Supplementary Information

Flavin–Iodine Coupled Organocatalysis for Aerobic Oxidative Direct Sulfenylation of Indoles with Thiols under Mild Conditions

Ryoma Ohkado, Tatsuro Ishikawa, and Hiroki Iida*

Department of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue, 690-8504, Japan

E-mail address: iida@riko.shimane-u.ac.jp

1. General

Melting points (M.p.) were determined on a SANSYO SMP-300 (SANSYO, Tokyo, Japan) and are uncorrected. The IR spectra were recorded on a JASCO FT/IR-660plus spectrophotometer (JASCO, Tokyo, Japan). The NMR spectra were measured using JEOL JNM-L400 and JNM ECX-500 spectrometers (JEOL, Akishima, Japan) operating at 400 and 500 MHz, respectively, for ^{1}H and 100 and 126 MHz, respectively, for ^{13}C using tetramethylsilane (TMS) or a solvent residual peak as the internal standard. The electrospray ionization mass (ESI-MS) spectra were recorded using a Bruker microTOFII-SHIY3 mass spectrometer (Bruker, Billerica, MA). The GC measurements were performed on a Shimadzu GC-2014 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) using Supelco Equity-5 (30 m x 0.25 mm) column.

2. Materials

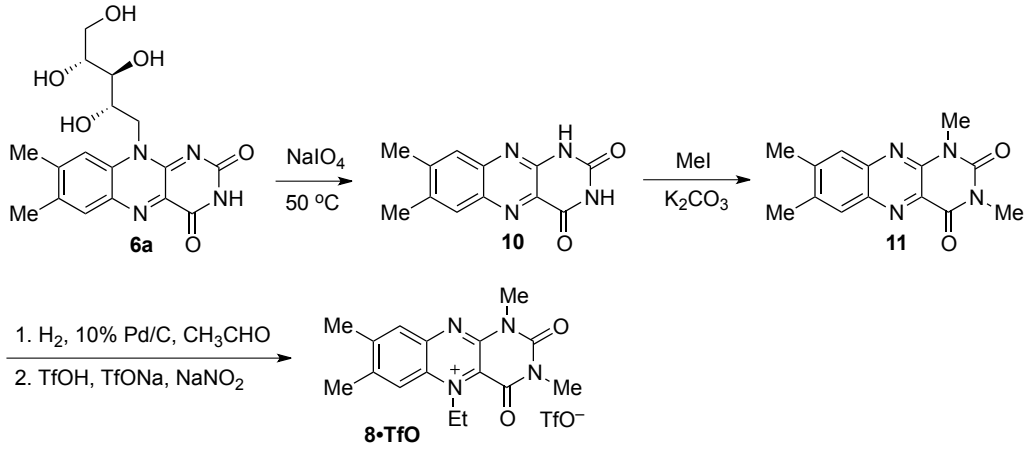
All starting materials were purchased from Aldrich (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Kasei (TCI, Tokyo, Japan) and were used as received. Riboflavin tetraacetate (**6b**),[S1] 5-ethyl-10-(2-hydroxylethyl)-3,7,8-trimethylisoalloxazinium

triflate (**7•TfO**),[S2] and 1,10-ethylene-7,8-dimethylisoalloxazinium triflate (**9•TfO**)[S3] were synthesized according to the previously reported methods.

3. Experimental Procedures

Synthesis of 5-ethyl-1,3,7,8-tetramethylalloxazinium triflate (8•TfO).

According to Scheme S1, novel **8•TfO** could be synthesized from a known compound **11** which can be prepared from commercially available riboflavin (**6a**).[S1]



Scheme S1 Preparation of **8•TfO** from **6a**.

Synthesis of 7,8-dimethylalloxazine (10). To a suspension of **6a** (3.00 g, 8.0 mmol) in water (120 mL) was added sodium periodate (4.77 g, 22 mmol). The mixture was stirred at 50 ˚C for 24 h. The brown precipitate was collected by filtration, washed with water (180 mL), MeOH (130 mL), and Et_2O (20 mL), and dried in vacuum to give **10** (1.34 g, 70% yield) as a yellow powder. The spectral property of **10** was in good agreement with the reported data.[S4]

Synthesis of 1,3,7,8-tetramethylalloxazine (11). A mixture of **10** (4.00 g, 17 mmol), K_2CO_3 (11.8 g, 86 mmol), and methyl iodide (2.40 mL, 39 mmol) in dry DMF (150 mL) was stirred for 3 h at room temperature. After most of the solvent was evaporated under reduced pressure at 50 ˚C, H_2O (200 mL) was added to the residue, and the crude mixture was extracted with $CHCl_3$ (700 mL). The organic layer was washed with brine (200 mL) and dried over $MgSO_4$, filtrated, and

evaporated to dryness. No further purification was required in order to obtain **11** as a yellow solid (3.48 g, 78% yield). The spectral property of **11** was in good agreement with the reported data.[S5]

Synthesis of 5-ethyl-1,3,7,8-tetramethylalloxazinium triflate (8•TfO). A mixture of **11** (1.02 g, 3.7 mmol), 10% Pd-C (400 mg), acetaldehyde (8.50 mL, 0.15 mol), H_2O (12.5 mL), and acetic acid (125 mL) was stirred for 2 days under molecular hydrogen. The reaction mixture was filtered through a pad of Celite under molecular nitrogen, and most of the solvents were evaporated under reduced pressure. After successive addition of 2 M aqueous TfOH solution (10 mL, 20 mmol), TfONa (5.07 g, 30 mmol), and $NaNO_2$ (1.07 g, 16 mmol), the mixture was stirred under air at 0 ˚C for 30 min. The resulting purple precipitate was collected by filtration, washed with cold H_2O (10 mL) and Et_2O (200 mL) to give the crude product (1.11 g). The product (680 mg) was then purified by the reprecipitation from CH_3Cl to Et_2O to give **8•TfO** (533 mg, 51%) as a yellow powder. Mp: 171 ˚C (dec). IR (KBr, cm^{-1}): 1685, 1373, 1254, 1031, 638. ^1H NMR (500 MHz, $CDCl_3$, r.t.): δ 8.10 (s, 1H, ArH), 8.05 (s, 1H, ArH), 6.12 (br, 1H, N^+CHHCH_3), 5.34 (br, 1H, N^+CHHCH_3), 3.85 (s, 3H, 1-NCH_3), 3.57 (s, 3H, 3-NCH_3), 2.68 (s, 3H, $ArCH_3$), 2.61(s, 3H, $ArCH_3$), 1.85 (t, J = 7.2 Hz, 3H, NCH_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, r.t.): δ 155.27, 149.25, 148.70, 148.62, 147.25, 146.10, 129.13, 128.95, 120.01 (q, J = 320 Hz, CF_3), 119.63, 117.40, 51.57, 30.88, 30.01, 21.76, 20.65, 15.23. HRMS (ESI+): m/z calcd for $C_{17}H_{19}F_3N_4O_5S$ ($M - TfO^-$), 299.1503; found, 299.1503.

Typical procedure for catalytic sulfenylation of 1a with 2a in the presence of 8•TfO and I_2. A mixture of **1a** (70.3 mg, 0.60 mmol), **2a** (89.4 mg, 0.72 mmol), I_2 (3.05 mg, 0.012 mmol), **8•TfO** (5.38. mg, 0.012 mmol), and CH_3CN (0.4 mL) was stirred at 25 ˚C for 20 h under O_2. After an addition of water (10 mL), the mixture was extracted with $CHCl_3$ (10 mL x 3), and the organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and filtered. After the solvent was removed by evaporation, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 100/0 to 20/1, v/v) to give **3a** (136 mg, 94%) as a white solid. These results are summarized in Tables 1 and 2.

Spectroscopic data of **3a**[S6]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) : δ 8.29 (br s, 1H, N*H*), 7.61 (d, J = 7.9 Hz, 1H, Ar*H*), 7.43 (d, J = 2.4 Hz, 1H, Ar*H*), 7.40 (d, J = 8.2 Hz, 1H, Ar*H*), 7.25 (dd, J = 7.6, 7.6 Hz, 1H, Ar*H*), 7.15 (dd, J = 7.5, 7.5 Hz, 1H, Ar*H*), 7.03 (d, J = 8.2 Hz, 2H, ArH), 6.96 (d, J = 8.1 Hz, 2H, ArH), 2.24 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ 136.58, 135.59, 134.79, 130.55, 129.62, 129.23, 126.39, 123.10, 120.96, 119.80, 111.67, 103.59, 20.98.

Spectroscopic data of **3b**[S6]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) : δ 8.34 (br s, 1H, N*H*), 7.61 (d, J = 8.0 Hz, 1H, Ar*H*), 7.45 (d, J = 2.6 Hz, 1H, Ar*H*), 7.41 (d, J = 8.2 Hz, 1H, Ar*H*), 7.26 (dd, J = 7.2, 7.2 Hz, 1H, Ar*H*), 7.17-7.13 (m, 3H, Ar*H*), 7.10 (d, J = 7.1 Hz, 2H, Ar*H*), 7.05 (dd, J = 7.1, 7.1 Hz, 1H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ 139.34, 136.61, 130.81, 129.22, 128.83, 125.98, 124.91, 123.18, 121.04, 119.79, 111.71, 102.94.

Spectroscopic data of **3c**[S6]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) : δ 8.38 (br s, 1H, N*H*), 7.56 (d, J = 7.9 Hz, 1H, Ar*H*), 7.46 (d, J = 2.6 Hz, 1H, Ar*H*), 7.43 (d, J = 8.4 Hz, 1H, Ar*H*), 7.27 (dd, J = 7.4, 7.4 Hz, 1H, Ar*H*), 7.17 (dd, J = 7.5, 7.5 Hz, 1H, Ar*H*), 7.11 (d, J = 8.6 Hz, 2H, Ar*H*), 7.01 (d, J = 8.6 Hz, 2H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ 137.94, 136.63, 130.83, 130.68, 128.92, 128.89, 127.24, 123.36, 121.20, 119.64, 111.80, 102.59.

Spectroscopic data of **3d**[S7]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) : δ 8.63 (br s, 1H, N*H*), 8.01 (dd, J = 7.7, 1.5 Hz, 1H, Ar*H*), 7.55 (d, J = 8.0 Hz, 1H, Ar*H*), 7.49 (d, J = 2.7 Hz, 1H, Ar*H*), 7.47 (d, J = 8.2 Hz, 1H, Ar*H*), 7.27 (ddd, J = 7.7 Hz, 1H, Ar*H*), 7.15 (dd, J = 7.1, 7.1 Hz, 1H, Ar*H*), 7.11 (dd, J = 8.1, 1.6 Hz, 1H, Ar*H*), 7.06 (ddd, J = 8.0, 6.8, 0.5 Hz, 1H, Ar*H*), 6.84 (dd, J_1 = 1.0 Hz, J_2 = 8.1 Hz, 1H, Ar*H*), 3.99 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ 167.27, 144.49, 136.86, 132.46, 131.44, 131.31, 129.19, 126.46, 125.96, 123.80, 123.24, 121.10, 119.82, 111.84, 102.83, 52.30.

Spectroscopic data of **3e**: Pale brown solid. Mp : 70.4-73.2 ˚C. IR (KBr, cm^{-1}): 3395, 3288, 1661, 1591, 1523, 1492, 1454, 1396, 1314, 1087, 744. ^{1}H NMR (500 MHz, DMSO-d_6 , 25 ˚C) : δ 11.64 (s, 1H, N*H*), 9.89 (s, 1H, N*H*), 7.75 (d, J = 2.7 Hz, 1H, Ar*H*), 7.49 (d, J =8.2 Hz, 1H, Ar*H*), 7.47-7.7.40 (m, 3H, Ar*H*), 7.17 (dd, J = 7.1, 7.1 Hz, 1H, Ar*H*), 7.08-7.00 (m, 3H, Ar*H*), 2.01 (s, 3H, CH_3). ^{13}C NMR (126 MHz, DMSO-d_6, 25 °C): δ 168.09, 136.82, 136.68, 132.38, 132.04, 128.59, 126.55, 122.05, 120.00, 119.68, 118.33, 112.28, 100.32, 23.88. HRMS (ESI-): m/z calculated for $C_{16}H_{14}N_2OS$ ($M - H^+$), 281.0743; found, 281.0748.

Spectroscopic data of **3f**[S8]: ^{1}H NMR (500 MHz, DMSO-d_6) : δ 11.53 (s, 1H, N*H*), 9.34 (s, 1H, O*H*), 7.68 (d, J = 2.5 Hz, 1H, Ar*H*), 7.44 (d, J = 8.7 Hz, 2H, Ar*H*), 7.15 (dd, J = 8.1, 8.1 Hz, 1H, Ar*H*), 7.05 (dd, J = 7.8, 7.8 Hz, 1H, Ar*H*), 7.00 (d, J = 8.7 Hz, 2H, Ar*H*), 6.64 (d, J = 8.7 Hz, 2H, Ar*H*)). ^{13}C NMR (126 MHz, DMSO-d_6, 25 °C): δ 155.68, 136.58, 131.45, 128.91,128.65, 126.95, 121.94, 119.86, 118.42, 115.94, 112.18, 102.11.

Spectroscopic data of **3g**[S6]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 ˚C) : δ 8.25 (br s, 1H, N*H*), 7.65 (d, J = 7.9 Hz, 1H, Ar*H*), 7.34-7.30 (m, 2H, Ar*H*), 7.23-7.16 (m, 2H, Ar*H*), 7.14 (dd, J = 7.2 Hz, 1H, Ar*H*), 6.99 (ddd, J = 8.3, 6.9, 0.7 Hz, 1H, Ar*H*), 6.66 (dd, J = 8.0, 1.3 Hz, 1H, Ar*H*), 6.60 (ddd, J = 8.1, 6.9, 0.5 Hz, 1H, ArH), 4.22 (br s, 2H, NH_2). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ 145.73, 136.44, 132.05, 129.11, 128.86, 128.16, 123.00, 120.84, 120.80, 119.57, 119.03, 115.49, 111.66, 104.44.

Spectroscopic data of **3h**[S9]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.25 (br s, 1H, N*H*), 7.32 (d, J = 2.7 Hz, 1H, Ar*H*), 7.21 (d, J = 8.8 Hz, 1H, Ar*H*), 7.05 (d, J = 2.4 Hz, 1H, Ar*H*), 7.01 (d, J = 8.3 Hz, 2H, Ar*H*), 6.95 (d, J = 8.1 Hz, 2H, Ar*H*), 6.88 (dd, J = 8.8, 2.5 Hz, 1H, Ar*H*), 3.74 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 155.08, 135.69, 134.69, 131.45, 131.34, 130.03, 129.62, 126.10, 113.51, 112.56, 102.64, 100.91, 55.86, 20.91.

Spectroscopic data of **3i**[S9]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.32 (br s, 1H, N*H*), 7.74 (d, J = 1.9 Hz, 1H, Ar*H*), 7.39 (d, J = 2.6 Hz, 1H, Ar*H*), 7.31 (dd, J = 8.6, 1.6 Hz, 1H, Ar*H*), 7.23 (d, J = 8.1 Hz, 1H, Ar*H*), 7.03-6.92 (m, 4H, ArH), 2.24 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 135.18, 135.12, 135.03, 131.74, 131.06, 129.74, 126.44, 126.12, 122.30, 114.49, 113.18, 103.48, 20.97.

Spectroscopic data of **3j**[S6]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.97 (br s, 1H, N*H*), 7.54 (d, J = 7.7 Hz, 1H, Ar*H*), 7.24 (d, J = 7.9 Hz, 1H, Ar*H*), 7.15 (dd, J = 7.0, 7.0 Hz, 1H, Ar*H*), 7.09 (dd, J = 7.0, 7.0 Hz, 1H, Ar*H*), 6.97-6.88 (m, 4H, Ar*H*), 2.40 (s, 3H, CH_3), 2.21 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): δ 141.08, 135.75, 135.48, 134.43, 130.38, 129.59, 125.88, 122.18, 120.72, 119.03, 110.78, 99.80, 20.92, 12.14.

Spectroscopic data of **3k**[S9]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.60 (d, J = 8.0 Hz, 1H, Ar*H*), 7.34 (d, J = 8.2 Hz, 1H, Ar*H*), 7.30-7.22 (m, 2H, Ar*H*), 7.14 (dd, J = 7.5, 7.5 Hz, 1H, Ar*H*), 7.01 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H, Ar*H*), 3.78 (s, 3H, CH_3), 2.23 (s, 3H, CH_3). ^{13}C

NMR (126 MHz, $CDCl_3$): δ 137.58, 136.04, 134.93, 134.57, 129.90, 129.52, 126.22, 122.55, 120.48, 119.79, 109.78, 101.21, 33.09, 20.93.

Spectroscopic data of **3l**[S10]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.56 (d, J = 7.9 Hz, 1H, Ar*H*), 7.36 (d, J = 8.2 Hz, 1H, Ar*H*), 7.32-7.24 (m, 2H, Ar*H*), 7.15 (dd, J = 7.5, 7.5 Hz, 1H, Ar*H*), 7.08 (d, J = 8.7 Hz, 2H, Ar*H*), 6.99 (d, J = 8.7 Hz, 2H, Ar*H*), 3.80 (s, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ 138.42, 137.69, 135.19, 130.51, 129.65, 128.81, 127.10, 122.83, 120.76, 119.67, 109.95, 100.17, 33.26.

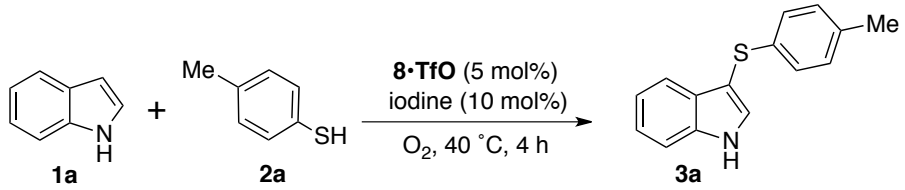
Spectroscopic data of **3m**[S6]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H, N*H*), 7.69 (d, J = 7.7 Hz, 1H, Ar*H*), 7.25 (d, J = 7.7 Hz, 1H, Ar*H*), 7.21-7.13 (m, 5H, Ar*H*), 7.08-7.01 (m, 2H, Ar*H*), 6.88 (d, J = 2.5 Hz, 1H, Ar*H*), 3.83 (s, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.07, 136.20, 129.94, 129.24, 129.04, 128.28, 126.83, 122.68, 120.51, 119.30, 111.58, 105.08, 41.03.

Spectroscopic data of **3n**[S11]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H, N*H*), 7.77 (d, J = 7.4 Hz, 1H, Ar*H*), 7.31 (d, J = 7.3 Hz, 1H, Ar*H*), 7.26-7.14 (m, 3H, Ar*H*), 2.68 (t, J = 7.4 Hz, 2H, CH_2), 1.53 (q, J = 7.4 Hz, 2H, CH_2), 1.35 (q, J = 7.1 Hz, 2H, CH_2), 1.31-1.15 (m, 8H, CH_2), 0.86 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.34, 129.53, 129.31, 122.70, 120.44, 119.47, 111.57, 106.21, 36.54, 31.90, 30.00, 29.30, 28.66, 22.74, 14,20.

Effects of solvents and iodine sources on catalytic sulfenylation of 1a with 2a.

The reaction condition of the flavin-iodine-catalyzed direct sulfenylation was optimized as shown in Table S1.

Table S1 Screening of solvents and iodine sources [a]



entry	solvent	iodine	yield (%)[b]
1	$CHCl_3$	I_2	43
2	1,2-dichloroethane	I_2	50
3	AcOEt	I_2	7
4	THF	I_2	13
5	1,4-dioxane	I_2	14
6	DMC	I_2	32
7	DMAc	I_2	28
8	DMF	I_2	52
9	*t*-BuOH	I_2	37
10	MeOH	I_2	40
11	CH_3CN	I_2	57
12	CH_3CN	TBAI[c]	30
13	CH_3CN	NH_4I[c]	30
14	CH_3CN	KI[c]	30

[a] Conditions: **1a** (0.6 M), **2a** (0.5 M), **8•TfO** (5 mol%), and iodine (10 mol%) under O_2 (1 atm) at 40 ˚C for 4 h. [b] Yield was calculated on the basis of **2a**, as determined by GC. [c] 20 mol% of iodine source was used.

Time-course of the aerobic sulfenylation of indole

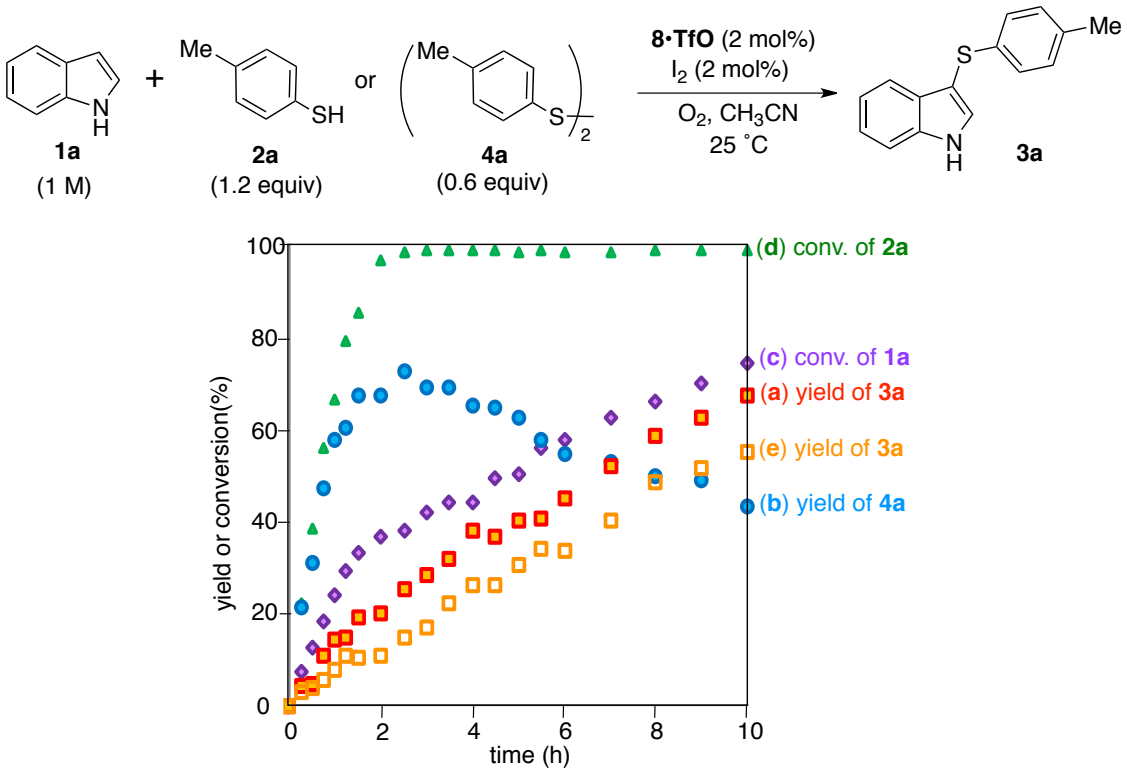
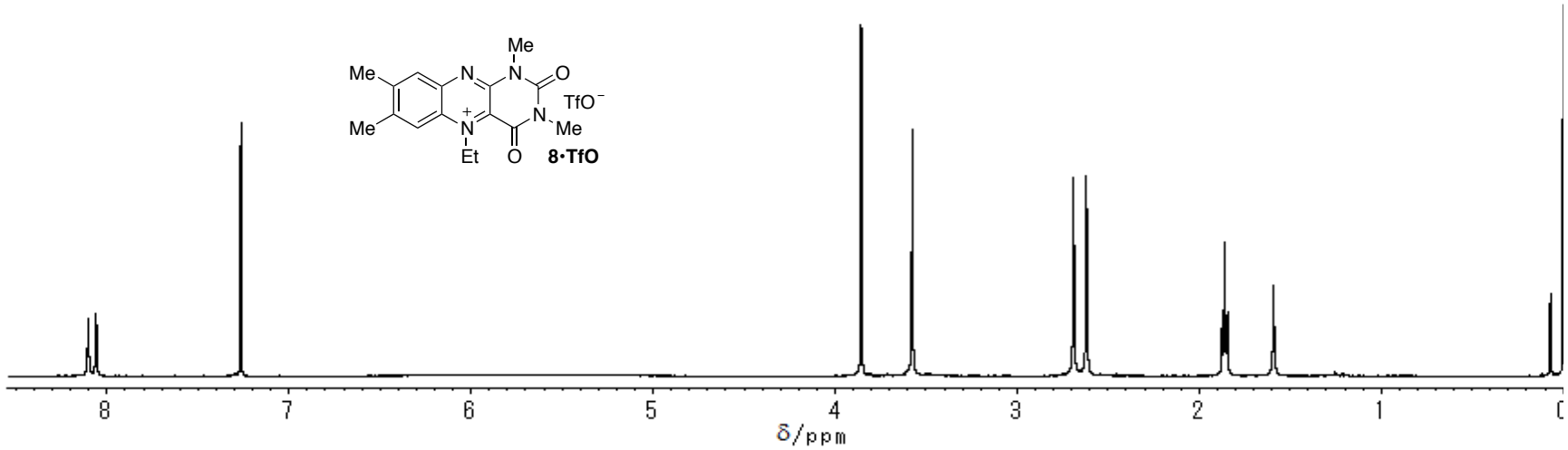
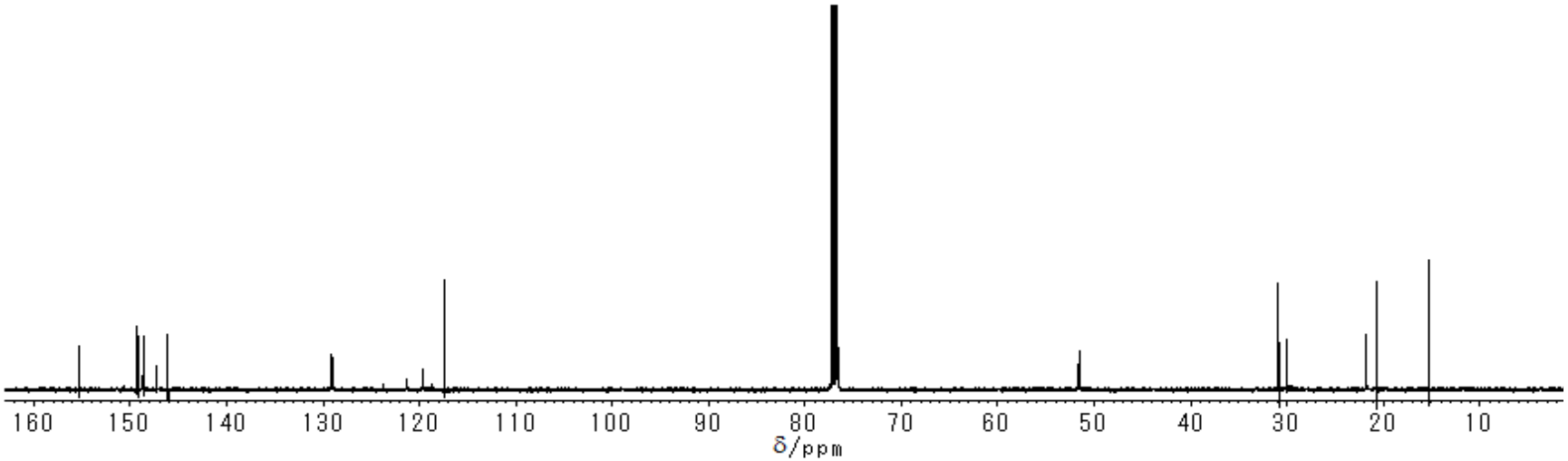


Fig. S1 Time-course of the yields and conversions of the products and substrates in aerobic sulfenylation of **1a** with **2a** (a-d) and **4a** (e) catalyzed by **8•TfO** and I_2. The plotted values are average of three (a-d) or two runs (e).

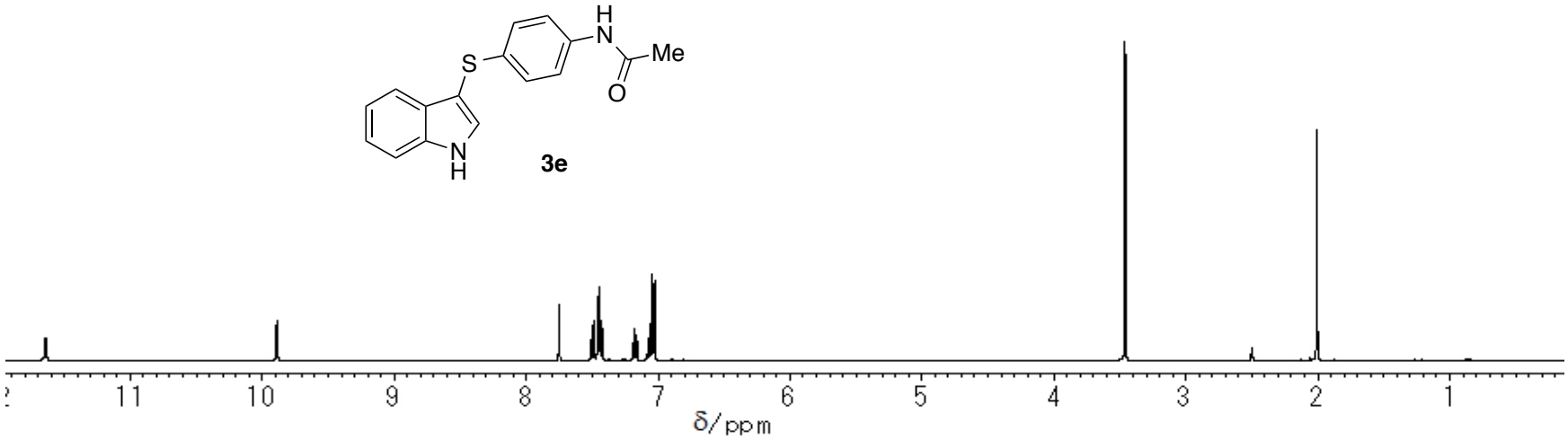
4. ^{1}H and ^{13}C NMR Spectra of Novel Compounds



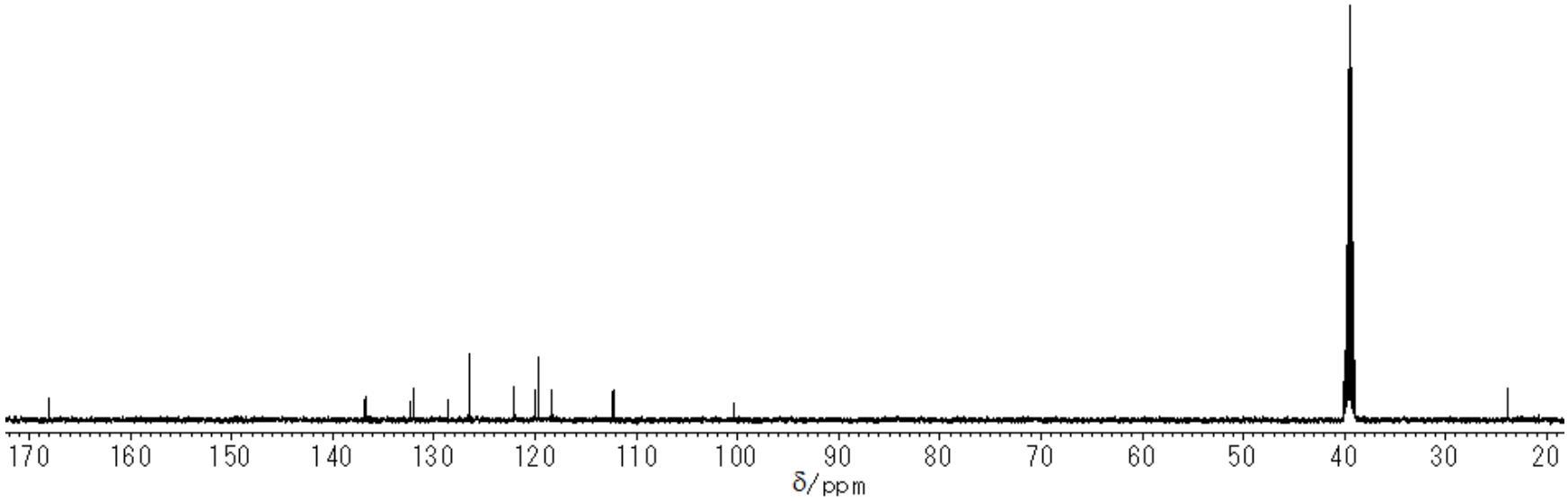
Spectrum S1. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **8•TfO**.



Spectrum S2. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **8•TfO**.

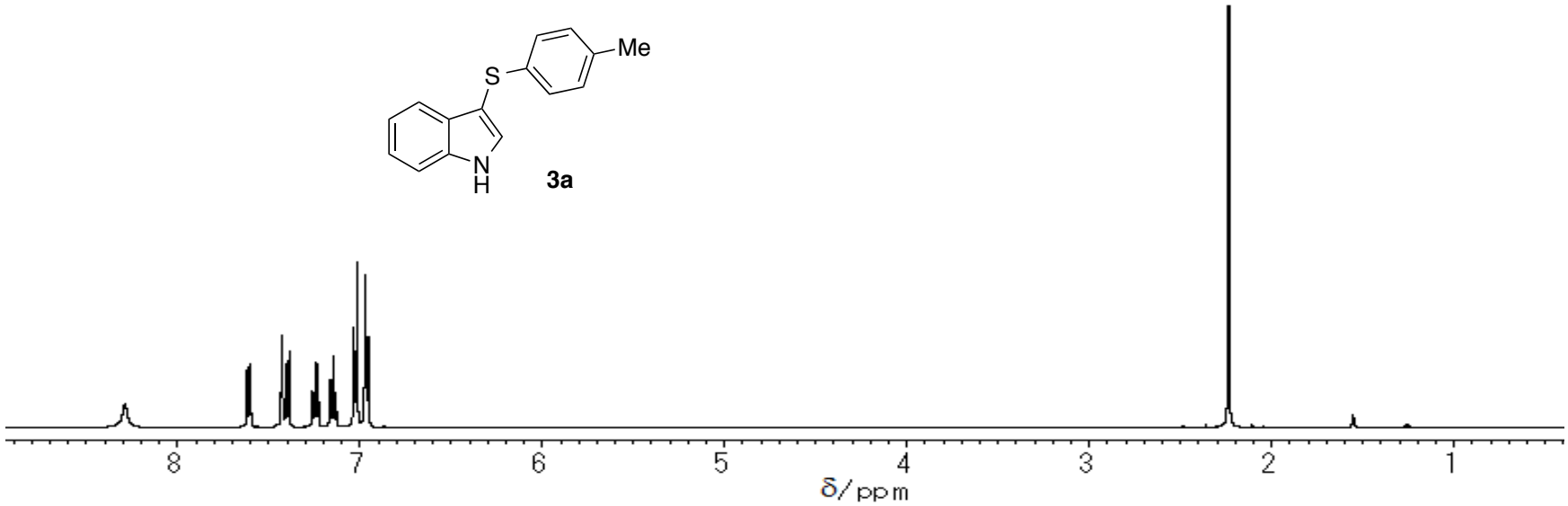


Spectrum S3. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **3e**.

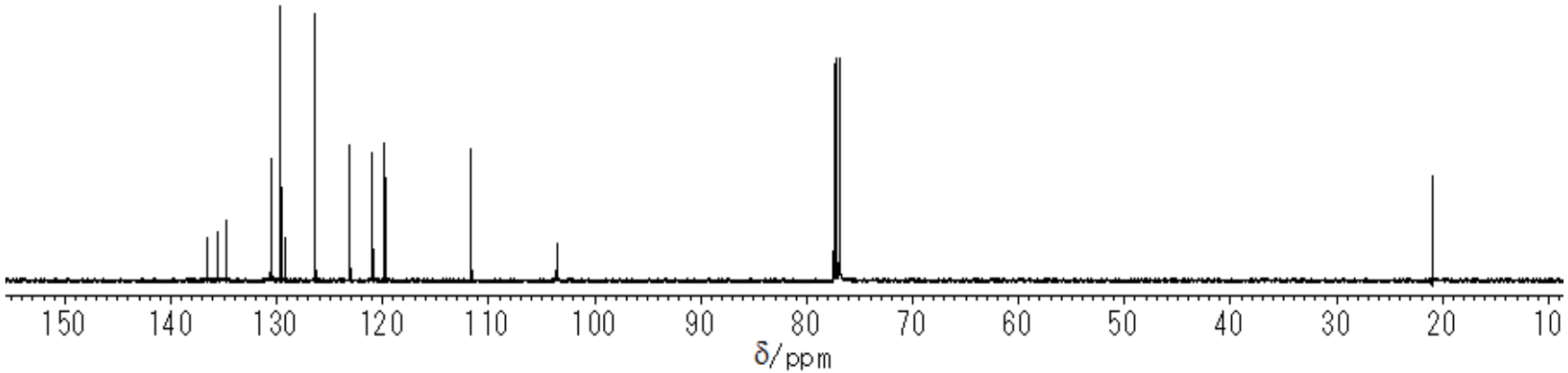


Spectrum S4. ^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of compound **3e**.

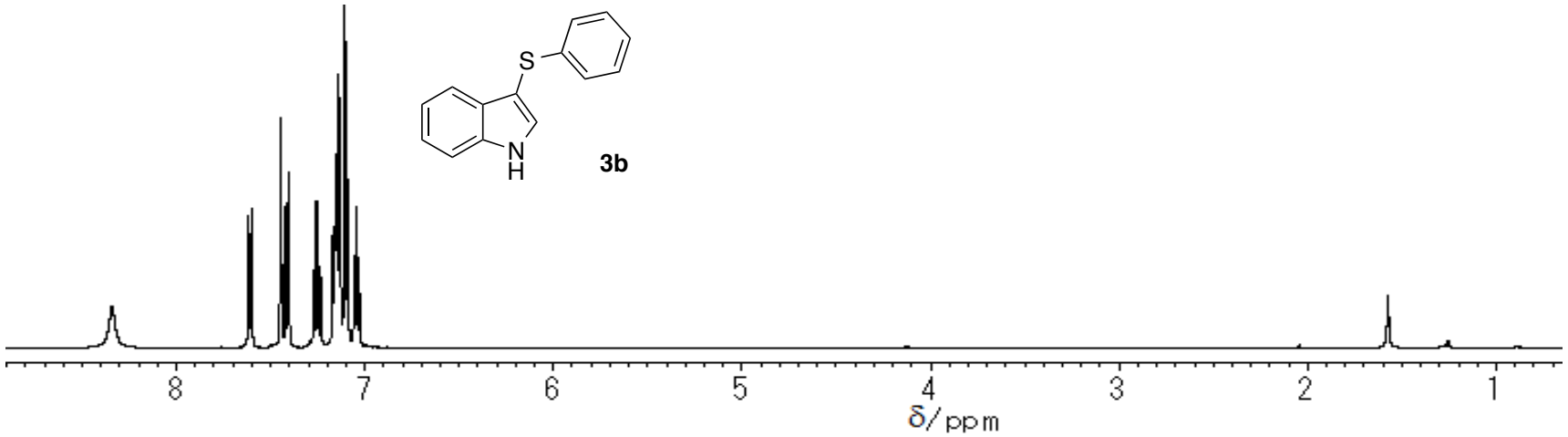
5. ^{1}H and ^{13}C NMR Spectra of Known Compounds



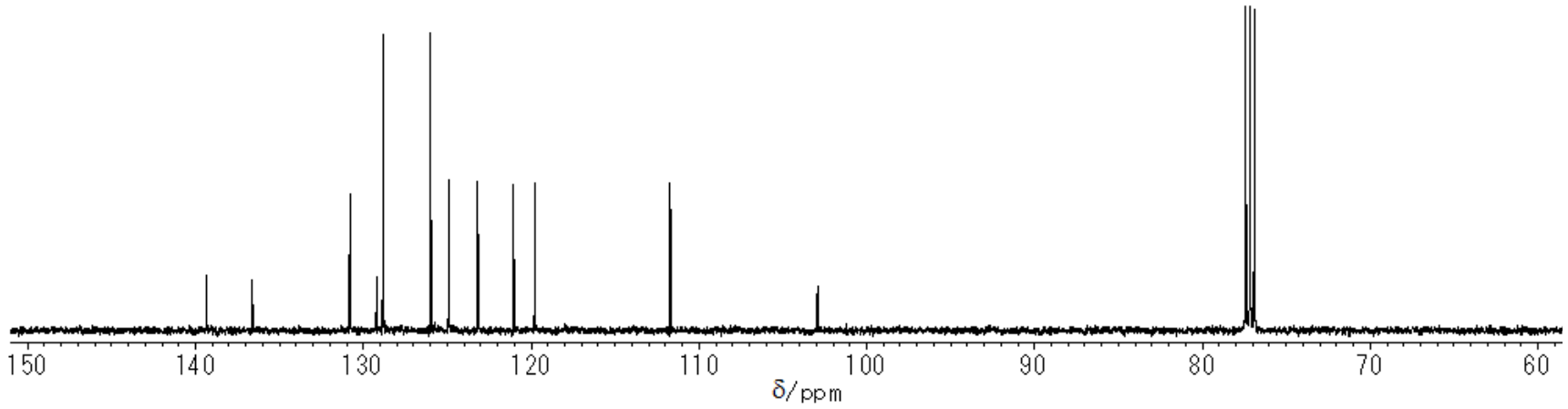
Spectrum S5. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3a**.



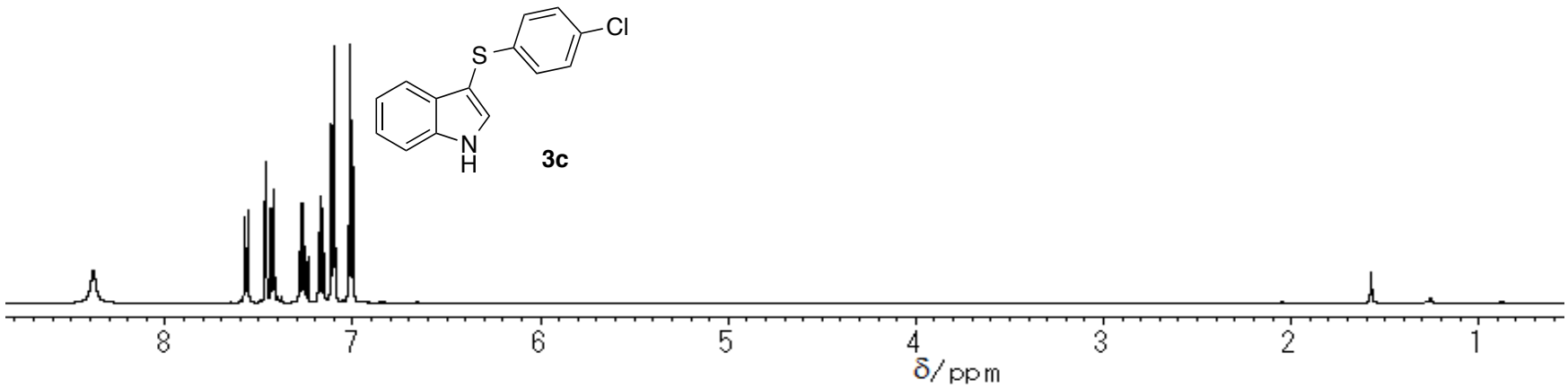
Spectrum S6. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3a**.



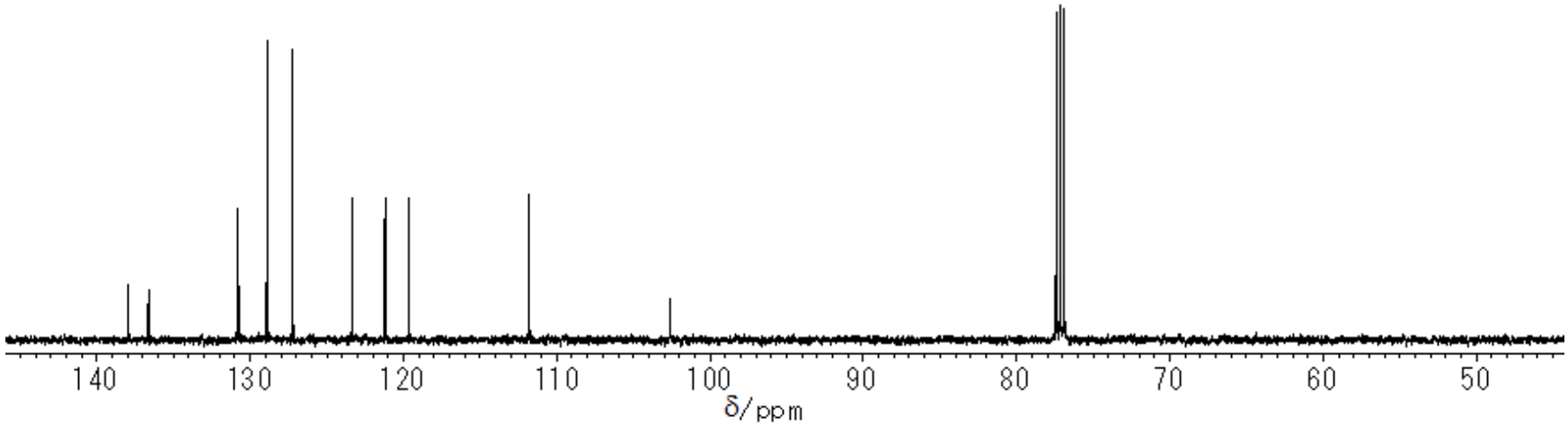
Spectrum S7. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3b**.



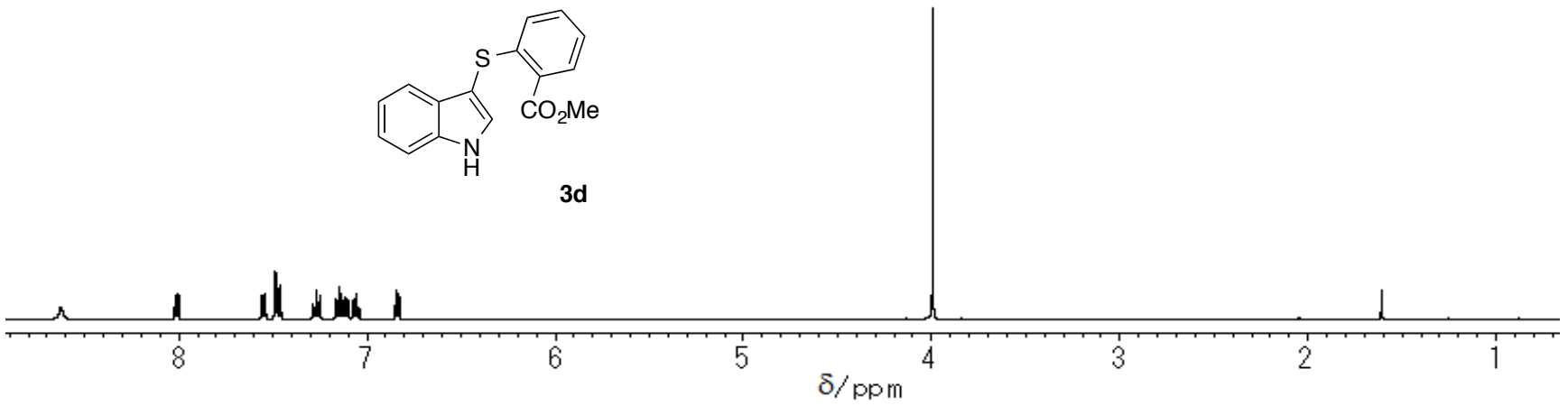
Spectrum S8. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3b**.



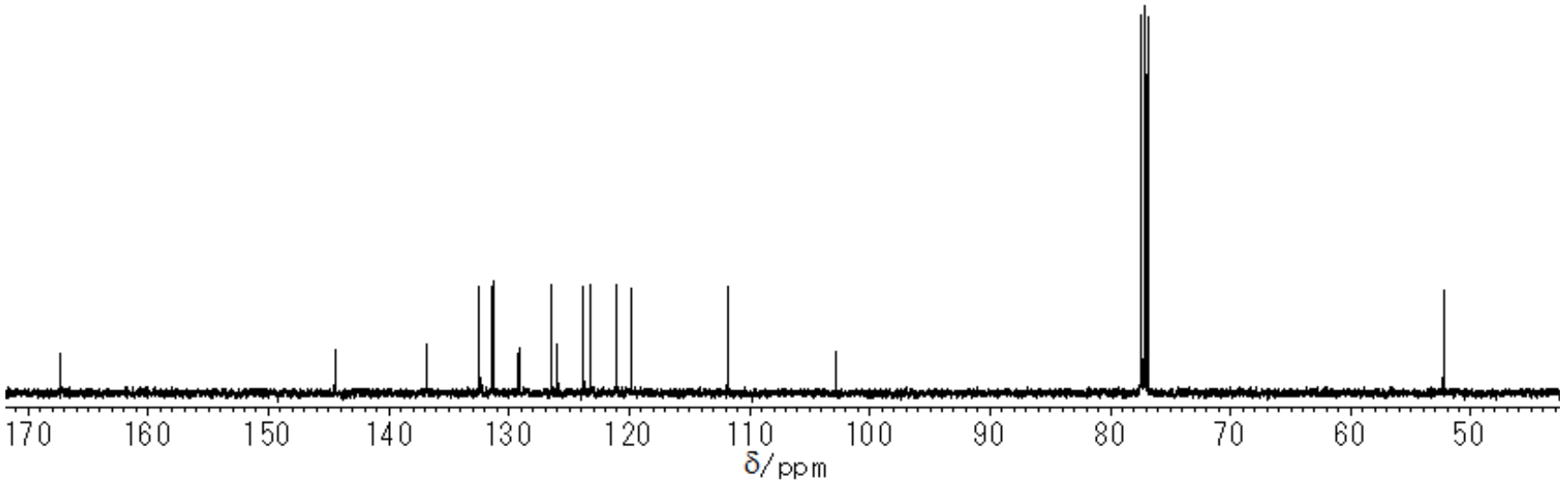
Spectrum S9. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3c**.



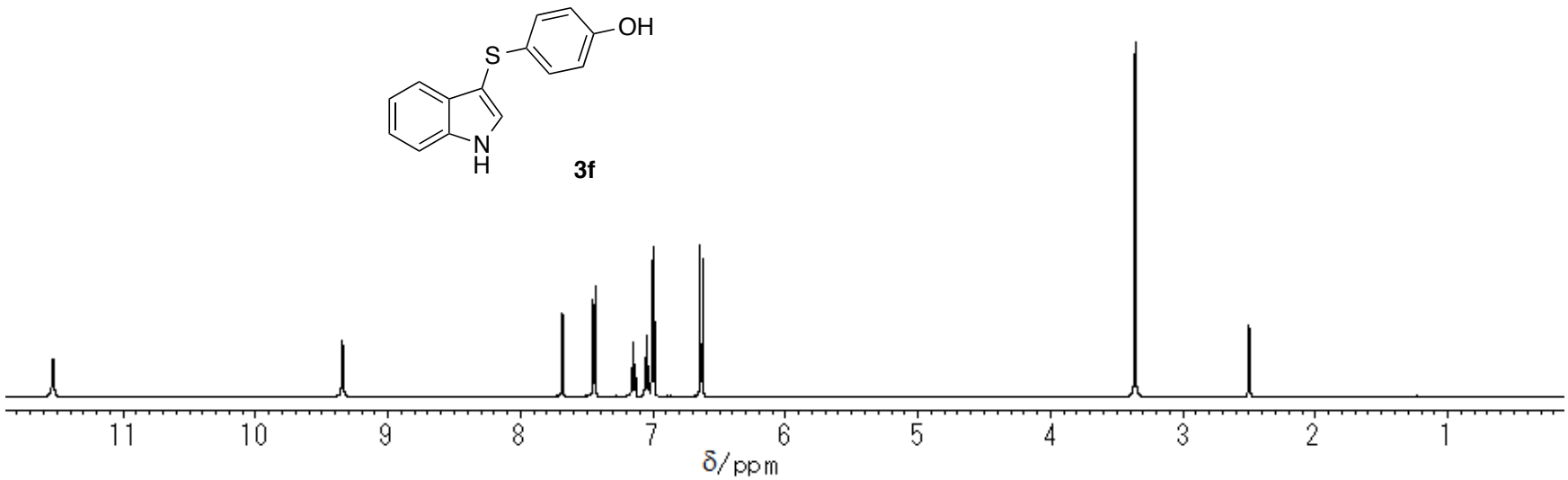
Spectrum S10. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3c**.



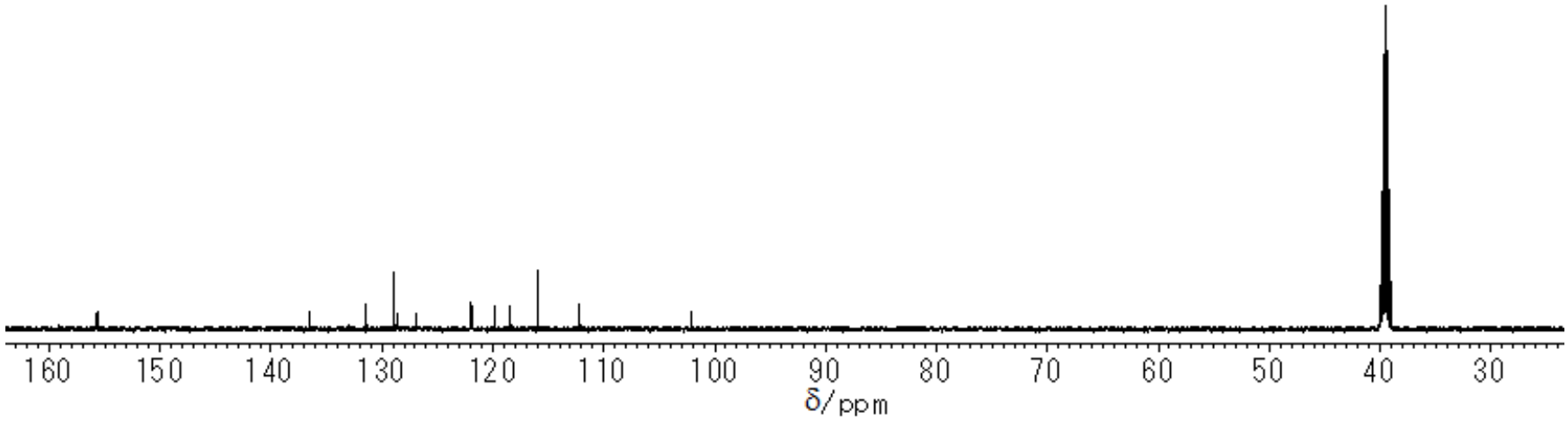
Spectrum S11. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3d**.



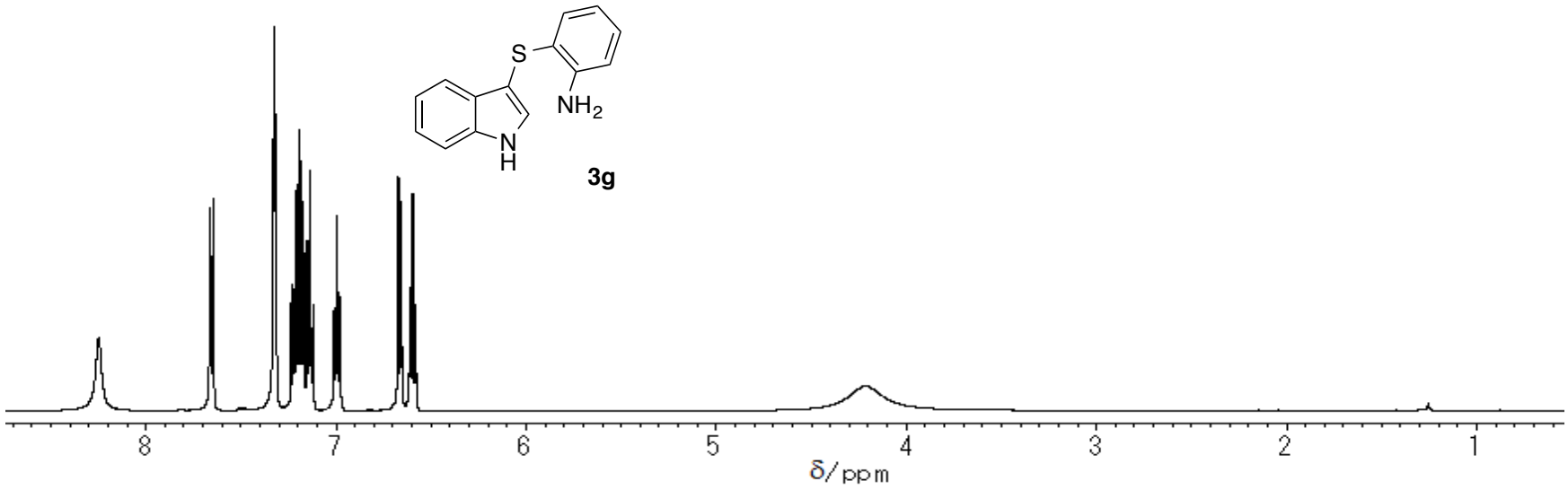
Spectrum S12. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3d**.



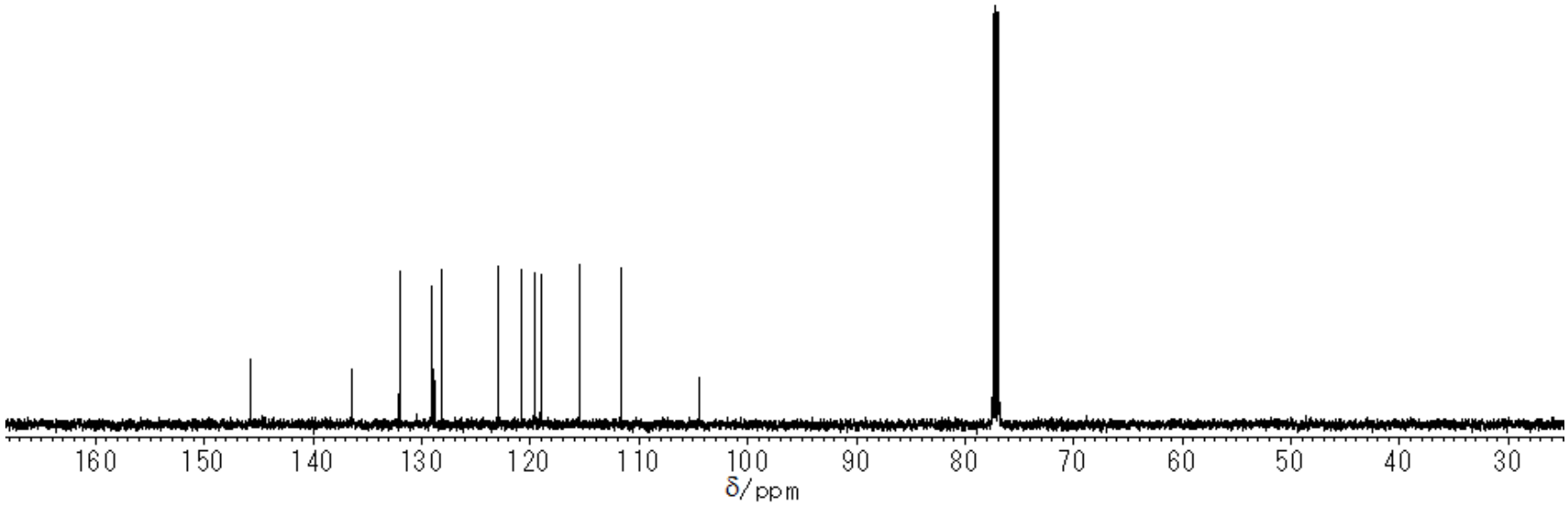
Spectrum S13. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of compound **3f**.



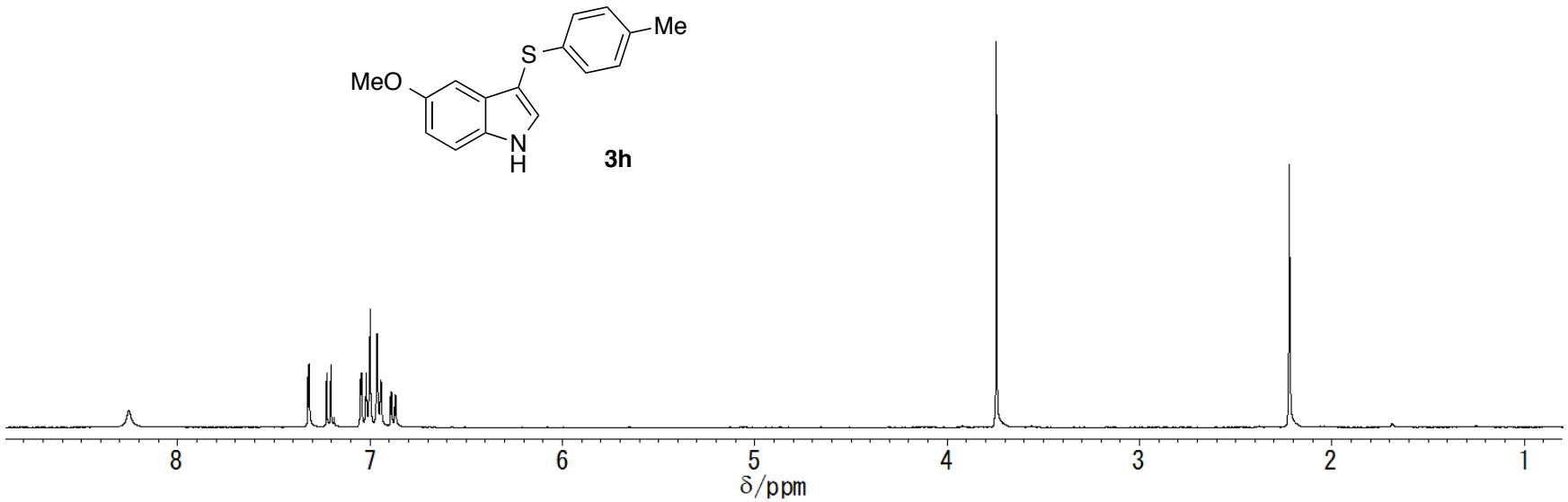
Spectrum S14. ^{13}C NMR (DMSO-d_6, 126 MHz) spectrum of compound **3f**.



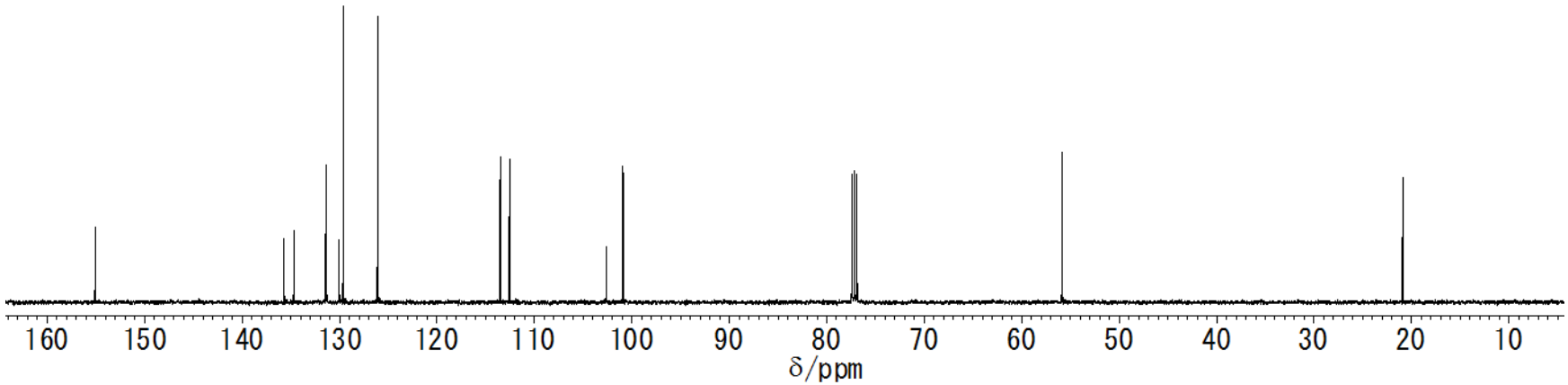
Spectrum S15. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3g**.



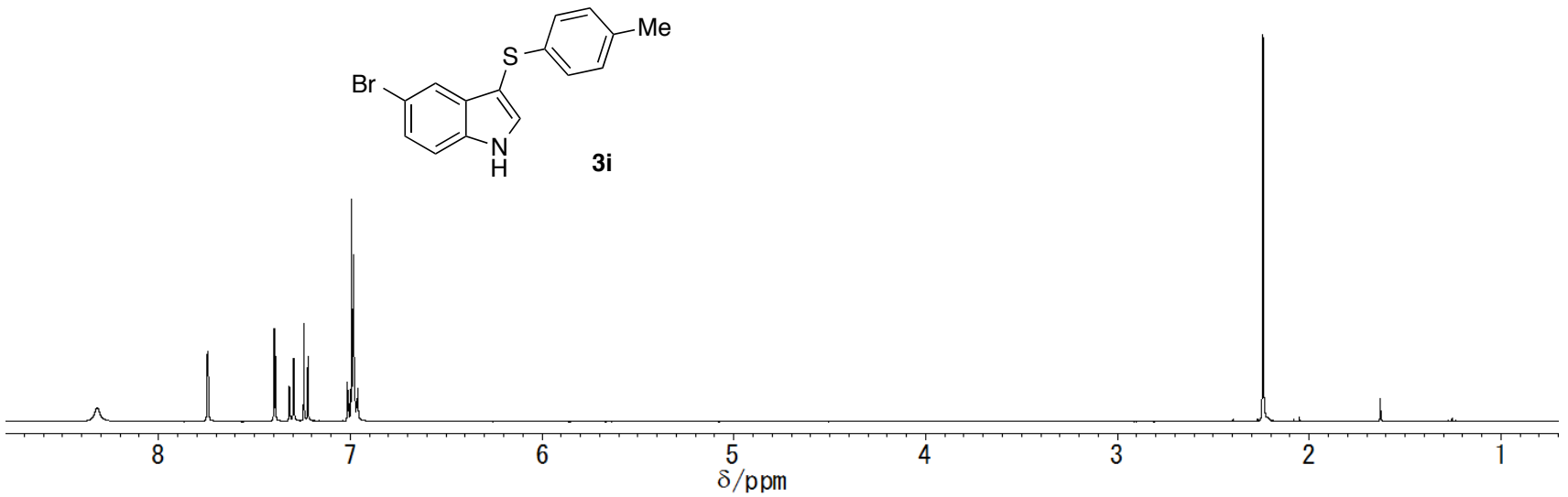
Spectrum S16. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3g**.



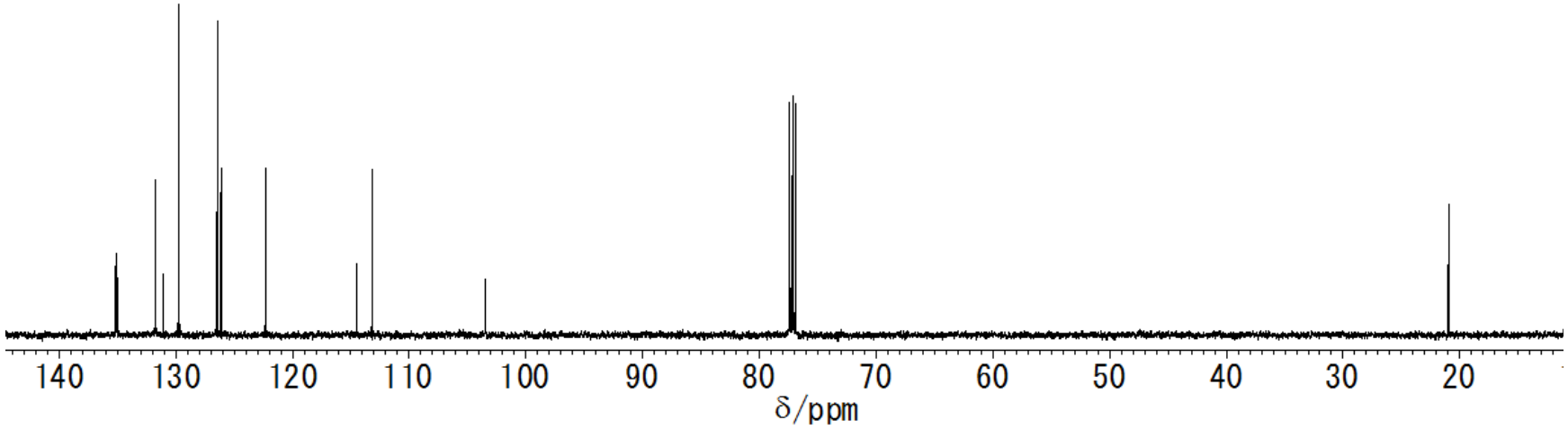
Spectrum S17. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3h**.



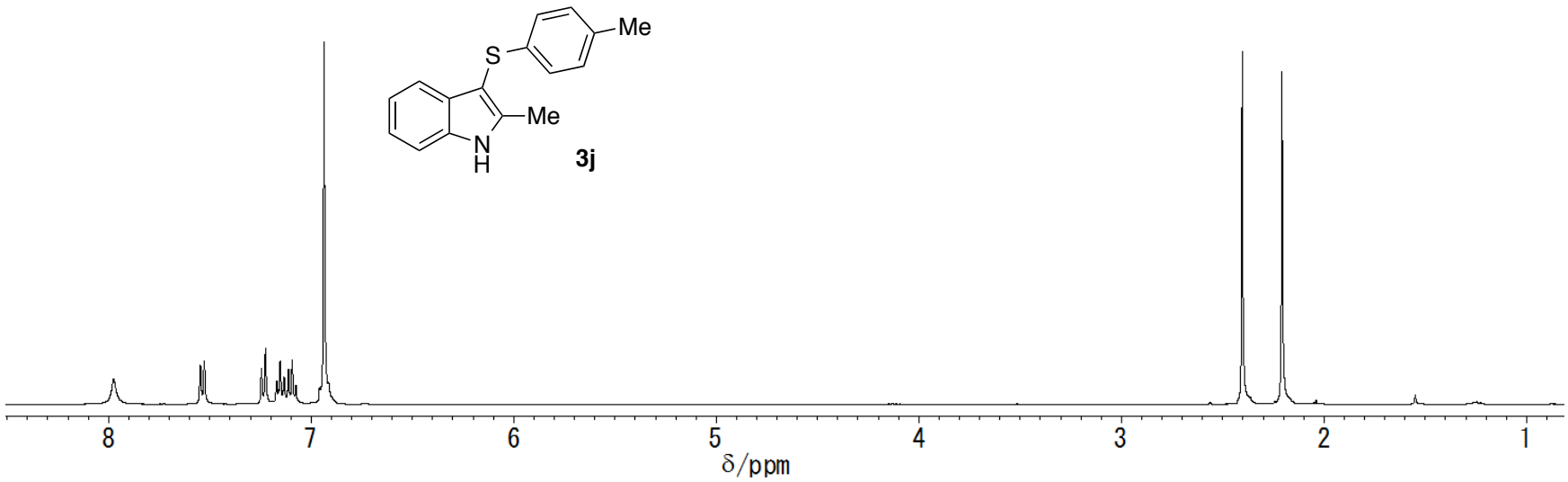
Spectrum S18. ^{13} NMR ($CDCl_3$, 126 MHz) spectrum of compound **3h**.



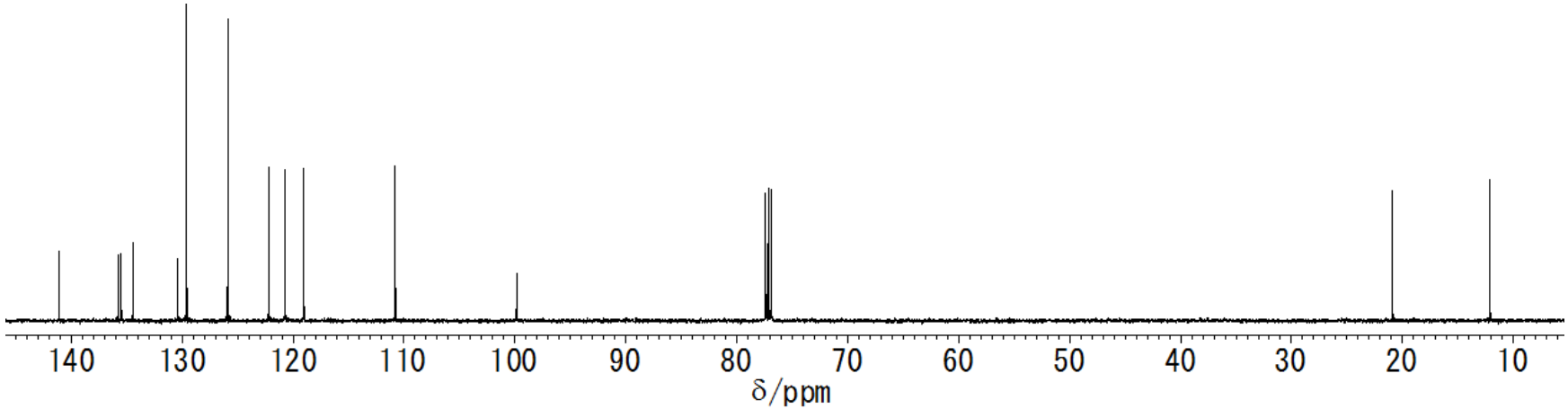
Spectrum S19. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3i**.



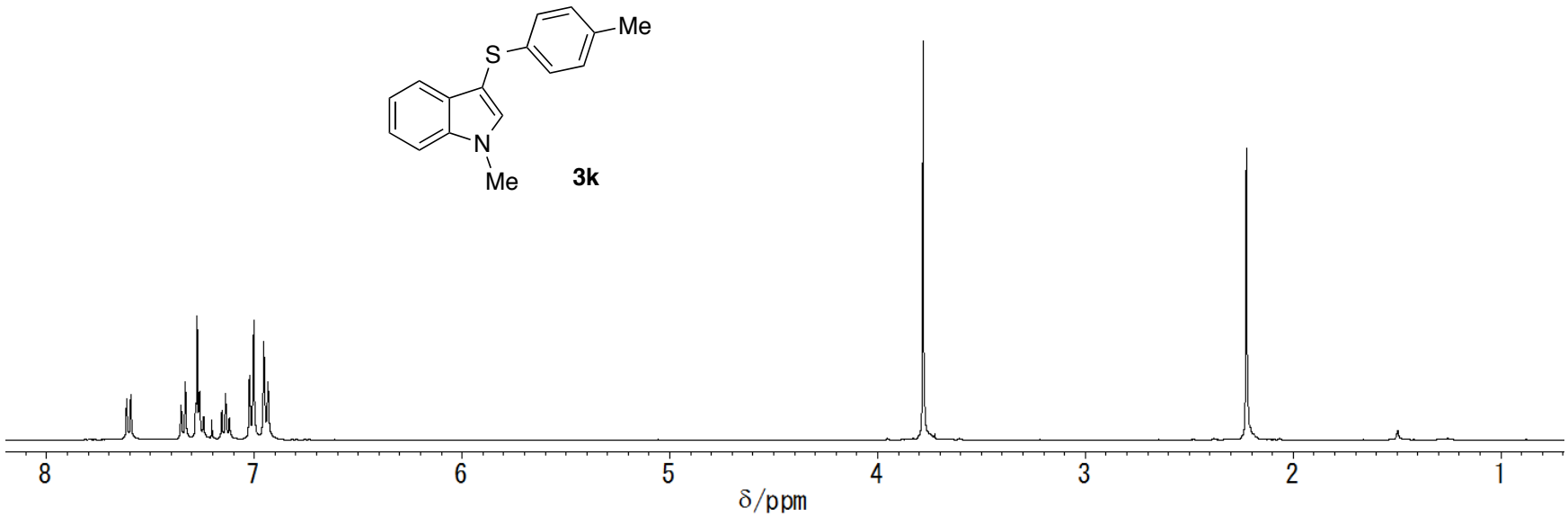
Spectrum S20. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3i**.



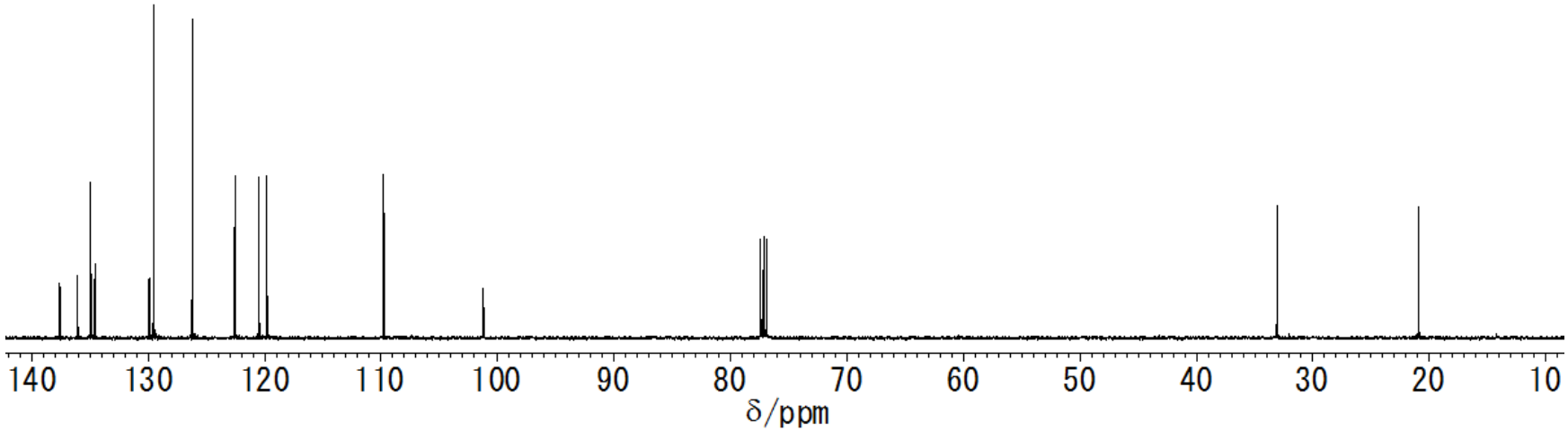
Spectrum S21. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3j**.



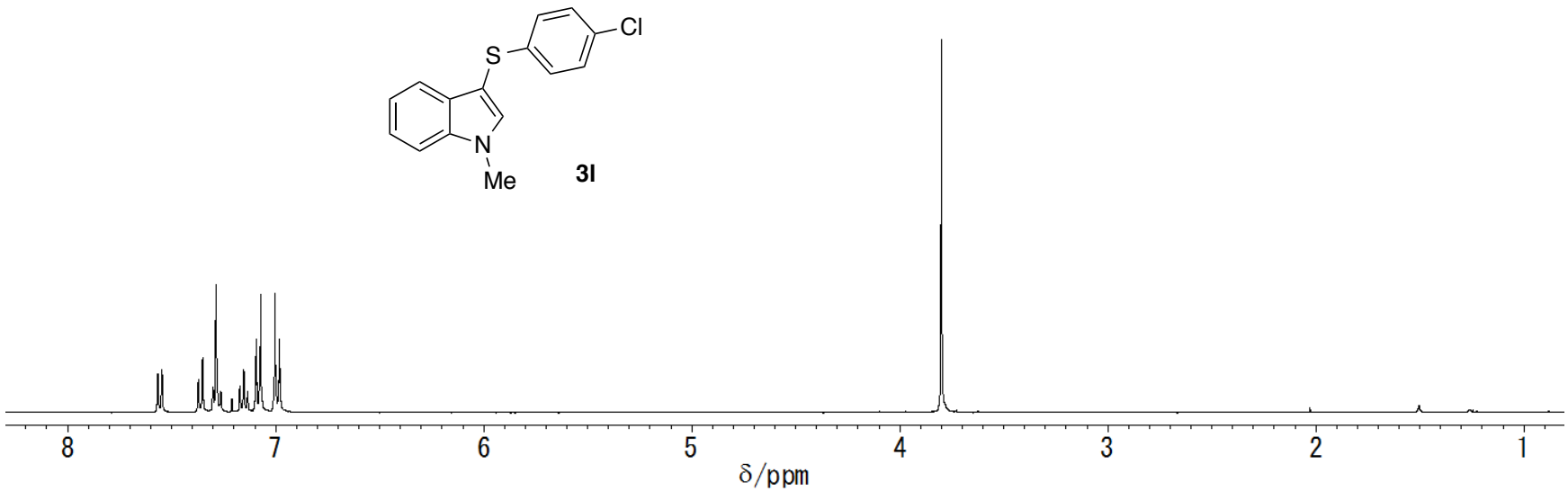
Spectrum S22. ^{13}H NMR ($CDCl_3$, 126 MHz) spectrum of compound **3j**.



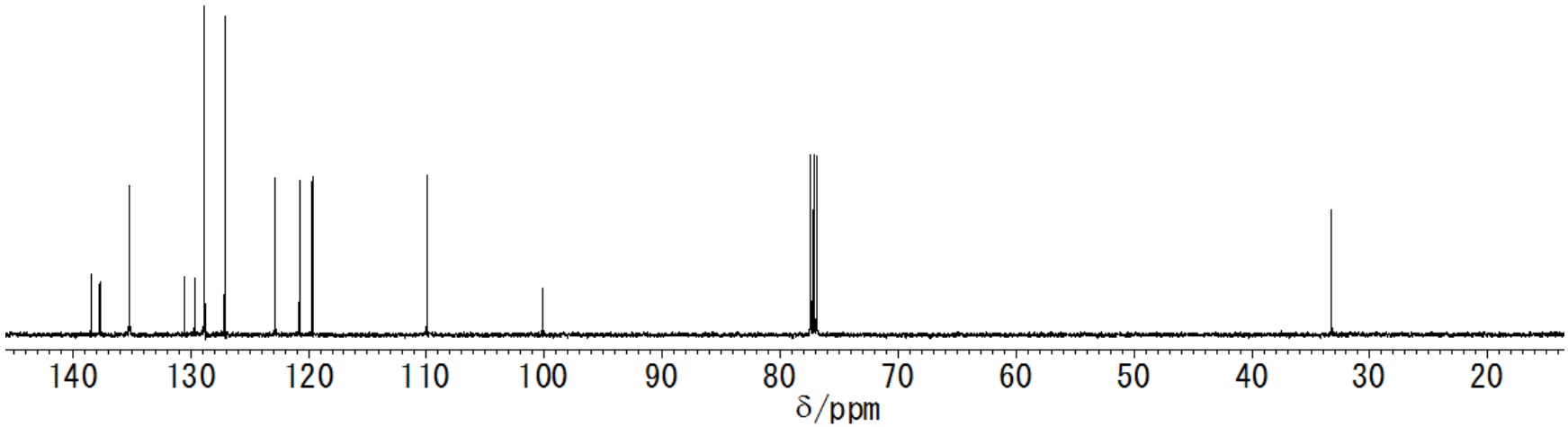
Spectrum S23. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3k**.



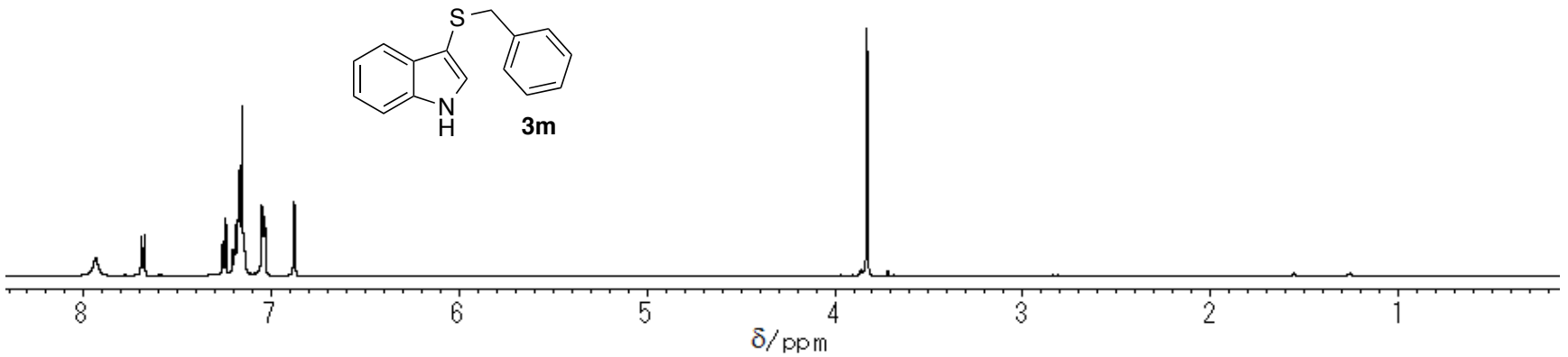
Spectrum S24. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3k**.



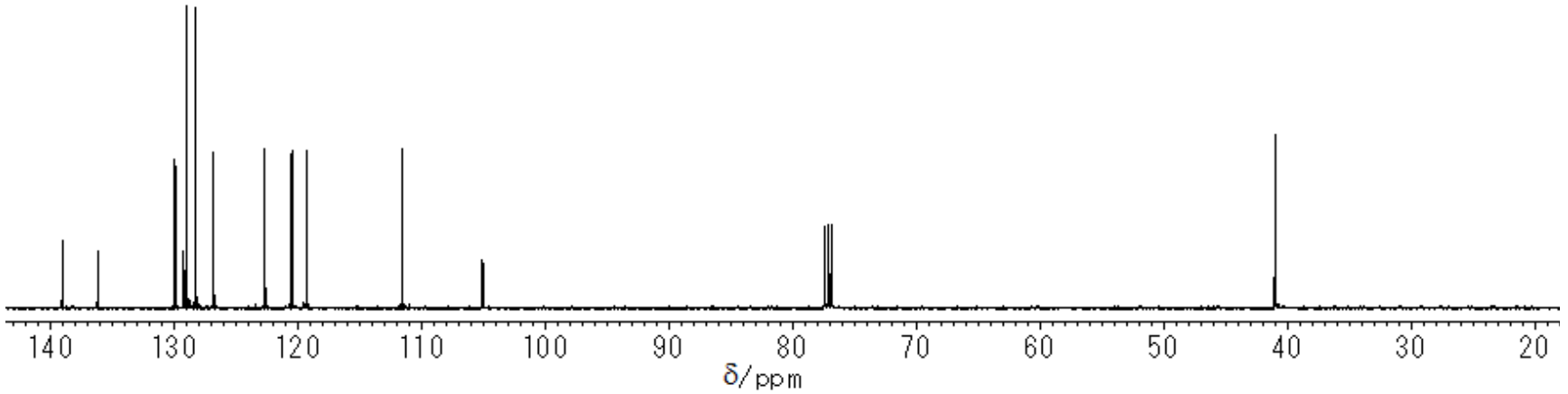
Spectrum S25. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3l**.



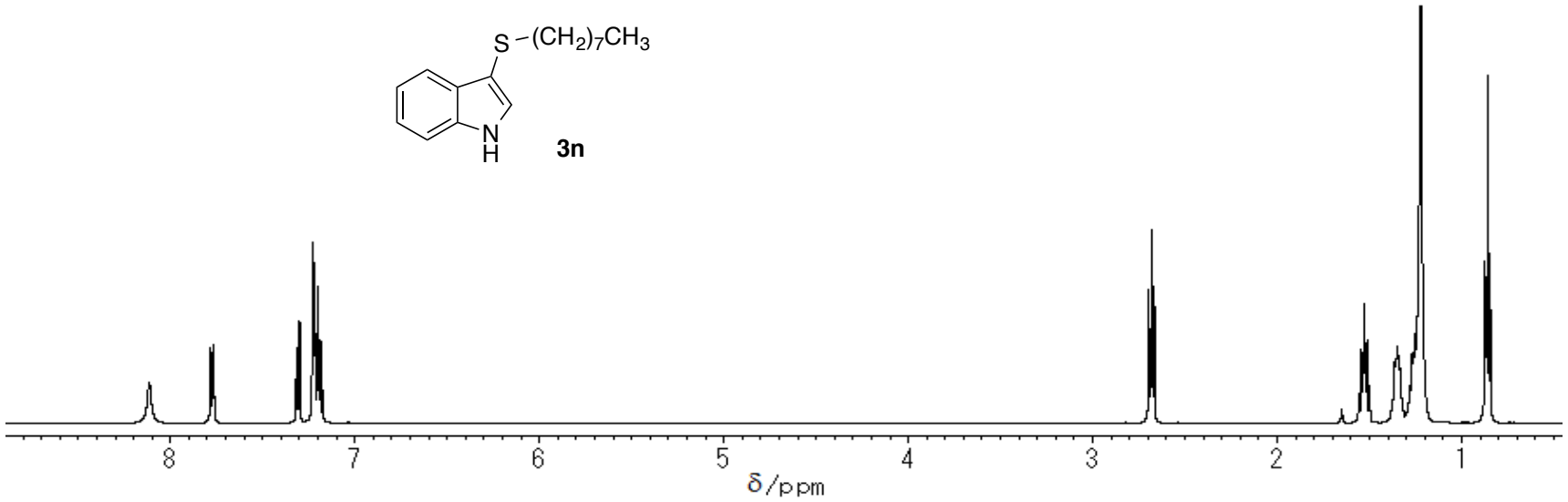
Spectrum S26. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3l**.



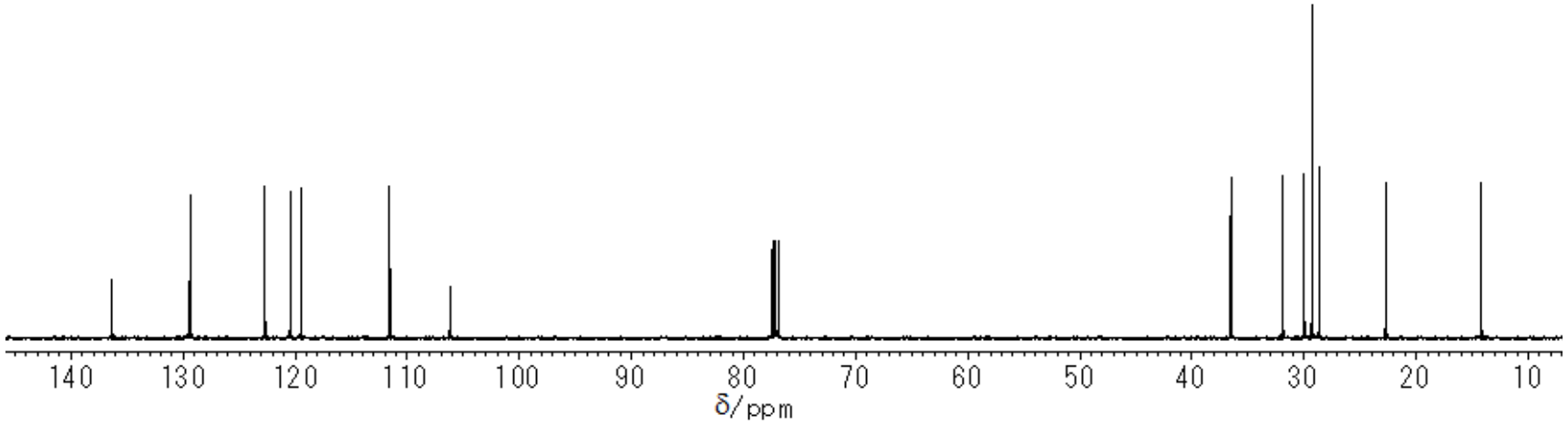
Spectrum S27. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3m**.



Spectrum S28. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3m**.



Spectrum S29. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of compound **3n**.



Spectrum S30. ^{13}C NMR ($CDCl_3$, 126 MHz) spectrum of compound **3n**

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