Supporting Information

Visible Light Driven, Persulfate-Mediated Dual C-H Sulfenylation of Imidazopyridines using Thiocyanate Salt

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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 3-((1*H*-indol-3-yl)thio)-2-aryl imidazo[1,2-*a*]pyridines (3a-3k):

An oven-dried round bottom flask was charged with the corresponding 2-aryl imidazo[1,2-*a*]pyridines (**1a-g**, 1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8 h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by addition of indole (**2a-2e**, 1 equiv.) to it. The entire reaction was continued up to 20 h. On completion of the reaction, next 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 3-((1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)thio)-2-phenylimidazo[1,2-*a*]pyridine (4a):

An oven-dried round bottom flask was charged with the corresponding 2-phenyl imidazo[1,2-*a*]pyridine (**1a**, 1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 ml of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by further addition of 7-aza indole (1 equiv.) to it. The entire reaction was continued up to 20 h. On completion of the reaction, next 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 2-((7-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)thio)benzo[*d*]thiazole (4b):

An oven-dried round bottom flask was charged with the corresponding 7-methyl 2-phenyl imidazo[1,2-*a*]pyridine (**1b**, 1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 ml of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by addition of benzothiazole (1 equiv.) to it. The entire reaction was continued up to 20h. On completion of the reaction, next 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 bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)sulfane (4c):

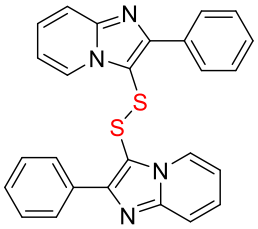
An oven-dried round bottom flask was charged with the corresponding 2-phenyl imidazo[1,2-*a*]pyridine (**1a**, 1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8h under irradiation of blue LED light

(24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8 h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by further addition of 2-phenyl imidazo[1,2-*a*]pyridines (**1a**, 1 equiv.) to it. The entire reaction was continued up to 20 h. On completion of the reaction, next 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.

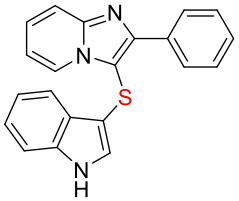
General procedure for the synthesis of 3-((1*H*-indol-3-yl)thio)-2-phenyl imidazo[1,5-*a*]pyridines (5a-c):

An oven-dried round bottom flask was charged with the corresponding 3-phenyl imidazo[1,5-*a*]pyridines (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8 h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by addition of indole (**2a**, 1 equiv.) to it. The entire reaction was continued up to 20 h. On completion of the reaction, next 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.

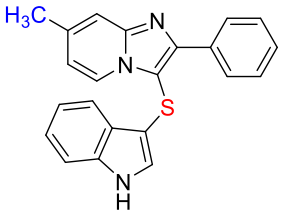
Spectral Data



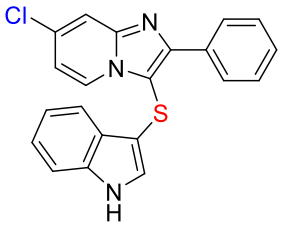
2-Phenyl-3-((2-phenyl-1,8a-dihydroimidazo[1,2-a]pyridin-3-yl)disulfanyl)imidazo[1,2-*a*]pyridine (1ab): ^{1}H NMR ($CDCl_3$,600 MHz) δ= 8.10 (d, *J* = 5.4 Hz, 2H), 7.63 (s, 4H), 7.36 (d, *J* = 5.4 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.13-7.09 (m, 6H), 6.74 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ =147.3, 131.9, 128.1, 127.9, 127.7, 127.0, 124.4, 117.6, 113.0.



3-((1*H*-indol-3-yl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3a): ^{1}H NMR ($CDCl_3$,500 MHz) δ= 8.63-8.60 (m, 3H), 8.39-8.37 (m, 2H), 7.62 (d, *J* = 9 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.48-7.45 (m, 1H), 7.37 (d, *J* = 8 Hz, 1H), 7.29-7.23 (m, 2H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.16-7.13 (m, 1H), 7.03-7.00 (m, 1H), 6.89 (td, *J* = 7 Hz, 1Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 149.4, 146.1, 136.0, 133.9, 129.0, 128.9, 128.4, 127.9, 127.2, 127.1, 125.1, 124.6, 122.8, 120.6, 119.3, 117.5, 112.5, 111.5, 110.4, 104.3.

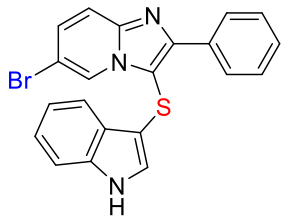


3-((1*H*-indol-3-yl)thio)-7-methyl-2-phenylimidazo[1,2-*a*]pyridine (3b): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 8.38 (d, *J* = 7.2 Hz, 1H), 8.27-8.26 (m, 2H), 8.24 (s, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.30 (s, 1H), 7.20-7.19 (m, 2H), 7.09 (d, *J* = 2.4 Hz, 1H), 7.07-7.05 (m, 1H), 6.94-6.92 (m, 1H), 6.62 (dd, *J* = 7.2 Hz, 1.8 Hz, 1H), 2.31 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 146.5, 137.1, 37.0, 128.9, 128.3, 128.2, 127.9, 126.8, 123.7, 122.8, 120.6, 119.3, 116.0, 115.2, 111.4, 104.9, 21.3.

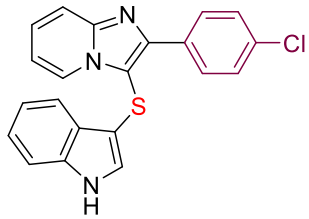


3-((1*H*-indol-3-yl)thio)-7-chloro-2-phenylimidazo[1,2-*a*]pyridine (3c): ^{1}H NMR ($CDCl_3$, 500 MHz) δ= 8.50 (dd, *J* = 7.5 Hz, 1Hz, 1H), 8.34-8.31 (m, 3H), 7.59 (dd, *J* = 2 Hz, 0.5 Hz, 1H), 7.55-7.51 (m, 2H), 7.47-7.44 (m, 1H), 7.32-7.27 (m, 2H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.16-

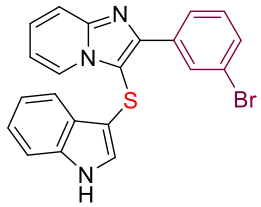
7.13 (m, 1H), 7.02-6.98 (m, 1H), 6.84 (dd, J = 7 Hz, 2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 190.1, 145.8, 136.0, 134.0, 132.5, 128.9, 128.8, 128.5, 127.8, 127.2, 124.9, 123.0, 120.8, 119.2, 116.4, 114.1, 111.5, 110.9, 104.0.



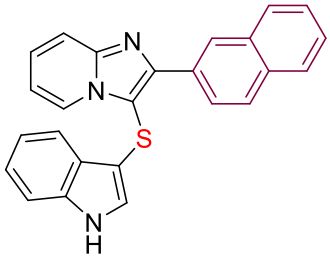
3-((1*H*-indol-3-yl)thio)-6-bromo-2-phenylimidazo[1,2-*a*]pyridine (3d): ^{1}H NMR ($CDCl_3$, 500 MHz) δ= 8.76 (s, 1H), 8.54 (s, 1H), 8.36 (d, J = 8 Hz, 1H), 7.57-7.55 (m, 2H), 7.50 (d, J = 9.5 Hz, 2H), 7.31-7.49 (m, 4H), 7.16 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ= 150.0, 144.5, 136.1, 133.5, 129.3, 129.0, 128.9, 128.6, 128.5, 127.9, 127.6, 124.8, 123.0, 120.8, 119.3, 118.1, 111.5, 111.0, 107.4, 103.6.



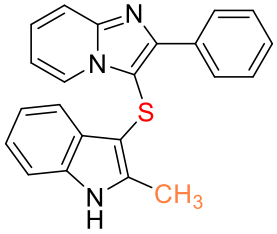
3-((1*H*-indol-3-yl)thio)-2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (3e): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 7.03 (d, J = 7.2 Hz, 1H), 8.37 (s, 1H), 8.27 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 9 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 1H), 7.21-7.16 (m, 2H), 7.13 (d, J = 1.8 Hz, 1H), 7.07 (t, J = 7.2 Hz, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.81 (t, J = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ= 148.0, 146.1, 136.1, 134.3, 132.4, 130.1, 128.6, 127.8, 127.2, 126.2, 124.6, 123.0, 120.8, 119.2, 117.5, 112.8, 111.5, 110.5, 104.2.



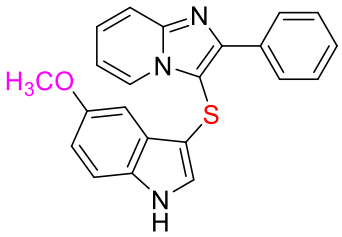
3-((1*H*-indol-3-yl)thio)-2-(3-bromophenyl)imidazo[1,2-*a*]pyridine (3f): ^{1}H NMR (DMSO-d_6, 600 MHz) δ= 11.49 (s, 1H), 8.91 (d, J = 7.8 Hz, 1H), 8.57 (t, J = 1.8 Hz, 1H), 8.45 (d, J = 9.6 Hz, 1H), 7.88 44 (t, J = 3 Hz, 1H), 7.70-7.68 (m, 1H), 7.65 (d, J = 10.5 Hz, 1H), 7.57 (d, J = 9 Hz, 1H), 7.41-7.38 (m, 1H), 7.34 (d, J = 9.26 Hz, 1H), 7.10 44 (td, J = 8.4 Hz, 1.2 Hz, 1H), 7.06-7.02 (m, 2H), 6.85-6.81 (m, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ= 146.1, 145.8, 136.7, 136.6, 131.1, 131.1, 130.9, 128.1, 127.1, 127.6, 125,6, 122.5, 122.2, 120.4, 120.3, 117.7, 114.2, 113.8, 112.7, 111.4, 100.7.



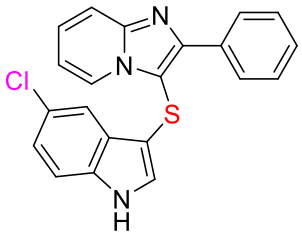
3-((1*H*-indol-3-yl)thio)-2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine (3g): ^{1}H NMR (DMSO-d_6, 600 MHz) δ= 11.68-11.65 (m, 1H), 9.29-9.27 (m, 1H), 8.83 (s, 1H), 8.41 (d, J = 7.9 Hz, 1H), 8.24 (d, J = 9 Hz, 1H), 8.13 (d, J = 7.2 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.99-7.98 (m, 1H), 7.94 (t, J = 9 Hz, 1H), 7.89-7.87 (m, 1H), 7.70-7.66 (m, 2H), 7.53-7.50 (m, 1H), 7.32 (d, J = 7.8 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 6.86-6.85 (m, 1H), 6.66 (t, J = 7.2 Hz, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ= 136.7, 133.8, 133.1, 133.0, 129.4, 129.1, 128.3, 128.0, 127.6, 127.0, 126.3, 126.3, 122.5, 120.4, 118.2, 117.1, 114.3, 112.8, 98.9.



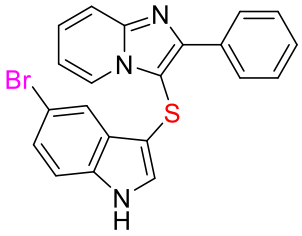
3-((2-Methyl-1H-indol-3-yl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3h): ^{1}H NMR (DMSO-d_6, 600 MHz) δ= 11.41 (s, 1H), 8.61 (d, J = 6.6 Hz, 1H), 8.32 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 9 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.39-7.37 (m, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.09 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 7.2 Hz, 1H), 6.83-6.81 (m, 1H), 2.47 (s, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ= 148.7, 145.6, 140.4, 135.6, 134.5, 129.2, 129.1, 128.8, 128.7, 126.7, 125.2, 121.6, 120.1, 117.9, 117.6, 113.5, 111.6, 111.0, 98.1, 12.4.



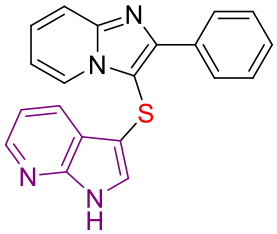
3-((5-Methoxy-1H-indol-3-yl)thio)-2-phenylimidazo[1,2-a]pyridine (3i): ^{1}H NMR (DMSO-d_6 +Di-ethyl ether, 600 MHz) δ= 11.34 (s, 1H), 8.98 (d, J = 6.6 Hz, 1H), 8.50 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 2.4 Hz, 1H), 7.69-7.64 (m, 3H), 7.52 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.13 (t, J = 6.6 Hz, 1H), 6.64 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 6.49 (d, J = 1.8 Hz, 1H), 3.20 (s, 3H); ^{13}C NMR (DMSO-d_6 +Di-ethyl ether, 150 MHz) δ= 154.0, 147.5, 145.3, 134.0, 131.0, 128.4, 128.3, 126.5, 125.1, 117.0, 113.0, 110.1, 99.9, 99.1, 54.2.



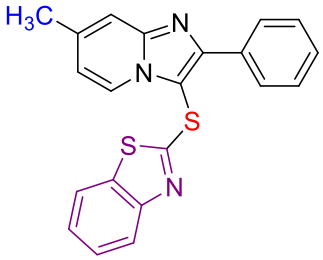
3-((5-Chloro-1*H*-indol-3-yl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3j): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 8.02 (d, *J* = 4.8 Hz, 3H), 7.54 (t, *J* = 7.8 Hz, 3H), 7.49 (t, *J* = 7.8 Hz, 3H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.18 (s, 1H), 7.04 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 150.8, 146.5, 133.7, 129.6, 129.1, 129.0, 128.6, 128.5, 126.5, 125.4, 123.2, 117.3, 112.9, 107.5.



3-((5-Bromo-1*H*-indol-3-yl)thio)-2-phenylimidazo[1,2-*a*]pyridine (3k): ^{1}H NMR ($CDCl_3$, 500 MHz) δ= 8.65 (s, 1H), 8.60 (dt, *J* = 7 Hz, 1 Hz, 1H); 8.29-8.27 (m, 2H), 7.63 (d, *J* = 9 Hz, 1H), 7.59-7.56 (m, 2H), 7.52-7.48 (m, 1H), 7.38 (d, *J* = 1.5 Hz, 1H), 7.29-7.27 (m, 1H), 7.22-7.20 (m, 2H), 7.12 (d, *J* = 8.5 Hz, 1H); 6.93 (td, *J* = 6.5 Hz, 1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 150.0, 146.2, 134.6, 133.7, 129.7, 129.1, 129.0, 128.6, 128.3, 126.1, 125.8, 124.4, 122.2, 117.6, 114.1, 112.8, 110.1.

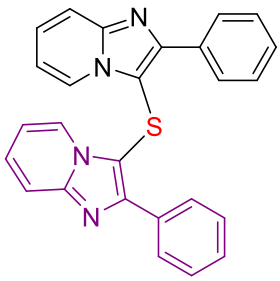


3-((1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)thio)-2-phenylimidazo[1,2-*a*]pyridine (4a): ^{1}H NMR (DMSO-d_6, 600 MHz) δ= 12.02 (s, 1H), 8,91 (d, *J* = 6.6 Hz, 1H), 8.34 (d, *J* = 7.8 Hz, 2H), 8.13 (dd, *J* = 4.8 Hz,1.2 Hz, 1H), 8.01 (d, *J* = 2,4 Hz, 1H), 7.79 (d, *J* = 9 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.25-7.23 (m, 1H), 7.09 (t, *J* = 6.6 Hz, 1H), 6.86-6.84 (m, 1H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ= 148.8. 148.5, 134.2, 131,4, 128.9, 127.1, 126.8, 125.5, 120.4, 117.5, 116.6, 113.7, 110.2, 100.5.

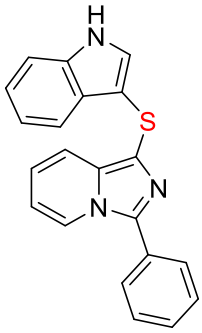


2-((7-Methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)thio)benzo[d]thiazole (4b): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 8.3 (d, *J* = 7.2 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz,

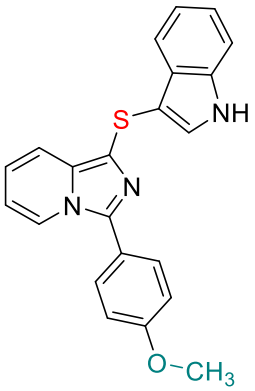
1H), 7.56-7.53 (m, 2H), 7.44-7.34 (m, 4H), 7.23 (t, *J* = 7.8 Hz, 1H),6.76 (d, *J* = 6.6 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ=168.8, 154.7, 152.4, 148.2, 139.0, 135.5, 132.8, 129.0, 129.5, 129.4, 126.3, 124.6, 123.5, 122.1, 121.1, 116.5, 116.4, 103.3, 21.5.



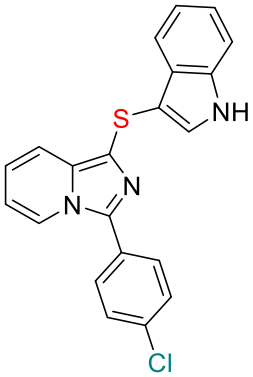
Bis(2-phenylimidazo[1,2-*a*]pyridin-3-yl)sulfane (4c): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 8.03 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 4H), 7.49-7.47 (m, 4H), 7.42 (d, *J* = 9 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.27 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 150.9, 146.5, 133.8, 129.6, 128.9, 128.6, 126.4, 125.4, 117.4, 112.6, 107.5.



1-((1*H*-indol-3-yl)thio)-3-phenylimidazo[1,5-*a*]pyridine (5a) : ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 8.84 (s, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 9 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.66-7.65 (m, 2H), 7.34-7.31 (m, 2H), 7.24-7.23 (m, 1H), 7.09-7.04 (m, 2H), 6.79-6.76 (m, 1H), 6.52-6.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 138.2, 137.0, 136.2, 133.0, 129.4, 129.5, 129.0, 128.8, 128.3, 124.0, 122.3, 121.7, 120.2, 119.5, 118.8, 113.6, 111.5, 106.3.



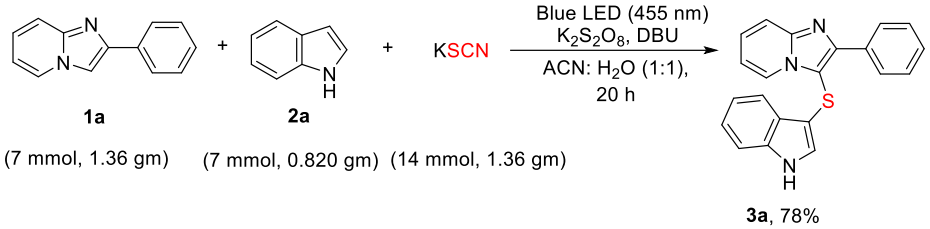
1-((1*H*-indol-3-yl)thio)-3-(4-methoxyphenyl)imidazo[1,5-*a*]pyridine (5b): ^{1}H NMR (DMSO-d_6, 500 MHz) δ= 11.39 (s, 1H), 8.31 (d, *J* = 6 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.75-7.69 (m, 4H), 7.36 (d, *J* = 7 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.05-6.98 (m, 2H), 6.79 (s, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ= 160.3, 138.1, 136.2, 132.8, 130.2, 129.8, 128.7, 123.3, 122.1, 121.7, 121.3, 120.3, 120.0, 119.2, 118.8, 114.5, 113.8, 111.8, 105.3, 55.4.



1-((1*H*-indol-3-yl)thio)-3-(4-chlorophenyl)imidazo[1,5-*a*]pyridine (5c): ^{1}H NMR ($CDCl_3$, 600 MHz) δ= 8.47 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.82-7.89 (m, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.46 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.11-7.05 (m, 2H), 6.81-6.78 (m, 1H), 6.54 (t, *J* = 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ= 136.8, 136.1, 135.0, 133.2, 130.9, 129.5, 129.2, 128.8, 122.5, 121.5, 120.3, 119.5, 118.9, 114.0, 111.4.

Gram Scale Synthesis

An oven-dried round bottom flask was charged with 2-phenyl imidazo[1,2-*a*]pyridine (**1a**, 1 equiv., 7 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8 h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by addition of indole (**2a**, 1 equiv., 7 mmol) to it. The entire reaction was continued up to 20 h. On completion of the reaction, next 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 in 78 % yield.



Scheme 1. Gram scale synthesis [a]Reaction conditions: **1a** (7 mmol), **2a** (7 mmol), KSCN (14 mmol), DBU (1 equiv.), $K_2S_2O_8$ (2 equiv.), Blue LED (455 nm), solvent: 20 mL, rt.

Control Experiments

a) Reaction for 9h:

An oven-dried round bottom flask was charged with 2-phenyl imidazo[1,2-*a*]pyridine (**1a**, 1 equiv., 1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8 h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by addition of indole (**2a**, 1 equiv., 1 mmol) to it. The entire reaction was continued up to 9 h.

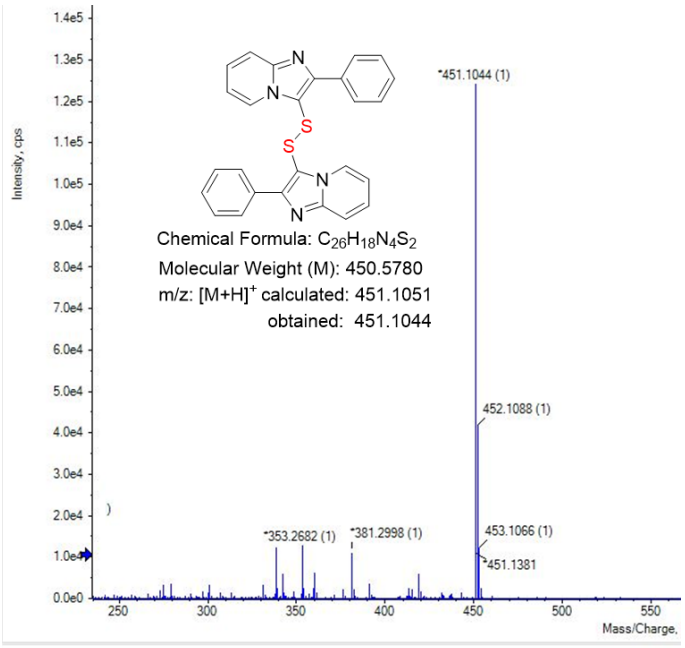


Figure 1. HRMS spectra of diimidazopyridinyl disulfide.

b) Reaction in absence of DBU:

An oven-dried round bottom flask was charged with 2-phenyl imidazo[1,2-*a*]pyridine (**1a**, 1 equiv., 1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8 h of continuation of reaction, indole (**2a**, 1 equiv.) was added to the same on-going reaction mixture. The entire reaction was continued up to 20 h.

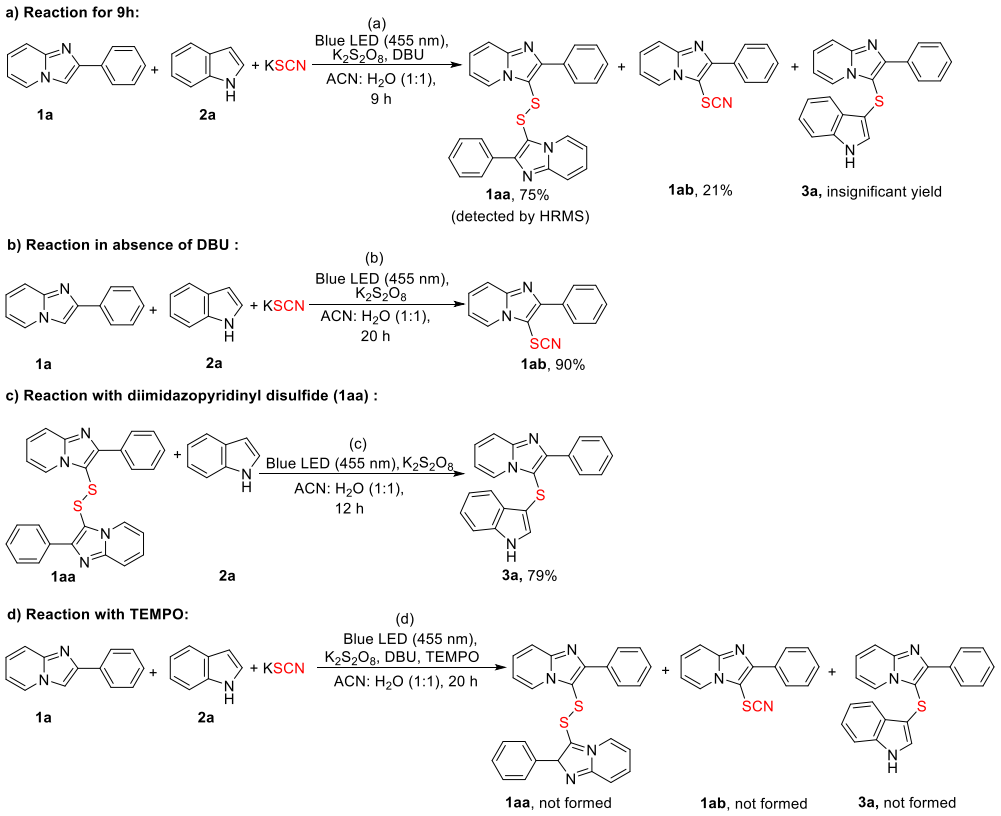
c) Reaction with diimidazopyridinyl disulfide (1aa):

An oven-dried round bottom flask was charged with the diimidazopyridinyl disulfide (**1aa**, 1 equiv., 1 mmol), indole (2 equiv.), $K_2S_2O_8$ (1.5 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 12 h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air.

d) **Reaction with TEMPO:**

An oven-dried round bottom flask was charged with 2-phenyl imidazo[1,2-*a*]pyridine (**1a**, 1 equiv., 1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.) TEMPO (4.5 equiv.) in 5 mL of ACN:H_2O in 1:1 ratio. The reaction mixture was stirred at room temperature for 8h under irradiation of blue LED light (24 W, 455 nm), at a distance of 2 cm away from light source, in open air. After 8 h of continuation of reaction, DBU (1 equiv.) was added to the same on-going reaction mixture, followed by addition of indole (**2a**, 1 equiv.) to it. The entire reaction was continued up to 20 h.

Scheme 2. Control experiments[a].



[a]Reaction conditions: (a) **1a** (1 mmol), **2a** (1 mmol), KSCN (2 equiv.), DBU (1 equiv.), $K_2S_2O_8$ (2 equiv.), Blue LED (455 nm), solvent: 5 mL, rt, 9 h; (b) **1a** (1 mmol), **2a** (1 mmol), KSCN (2 equiv.), $K_2S_2O_8$ (2 equiv.), Blue LED (455 nm), solvent: 5 mL, rt, 20 h; (c) **1aa** (1 mmol), **2a** (2 mmol), $K_2S_2O_8$ (2 equiv.), Blue LED (455 nm), solvent: 5 mL, rt, 12 h; (d) **1a** (1 mmol), **2a** (1 mmol), KSCN (2 mmol, 2 equiv.), DBU (1 equiv.), $K_2S_2O_8$ (2 equiv.), TEMPO (4.5 equiv.), Blue LED (455 nm), solvent: 5 mL, rt, 20 h.

***In vitro* anti-oxidant activity**

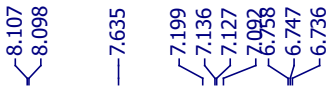
The selected synthesized compounds were screened for anti-oxidant activity via DPPH assay method. Compounds **3h** (0.264 µmol/mL; 65.15±0.185***inhibition at 500µg/mL) and **3j (**IC_{50} value of 0.244 µmol/mL; 87.49±0.051***inhibition at 500µg/mL) have showed the maximum anti-oxidant potential in comparison to the standard compound ascorbic acid (99.91±0.016***µmol/mL) (Table 1). Compounds **3c, 3f** also displayed higher anti-oxidant activity with IC_{50} value of 0.421 and 0.418 µmol/mL respectively. Compounds **4b, 3a, 3k, 3d, 3b** were observed as least active compounds amongst the synthesized compounds with IC_{50} values of 2.418, 1.719, 1.424, 1.272, 1.206 µmol/mL, respectively.

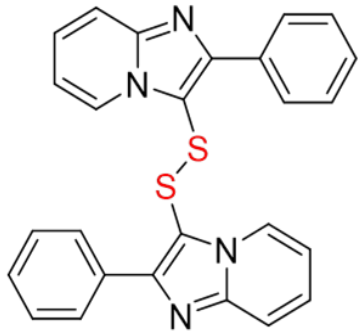
Table 1: Anti-oxidant activity (µmol/mL) of synthesized C-H sulfenylated of imidazopyridines:

Comp.	Conc.	%Inhibition±SEM	IC_{50}	Comp.	Conc.	%Inhibition±SEM	IC_{50}
3a	500	42.29±0.040***	1.719	**3b**	500	67.73±0.138***	1.206
	250	36.63±0.069***			250	48.03±0.348***	
	125	31.64±0.170***			125	34.32±0.403***	
	62.5	28.08±0.087***			62.5	31.17±0.346***	
	31.25	25.39±0.143***			31.25	27.30±0.106***	
3c	500	84.75±0.206***	0.421	**3d**	500	42.46±0.03***	**3d**
	250	71.47±0.092***			250	35.76±0.07***	
	125	55.15±0.059***			125	28.21±0.06***	
	62.5	42.37±0.179***			62.5	25.62±0.06***	
	31.25	31.83±0.179***			31.25	21.47±0.11***	
3e	500	68.27±0.501***	0.957	**3f**	500	65.72±0.117***	0.418
	250	44.76±0.289***			250	51.30±0.070***	
	125	29.98±0.062***			125	37.41±0.070***	
	62.5	27.91±0.074***			62.5	21.23±0.061***	
	31.25	25.02±0.037***			31.25	15.49±0.120***	
3g	500	70.10±0.346***	0.771	**3h**	500	65.15±0.185***	0.264
	250	48.91±0.068***			250	62.08±0.142***	
	125	31.45±0.113***			125	52.96±0.048***	
	62.5	25.58±0.048***			62.5	46.42±0.040***	

	31.25	22.64±0.442***			31.25	38.86±0.055***	
3i	500	76.06±0.133***	0.842	**3j**	500	87.49±0.051***	0.244
	250	56.11±0.128***			250	74.58±0.053***	
	125	39.04±0.221***			125	67.47±0.247***	
	62.5	28.76±0.088***			62.5	46.24±0.155***	
	31.25	24.38±0.154***			31.25	31.52±0.184***	
3k	500	74.36±0.007***	1.424	**4a**	500	61.89±0.136***	0.536
	250	41.04±0.044***			250	56.22±0.079***	
	125	20.41±0.071***			125	33.33±0.031***	
	62.5	17.71±0.096***			62.5	30.08±0.026***	
	31.25	10.45±0.118***			31.25	28.33±0.073***	
4b	500	54.45±0.535***	2.418	**5a**	500	58.05±0.044***	0.602
	250	37.68±0.038***			250	48.10±0.071***	
	125	24.61±0.105***			125	41.69±0.044***	
	62.5	17.94±0.121***			62.5	31.02±0.109***	
	31.25	12.56±0.041***			31.25	25.39±0.005***	
Ascorbic Acid (**STD.**)	500	99.91±0.016***	0.406				
	250	88.95±0.001***					
	125	75.19±0.076***					
	62.5	57.12±0.101***					
	31.25	40.90±0.163***					

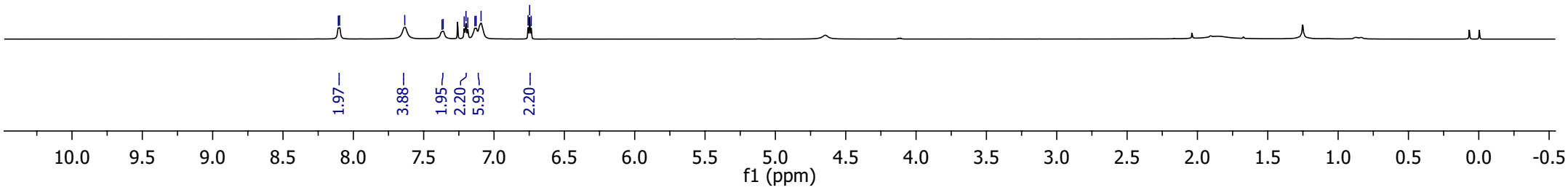
This data is represented as Mean±SEM, n=3, values are significantly different as compared to positive control (STD) Ascorbic acid (500µg/mL) (***P<0.001).

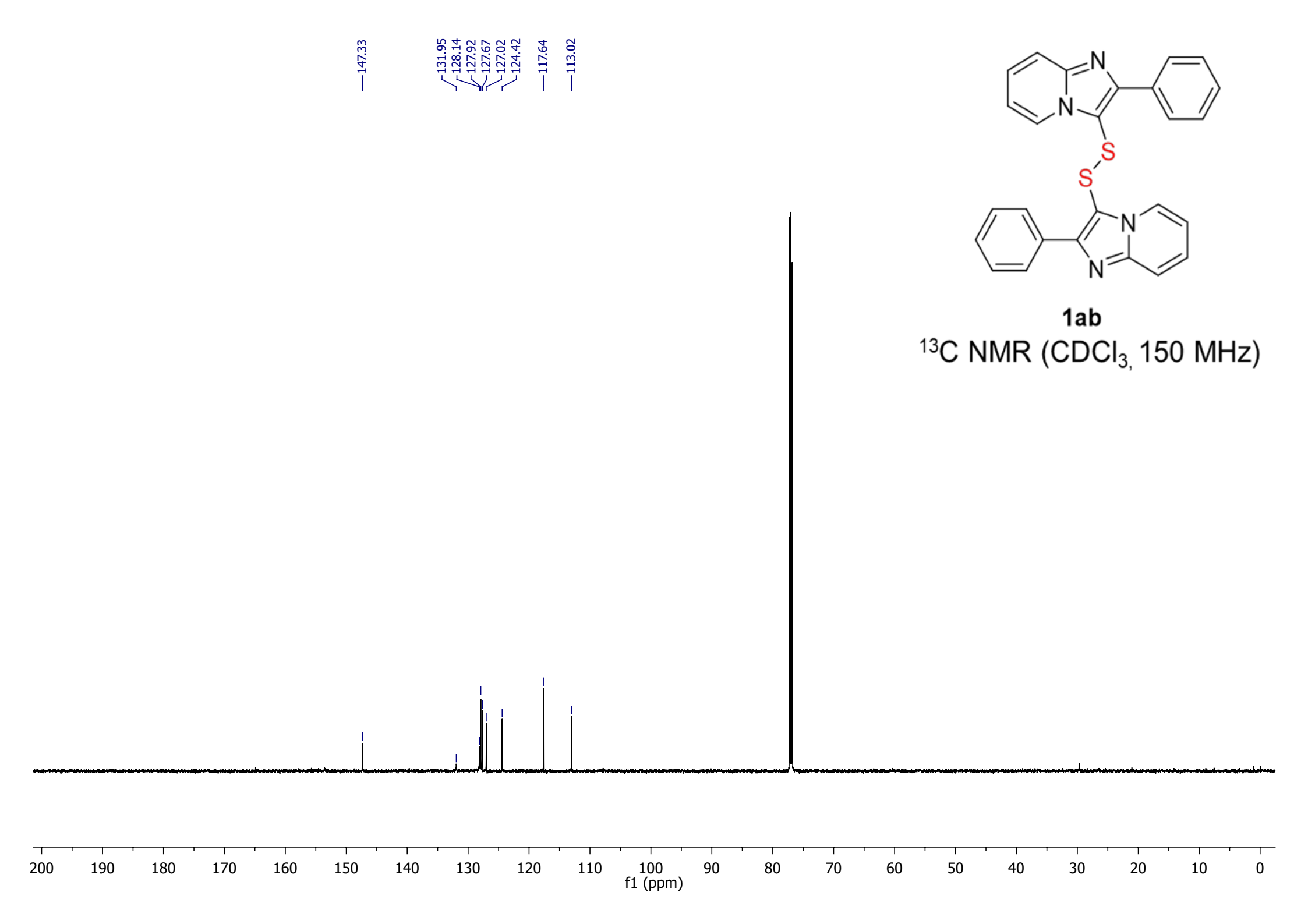




1ab

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

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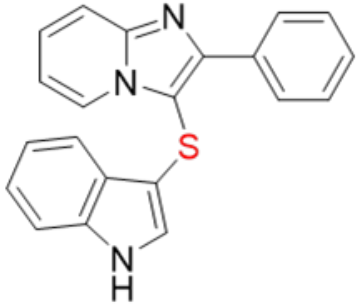
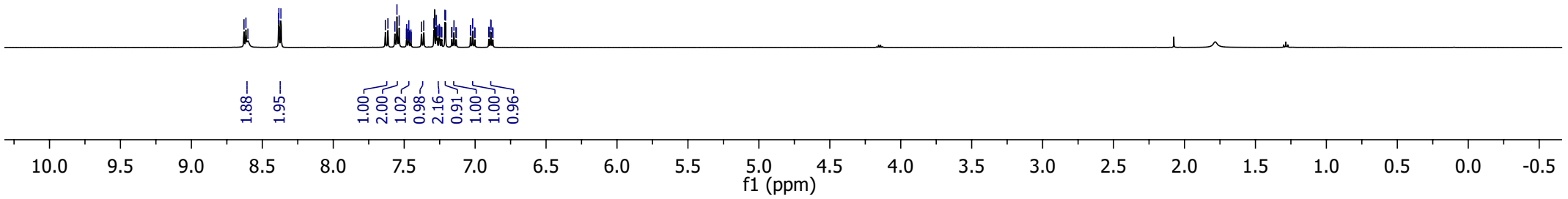
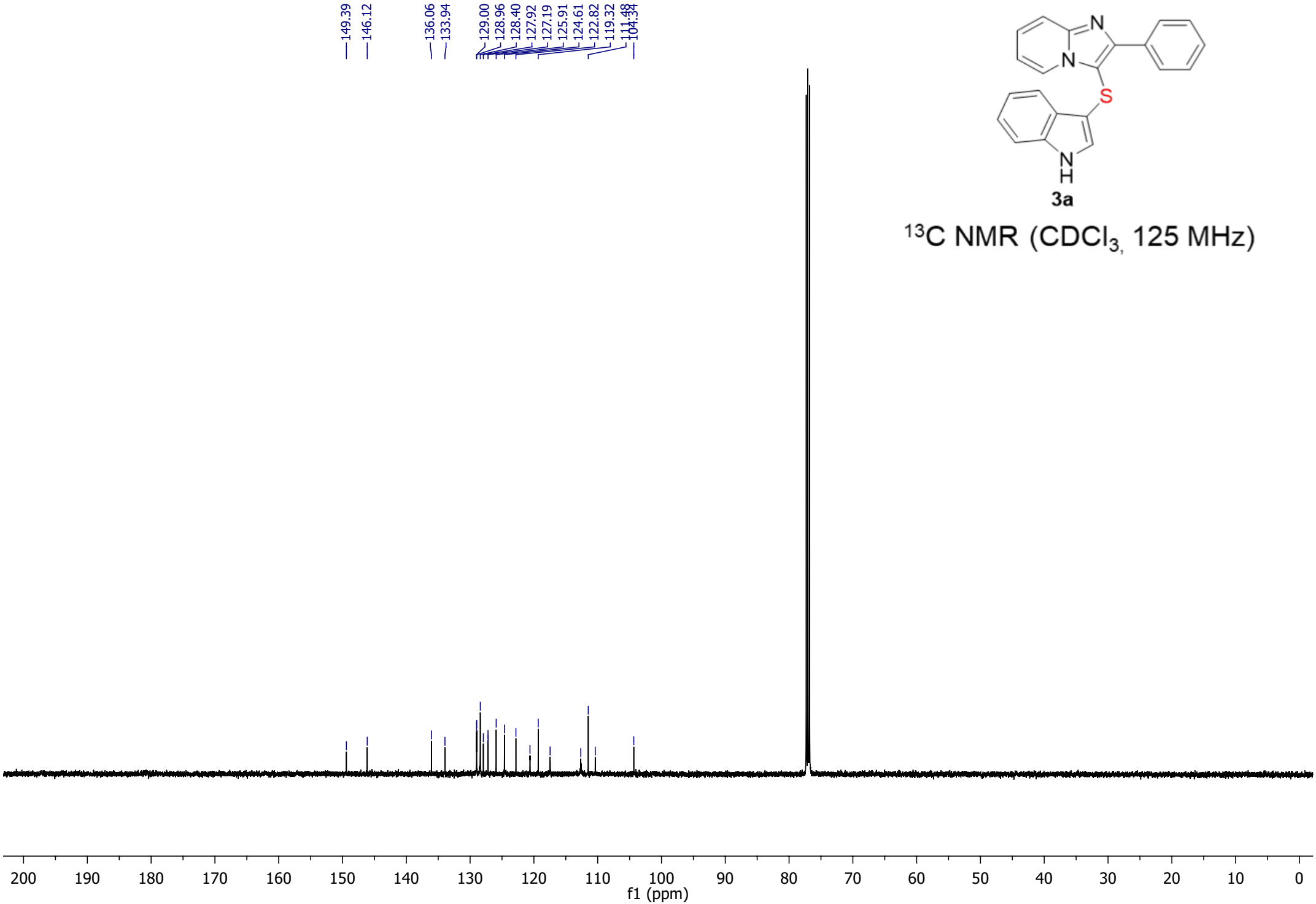
128.14
127.92
127.67
127.02
124.42
117.64
113.02
N
N
S
S
N
N
1ab
^{13}C NMR ($CDCl_3$, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3a

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

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127.92
127.19
125.91
124.61
122.82
119.32
111.48
104.34
N
N
S
N
H
3a
^{13}C NMR ($CDCl_3$, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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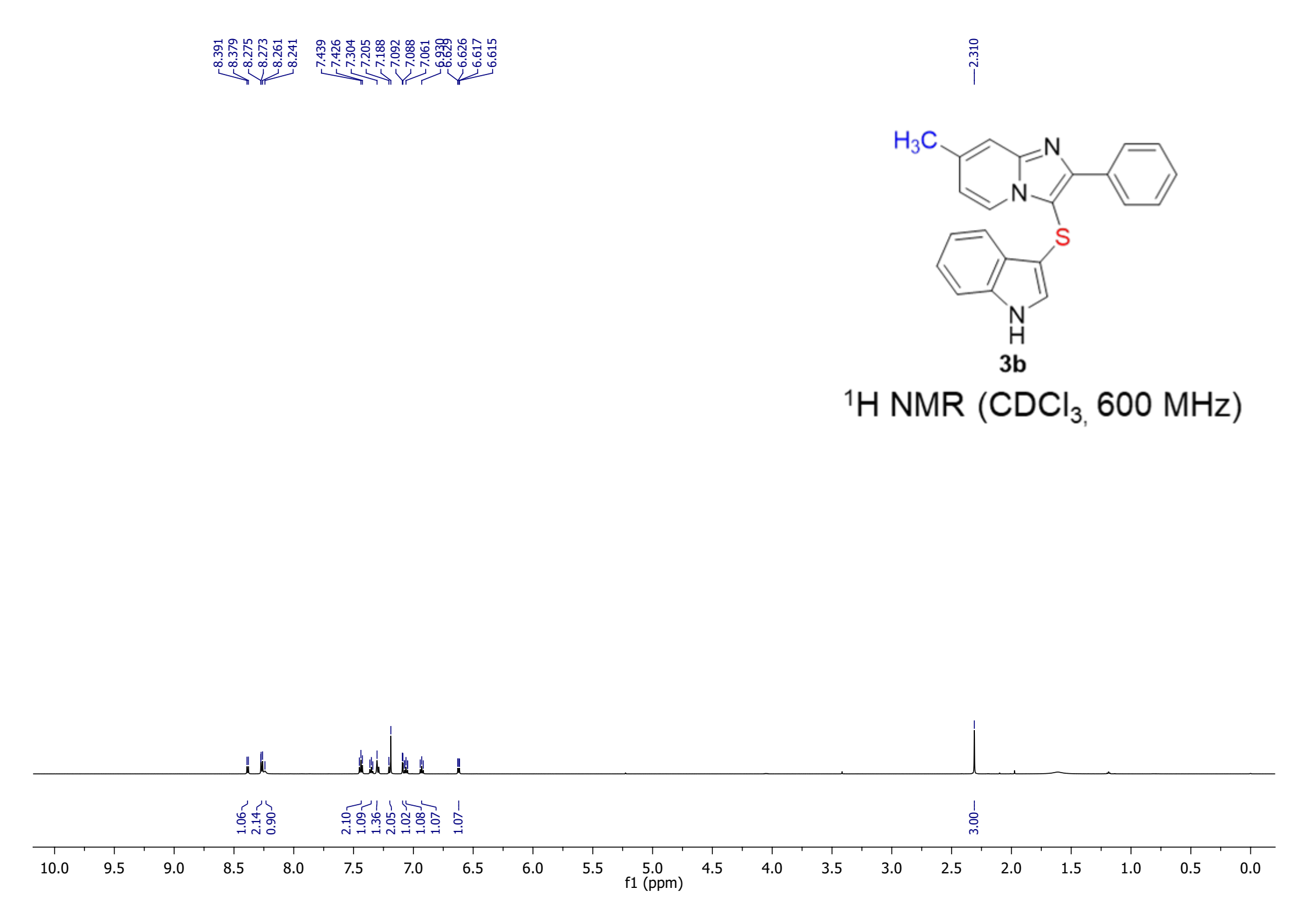
50
40
30
20
10
0
f1 (ppm)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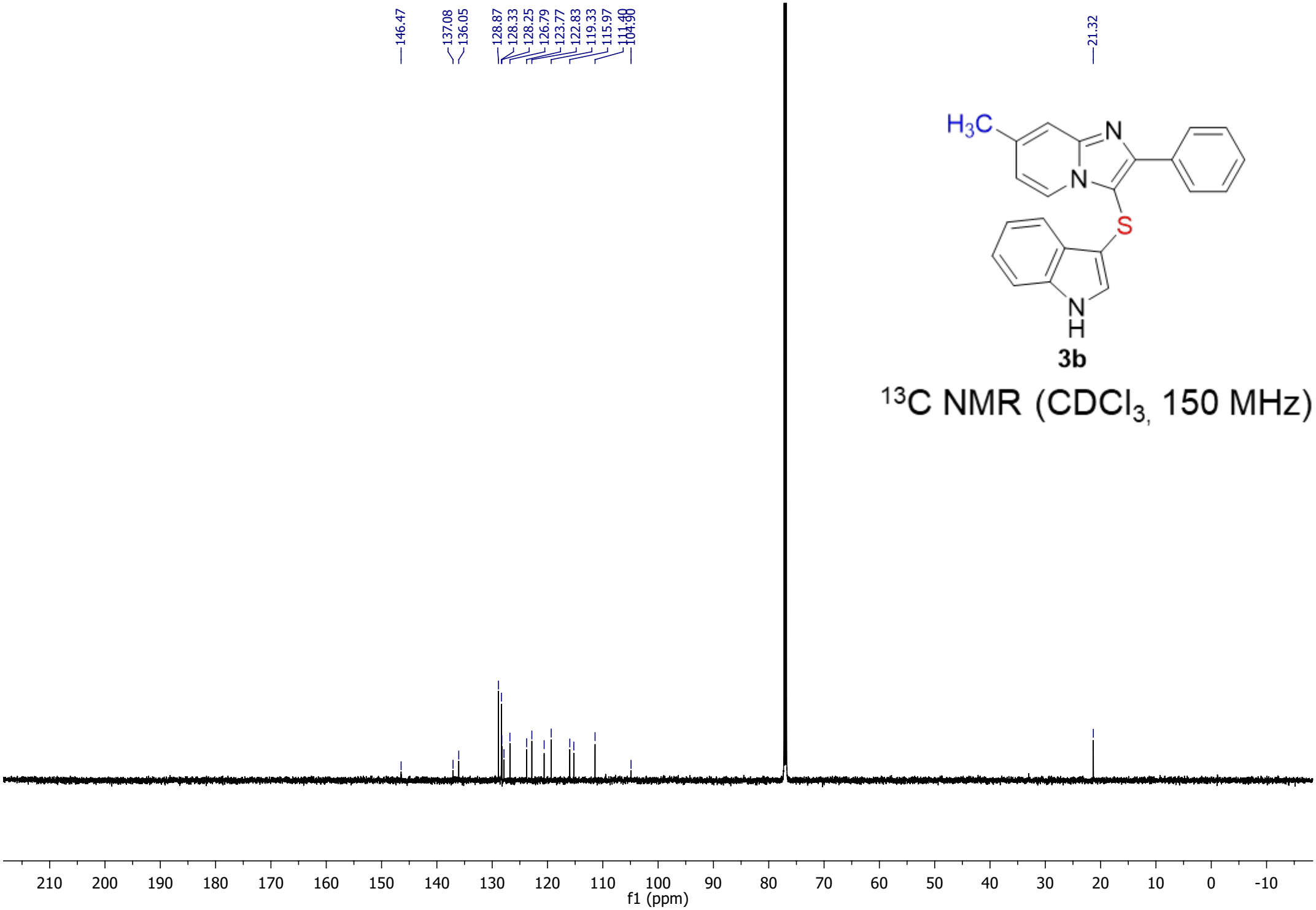
7.205
7.188
7.092
7.088
7.061
6.626
6.617
6.615
2.310
H3C
N
N
S
N
H
3b
1H NMR (CDCl3, 600 MHz)
1.06
2.14
0.90
2.10
1.09
1.36
2.05
1.02
1.08
1.07
1.07
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.33
128.25
126.79
123.77
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119.33
115.97
111.40
104.90
21.32
H3C
N
N
S
N
H
3b
13C NMR (CDCl3, 150 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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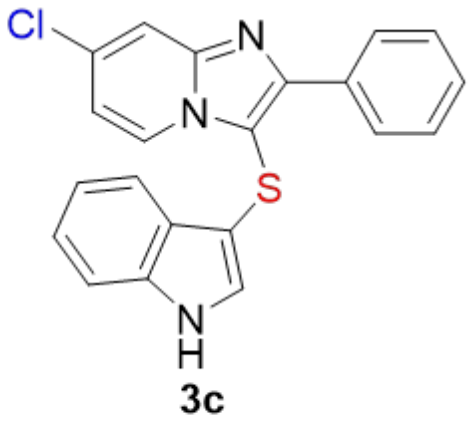
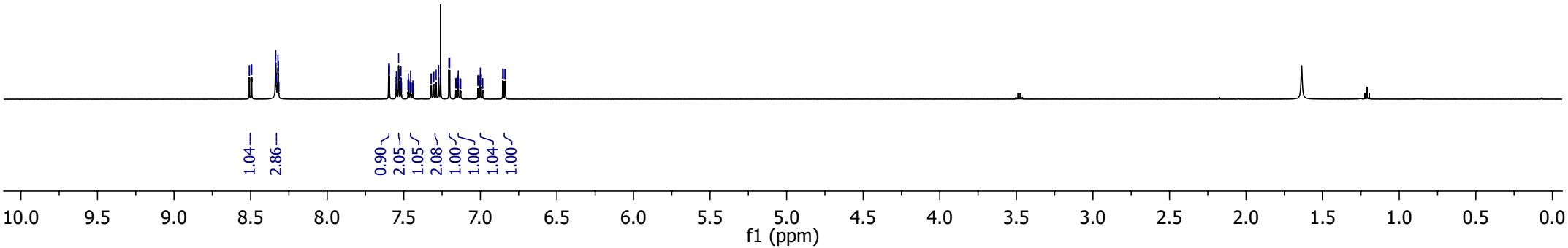
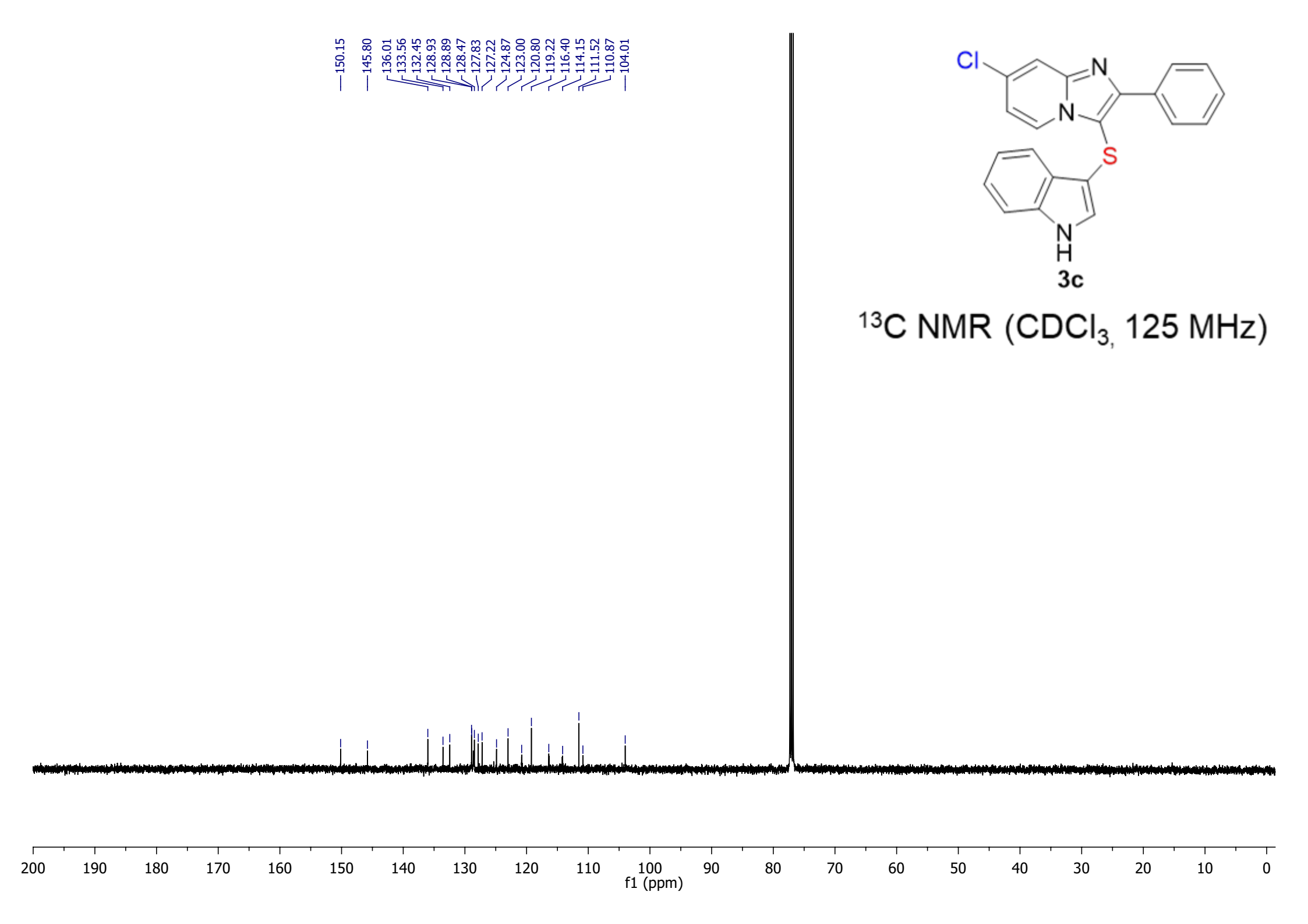
50
40
30
20
10
0
-10
f1 (ppm)



3c

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

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133.56
132.45
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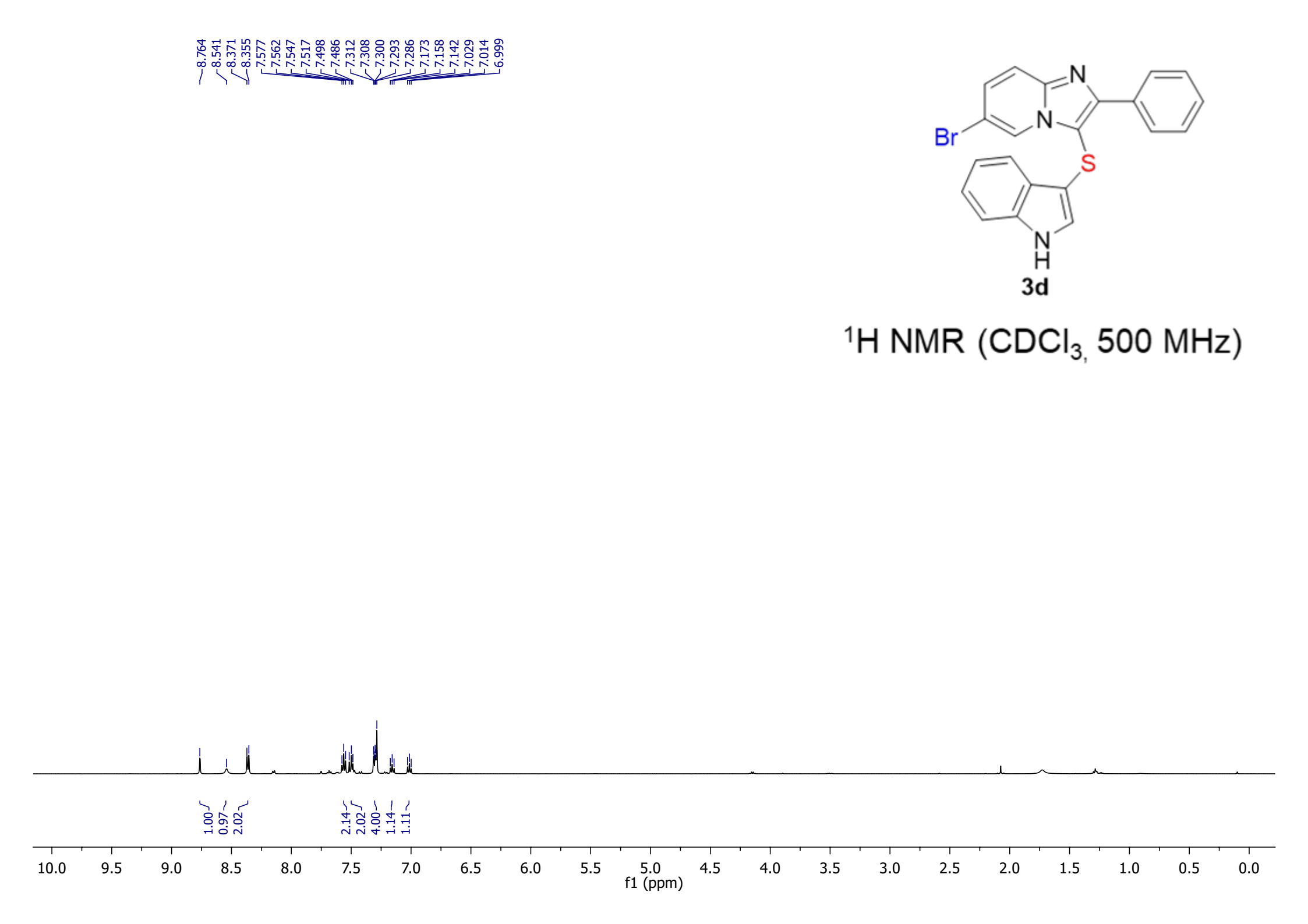
127.83
127.22
124.87
123.00
120.80
119.22
116.40
114.15
111.52
110.87
104.01
Cl
N
N
S
N
H
3c
^{13}C NMR ($CDCl_3$, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.293
7.286
7.173
7.158
7.142
7.029
7.014
6.999
Br
N
N
S
N
H
3d
^{1}H NMR ($CDCl_3$, 500 MHz)
1.00
0.97
2.02
2.14
2.02
4.00
1.14
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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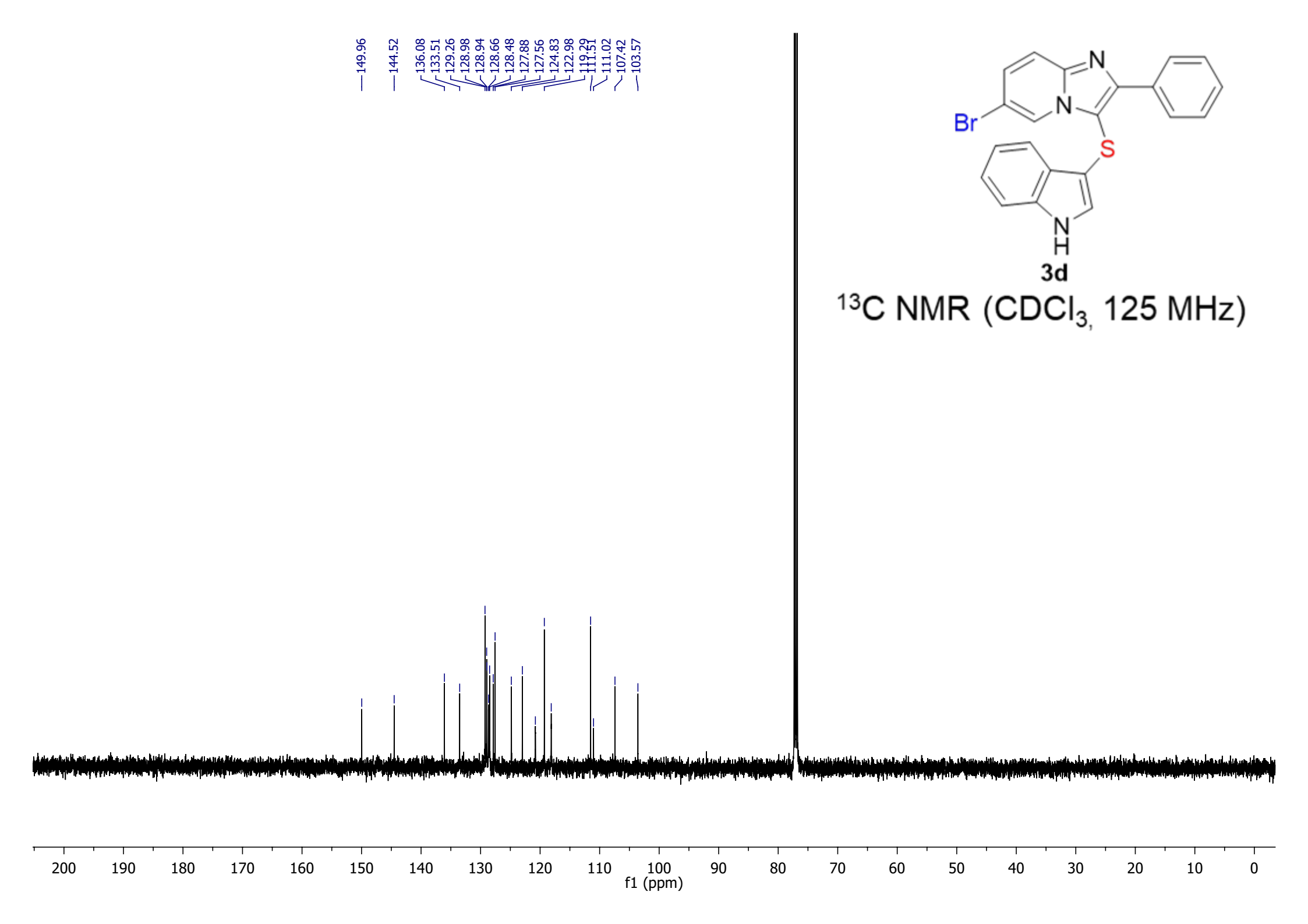
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.96
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133.51
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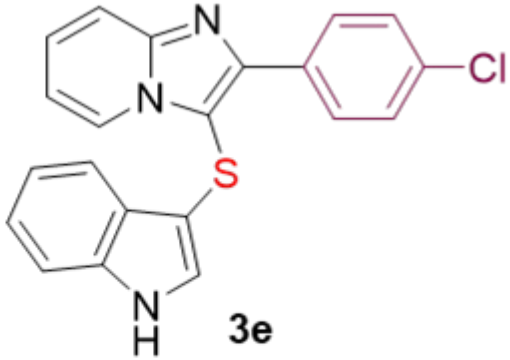
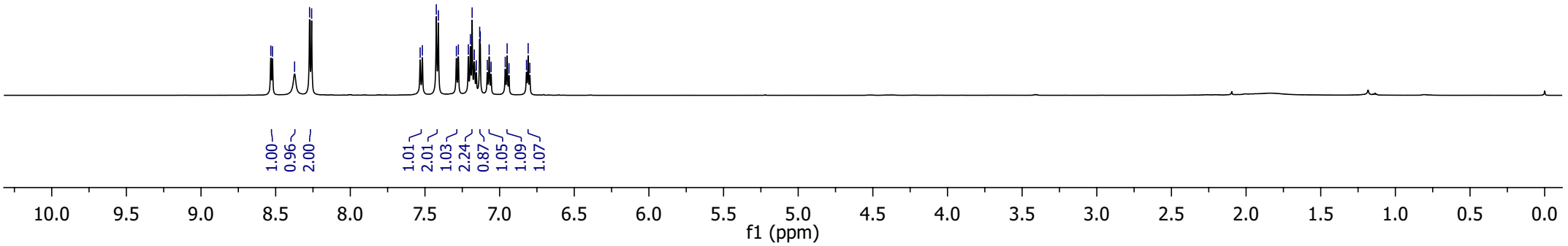
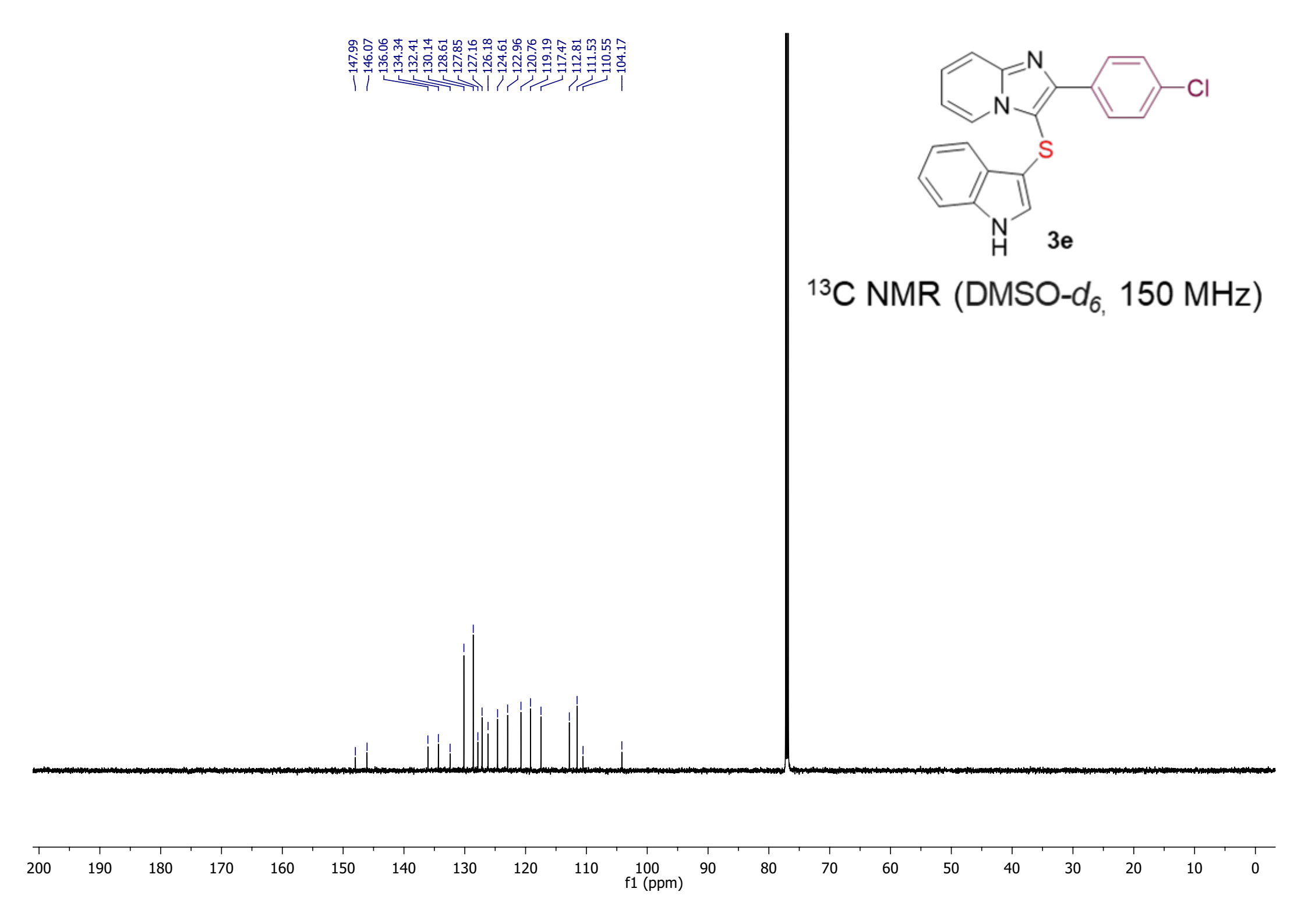
111.51
111.02
107.42
103.57
Br
N
N
S
N
H
3d
^{13}C NMR ($CDCl_3$, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

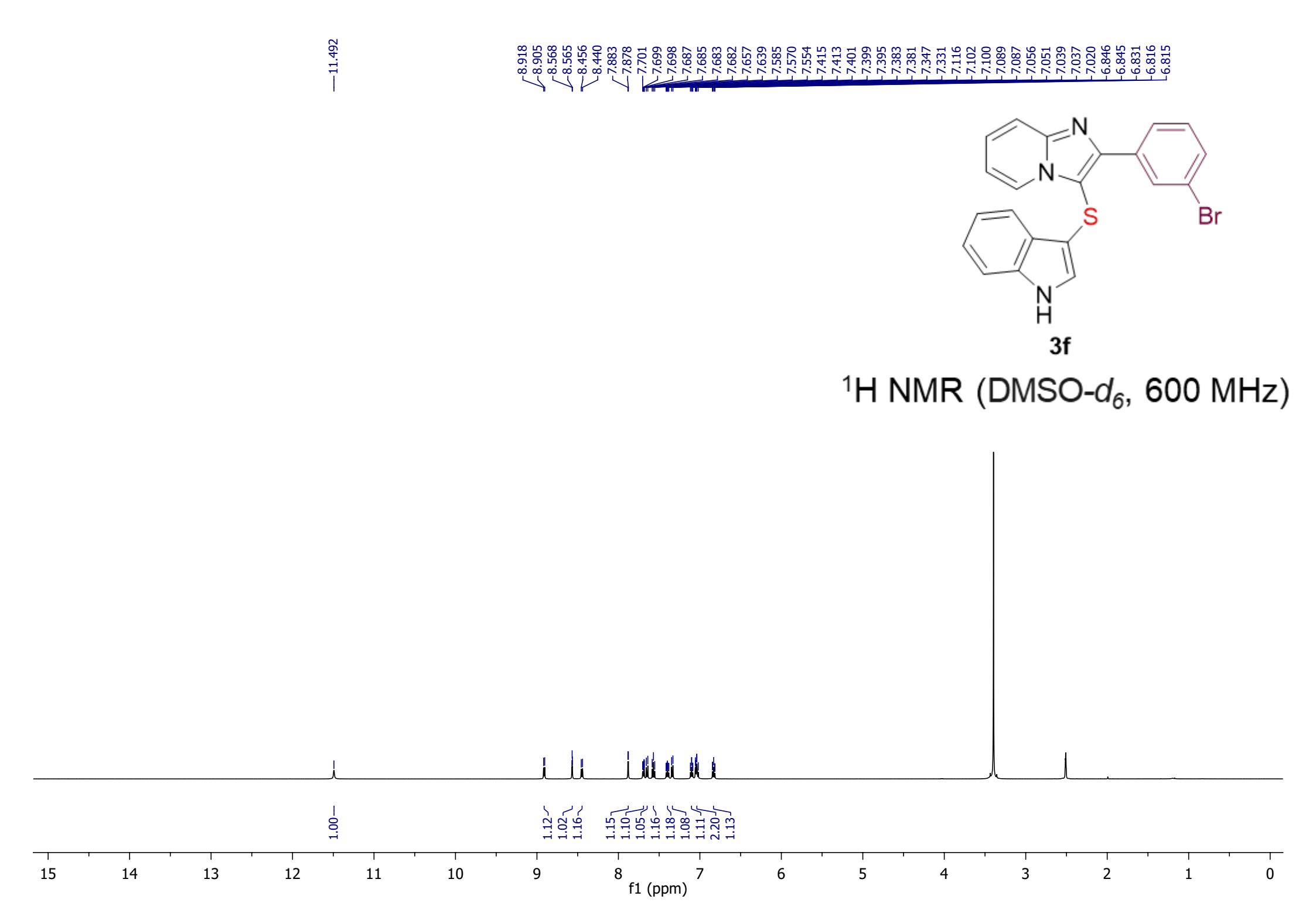


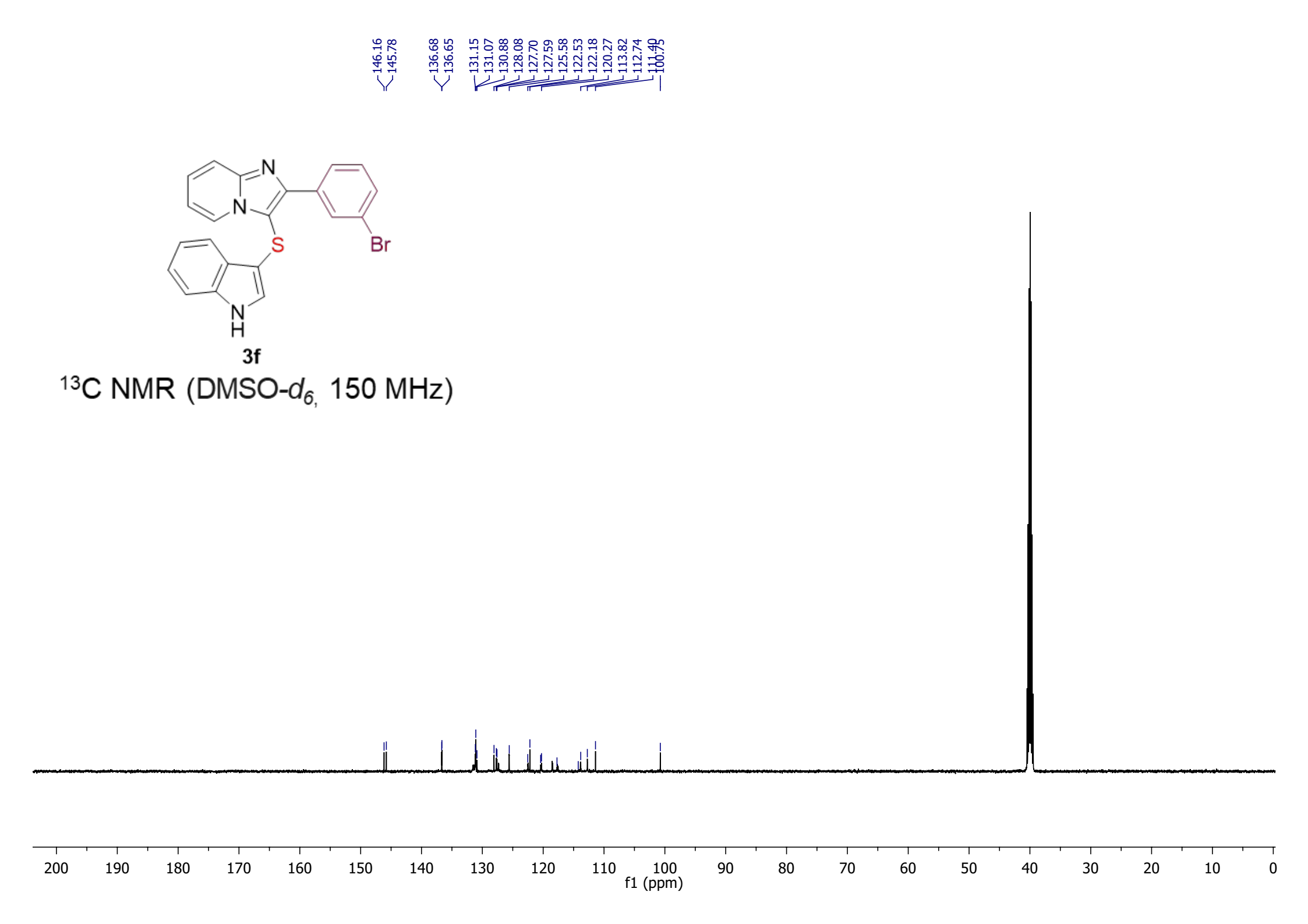
3e

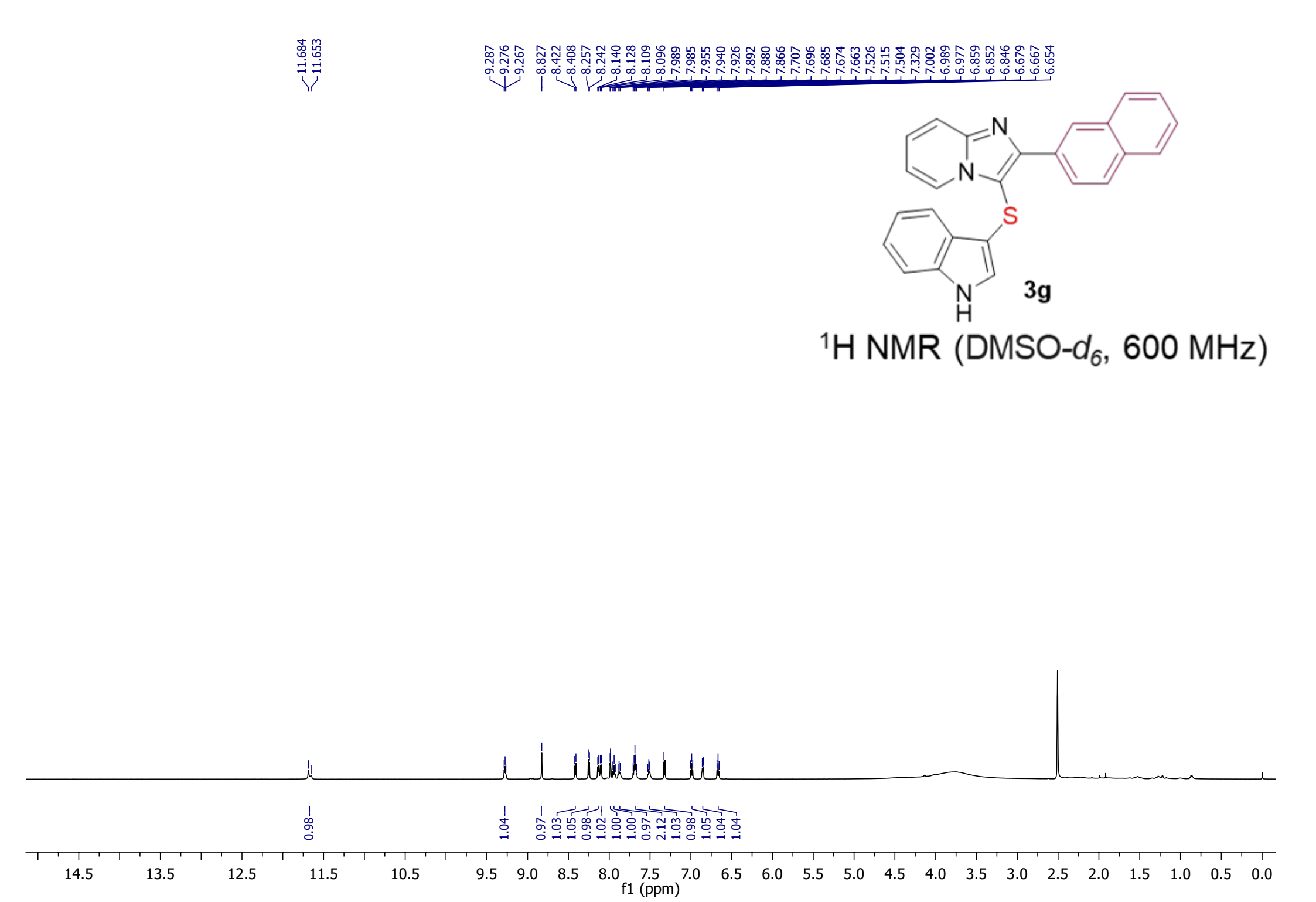
^{1}H NMR ($CDCl_3$, 600 MHz)



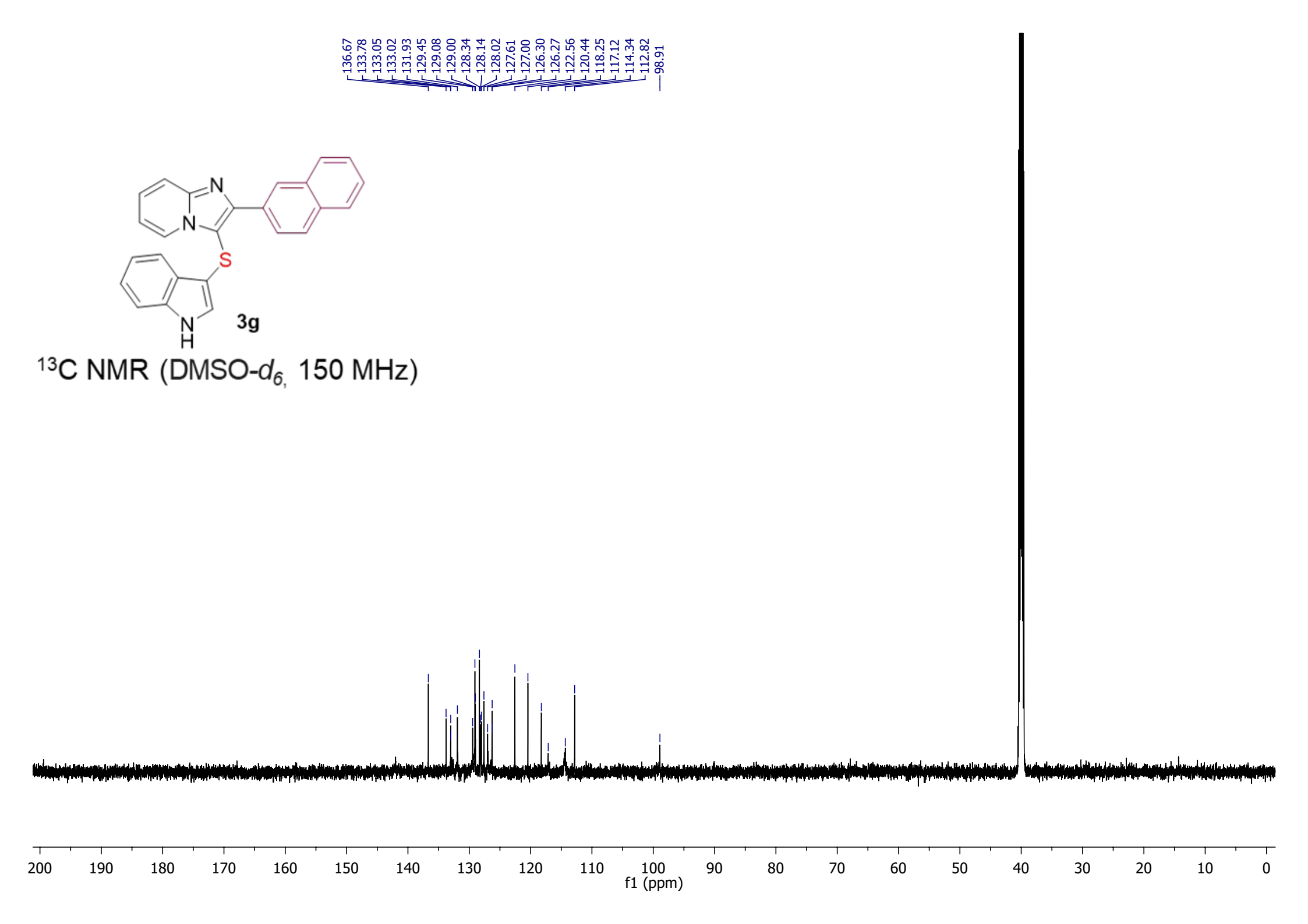

147.99
146.07
136.06
134.34
132.41
130.14
128.61
127.85
127.16
126.18
124.61
122.96
120.76
119.19
117.47
112.81
111.53
110.55
104.17
N
N
Cl
S
N
H
3e
^{13}C NMR (DMSO-d_6, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

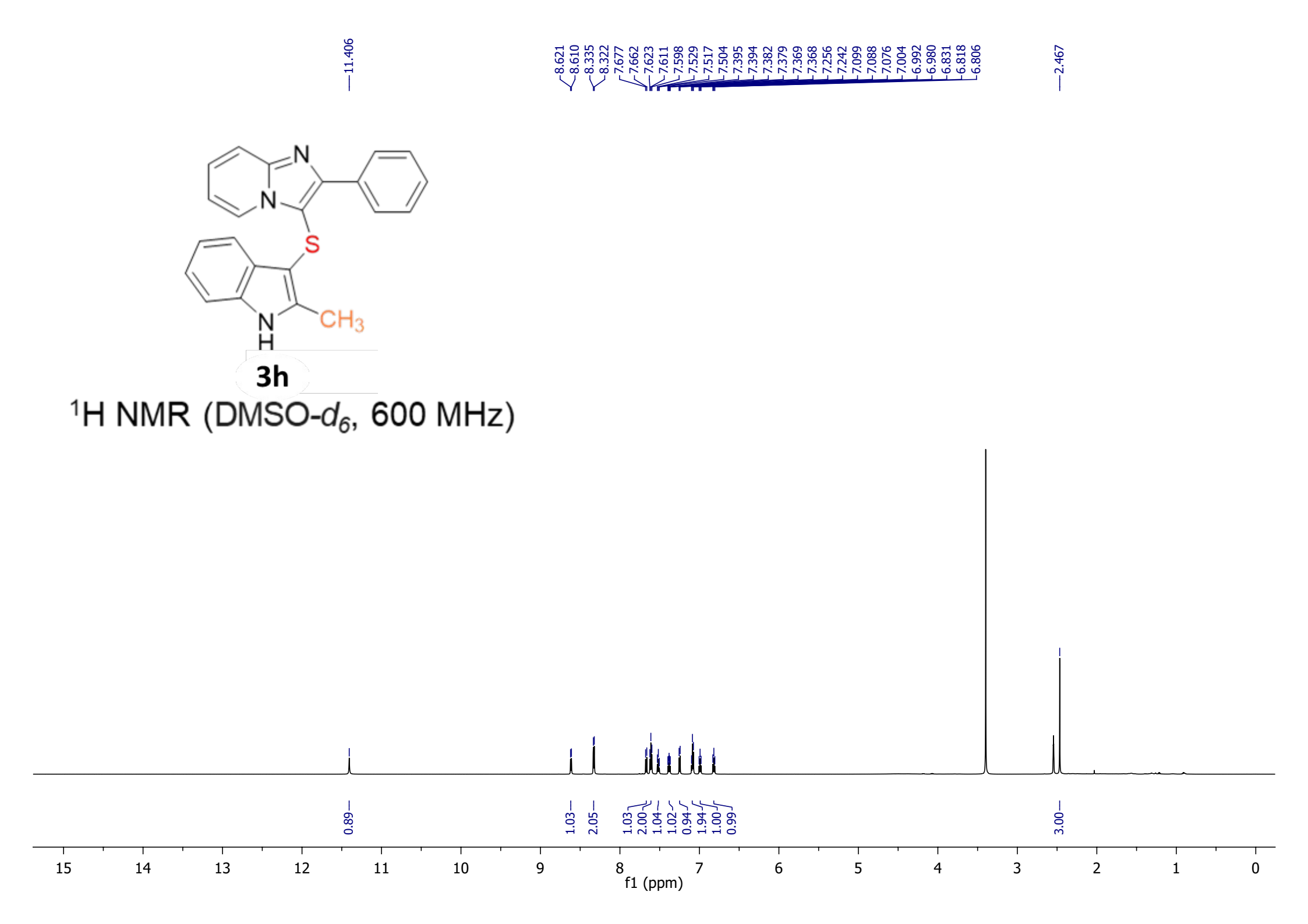

11.492
8.918
8.905
8.568
8.565
8.456
8.440
7.883
7.878
7.701
7.699
7.698
7.687
7.685
7.683
7.682
7.657
7.639
7.585
7.570
7.554
7.415
7.413
7.401
7.399
7.395
7.383
7.381
7.347
7.331
7.116
7.102
7.100
7.089
7.087
7.056
7.051
7.039
7.037
7.020
6.846
6.845
6.831
6.816
6.815
N
N
S
Br
N
H
3f
1H NMR (DMSO-d6, 600 MHz)
1.00
1.12
1.02
1.16
1.15
1.10
1.05
1.16
1.18
1.08
1.11
2.20
1.13
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

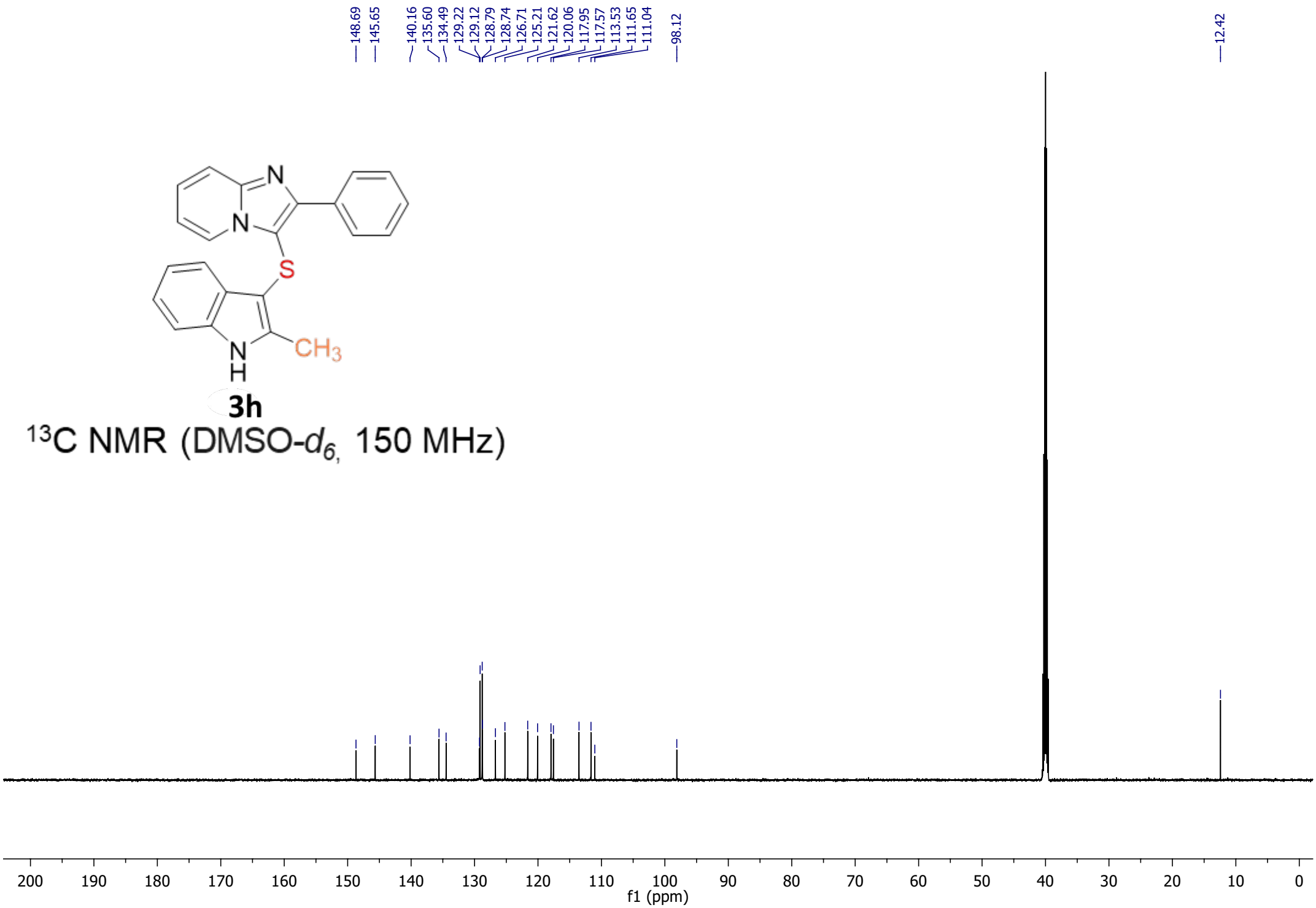

146.16
145.78
136.68
136.65
131.15
131.07
130.88
128.08
127.70
127.59
125.58
122.53
122.18
120.27
113.82
112.74
111.40
100.75
N
N
S
Br
N
H
3f
13C NMR (DMSO-d6, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

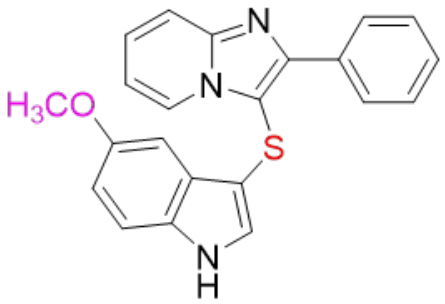


^{1}H NMR (DMSO-d_6, 600 MHz)


136.67
133.78
133.05
133.02
131.93
129.45
129.08
129.00
128.34
128.14
128.02
127.61
127.00
126.30
126.27
122.56
120.44
118.25
117.12
114.34
112.82
98.91
N
N
S
N
H
3g
^{13}C NMR (DMSO-d_6, 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)

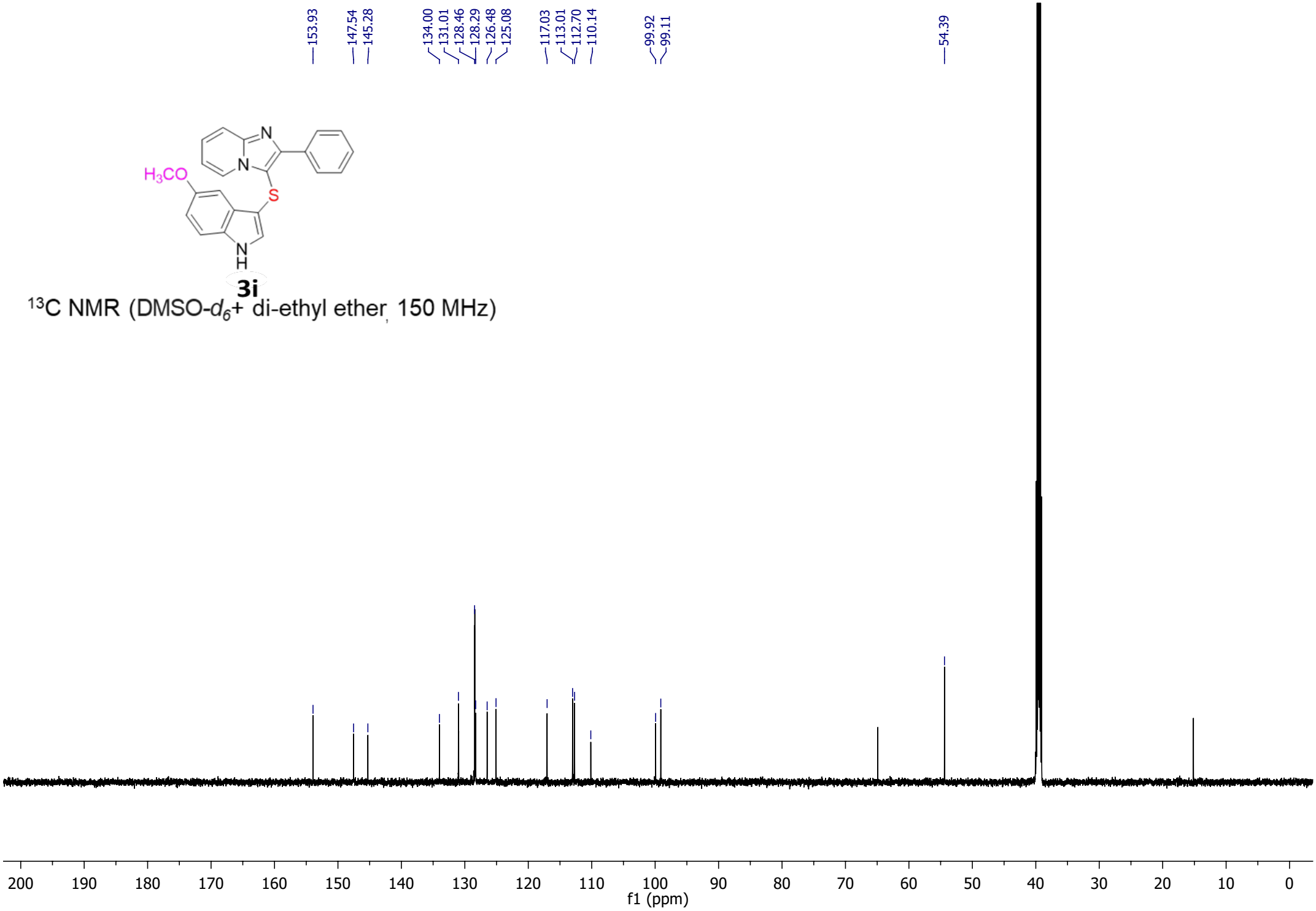

11.406
8.621
8.610
8.335
8.322
7.677
7.662
7.623
7.611
7.598
7.529
7.517
7.504
7.395
7.394
7.382
7.379
7.369
7.368
7.256
7.242
7.099
7.088
7.076
7.004
6.992
6.980
6.831
6.818
6.806
2.467
N
N
S
N
H
CH3
3h
1H NMR (DMSO-d6, 600 MHz)
0.89
1.03
2.05
1.03
2.00
1.04
1.02
0.94
1.94
1.00
0.99
3.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

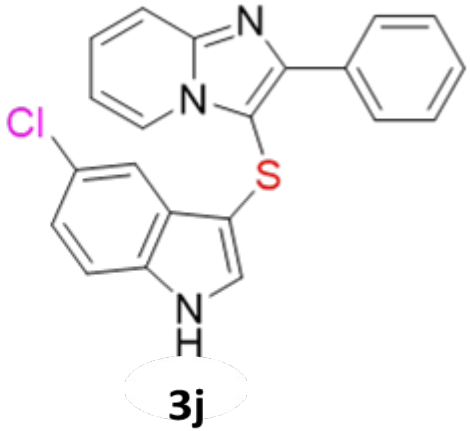

148.69
145.65
140.16
135.60
134.49
129.22
129.12
128.79
128.74
126.71
125.21
121.62
120.06
117.95
117.57
113.53
111.65
111.04
98.12
12.42
N
N
S
N
H
CH3
3h
13C NMR (DMSO-d6, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3i

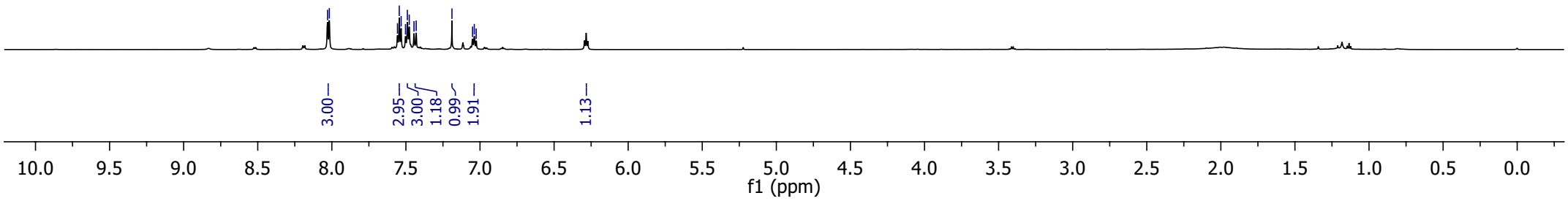
^{1}H NMR (DMSO-d_6+ di-ethyl ether, 600 MHz)

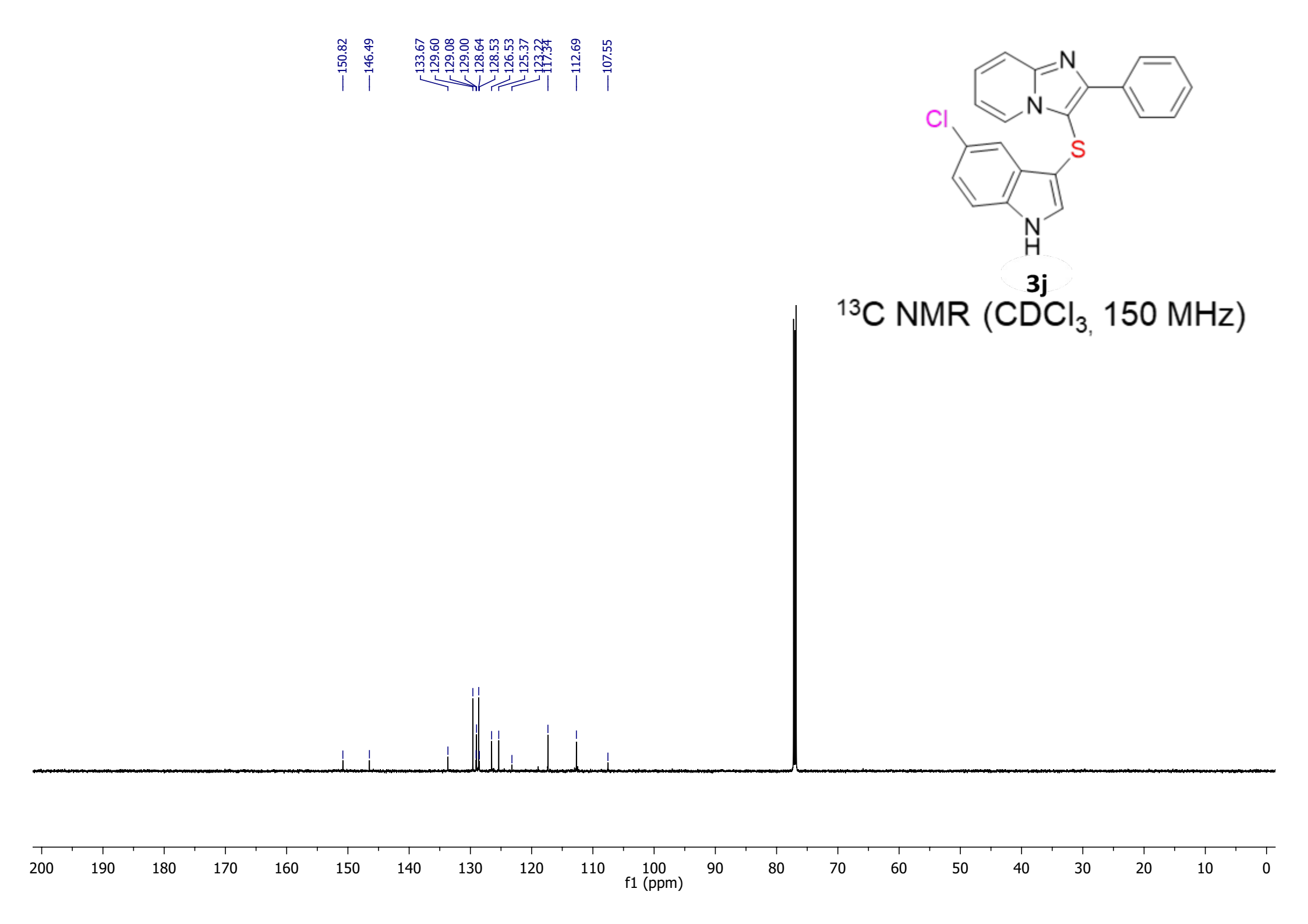

153.93
147.54
145.28
134.00
131.01
128.46
128.29
126.48
125.08
117.03
113.01
112.70
110.14
99.92
99.11
54.39
H3CO
N
N
S
N
H
3i
13C NMR (DMSO-d6+ di-ethyl ether, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

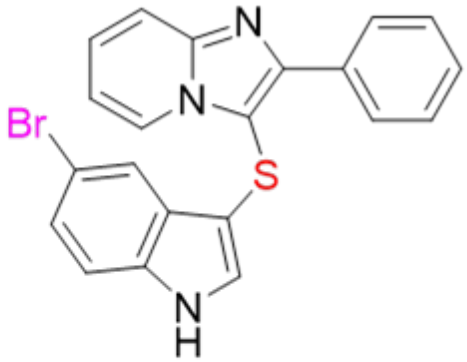


3j

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

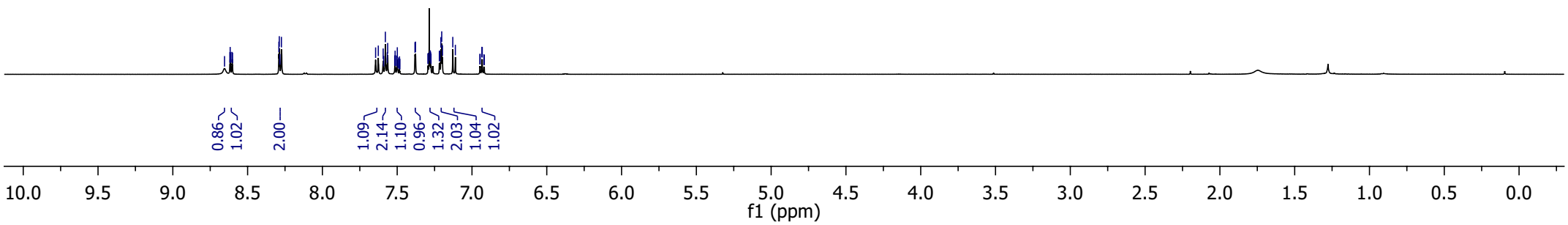


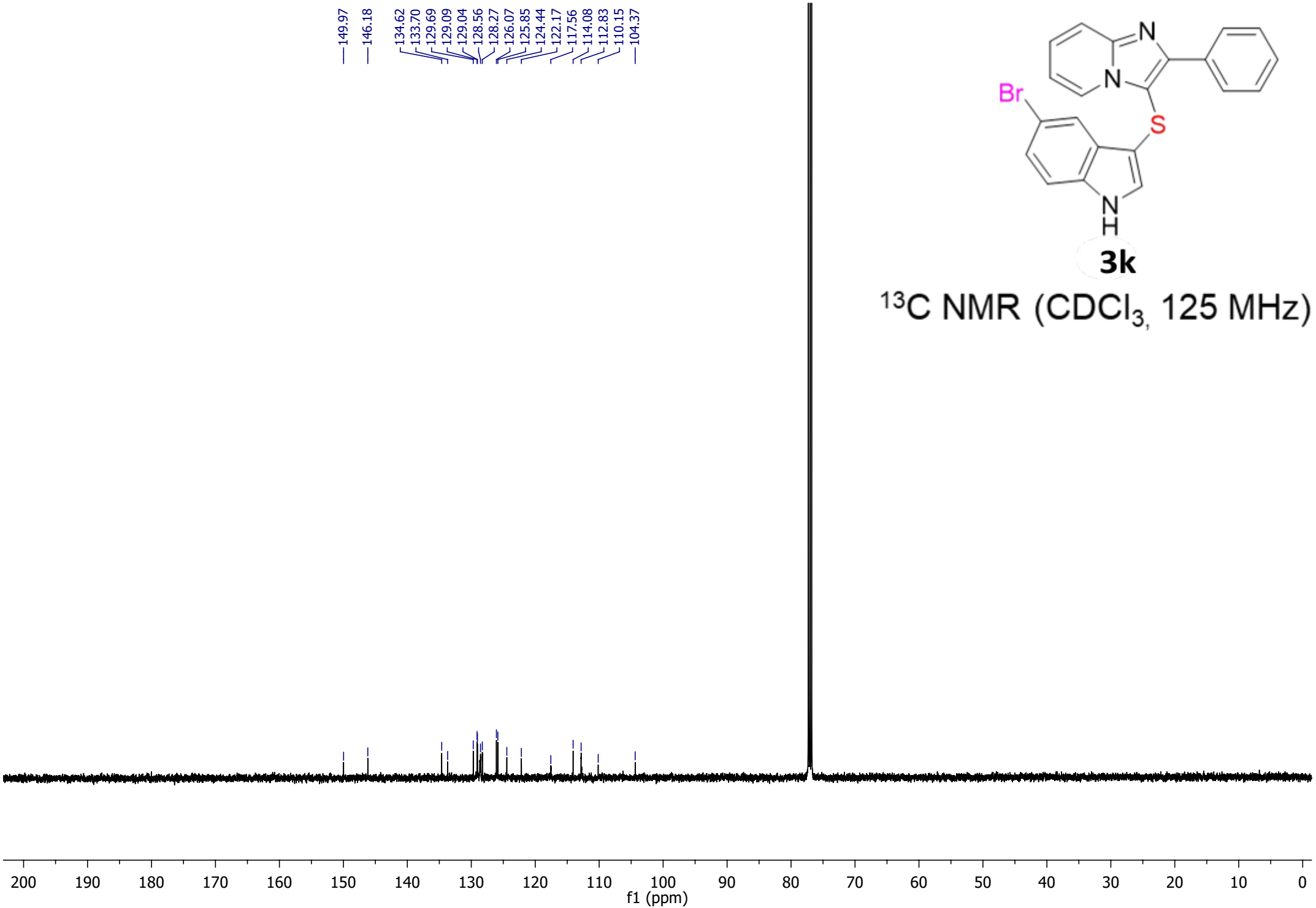

150.82
146.49
133.67
129.60
129.08
129.00
128.64
128.53
126.53
125.37
112.69
107.55
Cl
S
N
N
H
3j
^{13}C NMR ($CDCl_3$, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

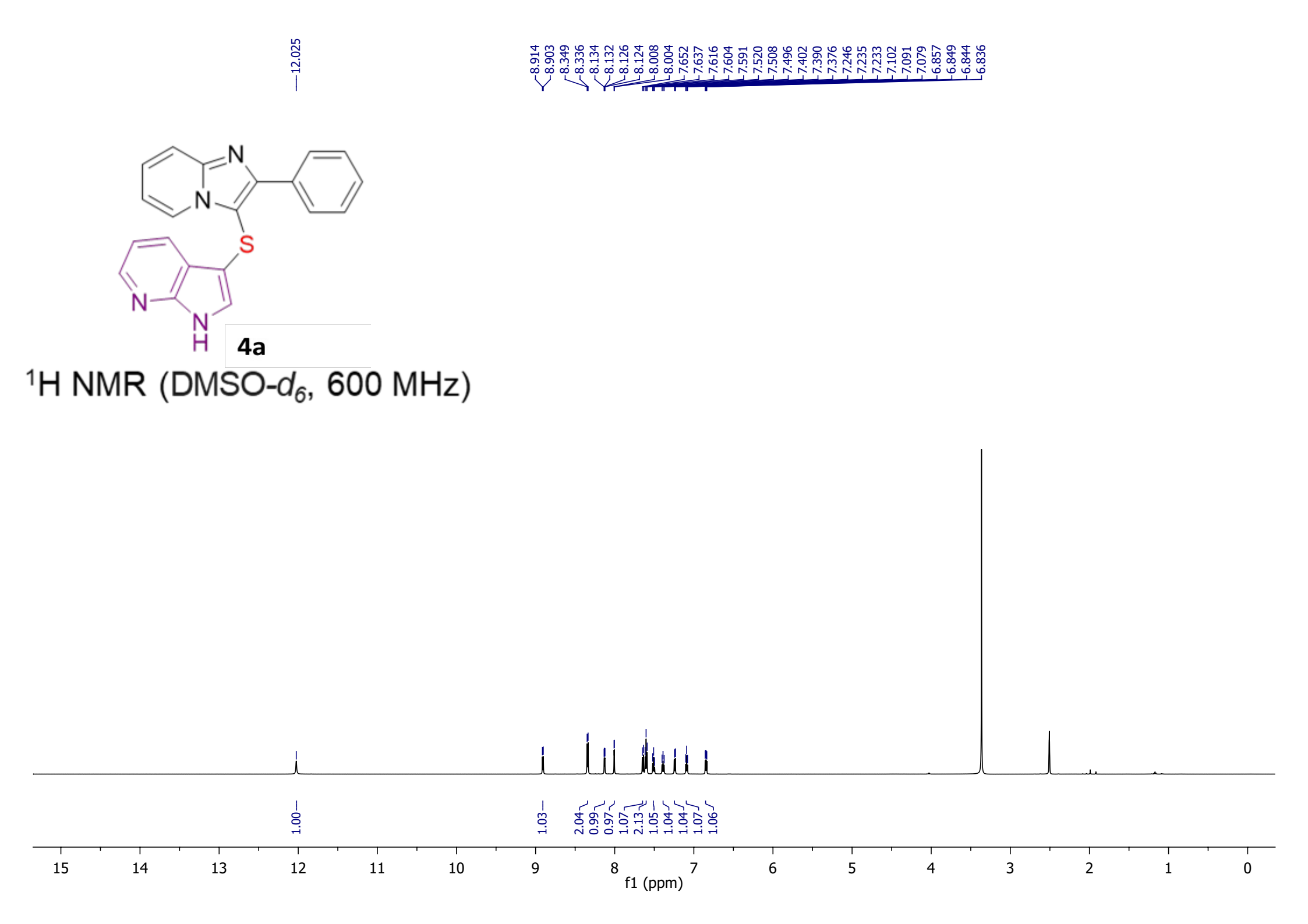


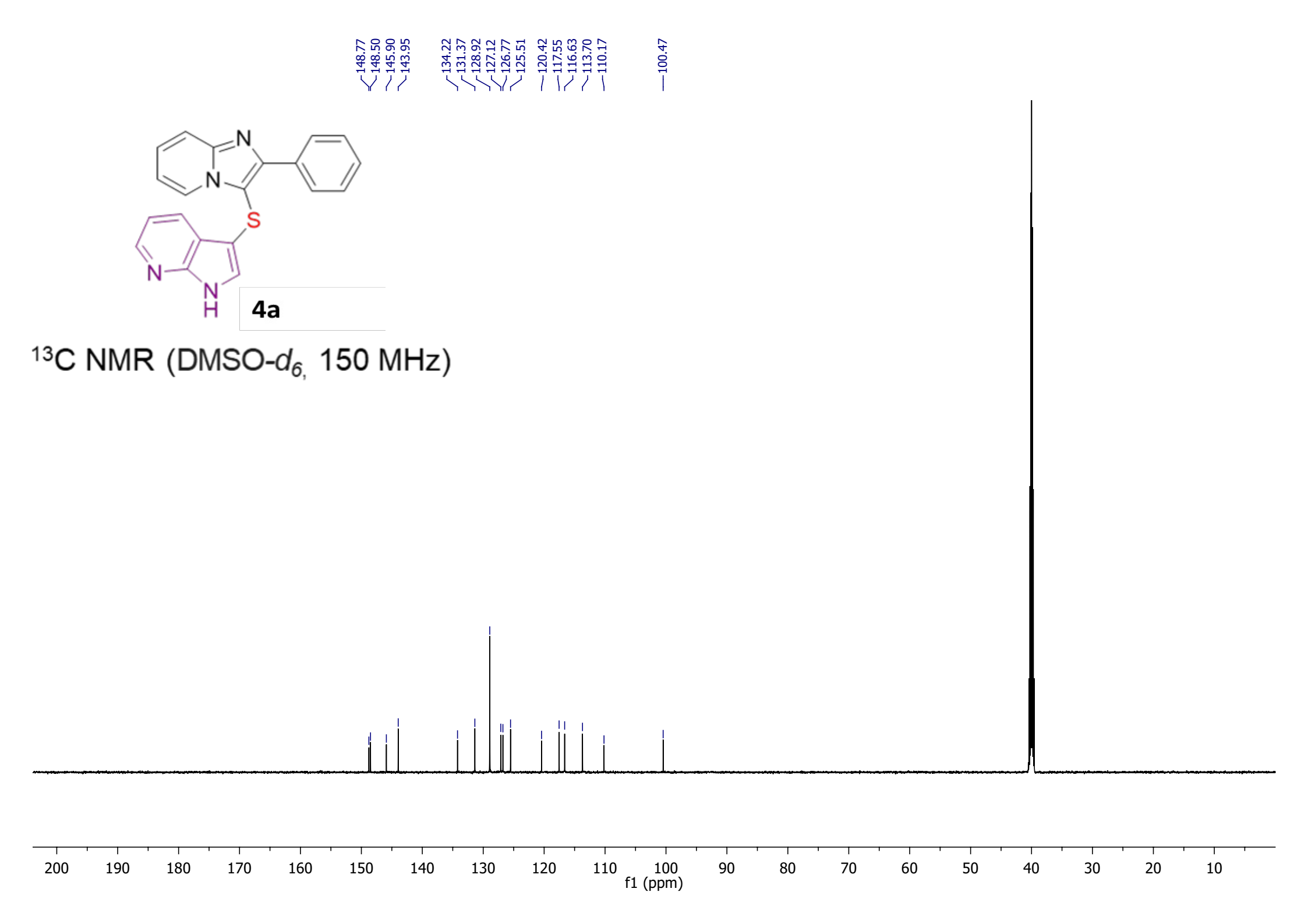
3k

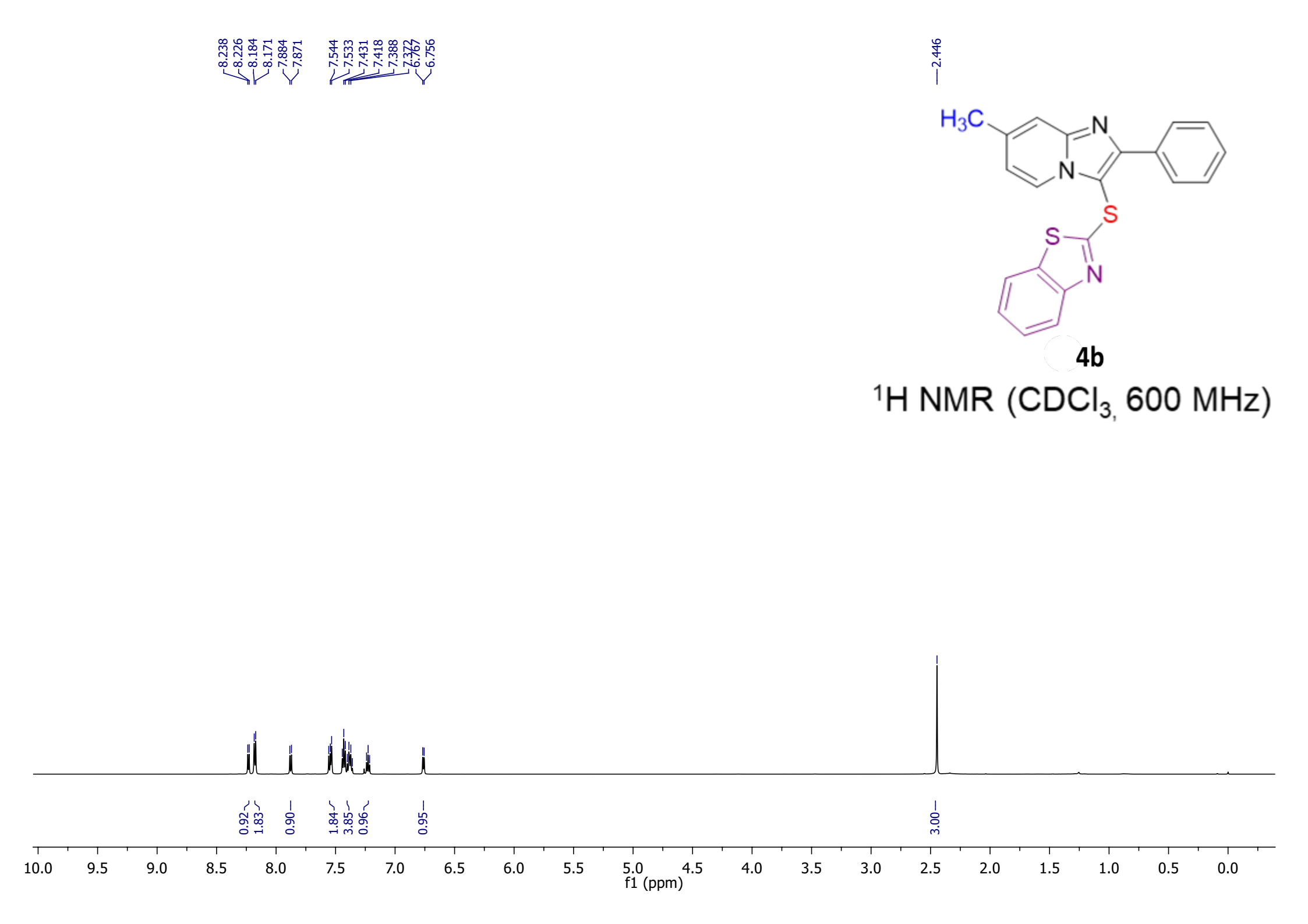
^{1}H NMR ($CDCl_3$, 500 MHz)

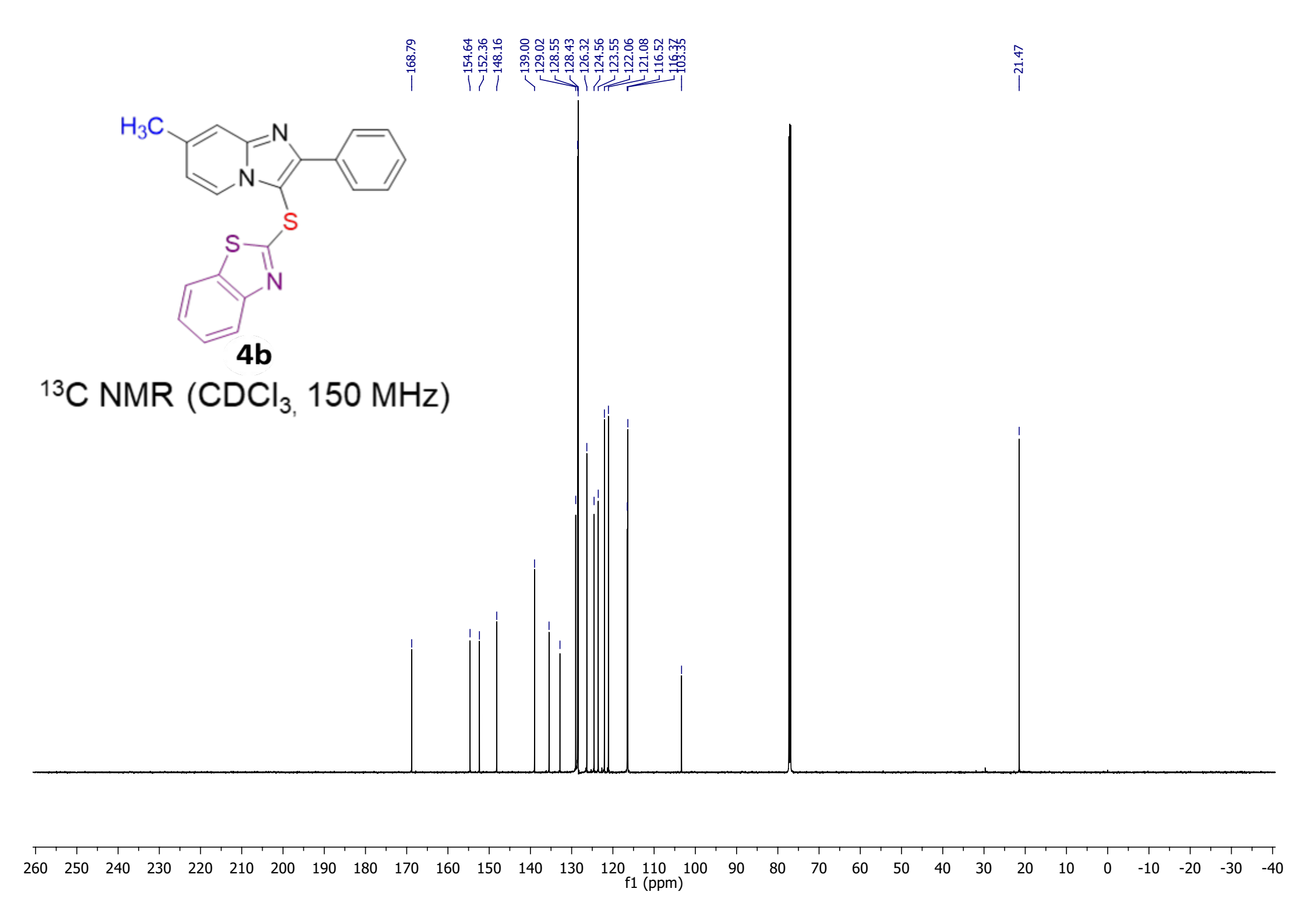


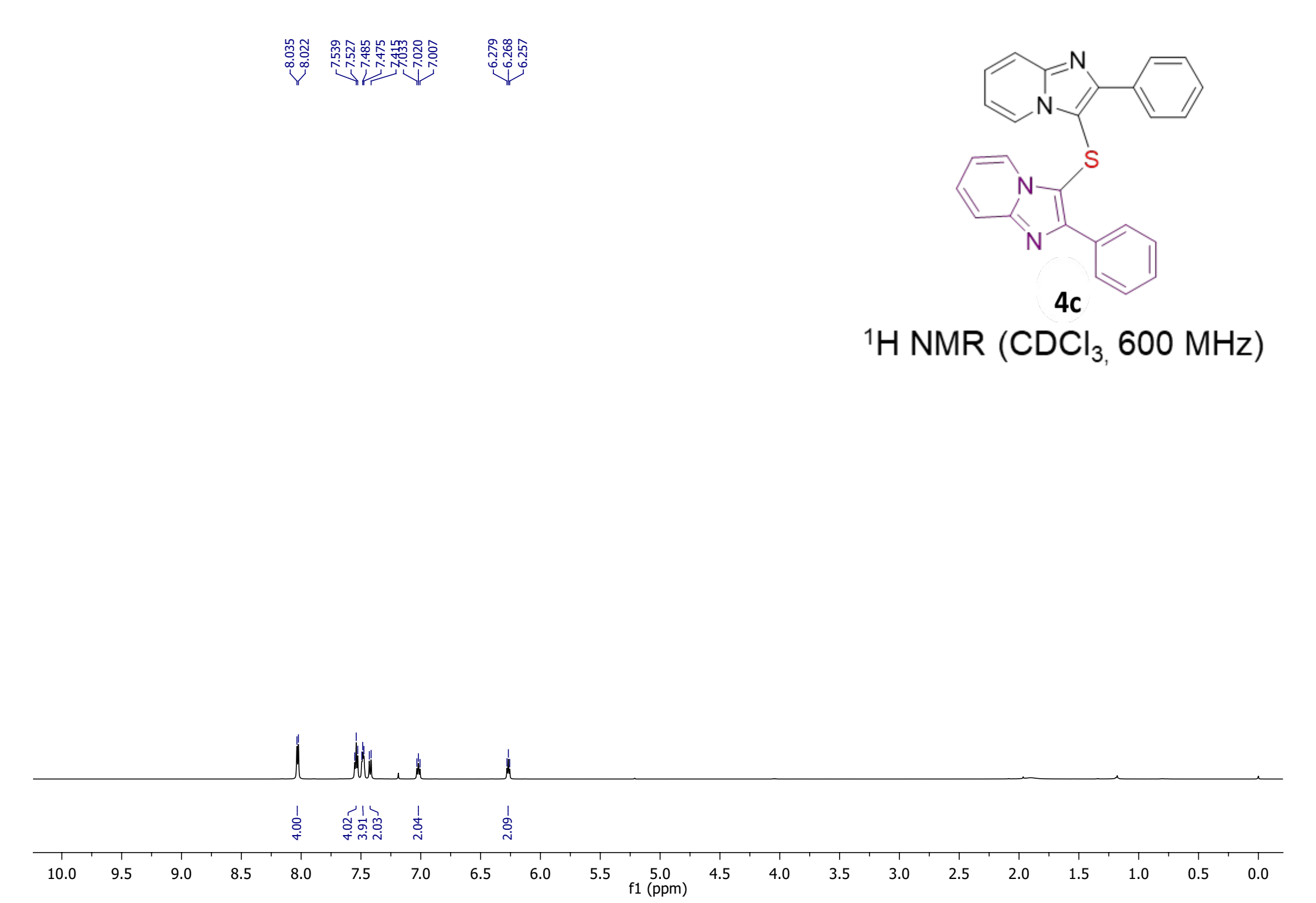

149.97
146.18
134.62
133.70
129.69
129.09
129.04
128.56
128.27
126.07
125.85
124.44
122.17
117.56
114.08
112.83
110.15
104.37
Br
S
N
N
H
3k
^{13}C NMR ($CDCl_3$, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

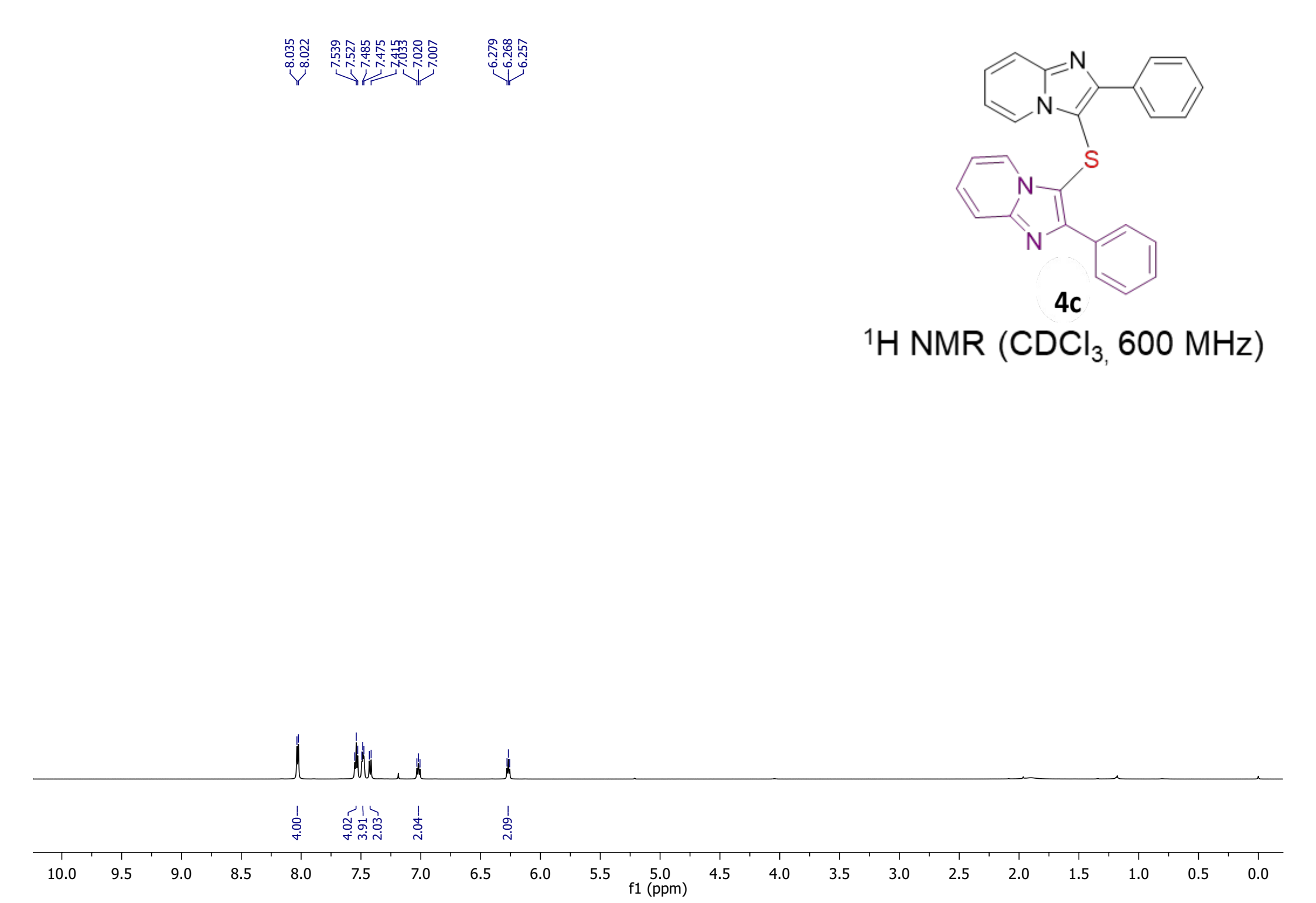

12.025
8.914
8.903
8.349
8.336
8.134
8.132
8.126
8.124
8.008
8.004
7.652
7.637
7.616
7.604
7.591
7.520
7.508
7.496
7.402
7.390
7.376
7.246
7.235
7.233
7.102
7.091
7.079
6.857
6.849
6.844
6.836
N
N
S
N
N
H
4a
1H NMR (DMSO-d6, 600 MHz)
1.00
1.03
2.04
0.99
0.97
1.07
2.13
1.05
1.04
1.04
1.07
1.06
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

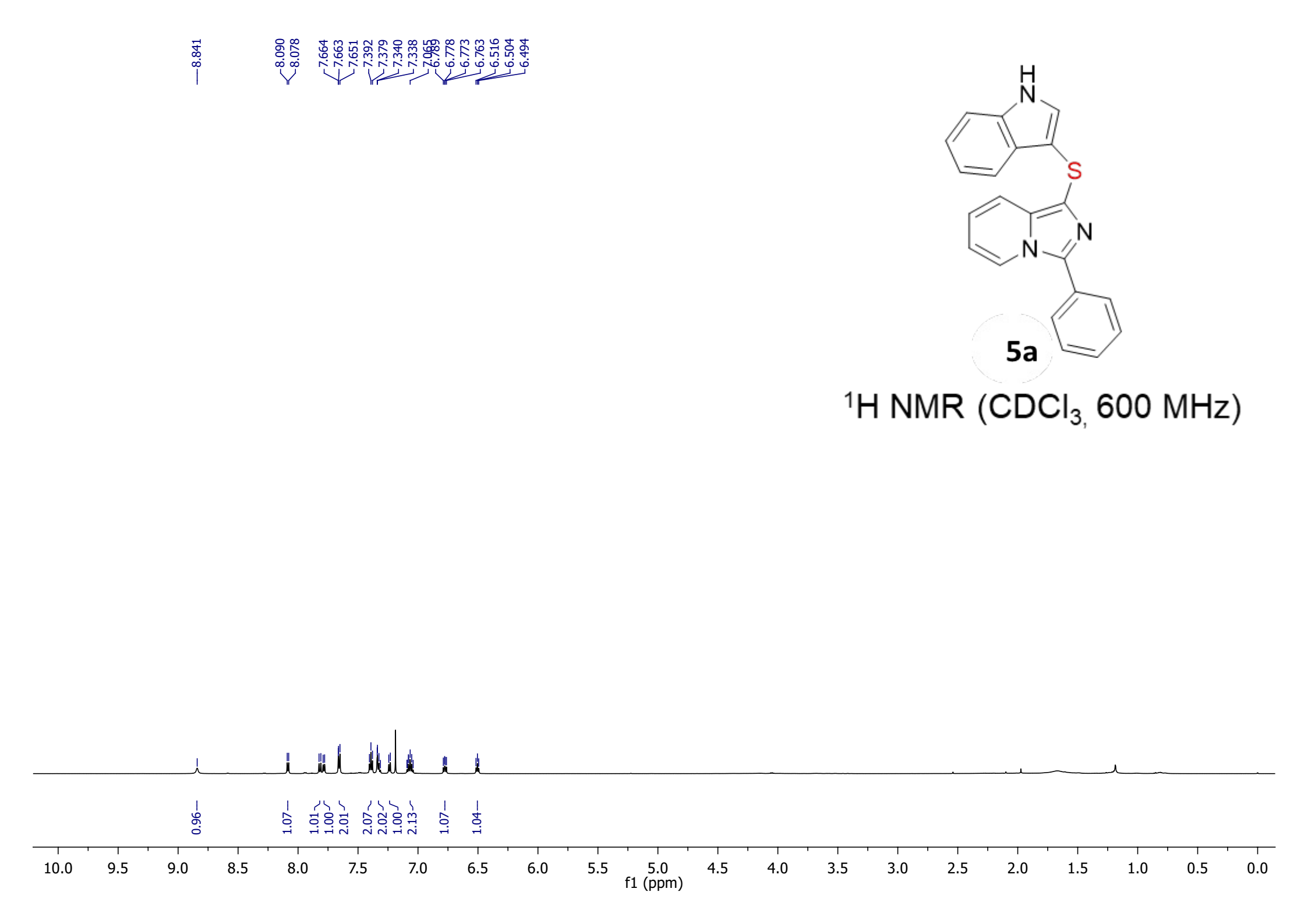

148.77
148.50
145.90
143.95
134.22
131.37
128.92
127.12
126.77
125.51
120.42
117.55
116.63
113.70
110.17
100.47
N
N
S
N
N
H
4a
13C NMR (DMSO-d6, 150 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.238
8.226
8.184
8.171
7.884
7.871
7.544
7.533
7.431
7.418
7.388
7.372
6.767
6.756
2.446
H3C
N
N
S
S
N
4b
1H NMR (CDCl3, 600 MHz)
0.92
1.83
0.90
1.84
3.85
0.96
0.95
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)

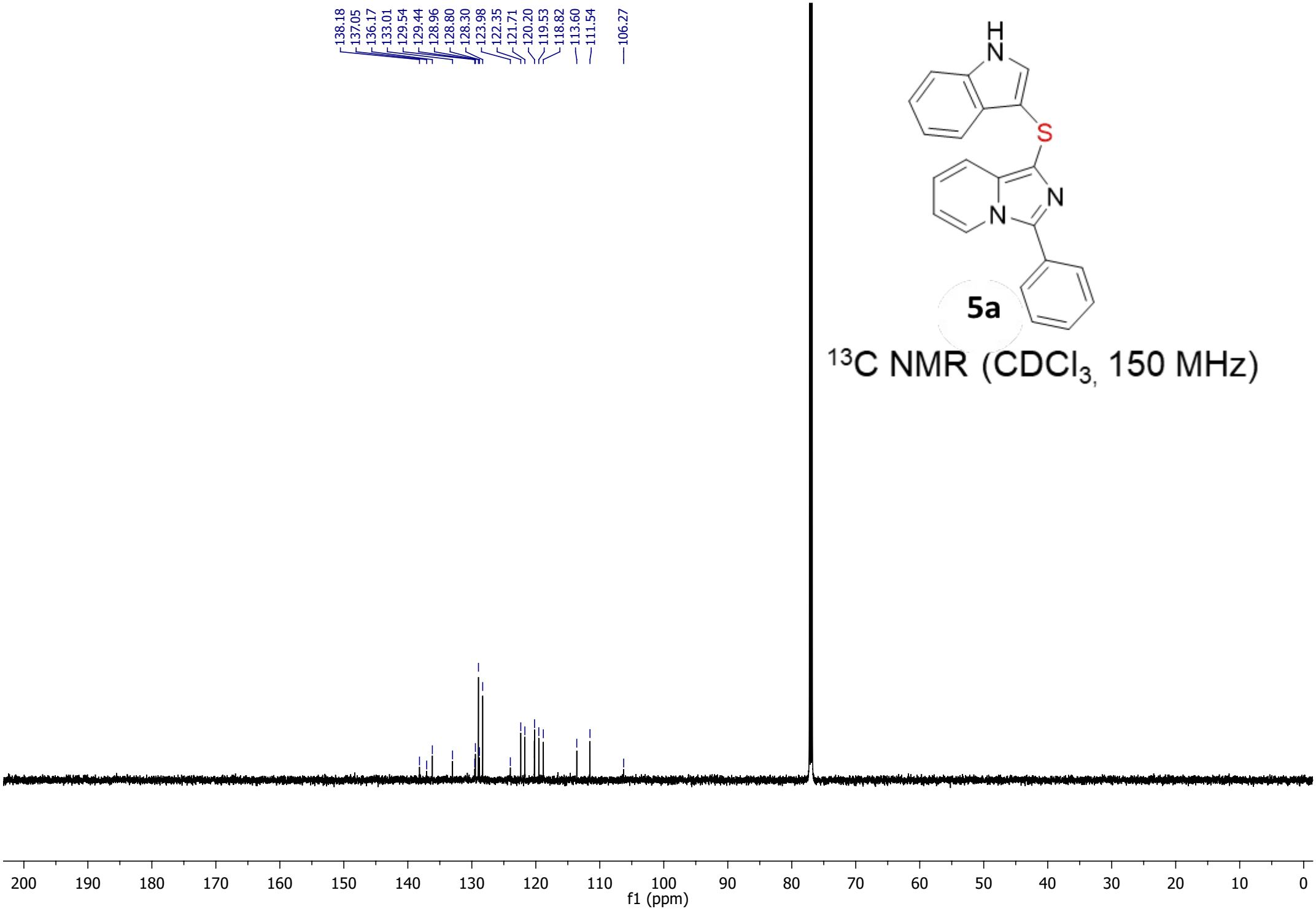

168.79
154.64
152.36
148.16
139.00
129.02
128.55
128.43
126.32
124.56
123.55
122.06
121.08
116.52
116.37
103.35
21.47
H3C
N
N
S
S
N
4b
13C NMR (CDCl3, 150 MHz)
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

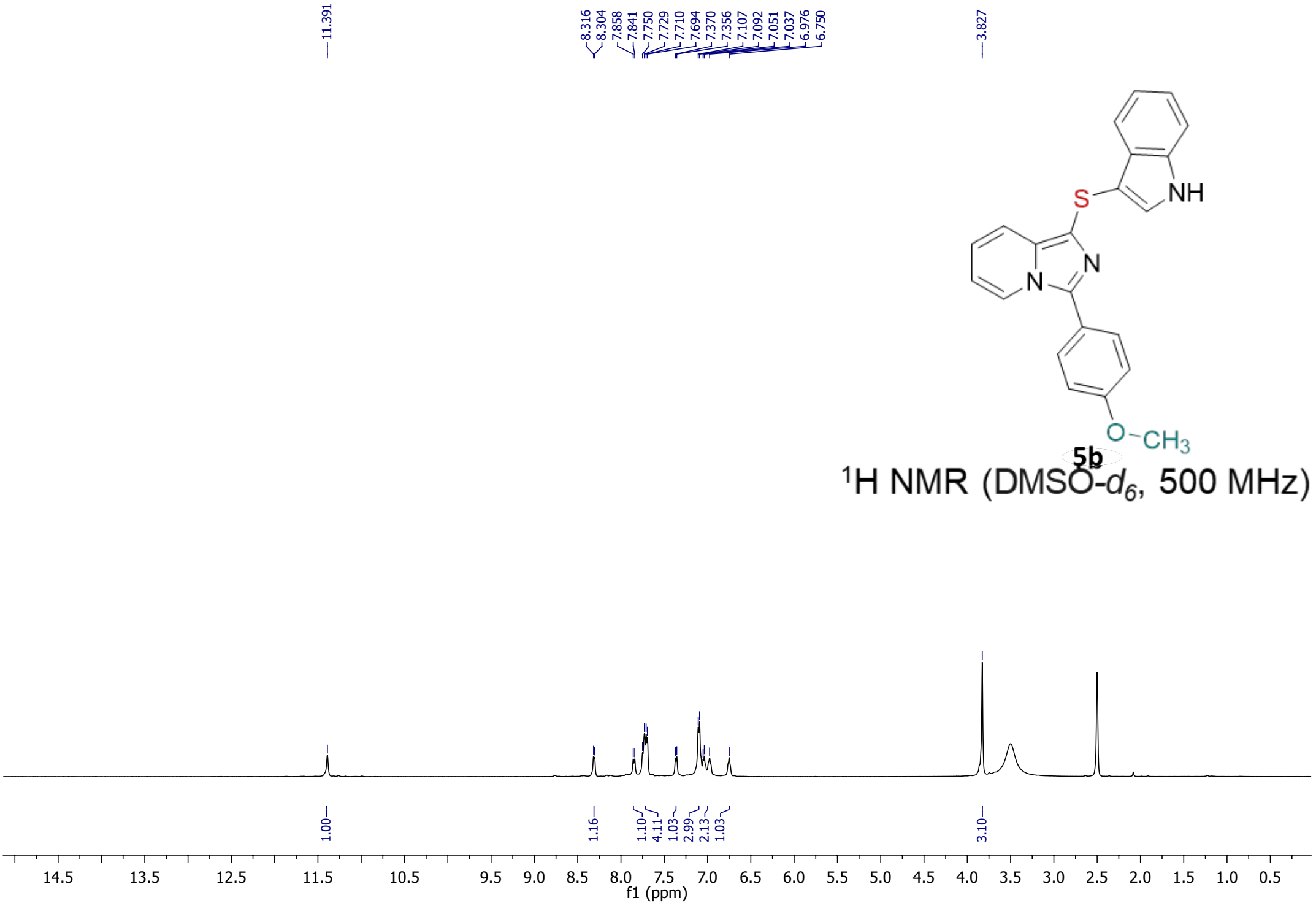

8.035
8.022
7.539
7.527
7.485
7.475
7.415
7.033
7.020
7.007
6.279
6.268
6.257
N
N
S
N
N
4c
1H NMR (CDCl3, 600 MHz)
4.00
4.02
3.91
2.03
2.04
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

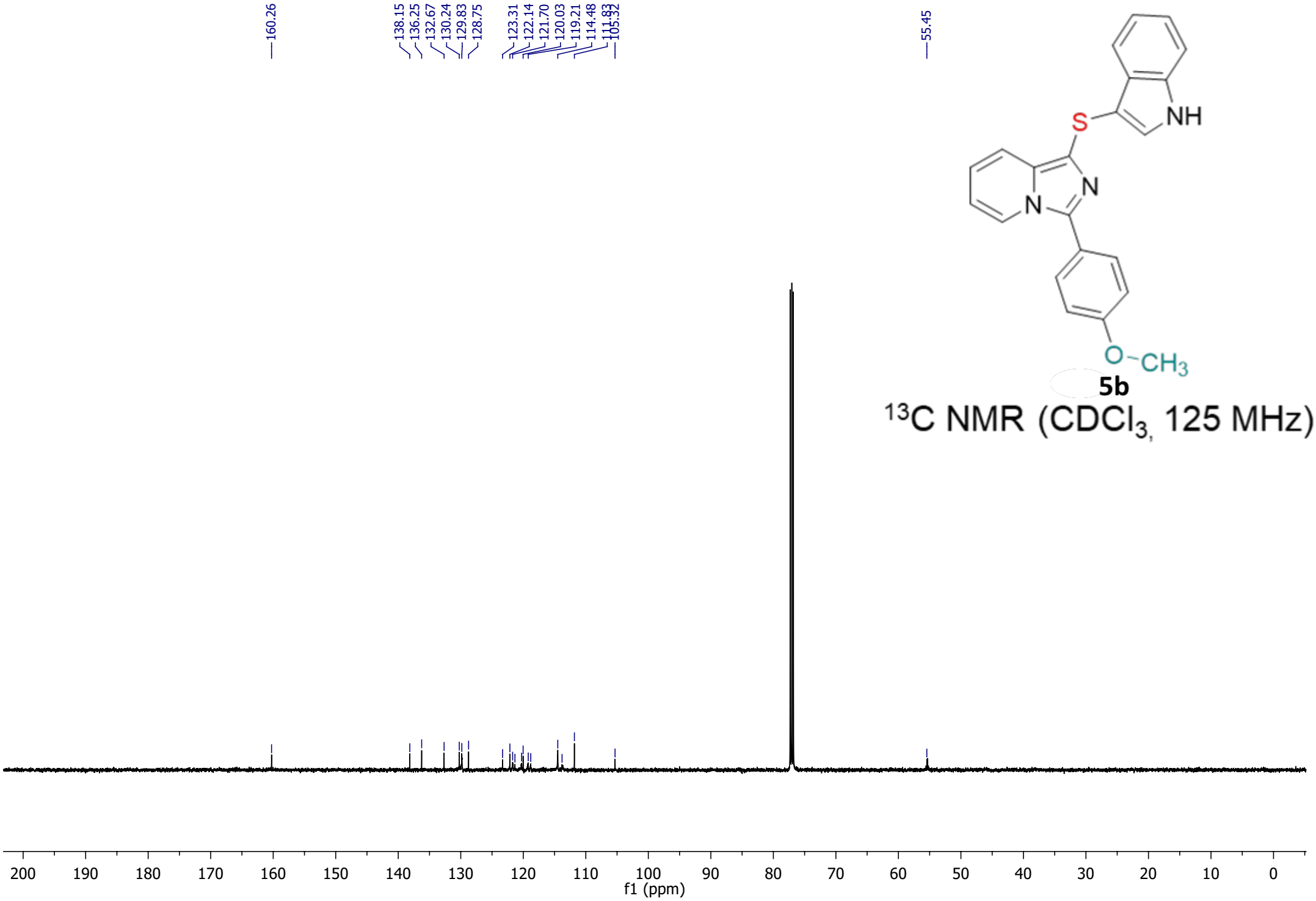

8.035
8.022
7.539
7.527
7.485
7.475
7.415
7.033
7.020
7.007
6.279
6.268
6.257
N
N
S
N
N
4c
1H NMR (CDCl3, 600 MHz)
4.00
4.02
3.91
2.03
2.04
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

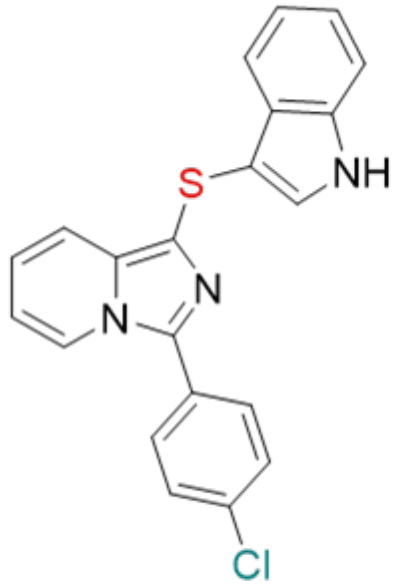


^{1}H NMR ($CDCl_3$, 600 MHz)


138.18
137.05
136.17
133.01
129.54
129.44
128.96
128.80
128.30
123.98
122.35
121.71
120.20
119.53
118.82
113.60
111.54
106.27
H
N
S
N
N
5a
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)

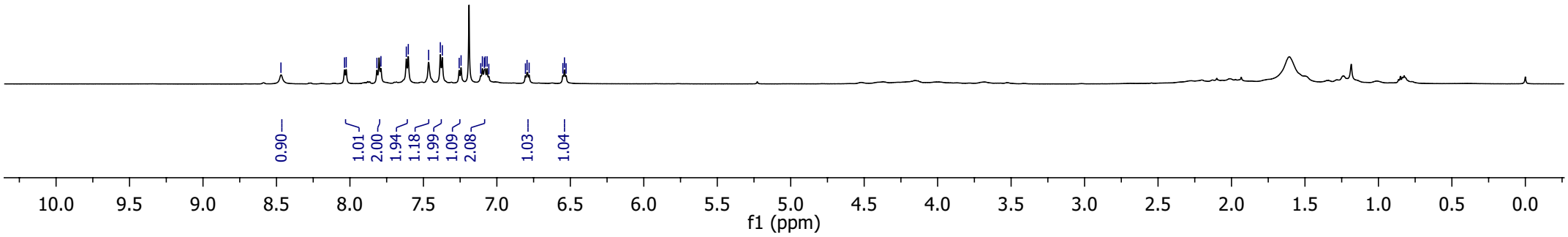

11.391
8.316
8.304
7.858
7.841
7.750
7.729
7.710
7.694
7.370
7.356
7.107
7.092
7.051
7.037
6.976
6.750
3.827
S
NH
N
N
O
CH3
5b
1H NMR (DMSO-d6, 500 MHz)
1.00
1.16
1.10
4.11
1.03
2.99
2.13
1.03
3.10
14.5
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

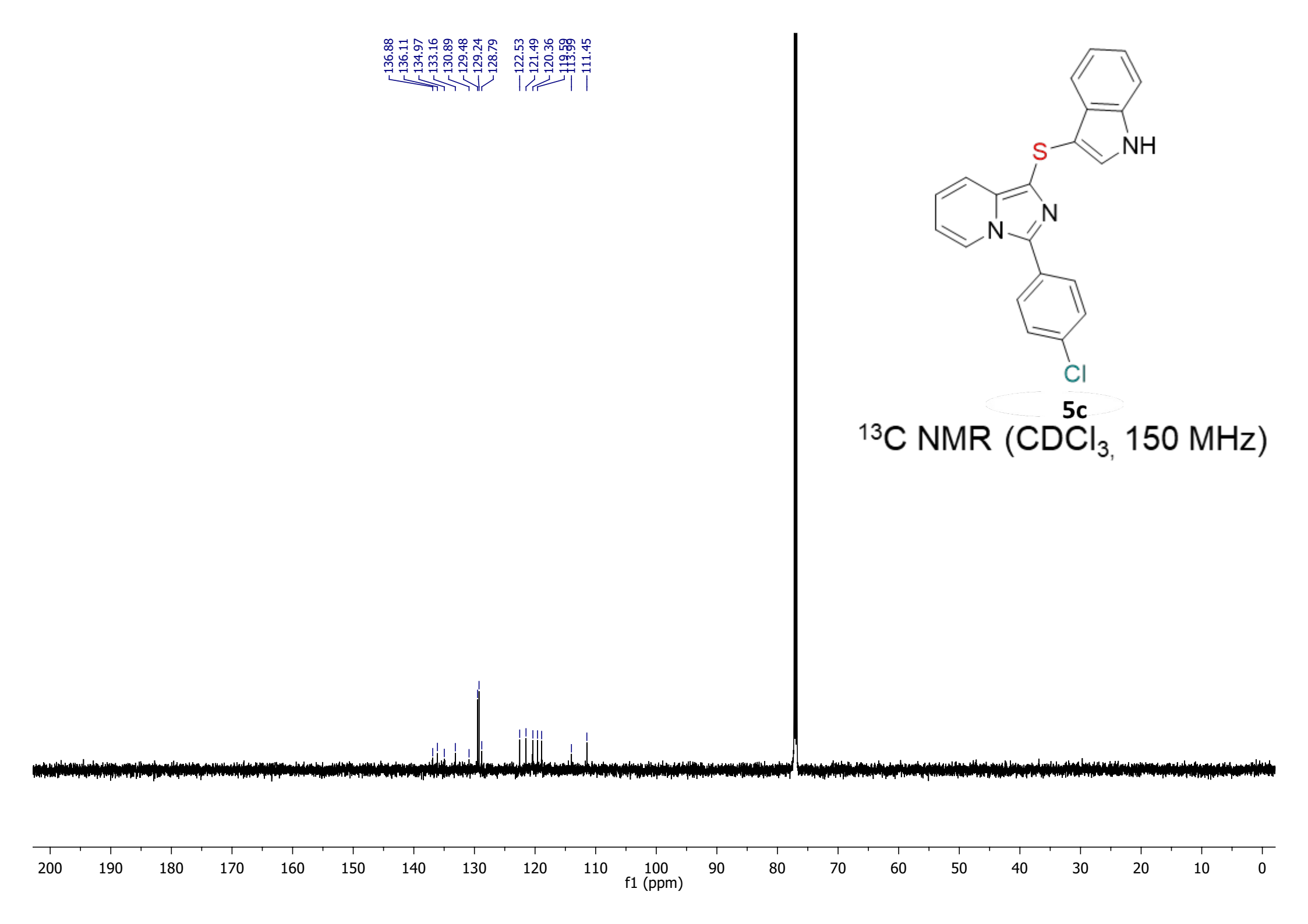

160.26
138.15
136.25
132.67
130.24
129.83
128.75
123.31
122.14
121.70
120.03
119.21
114.48
111.83
105.32
55.45
NH
S
N
N
O
CH3
5b
13C NMR (CDCl3, 125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5c

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




136.88
136.11
134.97
133.16
130.89
129.48
129.24
128.79
122.53
121.49
120.36
111.45
S
NH
N
N
Cl
5c
^{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)