

Supporting Information

Visible Light Induced Regioselective C-3 Thiocyanation of Imidazoheterocycles Through Naphthalimide Dye Based Photoredox Catalysis

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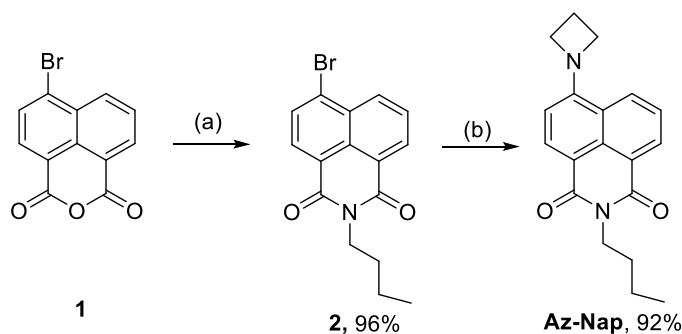
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General information

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 ^1H 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).



6-bromo-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**2**) & 6-(azetidin-1-yl)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**Az-Nap**):

An oven-dried round bottom flask was charged with **1** (1.20 g, 7.21 mmol) and n-butyl amine (1.05 g, 14.42 mmol) in 50 ml of ethanol. The reaction mixture was refluxed for 12 h. After completion of reaction, the reaction mixture was cooled to room temperature, filtered and washed with ethanol to obtain the product **2** (2.30g, 96%). Next, oven-dried round bottom flask was charged with **2** (2.30 g, 6.92 mmol), azetidine (0.59 g, 10.38 mmol), caesium carbonate (5.84 mmol, 4.50 g), tris(dibenzylideneacetone)dipalladium(0) (0.04 equiv., 0.25 g), xantphos (0.04 equiv., 0.16 g) in 22 ml of toluene. The reaction mixture was stirred at 70 °C for 12 h in inert atmosphere. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by using 30% ethyl acetate in *n*-hexane to afford the desired product **Az-Nap** as red solid (92%, 1.96 g).

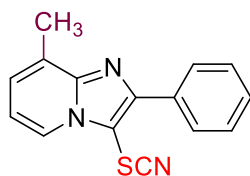
Compound 2: ¹H NMR (DMSO-*d*₆, 600 MHz) δ (ppm) 8.58-8.54 (m, 2H), 8.34 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 1H), 4.03 (t, *J* = 7.2 Hz, 2H), 1.64-1.59 (m, 2H), 1.37-1.31 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 150 MHz) δ (ppm) 163.4, 163.3, 133.1, 132.1, 131.8, 131.5, 130.3, 129.6, 129.3, 128.9, 123.3, 122.5, 41.7, 30.0, 20.2, 14.2.

Az-Nap: ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.57 (d, *J* = 7.5 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 8 Hz, 1H), 4.51 (t, *J* = 7.5 Hz, 4H), 4.18 (t, *J* = 7.5 Hz, 2H), 2.62-2.58 (m, 2H), 1.76-1.70 (m, 2H), 1.48-1.44 (m, 2H), 1.00-0.97 (m, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 164.8, 164.1, 152.6, 133.3, 131.1, 130.6, 130.0, 123.7, 122.8, 121.0, 110.4, 106.3, 55.4, 40.0, 30.3, 20.4, 17.1, 14.3, 13.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₉H₂₀N₂O₂: 309.1525; found: 309.1583.



2-Phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3a):

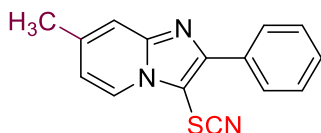
An oven-dried round bottom flask was charged with the 2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 194.08 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 20% ethyl acetate in *n*-hexane to afford the desired product **3a** as a white solid (95%, 238.73 mg, m.p. 110-112 °C). ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₁₄H₁₀N₃S: 252.0595; found: 252.0591.¹



8-Methyl-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3b):

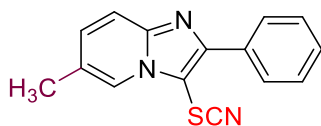
An oven-dried round bottom flask was charged with the 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 208.30 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 20% ethyl acetate in *n*-hexane to afford the desired product as white solid (76 %, 158.30 mg, m.p. 110-112 °C). ¹H NMR (CDCl₃, 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), 3.80 (s, 3H); ¹³C NMR (CDCl₃, 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, 15.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₅H₁₂N₃S: 266.0750; found: 266.0746.¹

201.44 mg, m.p. 98-100 °C) ^1H NMR (CDCl_3 , 500 MHz) δ (ppm) 8.29-8.27 (m, 1H), 8.10-8.08 (m, 2H), 7.56-7.53 (m, 2H), 7.49-7.46 (m, 1H), 7.23-7.22 (m, 1H), 7.02-6.98 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ (ppm) 152.5, 148.2, 132.3, 129.3, 128.9, 128.7, 128.5, 126.7, 122.1, 114.4, 108.3, 94.8, 16.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_3\text{S}$: 266.0752; found: 266.0744.¹



7-Methyl-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3c):

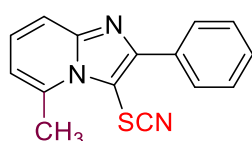
An oven-dried round bottom flask was charged with the 7-methyl-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 208.30 mg), NH_4SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH_3CN . The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 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 20% ethyl acetate in *n*-hexane to afford the desired product as white solid (73%, 193.49 mg, m.p. 104–106 °C). ^1H NMR (CDCl_3 , 500 MHz) δ (ppm) 8.28 (d, $J = 7$ Hz, 1H), 8.07-8.95 (m, 2H), 7.54-7.46 (m, 4H), 6.92 (d, $J = 7$ Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ (ppm) 153.0, 148.3, 139.5, 132.2, 129.3, 128.7, 128.6, 123.5, 116.9, 116.8, 108.3, 93.8, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_3\text{S}$: 266.0752; found: 266.0749.¹



6-Methyl-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3d):

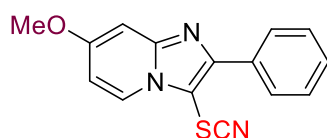
An oven-dried round bottom flask was charged with the 6-methyl-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 208.3 mg), NH_4SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH_3CN . The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 20% ethyl acetate in *n*-hexane to afford the desired product as white solid (77%, 204.30 mg, m.p. 176 – 178 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.24 (s, 1H), 8.07-8.06 (m, 2H), 7.67 (d, *J* = 9 Hz, 1H), 7.56-7.53 (m, 2H), 7.49-7.47 (m, 1H), 7.33 (d, *J* = 9 Hz, 1H), 2.48 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 152.8, 147.0, 132.2, 131.0, 129.3, 128.7, 128.7, 124.5, 122.2, 117.6, 108.3, 94.1, 18.5. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₅H₁₂N₃S: 266.0746; found: 266.0739.¹



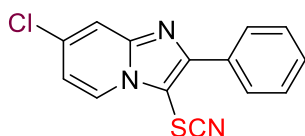
5-Methyl-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3e):

An oven-dried round bottom flask was charged with the 5-methyl-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 208.30 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 20% ethyl acetate in *n*-hexane to afford the desired product as white solid (78 %, 206.95 mg, m.p. 96-98 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 7.96-7.94 (m, 2H), 7.57 (d, *J* = 9 Hz, 1H), 7.55-7.52 (m, 2H), 7.49-7.46 (m, 1H), 7.33-7.31 (m, 1H), 6.74 (d, *J* = 7 Hz, 1H), 3.22 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz,) δ (ppm) 156.0, 149.7, 138.2, 132.3, 129.5, 129.3, 128.5, 128.4, 116.7, 116.2, 111.3, 95.7, 21.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₅H₁₂N₃S: 266.0751; found: 266.0743.



7-Methoxy-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3f):

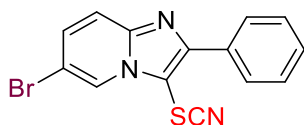
An oven-dried round bottom flask was charged with the 7-methoxy-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 224.30 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 30% ethyl acetate in *n*-hexane to afford the desired product as white solid (77 %, 216.62 mg, m.p. 106-108 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.55 (d, *J* = 7.5 Hz, 1H), 8.07-8.05 (m, 2H), 7.55-7.52 (m, 2H), 7.49-7.46 (m, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.82 (dd, *J* = 7.5 Hz, 2.5 Hz, 1H), 3.93 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 180.3, 153.3, 149.9, 132.1, 129.3, 128.7, 128.6, 124.7, 109.1, 108.4, 95.8, 92.9, 55.9. Calcd. for C₁₅H₁₂ON₃S: 282.0701; found: 282.0696.



7-Chloro-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3g):

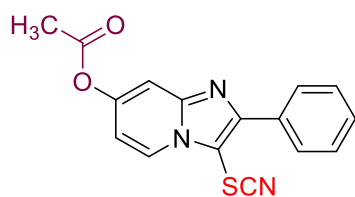
An oven-dried round bottom flask was charged with the 7-chloro-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 228.70 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 18% ethyl acetate in *n*-hexane to afford the desired product as yellow solid (67 %, 191.44 mg, m.p. 183–184 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.39 (d, *J* = 7 Hz, 1H), 8.07-8.10 (m, 2H), 7.79-7.77 (m, 1H), 7.58-7.55 (m, 2H), 7.53-7.50 (m, 1H), 7.14 (dd, *J* = 7.5 Hz, 1.2 Hz 1H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 154.0, 147.8, 134.9, 131.6, 129.8, 128.8, 127.2, 125.0, 124.7,

117.2, 116.0, 107.4, 95.3. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd. for $C_{14}H_9ClN_3S$: 286.0200; found, 286.0199.²



6-Bromo-2-phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (3h):

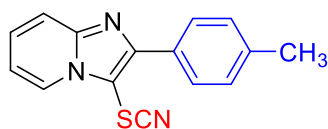
An oven-dried round bottom flask was charged with the 6-bromo-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 273.10 mg), NH_4SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH_3CN . The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 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 18% ethyl acetate in *n*-hexane to afford the desired product as pale-yellow solid (66 %, 217.93 mg, m.p. 128–130 °C). 1H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.56 (s, 1H), 8.03 (d, $J = 7.2$ Hz, 2H), 7.64 (d, $J = 7.5$ Hz, 1H), 7.54-7.51 (m, 3H), 7.49-7.47 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 152.4, 145.3, 130.6, 130.4, 128.7, 127.8, 127.7, 117.8, 108.3, 106.6, 94.4. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd. for $C_{14}H_9BrN_3S$: 329.9701; found: 329.9692.¹



2-Phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridin-7-yl acetate (3i):

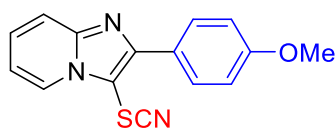
An oven-dried round bottom flask was charged with the 6-bromo-2-phenylimidazo[1,2-*a*]pyridine (1 mmol, 309.34 mg), NH_4SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH_3CN . The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 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 30%

ethyl acetate in *n*-hexane to afford the desired product as white solid (70%, 216.53mg, m.p. 134-138 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.42 (d, *J* = 7.2 Hz, 1H) 8.39 (s, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.49-7.47 (m, 2H), 7.44-7.42 (m, 1H), 4.01 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ (ppm) 164.8, 154.5, 147.0, 131.5, 129.8, 129.5, 128.9, 128.8, 124.2, 120.4, 113.7, 107.5, 97.0, 53.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₆H₁₂N₃O₂S: 310.0650; found: 310.0641.



3-Thiocyanato-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (3j):

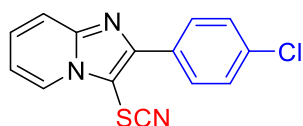
An oven-dried round bottom flask was charged with the 2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (1 mmol, 208.3 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 20% ethyl acetate in *n*-hexane to afford the desired product as white solid (87%, 230.83mg, m.p. 99–101 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.41-8.39 (m, 1H), 7.97 (d, *J* = 8 Hz, 2H), 7.74-7.72 (m, 1H), 7.44-7.40 (m, 1H), 7.33 (d, *J* = 8 Hz, 2H), 7.09-7.06 (m, 1H), 2.44 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 153.1, 147.9, 139.6, 129.5, 129.3, 128.6, 127.9, 124.3, 118.1, 114.2, 108.2, 94.3, 21.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₅H₁₂N₃S: 266.0752; found: 266.0745.¹



2-(4-Methoxyphenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (3k):

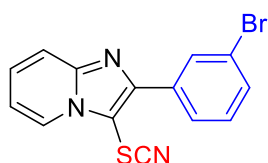
An oven-dried round bottom flask was charged with the 2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (1 mmol, 224.26 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was

stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 25% ethyl acetate in *n*-hexane to afford the desired product as pale-yellow solid (83 %, 233.50mg, m.p. 102-104 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.43 (d, *J* = 6.5 Hz, 1H), 8.29 (d, *J* = 9 Hz, 2H), 7.73 (d, *J* = 9 Hz, 1H), 7.47-7.44 (m, 1H), 7.12-7.09 (m, 1H), 7.07-7.06 (m, 2H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 160.7, 152.9, 147.9, 130.9, 127.9, 124.5, 124.3, 118.0, 114.2, 114.1, 108.3, 93.7, 55.4. Calcd. for C₁₅H₁₂ON₃S: 282.0701; found: 282.0696.¹



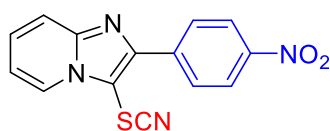
2-(4-Chlorophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (3I):

An oven-dried round bottom flask was charged with the 2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (1 mmol, 228.7 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 3). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 18% ethyl acetate in *n*-hexane to afford the desired product as white solid (80 %, 228.59 mg, m. p. 109-111 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.43 (d, *J* = 6.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 9 Hz, 1H), 7.50-7.46 (m, 3H), 7.13 (t, *J* = 7 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 151.7, 147.9, 135.6, 130.5, 129.9, 129.0, 128.2, 124.4, 118.3, 114.6, 107.8, 94.8. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₄H₉ClN₃S: 286.0206; found: 286.0201.¹



2-(3-Bromophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (3m):

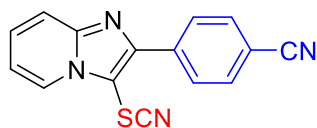
An oven-dried round bottom flask was charged with the 2-(3-bromophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (1 mmol, 273.1 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 18% ethyl acetate in *n*-hexane to afford the desired product as white solid (78 %, 257.55 mg, m.p. 159.7–160.5 °C). ¹H NMR (CDCl₃, 600 MHz) δ (ppm) 8.45 (d, *J* = 7.2 Hz, 1H), 8.22 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 9 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 6.6 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ (ppm) 150.3, 146.9, 132.9, 131.4, 130.9, 129.2, 127.3, 126.2, 123.4, 121.9, 117.3, 113.4, 106.7, 94.1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₄H₉BrN₃S: 329.9695; found 329.9700.³



2-(4-Nitrophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (3n):

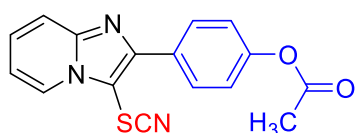
An oven-dried round bottom flask was charged with the 2-(4-nitrophenyl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (1 mmol, 239.23 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 40% ethyl acetate in *n*-hexane to afford the desired product as yellow solid (77 %, 228.15 mg, m.p. 210- 212 °C). ¹H NMR (CDCl₃, 600 MHz) δ (ppm) 8.45 (d, *J* = 7.2 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 2H), 8.25 (d, *J* = 9 Hz, 1H), 7.77 (d, *J* = 9 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 6.6 Hz, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ (ppm) 150.3, 148.2,

148.1, 138.2, 129.5, 128.7, 124.5, 124.0, 118.7, 115.2, 107.3, 96.3. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd. for $C_{14}H_9N_4O_2S$: 297.0446; found 297.0418.



4-(3-Thiocyanatoimidazo[1,2-*a*]pyridin-2-yl)benzonitrile (3o):

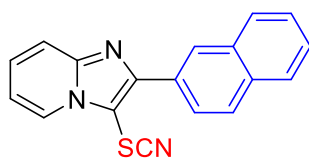
An oven-dried round bottom flask was charged with the 4-(imidazo[1,2-*a*]pyridin-2-yl)benzonitrile (1 mmol, 219.24 mg), NH_4SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH_3CN . The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 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 50% ethyl acetate in *n*-hexane to afford the desired product as pale-yellow solid (79%, 218.28 mg, m.p. 142–144 °C). 1H NMR ($CDCl_3$, 600 MHz) δ (ppm) 8.45 (d, $J = 7.2$ Hz, 1H), 8.19 (d, $J = 7.8$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 9$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 1H), 7.17 (t, $J = 5.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ (ppm) 150.6, 148.1, 136.4, 132.5, 129.2, 128.7, 124.5, 119.0, 118.6, 115.3, 112.9, 96.0. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd. for $C_{15}H_9N_4S$: 277.0548; found: 277.0547.¹



4-(3-Thiocyanatoimidazo[1,2-*a*]pyridin-2-yl)phenyl acetate (3p):

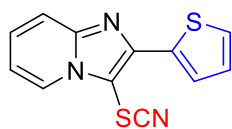
An oven-dried round bottom flask was charged with the 4-(imidazo[1,2-*a*]pyridin-2-yl)phenyl acetate (1 mmol, 252.30 mg), NH_4SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH_3CN . The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 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 30%

ethyl acetate in *n*-hexane to afford the desired product as white solid (78 %, 241.28 mg, m.p. 174–176 °C). ¹H NMR (CDCl₃, 600 MHz) δ (ppm) 8.46 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 9 Hz, 2H), 7.77 (d, *J* = 9 Hz, 1H), 7.50–7.47 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.349 (t, *J* = 6.6 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ (ppm) 169.3, 152.1, 151.6, 148.0, 130.0, 129.6, 128.2, 124.4, 122.0, 118.3, 114.5, 108.0, 94.7, 21.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₆H₁₁N₃O₃S: 309.0572; found 309.0565.



2-(Naphthalen-2-yl)-3-thiocyanatoimidazo[1,2-*a*]pyridine (3q):

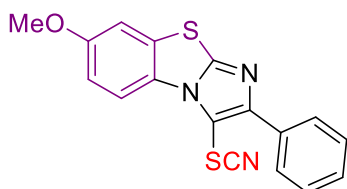
An oven-dried round bottom flask was charged with the 2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine (1 mmol, 244.1 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10–12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 25% ethyl acetate in *n*-hexane to afford the desired product as yellow solid (83 %, 150.12 mg, m.p. 118–120 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.54 (s, 1H), 8.30 (d, *J* = 6.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.94–7.92 (m, 2H), 7.85–7.83 (m, 1H), 7.38–8.29 (d, *J* = 8.5 Hz, 1H), 7.52–7.50 (m, 2H), 7.370–7.340 (m, 1H), 6.99–6.66 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 152.5, 147.8, 133.5, 133.1, 129.3, 128.7, 128.5, 128.4, 128.1, 127.7, 127.0, 126.5, 125.7, 124.3, 118.0, 114.4, 108.2, 95.0. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₈H₁₂N₃S: 302.0752; found: 302.0747.¹



3-Thiocyanato-2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine (3r):

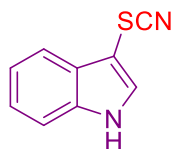
An oven-dried round bottom flask was charged with the 2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine (1 mmol, 200.26 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5

mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 25% ethyl acetate in *n*-hexane to afford the desired product as yellow solid (72%, 185.04 mg, m.p. 108–110 °C). ¹H NMR (CDCl₃, 500 MHz) δ (ppm) 8.29 (d, *J* = 6.5 Hz, 1H), 7.90 (dd, *J* = 3.5 Hz, 1 Hz, 1H), 7.63 (d, *J* = 9 Hz, 1H), 7.45 (dd, *J* = 5 Hz, 1 Hz, 1H), 7.37-7.34 (m, 1H), 7.16-7.15 (m, 1H), 7.00 (td, *J* = 7 Hz, 1 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 147.8, 147.6, 134.7, 128.2, 128.1, 128.0, 127.6, 124.2, 117.8, 114.4, 107.6, 93.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd. for C₁₂H₈N₃S₂: 258.0160; found: 258.0153.¹



7-Methoxy-2-phenyl-3-thiocyanatobenzo[*d*]imidazo[2,1-*b*]thiazole (5a):

An oven-dried round bottom flask was charged with the 7-methoxy-2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazole (**4a**, 1 mmol, 280.34 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 20% ethyl acetate in *n*-hexane to afford the desired product as white solid (89 %, 300.29 mg, m.p. 200-202 °C). ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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 C₁₇H₁₂N₃OS₂: 337.0344; found: 337.0341.



3-Thiocyanato-1H-indole (5b):

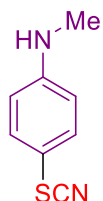
An oven-dried round bottom flask was charged with the indole (**4b**, 1 mmol, 117.15 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 12% ethyl acetate in *n*-hexane to afford the desired product as brown solid (92 %, 160.28 mg, m.p. 72–74 °C). ¹H NMR (CDCl₃, 600 MHz) δ (ppm) 8.83 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.99-6.94 (m, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ (ppm) 134.9, 130.4, 126.3, 122.4, 120.3, 117.1, 111.8, 111.3, 89.4. HRMS (ESI) *m/z*: Calcd. for [M + H]⁺ C₉H₇N₂S 175.0330; found 175.0322.²⁵



3-Thiocyanato-1H-pyrrolo[2,3-*b*]pyridine (5c):

An oven-dried round bottom flask was charged with the 7-aza-indole (**4c**, 1 mmol, 118.14 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 16% ethyl acetate in *n*-hexane to afford the desired product as white solid (93 %, 162.02 mg, m.p. 197–199 °C). ¹H NMR (DMSO-*d*₆, 600 MHz) δ (ppm) 12.6 (s, 1H), 8.39 (d, *J* = 4.2 Hz, 1H), 8.15 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.23-7.28 (m, 1H); ¹³C NMR (DMSO-*d*₆, 125 MHz) δ (ppm) 148.8, 145.0, 134.4, 126.9, 120.3,

117.8, 113.0, 89.5. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd. for $C_8H_6N_3S$: 176.0282; found: 176.0275.



***N*-methyl-4-thiocyanatoaniline (5d):**

An oven-dried round bottom flask was charged with the *N*-methyl aniline (**4d**, 1 mmol, 107.15 mg), NH_4SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH_3CN . The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After completion of reaction, the reaction mixture was extracted with ethyl acetate (15 mL \times 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 16% ethyl acetate in *n*-hexane to afford the desired product as yellow liquid (90 %, 147.79 mg). 1H NMR ($CDCl_3$, 600 MHz) δ (ppm) 7.38 (d, $J = 8.4$ Hz, 2H), 6.58 (d, $J = 8.4$ Hz, 2H), 4.09 (s, 1H), 2.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ (ppm) 190.1, 133.7, 112.4, 111.6, 106.5, 29.2. HRMS (ESI) m/z : Calcd. for $[M + H]^+ C_8H_8N_2S$ 164.0408; found 164.0400.

Optical and Redox Potential Characterization

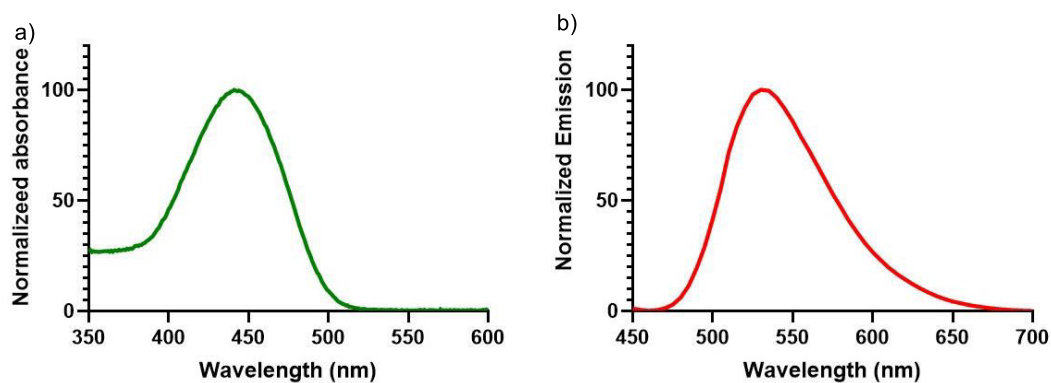


Figure 1: (a) UV-Vis absorbance peak at 441 nm, (b) Fluorescence emission peak at 505 nm.

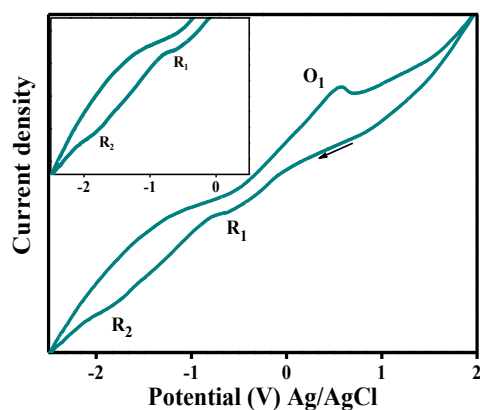


Figure 2: The CV profiles of the Az-Nap showed two redox peaks corresponding to the reduction and one peak for the oxidation process.

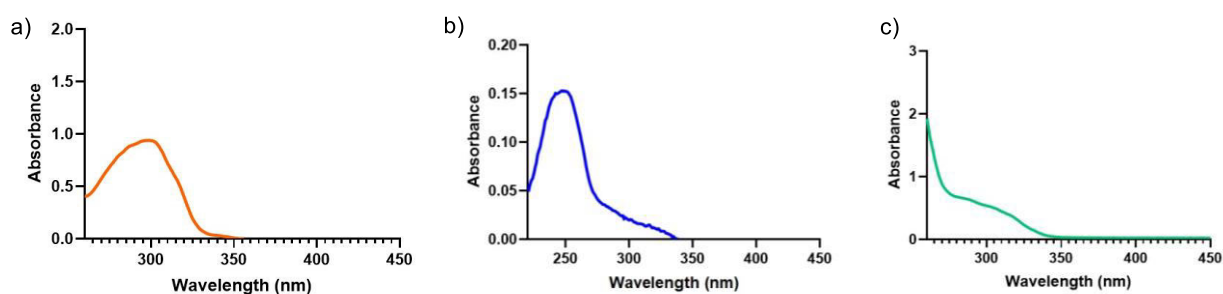


Figure 3. EDA complex studies. Absorption spectra of a) **3**, b) **3a**, c) reaction mixture of **3** + NH₄SCN.

Gram Scale Synthesis

An oven-dried round bottom flask was charged with the 2-phenyl imidazo[1,2-*a*]pyridine (7.0 mmol, 1359.61 mg), NH₄SCN (14.0 mmol, 2 equiv., 1065.68 mg), Az-Nap photocatalyst (5 mol %, 107.94 mg) in 14 ml of CH₃CN. The reaction mixture was stirred at room temperature for 5 h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to afford the desired product **3a** in 90% yield.

Control Experiments

TEMPO addition in the general procedure:

An oven-dried round bottom flask was charged with the respective 2-aryl imidazo[1,2-*a*]pyridine (1 mmol, 194.08 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg), TEMPO (2.5 equiv., 390.62 mg) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm.

BHT addition in the general procedure:

An oven-dried round bottom flask was charged with the respective 2-aryl imidazo[1,2-*a*]pyridine (1 mmol, 194.08 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg), BHT (2.5 equiv., 550.87 mg) in 3ml of CH₃CN. The reaction mixture was stirred at room temperature for 3 h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm.

Reaction in darkness:

An oven-dried round bottom flask was charged with 2-aryl imidazo[1,2-*a*]pyridine (1 mmol, 194.08 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg), in 3 ml of CH₃CN. 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.

Reaction in presence of DABCO:

An oven-dried round bottom flask was charged with 2-aryl imidazo[1,2-*a*]pyridine (1 mmol, 194.08 mg), NH₄SCN (2 equiv.), Az-Nap photocatalyst (5 mol %, 15.42 mg), DABCO (243.30 mg, 1 equiv.) in 3 ml of CH₃CN. The reaction mixture was stirred at room temperature for 3 h under irradiation of blue LED light (450 nm, 24 W) in open air. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. 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 Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica gel using a solvent system of 20% ethyl acetate in *n*-hexane to afford the desired product **3a** as a white solid with 93 % yield.

The starch iodide tests for detection of H₂O₂:

100 mg of Corn starch was added in 30 ml of distilled water in a 100 ml beaker followed by uniform mixing. Next, the mixture was boiled for 10 minutes and then cooled down to room temperature. Once the temperature of the solution was reduced to ambient temperature, 100 mg of potassium iodide was added to it and uniformly mixed. The reaction of 2-phenyl imidazo[1,2- *a*]pyridine (1 mmol, 194.08 mg), NH₄SCN (2 equiv., 152.24 mg), Az-Nap photocatalyst (5 mol %, 15.42 mg) in 3 ml of CH₃CN was carried under irradiation of blue LED light (450 nm, 24 W) in open air for 3 h. The approximate distance between the reaction flask and lamp was measured to be 10-12 cm. After 3 h, the reaction mixture was taken out and transferred into a small glass vial. Then the prepared starch iodide solution was added to it. The vial was shaken vigorously. Following 1 minute of standing, a change in color of the resulting reaction mixture was noted down, indicating the release of H₂O₂ during the course of reaction.

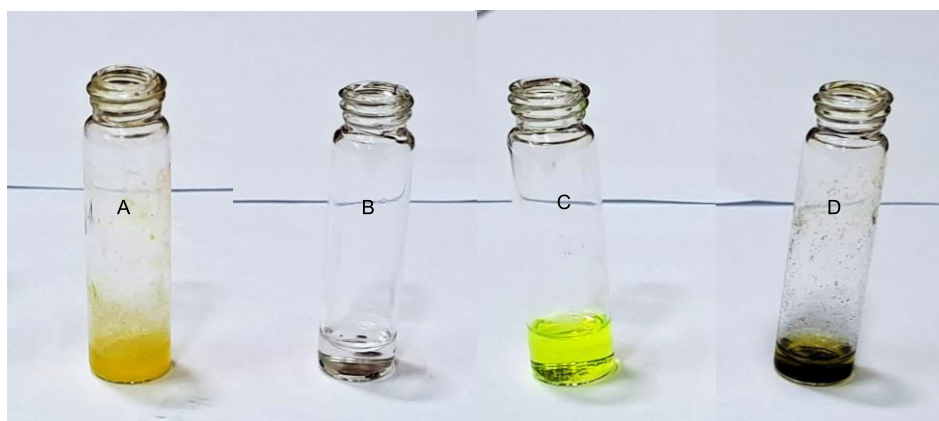


Figure 4: Detection of H₂O₂. A) reaction mixture at 3h, B) starch iodide solution, C) reaction mixture at 0 h + starch iodide solution, D) reaction mixture at 3 h + starch iodide solution.

Quantum Yield Experiment.

The quantum yield of the reaction was calculated in two steps:

(i) Determination of light available to the reaction system via actinometry:

The photon flux of blue LEDs was determined using the traditional potassium ferrioxalate actinometer method⁴⁻⁹. The potassium trisoxalato ferrate (III) trihydrate complex, an iron(III) actinometer, was synthesized according to literature reports.⁵ An experiment was conducted to assess light intensity by dissolving 0.737 g of potassium trisoxalato ferrate trihydrate complex in 10 mL of a 0.05 M H₂SO₄ solution to make a 0.15 M ferrioxalate actinometer solution. In another solution formed by dissolving 5.63 g of sodium acetate in 25 mL of a 0.05 M H₂SO₄ solution, a 0.2% by weight of 1,10-phenanthroline ligand was included. Both solutions were kept in a dark place.

The actinometer measurement was done as follows:

Following a 90-second exposure to blue LED light, 2.0 mL of the prepared actinometer solution was subjected to irradiation. Subsequently, 0.35 mL of the prepared phenanthroline solution was introduced, and the mixture was stirred in the dark for 1.0 hour to enable the formation of a red-colored [Fe(phen)₃]²⁺ complex through the binding of phenanthroline ligands with the photogenerated ferrous ions. The absorbance of the resulting [Fe(phen)₃]²⁺ complex was measured at 510 nm, with a reagent blank as a reference. Additionally, a non-irradiated sample was prepared, containing the actinometer solution, buffer, and phenanthroline ligand in the same proportions but without any exposure to irradiation. This non-irradiated sample's absorbance at λ 510 nm was measured under similar conditions.

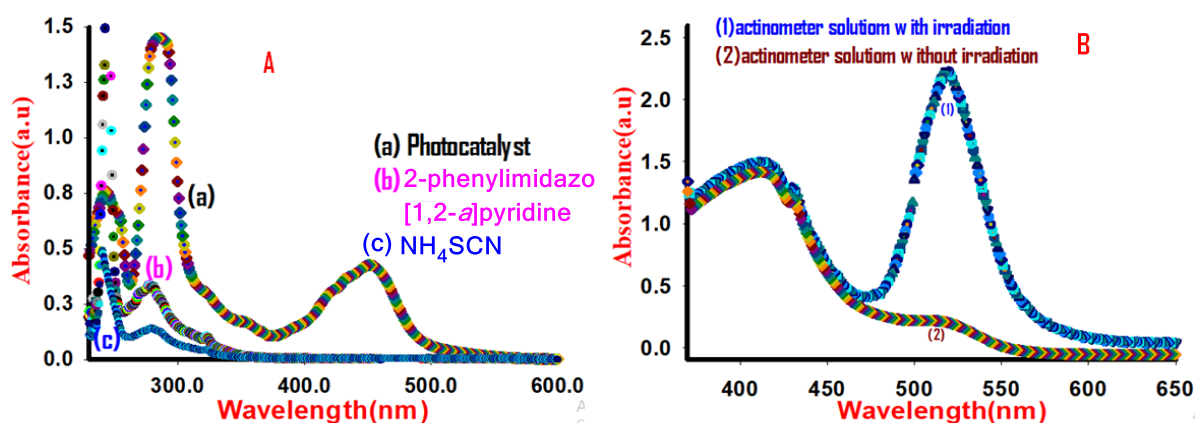


Figure 3: Initial absorption spectra of reaction mixture showing no absorption by 2-phenylimidazo[1,2-*a*]pyridine and NH₄SCN in the blue LED region, indicating that essentially all the incident light is absorbed by the photocatalyst and, therefore (*f*~0.999).; **B.** Absorption spectra of actinometer solution without and after irradiation for 90seconds.

The moles of Fe²⁺ formed can be determined according to Beer's Laws using the equation:

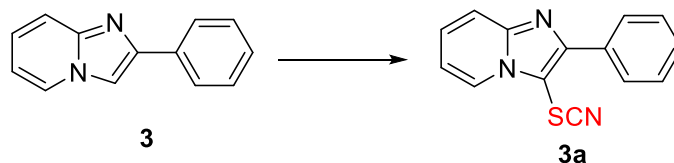
$$\text{moles of Fe}^{2+} = \frac{V(L) \times \Delta A}{1\text{cm} \times \epsilon (\text{L mol}^{-1}\text{cm}^{-1})} = 4.29 \times 10^{-7}$$

Where *V* is the total volume of the solution (0.00235 L) after adding all reagents, ΔA is the difference in absorbance at λ 510 nm between the irradiated and non-irradiated actinometer solutions (2.24 - 0.21). *l* is the path length (1.00 cm), and ϵ is the molar absorptivity of the ferrioxalate actinometer² at λ 510 nm (11,100 L mol⁻¹cm⁻¹). The photon flux of the blue LEDs was calculated as under:

$$\text{Photon flux} = \frac{\text{moles of Fe}^{2+}}{\phi \times t \times f} = 4.2 \times 10^{-9}$$

Where Φ is the quantum yield for the ferrioxalateactinometer (1.12), *t* is the irradiation time (90 s), and *f* is the fraction of light absorbed by the ferrioxalate actinometer. The absorption spectrum gave no absorbance value for the 2-phenylimidazo[1,2-*a*]pyridine and NH₄SCN as reaction ingredients in the blue LED region, indicating that the fraction of absorbed light (*f*) can be taken >0.999 for the photocatalyst. The photon flux was thus calculated (average of three experiments) to be 4.2 x 10⁻⁹ Einsteins s⁻¹.

(ii). *Determination of the reaction quantum yield:*



Compound **3** (20 mg, 0.08 mmol, 1.0 equiv), NH₄SCN (12 mg, 0.16 mmol, 2.0 equiv), and Az-Nap catalyst (1.2 mg) were placed in a quartz cuvette. The sample was stirred and irradiated for the 90 s. After irradiation, the yield of product **3a** formed was determined using the peak area analysis method of the Gas Chromatography technique.⁹ The yield of product **3a** formed after the 90 s of irradiation, as determined from quantitative analysis by gas chromatography,

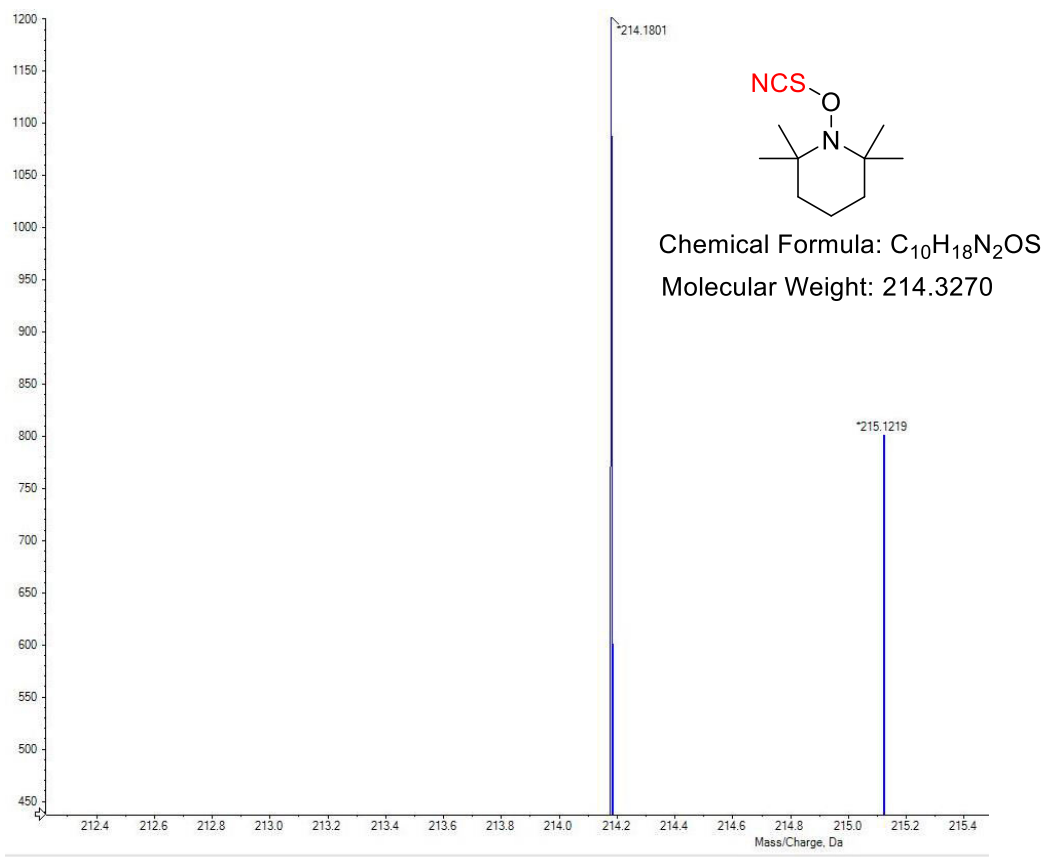
was found to be 0.13% corresponding to (1×10^{-6} mol). The reaction quantum yield (Φ) was then arrived at using the equation:

$$\phi = \frac{\text{moles of product formed}}{\text{Photon flux} \times t \times f} = 0.36$$

Where the photon flux is 4.2×10^{-9} einsteins s^{-1} (as determined by actinometry in step 1), t is the reaction time (90s), and f is the fraction of incident light absorbed by the reaction mixture. An initial absorption spectrum of the aforementioned reaction mixture gave an absorbance value of >3 at 420 nm, indicating that essentially all the incident light is absorbed by the photocatalyst in the reaction mixture, therefore (f) is > 0.999 .¹⁰ Therefore quantum yield was found to be less than 1, which shows inefficient radical chain mechanism.¹¹

HRMS of SCN-TEMPO adduct

(M + H)⁺ peak due to SCN-TEMPO adduct at 215.1219



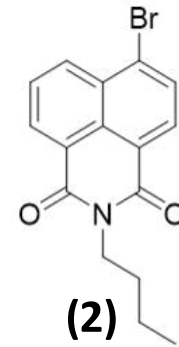
References:

1. S. Mitra, M. Ghosh, S. Mishra and A. Hajra, *J. Org. Chem.*, 2015, **80**, 8275–8281.
2. D. Yang, K. Yan, W. Wei, G. Li, S. Lu, C. Zhao, L. Tian and H. Wang, *J. Org. Chem.*, 2015, **80**, 11073–11079.
3. H. Zhang, Q. Wei, S. Wei, J. Qu and B. Wang, *Eur. J. Org. Chem.*, 2016, **2016**, 3373–3379.
4. C. G. Hatchard, C. A. Parker, *Proc. Roy. Soc. (London)* **1956**, *A23*, 518-531.
5. M. Montalti, A. Cerdi, L. Prodi, M. T. Gandolfi, *Chemical Actinometry. Handbook of Photochemistry*, III (Eds.: Taylor & Francis Group), LLC. Boca Raton, FL, **2006**, 601.
6. H. J. Kuhn, E. J.; Braslavsky, R. Schmidt, Chemical actinometry (IUPAC Technical Report) *Pure Appl. Chem.* 2004, **76**, 2105-2146.
7. I. P. Pozdnyakov, O. V. Kel, V. F. Plyusnin, V. P. Grivin, N. M. Bazhin, *J. Phys. Chem. A*. 2008, **112**, 8316–8322.
8. W. D. Bowman, J. N. Demas, *J. Phys. Chem.* 1976, **80**, 2434–2435.
9. G. Guiochon, C. L. Guillemin, *Journal of Chromatography Library*. 1988, **42**, 629-659.
10. M. Teders, L. Pitzer, S. Buss, F. Glorius, *ACS Catal.* 2017, **7**, 4053-4056.
11. M. A. Cismesia, T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426-5434.

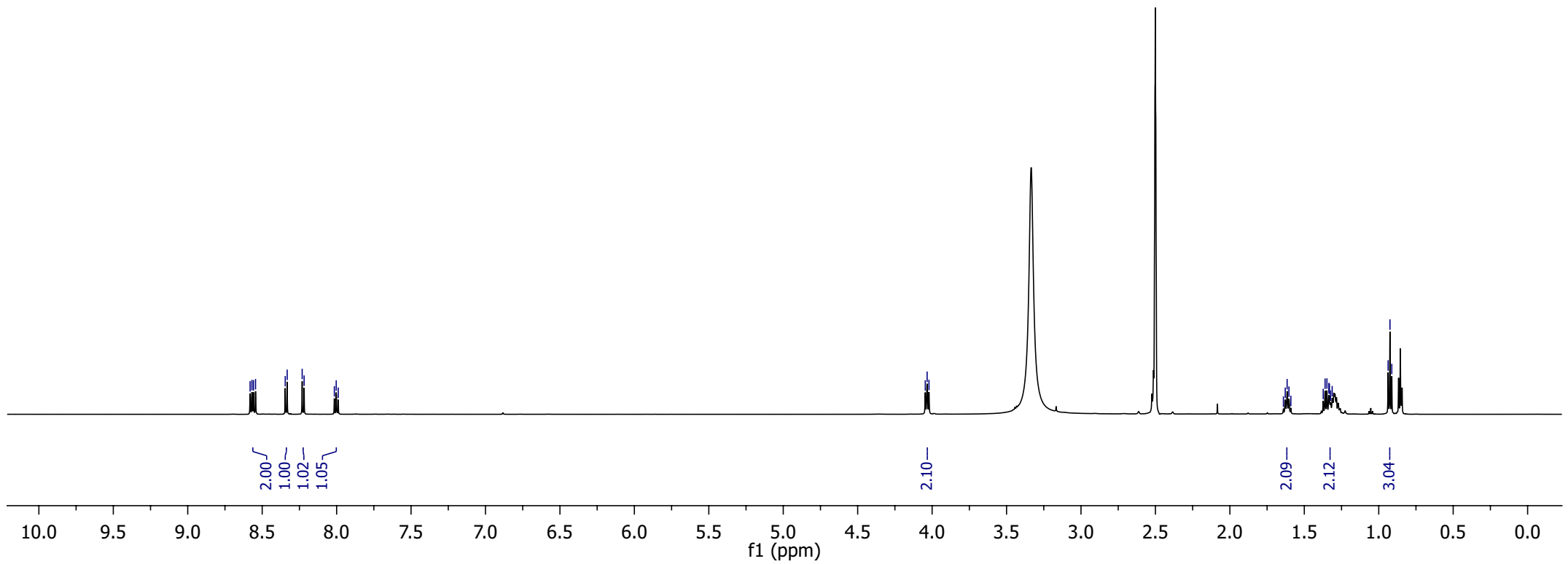
8.581
8.569
8.559
8.545
8.345
8.332
8.231
8.218
8.015
8.003
7.989

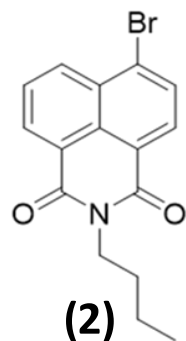
4.046
4.034
4.021

1.640
1.628
1.615
1.603
1.590
1.373
1.361
1.348
1.335
1.331
1.323
1.313
0.937
0.925
0.912



¹H NMR (DMSO-d₆, 600 MHz)





^{13}C NMR (DMSO- d_6 , 150 MHz)

163.41
163.36

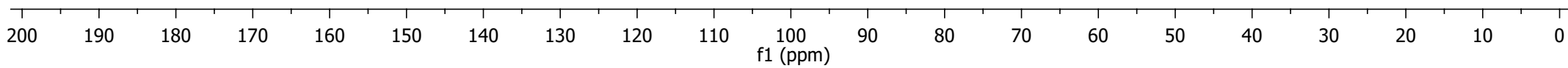
133.11
132.09
131.88
131.49
130.34
129.57
129.34
128.86
123.33
122.55

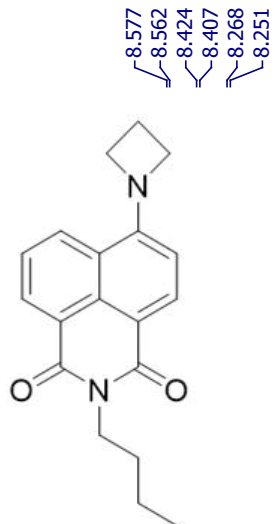
41.72

30.05

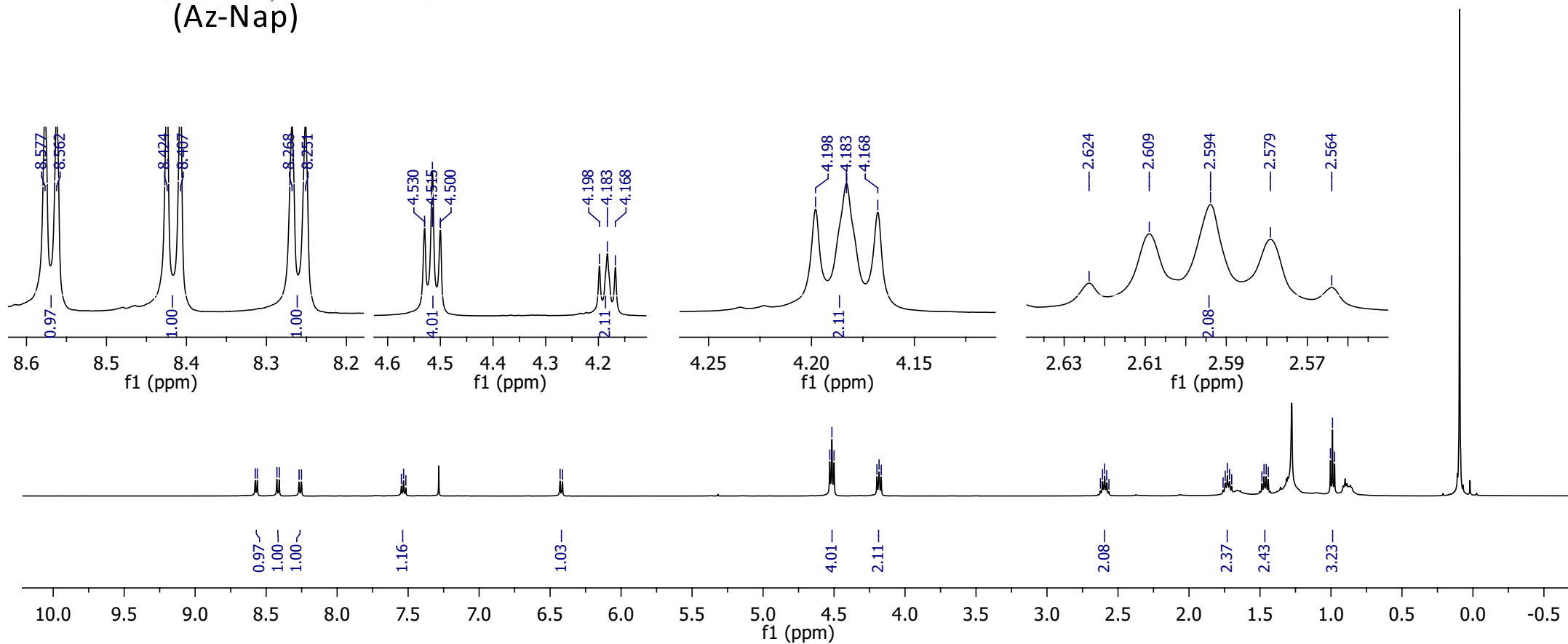
20.25

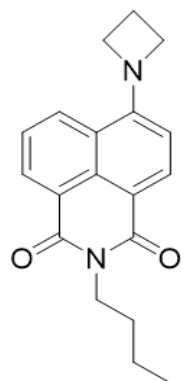
14.18





¹H NMR (CDCl₃, 500 MHz)
(Az-Nap)





^{13}C NMR (CDCl_3 , 125 MHz)
(Az-Nap)

164.763
164.132

152.566

133.277
131.101
130.577
129.971
123.723
122.839
120.978

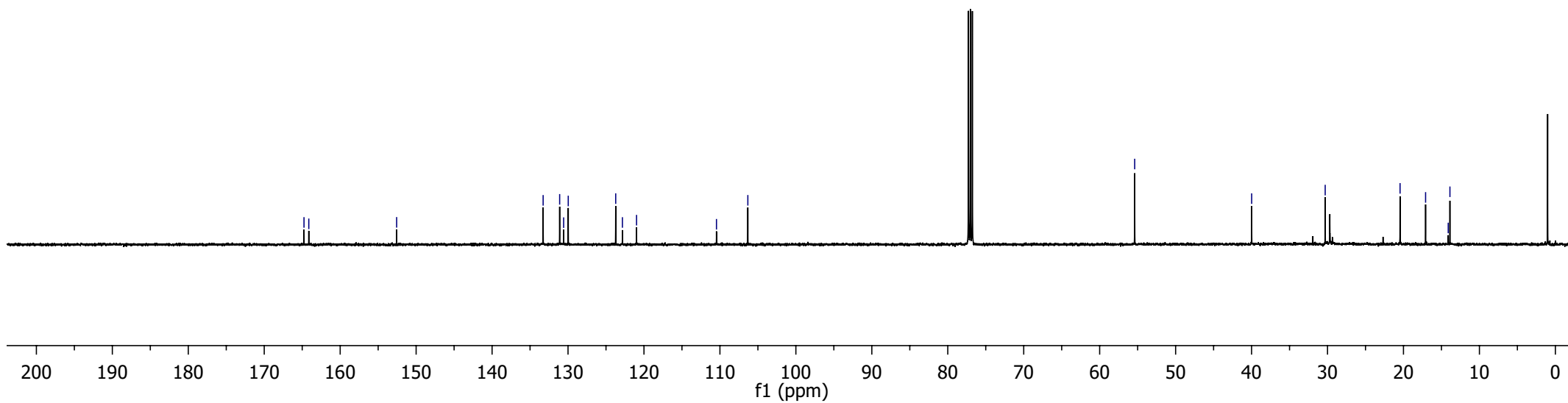
110.455
106.325

55.390

39.987

30.306

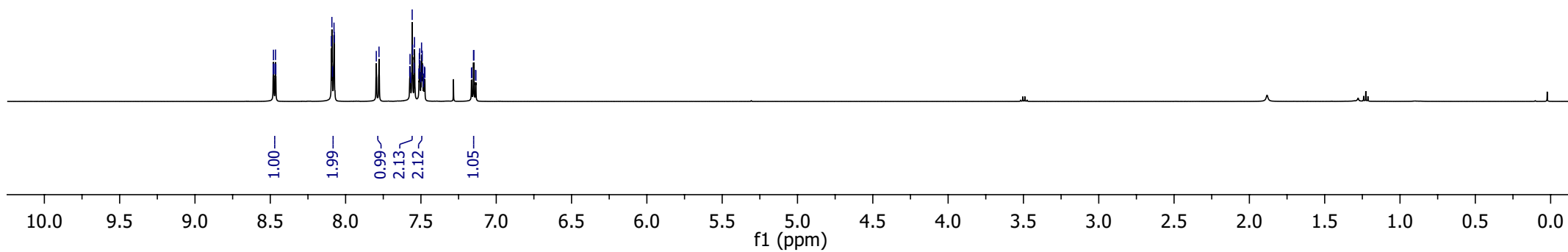
20.449
17.087
14.107
13.883



8.481
8.479
8.477
8.467
8.465
8.463
8.091
8.077
7.558
7.555
7.543
7.496
7.464
7.162
7.151
7.149
7.137
7.135



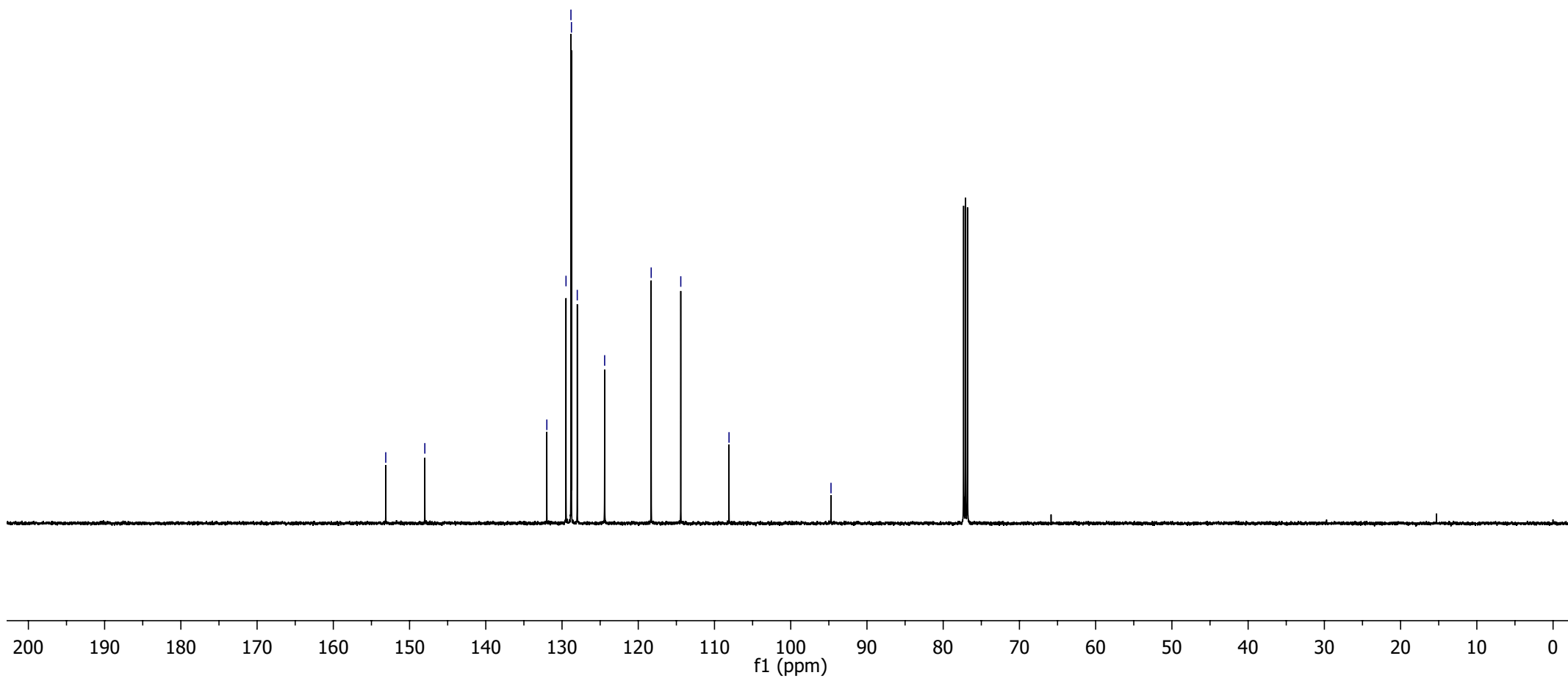
$^1\text{H NMR}$ (CDCl_3 , 500 MHz)
(3a)

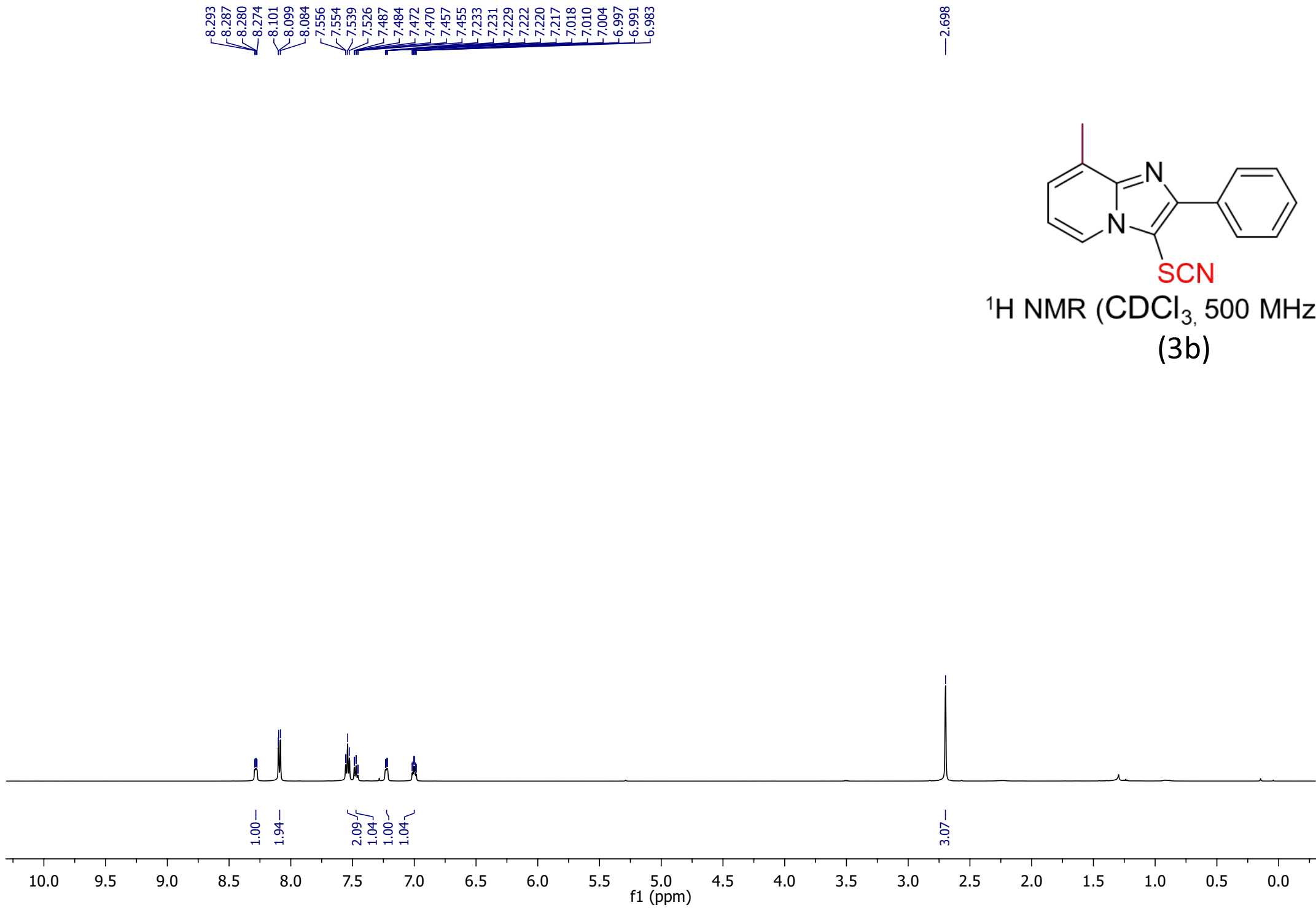


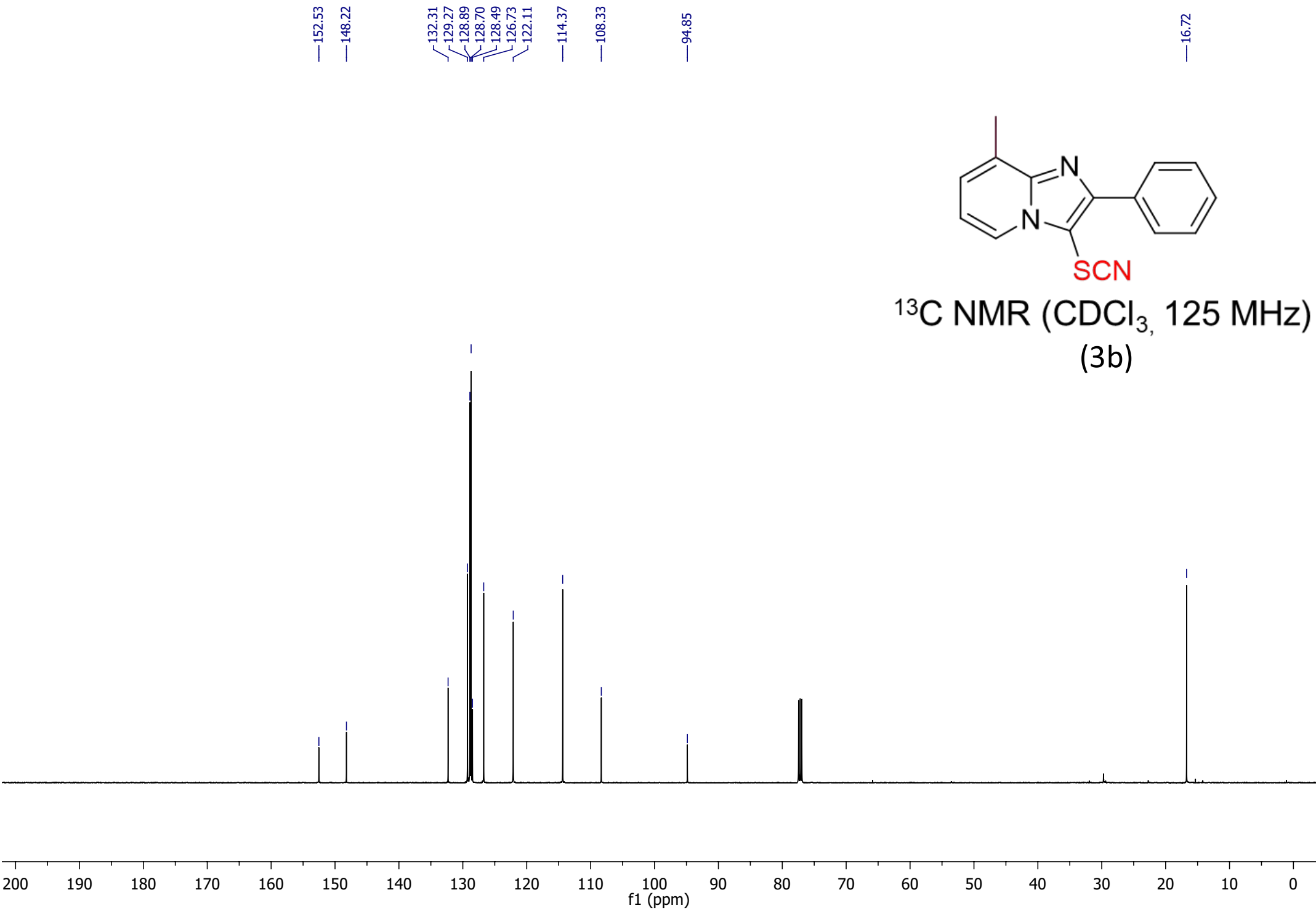


^{13}C NMR (CDCl_3 , 125 MHz)
(3a)

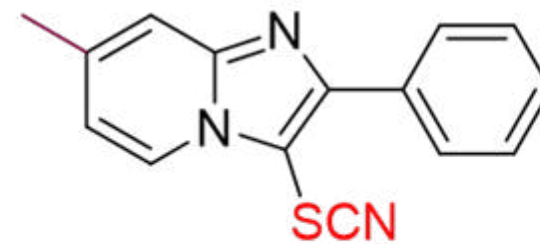
—153.12
—148.00
—131.99
—129.48
—128.83
—128.76
—128.00
—124.41
—118.30
—114.42
—108.09
—94.72





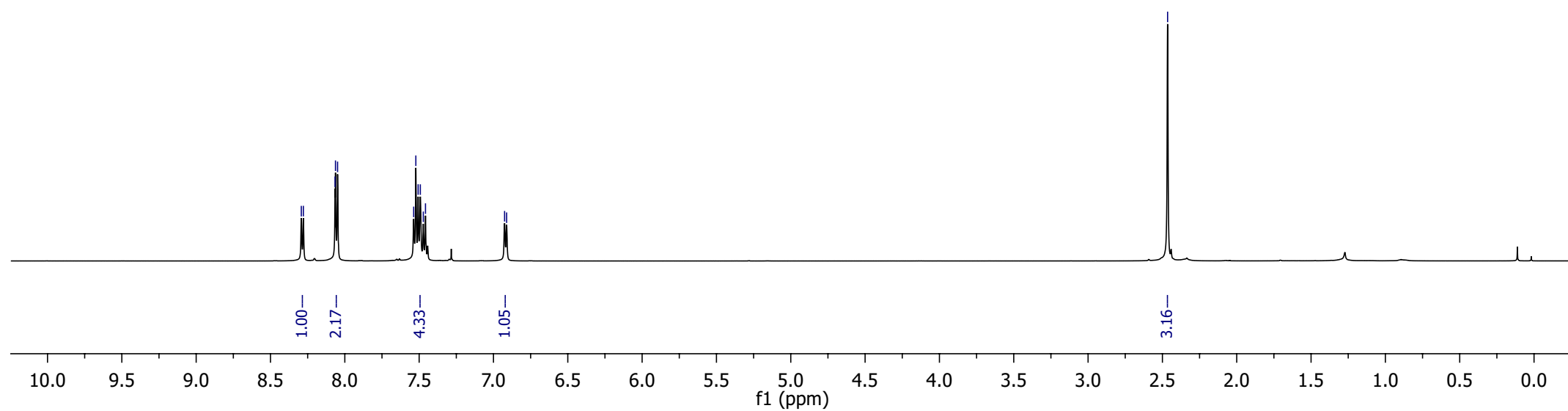


8.293
8.279
8.066
8.063
8.049
7.537
7.522
7.507
7.492
7.472
7.457
6.925
6.911

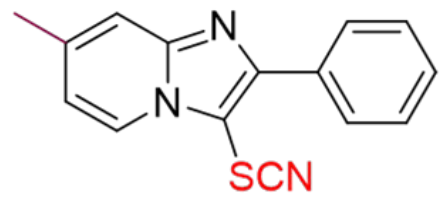


^1H NMR (CDCl_3 , 500 MHz)
(3c)

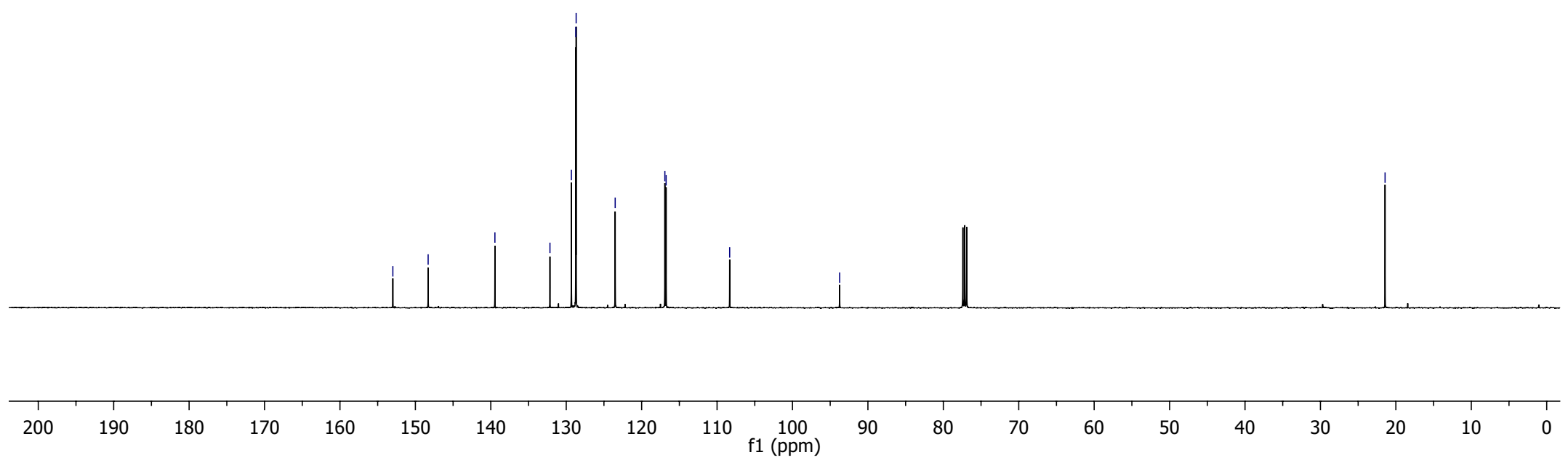
2.465



—152.99
—148.31
—139.46
/132.16
/129.32
/128.73
/128.68
—123.51
/116.92
/116.75
—108.33
—93.75
—21.43

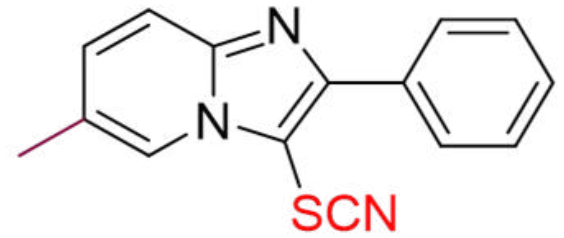


¹³C NMR (CDCl₃, 125 MHz)
(3c)

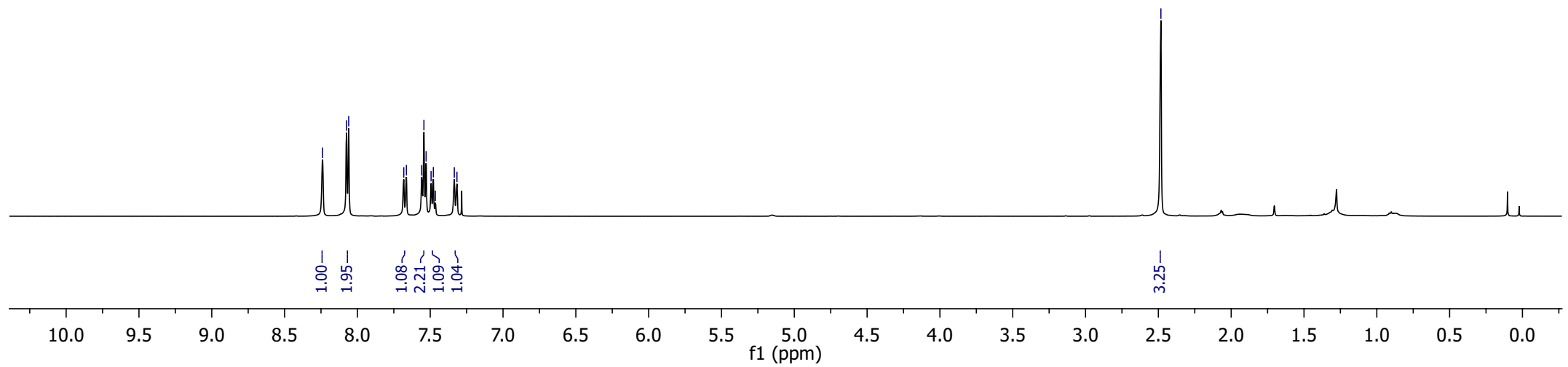


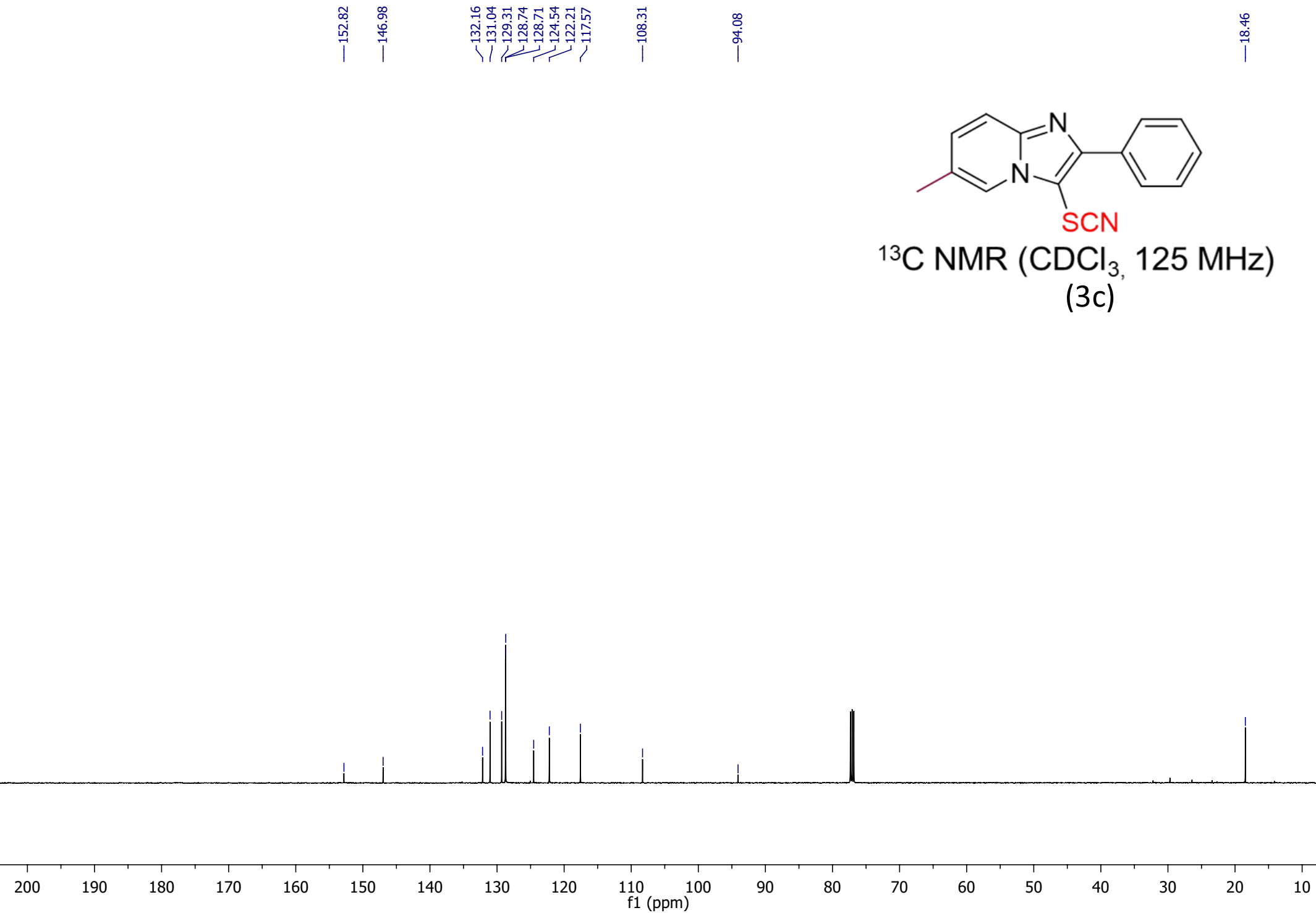
8.239
8.074
8.060
7.682
7.664
7.558
7.543
7.528
7.494
7.478
7.465
7.335
7.317

2.483



^1H NMR (CDCl_3 , 500 MHz)
(3d)



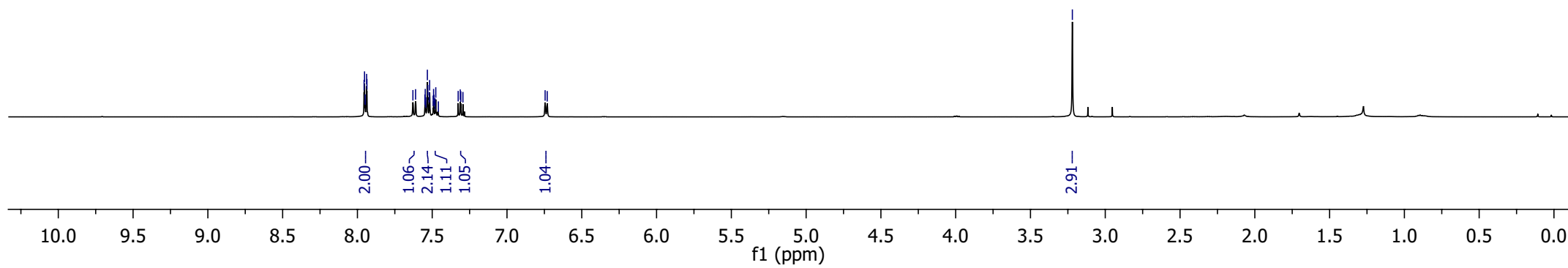


7.955
7.953
7.949
7.939
7.936
7.611
7.546
7.532
7.529
7.517
7.491
6.745
6.731

3.220



¹H NMR (CDCl₃, 500 MHz)
(3e)

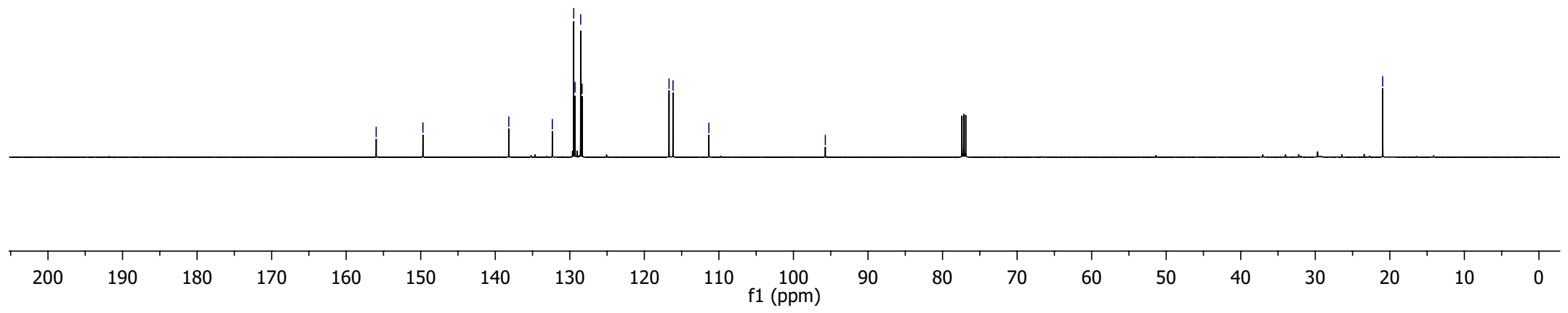


—155.974
—149.703
—138.183
—132.346
—129.473
—129.293
—128.543
—128.354
—116.686
—116.155
—111.343
—95.722

—20.957

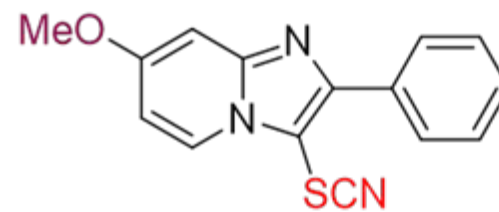


¹³C NMR (CDCl₃, 125 MHz)
(3e)

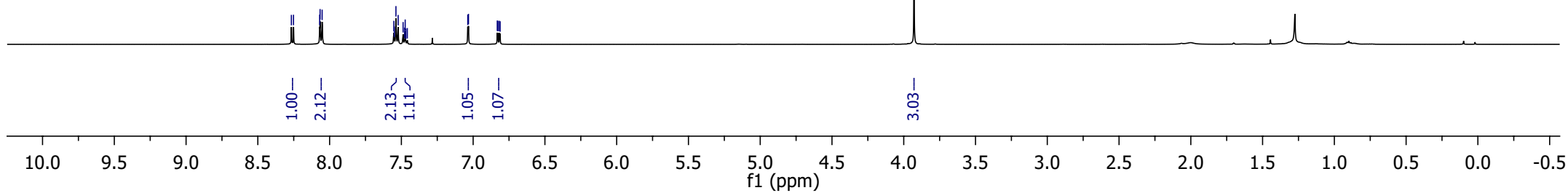


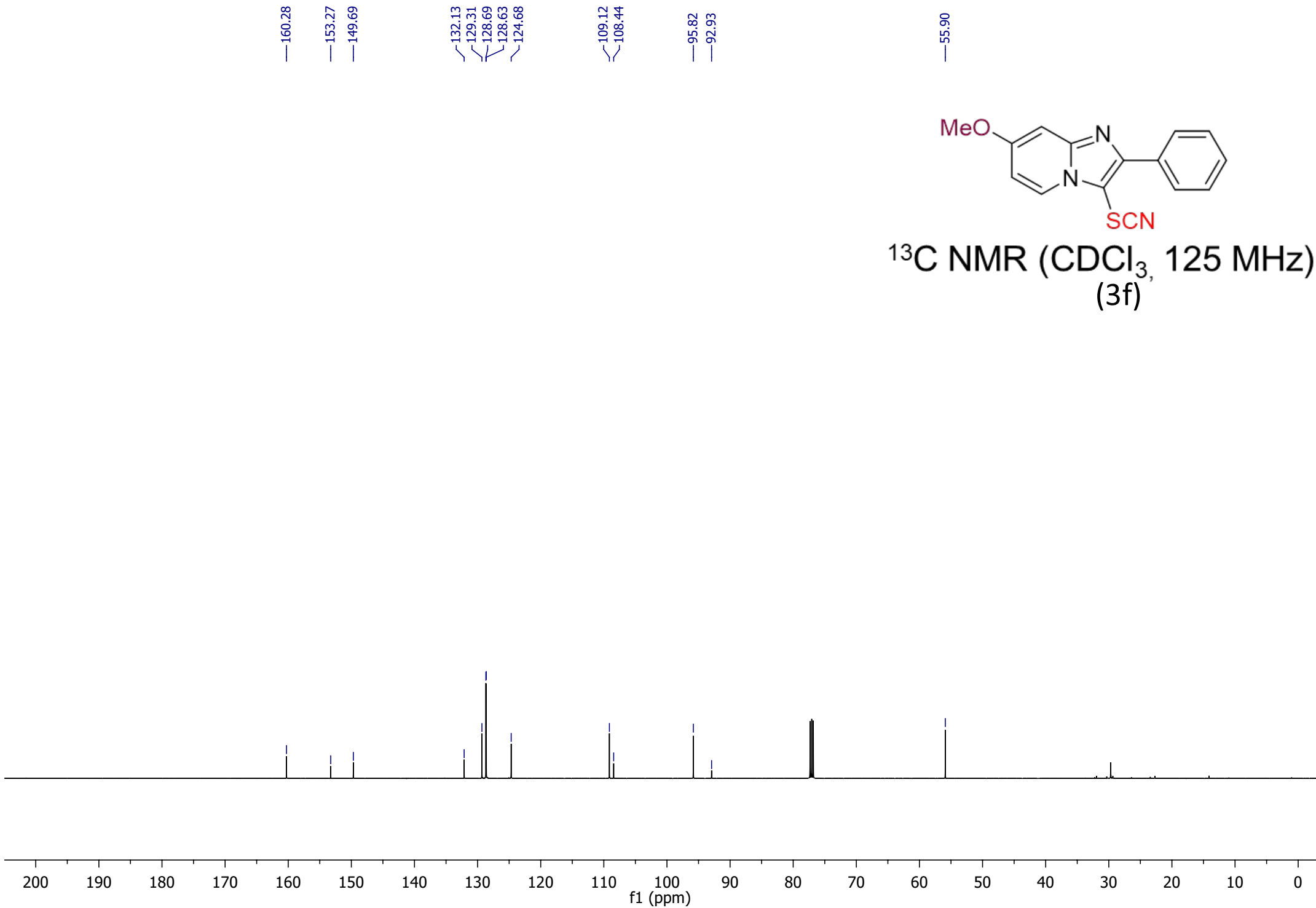
8.266
8.251
8.069
8.066
8.052
7.552
7.538
7.522
7.503
7.032
6.832
6.827
6.817
6.812

3.928

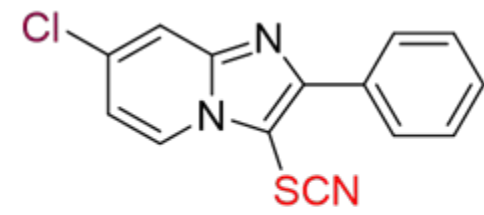


¹H NMR (CDCl₃, 500 MHz)
(3f)

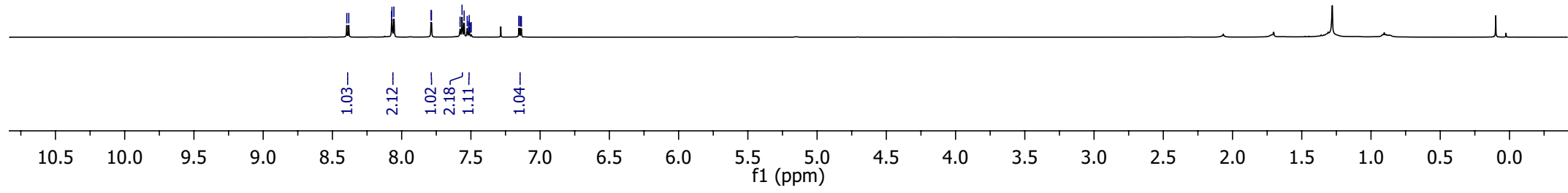
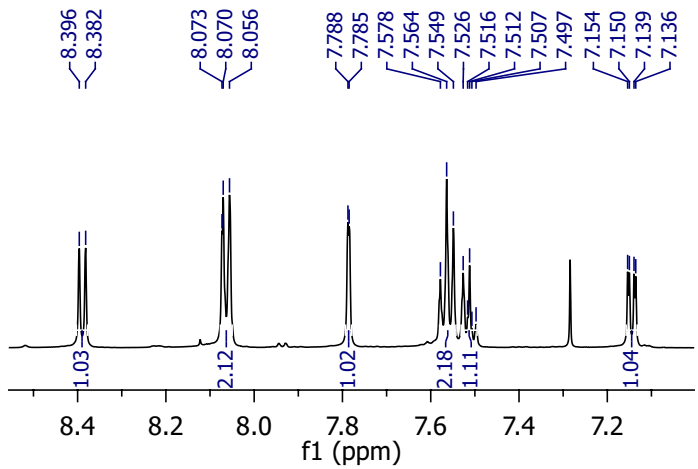




8.396
8.382
8.070
8.056
7.788
7.785
7.564
7.549
7.544
7.150
7.139
7.136



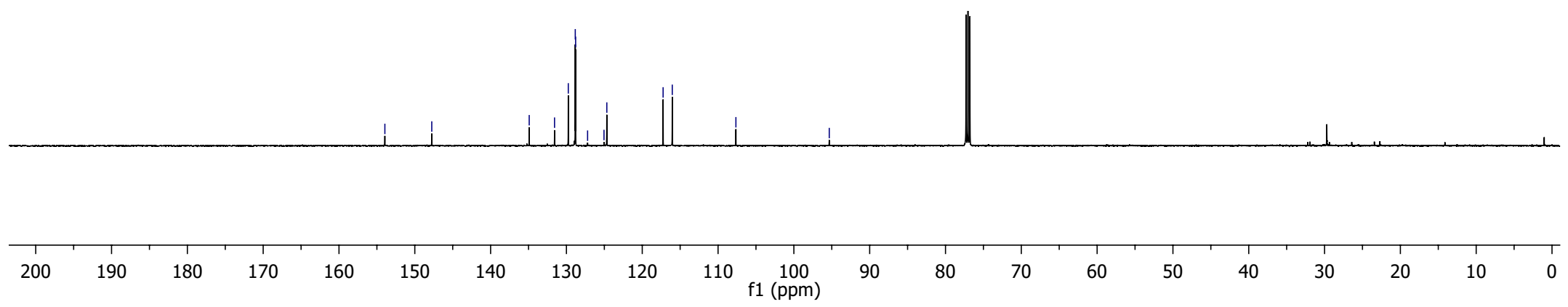
¹H NMR (CDCl₃, 500 MHz)
(3g)

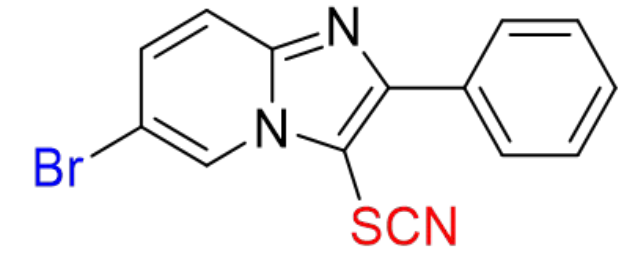




^{13}C NMR (CDCl_3 , 125 MHz)
(3g)

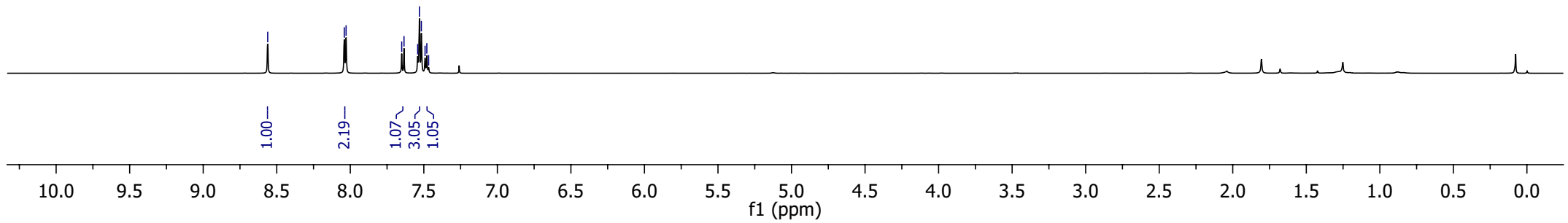
- 153.95
- 147.76
- 134.91
- 131.57
- 129.75
- 128.83
- 128.79
- 127.21
- 125.05
- 124.67
- 117.25
- 116.04
- 107.65
- 95.33

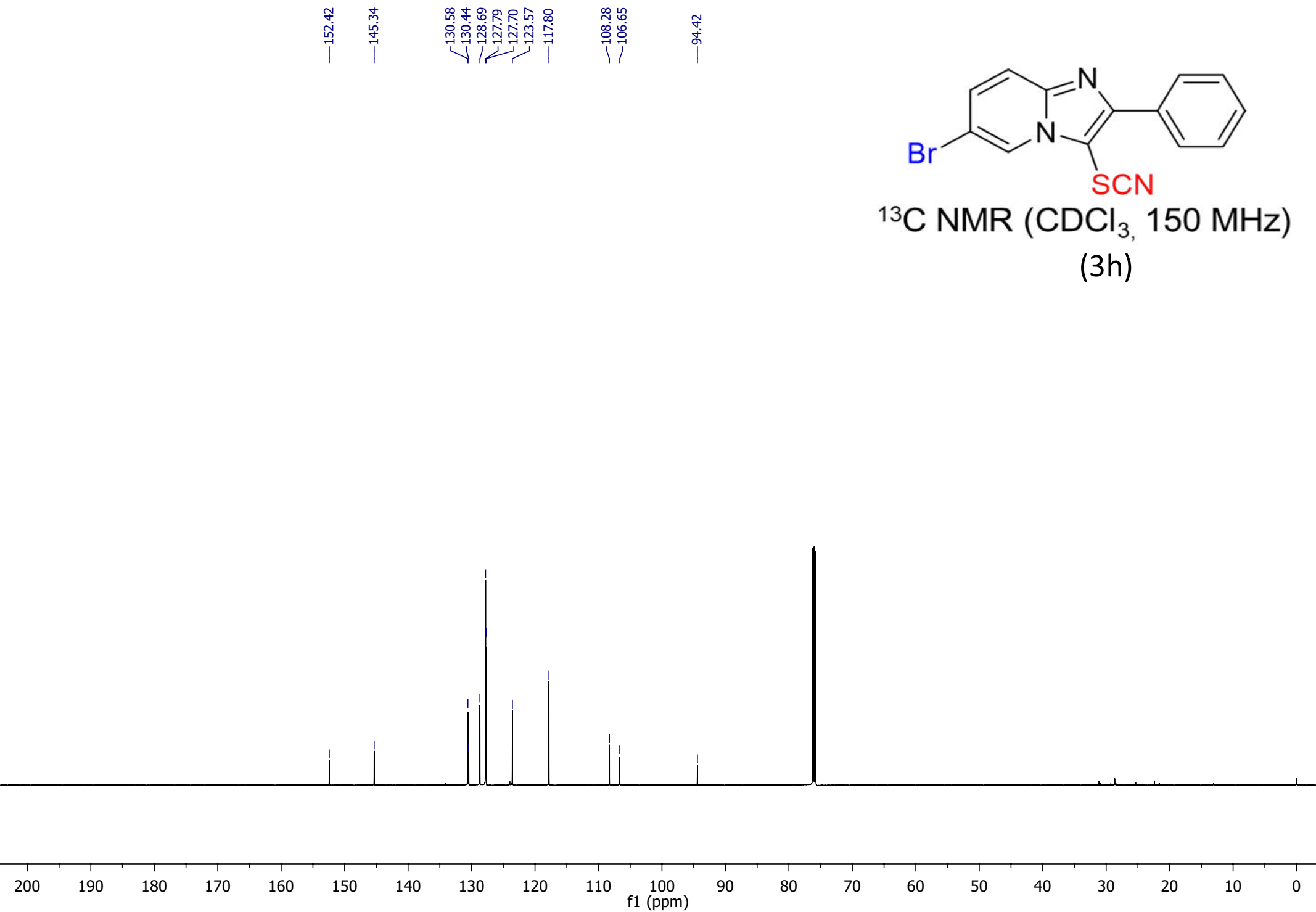
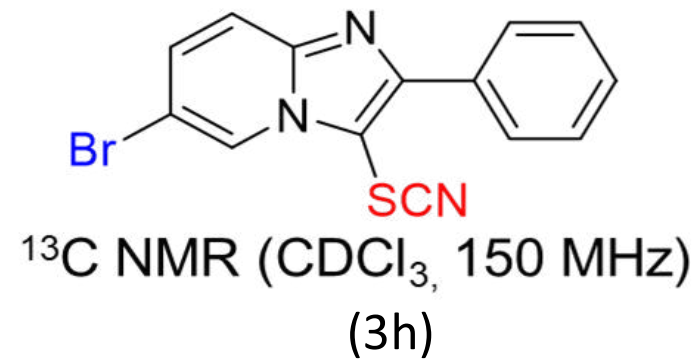




^1H NMR (CDCl_3 , 600 MHz)
(3h)

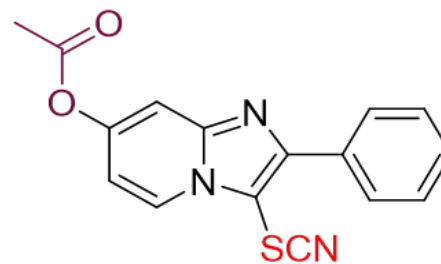
8.561
8.041
8.029
7.650
7.635
7.542
7.530
7.517
7.492
7.480
7.467



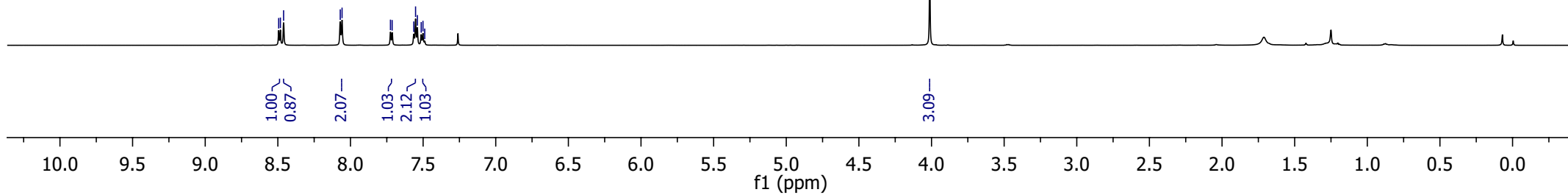


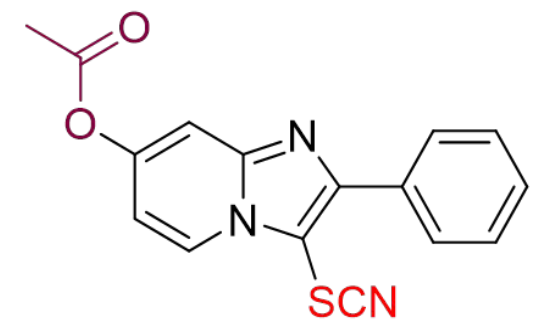
8.494
8.482
8.460
8.070
8.058
7.725
7.713
7.564
7.552
7.539
7.513
7.501
7.489

4.012

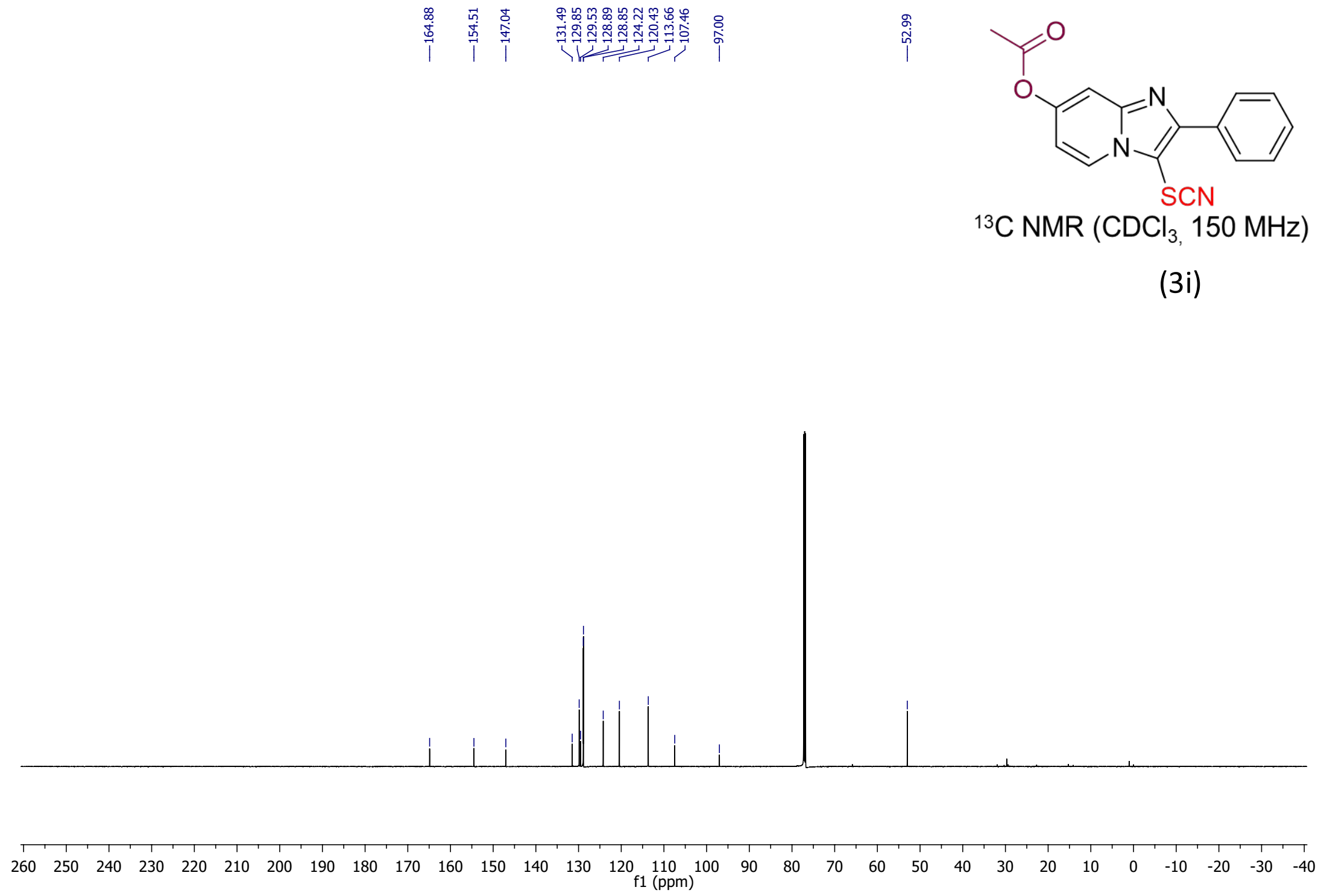


¹H NMR (CDCl₃, 600 MHz)
(3i)





¹³C NMR (CDCl₃, 150 MHz)
(3i)

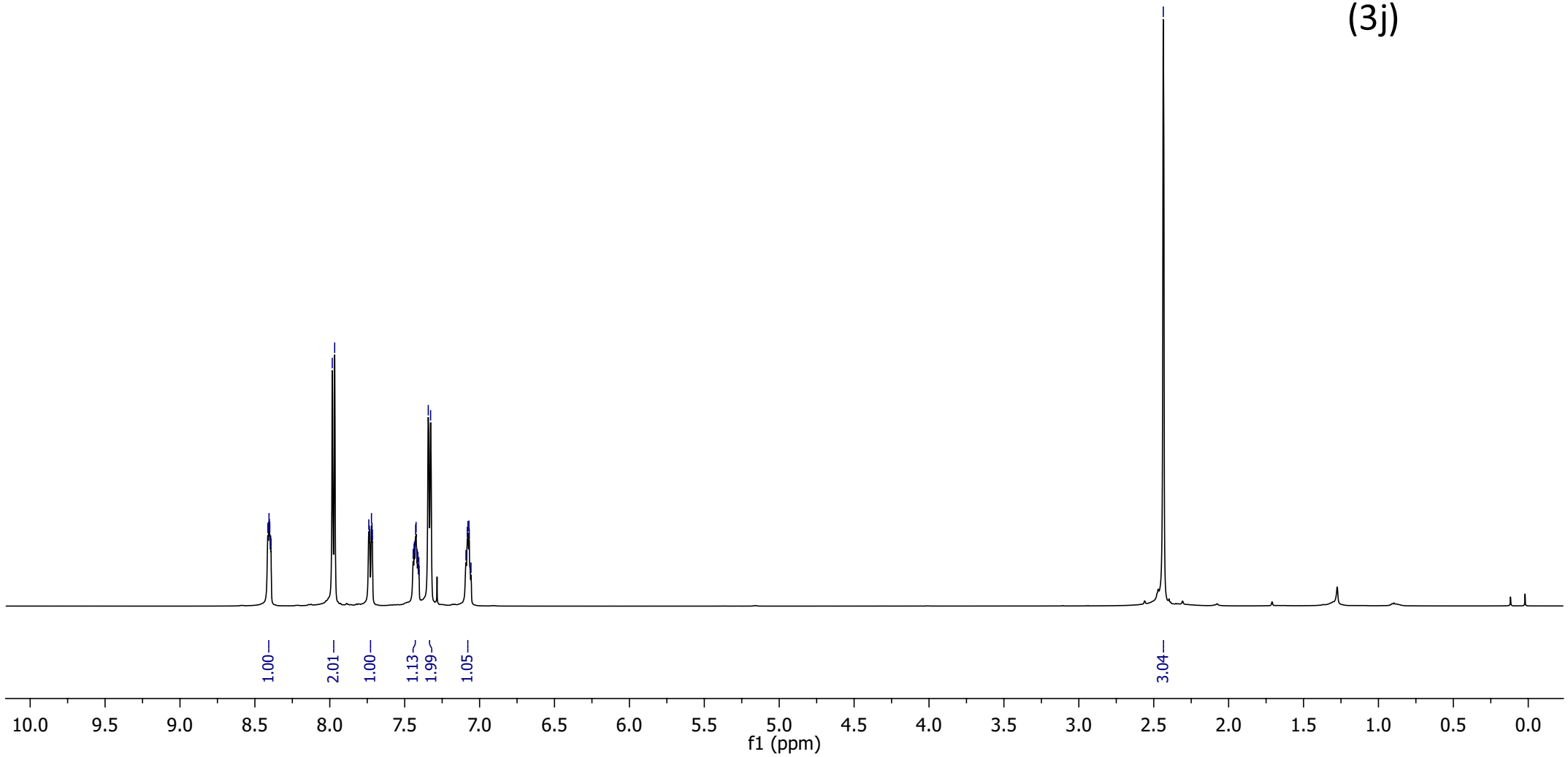


8.413
8.408
8.406
8.403
8.400
8.394
8.392
7.983
7.967
7.739
7.722
7.743
7.437
7.435
7.427
7.424
7.417
7.412
7.406
7.404
7.343
7.327
7.091
7.082
7.078
7.071
7.069
7.057

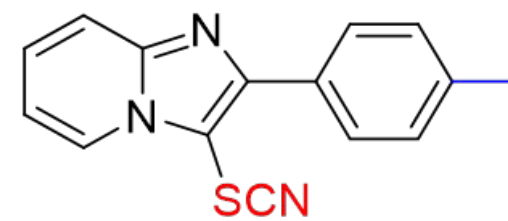
2.436



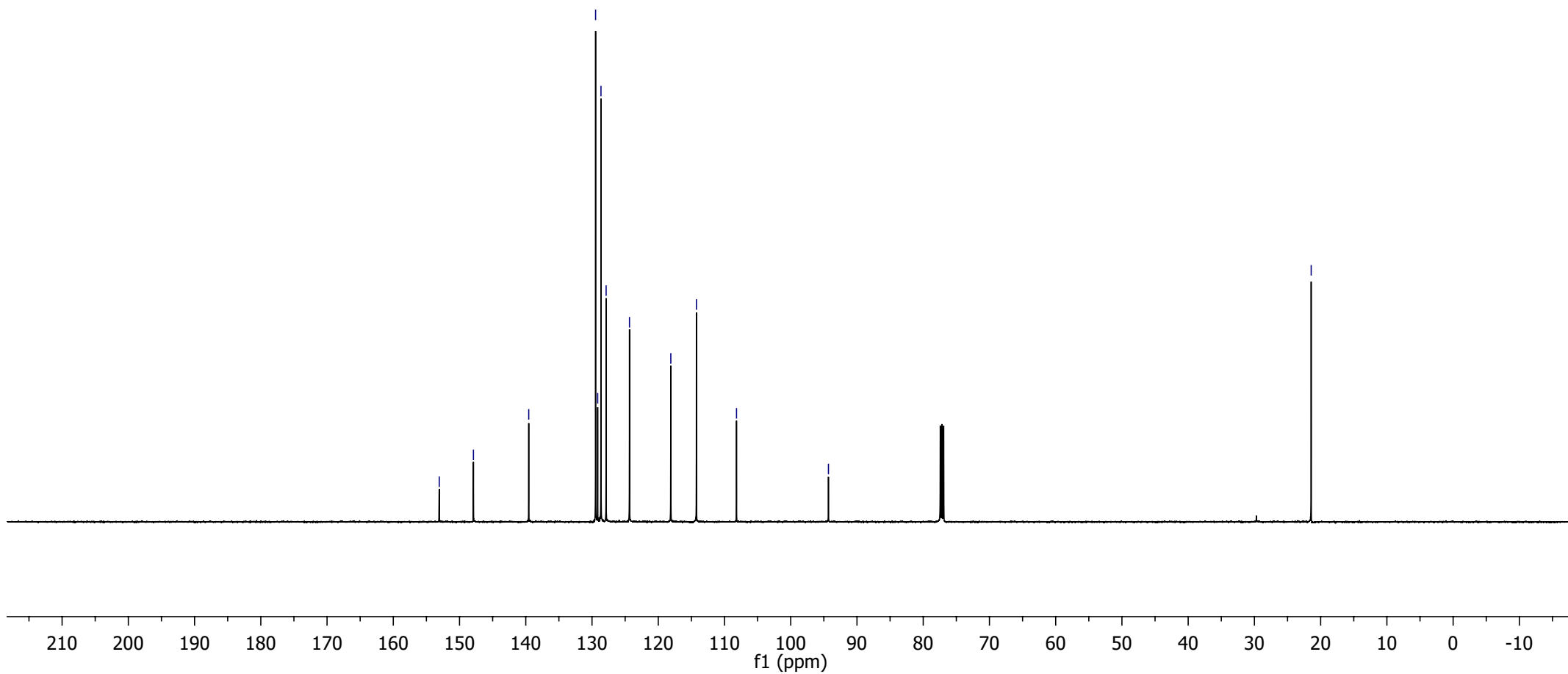
¹H NMR (CDCl₃, 500 MHz)
(3j)



—153.06
—147.90
—139.55
—129.46
—129.14
—128.65
—127.87
—124.34
—118.10
—114.24
—108.18
—94.31

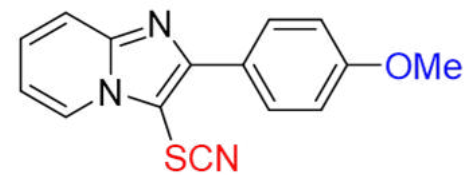


^{13}C NMR (CDCl_3 , 125 MHz)
(3j)



8.435
8.422
8.058
8.040
7.746
7.728
7.455
7.453
7.118
7.117
7.104
7.091
7.073
7.056

3.893



¹H NMR (CDCl₃, 500 MHz)

(3k)

1.00

2.14

1.10

1.07

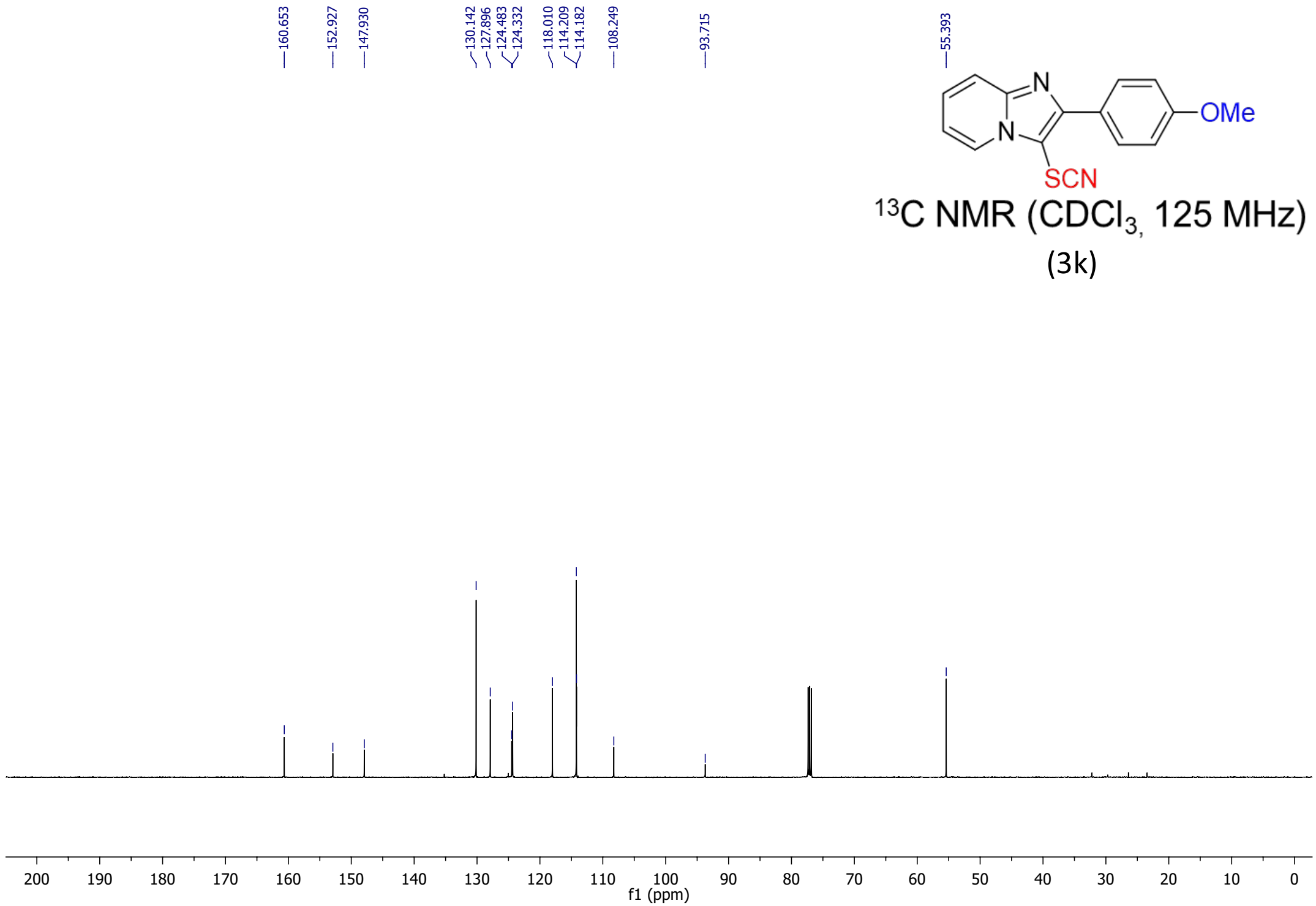
1.12

1.99

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

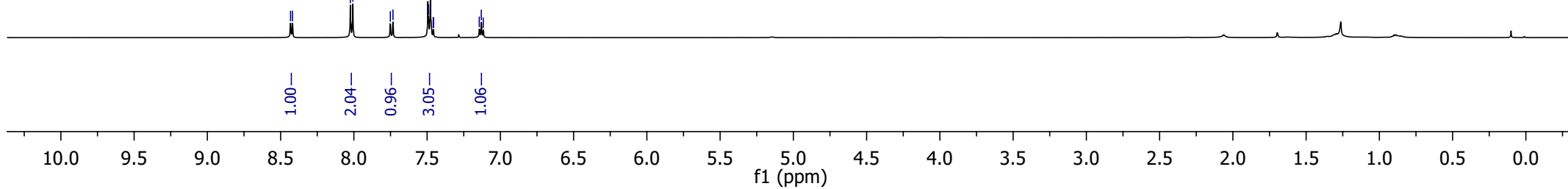
f1 (ppm)



8.432
8.419
8.024
8.007
7.751
7.733
7.495
7.491
7.478
7.144
7.130
7.117



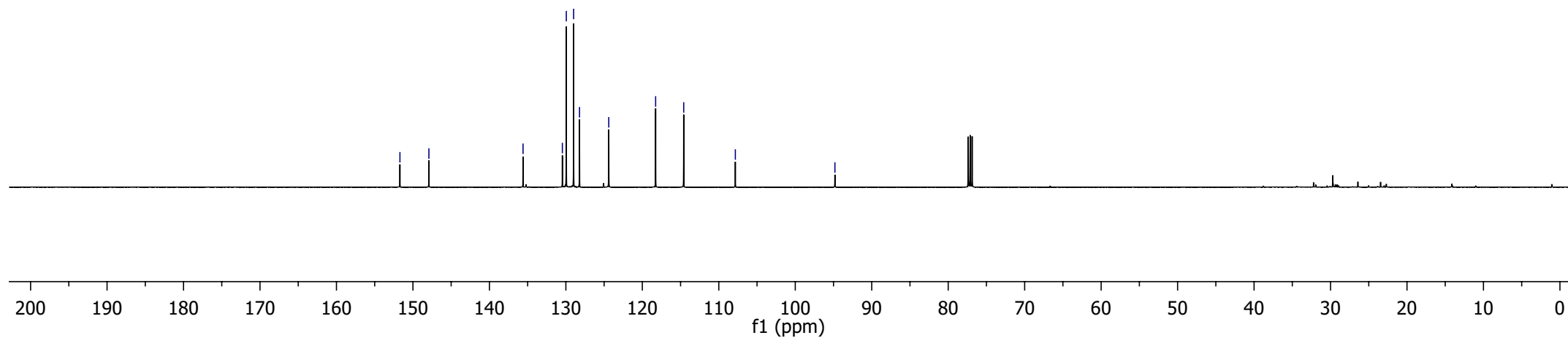
$^1\text{H NMR}$ (CDCl_3 , 500 MHz)
(3I)



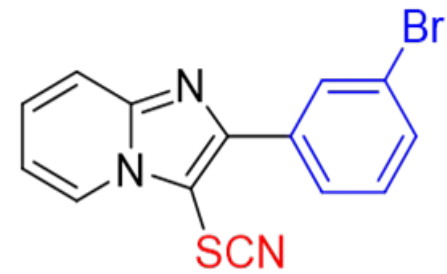


^{13}C NMR (CDCl_3 , 125 MHz)
(3l)

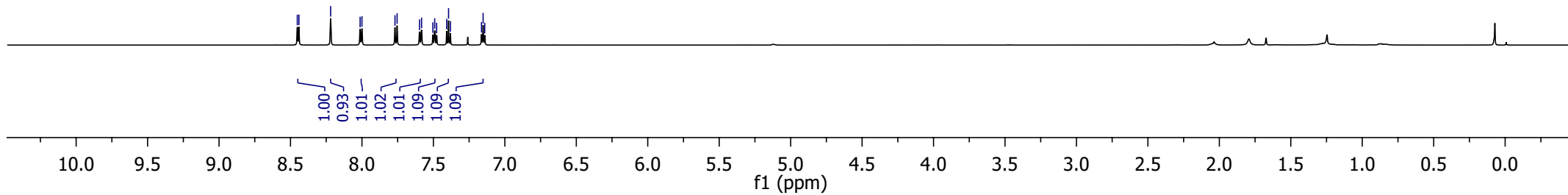
- 151.700
- 147.912
- 135.601
- 130.457
- 129.943
- 128.986
- 128.216
- 124.390
- 118.260
- 114.588
- 107.837
- 94.815



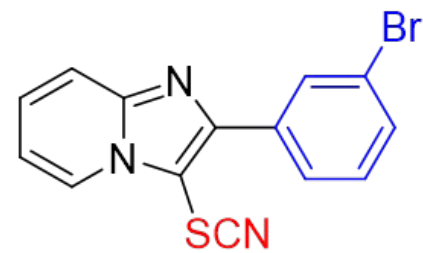
8.453
8.441
8.219
8.013
8.000
7.769
7.754
7.597
7.583
7.504
7.491
7.477
7.407
7.394
7.381
7.163
7.152
7.141



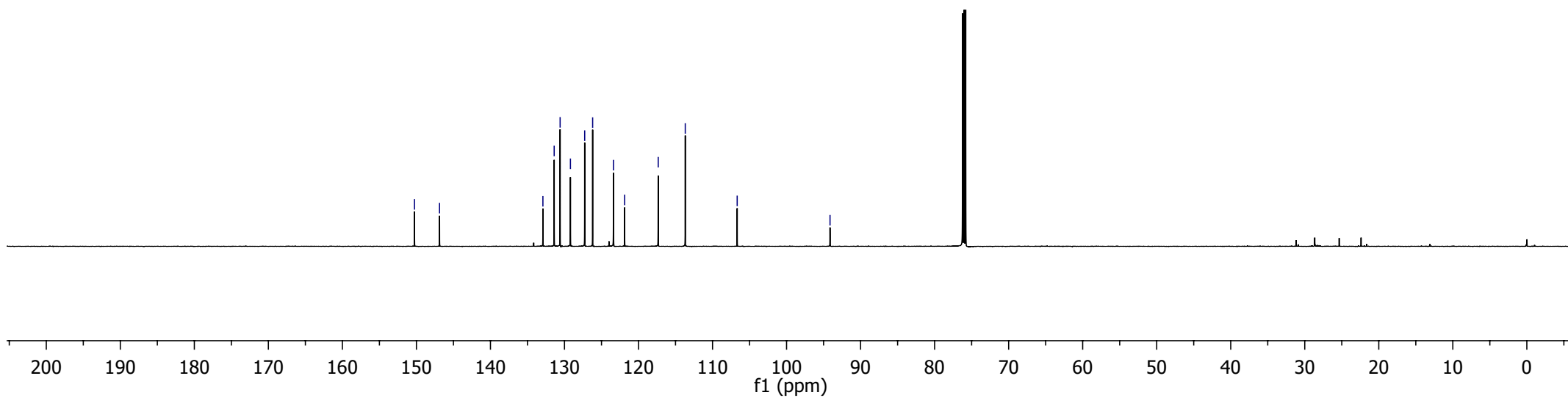
$^1\text{H NMR}$ (CDCl_3 , 600 MHz)
(3m)



150.26
146.88
132.91
131.39
130.59
129.20
127.27
126.19
123.38
121.88
117.34
113.68
106.67
94.13



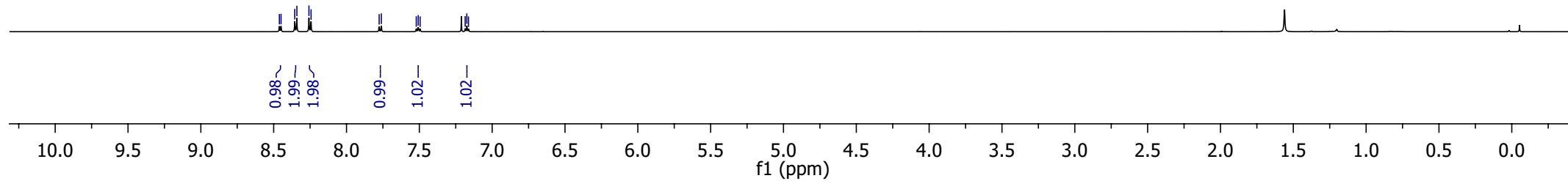
^{13}C NMR (CDCl_3 , 150 MHz)
(3m)



8.461
8.449
8.355
8.341
8.258
8.243
7.776
7.761
7.521
7.508
7.495
7.185
7.174
7.163



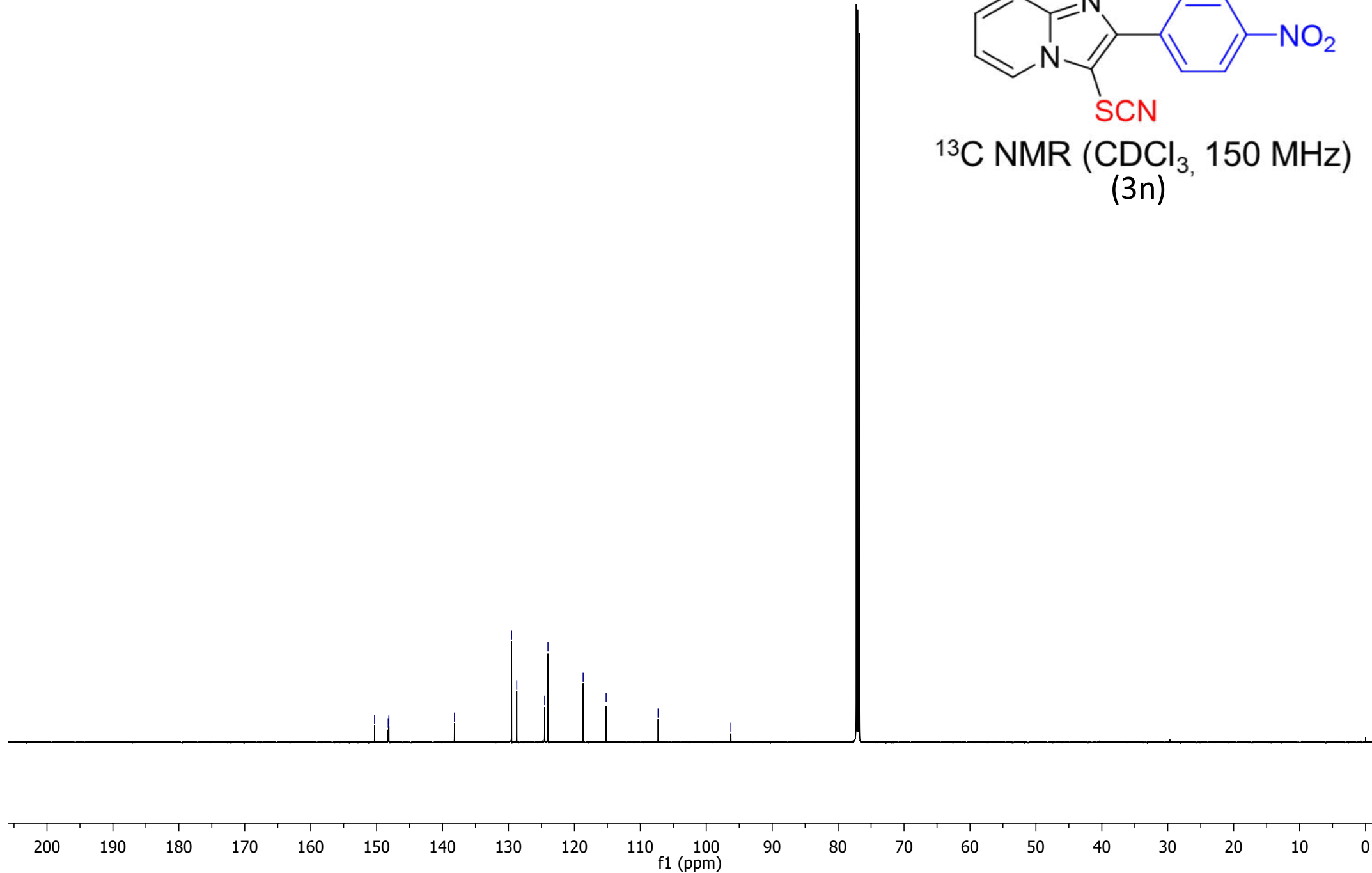
¹H NMR (CDCl₃, 600 MHz)
(3n)



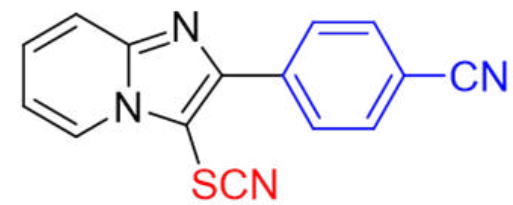
150.31
148.23
148.14
138.19
129.53
128.74
124.51
124.01
118.67
115.19
107.30
96.26



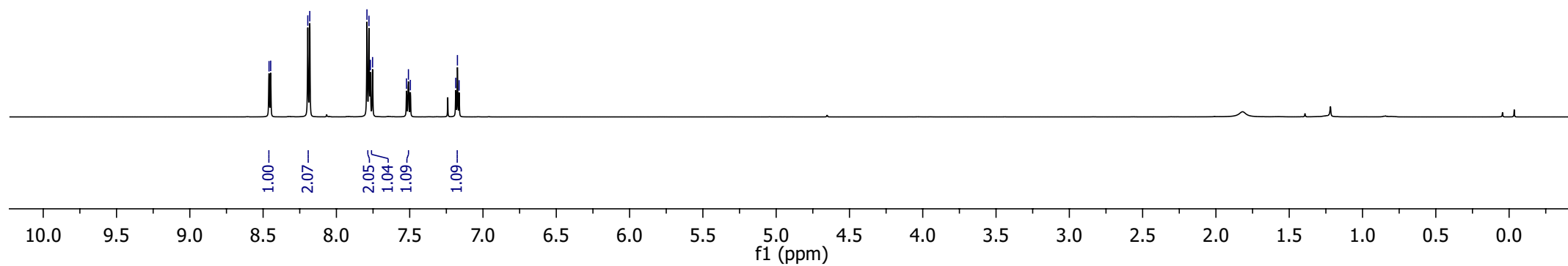
¹³C NMR (CDCl₃, 150 MHz)
(3n)



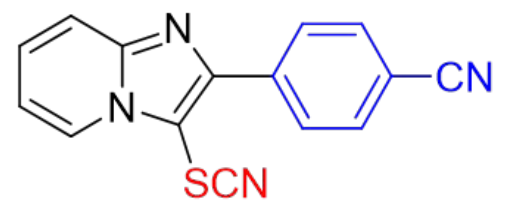
8.460
8.448
8.195
8.182
7.792
7.778
7.768
7.753
7.599
7.186
7.174
7.163



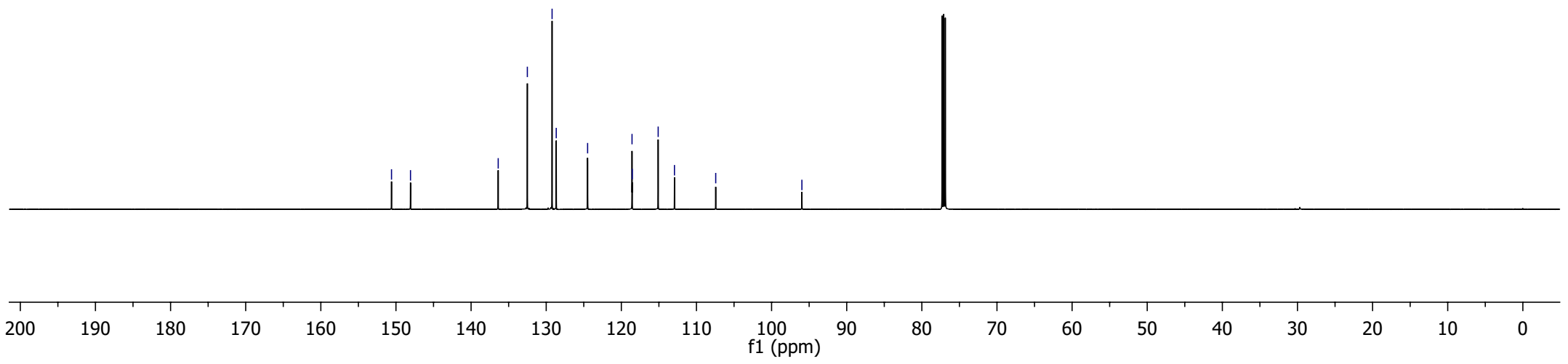
^1H NMR (CDCl_3 , 600 MHz)
(3o)



—150.59
—148.06
—136.39
—132.51
—129.22
—128.66
—124.49
—118.58
—118.55
—115.10
—112.93
—107.44
—95.97

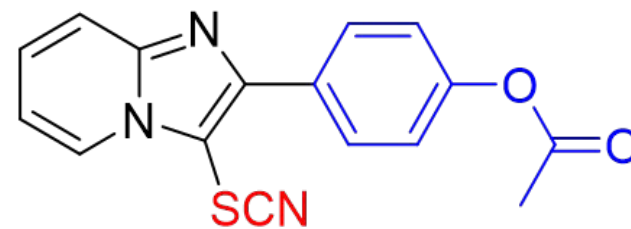


¹³C NMR (CDCl₃, 150 MHz)
(3o)



8.464
8.452
8.112
8.097
7.777
7.762
7.502
7.490
7.488
7.476
7.474
7.287
7.273
7.160
7.149
7.138

2.348



¹H NMR (CDCl₃, 600 MHz)
(3p)

0.96

2.02

0.98

1.01

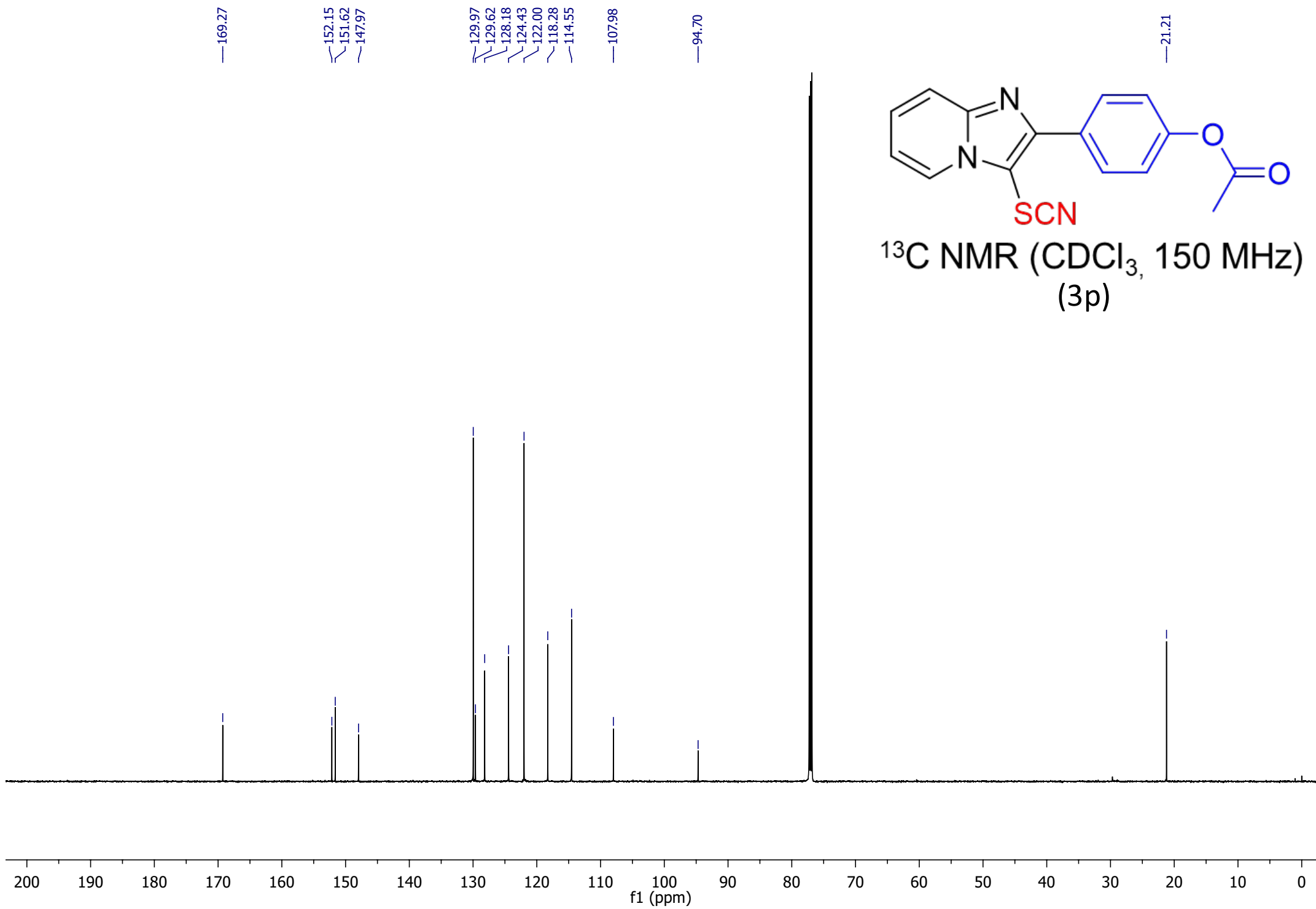
1.91

1.00

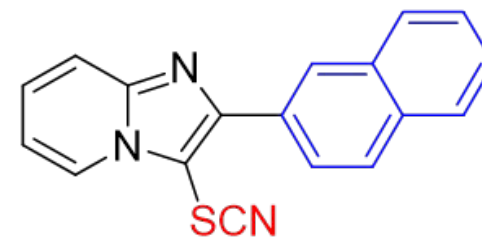
3.00

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

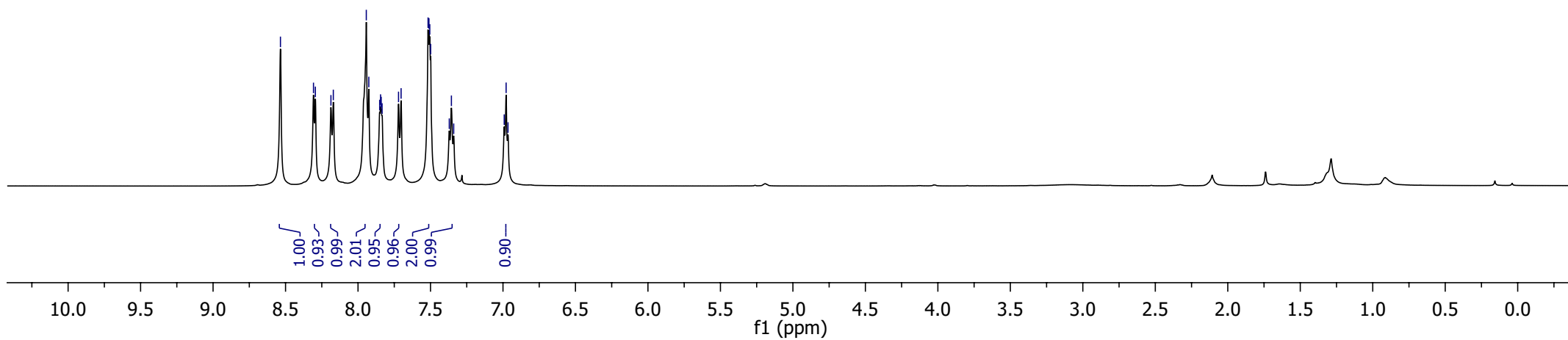
f1 (ppm)



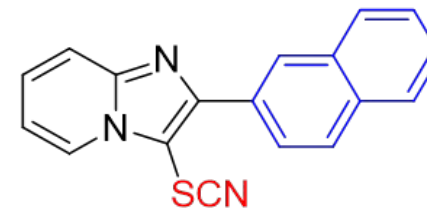
8.535
8.307
8.294
8.187
8.170
7.943
7.926
7.851
7.845
7.840
7.834
7.720
7.703
7.517
7.511
7.505
7.499
7.370
7.356
7.340
6.991
6.978
6.965



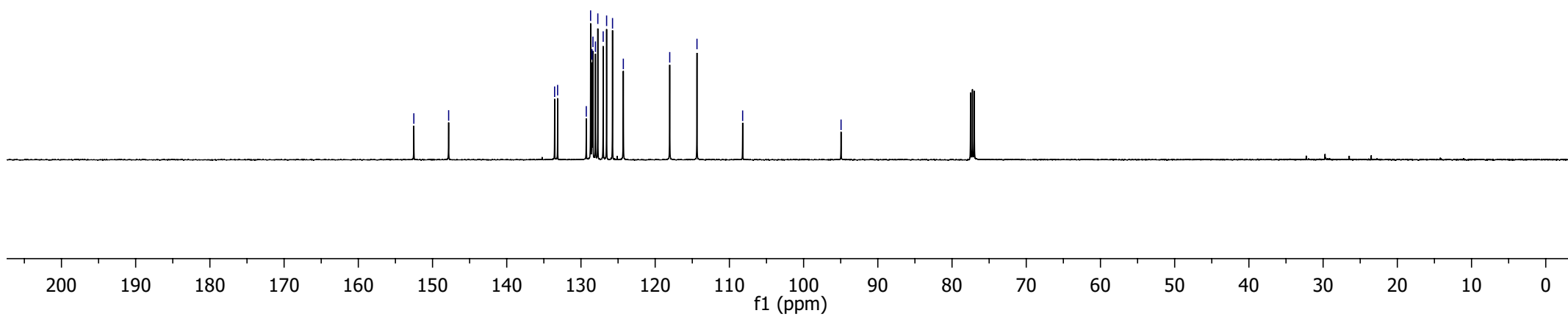
$^1\text{H NMR}$ (CDCl_3 , 500 MHz)
(3q)



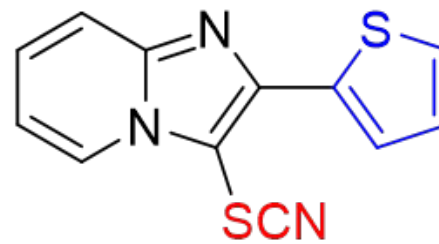
152.52
147.83
133.55
133.15
128.70
128.51
128.39
128.05
127.73
127.01
126.54
125.75
118.04
114.37
108.21



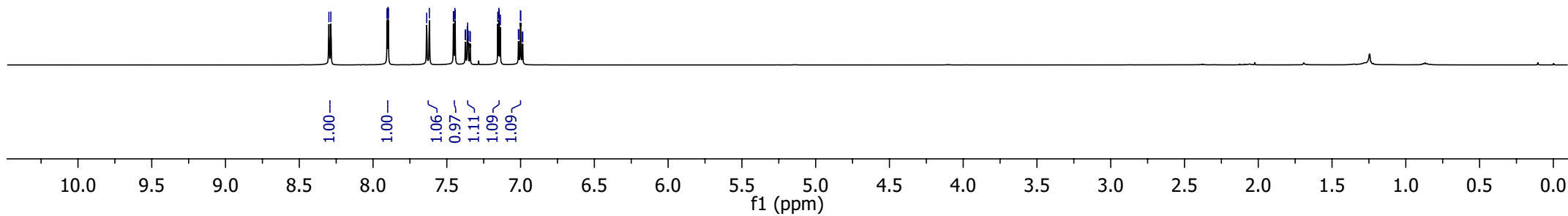
^{13}C NMR (CDCl_3 , 125 MHz)
(3q)



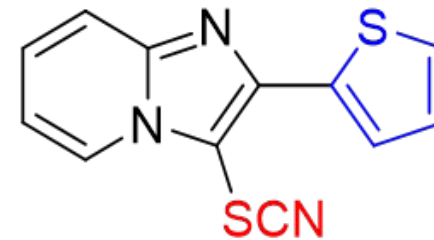
8.299
8.286
7.903
7.898
7.896
7.636
7.618
7.455
7.453
7.445
7.443
7.375
7.373
7.361
7.359
7.355
7.343
7.341
7.155
7.147
7.145
7.137
7.015
7.013
7.001
6.999
6.987
6.985



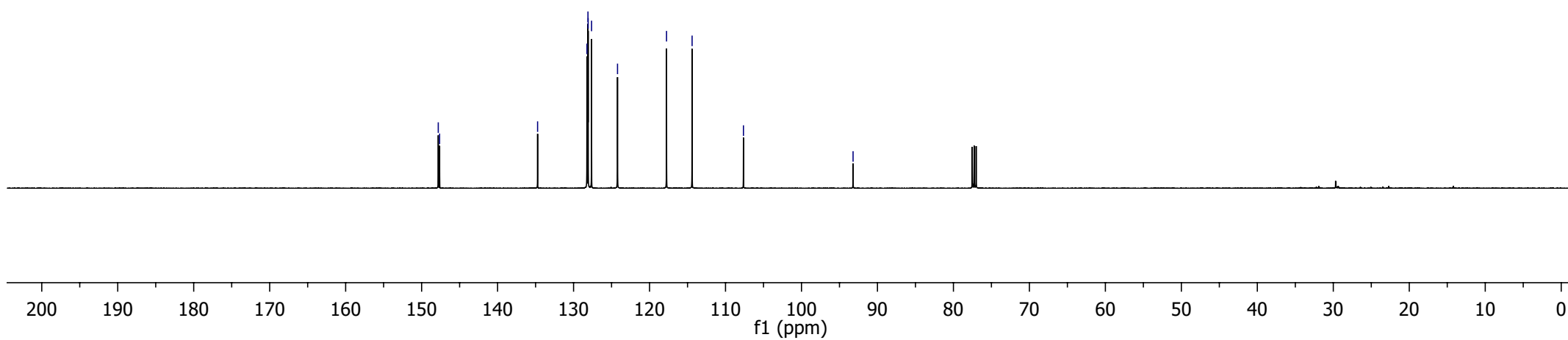
^1H NMR (CDCl_3 , 500 MHz)
(3r)



147.81
147.63
134.74
128.24
128.10
128.08
127.63
124.22
117.76
114.40
107.64
93.21

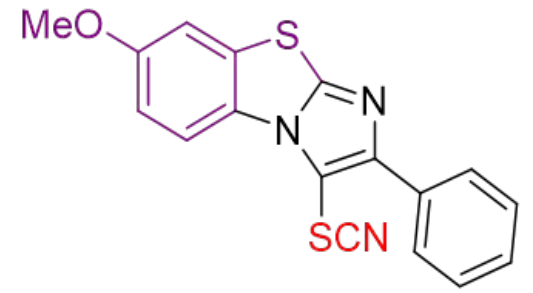


^{13}C NMR (CDCl_3 , 125 MHz)
(3r)

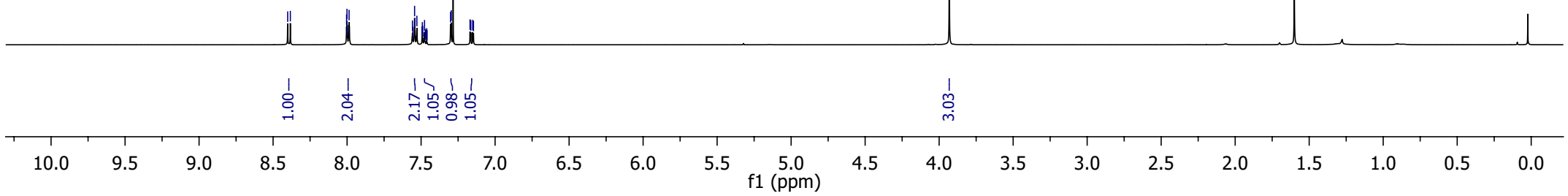


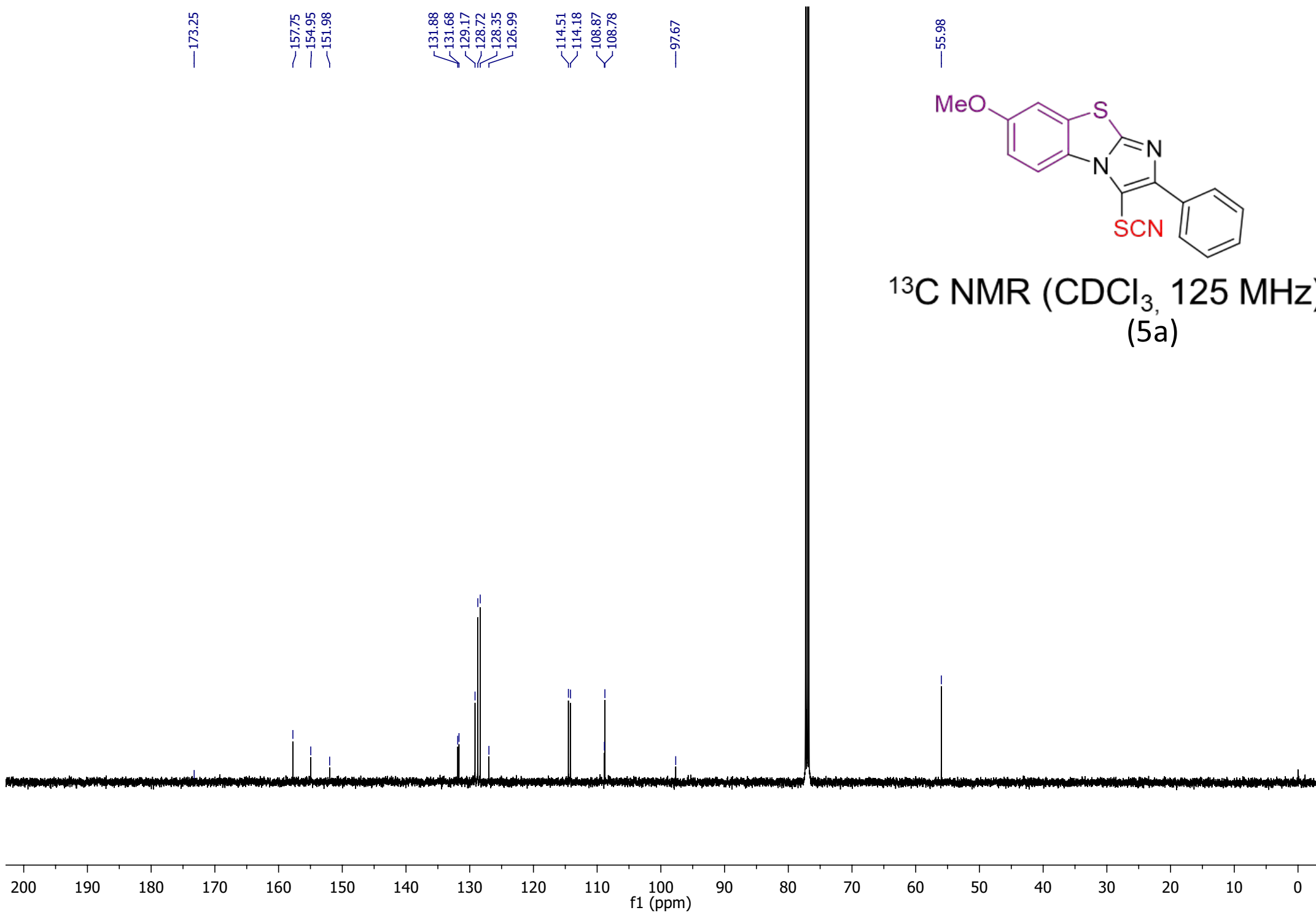
8.401
8.383
8.003
8.001
7.987
7.558
7.555
7.544
7.541
7.529
7.494
7.492
7.489
7.477
7.472
7.464
7.462
7.460
7.301
7.296
7.169
7.164
7.151
7.146

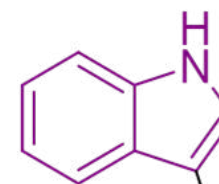
3.931



¹H NMR (CDCl₃, 500 MHz)
(5a)







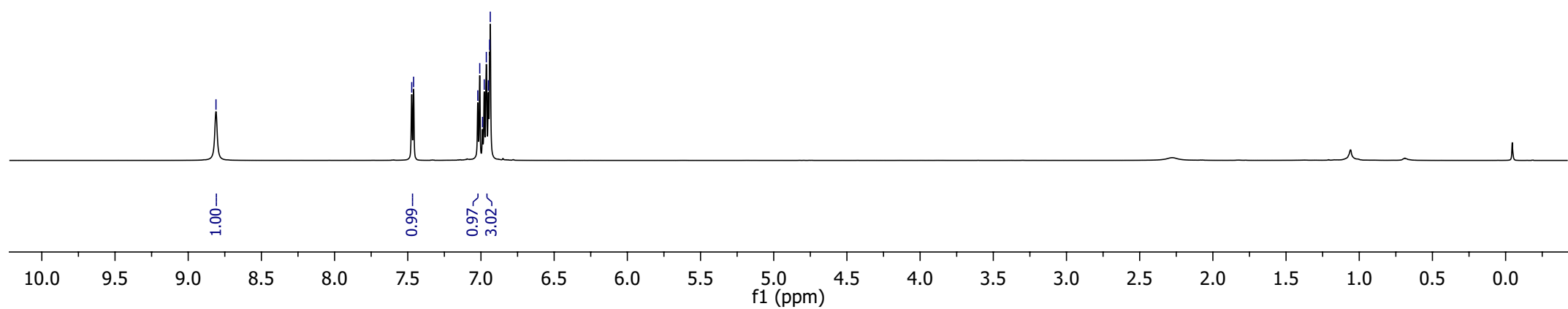
SCN

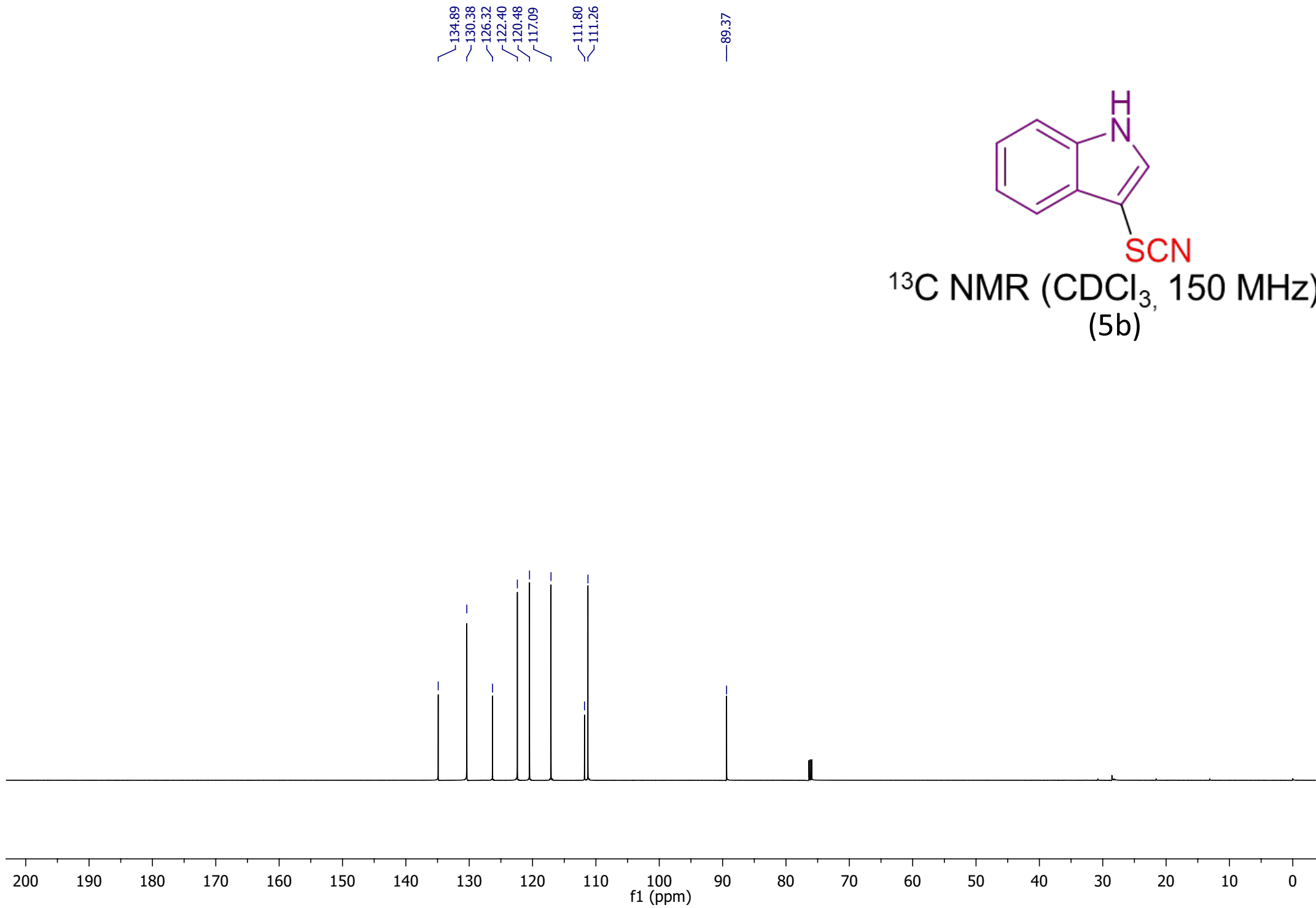
^1H NMR (CDCl_3 , 600 MHz)

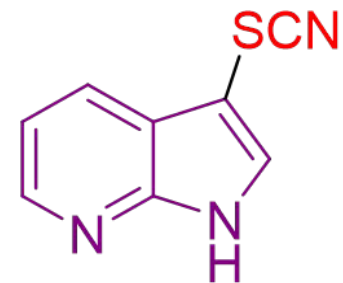
(5b)

8.810

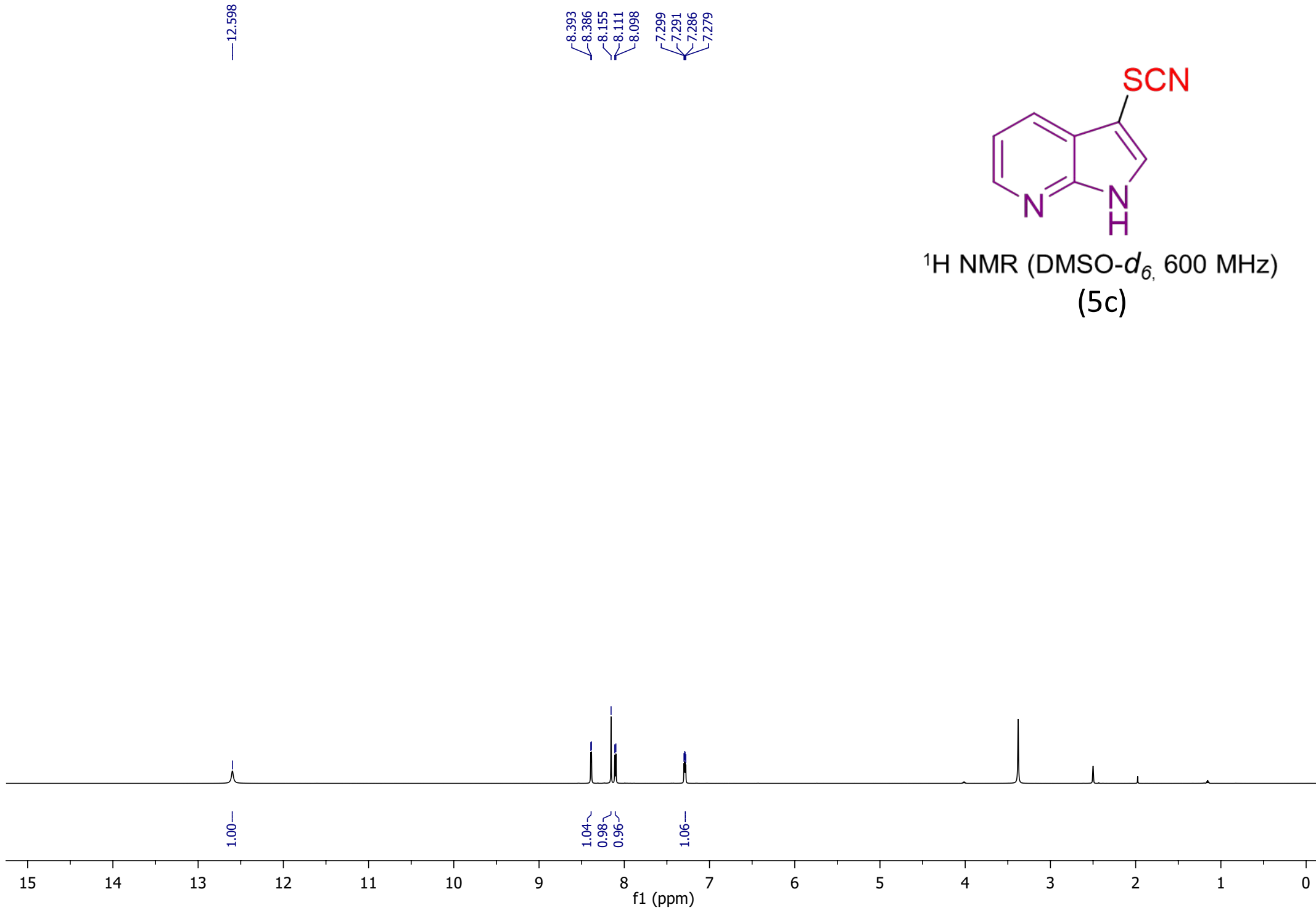
7.473
7.460
7.022
7.008
6.989
6.978
6.963
6.949
6.941
6.936







^1H NMR (DMSO- d_6 , 600 MHz)
(5c)

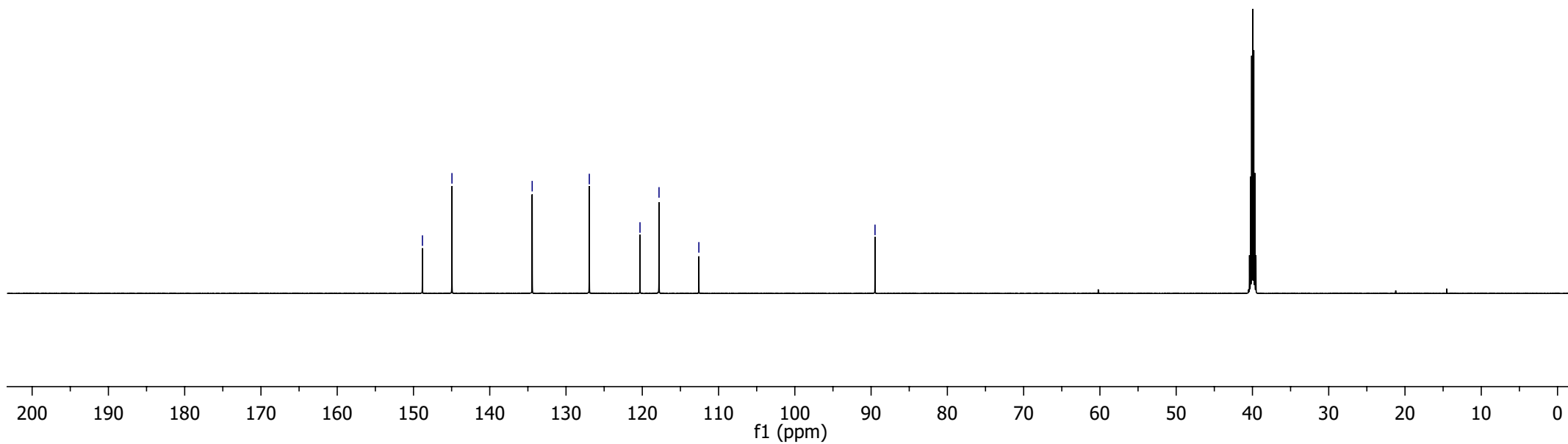


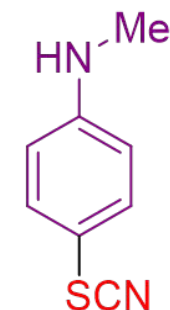
— 148.83
— 144.96
— 134.44
— 126.95
— 120.30
— 117.81
— 112.58

— 89.49

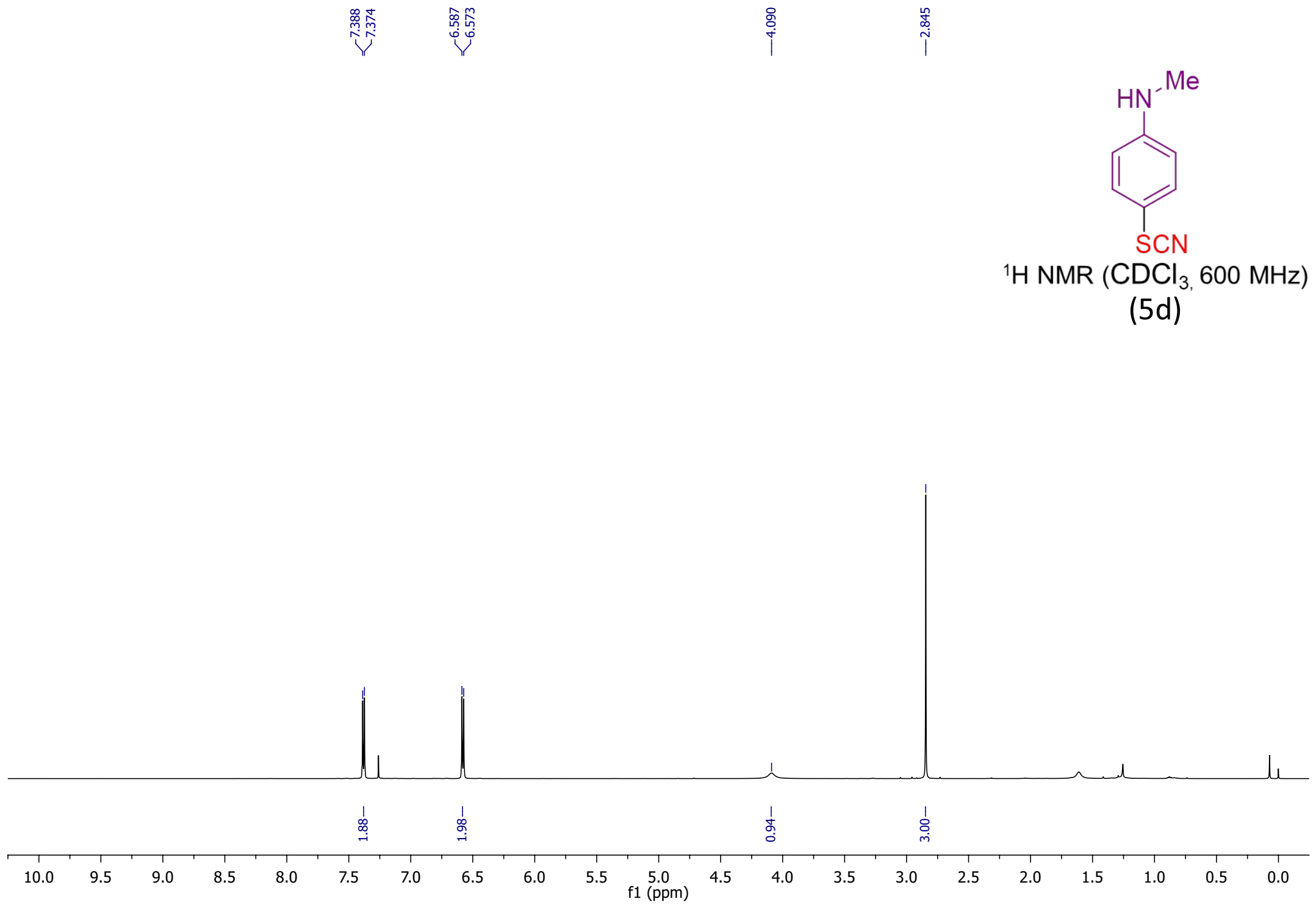


^{13}C NMR (DMSO- d_6 , 150 MHz)
(5c)





¹H NMR (CDCl₃, 600 MHz)
(5d)



—150.08

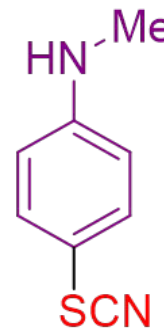
—133.72

—112.36

—111.63

—106.49

—29.23



¹³C NMR (CDCl₃, 150 MHz)
(5d)

