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TfNHNHBoc as a SCF_3 source in the sulfenylation of indoles

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Supporting information

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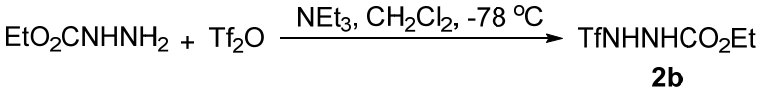
General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) and were referenced internally with tetramethylsilane (δ H 0.00), $CDCl_3$ (δ C 77.16), and acetone-d_6 (δ H 2.05, δ C 29.84). ^{19}F NMR was recorded on a Bruker AC-400 FT spectrometer (376 MHz, $CFCl_3$ as an external standard). Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Electrospray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. Melting points are uncorrected.

Trifluoromethanesulfonyl hydrazides **2a** and **2c**-**f** were prepared according to literature procedures.[1] The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, Adamas, and TCI, and used as received.

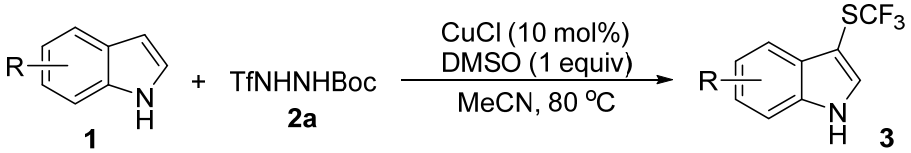
Abbreviations: Bn = benzyl, Boc = *tert*-butoxycarbonyl, Cbz = benzyloxycarbonyl, DCE = 1,2-dichloroethane, DMF = *N,N*-dimethylformamide, DMSO = dimethyl sulfoxide, TBHP = *tert*-butyl hydroperoxide, Tf = trifluoromethylsulfonyl, Ts = *p*-toluenesulfonyl.

Preparation of $TfNHNHCO_2Et$



To a solution of triflic anhydride (5.64 g, 3.36 mL, 20.0 mmol) in dichloromethane (20 mL) was added dropwise to a mixture of EtO_2CNHNH_2 (2.08 g, 20.0 mmol) and triethylamine (2.23 g, 3.05 mL, 22.0 mmol) in dichloromethane (100 mL) under nitrogen at -78 °C. The mixture was allowed to warm to room temperature and stirred for 2 h, then washed twice with water, once with 5% aqueous hydrochloric acid, and once with water, dried over anhydrous sodium sulfate, and the solvent was evaporated in vacuum. The residue was purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (4:1 v/v), to give $TfNHNHCO_2Et$ (**2b**) as a white solid (1.30 g, 28% yield). m.p. 80-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, br, 1H), 6.87 (s, br, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 119.4 (q, J = 321.8 Hz), 63.9, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.94; HRMS (ESI) calcd for $C_4H_8F_3N_2O_4S^+$ $(M + H)^+$ 237.0151, found 237.0144.

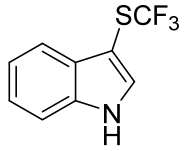
General procedure for the sulfenylation of indoles with TfNHNHBoc (Scheme 1)



To a reaction tube equipped with a magnetic stir bar was charged with TfNHNHBoc (**2a**) (211 mg, 0.80 mmol), indole **1** (0.40 mmol), and CuCl (4.0 mg, 10 mol%). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. DMSO (31.2 mg, 28 μL, 0.40 mmol) and MeCN (2.0 mL) were added via syringe with gentle stirring. The reaction vessel was allowed to stir at 80 °C for 10 h. The mixture was cooled to room temperature and purified directly by silica gel

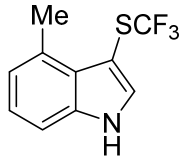
chromatography, eluting with ethyl acetate/petroleum ether (1:10~1:5 v/v), to give thioether **3**.

Analytical data for the products shown in Scheme 1



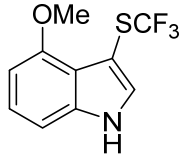
3a

3-((Trifluoromethyl)thio)-1*H*-indole (**3a**)[2] was obtained in 80% yield (69.4 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, br, 1H), 7.83-7.78 (m, 1H), 7.45-7.43 (m, 1H), 7.38-7.33 (m, 1H), 7.30-7.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 132.9, 129.6 (q, J = 309.9 Hz), 129.5, 123.5, 121.7, 119.3, 111.9, 95.3 (q, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.35.



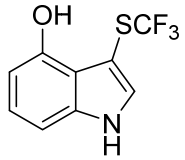
3b

4-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3b**)[3] was obtained in 64% yield (59.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, br, 1H), 7.38 (s, 1H), 7.17-7.13 (m, 2H), 6.97 (d, J = 6.0 Hz, 1H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.2, 131.7, 129.3 (q, J = 309.3 Hz), 126.8, 123.5, 109.9, 95.0 (q, J = 2.4 Hz), 19.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.76.



3c

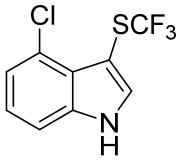
4-Methoxy-3-((trifluoromethyl)thio)-1*H*-indole (**3c**)[3] was obtained in 66% yield (65.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, br, 1H), 7.31 (s, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 138.0, 132.6, 129.6 (q, J = 309.4 Hz), 124.4, 118.6, 105.0, 102.2, 94.4 (q, J = 2.5 Hz), 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.40.



3d

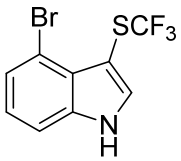
3-((Trifluoromethyl)thio)-1*H*-indol-4-ol (**3d**)[4] was obtained in 54% yield (50.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, br, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.78-6.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 137.8, 132.9, 128.4 (q, J = 311.0 Hz), 125.2, 116.6, 107.2, 104.6, 91.5 (q, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$)

δ -45.73.



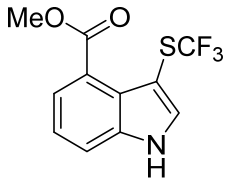
3e

4-Chloro-3-((Trifluoromethyl)thio)-1*H*-indole (**3e**) was obtained in 74% yield (74.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, br, 1H), 7.53 (d, J = 2.8 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.22-7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 135.1, 129.2 (q, J = 309.5 Hz), 126.8, 125.1, 124.1, 123.2, 110.8, 95.4 (q, J = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.46; HRMS (ESI) calcd for $C_9H_6ClF_3NS^+$ $(M + H)^+$ 251.9856, found 251.9862.



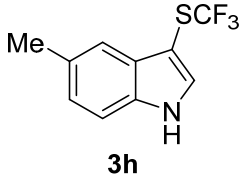
3f

4-Bromo-3-((trifluoromethyl)thio)-1*H*-indole (**3f**)[2] was obtained in 54% yield (64.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, br, 1H), 7.55 (d, J = 1.2 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.5, 129.1 (q, J = 309.5 Hz), 126.8, 126.1, 124.4, 114.4, 111.5, 96.3 (q, J = 2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.40.



3g

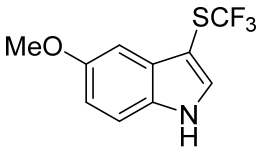
Methyl 3-((trifluoromethyl)thio)-1*H*-indole-4-carboxylate (**3g**) was obtained in 71% yield (78.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, br, 1H), 7.60-7.57 (m, 1H), 7.48-7.43 (m, 2H), 7.21 (t, J = 7.8 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 137.4, 136.2, 129.6 (q, J = 309.3 Hz), 125.6, 124.4, 123.3, 122.4, 115.9, 94.6 (d, J = 2.3 Hz), 52.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.10; HRMS (ESI) calcd for $C_{11}H_9F_3NO_2S^+$ $(M + H)^+$ 276.0301, found 276.0306.



3h

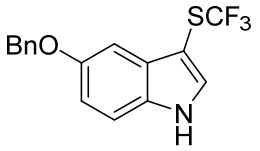
5-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3h**)[2] was obtained in 68% yield (62.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, br, 1H), 7.58 (s, 1H), 7.36 (d, J = 2.8 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.09 (dd, J = 8.4, 1.2 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4,

133.0, 131.4, 129.8, 129.6 (q, J = 309.9 Hz), 125.2, 118.9, 111.5, 94.8 (q, J = 2.3 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.50.



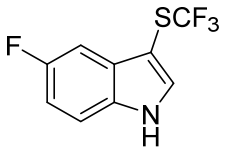
3i

5-Methoxy-3-((trifluoromethyl)thio)-1*H*-indole (**3i**)[2] was obtained in 76% yield (75.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, br, 1H), 7.43 (d, J = 2.8 Hz, 1H), 7.26-7.22 (m, 2H), 6.93 (d, J = 8.8 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 133.4, 131.0, 130.4, 129.6 (q, J = 309.9 Hz), 114.1, 112.7, 100.6, 95.0, 55.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.59.



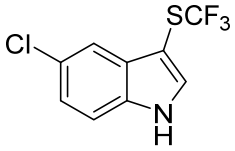
3j

5-(Benzyloxy)-3-((trifluoromethyl)thio)-1*H*-indole (**3j**) was obtained in 52% yield (67.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, br, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.33-7.27 (m, 3H), 7.17-7.13 (m, 1H), 6.96 (dd, J = 8.8, 2.4 Hz, 1H), 5.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 137.2, 133.6, 131.2, 130.3, 129.6 (d, J = 310.0 Hz), 128.7, 128.2, 128.0, 114.5, 112.8, 102.1, 94.8 (d, J = 2.3 Hz), 71.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.47; HRMS (ESI) calcd for $C_{16}H_{13}F_3NOS^+$ $(M + H)^+$ 324.0664, found 324.0682.



3k

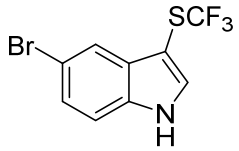
5-Fluoro-3-((trifluoromethyl)thio)-1*H*-indole (**3k**)[3] was obtained in 86% yield (81.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, br, 1H), 7.51 (s, 1H), 7.43 (d, J = 9.2 Hz, 1H), 7.30 (dd, J = 8.8, 4.0 Hz, 1H), 7.01 (t, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J = 237.5 Hz), 134.5, 132.6, 130.5 (d, J = 10.4 Hz), 129.5 (q, J = 310.0 Hz), 112.7 (d, J = 9.6 Hz), 112.2 (d, J = 26.6 Hz), 104.6 (d, J = 24.7 Hz), 95.8 (d, J = 2.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.55, -121.64.



3l

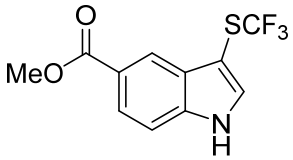
5-Chloro-3-((trifluoromethyl)thio)-1*H*-indole (**3l**)[3] was obtained in 75% yield (75.5 mg) as a

yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, br, 1H), 7.74 (d, J = 1.2 Hz, 1H), 7.46 (d, J = 2.8 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 8.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 134.2, 130.7, 129.4 (q, J = 310.0 Hz), 127.7, 124.0, 118.9, 113.0, 95.4 (q, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.38.



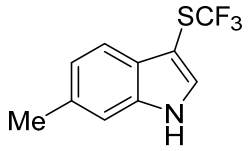
3m

5-Bromo-3-((trifluoromethyl)thio)-1*H*-indole (**3m**)[2] was obtained in 61% yield (72.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, br, 1H), 7.91 (s, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.25-7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 133.9, 131.3, 129.4 (q, J = 310.0 Hz), 126.6, 122.0, 115.3, 113.3, 95.4 (q, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.44.



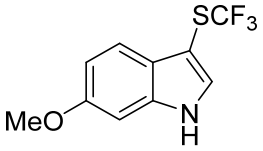
3n

Methyl 3-((trifluoromethyl)thio)-1*H*-indole-5-carboxylate (**3n**)[4] was obtained in 58% yield (63.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, acetone-d_6) δ 11.41 (s, br, 1H), 8.46 (s, 1H), 7.99 (d, J = 2.8 Hz, 1H), 7.94 (dd, J = 8.8, 1.6 Hz, 1H), 7.66-7.62 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 167.8, 140.2, 137.2, 130.5 (q, J = 308.9 Hz), 130.0, 124.8, 124.3, 121.8, 113.3, 95.33 (q, J = 2.4 Hz), 52.2; ^{19}F NMR (376 MHz, acetone-d_6) δ -45.70.



3o

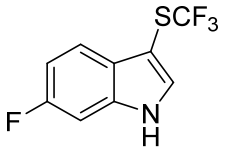
6-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3o**) was obtained in 75% yield (68.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.42-7.40 (m, 1H), 7.18 (s, 1H), 7.11 (d, J = 8.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 133.6, 132.3, 129.6 (q, J = 309.8 Hz), 127.4, 123.6, 119.1, 111.7, 95.4, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.58; HRMS (ESI) calcd for $C_{10}H_9F_3NS^+$ $(M + H)^+$ 232.0402, found 232.0410.



3p

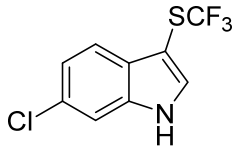
6-Methoxy-3-((trifluoromethyl)thio)-1*H*-indole (**3p**)[3] was obtained in 63% yield (62.5 mg) as a

yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.43 (d, J = 2.4 Hz, 1H), 6.94 (dd, J = 8.8, 2.0 Hz, 1H), 6.89 (d, J = 2.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 137.0, 131.7, 129.5 (q, J = 310.1 Hz), 123.7, 120.2, 111.8, 95.7, 95.1, 55.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.62.



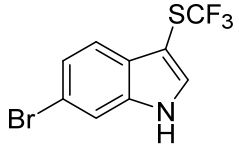
3q

6-Fluoro-3-((trifluoromethyl)thio)-1*H*-indole (**3q**)[2] was obtained in 52% yield (48.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, br, 1H), 7.70 (dd, J = 8.4, 5.2 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.10-7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, J = 240.0 Hz), 136.1 (d, J = 12.6 Hz), 133.3, 129.5 (q, J = 309.9 Hz), 126.0, 120.5 (d, J = 10.1 Hz), 110.7 (d, J = 24.7 Hz), 98.2 (d, J = 26.6 Hz), 96.0 (q, J = 2.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.48, -119.06.



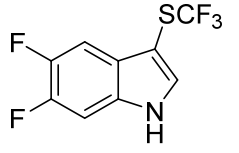
3r

6-Chloro-3-((trifluoromethyl)thio)-1H-indole (**3r**)[3] was obtained in 70% yield (70.4 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, br, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.46 (d, J = 2.8 Hz, 1H), 7.34 (d, J = 1.2 Hz, 1H), 7.22 (dd, J = 8.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 133.5, 129.5, 129.4 (q, J = 309.9 Hz), 128.1, 122.6, 120.4, 111.8, 96.1 (q, J = 2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.39.



3s

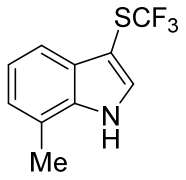
6-Bromo-3-((trifluoromethyl)thio)-1H-indole (**3s**) was obtained in 52% yield (61.4 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, br, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.47 (s, 1H), 7.43 (d, J = 1.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 133.4, 129.4 (q, J = 309.9 Hz), 128.4, 125.1, 120.8, 117.1, 114.7, 96.1 (q, J = 2.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.34; HRMS (ESI) calcd for $C_9H_6BrF_3NS^+$ $(M + H)^+$ 295.9351, found 295.9352.



3t

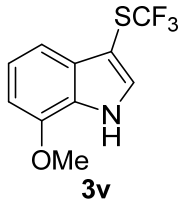
5,6-Difluoro-3-((trifluoromethyl)thio)-1*H*-indole (**3t**) was obtained in 45% yield (45.6 mg) as a

yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.58-7.49 (m, 2H), 7.22 (dd, J = 10.0, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0 (dd, J = 243.6, 16.0 Hz), 148.0 (dd, J = 241.2, 14.8 Hz), 134.2, 131.0 (d, J = 10.7 Hz), 129.4 (q, J = 309.9 Hz), 125.3 (d, J = 8.1 Hz), 106.4 (d, J = 20.2 Hz), 100.0 (d, J = 22.3 Hz), 96.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.55, -141.44 (d, J = 20.6 Hz), -144.28 (d, J = 20.6 Hz); HRMS (ESI) calcd for $C_9H_5F_5NS^+$ $(M + H)^+$ 254.0057, found 254.0057.



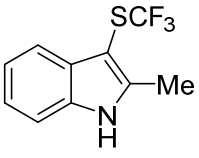
3u

7-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3u**)[2] was obtained in 78% yield (72.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, br, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 2.8 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 132.7, 129.7 (q, J = 309.9 Hz), 129.2, 124.0, 121.9, 121.1, 117.0, 95.9 (dd, J = 2.4 Hz), 16.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.38.



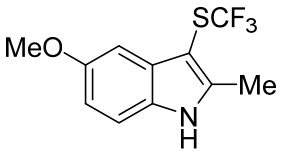
3v

7-Methoxy-3-((trifluoromethyl)thio)-1*H*-indole (**3v**)[5] was obtained in 85% yield (84.3 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, br, 1H), 7.43-7.37 (m, 2H), 7.18 (dd, J = 10.4, 8.0 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 132.4, 130.9, 129.6 (q, J = 310.0 Hz), 126.8, 122.2, 111.8, 103.2, 95.8 (d, J = 2.4 Hz), 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.60.



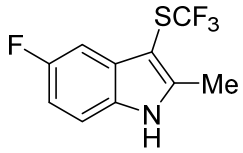
3w

2-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3w**)[2] was obtained in 46% yield (42.5 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, br, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.28-7.19 (m, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 135.1, 130.7, 129.9 (q, J = 310.7 Hz), 122.7, 121.5, 118.8, 110.9, 92.6 (q, J = 2.2 Hz), 12.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.39.



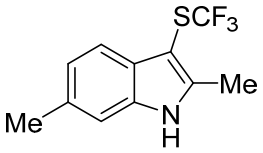
3x

5-Methoxy-2-methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3x**)[6] was obtained in 52% yield (54.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, br, 1H), 7.19-7.14 (m, 2H), 6.84 (dd, J = 8.8, 2.4 Hz, 1H), 3.88 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 144.2, 131.6, 123.0 (q, J = 310.9 Hz), 129.9, 112.6, 111.7, 100.6, 92.2, 56.0, 12.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.50.



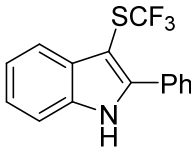
3y

5-Fluoro-2-methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3y**) was obtained in 69% yield (68.6 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, br, 1H), 7.34 (dd, J = 8.8, 1.6 Hz, 1H), 7.20 (dd, J = 8.8, 4.0 Hz, 1H), 6.93 (td, J = 11.2, 2.4 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1 (d, J = 236.6 Hz), 145.5, 131.6 (d, J = 10.3 Hz), 131.5, 129.8 (q, J = 310.7 Hz), 111.7 (d, J = 9.6 Hz), 111.0 (d, J = 26.3 Hz), 104.2 (d, J = 24.7 Hz), 92.9 (q, J = 2.4 Hz), 12.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.46, -122.26; HRMS (ESI) calcd for $C_{10}H_8F_4NS^+$ $(M + H)^+$ 250.0308, found 250.0312.



3z

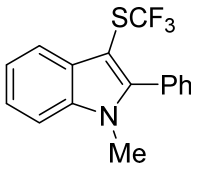
2,6-Dimethyl-3-((trifluoromethyl)thio)-1*H*-indole (**3z**) was obtained in 43% yield (41.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, br, 1H), 7.48 (s, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.02 (d, J = 8.2 Hz, 1H), 2.52 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 133.4, 131.0, 130.9, 129.9 (d, J = 310.3 Hz), 124.2, 118.5, 110.6, 92.0 (d, J = 1.9 Hz), 21.6, 12.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.46; HRMS (ESI) calcd for $C_{11}H_{11}F_3NS^+$ $(M + H)^+$ 246.0559, found 246.0559.



3aa

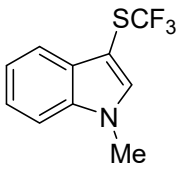
2-Phenyl-3-((trifluoromethyl)thio)-1*H*-indole (**3aa**)[2] was obtained in 70% yield (82.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, br, 1H), 7.85-7.82 (m, 1H), 7.71-7.67 (m, 2H), 7.48-7.39 (m, 3H), 7.34-7.30 (m, 1H), 7.28-7.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 135.4, 131.5, 130.7, 129.9 (q, J = 311.4 Hz), 129.4, 128.9, 128.8, 123.8, 121.9, 119.9, 111.4, 92.4 (d,

J = 2.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.28.



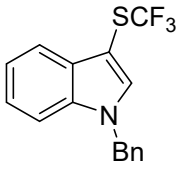
3ab

1-Methyl-2-phenyl-3-((trifluoromethyl)thio)-1*H*-indole (**3ab**)[7] was obtained in 64% yield (78.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.2 Hz, 1H), 7.53-7.47 (m, 3H), 7.44-7.38 (m, 3H), 7.36-7.28 (m, 2H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 137.2, 130.9, 130.3, 129.9, 129.8 (q, J = 311.2 Hz), 129.3, 128.5, 123.3, 121.8, 119.7, 110.1, 92.7 (d, J = 2.2 Hz), 31.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -43.86.



3ac

1-Methyl-3-((trifluoromethyl)thio)-1*H*-indole (**3ac**)[2] was obtained in 61% yield (56.4 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 1H), 7.35-7.24 (m, 4H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 137.1, 130.3, 129.6 (q, J = 310.1 Hz), 123.0, 121.4, 119.5, 110.0, 93.1 (q, J = 2.4 Hz), 33.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.89.

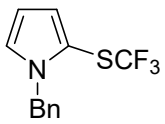


3ad

1-Benzyl-3-((trifluoromethyl)thio)-1*H*-indole (**3ad**)[8] was obtained in 69% yield (84.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 1H), 7.38 (s, 1H), 7.29-7.22 (m, 6H), 7.09-7.06 (m, 2H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.5, 136.2, 130.5, 129.6 (q, J = 310.1 Hz), 129.1, 128.2, 127.1, 123.2, 121.6, 119.7, 110.6, 94.0 (q, J = 2.3 Hz), 50.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.59.

Sulfenylation of pyrole 5 with TfNHNHBoc (eqn (1))

The procedure for the sulfenylation of pyrole **5** with TfNHNHBoc is the same as that for the sulfenylation of indoles (see above).



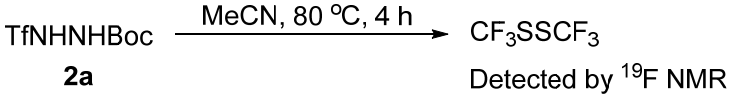
5

1-Benzyl-2-((trifluoromethyl)thio)-1*H*-pyrrole (**5**)[9] was obtained in 30% yield (30.5 mg) as a

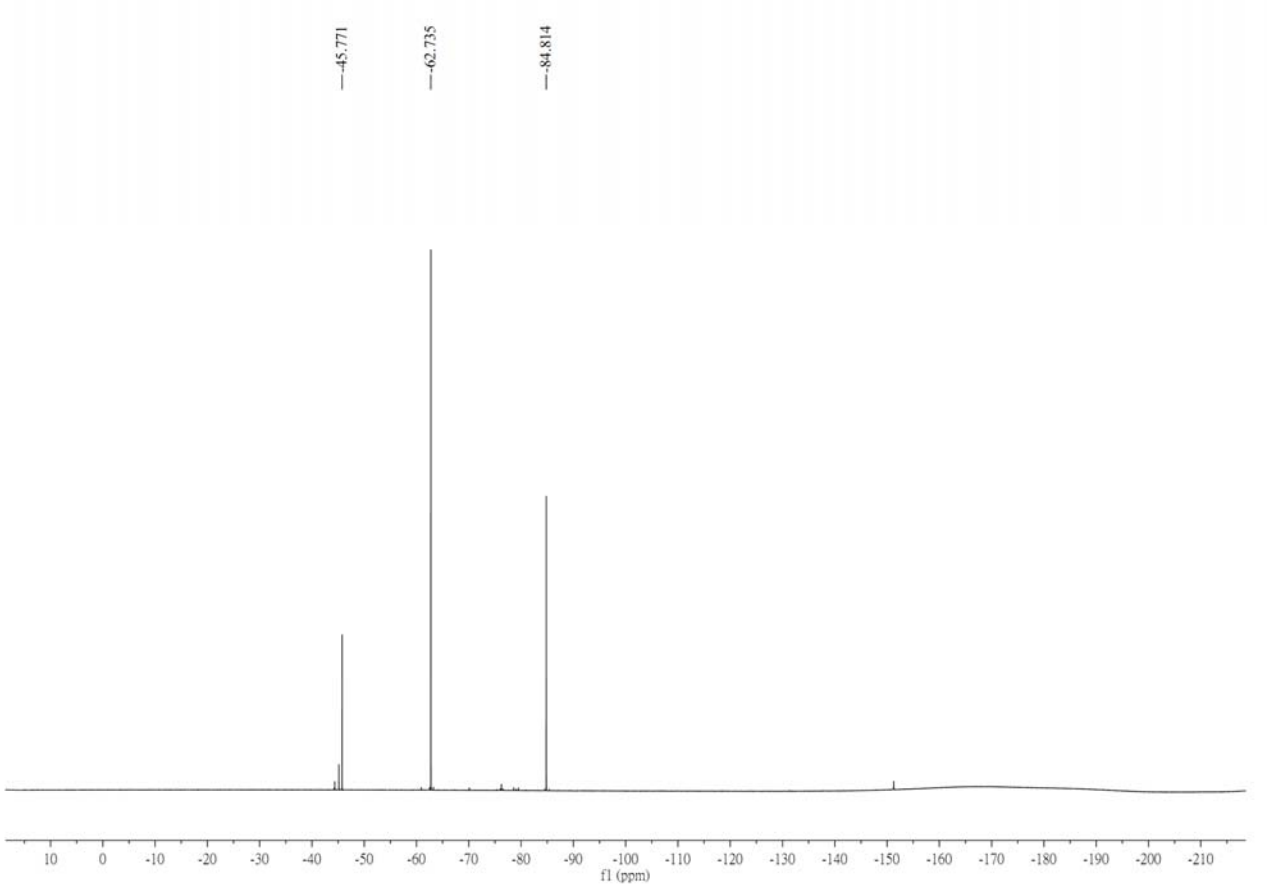
yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 3H), 7.08-7.04 (m, 2H), 6.91 (s, 1H), 6.72 (s, 1H), 6.26 (d, J = 2.8 Hz, 1H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 128.9, 128.4 (q, J = 311.4 Hz), 127.9, 127.6, 127.2, 123.1, 109.9, 109.8 (q, J = 2.3 Hz), 50.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.34.

Mechanistic studies

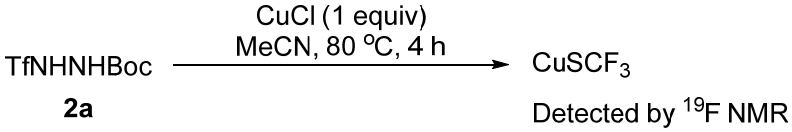
eqn (2)



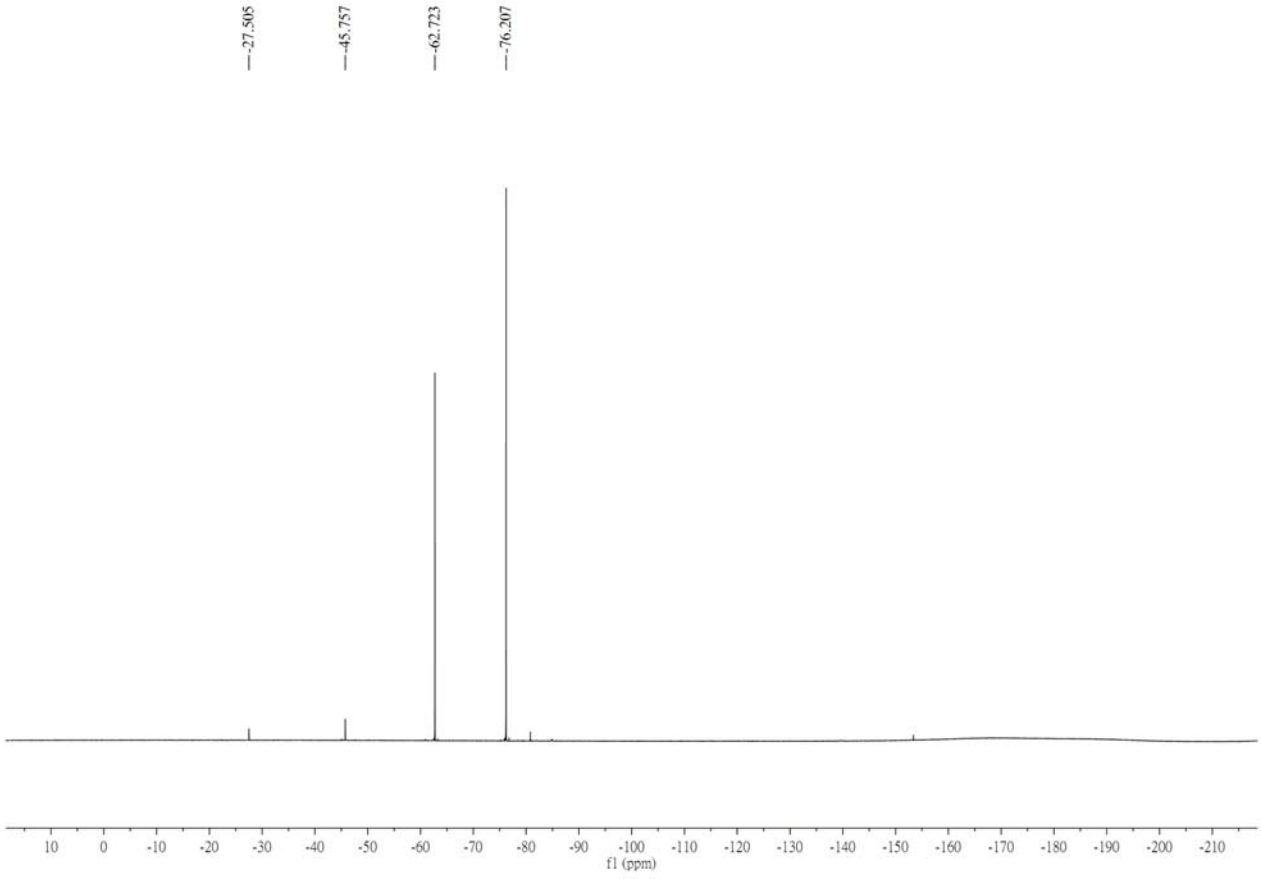
To a reaction tube equipped with a magnetic stir bar was charged with TfNHNHBoc (**2a**) (211 mg, 0.80 mmol). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Acetonitrile (2.0 mL) was added via syringe with gentle stirring. The reaction vessel was allowed to stir at 80 °C for 4 h. A small portion of the mixture was subjected to ^{19}F NMR spectroscopic analysis (using $PhCF_3$ as an internal standard), and CF_3SSCF_3 was identified. CF_3SSCF_3: ^{19}F NMR (376 MHz, $CDCl_3$) δ -45.77.[4]



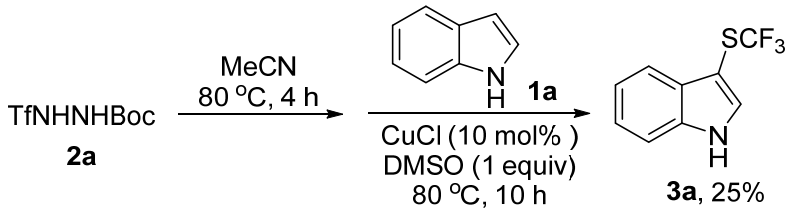
eqn (3)



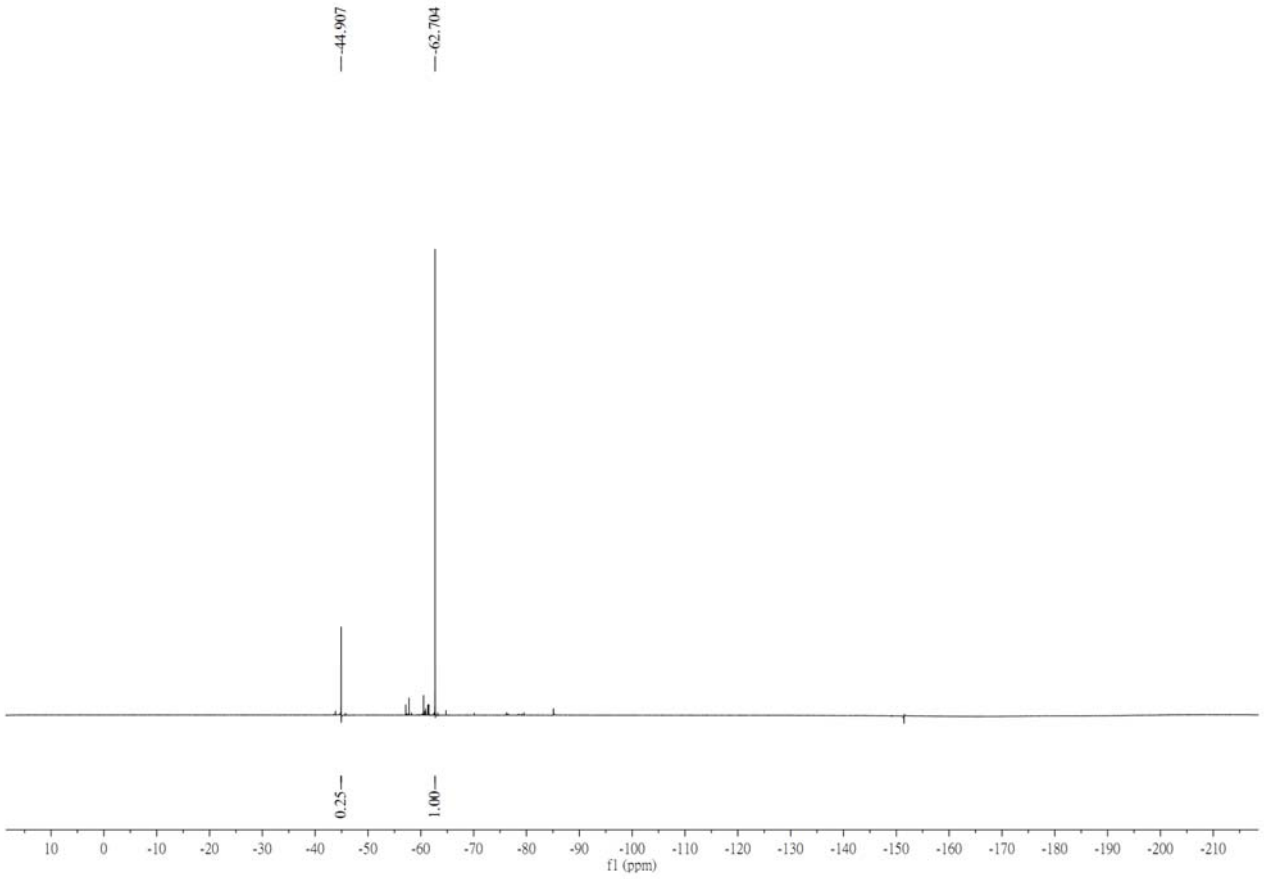
To a reaction tube equipped with a magnetic stir bar was charged with TfNHNHBoc (**2a**) (211 mg, 0.80 mmol) and CuCl (79.2 mg, 0.80 mmol). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Acetonitrile (2.0 mL) was added via syringe with gentle stirring. The reaction vessel was allowed to stir at 80 °C for 0.5 h. A small portion of the mixture was subjected to ^{19}F NMR spectroscopic analysis (using $PhCF_3$ as an internal standard), and $CuSCF_3$ was identified. $CuSCF_3$: ^{19}F NMR (376 MHz, $CDCl_3$) δ -27.50.[10]



eqn (4)

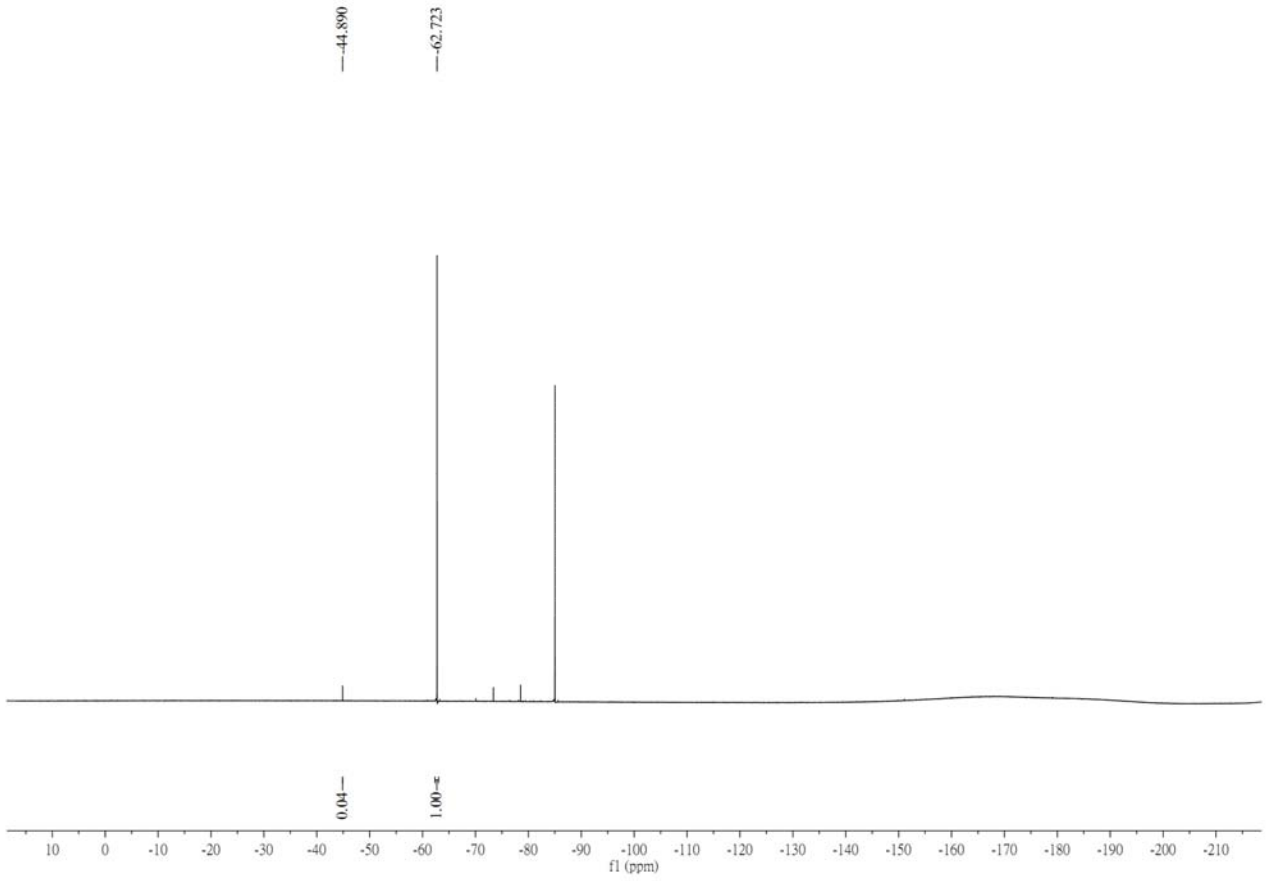


To a reaction tube equipped with a magnetic stir bar was charged with TfNHNHBoc (**2a**) (211 mg, 0.80 mmol). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. Acetonitrile (2.0 mL) was added via syringe with gentle stirring. After stir at 80 °C for 4 h, indole (**1a**) (46.9 mg, 0.40 mmol), CuCl (4.0 mg, 10 mol%), and DMSO (31.2 mg, 28 μL, 0.40 mmol) was added to the reaction tube. The mixture was stirred at 80 °C for 10 h to give thioether **3a** in 25% yield (determined by ^{19}F NMR spectroscopic analysis using $PhCF_3$ as an internal standard).

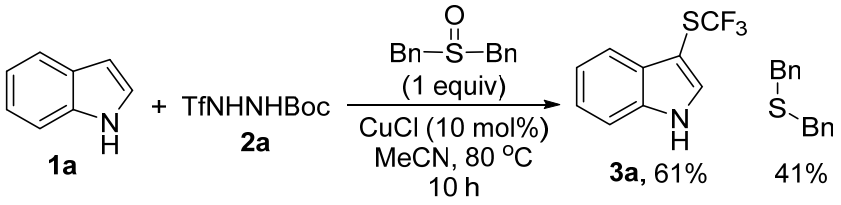


eqn (5)

To a reaction tube equipped with a magnetic stir bar was charged with TfNHNHBoc (**2a**) (211 mg, 0.80 mmol) and indole (**1a**) (46.9 mg, 0.40 mmol). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. DMSO (31.2 mg, 28 μL, 0.4 mmol) and MeCN (2.0 mL) were added via syringe with gentle stirring. The reaction vessel was allowed to stir at 80 °C for 10 h. Only a trace amount of thioether **3a** was determined by ^{19}F NMR spectroscopic analysis.



eqn (6)



To a reaction tube equipped with a magnetic stir bar was charged with TfNHNHBoc (**2a**) (211 mg, 0.80 mmol), indole (**1a**) (46.9 mg, 0.40 mmol), dibenzyl sulfoxide (92.1 mg, 0.40 mmol), and CuCl (4.0 mg, 10 mol%). The tube was sealed with a septum, evacuated, and backfilled with nitrogen three times. MeCN (2.0 mL) was added via syringe with gentle stirring. The reaction vessel was allowed to stir at 80 °C for 10 h. The mixture was cooled to room temperature and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:10), to give thioether **3a** in 61% yield (52.9 mg) and BnSBn in 41% yield (35.0 mg). BnSBn: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 10H), 3.59 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 129.1, 128.6, 127.1, 35.6.[11]

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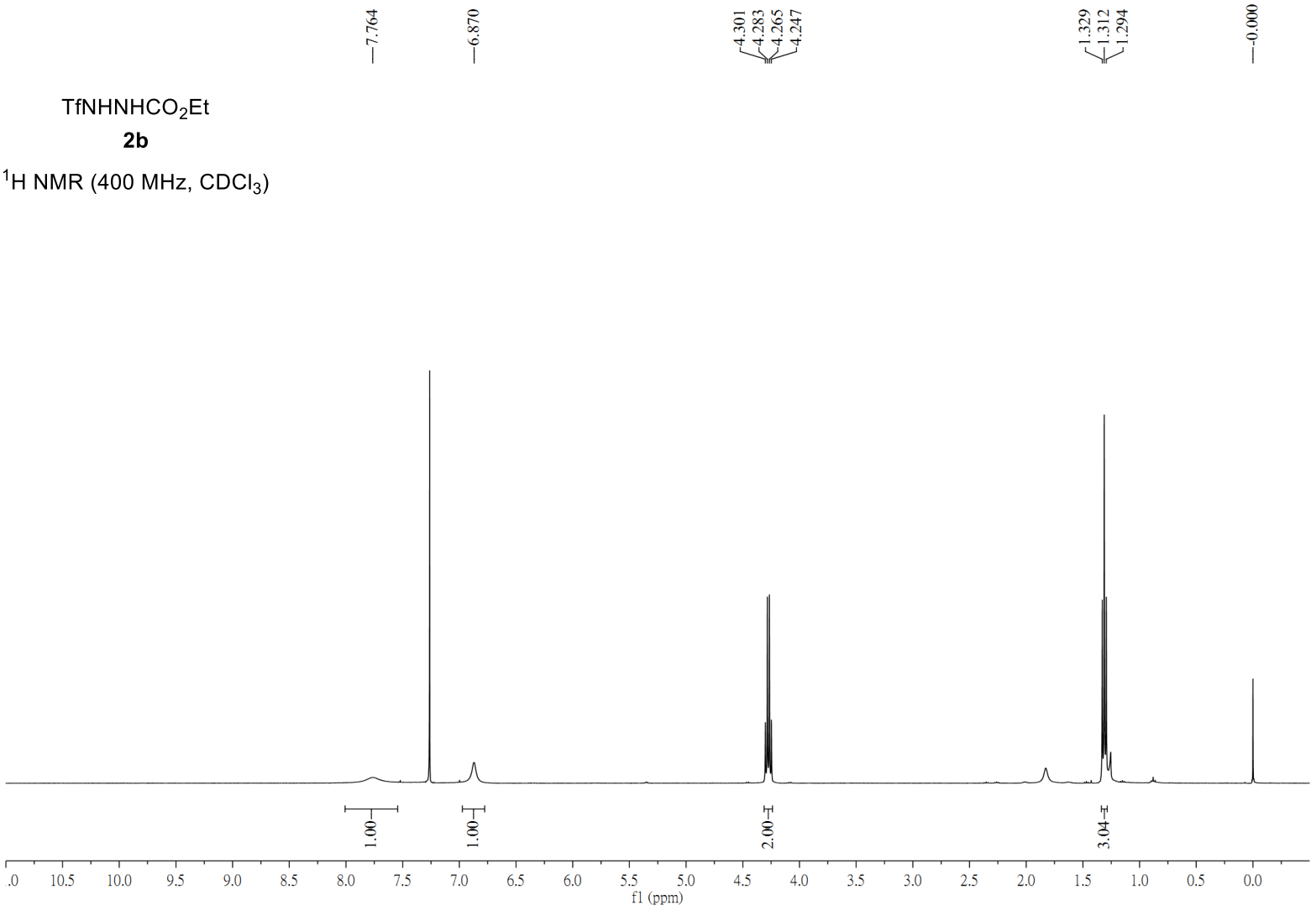
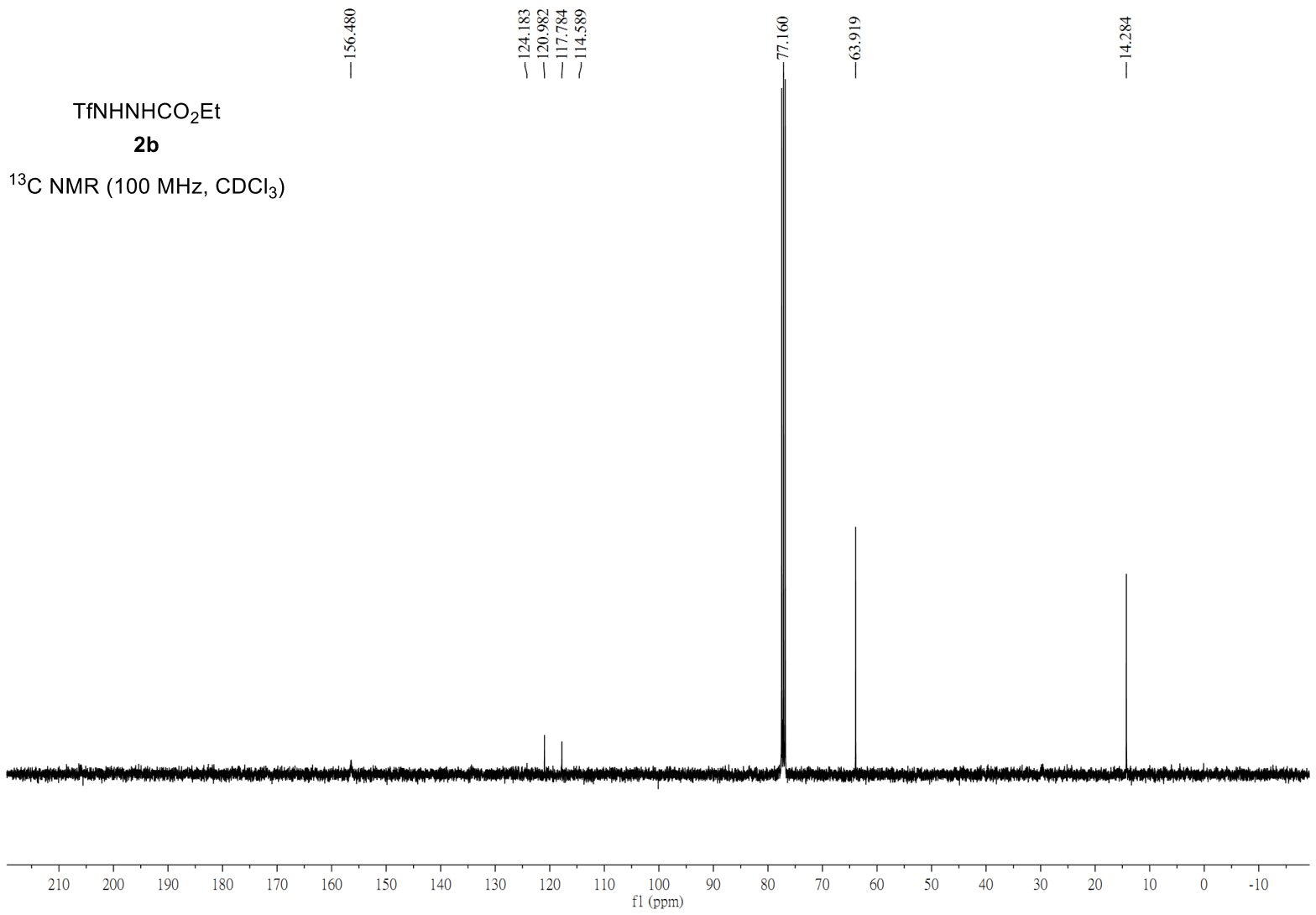
$TfNHNHCO_2Et$

2b

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

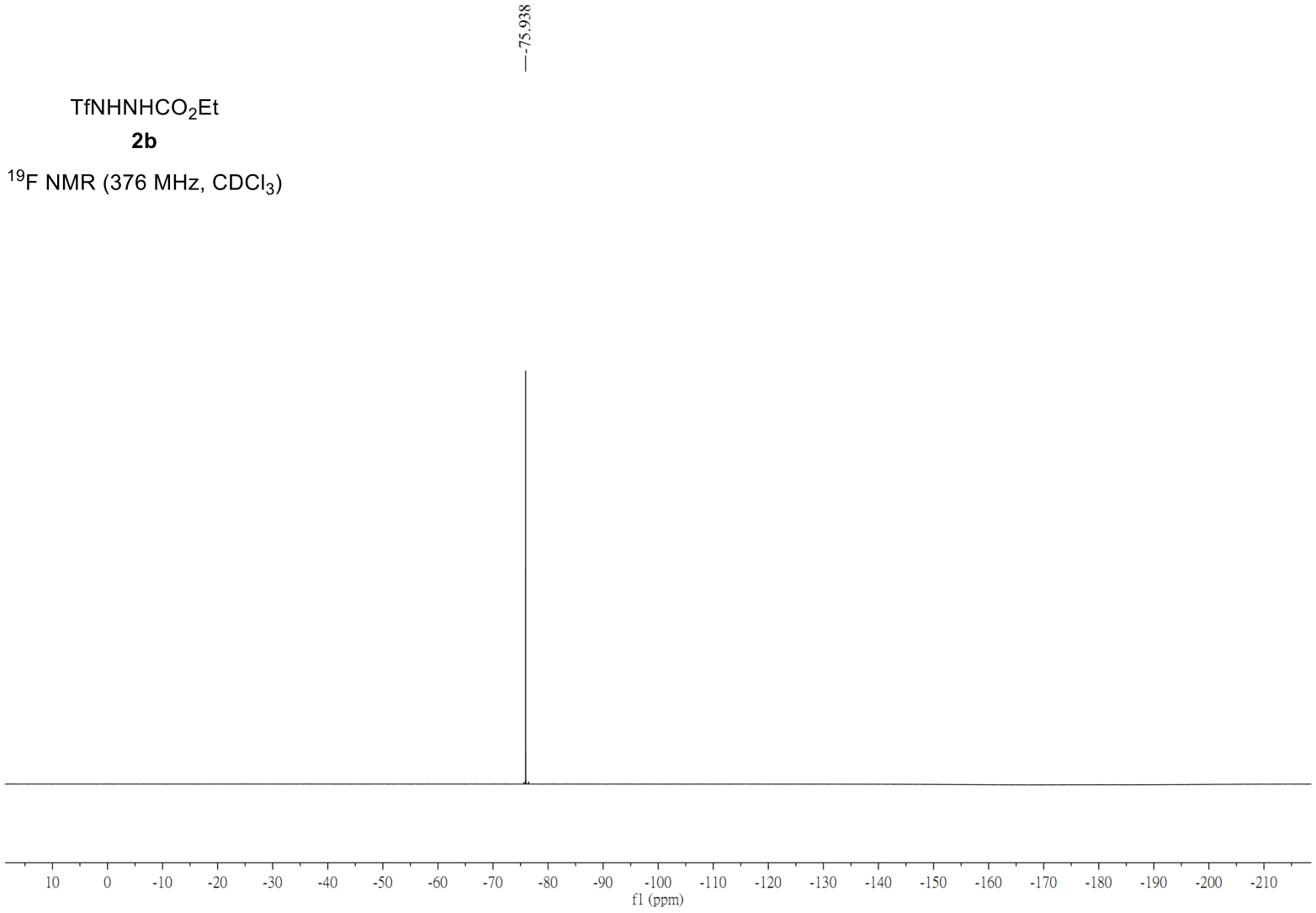


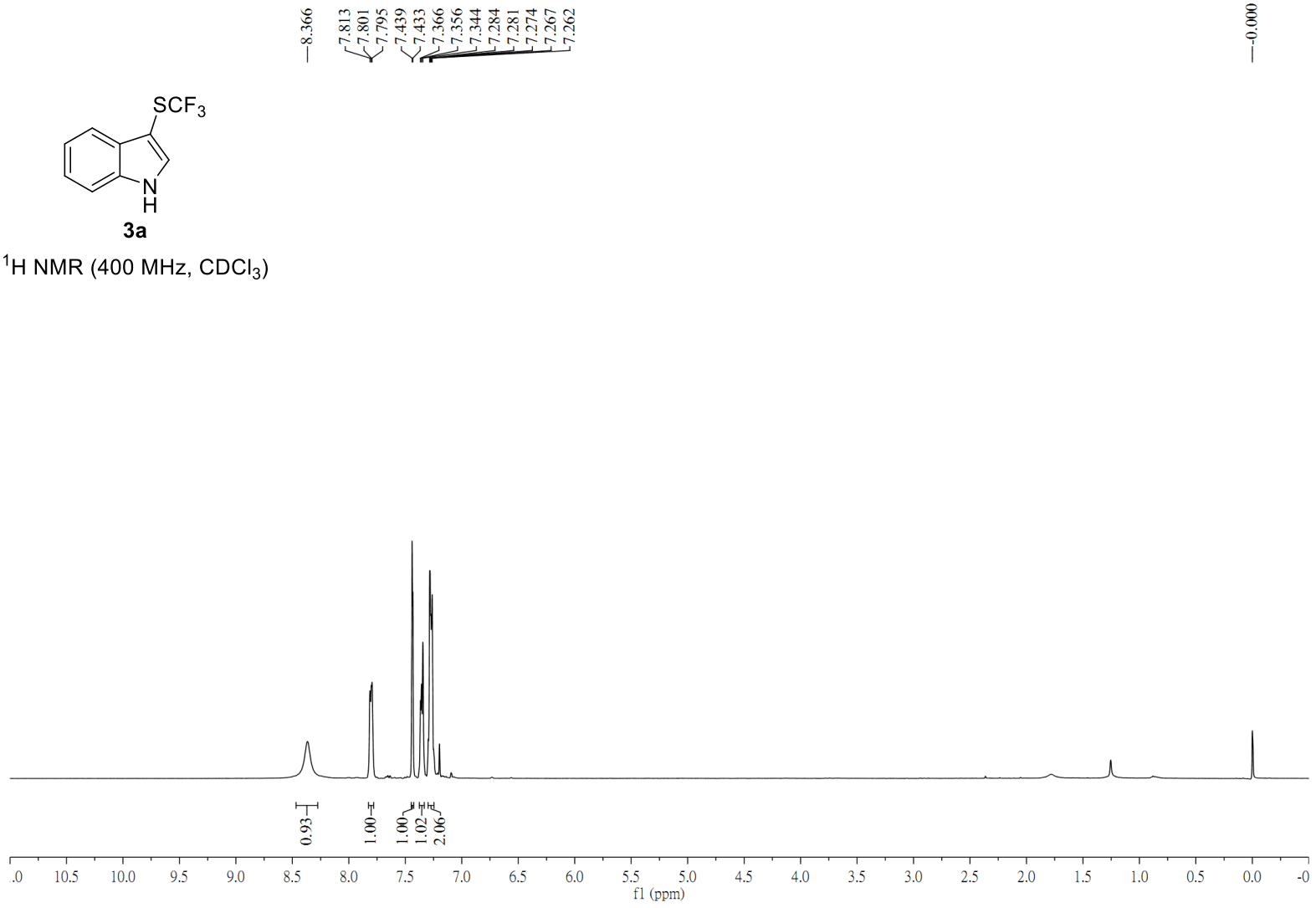

156.480
124.183
120.982
117.784
114.589
77.160
63.919
14.284
TfNHNHCO2Et
2b
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

TfNHNHCO$_2$Et

2b

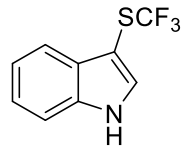
^{19}F NMR (376 MHz, CDCl$_3$)





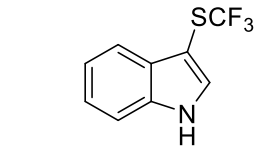
3a

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



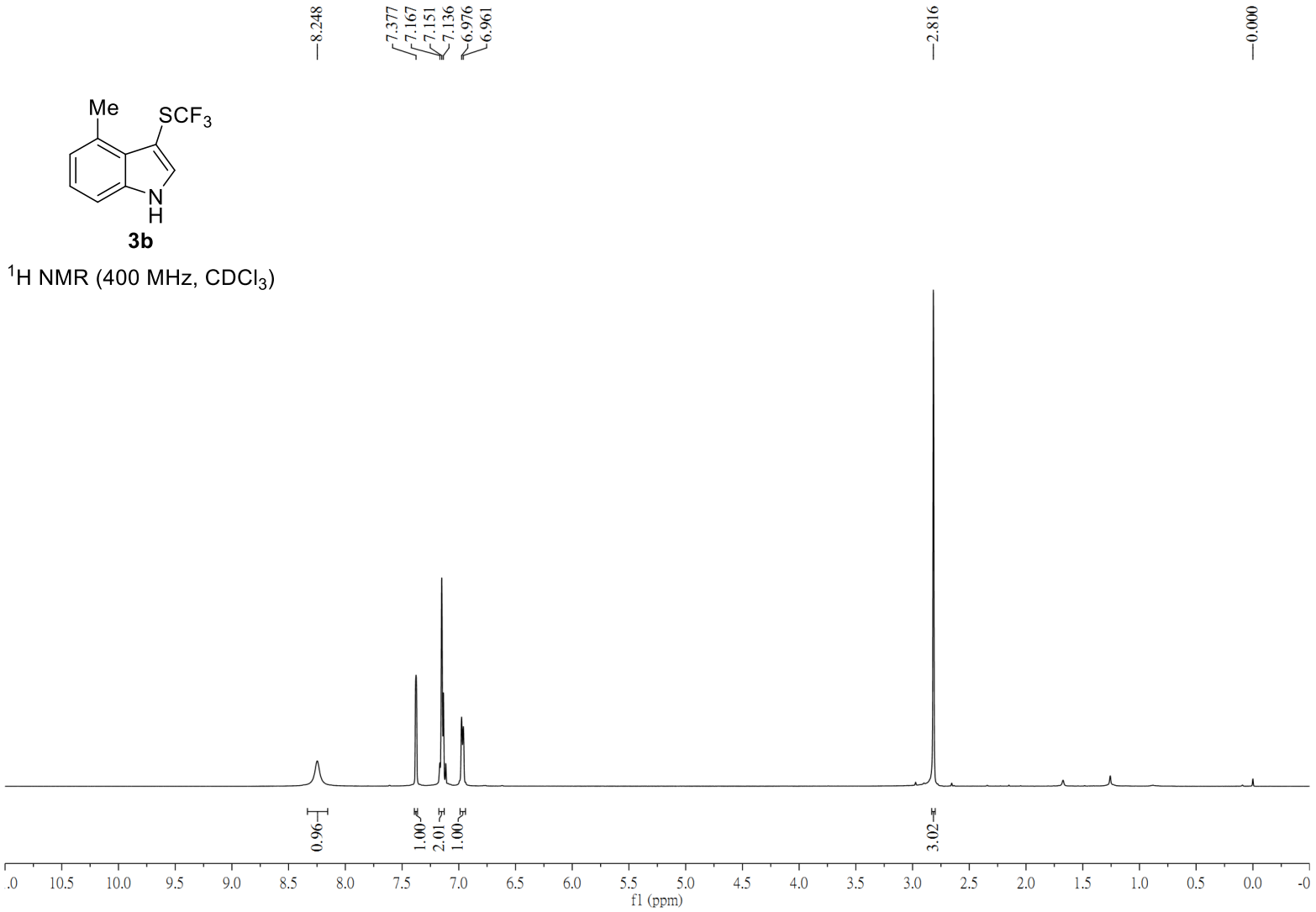
3a

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



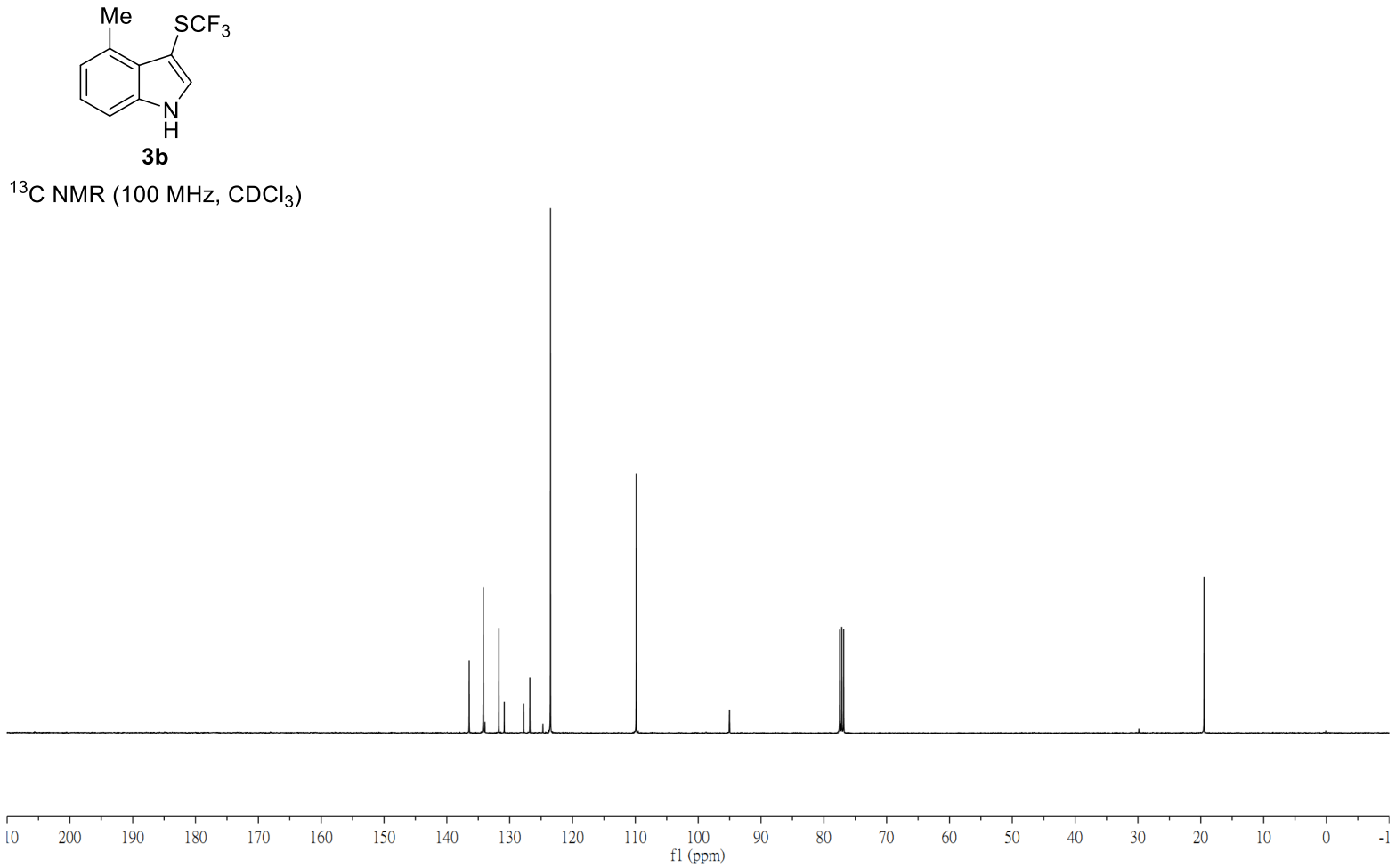
3a

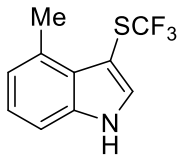
^{19}F NMR (376 MHz, $CDCl_3$)



3b

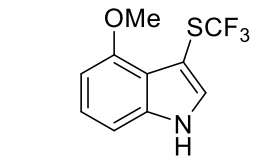
^{1}H NMR (400 MHz, $CDCl_3$)


136.449
134.208
133.937
131.734
130.862
127.787
126.794
124.711
123.513
109.878
95.055
95.033
95.008
94.984
77.160
19.476
Me
SCF3
N
H
3b
13C NMR (100 MHz, CDCl3)
f1 (ppm)



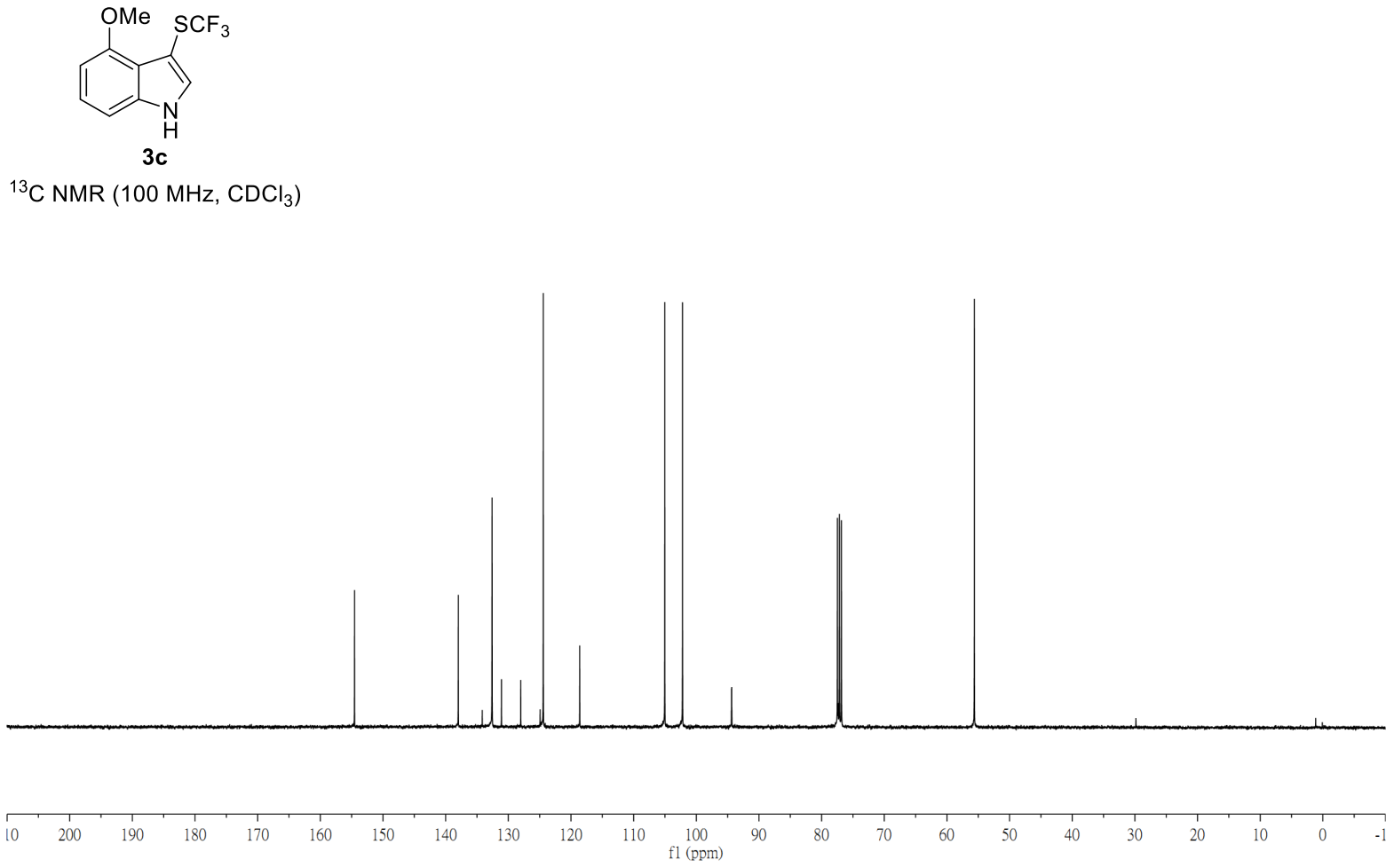
3b

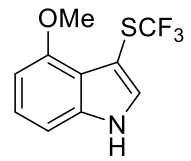
^{19}F NMR (376 MHz, $CDCl_3$)



3c

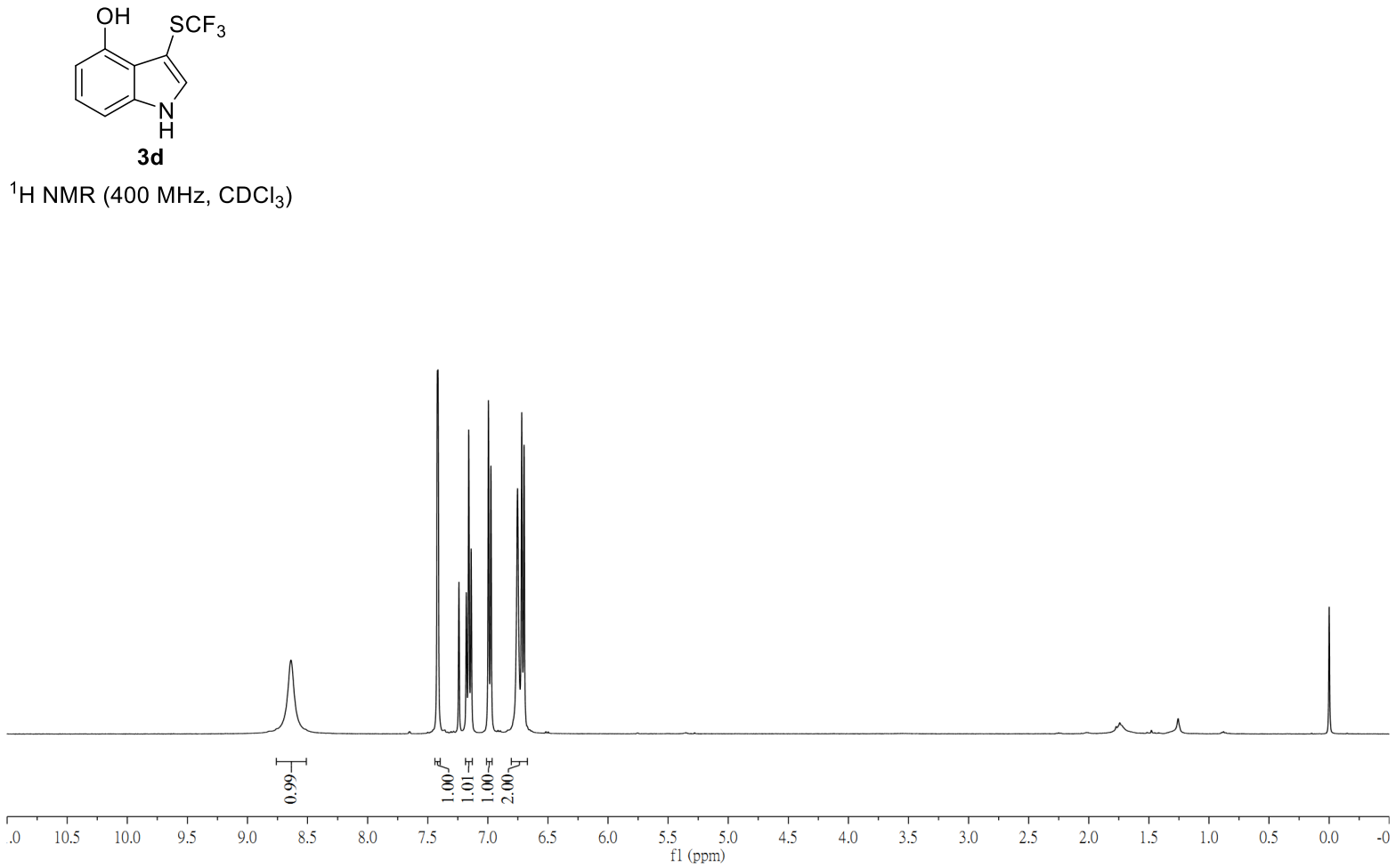
^{1}H NMR (400 MHz, $CDCl_3$)


154.554
137.985
134.168
132.596
131.092
128.017
124.941
124.420
118.606
105.031
102.197
94.400
94.375
94.348
94.323
77.160
55.622
OMe
SCF3
N
H
3c
13C NMR (100 MHz, CDCl3)
f1 (ppm)



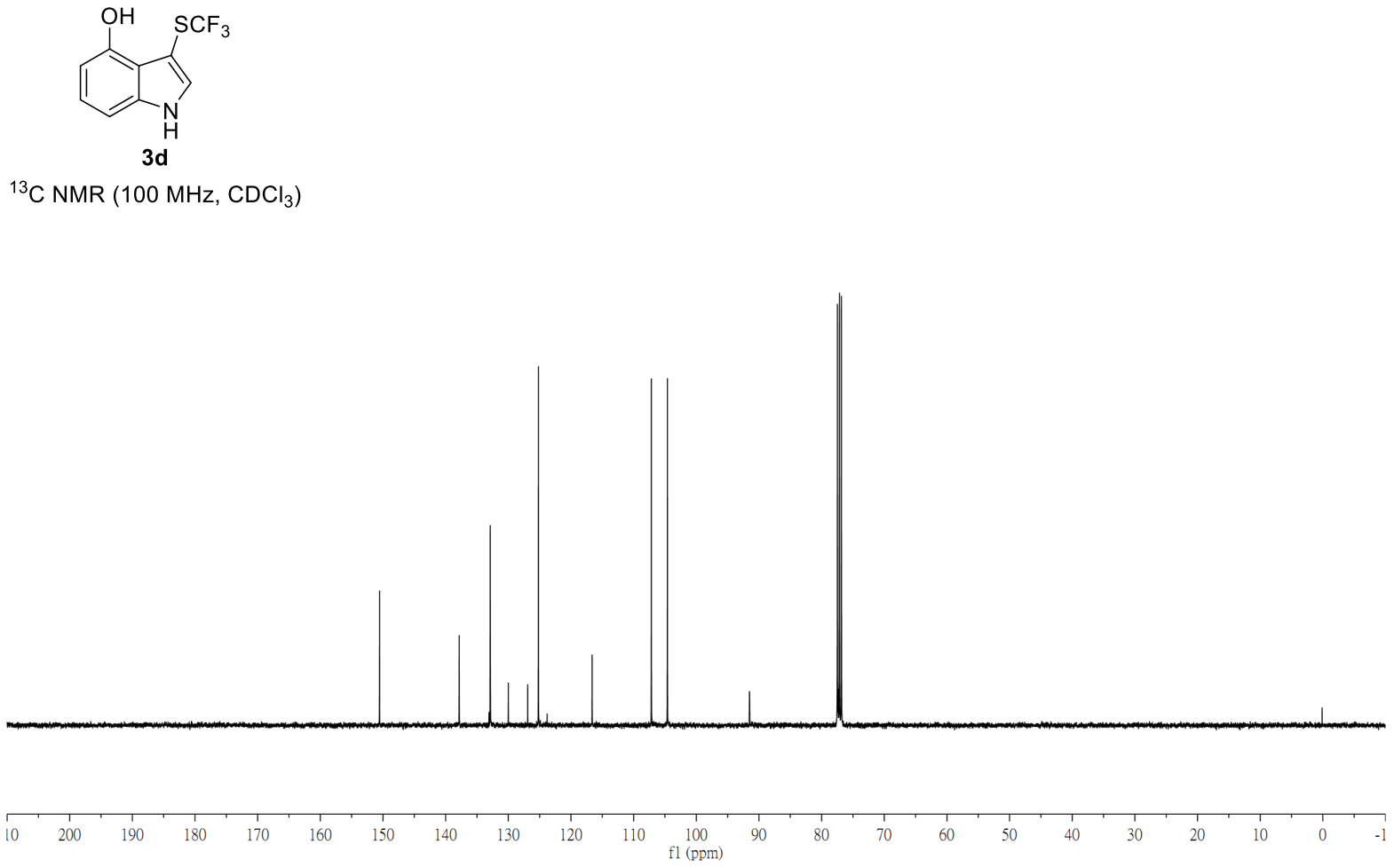
3c

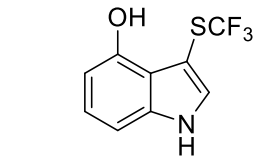
^{19}F NMR (376 MHz, $CDCl_3$)



3d

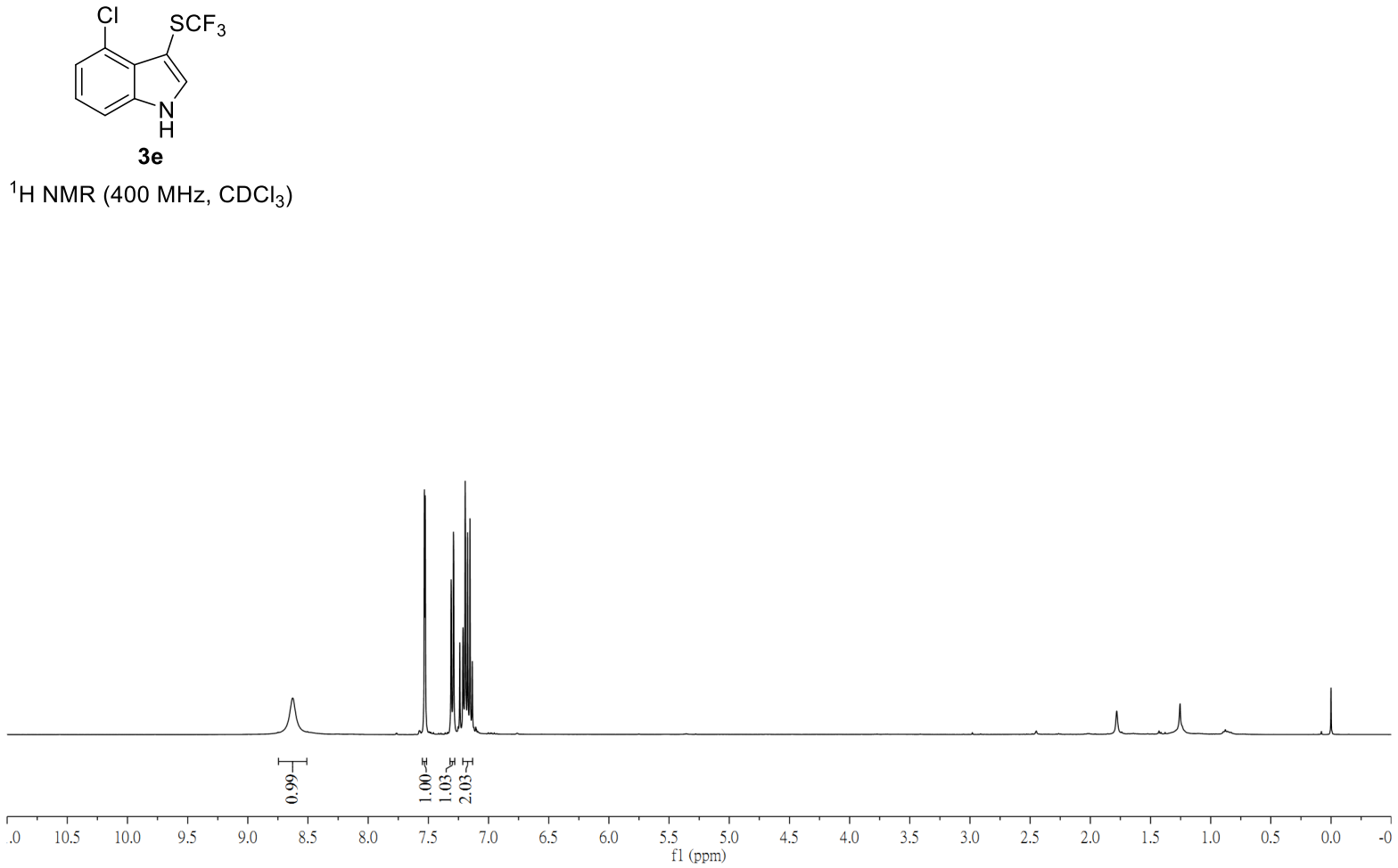
^{1}H NMR (400 MHz, $CDCl_3$)


150.560
137.845
133.087
132.888
129.996
126.905
125.202
123.813
116.628
107.170
104.612
91.516
91.492
91.472
77.160
OH
SCF3
N
H
3d
13C NMR (100 MHz, CDCl3)
f1 (ppm)



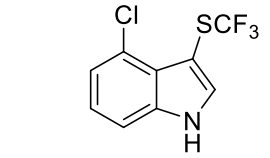
3d

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



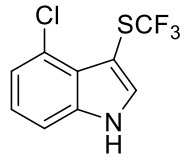
3e

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



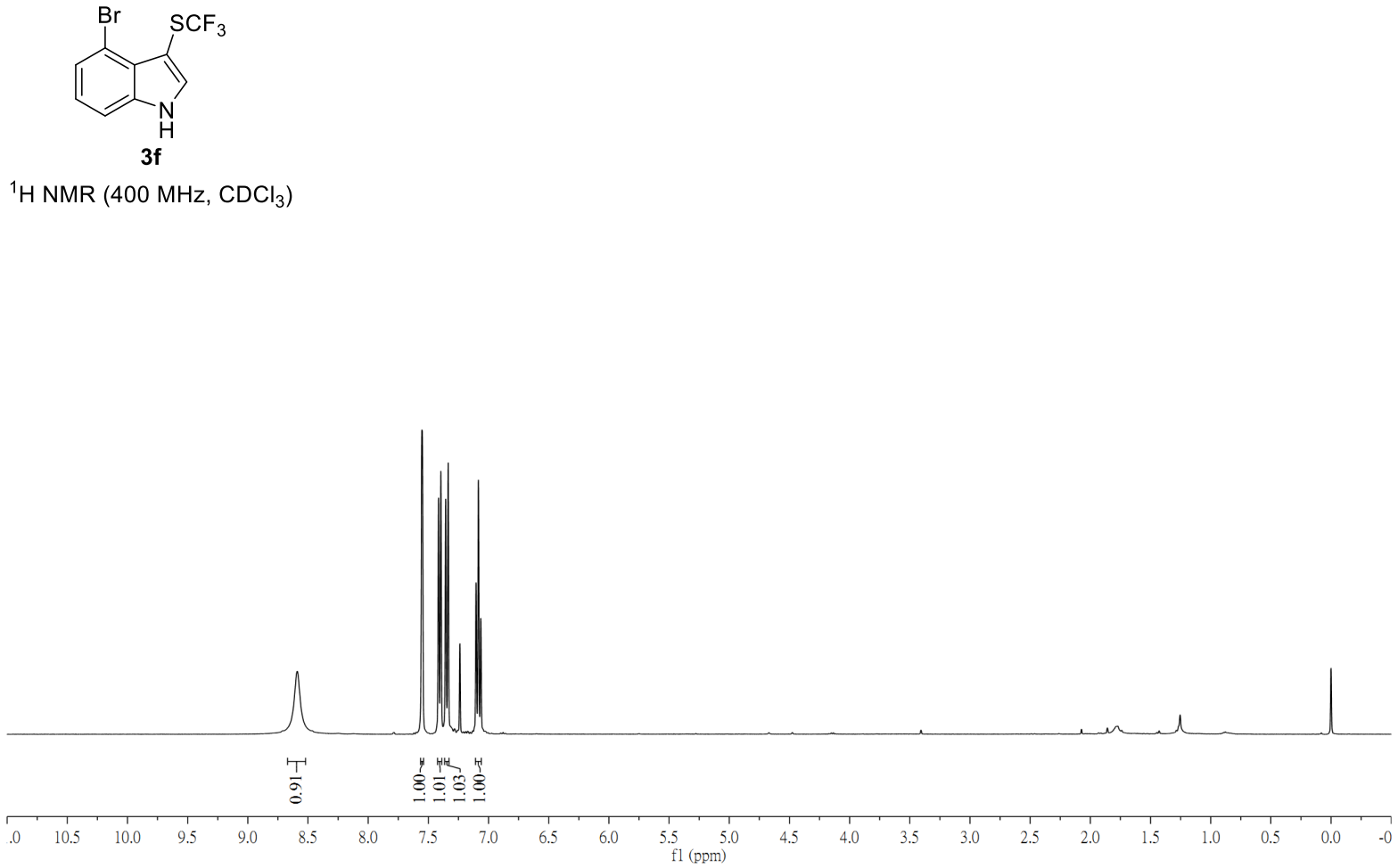
3e

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



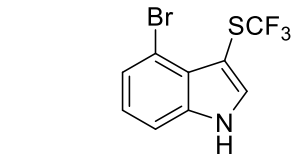
3e

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



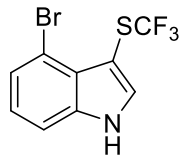
3f

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



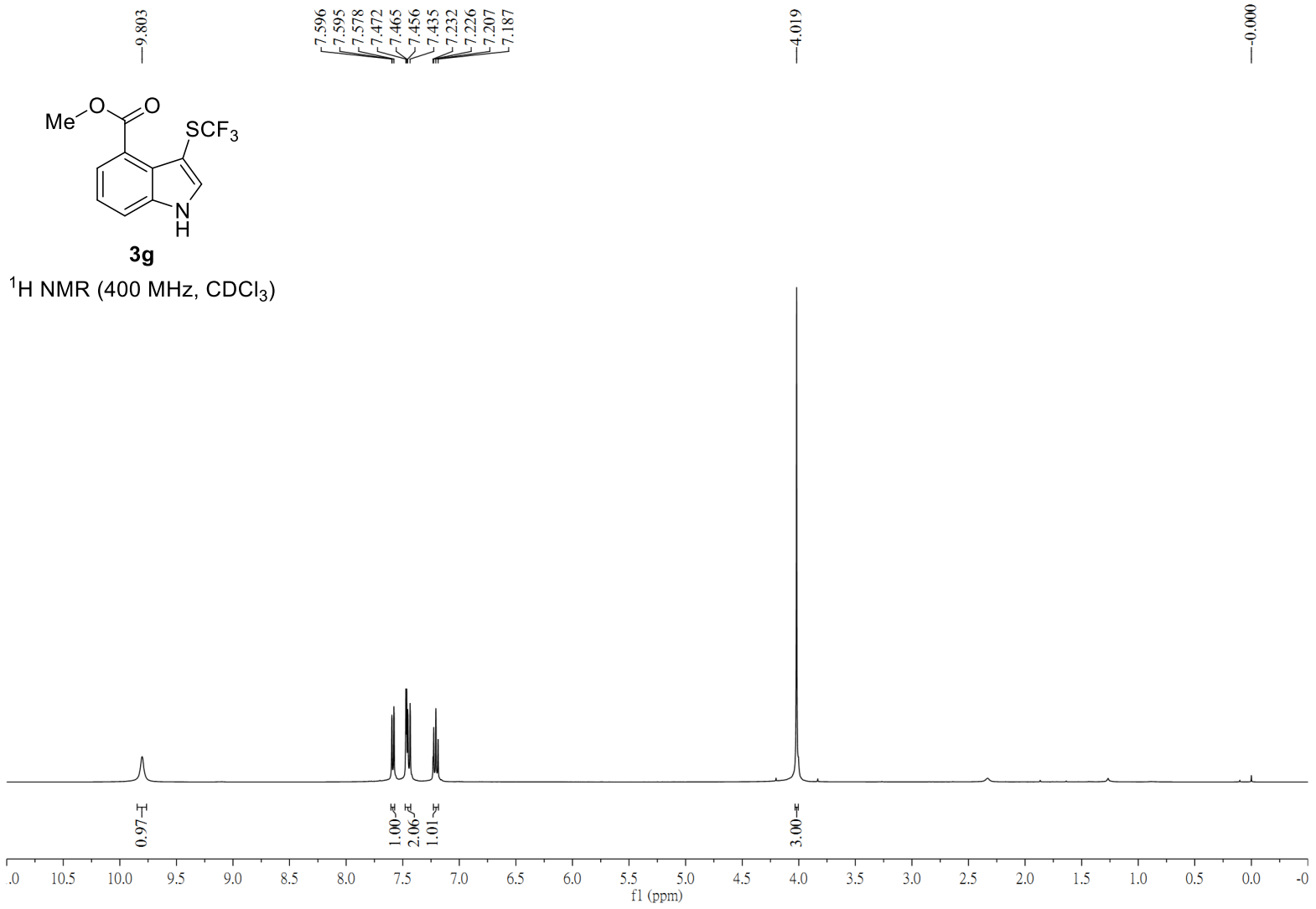
3f

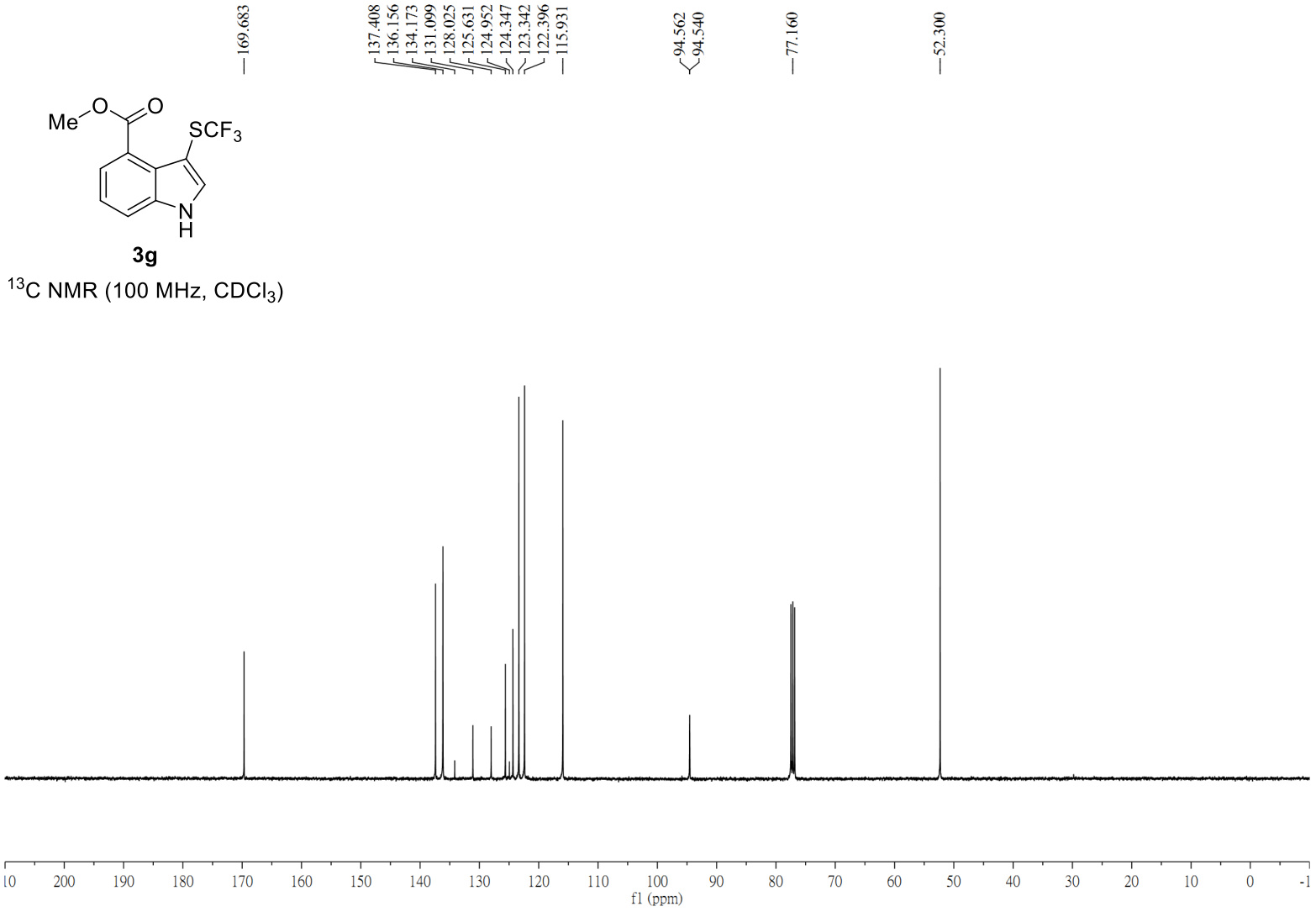
^{13}C NMR (100 MHz, $CDCl_3$)

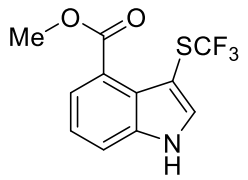


3f

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

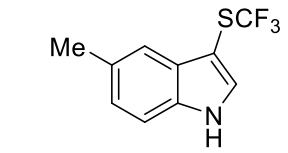

9.803
7.596
7.595
7.578
7.472
7.465
7.456
7.435
7.232
7.226
7.207
7.187
4.019
0.000
Me
O
O
SCF3
N
H
3g
1H NMR (400 MHz, CDCl3)
0.97
1.00
2.06
1.01
3.00
f1 (ppm)


169.683
137.408
136.156
134.173
131.099
128.025
125.631
124.952
124.347
123.342
122.396
115.931
94.562
94.540
77.160
52.300
Me
O
O
SCF3
N
H
3g
13C NMR (100 MHz, CDCl3)
f1 (ppm)



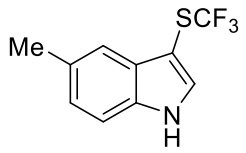
3g

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



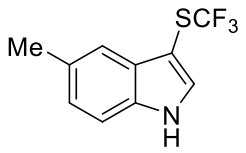
3h

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



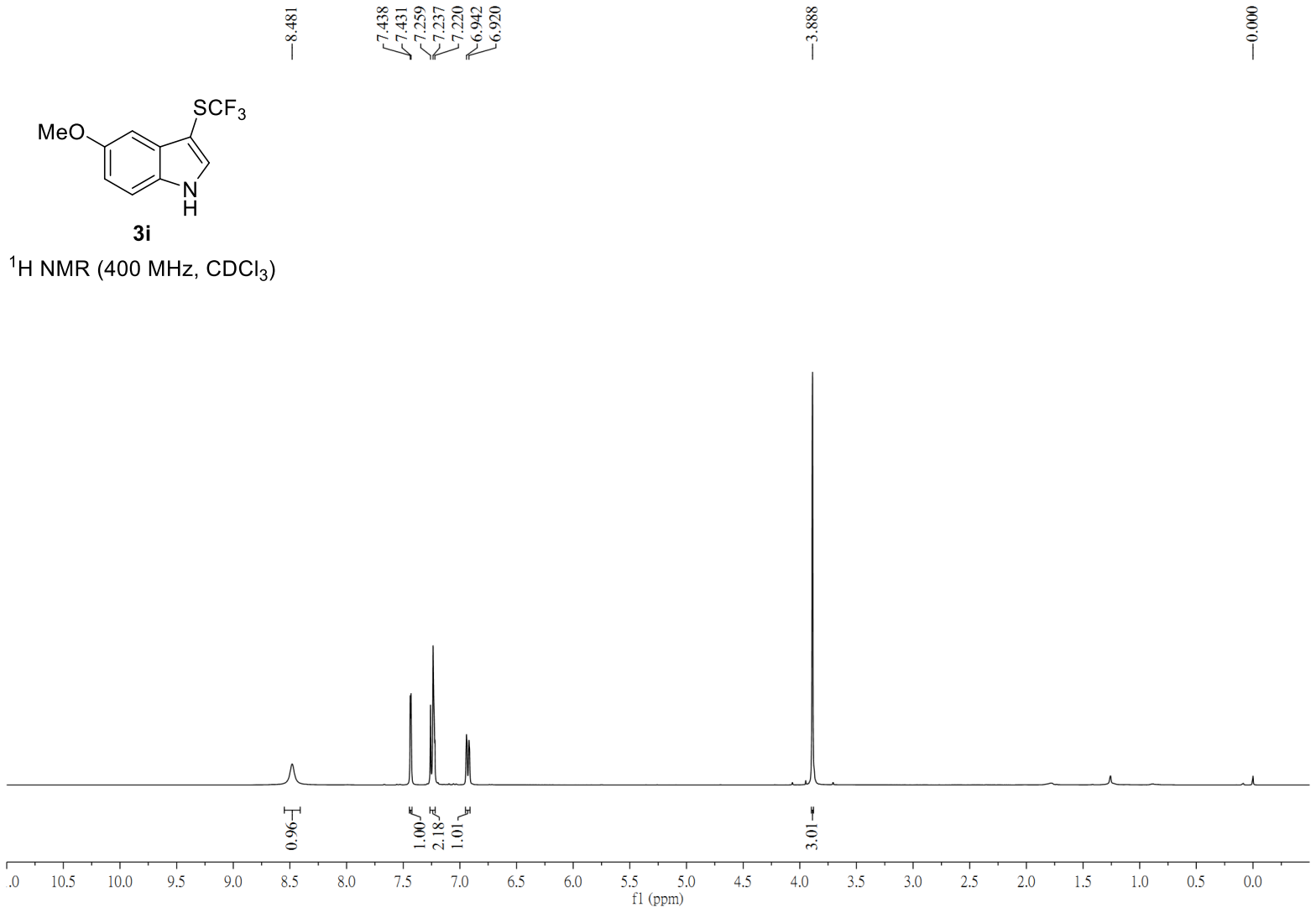
3h

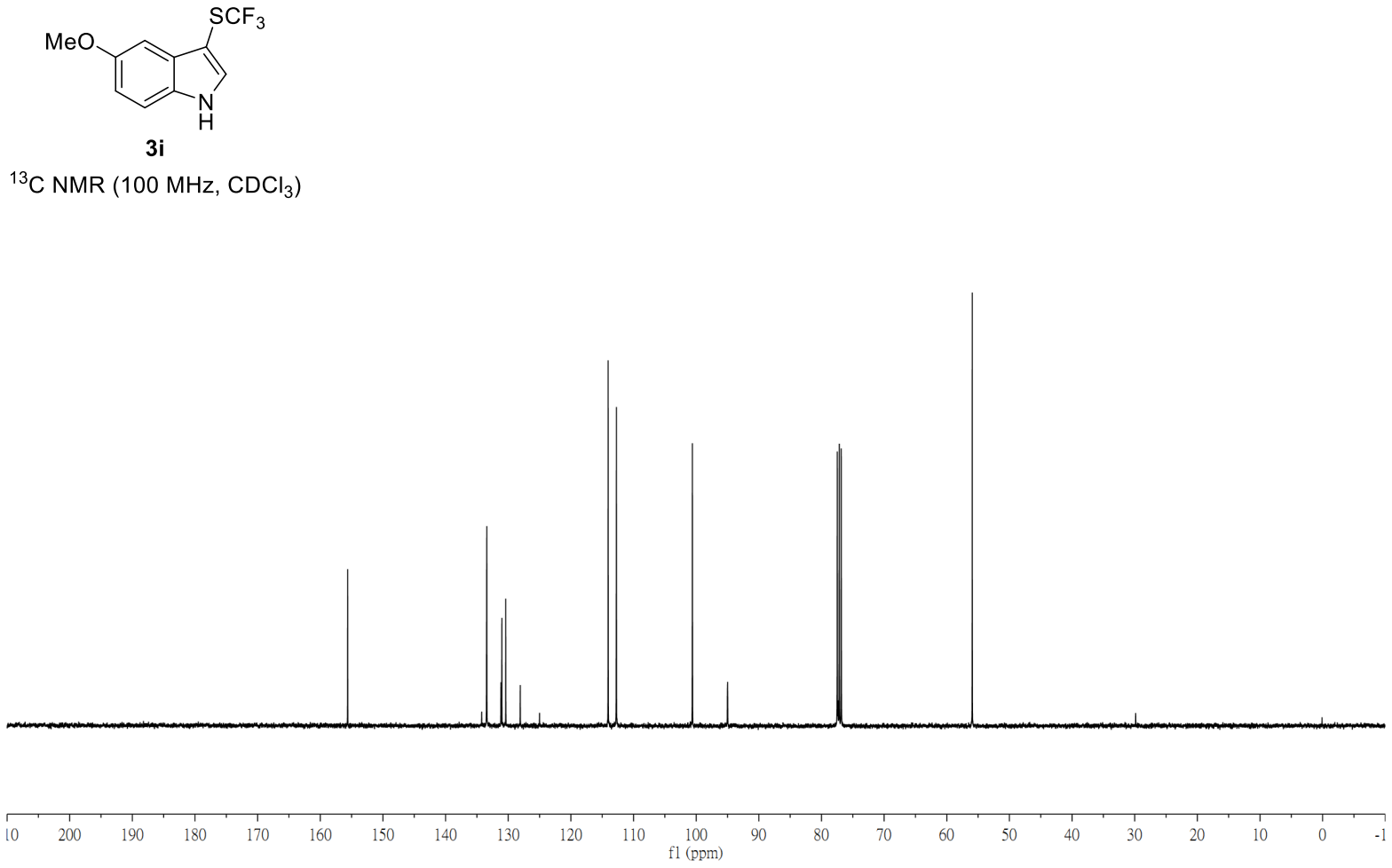
^{13}C NMR (100 MHz, $CDCl_3$)

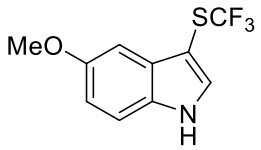


3h

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

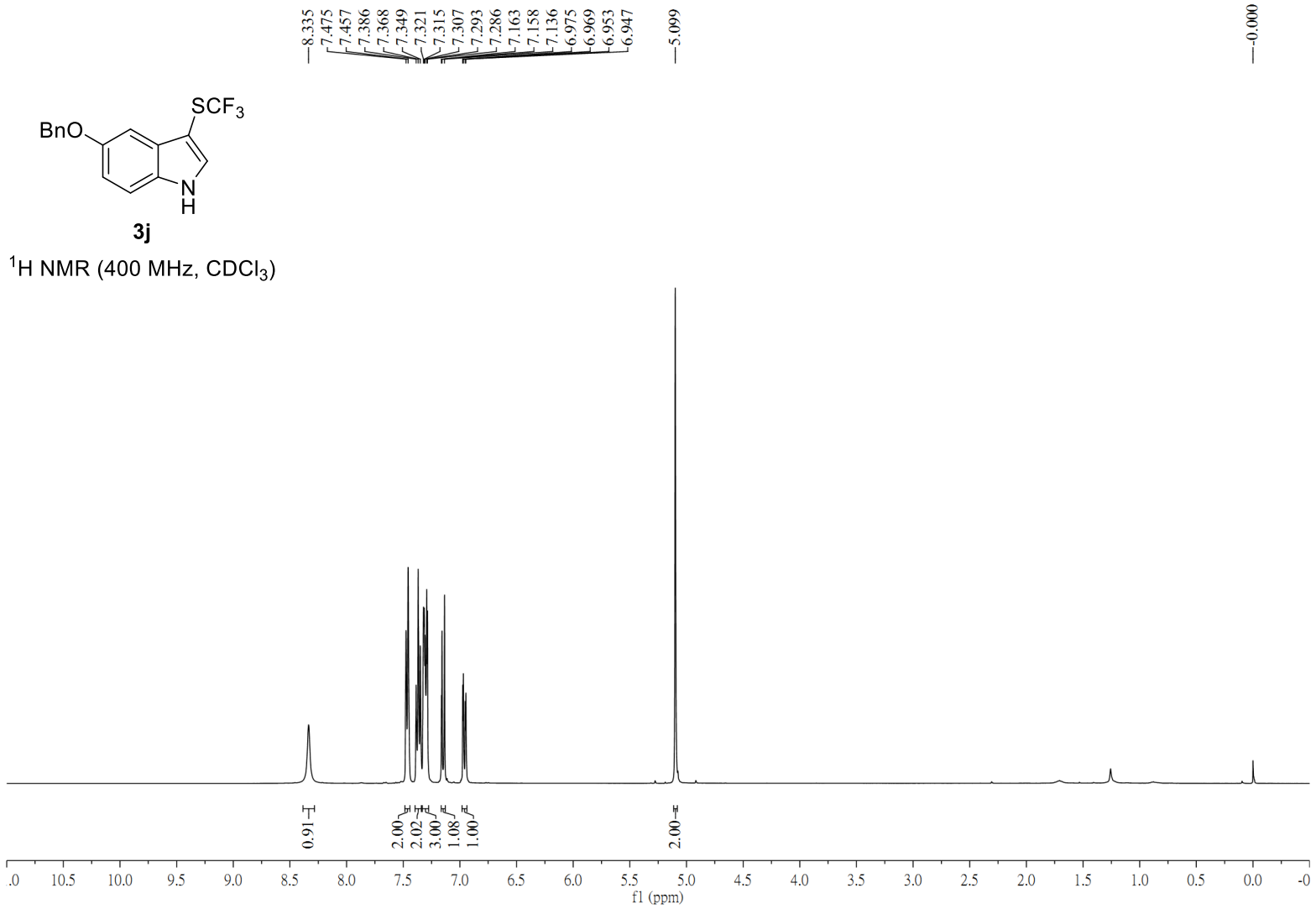

8.481
7.438
7.431
7.259
7.237
7.220
6.942
6.920
3.888
0.000
SCF3
MeO
N
H
3i
1H NMR (400 MHz, CDCl3)
0.96
1.00
2.18
1.01
3.01
f1 (ppm)

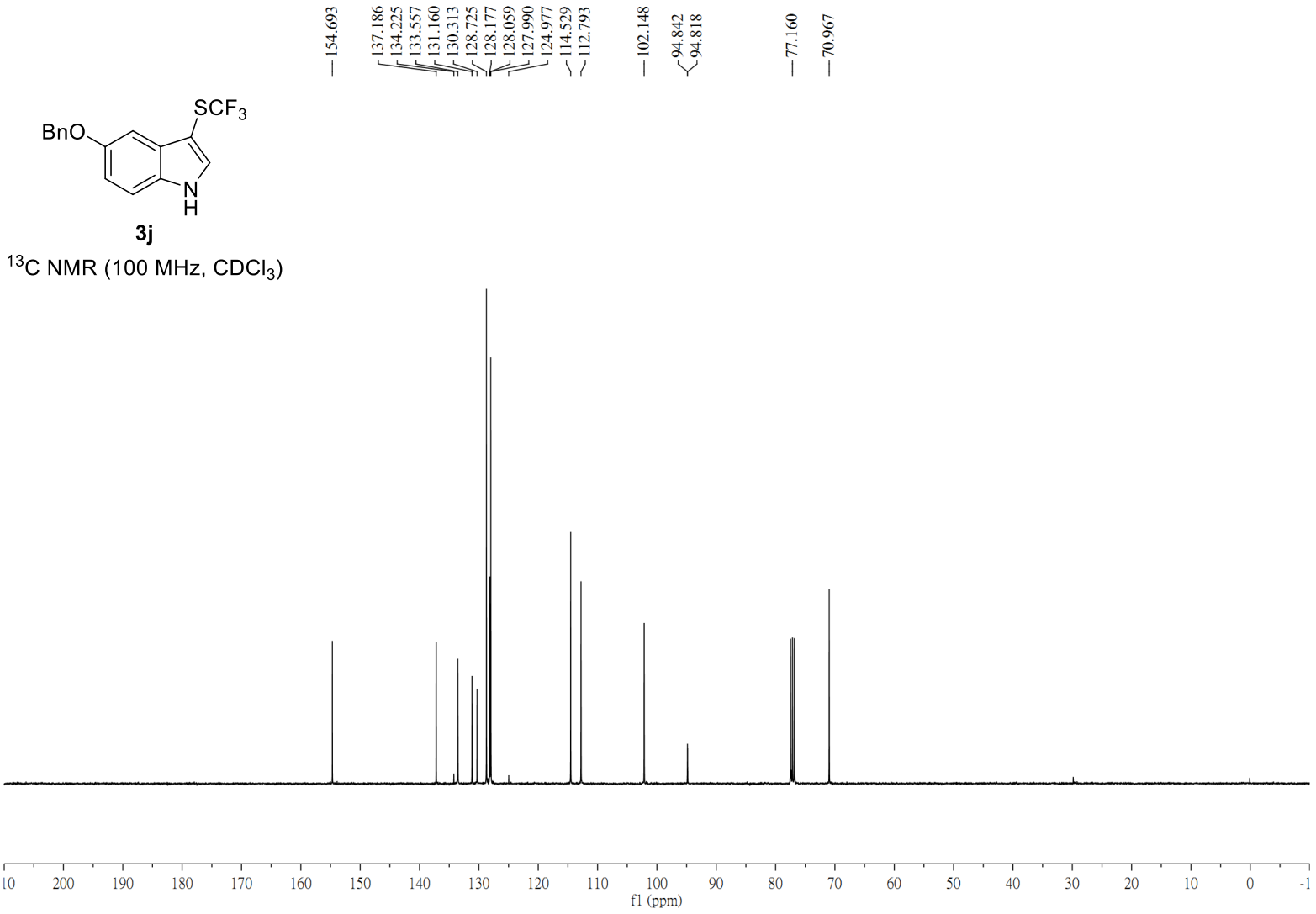

155.638
134.245
133.434
131.164
131.024
130.397
128.083
125.003
114.056
112.738
100.606
94.994
77.160
55.933
SCF3
MeO
N
H
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)

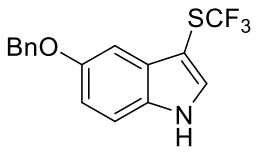


3i

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

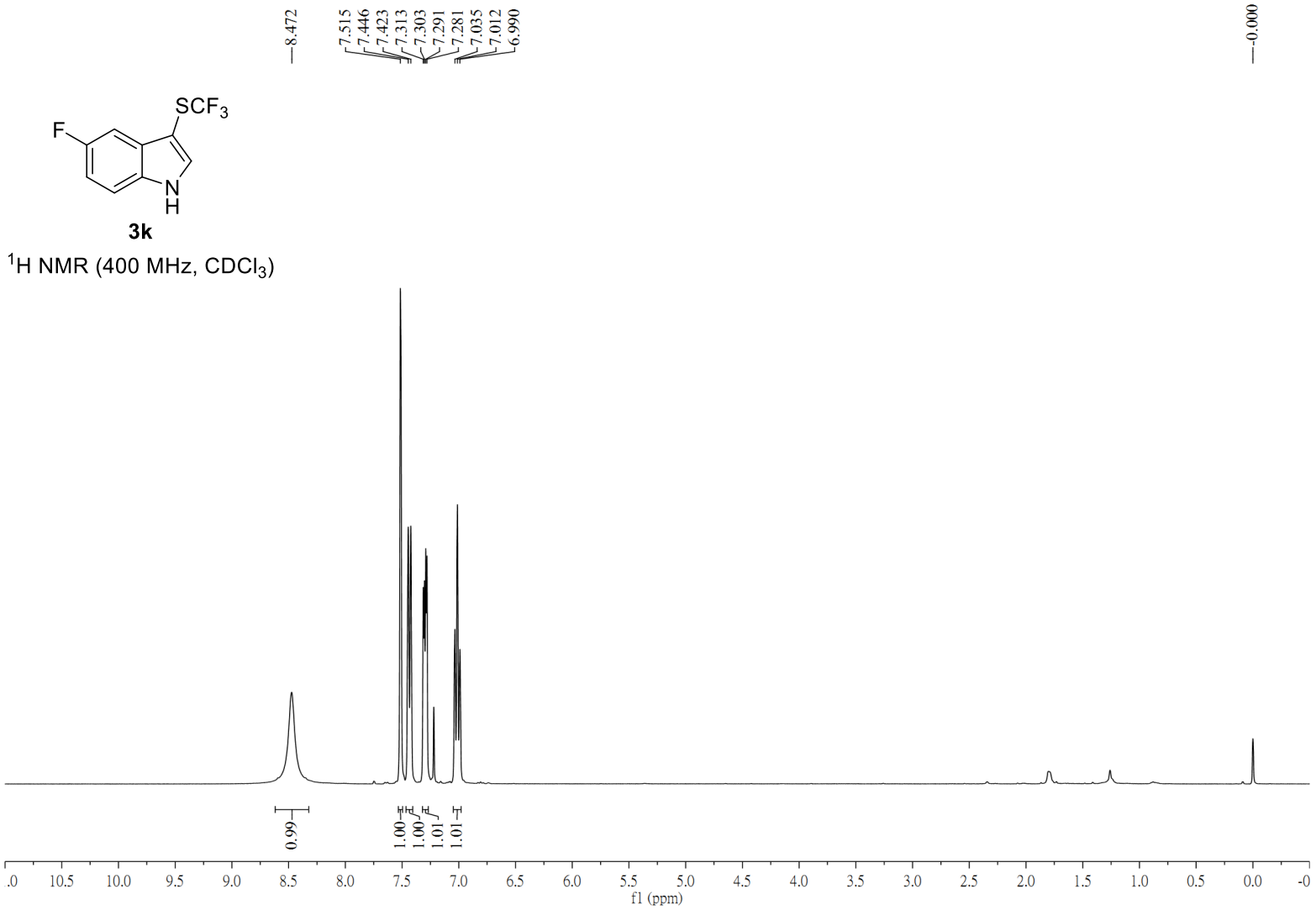

8.335
7.475
7.457
7.386
7.368
7.349
7.321
7.315
7.307
7.293
7.286
7.163
7.158
7.136
6.975
6.969
6.953
6.947
5.099
-0.000
SCF3
BnO
N
H
3j
1H NMR (400 MHz, CDCl3)
0.91
2.00
2.02
3.00
1.08
1.00
2.00
f1 (ppm)

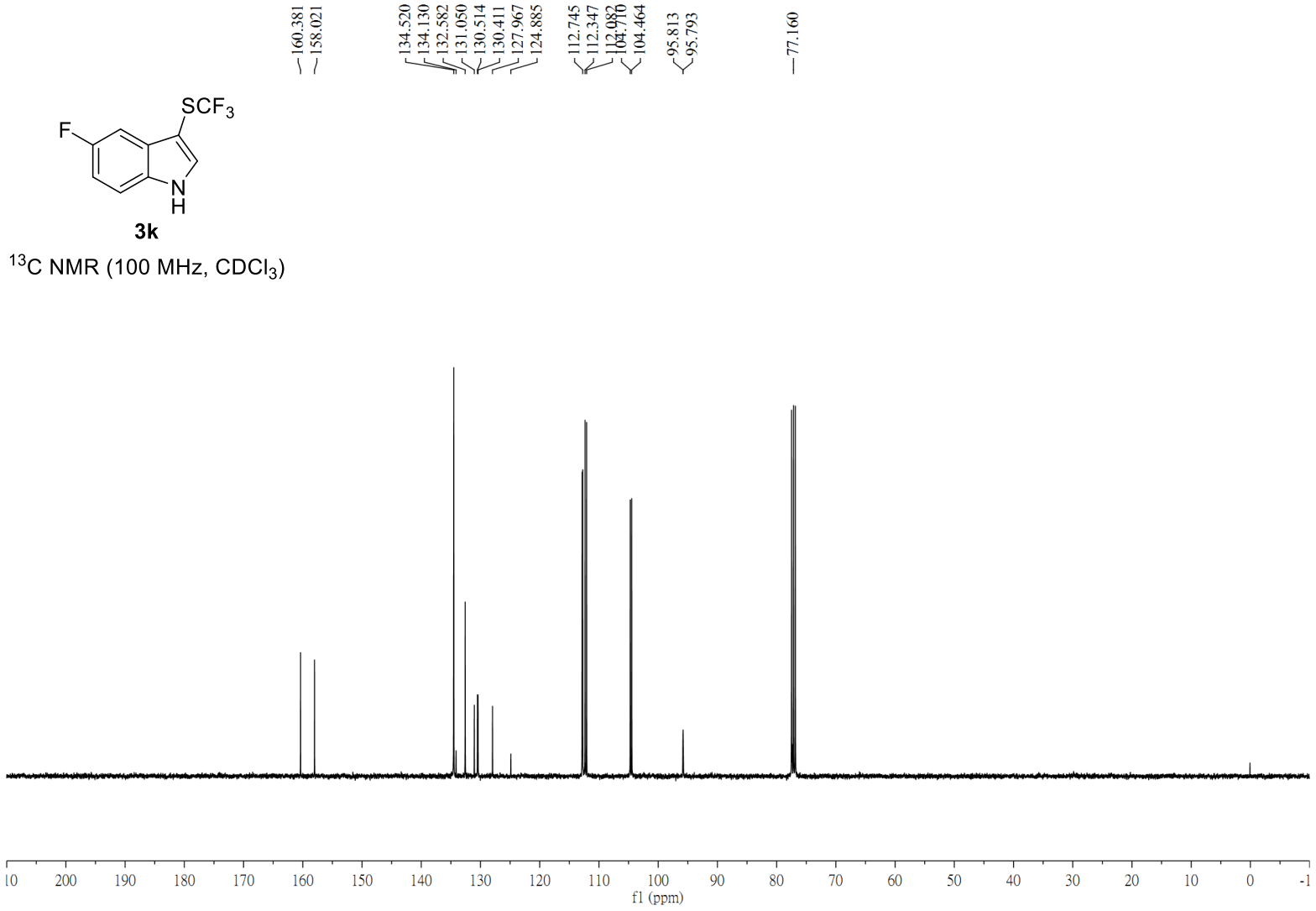

154.693
137.186
134.225
133.557
131.160
130.313
128.725
128.177
128.059
127.990
124.977
114.529
112.793
102.148
94.842
94.818
77.160
70.967
SCF3
BnO
N
H
3j
13C NMR (100 MHz, CDCl3)
f1 (ppm)

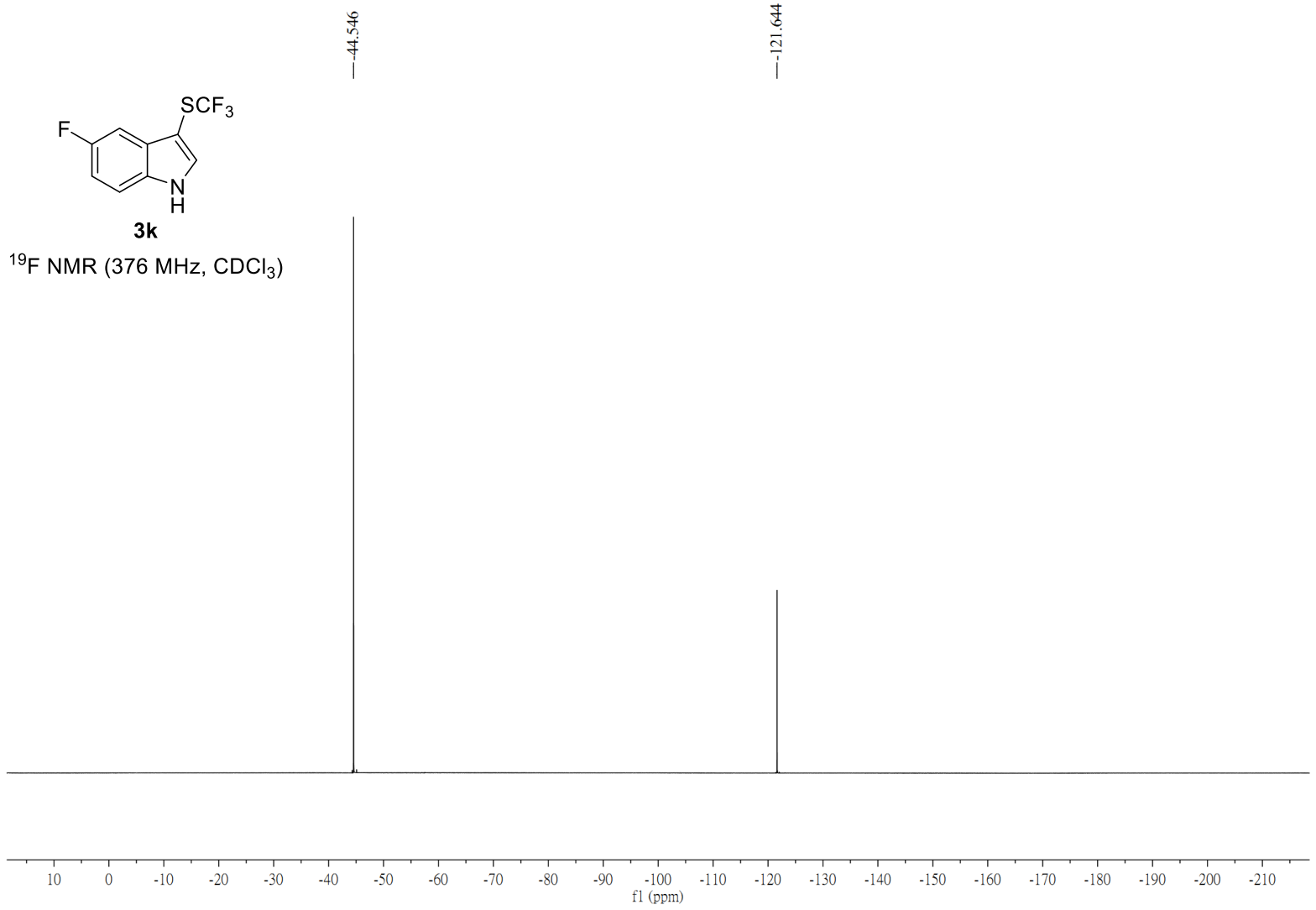


3j

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

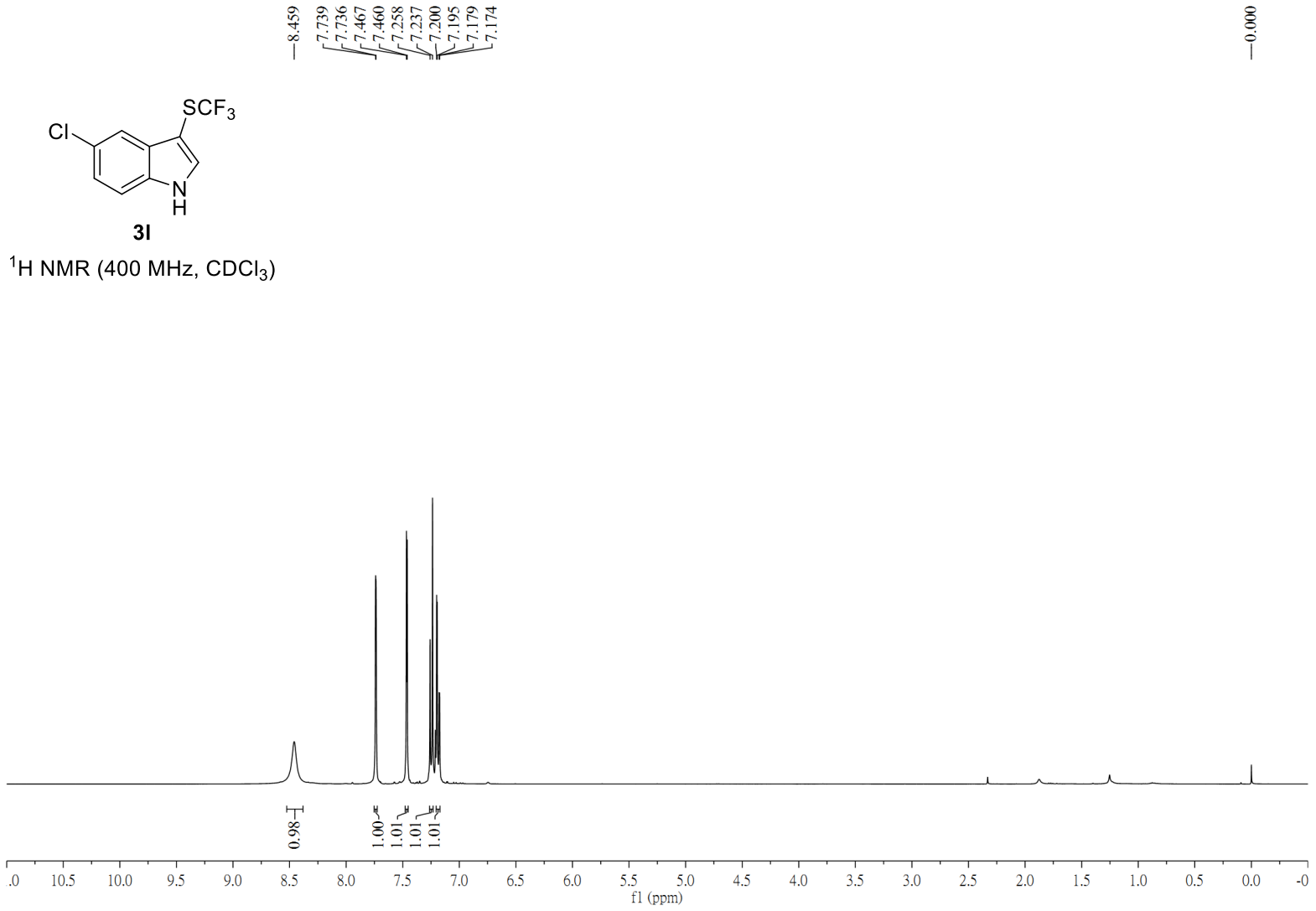

8.472
7.515
7.446
7.423
7.313
7.303
7.291
7.281
7.035
7.012
6.990
-0.000
SCF3
F
N
H
3k
1H NMR (400 MHz, CDCl3)
0.99
1.00
1.00
1.01
1.01
f1 (ppm)


160.381
158.021
134.520
134.130
132.582
131.050
130.514
130.411
127.967
124.885
112.745
112.347
104.710
104.464
95.813
95.793
77.160
SCF3
F
N
H
3k
13C NMR (100 MHz, CDCl3)
f1 (ppm)



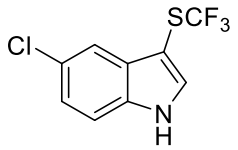
3k

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



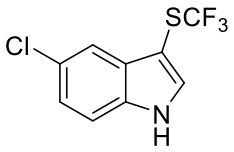
3l

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



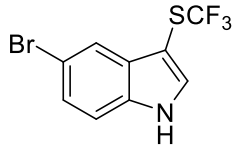
3l

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



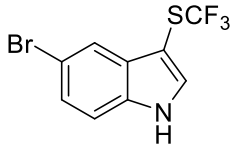
3l

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



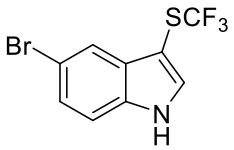
3m

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



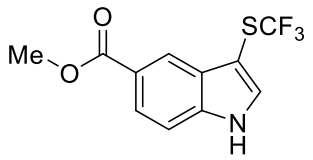
3m

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



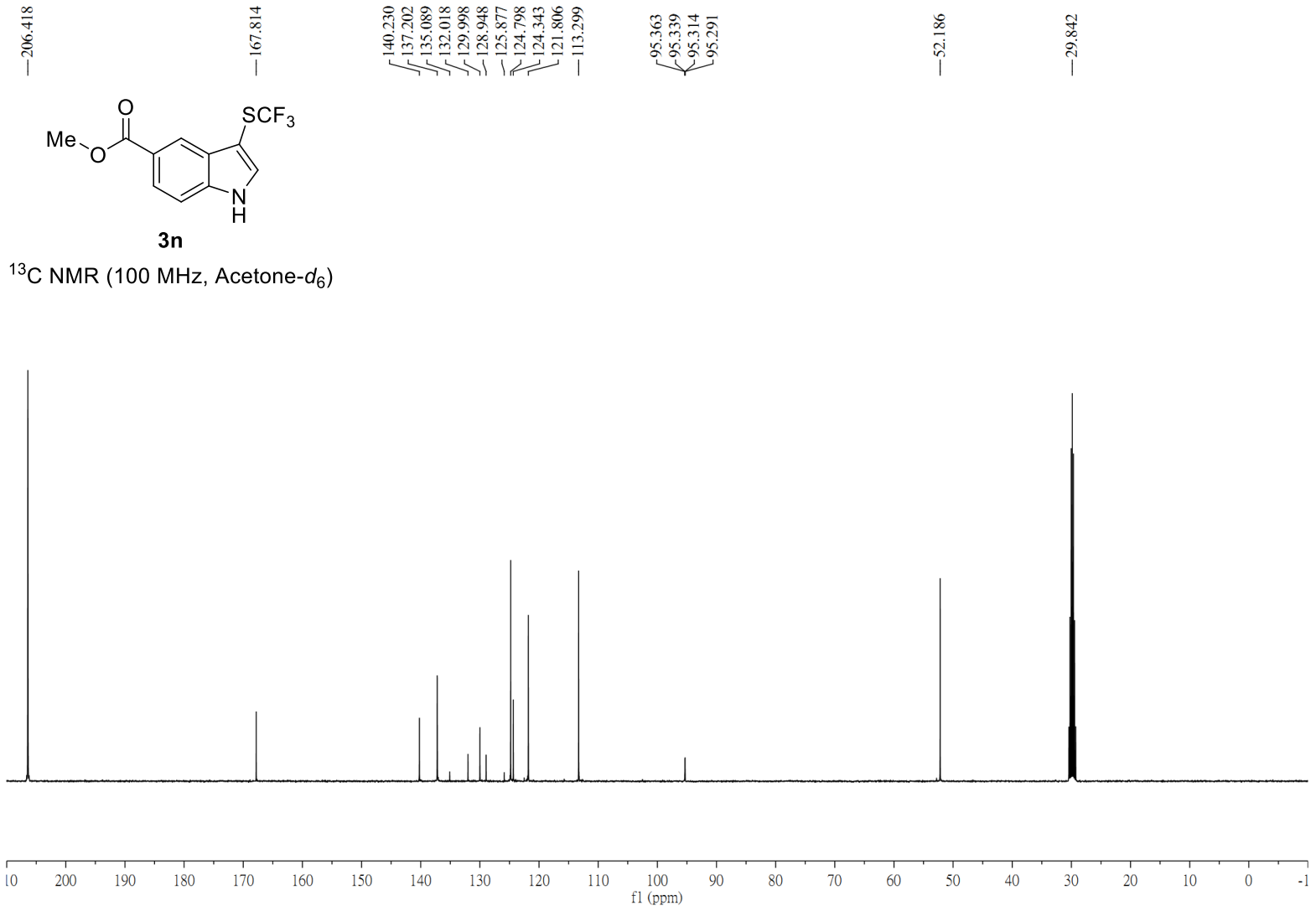
3m

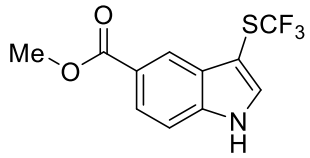
^{19}F NMR (376 MHz, $CDCl_3$)



3n

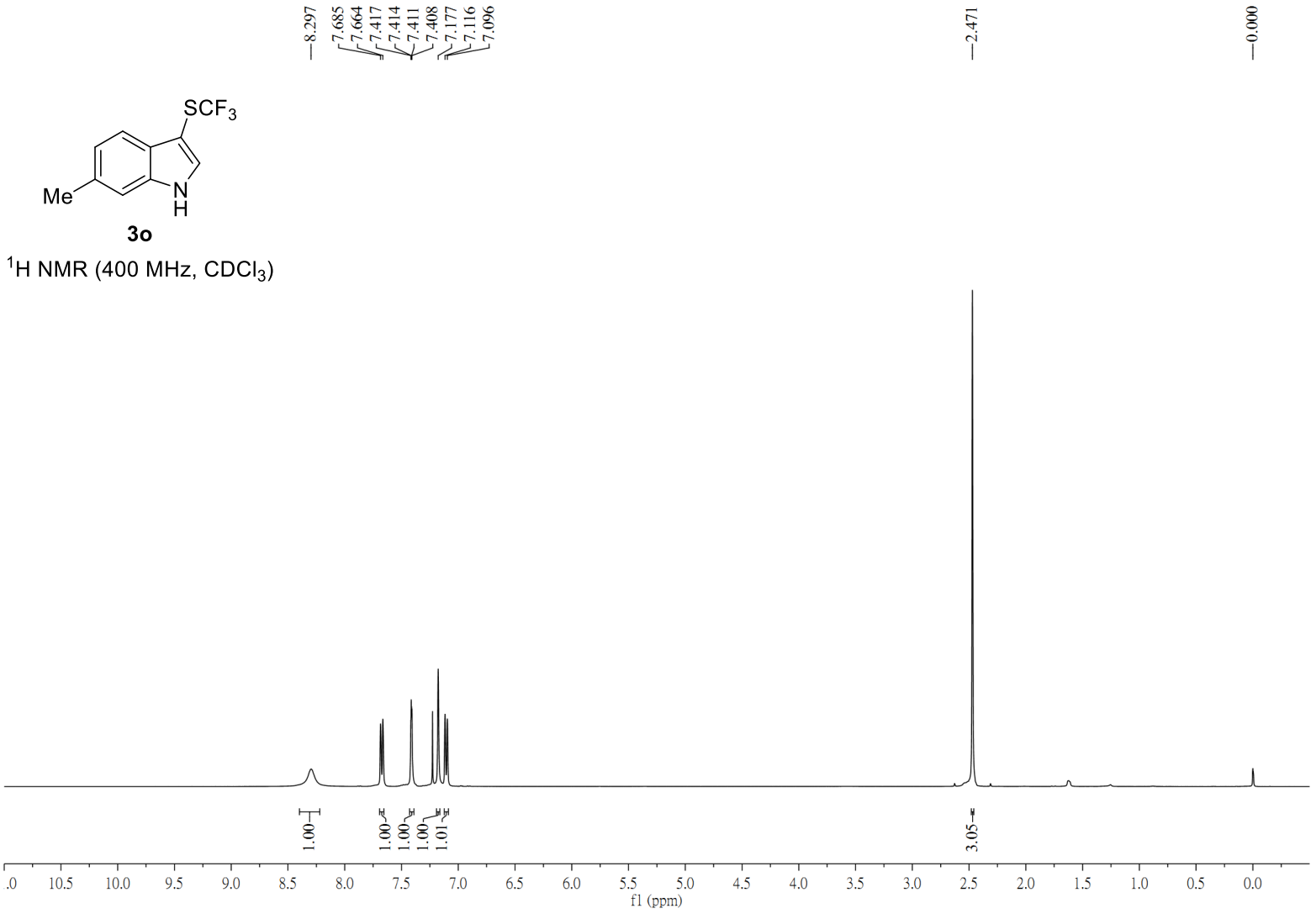
^{1}H NMR (400 MHz, Acetone-d_6)


206.418
167.814
140.230
137.202
135.089
132.018
129.998
128.948
125.877
124.798
124.343
121.806
113.299
95.363
95.339
95.314
95.291
52.186
29.842
O
Me
O
SCF3
N
H
3n
13C NMR (100 MHz, Acetone-d6)
f1 (ppm)



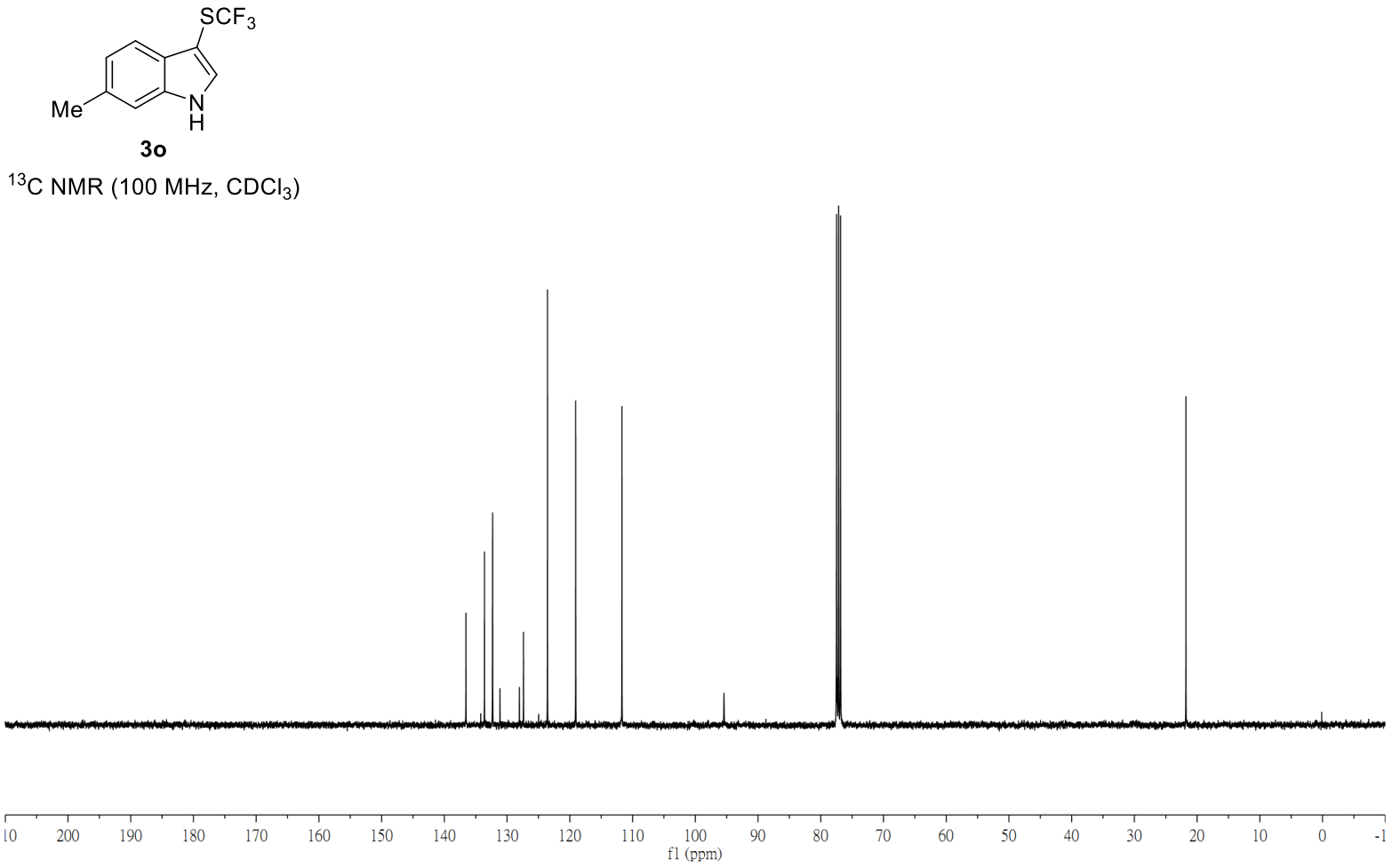
3n

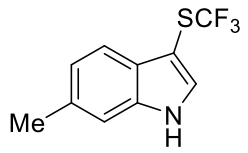
^{19}F NMR (376 MHz, Acetone-d_6)



3o

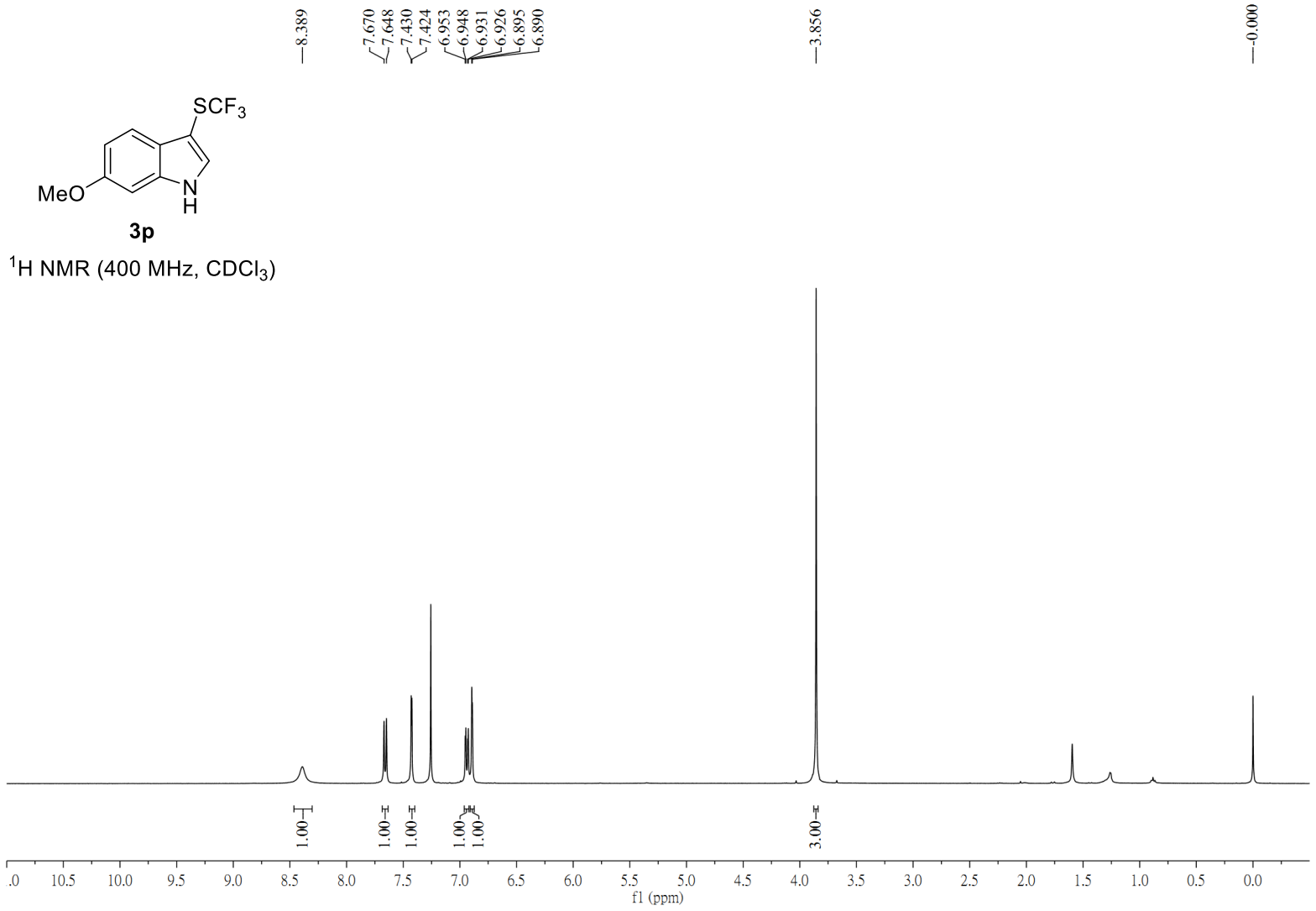
^{1}H NMR (400 MHz, $CDCl_3$)

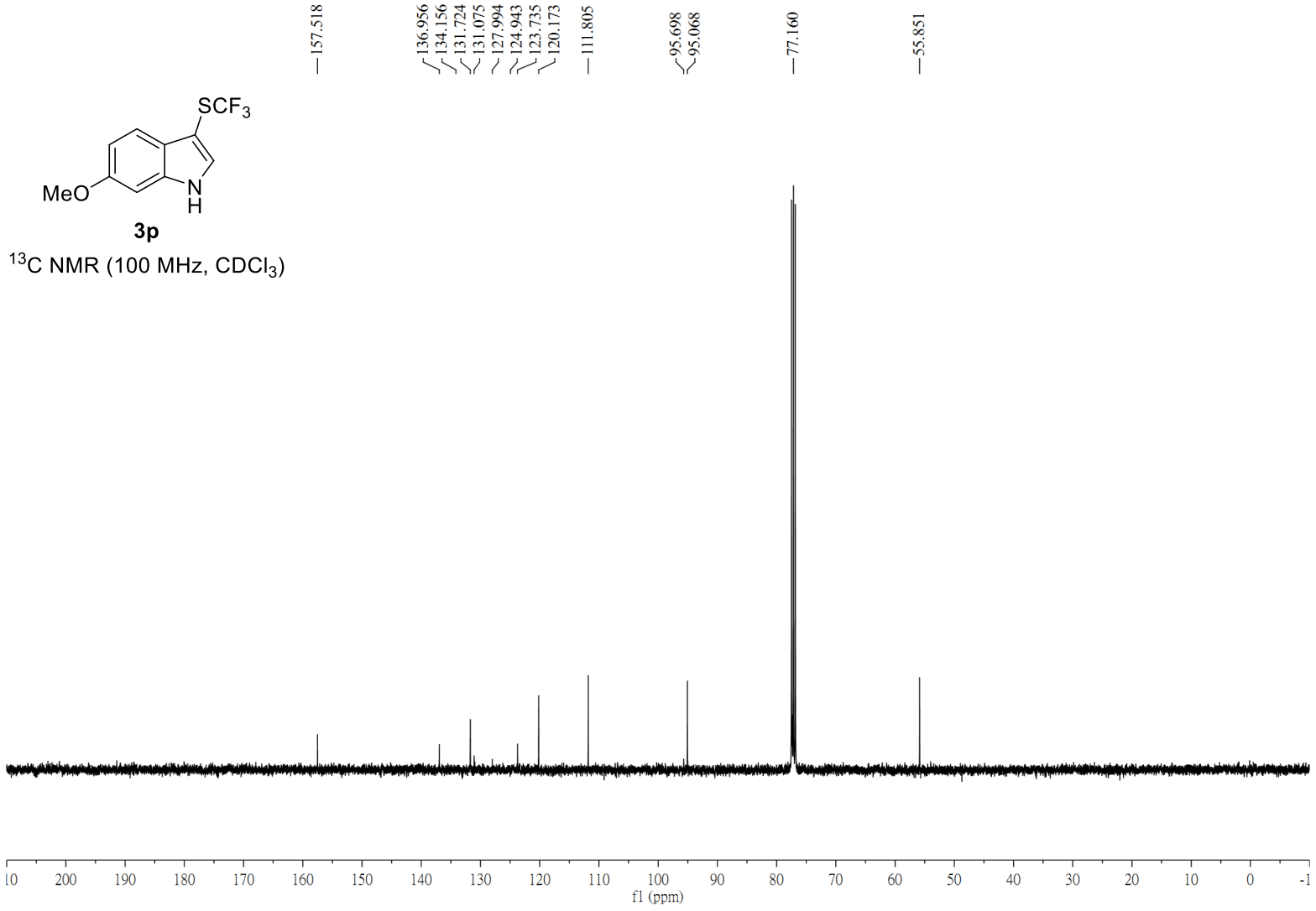

136.565
134.212
133.608
132.314
131.133
128.053
127.392
124.974
123.563
119.061
111.698
95.424
77.160
21.782
SCF3
Me
N
H
3o
13C NMR (100 MHz, CDCl3)
f1 (ppm)

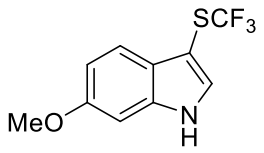


3o

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

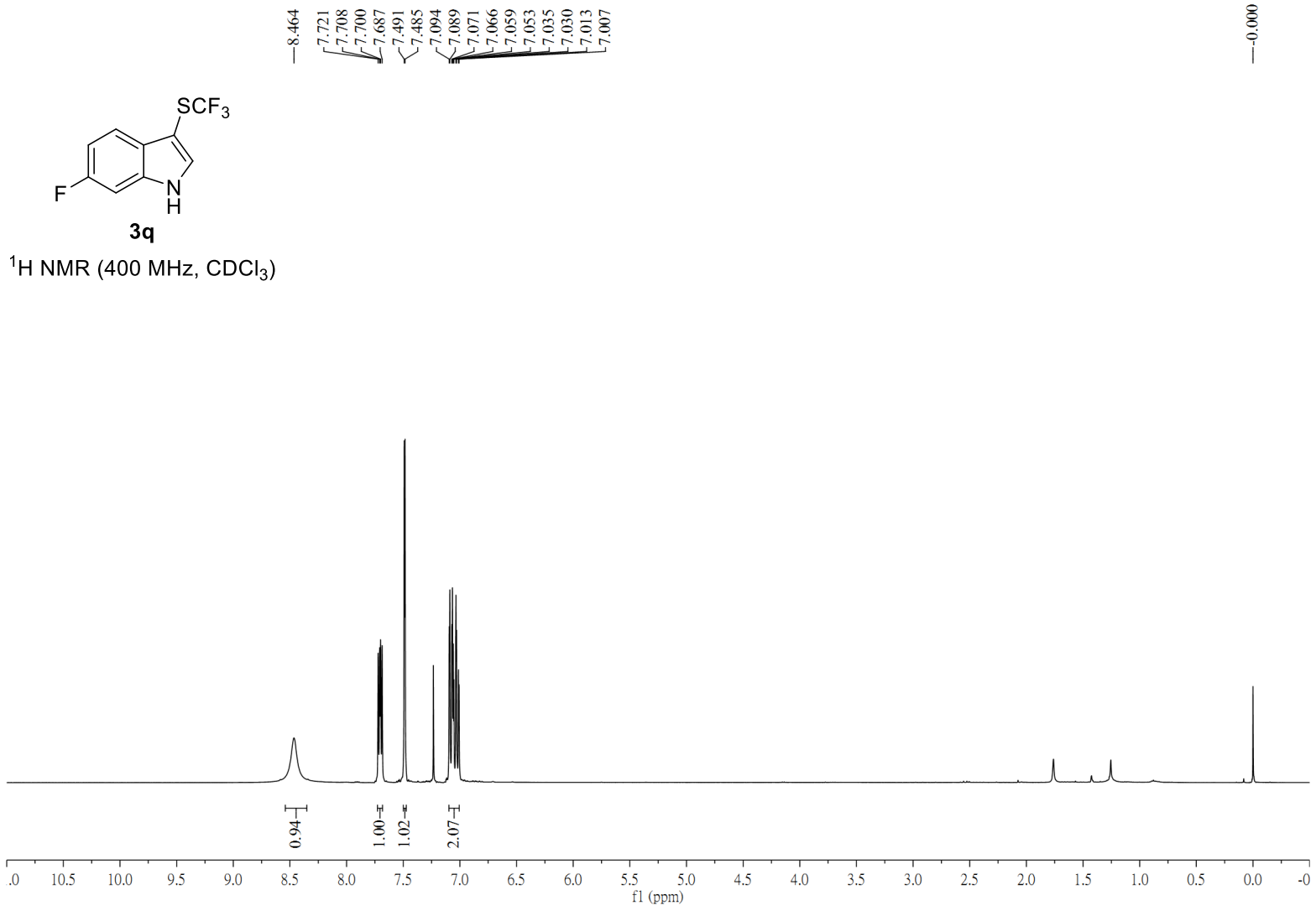

8.389
7.670
7.648
7.430
7.424
6.953
6.948
6.931
6.926
6.895
6.890
3.856
-0.000
SCF3
MeO
N
H
3p
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)


157.518
136.956
134.156
131.724
131.075
127.994
124.943
123.735
120.173
111.805
95.698
95.068
77.160
55.851
SCF3
MeO
N
H
3p
13C NMR (100 MHz, CDCl3)
f1 (ppm)



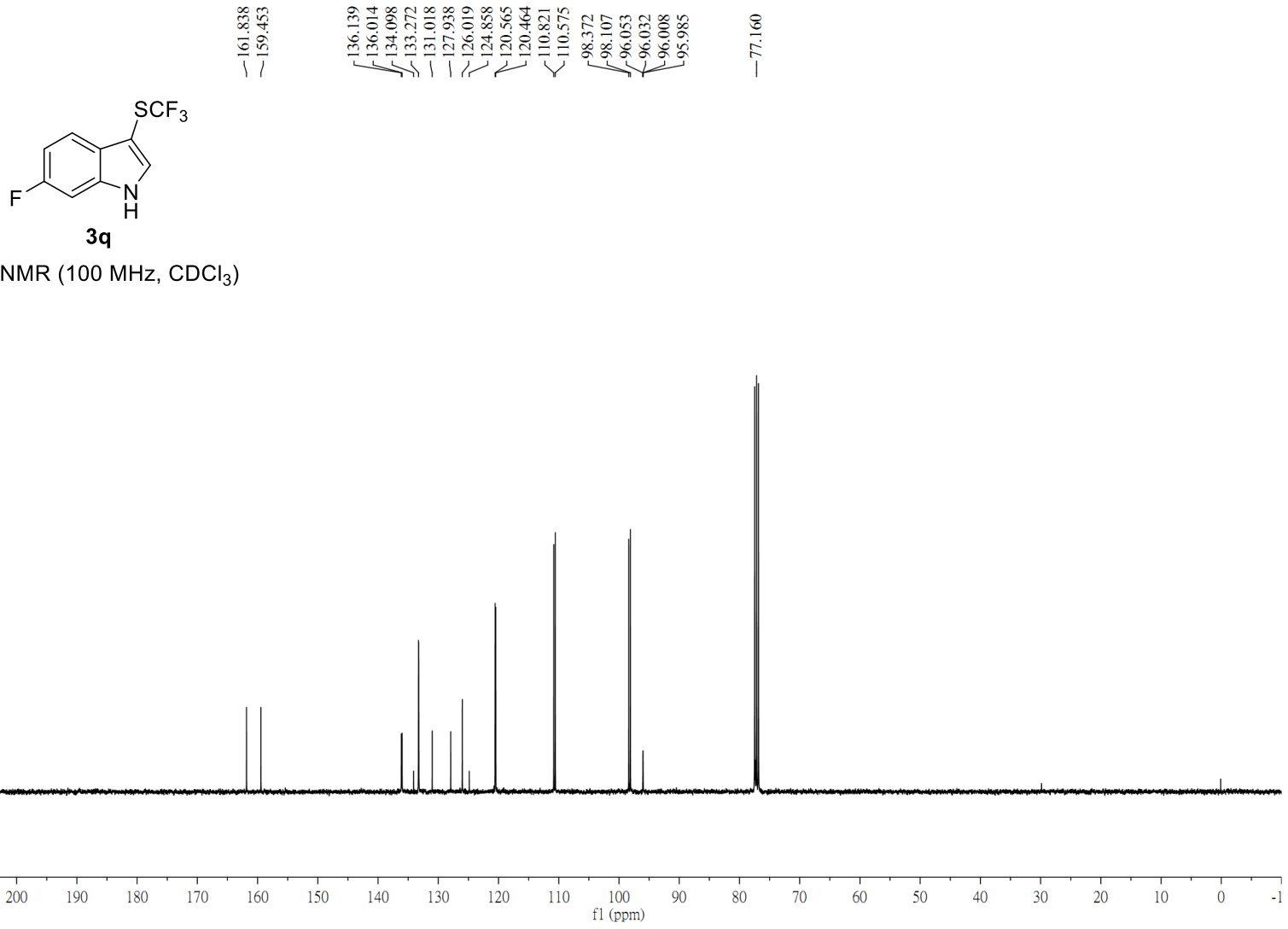
3p

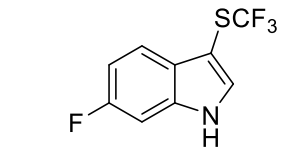
^{19}F NMR (376 MHz, $CDCl_3$)



3q

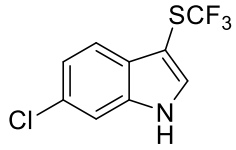
^{1}H NMR (400 MHz, $CDCl_3$)


161.838
159.453
136.139
136.014
134.098
133.272
131.018
127.938
126.019
124.858
120.565
120.464
110.821
110.575
98.372
98.107
96.053
96.032
96.008
95.985
77.160
SCF3
F
N
H
3q
13C NMR (100 MHz, CDCl3)
f1 (ppm)



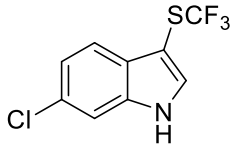
3q

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



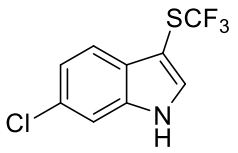
3r

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



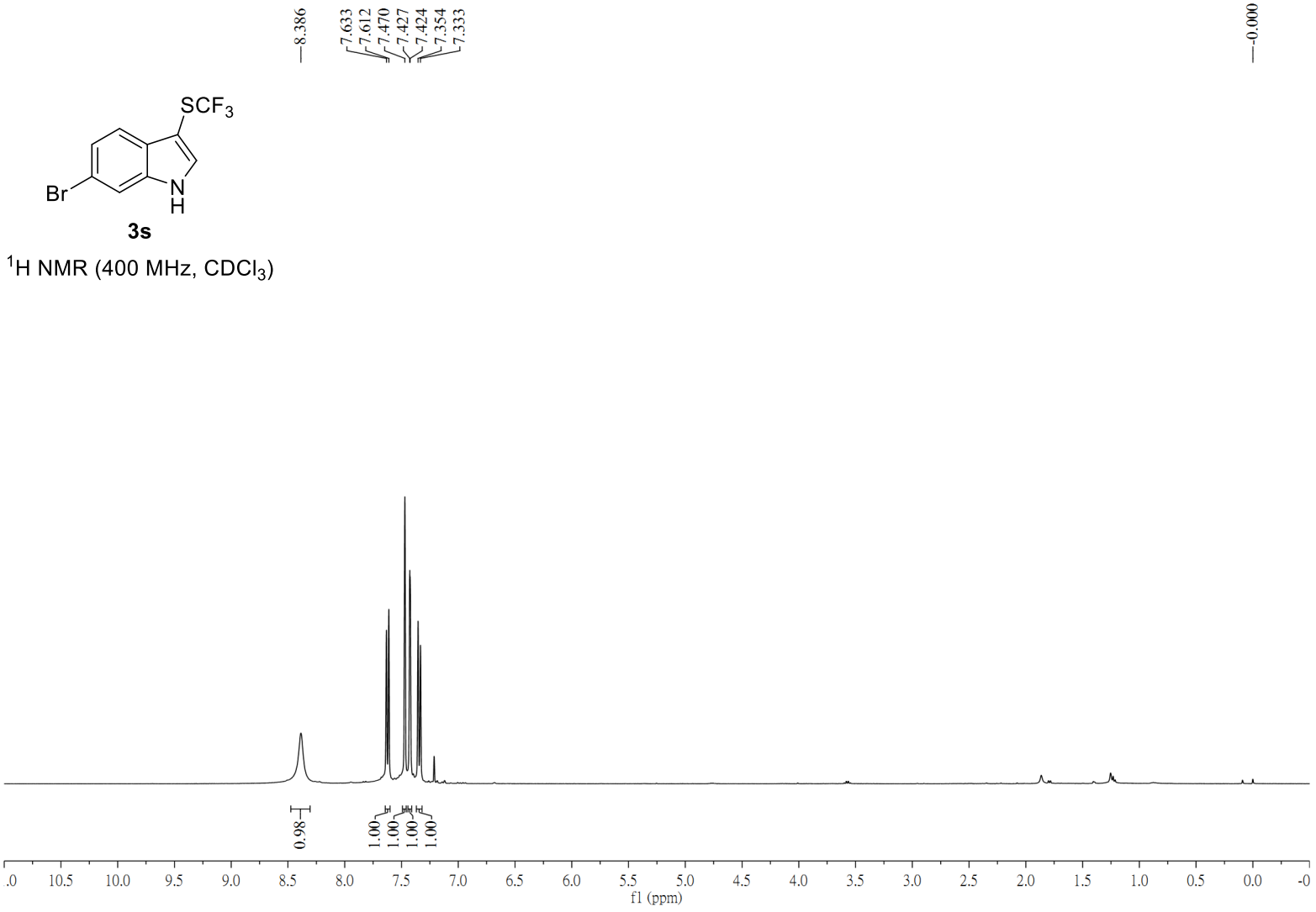
3r

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



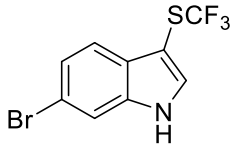
3r

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



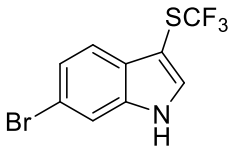
3s

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



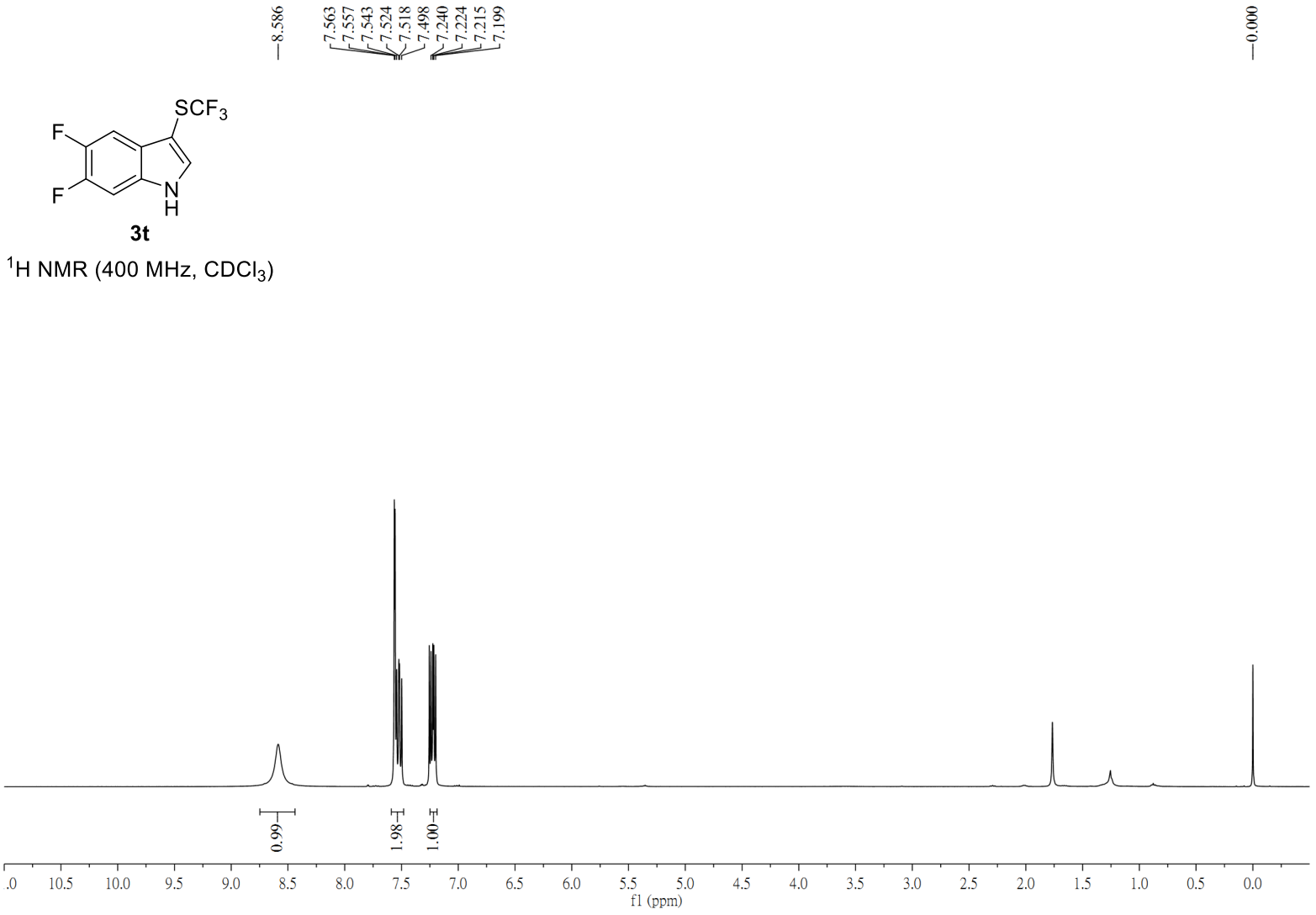
3s

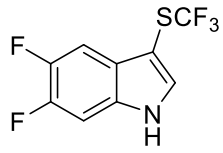
^{13}C NMR (100 MHz, $CDCl_3$)



3s

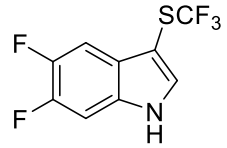
^{19}F NMR (376 MHz, $CDCl_3$)


8.586
7.563
7.557
7.543
7.524
7.518
7.498
7.240
7.224
7.215
7.199
0.000
SCF3
F
F
N
H
3t
1H NMR (400 MHz, CDCl3)
0.99
1.98
1.00
f1 (ppm)



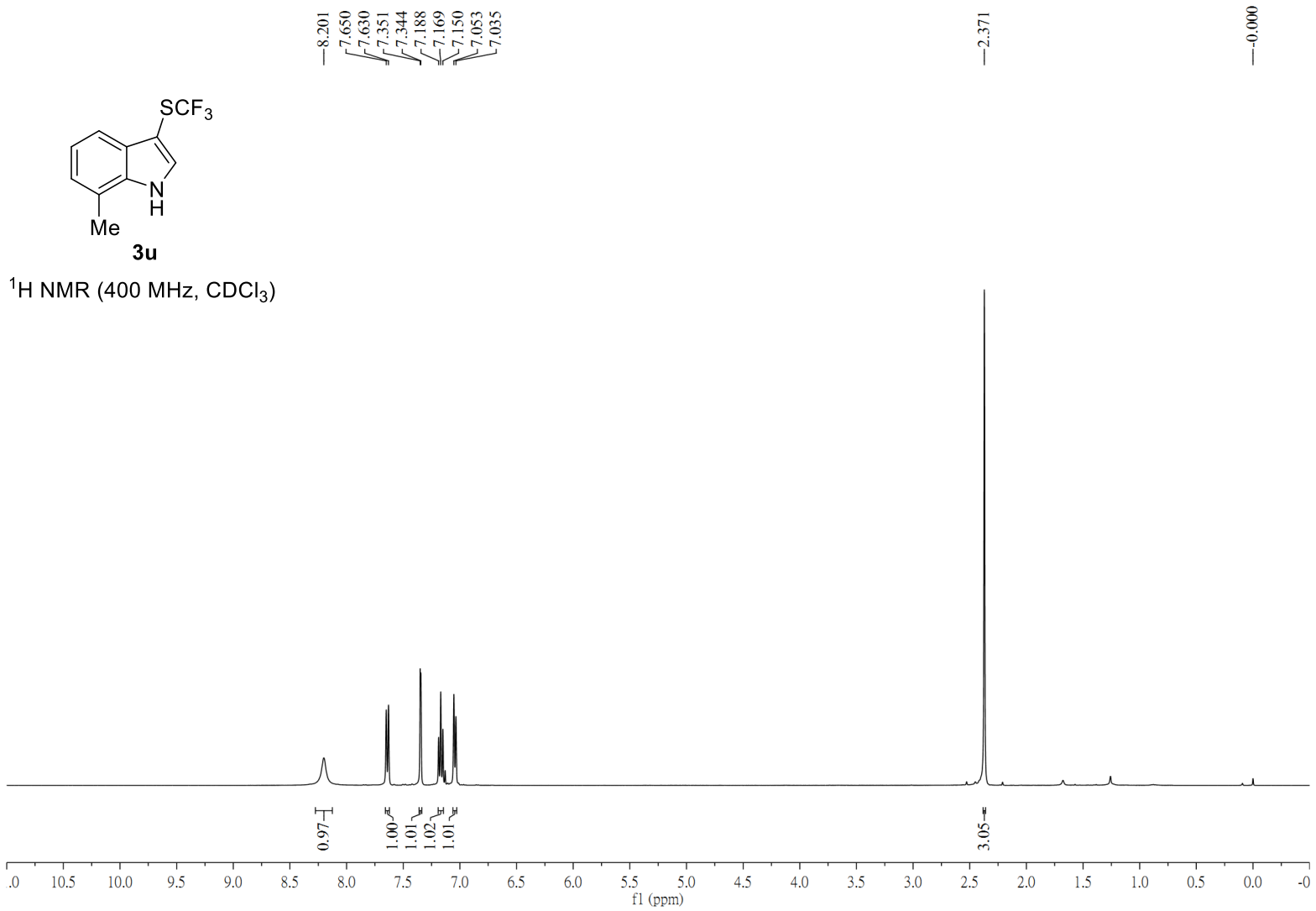
3t

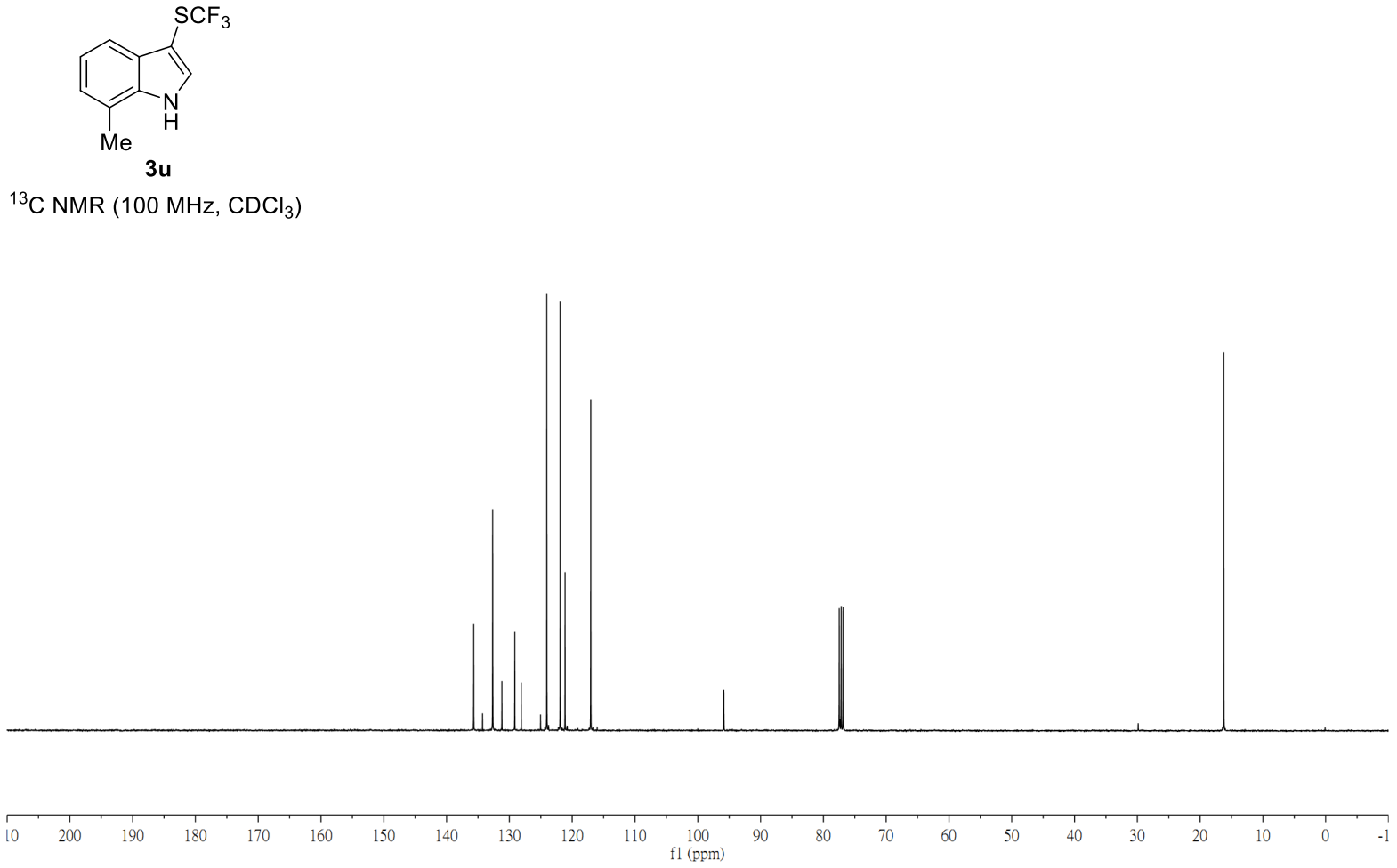
^{13}C NMR (100 MHz, $CDCl_3$)



3t

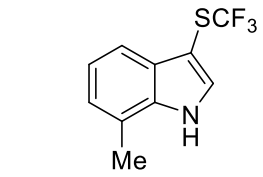
^{19}F NMR (376 MHz, $CDCl_3$)


8.201
7.650
7.630
7.351
7.344
7.188
7.169
7.150
7.053
7.035
2.371
-0.000
SCF3
N
H
Me
3u
1H NMR (400 MHz, CDCl3)
0.97
1.00
1.01
1.02
1.01
3.05
f1 (ppm)



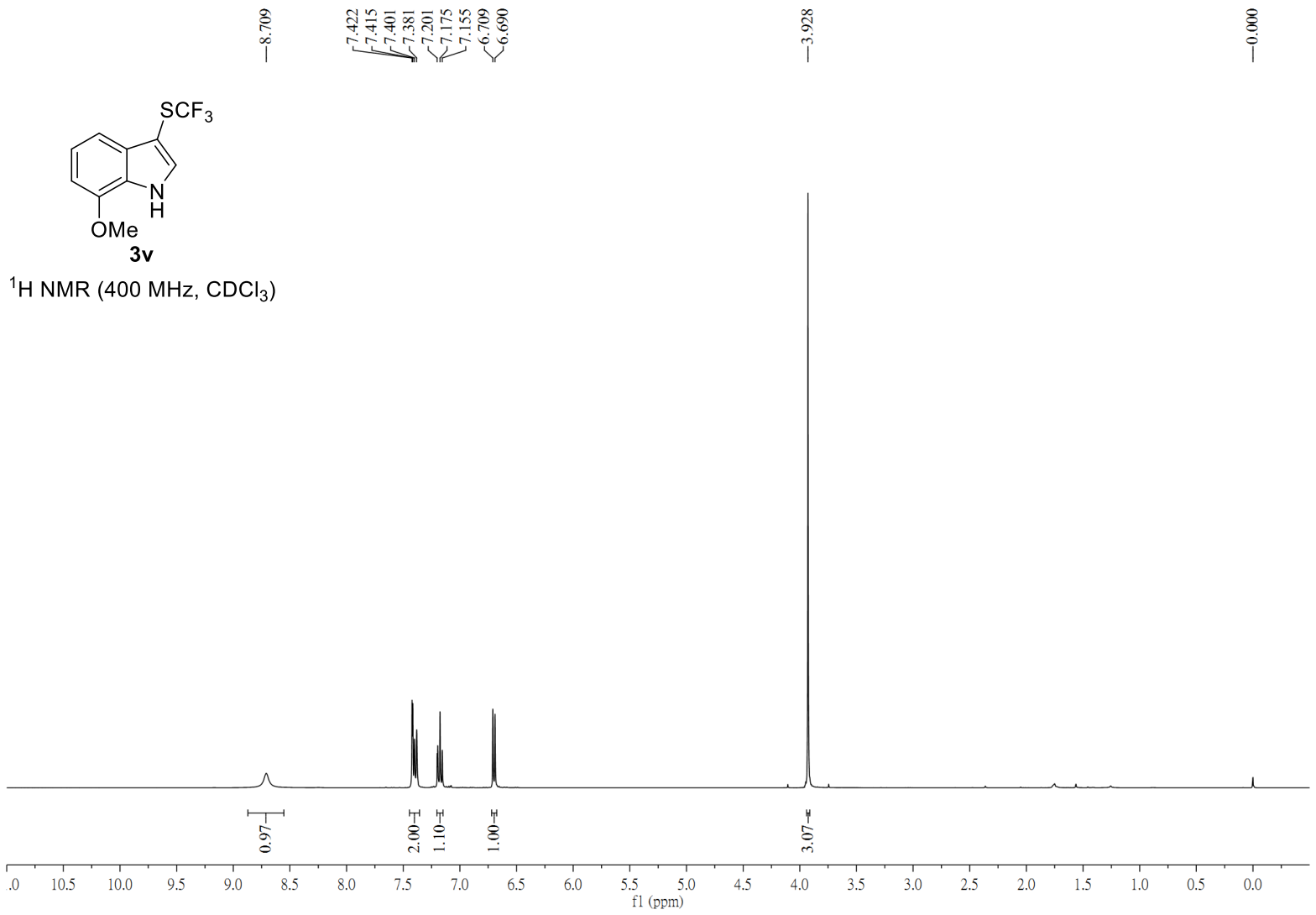
3u

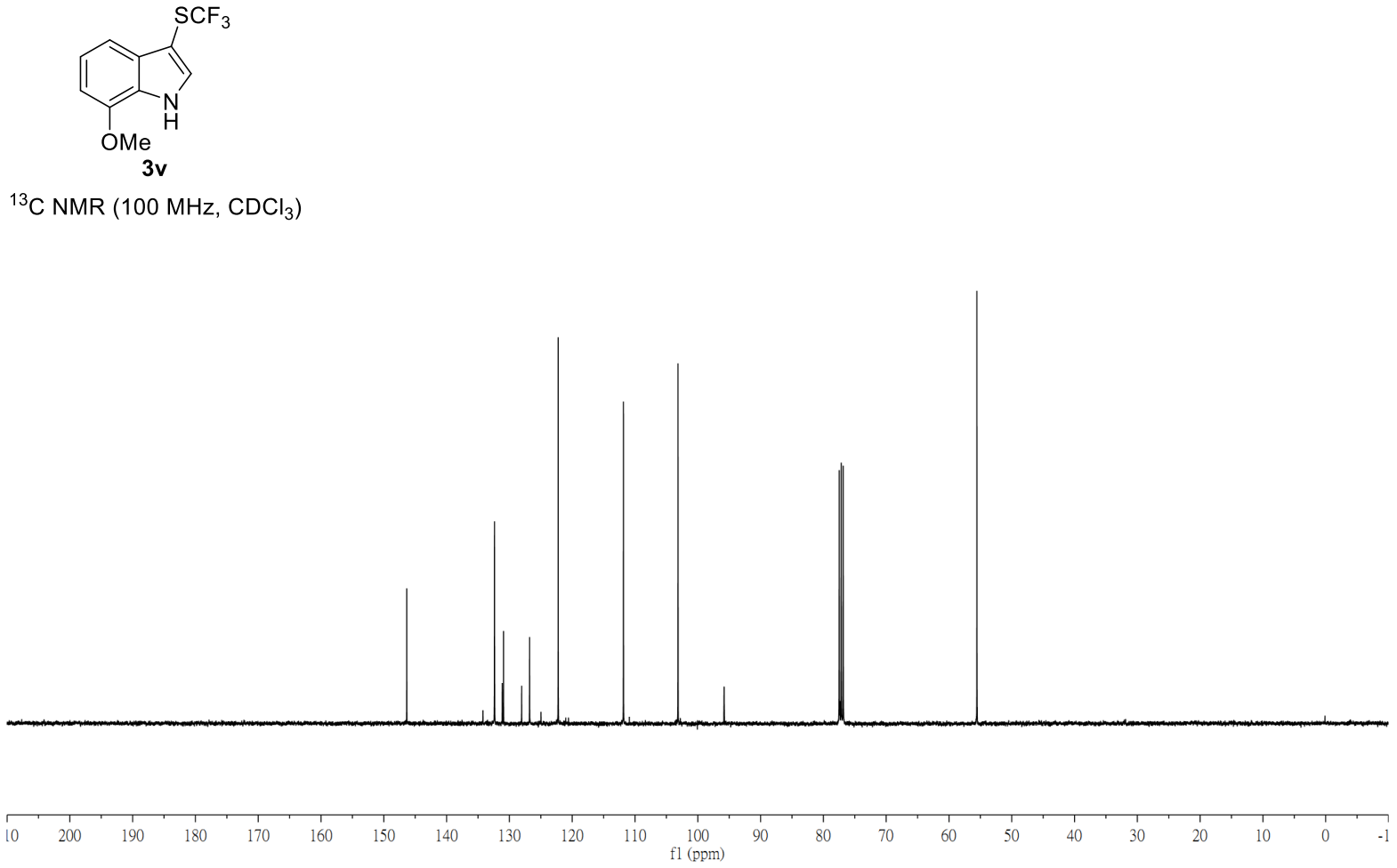
^{13}C NMR (100 MHz, $CDCl_3$)



3u

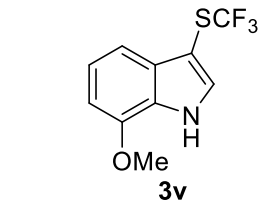
^{19}F NMR (376 MHz, $CDCl_3$)


8.709
7.422
7.415
7.401
7.381
7.201
7.175
7.155
6.709
6.690
3.928
0.000
SCF3
N
H
OMe
3v
1H NMR (400 MHz, CDCl3)
0.97
2.00
1.10
1.00
3.07
f1 (ppm)



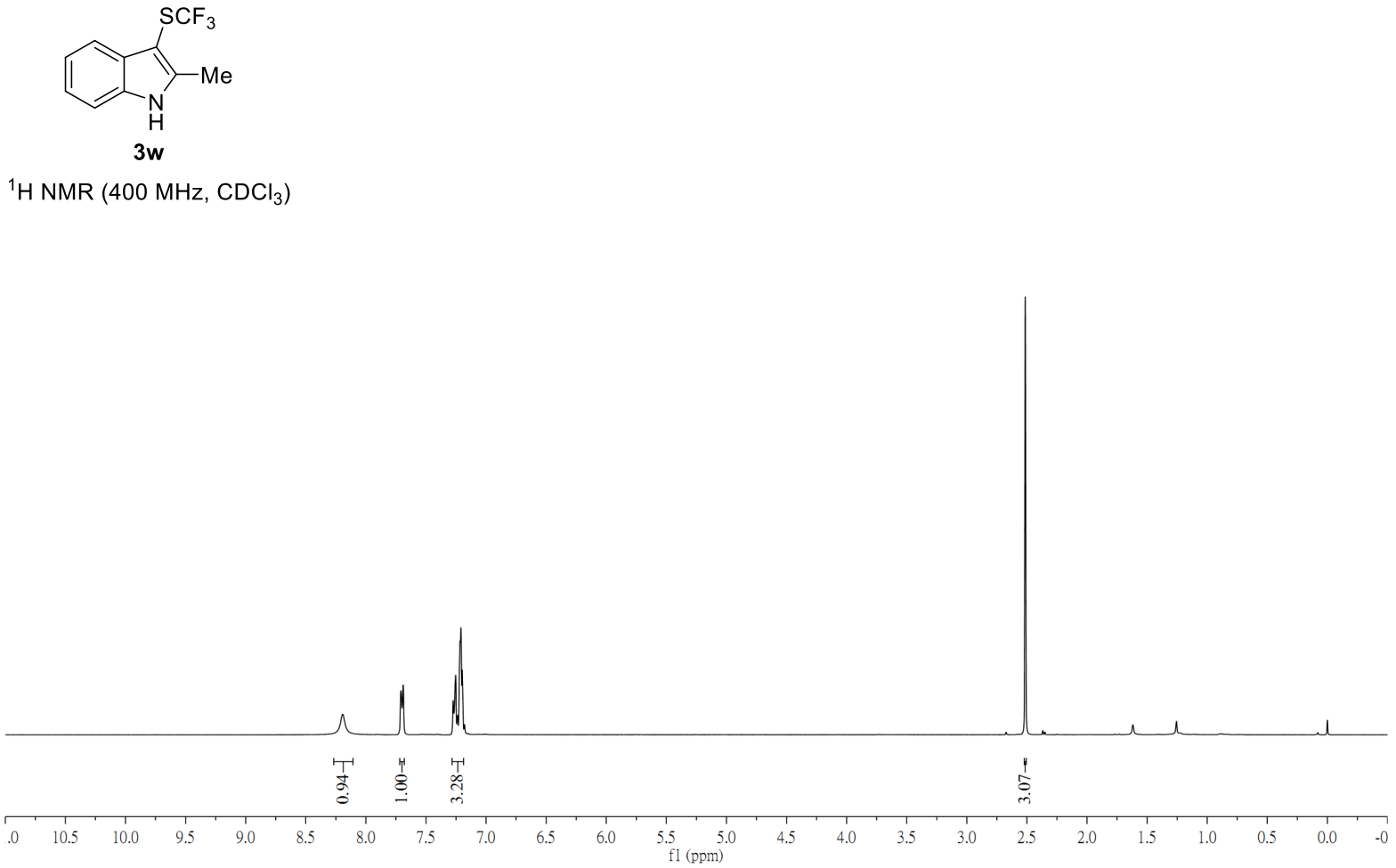
3v

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



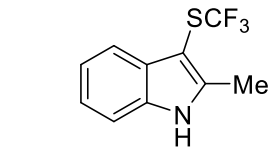
3v

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



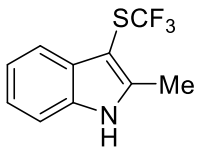
3w

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



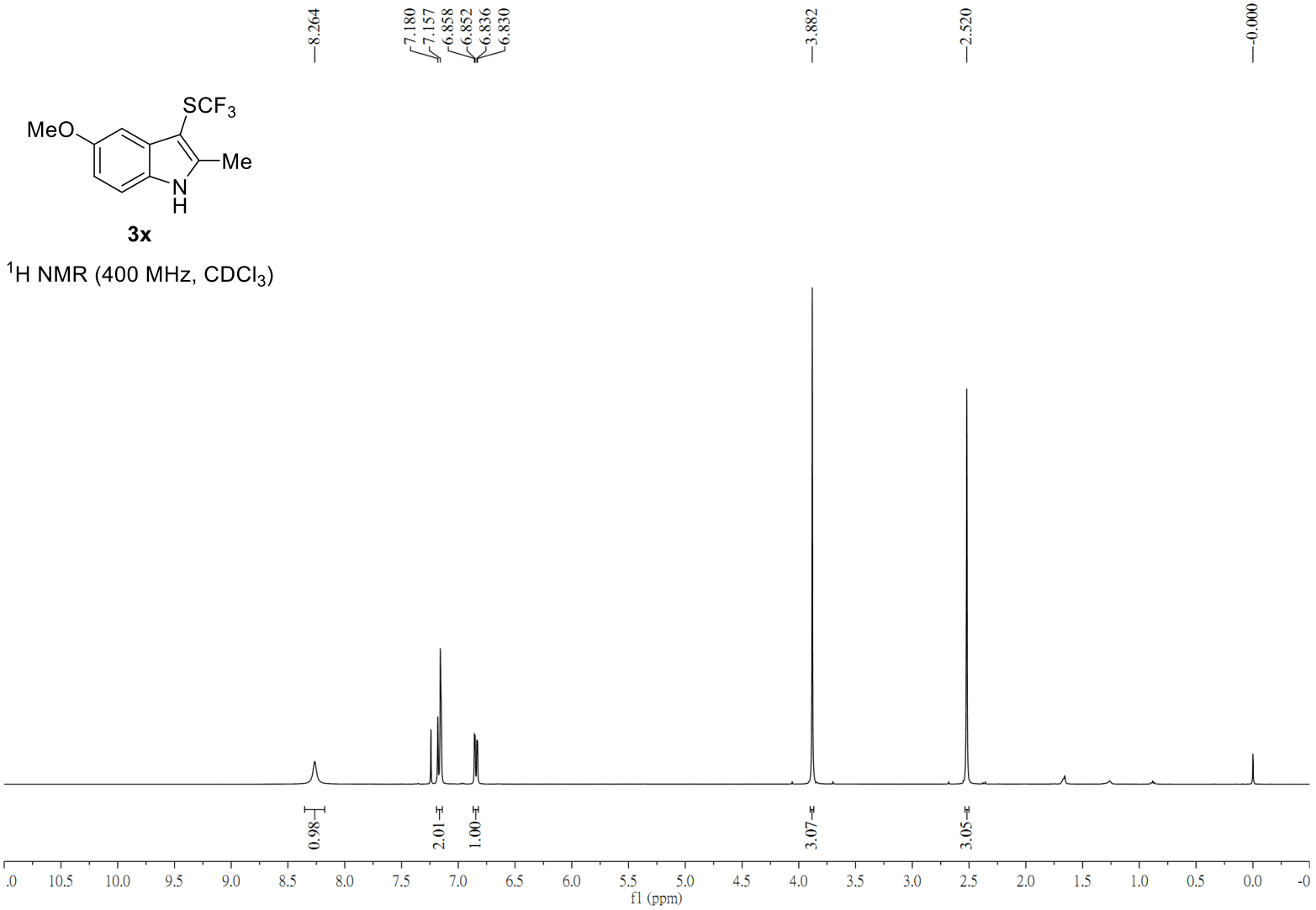
3w

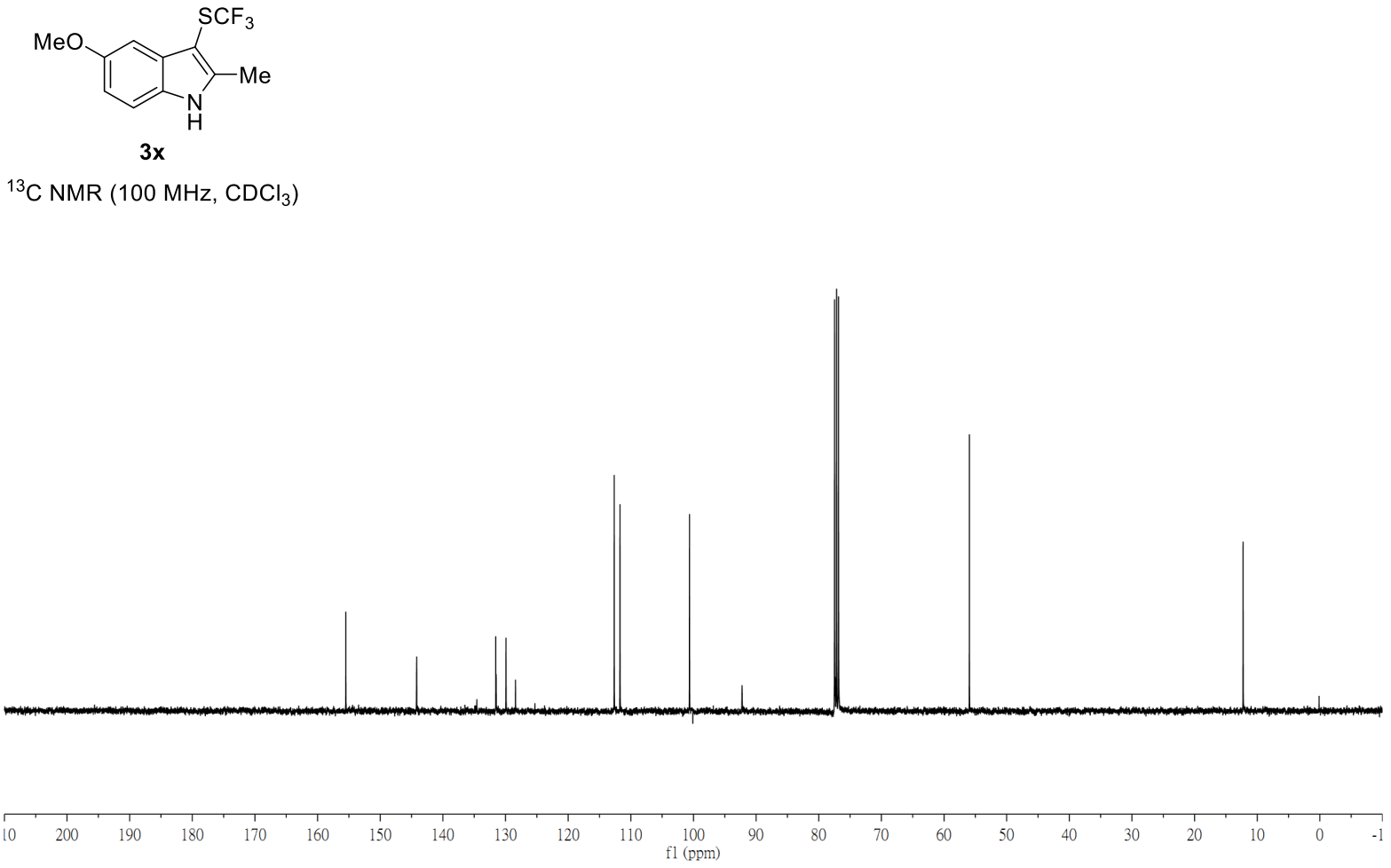
^{13}C NMR (100 MHz, $CDCl_3$)



3w

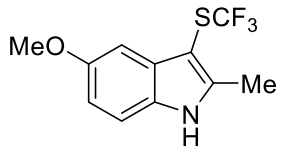
^{19}F NMR (376 MHz, $CDCl_3$)


8.264
7.180
7.157
6.858
6.852
6.836
6.830
3.882
2.520
0.000
SCF3
MeO
Me
N
H
3x
1H NMR (400 MHz, CDCl3)
0.98
2.01
1.00
3.07
3.05
f1 (ppm)



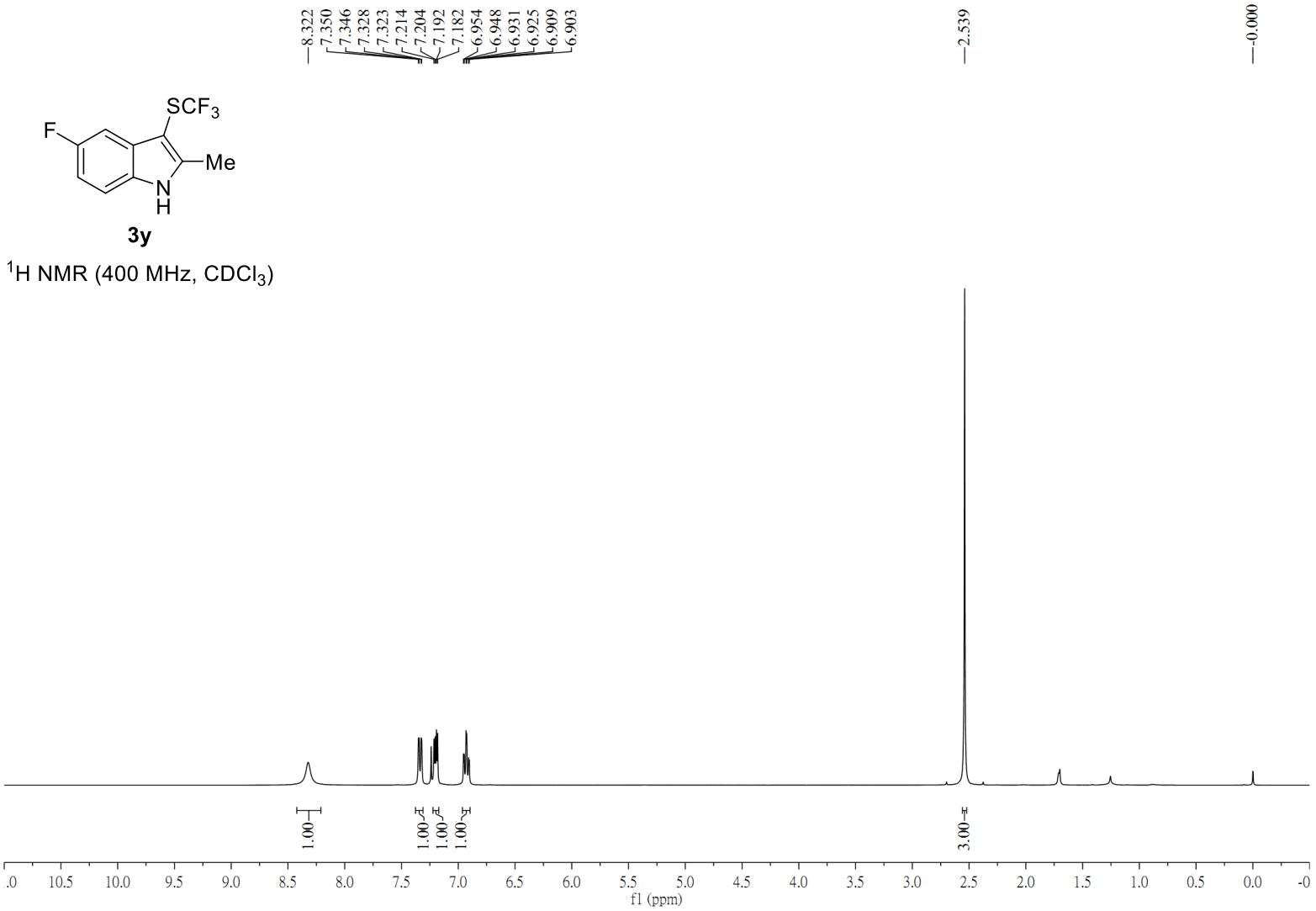
3x

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



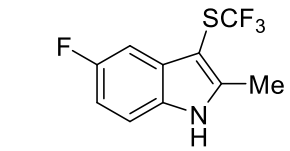
3x

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



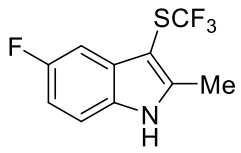
3y

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



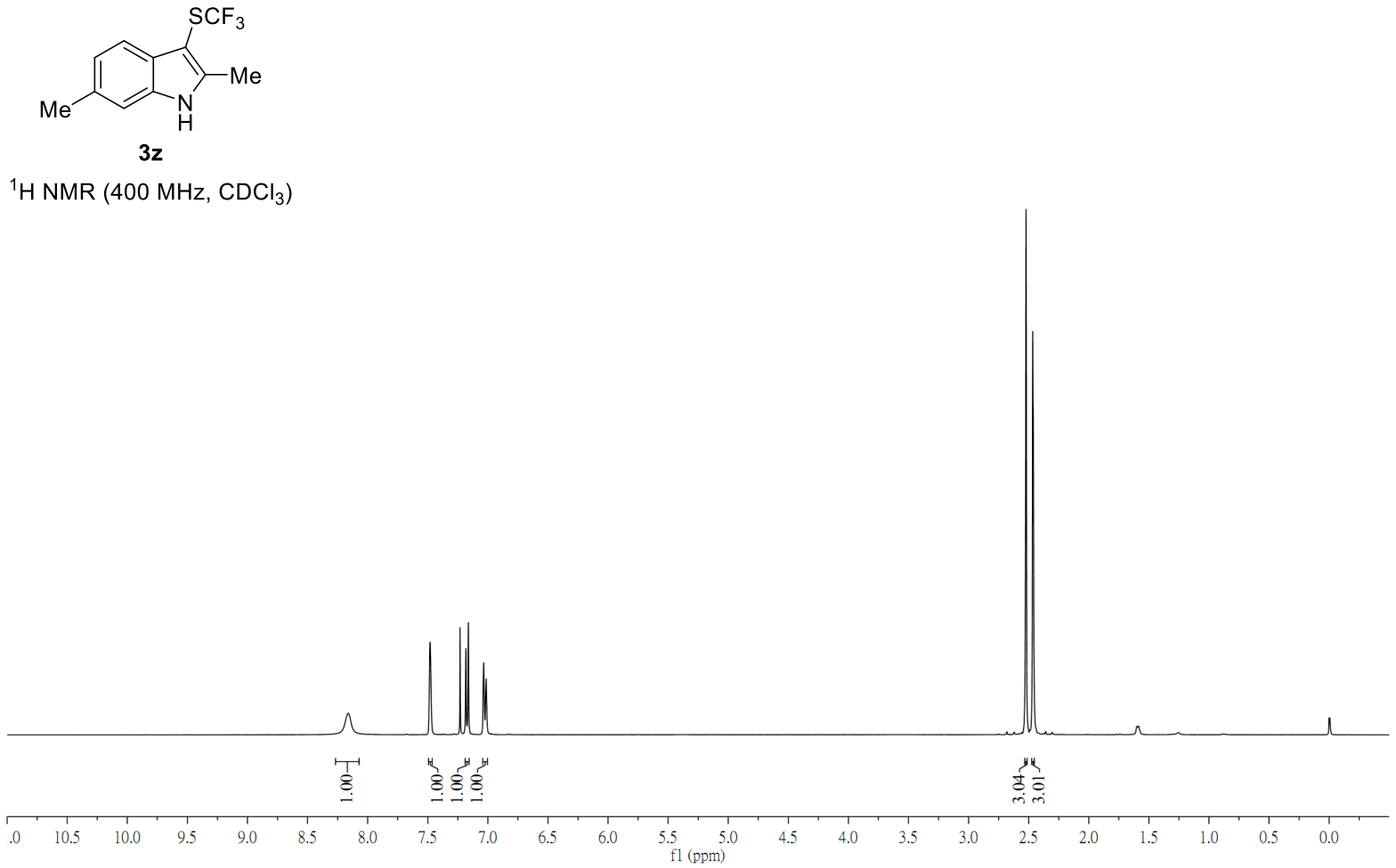
3y

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



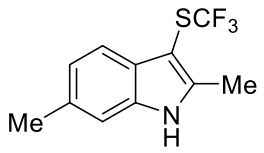
3y

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



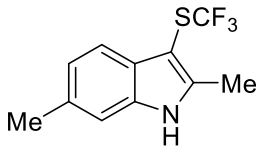
3z

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



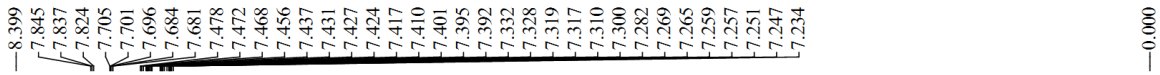
3z

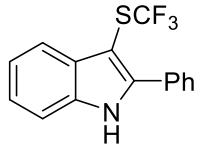
^{13}C NMR (100 MHz, $CDCl_3$)



3z

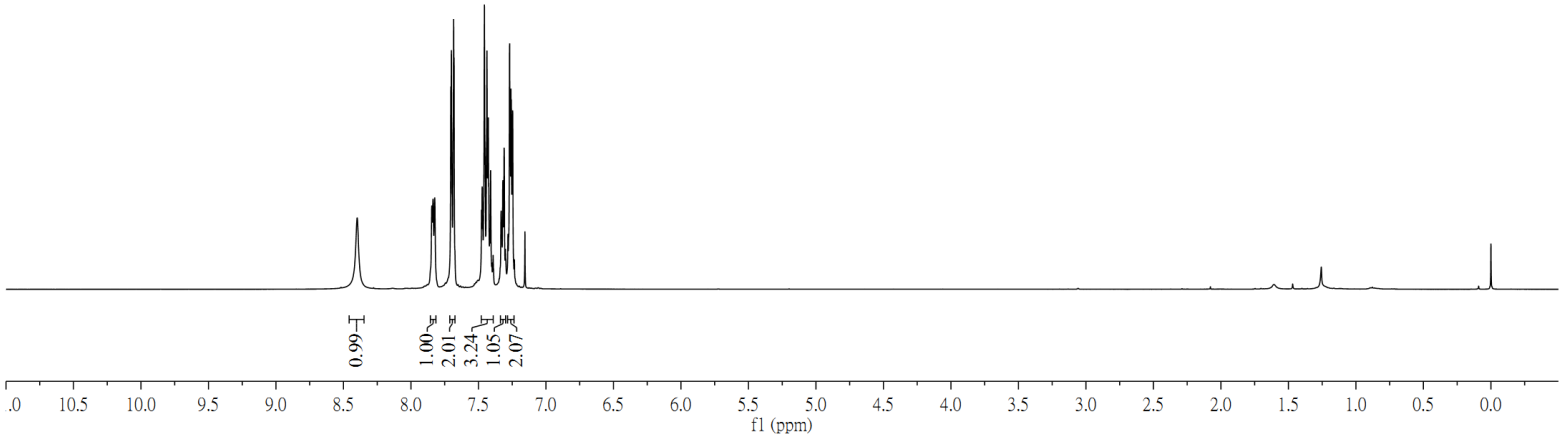
^{19}F NMR (376 MHz, $CDCl_3$)

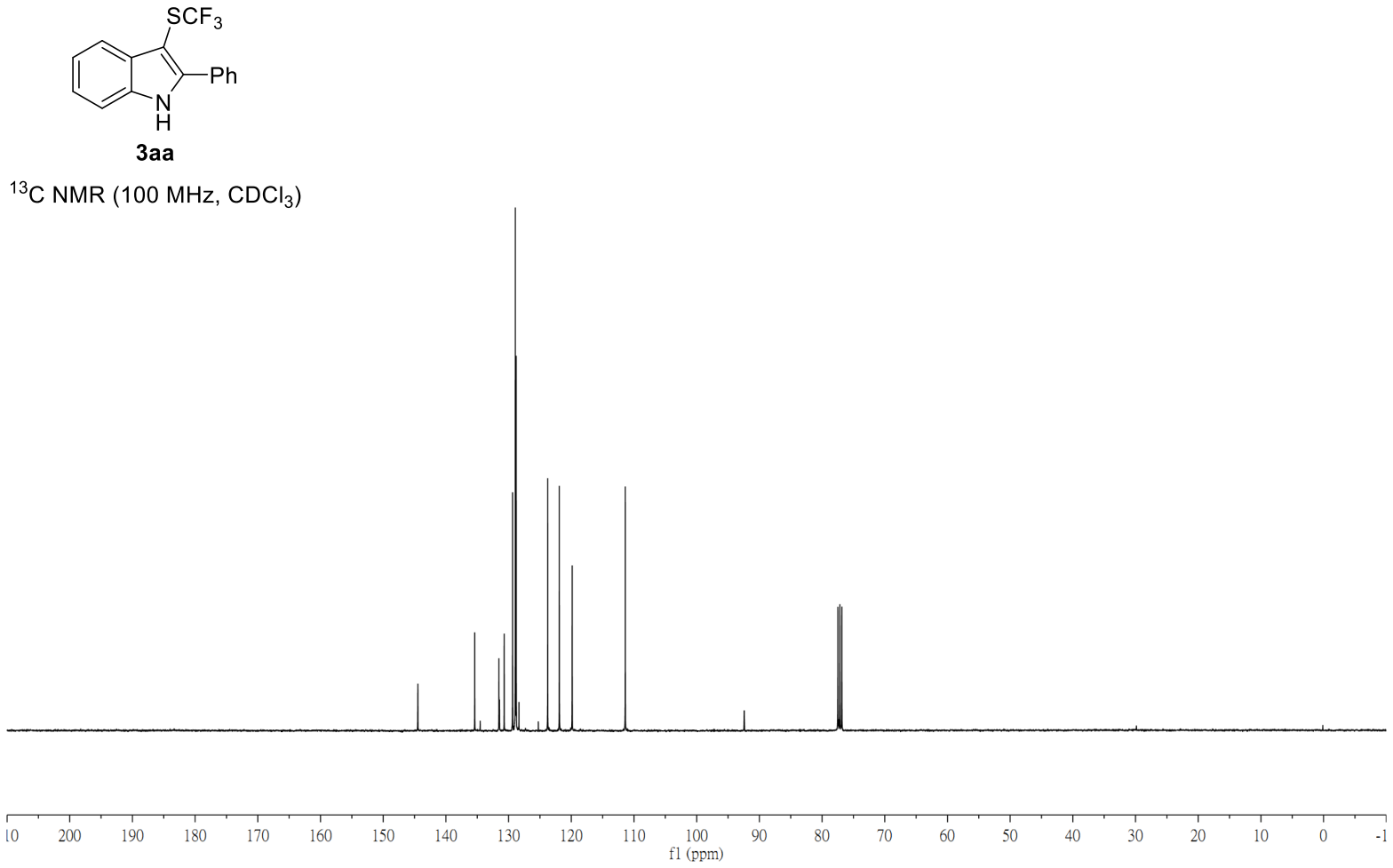


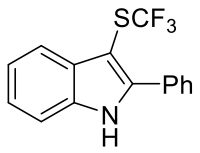


3aa

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

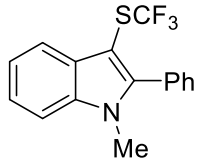



144.480
135.401
131.544
130.706
129.366
128.930
128.794
123.768
121.905
119.859
111.390
92.431
92.408
92.386
77.160
SCF3
Ph
N
H
3aa
13C NMR (100 MHz, CDCl3)
f1 (ppm)



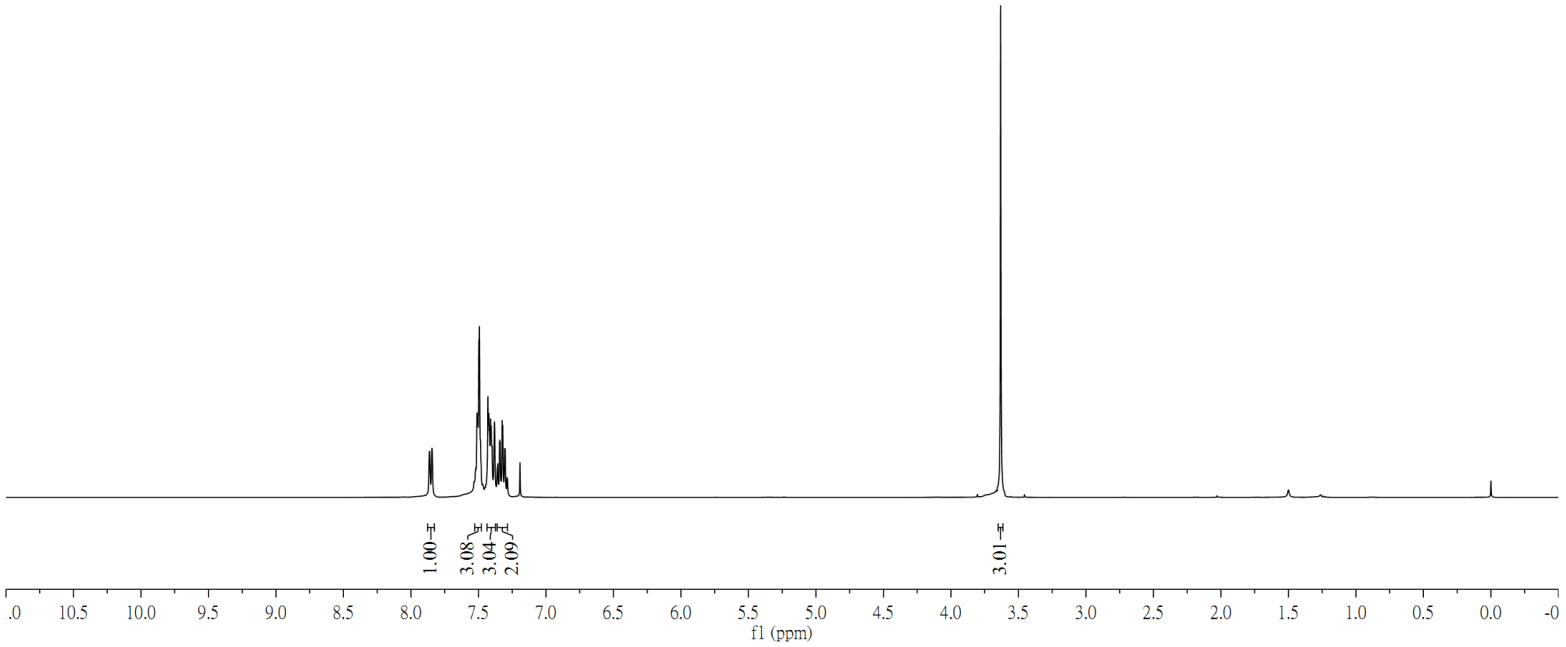
3aa

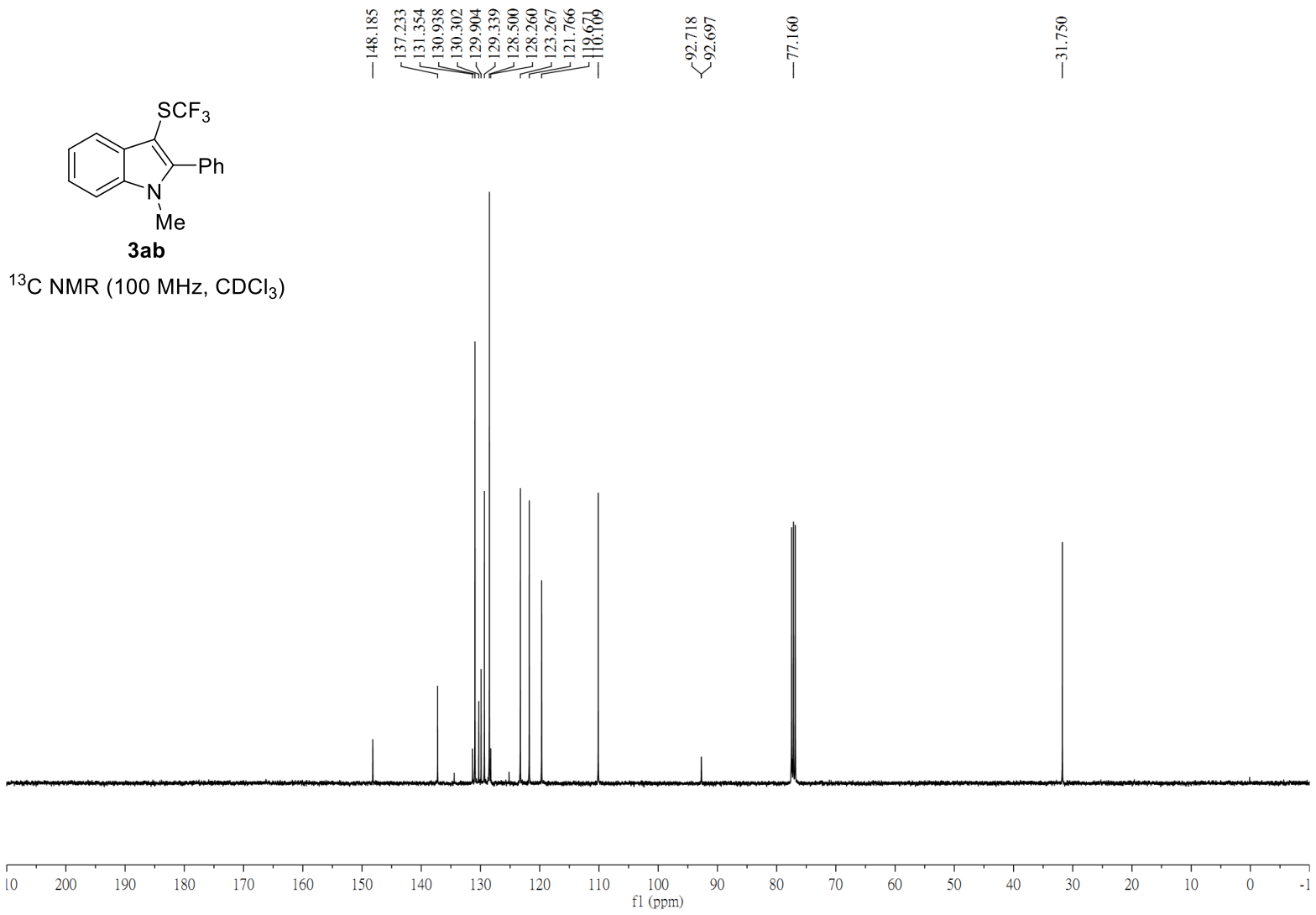
^{19}F NMR (376 MHz, $CDCl_3$)

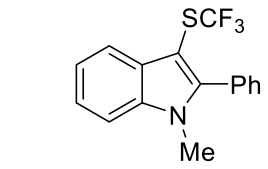


3ab

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

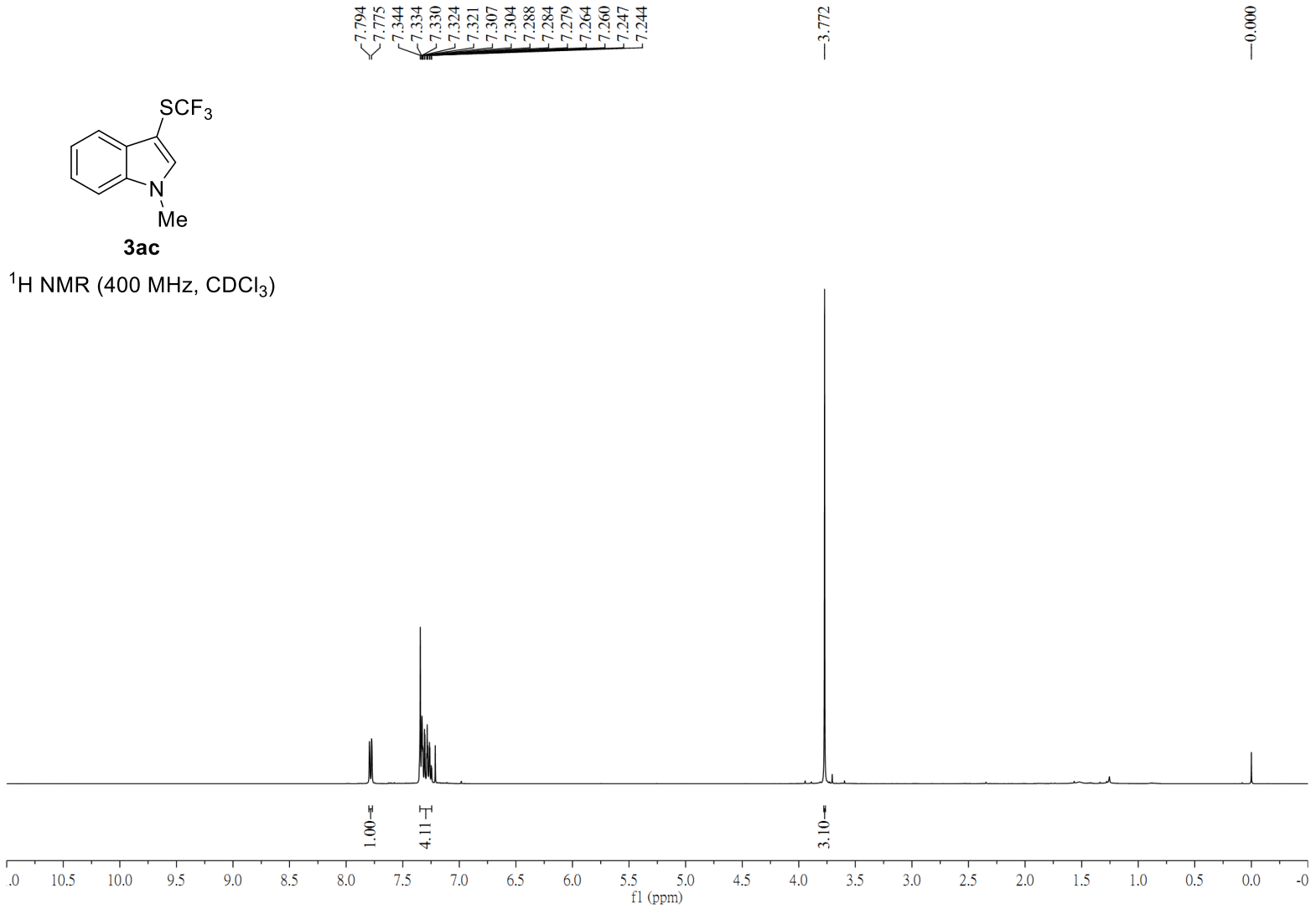


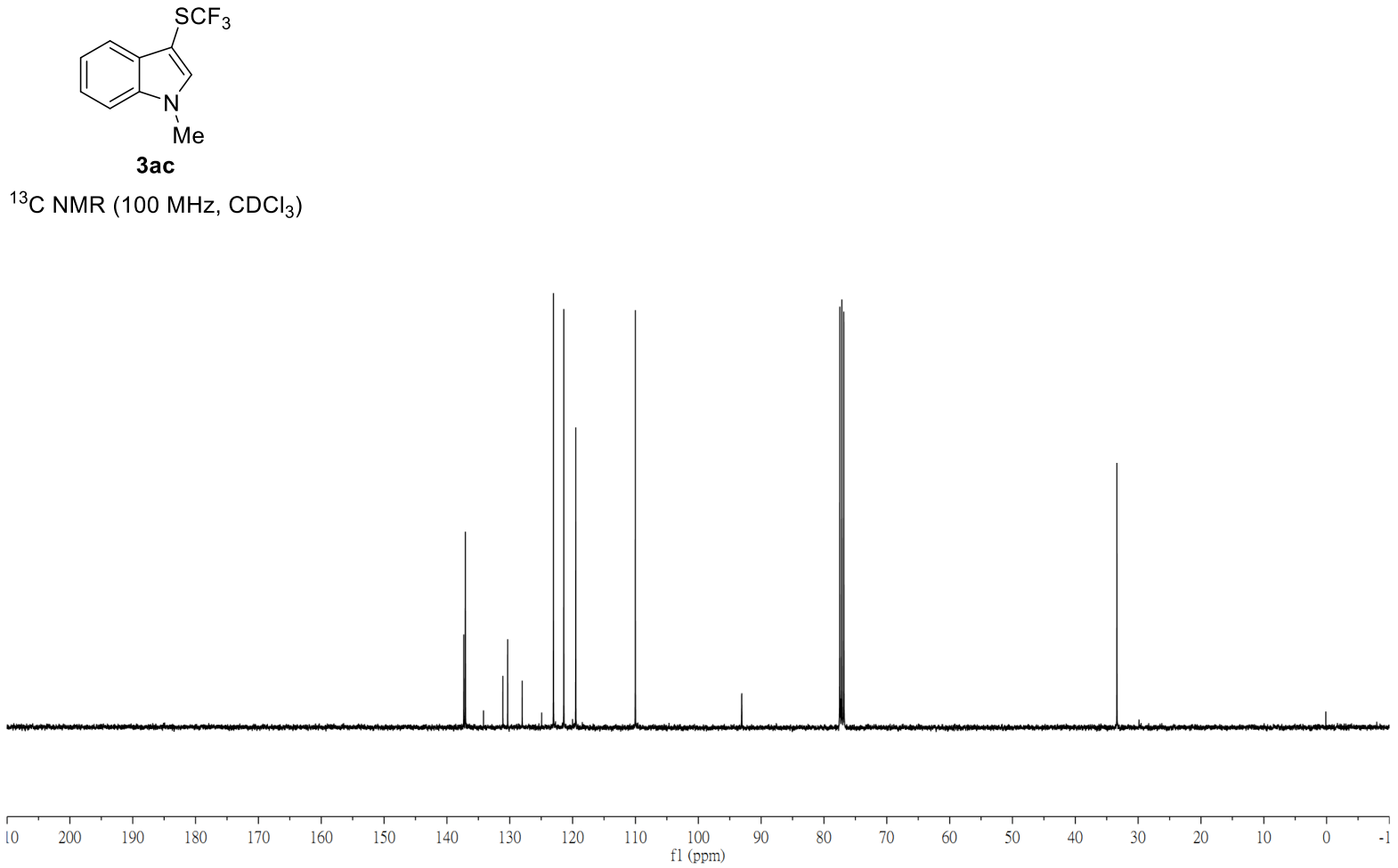

148.185
137.233
131.354
130.938
130.302
129.904
129.339
128.500
128.260
123.267
121.766
92.718
92.697
77.160
31.750
SCF3
Ph
N
Me
3ab
13C NMR (100 MHz, CDCl3)
f1 (ppm)

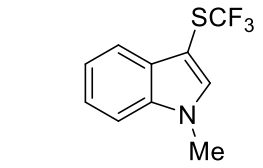


3ab

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

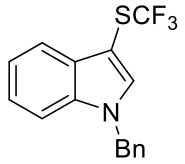

7.794
7.775
7.344
7.334
7.330
7.324
7.321
7.307
7.304
7.288
7.284
7.279
7.264
7.260
7.247
7.244
3.772
0.000
SCF3
N
Me
3ac
1H NMR (400 MHz, CDCl3)
1.00
4.11
3.10
f1 (ppm)


137.322
137.074
134.183
131.101
130.339
128.019
124.937
123.052
121.404
119.507
110.016
93.126
93.103
93.078
93.054
77.160
33.374
SCF3
N
Me
3ac
13C NMR (100 MHz, CDCl3)
f1 (ppm)



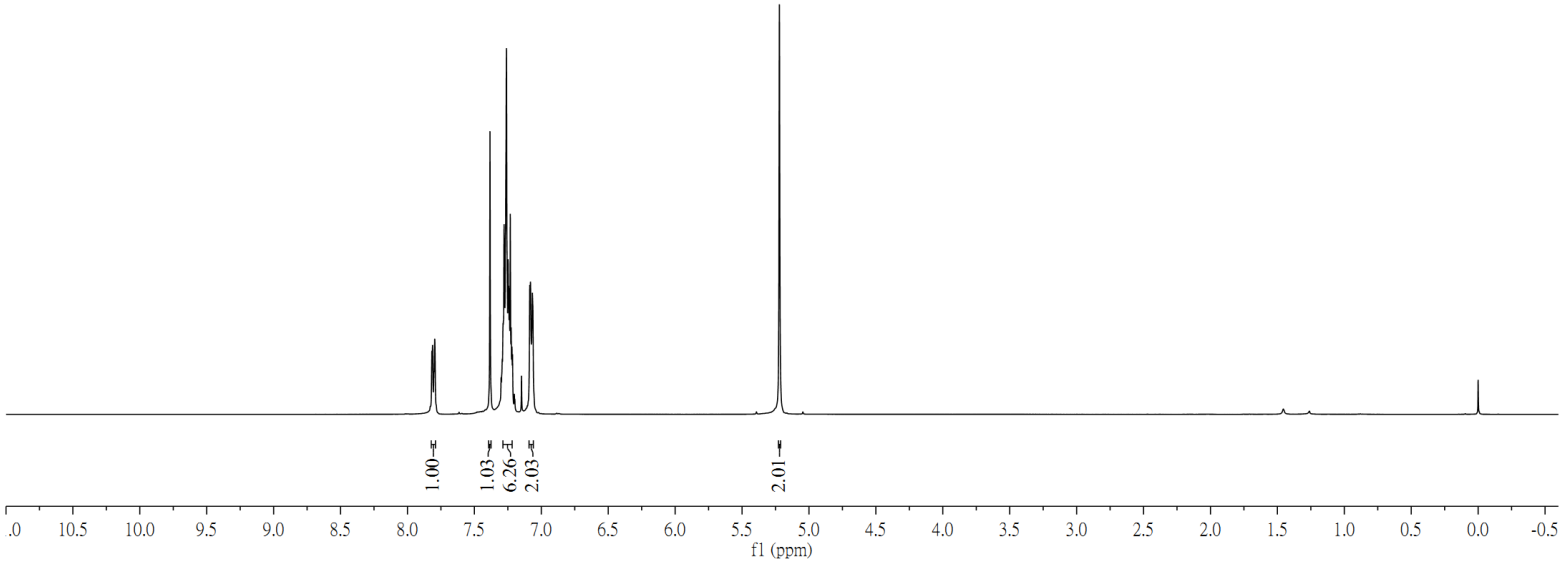
3ac

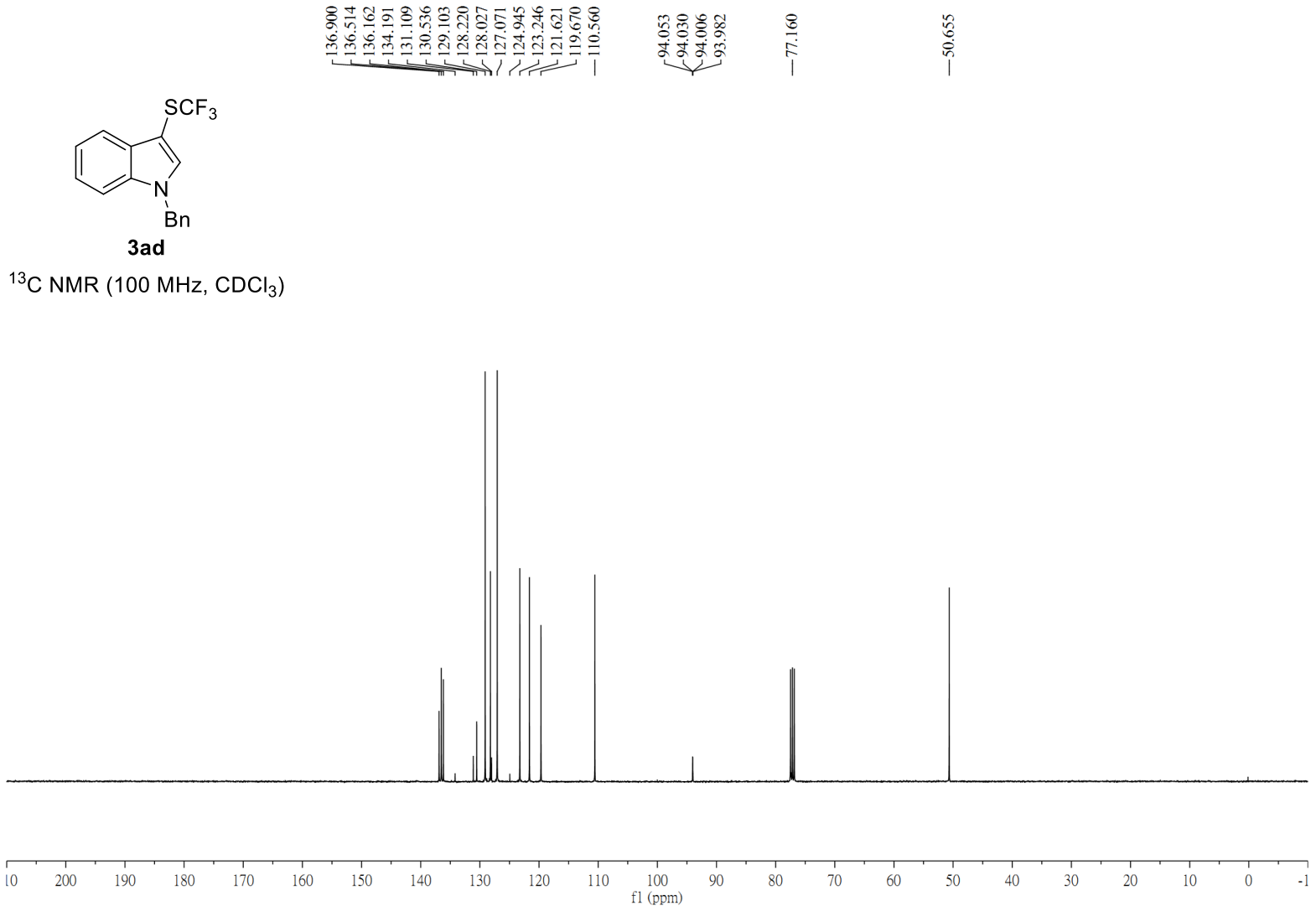
^{19}F NMR (376 MHz, $CDCl_3$)



3ad

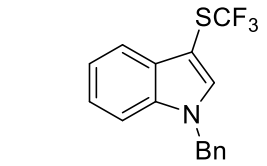
^{1}H NMR (400 MHz, $CDCl_3$)





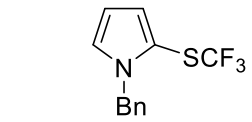
3ad

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



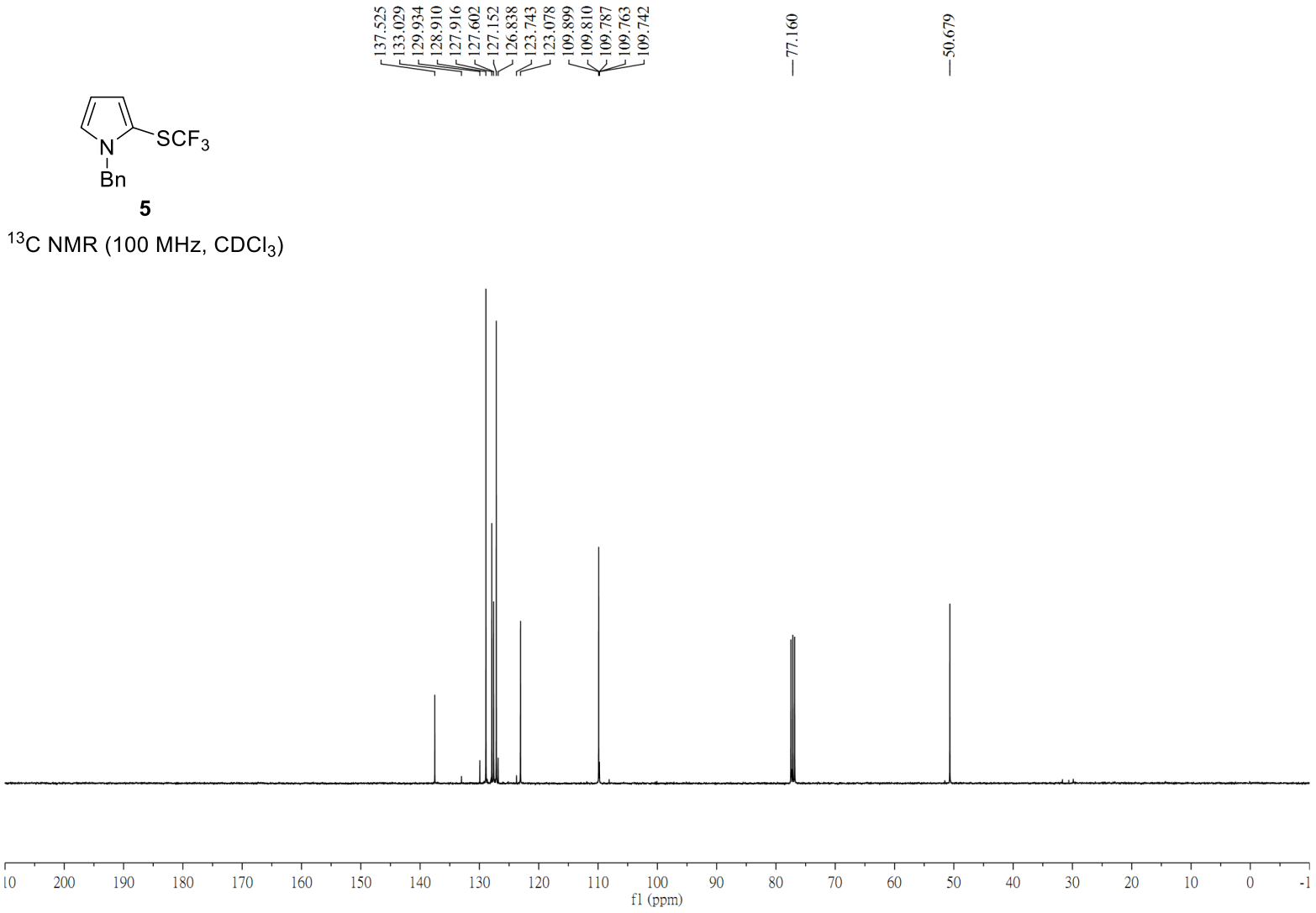
3ad

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



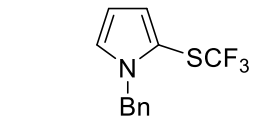
5

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



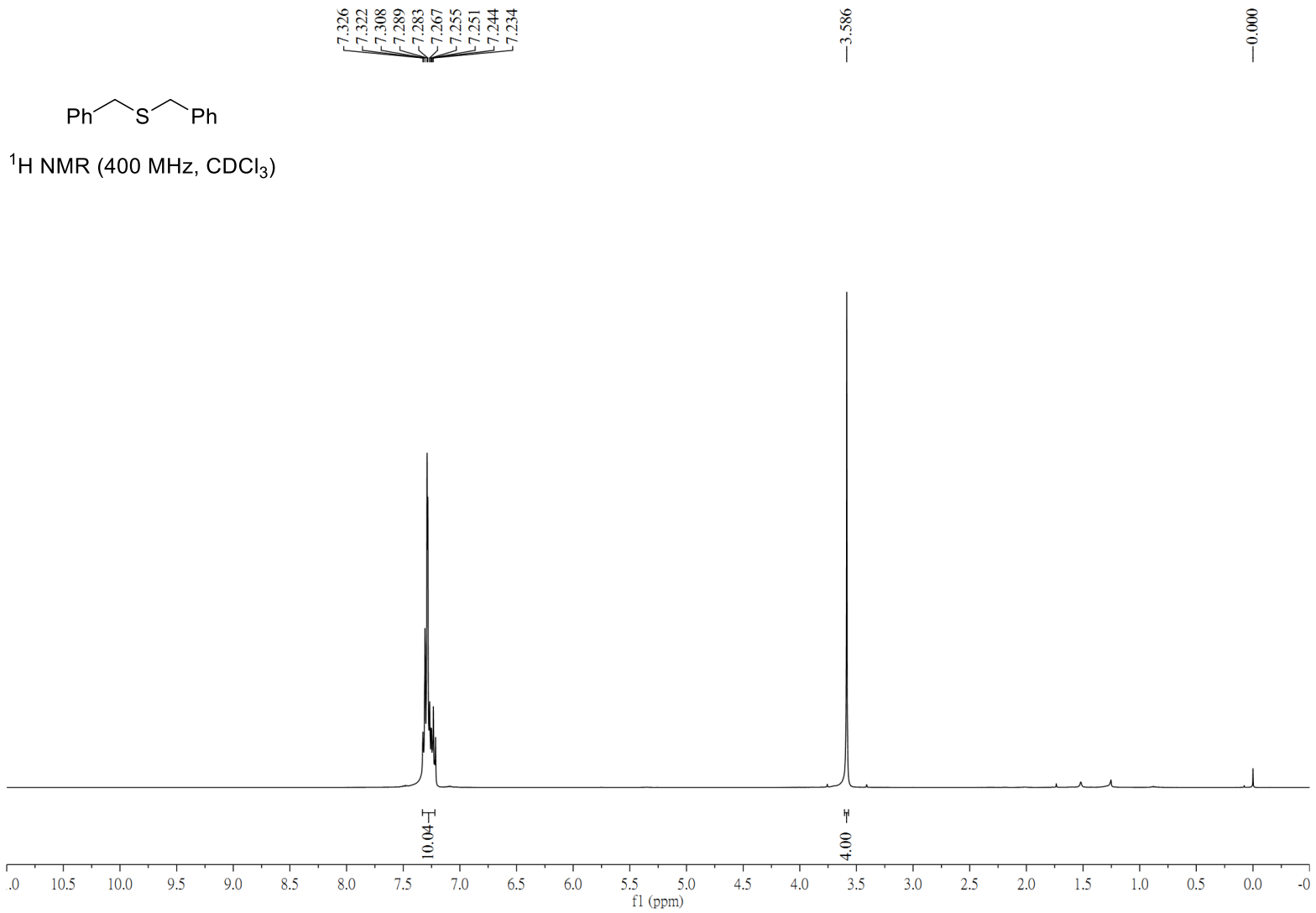
5

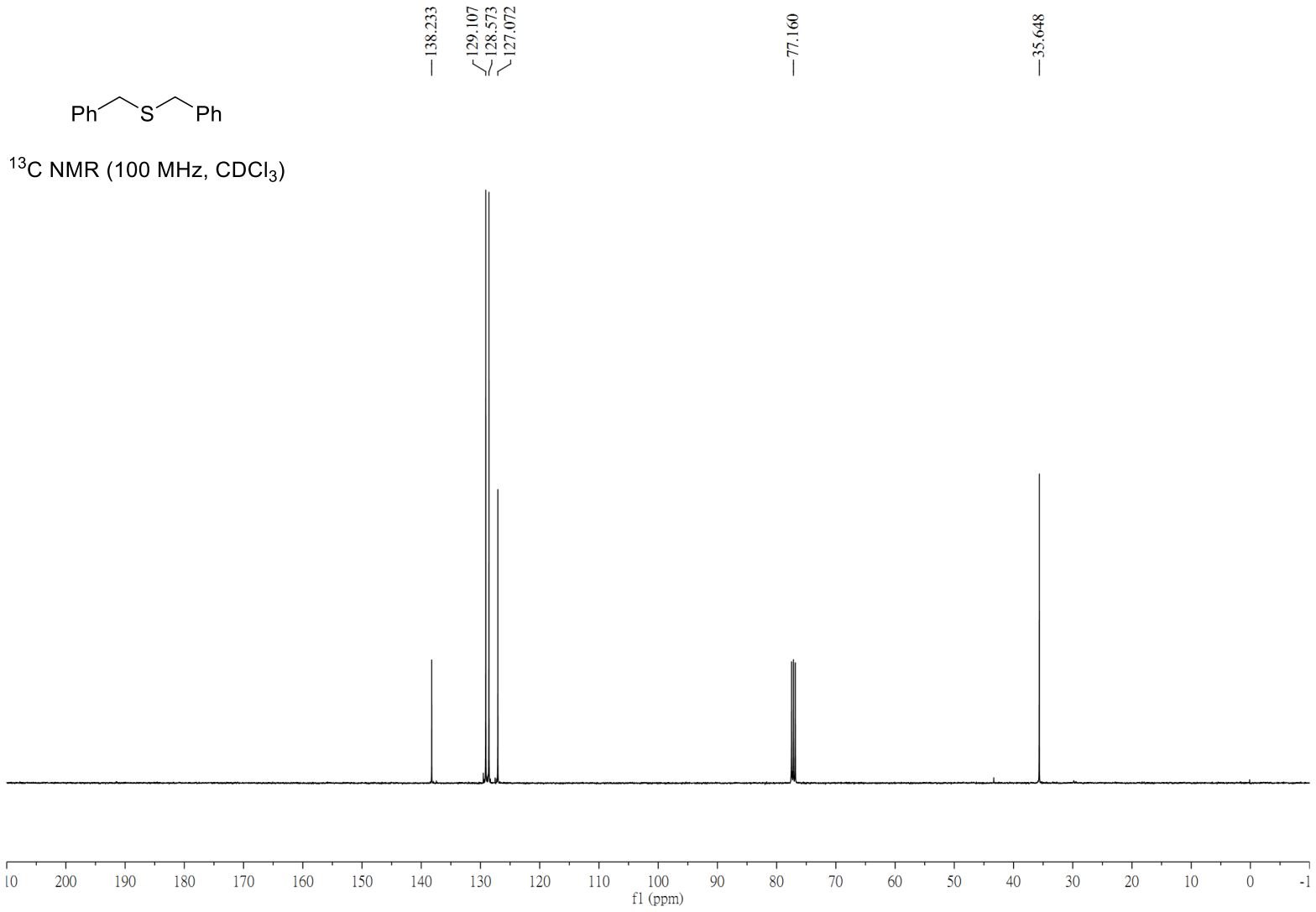
^{13}C NMR (100 MHz, $CDCl_3$)



5

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


7.326
7.322
7.308
7.289
7.283
7.267
7.255
7.251
7.244
7.234
3.586
0.000
Ph
S
Ph
^{1}H NMR (400 MHz, $CDCl_3$)
10.04
4.00
f1 (ppm)


138.233
129.107
128.573
127.072
77.160
35.648
Ph
S
Ph
13C NMR (100 MHz, CDCl3)
f1 (ppm)