**Supporting information**

# Complementary Strategies for Synthesis of Sulfinamides from Sulfur-Based Feedstock

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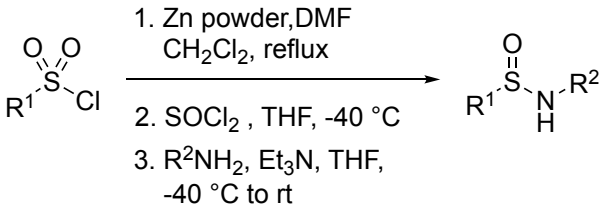
## 1. General

All starting reagents were commercially available and of analytical purity, which were used without further treatment unless otherwise stated. Sulfuryl chloride was freshly distilled at 68 °C - 69 °C under argon atmosphere. Thionyl chloride was freshly distilled at 76 °C - 78 °C under argon atmosphere. Zinc powder was activated using a standard method.[1] Solvents were dried according to standard methods. Triethylamine and benzylamine were stored over 4 Å molecular sieves. $^{1}$H NMR spectra were recorded at 400 MHz. $^{13}$C NMR spectra were recorded at 101 MHz and were $^{1}$H decoupled. Chemical shifts ($\delta$) are reported in ppm relative to solvent ($CDCl_3$: $\delta$C = 77.0 ppm, $(CD_3)_2SO$: $\delta$C = 39.5 ppm) or residual solvent peak ($CHCl_3$: $\delta$H = 7.26 ppm, $(CH_3)_2SO$: $\delta$H = 2.50 ppm). Accurate mass measurements (HRMS) were obtained by ESI on Agilent 6530 Q-TOF MS spectrometer. Analytical HPLC was performed under the following conditions: Agilent Eclipse plus C18 column (3.5 µL, 4.6×100 mm); UV/Vis detection at $\lambda_{obs}$ = 254 or 220 nm; flow rate 0.4 mL/min; gradient elution method (5 to 100 % of $CH_3CN$ in 0.1% aqueous formic acid over 13 min). Analytical TLC was performed using a pre-coated silica gel 60 Å F254 plates (0.2 mm thickness) and visualized by irradiation with UV light at 254 nm and by dipping in a stain solution ($KMnO_4$, cerium molybdate) followed by heating. Preparative column chromatography was carried out using silica gel 60 Å (particle size 0.063–0.200 mm). Infrared spectra were recorded on Nicolet Avatar 370 FTIR ATR (thin film). IR absorptions are given in wavenumbers as $cm^{-1}$.

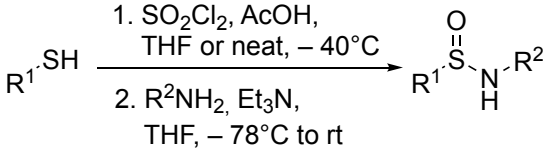
## 2. Synthesis of Sulfinamides

General procedure A (reductive pathway):

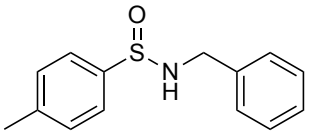



Sulfonyl chloride (0.81 mmol) was dissolved in $CH_2Cl_2$ (3 mL) in 25 mL round-bottom flask and DMF (94 µL, 1.22 mmol) was added. The resulting mixture was stirred for 10 minutes. Powdered zinc (58.5 mg, 0.89 mmol) was added (caution: vigorous initial reaction) and the mixture was refluxed until all the starting sulfonyl chloride was consumed (typically 1 h). Then the mixture was filtered (except for **1e**, **1h**, **1i**) and residues washed with MeOH (10 mL). The filtrate was concentrated under reduced pressure, redissolved in THF (3 mL) and $SOCl_2$ (118 µL, 1.63 mmol) was added dropwise at -40 °C. The resulting mixture was stirred for 45 min at -40 °C, then volatiles were evaporated under reduced pressure, the residue dissolved in THF (3 mL) and $Et_3N$ (170 µL, 1.22 mmol) and benzylamine (133 µL, 1.22 mmol) were added at -40 °C. The reaction mixture was stirred at rt overnight, then diluted with $CH_2Cl_2$ (10 mL) and washed with saturated aq. $NaHCO_3$ solution (20 mL). The combined organic phase was dried over anhydrous $MgSO_4$, concentrated under reduced pressure. Purification with column chromatography on silica gel afforded the product.

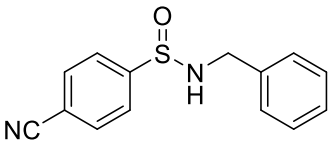
General procedure B (oxidative pathway):



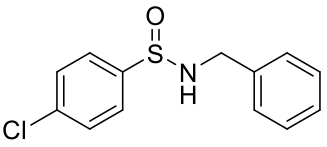

To an oven dried Schlenk flask, thiol (1 mmol), AcOH (120 µL, 2.1 mmol) and THF (1 mL) were added. $SO_2Cl_2$ (275 µL, 3.5 mmol) was added dropwise within 10 min at –40 °C under argon atmosphere. The reaction mixture was allowed to warm to rt and stirred for additional 120 min. Volatiles were evaporated under reduced pressure at rt and the residue was dissolved in THF (5 mL). The resulting solution was added dropwise to the solution of benzylamine (170 µL, 1.55 mmol) and $Et_3N$ (280 µL, 2 mmol) in THF (2.5 mL) at –78 °C and the reaction mixture was stirred at rt overnight. Then the reaction mixture was diluted with $CH_2Cl_2$ (20 mL) and washed with saturated aq. $NaHCO_3$ solution (10 mL). The aqueous phase was extracted with $CH_2Cl_2$ (2 × 20 mL). The combined organic phase was washed with brine (15 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification with column chromatography on silica gel afforded the product. This reaction sequence was also performed with a modification that did not use any solvent in the initial thiol oxidation step.



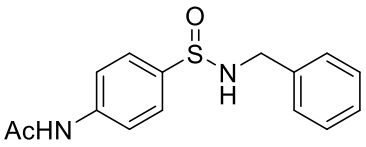

*N*-benzyl-4-methylbenzenesulfinamide (**1a**). Prepared according to the general procedure A using TsCl (155 mg, 0.81 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (160 mg, 80%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 – 7.59 (m, 2H), 7.36 – 7.21 (m, 7H), 4.46 – 4.31 (m, 1H), 4.23 (dd, $J$ = 13.5, 5.2 Hz, 1H), 3.89 (dd, $J$ = 13.5, 7.2 Hz, 1H), 2.41 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 141.4, 141.0, 137.9, 129.7, 128.7, 128.4, 127.7, 126.1, 44.6, 21.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{16}NOS^+$ 246.0947; found 246.0938; IR ($\nu_{max}$/cm$^{-1}$) 3215, 1415, 1051, 804, 739, 692. The spectra are in agreement with reported data.[2]



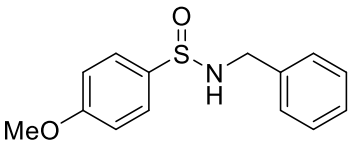

*N*-benzyl-4-cyanobenzenesulfinamide (**1b**). Prepared according to the general procedure A using 4-cyanobenzenesulfonyl chloride (164 mg, 0.81 mmol). Purification by column chromatography (15% of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (132 mg, 63%). Also prepared according to the general procedure B (neat) using 4-mercaptobenzonitrile (135 mg, 1 mmol, 1.0 eq). Purification by column chromatography (15 % of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (208 mg, 81 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 – 7.87 (m, 2H), 7.87 – 7.78 (m, 2H), 7.41 – 7.23 (m, 5H), 5.13 (dd, $J$ = 7.0, 5.0 Hz, 1H), 4.25 (dd, $J$ = 13.6, 5.0 Hz, 1H), 3.87 (dd, $J$ = 13.7, 7.0 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 149.1, 137.2, 132.5, 128.6, 128.2, 127.7, 127.1, 117.8, 114.6, 44.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{12}N_2OS$ 257.0743 ; found 257.0737; IR ($\nu_{max}$/cm$^{-1}$) 3213, 2871, 2233, 1082, 1055, 1020, 831, 704.



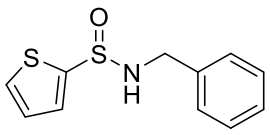
*N*-benzyl-4-chlorobenzenesulfinamide (**1c**). Prepared according to the general procedure A using 4-chlorobenzenesulfonyl chloride (172 mg, 0.81 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (143 mg, 66%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52 – 7.41 (m, 2H), 7.31 – 7.21 (m, 2H), 7.15 – 6.97 (m, 5H), 4.58 (dd, $J$ = 7.1, 5.0 Hz, 1H), 3.99 (dd, $J$ = 13.6, 5.1 Hz, 1H), 3.64 (dd, $J$ = 13.6, 7.1 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 142.6, 137.6, 137.5, 129.2, 128.8, 128.4, 127.9, 127.7, 44.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{12}ClNOS$ 266.0400; found 266.0407; IR ($\nu_{max}$/cm$^{-1}$) 3201, 2925, 2870, 2856, 1473, 1454, 1082, 1049, 1012, 818, 694. The spectra are in agreement with reported data.[2]



*N*-(4-((benzylamino) sulfinyl)phenyl)acetamide (**1d**). Prepared according to the general procedure A using 4-acetamidobenzenesulfonyl chloride (190 mg, 0.81 mmol, 1.0 eq). Purification by column chromatography (EtOAc) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (132 mg, 53%). Also prepared according to the general procedure B (neat) using *N*-(4-sulfanylphenyl)acetamide (167 mg, 1 mmol, 1.0 eq). Purification by column chromatography (EtOAc) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (202 mg, 70%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.75 – 7.67 (m, $J$ = 2.0 Hz, 4H), 7.57 (s, 1H), 7.39 – 7.21 (m, 5H), 4.34 (dd, $J$ = 7.0, 5.2 Hz, 1H), 4.26 (dd, $J$ = 13.3, 5.2 Hz, 1H), 3.92 (dd, $J$ = 13.3, 7.0 Hz, 1H), 2.23 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 168.5, 140.6, 138.8, 137.6, 128.7, 128.3, 127.8, 127.1, 119.7, 44.6, 24.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_{16}N_2O_2S$ 289.1005 ; found 289.1001; IR ($\nu_{max}$/cm$^{-1}$) 3244, 3182, 3109, 1674, 1589, 1531, 1311, 1086, 1038, 1026, 831, 696.

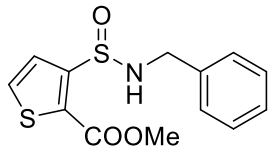


*N*-benzyl-4-methoxybenzenesulfinamide (**1e**). Prepared according to the general procedure A using 4-methoxybenzenesulfonyl chloride (168 mg, 0.81 mmol). Purification by column chromatography (40 % of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (149 mg, 70%). Also prepared according to the general procedure B (THF) using 4-mercaptoanisole (140 mg, 1 mmol). Purification by column chromatography (50 to 100% of EtOAc in cyclohexane) afforded the product as a white solid (227 mg, 87%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.76 – 7.64 (m, 2H), 7.40 – 7.21 (m, 5H), 7.09 – 6.97 (m, 2H), 4.72 (dd, $J$ = 7.2, 5.2 Hz, 1H), 4.23 (dd, $J$ = 13.6, 5.2 Hz, 1H), 3.92 (dd, $J$ = 13.6, 7.2 Hz, 1H), 3.87 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.0, 138.0, 135.3, 128.8, 128.4, 127.8, 127.8, 114.5, 55.6, 44.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{15}NO_2S$ 262.0896; found 262.0901; IR ($\nu_{max}$/cm$^{-1}$) 3207, 2992, 1595, 1495, 1051, 1024, 692. The spectra are in agreement with reported data.[2]

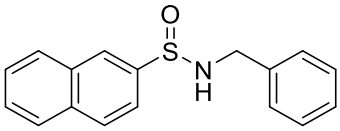


*N*-benzylthiophene-2-sulfinamide (**1f).** Prepared according to the general procedure A using 2-thiophenesulfonyl chloride (149 mg, 0.81 mmol). Purification by column chromatography (40% of EtOAc in cyclohexane) afforded the product as an off-white solid (18 mg, 94%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53 (dd, $J$ = 5.0, 1.4 Hz, 1H), 7.39 (dd, $J$ = 3.7, 1.4 Hz, 1H), 7.30 – 7.14 (m, 5H), 7.06 (dd, $J$ = 5.0, 3.7 Hz, 1H), 4.54 – 4.50 (m, 1H), 4.26 (dd, $J$ = 13.6, 5.1 Hz, 1H), 4.04 (dd, $J$ = 13.6, 7.2 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.7, 137.6, 131.5, 130.2, 128.7, 128.3, 128.0, 127.7, 44.6. HRMS

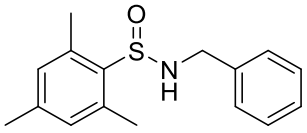
(ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{12}NOS_2^+$ 238.0355; found 238.0353; IR ($\nu_{max}$/cm$^{-1}$) 3143, 1495, 1404, 1051, 1039, 1028. The spectra are in agreement with reported data.[2]



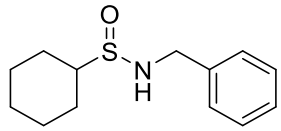
Methyl 3-((benzylamino)sulfinyl)thiophene-2-carboxylate (**1g**). Prepared according to the general procedure A using methyl 3-(chlorosulfonyl)thiophene-2-carboxylate (196 mg, 0.81 mmol) without $NaHCO_3$ wash step in the workup. Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (150 mg, 63%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.72 (d, $J$ = 5.2 Hz, 1H), 7.61 (d, $J$ = 5.2 Hz, 1H), 7.35 – 7.23 (m, 5H), 4.76 (dd, $J$ = 6.7, 5.9 Hz, 1H), 4.36 (dd, $J$ = 13.7, 6.7 Hz, 1H), 3.99 (dd, $J$ = 13.7, 5.9 Hz, 1H), 3.93 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 161.1, 151.9, 137.9, 130.9, 129.7, 128.6, 128.1, 127.7, 127.6, 52.7, 45.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{14}NO_3S_2^+$ 296.0410; found 296.0411; IR ($\nu_{max}$/cm$^{-1}$) 3207, 1707, 1435, 1406, 1255, 1061, 769, 731, 698, 644.



*N*-benzylnaphthalene-2-sulfinamide (**1h**)**.** Prepared according to the general procedure A using 2-naphtalenesulfonyl chloride (184 mg, 0.81 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a white solid (160 mg, 70%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.43 – 8.29 (m, 1H), 8.01 – 7.86 (m, 3H), 7.71 (dd, $J$ = 8.6, 1.8 Hz, 1H), 7.65 – 7.52 (m, 2H), 7.36 – 7.20 (m, 5H), 4.43 – 4.33 (m, 1H), 4.29 (dd, $J$ = 13.3, 5.0 Hz, 1H), 3.89 (dd, $J$ = 13.3, 7.2 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 141.1, 137.8, 134.5, 132.9, 129.1, 128.9, 128.8, 128.5, 128.0, 128.0, 127.8, 127.2, 127.0, 122.2, 44.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}NOS^+$ 282.0947; found 282.0946; IR ($\nu_{max}$/cm$^{-1}$) 3192, 2922, 1427, 1066, 1045, 1027, 812, 746. The spectra are in agreement with reported data.[2]

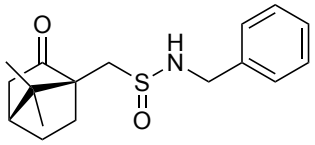


*N*-benzyl-2,4,6-trimethylbenzenesulfinamide (**1i**). Prepared according to the general procedure A using 2-mesitylenesulfonyl chloride (178 mg, 0.81 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a white solid (157 mg, 71%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39 – 7.17 (m, 5H), 6.85 (s, 2H), 4.57 (dd, $J$ = 6.5, 5.8 Hz, 1H), 4.35 (dd, $J$ = 13.6, 6.5 Hz, 1H), 4.27 (dd, $J$ = 13.6, 5.8 Hz, 1H), 2.58 (s, 6H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 140.5, 138.1, 137.2, 136.8, 130.8, 128.5, 128.1, 127.6, 48.1, 20.9, 19.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{20}NOS^+$ 274.1256; found 274.1260; IR ($\nu_{max}$/cm$^{-1}$) 3176, 2914, 1452, 1063, 1036, 729, 692. The spectra are in agreement with reported data.[3]

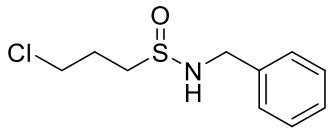


*N*-benzylcyclohexanesulfinamide (**1j**)**.** Prepared according to the general procedure A using cyclohexanesulfonyl chloride (149 mg, 0.81 mmol). Purification by column chromatography (70 to 100% of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (164 mg, 85%). Also prepared according to the general procedure A (THF) using cyclohexanethiol (126 µL, 1 mmol). Purification by column chromatography (70 to 100% of EtOAc in cyclohexane) afforded the product as an off-white solid (152 mg, 62%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.36 – 7.12 (m, 5H), 4.23 – 4.11 (m, 3H), 2.58–2.48 (m, 1H), 2.07 – 1.86 (m, 2H), 1.86 – 1.66 (m, 2H), 1.66 – 1.50 (m, 1H), 1.46 – 0.96 (m, 5H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.4, 128.5, 128.0, 127.4, 61.6, 46.9, 26.3, 26.1, 25.4, 25.2, 25.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{20}NOS^+$

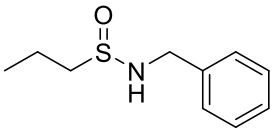
238.1260 ; found 238.1267; IR ($\nu_{max}$/cm$^{-1}$) 3176, 2927, 2854, 1448, 1032, 1014. The spectra are in agreement with reported data.[2]



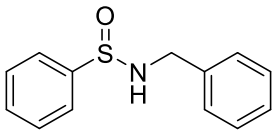
*N*-benzyl-1-((*1R*,*4R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfinamide (**1k**). Prepared according to the general procedure A using (*1S*)-(+)-10-camphorsulfonyl chloride (204 mg, 0.81 mmol) Purification by column chromatography (50% of EtOAc in cyclohexane) afforded the product as a yellowish oil (196 mg, 79%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.14 (m, 10H), 4.72 – 4.65 (m, 2H), 4.32– 4.15 (m, 4H), 3.10 (d, $J$ = 13.5 Hz, 1H), 2.93 (s, 2H), 2.61 (d, $J$ = 13.5 Hz, 1H), 2.40–2.28 (m, 2H), 2.16 – 1.91 (m, 6H), 1.88 (s, 1H), 1.83 (s, 1H), 1.69–1.50 (m, 2H), 1.43 – 1.30 (m, 2H), 0.99 (d, $J$ = 15.9 Hz, 6H), 0.85 (d, $J$ = 22.8 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 216.5, 216.1, 138.2, 138.2, 128.5, 128.5, 128.1, 128.0, 127.5, 127.5, 58.8, 58.3, 53.9, 53.6, 48.4, 48.1, 46.7, 46.7, 43.0, 42.8, 42.7, 42.4, 27.1, 26.9, 26.7, 25.7, 20.1, 19.7, 19.7, 19.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{24}NO_2S^+$ 306.1522; found 306.1526; IR ($\nu_{max}$/cm$^{-1}$) 3465, 3176, 2956, 2885, 1739, 1454, 1041, 1024, 733, 698.



*N*-benzyl-3-chloropropane-1-sulfinamide (**1l**)**.** Prepared according to the general procedure A using 3-chloropropanesulfonyl chloride (144 mg, 0.81 mmol) without $NaHCO_3$ wash step in the workup. Purification by column chromatography (EtOAc) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (123 mg, 65%). Also prepared according to the general procedure B (THF) using 3-chloro-1-propanethiol (111 mg, 1 mmol). Purification by column chromatography (EtOAc) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (184 mg, 80%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.10 (m, 5H), 4.58 – 4.50 (m, 1H), 4.26 – 4.10 (m, 2H), 3.57 – 3.47 (m, 2H), 2.95 – 2.85 (m, 1H), 2.85 – 2.75 (m, 1H), 2.13 – 1.99 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.1, 128.7, 128.1, 127.7, 51.9, 46.2, 43.3, 26.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{10}H_{15}ClNOS$ 232.0557; found 232.0557; IR ($\nu_{max}$/cm$^{-1}$) 3168, 2958, 2925, 1454, 1057, 1045, 1032, 746, 696.

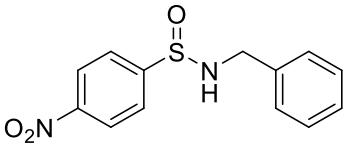


*N*-benzylpropane-1-sulfinamide (**1m**). Prepared according to the general procedure A using 1-propylsulfonyl chloride (113 µL, 1.0 mmol). Purification by column chromatography (50% of EtOAc in cyclohexane) afforded the product as a brownish oil, which solidified on standing to a brownish solid (145 mg, 74%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 – 7.17 (m, 5H), 4.35 – 4.19 (m, 2H), 4.07 – 4.03 (m, 1H), 2.84 – 2.64 (m, 2H), 1.76 – 1.69 (m, 2H), 1.04 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.3, 128.8, 128.3, 127.9, 57.4, 46.5, 17.0, 13.4; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{10}H_{16}NOS^+$ 198.0947; found 198.0946; IR ($\nu_{max}$/cm$^{-1}$) 3224, 2958, 1456, 1043, 1016, 742, 700. The spectra are in agreement with reported data.[2]

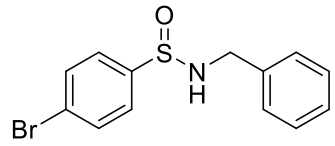


*N*-benzylbenzenesulfinamide (**1n**). Prepared according to the general procedure B using thiophenol (110 mg, 1 mmol). Purification by column chromatography (50% of EtOAc in cyclohexane) afforded the product as a white solid (179 mg, 77%).$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.84 – 7.77 (m, 2H), 7.59 – 7.49 (m, 3H), 7.38 – 7.25 (m, 5H), 4.39 – 4.32 (m, 1H), 4.28 (dd, $J$ = 13.3, 5.2 Hz, 1H), 3.93 (dd, $J$ = 13.3, 7.0 Hz, 1H).$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 144.0, 137.7, 131.0, 128.9, 128.7, 128.3, 127.8,

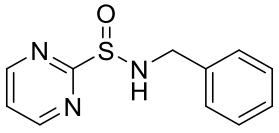
126.1, 44.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{14}NOS^+$ 232,0791; found 232.0790; IR ($\nu_{max}$/$cm^{-1}$) 3213, 1417, 1086, 1070, 1024. The spectra are in agreement with reported data.[2]



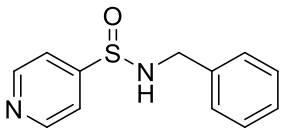
*N*-benzyl-4-nitrobenzenesulfinamide (**1o**). Prepared according to the general procedure B (neat) using 4-nitrophenyl disulphide (77 mg, 0.25 mmol). Purification by column chromatography (30 to 50% of EtOAc in cyclohexane) afforded the product as white a solid (107 mg, 78%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.43 – 8.34 (m, 2H), 8.04 – 7.95 (m, 2H), 7.40 – 7.23 (m, 5H), 4.51 (t, *J* = 6.0 Hz, 1H), 4.30 (dd, *J* = 13.5, 5.1 Hz, 1H), 3.89 (dd, *J* = 13.4, 7.0 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 150.9, 149.6, 137.0, 128.9, 128.3, 128.1, 127.5, 124.0, 44.8. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{13}N_2O_3S^+$ 277.0641; found 277.0598; IR ($\nu_{max}$/$cm^{-1}$) 3180,1604, 1518, 1338, 1082,1055, 1034, 1026. The spectra are in agreement with reported data.[4]



*N*-benzyl-4-bromobenzenesulfinamide (**1p**). Prepared according to the general procedure B (THF) using 4-bromobenzenethiol (189 mg, 1 mmol). Purification by column chromatography (50% of EtOAc in cyclohexane) afforded the product as a white solid (279 mg, 90%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.77 – 7.57 (m, 4H), 7.40 – 7.19 (m, 5H), 4.44 – 4.31 (m, 1H), 4.27 (dd, *J* = 13.4, 5.1 Hz, 1H), 3.90 (dd, *J* = 13.4, 7.1 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 143.1, 137.4, 132.2, 128.8, 128.3, 127.9, 127.8, 125.8, 44.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{13}BrNOS^+$ 309,9896; found 309.9878; IR ($\nu_{max}$/$cm^{-1}$) 3176, 1469, 1383, 1084, 1057. The spectra are in agreement with reported data.[2]

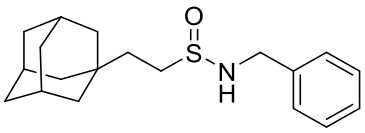


*N*-benzylpyrimidine-2-sulfinamide (**1q**). Prepared according to a modified general procedure B (THF or neat) using pyrimidine-2-thiol (112 mg, 1 mmol). After the overnight reaction, the reaction mixture was precipitated by the addition of $Et_2O$ (20 mL). The precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residue was dissolved in $CH_2Cl_2$ (10 mL) and *m*CPBA (222 mg, 1 mmol, ≤77%) was added portionwise at – 40 °C and the reaction mixture was stirred at – 40 °C for 30 min. The resulting mixture was diluted with $CH_2Cl_2$ (20 mL), washed with 10 % aq. $Na_2S_2O_3$ solution (30 mL), saturated aq. $NaHCO_3$ solution (30 mL) and brine (30 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (5% of MeOH and 1% $Et_3N$ in $CH_2Cl_2$) afforded the product as a colorless oil, which solidified on standing to a white solid (154 mg, 66%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.90 (d, *J* = 4.9 Hz, 2H), 7.43 (t, *J* = 4.8 Hz, 1H), 7.35 – 7.24 (m, 5H), 5.04 (t, *J* = 6.1 Hz, 1H), 4.43 (dd, *J* = 13.8, 6.5 Hz, 1H), 4.26 (dd, *J* = 13.8, 5.6 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 171.7, 158.6, 137.5, 128.7, 128.3, 127.8, 122.4, 46.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{12}N_3OS^+$ 234.0696; found 234.0704; IR ($\nu_{max}$/$cm^{-1}$) 3176, 1560, 1552, 1387, 1072, 1024.

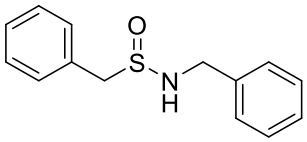


*N*-benzylpyridine-4-sulfinamide (**1r**). Prepared according to a modified general procedure B (THF) using pyridine-4-thiol (111 mg, 1 mmol). AcOH was omitted and THF was substituted to $CH_2Cl_2$. After the overnight reaction, *m*CPBA (333 mg, 1.5 mmol, ≤77%) in $CH_2Cl_2$ (2.5 mL) was added dropwise at –78 °C. The reaction mixture was allowed to warm up to rt and the progress of the reaction was monitored by TLC. After the intermediate sulfenamide consumption, the reaction mixture was processed as in the case on the product **1q**. Purification by column chromatography (50 to 100% of EtOAc and 1% $Et_3N$ in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a

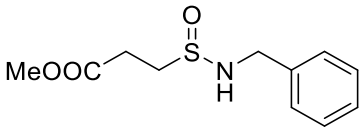
yellowish solid (135 mg, 58%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.85 – 8.77 (m, 2H), 7.74 – 7.67 (m, 2H), 7.39 – 7.24 (m, 5H), 4.57 (t, $J$ = 6.0 Hz, 1H), 4.28 (dd, $J$ = 13.4, 5.0 Hz, 1H), 3.88 (dd, $J$ = 13.4, 7.0 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 153.6, 150.5, 137.1, 128.8, 128.4, 128.0, 120.5, 45.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{13}N_2OS^+$ 233,0743; found 233.0737; IR ($\nu_{max}$/cm$^{-1}$) 3199, 1568, 1452, 1400, 1218, 1051, 1018, 976.



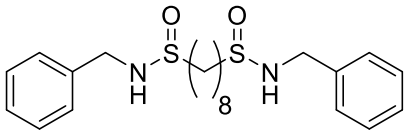
2-((3r,5r,7r)-adamantan-1-yl)-*N*-benzylethane-1-sulfinamide (**1s**). Prepared according to the general procedure B (neat) using adamantanylethanthiol (98 mg, 0.5 mmol). Purification by column chromatography (20% of EtOAc in cyclohexane) afforded the product as a white solid (103 mg, 65%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.26 (m, 5H), 4.32 – 4.22 (m, 2H), 4.18 – 4.08 (m, 1H), 2.85 – 2.67 (m, 2H), 2.00 – 1.94 (m, 3H), 1.77 – 1.67 (m, 3H), 1.67 – 1.58 (m, 3H), 1.52 – 1.47 (m, 6H), 1.47 – 1.35 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.2, 128.7, 128.2, 127.7, 49.7, 46.2, 42.2, 36.9, 36.8, 32.1, 28.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{28}NOS^+$ 318.1886; found 318.1845; IR ($\nu_{max}$/cm$^{-1}$) 3155, 2898, 2844,1450, 1039, 1026.



*N*-benzyl-1-phenylmethanesulfinamide (**1t**). Prepared according to the general procedure B (neat) using benzyl mercaptan (117 µL, 1 mmol). Purification by column chromatography (66 to 100% of EtOAc in cyclohexane) afforded the product as a white solid (184 mg, 75%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.47 – 7.24 (m, 10H), 4.36 – 4.22 (m, 2H), 4.09 (d, $J$ = 12.9 Hz, 1H), 4.00 (d, $J$ = 12.9 Hz, 1H), 3.86 – 3.76 (m, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 138.0, 130.6, 129.2, 128.9, 128.7, 128.3, 128.0, 127.7, 60.9, 47.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{16}NOS^+$ 246.0947; found 246.0947; IR ($\nu_{max}$/cm$^{-1}$) 3194, 1495, 1452, 1041, 1024.

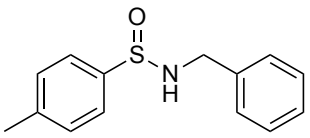


*N*-benzyl-4-methoxybenzenesulfinamide (**1u**). Prepared according to the general procedure B (neat) using methyl 3-mercaptopropionate (113 µL, 1 mmol). Purification by column chromatography (50 to 100% of EtOAc in cyclohexane) afforded the product as a white solid (162 mg, 67%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.29 (m, 5H), 4.34 – 4.22 (m, 3H), 3.72 (s, 3H), 3.20 – 3.11 (m, 1H), 3.11 – 3.01 (m, 1H), 2.85 – 2.67 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 172.0, 137.9, 128.8, 128.2, 127.6, 52.2, 49.4, 46.7, 27.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{16}NO_3S^+$ 242.0845; found 242.0854; IR ($\nu_{max}$/cm$^{-1}$) 3180, 1738, 1439, 1425, 1236, 1163, 1097, 1068, 1024.

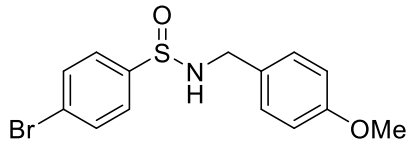


$N^1$,$N^8$-dibenzyloctane-1,8-disulfinamide (**1v**). Prepared according to General procedure B using 1,8-octanedithiol (189 µL, 97%, 1 mmol) and using a double amount of other reagents. Purification by column chromatography (50 to 100% of EtOAc in cyclohexane, then 5 to 10% of MeOH in EtOAc) afforded the product as pale solid (274 mg, 65%).$^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 10H), 4.37 – 4.23 (m, 4H), 4.05 –3.93 (m, 2H), 2.88 – 2.71 (m, 4H), 1.80 – 1.64 (m, 4H), 1.52 – 1.29 (m, 8H).$^{13}$C NMR (101 MHz, $CDCl_3$) δ 138.1, 128.7, 128.2, 127.8, 55.35, 55.32, 46.43, 46.41, 28.94, 28.85, 28.53, 28.49, 23.16, 23.12. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{33}N_2O_2S_2^+$ 421,1978; found 421.1972; IR ($\nu_{max}$/cm$^{-1}$) 3188, 2925, 2850, 1469, 1086, 1068, 1053, 1020.)

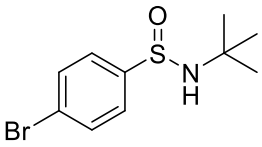
## 3. Synthesis of Sulfinamides with Different Amines



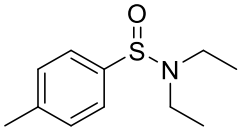
*N*-benzyl-4-methylbenzenesulfinamide (**1a**). Prepared according to the general procedure A using TsCl (155 mg, 0.81 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a yellowish oil, which solidified on standing to a yellowish solid (160 mg, 80%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69 – 7.59 (m, 2H), 7.36 – 7.21 (m, 7H), 4.46 – 4.31 (m, 1H), 4.23 (dd, $J$ = 13.5, 5.2 Hz, 1H), 3.89 (dd, $J$ = 13.5, 7.2 Hz, 1H), 2.41 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 141.4, 141.0, 137.9, 129.7, 128.7, 128.4, 127.7, 126.1, 44.6, 21.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{16}NOS^+$ 246.0947; found 246.0938; IR ($\nu_{max}$/cm$^{-1}$) 3215, 1415, 1051, 804, 739, 692. The spectra are in agreement with reported data.[2]



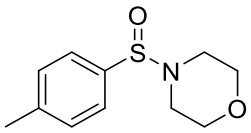
4-bromo-*N*-(4-methoxybenzyl)benzenesulfinamide (**2b**). Prepared according to the general procedure B (neat) using 4-bromobenzenethiol (189 mg, 1 mmol). Purification by column chromatography (50 to 100% of EtOAc in cyclohexane) afforded the product as a white solid (282 mg, 83%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68 – 7.59 (m, 4H), 7.20 – 7.14 (m, 2H), 6.88 – 6.81 (m, 2H), 4.55 – 4.40 (m, 1H), 4.17 (dd, $J$ = 13.2, 4.8 Hz, 1H), 3.84 – 3.74 (m, 4H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 159.2, 143.2, 132.1, 129.7, 129.5, 127.9, 125.7, 114.1, 55.3, 44.0. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{15}BrNO_2S^+$ 340.0001; found 339.9992; IR ($\nu_{max}$/cm$^{-1}$) 3205, 1610, 1512, 1246, 1051, 1024, 1009.



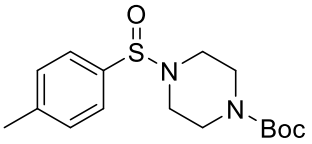
4-bromo-N-(*tert*-butyl)benzenesulfinamide (**2c**). Prepared according to the general procedure B using 4-bromobenzenethiol (189 mg, 1 mmol). Purification by column chromatography (50% of EtOAc in cyclohexane) afforded the product as a white solid (197 mg, 71%).$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.67 – 7.61 (m, 2H), 7.61 – 7.54 (m, 2H), 3.87 (brs, 1H), 1.43 (s, 9H).$^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 145.7, 131.9, 127.5, 125.4, 54.5, 31.1. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{10}H_{15}BrNOS^+$ 276.0052; found 276.0043; IR ($\nu_{max}$/cm$^{-1}$) 3186, 2970, 1568, 1468, 1385, 1365, 1228, 1043, 1036, 1005. The spectra are in agreement with reported data.[6]



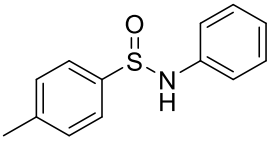
*N,N*-diethyl-4-methylbenzenesulfinamide (**2d**). Prepared according to the general procedure A using TsCl (191 mg, 1 mmol). Purification by column chromatography (33% of EtOAc in cyclohexane) afforded the product as a yellow oil (134 mg, 64%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.63 – 7.44 (m, 2H), 7.33 – 7.22 (m, 2H), 3.16 – 3.07 (m, 4H), 2.40 (s, 3H), 1.11 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 141.3, 140.9, 129.5, 126.3, 42.0, 21.4, 14.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{18}NOS^+$ 212.1104; found 212.1104; IR ($\nu_{max}$/cm$^{-1}$) 3224, 2958, 1456, 1043, 1016, 742, 700. The spectra are in agreement with reported data.[2]



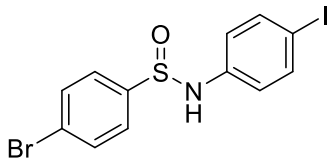
4-(p-tolylsulfinyl)morpholine (**2e**). Prepared according to the general procedure A using TsCl (155 mg, 0.81 mmol). Purification by column chromatography (30 to 100% of EtOAc in cyclohexane) afforded the product as a white solid (132 mg, 74%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54 – 7.42 (m, 1H), 7.31 – 7.17 (m, 1H), 3.71 – 3.55 (m, 2H), 3.12 – 3.02 (m, 1H), 2.93 – 2.83 (m, 1H), 2.34 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.4, 139.1, 129.6, 126.1, 66.8, 45.6, 21.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{16}NO_2S^+$ 226.0896; found 226.0897; IR ($\nu_{max}$/cm$^{-1}$) 2862, 2850, 1448, 1107, 1086, 1063, 903, 818. The spectra are in agreement with reported data.[2]



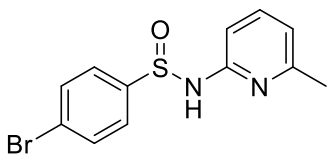
*tert*-butyl 4-(p-tolylsulfinyl)piperazine-1-carboxylate (**2f**). Prepared according to the general procedure A using TsCl (155 mg, 0.81 mmol). Purification by column chromatography (60% of EtOAc in cyclohexane) afforded the product as a white solid (203 mg, 77%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.49 – 7.39 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 3.48-3.26 (m, 4H), 3.01 (ddd, J = 10.9, 6.4, 3.6 Hz, 2H), 2.84 (ddd, J = 11.6, 6.4, 3.6 Hz, 2H), 2.31 (s, 3H), 1.34 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 154.4, 141.5, 139.3, 129.6, 126.0, 80.0, 45.5, 28.3, 21.3. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{25}N_2O_3S^+$ 325.1580; found 325.1587; IR ($\nu_{max}$/cm$^{-1}$) 2974, 2922, 2856, 1693, 1417, 1248, 1167, 1090, 1068. The spectra are in agreement with reported data.[7]



4-methyl-*N*-phenylbenzenesulfinamide (**2g**). Prepared according to the general procedure A using TsCl (155 mg, 0.81 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a yellowish solid (117 mg, 62%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.71 – 7.61 (m, 2H), 7.37 – 7.21 (m, 4H), 7.14 – 6.99 (m, 3H), 6.23 (s, 1H), 2.43 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 142.0, 141.6, 140.9, 129.9, 129.6, 125.6, 123.6, 118.9, 21.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{14}NOS^+$ 232.0791; found 232.0795; IR ($\nu_{max}$/cm$^{-1}$) 3089, 3070, 3043, 2858, 1088, 1053, 1043, 758. The spectra are in agreement with reported data.[2]



4-bromo-*N*-(4-iodophenyl)benzenesulfinamide (**2h**). Prepared according to the general procedure B (neat) using 4-bromobenzenethiol (189 mg, 1 mmol). Purification by column chromatography (1% of MeOH in $CH_2Cl_2$) afforded the product as a white solid (144 mg, 34%). $^{1}$H NMR (400 MHz, DMSO) $\delta$ 9.53 (s, 1H), 7.84 – 7.76 (m, 2H), 7.70 – 7.61 (m, 2H), 7.60 – 7.51 (m, 2H), 6.95 – 6.82 (m, 2H); $^{13}$C NMR (101 MHz, DMSO) $\delta$ 144.1, 141.9, 138.2, 132.6, 128.3, 125.3, 120.6, 85.9. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{10}BrINOS^+$ 421.8706; found 421.8696; IR ($\nu_{max}$/cm$^{-1}$) 3126, 1088, 1053, 1005.

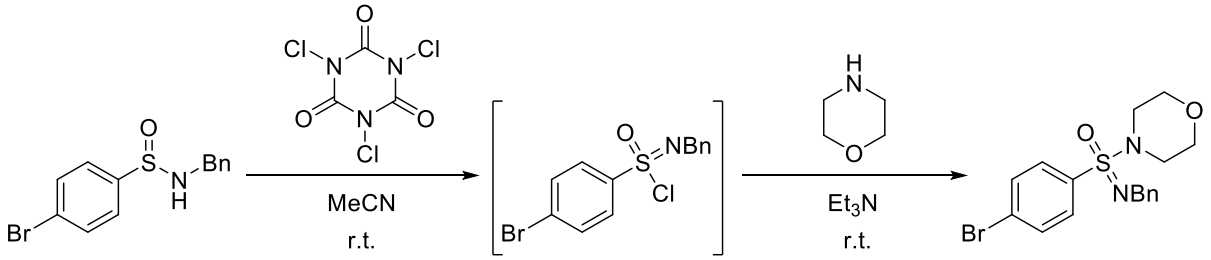


4-bromo-*N*-(6-methylpyridin-2-yl)benzenesulfinamide (**2i**). Prepared according to the general procedure B (neat) using 4-bromobenzenethiol (189 mg, 1 mmol). Purification by column chromatography (50 to 100% of EtOAc and 1% $Et_3N$ in cyclohexane) afforded the product as a white solid (182 mg, 59%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.70 – 7.62 (m, 4H), 7.52 – 7.43 (m, 1H), 7.08 (s, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 158.0, 153.0, 143.7, 138.8, 132.5, 127.3, 126.4, 118.1, 107.3, 24.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_{12}BrN_2OS^+$ 310.9848; found 310.9848; IR ($\nu_{max}$/cm$^{-1}$) 3109, 1597, 1570, 1450, 1375, 1294, 1225, 1095, 1065.

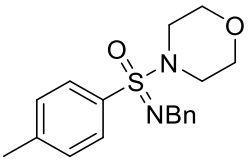
## 4. Synthesis of Sulfonimidamides

General procedure C:

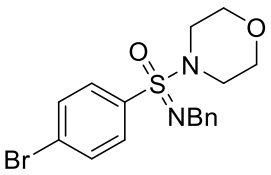
Sulfonimidamides were prepared according to a modified protocol.[5]



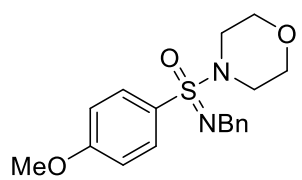

A sulfinamide (0.1 mmol) was dissolved in MeCN (2 mL) and trichloroisocyanuric acid (8 mg, 0.033mmol) was added. The reaction mixture was stirred at rt for 30 min. Then, a solution of morpholine (18 µL, 0.2 mmol) and $Et_3N$ (28 µL, 0.2 mmol) in MeCN (0.2 mL) was added and the resulting mixture was stirred at rt for 60 min. The reaction mixture was diluted with EtOAc (20 mL), washed with saturated aq. $NaHCO_3$ solution (10 mL) and brine (10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, concentrated under reduced pressure. Purification with column chromatography on silica gel afforded the product.



4-(4-methyl-*N*-phenylphenylsulfonimidoyl)morpholine (**3a**). Prepared according to the general procedure C using **1a** (25 mg, 0.1 mmol). Purification by column chromatography (40% of EtOAc in cyclohexane) afforded the product as a colorless oil, which solidified on standing to a white solid (25 mg, 73%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.85 – 7.71 (m, 2H), 7.50 – 7.43 (m, 2H), 7.36 – 7.17 (m, 5H), 4.49 (d, $J$ = 14.7 Hz, 1H), 4.35 (d, $J$ = 14.8 Hz, 1H), 3.68 – 3.53 (m, 4H), 2.93 (ddd, $J$ = 11.9, 5.5, 3.5 Hz, 2H), 2.83 (ddd, $J$ = 11.8, 5.8, 3.6 Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 143.3, 141.6, 132.0, 129.6, 128.4, 128.2, 127.7, 126.7, 66.5, 47.1, 45.5, 21.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{23}N_2O_2S^+$ 331.1475; found 321.1479; IR ($\nu_{max}$/cm$^{-1}$) 2966, 2854, 1452, 1257, 1146, 1113, 1065, 931, 715.

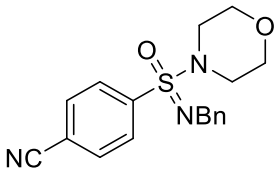


4-(*N*-benzyl-4-bromophenylsulfonimidoyl)morpholine (**3b**). Prepared according to the general procedure C using **1p** (31 mg, 0.1 mmol). Purification by column chromatography (50% of EtOAc in cyclohexane) afforded the product as a white solid (34 mg, 86%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.82 – 7.75 (m, 2H), 7.70 – 7.65 (m, 2H), 7.51 – 7.44 (m, 2H), 7.39 – 7.31 (m, 2H), 7.28 – 7.22 (m, 1H), 4.50 (d, $J$ = 14.6 Hz, 1H), 4.35 (d, $J$ = 14.7 Hz, 1H), 3.70 – 3.58 (m, 4H), 2.96 (ddd, $J$ = 11.9, 5.8, 3.7 Hz, 2H), 2.85 (ddd, $J$ = 11.7, 5.8, 3.4 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 141.0, 134.1, 132.1, 129.5, 128.3, 127.52, 127.48, 126.7, 66.3, 46.9, 45.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{20}BrN_2O_2S^+$ 395.0423; found 395.0412; IR ($\nu_{max}$/cm$^{-1}$) 3259, 2854, 1703, 1574, 1452, 1257, 1147, 1111, 1066, 1009, 931.

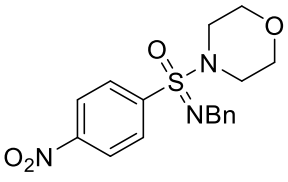


4-(*N*-benzyl-4-methoxyphenylsulfonimidoyl)morpholine (**3c**). Prepared according to the general procedure C using **1e** (26 mg, 0.1 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as an off-white solid (21 mg, 61%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.90 – 7.82 (m, 2H), 7.53 – 7.45 (m, 2H), 7.38 – 7.31 (m,

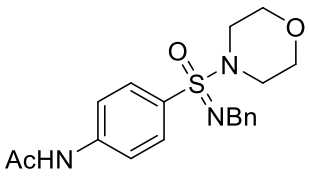
2H), 7.27 – 7.21 (m, 1H), 7.04 – 6.97 (m, 2H), 4.55 (d, $J$ = 14.8), 4.36 (d, $J$ = 14.7 Hz, 1H), 3.73 – 3.58 (m, 4H), 3.01 – 2.90 (m, 2H), 2.90 – 2.80 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.8, 141.4, 130.1, 128.3, 127.5, 126.5, 126.5, 114.0, 66.3, 55.6, 47.0, 45.5. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{23}N_2O_3S^+$ 347.1424; found 347.1423; IR ($\nu_{max}$/cm$^{-1}$) 3253, 2843,1593, 1495, 1441, 1255, 1146, 1111, 1065, 1026, 930.



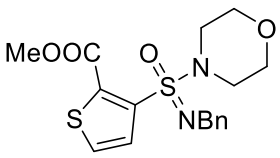

4-(*N*-benzylmorpholine-4-sulfonimidoyl)benzonitrile (**3d**). Prepared according to the general procedure C using **1b** (26 mg, 0.1 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as an off-white solid (30 mg, 88%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.08 – 8.00 (m, 2H), 7.87 – 7.80 (m, 2H), 7.50 – 7.42 (m, 2H), 7.41 – 7.32 (m, 2H), 7.31 – 7.24 (m, 1H), 4.51 (d, $J$ = 14.6 Hz, 1H), 4.36 (d, $J$ = 14.6 Hz, 1H), 3.73 – 3.55 (m, 4H), 2.98 (ddd, $J$ = 11.9, 5.9, 3.6 Hz, 2H), 2.88 (ddd, $J$ = 11.8, 5.8, 3.3 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 140.7, 139.7, 132.6, 128.5, 128.4, 127.5, 126.9, 117.5, 116.1, 66.2, 46.9, 45.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{20}BrN_3O_2S^+$ 342.1271; found 342.1274; IR ($\nu_{max}$/cm$^{-1}$) 3093, 2848, 2237, 1485, 1275, 1255, 1140, 1113, 1065, 937.




4-(*N*-benzyl-4-nitrophenylsulfonimidoyl)morpholine (**3e**)**.** Prepared according to the general procedure C using **1o** (27.7 mg, 0.1 mmol). Purification by column chromatography (20% of EtOAc in cyclohexane) afforded the product as a white solid (30 mg, 81%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.41 – 8.35 (m, 2H), 8.14 – 8.08 (m, 2H), 7.50 – 7.44 (m, 2H),, 7.40 – 7.33 (m, 2H), 7.31 – 7.24 (m, 1H), 4.525 (d, $J$ = 14.6, 1H), 4.38 (d, $J$ = 14.6 Hz, 1H), 3.72 – 3.58 (m, 4H), 3.00 (ddd, $J$ = 12.0, 5.8, 3.6 Hz, 2H), 2.91 (ddd, $J$ = 11.8, 6.0, 3.6 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 150.0, 141.2, 140.6, 129.1, 128.4, 127.5, 126.9, 124.0, 66.2, 46.9, 45.4. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{20}N_3O_4S^+$ 362.1169; found 362.1163; IR ($\nu_{max}$/cm$^{-1}$) 3103, 2846, 1604, 1520, 1346, 1282, 1257, 1165, 1122, 1065, 935.

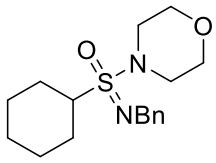



*N*-(4-(*N*-benzylmorpholine-4-sulfonimidoyl)phenyl)acetamide (**3f**). Prepared according to the general procedure C using **1d** (29 mg, 0.1 mmol). Purification by column chromatography (50 to 100% of EtOAc in cyclohexane) afforded the product as a white solid (25 mg, 67%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.88 – 7.80 (m, 2H), 7.73 (s, 1H), 7.70 – 7.62 (m, 2H), 7.51 – 7.44 (m, 2H), 7.38 – 7.31 (m, 2H), 7.27 – 7.21 (m, 1H), 4.50 (d, $J$ = 14.6 Hz, 1H), 4.36 (d, $J$ = 14.7 Hz, 1H), 3.73 – 3.56 (m, 4H), 3.02 – 2.90 (m, 2H), 2.85 (ddd, $J$ = 11.8, 5.7, 3.6 Hz, 2H), 2.20 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 168.6, 141.8, 141.2, 129.6, 129.2, 128.3, 127.6, 126.7, 119.1, 66.3, 47.0, 45.5, 24.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{20}N_3O_4S^+$ 374.1533; found 374.1529; IR ($\nu_{max}$/cm$^{-1}$) 3317, 2852, 1699, 1674, 1589, 1527, 1255, 1136, 1111, 1065, 928.

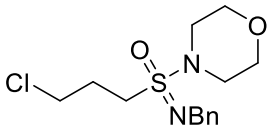



Methyl 3-(*N*-phenylmorpholine-4-sulfonimidoyl)thiophene-2-carboxylate (**3g**). Prepared according to the general procedure C using **1g** (29 mg, 0.1 mmol). Purification by column chromatography (2.5% of MeOH in $CH_2Cl_2$) afforded the product as a colorless oil, which solidified on standing to a white solid (25 mg, 68%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.45 (d, $J$ = 5.3 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 1H), 4.44 – 4.37 (m, 1H), 4.30 – 4.23 (m, 1H), 3.81 (s, 3H), 3.69 – 3.59 (m, 4H), 3.27 – 3.16 (m, 4H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 161.4, 141.1, 138.1, 135.4, 130.4, 128.3, 127.7, 127.4, 126.7, 66.7, 53.2, 47.1, 46.0, 29.8. HRMS (ESI): *m/z* $[M+H]^+$

calcd for $C_{17}H_{21}N_2O_4S_2^+$ 381.0937; found 381.0937; IR ($\nu_{max}$/cm$^{-1}$) 2954, 2852, 1734, 1439, 1282, 1257, 1236, 1066, 939, 735.



4-(*N*-benzylcyclohexanesulfonimidoyl)morpholine (**3h**). Prepared according to the general procedure C using **1j** (24 mg, 0.1 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a white solid (23 mg, 72%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.44 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.17 (m, 1H), 4.36 (d, $J$ = 14.7 Hz, 1H), 4.09 (d, $J$ = 14.7 Hz, 1H), 3.69 – 3.53 (m, 4H), 3.41 – 3.24 (m, 4H), 3.13 – 3.00 (m, 1H), 2.36 – 2.26 (m, 1H), 2.13 – 2.03 (m, 1H), 1.97 – 1.85 (m, 2H), 1.77 – 1.67 (m, 1H), 1.67 – 1.50 (m, 2H), 1.38 – 1.15 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 141.7, 128.2, 127.4, 126.4, 67.2, 62.1, 47.1, 45.2, 27.4, 26.7, 25.4, 25.4, 25.2. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{21}N_2O_4S_2^+$ 323.1788; found 323.1793 IR ($\nu_{max}$/cm$^{-1}$) 2933, 2852, 1495, 1284, 1255, 1142, 1111, 1066, 939.



4-(*N*-benzyl-3-chloropropylsulfonimidoyl)morpholine (**3i**). Prepared according to the general procedure C using **1l** (23 mg, 0.1 mmol). Purification by column chromatography (30% of EtOAc in cyclohexane) afforded the product as a white solid (20 mg, 63%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 2H), 7.26 – 7.20 (m, 1H), 4.32 (d, $J$ = 14.4 Hz, 1H), 4.11 (d, $J$ = 14.4 Hz, 1H), 3.81 – 3.58 (m, 6H), 3.34 – 3.08 (m, 5H), 3.01 (ddd, $J$ = 13.5, 8.5, 6.2 Hz, 1H), 2.50 – 2.29 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 141.1, 128.3, 127.6, 126.6, 66.7, 46.6, 46.1, 45.3, 43.3, 26.7. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{22}ClN_2O_2S^+$ 317.1090; found 317.1088; IR ($\nu_{max}$/cm$^{-1}$) 3388, 2856, 1495, 1255, 1111, 1066, 935.

## 5. References


(1) Smith, C. R. *Synlett* **2009**, *2009* (9), 1522–1523.
(2) Wen, D.; Zheng, Q.; Wang, C.; Tu, T. *Org. Lett.* **2021**, *23* (9), 3718–3723.
(3) Zhang, Y.; Chitale, S.; Goyal, N.; Li, G.; Han, Z. S.; Shen, S.; Ma, S.; Grinberg, N.; Lee, H.; Lu, B. Z.; Senanayake, C. H. *J. Org. Chem.* **2012**, *77* (1), 690–695.
(4) Revés, M.; Riera, A.; Verdaguer, X. *Eur. J. Inorg. Chem.* **2009**, *2009* (29–30), 4446–4453.
(5) Lo, P. K. T.; Willis, M. C. *J. Am. Chem. Soc.* **2021**, *143* (38), 15576–15581.
(6) Taniguchi, N. *Eur. J. Org. Chem.* **2016**, *2016* (12), 2157–2162.
(7) Yu, H.; Li, Z.; Bolm, C. *Angew. Chem. Int. Ed.* **2018**, *57* (47), 15602-15605.

## 6. $^{1}H$ and $^{13}C$ NMR Spectra

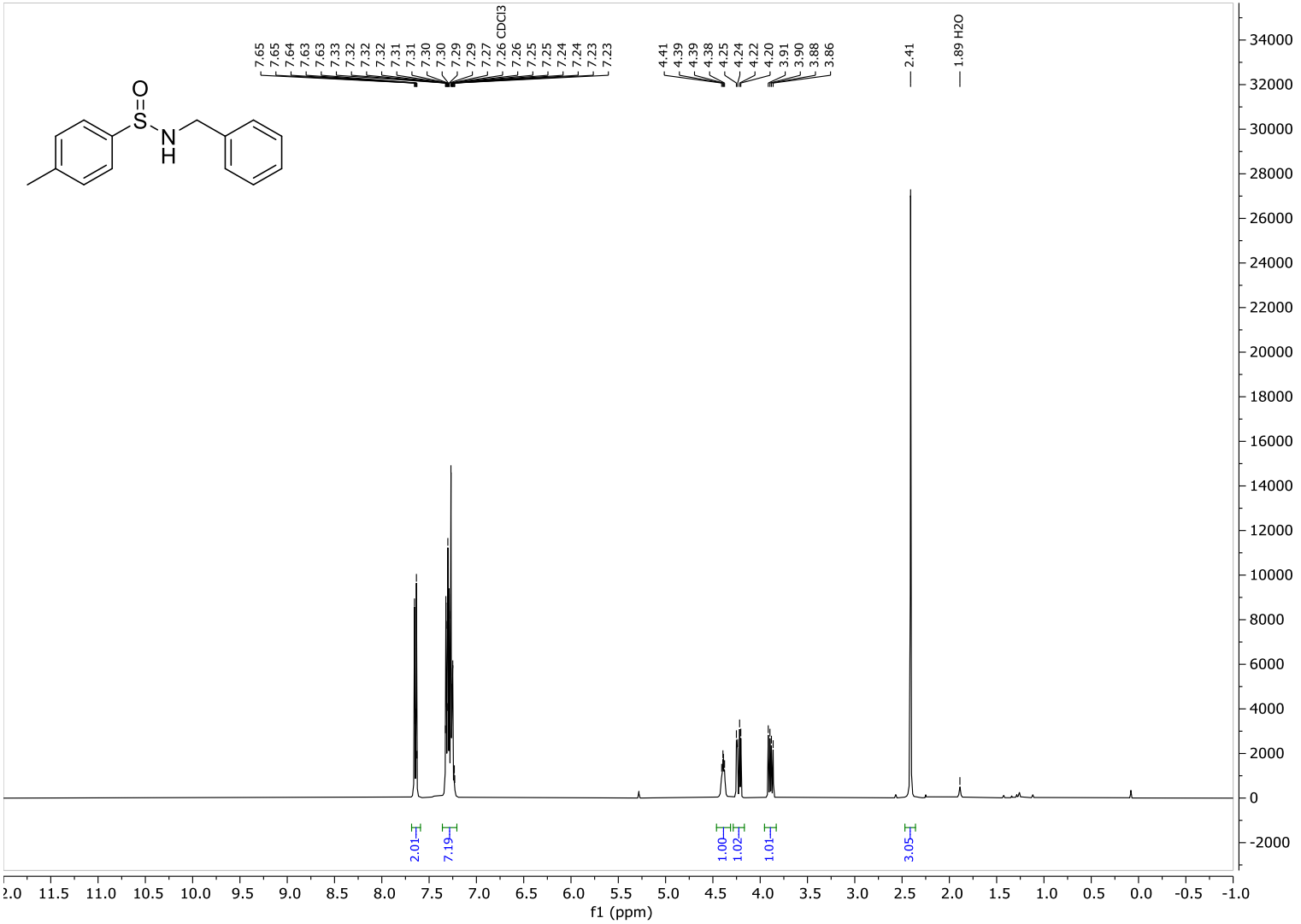



**Figure S1.** $^{1}H$ NMR of **1a** in $CDCl_3$.

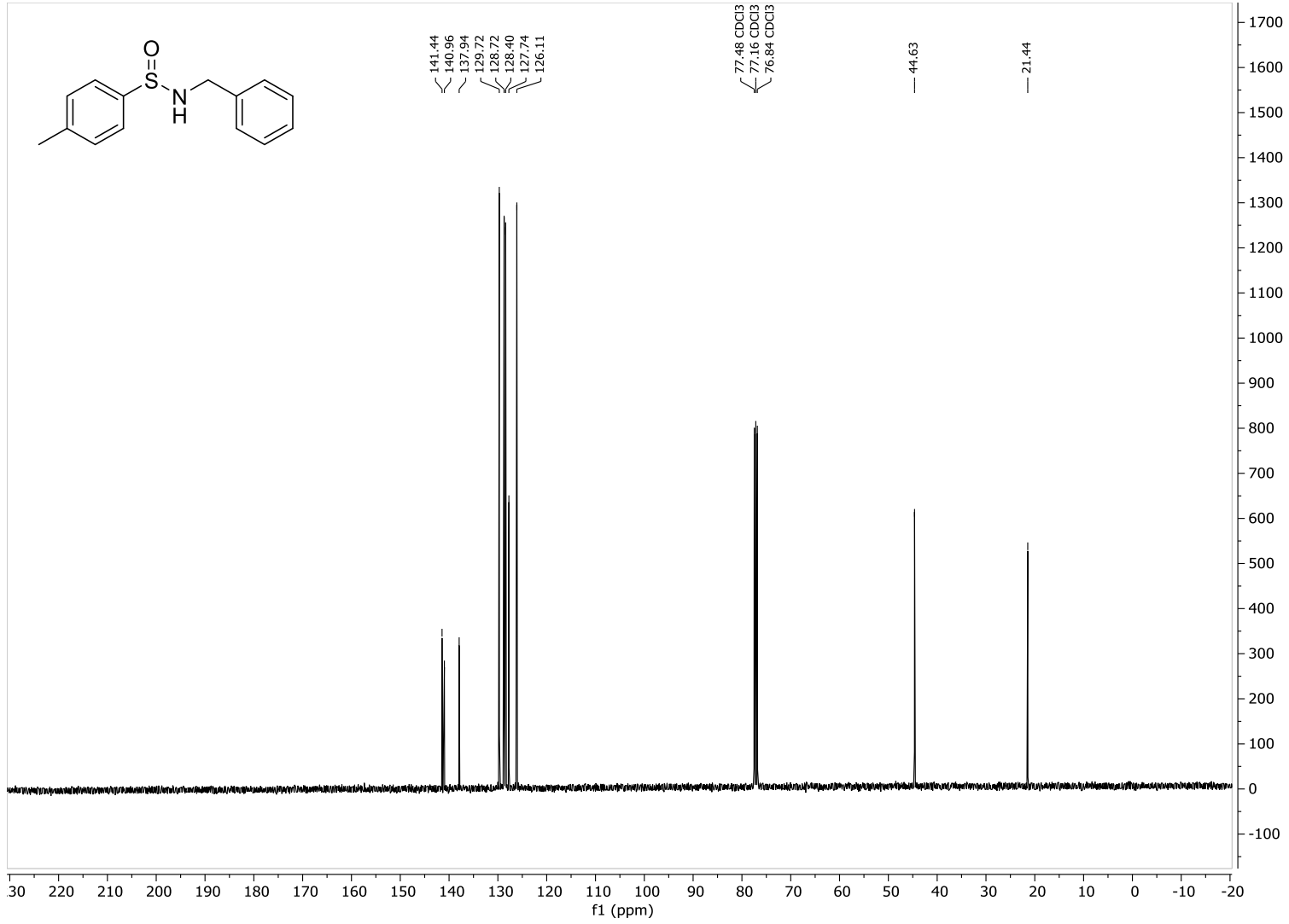



**Figure S2.** $^{13}C$ NMR of **1a** in $CDCl_3$.

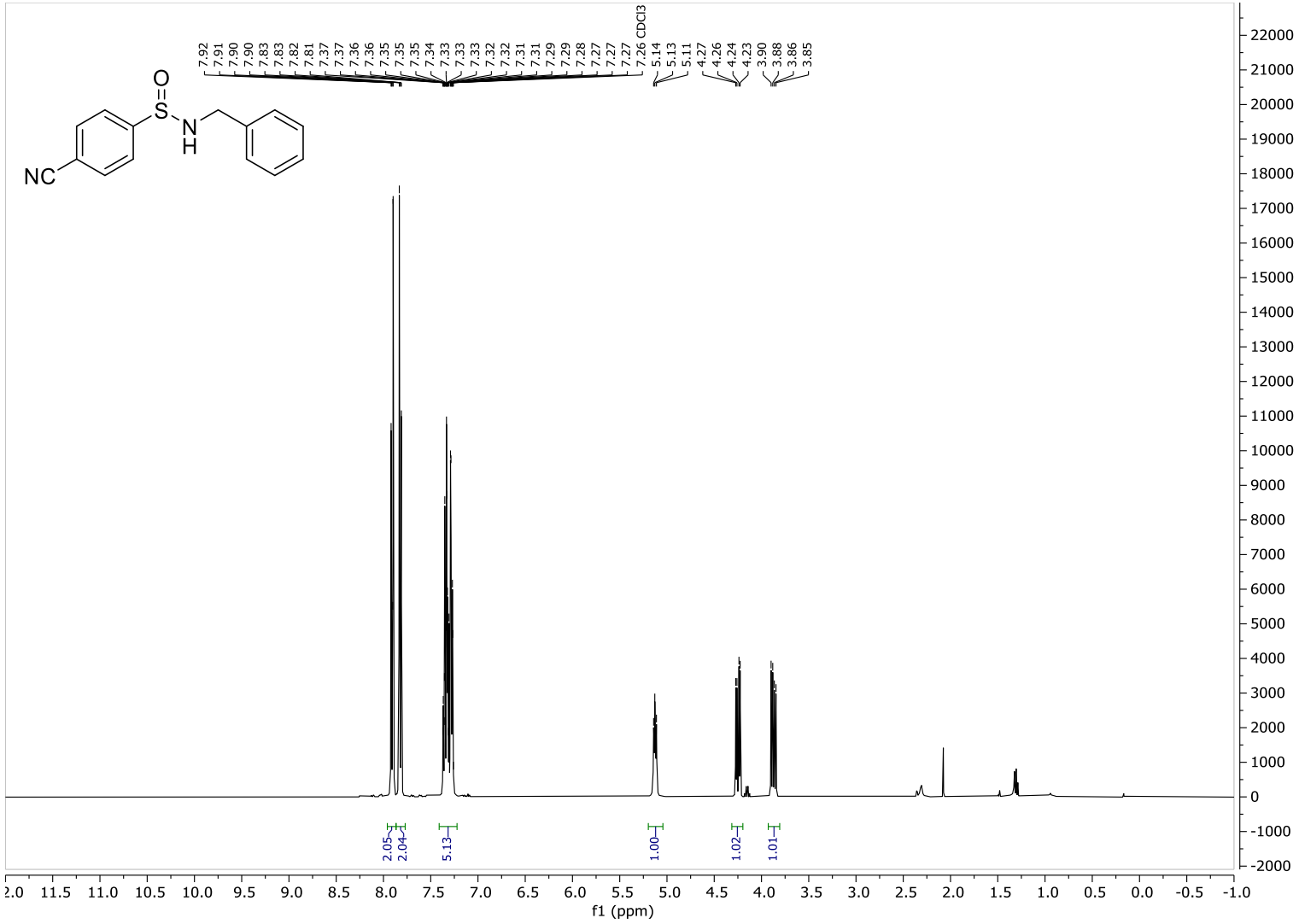



**Figure S3.** $^{1}$H NMR of **1b** in $CDCl_3$.

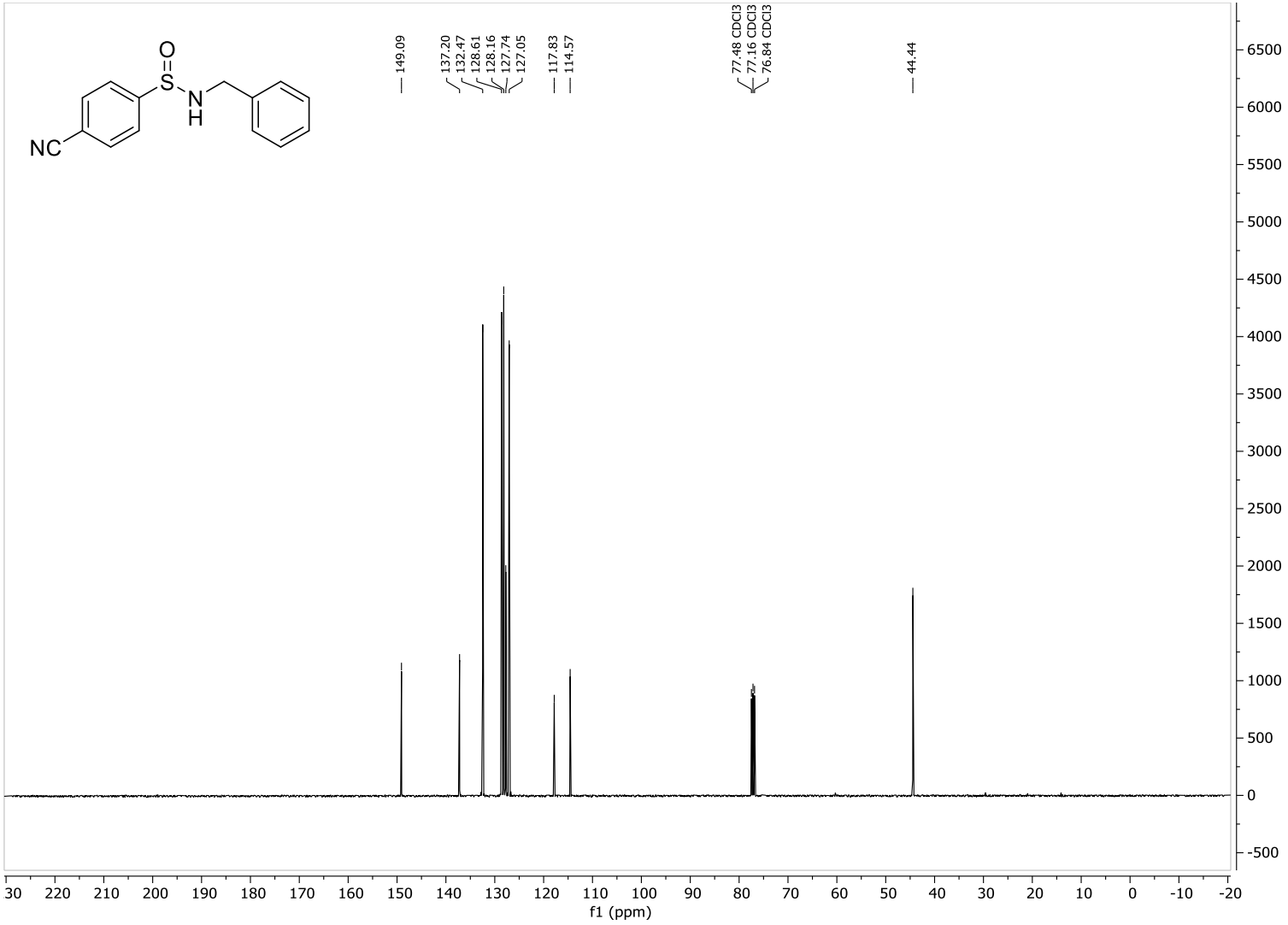



**Figure S4.** $^{13}C$ NMR of **1b** in $CDCl_3$.

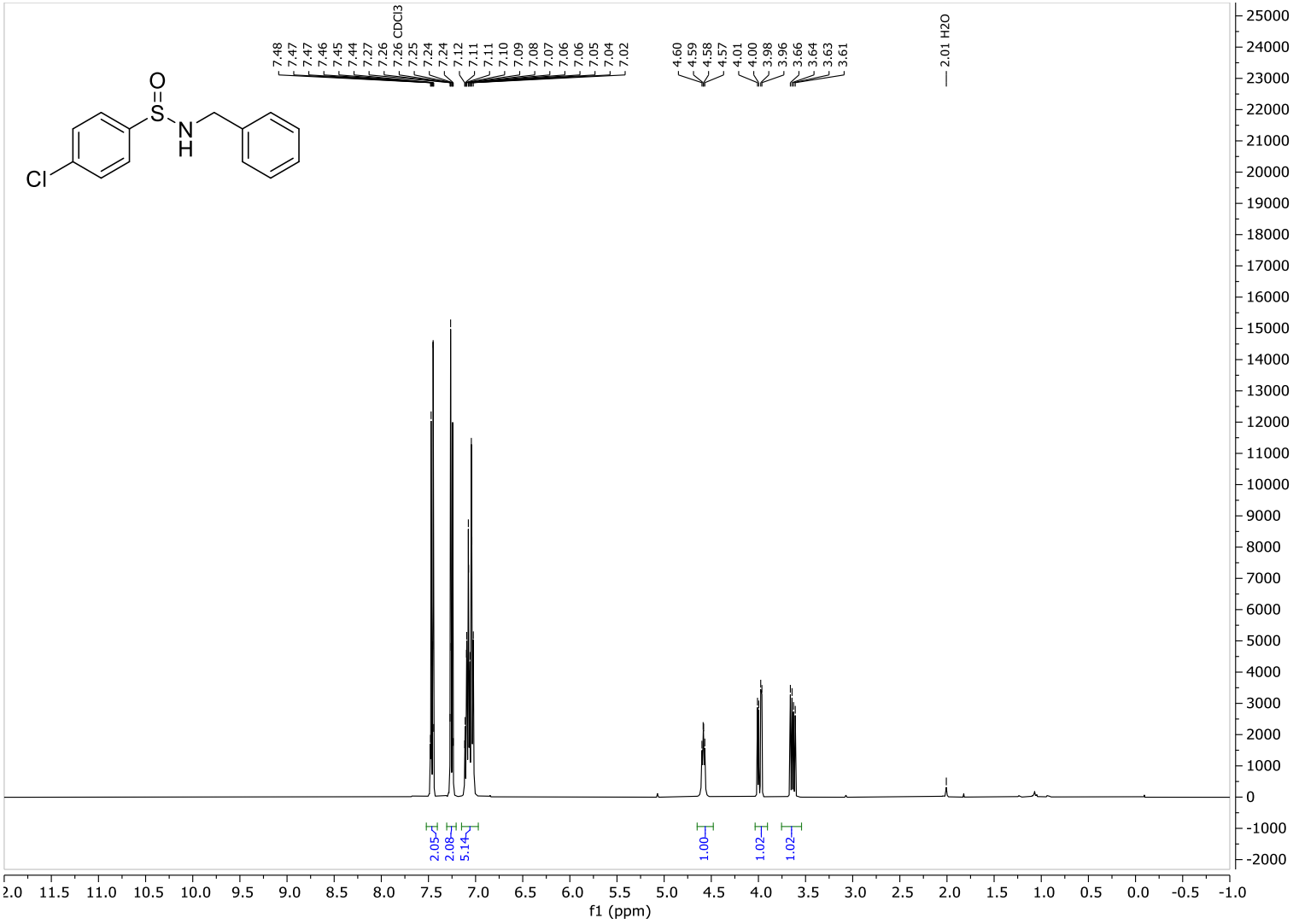



**Figure S5.** $^{1}$H NMR of **1c** in $CDCl_3$.

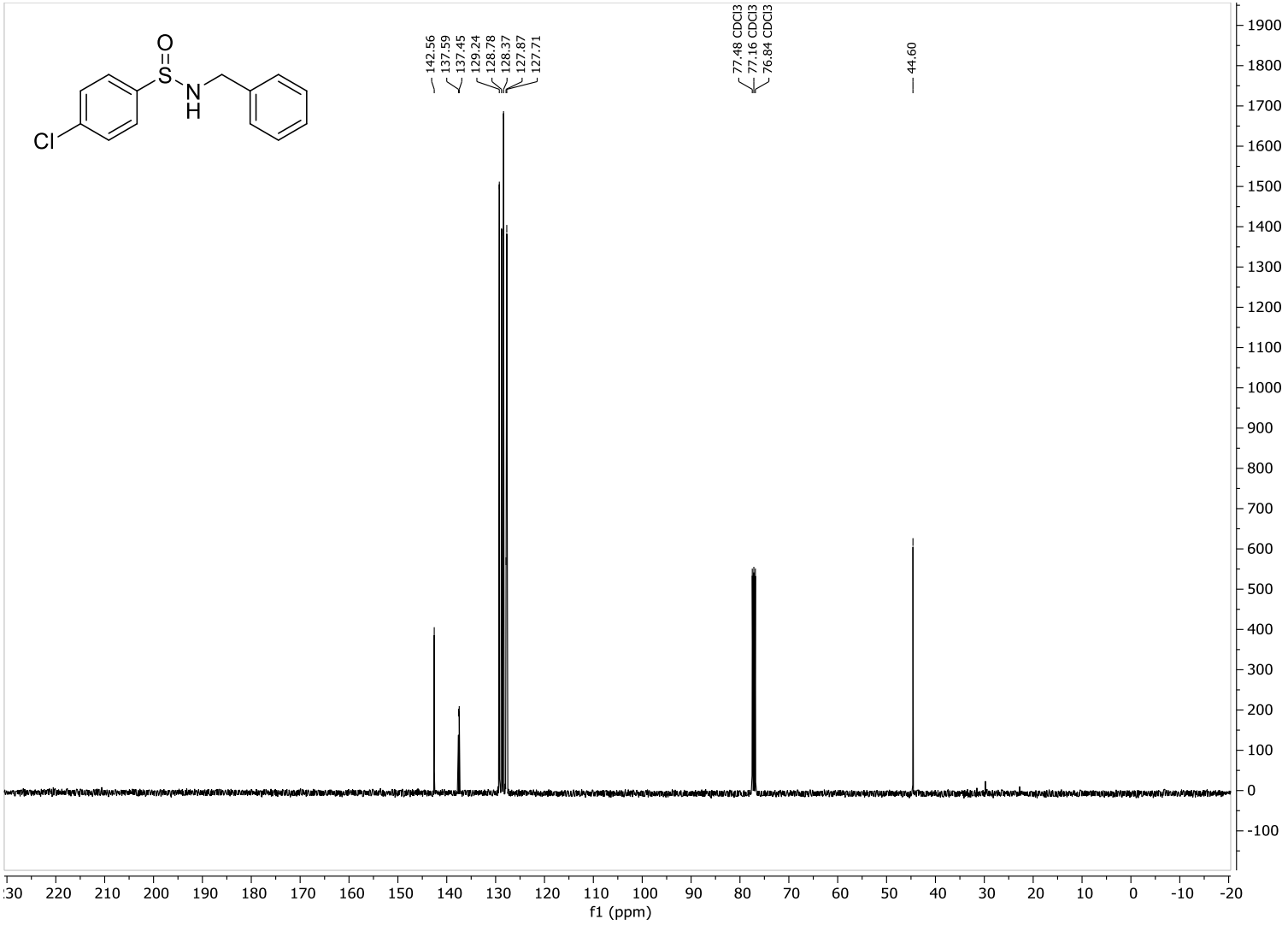



**Figure S6.** $^{13}C$ NMR of **1c** in $CDCl_3$.

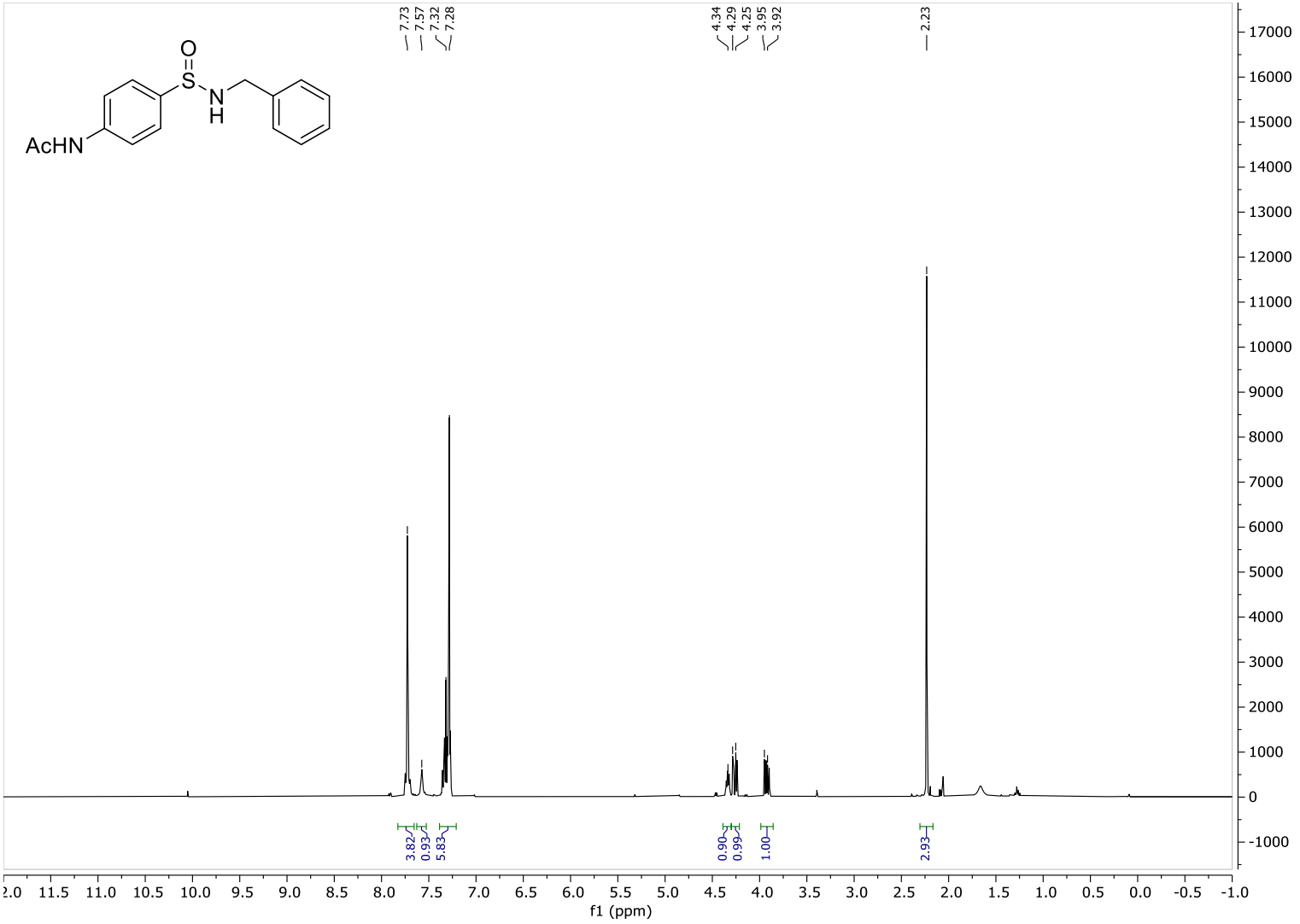



**Figure S7.** $^{1}$H NMR of **1d** in $CDCl_3$.

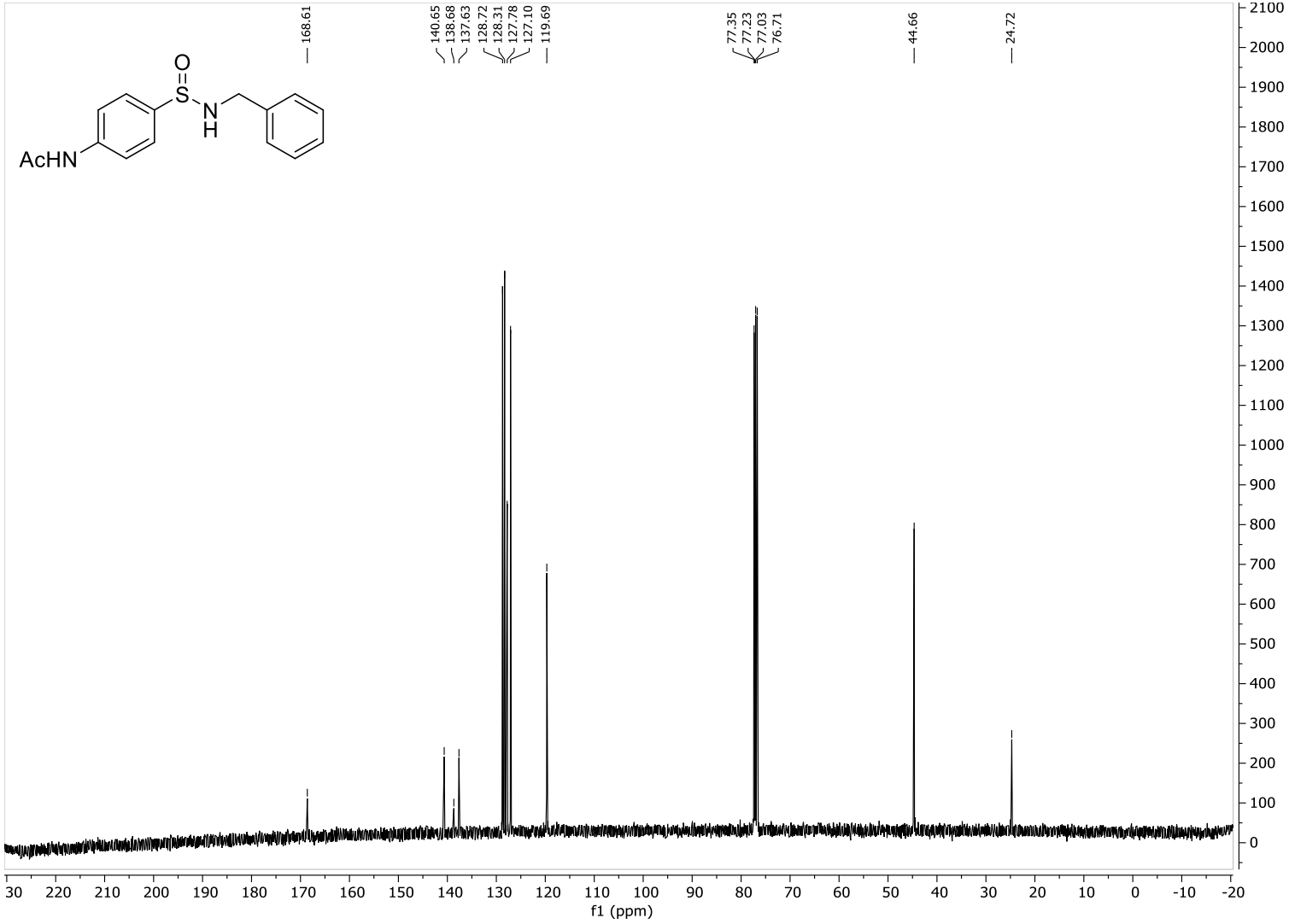



**Figure S8.** $^{13}C$ NMR of **1d** in $CDCl_3$.

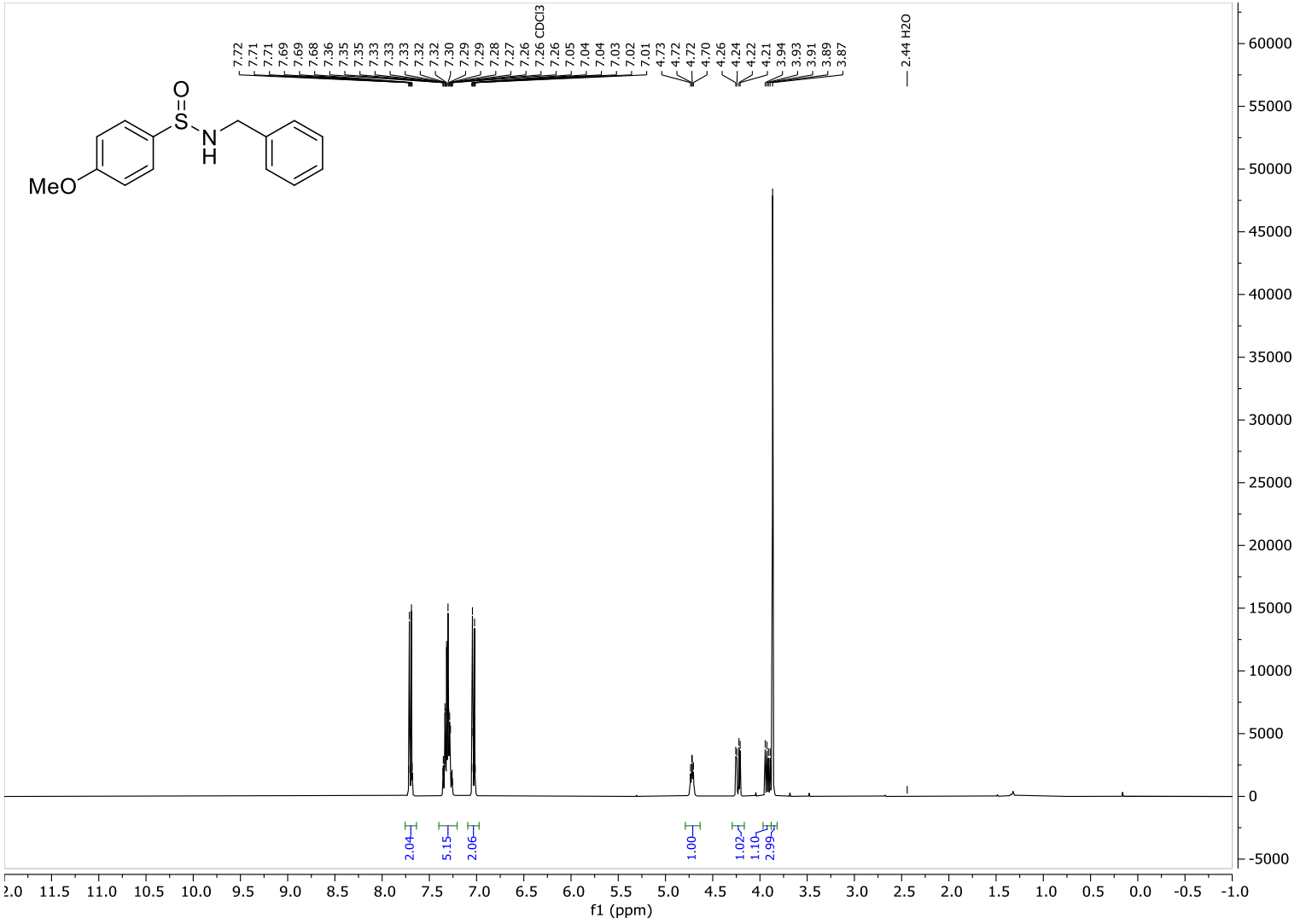



**Figure S9.** $^{1}H$ NMR of **1e** in $CDCl_3$.

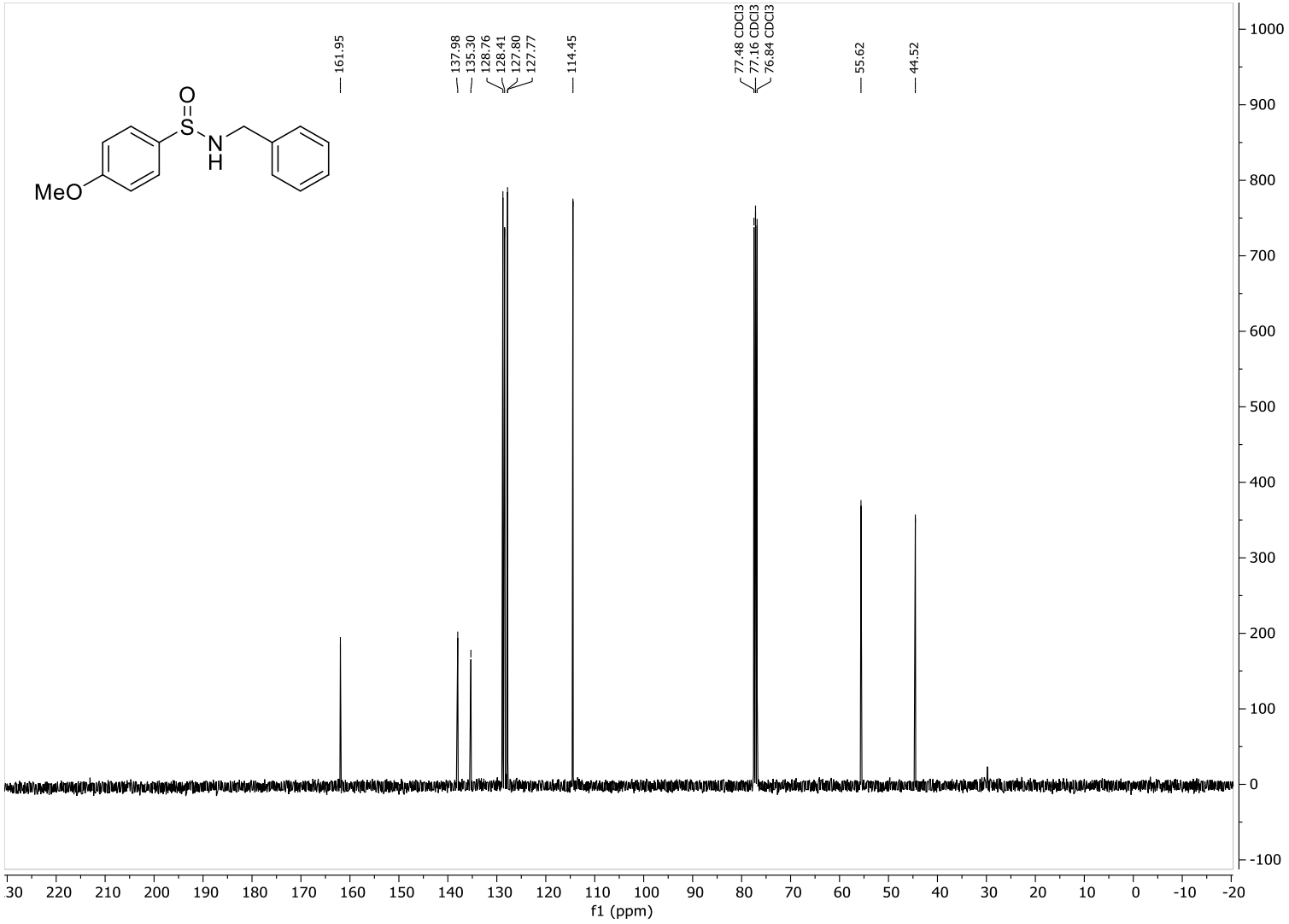



**Figure S10.** $^{13}C$ NMR of **1e** in $CDCl_3$.

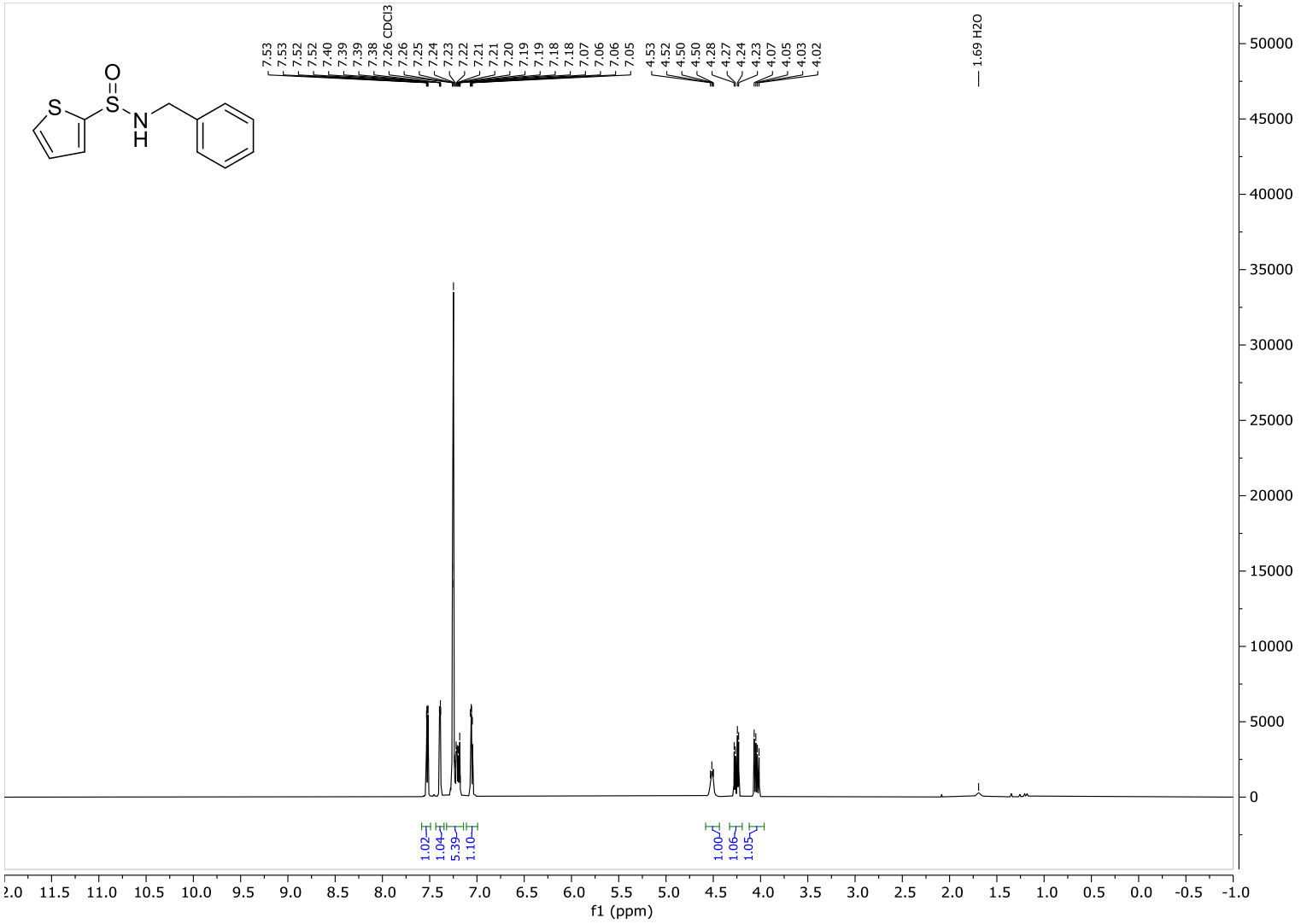



**Figure S11.** $^{1}$H NMR of **1f** in $CDCl_3$.

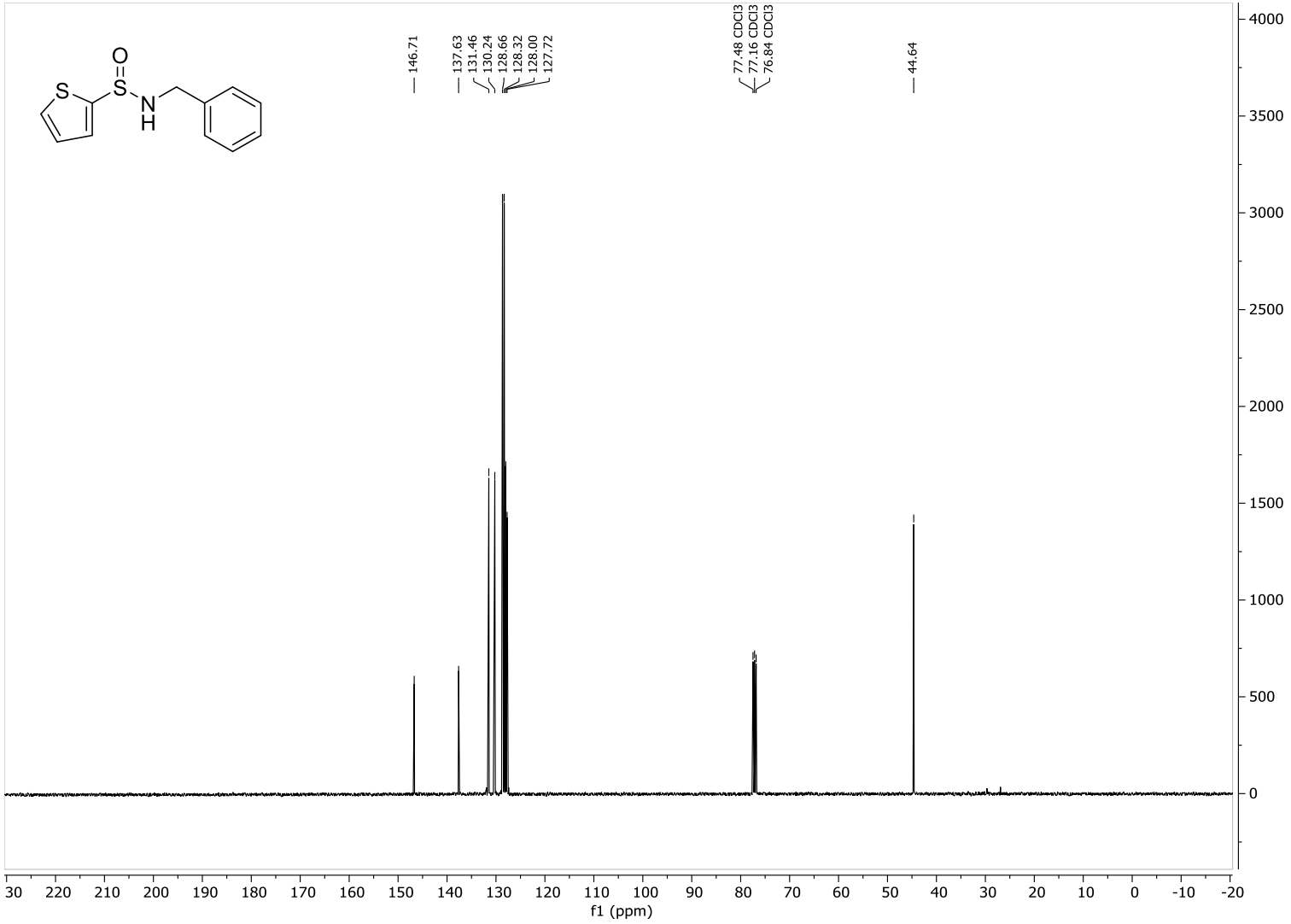



**Figure S12.** $^{13}C$ NMR of **1f** in $CDCl_3$.

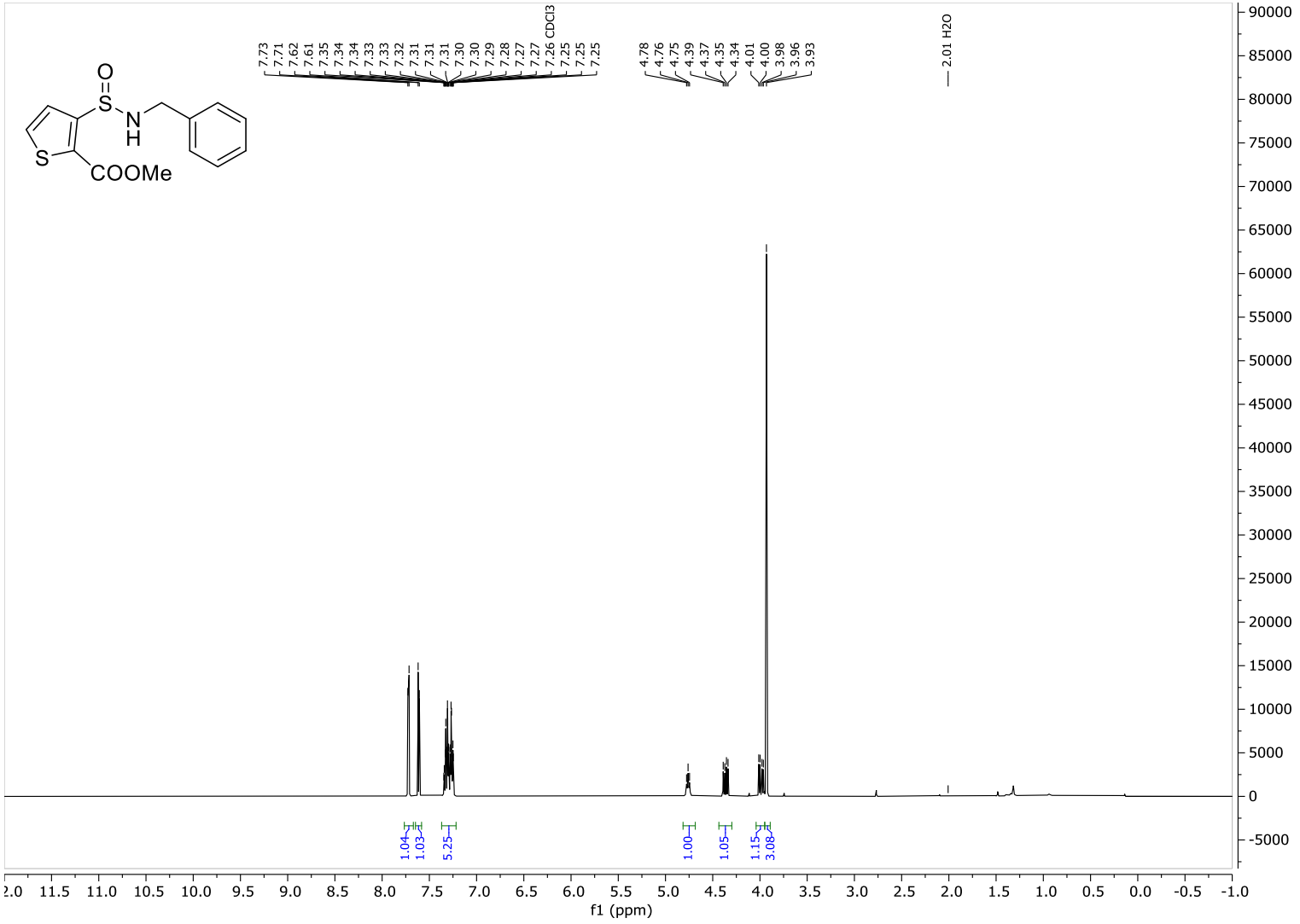



**Figure S13.** $^{1}$H NMR of **1g** in $CDCl_3$.

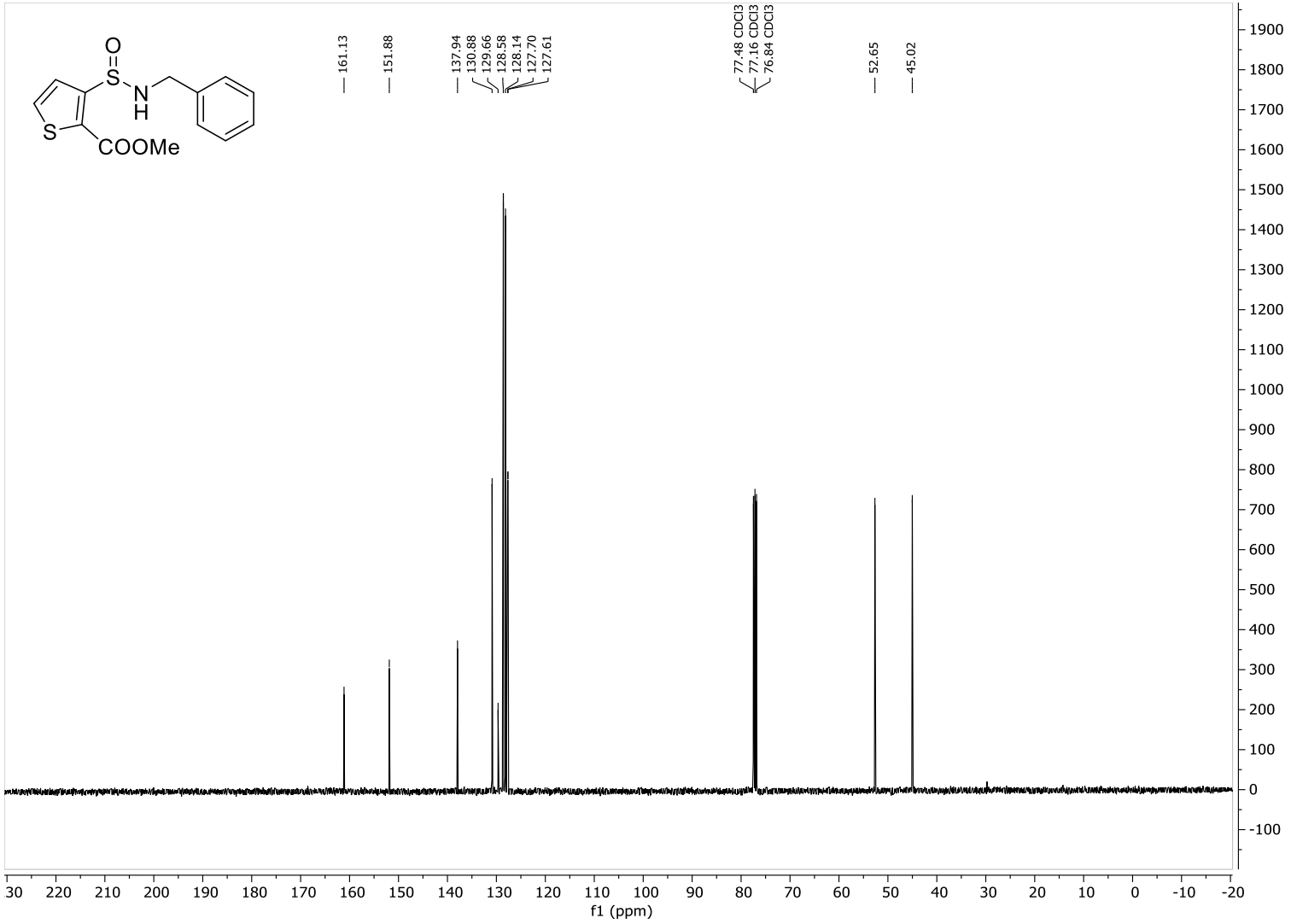



**Figure S14.** $^{13}C$ NMR of **1g** in $CDCl_3$.

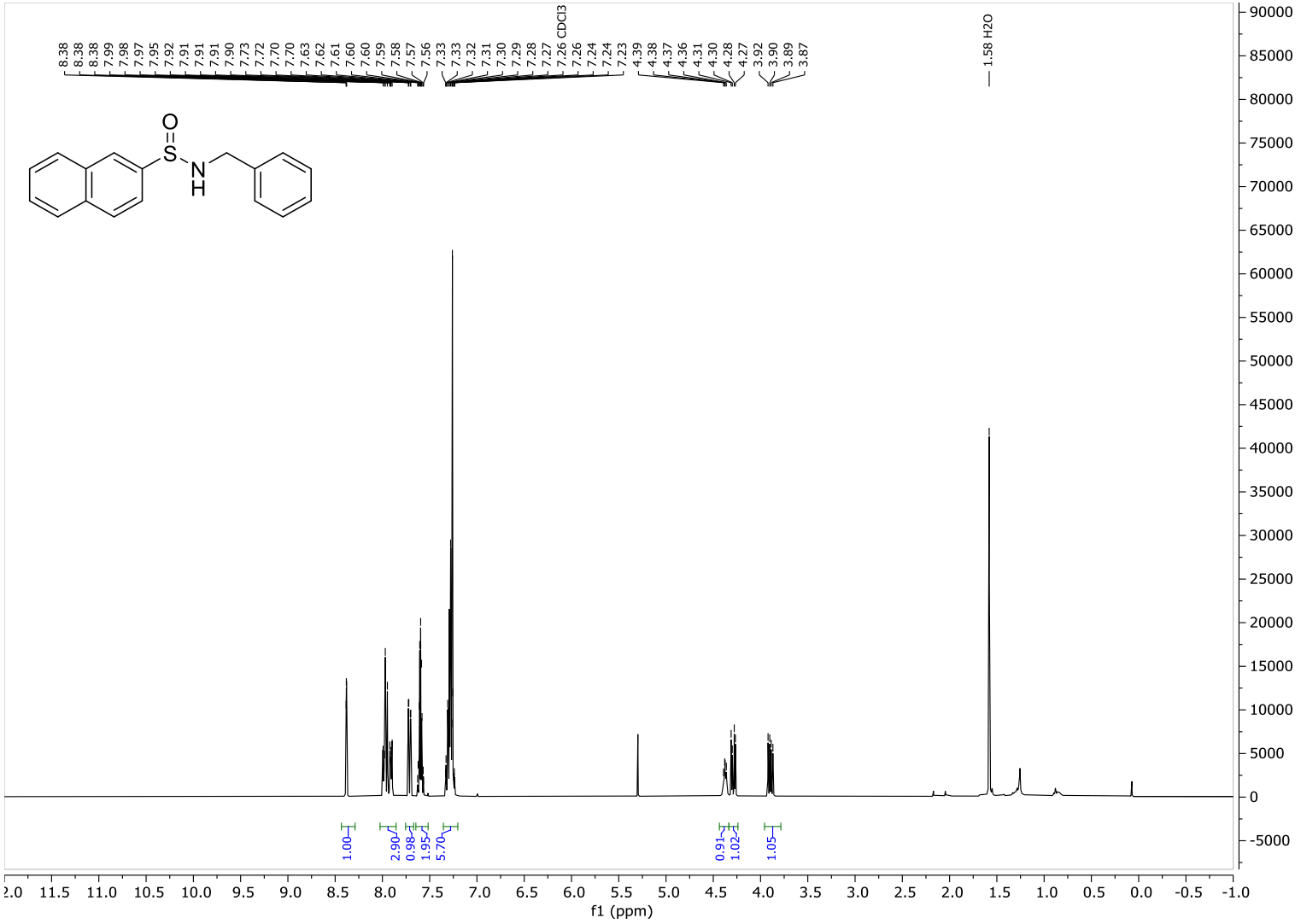



**Figure S15.** $^{1}$H NMR of **1h** in $CDCl_3$.

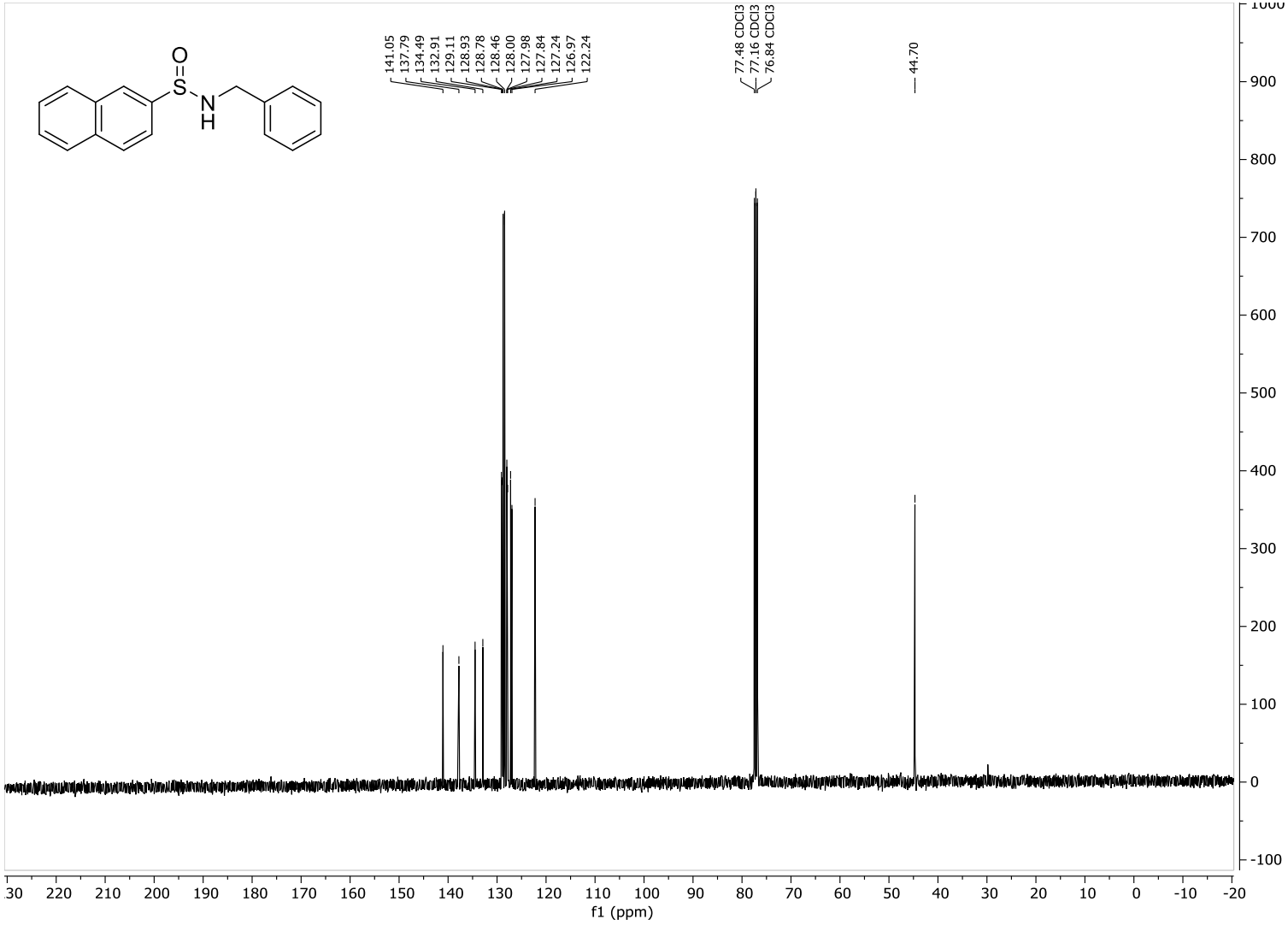



**Figure S16.** $^{13}C$ NMR of **1h** in $CDCl_3$.

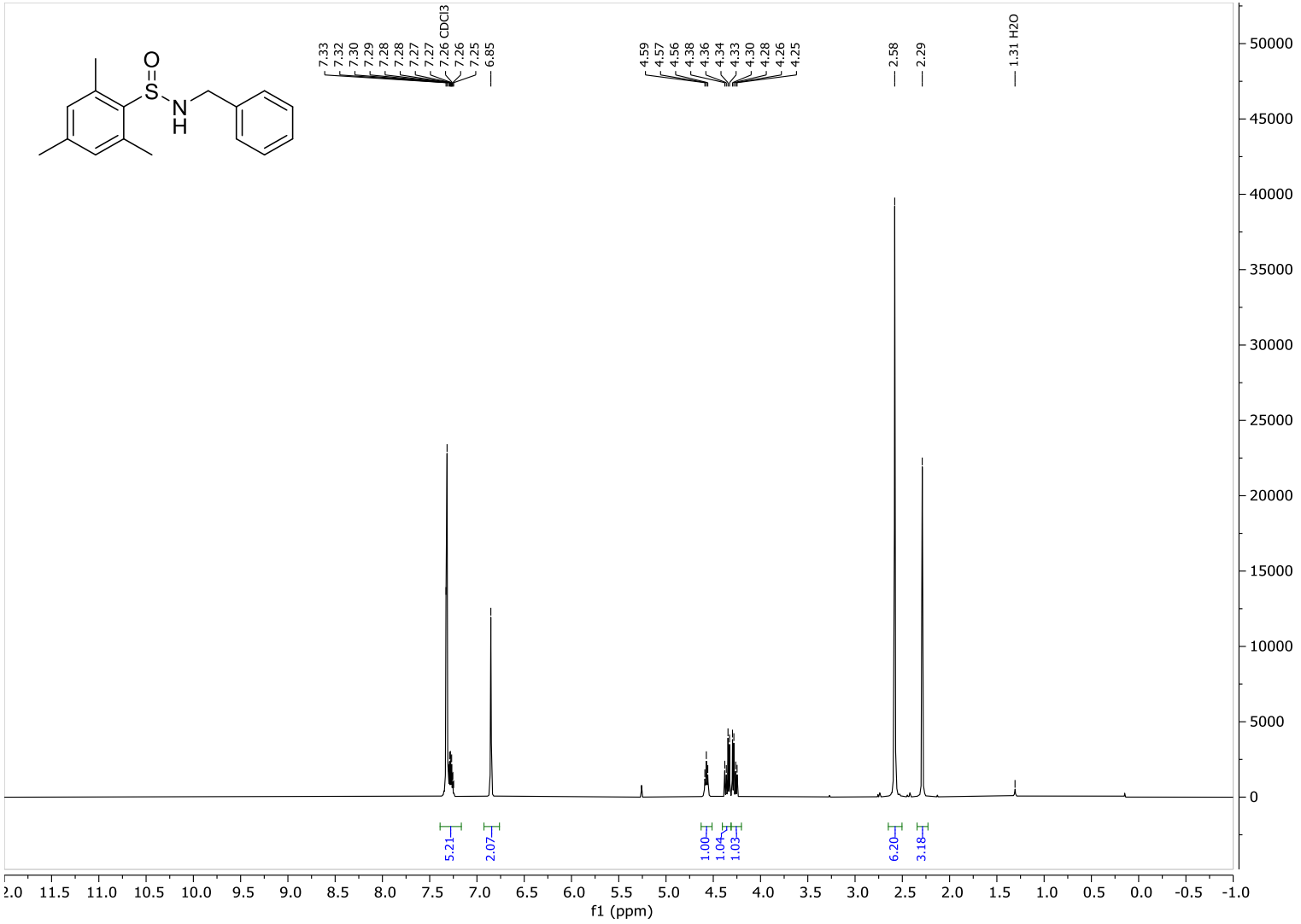



**Figure S17.** $^{1}$H NMR of **1i** in $CDCl_3$.

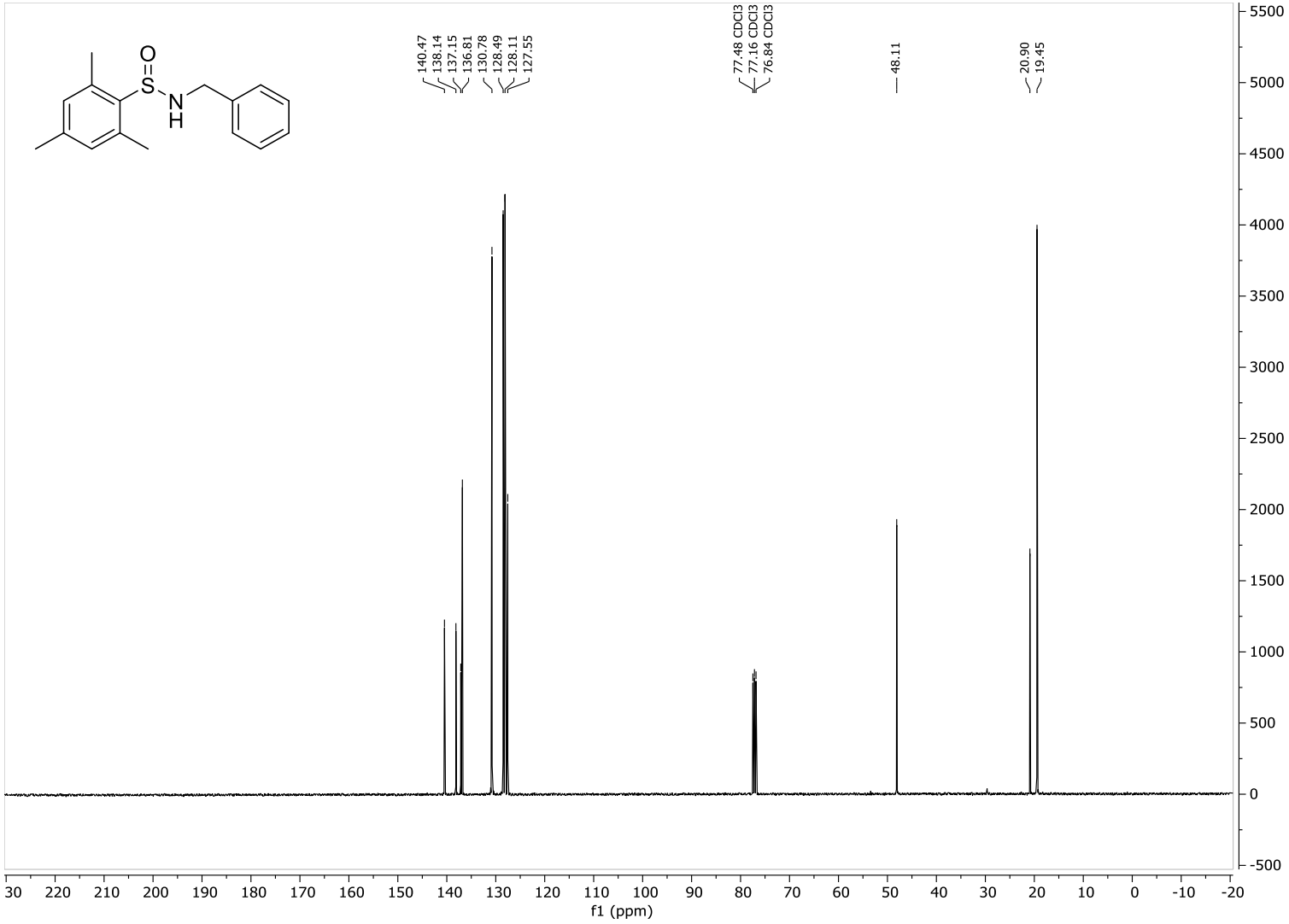



**Figure S18.** $^{13}C$ NMR of **1i** in $CDCl_3$.

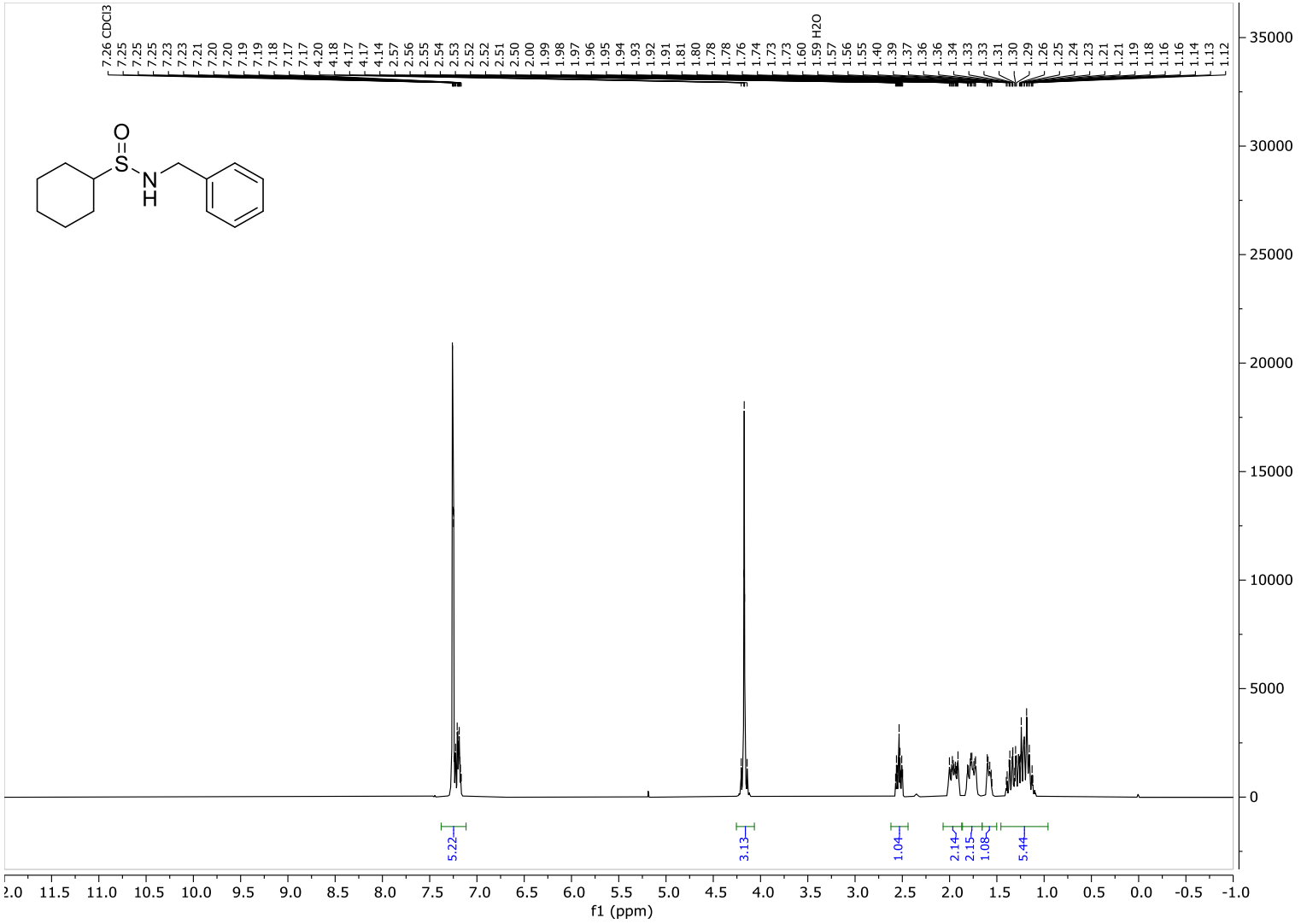



**Figure S19.** $^{1}H$ NMR of **1j** in $CDCl_3$.

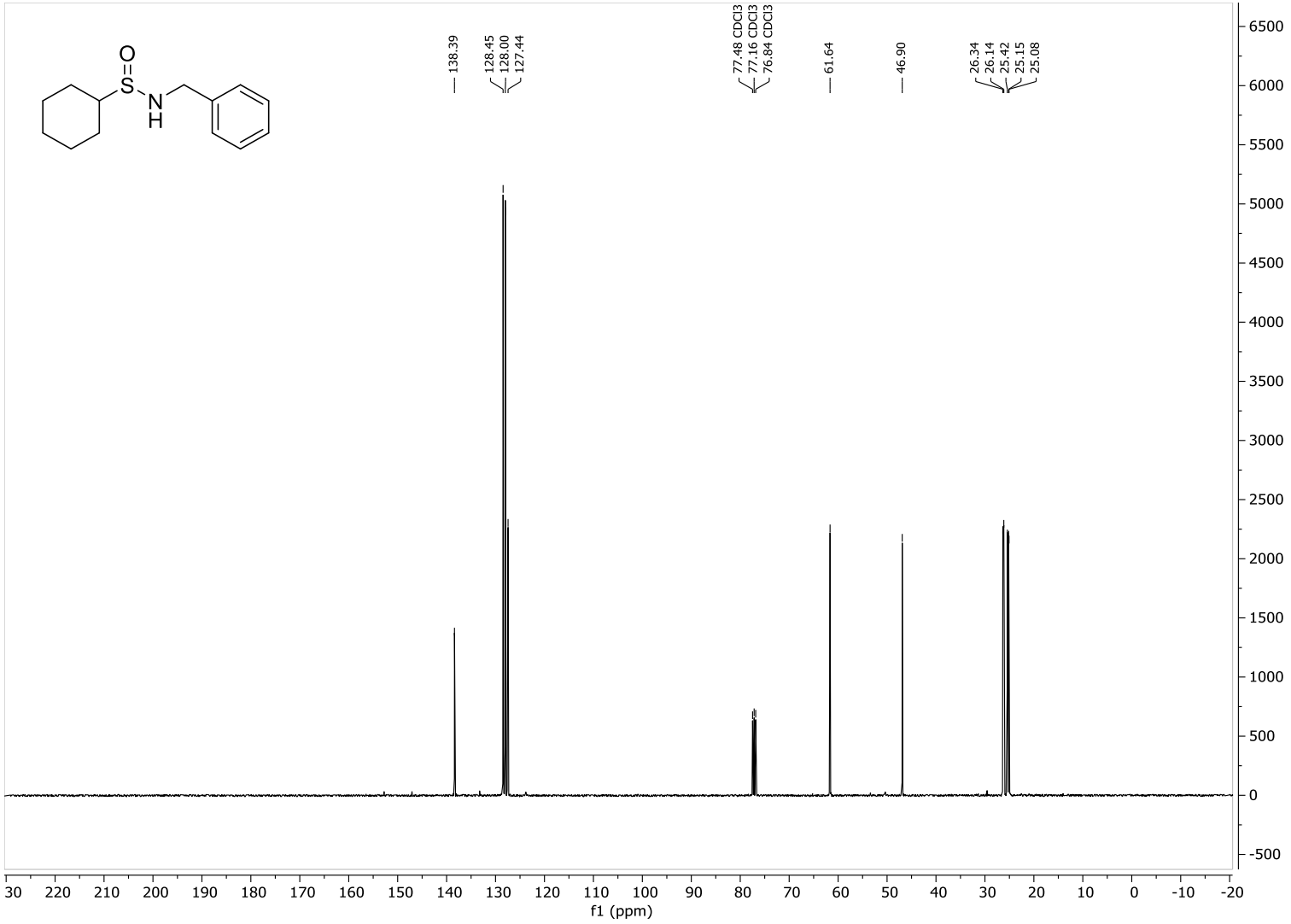



**Figure S20.** $^{13}C$ NMR of **1j** in $CDCl_3$.

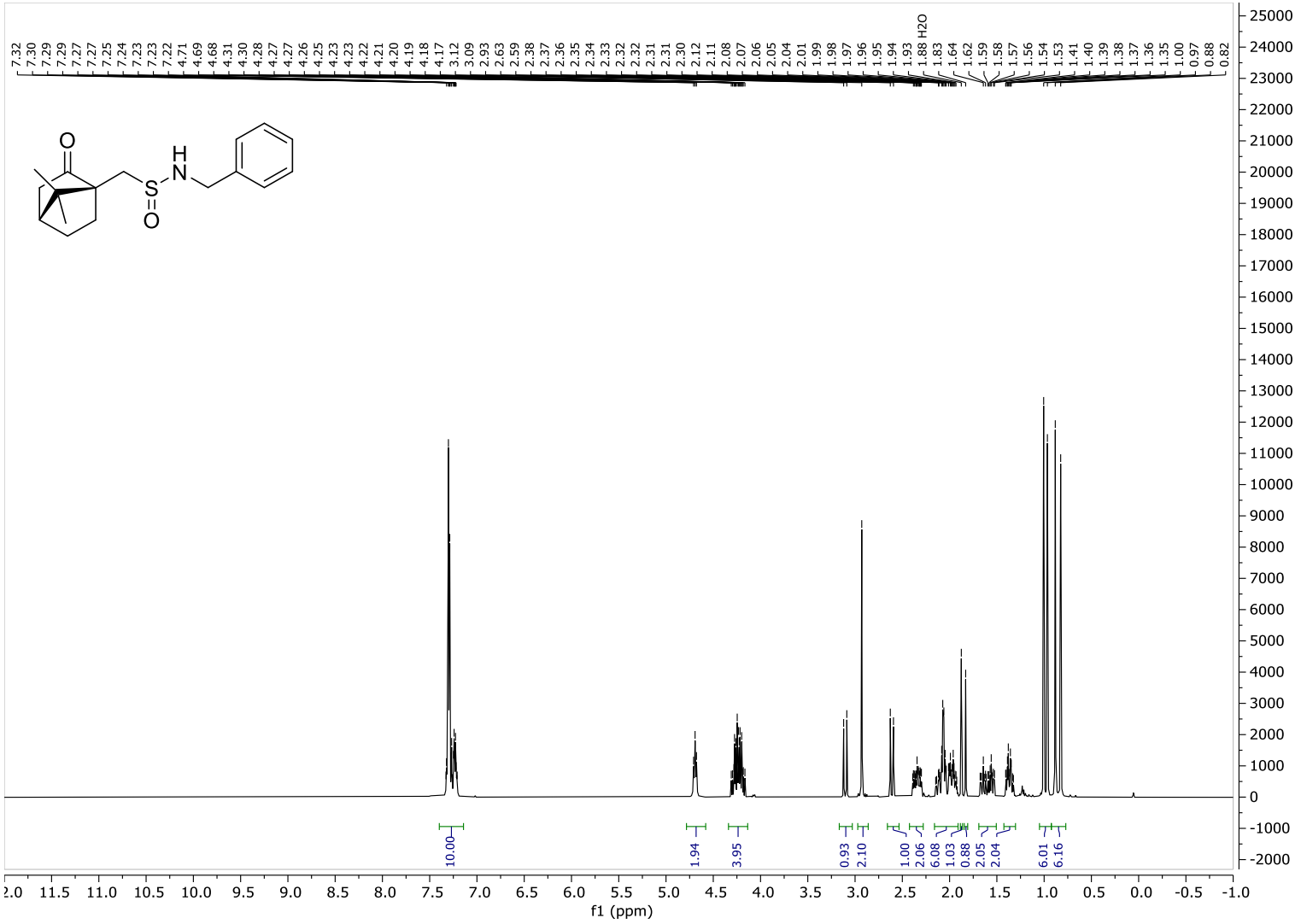



**Figure S21.** $^{1}$H NMR of **1k** in $CDCl_3$.

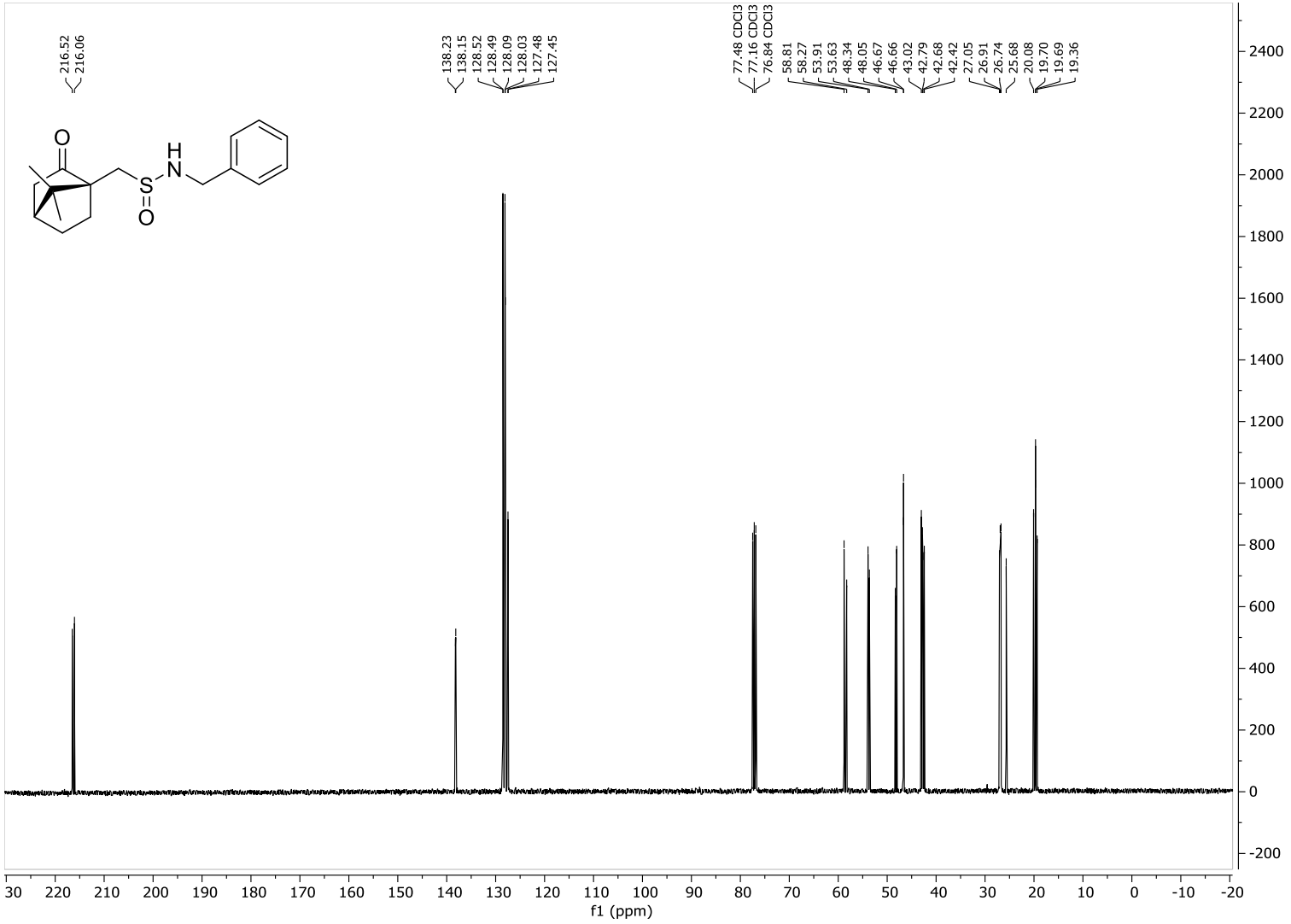



**Figure S22.** $^{13}C$ NMR of **1k** in $CDCl_3$.

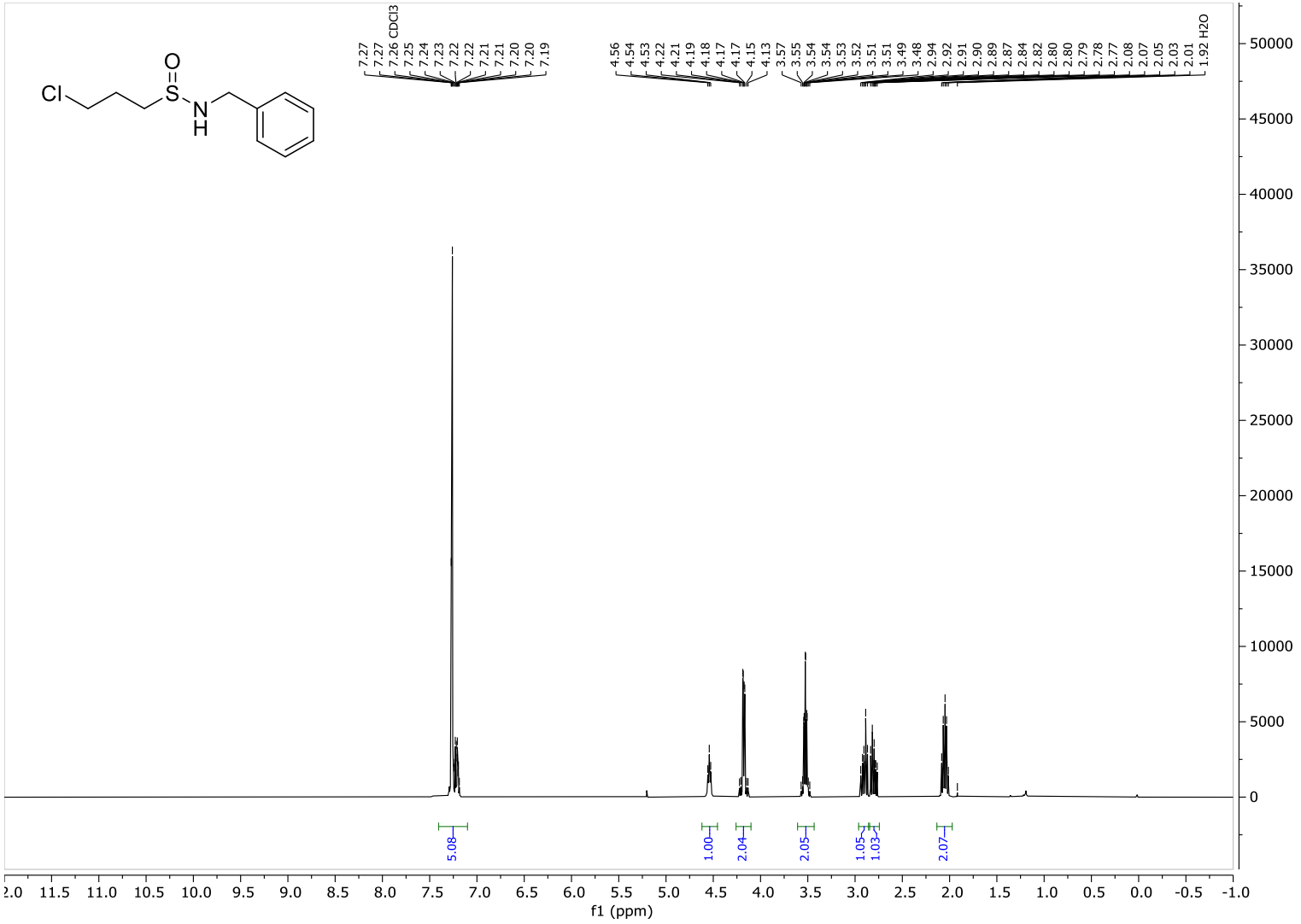



**Figure S23.** $^{1}$H NMR of **1l** $CDCl_3$.

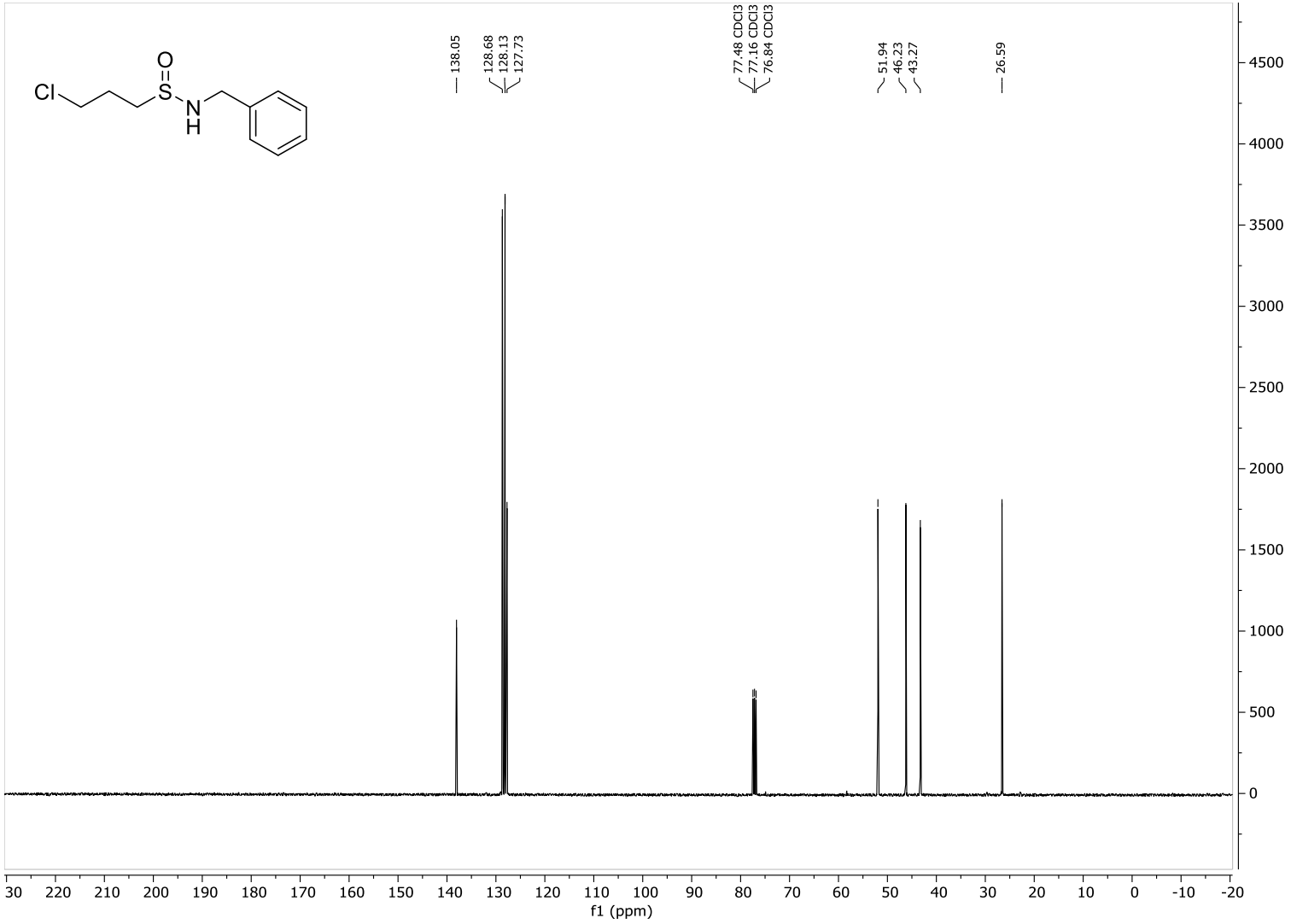



**Figure S24.** $^{13}C$ NMR of **1l** in $CDCl_3$.

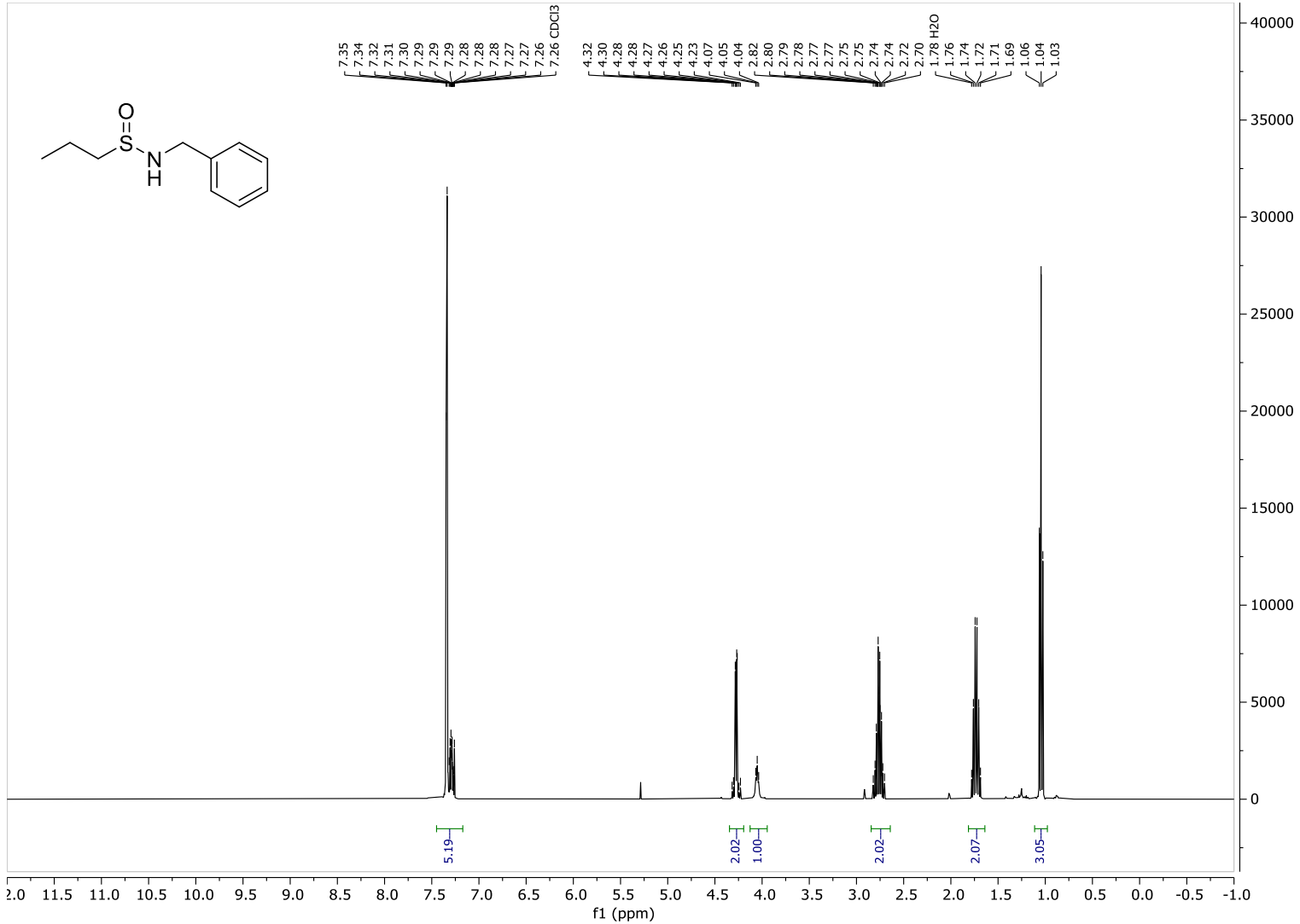



**Figure S25.** $^{1}H$ NMR of **1m** in $CDCl_3$.

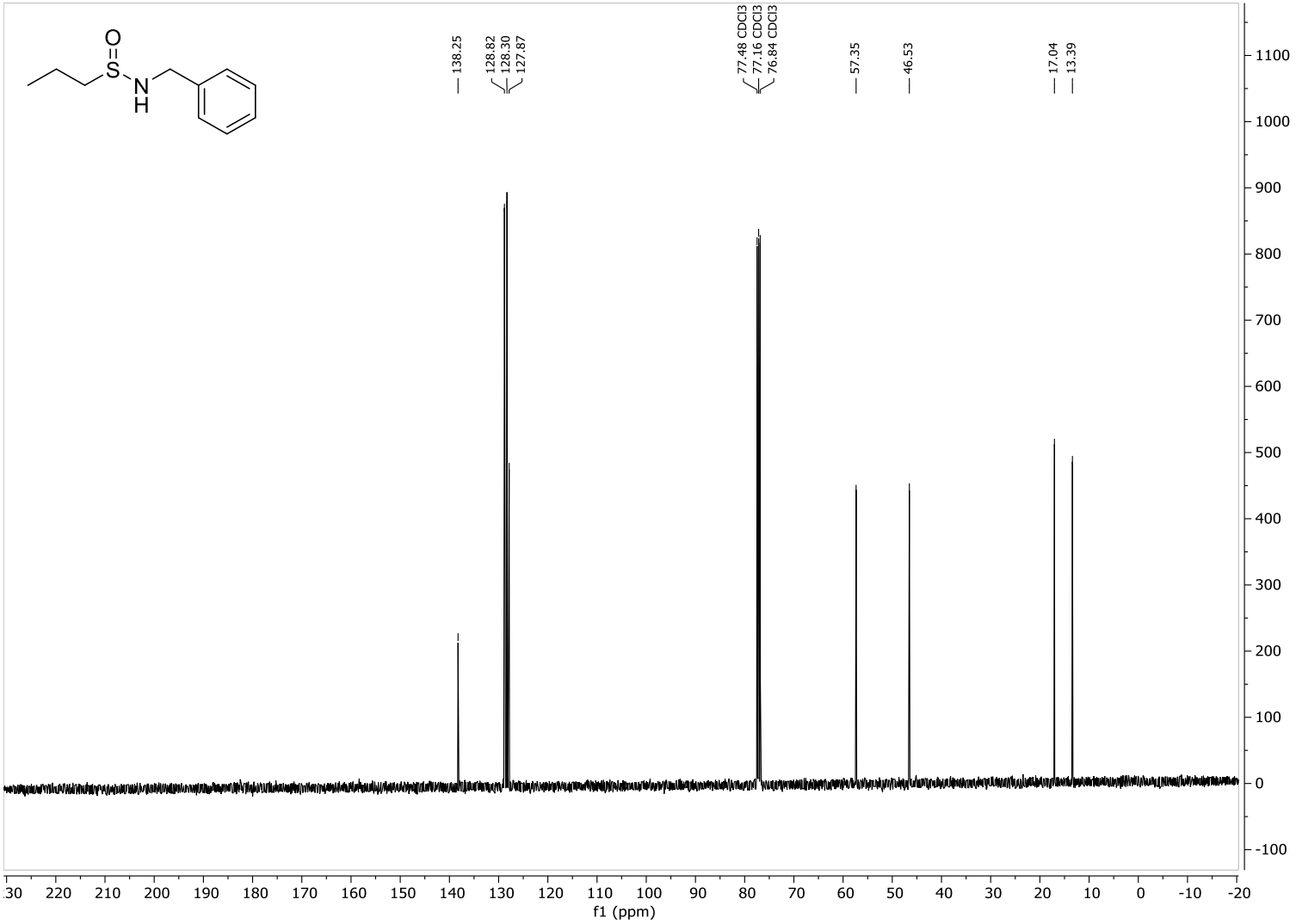



**Figure S26.** $^{13}C$ NMR of **1m** in $CDCl_3$.

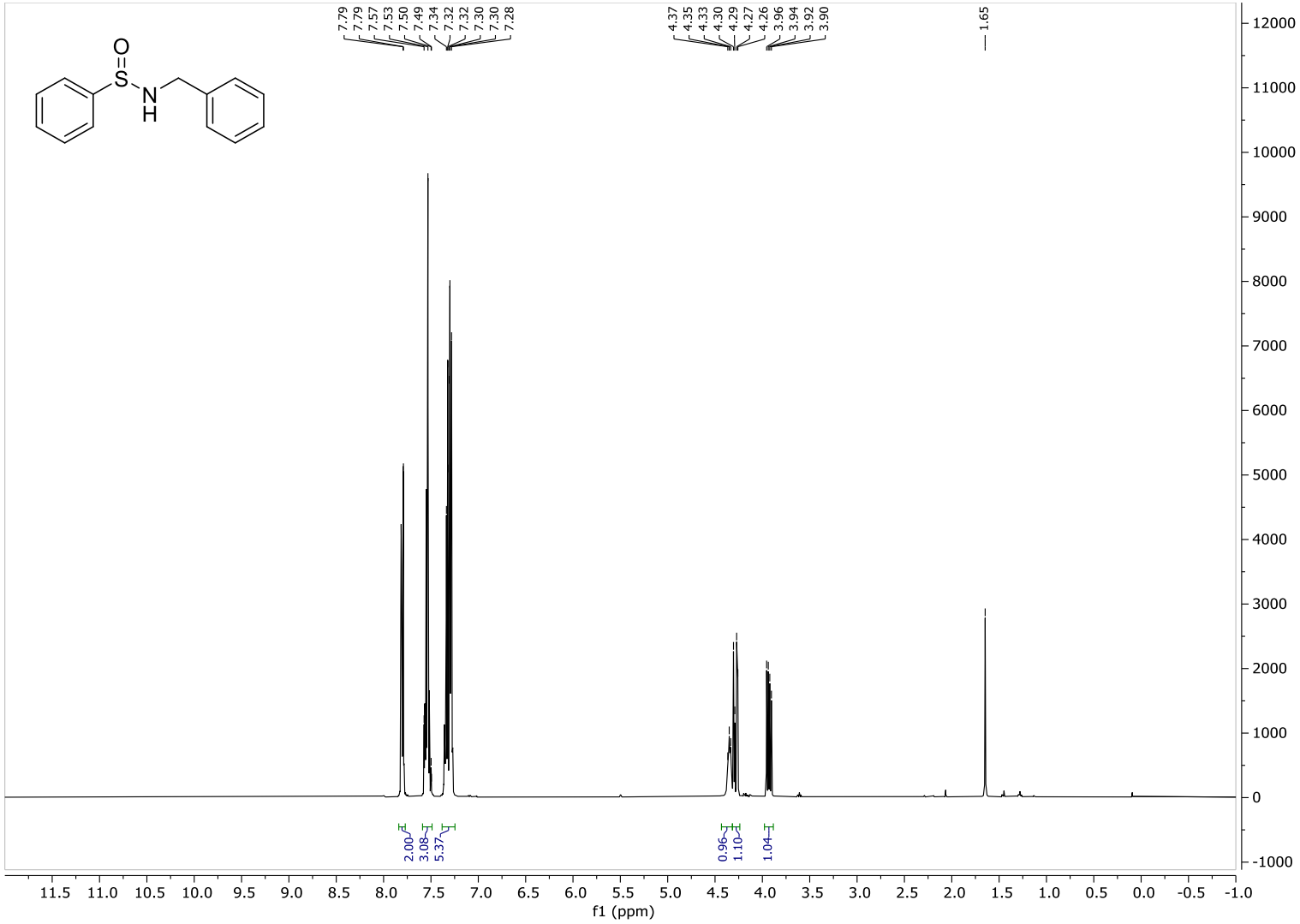



**Figure S27.** $^{1}$H NMR of **1n** in $CDCl_3$.

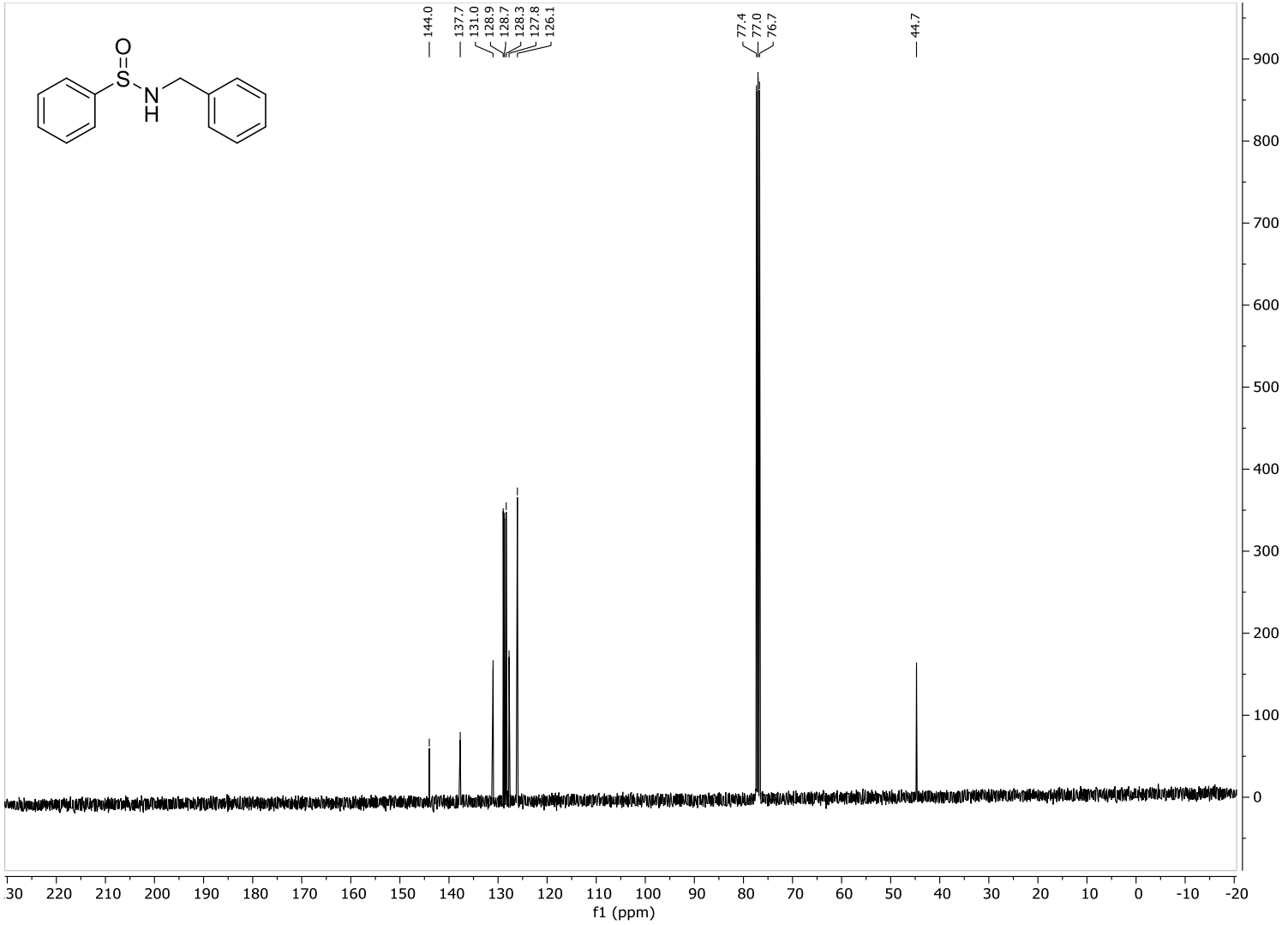



**Figure S28.** $^{13}C$ NMR of **1n** in $CDCl_3$.

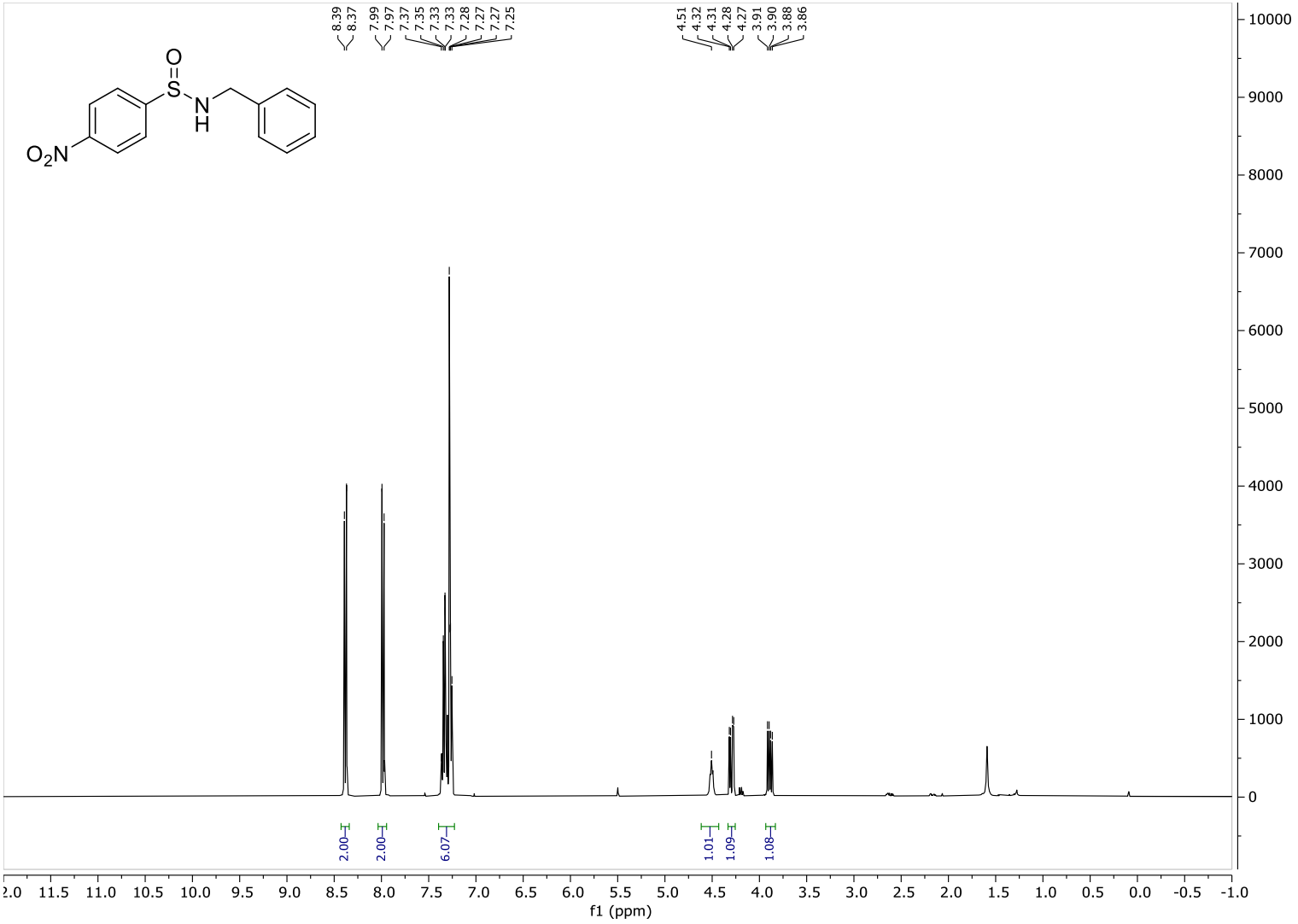



**Figure S29.** $^{1}$H NMR of **1o** in $CDCl_3$.

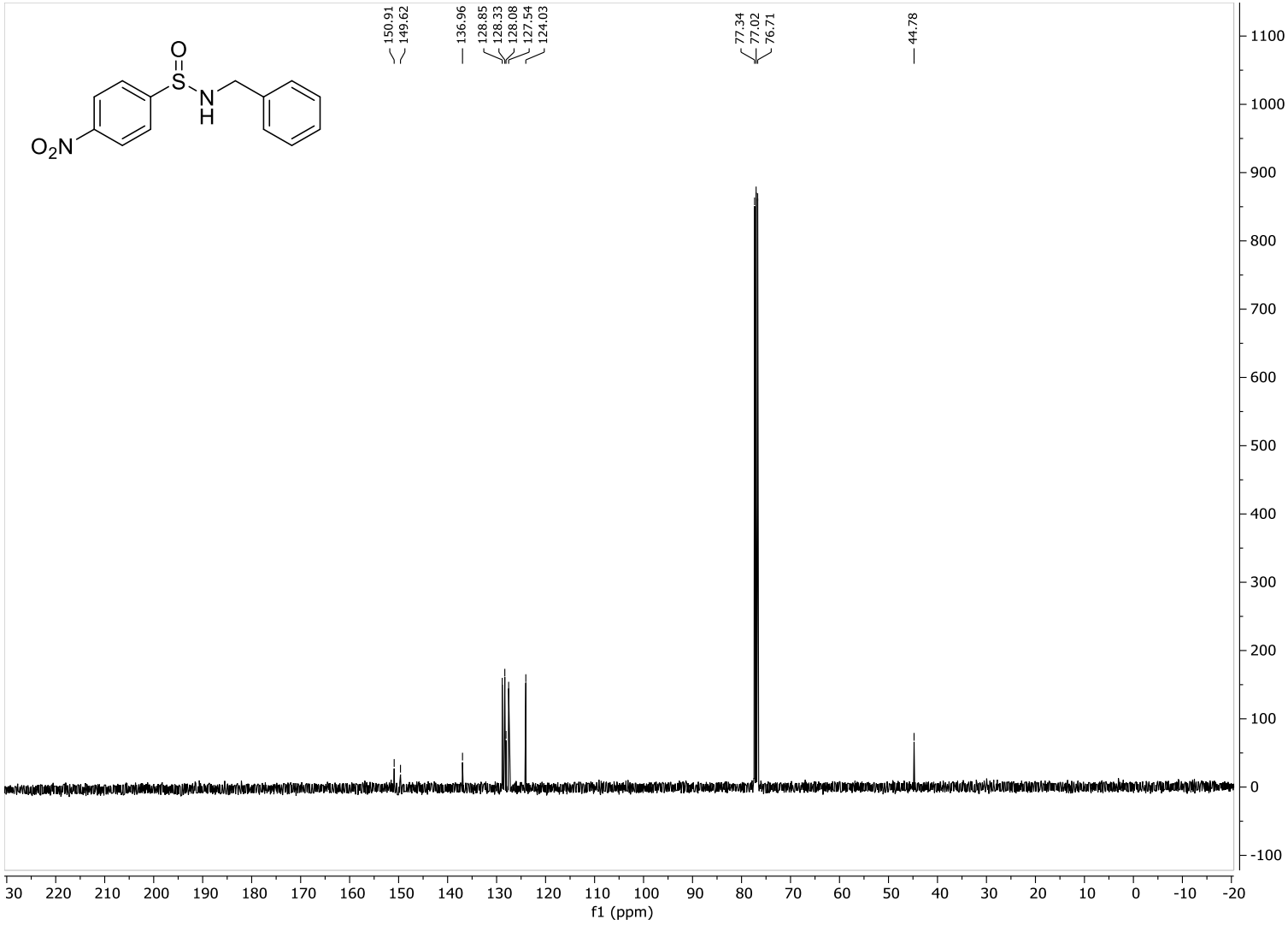



**Figure S30.** $^{13}C$ NMR of **1o** in $CDCl_3$.

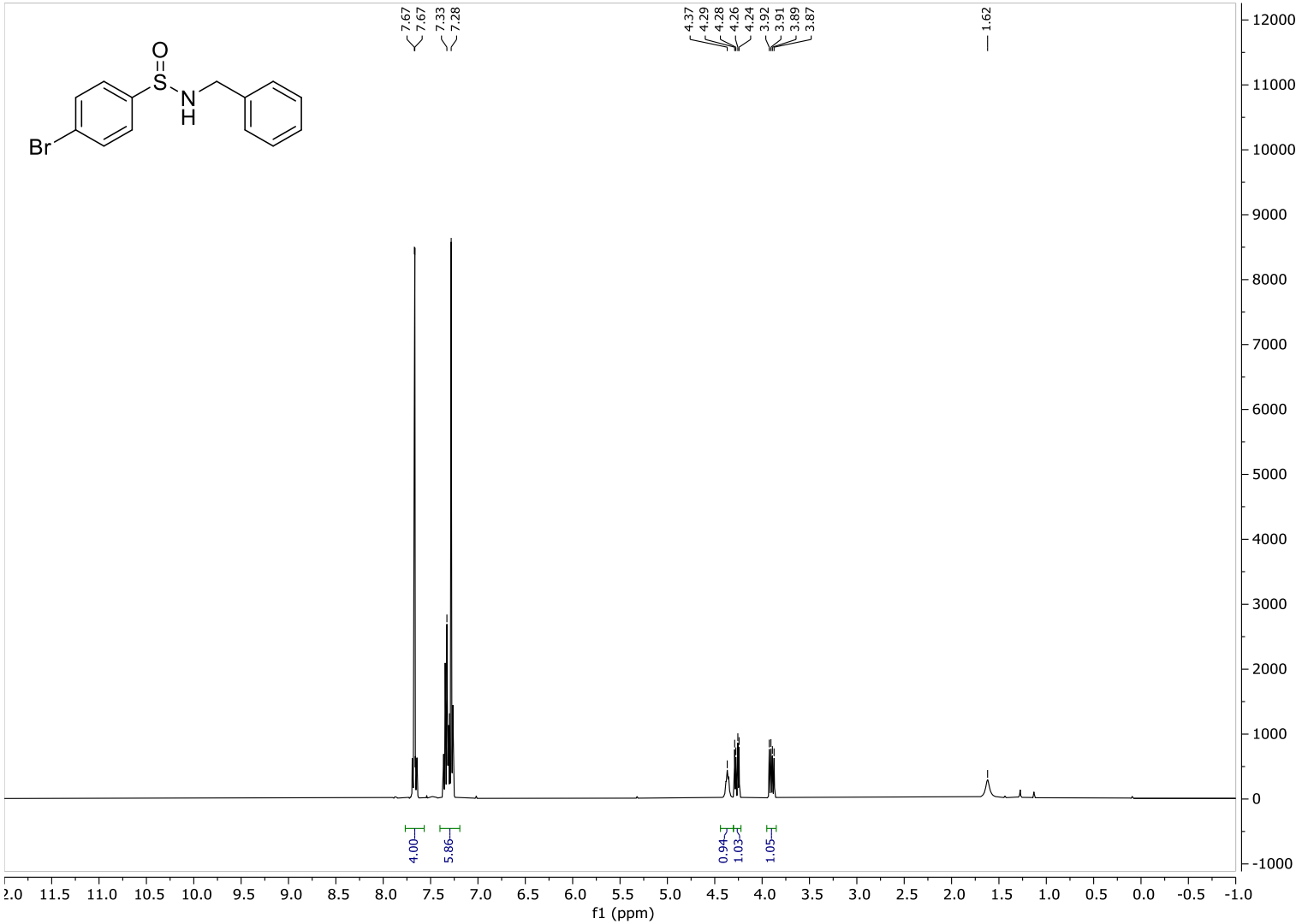



**Figure S31.** $^{1}$H NMR of **1p** in $CDCl_3$.

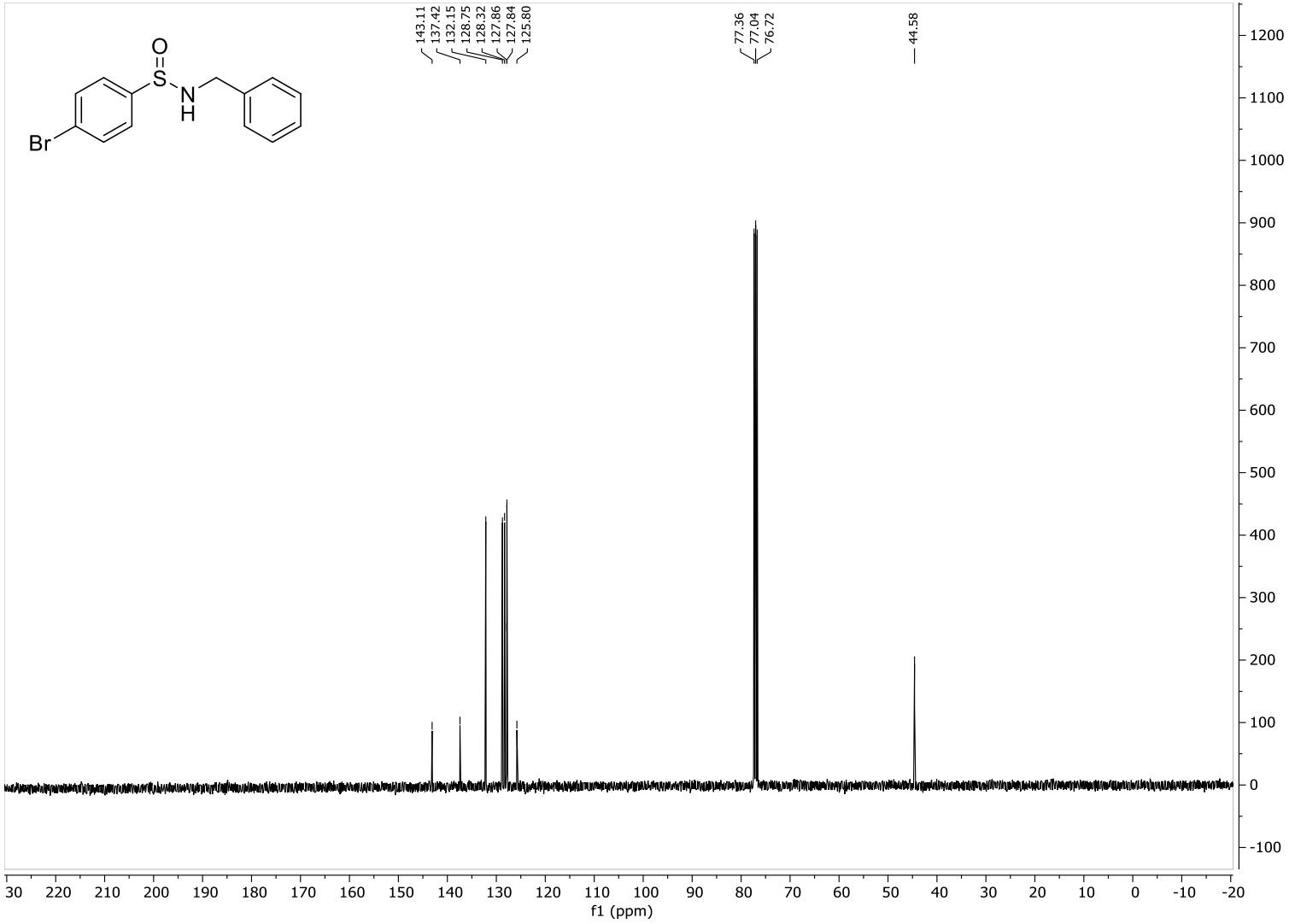



**Figure S32.** $^{13}C$ NMR of **1p** in $CDCl_3$.

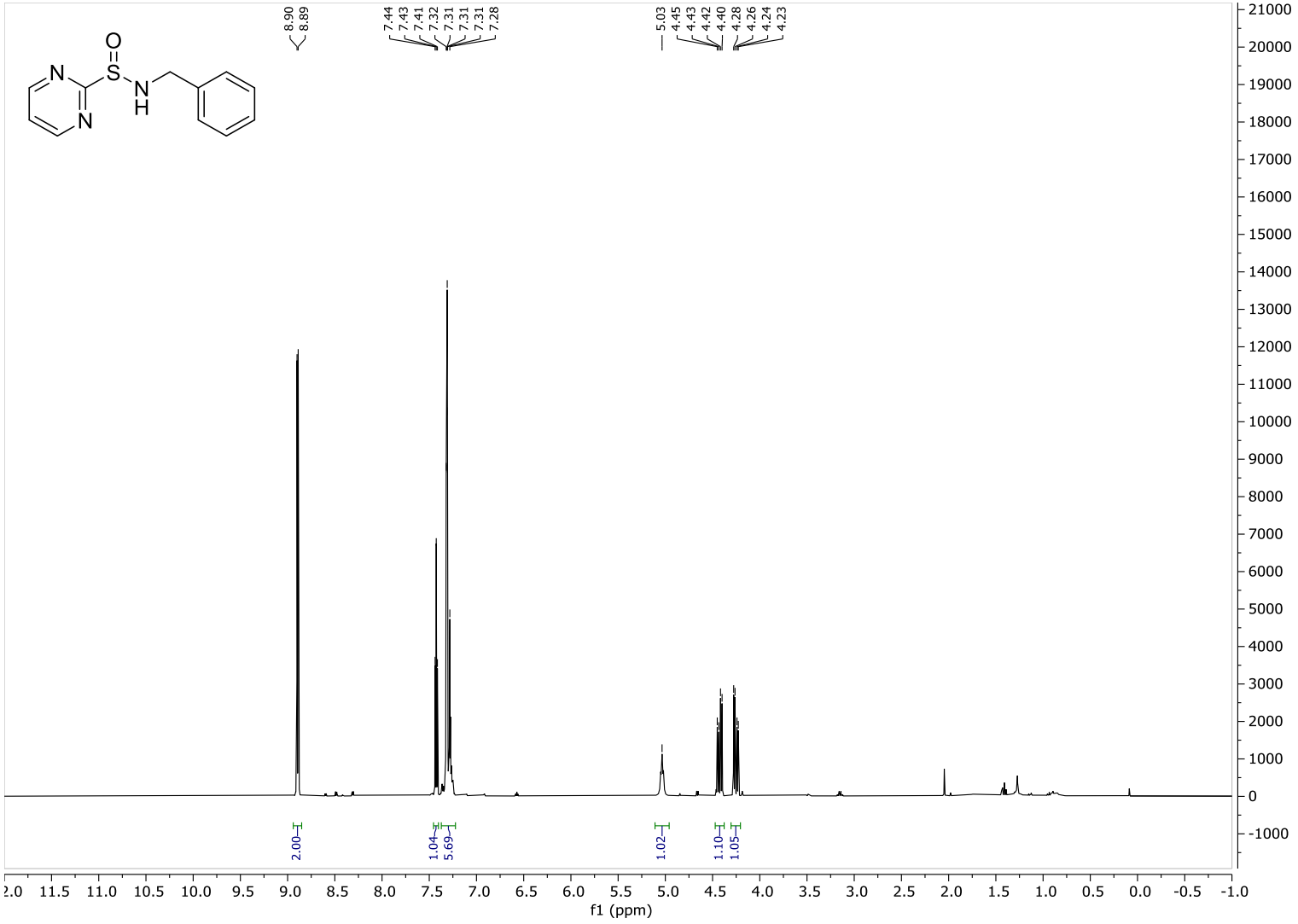



**Figure S33.** $^{1}$H NMR of **1q** in $CDCl_3$.

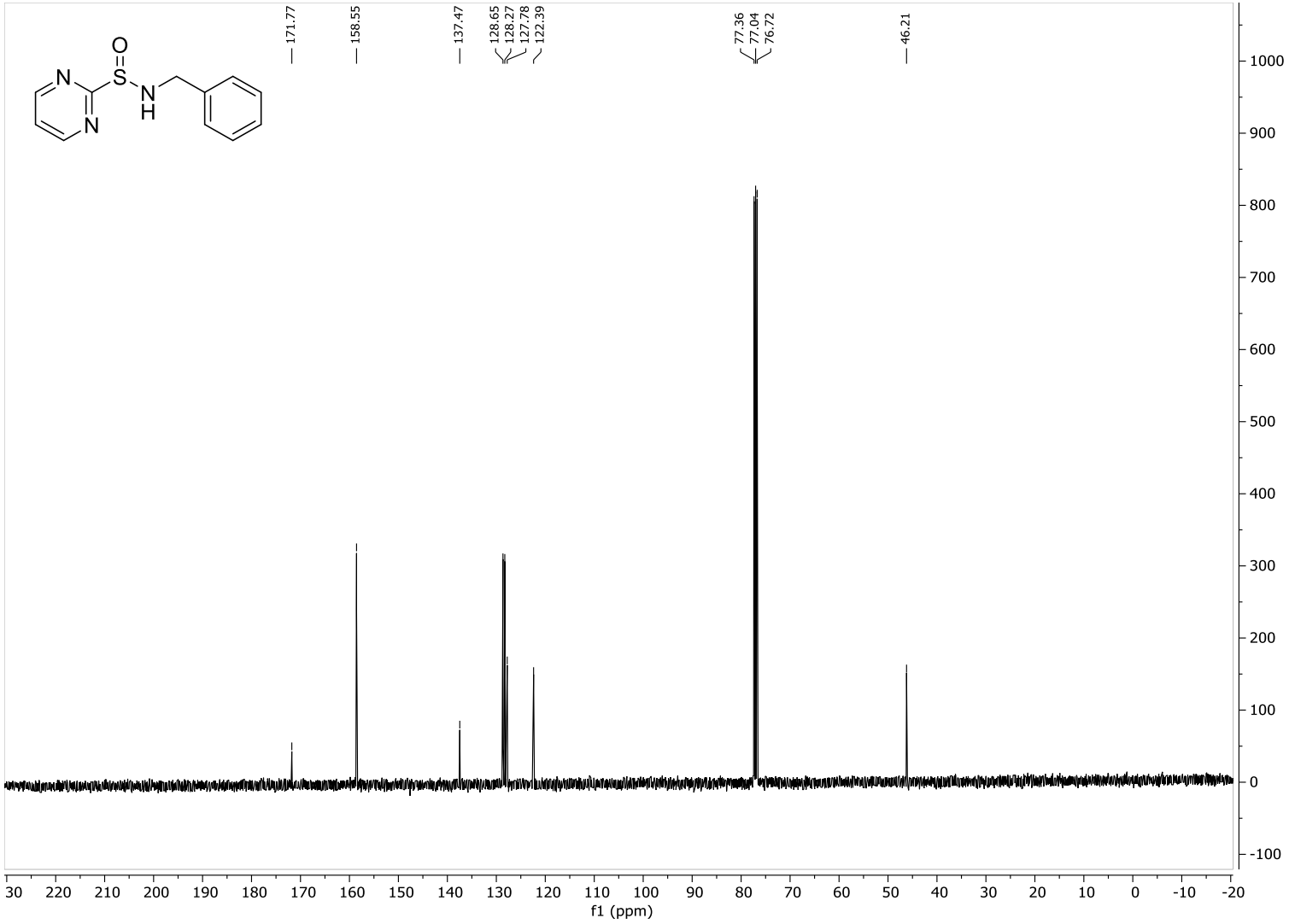



**Figure S34.** $^{13}C$ NMR of **1q** in $CDCl_3$.

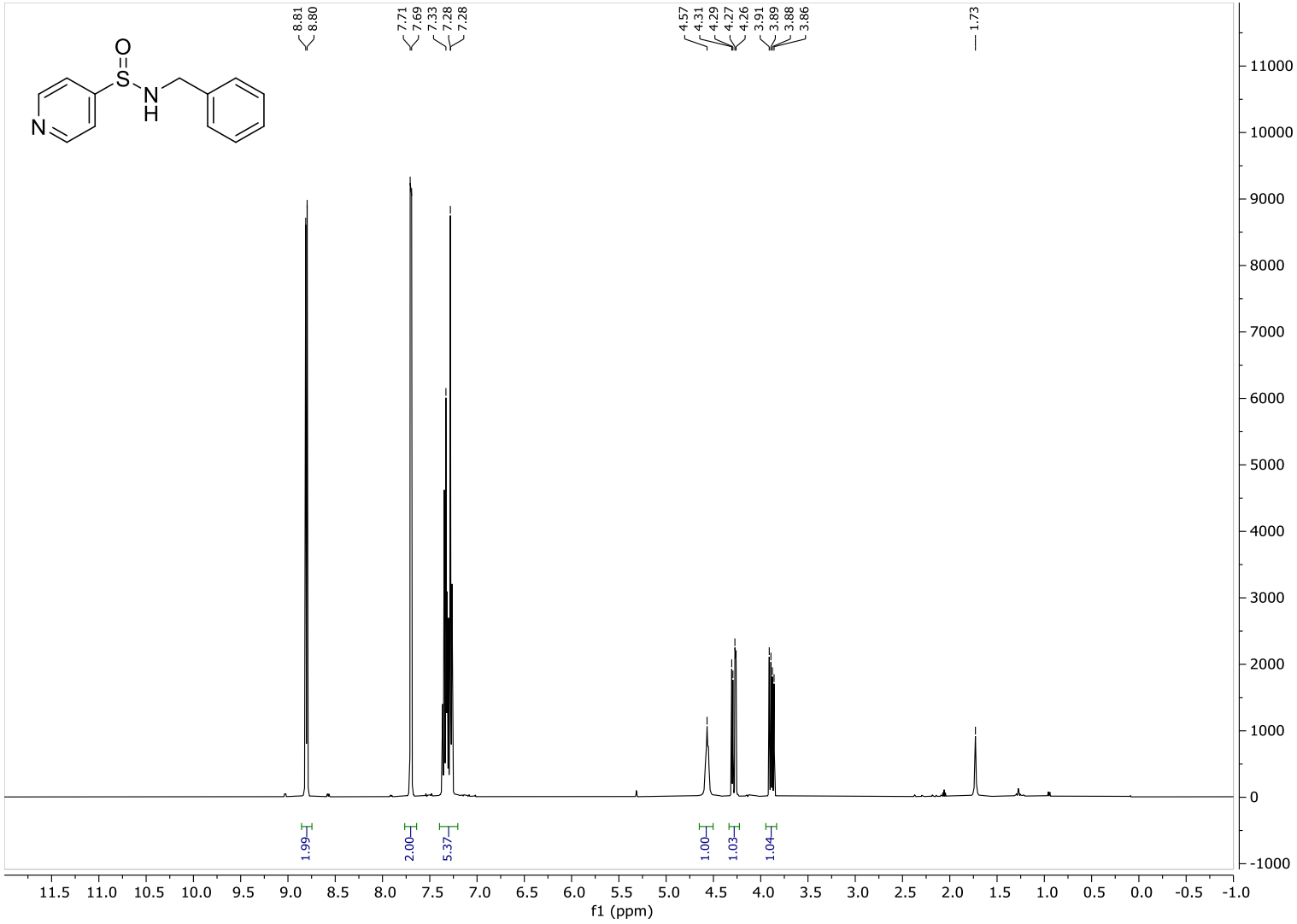



**Figure S35.** $^{1}$H NMR of **1r** in $CDCl_3$.

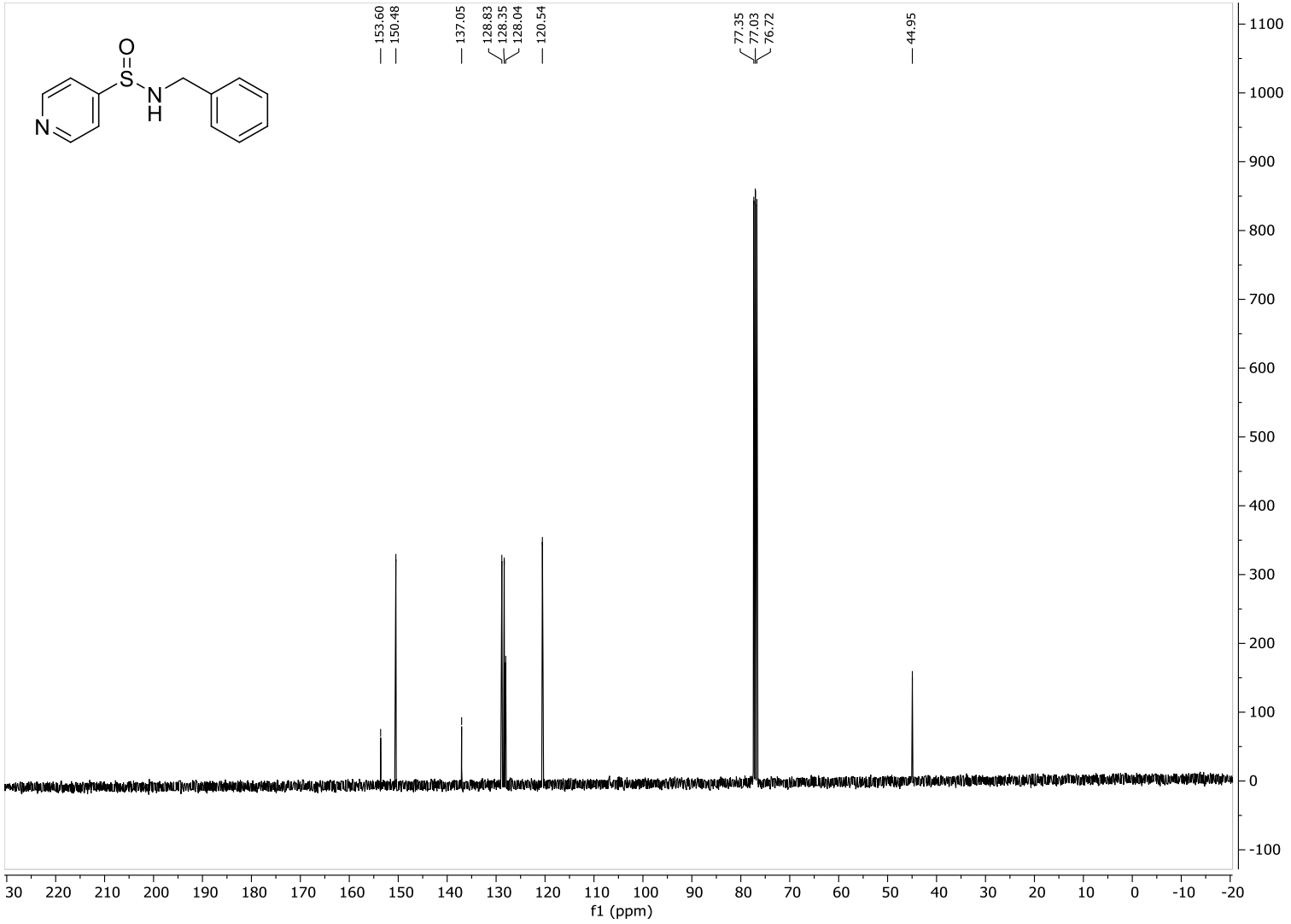



**Figure S36.** $^{13}C$ NMR of **1r** in $CDCl_3$.

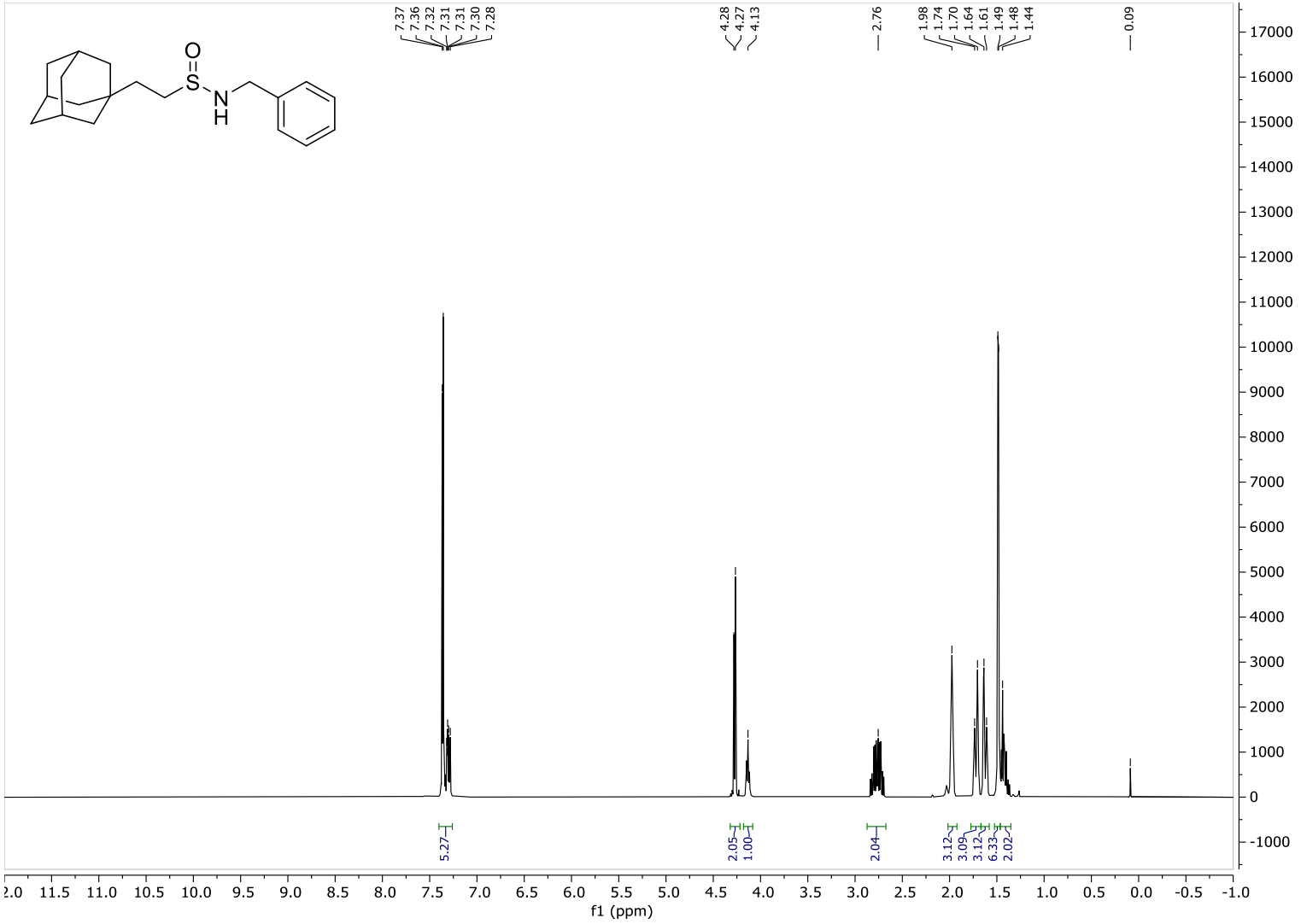



**Figure S37.** $^{1}$H NMR of **1s** in $CDCl_3$.

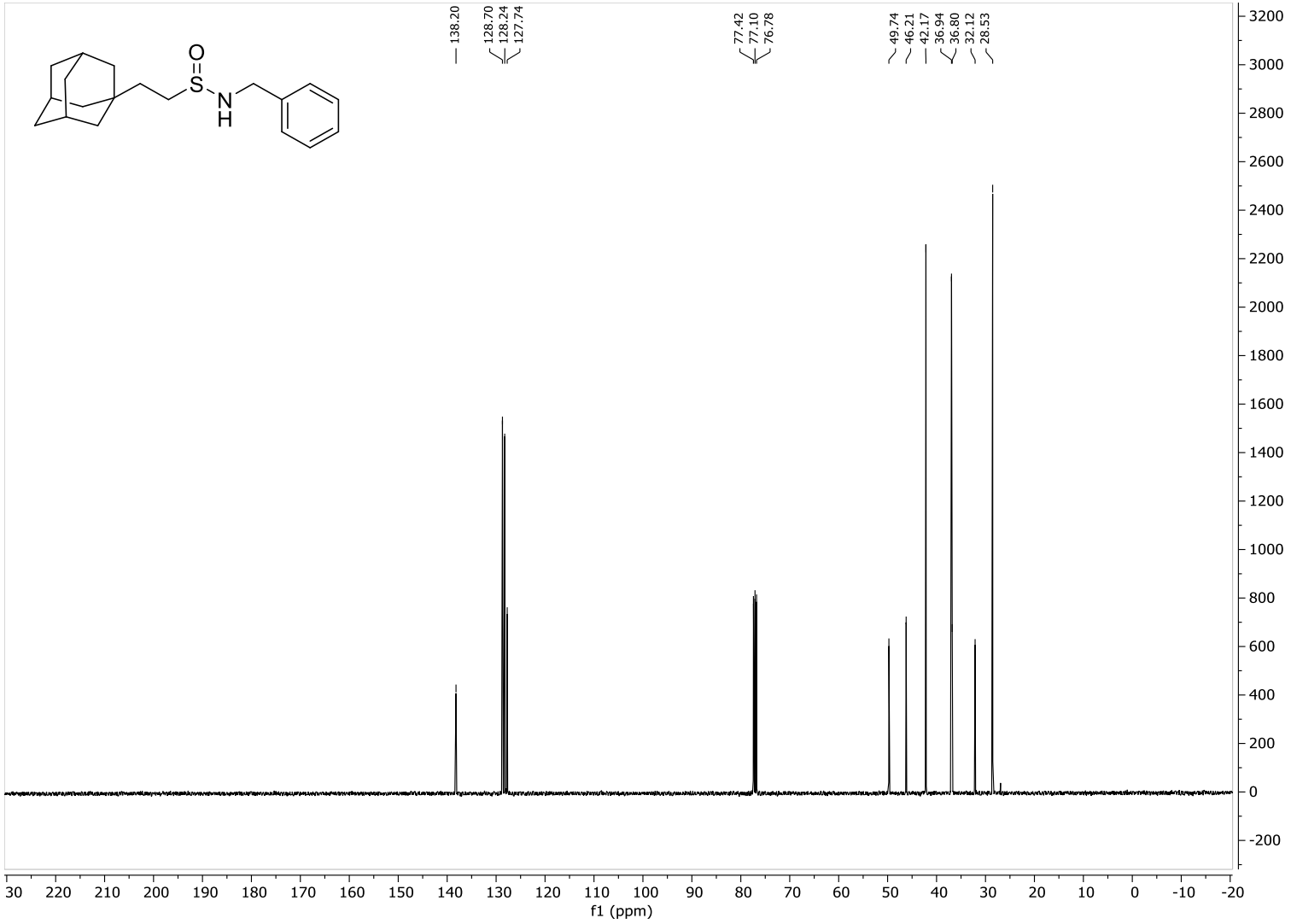



**Figure S38.** $^{13}C$ NMR of **1s** in $CDCl_3$.

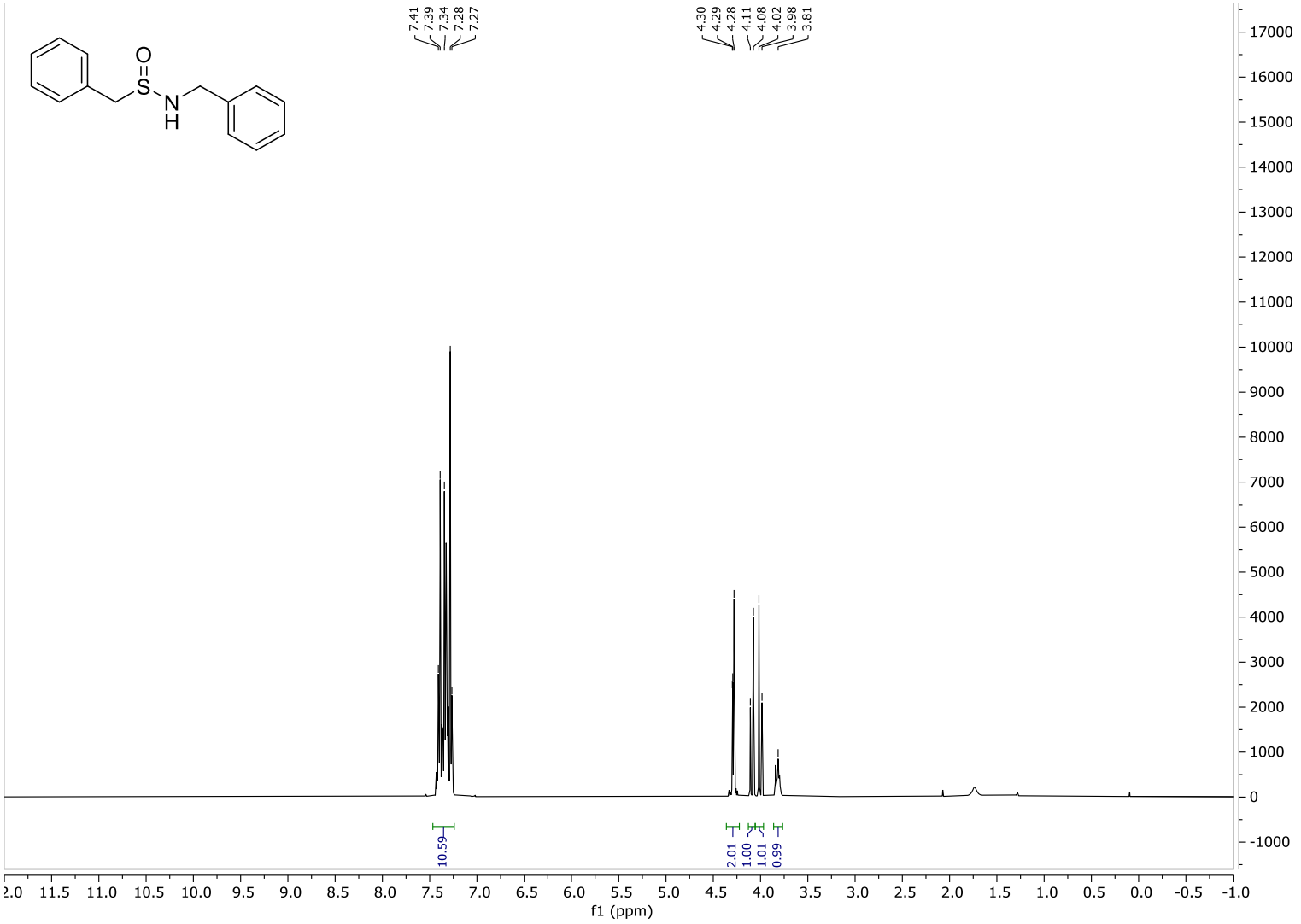



**Figure S39.** $^{1}$H NMR of **1t** in $CDCl_3$.

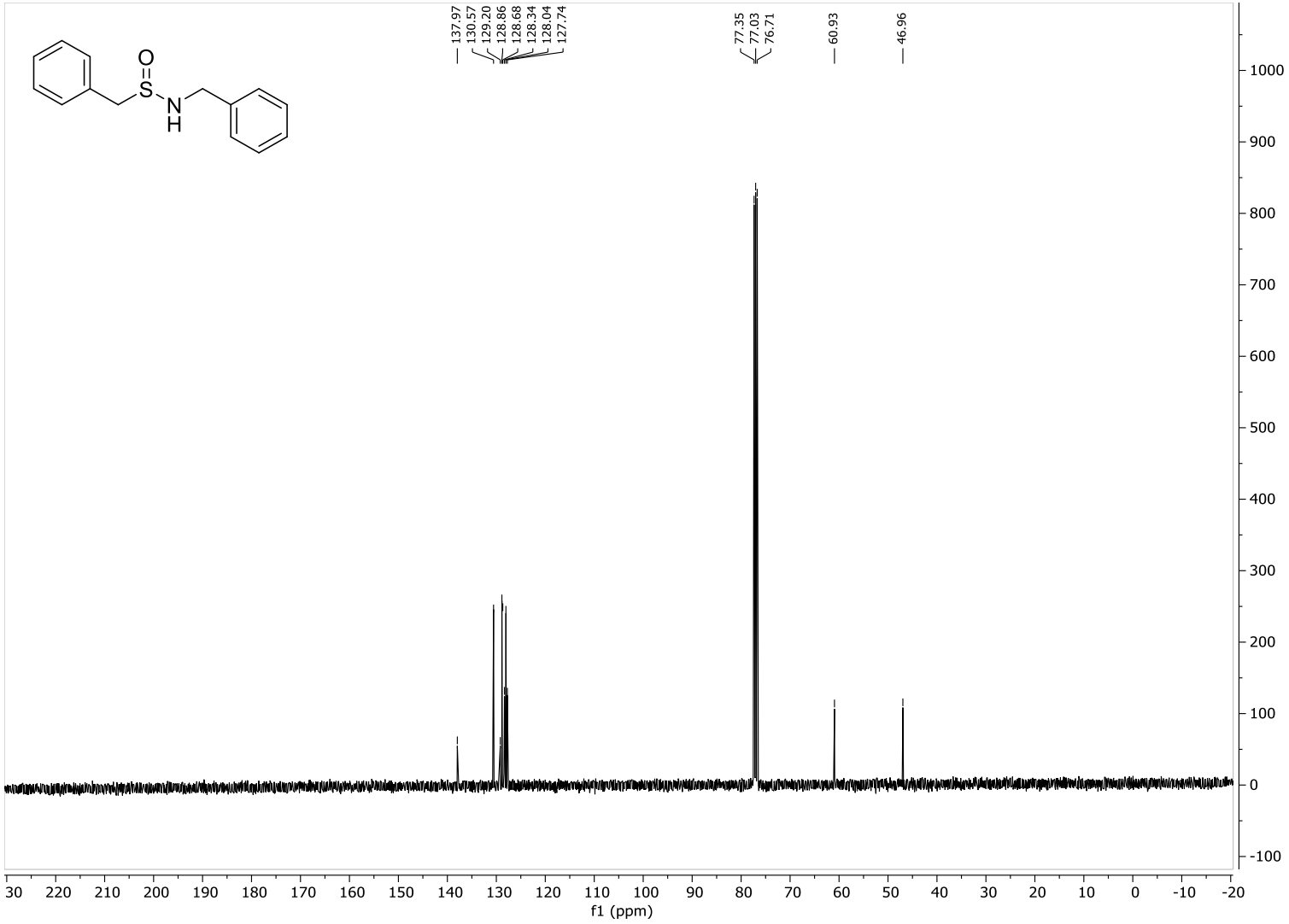



**Figure S40.** $^{13}C$ NMR of **1t** in $CDCl_3$.

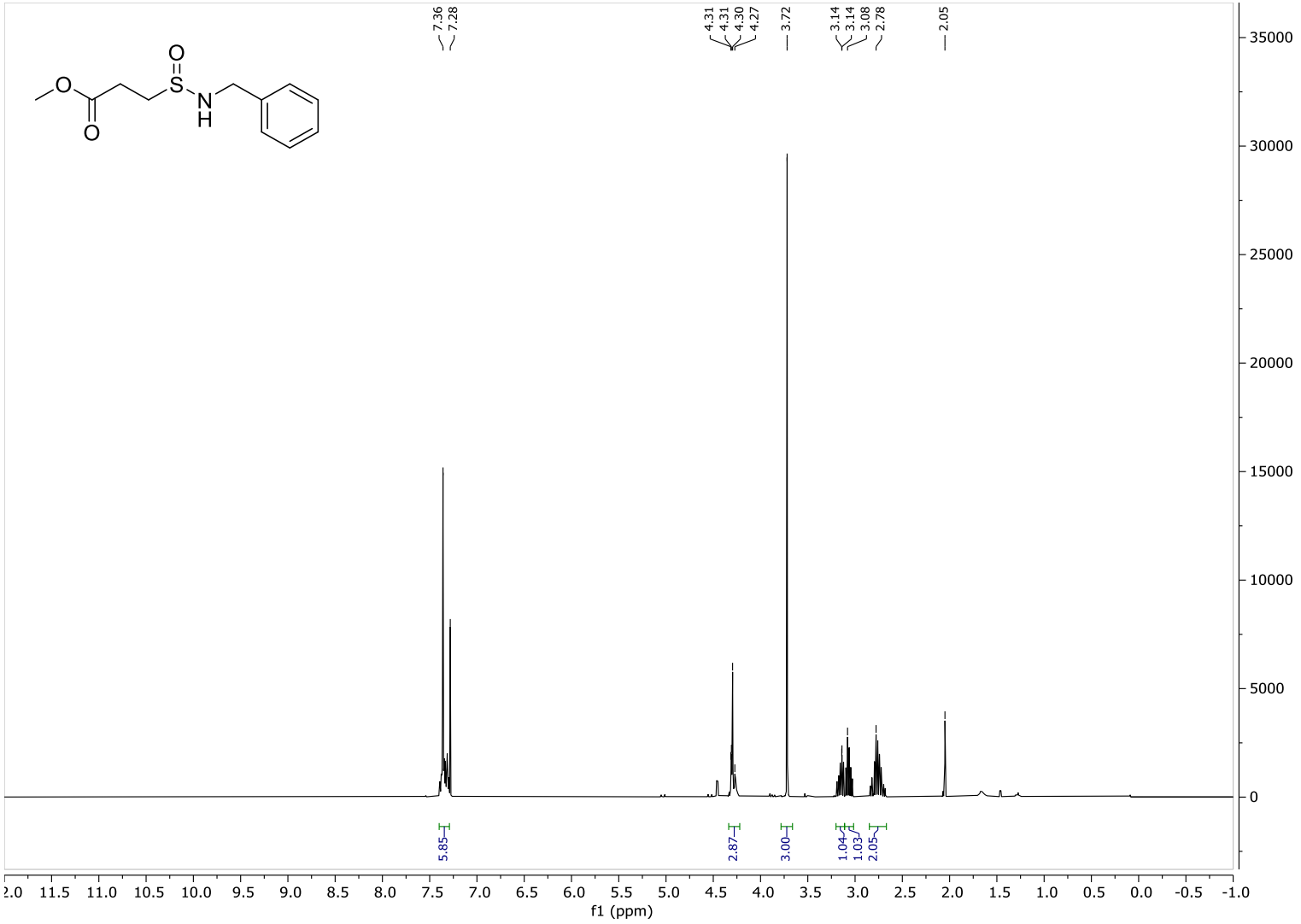



**Figure S41.** $^{1}$H NMR of **1u** in $CDCl_3$.

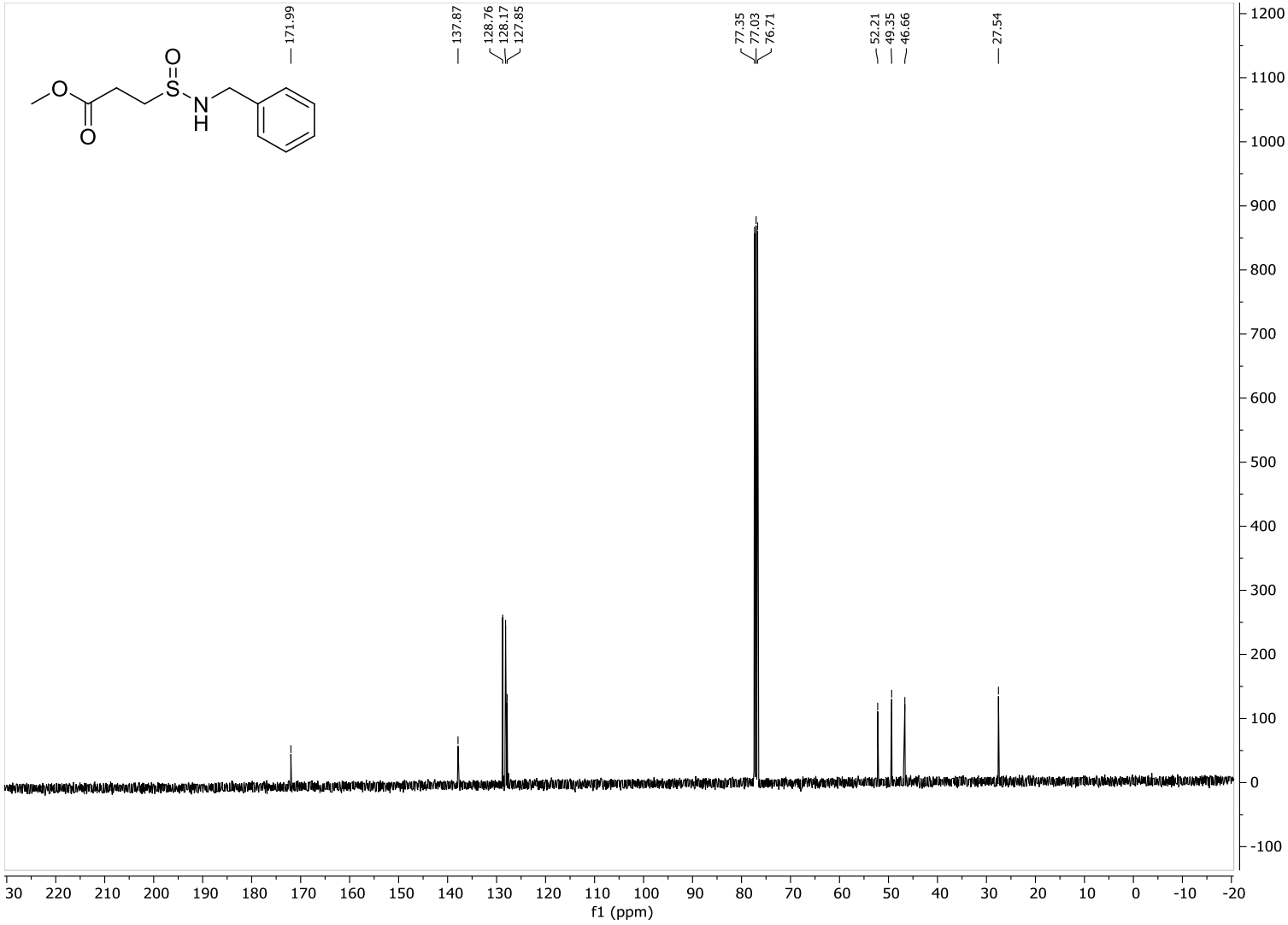



**Figure S42.** $^{13}C$ NMR of **1u** in $CDCl_3$.

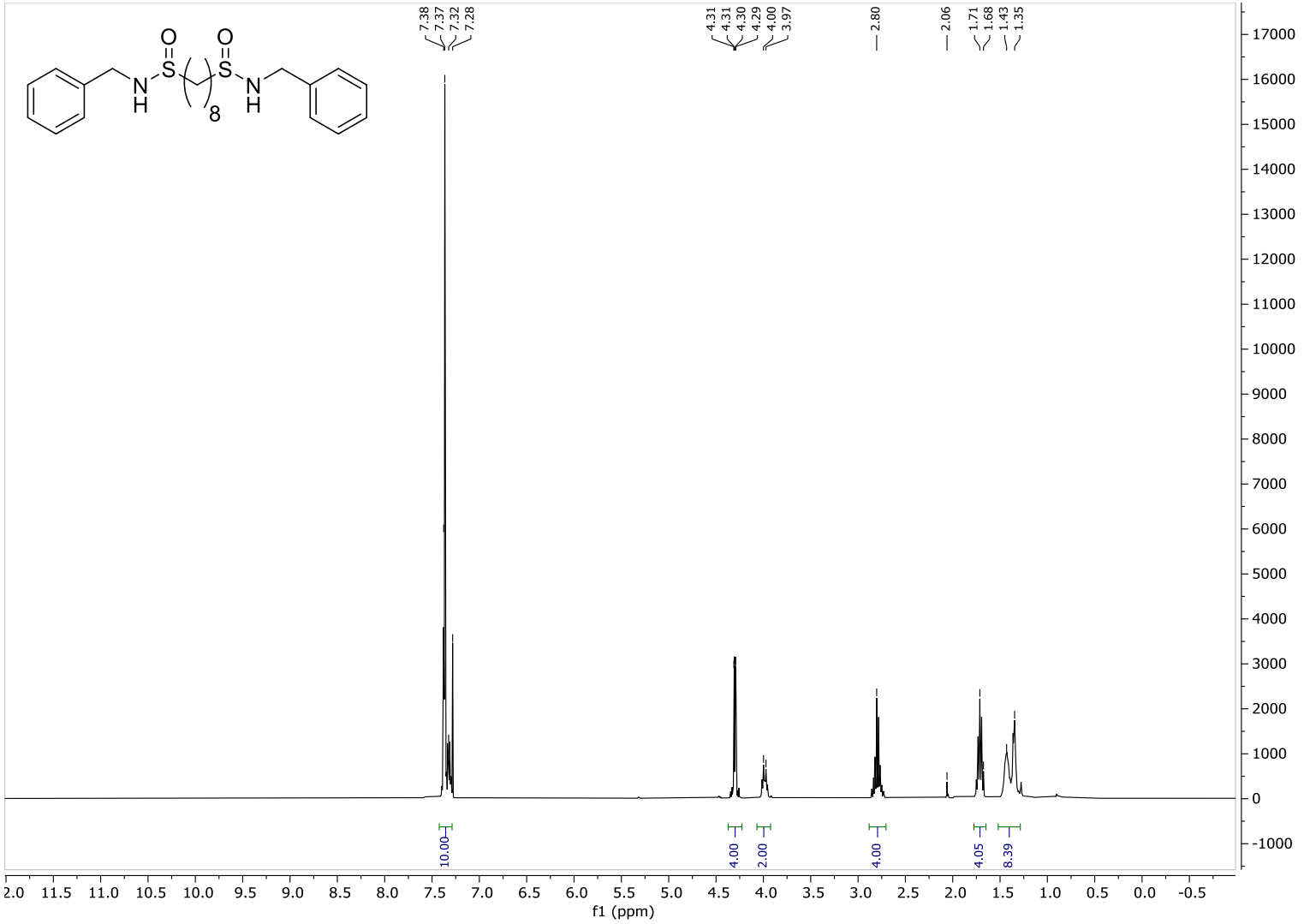



**Figure S43.** $^{1}$H NMR of **1v** in $CDCl_3$.

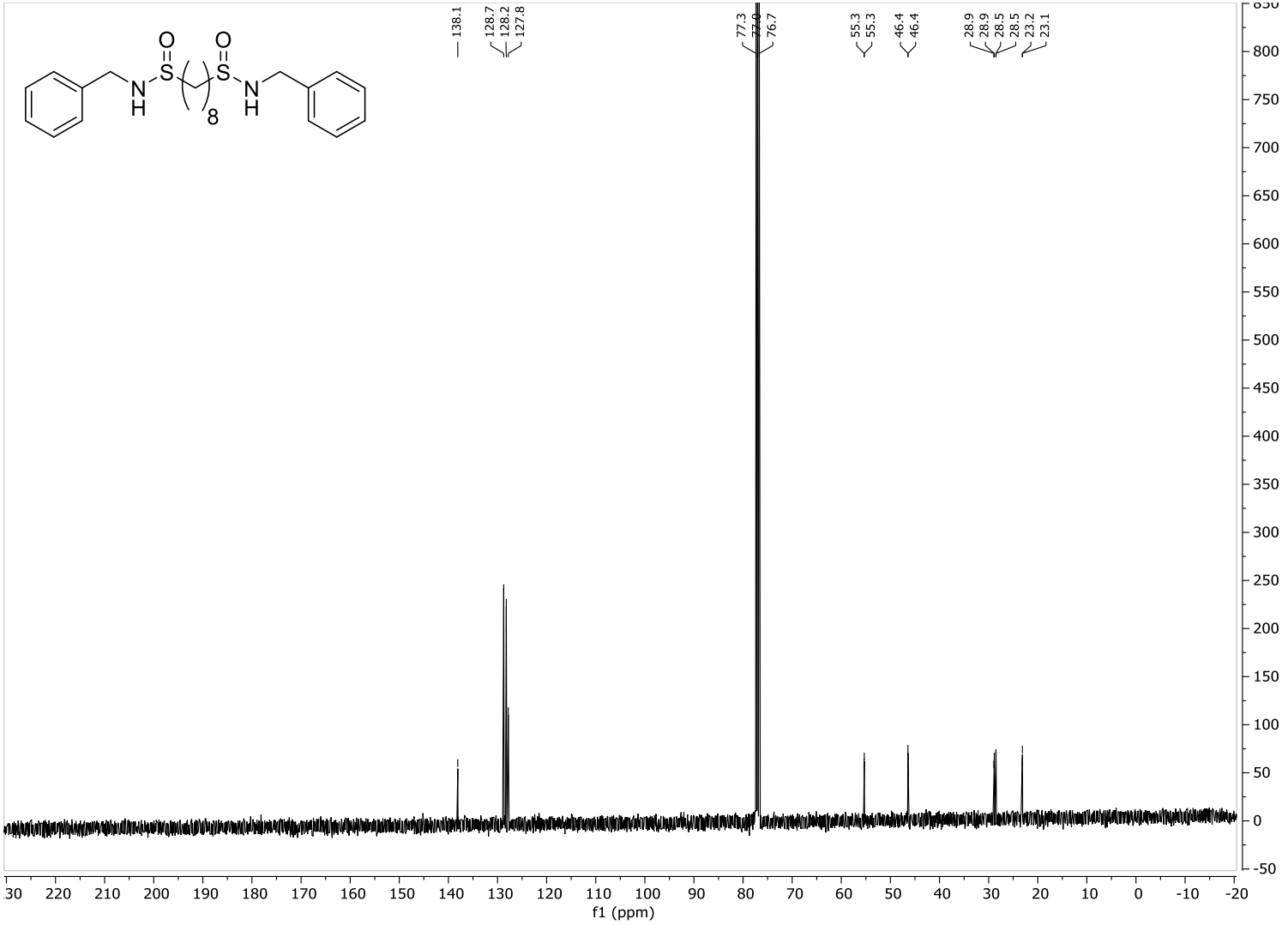



**Figure S44.** $^{13}C$ NMR of **1v** in $CDCl_3$.

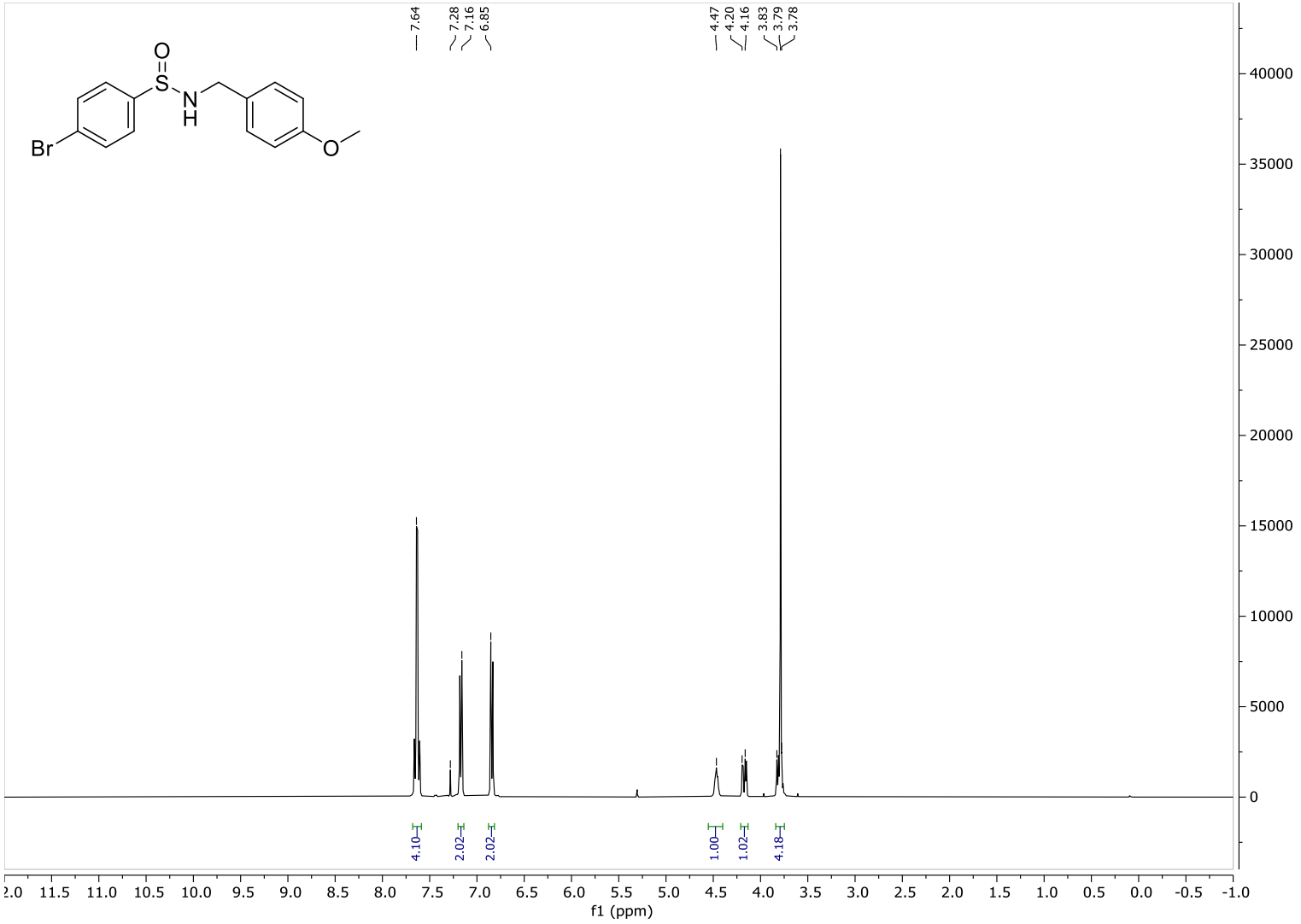



**Figure S45.** $^{1}$H NMR of **2b** in $CDCl_3$.

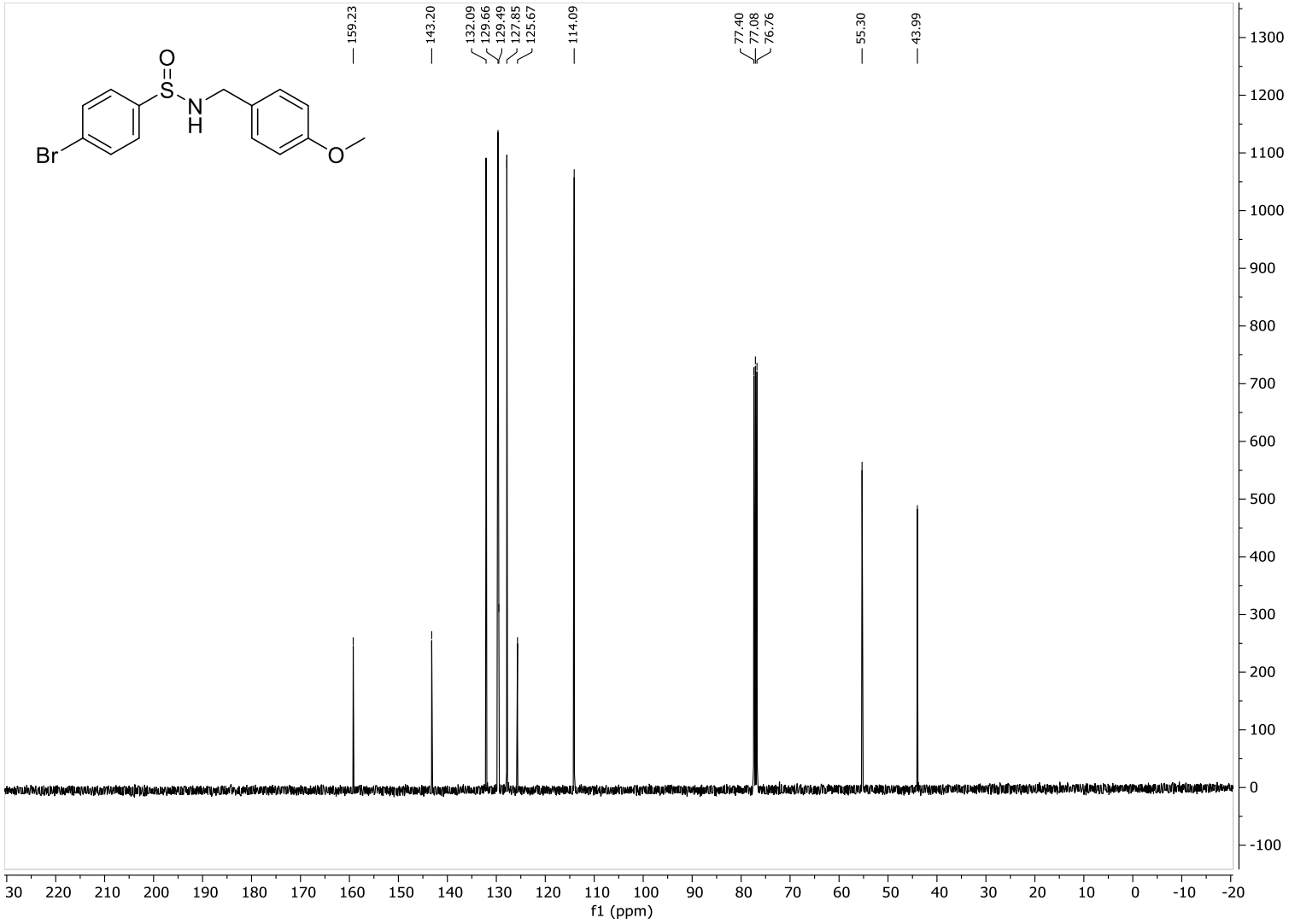



**Figure S46.** $^{13}C$ NMR of **2b** in $CDCl_3$.

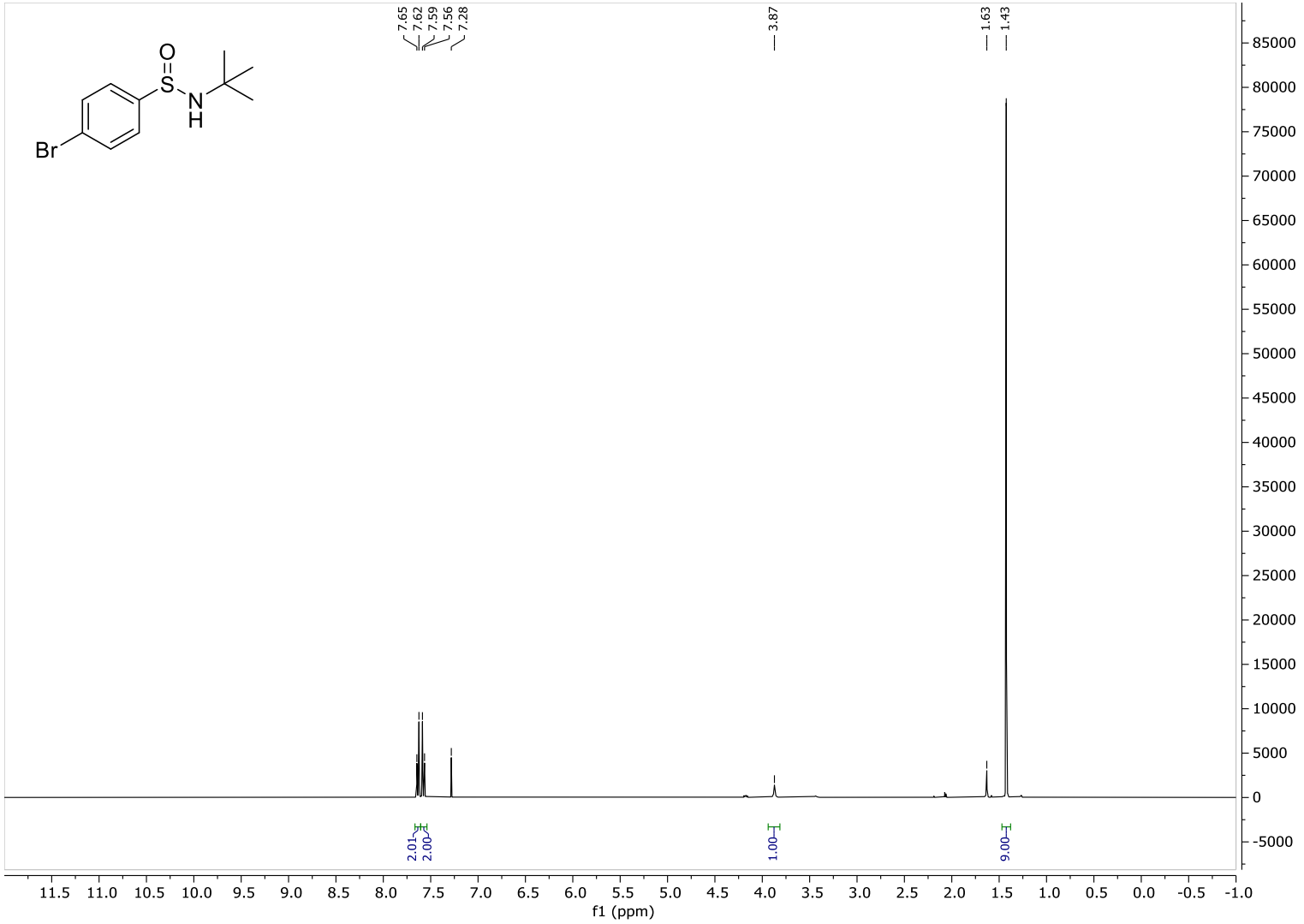



**Figure S47.** $^{1}$H NMR of **2c** in $CDCl_3$.

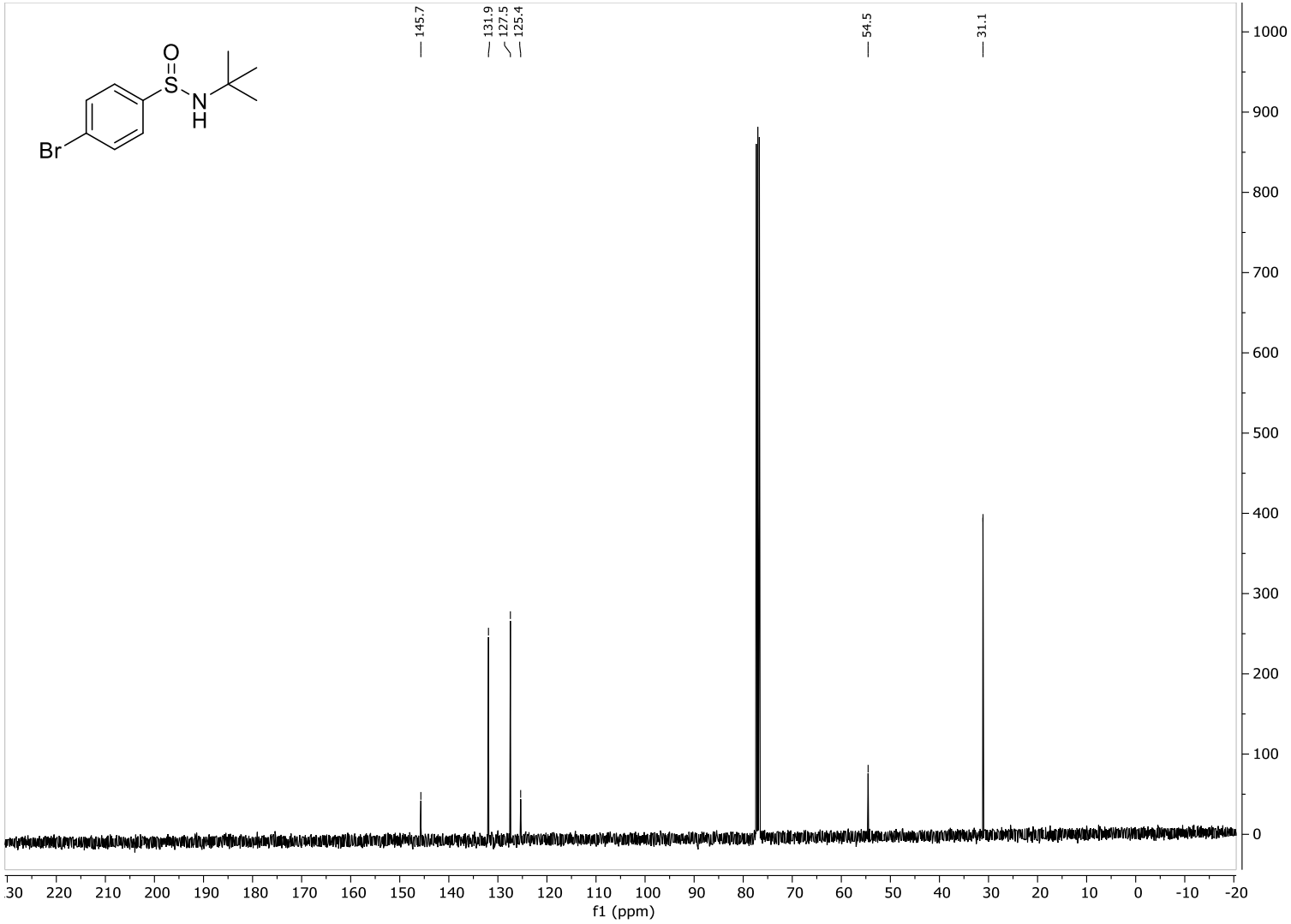



**Figure S48.** $^{13}C$ NMR of **2c** in $CDCl_3$.

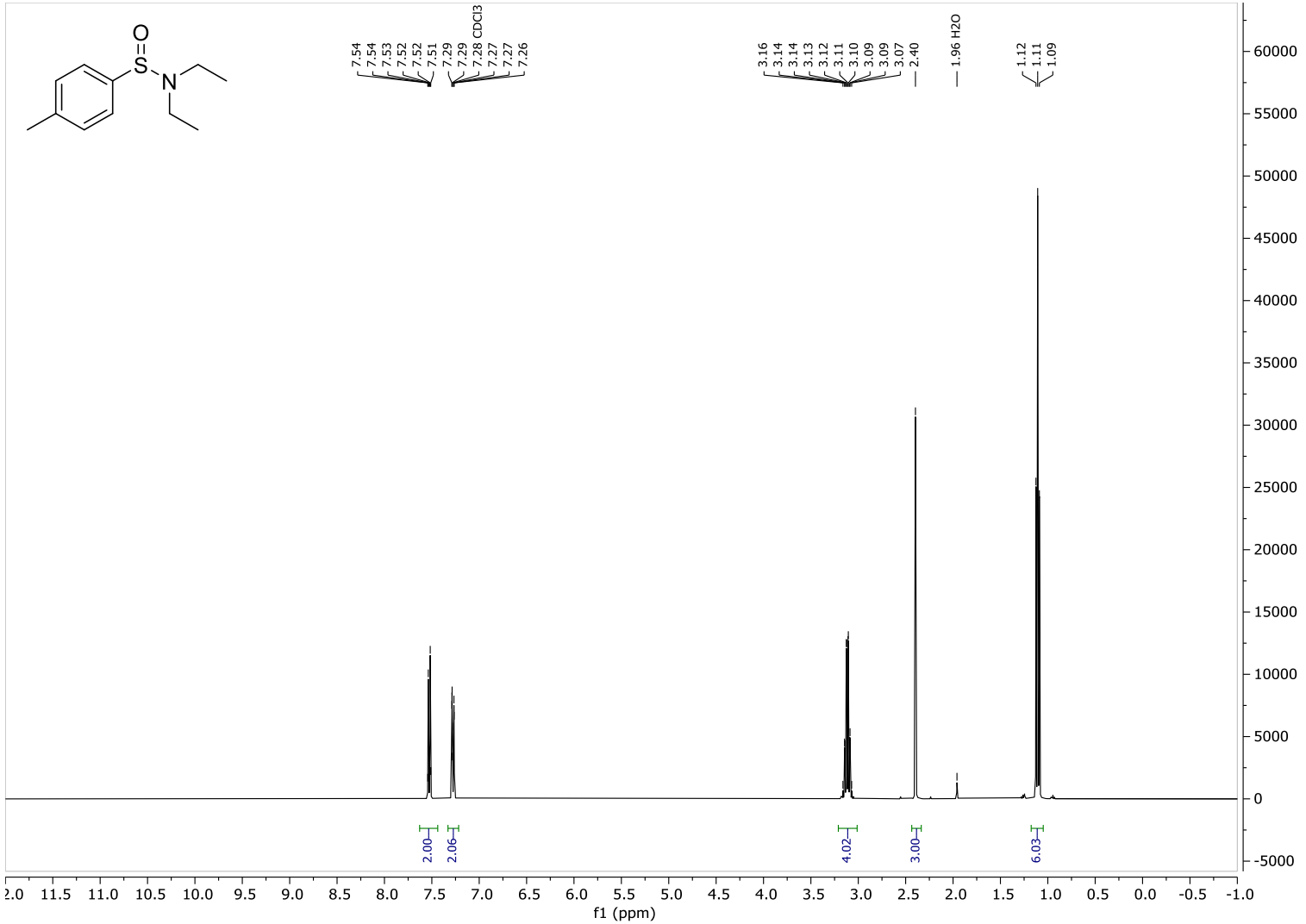



**Figure S49.** $^{1}$H NMR of **2d** in $CDCl_3$.

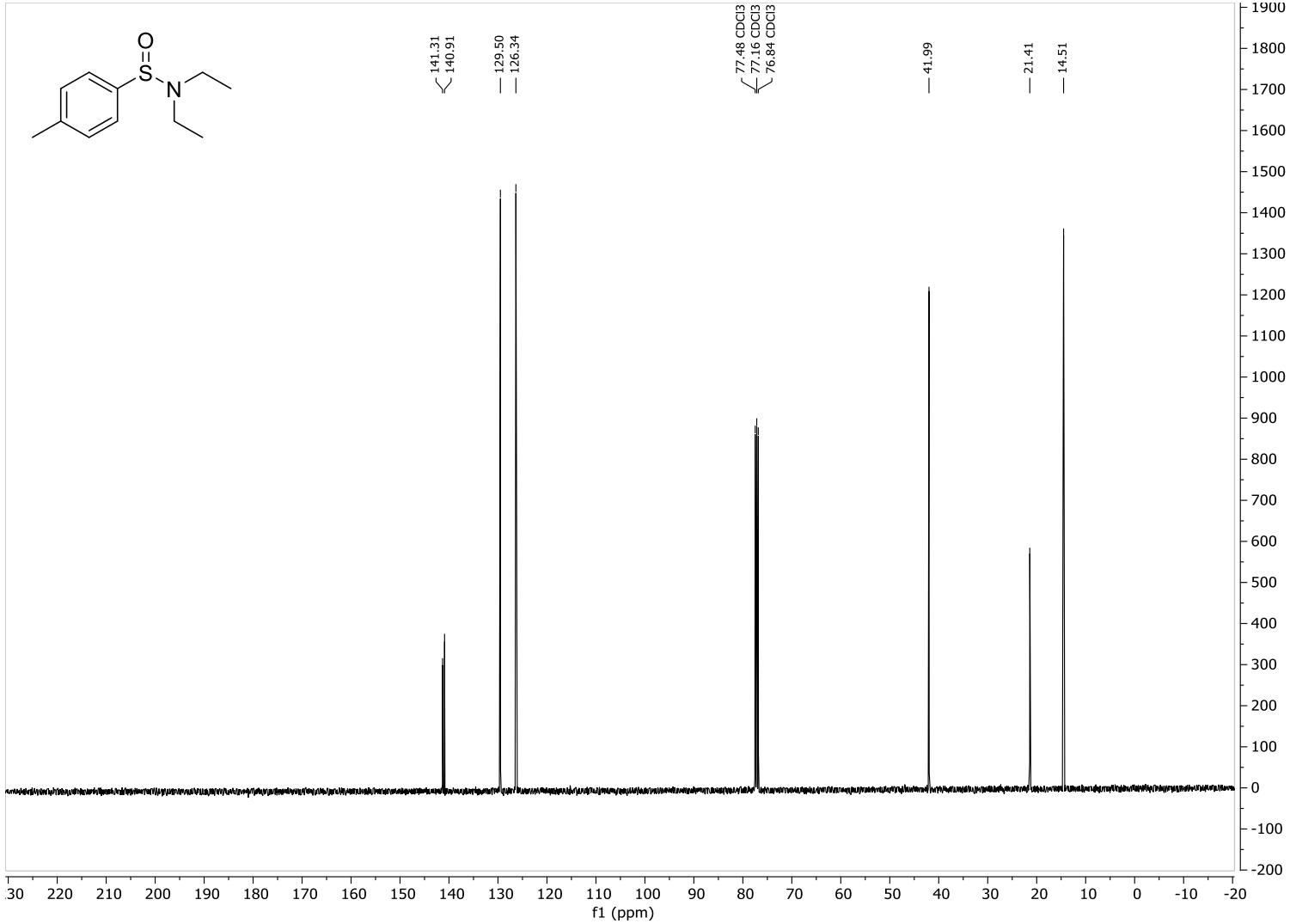



**Figure S50.** $^{13}C$ NMR of **2d** in $CDCl_3$.

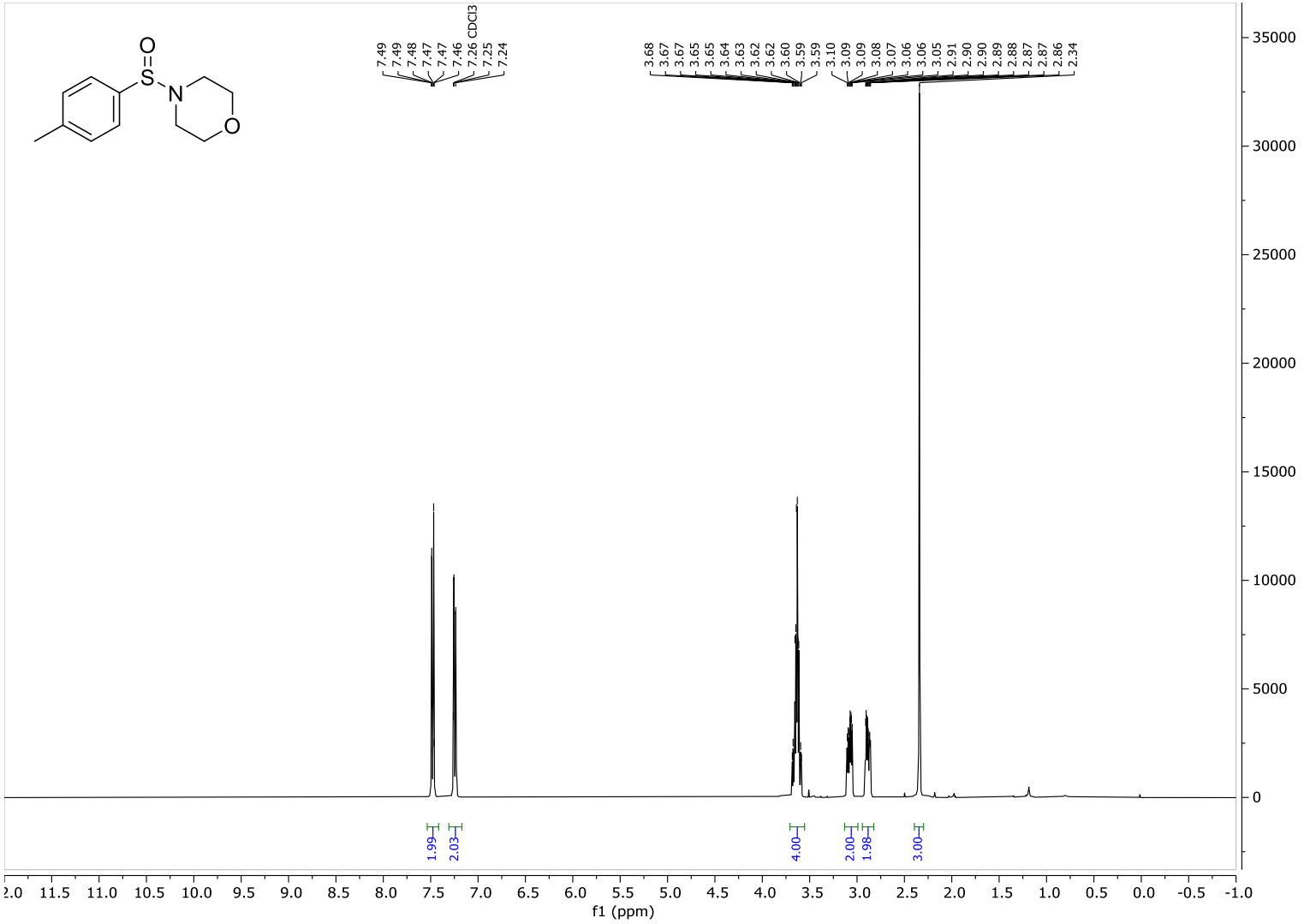



**Figure S51.** $^{1}$H NMR of **2e** in $CDCl_3$.

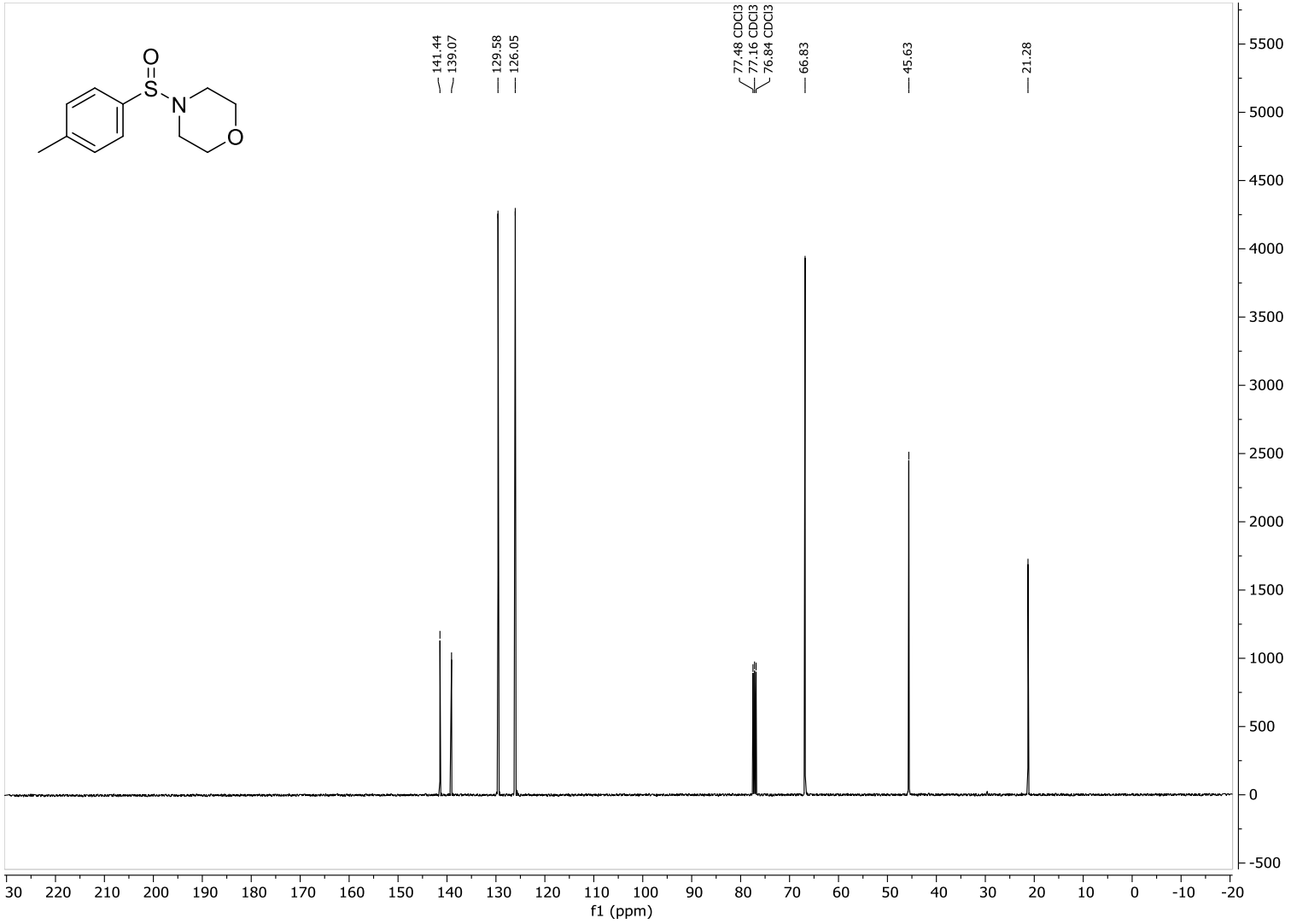



**Figure S52.** $^{13}C$ NMR of **2e** in $CDCl_3$.

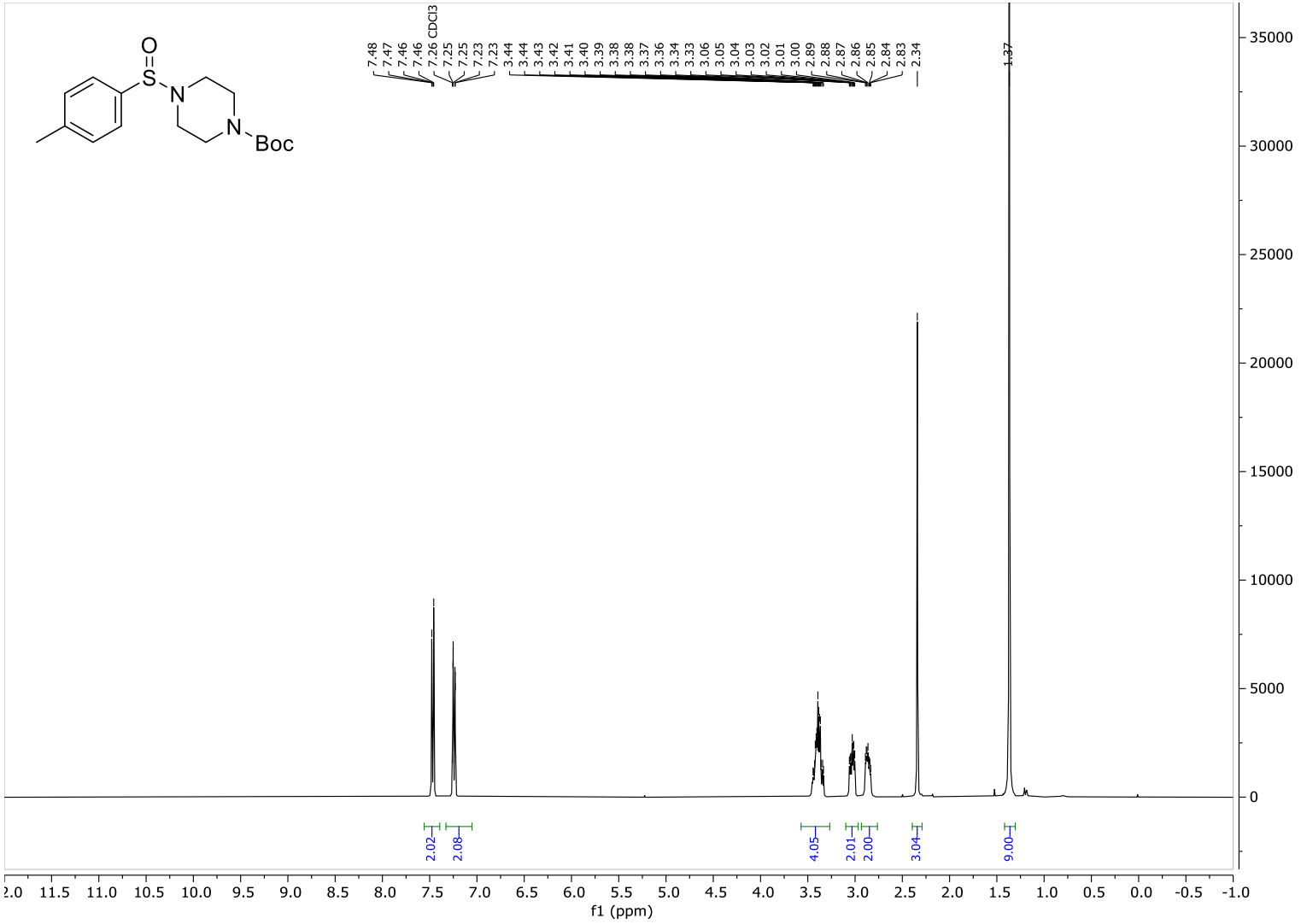



**Figure S53.** $^{1}$H NMR of **2f** in $CDCl_3$.

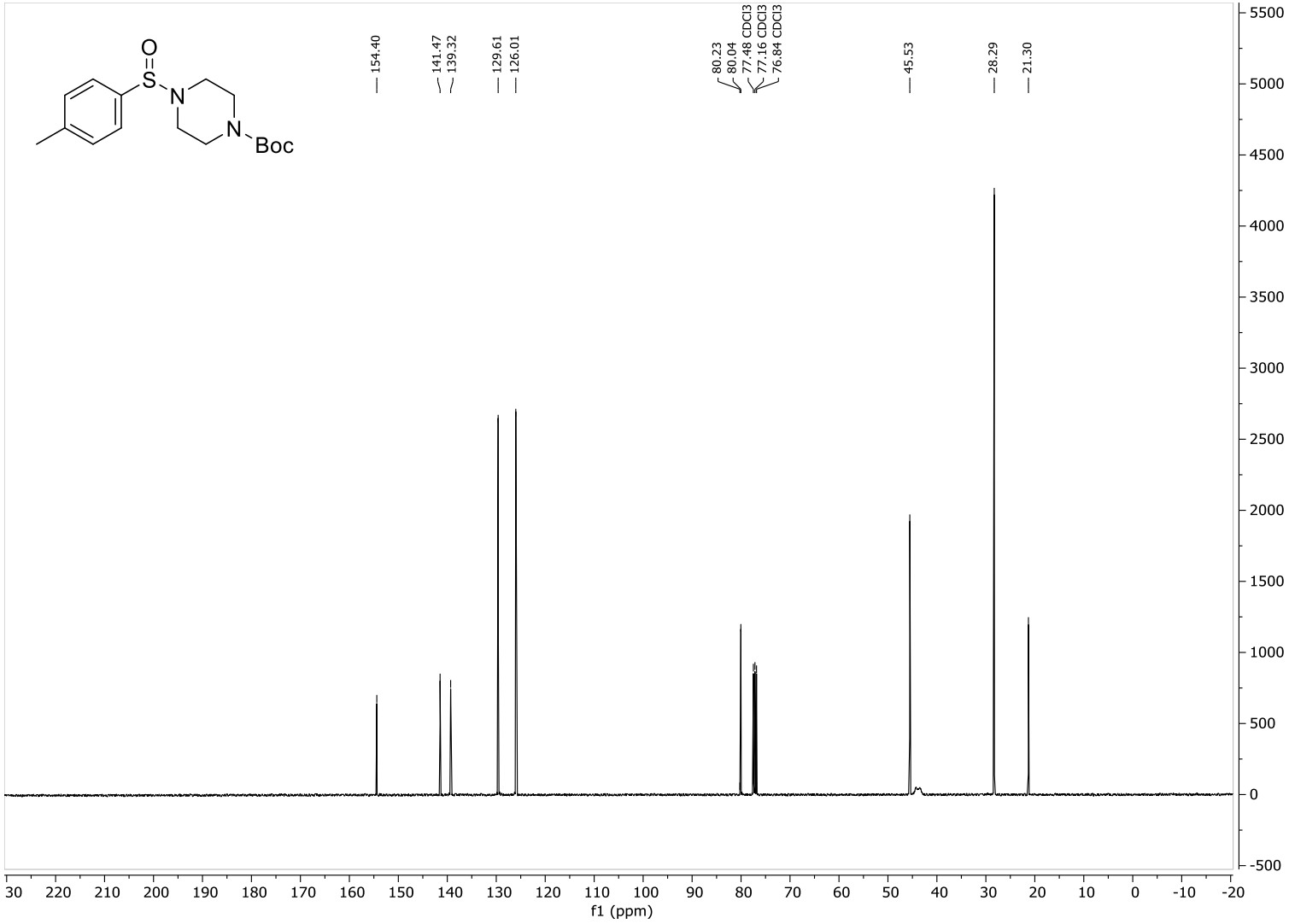



**Figure S54.** $^{13}C$ NMR of **2f** in $CDCl_3$.

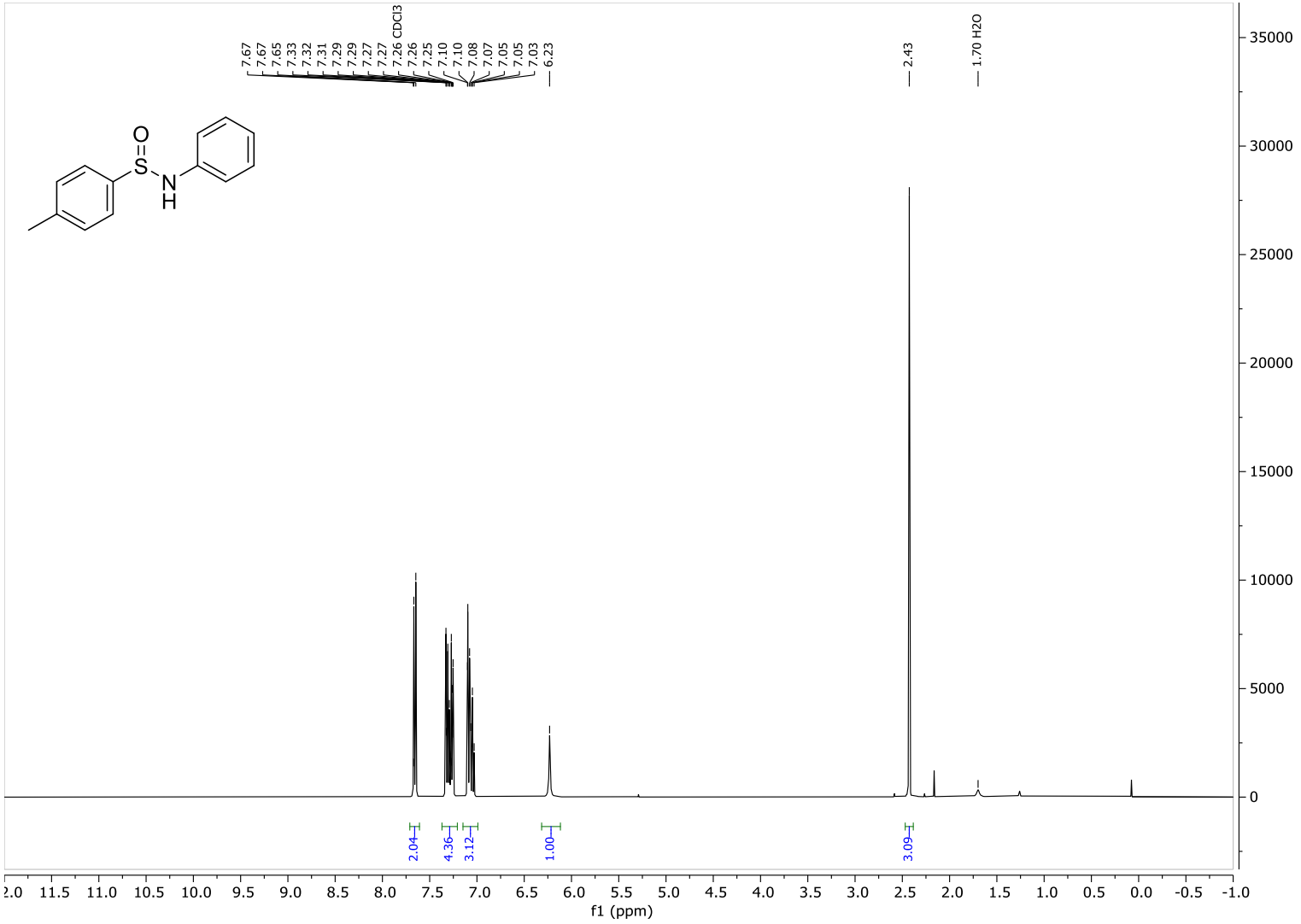



**Figure S55.** $^{1}$H NMR of **2g** in $CDCl_3$.

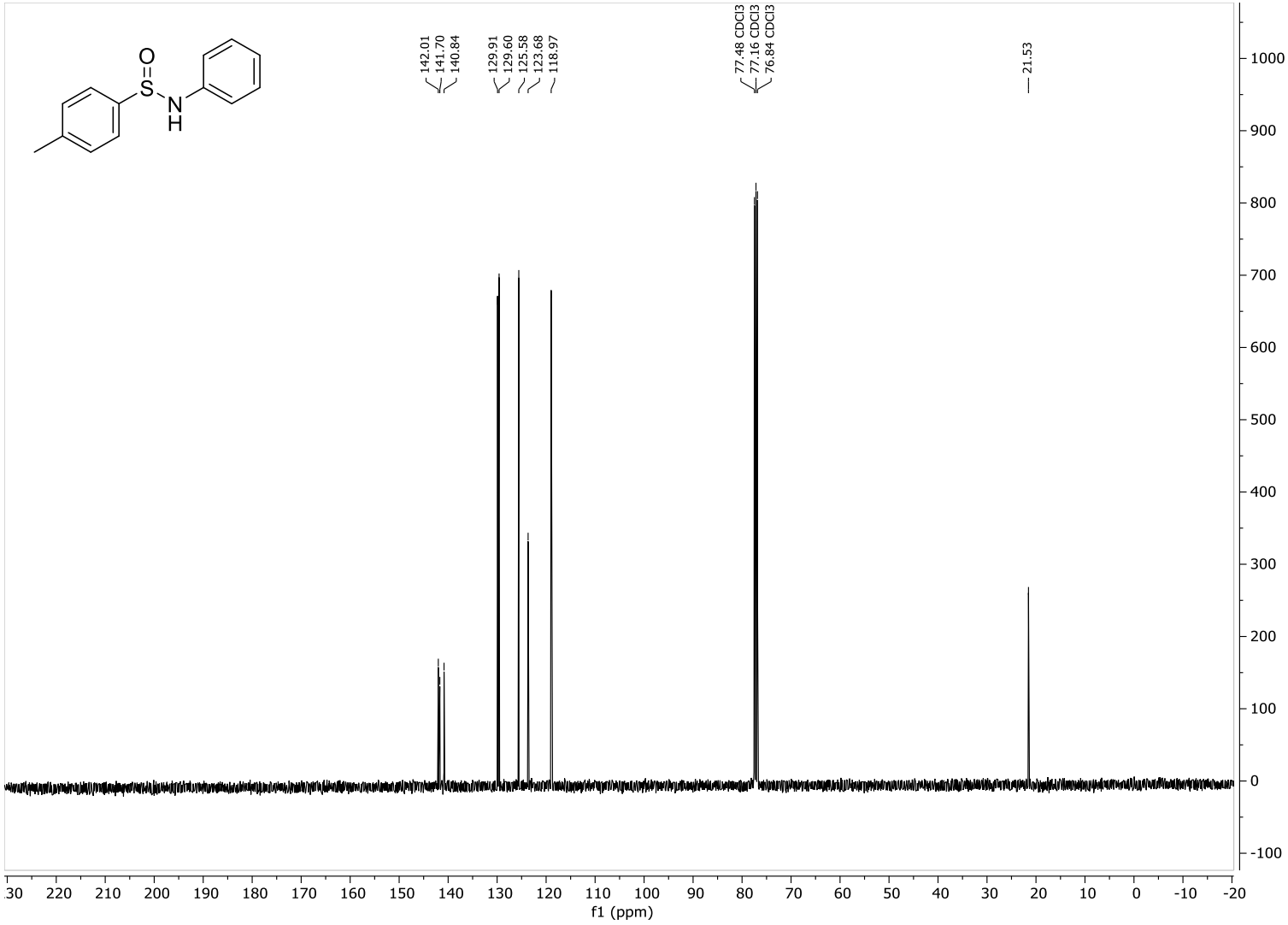



**Figure S56.** $^{13}C$ NMR of **2g** in $CDCl_3$.

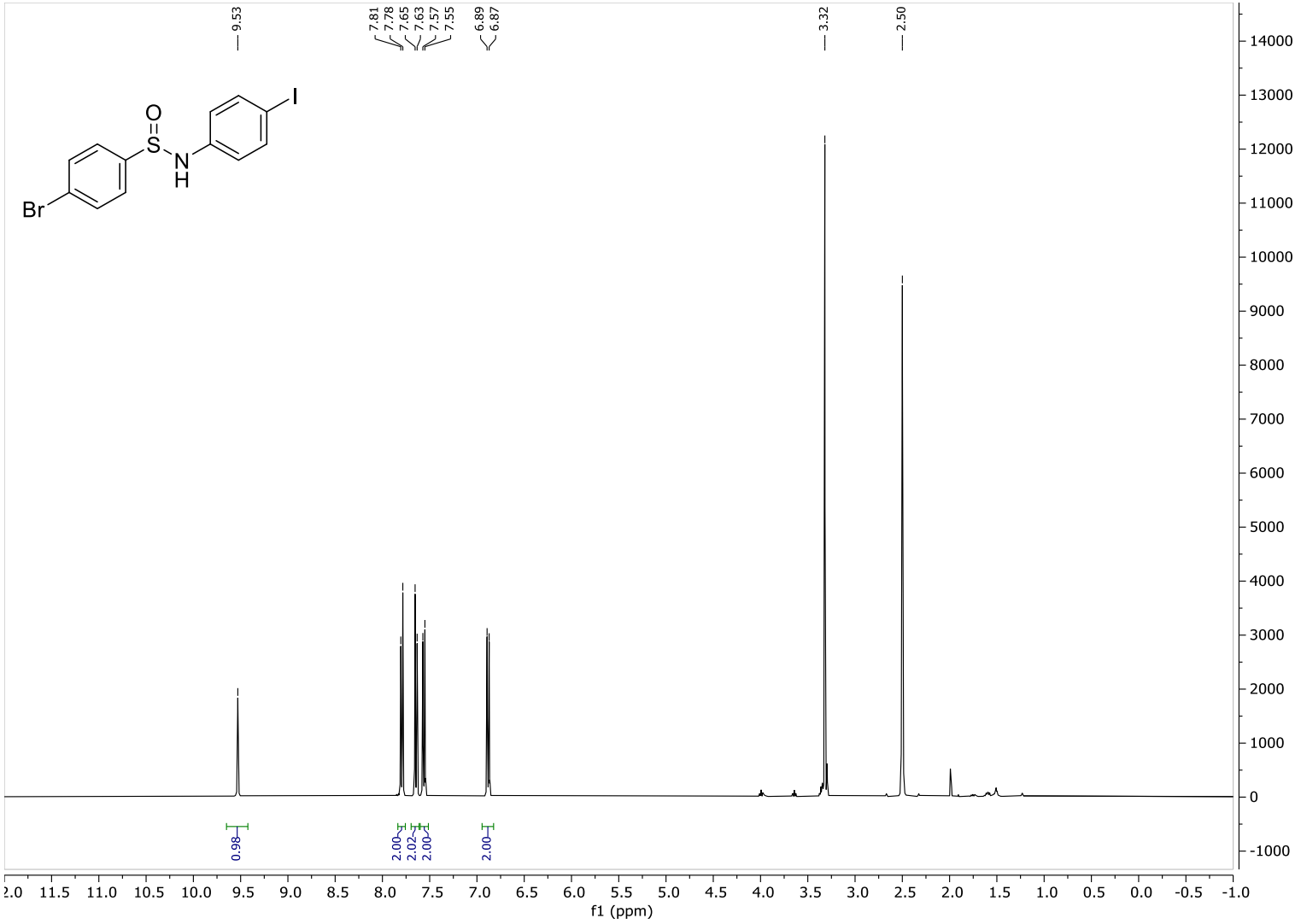



**Figure S57.** $^{1}$H NMR of **2h** in DMSO.

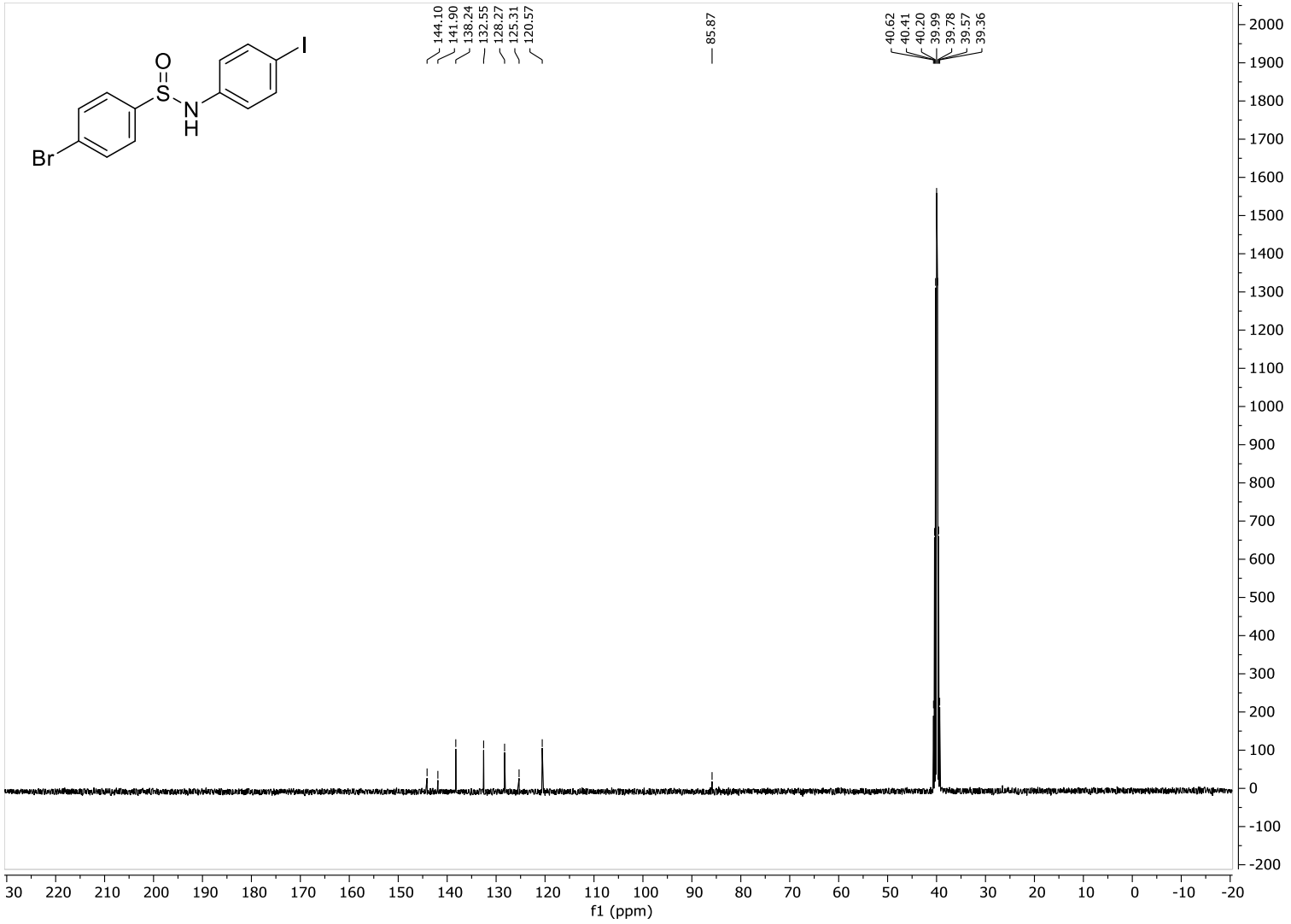



**Figure S58.** $^{13}$C NMR of **2h** in DMSO.

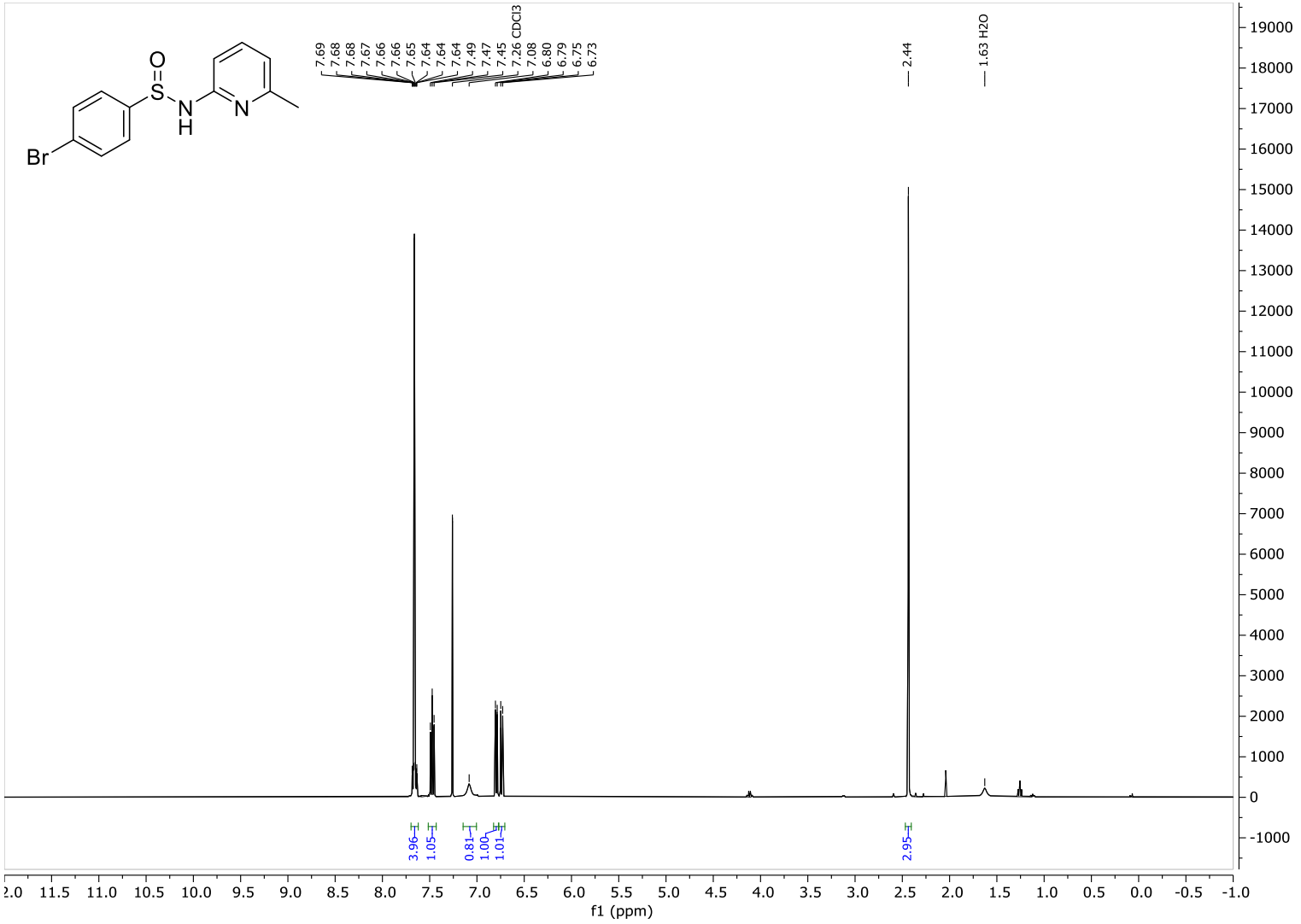



**Figure S59.** $^{1}$H NMR of **2i** in $CDCl_3$.

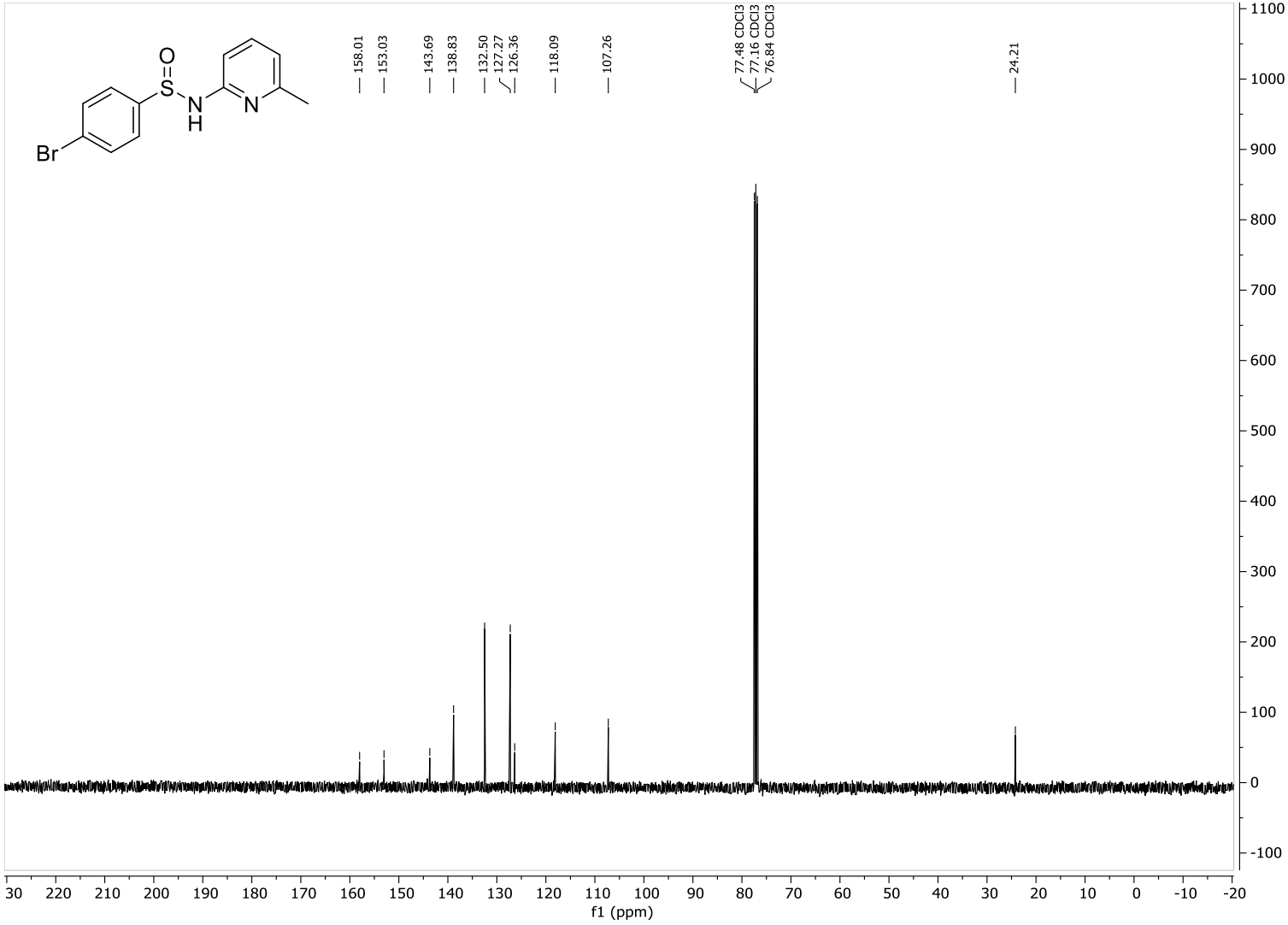



**Figure S60.** $^{13}C$ NMR of **2i** in $CDCl_3$.

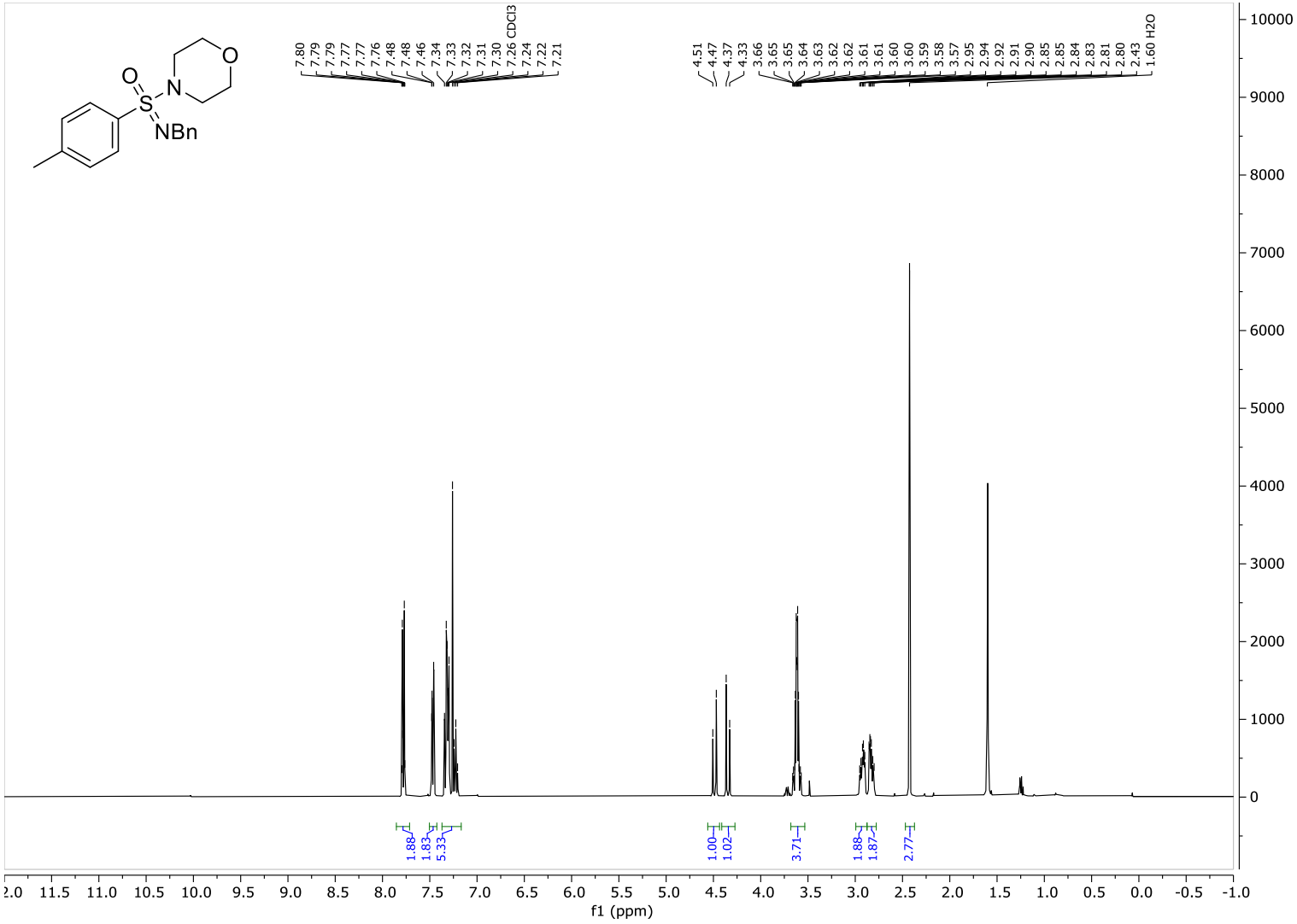



**Figure S61.** $^{1}$H NMR of **3a** in $CDCl_3$.

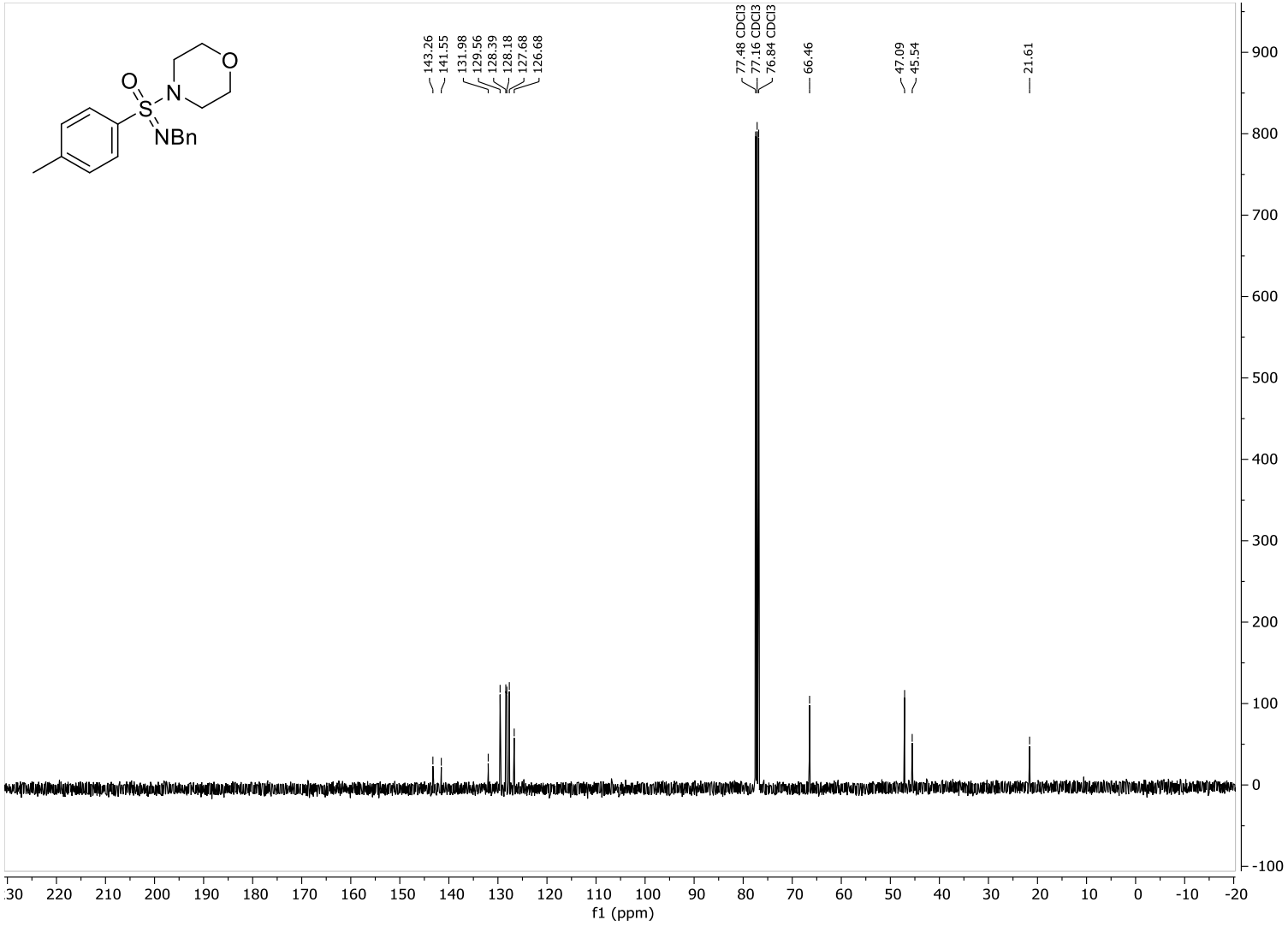



**Figure S62.** $^{13}C$ NMR of **3a** in $CDCl_3$.

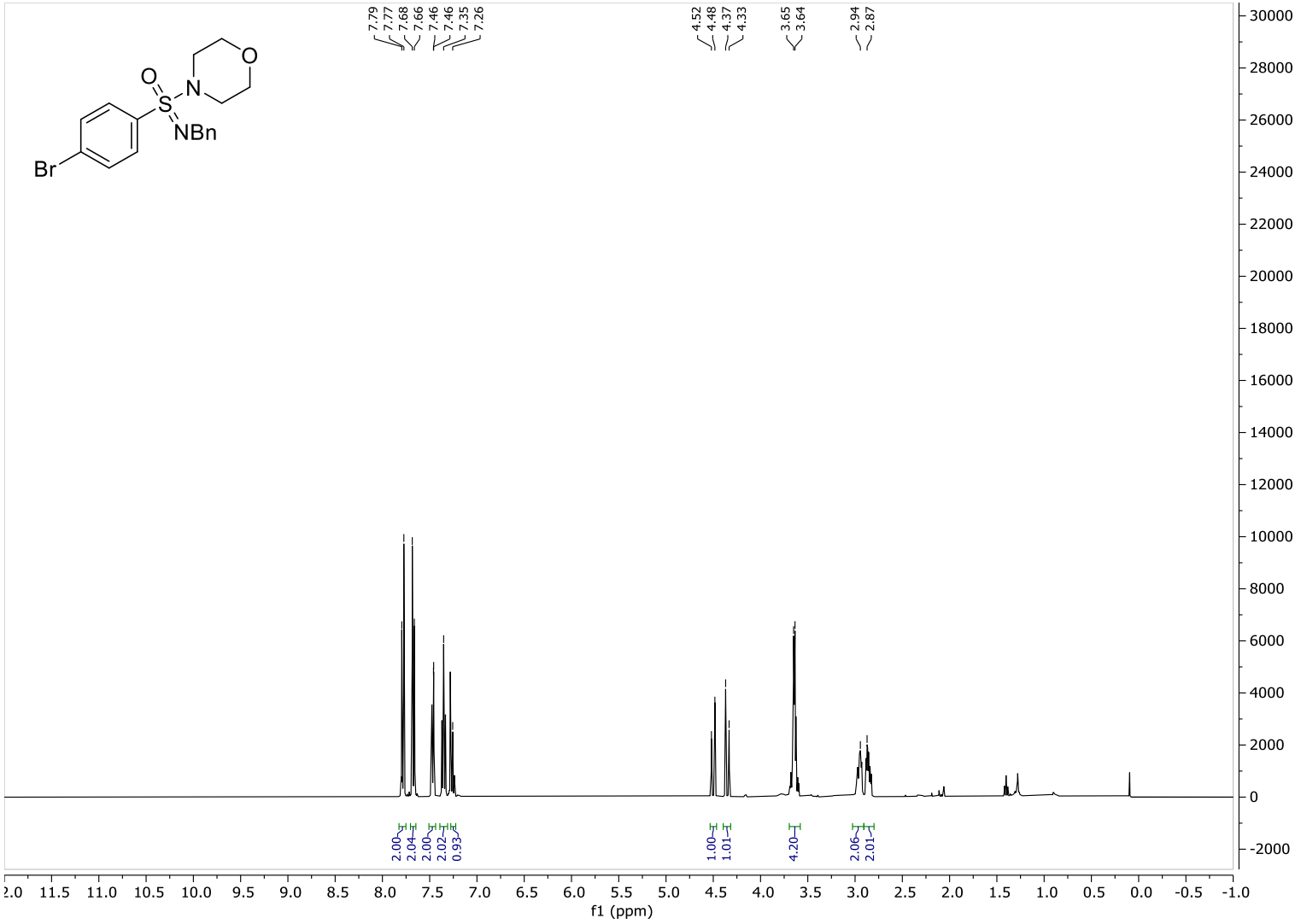



**Figure S63.** $^{1}$H NMR of **3b** in $CDCl_3$.

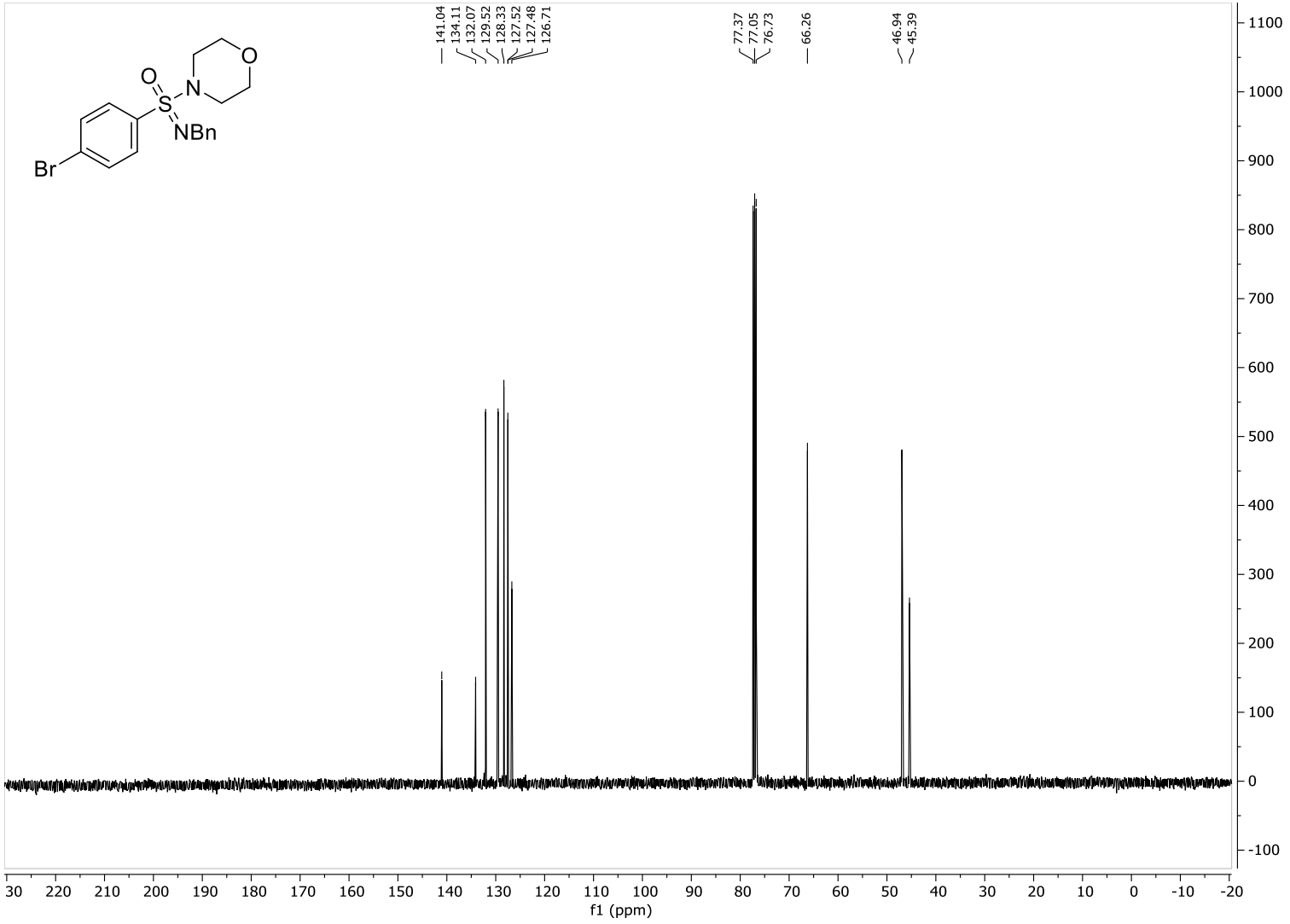



**Figure S64.** $^{13}C$ NMR of **3b** in $CDCl_3$.

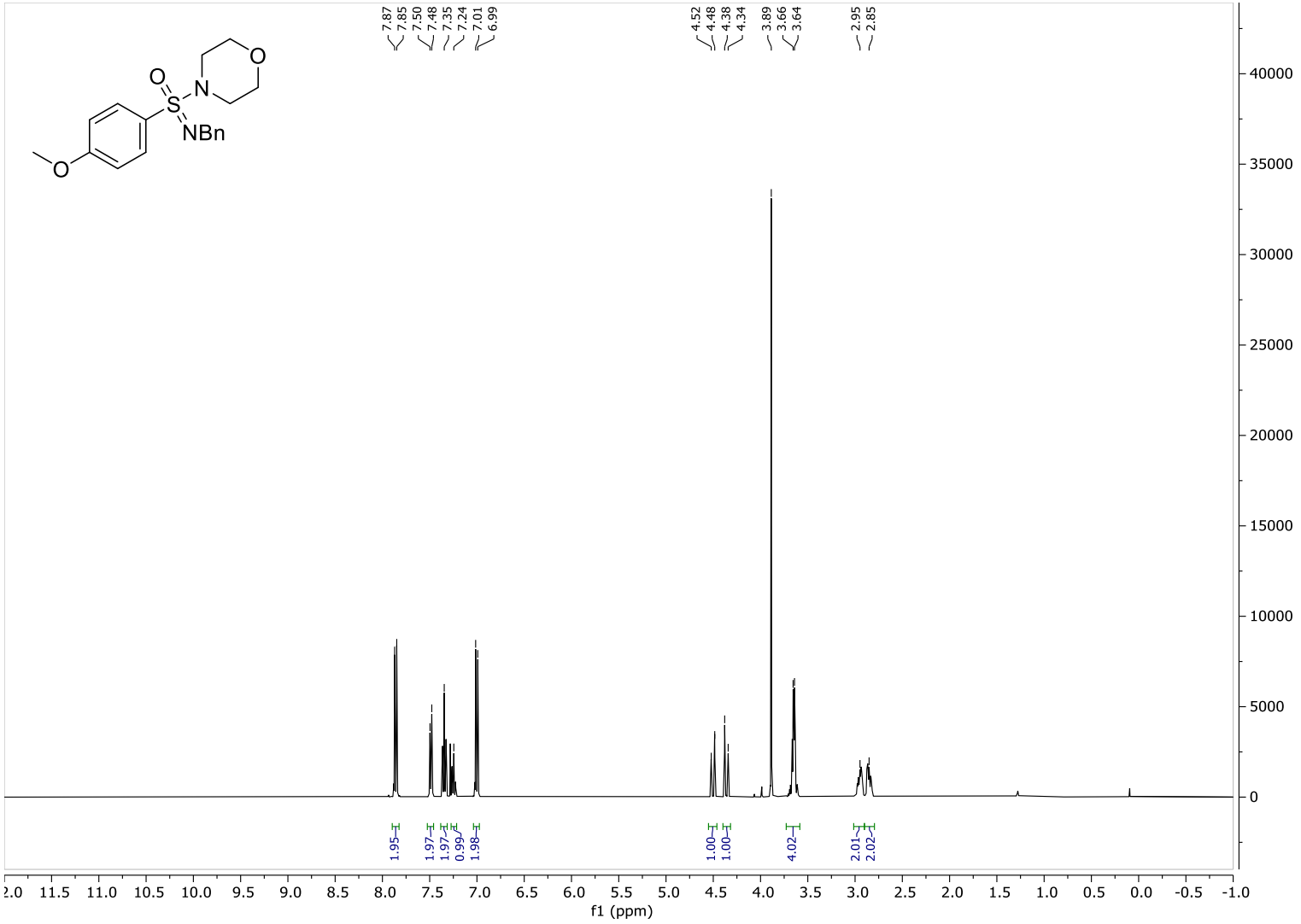



**Figure S65.** $^{1}$H NMR of **3c** in $CDCl_3$.

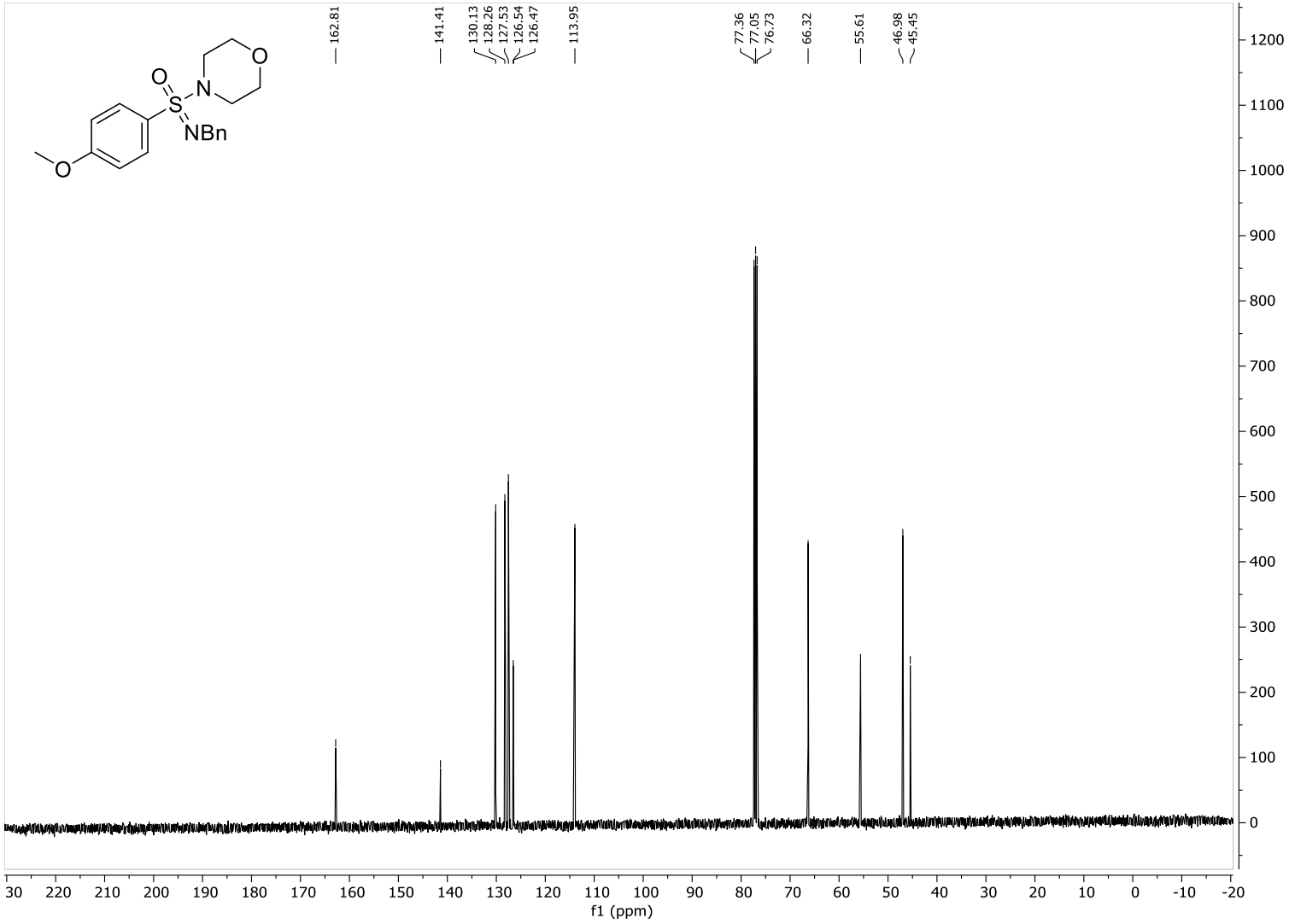



**Figure S66.** $^{13}C$ NMR of **3c** in $CDCl_3$.

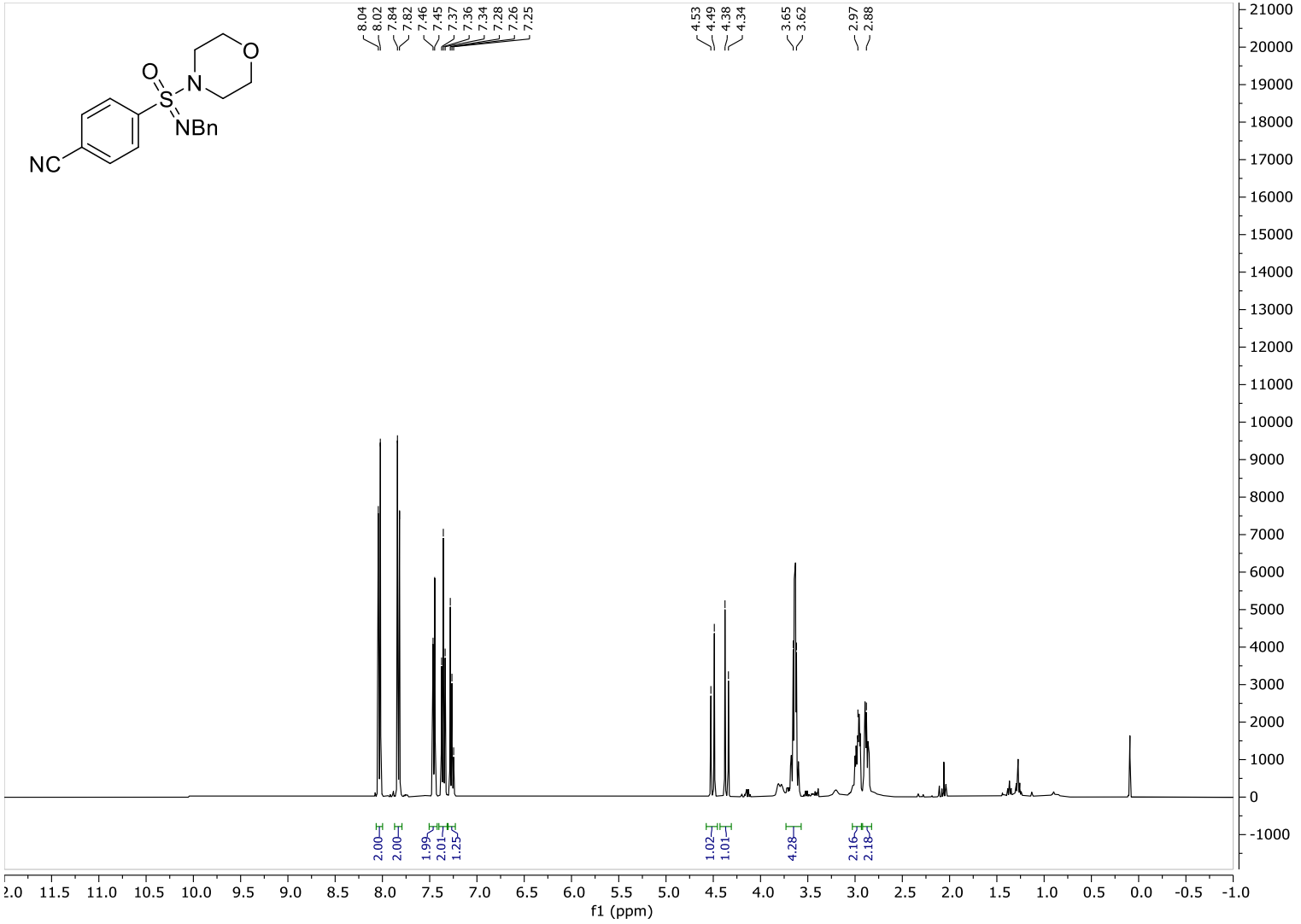



**Figure S67.** $^{1}$H NMR of **3d** in $CDCl_3$.

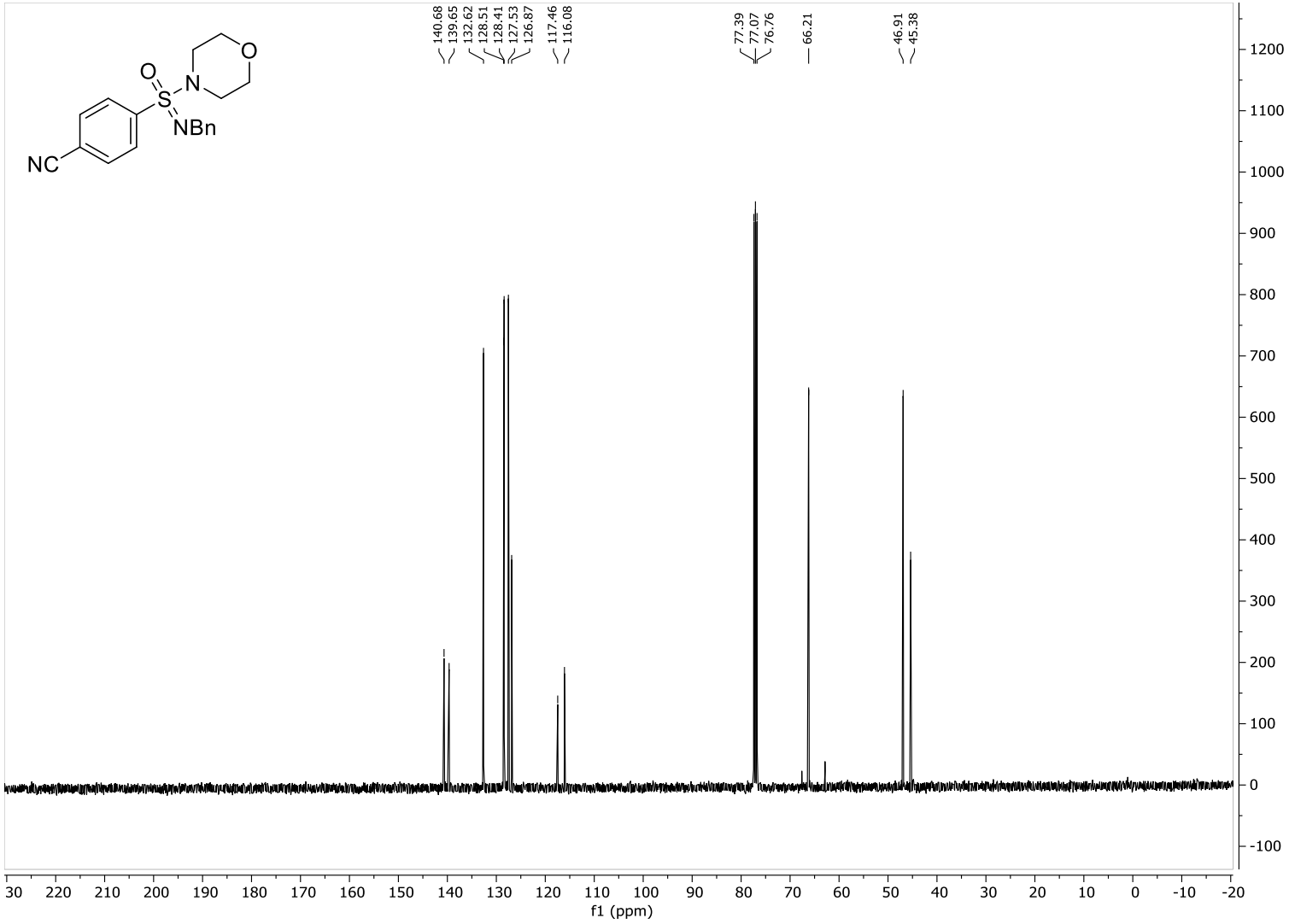



**Figure S68.** $^{13}C$ NMR of **3d** in $CDCl_3$.

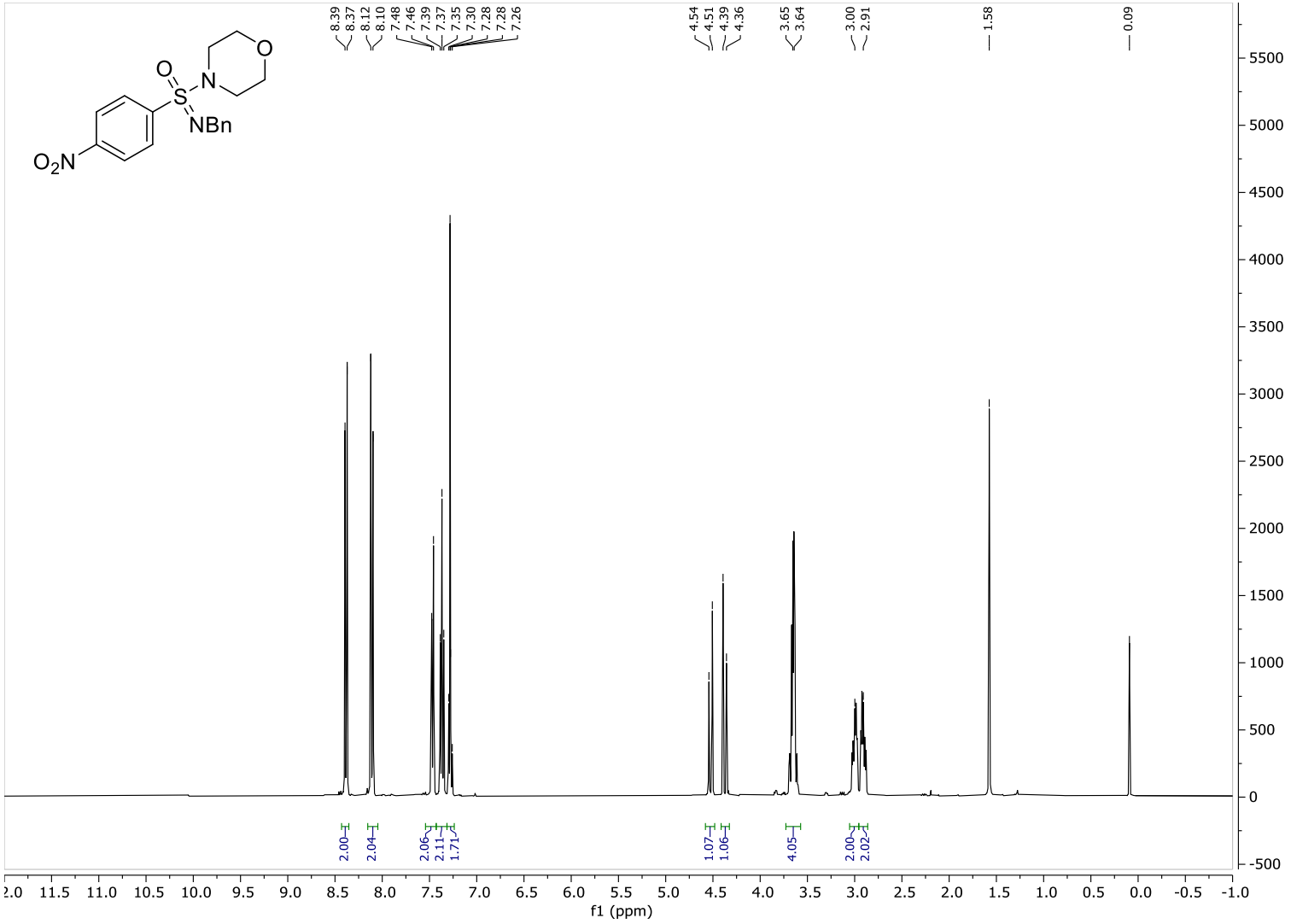



**Figure S69.** $^{1}$H NMR of **3e** in $CDCl_3$.

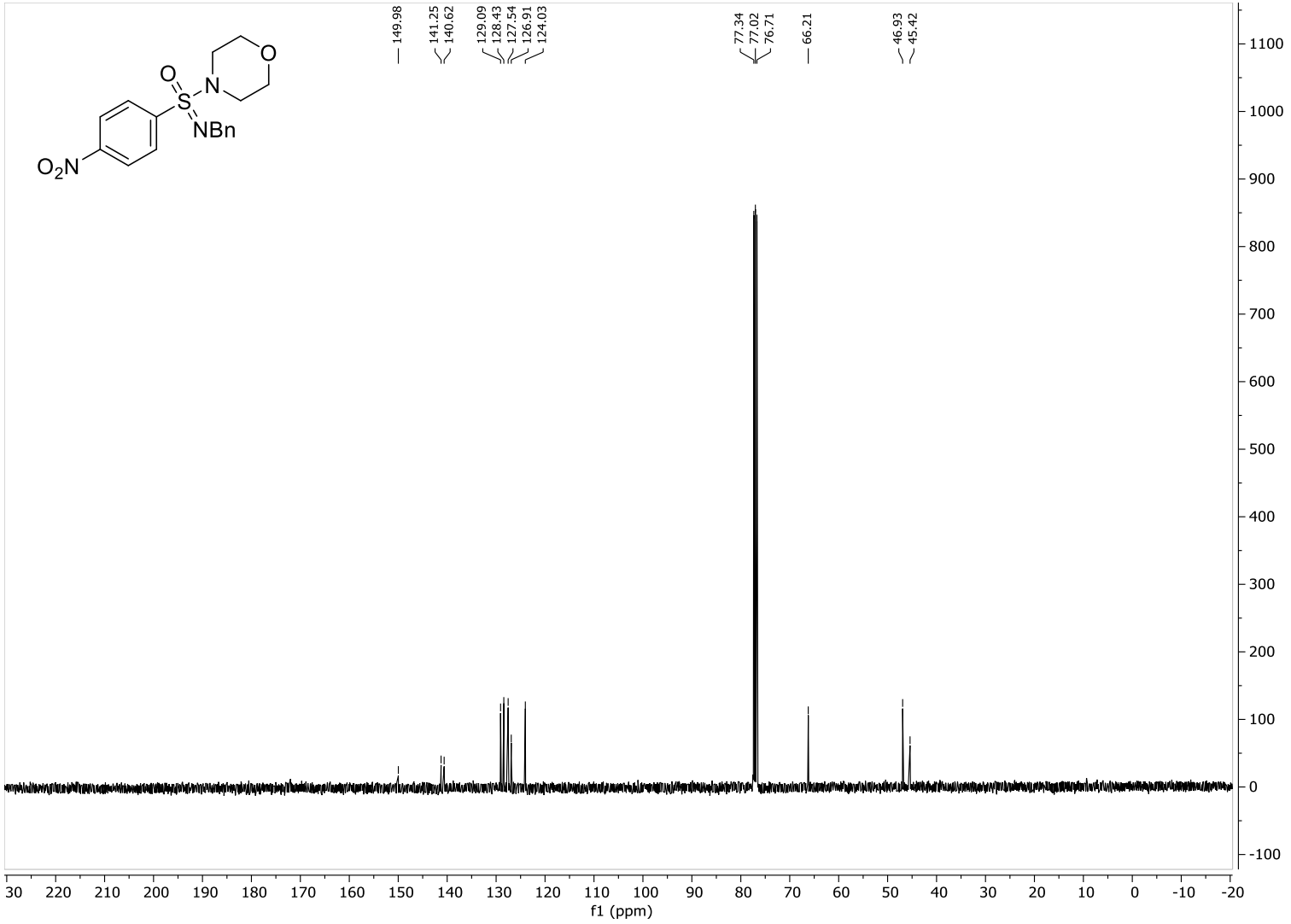



**Figure S70.** $^{13}C$ NMR of **3e** in $CDCl_3$.

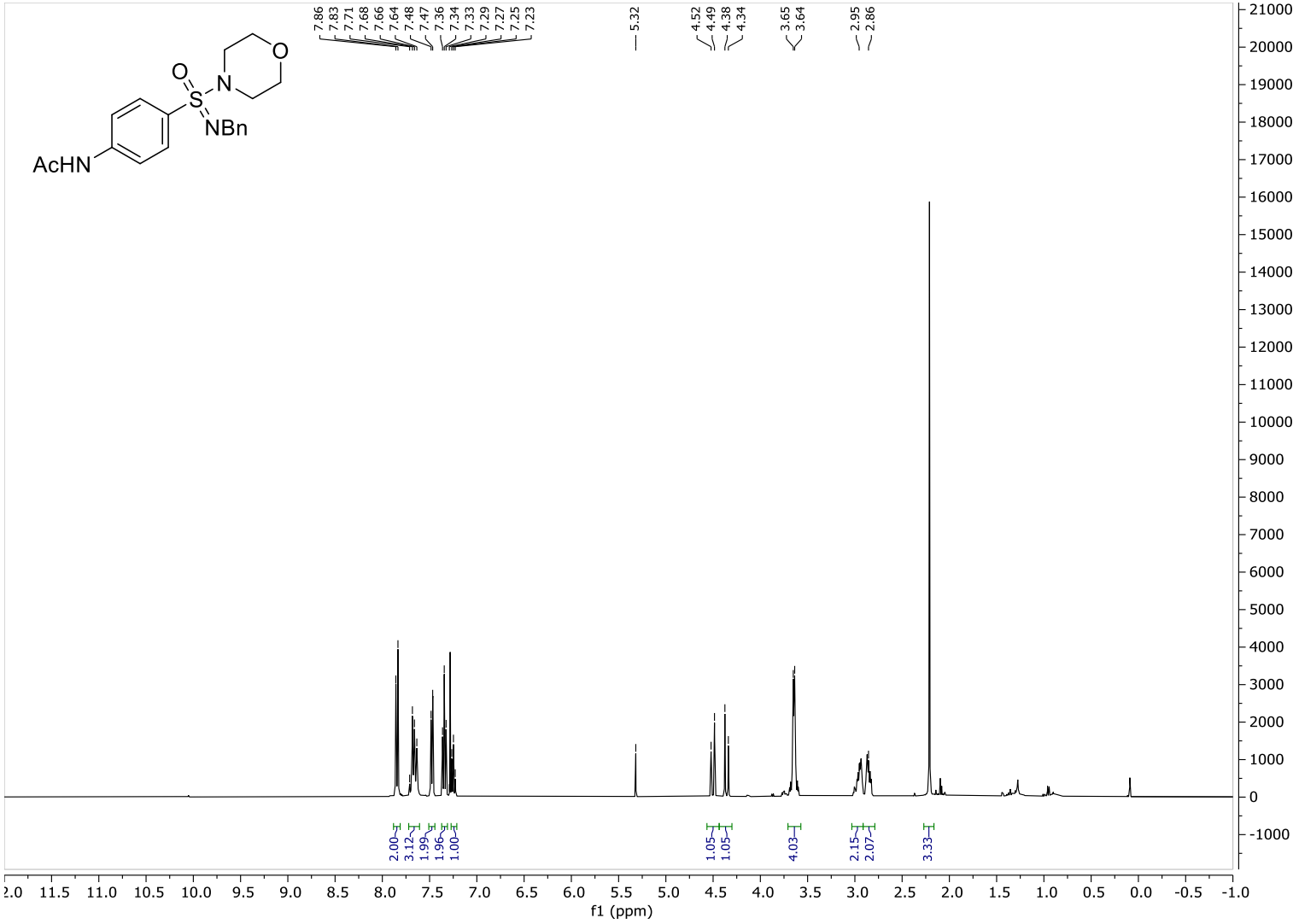



**Figure S71.** $^{1}$H NMR of **3f** in $CDCl_3$.

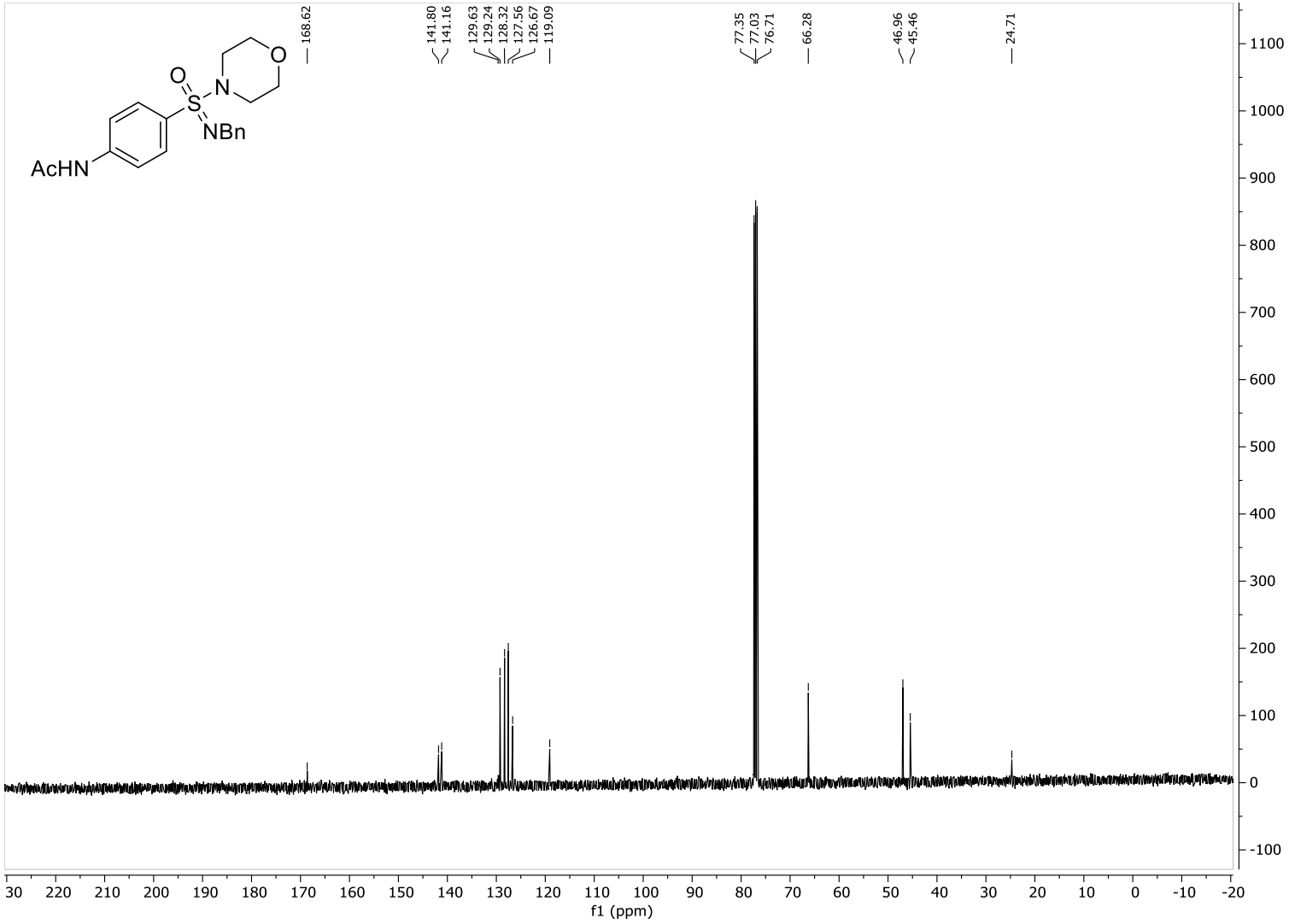



**Figure S72.** $^{13}C$ NMR of **3f** in $CDCl_3$.

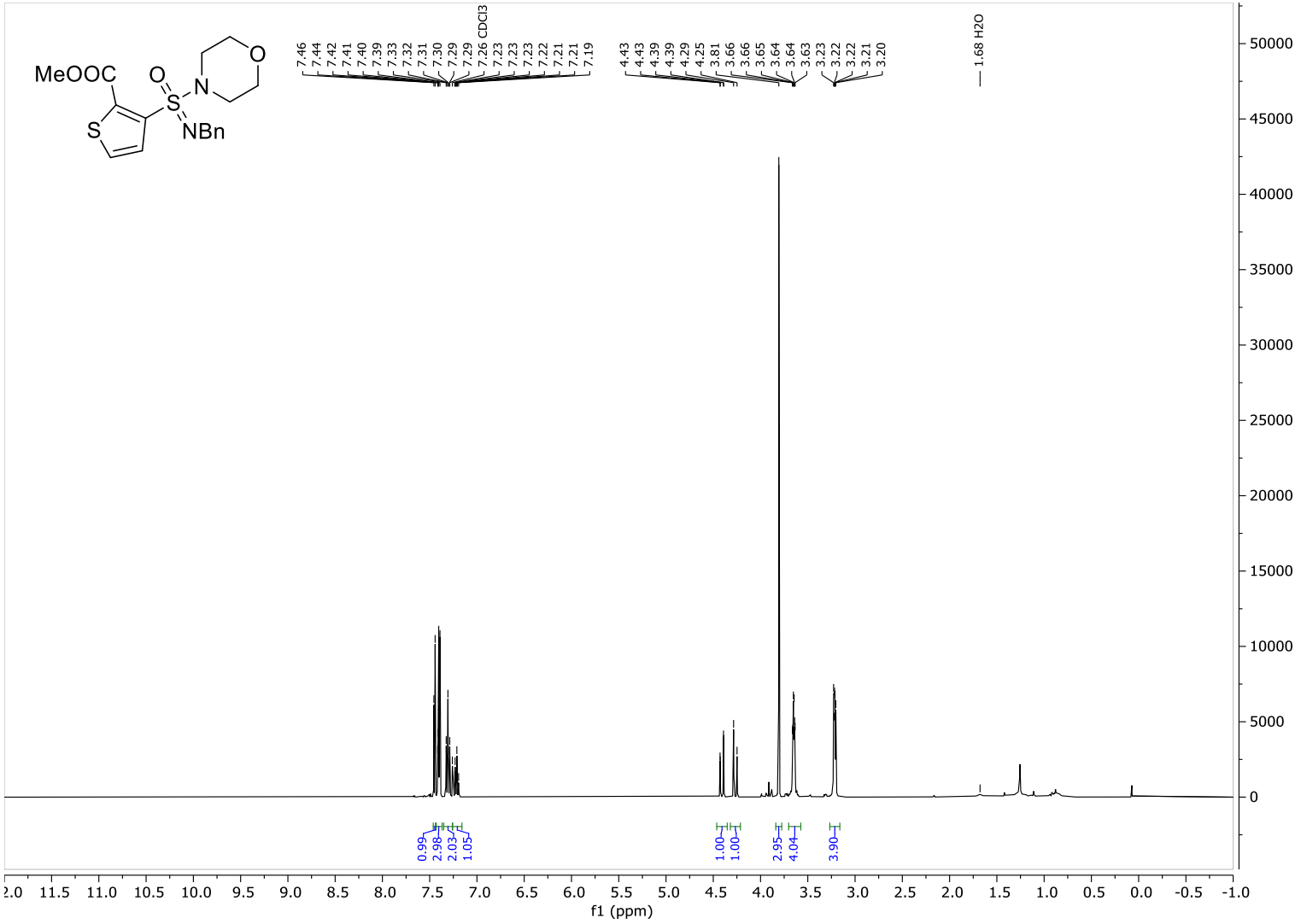



**Figure S73.** $^{1}$H NMR of **3g** in $CDCl_3$.

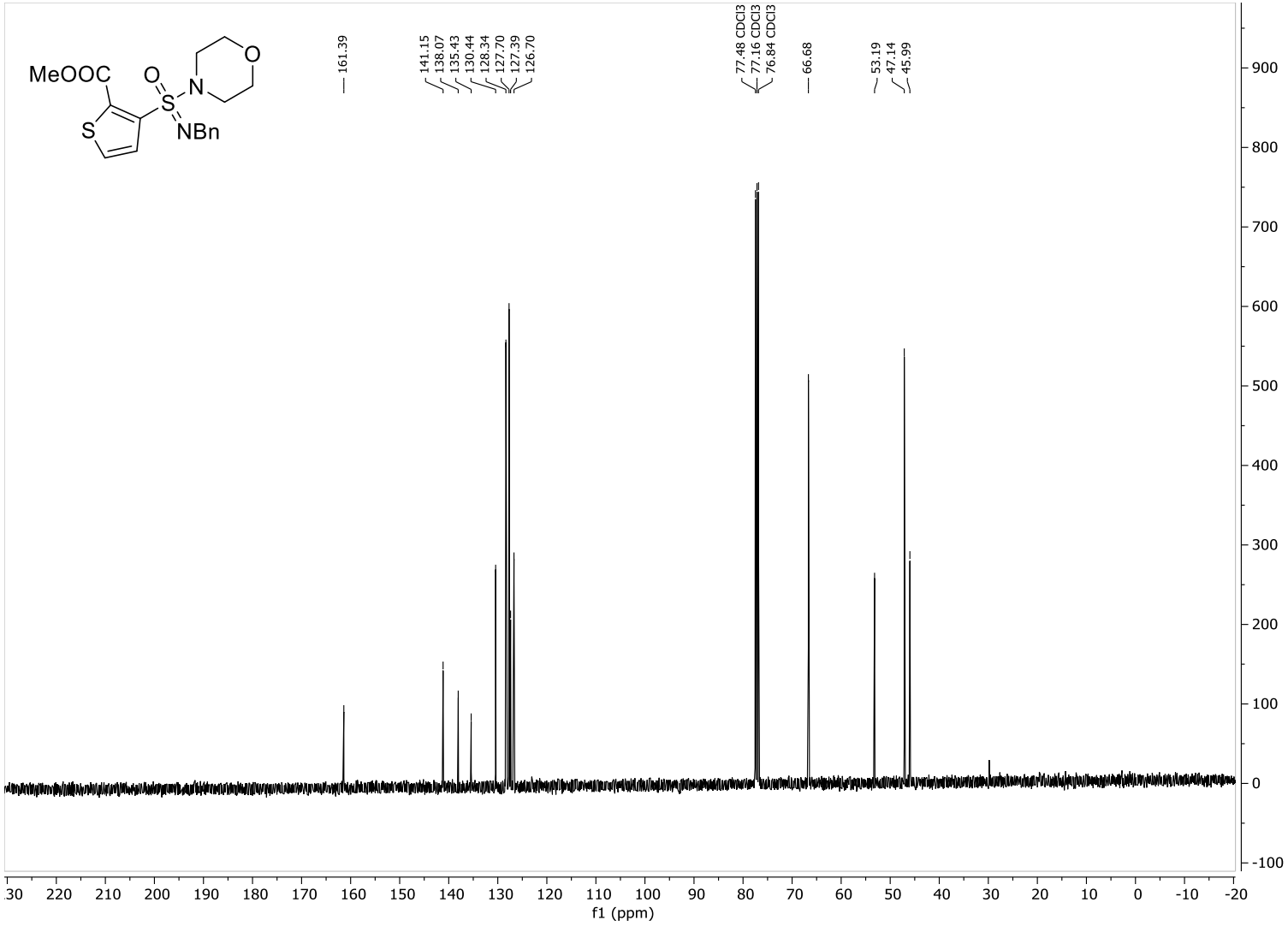



**Figure S74.** $^{13}C$ NMR of **3g** in $CDCl_3$.

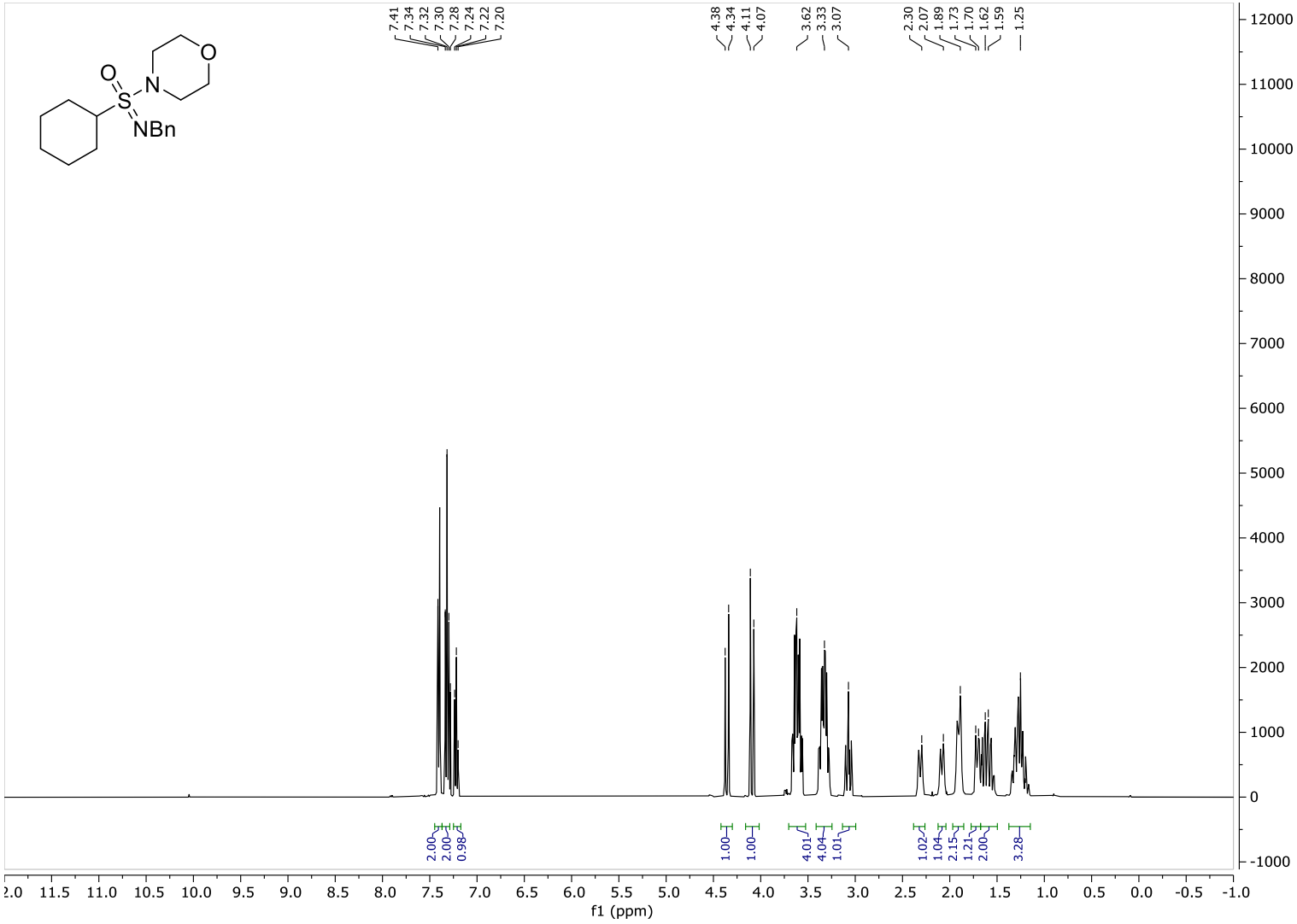



**Figure S75.** $^{1}$H NMR of **3h** in $CDCl_3$.

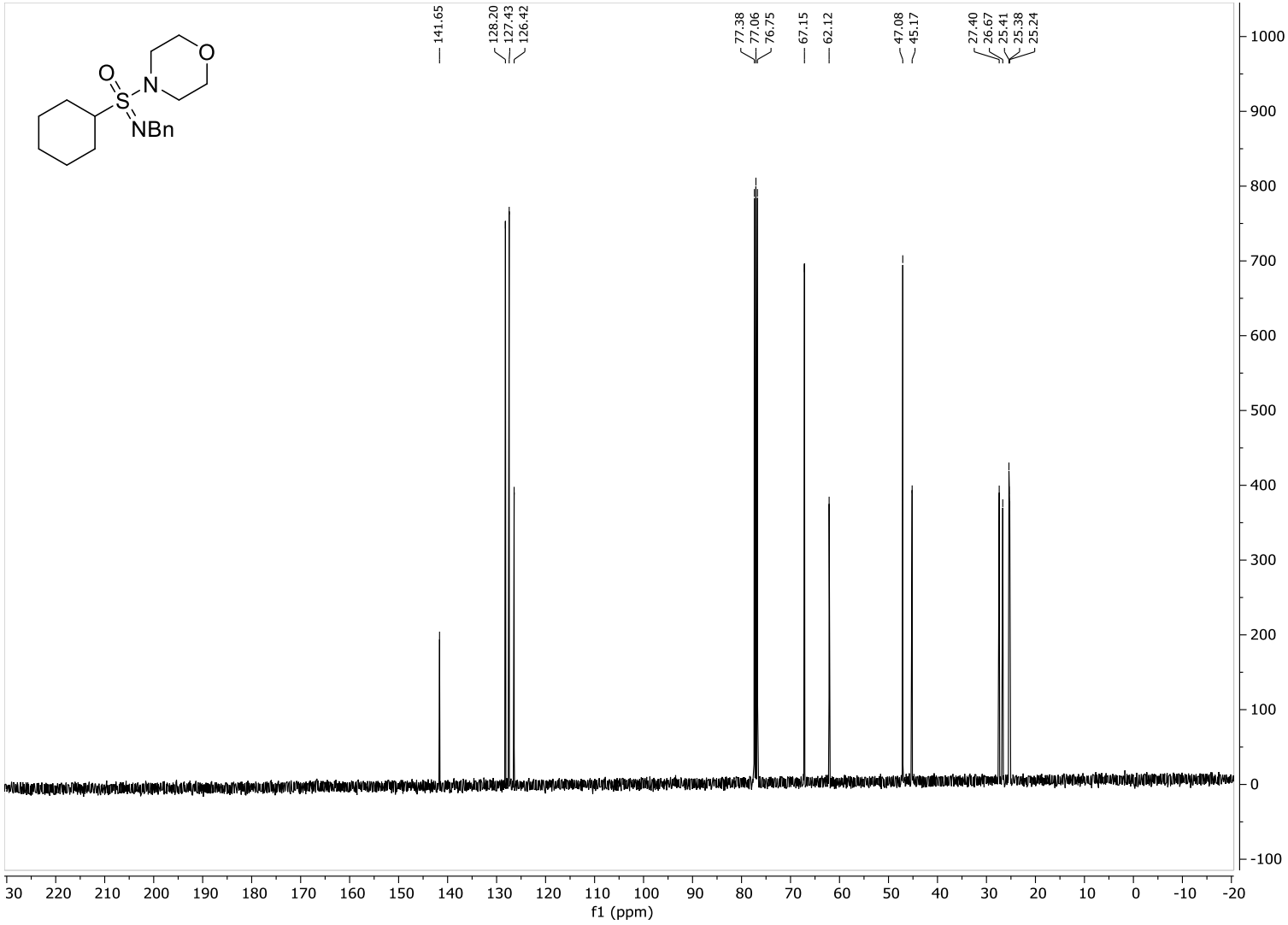



**Figure S76.** $^{13}C$ NMR of **3h** in $CDCl_3$.

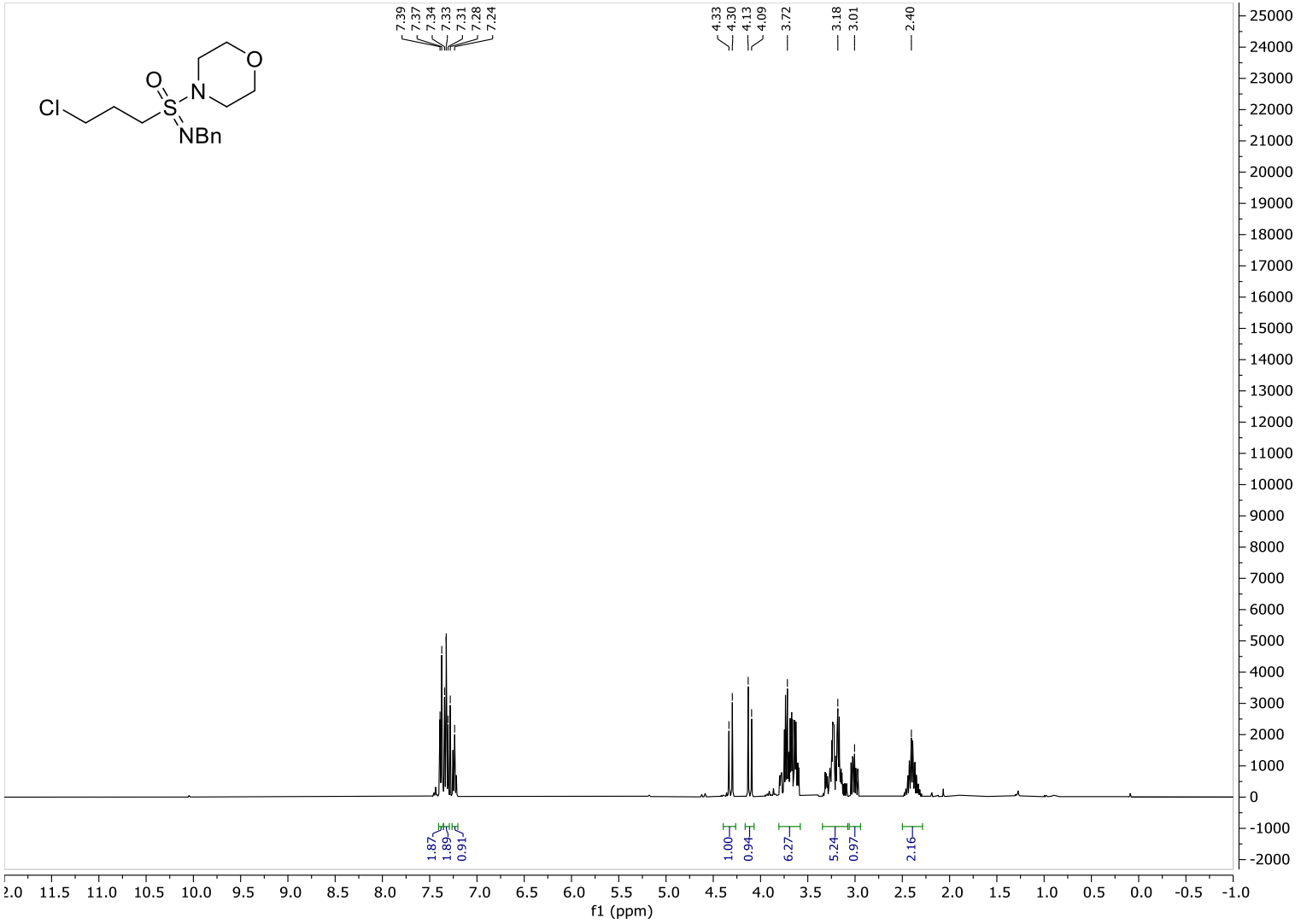



**Figure S77.** $^{1}H$ NMR of **3i** in $CDCl_3$.

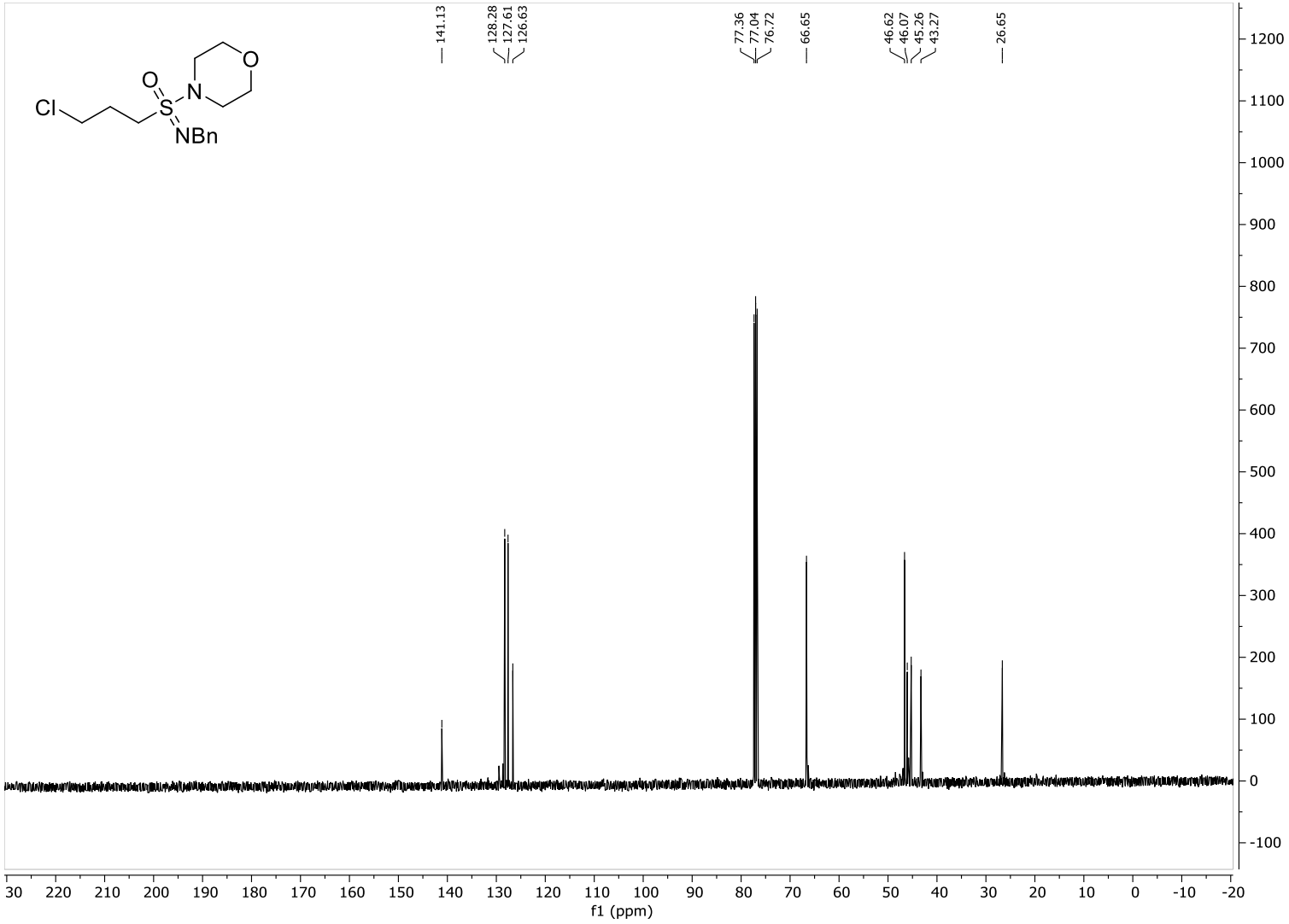



**Figure S78.** $^{13}C$ NMR of **3i** in $CDCl_3$.