Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Persulfate promoted C-1 thiocyanation of imidazo[1,5-*a*]pyridines under visible light irradiation in water

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General information

All chemicals were purchased from Sigma-Aldrich, TCI Chemicals, SRL Chemicals, and Avra, and used as received. Molychem silica gel (60-120 mesh) was used for column chromatography, and thin-layer chromatography was performed on Merck pre-coated silica gel 60-F254 plates. All other chemicals and solvents were obtained from commercial sources and purified using standard methods. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Advance spectrometers. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, dd= doublet of doublet, dt= doublet of triplet, td= triplet of doublet and m = multiplet), and coupling constants in hertz (Hz).

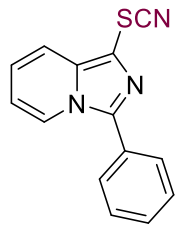
General procedure for the synthesis of 2a-2r:

An oven-dried round bottom flask was charged with the corresponding 3-aryl/heteroaryl/alkyl substituted imidazo[1,5-*a*]pyridine (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.) in 2 mL of H_2O. The reaction mixture was stirred at room temperature for 6 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 10-12cm away from light source, in open air. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of ethyl acetate/*n*-hexane to afford the desired product.

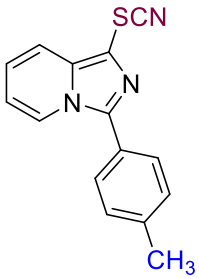
General procedure for the synthesis of 3aa-3ca:

An oven-dried round bottom flask was charged with the corresponding imidazoheterocycle (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.) in 2 mL of H_2O. The reaction mixture was stirred at room temperature for 6 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 10-12 cm away from light source, in open air. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of ethyl acetate/*n*-hexane to afford the desired product.

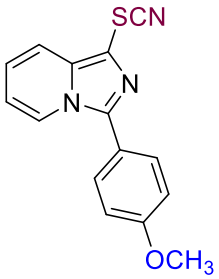
Spectral Data



3-Phenyl-1-thiocyanatoimidazo[1,5-*a*]pyridine (2a): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.30 (d, *J*= 7.2 Hz, 1H), 7.75 (d, *J*= 7.2 Hz, 2H), 7.70 (d, *J*= 9 Hz, 1H), 7.55-7.52 (m, 2H), 7.50-7.47 (m, 1H), 7.09-7.06 (m, 1H), 6.77 (t, *J*= 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 140.2, 135.4, 129.8, 129.2, 128.7, 128.3, 123.4, 122.7, 114.5, 110.6, 108.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{10}N_3S$: 252.0595; found: 252.0591.

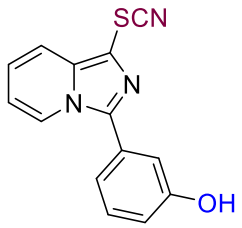


1-Thiocyanato-3-(*p*-tolyl)imidazo[1,5-*a*]pyridine (2b): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.46-8.45 (m, 1H), 7.98 (d, *J*= 7.2 Hz, 2H), 7.78 (d, *J*= 9 Hz, 1H), 7.49-7.46 (m, 1H), 7.34 (d, *J*= 7.5 Hz, 2H), 7.15-7.12 (m, 1H), 7.14-7.12 (m, 1H), 2.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 153.2, 147.9,139.6, 129.5, 129.1, 128.7, 128.0, 124.4, 118.2, 114.3, 108.2, 94.3, 21.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{12}N_3S$: 266.0752; found: 266.0744.

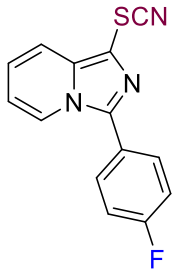


3-(4-Methoxyphenyl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2c): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.27 (d, *J*= 7.2 Hz, 1H), 7.73-7.70 (m, 2H), 7.09-7.08 (m, 3H), 6.777 (d, *J*= 7.08 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 160.7, 140.3, 135.2, 129.8, 123.1,

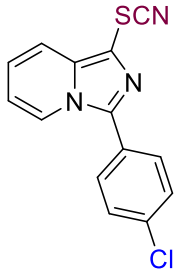
122.7, 121.1, 117.3, 114.6, 114.2, 110.6, 107.6, 55.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{12}ON_3S$: 282.0701; found: 282.0696.



4-(1-Thiocyanatoimidazo[1,5-*a*]pyridin-3-yl)phenol (2d): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.16 (d, *J*= 7.2 Hz, 1H), 7.60 (d, *J*= 9.6 Hz, 1H), 7.18-7.13 (m, 2H), 7.05 (d, *J*= 7.8 Hz, 1H), 7.02-6.99 (m, 1H), 6.82-6.80 (M, 1H), 6.69-6.66 (M, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 157.5, 140.4, 135.3, 130.3, 128.8, 123.9, 123.1, 119.6, 117.8, 117.1, 116.0, 114.7, 110.4, 107.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{10}N_3OS$: 268.3140; found: 268.3136.

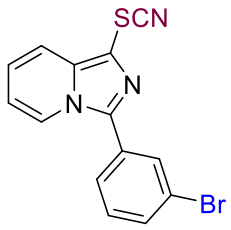


3-(4-Fluorophenyl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2e): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.27 (d, *J*= 7.5 Hz, 1H), 7.80-7.74 (m, 3H), 7.29-7.28 (m, 2H), 7.14-7.11 (m, 1H), 6.84-6.81 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 163.4 (d, J_{F-C} = 250 Hz), 139.3, 135.3, 130.4 (d, J_{F-C} = 8.75 Hz), 124.9 4 (d, J_{F-C} = 3.75 Hz), 123.3, 122.4, 117.4, 116.5 4 (d, J_{F-C} = 22.5 Hz), 114.6, 110.4, 108.3; ^{19}F NMR ($CDCl_3$, 471 MHz) δ (ppm) -109.95 (m, 1F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_8FN_3S$: 269.2974; found: 269.2972.

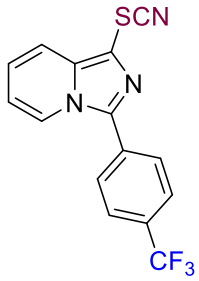


3-(4-Chlorophenyl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2f): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.19 (d, *J*= 7.2 Hz, 1H), 7.67-7.64 (m, 3H), 7.45 (d, *J*= 8.4 Hz, 2H), 7.05-7.02 (m, 1H), 6.74 (t, *J*= 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 139.1, 135.8, 135.5, 129.5,

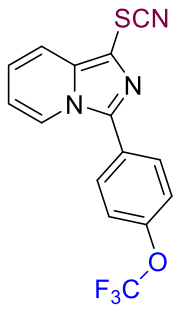
127.2, 123.5, 122.5, 117.5, 114.8, 110.4, 108.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_9ClN_3S$: 286.0200; found, 286.0199.



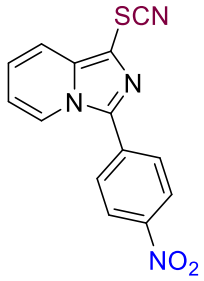
3-(3-Bromophenyl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2g): ^1H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.31 (d, *J*= 7.2 Hz, 1H), 7.94 (s, 1H), 7.75-7.71 (m, 2H), 7.63 (d, *J*= 7.8 Hz, 1H), 7.43 (t, *J*= 7.8 Hz, 1H), 7.14-7.11 (m, 1H), 6.84 (t, *J*= 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 138.5, 135.5, 132.8, 131.2, 130.7, 130.6, 126.7, 123.6, 123.3, 122.5, 117.5, 114.9, 110.3, 108.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_9BrN_3S$: 329.9701; found: 329.9692.



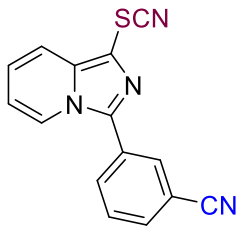
1-Thiocyanato-3-(4-(trifluoromethyl)phenyl)imidazo[1,5-*a*]pyridine (2h): ^1H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.27 (d, *J*= 6.6 Hz, 1H), 7.87 (d, *J*= 7.8 Hz, 2H), 7.75 (d, *J*= 8.4 Hz, 2H), 7.71 (d, *J*= 9.6 Hz, 1H), 7.10-7.07 (m, 1H), 6.79 8.29 (t, *J*= 7.2 Hz, 1H), ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 138.6, 135.7, 132.3, 131.6, 131.4, 128.5, 126.2 (q, $J_{F\text{-}C}$ = 4.5 Hz), 123.7, 122.4, 117.6, 115.1, 110.2, 109.3. ^{19}F NMR ($CDCl_3$, 471 MHz) δ= -61.339 (s, 1F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_9F_3N_3S$: 320.3032; found: 335.3015.



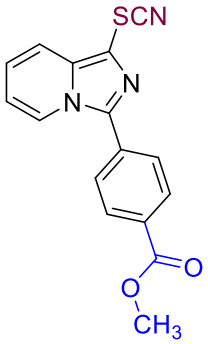
1-thiocyanato-3-(4-(trifluoromethoxy)phenyl)imidazo[1,5-*a*]pyridine (2i): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.29 (d, *J*= 7.2 Hz, 1H), 7.83 (d, *J*= 9 Hz, 2H), 7.75 (d, *J*= 9 Hz, 1H), 7.41 (d, *J*= 8.4 Hz, 1H), 7.14-7.11 (m, 1H), 6.83 (t, *J*= 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 150.0, 138.8, 135.5, 129.9, 127.4, 123.5, 122.4, 121.6, 120.4 (d, J_{F-C} = 256.5 Hz), 117.5, 114.8, 110.3, 108.6; ^{19}F NMR ($CDCl_3$, 471 MHz) δ= -57.72 (s, 3F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_9F_3N_3OS$: 335.3042; found: 335.3038.



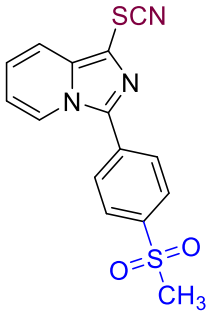
3-(4-Nitrophenyl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2j): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.45-8.42 (m, 3H), 8.07-8.05 (m, 2H), 7.84 (d, *J*= 9.6 Hz, 1H), 7.25-7.22 (m, 1H), 6.98-6.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ (ppm) 147.9, 137.7, 136.0, 134.8, 128.7, 124.5, 124.1, 122.4, 117.8, 115.6, 110.3, 109.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_9N_4O_2S$: 297.0446; found 297.0418.



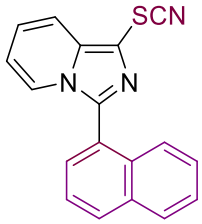
3-(1-Thiocyanatoimidazo[1,5-*a*]pyridin-3-yl)benzonitrile (2k): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.33 (dt, *J*= 7 Hz, 1Hz, 1H), 8.12-8.11 (m, 1H), 8.09-8.07 (m, 1H), 7.81-7.79 (m, 1H), 7.71 (td, *J*= 7 Hz, 1 Hz, 1H), 7.21-7.18 (m, 1H), 6.94-6.91 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz,) δ (ppm) 137.6, 135.8, 132.9, 132.3, 131.4, 130.2, 123.9, 122.2, 117.9, 117.6, 115.4, 113.7, 110.1, 109.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_9N_4S$: 277.0548; found: 277.0547.



Methyl 4-(1-thiocyanatoimidazo[1,5-*a*]pyridin-3-yl)benzoate (2l): ^{1}H NMR (DMSO-d_6, 600 MHz) δ (ppm) 8.71 (d, *J*= 7.2 Hz, 1H), 8.16-8.14 (m, 2H), 8.07-8.06 (m, 2H), 7.87 (d, *J*= 9 Hz, 1H), 7.34-7.31 (m, 1H), 7.06-7.04 (m, 1H), 3.92 (s, 3H); (d, *J*= 7.8 Hz, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz,) δ (ppm) 166.2, 143.0, 141.0, 138.7, 135.8, 133.4, 130.3, 128.6, 125.2, 124.5, 117.2, 115.8, 111.8, 52.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{16}H_{11}N_3O_3S$: 309.0572; found 309.0565.

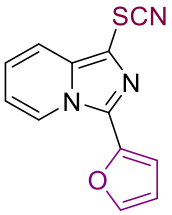


3-(4-(Methylsulfonyl)phenyl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2m): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.31 (d, *J*= 7.2 Hz, 1H), 8.06 (d, *J*= 8.4 Hz, 2H), 7.96 (d, *J*= 8.4 Hz, 1H), 7.73 (d, *J*= 9 Hz, 1H), 7.13-7.10 (m, 1H), 6.85-6.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ (ppm) 141.2, 138.0, 135.9, 134.0, 128.8, 128.4, 124.0, 122.4, 117.7, 115.5, 110.0, 109.9, 44.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{12}N_3O_2S_2$: 330.4000; found 309.3996.

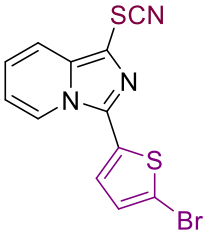


3-(Naphthalen-1-yl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2n):^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.01 (d, *J*= 7.8 Hz, 1H), 7.94 (d, *J*= 7.8 Hz, 1H), 7.75 (d, *J*= 9 Hz, 1H), 7.71 (t,

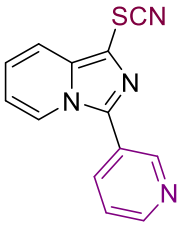
J= 8.4 Hz, 2H), 7.63-7.58 (m, 2H), 7.53 (t, *J*= 7.2 Hz, 1H), 7.47 (t, *J*= 7.2 Hz, 2H); (d, *J*= 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ (ppm)139.0, 135.1, 133.9, 131.5, 130.8, 129.0, 128.8, 127.5, 126.7, 125.6, 125.3, 125.0, 123.5, 123.3, 117.1, 114.2, 110.7, 107.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{12}N_3S$: 302.0752; found: 302.0747.



3-(Furan-2-yl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2o): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.77 (d, *J*= 7.2 Hz, 1H), 7.70 (d, *J*= 9 Hz, 1H), 7.61 (d, *J*= 1.2 Hz, 1H), 7.12-7.09 (m, 2H), 6.87 (t, *J*= 6.6 Hz, 1H), 6.6 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ (ppm) 145.0, 142.9, 134.8, 132.2, 124.3, 123.5, 117.1, 114.9, 112.0, 110.2, 108.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{12}H_8N_3OS$: 242.2762; found: 242.2753.

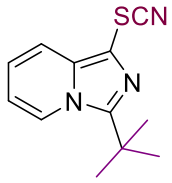


3-(5-Bromothiophen-2-yl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2p): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.35 (d, *J*= 7.2 Hz, 1H), 7.75 (d, *J*= 9.6 Hz, 1H), 7.3 (d, *J*= 4.2 Hz, 1H), 7.16 (d, *J*= 4.2 Hz, 1H), 7.15-7.12 (m, 1H), 6.90 (t, *J*= 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 135.4, 133.7, 132.0, 130.7, 126.6, 123.5, 117.6, 115.3, 114.9, 110.1, 109.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{12}H_6BrN_3OS$: 336.2250; found: 242.2245.



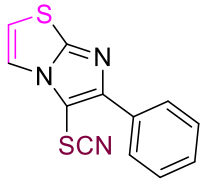
3-(Pyridin-3-yl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (**2q**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 9.07 (s, 1H), 8.76 (d, *J*= 4 Hz, 1H), 8.33 (d, *J*= 7 Hz, 1H), 8.15 (dt, *J*= 8 Hz, 2 Hz, 1H), 7.79 (d, *J*= 9.5 Hz, 1H), 7.54-7.52 (m, 1H), 7.19-7.16 (m, 1H), 6.90-6.88 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 150.6, 148.7, 137.2, 136.0, 135.7, 125.3, 124.1, 123.8, 122.2, 117.6,

115.2, 110.2, 109.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{13}H_8N_4S$: 252.2950; found: 252.2947.

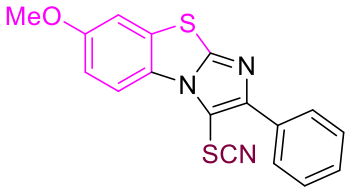


3-(*Tert*-butyl)-1-thiocyanatoimidazo[1,5-*a*]pyridine (2r): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.18 (d, *J*= 7.5 Hz, 1H), 7.67 (d, *J*= 9 Hz, 1H), 7.04-7.01 (m, 1H), 6.76-6.73 (m, 1H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 147.5, 135.9, 124.2, 122.0, 111.0, 105.0, 33.8, 28.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{12}H_{13}N_3S$: 231.3170; found: 231.3168.

2-Phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3aa): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.47 (dt, *J* = 6.5 Hz,1Hz, 1H), 8.09-8.07 (m, 2H), 7.79 (d, *J* = 9 Hz, 1H), 7.57-7.54 (m, 2H), 7.51-7.47 (m, 2H), 7.15 (td, *J* = 6.5 Hz,1Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 153.1, 148.0, 132.0, 129.5, 128.8, 128.7, 128.0, 124.4, 118.3, 114.4, 108.1, 94.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{10}N_3S$: 252.0595; found: 252.0591.



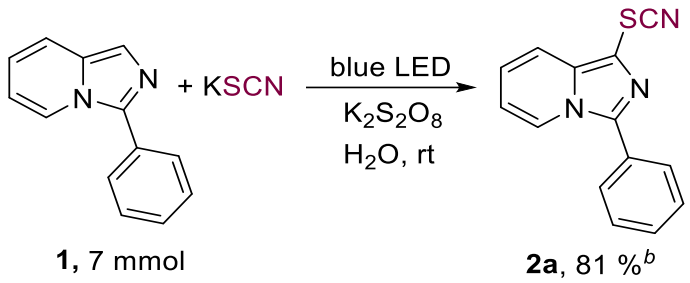
6-Phenyl-5-thiocyanatoimidazo[2,1-*b*]thiazole (3ba): ^{1}H NMR (DMSO-d_6, 600 MHz) δ (ppm) 8.23 (d, *J*= 4 Hz, 1H), 8.00-7.98 (m, 2H), 7.58 (d, *J*= 4.5 Hz, 1H), 7.57-7.53 (m, 2H), 7.48-7.45 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 152.7, 152.2, 132.8, 129.3, 128.1, 127.9, 119.7, 116.6, 111.1, 90.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{12}H_7N_3S_2$: 257.3290; found: 257.3286.



7-Methoxy-2-phenyl-3-thiocyanatobenzo[*d*]imidazo[2,1-*b*]thiazole (3ca): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.39 (d, *J* = 9 Hz, 1H), 8.00-7.99 (m, 2H), 7.56-7.53 (m, 2H), 7.49-7.46 (m, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 9 Hz, 2.5 Hz 1H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 157.8, 155.0, 131.9, 131.8, 129.2, 128.7, 128.3, 127.0, 114.5, 114.2, 108.9, 108.8, 97.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{12}N_3OS_2$: 337.0344; found: 337.0341.

Gram Scale Synthesis

An oven-dried round bottom flask was charged with the 3-phenyl imidazo[1,5-*a*]pyridine (7.0 mmol, 1.35 gm), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.) in 10 mL of H_2O. The reaction mixture was stirred at room temperature for 9 h under irradiation of blue LED light (24 W, 455 nm) in open air. The reaction mixture was kept at a distance of 2 cm from the light source for irradiation. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to afford the desired product **2a** in 89% yield (Scheme 1).



Scheme 1: Gram-scale reaction.
[a]**Reaction conditions:** 1 (7 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), H_2O (10 mL), 9 h, rt, open air, blue LED (24 W, 455 nm). [b]Isolated yield.

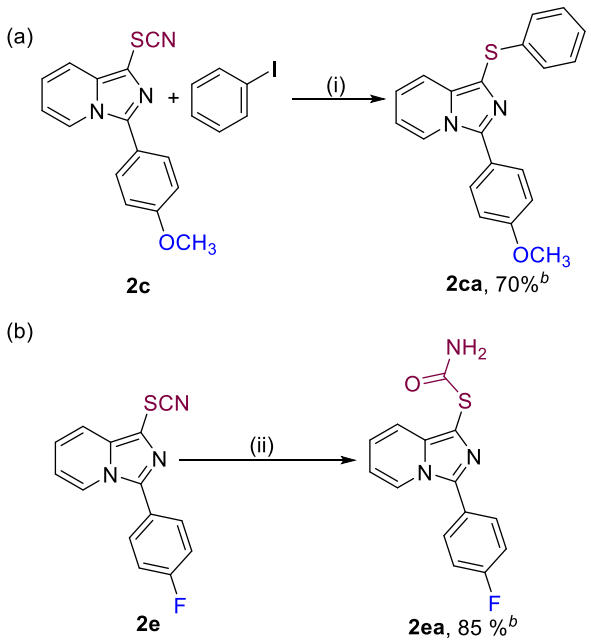
Conversion of thiocyanated imidazo[1,5-*a*]pyridines to thioether and thiocarbamate:

General procedure for the synthesis of 2ca:

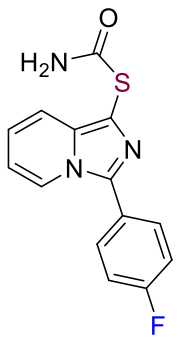
To an oven-dried round bottom flask **2c** (1 equiv., 0.2 mmol) was added in 2 mL of water. Iodobenzene (1 equiv.), $CuCl_2$•$2H_2O$ (0.1 equiv.), 1,10-Phenanthroline (0.1 equiv.), Cs_2CO_3 (2 equiv.), $(nBu)_4NF$ (0.2 equiv.) was further added and the entire reaction mixture was subjected to uniform stirring at 100°C for 12 h. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of ethyl acetate/*n*-hexane to afford the desired product.

General procedure for the synthesis of 2ea:

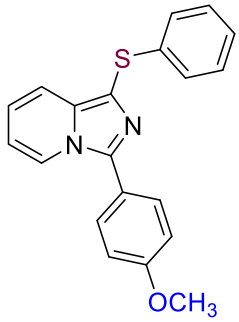
To an oven-dried round bottom flask, **2e** (1 equiv., 0.2 mmol) was added in 2 mL of DCM. To it 0.1 mL of H_2SO_4 (18 M) was added and the entire reaction mixture was subjected to uniform stirring for 4 h in ice bath. On competition of the reaction, 10 mL of DCM was added to it for further dilution and the entire reaction mixture was washed with saturated aqueous $NaHCO_3$ solution (5 mL × 3), brine (5 mL × 2), dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of ethyl acetate/*n*-hexane to afford the desired product.



Scheme 2: Application of C-1 thiocynated of imidazo[1,5-*a*]pyridines. [a]Reaction conditions: (i) **2c** (1 equiv.), Iodobenzene (1 equiv.), $CuCl_2$•$2H_2O$ (0.1 equiv.), 1,10-Phenanthroline (0.1 equiv.), Cs_2CO_3 (2 equiv.), $(nBu)_4NF$ (0.2 equiv.), H_2O (5 mL). (ii) **2e** (1 equiv., 0.2 mmol), H_2SO_4 (0.1mL, 18 M), CH_2Cl_2(2 mL), 0°C, 4h. [b]Isolated yield.



***S*-(3-(4-fluorophenyl)imidazo[1,5-*a*]pyridin-1-yl) carbamothioate (2ea):** ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.06 (d, *J*= 4 Hz, 1H), 7.70-7.68 (m, 2H), 7.14 (t, *J*= 9 Hz, 3H), 6.60-6.58 (m, 1H), 6.51 (t, *J*= 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 163.1(d, J_{F-C} = 248.5 Hz), 138.4, 135.9, 130.2 (d, J_{F-C} = 7.5 Hz), 125.7 (d, J_{F-C} = 3 Hz), 124.1, 121.8, 121.3, 118.6, 116.2 (d, J_{F-C} = 21 Hz), 113.9; ^{19}F NMR ($CDCl_3$, 471 MHz) δ (ppm) -107.870 (m, 1F). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{11}FN_3OS$: 288.3204; found: 288.3200.

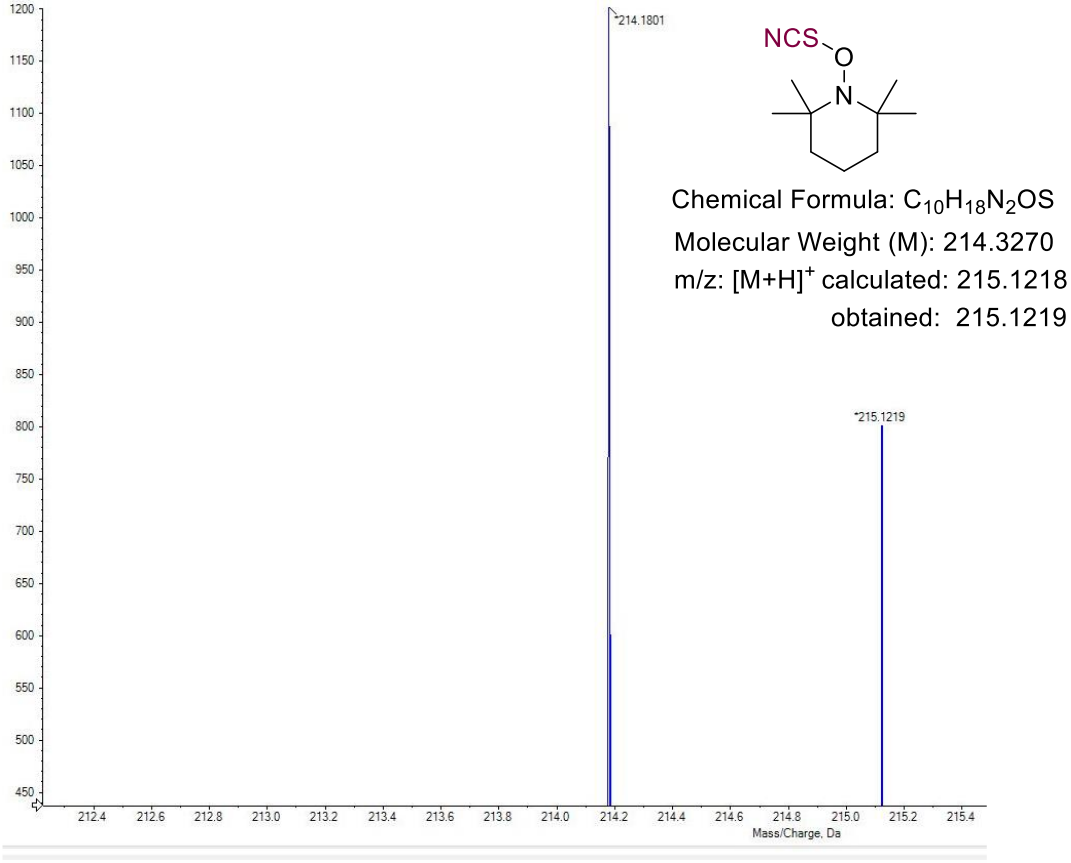


3-(4-Methoxyphenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine (2ca): ^{1}H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.17 (d, *J*= 7.2 Hz, 1H), 7.68 (d, *J*= 8.4 Hz, 1H), 7.55 (d, *J*= 9 Hz, 1H), 7.14-7.09 (m, 4H), 7.02-6.97 (m, 3H), 6.78-6.75 (m, 1H), 6.57 (t, *J*= 7.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 160.3, 139.3, 138.5, 134.9, 130.6, 129.7, 128.8, 127.0, 125.4, 122.0, 120.8, 119.5, 118.4, 114.4, 113.7, 55.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{16}N_2OS$: 332.4210; found: 332.4208.

Control Experiments

TEMPO addition in the general procedure:

An oven-dried round bottom flask was charged with the 3-phenylimidazo[1,5-*a*]pyridine (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), TEMPO (4 equiv.) in 2 mL of H_2O. The reaction mixture was stirred at room temperature for 6 h under irradiation of blue LED light (24 W, 455 nm) at a distance of 2 cm away from light source, in open air (Scheme 2a).



BHT addition in the general procedure:

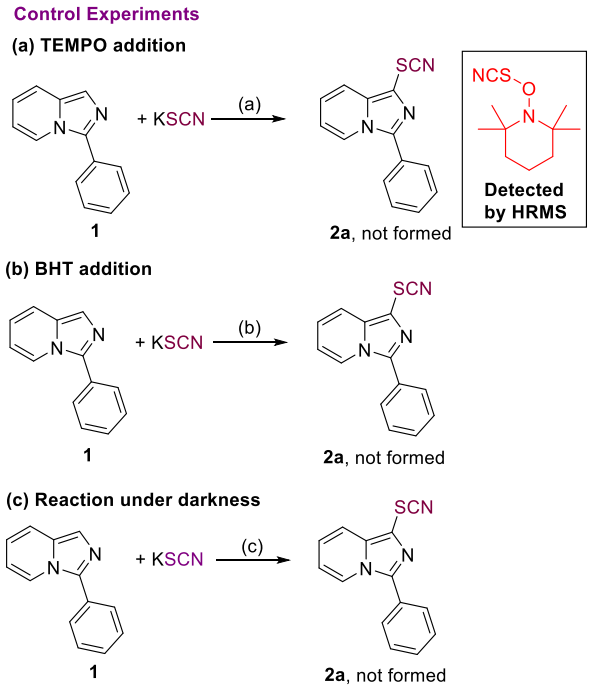
An oven-dried round bottom flask was charged with 3-phenylimidazo[1,5-*a*]pyridine (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), BHT (4 equiv.) in 2 mL of H_2O. The reaction mixture was stirred at room temperature for 6 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air (Scheme 2b).

Reaction in darkness:

An oven-dried round bottom flask was charged with 3-phenylimidazo[1,5-*a*]pyridine (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), in 2 mL of H_2O. The reaction mixture was stirred at room temperature for 3 h in open air and in absence of any light source *i.e*, in darkness (Scheme 2c).

Light on-off experiment:

Six standard oven-dried round bottom flask were charged with 3-phenyl imidazo[1,5-*a*]pyridine (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), in 2 mL of H_2O. The mixtures were stirred uniformly under irradiated of blue LEDs (approximately 2 cm away from the light source) at room temperature. After 1hr LEDs were turned off, and one round bottom flask was removed from the irradiation setup for analysis. The remaining five reactions were stirred in the absence of light for another 1 hr. After 2 h, one reaction was removed for analysis, and the LED lamps were turned back on to irradiate the remaining four reaction mixtures. After an additional 1 h of irradiation, the blue LEDs were turned off, and one round bottom flask was removed for analysis. The remaining three reactions were stirred in the absence of light for an additional 1 h. After 4 h another reaction was removed for analysis, and the LEDs were turned back on to irradiate the remaining two reaction mixtures. After 5 h, the LEDs were turned off, and one round bottom flask was removed for analysis. The remaining one reaction was stirred in the absence of light for an additional 1 h, then, it was analyzed. The yield of each reaction was determined by column chromatography at the respective time intervals (Fig. 1).



Scheme 3: Control Experiments Scheme.

[a]**Reaction conditions:** (a) **1** (1 mmol,), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), TEMPO (4 equiv.), blue LED (24 W, 455 nm), H_2O (2 mL), 6 h, rt, open air; (b) **1** (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), BHT (4 equiv.), blue LED (24 W, 455 nm), H_2O (2 mL), 6 h, rt, open air; (c) **1** (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (1 equiv.), H2O (2 mL), 6 h, rt, open air.

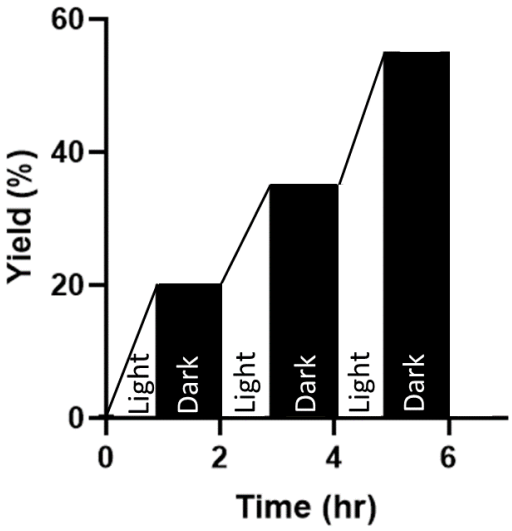
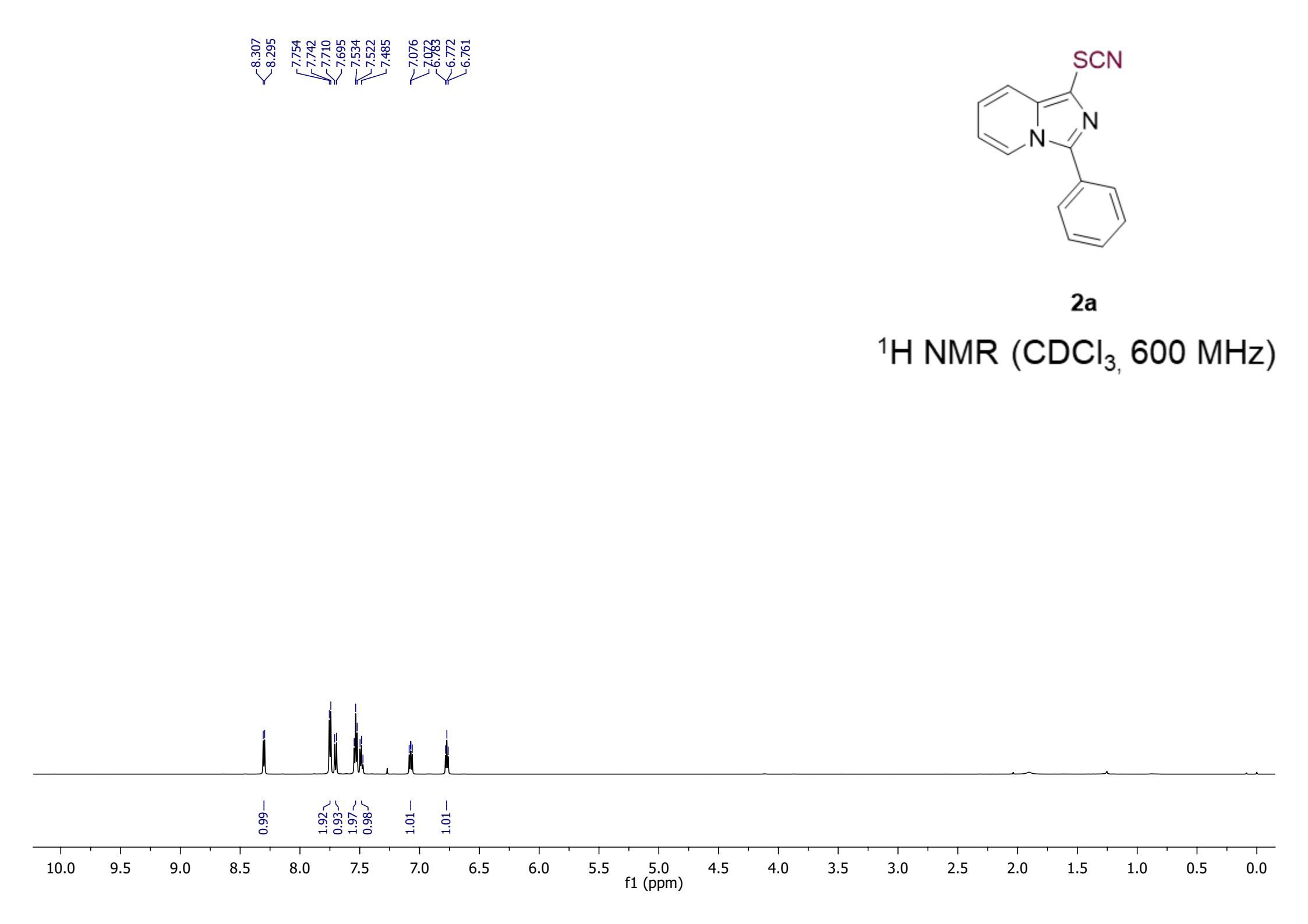
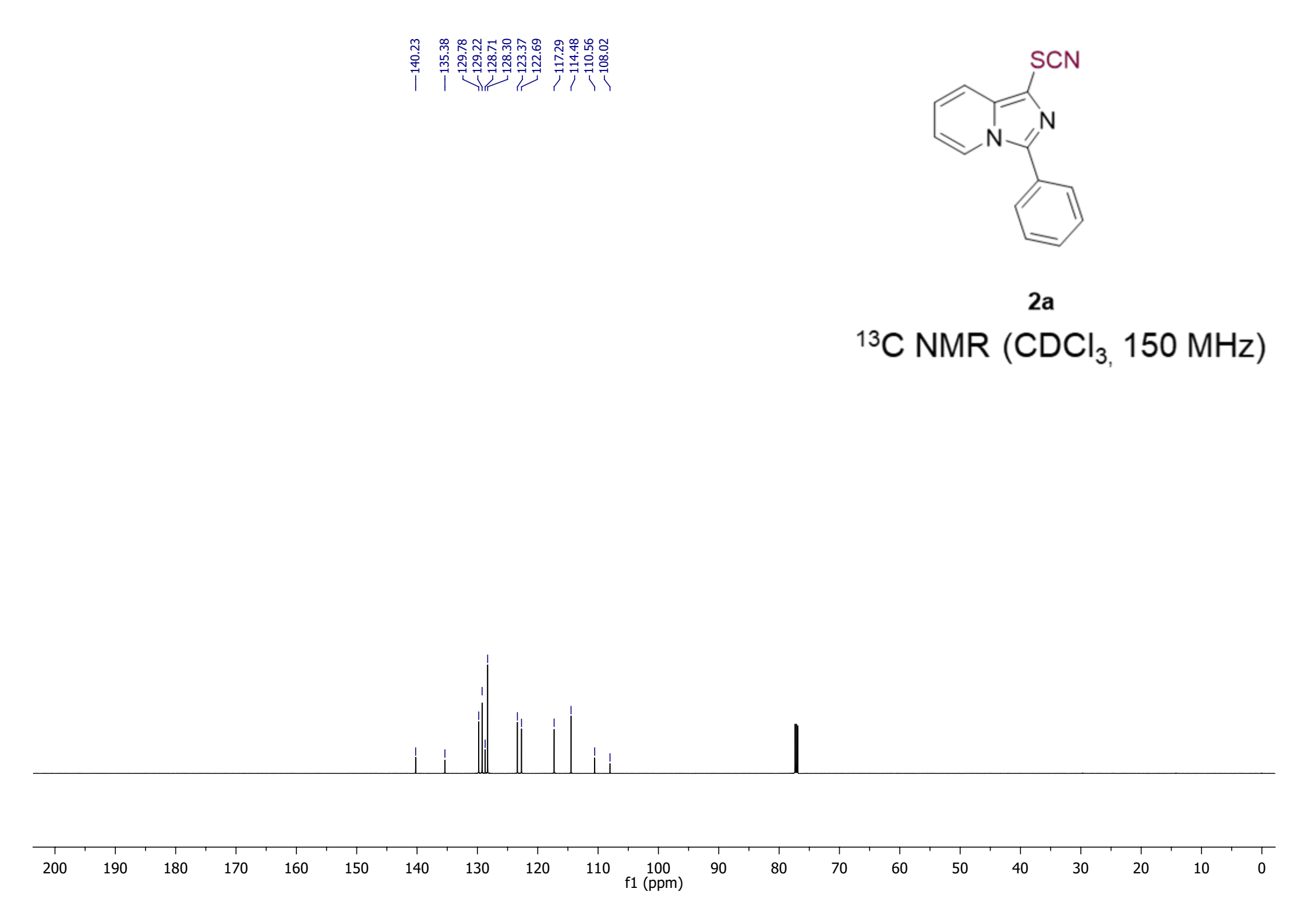
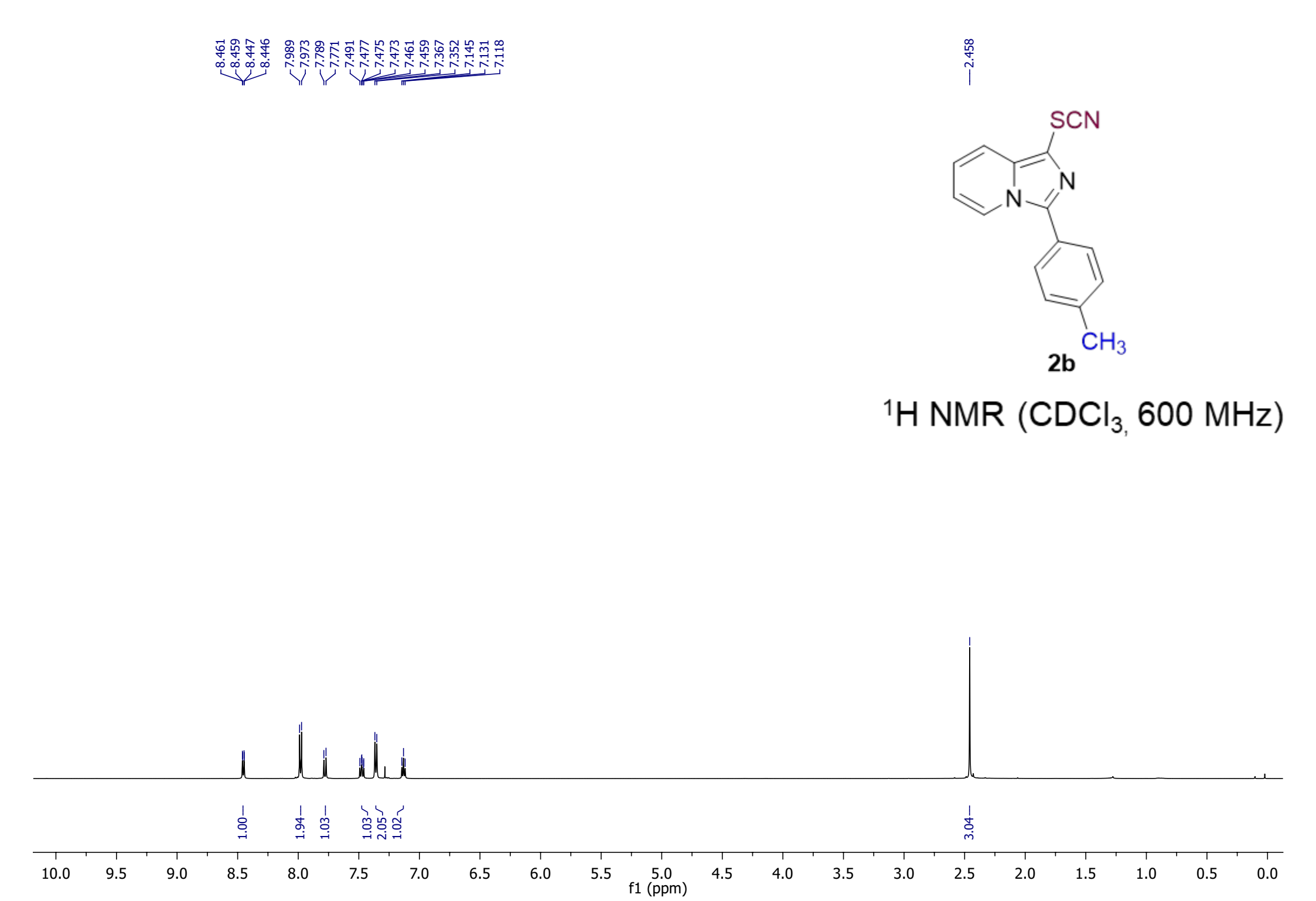


Figure 1: Light on-off experiment.


8.307
8.295
7.754
7.742
7.710
7.695
7.534
7.522
7.485
7.076
7.072
6.783
6.772
6.761
SCN
N
N
2a
1H NMR (CDCl3, 600 MHz)
0.99
1.92
0.93
1.97
0.98
1.01
1.01
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)


140.23
135.38
129.78
129.22
128.71
128.30
123.37
122.69
117.29
114.48
110.56
108.02
SCN
N
N
2a
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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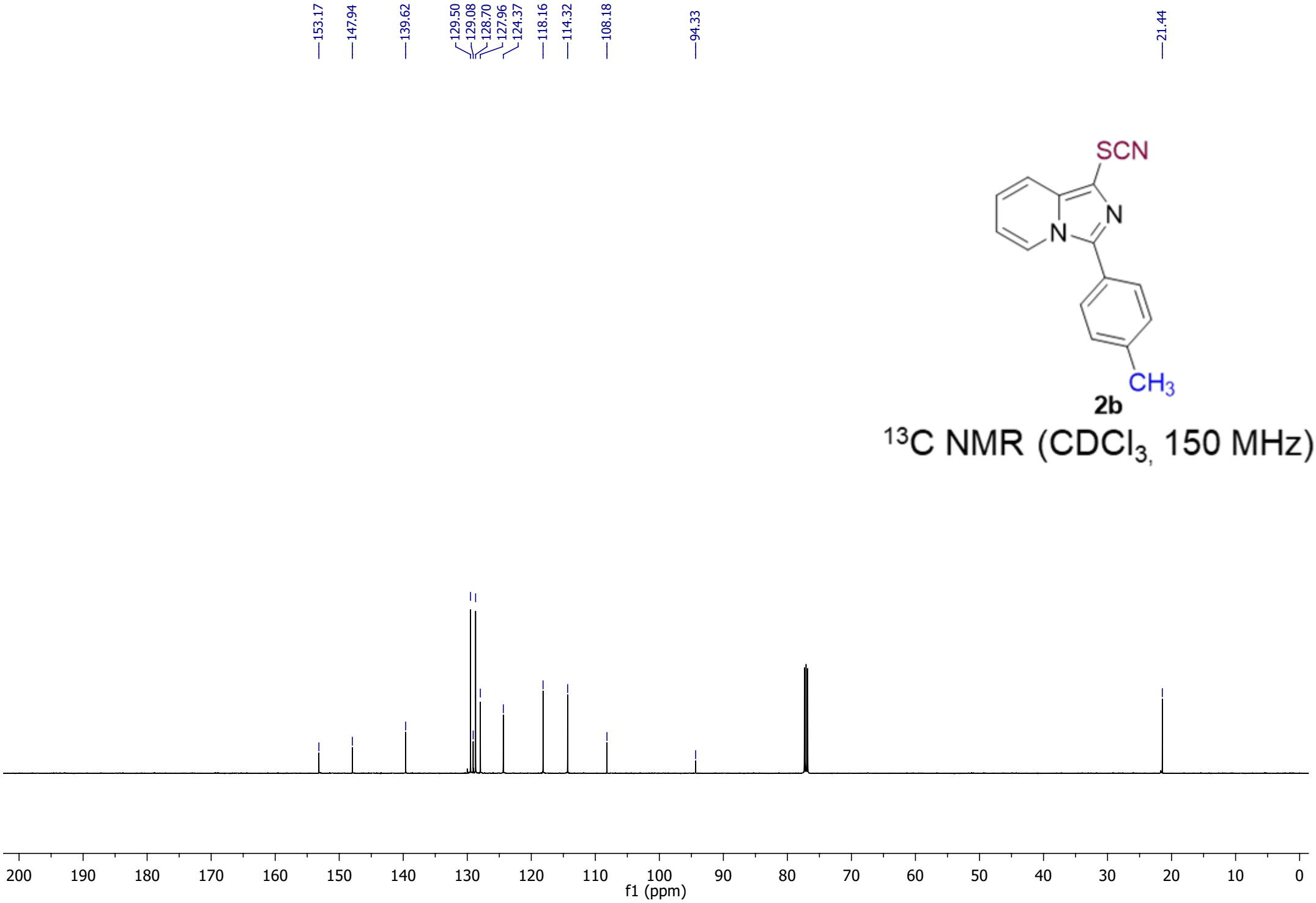
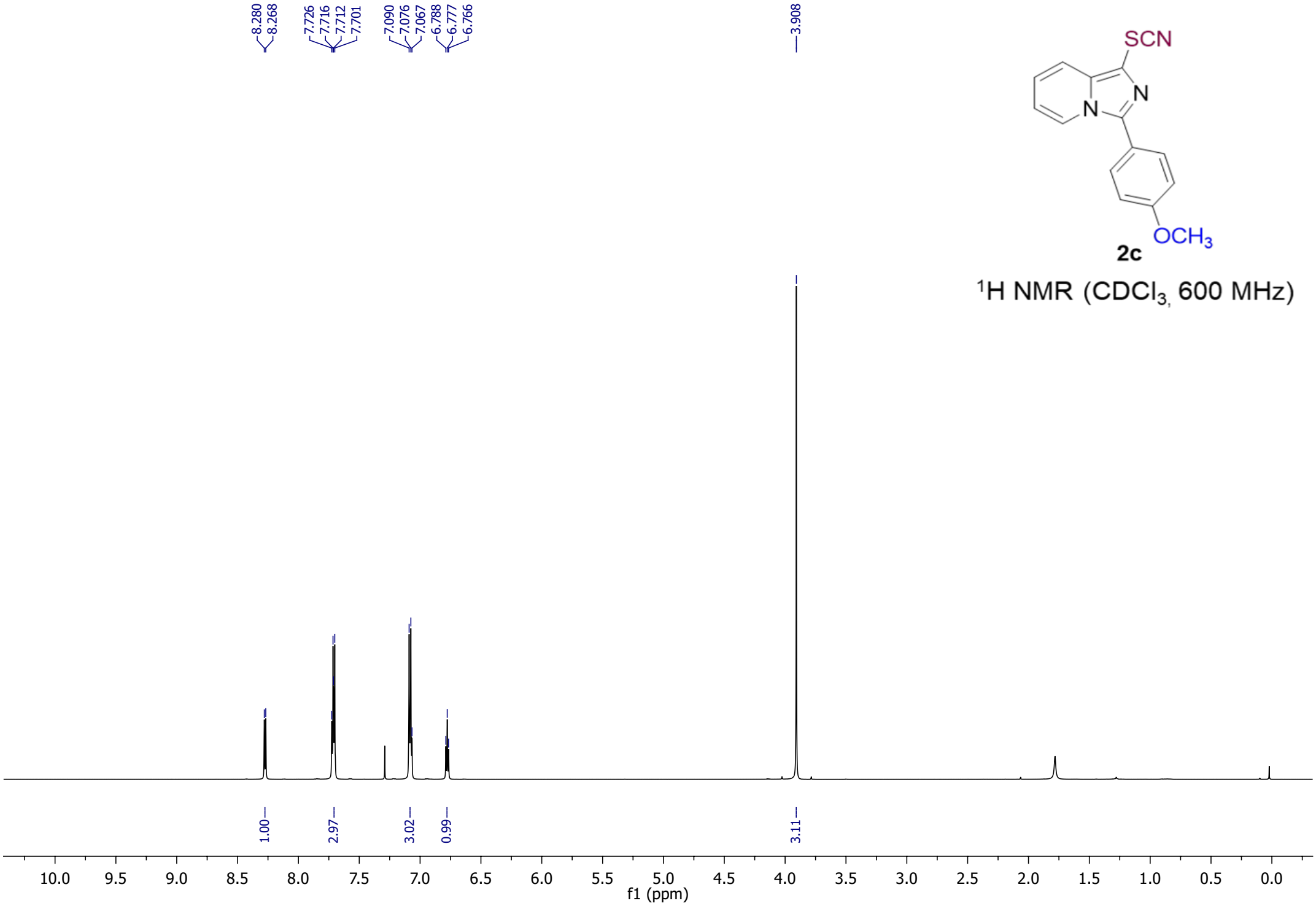
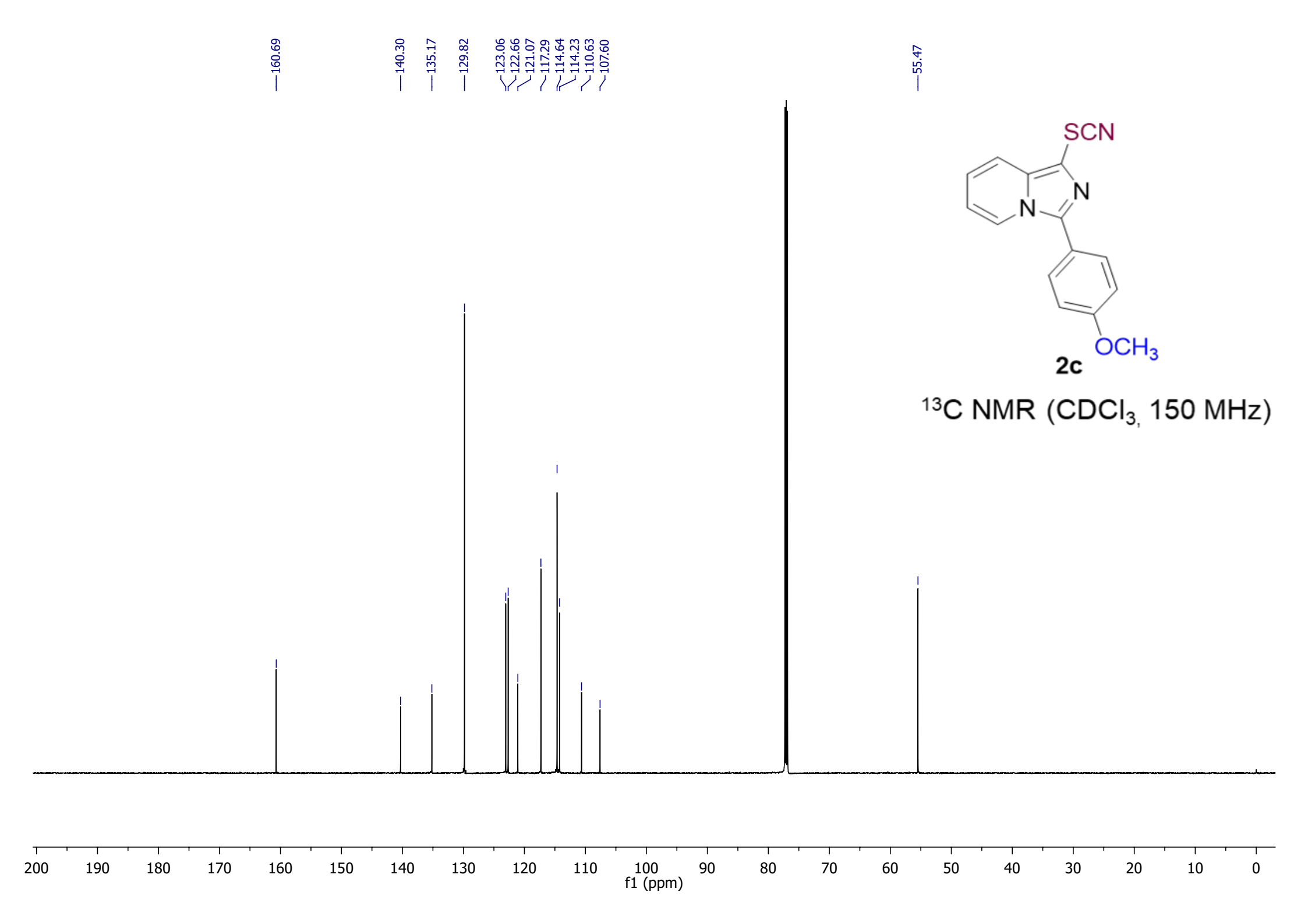
8.459
8.447
8.446
7.989
7.973
7.789
7.771
7.491
7.477
7.475
7.473
7.461
7.459
7.367
7.352
7.145
7.131
7.118
2.458
SCN
N
N
CH3
2b
1H NMR (CDCl3, 600 MHz)
1.00
1.94
1.03
1.03
2.05
1.02
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.17
147.94
139.62
129.50
129.08
128.70
127.96
124.37
118.16
114.32
108.18
94.33
21.44
SCN
N
N
CH3
2b
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.280
8.268
7.726
7.716
7.712
7.701
7.090
7.076
7.067
6.788
6.777
6.766
3.908
SCN
N
N
OCH3
2c
1H NMR (CDCl3, 600 MHz)
1.00
2.97
3.02
0.99
3.11
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)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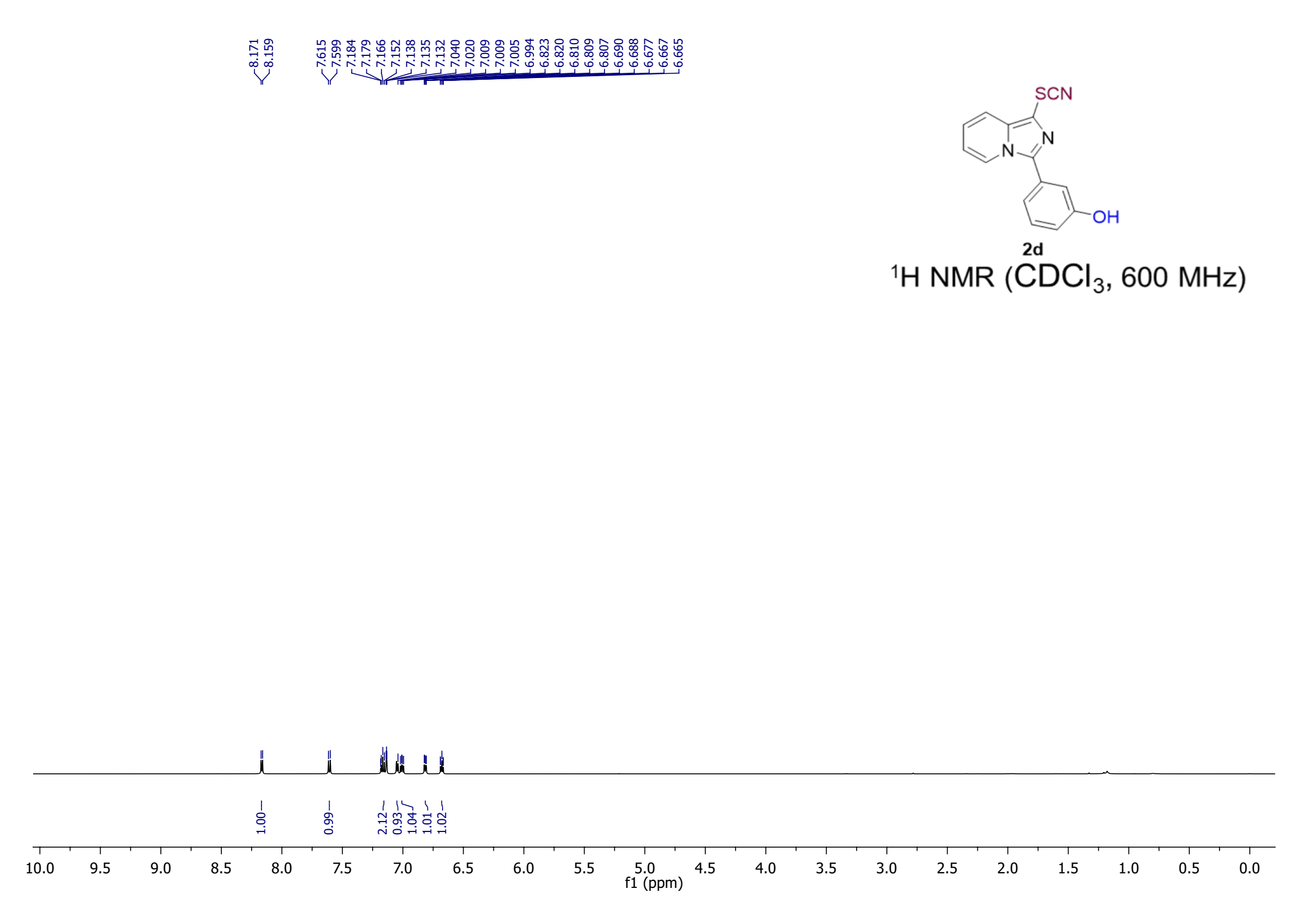
140.30
135.17
129.82
123.06
122.66
121.07
117.29
114.64
114.23
110.63
107.60
55.47
SCN
N
N
OCH3
2c
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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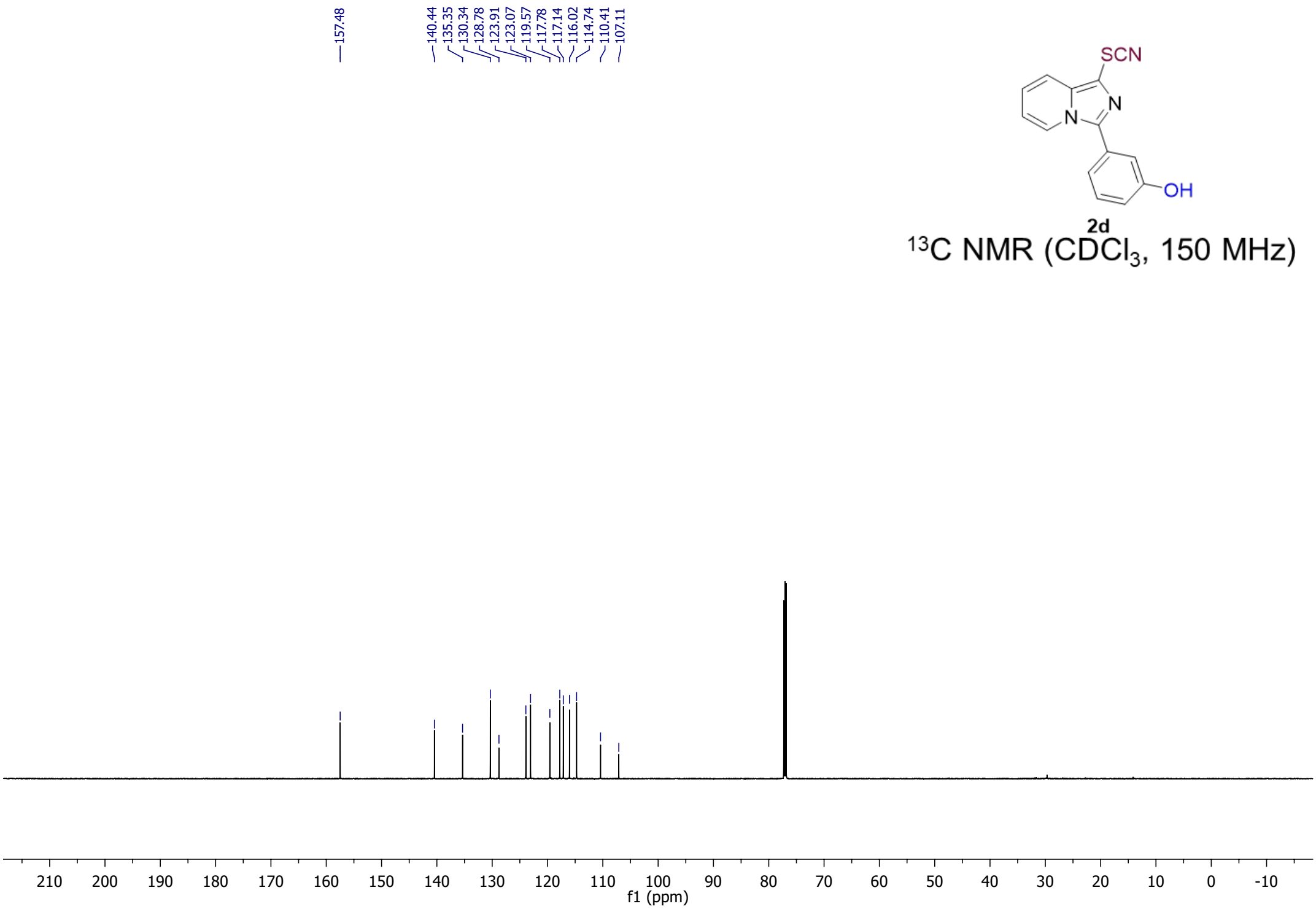
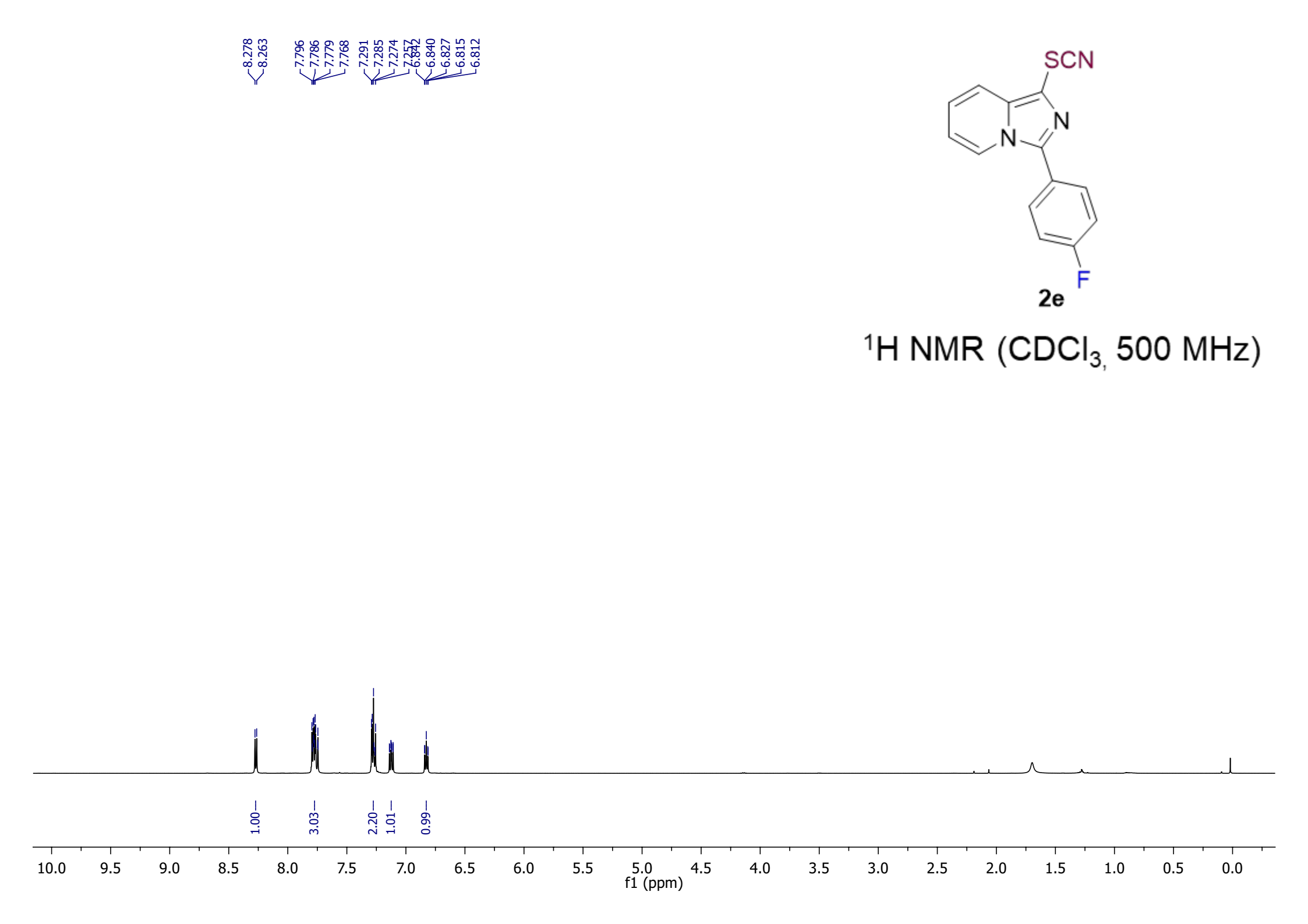
8.159
7.615
7.599
7.184
7.179
7.166
7.152
7.138
7.135
7.132
7.040
7.020
7.009
7.009
7.005
6.994
6.823
6.820
6.810
6.809
6.807
6.690
6.688
6.677
6.667
6.665
SCN
N
N
OH
2d
1H NMR (CDCl3, 600 MHz)
1.00
0.99
2.12
0.93
1.04
1.01
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.48
140.44
135.35
130.34
128.78
123.91
123.07
119.57
117.78
117.14
116.02
114.74
110.41
107.11
SCN
N
N
OH
2d
^{13}C NMR ($CDCl_3$, 150 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.263
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7.786
7.779
7.768
7.291
7.285
7.274
7.257
6.842
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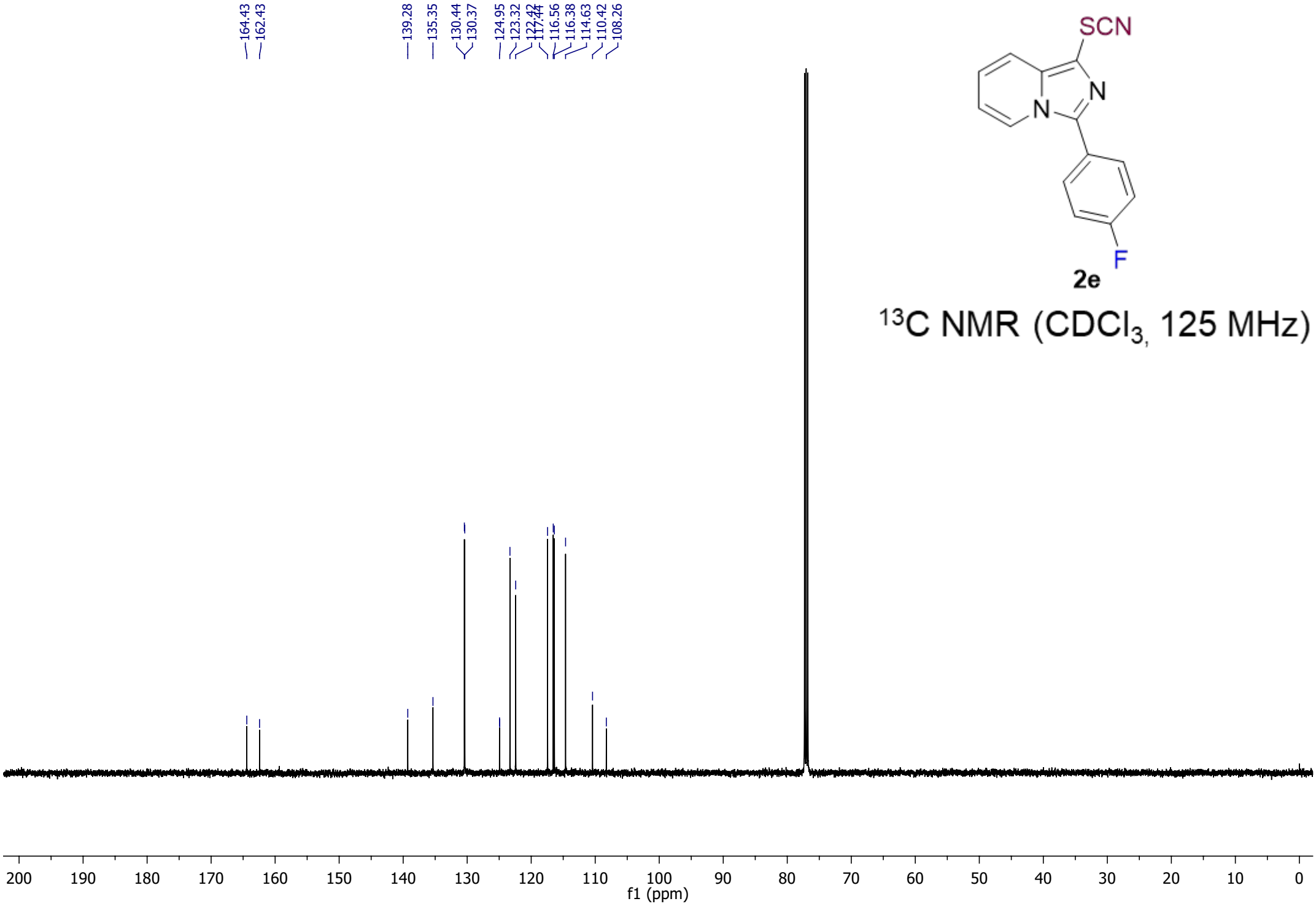
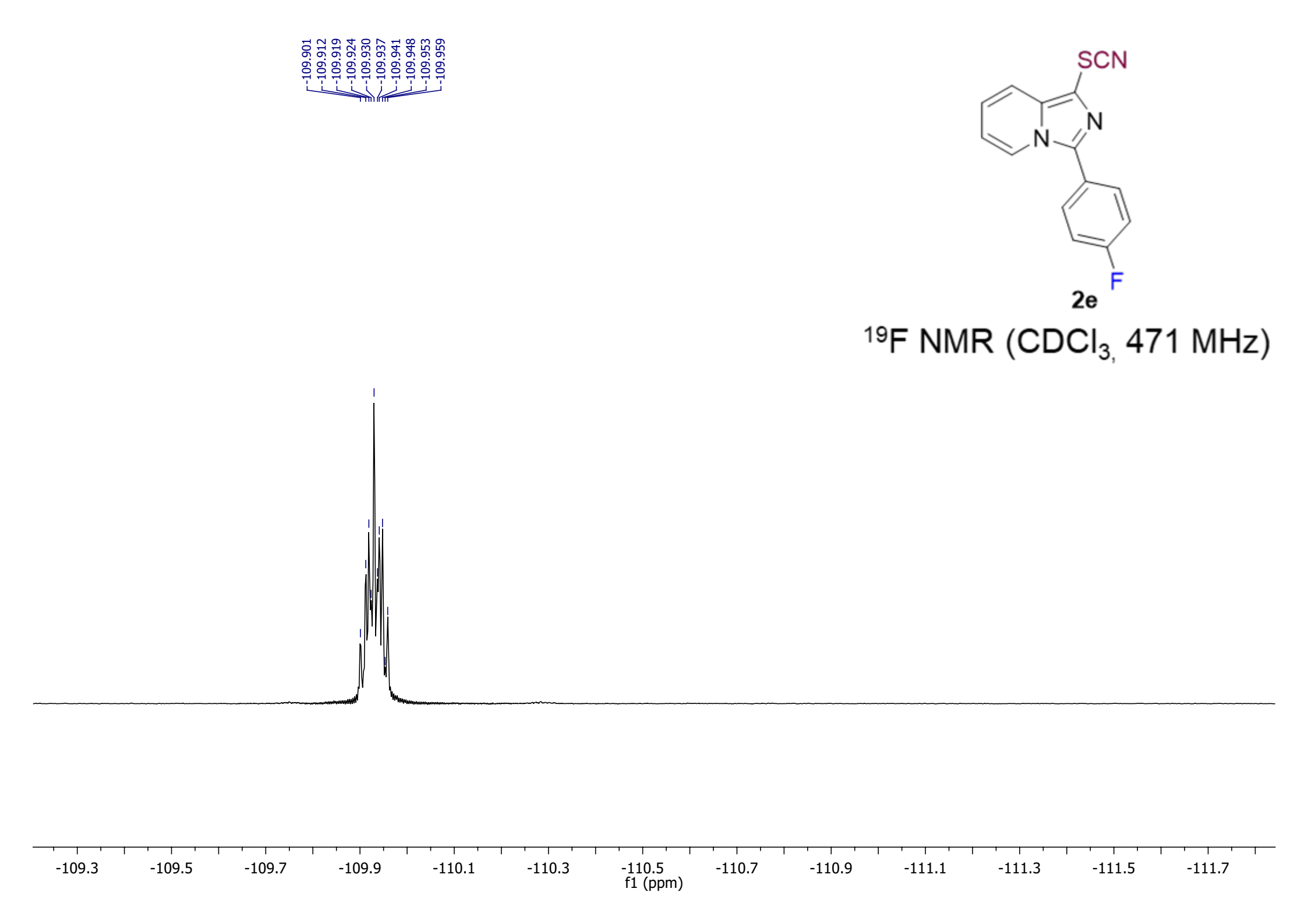
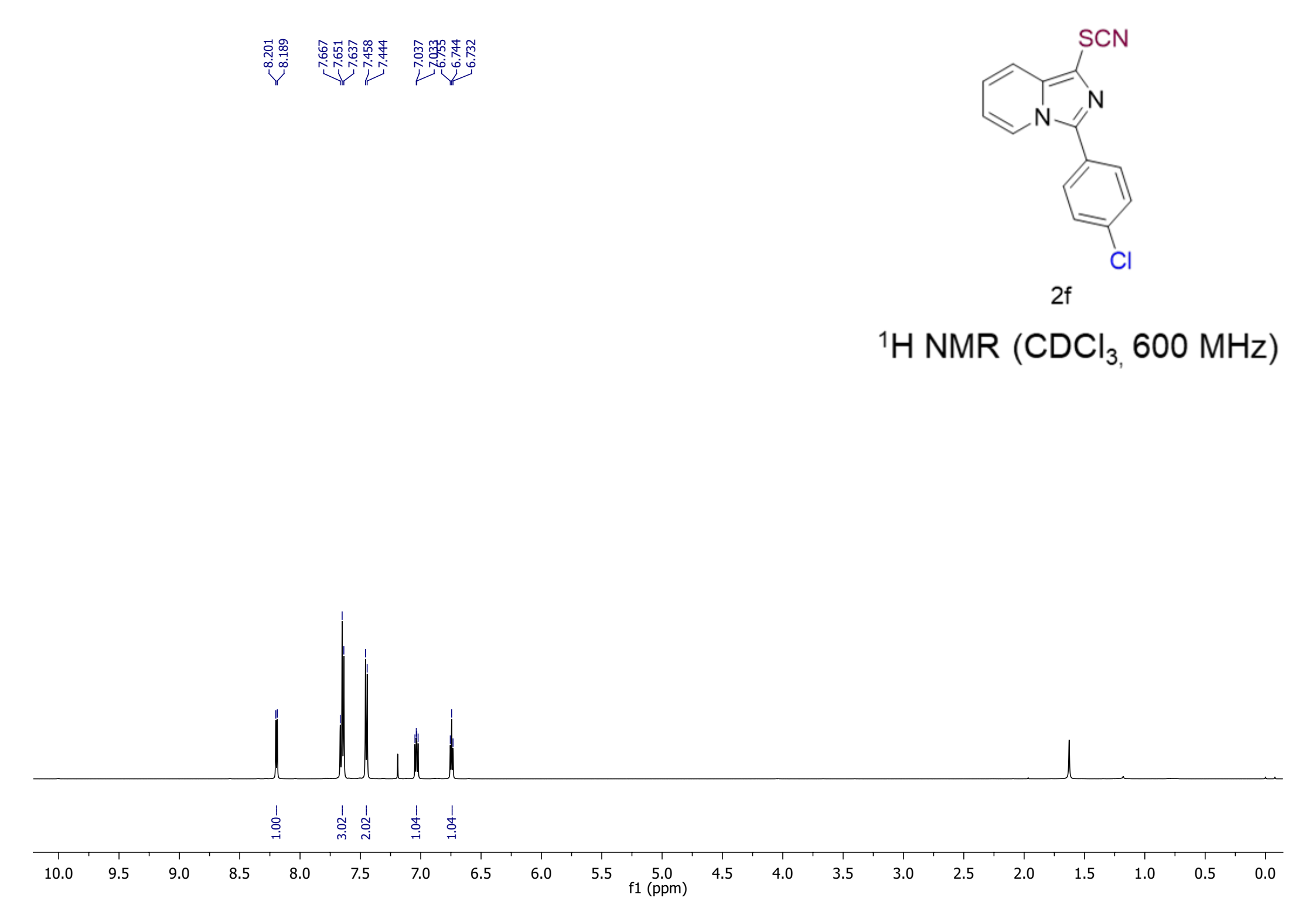
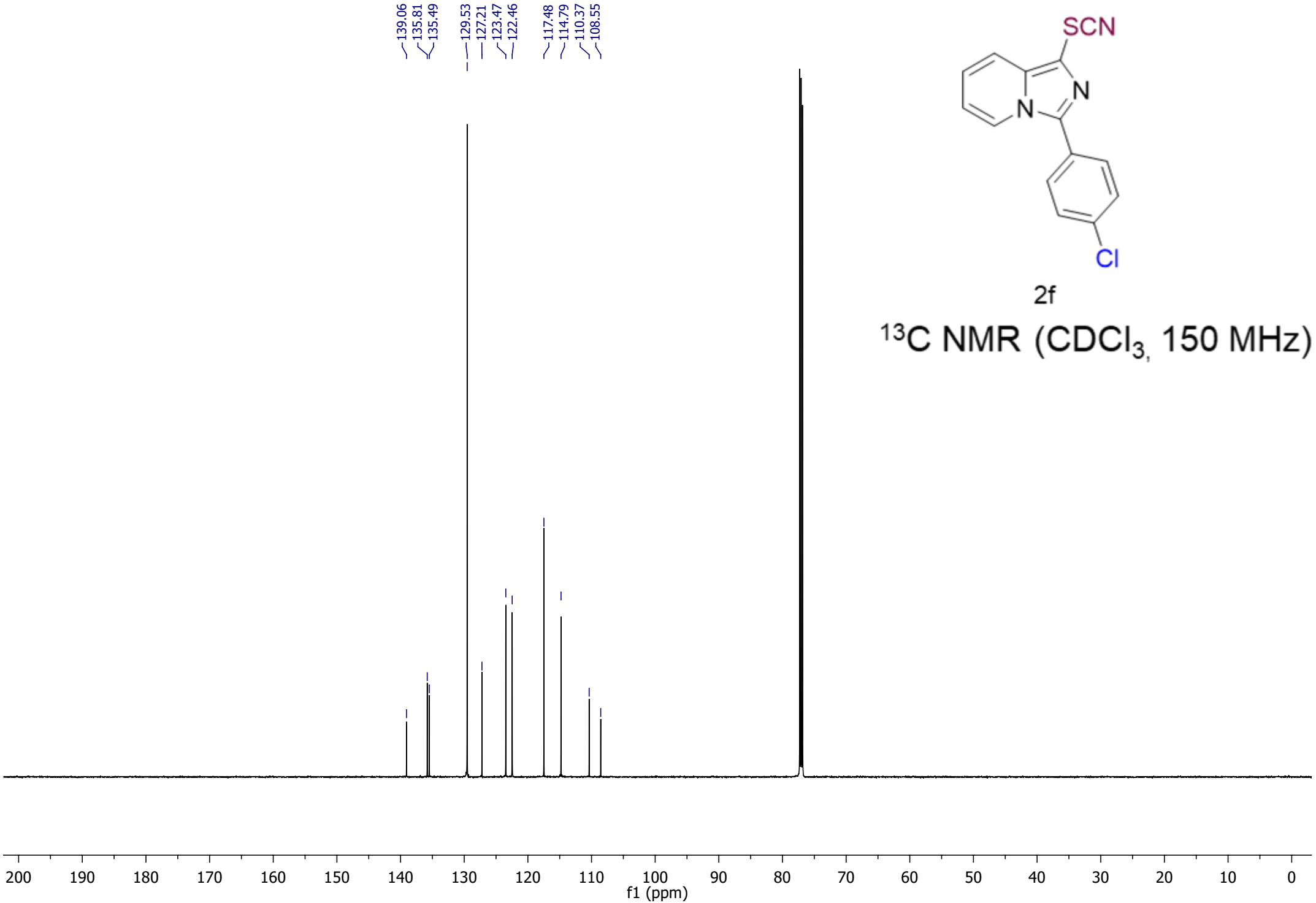
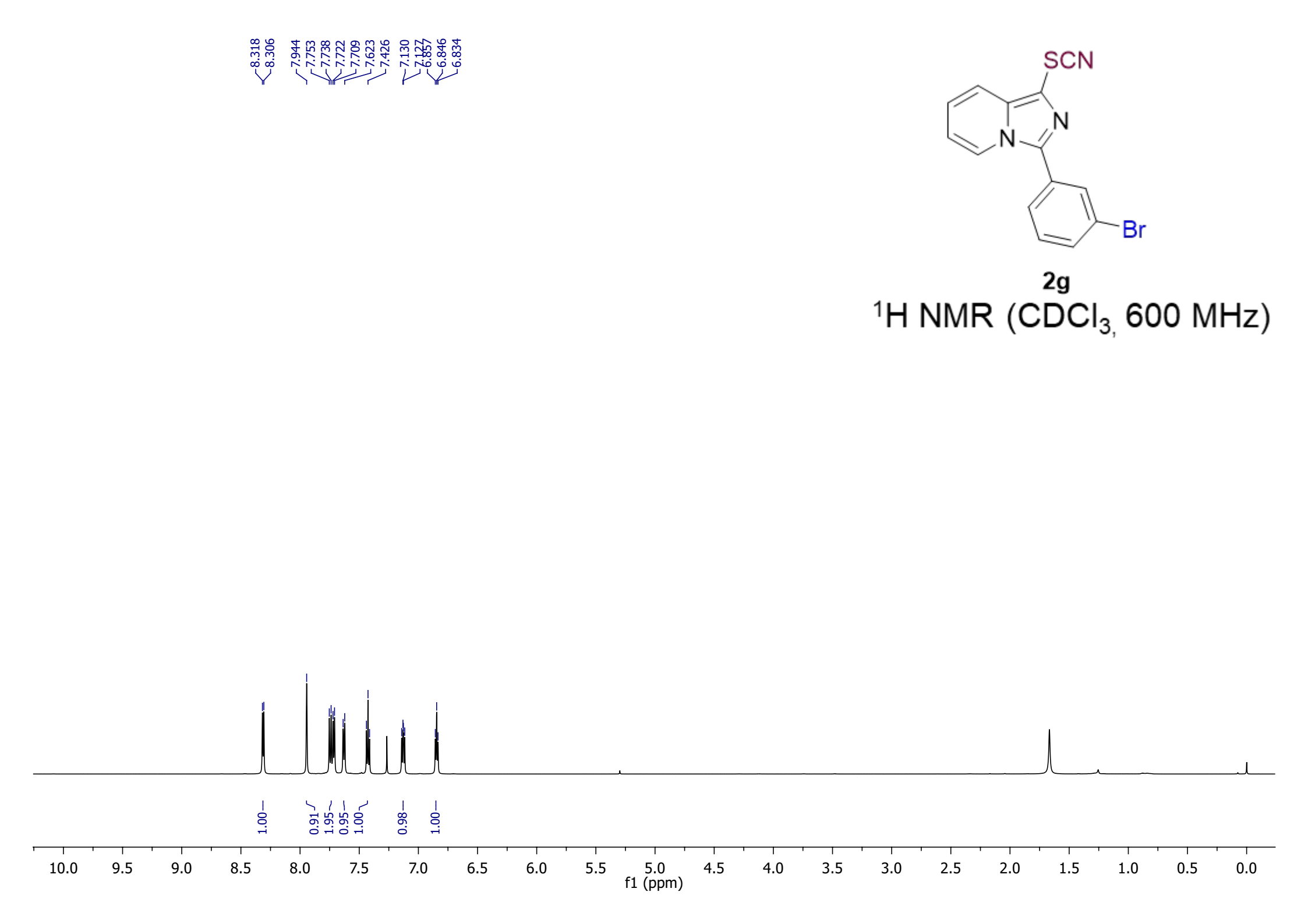
6.827
6.815
6.812
SCN
N
N
F
2e
1H NMR (CDCl3, 500 MHz)
1.00
3.03
2.20
1.01
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

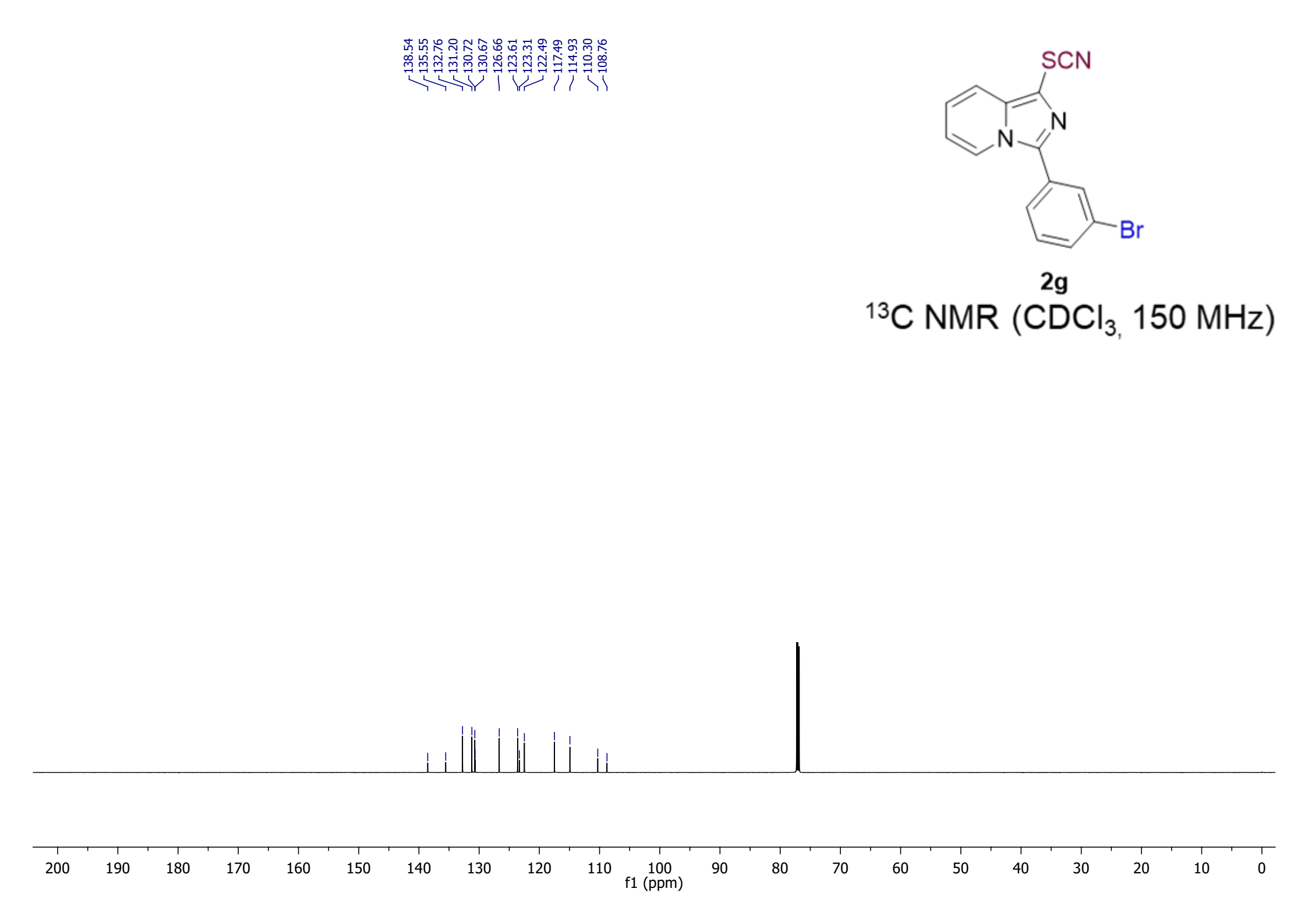

164.43
162.43
139.28
135.35
130.44
130.37
124.95
123.32
122.42
117.44
116.56
116.38
114.63
110.42
108.26
SCN
N
N
F
2e
^{13}C NMR ($CDCl_3$, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

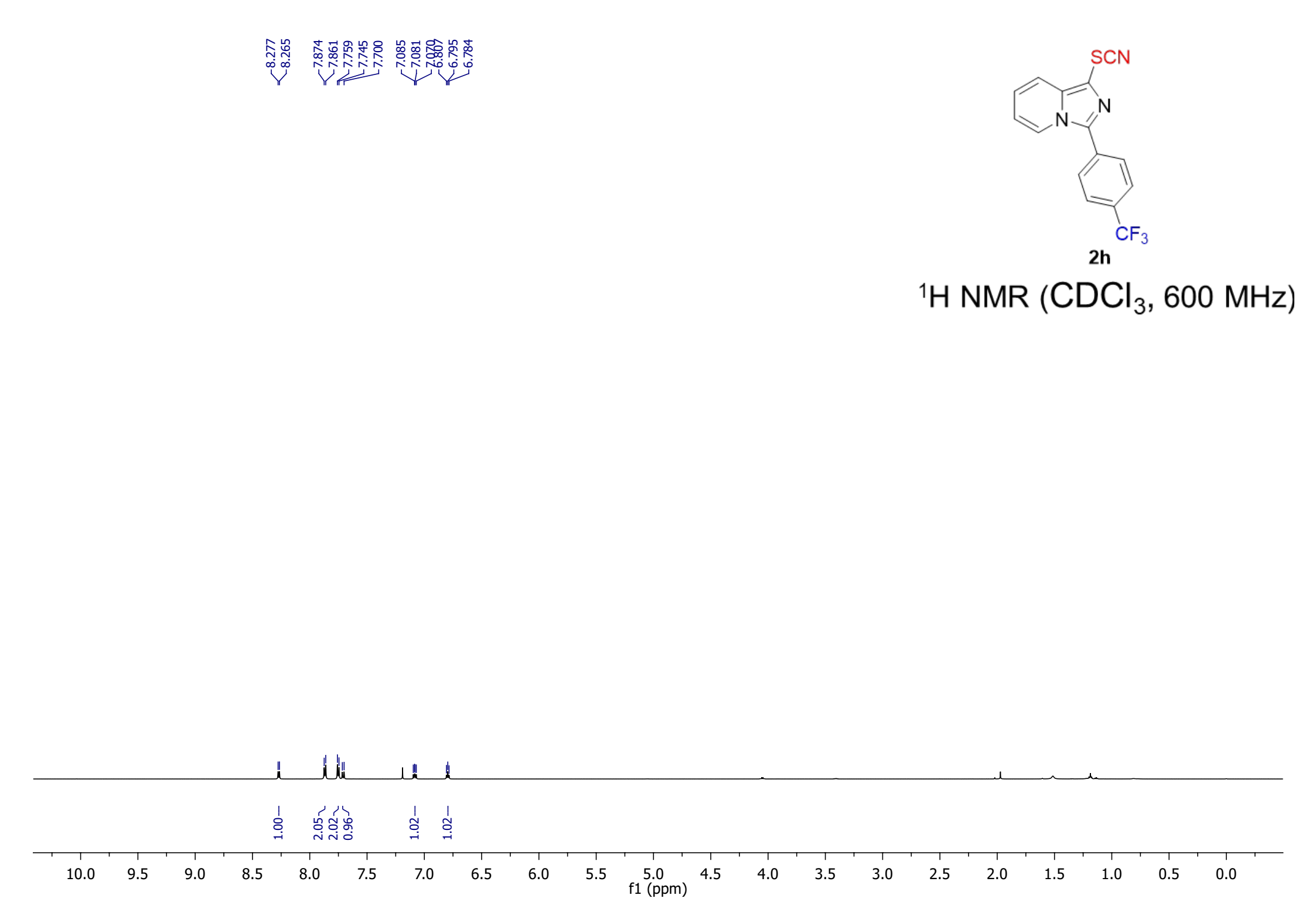

-109.901
-109.912
-109.919
-109.924
-109.930
-109.937
-109.941
-109.948
-109.953
-109.959
SCN
N
N
F
2e
19F NMR (CDCl3, 471 MHz)
-109.3
-109.5
-109.7
-109.9
-110.1
-110.3
-110.5
-110.7
-110.9
-111.1
-111.3
-111.5
-111.7
f1 (ppm)

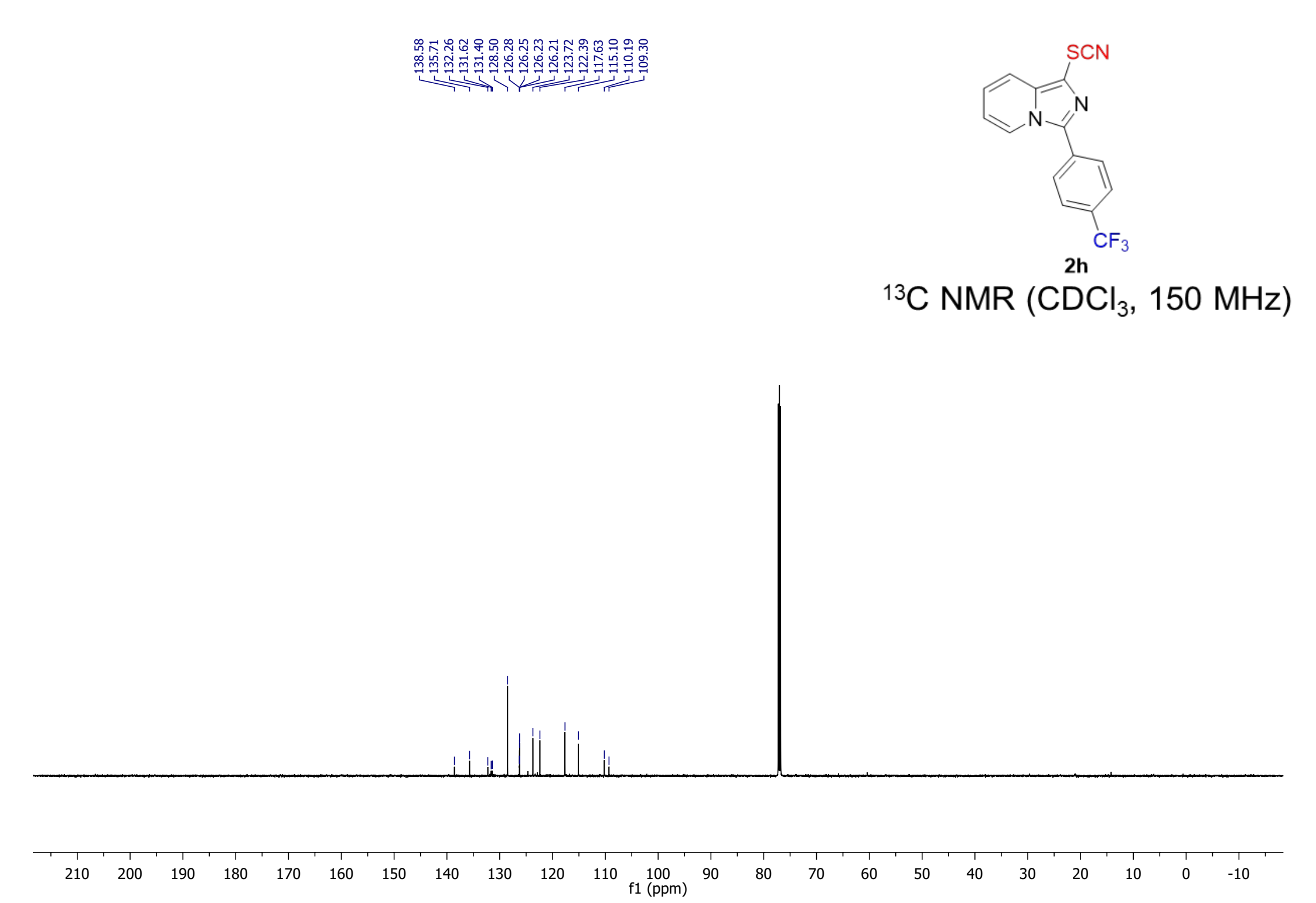

8.201
8.189
7.667
7.651
7.637
7.458
7.444
7.037
7.033
6.735
6.744
6.732
SCN
N
N
Cl
2f
1H NMR (CDCl3, 600 MHz)
1.00
3.02
2.02
1.04
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

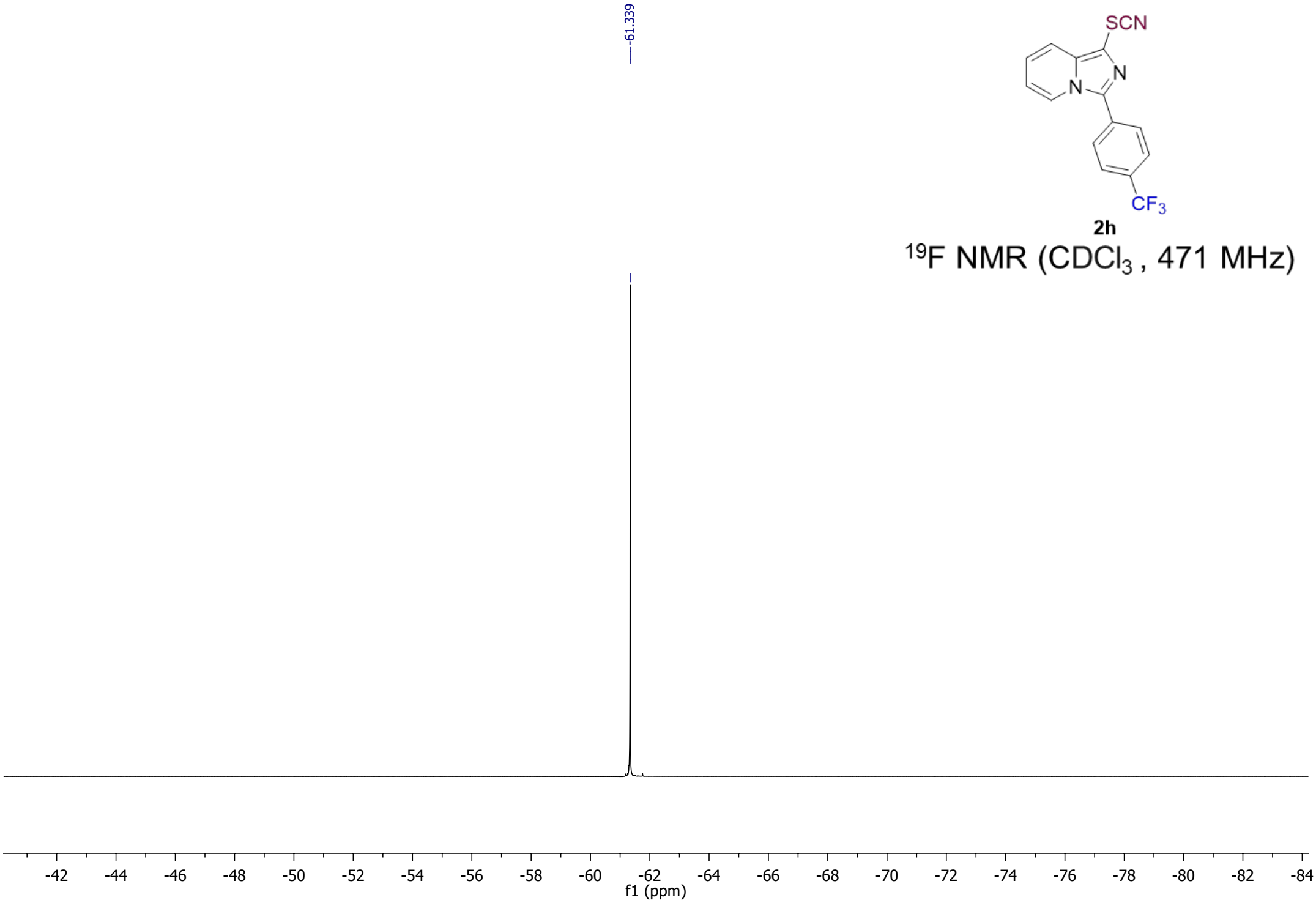

139.06
135.81
135.49
129.53
127.21
123.47
122.46
117.48
114.79
110.37
108.55
SCN
N
N
Cl
2f
^{13}C NMR ($CDCl_3$, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.318
8.306
7.944
7.753
7.738
7.722
7.709
7.623
7.426
7.130
7.127
6.857
6.846
6.834
SCN
N
N
Br
2g
1H NMR (CDCl3, 600 MHz)
1.00
0.91
1.95
0.95
1.00
0.98
1.00
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)


138.54
135.55
132.76
131.20
130.72
130.67
126.66
123.61
123.31
122.49
117.49
114.93
110.30
108.76
SCN
N
N
Br
2g
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

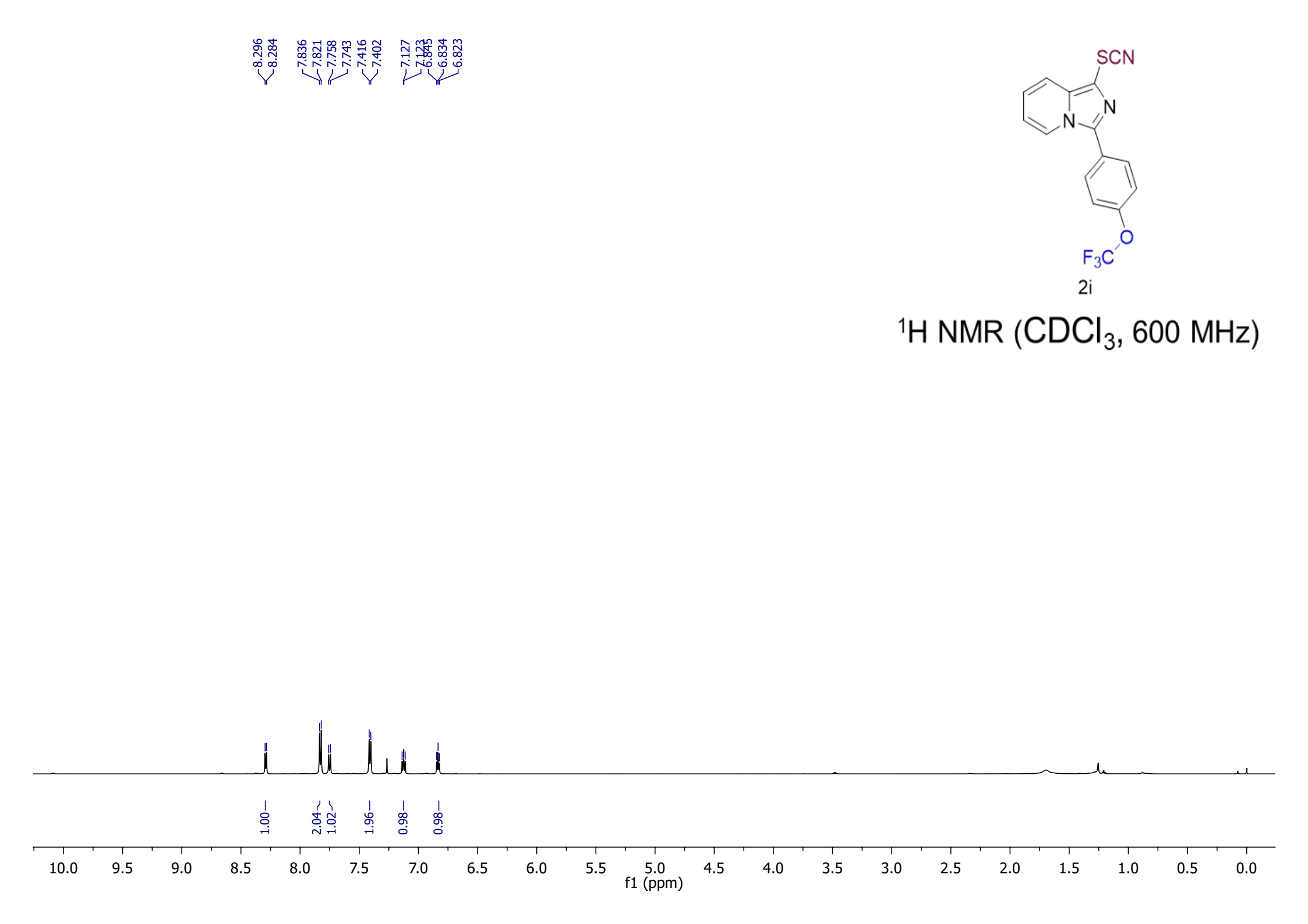

8.277
8.265
7.874
7.861
7.759
7.745
7.700
7.085
7.081
7.070
6.807
6.795
6.784
SCN
N
N
CF3
2h
1H NMR (CDCl3, 600 MHz)
1.00
2.05
2.02
0.96
1.02
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

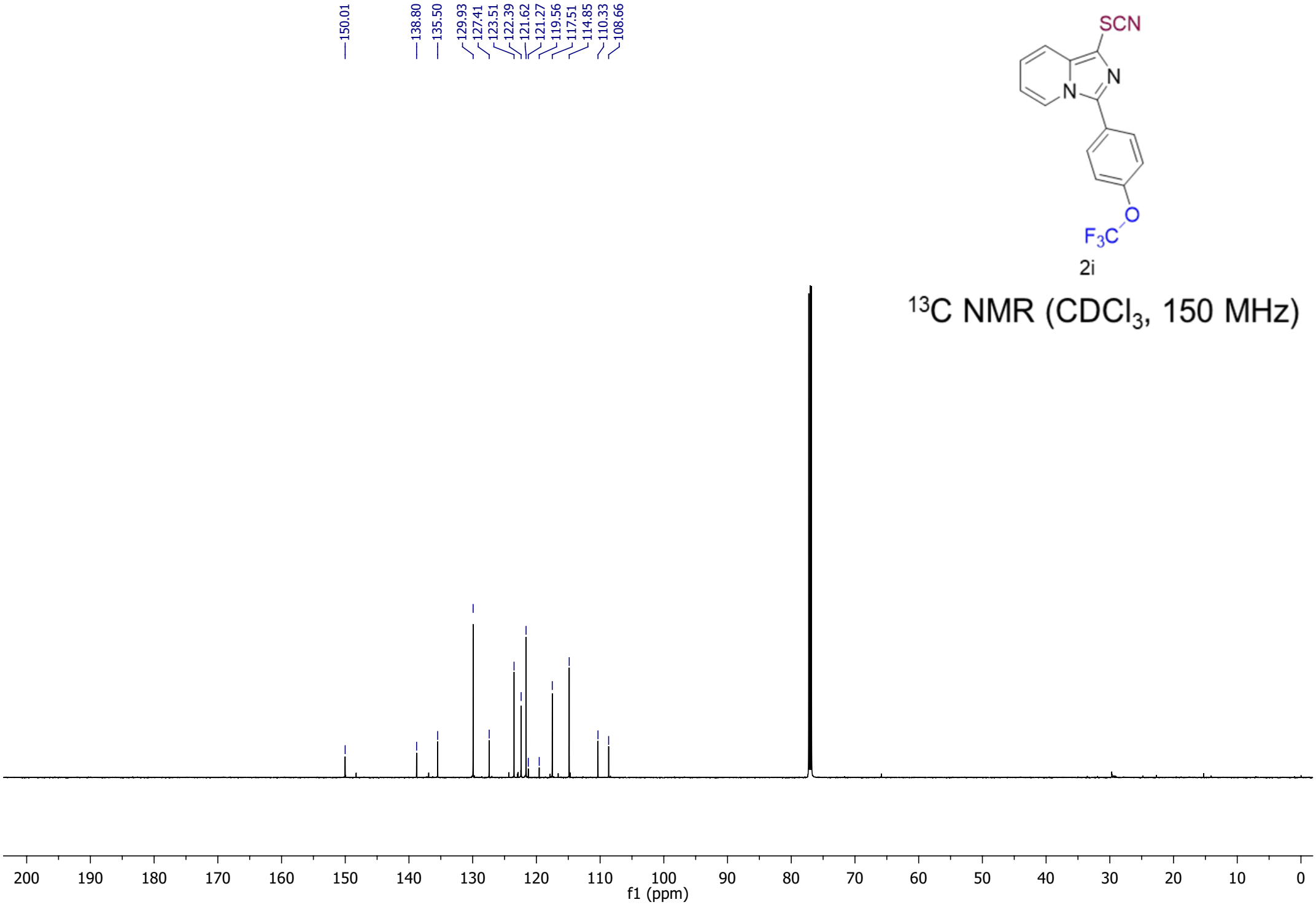

138.58
135.71
132.26
131.62
131.40
128.50
126.28
126.25
126.23
126.21
123.72
122.39
117.63
115.10
110.19
109.30
SCN
N
N
CF3
2h
13C NMR (CDCl3, 150 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

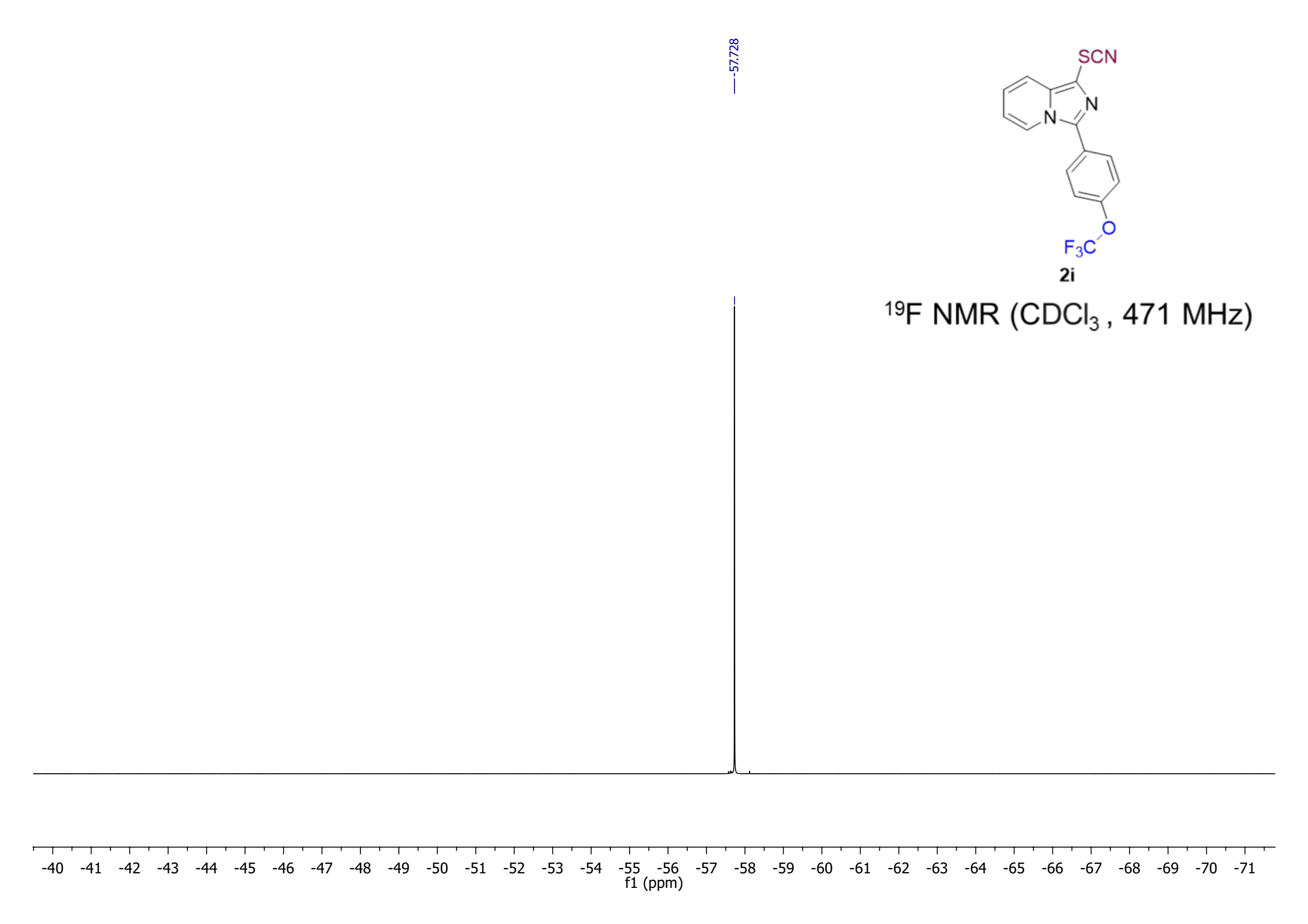


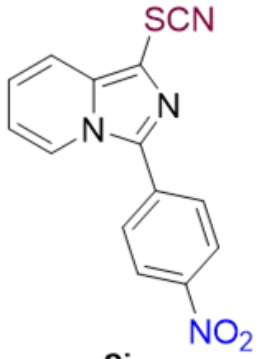
2h

^{19}F NMR ($CDCl_3$, 471 MHz)


8.296
8.284
7.836
7.821
7.758
7.743
7.416
7.402
7.127
7.123
6.845
6.834
6.823
SCN
N
N
O
F3C
2i
1H NMR (CDCl3, 600 MHz)
1.00
2.04
1.02
1.96
0.98
0.98
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)

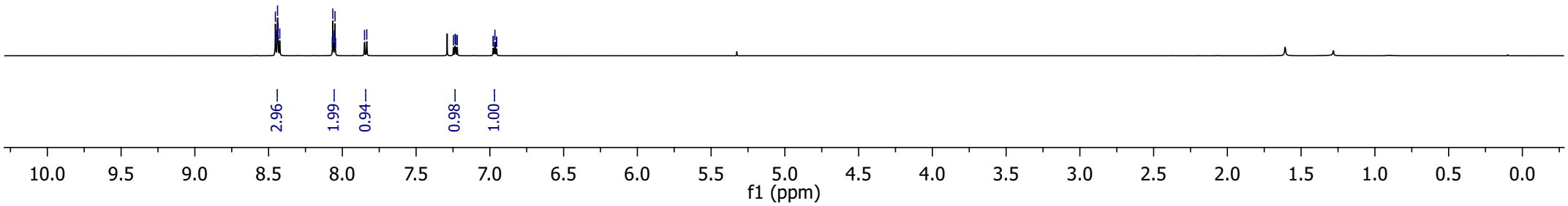

150.01
138.80
135.50
129.93
127.41
123.51
122.39
121.62
121.27
119.56
117.51
114.85
110.33
108.66
SCN
N
N
O
F3C
2i
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

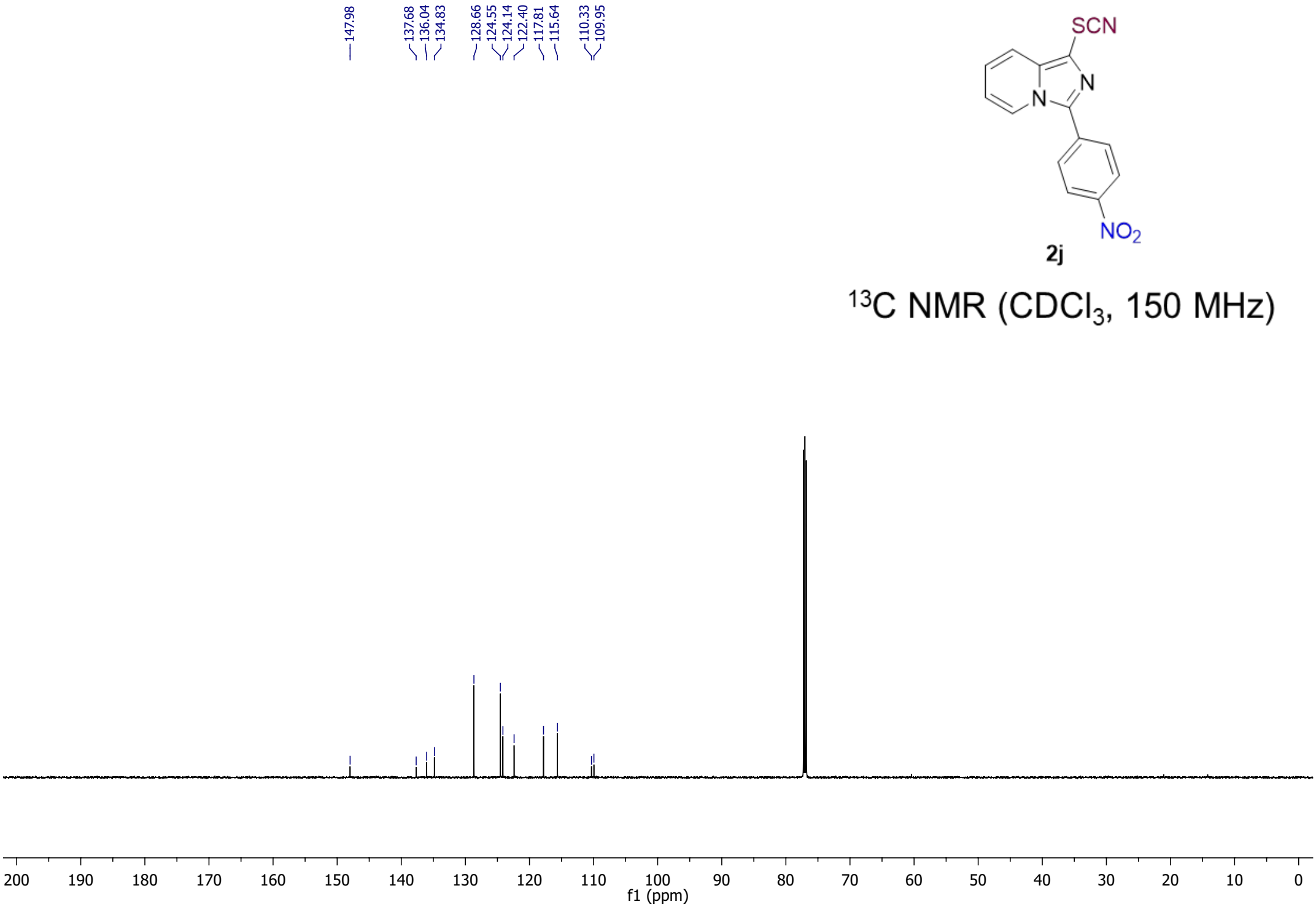

-57.728
SCN
N
N
O
F3C
2i
19F NMR (CDCl3 , 471 MHz)
-40 -41 -42 -43 -44 -45 -46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71
f1 (ppm)

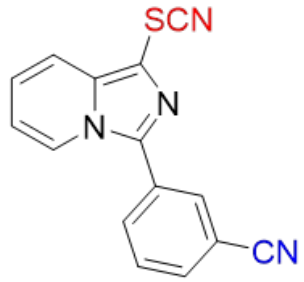


2j

^{1}H NMR ($CDCl_3$, 600 MHz)

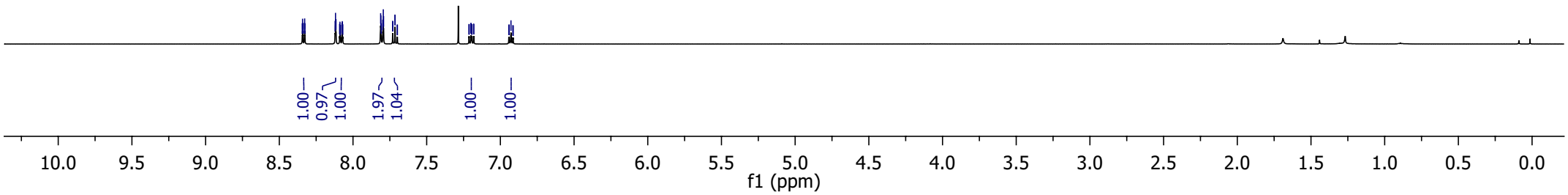



147.98
137.68
136.04
134.83
128.66
124.55
124.14
122.40
117.81
115.64
110.33
109.95
SCN
N
N
NO2
2j
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

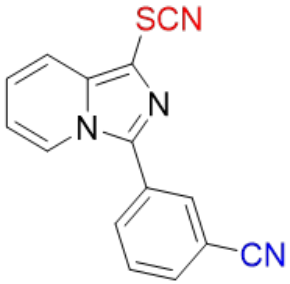


2k

^{1}H NMR ($CDCl_3$, 500 MHz)

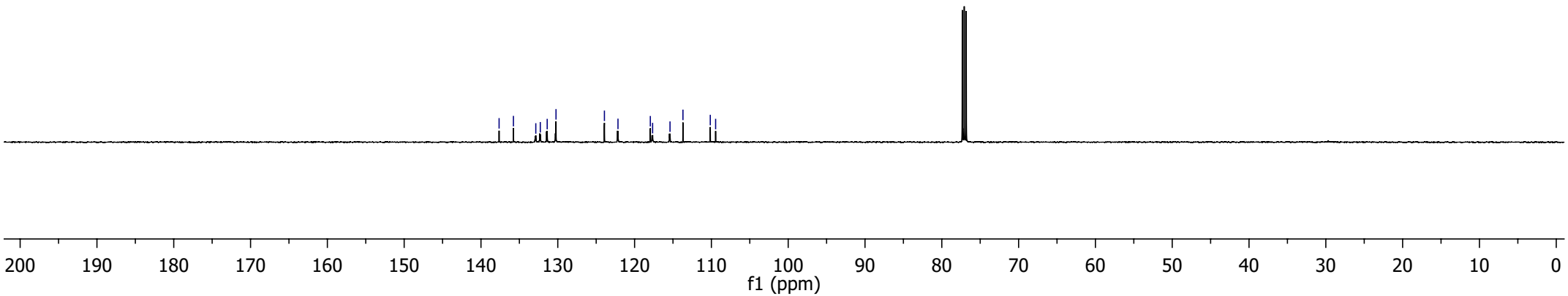


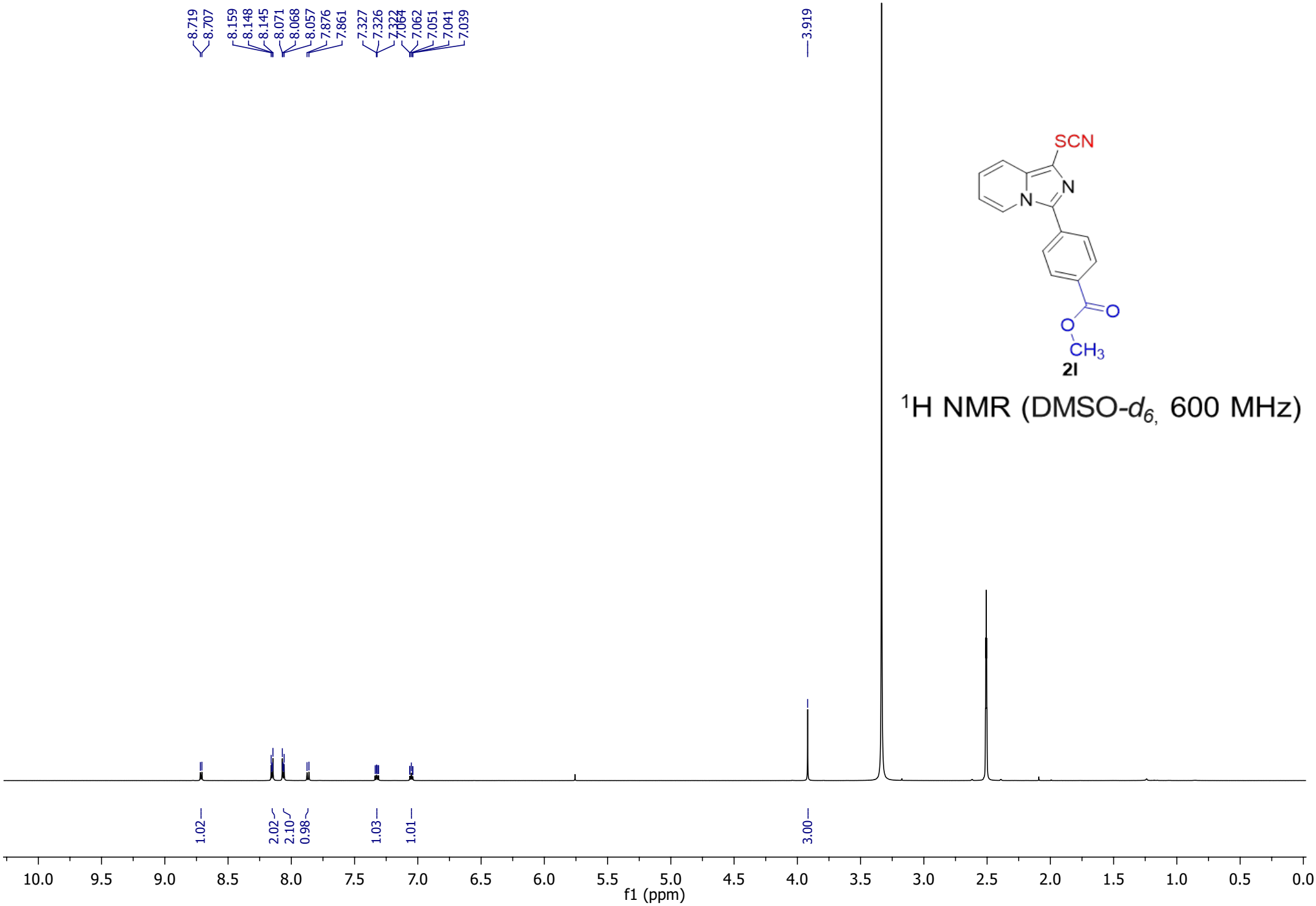
137.64
135.78
132.86
132.28
131.38
130.23
123.93
122.16
117.95
117.65
115.39
113.70
110.14
109.45

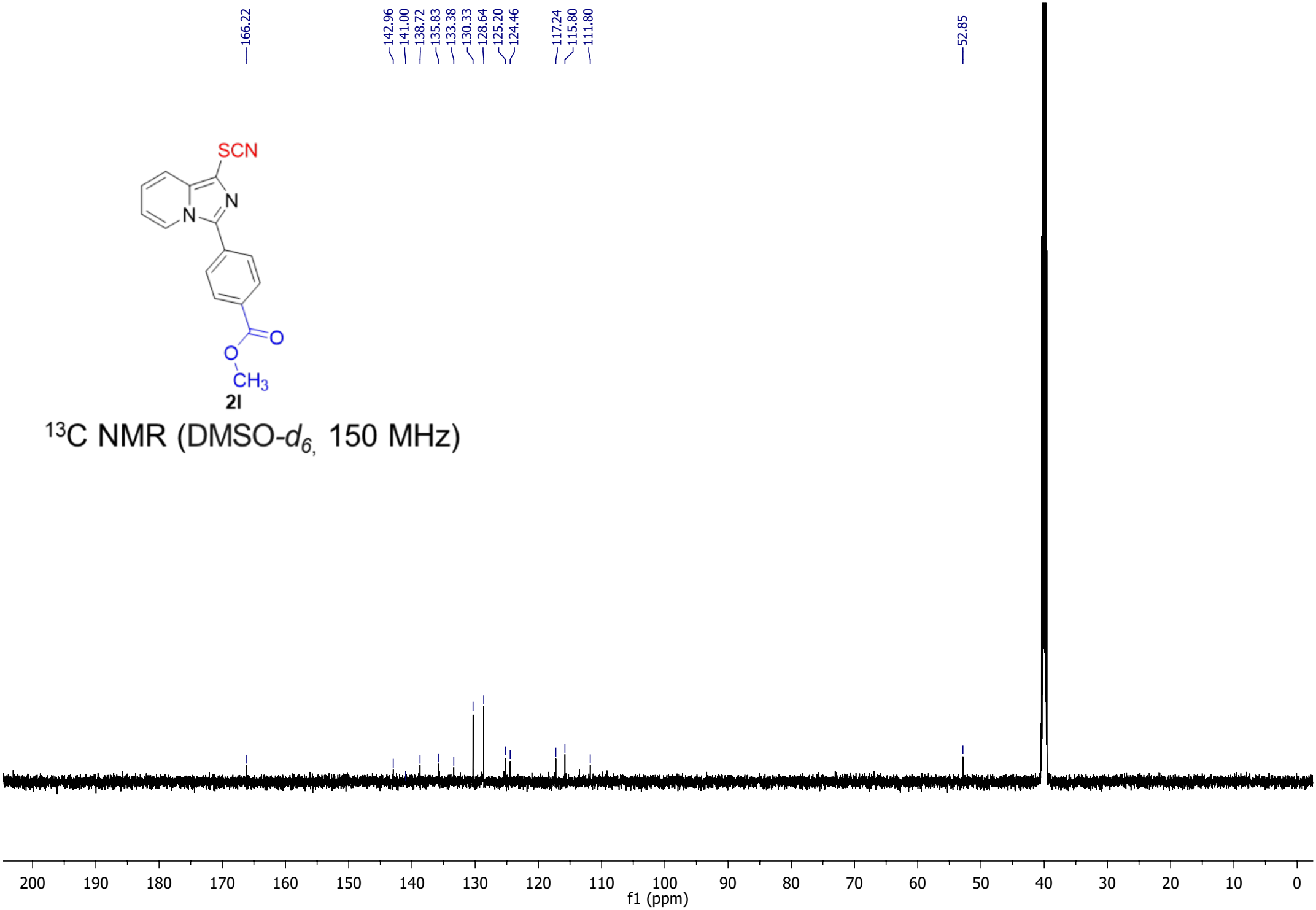


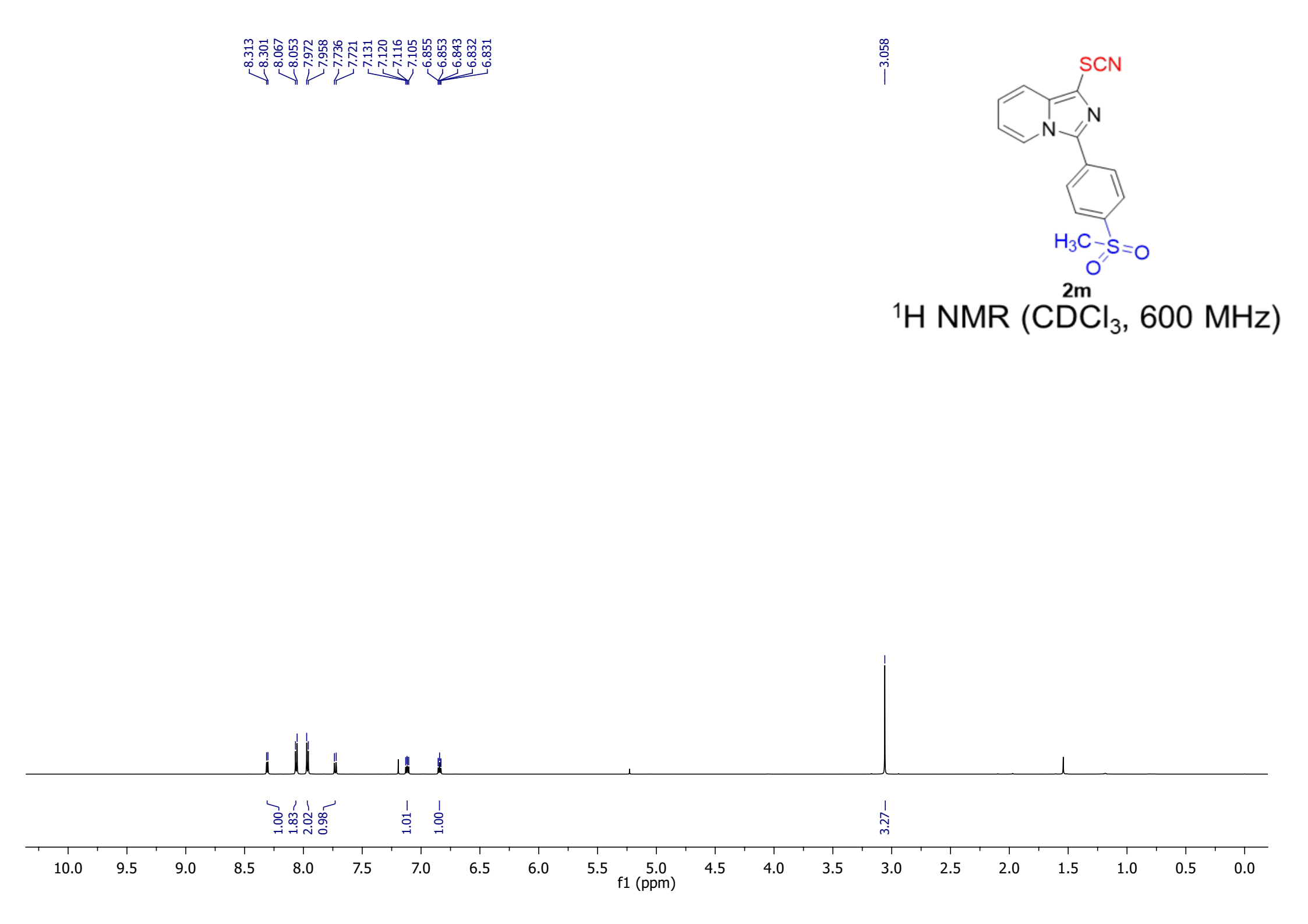
2k

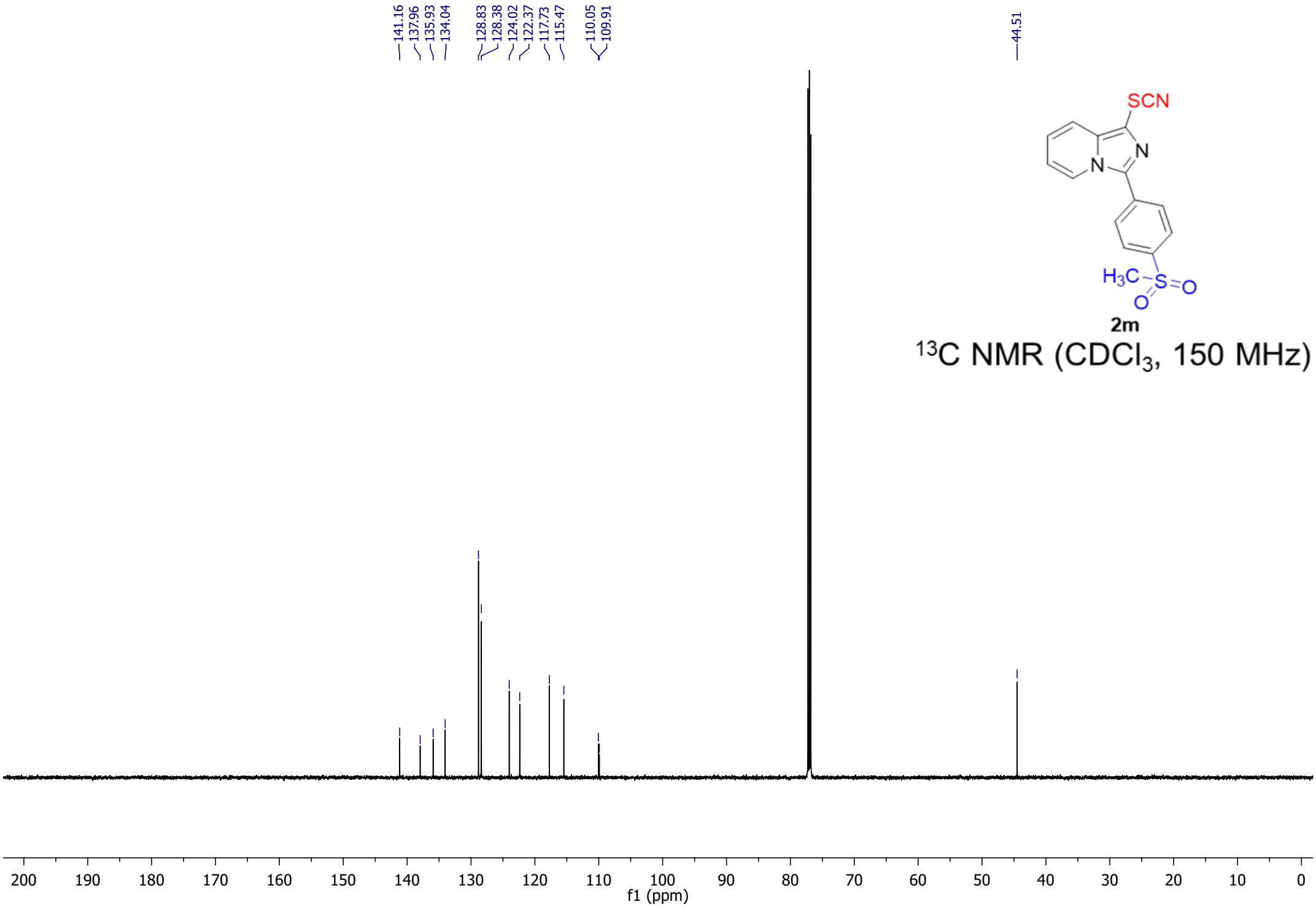
^{13}C NMR ($CDCl_3$, 125 MHz)

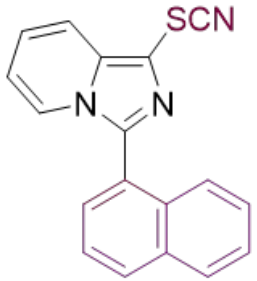



8.719
8.707
8.159
8.148
8.145
8.071
8.068
8.057
7.876
7.861
7.327
7.326
7.322
7.064
7.062
7.051
7.041
7.039
3.919
SCN
N
N
O
O
CH3
2l
1H NMR (DMSO-d6, 600 MHz)
1.02
2.02
2.10
0.98
1.03
1.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.22
142.96
141.00
138.72
135.83
133.38
130.33
128.64
125.20
124.46
117.24
115.80
111.80
52.85
SCN
N
N
O
O
CH3
2l
13C NMR (DMSO-d6, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

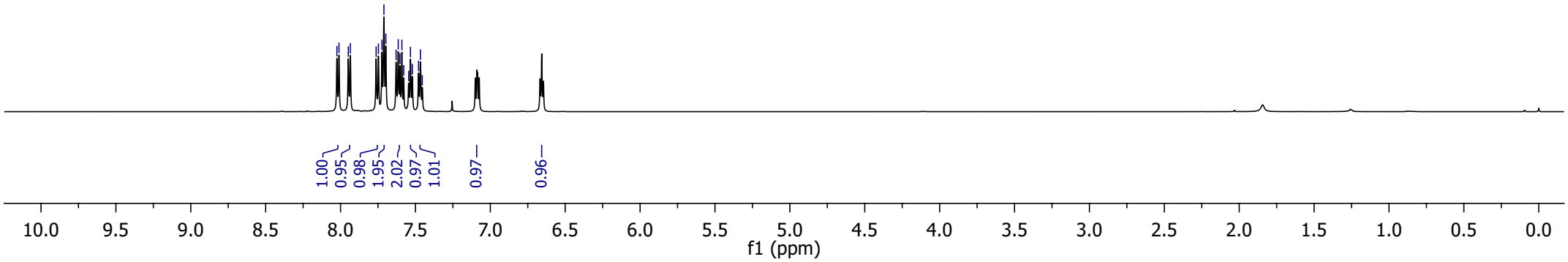

8.313
8.301
8.067
8.053
7.972
7.958
7.736
7.721
7.131
7.120
7.116
7.105
6.855
6.853
6.843
6.832
6.831
3.058
SCN
N
N
H3C
S
O
O
2m
1H NMR (CDCl3, 600 MHz)
1.00
1.83
2.02
0.98
1.01
1.00
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

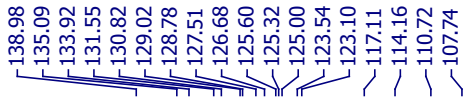

141.16
137.96
135.93
134.04
128.83
128.38
124.02
122.37
117.73
115.47
110.05
109.91
44.51
SCN
N
N
H3C
S
O
O
2m
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

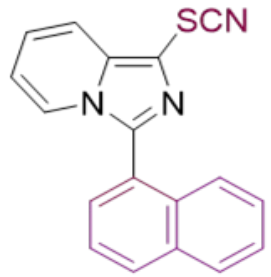


2n

^{1}H NMR ($CDCl_3$, 600 MHz)

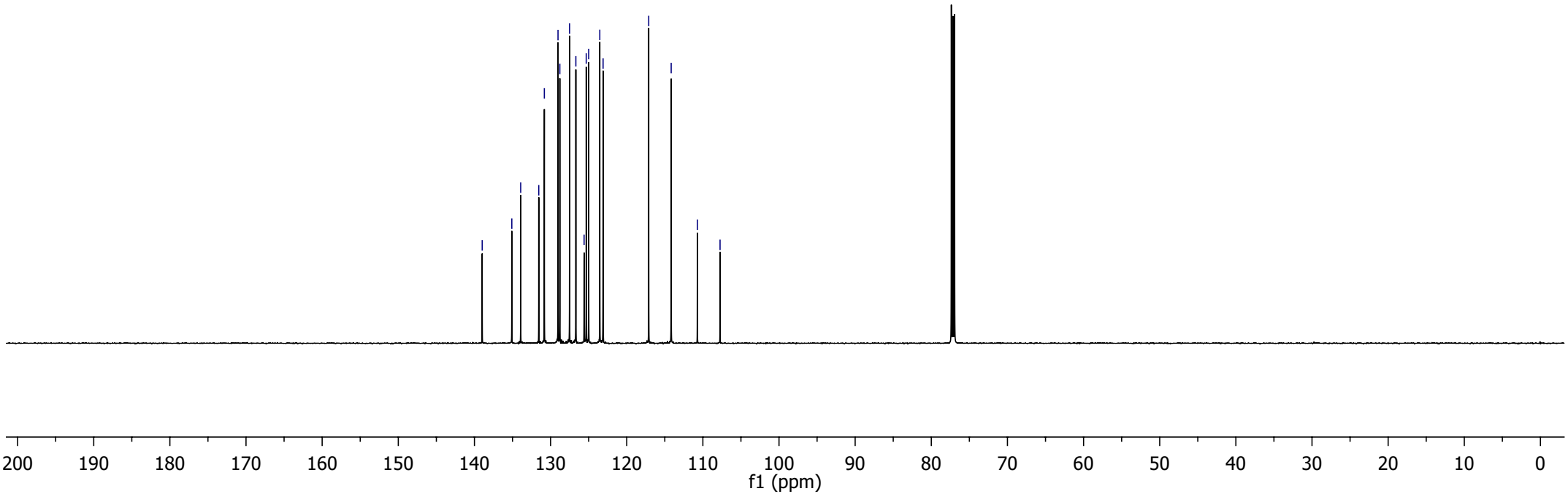


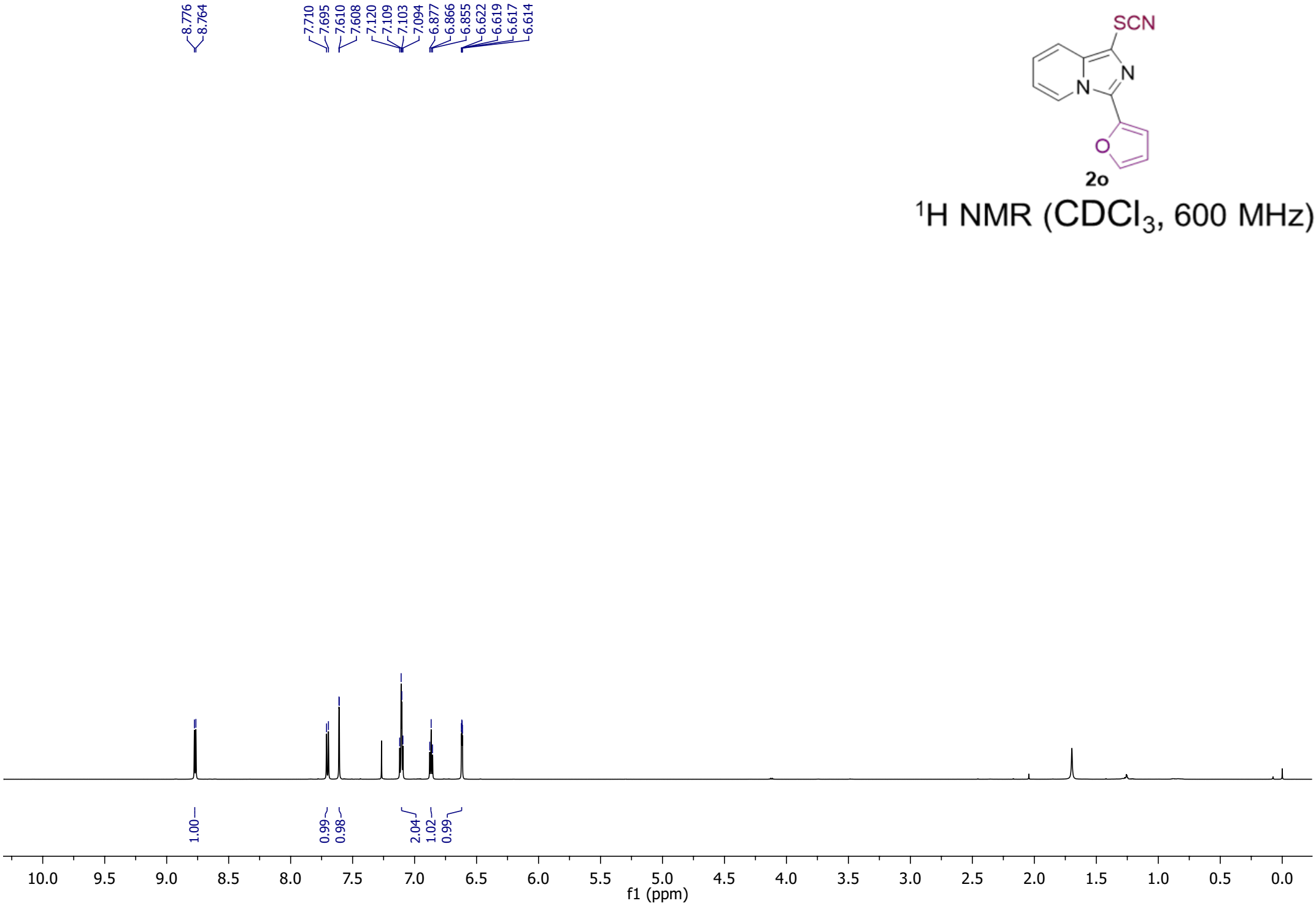


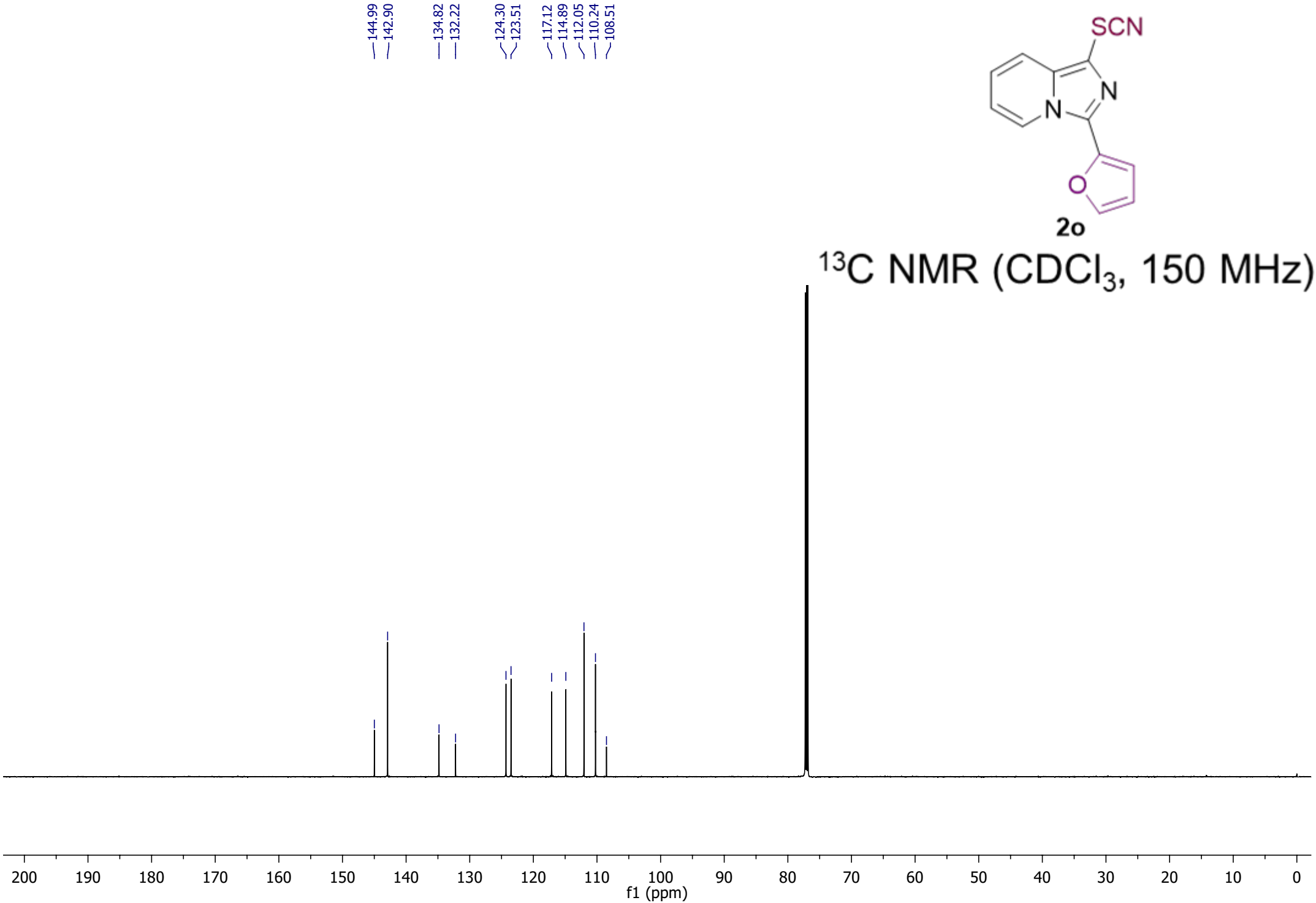


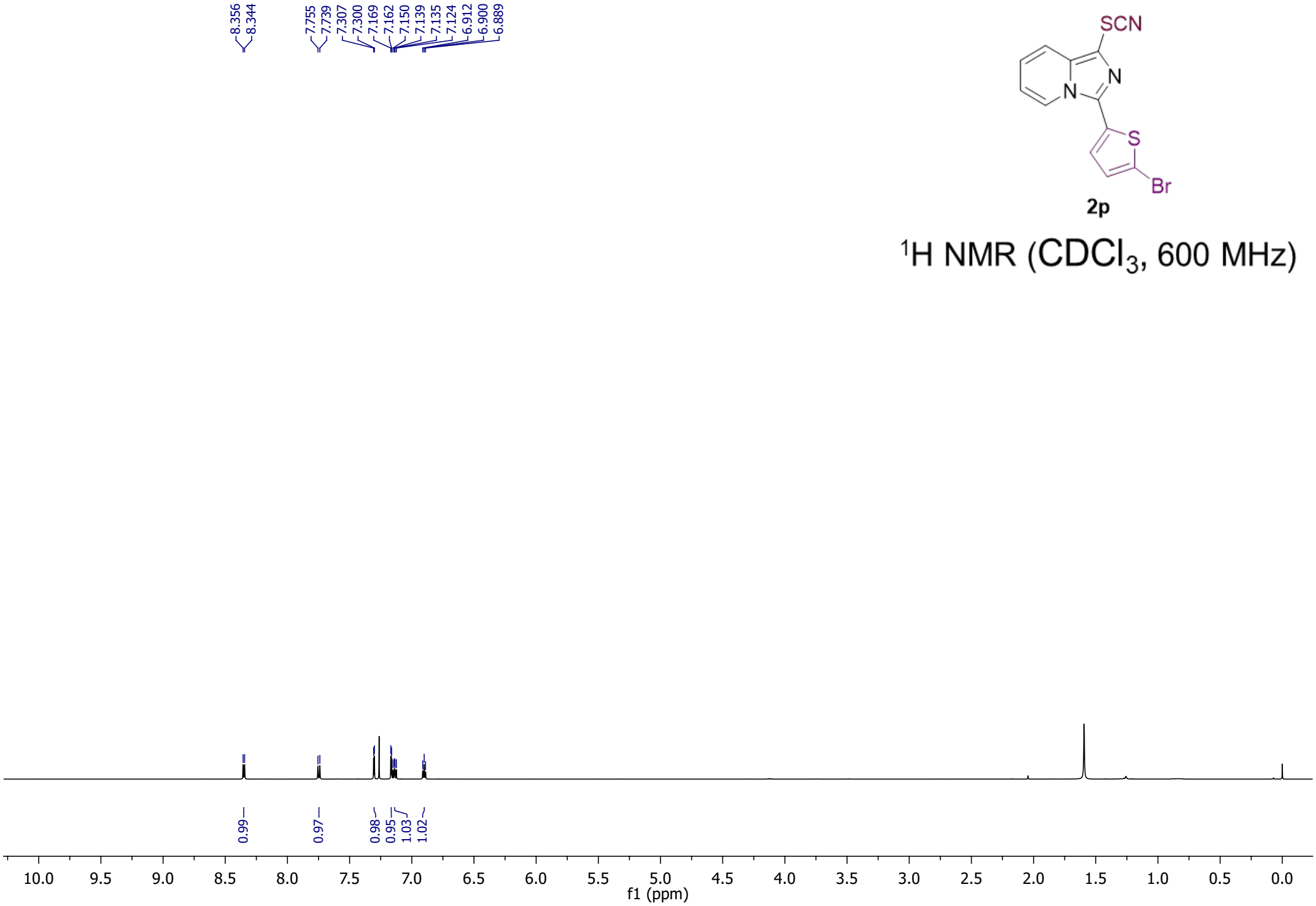
2n

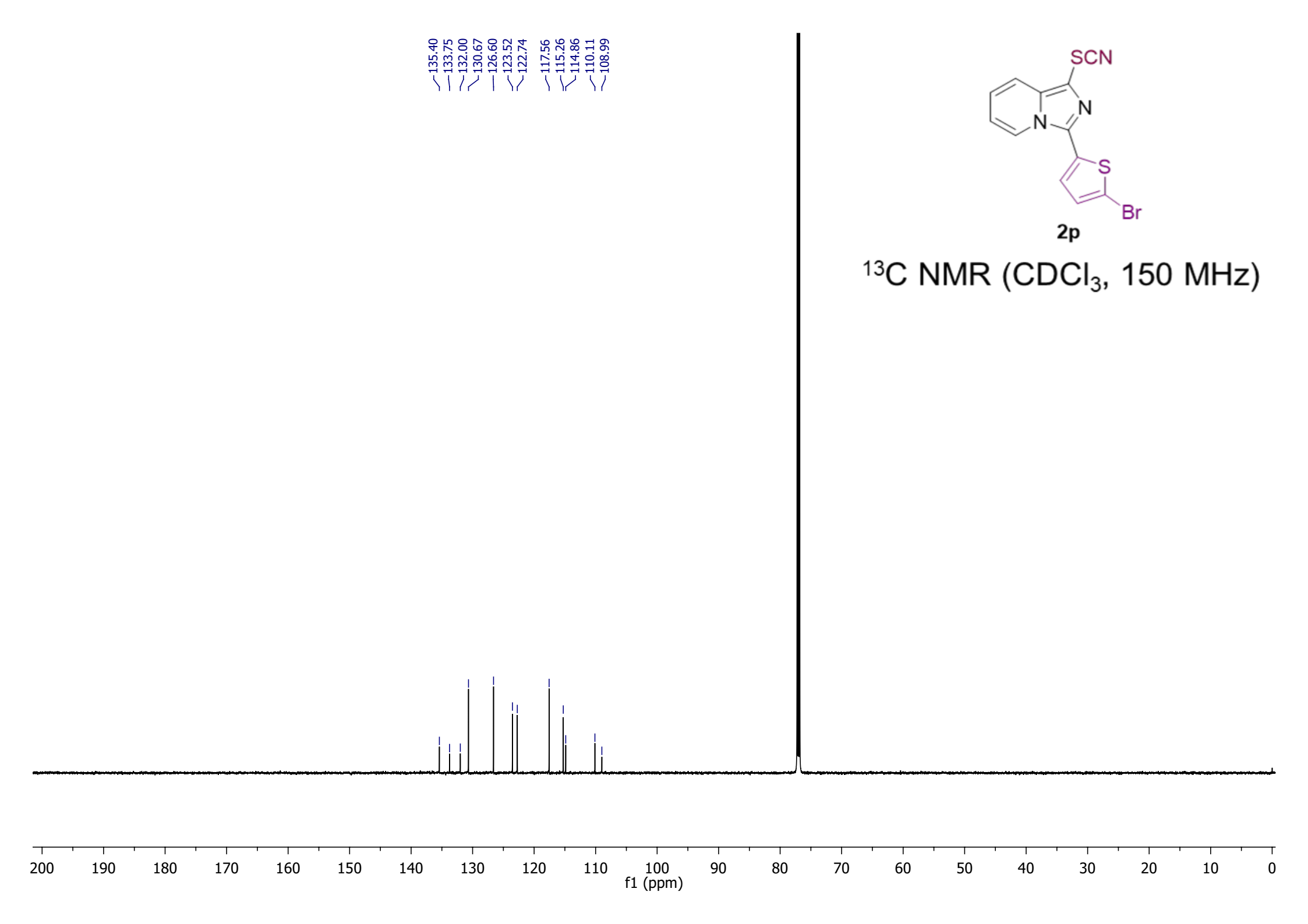
^{13}C NMR ($CDCl_3$, 150 MHz)

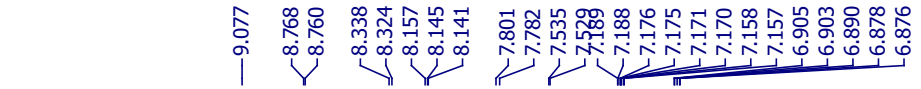


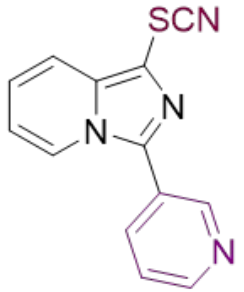

8.776
8.764
7.710
7.695
7.610
7.608
7.120
7.109
7.103
7.094
6.877
6.866
6.855
6.622
6.619
6.617
6.614
SCN
N
N
O
2o
1H NMR (CDCl3, 600 MHz)
1.00
0.99
0.98
2.04
1.02
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.99
142.90
134.82
132.22
124.30
123.51
117.12
114.89
112.05
110.24
108.51
SCN
N
N
O
2o
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.356
8.344
7.755
7.739
7.307
7.300
7.169
7.162
7.150
7.139
7.135
7.124
6.912
6.900
6.889
SCN
N
N
S
Br
2p
^{1}H NMR ($CDCl_3$, 600 MHz)
0.99
0.97
0.98
0.95
1.03
1.02
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)

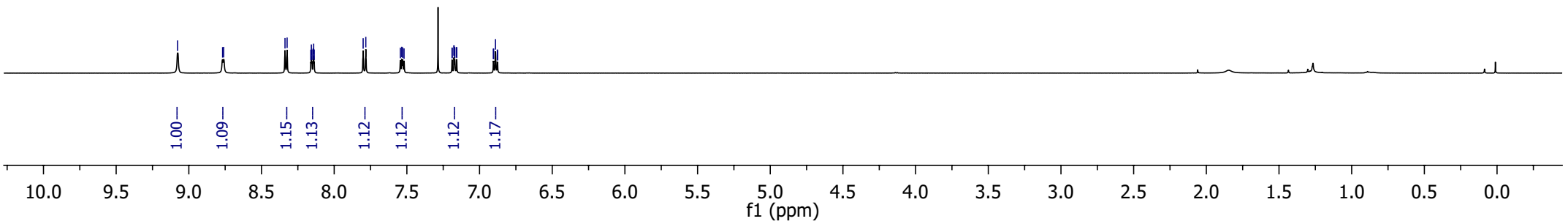

135.40
133.75
132.00
130.67
126.60
123.52
122.74
117.56
115.26
114.86
110.11
108.99
SCN
N
N
S
Br
2p
^{13}C NMR ($CDCl_3$, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

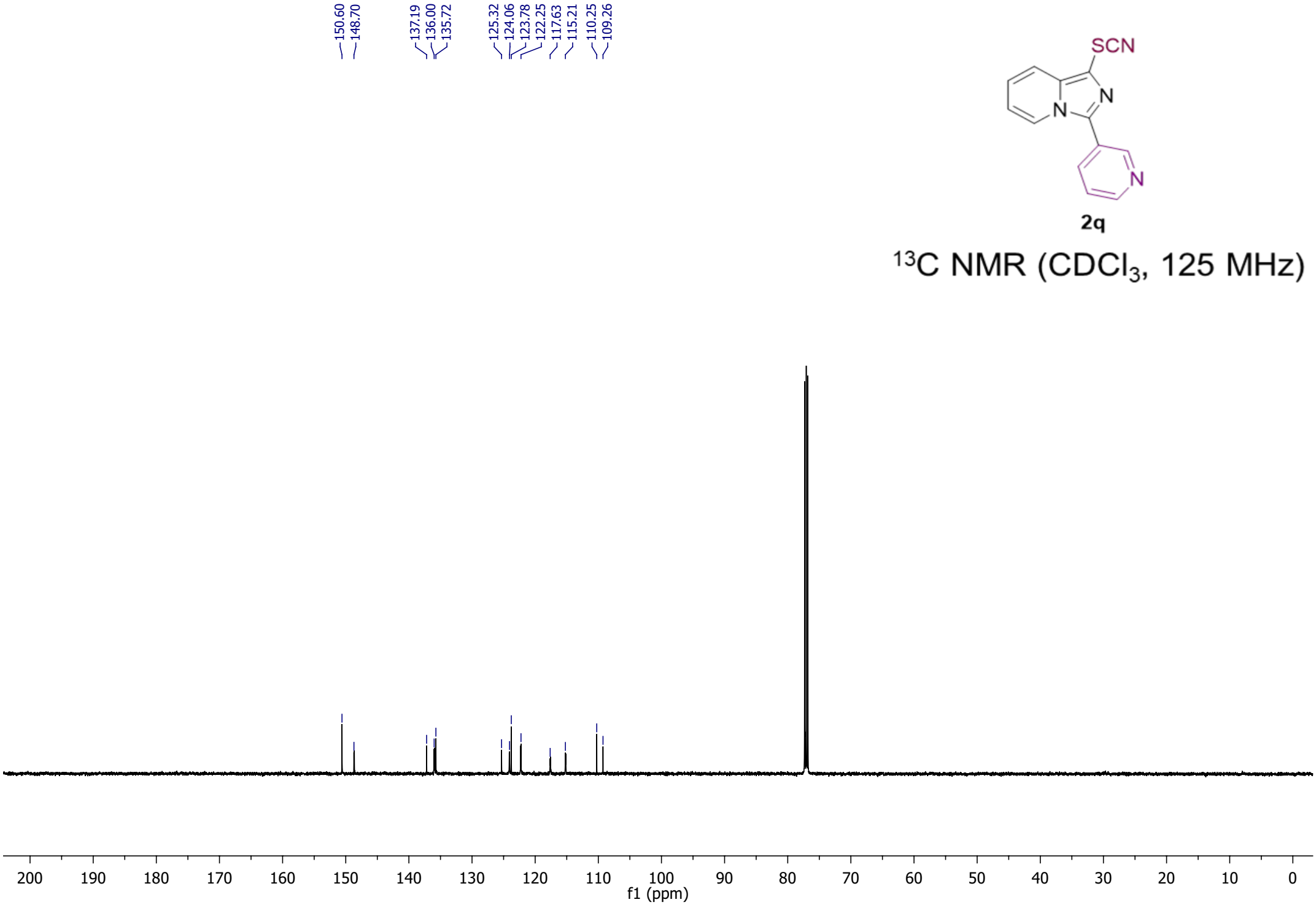


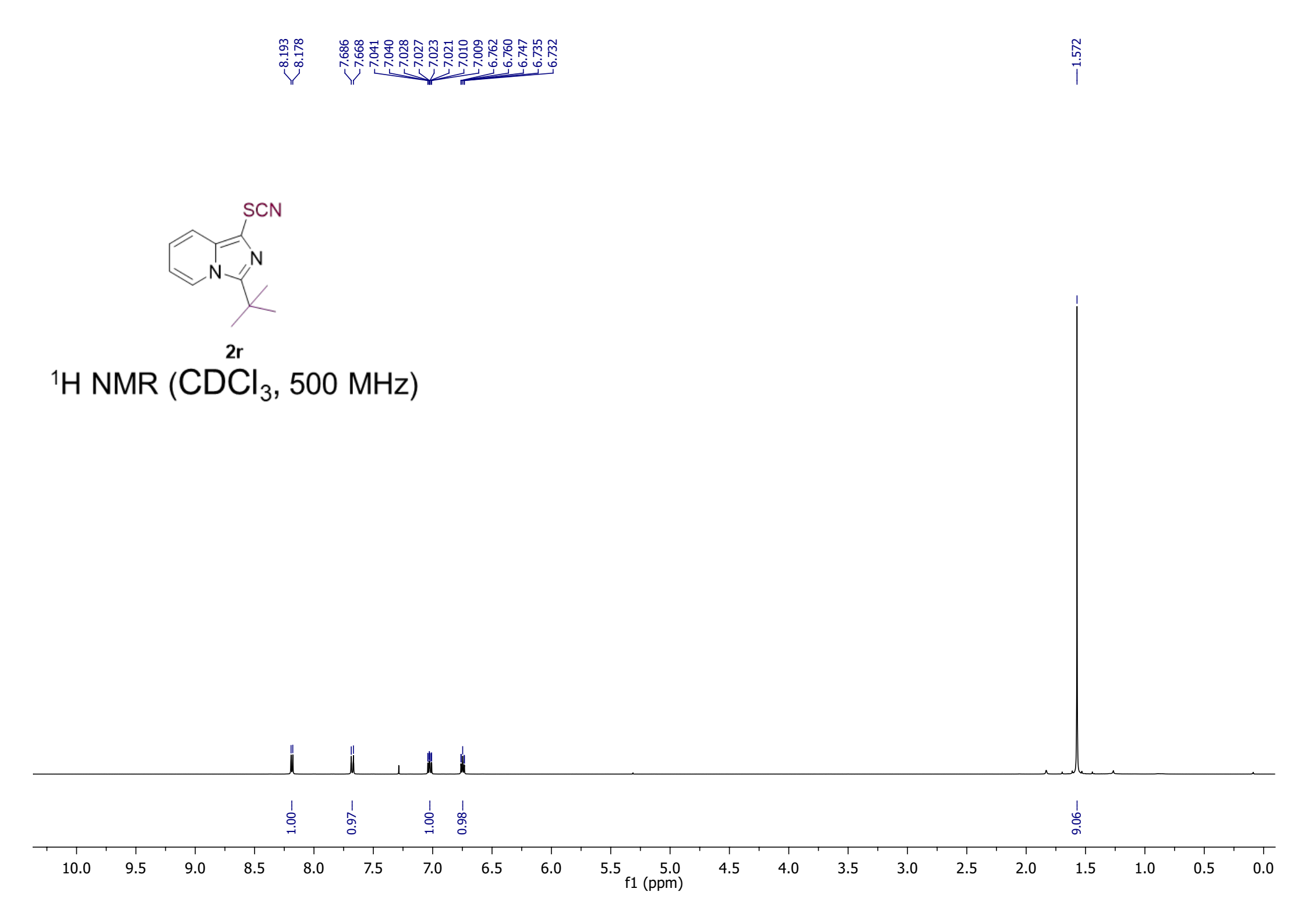


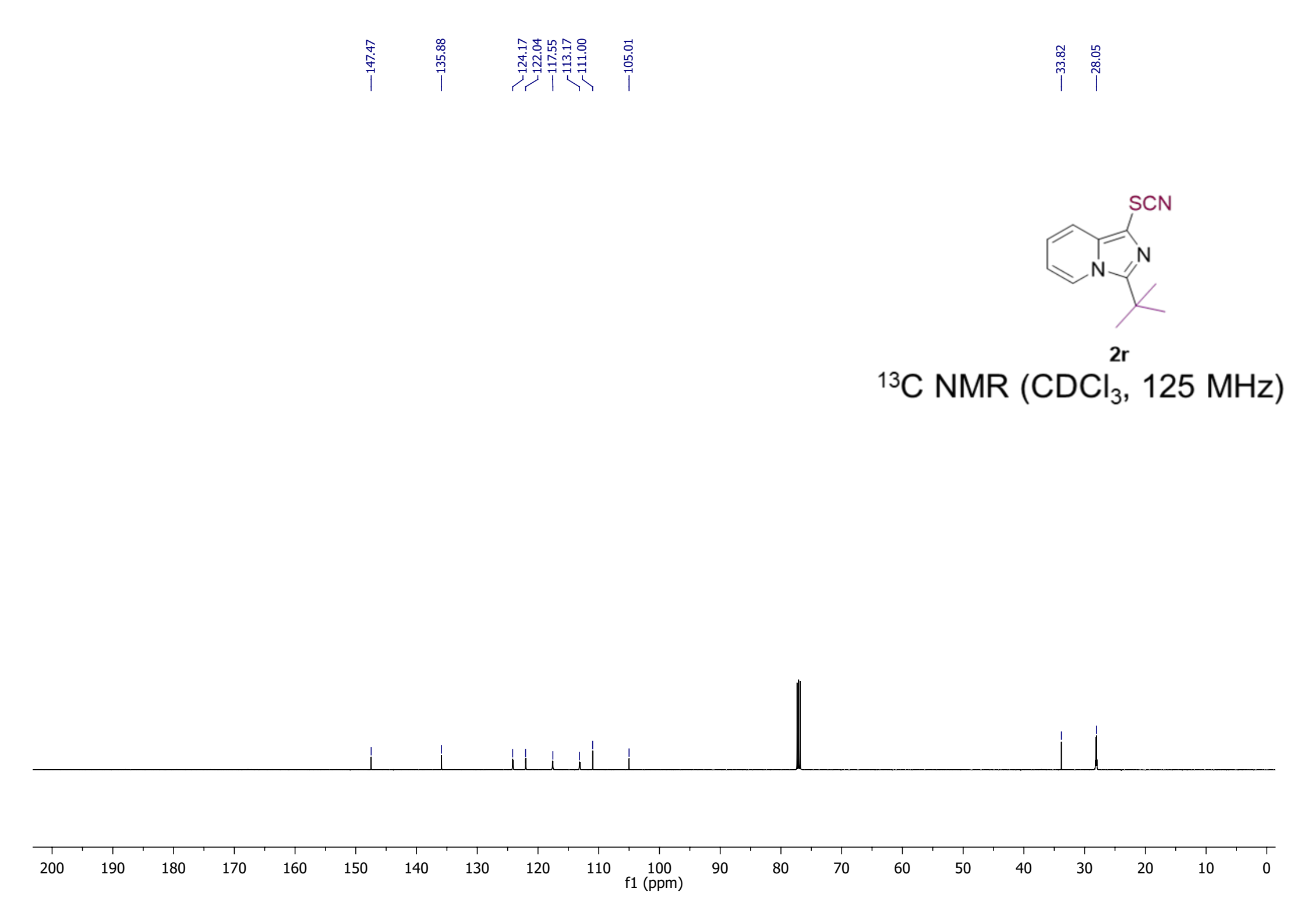
2q

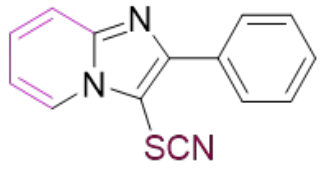
^{1}H NMR ($CDCl_3$, 500 MHz)




150.60
148.70
137.19
136.00
135.72
125.32
124.06
123.78
122.25
117.63
115.21
110.25
109.26
SCN
N
N
N
2q
^{13}C NMR ($CDCl_3$, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.193
8.178
7.686
7.668
7.041
7.040
7.028
7.027
7.023
7.021
7.010
7.009
6.762
6.760
6.747
6.735
6.732
1.572
SCN
N
N
2r
1H NMR (CDCl3, 500 MHz)
1.00
0.97
1.00
0.98
9.06
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)


147.47
135.88
124.17
122.04
117.55
113.17
111.00
105.01
33.82
28.05
SCN
N
N
2r
13C NMR (CDCl3, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

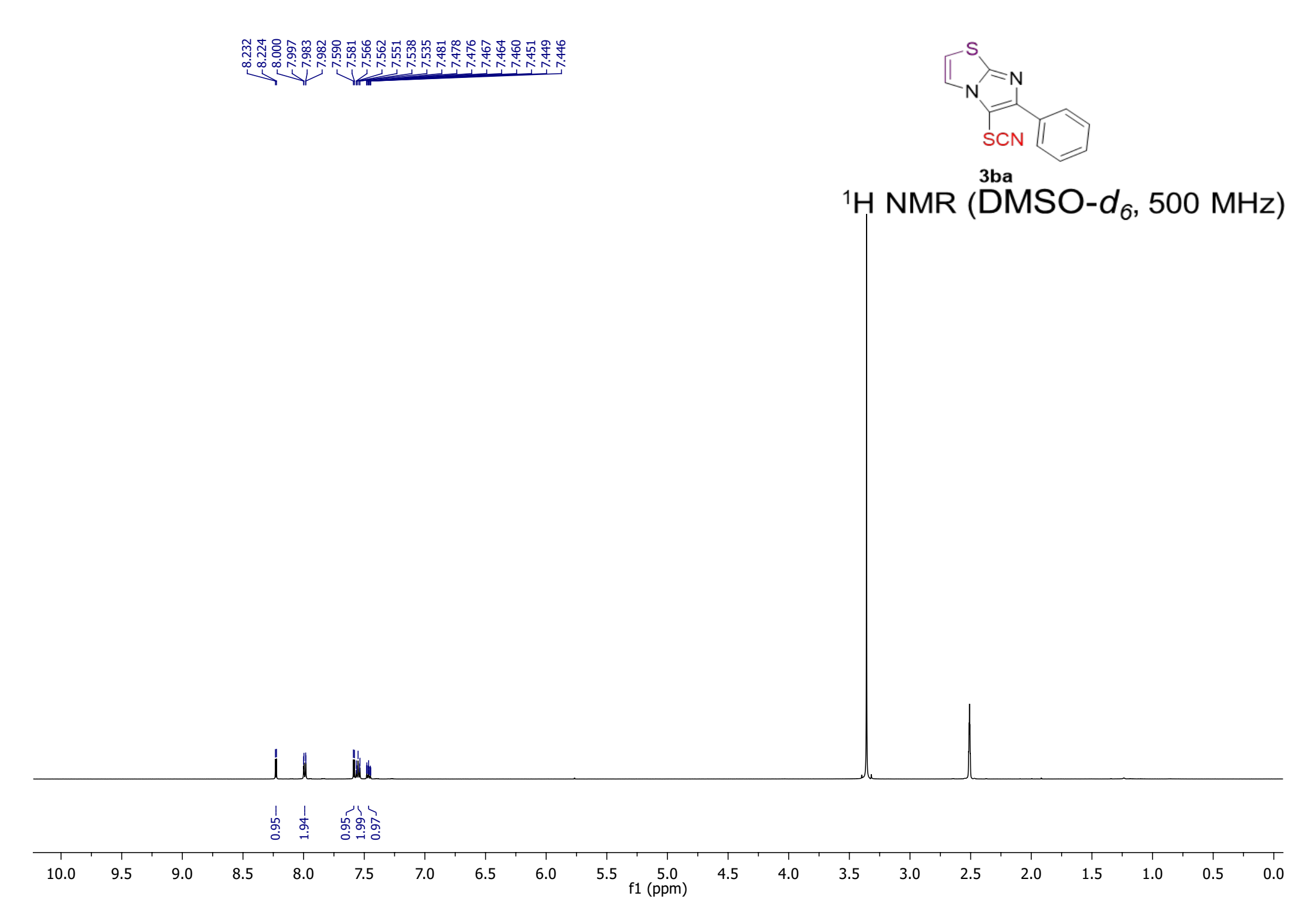


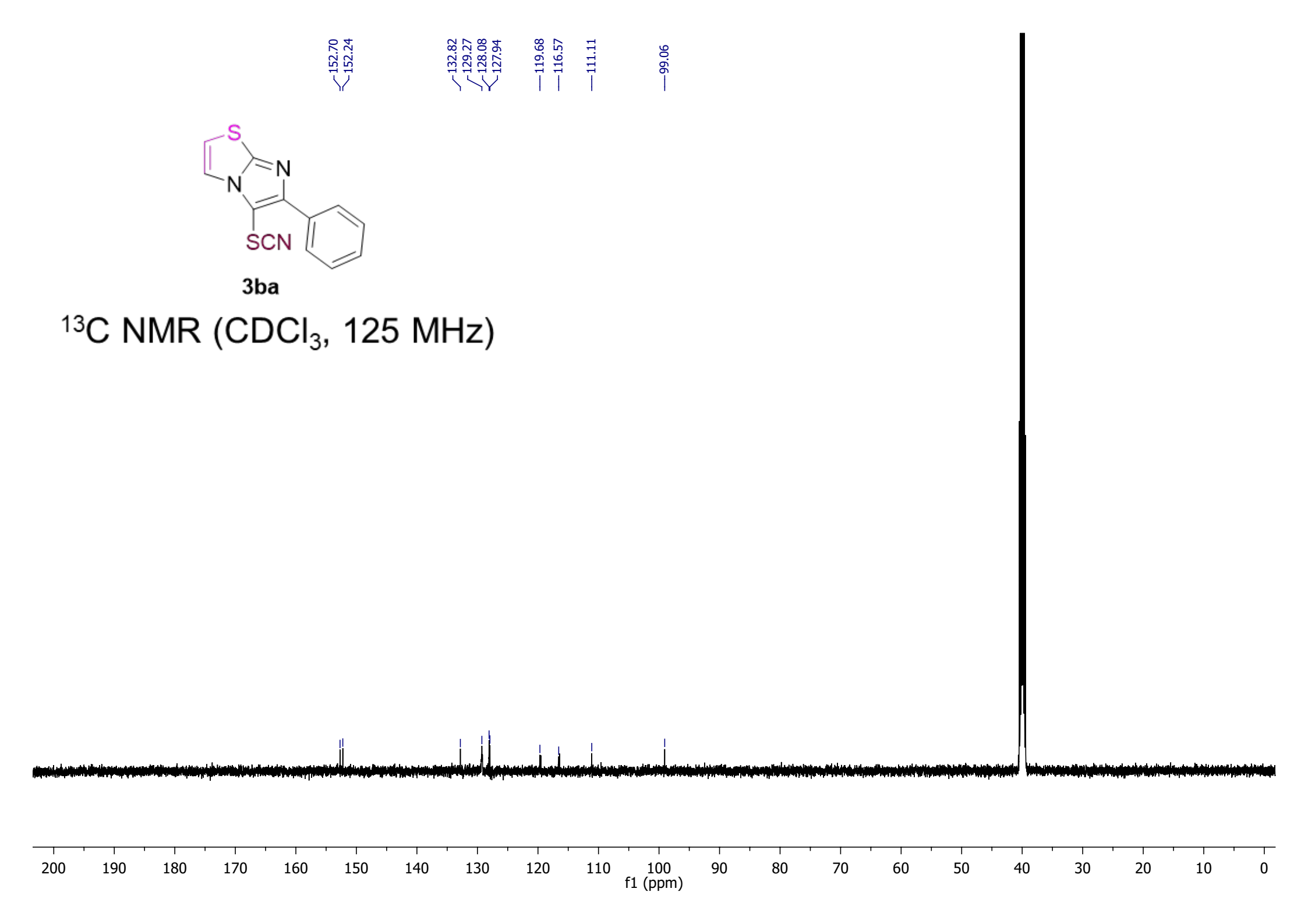
3aa

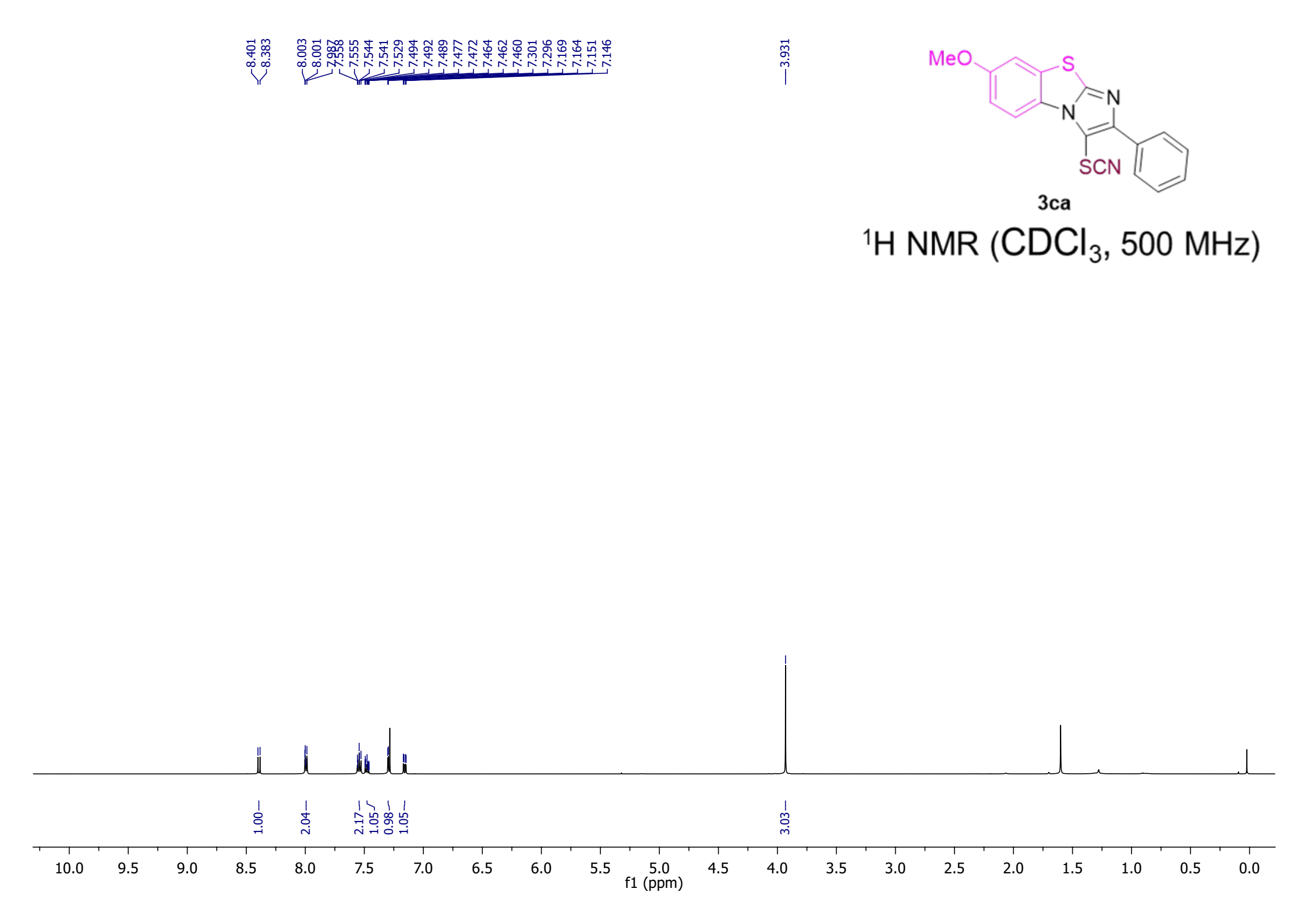
^{1}H NMR ($CDCl_3$, 500 MHz)

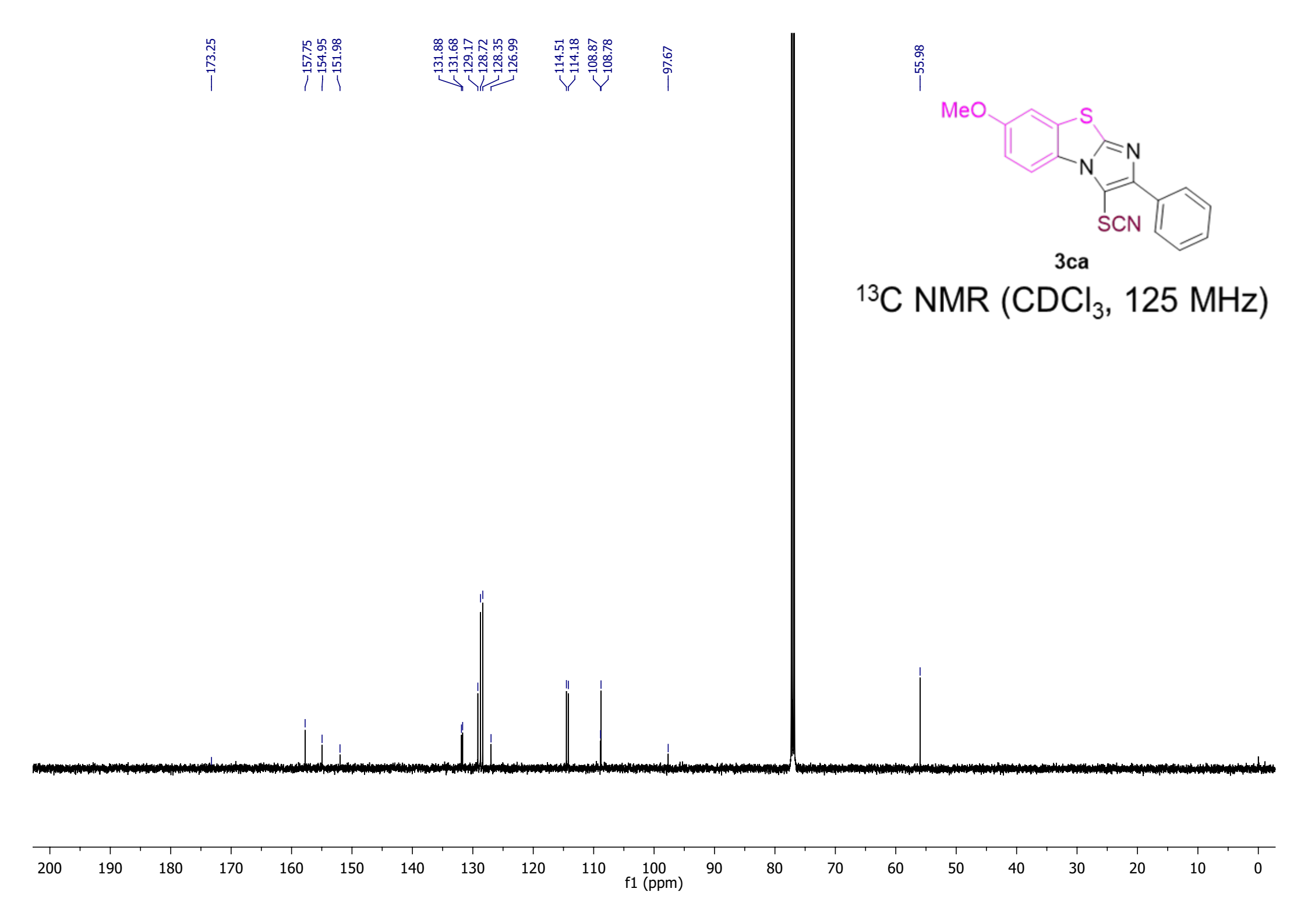
3aa

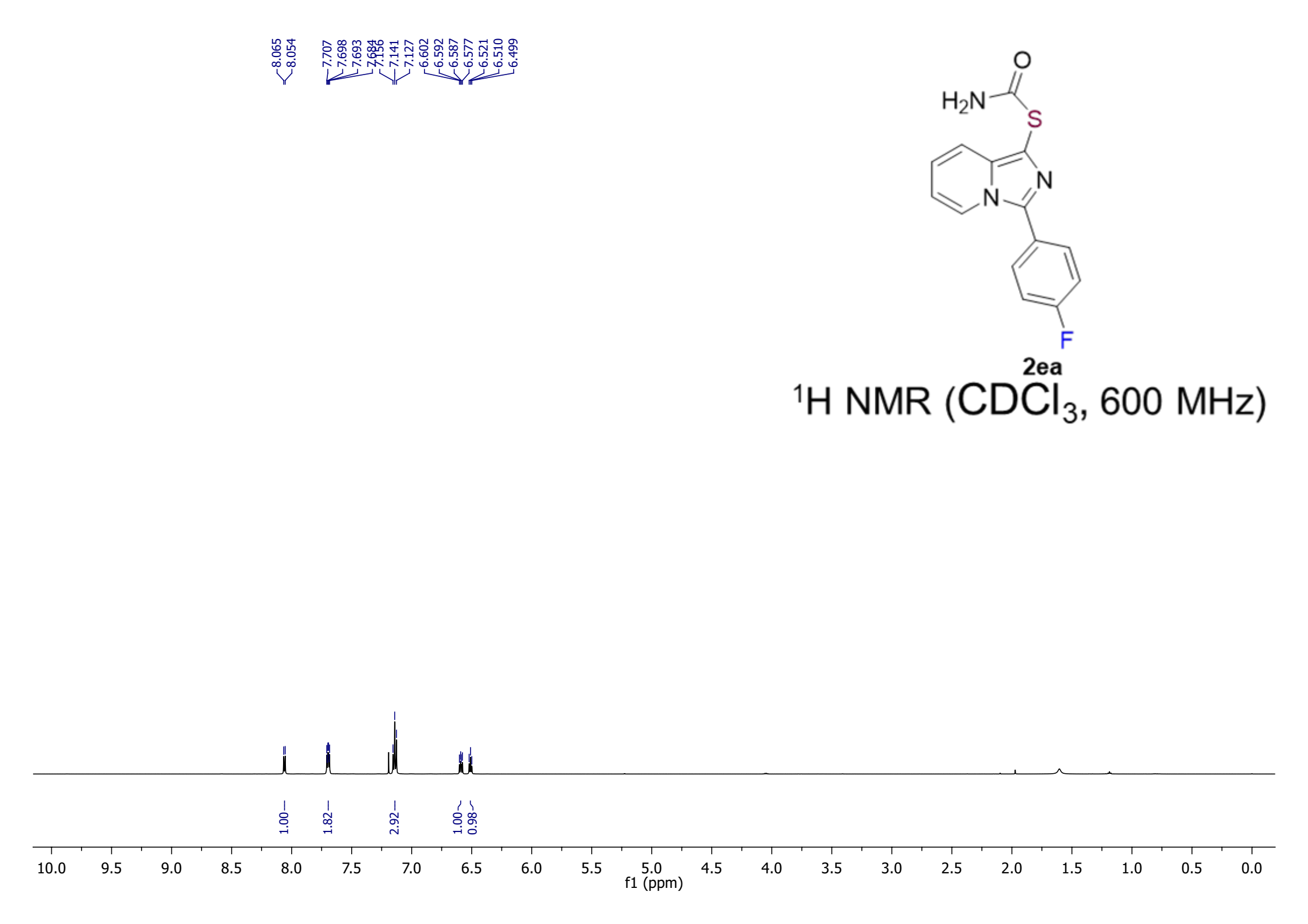
^{13}C NMR ($CDCl_3$, 125 MHz)

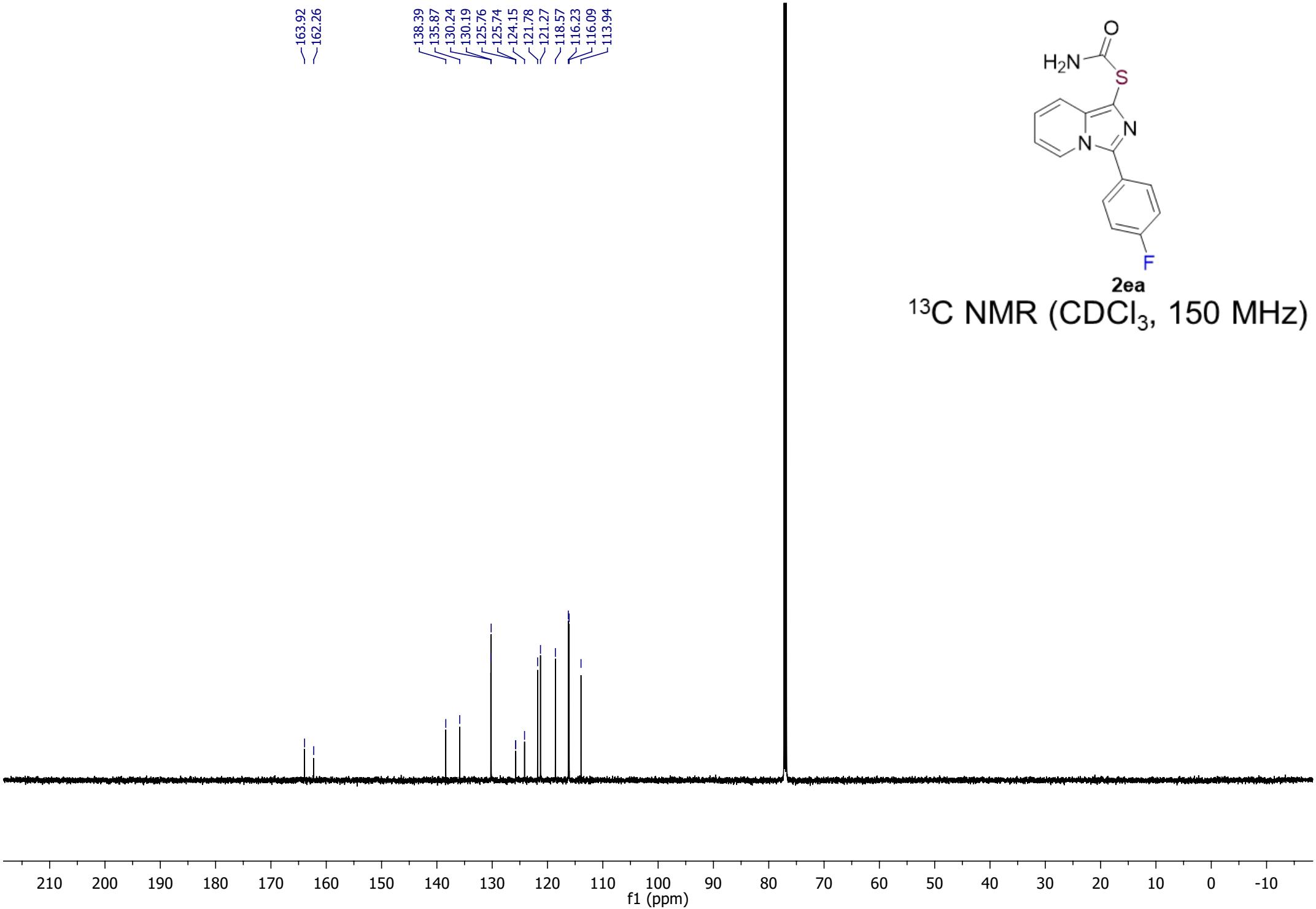

8.232
8.224
8.000
7.997
7.983
7.982
7.590
7.581
7.566
7.562
7.551
7.538
7.535
7.481
7.478
7.476
7.467
7.464
7.460
7.451
7.449
7.446
S
N
N
SCN
3ba
^{1}H NMR (DMSO-d_6, 500 MHz)
0.95
1.94
0.95
1.99
0.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

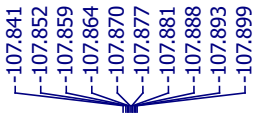

152.70
152.24
132.82
129.27
128.08
127.94
119.68
116.57
111.11
99.06
S
N
N
SCN
3ba
13C NMR (CDCl3, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

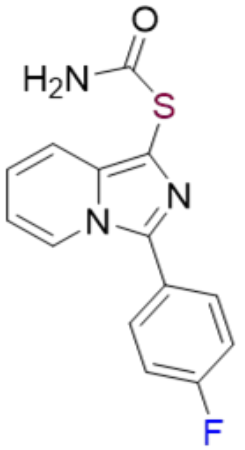

8.401
8.383
8.003
8.001
7.987
7.558
7.555
7.544
7.541
7.529
7.494
7.492
7.489
7.477
7.472
7.464
7.462
7.460
7.301
7.296
7.169
7.164
7.151
7.146
3.931
MeO
S
N
N
SCN
3ca
1H NMR (CDCl3, 500 MHz)
1.00
2.04
2.17
1.05
0.98
1.05
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.25
157.75
154.95
151.98
131.88
131.68
129.17
128.72
128.35
126.99
114.51
114.18
108.87
108.78
97.67
55.98
MeO
S
N
N
SCN
3ca
13C NMR (CDCl3, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.065
8.054
7.707
7.698
7.693
7.684
7.156
7.141
7.127
6.602
6.592
6.587
6.577
6.521
6.510
6.499
O
H2N
S
N
N
F
2ea
1H NMR (CDCl3, 600 MHz)
1.00
1.82
2.92
1.00
0.98
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)

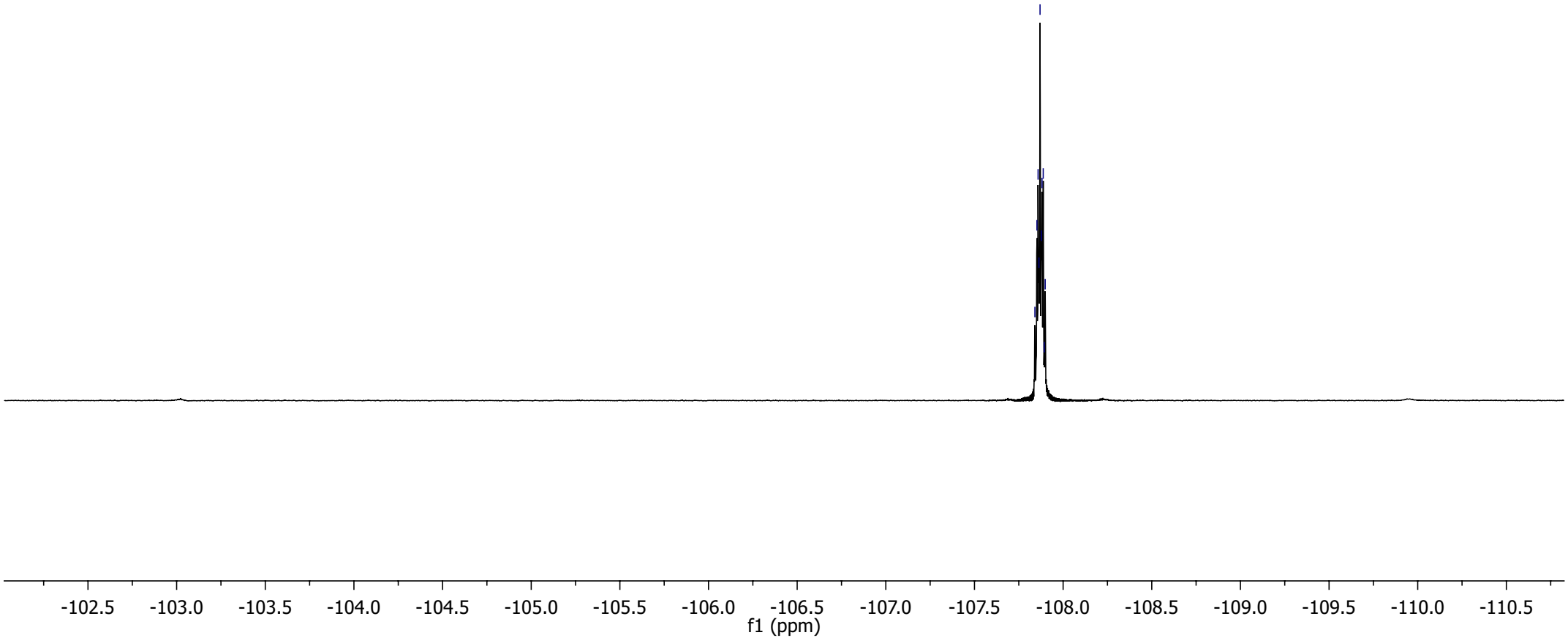

163.92
162.26
138.39
135.87
130.24
130.19
125.76
125.74
124.15
121.78
121.27
118.57
116.23
116.09
113.94
O
H2N
S
N
N
F
2ea
13C NMR (CDCl3, 150 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

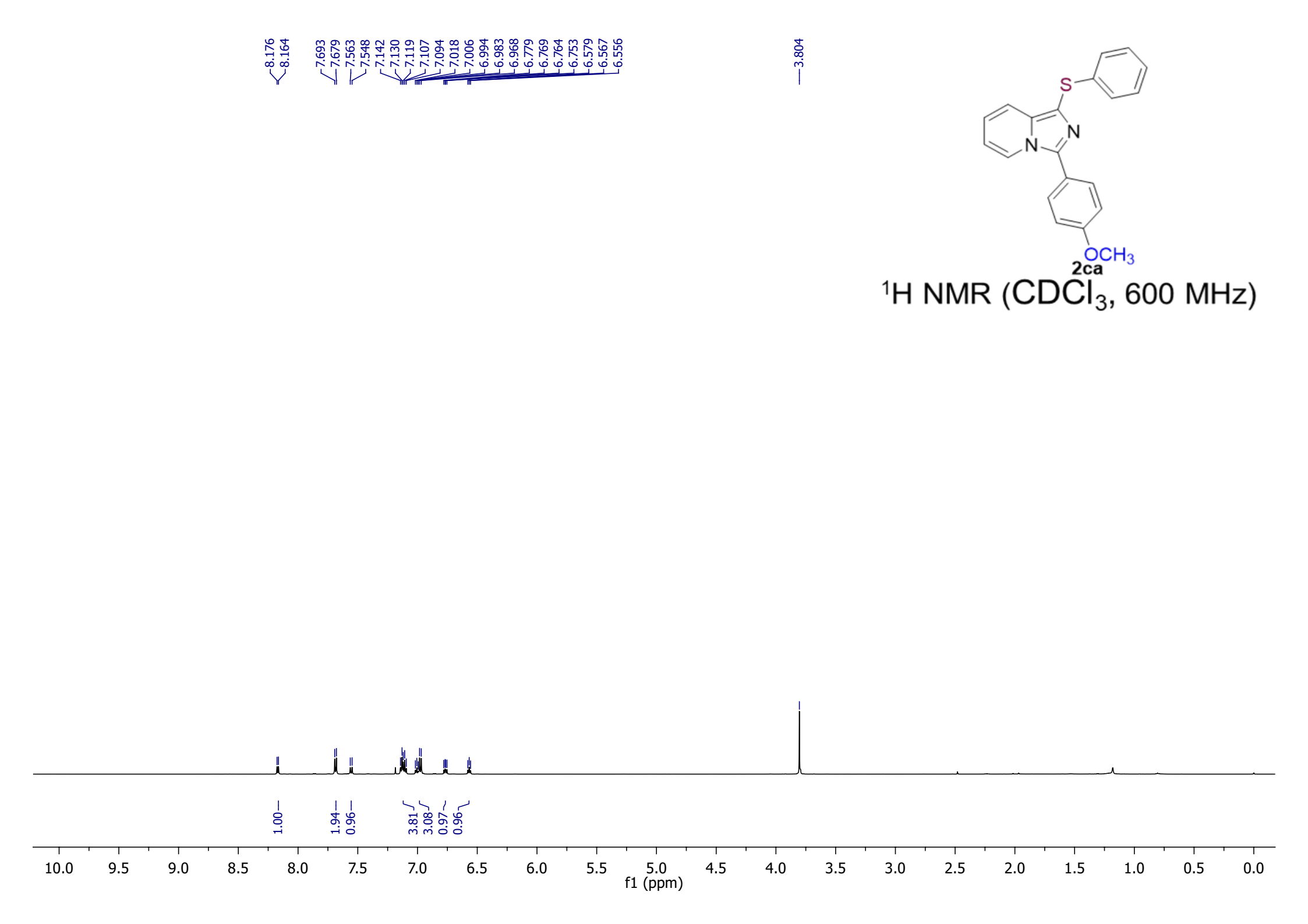


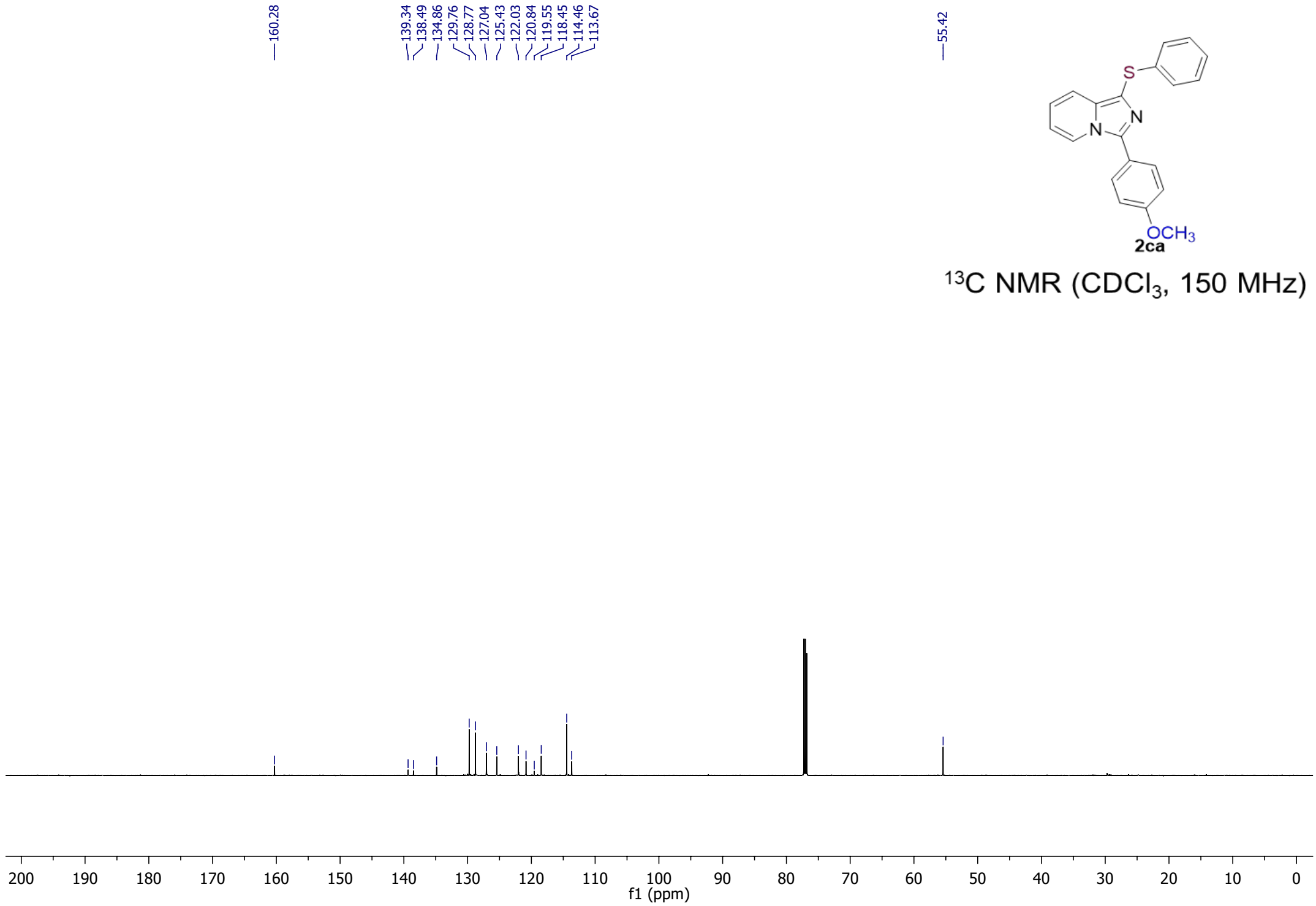


2ea

^{19}F NMR ($CDCl_3$, 471 MHz)




8.176
8.164
7.693
7.679
7.563
7.548
7.142
7.130
7.119
7.107
7.094
7.018
7.006
6.994
6.983
6.968
6.779
6.769
6.764
6.753
6.579
6.567
6.556
3.804
S
N
N
OCH3
2ca
1H NMR (CDCl3, 600 MHz)
1.00
1.94
0.96
3.81
3.08
0.97
0.96
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)


160.28
139.34
138.49
134.86
129.76
128.77
127.04
125.43
122.03
120.84
119.55
118.45
114.46
113.67
55.42
S
N
N
OCH3
2ca
13C NMR (CDCl3, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)