

Supporting Information

Copper-catalyzed sequential *N*-arylation of *C*-amino-*NH*-azoles

D. Nageswar Rao,^{a,b} Sk. Rasheed,^{a,b} Ram A. Vishwakarma^b and Parthasarathi Das^{a,b,*}

^a Academy of Scientific and Innovative Research (AcSIR)

^b Medicinal Chemistry Division, Indian Institute of Integrative Medicine (CSIR), Jammu 180001, India

Email: partha@iiim.ac.in

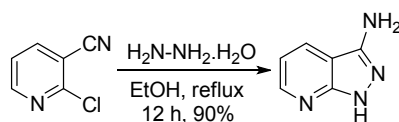
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1. General information

All purchased chemicals were used without further purification. All reactions were performed under open air. Analytical thin layer chromatography was performed using TLC pre-coated silica gel 60 F254 MERCK (20x20 cm). TLC plates were visualized by exposing UV light or by iodine vapors. Organic solutions were concentrated by rotary evaporation on BUCHI-Switzerland; R-120 rotary evaporator and vacuum pump V-710. Flash column chromatography was performed on Merck flash silica gel 100-200 mesh size. Melting points of solid compounds were determined on BUCHI-B-545-Switzerland melting point apparatus. ^1H and ^{13}C NMR spectra were recorded with BRUCKER 500 and 400 MHz NMR instruments. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl_3 as the internal standard (^1H NMR: TMS at 0.00 ppm, CHCl_3 at 7.24 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of $\text{DMSO}-d_6$ as the internal standard (^1H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 40.0 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of Acetone- d_6 as the internal standard (^1H NMR: TMS at 0.00 ppm, Acetone at 2.09 ppm; ^{13}C NMR: Acetone at 29.9 ppm, 206.7 ppm). All the NMR spectra were processed in MestReNova. HRMS spectra were recorded with LCMS-QTOF Module No. G6540 A (UHD) instrument.

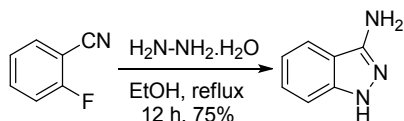
2. General procedure for the synthesis of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine



A round bottom flask equipped with a magnetic stirrer bar was charged with 2-chloronicotinonitrile (5 gr, 1 equiv), in 20 mL of ethanol and hydrazine hydrate (8.78 mL, 5 equiv) was added into the flask. The reaction mixture was stirred for 12 h at reflux temperature of ethanol. The progress of the reaction was monitored by TLC and after completion of the reaction the solvent was removed with an aid of rotatory evaporator. 10 ml of water was added to the crude reaction mixture and stirred at room temperature for 1 h to remove the extra amount of hydrazine hydrate. The crude reaction mixture was filtered through Buchner funnel to give the pure yellow color solid product with 90% yield.

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.92 (s, 1H), 8.34 (dd, $J = 4.5, 1.5$ Hz, 1H), 8.25 – 7.87 (m, 1H), 6.95 (dd, $J = 7.9, 4.6$ Hz, 1H), 5.55 (s, 2H).

3. General procedure for the synthesis of 1*H*-indazol-3-amine

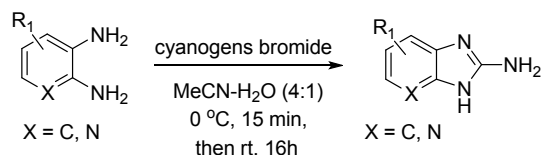


A round bottom flask equipped with a magnetic stirrer bar was charged with 2-fluorobenzonitrile (1 gr, 1 equiv), in 5 mL of ethanol and hydrazine hydrate (2.01 mL, 5 equiv) was added into the flask. The reaction mixture was stirred for 12 h at reflux temperature of ethanol. The progress of the reaction was

monitored by TLC and after completion of the reaction the solvent was removed with an aid of rotatory evaporator. 5 ml of water was added to the crude reaction mixture and stirred at room temperature for 1 h to remove the extra amount of hydrazine hydrate. The crude reaction mixture was filtered through Buchner funnel to give the off white colour solid product with 75% yield.

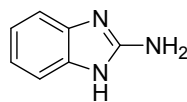
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 11.35 (s, 1H), 7.63 – 7.61 (m, 1H), 7.28 – 7.24 (m, 2H), 6.95 – 6.92 (m, 1H), 5.23 (s, 2H).

4. General procedure for the synthesis of 2-aminobenzimidazoles^[1]



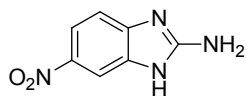
To a stirred solution of 1,2-diaminobenzene derivative (1.0 equiv) in MeCN-H₂O (4:1) was added cyanogens bromide (1.1 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and then warmed to room temperature and stirred for 16 h. The progress of the reaction was monitored by TLC and after completion of the reaction, the reaction mixture was extracted with EtOAc and the organic phase was washed with sat. aq. NaHCO₃ dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography to give pure 2-aminobenzimidazole derivative.

1H-benzo[d]imidazol-2-amine



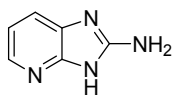
Following general procedure for the synthesis of 2-amino benzimidazoles, a mixture of benzene 1,2-diamine (100 mg, 0.925 mmol), cyanogens bromide (108 mg, 1.018 mmol) and MeCN-H₂O (4:1, 5 mL) was stirred at room temperature for 16 h. the crude product was purified via flash chromatography (EtOAc/MeOH, 10:1) to provide the title compound as a light brown colour solid (80% yield). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 10.70 (br, 1H), 7.13 – 7.06 (m, 2H), 6.85 (dd, $J = 5.7, 3.2$ Hz, 2H), 6.13 (br, 2H).

6-nitro-1H-benzo[d]imidazol-2-amine



Following general procedure for the synthesis of 2-amino benzimidazoles, a mixture of 4-nitro benzene 1,2-diamine (100 mg, 0.653 mmol), cyanogens bromide (76.2 mg, 0.718 mmol) and MeCN-H₂O (4:1, 5 mL) was stirred at room temperature for 16 h. the crude product was purified via flash chromatography (EtOAc/MeOH, 9:2) to provide the title compound as a thick yellow colour solid (75% yield). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.99 (d, $J = 2.0$ Hz, 1H), 7.92 (dd, $J = 8.7, 2.2$ Hz, 1H), 7.23 (d, $J = 8.7$ Hz, 1H), 6.99 (br, 2H).

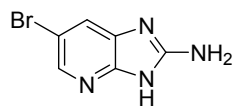
3H-imidazo[4,5-b]pyridin-2-amine



Following general procedure for the synthesis of 2-amino benzimidazoles, a mixture of pyridine-2,3-diamine (100 mg, 0.917 mmol), cyanogens bromide (107 mg, 1.009 mmol) and MeCN-H₂O (4:1, 5 mL) was stirred at room temperature for 24 h. the crude product was purified via flash chromatography (EtOAc/MeOH, 8:2) to provide the title compound as a brown

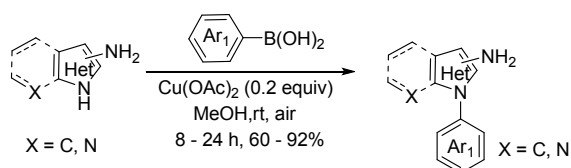
colour solid (55% yield). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.86 (d, $J = 4.1$ Hz, 1H), 7.35 (dd, $J = 7.6$, 1.3 Hz, 1H), 6.83 (dd, $J = 7.5$, 5.1 Hz, 1H), 6.52 (br, 2H).

6-bromo-3H-imidazo[4,5-b]pyridin-2-amine



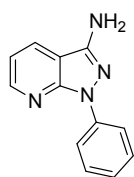
Following general procedure for the synthesis of 2-amino benzimidazoles, a mixture of 5-bromo pyridine-2,3-diamine (100 mg, 0.534 mmol), cyanogens bromide (62.3 mg, 0.588 mmol) and $\text{MeCN-H}_2\text{O}$ (4:1, 5 mL) was stirred at room temperature for 24 h. the crude product was purified via flash chromatography (EtOAc/MeOH , 8:2) to provide the title compound as a brown colour solid (50% yield). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.92 (s, 1H), 7.53 (s, 1H), 6.81 (br, 2H).

5 General procedure A: Sequential *N*-arylation of *C*-amino-NH-azoles



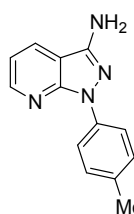
To a stirred solution of *C*-amino-*NH*-azole derivative (1.0 equiv) in MeOH (2 mL) was added aryl/hetero aryl boronic acid (1.1 equiv) and Cu(OAc)_2 (0.2 equiv) at room temperature. The reaction mixture was stirred at room temperature for 8-24 h. The progress of the reaction was monitored by TLC and after completion of the reaction. The crude product was purified by column chromatography without any extraction to give pure aryl amino azole derivative.

1-phenyl-1H-pyrazolo[3,4-*b*]pyridin-3-amine(2a)



Following general procedure A, a mixture of 1H-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), phenylboronic acid (100 mg, 0.82 mmol), Cu(OAc)_2 (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 8h. The crude product was purified via flash chromatography (Hexanes/EtOAc , 7:3) to provide the title compound as a light brown colour solid (141 mg, 90%), mp 186-188 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.58 (dd, $J = 4.6$, 1.5 Hz, 1H), 8.24 – 8.19 (m, 2H), 7.95 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.10 (dd, $J = 8.0$, 4.6 Hz, 1H), 4.30 (br, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 149.4, 148.5, 145.9, 138.6, 127.9, 127.7, 123.5, 118.9, 114.7, 108.0. **HRMS** (ESI): calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_4$ $[\text{M}+\text{H}]^+$, 211.0978; found: 211.0973.

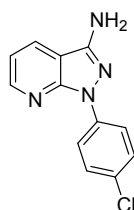
1-(*p*-tolyl)-1H-pyrazolo[3,4-*b*]pyridin-3-amine(2b)



Following general procedure A, a mixture of 1H-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), 4-methyl phenylboronic acid (111 mg, 0.82 mmol), Cu(OAc)_2 (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 9h. The crude product was purified via flash chromatography (Hexanes/EtOAc , 7:3) to provide the title compound as a off white colour solid (145 mg, 87%), mp 123-125 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 (dd, $J = 4.6$, 1.5 Hz, 1H), 8.05 (d, $J = 8.5$ Hz, 2H), 7.94 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.07 (dd, $J = 8.0$, 4.6 Hz, 1H), 4.26 (br, 2H), 2.38 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.5, 146.7, 137.2,

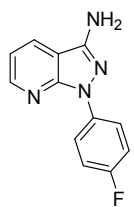
135.7, 134.3, 129.5, 128.6, 120.2, 115.5, 108.8, 20.9. **HRMS** (ESI): calcd. for C₁₃H₁₃N₄ [M+H]⁺, 225.1135; found: 225.1130.

1-(4-chlorophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(2c)



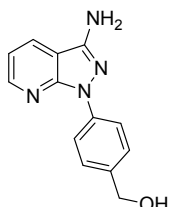
Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), 4-chloro phenylboronic acid (128 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 9h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a off white colour solid (147 mg, 81%), mp 182-184 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.58 (dd, *J* = 4.6, 1.3 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.95 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.12 (dd, *J* = 7.9, 4.6 Hz, 1H), 4.30 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 149.6, 147.2, 136.9, 129.4, 128.9, 128.8, 128.4, 120.8, 116.0, 109.3. **HRMS** (ESI): calcd. for C₁₂H₁₀ClN₄ [M+H]⁺, 245.0589; found: 245.0588.

1-(4-fluorophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(2d)



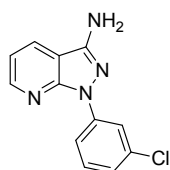
Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), 4-fluoro phenylboronic acid (115 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 10h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a thick brown colour solid (146 mg, 86%), mp 150-152 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.56 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.23 – 8.12 (m, 2H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.23 – 7.12 (m, 2H), 7.10 (dd, *J* = 8.0, 4.6 Hz, 1H), 4.30 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 160.7, 158.8, 150.3, 149.6, 147.0, 128.8, 121.5 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 12.5 Hz), 115.5, 108.9. **HRMS** (ESI): calcd. for C₁₂H₁₀FN₄ [M+H]⁺, 229.0884; found: 229.0879.

(4-(3-amino-1*H*-pyrazolo[3,4-*b*]pyridin-1-yl)phenyl)methanol(2e)



Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), 4-hydroxy methyl phenylboronic acid (125 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 18h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a yellow colour semi solid (147 mg, 82%). **¹H NMR** (400 MHz, CDCl₃) δ 8.61 – 8.53 (m, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.10 (dd, *J* = 7.9, 4.6 Hz, 1H), 4.73 (d, *J* = 9.7 Hz, 2H), 4.60 (s, 1H), 4.34 (br, 2H). **¹³C NMR** (125 MHz, Acetone-*d*₆) δ 150.0, 140.2, 138.5, 134.9, 130.5, 129.0, 127.9, 119.3, 116.4, 115.7, 64.4. **HRMS** (ESI): calcd. for C₁₃H₁₃N₄O [M+H]⁺, 241.1084; found: 241.1079.

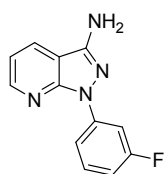
1-(3-chlorophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(2f)



Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), 3-chloro phenylboronic acid (128 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 10h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a light brown colour solid (162 mg, 89%), mp 184-186 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.60 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.35 (t, *J* = 2.0 Hz, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.4 Hz, 1H),

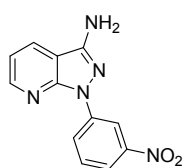
7.39 (t, $J = 8.1$ Hz, 1H), 7.20 – 7.08 (m, 2H), 4.32 (br, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.8, 149.6, 147.3, 140.8, 134.6, 129.9, 128.7, 124.1, 119.5, 117.3, 116.1, 109.5. HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{10}\text{ClN}_4$ $[\text{M}+\text{H}]^+$, 245.0589; found: 245.0583.

1-(3-fluorophenyl)-1H-pyrazolo[3,4-b]pyridin-3-amine(2g)



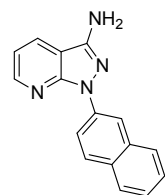
Following general procedure A, a mixture of 1H-pyrazolo[3,4-b]pyridin-3-amine (100 mg, 0.746 mmol), 3-fluoro phenylboronic acid (115 mg, 0.82 mmol), $\text{Cu}(\text{OAc})_2$ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a off white colour solid (145 mg, 85%), mp 128-130°C. ^1H NMR (400 MHz, CDCl_3) δ 8.61 – 8.55 (m, 1H), 8.14 – 8.06 (m, 2H), 7.94 (d, $J = 7.9$ Hz, 1H), 7.41 (dd, $J = 15.0, 8.3$ Hz, 1H), 7.11 (dd, $J = 7.9, 4.6$ Hz, 1H), 6.88 (td, $J = 8.2, 2.1$ Hz, 1H), 4.36 (br, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 164.0, 162.1, 150.7, 149.6, 147.3, 130.1 (d, $J = 9.2$ Hz), 128.8, 116.2, 114.7 (d, $J = 2.8$ Hz), 110.8 (d, $J = 21.3$ Hz), 109.5, 106.8 (d, $J = 27.0$ Hz). HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{10}\text{FN}_4$ $[\text{M}+\text{H}]^+$, 229.0884; found: 229.0883.

1-(3-nitrophenyl)-1H-pyrazolo[3,4-b]pyridin-3-amine(2h)



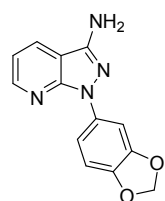
Following general procedure A, a mixture of 1H-pyrazolo[3,4-b]pyridin-3-amine (100 mg, 0.746 mmol), 3-nitro phenylboronic acid (137 mg, 0.82 mmol), $\text{Cu}(\text{OAc})_2$ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 15h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 6:4) to provide the title compound as a yellow solid (152 mg, 80%), mp 232-234 °C. ^1H NMR (400 MHz, Acetone- d_6) δ 9.31 (t, $J = 2.0$ Hz, 1H), 8.93 – 8.86 (m, 1H), 8.66 (dd, $J = 4.6, 1.3$ Hz, 1H), 8.35 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.99 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.75 (t, $J = 8.2$ Hz, 1H), 7.28 (dd, $J = 7.9, 4.7$ Hz, 1H), 5.88 (br, 2H). ^{13}C NMR (125 MHz, Acetone- d_6) δ 152.1, 150.5, 150.4, 149.6, 142.2, 131.1, 130.8, 124.3, 118.0, 117.5, 113.2, 111.7. HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_5\text{O}_2$ $[\text{M}+\text{H}]^+$, 256.0829; found: 256.0840.

1-(naphthalen-2-yl)-1H-pyrazolo[3,4-b]pyridin-3-amine(2i)



Following general procedure A, a mixture of 1H-pyrazolo[3,4-b]pyridin-3-amine (100 mg, 0.746 mmol), 2-naphthyl boronic acid (141 mg, 0.82 mmol), $\text{Cu}(\text{OAc})_2$ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 8h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a brown colour solid (155 mg, 80%), mp 126-128 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.66 (d, $J = 1.9$ Hz, 1H), 8.62 (dd, $J = 4.6, 1.5$ Hz, 1H), 8.49 (dd, $J = 9.0, 2.1$ Hz, 1H), 7.98 – 7.89 (m, 3H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.51 – 7.46 (m, 1H), 7.45 – 7.40 (m, 1H), 7.11 (dd, $J = 7.9, 4.6$ Hz, 1H), 4.35 (br, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 150.7, 149.6, 147.2, 137.3, 133.8, 130.8, 128.8, 128.8, 128.0, 127.68, 126.4, 125.0, 119.7, 116.6, 115.9, 109.3. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_4$ $[\text{M}+\text{H}]^+$, 261.1135; found: 261.1131.

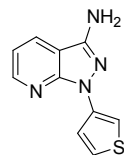
1-(benzo[d][1,3]dioxol-5-yl)-1H-pyrazolo[3,4-b]pyridin-3-amine(2j)



Following general procedure A, a mixture of 1H-pyrazolo[3,4-b]pyridin-3-amine (100 mg, 0.746 mmol), benzo[d][1,3]dioxol-5-ylboronic acid (136 mg, 0.82 mmol), $\text{Cu}(\text{OAc})_2$ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as

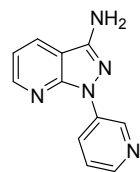
a brown colour solid (161 mg, 85%), mp 146-148 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.55 (dd, *J* = 4.6, 1.6 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (d, *J* = 2.1 Hz, 1H), 7.62 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.08 (dd, *J* = 8.0, 4.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.00 (s, 2H), 4.26 (br, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 149.5, 147.8, 146.7, 144.7, 134.1, 128.7, 115.6, 113.7, 108.7, 108.1, 102.8, 101.3. HRMS (ESI): calcd. for C₁₃H₁₁N₄O₂ [M+H]⁺, 255.0877; found: 255.0882.

1-(thiophen-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(2k)



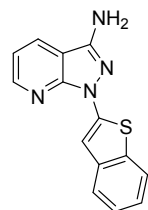
Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), thiophen-3-ylboronic acid (105 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 8h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a brown colour solid (145 mg, 90%), mp 103-105 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.58 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.89 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.82 (dd, *J* = 3.2, 1.2 Hz, 1H), 7.38 (dd, *J* = 5.2, 3.3 Hz, 1H), 7.08 (dd, *J* = 8.0, 4.6 Hz, 1H), 4.28 (br, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 149.8, 146.9, 138.0, 128.7, 125.0, 121.0, 115.7, 109.0, 108.4 (signals for pyrazolopyridine carbons were too weak to observe). HRMS (ESI): calcd. for C₁₀H₉N₄S [M+H]⁺, 217.0543; found: 217.0535.

1-(pyridin-3-yl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(2l)



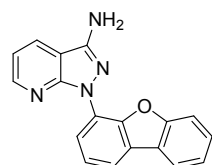
Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), pyridin-3-ylboronic acid (101 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 24h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 5:5) to provide the title compound as a light brown colour semi solid (94.4 mg, 60%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.46 (d, *J* = 2.1 Hz, 1H), 8.67 – 8.52 (m, 2H), 8.39 – 8.29 (m, 2H), 7.50 (dd, *J* = 8.4, 4.7 Hz, 1H), 7.24 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.37 (br, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 150.4, 149.8, 149.5, 143.9, 139.3, 130.8, 124.6, 123.7, 116.2, 110.1, 105.2. HRMS (ESI): calcd. for C₁₁H₁₀N₅ [M+H]⁺, 212.0931; found: 212.0985.

1-(benzo[*b*]thiophen-2-yl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(2m)



Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), benzo[*b*]thiophen-2-ylboronic acid (146 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 6:4) to provide the title compound as a brown colour solid (183 mg, 92%), mp 180-182 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, *J* = 3.9 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.90 (s, 1H), 7.76 (dd, *J* = 17.6, 7.8 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.26 (s, 1H), 7.16 (dd, *J* = 7.6, 4.7 Hz, 1H), 4.43 (br, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 150.0, 149.9, 149.6, 141.1, 139.3, 133.3, 131.0, 124.7, 122.7, 122.4, 121.8, 116.6, 110.4, 105.1. HRMS (ESI): calcd. for C₁₄H₁₁N₄S [M+H]⁺, 267.0699; found: 267.0701.

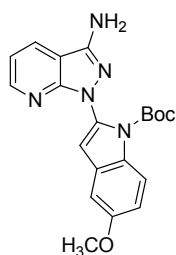
1-(dibenzo[*b,d*]furan-4-yl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(2n)



Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), dibenzo[*b,d*]furan-4-ylboronic acid (174 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 8h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 6:4) to provide the

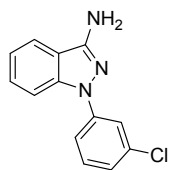
title compound as a brown colour solid (201 mg, 90%), mp 188-190 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.55 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.05 – 7.93 (m, 3H), 7.92 – 7.86 (m, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.46 (ddd, *J* = 12.2, 9.7, 4.5 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.12 (dd, *J* = 8.0, 4.6 Hz, 1H), 4.42 (br, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 156.4, 151.5, 149.9, 149.4, 147.7, 128.8, 127.4, 126.6, 124.1, 123.6, 123.5, 123.1, 122.9, 120.7, 119.3, 116.0, 112.2, 108.4. **HRMS** (ESI): calcd. for C₁₈H₁₃N₄O [M+H]⁺, 301.1084; found: 301.1079.

tert-butyl 2-(3-amino-1*H*-pyrazolo[3,4-*b*]pyridin-1-yl)-5-methoxy-1*H*-indole-1-carboxylate(2o)



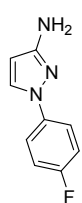
Following general procedure A, a mixture of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (100 mg, 0.746 mmol), (1-(tert-butoxycarbonyl)-5-methoxy-1*H*-indol-2-yl)boronic acid (239 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 6:4) to provide the title compound as a brown colour solid (249 mg, 88%), mp 168-170 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.51 (dd, *J* = 4.5, 1.3 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.11 (dd, *J* = 7.9, 4.6 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.78 (s, 1H), 4.29 (br, 2H), 3.86 (s, 3H), 1.15 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 155.9, 152.7, 149.9, 149.1, 147.4, 131.5, 130.4, 128.7, 127.8, 116.5, 115.9, 114.1, 108.1, 107.9, 103.4, 83.3, 55.6, 27.5. **HRMS** (ESI): calcd. for C₂₀H₂₂N₅O₃ [M+H]⁺, 380.1717; found: 380.1704.

1-(3-chlorophenyl)-1*H*-indazol-3-amine(2p)



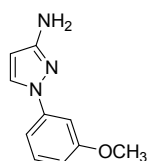
Following general procedure A, a mixture of 1*H*-indazol-3-amine (100 mg, 0.751 mmol), 3-chloro phenylboronic acid (129 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a brown colour semi solid (132 mg, 72%). **¹H NMR** (400 MHz, CDCl₃) δ 7.68 (dd, *J* = 7.5, 5.3 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.46 – 7.39 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.18 (dd, *J* = 10.0, 2.8 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 4.33 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 149.5, 141.6, 139.6, 135.0, 130.3, 128.2, 124.8, 121.1, 120.4, 119.8, 118.9, 117.0, 110.3. **HRMS** (ESI): calcd. for C₁₃H₁₁ClN₃ [M+H]⁺, 244.0636; found: 244.0631.

1-(4-fluorophenyl)-1*H*-pyrazol-3-amine(2q)



Following general procedure A, a mixture of 1*H*-pyrazol-3-amine (100 mg, 1.204 mmol), 4-fluoro phenylboronic acid (185 mg, 1.324 mmol), Cu(OAc)₂ (44 mg, 0.240 mmol) and MeOH (2 mL) was stirred at rt for 15h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 8:2) to provide the title compound as a brown colour solid (187 mg, 88%), mp 100-102 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.61 (d, *J* = 2.4 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 5.84 (d, *J* = 2.4 Hz, 1H), 4.06 (s, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 161.2, 159.3, 155.8, 127.9, 119.5 (d, *J* = 8.2 Hz), 116.1 (d, *J* = 22.9 Hz), 96.1. **HRMS** (ESI): calcd. for C₉H₉FN₃ [M+H]⁺, 178.0775; found: 178.0773.

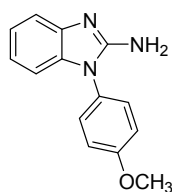
1-(3-methoxyphenyl)-1*H*-pyrazol-3-amine(2r)



Following general procedure A, a mixture of 1*H*-pyrazol-3-amine (100 mg, 1.204 mmol), 3-methoxy phenylboronic acid (201mg, 1.324 mmol), Cu(OAc)₂ (44 mg, 0.150 mmol) and

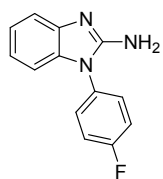
MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a brown colour liquid (186 mg, 82%). **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 2.4 Hz, 1H), 7.26 (t, *J* = 8.2 Hz, 1H), 7.17 (t, *J* = 2.0 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.72 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.81 (d, *J* = 2.4 Hz, 1H), 4.28 – 3.84 (br, 2H), 3.83 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 160.5, 155.8, 141.2, 130.1, 128.0, 111.0, 109.8, 103.7, 96.3, 55.4. **HRMS** (ESI): calcd. for C₁₀H₁₂N₃O [M+H]⁺, 190.0975; found: 190.0979.

1-phenyl-1*H*-benzo[*d*]imidazol-2-amine(3a)



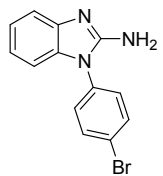
Following general procedure A, a mixture of 1*H*-benzo[*d*]imidazol-2-amine (100 mg, 0.751 mmol), 4-methoxy phenylboronic acid (126 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 4:6) to provide the title compound as a brown colour solid (165 mg, 92%), mp 176-178 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.23 (br, 2H), 3.80 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 158.7, 152.4, 140.9, 134.3, 127.2, 126.2, 120.8, 118.9, 115.2, 114.4, 107.2, 54.5. **HRMS** (ESI): calcd. for C₁₄H₁₄N₃O [M+H]⁺, 240.1132; found: 240.1130.

1-(4-fluorophenyl)-1*H*-benzo[*d*]imidazol-2-amine(3b)



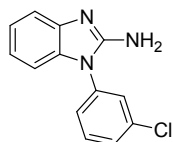
Following general procedure A, a mixture of 1*H*-benzo[*d*]imidazol-2-amine (100 mg, 0.751 mmol), 4-fluoro phenylboronic acid (116 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 4:6) to provide the title compound as a off white colour solid (150 mg, 88%), mp 158-160 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.50 – 7.40 (m, 3H), 7.31 (t, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 5.93 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 163.5, 153.2, 140.0, 134.3, 130.1 (d, *J* = 3.1 Hz), 128.9 (d, *J* = 8.8 Hz), 122.6, 120.6, 117.5 (d, *J* = 23.0 Hz), 115.6, 108.3. **HRMS** (ESI): calcd. for C₁₃H₁₁FN₃ [M+H]⁺, 228.0932; found: 228.0938.

1-(4-bromophenyl)-1*H*-benzo[*d*]imidazol-2-amine(3c)



Following general procedure A, a mixture of 1*H*-benzo[*d*]imidazol-2-amine (100 mg, 0.751 mmol), 4-bromo phenylboronic acid (166 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 14h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 4:6) to provide the title compound as a off white colour solid (183 mg, 85%), mp 180-182 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.20 – 7.13 (m, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 4.94 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 152.8, 142.1, 134.6, 133.9, 133.6, 128.3, 122.6, 122.3, 120.3, 116.5, 108.2. **HRMS** (ESI): calcd. for C₁₃H₁₁BrN₃ [M+H]⁺, 288.0131; found: 288.0129.

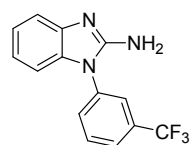
1-(3-chlorophenyl)-1*H*-benzo[*d*]imidazol-2-amine(3d)



Following general procedure A, a mixture of 1*H*-benzo[*d*]imidazol-2-amine (100 mg, 0.751 mmol), 3-chloro phenylboronic acid (129 mg, 0.826 mmol), Cu(OAc)₂ (27 mg,

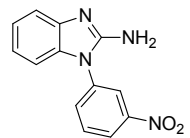
0.150 mmol) and MeOH (2 mL) was stirred at rt for 14h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 4:6) to provide the title compound as a yellow colour thick liquid (163 mg, 89%). **¹H NMR** (400 MHz, CDCl₃) δ 7.52 – 7.38 (m, 3H), 7.32 (ddd, *J* = 8.6, 7.6, 4.8 Hz, 2H), 7.12 – 7.05 (m, 1H), 7.00 – 6.89 (m, 2H), 5.23 (s, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 151.8, 140.5, 134.9, 134.9, 133.3, 130.3, 128.0, 125.8, 123.8, 121.4, 119.3, 115.2, 107.2. **HRMS** (ESI): calcd. for C₁₃H₁₁ClN₃ [M+H]⁺, 244.0636; found: 244.0630.

1-(3-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-2-amine(3e)



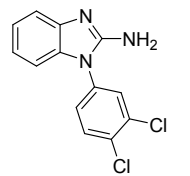
Following general procedure A, a mixture of 1H-benzo[d]imidazol-2-amine (100 mg, 0.751 mmol), 3-trifluoromethyl phenylboronic acid (157 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 16h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 4:6) to provide the title compound as a off white colour solid (170 mg, 82%), mp 123-125 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.72 (m, 3H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.41 (br, 2H). **¹³C NMR** (125 MHz, CDCl₃) δ 177.6, 153.0, 141.1, 135.4, 134.0, 133.0 (dd, *J* = 66.5, 33.2 Hz), 131.2, 130.0, 125.6 (dd, *J* = 7.1, 3.4 Hz), 123.7 (dd, *J* = 7.3, 3.6 Hz), 122.7, 120.5, 116.1, 108.1. **HRMS** (ESI): calcd. for C₁₄H₁₁F₃N₃ [M+H]⁺, 278.0900; found: 278.0892.

1-(3-nitrophenyl)-1H-benzo[d]imidazol-2-amine(3f)



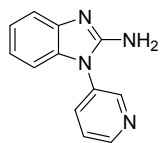
Following general procedure A, a mixture of 1H-benzo[d]imidazol-2-amine (100 mg, 0.751 mmol), 3-nitro phenylboronic acid (138 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 18h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 3:7) to provide the title compound as a yellow solid (162 mg, 85%), mp 214-216 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.38 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 5.17 (br, 2H). **¹³C NMR** (125 MHz, Acetone-*d*₆) δ 155.0, 150.2, 143.8, 137.5, 135.6, 134.2, 132.4, 123.8, 122.9, 122.8, 120.4, 116.6, 108.6. **HRMS** (ESI): calcd. for C₁₃H₁₁N₄O₂ [M+H]⁺, 255.0877; found: 255.0884.

1-(3,4-dichlorophenyl)-1H-benzo[d]imidazol-2-amine(3g)



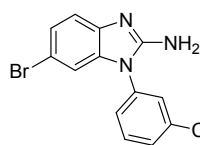
Following general procedure A, a mixture of 1H-benzo[d]imidazol-2-amine (100 mg, 0.751 mmol), 3,4 dichloro phenylboronic acid (158 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 14h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 4:6) to provide the title compound as a off white colour solid (173 mg, 83%), mp 178-180 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 5.50 (br, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 181.9, 152.8, 142.0, 134.4, 134.3, 133.1, 132.0, 128.6, 126.0, 122.6, 120.4, 116.5, 108.1. **HRMS** (ESI): calcd. for C₁₃H₁₀Cl₂N₃ [M+H]⁺, 278.0247; found: 278.0241.

1-(pyridin-3-yl)-1*H*-benzo[*d*]imidazol-2-amine(3h)



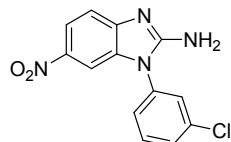
Following general procedure A, a mixture of 1*H*-benzo[*d*]imidazol-2-amine (100 mg, 0.751 mmol), 3-pyridyl boronic acid (102 mg, 0.826 mmol), Cu(OAc)₂ (27 mg, 0.150 mmol) and MeOH (2 mL) was stirred at rt for 24h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 2:8) to provide the title compound as a light brown colour solid (118 mg, 75%), mp 175-177 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.72 (s, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.26 (s, 1H), 7.04 (s, 1H), 6.93 – 6.82 (m, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 174.4, 172.3, 149.1, 147.7, 142.7, 134.9, 131.8, 124.9, 121.6, 119.1, 115.1, 107.5. HRMS (ESI): calcd. For C₁₂H₁₁N₄ [M+H]⁺, 211.0978; found: 211.0999.

6-bromo-1-(3-chlorophenyl)-1*H*-benzo[*d*]imidazol-2-amine(3i)



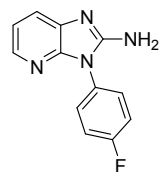
Following general procedure A, a mixture of 6-bromo-1*H*-benzo[*d*]imidazol-2-amine (100 mg, 0.473 mmol), 3-chloro phenylboronic acid (81 mg, 0.520 mmol), Cu(OAc)₂ (17 mg, 0.094 mmol) and MeOH (2 mL) was stirred at rt for 12h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 4:6) to provide the title compound as a brown colour thick liquid (125 mg, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.44 (m, 3H), 7.39 (d, *J* = 10.1 Hz, 1H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.09 (br, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 153.0, 141.2, 135.9, 135.9, 134.2, 131.4, 129.1, 126.9, 124.8, 122.5, 120.4, 116.0, 108.3. HRMS (ESI): calcd. for C₁₃H₁₀BrClN₃ [M+H]⁺, 321.9741; found: 321.9735.

1-(3-chlorophenyl)-6-nitro-1*H*-benzo[*d*]imidazol-2-amine(3j)



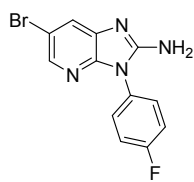
Following general procedure A, a mixture of 6-nitro-1*H*-benzo[*d*]imidazol-2-amine (100 mg, 0.561 mmol), 3-chloro phenylboronic acid (96 mg, 0.617 mmol), Cu(OAc)₂ (20 mg, 0.112 mmol) and MeOH (2 mL) was stirred at rt for 15h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 3:7) to provide the title compound as a yellow solid (129 mg, 80%), mp 228-230 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.02 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.69 (dd, *J* = 14.6, 7.4 Hz, 3H), 7.55 (d, *J* = 6.9 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.23 (br, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 149.7, 139.2, 134.9, 134.3, 131.8, 129.3, 127.3, 126.0, 118.7, 115.4, 113.9, 107.3, 103.2. HRMS (ESI): calcd. for C₁₃H₁₀ClN₄O₂ [M+H]⁺, 289.0487; found: 289.0492.

3-(4-methoxyphenyl)-3*H*-imidazo[4,5-*b*]pyridin-2-amine(3k)



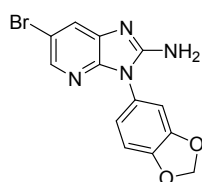
Following general procedure A, a mixture of 3*H*-imidazo[4,5-*b*]pyridin-2-amine (100 mg, 0.746 mmol), 4-fluoro phenylboronic acid (115 mg, 0.82 mmol), Cu(OAc)₂ (27 mg, 0.149 mmol) and MeOH (2 mL) was stirred at rt for 18h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 3:7) to provide the title compound as a light brown colour semi solid (128 mg, 75%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.81 (d, *J* = 4.6 Hz, 1H), 7.54 (dd, *J* = 8.3, 5.0 Hz, 3H), 7.43 (t, *J* = 8.7 Hz, 2H), 7.04 (s, 1H), 6.72 (br, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 171.9, 162.7, 160.3, 138.0, 129.8 (d, *J* = 9.1 Hz), 120.7, 117.7, 116.4 (d, *J* = 22.9 Hz) (signals for pyridoimidazole carbons were too weak to observe). HRMS (ESI): calcd. for C₁₂H₁₀FN₄ [M+H]⁺, 229.0884; found: 229.0878.

6-bromo-3-(4-fluorophenyl)-3*H*-imidazo[4,5-*b*]pyridin-2-amine(3l)



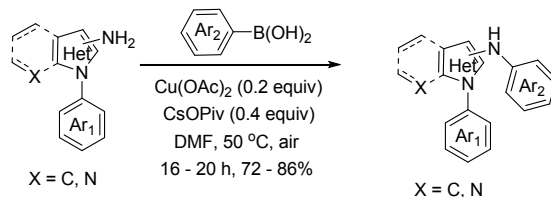
Following general procedure A, a mixture of 6-bromo-3*H*-imidazo[4,5-*b*]pyridin-2-amine (100 mg, 0.471 mmol), 4-fluoro phenylboronic acid (73 mg, 0.518 mmol), Cu(OAc)₂ (17 mg, 0.094 mmol) and MeOH (2 mL) was stirred at rt for 16h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 3:7) to provide the title compound as a light brown colour semi solid (112 mg, 78%), ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.86 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.54 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.43 (t, *J* = 8.7 Hz, 2H), 6.94 (br, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 162.9, 160.5, 156.2, 147.4, 137.5, 129.9 (d, *J* = 9.1 Hz), 129.4 (d, *J* = 2.8 Hz), 122.6, 116.5 (d, *J* = 22.9 Hz), 112.5. HRMS (ESI): calcd. for C₁₂H₉BrFN₄ [M+H]⁺, 306.9989; found: 306.9964.

3-(benzo[d][1,3]dioxol-5-yl)-6-bromo-3*H*-imidazo[4,5-*b*]pyridin-2-amine(3m)



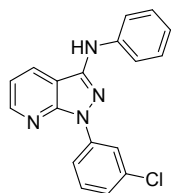
Following general procedure A, a mixture of 6-bromo-3*H*-imidazo[4,5-*b*]pyridin-2-amine (100 mg, 0.471 mmol), 3,4-(methylenedioxy)phenylboronic acid (86 mg, 0.518 mmol), Cu(OAc)₂ (17 mg, 0.094 mmol) and MeOH (2 mL) was stirred at rt for 18h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 3:7) to provide the title compound as a light brown colour semi solid (112 mg, 72%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.85 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.93 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.86 (s, 2H), 6.14 (br, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 156.4, 147.8, 147.6, 147.4, 137.5, 137.4, 126.5, 122.3, 121.4, 112.3, 108.7, 108.5, 101.8. HRMS (ESI): calcd. for C₁₃H₁₀BrN₄O₂ [M+H]⁺, 332.9982; found: 332.9978.

6 General procedure B: C-NH₂-arylation of N¹-aryl C-NH₂-azoles



To a stirred solution of N¹-aryl C-NH₂-azoles derivative (1.0 equiv) in DMF (1 mL) was added aryl/hetero aryl boronic acid (1.2 equiv) and Cu(OAc)₂ (0.2 equiv) and CsOPiv (0.4 equiv) at room temperature. The reaction mixture was stirred at 50 °C temperature for 16-20 h. The progress of the reaction was monitored by TLC and after completion of the reaction. 10 ml of ice cooled water was added to the reaction mixture at room temperature. The mixture was extracted with EtOAc (10 mL) further extracted two times with EtOAc (2 x 10 mL) and the combined organic phase was washed with sat. aq. NaHCO₃ dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography to give pure diaryl amino azole derivatives.

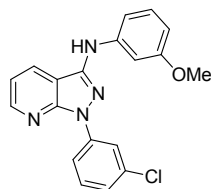
1-(3-chlorophenyl)-*N*-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(4a)



Following general procedure A, a mixture of 1-(3-chlorophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (50 mg, 0.205 mmol), phenylboronic acid (30 mg, 0.245 mmol), Cu(OAc)₂ (7.5 mg, 0.041 mmol), cesium pivalate (19 mg, 0.082 mmol) and DMF (1 mL) was stirred at 50 °C for 16 h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 8:2) to provide the title compound as a light brown semi solid (56 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, *J* = 3.7 Hz, 1H), 8.46 (d, *J* = 1.9 Hz, 1H),

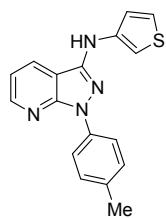
8.33 (d, $J = 8.2$ Hz, 1H), 7.98 (d, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 10.0$ Hz, 2H), 7.48 – 7.32 (m, 3H), 7.24 – 7.10 (m, 2H), 7.04 (t, $J = 7.3$ Hz, 1H), 6.47 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.3, 149.8, 144.2, 140.9, 140.91, 134.6, 129.9, 129.3, 128.8, 124.3, 121.7, 119.6, 117.5, 117.4, 116.3, 110.1. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{14}\text{ClN}_4$ $[\text{M}+\text{H}]^+$, 321.0902; found: 321.0896.

1-(3-chlorophenyl)-*N*-(3-methoxyphenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(4b)



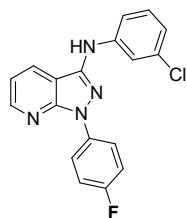
Following general procedure A, a mixture of 1-(3-chlorophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (50 mg, 0.205 mmol), 3-methoxy phenylboronic acid (37 mg, 0.245 mmol), $\text{Cu}(\text{OAc})_2$ (27 mg, 0.149 mmol), cesium pivalate (19 mg, 0.082 mmol) and DMF (1 mL) was stirred at 50 °C for 18h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 8:2) to provide the title compound as a brown colour thick liquid (59 mg, 82%). ^1H NMR (400 MHz, CDCl_3) δ 8.51 (d, $J = 3.1$ Hz, 1H), 8.34 (s, 1H), 8.23 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 7.7$ Hz, 1H), 7.31 (t, $J = 8.1$ Hz, 1H), 7.25 (s, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 7.8$ Hz, 1H), 7.02 (dd, $J = 7.5, 4.6$ Hz, 1H), 6.92 (d, $J = 7.7$ Hz, 1H), 6.50 (d, $J = 7.7$ Hz, 1H), 6.44 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 159.4, 149.0, 148.7, 142.9, 141.1, 139.8, 133.5, 128.9, 127.6, 123.1, 118.4, 116.3, 115.3, 109.1, 108.6, 106.1, 102.0, 54.2. HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{16}\text{ClN}_4\text{O}$ $[\text{M}+\text{H}]^+$, 351.1007; found: 351.1005.

N-(thiophen-3-yl)-1-(*p*-tolyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(4c)



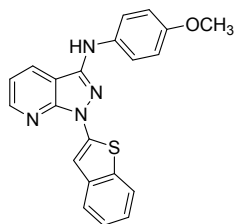
Following general procedure A, a mixture of 1-(*p*-tolyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (50 mg, 0.223 mmol), 3-thienyl boronic acid (34 mg, 0.267 mmol), $\text{Cu}(\text{OAc})_2$ (8 mg, 0.044 mmol), cesium pivalate (21 mg, 0.089 mmol) and DMF (1 mL) was stirred at 50 °C for 20h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 8:2) to provide the title compound as a brown colour semi solid (54.5 mg, 80%). ^1H NMR (500 MHz, CDCl_3) δ 8.51 (br, 1H), 8.08 (br, 2H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.23 (d, $J = 7.5$ Hz, 2H), 7.09 (br, 2H), 7.00 (br, 1H), 6.28 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, Acetone- d_6) δ 150.6, 150.3, 145.5, 140.3, 139.0, 134.1, 130.5, 130.20, 130.1, 119.9, 117.7, 116.7, 110.9, 79.2, 20.9. HRMS (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_4\text{S}$ $[\text{M}+\text{H}]^+$, 307.1012; found: 307.1019.

1-(3-chlorophenyl)-1-(4-fluorophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(4d)



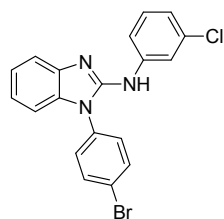
Following general procedure A, a mixture of 1-(4-fluorophenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (50 mg, 0.219 mmol), 3-chloro phenylboronic acid (41 mg, 0.263 mmol), $\text{Cu}(\text{OAc})_2$ (8 mg, 0.043 mmol), cesium pivalate (20 mg, 0.087 mmol) and DMF (1 mL) was stirred at 50 °C for 18h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 8:2) to provide the title compound as a off white colour solid (58 mg, 78%), mp 168-170 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.53 (br, 1H), 8.19 (br, 2H), 7.88 (d, $J = 6.5$ Hz, 1H), 7.52 (br, 1H), 7.29 (br, 1H), 7.22 – 7.04 (m, 4H), 6.90 (br, 1H), 6.44 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 159.9, 157.9, 148.8 (d, $J = 18.0$ Hz), 142.0, 141.3, 134.7, 133.8, 129.2, 127.5, 120.6 (d, $J = 8.2$ Hz), 120.2, 115.8, 115.2, 114.7 (d, $J = 22.5$ Hz), 113.9, 108.4. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{13}\text{ClFN}_4$ $[\text{M}+\text{H}]^+$, 339.0808; found: 339.0804.

1-(benzo[*b*]thiophen-2-yl)-*N*-(4-methoxyphenyl)-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine(4e)



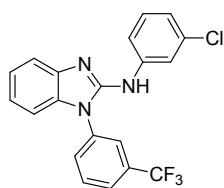
Following general procedure A, a mixture of 1-(benzo[b]thiophen-2-yl)-1H-pyrazolo[3,4-b]pyridin-3-amine (50 mg, 0.187 mmol), 4-methoxy phenylboronic acid (34 mg, 0.225 mmol), Cu(OAc)₂ (7 mg, 0.037 mmol) and DMF (1 mL) was stirred at 50 °C for 20h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 8:2) to provide the title compound as a brown colour semi solid (57 mg, 81%). ¹H NMR (500 MHz, CDCl₃) δ 8.67 (d, *J* = 4.2 Hz, 1H), 7.94 (br, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.3 Hz, 1H), 7.51 (br, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.26 (br, 1H), 7.12 (br, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.40 (s, 1H), 3.84 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 153.6, 150.4, 145.6, 140.8, 139.2, 134.5, 133.5, 131.0, 124.8, 122.9, 122.6, 122.0, 118.2, 117.4, 117.1, 114.2, 113.4, 110.6, 55.2. HRMS (ESI): calcd. for C₂₁H₁₇N₄OS [M+H]⁺, 373.1118; found: 373.1097.

1-(4-bromophenyl)-N-(3-chlorophenyl)-1H-benzo[d]imidazol-2-amine(4f)



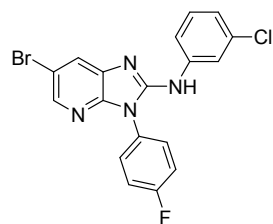
Following general procedure A, a mixture of 1-(4-bromophenyl)-1H-benzo[d]imidazol-2-amine (50 mg, 0.174 mmol), 3-chloro phenylboronic acid (32.5 mg, 0.208 mmol), Cu(OAc)₂ (6.3 mg, 0.034 mmol), cesium pivalate (16.2 mg, 0.069 mmol) and DMF (1 mL) was stirred at 50 °C for 18h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a off white colour solid (48.5 mg, 70%), mp 130-132 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.56 (dd, *J* = 6.9, 4.9 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.10 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.99 – 6.86 (m, 2H), 6.20 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 139.2, 133.7, 132.9, 132.2, 131.6, 129.1, 127.8, 123.6, 122.3, 121.6, 121.5, 120.4, 117.2, 116.6, 115.3, 107.3. HRMS (ESI): calcd. for C₁₉H₁₄BrClN₃ [M+H]⁺, 400.0034; found: 400.0074.

N-(3-chlorophenyl)-1-(3-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-2-amine(4g)



Following general procedure A, a mixture of 1-(3-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-2-amine (50 mg, 0.180 mmol), 3-chloro phenylboronic acid (33.6 mg, 0.216 mmol), Cu(OAc)₂ (6.5 mg, 0.036 mmol), cesium pivalate (16.8 mg, 0.072 mmol) and DMF (1 mL) was stirred at 50 °C for 20h. The crude product was purified via flash chromatography (Hexanes/EtOAc, 7:3) to provide the title compound as a brown colour semi solid (49.5 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.65 (m, 4H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.55 (br, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.15 (dd, *J* = 16.1, 7.8 Hz, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.97 (br, 1H), 6.91 (d, *J* = 7.8 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 177.6, 153.0, 141.1, 135.4, 134.0, 133.4, 133.0 (dd, *J* = 66.5, 33.2 Hz), 131.2, 130.0, 129.1, 126.5, 125.6 (dd, *J* = 7.1, 3.4 Hz), 124.3, 123.7 (dd, *J* = 7.3, 3.6 Hz), 122.7, 122.2, 120.5, 120.0, 116.1, 108.1. HRMS (ESI): calcd. for C₂₀H₁₄ClF₃N₃ [M+H]⁺, 388.0823; found: 388.0807.

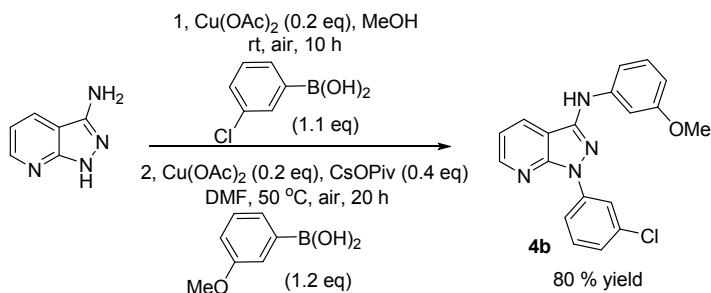
N-(4-bromophenyl)-3-(3-methoxyphenyl)-3H-imidazo[4,5-b]pyridin-2-amine(4h)



Following general procedure A, a mixture of 6-bromo-3-(4-fluorophenyl)-3H-imidazo[4,5-b]pyridin-2-amine (50 mg, 0.163 mmol), 3-chloro phenylboronic acid (31 mg, 0.196 mmol), Cu(OAc)₂ (6 mg, 0.032 mmol) and cesium pivalate (15.2 mg, 0.065 mmol) in DMF (1 mL) was stirred at 50 °C for 20h. The crude

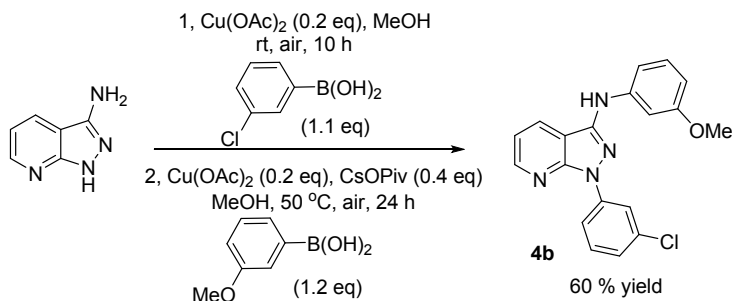
product was purified via flash chromatography (Hexanes/EtOAc, 8:2) to provide the title compound as a light brown colour semi solid (51.5 mg, 76%). ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 1.6 Hz, 1H), 7.97 (s, 1H), 7.76 (s, 1H), 7.54 – 7.48 (m, 3H), 7.36 (t, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 161.8, 141.8, 139.1, 136.0, 134.9, 130.2, 129.7 (d, *J* = 9.0 Hz), 128.1 (d, *J* = 3.5 Hz), 126.7, 123.9, 123.5, 118.9, 117.9 (d, *J* = 23.1 Hz), 116.8, 114.1. HRMS (ESI): calcd. for C₁₈H₁₂BrClFN₄ [M+H]⁺, 418.9892; found: 418.9878.

7 General procedures for the one-pot selective *N*-arylation of *C*-amino-*NH*-azoles



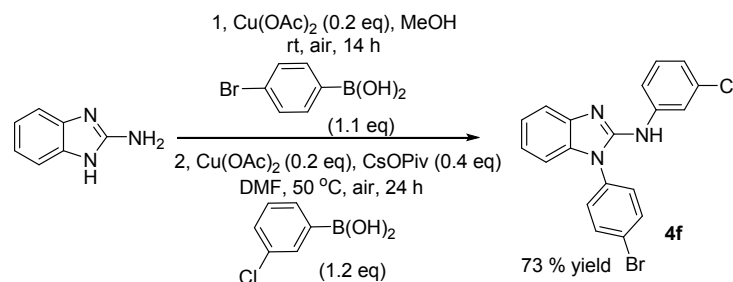
To a stirred solution of 1*H*-pyrazolo [3,4-*b*]pyridin-3-amine (50 mg, 0.373 mmol) in MeOH (2 mL) was added 3-chlorophenyl boronic acid (64 mg, 0.410 mmol) and Cu(OAc)₂ (13.5 mg, 0.074 mmol) at room temperature. The reaction mixture was stirred at room temperature for 10 h and after completion of the reaction. The solvent was removed with an aid of rotatory evaporator and then 3-methoxyphenyl boronic acid (68 mg, 0.447 mmol) and Cu(OAc)₂ (13.5 mg, 0.074 mmol) and CsOPiv (35 mg, 0.148 mmol) and DMF(1 mL) was added to the reaction mixture. The reaction mixture was stirred at 50 °C temperature for 20 h. The progress of the reaction was monitored by TLC and after completion of the reaction 10 ml of ice cooled water was added to the reaction mixture and mixture was extracted with EtOAc (10 mL) further extracted two times with EtOAc (2 x 10 mL) and the combined organic phase was washed with sat. aq. NaHCO₃, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography to give the final compound **4b** (101 mg, 80% yield).

One-pot sequential reaction in methanol as solvent instead of changing to DMF: Comparison of the yields (**4b**)



To a stirred solution of 1*H*-pyrazolo [3,4-*b*]pyridin-3-amine (50 mg, 0.373 mmol) in MeOH (2 mL) was added 3-chlorophenyl boronic acid (64 mg, 0.410 mmol) and Cu(OAc)₂ (13.5 mg, 0.074 mmol) at room temperature. The reaction mixture was stirred at room temperature for 10 h and after completion of the reaction. 3-methoxyphenyl boronic acid (68 mg, 0.447 mmol) and Cu(OAc)₂ (13.5 mg, 0.074 mmol) and

CsOPiv (35 mg, 0.148 mmol) was added to the crude reaction mixture. The reaction mixture was stirred at 50 °C temperature for 20 h. The progress of the reaction was monitored by TLC and after completion of the reaction 10 ml of ice cooled water was added to the reaction mixture and mixture was extracted with EtOAc (10 mL) further extracted two times with EtOAc (2 x 10 mL) and the combined organic phase was washed with sat. aq. NaHCO₃, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography to give the final compound **4b** (76 mg, 60% yield).



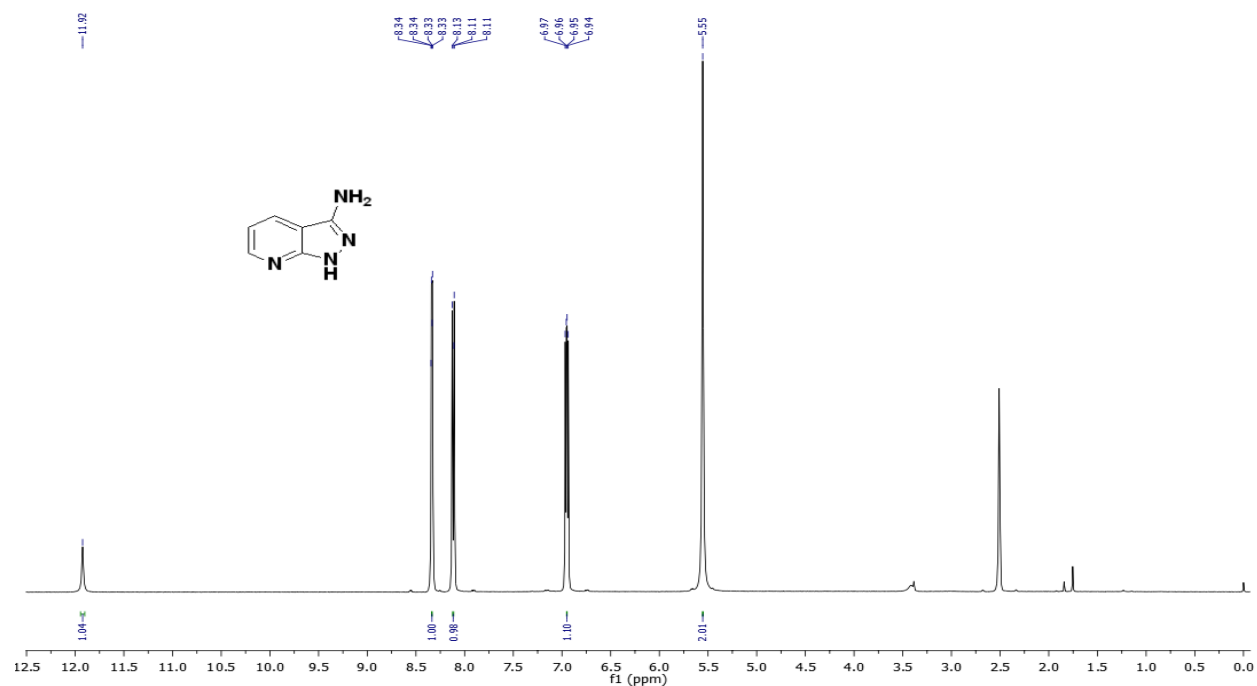
To a stirred solution of 1*H*-benzo[d]imidazol-2-amine (50 mg, 0.375 mmol) in MeOH (2 mL) was added 4-bromo phenyl boronic acid (83 mg, 0.413 mmol) and Cu(OAc)₂ (13.5 mg, 0.075 mmol) at room temperature. The reaction mixture was stirred at room temperature for 14 h and after completion of the reaction. The solvent was removed with an aid of rotatory evaporator and then 3-chlorophenyl boronic acid (70 mg, 0.450 mmol) and Cu(OAc)₂ (13.5 mg, 0.075 mmol) and CsOPiv (35 mg, 0.15 mmol) and DMF(1 mL) was added to the reaction mixture. The reaction mixture was stirred at 50 °C temperature for 24 h. The progress of the reaction was monitored by TLC and after completion of the reaction 10 ml of ice cooled water was added to the reaction mixture and mixture was extracted with EtOAc (10 mL) further extracted two times with EtOAc (2 x 10 mL) and the combined organic phase was washed with sat. aq. NaHCO₃, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography to give the final compound **4f** (100 mg, 73%).

8. References

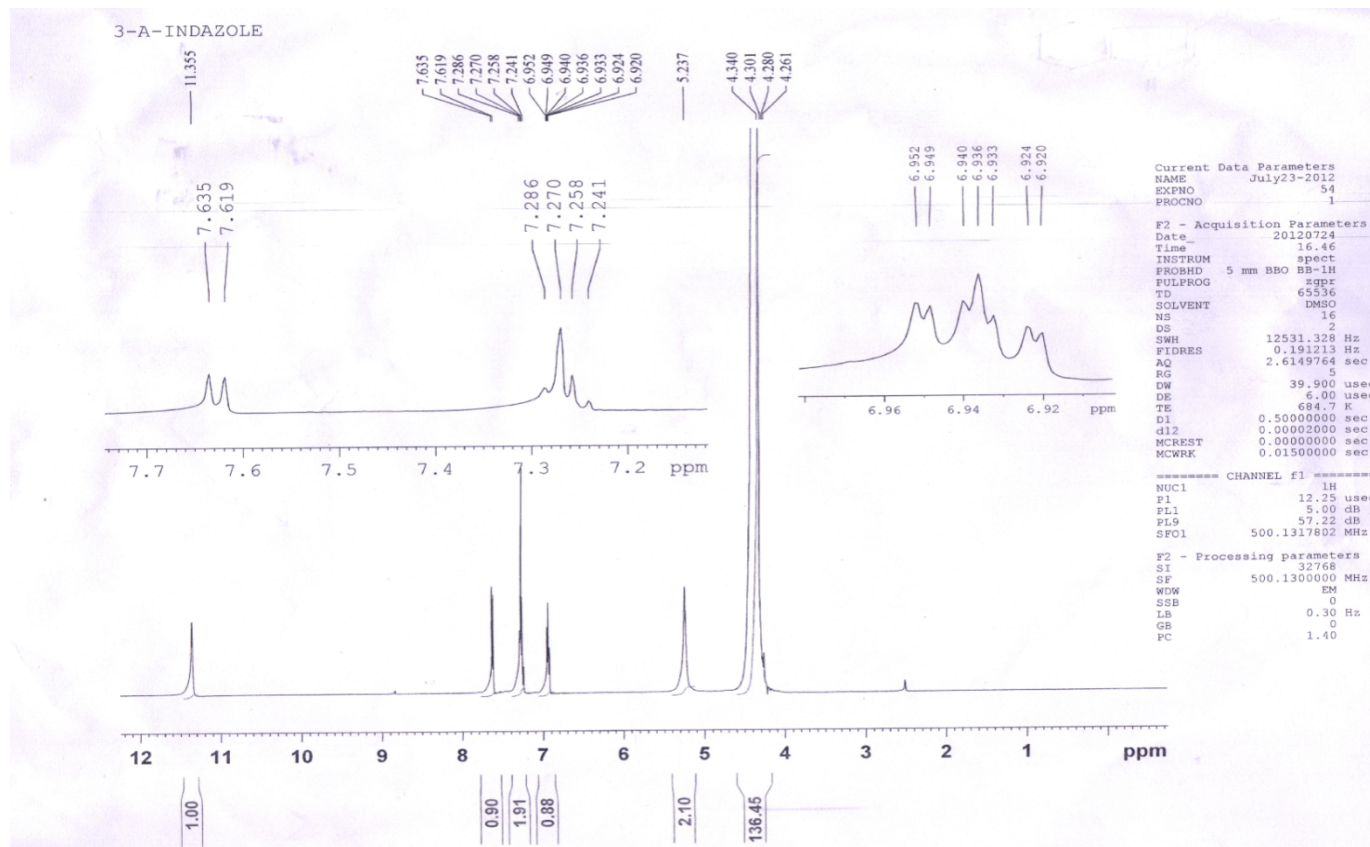
[1]. Ueda, S. Buchwald, S. L. *Angew. Chem. Int. Ed.*, **2012**, *51*, 10364.

10. Copies of ^1H -NMR and ^{13}C -NMR spectra

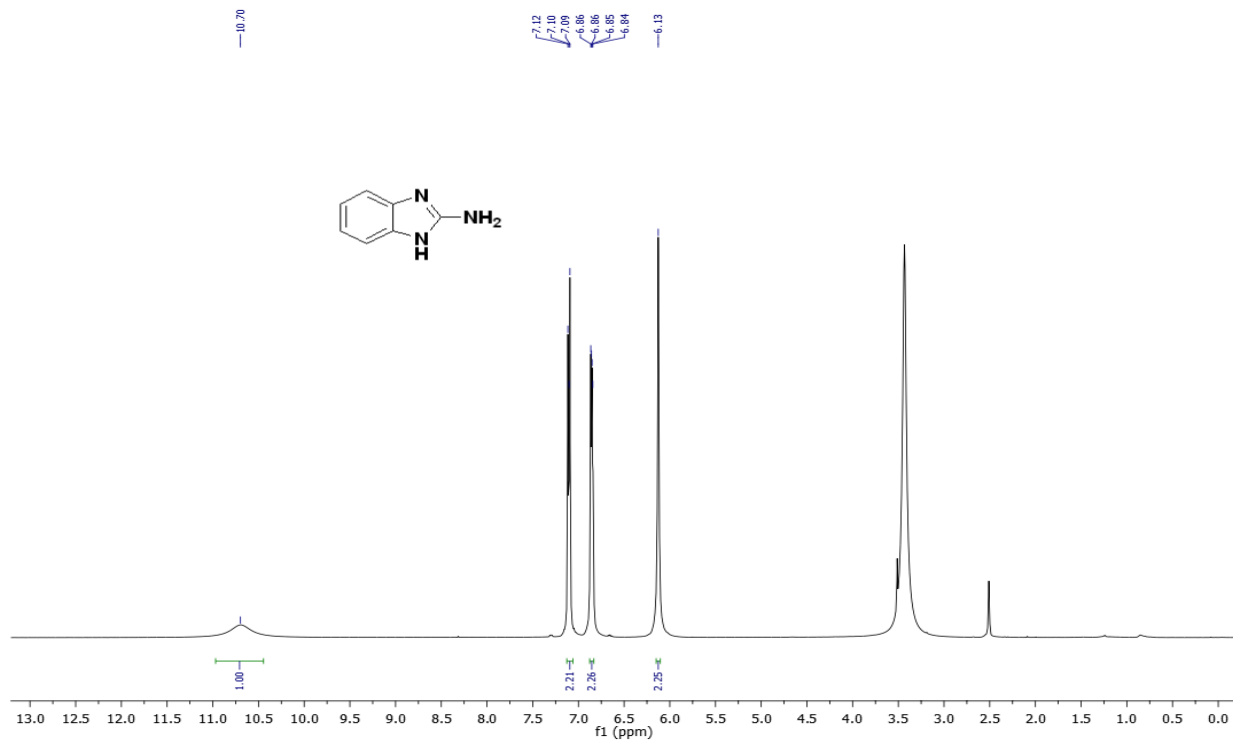
^1H -NMR of 1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (400 MHz, $\text{DMSO-}d_6$)



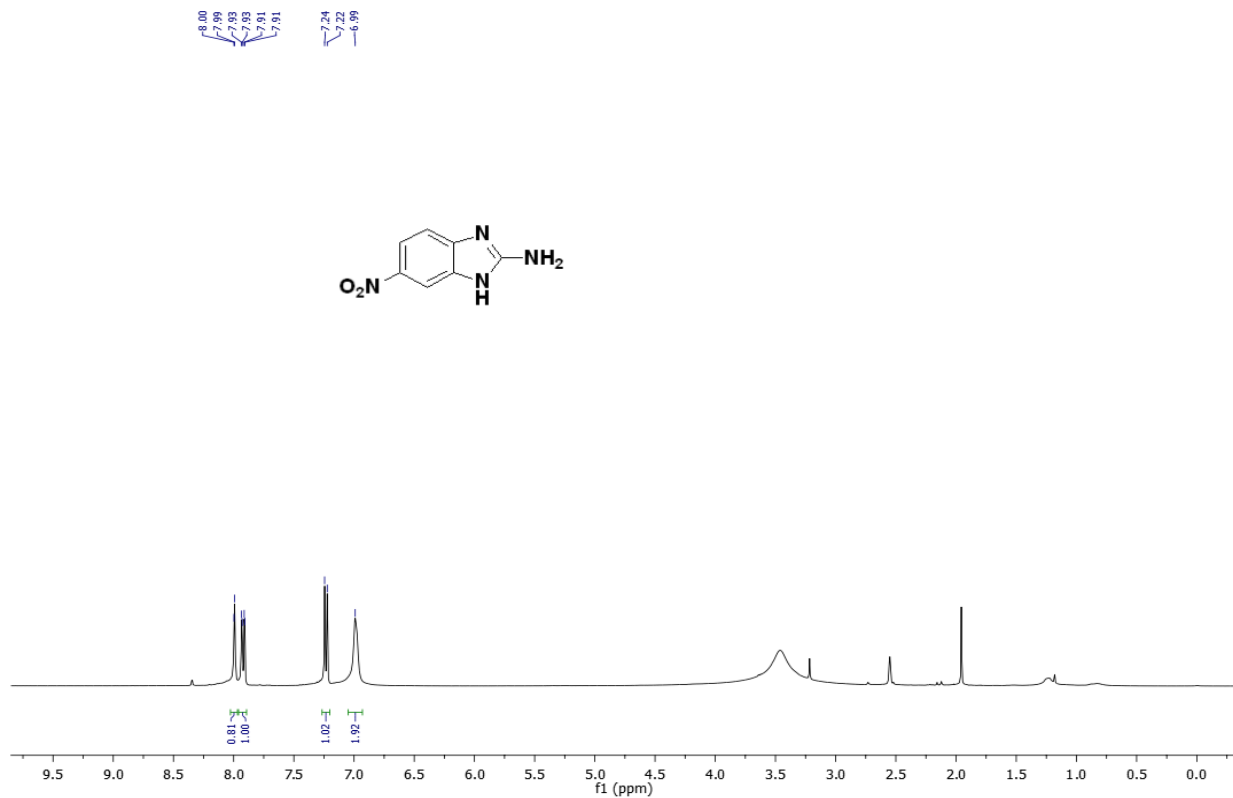
^1H -NMR of 1*H*-indazol-3-amine (500 MHz, $\text{DMSO-}d_6$)



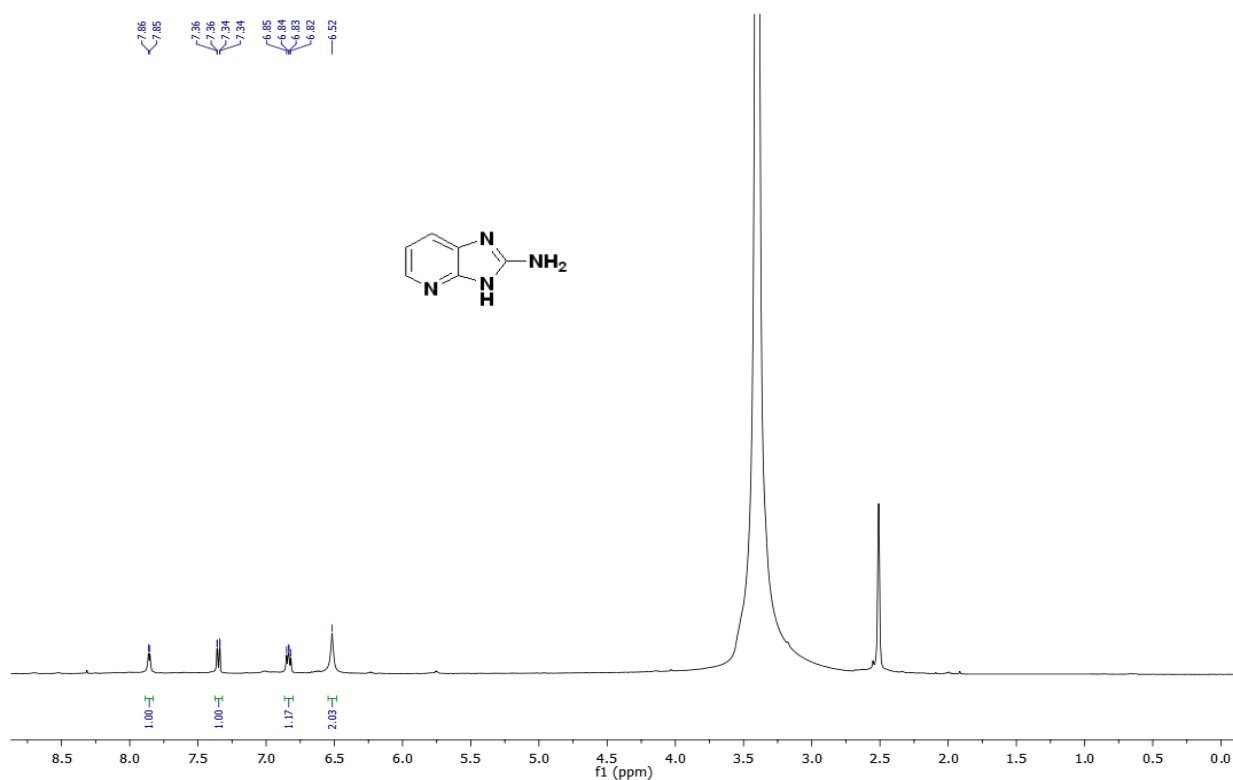
¹H-NMR of 1*H*-benzo[d]imidazol-2-amine (400 MHz, DMSO-*d*₆)



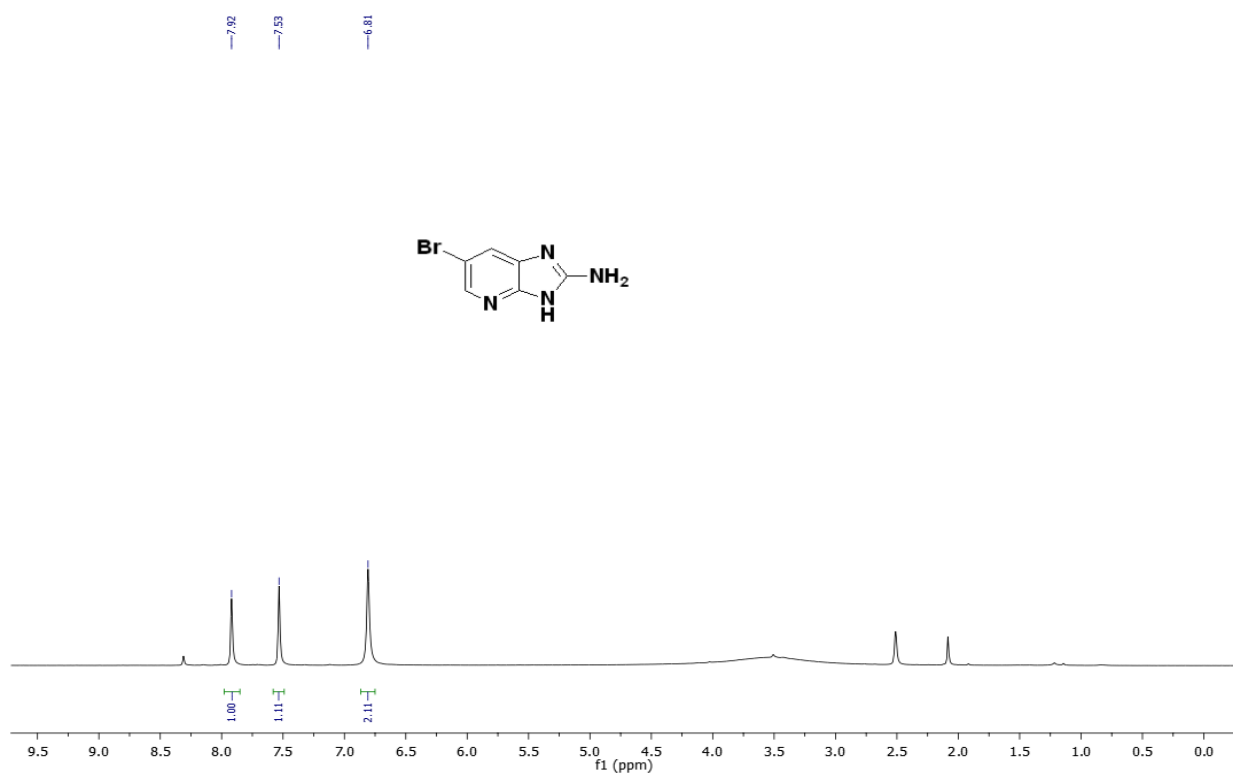
¹H-NMR of 6-nitro-1*H*-benzo[d]imidazol-2-amine (400 MHz, DMSO-*d*₆)



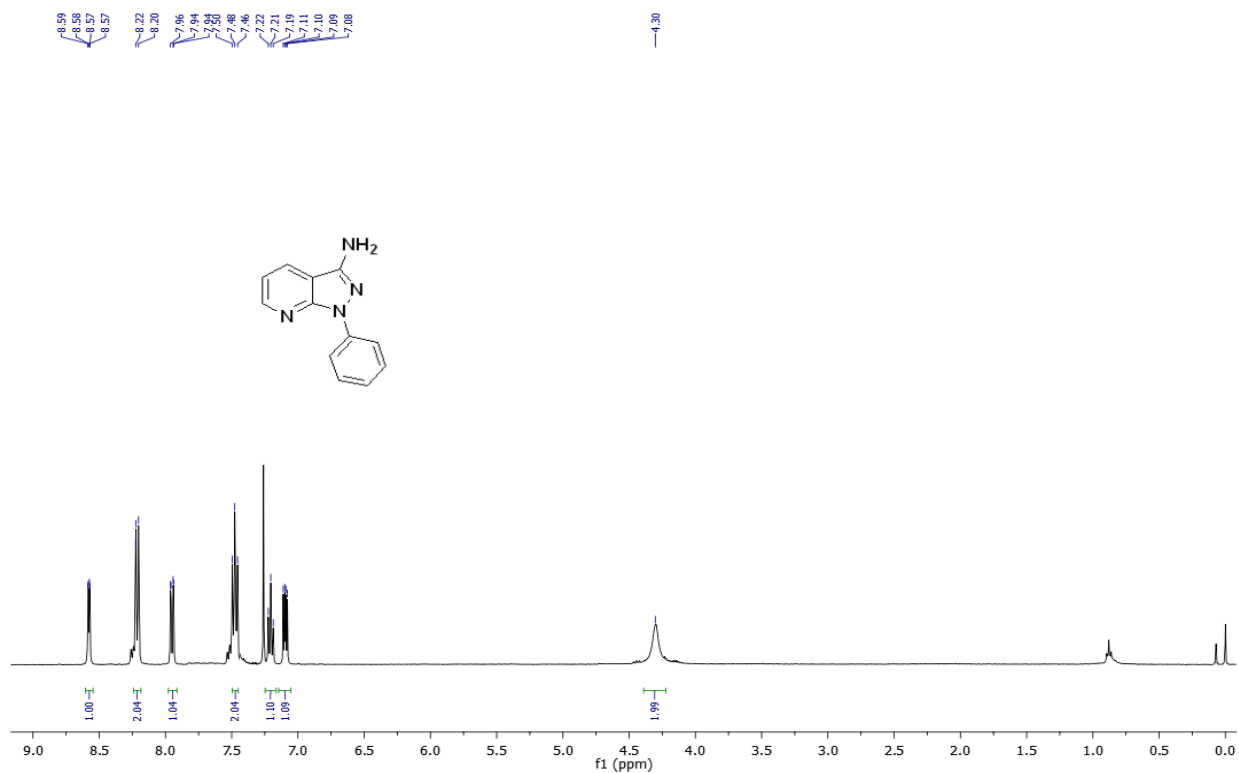
¹H-NMR of 3H-imidazo[4,5-b]pyridin-2-amine (400 MHz, DMSO-*d*₆)



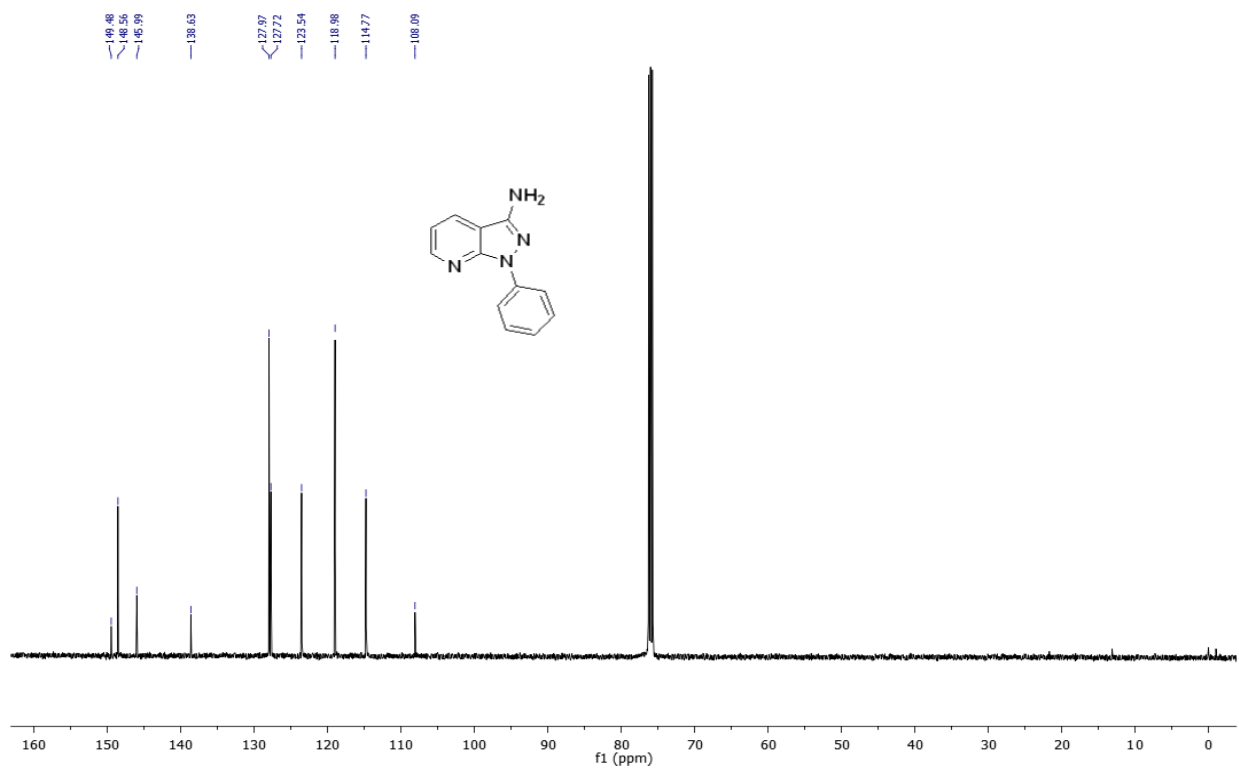
¹H-NMR of 6-bromo-3H-imidazo[4,5-b]pyridin-2-amine (400 MHz, DMSO-*d*₆)



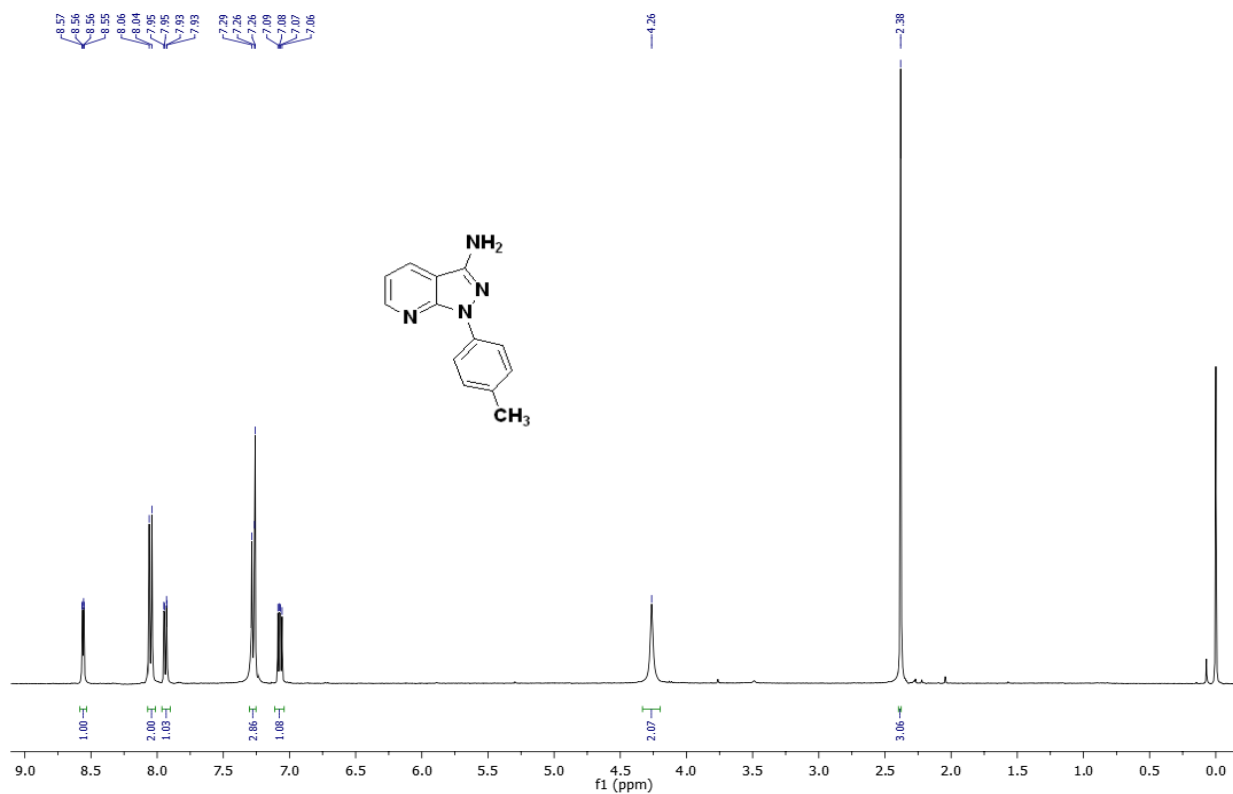
¹H-NMR of 2a (400 MHz, CDCl₃)



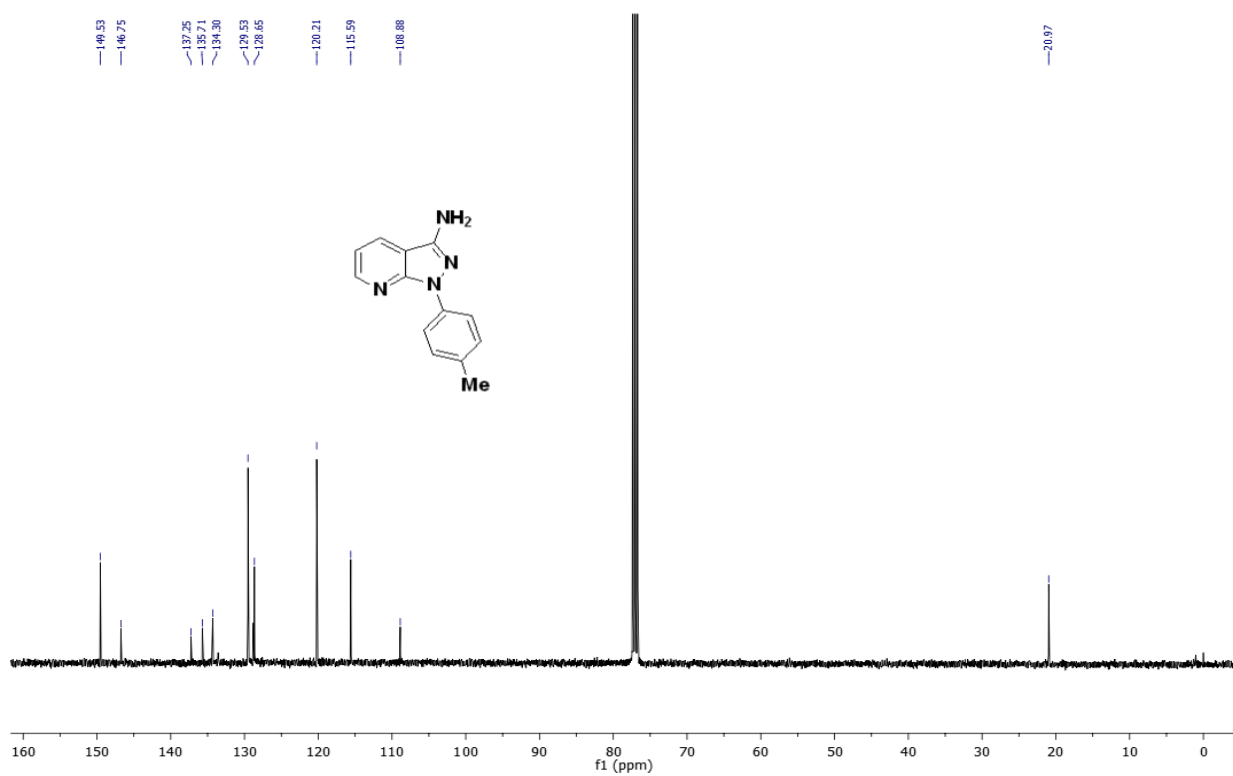
¹³C-NMR of 2a (125 MHz, CDCl₃)



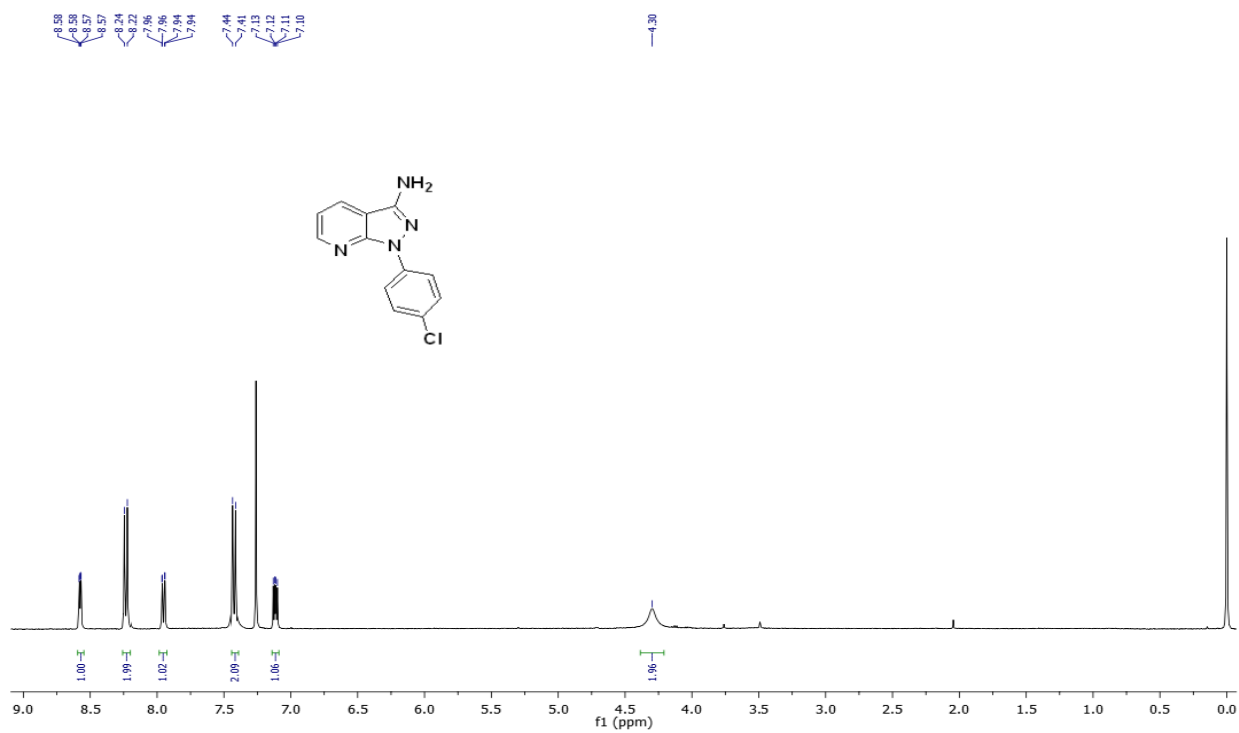
$^1\text{H-NMR}$ of 2b (400 MHz, CDCl_3)



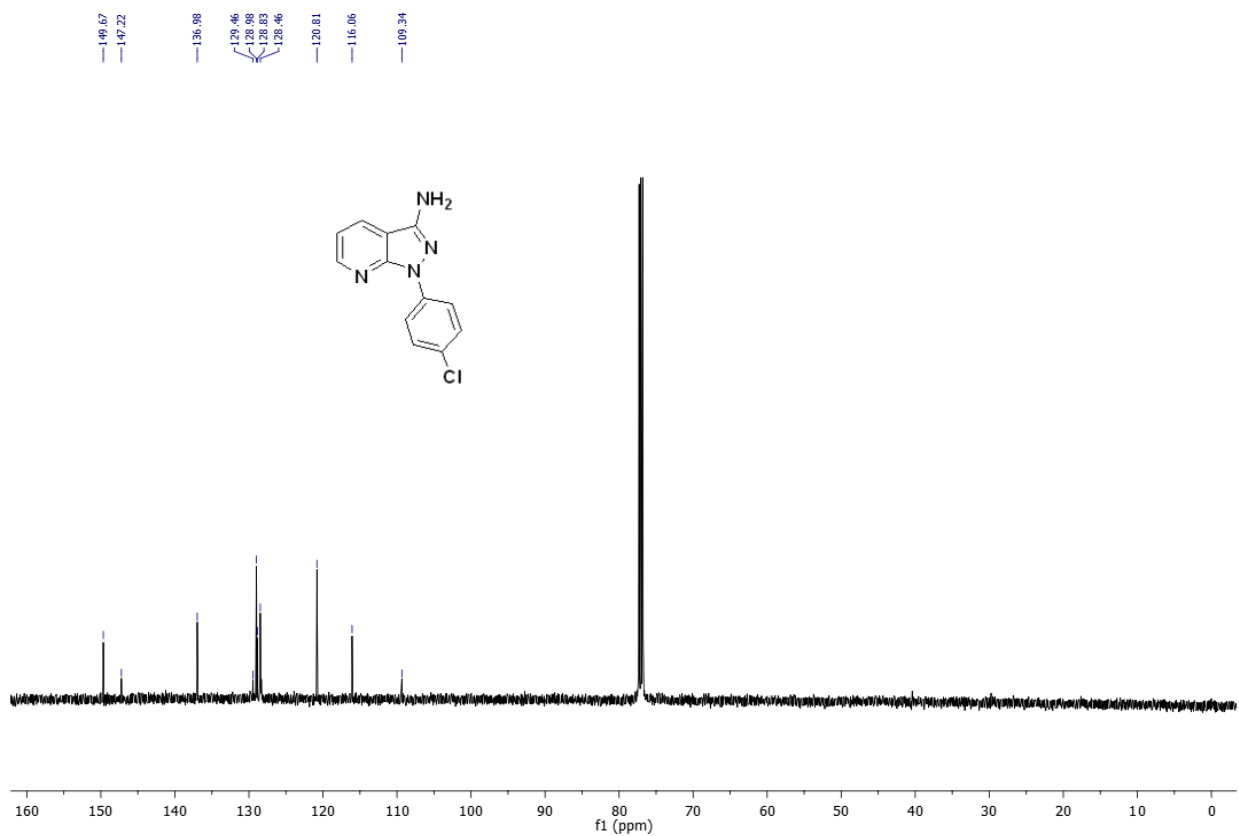
$^{13}\text{C-NMR}$ of 2b (100 MHz, CDCl_3)



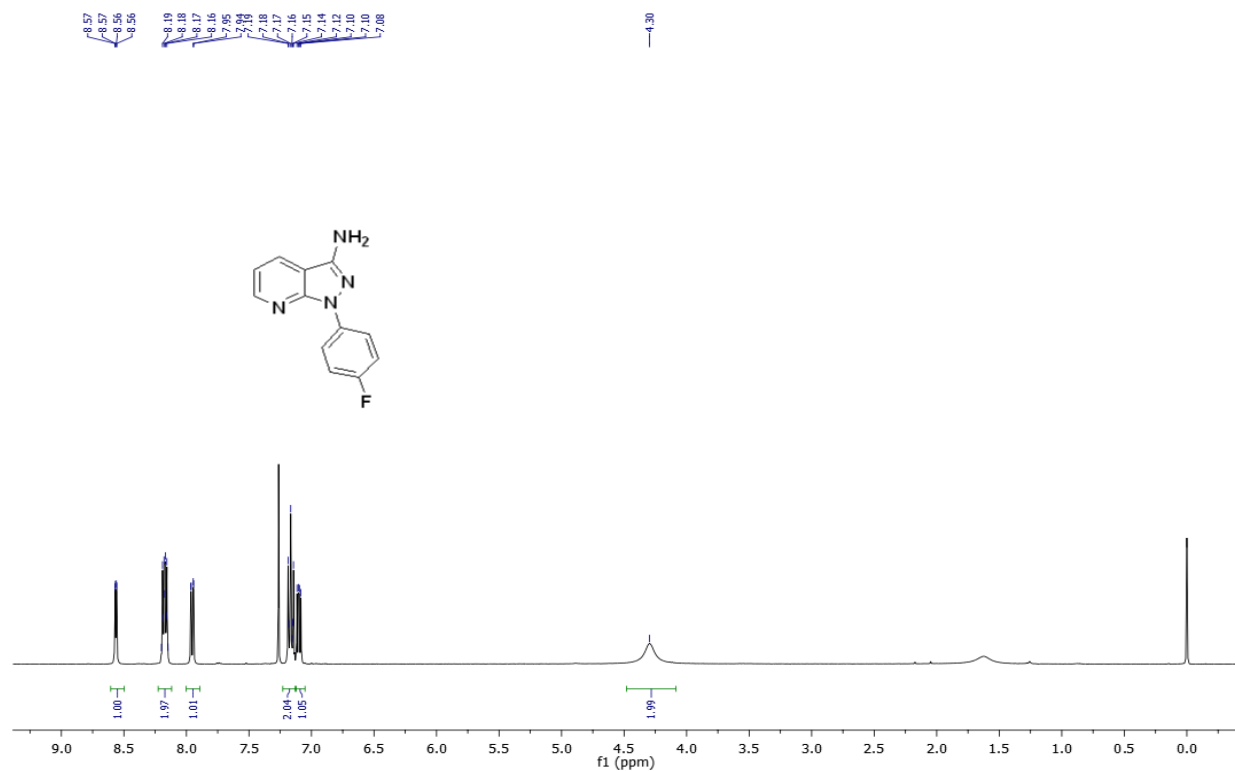
$^1\text{H-NMR}$ of 2c (400 MHz, CDCl_3)



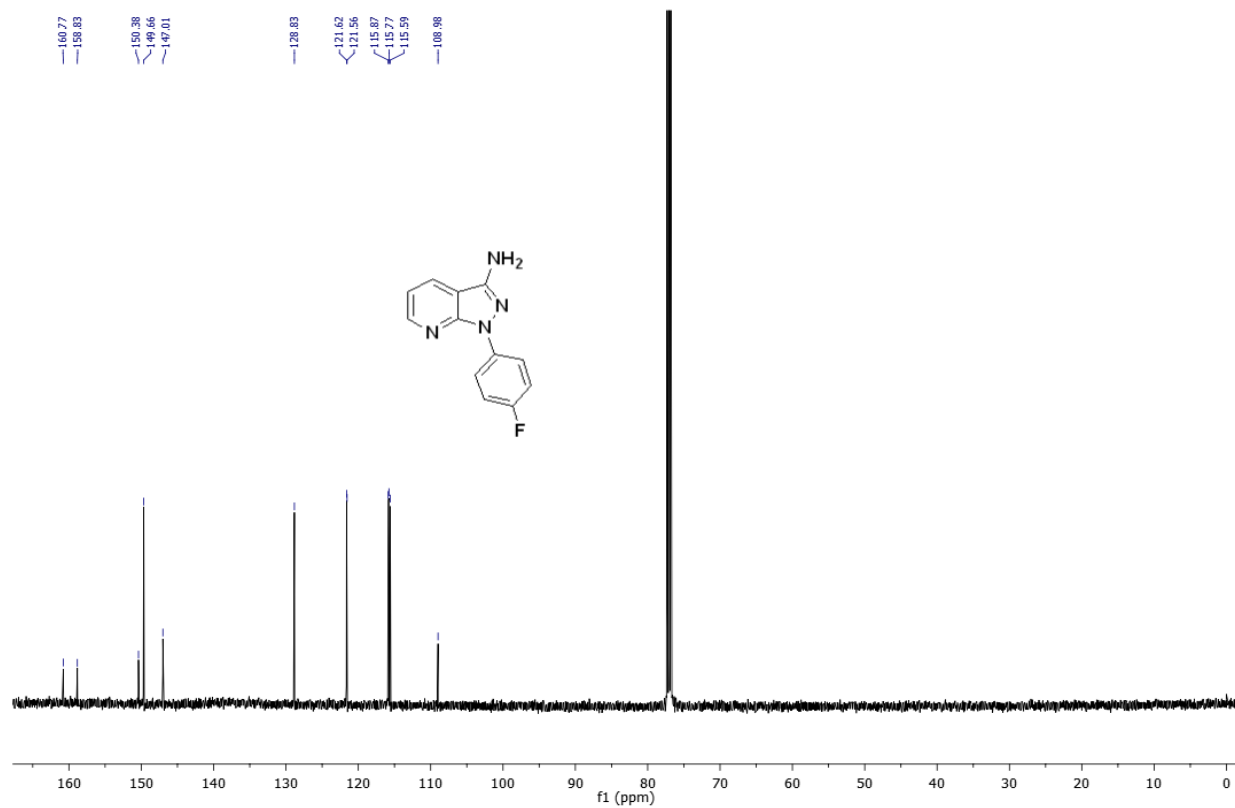
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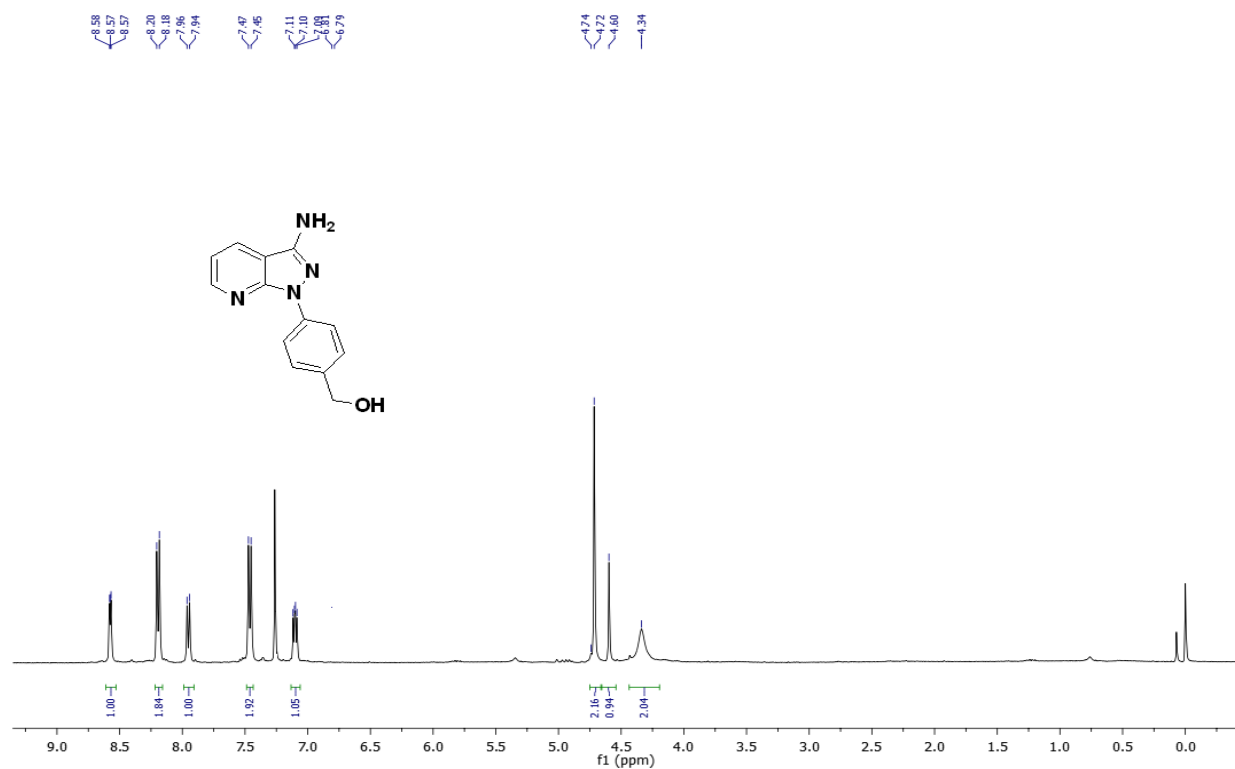
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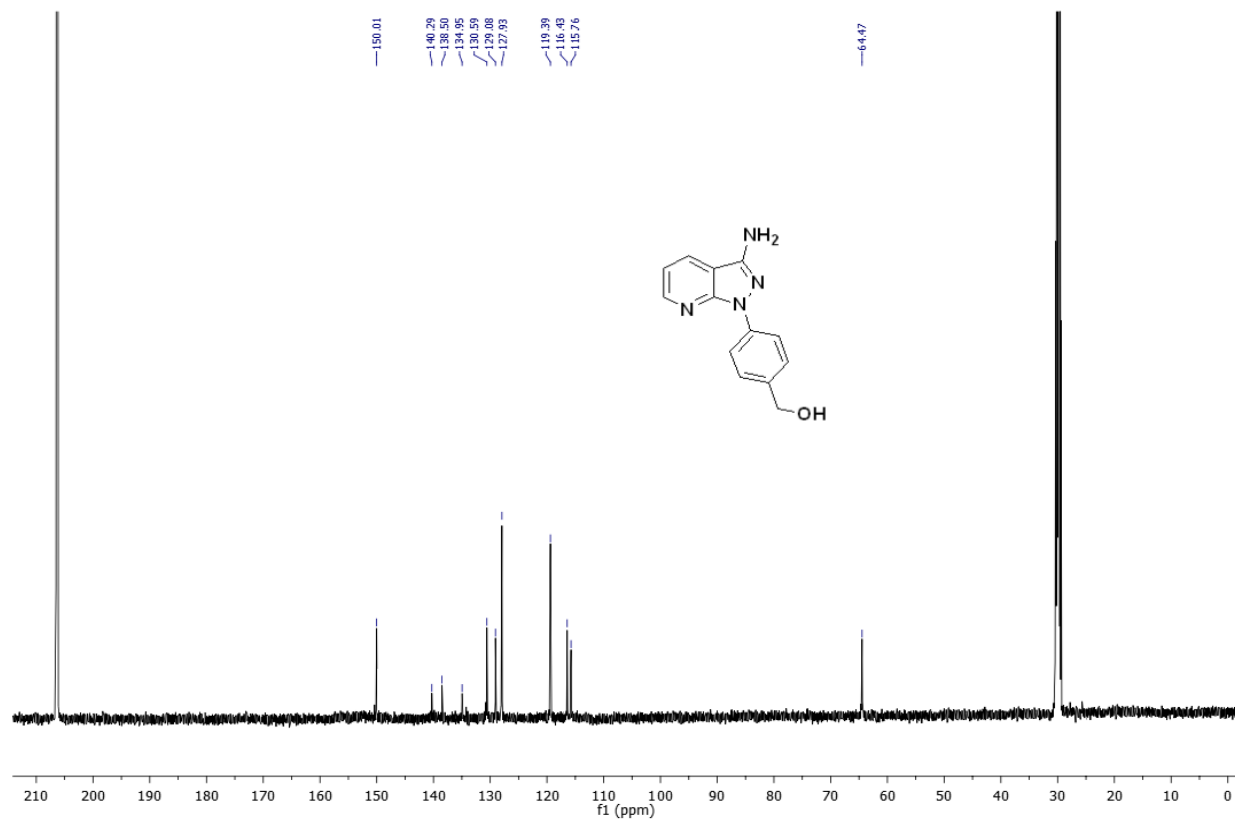
$^{13}\text{C-NMR}$ of 2d (125 MHz, CDCl_3)



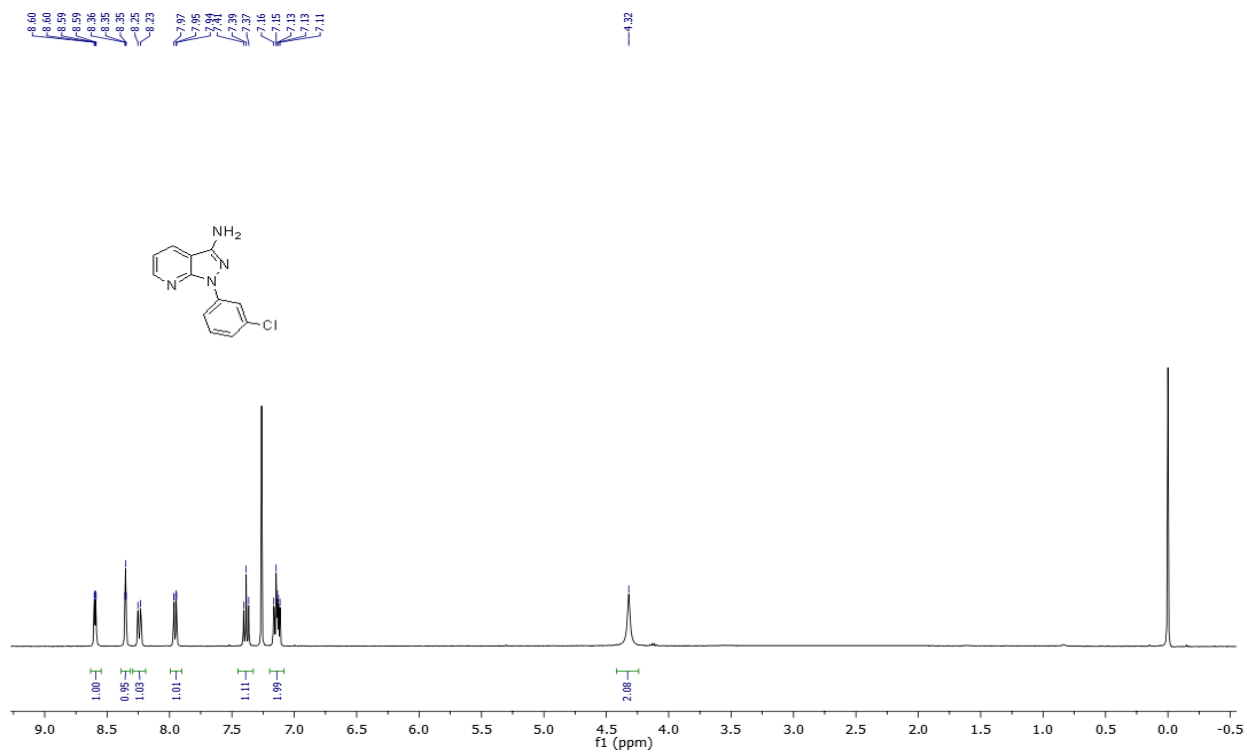
¹H-NMR of 2e (400 MHz, CDCl₃)



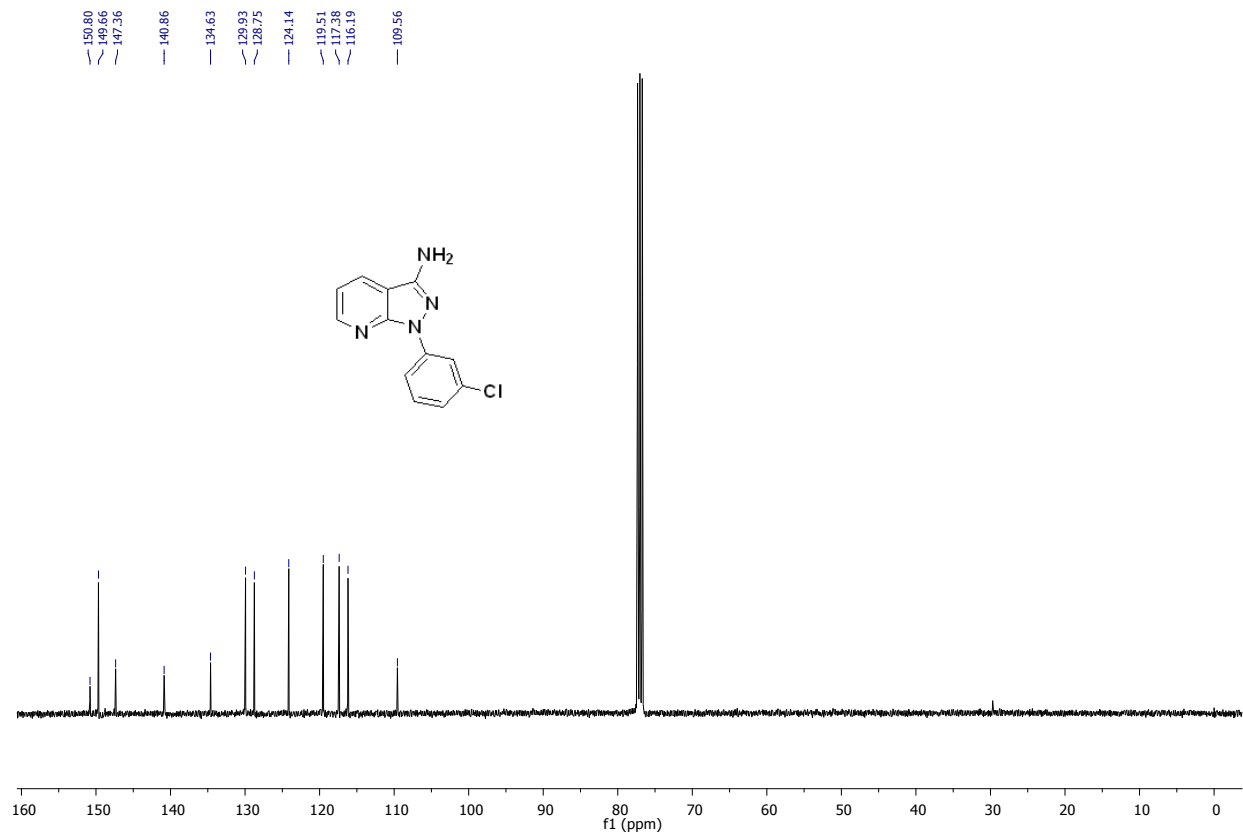
¹³C-NMR of 2e (125 MHz, Acetone-*d*₆)



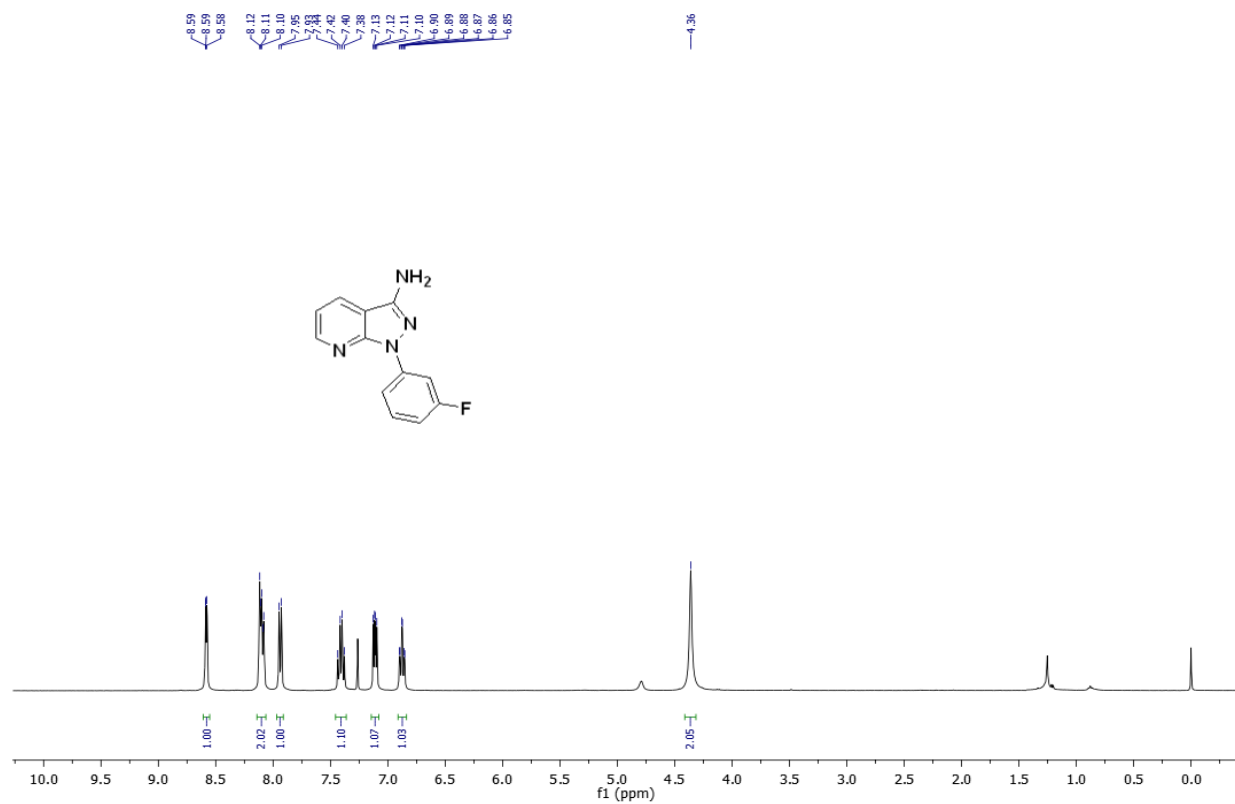
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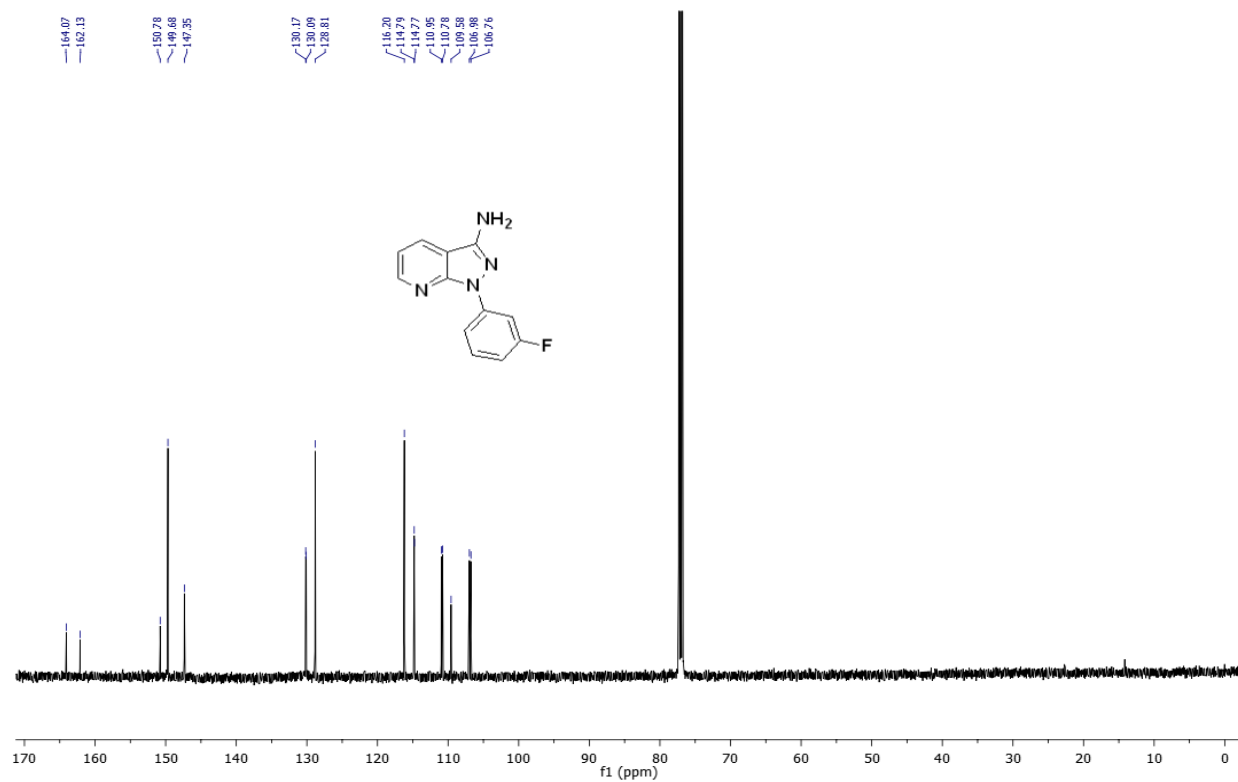
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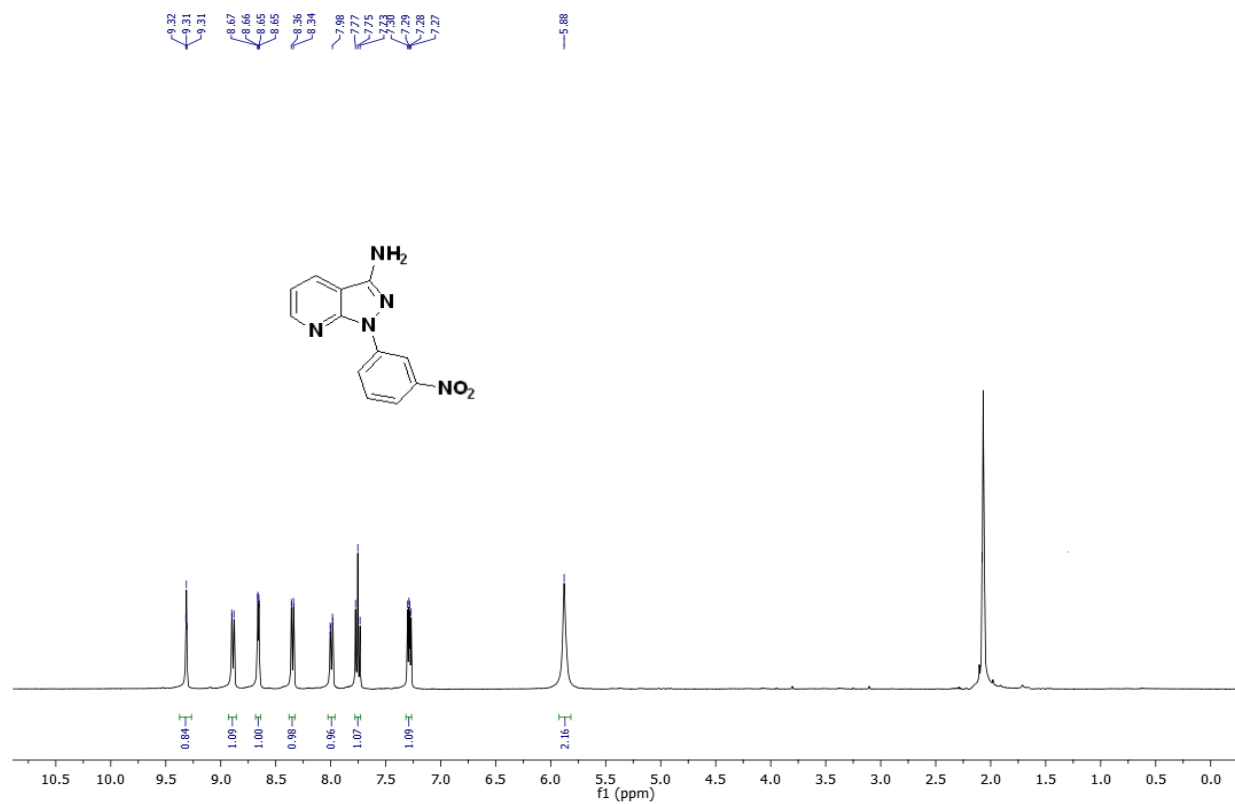
$^1\text{H-NMR}$ of 2g (400 MHz, CDCl_3)



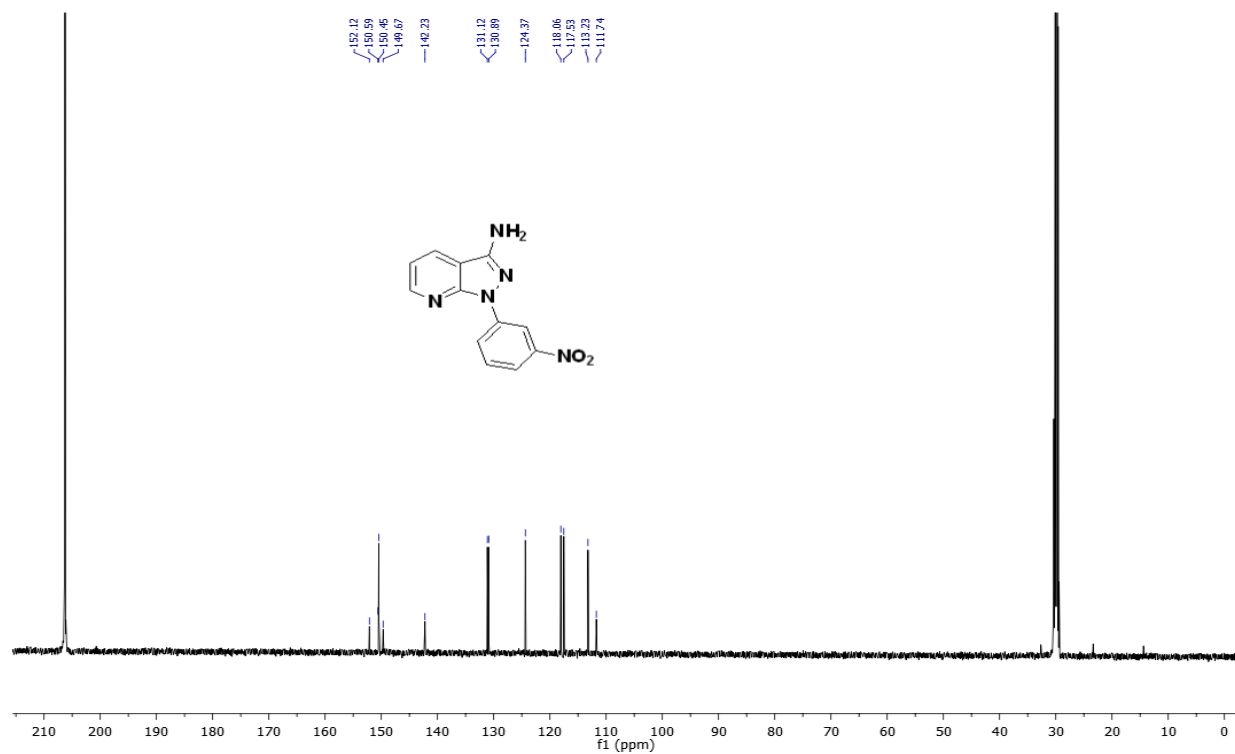
$^{13}\text{C-NMR}$ of 2g (125 MHz, CDCl_3)



¹H-NMR of 2h (400 MHz, Acetone-*d*₆)



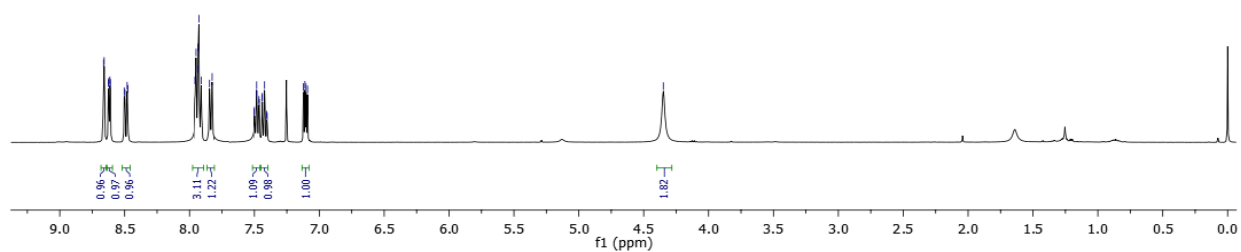
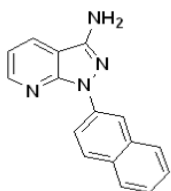
¹³C-NMR of 2h (125 MHz, Acetone-*d*₆)



$^1\text{H-NMR}$ of 2i (400 MHz, CDCl_3)

8.66
8.65
8.63
8.62
8.61
8.50
8.50
8.48
7.85
7.85
7.83
7.93
7.49
7.48
7.45
7.11
7.10
7.09

4.35

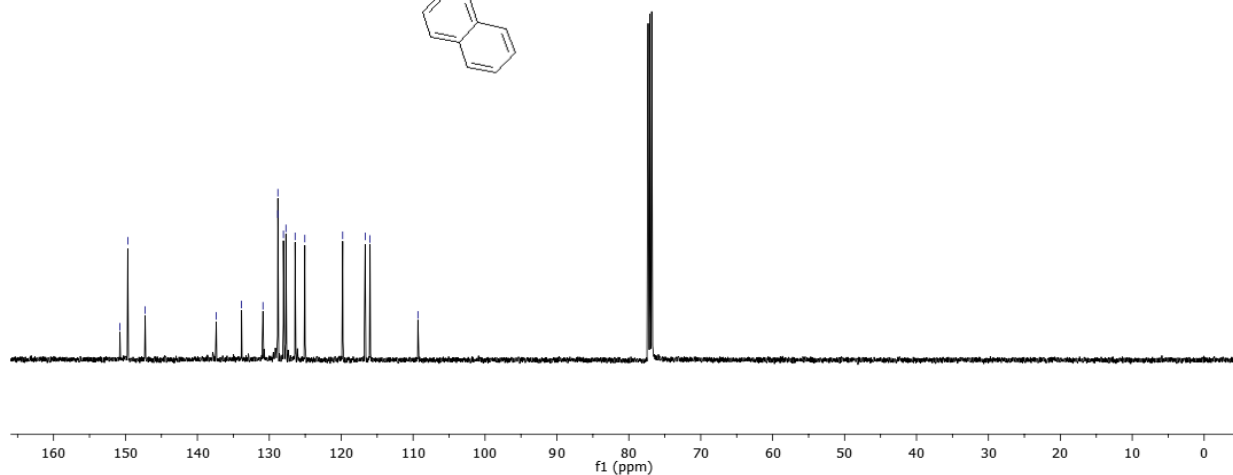
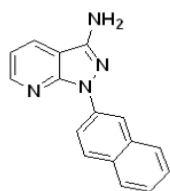


$^{13}\text{C-NMR}$ of 2i (125 MHz, CDCl_3)

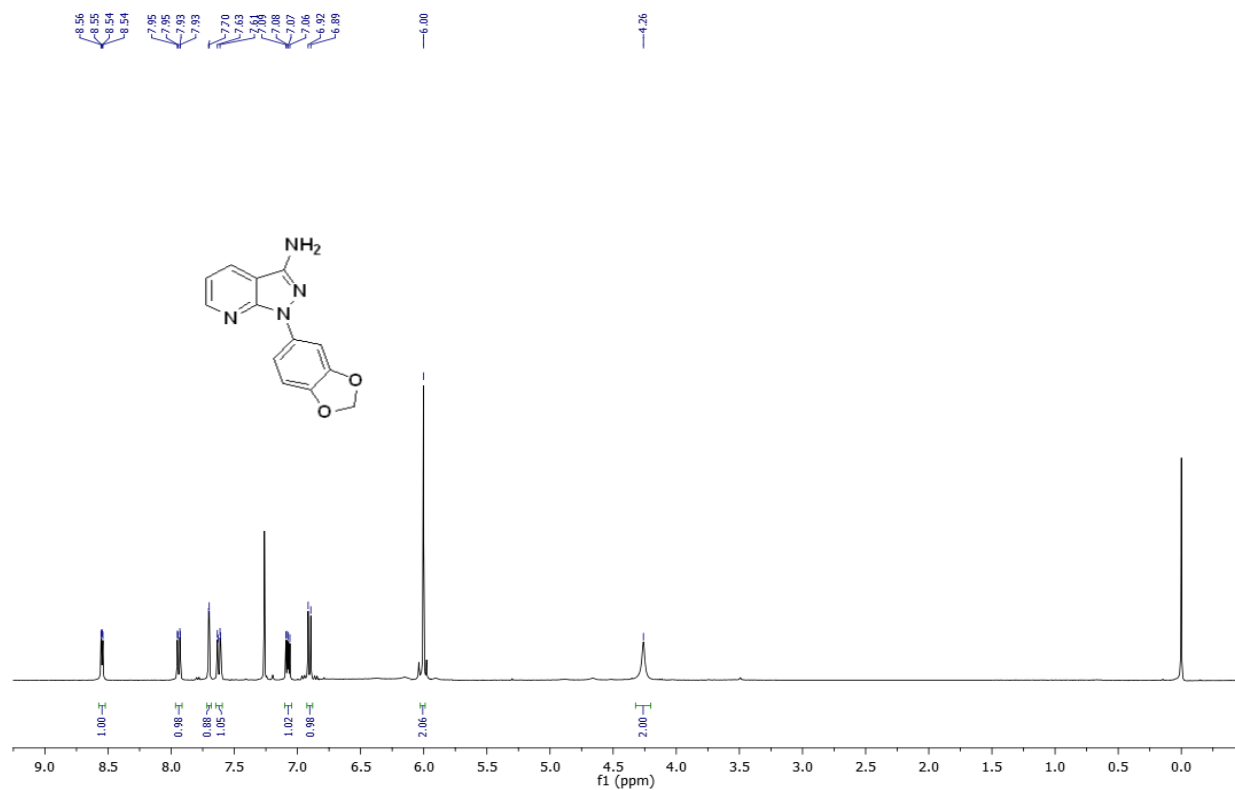
150.77
149.68
147.26

137.37
133.86
130.88
128.82
128.81
128.83
127.68
126.41
125.06
119.79
116.66
115.99

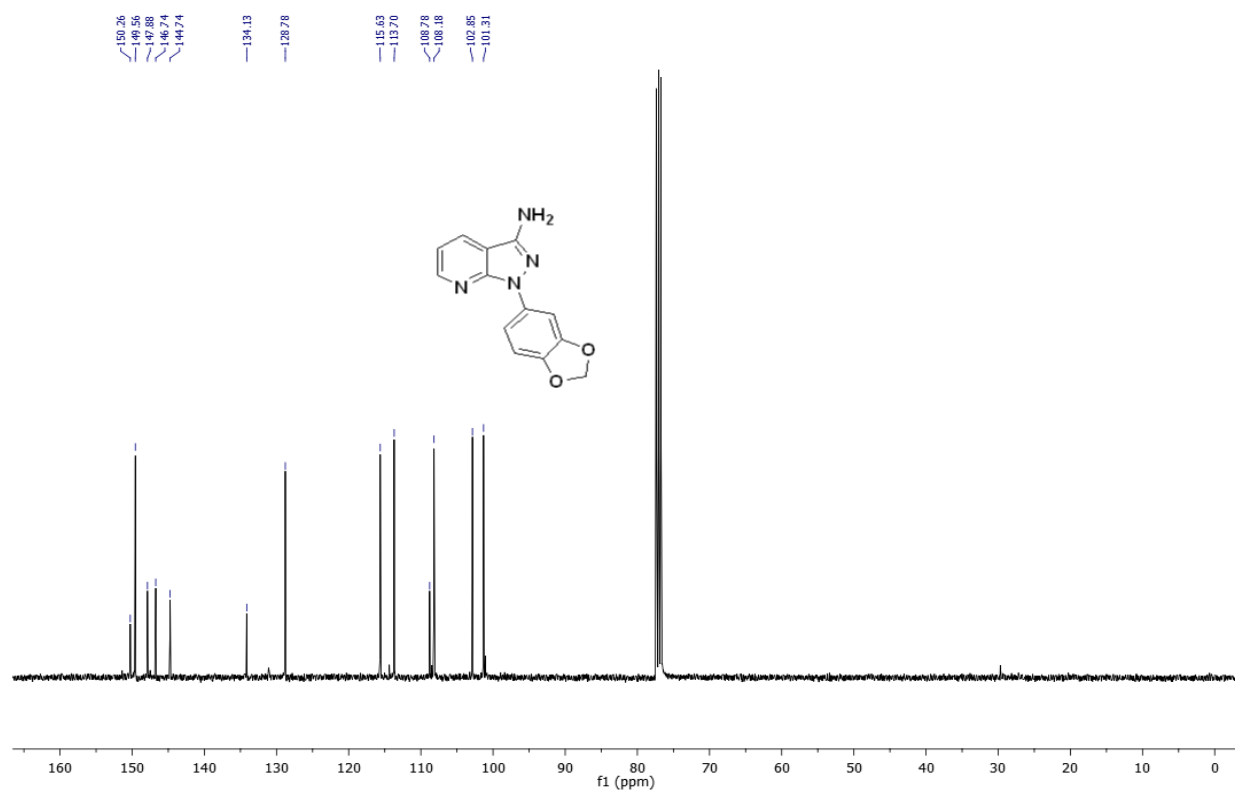
109.33



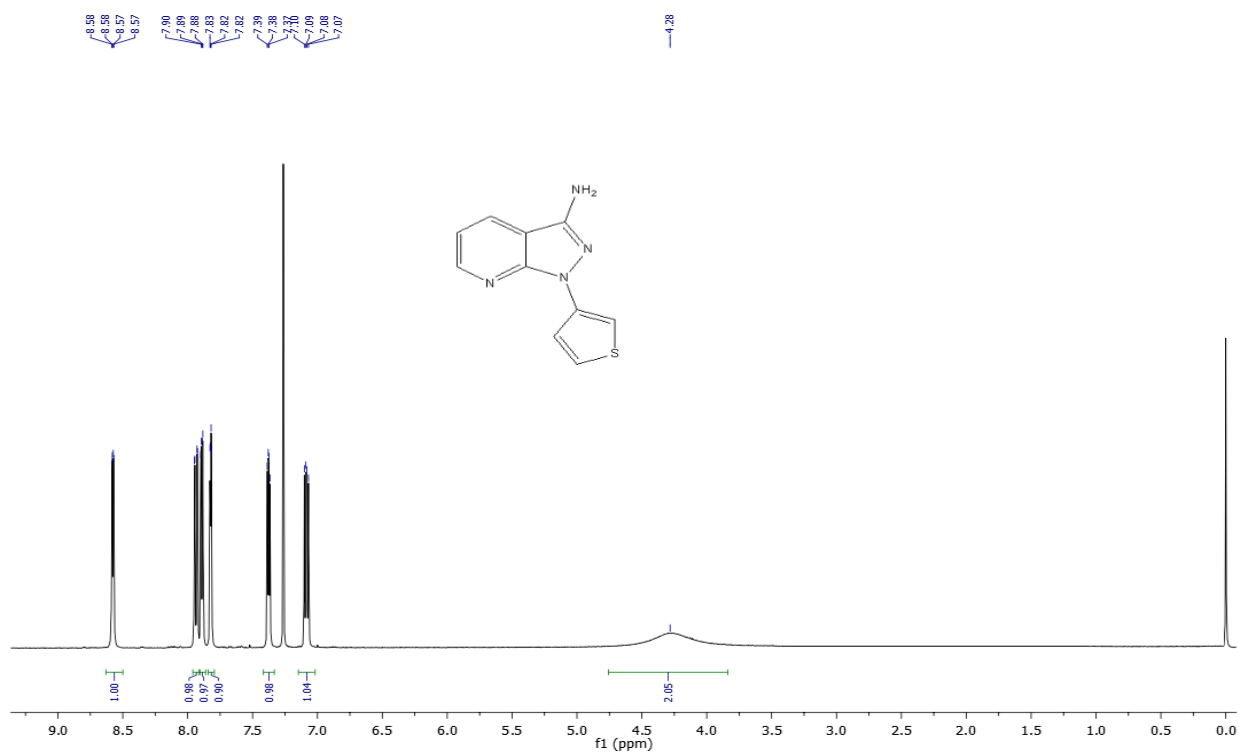
¹H-NMR of 2j (400 MHz, CDCl₃)



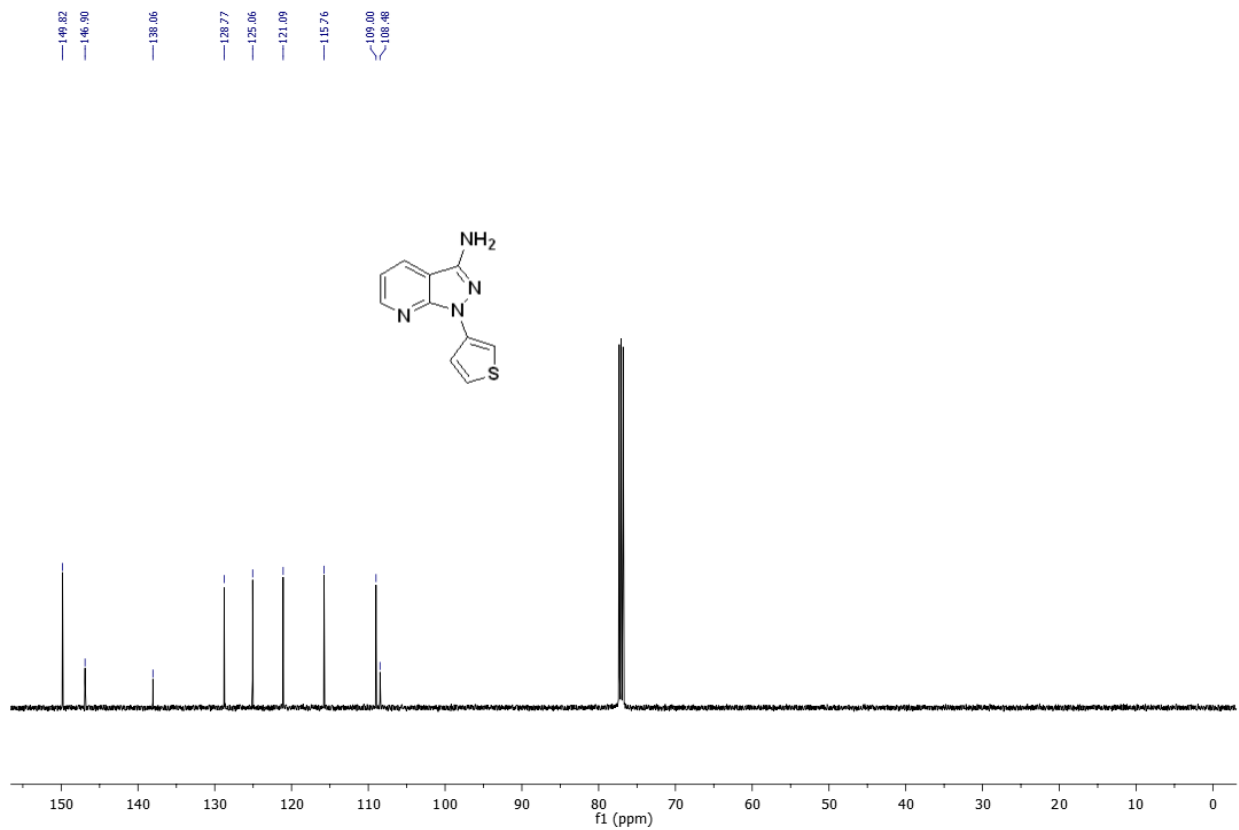
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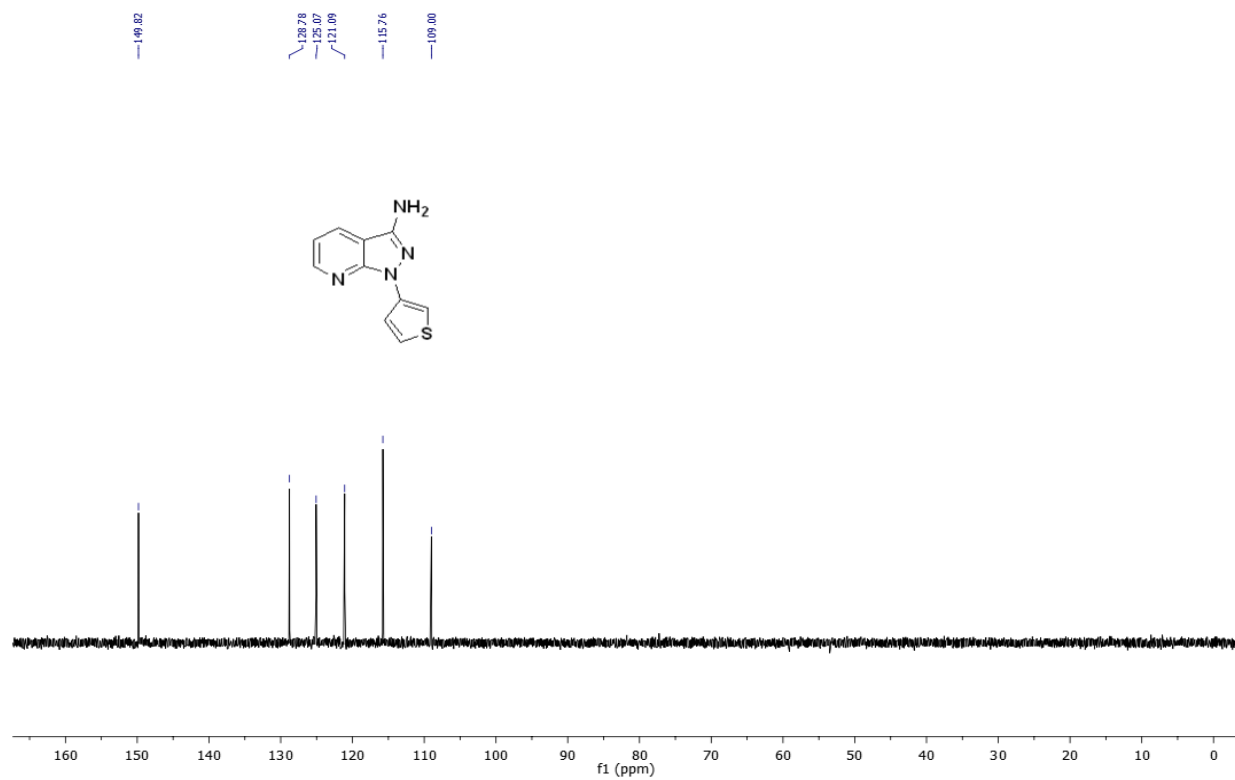
¹H-NMR of 2k (400 MHz, CDCl₃)



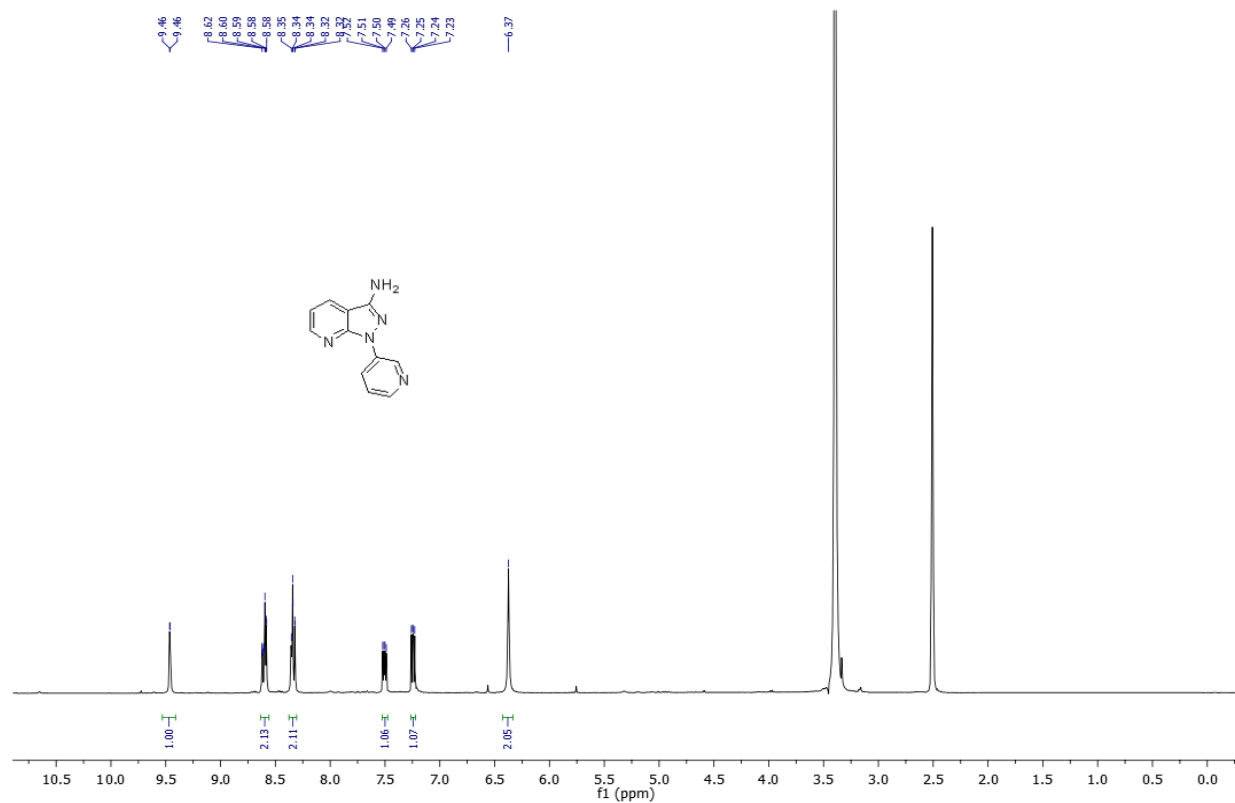
¹³C-NMR of 2k (125 MHz, CDCl₃)



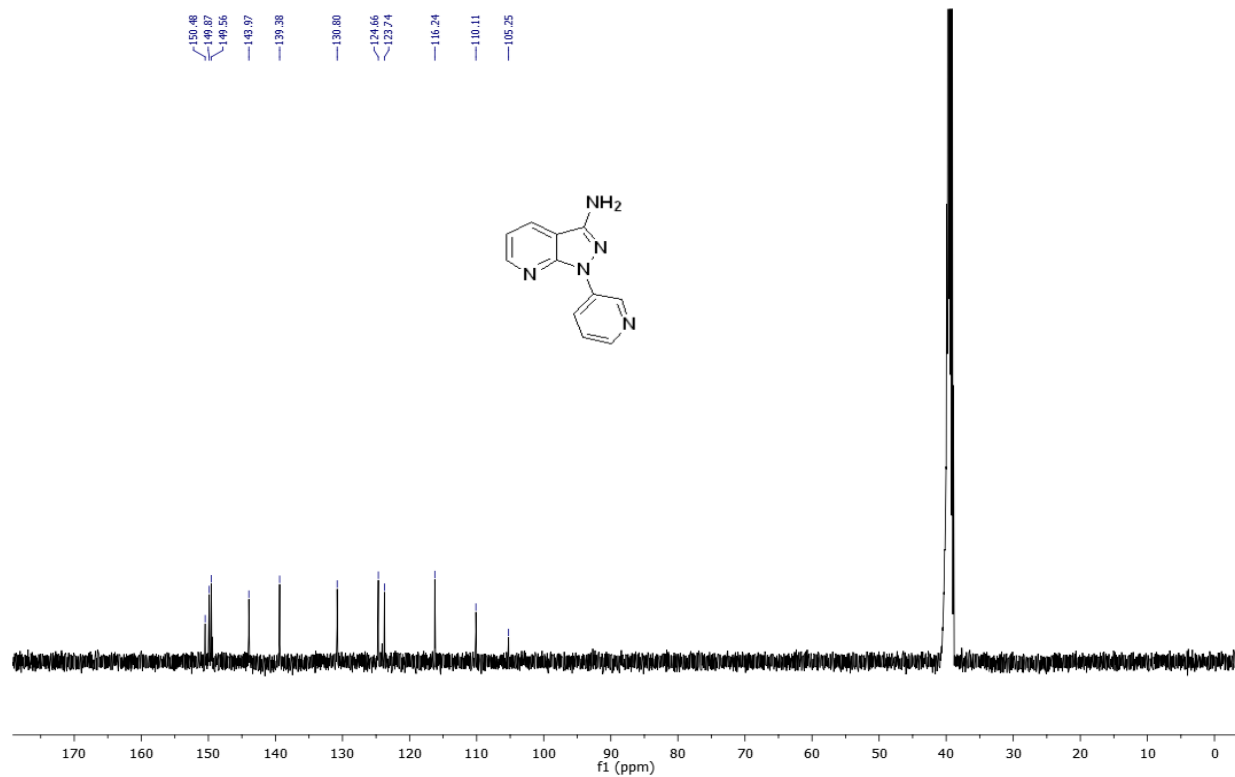
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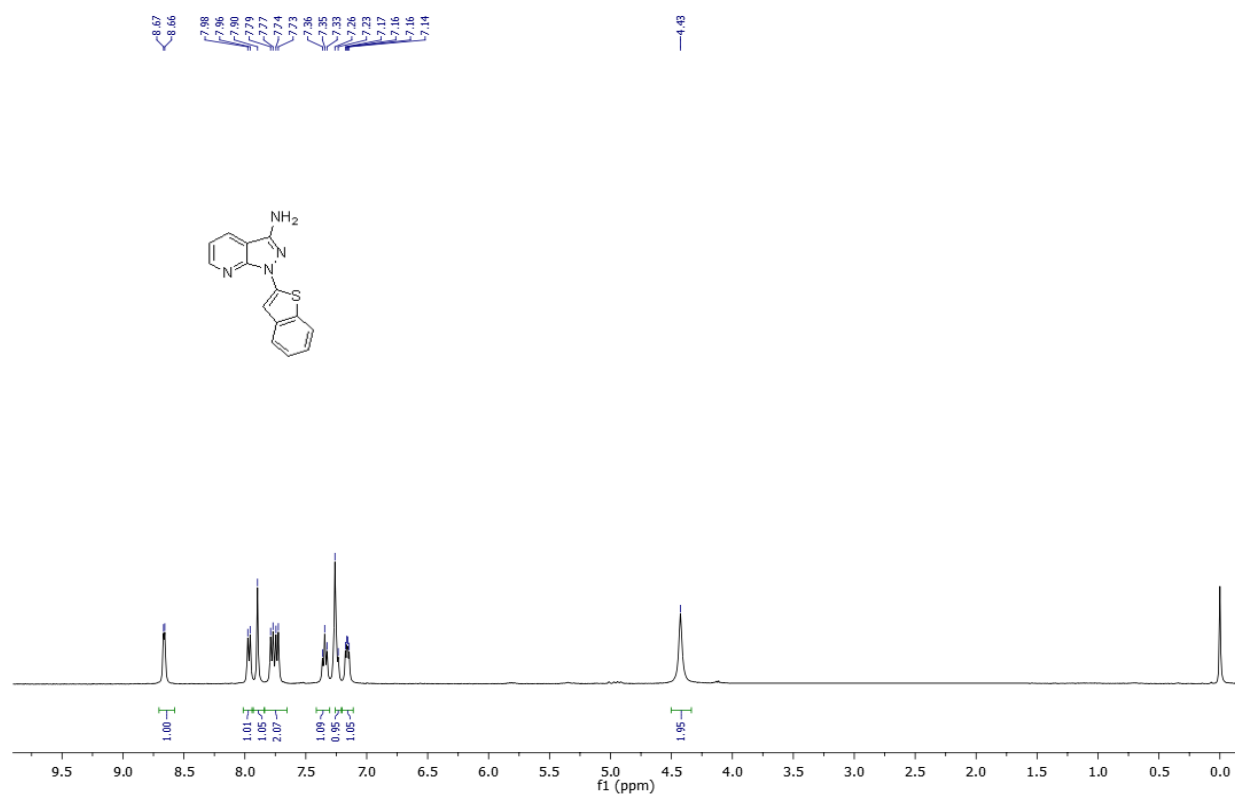
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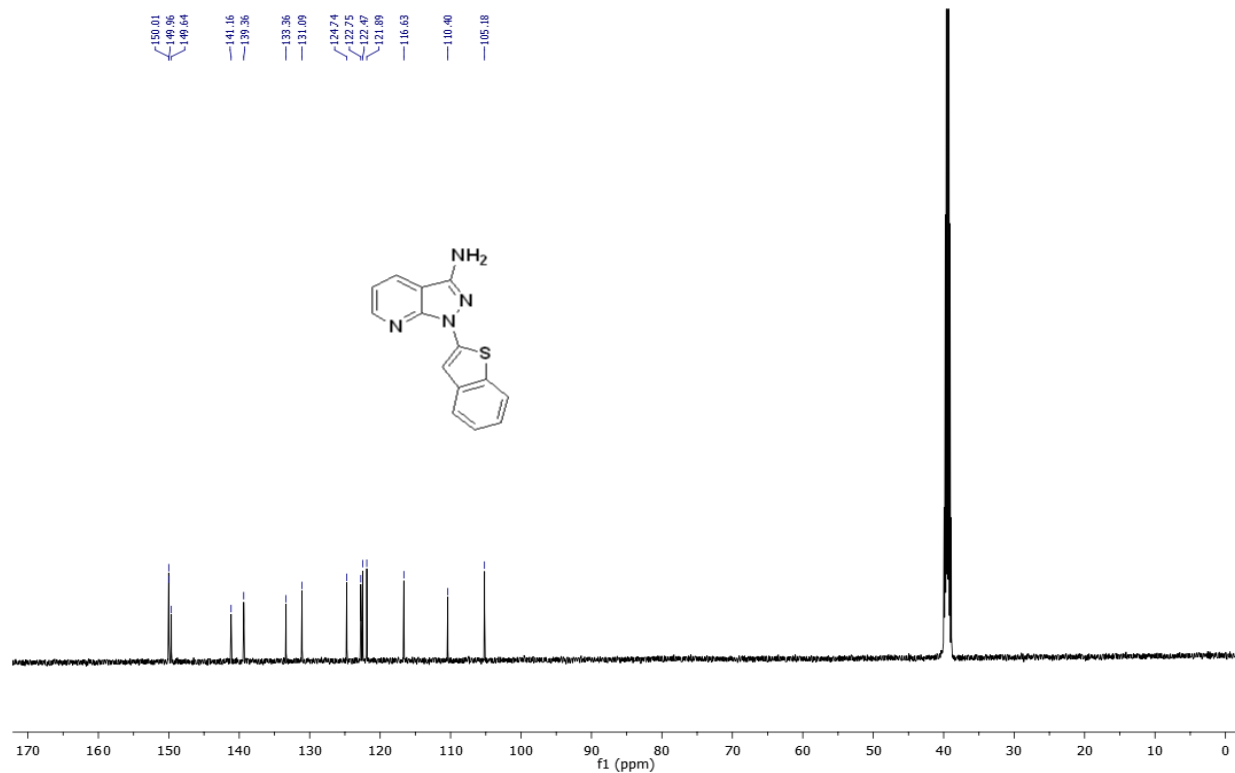
^{13}C -NMR of 2l (125 MHz, $\text{DMSO-}d_6$)



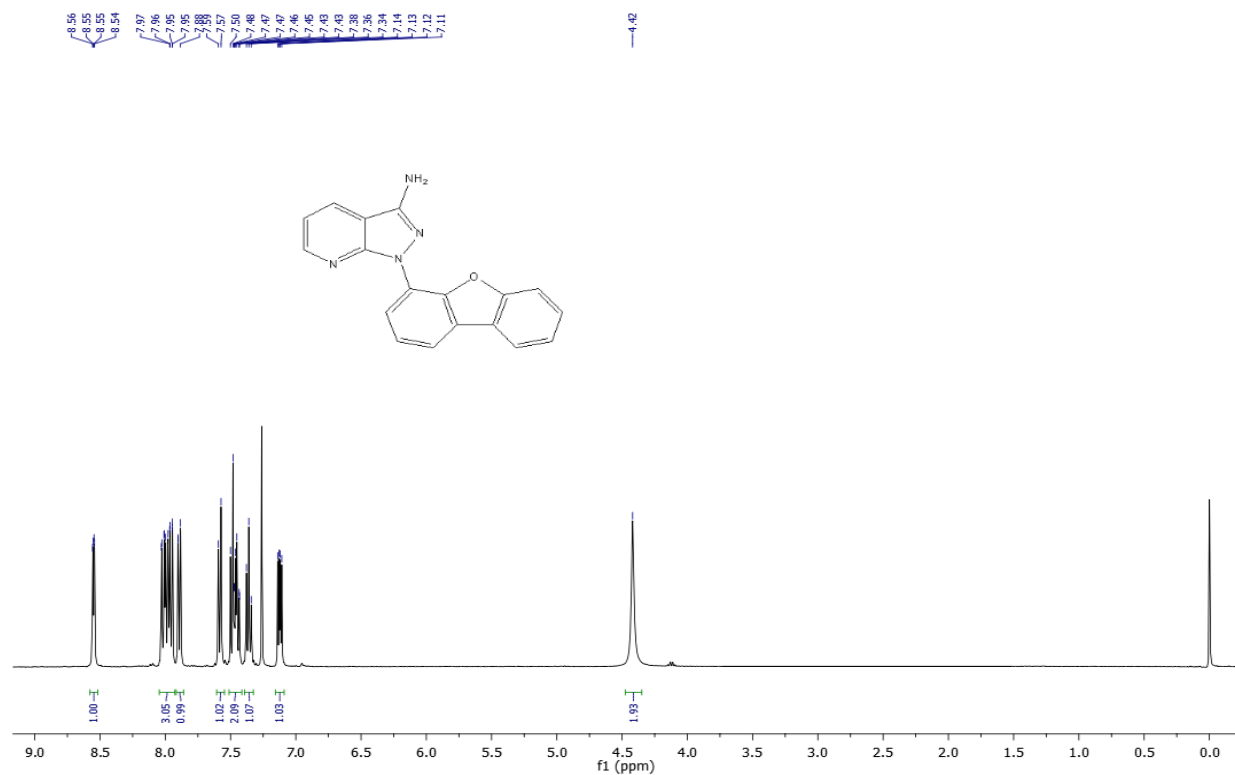
^1H -NMR of 2m (400 MHz, CDCl_3)



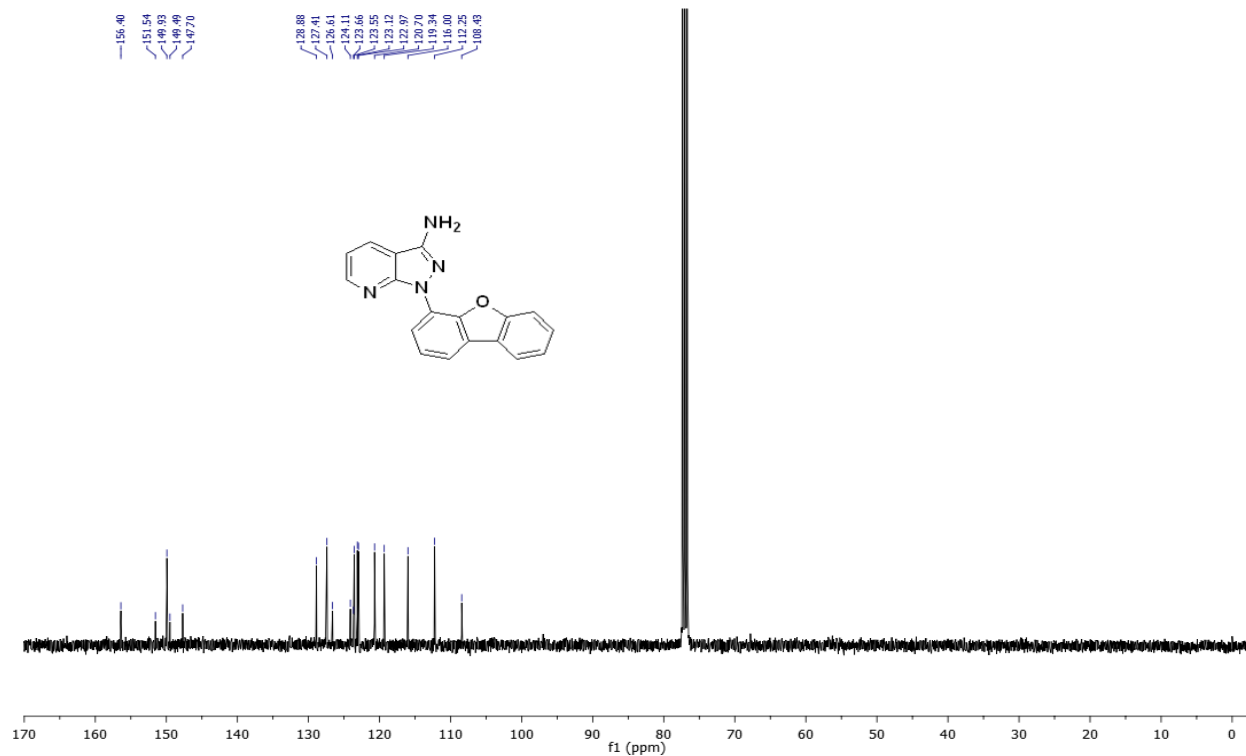
¹³C-NMR of 2m (125 MHz, DMSO-*d*₆)



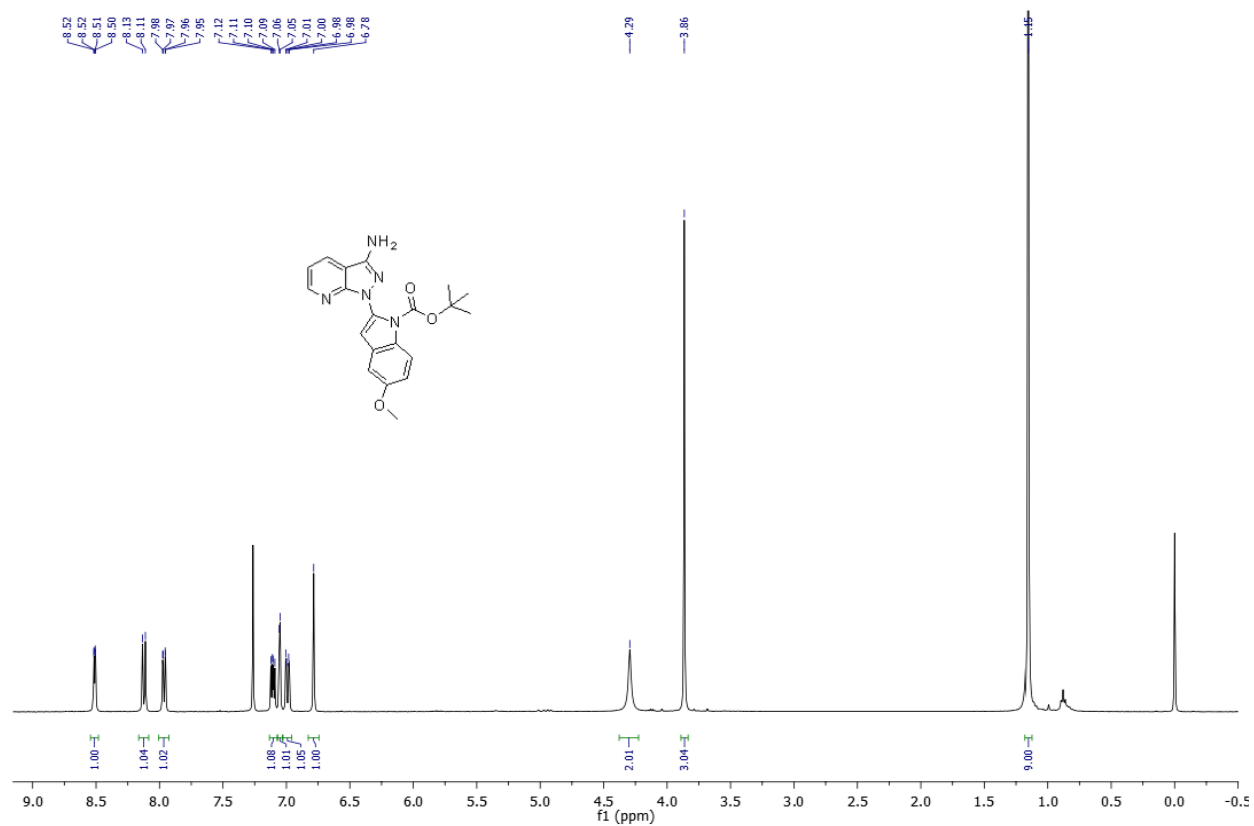
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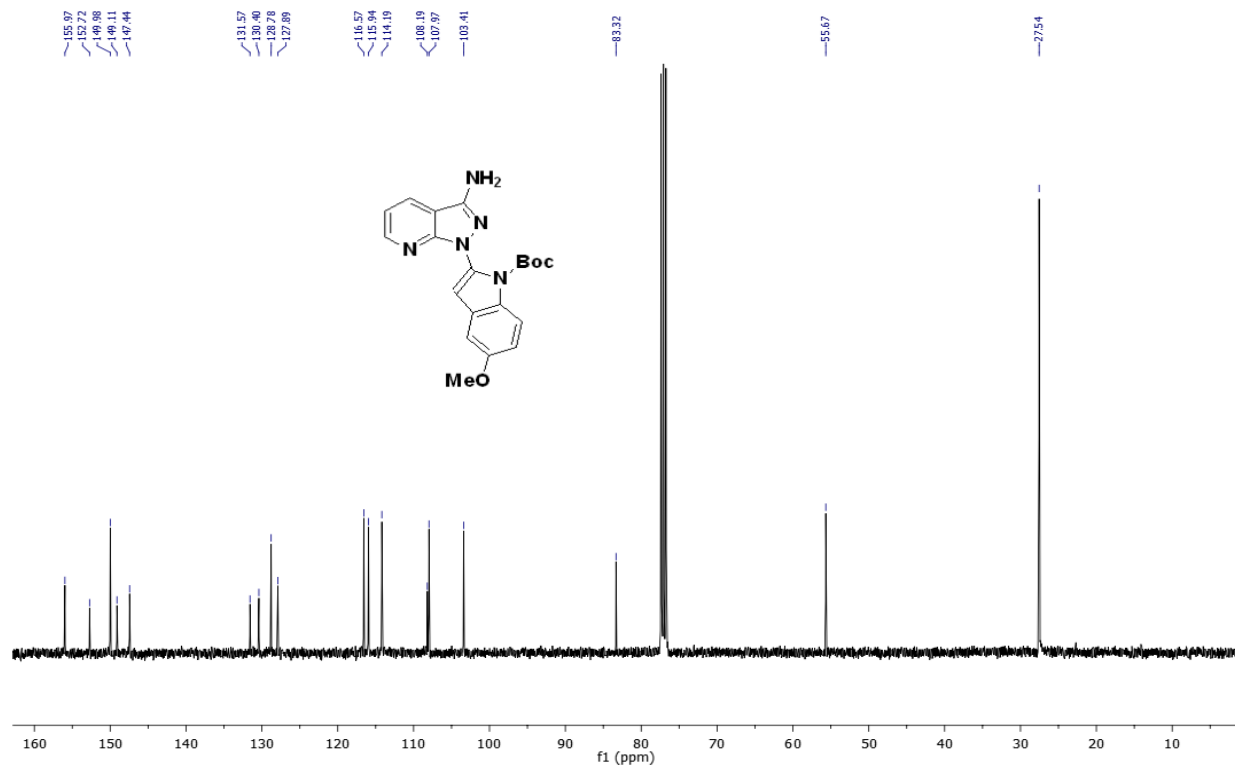
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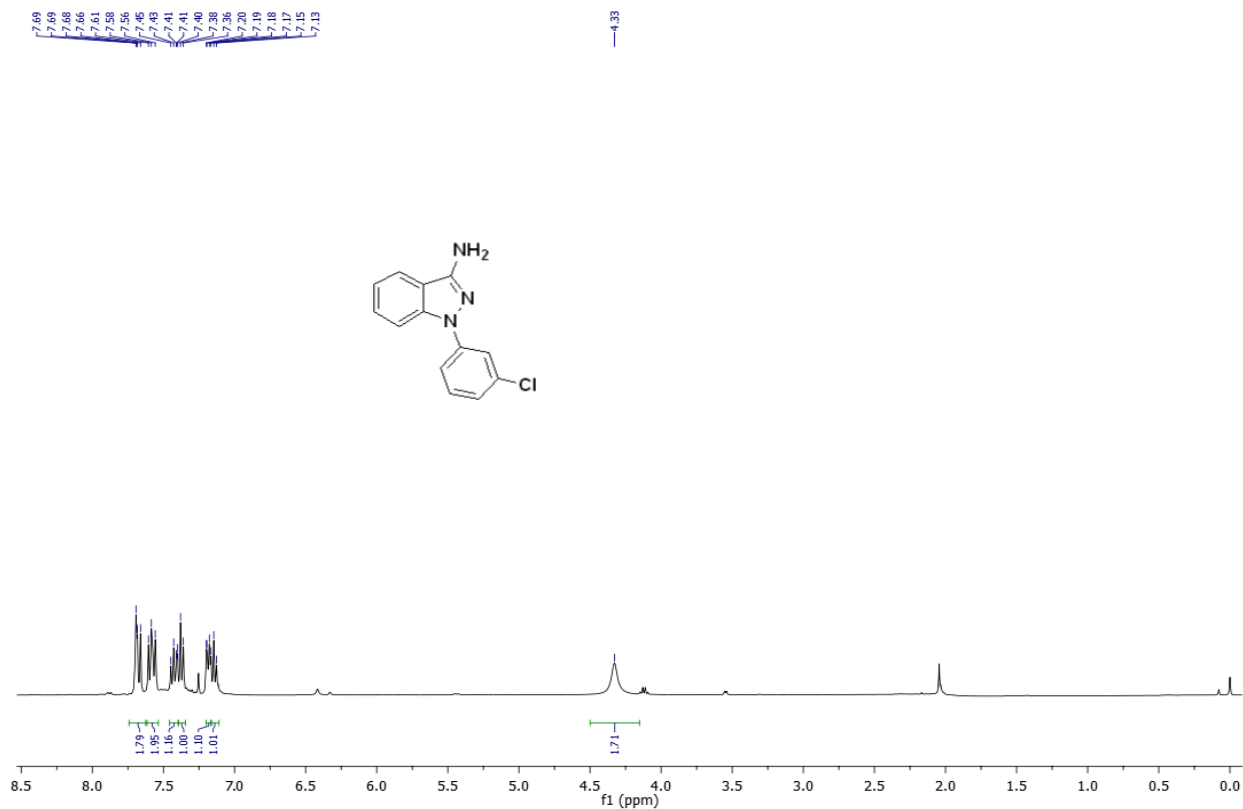
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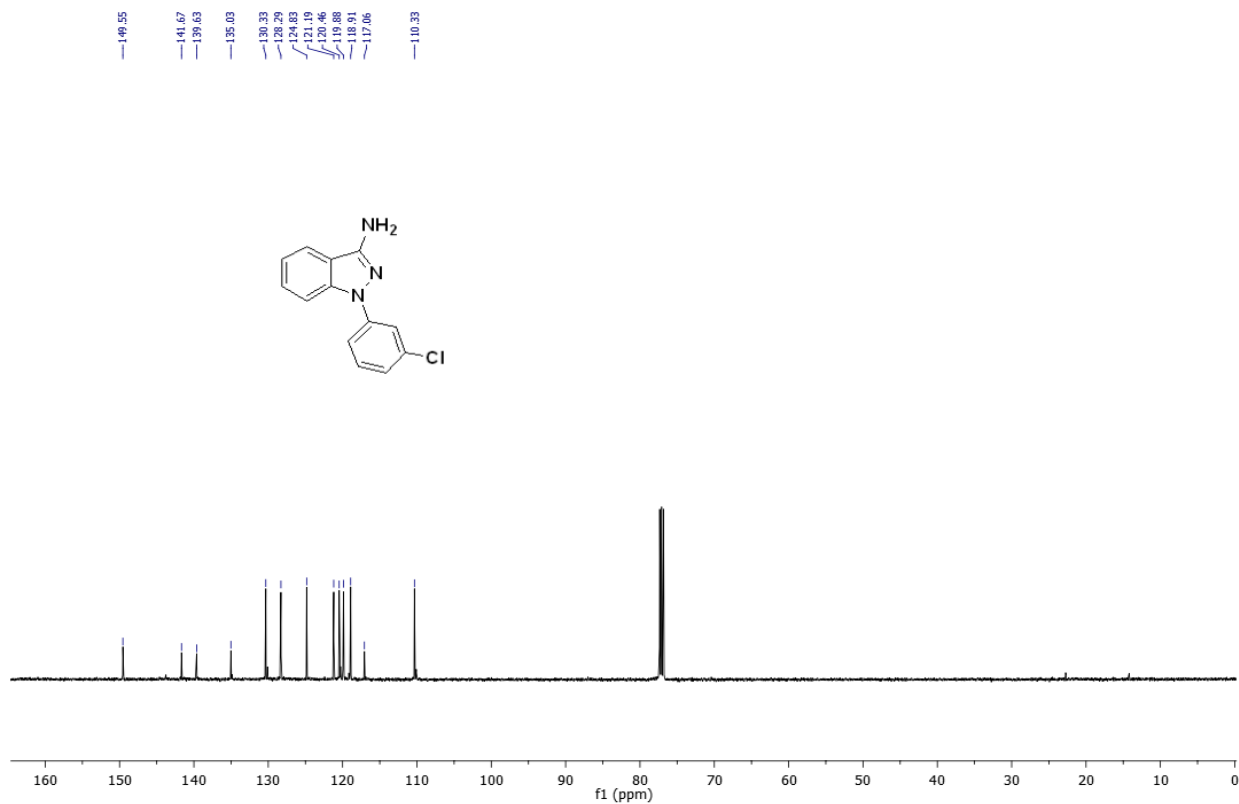
$^{13}\text{C-NMR}$ of 2o (100 MHz, CDCl_3)



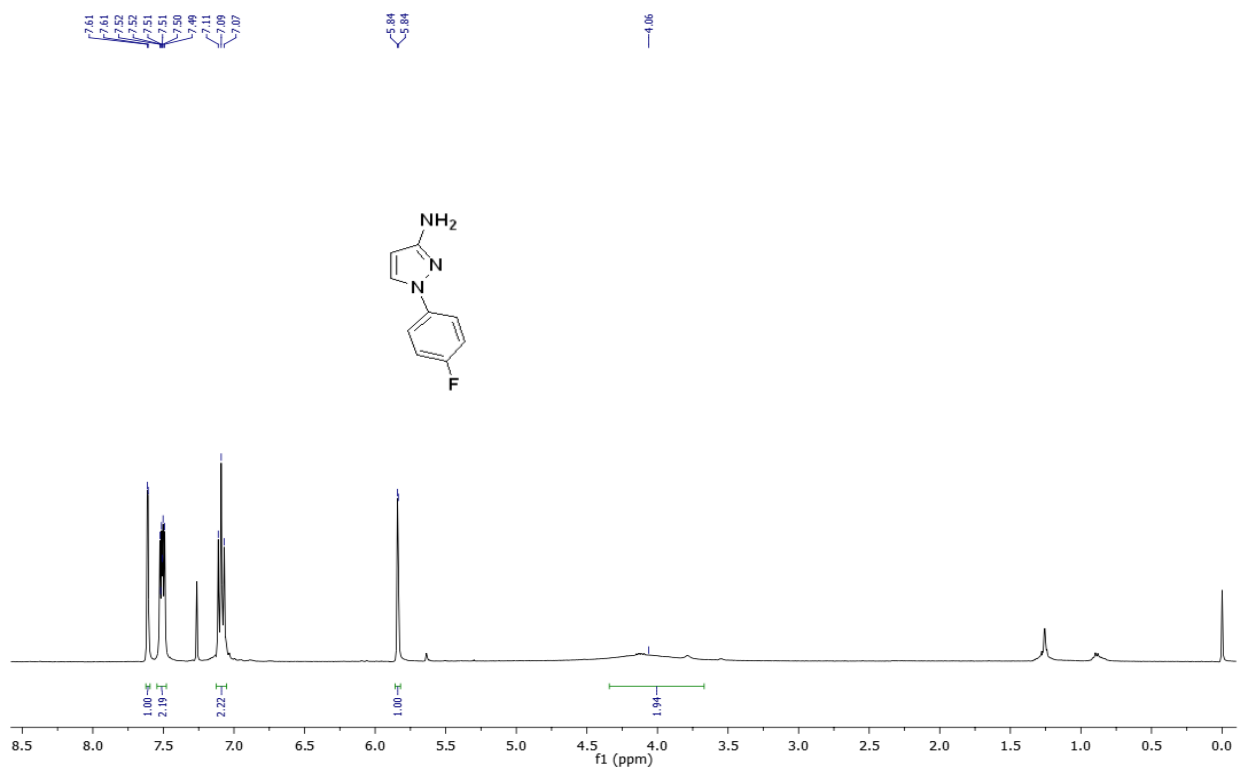
$^1\text{H-NMR}$ of 2p (400 MHz, CDCl_3)



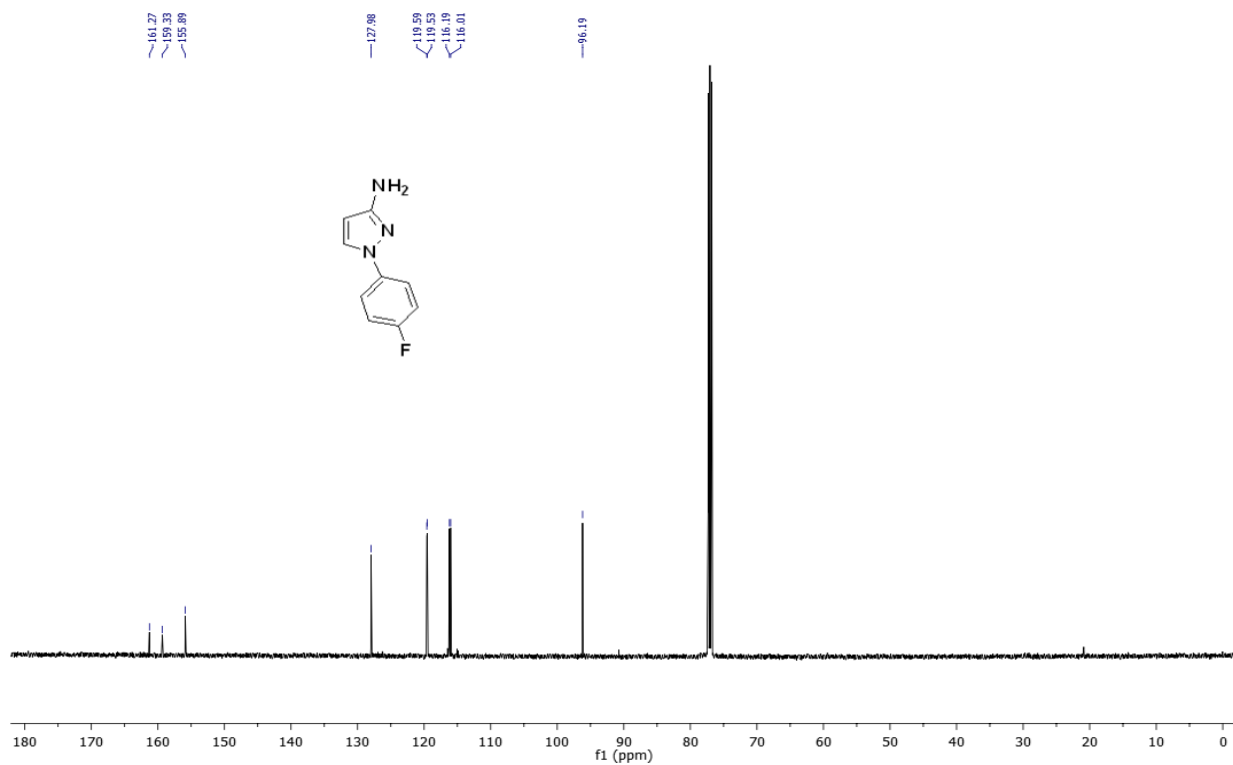
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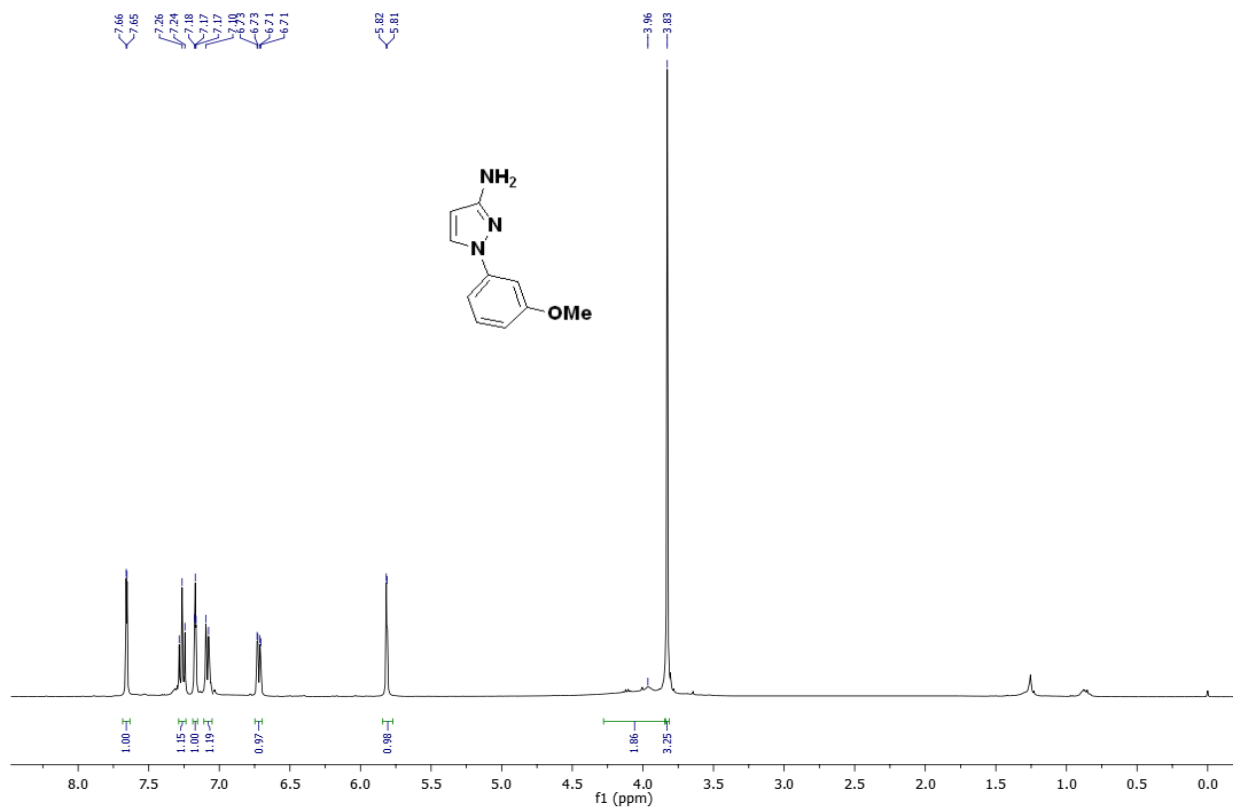
^1H -NMR of 2q (400 MHz, CDCl_3)



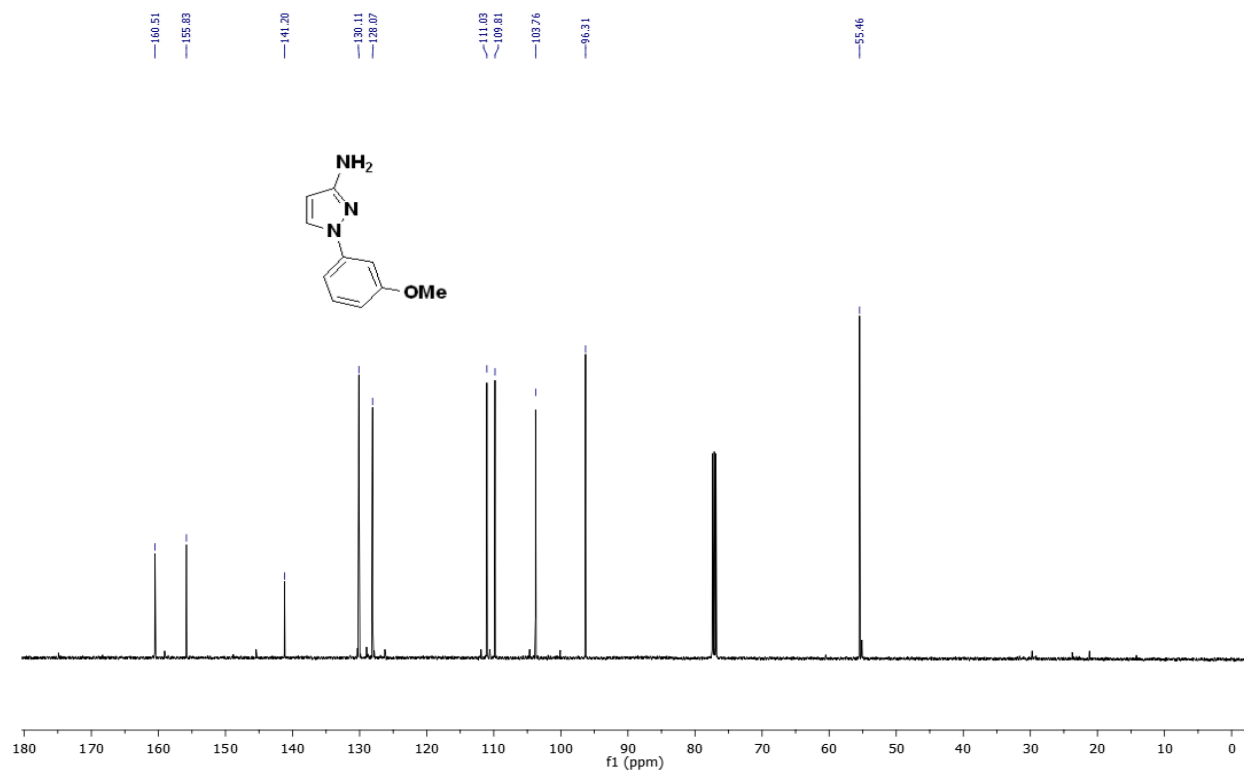
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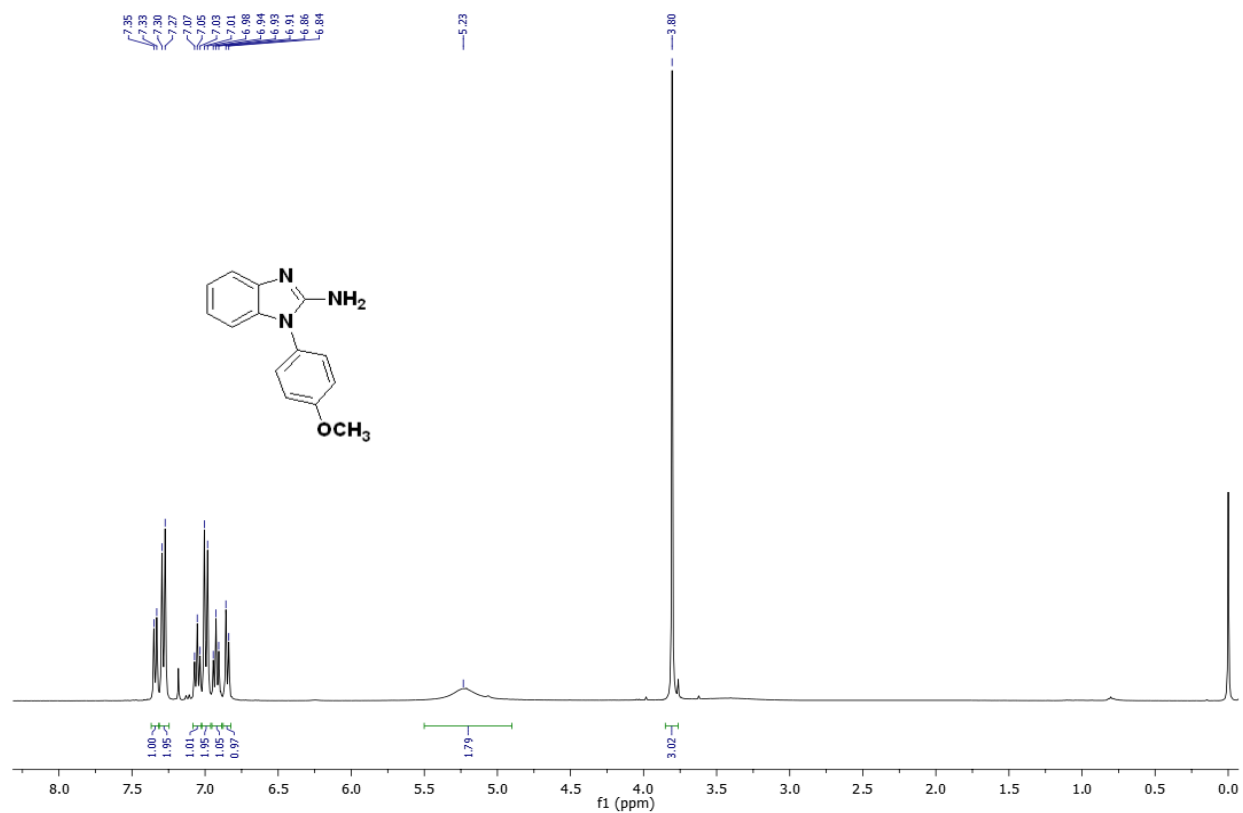
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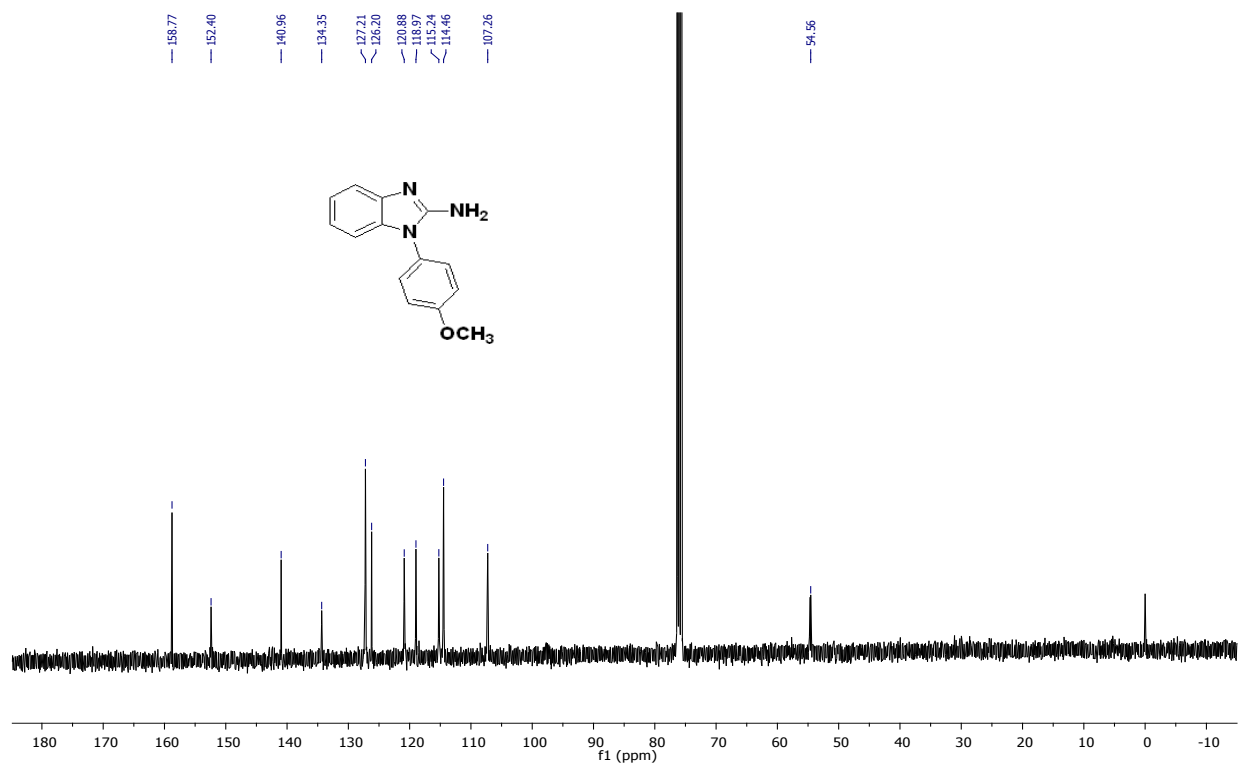
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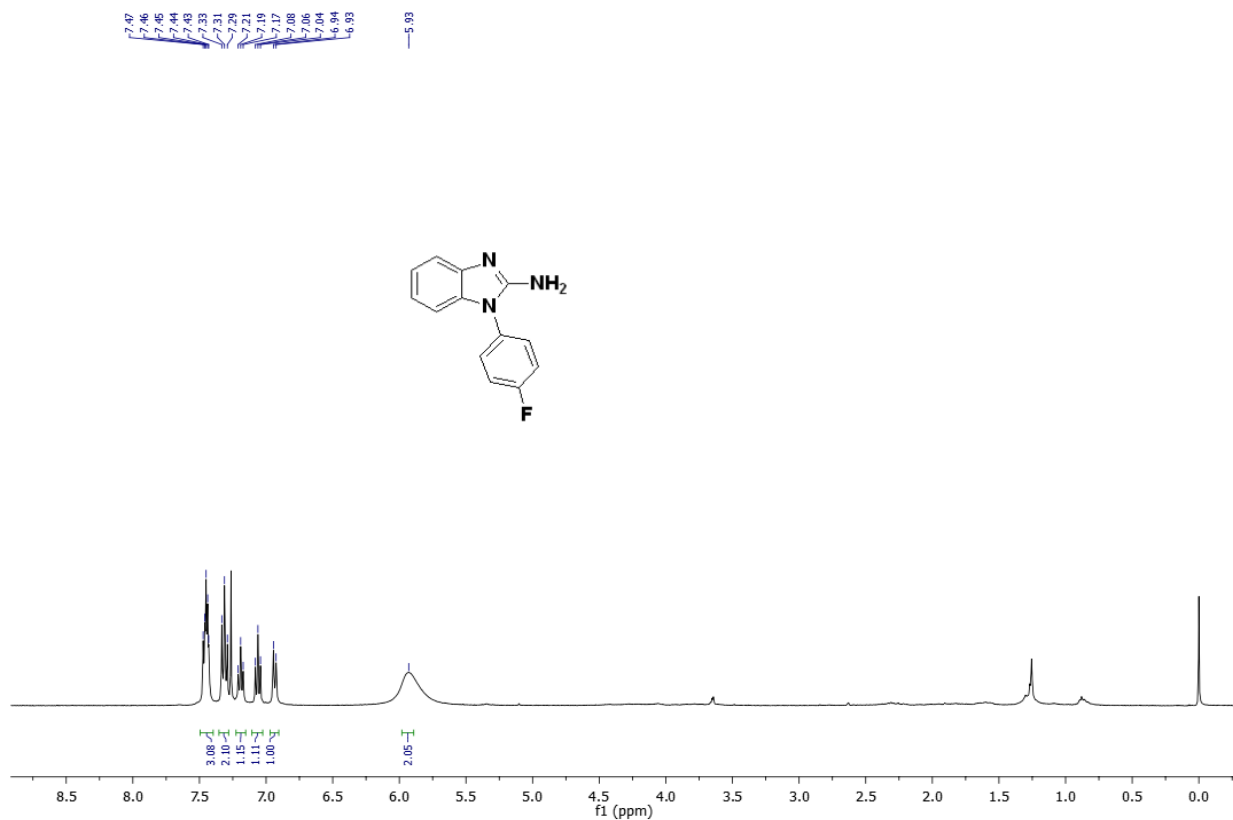
¹H-NMR of 3a (400 MHz, CDCl₃)



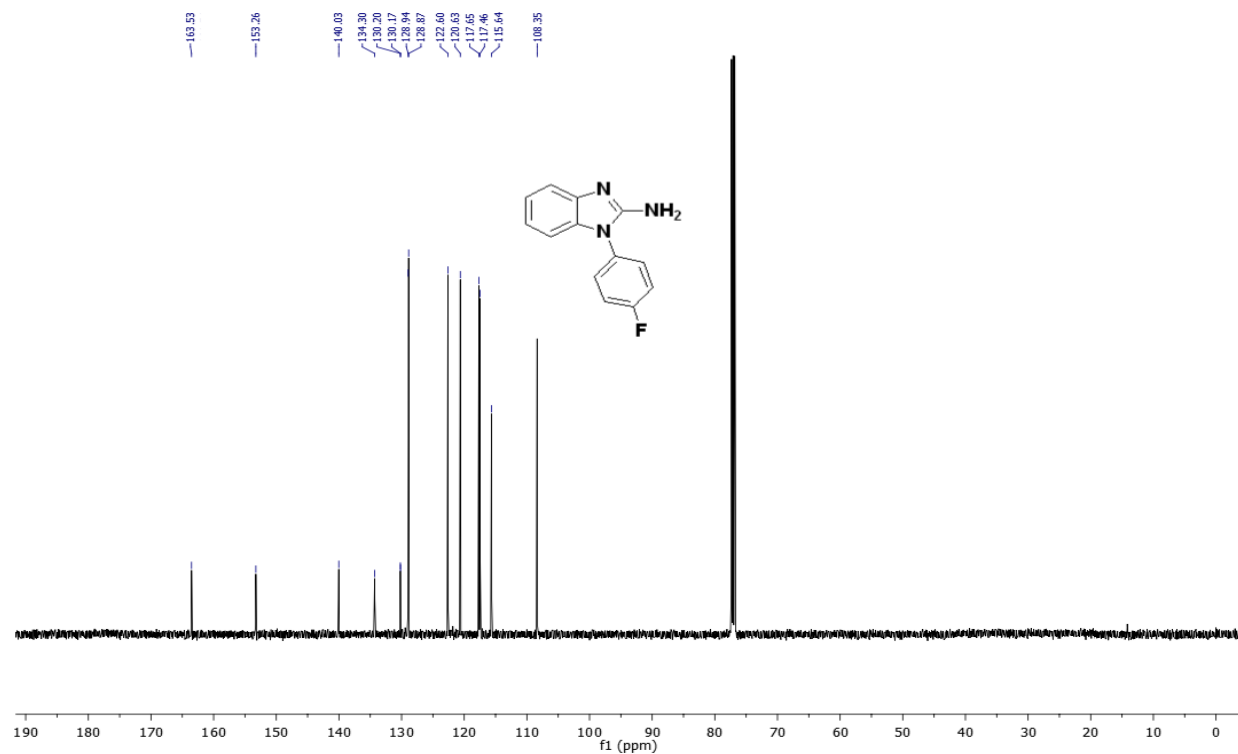
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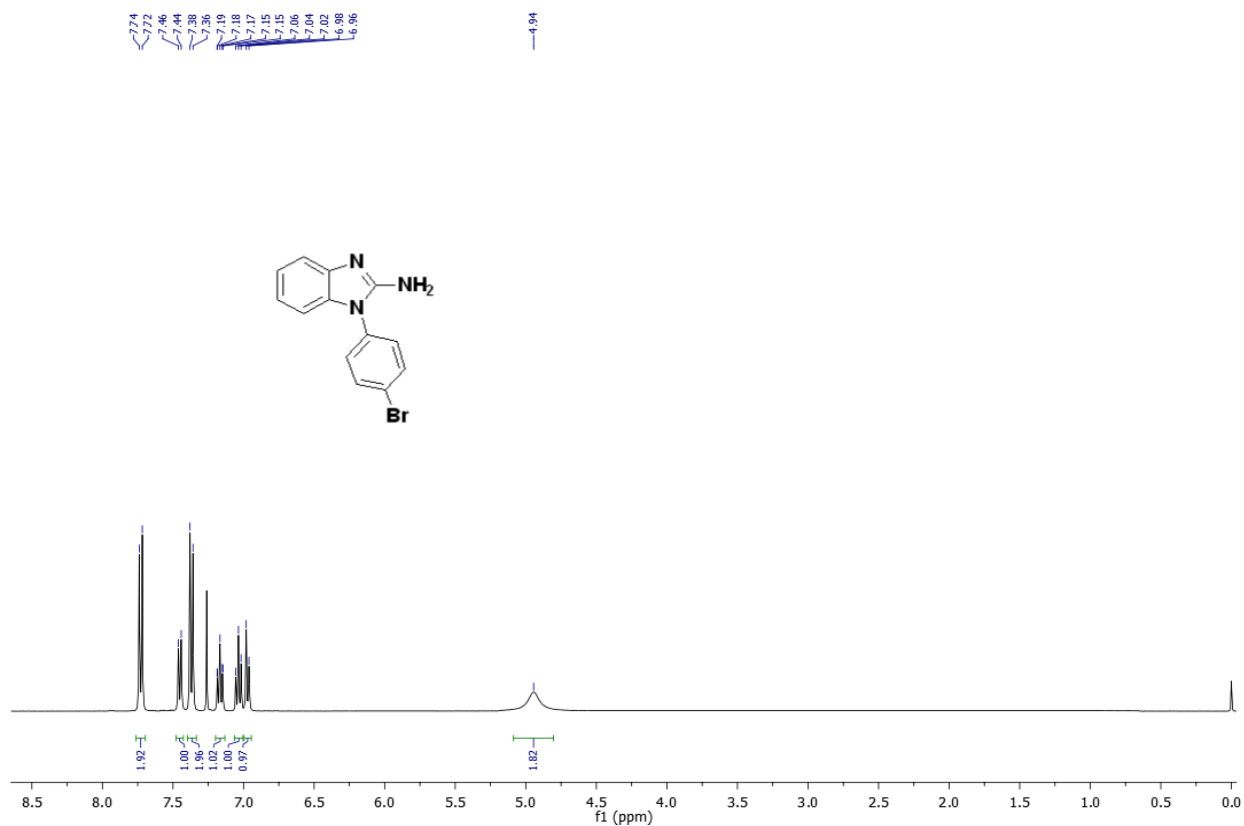
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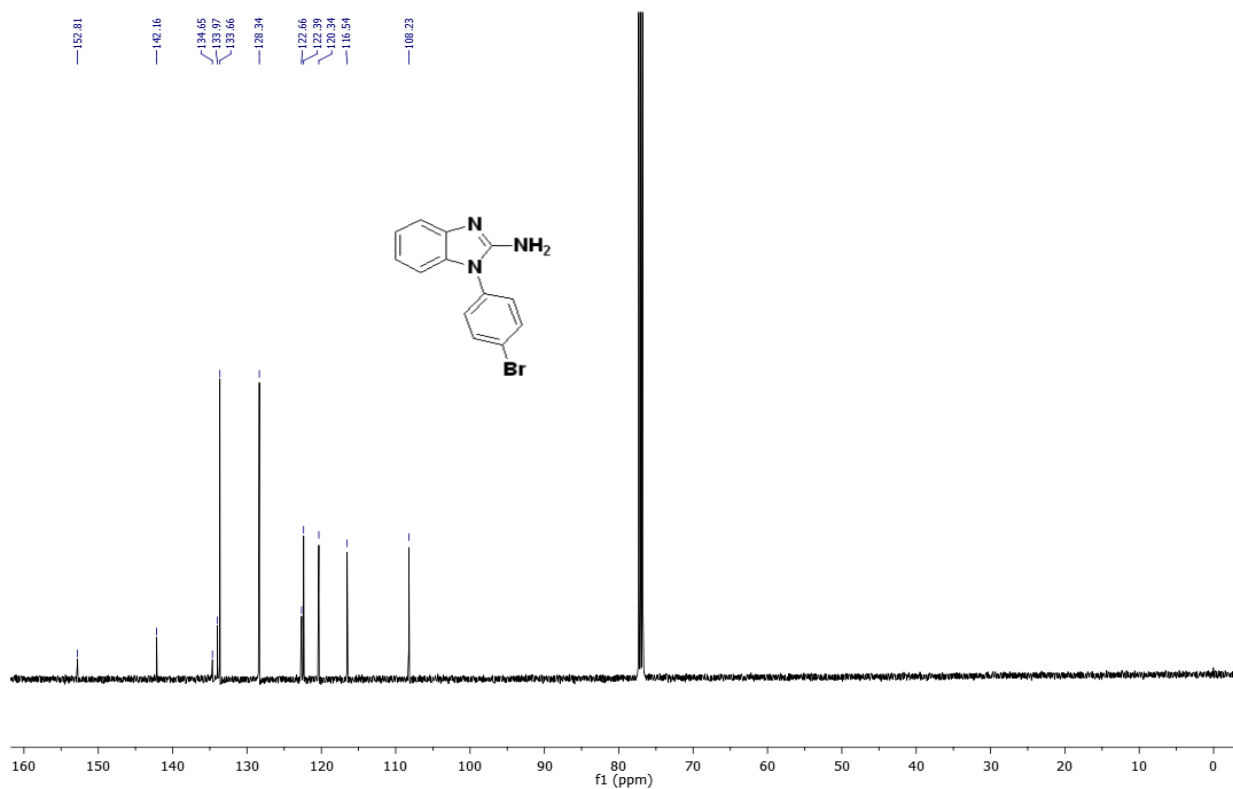
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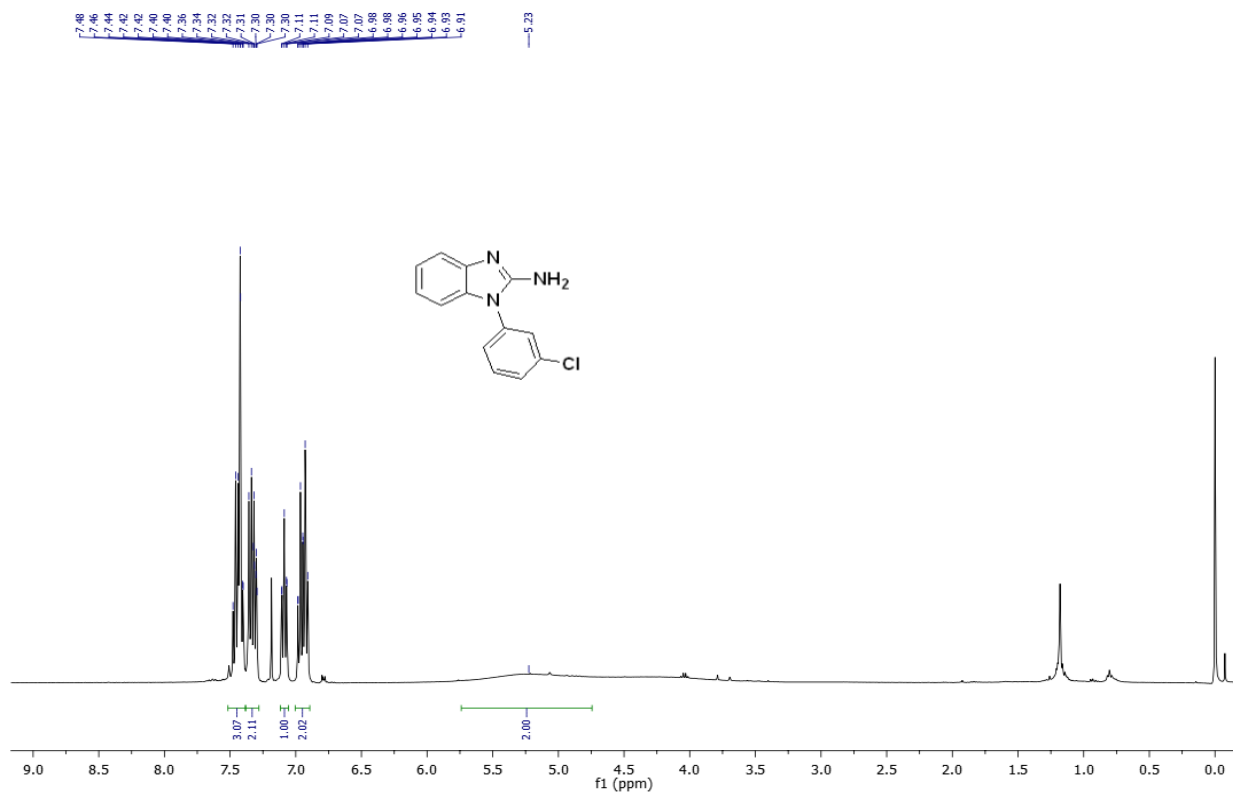
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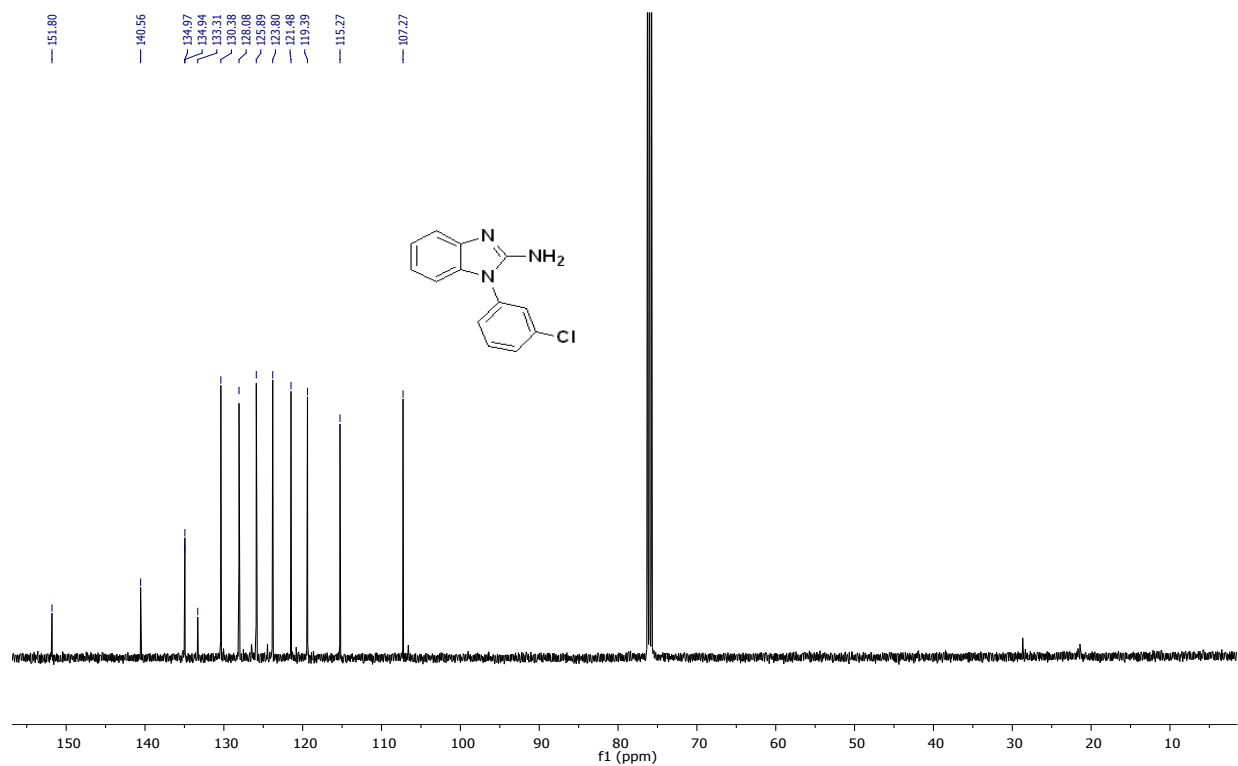
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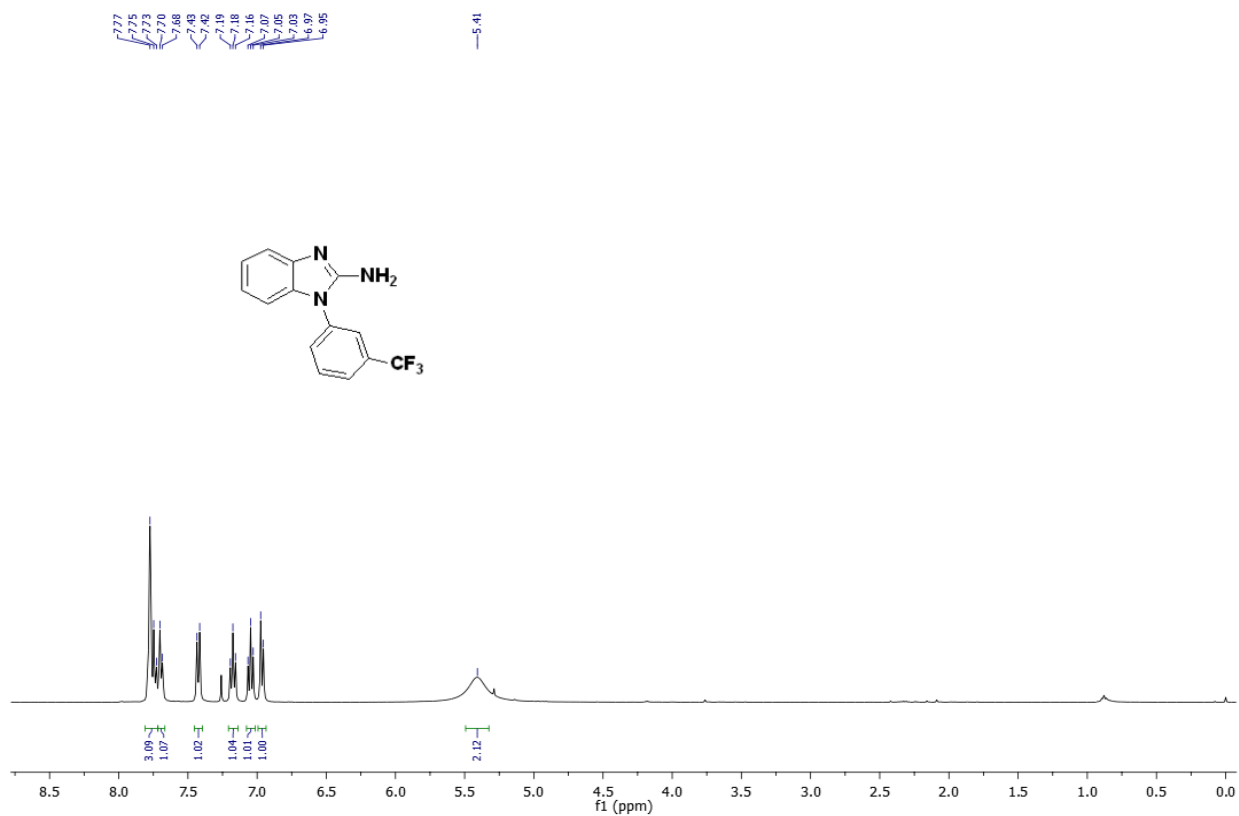
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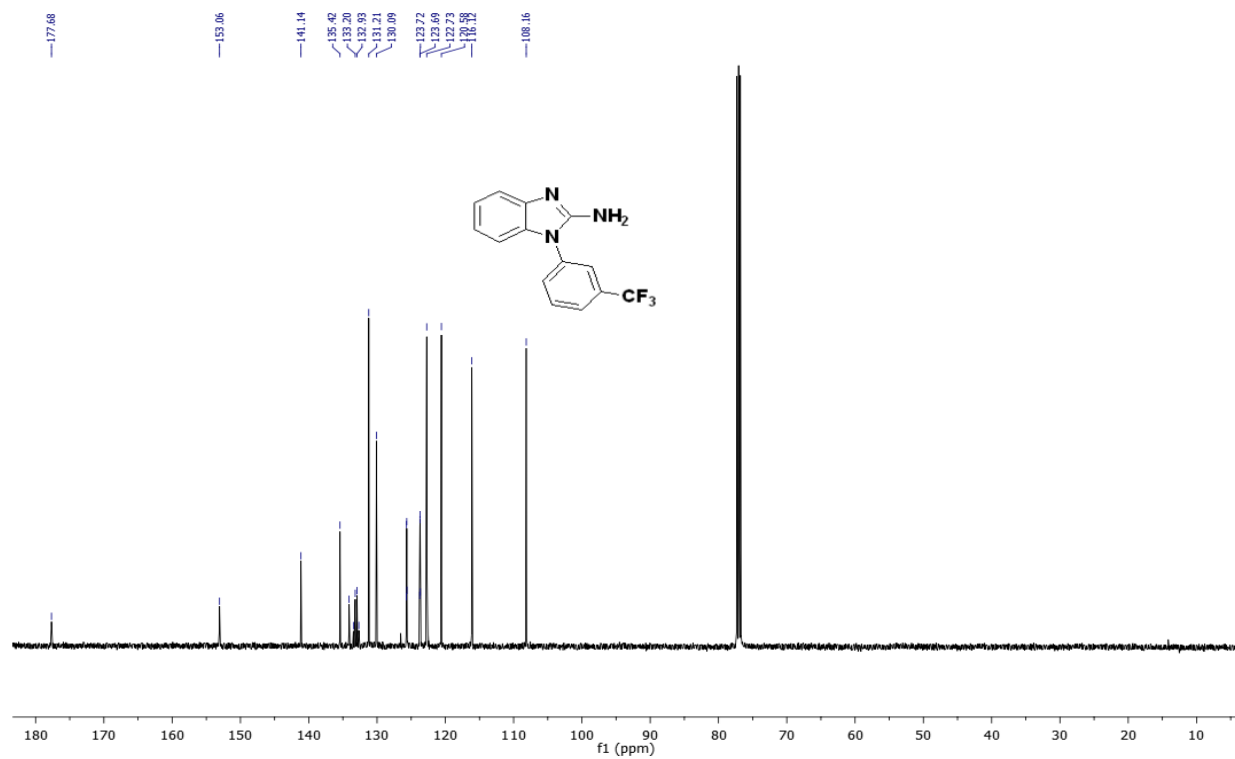
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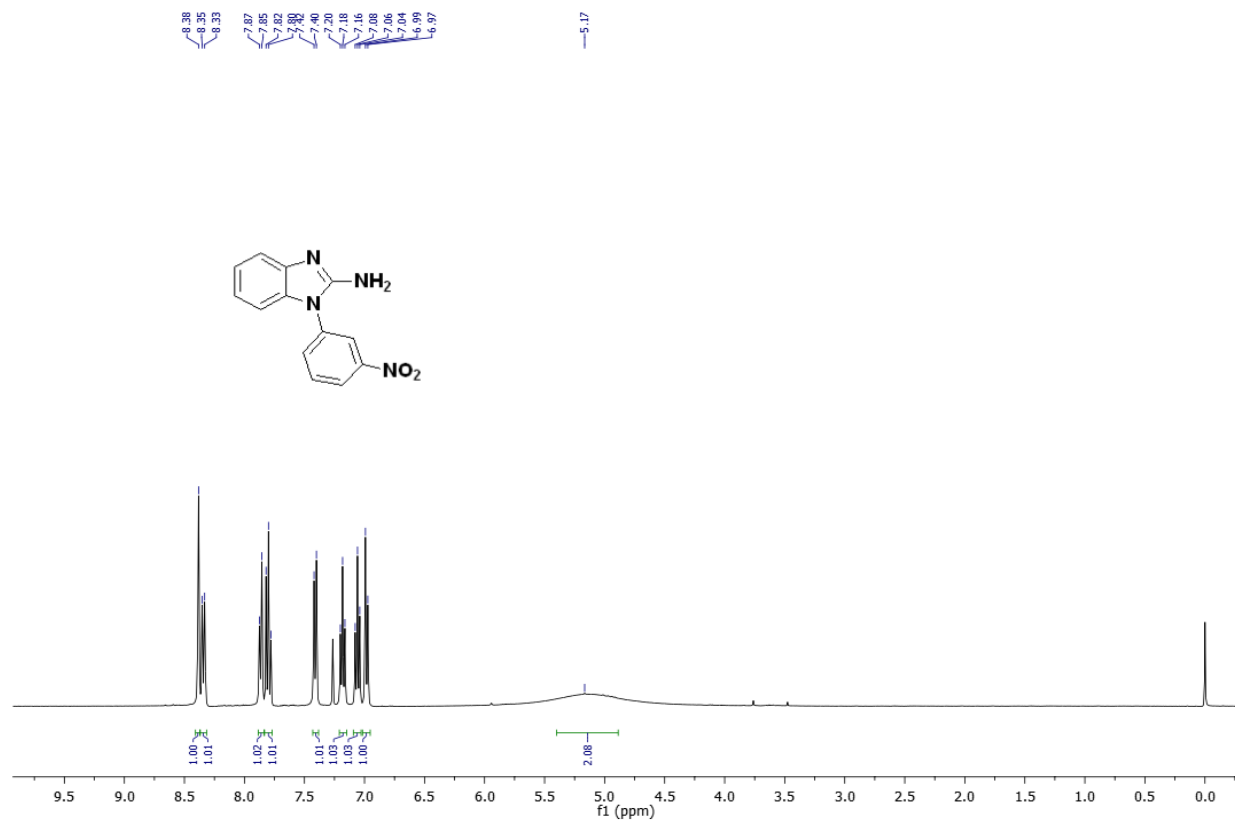
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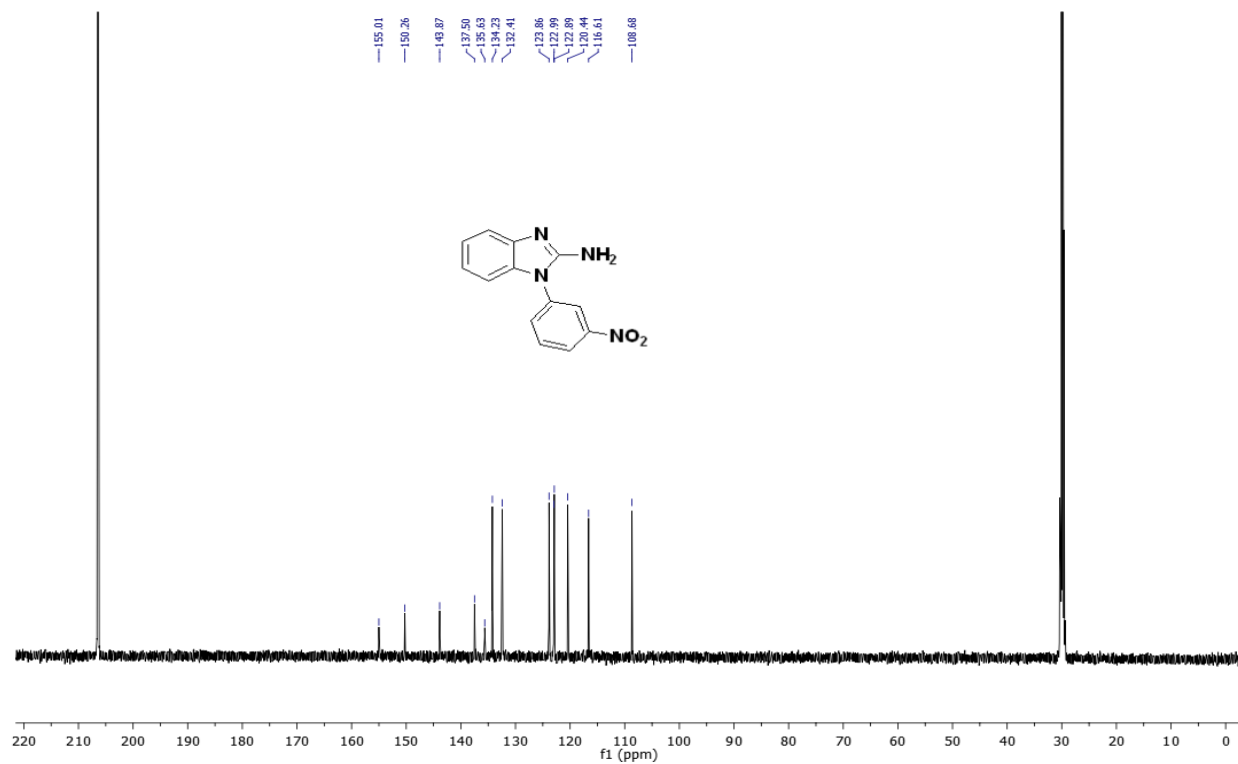
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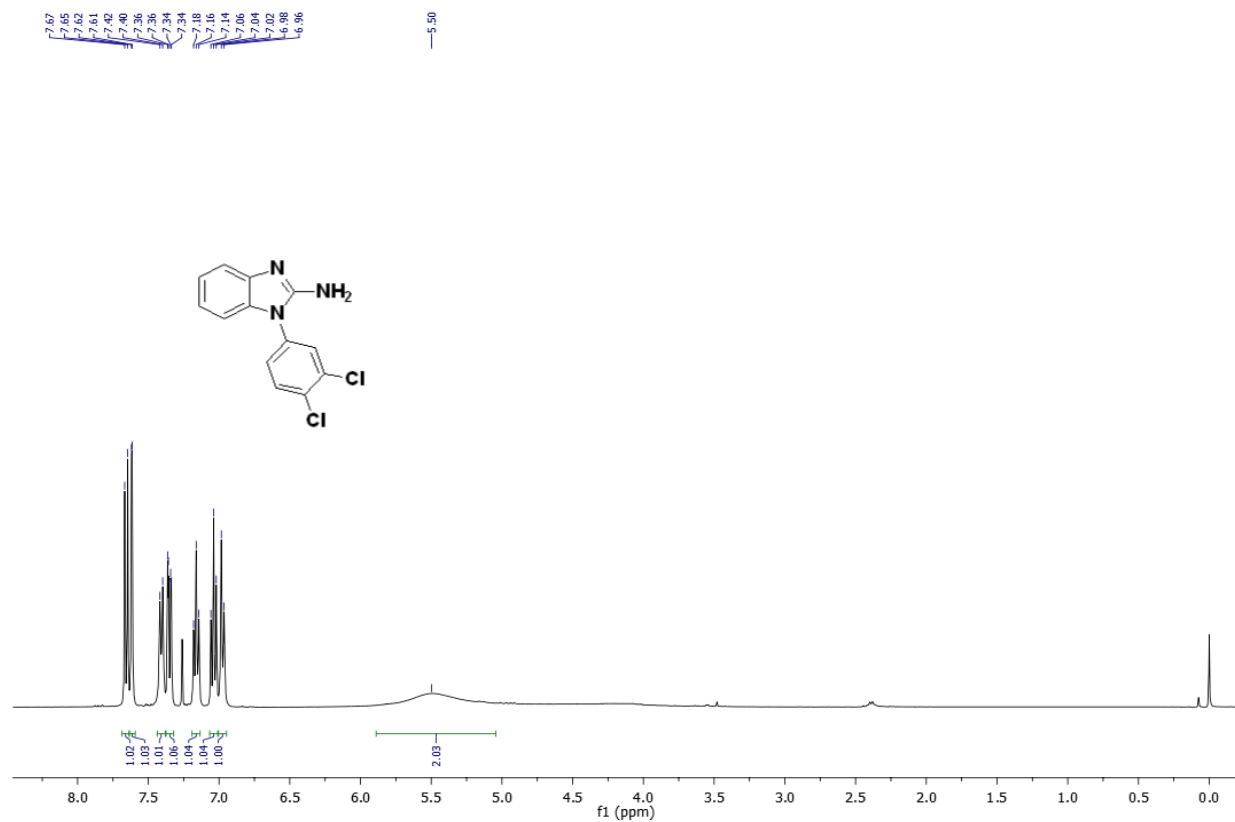
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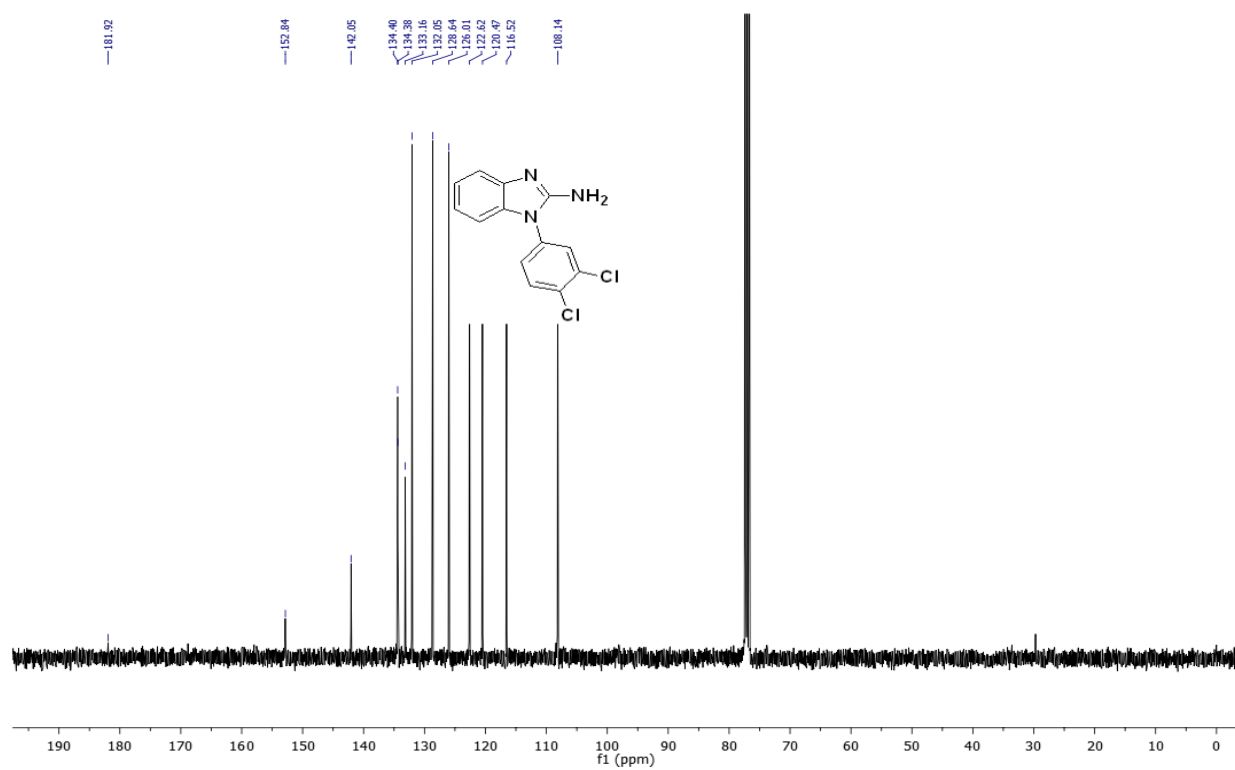
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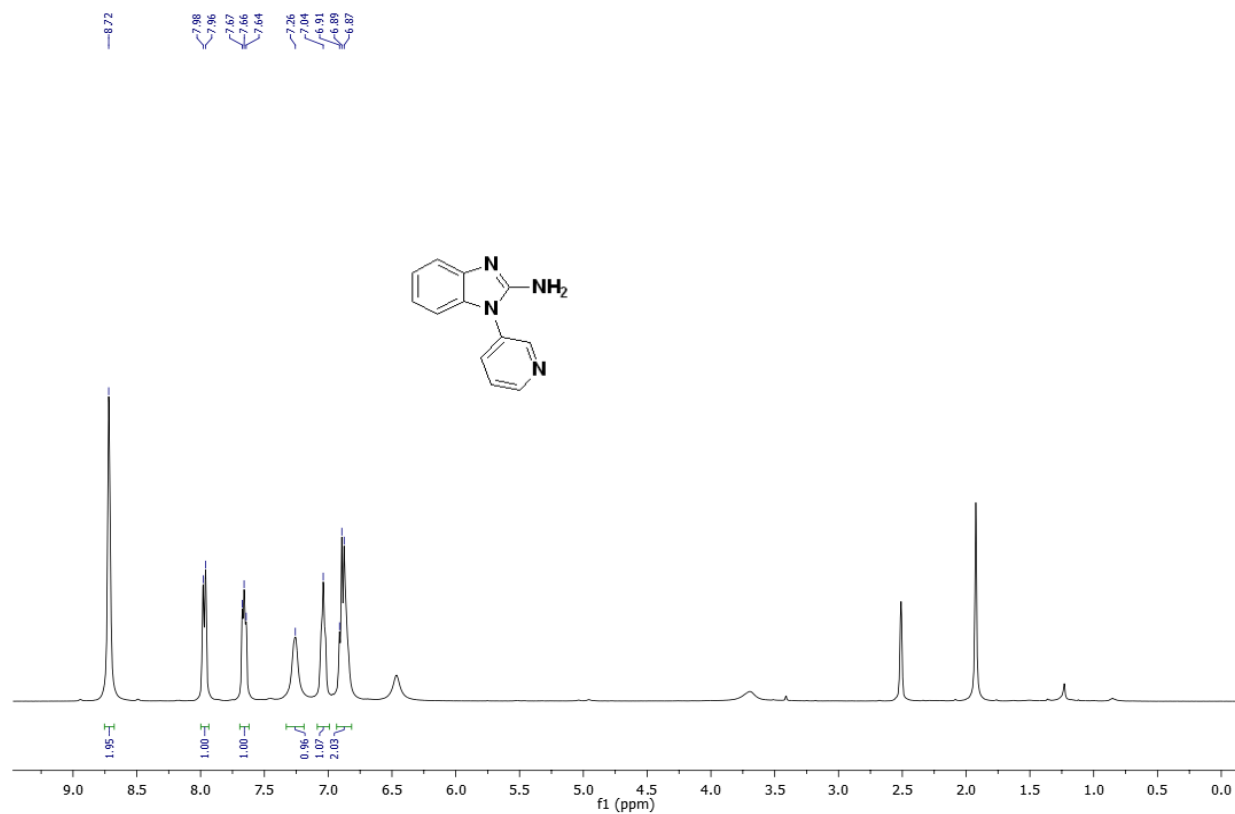
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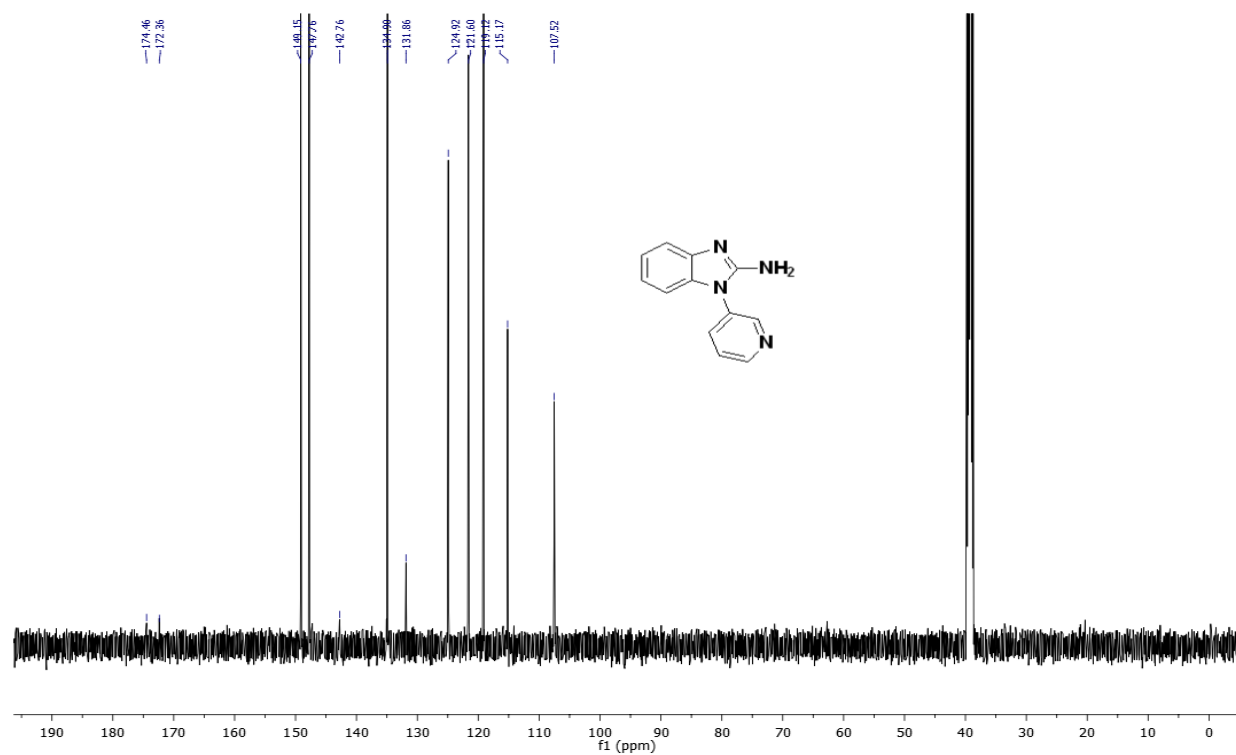
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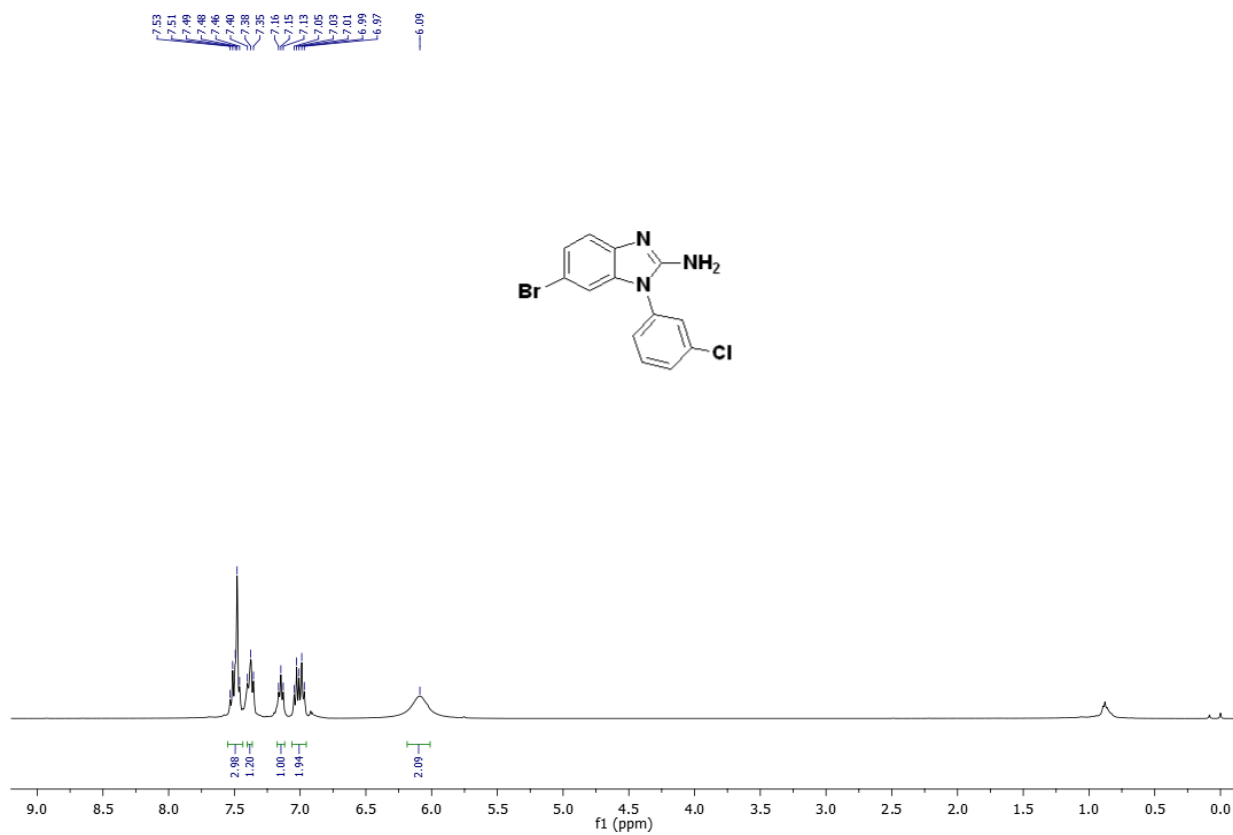
^1H -NMR of 3h (400 MHz, $\text{DMSO-}d_6$)



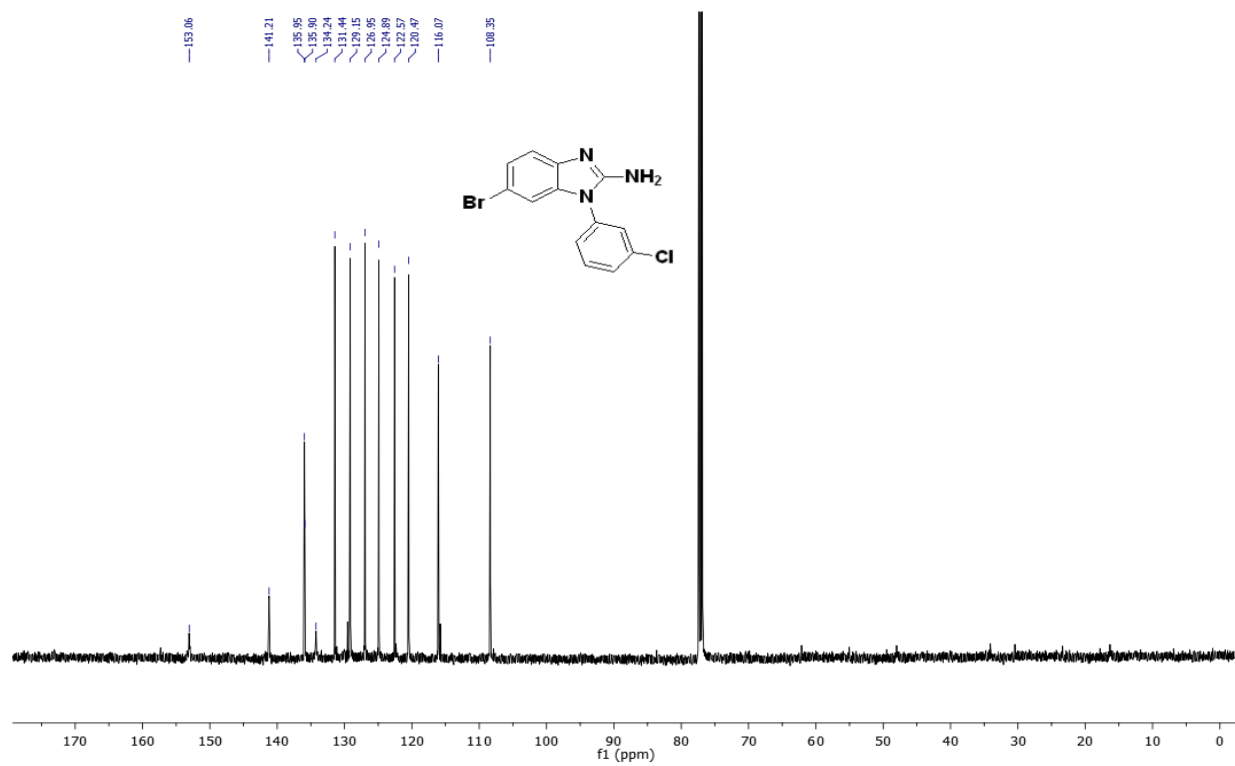
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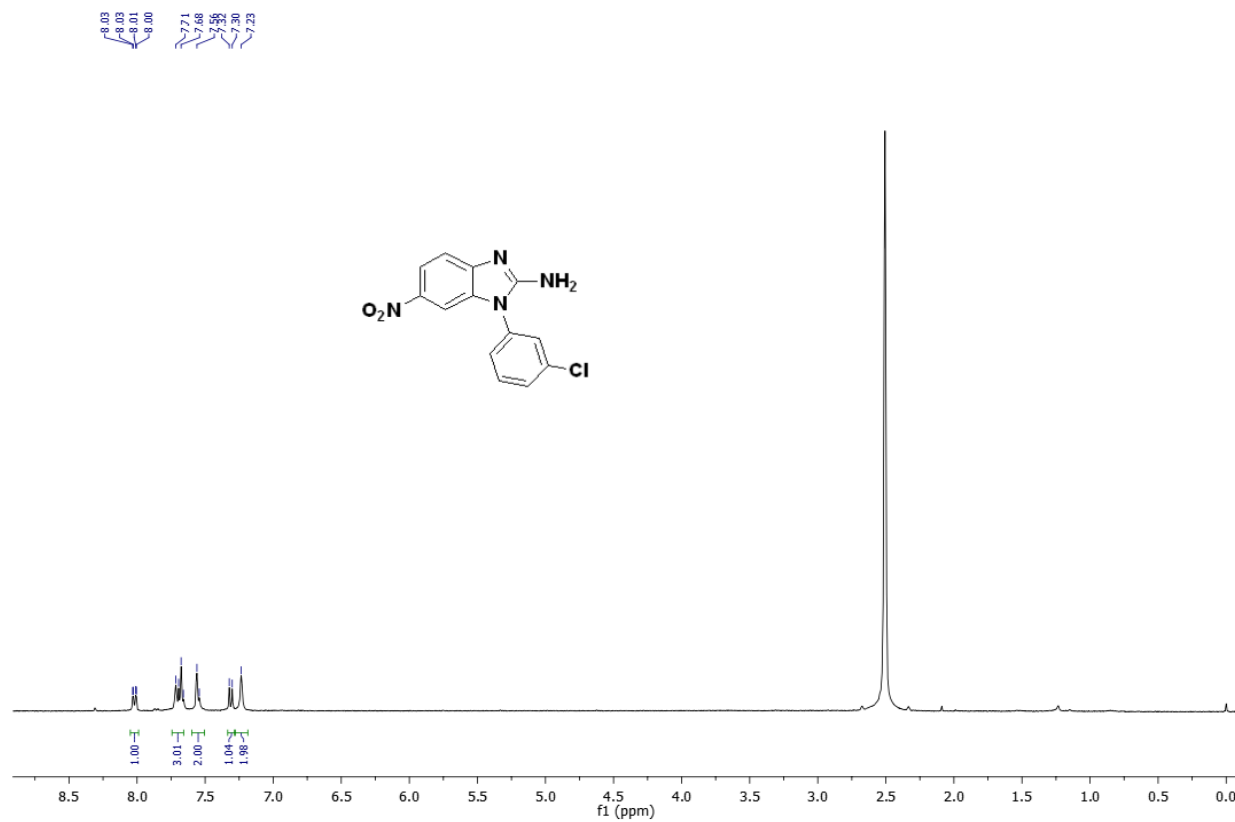
¹H-NMR of 3i (400 MHz, CDCl₃)



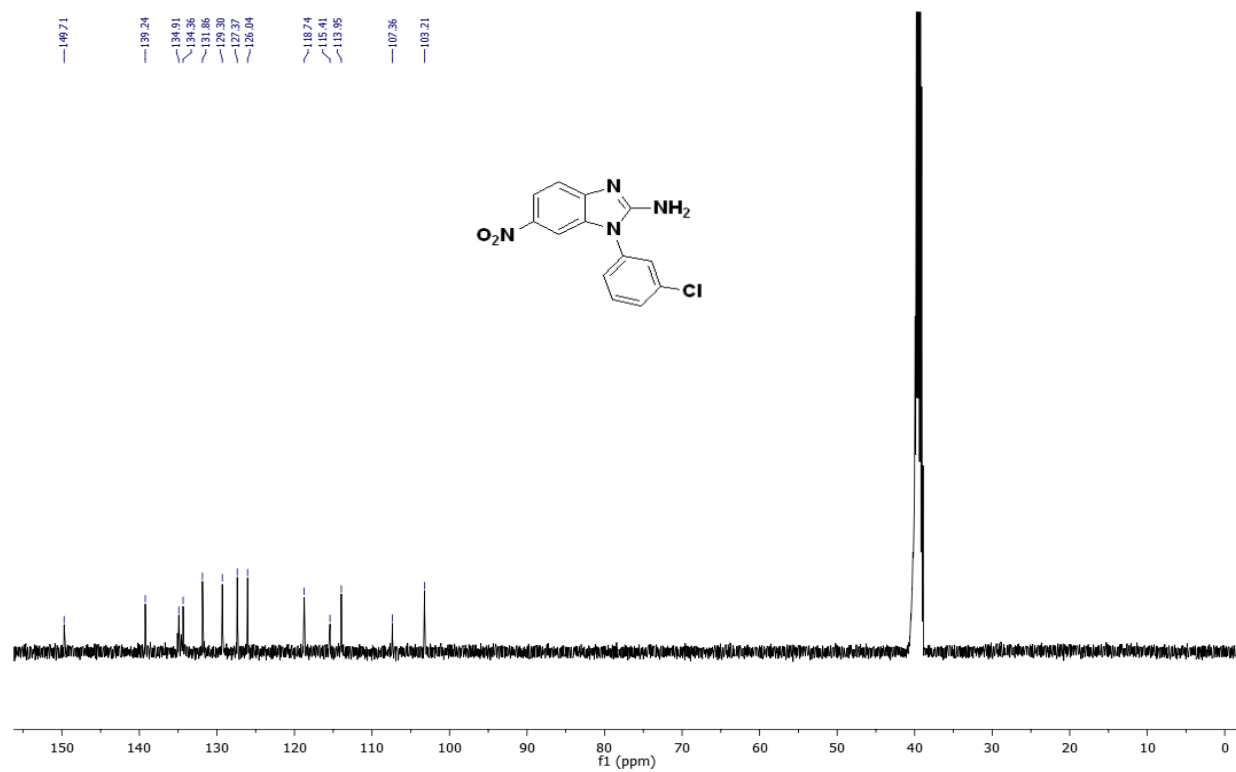
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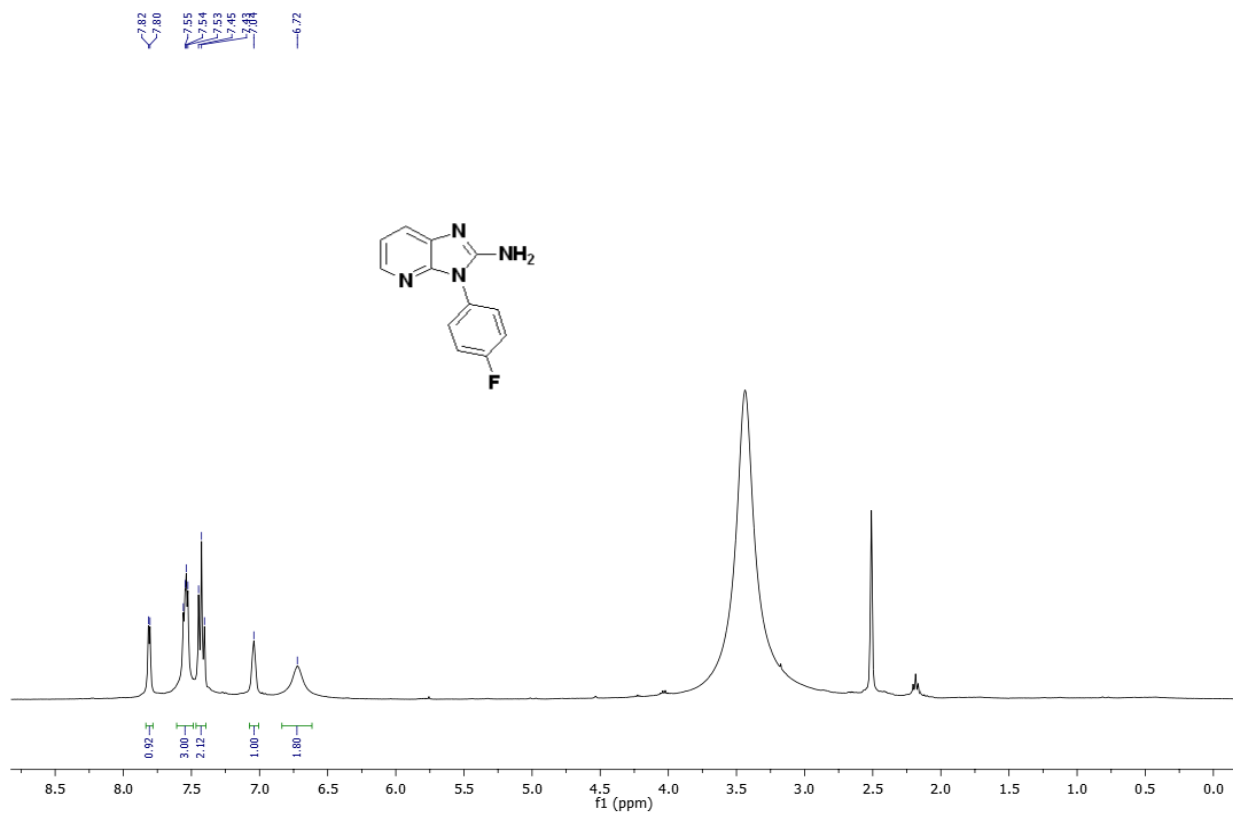
^1H -NMR of 3j (400 MHz, $\text{DMSO-}d_6$)



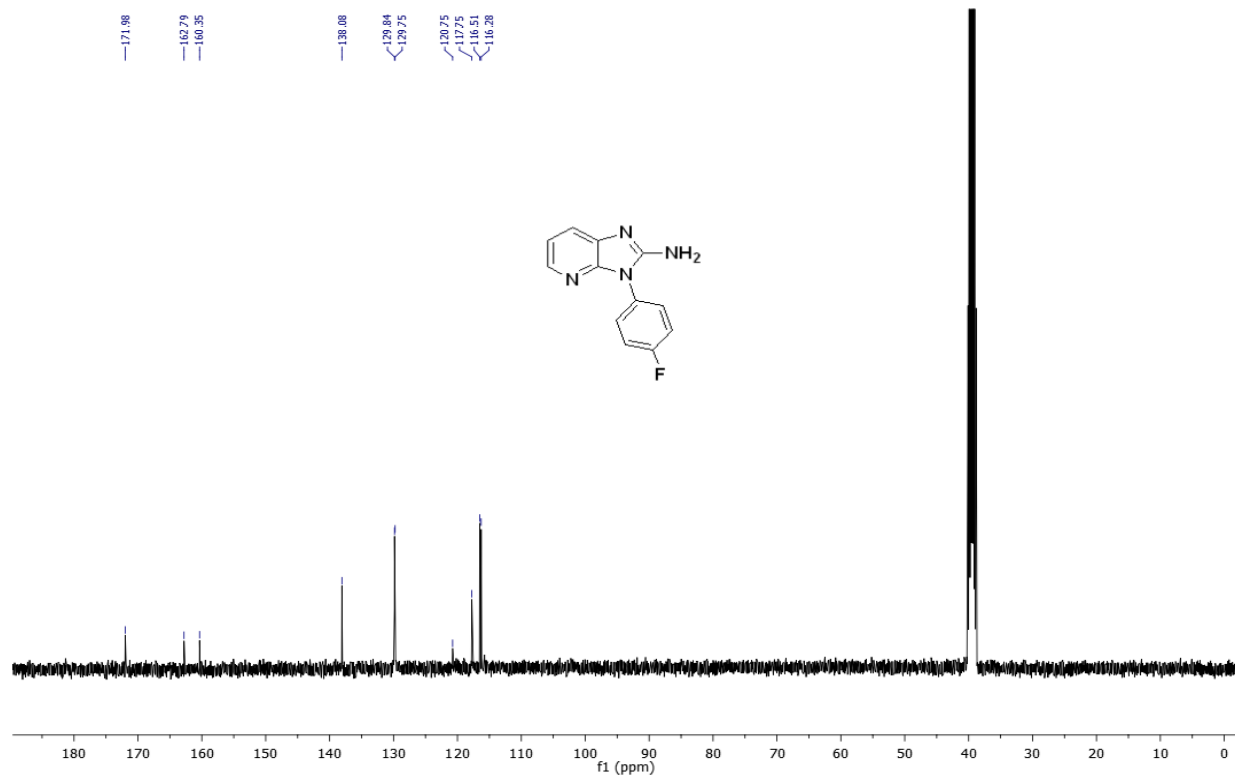
¹³C-NMR of 3j (125 MHz, DMSO-*d*₆)



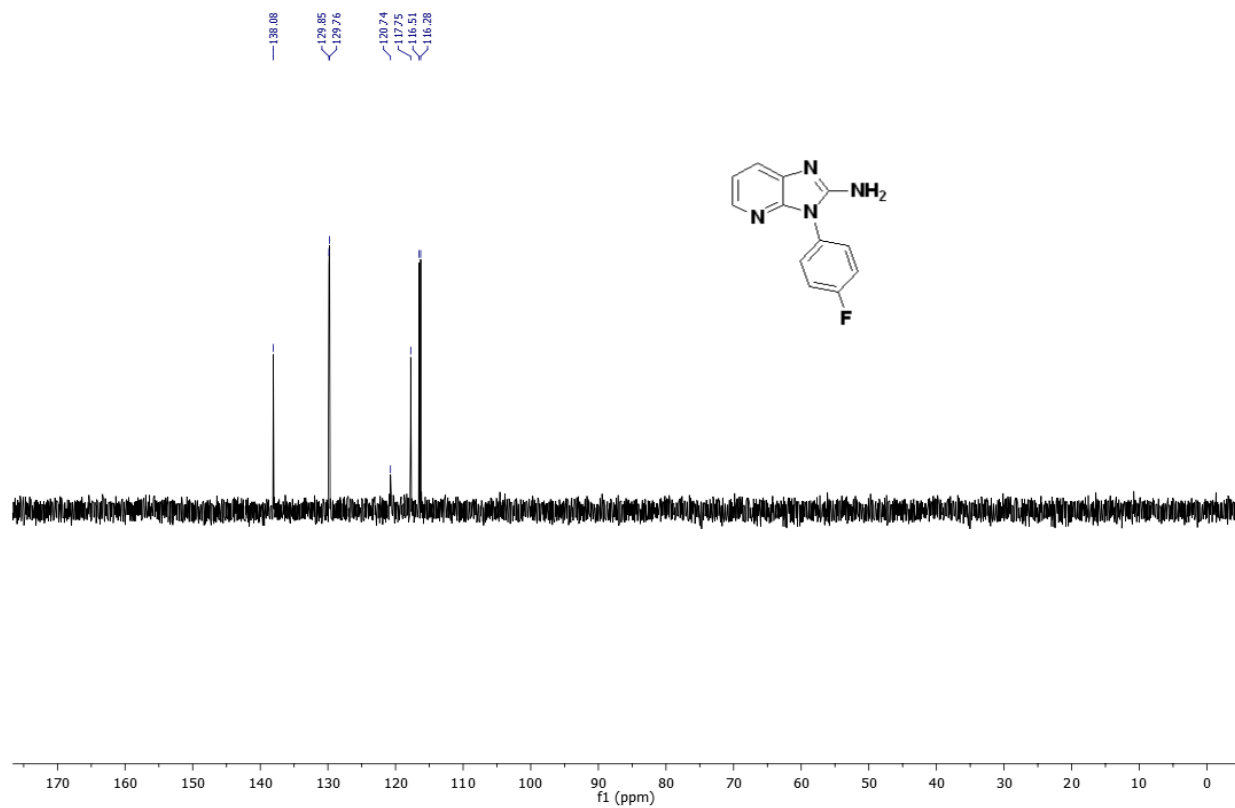
¹H-NMR of 3k (400 MHz, DMSO-*d*₆)



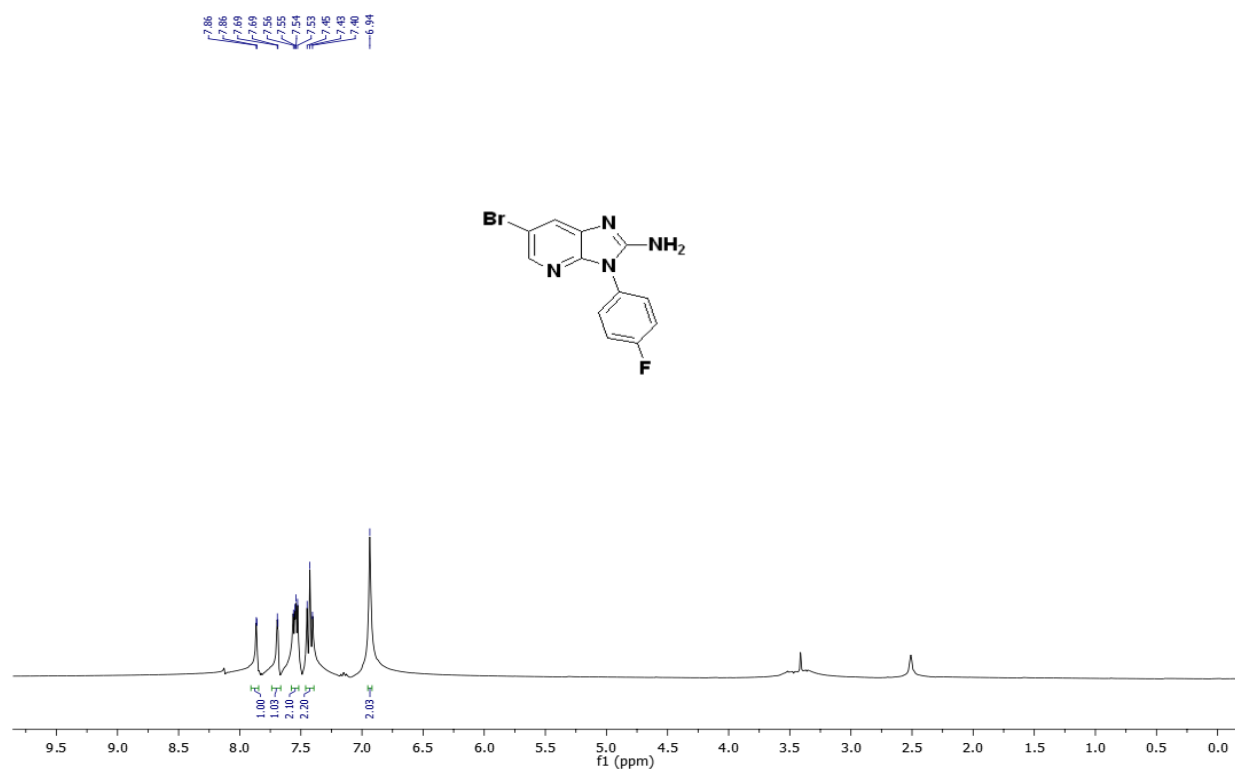
¹³C-NMR of 3k (100 MHz, DMSO-*d*₆)



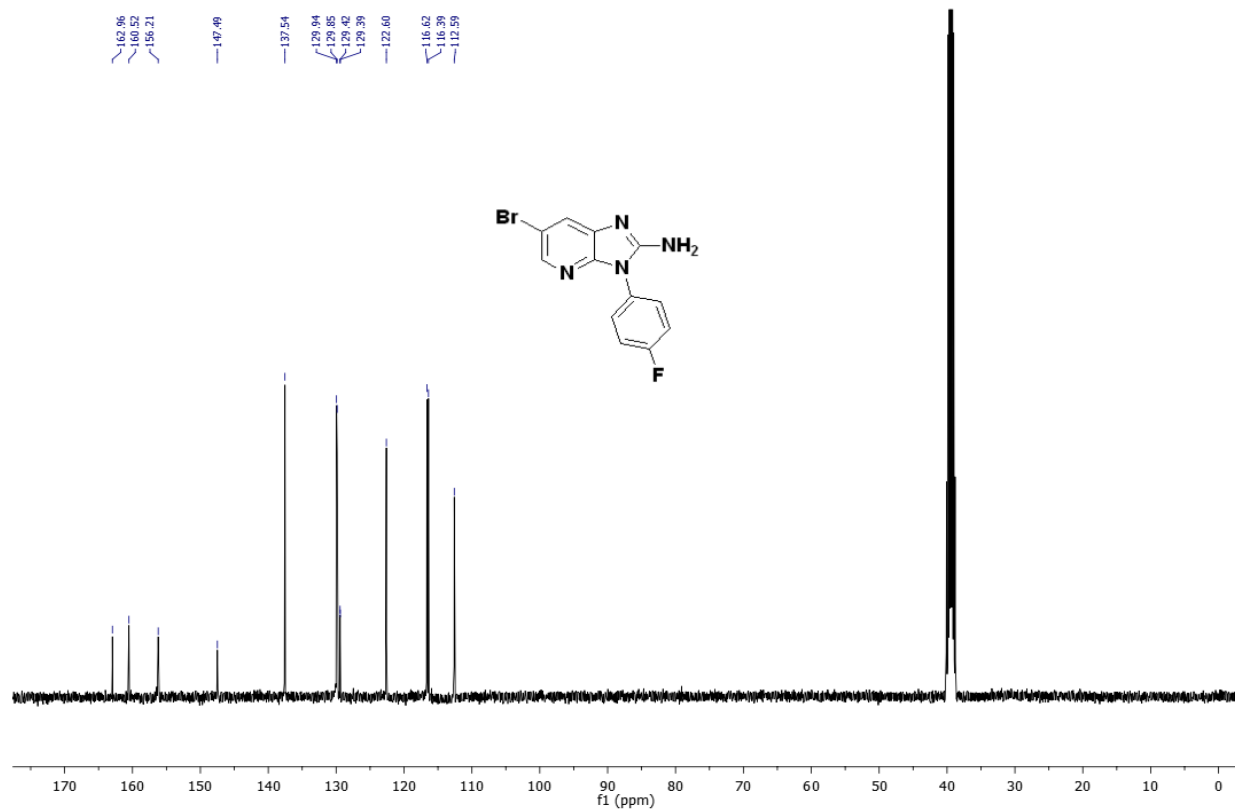
¹³C-NMR DEPT of 3k (100 MHz, DMSO-*d*₆)



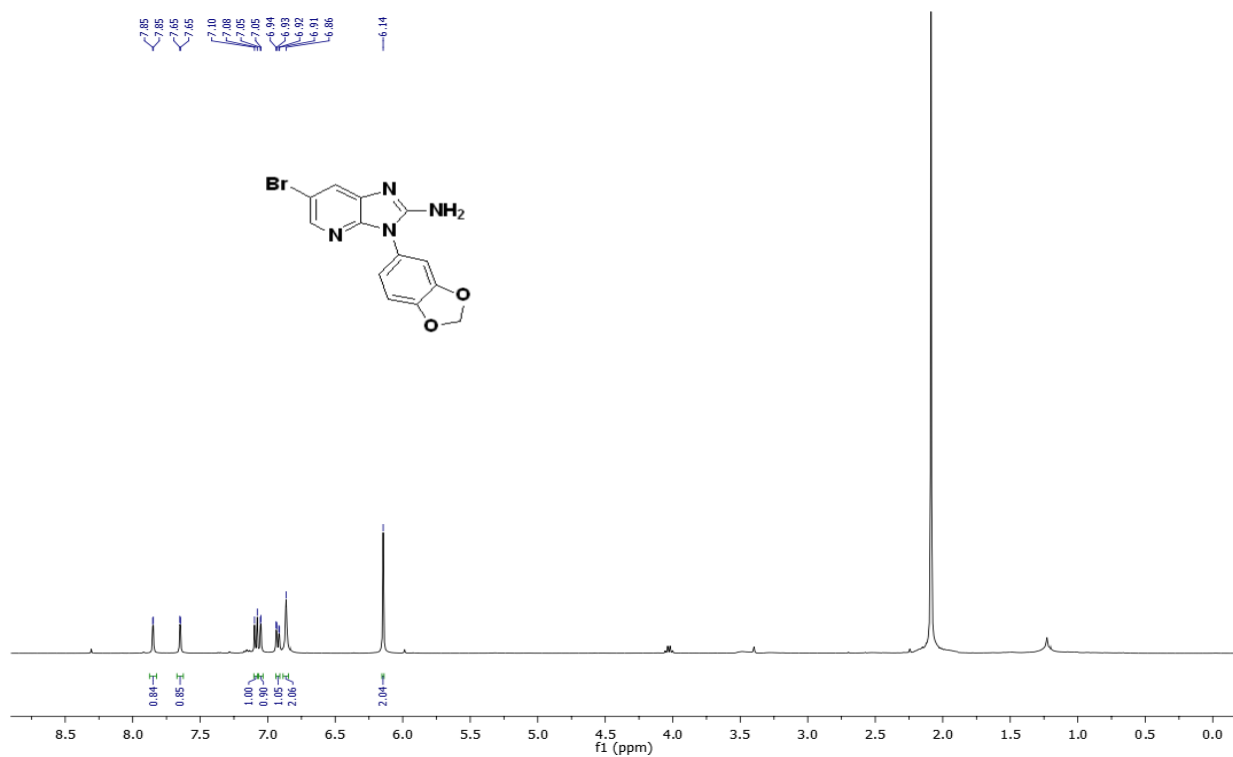
¹H-NMR of 31 (400 MHz, DMSO-*d*₆)



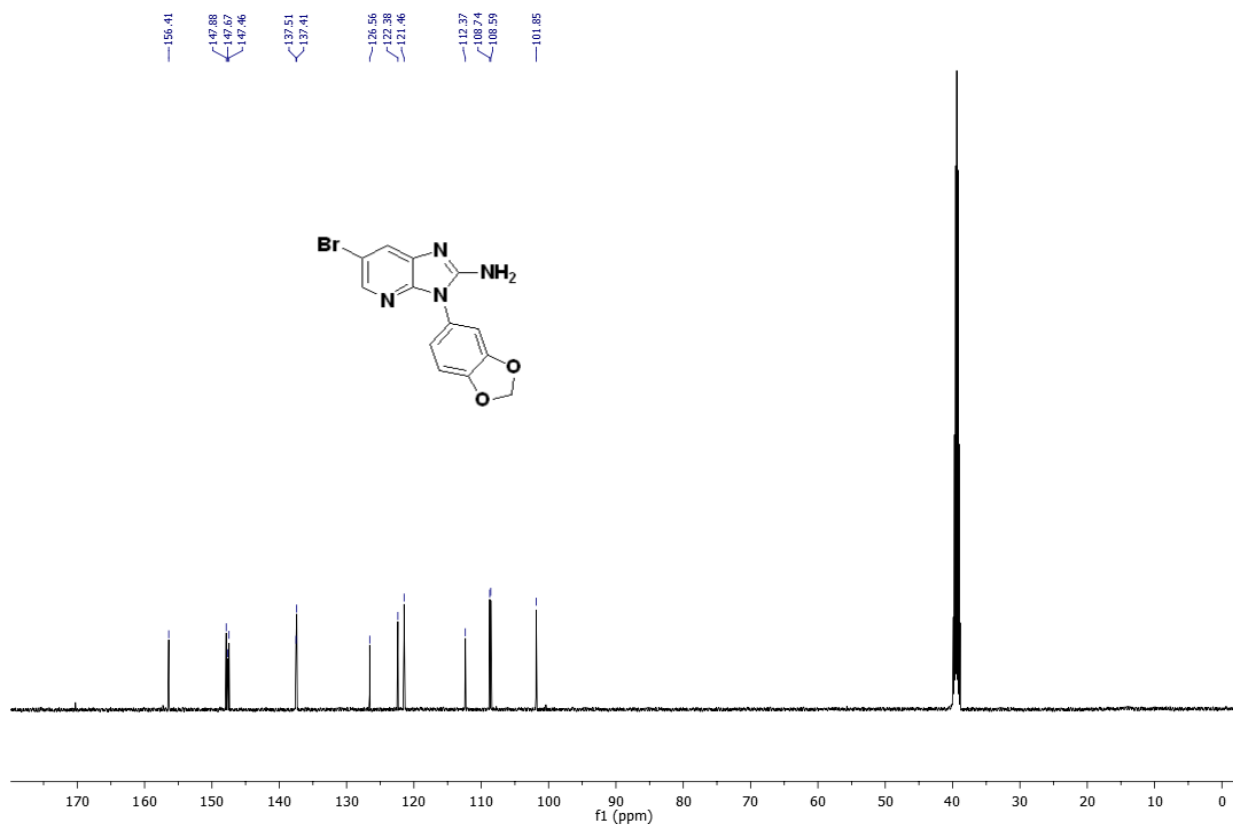
¹³C-NMR of 31 (100 MHz, DMSO-*d*₆)



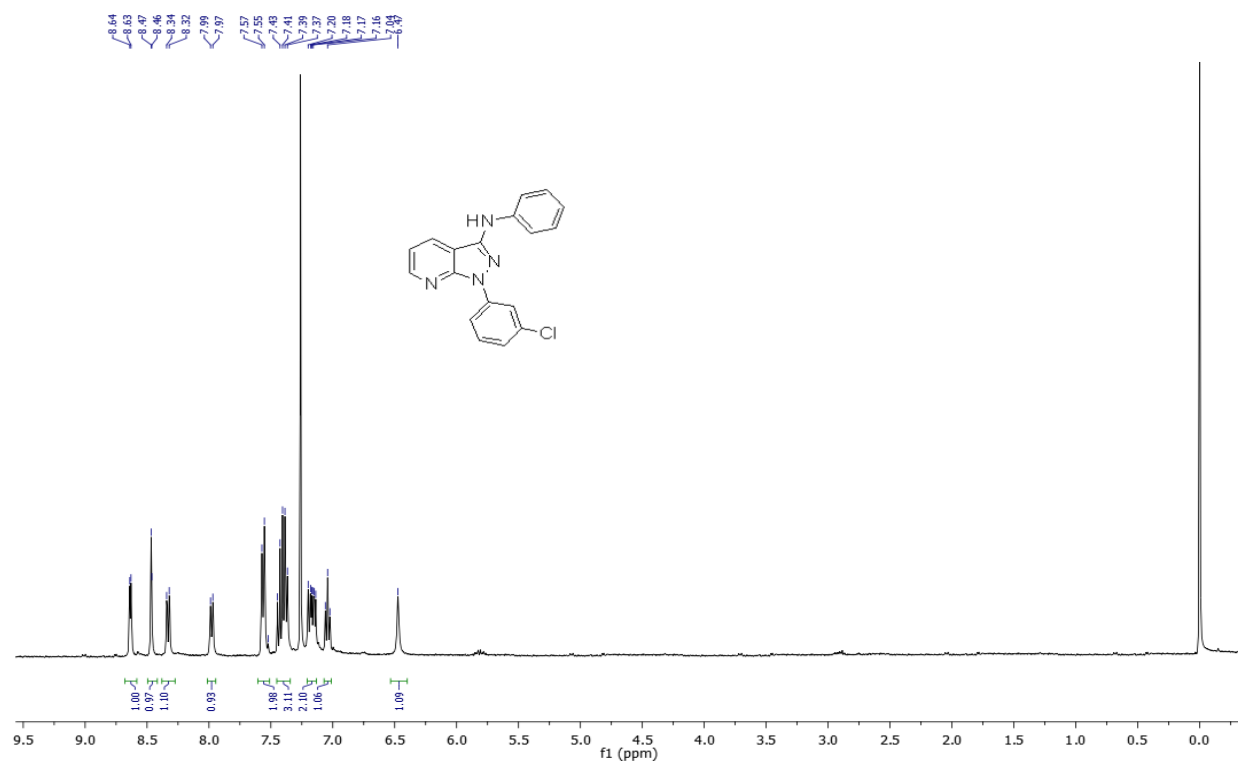
¹H-NMR of 3m (400 MHz, DMSO-*d*₆)



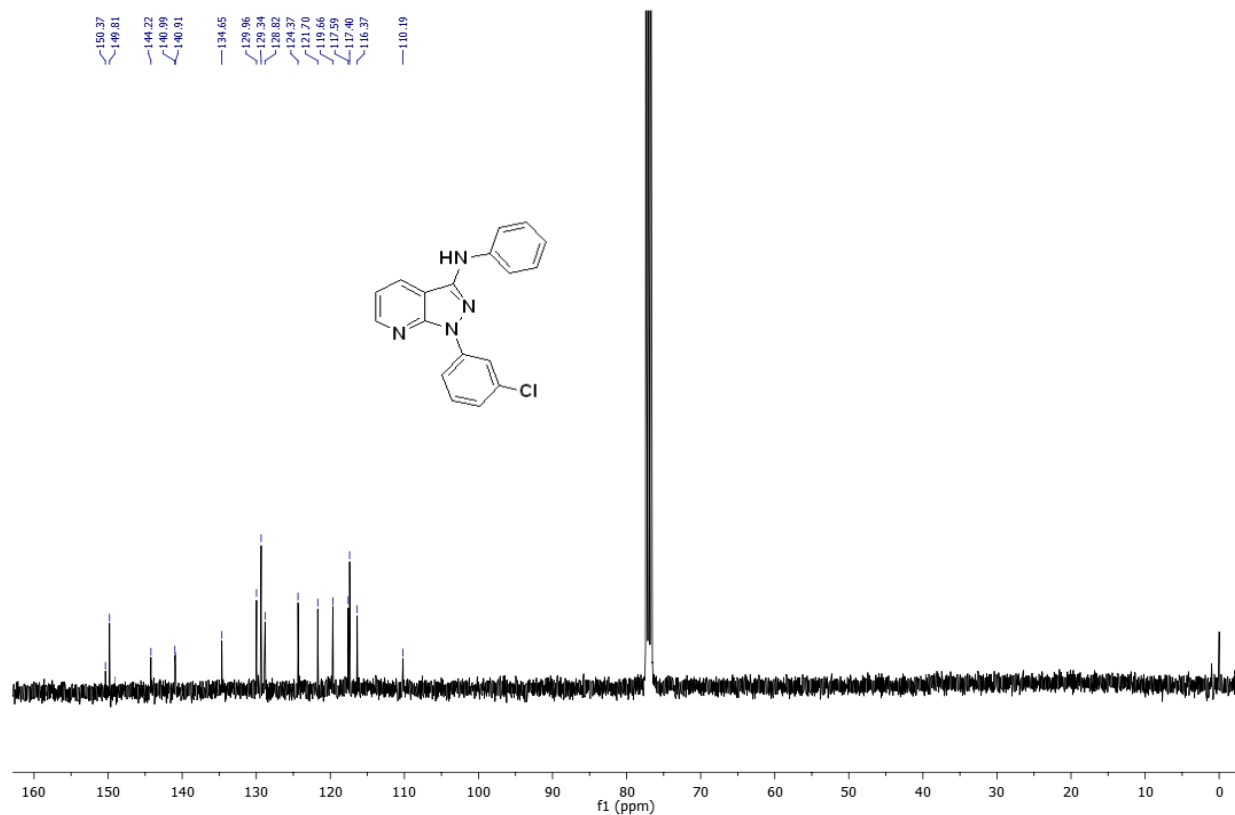
¹³C-NMR of 3m (125 MHz, DMSO-*d*₆)



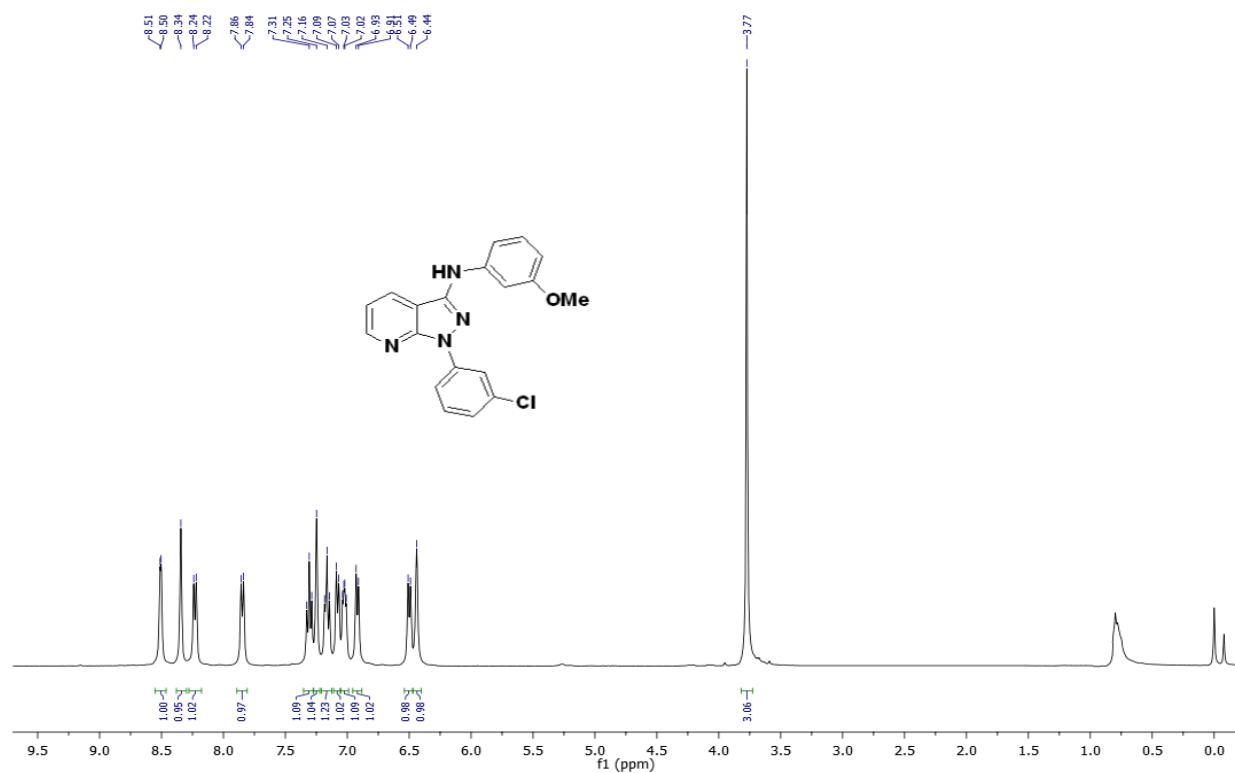
¹H-NMR of 4a (400 MHz, CDCl₃)



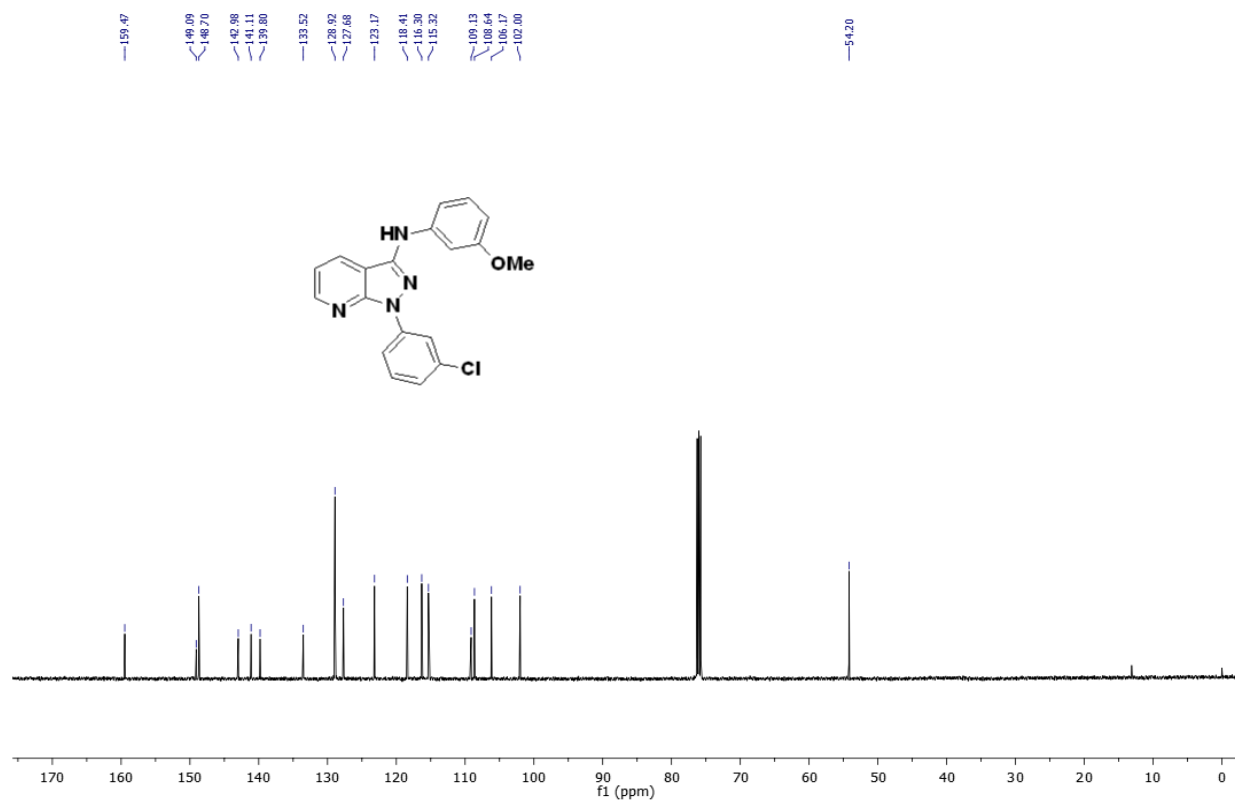
¹³C-NMR of 4a (100 MHz, CDCl₃)



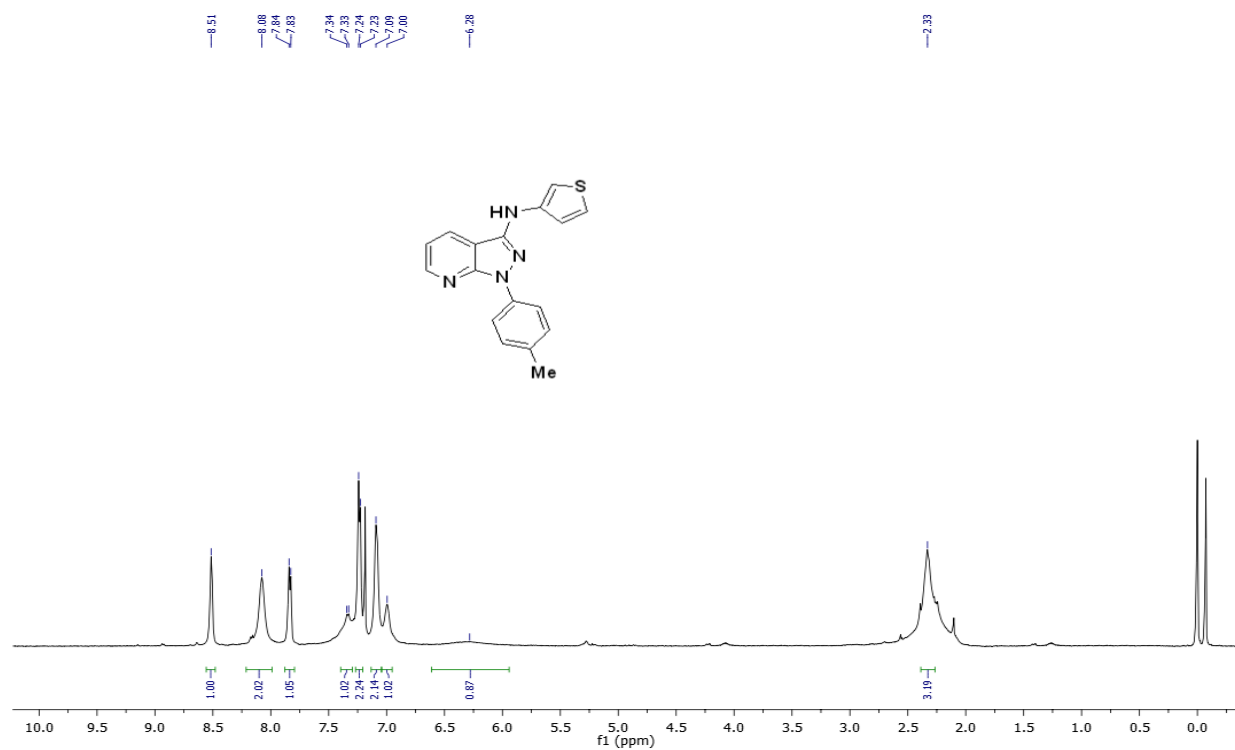
$^1\text{H-NMR}$ of 4b (400 MHz, CDCl_3)



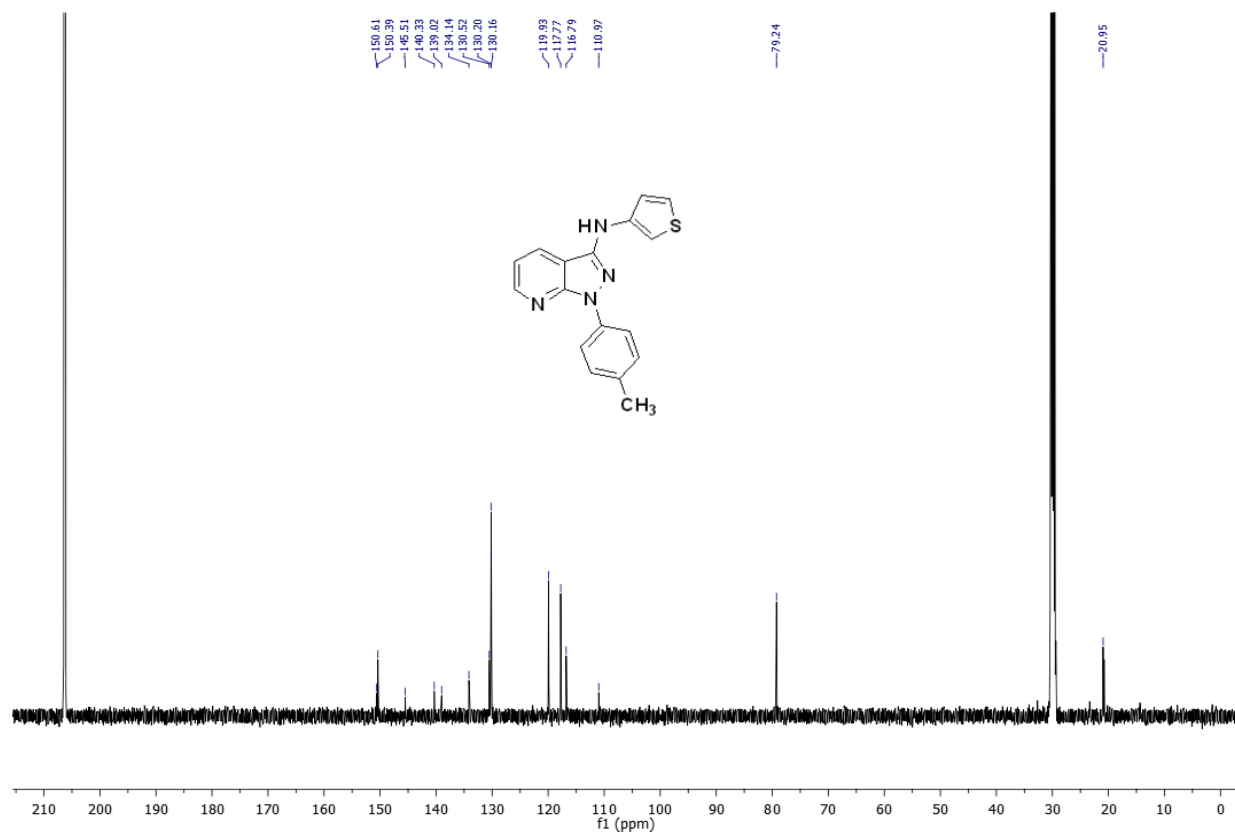
$^{13}\text{C-NMR}$ of 4b (125 MHz, CDCl_3)



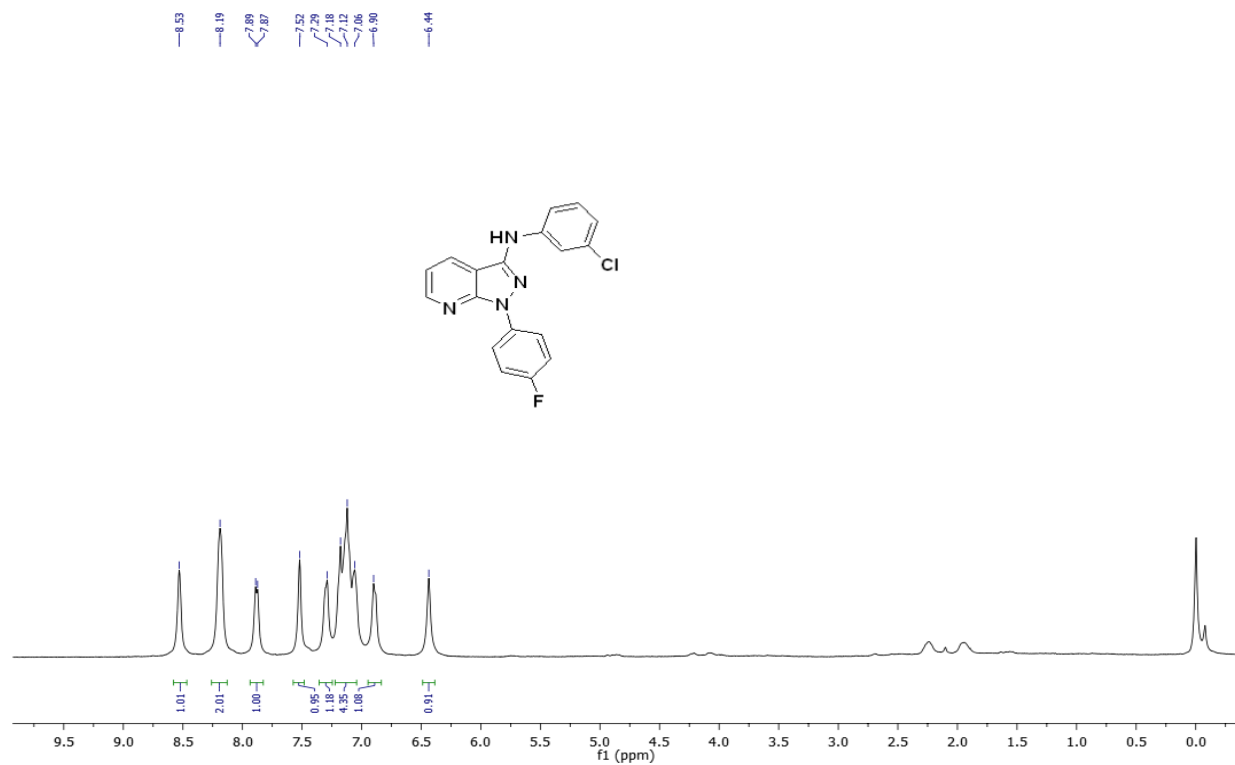
¹H-NMR of 4c (500 MHz, CDCl₃)



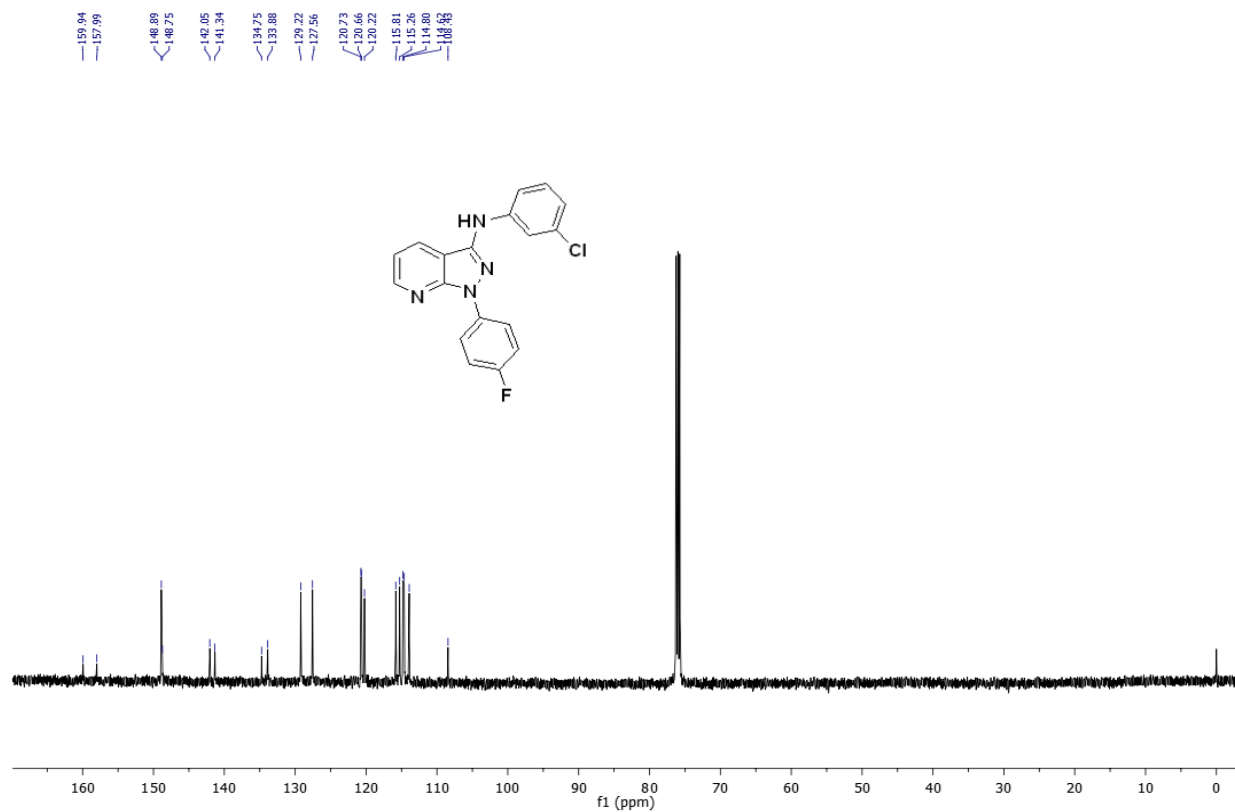
¹³C-NMR of 4c (125 MHz, Acetone-*d*₆)



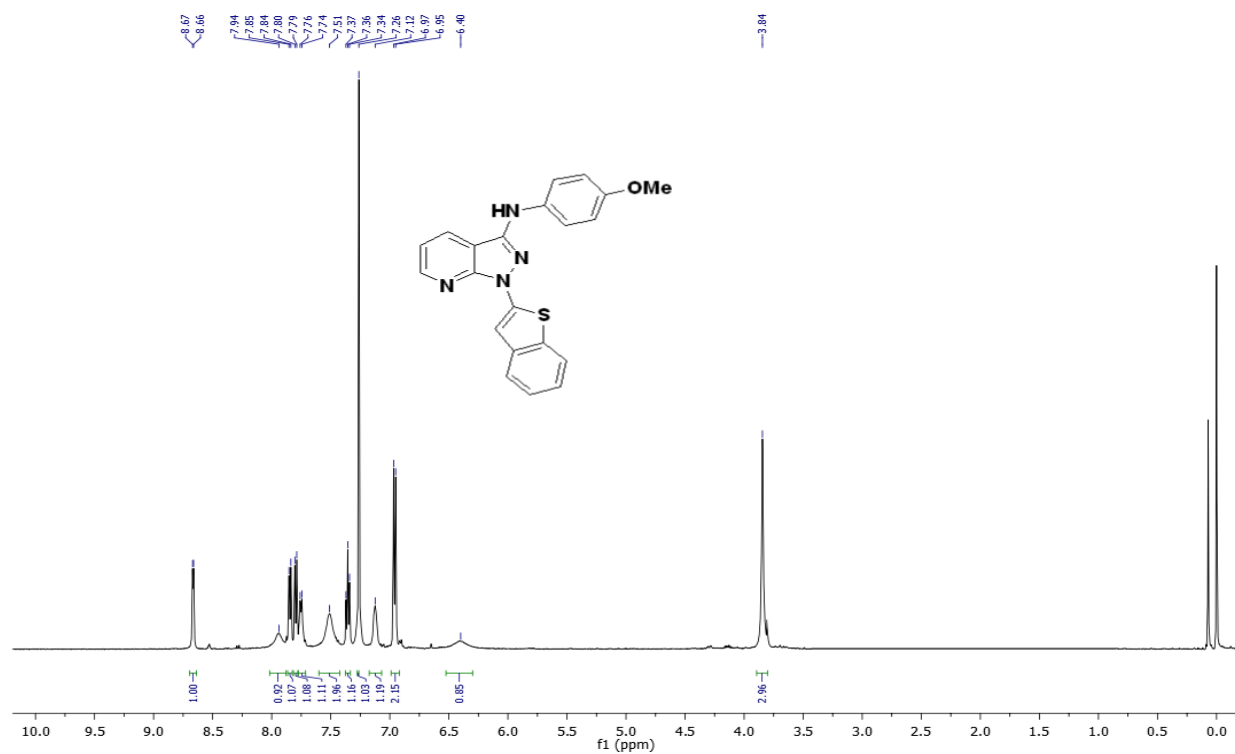
¹H-NMR of 4d (400 MHz, CDCl₃)



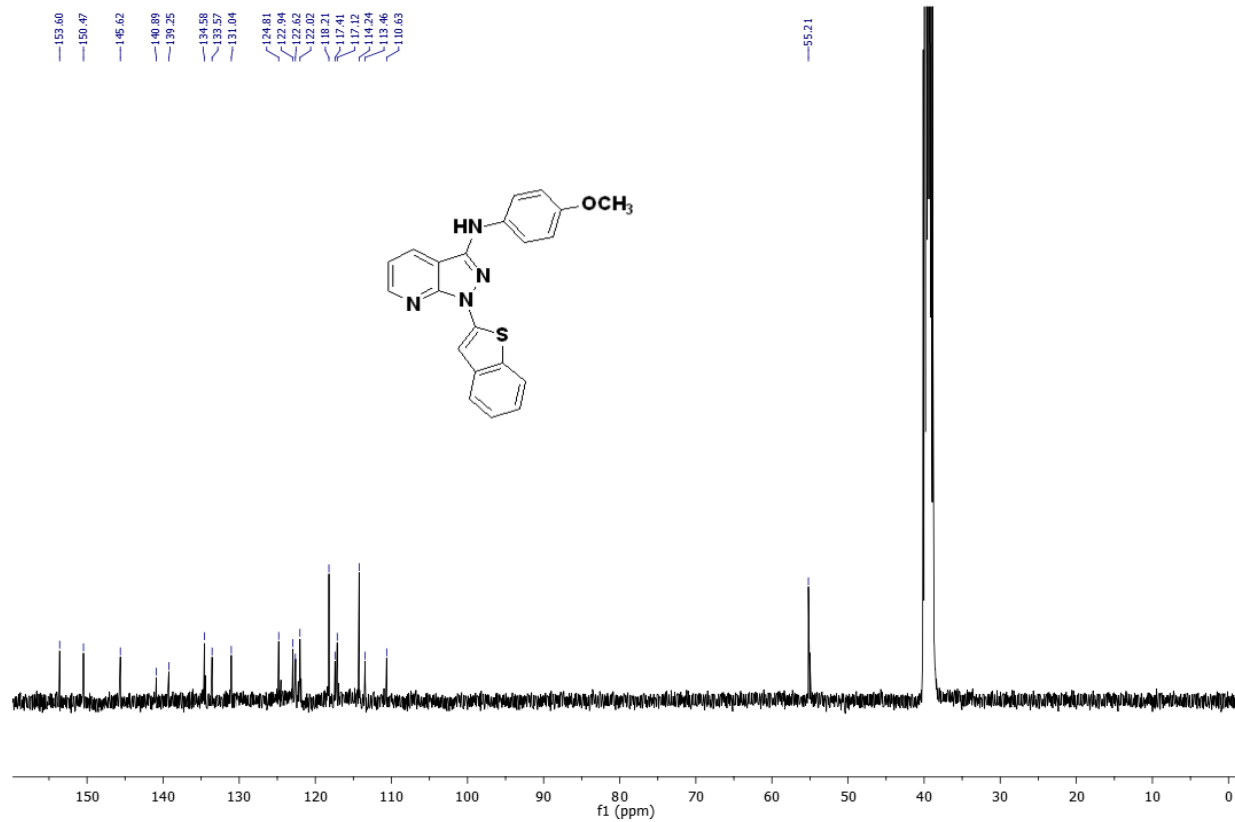
¹³C-NMR of 4d (125 MHz, CDCl₃)



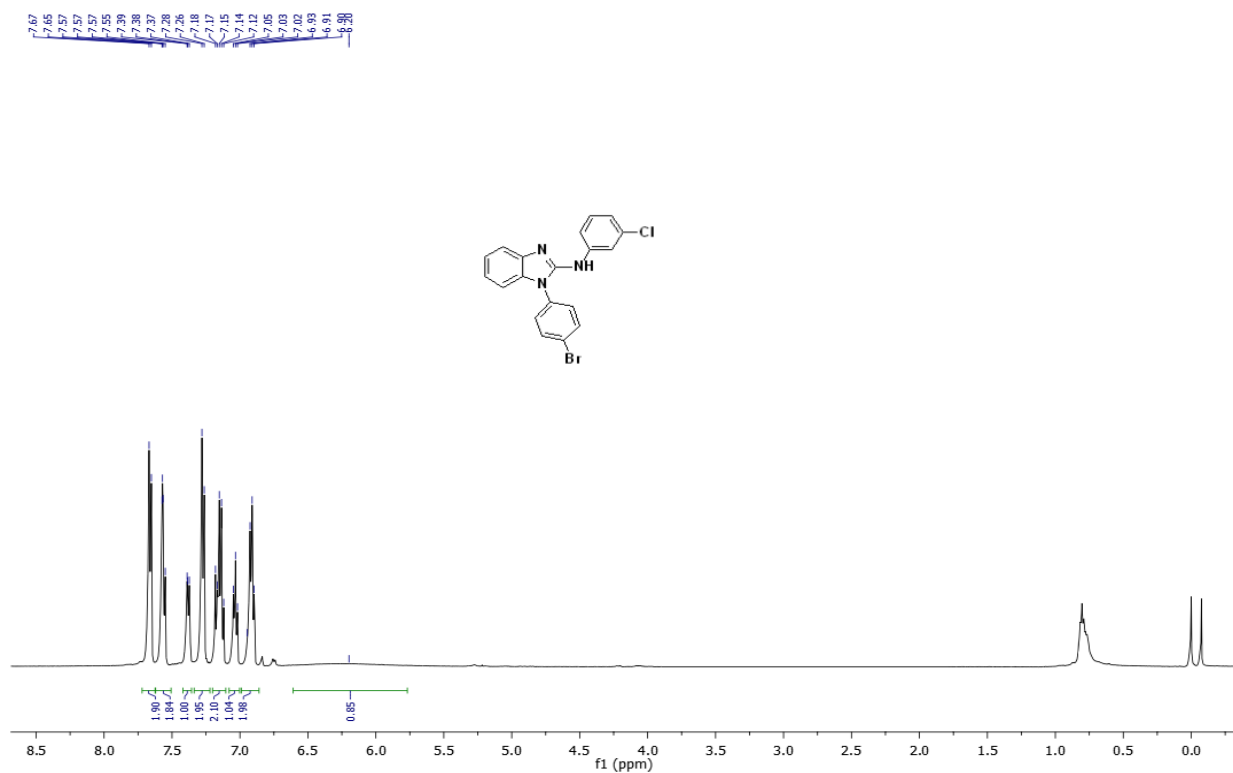
¹H-NMR of 4e (500 MHz, CDCl₃)



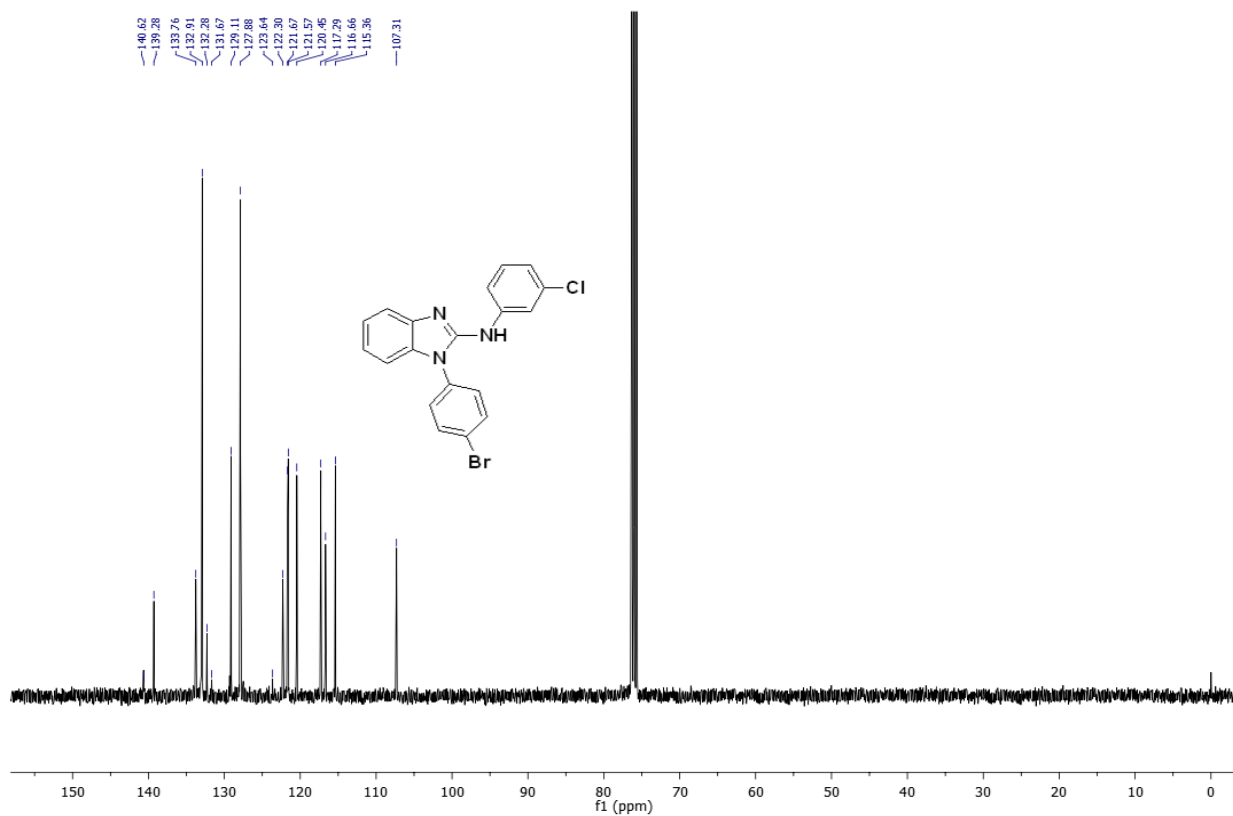
¹H-NMR of 4e (100 MHz, DMSO-*d*₆)



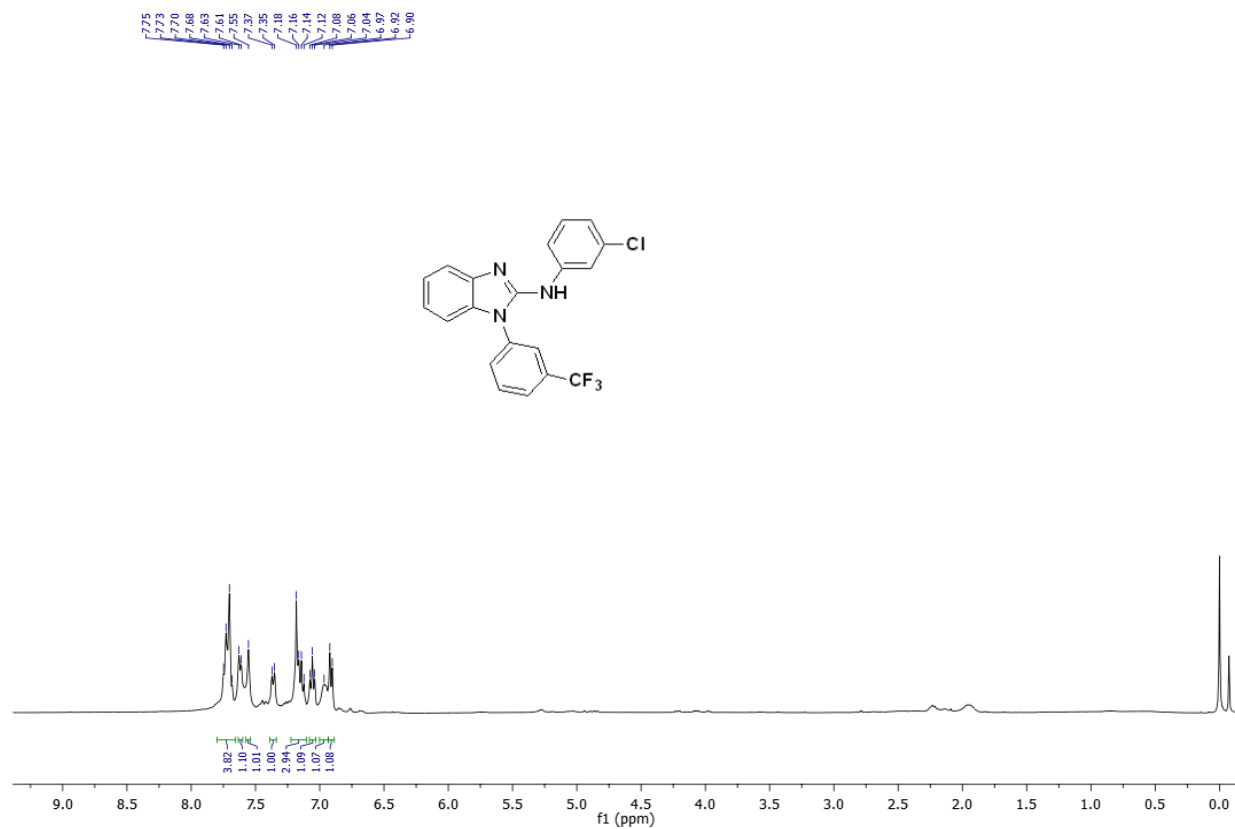
¹H-NMR of 4f (500 MHz, CDCl₃)



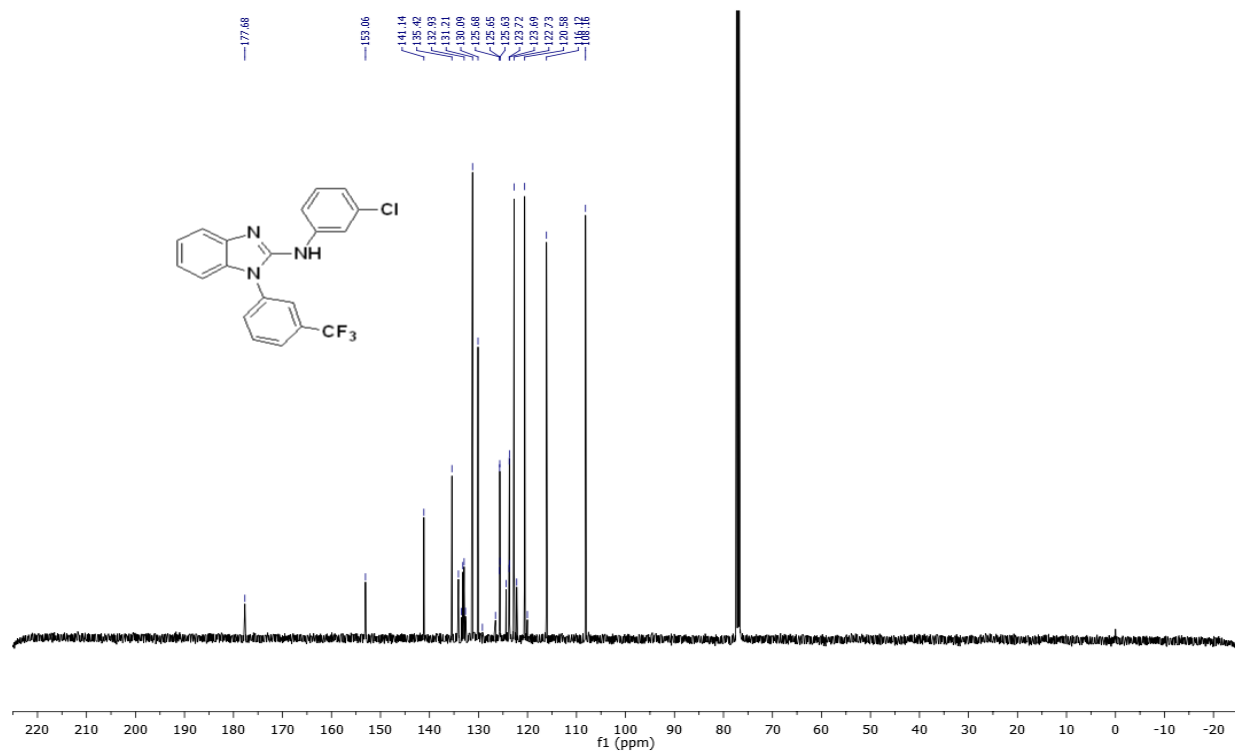
¹³C-NMR of 4f (100 MHz, CDCl₃)



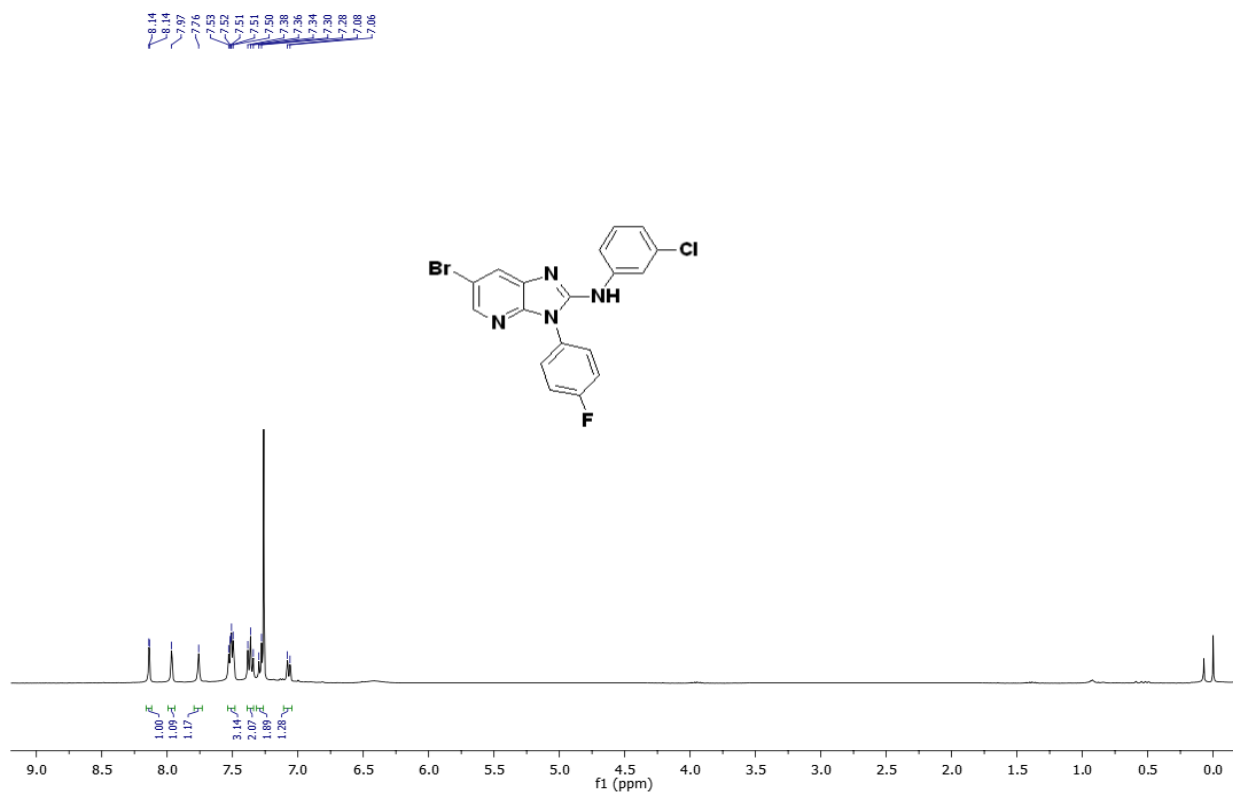
¹H-NMR of 4g (400 MHz, CDCl₃)



¹³C-NMR of 4g (125 MHz, CDCl₃)



¹H-NMR of 4h (400 MHz, CDCl₃)



¹H-NMR of 4h (100 MHz, CDCl₃)

