Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Visible-light-induced regioselective sulfenylation of imidazopyridines with thiols under transition metal-free conditions

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General Information

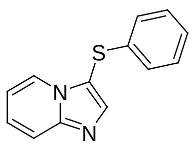
All reactions were performed in an oven-dried flask under air atmosphere. Solvents used as reaction media were dried over pre-dried molecular sieves (4 Å). Solvents for extraction and chromatography were reagent grade and used as received. All the chemicals/reagents including imidazopyridines, thiols were purchased from Alfa Aesar, Sigma-Aldrich and E. Merck; and were used without further purification. TLC was done on silica gel coated glass slide (Merck silica gel G for TLC). For column chromatography silica gel 60–120 mesh (SRL, India) was used with a mixture of EtOAc/hexane as eluent. Elemental analyses were performed on a Flash 2000 Thermo Scientific instrument at NIT Silchar. The yields are based on isolated compounds after purification. Melting points were recorded on an electro thermal digital melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were, respectively, recorded on a JEOL ECS-400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR) and BRUKER 400, 500 and 800 MHz (^{1}H NMR), 100, 125 and 201 MHz (^{13}C NMR) spectrometer in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal reference. The chemical shifts (δ) were expressed in parts per million. Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constant(s) in Hz, integration). Mass analyses and HRMS were obtained on an Agilent 6530 Accurate-Mass Q-TOF mass analyzer by the ESI method.

General procedure for visible-light-promoted synthesis of 3-sulfenyalted imidazopyridines

An oven-dried 10 mL round-bottom flask was charged with 2-phenylimidazo[1,2-a]pyridine **1a** (0.5 mmol, 97 mg), thiophenol **2a** (0.6 mmol, 66 mg), and rose bengal (5 mol %, 24 mg) in DMSO (2 mL), and the reaction mixture was stirred under blue LED irradiation for 6 h under ambient air. The progress of the reaction was monitored by TLC. After completion of the reaction water was added and the reaction mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum to get the crude residue, which was purified by column chromatography on silica gel (60−120 mesh) using petroleum ether/ethyl acetate = 3:1-9:1 as an eluent to afford the desired pure thiolated product **3a** (95%) as a white solid.

Characterization data for all synthesized compounds

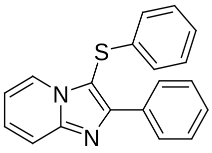
3-(Phenylthio)imidazo[1,2-*a*]pyridine (4a)[1]



4a

Afforded **4a** in 85% yield as a white solid; mp 84-87 °C (Lit. mp 85-88 °C); (Eluent: 25% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 6.8 Hz, 1H), 7.96 (s, 1H), 7.67 (d, J = 6.8 Hz, 1H), 7.26 (t, J = 6.8 Hz, 1H), 7.16 (t, J = 7.2 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 6.82 (t, J = 6.8 Hz, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 148.1, 142.4, 135.2, 129.3, 126.2, 126.0, 124.9, 124.3, 118.1, 113.2, 110.7; Anal. Calcd for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38%. Found: C, 68.95; H, 4.42; N, 12.36%; HRMS (ESI) ($[M+H]^+$) Calcd for $C_{13}H_{11}N_2S$: 227.0637; Found: 227.0636.

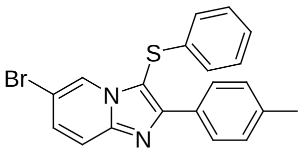
2-Phenyl-3-phenylsulfanyl-imidazo[1,2-*a*]pyridine (**3a**)[2]



3a

Afforded **3a** in 95% yield as a white solid; mp 95-97 °C (Lit. mp 95-98 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 6.8 Hz, 1H), 8.13 (d, J = 8.8 Hz, 2 H), 7.75 (d, J = 8.8 Hz, 1H), 7.58–7.53 (m, 3H), 7.36 (t, J = 8.0 Hz, 1H), 7.23 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 7.6 Hz, 2H), 6.90 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ =148.1, 142.5, 133.6, 132.4, 131.8, 130.8, 129.0, 128.8, 127.7, 126.8, 125.8, 124.3, 118.1, 113.2, 110.6; Anal. Calcd for $C_{19}H_{14}N_2S$: C, 75.47; H, 4.67; N, 9.26%. Found: C, 75.44; H, 4.68; N, 9.24%.

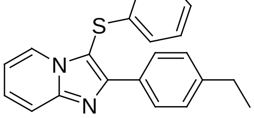
6-Bromo-3-phenylsulfanyl-2-*p*-tolyl-imidazo[1,2-*a*]pyridine (**3b**)[3]



3b

Afforded **3b** in 91% yield as a white amorphous; mp 150-152 °C; (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 6.8 Hz, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8, 1H), 7.57–7.52 (m, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.91–6.84 (m, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ = 149.8, 146.9, 136.2, 132.4, 131.5, 130.2, 129.8, 128.8, 126.8, 125.8, 124.5, 122.8, 117.6, 113.1, 107.1, 20.9; Anal. Calcd for $C_{20}H_{15}BrN_2S$: C, 60.77; H, 3.82; N, 7.09%. Found: C, 60.75; H, 3.83; N, 7.07%. HRMS (ESI) ($[M+H]^+$) Calcd for $C_{20}H_{16}BrN_2S$: 395.0212, Found: 395.0215.

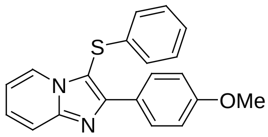
2-(4-Ethylphenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (3c)[2]



3c

Afforded **3c** in 92% yield as a white solid; mp 97-100 °C (Lit. mp 98-100 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.27 (d, J = 7.2 Hz, 1H), 8.12 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.55-7.52 (m, 3H), 7.34 (t, J = 6.4 Hz, 1H), 7.02 (d, J = 7.2 Hz, 2H), 6.89-6.86 (m, 3H), 2.63 (m, 2H), 1.25 (t, J = 8.0 Hz, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 149.9, 147.0, 143.6, 136.2, 131.6, 131.1, 130.3, 129.8, 128.8, 126.8, 125.8, 124.5, 117.6, 113.2, 107.1, 28.9, 14.1; Anal. Calcd for $C_{21}H_{18}N_2S$: C, 76.33; H, 5.49; N, 8.48%. Found: C, 76.28; H, 5.46; N, 8.45%.

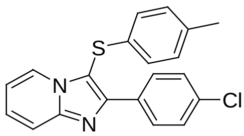
2-(4-Methoxyphenyl)-3-(phenylthio)imidazo[1,2-*a*]pyridine (3d)[1]



3d

Afforded **3d** in 90% yield as a white solid; mp 108-110 °C (Lit. mp 109-110 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 6.8 Hz, 1H), 8.15 (d, J = 9.2 Hz, 2H), 7.70-7.66 (m, 2H), 7.56 (d, J = 9.2 Hz, 2H), 7.32 (t, J = 8.4 Hz, 1H), 6.97 (d, J = 9.6 Hz, 2H), 6.87 (t, J = 6.8 Hz, 1H), 6.74 (d, J = 9.6 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 145.5, 138.2, 134.6, 131.8, 131.4, 130.2, 129.7, 128.2, 127.5, 126.5, 125.9, 124.3, 118.3, 108.3, 55.4; Anal. Calcd for $C_{20}H_{16}N_2OS$: C, 72.26; H, 4.85; N, 8.43%. Found: C, 72.24; H, 4.86; N, 8.42%.

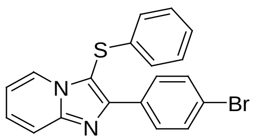
2-(4-Chloro-phenyl)-3-*p*-tolylsulfanyl-imidazo[1,2-*a*]pyridine (**3e**)[2]



3e

Afforded **3e** in 89% yield as a yellow solid; mp 136-138 °C (Lit. mp 135-138 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 6.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.56–7.52 (m, 2H), 7.36–7.30 (m, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.88–6.84 (m, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 147.0, 136.3, 134.6, 132.5, 132.3, 131.8, 130. 3, 129.9, 128.8, 125.9, 124.6, 117.6, 113.3, 107.2, 20.9; Anal. Calcd for $C_{20}H_{15}ClN_2S$: C, 68.46; H, 4.31; N, 7.98%. Found: C, 68.44; H, 4.32; N, 7.96%.

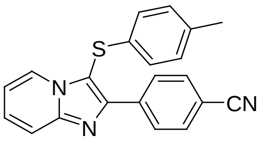
2-(4-Bromophenyl)-3-(phenylthio)imidazo[1,2-*a*]pyridine (3f)[2]



3f

Afforded **3f** in 89% yield as a white solid; mp 148-150 °C (Lit. mp 148-150 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 6.8 Hz, 1H), 8.10 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 9.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 6.8 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 6.8 Hz, 2H), 6.88 (t, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.2, 134.8, 132.3, 131.6, 130.9, 129.9, 129.6, 126.3, 125.6, 124.6, 123.0, 117.7, 113.3, 106.6; Anal. Calcd for $C_{19}H_{13}BrN_2S$: C, 59.85; H, 3.44; N, 7.35%. Found: C, 59.83; H, 3.43; N, 7.37%. HRMS (ESI) ($[M+H]^+$) Calcd for $C_{19}H_{14}BrN_2S$: 388.0056, Found: 388.0051.

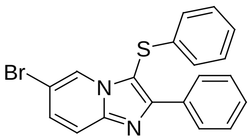
2-(4-Benzonitrile)-3-(p-tolylthio)imidazo[1,2-*a*]pyridine (3g)[4]



3g

Afforded **3g** in 96% yield as a yellow solid; mp 172-174 °C; (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 6.90–6.82 (m, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 147.2, 137.7, 134.0, 132.5, 131.6, 130.8, 129.7, 128.8, 127.1, 125.8, 124.3, 120.0, 117.7, 113.4, 105.7, 21.0; Anal. Calcd for $C_{21}H_{15}N_3S$: C, 73.87; H, 4.43; N, 12.31%. Found: C, 73.84; H, 4.40; N, 12.29%.

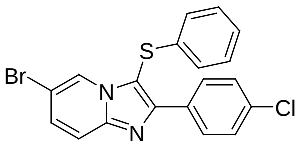
6-Bromo-2-phenyl-3-phenylsulfanyl-imidazo[1,2-*a*]pyridine (3h)[5]



3h

Afforded **3h** in 84% yield as a light yellow solid; mp 145-148 °C; (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 6.8 Hz, 1H), 8.09 (d, *J* = 9.2 Hz, 2H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.54 (d, *J* = 9.6 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.21 (m, 2H), 7.14 (m, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.88 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.4, 134.9, 132.5, 131.7, 131.0, 130.0, 129.6. 128.8, 125.9, 124.8, 123.4, 117.9, 113.5, 106.8; Anal. Calcd for $C_{19}H_{13}BrN_2S$: C, 59.85; H, 3.44; N, 7.35%. Found: C, 59.81; H, 3.41; N, 7.32%.

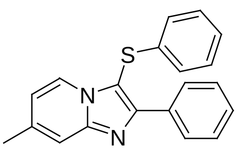
6-Bromo-2-(4-chloro-phenyl)-3-phenylsulfanyl-imidazo[1,2-*a*]pyridine (**3i**)[3]



3i

Afforded **3i** in 82% yield as a yellow solid; mp 168-171 °C; (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.8 Hz, 1H), 8.06 (d, *J* = 6.8 Hz, 2H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 6.8 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.93-6.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.1, 133.2, 132.3, 131.7, 130.9, 129.8, 129.7, 128.8, 127.4, 126.9, 124.4,117.7, 113.7, 106.1; Anal. Calcd for $C_{19}H_{12}BrClN_2S$: C, 54.89; H, 2.91; N, 6.74%. Found: C, 54.85; H, 2.90; N, 6.71%.

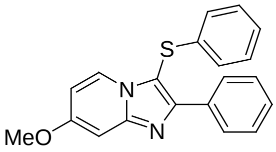
7-Methyl-2-phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (3j)[1]



3j

Afforded **3j** in 90% yield as a white solid; mp 168-171 °C (Lit. mp 170-172 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 6.8 Hz, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.71 (s, 1H), 7.57 -7.51 (m, 4H), 7.40-7.31 (m, 4H), 7.15 (d, J = 8.4 Hz, 1H), 6.84 (d, J = 6.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 146.8, 137.1, 134.2, 132.8, 129.1, 129.0, 128.8, 127.7, 126.5, 125.6, 124.9, 116.4, 115.7, 105.6, 21.9; Anal. Calcd for $C_{20}H_{16}N_2S$: C, 75.92; H, 5.10; N, 8.85%. Found: C, 75.88; H, 5.07; N, 8.82%.

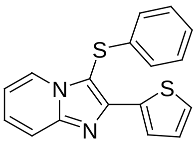
7-Methoxy-2-phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine (3k)[6]



3k

Afforded **3k** in 86% yield as a white solid; mp 112-115 °C; (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 6.8 Hz, 1H), 8.17 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.8 Hz, 1H), 7.58-7.51 (m, 3H), 7.33 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 6.88 (t, J = 6.8 Hz, 1H), 6.76 (d, J = 8.8 Hz, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 145.2, 135.7, 133.7, 130.9, 129.9, 129.2, 128.9, 128.3, 127.8, 126.0, 125.1, 124.4, 106.5, 101.5, 55.8; Anal. Calcd for $C_{20}H_{16}N_2OS$: C, 72.26; H, 4.85; N, 8.43%. Found: C, 72.22; H, 4.83; N, 8.39%.

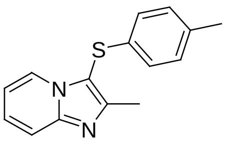
3-(Phenylthio)-2-(thiophen-2-yl)imidazo[1,2-a]pyridine (3l)[1]



3l

Afforded **3l** in 92% yield as a white solid; mp 157-159 °C (Lit. mp 158-160 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 7.0 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.74-7.68 (m, 3H), 7.60 (d, J = 7.5 Hz, 1H), 7.43-7.38 (m, 3H), 7.32 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 9.0 Hz, 1H), 6.85 (t, J = 7.0 Hz, 1H); ^{13}C NMR (225 MHz, $CDCl_3$) δ 147.8, 146.6, 136.5, 134.4, 129.3, 127.3, 126.4, 126.0, 125.3, 123.0, 117.4, 113.3, 105.4; Anal. Calcd for $C_{17}H_{12}N_2S_2$: C, 66.20; H, 3.92; N, 9.08%. Found: C, 66.16; H, 3.89; N, 9.06%.

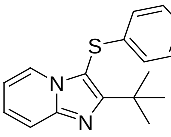
2-Methyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine (3m)[7]



3m

Afforded **3m** in 80% yield as a white solid; mp 101-103 °C (Lit. mp 102.5-103.8 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 6.8 Hz, 1H), 7.70 (d, J = 9.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.86 (t, J = 6.8 Hz, 1H), 2.59 (s, 3H), 2.2 5 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 146.3, 135.4, 131.2, 129.7, 127.4, 127.3, 124.1, 117.0, 113.0, 107.9, 21.0, 14.0; Anal. Calcd for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01%. Found: C, 70.80; H, 5.51; N, 10.98%.

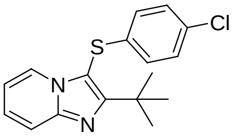
2-(Tert-butyl)-3-(phenylthio)imidazo[1,2-*a*]pyridine (3n)[5]



3n

Afforded **3n** in 75% yield as a white solid; mp 115-117 °C (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 6.8 Hz, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.26-7.22 (m, 1H), 7.16-7.12 (m, 2H), 7.09 (t, J = 6.8 Hz, 1H), 6.95 (d, J = 6.8 Hz, 2H), 6.82 (t, J = 6.8 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 148.1, 135.2, 130.9, 129.3, 126.27, 126.21, 126.08, 124.3, 118.1, 113.2, 32.0, 30.4; Anal. Calcd for $C_{17}H_{18}N_2S$: C, 72.30; H, 6.42; N, 9.92%. Found: C, 72.25; H, 6.38; N, 9.88%.

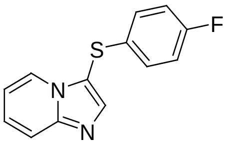
2-(Tert-butyl)-3-((4-chlorophenyl)thio)imidazo[1,2-*a*]pyridine (3o)[7]



3o

Afforded **3o** in 78% yield as a white solid; mp 110-113 °C (Lit. mp 111.2-113.0 °C); (Eluent: 25% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 6.8 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 6.92−6.85 (m, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 134.4, 132.3, 130.9, 128.8, 127.6, 126.2, 124.1, 118.2, 113.3, 109.9, 32.5, 30.3; Anal. Calcd for $C_{17}H_{17}ClN_2S$: C, 64.44; H, 5.41; N, 8.84%. Found: C, 64.41; H, 5.37; N, 8.80%.

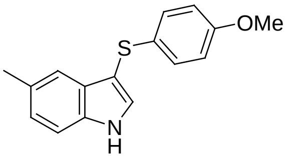
3-((4-Fluorophenyl)thio)imidazo[1,2-*a*]pyridine (3p)[7]



3p

Afforded **3p** in 69% yield as a white solid; mp 82.3-83.5 °C (Lit. mp 82.3-83.5 °C); (Eluent: 15% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 6.8 Hz, 1H), 7.97 (s, 1H), 7.69 (t, J = 3.6 Hz, 1H), 7.50 (d, J = 2.4 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 6.91−6.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J = 242.2 Hz), 148.2, 142.6, 130.9 (d, J = 4.8 Hz), 128.8 (d, J = 7.6 Hz), 126.3, 124.2, 118.3, 116.5 (d, J = 22.4 Hz), 113.4, 110.2; Anal. Calcd for $C_{13}H_9FN_2S$: C, 63.92; H, 3.71; N, 11.47%. Found: C, 63.88; H, 3.69; N, 11.45%.

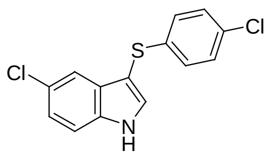
5-Choro-3-((4-Methoxyphenyl)thio)-*1H*-indole (3q)[8]



3q

Afforded **3q** in 81% yield as a white solid; mp 106-109 °C (Eluent: 10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 6.4 Hz, 1H), 7.93 (s, 1H), 7.67 (s, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 141.4, 132.4, 130.9, 129.3, 128.8, 126.2, 124.3, 118.0, 115.0, 113.3, 101.0, 55.4, 20.8; Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20%. Found: C, 71.31; H, 5.57; N, 5.17%.

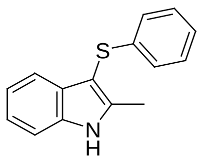
5-Choro-3-((4-chlorophenyl)thio)-*1H*-indole (3r)[8]



3r

Afforded **3r** in 68% yield as a white solid; mp 135-138 °C (Eluent: 10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.32-7.27 (m, 3H), 6.83 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 142.5, 134.4, 132.5, 128.8, 127.7, 126.4, 124.2, 120.1, 118.3, 113.5, 101.9; Anal. Calcd for $C_{14}H_9Cl_2NS$: C, 57.16; H, 3.08; N, 4.76%. Found: C, 57.13; H, 3.05; N, 4.71%.

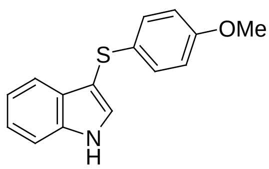
2-Methyl-3-(phenylthio)-*1H*-indole (3s)[8]



3s

Afforded **3s** in 69% yield as a white solid; mp 107-110 °C (Lit. mp 109-111 °C) (Eluent: 10% EtOAc/hexane); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 6.8 Hz, 1H), 7.69-7.64 (m, 2H), 7.26 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.4 Hz, 1H), 6.83 (t, J = 6.8 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 142.1, 136.3, 132.5, 130.1, 128.8, 126.7, 125.9, 124.3, 118.1, 113.1, 102.4, 20.9; Anal. Calcd for $C_{15}H_{13}NS$: C, 75.28; H, 5.47; N, 5.85%. Found: C, 75.24; H, 5.44; N, 5.81%.

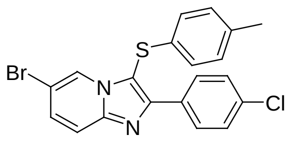
3-((4-Methoxyphenyl)thio)-*1H*-indole (3t)[8]



3t

Afforded **3t** in 91% yield as a white solid; mp 110-113 °C (Lit. mp 111-113 °C); (Eluent: 10% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 6.8 Hz, 1H), 7.94 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.28-7.21 (m, 1H), 7.05 (d, J = 8.8 Hz, 2H), 6.84-6.80 (m, 1H), 6.75 (d, J = 8.8 Hz, 2H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 147.7, 132.4, 130.8, 129.1, 128.7, 125.8, 125.1, 124.2, 117.9, 114.9, 100.0, 55.3; Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20%. Found: C, 71.31; H, 5.57; N, 5.17%.

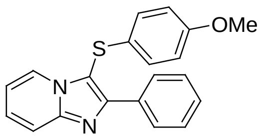
6-Bromo-2-(4-chloro-phenyl)-3-p-tolylsulfanyl-imidazo[1,2-*a*]pyridine (3u)[3]



3u

Afforded **3u** in 87% yield as a white solid; mp 175-178 °C (Eluent: 20% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 4.8 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 4.8 Hz, 2H), 7.39 (t, J = 6.8 Hz, 1H), 7.17 (d, J = 4.4 Hz, 2H), 6.89 (d, J = 4.8 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 147.5, 136.6, 133.8, 132.4, 131.9, 130.5, 130.2, 129.3, 127.3, 126.6, 123.3, 118.2, 106.9, 21.6; Anal. Calcd for $C_{20}H_{14}BrClN_2S$: C, 55.89; H, 3.28; N, 6.52%. Found: C, 55.85; H, 3.26; N, 6.51%.

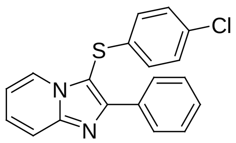
3-((4-Methoxyphenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3v)[2]



3v

Afforded **3v** in 88% yield as a white solid; mp 114-117 °C (Lit. mp 115-118 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, J = 6.8 Hz, 1H), 8.15 (d, J = 8.0, 2H), 7.68 (d, J = 9.2 Hz, 1H), 7.56-7.49 (m, 3H), 7.32 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.4 Hz, 2H), 6.87 (t, J = 6.8 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 3.69 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 158.7, 149.6, 146.9, 132.5, 131.6, 129.9, 128.8, 128.1, 126.8, 125.1, 124.5, 117.7, 115.2, 113.2, 108.1, 55.4; Anal. Calcd for $C_{20}H_{16}N_2OS$: C, 72.26; H, 4.85; N, 8.43%. Found: C, 72.21; H, 4.82; N, 8.41%.

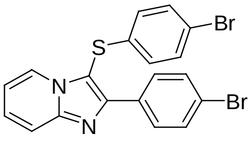
3-((4-Chlorophenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3w)[9]



3w

Afforded **3w** in 86% yield as a white solid; mp 118-120 °C (Lit. mp 117-119 °C); (Eluent: 20% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (d, J = 7.2 Hz, 1H), 8.07 (d, J = 8.8 Hz, 2H), 7.70-7.68 (m, 1H), 7.56-7.49 (m, 3H), 7.38-7.29 (m, 3H), 6.92 (t, J = 6.8 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.2, 147.1, 134.0, 132.6, 132.5, 131.7, 130.9, 130.0, 129.8, 128.8, 127.1, 124.4, 117.8, 113.7, 105.9; Anal. Calcd for $C_{19}H_{13}ClN_2S$: C, 67.75; H, 3.89; N, 8.32%. Found: C, 67.71; H, 3.86; N, 8.27%.

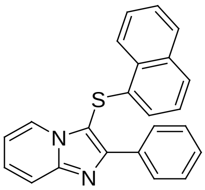
2-(4-Bromophenyl)-3-((4-bromophenyl)thio)-imidazo[1,2-*a*]pyridine (3x) (New compound)



3x

Afforded **3x** in 90% yield as a white solid; mp 169-172 °C; (Eluent: 20% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 800 MHz): δ 8.24 (d, *J* = 6.4 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.4, 147.2, 134.0, 132.5, 132.4, 132.0, 131.7, 130.9, 130.0, 129.8, 128.8, 127.0, 123.1, 120.0, 117.8; HRMS (ESI) ($[M+H]^+$) Calcd for $C_{19}H_{13}Br_2N_2S$: 458.9161, Found: 458.9160.

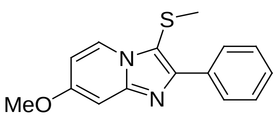
3-(Naphthalen-1-ylthio)-2-phenylimidazo[1,2-*a*]pyridine (3y)[5]



3y

Afforded **3y** in 94% yield as a white solid; mp 162-165 °C (Eluent: 25% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 6.8 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.74-7.67 (m, 4H), 7.56-7.49 (m,4H), 7.40-7.37 (m, 2H), 7.35-7.34 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.3, 133.9, 132.5, 132.4, 132.2, 131.7, 130.9, 129.9, 129.4, 128.9, 127.8, 127.1, 126.9, 125.9, 124.6, 123.8, 123.6, 117.8, 113.4, 106.5; Anal. Calcd for $C_{23}H_{16}N_2S$: C, 78.38; H, 4.58; N, 7.95%. Found: C, 78.35; H, 4.56; N, 7.91%.

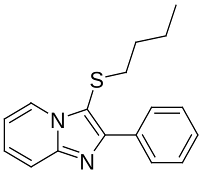
7-Methoxy-3-(methylthio)-2-phenylimidazo[1,2-*a*]pyridine (3z)[6]



3z

Afforded **3z** in 84% yield as a white solid; mp 71-74 °C; (Eluent: 15% EtOAc/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.8 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 6.4 Hz, 1H), 3.85 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 148.0, 146.7, 133.4, 129.1, 127.5, 127.1, 124.5, 109.3, 107.0, 95.1, 55.2, 17.5; Anal. Calcd for $C_{15}H_{14}N_2OS$: C, 66.64; H, 5.22; N, 10.36%. Found: C, 66.59; H, 5.17; N, 10.32%.

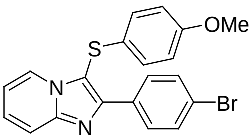
3-(Butylthio)-2-phenylimidazo[1,2-a]pyridine (3aa)[1]



3aa; 72%

Afforded **3z** in 72% yield as yellow oil; (Eluent: 15% EtOAc/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 7.0 Hz, 1H), 7.97 (d, J = 9.0 Hz, 2H), 7.68 (d, J = 9.0 Hz, 1H), 7.47 (t, J = 7.0 Hz, 2H), 7.30 (t, J = 7.0 Hz, 1H), 7.07 (t, J = 5.0 Hz, 1H), 6.88 (t, J = 7.0 Hz, 1H), 2.73 (t, J = 7.5 Hz, 2H), 1.46-1.41 (m, 2H), 1.32-1.25 (m, 2H), 0.81 (t, J = 8.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 146.2, 132.3, 129.2, 129.0, 128.6, 125.4, 124.1, 117.1, 111.9, 109.7, 36.3, 32.1, 21.5, 13.2; Anal. Calcd for $C_{17}H_{18}N_2S$: C, 72.30; H, 6.42; N, 9.92%. Found: C, 72.25; H, 6.38; N, 9.88%.

2-(4-Bromophenyl)-3-((4-(methoxyphenyl)thio)imidazo[1,2-*a*]pyridine (3ab) (New Compound)



3ab; 85%

Afforded **3ab** in 86% yield as a white solid; mp 160-163 °C; (Eluent: 20% EtOAc/hexane); ^{1}H NMR ($CDCl_3$, 800 MHz): δ 8.31 (d, J = 7.2 Hz, 1H), 8.16 (d, J = 8.0, 2H), 7.69 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.33 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 6.88 (t, J = 7.2 Hz, 1H), 6.75 (d, J = 8.8 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$, 201 MHz): δ 158.6, 149.5, 146.8, 132.4, 131.6, 130.9, 129.8, 128.8, 128.0, 126.7, 125.0, 124.5, 122.8, 117.6, 115.2, 55.3; HRMS (ESI) ($[M+H]^+$) Calcd for $C_{20}H_{16}BrN_2OS$: 411.0161, Found: 411.0159.

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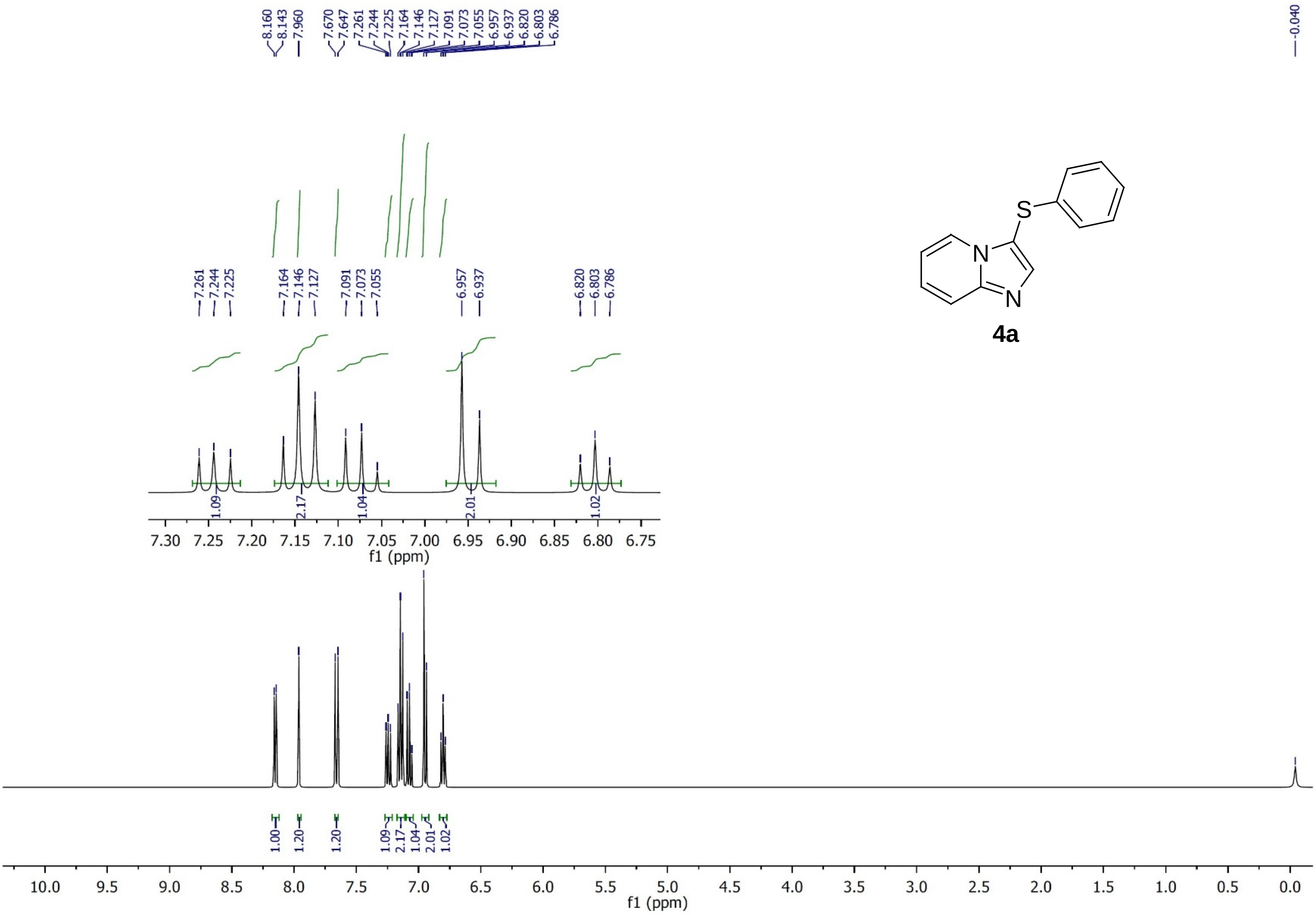
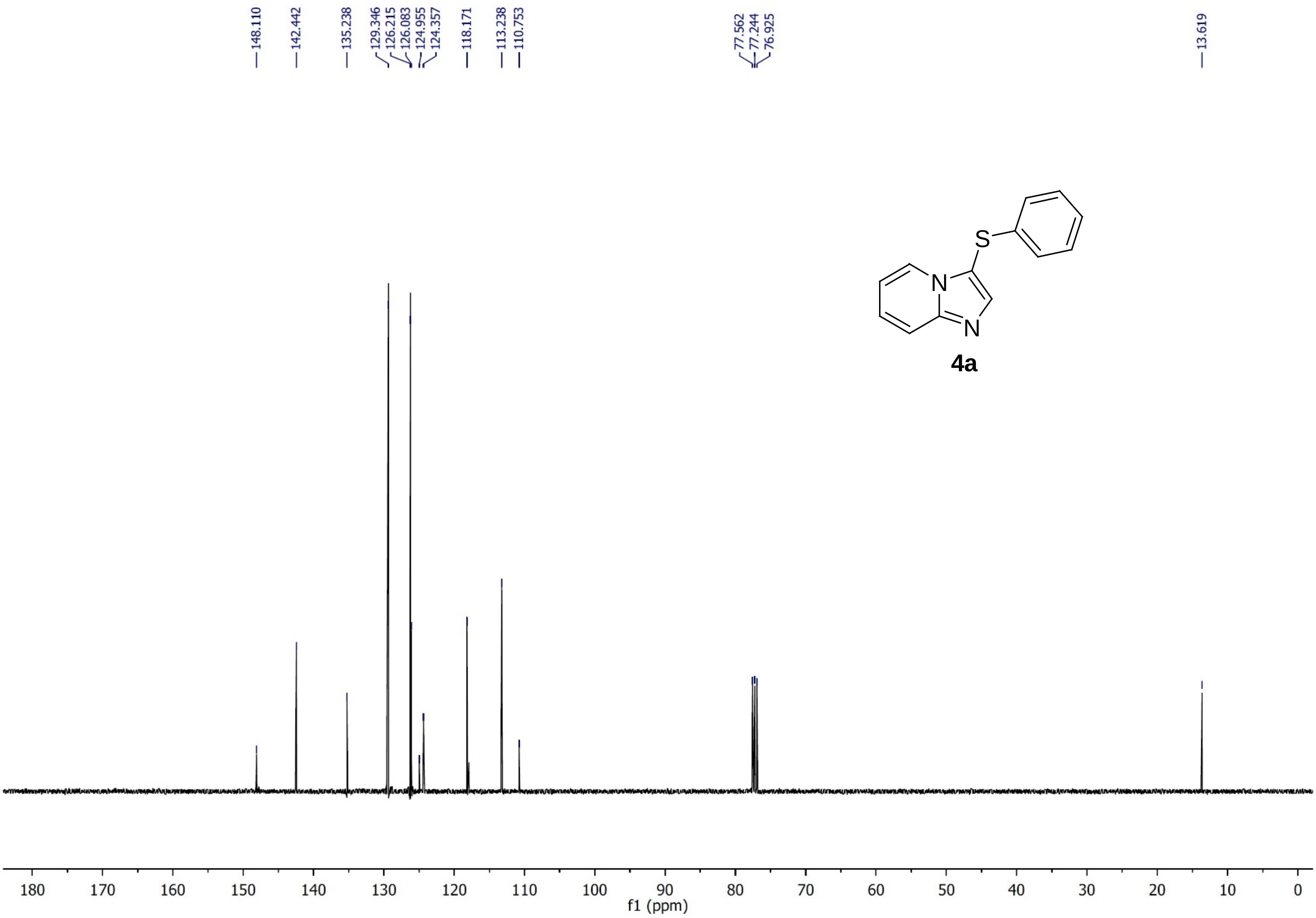
^{1}H and ^{13}C NMR spectra of synthesized compounds

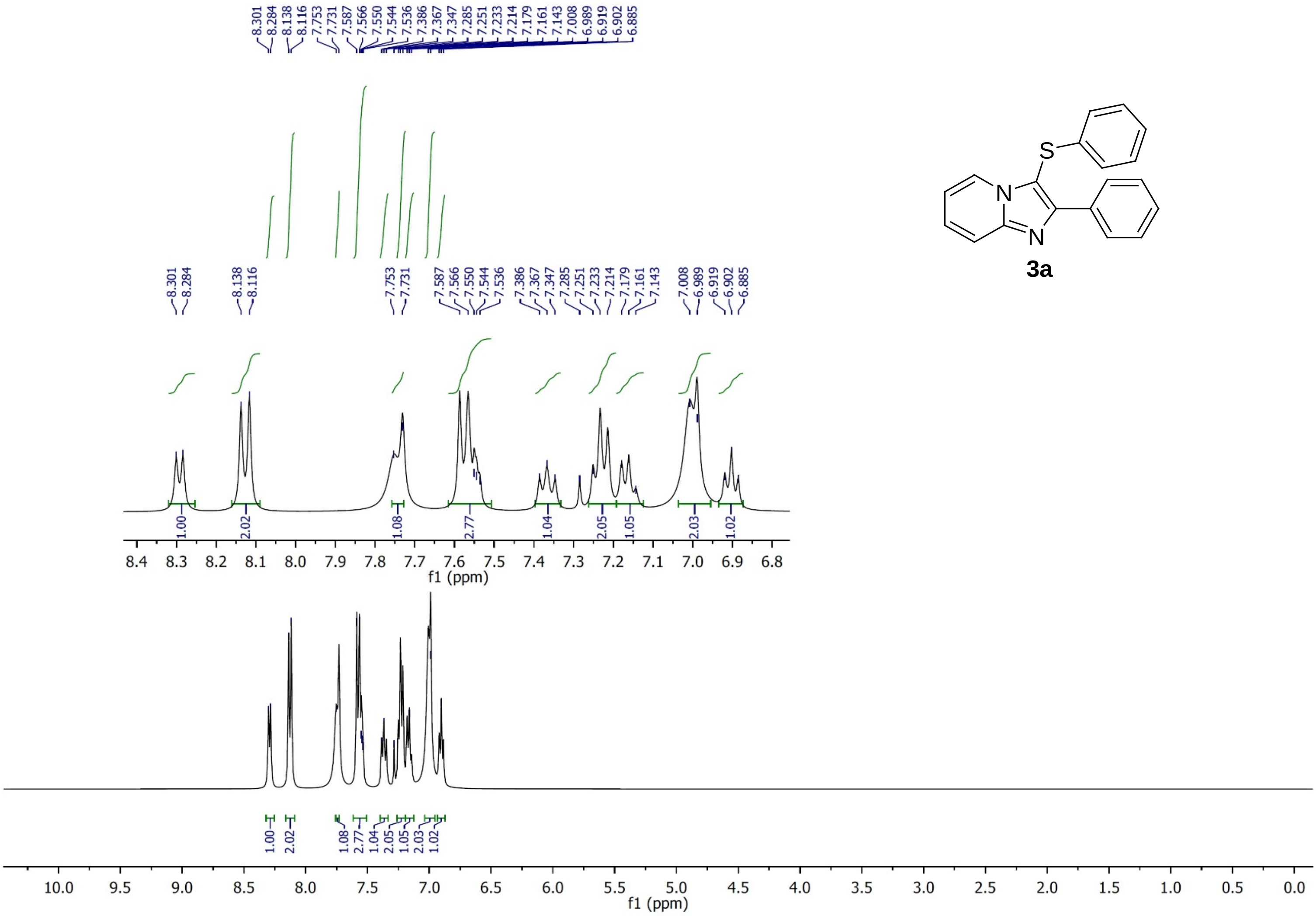
^{1}H NMR of compound **4a** ($CDCl_3$, 400 MHz)



^{13}C NMR of compound **4a** ($CDCl_3$, 100 MHz)

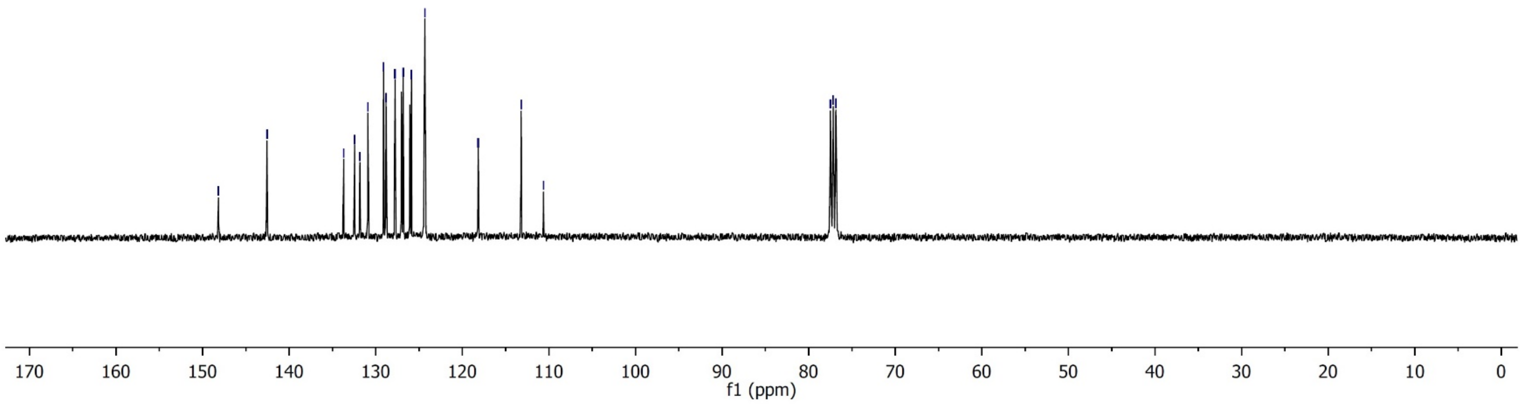


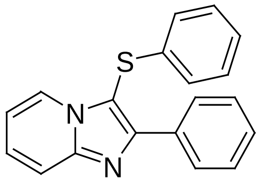
^{1}H NMR of compound **3a** ($CDCl_3$, 400 MHz)



3a

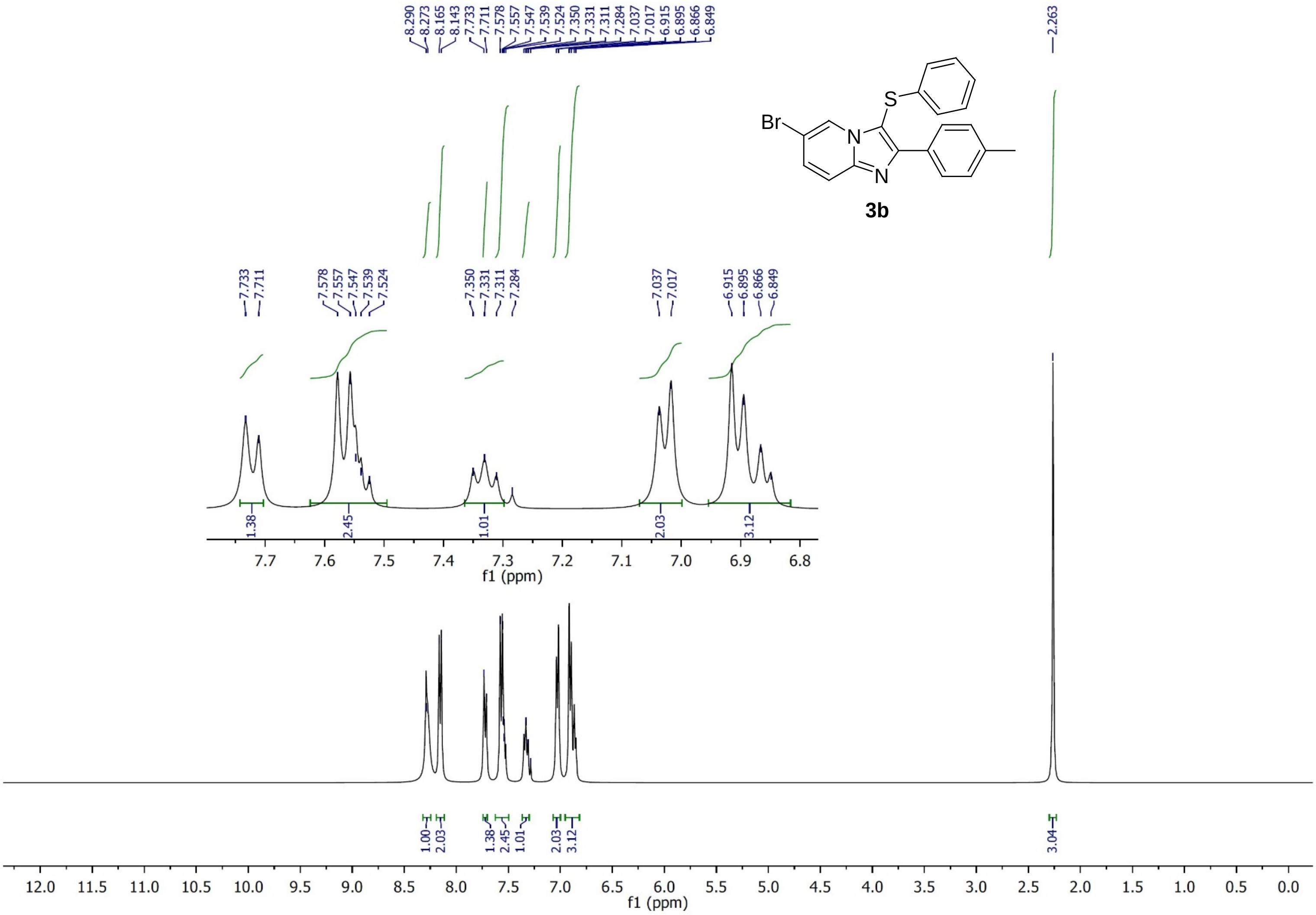
^{13}C NMR of compound **3a** ($CDCl_3$, 100 MHz)



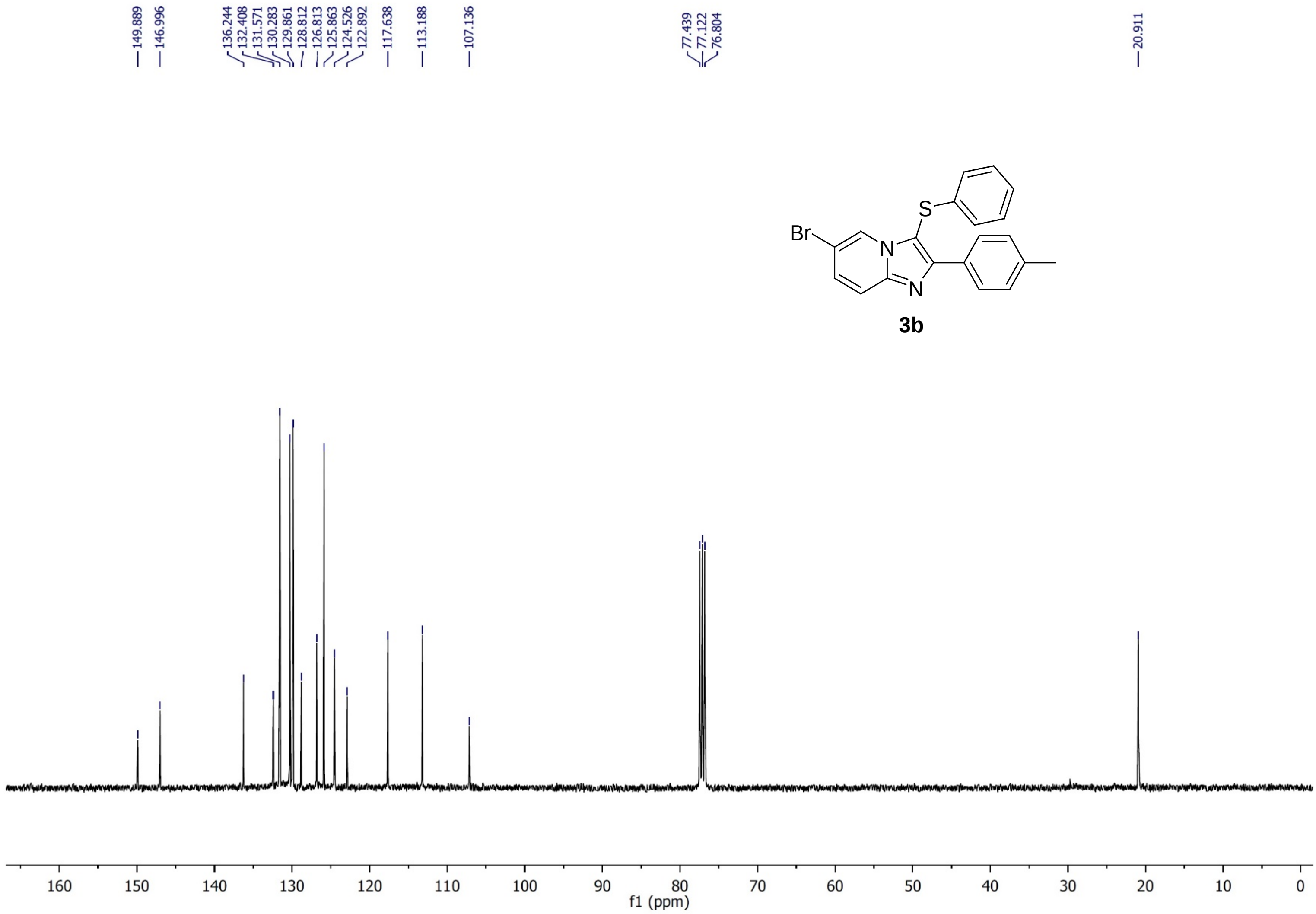


3a

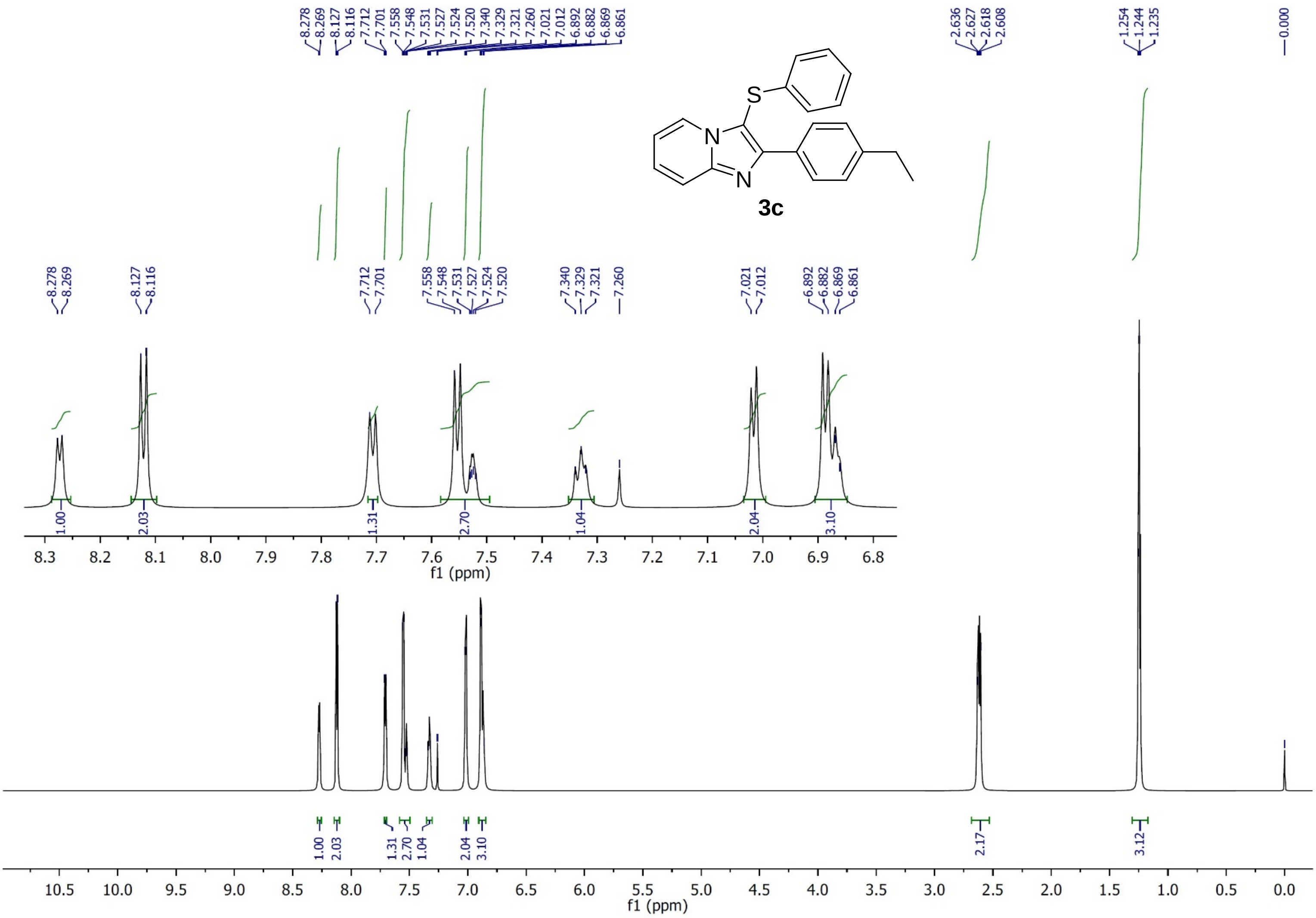
[1]H NMR of compound **3b** ($CDCl_3$, 400 MHz)



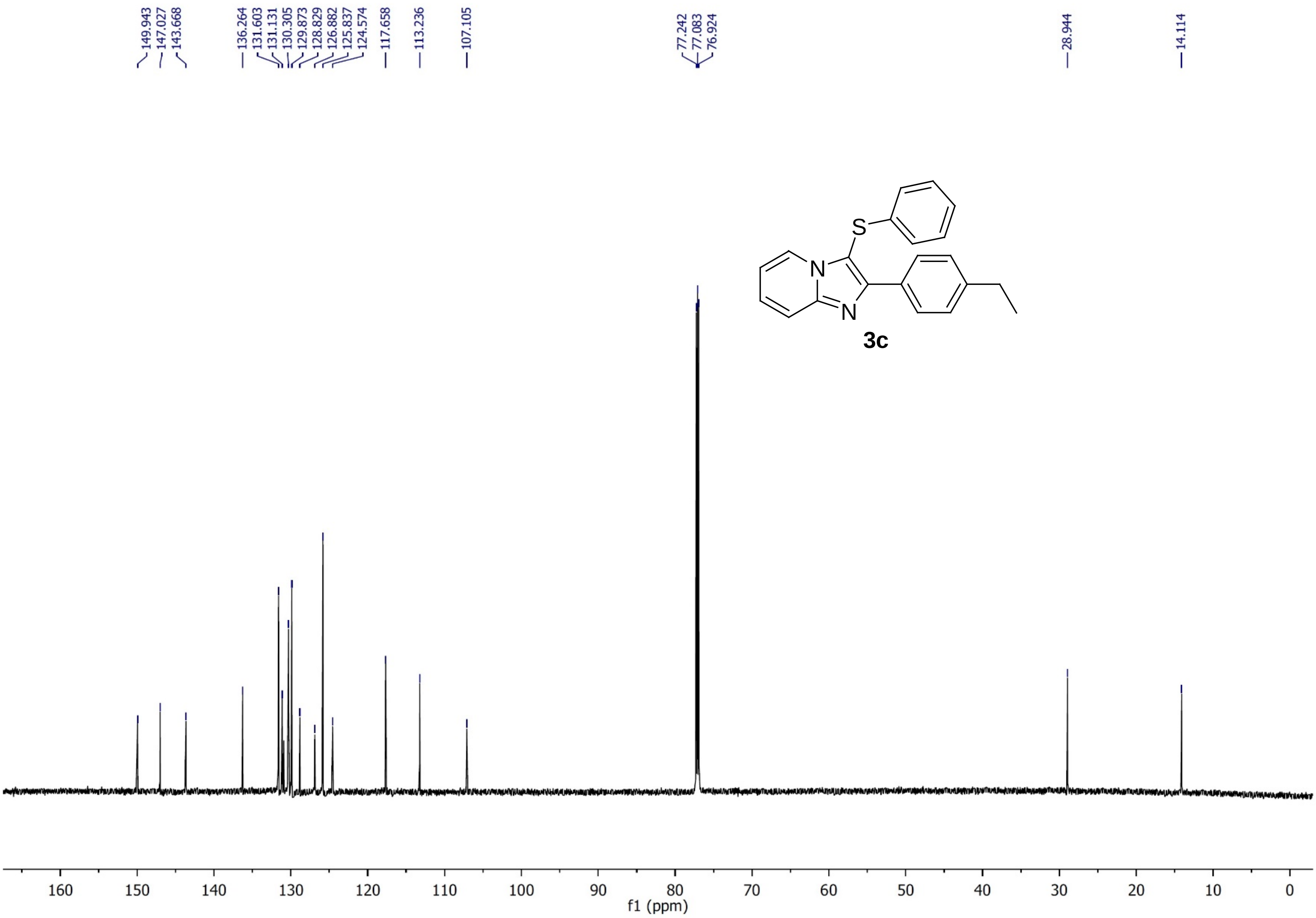
[13]C NMR of compound **3b** ($CDCl_3$, 100 MHz)



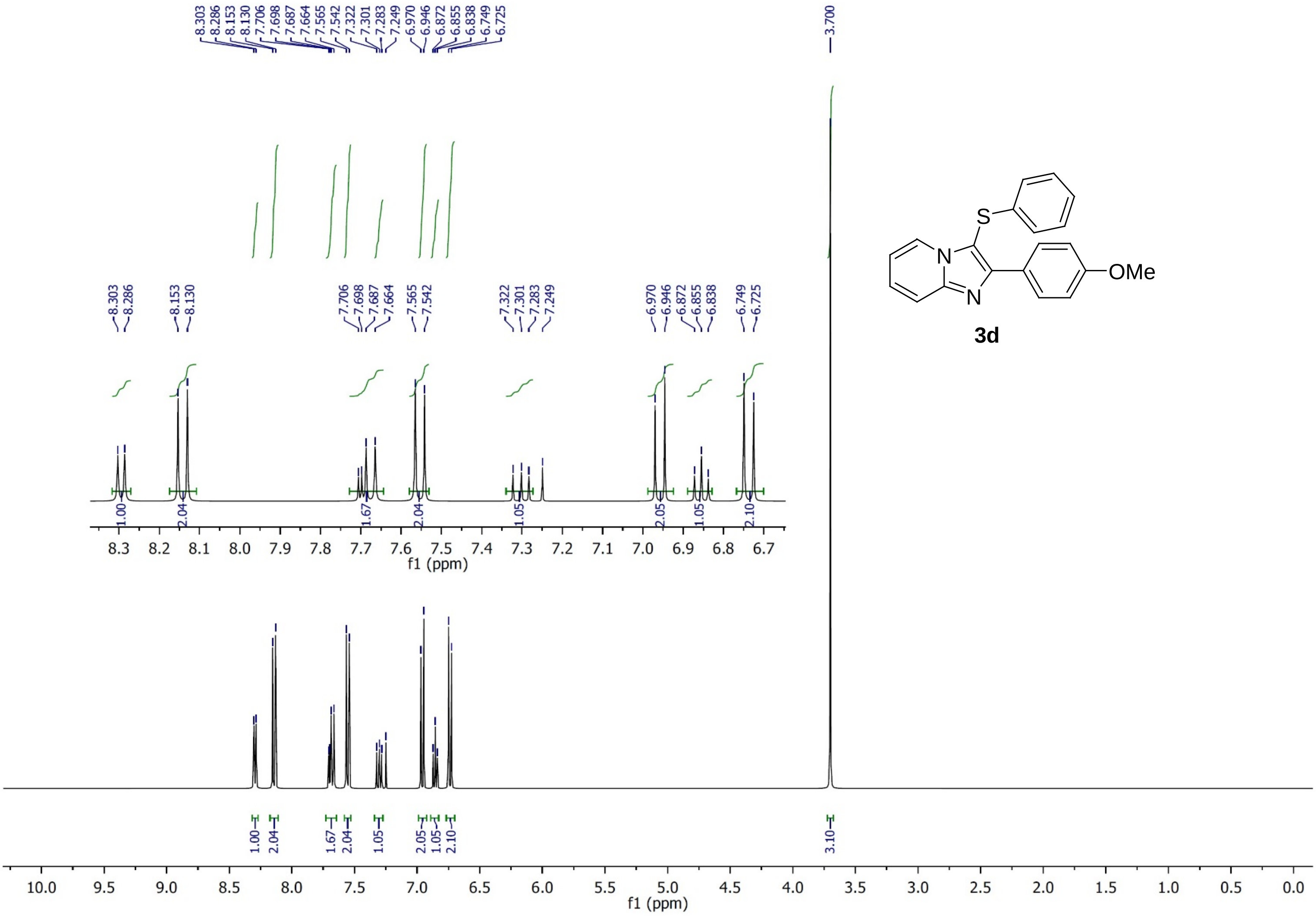
[1]H NMR of compound **3c** ($CDCl_3$, 800 MHz)



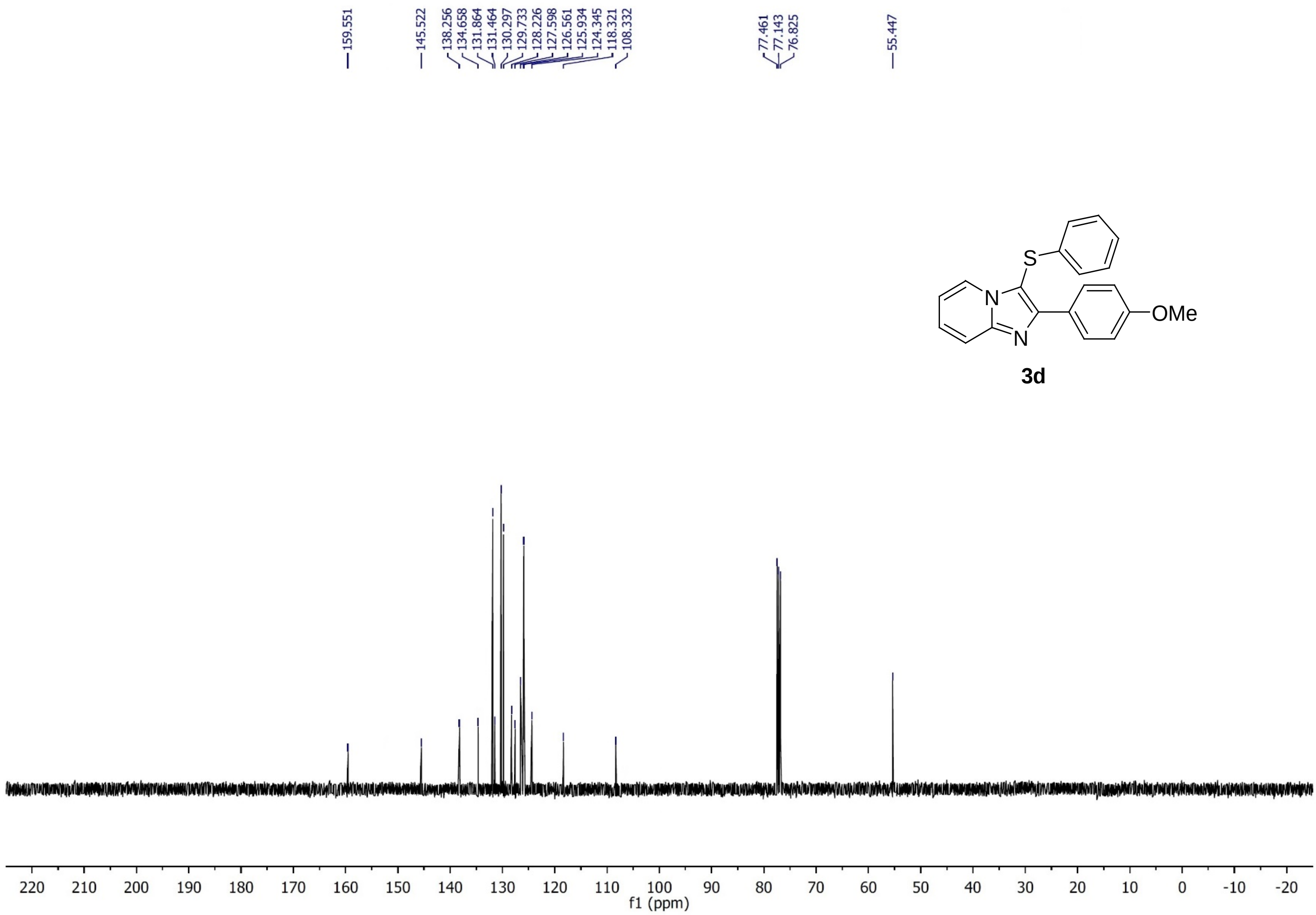
[13]C NMR of compound **3c** ($CDCl_3$, 201 MHz)



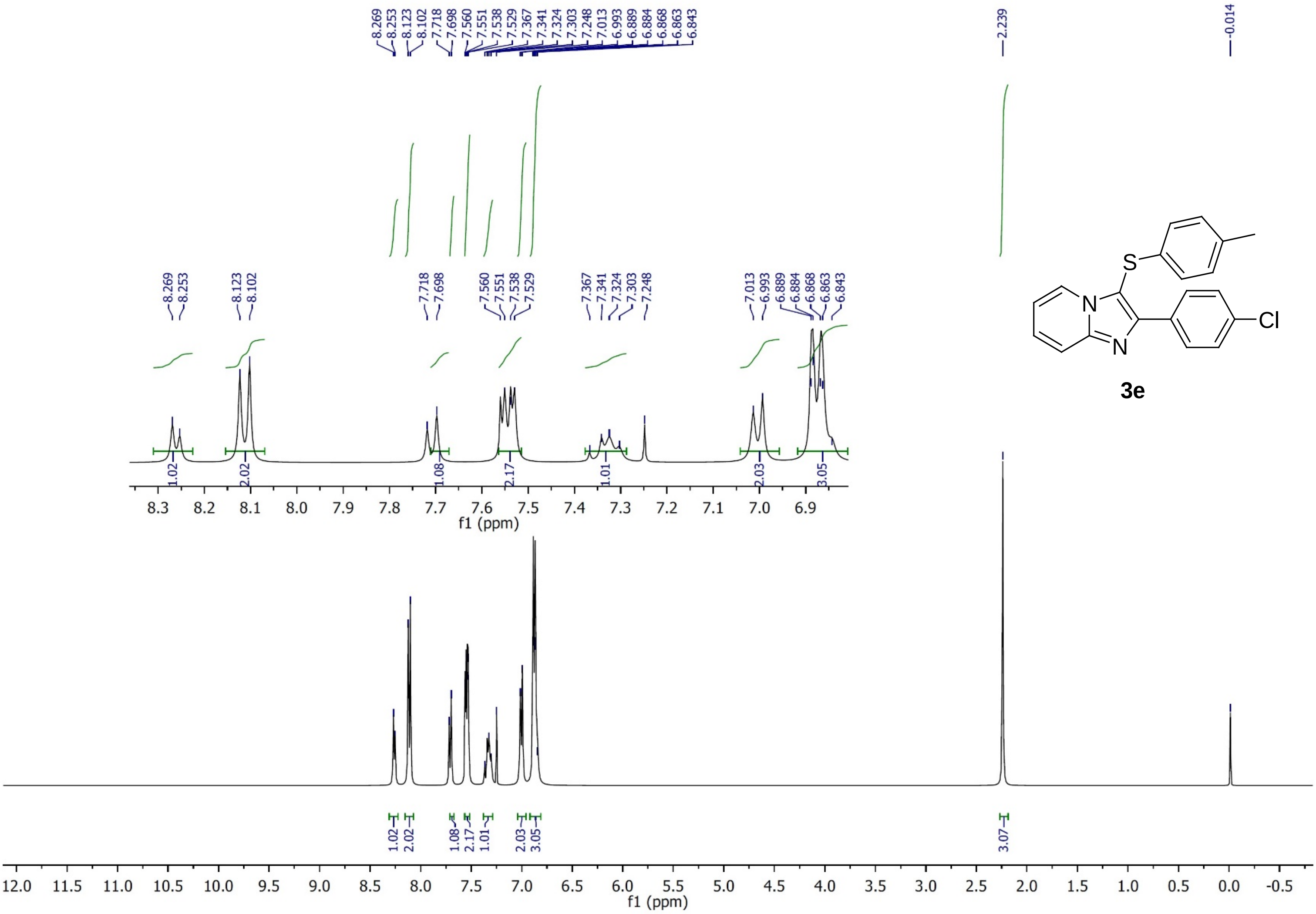
[1]H NMR of compound **3d** ($CDCl_3$, 400 MHz)



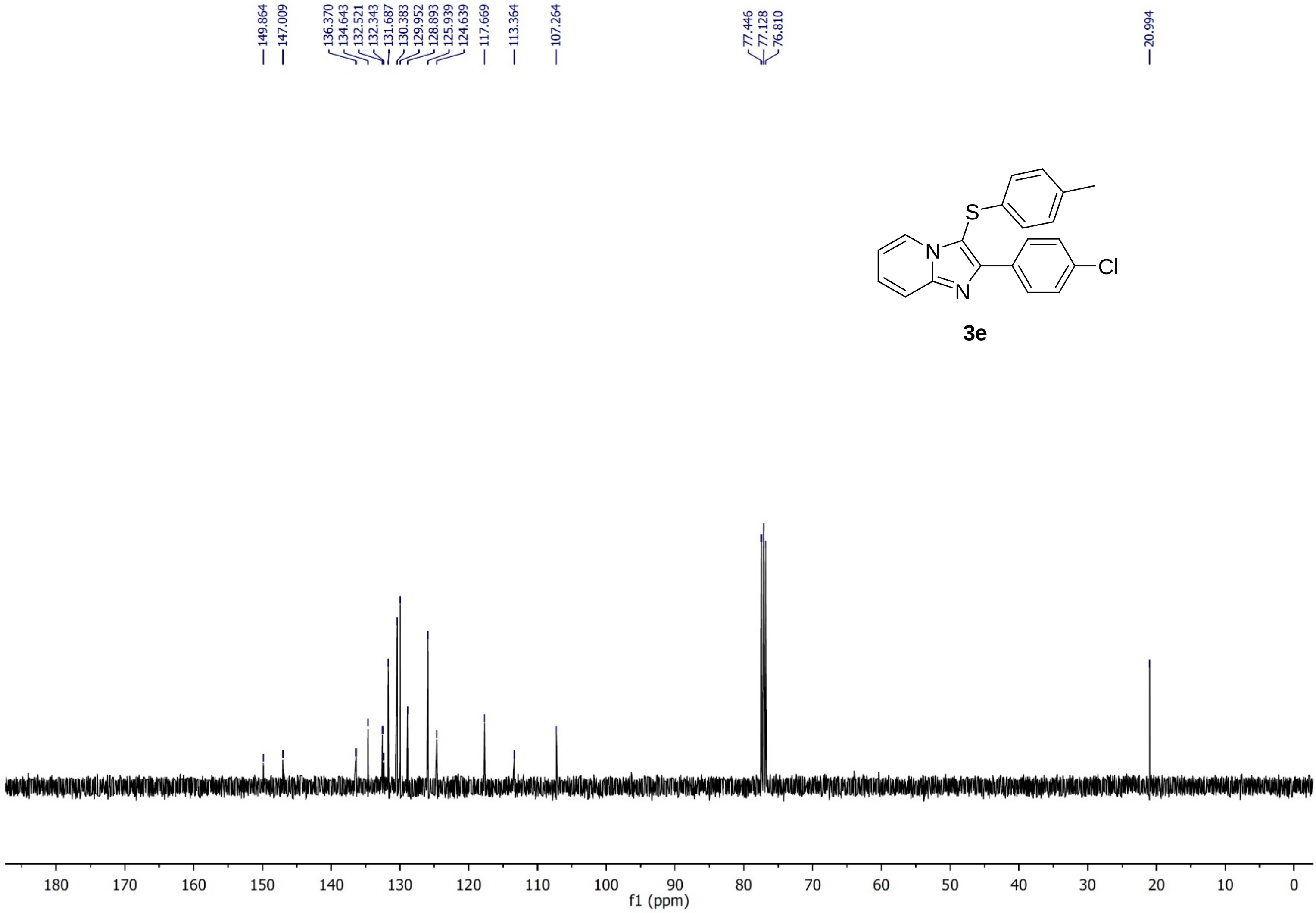
^{13}C NMR of compound **3d** ($CDCl_3$, 100 MHz)



[1]H NMR of compound **3e** ($CDCl_3$, 400 MHz)

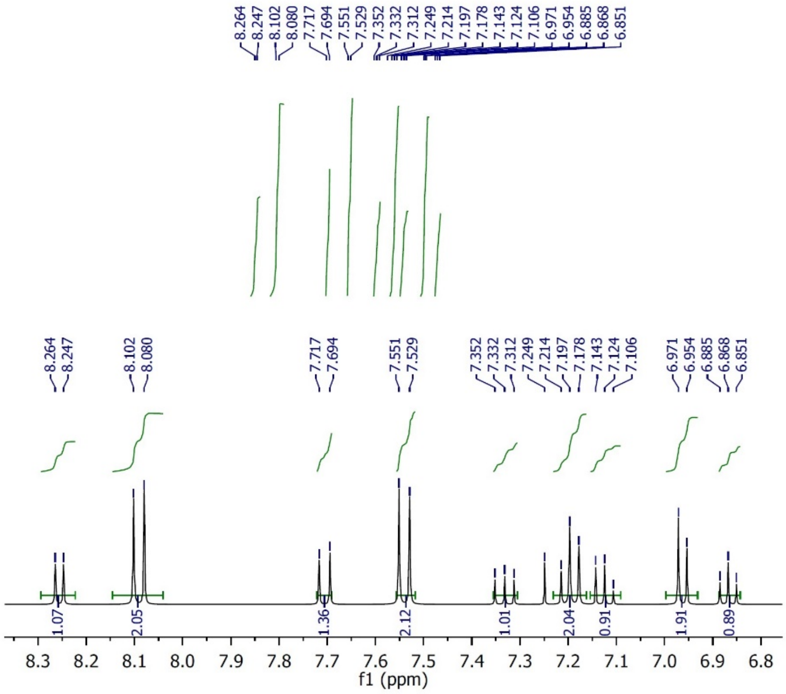


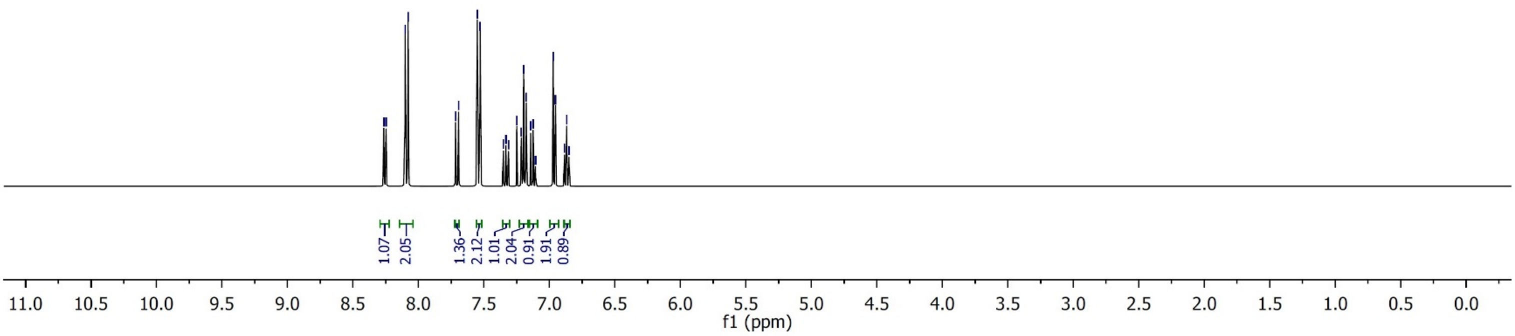
^{13}C NMR of compound **3e** ($CDCl_3$, 100 MHz)

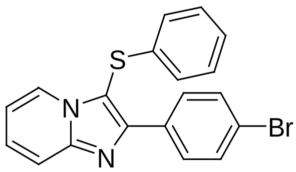


3e

^1H NMR of compound **3f** ($CDCl_3$, 400 MHz)

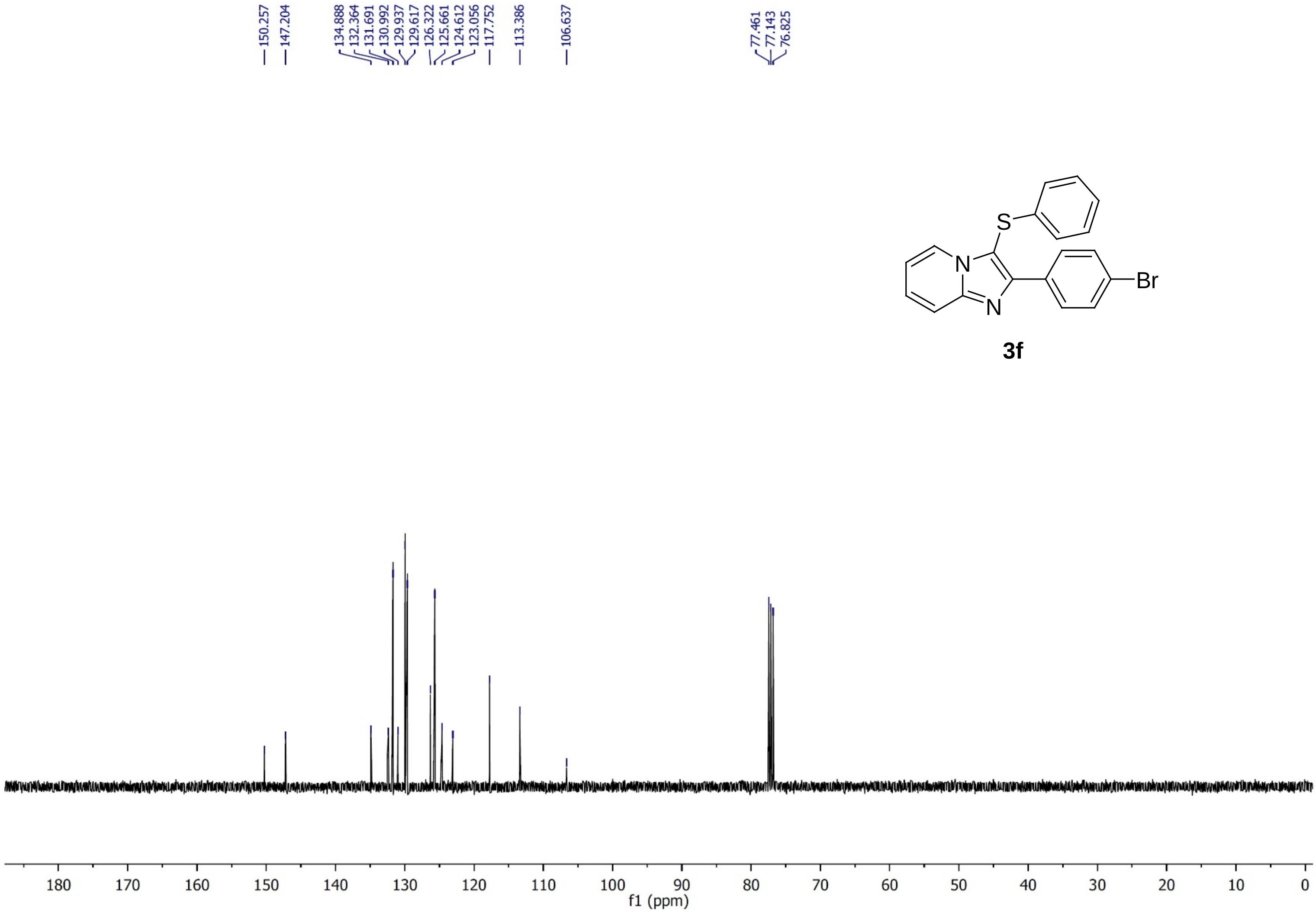






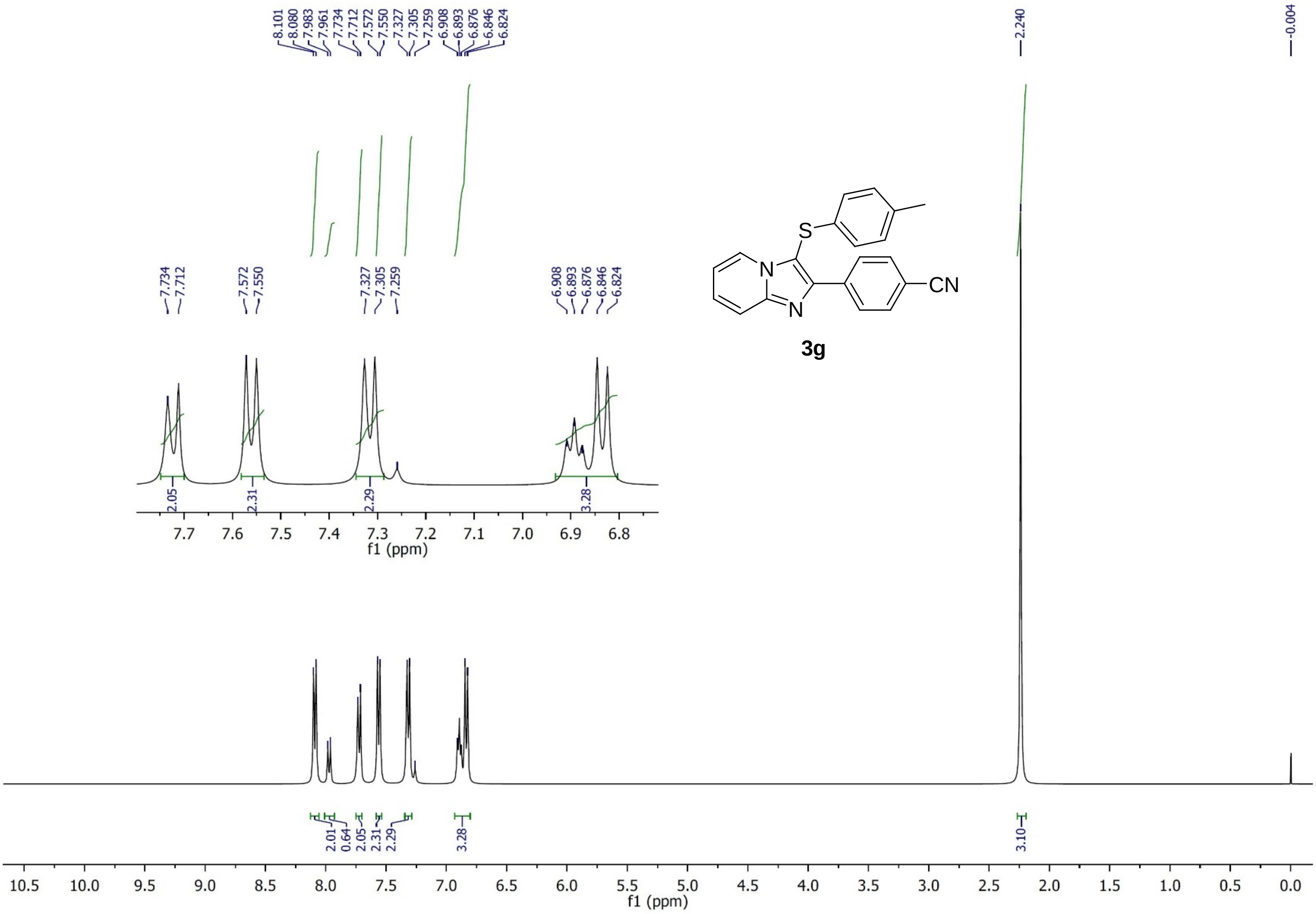
3f

^{13}C NMR of compound **3f** ($CDCl_3$, 100 MHz)

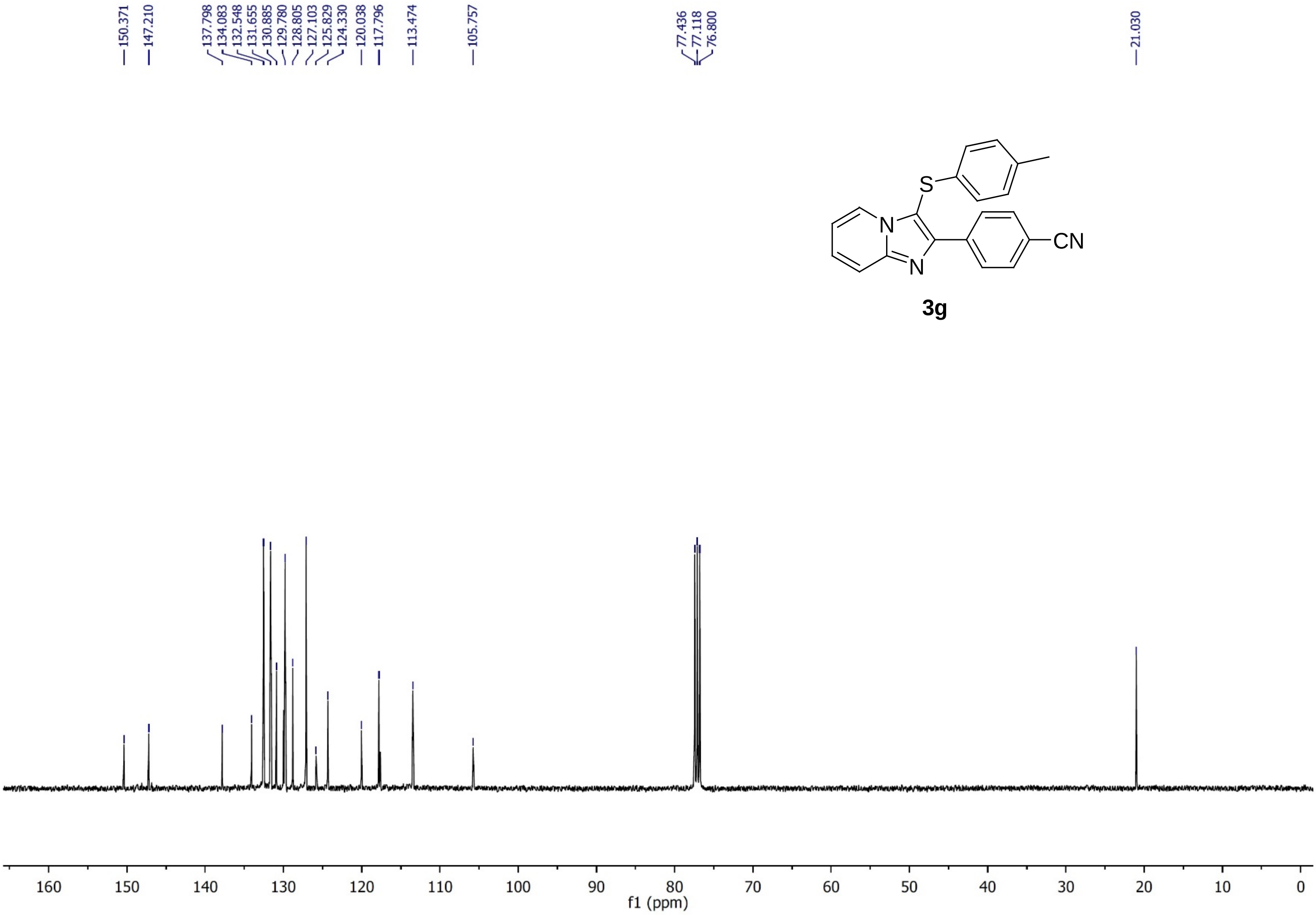


3f

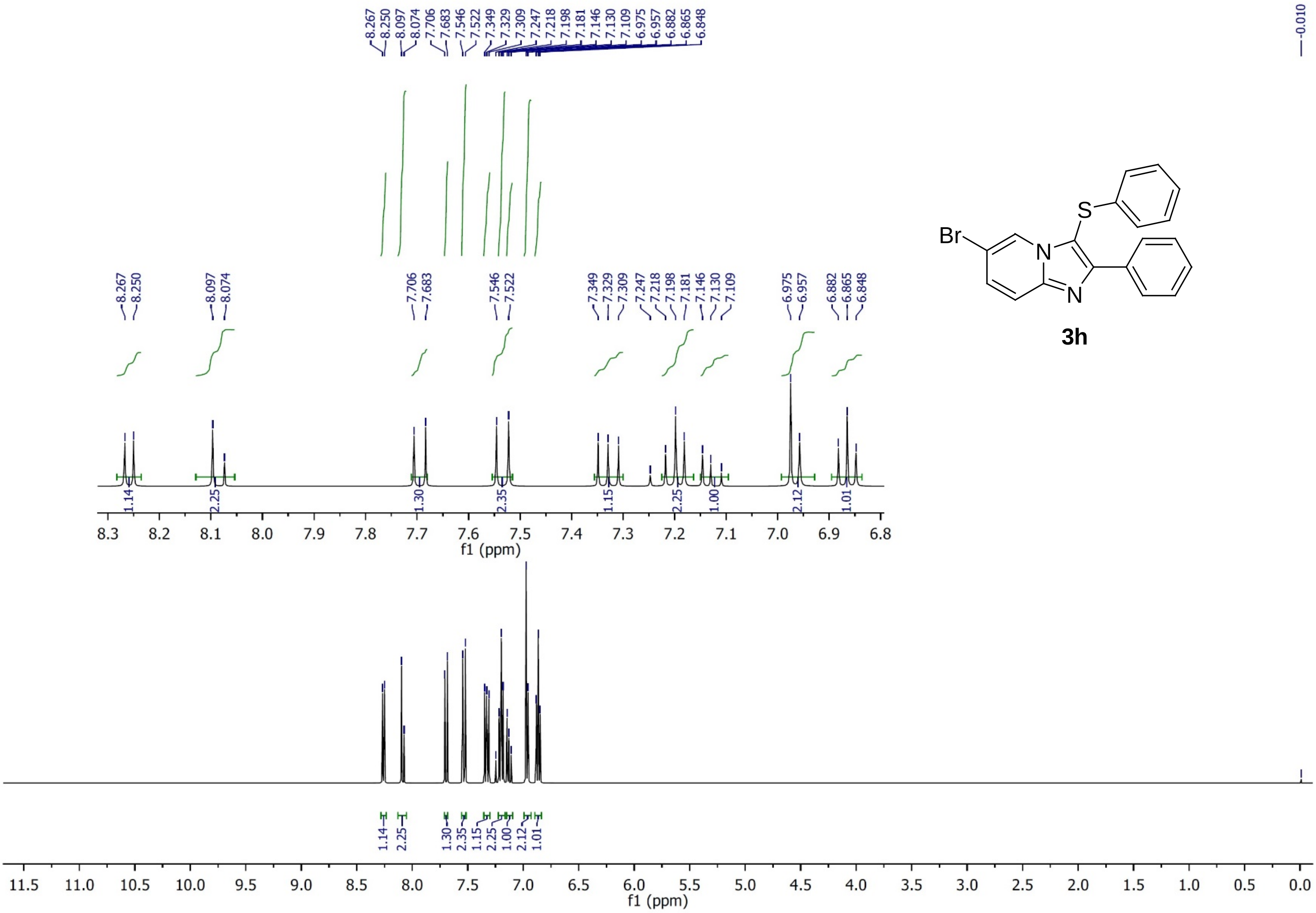
^1H NMR of compound **3g** ($CDCl_3$, 400 MHz)



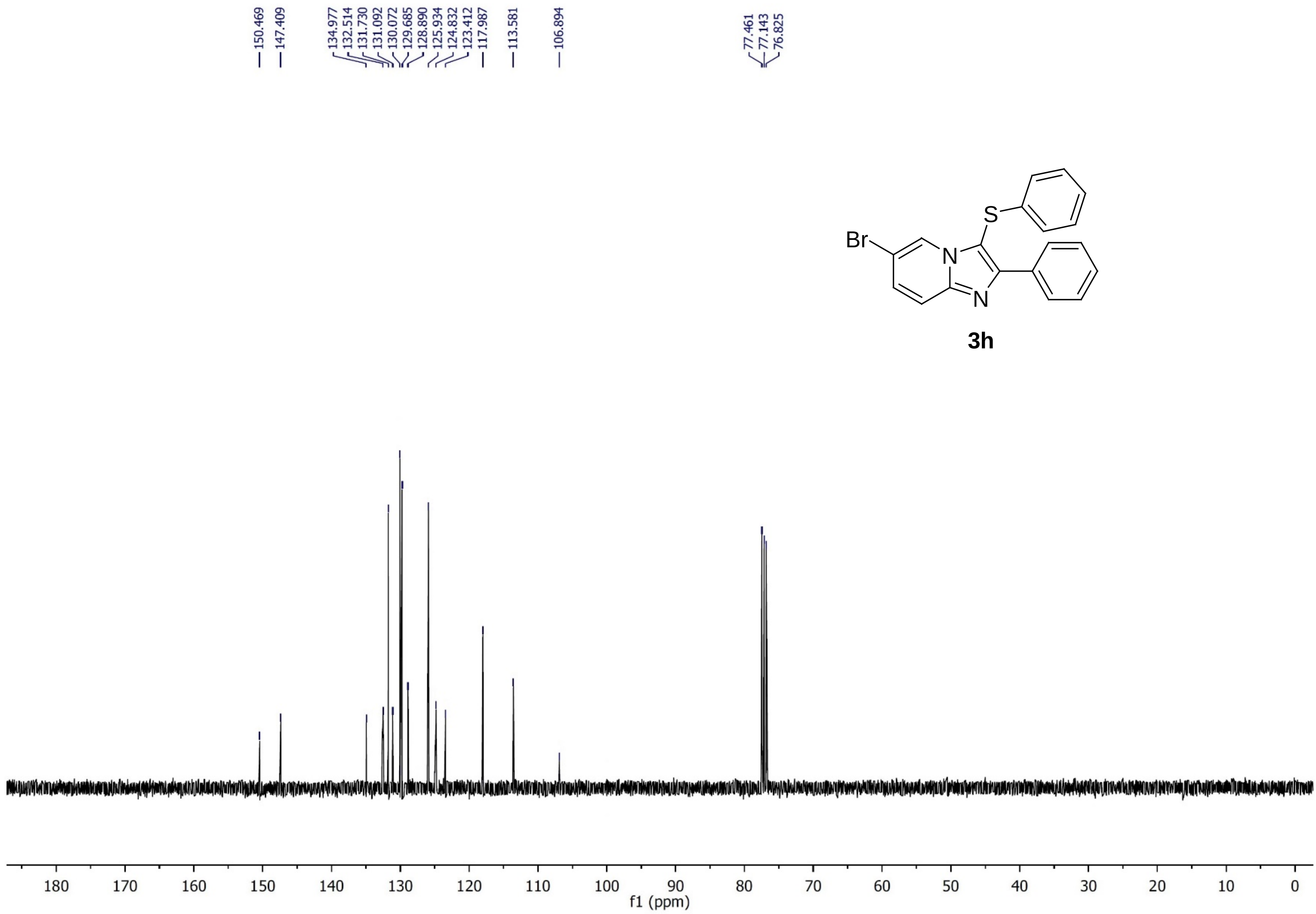
^{13}C NMR of compound **3g** ($CDCl_3$, 100 MHz)



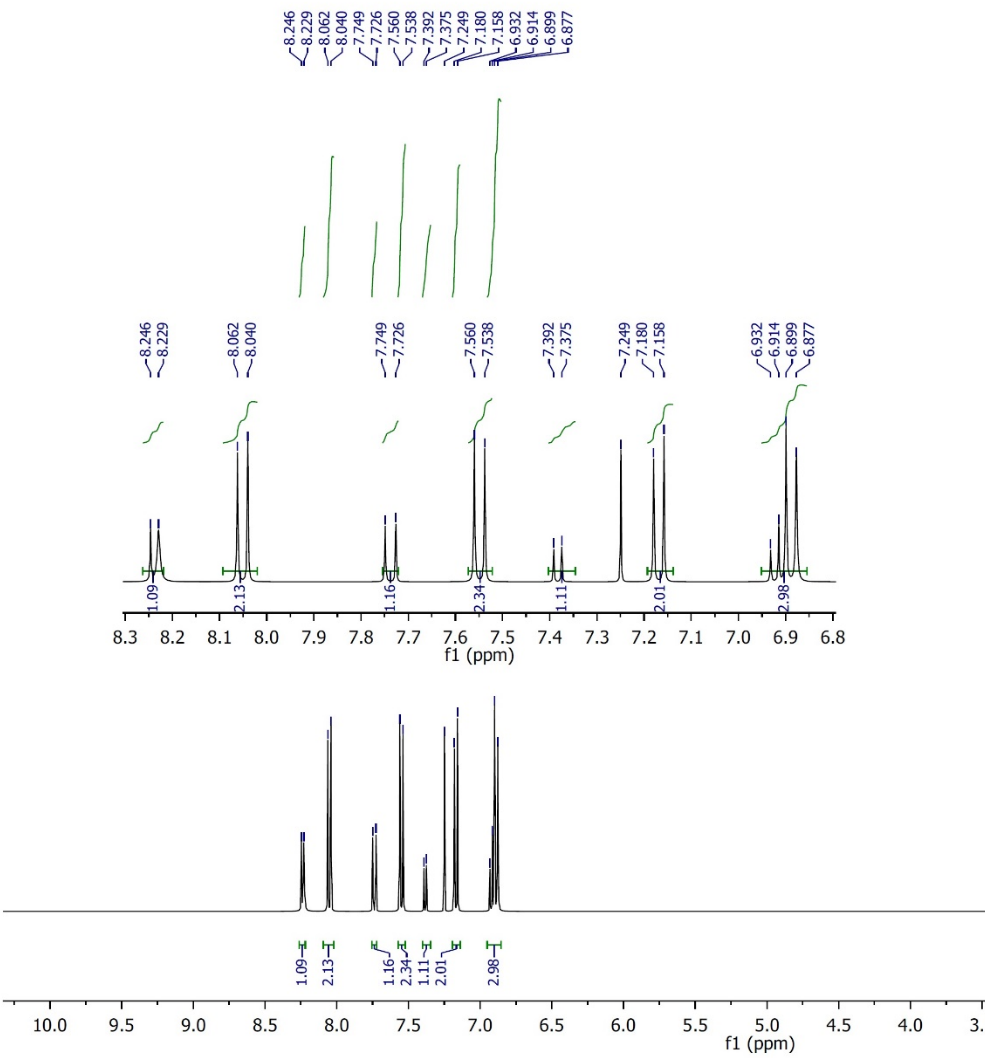
[1]H NMR of compound **3h** ($CDCl_3$, 400 MHz)

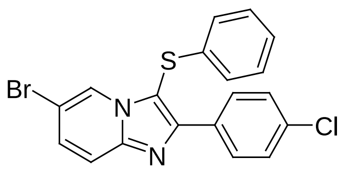


^{13}C NMR of compound **3h** ($CDCl_3$, 100 MHz)



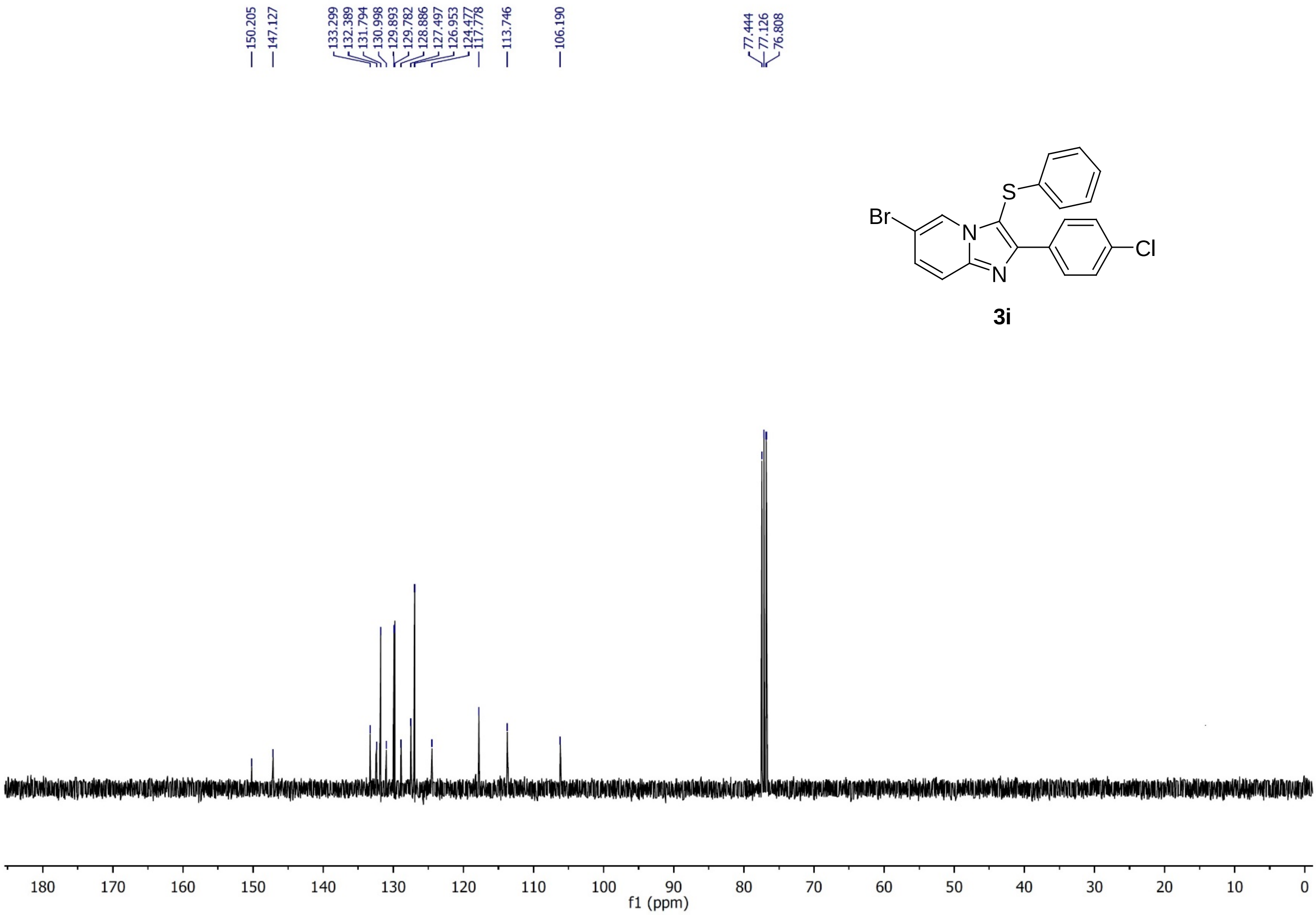
[1]H NMR of compound **3i** ($CDCl_3$, 400 MHz)





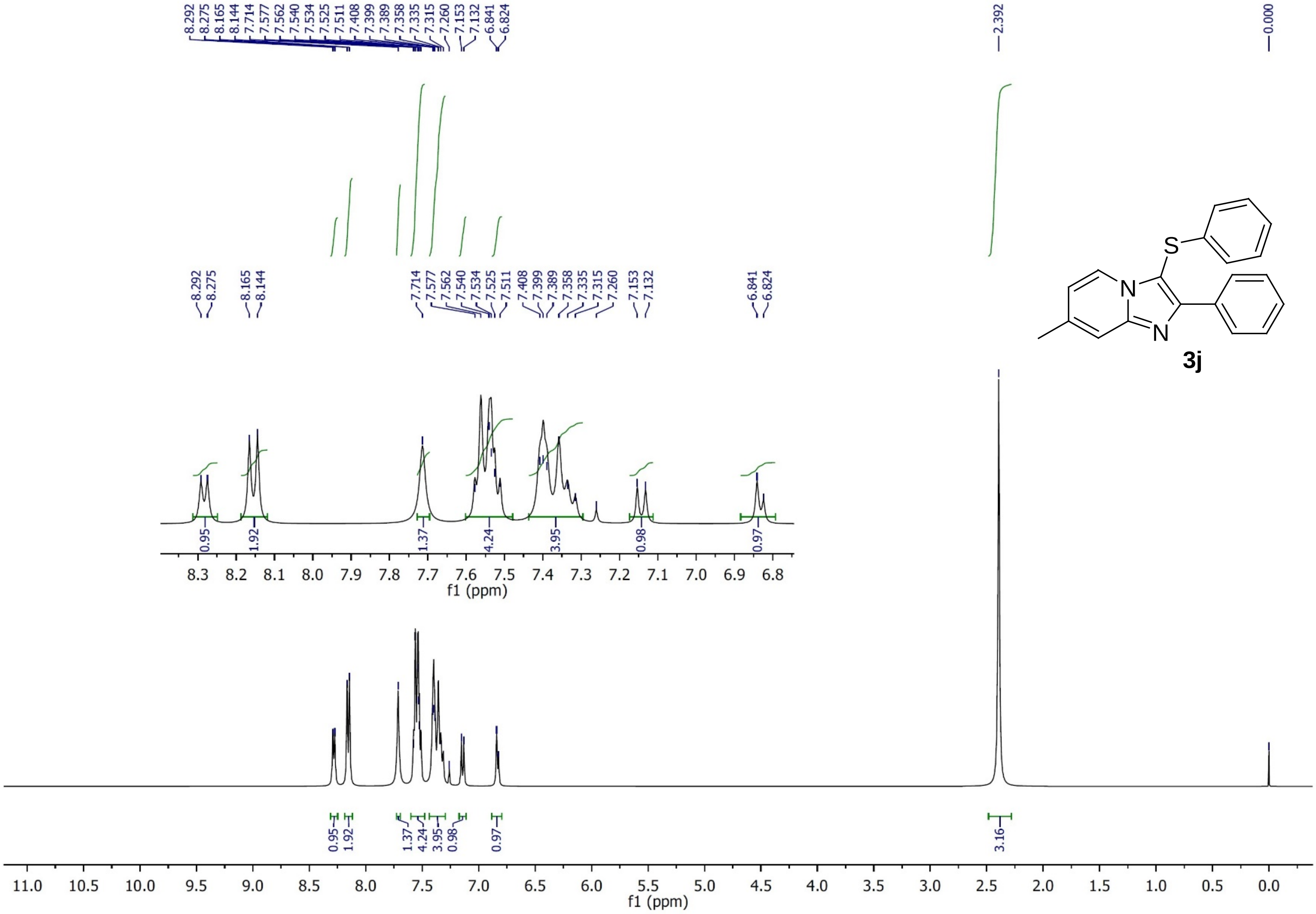
3i

^{13}C NMR of compound **3i** ($CDCl_3$, 100 MHz)

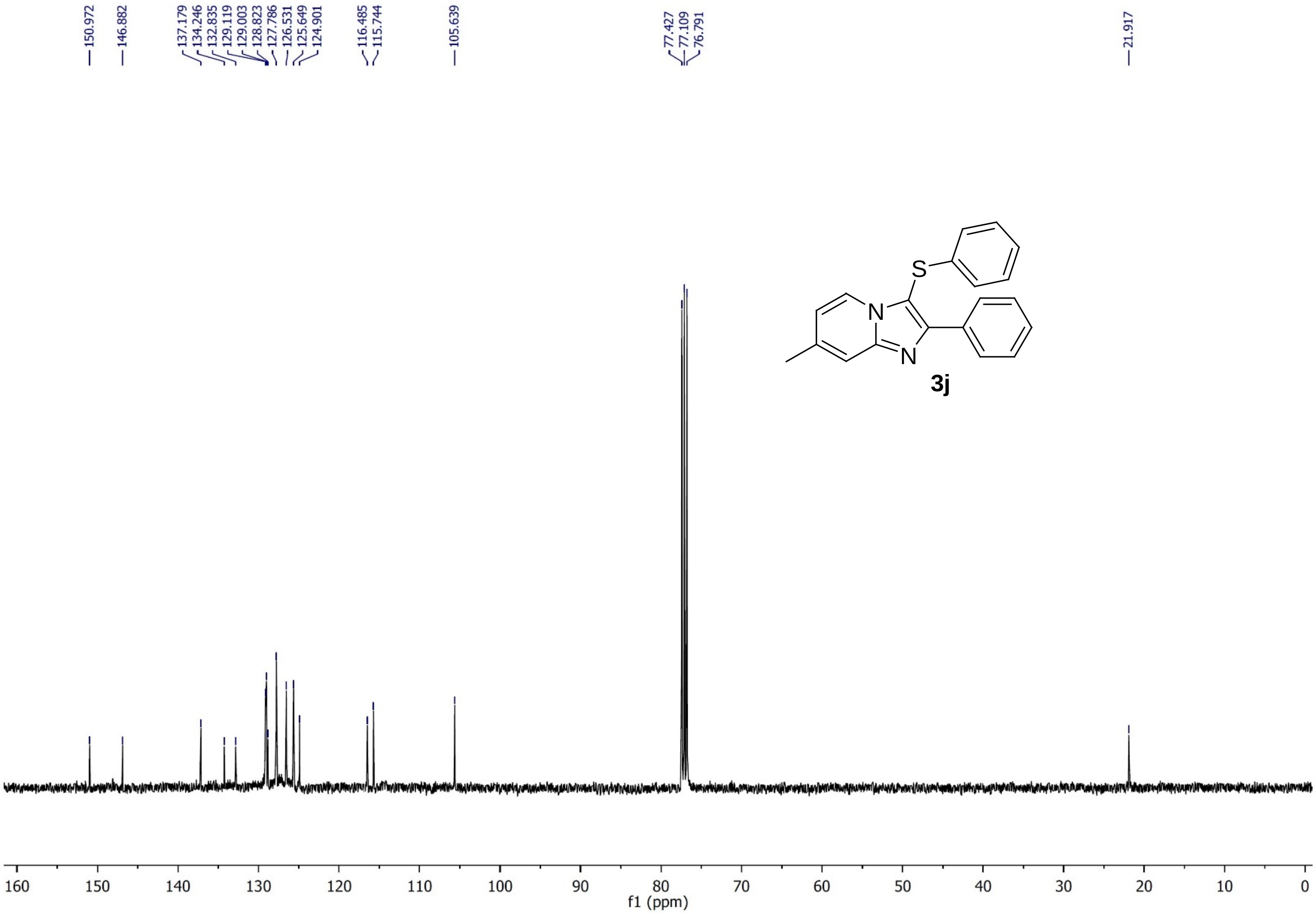


3i

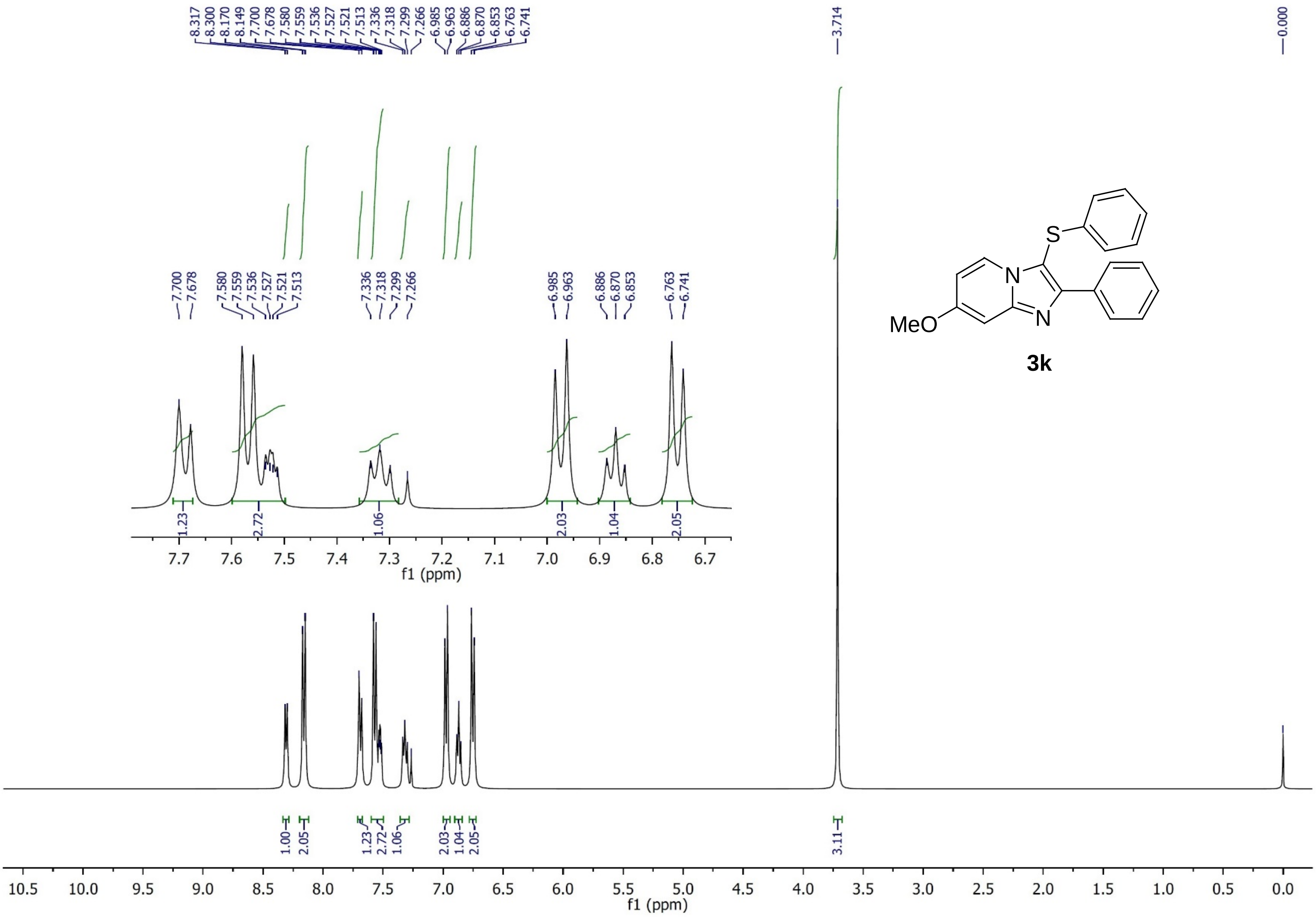
^{1}H NMR of compound **3j** ($CDCl_3$, 400 MHz)



^{13}C NMR of compound **3j** ($CDCl_3$, 100 MHz)

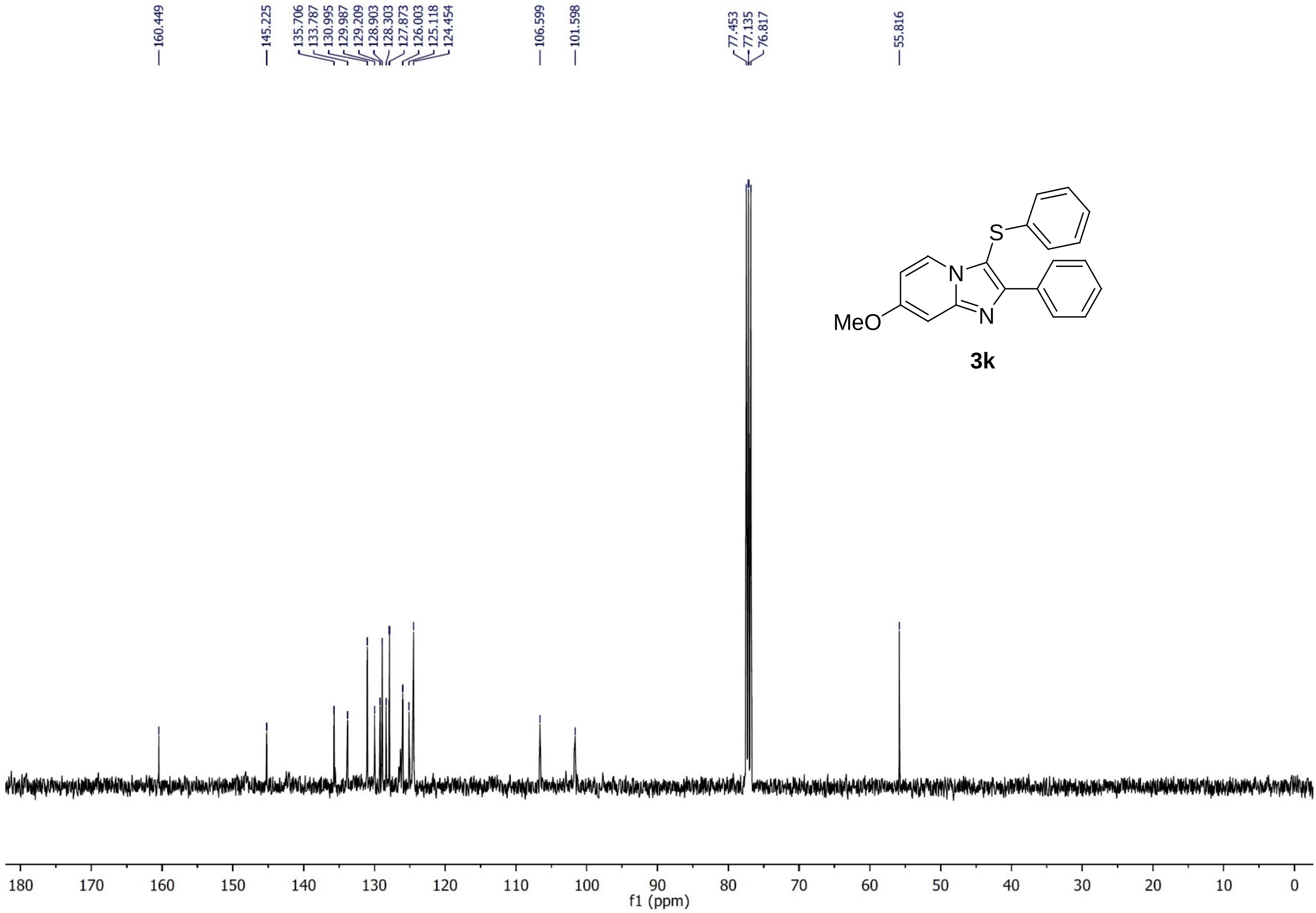


[1]H NMR of compound **3k** ($CDCl_3$, 400 MHz)

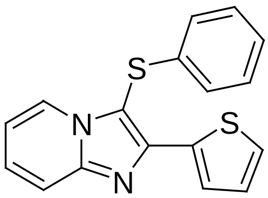


3k

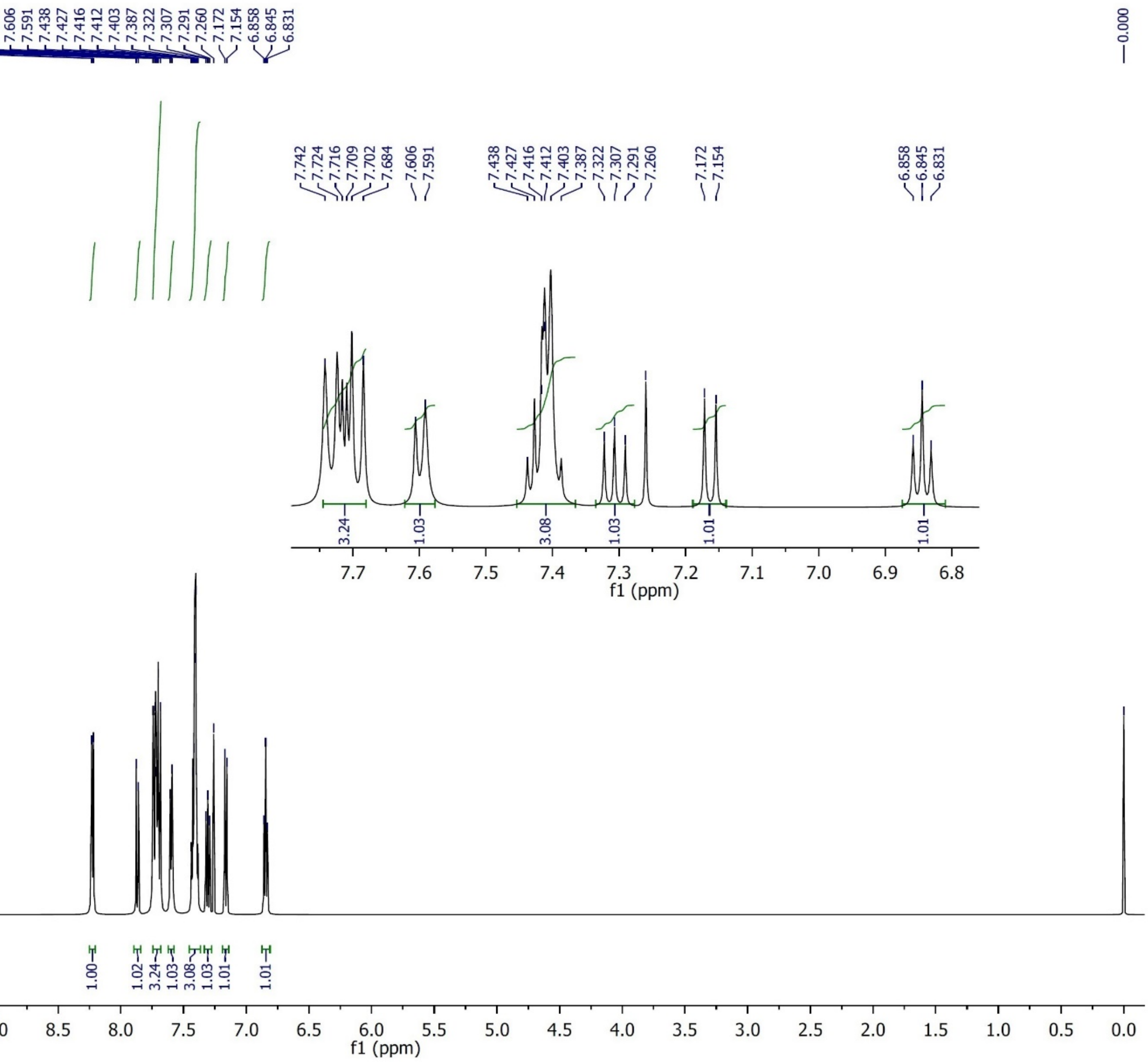
^{13}C NMR of compound **3k** ($CDCl_3$, 100 MHz)



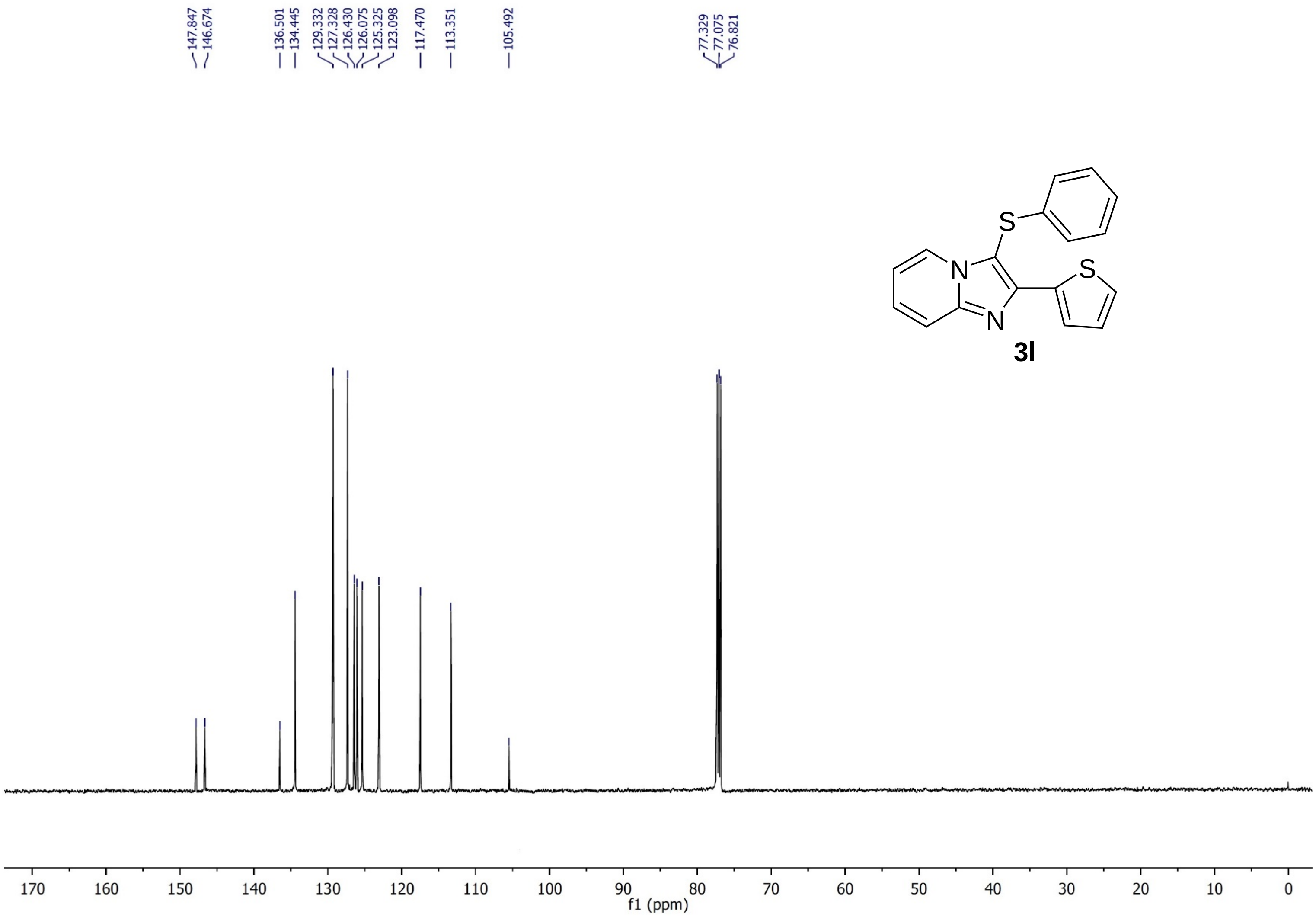
[1]H NMR of compound **3l** ($CDCl_3$, 500 MHz)



3l

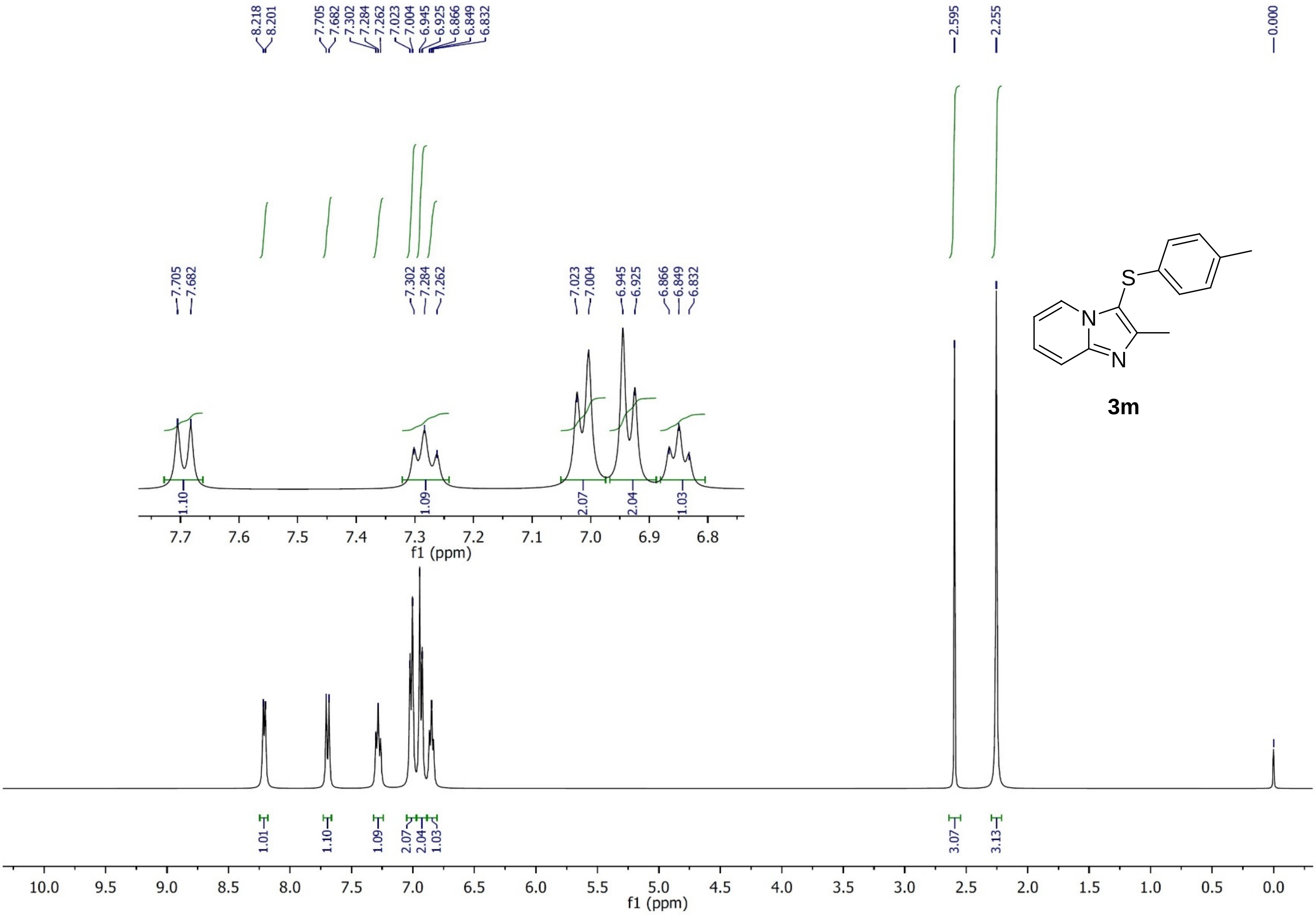


^{13}C NMR of compound **3l** ($CDCl_3$, 125 MHz)

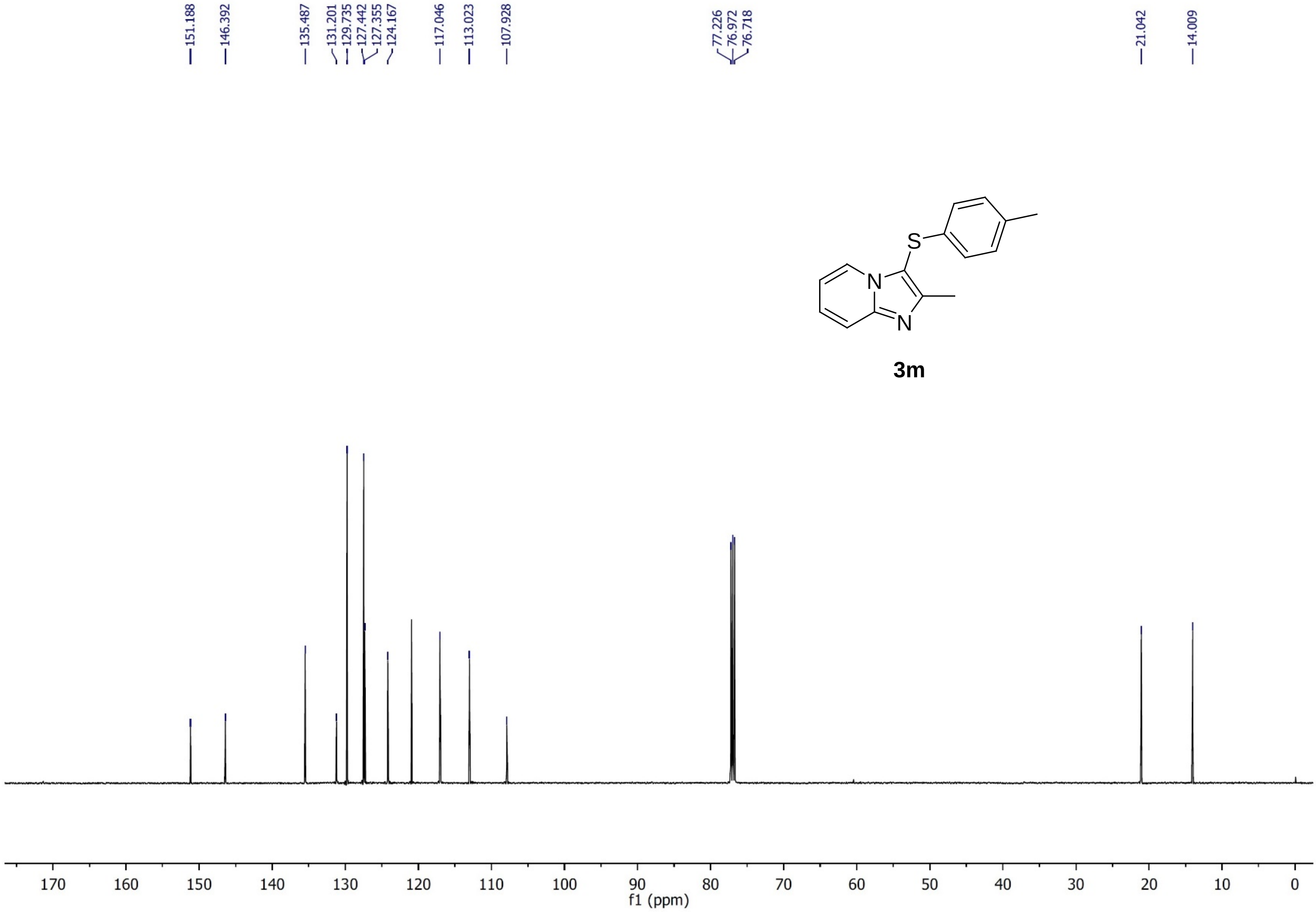


3l

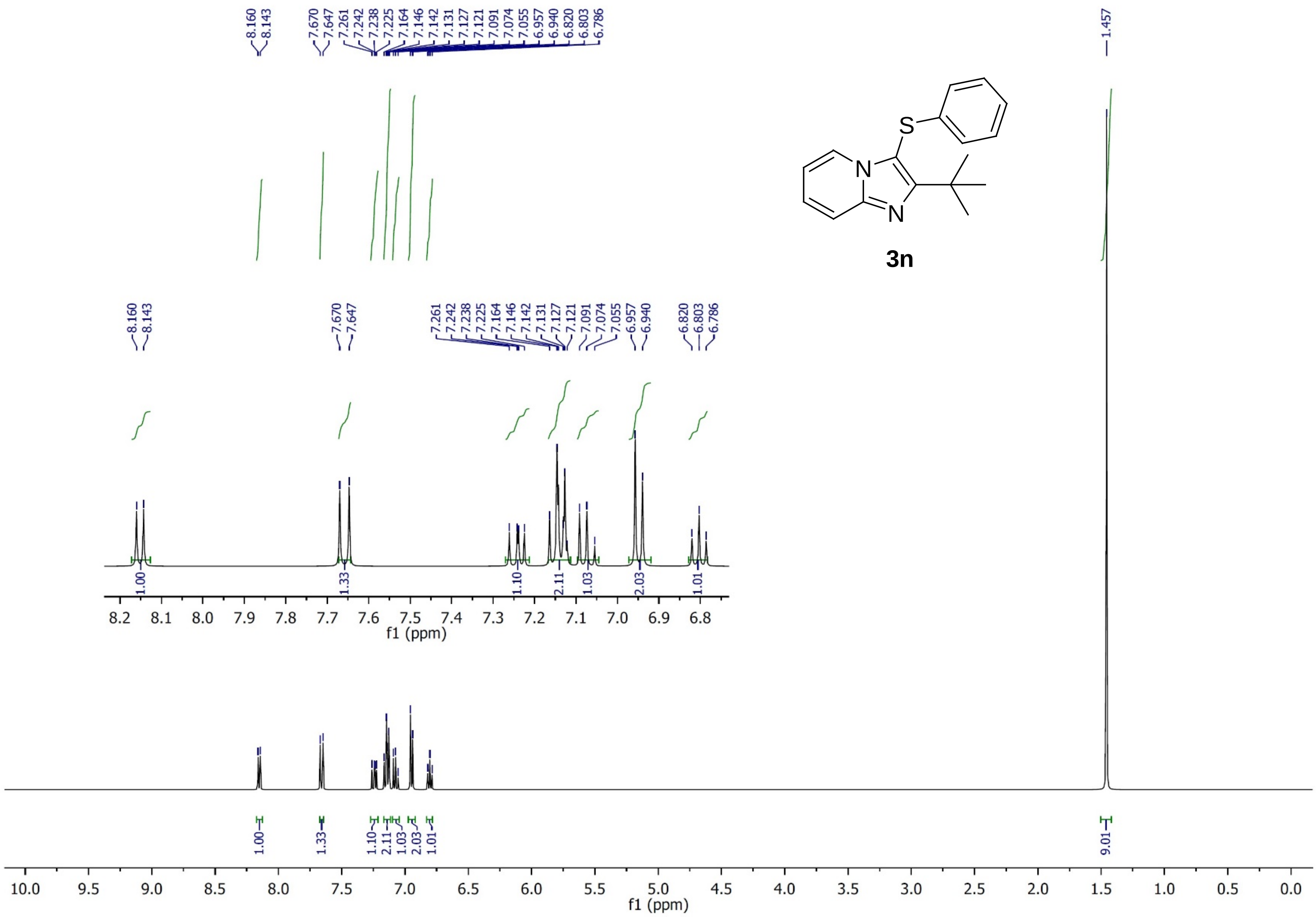
[1]H NMR of compound **3m** ($CDCl_3$, 400 MHz)



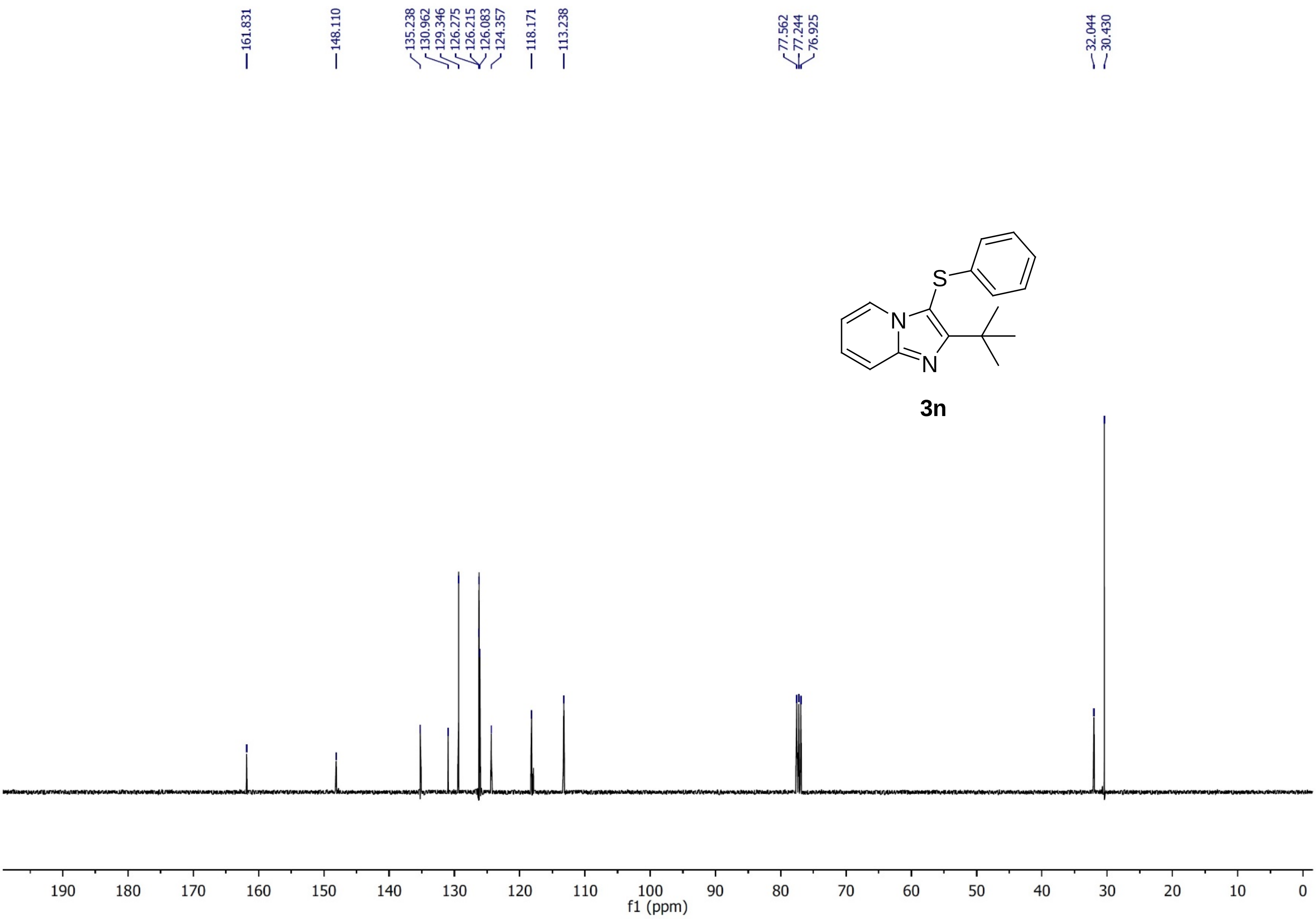
^{13}C NMR of compound **3m** ($CDCl_3$, 100 MHz)



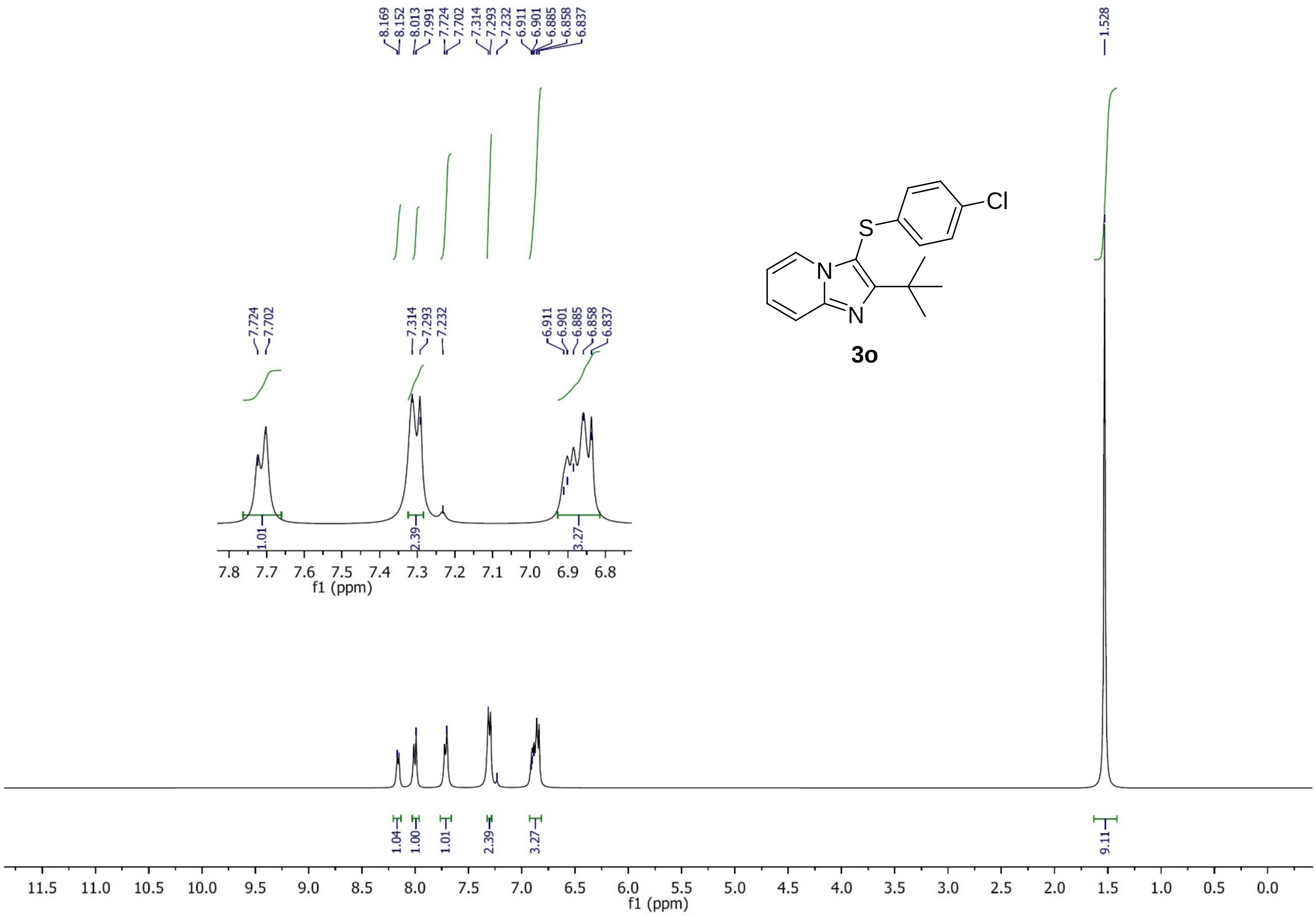
^{1}H NMR of compound **3n** ($CDCl_3$, 400 MHz)



^{13}C NMR of compound **3n** ($CDCl_3$, 100 MHz)

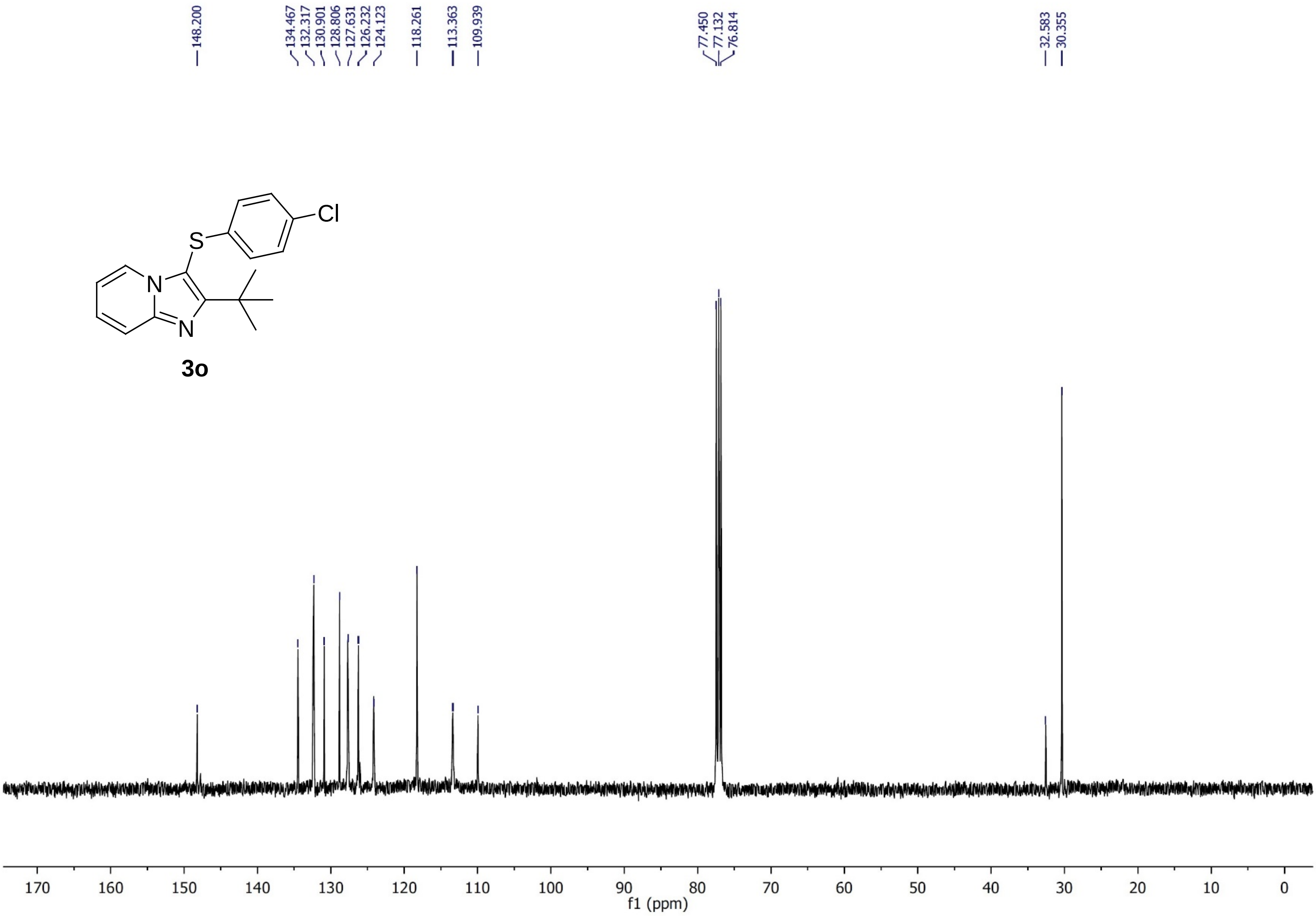


[1]H NMR of compound **3o** ($CDCl_3$, 400 MHz)

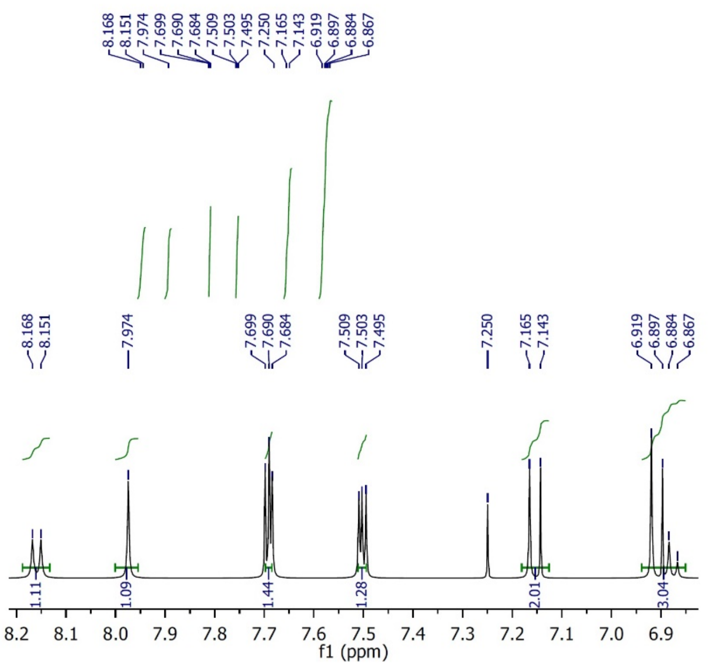


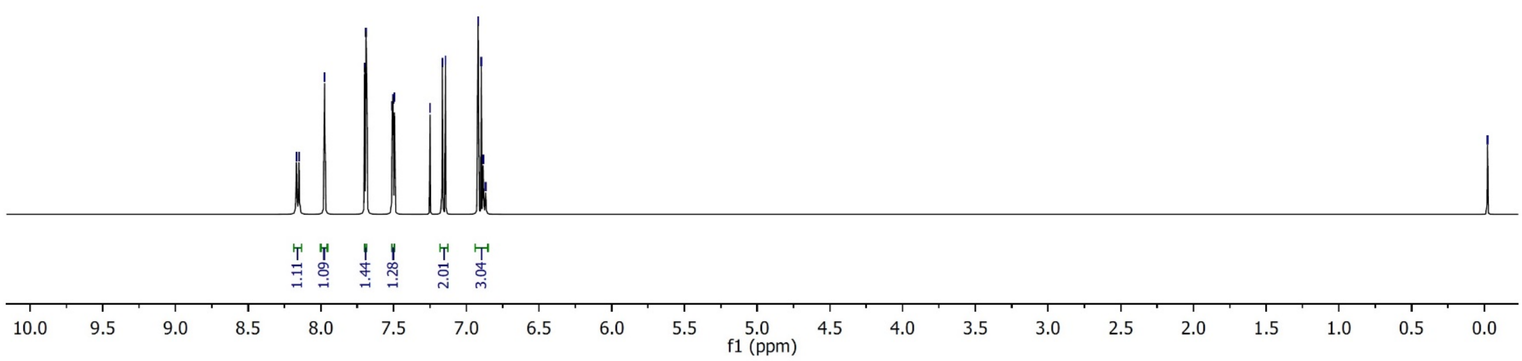
3o

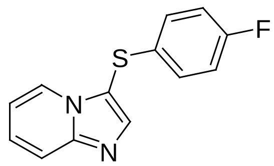
^{13}C NMR of compound **3o** ($CDCl_3$, 100 MHz)



^{1}H NMR of compound **3p** ($CDCl_3$, 400 MHz)

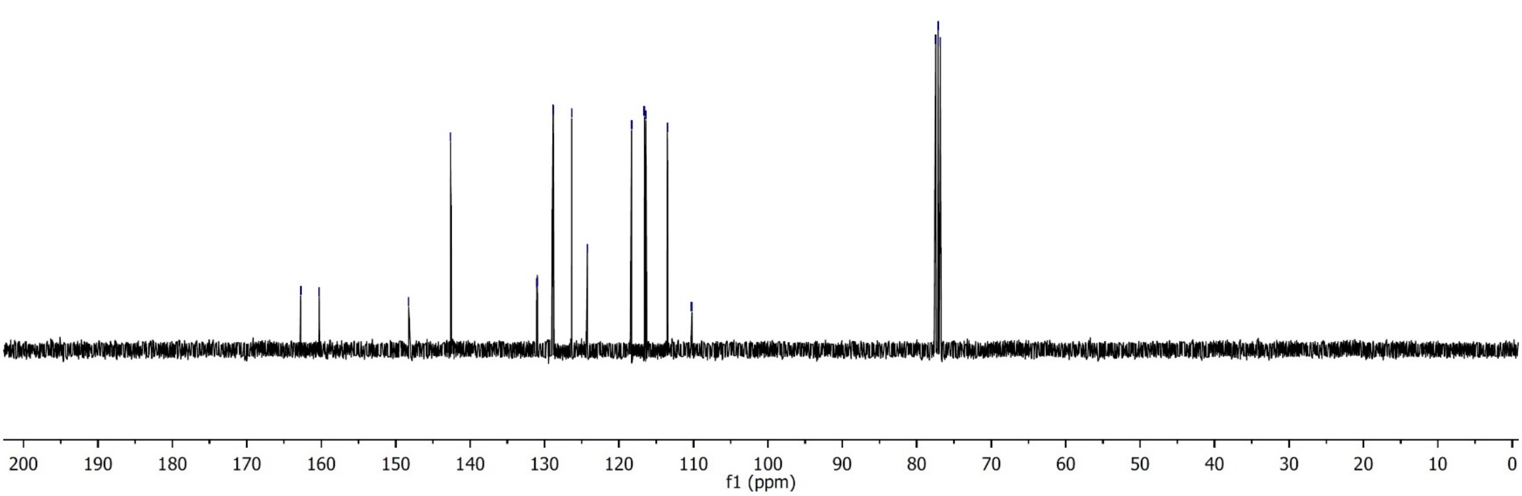


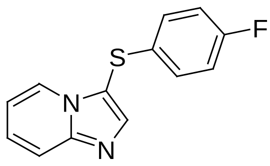




3p

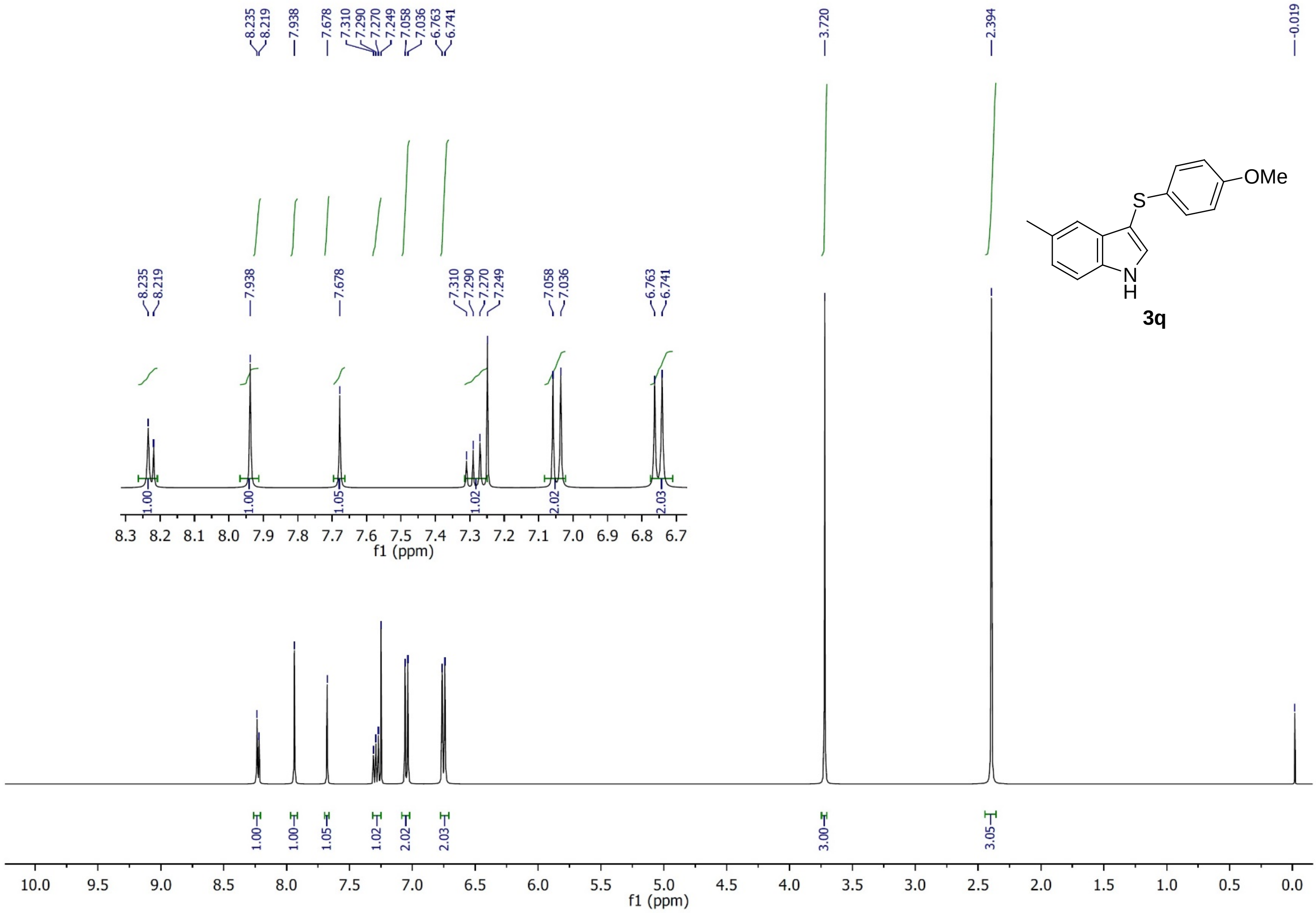
^{13}C NMR of compound **3p** ($CDCl_3$, 100 MHz)



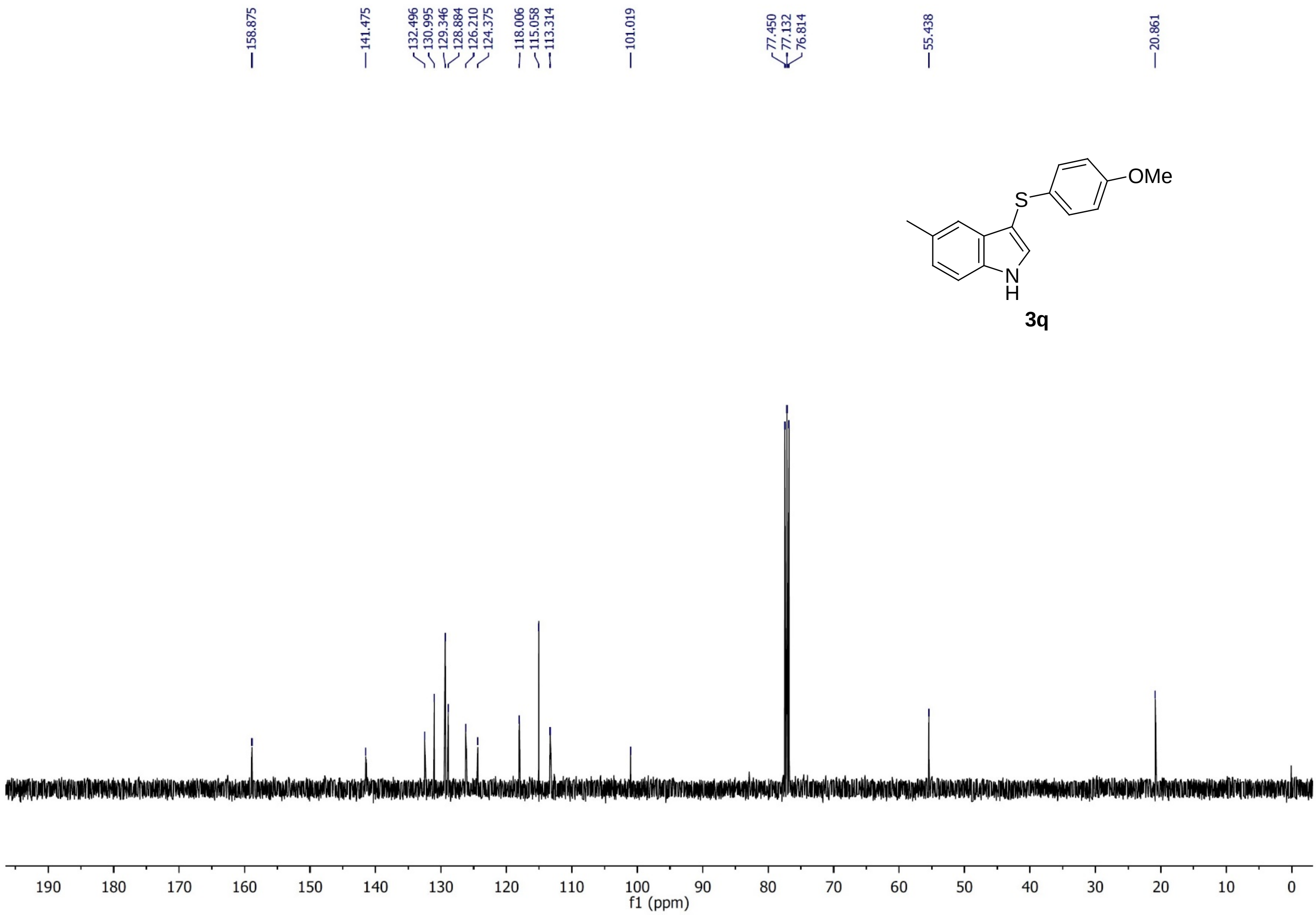


3p

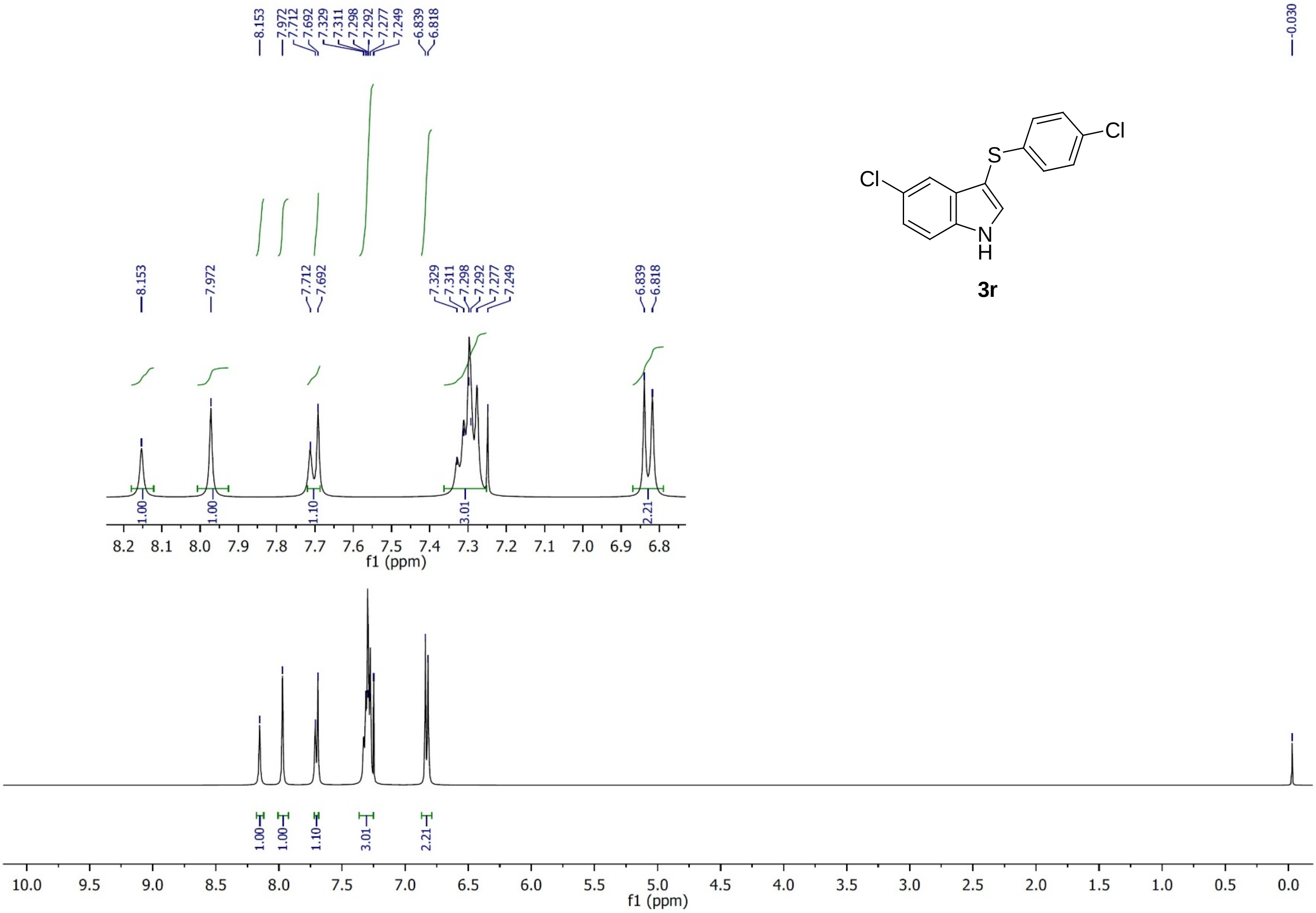
^{1}H NMR of compound **3q** ($CDCl_3$, 400 MHz)



^{13}C NMR of compound **3q** ($CDCl_3$, 100 MHz)

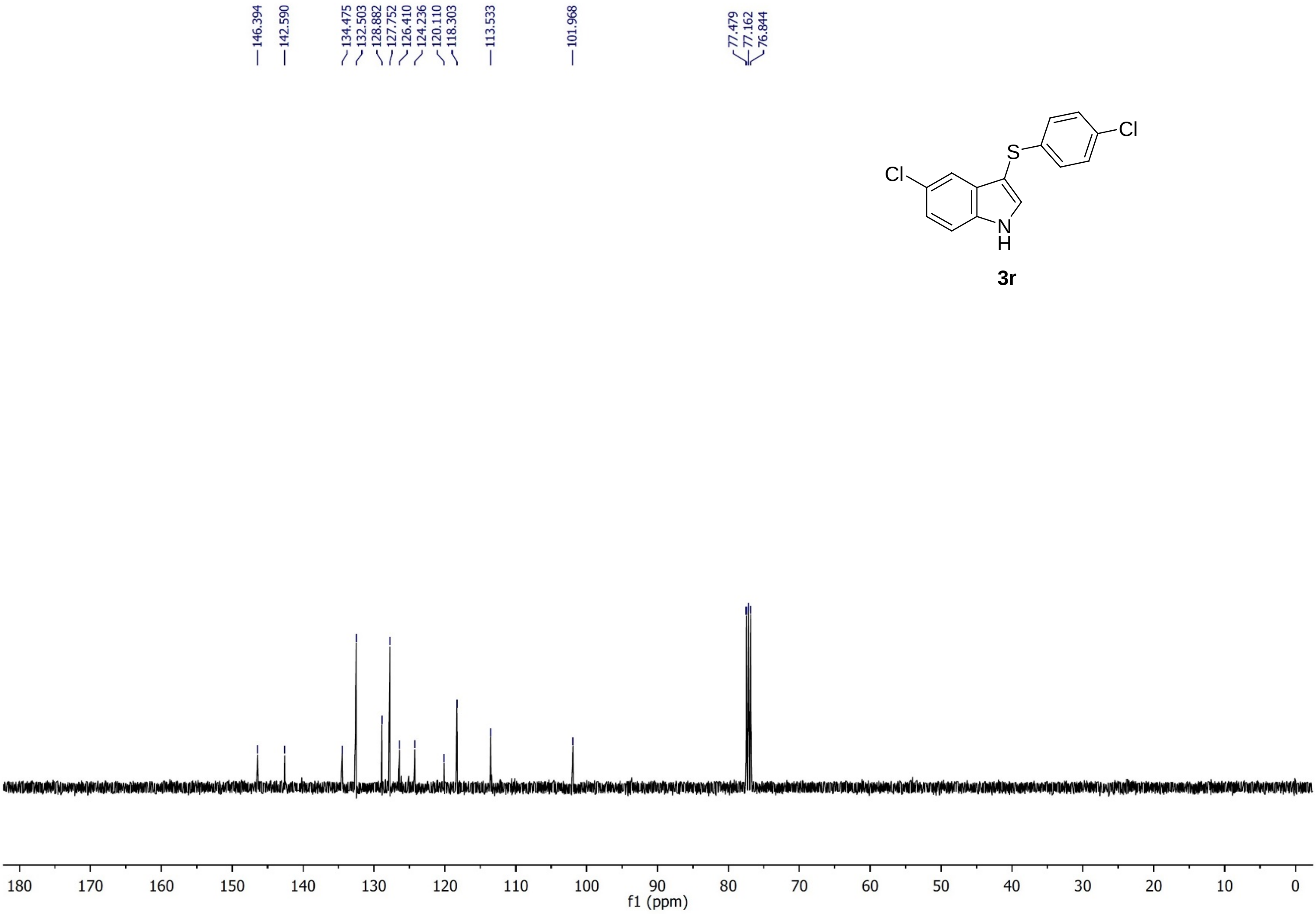


^{1}H NMR of compound **3r** ($CDCl_3$, 400 MHz)



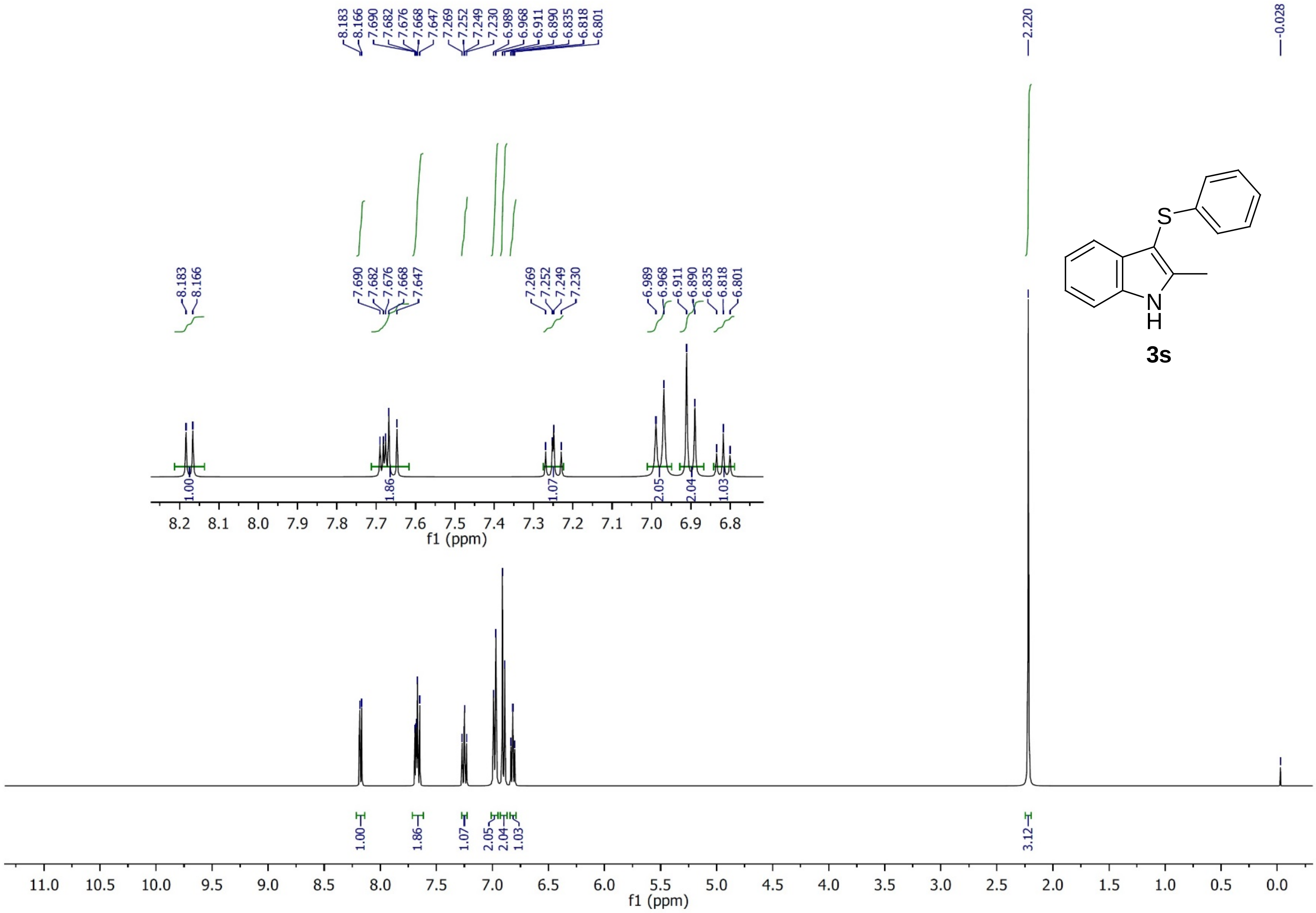
3r

^{13}C NMR of compound **3r** ($CDCl_3$, 100 MHz)



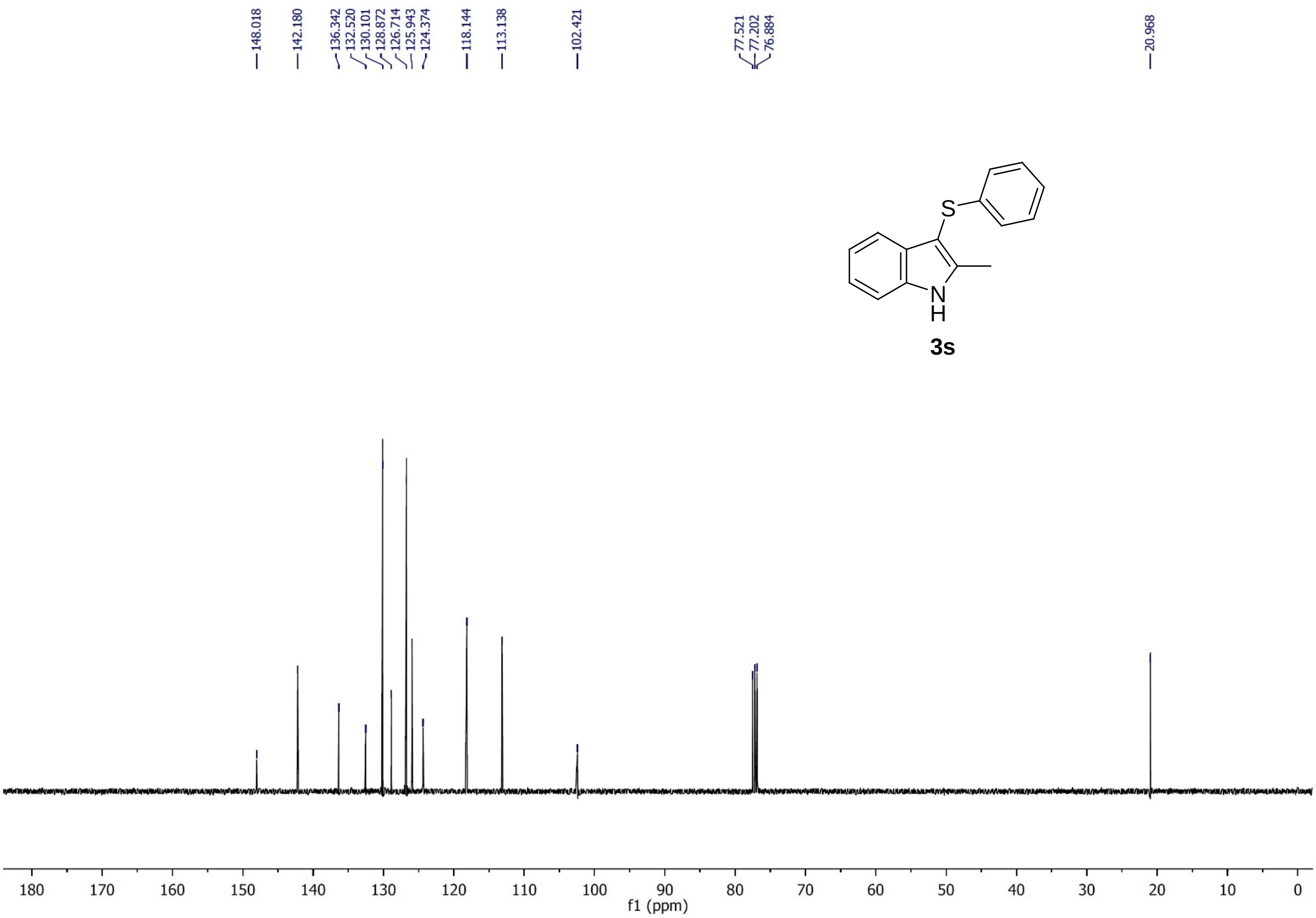
3r

^{1}H NMR of compound **3s** ($CDCl_3$, 400 MHz)

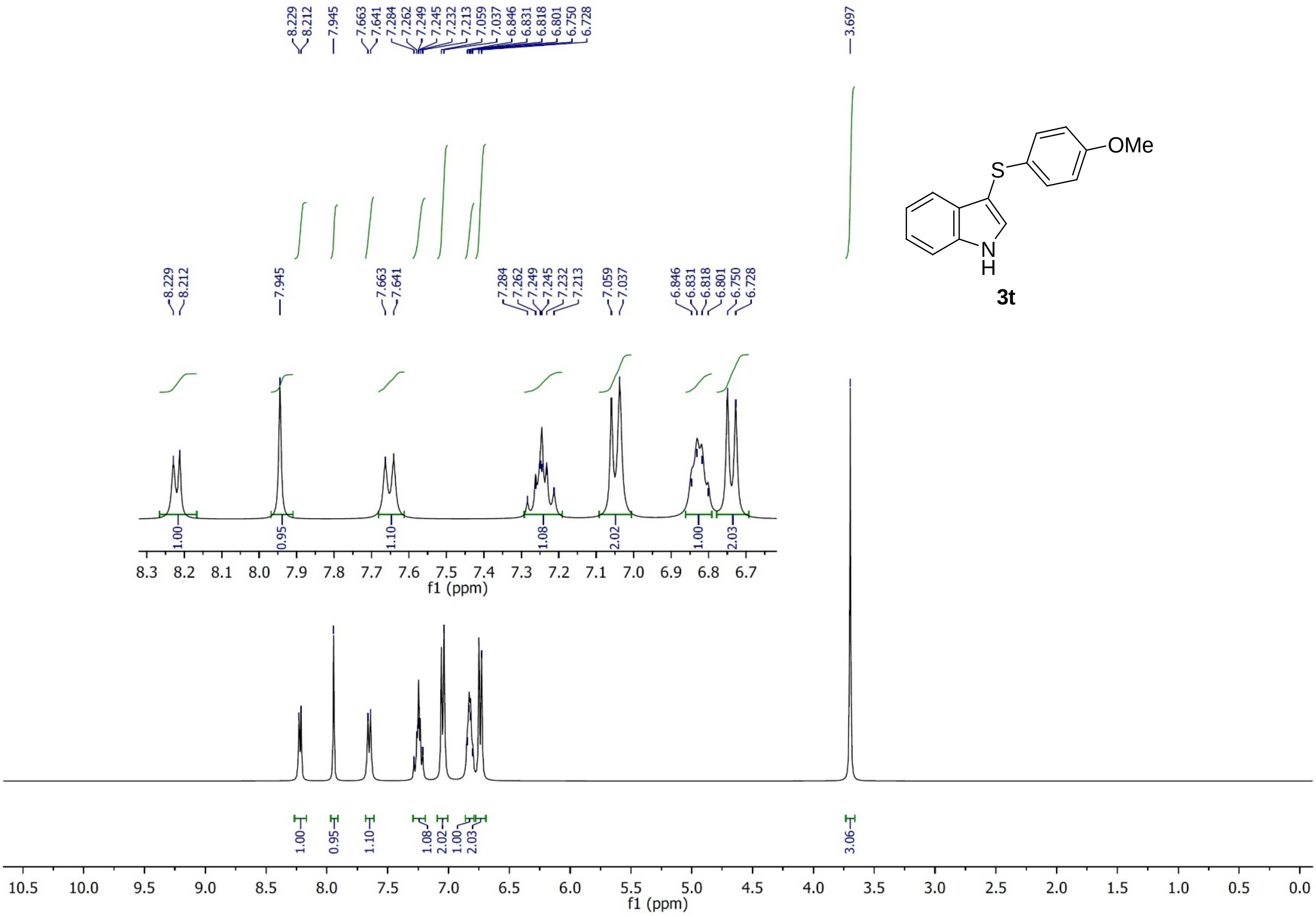


3s

^{13}C NMR of compound **3s** ($CDCl_3$, 100 MHz)

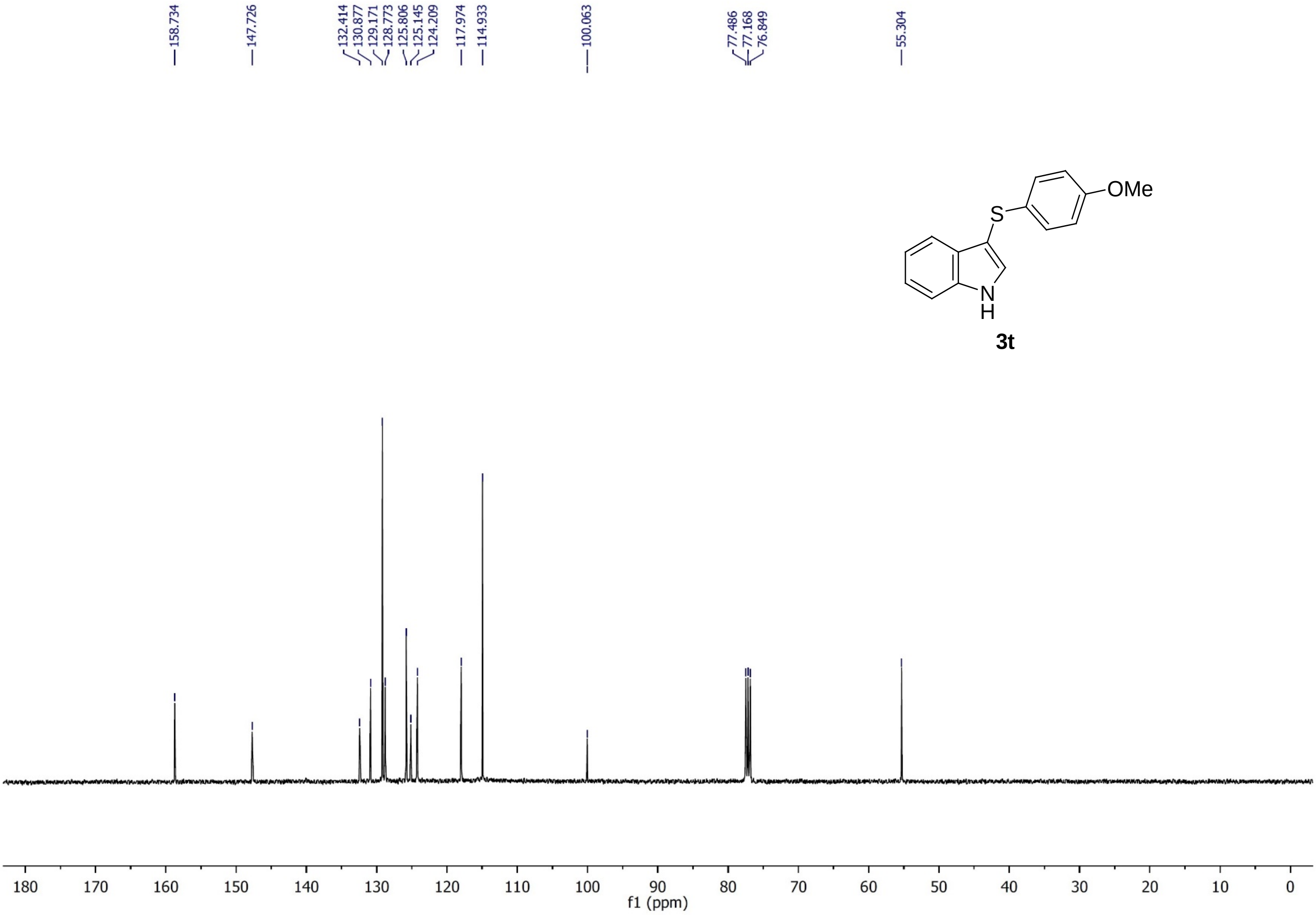


[1]H NMR of compound **3t** ($CDCl_3$, 400 MHz)



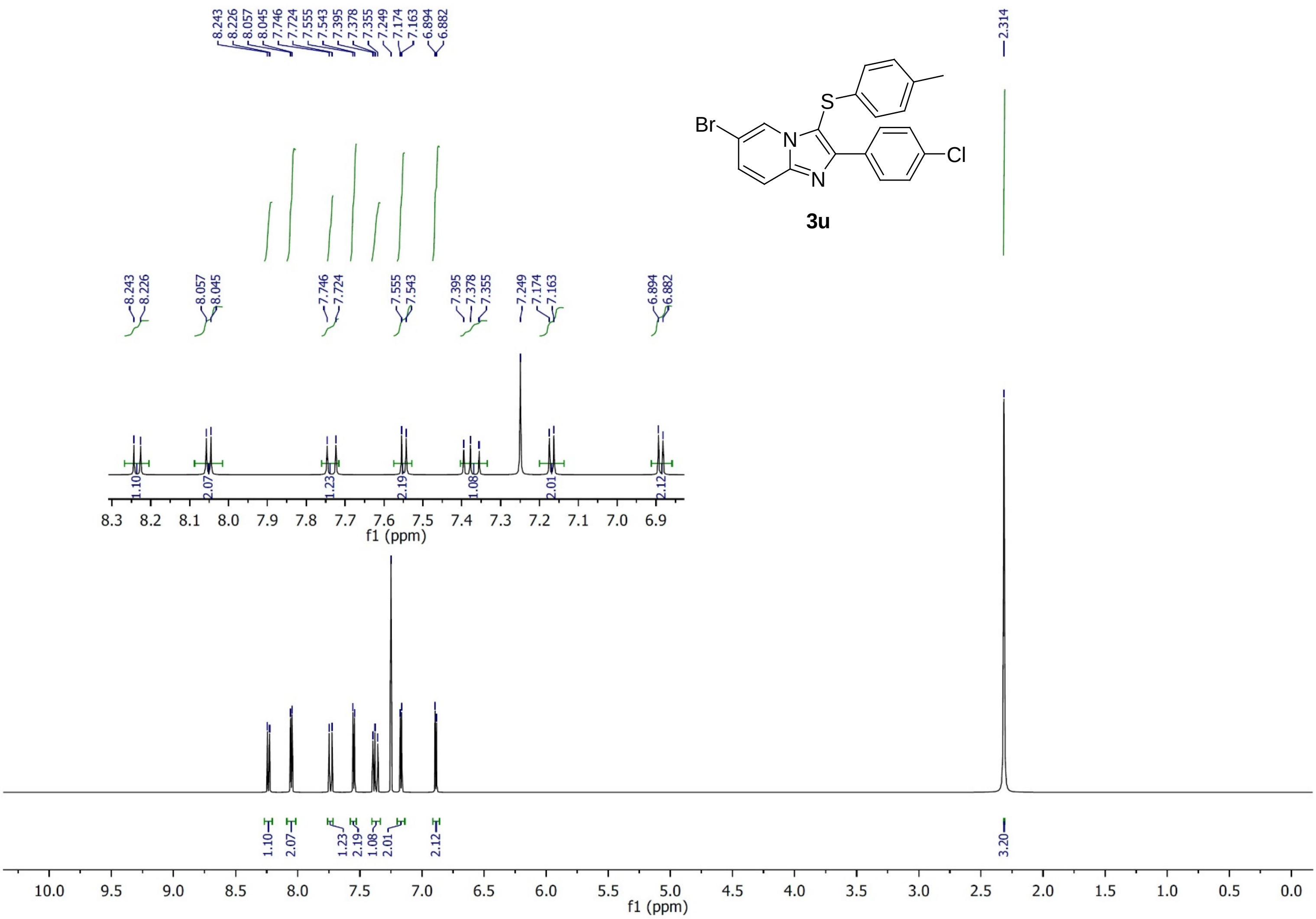
3t

^{13}C NMR of compound **3t** ($CDCl_3$, 100 MHz)

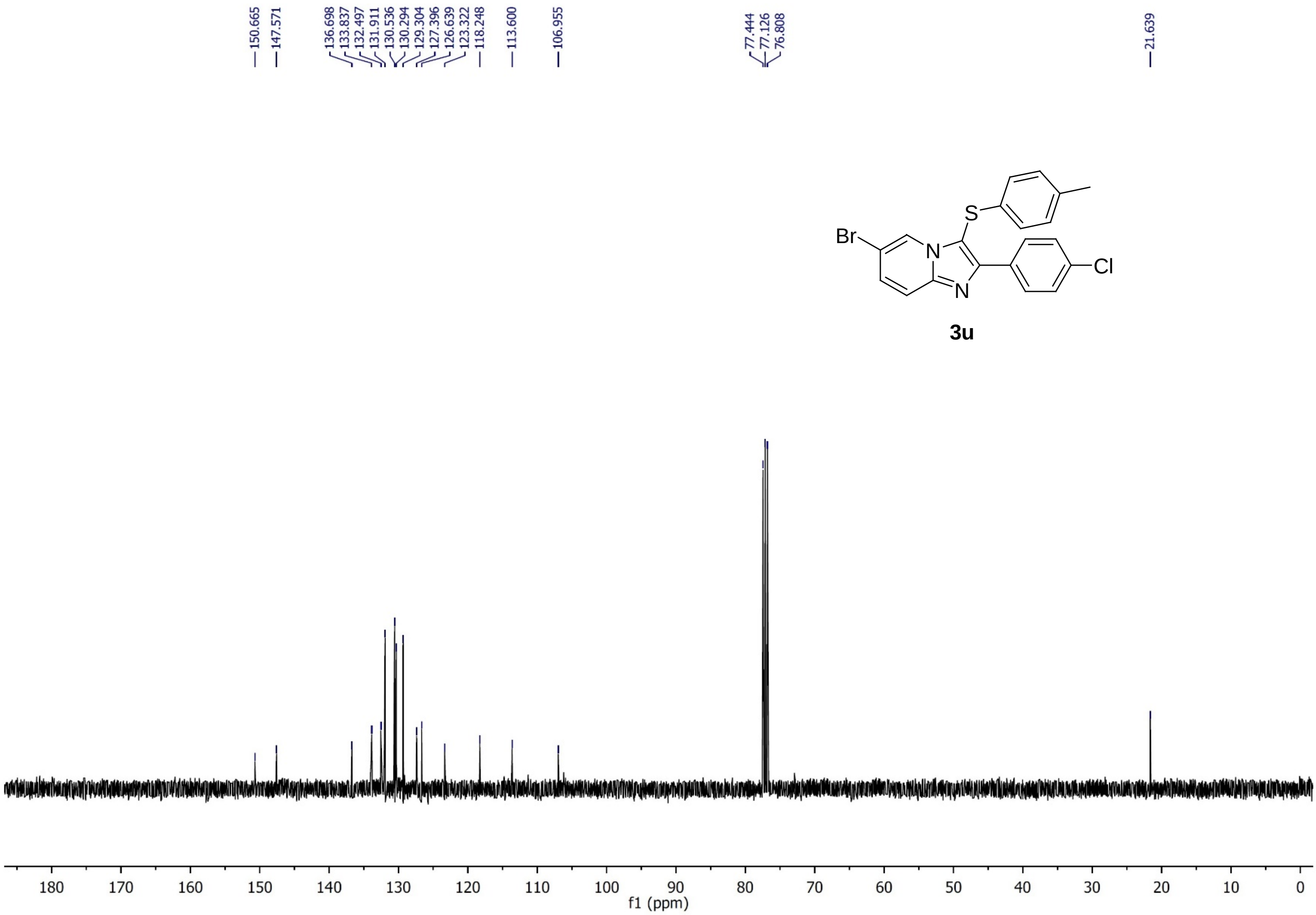


3t

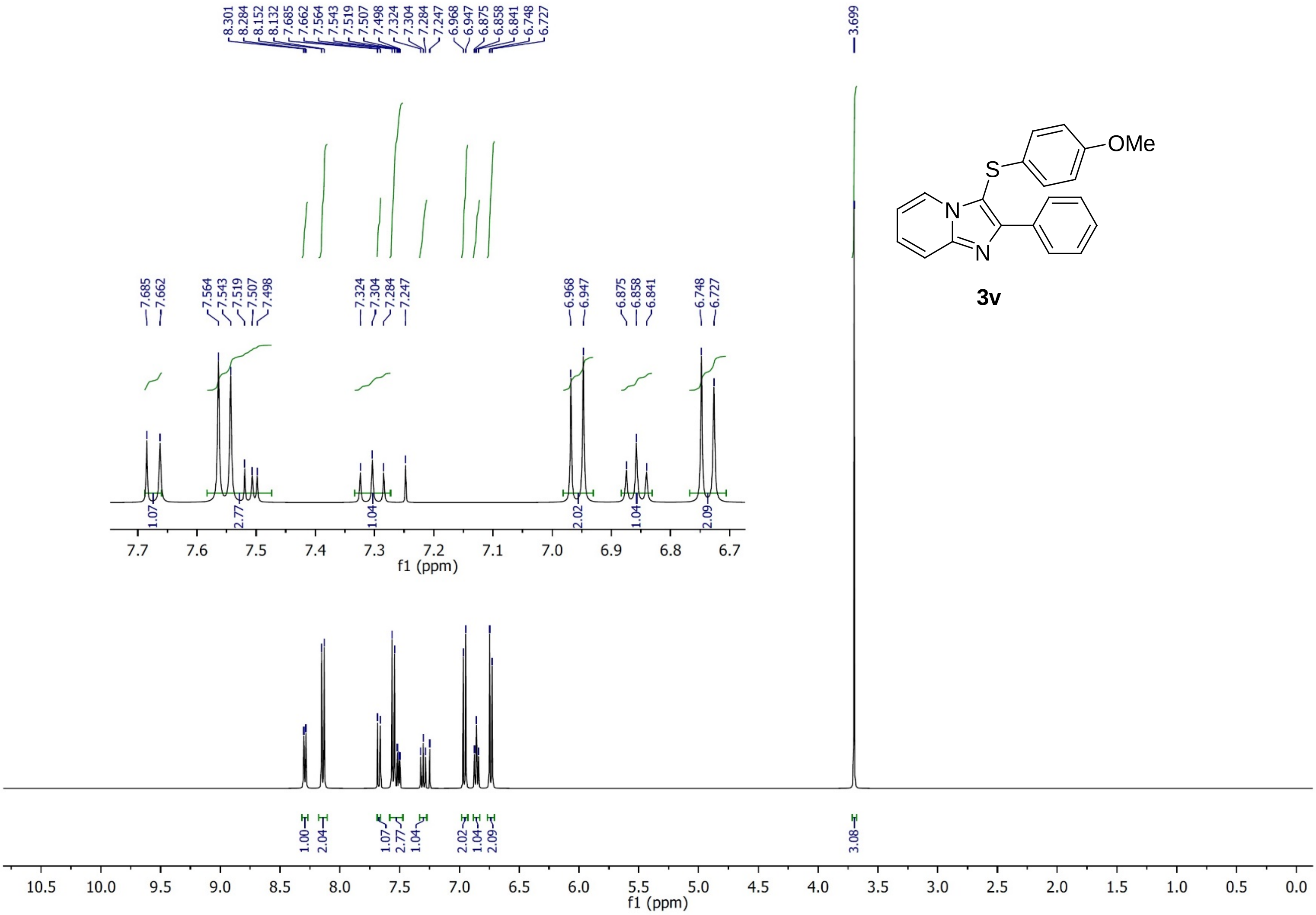
[1]H NMR of compound **3u** ($CDCl_3$, 400 MHz)



^{13}C NMR of compound **3u** ($CDCl_3$, 100 MHz)

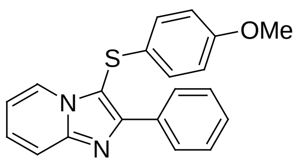


^1H NMR of compound **3v** ($CDCl_3$, 400 MHz)

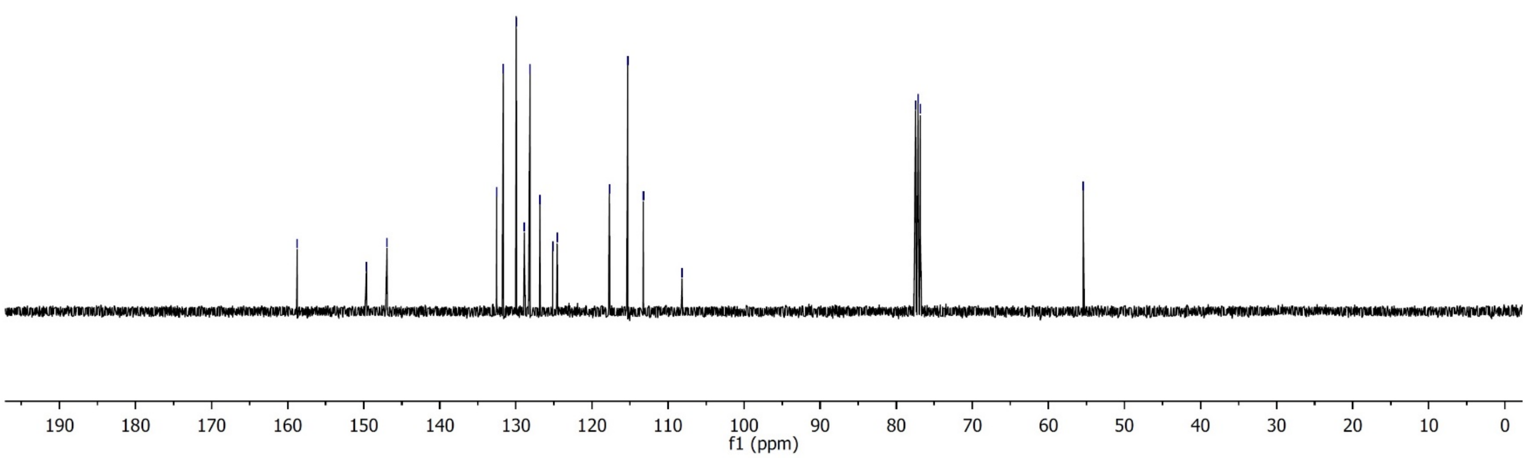


3v

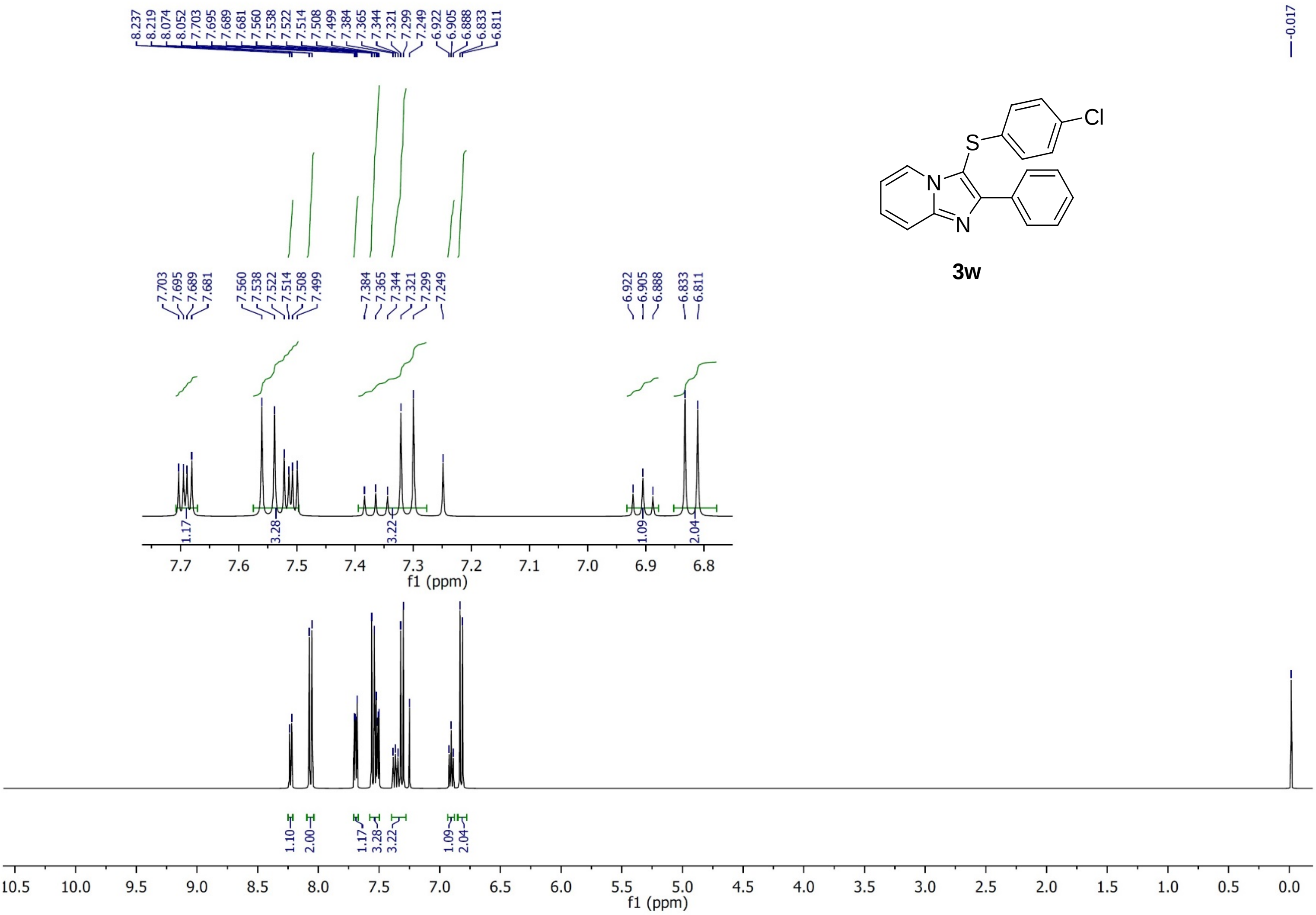
^{13}C NMR of compound **3v** ($CDCl_3$, 100 MHz)



3v

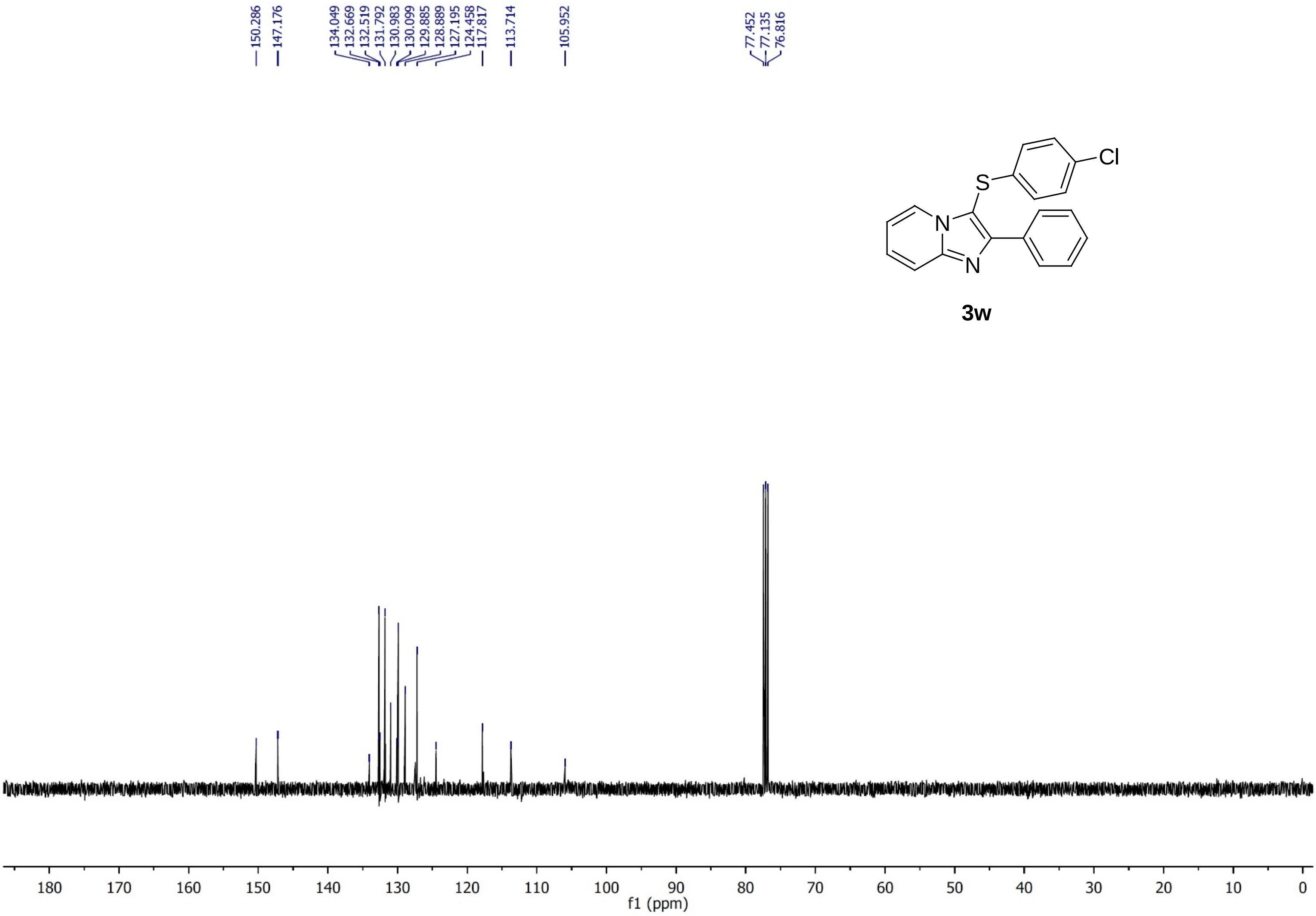


[1]H NMR of compound **3w** ($CDCl_3$, 400 MHz)



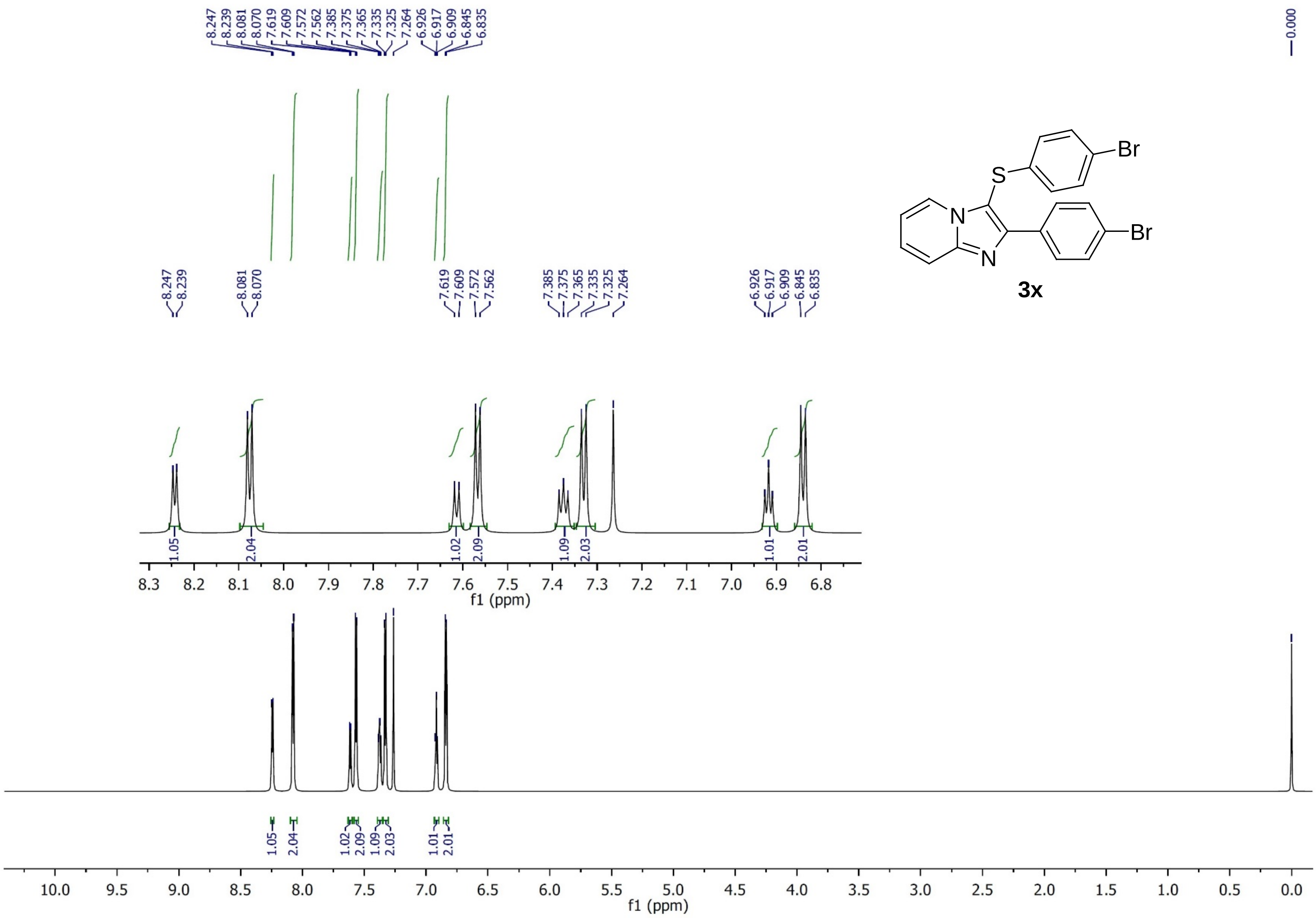
3w

^{13}C NMR of compound **3w** ($CDCl_3$, 100 MHz)

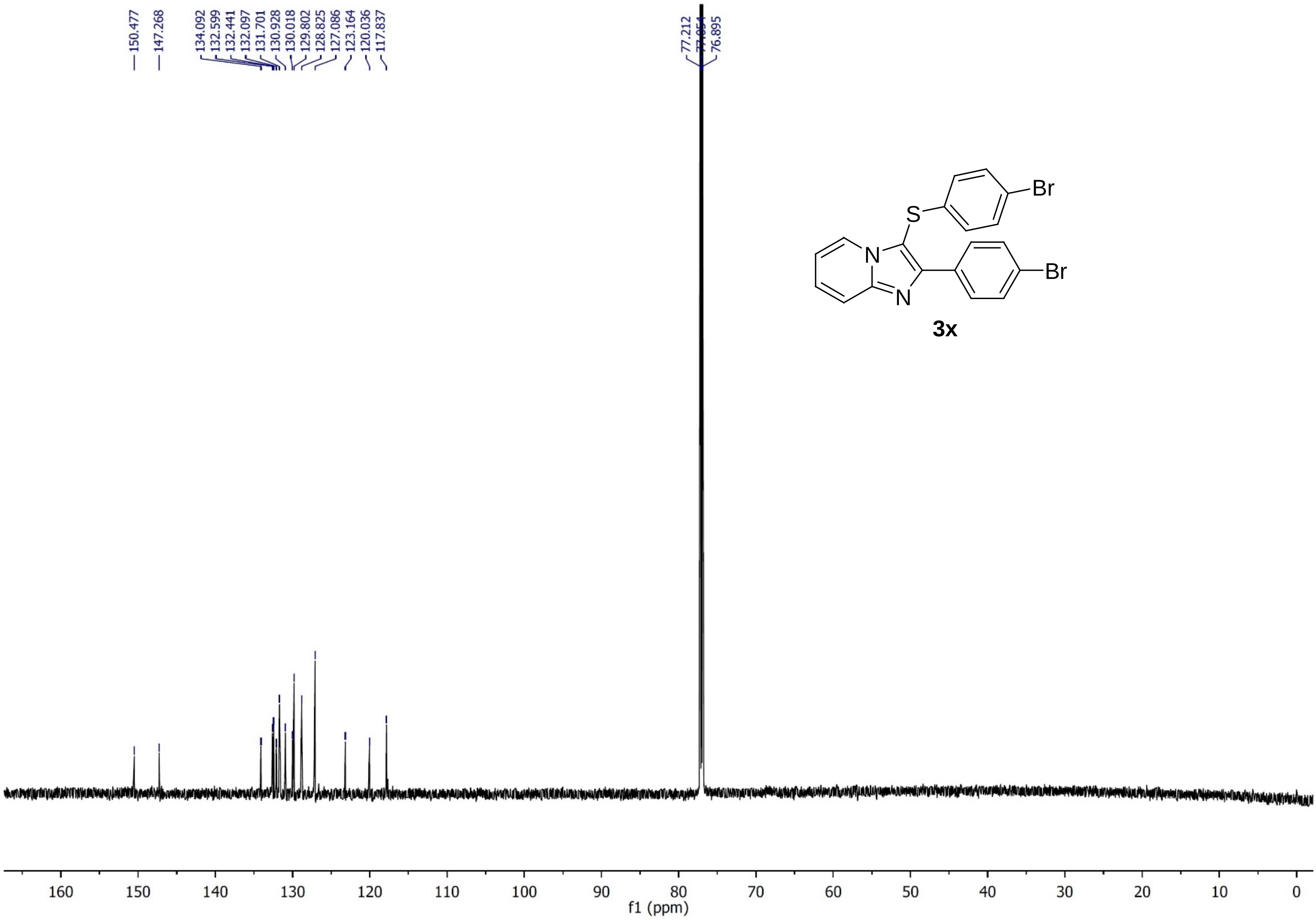


3w

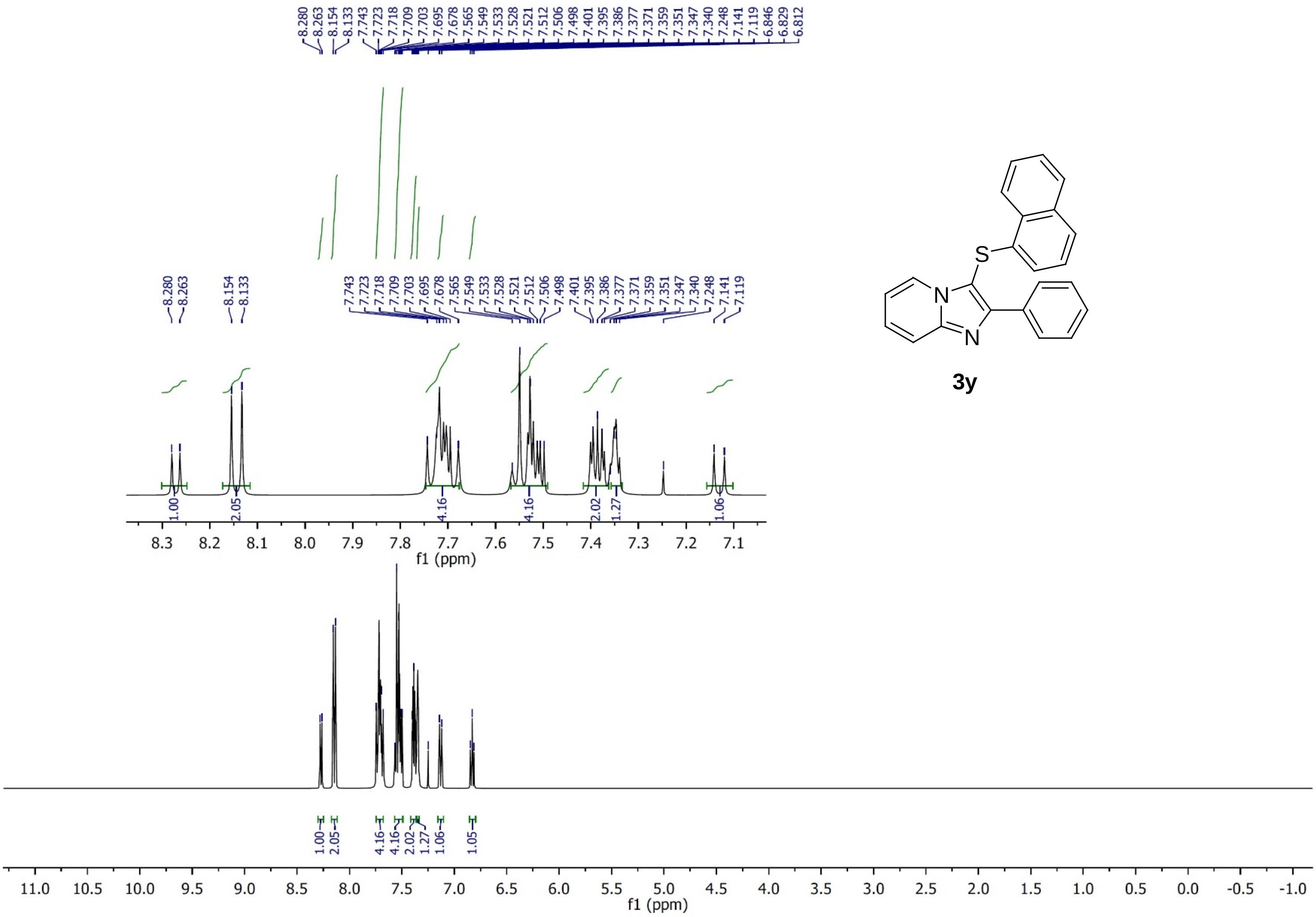
[1]H NMR of compound **3x** ($CDCl_3$, 800 MHz)



^{13}C NMR of compound **3x** ($CDCl_3$, 201 MHz)

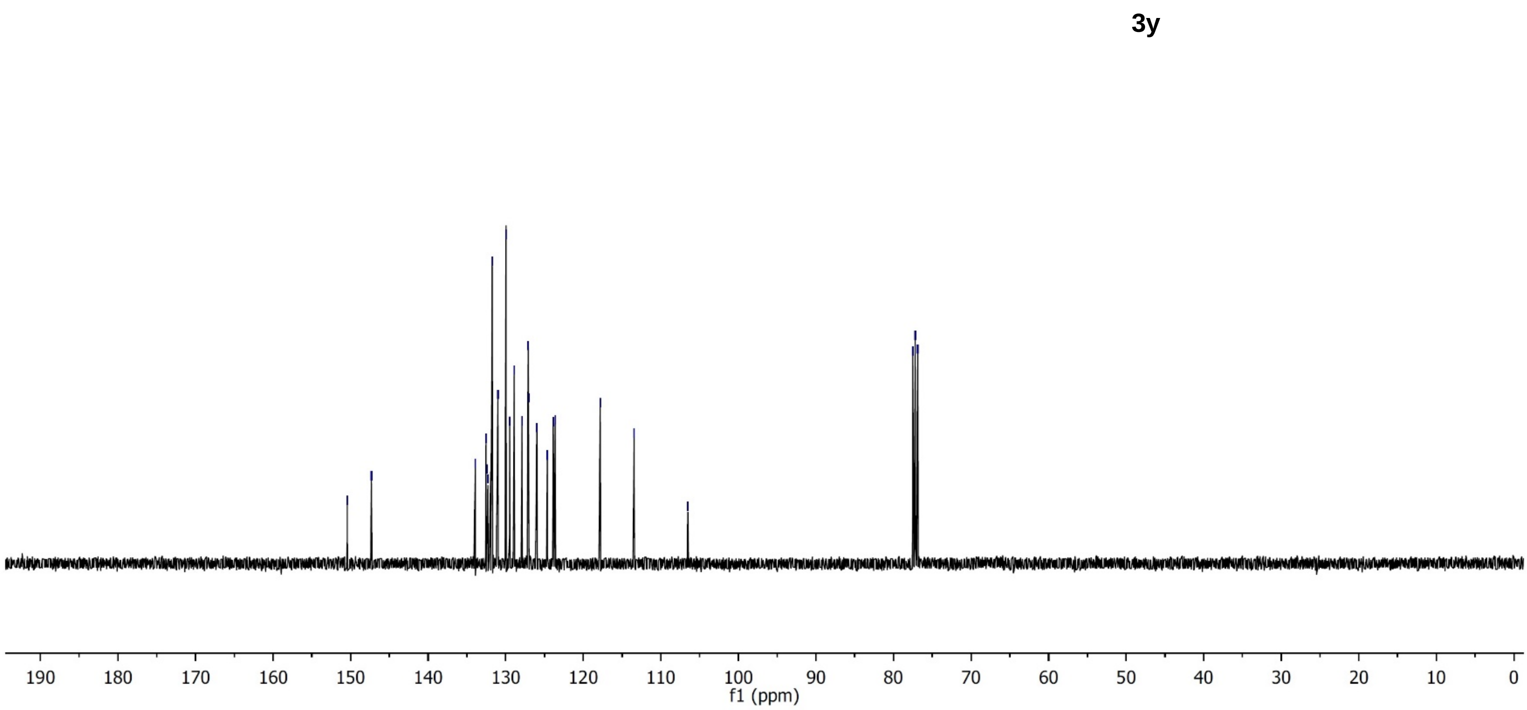


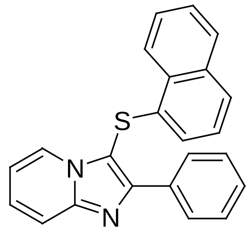
^{1}H NMR of compound **3y** ($CDCl_3$, 400 MHz)



3y

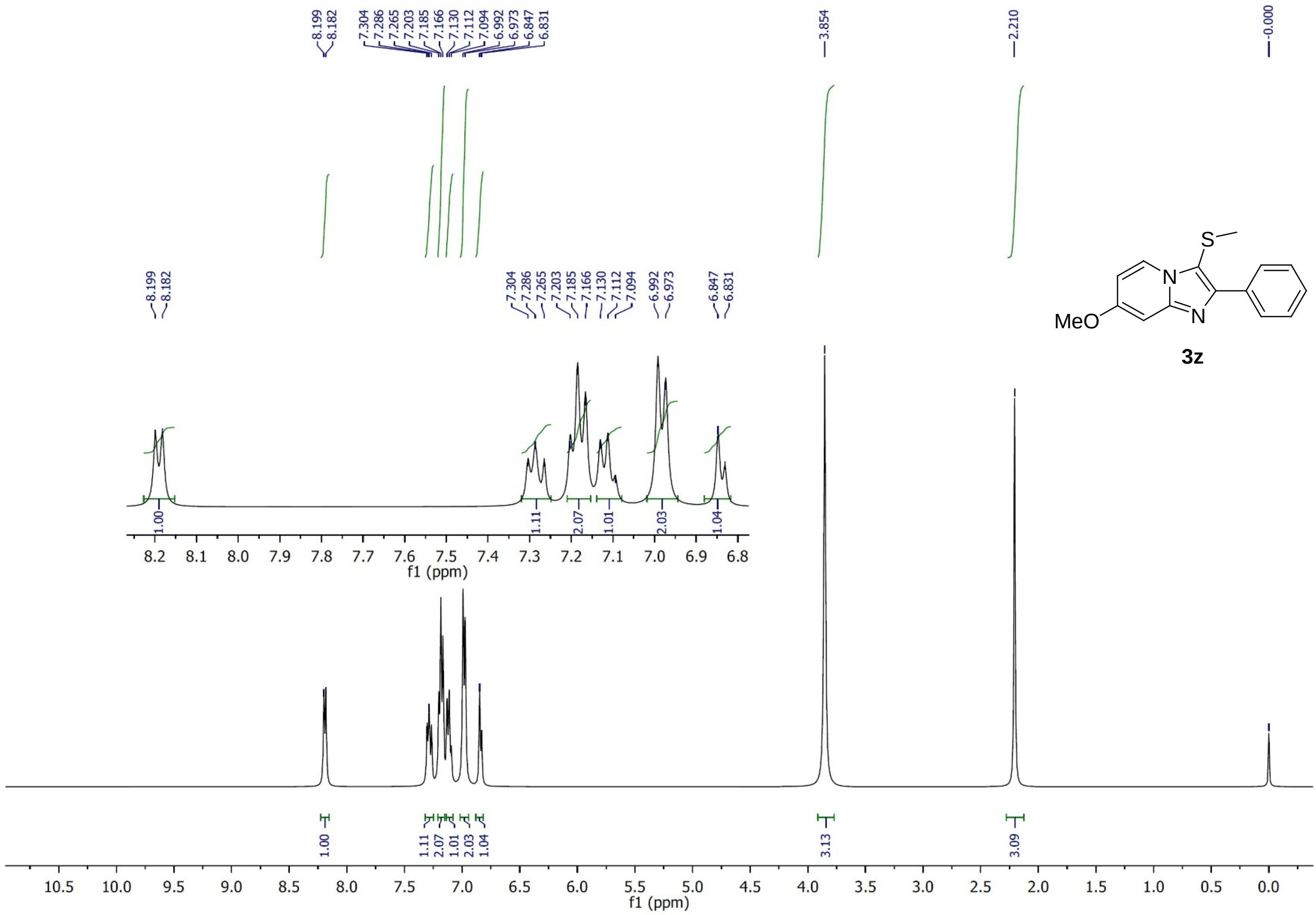
^{13}C NMR of compound **3y** ($CDCl_3$, 100 MHz)



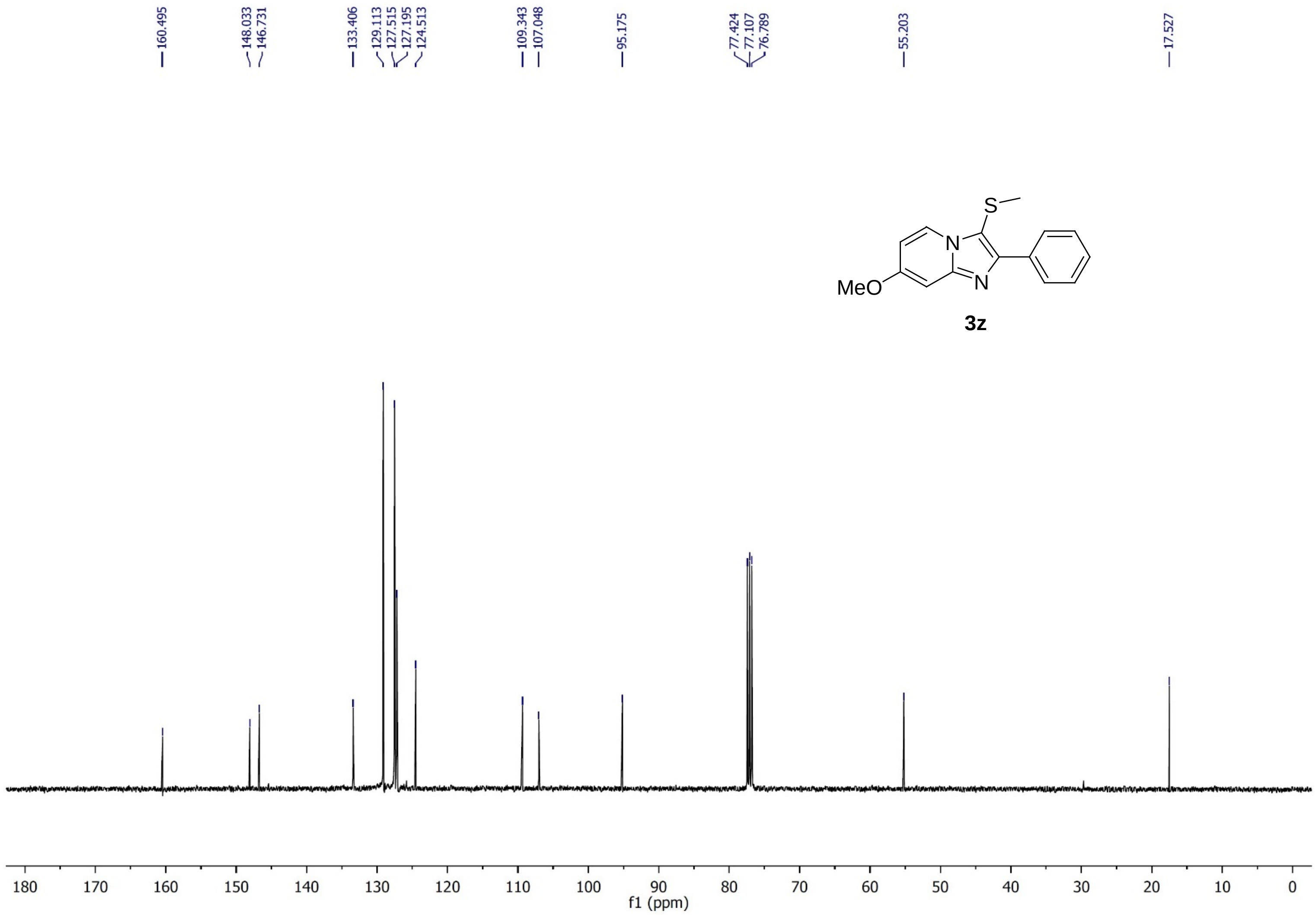


3y

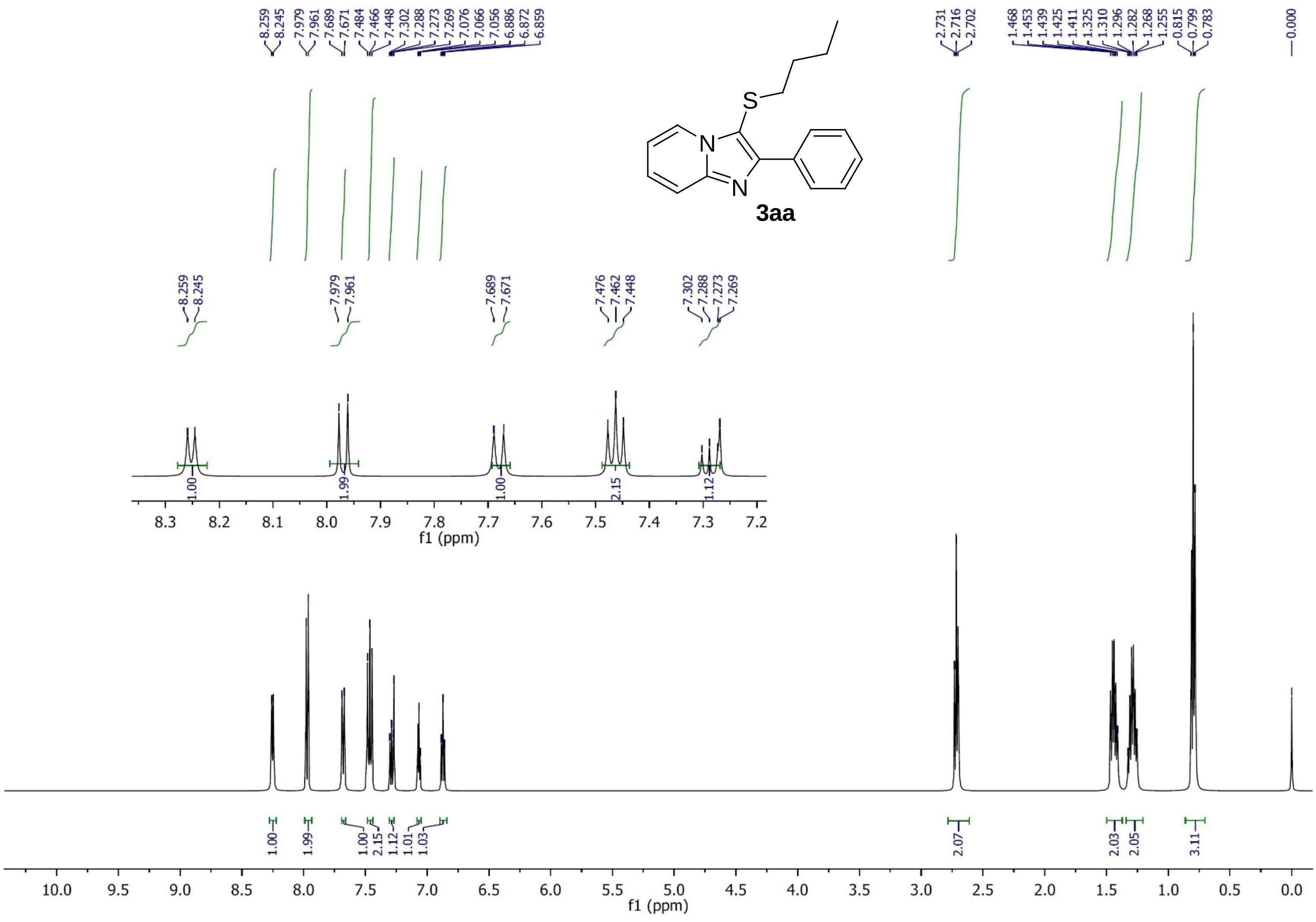
^{1}H NMR of compound **3z** ($CDCl_3$, 400 MHz)



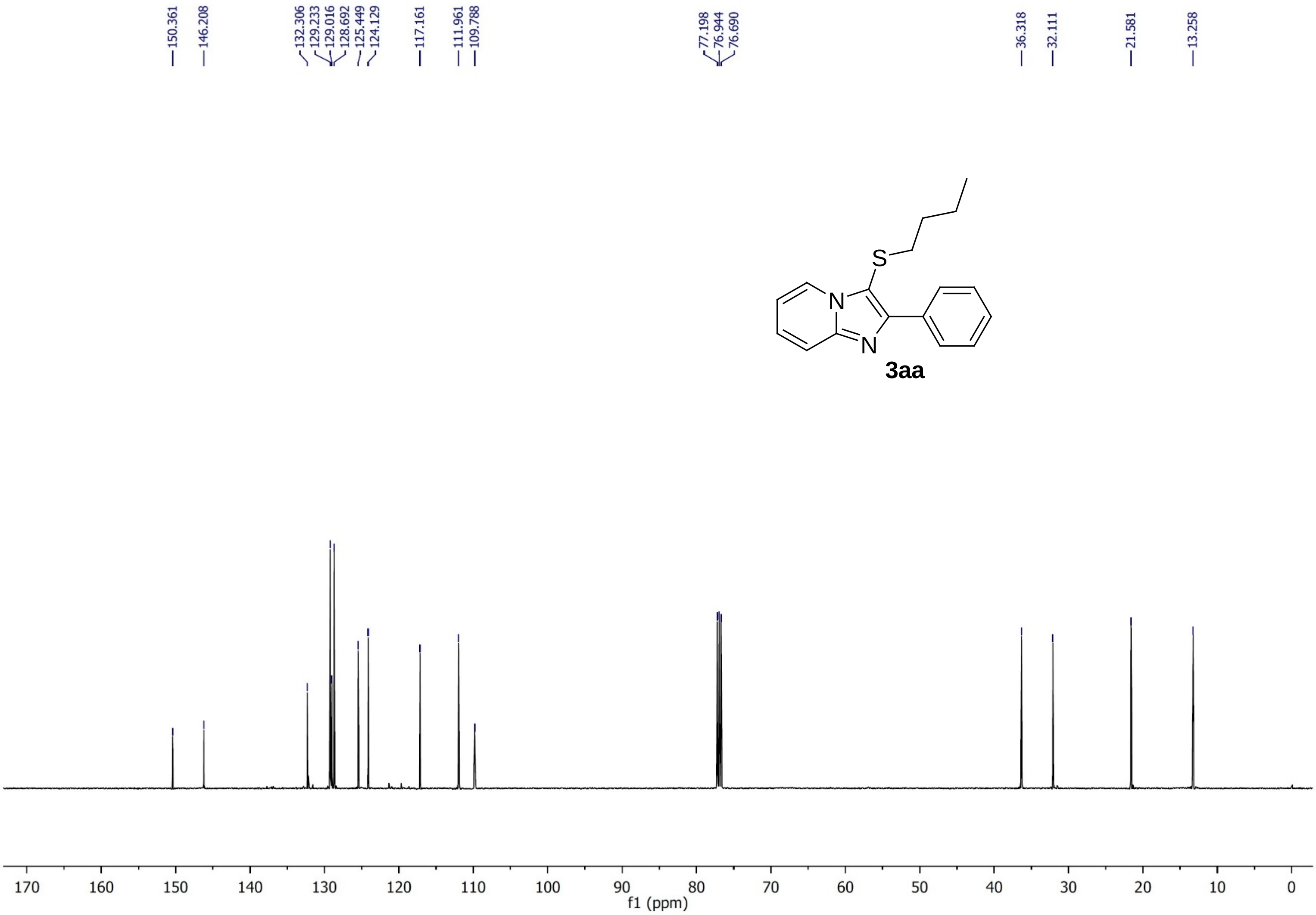
^{13}C NMR of compound **3z** ($CDCl_3$, 100 MHz)



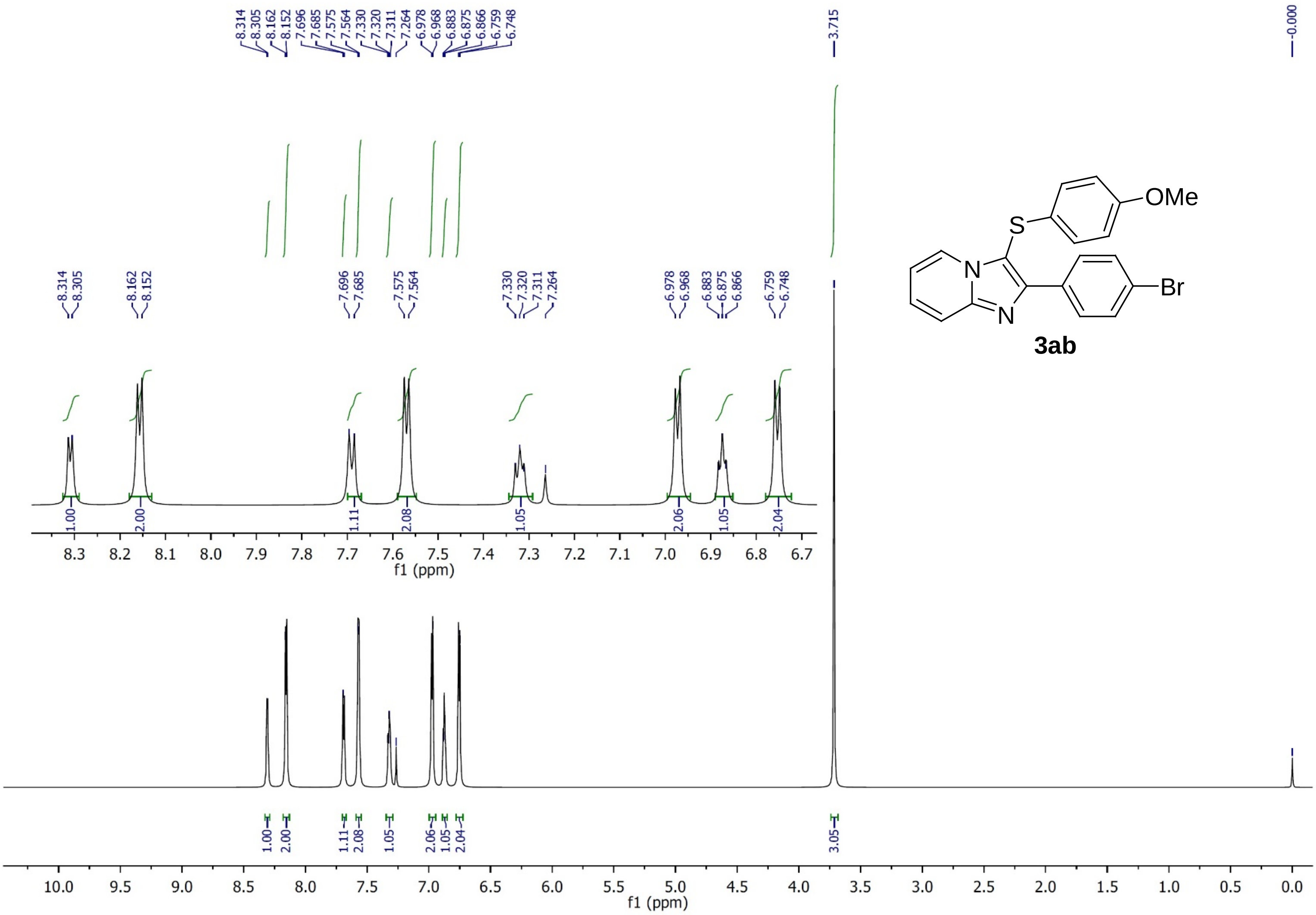
^{1}H NMR of compound **3aa** ($CDCl_3$, 500 MHz)



^{13}C NMR of compound **3aa** ($CDCl_3$, 125 MHz)



^{1}H NMR of compound **3ab** ($CDCl_3$, 800 MHz)



^{13}C NMR of compound **3ab** ($CDCl_3$, 201 MHz)