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N-Hydroxy sulfonamides as new sulfenylating agents for the functionalization of aromatic compounds

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Supporting information

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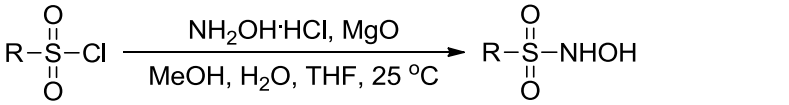
General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. Infrared spectra were recorded on a Nicolet MX-IE FT-IR spectrometer. 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. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump using a Daicel Chiralpak column (IC, 250 x 4.6 mm) with hexane/isopropanol as mobile phase, and the UV detection was monitored at 254 nm. Optical rotations were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\,℃}$ (c = g/100 mL, solvent). Melting points are uncorrected.

The preparation of some *N*-hydroxy sulfonamides is shown below. *N*-Hydroxy imide **H3**,[1] sulfinic acid **4a**,[2] sulfinate ester **5b**,[3] and thiosulfonate **6a**[2] were prepared according to literature procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI, and used as received.

Abbreviations: DMF = *N*,*N*-dimethylformamide, DMSO = dimethyl sulfoxide, Fmoc = fluorenylmethyloxycarbonyl, NIS = *N*-iodosuccinimide, TBAI = tetrabutylammonium iodide, TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, THF = tetrahydrofuran, Ts = *p*-toluenesulfonyl.

Preparation of some *N*-hydroxy sulfonamides[4]

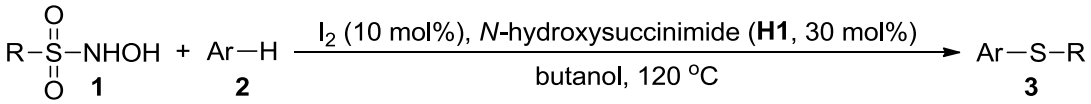


1c, R = 4-MeOC$_6$H$_4$, 80%
1d, R = F, 95%
1e, R = Cl, 90%
1g, R = I, 88%
1h, R = NO$_2$, 70%
1j, R = 1-naphthyl, 85%
1k, R = 2-naphthyl, 83%
1l, R = 2-thienyl, 72%

To a suspension of hydroxylamine hydrochloride (0.72 g, 10 mmol) and MgO (0.34 g, 8.6 mmol) in MeOH–H_2O (3:2, 5.0 mL) was treated with a solution of a sulfonyl chloride (4.3 mmol) in THF (30 mL) and then with MgO (0.17 g, 4.3 mmol). The mixture was vigorously stirred at room temperature until the sulfonyl chloride completely disappeared. Next, the mixture was filtered first through a pad of Celite, and then on a short plug of silica gel. The clear filtrate was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:0 to 1:5), to give *N*-hydroxy sulfonamide **1**.

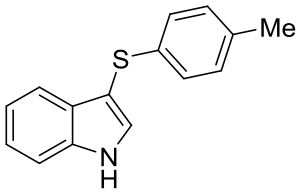
The *N*-hydroxy sulfonamides (**1c-e**, **1g, 1h**, and **1j-l**) we prepared are known compounds. Their melting points and NMR data were in agreement with those reported in the literature.

General procedure for the sulfenylation of aromatic compounds with *N*-hydroxy sulfonamides



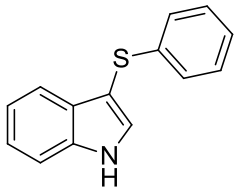
A mixture of *N*-hydroxy sulfonamide **1** (0.20 mmol), aromatic compound **2** (0.30 mmol), iodine (5.1 mg, 0.02 mmol, 10 mol%), and *N*-hydroxysuccinimide (**H1**) (6.9 mg, 0.06 mmol, 30 mol%) in butanol (2.0 mL) was heated under nitrogen in a sealed tube at 120 ^{o}C (oil bath) for 15 h. The mixture was cooled to room temperature, and purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (0:1 to 1:2), to give thioether **3**.

Analytical data for the products



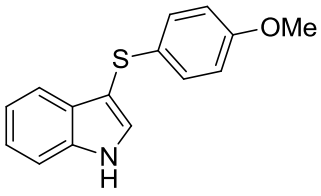
3a

3-(*p*-Tolylthio)-1*H*-indole (**3a**).[2] White solid (46.9 mg, 98%); m.p. 123-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, br, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.46-7.36 (m, 2H), 7.29-7.21 (m, 1H), 7.18-7.10 (m, 1H), 7.02 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.2 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.4, 134.6, 130.4, 129.5, 129.1, 126.2, 122.9, 120.8, 119.7, 111.5, 103.4, 20.8.



3b

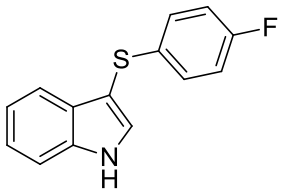
3-(Phenylthio)-1*H*-indole (**3b**).[2] White solid (41.4 mg, 92%); m.p. 151-153 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, br, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.31-7.26 (m, 1H), 7.21-7.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 136.5, 130.7, 129.1, 128.7, 125.8, 124.7, 123.0, 120.9, 119.7, 111.6, 102.8.



3c

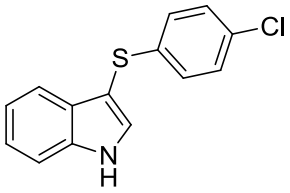
3-((4-Methoxyphenyl)thio)-1*H*-indole (**3c**).[2] Yellow solid (43.4 mg, 85%); m.p. 112-113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, br, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.41

(d, *J* = 8.0 Hz, 1H), 7.28-7.22 (m, 1H), 7.19-7.15 (m, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 136.4, 130.0, 129.5, 129.0, 128.5, 122.9, 120.8, 119.6, 114.5, 111.5, 104.5, 55.3.



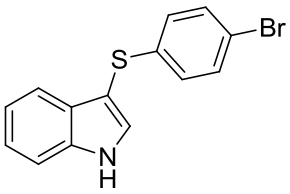
3d

3-((4-Fluorophenyl)thio)-1*H*-indole (**3d**).[2] White solid (47.2 mg, 97%); m.p. 133-135 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, br, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 2.8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.31-7.24 (m, 1H), 7.20-7.13 (m, 1H), 7.12-7.04 (m, 2H), 6.90-6.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9 (d, *J* = 242.5 Hz), 136.5, 134.0 (d, *J* = 3.1 Hz), 130.5, 128.8, 127.8 (d, *J* = 7.8 Hz), 123.1, 121.0, 119.5, 115.7 (d, *J* = 21.9 Hz), 111.6, 103.3.



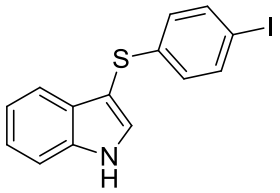
3e

3-((4-Chlorophenyl)thio)-1*H*-indole (**3e**).[2] White solid (50.8 mg, 98%); m.p. 129-131 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, br, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.32-7.25 (m, 1H), 7.21-7.13 (m, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.5, 130.7, 130.5, 128.8, 128.7, 127.1, 123.2, 121.0, 119.5, 111.7, 102.4.



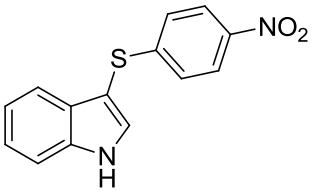
3f

3-((4-Bromophenyl)thio)-1*H*-indole (**3f**).[2] White solid (60.0 mg, 99%); m.p. 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, br, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 2.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.32-7.23 (m, 3H), 7.20-7.14 (m, 1H), 6.95 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 136.5, 131.6, 130.8, 128.7, 127.3, 123.2, 121.1, 119.5, 118.3, 111.7, 102.2.



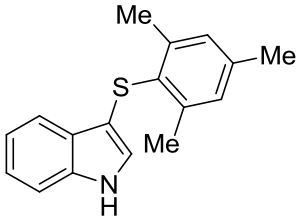
3g

3-((4-Iodophenyl)thio)-1*H*-indole (**3g**).[2] White solid (67.4 mg, 96%); m.p. 135-137 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, br, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 2.8 Hz, 1H), 7.46-7.40 (m, 3H), 7.32-7.25 (m, 1H), 7.21-7.13 (m, 1H), 6.82 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.5, 136.5, 130.8, 128.7, 127.6, 123.2, 121.1, 119.5, 111.7, 102.0, 89.0.



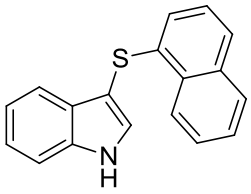
3h

3-((4-Nitrophenyl)thio)-1*H*-indole (**3h**).[2] Yellow solid (50.2 mg, 93%); m.p. 172-173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, br, 1H), 8.00 (d, J = 9.2 Hz, 2H), 7.56-7.48 (m, 3H), 7.35-7.29 (m, 1H), 7.22-7.17 (m, 1H), 7.13 (d, J = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 144.9, 136.6, 131.2, 128.4, 125.1, 123.9, 123.6, 121.4, 119.2, 111.9, 100.2.



3i

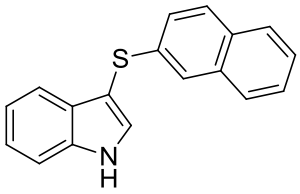
3-(Mesitylthio)-1*H*-indole (**3i**).[2] White solid (43.3 mg, 81%); m.p. 126-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, br, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.20-7.13 (m, 1H), 7.10-7.05 (m, 1H), 7.02 (d, J = 2.4 Hz, 1H), 6.90 (s, 2H), 2.52 (s, 6H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.8, 136.1, 130.0, 129.2, 128.1, 125.5, 122.5, 120.0, 119.5, 111.3, 107.9, 22.1, 21.0.



3j

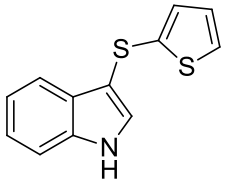
3-(Naphthalen-1-ylthio)-1*H*-indole (**3j**).[5] White solid (51.2 mg, 93%); m.p. 167-169 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.4 Hz, 1H), 8.44 (s, br, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.63-7.49 (m, 5H), 7.44 (d, J = 8.4 Hz, 1H), 7.31-7.22 (m, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.13 (d, J =

6.4 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.2, 133.7, 130.9, 130.7, 129.0, 128.4, 126.1, 126.0, 125.7, 125.2, 123.9, 123.3, 123.1, 120.9, 119.7, 111.6, 102.1.



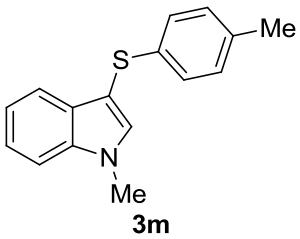
3k

3-(Naphthalen-2-ylthio)-1*H*-indole (**3k**).[2] White solid (49.5 mg, 90%); m.p. 141-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, br, 1H), 7.75-7.70 (m, 1H), 7.66-7.60 (m, 2H), 7.59-7.53 (m, 2H), 7.50-7.44 (m, 2H), 7.40-7.32 (m, 2H), 7.32-7.23 (m, 2H), 7.18-7.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 136.5, 133.7, 131.3, 130.7, 129.1, 128.2, 127.7, 126.9, 126.3, 125.0, 124.7, 123.5, 123.1, 121.0, 119.7, 111.6, 102.8.



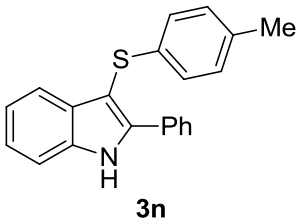
3l

3-(Thiophen-2-ylthio)-1*H*-indole (**3l**).[2] White solid (25.9 mg, 56%); m.p. 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, br, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.46 (s, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.24-7.06 (m, 4H), 6.91-6.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.2, 129.8, 129.2, 128.5, 127.3, 127.2, 123.0, 120.8, 119.4, 111.5, 106.8.



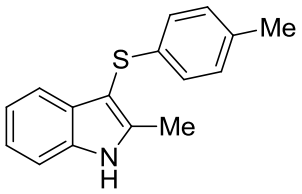
3m

1-Methyl-3-(*p*-tolylthio)-1*H*-indole (**3m**).[6] White solid (48.1 mg, 95%); m.p. 86-88 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.32-7.21 (m, 2H), 7.18-7.11 (m, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 135.9, 134.8, 134.5, 129.8, 129.4, 126.1, 122.5, 120.4, 119.8, 109.6, 101.2, 33.1, 20.8.



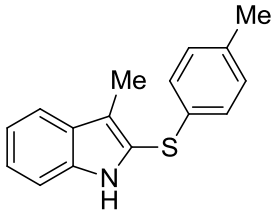
3n

2-Phenyl-3-(*p*-tolylthio)-1*H*-indole (**3n**).[6] Colorless oil (42.2 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, br, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.47-7.34 (m, 4H), 7.30-7.24 (m, 1H), 7.20-7.12 (m, 1H), 7.01 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 135.8, 135.6, 134.3, 131.4, 131.2, 129.6, 128.7, 128.6, 128.1, 125.7, 123.3, 121.1, 120.0, 111.1, 99.8, 20.9.



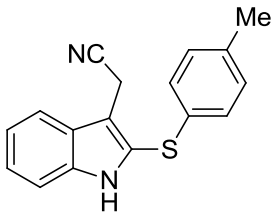
3o

2-Methyl-3-(*p*-tolylthio)-1*H*-indole (**3o**).[7] White solid (38.0 mg, 75%); m.p. 94-96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, br, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.21-7.14 (m, 1H), 7.14-7.07 (m, 1H), 6.97 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 2.50 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 135.7, 135.4, 134.3, 130.3, 129.5, 125.7, 122.1, 120.6, 119.0, 110.6, 99.8, 20.8, 12.1.



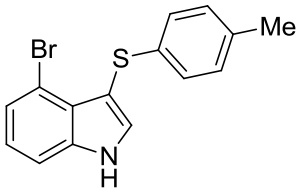
3p

3-Methyl-2-(*p*-tolylthio)-1*H*-indole (**3p**).[6] Colorless oil (32.4 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, br, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.25-7.21 (m, 1H), 7.17-7.11 (m, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 2.40 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.8, 135.7, 133.2, 129.8, 128.5, 127.1, 123.3, 122.2, 119.5, 119.3, 110.8, 20.9, 9.4.



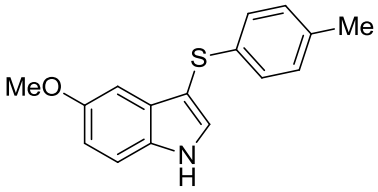
3q

2-(2-(*p*-Tolylthio)-1*H*-indol-3-yl)acetonitrile (**3q**). Colorless oil (35.6 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, br, 1H), 7.76-7.67 (m, 1H), 7.34-7.19 (m, 3H), 7.06 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 3.94 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 136.6, 131.4, 130.2, 128.0, 126.5, 125.0, 124.1, 120.8, 118.8, 117.6, 111.3, 110.8, 21.0, 13.8; IR (film): ν 3394, 3056, 2922, 2856, 2252, 1618, 1596, 1491, 1448, 1410, 1342, 1015, 806, 746 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}N_2S^+$ $(M+H)^+$ 279.0950, found 279.0950.



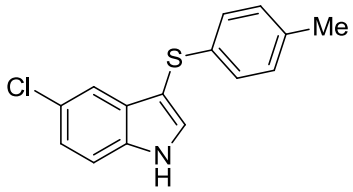
3r

4-Bromo-3-(*p*-tolylthio)-1*H*-indole (**3r**).[6] Colorless oil (61.5 mg, 97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, br, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.38-7.30 (m, 2H), 7.10-7.01 (m, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.2, 134.5, 132.9, 129.5, 126.2, 126.1, 125.7, 123.8, 114.6, 111.1, 104.2, 20.9.



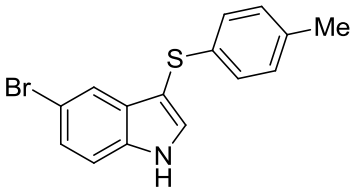
3s

5-Methoxy-3-(*p*-tolylthio)-1*H*-indole (**3s**).[6] White solid (52.2 mg, 97%); m.p. 77-78 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, br, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.90 (dd, J = 8.8, 2.4 Hz, 1H), 3.77 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 135.6, 134.5, 131.3, 131.2, 129.9, 129.5, 126.0, 113.5, 112.4, 102.6, 100.7, 55.8, 20.8.



3t

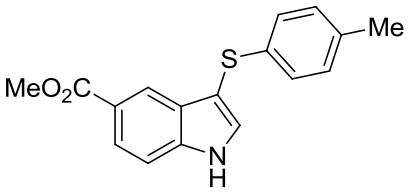
5-Chloro-3-(*p*-tolylthio)-1*H*-indole (**3t**).[7] White solid (53.5 mg, 98%); m.p. 134-136 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, br, 1H), 7.58 (d, J = 1.2 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.19 (dd, J = 8.8, 1.2 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.9, 134.8, 131.8, 130.3, 129.6, 126.8, 126.3, 123.4, 119.1, 112.6, 103.4, 20.9.



3u

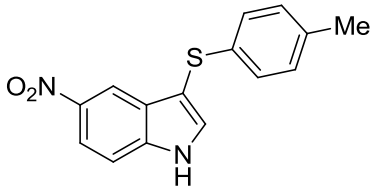
5-Bromo-3-(*p*-tolylthio)-1*H*-indole (**3u**).[7] White solid (60.9 mg, 96%); m.p. 144-146 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, br, 1H), 7.74 (d, J = 1.2 Hz, 1H), 7.44 (d, J = 2.4 Hz, 1H), 7.32

(dd, J = 8.8, 1.2 Hz, 1H), 7.27 (d, J = 8.8 Hz, 1H), 7.01 (d, J = 9.2 Hz, 2H), 6.98 (d, J = 9.2 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 135.0, 134.9, 131.6, 130.9, 129.6, 126.3, 126.0, 122.2, 114.4, 113.0, 103.3, 20.9.



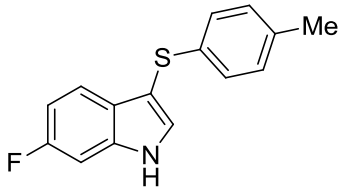
3v

Methyl 3-(*p*-tolylthio)-1*H*-indole-5-carboxylate (**3v**). White solid (54.7 mg, 92%); m.p. 174-178 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, br, 1H), 8.39 (d, J = 1.6 Hz, 1H), 7.96 (dd, J = 8.6, 1.6 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.02 (d, J = 8.3 Hz, 2H), 6.98 (d, J = 8.3 Hz, 2H), 3.90 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 139.1, 135.1, 135.0, 131.9, 129.6, 128.9, 126.4, 124.4, 123.0, 122.5, 111.4, 105.4, 52.0, 20.9; IR (film): v 3311, 2951, 2925, 2856, 1694, 1617, 1491, 1435, 1312, 1291, 1244, 1205, 1107, 804, 769, 749 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{16}NO_2S^+$ $(M+H)^+$ 298.0896, found 298.0897.



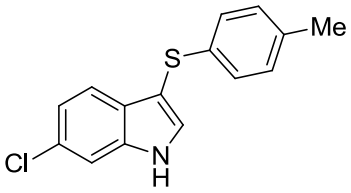
3w

5-Nitro-3-(*p*-tolylthio)-1*H*-indole (**3w**). Yellow solid (52.8 mg, 93%); m.p. 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, br, 1H), 8.57 (d, J = 2.2 Hz, 1H), 8.16 (dd, J = 9.0, 2.2 Hz, 1H), 7.64 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 139.4, 135.6, 134.0, 133.2, 129.7, 128.8, 127.0, 118.7, 116.9, 111.8, 107.4, 20.9; IR (film): v 3268, 2921, 2852, 1615, 1582, 1490, 1453, 1317, 1077, 803, 734 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2S^+$ $(M+H)^+$ 285.0692, found 285.0692.



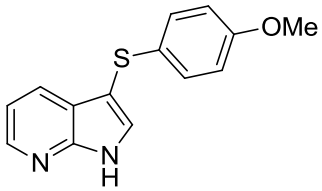
3x

6-Fluoro-3-(*p*-tolylthio)-1*H*-indole (**3x**).[7] White solid (50.9 mg, 99%); m.p. 124-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, br, 1H), 7.53-7.46 (m, 1H), 7.44 (d, J = 2.4 Hz, 1H), 7.13-7.06 (m, 1H), 7.02 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.95-6.86 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, J = 237.7 Hz), 136.3 (d, J = 12.5 Hz), 135.1, 134.9, 130.6 (d, J = 3.2 Hz), 129.5, 126.3, 125.5, 120.6 (d, J = 10.2 Hz), 109.7 (d, J = 24.5 Hz), 103.9, 98.0 (d, J = 26.3 Hz), 20.9.



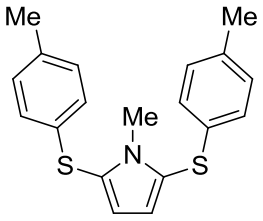
3y

6-Chloro-3-(*p*-tolylthio)-1*H*-indole (**3y**).[6] Colorless oil (51.9 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, br, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.43 (s, 1H), 7.39 (s, 1H), 7.10 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 134.9, 130.9, 129.9, 129.6, 129.0, 127.6, 126.4, 121.6, 120.6, 111.5, 104.0, 20.9.



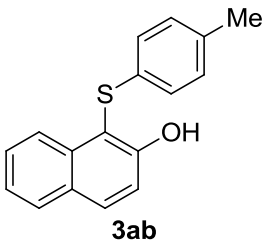
3z

3-((4-Methoxyphenyl)thio)-1*H*-pyrrolo[2,3-b]pyridine (**3z**).[5] White solid (48.1 mg, 94%); m.p. 173-175 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.61 (s, br, 1H), 8.40-8.35 (m, 1H), 7.99-7.93 (m, 1H), 7.67 (s, 1H), 7.17-7.15 (m, 1H), 7.14 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 148.8, 142.9, 131.1, 129.0, 128.8, 128.6, 122.1, 116.7, 114.5, 103.4, 55.3.



3aa

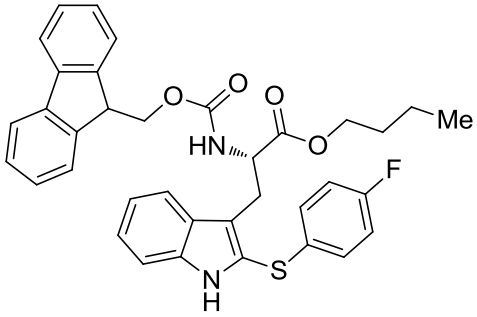
1-Methyl-2,5-bis(*p*-tolylthio)-1*H*-pyrrole (**3aa**). Colorless oil (39.0 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, J = 8.0 Hz, 4H), 6.89 (d, J = 8.0 Hz, 4H), 6.64 (s, 2H), 3.48 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.3, 129.8, 126.2, 122.5, 119.0, 31.4, 20.9; IR (film): ν 3018, 2924, 2855, 1597, 1492, 1432, 1400, 1377, 1293, 1084, 1015, 803, 765 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NS_2^+$ $(M+H)^+$ 326.1032, found 326.1033.



3ab

1-(*p*-Tolylthio)naphthalen-2-ol (**3ab**).[8] Yellow solid (34.1 mg, 64%); m.p. 72-73 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H),

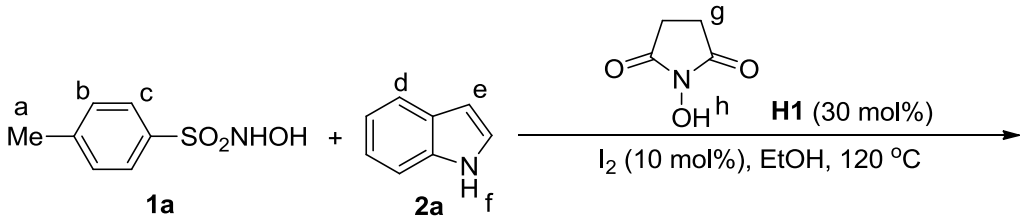
7.51-7.45 (m, 1H), 7.41-7.34 (m, 1H), 7.33 (d, *J* = 9.2 Hz, 1H), 7.21 (s, br, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 135.9, 135.4, 132.6, 131.7, 129.9, 129.4, 128.5, 127.9, 126.6, 124.7, 123.8, 116.8, 108.6, 20.9.

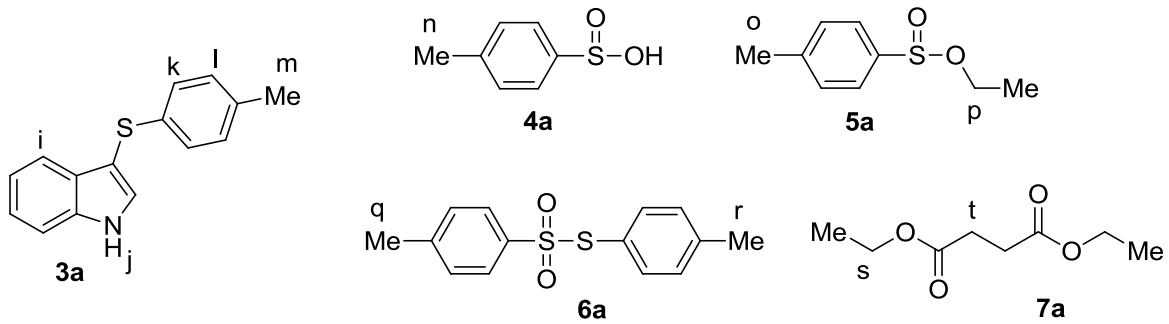


3ac

Butyl (*S*)-2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-3-(2-((4-fluorophenyl)thio)-1*H*-indol-3-yl)propanoate (**3ac**). Colorless oil (110.7 mg, 91%); >99 ee as determined by HPLC analysis (Chiralpak IC, λ = 254 nm, hexane/isopropanol = 85/15, flow rate 1.0 mL/min): t_R (major) = 10.7 min, t_R (minor) = 14.3 min; $[\alpha]_D^{20}$ = 50.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, br, 1H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58-7.50 (m, 2H), 7.43-7.35 (m, 2H), 7.32-7.20 (m, 5H), 7.18-7.11 (m, 1H), 7.10-7.04 (m, 2H), 6.96-6.88 (m, 2H), 5.47-5.39 (m, 1H), 4.76-4.67 (m, 1H), 4.33-4.26 (m, 2H), 4.20-3.96 (m, 2H), 3.47-3.32 (m, 2H), 1.57-1.48 (m, 2H), 1.31-1.21 (m, 2H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 161.6 (d, *J* = 245.1 Hz), 155.7, 143.8 (d, *J* = 5.5 Hz), 141.2, 136.9, 131.1, 129.3 (d, *J* = 7.9 Hz), 127.9, 127.7, 127.0, 125.2, 124.1, 123.8, 120.3, 119.9, 119.2, 117.2, 116.4 (d, *J* = 22.1 Hz), 111.1, 67.1, 65.6, 54.6, 47.1, 30.4, 28.0, 19.0, 13.7; IR (film): *v* 3405, 2958, 2925, 2857, 1710, 1619, 1595, 1572, 1509, 1492, 1460, 1449, 1387, 1258, 1200, 1083, 804, 749 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{34}N_2O_4SF^+$ $(M+H)^+$ 609.2218, found 609.2247.

^{1}H NMR spectroscopic analysis of the reaction mixture (Table 2)





A mixture of *N*-hydroxy sulfonamide **1a** (0.20 mmol), indole (**2a**) (0.30 mmol), iodine (5.1 mg, 0.02 mmol, 10 mol%), and *N*-hydroxysuccinimide (**H1**) (6.9 mg, 0.06 mmol, 30 mol%) in ethanol (2.0 mL) was heated under nitrogen at 120 ^{o}C (oil bath). The mixture was cooled to room temperature at set intervals and samples (200 μL) were withdrawn with a syringe. The samples were concentrated under reduced pressure, and the residues were subjected to ^{1}H NMR spectroscopic analysis and ESI-MS (positive mode) analysis.

(1) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for *N*-hydroxy sulfonamide **1a**, δ a: 2.45 (s, 3H), b: 7.83 (d, J = 8.0 Hz, 2H), c: 7.36 (d, J = 8.0 Hz, 2H).

(2) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for indole (**2a**), δ d: 7.65 (d, J = 7.6 Hz, 1H), e: 6.59-6.53 (m, 1H), f: 8.18 (s, br, 1H).

(3) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for *N*-hydroxysuccinimide (**H1**), δ g: 2.69 (s, 4H), h: 3.54 (s, br, 1H).

(4) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for thioether **3a**, δ i: 7.62 (d, J = 8.0 Hz, 1H), j: 8.39 (s, br, 1H), k: 7.02 (d, J = 8.0 Hz, 2H), l: 6.97 (d, J = 8.0 Hz, 2H), m: 2.24 (s, 3H).

(5) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for sulfinic acid **4a**, δ n: 2.39 (s, 3H); HRMS (ESI) calcd for $C_7H_9O_2S^+$ $(M + H)^+$ 157.0318, found 157.0317.

(6) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for sulfinate ester **5a**, δ o: 2.42 (s, 3H), p: 3.79-3.69 (m, 2H); HRMS (ESI) calcd for $C_9H_{13}O_2S^+$ $(M+H)^+$ 185.0631, found 185.0633.

(7) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for thiosulfonate **6a**, δ q: 2.41 (s, 3H), r: 2.38 (s, 3H); HRMS (ESI) calcd for $C_{14}H_{14}O_2S_2Na^+$ $(M + Na)^+$ 301.0327, found 301.0327.

(8) Partial ^{1}H NMR (400 MHz, $CDCl_3$) for diethyl succinate (**7a**), δ s: 4.15 (q, J = 7.2 Hz, 4H), t: 2.62 (s, 4H); HRMS (ESI) calcd for $C_8H_{15}O_4^+$ $(M+H)^+$ 175.0965, found 175.0967.

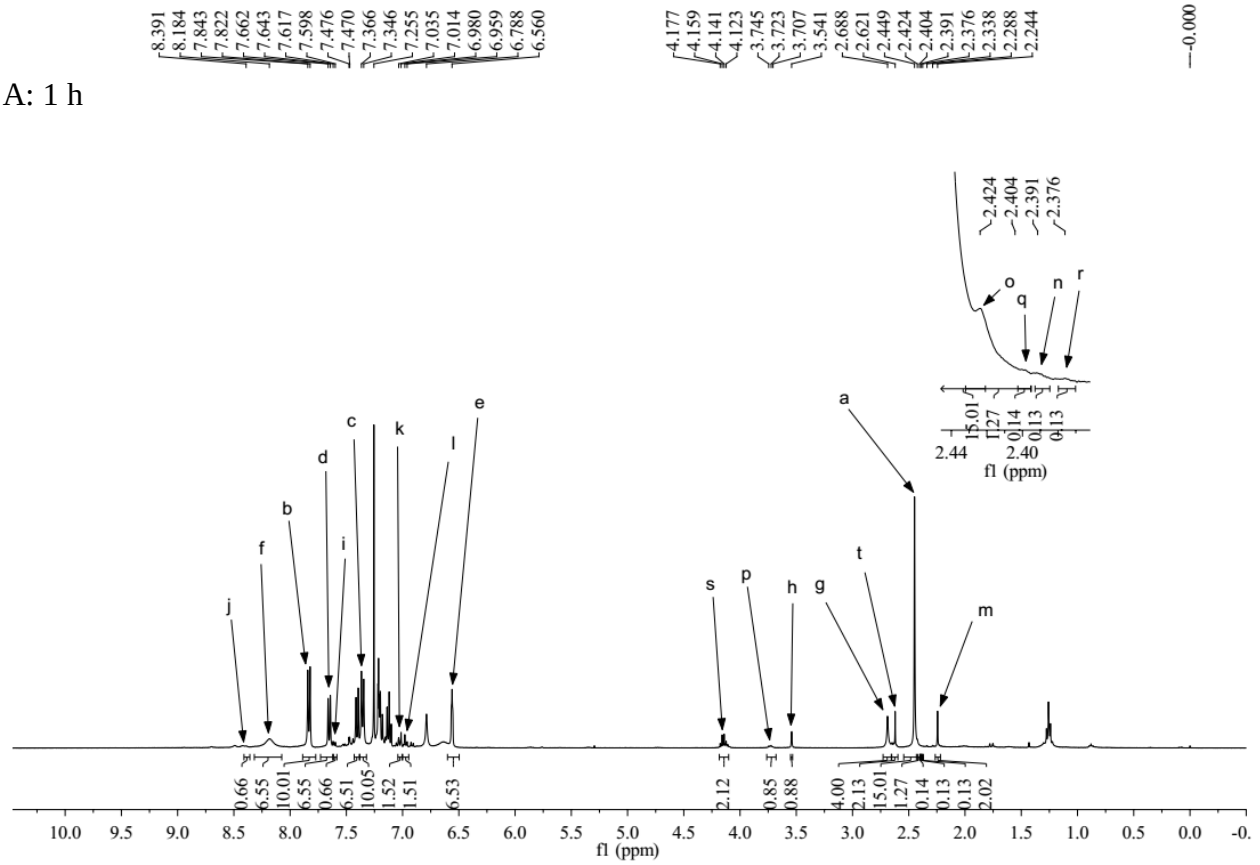
Calculation of the ratios between the starting materials, the intermediates, and the products is shown below.

1a : **3a** : **4a** : **5a** : **6a** = a/3 : m/3 : n/3 : o/3 : q/3

H1 : **7a** = g/4 : t/4

Entry	Time (h)	**1a** : **3a** : **4a** : **5a** : **6a**	**H1** : **7a**
1	1	80.8 : 10.9 : 0.7 : 6.8 : 0.8	65.3 : 34.7
2	5	14.9 : 70.7 : 2.8 : 8.5 : 3.1	49.0 : 51.0
3	15	0 : 93.6 : 3.5 : 0 : 2.9	47.1 : 52.9

A: 1 h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7.643
7.617
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7.476
7.470
7.366
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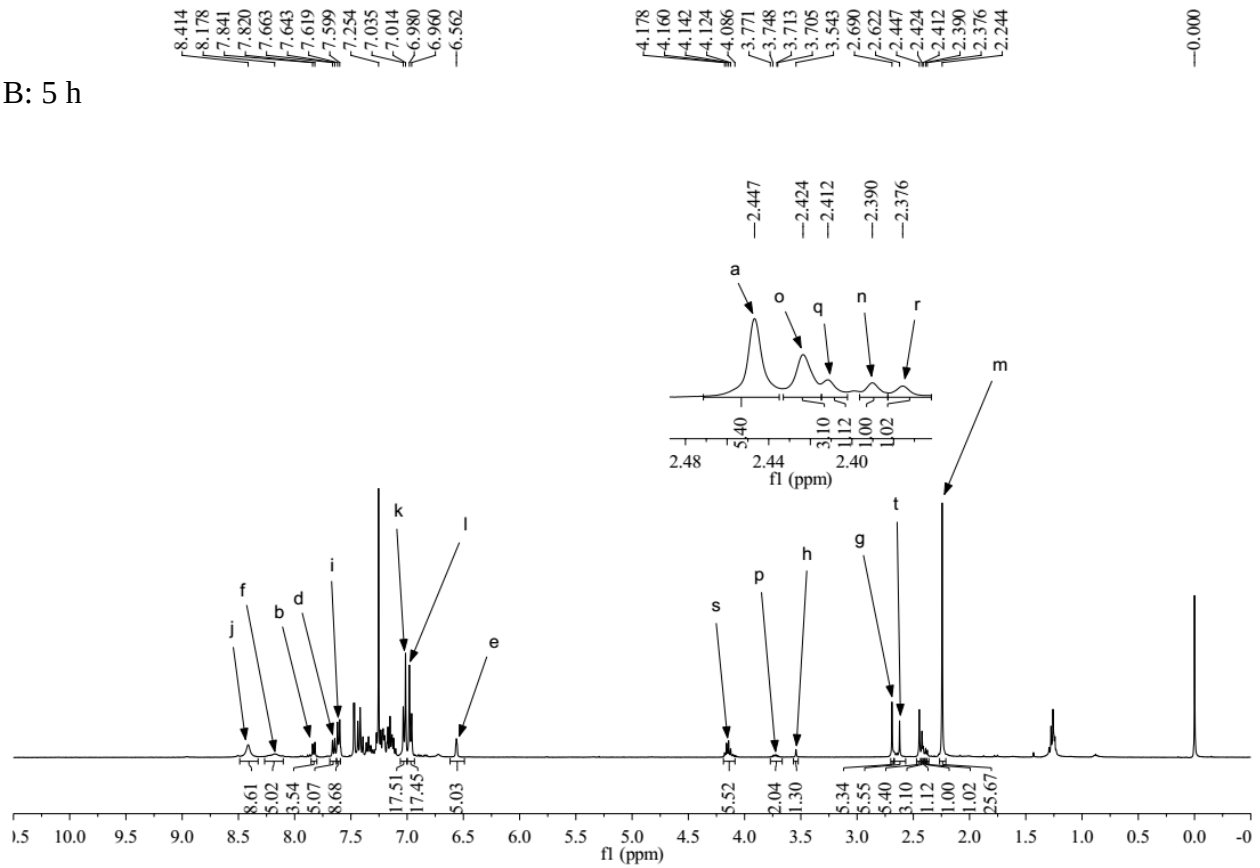
7.255
7.035
7.014
6.980
6.959
6.788
6.560
4.177
4.159
4.141
4.123
3.745
3.723
3.707
3.541
2.688
2.621
2.449
2.424
2.404
2.391
2.376
2.338
2.288
2.244
-0.000
a
b
c
d
e
f
g
h
i
j
k
l
m
n
o
p
q
r
s
t
fl (ppm)

B: 5 h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7.643
7.619
7.599
7.254
7.035
7.014
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3.748
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3.705
3.543
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2.622
2.447
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2.390
2.376
2.244
-0.000
a
b
d
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f
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i
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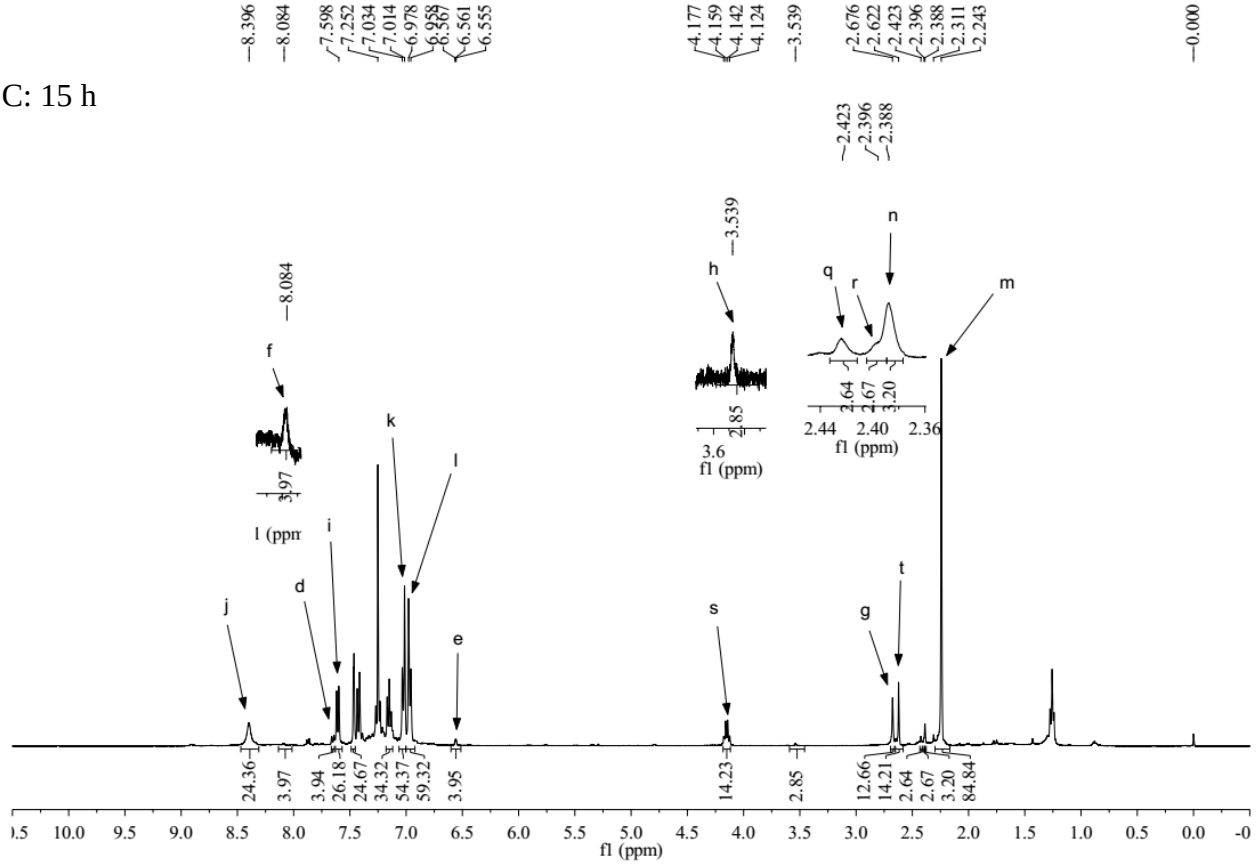
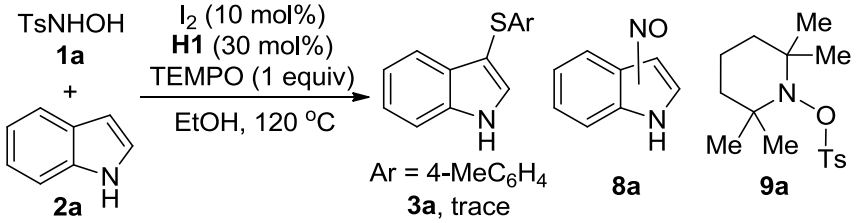
k
l
m
n
o
p
q
r
s
t
fl (ppm)

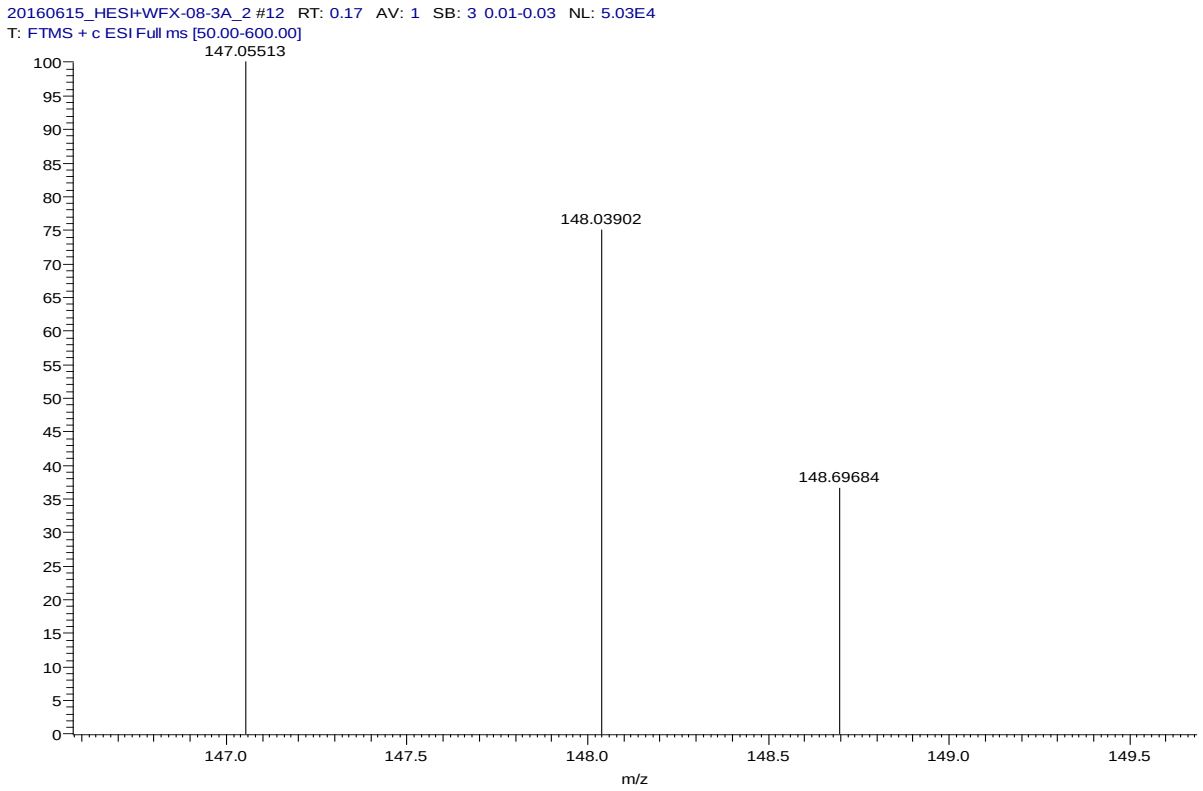
C: 15 h



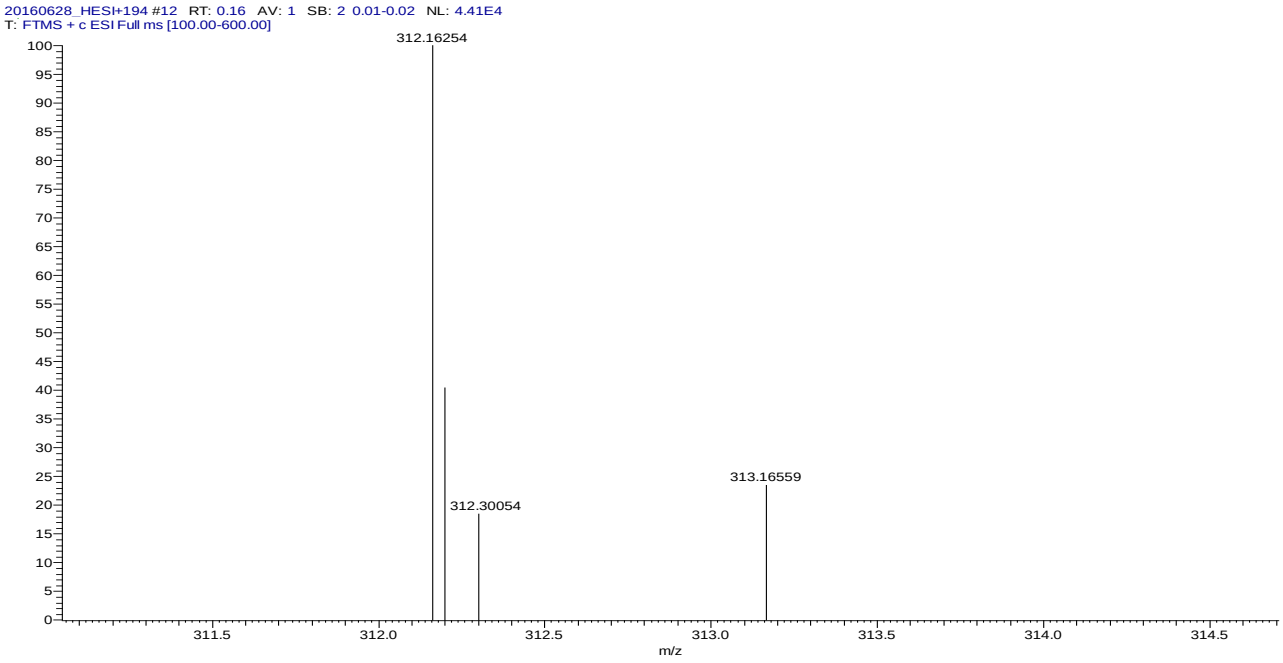
ESI-MS analysis of the reaction mixture (eqn (2))



A mixture of *N*-hydroxy sulfonamide **1a** (37.4 mg, 0.20 mmol), indole **2a** (35.1 mg, 0.30 mmol), iodine (5.1 mg, 0.02 mmol, 10 mol%), *N*-hydroxysuccinimide (**H1**) (6.9 mg, 0.06 mmol, 30 mol%), and TEMPO (31.3 mg, 0.20 mmol) in butanol (2.0 mL) was heated under nitrogen in a sealed tube at 120 ^{o}C (oil bath) for 15 h. The mixture was cooled to room temperature, and subjected to ESI-MS (positive mode) analysis. Copied below is the ESI-MS spectrum we obtained.



Nitroso-substituted indole **8a**: HRMS (ESI) calcd for $C_8H_7ON_2^+$ $(M+H)^+$ 147.0553, found 147.0551.



TEMPO-Ts (**9a**): HRMS (ESI) calcd for $C_{16}H_{26}NO_3S^+$ $(M+H)^+$ 312.1628, found 312.1625.

References

1 D. Kumar and Neelam, *J. Indian Chem. Soc.*, 2015, **92**, 319.
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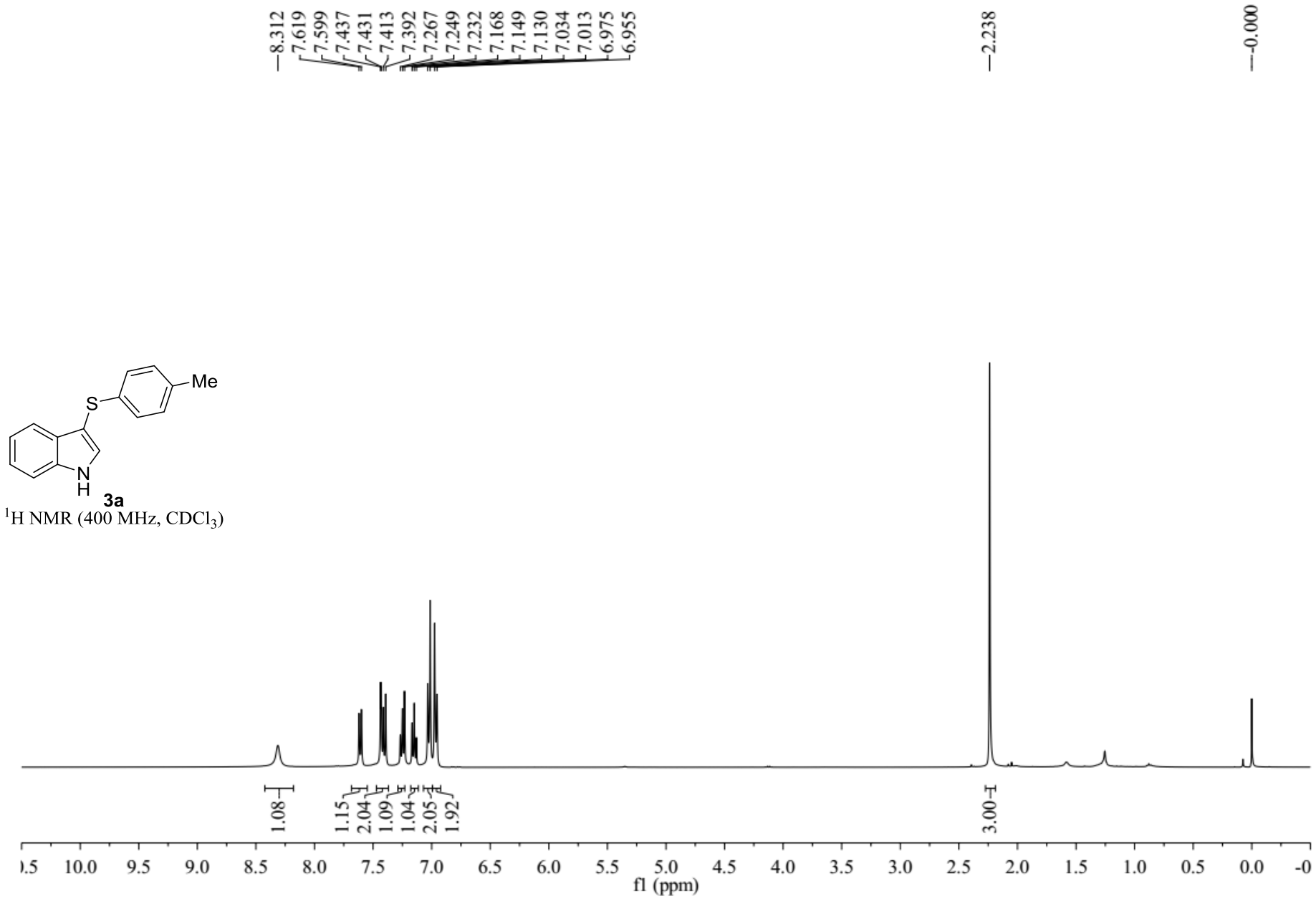
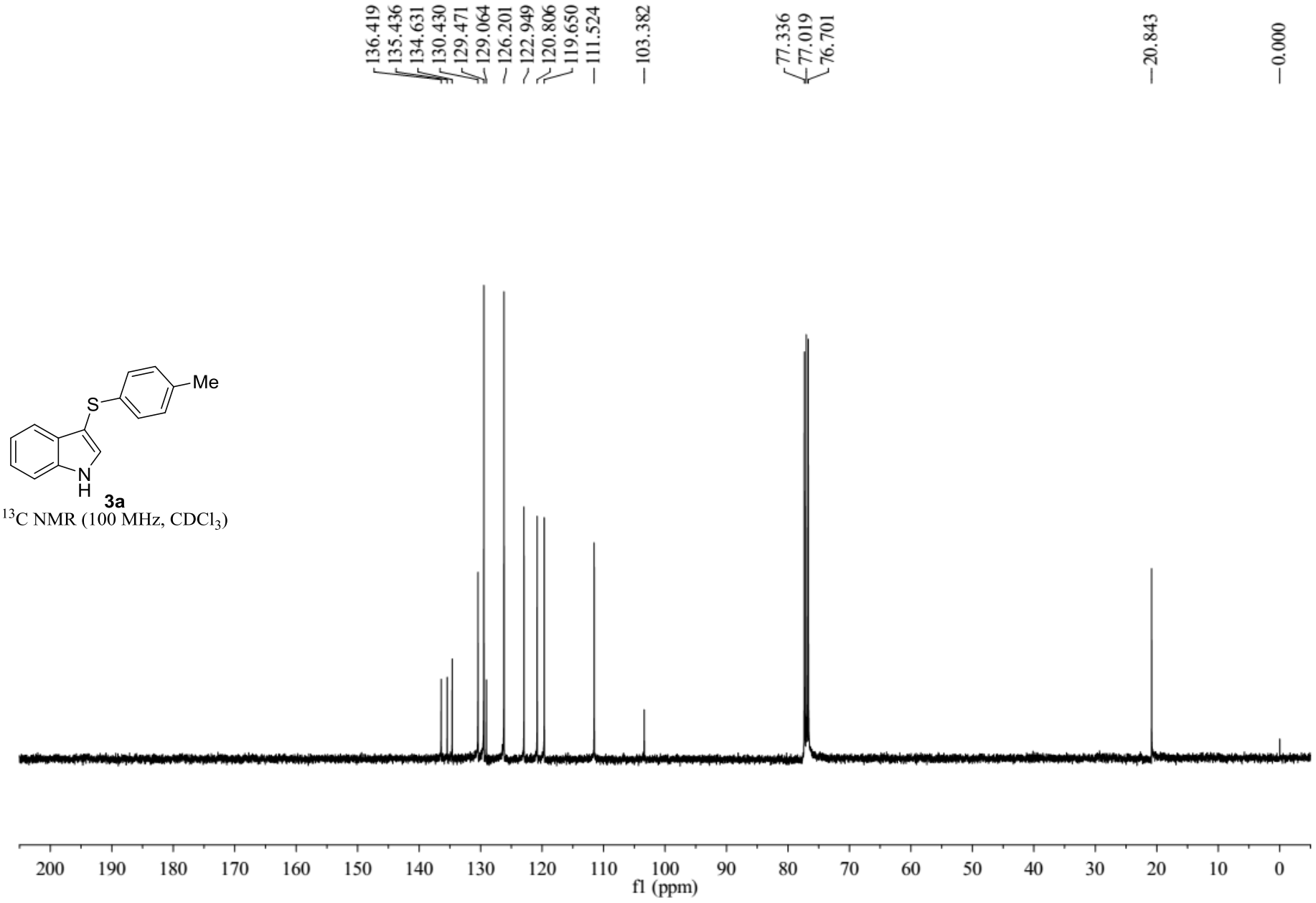


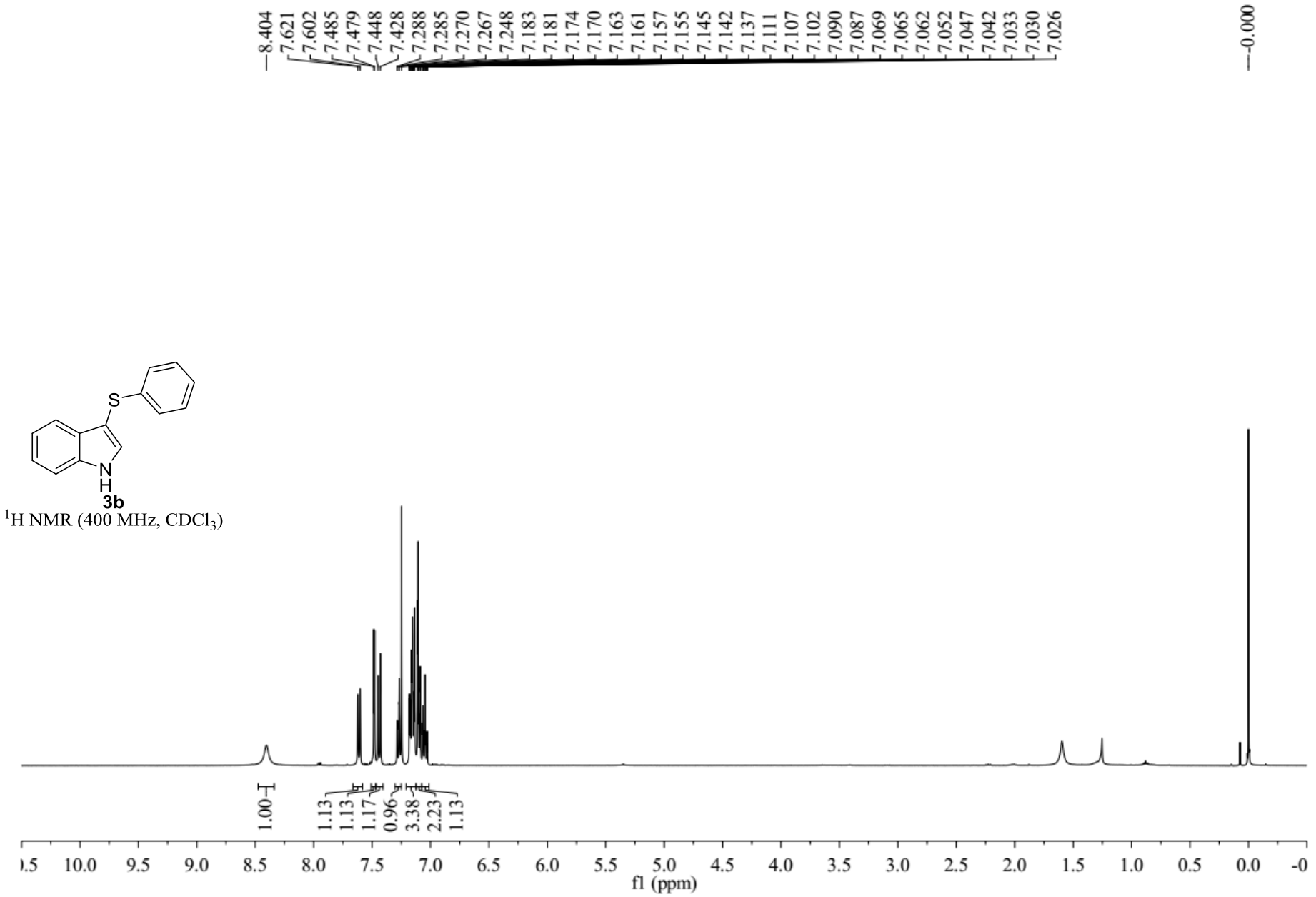
3a

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



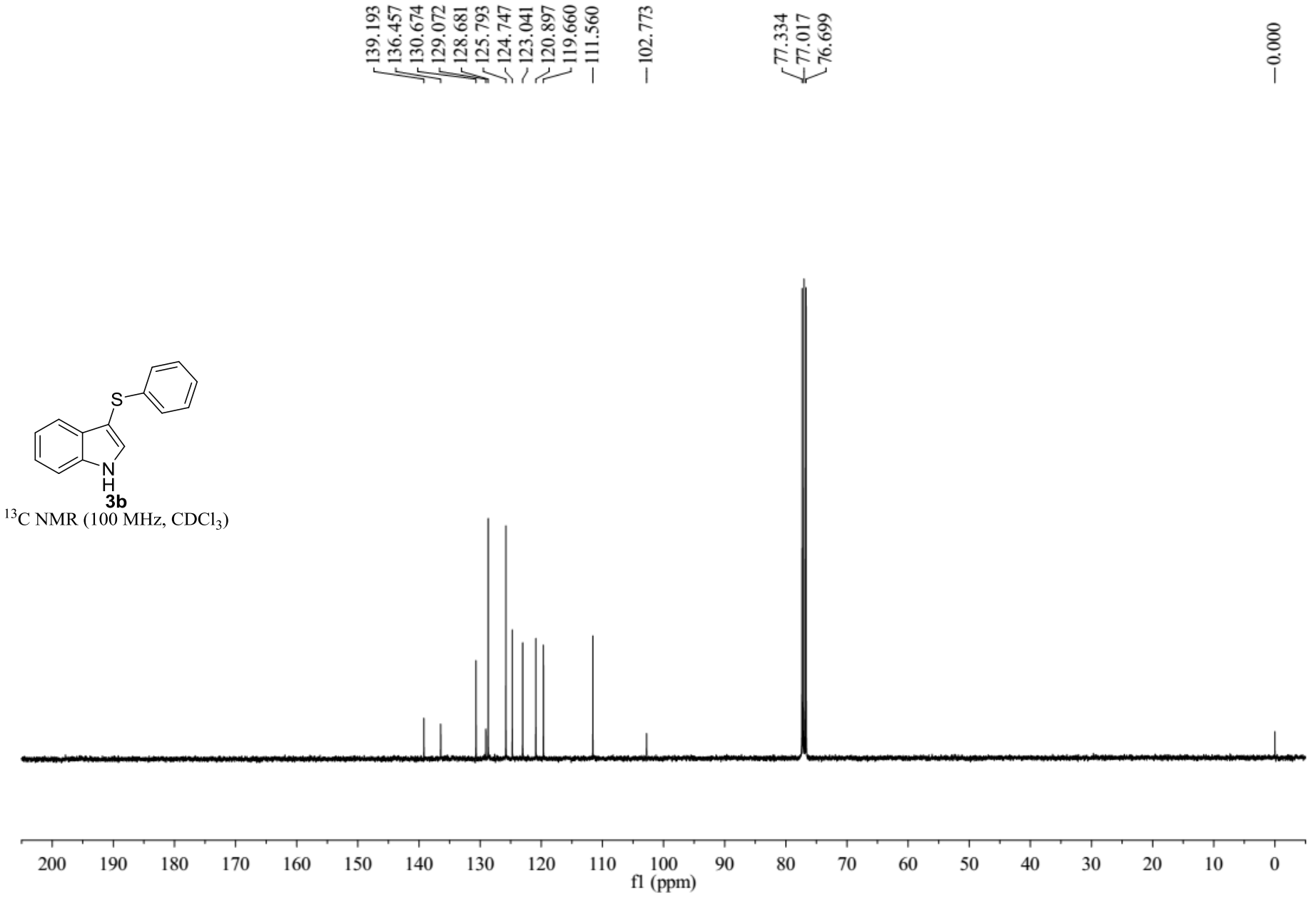
3a

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



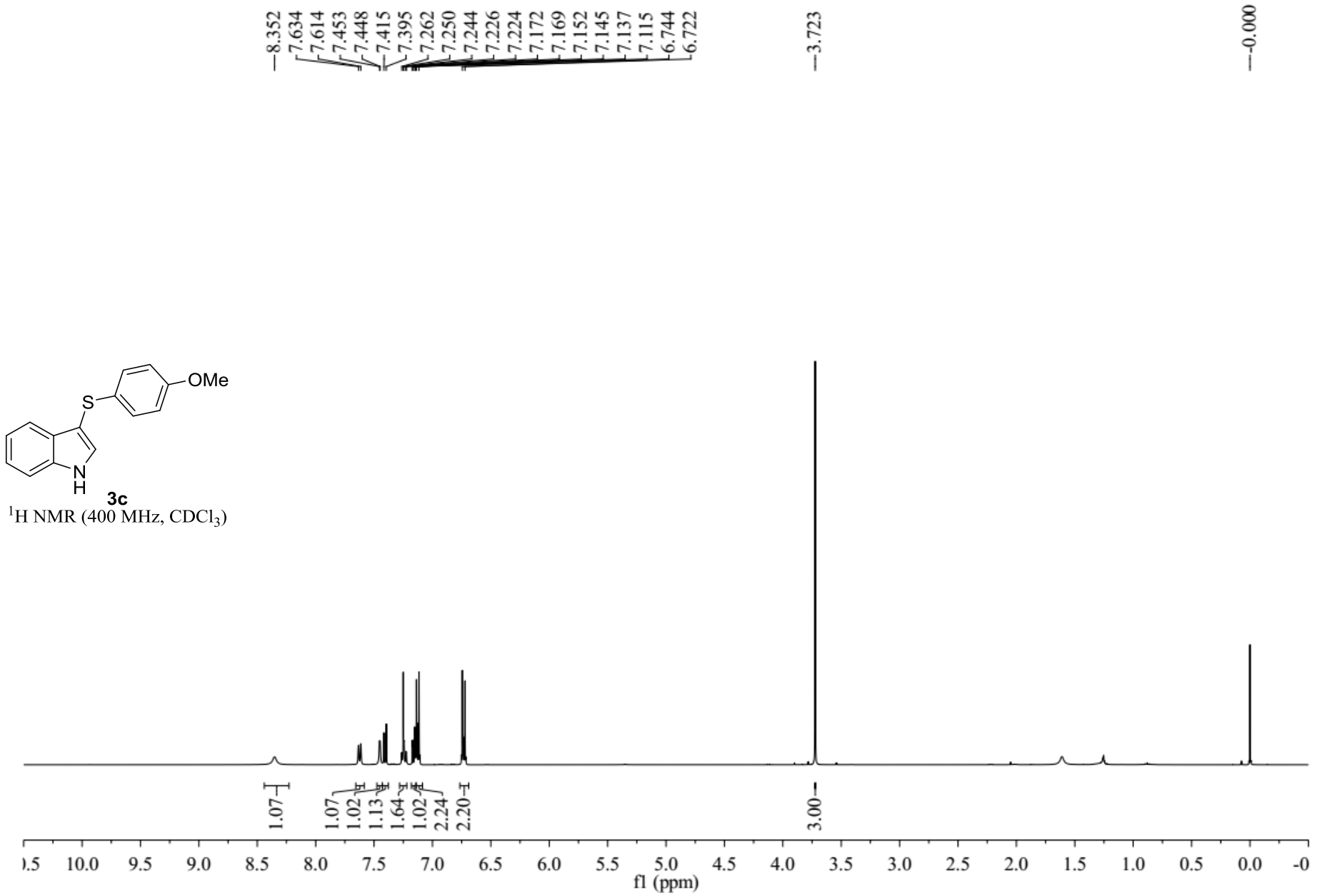
3b

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



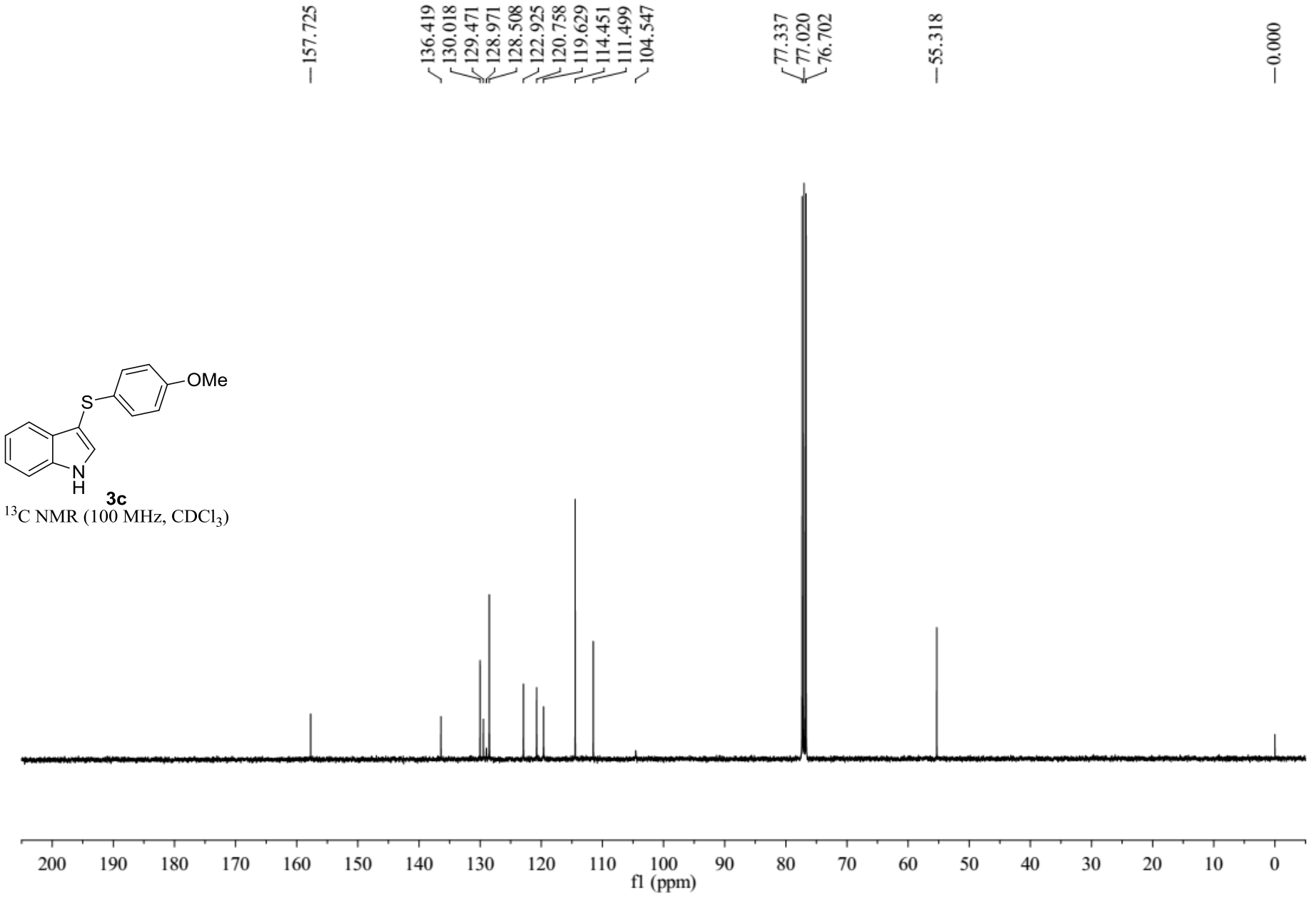
3b

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



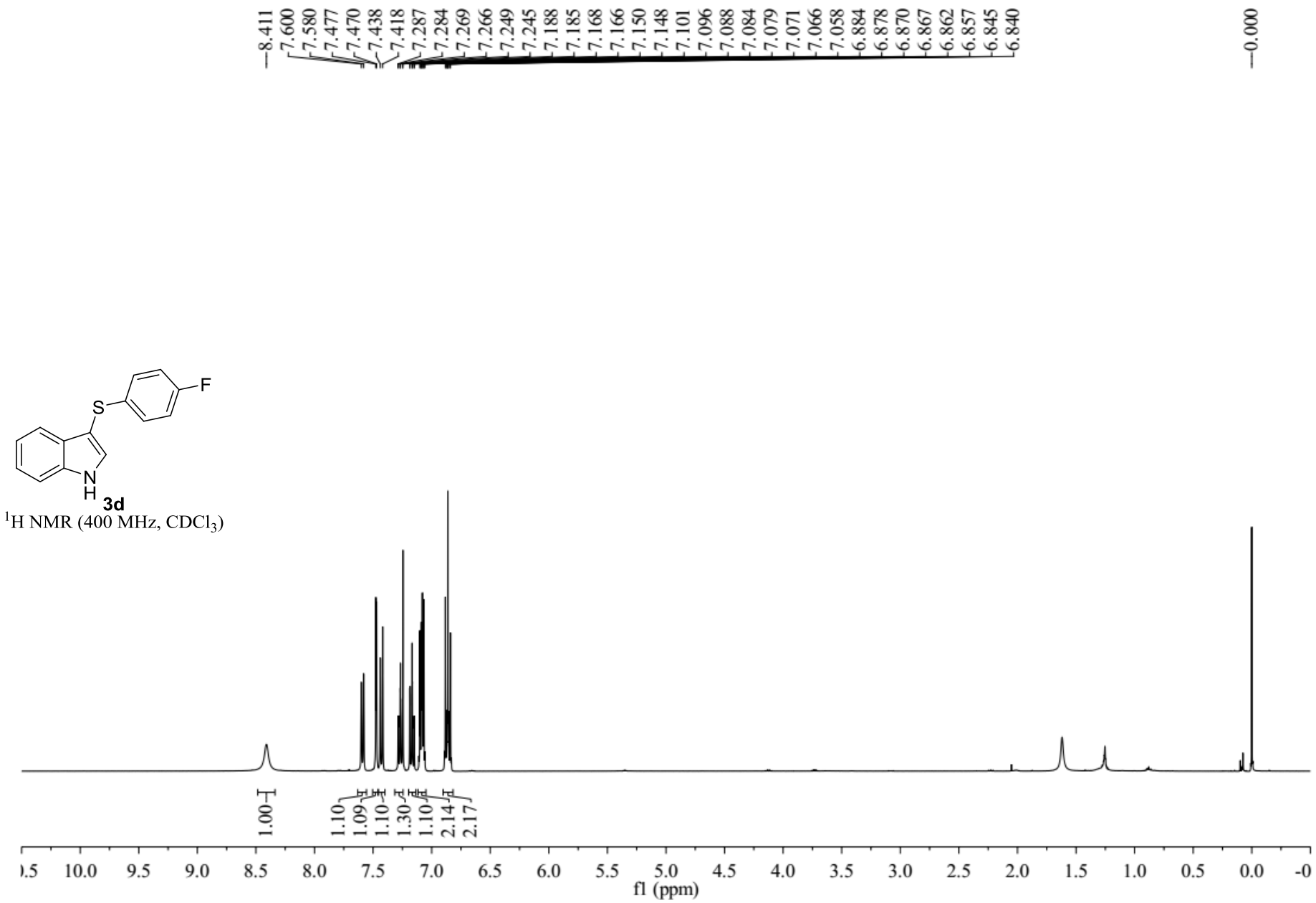
3c

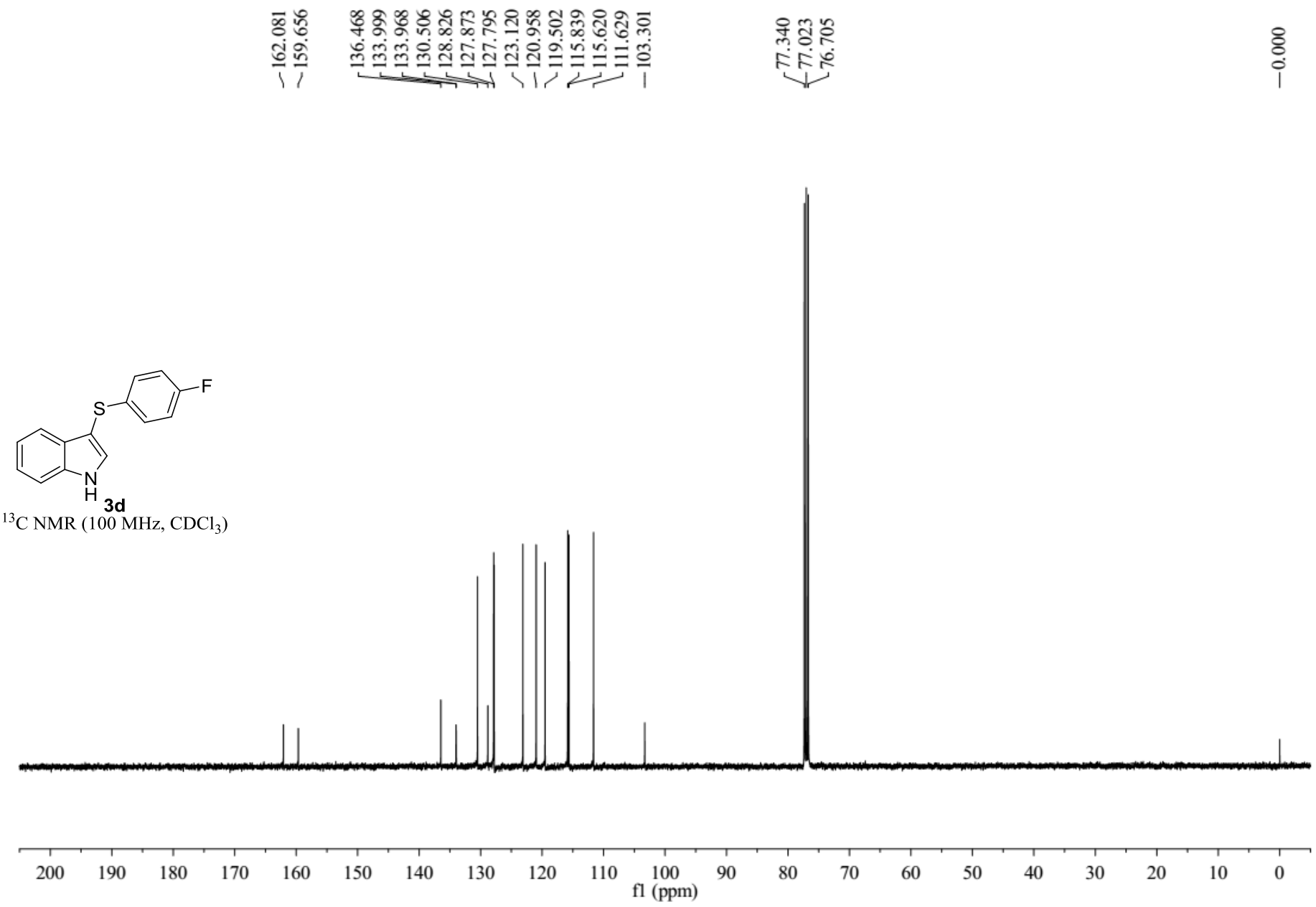
^{1}H NMR (400 MHz, $CDCl_3$)



3c

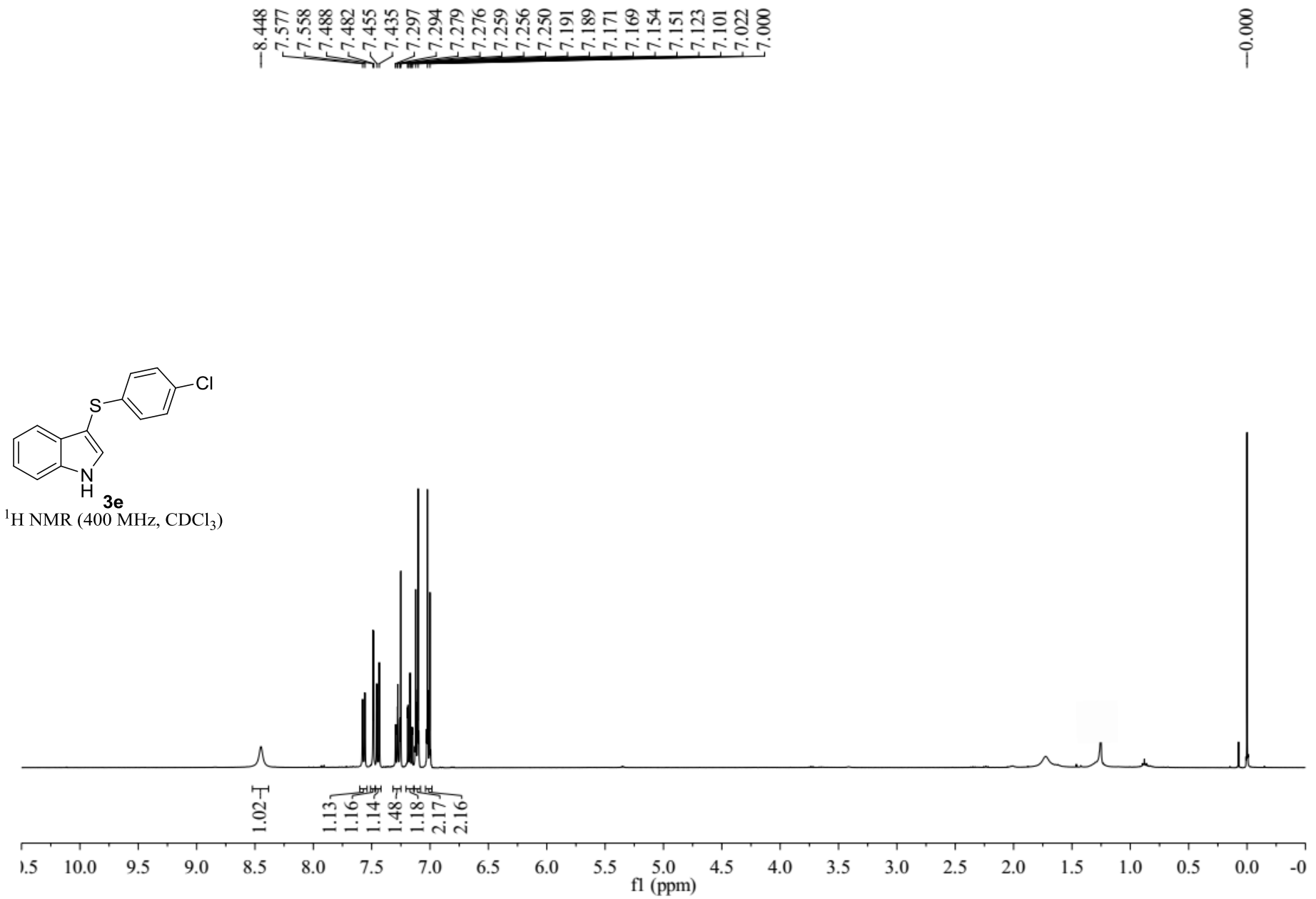
^{13}C NMR (100 MHz, $CDCl_3$)


8.411
7.600
7.580
7.477
7.470
7.438
7.418
7.287
7.284
7.269
7.266
7.249
7.245
7.188
7.185
7.168
7.166
7.150
7.148
7.101
7.096
7.088
7.084
7.079
7.071
7.066
7.058
6.884
6.878
6.870
6.867
6.862
6.857
6.845
6.840
0.000
F
S
N
H
3d
1H NMR (400 MHz, CDCl3)
1.00
1.10
1.09
1.10
1.30
1.10
2.14
2.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



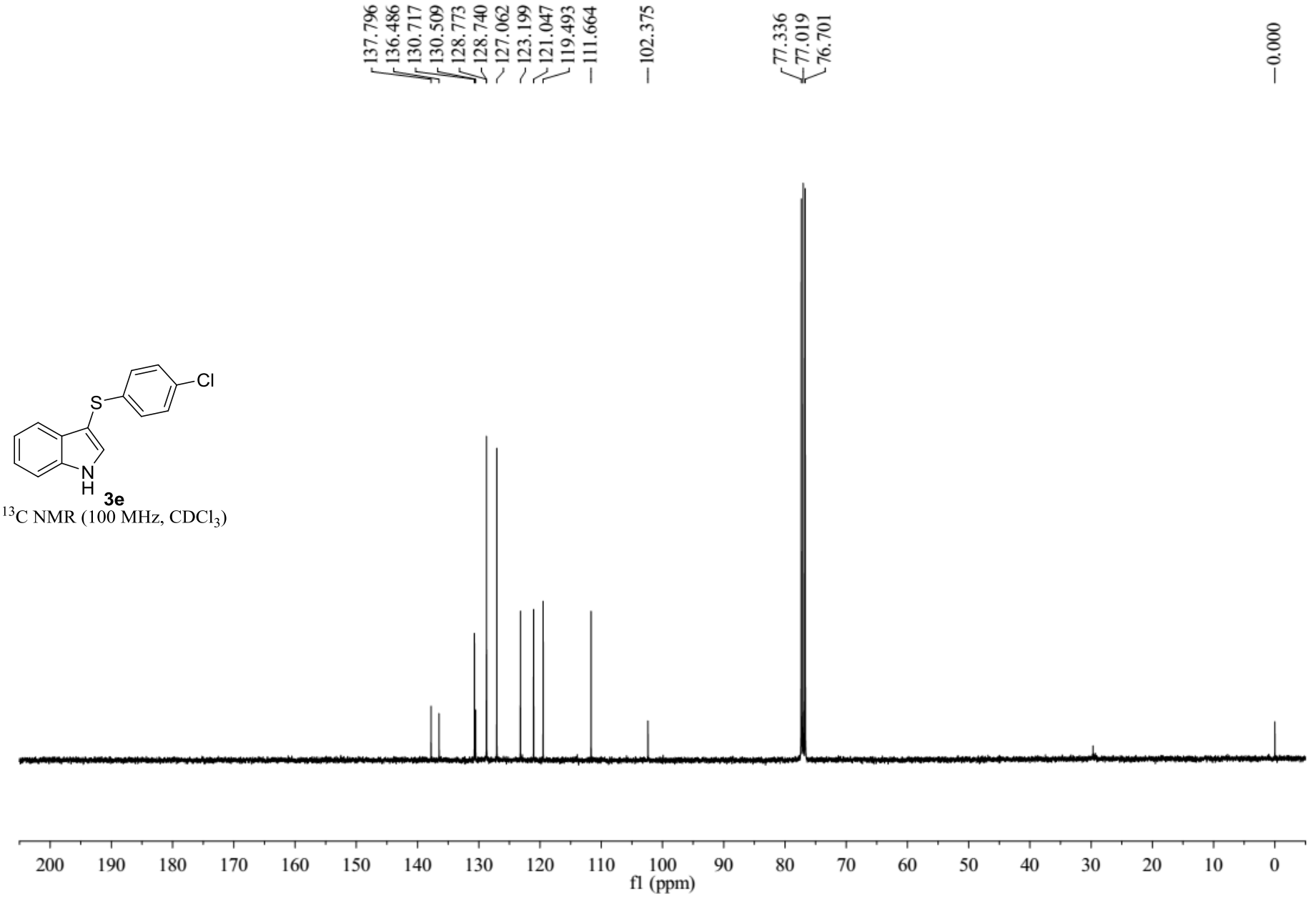
3d

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



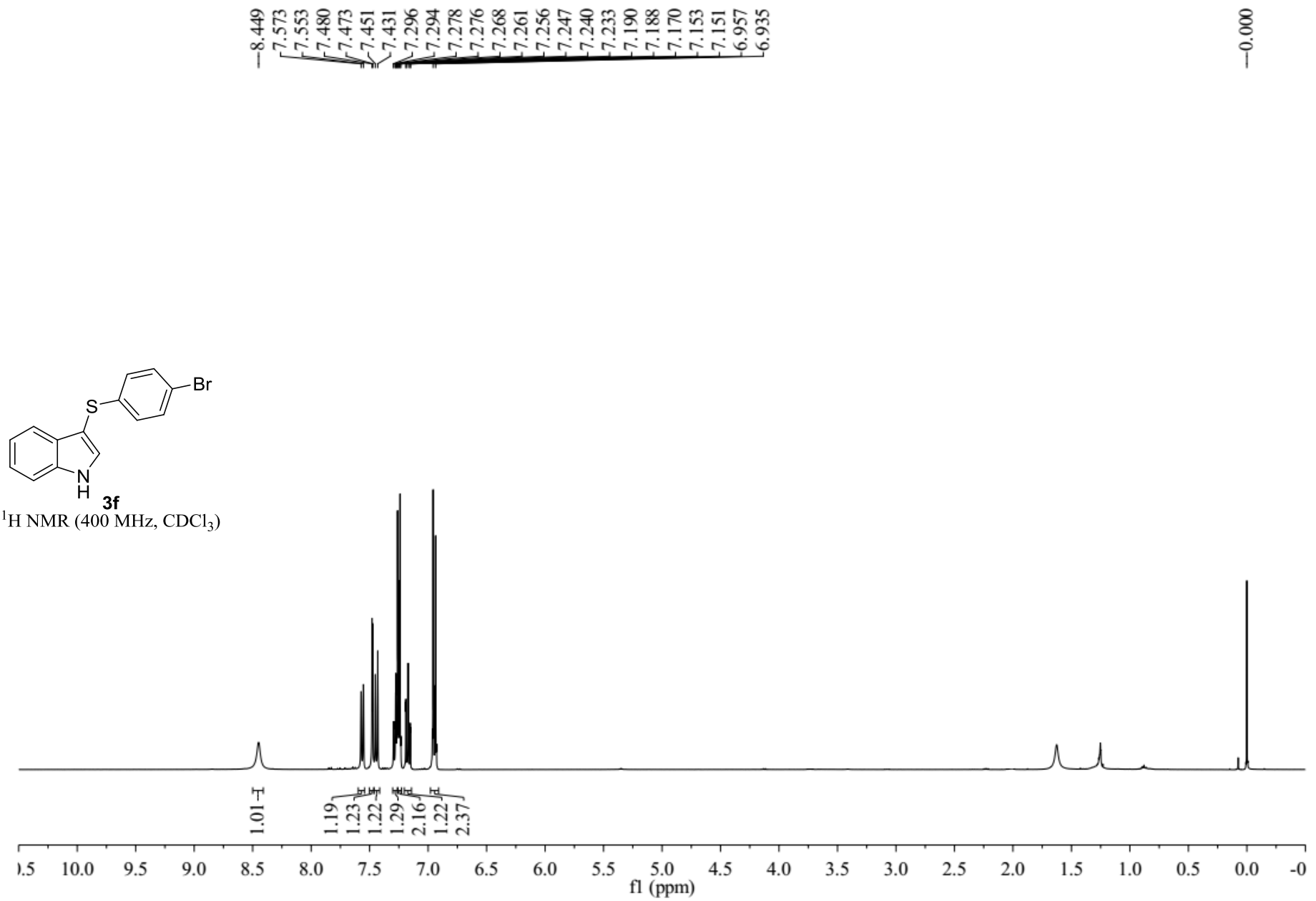
3e

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



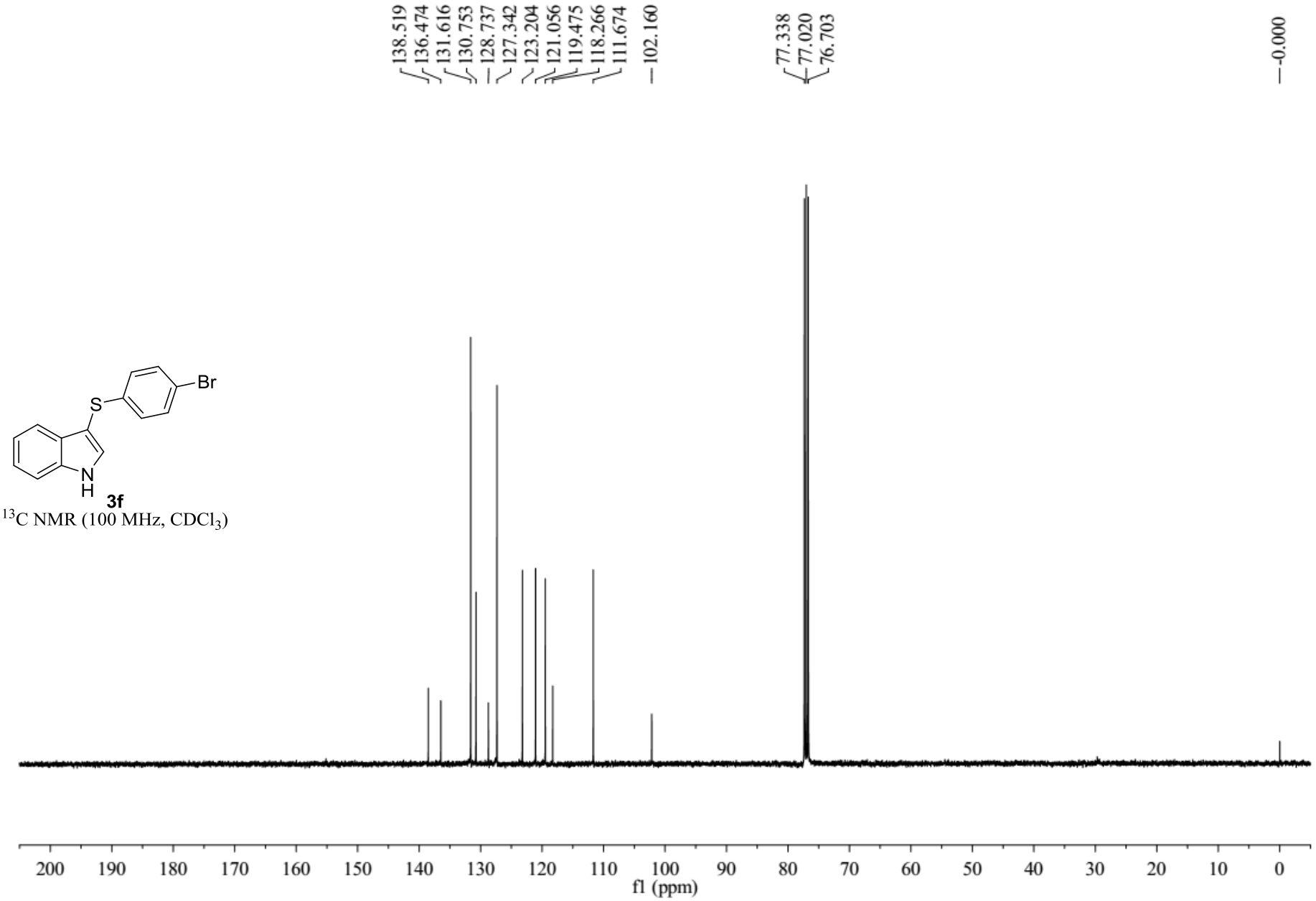
3e

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



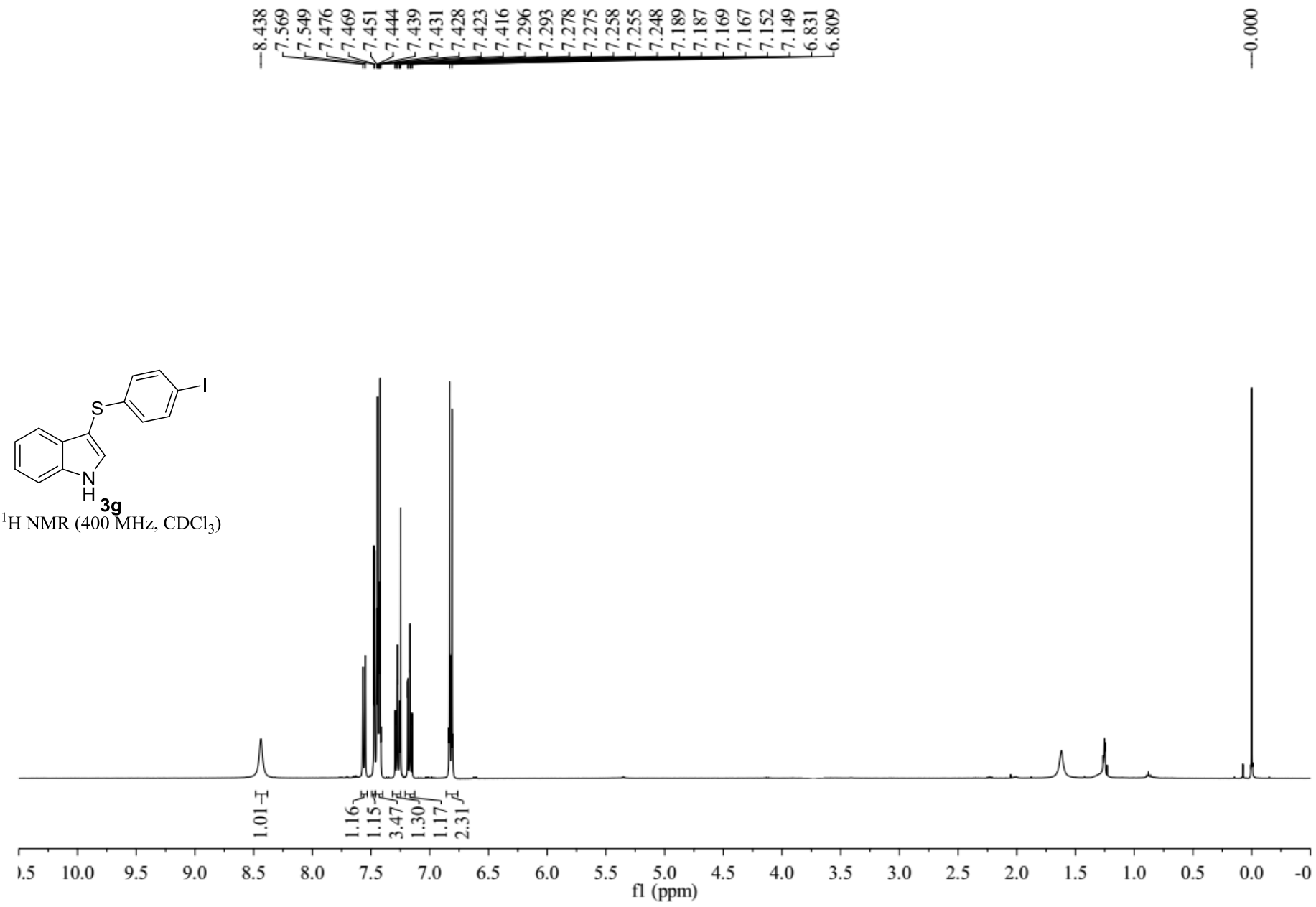
3f

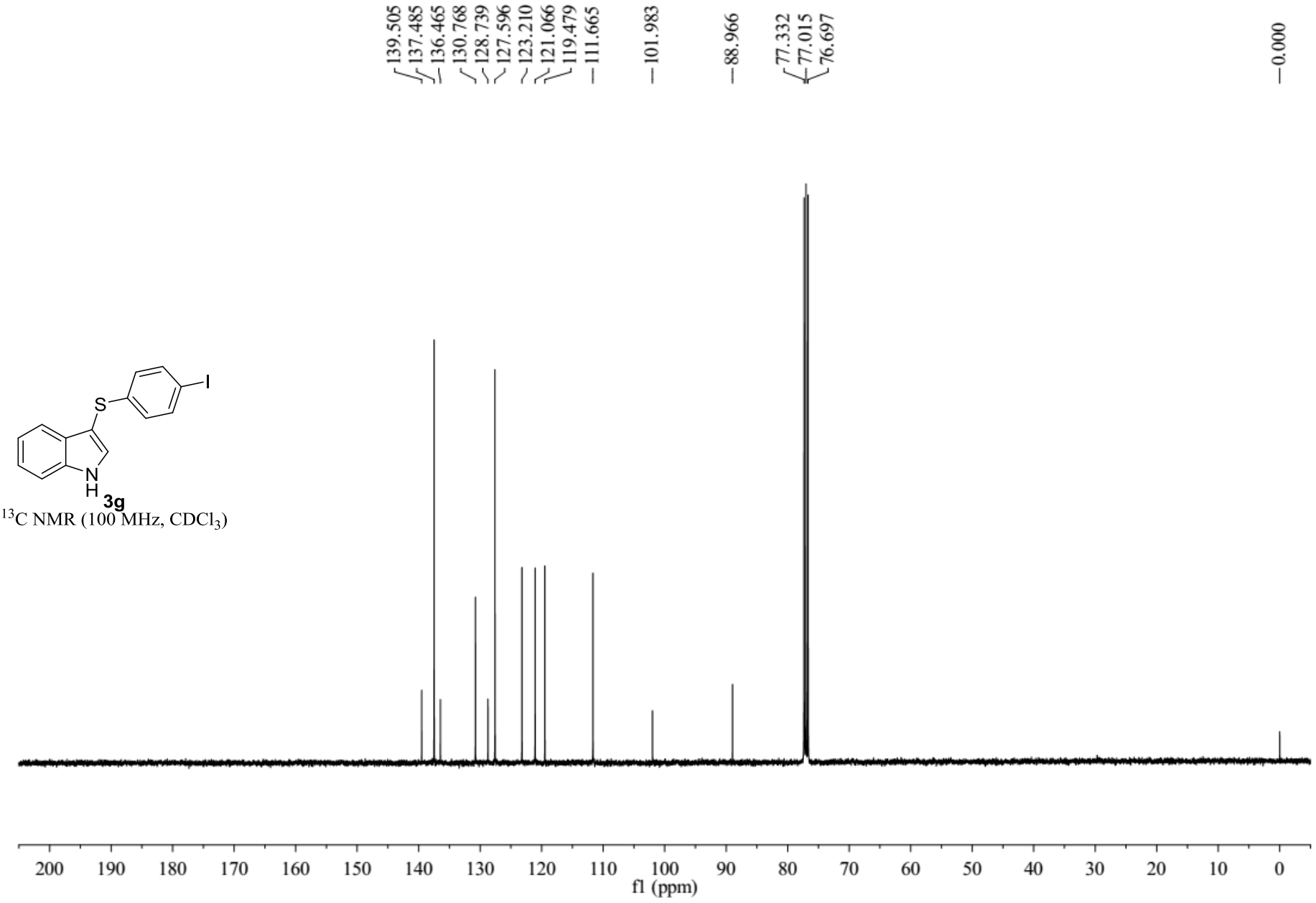
^{1}H NMR (400 MHz, $CDCl_3$)



3f

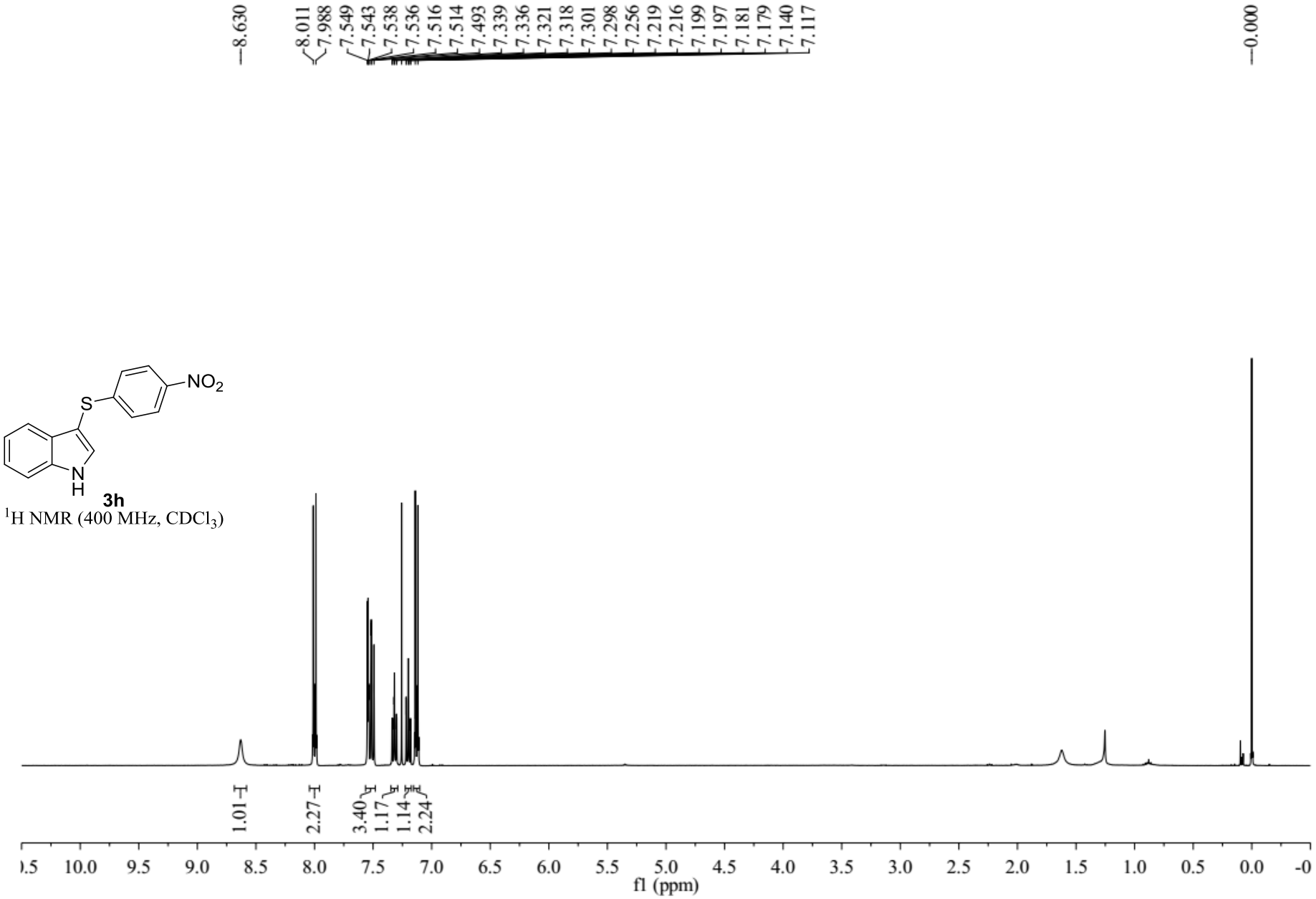
^{13}C NMR (100 MHz, $CDCl_3$)


8.438
7.569
7.549
7.476
7.469
7.451
7.444
7.439
7.431
7.428
7.423
7.416
7.296
7.293
7.278
7.275
7.258
7.255
7.248
7.189
7.187
7.169
7.167
7.152
7.149
6.831
6.809
0.000
S
I
N
H
3g
1H NMR (400 MHz, CDCl3)
1.01
1.16
1.15
3.47
1.30
1.17
2.31
f1 (ppm)



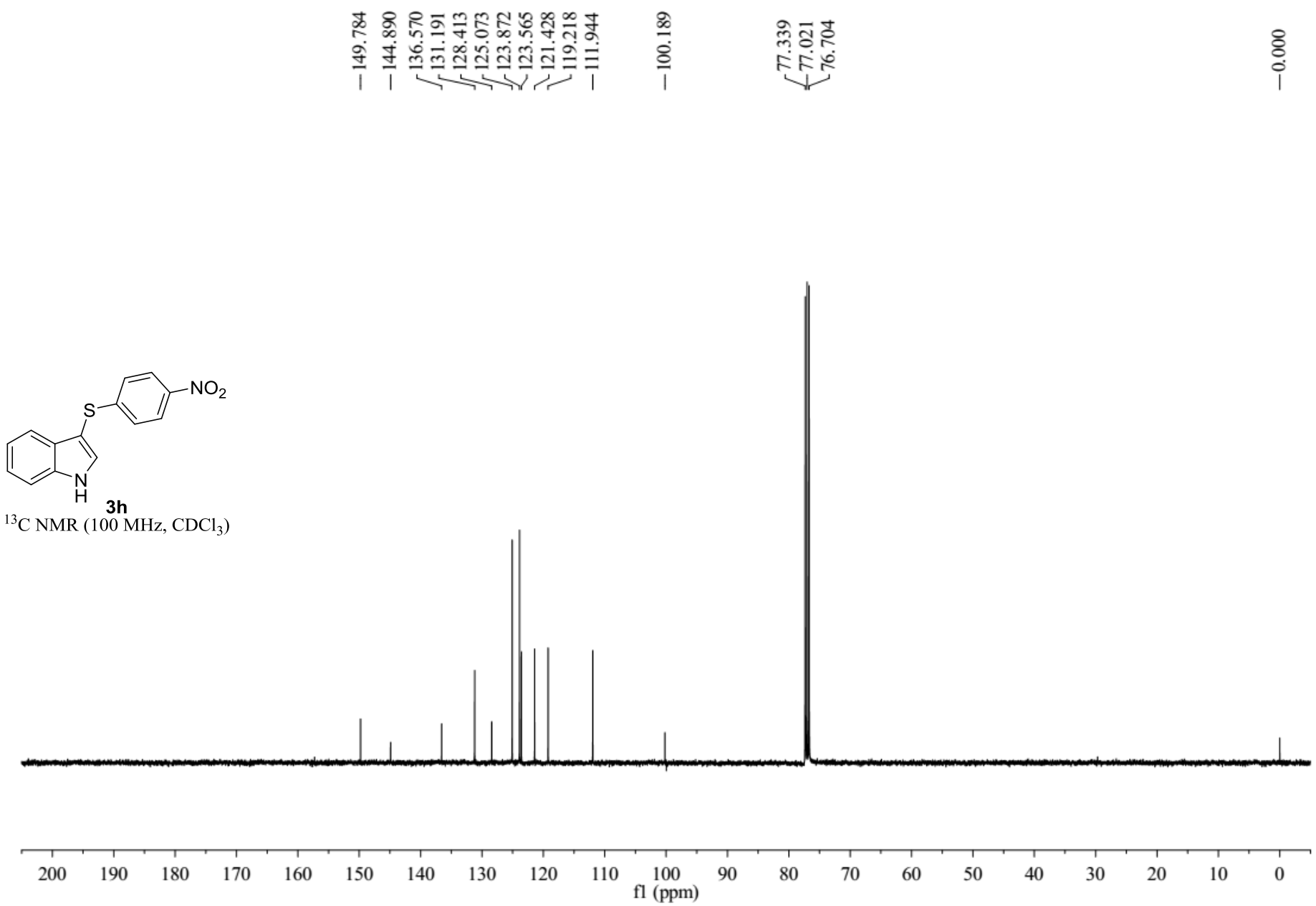
3g

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



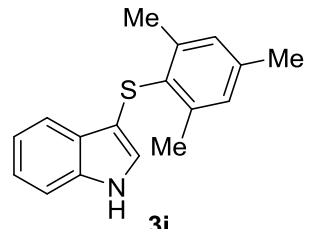
3h

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



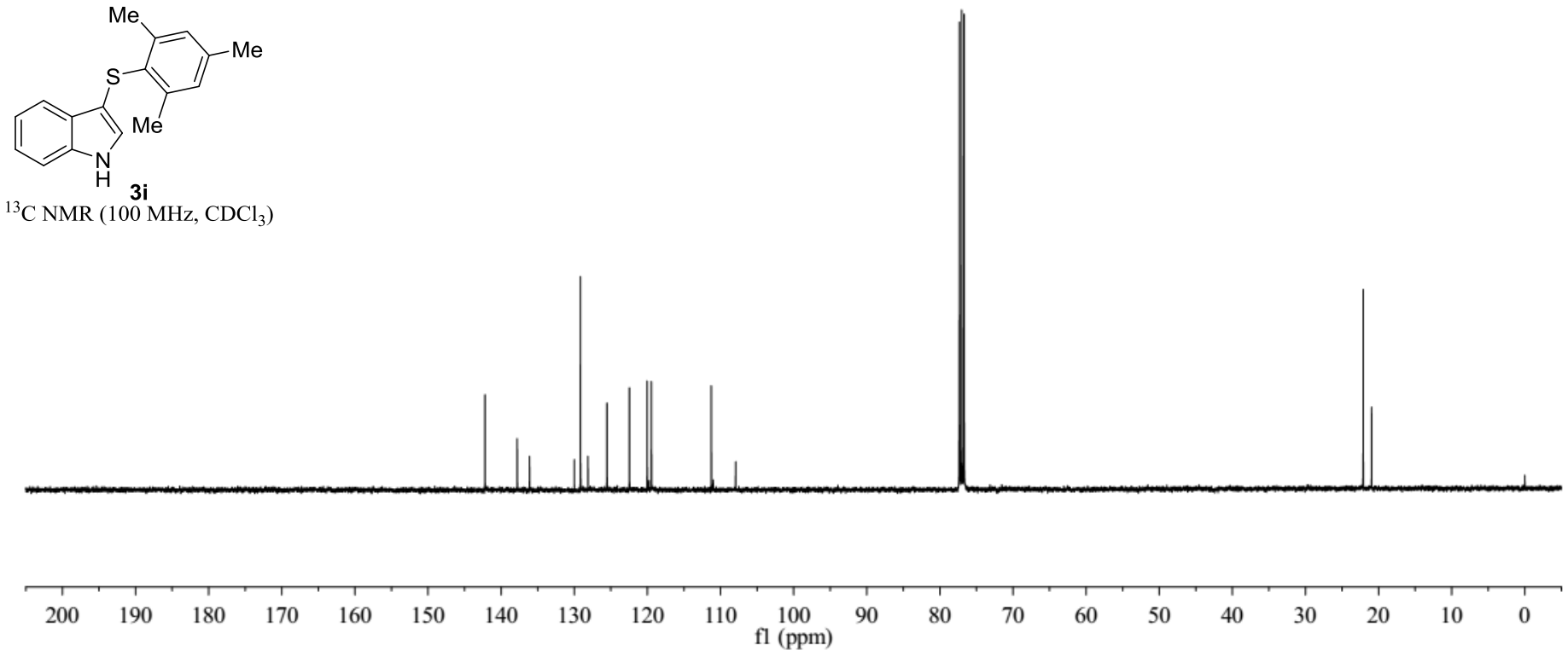
3h

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



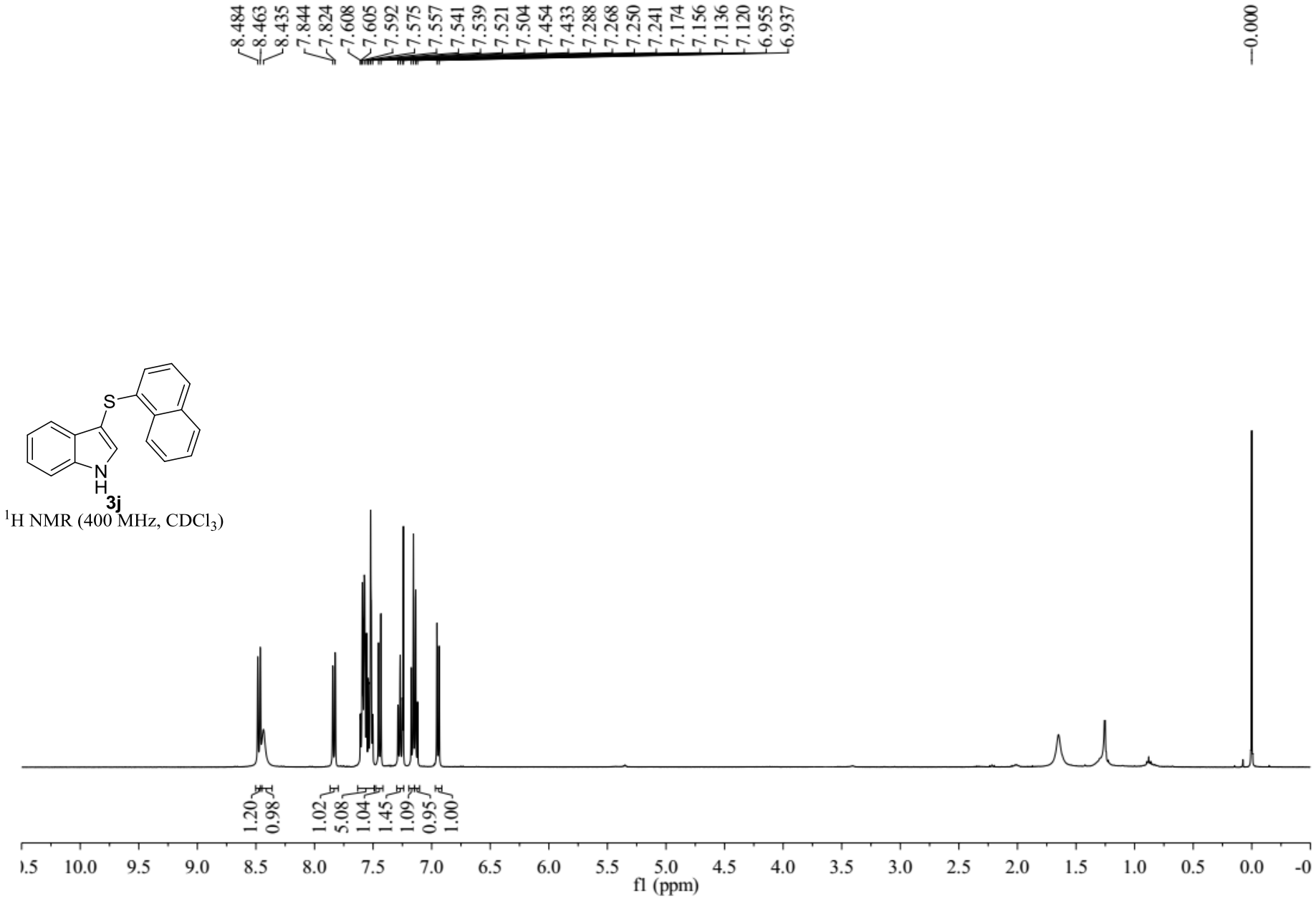
3i

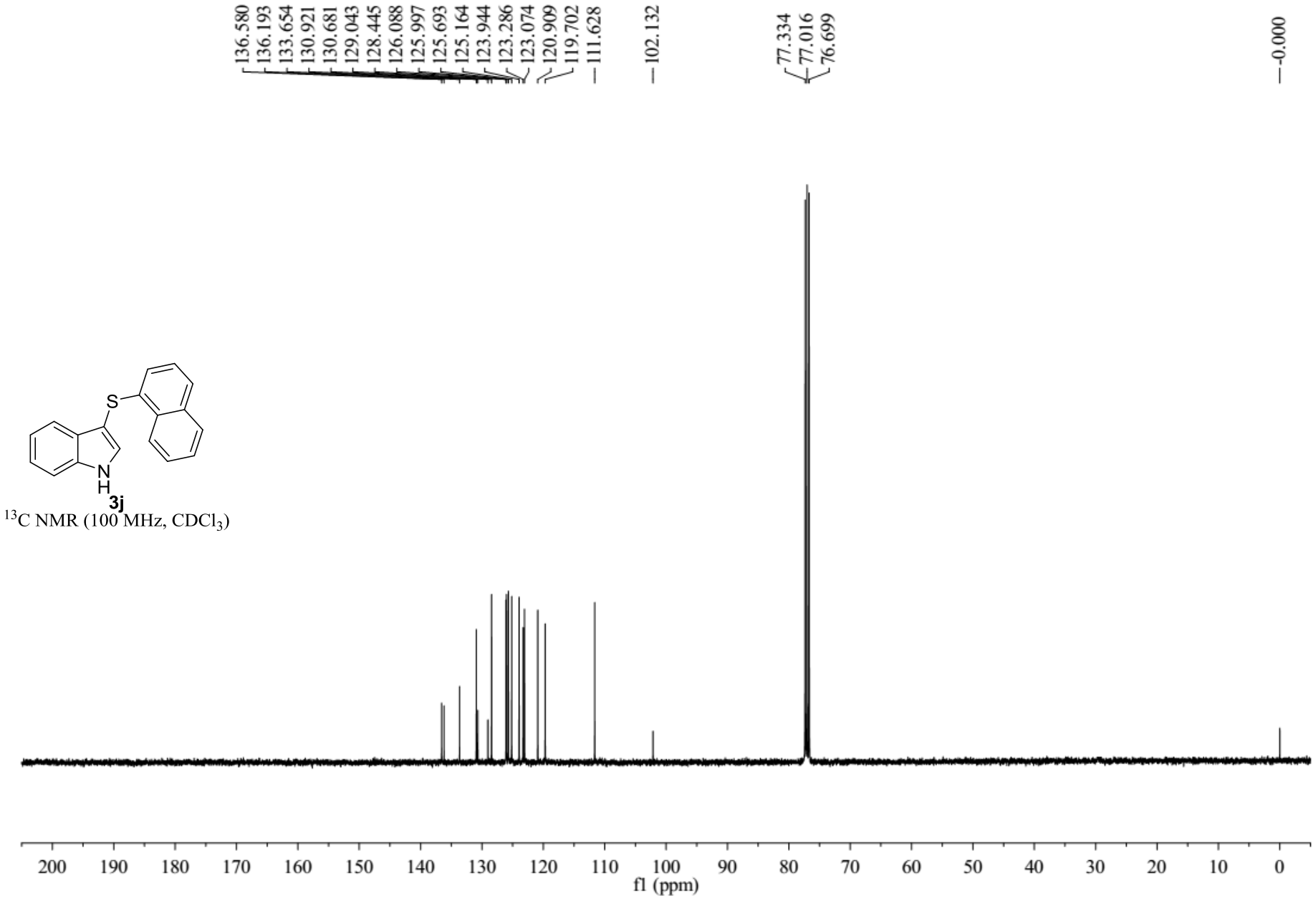
^{1}H NMR (400 MHz, $CDCl_3$)



3i

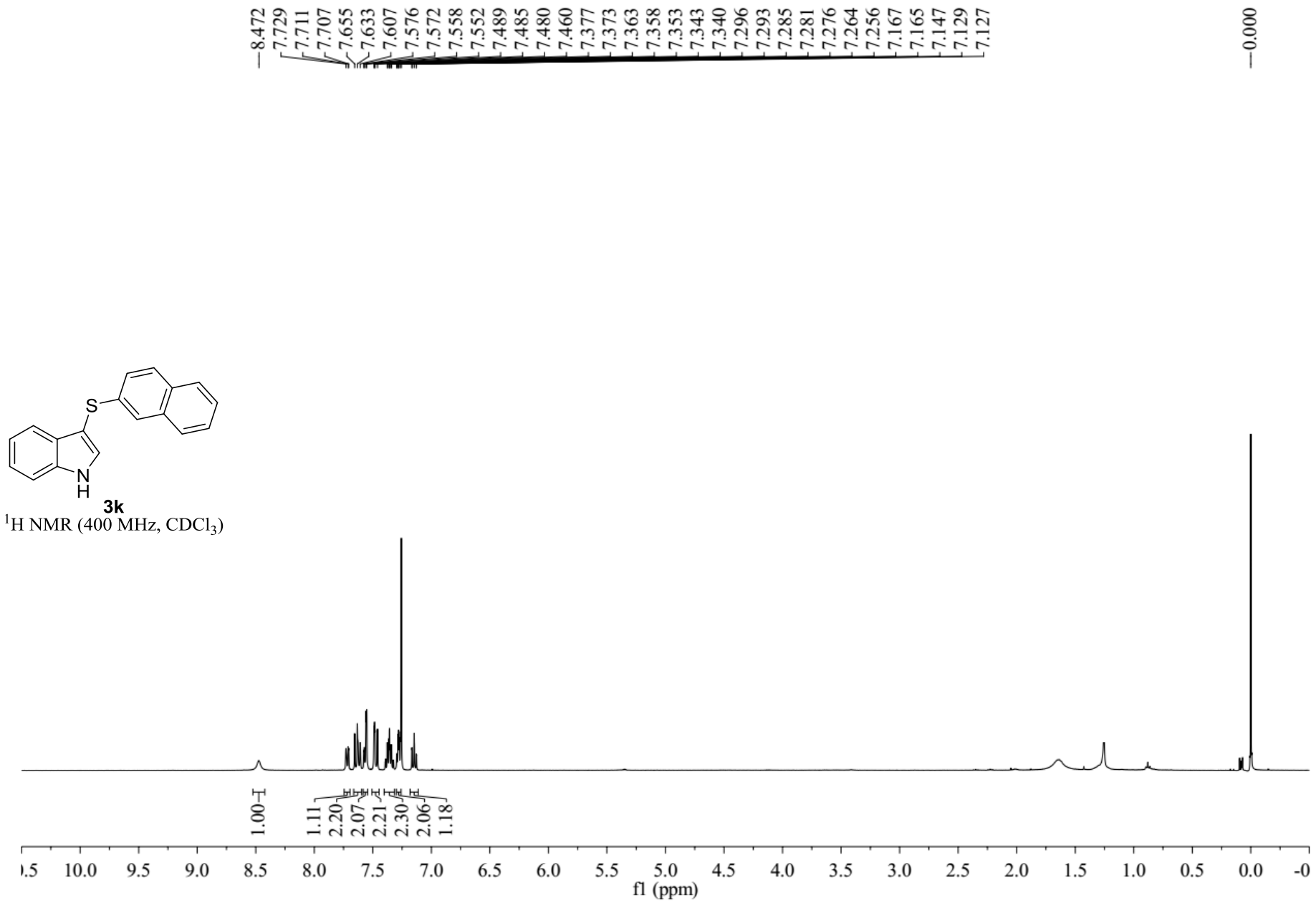
^{13}C NMR (100 MHz, $CDCl_3$)


8.484
8.463
8.435
7.844
7.824
7.608
7.605
7.592
7.575
7.557
7.541
7.539
7.521
7.504
7.454
7.433
7.288
7.268
7.250
7.241
7.174
7.156
7.136
7.120
6.955
6.937
0.000
S
N
H
3j
1H NMR (400 MHz, CDCl3)
1.20
0.98
1.02
5.08
1.04
1.45
1.09
0.95
1.00
f1 (ppm)



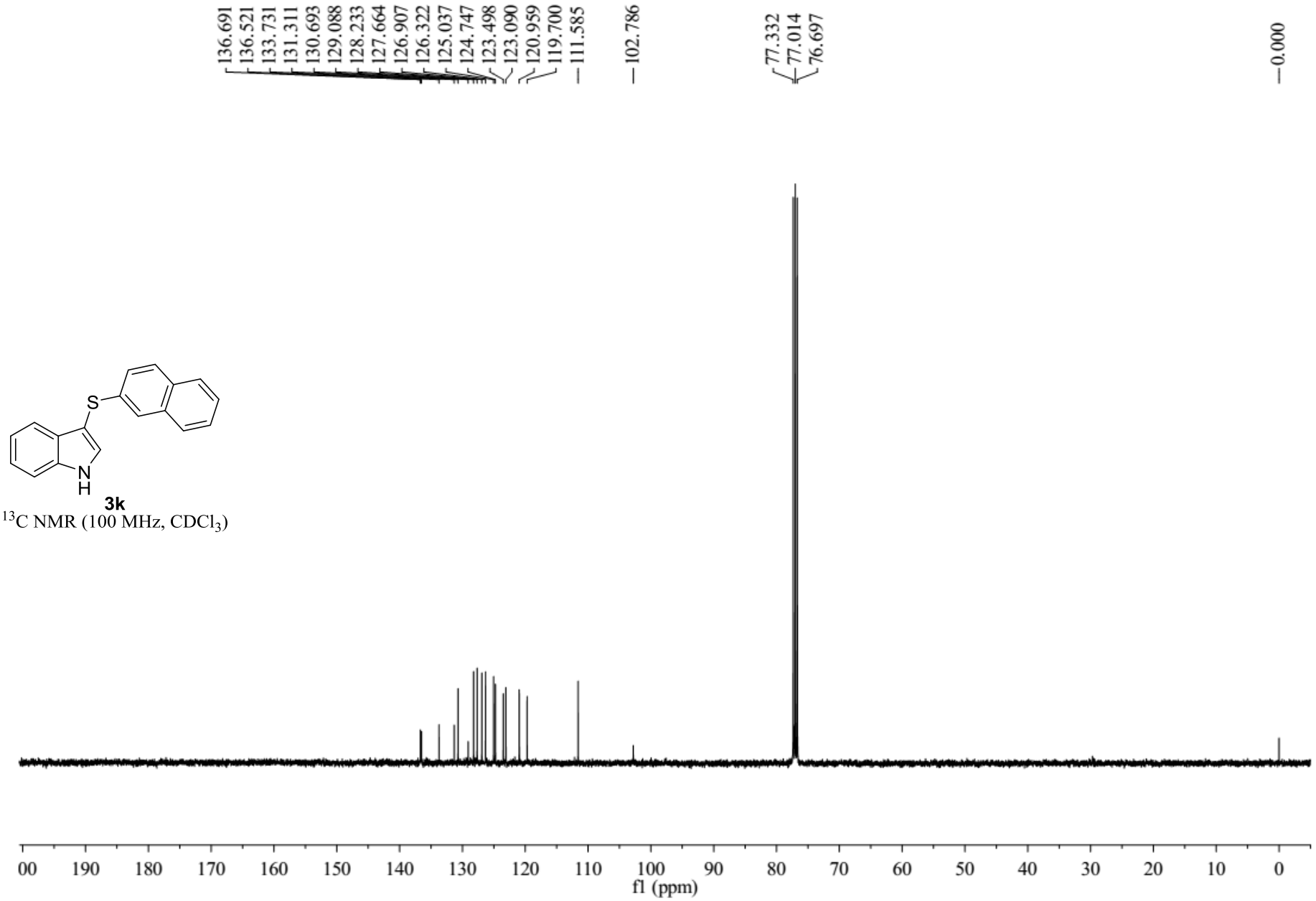
3j

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



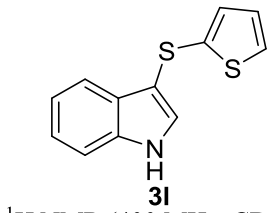
3k

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



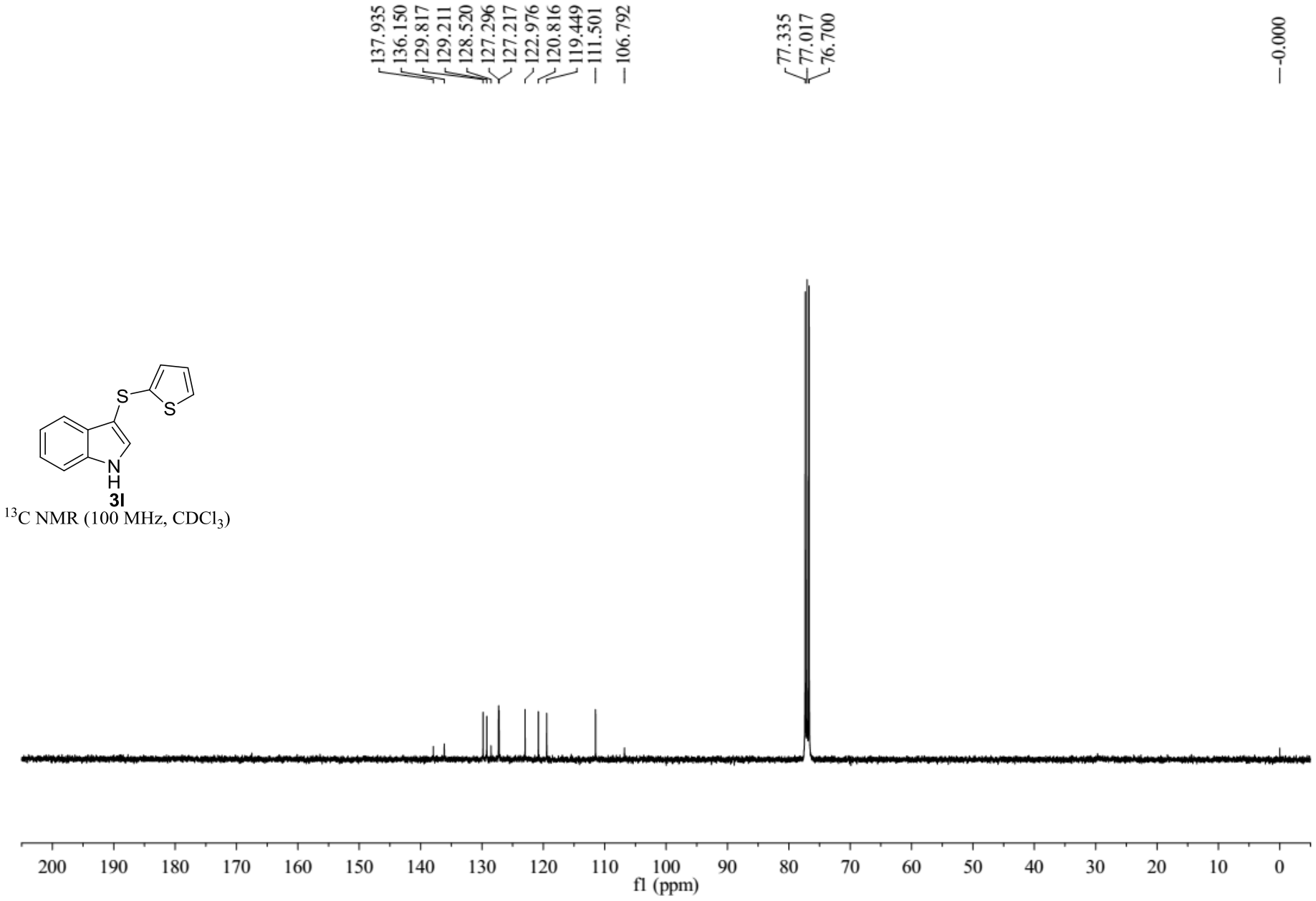
3k

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



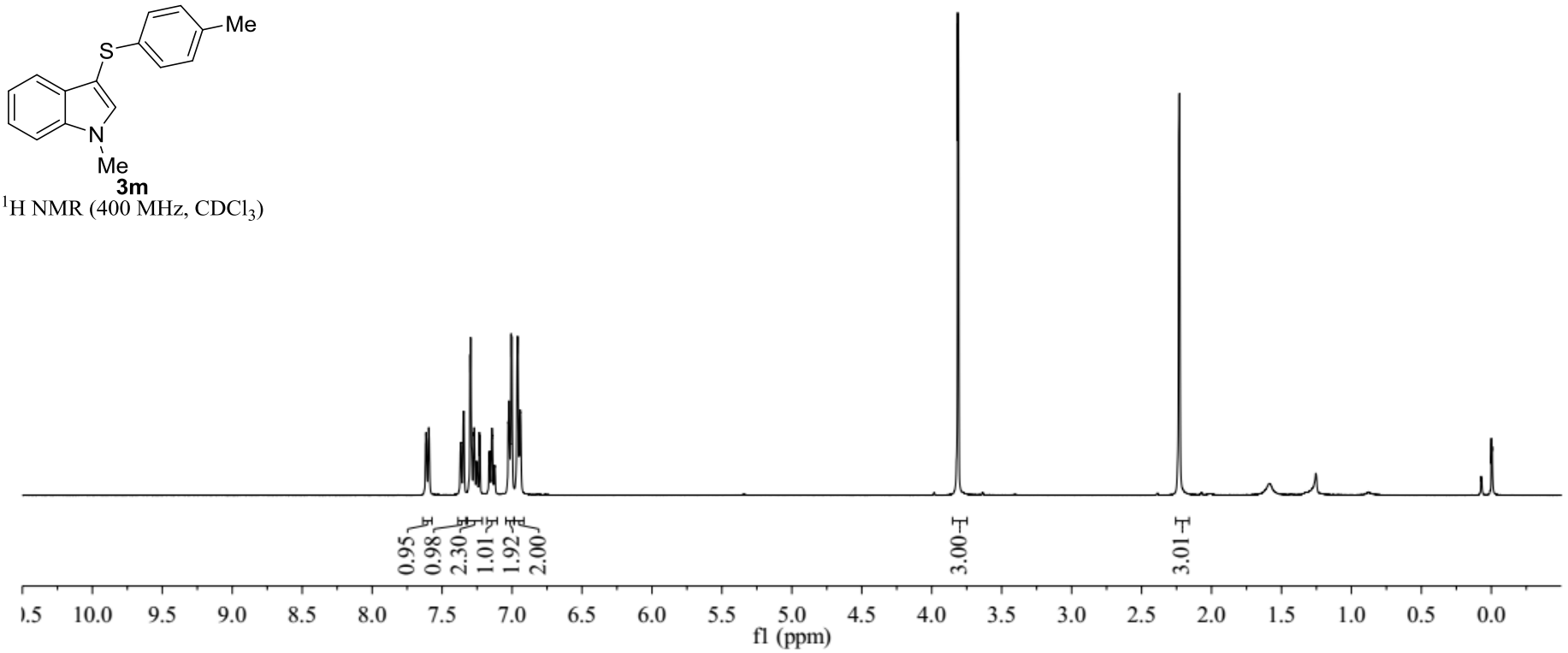
3l

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



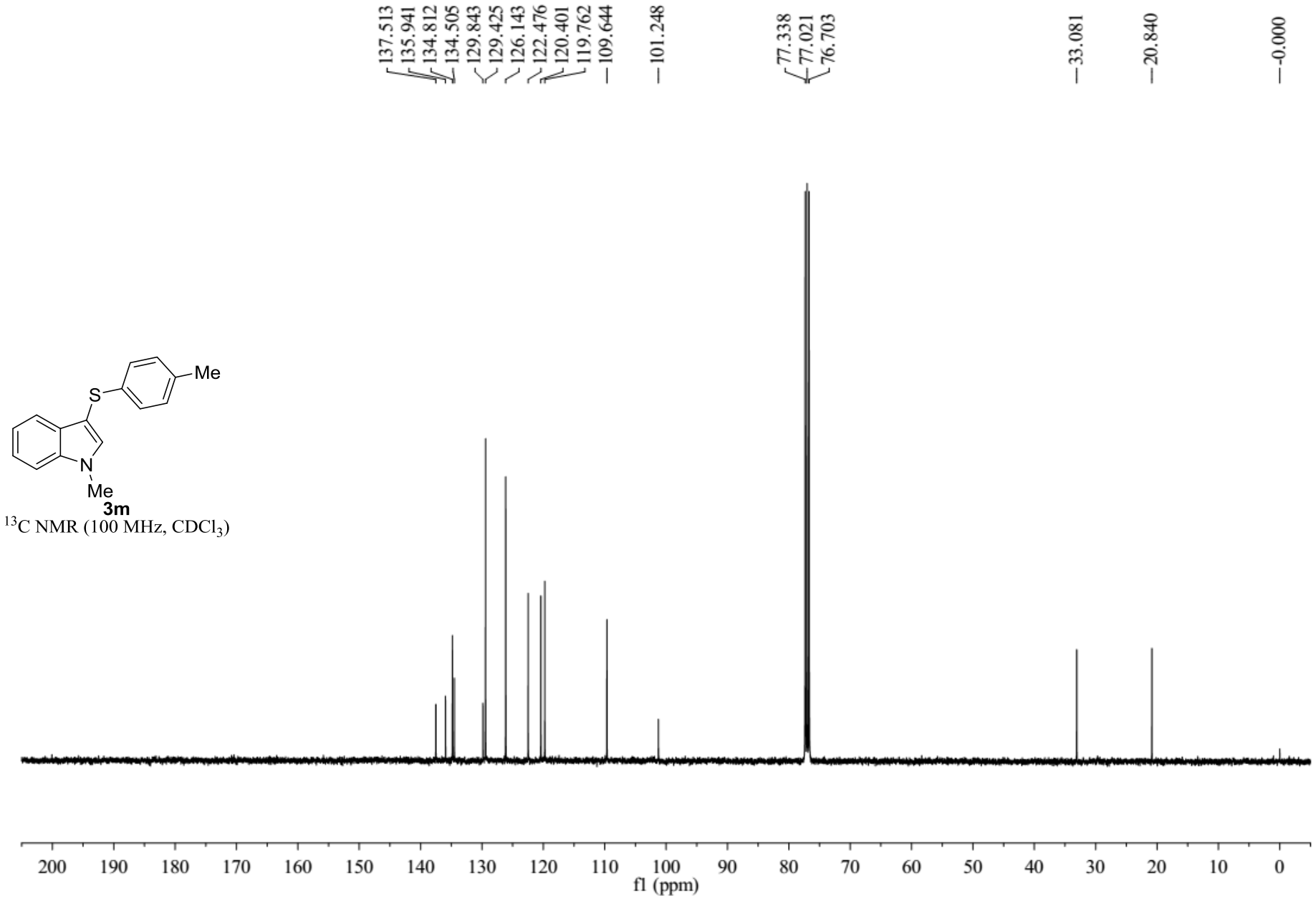
3l

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

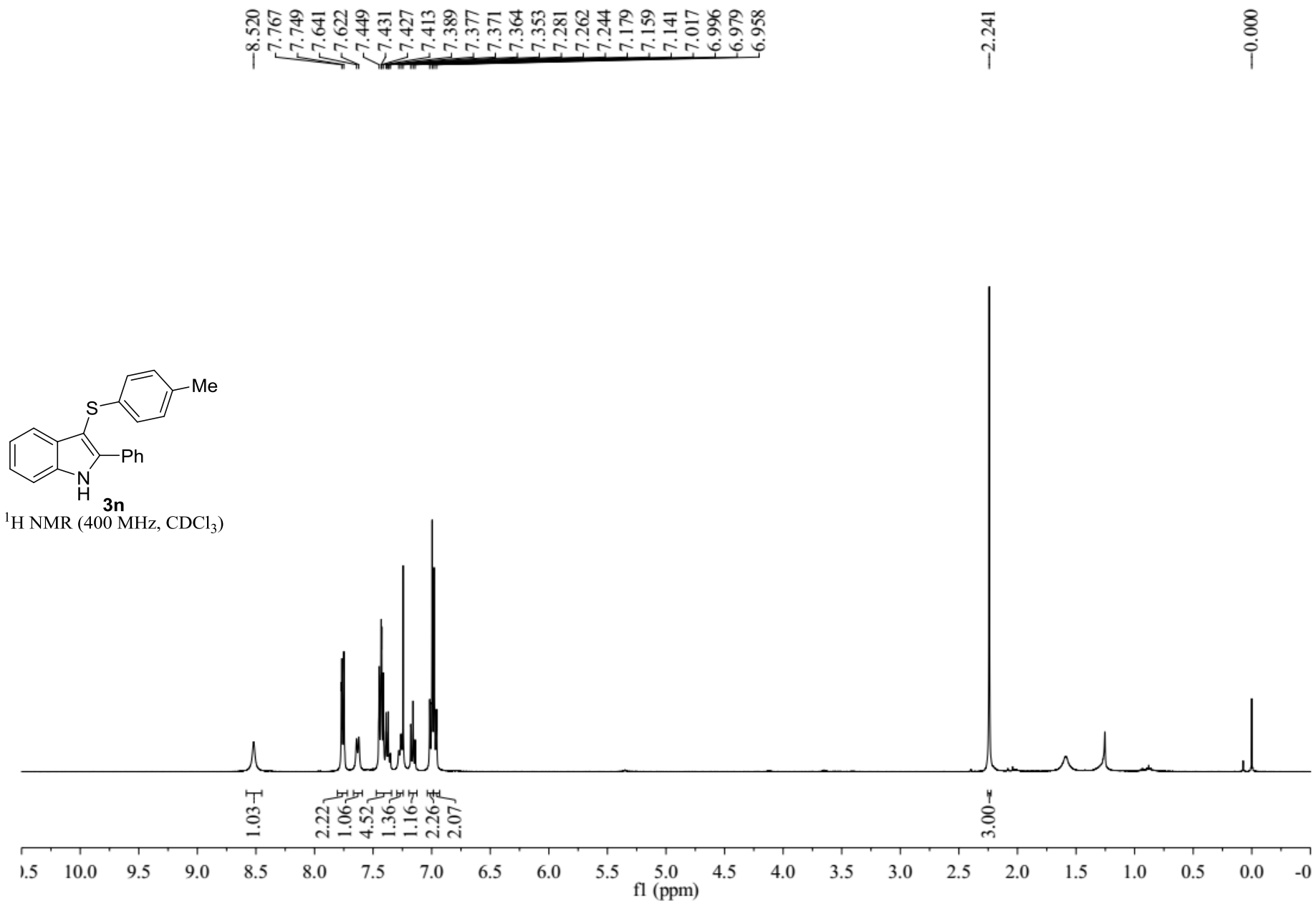


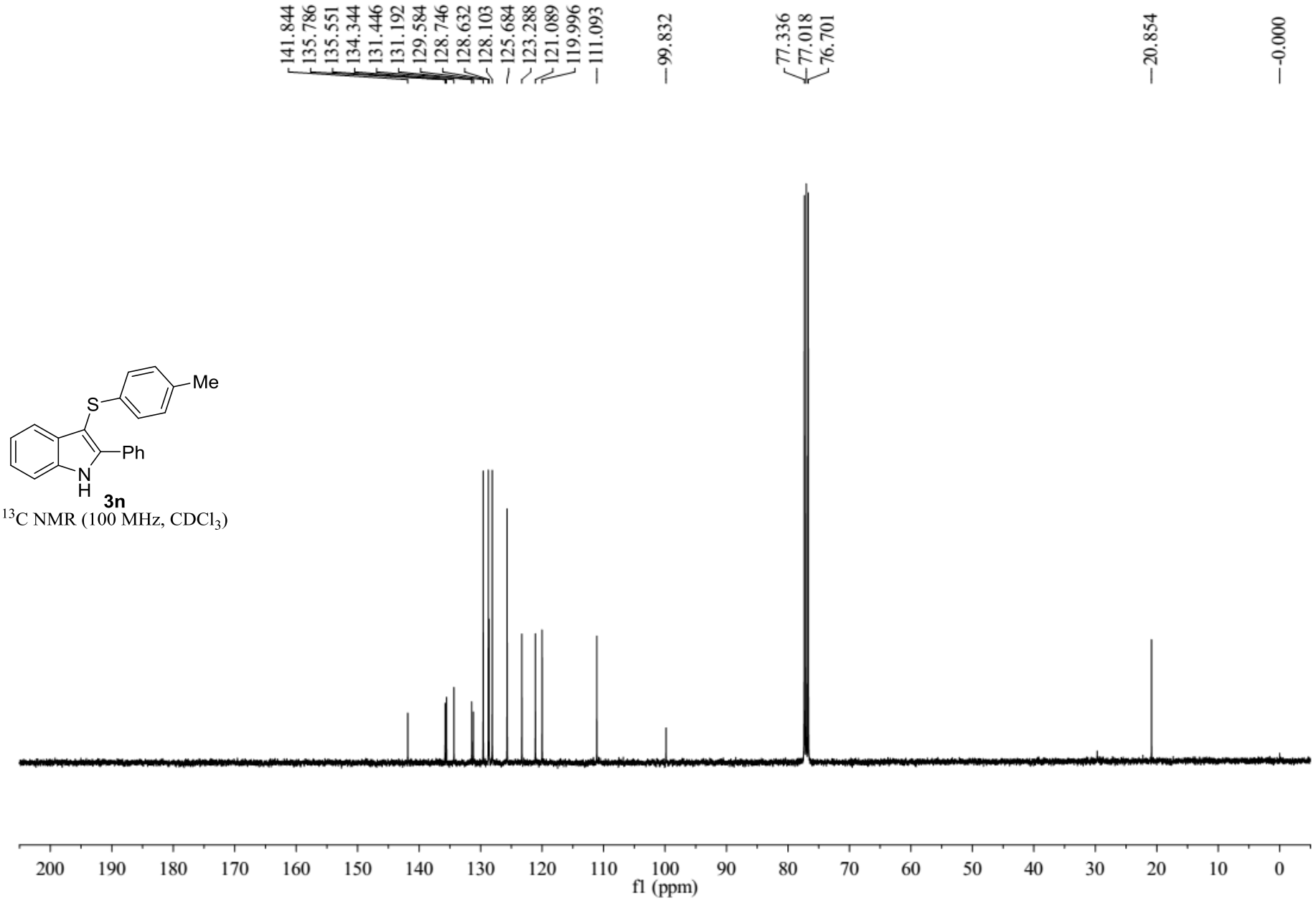
3m

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



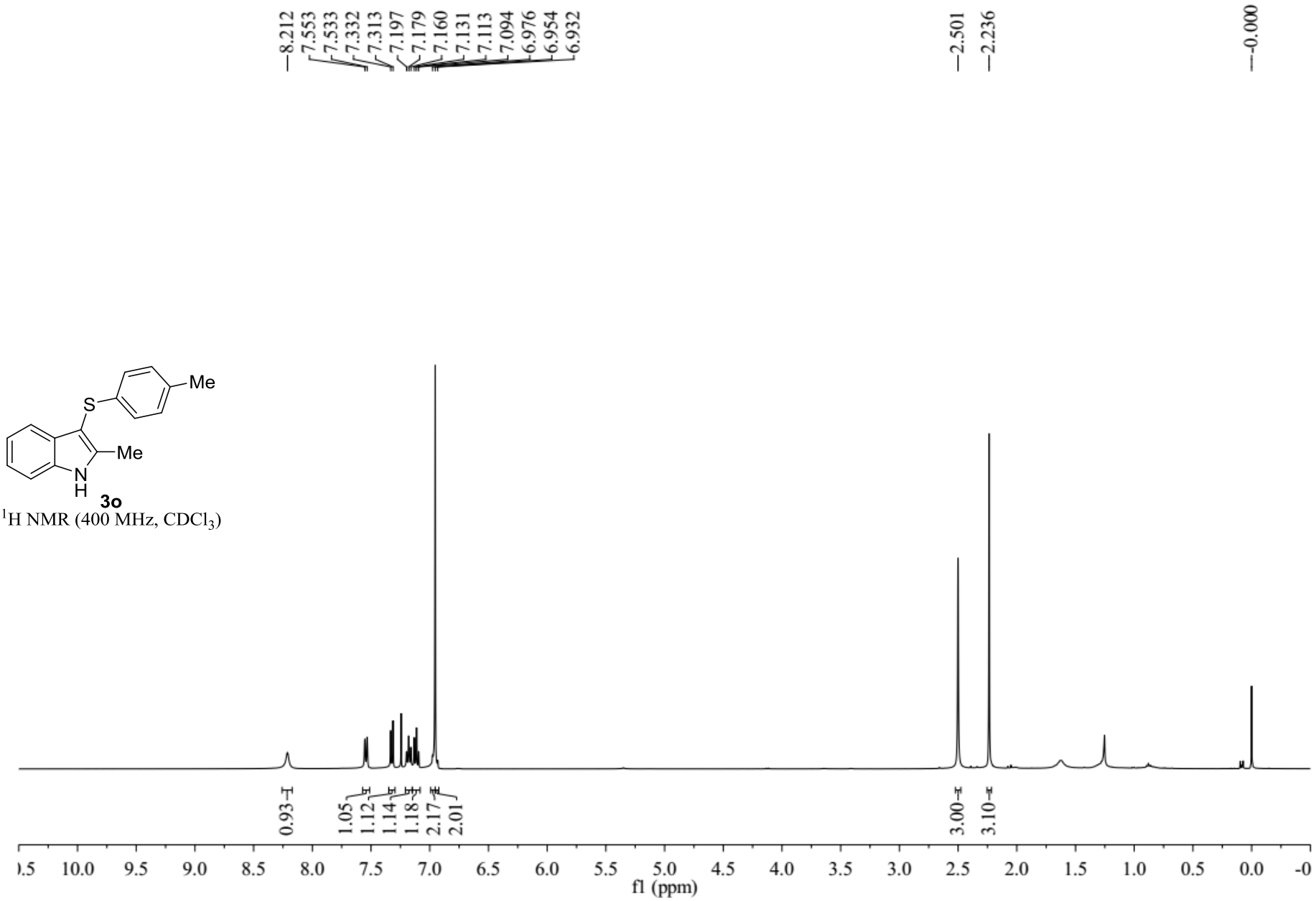
^{13}C NMR (100 MHz, $CDCl_3$)


8.520
7.767
7.749
7.641
7.622
7.449
7.431
7.427
7.413
7.389
7.377
7.371
7.364
7.353
7.281
7.262
7.244
7.179
7.159
7.141
7.017
6.996
6.979
6.958
2.241
0.000
Me
S
Ph
N
H
3n
1H NMR (400 MHz, CDCl3)
1.03
2.22
1.06
4.52
1.36
1.16
2.26
2.07
3.00
f1 (ppm)



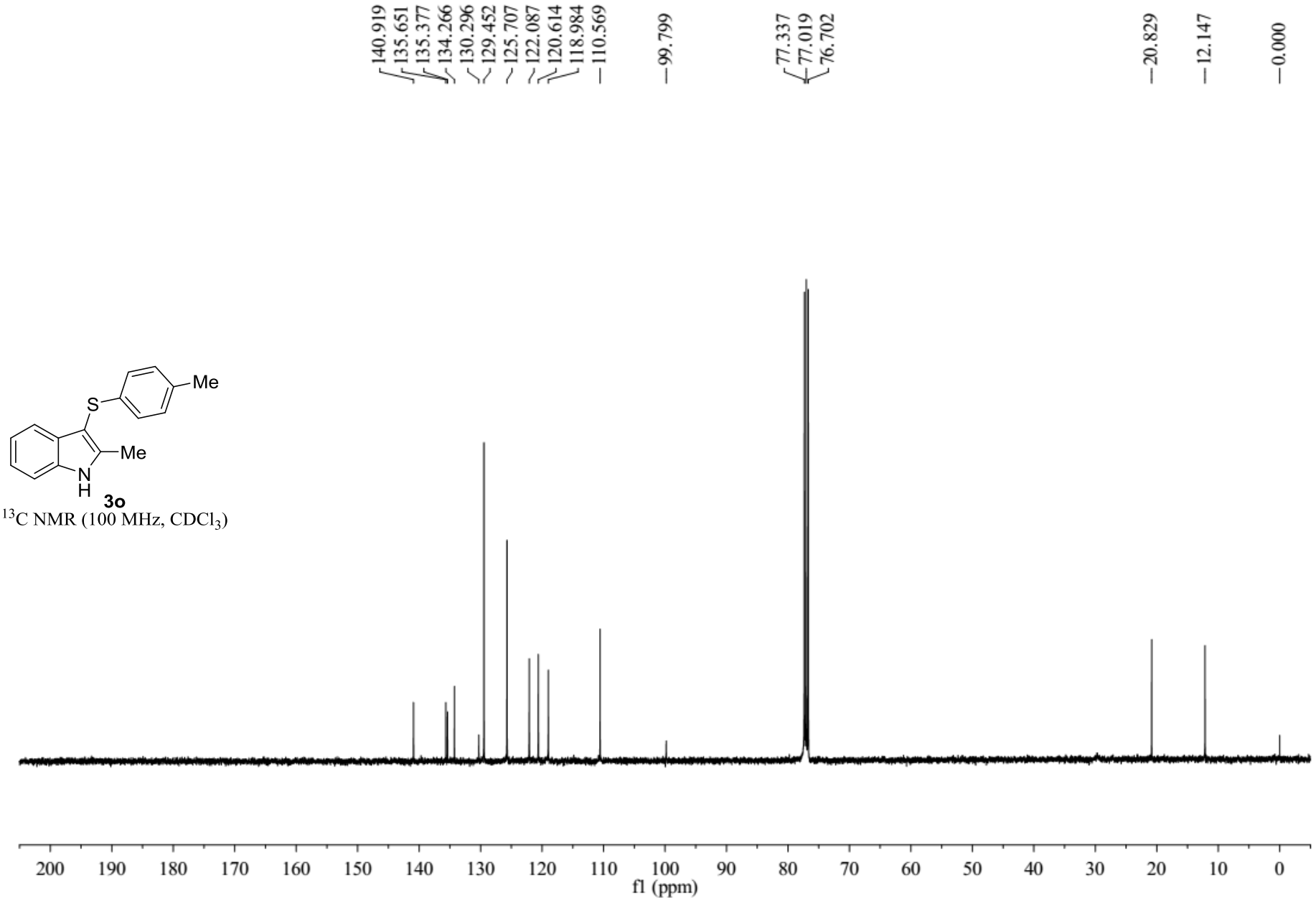
3n

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



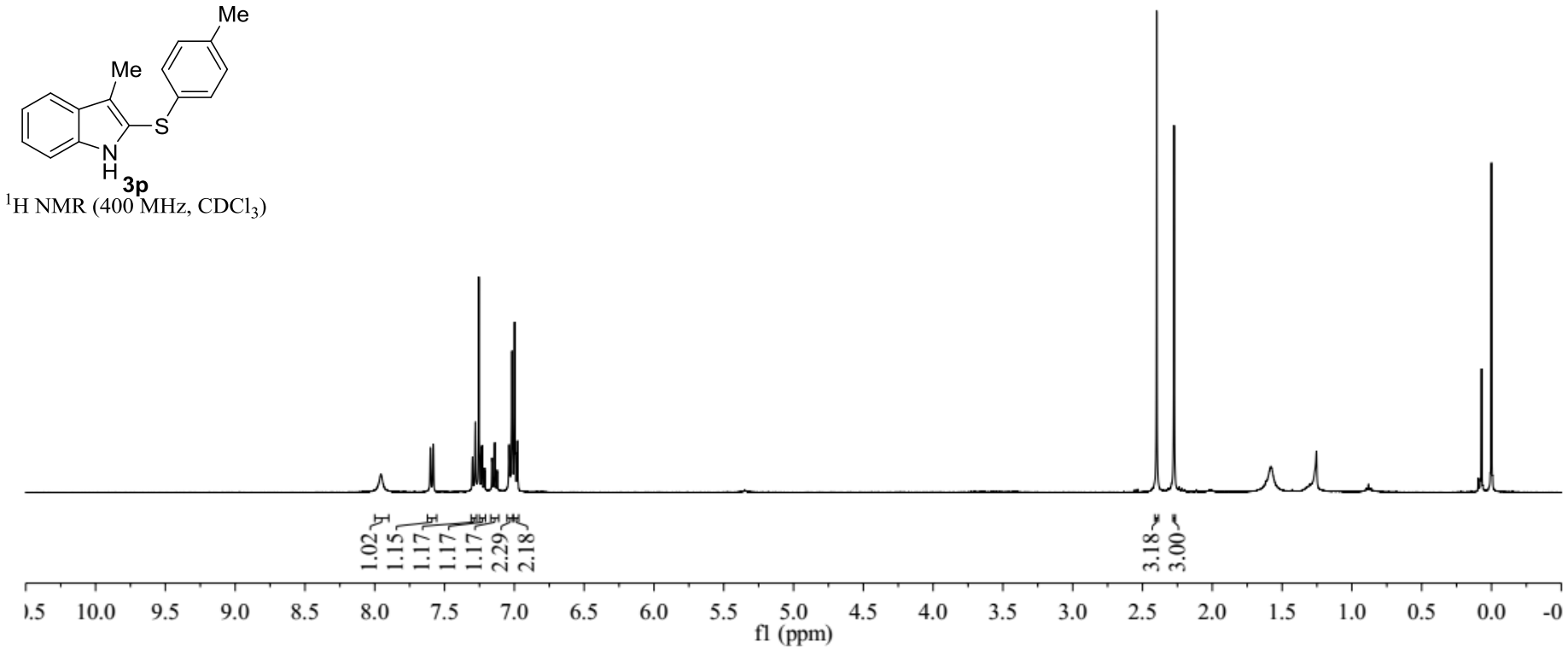
3o

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

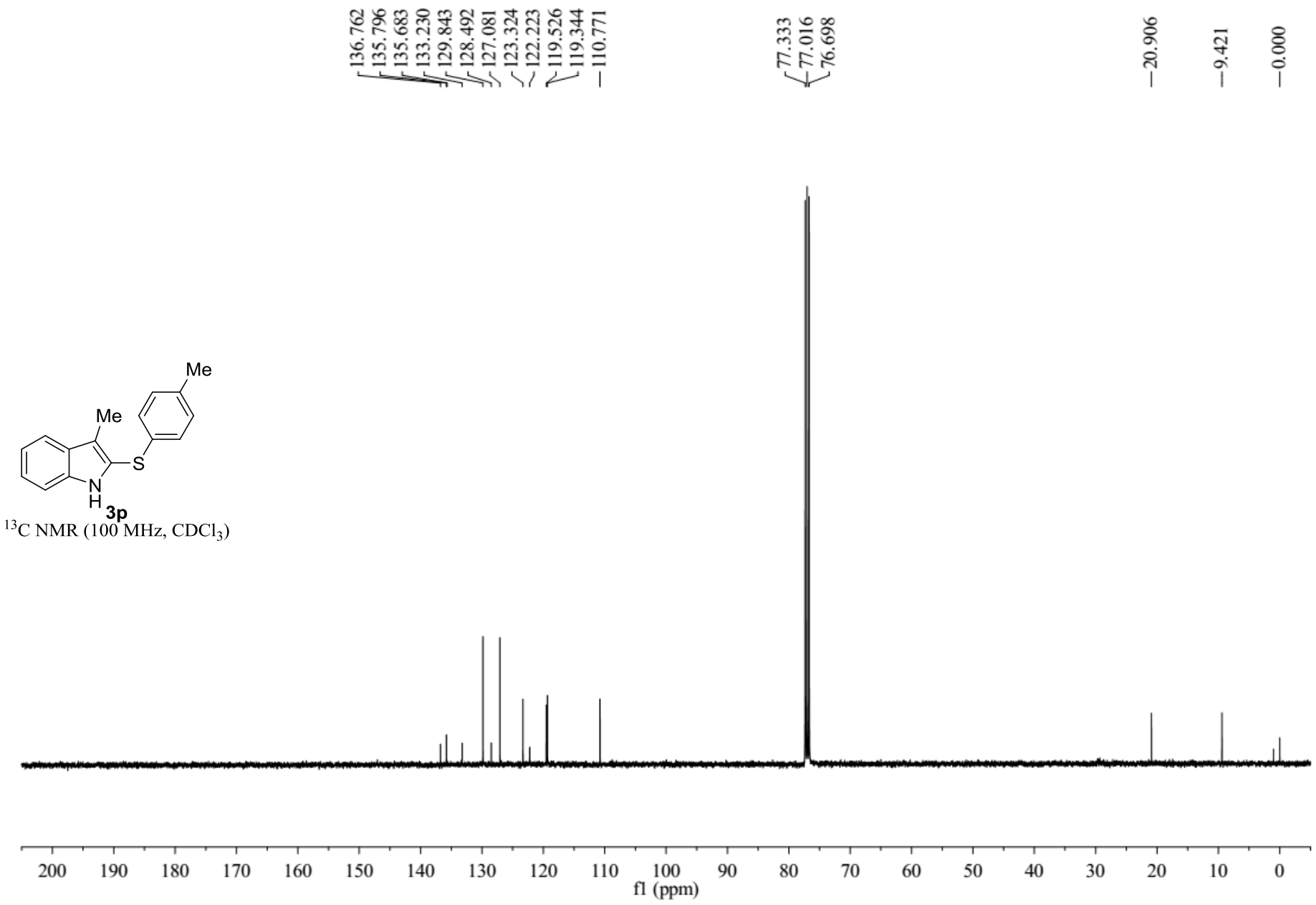


3o

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

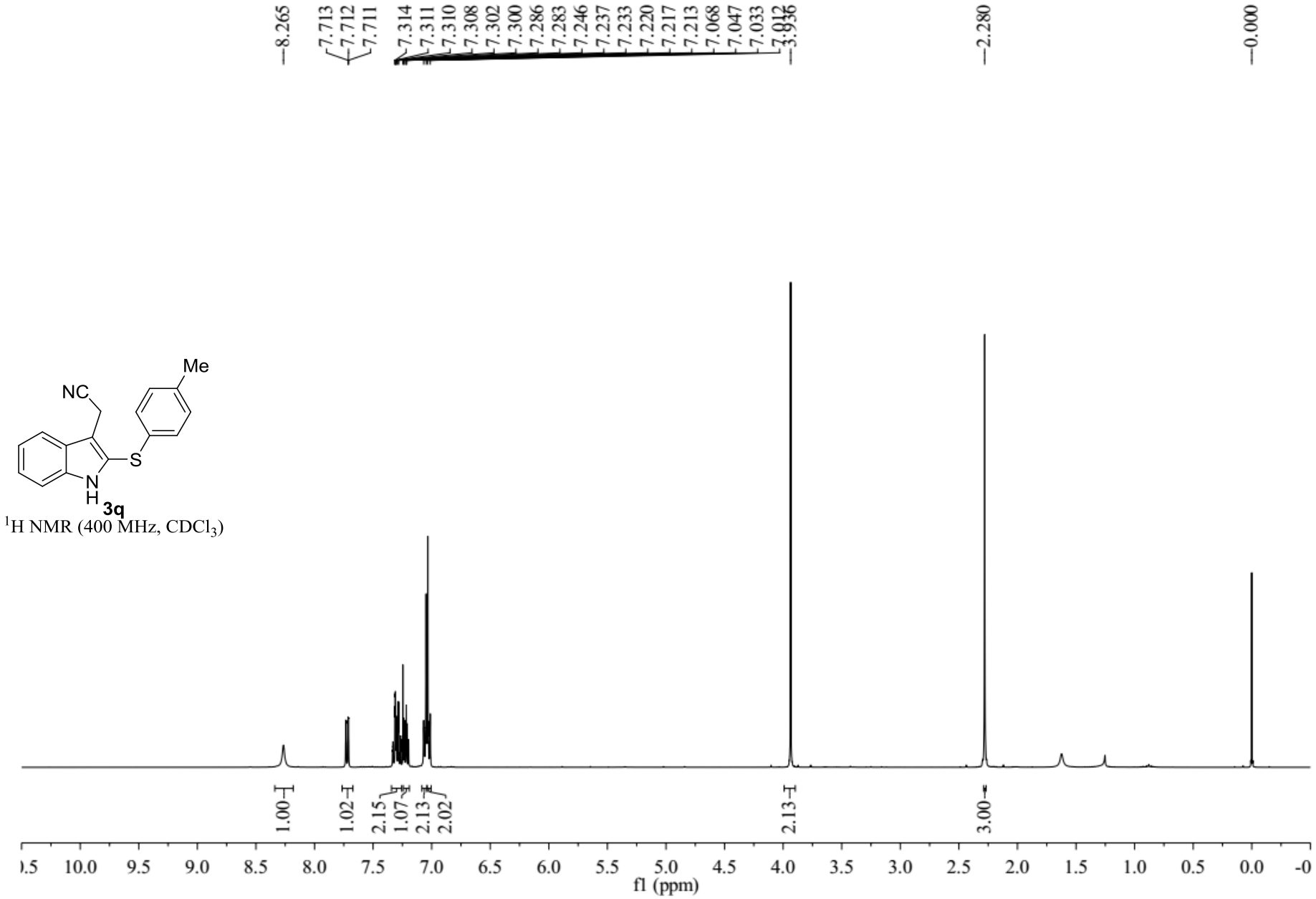


^{1}H NMR (400 MHz, $CDCl_3$)

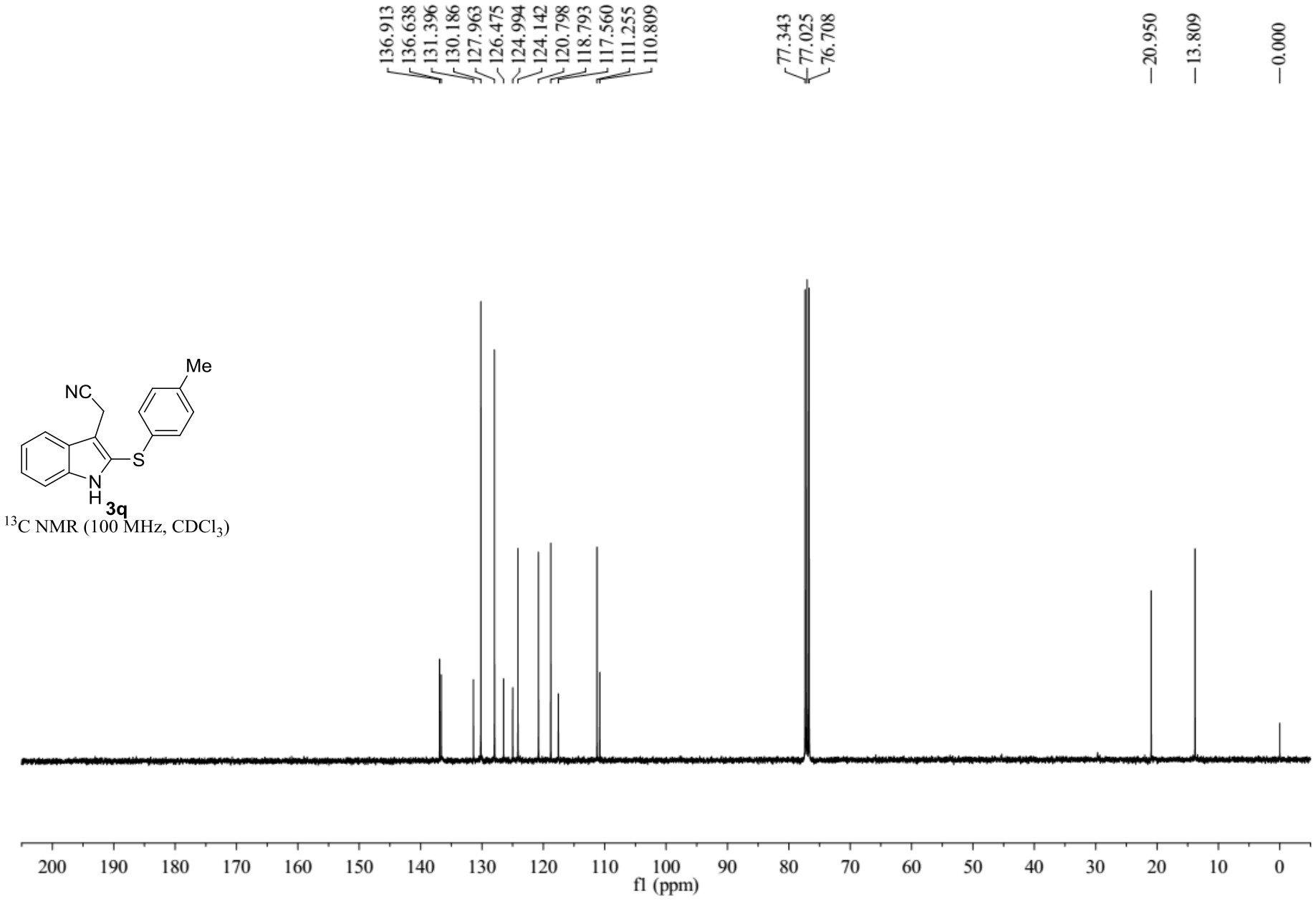


3p

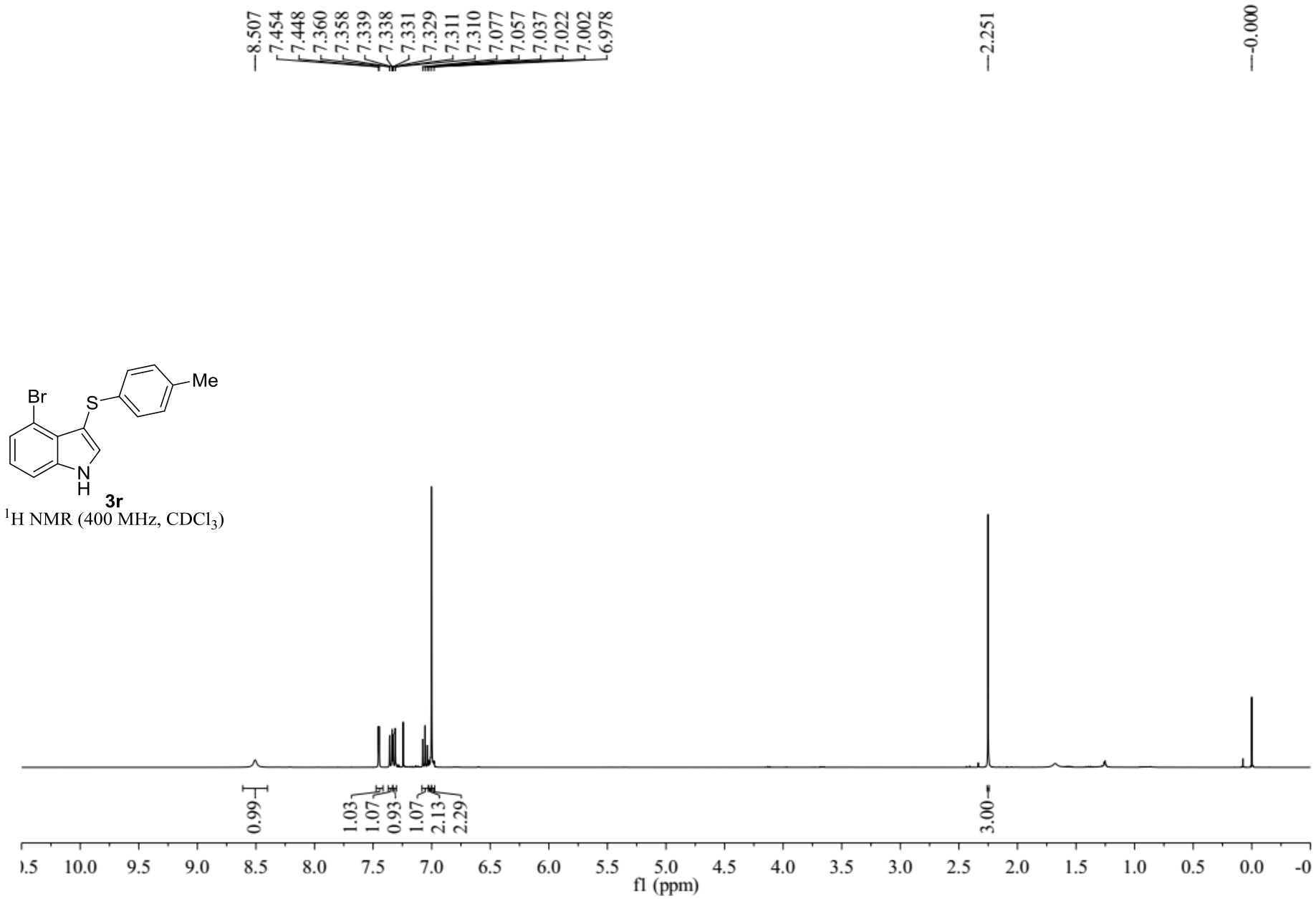
^{13}C NMR (100 MHz, $CDCl_3$)



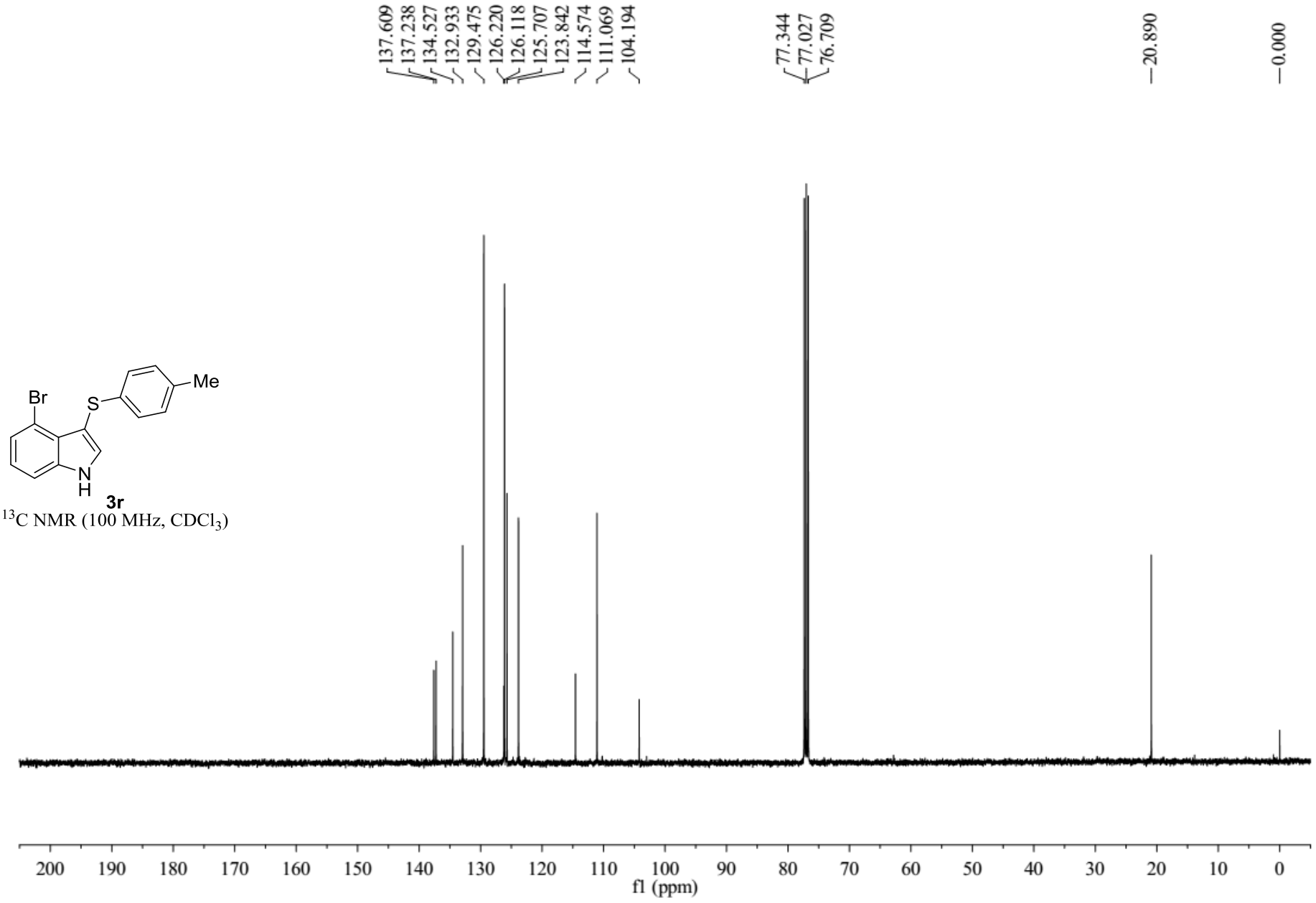
^{1}H NMR (400 MHz, $CDCl_3$)



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

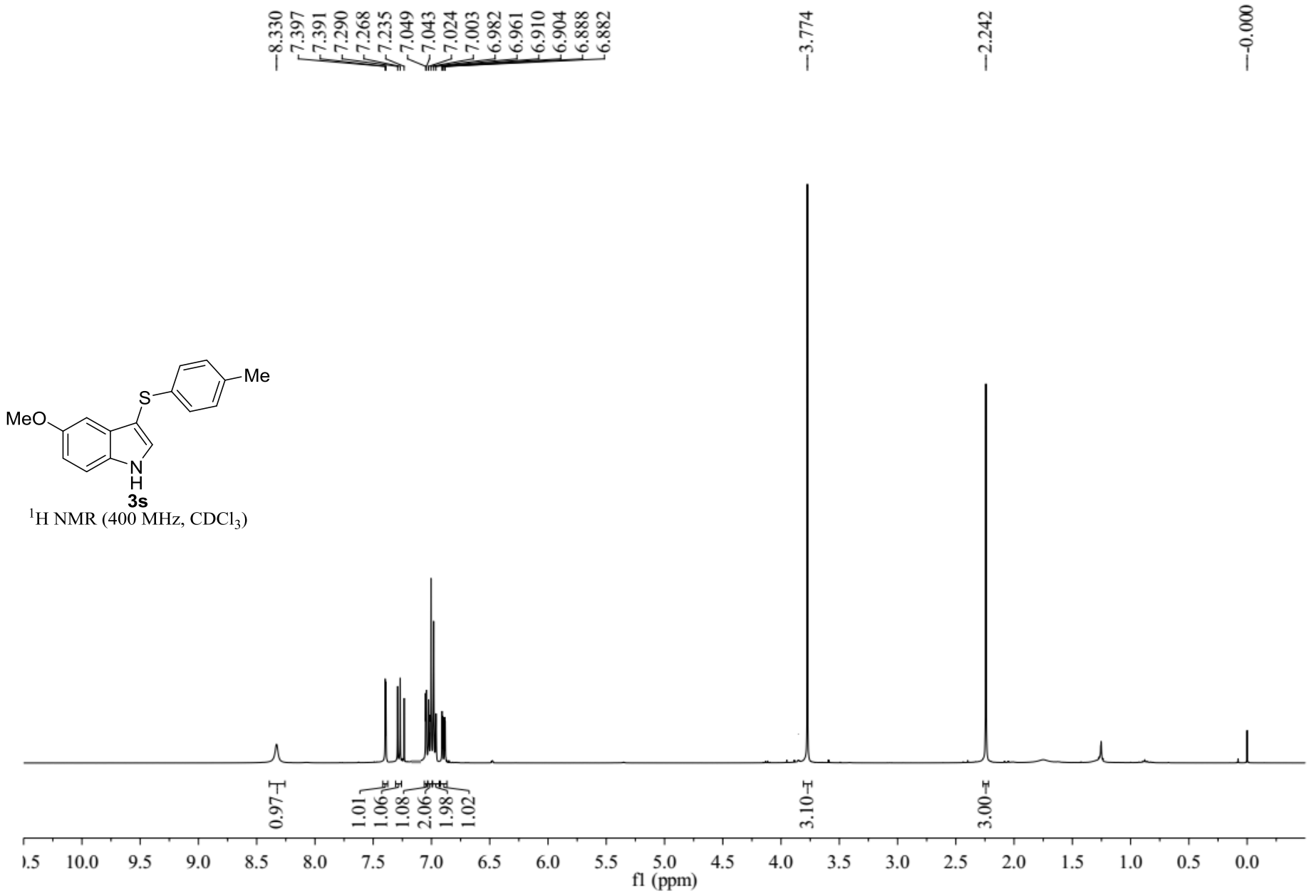


^{1}H NMR (400 MHz, $CDCl_3$)

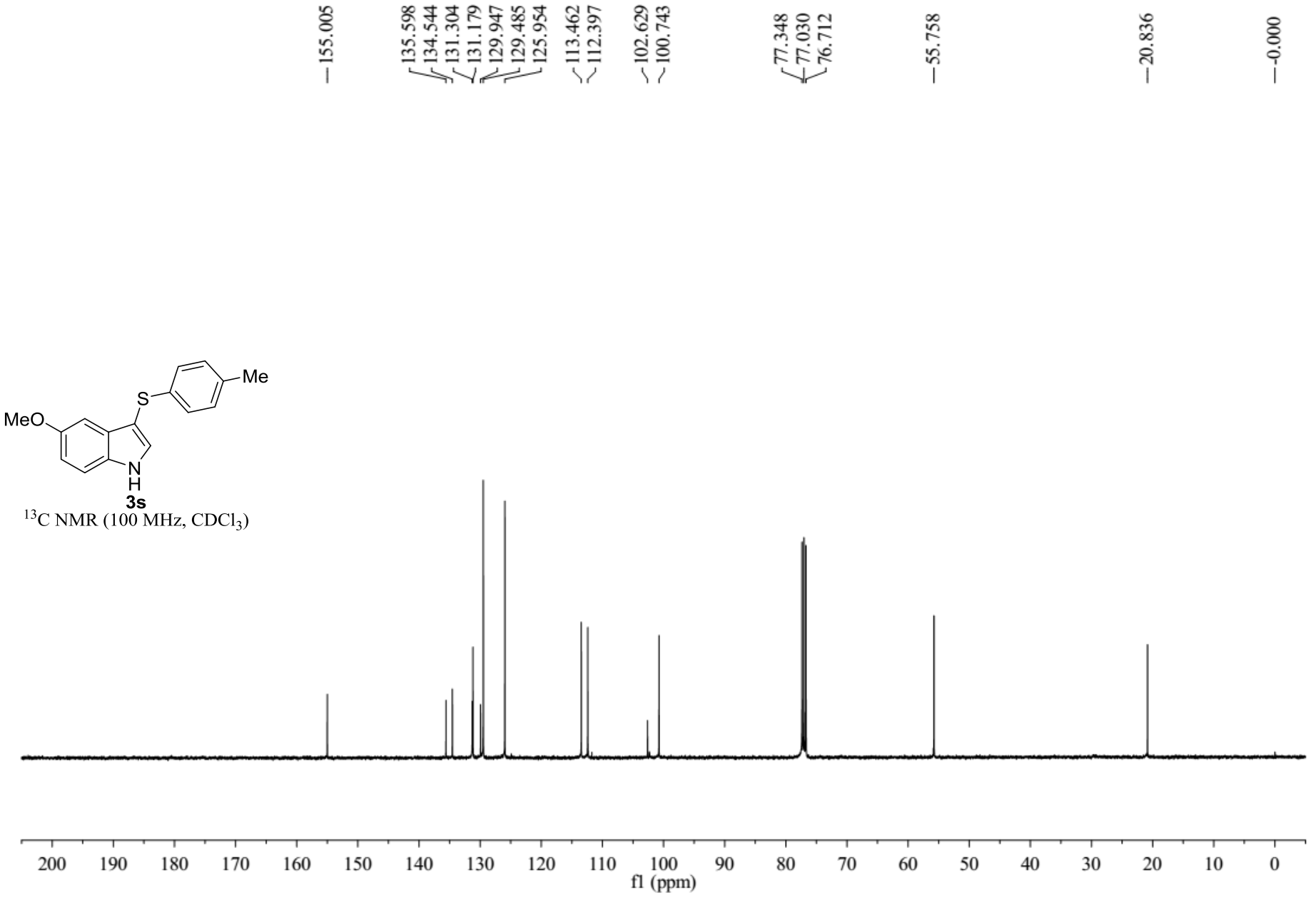


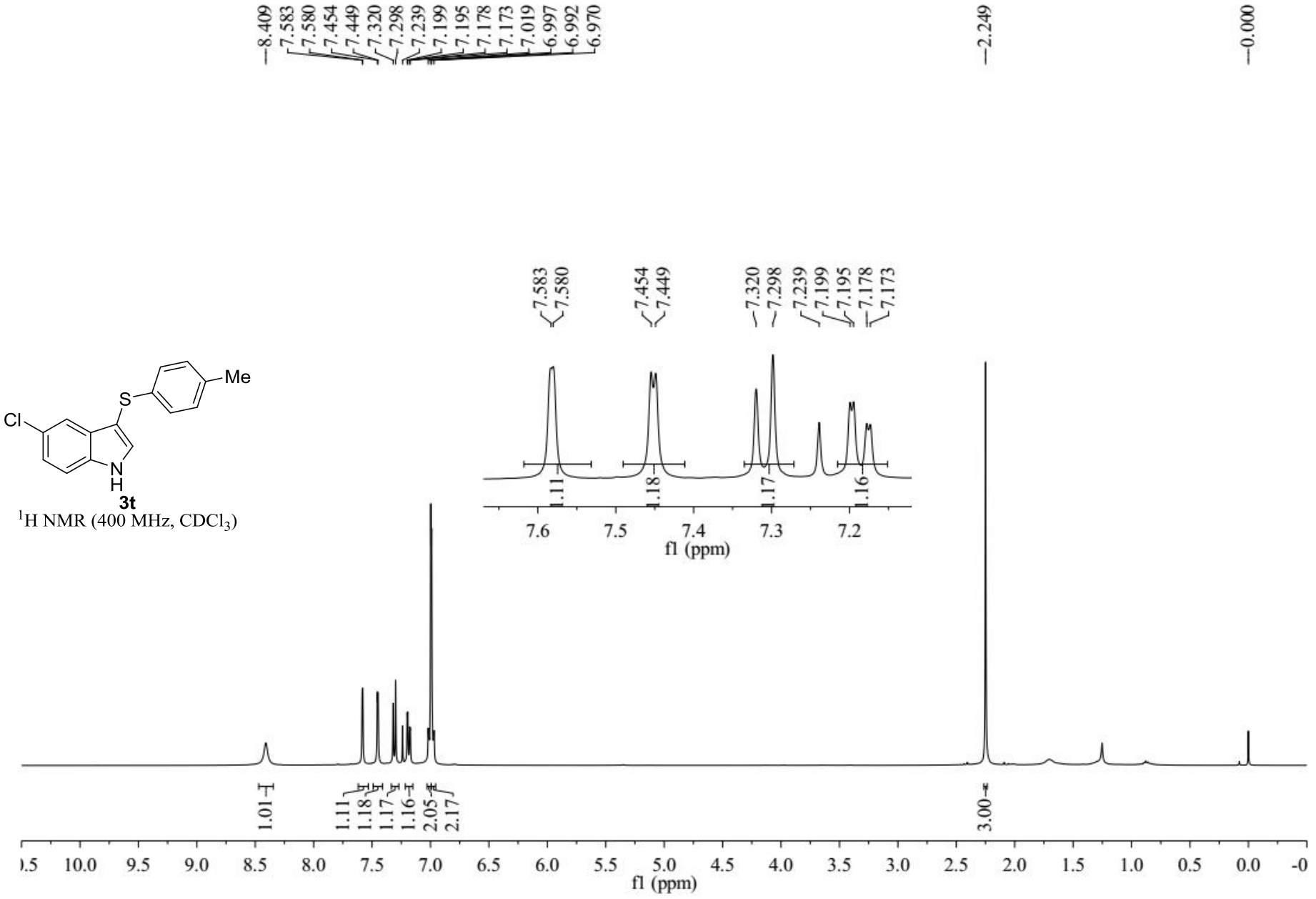
3r

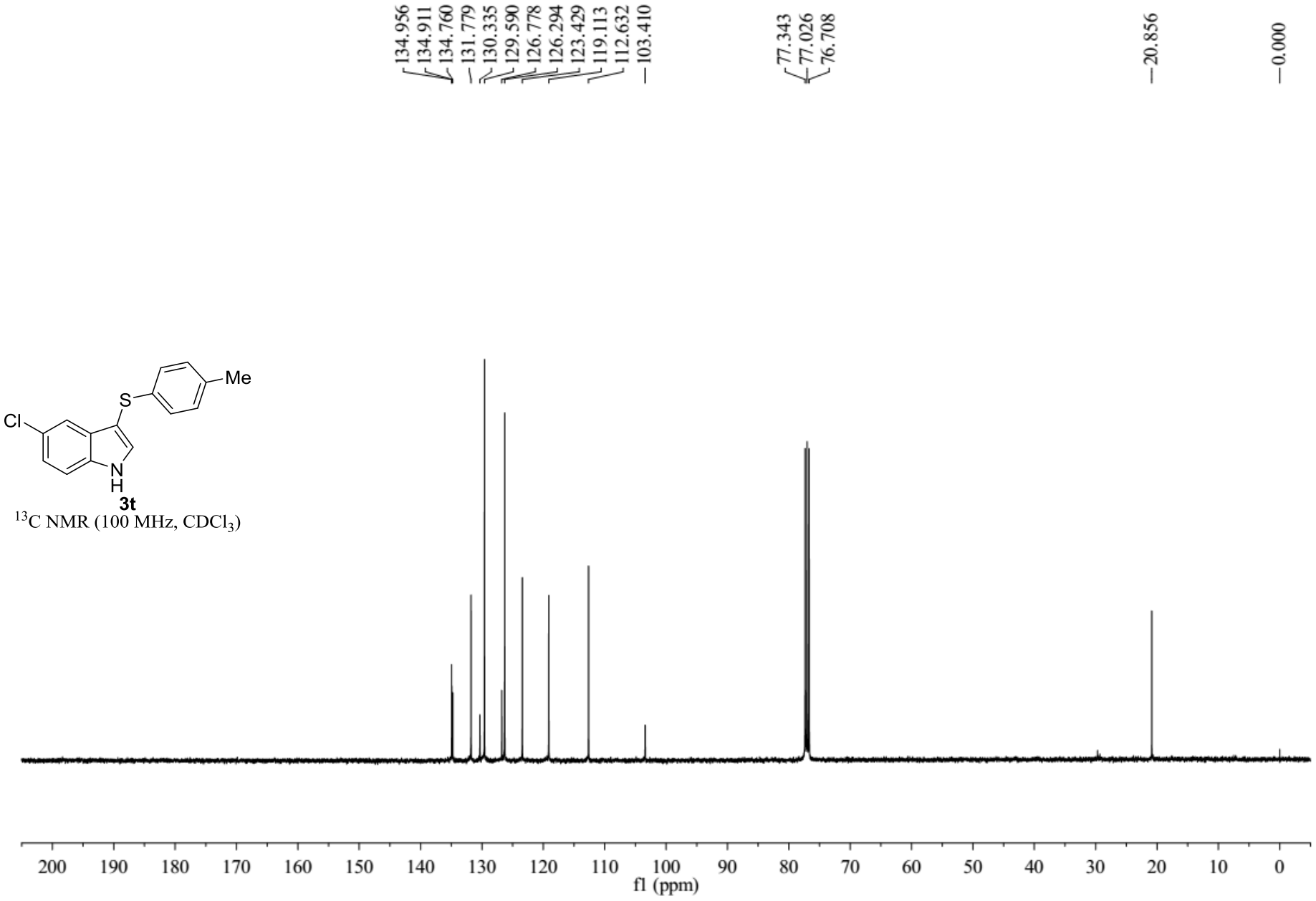
^{13}C NMR (100 MHz, $CDCl_3$)



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


155.005
135.598
134.544
131.304
131.179
129.947
129.485
125.954
113.462
112.397
102.629
100.743
77.348
77.030
76.712
55.758
20.836
-0.000
Me
S
MeO
N
H
3s
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.409
7.583
7.580
7.454
7.449
7.320
7.298
7.239
7.199
7.195
7.178
7.173
7.019
6.997
6.992
6.970
2.249
0.000
Me
S
Cl
N
H
3t
1H NMR (400 MHz, CDCl3)
1.11
1.18
1.17
1.16
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
1.01
1.11
1.18
1.17
1.16
2.05
2.17
3.00
f1 (ppm)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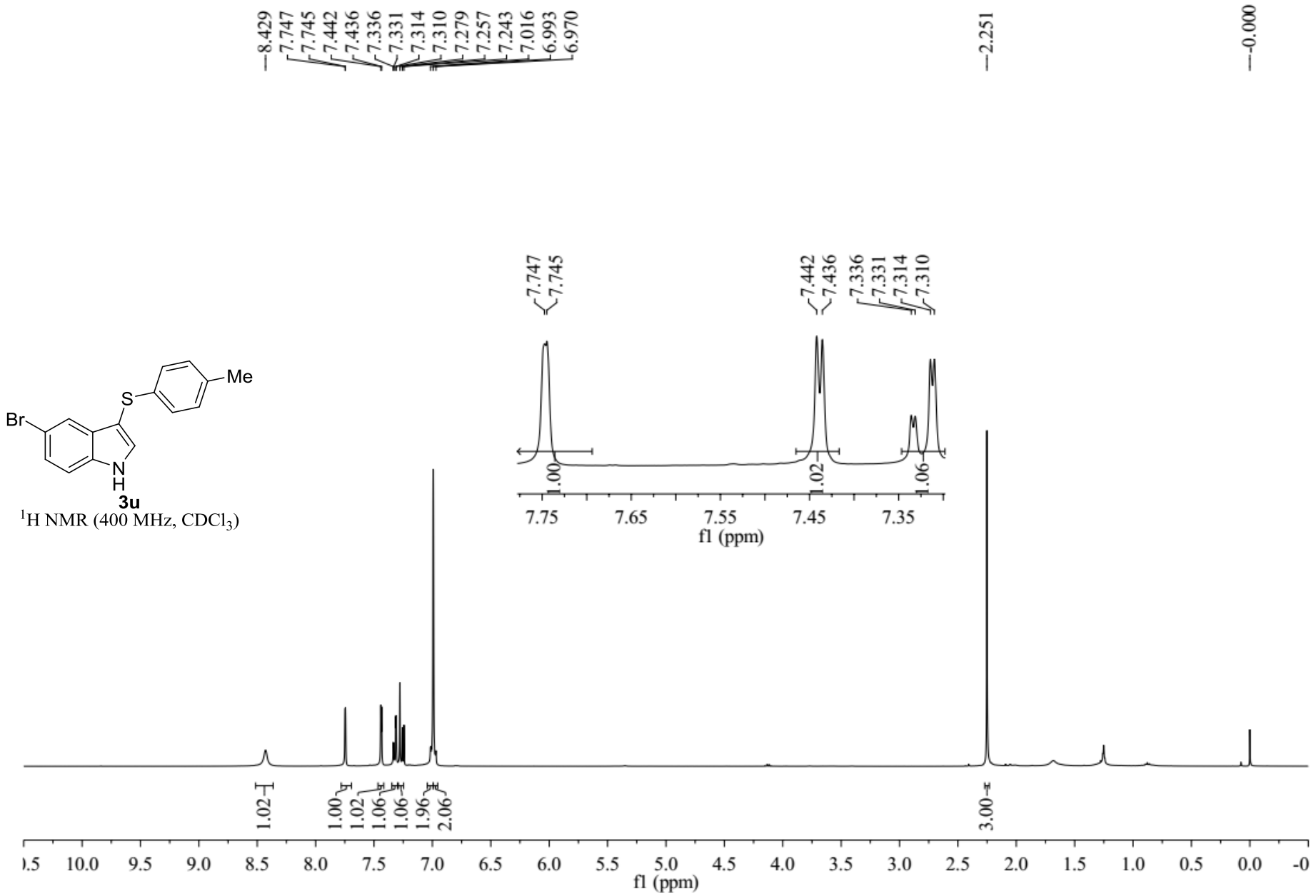
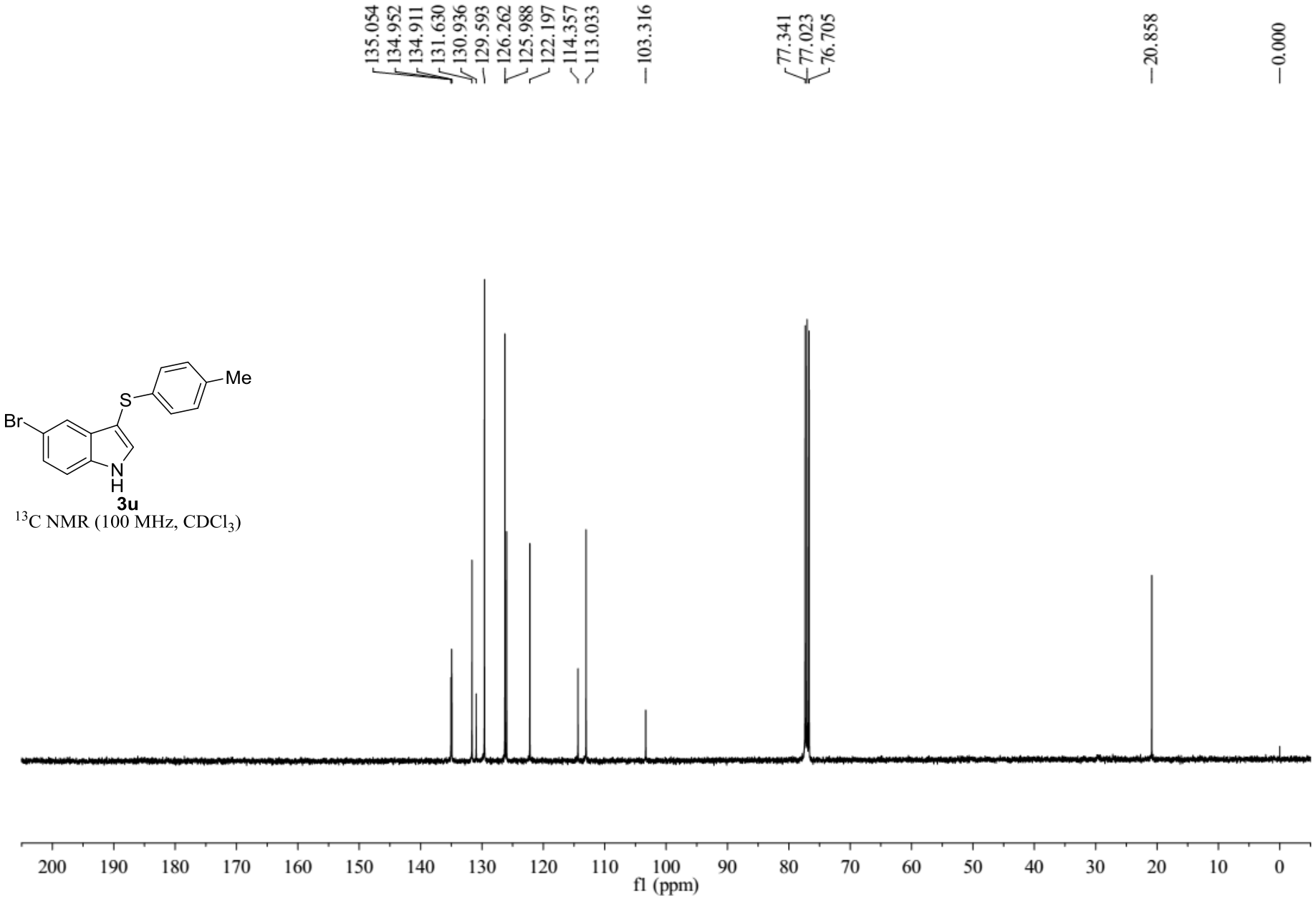
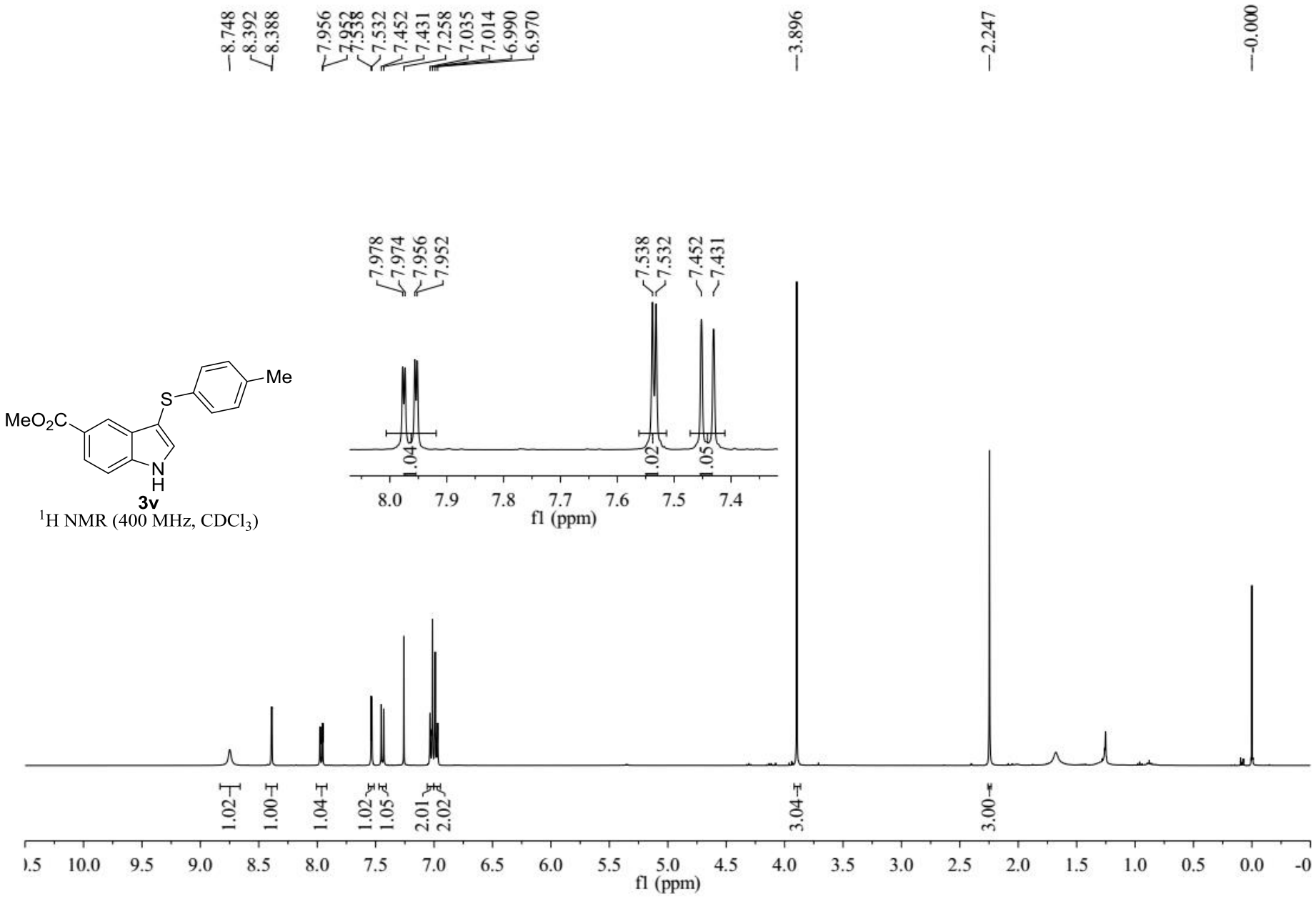
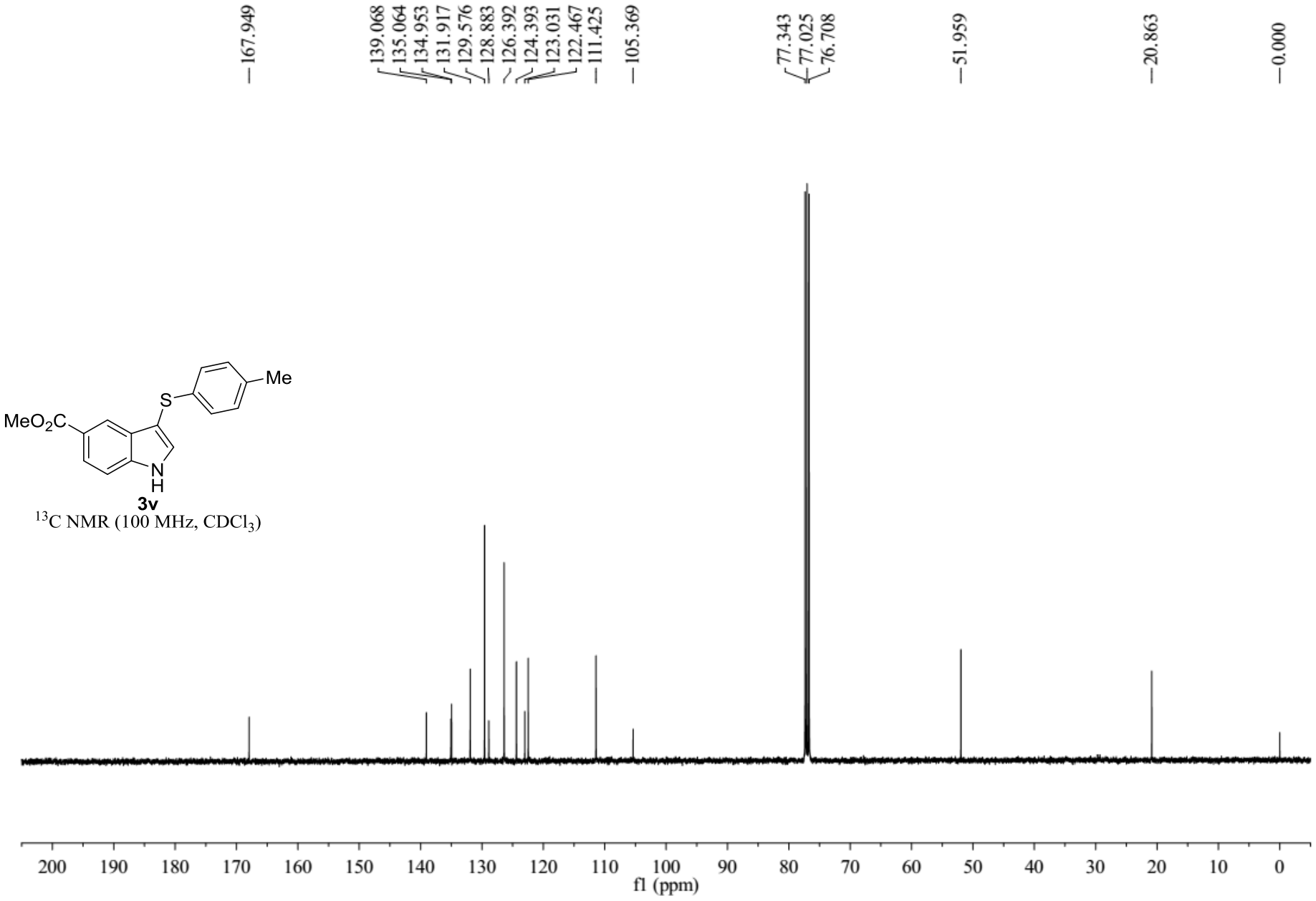
134.911
134.760
131.779
130.335
129.590
126.778
126.294
123.429
119.113
112.632
103.410
77.343
77.026
76.708
20.856
0.000
Me
S
Cl
N
H
3t
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.429
7.747
7.745
7.442
7.436
7.336
7.331
7.314
7.310
7.279
7.257
7.243
7.016
6.993
6.970
2.251
0.000
Br
S
Me
N
H
3u
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.06
1.06
1.96
2.06
3.00
fl (ppm)

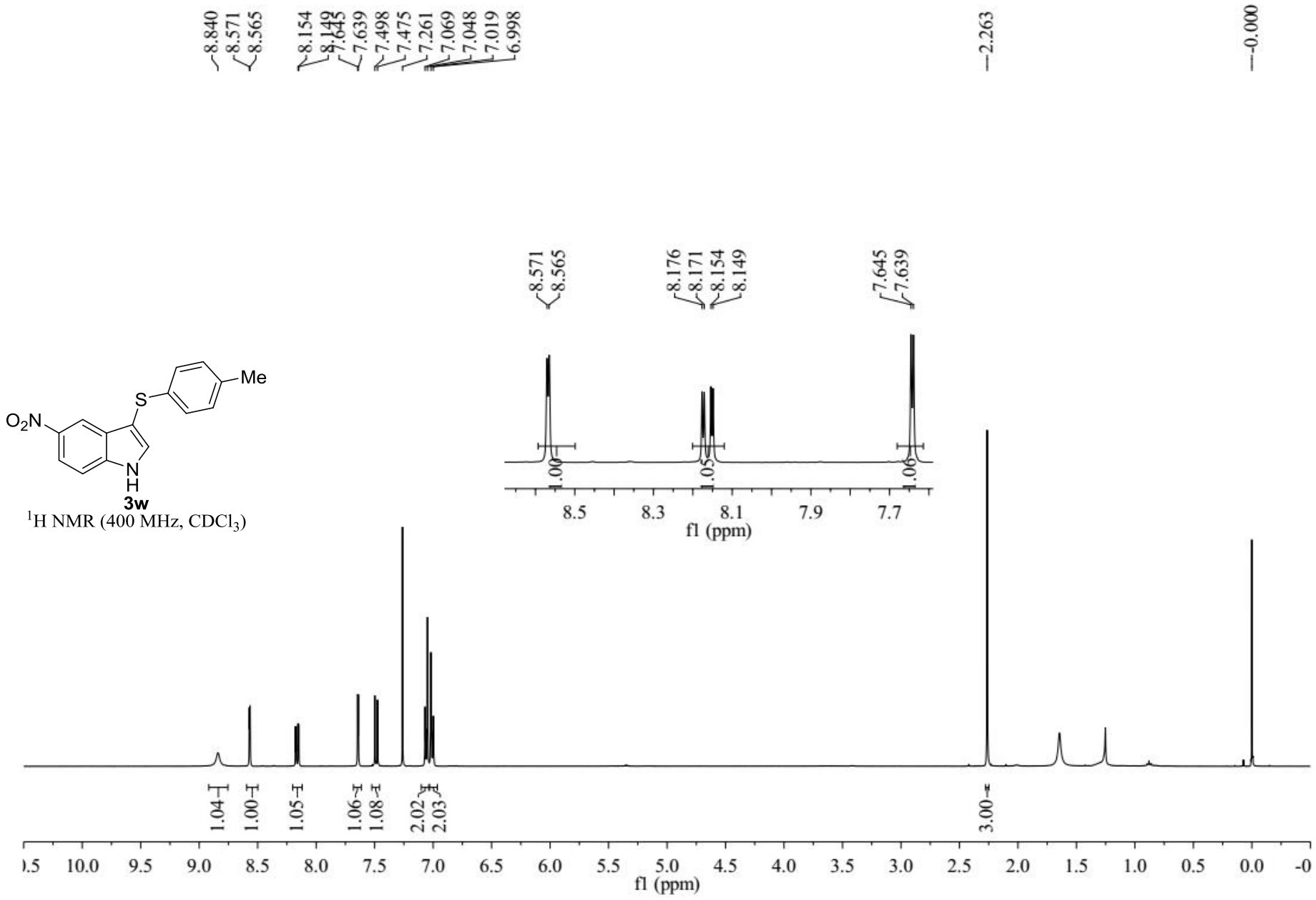

135.054
134.952
134.911
131.630
130.936
129.593
126.262
125.988
122.197
114.357
113.033
103.316
77.341
77.023
76.705
20.858
0.000
Br
S
Me
N
H
3u
^{13}C NMR (100 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

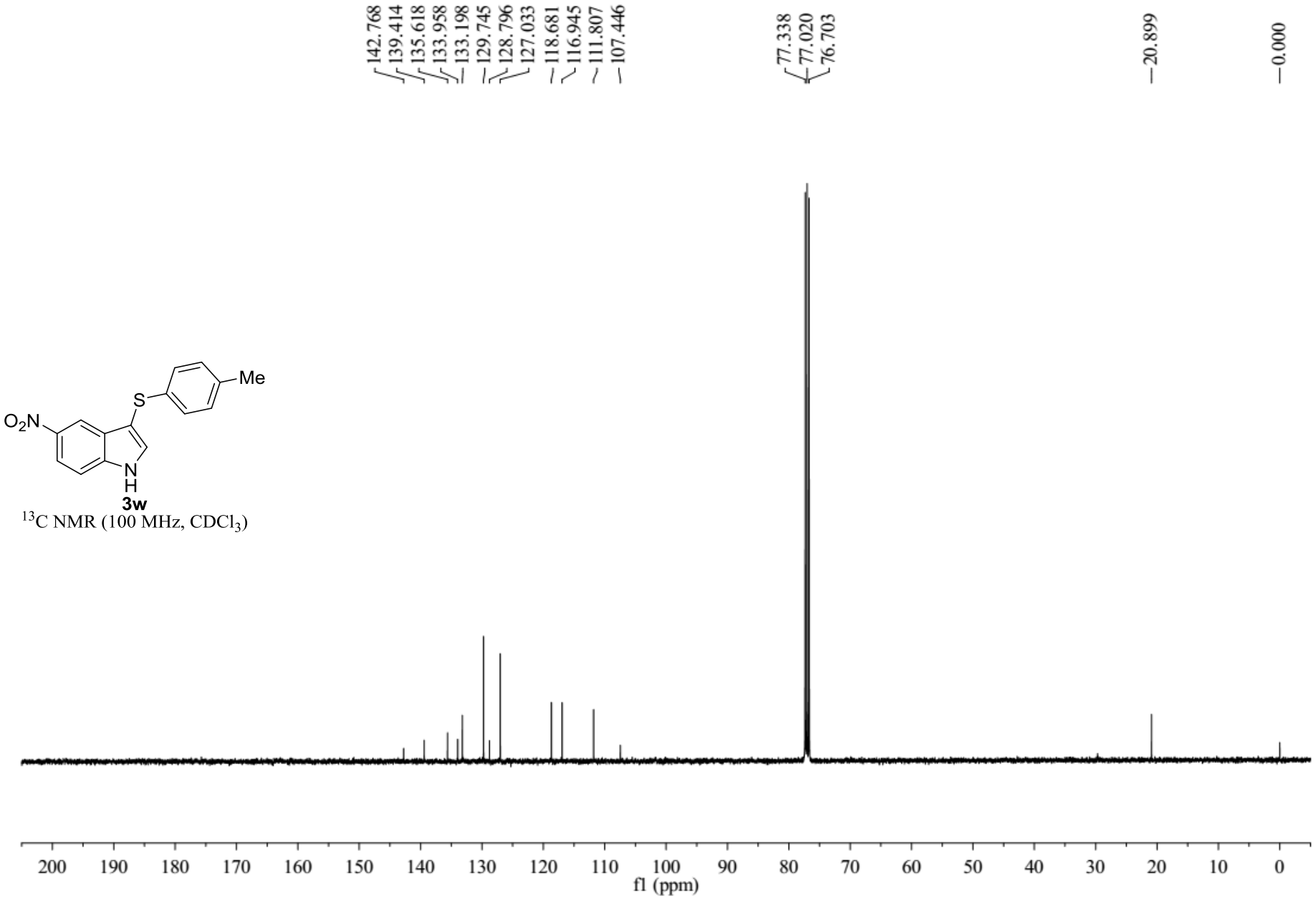

8.748
8.392
8.388
7.956
7.952
7.538
7.532
7.452
7.431
7.258
7.035
7.014
6.990
6.970
3.896
2.247
0.000
MeO2C
S
Me
N
H
3v
1H NMR (400 MHz, CDCl3)
7.978
7.974
7.956
7.952
7.538
7.532
7.452
7.431
1.04
1.02
1.05
8.0 7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
1.02
1.00
1.04
1.02
1.05
2.01
2.02
3.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



3v

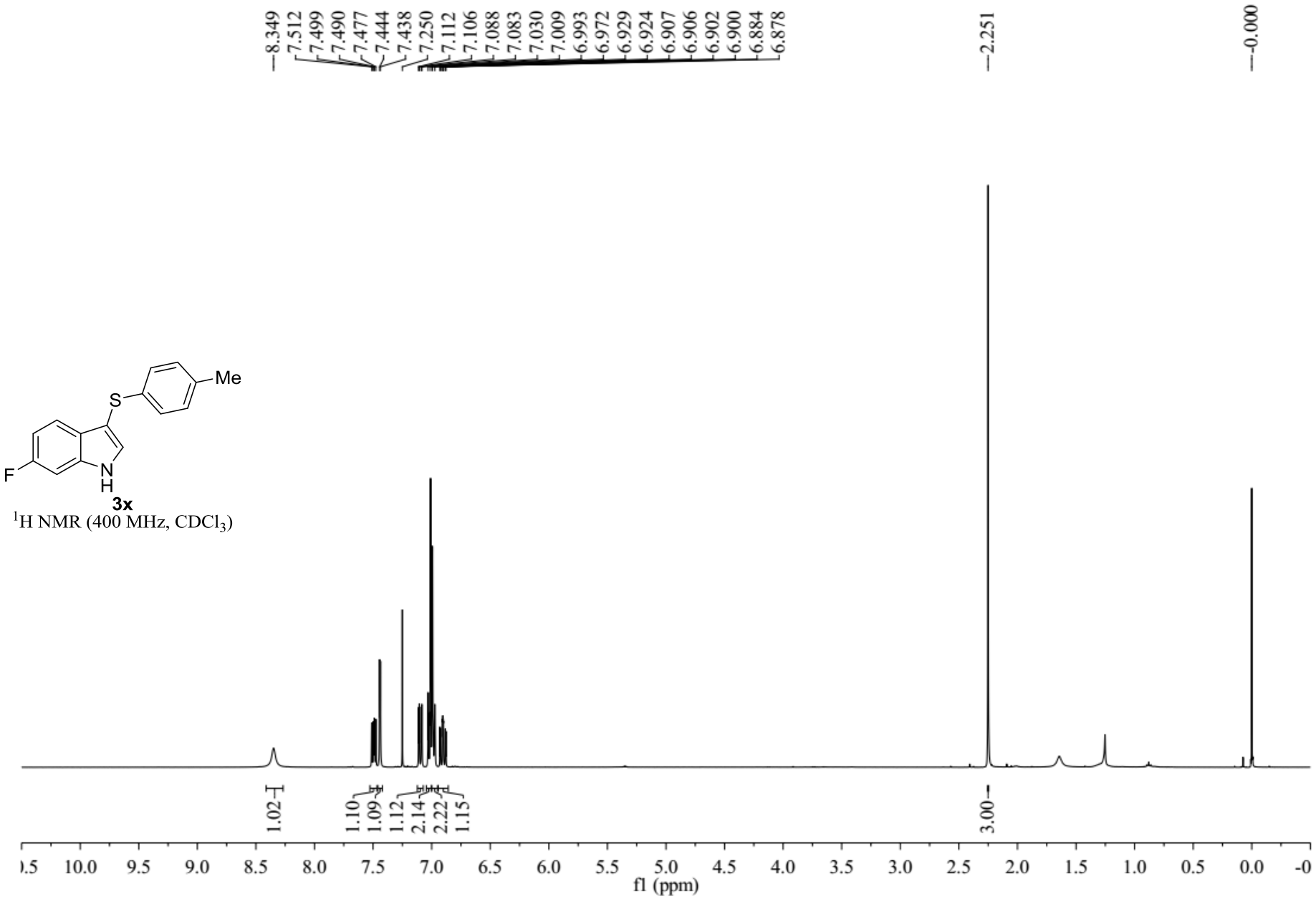
^{13}C NMR (100 MHz, $CDCl_3$)


8.840
8.571
8.565
8.154
8.149
7.645
7.639
7.498
7.475
7.261
7.069
7.048
7.019
6.998
2.263
0.000
O2N
S
Me
N
H
3w
1H NMR (400 MHz, CDCl3)
8.571
8.565
8.176
8.171
8.154
8.149
7.645
7.639
1.00
1.05
1.06
8.5
8.3
8.1
7.9
7.7
f1 (ppm)
1.04
1.00
1.05
1.06
1.08
2.02
2.03
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



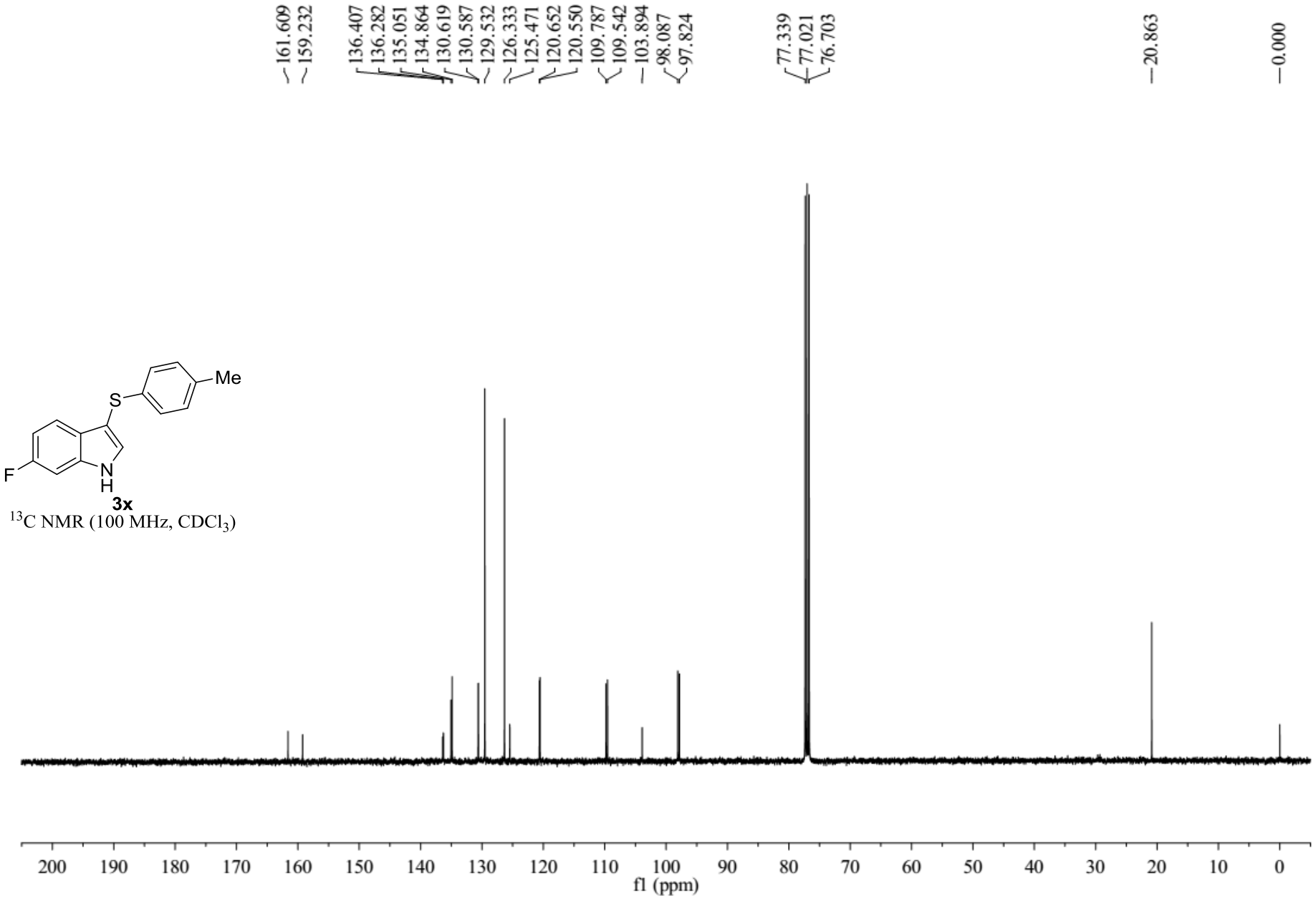
3w

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



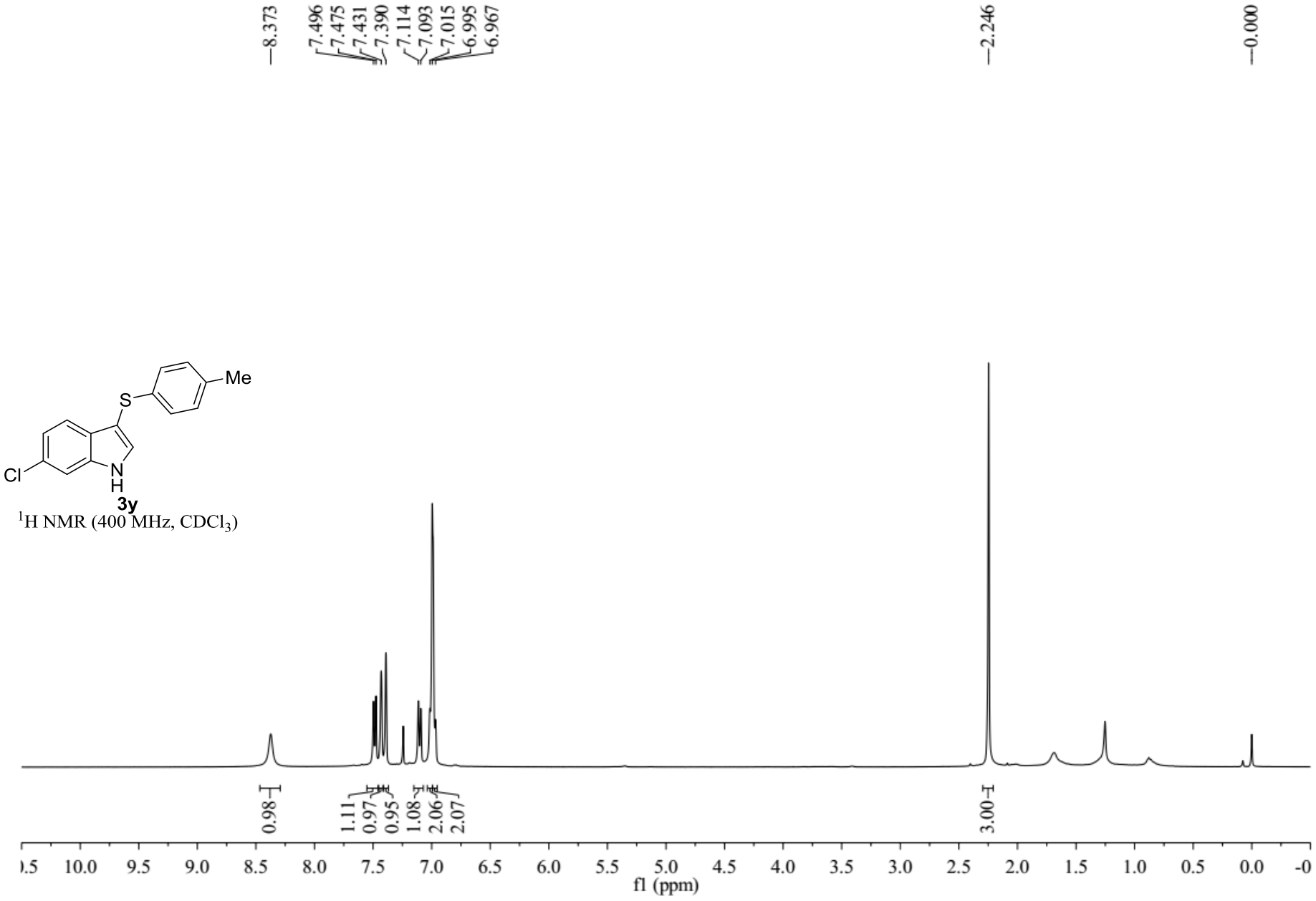
3x

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

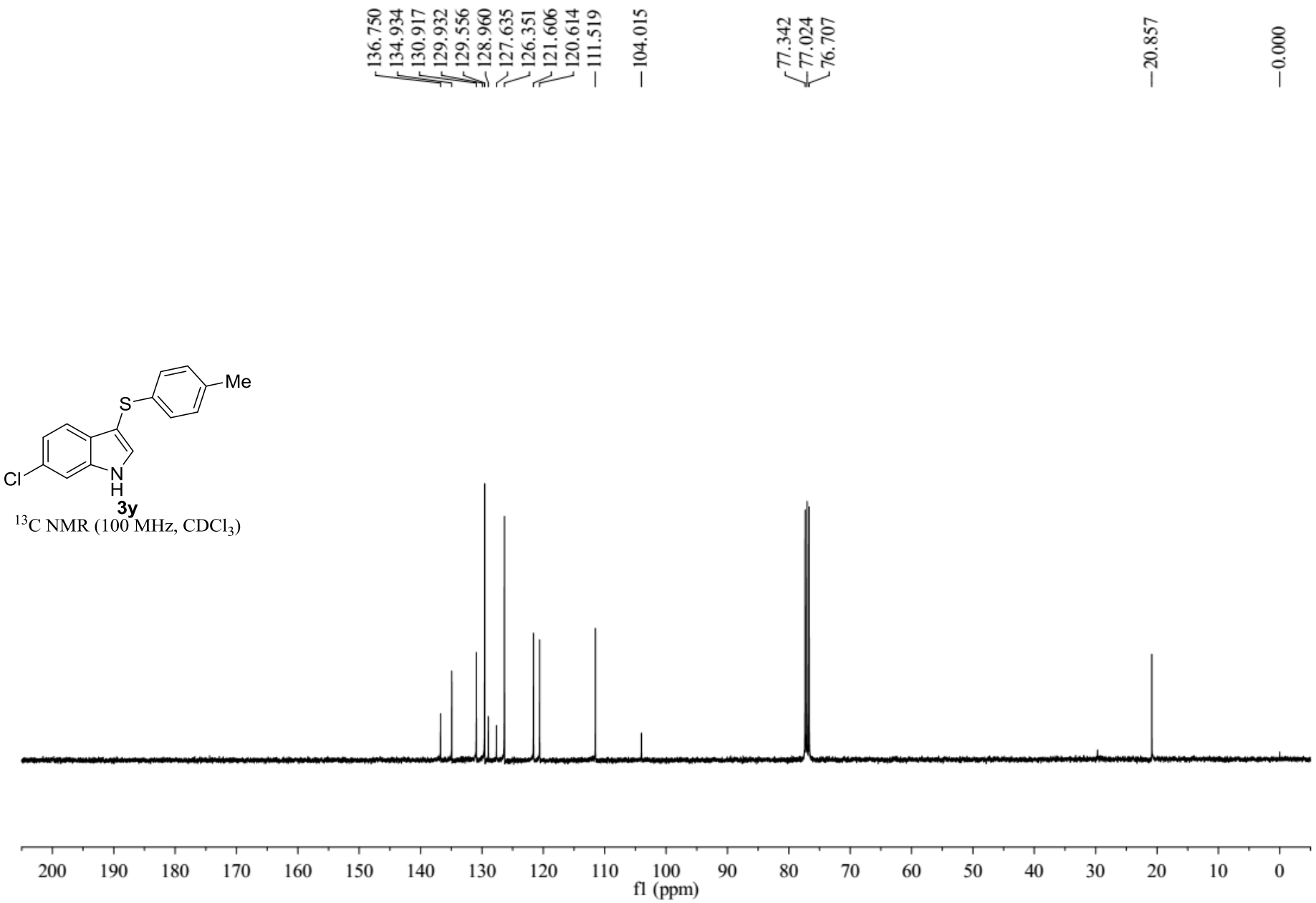


3x

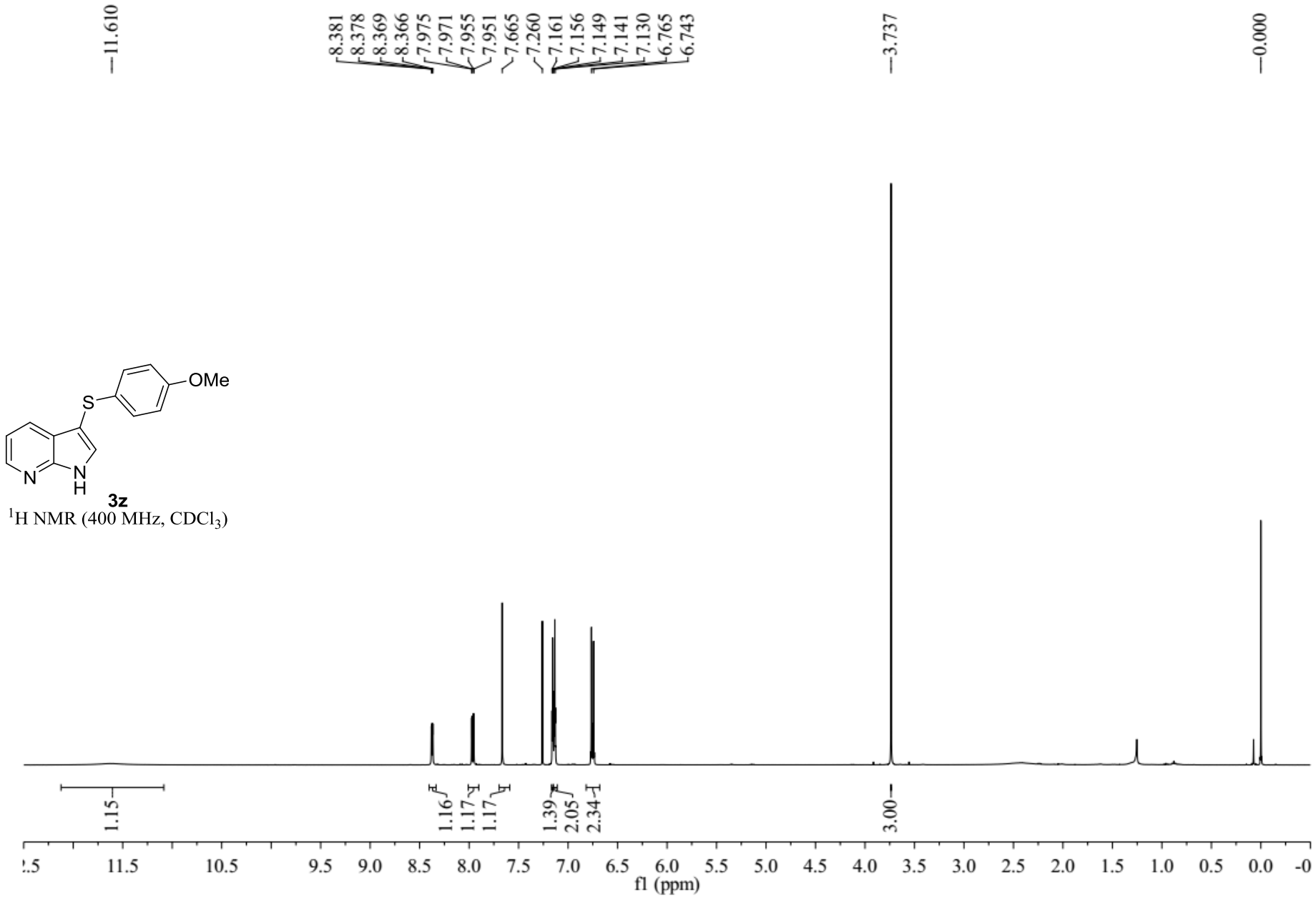
^{13}C NMR (100 MHz, $CDCl_3$)



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

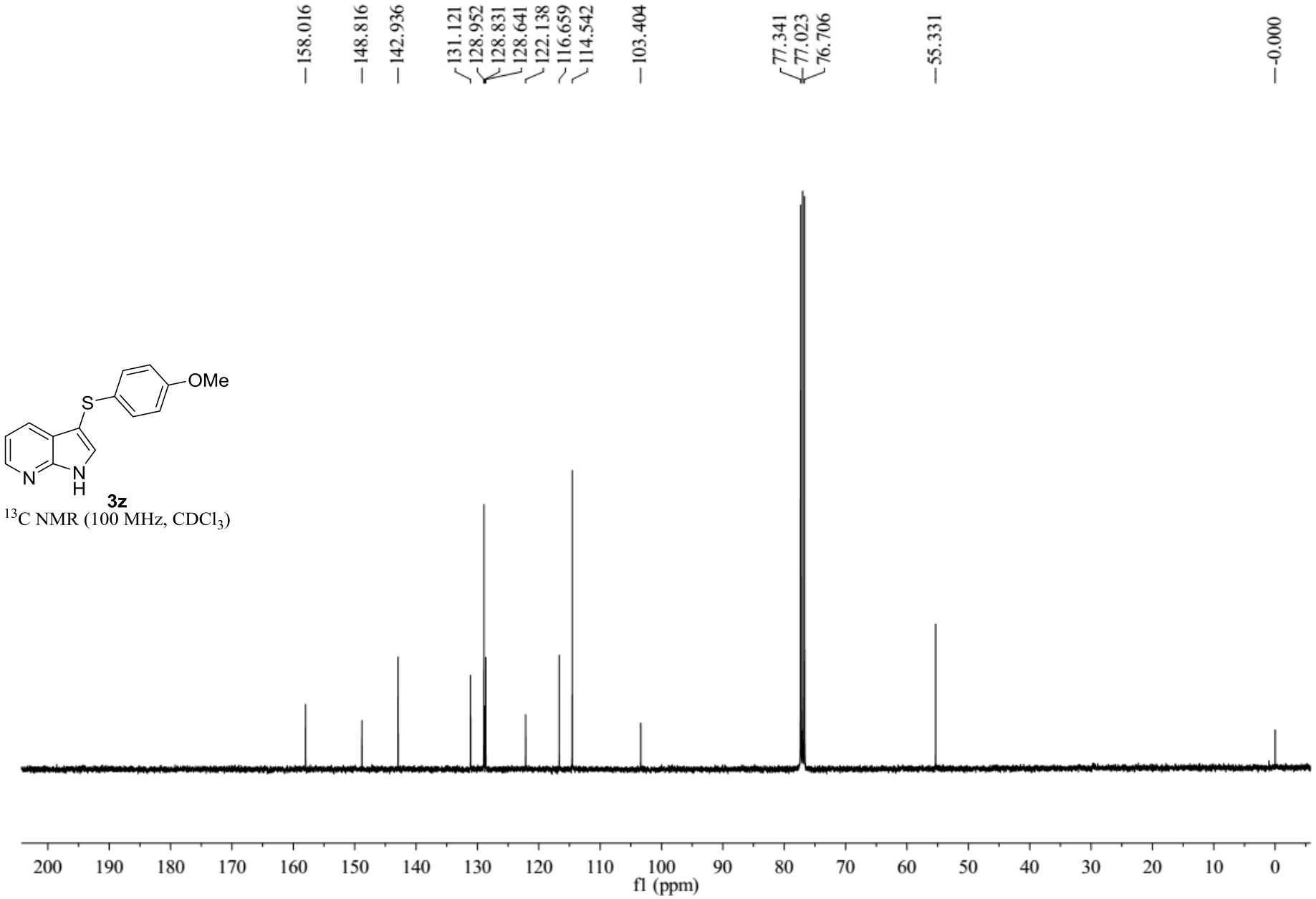


^{13}C NMR (100 MHz, $CDCl_3$)



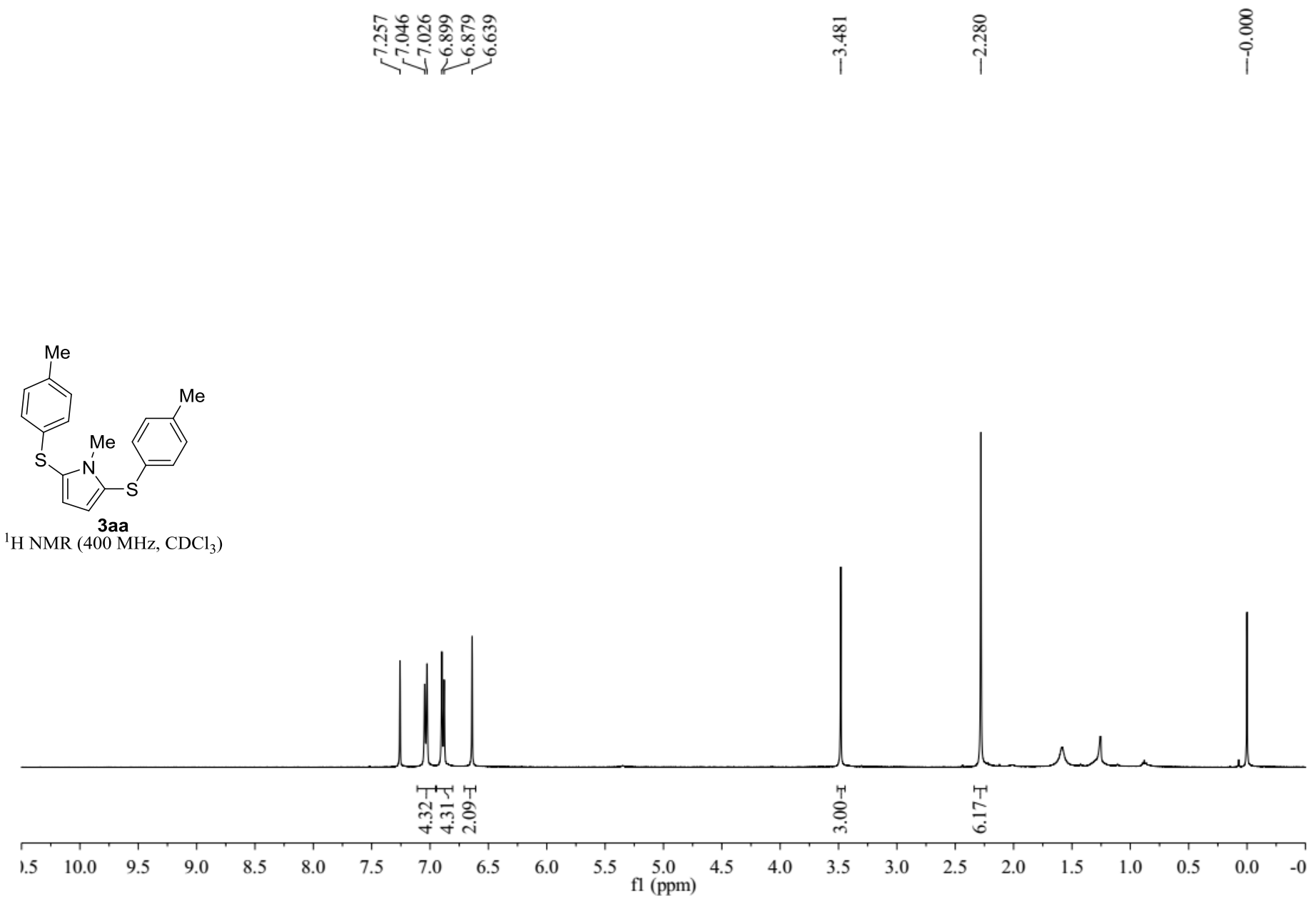
3z

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



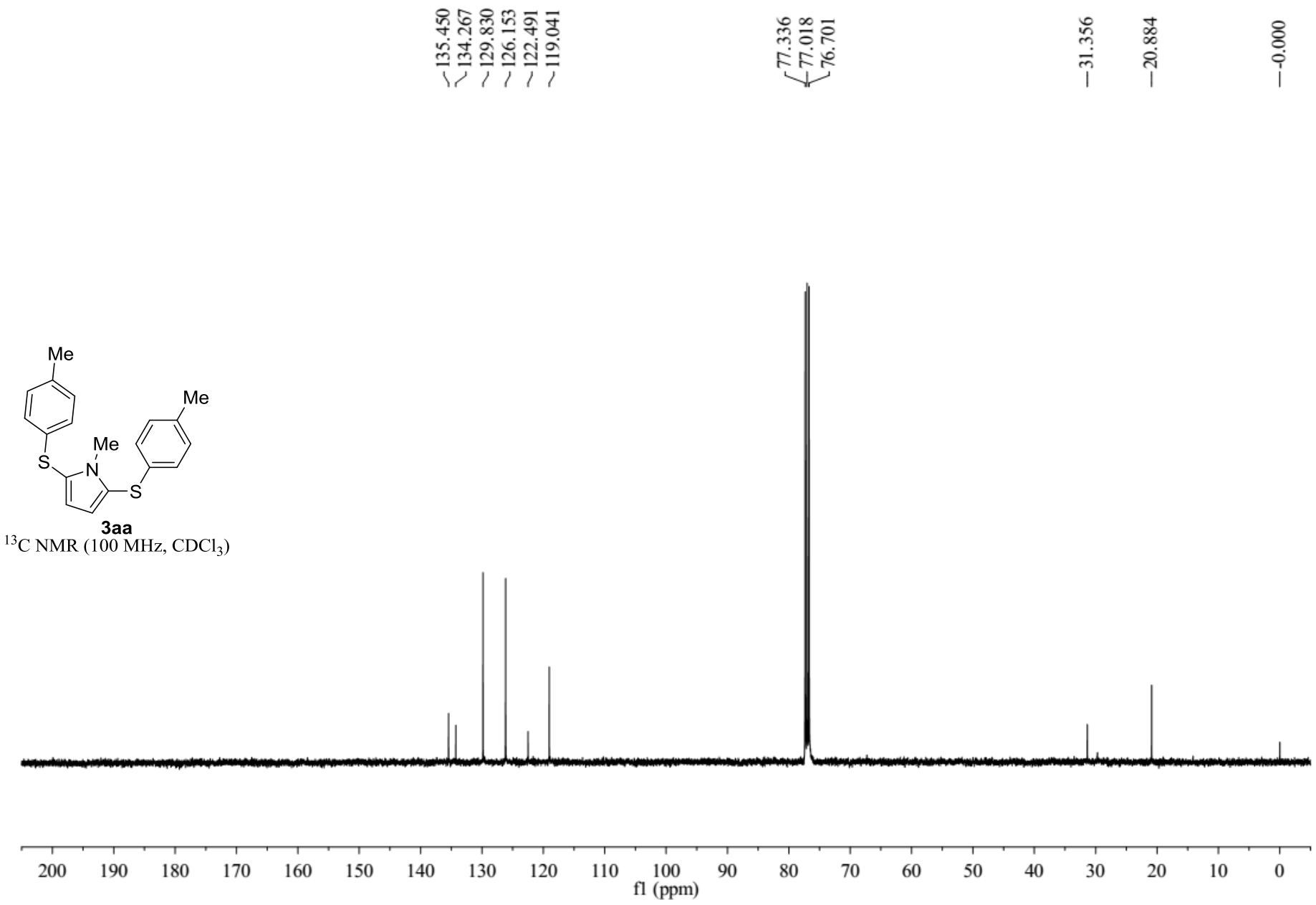
3z

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



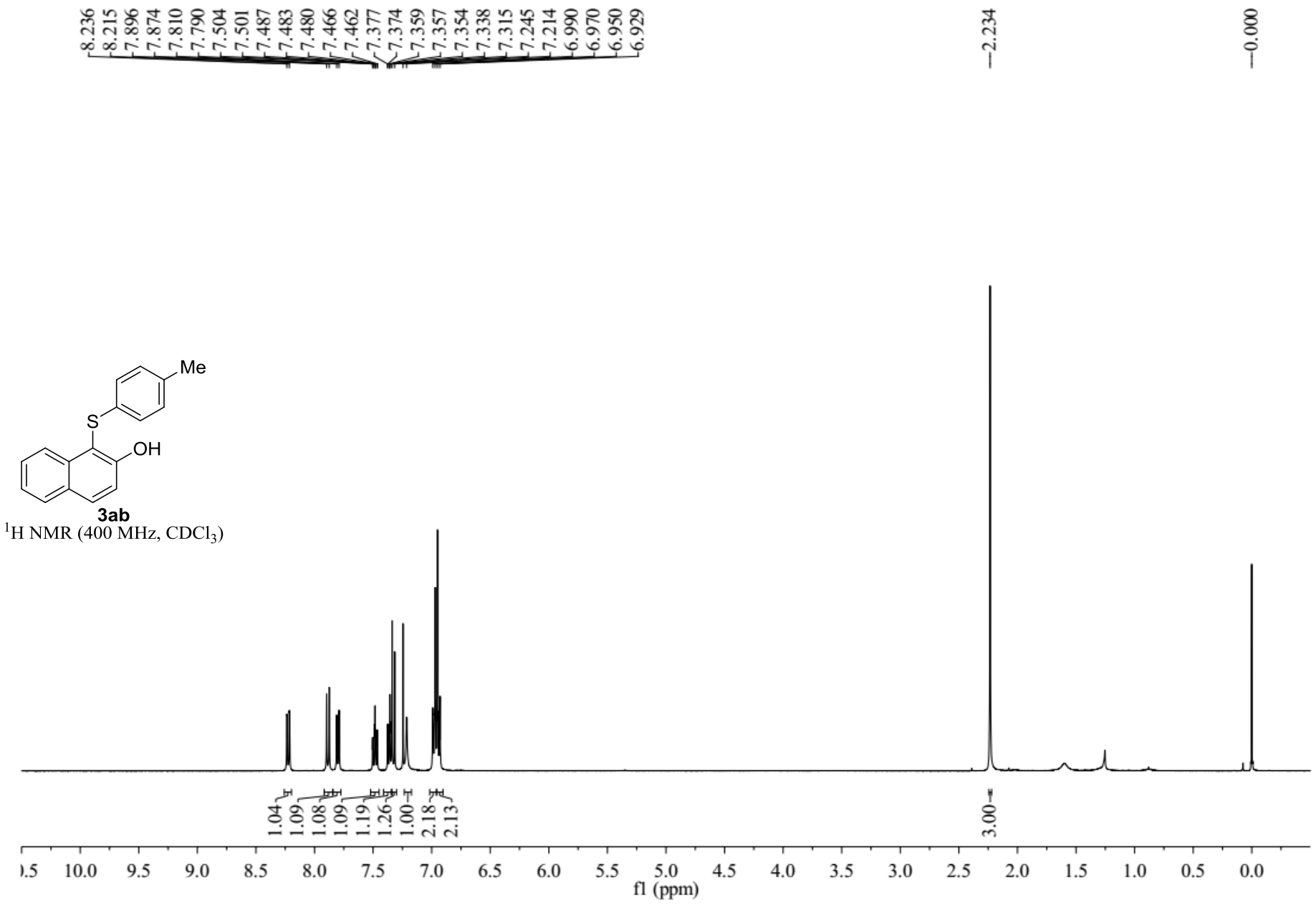
3aa

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



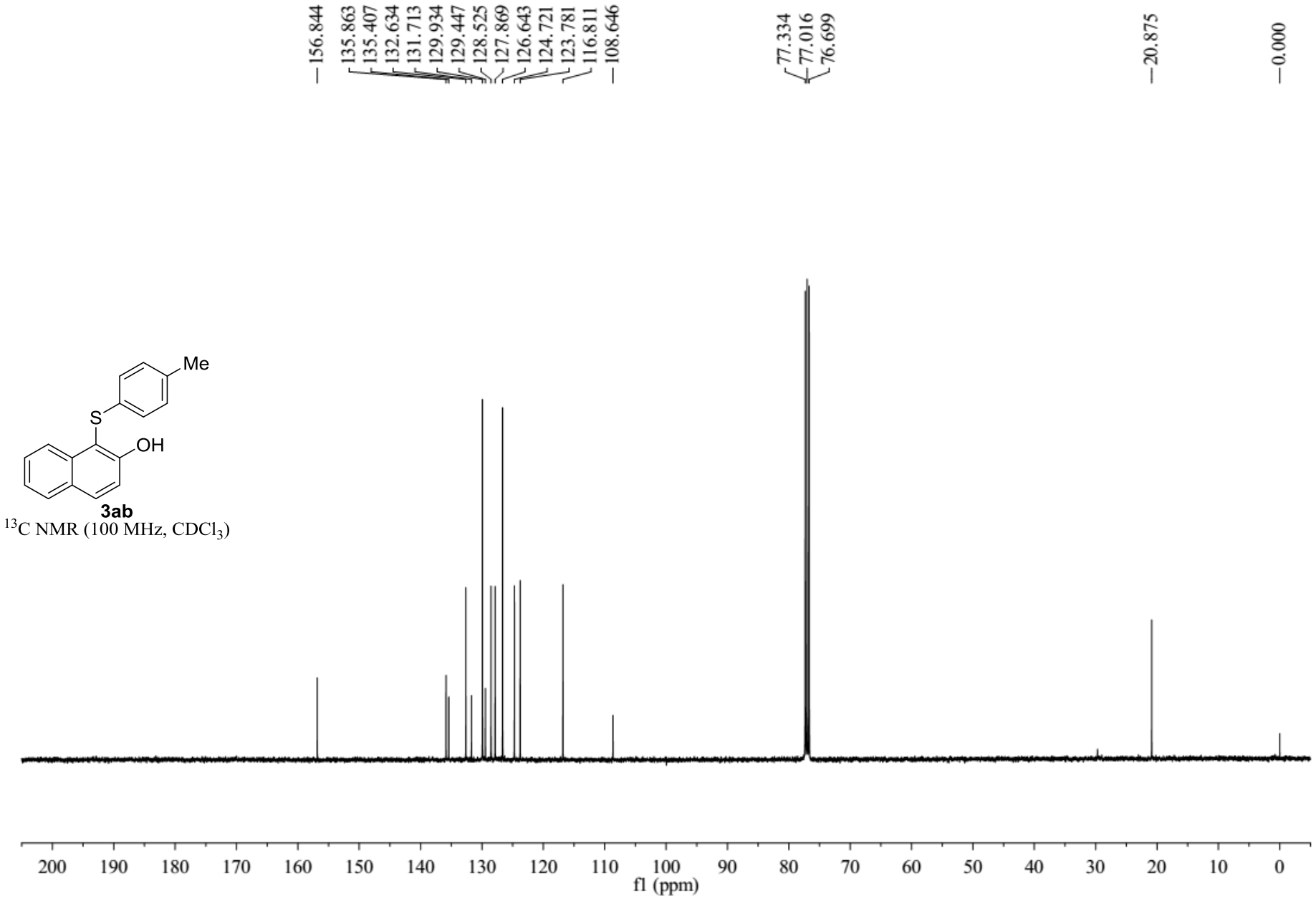
3aa

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



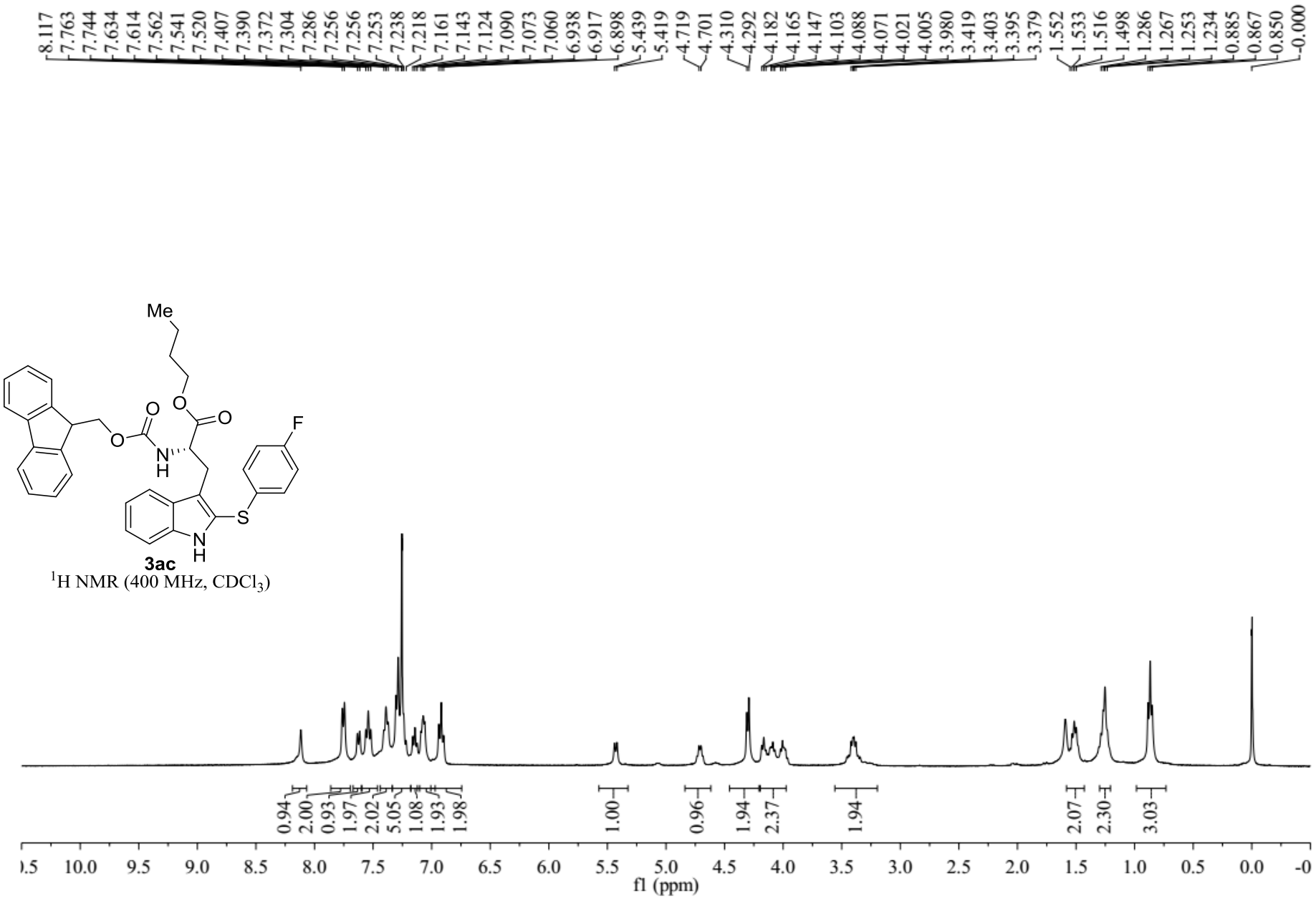
3ab

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



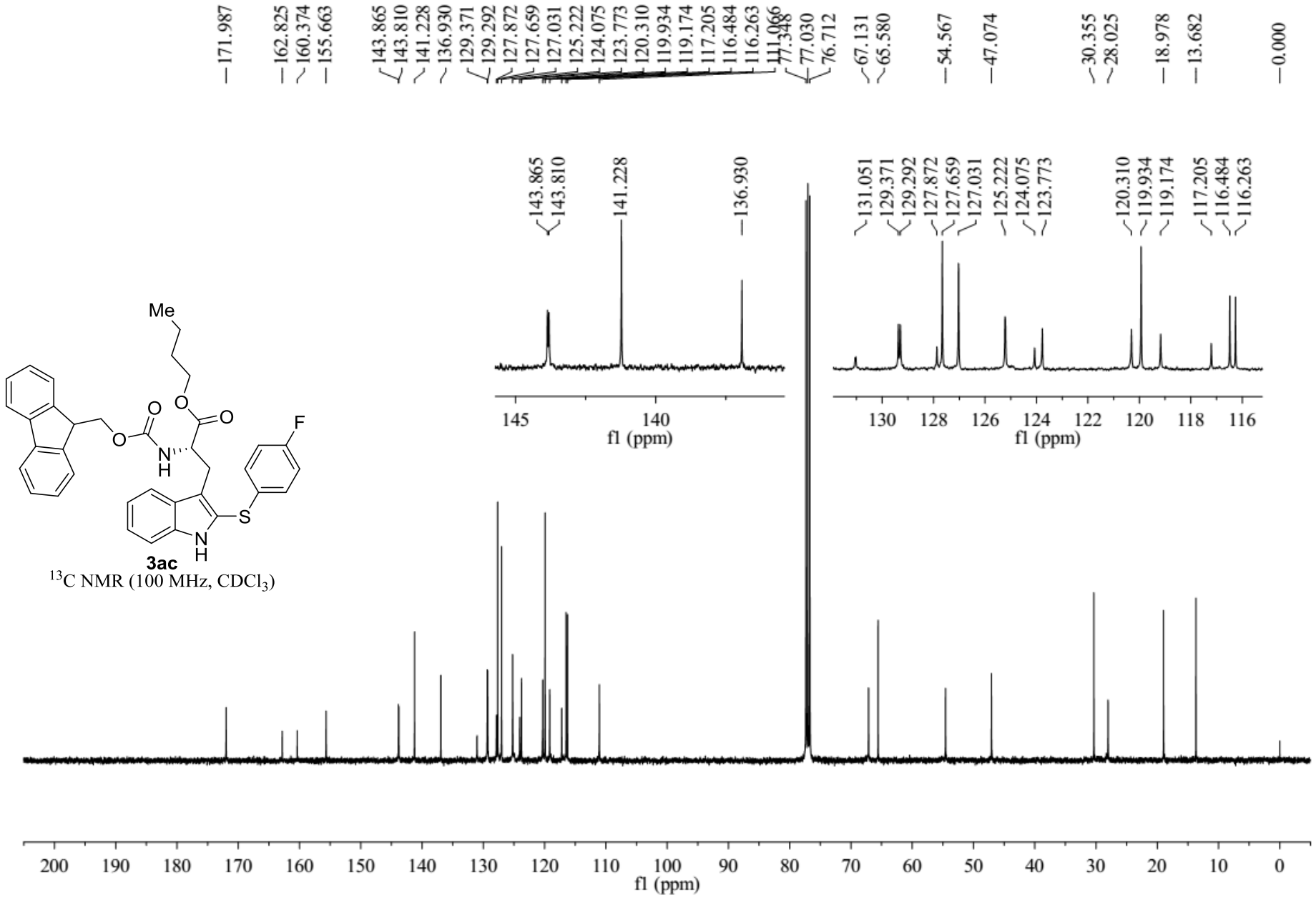
3ab

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

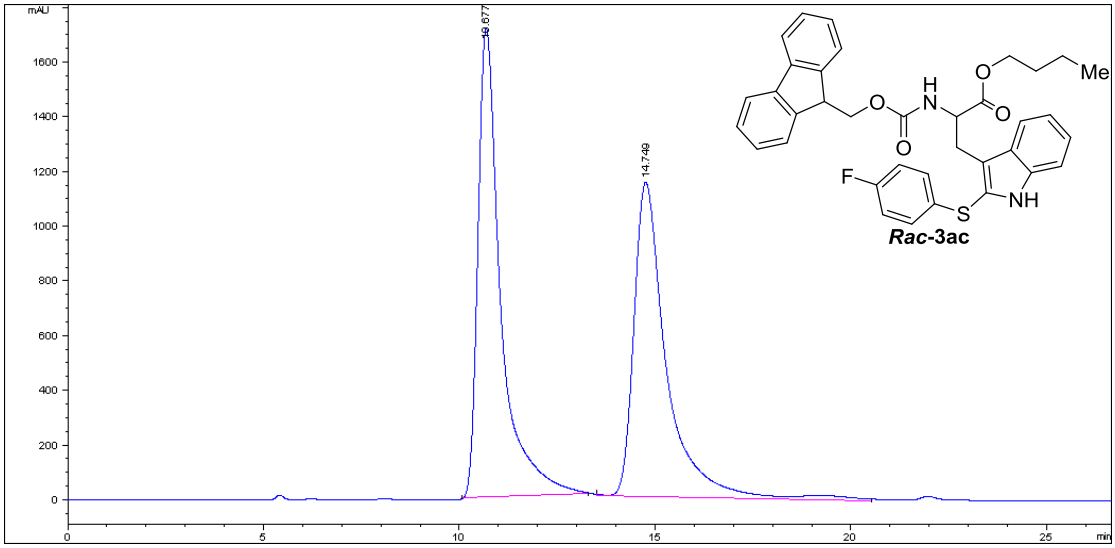


3ac

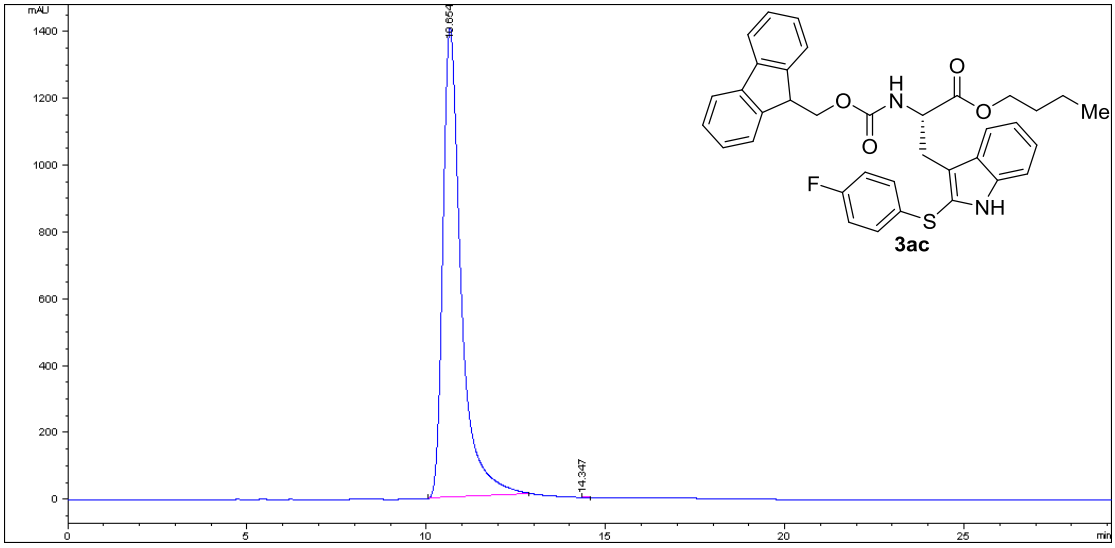
^{1}H NMR (400 MHz, $CDCl_3$)



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



Number	Time (min)	Area (mAU s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.677	69451.3	1716.1	0.6745	0.537	50.797
2	14.749	67272.4	1150.6	0.9744	0.53	49.203



Number	Time (min)	Area (mAU s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.654	49853.3	1405.6	0.5911	0.614	99.985
2	14.347	7.6	5.1E-1	0.2209	0	0.015