Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

$AgBF_4$-Catalyzed Deoxygenative C2-amination of Quinoline *N*-Oxides with Isothiocyanates

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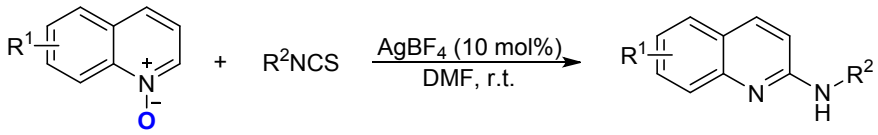
1. General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^{1}H NMR: $CDCl_3$ 7.26 ppm, ^{13}C NMR: $CDCl_3$ 77.0 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Mass spectra were performed on a spectrometer operating on ESI-TOF.

2. Experimental Section

(a) General procedure for the synthesis of 2-aminoquinolines

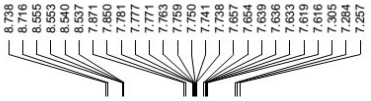


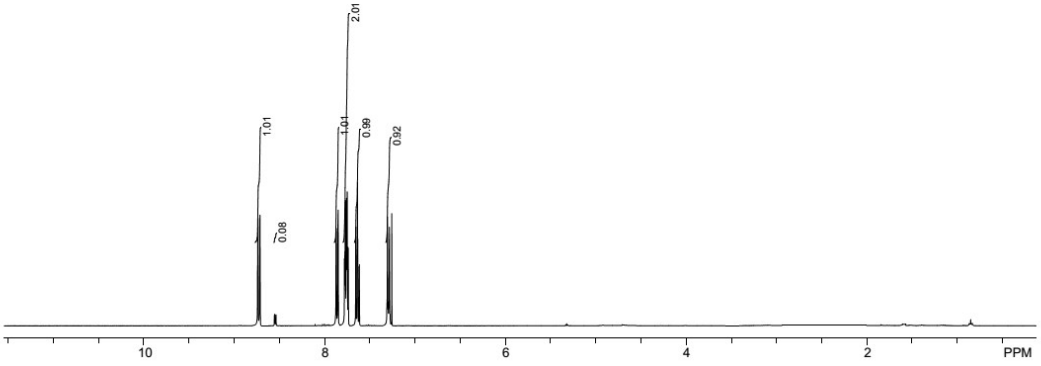
1 **2** **3**

In a tube was consecutively placed quinoline *N*-oxide (0.3 mmol), DMF (1.2mL), isothiocyanate (0.45 mmol) and $AgBF_4$ (0.03 mmol), then the mixtures were stirred at room temperature, the progress of the reaction was monitored by TLC. The reaction typically took 1h - 2h. Upon completion, water (5mL) was added to the reaction mixtue, it was extracted with CH_2Cl_2 (5 mL x 3) and the organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to obtain 2-aminoquinolines **3**

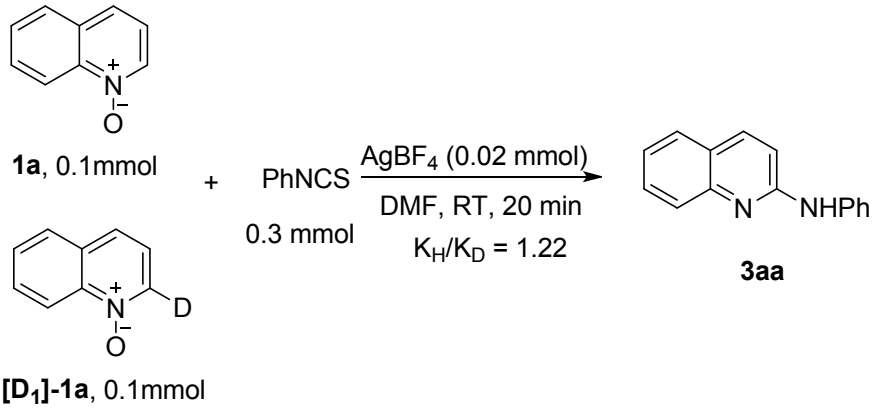
(b) Preparation of 2-*d*1-Quinoline-*N*-Oxide

D_2O (1.5 mL), NaOH (200 mg, 5 mmol), quinoline-*N*-oxide (258 mg, 2.0 mmol)were weighed into 30-mL pressure tube sealed with rubber plugs. The reaction mixture was stirred at 100 ℃ for overnight. After cooling to room temperature, the mixture was then extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with saturated NaCl solution (3 x 5 mL), dried over $MgSO_4$, and filtered. EtOAc was removed under reduced pressure to obtain the crude product 2 - d_1 - quinoline *N* - Oxide. It was further purified by flash column chromatography and percentage of *d* - incorporation was determined by ^{1}H NMR. Peak areas at 8.73 ppm and 8.55 ppm were compared to obtain the deuterium incorporation. Deuterium incorporation was detected to be 92% by ^{1}H NMR (see ^{1}H spectrum).

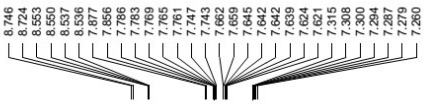


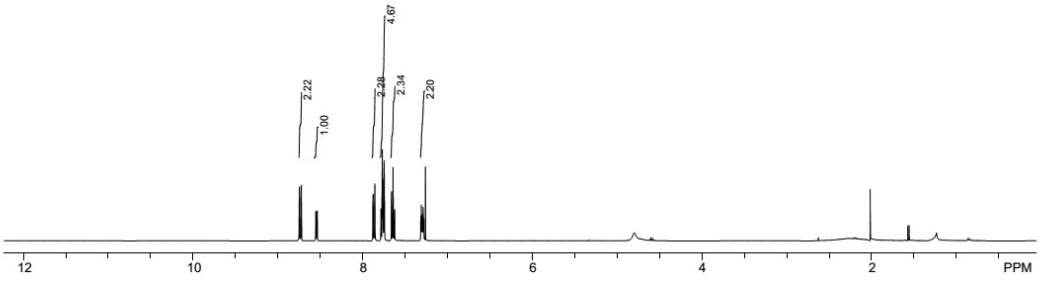


(c) KIE Experiment

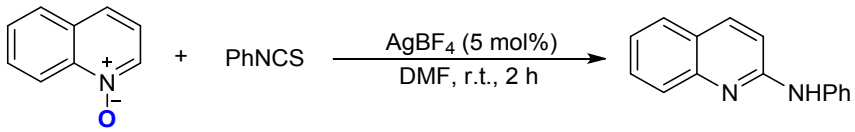


In a tube was consecutively placed Quinoline *N*-oxide **1a** and 2-d_1-quinoline *N*-oxide **[D$_1$]-1a** (1:1，totally 0.2 mmol, deuteration ratio has been calculated), DMF (0.8 mL), PhNCS (40.5 mg, 0.3mmol) and $AgBF_4$ (4 mg, 0.02 mmol), then the mixtures were stirred at room temperature for 20 min, the residual starting material (mixture of 2-d_1-quinoline-*N*-oxide and quinolone -*N*-oxide) was recovered by column chromatography on silica gel (200-300 mesh), which was characterized by ^{1}H NMR spectroscopy. The k_H/k_D= 1.22 was calculated by ^{1}H NMR of the isolated mixture of *N*‐oxides **1a** and **[D$_1$]-1a.**





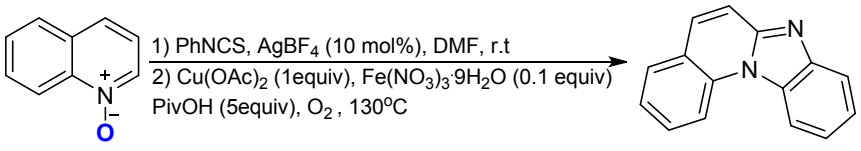
(d) Large scale experiment of preparation of 3aa



1a, 6mmol, 0.87g **3aa**, 82%, 1.08 g

In a round-bottom flask was consecutively placed quinoline *N*-oxide **1a** (0.87 g, 6 mmol), DMF (24 mL), phenyl isothiocyanate **2a** (1.22 g, 9 mmol) and $AgBF_4$ (58.2 mg, 0.3 mmol), then the mixtures were stirred at room temperature for 2 hours. Upon completion, water (30 mL) was added to the reaction mixtue, it was extracted with CH_2Cl_2 (20 mL x 3) and the organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to obtain 1.08 gram of **3aa,** yield 82%.

(e) One pot synthesis of benzo[4,5]imidazo[1,2-*a*]quinolone



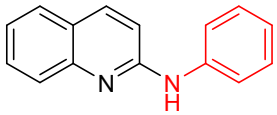
1a **4a**, 61%

In a pressure tube was consecutively placed quinoline *N*-oxide (72.5 mg, 0.5 mmol), DMF (2 mL), isothiocyanate (101.3 mg, 0.75 mmol) and $AgBF_4$ (9.8 mg, 0.05 mmol), the mixtures were stirred at room temperature for 2h, then, to the mixture was added $Cu(OAc)_2$ (62 mg, 0.5 mol), $Fe(NO_3)_3.9H_2O$ (20 mg, 0.05 mmol) and PivOH (255 mg, 2.5 mmol), it was allowed to heated to 130°C for 3 days under balloon pressure of O_2, The reaction was cooled down to room temperature after complete consumption of **3aa** 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, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to obtain product **4a**[1], yield 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (d, *J*= 8.4 Hz, 1 H), 8.44 (d, *J*= 7.6 Hz, 1 H), 8.07 – 8.05 (m, 1 H), 7.91– 7.89 (m, 1 H), 7.84– 7.73 (m, 3 H), 7.61– 7.52 (m, 3 H).

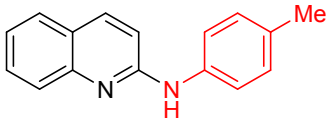
3. Characterization data of products

N-phenylquinolin-2-amine (3aa)[2]



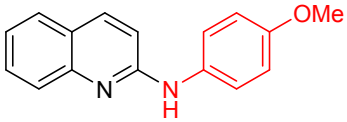
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J*= 9.2 Hz, 1 H), 7.80(d, *J*= 8.0 Hz, 1 H), 7.65 (dd, J_1= 8.0 Hz,J_2= 1.2 Hz,1 H), 7.62– 7.56 (m, 3 H), 7.40– 7.35 (m, 2 H), 7.32– 7.28(m, 1 H), 7.12– 7.08 (m, 1 H), 6.99(d, *J*= 8.8 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 147.6, 140.1, 137.7, 129.7, 129.2, 127.4, 126.6, 124.1, 123.1, 123.0, 120.5, 111.6.

N-(p-tolyl)quinolin-2-amine (3ab)[3]



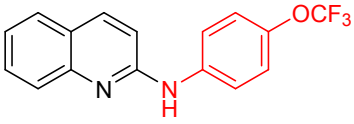
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J*= 9.2 Hz, 1 H), 7.76(d, *J*= 8.4 Hz, 1 H), 7.63 (d, *J*= 8.0 Hz, 1 H), 7.60–7.56 (m, 1 H), 7.41(d, *J*= 8.0 Hz,2 H), 7.30– 7.28(m, 1 H), 7.18 (d, *J*= 8.0 Hz,2 H), 6.96(d, *J*= 8.8 Hz ,1 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 147.7, 137.7, 137.4, 133.1, 129.8, 129.8, 127.4, 126.5, 124.0, 122.9, 121.3, 111.3, 20.8.

N-(4-methoxyphenyl)quinolin-2-amine (3ac)[3]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J*= 9.2 Hz, 1 H), 7.76(d, *J*= 8.4 Hz, 1 H), 7.63 (d, *J*= 8.0 Hz, 1 H), 7.60–7.56 (m, 1 H), 7.41 (d, *J*= 8.0 Hz,2 H), 7.30– 7.28(m, 1 H), 7.18 (d, *J*= 8.0 Hz,2 H), 6.96(d, *J*= 8.8 Hz ,1 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 147.7, 137.7, 137.4, 133.1, 129.8, 129.8, 127.4, 126.5, 124.0, 122.9, 121.3, 111.3, 20.8.

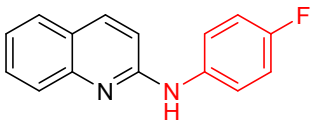
N-(4-(trifluoromethoxy)phenyl)quinolin-2-amine (3ad)[4]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J*= 8.4 Hz, 1 H), 7.79(d, *J*= 8.8 Hz, 1 H), 7.68– 7.65 (m, 3 H), 7.62–7.58(m, 1 H), 7.34 – 7.30 (m,1 H), 7.21(d, *J*= 8.8 Hz ,2 H), 6.91 (d, *J*= 8.8 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 147.2, 144.2 (q, $J_{C\text{-}F}$ = 2.2), 138.9, 138.0, 130.0, 127.5, 126.7, 124.1, 123.5, 122.0, 120.8, 112.0; ^{19}F

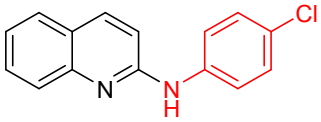
NMR (376 MHz, $CDCl_3$): δ = - 58.1.

N-(4-fluorophenyl)quinolin-2-amine (3ae)[5]



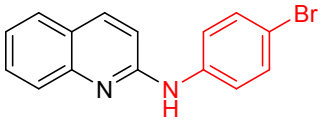
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J*= 8.8 Hz, 1 H), 7.77(d, *J*= 8.4 Hz, 1 H), 7.64 (d, *J*= 8.0 Hz, 1 H), 7.60–7.52(m, 3 H), 7.32– 7.28(m, 1 H), 7.08 – 7.04 (m,2 H), 6.87(d, *J*= 8.8 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 157.7, 154.5, 147.5, 137.8, 136.1, 136.1, 129.8, 127.4, 126.6, 124.0, 123.1, 122.6, 115.9, 115.7, 111.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 119.5.

N-(4-chlorophenyl)quinolin-2-amine (3af)[5]



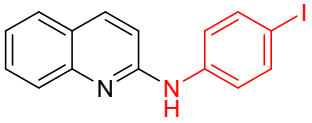
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J*= 8.8 Hz, 1 H), 7.80(d, *J*= 8.4 Hz, 1 H), 7.66– 7.56 (m, 4 H), 7.34–7.29(m,3 H), 6.88(d, *J*= 9.2 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 147.3, 138.8, 137.8, 129.9, 129.1, 127.5, 127.4, 126.7, 124.1, 123.4, 121.2, 111.9.

N-(4-bromophenyl)quinolin-2-amine (3ag)[4]



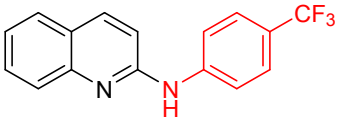
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J*= 8.8 Hz, 1 H), 7.80(d, *J*= 8.4 Hz, 1 H), 7.65 (dd, J_1= 8.0 Hz, J_2= 1.2 Hz, 1 H), 7.62– 7.53(m,3 H), 7.47 – 7.43 (m, 2 H), 7.34 – 7.30 (m, 1 H), 6.89(d, *J*= 8.8 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 147.4, 139.3, 137.8, 132.0, 129.9, 127.4, 126.8, 124.1, 123.4, 121.4, 114.9, 112.0.

N-(4-iodophenyl)quinolin-2-amine (3ah)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J*= 8.8 Hz, 1 H), 7.80(d, *J*= 7.6 Hz, 1 H), 7.66 – 7.58 (m, 4 H),7.47 – 7.43 (m, 2 H), 7.34 – 7.30 (m, 1 H), 6.90(d, *J*= 8.8 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 147.3, 140.1, 137.9, 137.8, 129.9, 127.4, 126.8, 124.1, 123.5, 121.7, 112.1, 85.0; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}IN_2[M+H]^+$: 347.0040, found 347.0043.

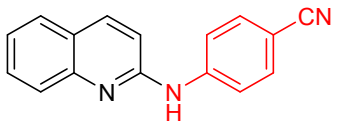
N-(4-(trifluoromethyl)phenyl)quinolin-2-amine (3ai)[5]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J*= 8.8 Hz, 1 H), 7.85(d, *J*= 8.0 Hz, 1 H), 7.78 (d, *J*= 8.0 Hz, 2 H),7.68 – 7.57 (m, 4 H), 7.38 – 7.34 (m, 1 H), 6.91(d, *J*= 8.8 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 147.2, 143.5, 138.0, 130.0, 127.4, 126.9, 126.3 (q, J_{C-F} = 3.7), 124.3, 123.8, 118.4, 112.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -

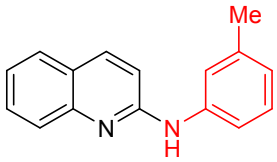
61.6.

4-(quinolin-2-ylamino)benzonitrile (3aj)[6]



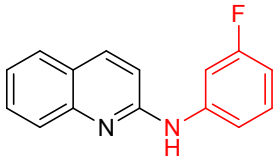
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J*= 8.8 Hz, 1 H), 7.92– 7.87 (m, 3 H), 7.71 – 7.62 (m, 4 H),7.39(t, *J*= 8.0 Hz, 1 H), 6.93(d, *J*= 8.8 Hz ,1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 147.0, 144.5, 138.1, 133.4, 130.1, 127.5, 127.2, 124.4, 124.2, 119.6, 118.3, 112.9, 104.1.

***N*-(m-tolyl)quinolin-2-amine (3ak)[3]**



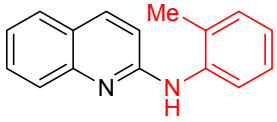
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J*= 8.8 Hz, 1 H), 7.78 (d, *J*= 8.8 Hz, 1 H), 7.65 (dd, J_1= 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.61 – 7.57(m, 1 H),7.37 – 7.24 (m, 4 H), 7.01 (d, *J*= 8.8 Hz, 1 H), 6.92(d, *J*= 7.6 Hz ,1 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 147.6, 140.0, 139.1, 137.7, 129.8, 129.1, 127.4, 126.6, 124.1, 124.1, 123.0, 121.3, 117.8, 111.5, 21.5.

***N*-(3-fluorophenyl)quinolin-2-amine (3al)**



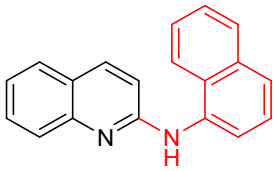
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J*= 8.4 Hz, 1 H), 7.84 (d, *J*= 8.8 Hz, 1 H), 7.75 – 7.71 (m, 1 H), 7.68 – 7.59 (m, 2 H),7.35– 7.25 (m, 2 H), 7.23– 7.20 (m, 1 H), 6.93(d, *J*= 8.8 Hz ,1 H), 6.78 – 6.73 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 162.1, 153.5, 147.3, 142.0, 141.9, 137.8, 130.1, 130.0, 129.9, 127.4, 127.0, 124.2, 123.5, 114.8, 114.8, 112.2, 109.2, 109.0, 106.8, 106.5;^{19}F NMR (376 MHz, $CDCl_3$): δ = - 111.7; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}FN_2[M+H]^+$: 239.0979, found 239.0985.

***N*-(o-tolyl)quinolin-2-amine (3am)[5]**



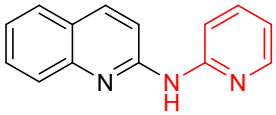
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J*= 9.2 Hz, 1 H), 7.73(d, *J*= 8.4 Hz, 1 H), 7.64(d, *J*= 8.0 Hz, 1 H),7.61 – 7.56 (m,2 H), 7.31 – 7.23 (m, 3 H), 7.14 – 7.10 (m, 1 H), 6.88 (d, *J*= 8.8 Hz, 1 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 147.8, 137.9, 131.6, 131.0, 129.9, 127.5, 126.9, 126.2, 124.8, 124.1, 123.5, 122.9, 110.6, 18.1.

***N*-(naphthalen-1-yl)quinolin-2-amine (3an)**



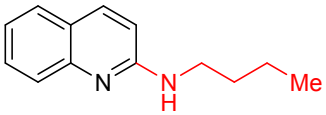
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J*= 8.0 Hz, 1 H), 7.92(d, *J*= 8.8 Hz, 1 H), 7.86(d, *J*= 8.8 Hz, 1 H),7.76 (d, *J*= 8.4 Hz, 2 H),7.69 – 7.58 (m, 3 H), 7.56 – 7.49 (m, 3 H), 7.32 – 7.28 (m, 1 H), 6.85 (d, *J*= 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 147.6, 138.0, 135.4, 134.7, 129.9, 129.5, 128.5, 127.5, 126.4, 126.1, 125.9, 125.8, 124.1, 123.0, 122.2, 121.2, 110.7; HRMS (ESI) *m/z* calcd. for $C_{19}H_{15}N_2[M+H]^+$: 271.1230, found 271.1227.

N-(pyridin-2-yl)quinolin-2-amine (3ao)[3]



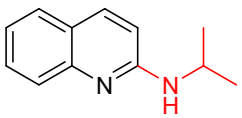
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J*= 8.0 Hz, 1 H), 8.36 – 8.34 (m, 1 H), 7.95 (d, *J*= 8.8 Hz, 1 H),7.88 (d, *J*= 8.8 Hz, 1 H),7.74– 7.59 (m, 3 H), 7.36 – 7.29 (m, 2 H), 6.96 – 6.93 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 152.9, 147.4, 138.0, 137.5, 129.6, 127.3, 126.7, 124.3, 123.5, 117.0, 113.8, 113.0.

N-butylquinolin-2-amine (3ap)[3]



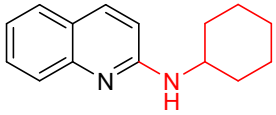
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J*= 8.8 Hz, 1 H), 7.67 (d, *J*= 8.4 Hz, 1 H), 7.58 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H),7.54 – 7.50 (m, 1 H),7.22 – 7.18 (m, 1 H), 6.64 (d, *J*= 8.8 Hz, 1 H), 3.49 – 3.45 (m, 2 H), 1.69 – 1.62 (m, 2 H), 1.51 – 1.49 (m, 2 H), 0.97 (t, *J*= 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 137.6, 129.7, 129.1, 127.4, 125.7, 123.2, 122.0, 110.9, 41.6, 31.8, 20.2, 13.9.

N-isopropylquinolin-2-amine (3aq)[3]



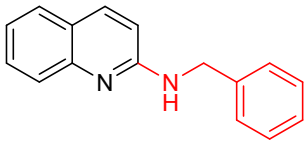
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J*= 9.2 Hz, 1 H), 7.66 (d, *J*= 8.4 Hz, 1 H), 7.59 – 7.57 (m, 1 H), 7.55 – 7.50 (m, 1 H),7.22 – 7.18 (m, 1 H), 6.63 (d, *J*= 8.8 Hz, 1 H), 4.23 – 4.14 (m, 1 H), 1.30 (d, *J*= 6.4 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 147.4, 137.7, 129.7, 127.4, 125.5, 123.1, 122.0, 111.0, 43.0, 23.1.

N-cyclohexylquinolin-2-amine (3ar)[7]



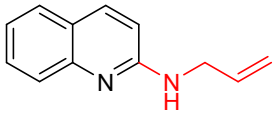
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J*= 8.8 Hz, 1 H), 7.64 (d, *J*= 8.4 Hz, 1 H), 7.57 – 7.56 (m, 1 H),7.53–7.49 (m, 1 H),7.21– 7.16 (m, 1 H), 6.63 (d, *J*= 9.2 Hz, 1 H), 3.87 – 3.78 (m, 1 H), 2.12 – 2.08 (m, 2 H), 1.81 – 1.76 (m, 2 H), 1.69 – 1.64 (m, 1 H), 1.50 – 1.39 (m, 2 H), 1.30 – 1.21 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 147.8, 137.5, 129.6, 127.4, 125.7, 123.2, 121.8, 110.9, 49.9, 33.5, 25.7, 24.9.

N-benzylquinolin-2-amine (3as)[3]



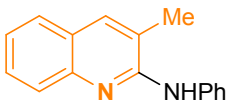
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J*= 8.8 Hz, 1 H), 7.73 (d, *J*= 9.2 Hz, 1 H), 7.60– 7.53 (m, 2 H),7.43– 7.41 (m,2 H), 7.37– 7.33 (m, 2 H), 7.31– 7.29 (m, 1 H), 7.25 – 7.21 (m, 1 H), 6.63 (d, *J*= 8.8 Hz, 1 H), 4.73 (d, *J*= 5.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 147.9, 139.3, 137.4, 129.6, 128.6, 127.7, 127.4, 127.3, 126.2, 123.5, 122.1, 111.3, 45.8.

N-allylquinolin-2-amine (3at)



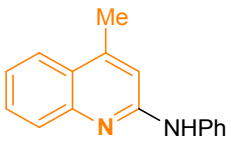
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J*= 8.8 Hz, 1 H), 7.68 (d, *J*= 8.4 Hz, 1 H), 7.60 – 7.58 (m, 1 H),7.55 – 7.51 (m,1 H), 7.23– 7.20 (m, 1 H), 6.65 (d, *J*= 8.8 Hz, 1 H), 6.07 – 5.97 (m, 1 H), 5.34 – 5.28 (m, 1 H), 5.20 – 5.16 (m, 1 H), 4.17 – 4.14 (m,2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 147.8, 137.5, 135.1, 129.6, 127.4, 126.0, 123.4, 122.2, 116.2, 111.1, 44.2; HRMS (ESI) *m/z* calcd. for $C_{12}H_{13}N_2[M+H]^+$: 185.1073, found 185.1071.

3-methyl-*N*-phenylquinolin-2-amine (3ba)[8]



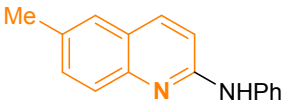
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90– 7.84 (m, 3 H), 7.74(s, 1 H), 7.61– 7.53(m, 2H),7.41– 7.37 (m,2 H), 7.32–7.28 (m, 1 H), 7.09 – 7.05 (m, 1 H), 6.51 (s, 1 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 146.3, 140.4, 136.4, 128.9, 128.6, 126.8, 126.5, 124.4, 123.1, 122.3, 119.9, 119.5, 17.7.

4-methyl-*N*-phenylquinolin-2-amine (3ca)[9]



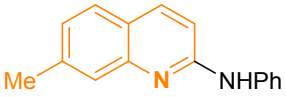
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83– 7.80 (m, 2 H), 7.61 – 7.55 (m, 3 H),7.39 – 7.31 (m,3 H), 7.12– 7.07 (m, 1 H), 6.83 (d, *J*= 1.2 Hz, 1 H), 2.58 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 147.5, 145.6, 140.3, 129.4, 129.1, 127.1, 124.4, 123.5, 122.9, 122.8, 120.5, 111.7, 18.8.

6-methyl-*N*-phenylquinolin-2-amine (3da)[3]



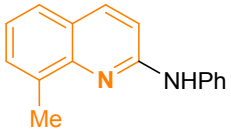
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J*= 8.8 Hz, 1 H), 7.70 (d, *J*= 9.2 Hz, 1 H),7.56– 7.54 (m,2 H), 7.44– 7.42 (m, 2 H), 7.38 – 7.34 (m, 2 H), 7.09 – 7.06 (m, 1 H), 6.97 (d, *J*= 8.8 Hz, 1 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 145.8, 140.3, 137.2, 132.7, 131.8, 129.2, 126.5, 126.3, 124.1, 122.9, 120.3, 111.6, 21.2.

7-methyl-*N*-phenylquinolin-2-amine (3ea)



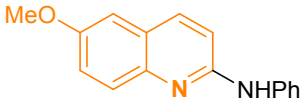
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J*= 8.8 Hz, 1 H), 7.70 (d, *J*= 9.2 Hz, 1 H),7.56– 7.54 (m,2 H), 7.44– 7.42 (m, 2 H), 7.38 – 7.34 (m, 2 H), 7.09 – 7.06 (m, 1 H), 6.97 (d, *J*= 8.8 Hz, 1 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 147.7, 140.0, 137.4, 129.2, 127.0, 126.0, 125.2, 123.0, 122.1, 120.5, 110.7, 21.8; HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}N_2[M+H]^+$: 235.1230, found 235.1225.

8-methyl-*N*-phenylquinolin-2-amine (3fa)



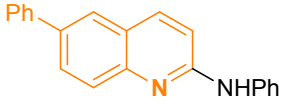
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J*= 8.8 Hz, 1 H), 7.76 (d, *J*= 8.0 Hz, 1 H),7.52– 7.48 (m,2 H), 7.41– 7.37 (m, 2 H), 7.23– 7.20 (m,1 H), 7.09 – 7.06 (m, 1 H), 6.89 (d, *J*= 8.8 Hz, 1 H), 2.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 149.2, 137.9, 136.4, 130.0, 129.0, 126.3, 125.3, 123.7, 122.8, 122.3, 119.4, 111.8, 18.2; HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}N_2[M+H]^+$: 235.1230, found 235.1226.

6-methoxy-*N*-phenylquinolin-2-amine (3ga)[3]



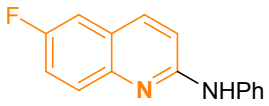
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J*= 8.8 Hz, 1 H), 7.72(d, *J*= 9.2 Hz, 1 H),7.54 (d, *J*= 8.4 Hz, 1 H), 7.37– 7.33 (m, 2 H), 7.28– 7.26 (m, 1 H), 7.09 – 7.04 (m, 1 H), 7.00 - 6.98 (m, 1 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 152.8, 143.1, 140.5, 136.7, 129.2, 128.1, 124.6, 122.6, 121.4, 120.0, 111.9, 106.2, 55.5.

***N*,6-diphenylquinolin-2-amine (3ha)**



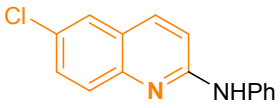
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J*= 8.8 Hz, 1 H), 7.87 – 7.85 (m,3 H),7.71 – 7.69 (m, 2 H), 7.50– 7.47 (m, 2 H), 7.41– 7.36 (m, 3 H), 7.13– 7.10 (m, 1 H), 7.01 (d, *J*= 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 147.1, 140.7, 140.1, 137.9, 135.9, 129.3, 129.2, 128.8, 127.1, 127.1, 125.3, 124.2, 123.1, 120.5, 112.0; HRMS (ESI) *m/z* calcd. for $C_{21}H_{17}N_2[M+H]^+$: 297.1386, found 297.1379.

6-fluoro-*N*-phenylquinolin-2-amine (3ia)



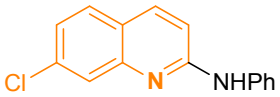
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J*= 8.8 Hz, 1 H), 7.78 – 7.74 (m,1 H),7.57 – 7.55 (m, 2 H), 7.39– 7.32 (m, 3 H), 7.29– 7.27 (m, 1 H), 7.11 – 7.08 (m, 1 H), 7.00 (d, *J*= 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 157.3, 153.9, 153.8, 144.4, 140.1, 137.0, 137.0, 129.2, 128.7, 128.6, 124.3, 124.2, 123.1, 120.4, 119.3, 119.1, 112.7, 110.9, 110.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 118.9; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}FN_2[M+H]^+$: 239.0979, found 239.0981.

6-chloro-*N*-phenylquinolin-2-amine (3ja)



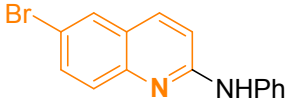
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J*= 8.8 Hz, 1 H), 7.70 (d, *J*= 8.8 Hz, 1 H),7.61 – 7.55 (m, 3 H), 7.52–7.49 (m, 1 H), 7.39– 7.35 (m, 2 H), 7.11 (t,*J*= 7.2 Hz, 1 H), 6.97 (d, *J*= 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 146.0, 139.8, 136.7, 130.4, 129.2, 128.3, 128.2, 126.1, 124.6, 123.4, 120.6, 112.6; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}ClN_2[M+H]^+$: 255.0684, found 255.0682.

7-chloro-*N*-phenylquinolin-2-amine (3ka)



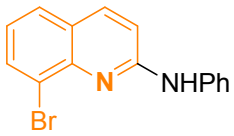
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85(d, *J*= 8.8 Hz, 1 H), 7.77(d, *J*= 2.0 Hz, 1 H),7.59– 7.53 (m, 3 H), 7.40– 7.36 (m, 2 H), 7.23 (dd, J_1= 8.8 Hz, J_2= 2.0 Hz, 1 H), 7.14– 7.09 (m,1 H), 6.92 (d, *J*= 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 148.2, 139.7, 137.3, 135.5, 129.2, 128.5, 125.8, 123.8, 123.4, 122.4, 120.7, 111.8; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}ClN_2[M+H]^+$: 255.0684, found 255.0681.

6-bromo-N-phenylquinolin-2-amine (3la)[3]



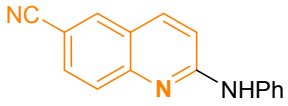
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J*= 8.8 Hz, 1 H), 7.77 – 7.76 (m, 1 H), 7.64– 7.63 (m, 2 H), 7.58– 7.55 (m, 2 H), 7.39 – 7.35 (m, 2 H), 7.13– 7.09 (m,1 H), 6.96 (d, *J*= 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 146.3, 139.7, 136.7, 132.9, 129.4, 129.3, 128.4, 125.2, 123.4, 120.6, 116.0, 112.6.

8-bromo-N-phenylquinolin-2-amine (3ma)



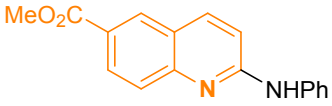
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.77 (m, 2 H), 7.64 – 7.63 (m, 2 H), 7.57 – 7.55 (m, 2 H), 7.39– 7.35 (m, 2 H), 7.11 (t, *J*= 7.6 Hz, 1 H), 6.96 (d, *J*= 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 146.3, 139.7, 136.7, 132.9, 129.4, 129.3, 128.4, 125.2, 123.4, 120.6, 116.0, 112.6; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}ClN_2[M+H]^+$: 255.0684, found 255.0681; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}BrN_2[M+H]^+$: 299.0178, found 299.0174.

2-(phenylamino)quinoline-6-carbonitrile (3na)



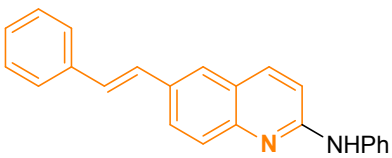
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J*= 1.2 Hz, 1 H), 7.89 (d, *J*= 9.2 Hz, 1 H), 7.76 (d, *J*= 8.8 Hz, 1 H), 7.69 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1 H), 7.60 (d, *J*= 8.0 Hz, 2 H), 7.42 – 7.38 (m, 3 H), 7.16 (t, *J*= 7.2 Hz, 1 H), 7.02 (d, *J*= 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 149.6, 137.6, 133.2, 131.0, 129.3, 127.7, 125.3, 124.2, 123.4, 121.2, 119.3, 113.4, 105.8; HRMS (ESI) *m/z* calcd. for $C_{16}H_{12}N_3[M+H]^+$: 246.1026, found 246.1026.

methyl 2-(phenylamino)quinoline-6-carboxylate (3oa)



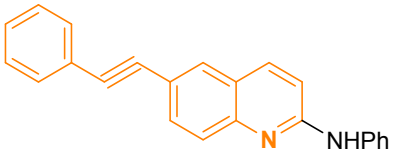
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J*= 1.6 Hz, 1 H), 8.17 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1 H), 7.95 (d, *J*= 8.8 Hz, 1 H), 7.75 (d, *J*= 8.8 Hz, 1 H), 7.59 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2 H), 7.40 – 7.36 (m, 2 H), 7.15 – 7.11 (m, 1 H), 6.99 (d, *J*= 8.8 Hz, 1 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 155.9, 150.3, 139.4, 138.7, 130.5, 129.7, 129.3, 126.6, 124.4, 123.8, 123.1, 121.1, 112.4, 52.1; HRMS (ESI) *m/z* calcd. for $C_{17}H_{15}N_2O_2[M+H]^+$: 279.1128, found 279.1133.

(E)-*N*-phenyl-6-styrylquinolin-2-amine (3pa)



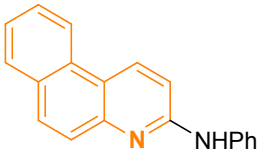
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J*= 8.8 Hz, 1 H), 7.86 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1 H), 7.76 (d, *J*= 8.8 Hz, 1 H), 7.68 (d, *J*= 1.6 Hz, 1 H), 7.58 – 7.54 (m, 4 H), 7.40 – 7.36 (m, 4 H), 7.29 – 7.27 (m, 1 H), 7.21 – 7.18 (m, 2 H), 7.13 – 7.09 (m, 1 H), 6.98 (d, *J*= 8.8 Hz, 1 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 147.5, 140.0, 137.7, 137.4, 132.3, 129.3, 128.7, 128.3, 128.2, 127.6, 127.5, 127.0, 126.4, 125.8, 124.2, 123.2, 120.5, 111.9; HRMS (ESI) *m/z* calcd. for $C_{23}H_{19}N_2[M+H]^+$: 323.1543, found 323.1536.

_N_-phenyl-6-(phenylethynyl)quinolin-2-amine (3qa)



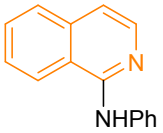
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.85 (m, 2 H), 7.75 – 7.69 (m, 2 H), 7.60 – 7.55 (m, 4 H), 7.40 – 7.35 (m, 5 H), 7.12 (t, *J*= 7.2 Hz, 1 H), 6.98 (d, *J* = 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 147.4, 139.8, 137.4, 132.7, 131.5, 130.8, 129.3, 128.4, 128.2, 126.8, 123.8, 123.4, 123.3, 120.7, 117.7, 112.3, 89.6, 89.3; HRMS (ESI) *m/z* calcd. for $C_{23}H_{17}N_2[M+H]^+$: 321.1386, found 321.1377.

_N_-phenylbenzo[f]quinolin-3-amine (3ra)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.18 (d, *J* = 8.0 Hz, 1 H), 7.96 (d, *J*= 8.8 Hz, 1 H), 7.89 – 7.87 (m, 1 H), 7.72 – 7.57 (m, 6 H), 7.46 – 7.42 (m, 2 H), 7.15 – 7.10 (m, 1 H), 7.02 (d, *J*= 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 145.7, 140.5, 137.8, 134.3, 130.7, 129.3, 127.8, 127.8, 126.3, 125.2, 124.6, 123.9, 122.7, 121.0, 120.0, 110.9; HRMS (ESI) *m/z* calcd. for $C_{19}H_{15}N_2[M+H]^+$: 271.1230, found 271.1225.

_N_-phenylisoquinolin-1-amine (3sa)[1]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J*= 6.0 Hz, 1 H), 7.95 – 7.92 (m, 1 H), 7.75 (d, *J*= 8.0 Hz, 1 H), 7.69 – 7.63 (m, 3 H), 7.56 – 7.52 (m, 1 H), 7.40 – 7.35 (m, 2 H), 7.14 (dd, J_1 = 6.0 Hz, J_2 = 0.8 Hz, 1 H), 7.09 – 7.05 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 140.8, 140.3, 137.4, 129.9, 129.0, 127.4, 126.5, 122.7, 121.4, 120.3, 118.8, 113.4;

4. References

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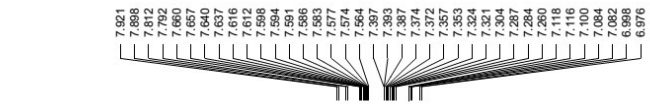
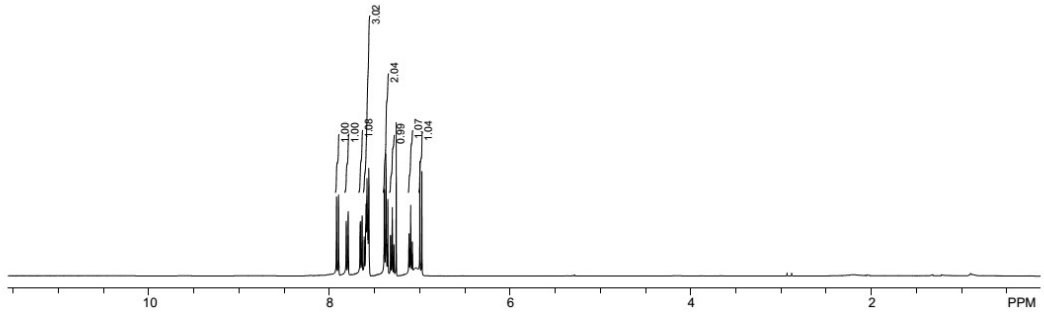
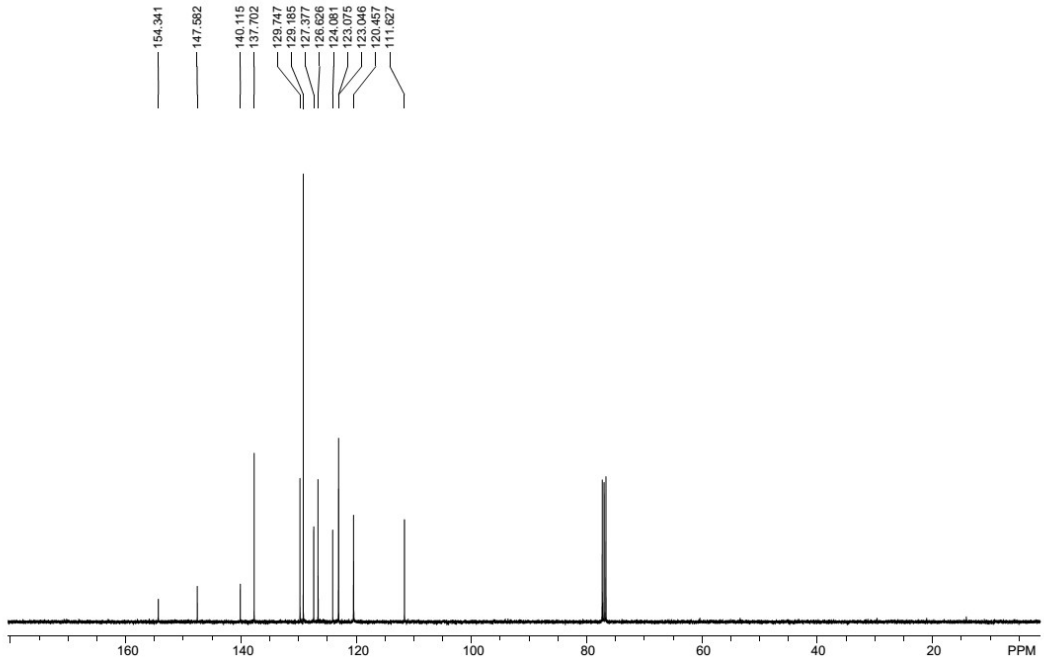
5. ^{1}H and ^{13}C NMR spectra of products

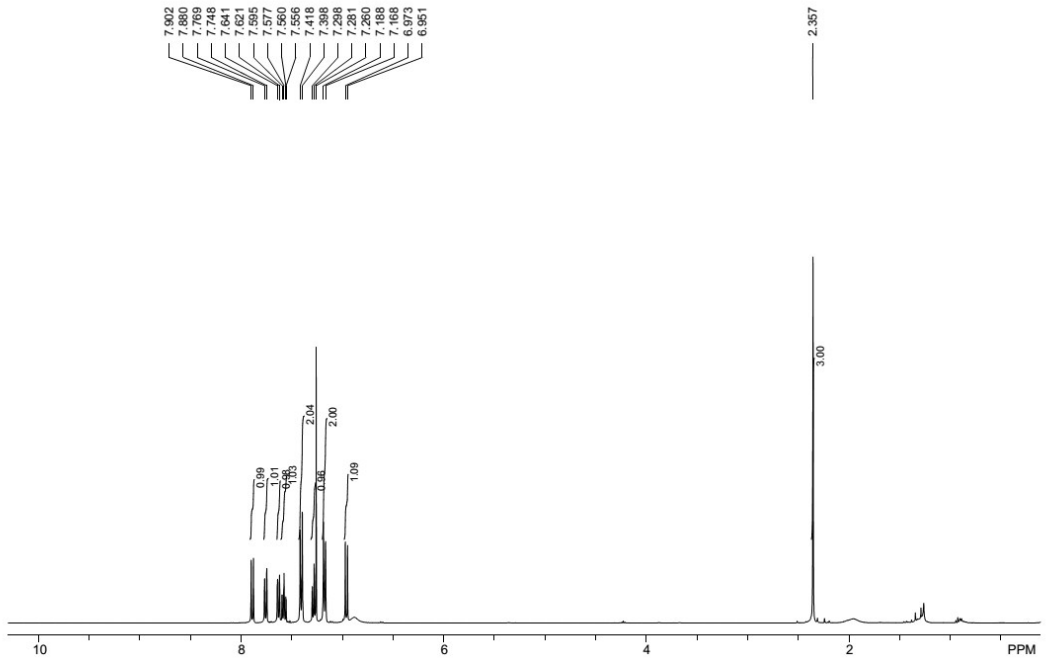
***N*-phenylquinolin-2-amine (3aa)**

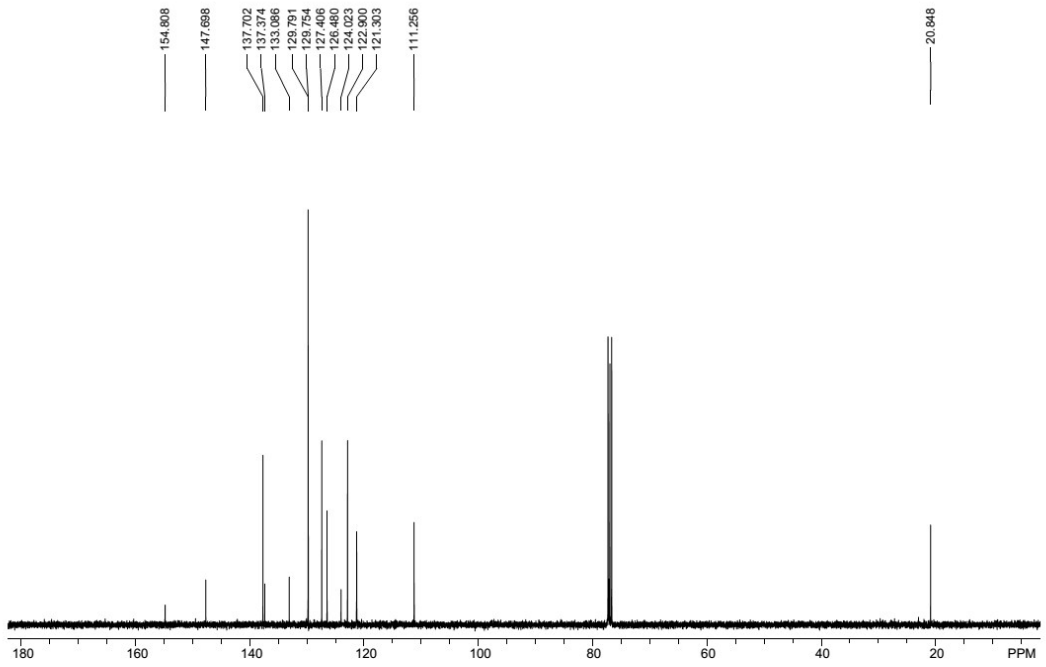




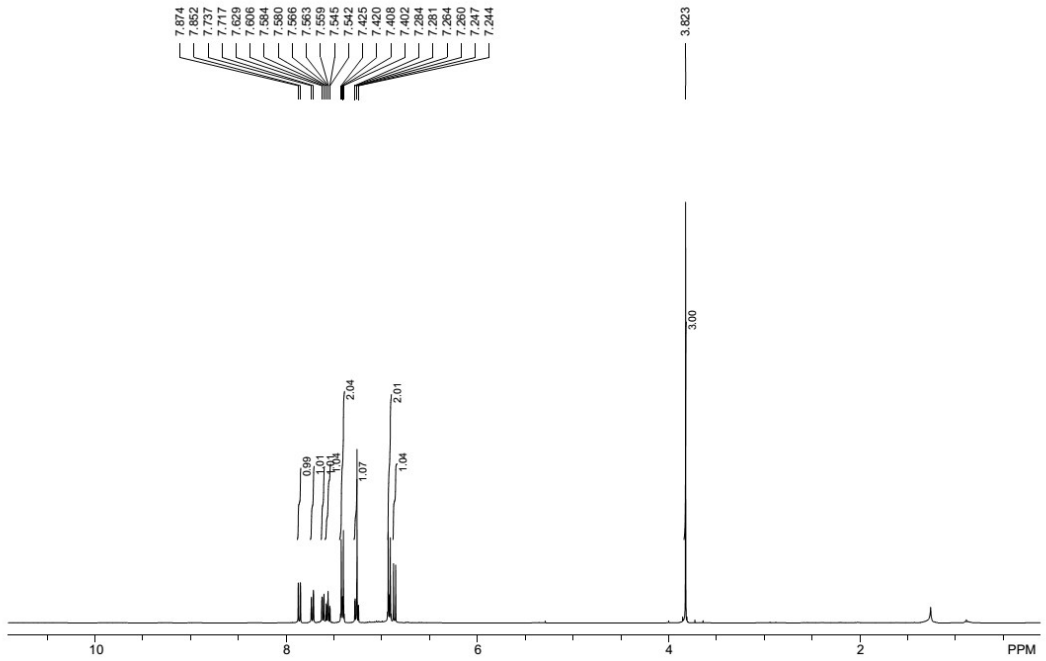


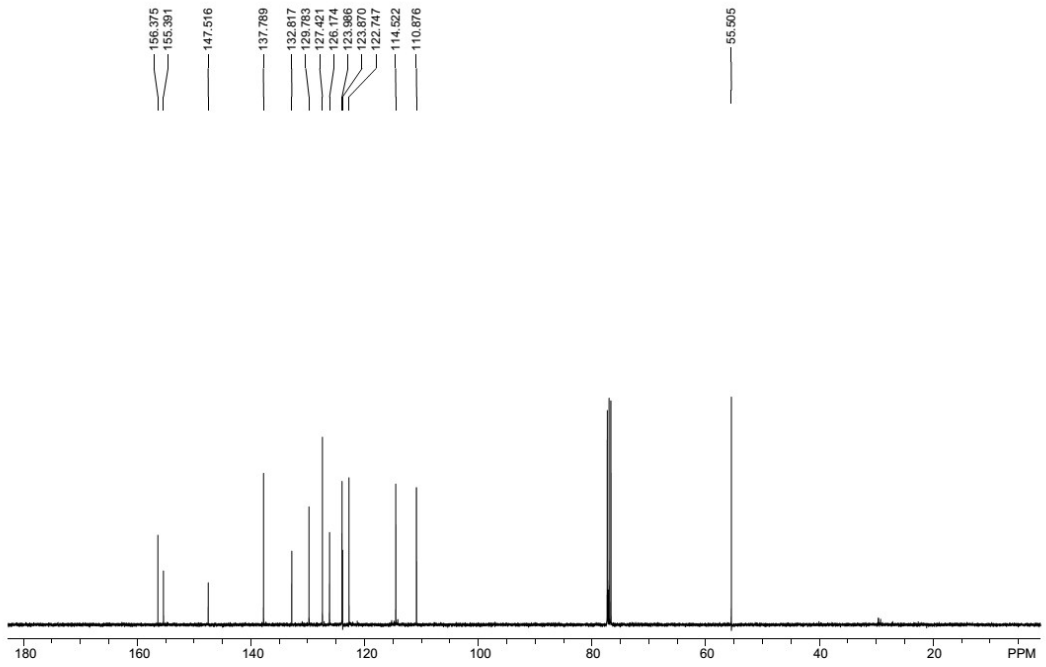
***N*-(p-tolyl)quinolin-2-amine (3ab)**



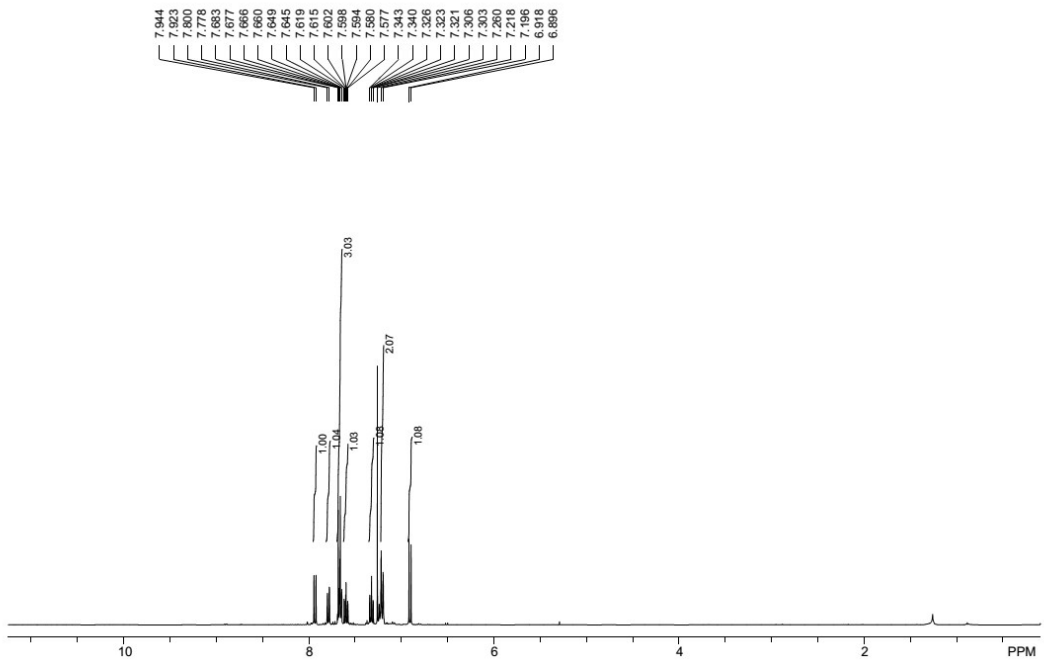


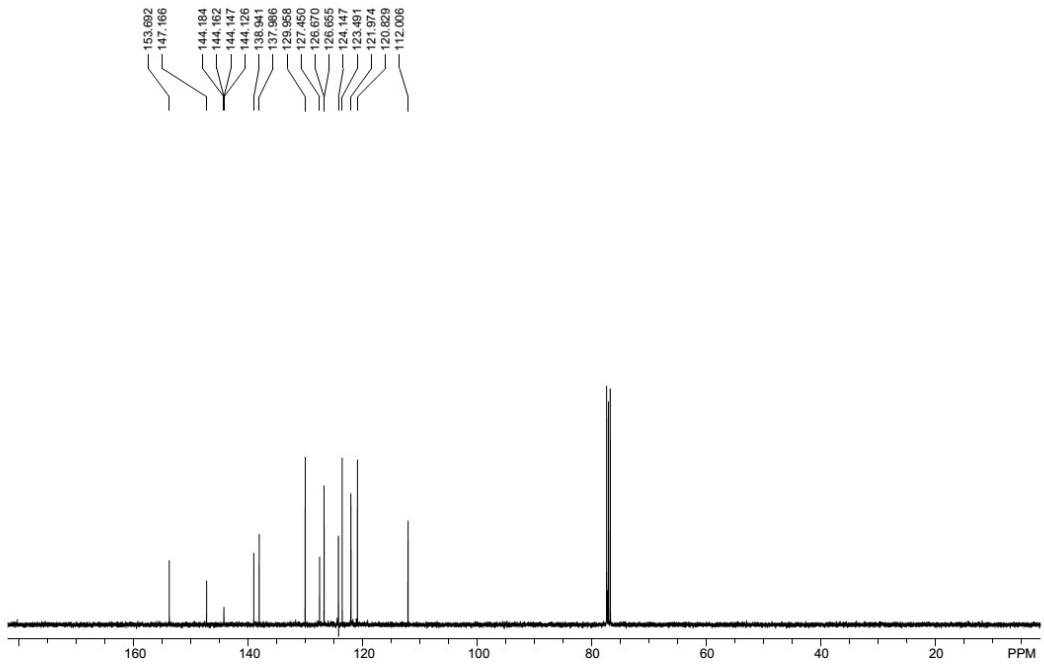
***N*-(4-methoxyphenyl)quinolin-2-amine (3ac)**



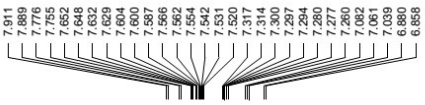


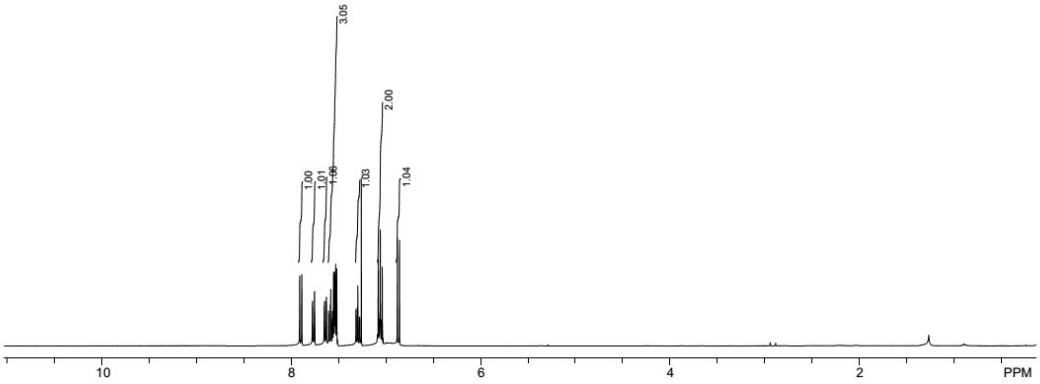
***N*-(4-(trifluoromethoxy)phenyl)quinolin-2-amine (3ad)**

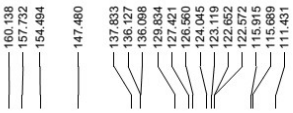


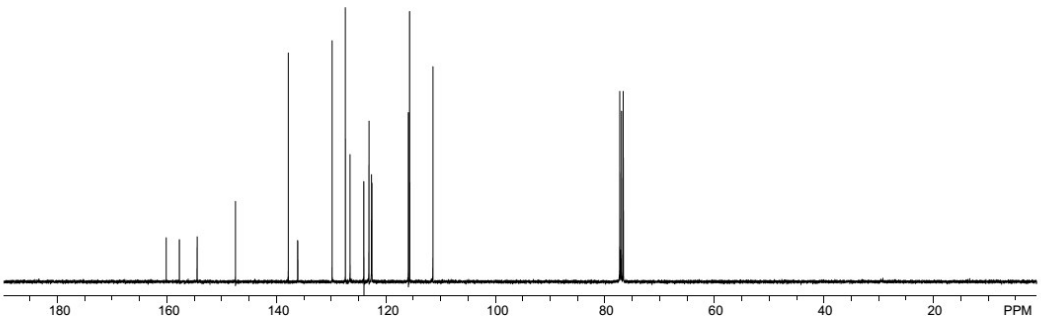


***N*-(4-fluorophenyl)quinolin-2-amine (3ae)**

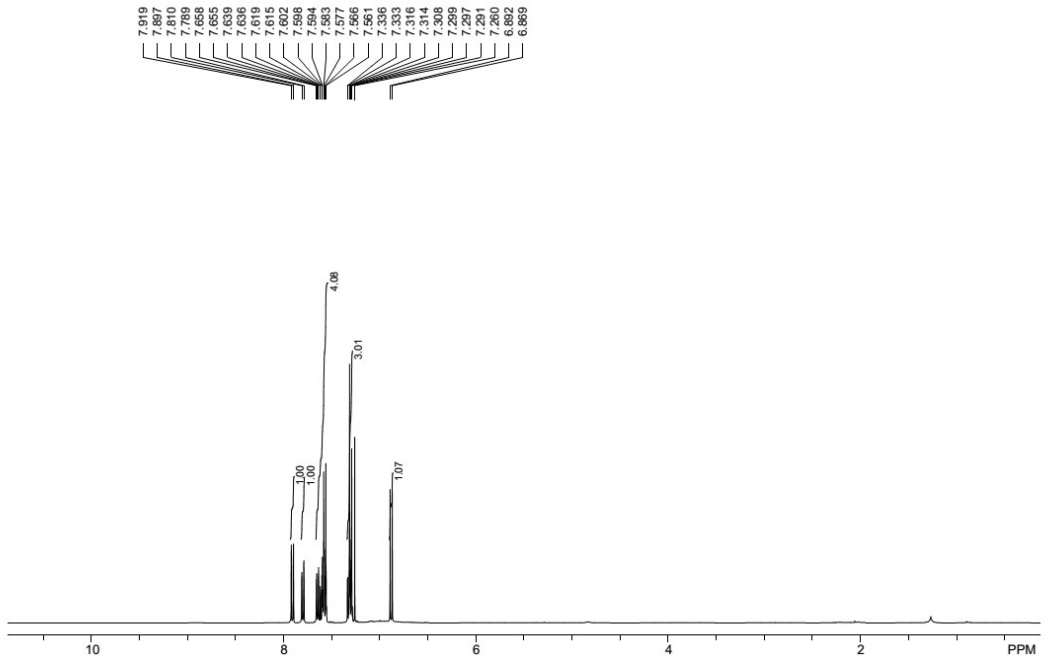


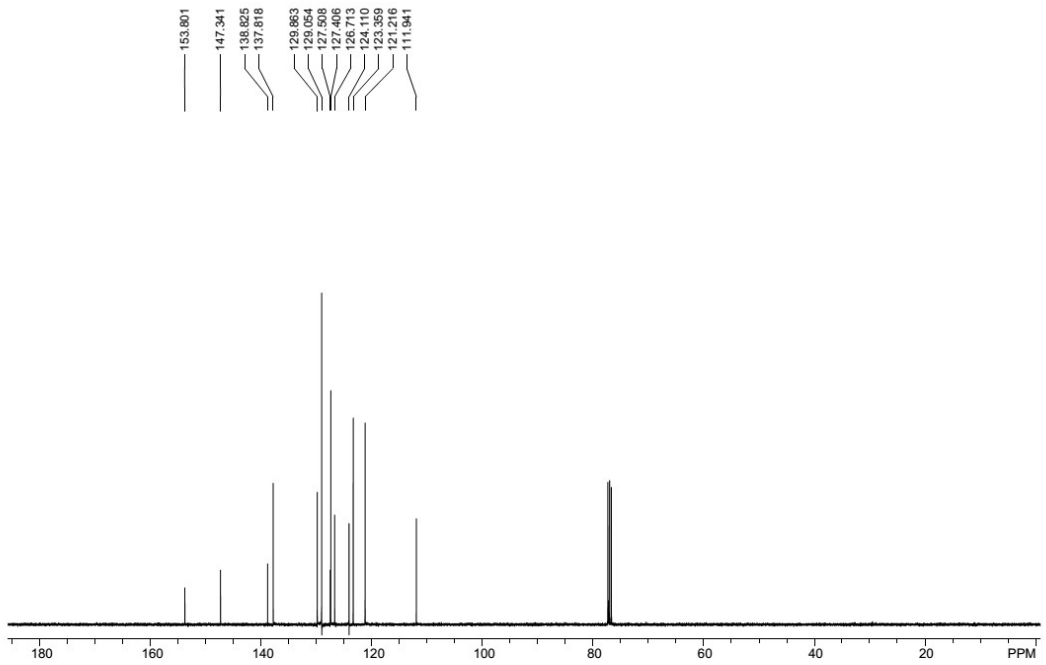




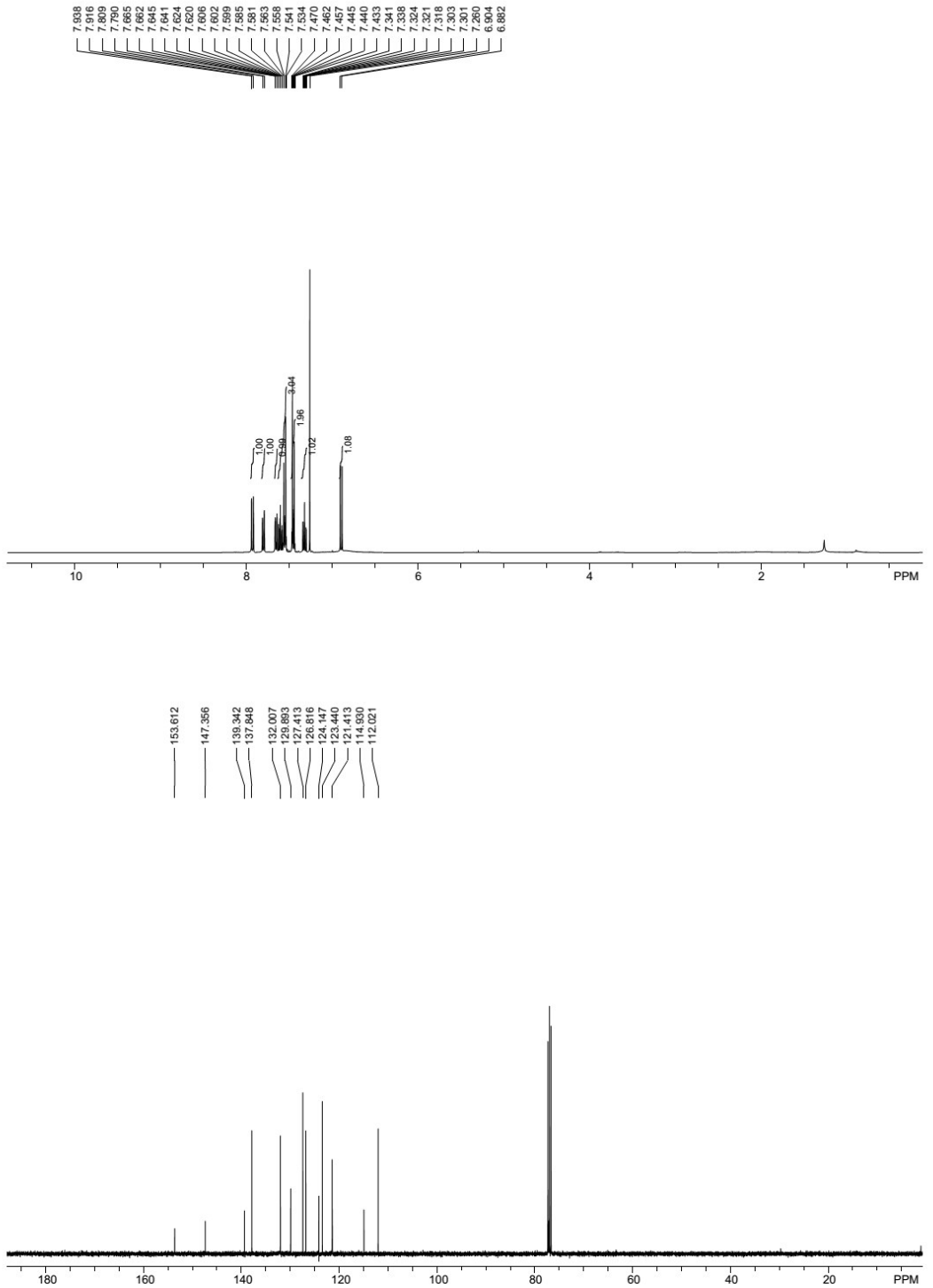


_N_-(4-chlorophenyl)quinolin-2-amine (3af)

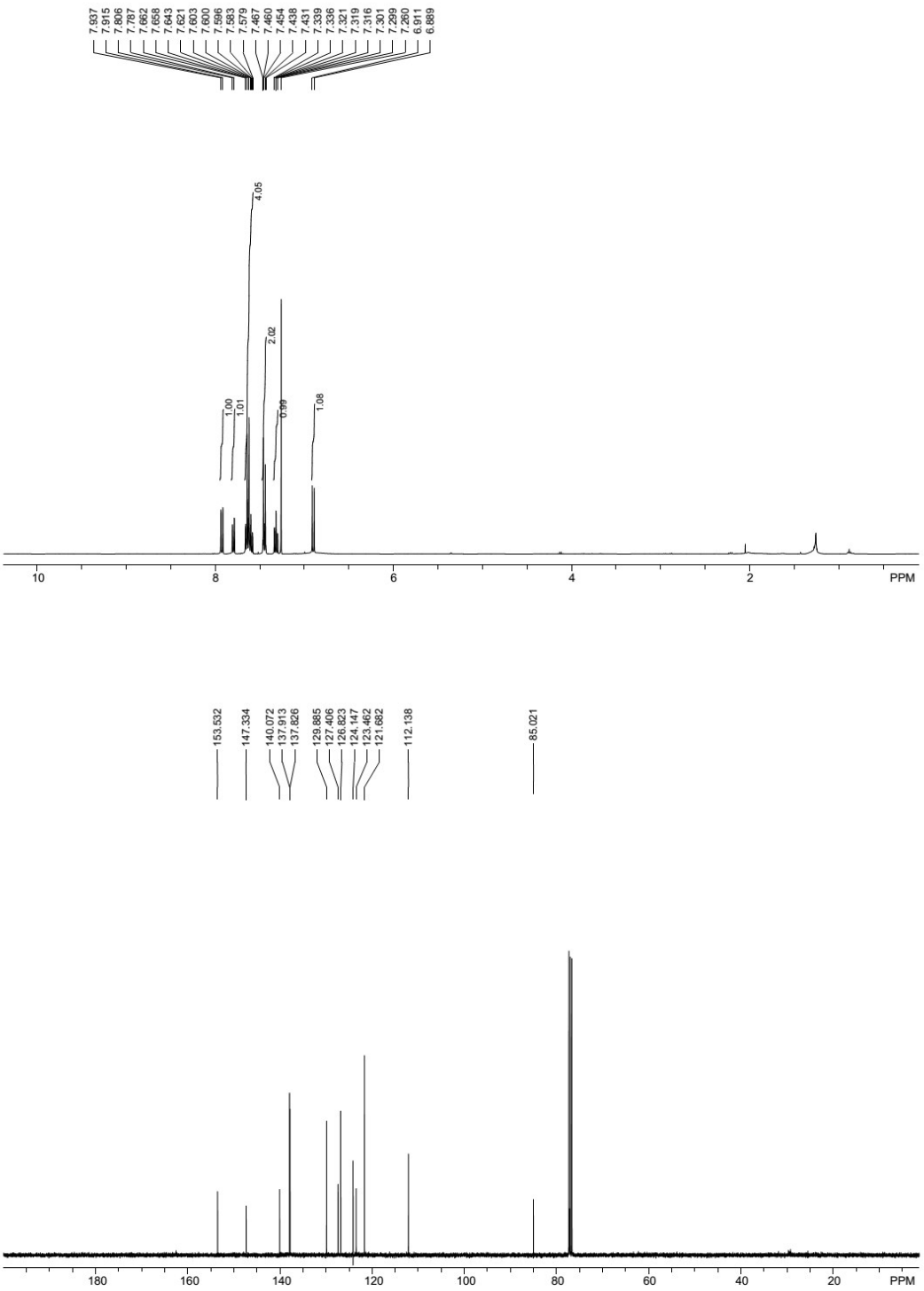




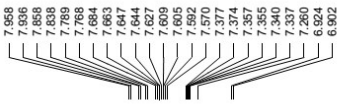
***N*-(4-bromophenyl)quinolin-2-amine (3ag)**

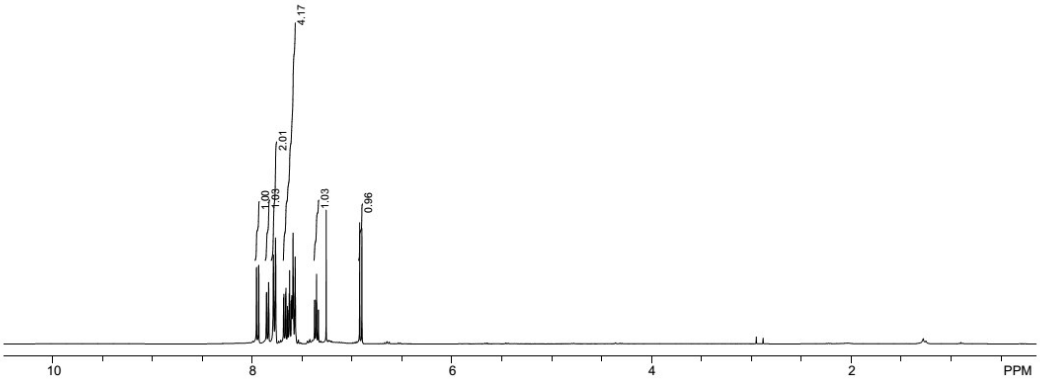


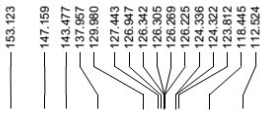
***N*-(4-iodophenyl)quinolin-2-amine (3ah)**

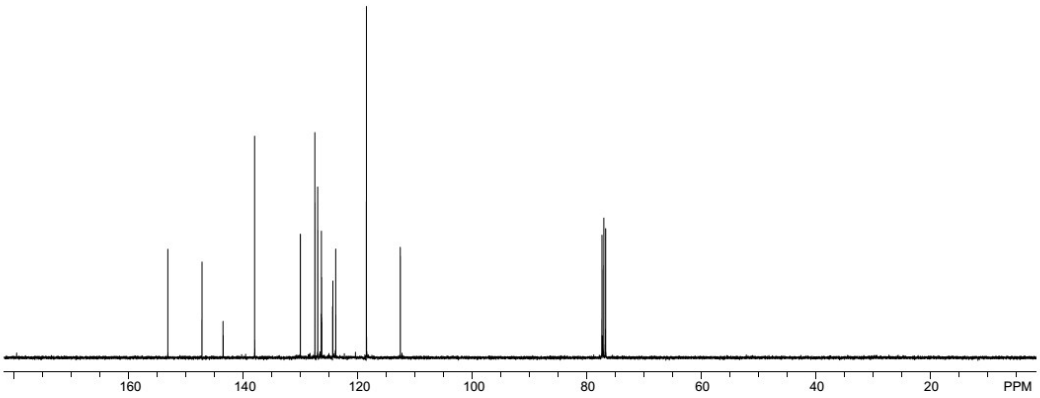


***N*-(4-(trifluoromethyl)phenyl)quinolin-2-amine (3ai)**

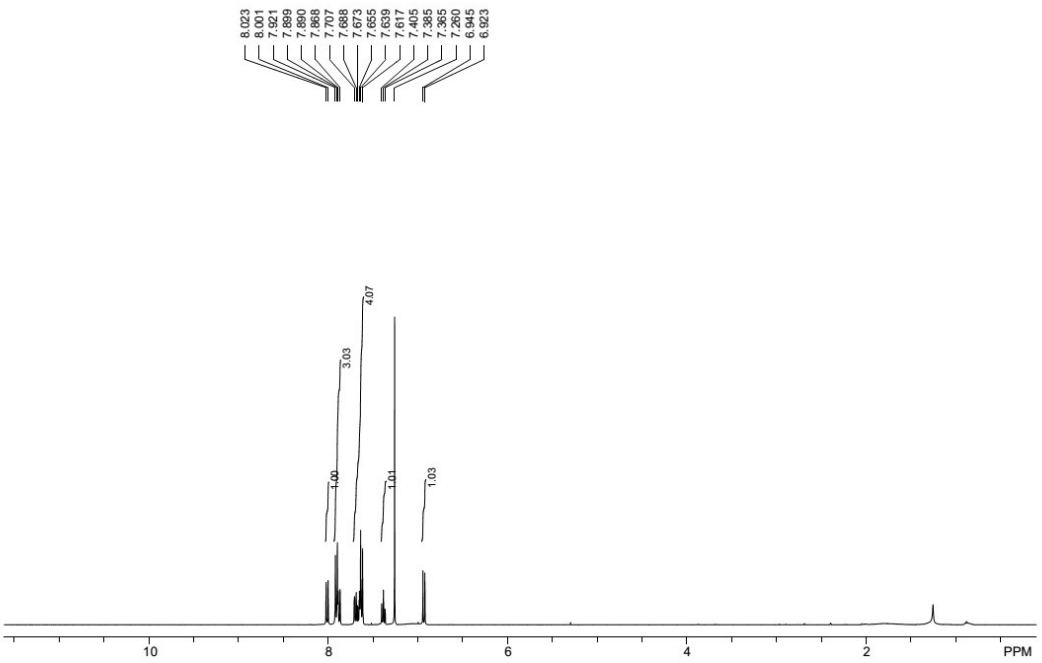


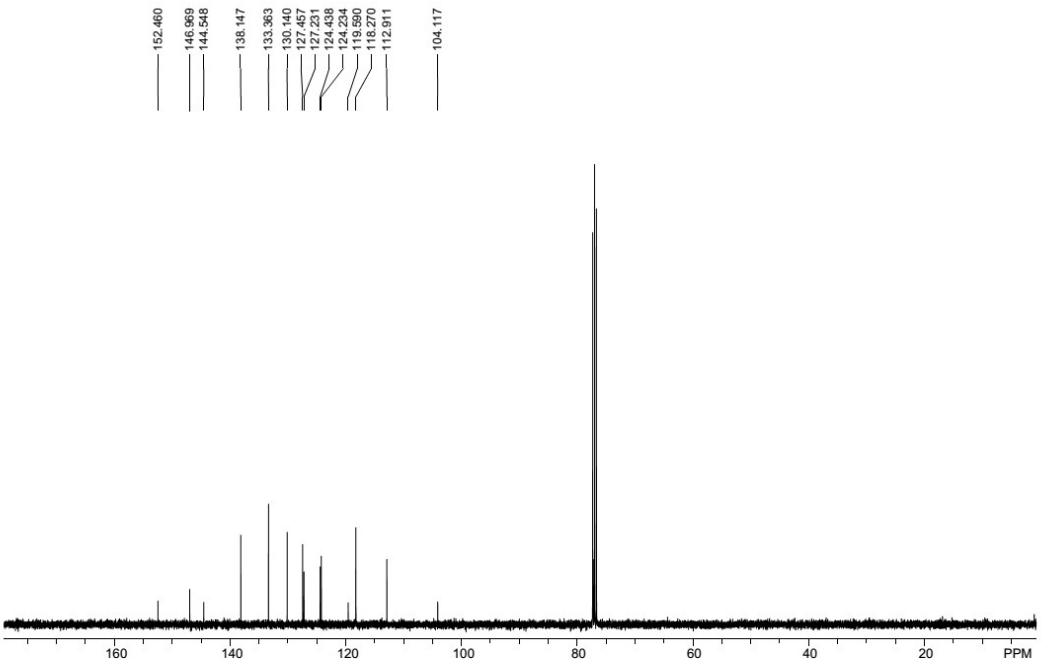




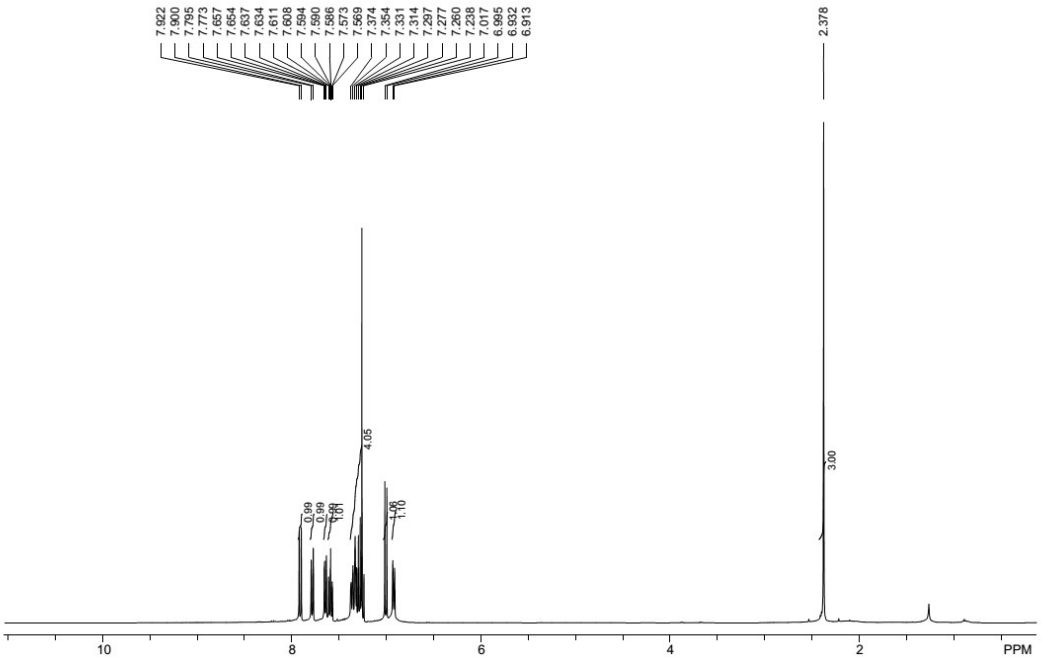


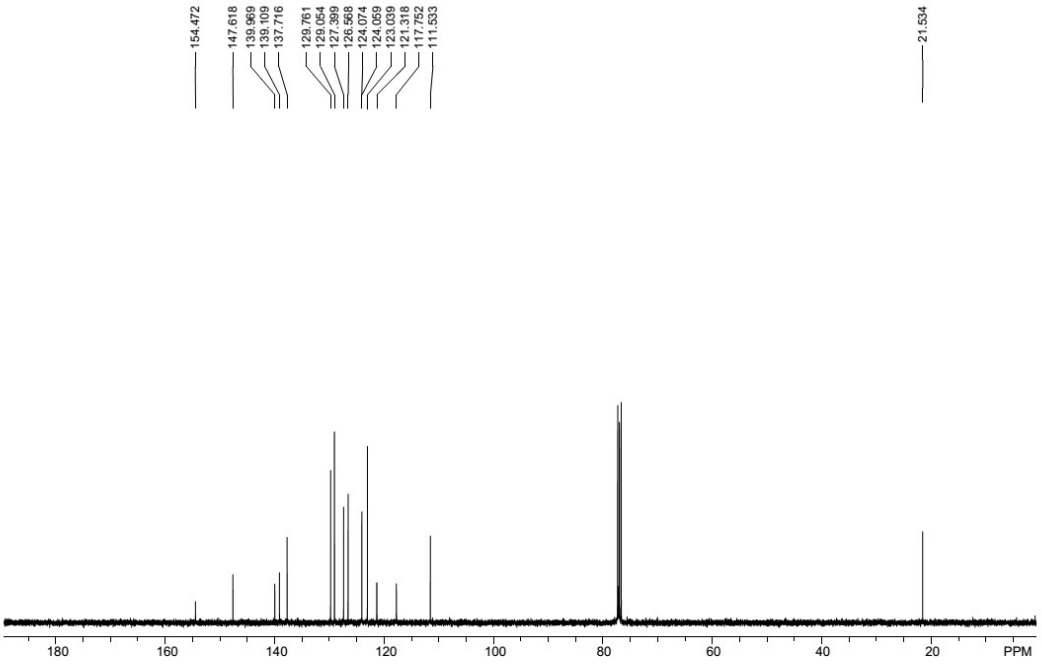
4-(quinolin-2-ylamino)benzonitrile (3aj)



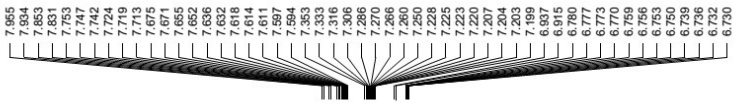


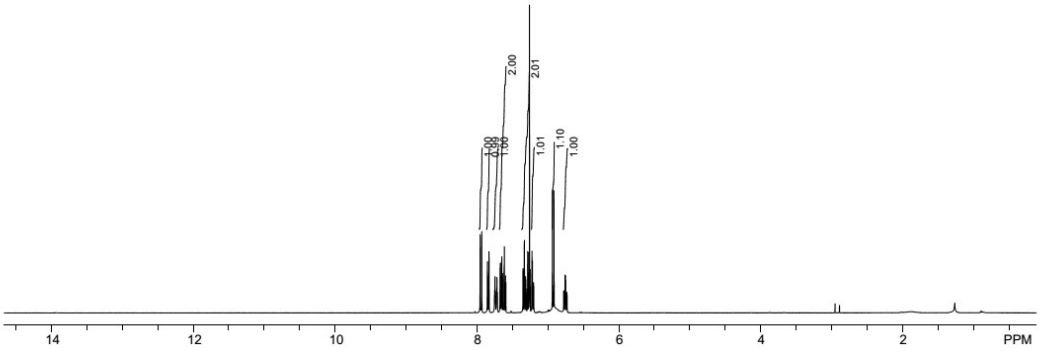
***N*-(m-tolyl)quinolin-2-amine (3ak)**

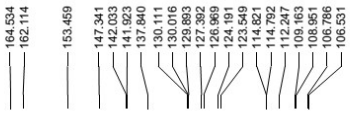


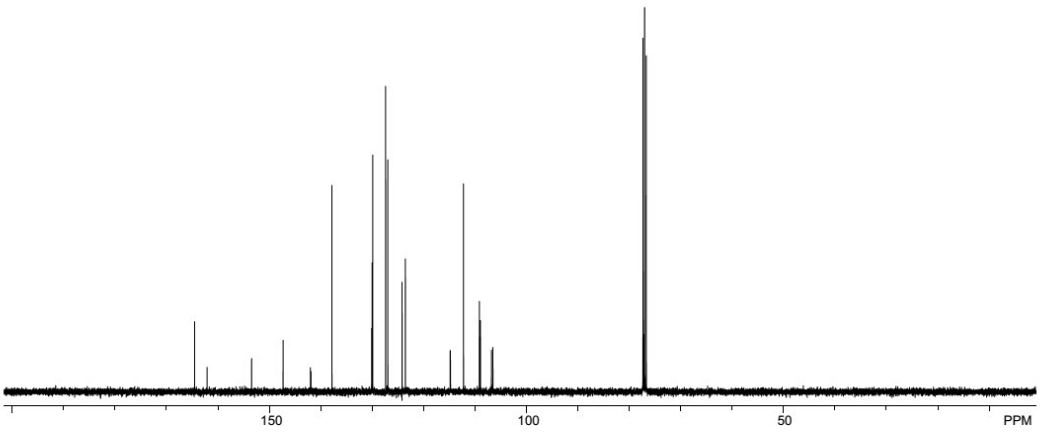


***N*-(3-fluorophenyl)quinolin-2-amine (3al)**

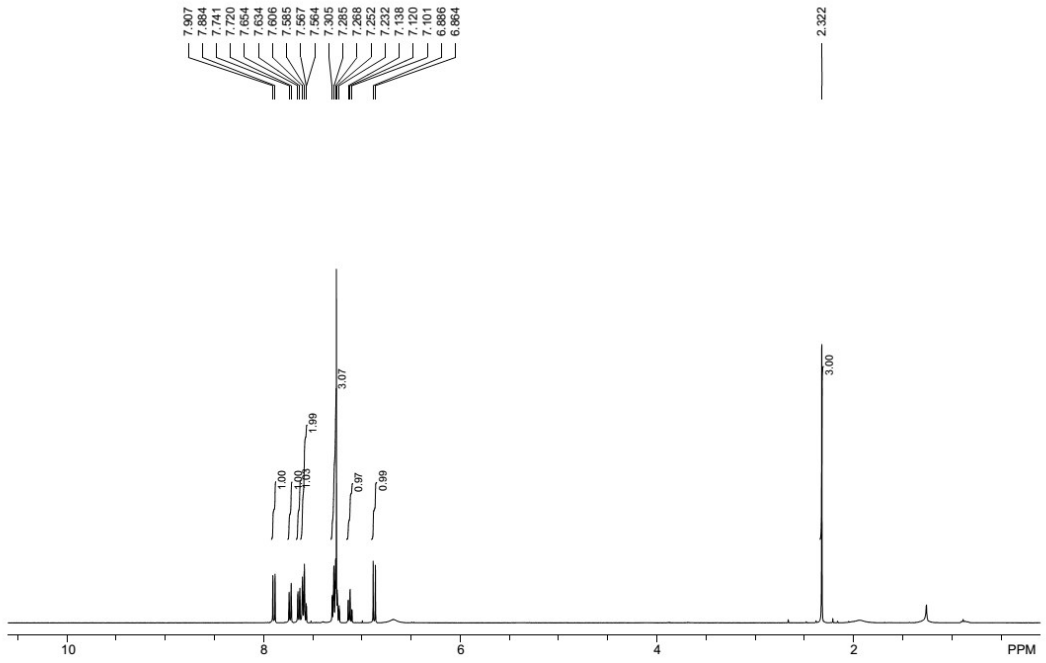


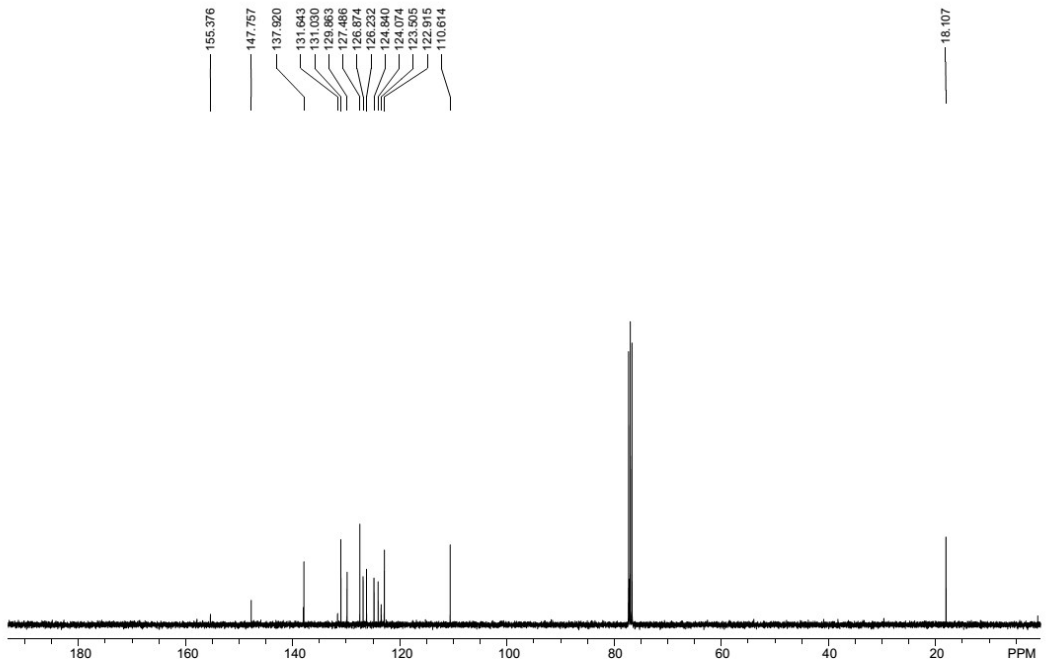




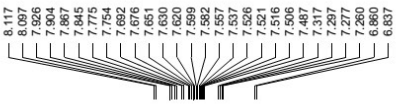


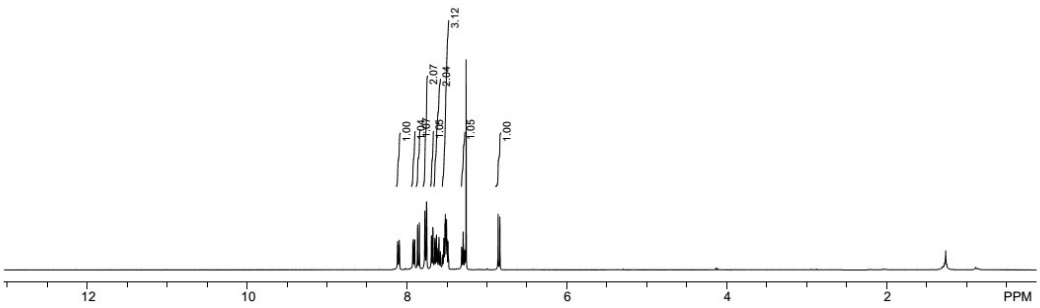
_N_-(o-tolyl)quinolin-2-amine (3am)

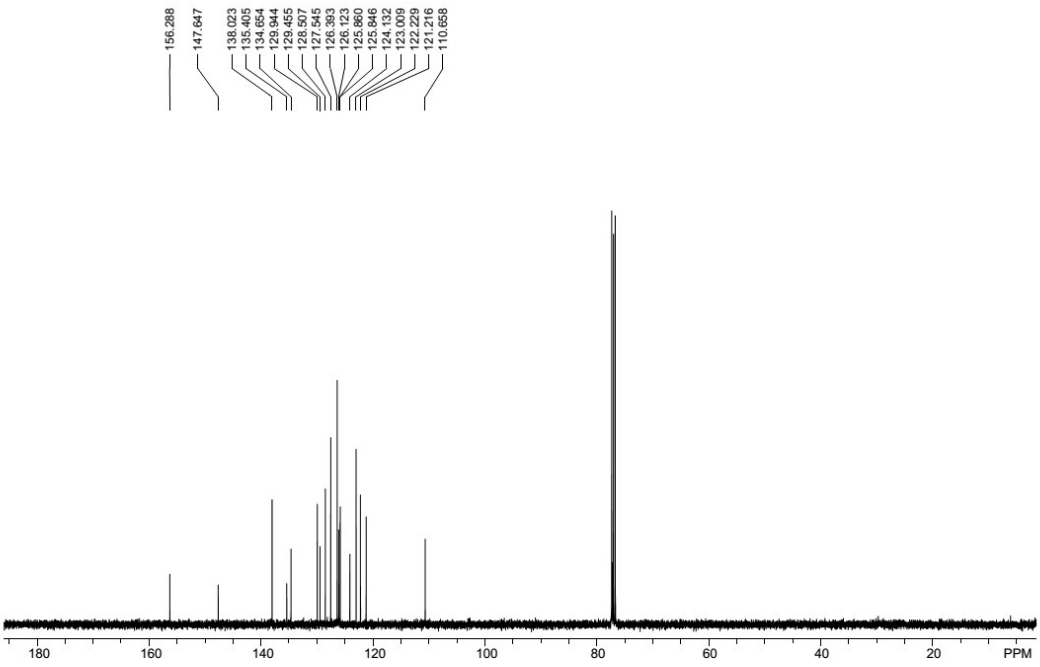




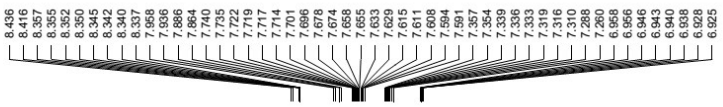
_N_-(naphthalen-1-yl)quinolin-2-amine (3an)

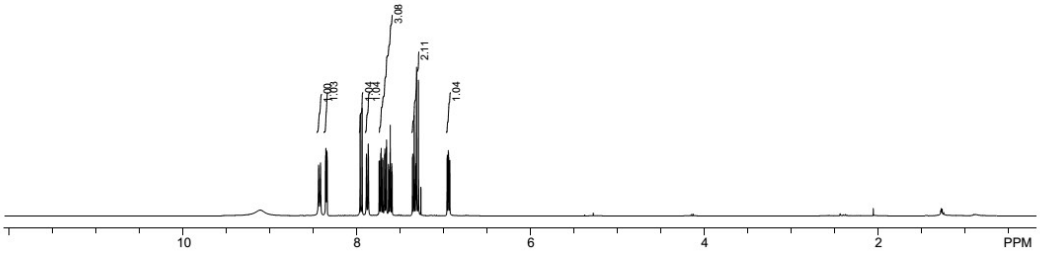


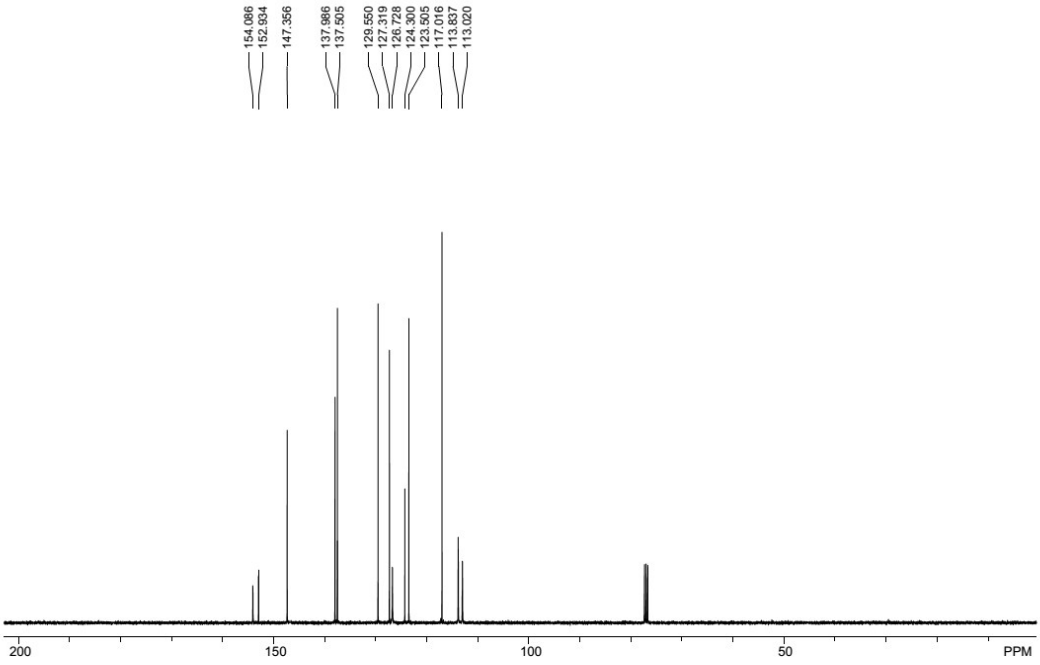




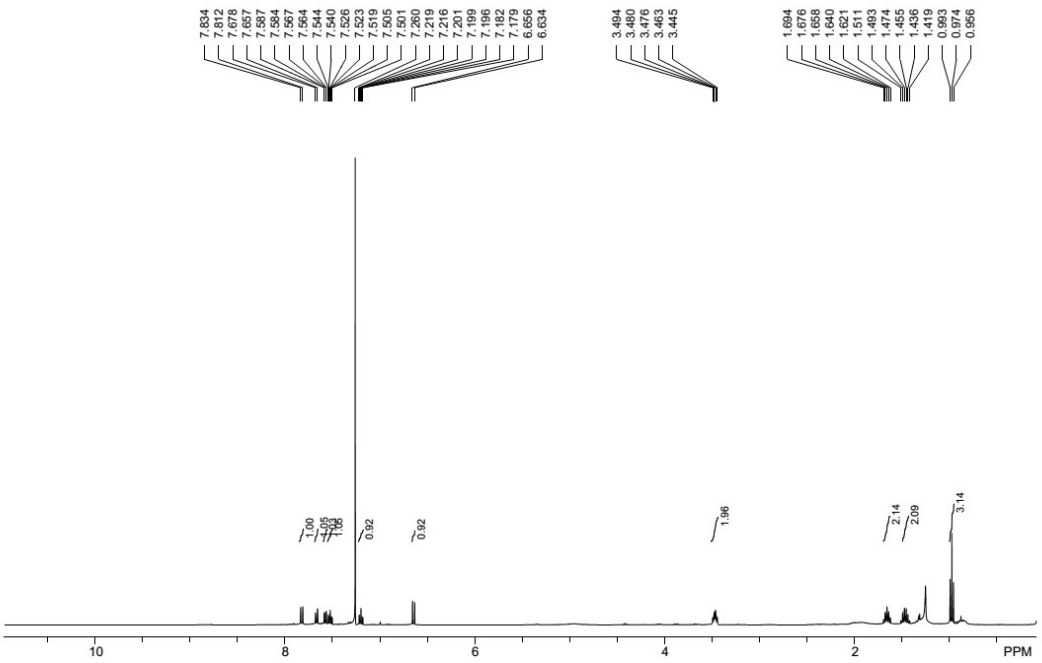
***N*-(pyridin-2-yl)quinolin-2-amine (3ao)**

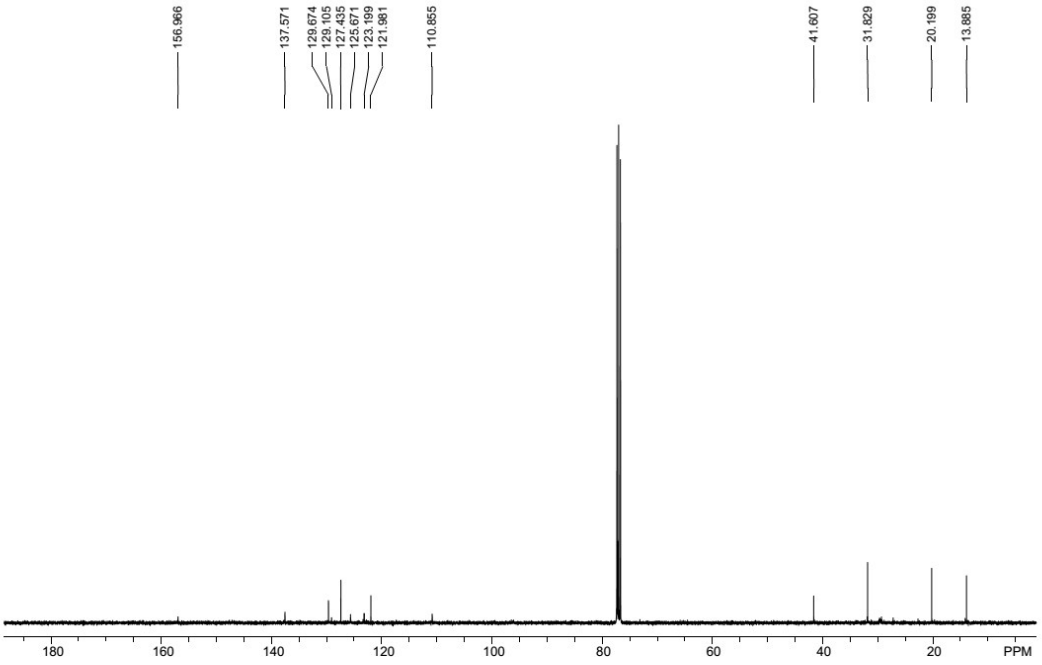




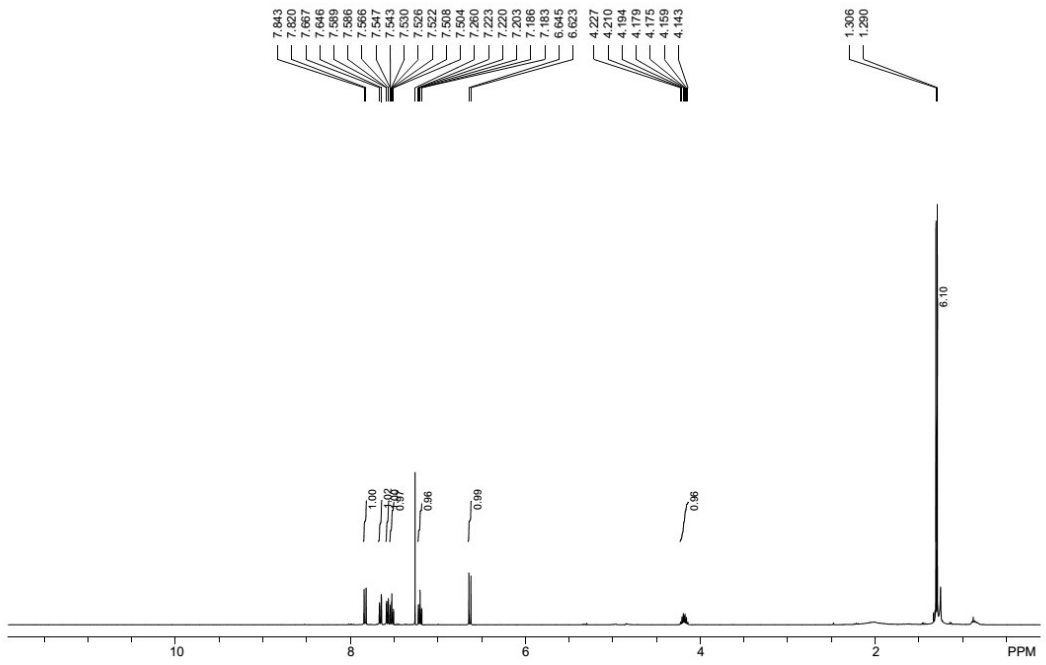


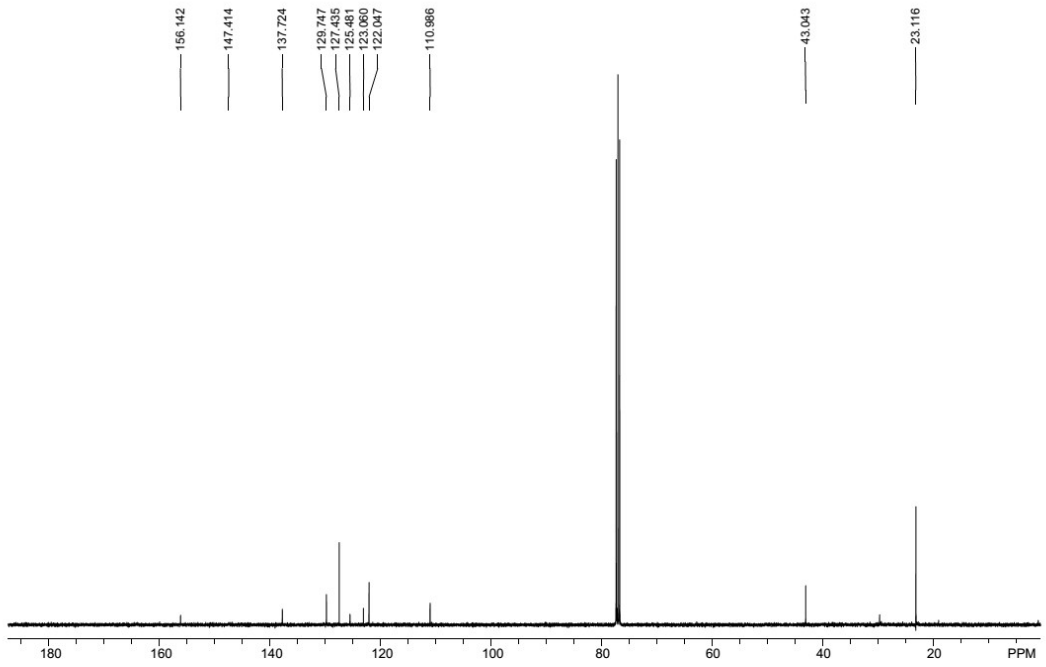
***N*-butylquinolin-2-amine (3ap)**



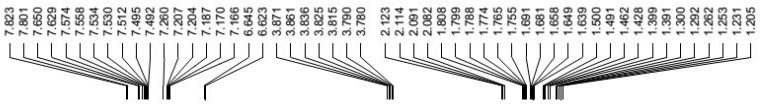


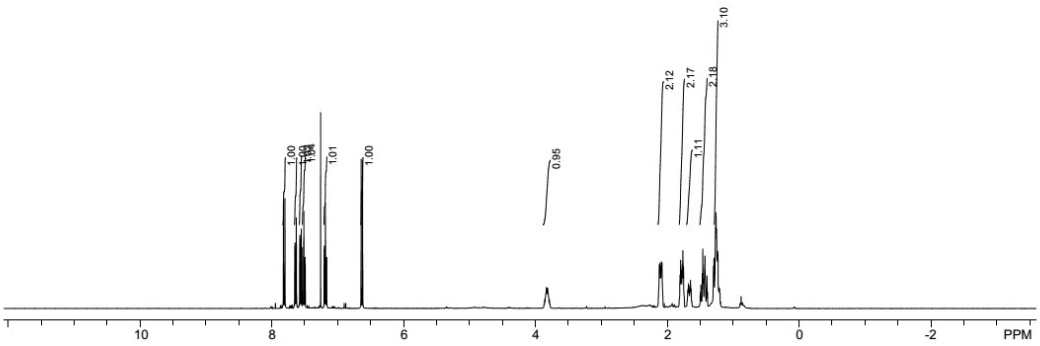
***N*-isopropylquinolin-2-amine (3aq)**

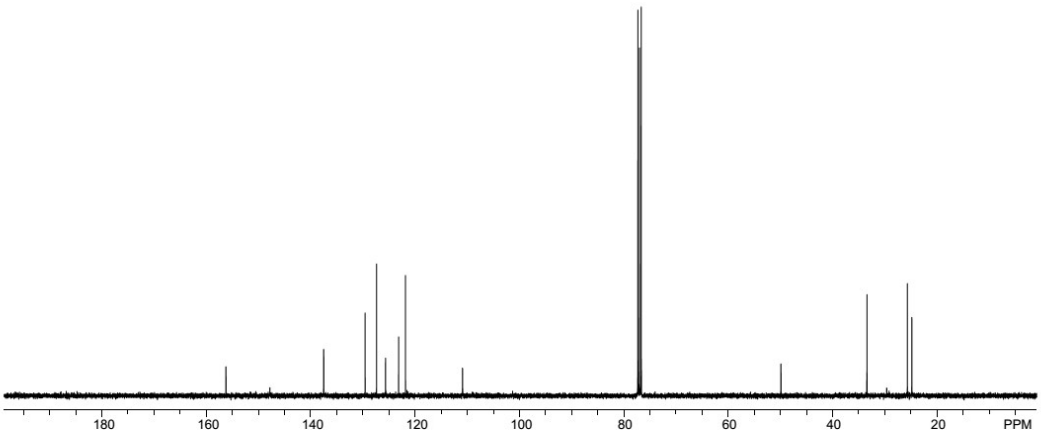




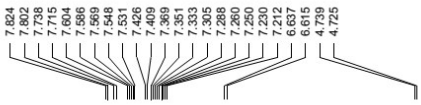
_N_-cyclohexylquinolin-2-amine (3ar)







***N*-benzylquinolin-2-amine (3as)**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7.586
7.569
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7.531
7.426
7.409
7.369
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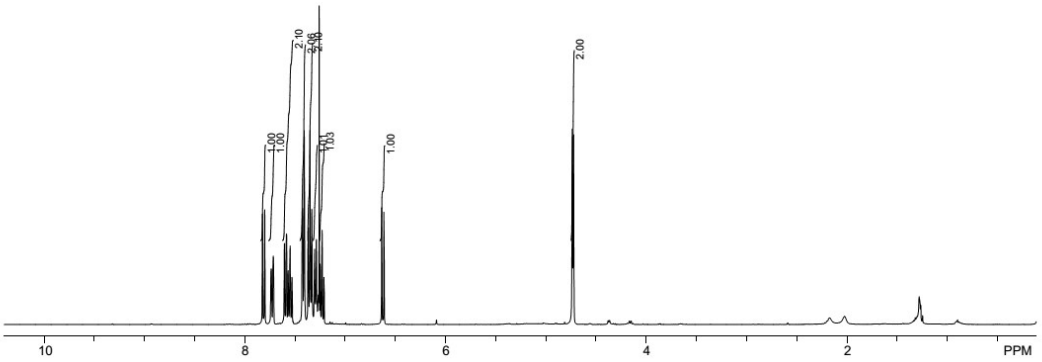
7.212
6.637
6.615
4.739
4.725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1.00
2.10
2.06
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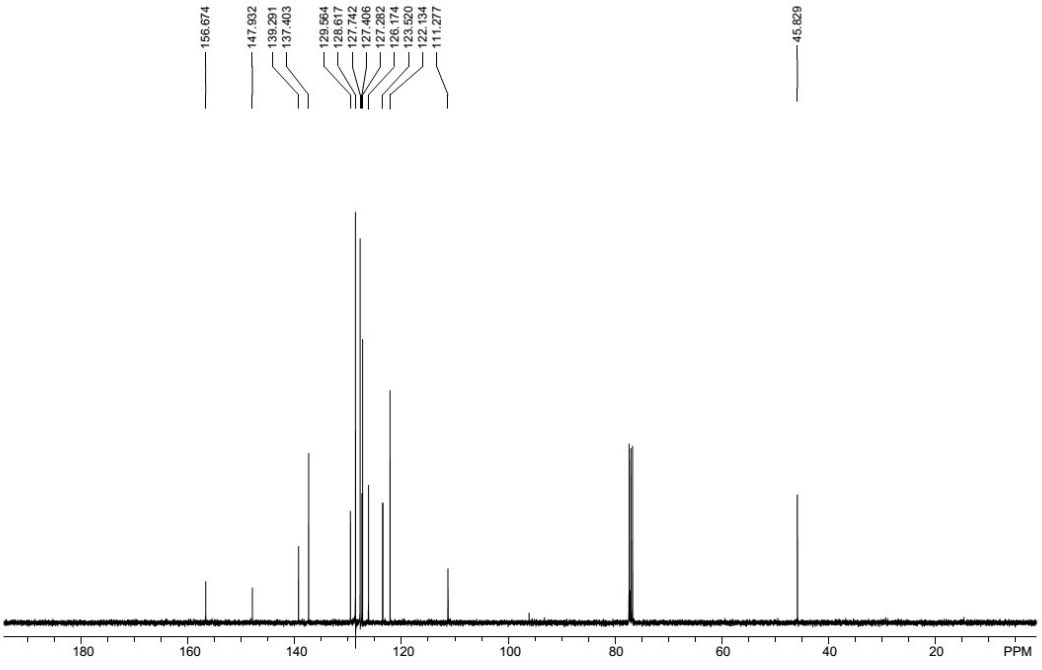
1.01
1.03
1.00
2.00
10
8
6
4
2
PPM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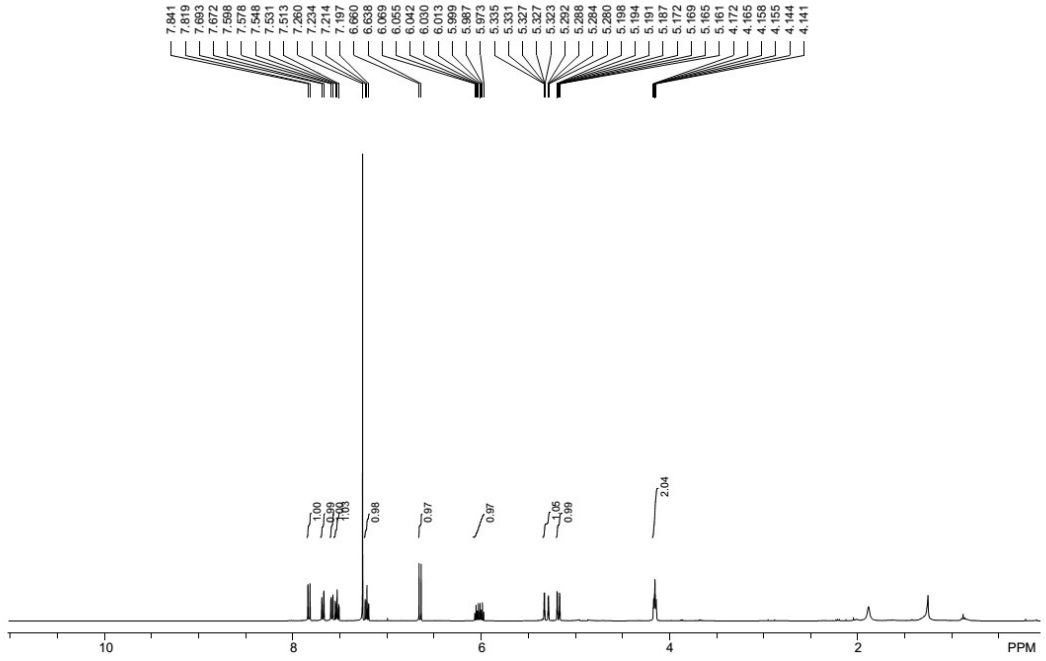
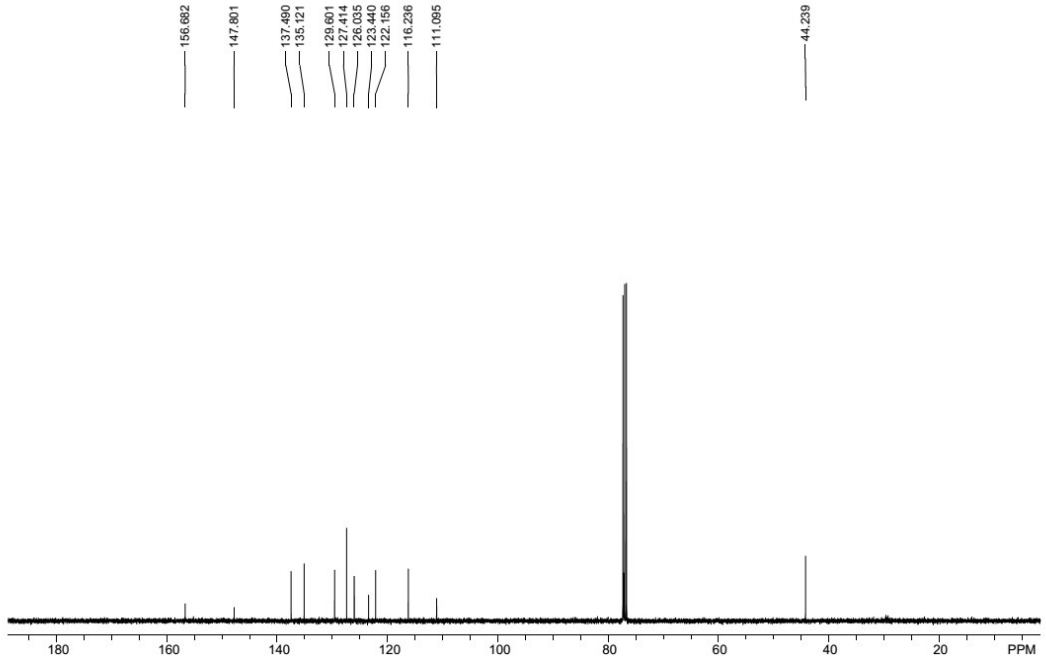
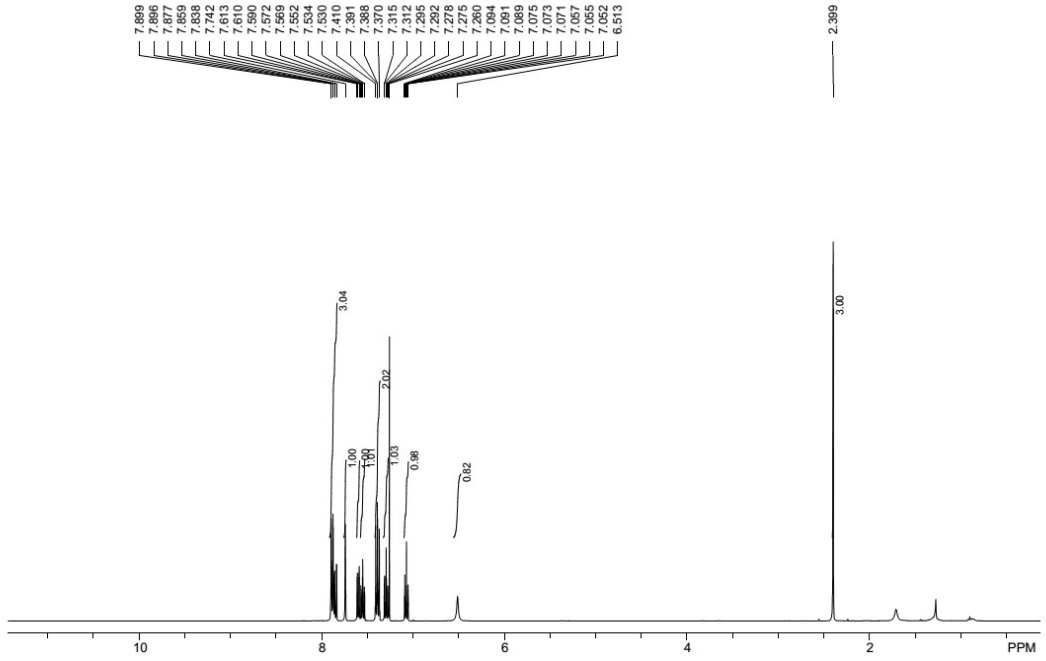
126.174
123.520
122.134
111.277
45.829
180
160
140
120
100
80
60
40
20
PPM

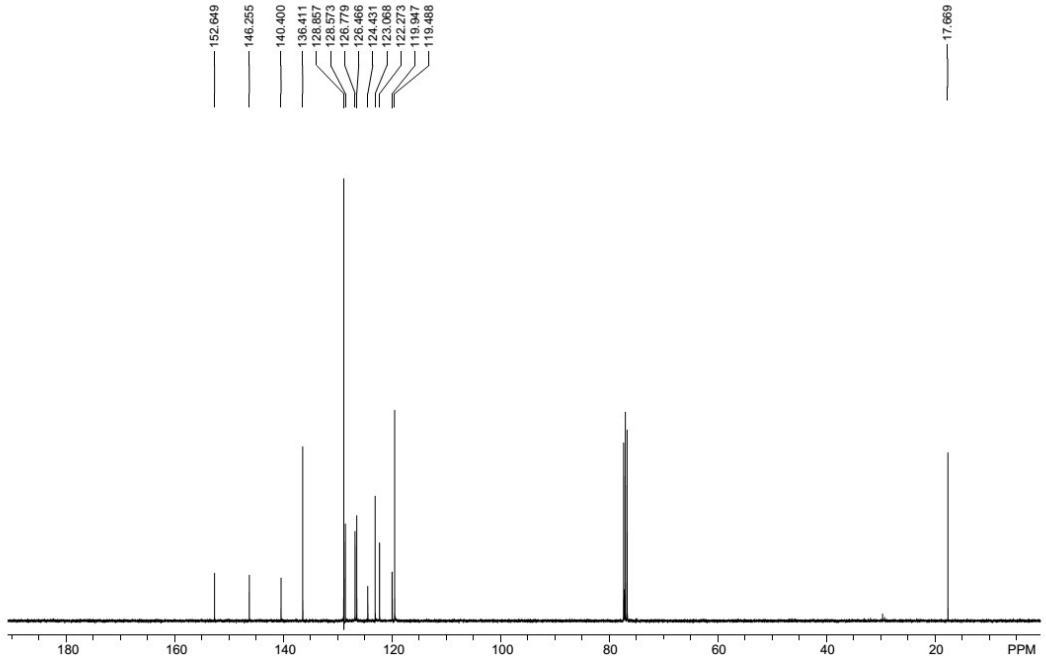
***N*-allylquinolin-2-amine (3at)**



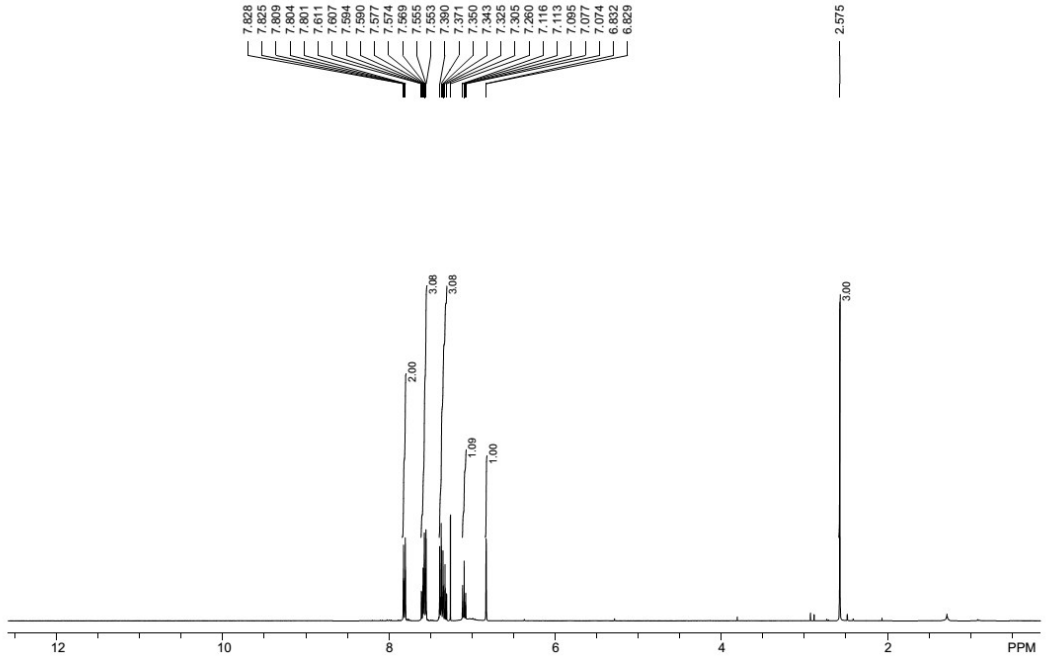


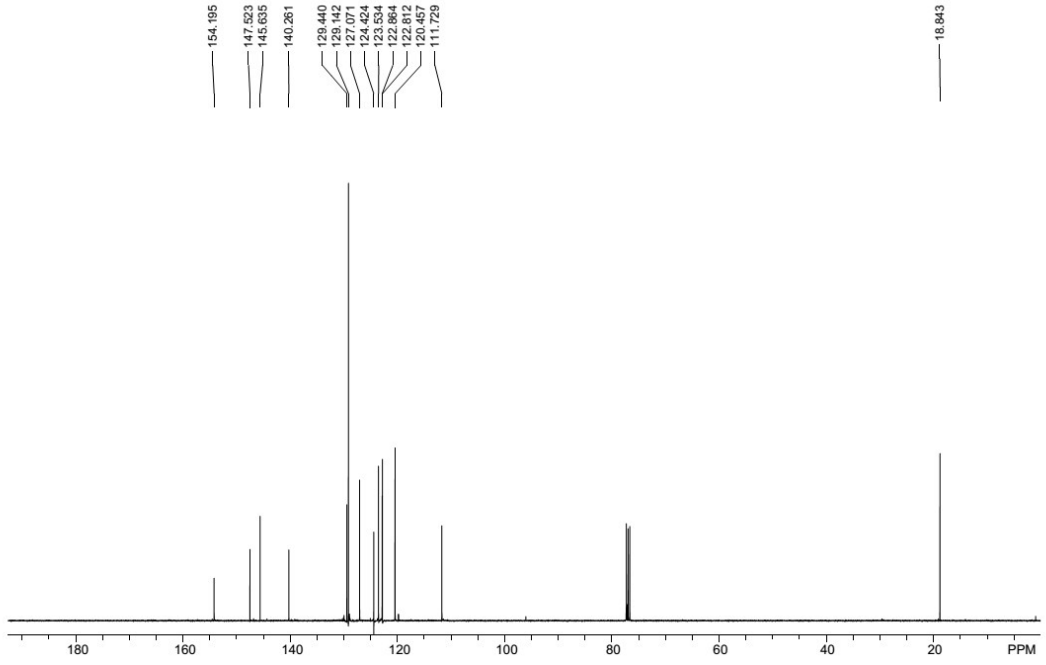
3-methyl-*N*-phenylquinolin-2-amine (3ba)



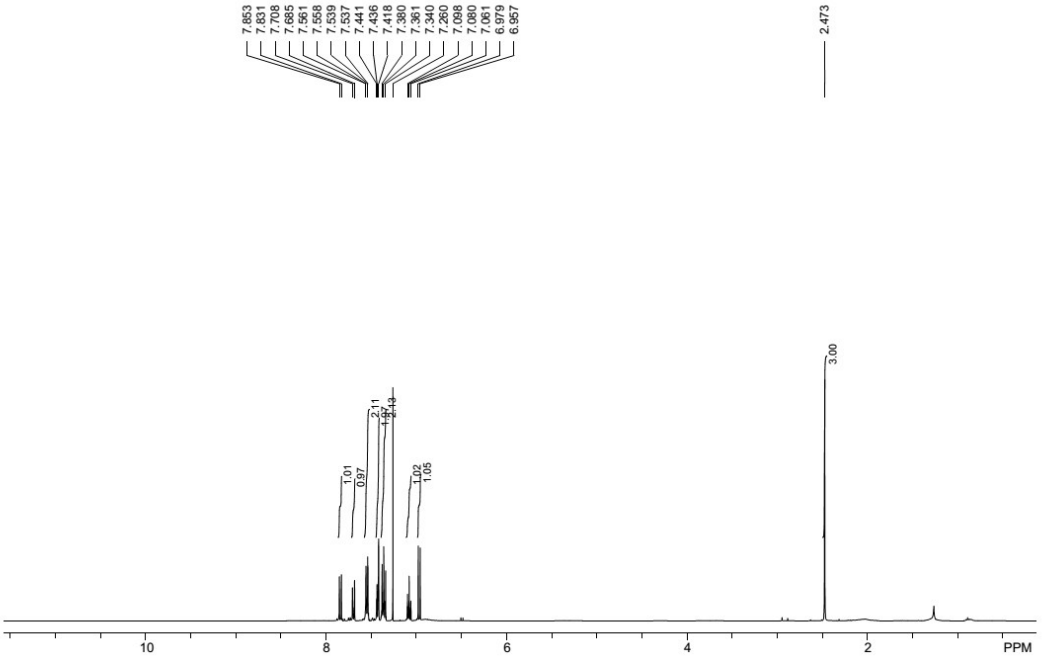


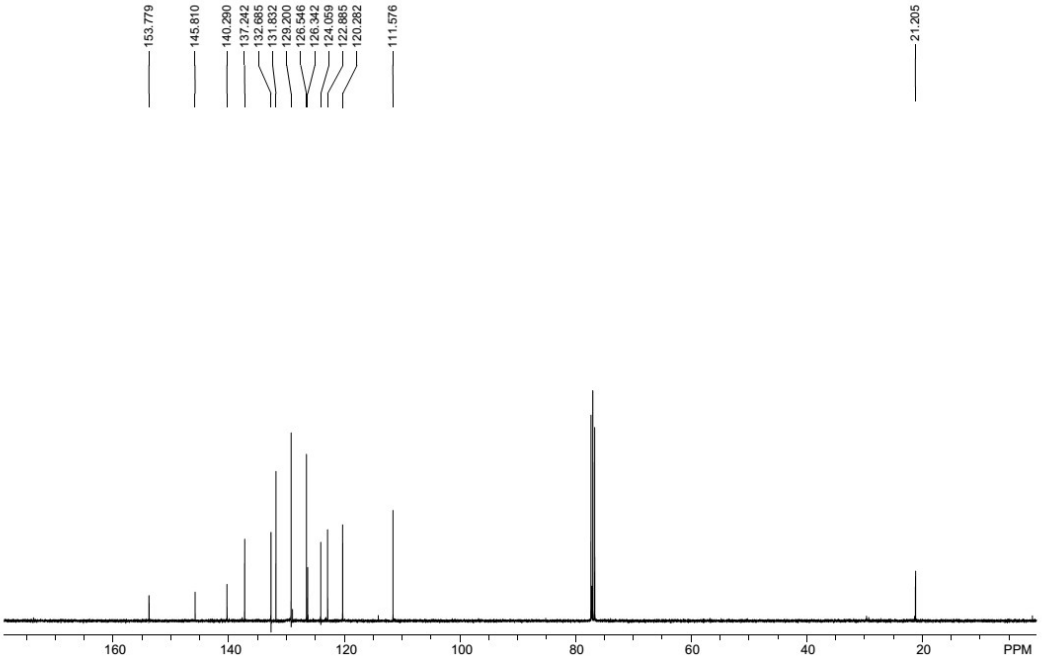
4-methyl-*N*-phenylquinolin-2-amine (3ca)



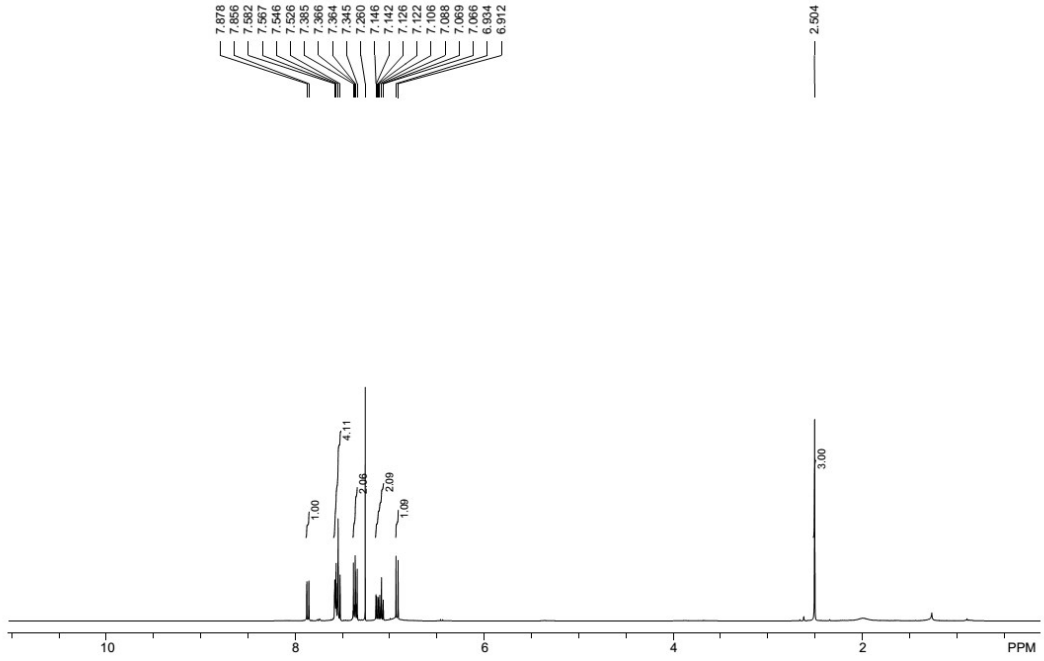


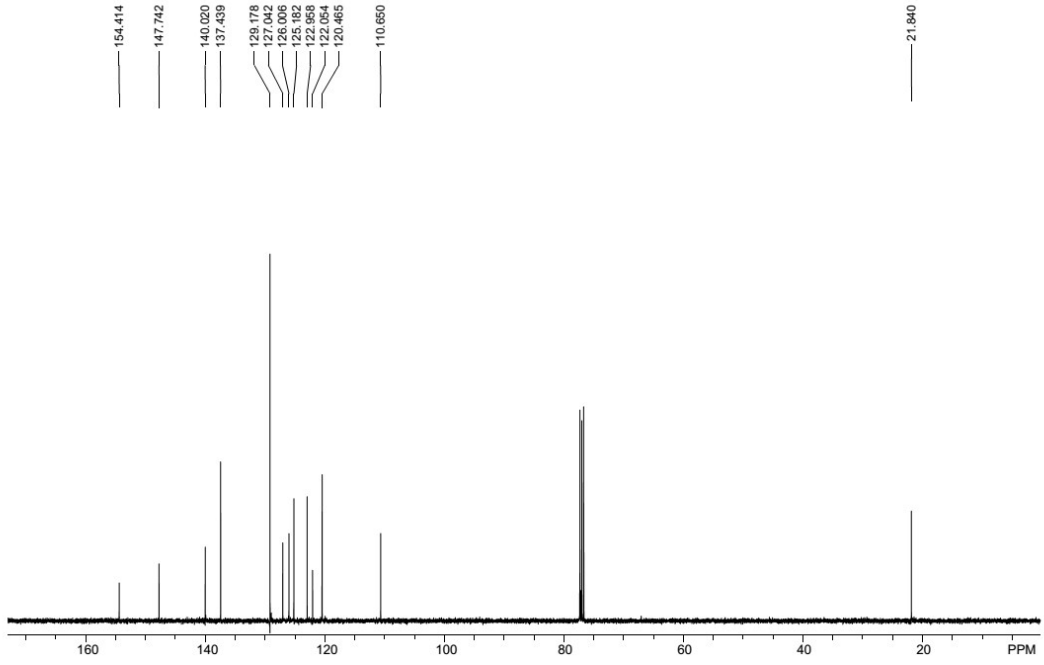
6-methyl-*N*-phenylquinolin-2-amine (3da)



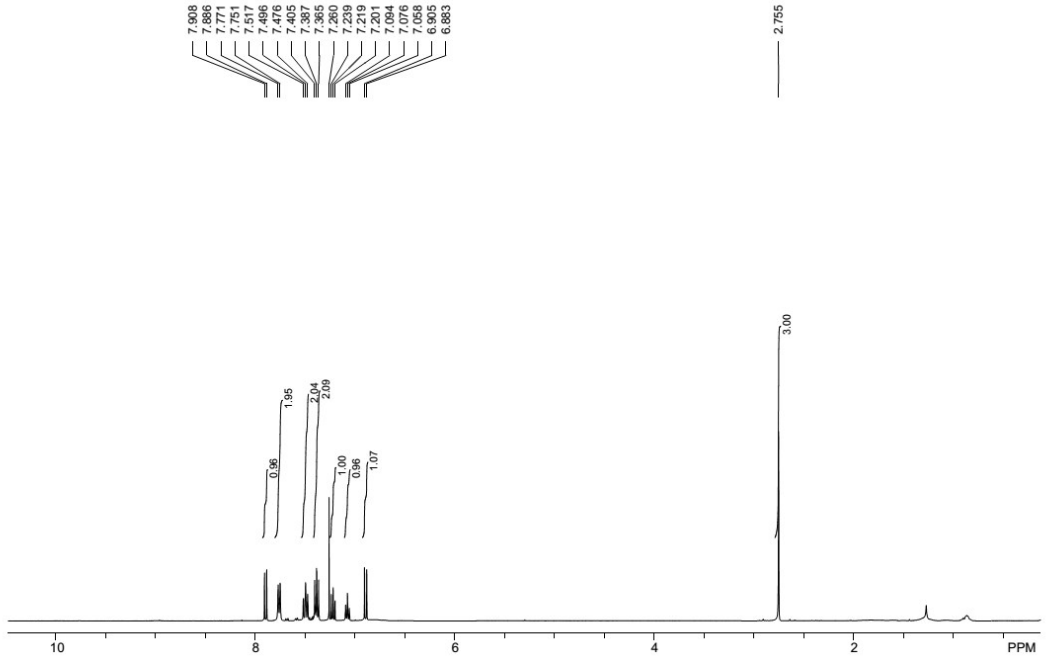


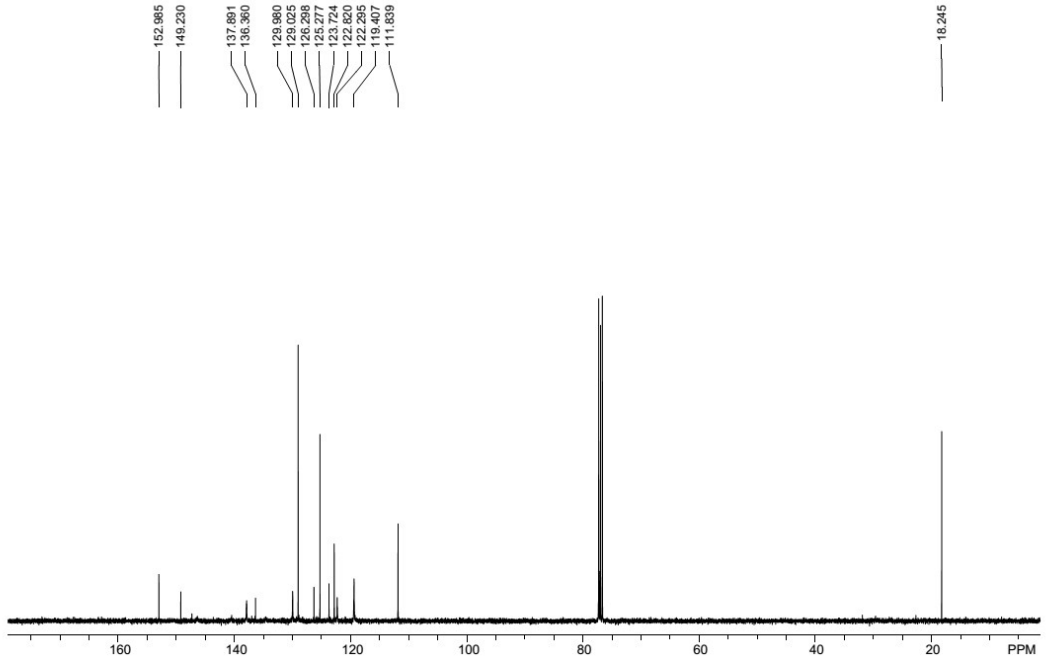
7-methyl-*N*-phenylquinolin-2-amine (3ea)



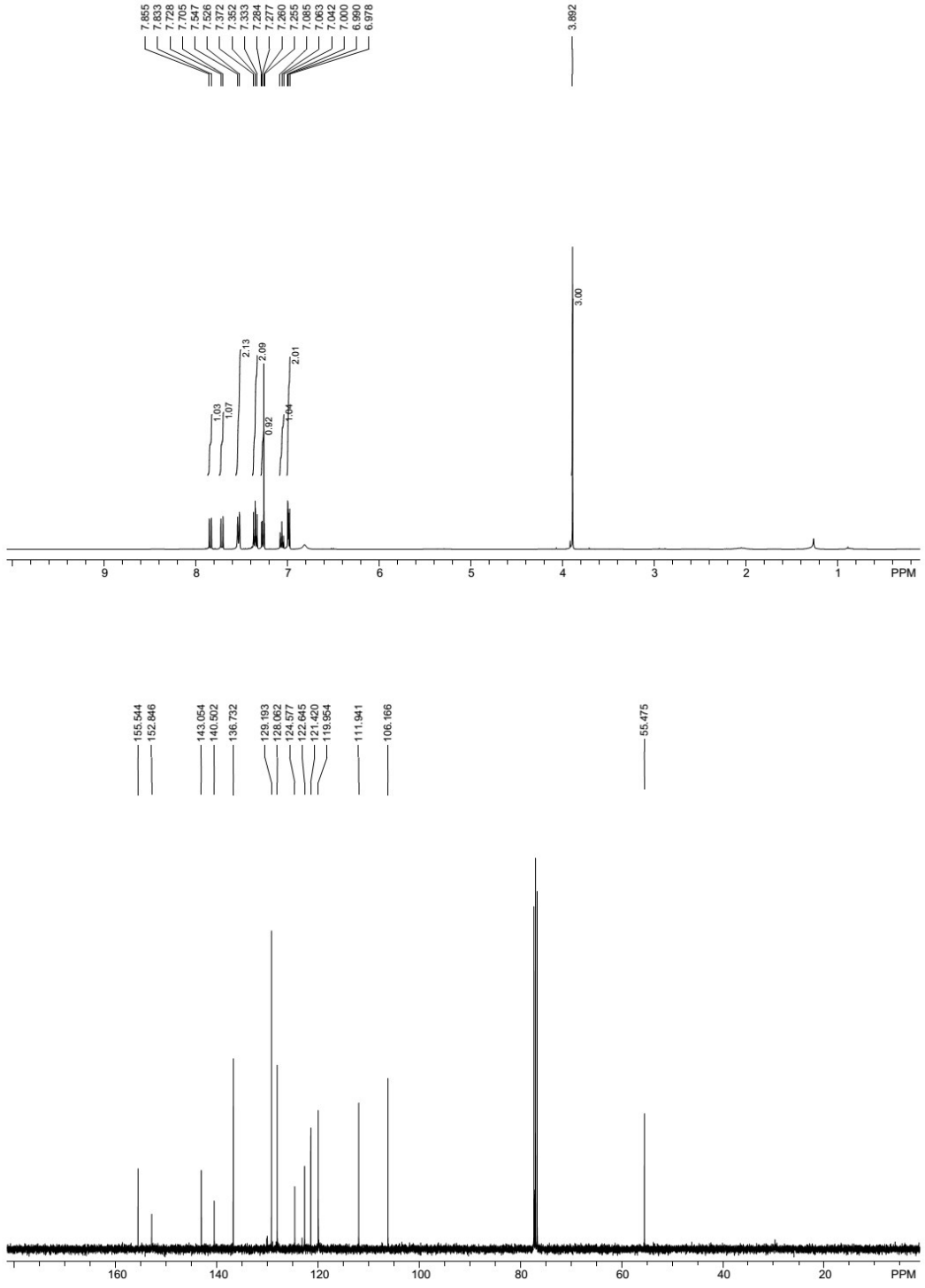


8-methyl-*N*-phenylquinolin-2-amine (3fa)

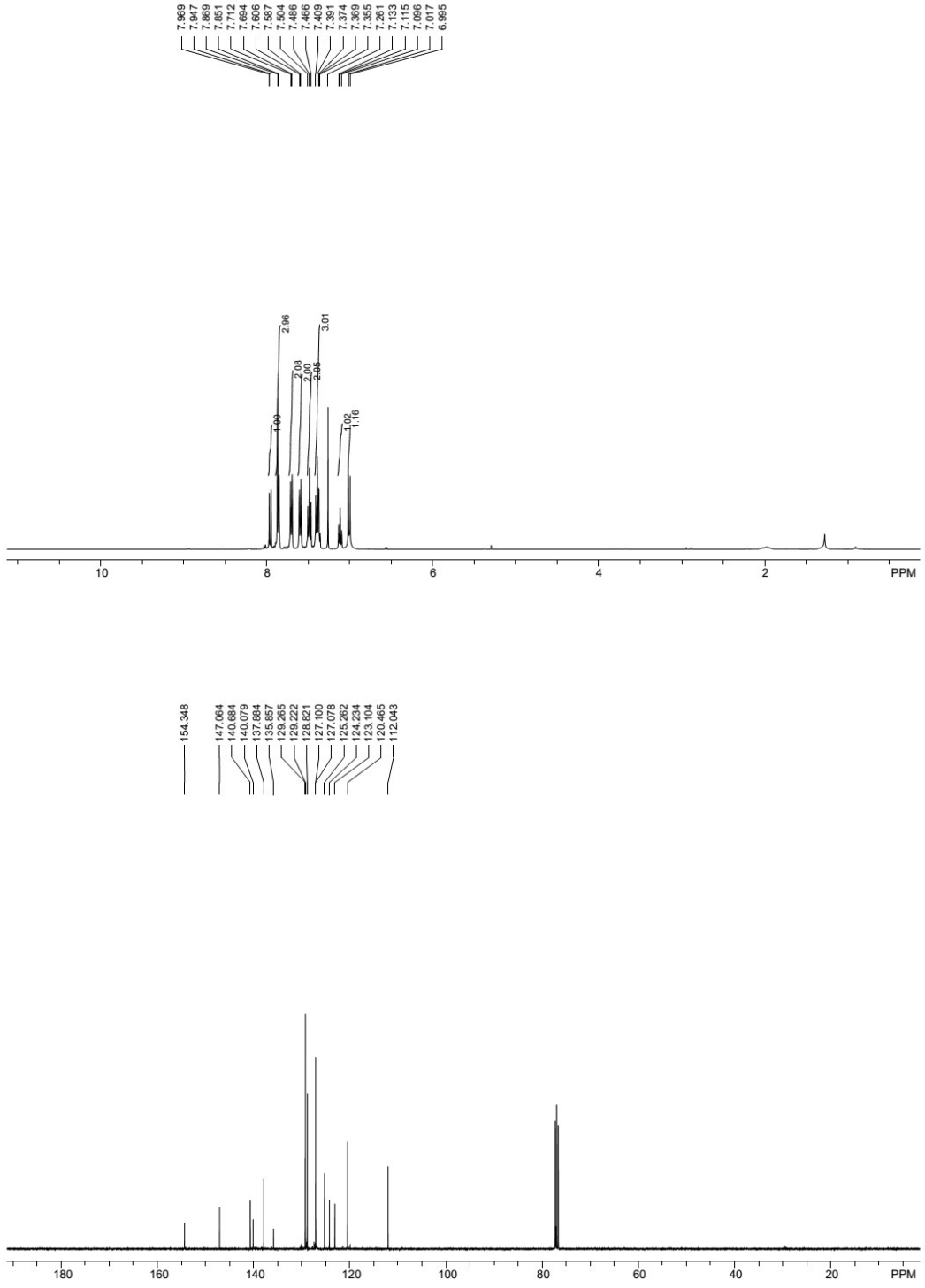




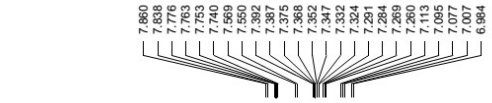
6-methoxy-*N*-phenylquinolin-2-amine (3ga)

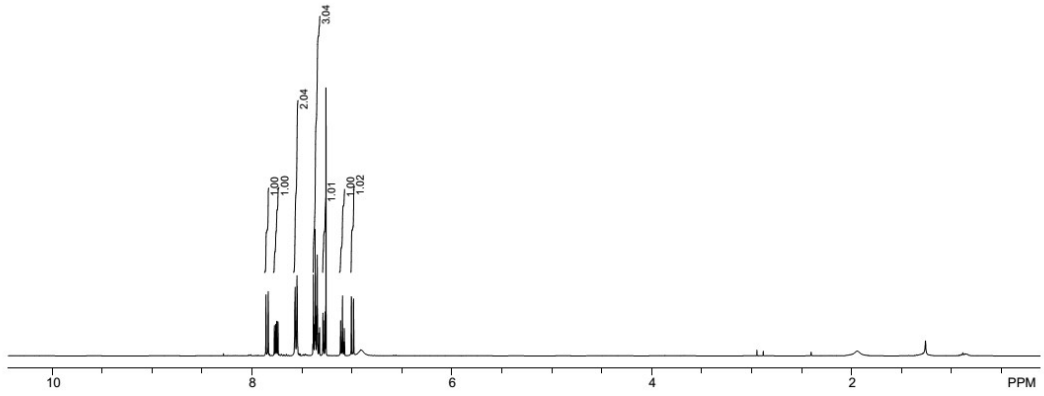


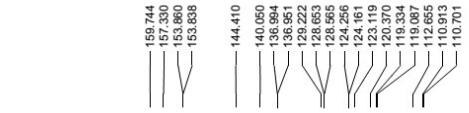
***N*,6-diphenylquinolin-2-amine (3ha)**

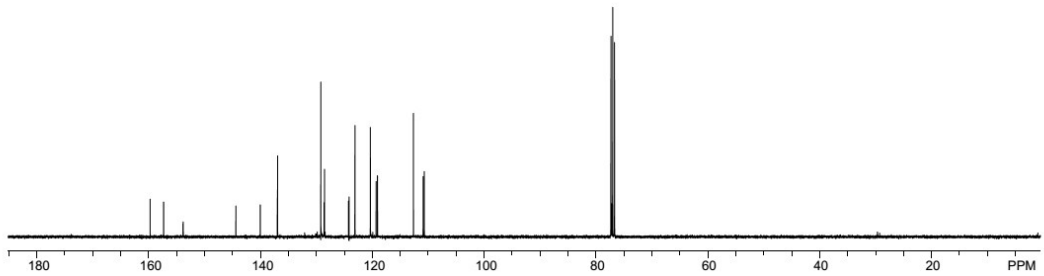


6-fluoro-*N*-phenylquinolin-2-amine (3ia)

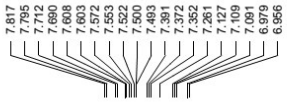


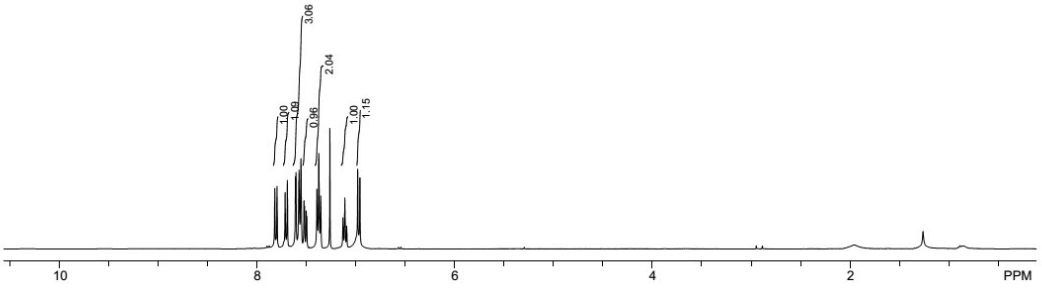


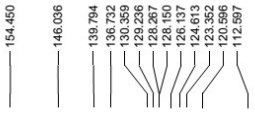


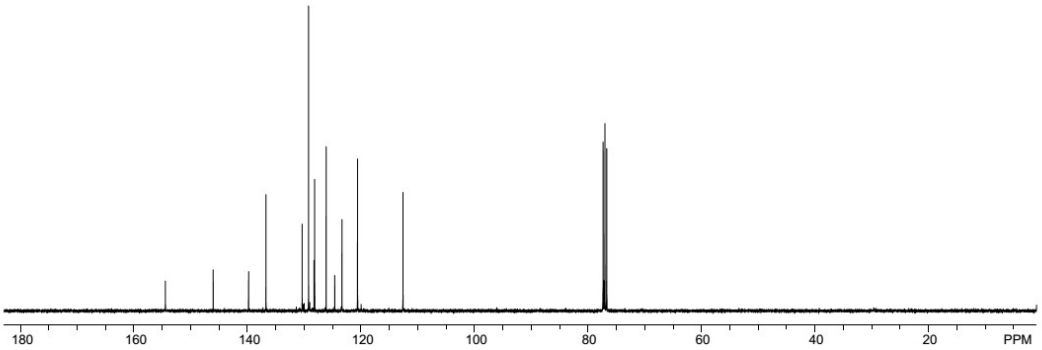


6-chloro-*N*-phenylquinolin-2-amine (3ja)

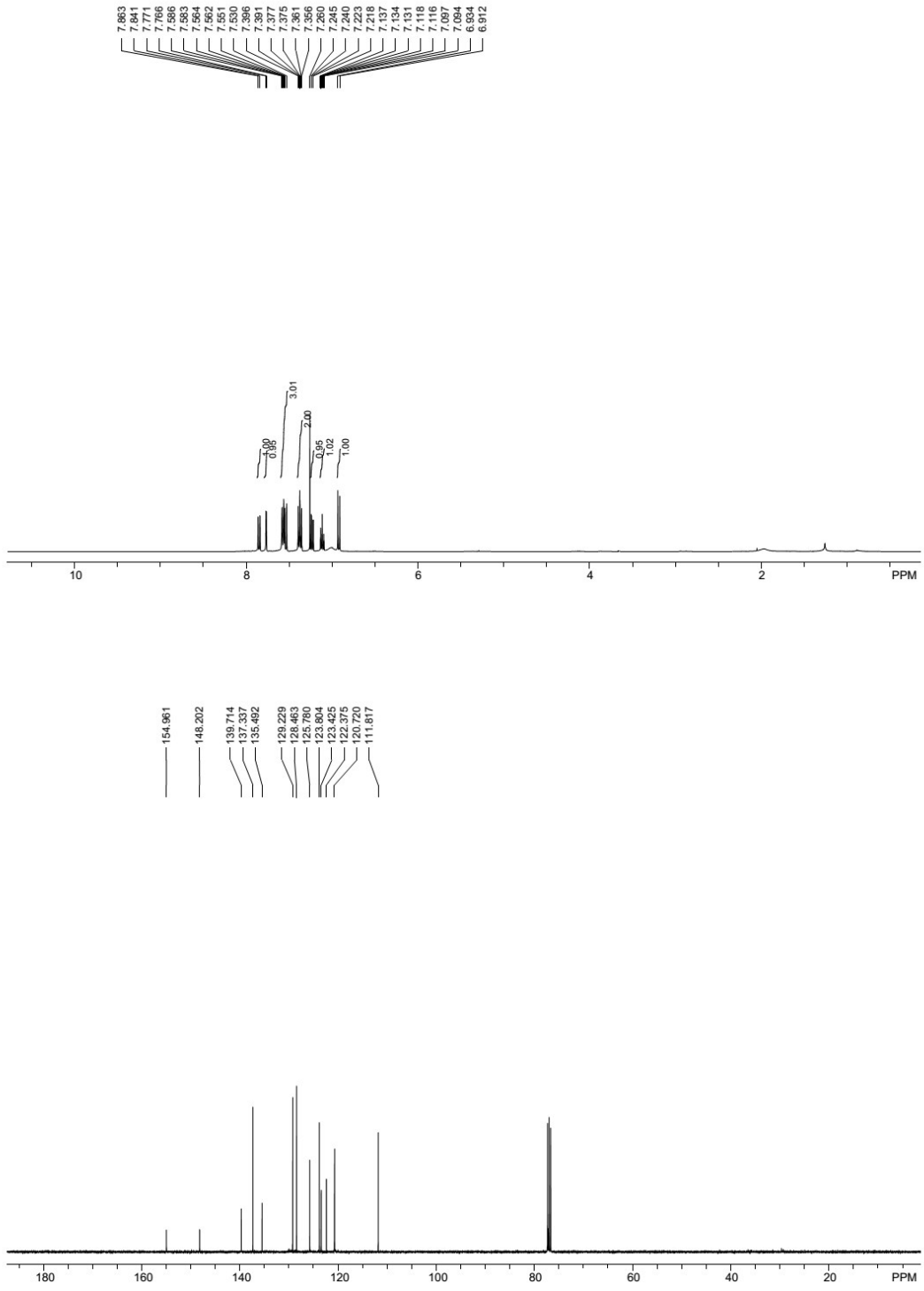




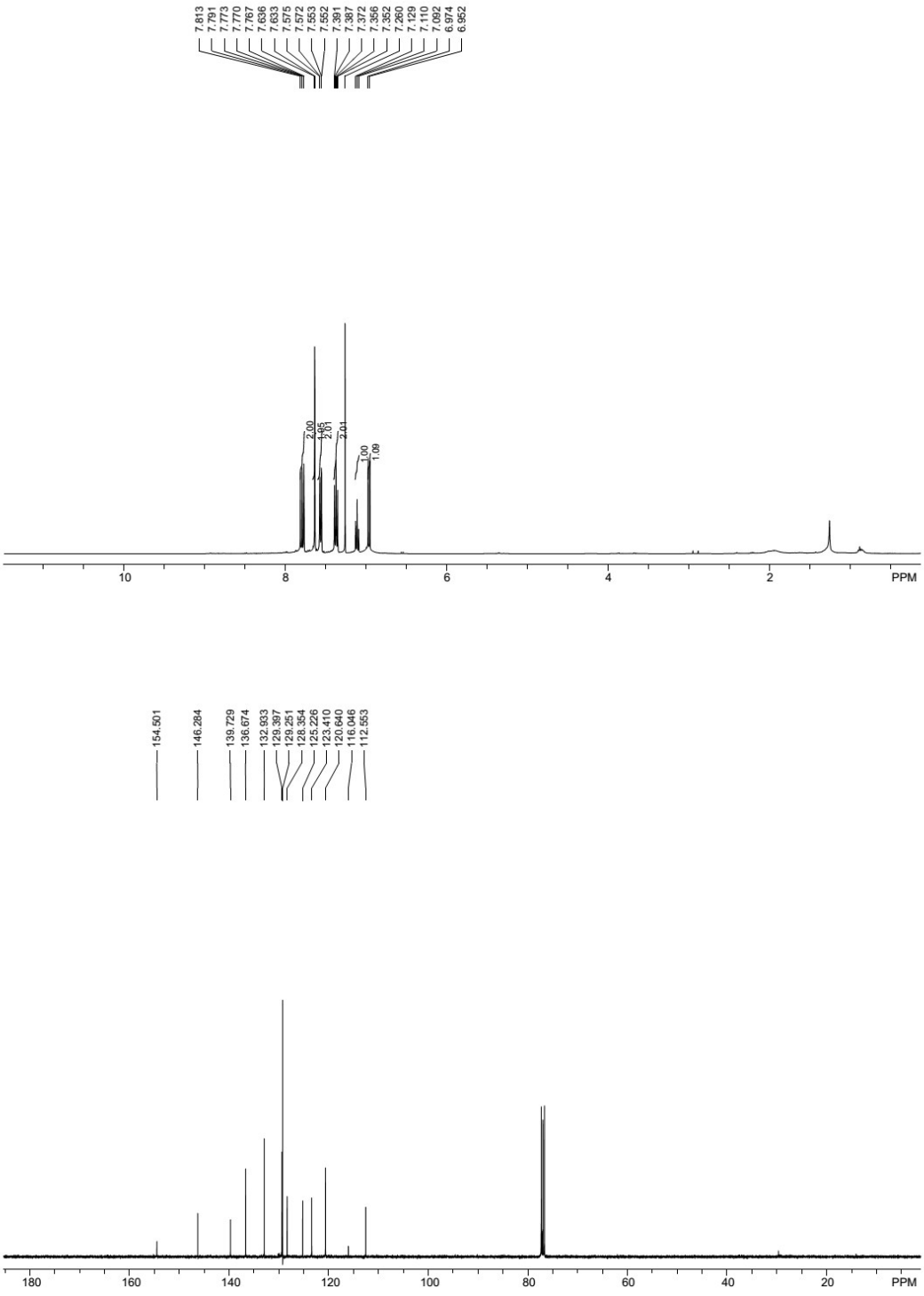




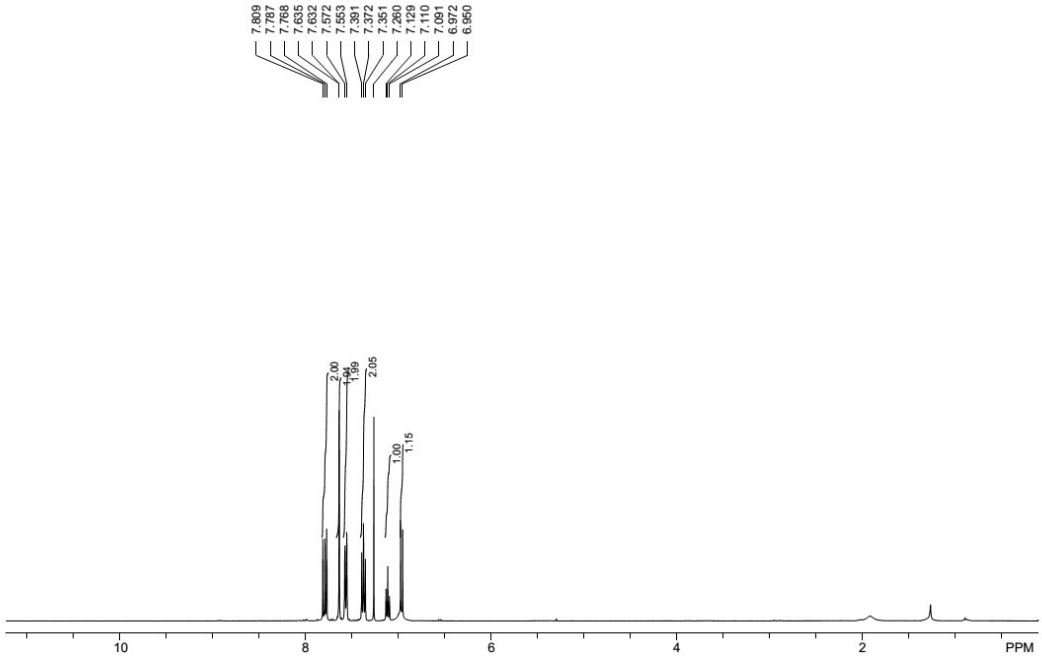
7-chloro-*N*-phenylquinolin-2-amine (3ka)

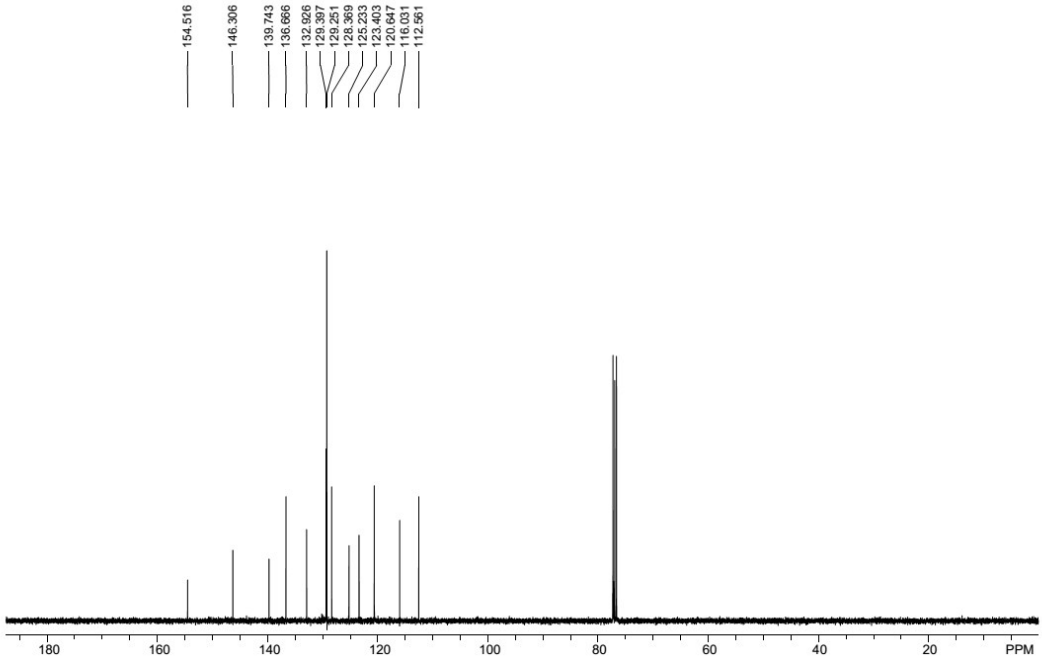


6-bromo-*N*-phenylquinolin-2-amine (3la)

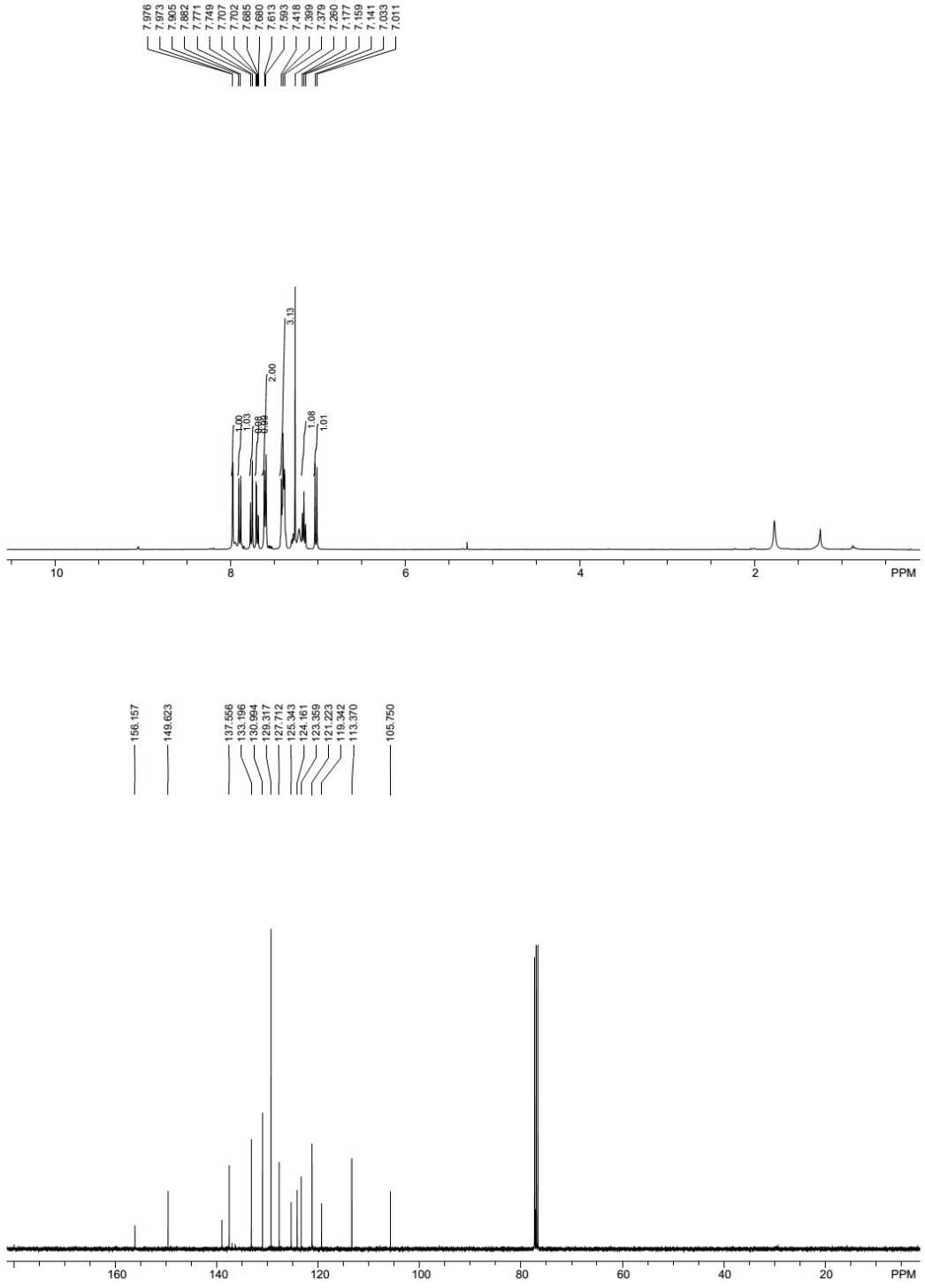


8-bromo-*N*-phenylquinolin-2-amine (3ma)

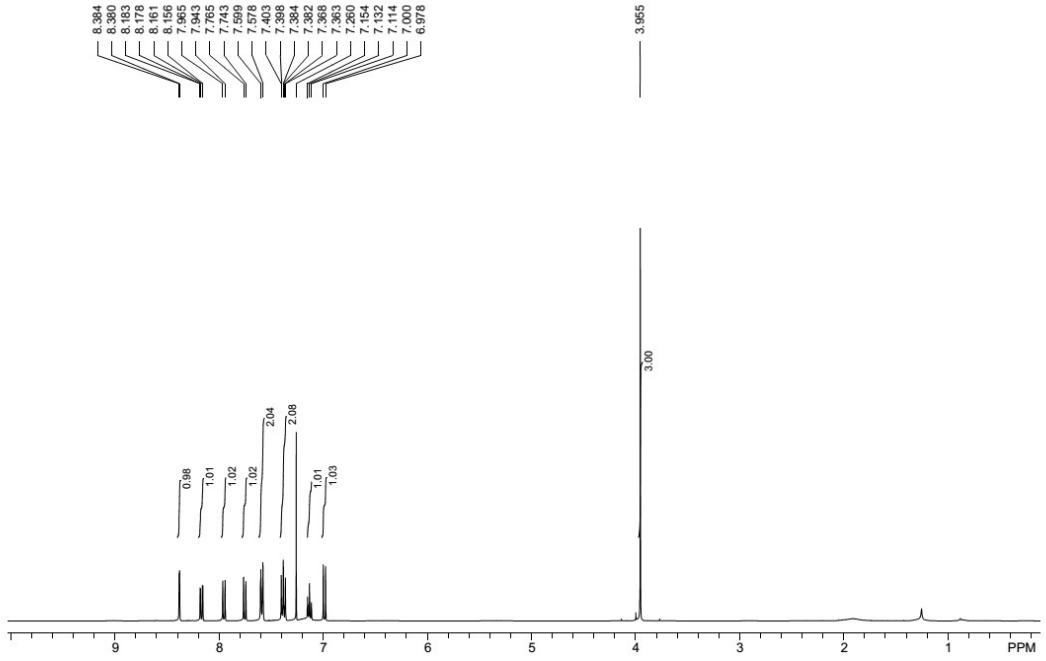


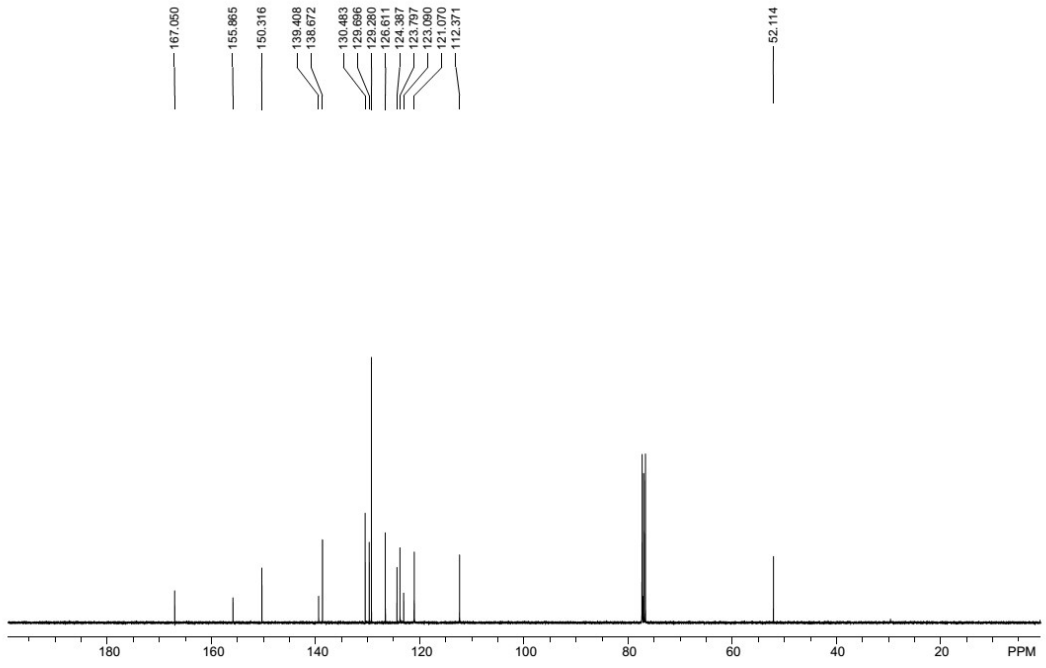


2-(phenylamino)quinoline-6-carbonitrile (3na)

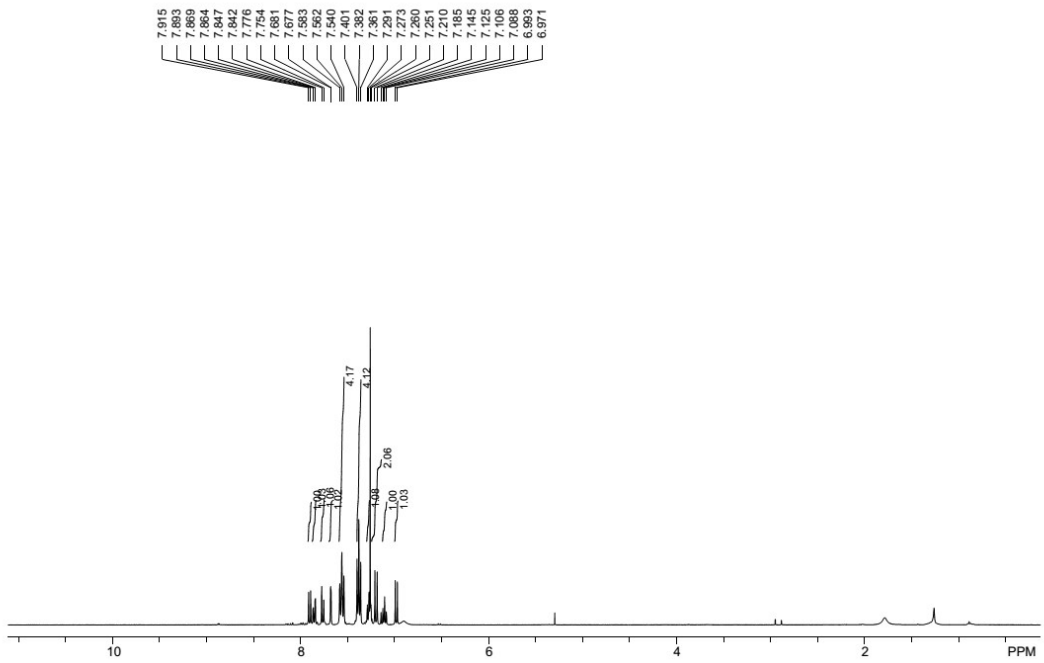


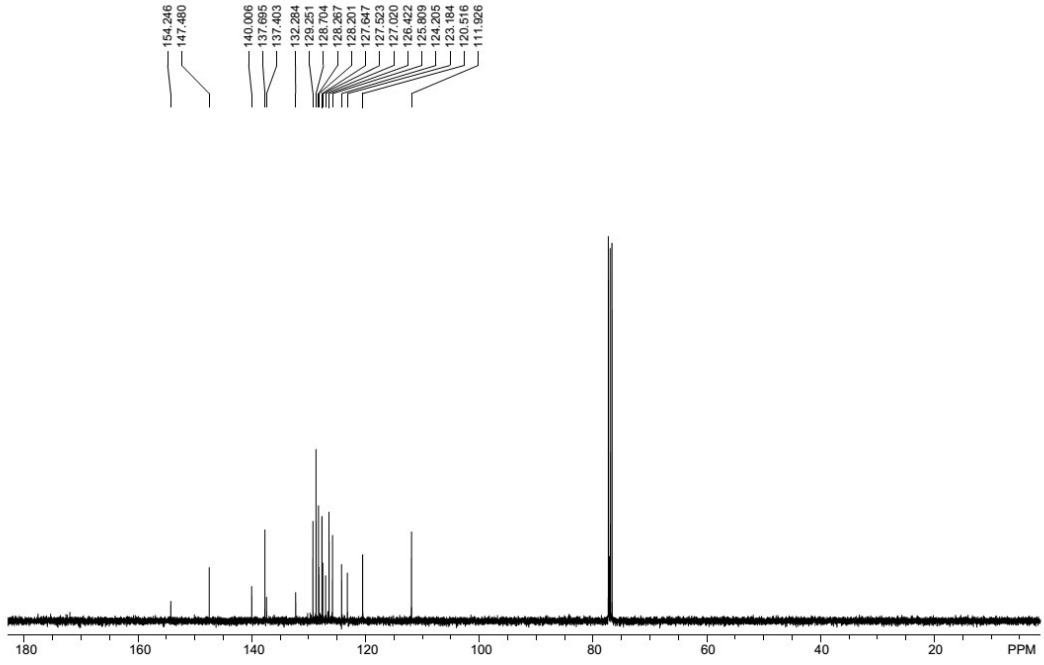
methyl 2-(phenylamino)quinoline-6-carboxylate (3oa)



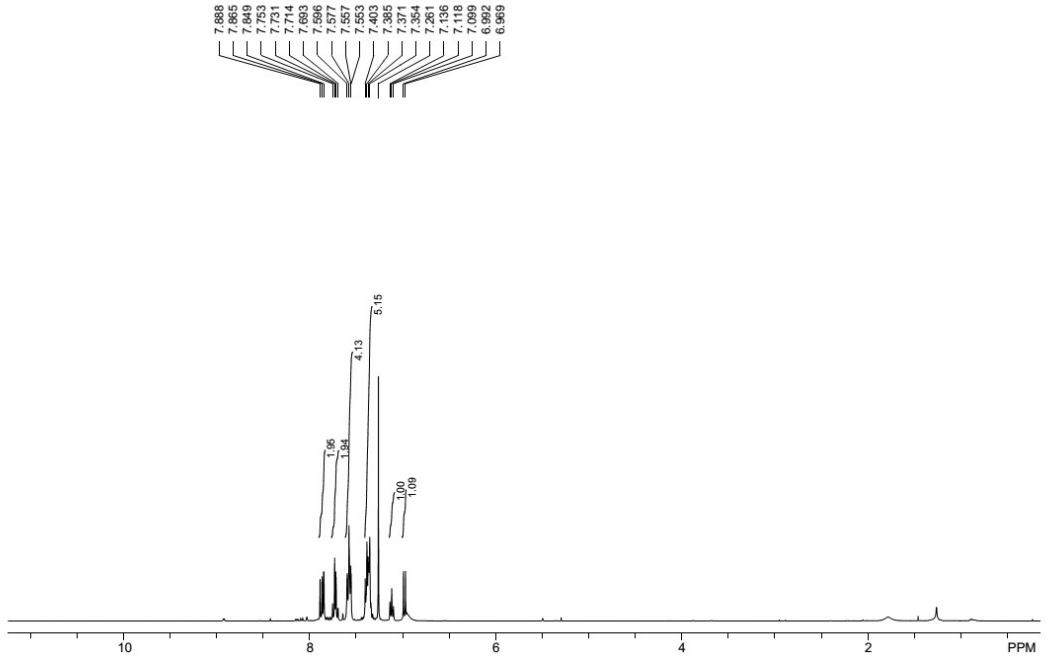


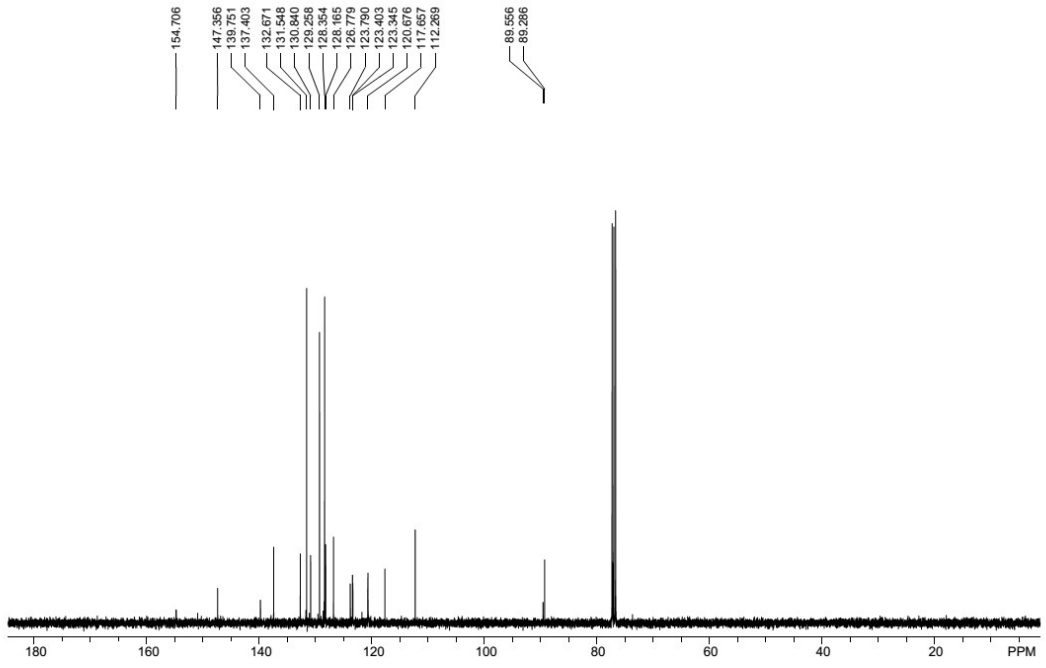
(E)-*N*-phenyl-6-styrylquinolin-2-amine (3pa)



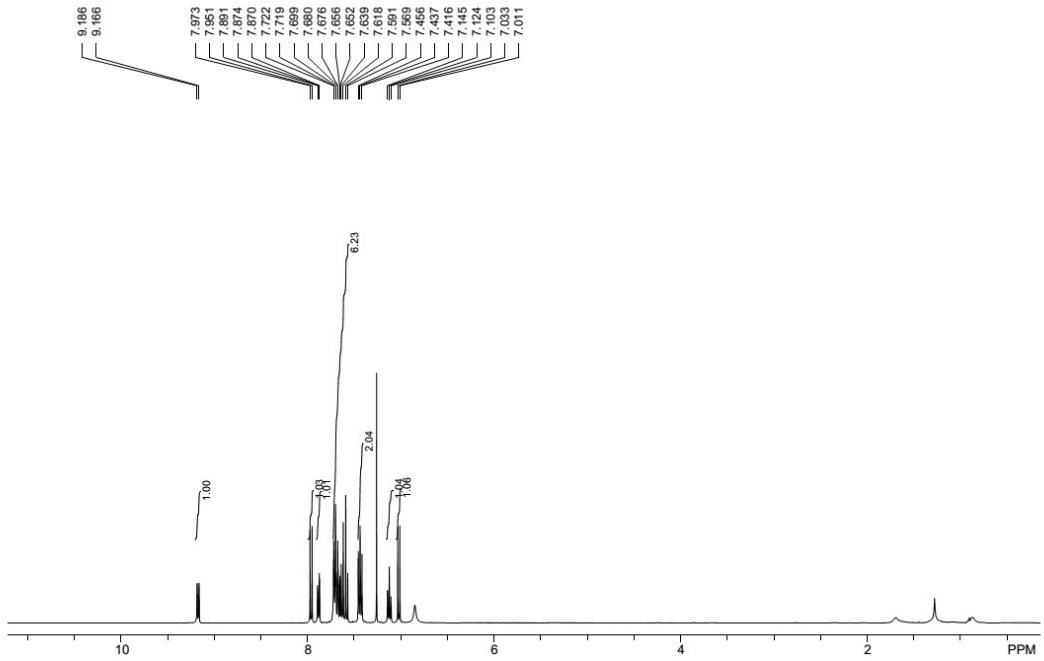


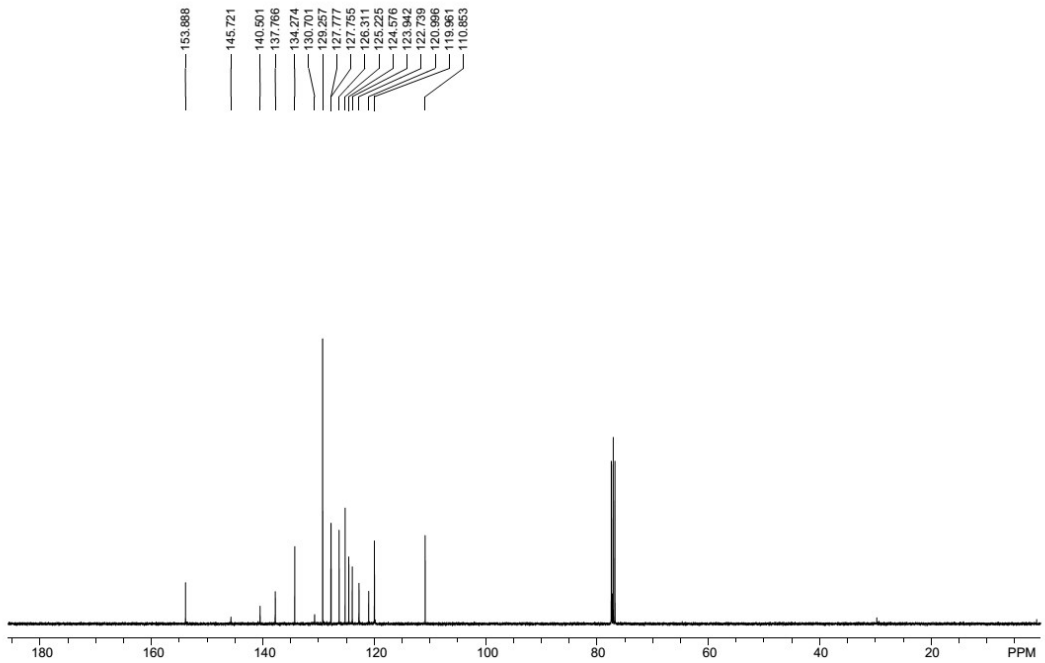
***N*-phenyl-6-(phenylethynyl)quinolin-2-amine (3qa)**



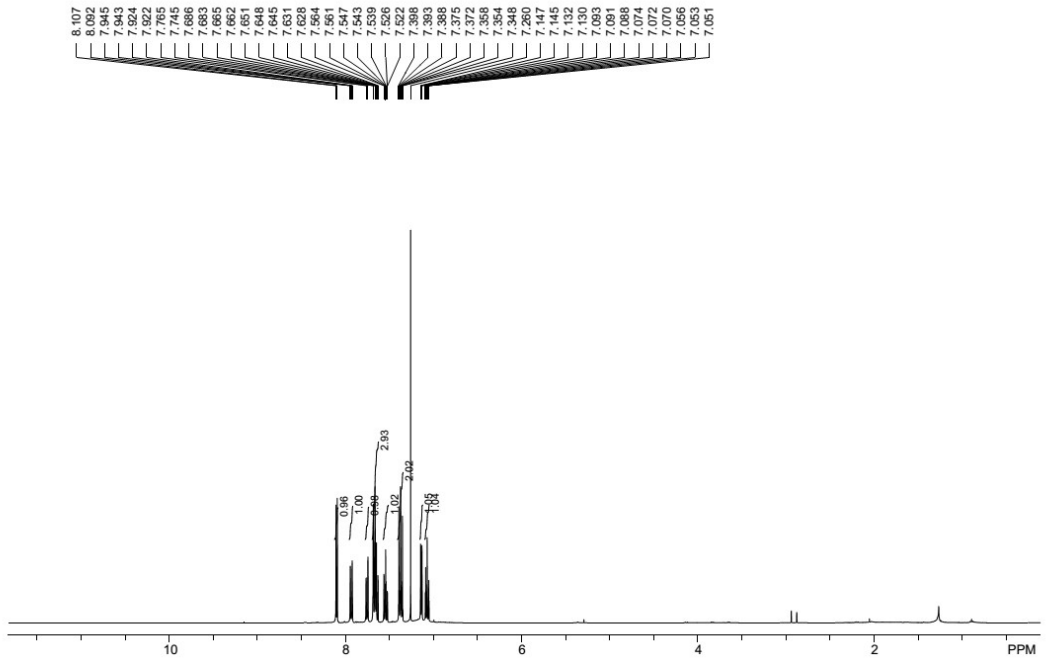


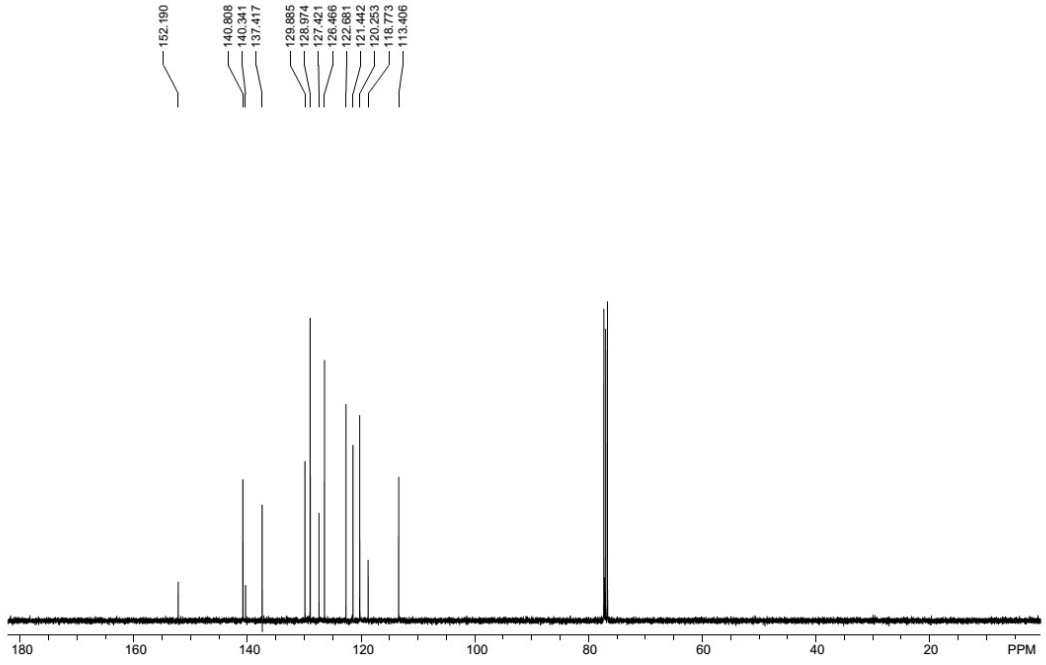
***N*-phenylbenzo[f]quinolin-3-amine (3ra)**





***N*-phenylisoquinolin-1-amine (3sa)**





benzo[4,5]imidazo[1,2-*a*]quinolone (4a)