Electronic Supplementary Information (ESI)

Base and ligand-free copper-catalyzed *N*-arylation of 2-amino-*N*-heterocycles with boronic acids in air

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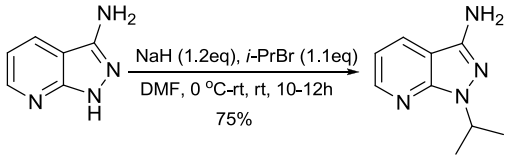
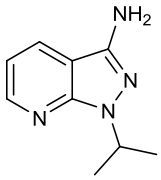
General experimental procedures

All purchased chemicals were used without further purification. All reactions were performed under air atmosphere. 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 or immersion in ninhydrin followed by heating on hot plate. 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 230-400 mesh size. Melting points of solid compounds were determined on BUCHI-B-545-Switzerland melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded with BRUCKER 500 and 400 MHz NMR instruments. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^{1}H 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 DMSO-d_6 as the internal standard (^{1}H 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 (^{1}H 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. Mass spectra were recorded with VARIAN GC-MS-MS instrument. HRMS spectra were recorded with LCMS-QTOF Module No. G6540 A (UHD) instrument.

General procedure for the synthesis of *N*-alkylated 3-amino pyrazolo pyridines



A dried round bottom flask equipped with a magnetic stirrer bar was charged 3-amino pyrazolo pyridine (0.1 g, 0.745 mmol) and dry DMF (2 mL) under nitrogen atmosphere. The reaction mixture was cool down to 0 ^{o}C and NaH (1.2eq) was added and stirred for 1h. After 1h stirring alkyl halide (isopropyl bromide) (1.1 eq) was added and continued the stirring for overnight. After completion of the reaction it was quenched by ice water and the solvent was removed with aid of a rotatory evaporator. The mixture was dilute with water (15 mL) and extracted with ethyl acetate (3x15mL). The combined organic layer was dried over Na_2SO_4, the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane/EtOAc, 2:3) to provide the desired product.

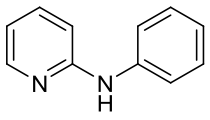


^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (dd, *J* = 4.5 Hz, 1.6 Hz, 1H), 7.81 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.00 – 6.90 (m, 1H), 5.22 (m, 1H), 1.57 (d, *J* = 6.7 Hz, 6H); GC MS (EI) m/z (relative intensity): 176.1 (M^+, 28.0), 161.2 (99.9), 134.3(15.0), 105.2 (10.0), 78.1 (15.0), 52.1 (7.5).

General procedure for the synthesis of copper-catalyzed *N*-Arylation of 2-amino-*N*-heterocycles with boronic acids

A round bottom flask equipped with a magnetic stirrer bar was charged with 2-amino-*N*-heterocycles (1 eq), boronic acids (1.1 eq), copper acetate (10 mol%) and dichloro ethane (2 mL), was added into the flask. The flask was kept open and the reaction mixture was stirred for 4-26 h in air at room temperature. The progress of the reaction was monitored by TLC and after completion of the reaction the solvent was removed with aid of a rotatory evaporator. The crude reaction mixture was diluted with 20mL of water and extracted with ethyl acetate (3x15 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (hexane/EtOAc) to provide the desired product.

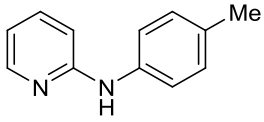
***N*-phenylpyridin-2-amine (1a)**[1]



1a

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and phenyl boronic acid (71.2 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL) , 4 h). Purification: Hexane/EtOAc (9: 1). Yield: 81 mg, 90%; white solid; mp. 106-108 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 4.3 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.24 (d, *J* = 1.9 Hz, 4H), 7.07 (s, 1H), 7.01 – 6.93 (m, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.70 – 6.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.1, 148.2, 140.5, 137.8, 129.3, 122.8, 120.6, 115.0, 108.2; HRMS(ESI): Calcd. for $C_{11}H_{11}N_2$ $[M+H]^+$ 171.0917; found: 171.0918.

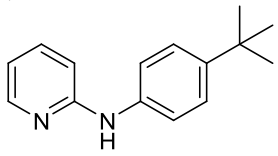
***N*-(*p*-tolyl)pyridin-2-amine (1b)**[2]



1b

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and *p*-tolyl boronic acid (79.4 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 5 h). Purification: Hexane/EtOAc (9:1). Yield: 80 mg, 82%; white solid; mp. 103-104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 4.5 Hz, 1H), 7.52 – 7.38 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.1Hz, 2H), 6.82 (d, *J* = 8.4Hz, 1H), 6.72 – 6.59 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.6, 148.3, 137.7, 132.7, 129.9, 121.3, 114.7, 107.7, 20.6; HRMS (ESI): Calcd. for $C_{12}H_{13}N_2$ $[M + H]^+$ 185.1073; found: 185.1068.

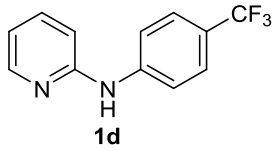
_N_-(4-(tert-butyl)phenyl)pyridin-2-amine (1c)[3]



1c

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 4-terbutylphenyl boronic acid (104 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 5 h). Purification: Hexane/EtOAc (9:1). Yield: 102 mg, 85%; light brown solid; mp. 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 6.7 Hz, 1H), 7.57 – 7.40 (m, 1H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 6.7 Hz, 2H), 7.08 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.77 – 6.61 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.5, 148.3, 146.1, 137.7, 137.5, 126.1, 120.7, 114.5, 107.8, 34.6, 31.4; HRMS (ESI): calcd. for $C_{15}H_{19}N_2$ $[M+H]^+$ 227.1543; found: 227.1542.

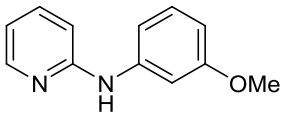
_N_-(4-(trifluoromethyl)phenyl)pyridin-2-amine (1d)



1d

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 4-trifluoromethyl phenyl boronic acid (111 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 8 h). Purification: Hexane/EtOAc (9:1). Yield: 112 mg, 89%; white solid; mp. 93-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 4.0 Hz, 1H), 7.56 (dd, *J*=12.1 Hz, 5.4 Hz, 3H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.01 (s, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.83 (dd, *J* = 6.6 Hz, 5.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.7, 148.2, 143.8, 137.9, 126.5, 125.5, 123.4, 118.1, 116.2, 109.8; HRMS (ESI): calcd. for $C_{12}H_{10}F_3N_2$ $[M+H]^+$ 239.0791; found: 239.0792.

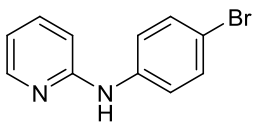
_N_-(3-methoxyphenyl)pyridin-2-amine (1e) [4]



1e

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 3-methoxyphenyl boronic acid (89 mg, 0.584 mmol), by fallowing general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 6 h). Purification: Hexane/EtOAc (9:1). Yields: 85 mg, 80%; semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 5.0 Hz, 1H), 7.56 – 7.38 (m, 2H), 7.20 (t, *J* = 8.1Hz, 1H), 6.98 – 6.81 (m, 3H), 6.76 – 6.65 (m, 1H), 6.65 – 6.53 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 156.2, 148.3, 142.0, 137.8, 130.0, 114.9, 112.7, 108.6, 108.0, 106.2, 55.2; HRMS (ESI): calcd. for $C_{12}H_{13}N_2O$ $[M+H]^+$ 201.1023; found: 201.1025.

_N_-(4-bromophenyl)pyridin-2-amine (1f) [4]

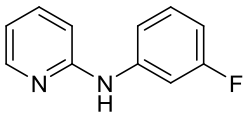


1f

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 4-bromophenyl boronic acid (117 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 6 h). Purification: Hexane/EtOAc (9:1). Yield: 116 mg, 88%; white solid; mp. 131-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 4.0 Hz, 1H), 7.52 – 7.37

(m, 1H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.96 (s, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.69 – 6.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.5, 148.3, 139.7, 137.8, 132.1, 121.5, 115.4, 114.7, 108.7; HRMS (ESI): calcd. for $C_{11}H_{10}BrN_2$ $[M+H]^+$ 249.0022; found: 249.0023.

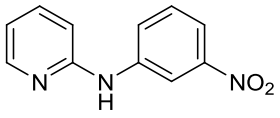
***N*-(3-fluorophenyl)pyridin-2-amine (1g)**



1g

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 3-fluorophenyl boronic acid (81.7 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 7 h). Purification: Hexane/EtOAc (9:1). Yield: 81 mg, 81%; white solid; mp. 66-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 4.9 Hz, 1H), 7.60 – 7.44 (m, 1H), 7.25 (dt, *J* = 12.1 Hz, 7.5 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.84 – 6.63 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.7, 162.2, 155.6, 148.2, 142.6, 137.9, 130.3, 115.6, 115.2, 109.1, 106.7; HRMS (ESI): calcd. for $C_{11}H_{10}FN_2$ $[M+H]^+$ 189.0823; found: 189.0824.

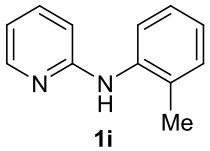
***N*-(3-nitrophenyl)pyridin-2-amine (1h)**



1h

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 3-Nitrophenyl boronic acid (97.5 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 9 h). Purification: Hexane/EtOAc (8:2). Yield: 86 mg, 75%; yellow solid; mp. 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41 (d, *J* = 2.1Hz, 1H), 8.30 (s, 1H), 7.82 (dd, *J* = 7.9 Hz, 1.7 Hz, 1H), 7.74 (dd, *J* = 8.1 Hz, 2.1 Hz, 1H), 7.59 (dd, *J* = 11.1 Hz, 4.5Hz, 1H), 7.45 (t, *J* = 8.2 Hz, 1H), 6.94 – 6.72 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.6, 149.0, 148.2, 142.0, 138.0, 129.8, 124.5, 116.4, 116.2, 113.1, 110.1; HRMS (ESI): calcd. for $C_{11}H_{10}N_3O_2$ $[M+H]^+$ 216.0768; found: 216.0767.

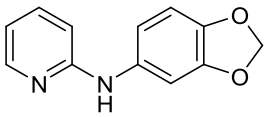
***N*-(*o*-tolyl)pyridin-2-amine (1i)** [4]



1i

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and *o*-tolyl boronic acid (79.4 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 10 h). Purification: Hexane/EtOAc (9:1).Yield: 77 mg, 79%; brown solid; mp. 76-77 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 5.7 Hz, 1H), 7.52 – 7.34 (m, 2H), 7.30 – 7.14 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.75 – 6.58 (m, 2H), 6.34 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.2, 147.9, 137.9, 137.2, 130.9, 130.5, 126.3, 123.9, 122.4, 114.1, 107.0, 17.5; HRMS (ESI): calcd. for $C_{12}H_{13}N_2$ $[M+H]^+$ 185.1073; found: 185.1075.

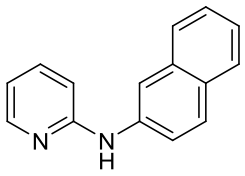
***N*-(benzo[*d*][1,3]dioxol-5-yl)pyridin-2-amine(1j)**



1j

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and benzo [*d*] [1,3] dioxol-5-yl boronic acid (96.9 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 7 h). Purification: Hexane/EtOAc (9:1). Yield: 101 mg, 89%; light brown solid; mp. 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 5.0, 1H), 7.51 – 7.38 (m, 1H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.75 – 6.63 (m, 3H), 6.49 (s, 1H), 5.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 148.2, 148.1, 144.0, 137.7, 134.6, 115.2, 114.4, 108.4, 107.5, 104.5, 101.2; HRMS (ESI): calcd. for $C_{12}H_{11}N_2O_2$ $[M+H]^+$ 215.0815; found: 215.0818.

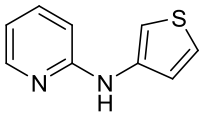
_N_-(naphthalen-2-yl)pyridin-2-amine (1k)



1k

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 2-naphthalene boronic acid (100.4 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 10h). Purification: Hexane/EtOAc (9:1). Yield: 96 mg, 82%; light brown solid; mp. 129-130 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 3.1Hz, 1H), 7.93 – 7.68 (m, 4H), 7.61 – 7.33 (m, 5H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.86 – 6.68 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.1, 148.4, 138.2, 137.8, 134.4, 130.0, 129.1, 127.6, 127.0, 126.4, 124.3, 121.4, 115.6, 115.2, 108.6; HRMS (ESI): calcd. for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073; found: 221.1071.

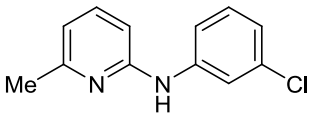
_N_-(thiophen-3-yl)pyridin-2-amine (1l)



1l

Synthesized from 2-aminopyridine (50 mg, 0.531 mmol) and 3-thienyl boronic acid (74.7 mg, 0.584 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 12 h). Purification: Hexane/EtOAc (9:1). Yield: 76 mg, 81%; brown solid; mp. 86-87 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 5.0 Hz, 1H), 7.55 – 7.40 (m, 1H), 7.29 – 7.24 (m, 1H), 7.21 (dd, *J* = 3.2 Hz, 1.5 Hz, 1H), 6.99 (d, *J* = 6.6 Hz, 1H), 6.89 (s, 1H), 6.82 – 6.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.1, 148.1, 138.7, 137.7, 124.8, 122.9, 114.6, 108.8, 108.1; HRMS (ESI): calcd for $C_9H_9N_2S$ $[M+H]^+$ 177.0481; found: 177.0483.

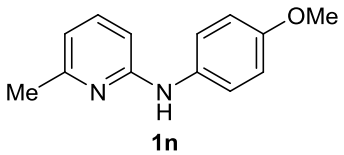
N-(3-chlorophenyl)-6-methylpyridin-2-amine (1m)



1m

Synthesized from 2-amino 6-methyl pyridine (50 mg, 0.462 mmol) and 3-chlorophenyl boronic acid (79.4 mg, 0.509 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 9 h). Purification: Hexane/EtOAc (9:1). Yield: 86 mg, 85%; brown liquid; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.39 (dd, *J* = 13.3 Hz, 4.9 Hz, 2H), 7.22 – 7.00 (m, 3H), 6.97 – 6.90 (m, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 154.7, 142.1, 138.4, 134.7, 130.2, 122.1, 119.3, 117.6, 114.9, 105.9, 24.0; HRMS (ESI): calcd. for $C_{12}H_{12}ClN_2$ $[M+H]^+$ 219.0684; found: 219.0687.

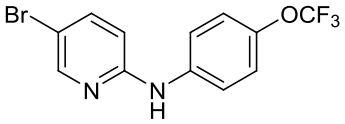
_N_-(3-methoxyphenyl)-6-methylpyridin-2-amine (1n)



1n

Synthesized from 2-amino 6-methyl pyridine (50 mg, 0.462 mmol) and 4-methoxyphenyl boronic acid (77.3 mg, 0.509 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 8h). Purification: Hexane/EtOAc (9:1). Yield: 87 mg, 88%; brown liquid; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.24 (m, 1H), 7.18 (d, *J* = 6.7 Hz, 2H), 6.95 – 6.77 (m, 3H), 6.48 (t, *J* = 8.3 Hz, 2H), 3.76 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.1, 157.0, 156.2, 138.1, 133.4, 124.3, 114.5, 113.5, 103.8, 55.4, 24.1; HRMS (ESI): calcd. for $C_{13}H_{15}N_2O$ $[M+H]^+$ 215.1179; found: 215.1180.

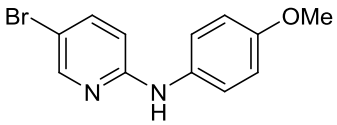
5-bromo-N-(4-(trifluoromethoxy)phenyl)pyridin-2-amine (1o)



1o

Synthesized from 2-amino 5-bromo pyridine (50 mg, 0.290 mmol) and 4-trifluoromethoxy phenyl boronic acid (65.7 mg, 0.319 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 14h). Purification: Hexane/EtOAc (9:1). Yield: 79 mg, 82%; brown solid; mp. 93-94 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 2.3 Hz, 1H), 7.59 (dt, *J* = 8.8 Hz, 2.3 Hz, 1H), 7.37 (dd, *J* = 9.0 Hz, 2.3 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.2, 148.8, 144.3, 140.2, 138.7, 122.1, 121.1, 110.1, 109.7, 29.7; HRMS (ESI): calcd. for $C_{12}H_9BrF_3N_2O$ $[M+H]^+$ 334.9825; found: 334.9833.

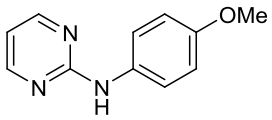
5-bromo-*N*-(4-methoxyphenyl)pyridin-2-amine (1p)



1p

Synthesized from 2-amino 5-bromo pyridine (50 mg, 0.290 mmol) and 4-methoxyphenyl boronic acid (48.4 mg, 0,319 mmol), by following general procedure (10mol% $Cu(OAc)_2$, DCE (2 mL), 12 h). Purification: Hexane/EtOAc (9:1). Yield: 65 mg, 80%; brown solid; mp. 83-84 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 5.9 Hz, 1H), 7.50 (dd, *J* = 10.3 Hz, 4.0 Hz, 1H), 7.26 – 7.15 (m, 2H), 6.96 – 6.83 (m, 2H), 6.62 – 6.44 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.7, 156.1, 148.7, 140.1, 132.5, 124.5, 116.1, 114.8, 108.6, 55.4; HRMS (ESI): calcd. for $C_{12}H_{12}BrN_2O$ $[M+H]^+$ 281.0107; found: 281.0112.

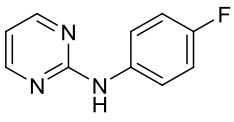
***N*-(4-methoxyphenyl)pyrimidin-2-amine (2a)**



2a

Synthesized from 2-aminopyrimidine (50 mg, 0.526 mmol) and 4-methoxyphenyl boronic acid (87.9 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 14h). Purification: Hexane/EtOAc (8:2). Yields: 79 mg, 75%; white solid; mp. 123-124^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 4.8Hz, 2H), 7.47 (d, *J* = 8.9Hz, 2H), 7.35 (s, 1H), 6.90 (d, *J* = 8.9Hz, 2H), 6.66 (t, *J* = 4.8Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.4, 158.0, 155.8, 132.2, 122.2, 116.0, 114.7, 114.2, 111.9, 55.5; HRMS (ESI): calcd. for $C_{11}H_{12}N_3O$ $[M+H]^+$ 202.0975; found: 202.0969.

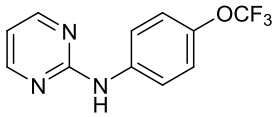
***N*-(4-fluorophenyl)pyrimidin-2-amine (2b)**



2b

Synthesized from 2-aminopyrimidine (50 mg, 0.526 mmol) and 4-fluorophenyl boronic acid (80.9 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 10 h). Purification: Hexane/EtOAc (8:2). Yield: 78 mg, 79%; white solid; mp. 141-142 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.40 (d, *J* =4.7 Hz, 2H), 7.62 – 7.51 (m, 2H), 7.50 (s, 1H), 7.04 (t, *J* = 8.7 Hz, 2H), 6.72 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.1, 159.6, 158.0, 135.2, 121.5, 115.5, 112.4; HRMS (ESI): calcd. for $C_{10}H_9FN_3$ $[M+H]^+$ 190.0775; found: 190.0769.

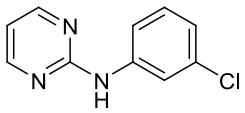
***N*-(4-(trifluoromethoxy)phenyl)pyrimidin-2-amine (2c)**



2c

Synthesized from 2-aminopyrimidine (50 mg, 0.526 mmol) and 4-trifluoromethoxyphenyl boronic acid (119 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 16 h). Purification: Hexane/EtOAc (8:2). Yield: 96 mg, 72%; white solid; mp. 95-96 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 4.8 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 4.8, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 159.7, 157.9, 144.3, 138.1, 121.7, 120.3, 112.8; HRMS (ESI): calcd. for $C_{11}H_9F_3N_3O$ $[M+H]^+$ 256.0692; found: 256.0690.

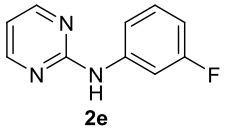
***N*-(3-chlorophenyl)pyrimidin-2-amine (2d)**



2d

Synthesized from 2-aminopyrimidine (50 mg, 0.526 mmol) and 3-chlorophenyl boronic acid (90.1 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 12 h). Purification: Hexane/EtOAc (8:2). Yield: 81 mg, 75%; white solid; mp. 93-94 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 4.8 Hz, 2H), 7.80 (t, *J* = 2.1 Hz, 1H), 7.45 (s, 1H), 7.33 (ddd, *J* = 8.2 Hz, 2.1 Hz, 0.9 Hz, 1H), 7.19 (s, 1H), 6.94 (ddd, *J* = 7.9 Hz, 2.0 Hz, 0.9 Hz, 1H), 6.70 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 159.2, 157.4, 140.1, 134.1, 129.3, 121.9, 118.6, 116.7, 112.5; HRMS (ESI): calcd. for $C_{10}H_9ClN_3$ $[M+H]^+$ 206.0480; found : 206.0481.

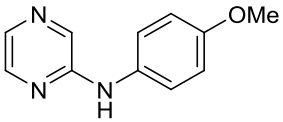
***N*-(3-fluorophenyl)pyrimidin-2-amine (2e)**



2e

Synthesized from 2-aminopyrimidine (50 mg, 0.526 mmol) and 3-fluorophenyl boronic acid (80.9 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 15 h). Purification: Hexane/EtOAc (8:2). Yield: 77 mg, 78%; white solid; mp. 98-99 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.44 (d, *J* = 4.8 Hz, 2H), 7.73 (dt, *J* = 11.6 Hz, 2.2 Hz, 1H), 7.61 (s, 1H), 7.34 – 7.15 (m, 3H), 6.77 (t, *J* = 4.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.6, 161.8, 159.1, 157.4, 140.6, 129.4, 113.9, 112.4, 108.6, 108.4, 105.8, 105.7; HRMS (ESI): calcd. for $C_{10}H_9FN_3$ $[M+H]^+$ 190.0775; found: 190.0774.

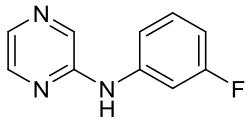
***N*-(4-methoxyphenyl)pyrazin-2-amine (2f)** [5]



2f

Synthesized from 2-aminopyrazine (50 mg, 0.526 mmol) and 4-methoxyphenyl boronic acid (87.9 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 14 h). Purification: Hexane/EtOAc (7:3). Yield: 76 mg, 72%; brown solid; mp. 124-125 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.10 (s, 1H), 8.04 (d, *J* = 1.2 Hz, 1H), 7.92 (d, *J* = 2.7 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.8, 153.2, 141.9, 134.3, 132.1, 131.7, 123.9, 114.7, 55.5; HRMS (ESI): calcd. for $C_{11}H_{12}N_3O$ $[M+H]^+$ 202.0975; found: 202.0973.

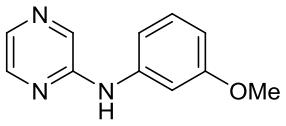
***N*-(3-fluorophenyl)pyrazin-2-amine (2g)**



2g

Synthesized from 2-aminopyrazine (50 mg, 0.526 mmol) and 3-fluorophenyl boronic acid (80.9 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 16 h). Purification: Hexane/EtOAc (7:3). Yield: 73 mg, 74%; yellow solid; mp. 93-94 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.26 (s, 1H), 8.15 (d, *J* = 1.3Hz, 1H), 8.03 (d, *J* = 2.5 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.82 (s, 1H), 6.81 – 6.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.7, 135.4, 133.4, 130.4, 130.3, 115.0, 109.9, 109.7, 106.9, 106.7; HRMS (ESI): calcd. for $C_{10}H_9FN_3$ $[M+H]^+$ 190.0775; found: 190.0778.

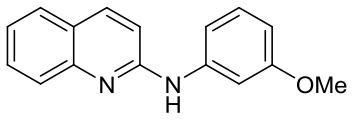
***N*-(3-methoxyphenyl)pyrazin-2-amine (2h)**



2h

Synthesized from 2-aminopyrazine (50 mg, 0.526 mmol) and 3-methoxyphenyl boronic acid (87.9 mg, 0.578 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 15 h). Purification: Hexane/EtOAc (7:3). Yield: 74 mg, 70%; yellow solid; mp. 107-108 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.29 (s, 1H), 8.14 (d, *J* = 2.6 Hz, 1H), 8.00 (d, *J* = 2.7Hz , 1H), 7.26 (t, *J* = 8.1 Hz, 1H), 7.08 (t, *J* = 2.2 Hz, 1H), 6.96 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.76 (s, 1H), 6.66 (dd, *J* = 8.3 Hz, 2.4 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 152.3, 142.1, 140.3, 134.3, 132.5, 130.1, 112.6, 109.0, 106.3, 55.3; HRMS (ESI): calcd. for $C_{11}H_{12}N_3O$ $[M+H]^+$ 202.0975; found: 202.0974.

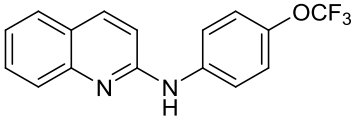
***N*-(3-methoxyphenyl)quinolin-2-amine (2i)**



2i

Synthesized from 2-aminoquinoline (50 mg, 0.347 mmol) and 3-methoxyphenyl boronic acid (58 mg, 0.381 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 18 h). Purification: Hexane/EtOAc (9:1). Yield: 70 mg, 80%; yellow solid; mp. 122-123 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.35 – 7.22 (m, 2H), 7.04 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.00 (dd, *J* = 8.9 Hz, 1.9 Hz, 1H), 6.84 (s, 1H), 6.64 (dd, *J* = 8.2 Hz, 2.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 159.9, 153.8, 147.1, 141.0, 137.2, 129.4, 129.3, 126.9, 126.29, 123.6, 122.7, 112.1, 111.5, 108.0, 105.6, 54.8; HRMS (ESI): calcd. for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1179; found: 251.1174.

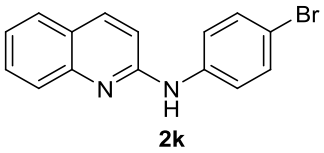
***N*-(4-(trifluoromethoxy)phenyl)quinolin-2-amine (2j)**



2j

Synthesized from 2-aminoquinoline (50 mg, 0.347 mmol) and 4-trifluoromethoxyphenyl boronic acid (78.4 mg, 0.381 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 15 h). Purification: Hexane/EtOAc (9:1). Yield: 87 mg, 82%; white solid; mp. 102-103 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.39 (m, 4H), 7.28 – 7.18 (m, 1H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.31 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 153.8, 146.8, 144.5, 138.8, 138.3, 127.3, 126.3, 124.1, 123.6, 122.5, 122.1, 121.3, 116.3, 111.8; HRMS (ESI): calcd. for $C_{16}H_{12}F_3N_2O$ $[M+H]^+$ 305.0896; found: 305.0896.

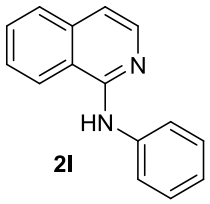
_N_-(4-bromophenyl)quinolin-2-amine (2k)



2k

Synthesized from 2-aminoquinoline (50 mg, 0.347 mmol) and 4-bromophenyl boronic acid (76.2 mg, 0.381 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 13 h). Purification: Hexane/EtOAc (9:1). Yield: 83 mg, 80%; white solid; mp. 150-151 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.53 (dd, *J* = 8.8 Hz, 1.7 Hz, 2H), 7.44 (dd, *J* = 8.8 Hz, 1.7 Hz, 2H), 7.35 – 7.27 (m, 1H), 6.87 (dd, *J* = 8.9 Hz, 1.6 Hz, 1H), 6.84 (d, *J* = 14.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.9, 153.9, 146.9, 139.1, 132.1, 130.2, 127.5, 126.2, 124.1, 123.6, 122.1, 117.6, 115.5, 111.8; HRMS (ESI): calcd. for $C_{15}H_{12}BrN_2$ $[M+H]^+$ 299.0179; found: 299.0181.

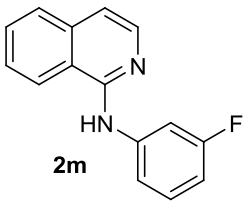
_N_-phenylisoquinolin-1-amine (2l)



2l

Synthesized from isoquinoline-1-amine (50 mg, 0.347 mmol) and phenyl boronic acid (46.4 mg, 0.381 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 12 h). Purification: Hexane/EtOAc (9:1). Yield: 61 mg, 80%; yellow solid; mp. 103-104 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 5.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.69 (dd, *J* = 8.6 Hz, 1.0 Hz, 3H), 7.63 – 7.51 (m, 1H), 7.40 (dd, *J* = 9.1 Hz, 6.9 Hz, 2H), 7.20 – 7.14 (m, 1H), 7.13 – 7.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 152.2, 140.8, 140.5, 137.4, 129.9, 129.0, 127.5, 126.4, 122.8, 121.6, 120.3, 118.8, 113.4; HRMS (ESI): calcd. for $C_{15}H_{13}N_2$ $[M+H]^+$ 221.1073; found: 221.1067.

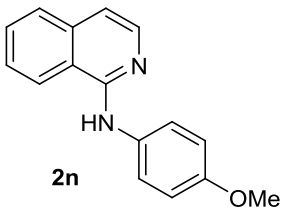
_N_-(3-fluorophenyl)isoquinolin-1-amine (2m)



2m

Synthesized from isoquinoline-1-amine (50 mg, 0.347 mmol) and 3-fluorophenyl boronic acid (53.3 mg, 0.381 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 18 h). Purification: Hexane/EtOAc (9:1). Yield: 65 mg, 79%; yellow solid; mp. 93-94 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 5.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.72 (s, 1H), 7.70 – 7.62 (m, 1H), 7.60 – 7.51 (m, 1H), 7.26 (dd, *J* = 3.9 Hz, 2.8 Hz, 2H), 7.18 (d, *J* = 5.8 Hz, 1H), 6.77 – 6.69 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.1, 162.2, 151.7, 140.7, 137.5, 130.0, 129.8, 127.6, 126.8, 121.3, 118.8, 114.9, 113.9, 109.1, 107.0; HRMS (ESI): calcd. for $C_{15}H_{12}FN_2$ $[M+H]^+$ 239.0979; found: 239.0982.

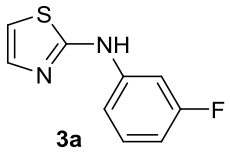
_N_-(4-methoxyphenyl)isoquinolin-1-amine (2n)



2n

Synthesized from isoquinoline-1-amine (50 mg, 0.347 mmol) and 4-methoxyphenyl boronic acid (58 mg, 0.381 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 16 h). Purification: Hexane/EtOAc (9:1). Yield: 71 mg, 82%; brown solid; mp. 129-130 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 5.8 Hz, 1H), 7.94 – 7.87 (m, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.63 (ddd, *J* = 8.1 Hz, 6.9 Hz, 1.1 Hz, 1H), 7.52 (dq, *J* = 5.3 Hz, 1.8 Hz, 3H), 7.07 (d, *J* = 5.8 Hz, 1H), 6.98 (s, 1H), 6.95 – 6.91 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.8, 152.9, 141.0, 137.4, 133.3, 129.8, 127.4, 126.3, 123.1, 121.4, 118.5, 114.3, 112.7, 55.5; HRMS (ESI): calcd. for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1179; found: 251.1181.

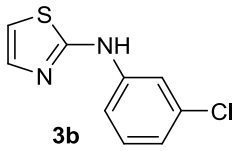
_N_-(3-fluorophenyl)thiazol-2-amine (3a)[6]



3a

Synthesized from 2-aminothiazole (50 mg, 0.5 mmol) and 3-fluorophenyl boronic acid (77 mg, 0.55 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 6 h). Purification: Hexane/EtOAc (8:2). Yield: 68 mg, 70%; brown solid; mp. 89-90 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 1H), 7.33 (t, *J* = 2.9 Hz, 1H), 7.29 (dd, *J* = 8.1 Hz, 1.6 Hz, 1H), 7.21 (dt, *J* = 10.9 Hz, 2.3 Hz, 1H), 7.07 (dd, *J* = 8.1 Hz, 2.0 Hz, 1H), 6.74 (td, *J* = 8.3 Hz, 2.3 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.5, 162.5, 142.3, 138.2, 130.6, 113.1, 109.3, 107.9, 104.9; HRMS (ESI): calcd. for $C_9H_8FN_2S$ $[M+H]^+$ 195.0387; found: 195.0389.

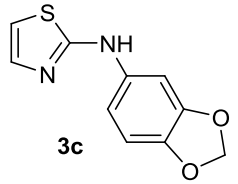
_N_-(3-chlorophenyl)thiazol-2-amine (3b)



3b

Synthesized from 2-aminothiazole (50 mg, 0.5 mmol) and 3-chlorophenyl boronic acid (85.8 mg, 0.55 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 8 h). purification: Hexane/EtOAc (8:2). Yields: 76 mg, 72%; brown solid; mp. 96-97 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.25 (s, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.33 (d, *J* = 3.5 Hz, 1H), 7.31 – 7.20 (m, 2H), 7.02 (dd, *J* = 7.3 Hz, 1.4 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H); ^{13}CNMR (100 MHz, $CDCl_3$) δ = 165.3, 141.9, 138.3, 135.1, 130.4, 122.6, 117.7, 115.7, 107.9; HRMS (ESI): calcd. for $C_9H_8ClN_2S$ $[M+H]^+$ 211.0091; found: 211.0093.

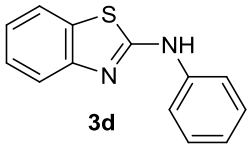
_N_-(benzo[*d*][1,3]dioxol-5-yl)thiazol-2-amine (3c)



3c

Synthesized from 2-aminothiazole (50 mg, 0.5 mmol) and benzo [*d*] [1,3] dioxol-5-yl boronic acid (91.3 mg, 0.55 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 7 h). Purification: Hexane/EtOAc (8:2). Yield: 79.2 mg, 72%; brown solid; mp. 102-103 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 3.4 Hz, 1H), 6.92 (br, 1H), 6.79 (br, 2H), 6.55 (d, *J* = 3.3 Hz, 1H), 5.97 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.8, 148.3, 144.3, 137.9, 134.9, 113.0, 108.6, 106.9, 102.4, 101.4; HRMS (ESI): calcd. for $C_{10}H_9N_2O_2S$ $[M+H]^+$ 221.0379; found: 221.0385.

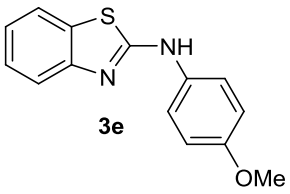
_N_-phenylbenzo[*d*]thiazol-2-amine (3d)



3d

Synthesized from 2-aminobenzothiazole (50 mg, 0.333 mmol) and phenyl boronic acid (44.6 mg, 0.366 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 13 h). Purification: Hexane/EtOAc (9:1). Yield: 58 mg, 70%; white solid; mp. 156-157 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ = 10.43 (s, 1H), 7.73 (t, *J* = 8.3 Hz, 3H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.32 (ddd, *J* = 12.8 Hz, 10.1 Hz, 4.4 Hz, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ = 162.6, 152.4, 140.9, 130.3, 129.7, 126.5, 123.1, 121.5, 119.8, 118.5, 55.1; HRMS (ESI): calcd. for $C_{13}H_{11}N_2S$ $[M+H]^+$ 227.0638; found: 227.0640.

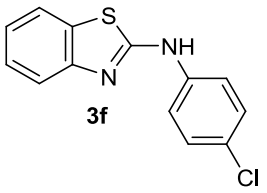
_N_-(4-methoxyphenyl)benzo[_d_]thiazol-2-amine (3e)



3e

Synthesized from 2-aminobenzothiazole (50 mg, 0.333 mmol) and 4-methoxyphenyl boronic acid (55.6 mg, 0.366 mmol), by following general procedure (10 mol% $Cu(OAC)_2$, DCE (2 mL), 12 h). Purification: Hexane/EtOAc (9:1). Yield: 61 mg, 72%; white solid; mp. 151-152 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ = 10.09 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 163.7, 155.8, 152.5, 134.3, 130.3, 126.7, 122.8, 121.6, 121.1, 119.4, 115.0, 55.9; HRMS (ESI): calcd. for $C_{14}H_{13}N_2OS$ $[M+H]^+$ 257.0743; found: 257.0747.

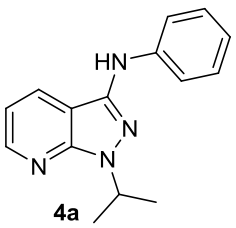
_N_-(4-chlorophenyl)benzo[d]thiazol-2-amine (3f)



3f

Synthesized from 2-aminobenzothiazole (50 mg, 0.333 mmol) and 4-chlorophenyl boronic acid (59.1 mg, 0.366 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 15h). Purification: Hexane/EtOAc (9:1). Yield: 60.6 mg, 70%; white solid; mp. 203-204 ^oC; ^1H NMR (400 MHz, Acetone-d_6) δ = 7.94 – 7.90 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.22 – 7.16 (m, 1H) ; ^{13}C NMR (125 MHz, Acetone-d_6) δ =162.3, 153.4, 140.7, 131.3, 129.7, 127.3, 126.9, 123.6, 121.7, 120.8, 120.3; HRMS (ESI): calcd. for $C_{13}H_{10}ClN_2S$ $[M+H]^+$ 261.0248; found: 261.0255.

1-isopropyl-_N_-phenyl-1_H_-pyrazolo[3,4-_b_]pyridin-3-amine (4a)

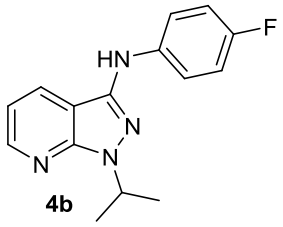


4a

Synthesized from 1-isopropyl-1H-pyrazolo [3,4-*b*] pyridin-3-amine (50 mg, 0.284 mmol) and phenyl boronic acid (38.1 mg, 0.312 mmol), by following general procedure(10 mol% $Cu(OAc)_2$, DCE (2 mL), 12h). Purification:

Hexane/EtOAc (9:1).Yield: 57 mg, 80%; yellow solid; mp. 114-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (dd, *J* = 4.5 Hz, 1.5 Hz, 1H), 7.86 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.29 (d, *J* = 4.3 Hz, 4H), 7.01 – 6.90 (m, 2H), 6.30 (s, 1H), 5.24 (m, 1H), 1.57 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.6, 148.8, 142.7, 141.7, 129.2, 129.1, 120.5, 116.2, 114.9, 108.1, 47.8, 21.9; HRMS (ESI): calcd. for $C_{15}H_{17}N_4$ $[M+H]^+$ 253.1448; found: 253.1441.

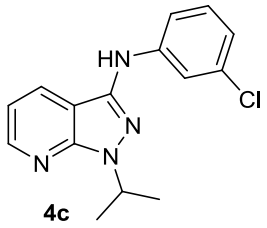
_N_-(4-fluorophenyl)-1-isopropyl-1_H_-pyrazolo[3,4-_b_]pyridin-3-amine (4b)



4b

Synthesized from 1-isopropyl-1*H*-pyrazolo [3,4-*b*] pyridin-3-amine (50 mg, 0.284 mmol) and 4-fluorophenyl boronic acid (43.6 mg, 0.312 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 15 h). Purification : Hexane/EtOAc (9:1).Yield: 54 mg, 70%; yellow solid; mp. 127-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (dd, *J* = 4.5 Hz, 1.6 Hz, 1H), 7.81 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.07 – 6.93 (m, 3H), 6.19 (s, 1H), 5.22-5.23 (m, 1H), 1.57 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.6, 148.9, 142.1, 138.7, 129.0, 117.8, 115.8, 115.6, 114.8, 107.7, 47.7, 21.9; HRMS (ESI): calcd. for $C_{15}H_{16}FN_4$ $[M+H]^+$ 271.1354; found: 271.1348.

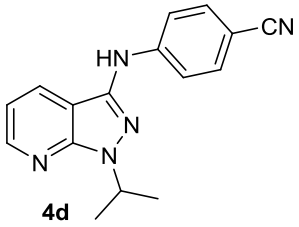
_N_-(3-chlorophenyl)-1-isopropyl-1_H_-pyrazolo[3,4-_b_]pyridin-3-amine (4c)



4c

Synthesized from 1-isopropyl-1*H*-pyrazolo [3,4-*b*] pyridin-3-amine (50 mg, 0.284 mmol) and 3-chlorophenyl boronic acid (48.6 mg, 0.312 mmol), by following general procedure (10mol% $Cu(OAc)_2$, DCE (2 mL), 13 h). Purification: Hexane/EtOAc (9:1). Yield: 59 mg, 72%; yellow solid; mp. 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (dd, *J* = 4.5 Hz, 1.4 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.36 (br, 1H), 7.18 (dd, *J* = 19.3 Hz, 11.4 Hz, 2H), 7.03 (d, *J* = 4.4 Hz, 1H), 6.90 (br, 1H), 6.29 (s, 1H), 5.26 (br, 1H), 1.58 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.5, 149.0, 143.9, 141.0, 134.8, 130.1, 128.8, 120.3, 115.8, 115.2, 114.0, 108.0, 48.0, 22.0; HRMS (ESI): calcd. for $C_{15}H_{16}ClN_4$ $[M+H]^+$ 287.1058; found: 287.1052.

4-((1-isopropyl-1H-pyrazolo[3,4-b]pyridin-3-yl)amino)benzonitrile (4d)



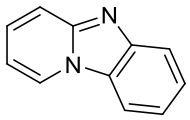
4d

Synthesized from 1-isopropyl-1*H*-pyrazolo [3,4-*b*] pyridin-3-amine (50 mg, 0.284 mmol) and 4-cyanophenyl boronic acid (45.8 mg, 0.312 mmol), by following general procedure (10 mol% $Cu(OAc)_2$, DCE (2 mL), 18 h). Purification: Hexane/EtOAc (8:2). Yields: 51 mg, 65%; yellow solid; mp. 169-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.54 (dd, *J* = 4.5 Hz, 1.4 Hz, 1H), 7.92 (dd, *J* = 8.1Hz, 1.5 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.07 (dd, *J* = 8.1 Hz, 4.6 Hz, 1H), 6.62 (s, 1H), 5.29-5.31 (m, 1H), 1.59 (d, *J* = 6.7 Hz, 6H); ^{13}C

NMR (125 MHz, CDCl3) δ = 149.3, 149.2, 146.6, 140.2, 133.5, 128.8, 120.2, 115.6, 108.1, 101.7, 48.1, 22.0; HRMS (ESI): calcd.for $C_{16}H_{16}N_5$ $[M+H]^+$ 278.1400; found: 278.1400.

General procedure for the one pot synthesis of Benzo[4,5]imidazo[1,2-a]pyridine 5

A round bottom flask equipped with a magnetic stirrer bar was charged 2-aminopyridine (50 mg, 0.531 mmol, 1 eq), phenyl boronic acid (71.2 mg, 0.584 mmol, 1.1 eq), copper acetate (10 mol%) and dichloro ethane (2 mL). The flask was kept open and the mixture was stirred for 4h, in air and at room temperature. After completion of the reaction (the reaction progress was monitored by TLC), the solvent was removed with aid of a rotatory evaporator. Subsequently, Fe $(NO_3)_3 \cdot 9H_2O$ (10 mol%), PivOH (2.5 mmol) and DMF (1.0 mL) was added into the flask and stirred at 130 ^oC for 28h under 1atm O_2. The reaction mixture was allowed to cool down to room temperature after complete consumption of starting material as monitored by TLC. Water (10 mL), triethylamine (1.0 mL), and EtOAc (10 mL) were added to the reaction mixture successively. The organic phase was separated, and the aqueous phase was further extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (Hexane/EtOAc; 2:3) to provide the desired product **5**.



5

Yield: 64.3 mg, 72%; brown solid; mp. 174-175 ^oC; ^1H NMR (500 MHz, Acetone-d_6) δ = 8.91 (d, *J* = 6.0 Hz, 1H), 8.20 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 6.6 Hz, 1H); ^{13}C NMR (125 MHz, Acetone-d_6) δ = 149.2, 145.6, 130.4, 129.8, 127.2, 126.1, 121.4, 120.3, 118.3, 112.1, 110.9; HRMS (ESI): calcd. for $C_{11}H_9N_2$ $[M+H]^+$ 169.0760; found: 169.0766.

X-ray crystallography of *N*-(4-methoxyphenyl) isoquinolin-1-amine (2n)

A single crystal of N-(4-methoxyphenyl) isoquinolin-1-amine was obtained by slow evaporation at room temperature, from a mixture of hexane/dichloromethane. The X-ray data was collected from a dry crystal mounted on an 'Xcalibur, Sapphire3', Oxford diffractometer. The crystal structure was solved by direct method using SHELXS-97[7] followed by Full matrix anisotropic least square refinement using SHELXL-97[7] All the hydrogen atoms were located from difference Fourier map except the methyl groups. For methyl group the hydrogen atom were fixed geometrically and refined in the final cycle as riding over the heavy atom they are bonded. All the relevant crystallographic data collection parameters and structure refinement details for **2n** is summarized in Table 1. Bond lengths and bond angles are given in Table 2.

Table 1. Crystal data and structure refinement for **2n**

Identification code	**2n**	
Empirical formula	C_{16} H_{14} N_2 O_1	
Formula weight	250.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1/n	
Unit cell dimensions	a = 13.4270(13) Å	α= 90°.
	b = 5.6126(5) Å	β= 91.685(10)°.
	c = 16.7627(19) Å	γ = 90°.
Volume	1262.7(2) $Å^3$	

Z	4
Density (calculated)	1.317 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F (000)	528
Crystal size	0.3 x 0.1 x 0.01 mm^3
Theta range for data collection	3.83 to 26.74°.
Index ranges	-17<=h<=15, -6<=k<=7, -21<=l<=14
Reflections collected	4561
Scan type	ω-scan
Unique reflections	2551 [R(int) = 0.065]
Observed reflection [|F| >4σ(F)]	874
Completeness to theta = 26.74°	95.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2551 / 0 / 228
Goodness-of-fit (S)	0.954
Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.0782
R indices (all data)	R1 = 0.2057, wR2 = 0.1153
Largest diff. peak and hole	0.168 and -0.168 $e.Å^{-3}$
CCDC number	**909445**

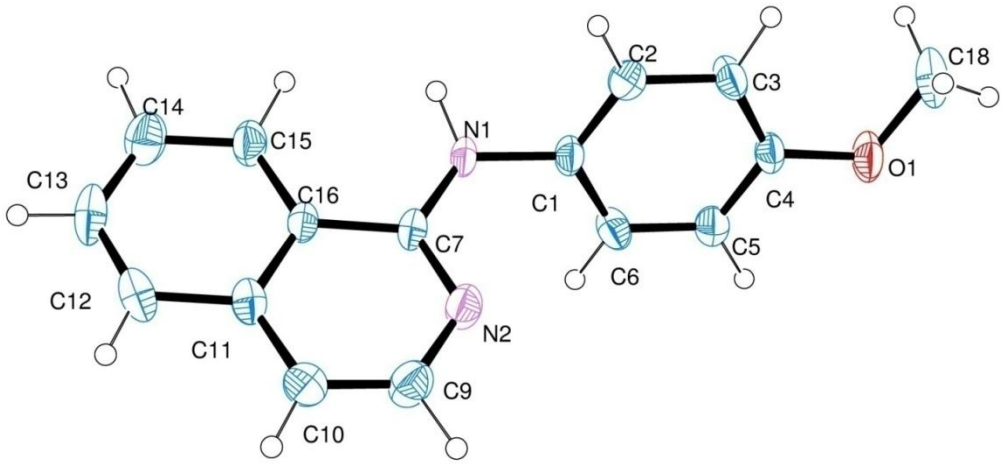
Table 2. Bond lengths [Å] and angles [°] for **2n**

O1	-C4	1.3862	C4	-C5	1.3795	C2	-H4	0.9900
O1	-C18	1.4322	C5	-C6	1.3784	C3	-H3	1.0200
N1	-C1	1.4316	C7	-C16	1.4523	C5	-H2	1.0400
N1	-C7	1.3724	C9	-C10	1.3581	C6	-H1	0.9600
N2	-C7	1.3129	C10	-C11	1.3979	C9	-H10	1.0400
N2	-C9	1.3553	C11	-C16	1.4065	C10	-H9	0.9600
N1	-H1N	0.9600	C11	-C12	1.4353	C12	-H8	0.9500
C1	-C6	1.4009	C12	-C13	1.3442	C13	-H7	0.9500
C1	-C2	1.3730	C13	-C14	1.3796	C14	-H6	1.0400
C2	-C3	1.3980	C14	-C15	1.3853			
C3	-C4	1.3706	C15	-C16	1.3973			

C4	-O1	-C18	117.49	C9	-C10	-C11	118.69	C10	-C9	-H10	121.00
C1	-N1	-C7	122.64	C12	-C11	-C16	117.69	C9	-C10	-H9	119.00
C7	-N2	-C9	118.24	C10	-C11	-C12	123.47	C11	-C10	-H9	122.00
C1	-N1	-H1N	112.00	C10	-C11	-C16	118.84	C11	-C12	-H8	112.00
C7	-N1	-H1N	115.00	C11	-C12	-C13	120.67	C13	-C12	-H8	128.00
C2	-C1	-C6	119.16	C12	-C13	-C14	121.89	C12	-C13	-H7	114.00
N1	-C1	-C2	121.50	C13	-C14	-C15	119.13	C14	-C13	-H7	124.00
N1	-C1	-C6	119.28	C14	-C15	-C16	120.97	C13	-C14	-H6	128.00
C1	-C2	-C3	120.89	C11	-C16	-C15	119.63	C15	-C14	-H6	113.00
C2	-C3	-C4	118.92	C7	-C16	-C15	123.03	C14	-C15	-H5	116.00

O1	-C4	-C5	115.62	C1	-C2	-H4	121.00	C16	-C15	-H5	122.00
O1	-C4	-C3	123.19	C3	-C2	-H4	118.00	O1	-C18	-H11	101.00
C3	-C4	-C5	121.15	C2	-C3	-H3	117.00	O1	-C18	-H12	109.00
C4	-C5	-C6	119.77	C4	-C3	-H3	124.00	O1	-C18	-H13	106.00
C1	-C6	-C5	120.08	C4	-C5	-H2	119.00	H11	-C18	-H12	115.00
N2	-C7	-C16	122.22	C6	-C5	-H2	121.00	H11	-C18	-H13	108.00
N1	-C7	-C16	119.12	C1	-C6	-H1	119.00	H12	-C18	-H13	117.00
N1	-C7	-N2	118.64	C5	-C6	-H1	120.00				
N2	-C9	-C10	124.62	N2	-C9	-H10	115.00				

The ORTEP diagram showing numbering scheme and the molecular conformation of **2n** in crystals.

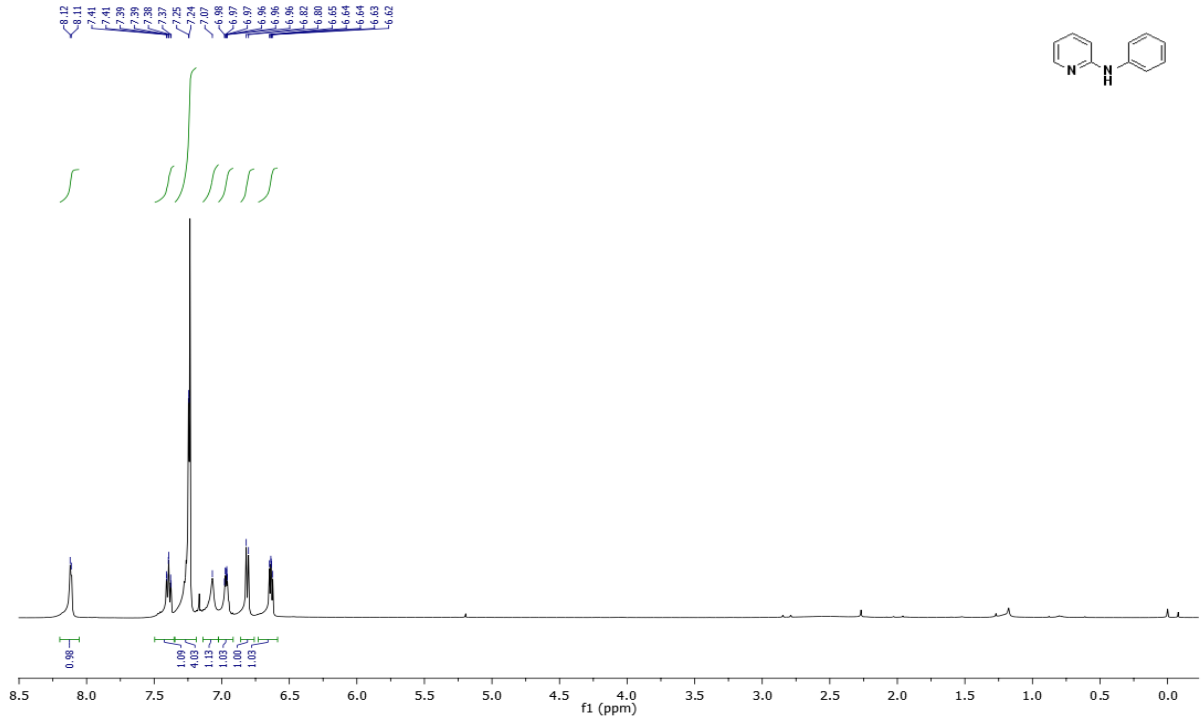


References:

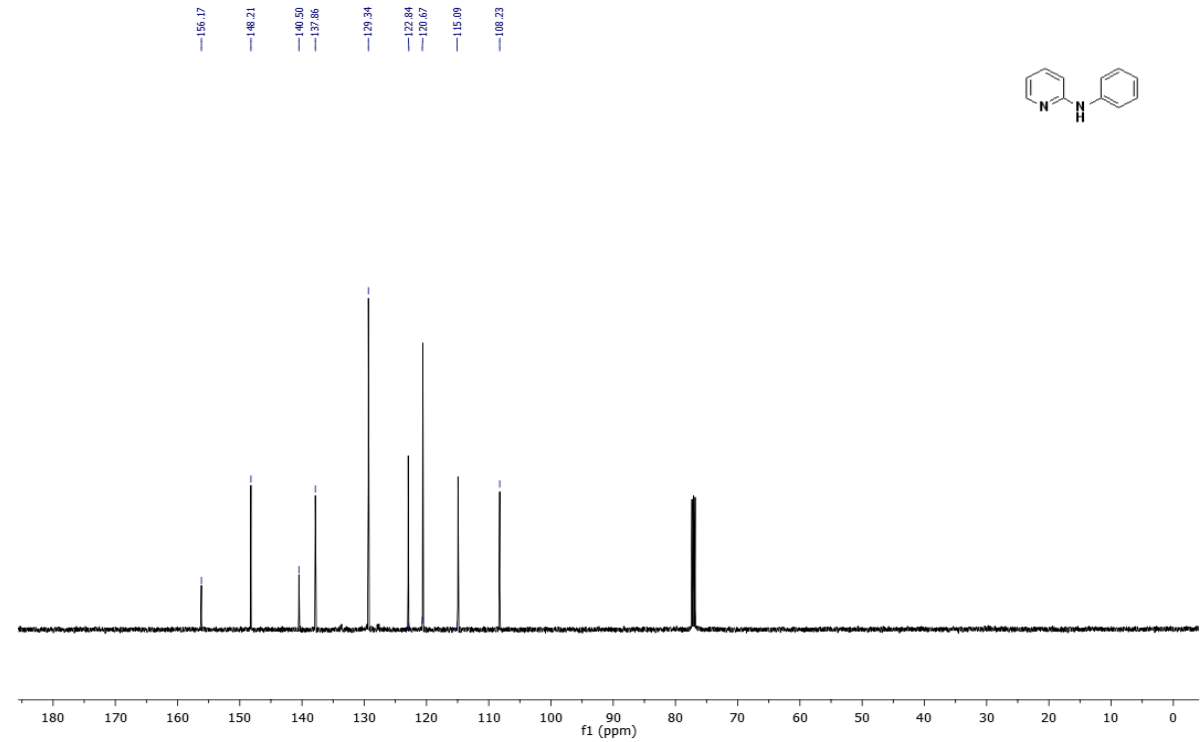
1 Y. Liu, Y. Bai, J. Zhang, Y.Li, J. Jiao, X. Qi, *Eur. J. Org. Chem.* 2007, 6084.
2 Q. Shen, J. F. Hartwig, *Org. Lett.*, 2008,**10**,4109.
3 R. J. Lundgren, A. S-Kumankumah, M. Stradiotto, *Chem. Eur. J.* 2010, **16**, 1983.
4 H. Wang, Y. Wang, C. Peng, J. Zhang, Q. Zhu, *J. Am. Chem. Soc*., 2010, **132**, *13217*
5 D. Maiti, B. P. Fors, J. L. Henderson, Y. Nakamura, S. L. Buchwald, *Chem. Sci*., 2011, **2**, 57
6 M. A. McGowan, J. L. Henderson, S. L. Buchwald, *Org. Lett*., 2012, **14**, 1432.
7 G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr*., 2008, *A64*, 112.

^{1}H NMR and ^{13}C NMR Spectra of Compounds (1a-1p; 2a-2n, 3a-3f, 4a-4d and 5)

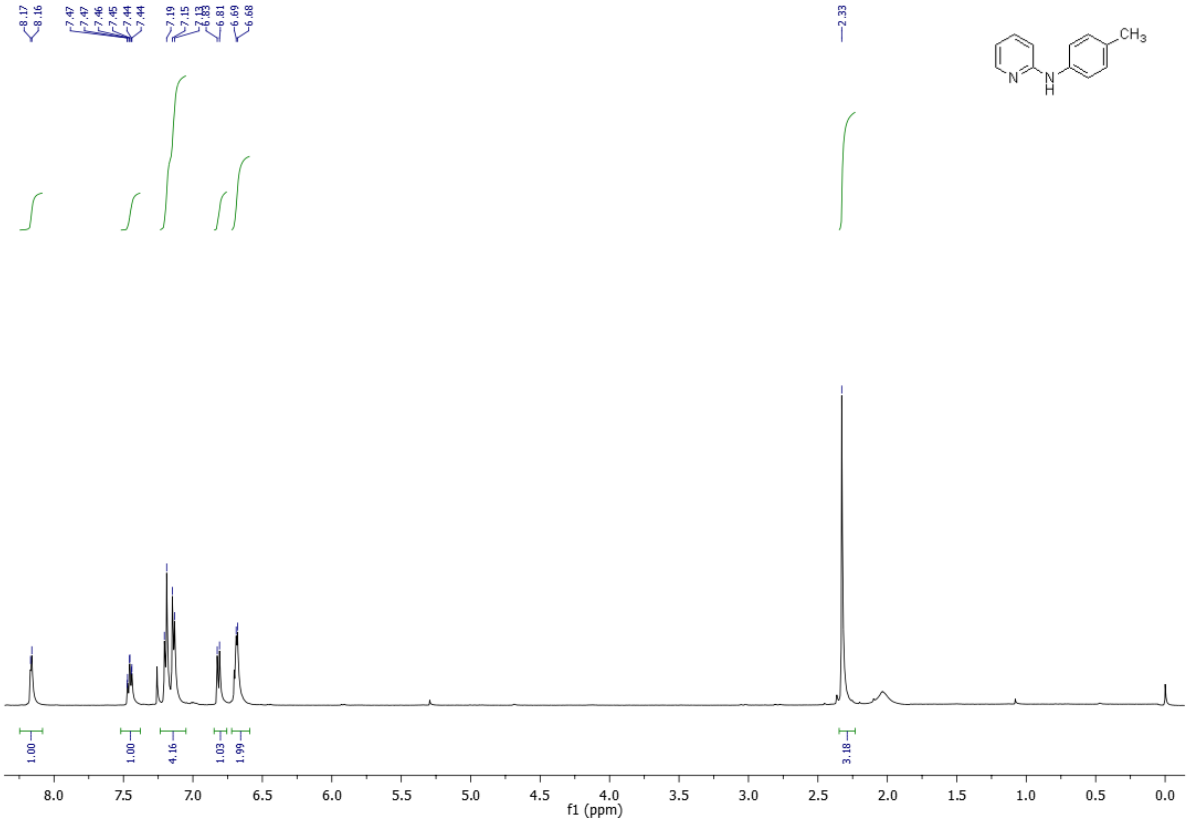
N-phenylpyridin-2-amine (1a) ^{1}H-NMR spectrum



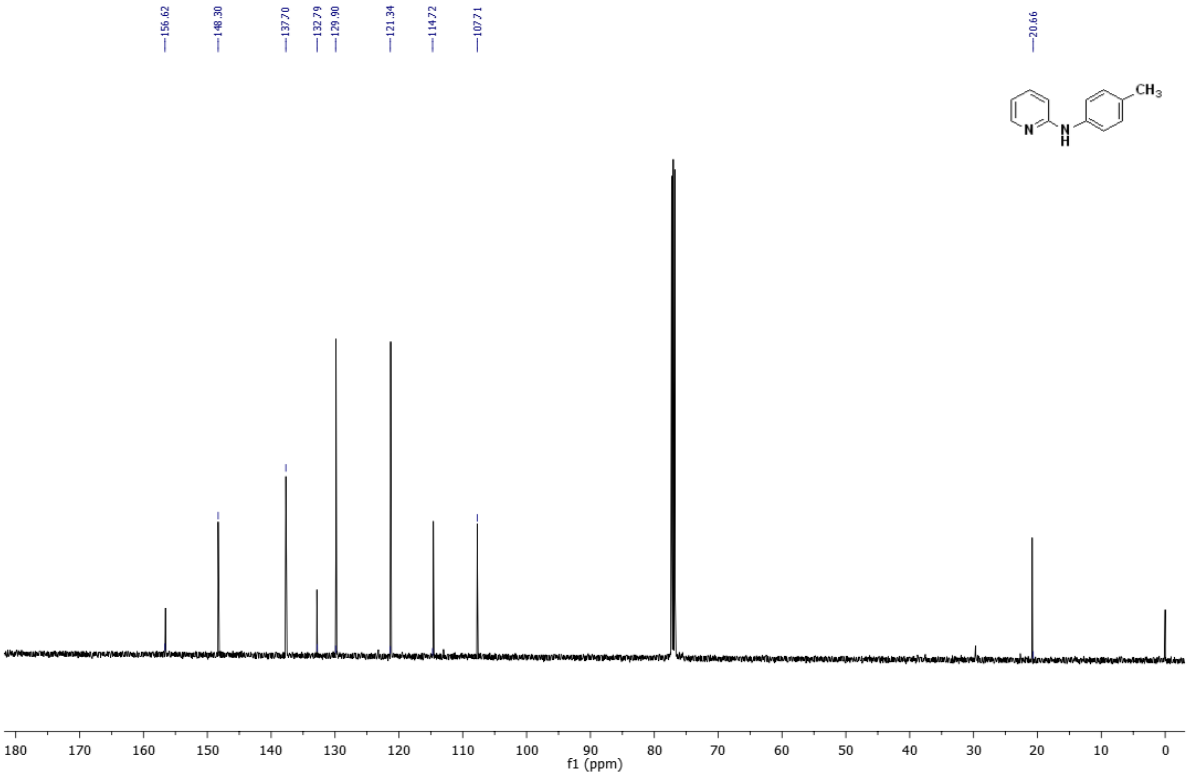
N-phenylpyridin-2-amine (1a) ^{13}C-NMR spectrum



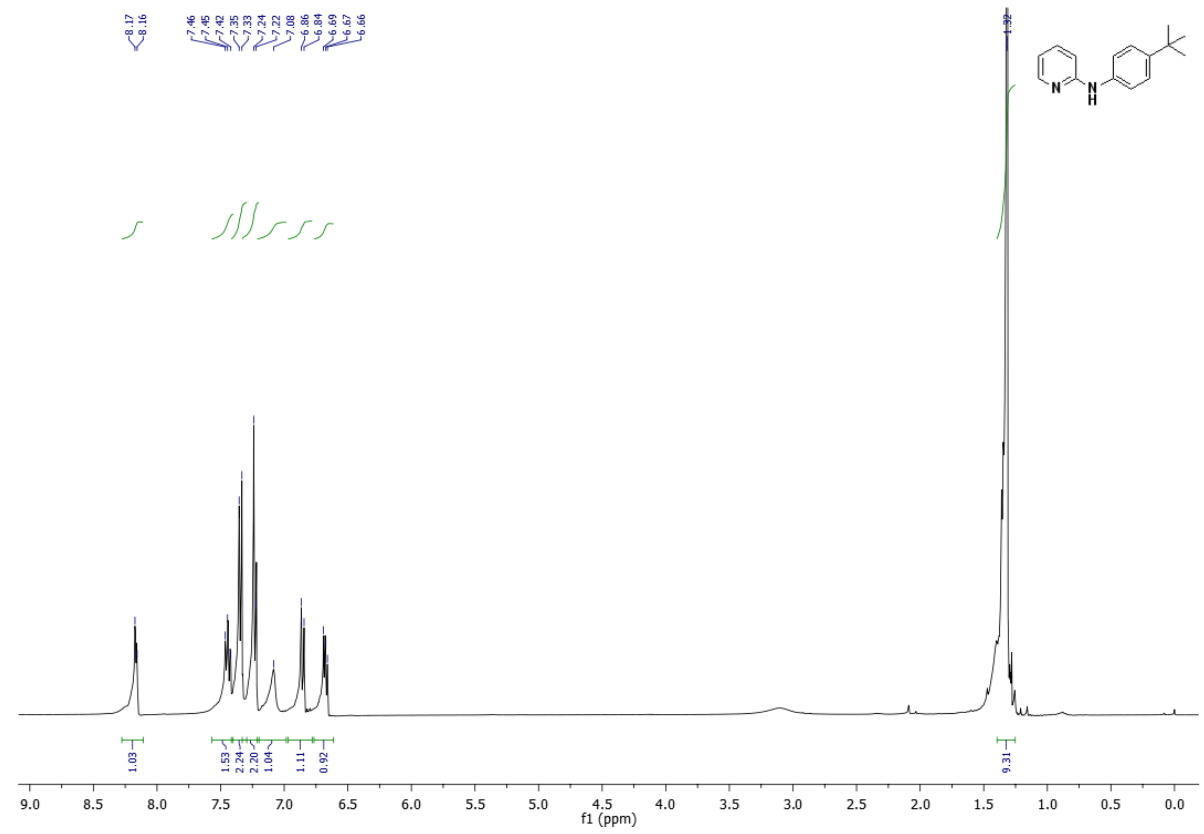
N-(*p*-tolyl)pyridin-2-amine (1b) ^{1}H-NMR spectrum



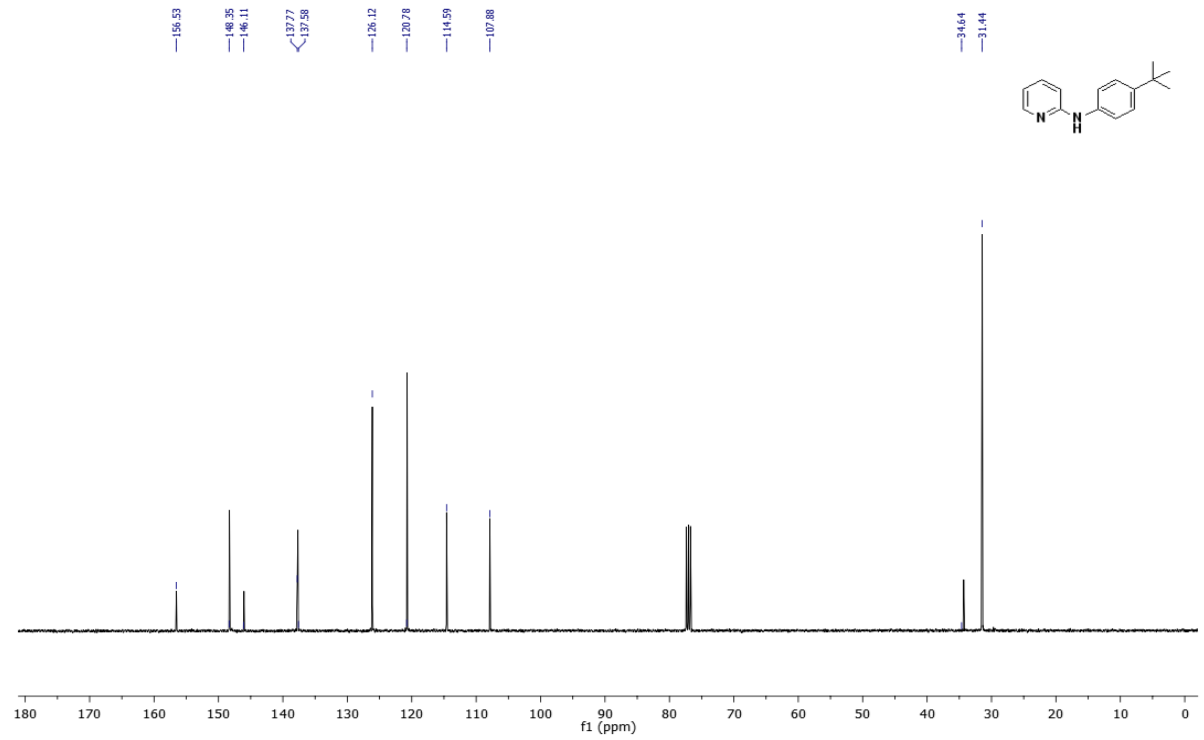
***N*-(p-tolyl)pyridin-2-amine (1b) ^{13}C-NMR spectrum**



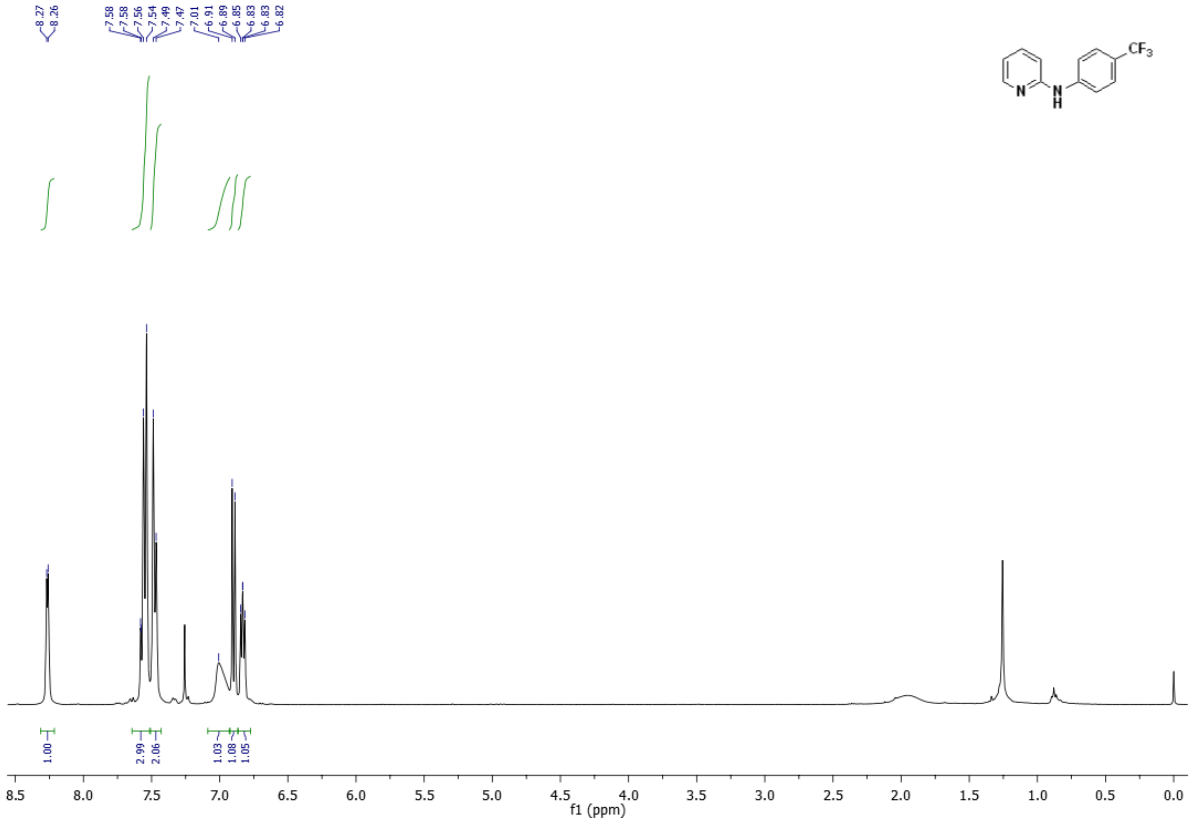
***N*-(4-(tert-butyl)phenyl)pyridin-2-amine (1c) ^{1}H-NMR spectrum**



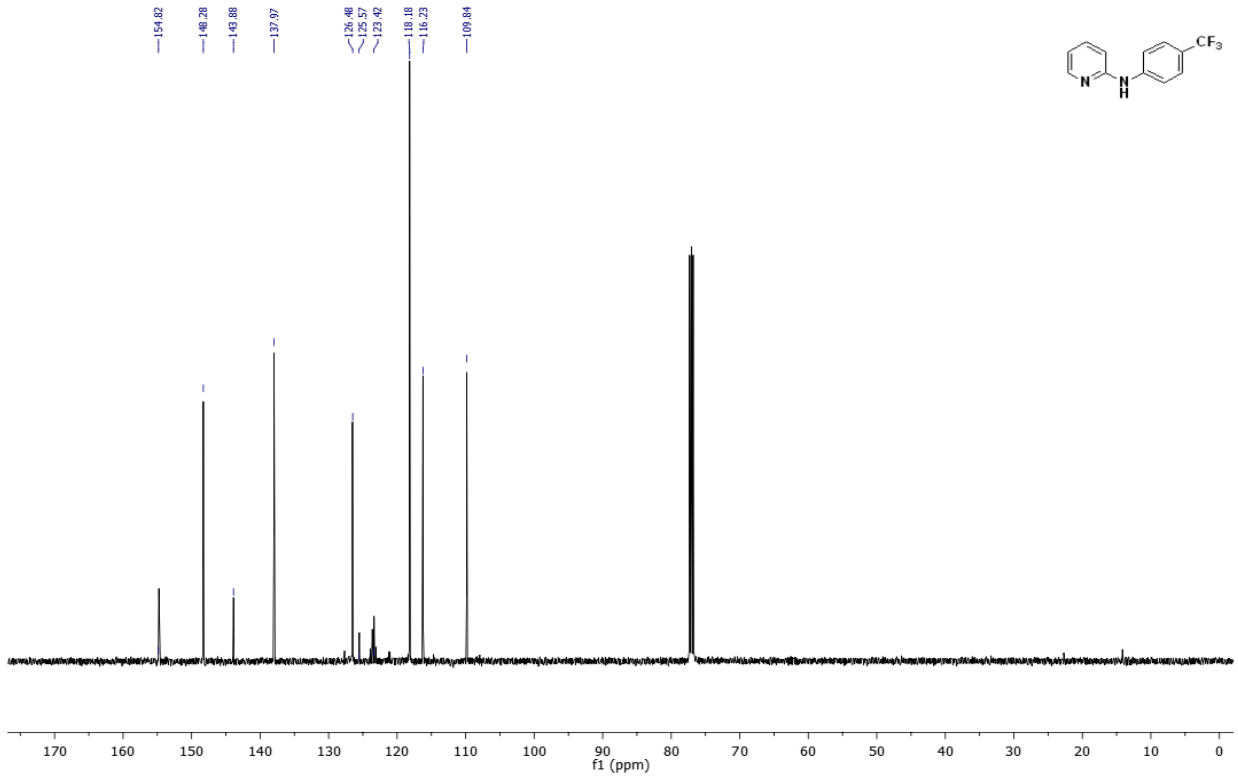
***N*-(4-(tert-butyl)phenyl)pyridin-2-amine (1c) ^{13}C-NMR spectrum**



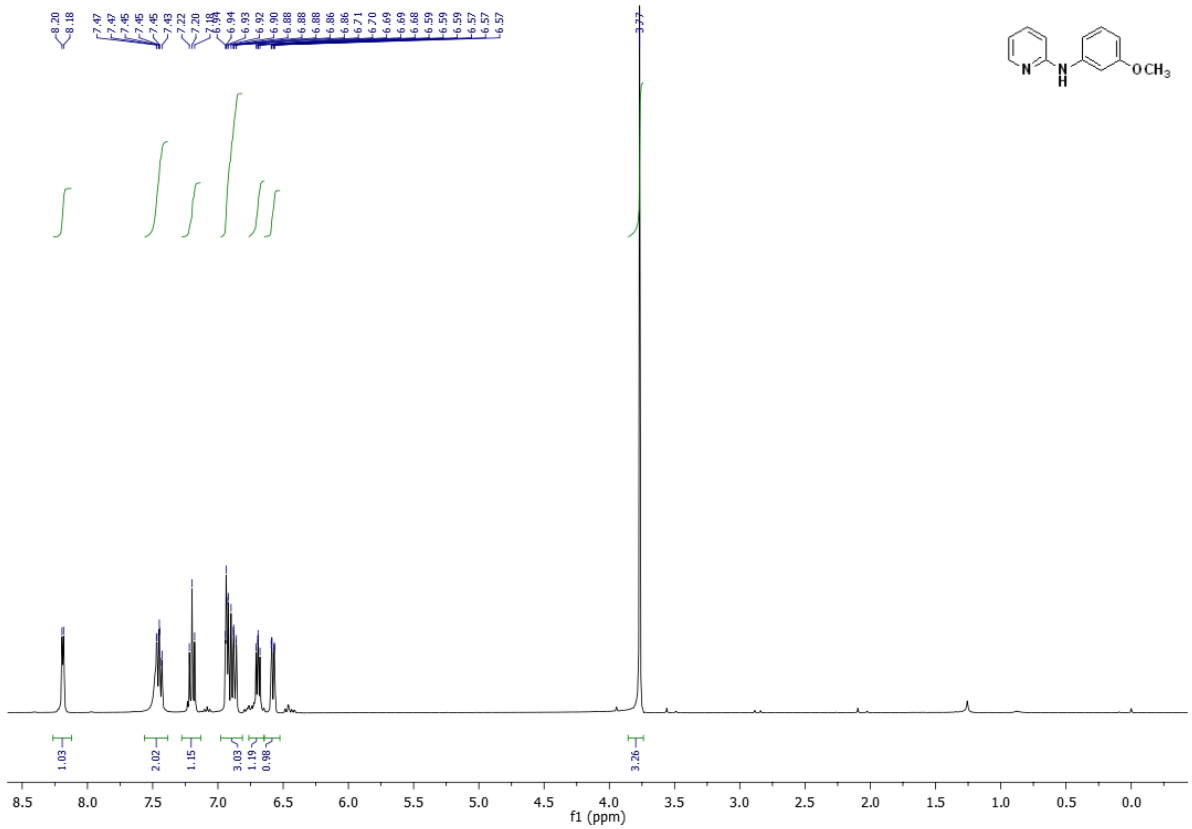
***N*-(4-(trifluoromethyl)phenyl)pyridin-2-amine (1d) ^{1}H-NMR spectrum**



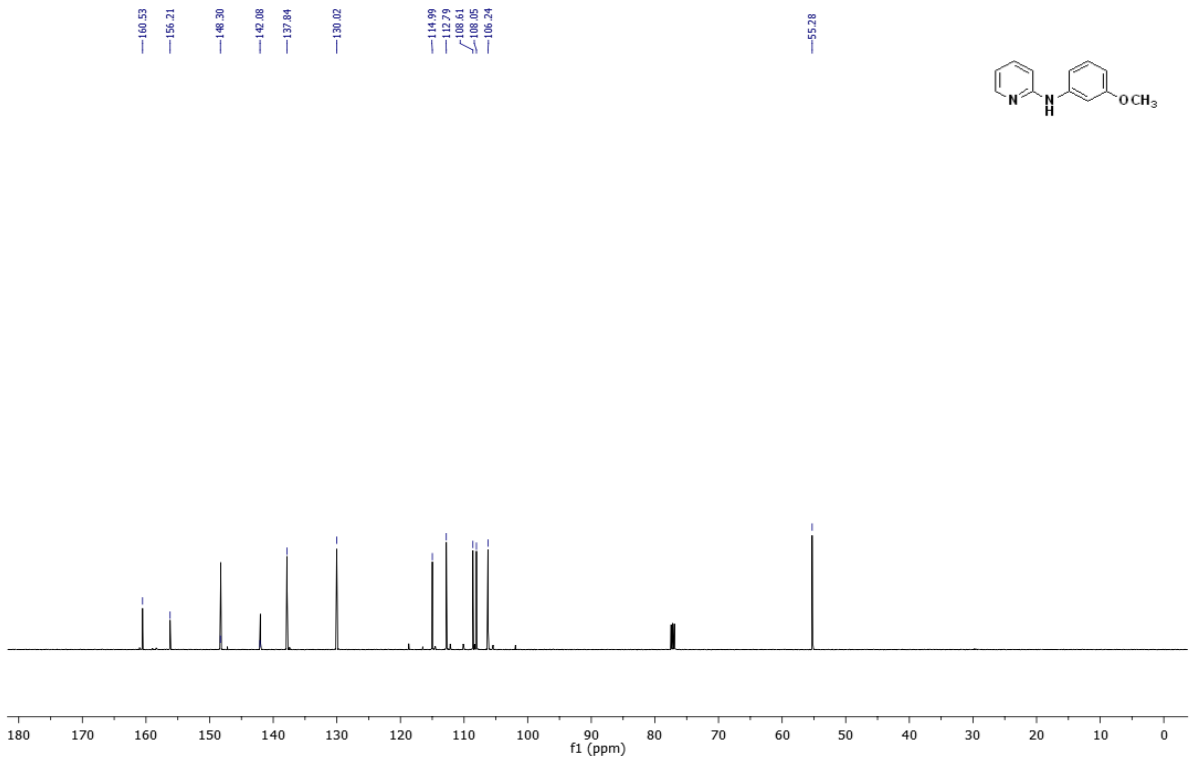
_N_-(4-(trifluoromethyl)phenyl)pyridin-2-amine (1d) ^{13}C-NMR spectrum



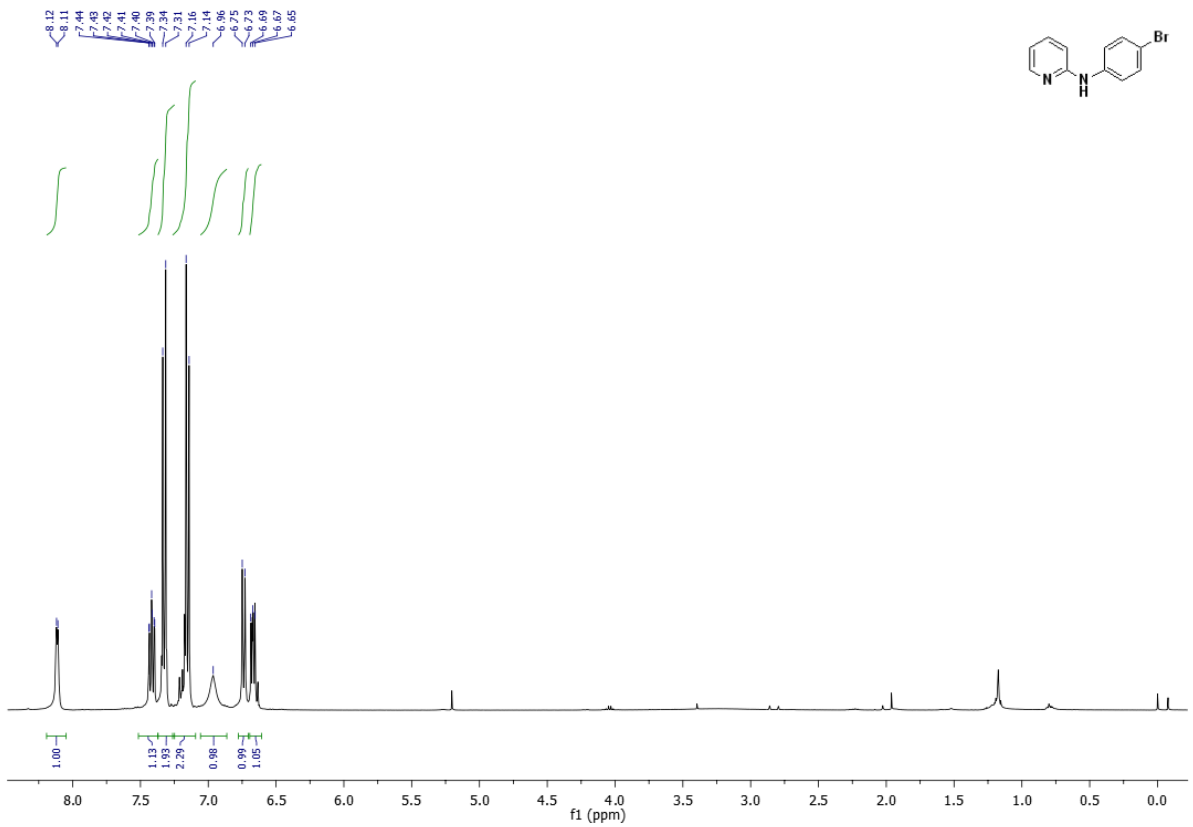
_N_-(3-methoxyphenyl)pyridin-2-amine (1e) ^{1}H-NMR spectrum



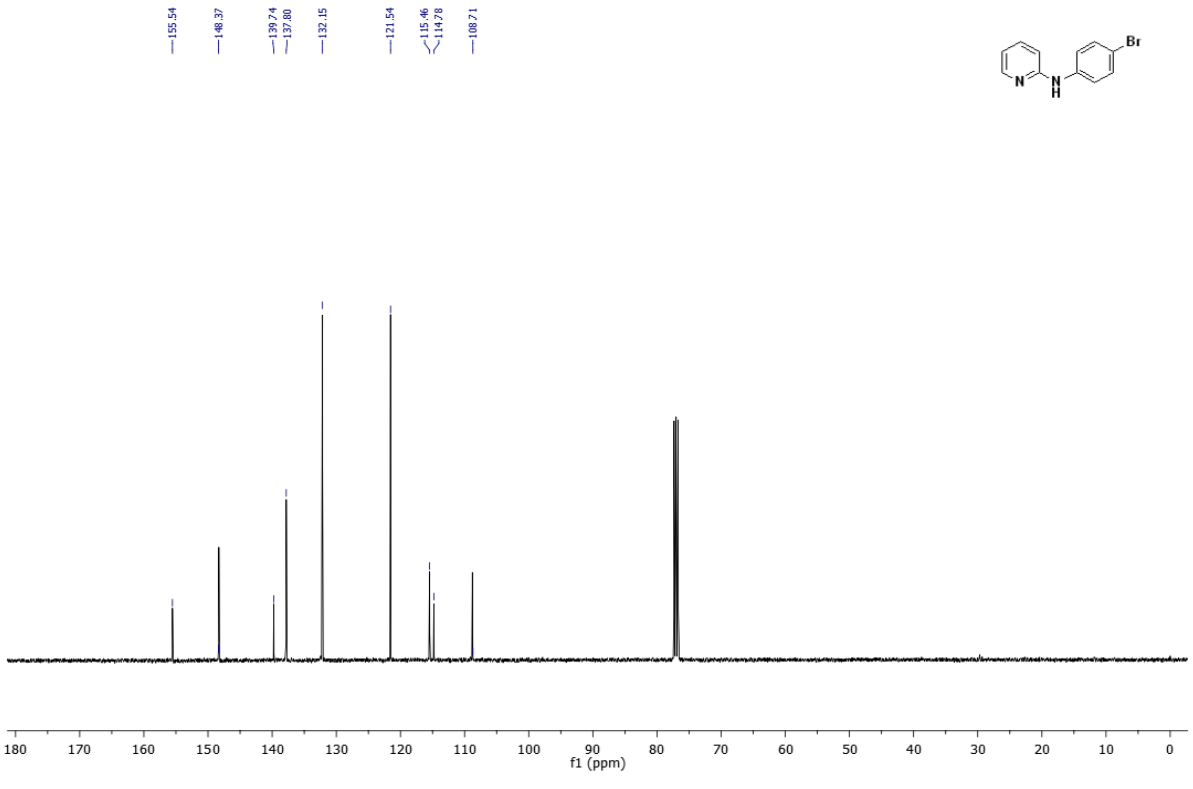
_N_-(3-methoxyphenyl)pyridin-2-amine (1e) ^{13}C-NMR spectrum



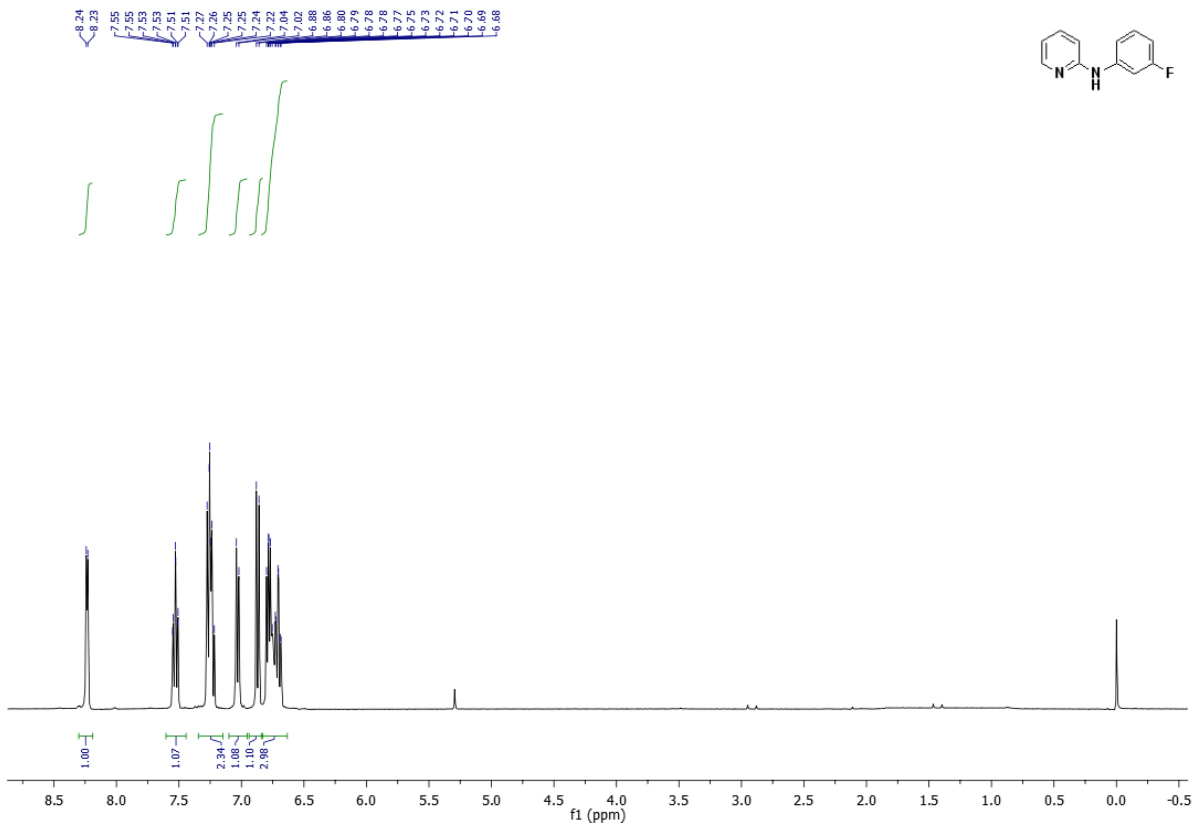
_N_-(4-bromophenyl)pyridin-2-amine (1f) ^{1}H-NMR spectrum



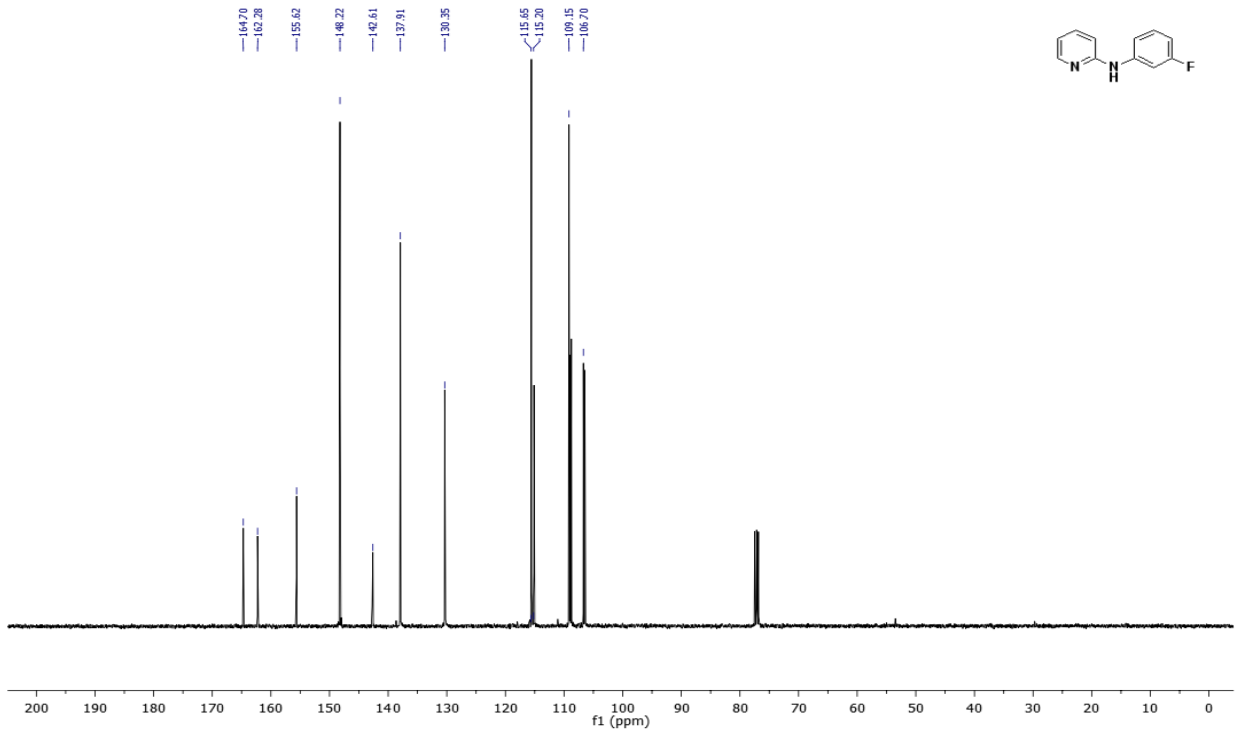
_N_-(4-bromophenyl)pyridin-2-amine (1f) ^{13}C-NMR spectrum



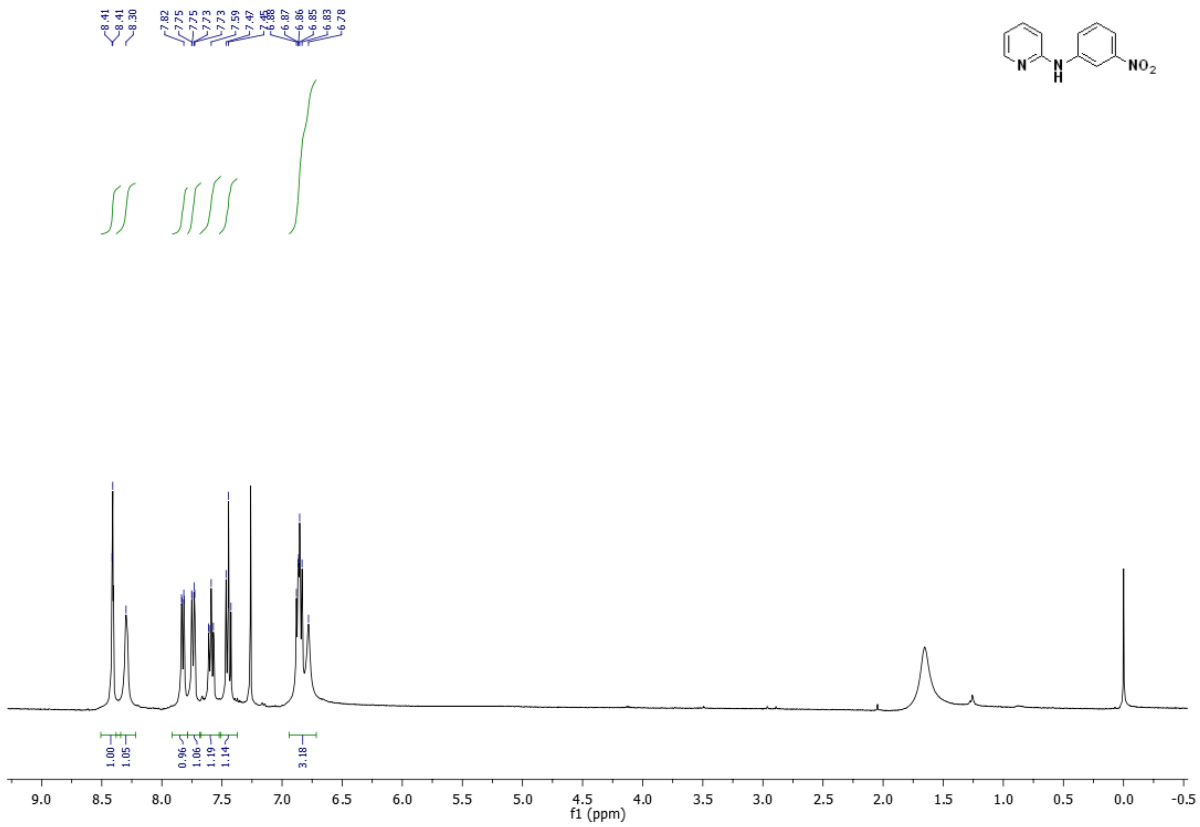
_N_-(3-fluorophenyl)pyridin-2-amine (1g) ^{1}H-NMR spectrum



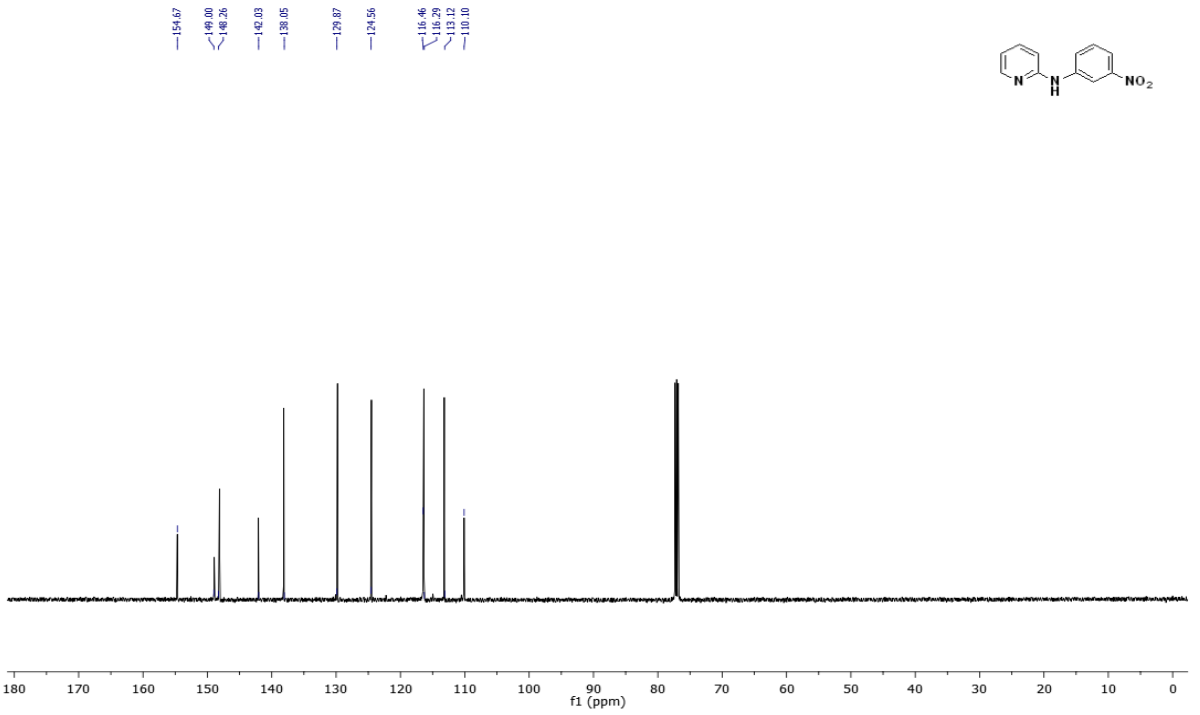
***N*-(3-fluorophenyl)pyridin-2-amine (1g) ^{13}C-NMR spectrum**



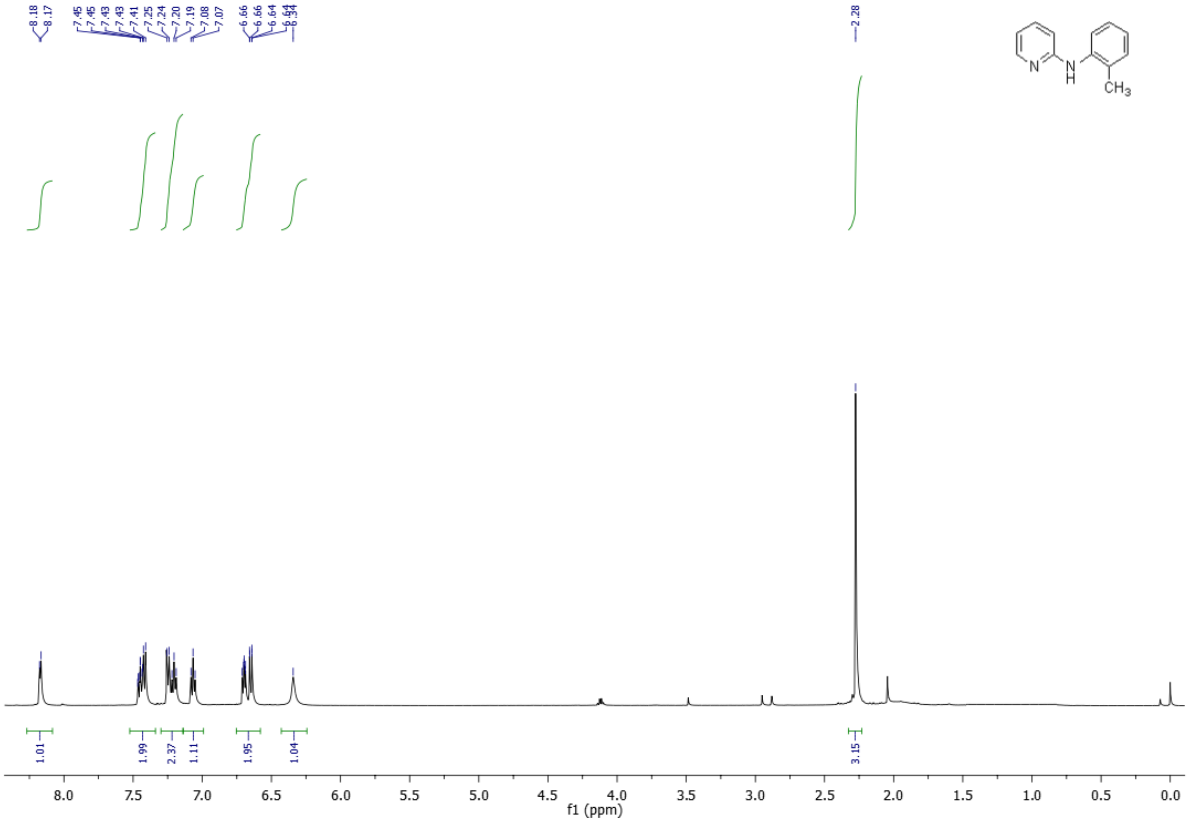
***N*-(3-nitrophenyl)pyridin-2-amine (1h) ^{1}H-NMR spectrum**



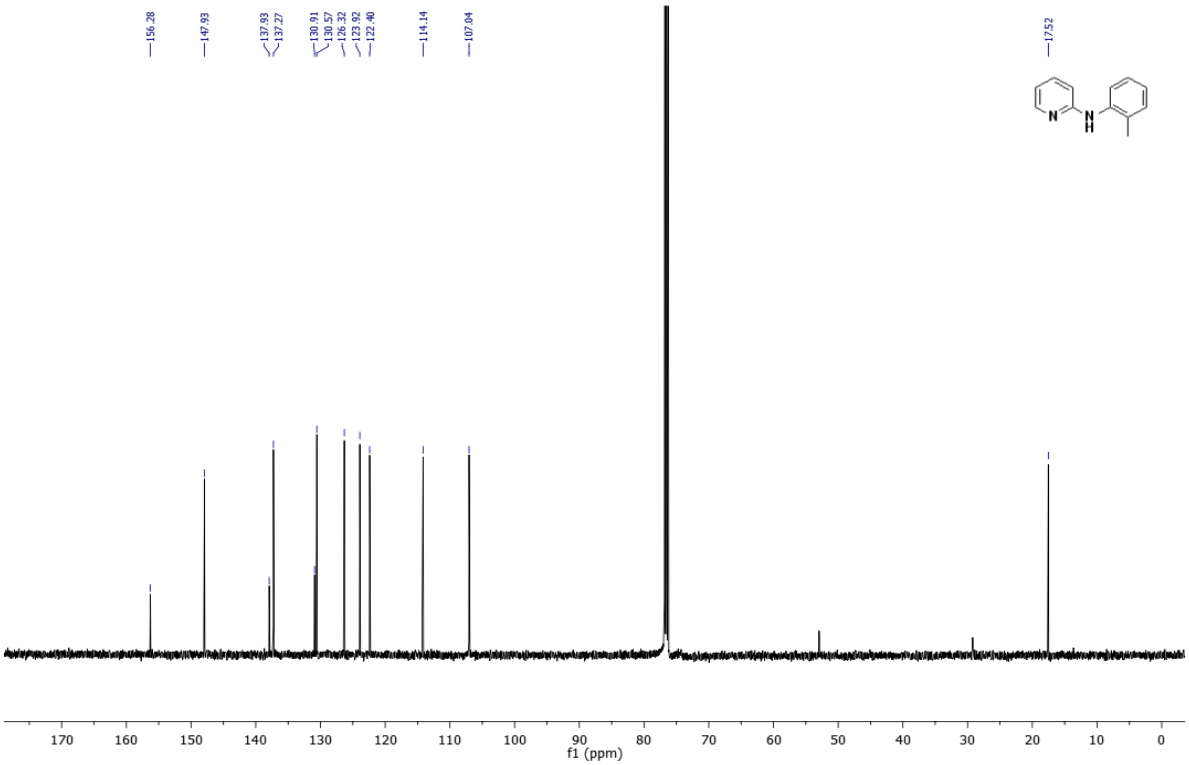
***N*-(3-nitrophenyl)pyridin-2-amine (1h) ^{13}C-NMR spectrum**



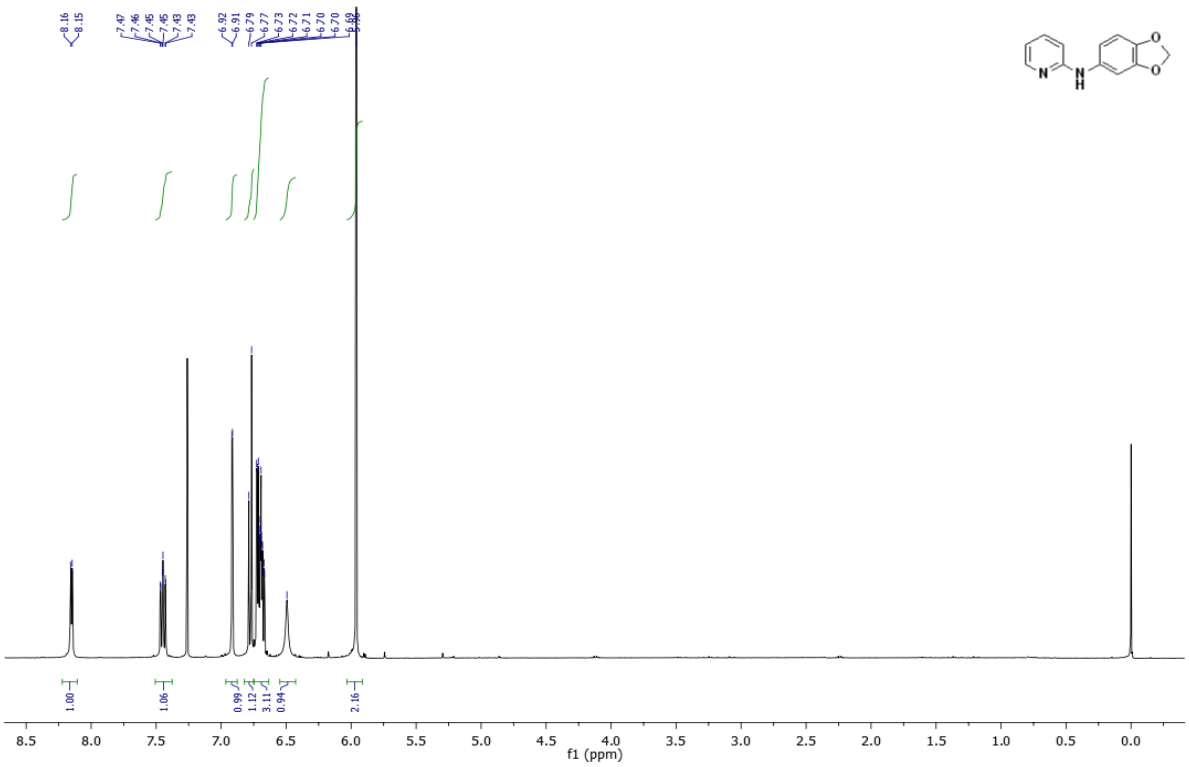
***N*-(o-tolyl)pyridin-2-amine (1i) ^{1}H-NMR spectrum**



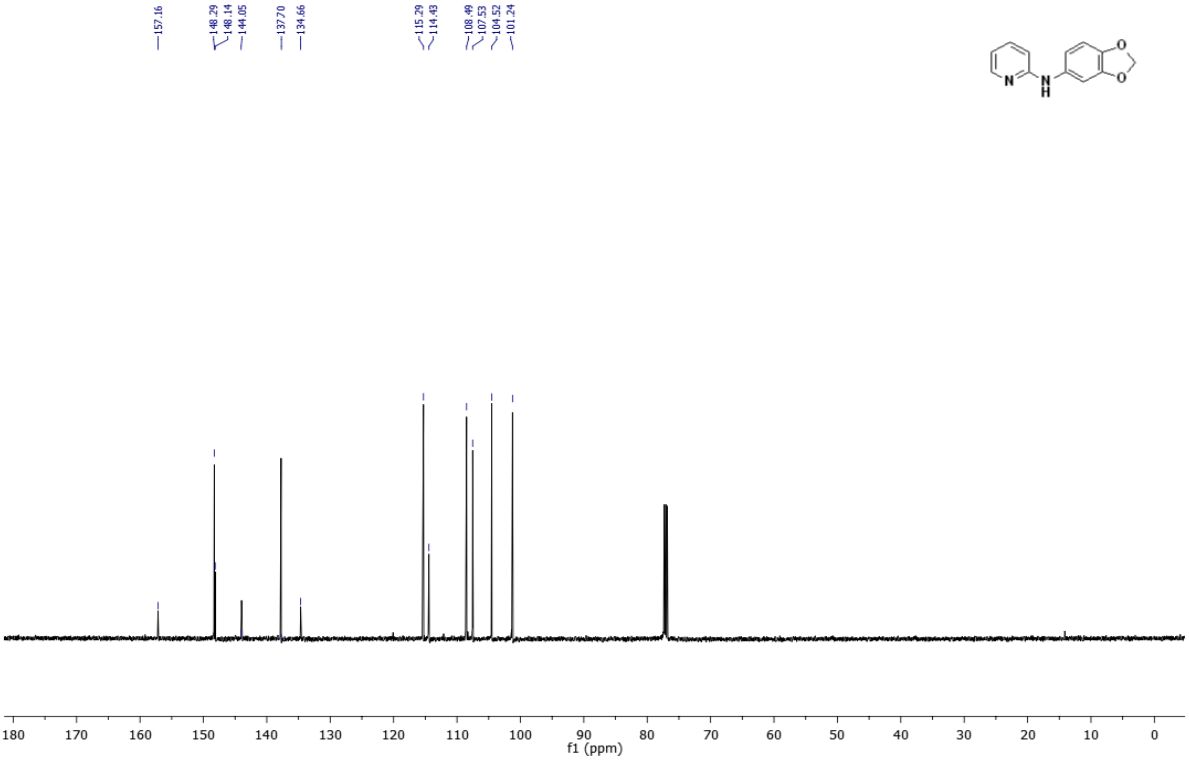
_N_-(_o_-tolyl)pyridin-2-amine (1i) ^{13}C-NMR spectrum



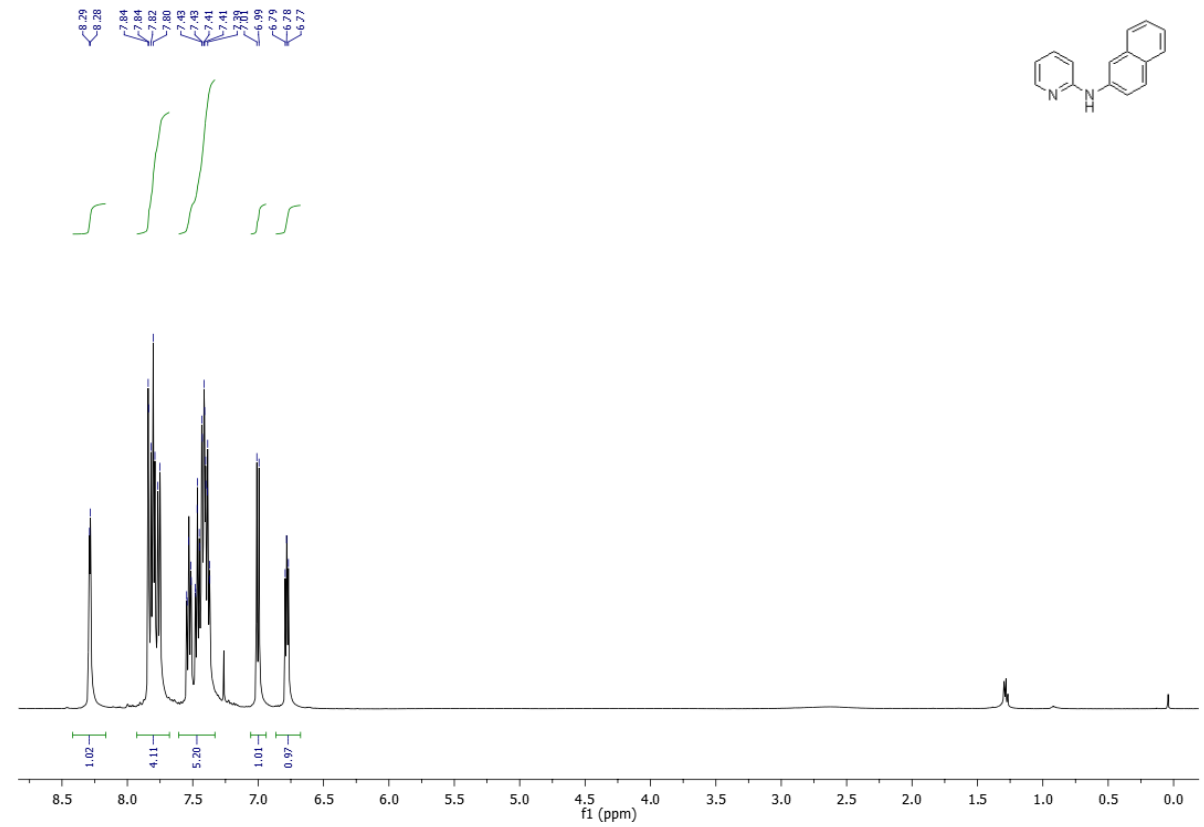
_N_-(benzo[_d_][1,3]dioxol-5-yl)pyridin-2-amine (1j) ^{1}H-NMR spectrum



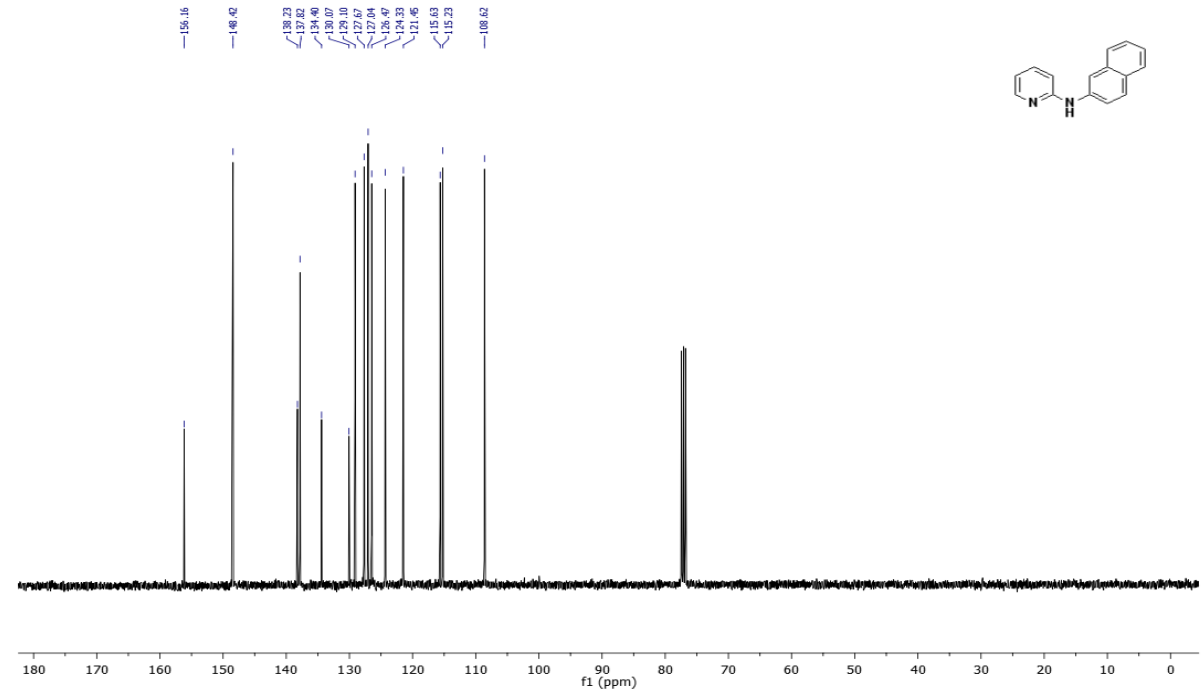
_N_-(benzo[_d_][1,3]dioxol-5-yl)pyridin-2-amine (1j) ^{13}C-NMR spectrum



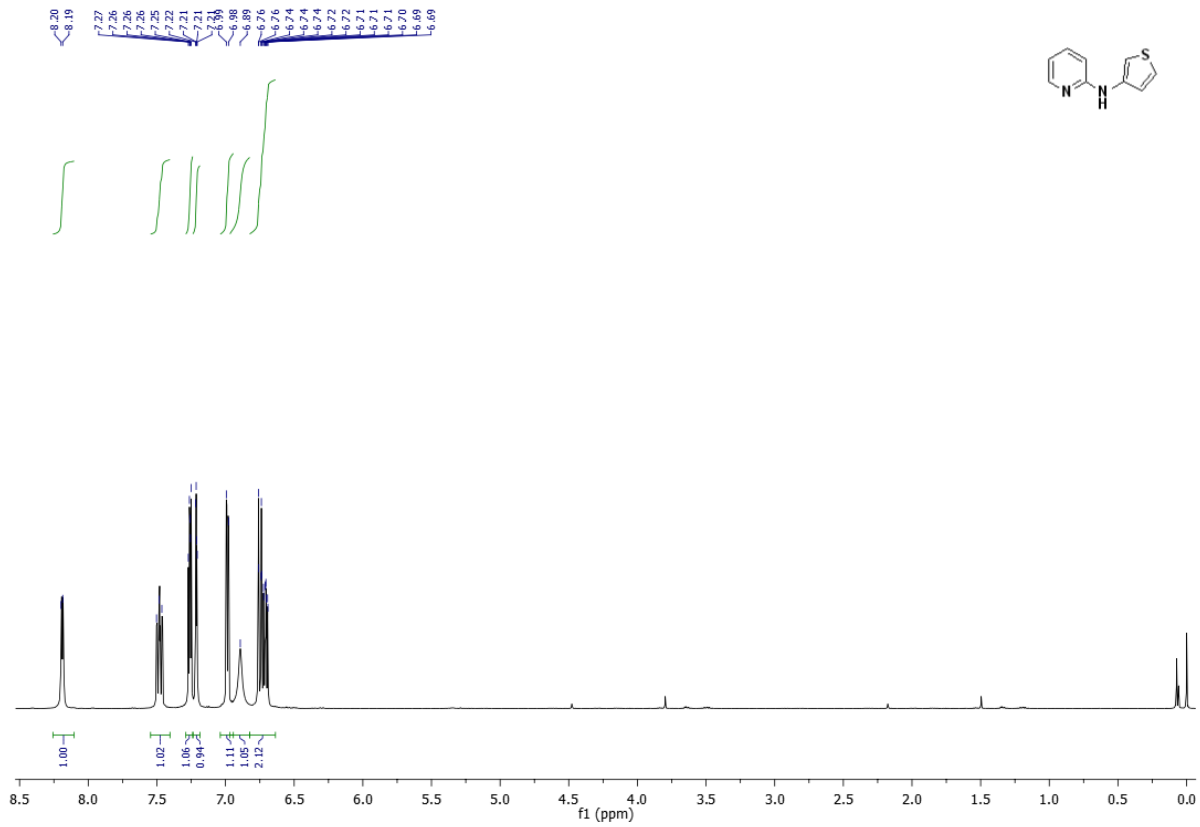
_N_-(naphthalen-2-yl)pyridin-2-amine (1k) ^{1}H-NMR spectrum



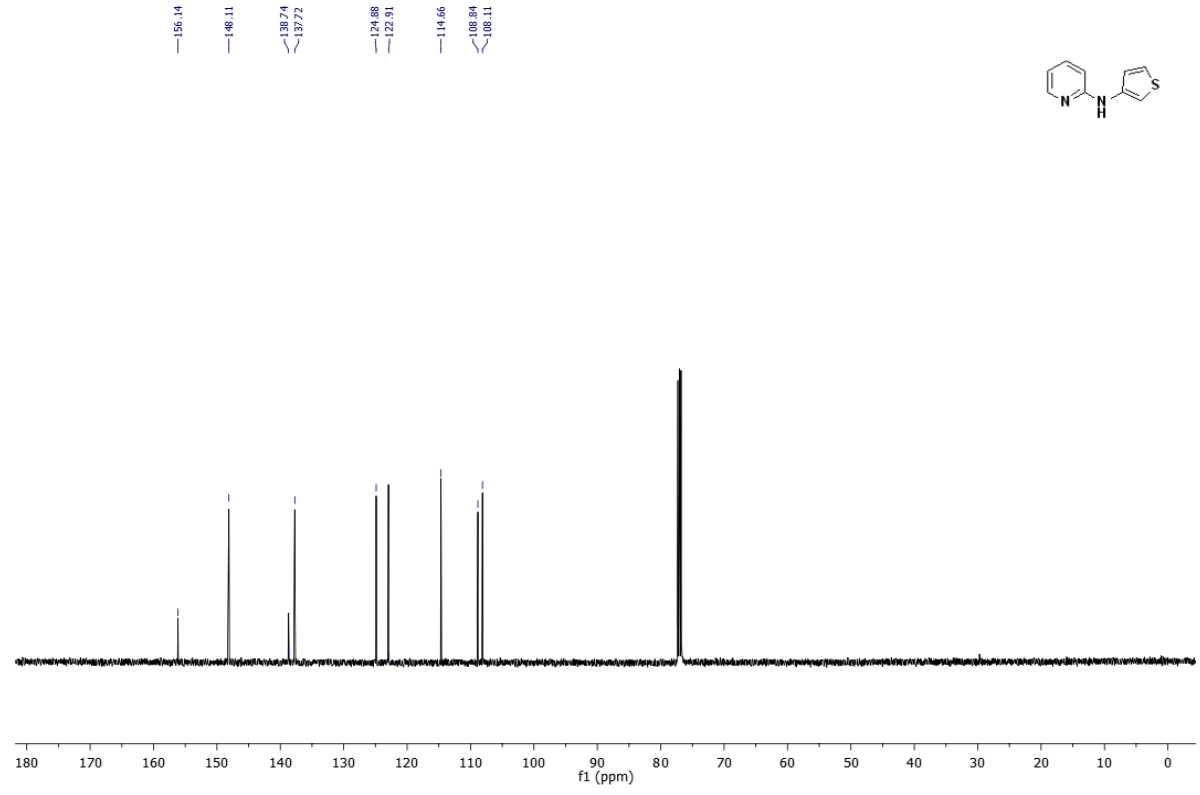
***N*-(naphthalen-2-yl)pyridin-2-amine (1k) ^{13}C-NMR spectrum**



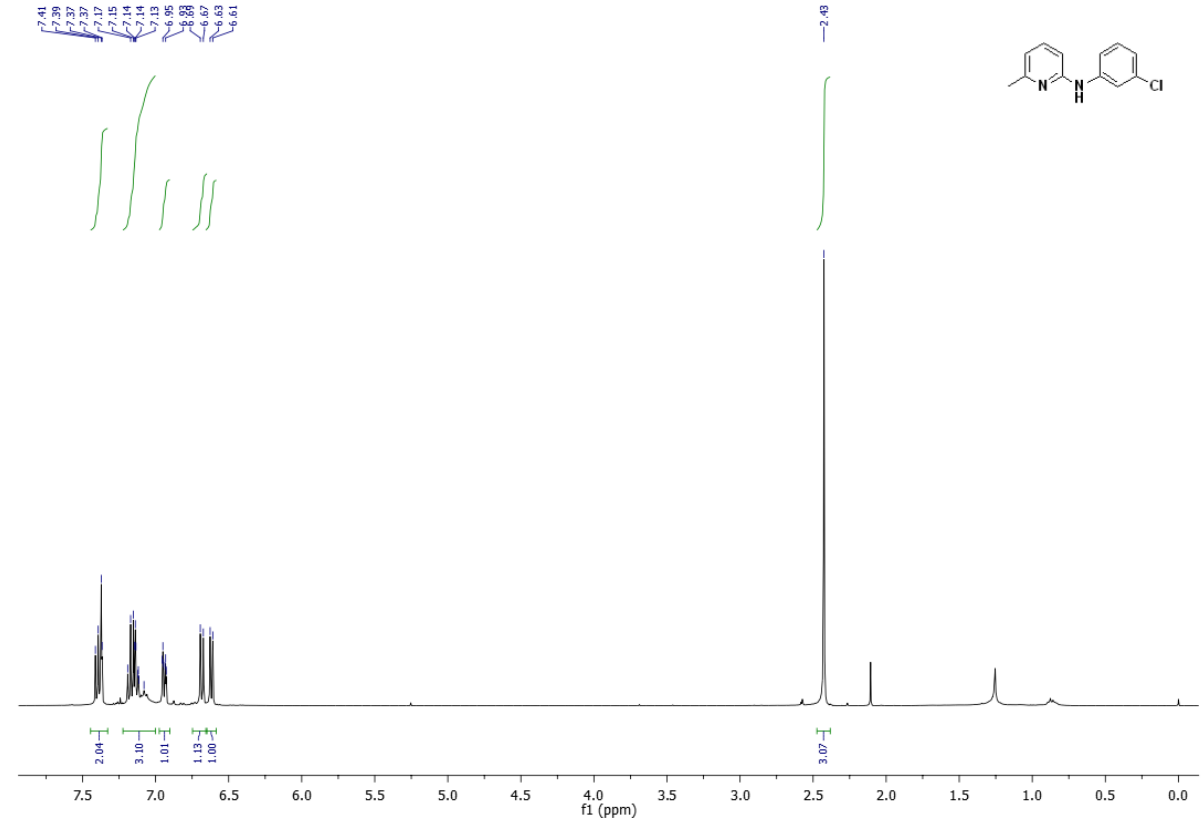
***N*-(thiophen-3-yl)pyridin-2-amine (1l) ^{1}H-NMR spectrum**



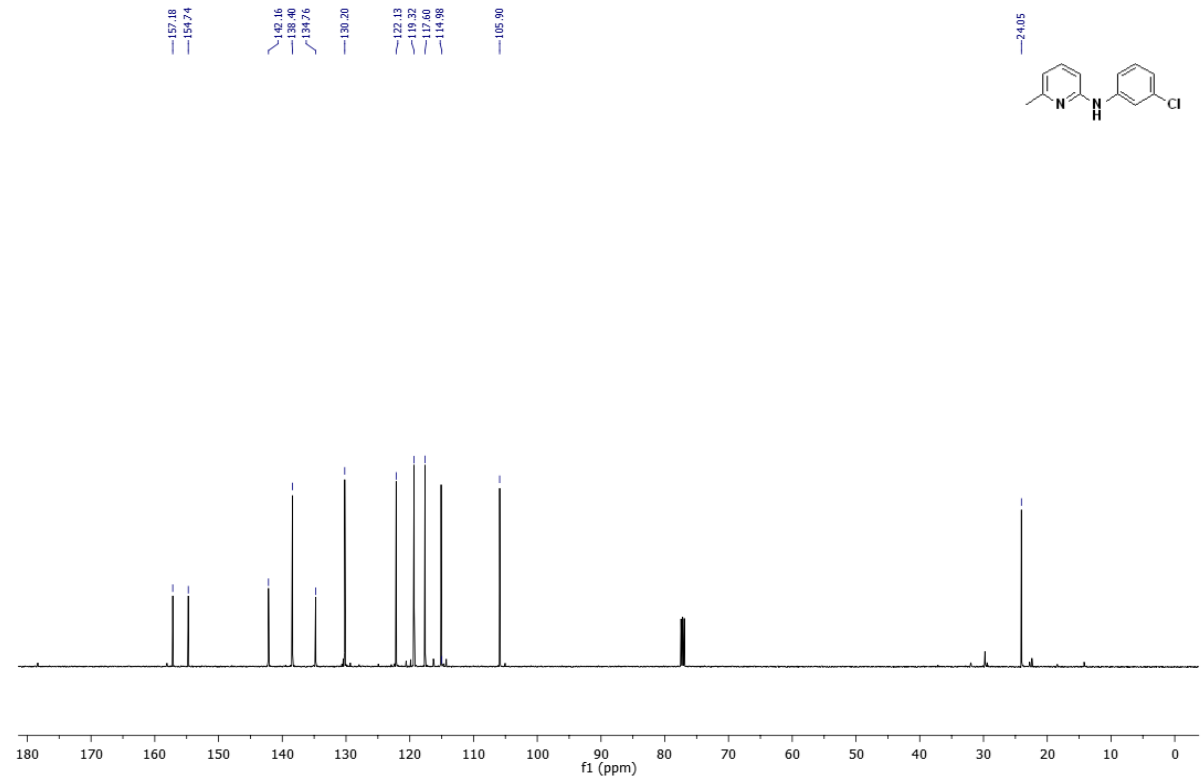
_N_-(thiophen-3-yl)pyridin-2-amine (1l) ^{13}C-NMR spectrum



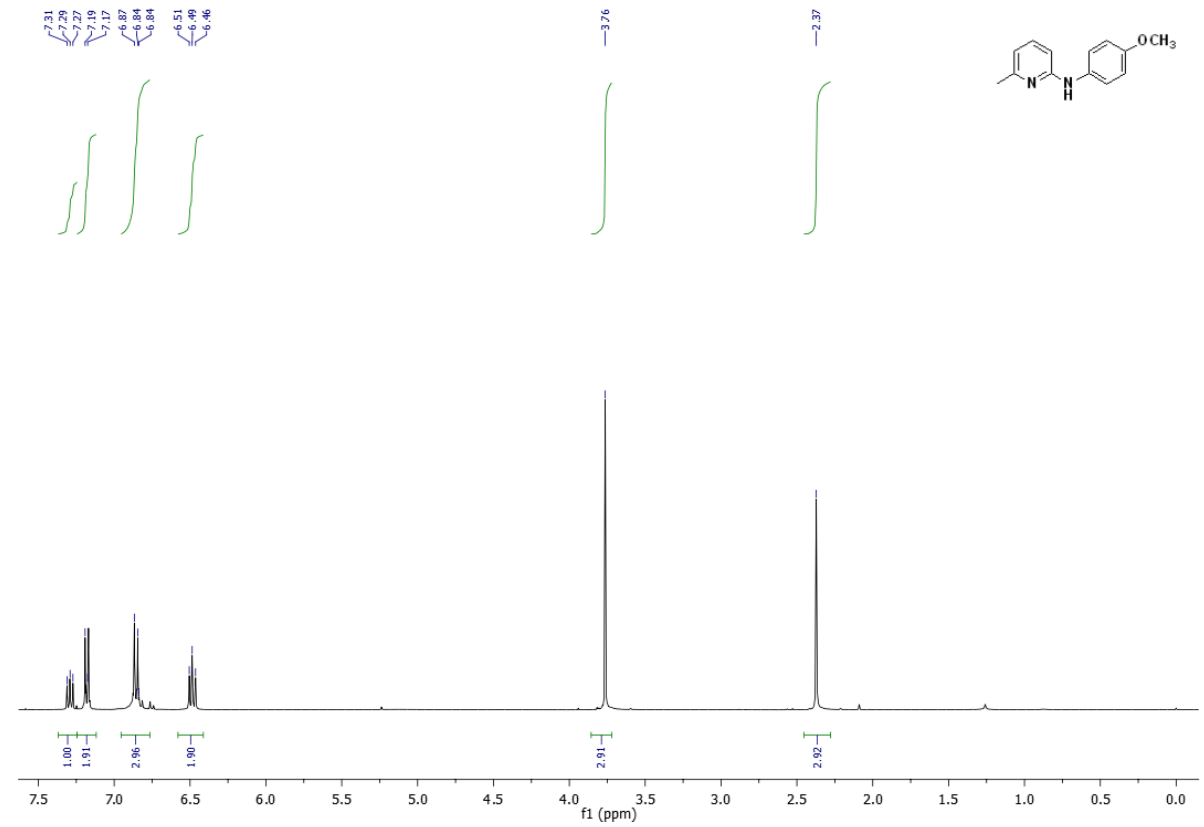
_N_-(3-chlorophenyl)-6-methylpyridin-2-amine (1m) ^{1}H-NMR spectrum



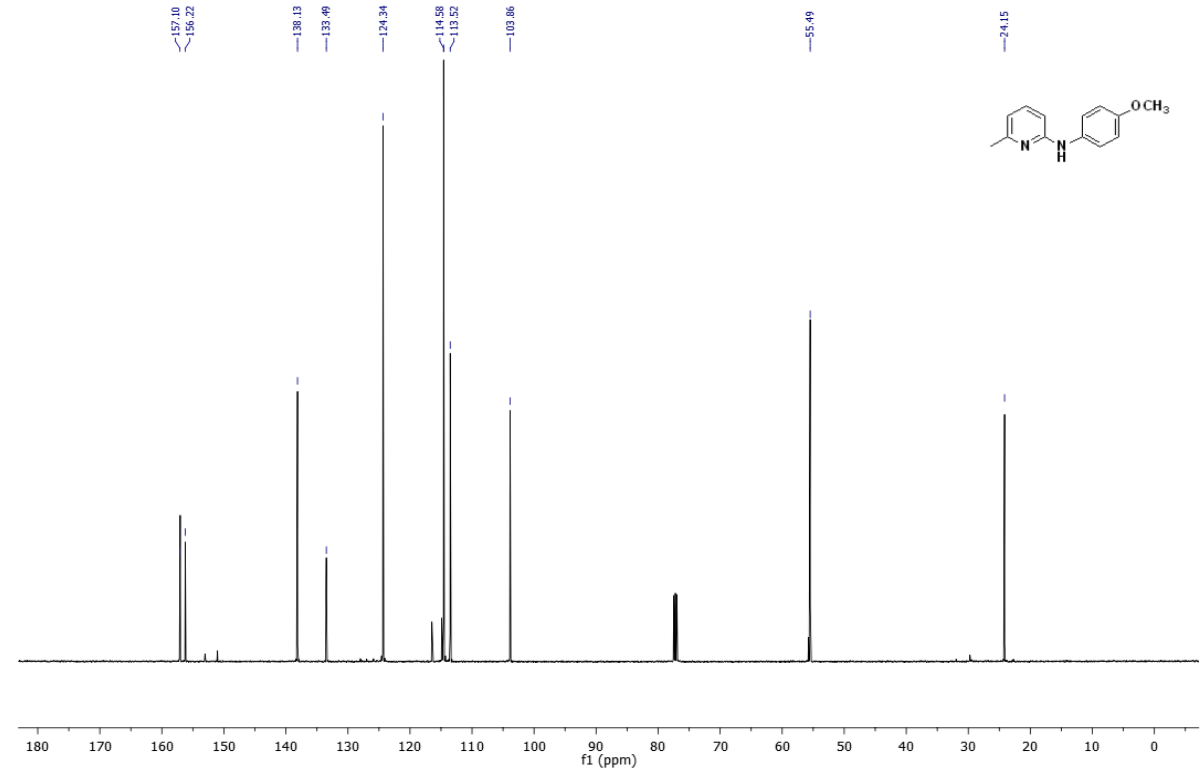
_N_-(3-chlorophenyl)-6-methylpyridin-2-amine (1m) ^{13}C-NMR spectrum



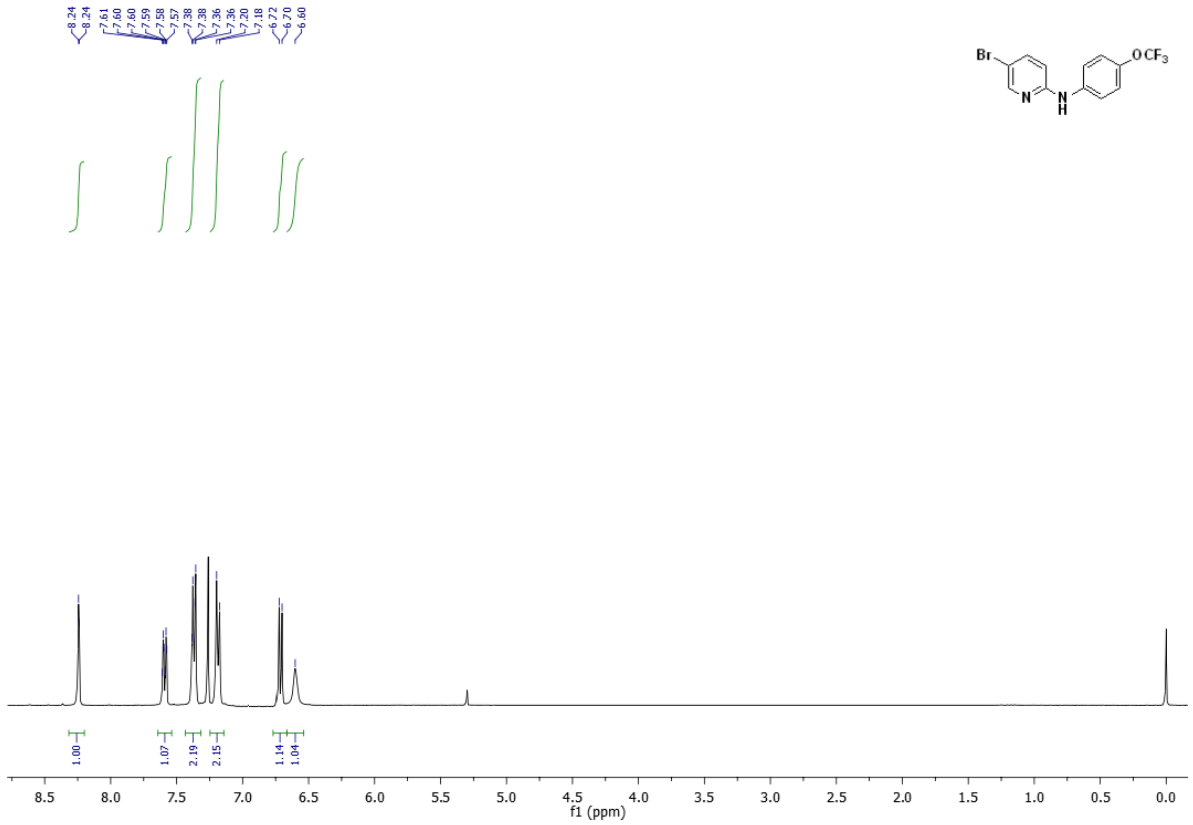
_N_-(3-methoxyphenyl)-6-methylpyridin-2-amine (1n) ^{1}H-NMR spectrum



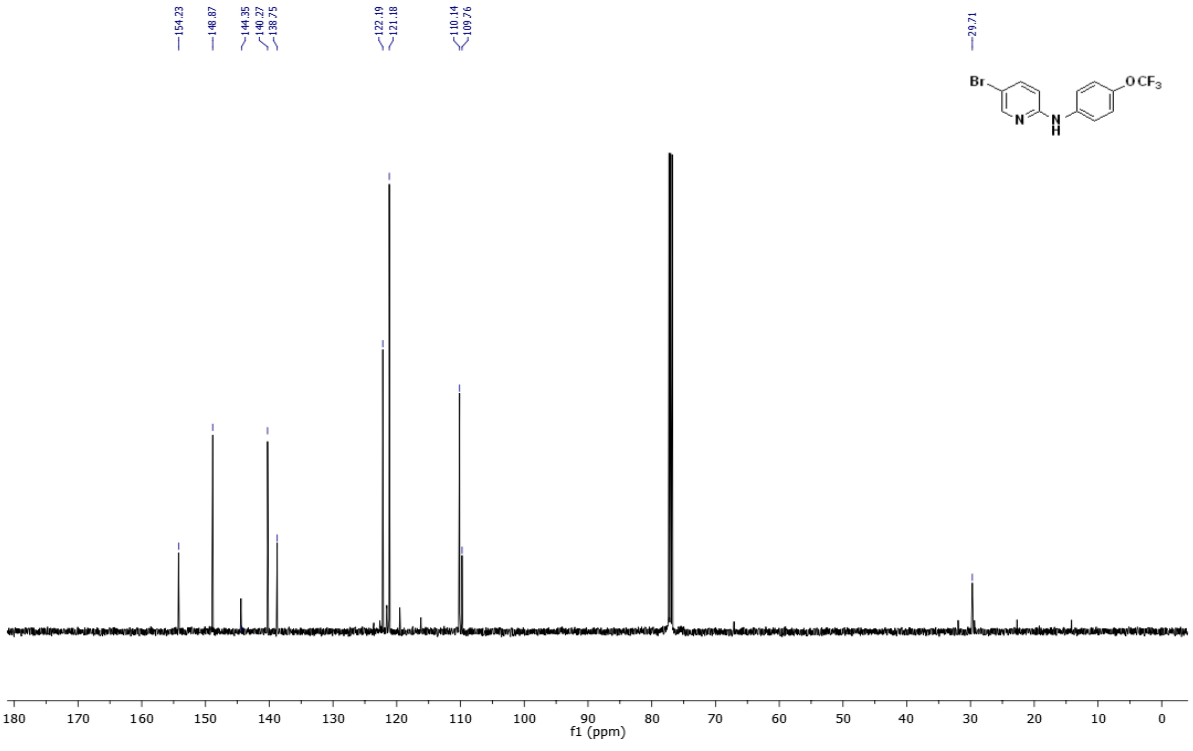
_N_-(3-methoxyphenyl)-6-methylpyridin-2-amine (1n) ^{13}C-NMR spectrum



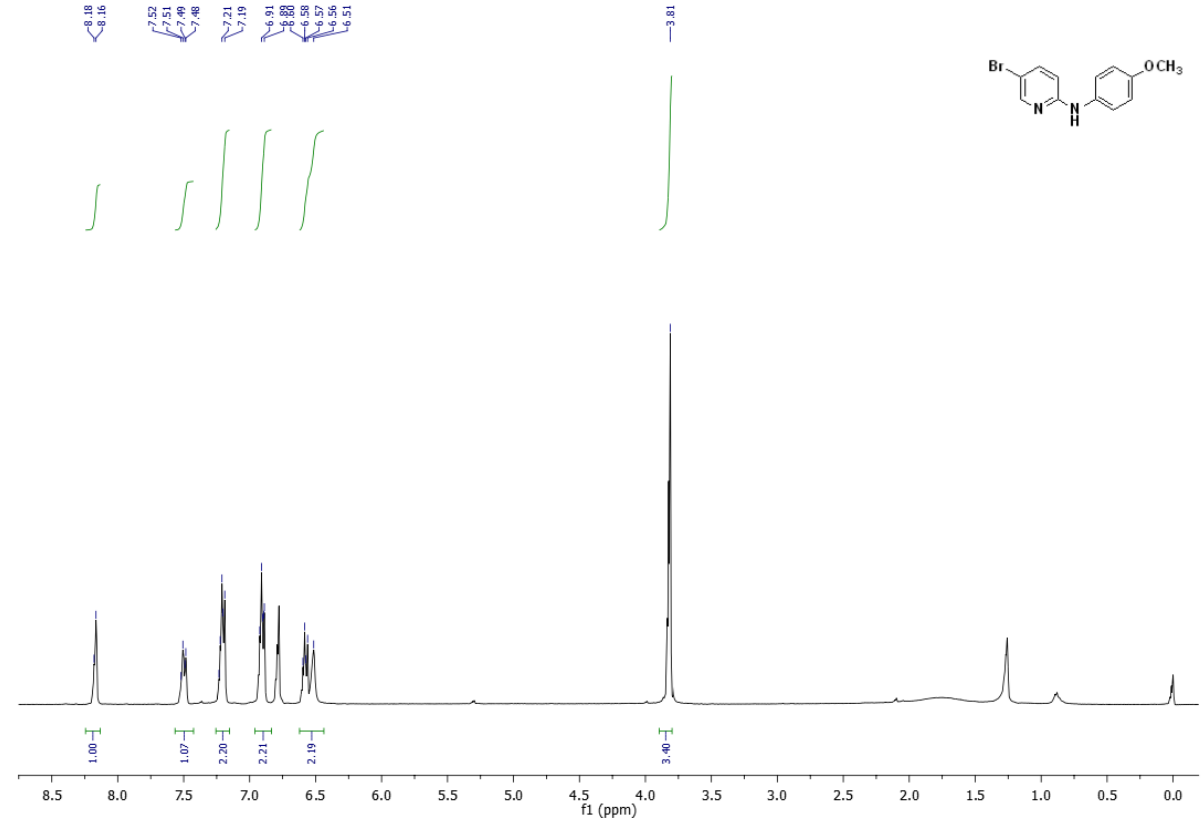
5-bromo-_N_-(4-(trifluoromethoxy)phenyl)pyridin-2-amine (1o) ^{1}H-NMR spectrum



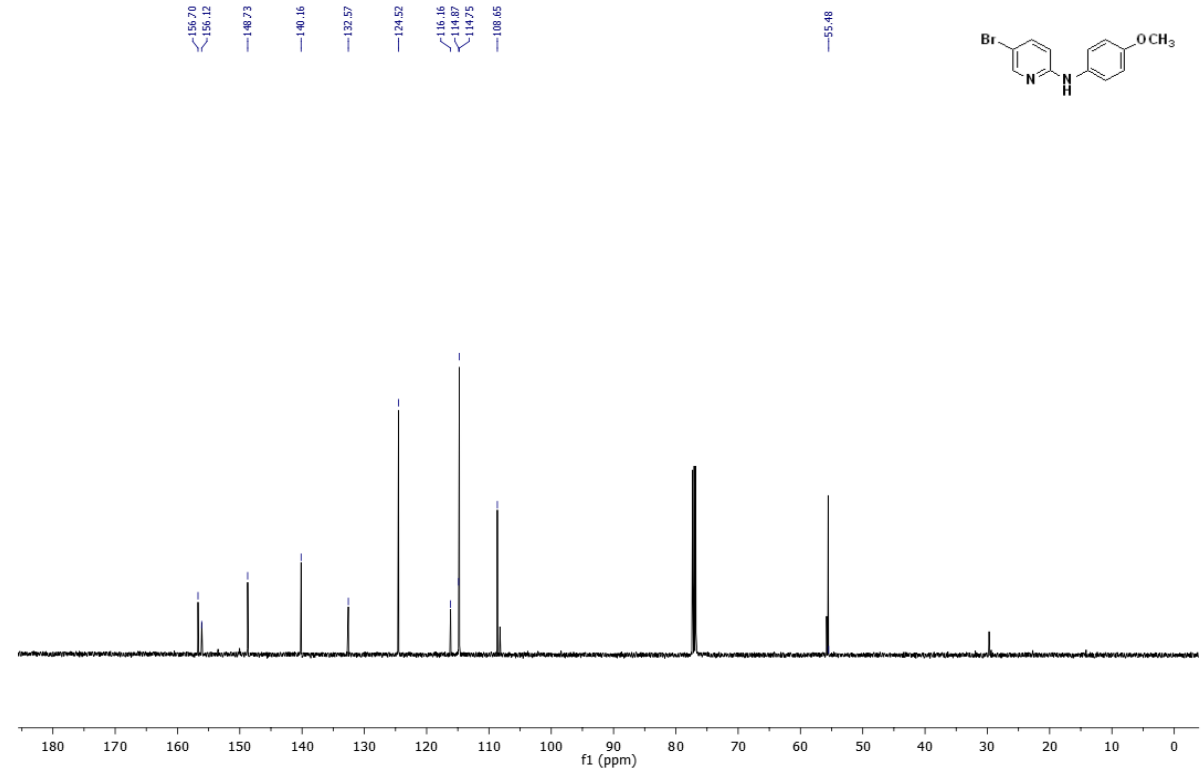
5-bromo-*N*-(4-(trifluoromethoxy)phenyl)pyridin-2-amine (1o) ^{13}C-NMR spectrum



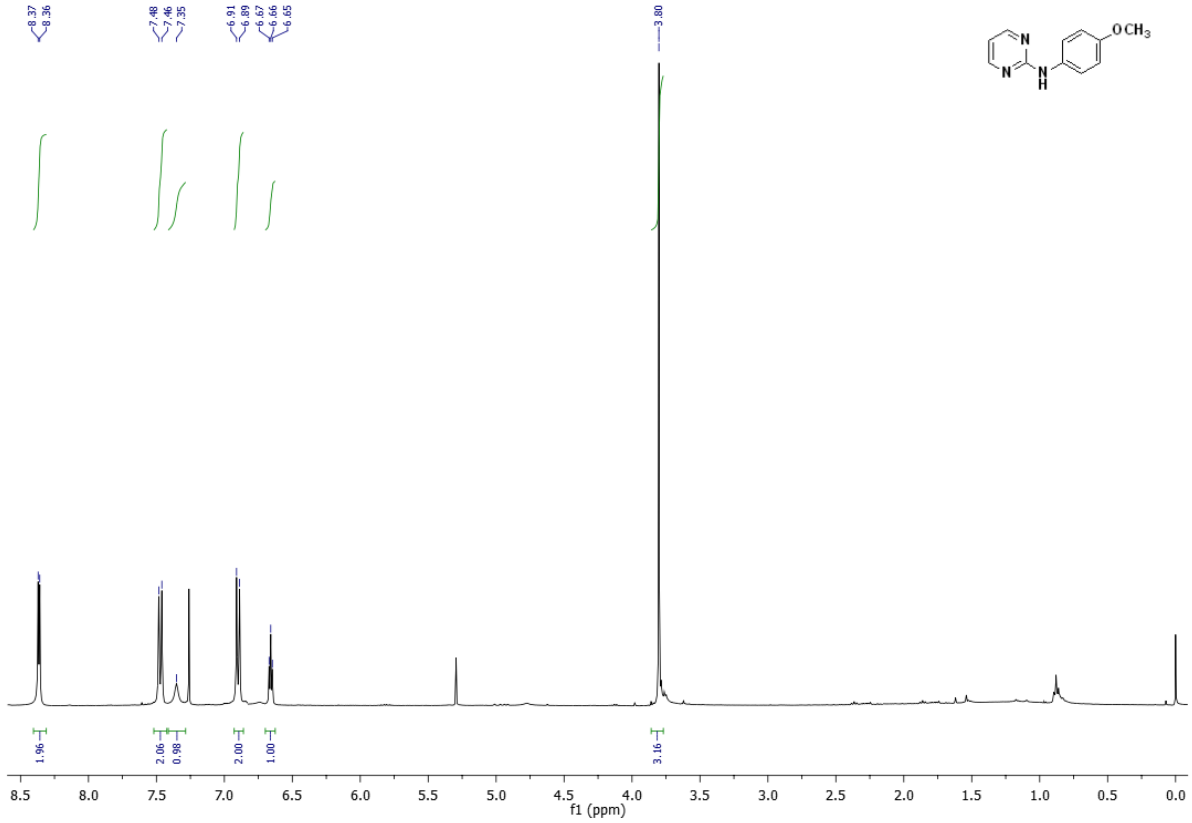
5-bromo-*N*-(4-methoxyphenyl)pyridin-2-amine (1p) ^{1}H-NMR spectrum



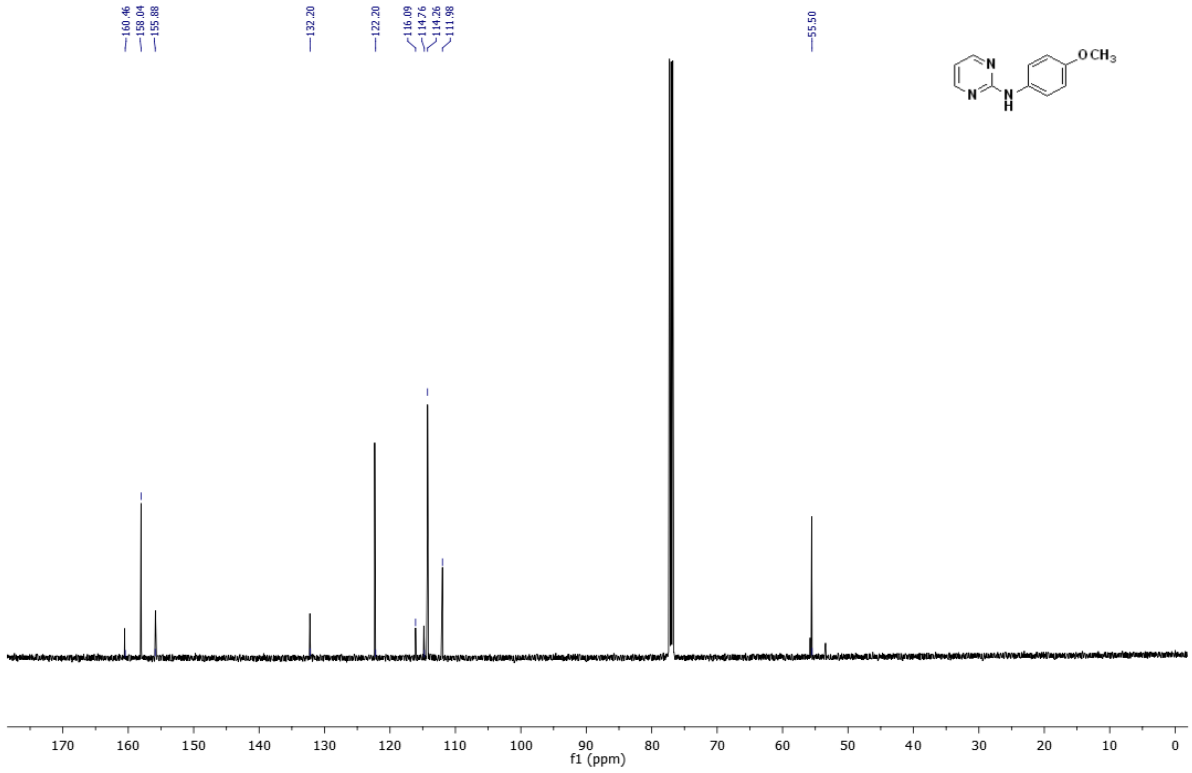
5-bromo-*N*-(4-methoxyphenyl)pyridin-2-amine (1p) ^{13}C-NMR spectrum



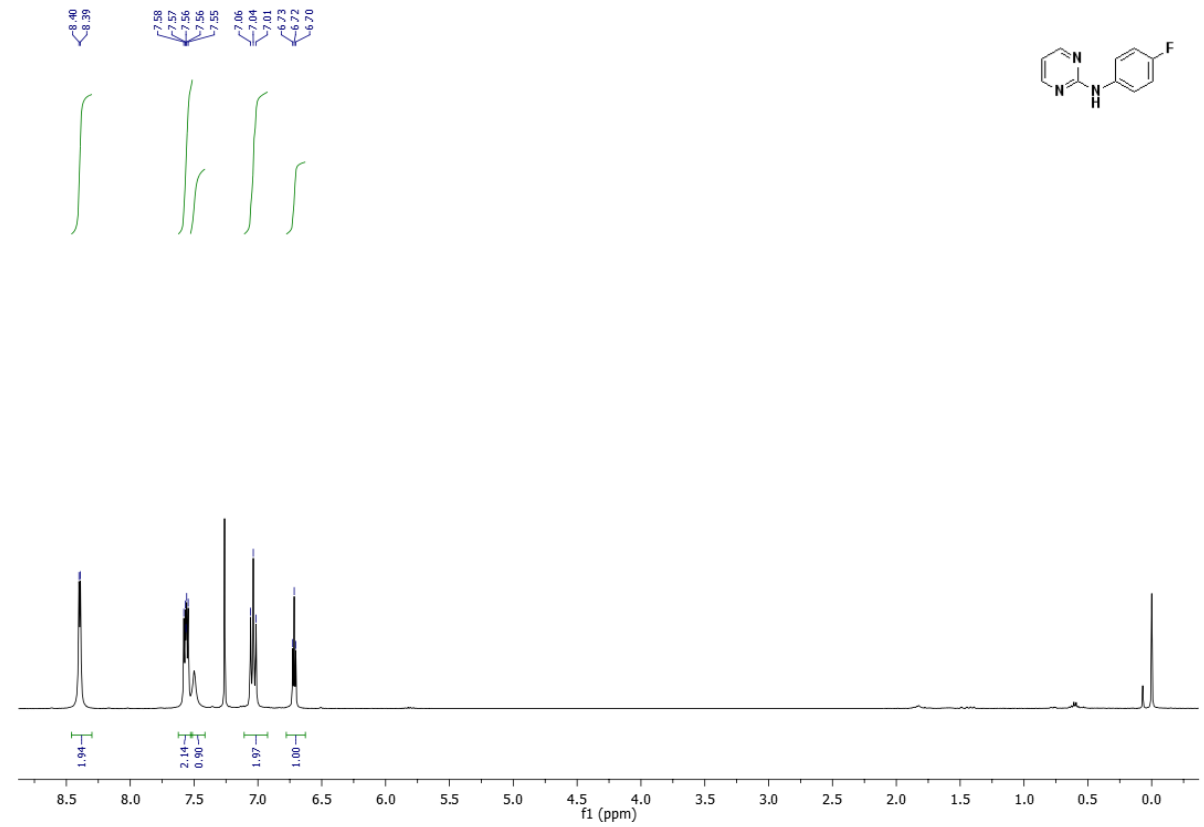
***N*-(4-methoxyphenyl)pyrimidin-2-amine (2a) ^{1}H-NMR spectrum**



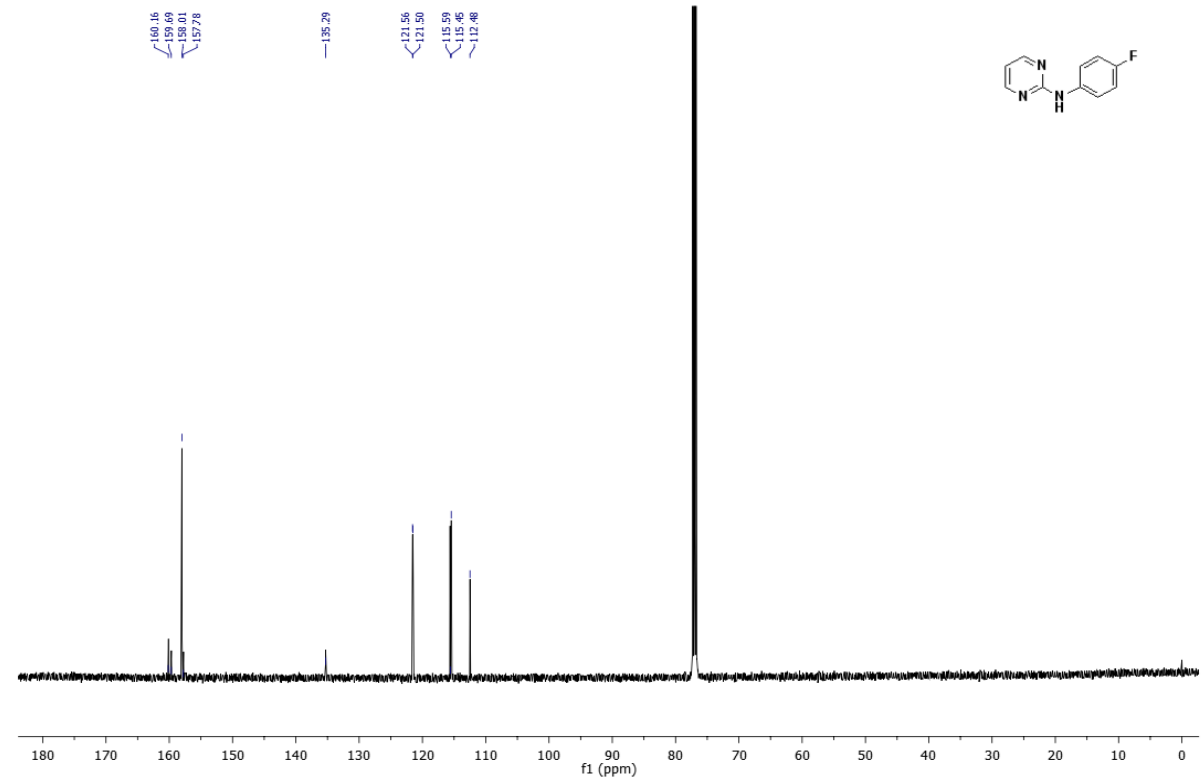
***N*-(4-methoxyphenyl)pyrimidin-2-amine (2a) ^{13}C-NMR spectrum**



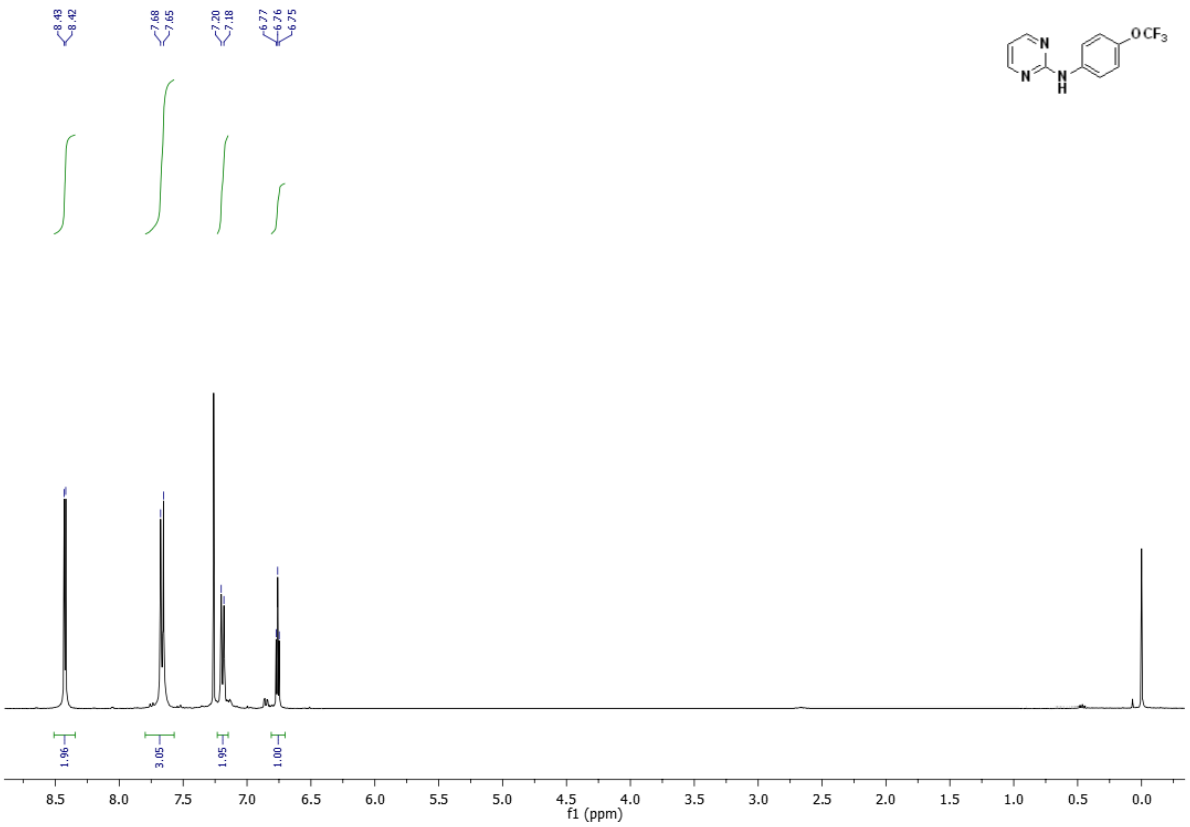
***N*-(4-fluorophenyl)pyrimidin-2-amine (2b) ^{1}H-NMR spectrum**



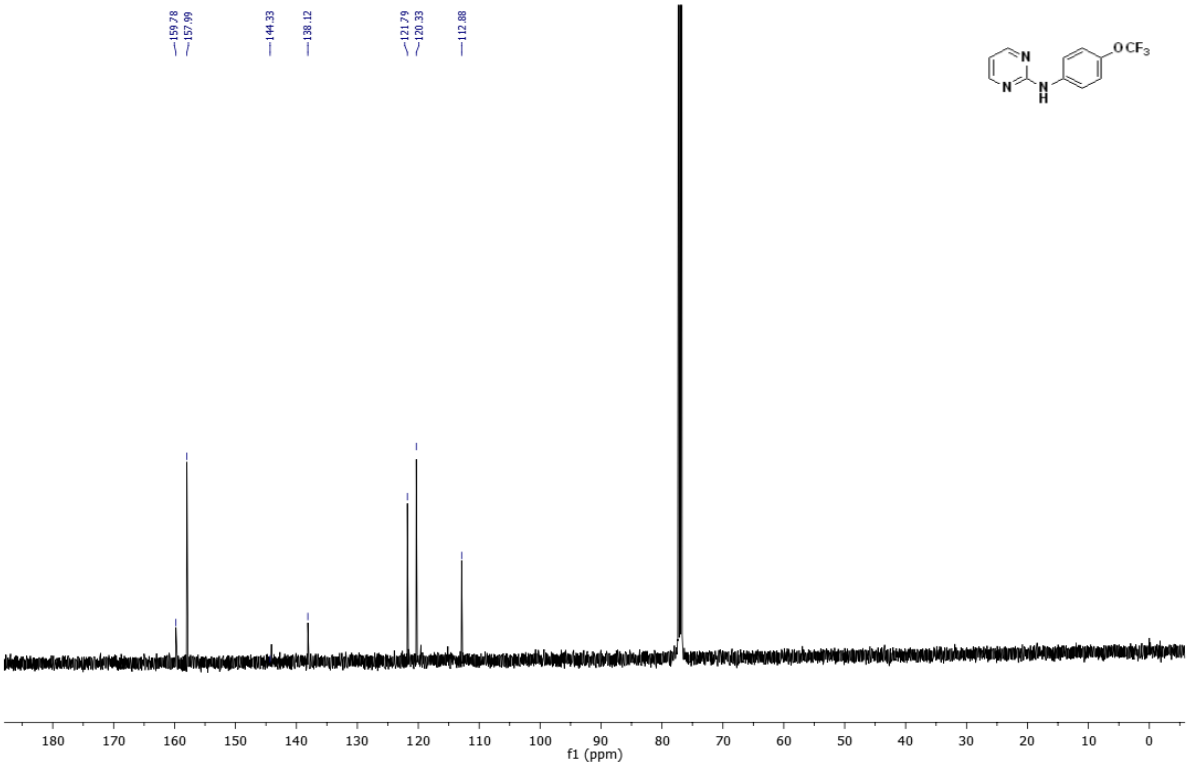
***N*-(4-fluorophenyl)pyrimidin-2-amine (2b) ^{13}C-NMR spectrum**



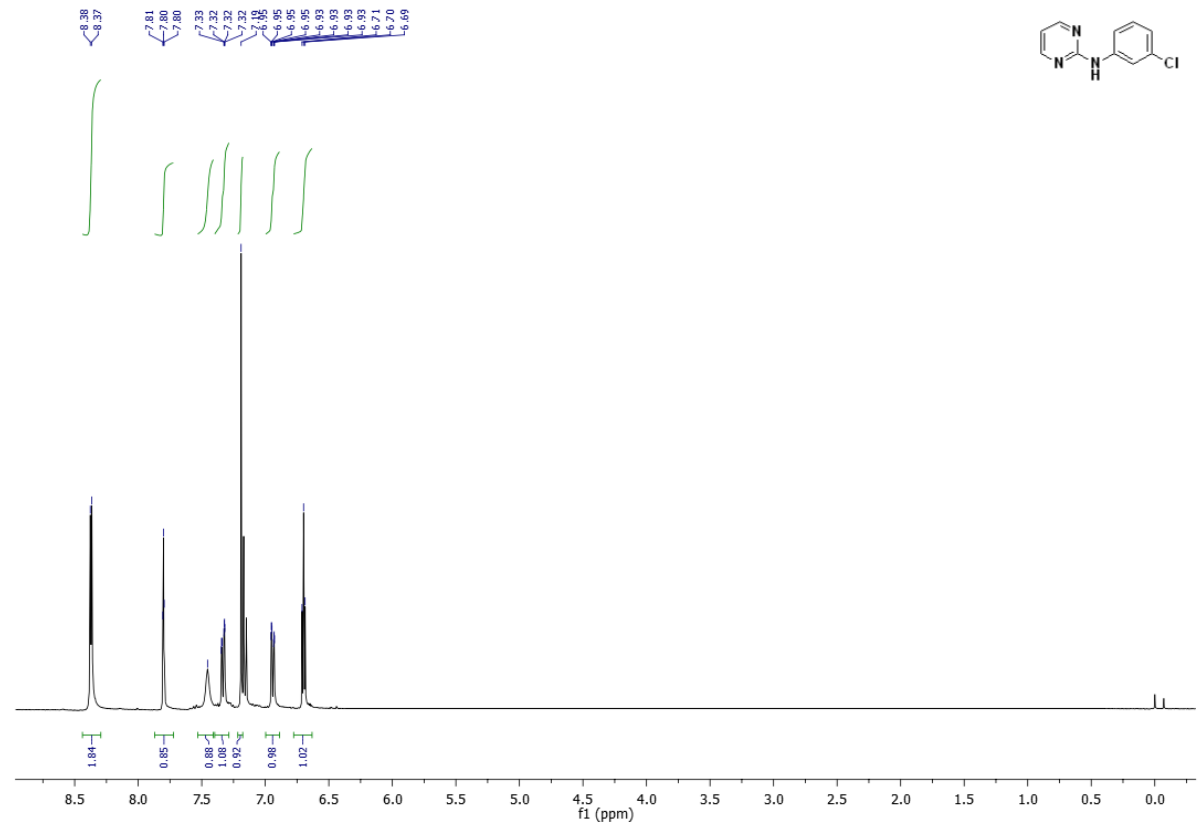
***N*-(4-(trifluoromethoxy)phenyl)pyrimidin-2-amine (2c) ^{1}H-NMR spectrum**



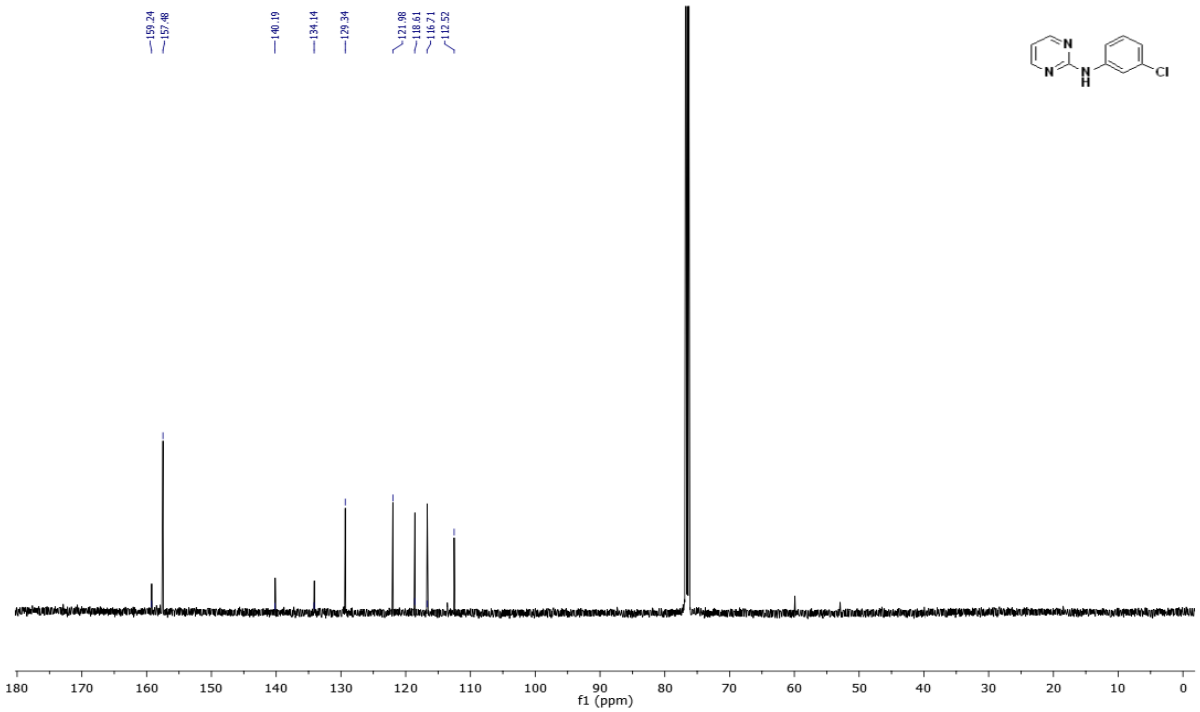
***N*-(4-(trifluoromethoxy)phenyl)pyrimidin-2-amine (2c) ^{13}C-NMR spectrum**



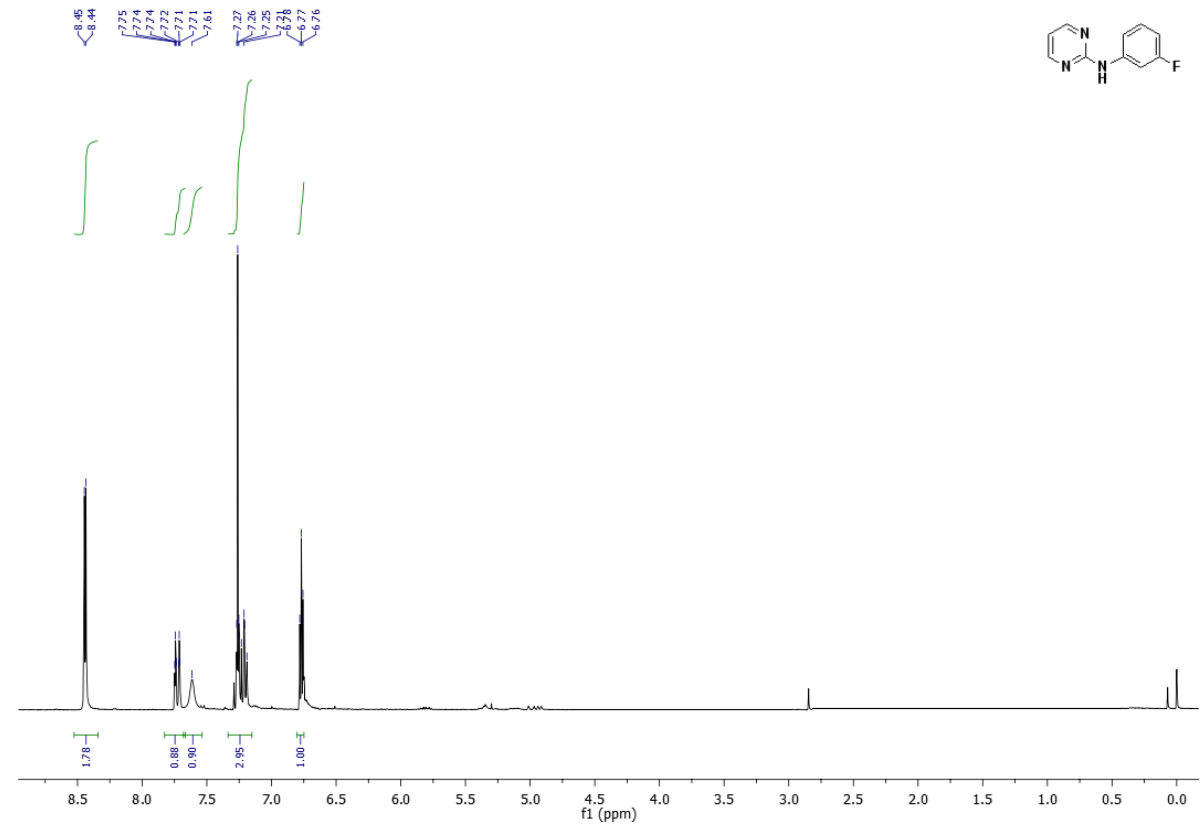
***N*-(3-chlorophenyl)pyrimidin-2-amine (2d) ^{1}H-NMR spectrum**



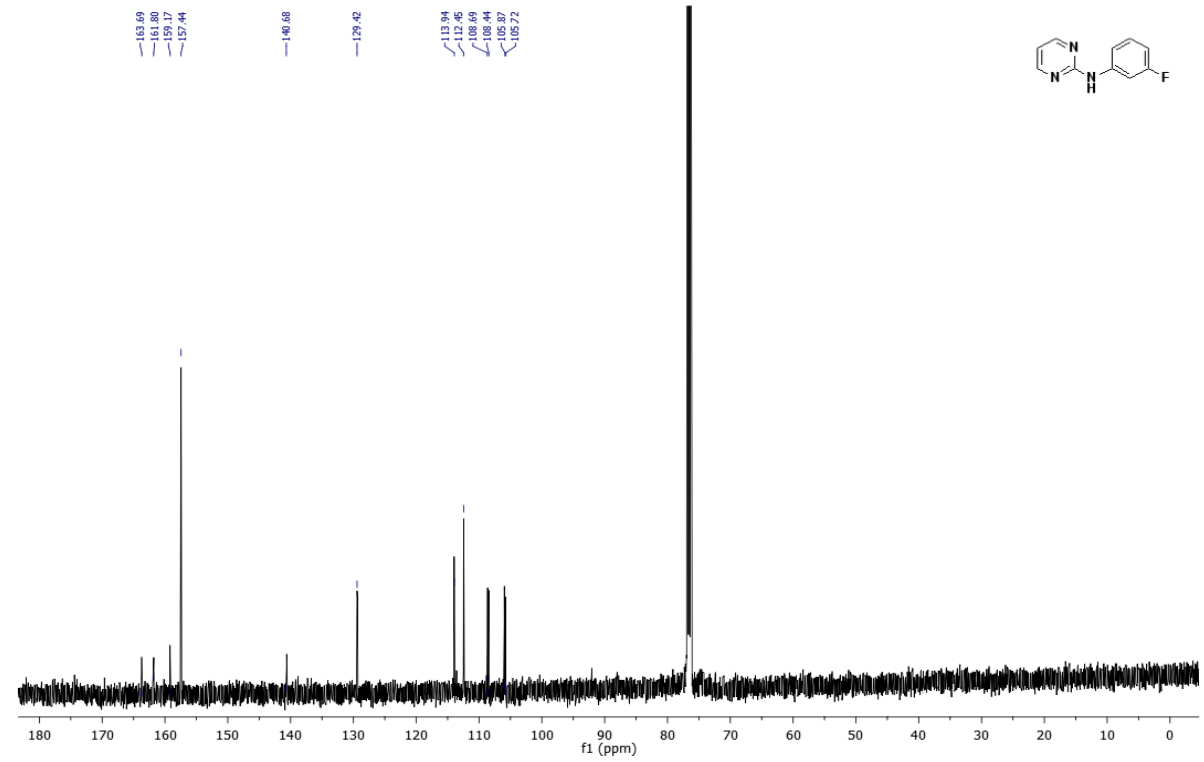
_N_-(3-chlorophenyl)pyrimidin-2-amine (2d) ^{13}C-NMR spectrum



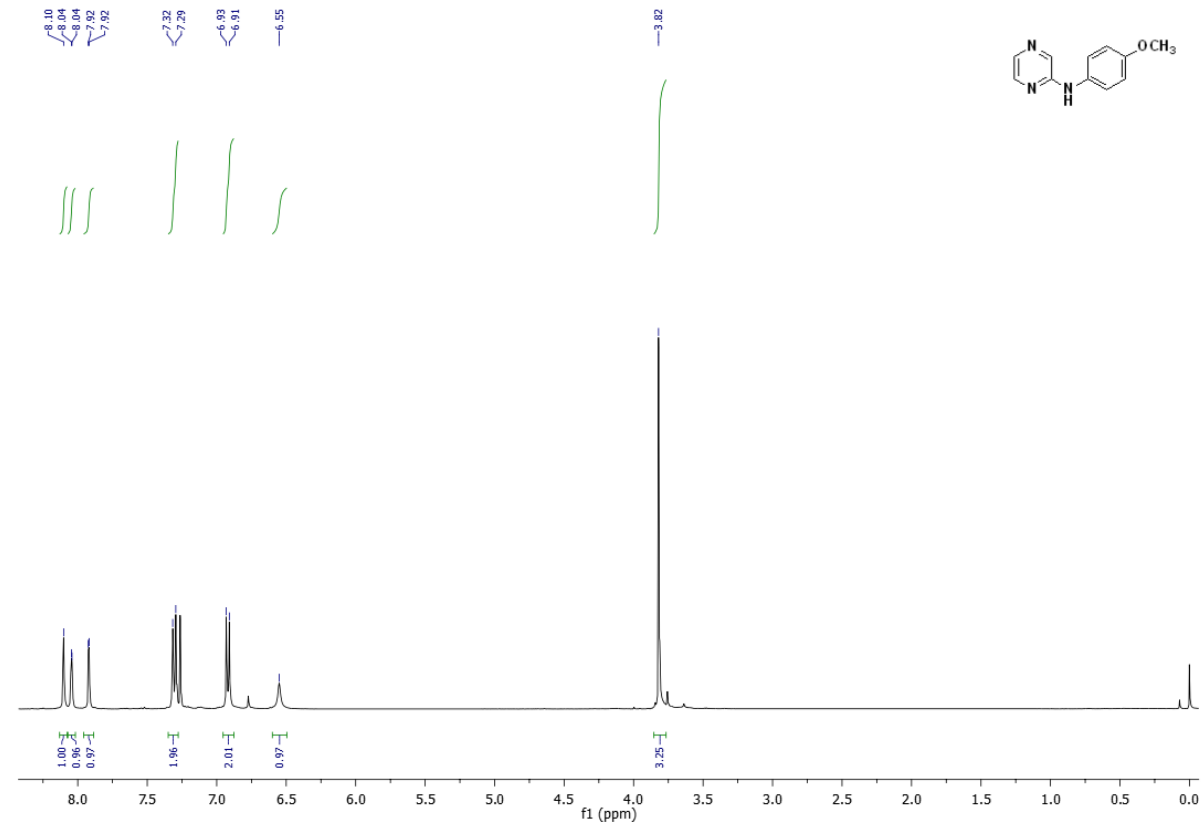
_N_-(3-fluorophenyl)pyrimidin-2-amine (2e) ^{1}H-NMR spectrum



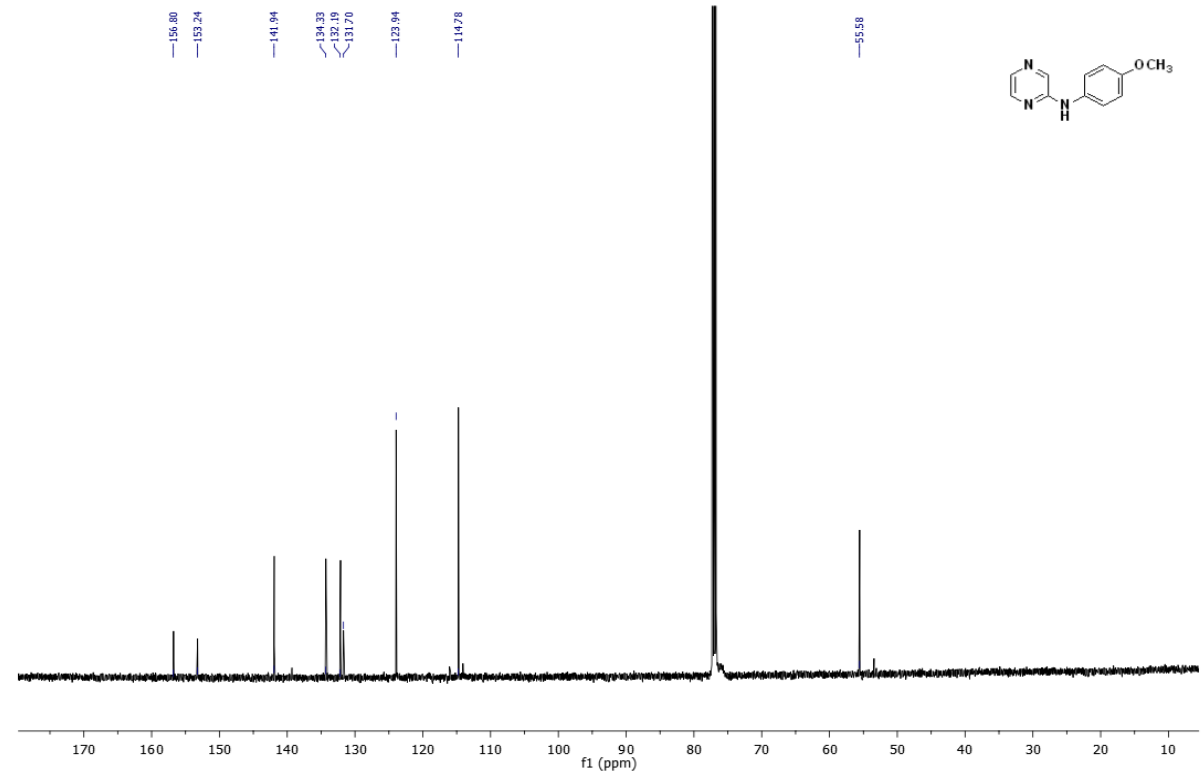
***N*-(3-fluorophenyl)pyrimidin-2-amine (2e) ^{13}C-NMR spectrum**



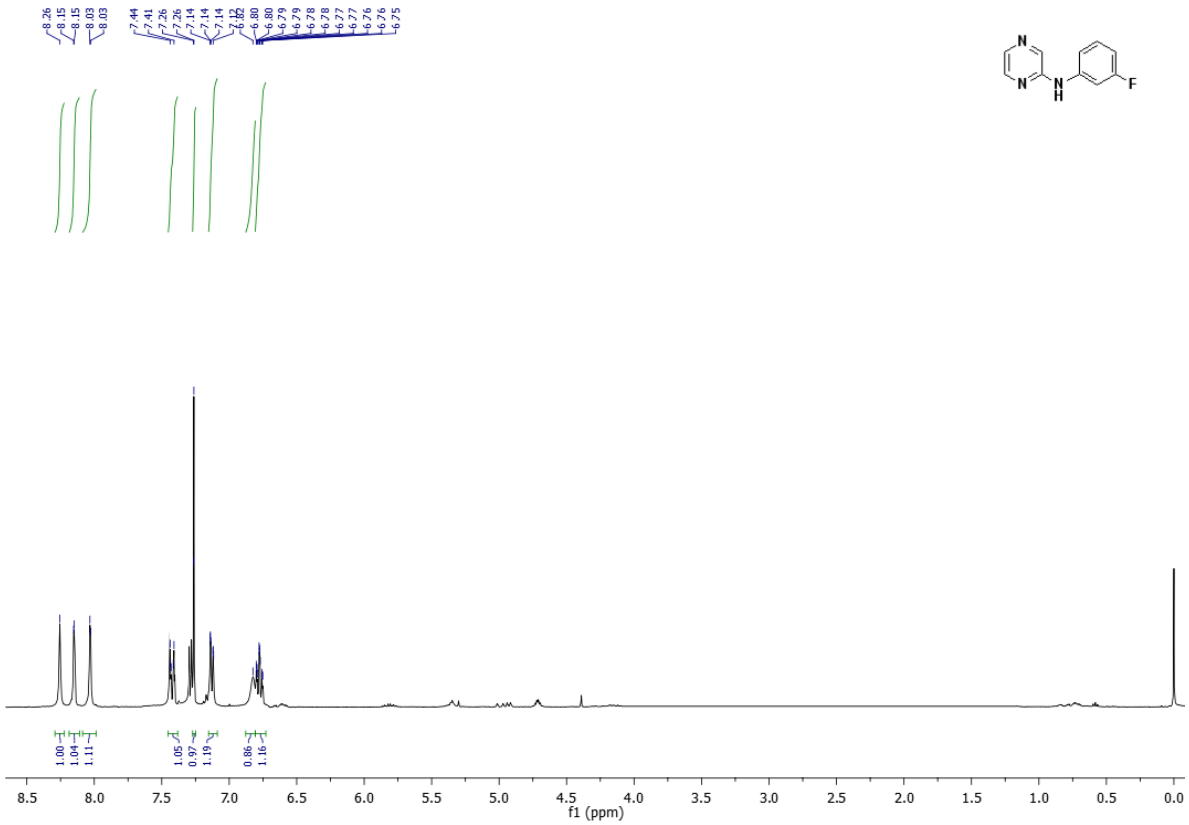
***N*-(4-methoxyphenyl)pyrazin-2-amine (2f)^{1}H-NMR spectrum**



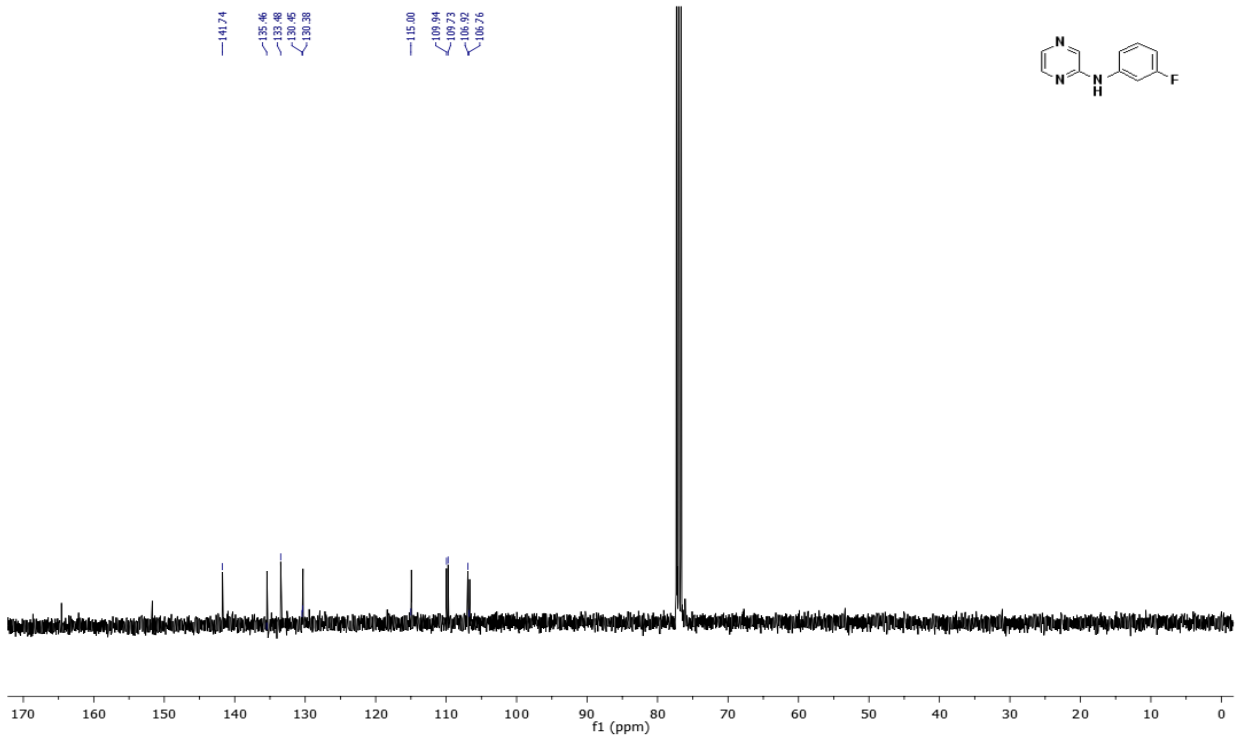
***N*-(4-methoxyphenyl)pyrazin-2-amine (2f) ^{13}C-NMR spectrum**



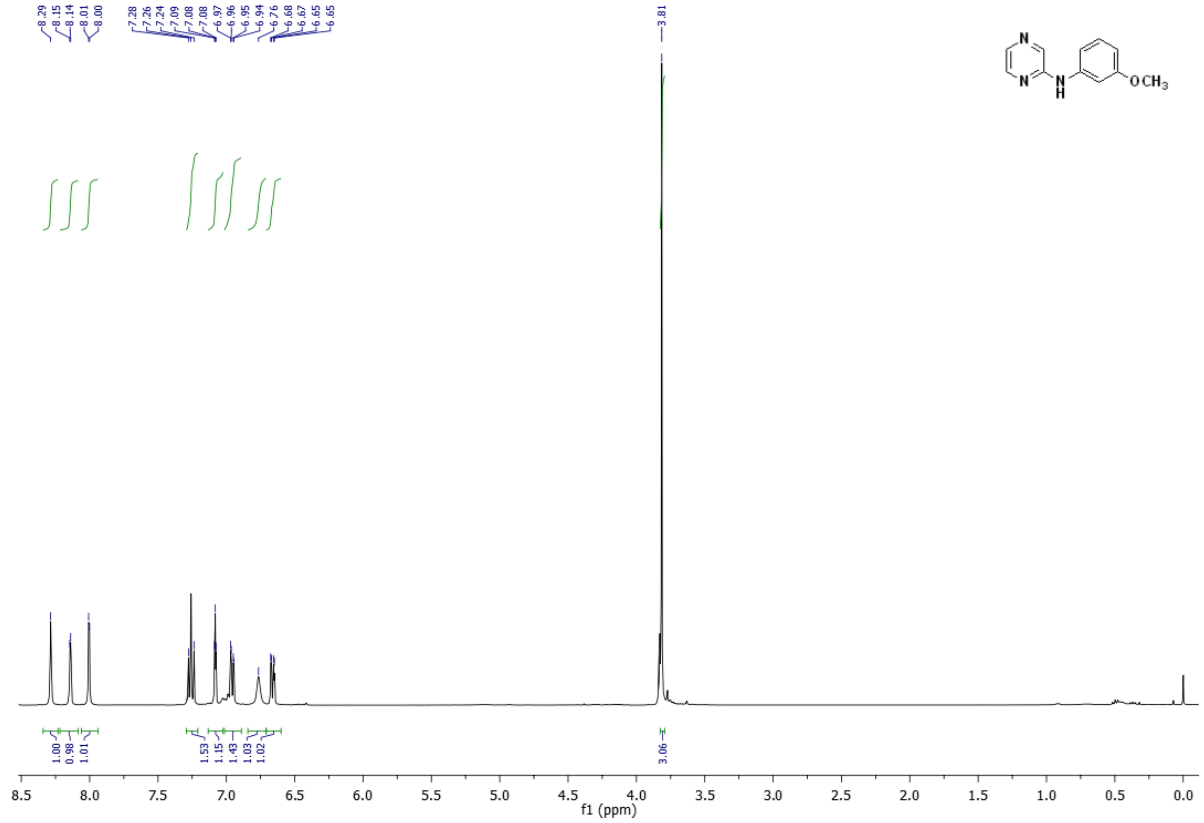
***N*-(3-fluorophenyl)pyrazin-2-amine (2g) ^{1}H-NMR spectrum**



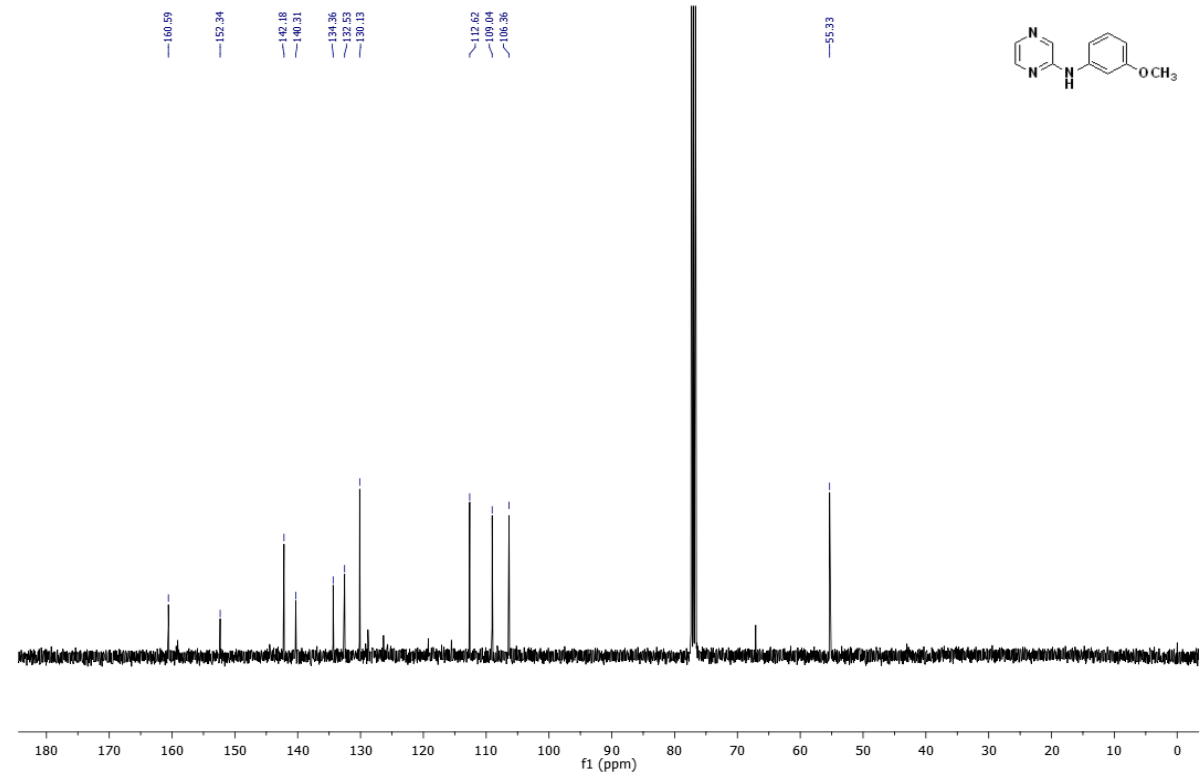
***N*-(3-fluorophenyl)pyrazin-2-amine (2g) ^{13}C-NMR spectrum**



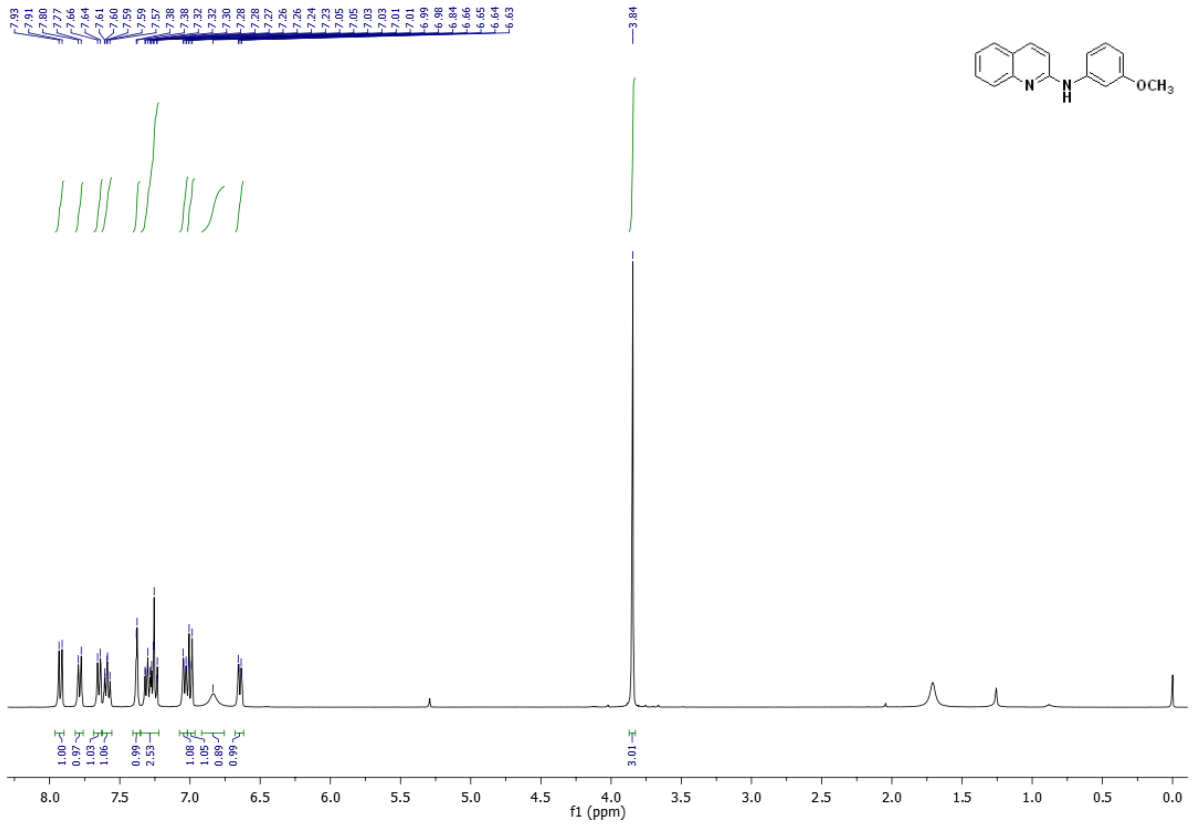
***N*-(3-methoxyphenyl)pyrazin-2-amine (2h) ^{1}H-NMR spectrum**



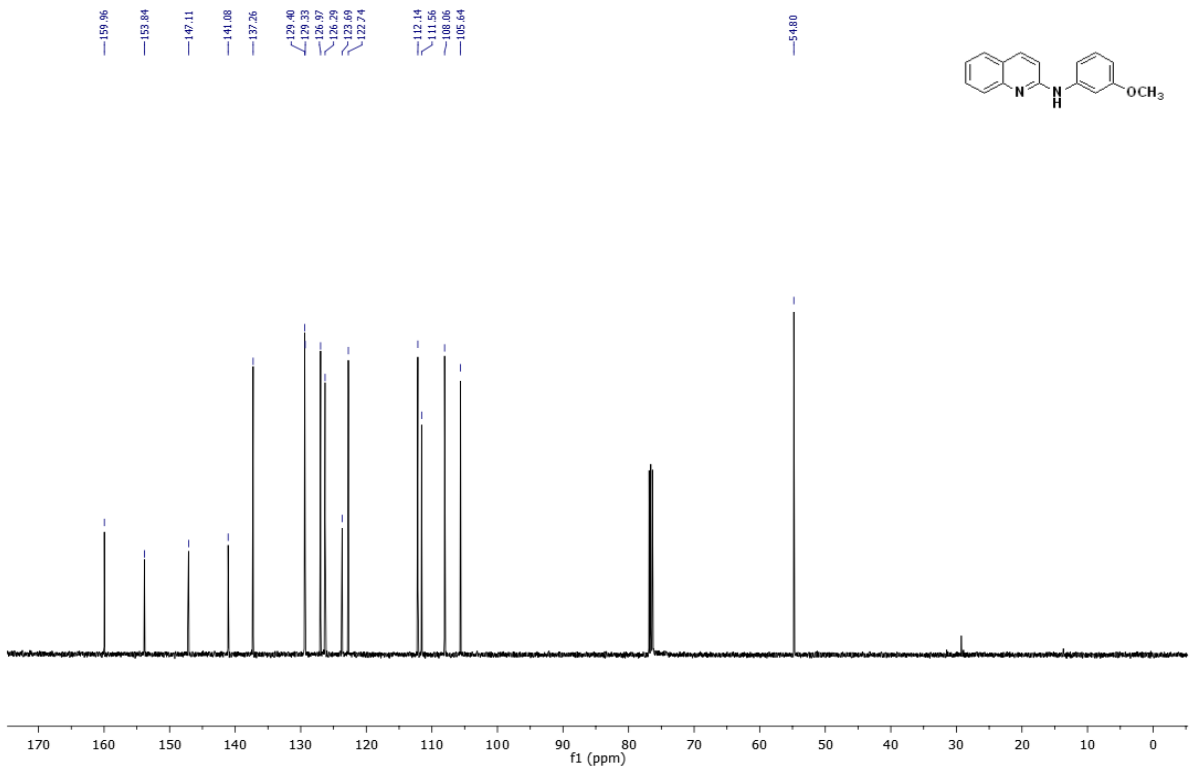
_N_-(3-methoxyphenyl)pyrazin-2-amine (2h) ^{13}C-NMR spectrum



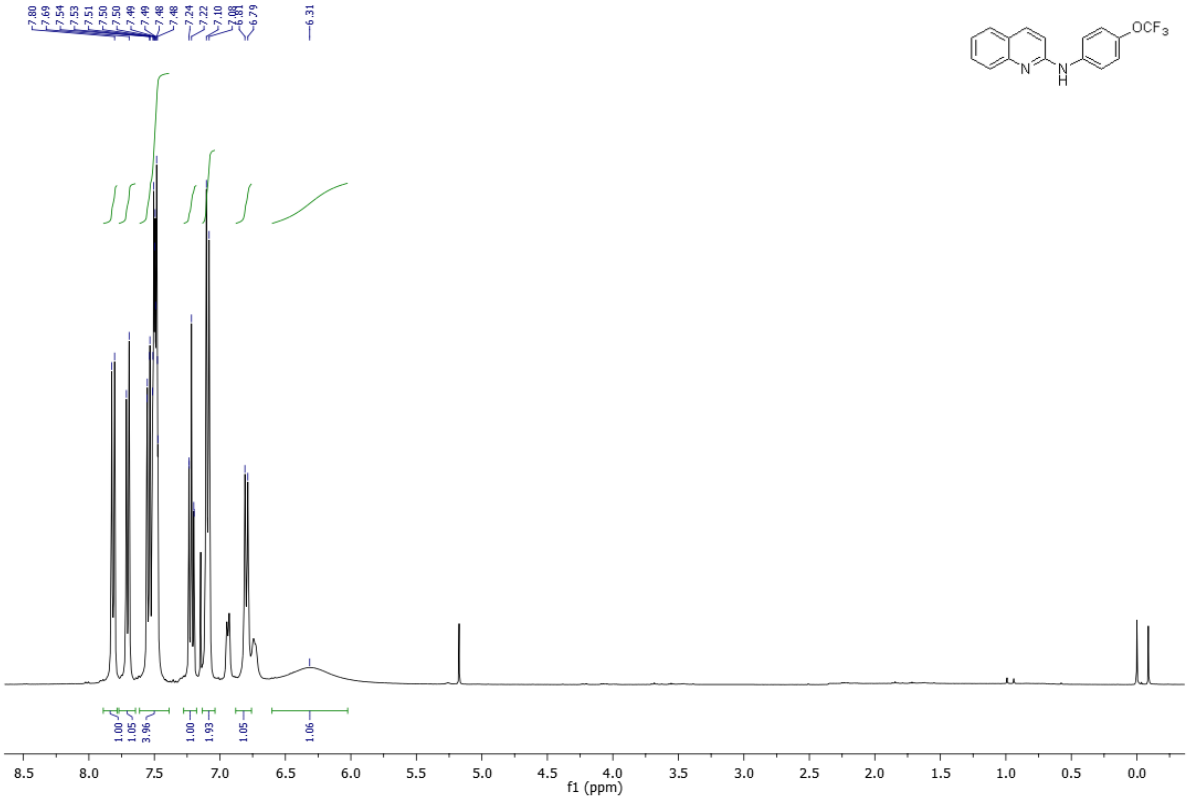
_N_-(3-methoxyphenyl)quinolin-2-amine (2i) ^{1}H-NMR spectrum



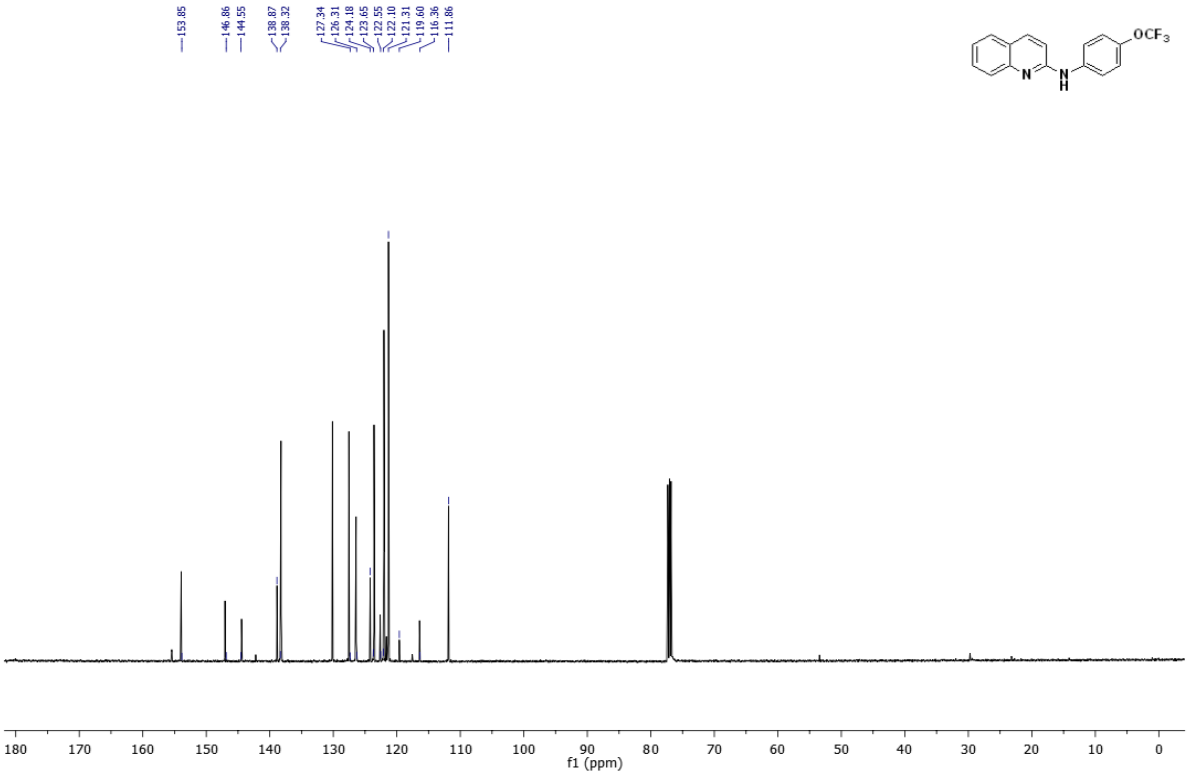
_N_-(3-methoxyphenyl)quinolin-2-amine (2i) ^{13}C-NMR spectrum



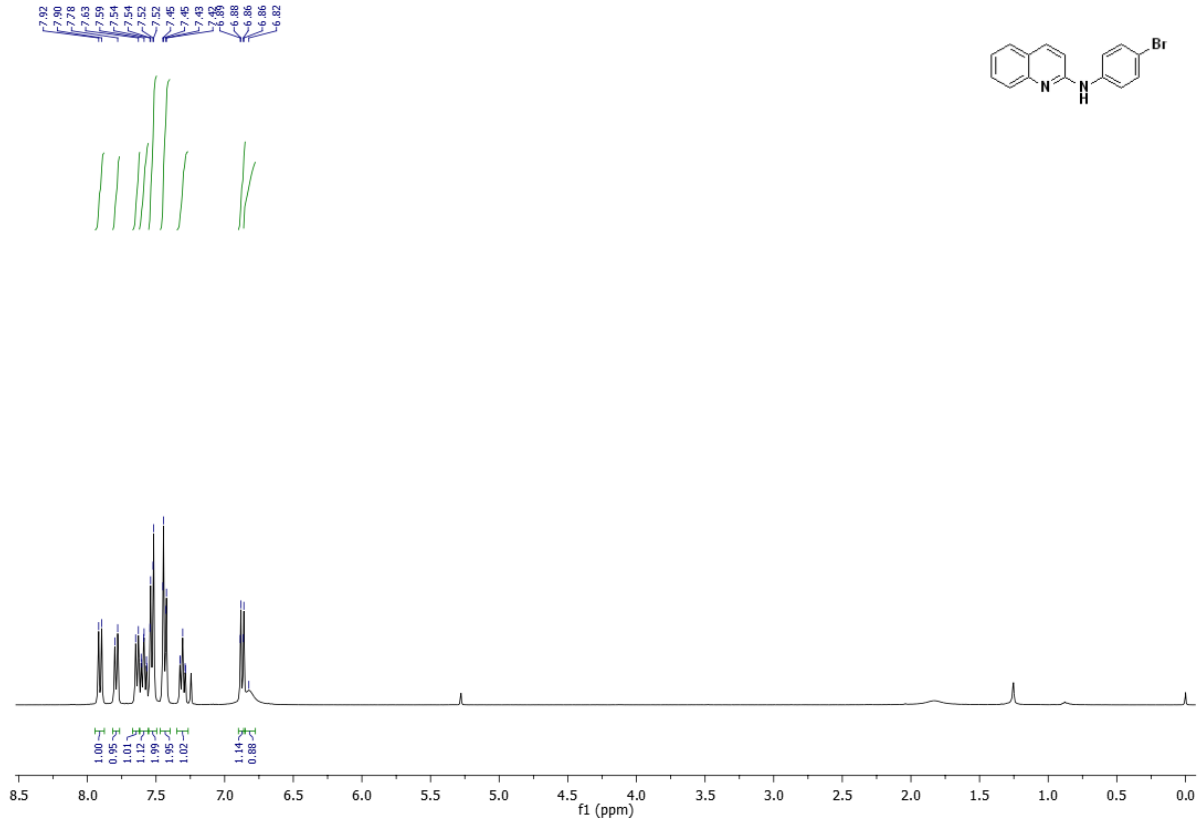
_N_-(4-(trifluoromethoxy)phenyl)quinolin-2-amine(2j) ^{1}H-NMR spectrum



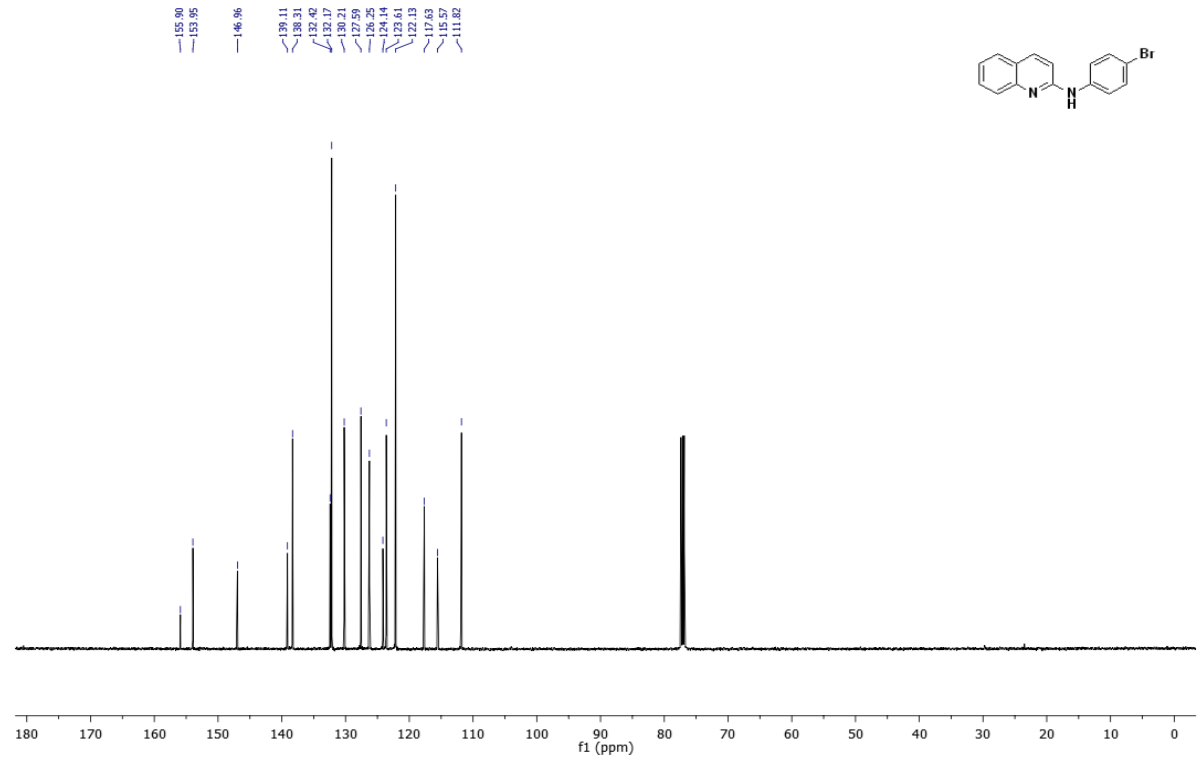
***N*-(4-(trifluoromethoxy)phenyl)quinolin-2-amine(2j) ^{13}C-NMR spectrum**



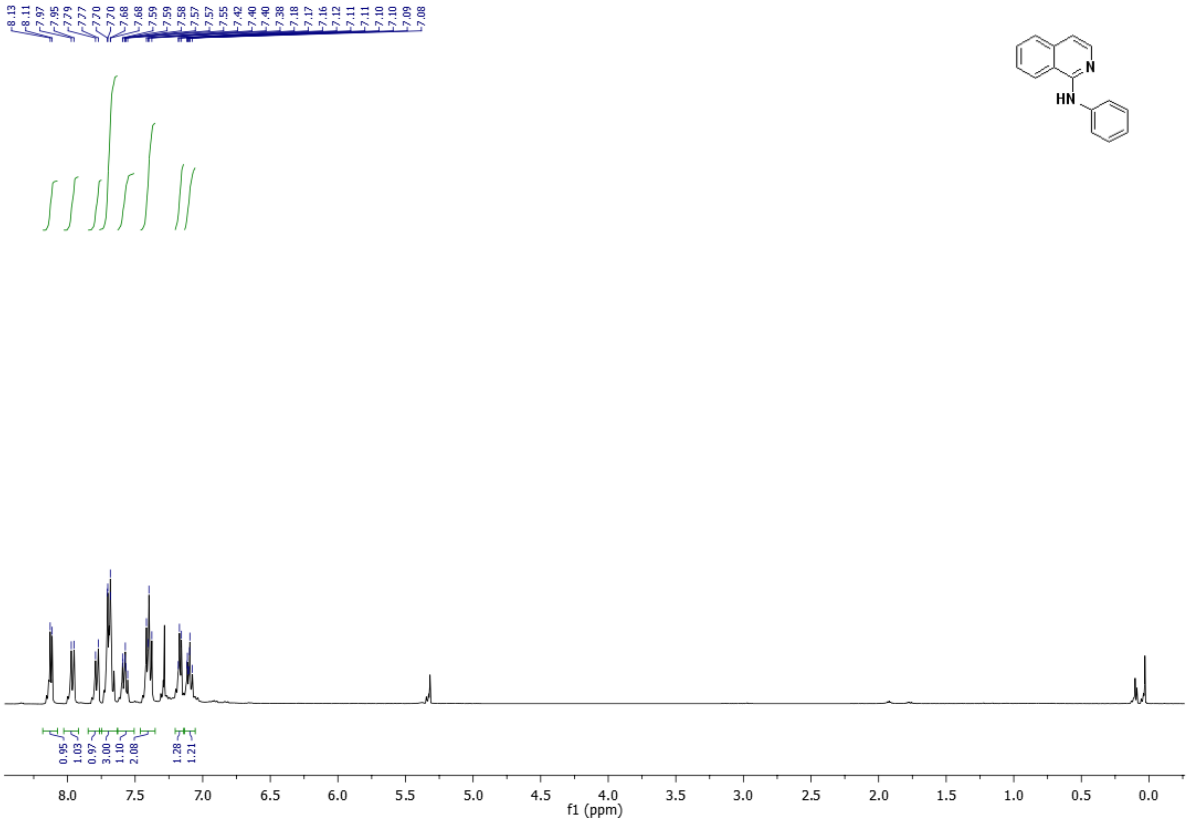
***N*-(4-bromophenyl)quinolin-2-amine (2k) ^{1}H-NMR spectrum**



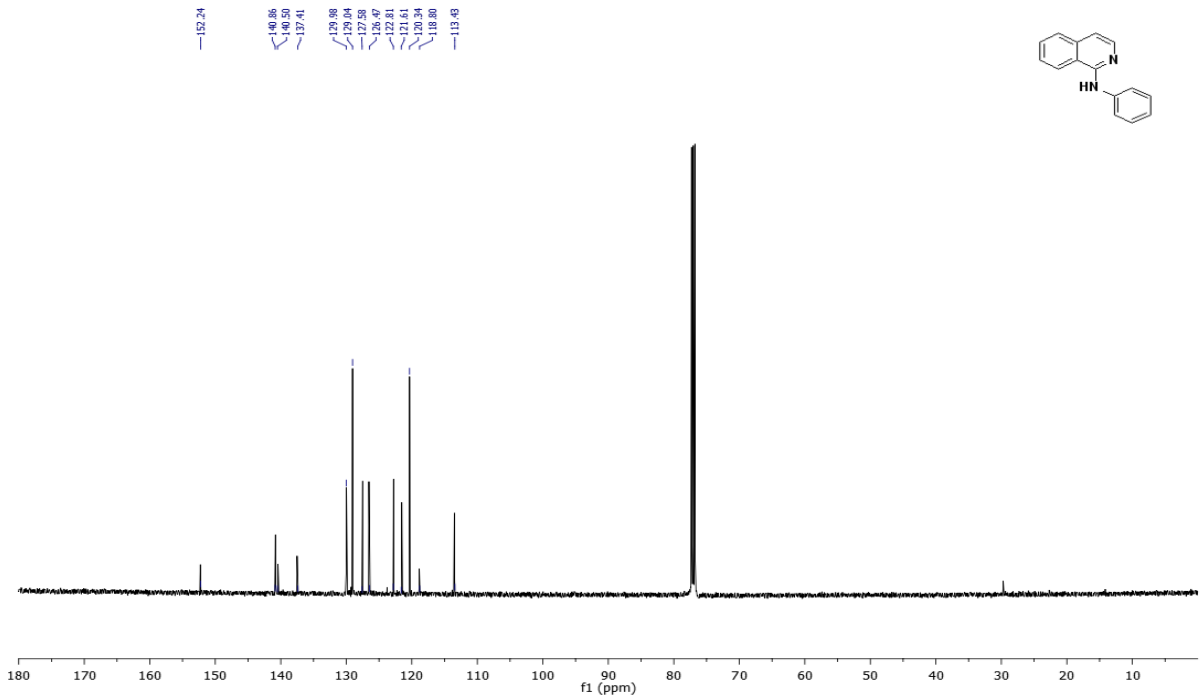
***N*-(4-bromophenyl)quinolin-2-amine (2k) ^{13}C-NMR spectrum**



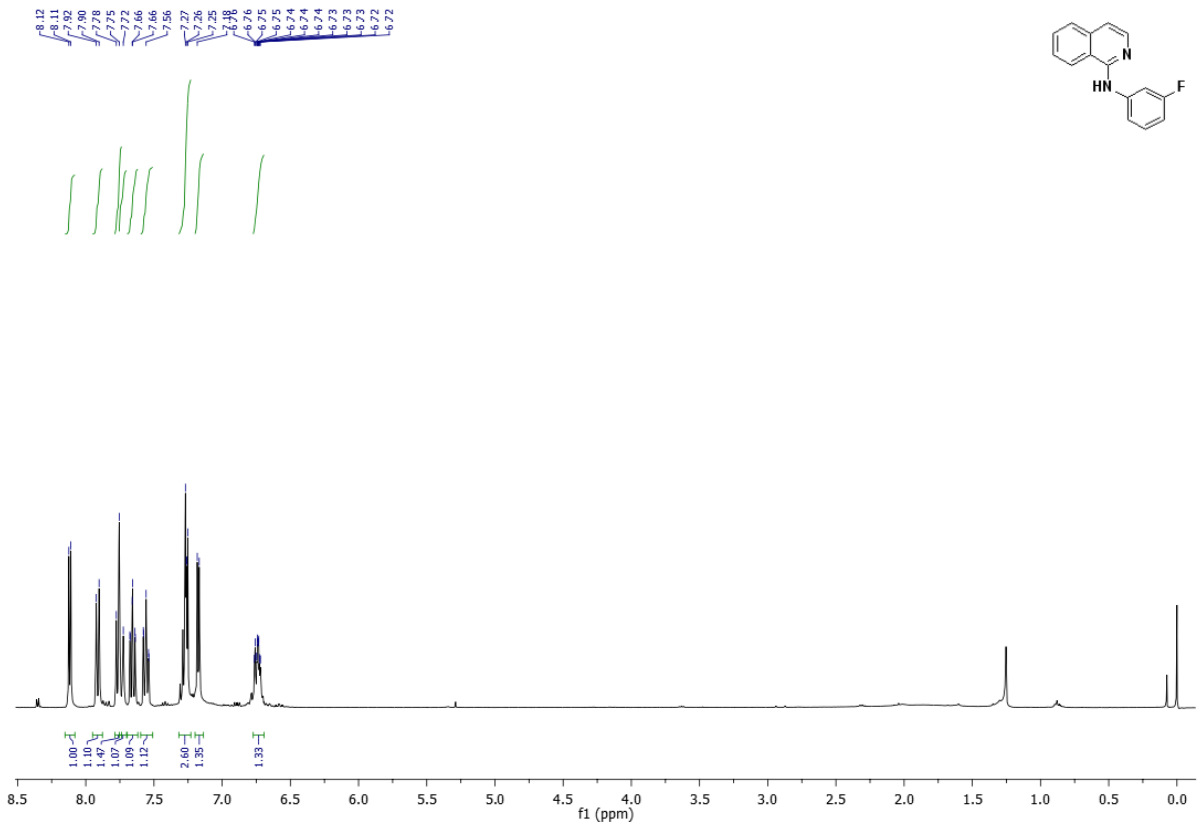
***N*-phenylisoquinolin-1-amine (2l) ^{1}H-NMR spectrum**



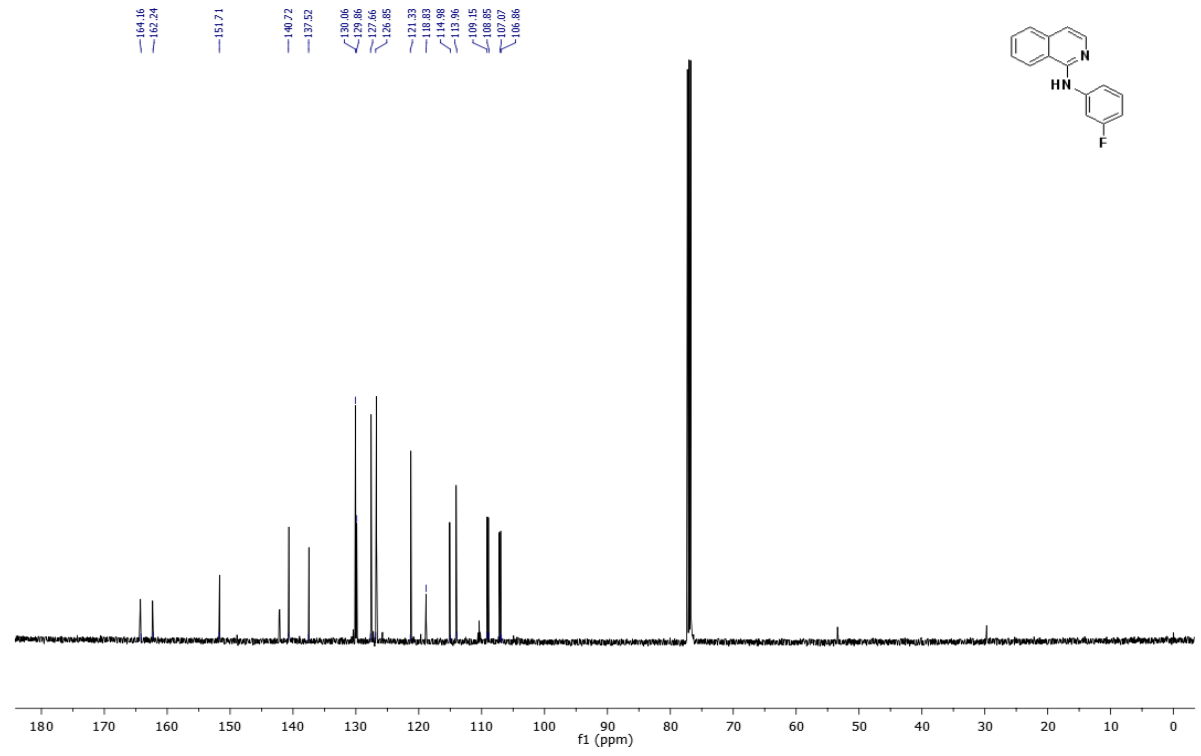
N-phenylisoquinolin-1-amine (2l) ^{13}C-NMR spectrum



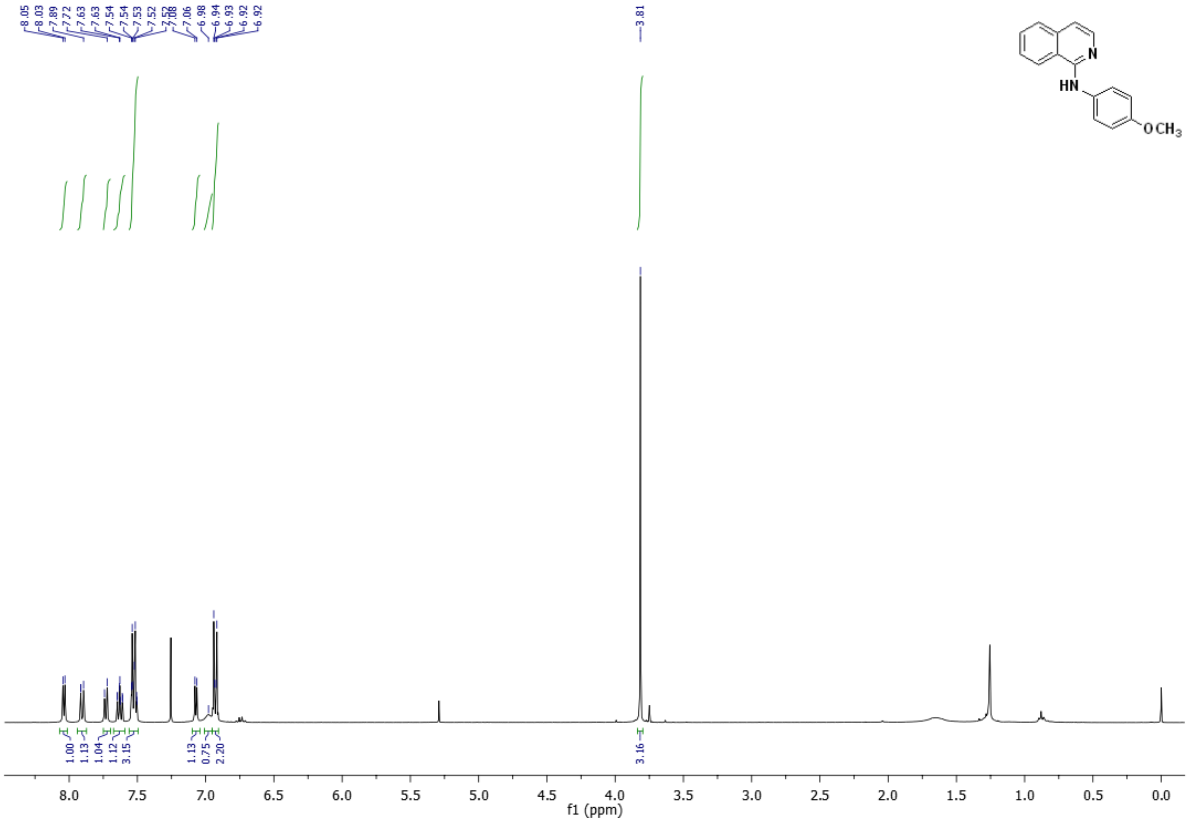
***N*-(3-fluorophenyl)isoquinolin-1-amine (2m) ^{1}H-NMR spectrum**



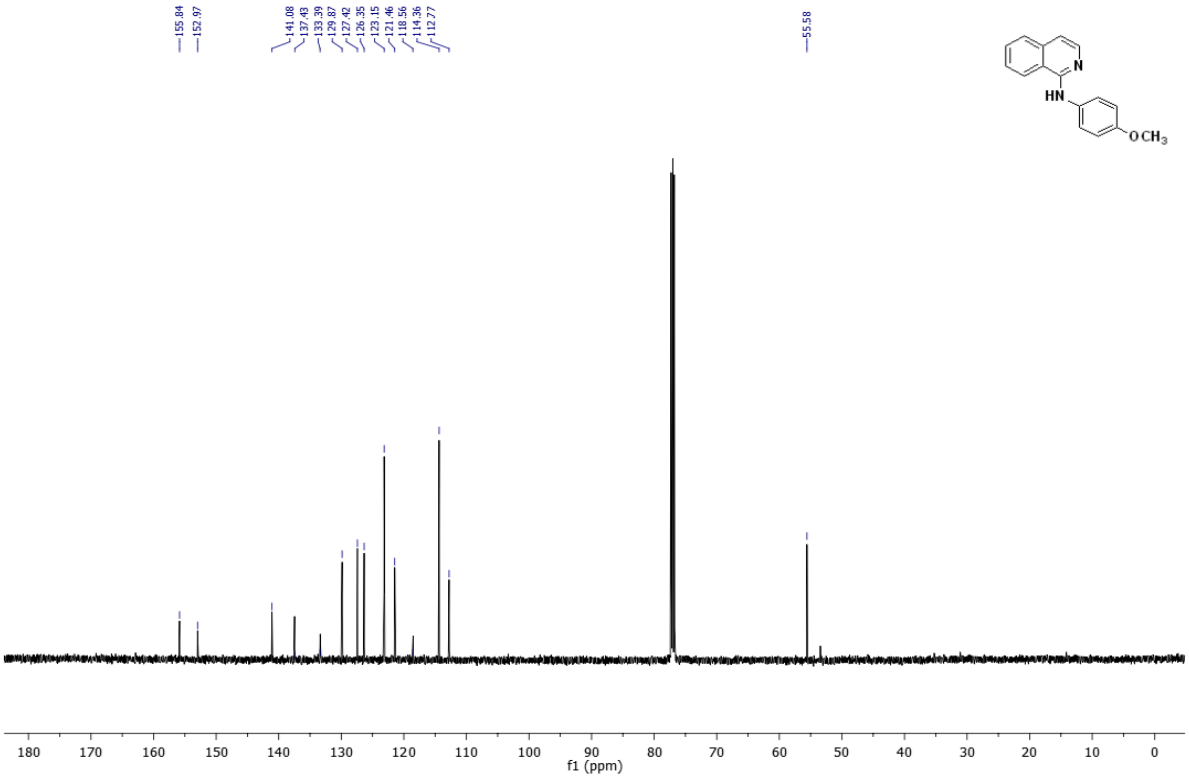
***N*-(3-fluorophenyl)isoquinolin-1-amine(2m) ^{13}C-NMR spectrum**



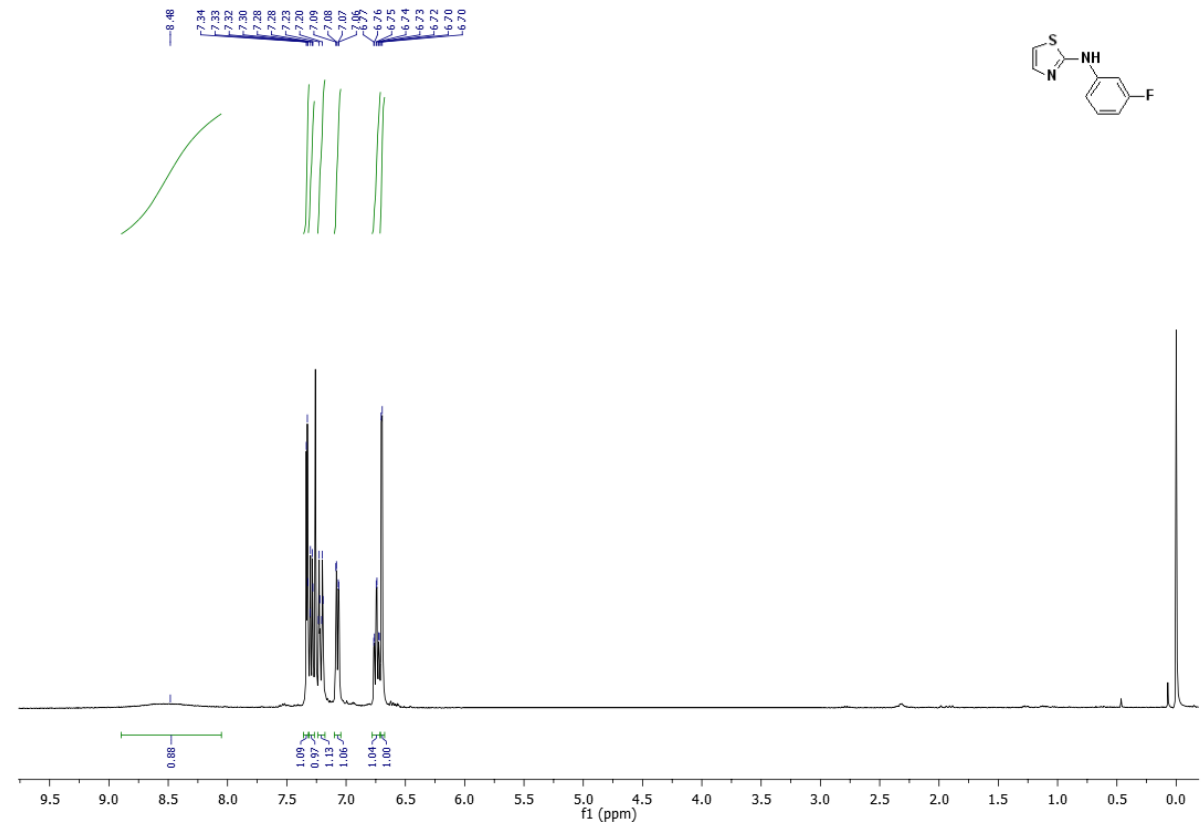
***N*-(4-methoxyphenyl)isoquinolin-1-amine(2n) ^{1}H-NMR spectrum**



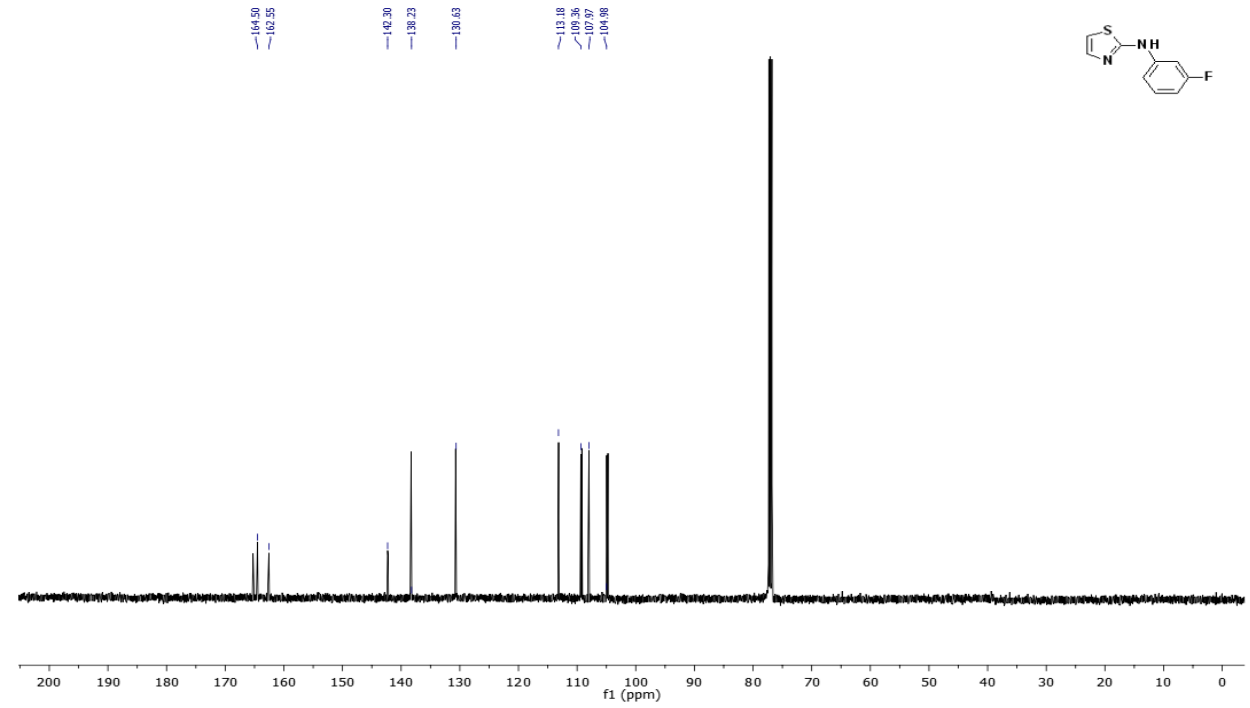
***N*-(4-methoxyphenyl)isoquinolin-1-amine (2n) ^{13}C-NMR spectrum**



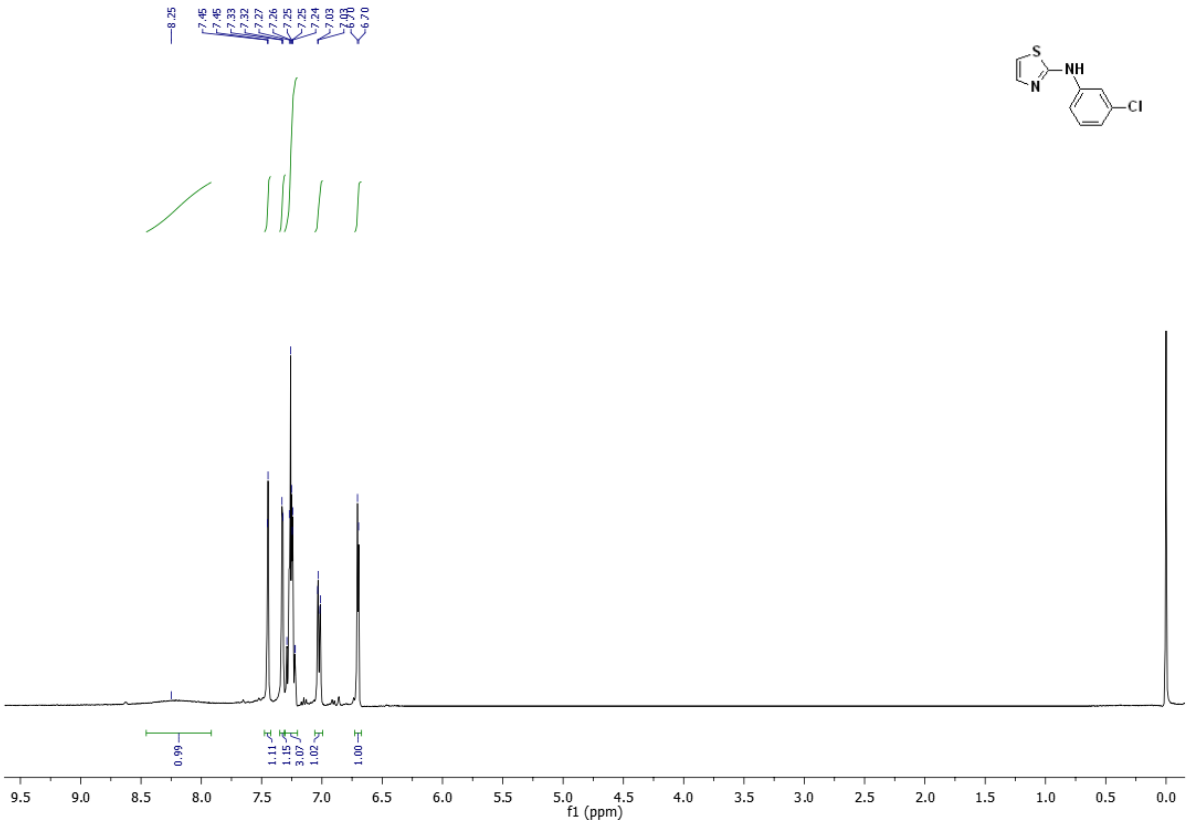
***N*-(3-fluorophenyl)thiazol-2-amine (3a) ^{1}H-NMR spectrum**



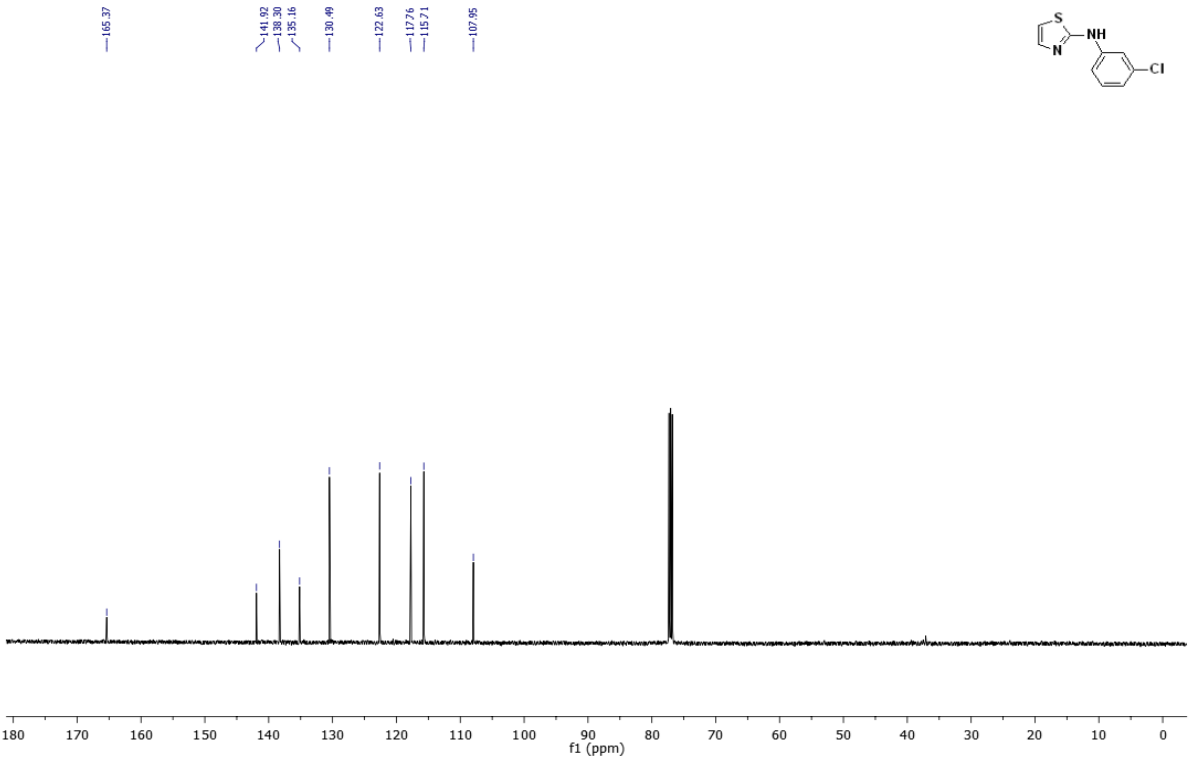
***N*-(3-fluorophenyl)thiazol-2-amine(3a) ^{13}C-NMR spectrum**



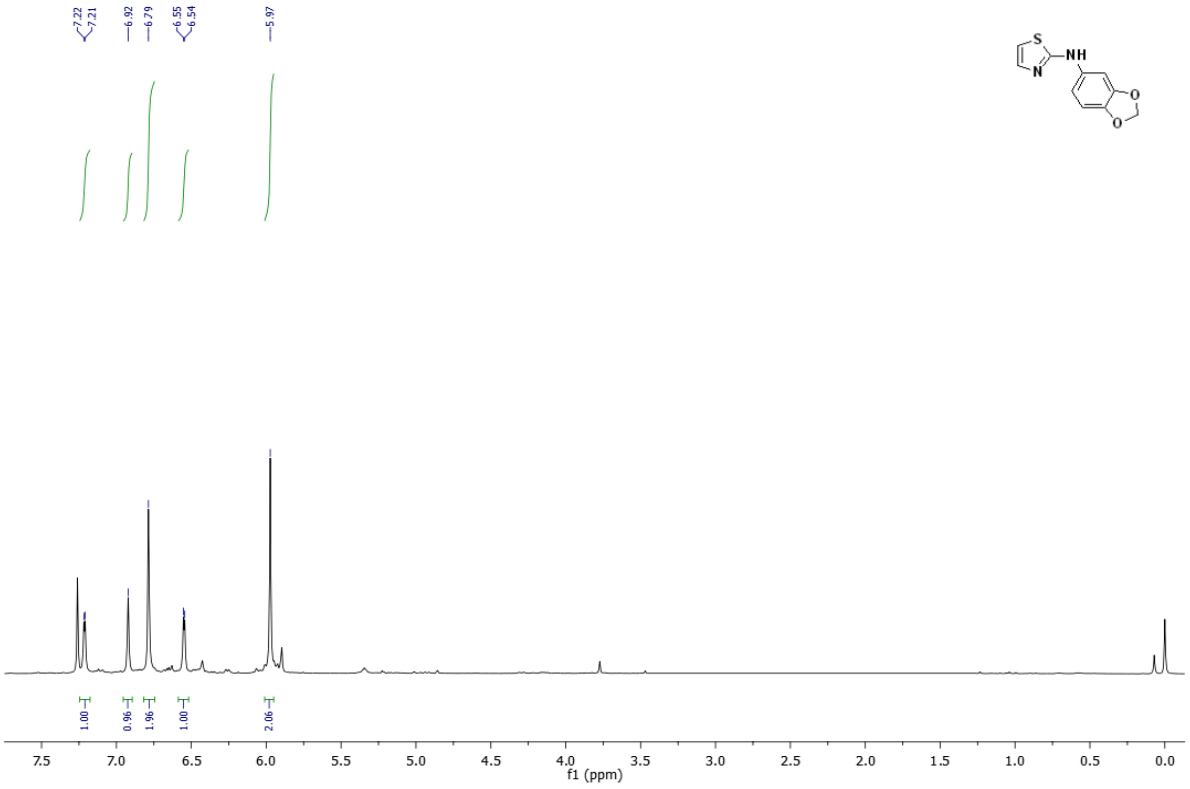
N-(3-chlorophenyl)thiazol-2-amine(3b) ^{1}H-NMR spectrum



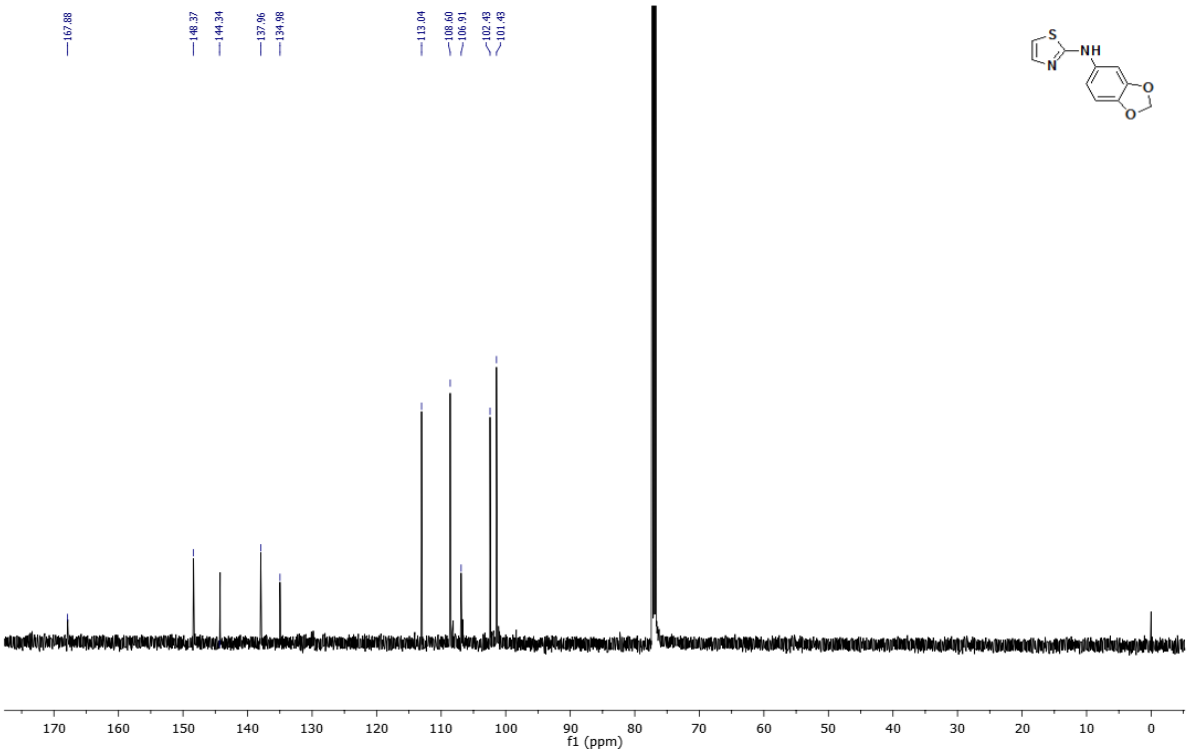
***N*-(3-chlorophenyl)thiazol-2-amine (3b)^{13}C-NMR spectrum**



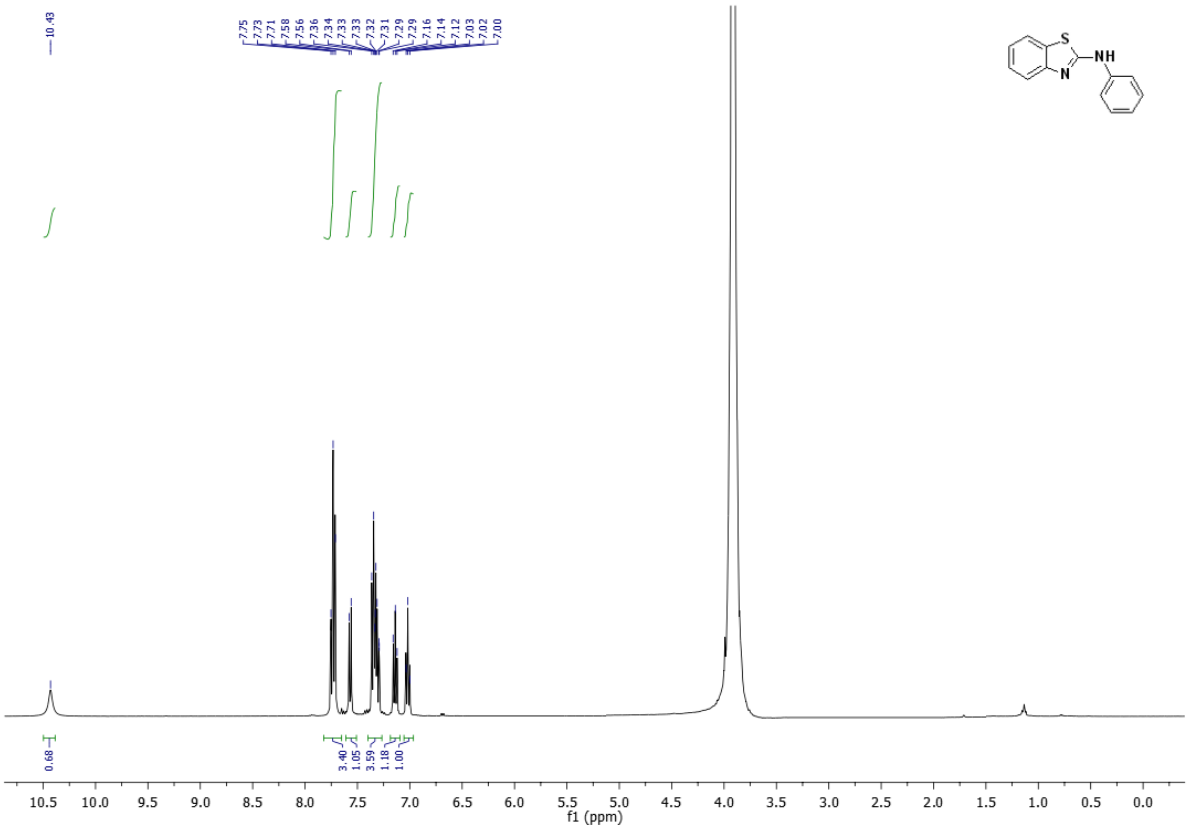
***N*-(benzo[*d*][1,3]dioxol-5-yl)thiazol-2-amine (3c) ^{1}H-NMR spectrum**



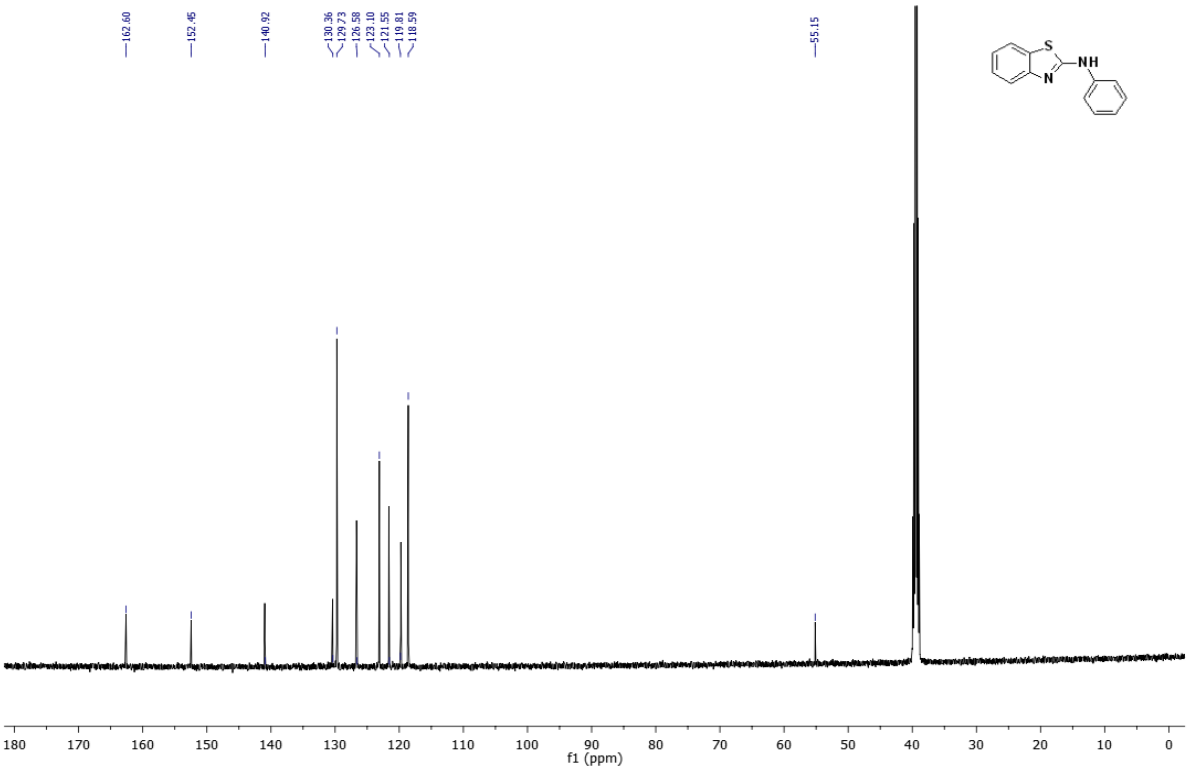
_N_-(benzo[_d_][1,3]dioxol-5-yl)thiazol-2-amine (3c) ^{13}C-NMR spectrum



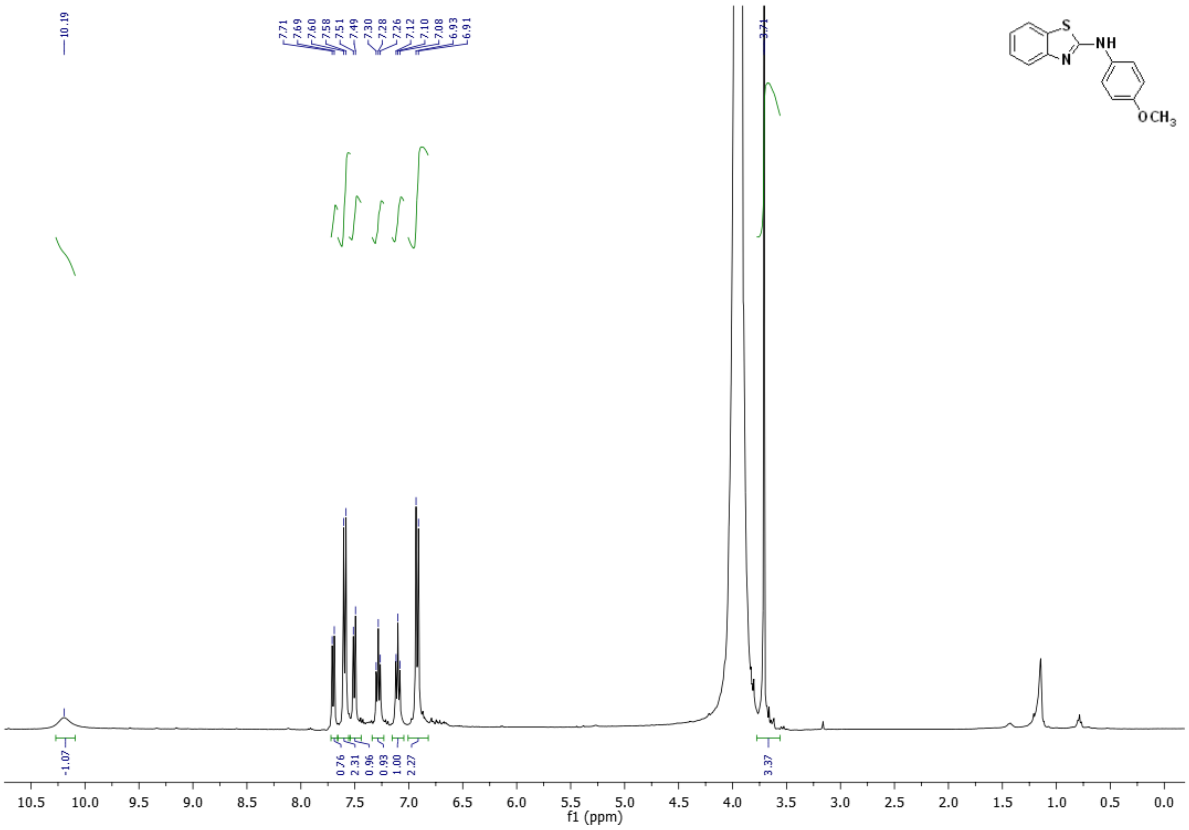
_N_-phenylbenzo[_d_]thiazol-2-amine(3d) ^{1}H-NMR spectrum



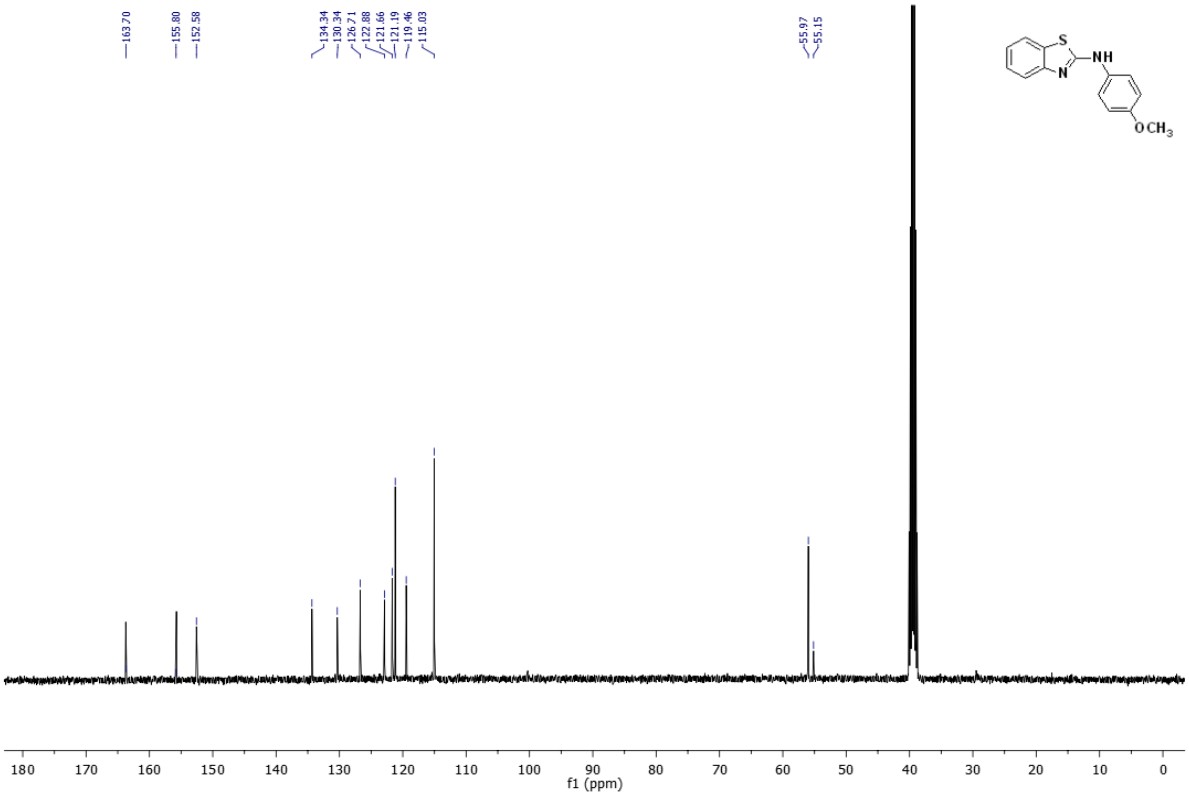
***N*-phenylbenzo[*d*]thiazol-2-amine (3d) ^{13}C-NMR spectrum**



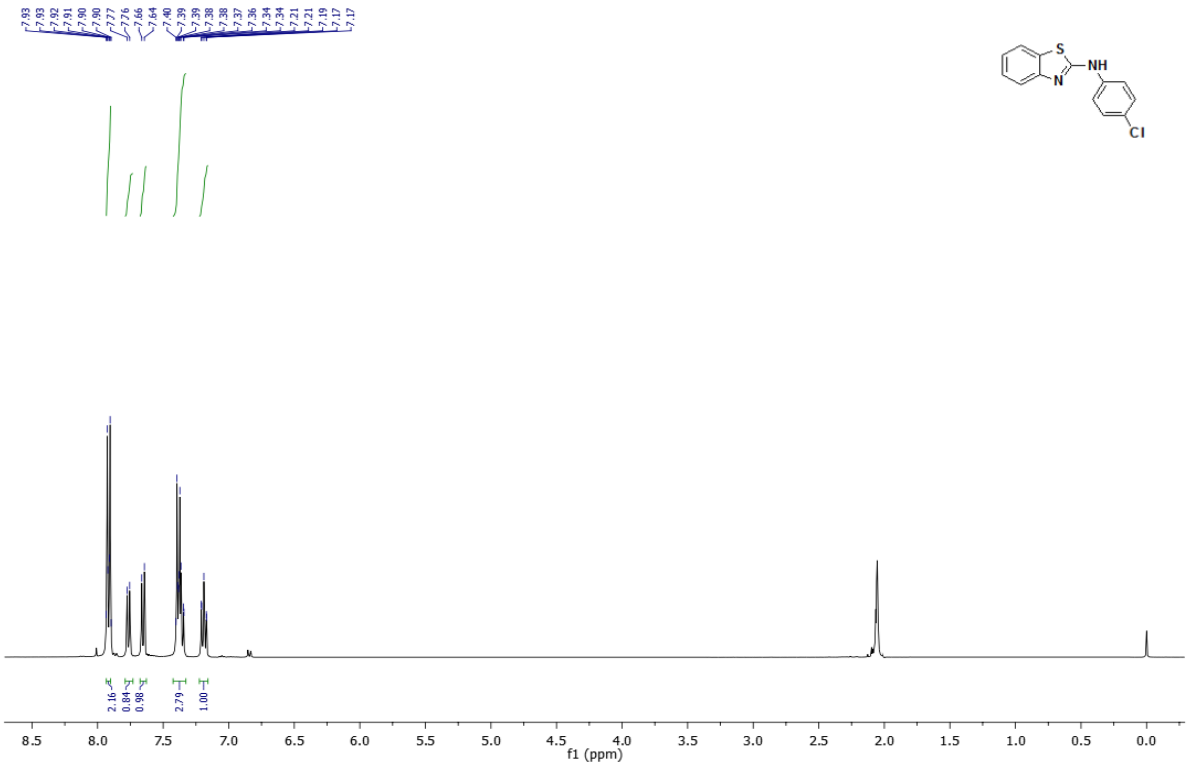
***N*-(4-methoxyphenyl)benzo[*d*]thiazol-2-amine (3e) ^{1}H-NMR spectrum**



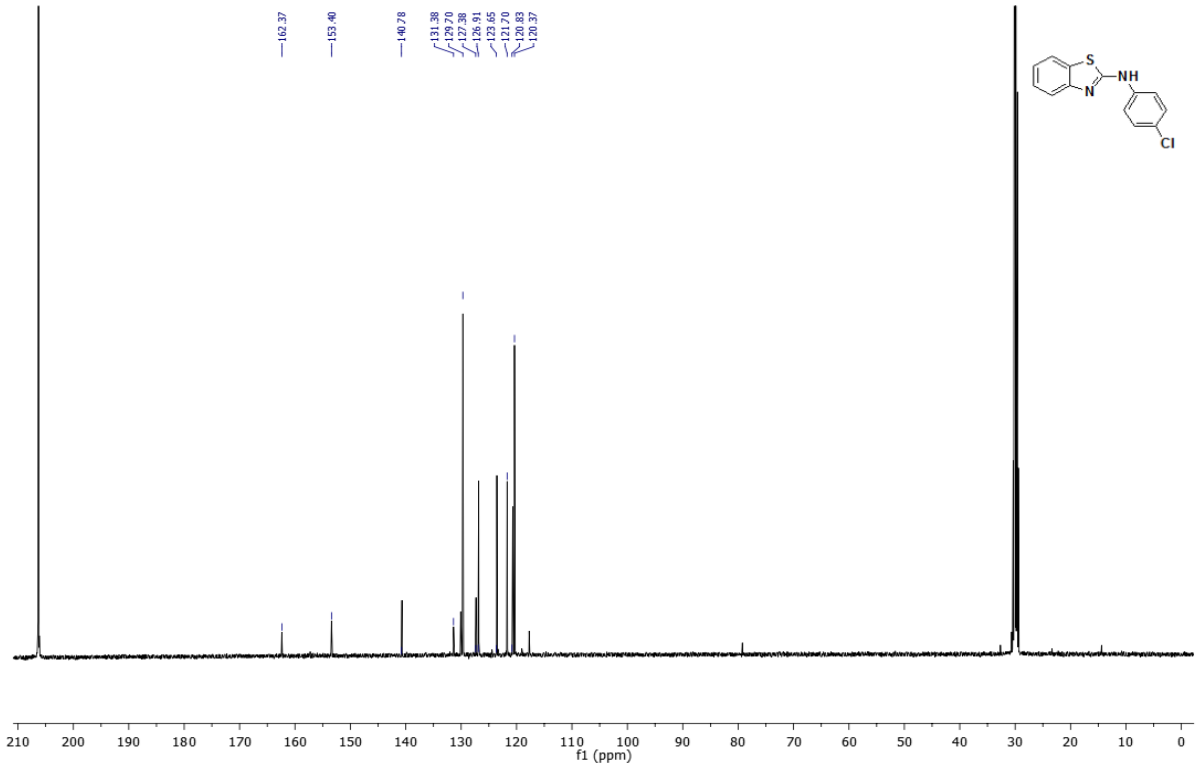
***N*-(4-methoxyphenyl)benzo[d]thiazol-2-amine(3e) ^{13}C-NMR spectrum**



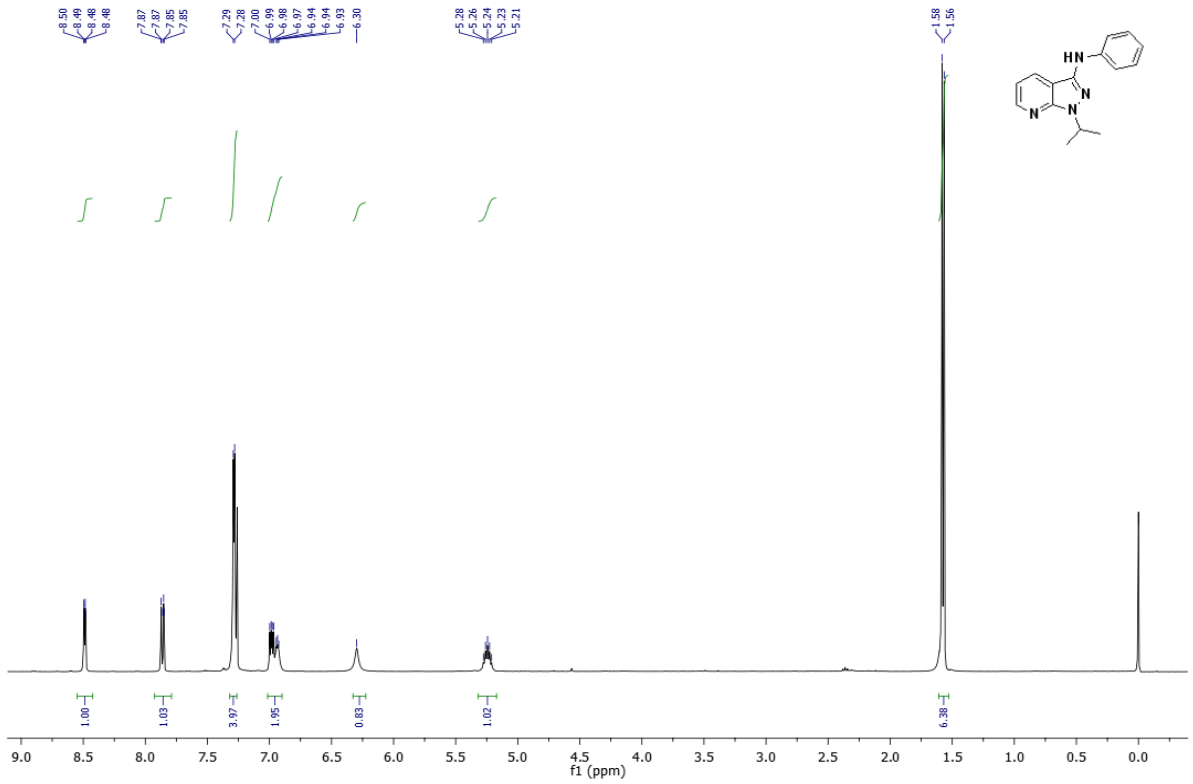
***N*-(4-chlorophenyl)benzo[*d*]thiazol-2-amine (3f) ^{1}H-NMR spectrum**



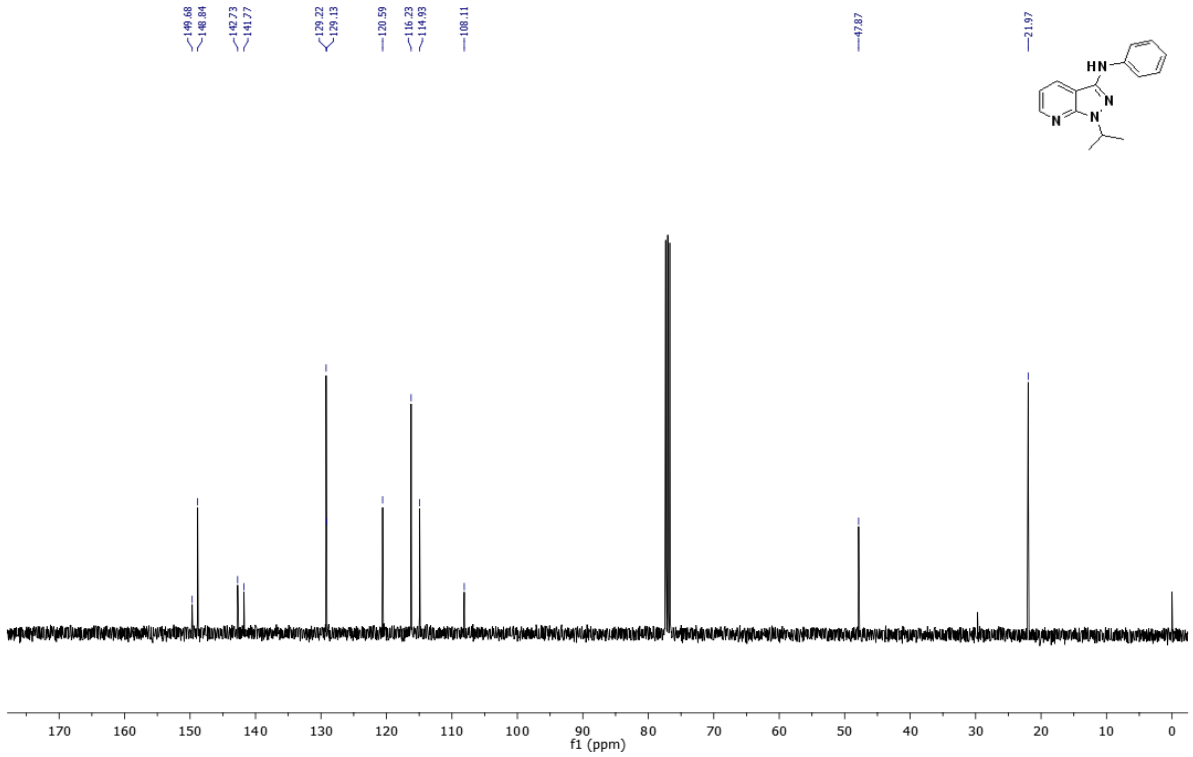
_N_-(4-chlorophenyl)benzo[_d_]thiazol-2-amine (3f) ^{13}C-NMR spectrum



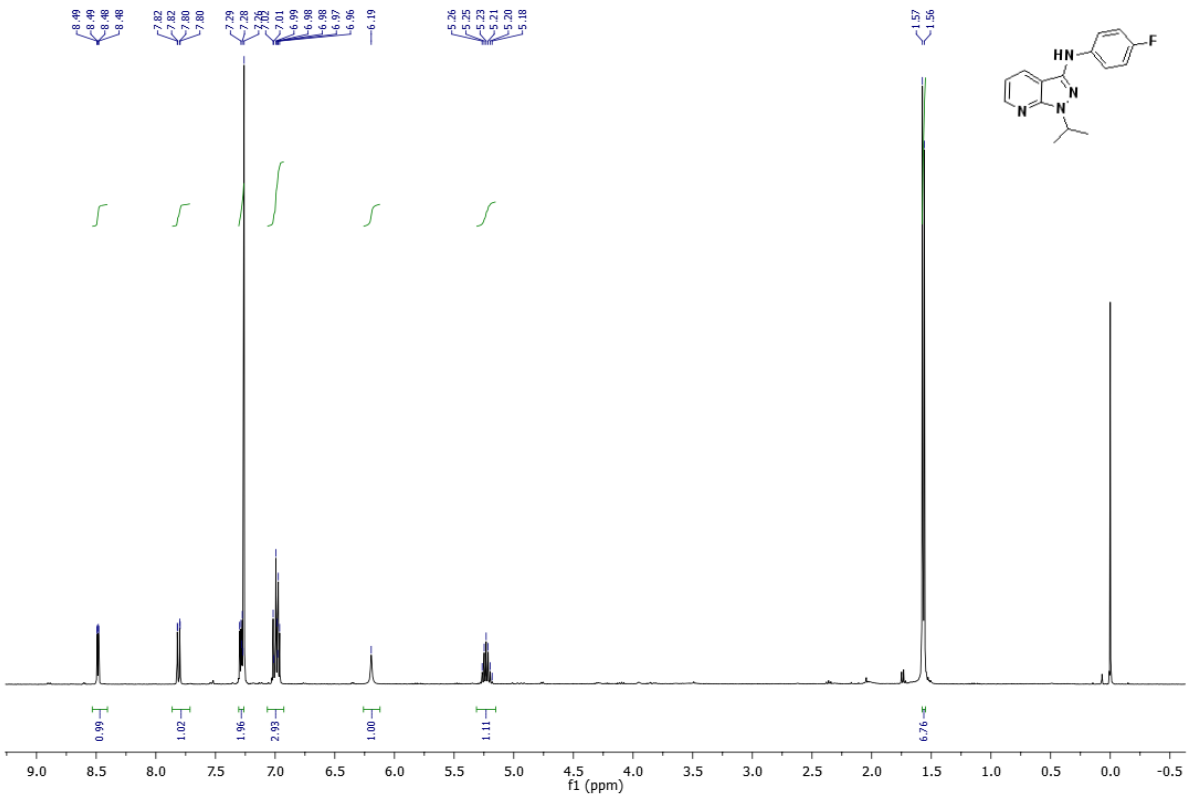
1-isopropyl-_N_-phenyl-1_H_-pyrazolo[3,4-_b_]pyridin-3-amine (4a) ^{1}H-NMR spectrum



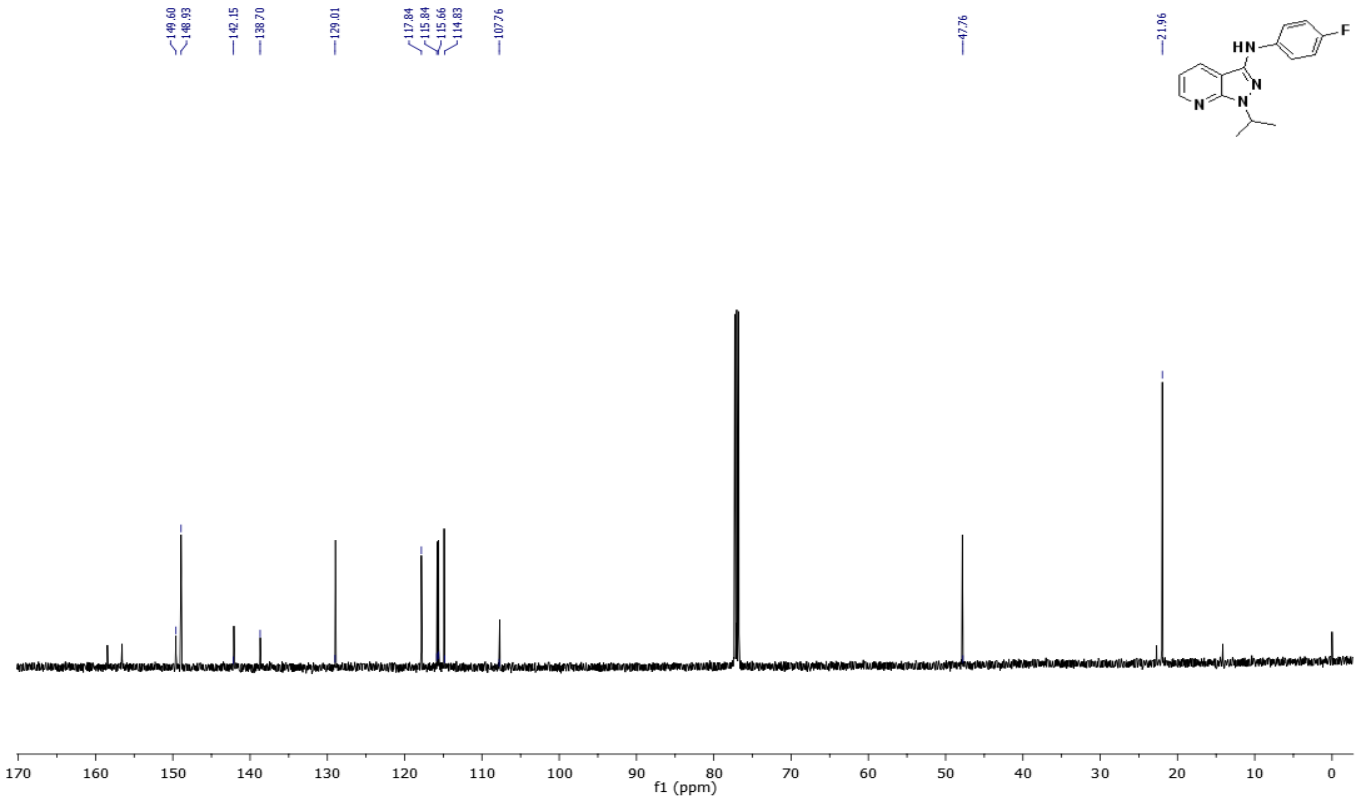
1-isopropyl-*N*-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (4a) ^{13}C-NMR spectrum



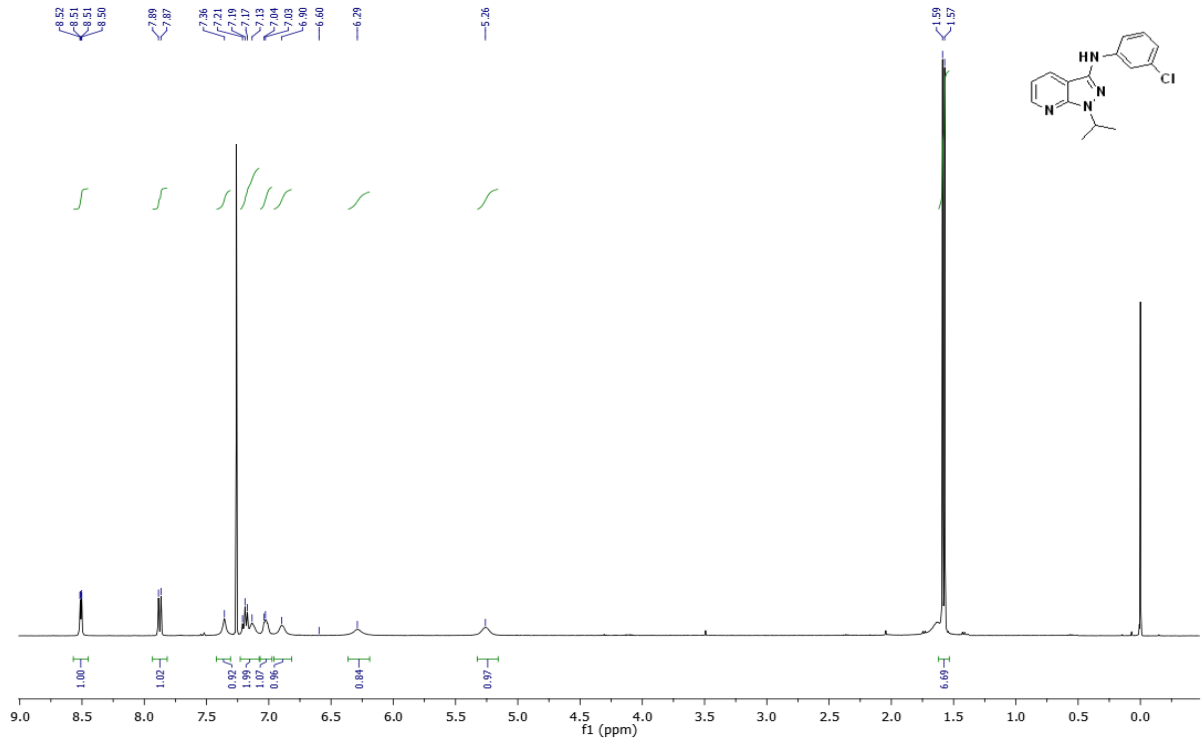
***N*-(4-fluorophenyl)-1-isopropyl-1*H*-pyrazolo[3,4-*b*]pyridin-3-amine (4b) ^{1}H-NMR spectrum**



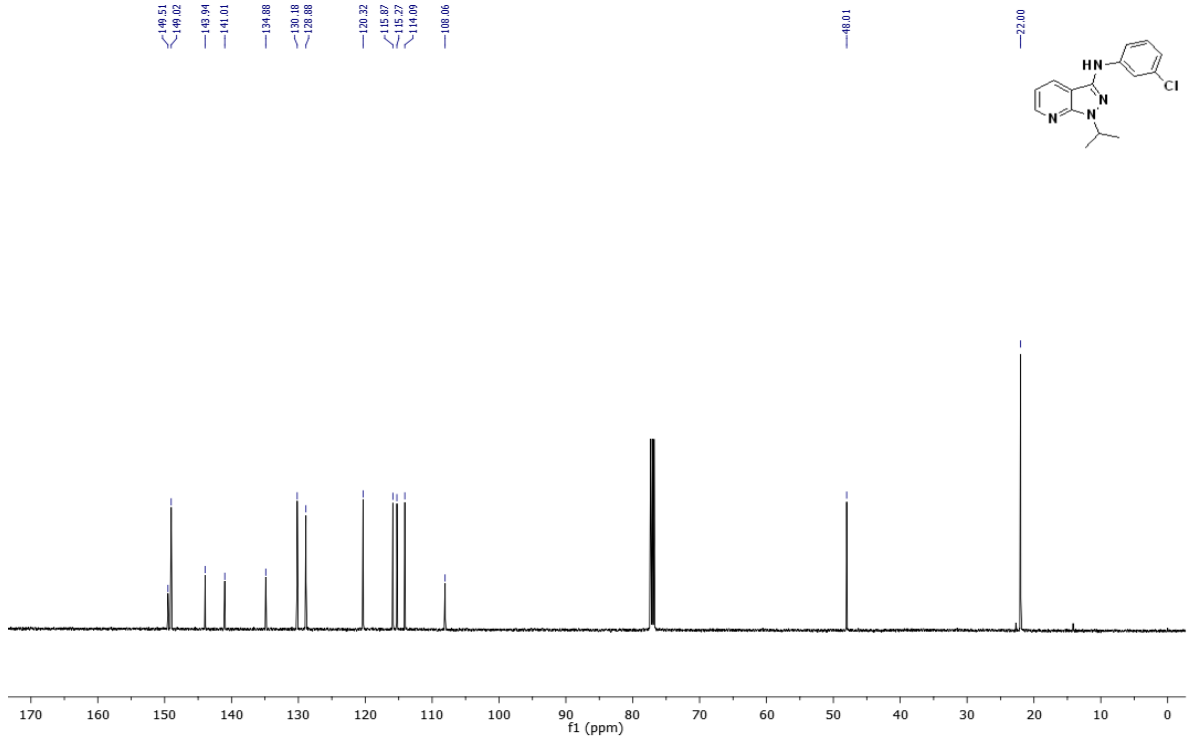
_N_-(4-fluorophenyl)-1-isopropyl-1_H_-pyrazolo[3,4-_b_]pyridin-3-amine (4b) ^{13}C-NMR spectrum



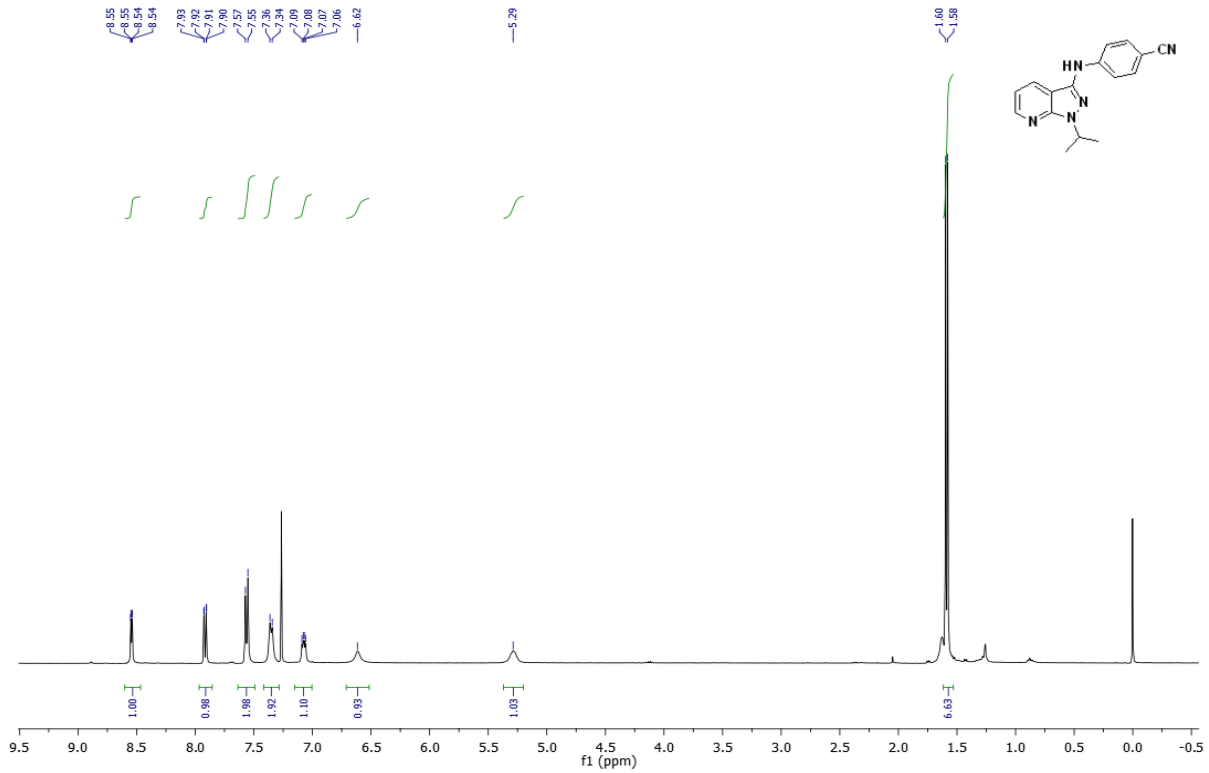
_N_-(3-chlorophenyl)-1-isopropyl-1H-pyrazolo[3,4-_b_]pyridin-3-amine (4c) ^{1}H-NMR spectrum



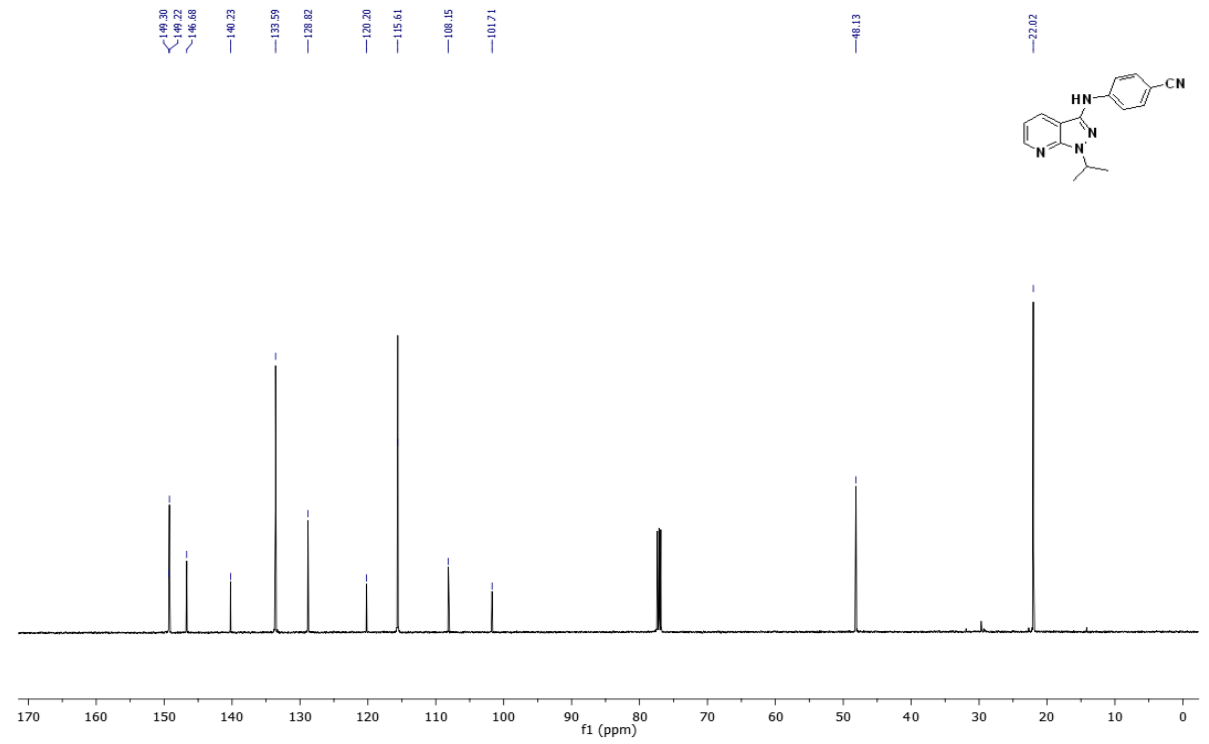
_N_-(3-chlorophenyl)-1-isopropyl-1_H_-pyrazolo[3,4-_b_]pyridin-3-amine (4c) ^{13}C-NMR spectrum



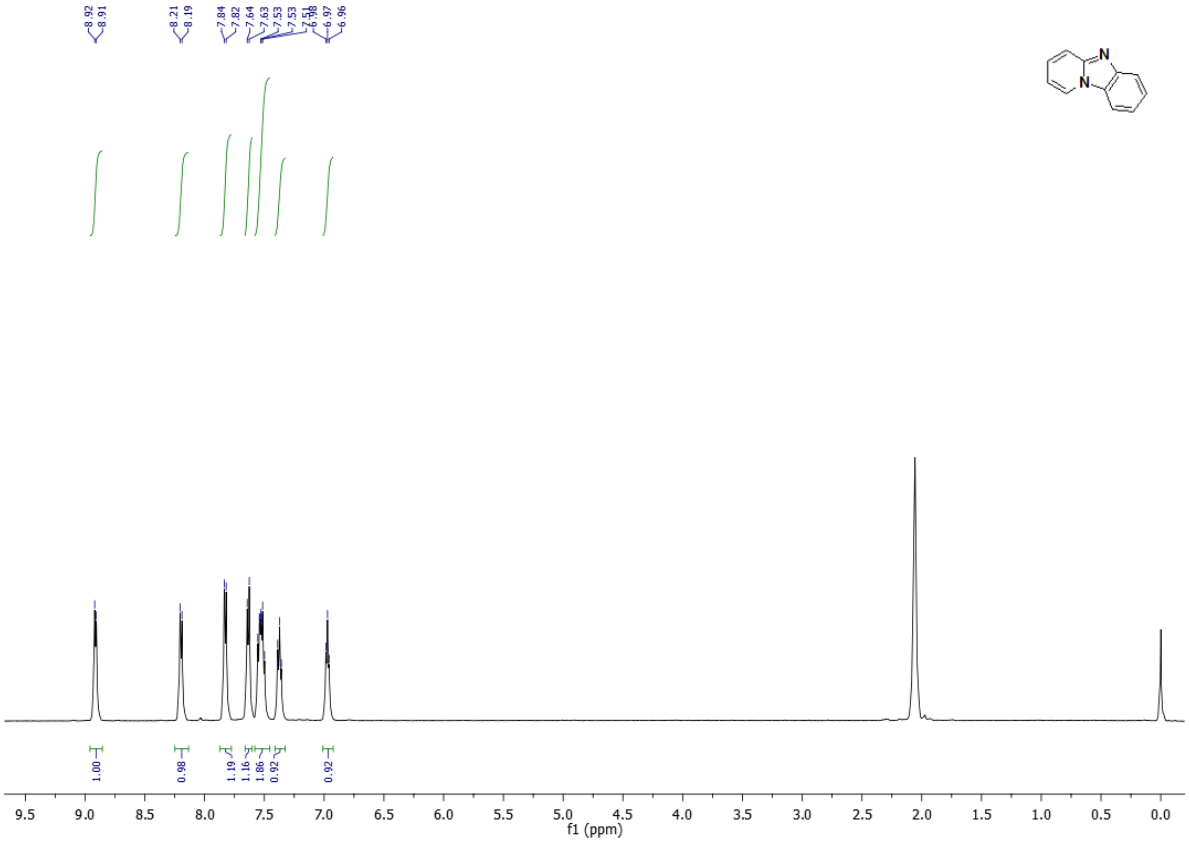
4-((1-isopropyl-1_H_-pyrazolo[3,4-_b_]pyridin-3-yl)amino)benzonitrile (4d) ^{1}H-NMR spectrum



4-((1-isopropyl-1*H*-pyrazolo[3,4-*b*]pyridin-3-yl)amino)benzonitrile (4d) ^{13}C-NMR spectrum



Benzo[4,5]imidazo[1,2-*a*]pyridine (5) ^{1}H-NMR spectrum



Benzo[4,5]imidazo[1,2-*a*]pyridine (5) ^{13}C-NMR spectrum