Supporting Information

Na_2S-Catalyzed Dehydrogenative Condensation of 2-Aminobenzyl Alcohols and Ketones: A Synthesis of Quinolines

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General information

Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanillin stains. Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.251 ppm for ^1H, 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

General procedure for synthesis of quinolines and 1,8-naphthyridines c1-c42

A mixture of 2-aminobenzyl alcohol **a** (0.5 mmol), ketone **b** (0.6 mmol) and $Na_2S•3H_2O$ (0.1 mmol, 14 mg) was stirred and heated at 120 ºC (copper or aluminum heating block) in a 7-mL test tube under an argon atmosphere (the tube was closed with a rubber septum mounted with a rubber balloon filled with argon to equilibrate the pressure. After 16 h of heating, the tube was cooled down to rt, the crude mixture was purified by column chromatography on silica gel (EtOAc:Hexane 3:97 for quinolines and CH_2Cl_2:EtOAc 5:1 to 1: for 1,8-naphthyridines) to afford the expected quinoline or 1,8-naphthyridine as a pale yellow or white solid.

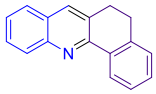
Procedure for the determination of hydrogen generated during the reaction

A mixture of 2-aminobenzyl alcohol **a1** (5 mmol, 615 mg), acetophenone **b** (6 mmol, 720 mg) and $Na_2S•3H_2O$ (1 mmol, 140 mg) was stirred and heated at 120 ºC (copper or aluminum heating block) in a 20-mL test tube under an argon atmosphere (the tube was closed with a rubber septum mounted with a rubber balloon filled with argon to equilibrate the pressure. After 16 h of heating, the tube was cooled down to rt, the gas inside the tube was taken with a 10-mL syringe (10 mL of gas). A sample of copper(II) oxide (CuO) (500 mg) was placed in the center of a glass tube (length × diameter = 20 cm×1 cm). The CuO was secured using glass wool plugs at both ends to prevent material displacement. Both ends of the glass tube were sealed with rubber septa, each equipped with a needle. Argon gas was swept through the tube for 5 minutes to purge any air (oxygen) from the system. After purging, one end of the tube was connected to an

argon-filled rubber balloon (acting as a reservoir/low-pressure exit), and the other end was connected to the syringe containing the reactant gas (presumably hydrogen, based on the conclusion). The central section of the glass tube containing the CuO was gently heated using a Bunsen burner. The gas from the syringe was then slowly and continuously passed through the heated tube. The black powder CuO was observed to turn brick-red (metallic Cu) upon contact with the incoming gas. In the cooler downstream section of the tube, droplets of water were visible, confirming that the gas introduced from the syringe contained hydrogen (H_2) which was oxidized to water (H_2O) by the copper(II) oxide.

Characterization of products

5,6-Dihydrobenzo[*c*]acridine (c1)[1]

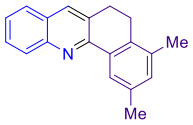


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (178 mg, 77%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (dd, J = 7.8, 1.1 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.64 – 7.61 (m, J = 8.1, 0.8 Hz, 1H), 7.60 – 7.56 (m, J = 8.4, 6.9, 1.4 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, J = 7.4, 1.4 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 3.01 – 2.95 (m, 2H), 2.92 – 2.86 (m, J = 8.4, 5.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.3, 147.7, 139.4, 134.7, 133.7, 130.5, 129.7, 129.4, 128.6, 128.0, 127.9, 127.3, 127.0, 126.1, 126.0, 28.8, 28.4.

2,4-Dimethyl-5,6-dihydrobenzo[*c*]acridine (c2)



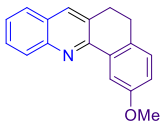
Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (200 mg, 77%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.85 (s, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.49 – 7.45 (m, 1H), 7.12 (s, 1H), 3.09 – 3.02 (m, 2H), 2.95 – 2.86 (m, 2H), 2.49 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 147.6, 136.0, 135.0, 134.9, 134.5, 133.3, 132.5, 130.4, 129.4, 128.5, 127.8, 126.9, 125.8, 124.4, 28.5, 23.9, 21.2, 19.6.

HRMS (ESI+) calcd for $C_{19}H_{18}N$ $[M + H]^+$ 260.1439. Found 260.1442.

2-Methoxy-5,6-dihydrobenzo[*c*]acridine (c3)[2]

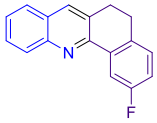


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (178 mg, 68%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 2H), 7.82 (s, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.44 – 7.39 (m, 1H), 7.13 (d, J = 8.3 Hz, 1H), 6.91 (dd, J = 8.2, 2.8 Hz, 1H), 3.92 (s, 3H), 3.05 – 2.97 (m, 2H), 2.91 – 2.85 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 153.3, 147.6, 135.7, 133.7, 131.9, 130.7, 129.4, 129.0, 128.6, 127.9, 127.0, 126.1, 116.9, 109.8, 55.6, 29.1, 27.6.

2-Fluoro-5,6-dihydrobenzo[*c*]acridine (c4)



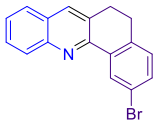
Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (177 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (dd, J = 10.0, 2.8 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.84 (s, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.50 – 7.43 (m 1H), 7.20 (dd, J = 8.3, 5.5 Hz, 1H), 7.07 – 7.02 (m, 1H), 3.08 – 3.03 (m, 2H), 2.95 – 2.88 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4 (d, J = 243.9 Hz), 152.3, 147.5, 136.7 (d, J = 7.2 Hz), 135.0 (d, J = 2.8 Hz), 133.9, 130.2, 129.5, 129.4 (*d*, J = 8.0 Hz), 128.8, 128.1, 127.0, 126.4, 116.4 (d, J = 22.2 Hz), 112.5 (d, J = 23.2 Hz), 28.7, 27.6.

HRMS (ESI+) calcd for $C_{17}H_{13}FN$ $[M + H]^+$ 250.1032. Found 250.1040.

2-Bromo-5,6-dihydrobenzo[*c*]acridine (c5)[3]

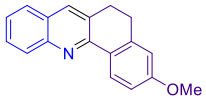


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (226 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, J = 2.2 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.81 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.48 – 7.45 (m, 1H), 7.42 (dd, J = 8.0, 2.2 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 3.06 – 3.00 (m, 2H), 2.92 – 2.86 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 147.5, 138.0, 136.6, 133.9, 132.3, 130.1, 129.6, 129.4, 128.8, 128.8, 128.0, 127.0, 126.4, 121.2, 28.4, 27.8.

3-Methoxy-5,6-dihydrobenzo[*c*]acridine (c6)[3]

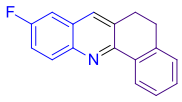


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (133 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, J = 8.6 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.81 (s, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.46 – 7.41 (m, 1H), 6.98 (dd, J = 8.6, 2.6 Hz, 1H), 6.79 (d, J = 2.6 Hz, 1H), 3.86 (s, 3H), 3.15 – 3.04 (m, 2H), 2.99 – 2.89 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.0, 153.4, 147.7, 141.3, 133.5, 130.0, 129.2, 128.6, 127.9, 127.8, 127.6, 127.0, 125.6, 113.1, 113.0, 55.3, 28.9, 28.8.

9-Fluoro-5,6-dihydrobenzo[*c*]acridine (c7)[4]



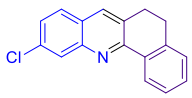
Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (142 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 7.6 Hz, 1H), 8.11 (dd, J = 9.1, 5.4 Hz, 1H), 7.83 (s, 1H), 7.45 – 7.32 (m, 4H), 7.27 (d, J = 7.6 Hz, 1H), 3.13 – 3.07 (m, 2H), 3.02 – 2.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (d, J = 246.7 Hz), 152.9, 144.7, 139.3, 134.5, 133.1 (d, J = 5.4 Hz), 131.8 (d, J = 9.3 Hz), 131.5, 129.7, 128.4 (d, J = 9.8 Hz), 128.0, 127.4, 125.9, 118.7 (d, J = 25.6 Hz), 110.0 (d, J = 21.6 Hz), 28.8, 28.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -115.28 (dd, J = 13.7, 8.1 Hz).

10-Chloro-5,6-dihydrobenzo[*c*]acridine (c8)



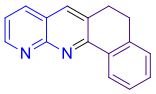
Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (170 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 1.2 Hz, 1H), 7.84 (s, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.50 – 7.38 (m, 3H), 7.29 (d, J = 6.9 Hz, 1H), 3.12 – 3.06 (m, 2H), 3.04 – 2.97 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 148.0, 139.6, 134.4, 134.3, 133.5, 130.9, 130.1, 128.4, 128.2, 128.1, 127.4, 127.0, 126.2, 28.8, 28.3. (1 signal missing due to overlap)

HRMS (ESI+) calcd for $C_{17}H_{13}ClN$ $[M + H]^+$ 266.0737. Found 266.0731.

5,6-Dihydronaphtho[1,2-*b*][1,8]naphthyridine (c9)[5]

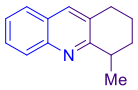


Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 4:1) (160 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (dd, J = 4.0, 1.7 Hz, 1H), 8.72 (d, J = 7.5 Hz, 1H), 7.98 (dd, J = 8.0, 1.7 Hz, 1H), 7.80 (s, 1H), 7.41 – 7.28 (m, 3H), 7.19 (d, J = 7.3 Hz, 1H), 3.06 – 3.00 (m, 2H), 2.95 – 2.90 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 155.5, 152.6, 139.4, 136.1, 134.5, 133.9, 131.7, 130.4, 127.8, 127.2, 126.9, 122.2, 121.4, 28.4, 28.0.

4-Methyl-1,2,3,4-tetrahydroacridine (c10)[6]

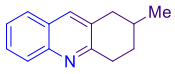


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (150 mg, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.5 Hz, 1H), 7.73 (s, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.43 – 7.38 (m, 1H), 3.24 – 3.15 (m, 1H), 3.00 – 2.85 (m, 2H), 2.15 – 2.08 (m, 1H), 1.98 – 1.90 (m, 1H), 1.83 – 1.75 (m, 1H), 1.75 – 1.69 (m, 1H), 1.49 (d, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2, 146.9, 134.8, 130.6, 128.6, 128.3, 127.1, 126.8, 125.5, 36.6, 31.4, 29.8, 21.6, 20.3.

2-Methyl-1,2,3,4-tetrahydroacridine (c11)[7]

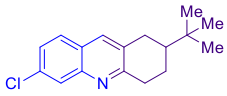


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (126 mg, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 8.5 Hz, 1H), 7.72 (s, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.43 – 7.37 (m, 1H), 3.24 – 3.16 (m, 1H), 3.11 – 3.04 (m, 1H), 2.99 – 2.94 (m, 1H), 2.55 (dd, J = 16.3, 10.8 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.99 – 1.88 (m, 1H), 1.65 – 1.51 (m, 1H), 1.10 (d, J = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 146.7, 135.0, 130.6, 128.5, 128.3, 127.2, 126.9, 125.5, 37.8, 33.1, 31.4, 29.1, 21.7.

2-(Tert-butyl)-6-chloro-1,2,3,4-tetrahydroacridine (c12)



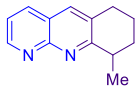
Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (139 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.70 (s, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 8.7 Hz, 1H), 3.27 – 3.14 (m, 1H), 3.07 – 2.87 (m, 2H), 2.75 – 2.51 (m, 1H), 2.17 – 2.08 (m, 1H), 1.61 – 1.40 (m, 2H), 0.97 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 146.9, 135.1, 134.1, 131.7, 128.2, 127.4, 126.5, 125.5, 44.6, 34.4, 32.6, 30.8, 27.3, 24.5.

HRMS (ESI+) calcd for $C_{17}H_{21}ClN$ $[M + H]^+$ 274.1363. Found 274.1372.

9-Methyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c13)



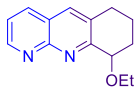
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 4:1) (121 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 1.9 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.73 (s, 1H), 7.31 (dd, J = 7.8, 4.1 Hz, 1H), 3.25 – 3.09 (m, 1H), 2.99 – 2.85 (m, 2H), 2.17 – 2.01 (m, 1H), 2.01 – 1.84 (m, 1H), 1.84 – 1.72 (m, 1H), 1.70 – 1.59 (m, 1H), 1.50 (d, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 154.9, 152.4, 136.0, 135.4, 132.1, 121.3, 121.2, 37.0, 31.2, 29.6, 21.1, 20.5.

HRMS (ESI+) calcd for $C_{13}H_{15}N_2$ $[M + H]^+$ 199.1235. Found 199.1227.

9-Ethoxy-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c14)



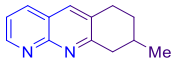
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 3:1) (114 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 3.4 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.84 (s, 1H), 7.36 (dd, J = 8.1, 4.2 Hz, 1H), 4.64 (t, J = 3.2 Hz, 1H), 3.87 – 3.73 (m, 2H), 3.13 – 3.00 (m, 1H), 2.92 – 2.78 (m, 1H), 2.33 – 2.23 (m, 1H), 2.21 – 2.07 (m, 1H), 1.93 – 1.83 (m, 1H), 1.82 – 1.72 (m, 1H), 1.14 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 154.5, 152.7, 136.3, 136.1, 132.5, 122.4, 121.9, 76.5, 65.1, 28.9, 28.2, 17.6, 15.5.

HRMS (ESI+) calcd for $C_{14}H_{17}N_2O$ $[M + H]^+$ 229.1341. Found 229.1345.

8-Methyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c15)



Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 3:1) (127 mg, 64%). Mixture 12:1 of two isomers.

^{1}H NMR signals of the major isomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 – 8.93 (m, 1H), 8.04 – 7.98 (m, 1H), 7.75 (s, 1H), 7.32 – 7.29 (m, 1H), 3.31 – 3.25 (m, 1H), 3.00 – 2.92 (m, 1H), 2.73 – 2.66 (m, 1H), 2.05 – 1.91 (m, 3H), 1.50 – 1.39 (m, 1H), 1.1 – 1.09 (m, 3H).

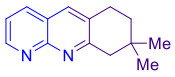
Some characteristic ^{1}H NMR signals of the minor isomer (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 3.15 – 3.16 (m, 2H), 1.13 – 1.34 (m, 4H).

^{13}C NMR signals of the major isomer (101 MHz, $CDCl_3$) δ 163.0, 154.7, 152.5, 136.0, 135.3, 131.6, 121.3, 121.2, 42.3, 30.9, 29.2, 28.4, 21.8.

Some characteristic ^{13}C-NMR signals of the minor isomer (101 MHz, $CDCl_3$) δ 154.7, 152.6, 137.4, 136.2, 134.5, 121.3, 34.2, 32.6, 31.0, 22.2, 20.4.

HRMS (ESI+) calcd for $C_{13}H_{15}N_2$ $[M + H]^+$ 199.1235. Found 199.1242.

8,8-Dimethyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c16)



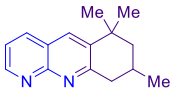
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 3:1) (132 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 – 8.86 (m, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.80 (s, 1H), 7.32 (dd, J = 7.8, 4.1 Hz, 1H), 2.98 (t, J = 6.8 Hz, 2H), 2.93 (s, 2H), 1.65 (t, J = 6.8 Hz, 2H), 1.02 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 154.9, 152.6, 136.1, 135.4, 130.8, 121.4, 121.2, 47.7, 35.5, 30.2, 28.2, 25.7.

HRMS (ESI+) calcd for $C_{14}H_{17}N_2$ $[M + H]^+$ 213.1392. Found 213.1398.

6,6,8-Trimethyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c17)



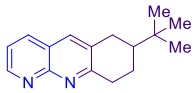
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 3:1) (143 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 3.8 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.95 (s, 1H), 7.31 (dd, J = 8.0, 4.2 Hz, 1H), 3.12 – 2.81 (m, 3H), 1.79 – 1.70 (m, 1H), 1.38 (d, J = 6.8 Hz, 3H), 1.36 – 1.25 (m, 1H), 1.06 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 154.6, 152.6, 136.3, 136.1, 133.8, 121.5, 121.2, 48.1, 45.6, 31.7, 30.5, 29.8, 25.8, 21.3.

HRMS (ESI+) calcd for $C_{15}H_{19}N_2$ $[M + H]^+$ 227.1548. Found 227.1539.

7-(*tert*-Butyl)-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c18)



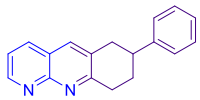
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 4:1) (161 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 2.5 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.31 (dd, J = 8.0, 4.2 Hz, 1H), 3.32 (d, J = 18.0 Hz, 1H), 3.13 – 2.93 (m, 2H), 2.67 (dd, J = 16.1, 11.5 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.59 – 1.41 (m, 2H), 0.95 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 154.8, 152.6, 136.0, 135.8, 132.6, 121.4, 121.2, 44.5, 34.6, 32.6, 30.6, 27.3, 24.3.

HRMS (ESI+) calcd for $C_{16}H_{21}N_2$ $[M + H]^+$ 241.1705. Found 241.1712.

7-Phenyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c19)



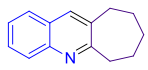
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 5:1) (169 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 – 8.94 (m, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.40 – 7.23 (m, 6H), 3.51 – 3.39 (m, 1H), 3.36 – 3.21 (m, 2H), 3.18 – 3.05 (m, 2H), 2.38 – 2.26 (m, 1H), 2.22 – 2.06 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 154.9, 152.8, 145.4, 136.1, 135.7, 131.7, 128.7, 126.8, 126.6, 121.4, 40.3, 37.1, 33.9, 30.1. (1 signal missing due to overlap)

HRMS (ESI+) calcd for $C_{21}H_{17}N_2$ $[M + H]^+$ 261.1392. Found 261.1388.

7,8,9,10-Tetrahydro-6*H*-cyclohepta[*b*]quinoline (c20)[8]

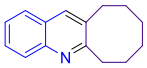


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (120 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 3.25 – 3.12 (m, 2H), 2.99 – 2.82 (m, 2H), 1.87 (d, J = 4.9 Hz, 2H), 1.82 – 1.70 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 146.3, 136.6, 134.7, 128.5, 127.4, 126.9, 125.8, 40.1, 35.5, 32.3, 28.9, 27.1. (1 signal missing due to overlap).

6,7,8,9,10,11-Hexahydrocycloocta[*b*]quinoline (c21)[8]

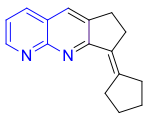


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (133 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 1H), 7.80 (s, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 3.19 – 3.08 (m, 2H), 2.96 – 2.86 (m, 2H), 1.88 (s, 2H), 1.75 (s, 2H), 1.38 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 147.0, 135.2, 135.1, 128.5, 127.7, 126.9, 125.6, 35.3, 32.8, 32.1, 31.0, 26.1, 26.0. (1 signal missing due to overlap).

3-Cyclopentylidene-2,3-dihydro-1H-cyclopenta[*b*]quinoline (c22)



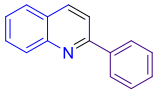
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 5:1) (99 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.77 (s, 1H), 7.30 (dd, J = 7.4, 4.2 Hz, 1H), 3.25 (s, 2H), 3.14 – 3.05 (m, 2H), 2.78 (s, 2H), 2.41 (s, 2H), 1.84 – 1.72 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 156.6, 152.0, 150.5, 139.9, 136.4, 130.7, 129.4, 121.2, 120.7, 34.4, 33.5, 28.8, 27.4, 27.2, 25.8.

HRMS (ESI+) calcd for $C_{17}H_{18}N$ $[M + H]^+$ 237.1392. Found 237.1390.

2-Phenylquinoline (c23)[9]

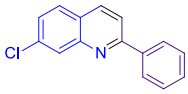


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (125 mg, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 – 8.17 (m, 4H), 7.87 (d, J = 8.6 Hz, 1H), 7.82 (dd, J = 8.1, 1.0 Hz, 1H), 7.76 – 7.72 (m, J = 8.4, 6.9, 1.4 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.50 – 7.46 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 148.4, 139.8, 136.9, 129.8, 129.7, 129.4, 128.9, 127.7, 127.6, 127.3, 126.4, 119.1.

7-Chloro-2-phenylquinoline[10] (c24)

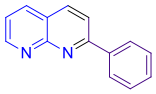


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (120 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.09 (m, 4H), 7.82 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.45 (dd, J = 8.8, 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 148.7, 139.2, 136.6, 135.5, 129.7, 129.0, 128.8, 128.7, 127.6, 127.3, 125.6, 119.1.

2-Phenyl-1,8-naphthyridine[11] (c25)

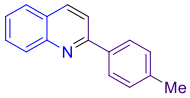


Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 4:1) (117 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, J = 2.3 Hz, 1H), 8.29 (d, J = 7.5 Hz, 2H), 8.18 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.41 (dd, J = 8.0, 4.2 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 156.2, 153.9, 138.5, 137.8, 136.8, 130.2, 128.9, 128.0, 121.8, 121.7, 119.7.

2-(*p*-Tolyl)quinoline[12] (c26)

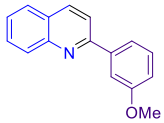


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (164 mg, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 – 8.19 (m, 1H), 8.17 (d, J = 8.6 Hz, 1H), 8.13 – 8.09 (m, 2H), 7.85 (d, J = 8.6 Hz, 1H), 7.80 (dd, J = 8.1, 1.2 Hz, 1H), 7.76 – 7.71 (m, 1H), 7.54 – 7.49 (m, 1H), 7.35 (dd, J = 8.4, 0.5 Hz, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.3, 148.4, 139.4, 136.9, 136.7, 129.7, 129.6, 127.5, 127.2, 126.1, 118.9, 21.4. (2 signals missing due to overlap).

2-(3-Methoxyphenyl)quinoline (c27)[13]

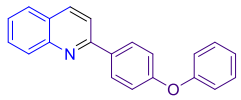


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (167 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 – 8.19 (m, 1H), 8.16 (d, J = 8.6 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.80 (dd, J = 8.1, 1.1 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.54 – 7.50 (m, 1H), 7.45 (t, J = 7.9 Hz, 1H), 7.06 – 7.02 (m, 1H), 3.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 157.0, 148.2, 141.1, 136.7, 129.8, 129.7, 129.6, 127.5, 127.3, 126.3, 120.0, 119.0, 115.4, 112.8, 55.4.

2-(4-Phenoxyphenyl)quinoline (c28)[14]

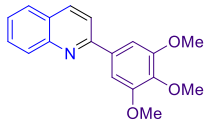


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (122 mg, 41%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 – 8.15 (m, 4H), 7.84 (d, J = 8.6 Hz, 1H), 7.81 (dd, J = 8.1, 1.2 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.54 – 7.50 (m, 1H), 7.41 – 7.36 (m, 2H), 7.19 – 7.15 (m, 3H), 7.12 – 7.09 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 157.0, 156.7, 148.4, 136.9, 134.8, 129.9, 129.8, 129.7, 129.2, 127.6, 127.1, 126.2, 123.7, 119.3, 119.0, 118.8.

2-(3,4,5-Trimethoxyphenyl)quinoline (c29)[15]

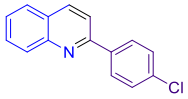


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (121 mg, 41%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (t, J = 7.5 Hz, 2H), 7.83 – 7.78 (m, 2H), 7.73 – 7.68 (m, 1H), 7.53 – 7.48 (m, 1H), 7.41 (s, 2H), 3.99 (s, 3H), 3.92 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 153.6, 148.2, 139.5, 136.8, 135.3, 129.8, 129.6, 127.5, 127.2, 126.3, 118.9, 104.9, 61.0, 56.3.

2-(4-Chlorophenyl)quinoline (c30)[16]

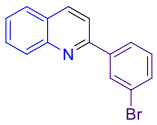


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (182 mg, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.11 – 8.08 (m, 2H), 7.78 (d, J = 8.2 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.53 – 7.50 (m, 1H), 7.49 – 7.46 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 148.3, 138.0, 136.9, 135.6, 129.8, 129.8, 129.0, 128.8, 127.5, 127.2, 126.5, 118.5.

2-(3-Bromophenyl)quinoline (c31)[14]

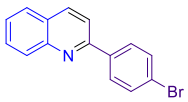


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (175 mg, 62%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, J = 1.6 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7.81 – 7.69 (m, 3H), 7.58 (dd, J = 7.9, 0.8 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.35 (t, J = 7.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.5, 148.2, 141.6, 137.0, 132.2, 130.6, 130.3, 129.9, 129.8, 127.5, 127.3, 126.6, 126.0, 123.2, 118.6.

2-(4-Bromophenyl)quinoline (c32)[14]

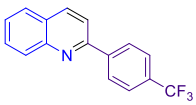


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (167 mg, 59%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.6 Hz, 1H), 8.04 – 8.01 (m, 2H), 7.78 (dd, J = 8.2, 0.9 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.64 – 7.61 (m, 2H), 7.54 – 7.50 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 148.3, 138.5, 136.9, 132.0, 129.8, 129.7, 129.1, 127.5, 127.3, 126.5, 124.0, 118.4.

2-(4-(Trifluoromethyl)phenyl)quinoline (c33)[17]

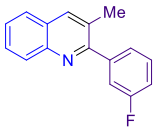


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (169 mg, 62%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, J = 8.1 Hz, 2H), 8.21 – 8.17 (m, 2H), 7.83 – 7.79 (m, 2H), 7.78 – 7.73 (m, 3H), 7.57 – 7.53 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 148.3, 142.9, 137.1, 131.1 (q, J = 32.8 Hz), 130.0, 129.9, 127.8, 127.5, 127.4, 126.8, 125.7 (q, J = 4.5 Hz), 124.3 (q, J = 272.1 Hz), 118.7.

2-(3-Fluorophenyl)-3-methylquinoline (c34)[18]

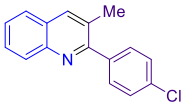


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (168 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.5, 0.6 Hz, 1H), 7.97 (s, 1H), 7.75 (dd, J = 8.2, 0.9 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.53 – 7.48 (m, 1H), 7.46 – 7.41 (m, 1H), 7.38 – 7.35 (m, 1H), 7.34 – 7.31 (m, 1H), 7.16 – 7.10 (m, 1H), 2.43 (d, J = 1.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7 (d, J = 246.5 Hz), 159.0, 146.6, 143.0 (d, J = 8.0 Hz), 137.0, 129.9 (d, J = 8.1 Hz), 129.3, 129.0, 128.9, 127.7, 126.8, 126.7, 124.7 (d, J = 3.3 Hz), 116.1 (d, J = 21.4 Hz), 115.2 (d, J = 21.1 Hz), 20.5.

2-(4-Chlorophenyl)-3-methylquinoline (c35)[18]

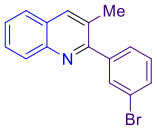


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (185 mg, 73%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 1H), 7.95 (s, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.54 – 7.48 (m, 3H), 7.46 – 7.43 (m, 2H), 2.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 146.6, 139.2, 136.9, 134.3, 130.3, 129.1, 128.9, 128.4, 128.2, 127.6, 126.7, 126.6, 20.5.

2-(3-Bromophenyl)-3-methylquinoline (c36)[18]

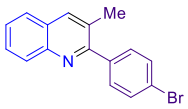


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (214 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 1H), 7.96 (s, 1H), 7.77 (t, J = 1.7 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.67 – 7.64 (m, 1H), 7.57 – 7.54 (m, 1H), 7.52 – 7.48 (m, 2H), 7.33 (t, J = 7.9 Hz, 1H), 2.42 (d, J = 1.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 146.5, 142.8, 137.0, 132.0, 131.2, 129.8, 129.2, 129.0, 128.9, 127.7, 127.5, 126.7, 126.7, 122.5, 20.5.

2-(4-Bromophenyl)-3-methylquinoline (c37)[18]

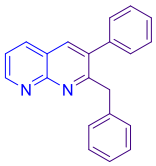


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (208 mg, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.62 – 7.59 (m, 2H), 7.52 – 7.49 (m, 1H), 7.48 – 7.45 (m, 2H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.1, 146.6, 139.7, 137.0, 131.4, 130.7, 129.2, 128.9, 128.9, 127.6, 126.8, 126.6, 122.6, 20.5.

2-Benzyl-3-phenyl-1,8-naphthyridine (c38)



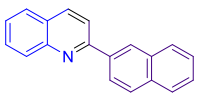
Purification of the crude mixture by column chromatography on silica gel (CH_2Cl_2:EtOAc 5:1) (124 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, J = 3.5 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H), 7.45 (dd, J = 7.9, 4.2 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.22 – 7.17 (m, 2H), 7.14 – 7.04 (m, 3H), 7.00 (d, J = 7.1 Hz, 2H), 4.38 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 155.3, 153.5, 138.9, 138.7, 137.6, 137.3, 136.8, 129.5, 129.2, 128.4, 128.2, 128.0, 126.1, 122.0, 121.3, 43.2.

HRMS (ESI+) calcd for $C_{21}H_{17}N_2$ $[M + H]^+$ 297.1392. Found 297.1392.

2-(Naphthalen-2-yl)quinoline (c39)[17]

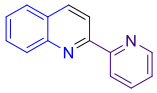


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (115 mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, J = 1.0 Hz, 1H), 8.39 (dd, J = 8.6, 1.8 Hz, 1H), 8.24 (t, J = 7.6 Hz, 2H), 8.05 – 7.98 (m, 3H), 7.93 – 7.89 (m, 1H), 7.85 (dd, J = 8.1, 1.2 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.57 – 7.52 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.32 (s), 148.56 (s), 137.14 (s), 136.93 (s), 134.03 (s), 133.68 (s), 129.91 (s), 129.86 (s), 128.97 (s), 128.71 (s), 127.87 (s), 127.64 (s), 127.39 (s), 127.29 (s), 126.85 (s), 126.85 (s), 126.48 (d, J = 1.4 Hz), 125.22 (s), 119.29 (s).

2-(Pyridin-2-yl)quinoline (c40)[19]

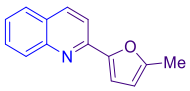


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3 to 4:1) (148 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 – 8.69 (m, 1H), 8.68 – 8.61 (m, 1H), 8.56 (d, J = 8.6 Hz, 1H), 8.24 (d, J = 8.6 Hz, 1H), 8.20 – 8.16 (m, 1H), 7.85 – 7.79 (m, 2H), 7.73 – 7.69 (m, 1H), 7.53 – 7.49 (m, 1H), 7.33 – 7.29 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 156., 149.2, 148.0, 137.0, 136.8, 129.9, 129.6, 128.3, 127.7, 126.8, 124.1, 121.9, 119.0.

2-(5-Methylfuran-2-yl)quinoline (c41)[20]

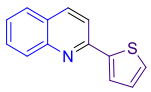


Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (138 mg, 66%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.68 – 7.64 (m, 1H), 7.46 – 7.41 (m, 1H), 7.11 (d, J = 3.3 Hz, 1H), 6.22 – 6.09 (m, 1H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 152.2, 149.2, 148.2, 136.5, 129.7, 129.3, 127.6, 127.0, 125.9, 117.3, 111.5, 108.7, 14.0.

2-(Thiophen-2-yl)quinoline (c42)[Error! Bookmark not defined.]



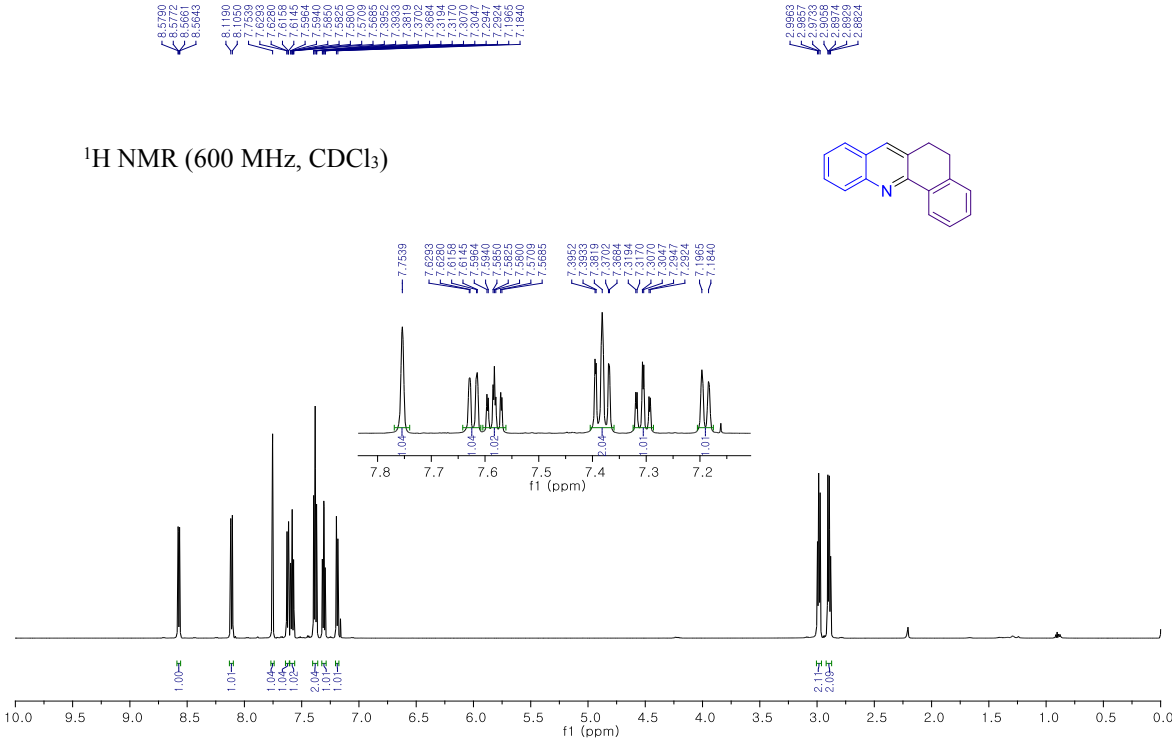
Purification of the crude mixture by column chromatography on silica gel (hexane:EtOAc 97:3) (148 mg, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 8.5 Hz, 1H), 8.07 (d, J = 8.6 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.72 – 7.68 (m, 2H), 7.49 – 7.44 (m, 2H), 7.15 (dd, J = 5.0, 3.7 Hz, 1H).

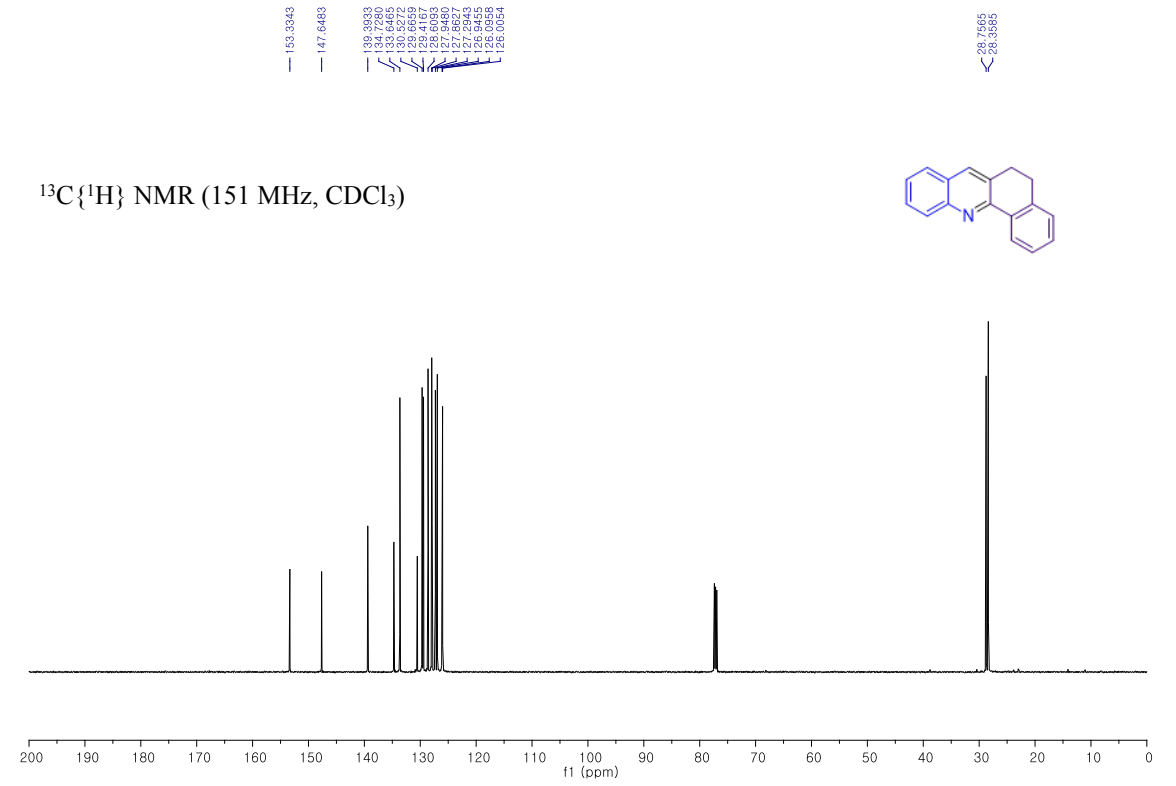
^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 148.2, 145.4, 136.6, 129.8, 129.3, 128.6, 128.1, 127.5, 127.2, 126.1, 125.9, 117.6.

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

5,6-Dihydrobenzo[*c*]acridine (c1)



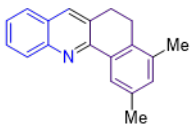
^{1}H NMR (600 MHz, $CDCl_3$)

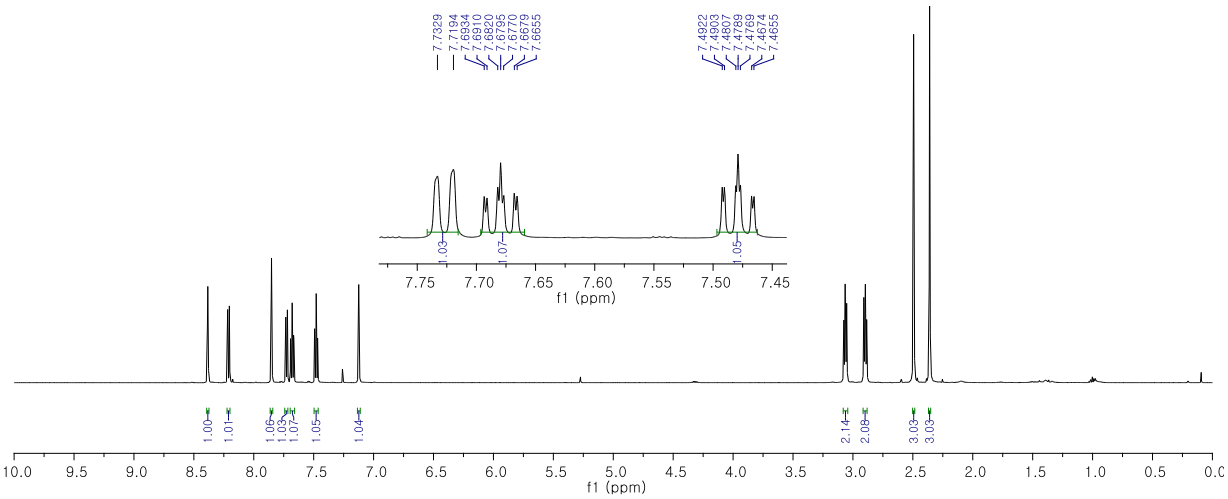


$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

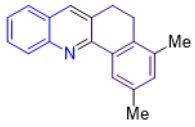
2,4-Dimethyl-5,6-dihydrobenzo[*c*]acridine (c2)

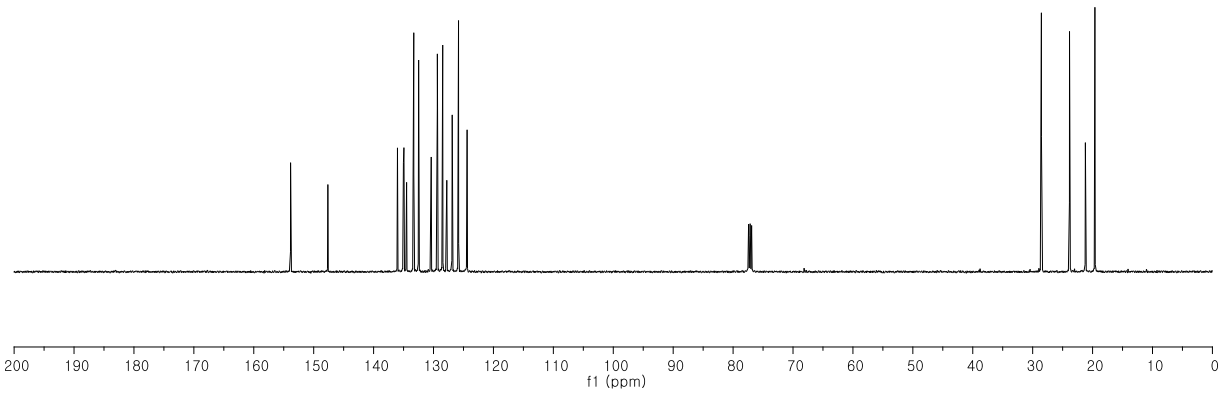
^{1}H NMR (600 MHz, $CDCl_3$)





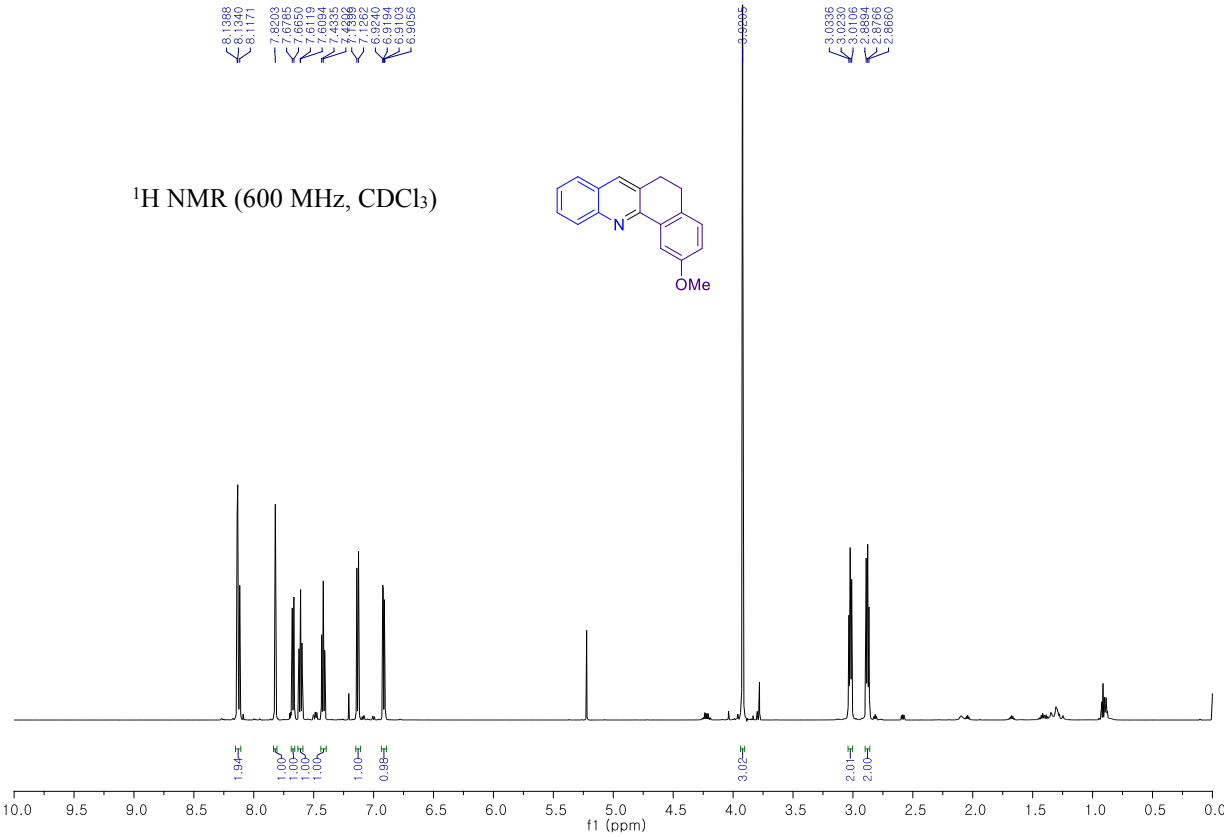
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



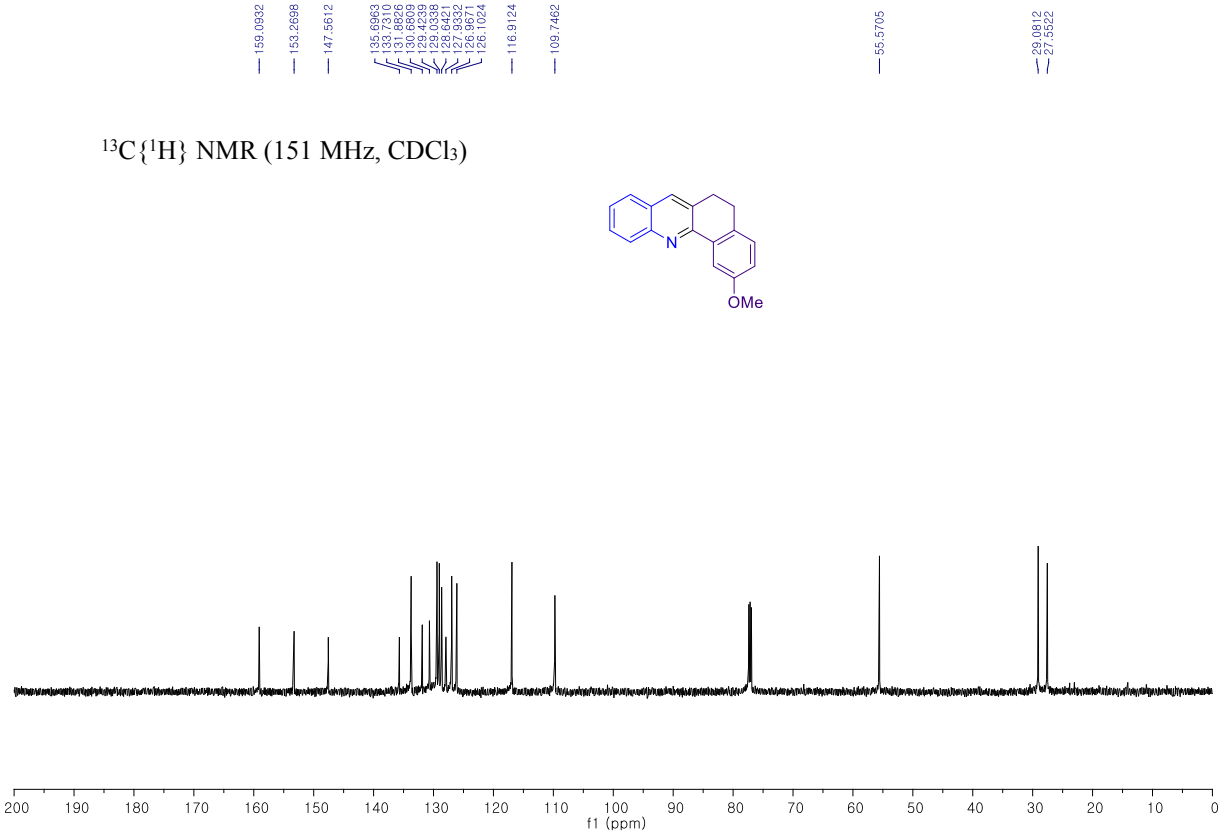


2-Methoxy-5,6-dihydrobenzo[*c*]acridine (c3)

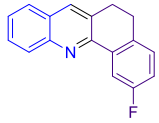
^{1}H NMR (600 MHz, $CDCl_3$)



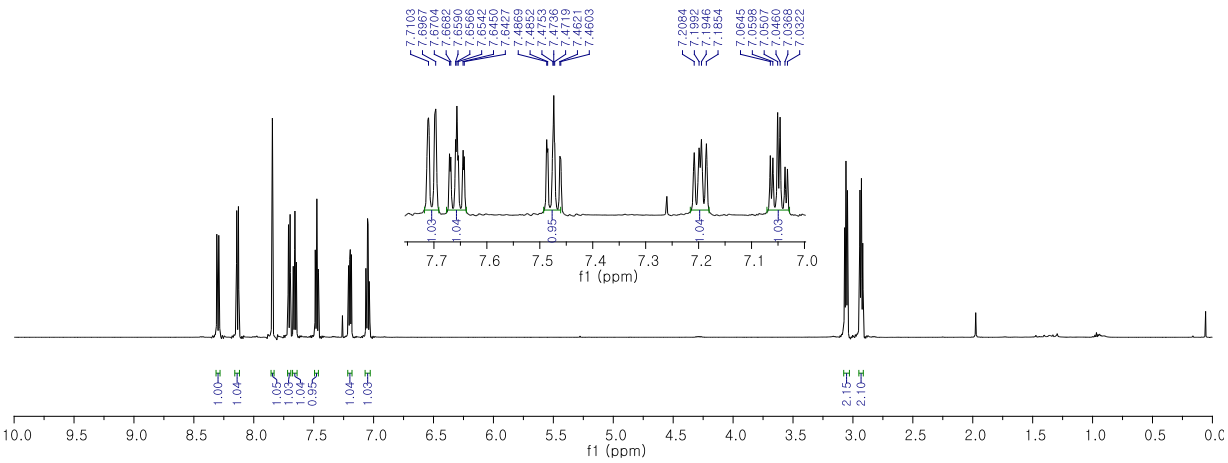
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

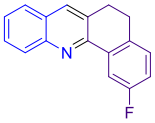


2-Fluoro-5,6-dihydrobenzo[*c*]acridine (c4)

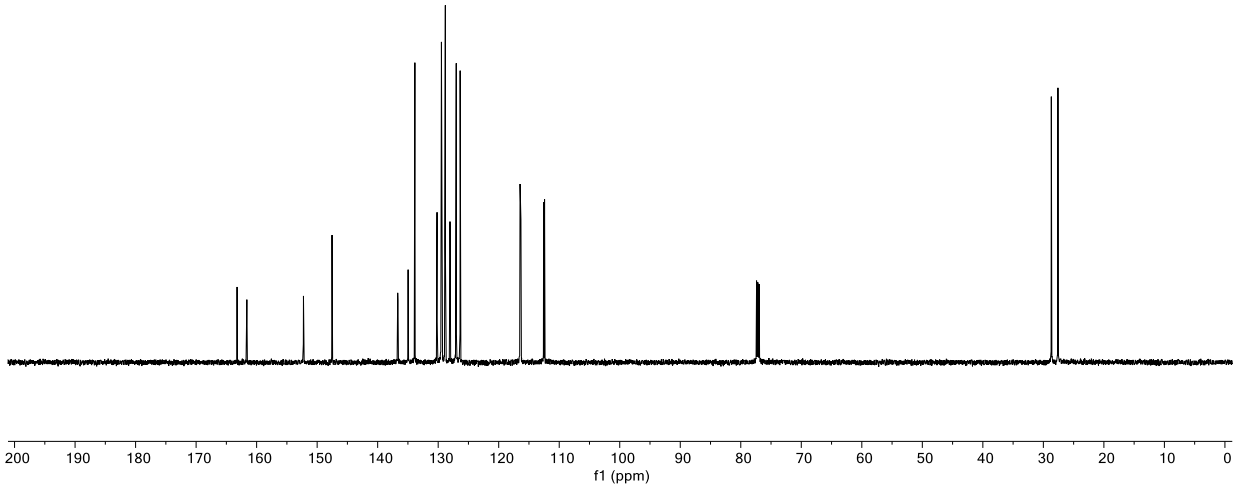


^{1}H NMR (600 MHz, $CDCl_3$)



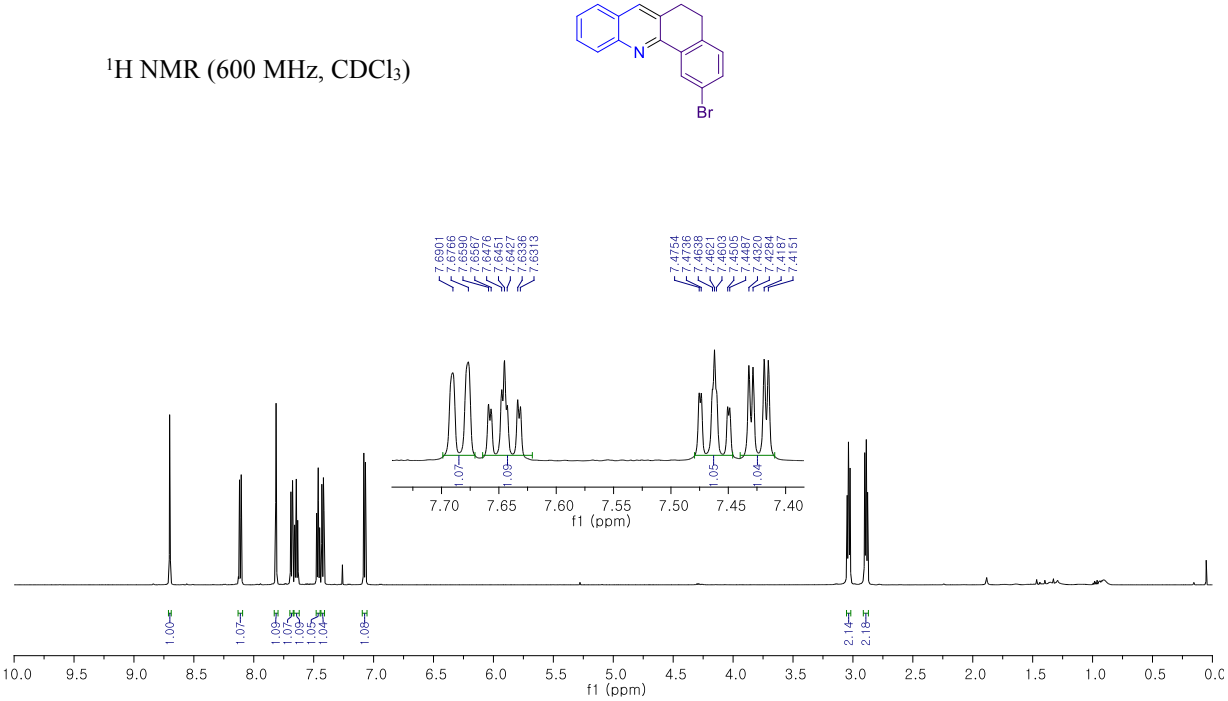


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

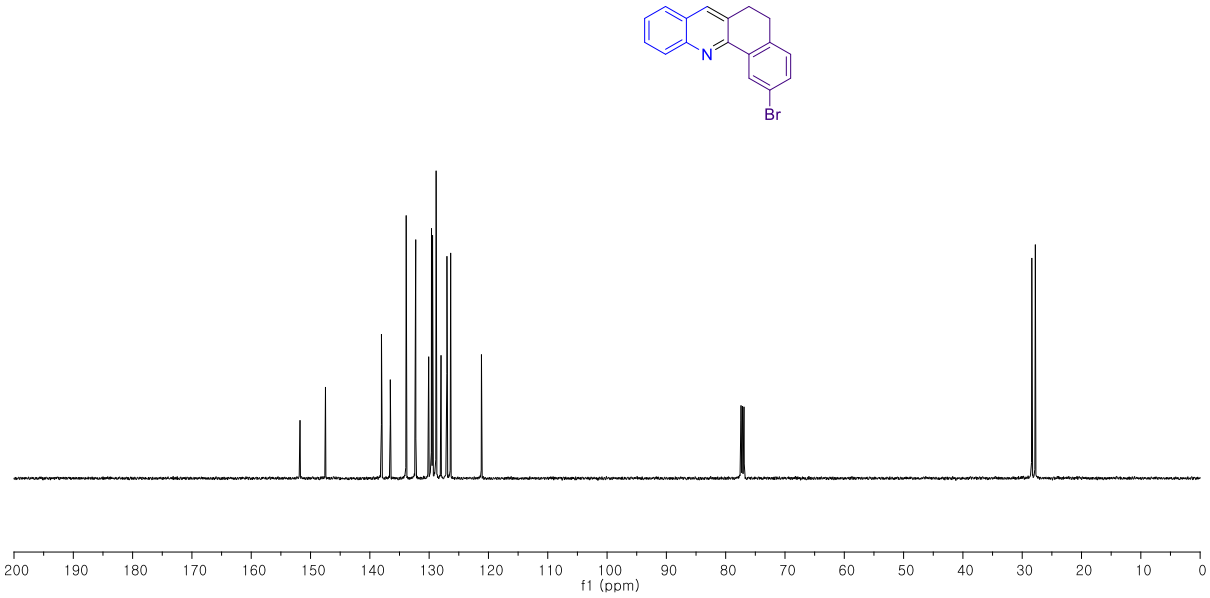


2-Bromo-5,6-dihydrobenzo[*c*]acridine (c5)

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

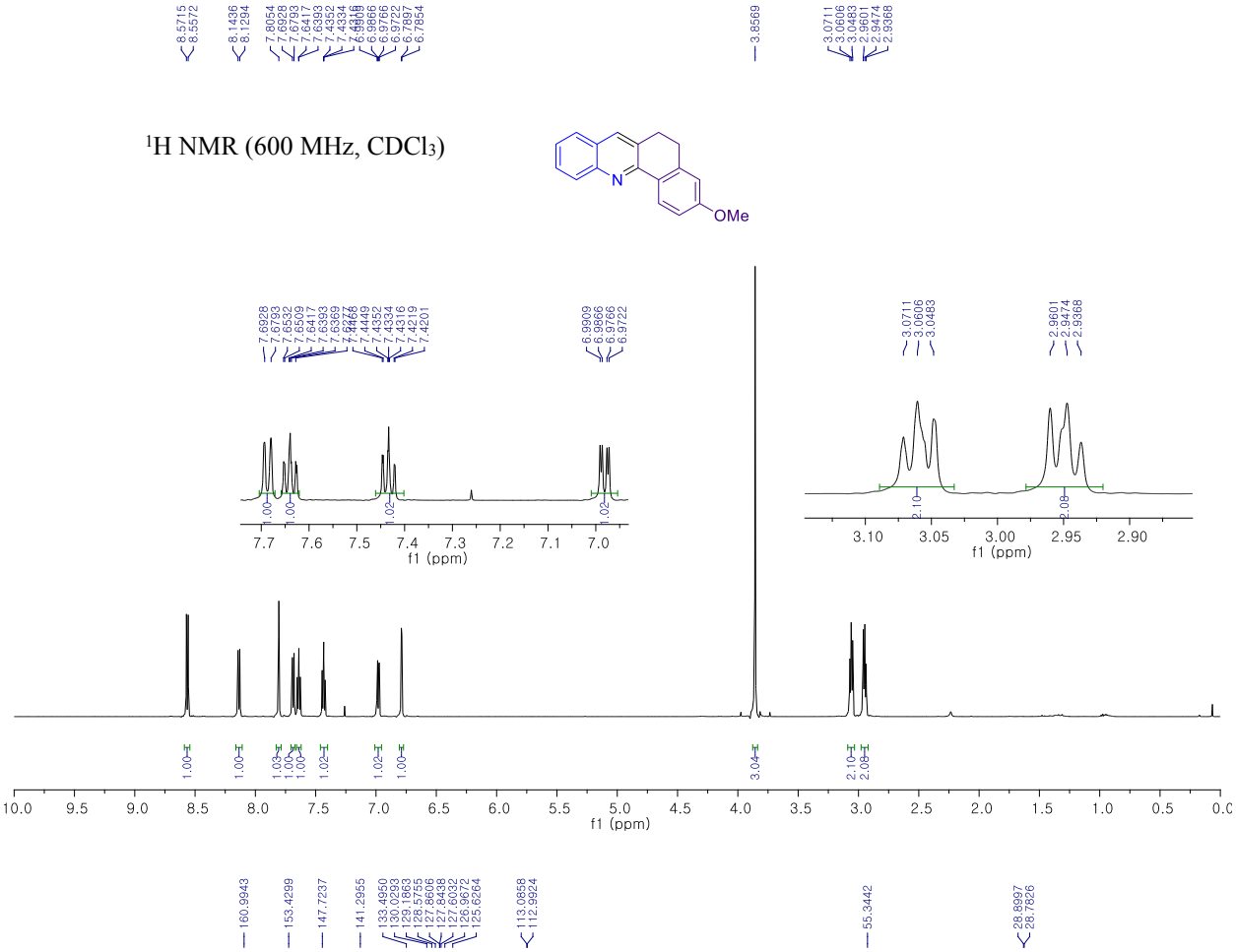


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

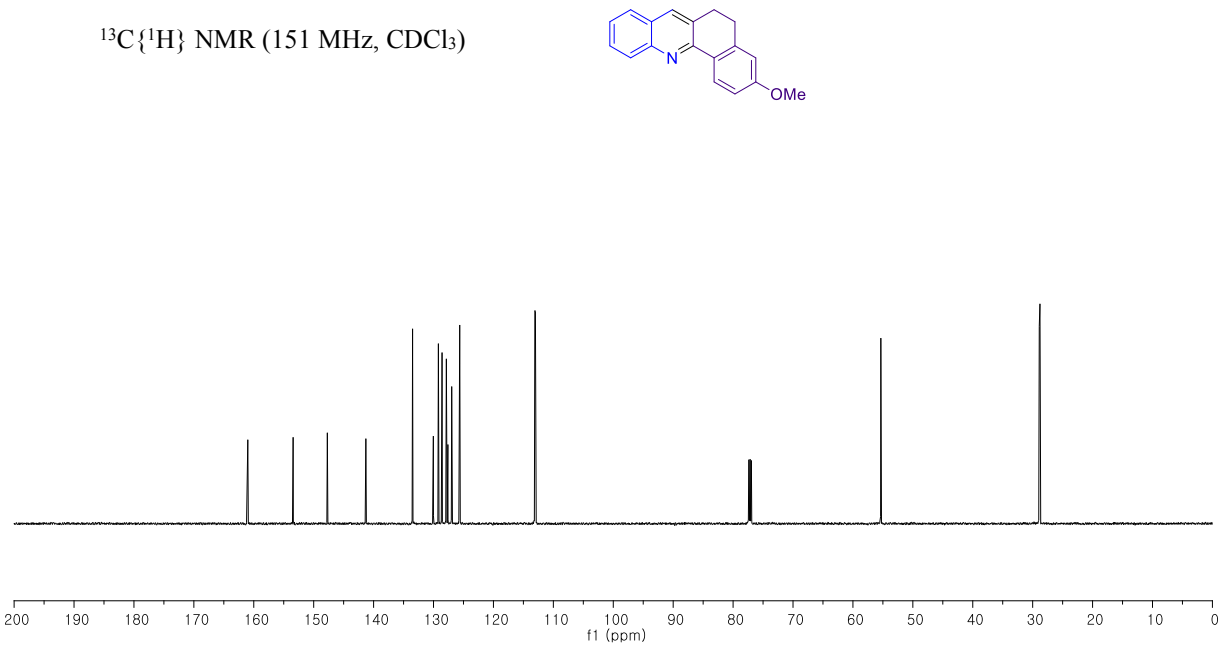


3-Methoxy-5,6-dihydrobenzo[*c*]acridine (c6)

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

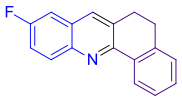


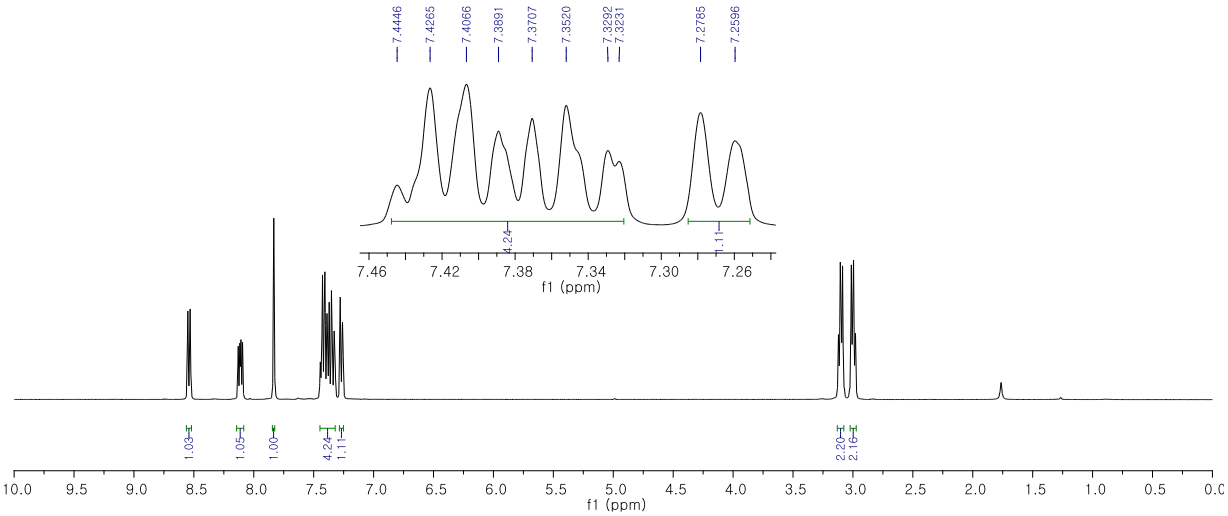
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



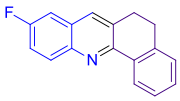
9-Fluoro-5,6-dihydrobenzo[*c*]acridine (c7)

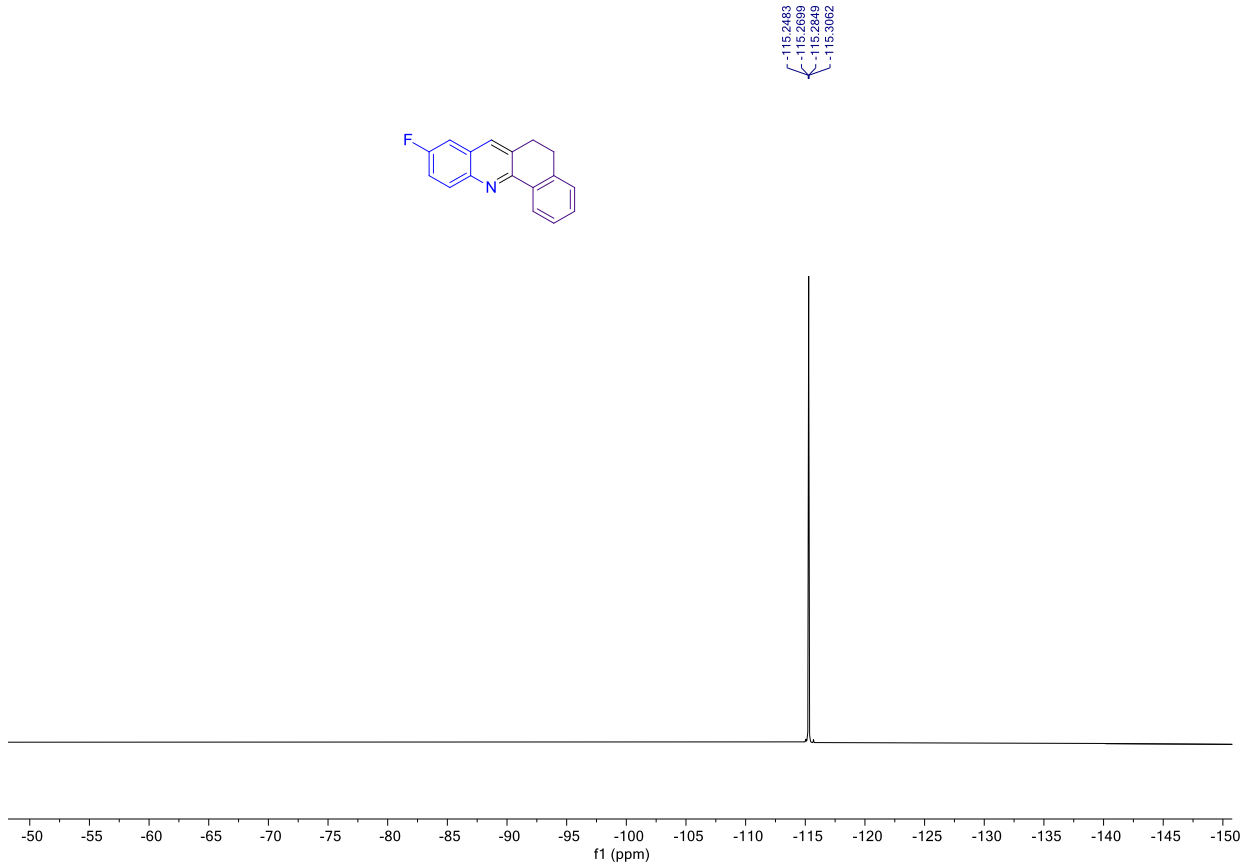
^{1}H NMR (400 MHz, $CDCl_3$)





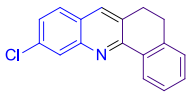
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

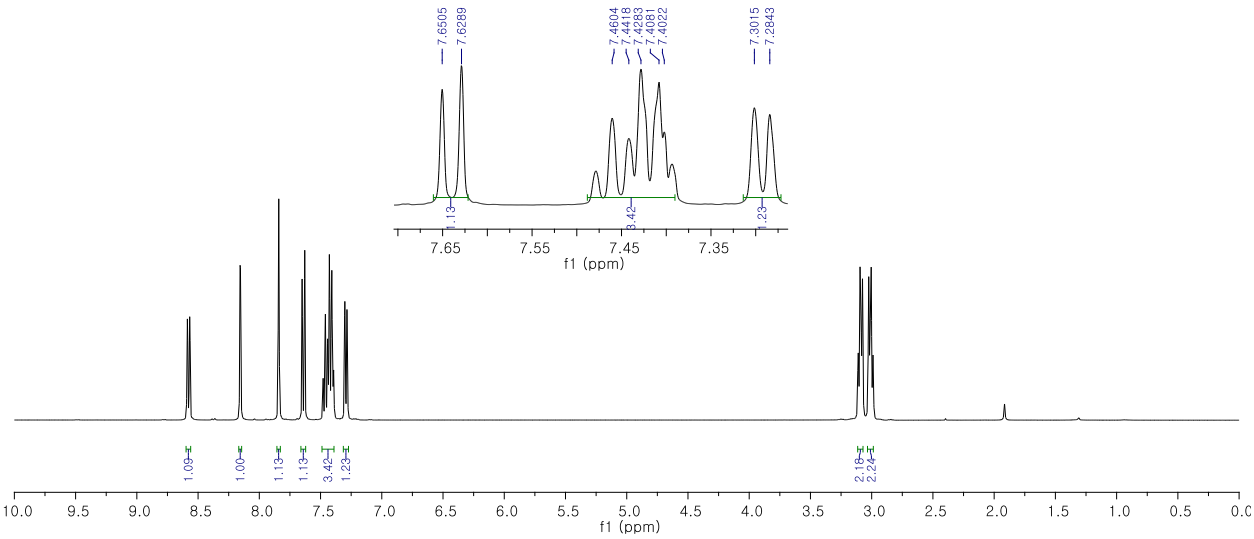



-115.2483
-115.2699
-115.2849
-115.3062
F
N
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)

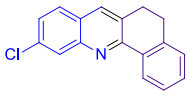
10-Chloro-5,6-dihydrobenzo[*c*]acridine (c8)

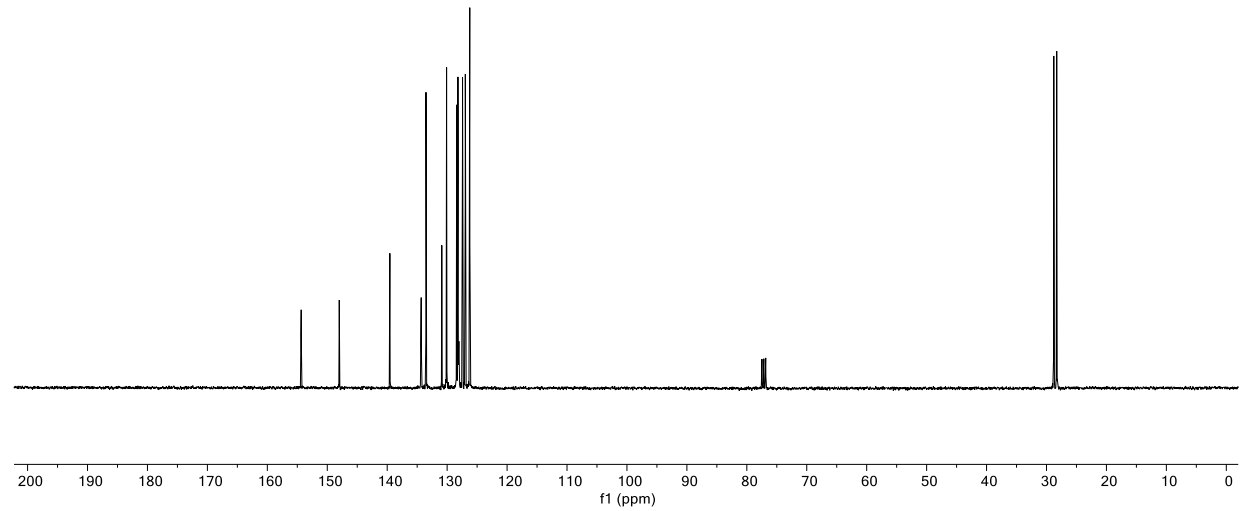
^{1}H NMR (400 MHz, $CDCl_3$)





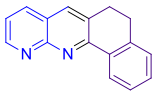
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

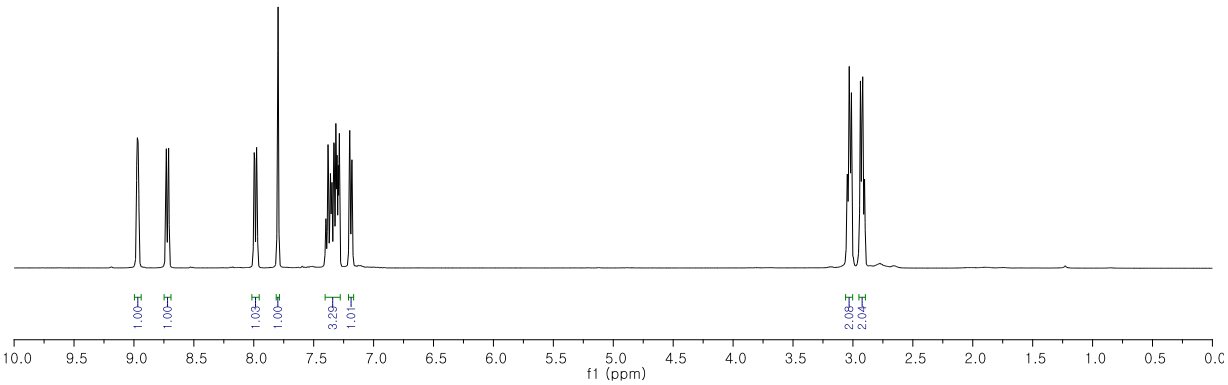




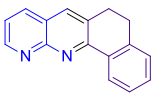
5,6-Dihydronaphtho[1,2-*b*][1,8]naphthyridine (c9)

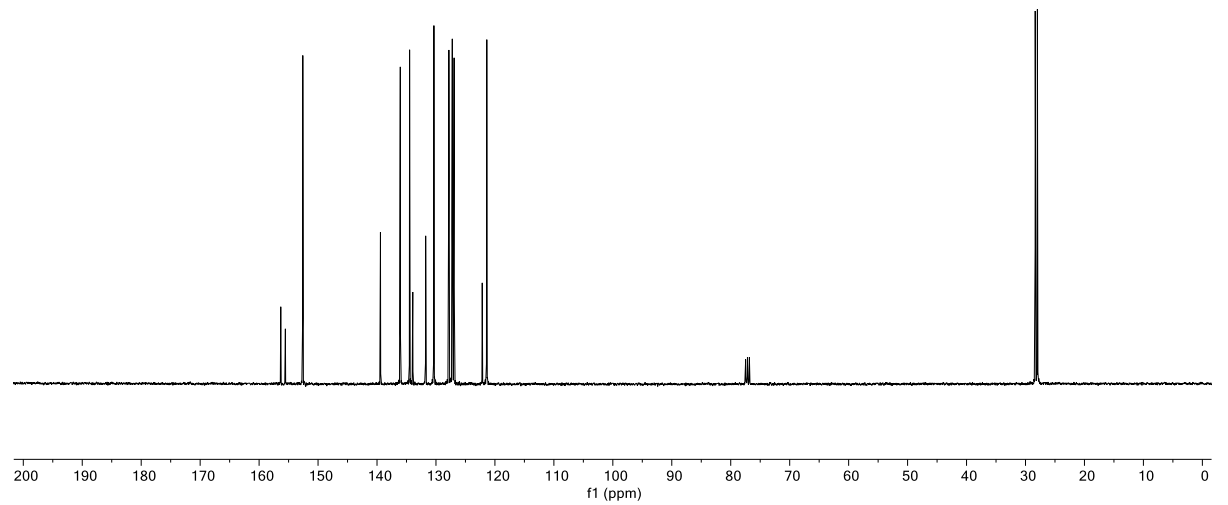
^{1}H NMR (400 MHz, $CDCl_3$)





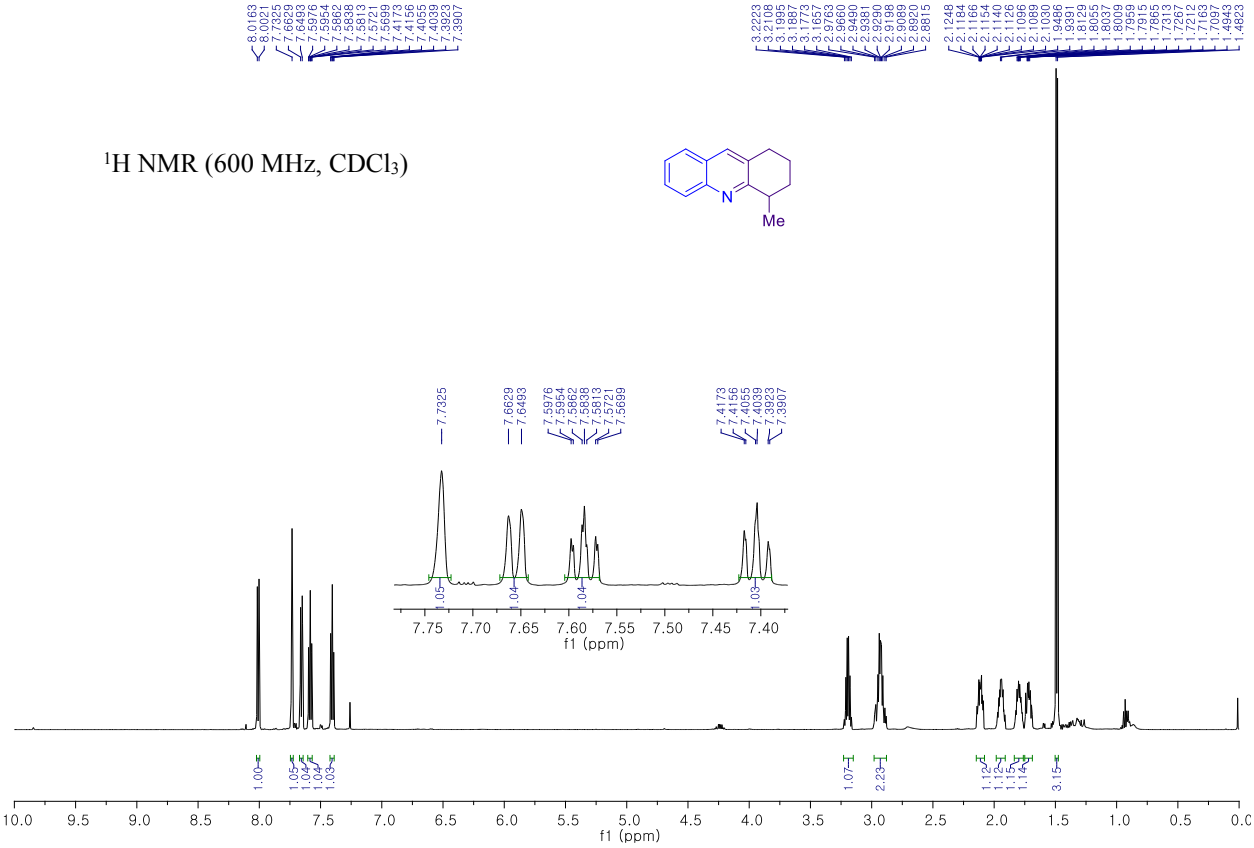
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



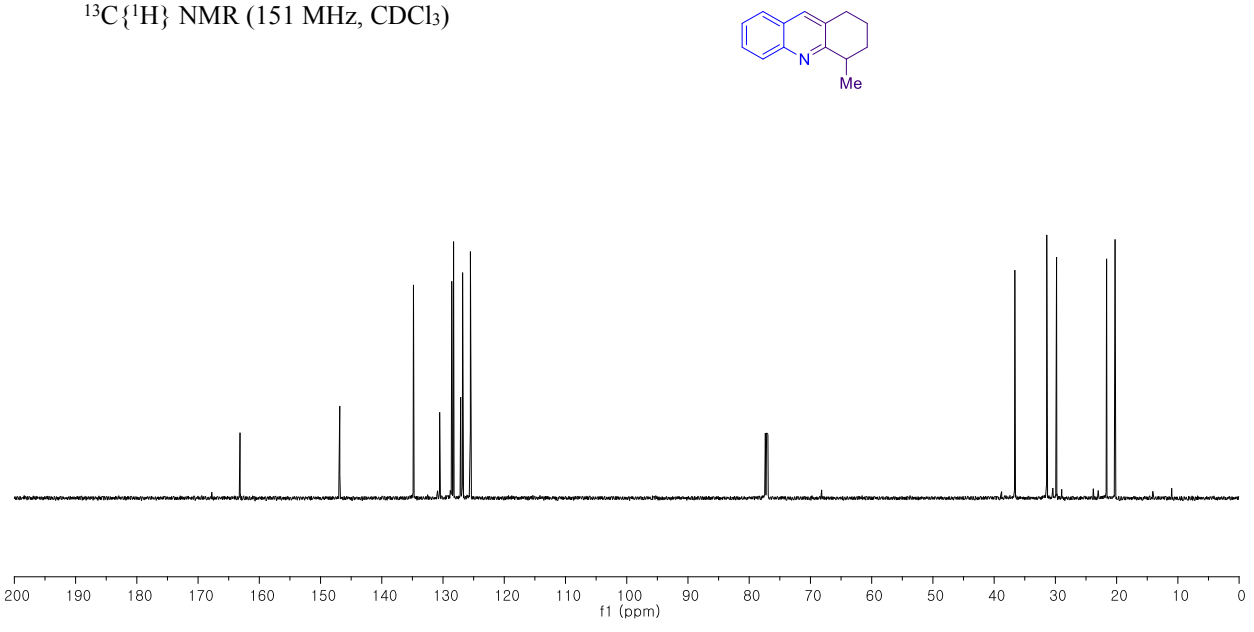


4-Methyl-1,2,3,4-tetrahydroacridine (c10)

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

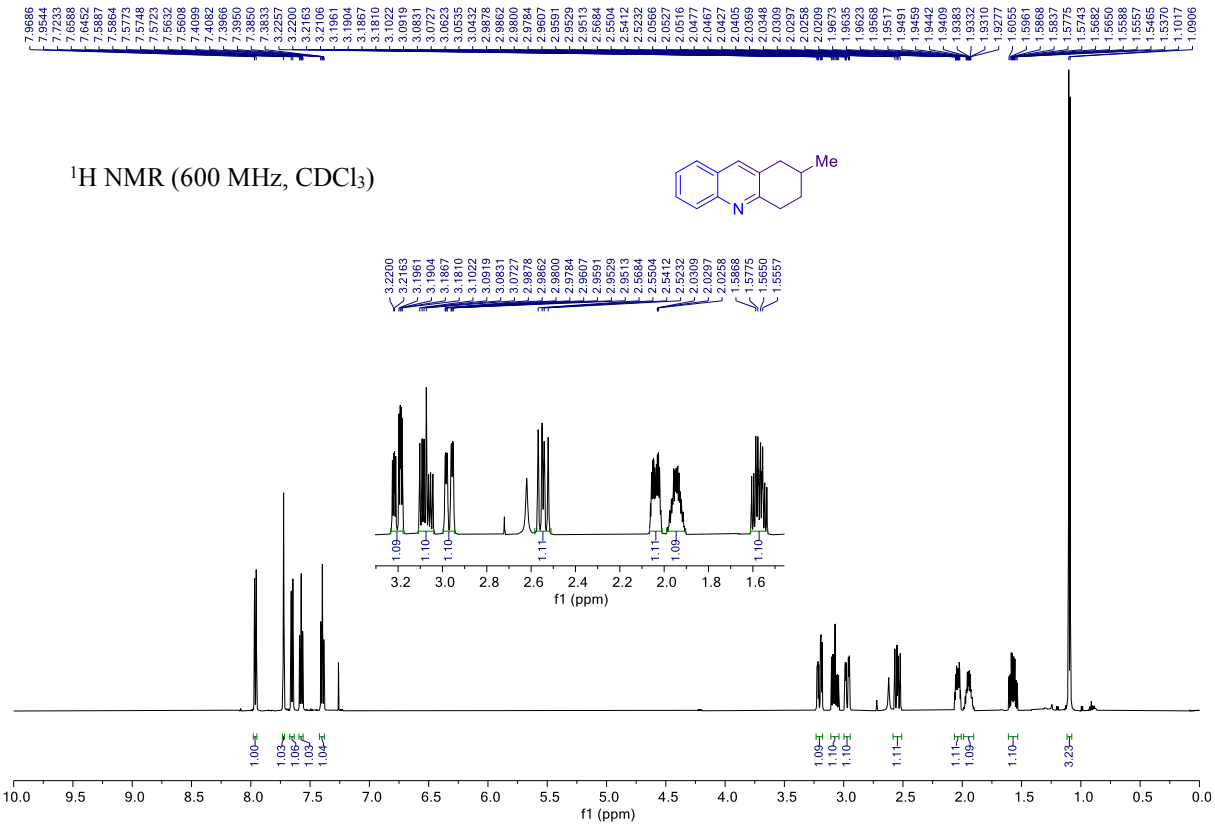


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

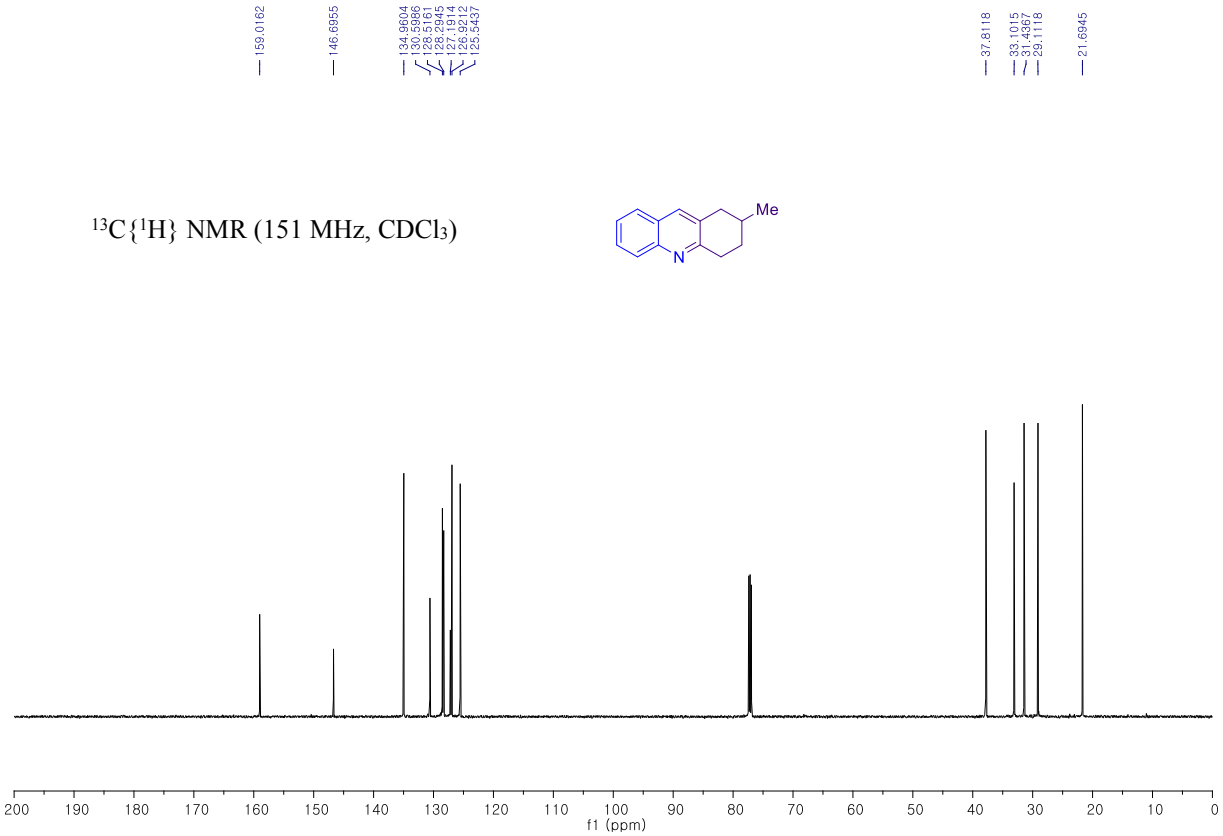


2-Methyl-1,2,3,4-tetrahydroacridine (c11)

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

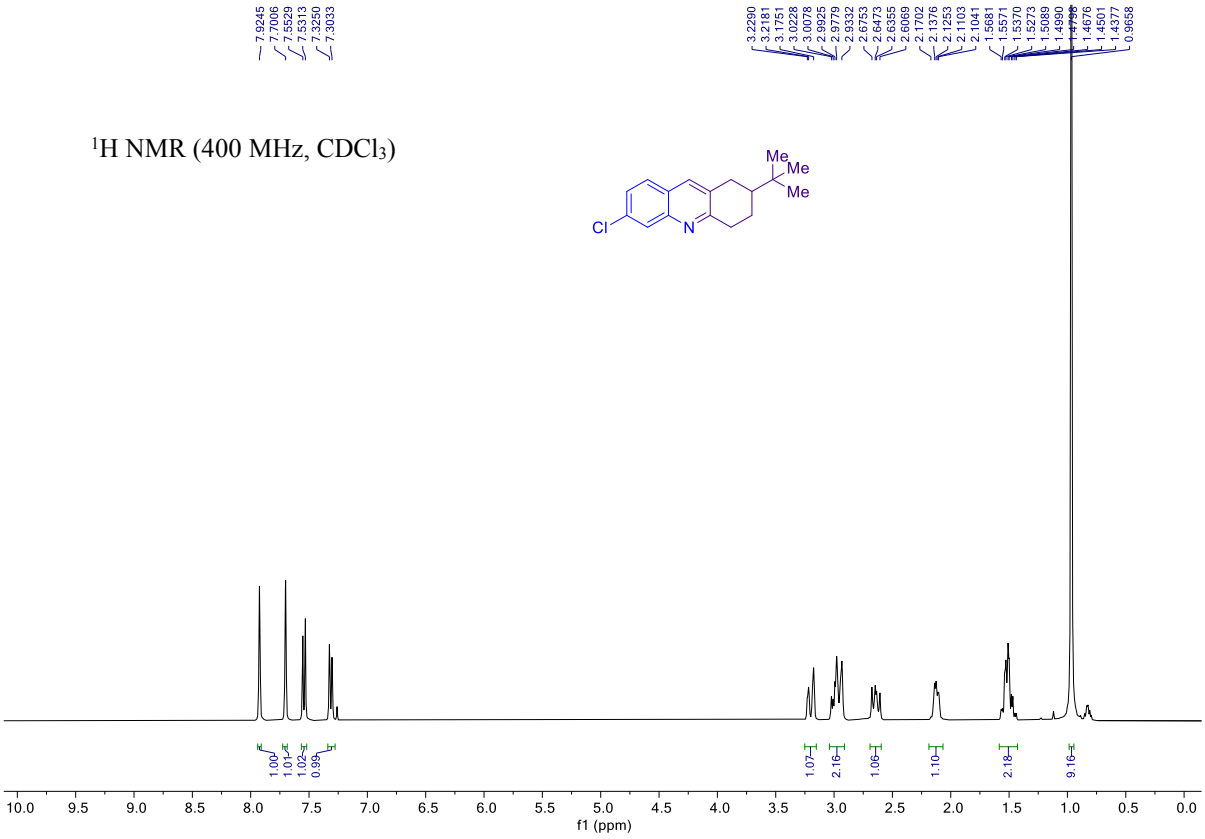


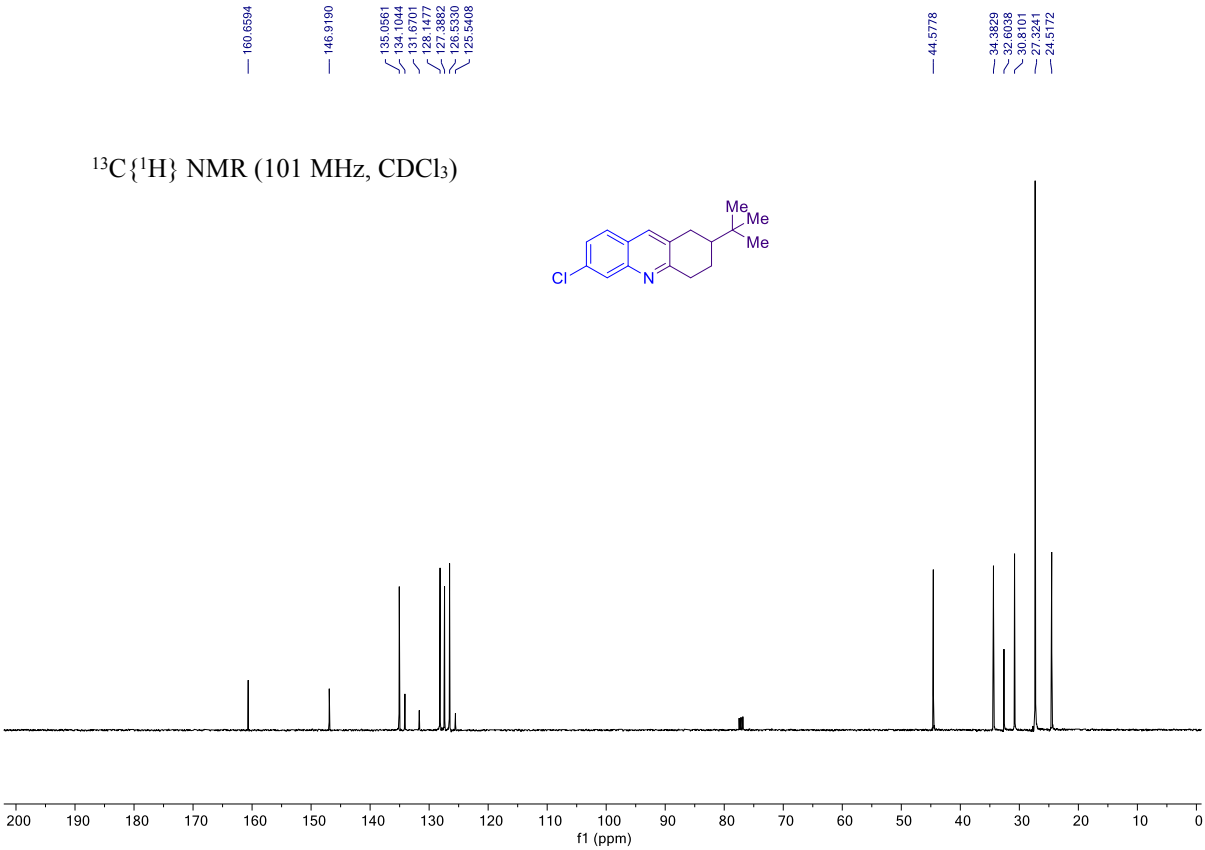
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



2-(Tert-butyl)-6-chloro-1,2,3,4-tetrahydroacridine (c12)

^{1}H NMR (400 MHz, $CDCl_3$)

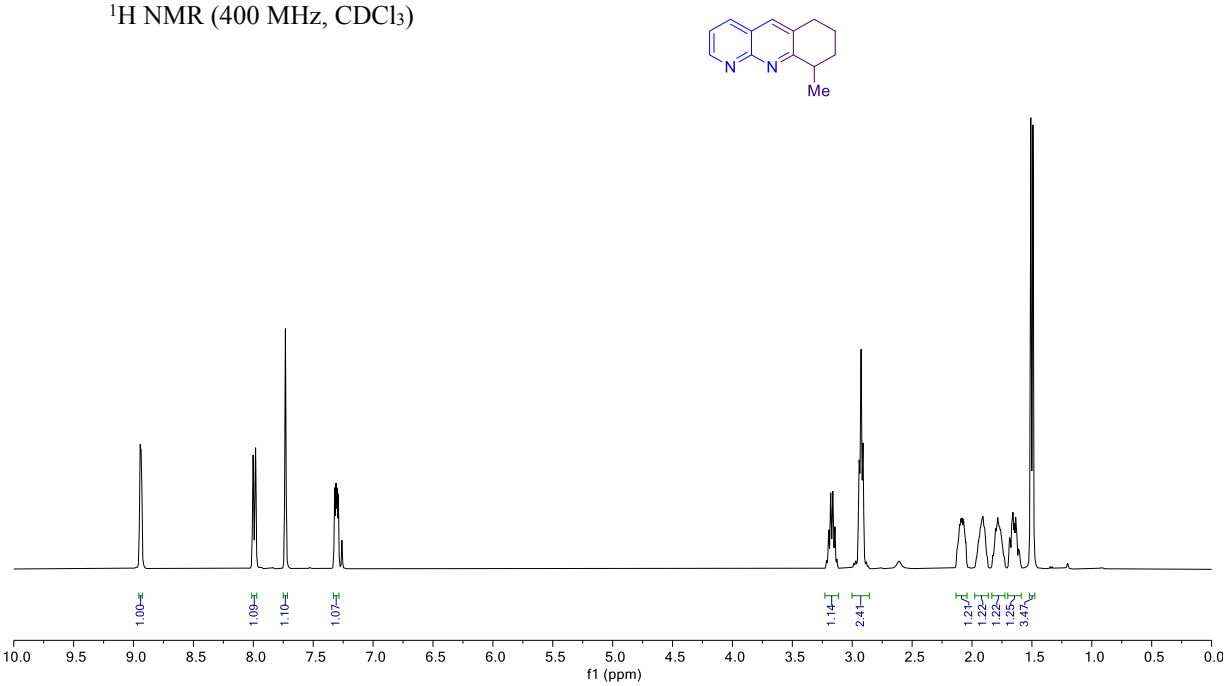




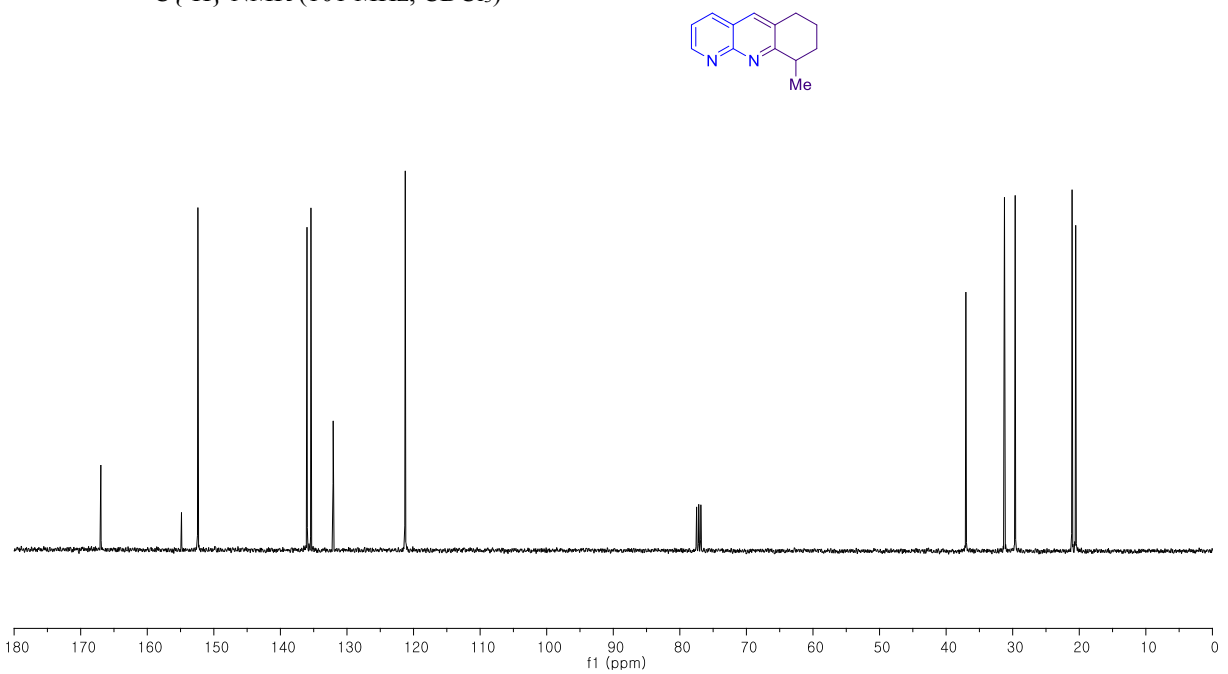
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

9-Methyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridinenew (c13)

^{1}H NMR (400 MHz, $CDCl_3$)

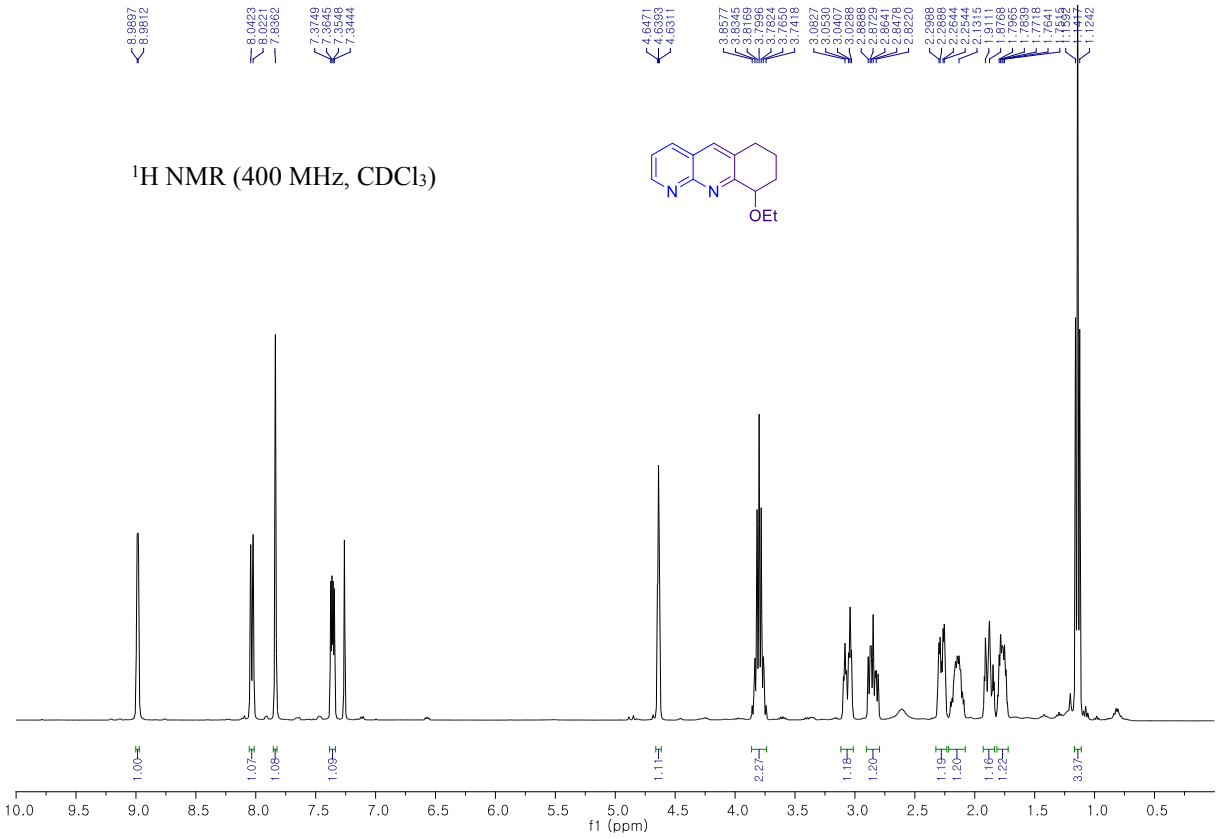


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

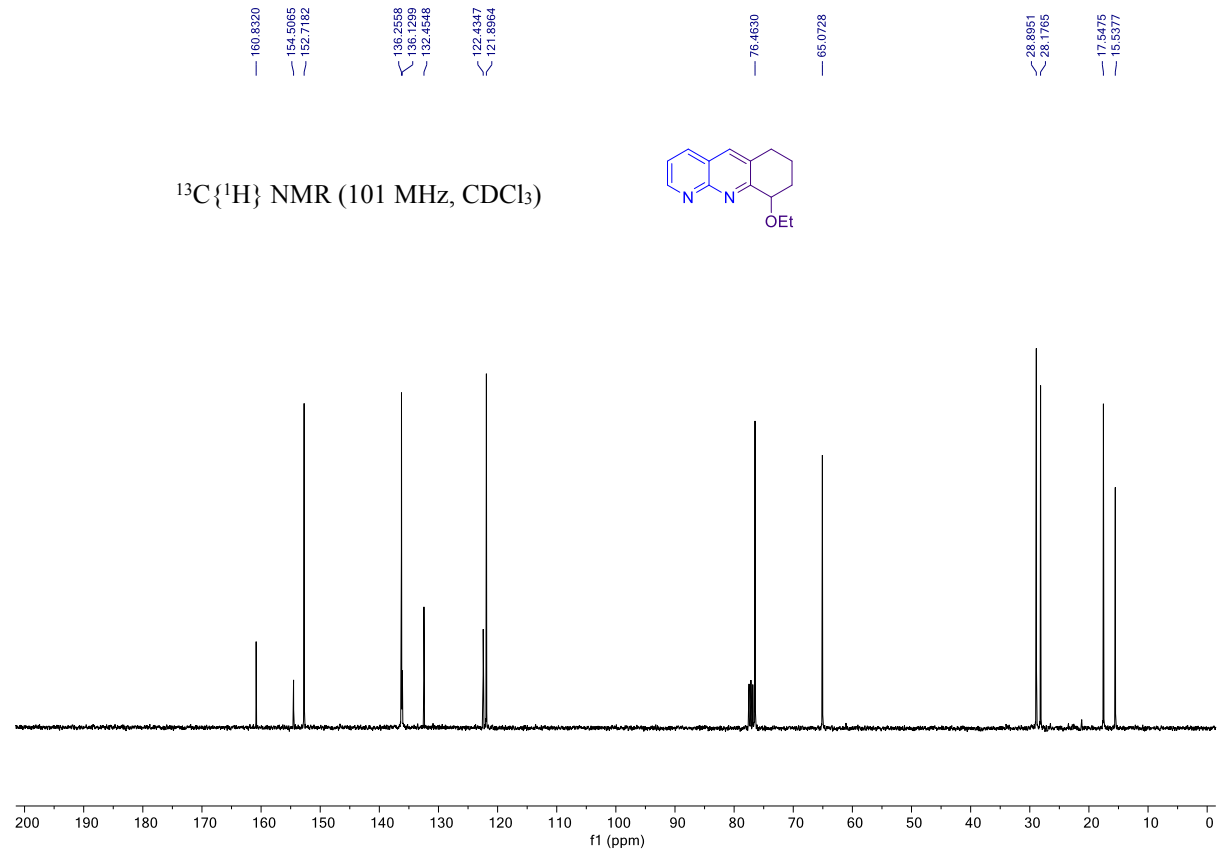


9-Ethoxy-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c14)

^{1}H NMR (400 MHz, $CDCl_3$)

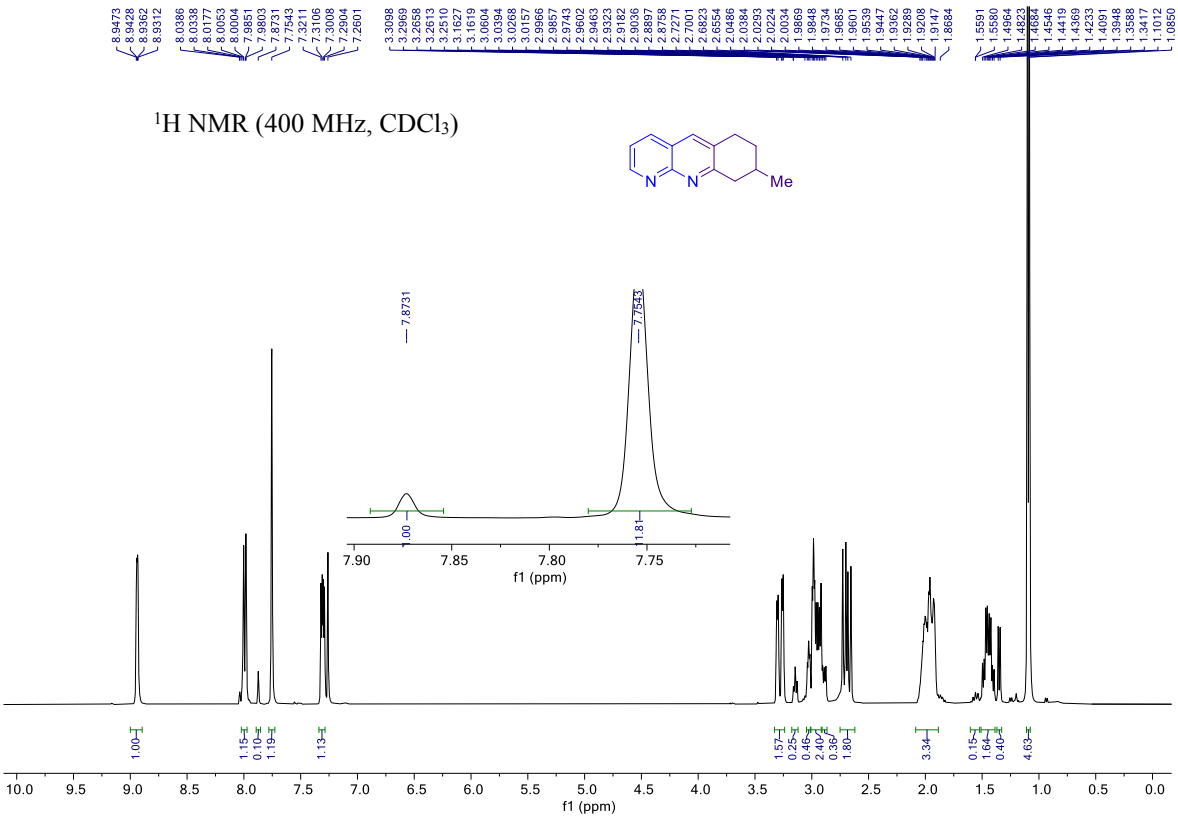


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

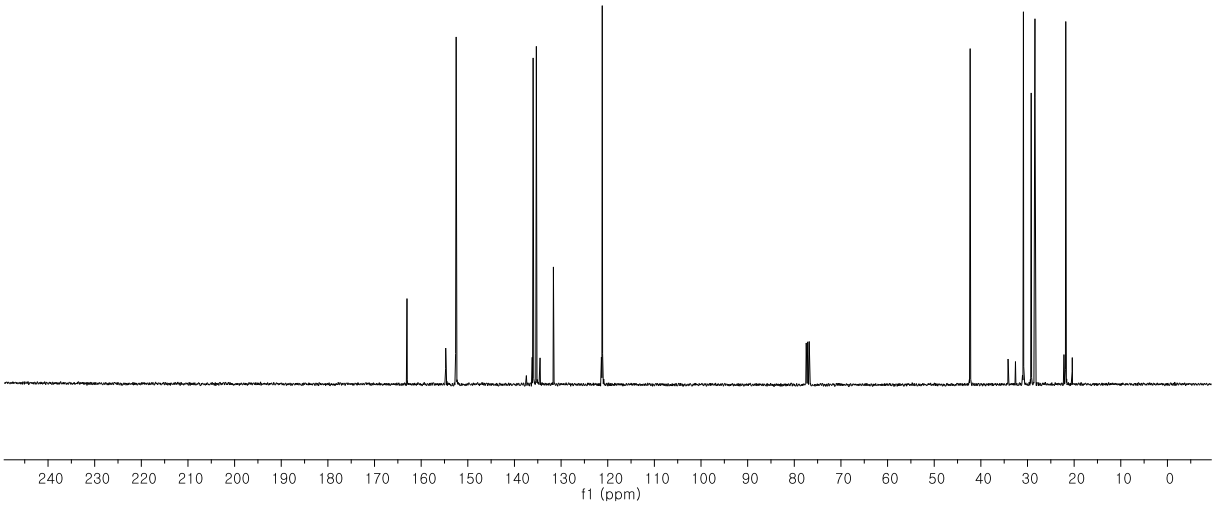


8-Methyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c15)

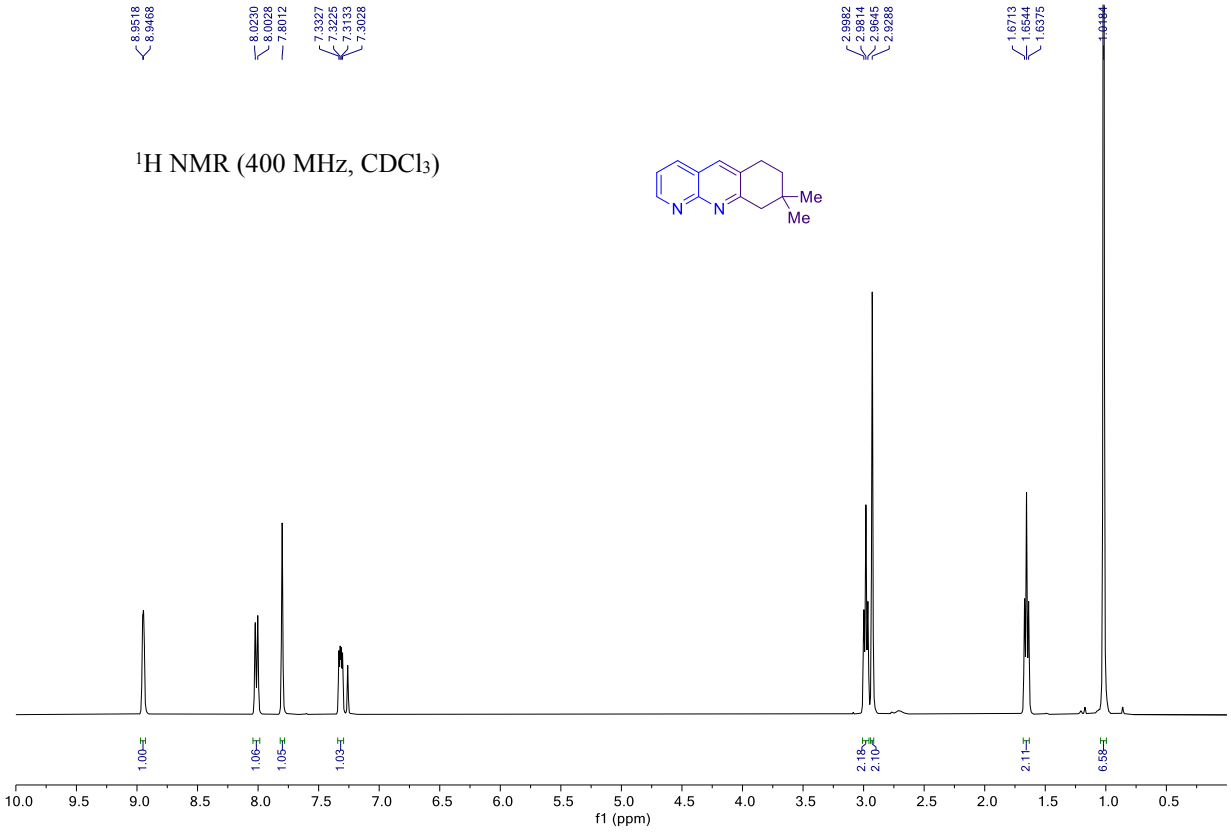
^{1}H NMR (400 MHz, $CDCl_3$)

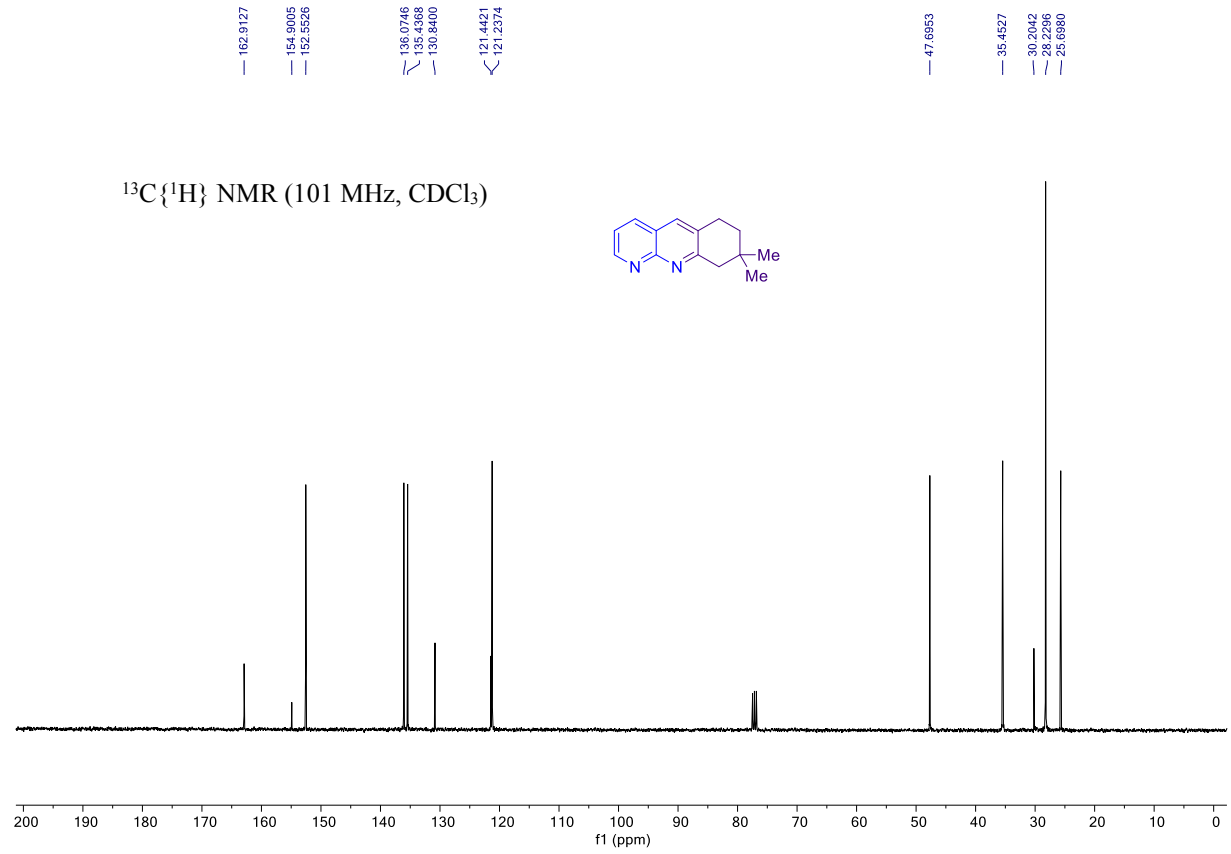


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

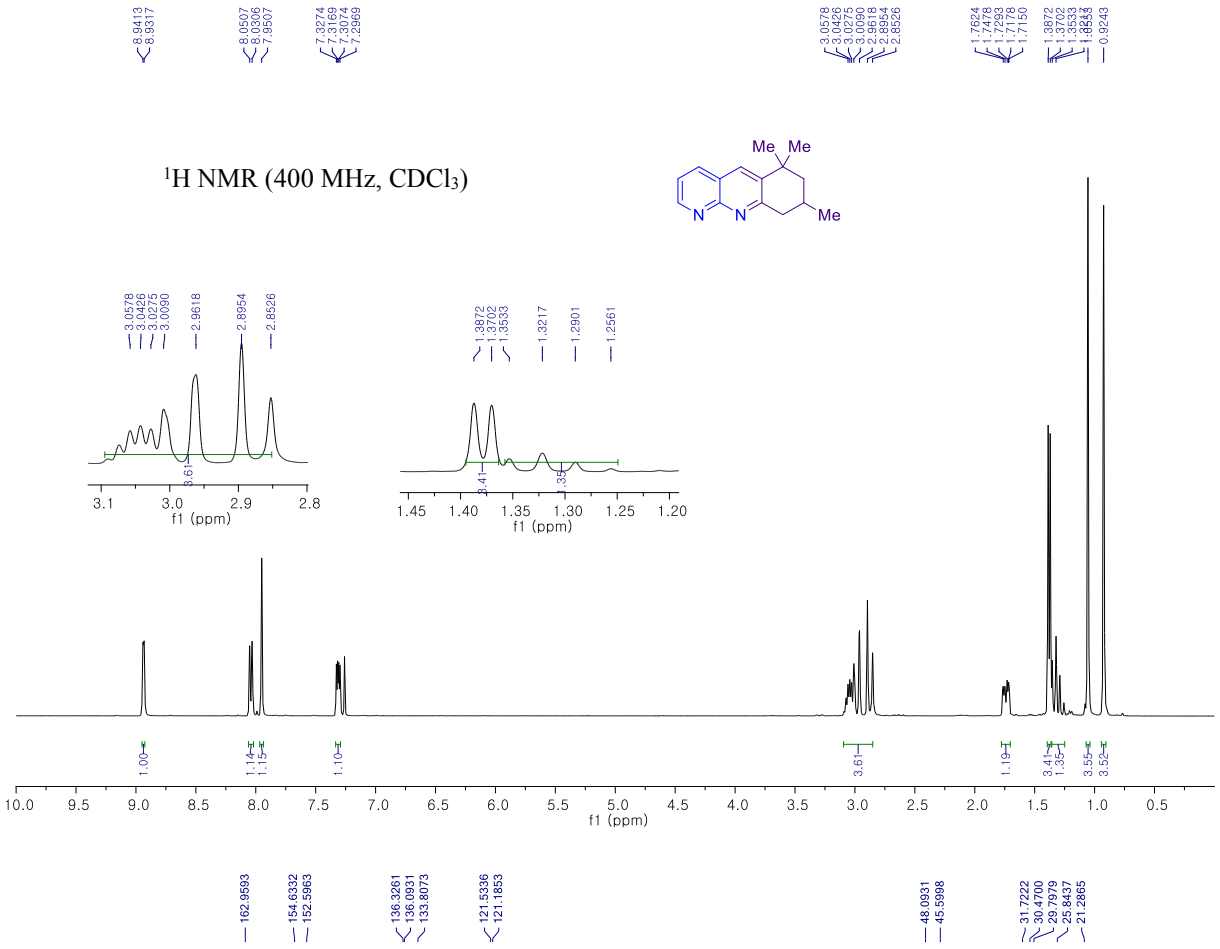


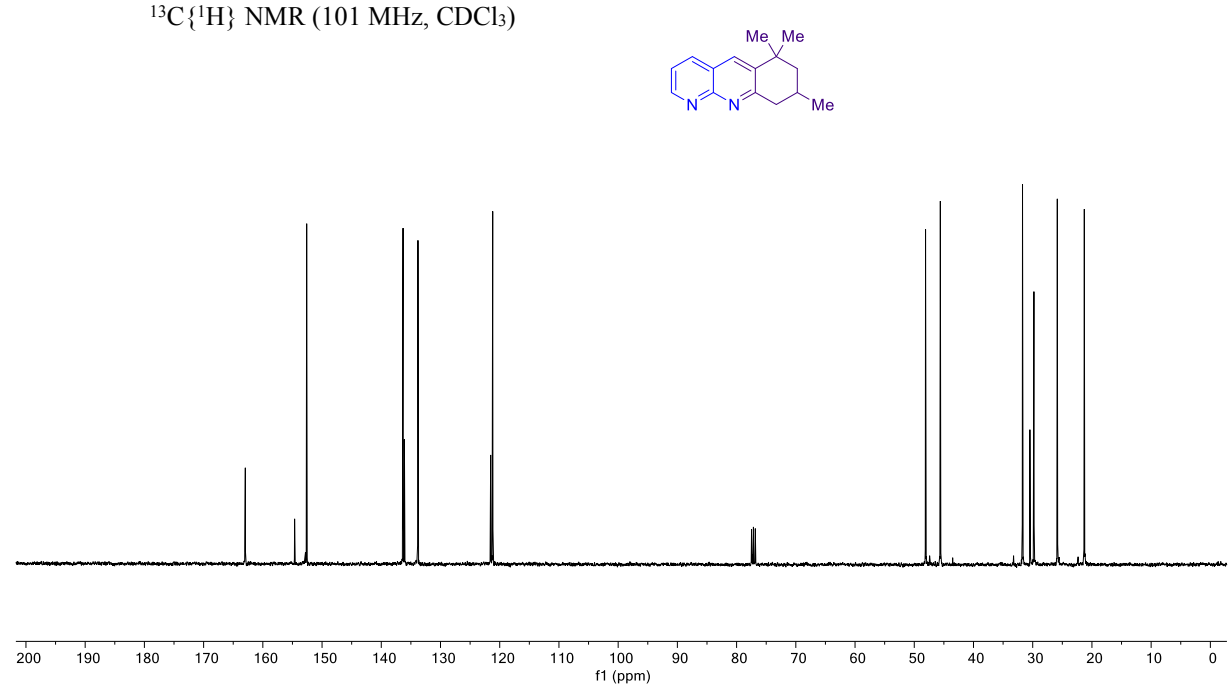
8,8-Dimethyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c16)





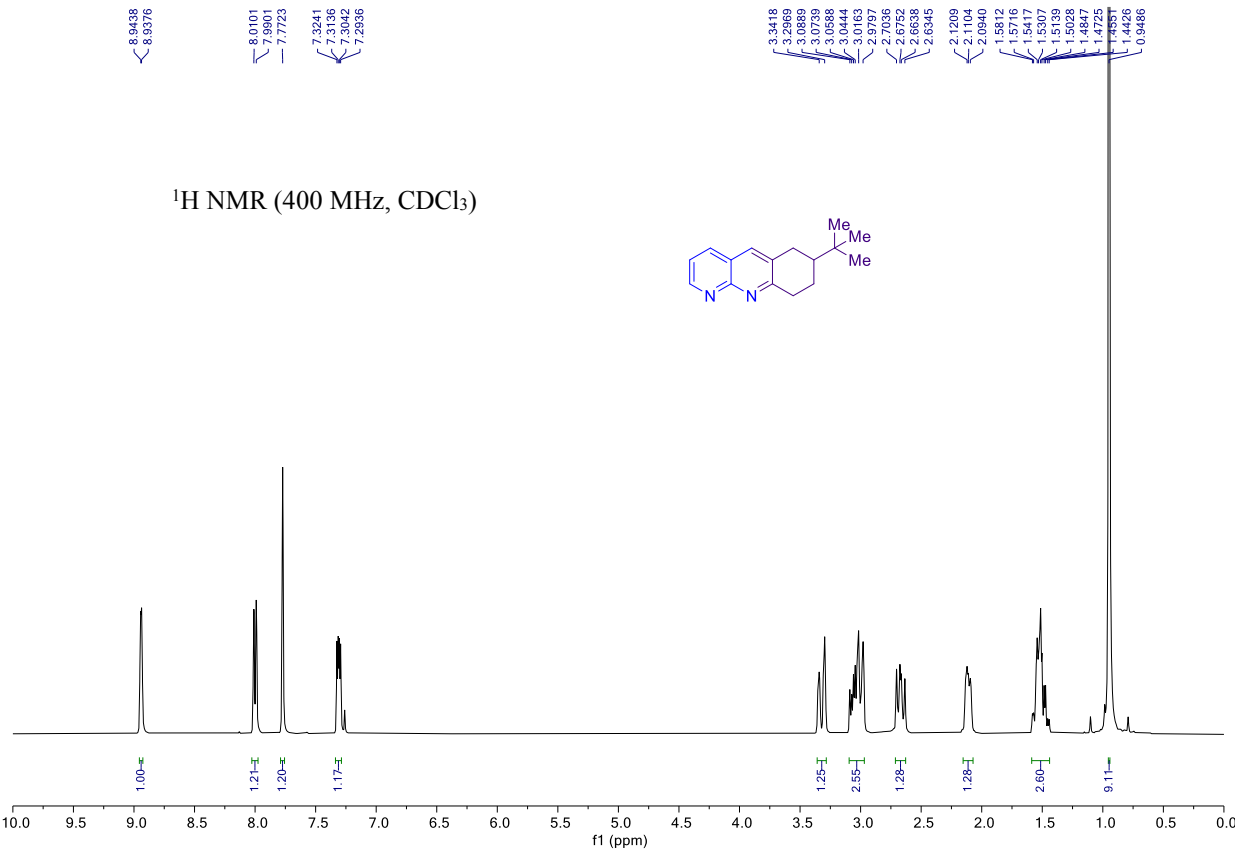
6,6,8-Trimethyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c17)



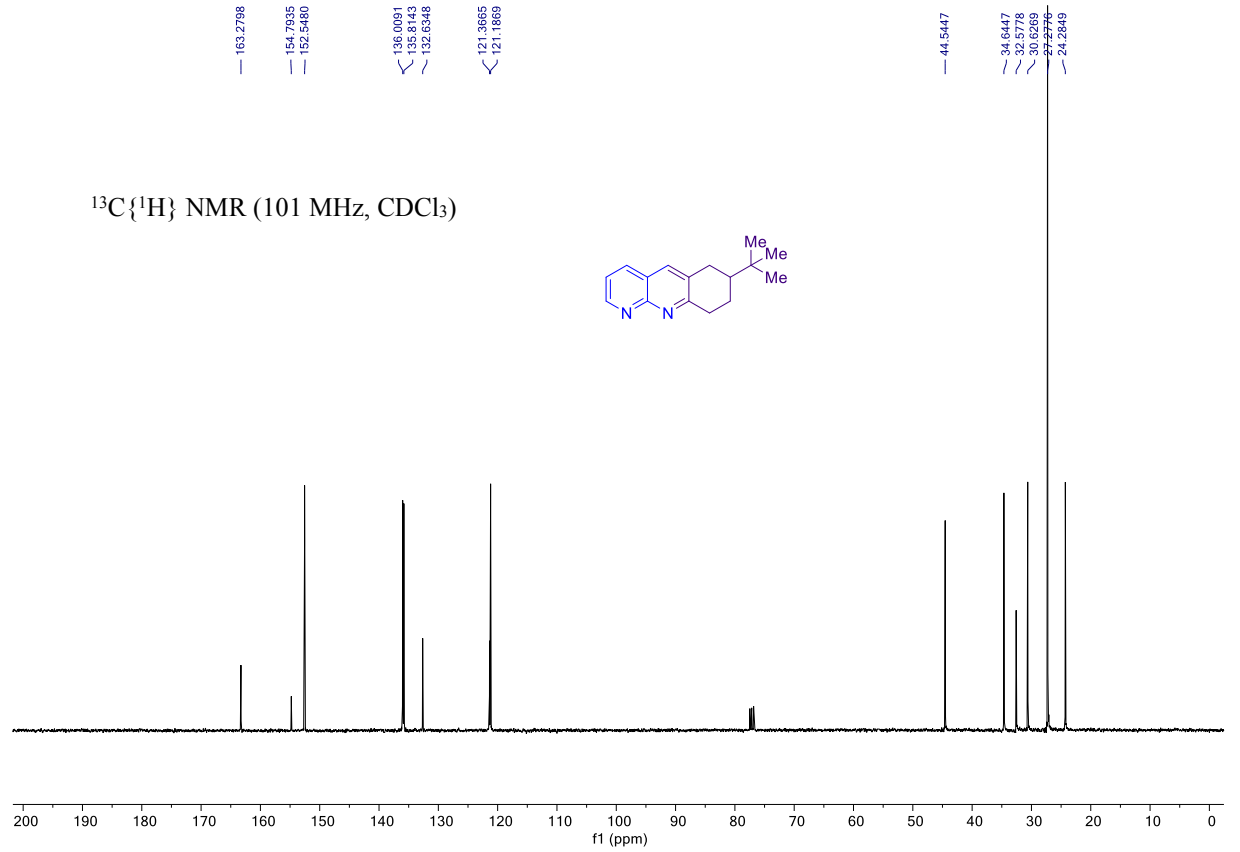


7-(Tert-butyl)-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c18)

^{1}H NMR (400 MHz, $CDCl_3$)

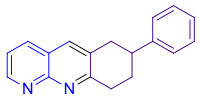


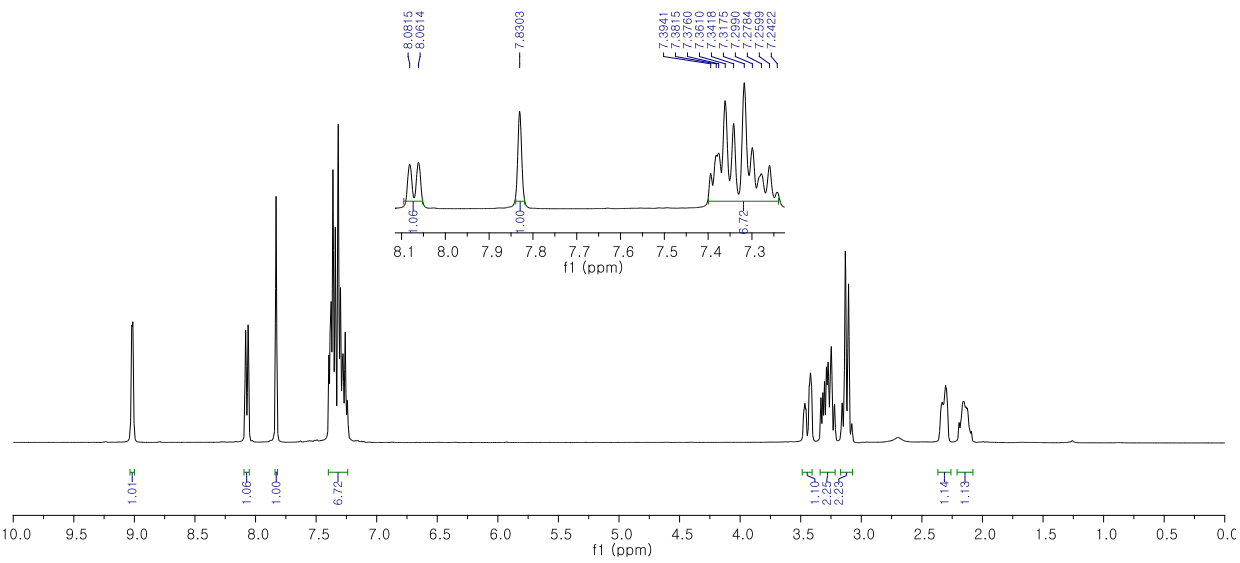
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



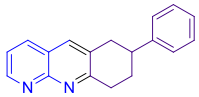
7-Phenyl-6,7,8,9-tetrahydrobenzo[*b*][1,8]naphthyridine (c19)

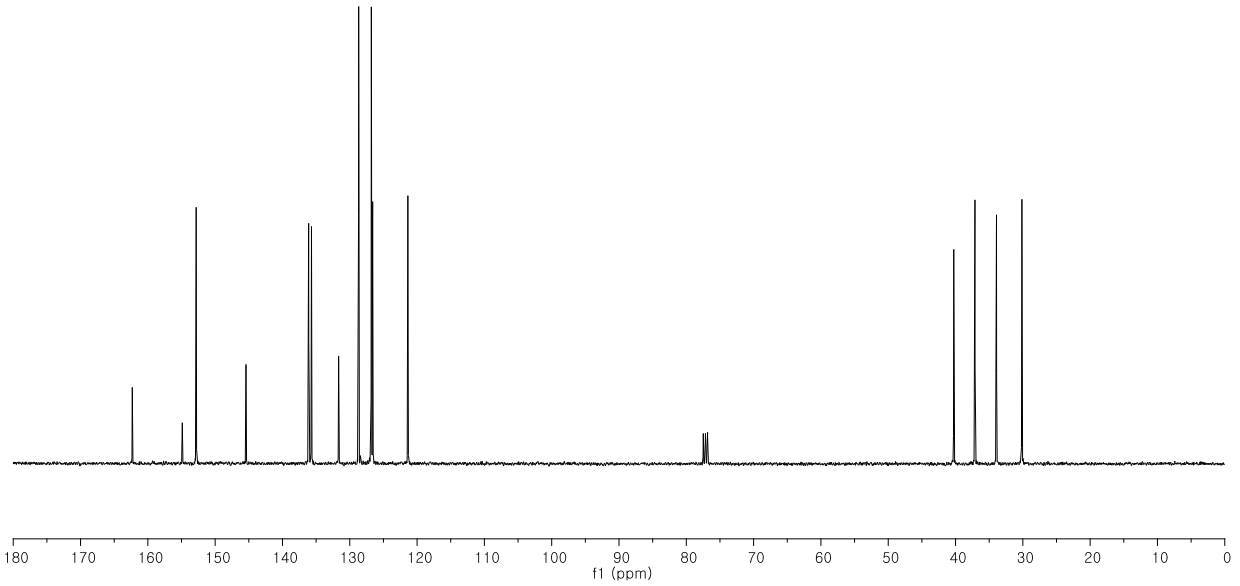
^{1}H NMR (400 MHz, $CDCl_3$)



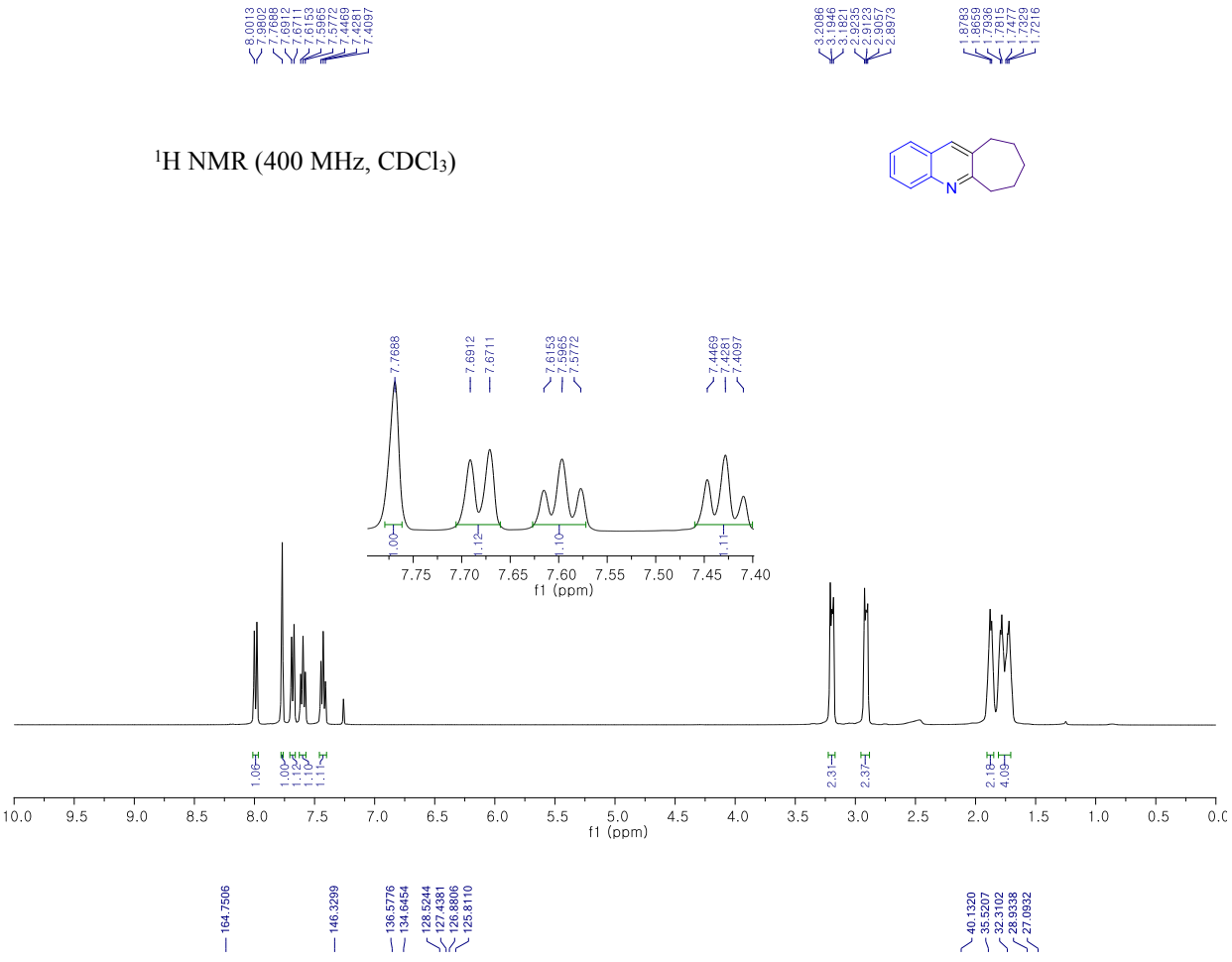


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

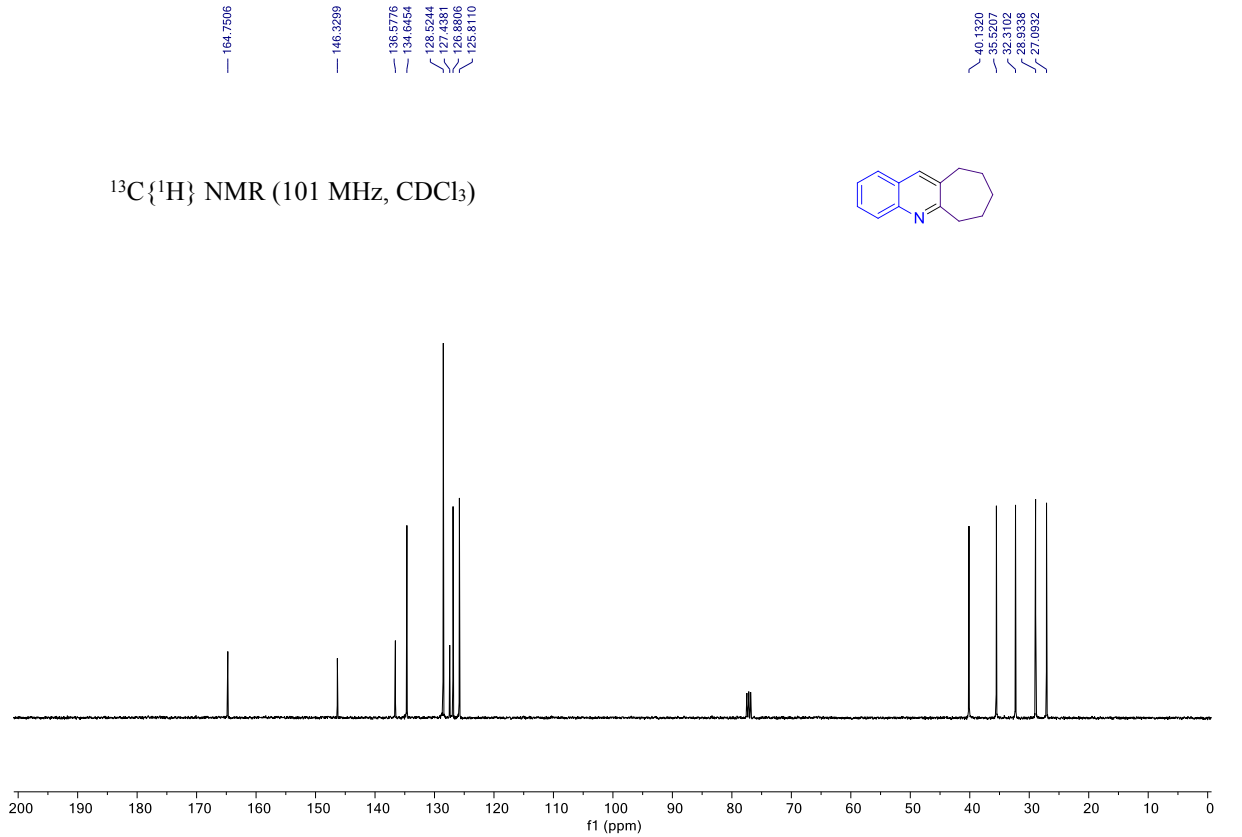




7,8,9,10-Tetrahydro-6*H*-cyclohepta[*b*]quinolone (c20)

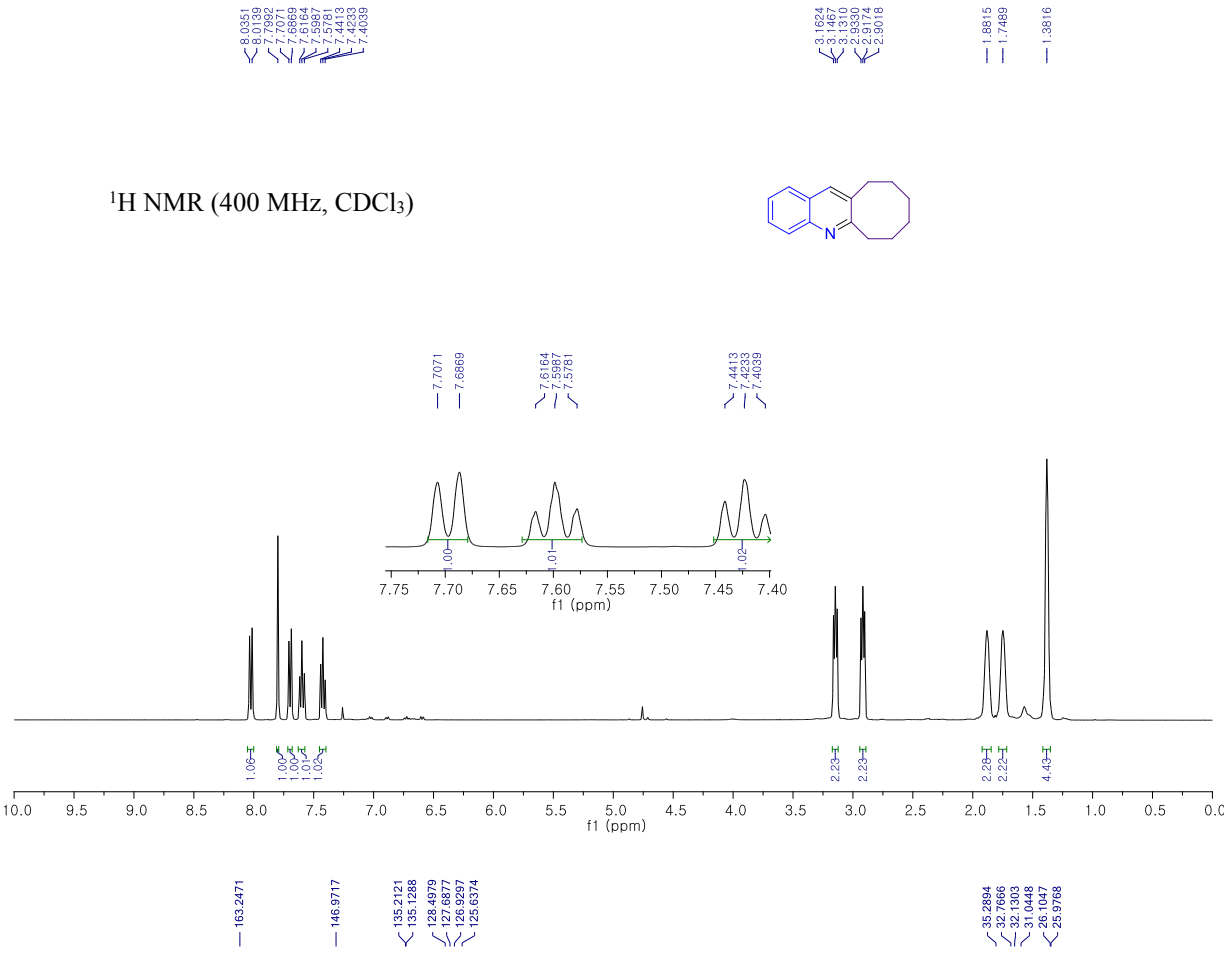


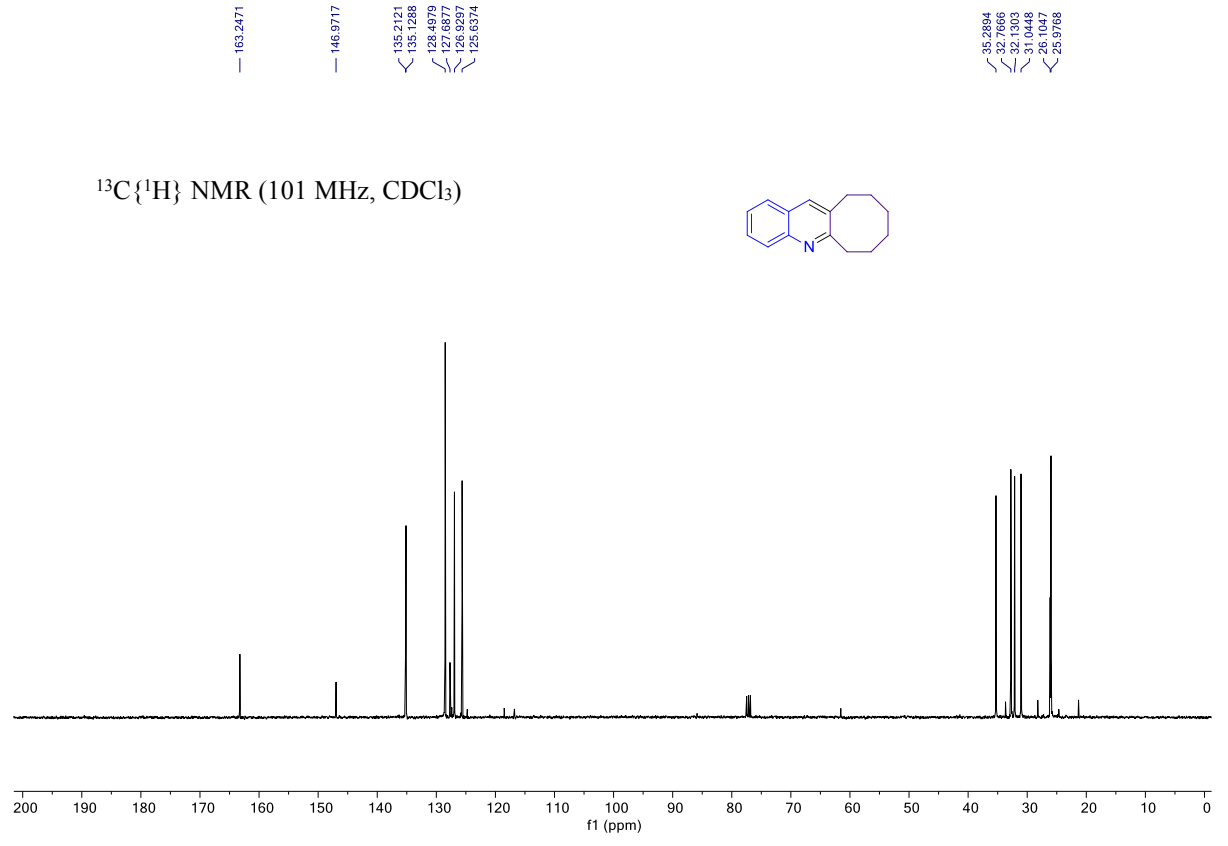
^{1}H NMR (400 MHz, $CDCl_3$)



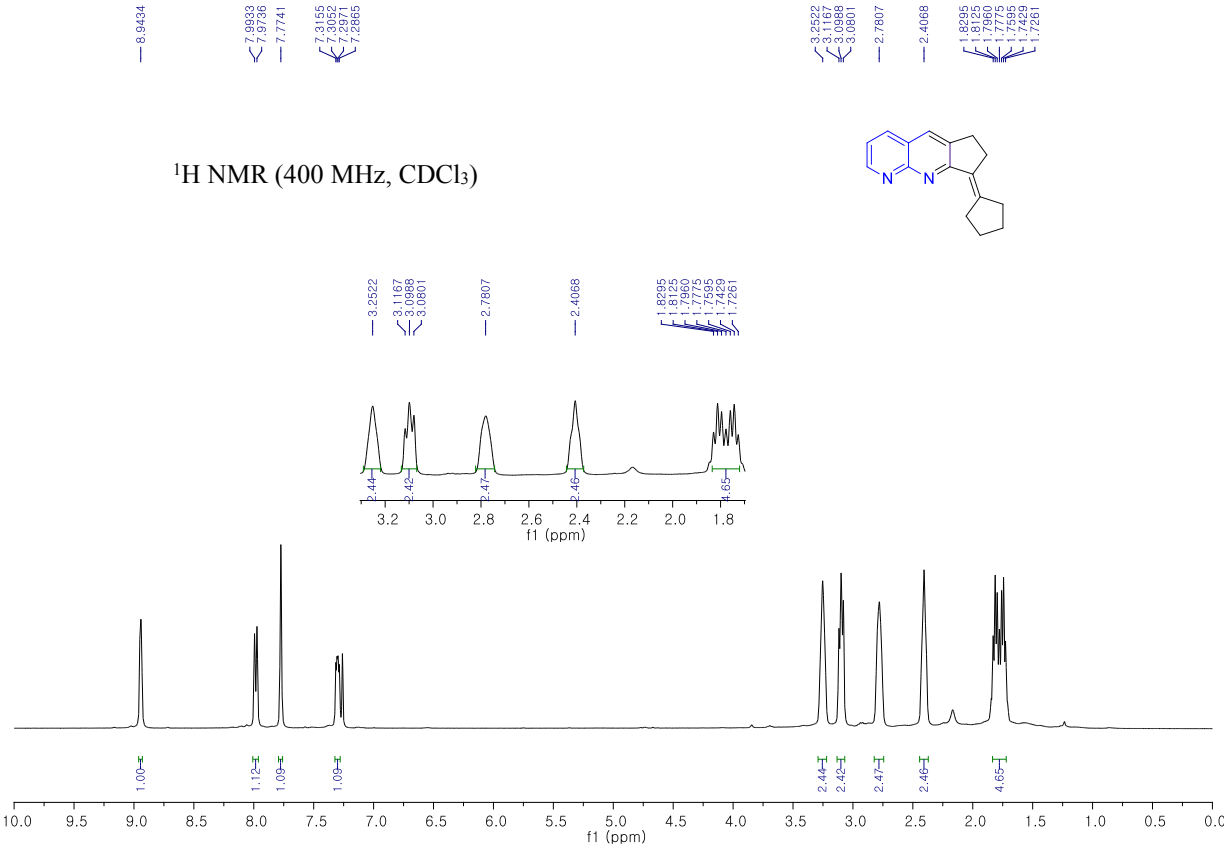
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

6,7,8,9,10,11-Hexahydrocycloocta[*b*]quinolone (c21)



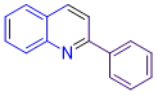


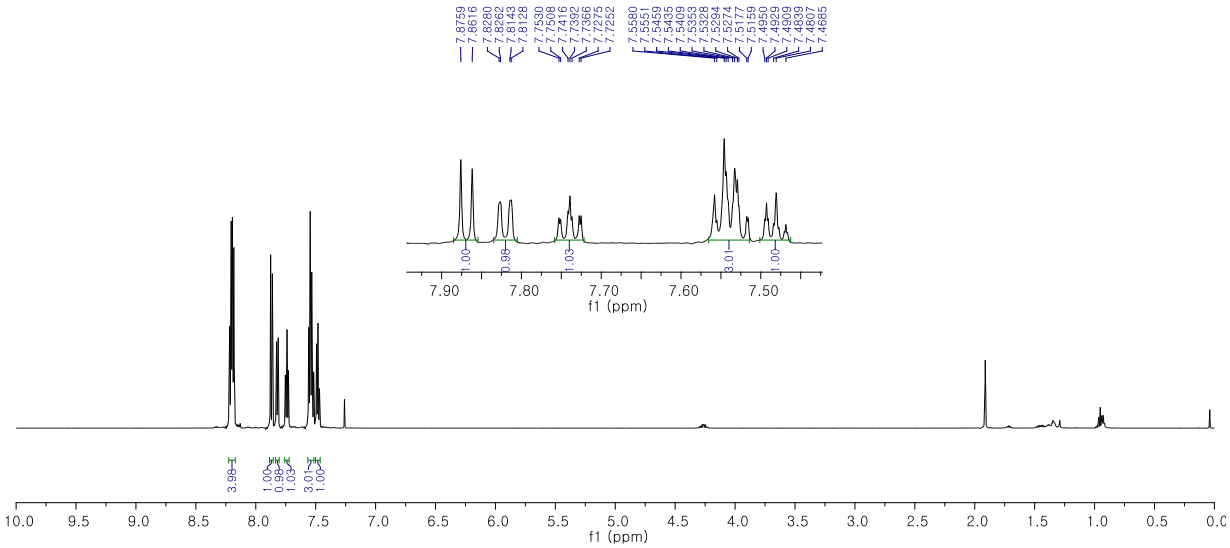
3-Cyclopentylidene-2,3-dihydro-1H-cyclopenta[b]quinoline (c22)

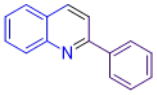


2-Phenylquinoline (c23)

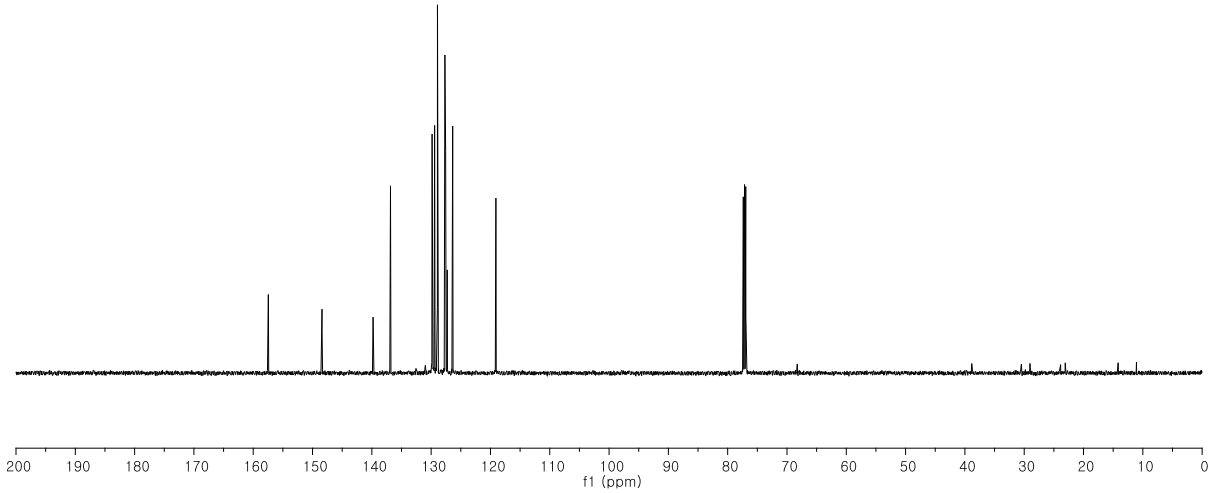
^{1}H NMR (600 MHz, $CDCl_3$)





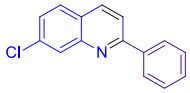


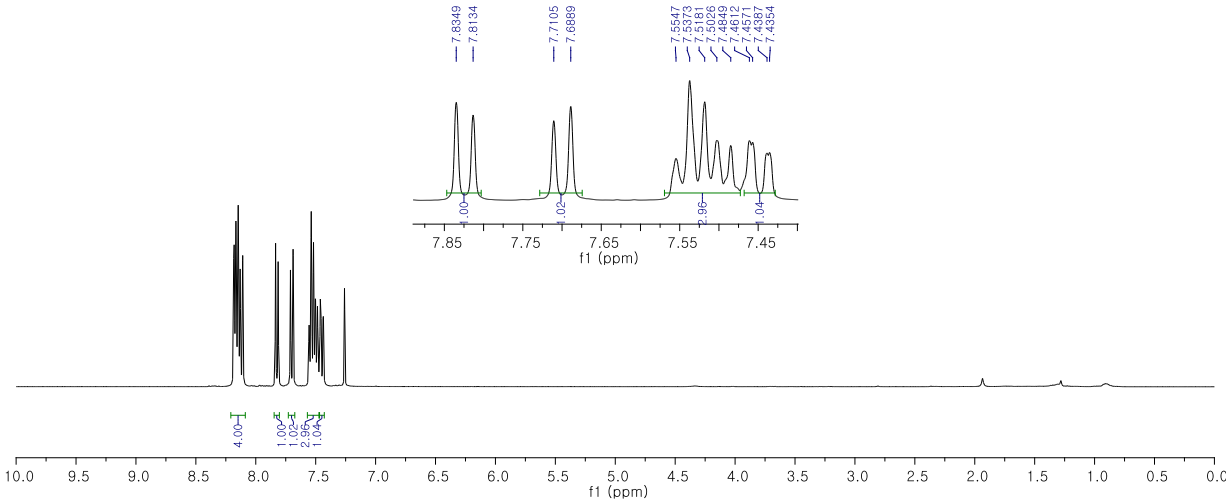
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



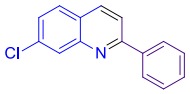
7-Chloro-2-phenylquinoline (c24)

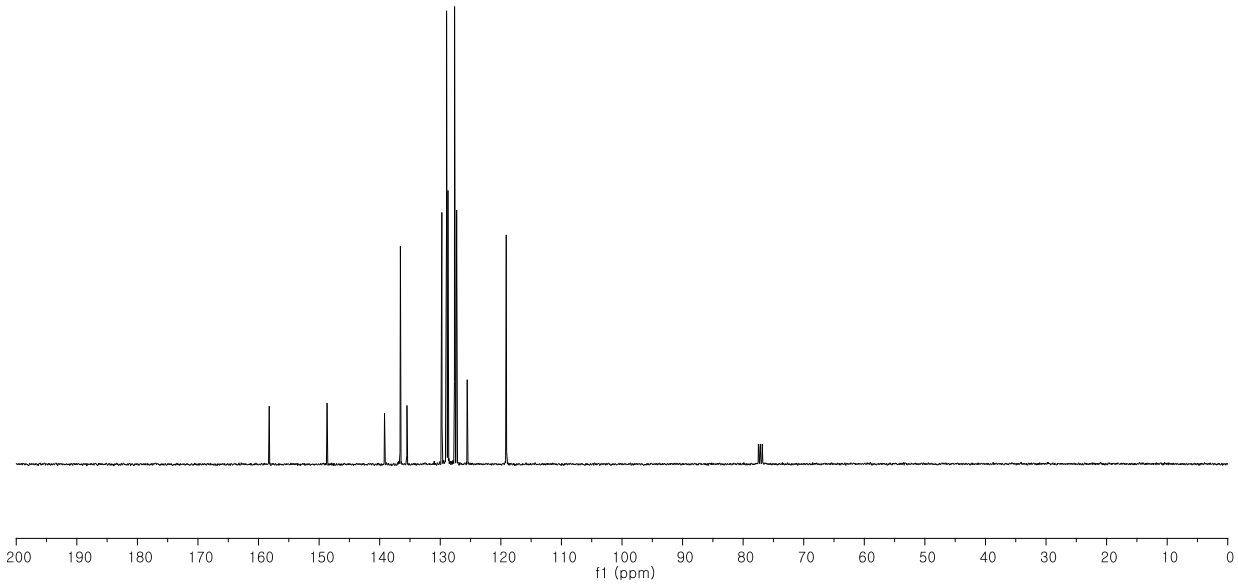
^{1}H NMR (400 MHz, $CDCl_3$)





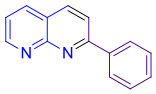
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

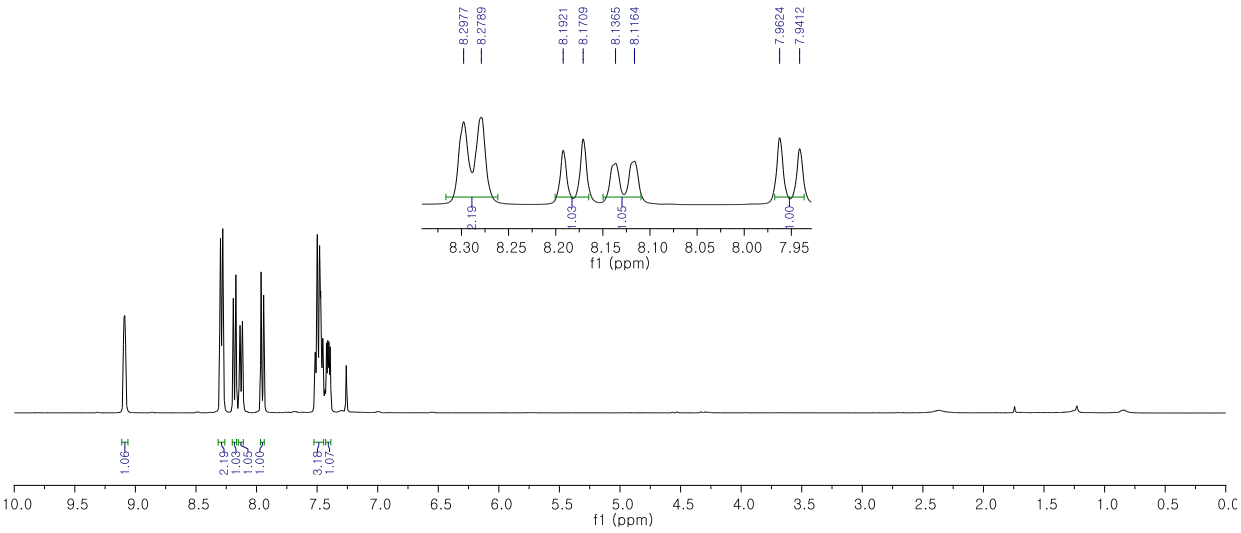




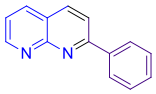
2-Phenyl-1,8-naphthyridine (c25)

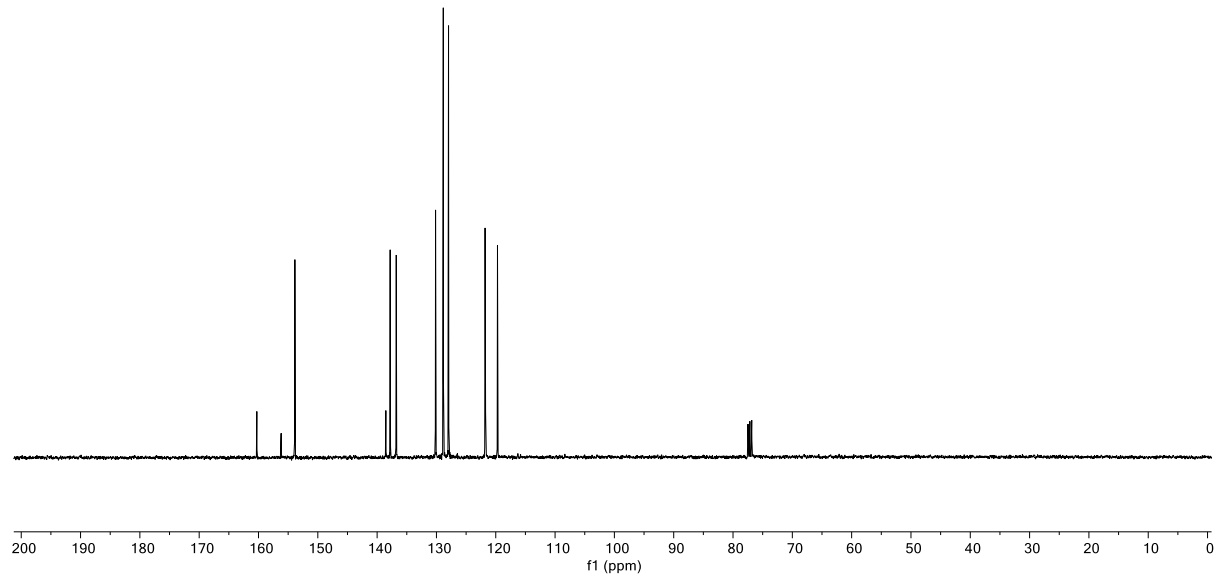
^{1}H NMR (400 MHz, $CDCl_3$)



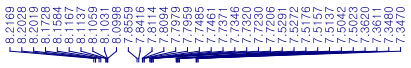


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

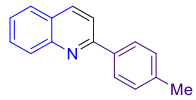


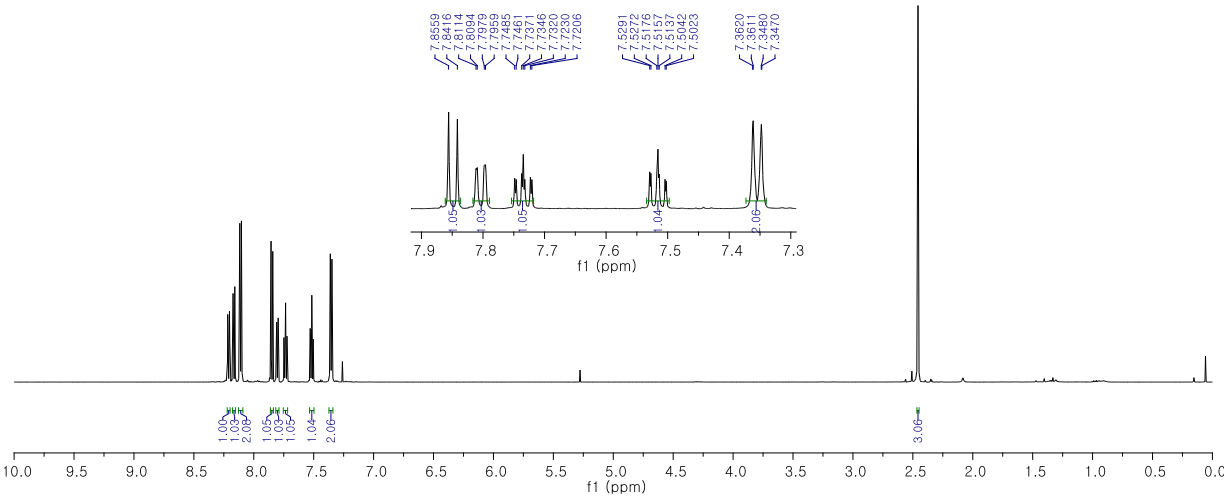


2-(*p*-Tolyl)quinoline (c26)

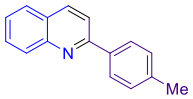


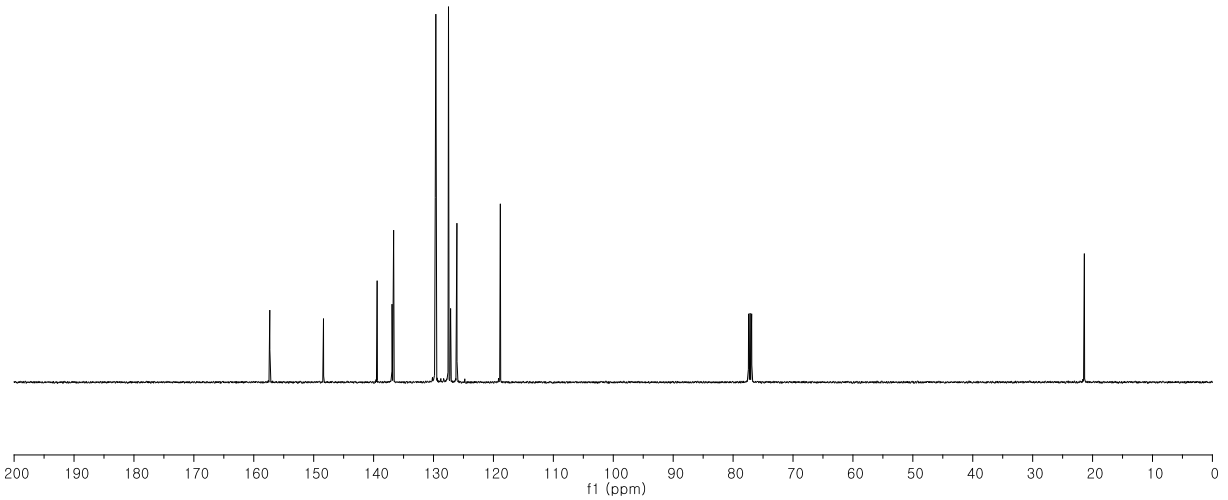
^{1}H NMR (600 MHz, $CDCl_3$)





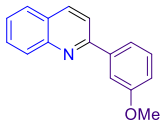
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

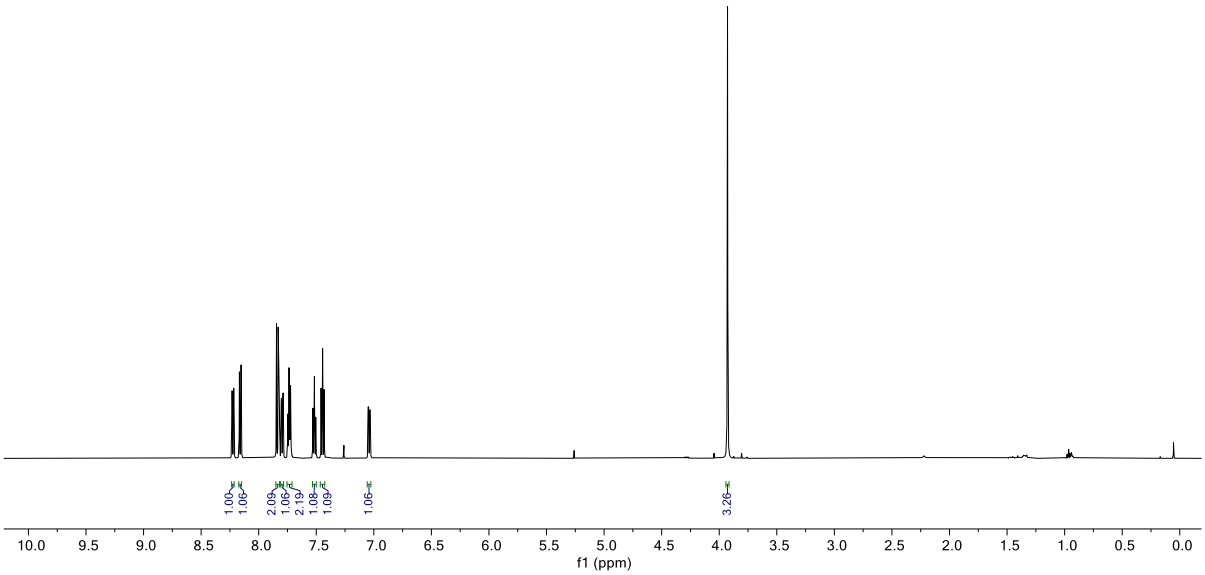




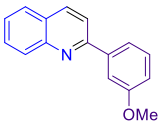
2-(3-Methoxyphenyl)quinoline (c27)

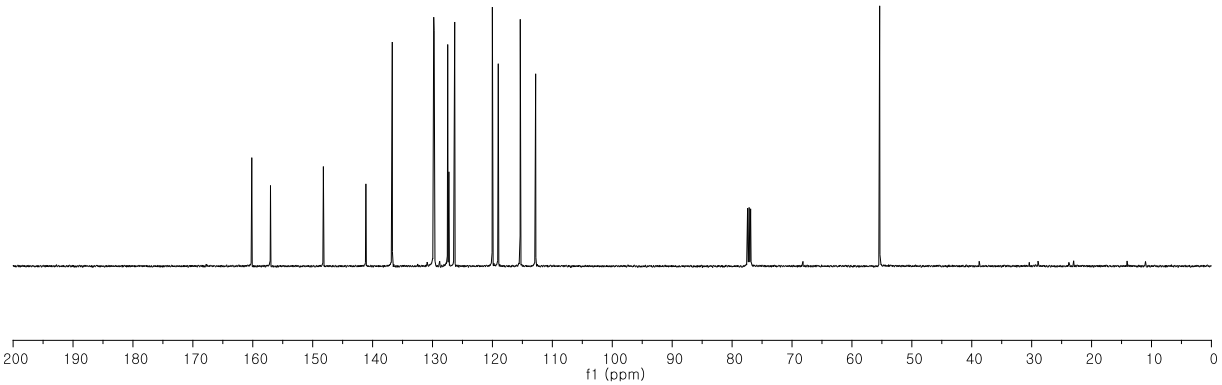
^{1}H NMR (600 MHz, $CDCl_3$)





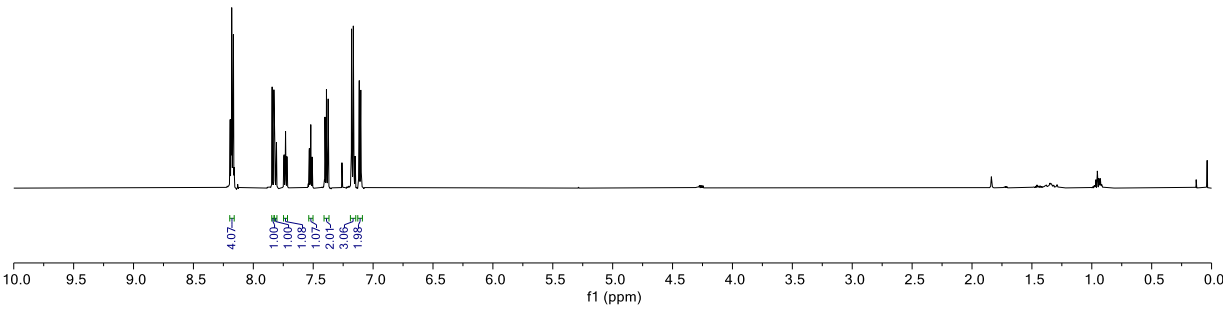
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



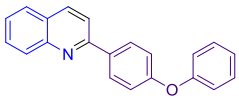


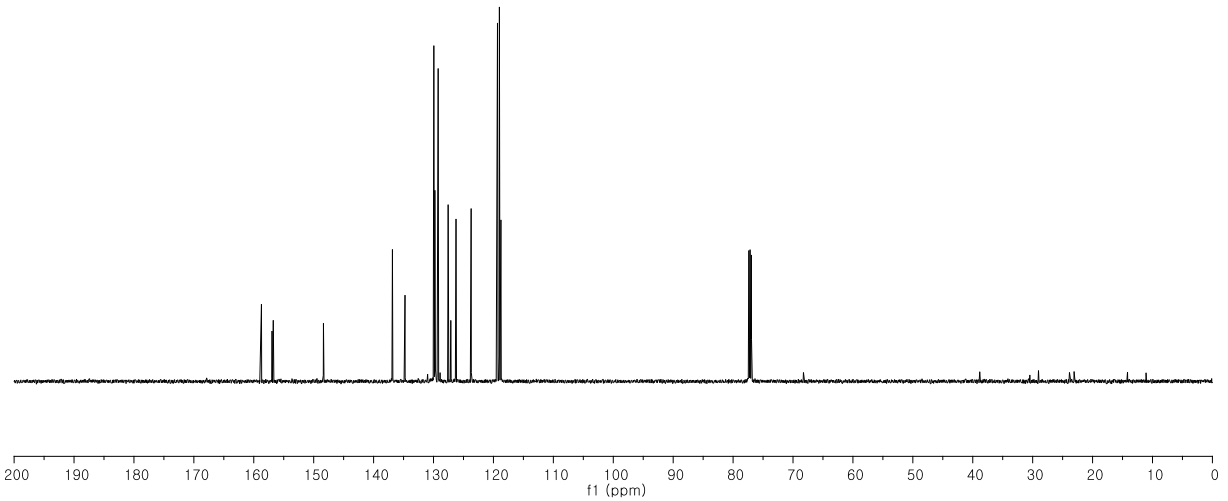
2-(4-Phenoxyphenyl)quinoline (c28)

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

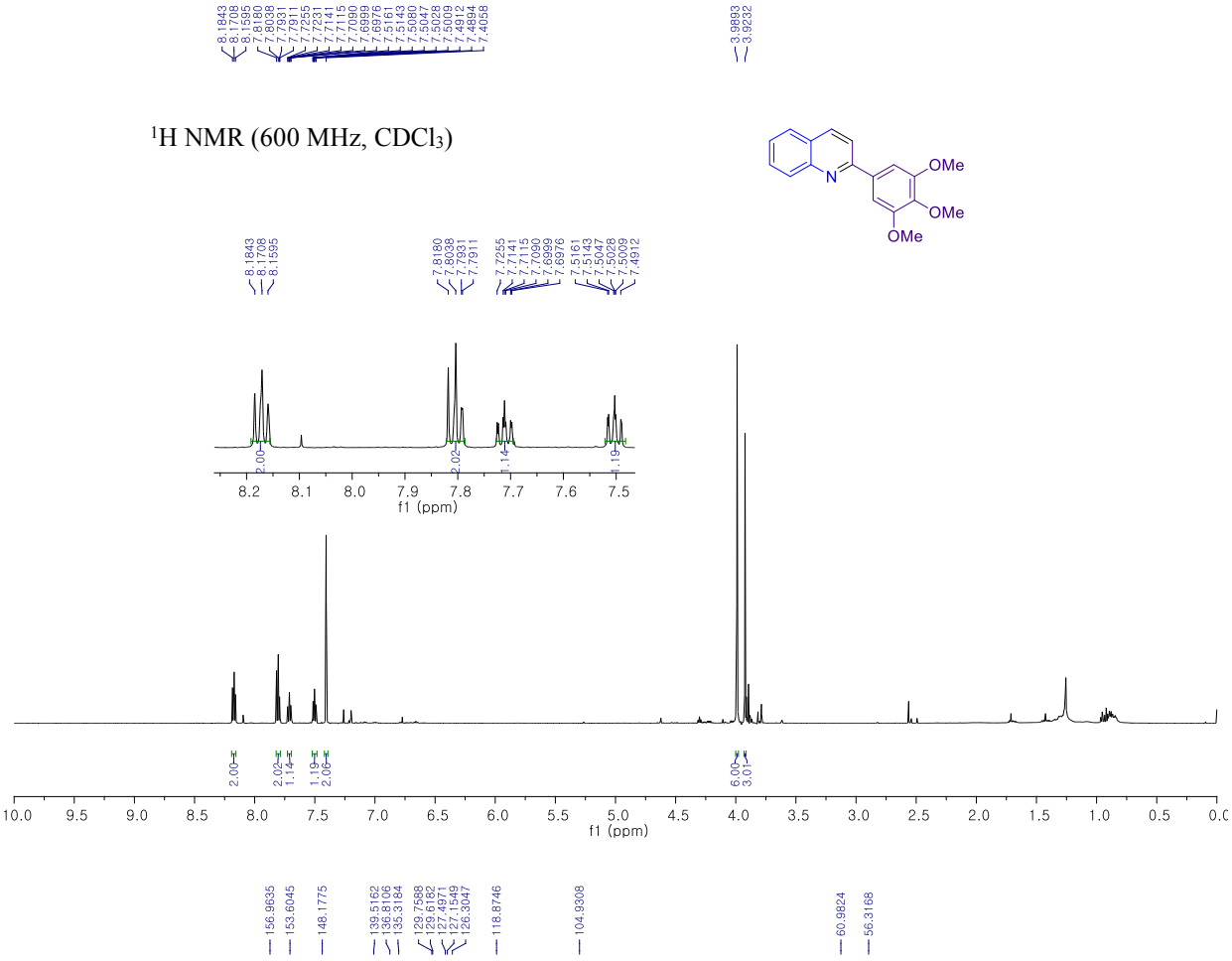


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

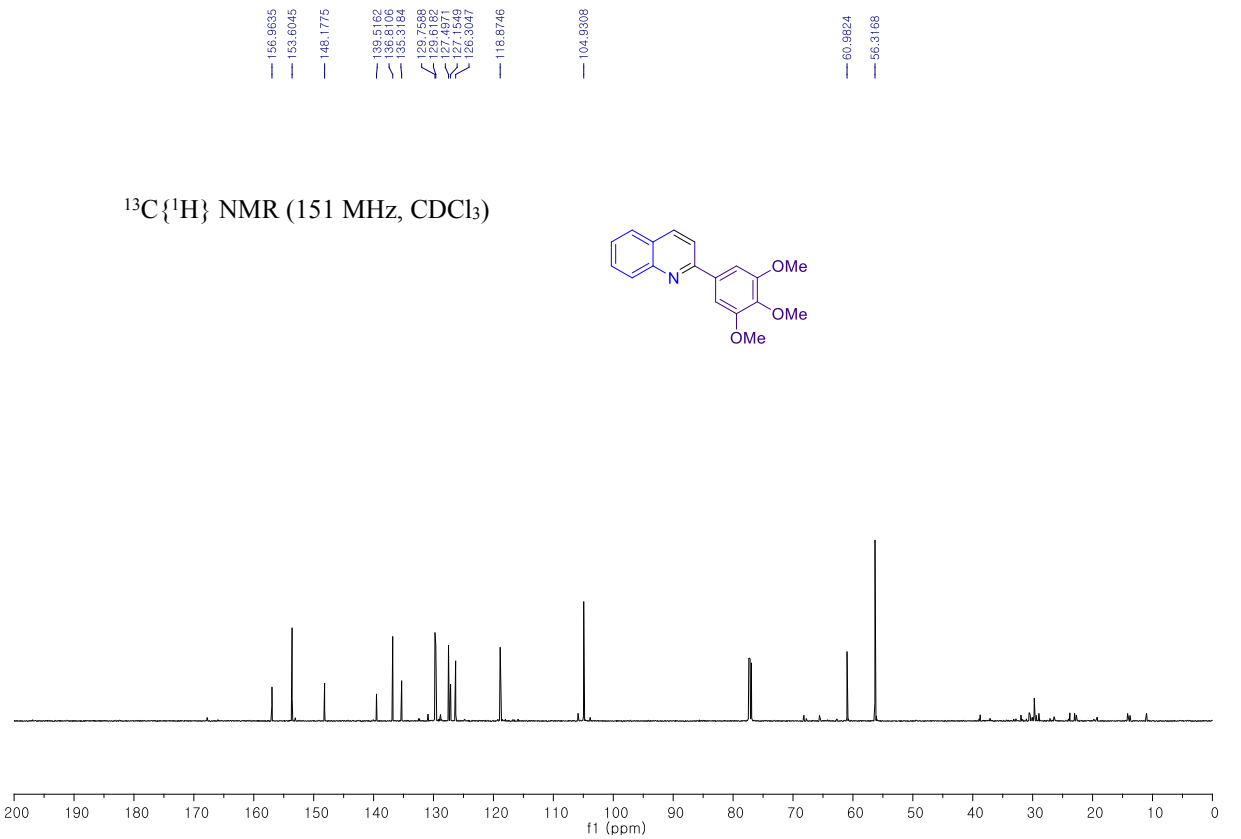




2-(3,4,5-Trimethoxyphenyl)quinoline (c29)



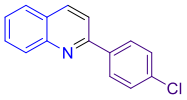
^{1}H NMR (600 MHz, $CDCl_3$)

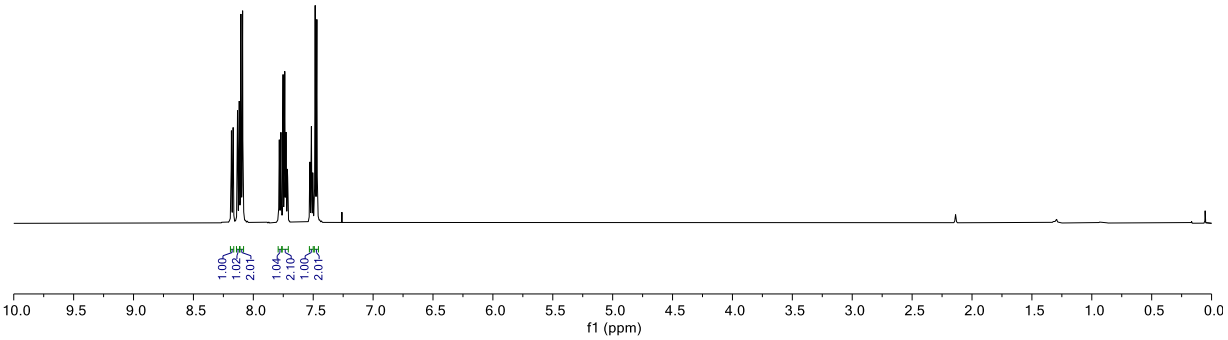


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

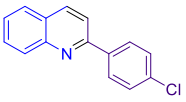
2-(4-Chlorophenyl)quinolone (c30)

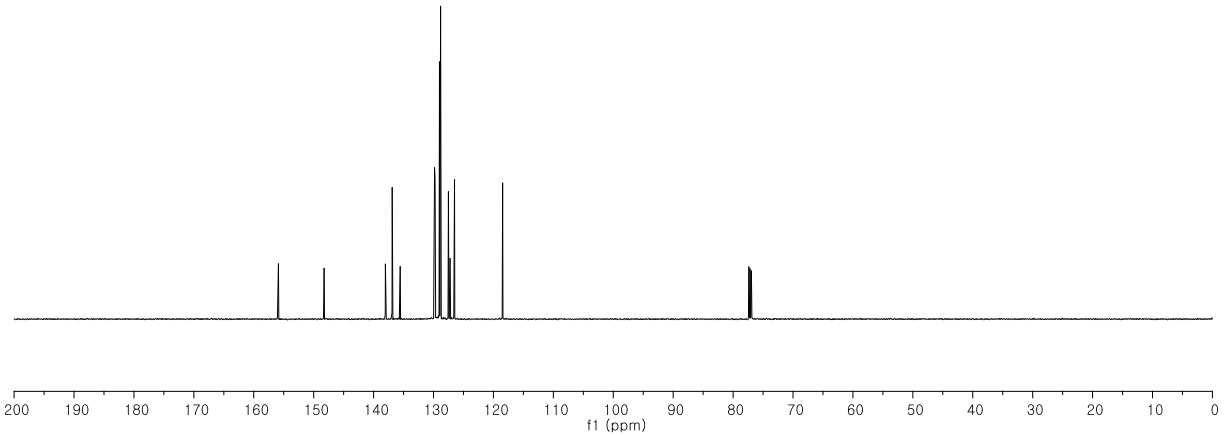
^{1}H NMR (600 MHz, $CDCl_3$)





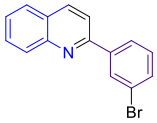
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

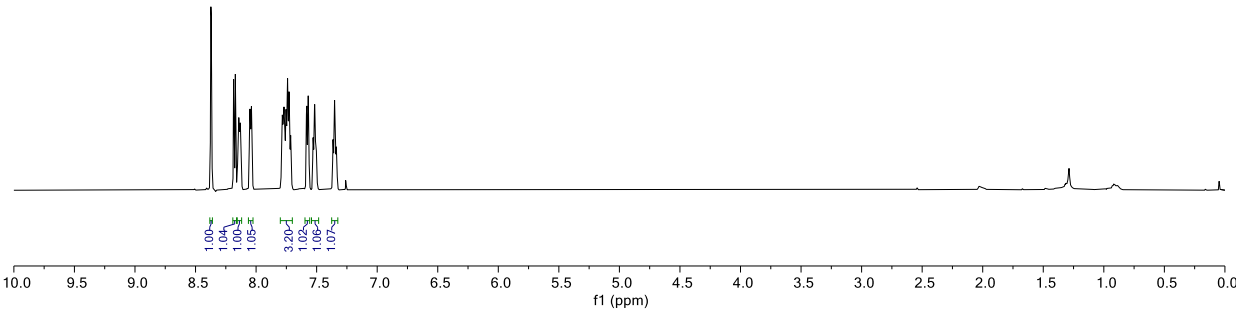




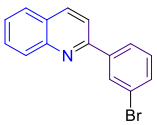
2-(3-Bromophenyl)quinoline (c31)

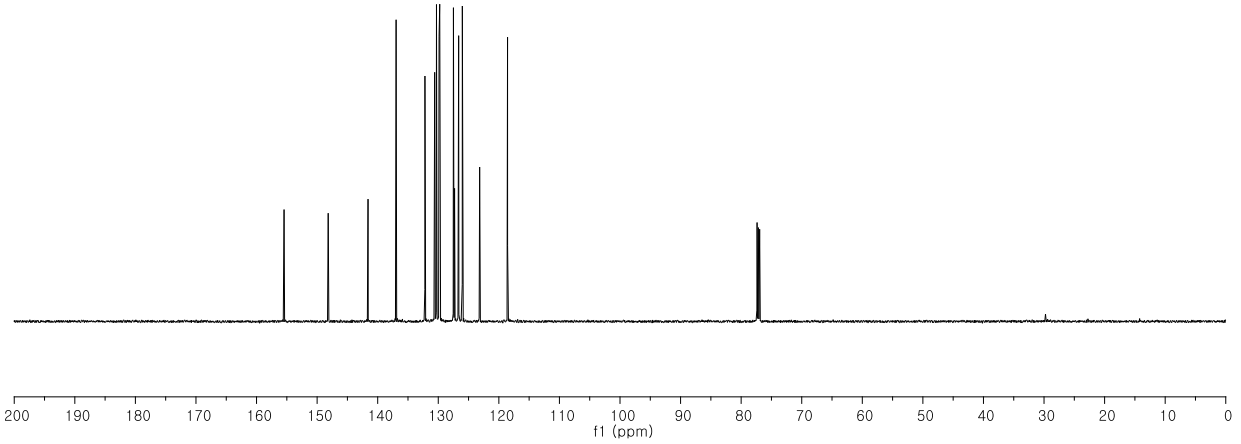
^{1}H NMR (600 MHz, $CDCl_3$)





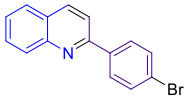
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

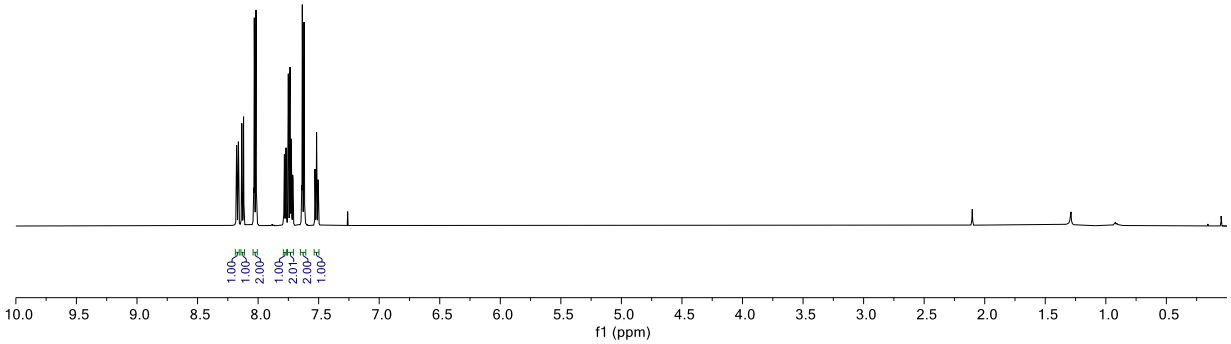




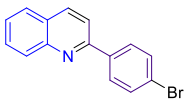
2-(4-Bromophenyl)quinolone (c32)

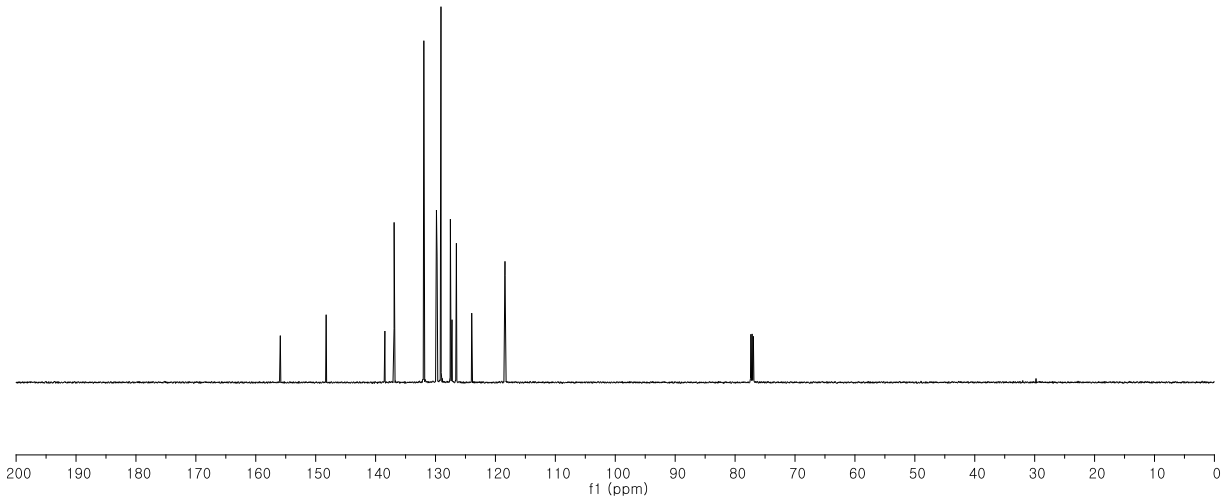
^{1}H NMR (600 MHz, $CDCl_3$)





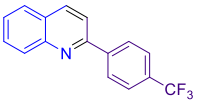
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

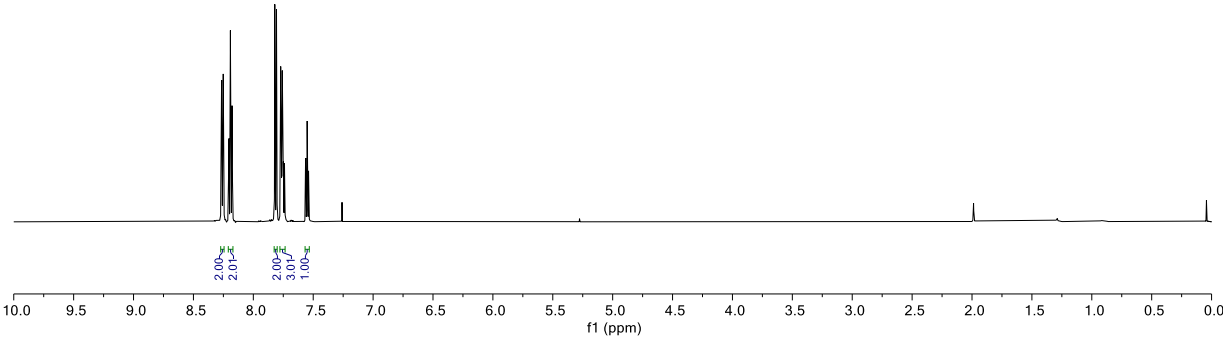




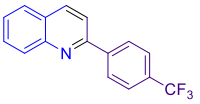
2-(4-(Trifluoromethyl)phenyl)quinoline (c33)

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



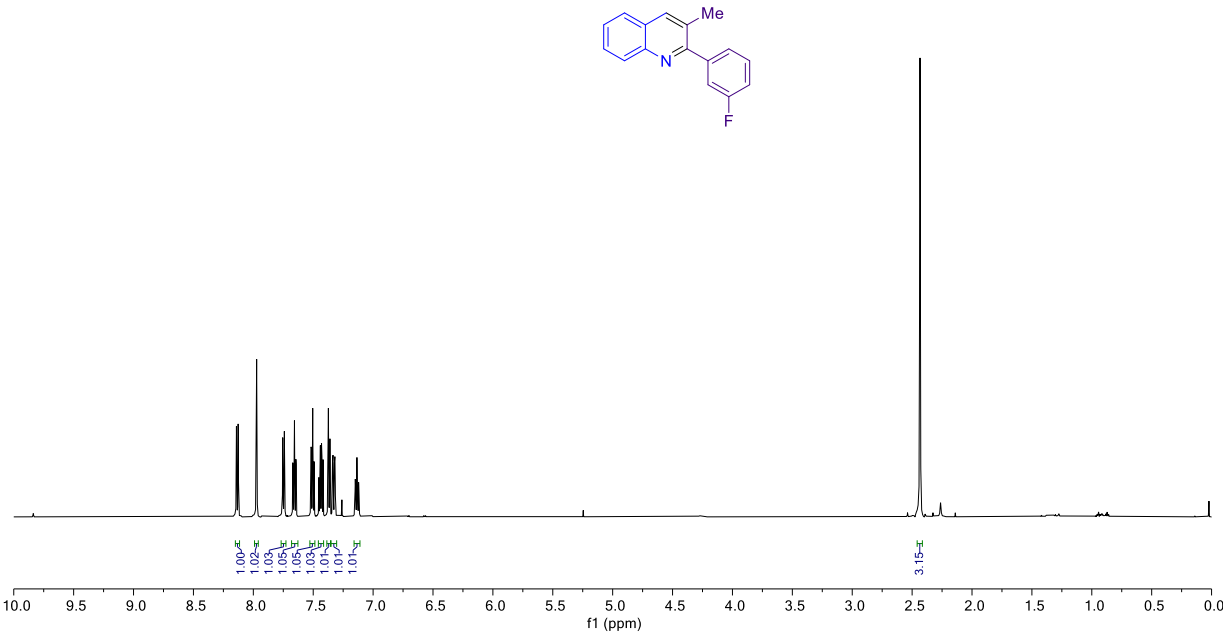


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

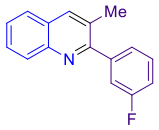


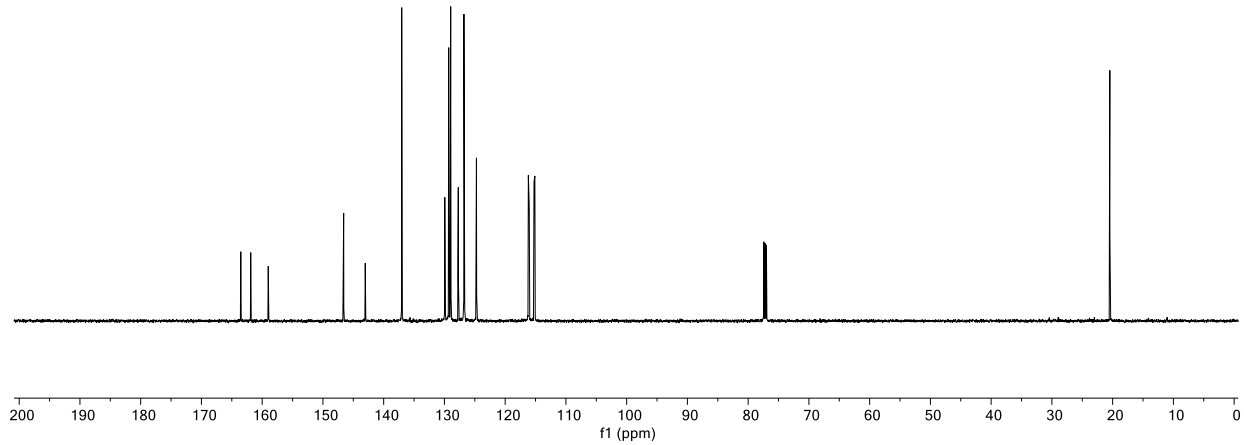
2-(3-Fluorophenyl)-3-methylquinoline (c34)

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



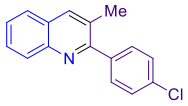
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

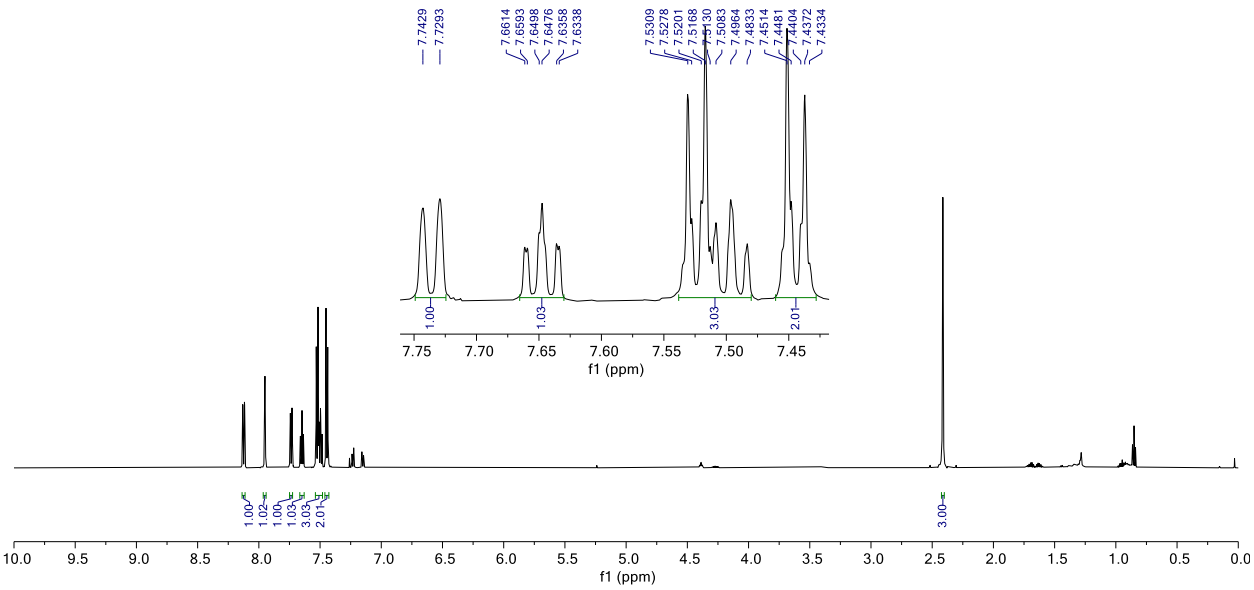




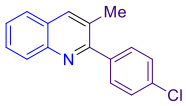
2-(4-Chlorophenyl)-3-methylquinoline (c35)

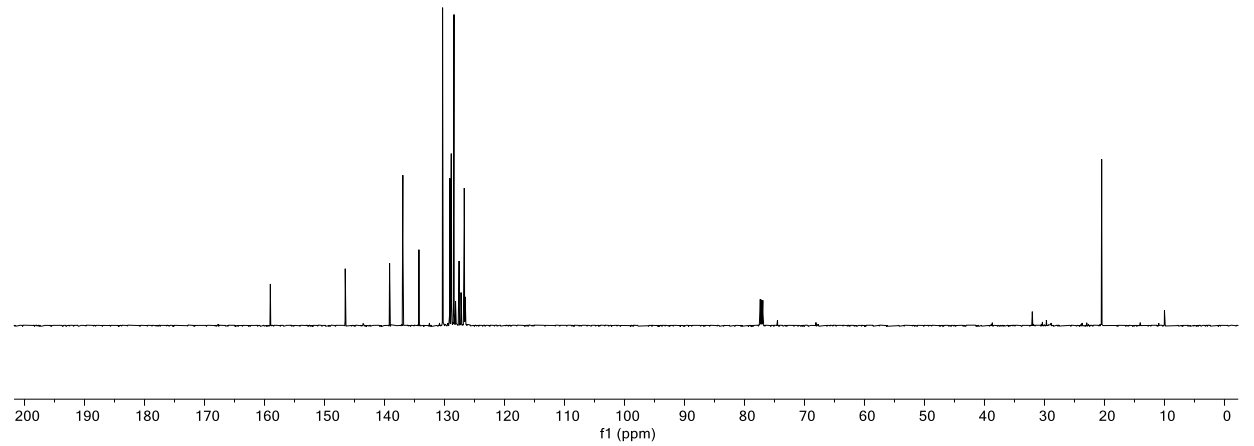
^{1}H NMR (600 MHz, $CDCl_3$)





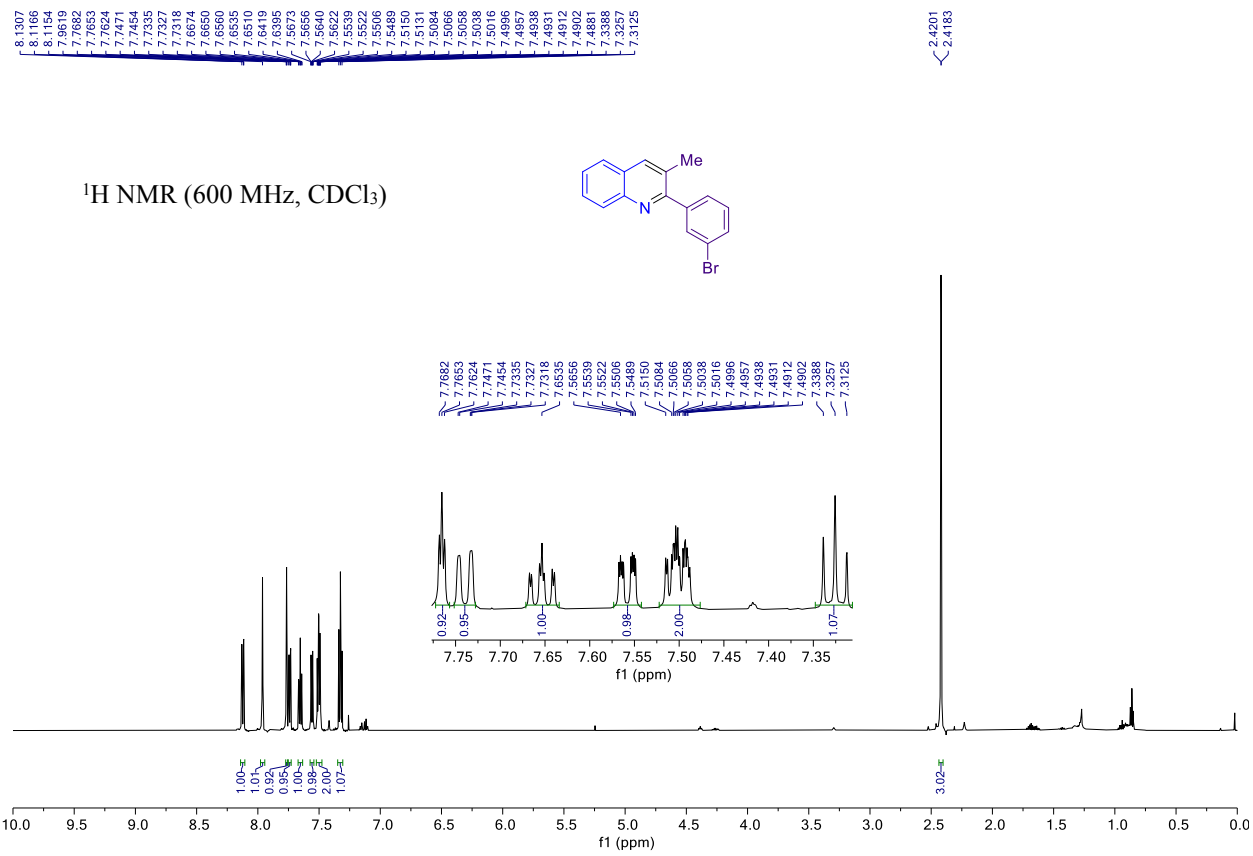
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



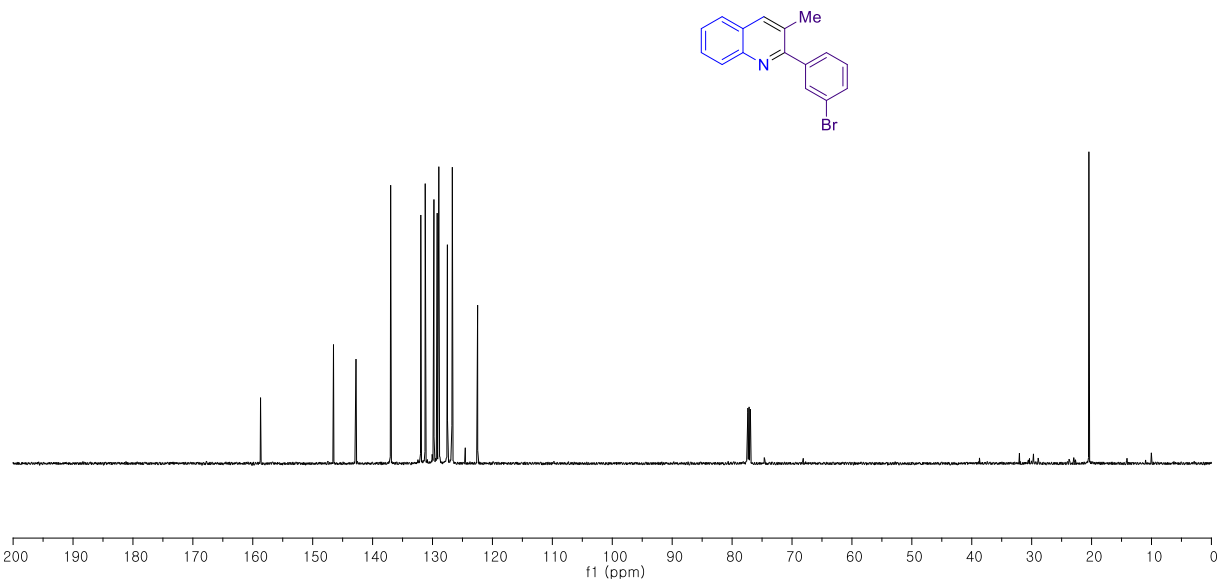


2-(3-Bromophenyl)-3-methylquinoline (c36)

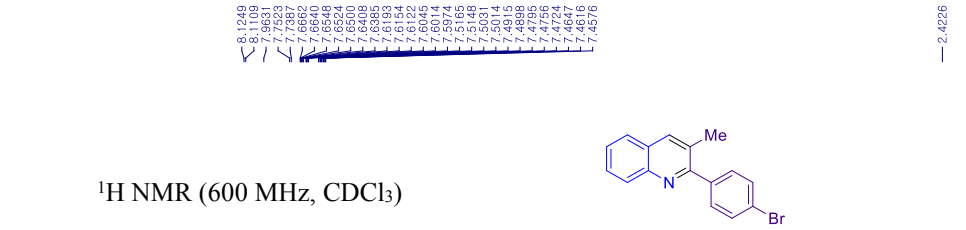
^{1}H NMR (600 MHz, $CDCl_3$)



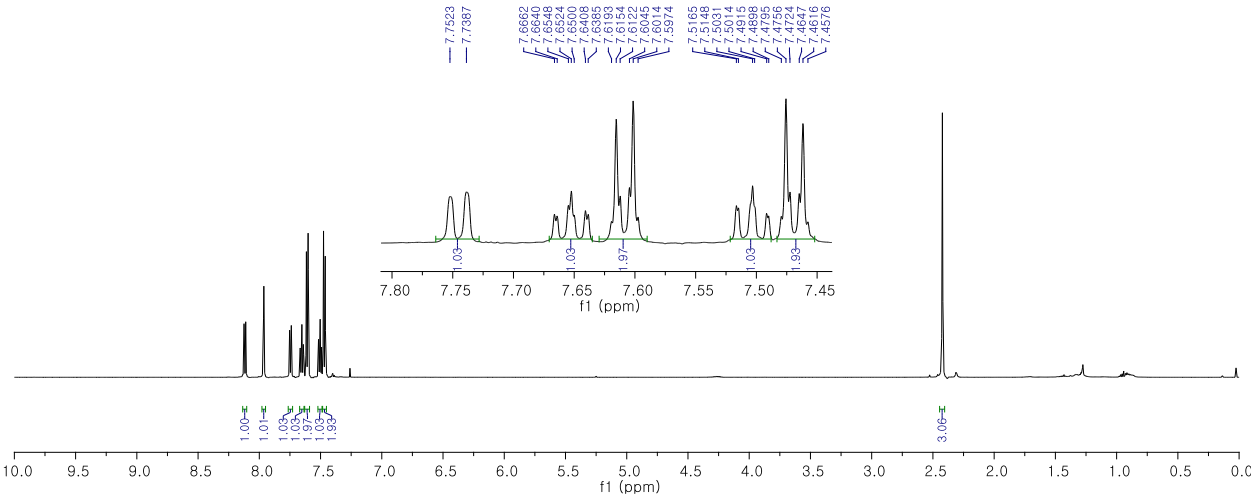
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



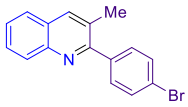
2-(4-Bromophenyl)-3-methylquinoline (c37)

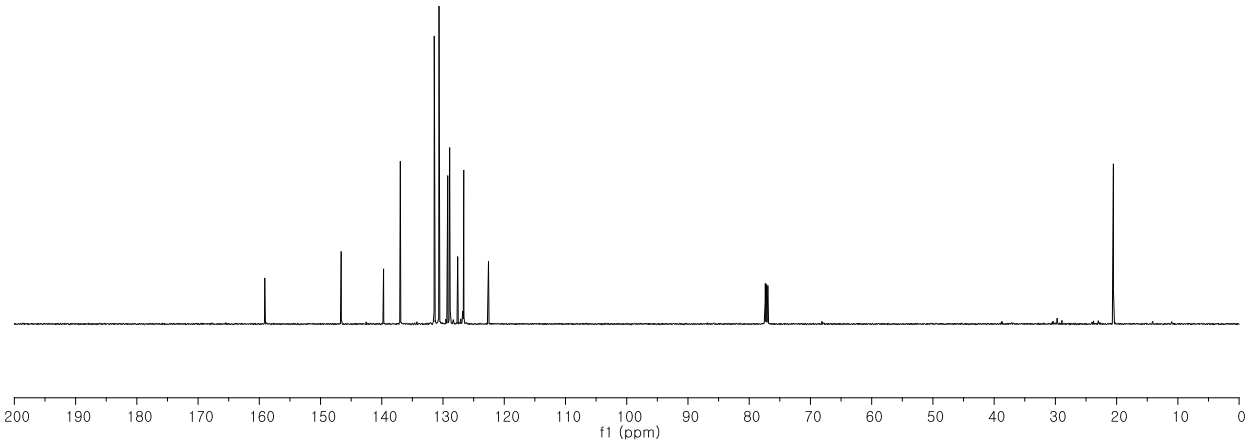


^{1}H NMR (600 MHz, $CDCl_3$)

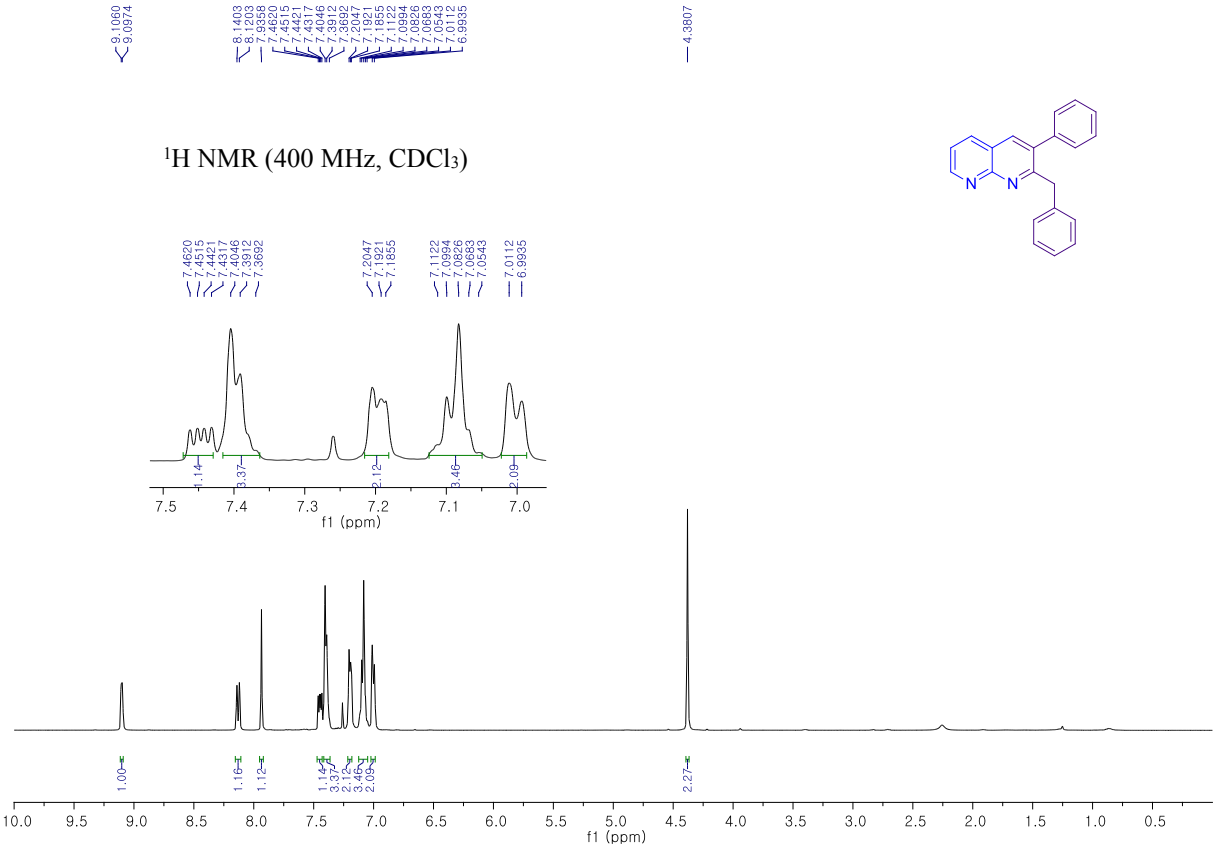


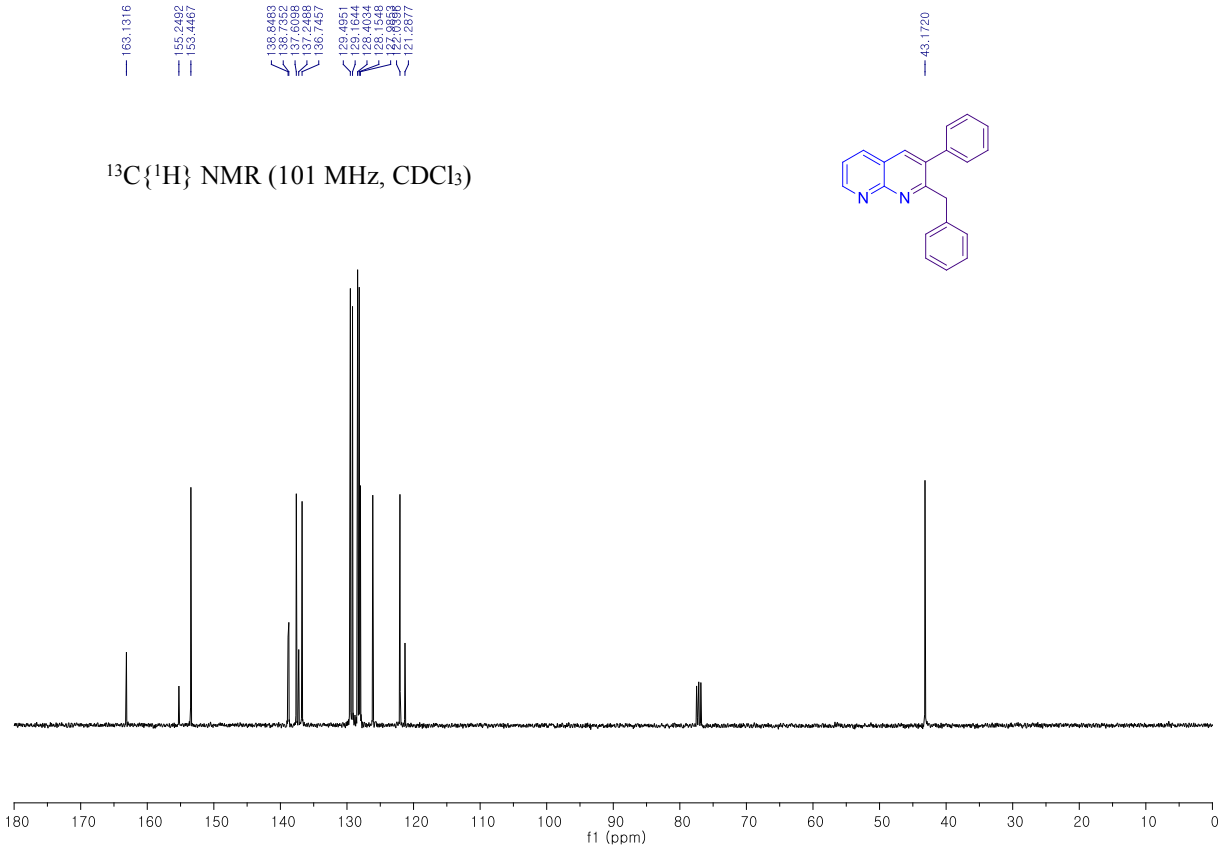
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)





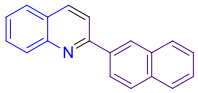
2-Benzyl-3-phenyl-1,8-naphthyridine (c38)

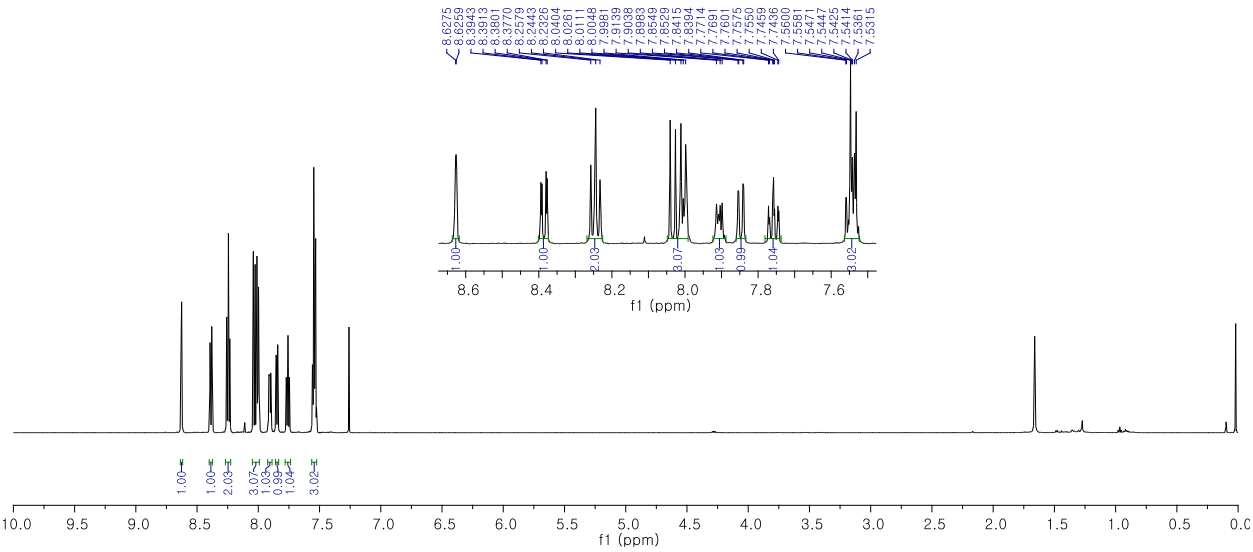


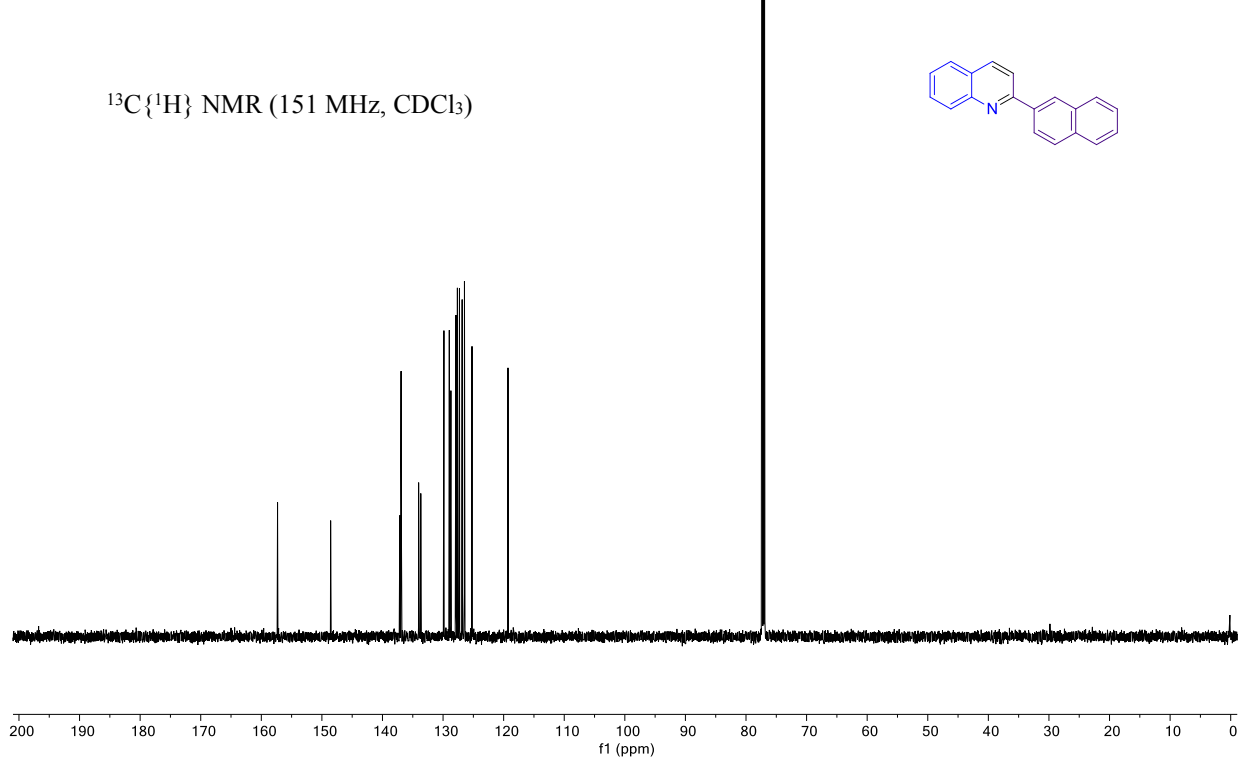


2-(Naphthalen-2-yl)quinoline (c39)

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



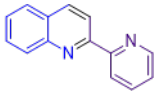


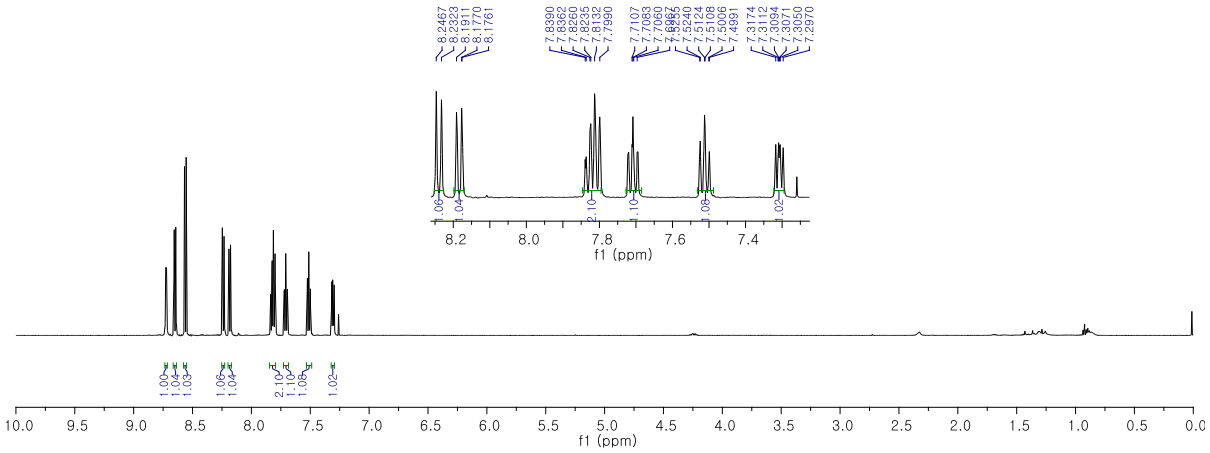


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

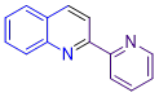
2-(Pyridin-2-yl)quinoline (c40)

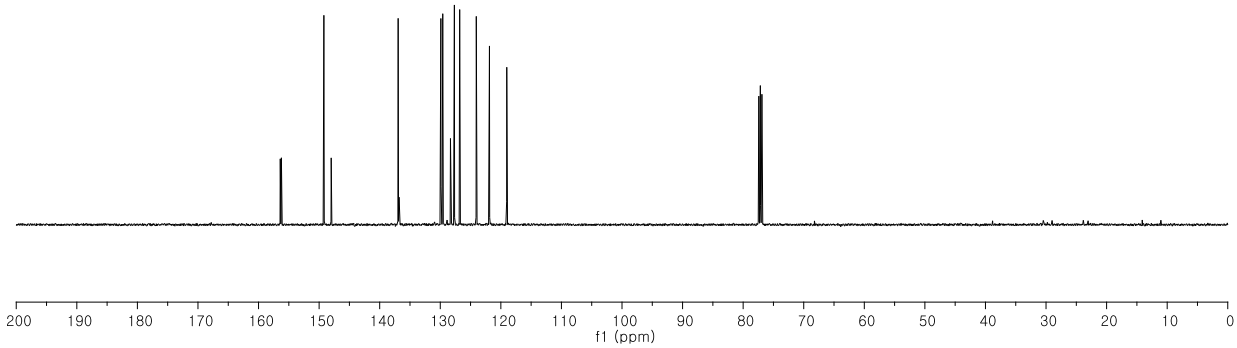
^{1}H NMR (600 MHz, $CDCl_3$)





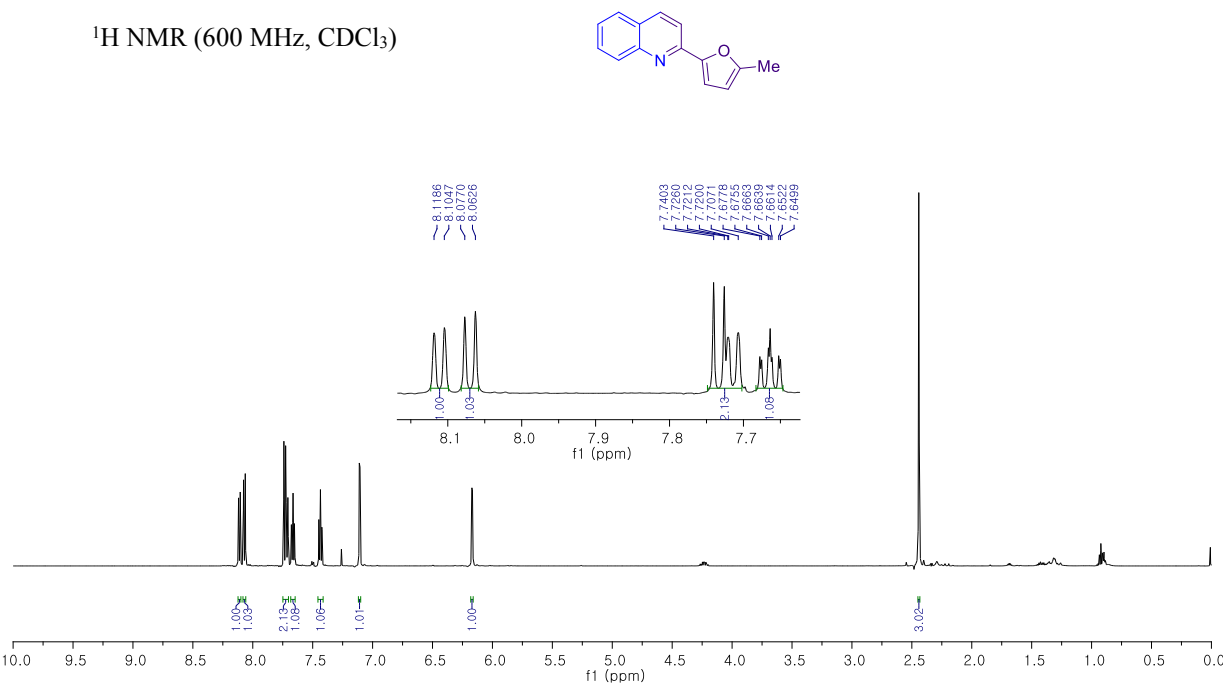
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



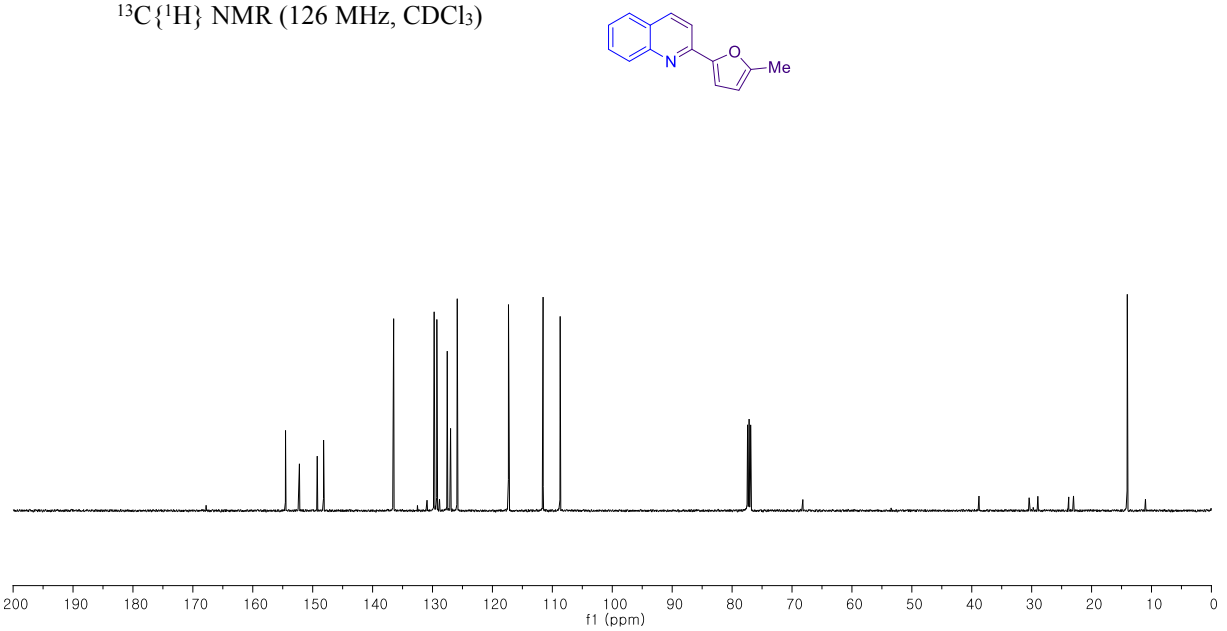


2-(5-Methylfuran-2-yl)quinoline (c41)

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

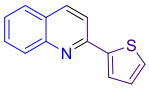


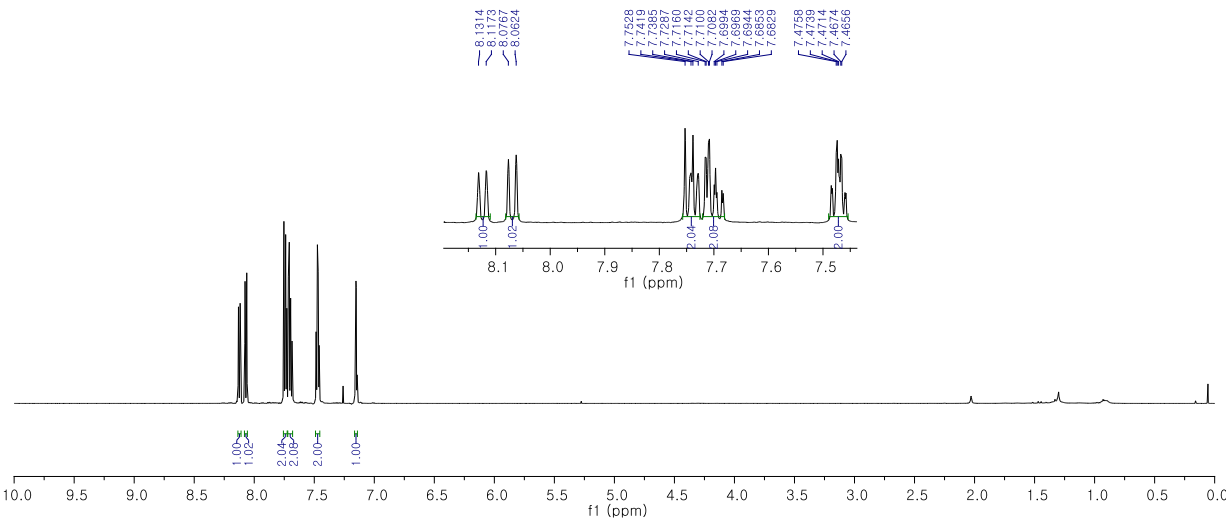
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



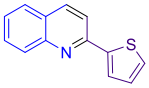
2-(thiophen-2-yl)quinolone (c42)

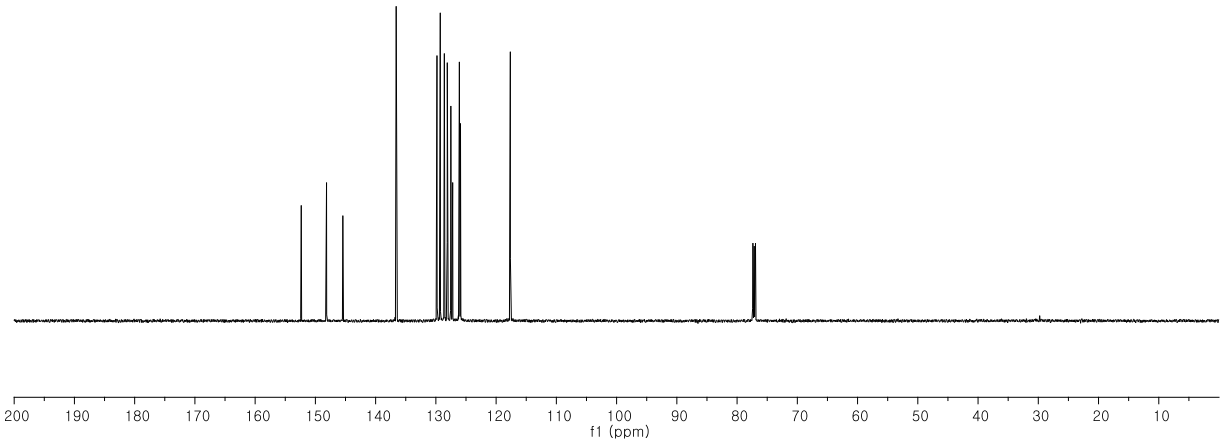
^{1}H NMR (600 MHz, $CDCl_3$)





$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)





[1] Tian, H.; Xue, W.; Wu, J.; Yang, Z.; Lu, H.; Tang, C. A general and practical bifunctional cobalt catalytic system for N-heterocycle assembly *via* acceptorless dehydrogenation. *Org. Chem. Front.* 2022, *9*, 4554-4560.

[2] Singh, K.; Vellakkaran, M.; Banerjee, D. A nitrogen-ligated nickel-catalyst enables selective intermolecular cyclisation of β- and γ-amino alcohols with ketones: access to five and six-membered N-heterocycles. *Green Chem.* **2018**, *20*, 2250- 2256.

[3] Zhang, X.; Chen, J.; Yong, S.; Zhao, Y. Acid/base-co-catalyzed cyclization of ketones with *o*-amino-benzylamines: Direct synthesis of quinoline compounds. *Tetrahedron Lett*. 2023, *128*, 154700.

[4] Xu, Z.; Chen, H.; Deng, G. J.; Huang, H. Copper-Catalyzed Formal [3 + 3] Annulations of Arylketoximes and *o*-Fluorobenzaldehydes: An Entry to Quinoline Compounds. *Org. Lett*. **2021**, *23*, 936-942.

[5] Xiong, B.; Zhang, S.; Jiang, H.; Zhang, M. Hydrogen-Transfer-Mediated Direct β-Alkylation of Aryl-1,8-naphthyridines with Alcohols under Transition Metal Catalyst Free Conditions. *Org. Lett*. **2016**, *18*, 724-727.

[6] Taguchi, K.; Sakaguchi, S.; Ishii, Y. Synthesis of quinolines from amino alcohol and ketones catalyzed by $[IrCl(cod)]_2$ or $IrCl_3$ under solvent-free conditions. *Tetrahedron Lett*. 2005, *46*, 4539-4542.

[7] Vander Mierde, H.; Van Der Voort, P.; De Vos, D.; Verpoort, F. A Ruthenium-Catalyzed Approach to the Friedländer Quinoline Synthesis. *Eur. J. Org. Chem*. **2008**, *9*, 1625-1631.

[8] Roy, S.; Das, S. K.; Khatua, H.; Das, S.; Singh, K. N.; Chattopadhyay, B. Iron-Catalyzed Radical Activation Mechanism for Denitrogenative Rearrangement Over C(sp3)–H Amination. *Angew. Chem. Ind. Ed*. **2021**, *133*, 8854- 8862.

[9] Lamola, J. L.; Moshapo, P. T.; Holzapfel, C. W.; Maumela, M. C. Evaluation of P-bridged biaryl phosphine ligands in palladium-catalysed Suzuki–Miyaura cross-coupling reactions. *RSC adv*. **2021**, *11*, 26883-26891.

[10] Zhou, X.; Li, X.; Le, C.; Li, J. Q. Base-Catalyzed Domino Isomerization/Oxidant-Free Dehydrogenative Annulation of Allylic Alcohols: Scope, Mechanism, and Application. *Adv. Synth. Catal*. **2024**, *366*, 3316-3324.

[11] Anderson, E. C.; Sneddon, H. F.; Hayes, C. J. A mild synthesis of substituted 1,8-naphthyridines. *Green Chem*. **2019**, *21*, 3050-3058.

[12] Kojima, M.; Kanai, M. Tris(pentafluorophenyl)borane-Catalyzed Acceptorless Dehydrogenation of N-Heterocycles. *Angew. Chem*. **2016**, *128*, 12412-12415.

[13] Nagy, B. S.; Maestro, A.; Chaudhari, M. B.; Kappe, C. O.; Ötvös, S. B. Enantioselective Flow Synthesis of a Tetrahydroquinoline SERM Enabled by Immobilized Chiral Phosphoric Acid Catalysis and Diboronic Acid Mediated Selective Nitro Reduction. *Adv. Synth. Catal*. **2024**, *366*, 1024-1030.

[14] Wani, A. A.; Bhujbal, S. M.; Sherpa, D.; Kathuria, D.; Chourasiya, S. S.; Sahoo, S. C.; Bharatam, P. V. An NNN Pd(ii) pincer complex with 1,1-diaminoazine: a versatile catalyst for acceptorless dehydrogenative coupling reactions. *Org. Biomol. Chem*. **2025**, *23*, 343-351.

[15] Elavarasan, S.; Bhaumik, A.; Sasidharan, M. An Efficient Mesoporous Cu-Organic Nanorod for Friedländer Synthesis of Quinoline and Click Reactions. *ChemCatChem*. **2019**, *11*, 4340-4350.

[16] Lee, S. Y.; Cheon, C. H. On-Water Synthesis of 2-Substituted Quinolines from 2-Aminochalcones Using Benzylamine as the Nucleophilic Catalyst. *J. Org. Chem*. **2018**, *83*, 13036-13044.

[17] Lu, Y.; Zhu, M.; Chen, S.; Yao, J.; Li, T.; Wang, X.; Tang, C. Single-Atom Fe-Catalyzed Acceptorless Dehydrogenative Coupling to Quinolines. *J. Am. Chem. Soc*. **2024**, *146*, 23338-23347.

[18] Hu, X. H.; Hu, X. P. Highly diastereo-and enantioselective Ir-catalyzed hydrogenation of 2, 3-disubstituted quinolines with structurally fine-tuned phosphine–phosphoramidite ligands. *Org. Lett*. **2019**, *21*, 10003-10006.

[19] Martinez, R.; Ramon, D. J.; Yus, M. Transition-Metal-Free Indirect Friedländer Synthesis of Quinolines from Alcohols. *J. Org. Chem*. **2008**, *73*, 9778-9780.

[20] Di Filippo, M.; Baumann, M. Continuous Flow Synthesis of Quinolines via a Scalable Tandem Photoisomerization-Cyclization Process. *Eur. J. Org. Chem*. **2020**, *2020*, 6199-6211.