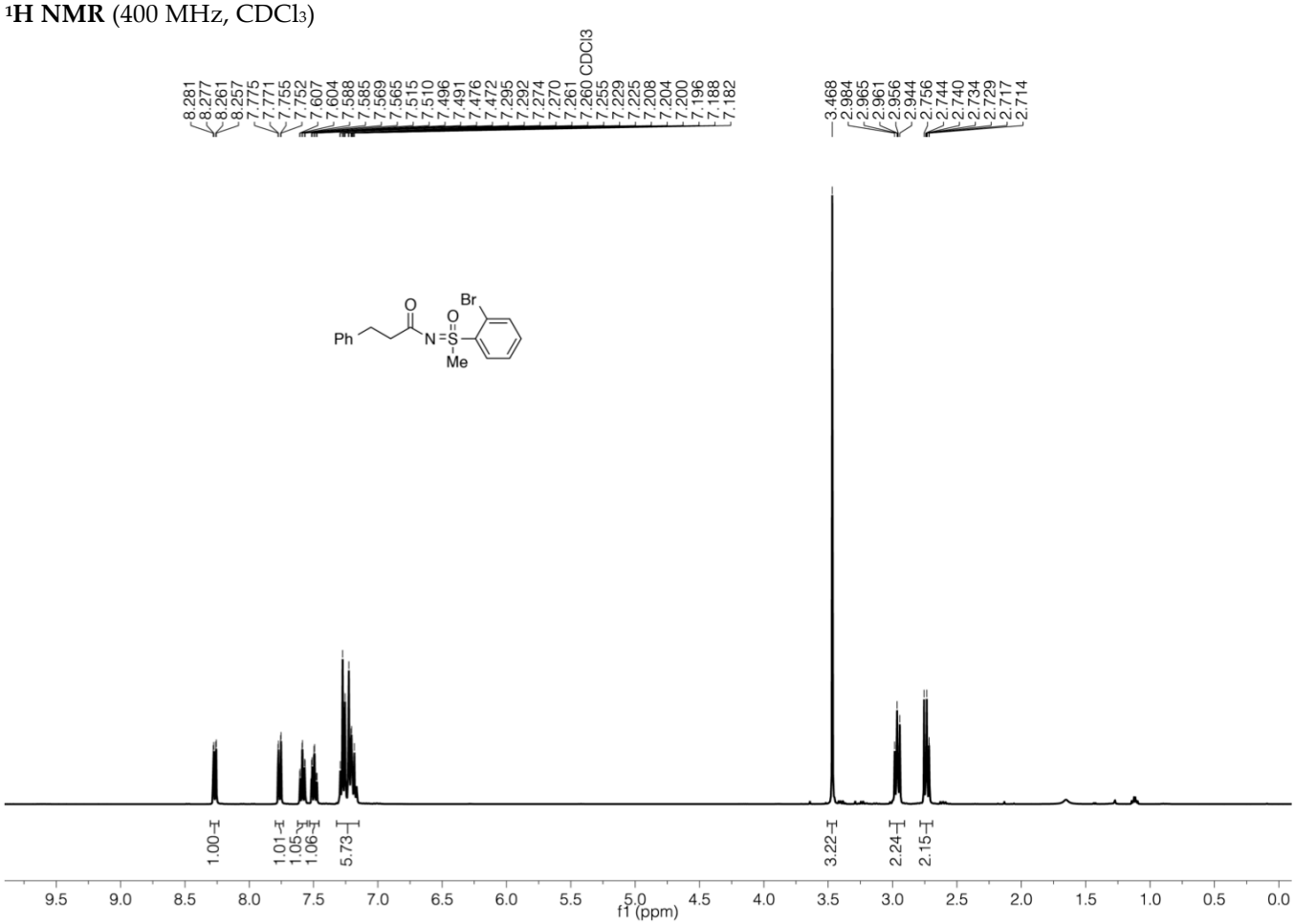
^{13}C NMR (100 MHz, $CDCl_3$)



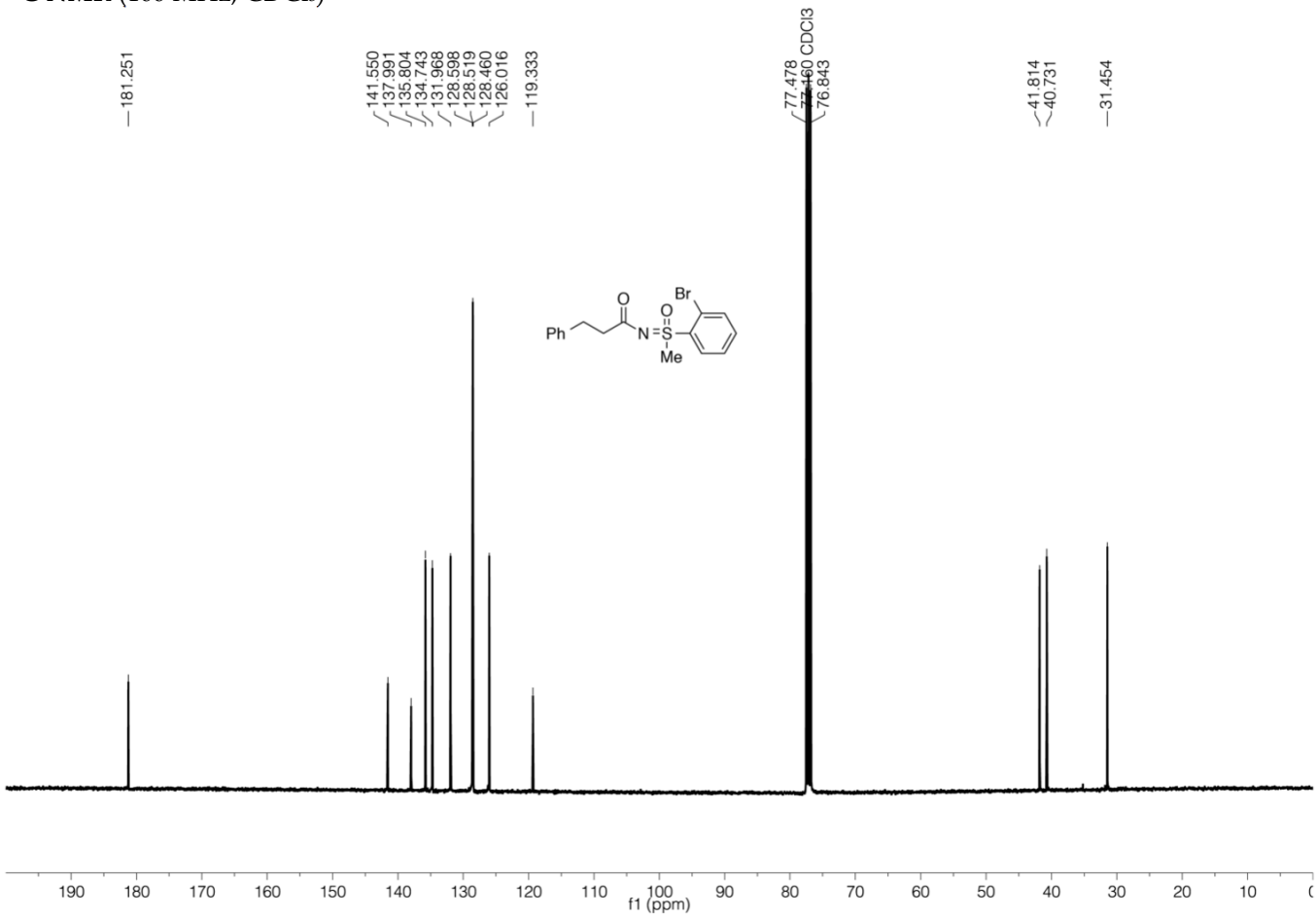


***N*-((2-Bromophenyl)(methyl)(oxo)-λ⁶-sulfanylidene)-3-phenylpropanamide (5ae):**

¹H NMR (400 MHz, $CDCl_3$)

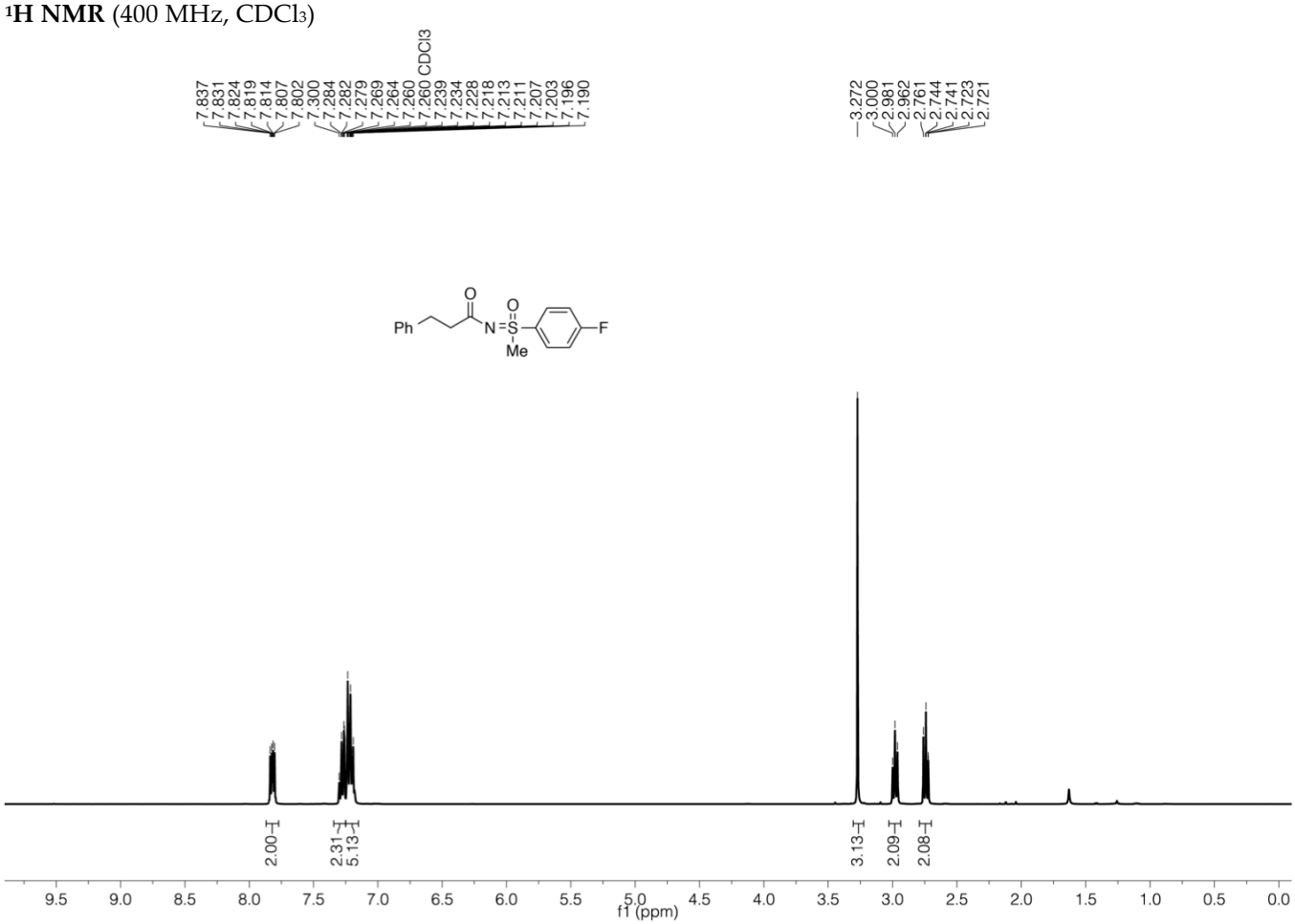


¹³C NMR (100 MHz, $CDCl_3$)

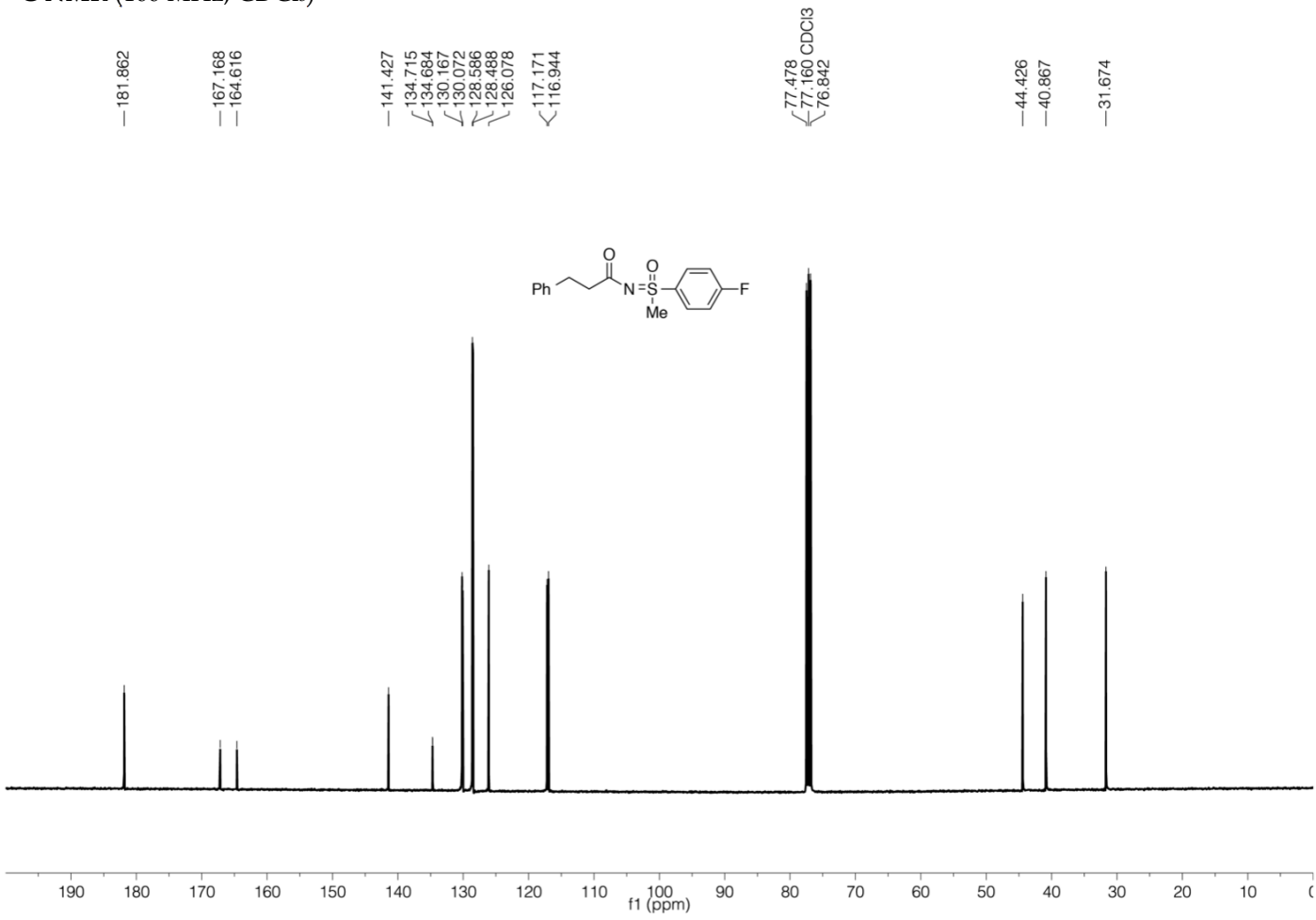


***N*-((4-Fluorophenyl)(methyl)(oxo)-λ⁶-sulfanylidene)-3-phenylpropanamide (5af):**

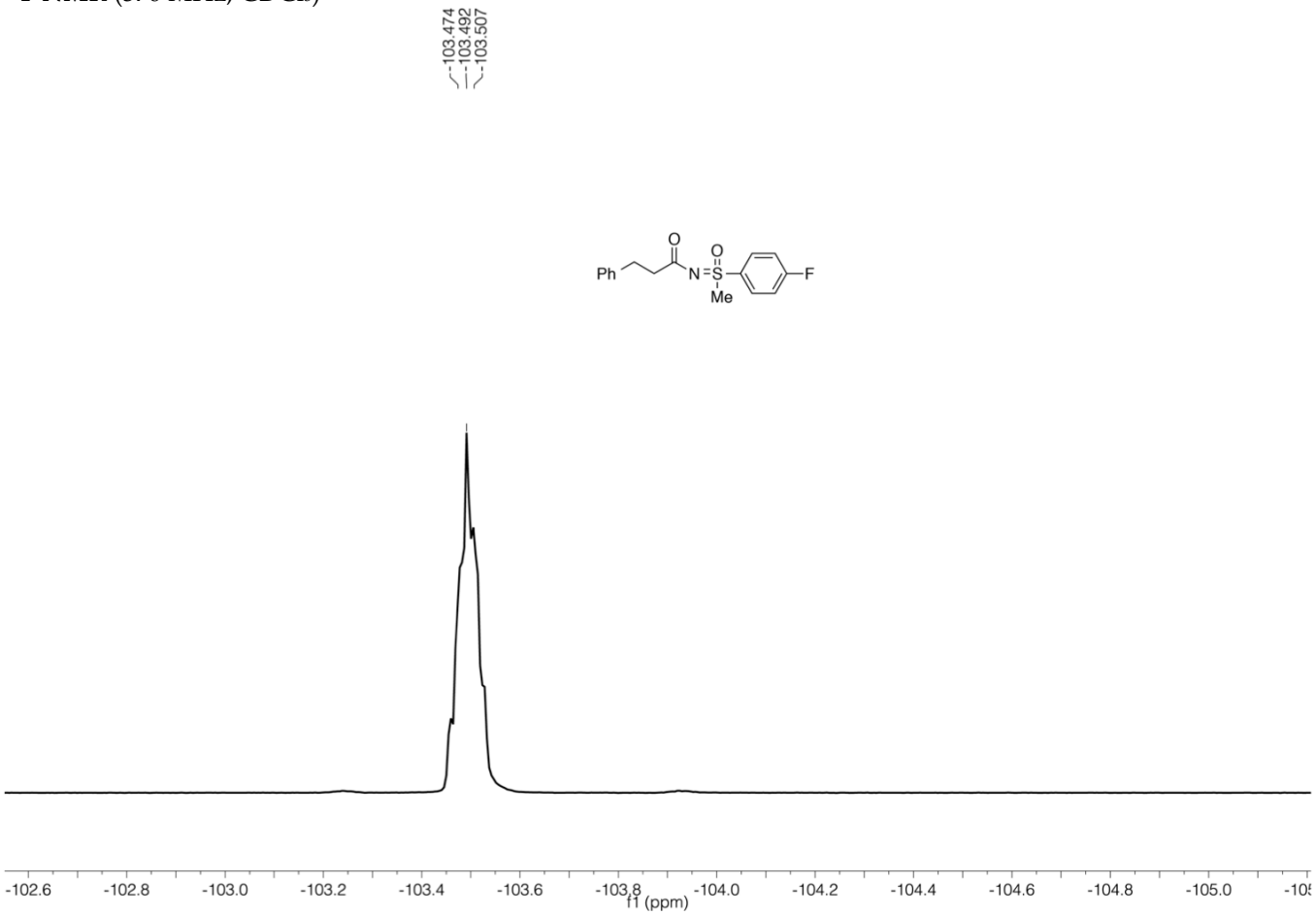
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

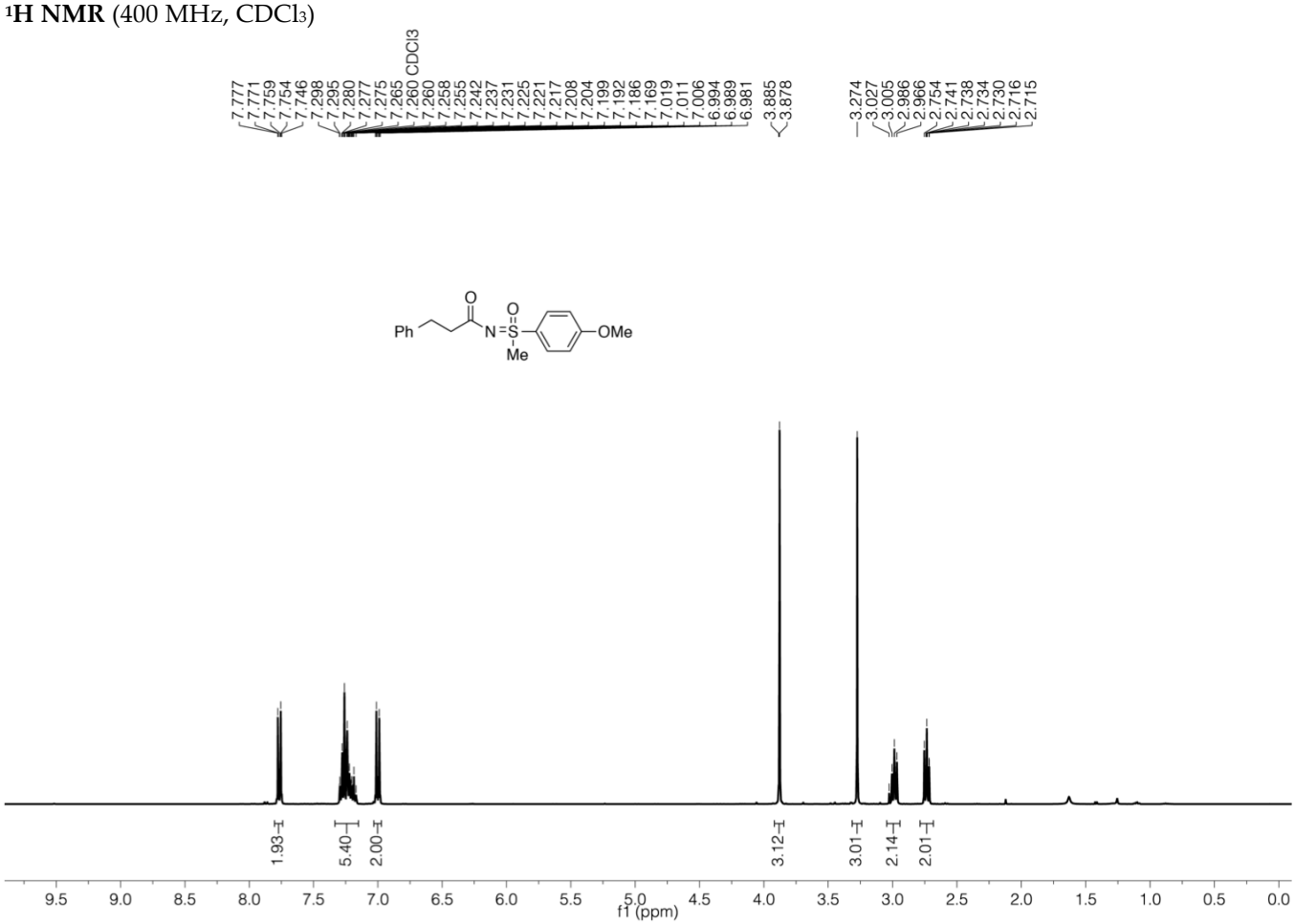


^{19}F NMR (376 MHz, $CDCl_3$)

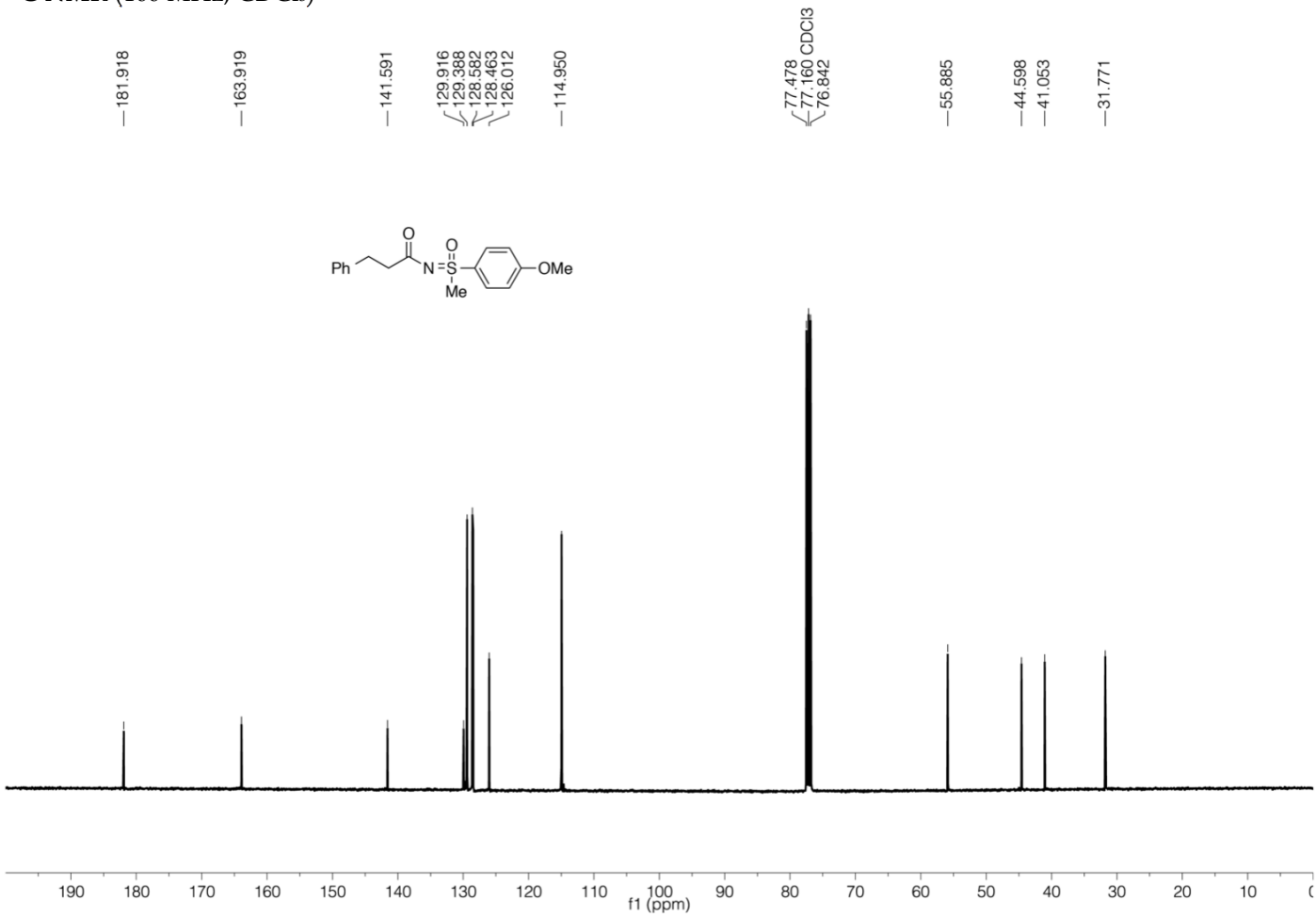


***N*-((4-Methoxyphenyl)(methyl)(oxo)-λ⁶-sulfanylidene)-3-phenylpropanamide (5ag):**

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

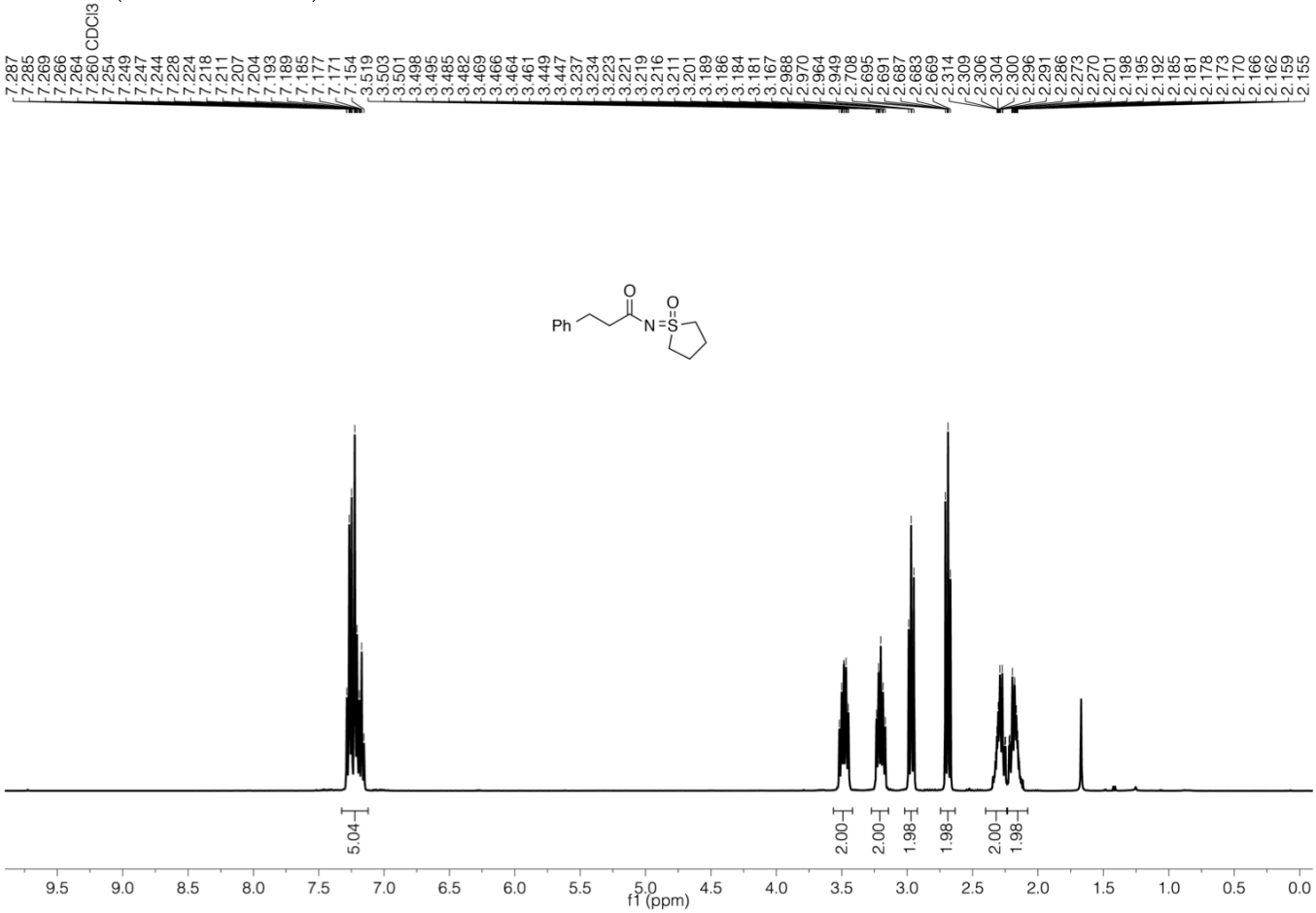


^{13}C NMR (100 MHz, $CDCl_3$)

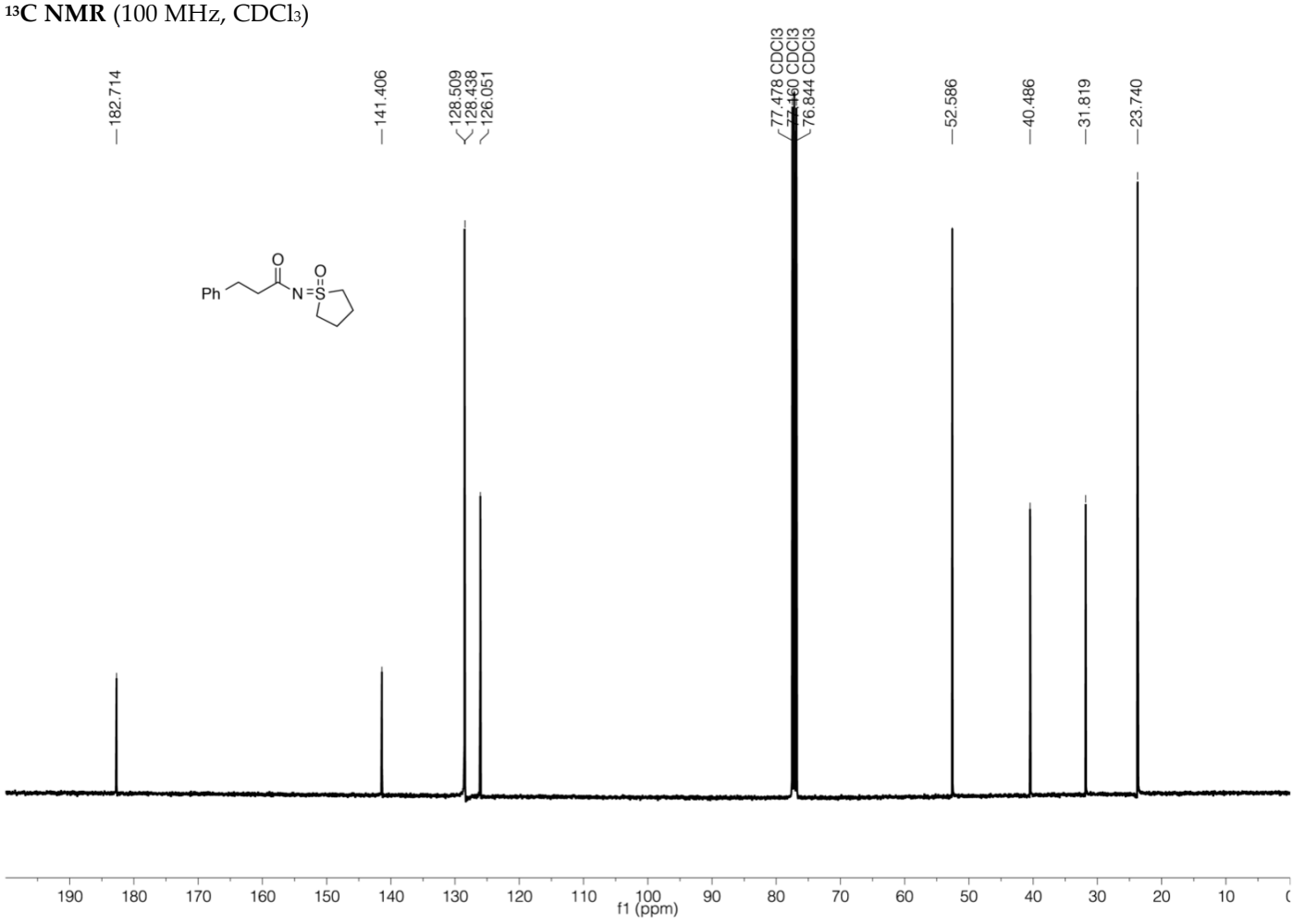


***N*-(1-Oxidotetrahydro-1λ⁶-thiophen-1-ylidene)-3-phenylpropanamide (5ah):**

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

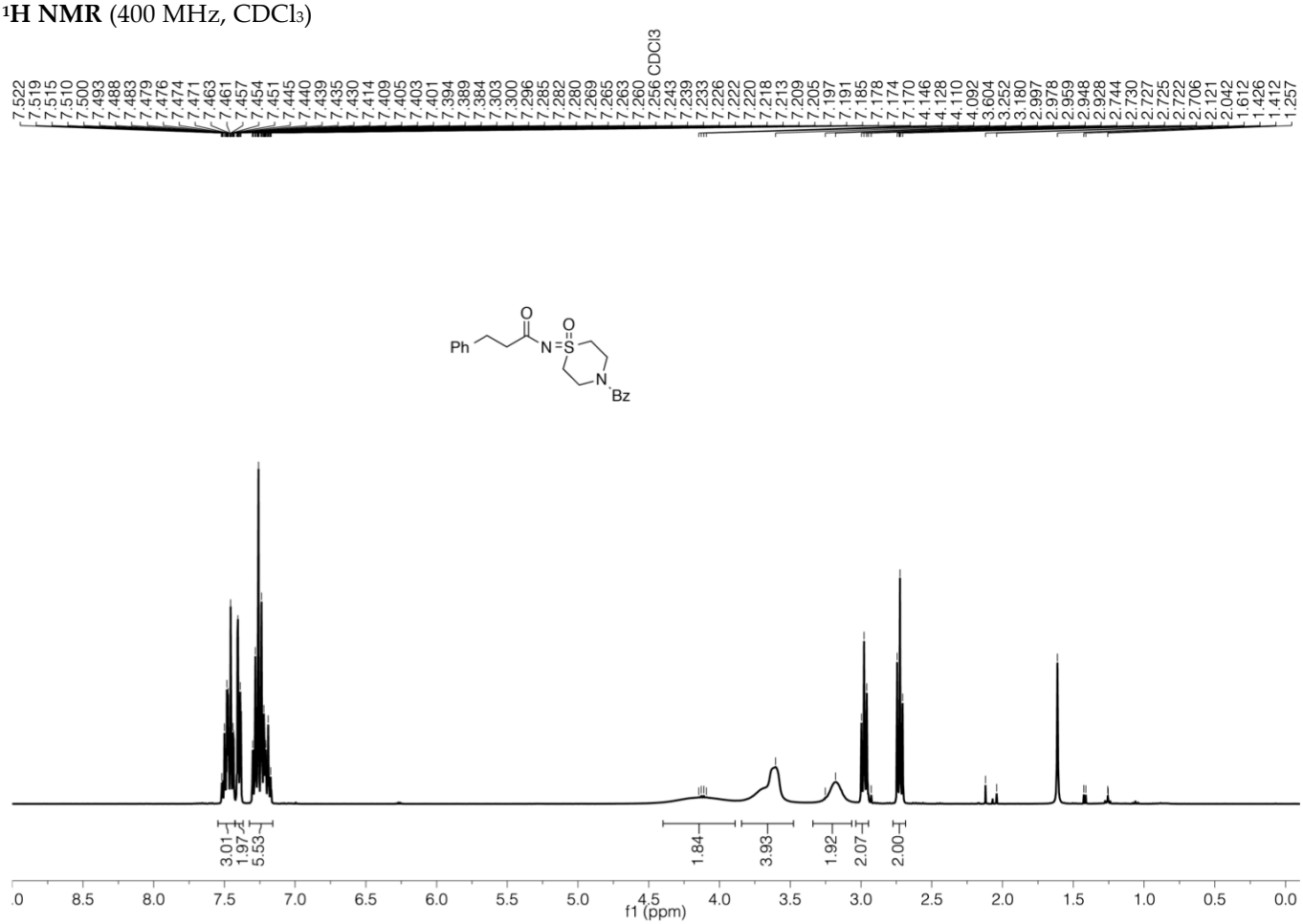


^{13}C NMR (100 MHz, $CDCl_3$)

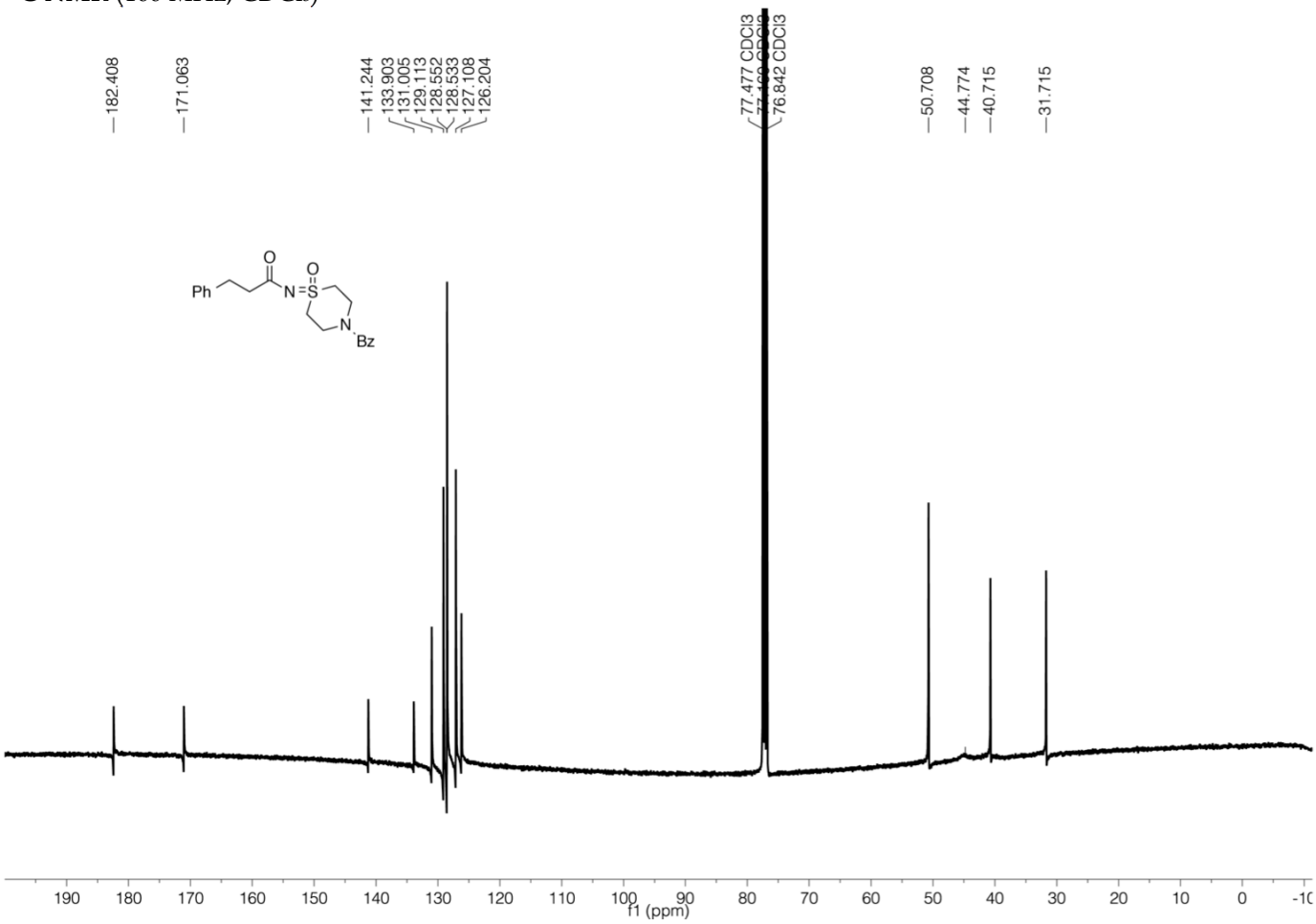


***N*-(4-Benzoyl-1-oxido-1λ⁶-thiomorpholin-1-ylidene)-3-phenylpropanamide (5ai):**

¹H NMR (400 MHz, $CDCl_3$)

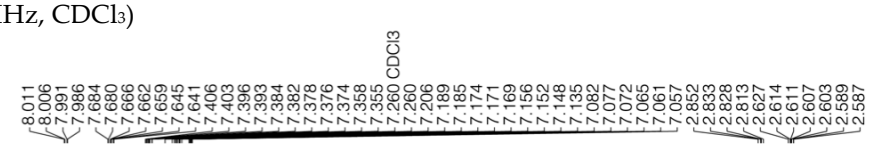


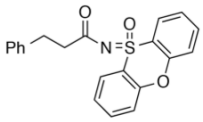
¹³C NMR (100 MHz, $CDCl_3$)

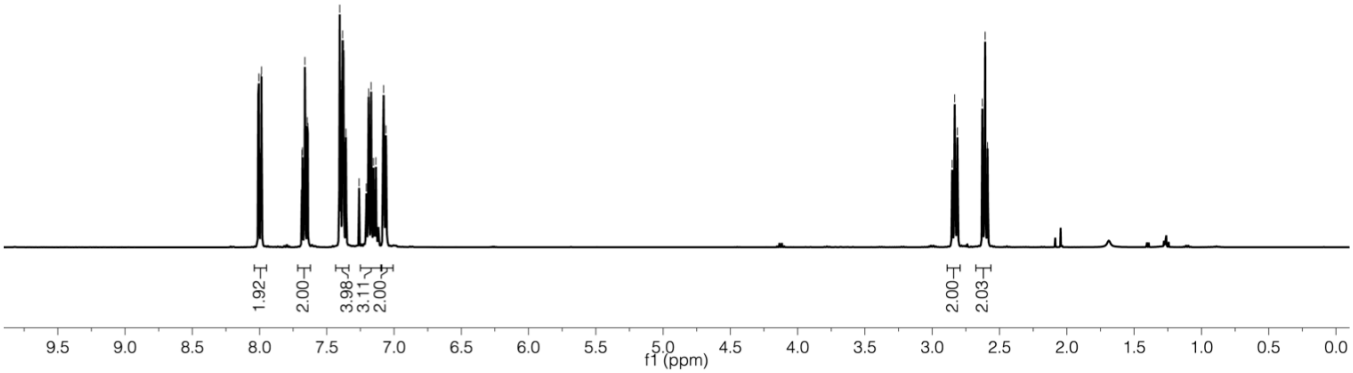


***N*-(10-Oxido-10λ⁴-phenoxathiin-10-ylidene)-3-phenylpropanamide (5aj):**

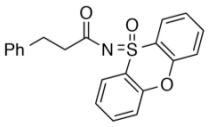
¹H NMR (400 MHz, $CDCl_3$)

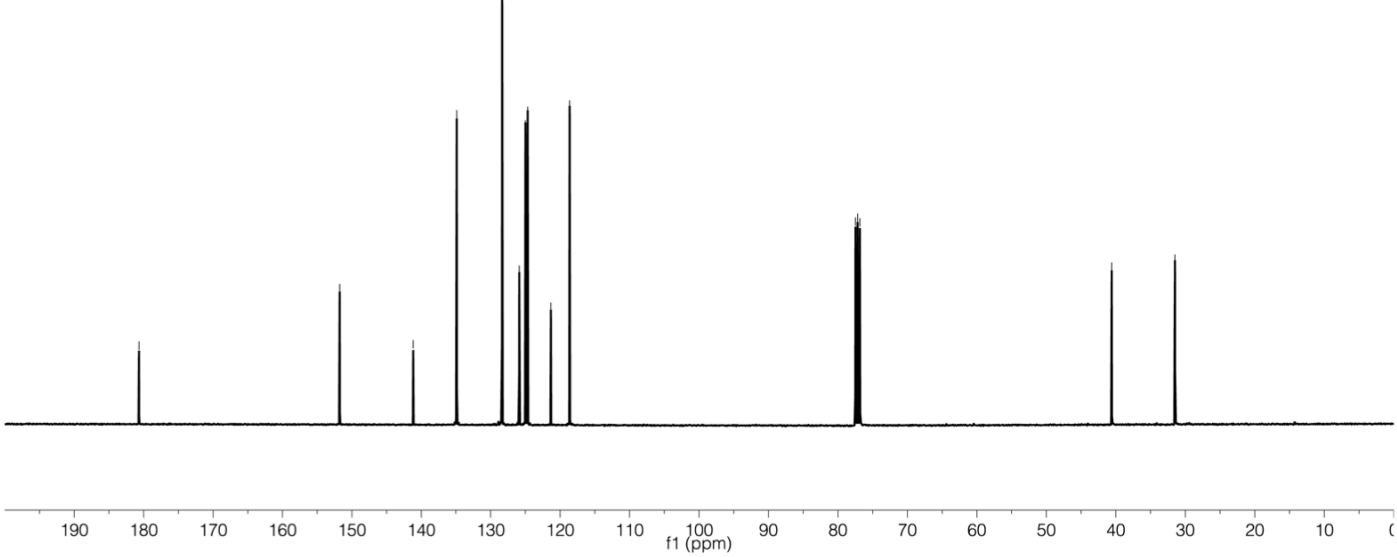






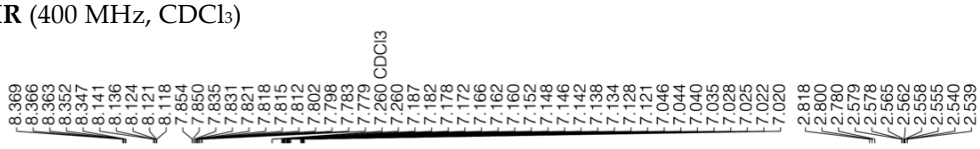
¹³C NMR (100 MHz, $CDCl_3$)

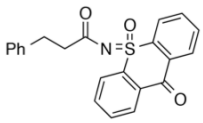


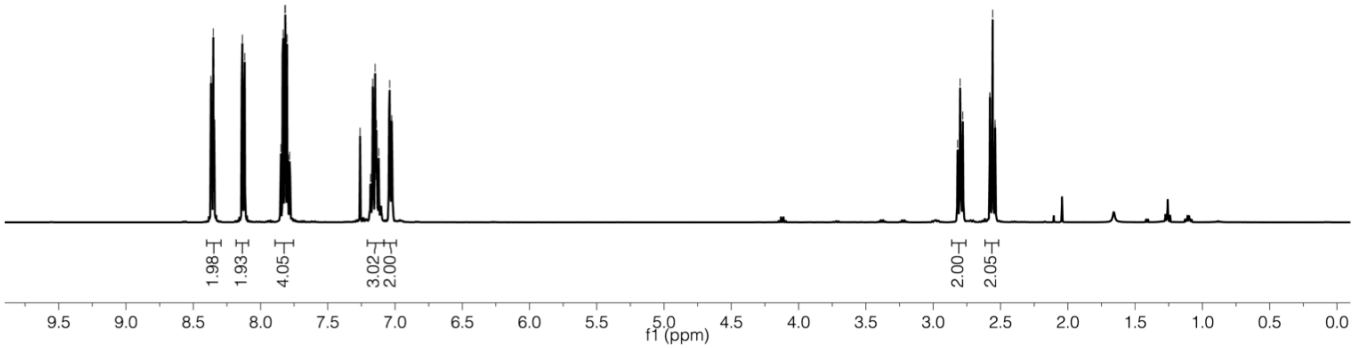


***N*-(10-Oxido-9-oxo-9H-10λ⁴-thioxanthen-10-ylidene)-3-phenylpropanamide (5ak):**

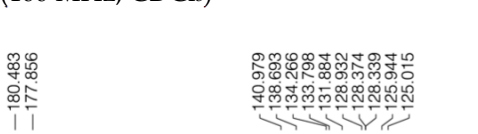
¹H NMR (400 MHz, $CDCl_3$)

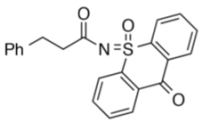


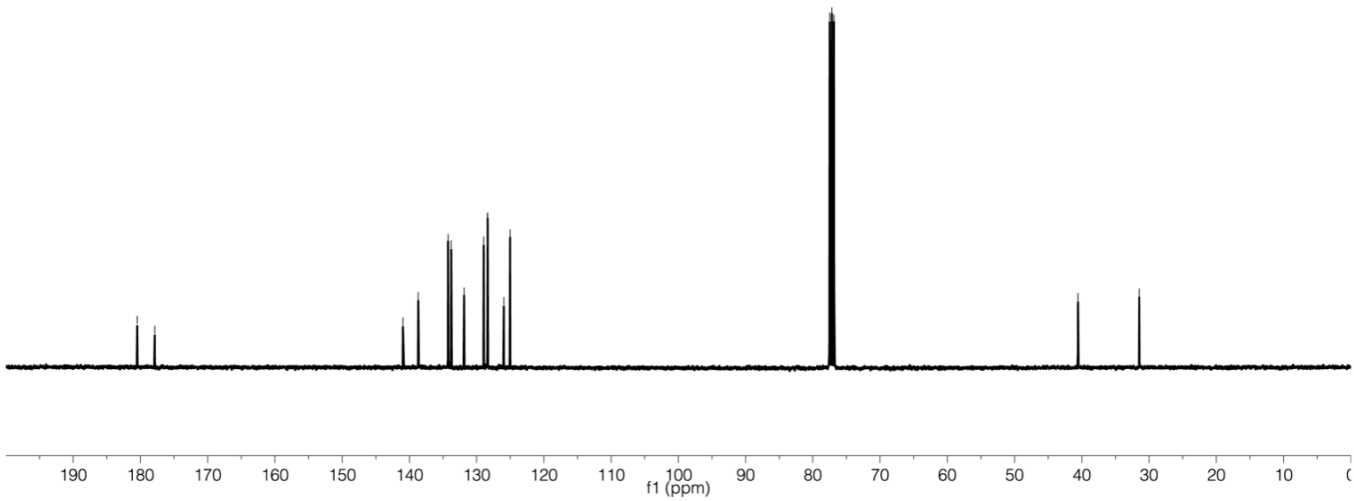




¹³C NMR (100 MHz, $CDCl_3$)

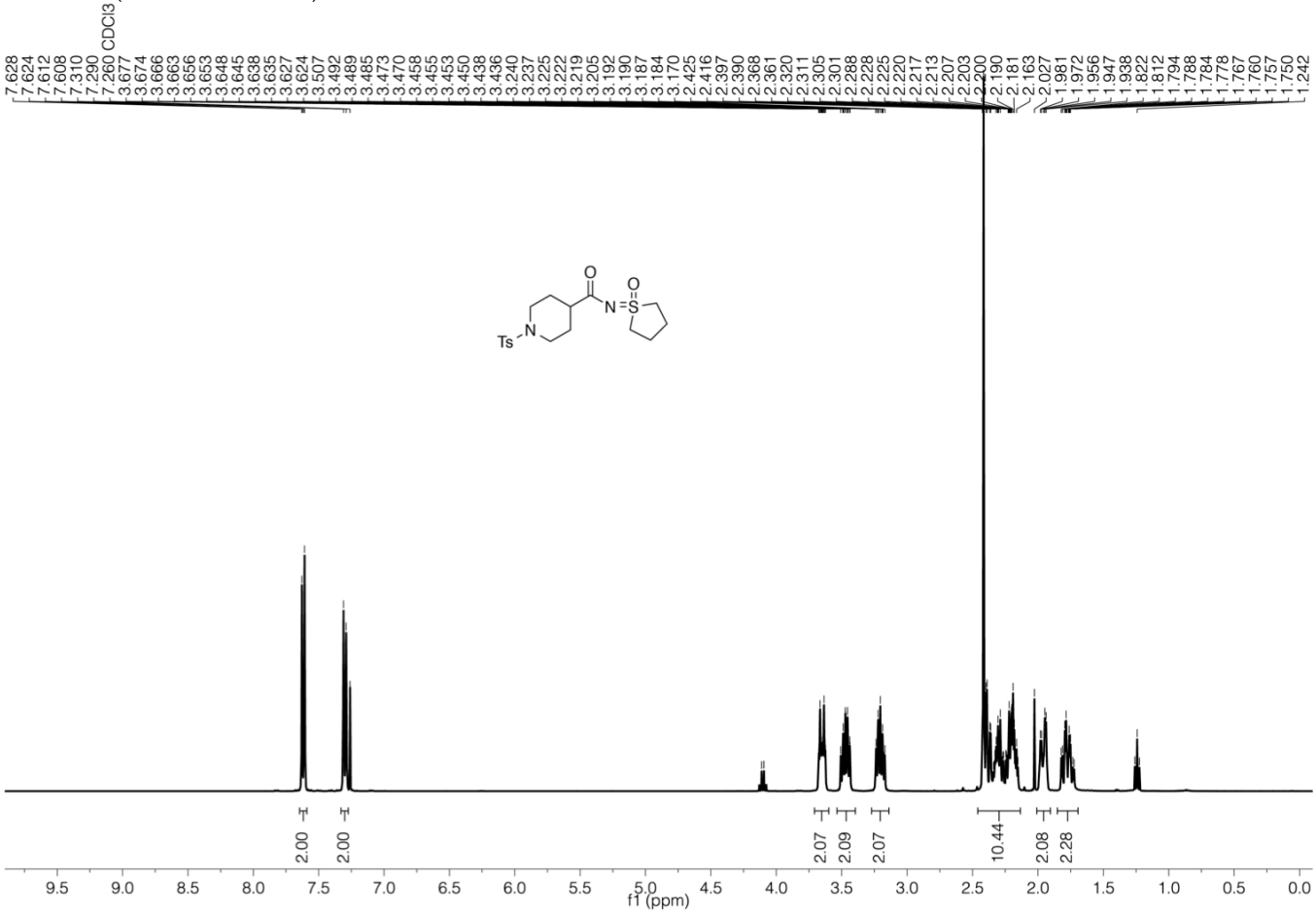




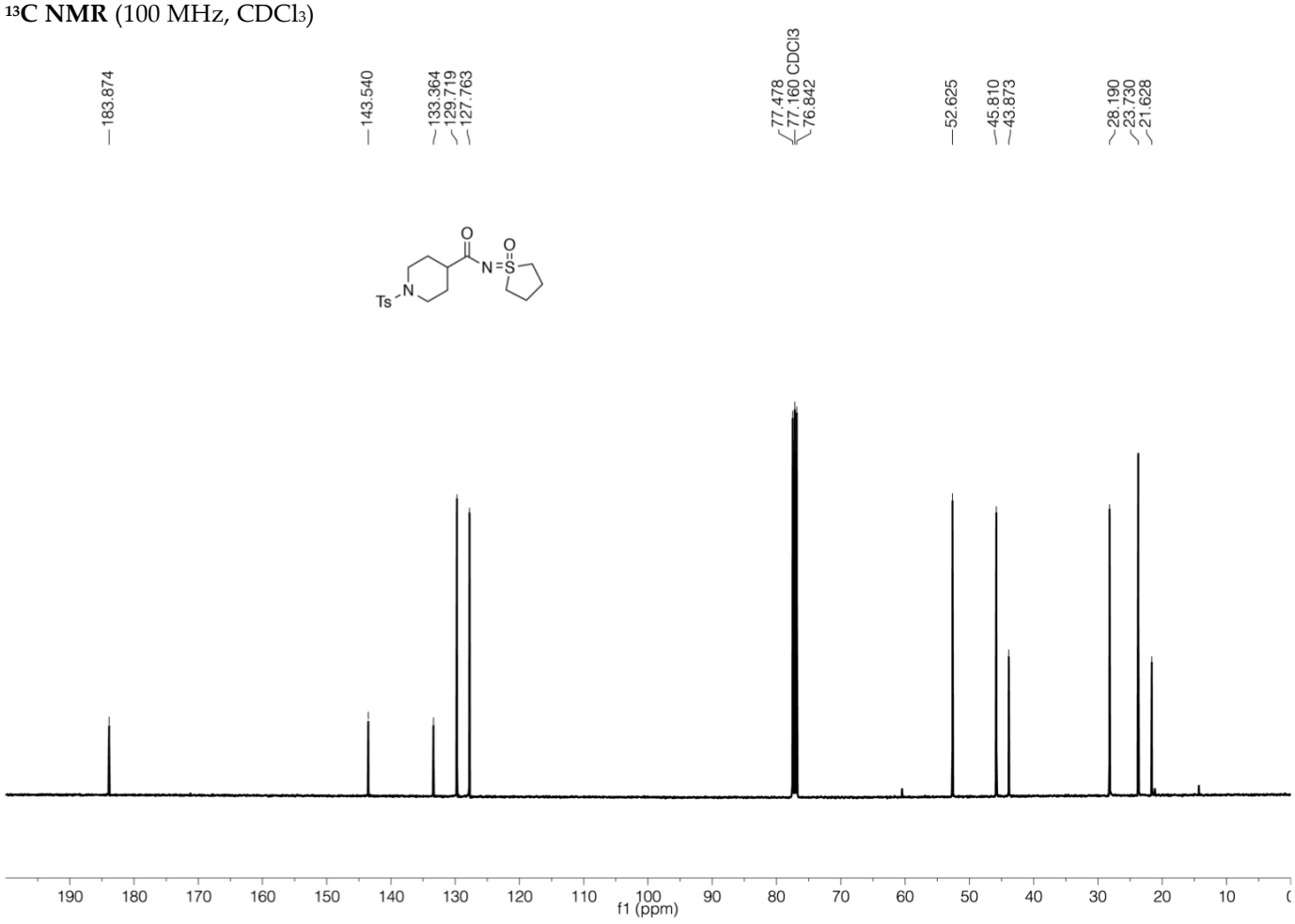


***N*-(1-oxidotetrahydro-1λ⁶-thiophen-1-ylidene)-1-tosylpiperidine-4-carboxamide (5bh):**

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

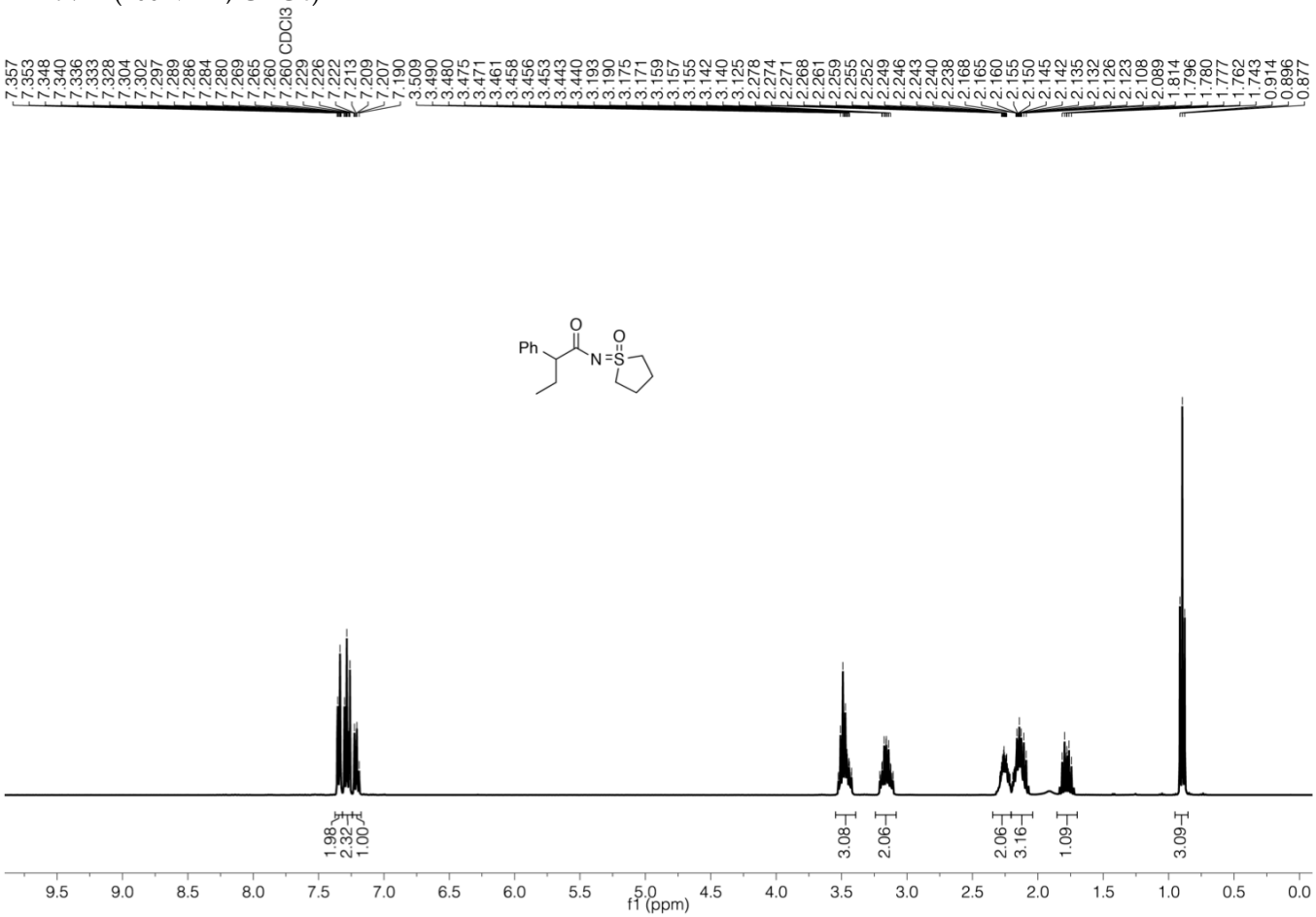


^{13}C NMR (100 MHz, $CDCl_3$)

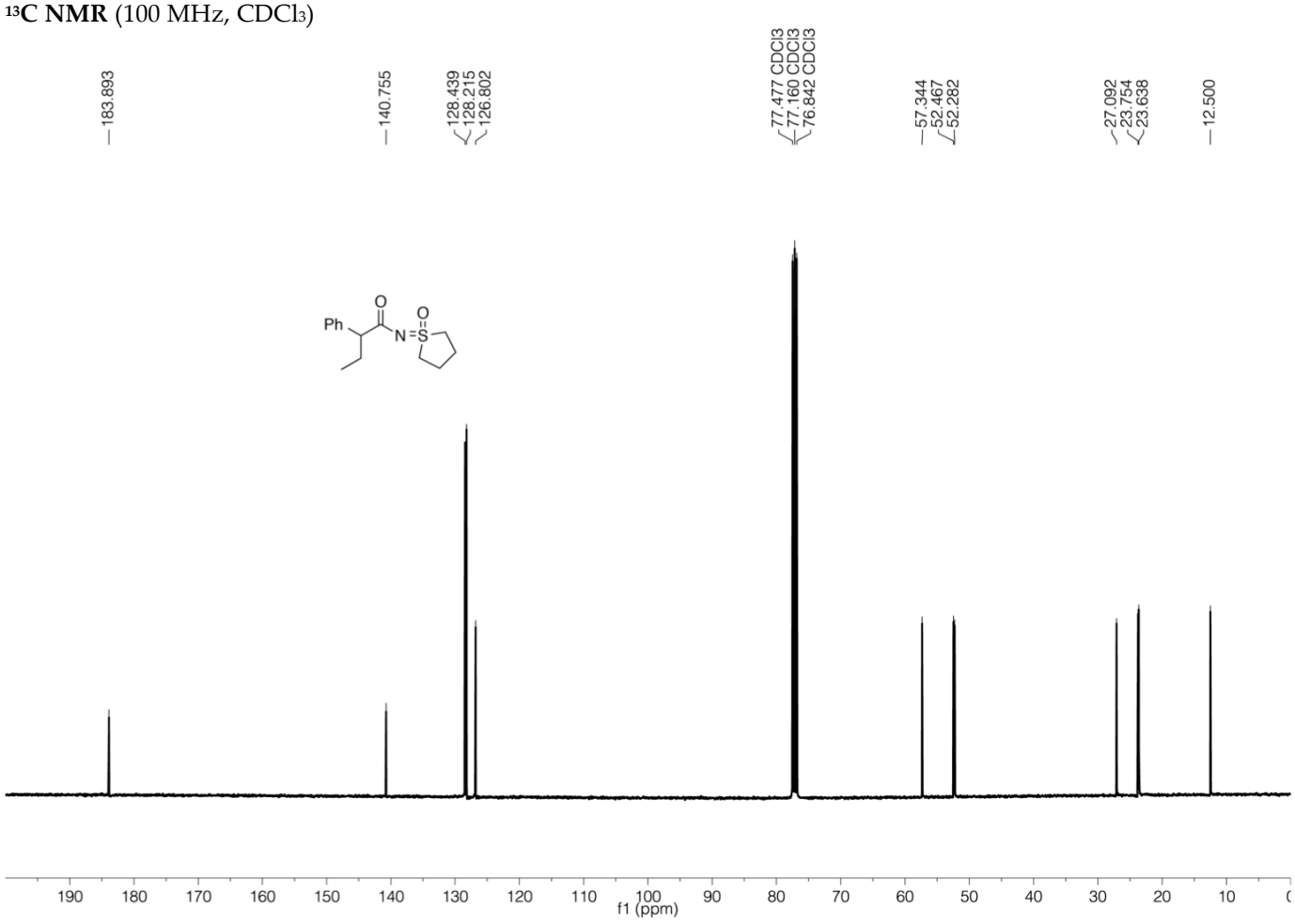


***N*-(1-Oxidotetrahydro-1λ⁶-thiophen-1-ylidene)-2-phenylbutanamide (5ch):**

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

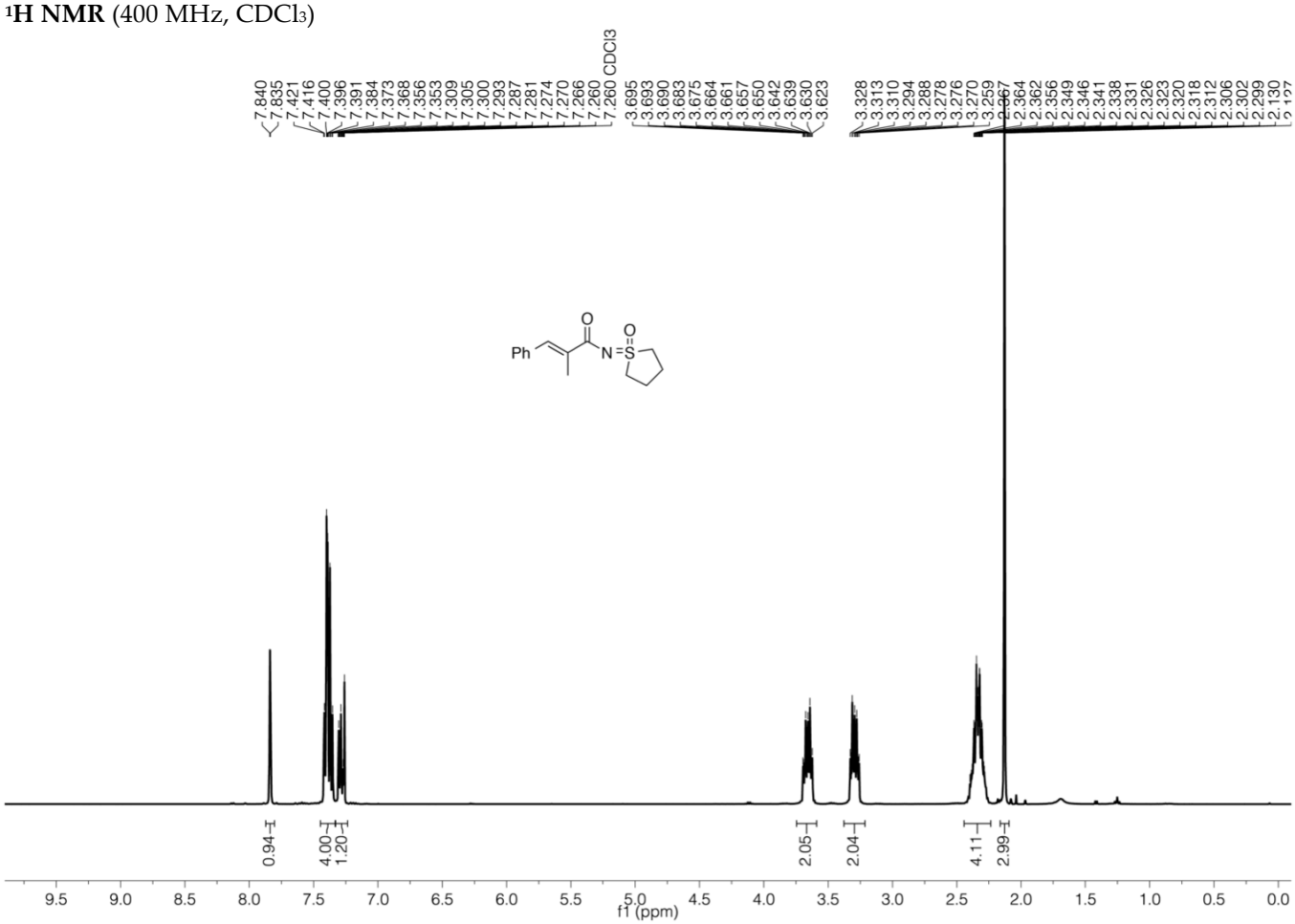


^{13}C NMR (100 MHz, $CDCl_3$)

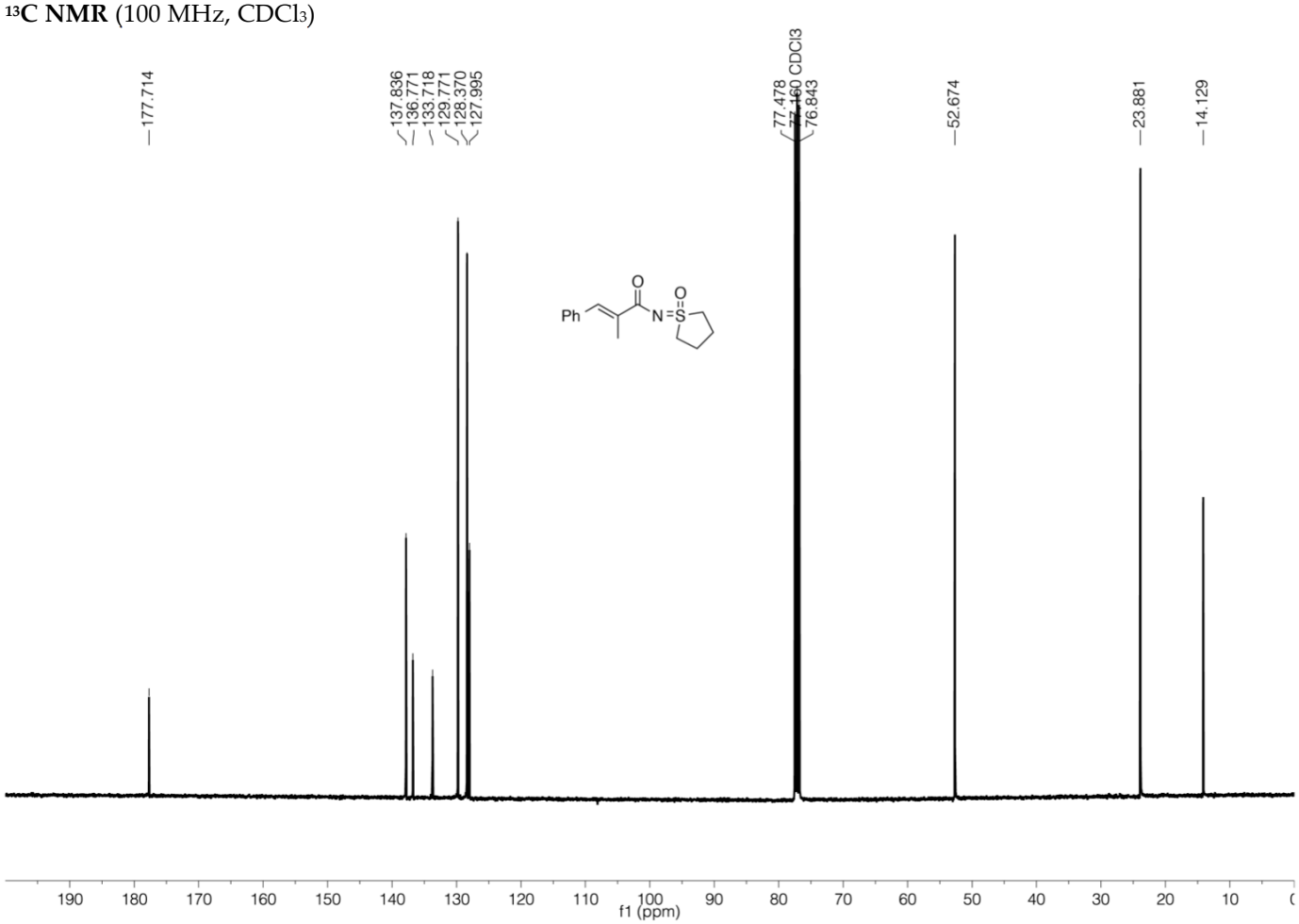


(*E*)-2-Methyl-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)-3-phenylacrylamide (5dh):

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

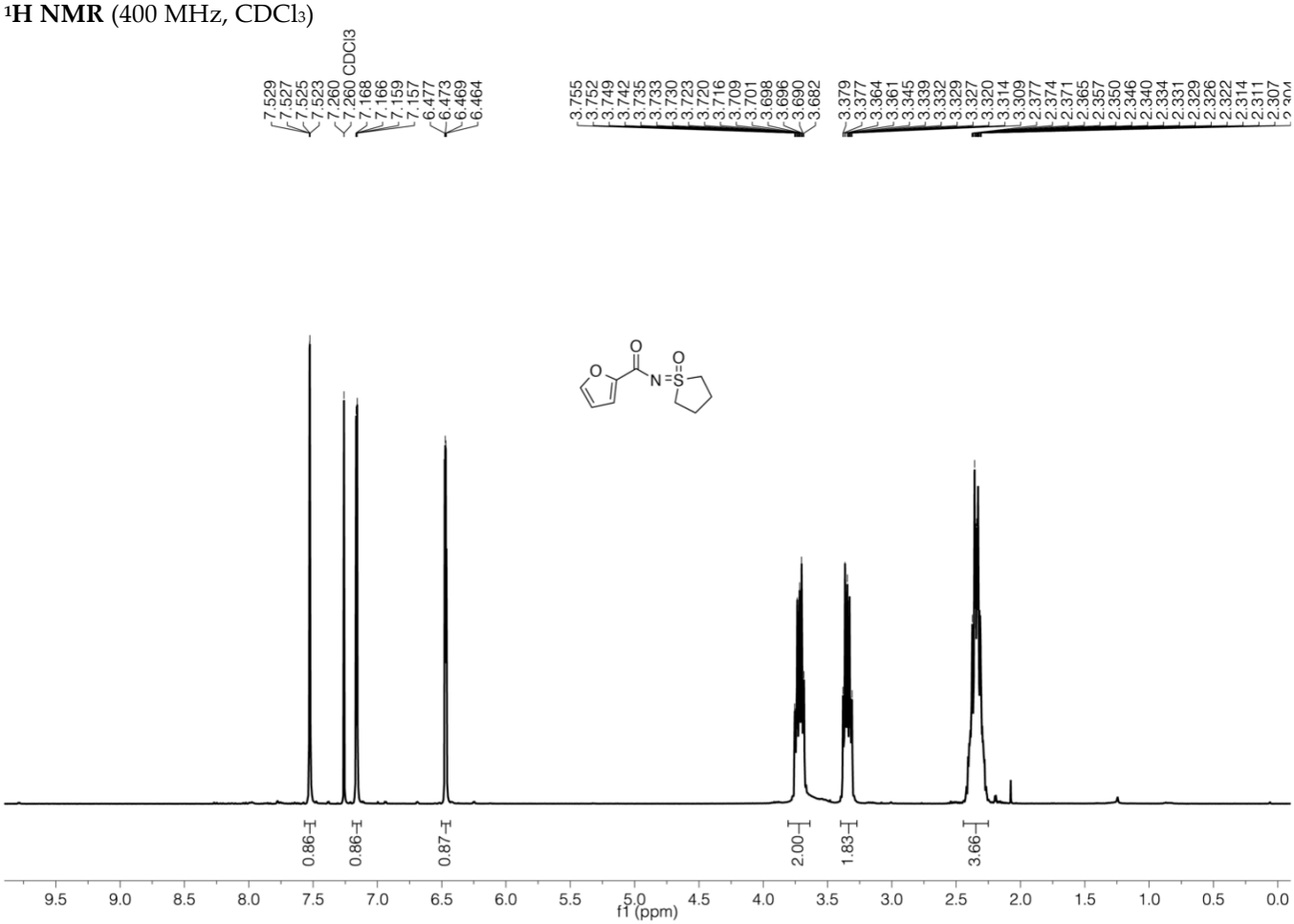


^{13}C NMR (100 MHz, $CDCl_3$)

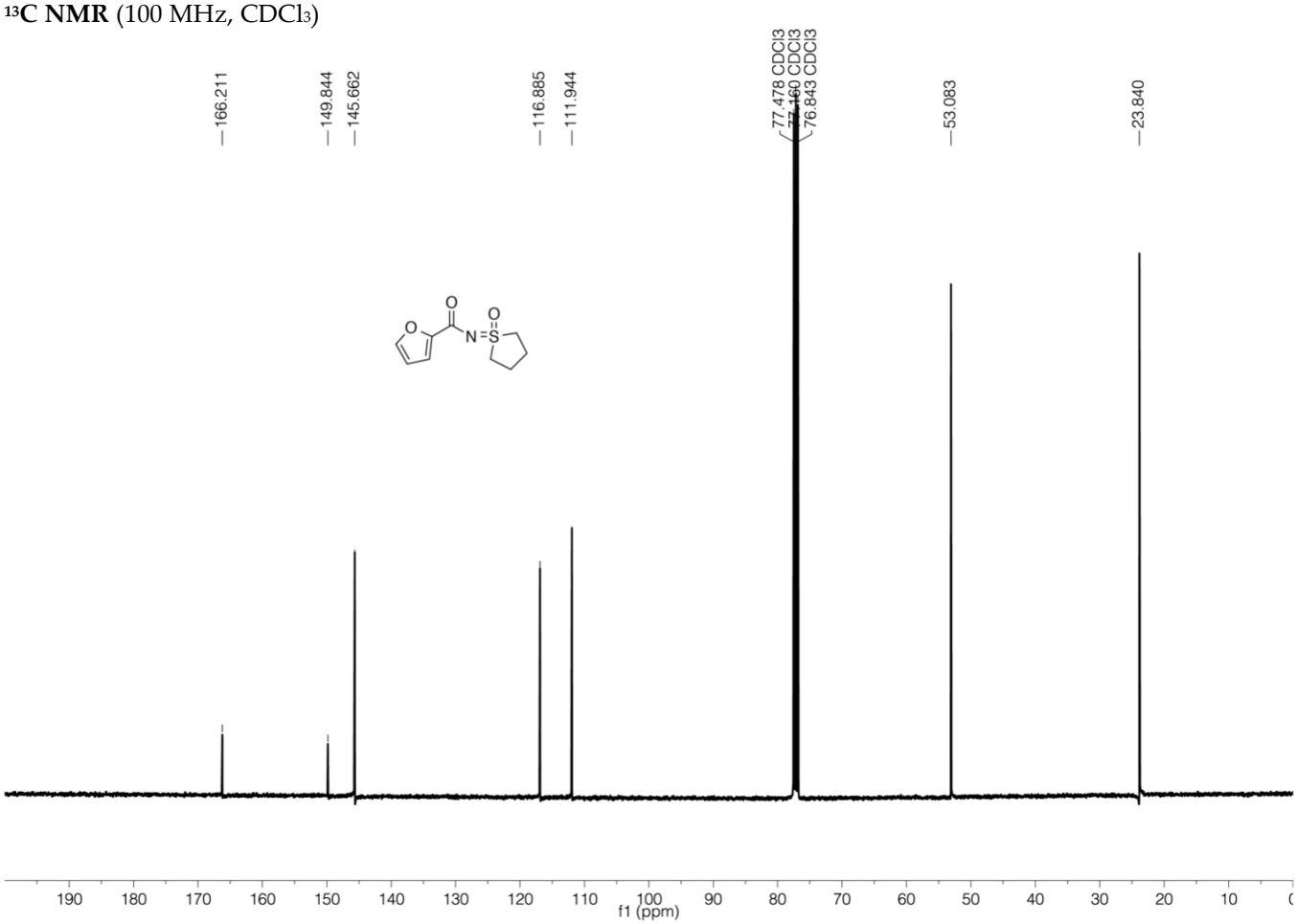


***N*-(1-Oxidotetrahydro-1λ⁶-thiophen-1-ylidene)furan-2-carboxamide (5eh):**

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

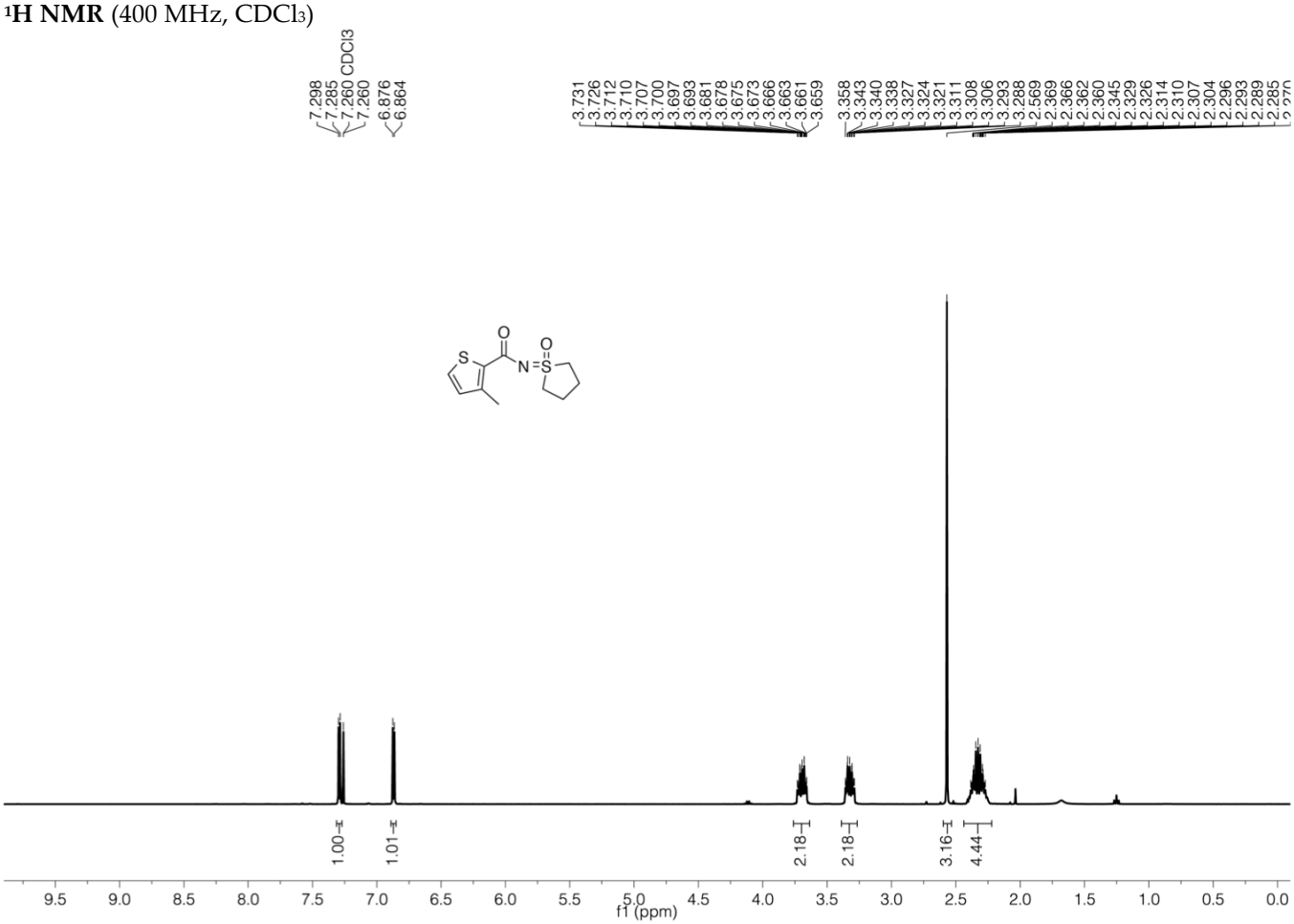


^{13}C NMR (100 MHz, $CDCl_3$)

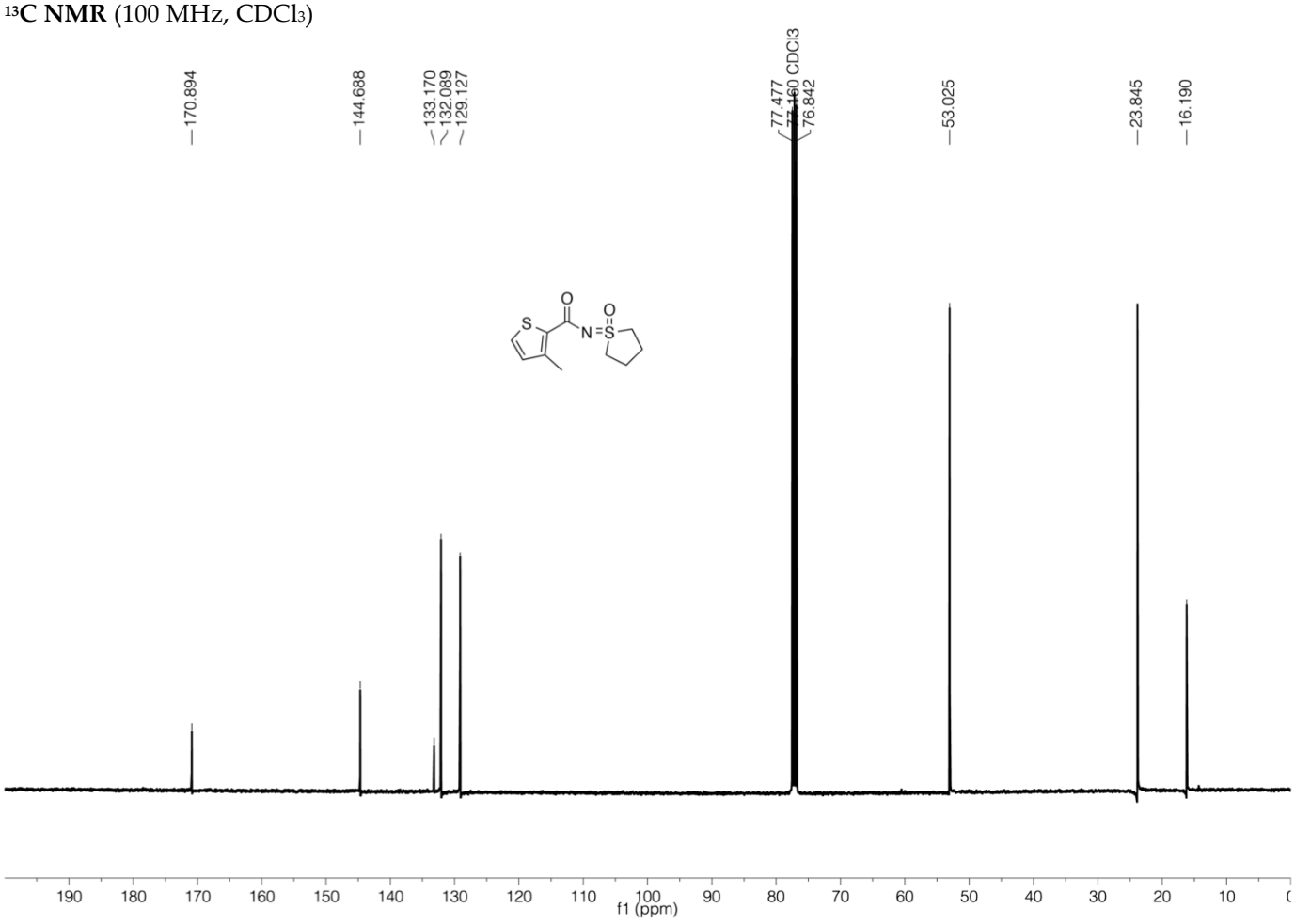


3-Methyl-*N*-(1-oxidotetrahydro-1λ⁶-thiophen-1-ylidene)thiophene-2-carboxamide (5fh):

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

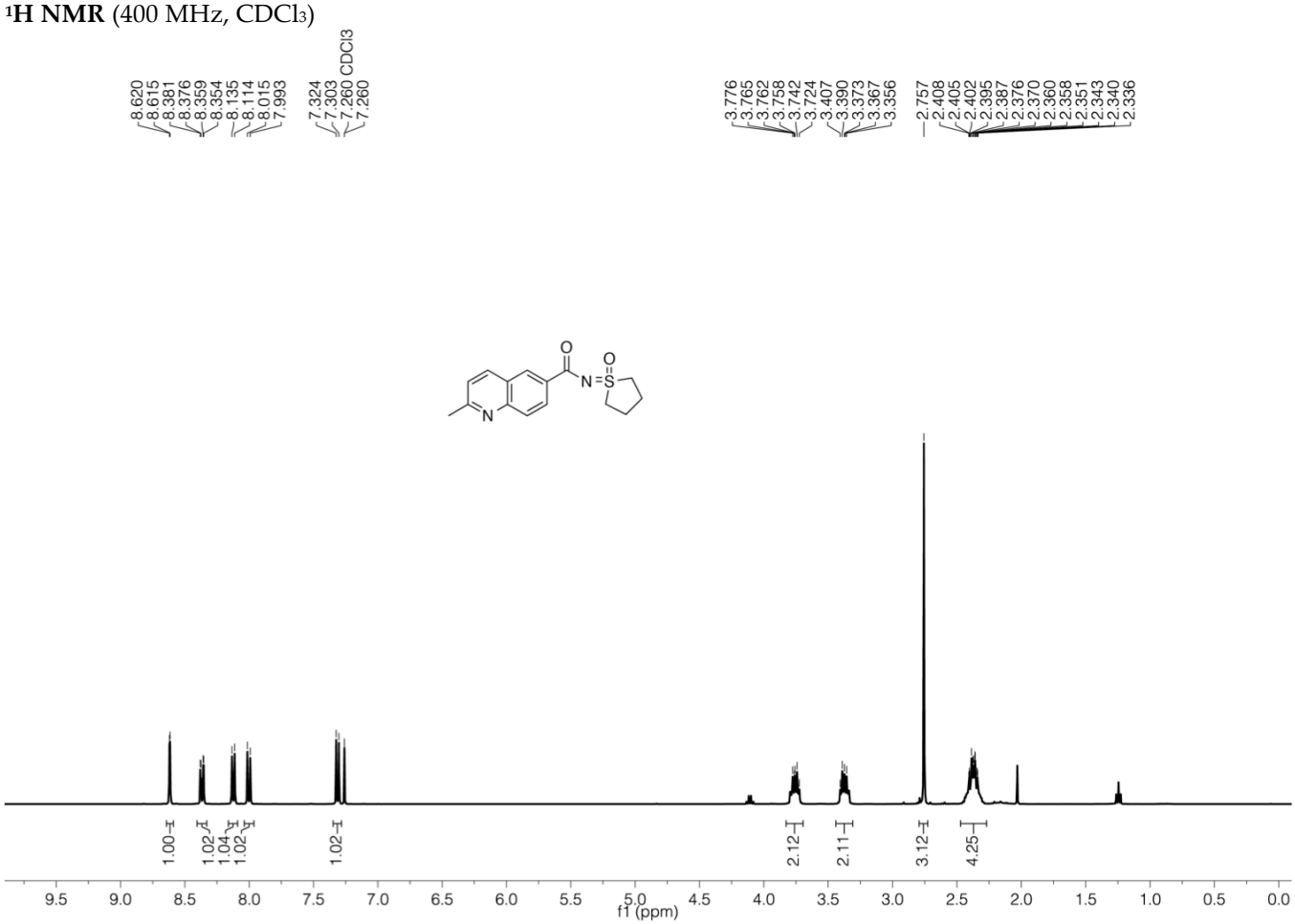


^{13}C NMR (100 MHz, $CDCl_3$)

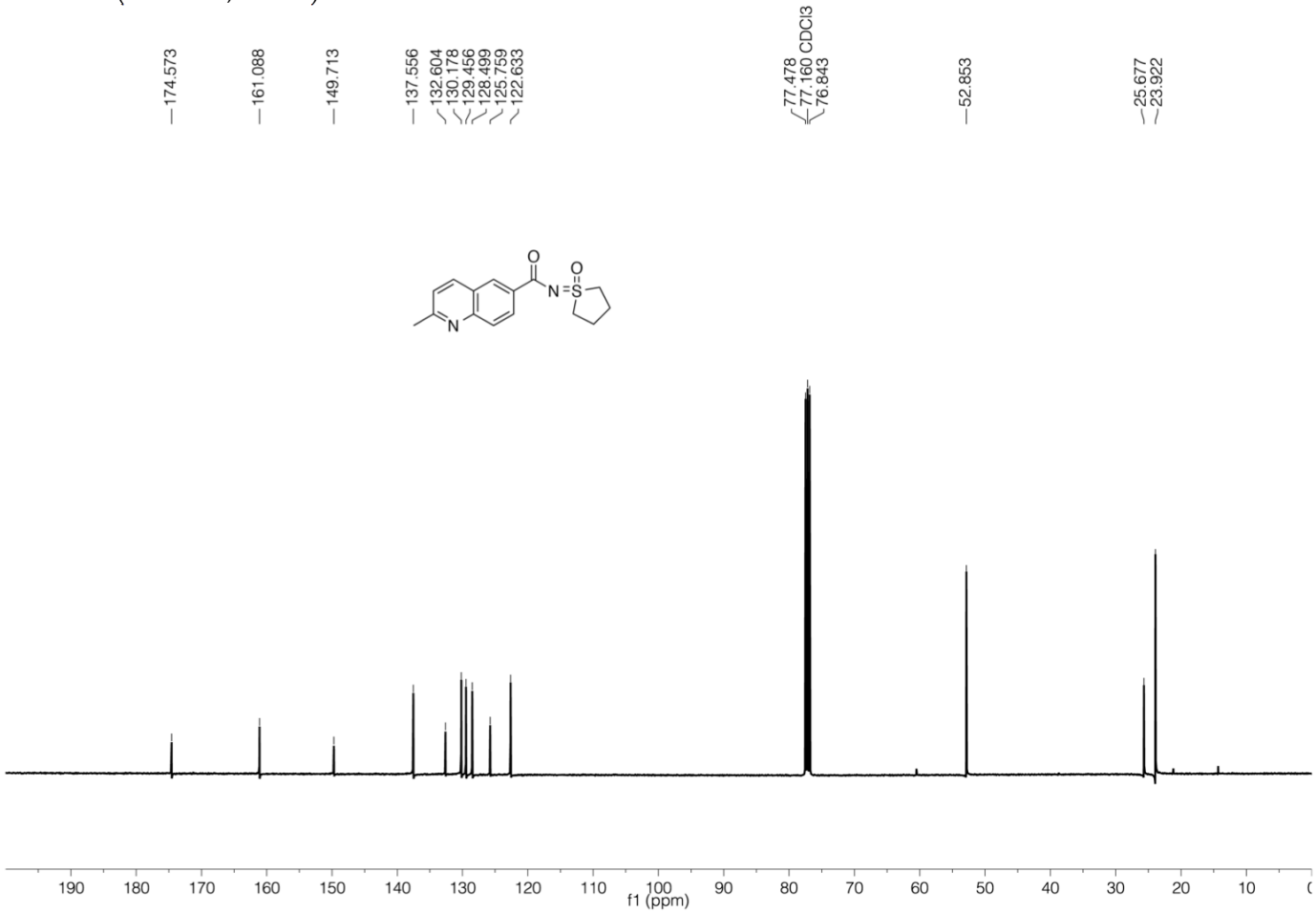


2-Methyl-*N*-(1-oxidotetrahydro-1λ⁶-thiophen-1-ylidene)quinoline-6-carboxamide (5gh):

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

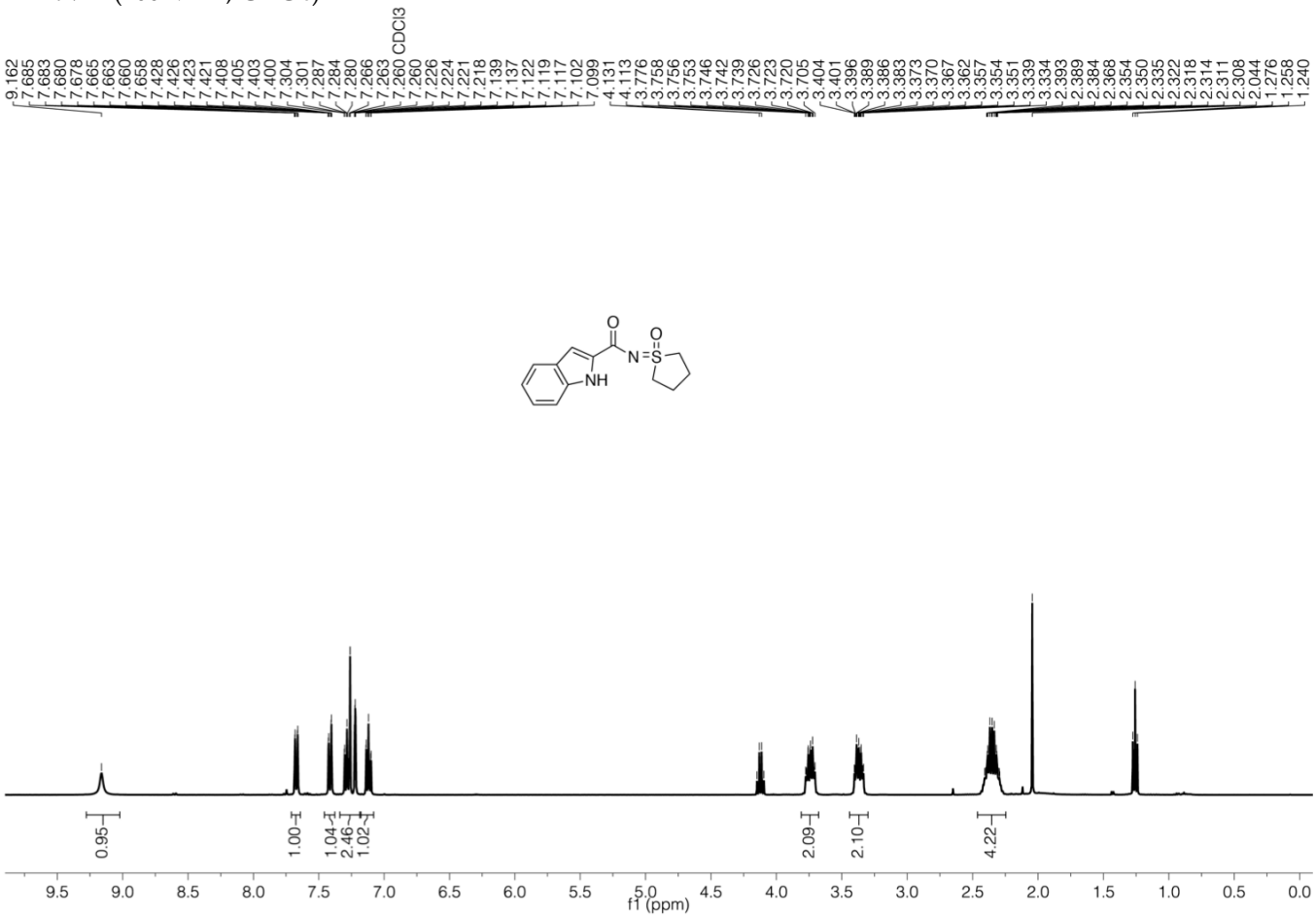


^{13}C NMR (100 MHz, $CDCl_3$)

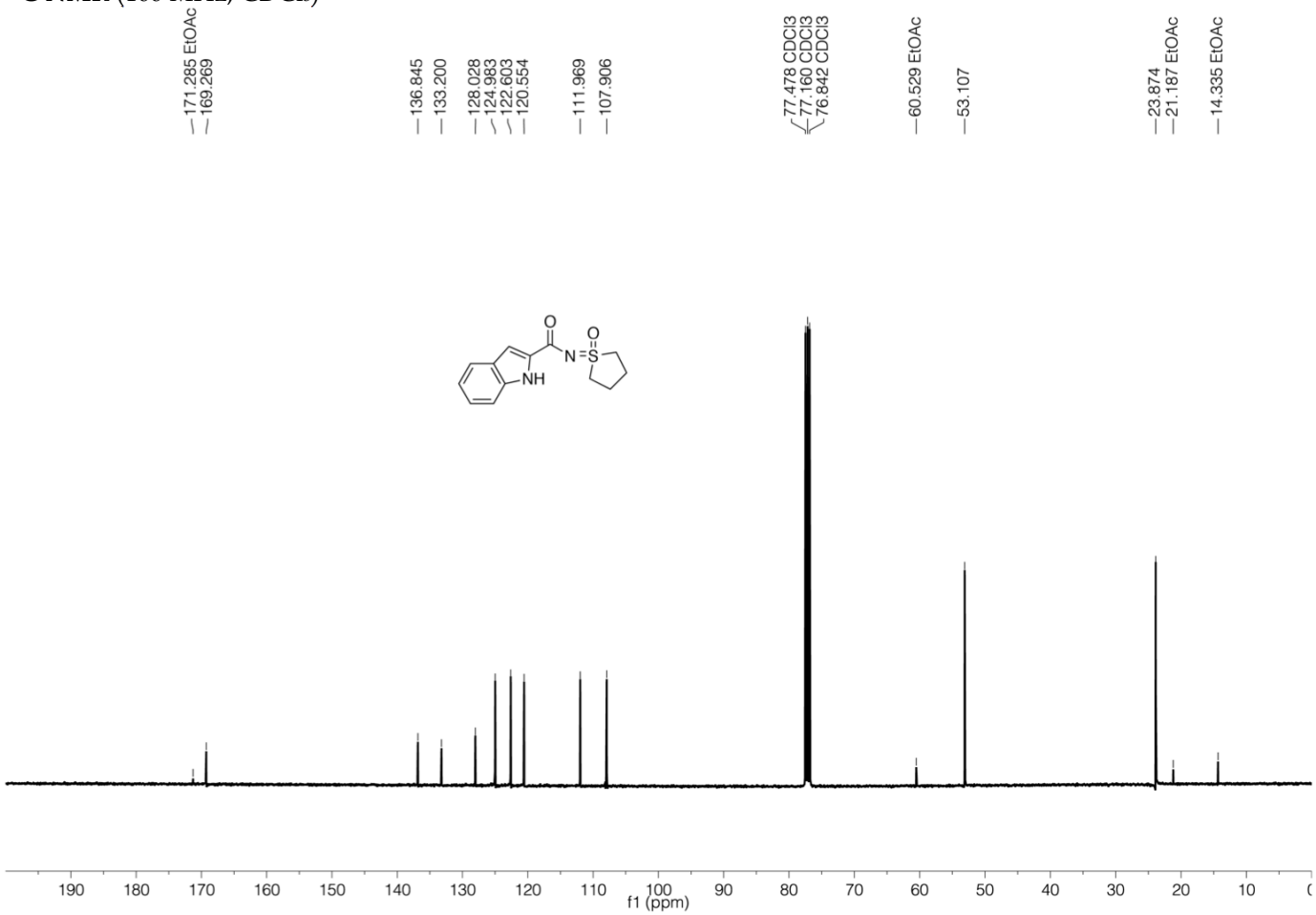


***N*-(1-Oxidotetrahydro-1λ⁶-thiophen-1-ylidene)-1*H*-indole-2-carboxamide (5hh):**

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

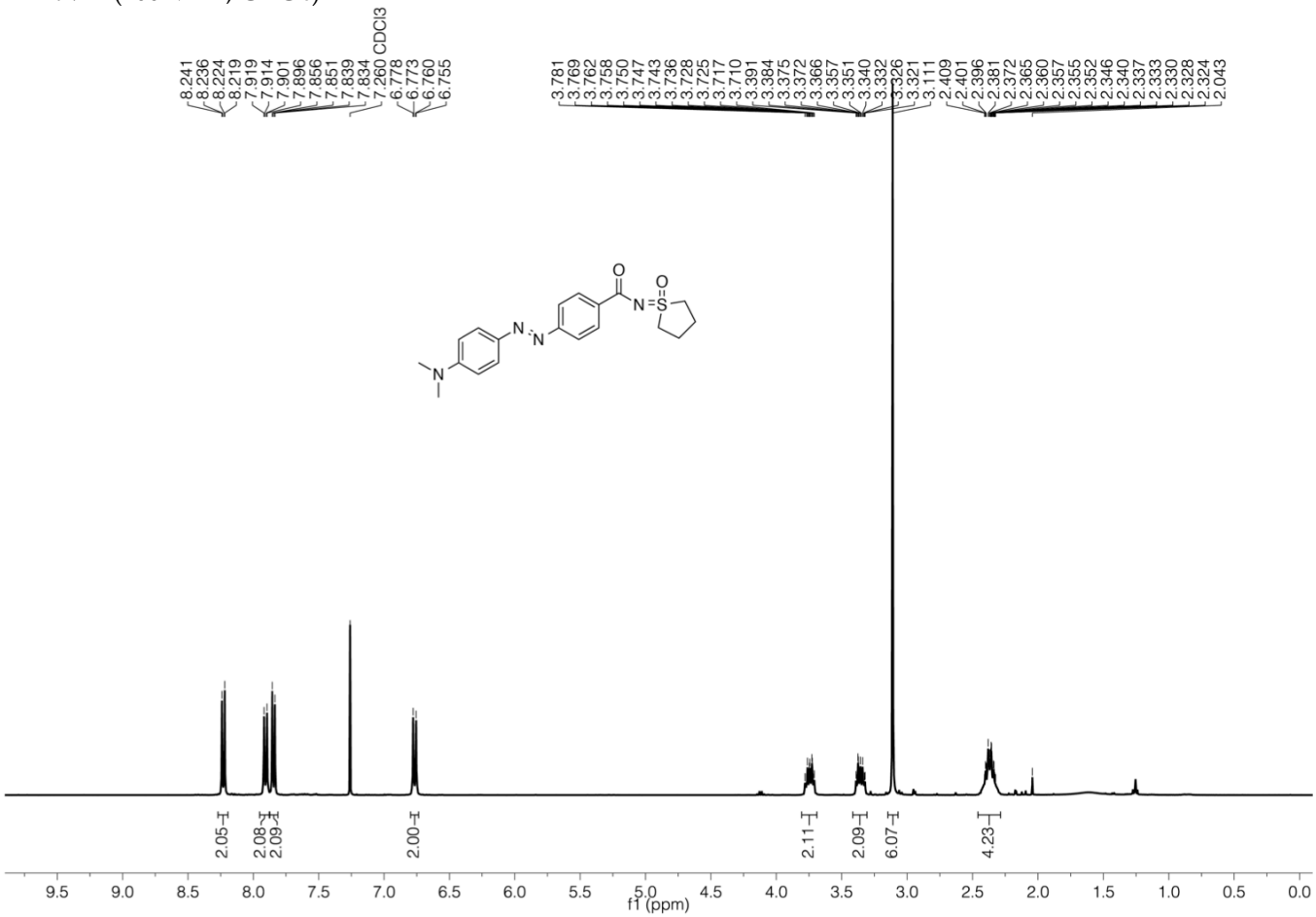


^{13}C NMR (100 MHz, $CDCl_3$)

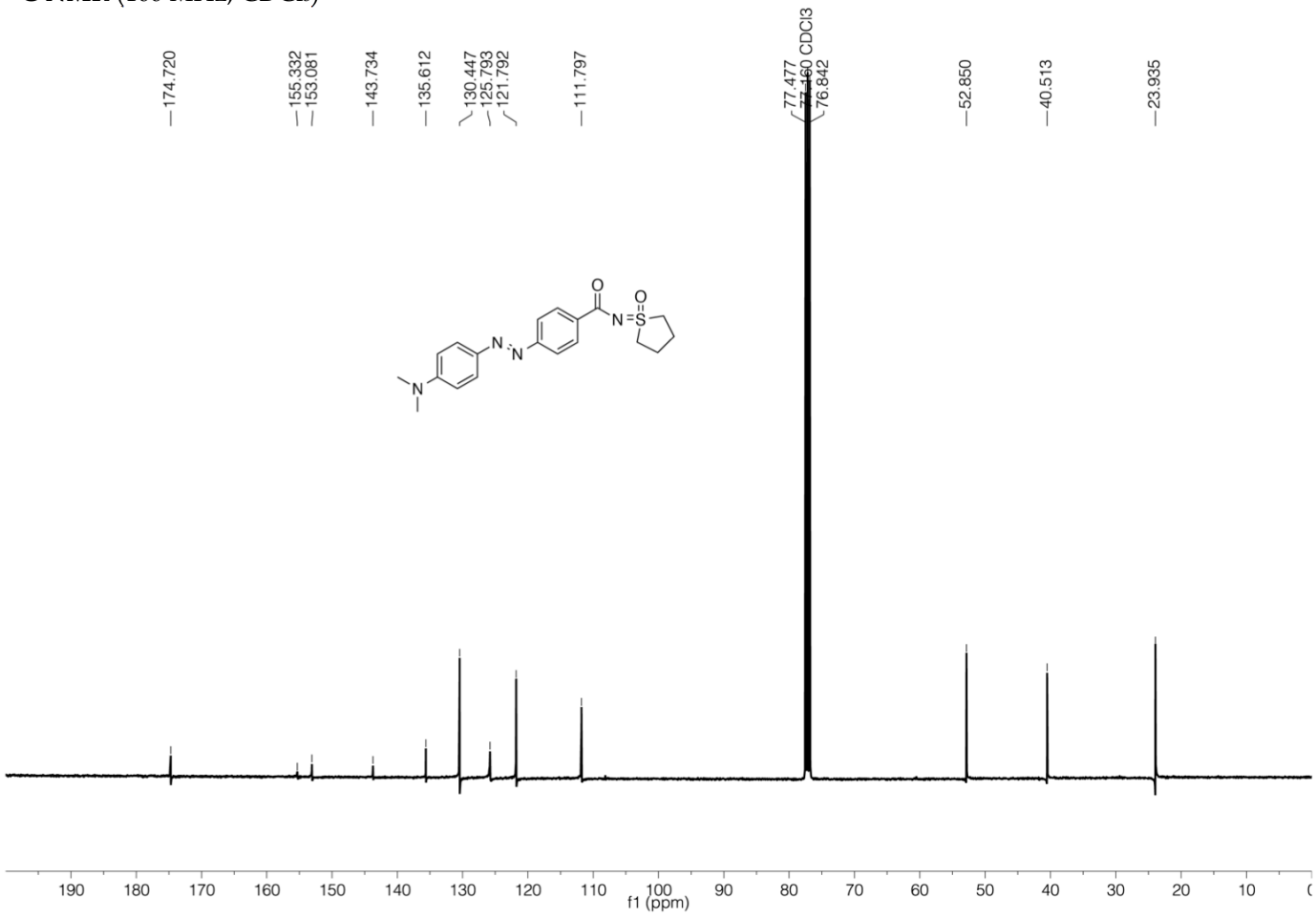


(*E*)-4-((4-(Dimethylamino)phenyl)diazenyl)-*N*-(1-oxidotetrahydro-1λ^6-thiophen-1-ylidene)benzamide (5ih):

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

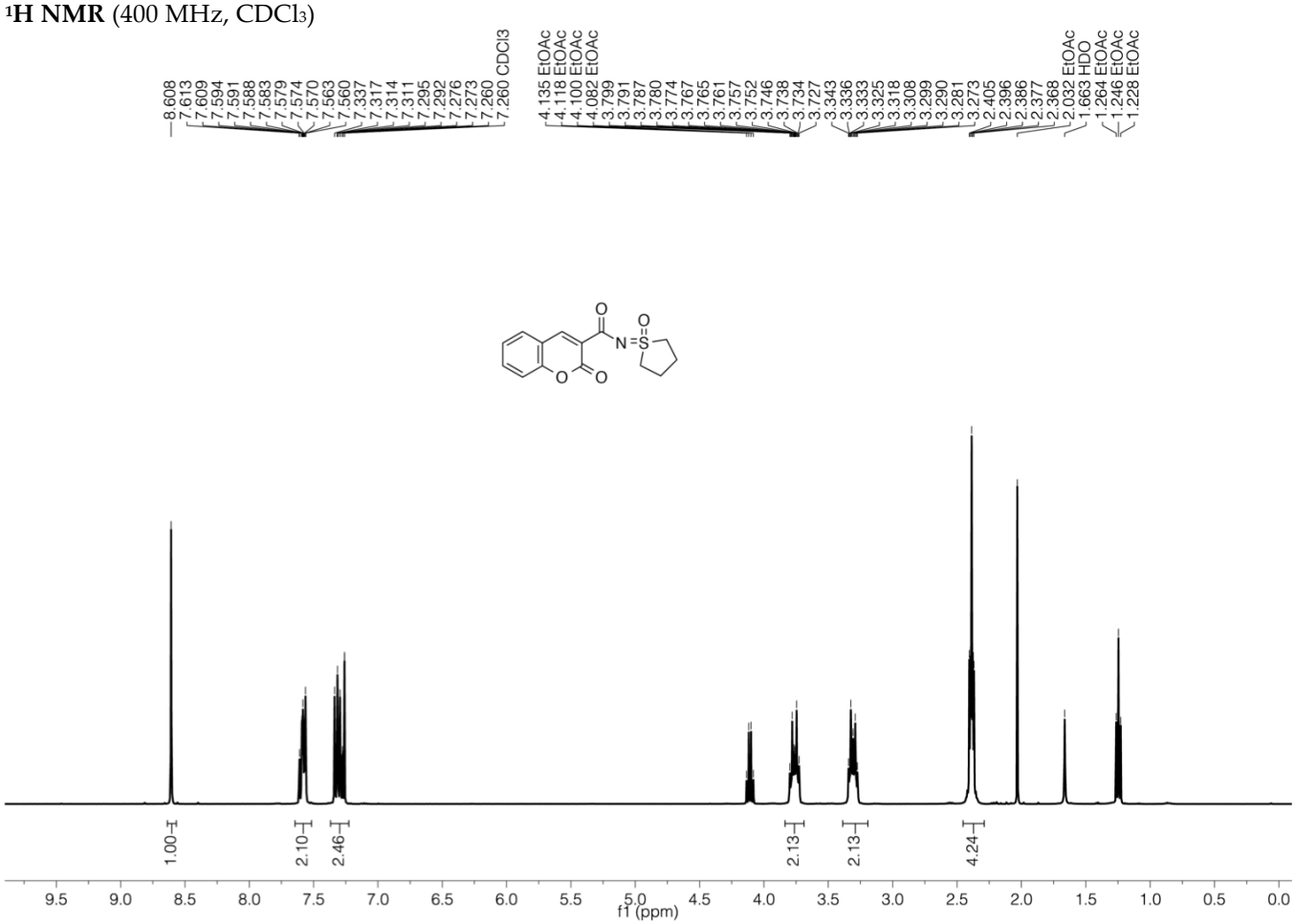


^{13}C NMR (100 MHz, $CDCl_3$)

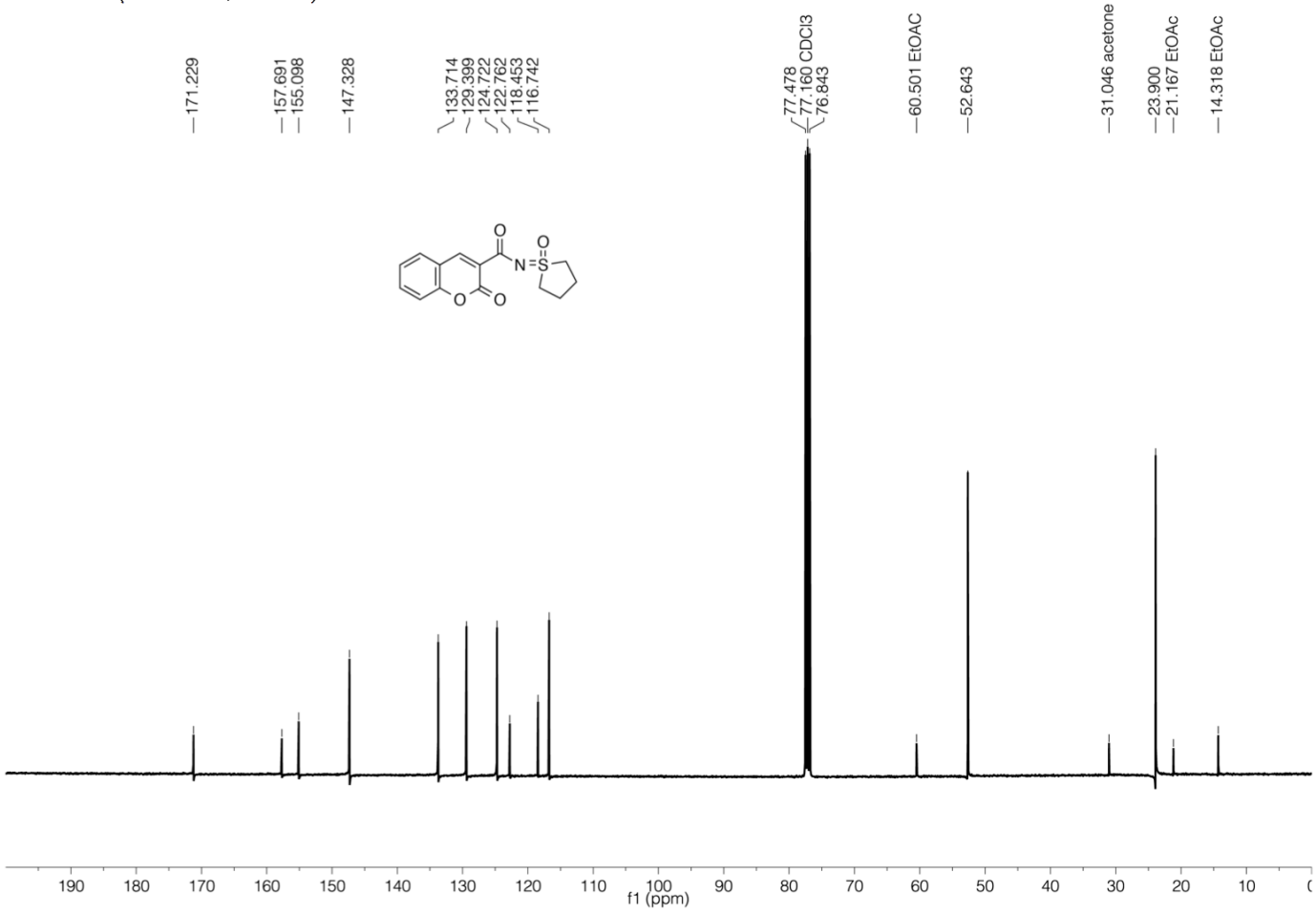


***N*-(1-Oxidotetrahydro-1λ⁶-thiophen-1-ylidene)-2-oxo-2*H*-chromene-3-carboxamide (5jh):**

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

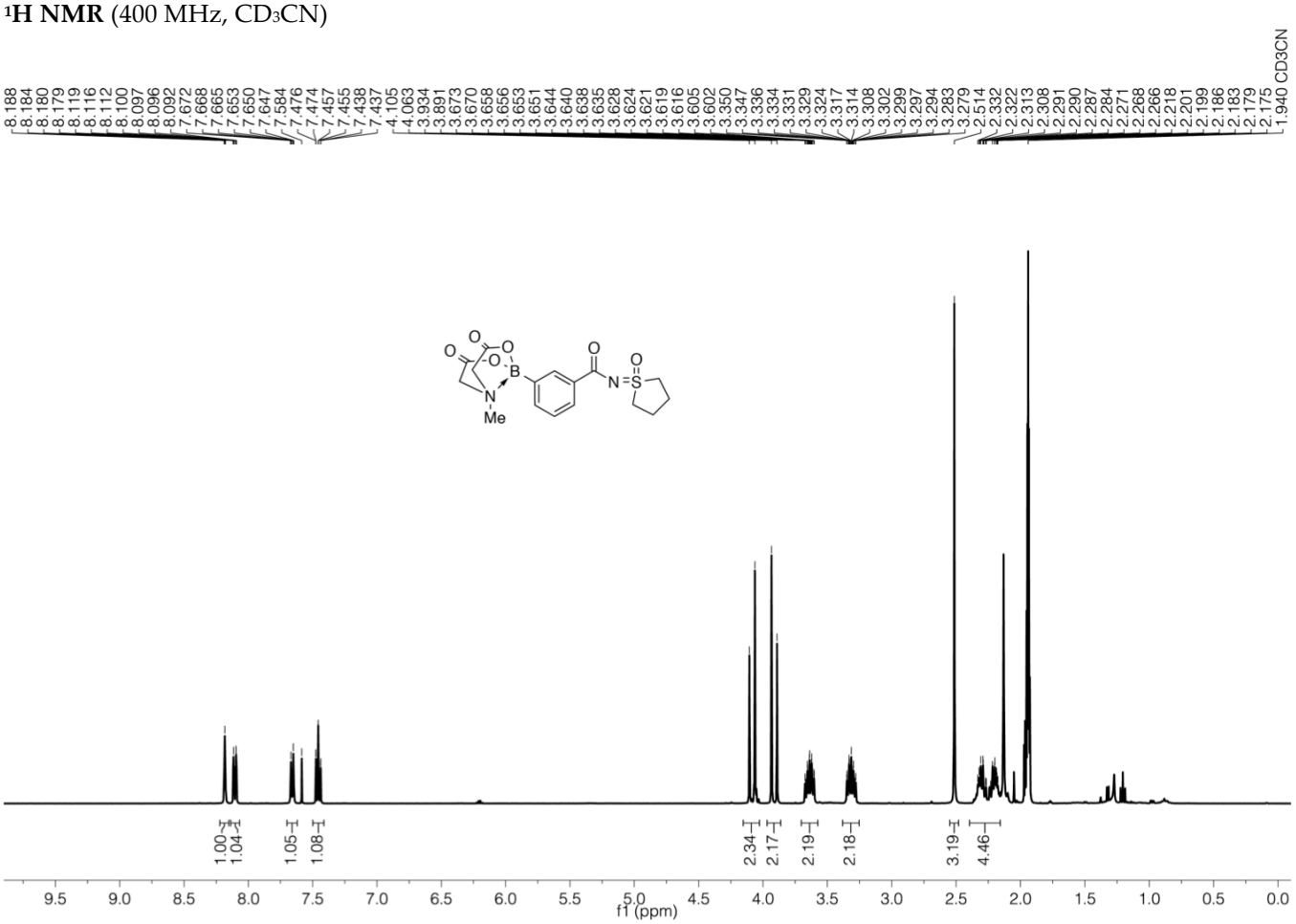


^{13}C NMR (100 MHz, $CDCl_3$)

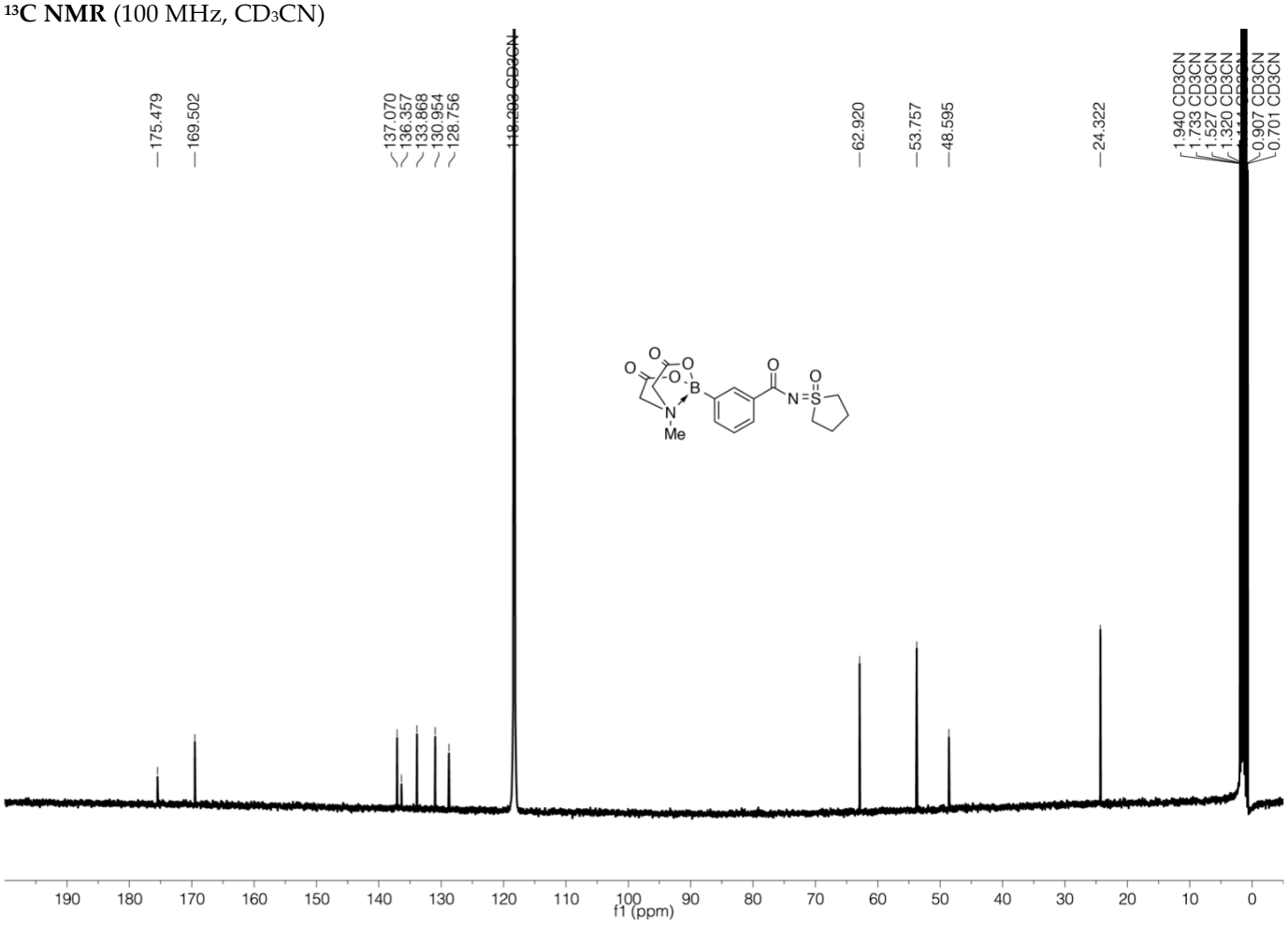


(3-((1-Oxidotetrahydro-1λ⁶-thiophen-1-ylidene)carbamoyl)phenyl)boronic acid MIDA ester (5kh):

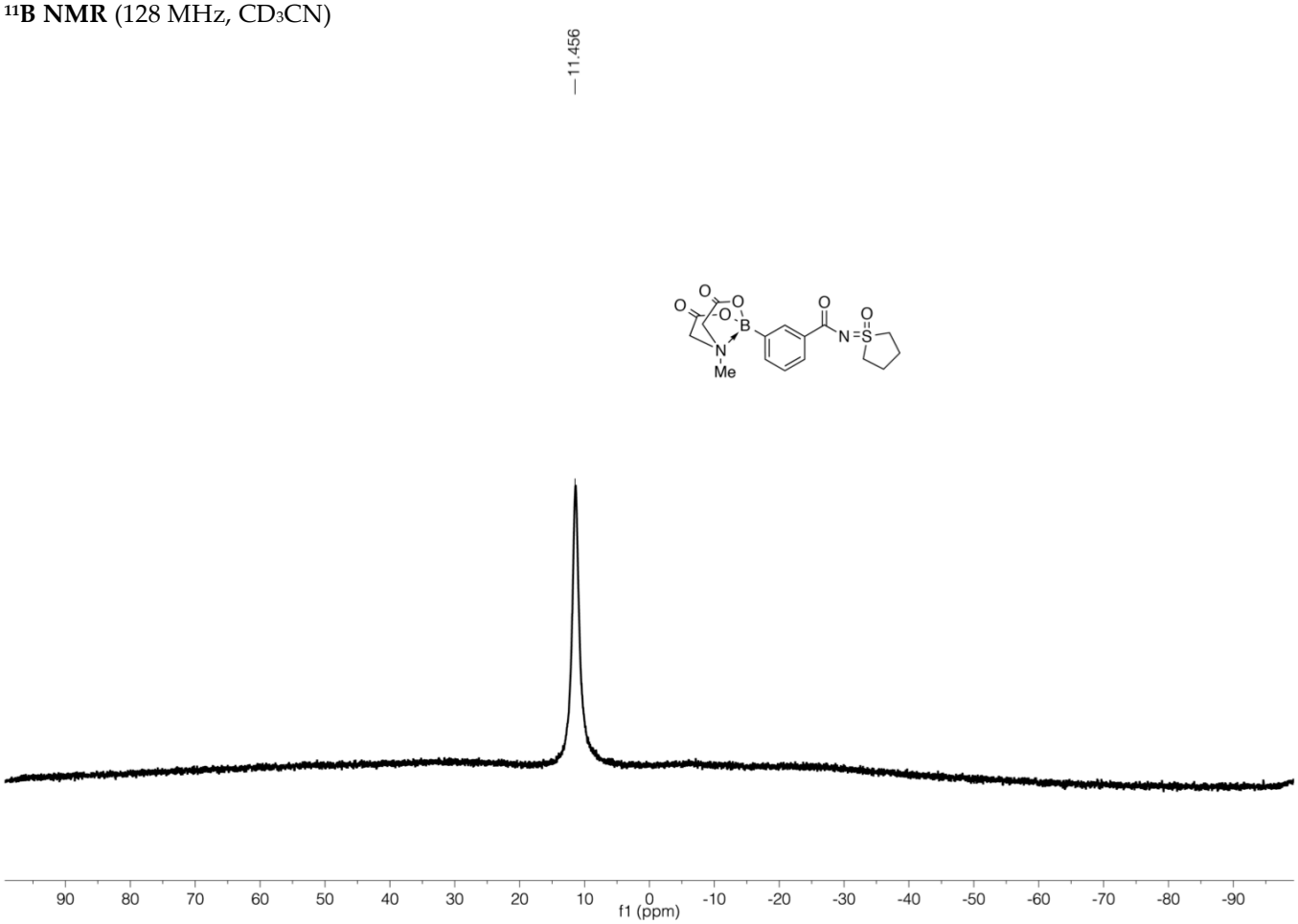
^{1}H NMR (400 MHz, CD_3CN)



^{13}C NMR (100 MHz, CD_3CN)

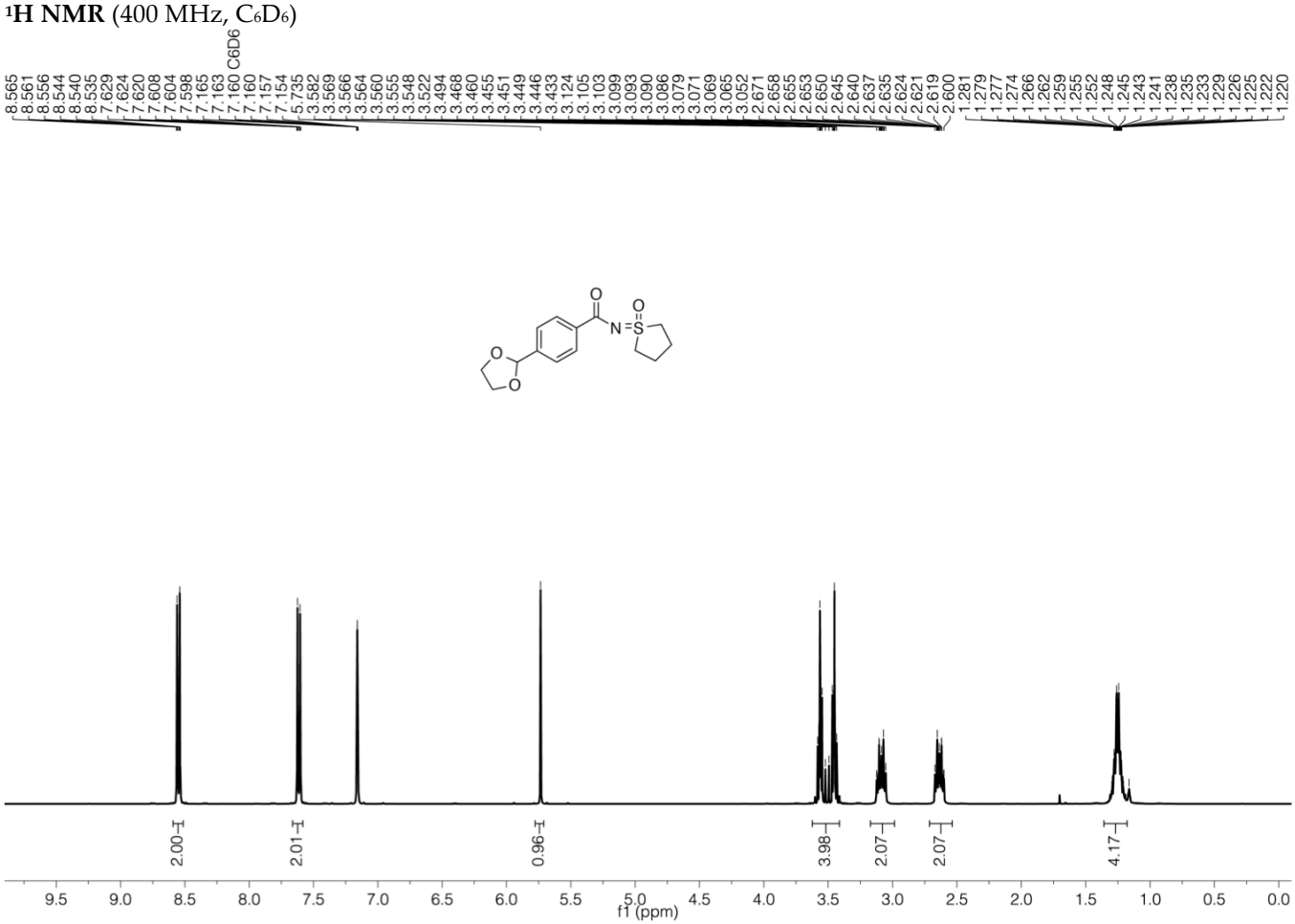


^{11}B NMR (128 MHz, CD_3CN)

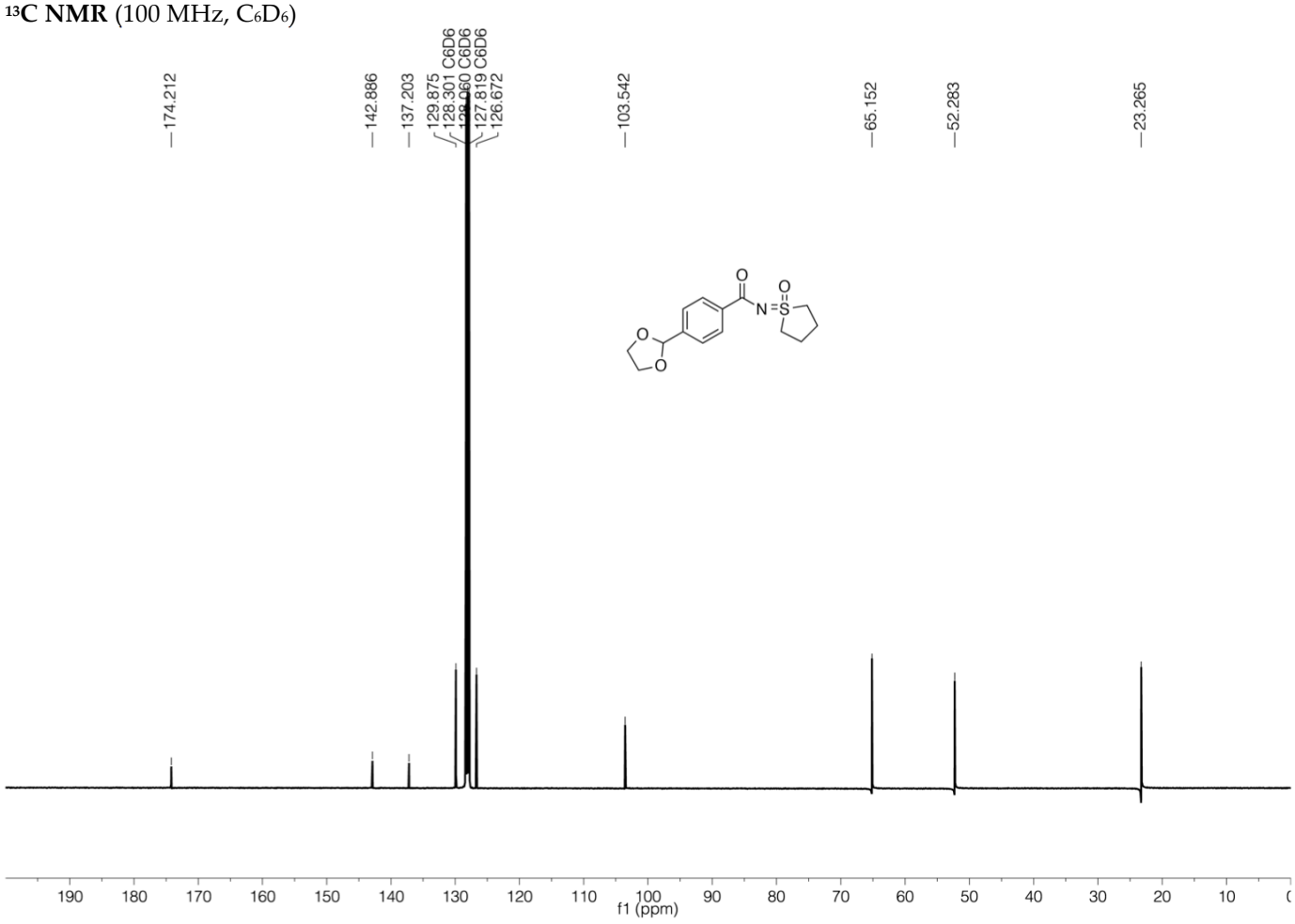


4-(1,3-Dioxolan-2-yl)-*N*-(1-oxidotetrahydro-1λ⁶-thiophen-1-ylidene)benzamide (5lh):

¹H NMR (400 MHz, C_6D_6)

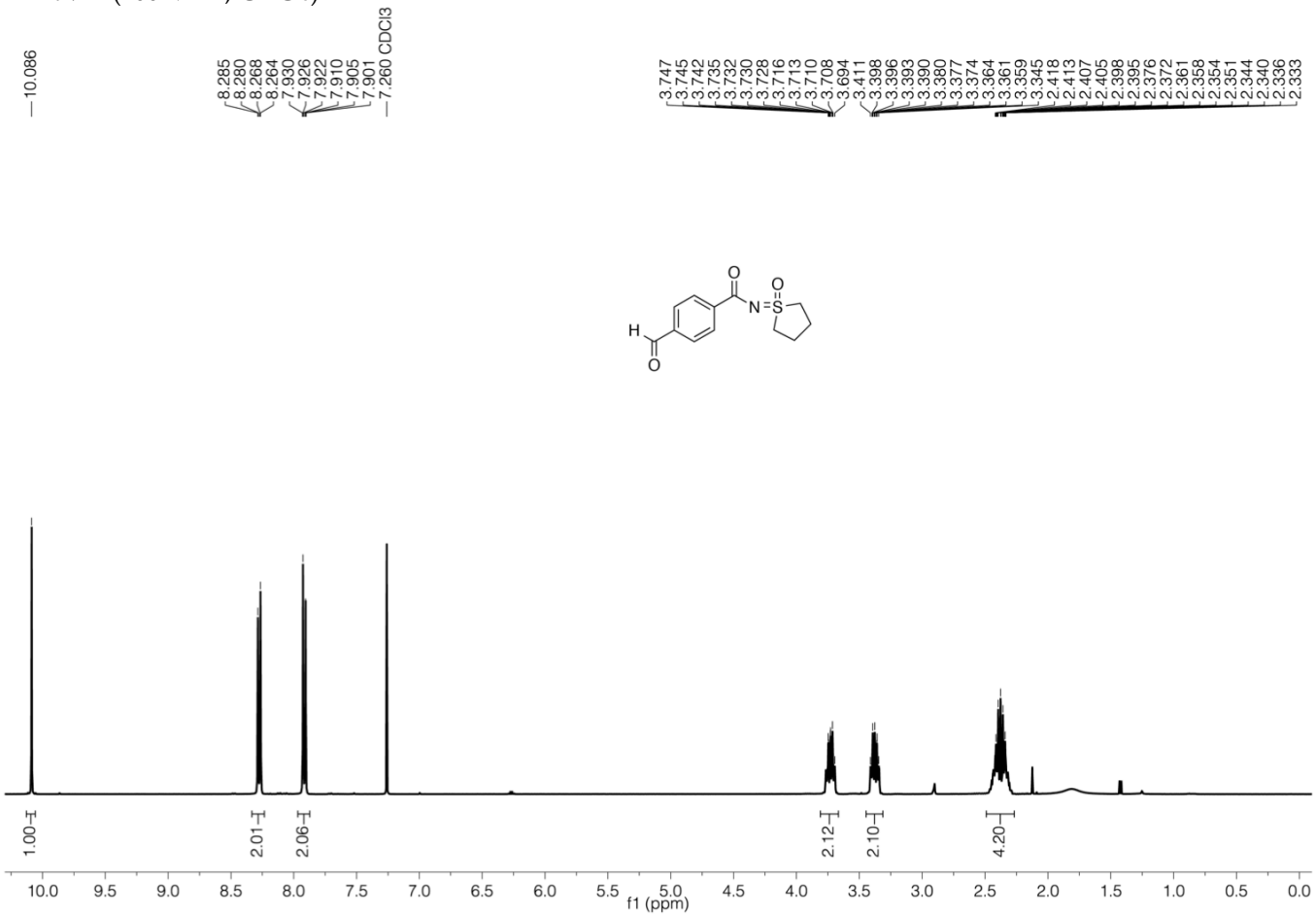


¹³C NMR (100 MHz, C_6D_6)

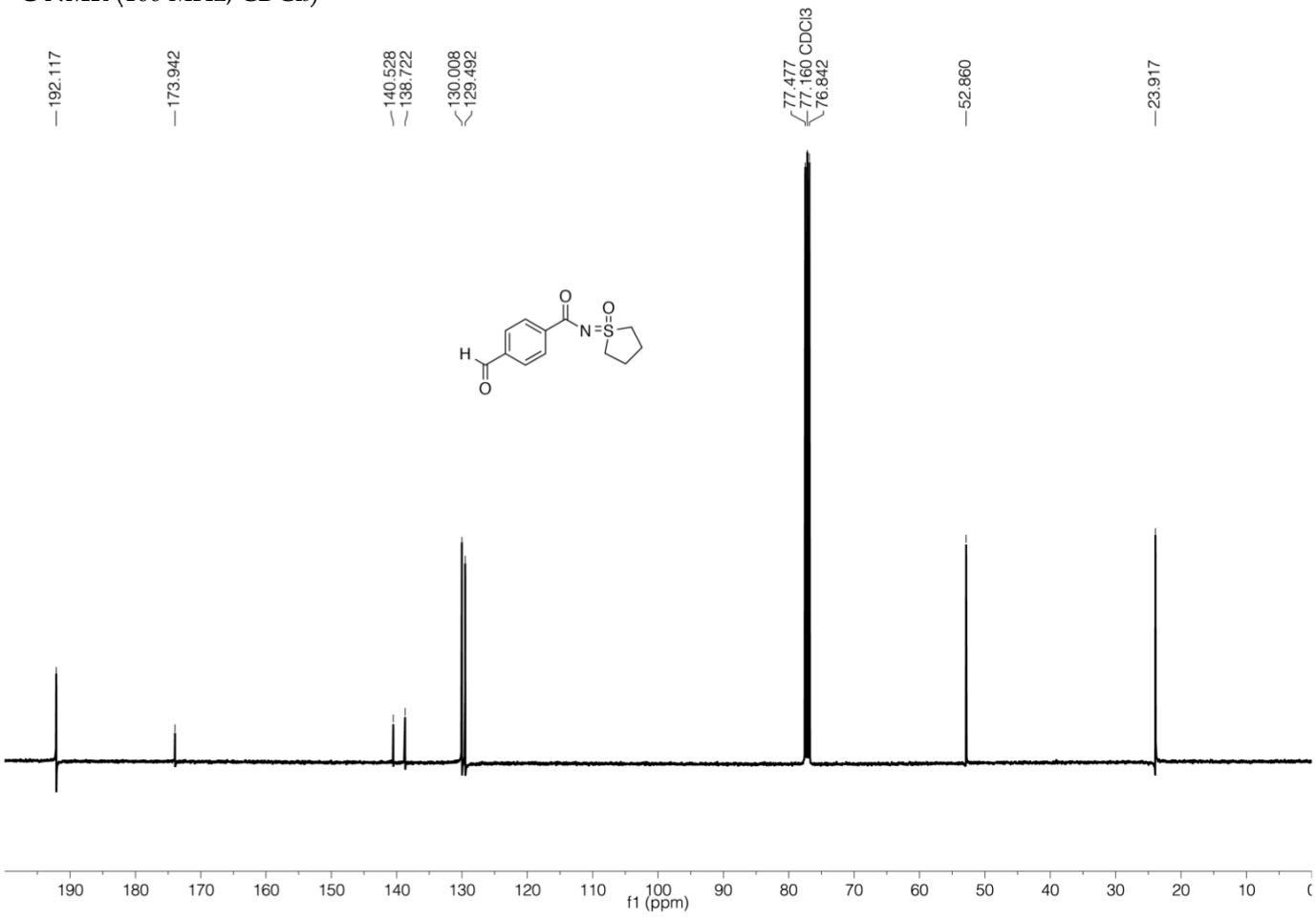


4-Formyl-*N*-(1-oxidotetrahydro-1λ⁶-thiophen-1-ylidene)benzamide (5mh):

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

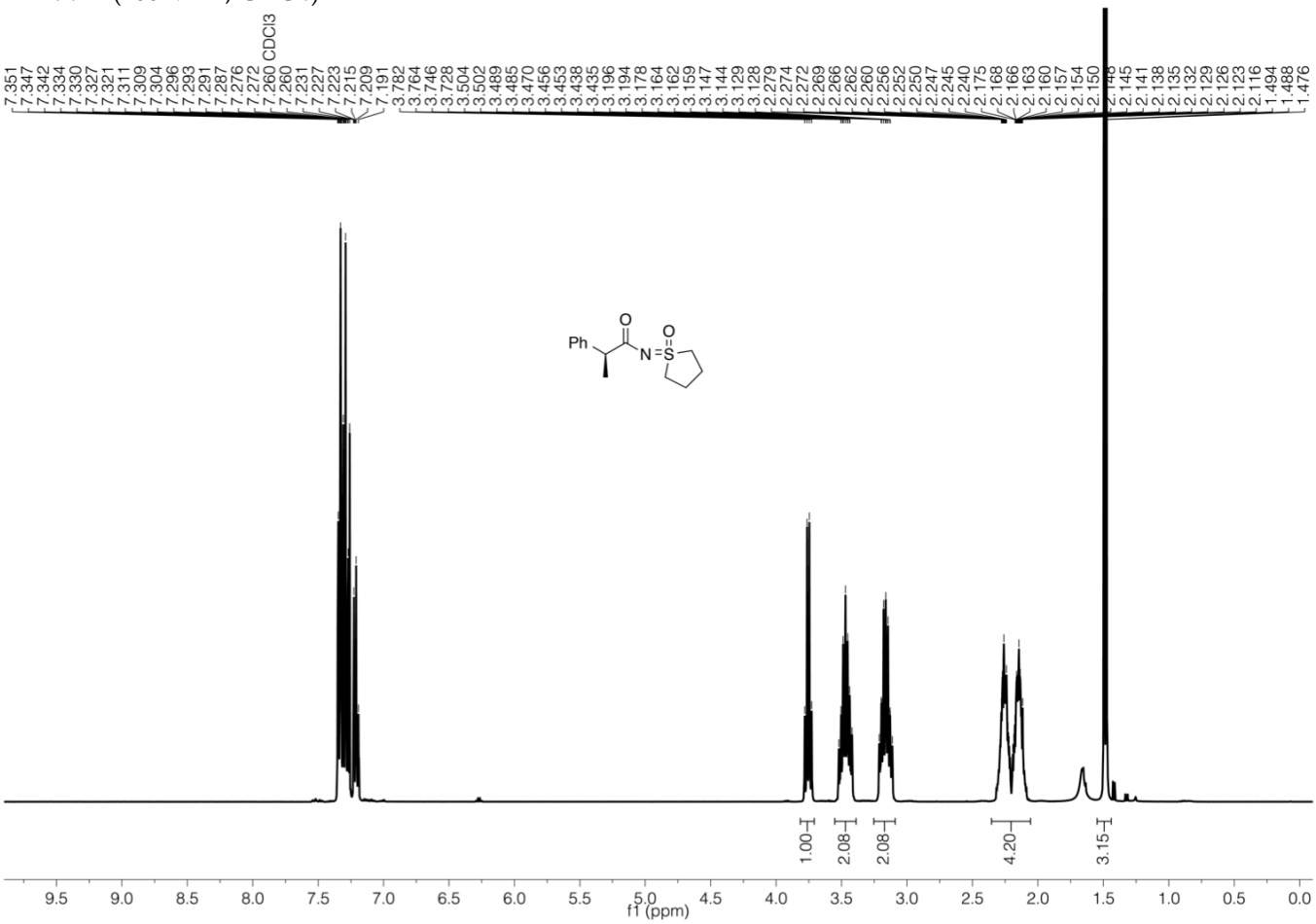


^{13}C NMR (100 MHz, $CDCl_3$)

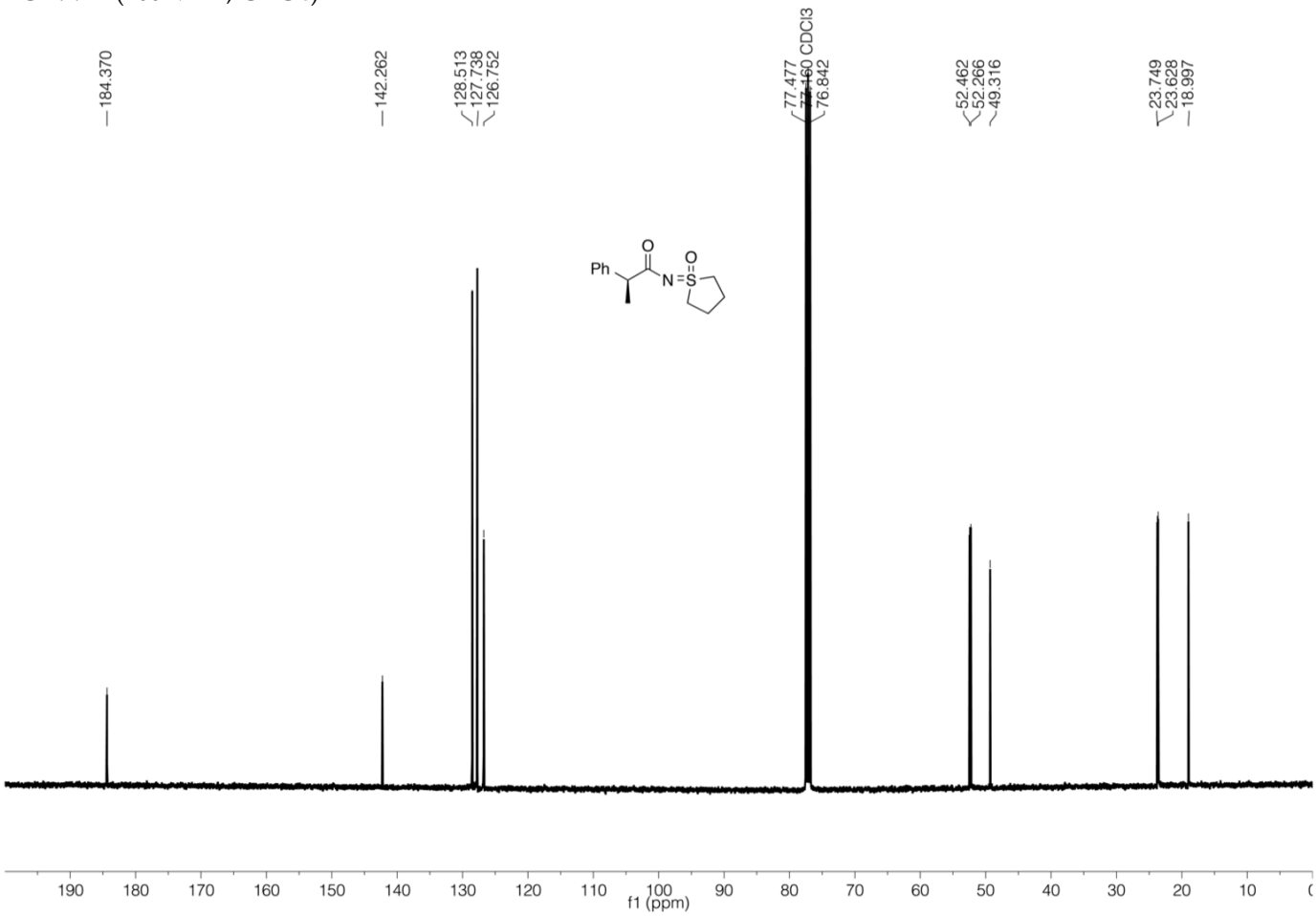


***(S)-N-(1*-Oxidotetrahydro-1λ⁶-thiophen-1-ylidene)-2-phenylpropanamide (5nh):**

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

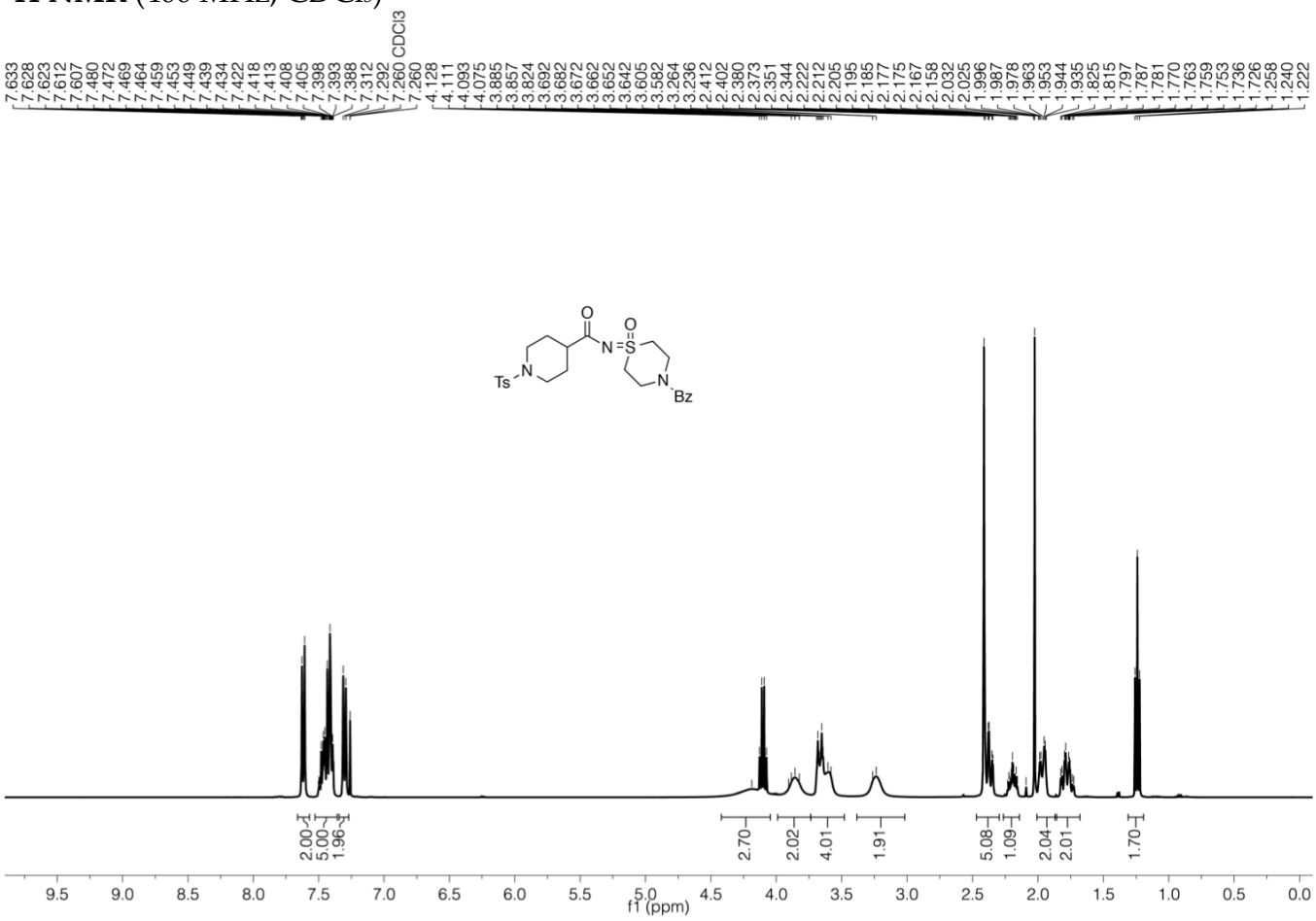


^{13}C NMR (100 MHz, $CDCl_3$)

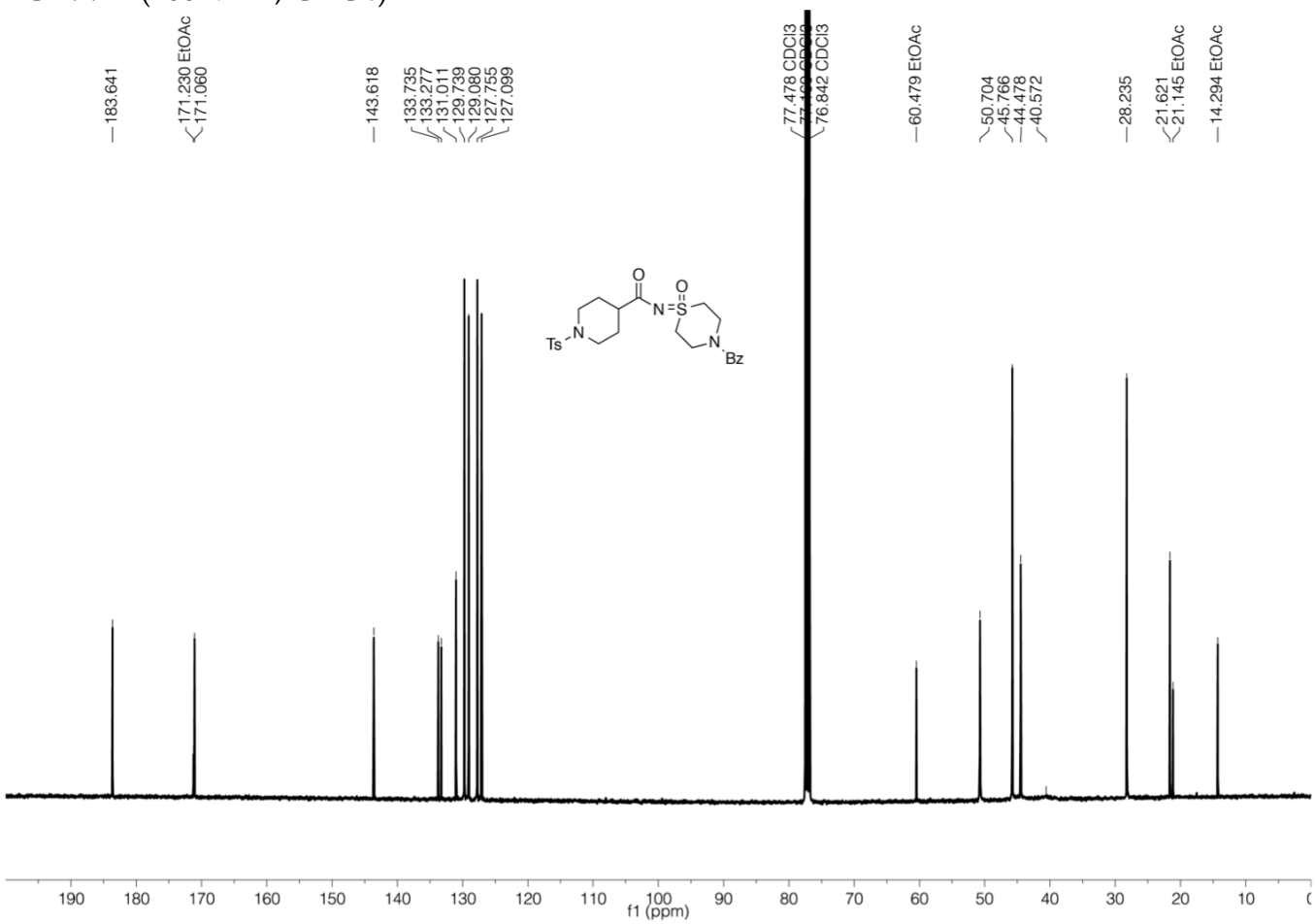


N-(4-benzoyl-1-oxido-1λ⁶-thiomorpholin-1-ylidene)-1-tosylpiperidine-4-carboxamide (5bi):

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

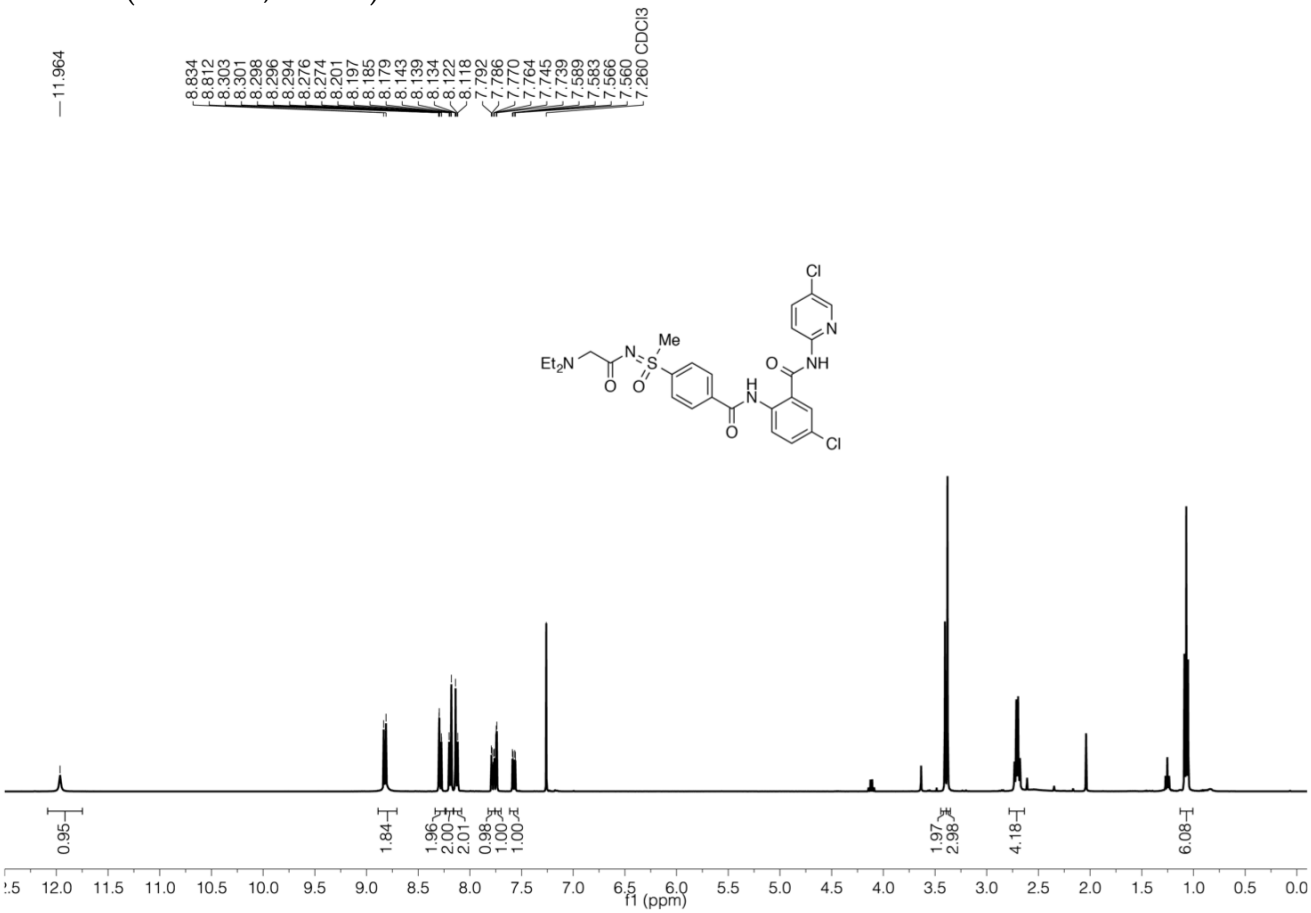


^{13}C NMR (100 MHz, $CDCl_3$)

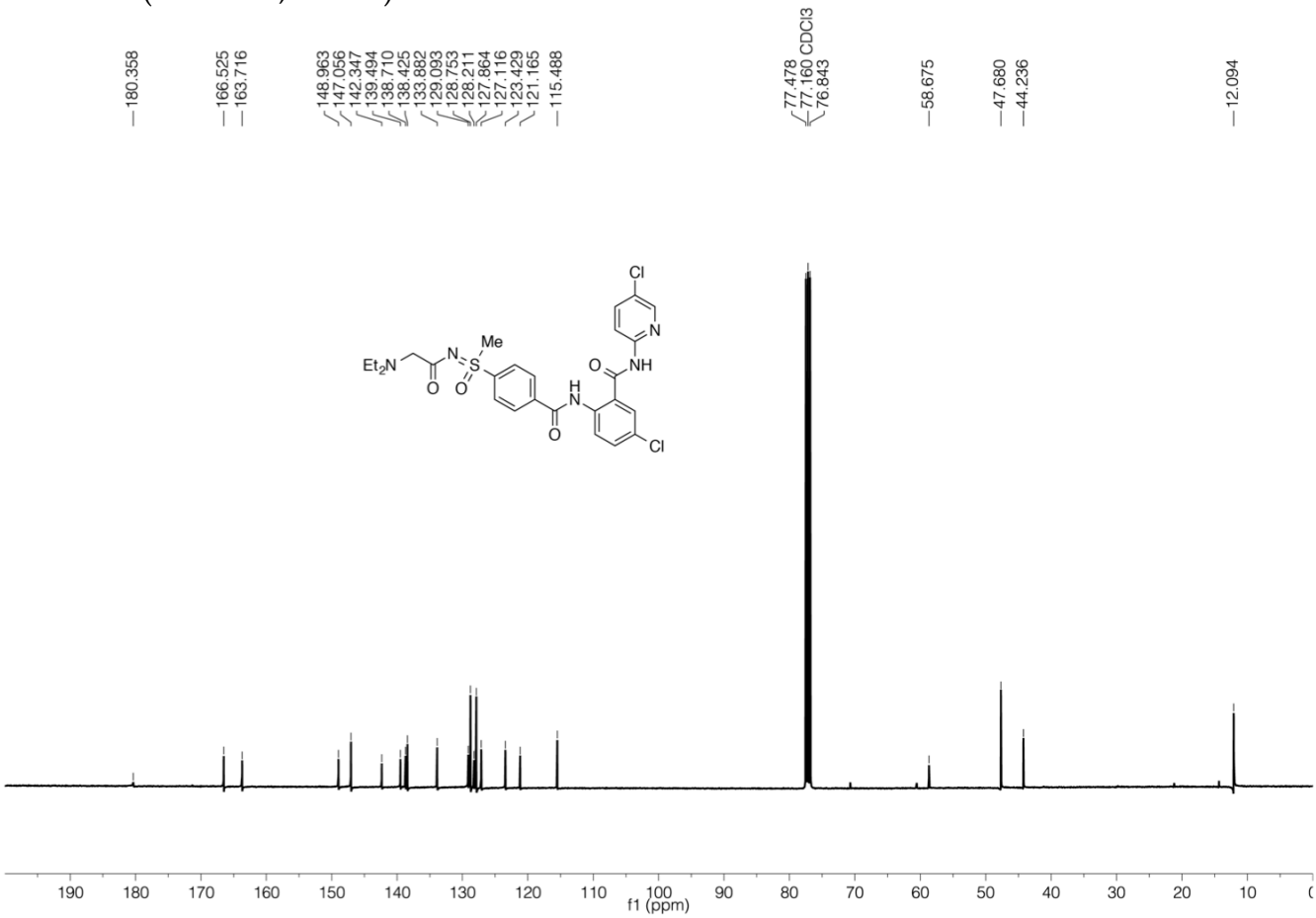


5-Chloro-*N*-(5-chloropyridin-2-yl)-2-(4-(*N*-(diethylglycyl)-*S*-methylsulfonimidoyl)benzamido)benzamide (2):

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

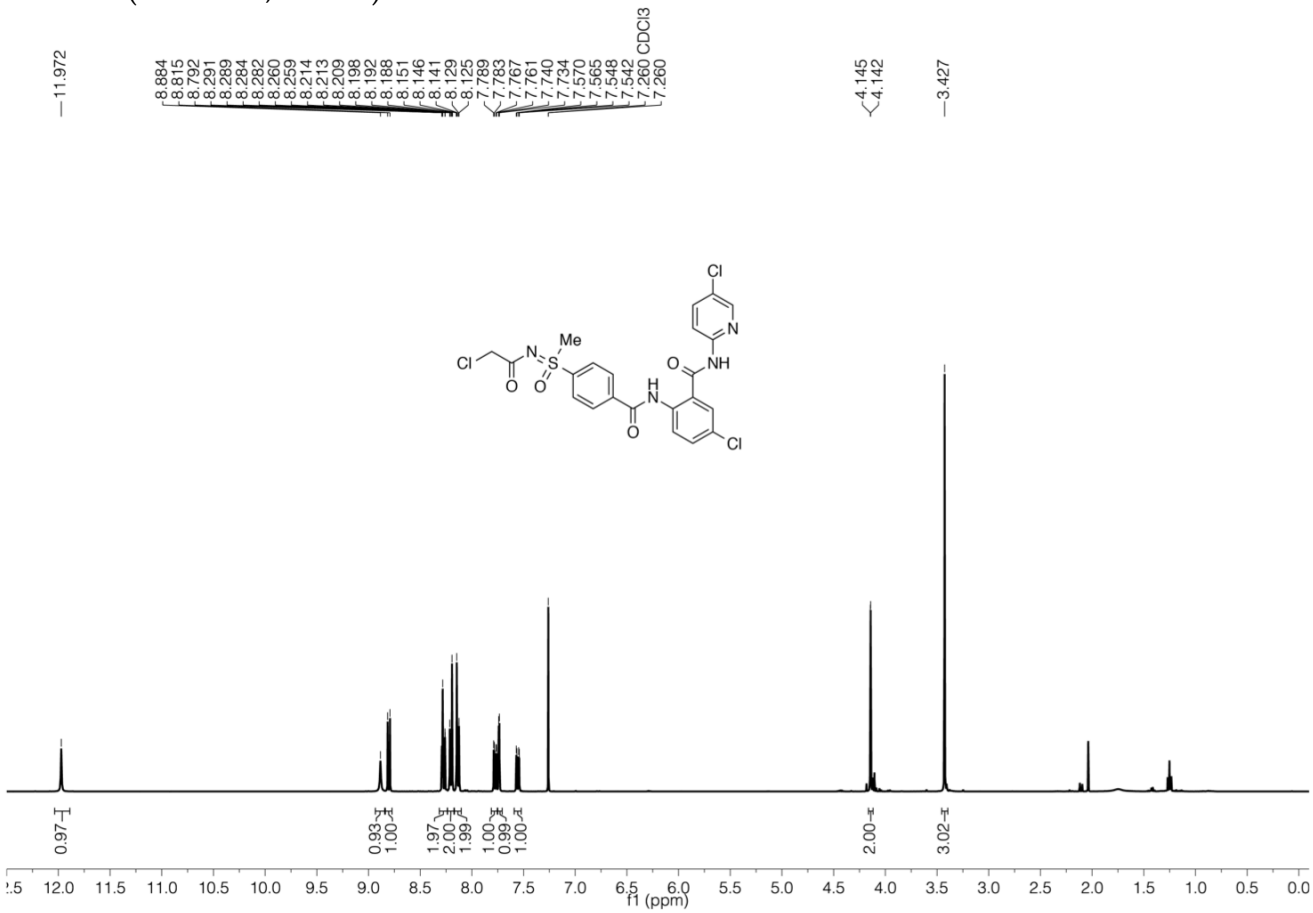


^{13}C NMR (100 MHz, $CDCl_3$)



5-Chloro-2-(4-(*N*-(2-chloroacetyl)-*S*-methylsulfonimidoyl)benzamido)-*N*-(5-chloropyridin-2-yl)benzamide (S2):

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



^{13}C NMR (100 MHz, $CDCl_3$)