Mechanistic Insights into the Potassium *tert*-Butoxide-Mediated Synthesis of *N*-Heterobiaryls

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General Procedures

Materials and methods: All heterocyclic *N*-oxides were synthesized from respective quinolines according to typical oxidation procedures.[1] Prior to use all heterocyclic *N*-oxides were dried under reduced pressure and elevated temperature to ensure complete exclusion of moisture. All chemicals were used as commercially available. Thermal reactions were conducted with continuous magnetic stirring under an atmosphere of argon in oven-dried glassware. Microwave-accelerated reactions were carried out in 2 mL vials, in 4×20 well plates using an Anton Paar Microwave PRO microwave reactor. 2-Methyltetrahydrofuran and *N,N*-dimethylformamide were subjected to three cycles of the freeze-pump-thaw degassing procedure before use. Reactions were monitored by TLC until deemed complete using silica gel-coated glass plates (Merck Kieselgel 60 F254). Plates were visualized under UV light (254 nm).

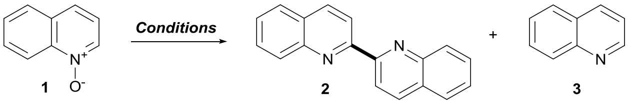
Purification: Column chromatography was performed using CombiFlash Rf-200 (Teledyne-Isco) automated flash chromatography system.

Characterization: ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded at 500 (^{1}H), 125 (^{13}C), and 282 MHz (^{19}F) on Varian Mercury VX 300 and Agilent Inova 500 instruments in $CDCl_3$ solutions. Chemical shifts (δ) are reported in parts per million (ppm) from the residual solvent peak and coupling constants (*J*) in Hz. Proton multiplicity is assigned using the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint.), septet (sept.), multiplet (m), broad (br). HRMS samples were analyzed by LSU Mass Spectrometry Facility.

EPR Spectra were collected on a Bruker EMX EPR spectrometer with ER041X Microwave X-band radiation.

Infrared measurements were carried out neat on a Bruker Vector 22 FT-IR spectrometer fitted with a Specac diamond attenuated total reflectance (ATR) module.

Table S1. Optimization of the KO*t*-Bu-mediated deoxygenative C2-homocoupling of quinoline *N*-oxide (**1**).[a]



Entry	Base (Equiv.)	Additive (Equiv.)	Solvent (M)	Temperature (°C)	Yield[b] **1**:**2**:**3**
1	NaOH (3)	–	THF (0.5)	100	100:0:0
2	Na_2CO_3 (3)	–	THF (0.5)	100	100:0:0
3	$NaHCO_3$ (3)	–	THF (0.5)	100	100:0:0
4	KO*t*-Bu (3)	–	THF (0.5)	100	15:41:44
5	KO*t*-Bu (3)	–	PhH (1)	100	34:31:35
6	KO*t*-Bu (3)	–	MeTHF (1)	100	17:54:29
7	KO*t*-Bu (3)	–	NMP (1)	100	17:21:62
8	KO*t*-Bu (3)	AIBN (1)	DMF (2)	65	12:77:11
9	KO*t*-Bu (3)	AIBN (0.2)	DMF (2)	65	7:76:17

[a] Reaction conditions: quinoline *N*-oxide (0.2 mmol), base, additive, solvent, 2 h. [b] Yields were obtained by ^1H NMR with 1,4-dimethoxybenzene as an internal standard. MeTHF = 2-methyltetrahydrofuran, AIBN = azobisisobutyronitrile, DMF = dimethylformamide, PhH = benzene, PhMe = toluene, THF = tetrahydrofuran.

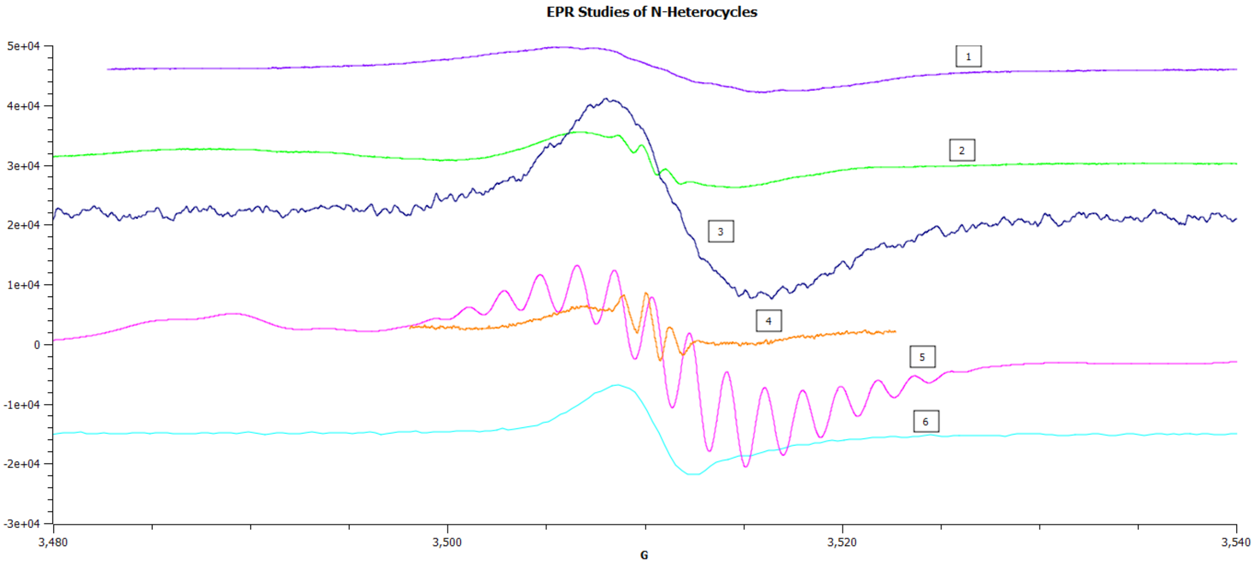


Figure S1. Electron paramagnetic resonance measurements of *N*-oxides and KO*t*-Bu. 1) 3-Methylisoquinoline *N*-oxide. 2) 2,2'-Biquinoline. 3) Phthalazine *N*-oxide. 4) Quinoline *N*-oxide. 5) Quinoxaline *N*-oxide. 6) Isoquinoline *N*-oxide.

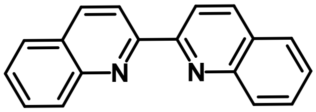
General Procedure for the thermal KO*t*-Bu-mediated deoxygenative C2-homocoupling of heterocyclic *N*-oxides (GP1):

An oven-dried and argon-flushed 10 mL Schleck flask was charged with heterocyclic *N*-oxide (1.0 mmol) and degassed MeTHF (2 mL) or *N,N*-dimethylformamide (2 mL) and the reaction mixture was heated to 65 °C. To the reaction mixture was added potassium *tert*-butoxide (336 mg, 3.0 mmol, 3 equiv.) and azobisisobutyronitrile (33 mg, 0.2 mmol, 20 mol%, if specified) in six portions over 10 min. The reaction was allowed to stir until deemed complete by ^{1}H NMR or TLC (1.5–12 h). A 10% aqueous solution of NH_4Cl (5 mL) was added, and the aqueous layer was extracted with EtOAc (5×5 mL). The combined organic layer was dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography [hexanes/EtOAc, silica gel] to yield the desired product.

General Procedure for the microwave-accelerated KO*t*-Bu-mediated deoxygenative C2-homocoupling of azine *N*-oxides (GP2):

Heterocyclic *N*-oxide (1 mmol), potassium *tert*-butoxide (336 mg, 3.0 mmol, 3 equiv.), azobisisobutyronitrile (33 mg, 0.2 mmol, 20 mol%) and MeTHF (2 mL) were divided between two 2 mL LCMS vials. The vials were heated to 65 °C in a microwave for 15 min before being combined and worked up according to GP1.

2,2'-Biquinoline[2] (2)



Small scale experiment: According to GP1, quinoline *N*-oxide (**1**) (145 mg, 1.0 mmol) in dimethylformamide (2 mL) was heated to 65 °C. KO*t*-Bu (224 mg, 2.0 mmol, 2 equiv.) was added in three portions over 10 min and the reaction heated for 3 h. Following aqueous work-up, the crude product was purified by column chromatography to yield 2,2'-biquinoline (**2**) (128 mg, 94%).

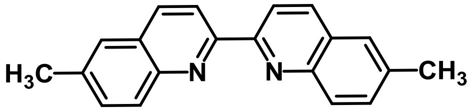
Gram-scale experiment: According to GP1, quinoline *N*-oxide (**1**) (5.0 g, 3.45 mol) in MeTHF (7 mL) was heated to 65 °C. KO*t*-Bu (7.73 g, 6.9 mol, 2 equiv.) and AIBN (113 mg, 0.69 mol, 20 mol%) were added in twenty portions over 10 min. After 3 h an aqueous work-up was performed, and the crude product was purified by column chromatography to yield product **2** (3.47 g, 78%).

Microwave experiment: According to GP2, quinoline *N*-oxide (**1**) (290 mg, 2.0 mmol), KO*t*-Bu (448 mg, 4.0 mmol, 2 equiv.), AIBN (66 mg, 0.4 mmol, 20 mol%), and MeTHF (4 mL) were divided into 4 vials and subjected to microwave conditions. After aqueous workup all vials were combined and the crude product purified by column chromatography to yield product **2** (168 mg, 65%).

Synthesis from quinoline by a tandem N-oxidation/C2-homocoupling reaction: To an oven dried round bottom flask was added quinoline (**3**) (2.0 g, 15.50 mmol), *meta*-chloroperoxybenzoic acid (2.67 g, 15.5 mmol, 1 equiv., 100% *m*CPBA), and MeTHF (30 mL). The reaction was heated to 40 °C and allowed to stir for 6 h. The reaction was then heated to 65 °C, and KO*t*-Bu (6.94 g, 62.0 mmol, 4 equiv.) and AIBN (508 mg, 3.10 mmol, 20 mol%) were added in ten portions over 20 min. The reaction was worked up according to GP1, and purified by column chromatography to yield 2,2'-biquinoline (**2**)

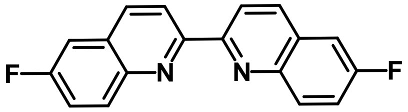
(1.61 g, 81%). – m.p.: 72–74°C (lit.[2] 70–72 °C). – ^{1}H NMR (500 MHz): 7.57 (2 H, dt, *J* = 1, 6.5 Hz), 7.76 (2 H, dt, *J* = 1, 6.5 Hz), 7.88 (2 H, d, *J* = 8 Hz), 8.24 (2 H, d, *J* = 9 Hz), 8.33 (2 H, d, *J* = 9 Hz), 8.85 (2 H, d, *J* = 9 Hz) ppm. – ^{13}C NMR (125 MHz): 119.4, 127.0, 127.7, 128.5, 129.5, 129.9, 136.7, 147.9, 156.2 ppm. – IR: 1057, 1125, 1245, 1325, 1487, 2850, 3029 cm^{-1}. – MS (ESI): 257.0, calcd: 257.1 [M+H$^+$].

6,6'-Dimethyl-2,2'-biquinoline[3] (4)



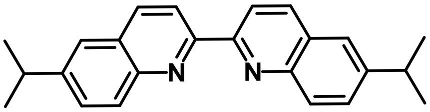
According to GP1, 6-methylquinoline *N*-oxide (80 mg, 0.50 mmol) and AIBN (16 mg, 0.1 mmol, 20 mol%) were treated with KO*t*-Bu (168 mg, 1.50 mmol, 3 equiv.) in three portions over 10 min in MeTHF (1 mL) at 65 °C. After the reaction mixture was stirred for 3 h at 65 °C, it was worked up, and the crude product was purified by column chromatography to yield biquinoline **4** (60 mg, 85%). – m.p.: >250 °C (lit.[3] 260–261). – ^{1}H NMR (500 MHz): 2.57 (6 H, s), 7.58 (2 H, dd, *J* = 2, 8.5 Hz), 7.64 (2 H, s), 8.11 (2 H, d, *J* = 8.5 Hz), 8.22 (2 H, d, *J* = 8.5 Hz), 8.78 (2 H, d, *J* = 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 21.7, 119.4, 126.5, 128.4, 129.6, 131.8, 136.0, 136.8, 146.5, 155.6 ppm. – IR: 1032, 1101, 1167, 1271, 1334, 1432, 1578, 1611, 2842, 2941, 3074 cm^{-1}. – MS (ESI): 285.2, calcd: 285.1 [M+H$^+$].

6,6'-Difluoro-2,2'-biquinoline (5)



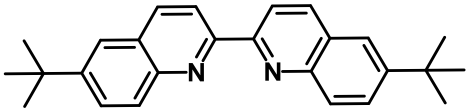
According to GP1, 6-fluoroquinoline *N*-oxide (82 mg, 0.50 mmol) in dimethylformamide (1 mL) was heated at 65 °C. KO*t*-Bu (112 mg, 1.0 mmol, 2 equiv.) was added in three portions over 10 min. After 3 h the reaction was worked up, and the crude product purified by column chromatography to yield product **5** (47 mg, 64%). – ^{1}H NMR (500 MHz): 7.48–7.54 (4 H, m), 8.21 (2 H, dd, *J* = 5.5, 9.5 Hz), 8.26 (2 H, d, *J* = 9 Hz), 8.82 (2 H, d, *J* = 9 Hz) ppm. – ^{13}C NMR (125 MHz): 110.7 (dd, *J* = 5, 21.5 Hz), 119.8 (m), 120.0 (m), 129.1 (d, *J* = 1 Hz), 132.4 (d, *J* = 9 Hz), 136.1 (d, *J* = 5.5 Hz), 145.0, 155.4 (d, *J* = 2.5 Hz), 159.8, 161.8 ppm. – ^{19}F NMR (282 MHz): –112.60 ppm. – IR: 1060, 1136, 1222, 1342, 1465, 1554, 1615, 2853, 3062 cm^{-1}. – MS (ESI): 293.0 calcd: 293.1 [M+H$^+$]. – HRMS: 293.0894 calcd: 293.0885 [M+H$^+$].

6,6'-Diisopropyl-2,2'-biquinoline (6)



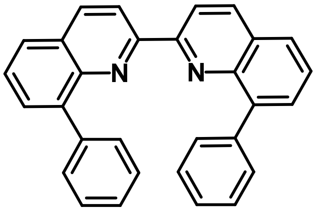
According to GP1, 6-isopropylquinoline *N*-oxide (1.0 g, 5.34 mmol) in MeTHF (11 mL) was heated to 65 °C. KO*t*-Bu (1.79 g, 16.02 mmol, 3 equiv.) and AIBN (175 mg, 1.06 mmol, 20 mol%) were added in six portions in 20 min. After 2 h an aqueous work-up was performed, and the crude product was purified by column chromatography to yield product **6** (755 mg, 83%). – ^{1}H NMR (500 MHz): 1.40 (12 H, d, *J* = 6.5 Hz), 3.15 (2 H, sept., *J* = 6.5 Hz), 7.65–7.68 (4 H, m), 8.16 (2 H, d, *J* = 9 Hz), 8.27 (2 H, d, *J* = 8.5 Hz), 8.80 (2 H, d, *J* = 9 Hz) ppm. – ^{13}C NMR (125 MHz): 23.9, 34.2, 119.4, 123.8, 128.5, 129.4, 129.5, 129.8, 146.9, 147.6, 155.7 ppm. – IR: 1040, 1146, 1253, 1341, 1452, 1552, 1625, 2865, 2954, 3065 cm^{-1}. – MS (ESI): 341.0, calcd: 341.2 [M+H$^+$]. – HRMS: 341.2017, calcd: 341.2012 [M+H$^+$].

6,6'-Di-*tert*-butyl-2,2'-biquinoline (7)



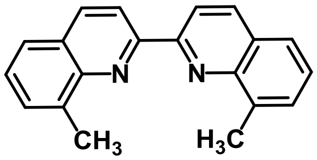
According to GP1, 6-*tert*-butylquinoline *N*-oxide (580 mg, 2.88 mmol) in MeTHF (7 mL) was heated at 65 °C. KO*t*-Bu (970 mg, 8.64 mmol, 3 equiv.) and AIBN (92 mg, 0.56 mmol, 20 mol%) were added in six portions in 20 min. After 2 h an aqueous work-up was performed, and the crude product was purified by column chromatography to yield product **7** (409 mg, 77%). – m.p. >250 °C. – ^{1}H NMR (500 MHz): 1.45 (18 H, s), 7.78 (2 H, s), 7.83 (2 H, d, *J* = 8.5 Hz), 8.14 (2 H, d, *J* = 9 Hz), 8.27 (2 H, d, *J* = 8.5 Hz), 8.78 (2 H, d, *J* = 9 Hz) ppm. – ^{13}C NMR (125 MHz): 31.2, 35.0, 119.4, 122.7, 128.1, 128.5, 129.3, 136.7, 146.4, 149.8, 155.8 ppm. – IR: 1110, 1214, 1367, 1445, 1543, 2890, 3021, 3204 cm^{-1}. – MS (ESI): 369.1, calcd: 369.2 [M+H$^+$]. – HRMS: 369.2327, calcd: 369.2325 [M+H$^+$].

8,8'-Diphenyl-2,2'-biquinoline[4] (8)



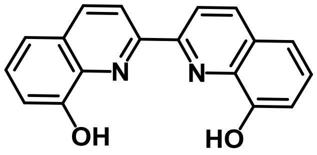
According to GP1, 8-phenylquinoline *N*-oxide (240 mg, 1.08 mmol) in MeTHF (2 mL) was heated to 65 °C. KO*t*-Bu (362 mg, 3.24 mmol, 3 equiv.) and AIBN (35 mg, 0.22 mmol, 20 mol%) were added in three portions over 10 min. After 2 h an aqueous workup was performed, and the crude product purified by column chromatography to yield biquinoline **8** (159 mg, 72%). – m.p.: 246–248 °C (lit.[4] 247–248 °C). – ^{1}H NMR (500 MHz): 7.50 (2 H, t, J = 7.5 Hz), 7.60 (4 H, t, J = 8 Hz), 7.63 (2 H, t, J = 7.5 Hz), 7.82 (2 H, d, J = 7 Hz), 7.85 (2 H, d, J = 8 Hz), 7.91 (4 H, d, J = 7.5 Hz), 8.28 (2 H, d, J = 9 Hz), 8.66 (2 H, d, J = 9 Hz) ppm. – ^{13}C NMR (125 MHz): 119.3, 126.8, 127.2, 127.3, 127.7, 128.9, 130.2, 131.2, 137.0, 139.6, 140.9, 145.1, 155.7 ppm. – IR: 1110, 1213, 1356, 1445, 1565, 2893, 2990, 3025 cm^{-1}. – MS (ESI): 409.1, calcd: 409.2 [M+H$^+$].

8,8'-Dimethyl-2,2'-biquinoline[5] (9)



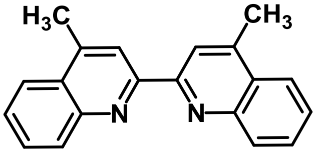
According to GP1, 8-methylquinoline *N*-oxide (350 mg, 2.20 mmol, 1 equiv.) in MeTHF (4.5 mL) was heated to 65 °C. KO*t*-Bu (616 mg, 5.50 mmol, 2.5 equiv.) was added in five portions over 10 min. After 6 h an aqueous workup was performed, and the crude product purified by column chromatography to yield biquinoline **9** (244 mg, 78%). – m.p.: 203–204 °C (Lit.[5] 209–210 °C). – ^{1}H NMR (300 MHz): 2.92 (6 H, s), 7.43 (2 H, t, J = 8 Hz), 7.59 (2 H, d, J = 8 Hz), 7.72 (2 H, d, J = 8 Hz), 8.28 (2 H, d, J = 10 Hz), 8.93 (2 H, d, J = 10 Hz) ppm. – ^{13}C NMR (75 MHz): 17.9, 119.0, 125.6, 126.6, 128.4, 129.5, 136.8, 137.9, 146.8, 155.2 ppm. – IR: 1086, 1163, 1327, 1494, 1615, 2850, 2922, 3043 cm^{-1}. – MS (ESI): 285.0, calcd: 285.1 [M+H$^+$].

[2,2'-Biquinoline]-8,8'-diol[6] (10)



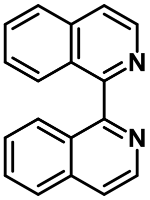
According to GP1, 8-hydroxyquinoline *N*-oxide (320 mg, 2.0 mmol, 1 equiv.) in DMF (4 mL) was reacted with AIBN (66 mg, 0.40 mmol, 20 mol%) and KO*t*-Bu (896 mg, 8.0 mmol, 4 equiv.) at 65 °C. The crude product was purified by column chromatography to yield **10** (378 mg, 65%). – ^{1}H NMR (300 MHz): 7.15 (1 H, dd, J = 1, 7.5 Hz), 7.27–7.41 (3 H, m), 8.03 (1 H, dd, J = 8.5 Hz) ppm. – ^{13}C NMR (75 MHz): 109.8, 117.56, 122.7, 126.5, 126.6, 136.1, 137.6, 151.7, 156.9 ppm. – IR: 1213, 1345, 1438, 1597, 2894, 2943, 3026 cm^{-1}. – MS (ESI): 289.0, calcd: 289.1 [M+H$^+$].

4,4'-Dimethyl-2,2'-biquinoline[7] (11)



According to GP1, 4-methylquinoline *N*-oxide (350 mg, 2.20 mmol, 1 equiv.) in MeTHF (5 mL) was heated to 65 °C. KO*t*-Bu (492 mg, 4.40 mmol, 2 equiv.) and AIBN (72 mg, 0.44 mmol, 20 mol%) was added in 6 portions over 10 min. After 3 h an aqueous workup was performed, and the crude product purified by column chromatography to yield biquinoline **11** (225 mg, 72%). – ^{1}H NMR (500 MHz): 2.85 (6 H, s), 7.60 (2 H, t, *J* = 9 Hz), 7.76 (2 H, t, *J* = 7.5 Hz), 8.06 (2 H, d, *J* = 9 Hz), 8.25 (2 H, d, *J* = 9 Hz), 8.67 (2 H, s) ppm. – ^{13}C NMR (125 MHz): 19.0, 120.0, 123.8, 126.6, 126.7, 128.5, 129.2, 130.4, 145.0, 147.8, 156.0 ppm. – IR: 1102, 1215, 1396, 1425, 2874, 2998, 3025 cm^{-1}. – MS (ESI): 285.0, calcd: 285.1 [M+H$^+$].

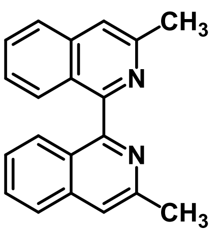
1,1'-Biisoquinoline[8] (12)



Small Scale Experiment: According to GP1, isoquinoline *N*-oxide (435 mg, 3.0 mmol) in MeTHF (6 mL) was heated to 65 °C. KO*t*-Bu (840 mg, 7.5 mmol, 2.5 equiv.) and AIBN (98 mg, 0.6 mmol, 20 mol%) were added in three portions over 10 min. After 4 h an aqueous workup was performed, and the crude product was purified by column chromatography to yield product **13** (371 mg, 96%).

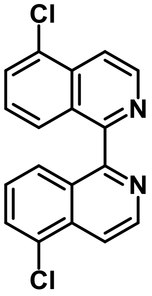
Gram Scale Experiment: According to GP1, isoquinoline *N*-oxide (2.0 g, 13.79 mmol) in MeTHF (28 mL) was heated to 65 °C. KO*t*-Bu (4.63 mg, 41.37 mmol, 3 equiv.) and AIBN (453 mg, 2.76 mmol, 20 mol%) were added in ten portions over 10 min. After 4 h an aqueous workup was performed, and the crude product was purified by column chromatography to yield 1,1'-biisoquinoline (**12**) (1.4 g, 76%). – ^{1}H NMR (500 MHz): 7.49 (2 H, dt, *J* = 1, 7 Hz), 7.69–7.77 (2 H, m), 7.81 (2 H, d, *J* = 6 Hz), 7.95 (2 H, d, *J* = 8 Hz), 8.72 (2 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 120.9, 126.7, 126.9, 127.4, 127.5, 130.2, 136.5, 141.6, 157.7 ppm. – IR: 1261, 1314, 1375, 1456, 1585, 1653, 2854, 2926, 3054 cm^{-1}. – MS (ESI): 257.1, calcd: 257.1 [M+H$^+$].

3,3'-Dimethyl-1,1'-biisoquinoline[9] (13)



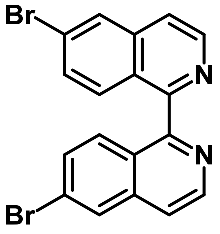
According to GP1, 3-methylisoquinoline *N*-oxide (150 mg, 0.94 mmol) in MeTHF (2 mL) was heated to 65 °C. KO*t*-Bu (316 mg, 2.82 mmol, 3 equiv.) and AIBN (31 mg, 0.19 mmol, 20 mol%) were added in three portions over 10 min. After 2 h an aqueous workup was performed, and the crude product was product purified by column chromatography to yield biisoquinoline **13** (72 mg, 54%). – ^{1}H NMR (500 MHz): 2.80 (6 H, s), 7.35 (2 H, t, *J* = 7.5 Hz), 7.53 (2 H, d, *J* = 8.5 Hz), 7.61–7.65 (4 H, m), 7.83 (2 H, d, *J* = 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 24.4, 119.1, 126.0, 126.3, 126.5, 127.1, 130.2, 137.5, 150.9, 157.8 ppm. – IR: 1026, 1177, 1205, 1311, 1438, 1561, 1656, 2923, 2959, 3040 cm^{-1}. – MS (ESI): 285.1, calcd: 285.1 [M+H^{+}].

5,5'-Dichloro-1,1'-biisoquinoline (14)



According to GP1, 5-chloroisoquinoline *N*-oxide (100 mg, 0.56 mmol) in MeTHF (1 mL) was heated to 65 °C. KO*t*-Bu (188 mg, 1.68 mmol, 3 equiv.) and AIBN (18 mg, 0.11 mmol, 20 mol%) were added in two portions over 5 min. After 3 h an aqueous work-up was performed, and the crude product purified by column chromatography to yield product **14** (49 mg, 54%). – ^{1}H NMR (500 MHz): 7.41 (2 H, t, *J* = 8 Hz), 7.64 (2 H, d, *J* = 8 Hz), 7.81 (2 H, d, *J* = 8 Hz), 8.24 (2 H, d, *J* = 6 Hz), 8.83 (2 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 117.6, 126.1, 127.5, 128.7, 130.4, 131.5, 134.8, 143.0, 158.0 ppm. – IR: 1039, 1221, 1381, 1491, 1595, 2913, 30076, 3281 cm^{-1}. – MS (ESI): 324.9, calcd: 325.0 [M+H^{+}]. – HRMS: 325.0299, calcd: 325.0294 [M+H^{+}].

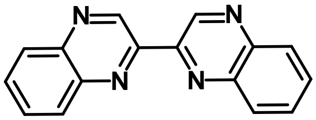
6,6'-Dibromo-1,1'-biisoquinoline (15)



According to GP1, 6-bromoisoquinoline *N*-oxide (50 mg, 0.22 mmol, 1 equiv.) in DMF (500 µL) was heated to 65 °C. KO*t*-Bu (74 mg, 0.66 mmol, 3 equiv.) and AIBN (36 mg, 1.0 mmol, 1 equiv.) were added in six portions over 10 min. After 3 h an aqueous workup was performed, and the crude product purified by column chromatography to yield product **15** (35 mg, 77%). – ^{1}H NMR (500 MHz): 7.49 (2 H, t, *J* = 1, 8 Hz), 7.65–7.95 (6

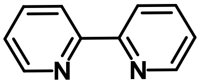
H, m), 8.72 (2 H, d, *J* = 8 Hz) ppm. – ^{13}C NMR (125 MHz): 121.0, 126.9, 127.2, 127.6, 127.8, 130.4, 136.9, 141.9, 158.1 ppm. – IR: 1169, 1215, 1374, 1445, 2892, 3028 cm^{-1}. – MS (ESI): 412.9, calcd: 412.9 [M+H$^+$]. – HRMS: 412.9283, calcd: 412.9283 [M+H$^+$].

2,2'-Biquinoxaline[10] (16)



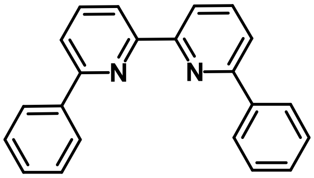
According to GP1, quinoxaline *N*-oxide (438 mg, 3.0 mmol) in MeTHF (6 mL) was heated at 65 °C. KO*t*-Bu (840 mg, 7.5 mmol, 2.5 equiv.) and AIBN (98 mg, 0.60 mmol, 20 mol%) were added in three portions over 10 min. After 3 h the reaction mixture was then worked up, and the crude product was purified by column chromatography to yield product **16** (318 mg, 82%). – ^{1}H NMR (500 MHz): 7.83–7.87 (4 H, m), 8.20–8.27 (4 H, m), 10.12 (2 H, s) ppm. – ^{13}C NMR (125 MHz): 129.4, 130.0, 130.5, 130.9, 141.6, 142.8, 144.3, 148.5 ppm. – IR: 1049, 1134, 1210 1366, 1488, 1543, 2888, 2956, 3060 cm^{-1}. – MS (ESI): 259.0, calcd: 259.1 [M+H$^+$].

2,2'-Bipyridine[11] (17)



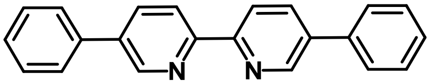
According to GP1, pyridine *N*-oxide (294 mg, 3.0 mmol), AIBN 98 mg, 0.6 mmol, 20 mol%), and KO*t*-Bu (840 mg, 7.5 mmol, 2.5 equiv.) were reacted in MeTHF (8 mL) at 65 °C. After 3 h an aqueous workup was performed, and the crude product was purified by column chromatography to yield product **17** (110 mg, 47%). – ^{1}H NMR (300 MHz): 7.20–7.40 (2 H, m), 7.80–7.90 (2 H, m), 8.43–8.44 (2 H, m), 8.77–8.83 (2 H, m) ppm. – ^{13}C NMR (125 MHz): 121.1, 123.7, 136.9, 149.2, 156.2 ppm. – IR: 1077, 1125, 1255, 1326, 1498, 1587, 1667, 2852, 2934, 3025 cm^{-1}. – MS (ESI): 157.0, calcd: 157.1 [M+H$^+$].

6,6'-Diphenyl-2,2'-bipyridine[12] (18)



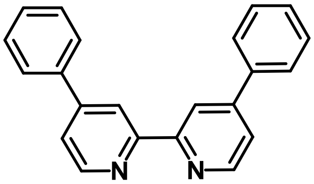
According to GP1, 2-phenylpyridine *N*-oxide (500 mg, 2.92 mmol, 1 equiv.) in MeTHF (6 mL) was heated at 65 °C. KO*t*-Bu (981 mg, 8.76 mmol, 3 equiv.) and AIBN (96 mg, 0.58 mmol, 20 mol%) were added in three portions over 10 min. After 3 h an aqueous work-up was performed, and the crude product was purified by column chromatography to yield product **18** (347 mg, 77%). – ^{1}H NMR (500 MHz): 7.45 (2 H, t, *J* = 6 Hz), 7.53 (4 H, dt, *J* = 1, 7.5 Hz), 7.79 (2 H, dd, *J* = 1, 7.5 Hz), 7.92 (2 H, dt, *J* = 1.5, 8 Hz), 8.19 (4 H, dd, *J* = 1.5, 7 Hz), 8.61 (2 H, dd, *J* = 1, 8 Hz) ppm. – ^{13}C NMR (125 MHz): 119.5, 120.3, 127.0, 128.7, 129.0, 137.6, 139.4, 155.9, 156.3 ppm. – IR: 1076, 1144, 1274, 1395, 1456, 2850, 3025 cm^{-1}. – MS (ESI): 309.0, calcd: 309.1 [M+H$^+$].

5,5'-Diphenyl-2,2'-bipyridine[13] (19)



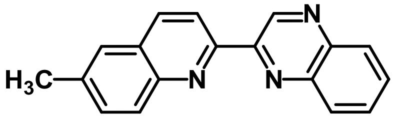
According to GP1, 3-phenylpyridine *N*-oxide (200 mg, 1.17 mmol) in MeTHF (2 mL) was heated to 65 °C. KO*t*-Bu (393 mg, 3.51 mmol, 3 equiv.) and AIBN (38 mg, 0.23 mmol, 20 mol%) were added in six portions over 10 min. After 1 h the reaction an aqueous workup was performed, and the crude product purified by column chromatography to yield product **19** (110 mg, 61%). – ^{1}H NMR (300 MHz): 7.44 (2 H, d, *J* = 7.5 Hz), 7.52 (4 H, t, *J* = 7.5 Hz), 7.64–7.72 (4 H, m), 8.05 (2 H, dd, *J* = 2, 8.5 Hz), 8.52 (2 H, d, *J* = 8.5 Hz), 8.95 (2 H, d, *J* = 2 Hz) ppm. – ^{13}C NMR (75 MHz): 120.9, 127.1, 128.2, 129.1, 135.2, 136.4, 137.6, 147.7, 154.6 ppm. – IR: 1077, 1261, 1362, 1456, 1586, 1684, 2852, 2924, 3059 cm^{-1}. – MS (ESI): 309.0, calcd: 309.1 [M+H$^+$].

4,4'-Diphenyl-2,2'-bipyridine[14] (20)



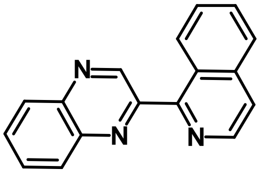
According to GP1, 4-phenylpyridine *N*-oxide (200 mg, 1.17 mmol) in MeTHF (2 mL) was heated to 65 °C. Potassium *tert*-butoxide (393 mg, 3.51 mmol, 3 equiv.) and AIBN (38 mg, 0.23 mmol, 20 mol%) were added in three portions over 10 min. After 3 h the reaction an aqueous workup was performed, and the crude product purified by column chromatography to yield product **20** (123 mg, 68%). ^{1}H NMR (500 MHz): 7.45–7.57 (8 H, m), 7.79 (4 H, dd, *J* = 1.5, 6.5 Hz), 8.73 (2 H, s), 8.75 (2 H, d, *J* = 5.5 Hz) ppm. – ^{13}C NMR (125 MHz): 119.2, 121.7, 127.2, 129.0, 129.1, 138.3, 149.4, 149.6, 156.6 ppm. – IR: 1260, 1360, 1352, 1554, 1635, 2925, 3022 cm^{-1}. – MS (ESI): 309.0, calcd: 309.1 [M+H$^+$].

2-(6-Methylquinolin-2-yl)quinoxaline (21)



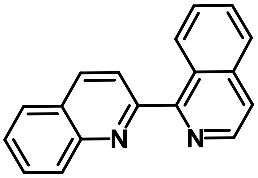
According to GP1, 6-methylquinoline *N*-oxide (143 mg, 0.90 mmol) and quinoxaline dioxide (300 mg, 1.80 mmol, 2 equiv.) was reacted with AIBN (30 mg, 0.18 mmol, 10 mol%) and KO*t*-Bu (504 mg, 4.5 mmol, 2.5 equiv.) in MeTHF (4 mL) at 65 °C. The crude product was purified by column chromatography to yield product **21** (56 mg, 36%). – ^{1}H NMR (500 MHz): 2.60 (3 H, s), 7.63 (1 H, dd, *J* = 2, 9 Hz), 7.66 (1 H, s), 7.80–7.83 (2 H, m), 8.16 (1 H, d, *J* = 8.5 Hz), 8.18–8.23 (1 H, m), 8.26 (1 H, d, *J* = 8 Hz), 8.71 (1 H, d, *J* = 8.5 Hz), 10.21 (1 H, s) ppm. – ^{13}C NMR (125 MHz): 21.7 (CH_3), 119.2 (CH), 126.6 (CH), 128.5 (C), 129.3 (CH), 129.4 (CH), 129.8 (CH), 130.00 (CH), 130.1 (CH), 132.2 (CH), 136.3 (CH), 137.6 (C), 141.8 (C), 142.6 (C), 144.7 (CH), 146.5 (C), 150.4 (C), 153.6 (C) ppm. – IR: 1075, 1213, 1337, 1449, 1547, 1608, 2853, 2927, 3025 cm^{-1}. – MS (ESI): 272.1, HRMS: 272.1195, calcd: 272.1182 [M+H$^+$].

2-(Isoquinolin-1-yl)quinoxaline (22)



According to GP1, isoquinoline (130 mg, 0.90 mmol, 1 equiv.) and quinoxaline dioxide (300 mg, 1.80 mmol, 2 equiv.) was reacted with AIBN (30 mg, 0.18 mmol, 10 mol%) and KO*t*-Bu (504 mg, 4.50 mmol, 2.5 equiv.) in MeTHF (4 mL) at 65 °C. The crude product was purified by column chromatography to yield cross-coupling product **22** (95 mg, 41%). – ^{1}H NMR (500 MHz): 7.69 (1 H, dt, *J* = 1.5, 8 Hz), 7.78 (1 H, dt, *J* = 1.5, 8.5 Hz), 7.82 (1 H, d, *J* = 6 Hz), 7.83–7.88 (2 H, m), 7.95 (1 H, d, *J* = 8.5 Hz), 8.21–8.29 (2 H, m), 8.75 (1 H, d, *J* = 5.5 Hz), 8.96 (1 H, dd, *J* = 1, 8 Hz), 9.66 (1 H, s) ppm. – ^{13}C NMR (125 MHz): 122.1, 127.2, 127.4, 128.3, 129.3, 129.8, 130.3, 130.4, 130.5, 130.6, 137.3, 141.0, 141.8, 142.1, 147.0, 152.5, 154.5 ppm. – IR: 1118, 1213, 1454, 1602, 2894, 2909, 3025 cm^{-1}. – MS (ESI): 258.1, HRMS: 258.1022, calcd: 258.1026 [M+H$^+$].

2-(Isoquinolin-1-yl)quinoline[15] (23)



To a solution of quinoline *N*-oxide (500 mg, 3.45 mmol) and isoquinoline *N*-oxide (1.5 g, 10.34 mmol, 3 equiv.) in dimethylformamide (17.3 mL) at 65 °C was added a solution of

KO*t*-Bu (1.56 g, 13.80 mmol, 4 equiv.) and AIBN (113 mg, 0.69 mmol, 20 mol%) in ten portions over 20 min. The reaction was heated for 30 min before an aqueous workup was performed, and the crude product was purified by column chromatography to yield cross-coupling product **23** (111 mg, 25%). – ^{1}H NMR (500 MHz): 6.62–7.82 (5 H, m), 7.93 (2 H, t, *J* = 8.5 Hz), 8.16 (1 H, d, *J* = 9 Hz), 8.26 (1 H, d, *J* = 8 Hz), 8.38 (1 H, d, *J* = 8.5 Hz), 8.70 (1 H, d, *J* = 5.5 Hz), 8.84 (1 H, d, *J* = 9 Hz) ppm. – ^{13}C NMR (125 MHz): 121.4 (CH), 122.8 (CH), 127.0 (C), 127.1 (CH), 127.6 (C), 127.7 (CH), 127.8 (CH), 128.0 (CH), 129.8 (CH), 129.9 (CH), 130.2 (CH), 136.8 (CH), 137.3 (C), 142.0 (CH), 147.4 (C), 157.5 (C), 158.1 (C) ppm. – IR: 1135, 1277, 1388, 1498, 1552, 3050 cm^{-1}. – MS (ESI): 257.0, calcd: 257.1 [M+H$^+$].

General Procedure for EPR spectroscopic studies:

To a vial was added heterocyclic *N*-oxide (0.5 mmol) and solvent (0.5M). The solution was degassed for 2 minutes under a high flow of argon, and KO*t*-Bu (3 equiv.) was added. The reaction was then either heated to 65 °C or sonicated at 23 °C for 5 min prior to acquiring the EPR spectrum.

X-Ray Crystallographic Data

6,6'-Diisopropyl-2,2'-biquinoline (6)

CCDC Number: 1474208

Bond precision: C–C = 0.0048 Å Wavelength = 0.71075

Cell:	a=12.648(15)	b=5.914(7)	c=13.125(17)
	α=90	β=94.02(2)	γ=90
Temperature:	293 K		

	Calculated	Reported
Volume	979(2)	979(2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{24}H_{24}N_2$	$C_{24}H_{24}N_2$
Sum formula	$C_{24}H_{24}N_2$	$C_{24}H_{24}N_2$
M_r	340.45	340.45
D_x, g cm^{-3}	1.155	1.155

Z	2	2
μ (mm^{-1})	0.067	0.067
F000	364.0	364.0
F000’	364.12	
h,k,l_{max}	15,7,15	15,7,15
N_{ref}	1725	1699
T_{min},T_{max}	0.987,0.987	0.383,1.000
T_{min}’	0.987	

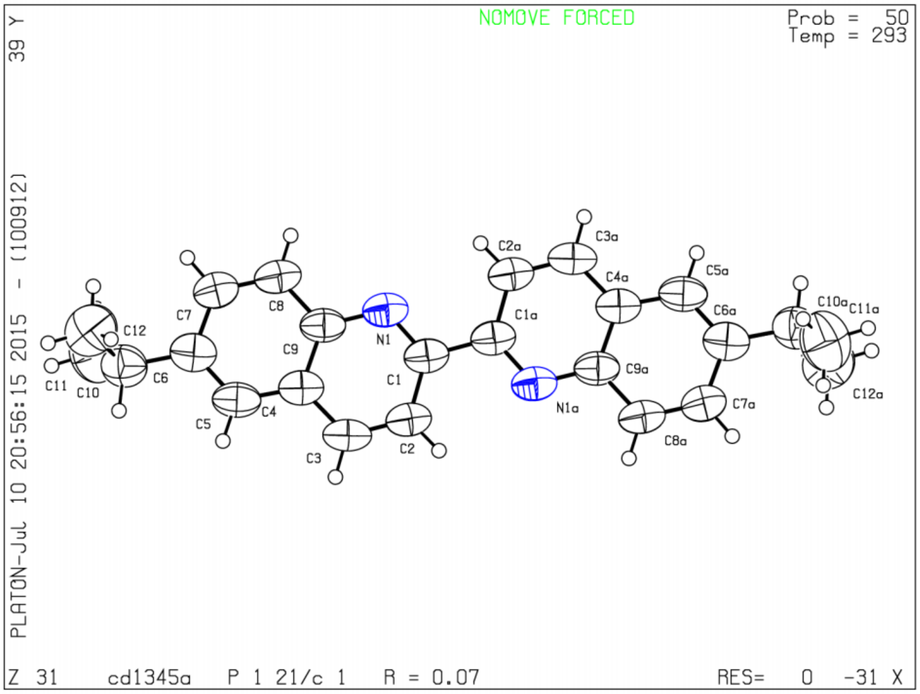
Correction method= # Reported T Limits: T_{min}=0.383 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.985 θ(max)= 25.045

R(reflections)= 0.0710(859) wR2(reflections)= 0.1519(1699) S = 1.022

N_{par}= 121



6,6'-Di-*tert*-butyl-2,2'-biquinoline (7)

CCDC Number: 1474212

Bond precision: C–C = 0.0032 Å Wavelength=0.71075

Cell:	a=18.301(11)	b=6.133(3)	c=18.738(11)
	α=90	β=94.032(6)	γ=90
Temperature:	293 K		

	Calculated	Reported
Volume	2098(2)	2098(2)
Space group	I 2/a	I 1 2/a 1
Hall group	-I 2ya	-I 2ya
Moiety formula	$C_{26}H_{28}N_2$	$C_{26}H_{28}N_2$
Sum formula	$C_{26}H_{28}N_2$	$C_{26}H_{28}N_2$
M_r	368.50	368.50
D_x,g cm^{-3}	1.167	1.167
Z	4	4
μ (mm^{-1})	0.068	0.068
F000	792.0	792.0
F000’	792.26	
h,k,l_{max}	22,7,22	22,7,22
N_{ref}	1951	1924
T_{min},T_{max}	0.966,0.989	0.527,1.000
T_{min}’	0.966	

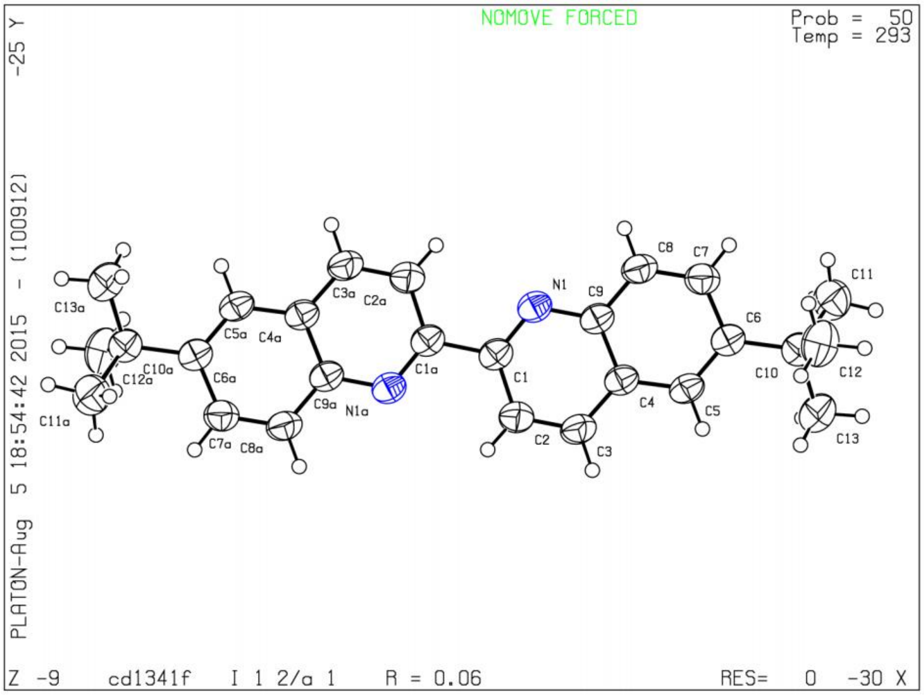
Correction method= # Reported T Limits: T_{min}=0.527 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.986 θ(max)= 25.493

R(reflections)= 0.0634(1474) wR2(reflections)= 0.1458(1924) S = 1.035

N_{par}= 130


NOMOVE FORCED
Prob = 50
Temp = 293
-25 Y
PLATON-Aug 5 18:54:42 2015 - (100912)
C13a
C12a
C10a
C11a
C5a
C4a
C6a
C7a
C8a
C3a
C2a
C9a
N1a
C1a
N1
C1
C9
C8
C7
C2
C3
C4
C5
C6
C10
C11
C12
C13
Z -9
cd1341f
I 1 2/a 1
R = 0.06
RES= 0 -30 X

6,6'-Diphenyl-2,2'-bipyridine (18)

CCDC Number: 1474211

Bond precision: C–C = 0.0039 Å Wavelength=0.71075

Cell:	a=20.260(12)	b=5.434(3)	c=16.088(9)
	α=90	β=110.528(9)	γ=90
Temperature:	293 K		

	Calculated	Reported
Volume	1658.7(16)	1658.7(16)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{22}H_{16}N_2$	$2(C_{11}H_8N)$
Sum formula	$C_{22}H_{16}N_2$	$C_{22}H_{16}N_2$
M_r	308.37	308.37
D_x,g cm^{-3}	1.235	1.235
Z	4	4
μ (mm^{-1})	0.073	0.073
F000	648.0	648.0
F000’	648.22	
h,k,l_{max}	24,6,19	24,6,19
N_{ref}	2942	2904
T_{min},T_{max}	0.962,0.978	0.691,1.000
T_{min}’	0.962	

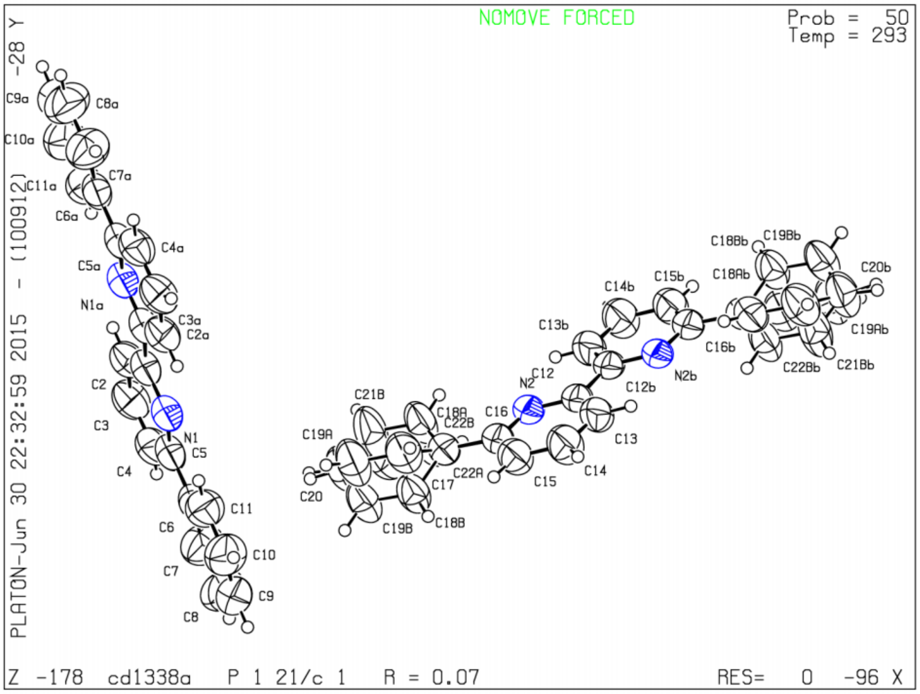
Correction method= # Reported T Limits: T_{min}=0.691 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.987 θ(max)= 25.047

R(reflections)= 0.0681(2142) wR2(reflections)= 0.1491(2904) S = 1.023

N_{par}= 253



2-Phenylpyridine *N*-Oxide
CCDC Number: 1474206

Bond precision: C–C = 0.0030 Å Wavelength = 0.71075

Cell:	a=5.8141(14)	b=23.591(5)	c=6.8413(16)
	α=90	β=114.257(3)	γ=90
Temperature:	293 K		

	Calculated	Reported
Volume	855.5(3)	855.5(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{11}H_9NO$	$C_{11}H_9NO$
Sum formula	$C_{11}H_9NO$	$C_{11}H_9NO$
M_r	171.19	171.19
D_x, g cm^{-3}	1.329	1.329
Z	4	4
μ (mm^{-1})	0.086	0.086
F000	360.0	360.0
F000’	360.15	

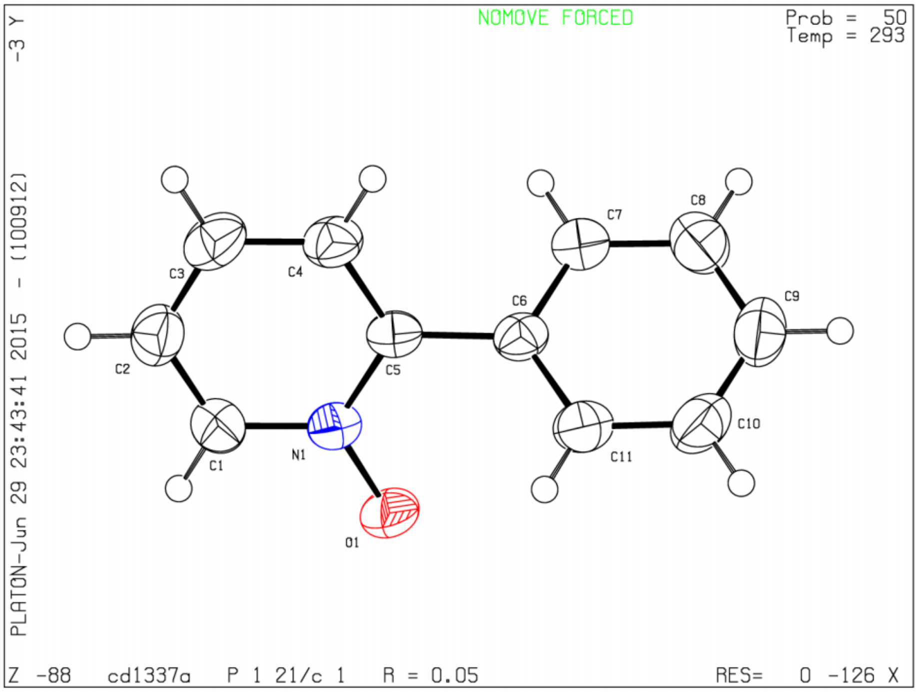
h,k,l_{max}	6,28,8	6,28,8
N_{ref}	1508	1458
T_{min},T_{max}	0.983,0.983	0.648,1.000
T_{min}'	0.983	

Correction method= # Reported T Limits: T_{min}=0.648 T_{max}=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.967 θ(max)= 25.047

R(reflections)= 0.0493(1310) wR2(reflections)= 0.1128(1458) S = 1.025

N_{par}= 118



3-Methylquinoline *N*-Oxide *meta*-Chlorobenzoic Acid (1:1) Complex

CCDC Number: 1474207

Bond precision: C–C = 0.0025 Å Wavelength = 0.71075

Cell:	a=15.840(4)	b=13.517(4)	c=7.047(2)
	α=90	β=101.395(5)	γ=90
Temperature:	293 K		

	Calculated	Reported
Volume	1479.1(7)	1479.2(7)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{10}H_9NO$, $C_7H_5ClO_2$	$C_7H_5ClO_2$, $C_{10}H_9NO$
Sum formula	$C_{17}H_{14}ClNO_3$	$C_{17}H_{14}ClNO_3$
M_r	315.74	315.74
D_x, g cm^{-3}	1.418	1.418
Z	4	4
μ (mm^{-1})	0.270	0.270
F000	656.0	656.0
F000’	656.89	
h,k,l_{max}	18,16,8	18,16,8
N_{ref}	2614	2574
T_{min},T_{max}	0.878,0.935	0.783,1.000
T_{min}’	0.874	

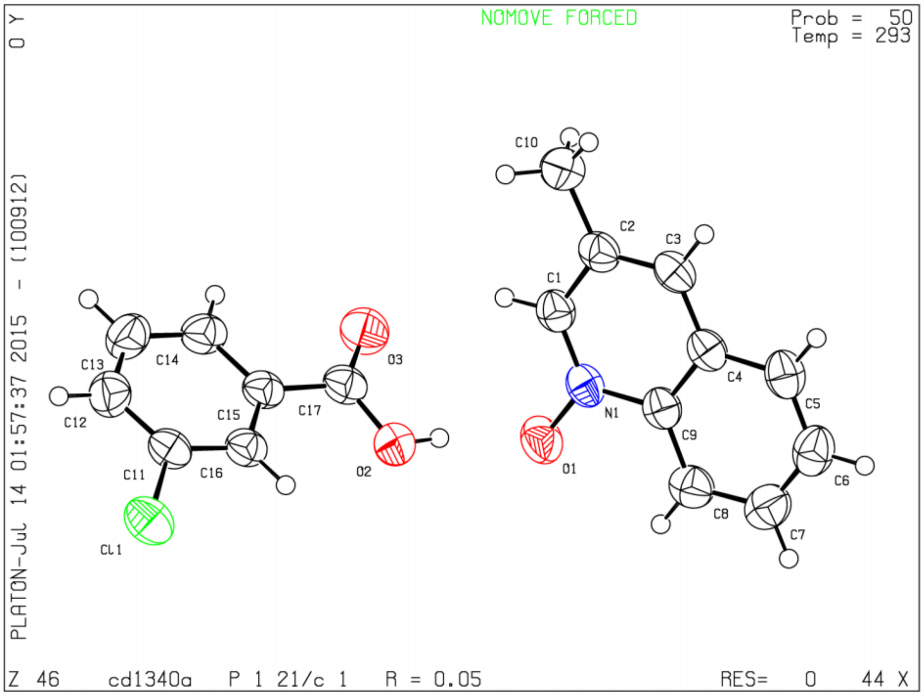
Correction method= # Reported T Limits: T_{min}=0.783 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.985 θ(max)= 25.047

R(reflections)= 0.0462(2325) wR2(reflections)= 0.1280(2574) S = 1.076

N_{par}= 201



3-Methylisoquinoline *N*-Oxide Dihydrate

CCDC Number: 1474213

Bond precision:	C–C = 0.0019 Å		Wavelength = 0.71075
Cell:	a=6.8201(14)	b=16.879(3)	c=9.0566(19)
	α=90	β=106.250(3)	γ=90
Temperature:	293 K		

	Calculated	Reported
Volume	1000.9(3)	1000.9(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{10}H_9NO, 2(H_2O)$	$C_{10}H_9NO, 2(H_2O)$
Sum formula	$C_{10}H_{13}NO_3$	$C_{10}H_{13}NO_3$
M_r	195.21	195.21
D_x, g cm^{-3}	1.296	1.295
Z	4	4
μ (mm^{-1})	0.096	0.096
F000	416.0	416.0
F000’	416.22	
h,k,l_{max}	8,20,10	8,20,10

N_{ref}	1768	1743
T_{min},T_{max}	0.952,0.972	0.844,1.000
T_{min}’	0.952	

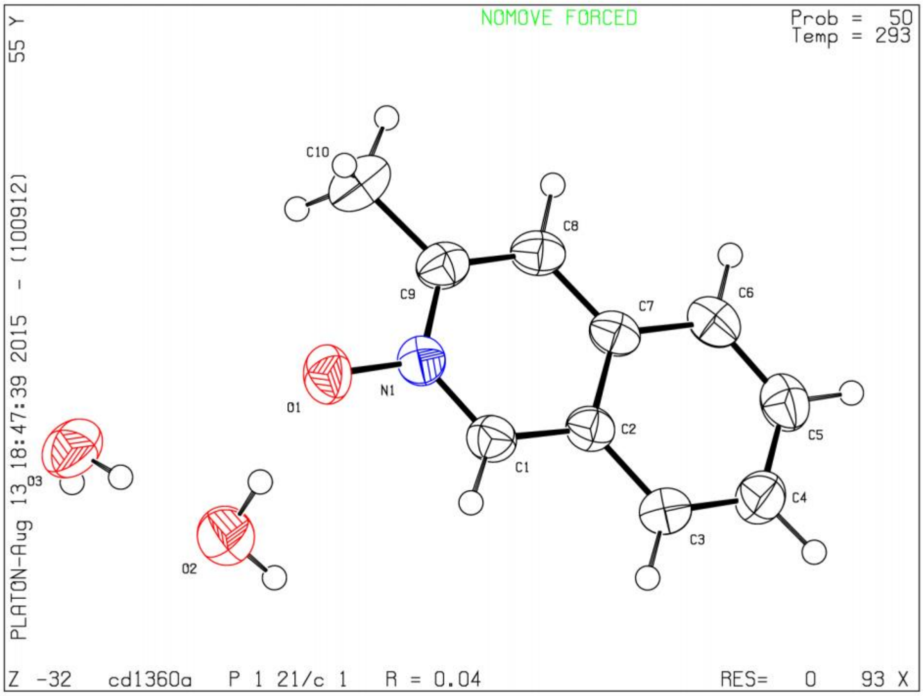
Correction method= # Reported T Limits: T_{min}=0.844 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.986 θ(max)= 25.043

R(reflections)= 0.0441(1611) wR2(reflections)= 0.1237(1743) S = 1.050

N^{par}= 166



6-Methoxyquinoline *N*-Oxide Dihydrate

CCDC Number: 1474209

Bond precision: C–C = 0.0030 Å Wavelength = 0.71075

Cell:	a=4.8503(12)	b=17.114(4)	c=6.4411(15)
	α=90	β=105.911(4)	γ=90
Temperature:	98 K		

	Calculated	Reported
Volume	514.2(2)	514.2(2)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	$C_{10}H_9NO_2$, 2(H_2O)	$C_{10}H_9NO_2$, 2(H_2O)
Sum formula	$C_{10}H_{13}NO_4$	$C_{10}H_{13}NO_4$
Mr	211.21	211.21
D_x, g cm^{-3}	1.364	1.364
Z	2	2
μ (mm^{-1})	0.106	0.106
F000	224.0	224.0
F000’	224.13	
h,k,l_{max}	6,22,8	6,22,8
N_{ref}	2364[1222]	2236
T_{min},T_{max}	0.971,0.982	0.883,1.000
T_{min}’	0.955	

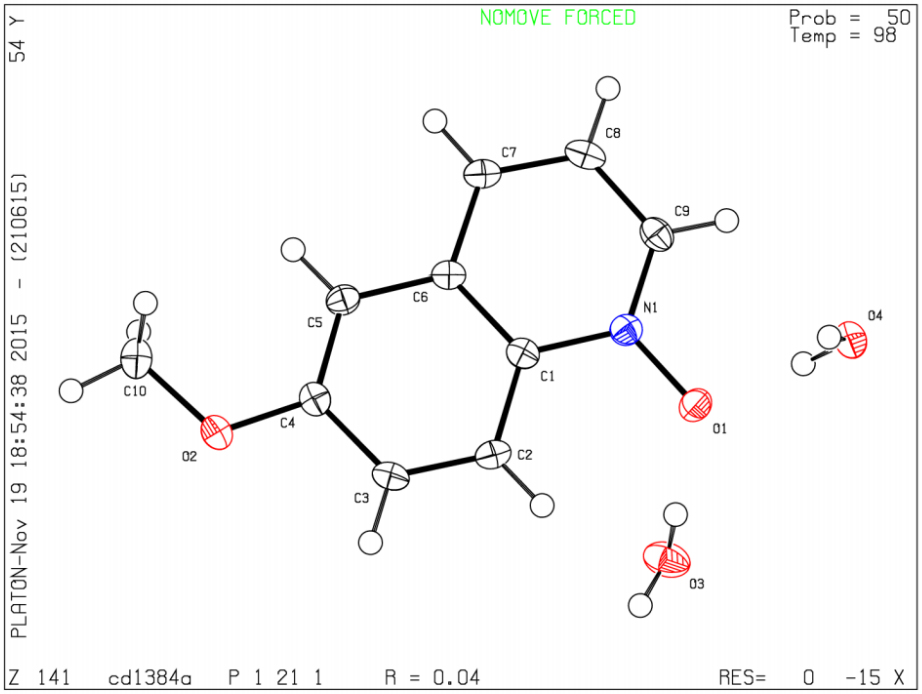
Correction method= # Reported T Limits: T_{min}=0.883 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.83/0.95 θ(max)= 27.488

R(reflections)= 0.0350(2205) wR2(reflections)= 0.0902(2236) S = 1.028

N_{par}= 149



4-Methylquinoline *N*-Oxide Dihydrate

CCDC Number: 1474210

Bond precision:	C–C = 0.0020 Å		Wavelength = 0.71075
Cell:	a=6.690(4)	b=8.863(5)	c=9.115(6)
	α=107.219(6)	β=111.191(11)	γ=92.478(5)
Temperature:	98 K		

	Calculated	Reported
Volume	474.4(5)	474.4(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	$C_{10}H_9NO$, $2(H_2O)$	$C_{10}H_9NO$, $2(H_2O)$
Sum formula	$C_{10}H_{13}NO_3$	$C_{10}H_{13}NO_3$
M_r	195.21	195.21
D_x, g cm^{-3}	1.367	1.366
Z	2	2
μ (mm^{-1})	0.101	0.101
F000	208.0	208.0
F000’	208.11	
h,k,l_{max}	8,11,11	8,11,11
N_{ref}	2166	2135
T_{min},T_{max}	0.973,0.990	0.533,1.000
T_{min}’	0.951	

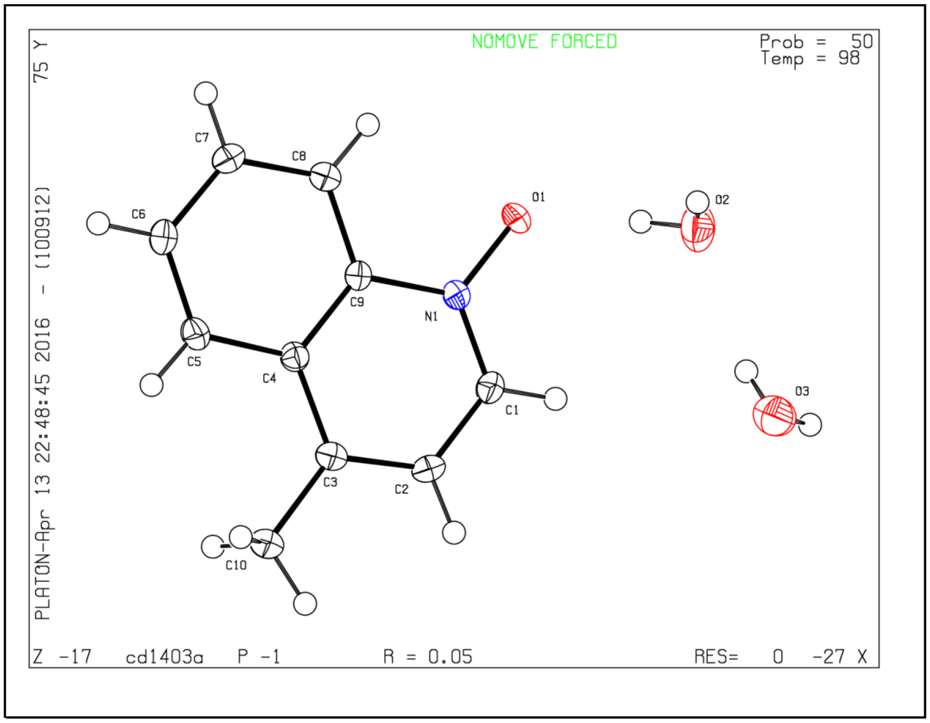
Correction method= # Reported T Limits: T_{min}=0.533 T_{max}=1.000

AbsCorr = MULTI-SCAN

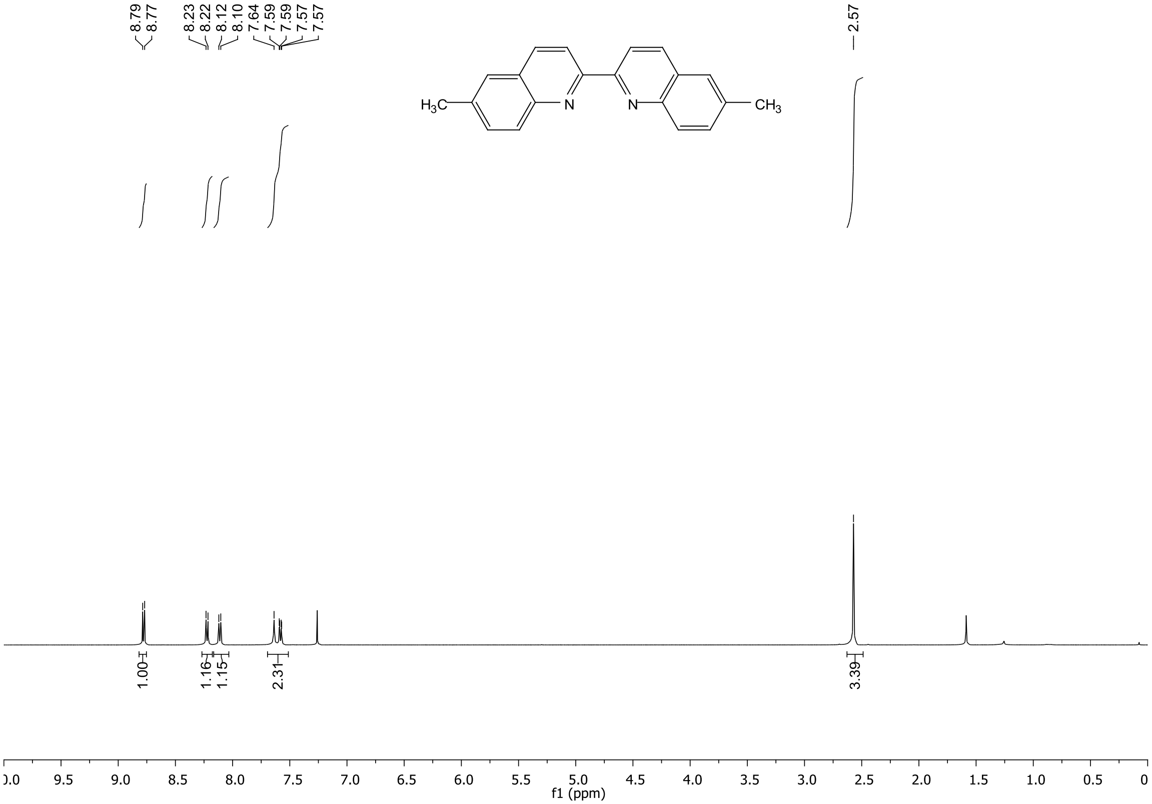
Data completeness= 0.986 θ(max)= 27.496

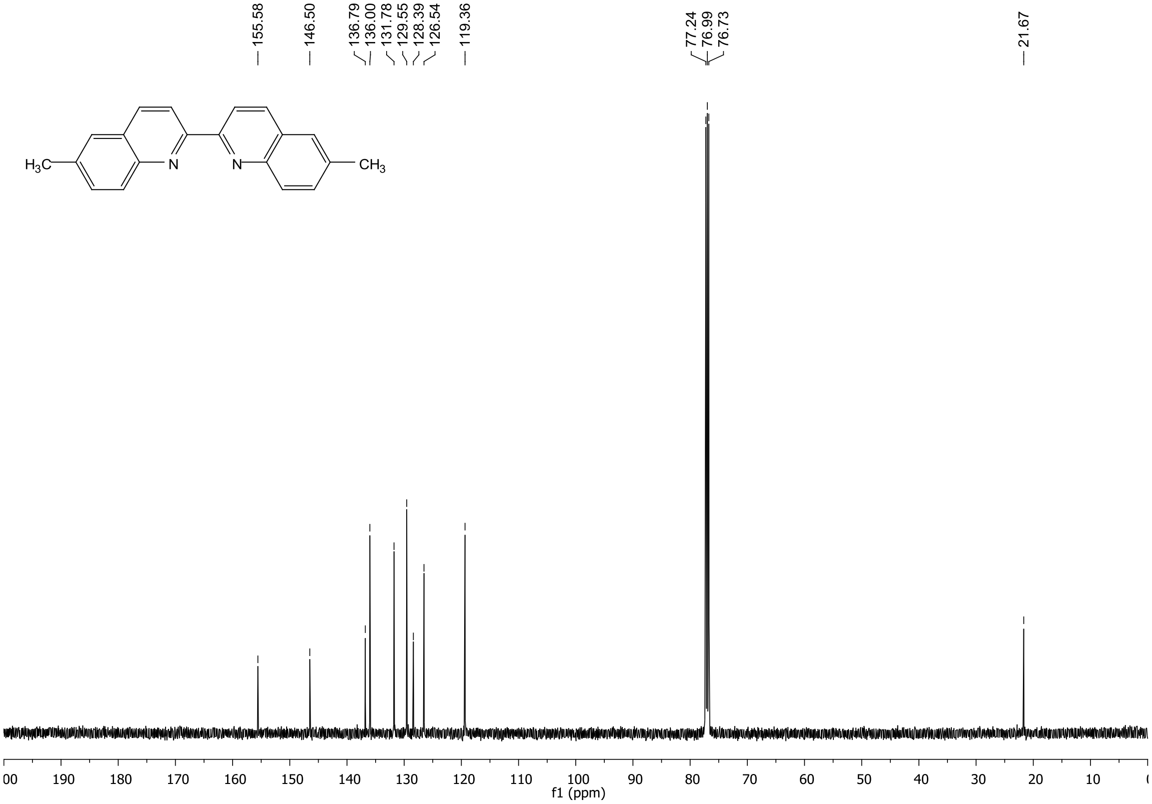
R(reflections)= 0.0486(1817) wR2(reflections)= 0.1186(2135) S = 0.991

N_{par}= 137

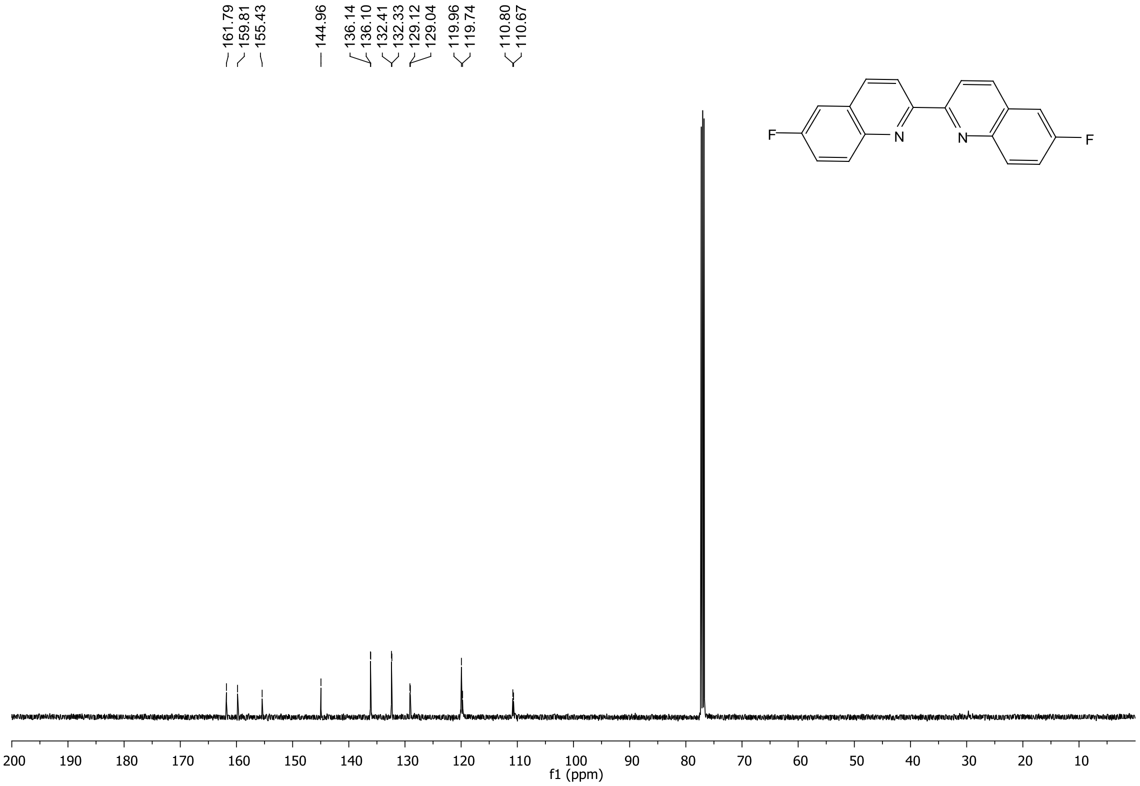


6,6'-Dimethyl-2,2'-biquinoline (4)

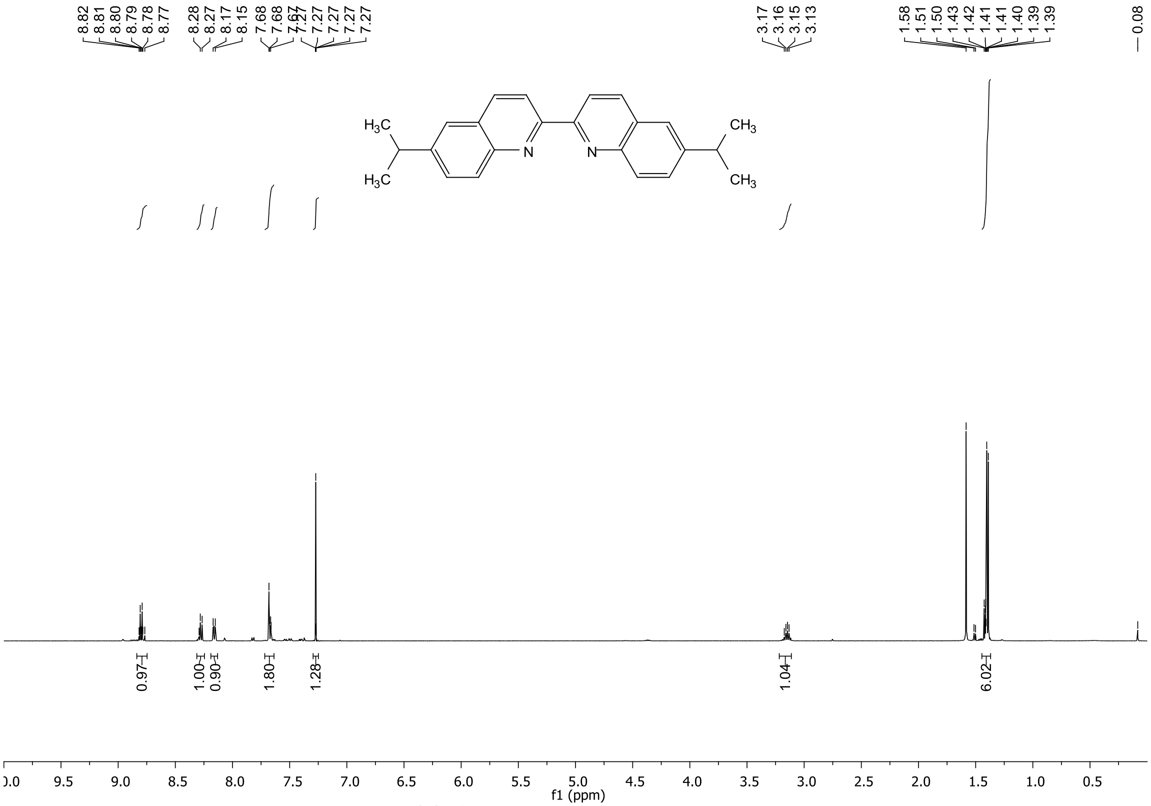


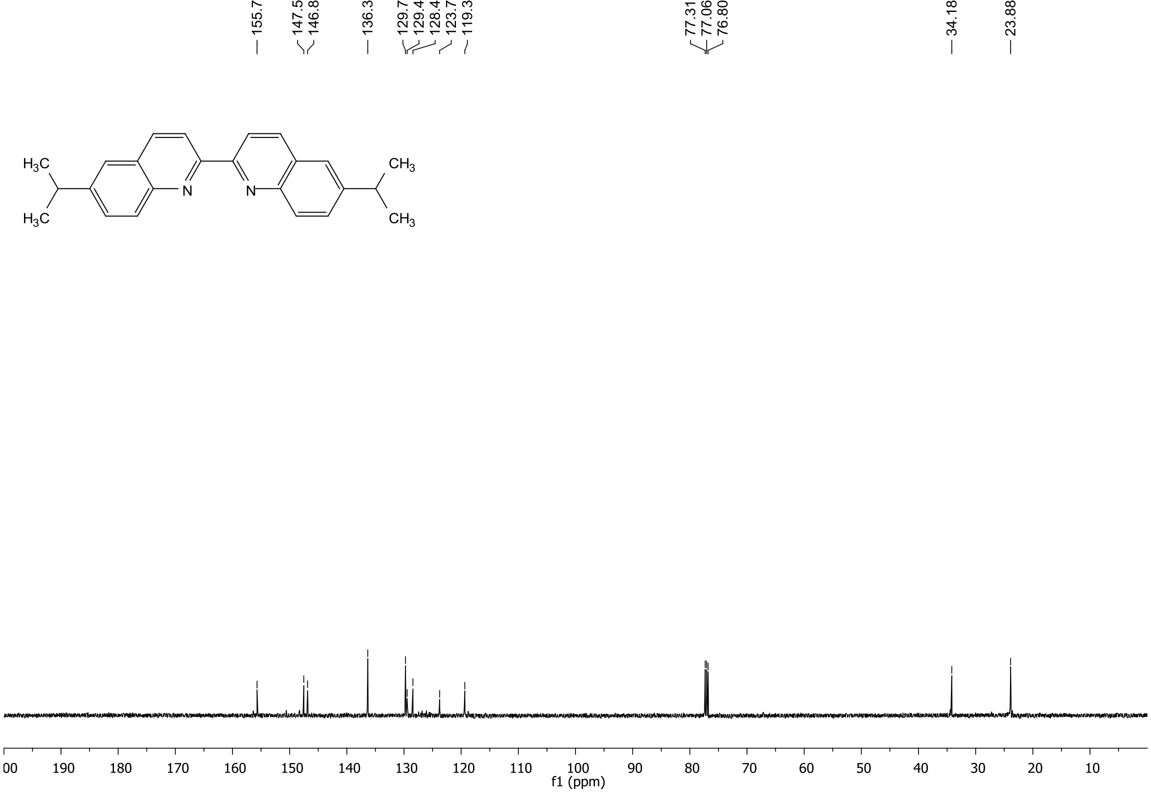


6,6'-Difluoro-2,2'-biquinoline (5)

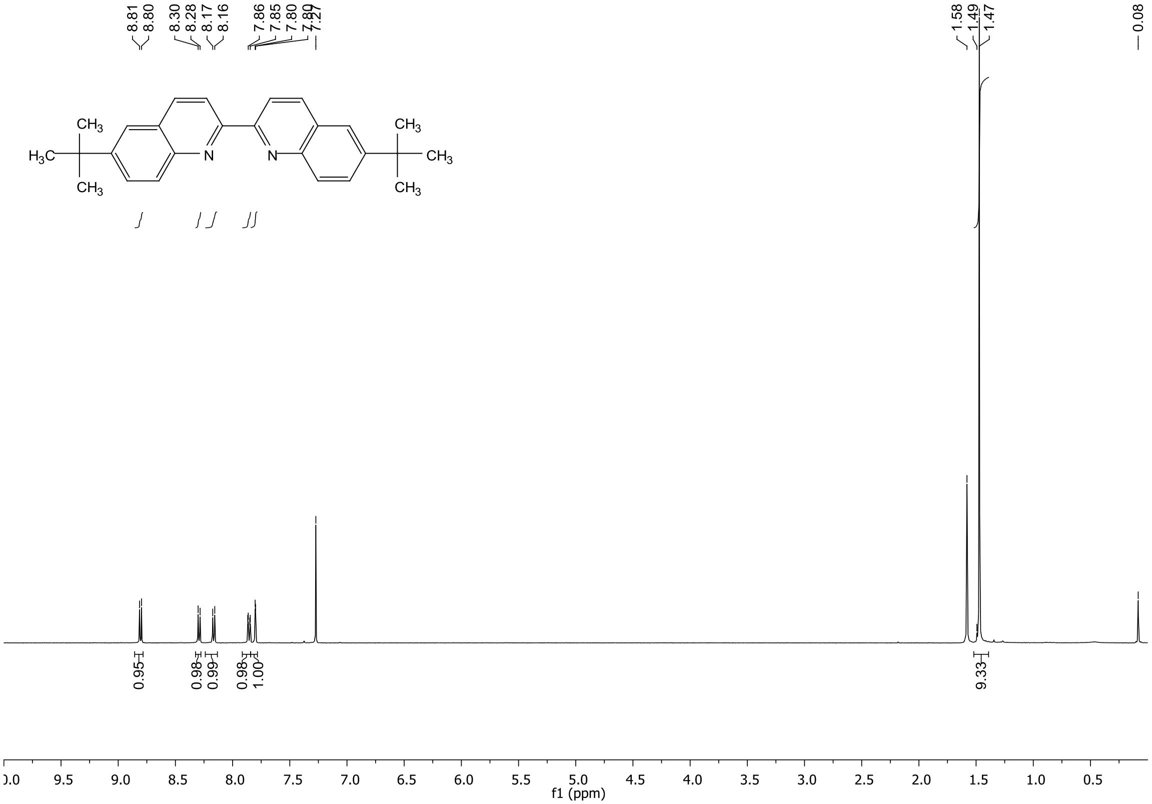


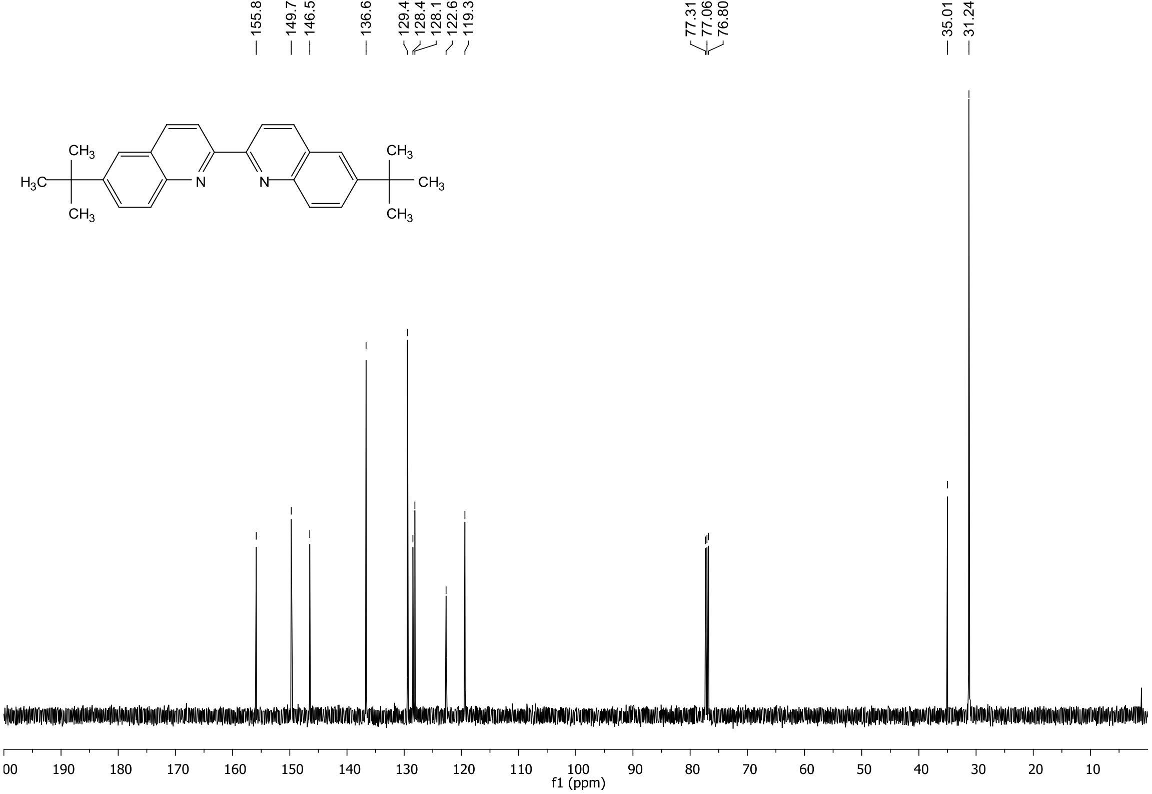
6,6'-Diisopropyl-2,2'-biquinoline (6)



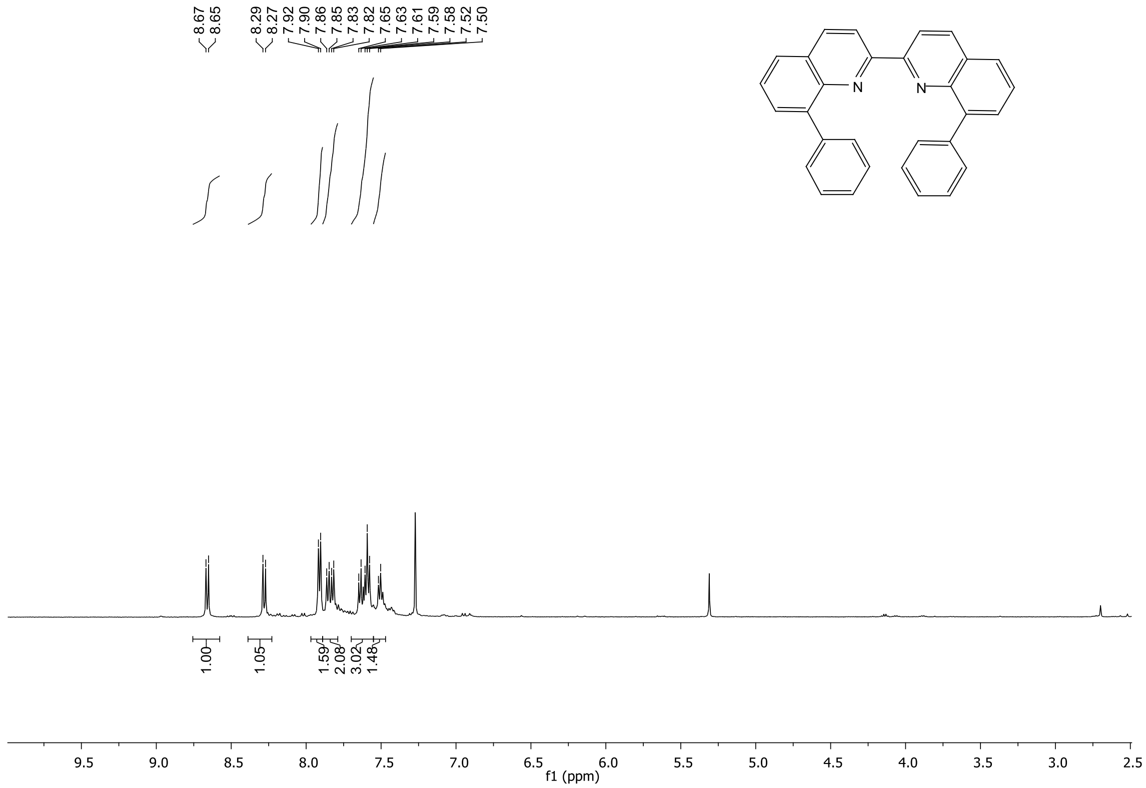


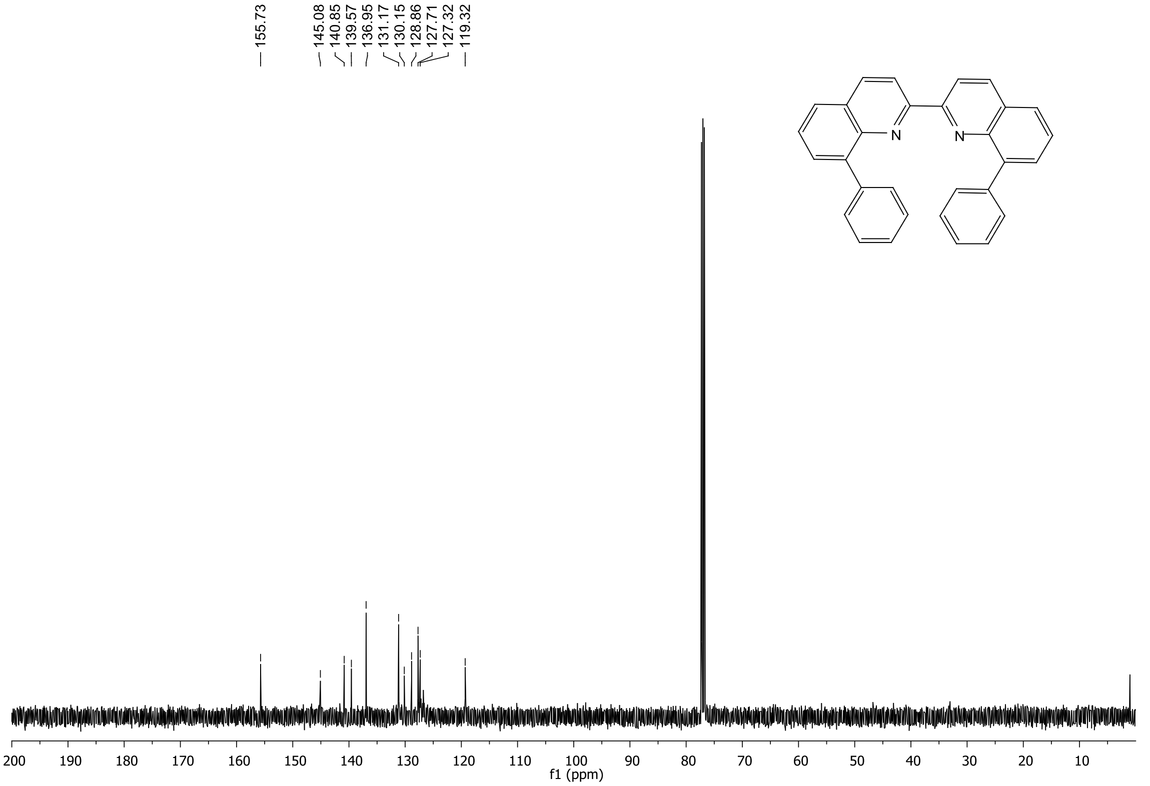
6,6'-Di-*tert*-butyl-2,2'-biquinoline (7)



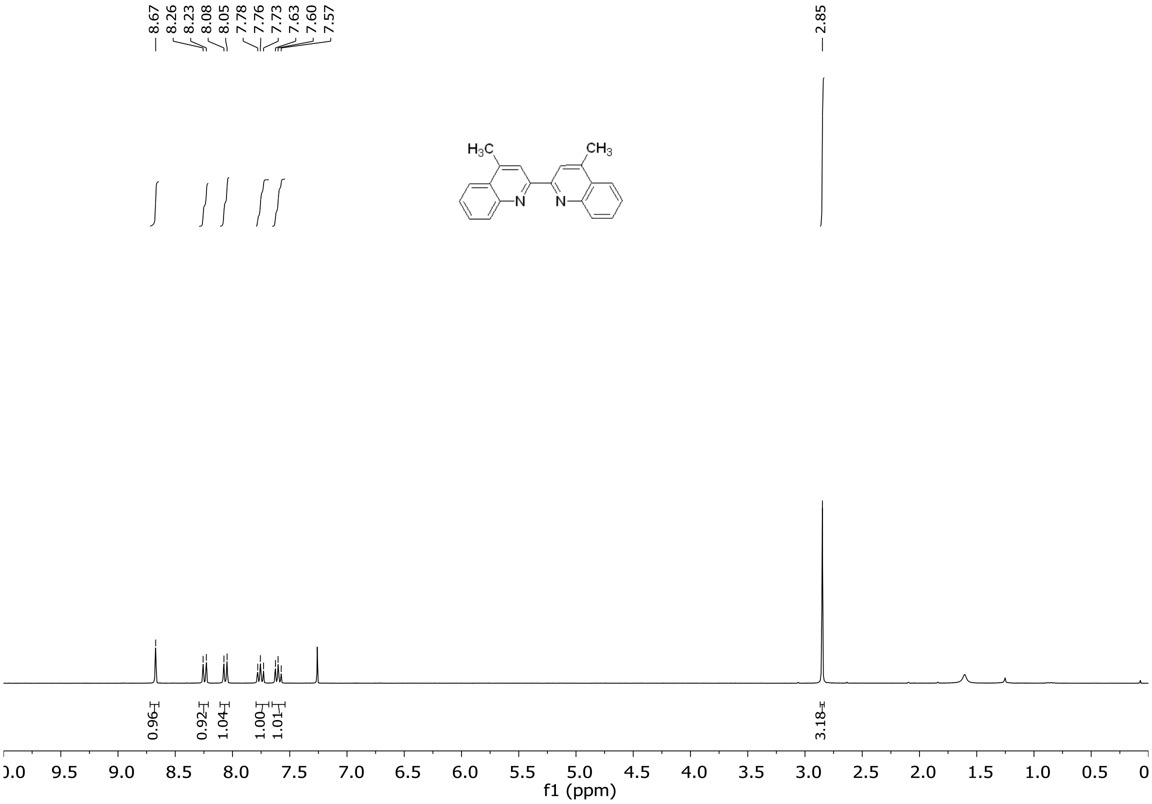


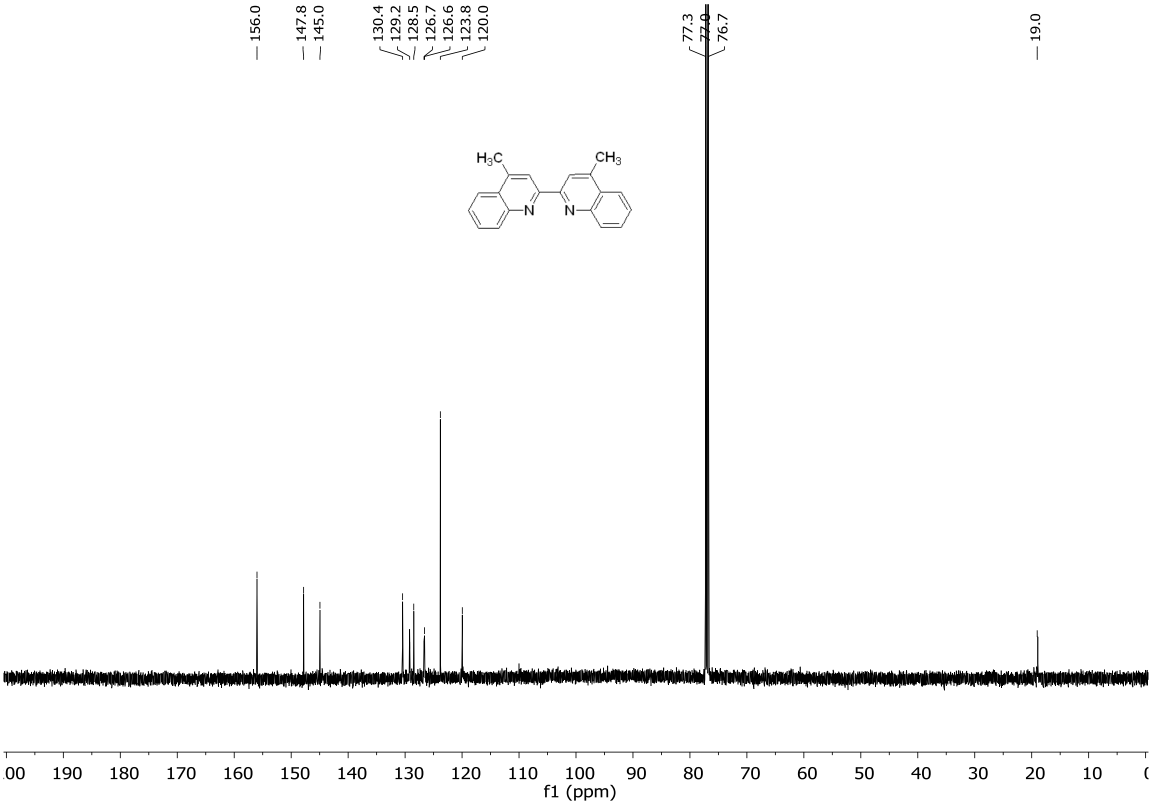
8,8'-Diphenyl-2,2'-biquinoline (8)



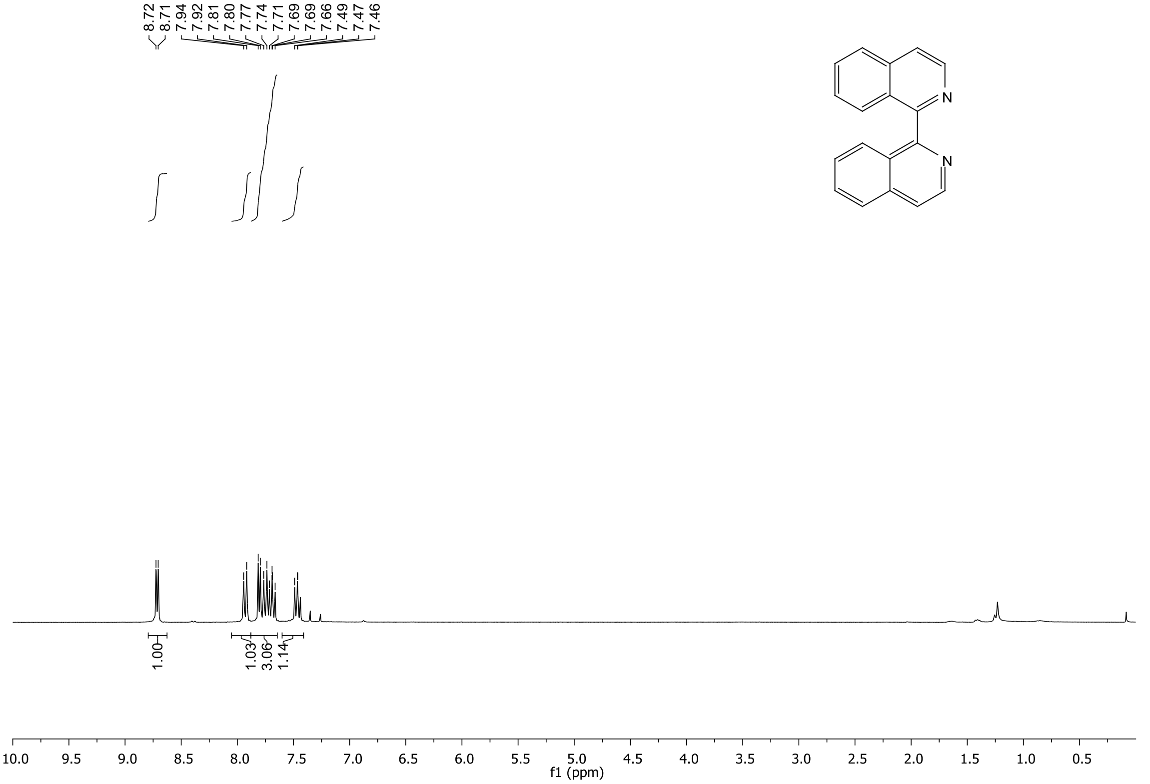


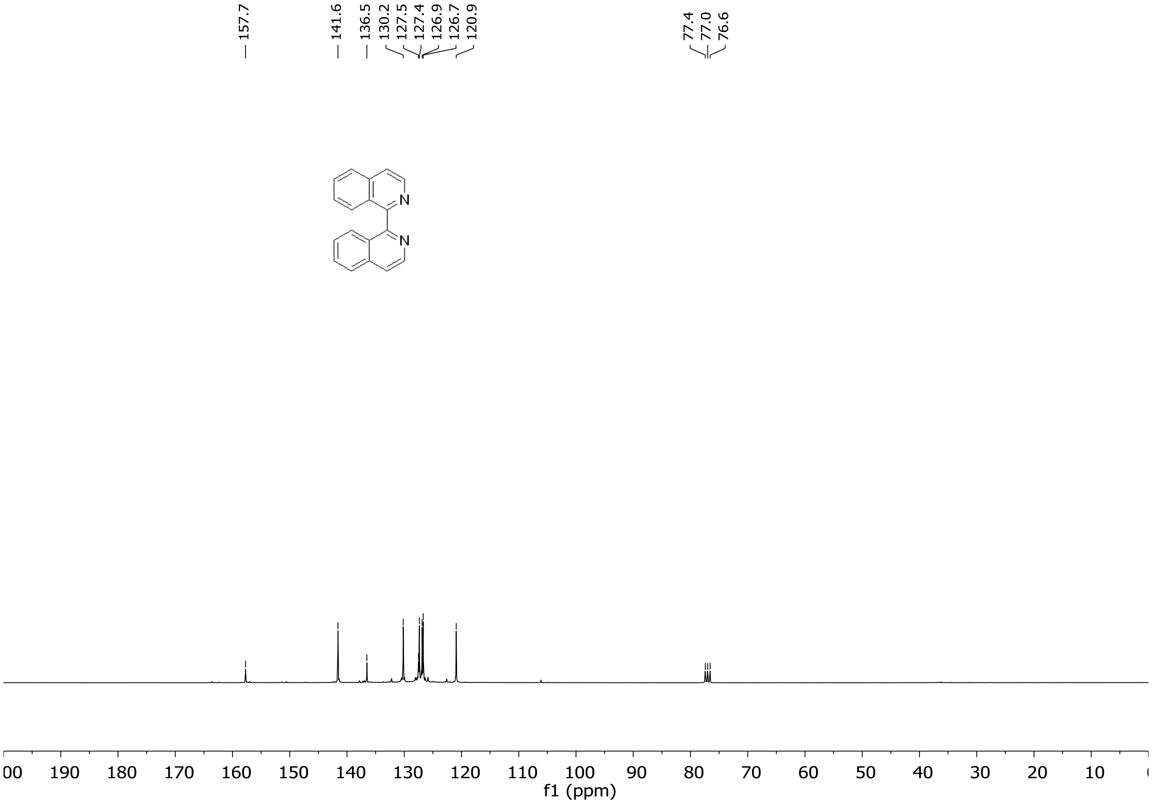
4,4'-Dimethyl-2,2'-biquinoline (11)



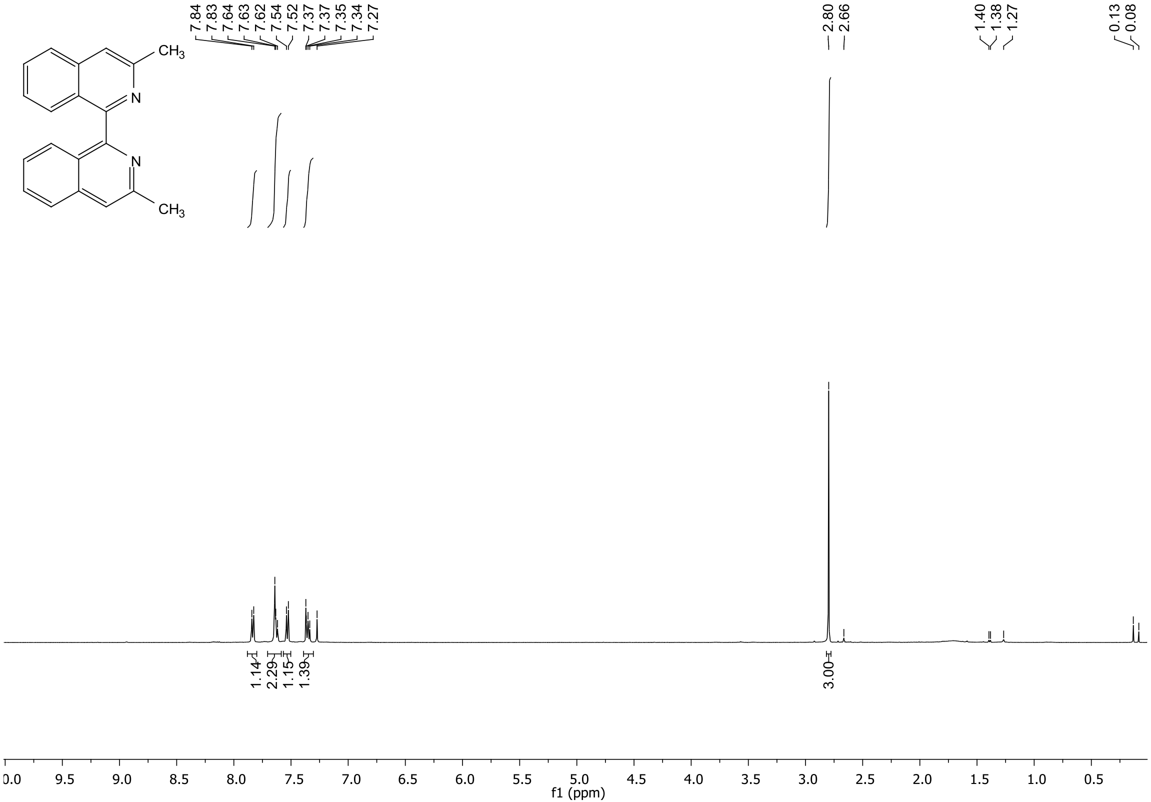


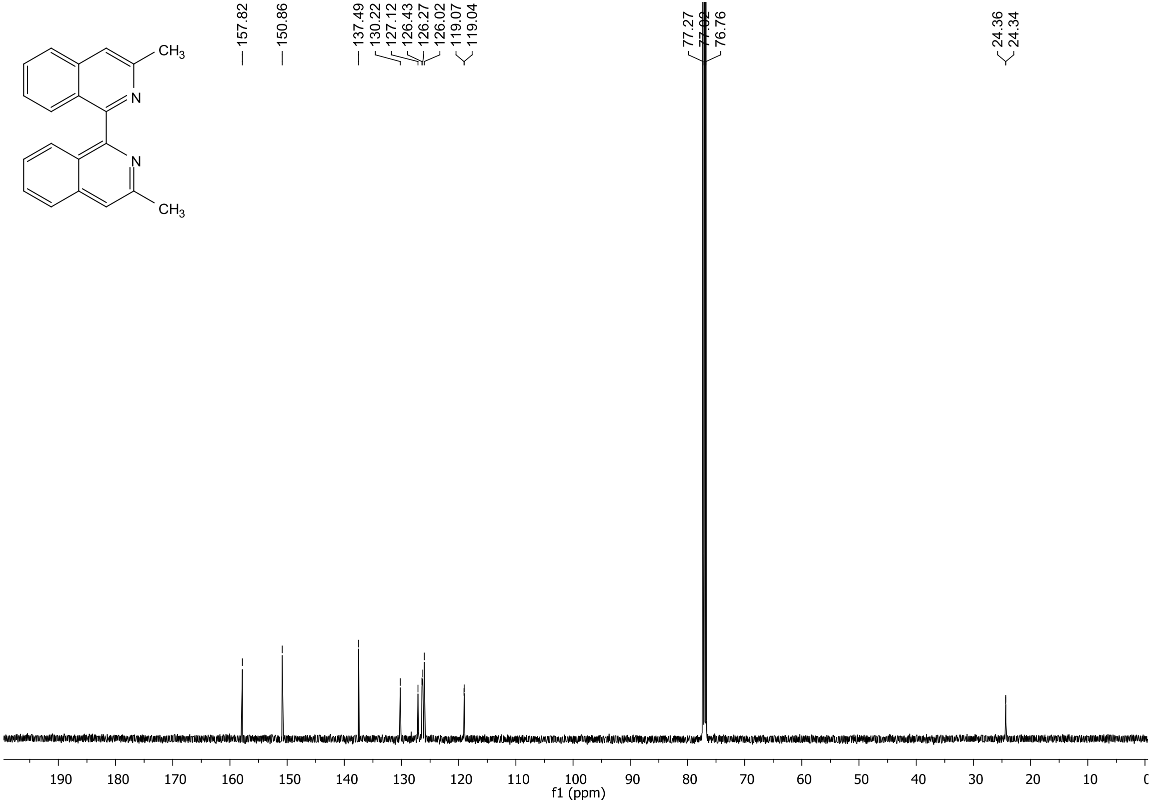
1,1'-Biisoquinoline (12)



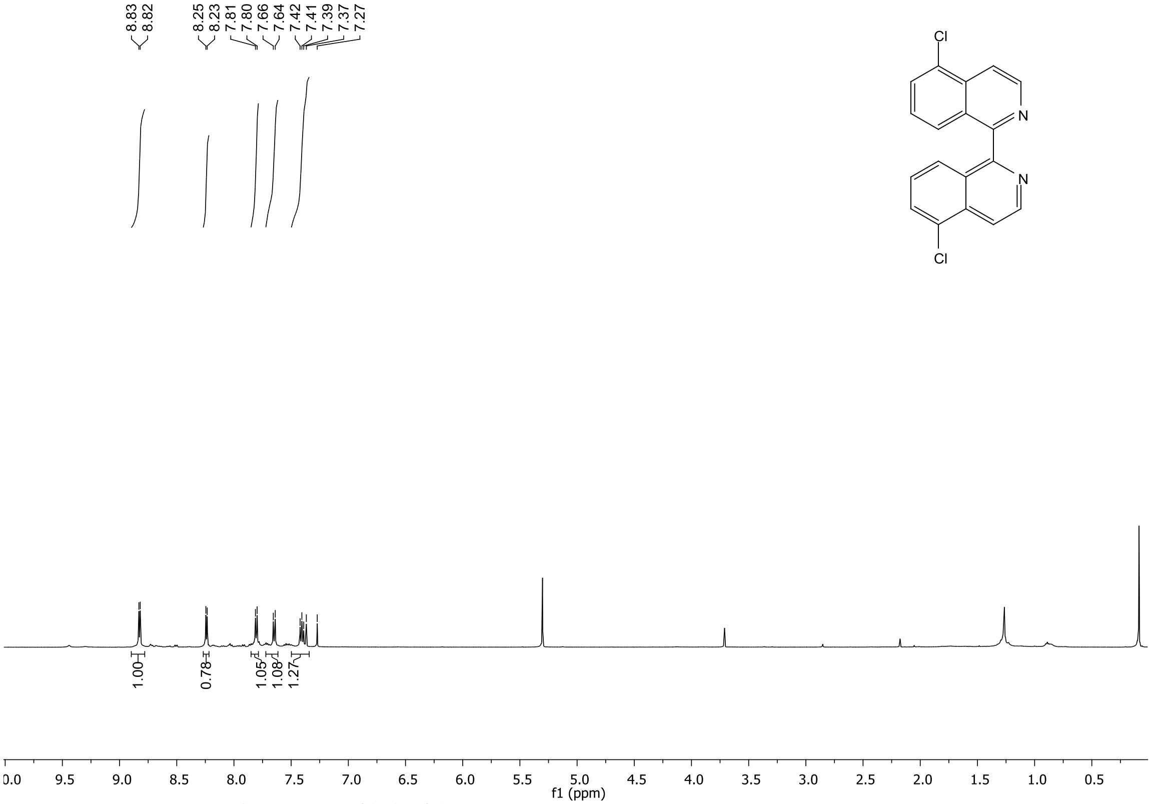


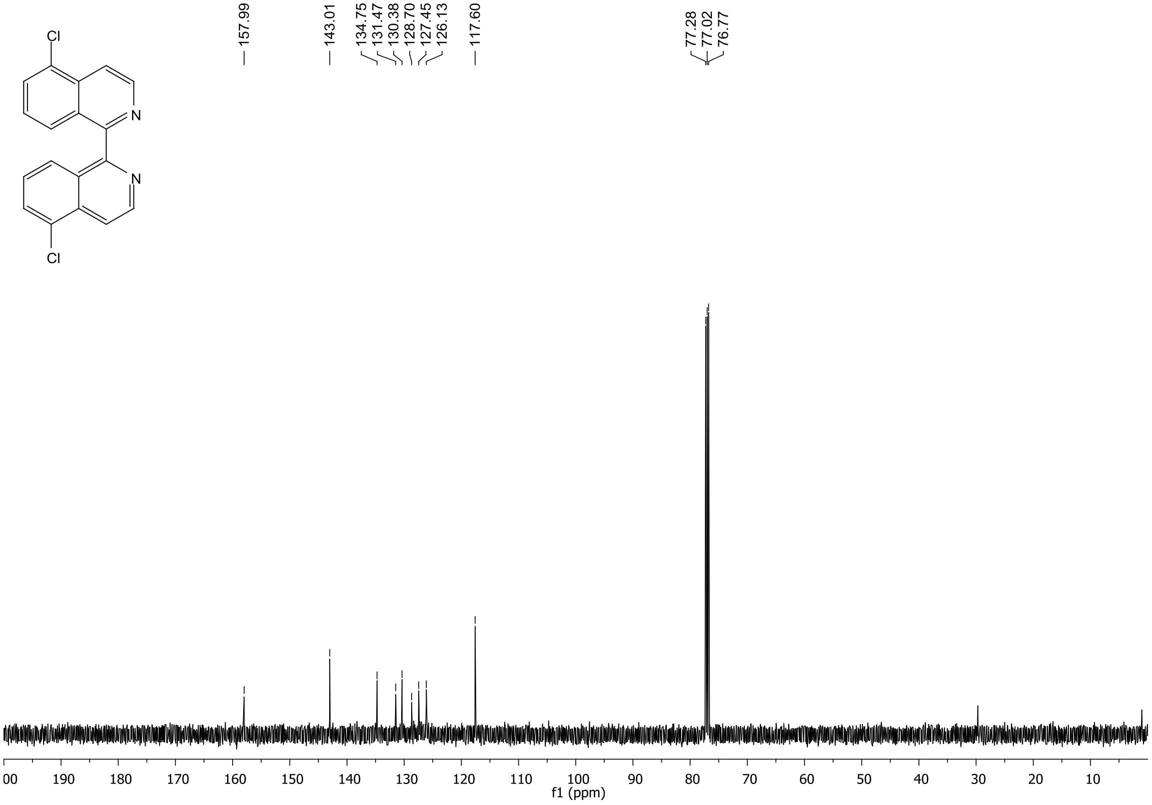
3,3'-Dimethyl-1,1'-biisoquinoline (13)



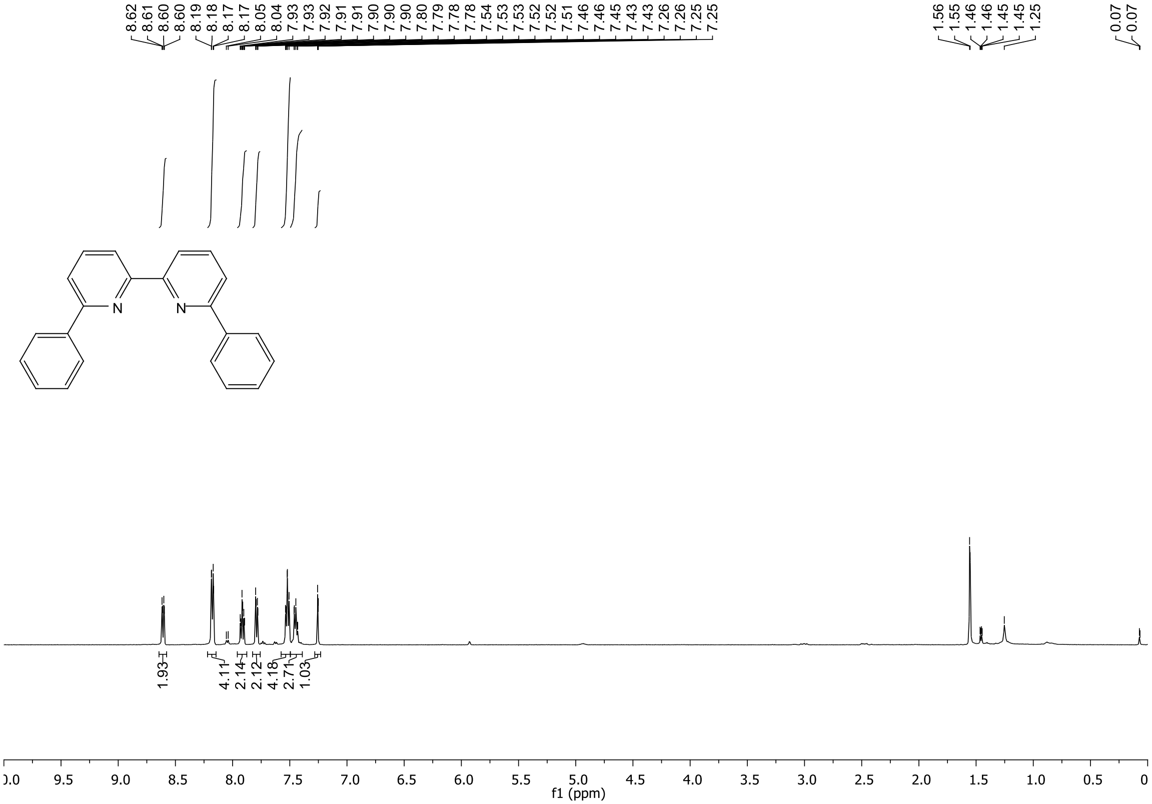


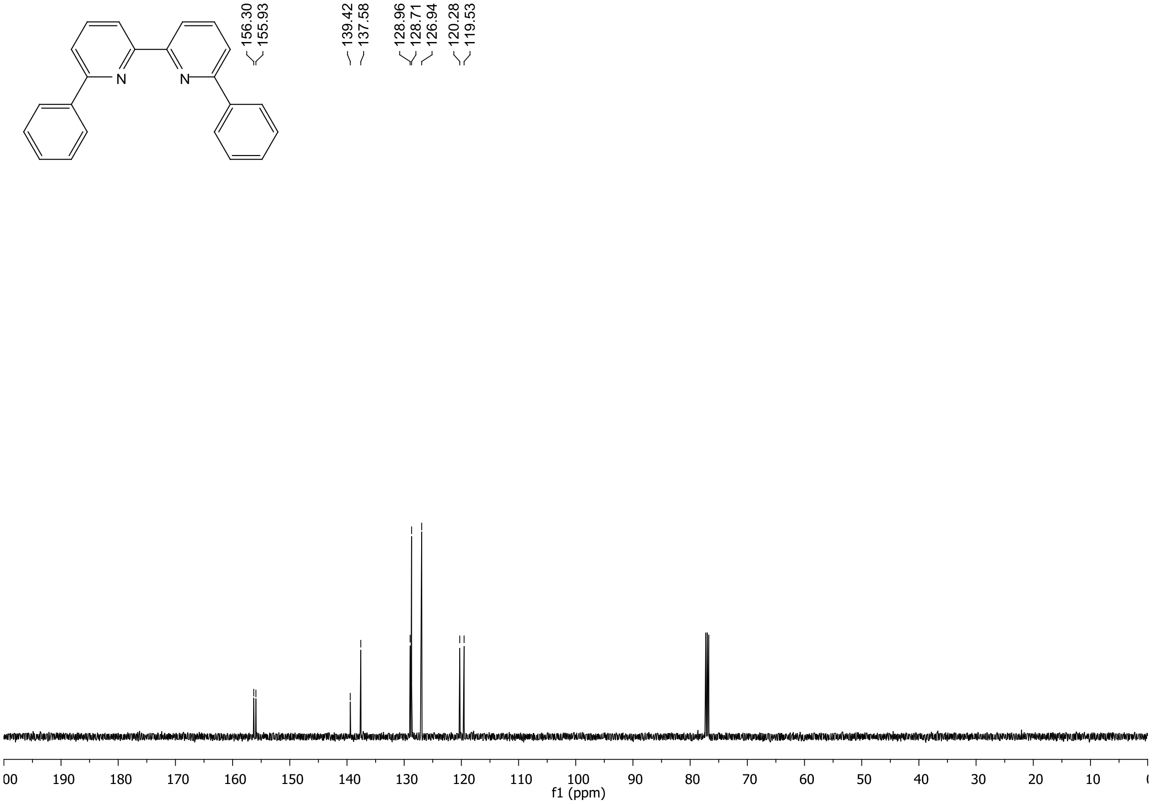
5,5'-Dichloro-1,1'-biisoquinoline (14)



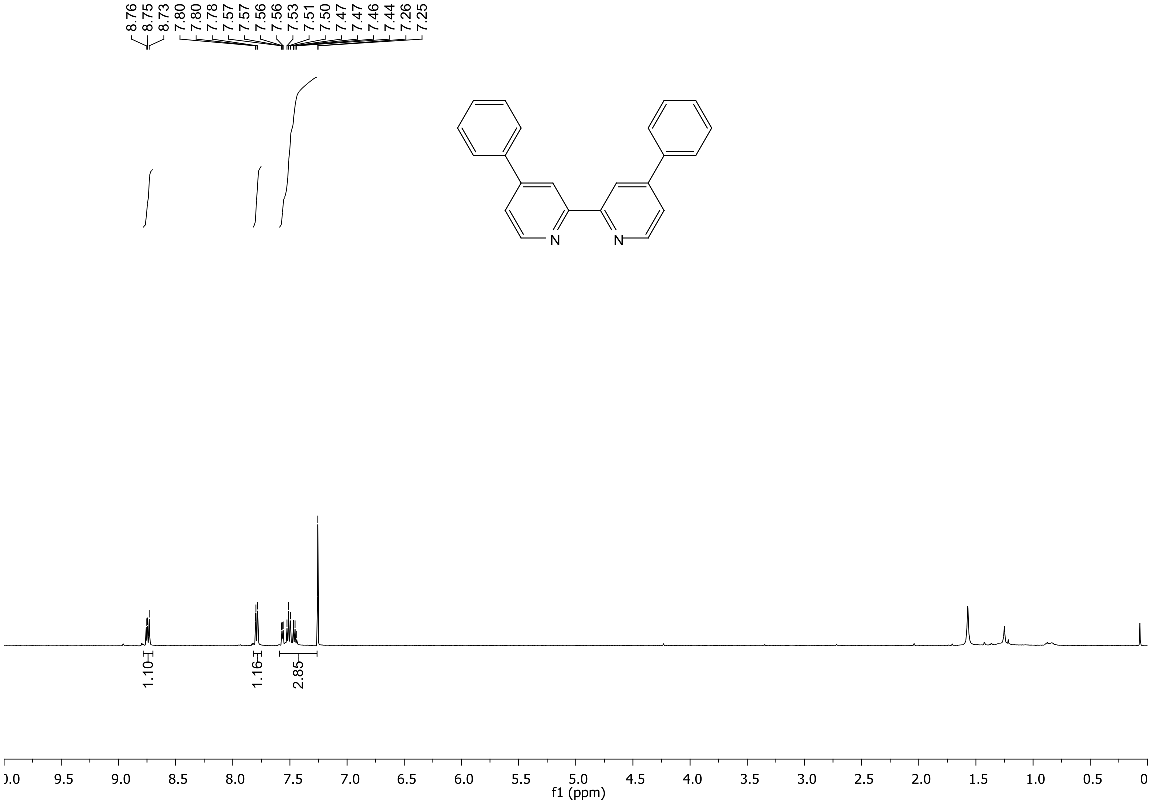


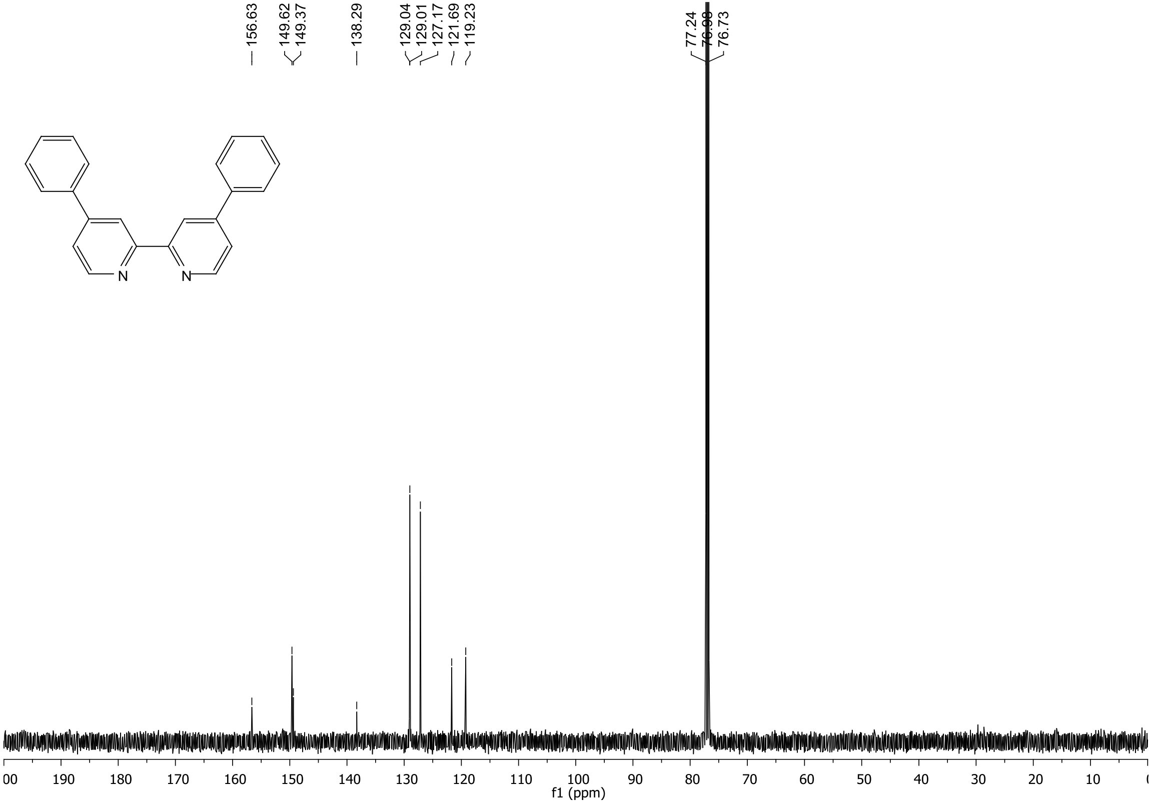
6,6'-Diphenyl-2,2'-bipyridine (18)



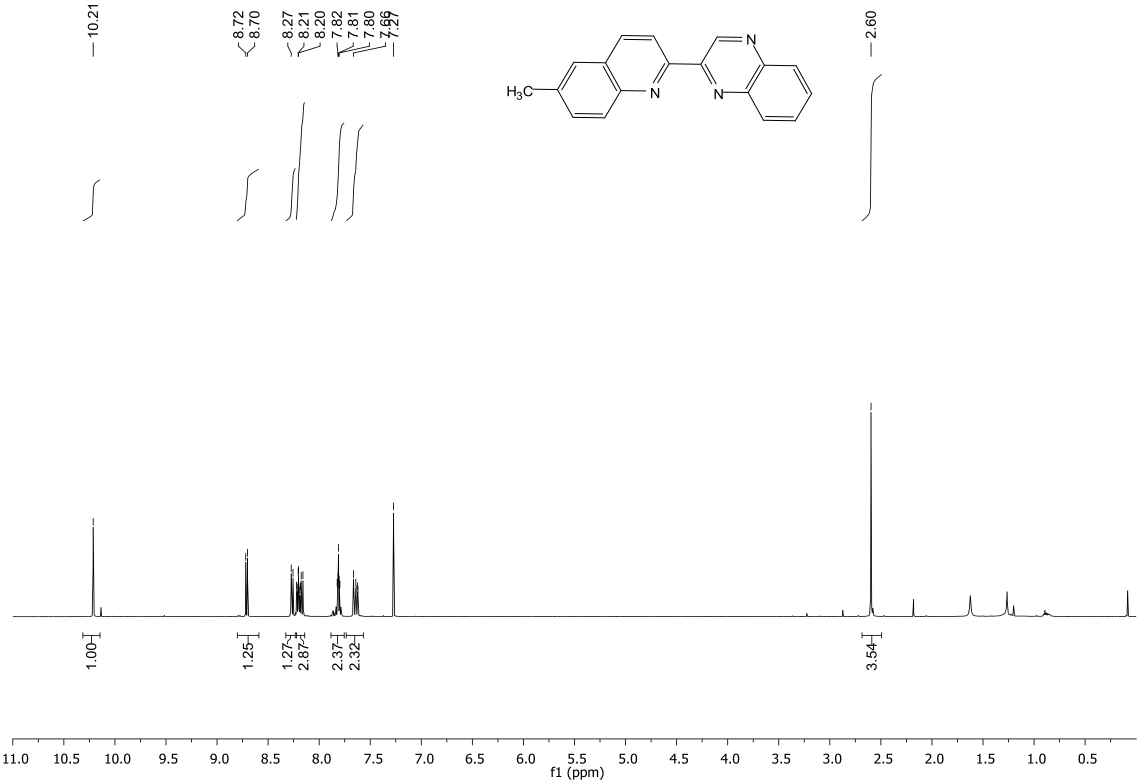


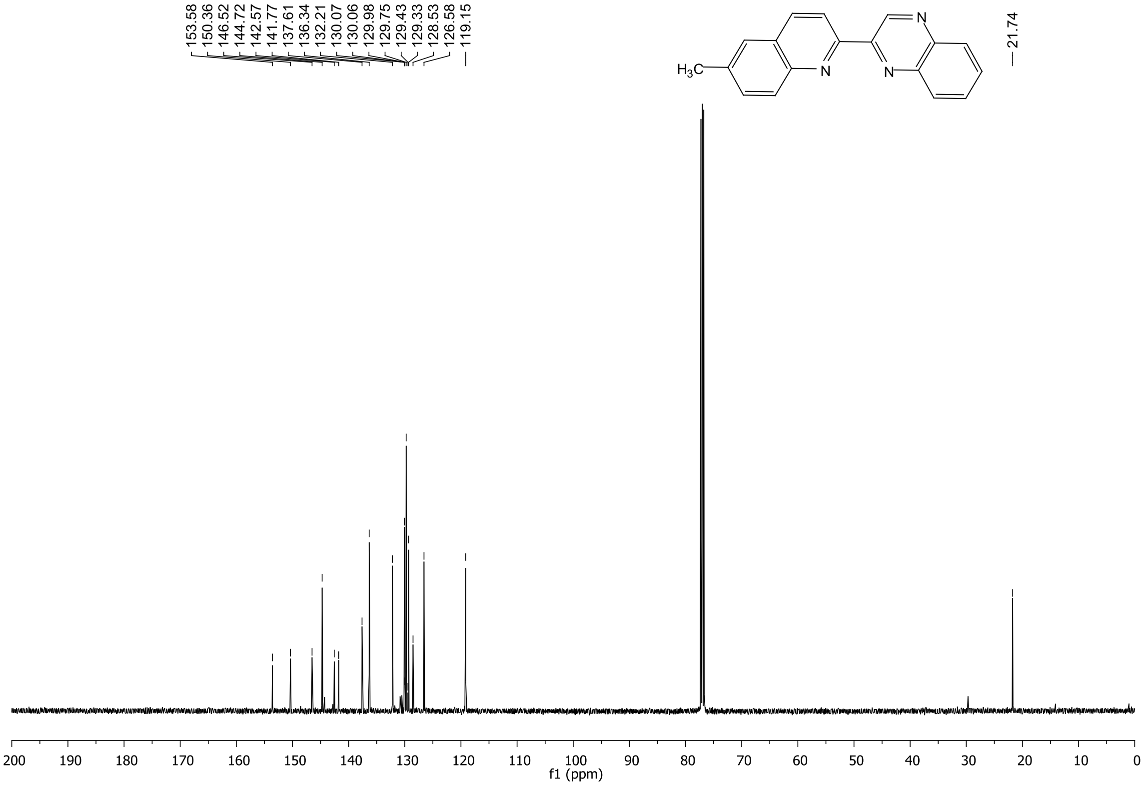
4,4'-Diphenyl-2,2'-bipyridine (20)



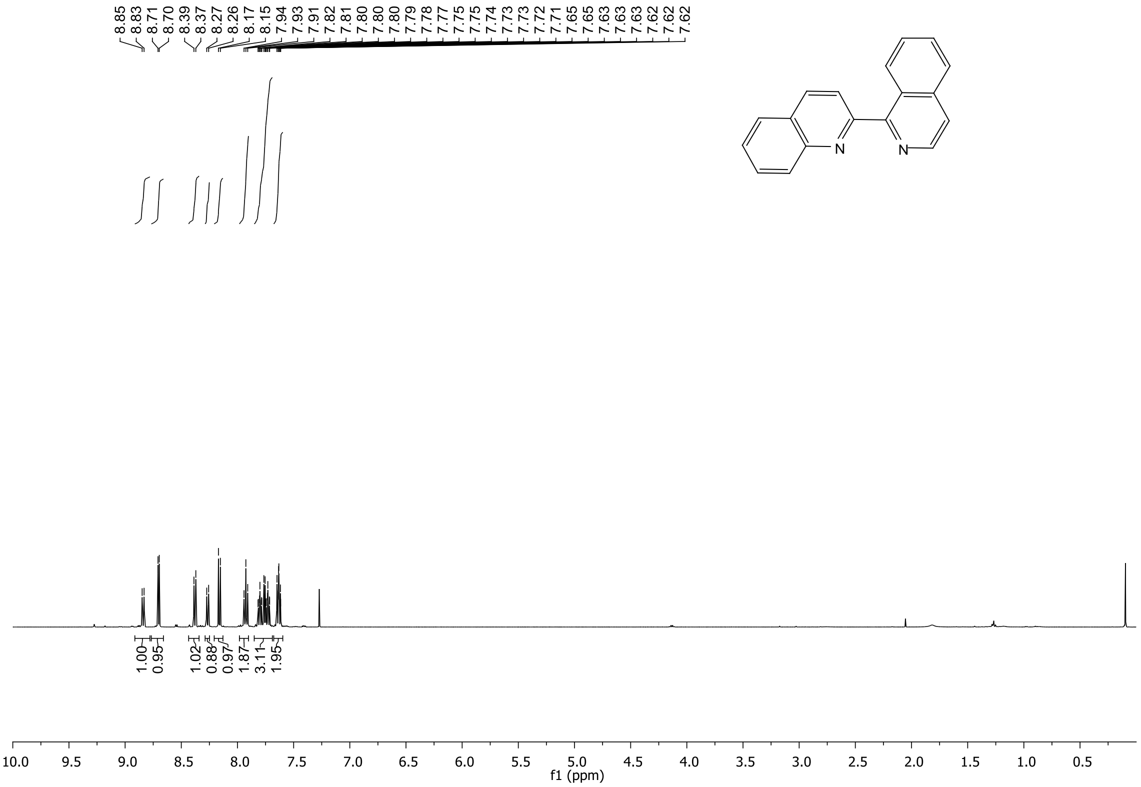


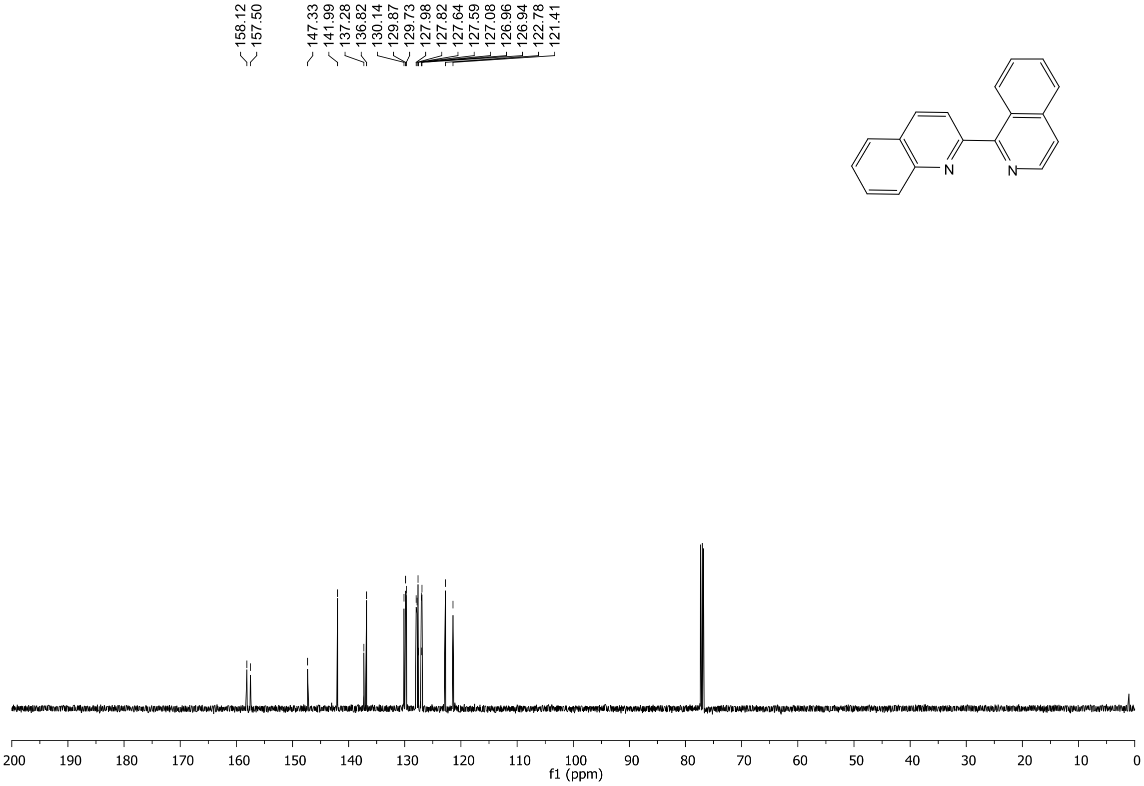
2-(6-Methylquinolin-2-yl)quinoxaline (21)





2-(Isoquinolin-1-yl)quinoline (23)





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