SUPPORTING INFORMATION

Palladium-Catalyzed C8-Selective C–H Arylation of Quinoline *N*-Oxides: Insights into the Electronic, Steric and Solvation Effects on the Site-Selectivity by Mechanistic and DFT Computational Studies

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General Procedures

Materials and methods: All quinoline *N*-oxides were synthesized from respective quinolines according to the typical oxidation procedures.[1] All chemicals were used as commercially available. All thermal reactions were conducted with continuous magnetic stirring under an atmosphere of argon in 2 dram vials (6 mL, FisherBrand).

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).

Microwave-assisted reactions: All microwave reactions were run in 2 mL vials (Chemglass, CV-1160-1232) with septa (Chemglass, CV-4060-0010) and closure (Chemglass, CV-3720-W010) with continuous magnetic stirring under an atmosphere of argon in an Anton Paar Multiwave PRO fitted with a Rotor 4x20 Well Plate. The method used is as follows: maximum wattage was 1500 W and max IR temperature 180 °C (avg. 375 W during run). A one minute hold was allowed for the microwave to ramp to

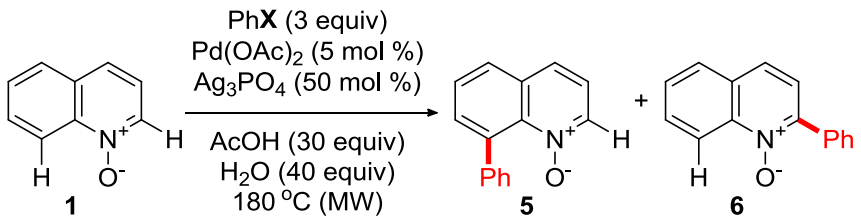
1500 W with no stirring, at which point stirring began and the well plates heated to 180 °C (avg. 178 °C), with low fan, for the time deemed necessary with low stirring. After the time was completed the vessels were cooled with high fan to 55 °C at which point they were removed from the microwave (approximately 20 min.)

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

Characterization: ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded at 500 (^{1}H), 125 and (^{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 (quart.), quintet (quint.), septet (sept.), multiplet (m), broad (br).

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. Comparison of Reactivity of Aryl Halides.[a]



Entry	X	%, **1**	%, **5** (C8)	%, **6** (C2)	C8/C2 (**5**/**6**) ratio
1	I	10	86	4	>20:1
2	Br	80	16	2	8:1
3	Cl	98	0	0	–

[a] Yields were determined by ^{1}H NMR analysis with 1,4-dimethoxybenzene as an internal standard added prior to work-up. Reactions were carried out with 0.2 mmol of **1** under microwave irradiation at 180 °C for 1 h.

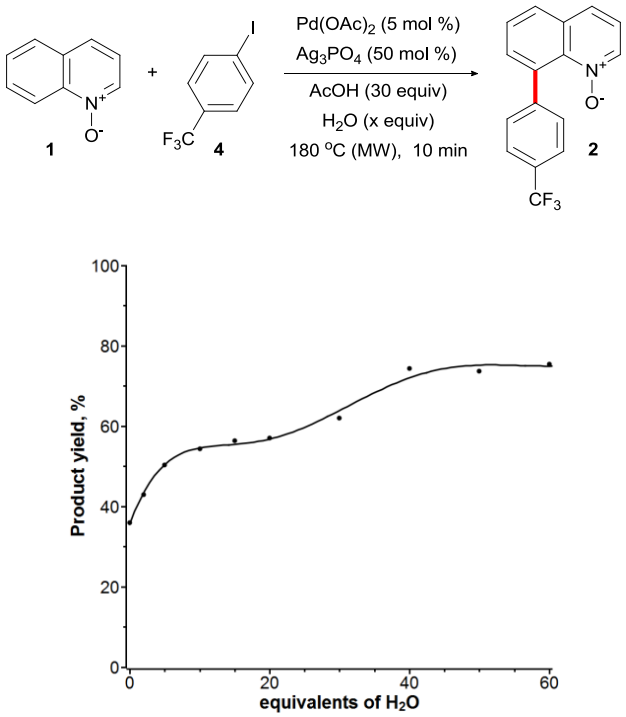


Figure S1. Influence of Added Water on the C8–H Arylation under Increasing Dilution Conditions (The reaction was carried out with 30 equiv AcOH under microwave irradiation at 180 °C, see Table S2 for experimental details).

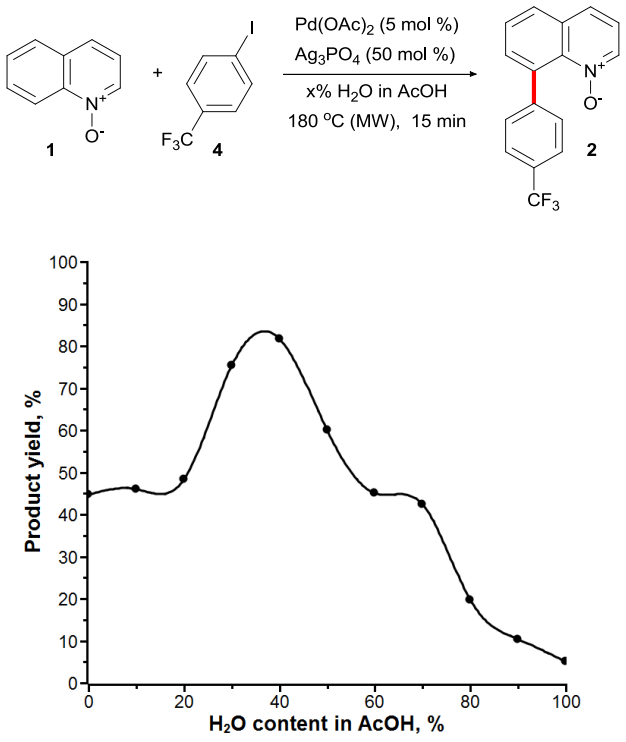


Figure S2. Influence of the Water Content on the C8–H Arylation under Constant Volume Conditions (The reaction was carried out under microwave irradiation at 180 °C, see Table S3 for experimental details).

Preparation of silver phosphate

Silver phosphate was prepared by adding a solution of tripotassium phosphate (11.16 g, 0.05 mol) in deionized water (15 mL) to a solution of silver nitrate (27 g, 0.16 mol) in deionized water (45 mL) in the dark. The reaction mixture was allowed to stir for 15 min at room temperature and then filtered through a Buchner funnel and the solids were washed consecutively with deionized water (3 x 30 mL), ethanol (3 x 30 mL), and methyl *tert*-butyl ether (5 x 15 mL). The solids were then dried in vacuo (0.5 mbar) at 90 °C for 4 h to yield silver phosphate (19.9 g, 95 %) that was stored in the dark.

General procedure 1 for the reaction development experiments (GP1)

An argon-flushed 6 mL (thermal conditions) or 2 mL (microwave conditions) vial was charged with quinoline *N*-oxide (29 mg, 0.2 mmol), palladium salt (5 mol %, 0.01 mmol) silver salt (50 mol %, 0.10 mmol), a degassed solvent (10 or 30 equiv.), an appropriate amount of degassed and deionized water , and 4-iodobenzotrifluoride (88 μL, 0.6 mmol, 3 equiv.). The vial was sealed, and the reaction mixture was stirred at 120 ^{o}C (thermal conditions) or at 180 ^{o}C (microwave conditions) for the specified time (10 min to 50 min). Work up was performed according to the general procedure 2.

General procedure 2 for the work-up of kinetic and reaction development experiments (GP2)

After completion of a reaction carried out with 0.2 mmol of quinoline *N*-oxide, a reaction mixture was charged with a 0.05M solution of 1,4-dimethoxybenzene (0.05 or 0.1 mmol) in dichloromethane (0.5 or 1 mL), and the mixture was stirred at room temperature for 5 min. Then a 1:3 v/v mixture of 30% aq. ammonia solution and saturated aq. solution of ammonium chloride (2 mL) was added, and the stirring was continued for 15 min. The organic phase was separated, dried over sodium sulfate and concentrated under reduced pressure. The conversion of the substrate to the C8-arylation product was determined from the ^{1}H NMR spectrum of the crude product in $CDCl_3$ by integration of the 2-H peak of the 8-arylquinoline *N*-oxide and 1,4-dimethoxybenzene (6.82 ppm, 1 H, s).

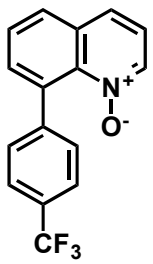
General Procedure 3 (GP3) for the thermal synthesis of 2, 5–21, 23–25

A 2-dram vial (6 mL), with magnetic stir bar, was degassed with argon for 1 min. Quinoline *N*-oxide (145 mg, 1 mmol, 1 equiv.), silver phosphate (209 mg, 0.5 mmol, 0.5 equiv.), and palladium acetate (11.2 mg, 0.05 mmol, 5 mol %) were added. Degassed acetic acid (1.73 mL, 30.0 mmol, 30 equiv.), degassed deionized water (720 μL, 40.0 mmol, 40 equiv.), and an iodoarene (3 equiv.) were added in order and the reaction was heated to 120 °C for 12 h. The reaction was cooled to 23 °C and diluted with 5 mL of a 1:3 v/v mixture of 30% aq. ammonia solution and saturated aq. solution of ammonium chloride. The aqueous layer was extracted with dichloromethane (5 x 5 mL), the organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel, gradient: dichloromethane/EtOAc–EtOH (1:1)] to yield the desired 8-arylquinoline-*N*-oxide.

General Procedure 4 (GP4) for the microwave-accelerated synthesis of 2, 5, 8–11, 16, 22, 23

Three 2 mL vials, with magnetic stir bar, were degassed with argon for 1 min. To each vial was added quinoline *N*-oxide (29 mg, 0.2 mmol, 1 equiv.), silver phosphate (41 mg, 0.1 mmol, 0.5 equiv.), and palladium acetate (2.2 mg, 0.01 mmol, 5 mol %). Degassed acetic acid (360 mL, 6.0 mmol, 30 equiv.), degassed deionized water (144 μL, 8.0 mmol, 40 equiv.), and an iodoarene (3 equiv.) were added in order and the reaction heated in a microwave at 180 °C for 50 min. The reactions were cooled to 23 °C, combined, and diluted with 5 mL of a 1:3 v/v mixture of 30% aq. ammonia solution and saturated aq. solution of ammonium chloride. The aqueous layer was extracted with dichloromethane (5 x 5 mL), the organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel, gradient: dichloromethane/EtOAc–EtOH (1:1)] to yield the desired 8-substituted quinoline *N*-oxide.

8-(4-(Trifluoromethyl)phenyl)quinoline 1-oxide (2)



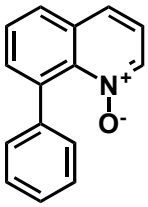
Thermal conditions: According to GP3, quinoline *N*-oxide (73 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.025 mmol, 5 mol %), acetic acid (900 μL, 15.0 mmol, 30 equiv.), water (120 μL, 20.0 mmol, 40 equiv.) and 4-iodobenzotrifluoride (220 μL, 1.50 mmol, 3 equiv.) was heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield **2** (120 mg, 83 %) as orange solid.

Microwave conditions: According to GP4, quinoline *N*-oxide (87 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol,30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 4-(trifluoromethyl)iodobenzene (264 μL, 1.80 mmol, 3 equiv.) was divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **2** (164 mg, 94 %).

Microwave conditions from 2-carboxyquinoline 1-oxide: According to GP4, 2-carboxyquinoline 1-oxide (38 mg, 0.2 mmol)), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol,30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 4-(trifluoromethyl)iodobenzene (264 μL, 1.80 mmol, 3 equiv.) was divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **2** (49 mg, 85 %).

– m.p.: 122-124 °C. – ^{1}H NMR (500 MHz): 7.32 (1 H, dd, *J* = 2, 6 Hz), 7.43 (2 H, d, *J* = 8.5 Hz), 7.50 (1 H, dd, *J* = 1, 7 Hz), 7.62–7.67 (3 H, m), 7.79 (1 H, 8.5 Hz), 7.93 (1 H, dd, *J* = 2, 8.5 Hz), 8.35 (1 H, 6 Hz) ppm. – ^{13}C NMR (125 MHz): 121.5, 123.4, 123.8 (quart., *J* = 2.5 Hz), 125.6, 126.2, 127.7, 128.0, 128.3, 129.1, 132.0, 134.0, 134.8, 136.8, 138.8 ppm. – ^{19}F NMR (282 MHz): –62.2 ppm. – IR: 1018, 1149, 1243, 1322, 1405, 1509, 2981, 3092 cm^{-1}. – MS (ESI): 289.9, calcd: 290.0787, HRMS: 290.1482 [M+H^{+}].

8-Phenylquinoline 1-oxide (5)

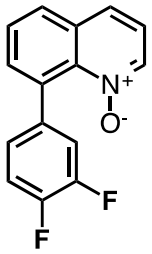


Thermal conditions: According to GP3, quinoline *N*-oxide (73 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.025 mmol, 5 mol %), acetic acid (900 μL, 15.0 mmol, 30 equiv.), water (120 μL, 12.0 mmol, 40 equiv.) and iodobenzene (167 μL, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield **5** (103 mg, 93 %).

Microwave conditions: According to GP4, quinoline *N*-oxide (87 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol,30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and iodobenzene (201 μL, 1.80 mmol, 3 equiv.) were divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **5** (116 mg, 87 %).

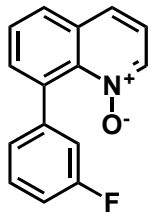
Gram-scale synthesis: Quinoline *N*-oxide (2.03 g, 14 mmol), acetic acid (24.23 mL, 420 mmol, 30 equiv.), and water (10.08 mL, 560 mmol, 40 equiv.) was divided between two screw cap storage tubes. The reaction was degassed with argon for 15 min. before silver phosphate (2.93 g, 7.0 mmol, 0.5 equiv.), palladium acetate (157 mg, 0.7 mmol, 5 mol %), and iodobenzene (4.76 mL, 42 mmol, 3 equiv.) was divided between the two storage tubes. The storage tubes were sealed and heated to 120 °C for 12 h before being cooled to 23 °C. The reactions were worked up following GP3, and the crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **5** (2.6 g, 82 %). – ^{1}H NMR (500 MHz): 7.32–7.39 (5 H, m), 7.54 (1 H, t, *J* = 8 Hz), 7.68–7.75 (2 H, m), 8.01 (1 H, d, *J* = 8 Hz), 8.25 (1 H, d, *J* = 8.5 Hz), 8.84 (1 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 121.2, 126.2, 126.9, 127.7, 128.1, 128.5, 132.1, 134.3, 136.3, 137.0, 142.8 ppm. – IR: 1030, 1134, 1201, 1305, 1417, 1512, 2992, 3029, 3055 cm^{-1}. – MS (ESI): 222.0, calcd: 222.0913, HRMS: 222.0962 [M+H^{+}].

8-(3,4-Difluorophenyl)quinoline 1-oxide (7)



Thermal conditions: According to GP3, quinoline *N*-oxide (73 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.025 mmol, 5 mol %), acetic acid (900 μL, 15.0 mmol, 30 equiv.), water (120 μL, 12.0 mmol, 40 equiv.) and 3,4-difluoroiodobenzene (180 μL, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **7** (94 mg, 73 %). – m.p.: 100–104 °C. – ^{1}H NMR (500 MHz): 7.0–7.03 (1 H, m), 7.11–7.16 (2 H, m), 7.31 (1 H, dd, *J* = 6, 8.5 Hz), 7.50 (1 H, dd, *J* = 1.5, 7.5 Hz), 7.62 (1 H, t, *J* = 7.5 Hz), 7.78 (1 H, d, *J* = 8.5 Hz), 7.90 (1 H, d, *J* = 1, 8 Hz), 8.36 (1 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 115.4 (d, *J* = 17.5 Hz), 117.4 (d, *J* = 17.5 Hz), 121.4, 124.3 (dd, *J* = 3.5, 5.5 Hz), 126.4, 127.7, 128.3, 129.2, 132.0, 133.9, 134.3, 137.0, 138.8, 139.6 (dd, *J* = 4.5, 6.5 Hz), 147.9 (d, *J* = 12.8 Hz), 138.1 (d, *J* = 12.6 Hz), 149.8 (d, *J* = 12.9 Hz), 150.1 (d, *J* = 12.5 Hz) ppm. – ^{19}F NMR (282 MHz): –141.9 – –141.8 (m), –140.1 – –139.9 (m) ppm. – IR: 1011, 1118, 1201, 1299, 1382, 1416, 1518, 2942, 2999, 3059, 3250cm^{-1}. – MS (ESI): 279.9 [M+Na+], calcd: 257.0652, HRMS: 257.0662 [M+H^{+}].

8-(3-Fluorophenyl)quinoline 1-oxide (8)

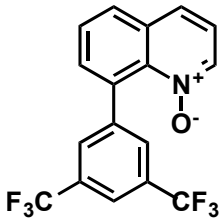


Thermal conditions: According to GP3, quinoline *N*-oxide (73 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.025 mmol, 5 mol %), acetic acid (900 μL, 15.0 mmol, 30 equiv.), water (120 μL, 12.0 mmol, 40 equiv.) and 3-fluoroiodobenzene (176 μL, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **8** (141 mg, 79 %).

Microwave conditions: According to GP4, quinoline *N*-oxide (87 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol,30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 3-fluoroiodobenzene (211 μL, 1.80 mmol, 3 equiv.) were divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was

purified by column chromatography to yield 8-substituted quinoline *N*-oxide **8** (158 mg, 74 %). – ^{1}H NMR (500 MHz): 7.02–7.10 (3 H, m), 7.28–7.34 (2 H, m), 7.50 (1 H, d, *J* = 1.5, 7 Hz), 7.62 (1 H, t, *J* = 7.5 Hz), 7.77 (1 H, d, *J* = 8 Hz), 7.90 (1 H, dd, *J* = 1.5, 8 Hz), 8.36 (1 H, dd, *J* = 1, 7 Hz) ppm. – ^{13}C NMR (125 MHz): 112.9 (d, *J* = 21 Hz), 115.3 (d, *J* = 22 Hz) 121.4, 124.1 (d, *J* = 2.5 Hz), 126.4, 127.7, 128.1 (d, 8.5 Hz), 129.0, 132.0, 134.1, 134.8, 137.0, 138.8, 144.9 (d, *J* = 8.5 Hz), 160.6, 162.6 ppm. – ^{19}F NMR (282 MHz): –115.1 ppm. – IR: 1004, 1089, 1134, 1170, 1295, 1349, 1417, 1514, 2970, 3031, 3067, 3364 cm^{-1}. – MS (ESI): 240.0, calcd: 240.0819, HRMS: 240.0867 [M+H^{+}].

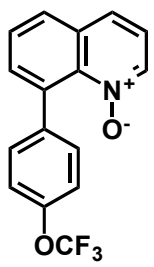
8-(3,5-Bis(trifluoromethyl)phenyl)quinoline 1-oxide (9)



Thermal conditions: According to GP3, quinoline *N*-oxide (73 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.025 mmol, 5 mol %), acetic acid (900 μL, 15.0 mmol, 30 equiv.), water (120 μL, 12.0 mmol, 40 equiv.) and 3,5-bis(trifluoromethyl)iodobenzene (268 μL, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **9** (140 mg, 78 %).

Microwave conditions: According to GP4, quinoline *N*-oxide (87 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol,30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 3,5-bis(trifluoromethyl)iodobenzene (322 μL, 1.80 mmol, 3 equiv.) were divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **9** (178 mg, 83 %). – **m.p.: 150–152 °C. –** ^{1}H NMR (500 MHz): 7.33 (1 H, dd, *J* = 6, 8.5 Hz), 7.50 (1 H, dd, *J* = 1, 7.5 Hz), 7.65 (1 H, t, *J* = 7.5 Hz), 7.78–7.82 (4 H, m), 7.97 (1 H, dd, *J* = 1.5, 8 Hz), 8.36 (1 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 120.0 (m), 121.7, 122.5, 124.6, 126.3, 127.8, 128.2, 129.6, 129.8, 129.9, 132.0, 133.2, 134.4, 136.9, 138.6, 144.6 ppm. – ^{19}F NMR (282 MHz): –62.5 ppm. – IR: 1019, 1106, 1150, 1246, 1330, 1405, 1508, 2956, 3024, 3098, 3399 cm^{-1}. – MS (ESI): 357.9, calcd: 358.0661, HRMS: 358.0114 [M+H^{+}].

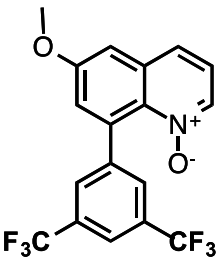
8-(4-(Trifluoromethoxy)phenyl)quinoline 1-oxide (10)



Thermal conditions: According to GP3, quinoline *N*-oxide (145 mg, 1 mmol), silver phosphate (209 mg, 0.5 mmol, 0.5 equiv.), palladium acetate (11 mg, 0.05 mmol, 5 mol %), acetic acid (1.7 mL, 30 mmol, 30 equiv.), water (720 μL, 40 mmol, 40 equiv.), and 4-(trifluoromethyoxy)iodobenzene (469 μL, 3 mmol, 3 equiv.) was heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **10** (257 mg, 84 %).

Microwave conditions: According to GP4, quinoline *N*-oxide (87 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol,30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 4-(trifluoromethyoxy)iodobenzene (281 μL, 1.80 mmol, 3 equiv.) were divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **10** (140 mg, 76 %). – m.p.: 107–110 °C. – ^{1}H NMR (500 MHz): 7.20 (2 H, d, *J* = 8.5 Hz), 7.28–7.34 (3 H, m), 7.50 (1 H, dd, *J* = 1, 7.5 Hz), 7.62 (1 H, t, *J* = 8 Hz), 7.78 (1 H, d, *J* = 8.5 Hz), 7.90 (1 H, dd, *J* = 1, 8 Hz), 8.36 (1 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 119.3, 119.6, 121.3, 121.6, 126.8, 127.7, 128.9, 128.4, 129.6, 132.0, 134.5, 134.9, 137.2, 138.8, 141.3, 147.7, 147.8, 173.9 ppm. – ^{19}F NMR (282 MHz): –57.7 ppm. – IR: 1029, 1082, 1163, 1223, 1349, 1408, 1504, 2938, 3020, 3065, 3410 cm^{-1}. – MS (ESI): 305.9, calcd: 306.0736, HRMS: 306.0761 [M+H^{+}].

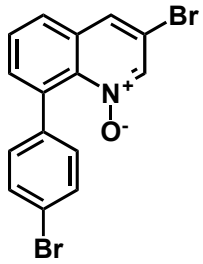
8-(3,5-Bis(trifluoromethyl)phenyl)-6-methoxyquinoline 1-oxide (11)



Thermal conditions: According to GP3, 6-methoxyquinoline *N*-oxide (175 mg, 1 mmol), silver phosphate (209 mg, 0.5 mmol, 0.5 equiv.), palladium acetate (11 mg, 0.05 mmol, 5 mol %), acetic acid (1.7 mL, 30 mmol, 30 equiv.), water (720 μL, 40 mmol, 40 equiv.), and 3,5-bis(trifluoromethyl)iodobenzene (536 μL, 3 mmol, 3 equiv.) was heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **11** (322 mg, 83 %).

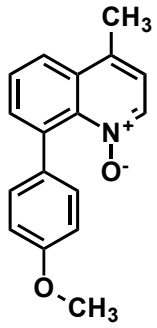
Microwave conditions: According to GP4, 6-methoxyquinoline *N*-oxide (105 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol, 30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 3,5-bis(trifluoromethyl)iodobenzene (322 μL, 1.80 mmol, 3 equiv.) were divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **11** (160 mg, 69 %) – ^{1}H NMR (500 MHz): 3.95 (3 H, s), 7.13 (1 H, s), 7.19 (1 H, s), 7.68 (1 H, d, *J* = 8.5 Hz), 7.78 (2 H, s), 7.82 (1 H, s), 8.20 (1 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (75 MHz): 55.9, 107.2, 120.3, 120.3, 120.3, 122.0, 122.4, 124.6, 127.1, 127.2, 128.2, 128.2, 129.5, 129.7, 130.0, 130.3, 133.5, 134.0, 134.8, 135.7, 144.0, 158.0, 175.0 ppm. – ^{19}F NMR (282 MHz): –62.6 ppm. – IR: 1032, 1138, 1212, 1360, 1412, 1464, 2924, 3006, 3099, 3228 cm^{-1}. – MS (ESI): 387.8, calcd: 388.0767, HRMS: 388.0815 [M+H^{+}].

3-Bromo-8-(4-bromophenyl)quinoline 1-oxide (12)



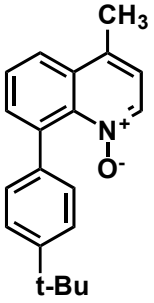
Thermal conditions: According to GP3, 3-bromoquinoline *N*-oxide (89 mg, 0.40 mmol), silver phosphate (84 mg, 0.20 mmol, 0.5 equiv.), palladium acetate (4.5 mg, 0.02 mmol, 5 mol %), acetic acid (700 μL, 1.20 mmol, 30 equiv.), water (288 μL, 1.60 mmol, 40 equiv.), and 1-bromo-4-iodobenzene (338 mg, 1.20 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **12** (86 mg, 57 %). – ^{1}H NMR (500 MHz): 7.16 (1 H, dd, *J* = 2, 6.5 Hz), 7.47–7.51 (4 H, m), 7.63 (1 H, t, *J* = 8 Hz), 7.80 (1 H, d, *J* = 8 Hz) 7.92 (1 H, d, *J* = 2 Hz), 8.43 (1 H, s) ppm. – ^{13}C NMR (125 MHz): 114.7, 120.7, 128.0, 128.2, 128.2, 128.7, 130.0, 131.7, 134.3, 135.2, 137.9, 138.4, 140.9 ppm. – IR: 1104, 1161, 1238, 1373, 1446, 1558, 2849, 2926, 3059, 3364 cm^{-1}. – MS (ESI): 377.7, calcd: 377.9124, HRMS: 378.1023 [M+H^{+}].

8-(4-Methoxyphenyl)-4-methylquinoline 1-oxide (13)



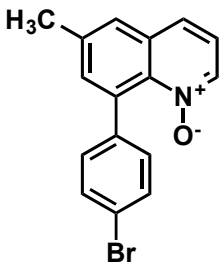
Thermal conditions: According to GP3, 4-methylquinoline *N*-oxide (80 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.03 mmol, 5 mol %), acetic acid (900 μL, 1.50 mmol, 30 equiv.), water (360 μL, 2.0 mmol, 40 equiv.), and 4-iodoanisole (351 mg, 1.50 mmol, 3 equiv.) was heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **13** (109 mg, 82 %). – ^{1}H NMR (500 MHz): 2.66 (3 H, s), 3.84 (3 H, s), 6.91 (2 H, d, *J* = 8.5 Hz), 7.09 (1 H, d, *J* = 6 Hz), 7.23 (2 H, d, *J* = 8.5 Hz), 7.52 (1 H, d, *J* = 7 Hz), 7.61 (1 H, t, *J* = 8 Hz), 7.95 (1 H, d, *J* = 8 Hz), 8.24 (1 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 19.1, 55.3, 112.4, 121.8, 124.5, 127.4, 129.0, 131.3, 134.1, 135.5, 136.3, 136.5, 138.9, 158.0 ppm. – IR: 1041, 1109, 1154, 1243, 1340, 1398, 1463, 1569, 2835, 2917, 3000, 3036, 3362 cm^{-1}. – MS (ESI): 266.0, calcd: 265.1103, HRMS: 266.1217 [M+H^{+}].

8-(4-(*tert*-Butyl)phenyl)-4-methylquinoline 1-oxide (14)



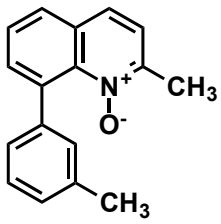
Thermal conditions: According to GP3, 4-methylquinoline *N*-oxide (80 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.03 mmol, 5 mol %), acetic acid (900 μL, 1.50 mmol, 30 equiv.), water (360 μL, 2.0 mmol, 40 equiv.), and 4-*tert*-butyliodobenzene (267 μL, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **14** (110 mg, 75 %). – ^{1}H NMR (500 MHz): 1.37 (9 H, s), 2.69 (3 H, s), 7.12 (1 H, d, *J* = 6.5 Hz), 7.23–7.25 (2 H, m), 7.26–7.40 (2 H, m), 7.55 (1 H, dd, *J* = 1, 7.5 Hz), 7.64 (1 H, dt, *J* = 1, 7.5 Hz), 7.98 (1 H, dd, *J* = 1, 7.5 Hz), 7.25 (1 H, d, *J* = 6.5 Hz) ppm. – ^{13}C NMR (125 MHz): 19.1, 31.5, 121.9, 123.8, 124.5, 127.4, 127.5, 127.5, 131.2, 133.8, 134.1, 136.1, 136.9, 138.8, 140.2, 148.6 ppm. – IR: 1018, 1098, 1207, 1269, 1364, 1450, 2856, 2965, 3025, 3232 cm^{-1}. – MS (ESI): 292.0, calcd: 292.1696, HRMS: 292.1732 [M+H^{+}].

8-(4-Bromophenyl)-6-methylquinoline 1-oxide (15)



Thermal conditions: According to GP3, 6-methylquinoline *N*-oxide (80 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.03 mmol, 5 mol %), acetic acid (900 μL, 1.50 mmol, 30 equiv.), water (360 μL, 2.0 mmol, 40 equiv.), and 1-bromo-4-iodobenzene (423 mg, 1.50 mmol, 3 equiv.) was heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **15** (140 mg, 90 %). – m.p.: 163–165 °C. – ^{1}H NMR (500 MHz): 2.50 (3 H, s), 7.17–7.23 (3 H, m), 7.30 (1 H, d, *J* = 2 Hz), 7.43–7.47 (2 H, m), 7.63 (1 H, s), 7.65 (1 H, d, *J* = 8.5 Hz), 8.25 (1 H, d, *J* = 5.5 Hz) ppm. – ^{13}C NMR (125 MHz): 21.2, 120.2, 121.4, 125.7, 127.8, 129.8, 132.2, 134.7, 136.2, 136.3, 137.4, 137.9, 141.7 ppm. – IR: 1012, 1154, 1209, 1323, 1387, 1437, 1511, 2906, 2970, 3038, 3357 cm^{-1}. – MS (ESI): 314.0, calcd: 313.0102, HRMS: 314.0229 [M+H^{+}].

2-Methyl-8-(*m*-tolyl)quinoline 1-oxide (16)

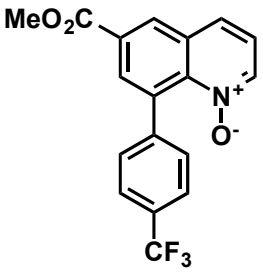


Thermal conditions: According to GP3, 2-methylquinoline *N*-oxide (83 mg, 0.52 mmol), silver phosphate (109 mg, 0.26 mmol, 0.5 equiv.), palladium acetate (5.8 mg, 0.03 mmol, 5 mol %), acetic acid (900 μL, 1.56 mmol, 30 equiv.), water (375 μL, 2.8 mmol, 40 equiv.), and 3-iodotoluene (200 μL, 1.58 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **16** (78 mg, 60 %).

Microwave conditions: According to GP4, 2-methylquinoline *N*-oxide (95 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol, 30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 3-iodotoluene (230 μL, 1.80 mmol, 3 equiv.) were divided into three vials and heated in a microwave at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **16** (107 mg, 72 %). – ^{1}H NMR (500 MHz): 2.38 (3 H, s), 2.59 (3 H, s), 7.10 – 7.14 (3 H, m), 7.24 –

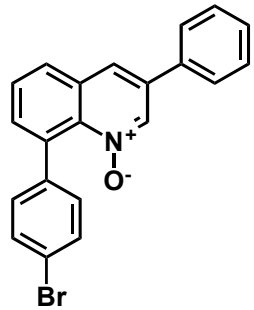
7.29 (1 H, m), 7.33 (1 H, d, *J* = 8.5 Hz), 7.49 (1 H, dd, *J* = 1.5, 7 Hz), 7.54 (1 H, t, *J* = 8 Hz), 7.69 (1 H, d, *J* = 8.5 Hz), 7.82 (1 H, dd, *J* = 1.5, 7.5 Hz) ppm. – ^{13}C NMR (125 MHz): 19.24, 21.58, 123.14, 125.4, 125.8, 126.6, 125.7, 126.8, 128.3, 128.6, 130.7, 134.5, 136.1, 136.3, 139.2, 143.4, 147.3 ppm. – IR: 1101, 1244, 1311, 1330, 1433, 1521, 1602, 2920, 29905, 3058 cm^{-1}. – MS (ESI): 250.0, calcd: 249.1154, HRMS: 250.1287 [M+H$^+$].

6-(Methoxycarbonyl)-8-(4-(trifluoromethyl)phenyl)quinoline 1-oxide (17)



Thermal conditions: According to GP3, 6-(methoxycarbonyl)quinoline *N*-oxide (204 mg, 1 mmol), silver phosphate (209 mg, 0.5 mmol, 0.5 equiv.), palladium acetate (11 mg, 0.05 mmol, 5 mol %), acetic acid (1.7 mL, 30 mmol, 30 equiv.), water (720 μL, 40 mmol, 40 equiv.), and 4-iodobenzotrifluoride (441 μL, 3 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **17** (223 mg, 64 %). – m.p: 132–135 °C. – ^{1}H NMR (500 MHz): 3.97 (3 H, s), 7.32 – 7.39 (3 H, m), 7.43 (2 H, d, *J* = 8 Hz), 7.61 (2 H, d, *J* = 8 Hz), 7.87 (1 H, d, *J* = 7.5 Hz), 8.06 (1 H, s), 8.41 (1 H, d, *J* = 4.5 Hz), 8.63 (1 H, s) ppm. – ^{13}C NMR (125 MHz): 52.8, 122.4, 123.9 (quart., *J* = 3.8 Hz), 127.1, 128.3, 129.3, 131.5, 131.7, 132.3, 135.5, 138.5, 140.4, 145.7, 160.3 ppm. – ^{19}F NMR (282 MHz): –62.3 ppm. – IR: 1039, 1137, 1209, 1307, 1412, 1518, 2939, 2986, 3088, 3392 cm^{-1}. – MS (ESI): 347.9, calcd: 348.0842, HRMS: 348.0792 [M+H$^+$].

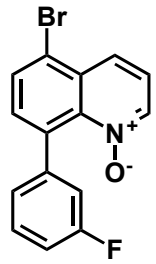
8-(4-Bromophenyl)-3-phenylquinoline 1-oxide (18)



Thermal conditions: According to GP3, 3-phenylquinoline *N*-oxide (80 mg, 0.36 mmol), silver phosphate (76 mg, 0.18 mmol, 0.5 equiv.), palladium acetate (4 mg, 0.02 mmol, 5 mol %), acetic acid (624 mL, 10.83 mmol, 30 equiv.), water (260 μL, 14.44 mmol, 40 equiv.), and 1-bromo-4-iodobenzene (304 mg, 1.08 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by

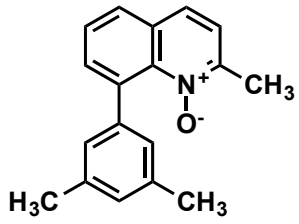
column chromatography to yield 8-substituted quinoline *N*-oxide **18** (100 mg, 74 %). – ^{1}H NMR (500 MHz): 7.23 (1 H, dd, *J* = 2, 6.5 Hz), 7.45–7.54 (7 H, m), 7.61–7.65 (3 H, m), 7.94 (2 H, dt, *J* = 1.5, 4 Hz), 8.64 (1 H, d, *J* = 1.5 Hz) ppm. – ^{13}C NMR (125 MHz): 120.5, 123.6, 127.0, 128.1, 128.3, 129.0, 129.1, 129.4, 129.8, 130.0, 131.9 133.9, 135.1, 135.2, 135.5, 136.2, 137.7, 141.5 ppm. – IR: 1011, 1140, 1224, 1338, 1445, 1576, 2925, 3058, 3367 cm^{-1}.

5-Bromo-8-(3-fluorophenyl)quinoline 1-oxide (19)



Thermal conditions: According to GP3, 5-bromoquinoline *N*-oxide (112 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.03 mmol, 5 mol %), acetic acid (900 mL, 1.50 mmol, 30 equiv.), water (50 μL, 2.75 mmol, 5.5 equiv.), and 3-fluoroiodobenzene (176 μL, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **19** (86 mg, 54 %). – m.p.: 126–128 °C. – ^{1}H NMR (500 MHz): 6.99–7.05 (2 H, m), 7.29–7.42 (4 H, m), 7.90 (1 H, d, *J* = 8 Hz), 8.17 (1 H, d, *J* = 8.5 Hz), 8.37 (1 H, d, *J* = 6 Hz) ppm. – ^{13}C NMR (125 MHz): 113.3 (d, *J* = 1.5 Hz), 114.9 (d, *J* = 1.5 Hz), 122.2, 122.6, 123.6, 123.7, 125.2, 128.4, 128.4, 131.0, 131.7, 133.7, 134.9, 137.2, 139.8, 144.2 (d, *J* = 0.5 Hz), 160.8, 162.7 ppm. – ^{19}F NMR (282 MHz): –114.6 (m) ppm. – IR: 1093, 1151, 1196, 1269, 1366, 1482, 2931, 3002, 3061, 3110, 3372 cm^{-1}. – MS (ESI): 317.8, calcd: 317.9924, HRMS: 317.9920 [M+H^{+}].

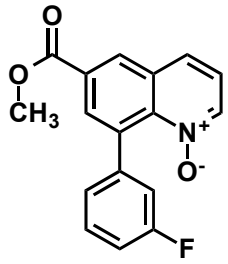
8-(3,5-Dimethylphenyl)-2-methylquinoline 1-oxide (20)



Thermal conditions: According to GP3, 2-methylquinoline *N*-oxide (100 mg, 0.63 mmol), silver phosphate (131 mg, 0.31 mmol, 0.5 equiv.), palladium acetate (7 mg, 0.03 mmol, 5 mol %), acetic acid (1.08 mL, 18.9 mmol, 30 equiv.), water (453 μL, 25.20 mmol, 40 equiv.), and 5-iodo-*m*-xylene (273 μL, 1.88 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **20** (142 mg, 86 %). –

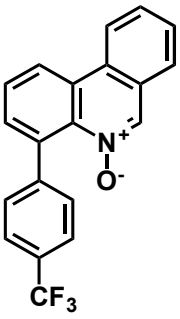
^{1}H NMR (500 MHz): 2.38 (6 H, s), 2.59 (3 H, s), 6.97 (2 H, s), 6.98 (1 H, s), 7.30 (1 H, d, *J* = 8.5 Hz), 7.45–7.53 (2 H, m), 7.64 (1 H, d, *J* = 8.5 Hz), 7.79 (1 H, dd, *J* = 1.5, 8 Hz) ppm. – ^{13}C NMR (125 MHz): 19.3, 21.6, 123.1, 125.2, 125.9, 126.6, 127.9, 128.2, 130.7, 134.3, 136.1, 136.3, 139.4, 143.6, 146.9 ppm. – IR: 1097, 1239, 1319, 1430, 1570, 2949, 3006, 3042, 3121, 2448 cm^{-1}. – MS (ESI): 286.0 [M+Na^{+}], calcd: 263.1310, HRMS: 263.0147 [M+H^{+}].

8-(3-Fluorophenyl)-6-(methoxycarbonyl)quinoline 1-oxide (21)



Thermal conditions: According to GP3, 6-(methoxycarbonyl)-quinoline *N*-oxide (101 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.03 mmol, 5 mol %), acetic acid (900 mL, 1.50 mmol, 30 equiv.), water (50 μL, 2.75 mmol, 5.5 equiv.), and 3-fluoroiodobenzene (176 μL, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **21** (80 mg, 54 %) . – ^{1}H NMR (500 MHz): 3.98 (3 H, s), 7.03–7.09 (3 H, m), 7.30–7.40 (2 H, m), 7.89 (1 H, d, *J* = 8.5 Hz), 8.08 (1 H, d, *J* = 2 Hz), 8.47 (1 H, d, *J* = 5.5 Hz), 8.62 (1 H, d, *J* = 2 Hz) ppm. – ^{13}C NMR (125 MHz): 52.8, 113.4 (d, *J* = 20.9 Hz), 115.3 (d, *J* = 22.5 Hz), 122.2, 124.0 (d, *J* = 2.8 Hz), 127.4, 128.3 (d, *J* = 8.5 Hz), 129.2, 131.3, 131.6, 133.4, 135.6, 138.8, 140.5, 143.9 (d, *J* = 8.5 Hz), 160.7, 162.7, 165.4 ppm. – ^{19}F NMR (282 MHz): –114.1 (m) ppm. – IR: 1011, 1201, 1225, 1326, 1445, 2989, 3029 cm^{-1}. – MS (ESI): 297.9, calcd: 297.0801, HRMS: 296.9133 [M+H^{+}].

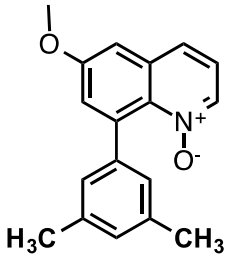
4-(4-(Trifluoromethyl)phenyl)phenanthridine 5-oxide (22)



Microwave conditions: According to GP4, phenanthridine *N*-oxide (39 mg, 0.20 mmol), silver phosphate (41 mg, 0.10 mmol, 0.5 equiv.), palladium acetate (2.2 mg, 0.01 mmol, 5 mol %), acetic acid (360 μL, 6.0 mmol, 30 equiv.), water (144 μL, 8.0 mmol, 40 equiv.) and 4-iodobenzotrifluoride (88 μL, 0.60 mmol, 3 equiv.) were heated in a microwave reactor at 180 °C for 50 min. The crude product was purified

by column chromatography to yield 8-substituted quinoline *N*-oxide **22** (33 mg, 61 %). – ^{1}H NMR (500 MHz): 7.32–7.41 (4 H, m), 7.61 (1 H, d, *J* = 7 Hz), 7.66 (1 H, d, *J* = 8 Hz), 7.71–7.73 (2 H, m), 7.78 (1 H, t, *J* = 7.5 Hz), 8.53 (1 H, d, *J* = 8.5 Hz), 8.64 (1 H, d, *J* = 8 Hz), 8.68 (1 H, s) ppm. – ^{13}C NMR (125 MHz): 122.5, 122.7, 125.5, 126.0, 126.7, 126.9, 127.0, 127.6, 128.0, 129.0, 134.0, 135.2, 137.4, 143.6 ppm. – IR: 1122, 1285, 1349, 1445, 1585, 2948, 3025, 3104 cm^{-1}. – MS (ESI): 272.0, calcd:272.1070, HRMS: 272.1071 [M+H^{+}].

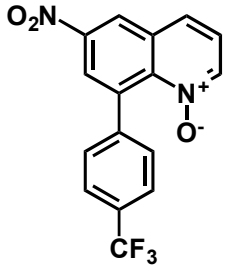
8-(3,5-Dimethylphenyl)-6-methoxyquinoline 1-oxide (23)



Thermal conditions: According to GP3, 6-methoxyquinoline *N*-oxide (175 mg, 1 mmol), silver phosphate (209 mg, 0.5 mmol, 0.5 equiv.), palladium acetate (11 mg, 0.05 mmol, 5 mol %), acetic acid (1.7 mL, 30 mmol, 30 equiv.), water (720 μL, 40 mmol, 40 equiv.), and 5-iodo-*m*-xylene (435 μL, 3 mmol, 3 equiv.) was heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **23** (213 mg, 76 %).

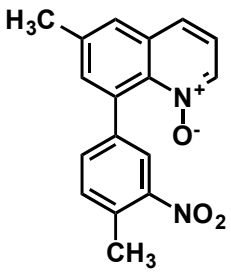
Microwave conditions: According to GP4, 6-methoxyquinoline *N*-oxide (105 mg, 0.60 mmol), silver phosphate (123 mg, 0.30 mmol, 0.5 equiv.), palladium acetate (6.6 mg, 0.03 mmol, 5 mol %), acetic acid (1.80 mL, 18.0 mmol, 30 equiv.), water (430 μL, 24.0 mmol, 40 equiv.) and 5-iodo-*m*-xylene (261 μL, 1.80 mmol, 3 equiv.) was divided into three vials and heated under microwave irradiation at 180 °C for 50 min. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **23** (133 mg, 79 %). – m.p.: 153–155 °C. – ^{1}H NMR (500 MHz): 2.35 (6 H, s), 3.93 (3 H, s), 6.94 (2 H, s), 6.96 (2 H, s), 7.10 (1 H, d, *J* = 2.5 Hz), 7.13 (1 H, d, *J* = 2.5 Hz), 7.20 (1 H, dd, *J* = 6, 8 Hz), 7.62 (1 H, dd) ppm. – ^{13}C NMR (125 MHz): 21.4, 55.7, 106.1, 121.4, 126.0, 126.6, 127.3, 128.1, 133.4, 134.7, 136.0, 136.2, 138.3, 142.0, 157.9, 174.7 ppm. – IR: 1045, 1133, 1207, 1309, 1417, 1513, 2988, 3024, 3056, 3121 cm^{-1}. – MS (ESI): 302.0 [M+Na^{+}], calcd: 280.1332, HRMS: 280.1161 [M+H^{+}].

6-Nitro-8-(4-(trifluoromethyl)phenyl)quinoline 1-oxide (24)



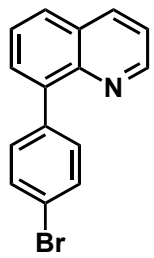
Thermal conditions: According to GP3, 6-nitroquinoline *N*-oxide (95 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.03 mmol, 5 mol %), acetic acid (900 mL, 15 mmol, 30 equiv.), water (360 μL, 20 mmol, 40 equiv.), and 4-iodobenzotrifluoride (220 μL, 1.5 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **24** (96 mg, 57 %). – m.p.: 117–119 °C. – ^{1}H NMR (500 MHz): 7.45 (2 H, d, *J* = 8.5 Hz), 7.50 (1 H, dd, *J* = 2.5, 8.5 Hz), 7.68 (2 H, d, *J* = 8.5 Hz, 7.96 (1 H, d, *J* = 8.5 Hz), 8.24 (1 H, d, *J* = 2.5 Hz), 8.47 (1 H, d, *J* = 6.5 Hz), 8.84 (1 H, d, *J* = 2.5 Hz) ppm. – ^{13}C NMR (125 MHz): 123.7, 124.2 (quart., *J* = 4 Hz), 124.8, 126.6, 127.1, 128.1, 128.3, 128.9, 129.2, 129.4, 131.6, 137.7, 139.5, 140.8, 144.3, 145.7 ppm. – ^{19}F NMR (282 MHz): –62.5 ppm. – IR: 1020, 1110, 1131, 1239, 1325, 1543, 2941, 2992, 3049, 3252 cm^{-1}. – MS (ESI): 334.8, calcd: 335.0638, HRMS: 335.0847 [M+H^{+}].

6-Methyl-8-(4-methyl-3-nitrophenyl)quinoline 1-oxide (25)



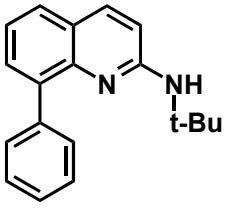
Thermal conditions: According to GP3, 6-methylquinoline *N*-oxide (80 mg, 0.50 mmol), silver phosphate (104 mg, 0.25 mmol, 0.5 equiv.), palladium acetate (5.6 mg, 0.03 mmol, 5 mol %), acetic acid (900 μL, 1.50 mmol, 30 equiv.), water (360 μL, 2.0 mmol, 40 equiv.), and 4-iodo-1-methyl-2-nitrobenzene (394 mg, 1.50 mmol, 3 equiv.) were heated at 120 °C for 12 h. The crude product was purified by column chromatography to yield 8-substituted quinoline *N*-oxide **25** (121 mg, 82 %). – m.p.: 183–185 °C. – ^{1}H NMR (500 MHz): 2.55 (3 H, s), 2.67 (3 H, s), 7.27–7.31 (3 H, m), 7.48 (1 H, dd, *J* = 2, 8 Hz), 7.69 (1 H, s), 7.71 (1 H, s), 7.99 (1 H, d, *J* = 2 Hz), 8.28 (1 H, dd, *J* = 0.5, 6 Hz) ppm. – ^{13}C NMR (125 MHz): 20.5, 21.1, 121.5, 123.9, 125.9, 128.2, 131.0, 135.6, 132.2, 133.2, 133.3, 136.3, 136.5, 137.3, 138.0, 141.7, 147.6 ppm. – IR: 1038, 1097, 1170, 1235, 1375, 1436, 1523, 2927, 2978, 3056, 3348 cm^{-1}. – MS (ESI): 295.0, calcd: 295.1077, HRMS: 295.1090 [M+H^{+}].

Experimental procedure for the tandem microwave-accelerated synthesis of 8-arylquinoline from quinoline: Synthesis of 8-(4-bromophenyl)quinoline (26)



Quinoline (77 mg, 0.6 mmol), hydrogen peroxide (93 μL, 1.20 mmol, 2 equiv., 30% solution in water), and acetic acid (1.08 mL) were divided into three 2 mL vials and heated in the microwave at 180 °C for 30 min. After the microwave reached 55 °C (avg. 20 min) each vial was degassed and stirred with silver phosphate (125 mg, 0.30 mmol, 0.5 equiv.) for 15 min before palladium acetate (6.7 mg, 0.03 mmol, 5 mol%), 1-bromo-4-iodobenzene (507 mg, 1.8 mmol, 3 equiv.), and deionized water (435 μL) were divided into the three vials. The vials where then heated in the microwave at 180 °C for 50 min before being cooled to 55 °C (avg. 20 min). Each vial was then degassed and hypophosphorous acid (158 μL, 3.6 mmol, 6 equiv., 50 wt % solution in water) was divided between the three vials. The vials were heated in the microwave at 120 °C for 0.5 h before cooling to 55 °C (avg. 20 min) and diluted with a saturated aqueous solution of ammonium chloride (5 mL). The aqueous layer was extracted with dichloromethane (5 x 5 mL), the organic layers combined, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography [silica gel, dichloromethane/EtOAc-EtOH (1:1)] to yield **26** (114 mg, 67 %). – ^{1}H NMR (500 MHz): 7.42 (1 H, dd, *J* = 4, 8 Hz), 7.57–7.63 (5 H, m), 7.71 (1 H, dd, *J* = 1.5, 7 Hz), 7.84 (1 H, dd, *J* = 1.5, 8 Hz), 8.21 (1 H, dd, *J* = 2, 8.5 Hz), 8.95 (1 H, dd, *J* = 2, 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 121.2, 121.8, 126.3, 127.9, 128.8, 130.1, 131.1, 132.3, 136.3, 138.4, 139.6, 145.8, 150.4 ppm. – IR: 1012, 1103, 1222, 1318, 1425, 1574, 2920, 3006, 3046, 3113 cm^{-1}. – MS (ESI): 283.9, calcd: 284.0069, HRMS: 284.1331 [M+H^{+}].

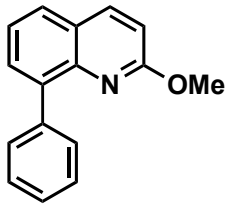
_N_-(_tert_-Butyl)-8-phenylquinolin-2-amine (27)



To a solution of 8-substituted quinoline *N*-oxide **5** (100 mg, 0.45 mmol) and *tert*-butylamine (283 μL, 2.7 mmol, 6 equiv.) in trifluorotoluene (4.5 mL) at 0 °C was added *p*-toluenesulfonic anhydride (308 mg, 0.945 mmol, 2.1 equiv.) in 3 portions. The

reaction mixture was allowed to stir at 0 °C for 1.5 h before being diluted with a saturated aqueous solution of sodium bicarbonate (5 mL). The aqueous layer was extracted with dichloromethane (4 x 5 mL), the organic layers combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel, hexanes/EtOAc] to yield 2,8-disubstituted quinoline **27** (88 mg, 70 %). – ^{1}H NMR (500 MHz): 1.4 (9 H, s), 4.46–4.53 (1 H, br s), 6.53 (1 H, d, *J* = 1, 9 Hz), 7.29 (1 H, dt, *J* = 1, 7 Hz), 7.40 (1 H, dt, *J* = 1.5, 7.5 Hz), 7.50 (2 H, dt, *J* = 1, 7.5 Hz), 7.62 (2 H, dt, *J* = 1.5, 7 Hz), 7.73 (2 H, dd, *J* = 1, 7 Hz), 7.79 (1 H, dd, *J* = 1, 9 Hz) ppm. – ^{13}C NMR (125 MHz): 29.1, 51.4, 113.3, 121.5, 123.3, 126.4, 127.1, 127.3, 130.1, 136.7, 138.3, 140.9, 145.8, 155.8 ppm. – IR: 1030, 1145, 1286, 1335, 1426, 1520, 2960, 3046, 3425 cm^{-1}. – MS (ESI): 277.0, calcd: 277.1699, HRMS: 277.1746 [M+H^{+}].

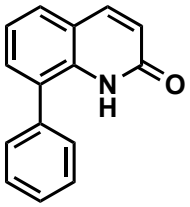
2-Methoxy-8-phenylquinoline[6] (28)



To a solution of 8-substituted quinoline *N*-oxide **5** (50 mg, 0.23 mmol) in methanol (2.5 mL) was added *p*-toluenesulfonic chloride (56 mg, 0.29 mmol, 1.3 equiv.) at 23 °C. The reaction mixture was allowed to stir for 15 min before triethylamine (63 μL, 0.45 mmol, 2 equiv.) was added and the reaction was allowed to stir 12 h. The reaction mixture was diluted with a 1M HCl (5 mL) and dichloromethane (5 mL). The layers were separated and the organic layer washed with a saturated aqueous solution of sodium carbonate. The aqueous layers were combined and extracted with dichloromethane (4 x 5 mL), the organic layers combined, dried over anhydrous sodium sulfate, concentrated under reduced pressure, and purified by column chromatography [silica gel, hexanes/dichloromethane] to yield 2,8-disubstituted quinoline **28** (45 mg, 83%). – ^{1}H NMR (500 MHz): 3.92 (3 H, s), 6.92 (1 H, d, *J* = 9 Hz), 7.36–7.49 (6 H, m), 7.71 (1 H, dt, *J* = 1.5, 8.5 Hz), 7.81 (1 H, dd, *J* = 1.5, 7.5 Hz), 8.02 (1 H, d, *J* = 9 Hz) ppm. – ^{13}C NMR (125 MHz): 53.3, 112.7, 123.8, 125.5, 126.9, 127.1, 127.5, 130.3, 130.6, 138.4, 139.1,

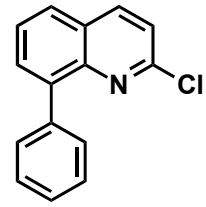
139.6, 143.8, 161.7 ppm. – IR: 1095, 1249, 1299, 1354, 1438, 2932, 3003, 3094 cm^{-1}. – MS (ESI): 236.0, calcd: 236.1070, HRMS: 236.1154 [$M+H^+$].

8-Phenylquinolin-2(1*H*)-one[2,3] (29)



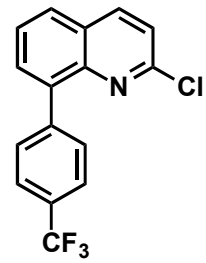
A solution of 8-substituted quinoline *N*-oxide **6** (112 mg, 0.51 mmol) in trifluoroacetic acid (2 mL) was heated at 40 °C for 12 h then cooled to 23 °C. The reaction mixture was concentrated under reduced pressure and purified by column chromatography [hexanes/EtOAc–EtOH (1:1), silica gel] to yield **29** (104 mg, 93 %). – ^{1}H NMR (500 MHz): 6.65 (1 H, d, *J* = 9.5 Hz), 7.24–7.28 (2 H, m), 7.34–7.54 (5 H, m), 7.56 (1 H, dd, *J* = 1.5, 7.5 Hz), 7.81 (1 H, d, *J* = 9.5 Hz), 8.82–8.85 (1 H, br s) ppm. – ^{13}C NMR (125 MHz): 120.0, 121.9, 122.4, 127.5, 128.6, 128.7, 129.2, 129.6, 131.4, 135.3, 135.8, 141.0, 162.4 ppm. – IR: 1065, 1139, 1247, 1325, 1406, 1610, 2728, 2884, 2978, 3057 cm^{-1}.

2-Chloro-8-phenylquinoline[4] (30)



A 6 mL vial containing 8-substituted quinoline *N*-oxide **5** (55 mg, 0.25 mmol) and thionyl chloride (2.5 mL) was heated at 50 °C for 12 h. It was then concentrated under reduced pressure and purified by column chromatography [neutral alumina, 5 vol % triethylamine in hexanes] to yield 2-chloroquinoline **30** (43 mg, 72 %). – ^{1}H NMR (500 MHz): 7.42–7.54 (4 H, m), 7.62 (1 H, t, *J* = 7.5 Hz), 7.75 (2 H, dd, *J* = 1, 8 Hz), 7.80 (2 H, dd, *J* = 1, 8 Hz), 8.12 (1 H, d, *J* = 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 122.4, 126.8, 127.1, 127.4, 127.5, 128.0, 128.1, 130.7, 131.3, 138.5, 139.1, 140.0, 145.4, 150.3 ppm. – IR: 1103, 1263, 1325, 1443, 2880, 3046 cm^{-1}. – MS (ESI): 239.9.

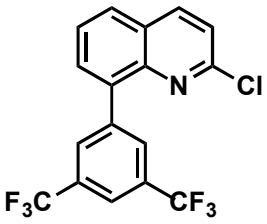
2-Chloro-8-(4-(trifluoromethyl)phenyl)quinoline[3a] (31)



A 6 mL vial containing 8-substituted quinoline *N*-oxide **2** (72 mg, 0.25 mmol) and thionyl chloride (2.5 mL) was heated at 50 °C for 12 h. It was then concentrated under reduced pressure and purified by column chromatography [neutral alumina, 5 vol % triethylamine in hexanes] to

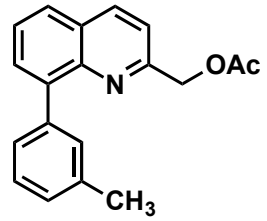
yield 2-chloroquinoline **31** (52 mg, 68 %). – ^{1}H NMR (500 MHz): 7.42 (1 H, d, *J* = 8.5 Hz), 7.65 (1 H, t, *J* = 7.5 Hz), 7.75 (2 H, d, *J* = 8 Hz), 7.79 (1 H, d, *J* = 7.5 Hz), 7.82–7.87 (3 H, m), 8.16 (1 H, d, *J* = 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 122.7, 124.8 (quart., *J* = 3.7 Hz), 126.8, 127.4, 128, 131.0, 131.4, 138.5, 139.1, 142.1, 145.1, 150.7 ppm. – ^{19}F NMR (282 MHz): –62.4 ppm. – IR: 967, 1066, 1168, 1323, 1403, 1457, 1568, 2867, 2981, 3088, 3106 cm^{-1}. – MS (ESI): 307.8, calcd: 307.0376, HRMS: 307.2292 [M+H^{+}].

8-(3,5-Bis(trifluoromethyl)phenyl)-2-chloroquinoline[3a] (32)



A 6 mL vial containing 8-substituted quinoline *N*-oxide **9** (89 mg, 0.25 mmol) and thionyl chloride (2.5 mL) was heated at 50 °C for 12 h before being concentrated under reduced pressure and purified by column chromatography [neutral alumina, hexanes-5 mol % triethylamine] to yield 2-chloroquinoline **32** (67 mg, 71 %). – ^{1}H NMR (500 MHz): 7.46 (1 H, d, *J* = 8.5 Hz), 7.67 (1 H, dt, *J* = 1, 8.5 Hz), 7.82 (1 H, dd, *J* = 1.5, 7.5 Hz), 7.91 (1 H, dd, *J* = 1.5, 8 Hz), 7.93 (1 H, s), 8.18 (2 H, d, *J* = 8.5 Hz), 8.21 (1 H, s) ppm. – ^{13}C NMR (125 MHz): 121.2 (m), 122.4, 123.0, 124.6, 126.8, 127.4, 128.3, 128.7, 130.9, 131.3, 136.7, 139.2, 140.3, 144.8, 151.1 ppm. – ^{19}F NMR (282 MHz): –62.7 ppm. – IR: 1103, 1130, 1262, 1325, 1442, 2960, 3025 cm^{-1}. – MS (ESI): 375.8, calcd: 376.0322, HRMS: 376.0301 [M+H^{+}].

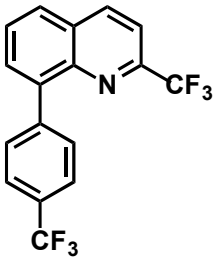
(8-(*m*-Tolyl)quinolin-2-yl)methyl acetate[5] (33)



A solution of 8-substituted quinoline *N*-oxide **16** (100 mg, 0.45 mmol) in acetic anhydride (2 mL) was heated to 130 °C. After 4 h the reaction mixture was concentrated under reduced pressure to yield **33** (118 mg, 94 %). –^{1}H NMR (500 MHz): 2.13 (3 H, s), 2.45 (3 H, s), 5.38 (2 H, s), 7.22 (1 H, dd, *J* = 1, 7.5 Hz), 7.36 (1 H, t, *J* = 7.5 Hz), 7.43 (1 H, d, *J* = 8.5 Hz), 7.52–7.6 (3 H, m), 7.74 (1 H, dd, *J* = 1, 7 Hz), 7.80 (1 H, dd, *J* = 1.5, 8 Hz), 8.20 (1 H, d, *J* = 8 Hz) ppm. – ^{13}C NMR (125 MHz): 20.9, 21.6,

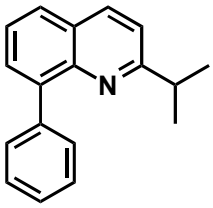
67.2, 118.7, 126.3, 127.2, 127.6, 127.9, 128.0, 128.2, 130.5, 131.6, 137.0, 137.2, 139.2, 140.6, 145.2, 155.6, 170.7 ppm. – IR: 1049, 1180, 1279, 1327, 1435, 1569, 2922, 3043 cm^{-1}. – MS (ESI): 291.9, calcd: 292.1332, HRMS: 292.1732 $[M+H^+]$.

2-(Trifluoromethyl)-8-(4-(trifluoromethyl)phenyl)quinoline[5] (34)



To a solution of 8-substituted quinoline *N*-oxide **2** (72 mg, 0.25 mmol) and trimethyl(trifluoromethyl)silane (300 μL, 1.50 mmol, 6 equiv.) in tetrahydrofuran (2.5 mL, dried over sodium and benzophenone) at –50 °C was added potassium *tert*-butoxide (168 mg, 1.50 mmol, 6 equiv.) in 3 portions over 1 h. The reaction was then quenched with a saturated aqueous solution of ammonium chloride (5 mL) and the aqueous layer extracted with dichloromethane (3 x 5 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel, hexanes/dichloromethane] to yield 2,8-disubstituted quinoline **34** (53 mg, 62 %). – ^{1}H NMR (500 MHz): 7.75 (2 H, d, *J* = 8 Hz), 7.78 (2 H, d, *J* = 8.5 Hz), 7.88–7.91 (3 H, m), 7.95 (1 H, dd, *J* = 1.5, 8 Hz), 8.41 (1 H, d, *J* = 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 117.0 (d, *J* = 1.75 MHz), 122.8 (d, *J* = 93.9 Hz) 124.7 (quart., *J* = 3.8 Hz), 125.5, 128.0, 128.3, 128.4, 128.6, 129.3, 129.6 (d, *J* = 32.1), 131.2, 131.5, 138.4, 139.8, 141.8, 144.4, 147.6 (quart., *J* = 34.7) ppm. – ^{19}F NMR (282 MHz): –62.5, –82.3 ppm. – IR: 1066, 1168, 1326, 1506, 2870, 2985, 3074 cm^{-1}.

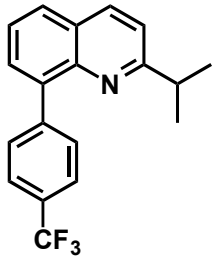
2-Isopropyl-8-phenylquinoline[4] (35)



To a solution of 8-substituted quinoline *N*-oxide **5** (100 mg, 0.45 mmol) in diethyl ether (2.3 mL) was added copper(I) chloride (4.5 mg, 0.05 mmol, 10 mol %), magnesium chloride (90 mg, 0.90 mmol, 2 equiv.) and isopropylmagnesium chloride (450 μL, 0.90 mmol, 2 equiv., 2 M in tetrahydrofuran) at 23 °C. The reaction was allowed to stir 12 h before being neutralized with a saturated aqueous solution of ammonium chloride (5 mL) and the aqueous layer was extracted with dichloromethane (3 x 5 mL).

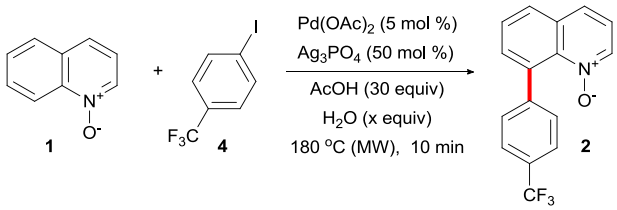
The combined organic fractions were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel, hexanes/dichloromethane] to yield quinoline **35** (104 mg, 94 %). – ^{1}H NMR (500 MHz): 1.28 (6 H, d, *J* = 7 Hz), 3.96 (1 H, sept., *J* = 7 Hz), 7.29–7.35 (6 H, m), 7.49 (1 H, dd, *J* = 1.5, 7 Hz), 7.55 (1 H, t, *J* = 8 Hz), 7.72 (1 H, d, *J* = 8.5 Hz), 7.82 (1 H, dd, *J* = 1.5, 8 Hz) ppm. – ^{13}C NMR (125 MHz): 20.4, 31.6, 119.0, 125.4, 126.0, 126.7, 126.8, 127.9, 128.2, 130.3, 134.5, 136.4, 139.3, 143.6 ppm. – IR: 905, 1092, 1239, 1280, 1387, 2892, 2974, 3034, 3273 cm^{-1}. – MS (ESI): 248.0, calcd: 248.1434, HRMS: 248.0247 [M+H^{+}].

2-Isopropyl-8-(4-(trifluoromethyl)phenyl)quinoline[4] (36)



To a solution of 8-substituted quinoline *N*-oxide **9** (144 mg, 0.5 mmol) in diethyl ether (1.3 mL) was added copper(I) chloride (5 mg, 0.05 mmol, 10 mol %), magnesium chloride (100 mg, 1.0 mmol, 2 equiv.) and isopropylmagnesium chloride (500 μL, 1.0 mmol, 2 equiv., 2 M in tetrahydrofuran) at 23 °C. The reaction was allowed to stir 12 h before being neutralized with a saturated aqueous solution of ammonium chloride (5 mL) and the aqueous layer was extracted with dichloromethane (3 x 5 mL). The combined organic fractions were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography [silica gel, hexanes/dichloromethane] to yield quinoline **36** (115 mg, 73 %). – ^{1}H NMR (500 MHz): 1.35 (6 H, d, *J* = 7 Hz), 3.22 (1 H, sept. *J* = 7 Hz), 7.36 (1 H, d, *J* = 8.5 Hz), 7.55 (1 H, t, *J* = 7.5 Hz), 7.73–7.80 (3 H, m), 7.82 (1 H, dd, *J* = 1, 8 Hz), 7.96 (2 H, d, *J* = 8 Hz), 8.12 (1 H, d, *J* = 8.5 Hz) ppm. – ^{13}C NMR (125 MHz): 22.3, 37.1, 120.0, 124.3 (quart., *J* = 3.7 Hz), 125.4, 127.3, 128.0, 130.0, 131.4, 136.4, 138.6, 143.3, 145.0, 167.2 ppm. – ^{19}F NMR (282 MHz): –62.2 ppm. – IR: 983, 1051, 1236, 1326, 1408, 1557, 2883, 2953, 3060 cm^{-1}.

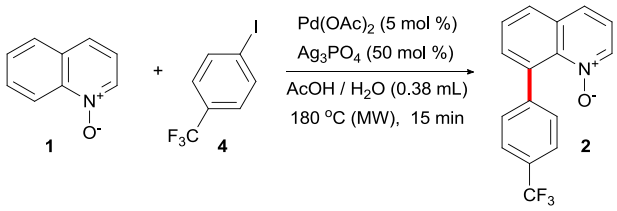
Table S2. Influence of added water on the C8–H arylation of quinoline *N*-oxide (1) with 4-iodobenzotrifluoride (4) under increasing dilution conditions.



entry	H_2O, equiv.	%, **2**
1	0	36.0
2	2	43.0
3	5	50.3
4	10	54.3
5	15	56.3
6	20	57.0
7	30	62.0
8	40	74.3
9	50	73.7
10	60	75.5

An argon-flushed 2 mL vial was charged with quinoline *N*-oxide (29 mg, 0.2 mmol), palladium acetate (5 mol %, 2.2 mg, 0.01 mmol) silver phosphate (50 mol %, 41 mg, 0.1 mmol), a degassed mixture of glacial acetic acid (30 equiv., 0.36 mL, 6.0 mmol) and an appropriate amount of deionized water, and 4-iodobenzotrifluoride (3 equiv., 88 μL, 0.60 mmol). The vial was sealed, and the reaction mixture was stirred under microwave irradiation (180 ^{o}C) for 10 min. Work up was performed according to the general procedure GP2. Each experiment was carried out in triplicate. An NMR yield of **2** (average of three runs) is reported in Table S2.

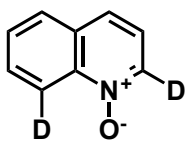
Table S3. Influence of the water content on the C8–H arylation of quinoline *N*-oxide (1) with 4-iodobenzotrifluoride (4) under constant volume conditions.



entry	H_2O in AcOH, vol %	%, **2**
1	0	44.7
2	10	46.0
3	20	48.3
4	30	75.3
5	40	81.7
6	50	60.0
7	60	45.0
8	70	42.3
9	80	19.7
10	90	10.3
11	100	5.0

An argon-flushed 2 mL vial was charged with quinoline *N*-oxide (29 mg, 0.2 mmol), palladium acetate (2.2 mg, 0.01 mmol, 5 mol %,) silver phosphate (41 mg, 0.10 mmol, 50 mol %), a degassed mixture of glacial acetic acid and deionized water of an appropriate composition (0.38 mL), and 4-iodobenzotrifluoride (88 μL, 0.60 mmol, 3 equiv.). The vial was sealed, and the reaction mixture was stirred under microwave irradiation (180 °C) for 15 min. Work up was performed according to the general procedure GP2. Each experiment was carried out in triplicate. An NMR yield of **2** (average of three runs) is reported in Table S3.

2,8-d_2-Quinoline *N*-oxide



A modification of Shibata's procedure[6] was used for the deuteration of quinoline *N*-oxide. An argon-flushed 6 mL vial was charged with $[Rh(cod)Cl]_2$ (20 mg, 0.0405 mmol) and degassed acetone (4 mL). Silver triflate (10.4 mg, 0.0405 mmol) was added, and the reaction mixture was stirred in the dark for 2 h at 23 °C. The mixture was filtered through a cotton wool plug, transferred into an argon-flushed 2-dram vial and *rac*-BINAP (25.2 mg, 0.0405 mmol) was added to the filtrate. The solution was stirred at 23 °C for 2 h and then concentrated under reduced pressure (0.5 mbar). Quinoline *N*-oxide (90 mg, 0.6 mmol) and a degassed mixture of chlorobenzene (2 mL) and D_2O (1 mL) were added, and the reaction mixture

was stirred at 120 ^{o}C for 16 h. For the work-up, the reaction mixture was diluted with chloroform, dried with sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography [silica gel, 5 vol% triethylamine solution in hexane / ethyl acetate (1:1)] to give 69.3 mg of 2,8-d_2-quinoline *N*-oxide (98% D in C2 and C8).

Kinetic isotope effect study

An argon-flushed 6 mL vial was charged with a degassed solution of quinoline *N*-oxide (or 2,8-d_2-quinoline *N*-oxide) (30 mg, 0.2 mmol) in glacial acetic acid (or CD_3COOD) (0.36 mL), palladium acetate (5 mol %, 2.2 mg, 0.01 mmol) silver phosphate (50 mol %, 41 mg, 0.1 mmol), degassed and deionized water (or D_2O) (5.5 equiv., 20 or 22 μL, 1.1 mmol), and 3,5-bis(trifluoromethyl)iodobenzene (3 equiv., 107 μL, 0.60 mmol). The vial was sealed, and the reaction mixture was stirred at 120 ^{o}C for 3 h. The experiment was carried out in triplicate for **1** and 2,8-d_2-**1**. Work-up was performed according to GP2. The average conversion of **1** to **9** and 2,8-d_2-**1** to 2-*d*-**9** over 3 runs was 41.4% and 20.3%.

H/D Exchange studies

Experiment 1: $Pd(OAc)_2$-catalyzed H/D exchange:

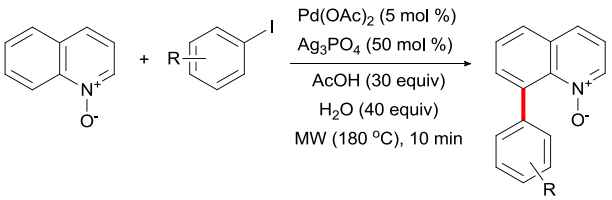
An argon-flushed 6 mL vial was charged with quinoline *N*-oxide (29 mg, 0.2 mmol), palladium acetate (5 mol %, 2.2 mg, 0.01 mmol), degassed CD_3COOD (30 equiv., 0.36 mL, 6.0 mmol), and D_2O (5.5 equiv., 20 □L, 1.1 mmol). The vial was sealed, and the reaction mixture was stirred at 120 ^{o}C for 3 h. A 1:3 v/v mixture of 30% aq. ammonia solution and saturated aq. solution of ammonium chloride (2 mL) was added, and the reaction mixture was extracted with chloroform. The organic phase was separated, dried over sodium sulfate and concentrated under reduced pressure. The extent of the H/D exchange was determined from the ^{1}H NMR spectrum of the isolated quinoline *N*-oxide in $CDCl_3$ by integration of the 2-H and 8-H peaks of quinoline *N*-oxide. 62% H/D exchange was observed for 8-H and <1% for 2-H.

Experiment 2: H/D exchange for the recovered substrate and the product of the $Pd(OAc)_2$-catalyzed C8-arylation of quinoline N-oxide:

An argon-flushed 6 mL vial was charged with quinoline *N*-oxide (29 mg, 0.2 mmol), palladium acetate (5 mol %, 2.2 g, 0.01 mmol), silver phosphate (50 mol %, 41 mg, 0.1 mmol), degassed CD_3COOD (30 equiv., 0.36 mL, 30 mmol), D_2O (5.5 equiv., 20 □L, 1.1 mmol), and 4-iodobenzotrifluoride (3 equiv., 88 μL, 0.60 mmol). The vial was sealed, and the reaction mixture was stirred at 120 ^oC for 3 h. A 1:3 v/v mixture of 30% aq. ammonia solution and saturated aq. solution of ammonium chloride (2 mL) was added, and the reaction mixture was extracted with chloroform. The organic phase was separated, dried over sodium sulfate and concentrated under reduced pressure. The unreacted quinoline *N*-oxide and product **2** were isolated by means of preparative TLC [silica gel, 4 cm x 10 cm, 5 vol% triethylamine solution in hexane / ethyl acetate (1:1)]. The extent of the H/D exchange was determined from the ^1H NMR spectra in $CDCl_3$ by integration of the 2-H and 8-H peaks of quinoline *N*-oxide, and 2-H of product **2**. 39% H/D exchange was observed for 8-H and <1% for 2-H for quinoline *N*-oxide. <1% H/D exchange was observed for 2-H in product **2**.

Table S4. Hammett correlation study for the C8-C–H arylation of quinoline *N*-oxide (1) with substituted iodoarenes.

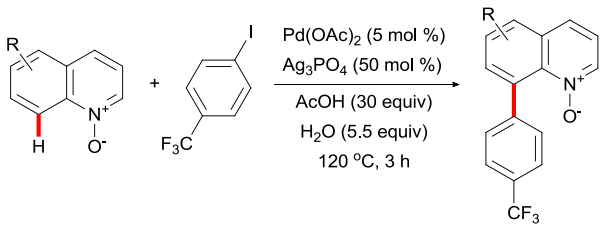
entry	Substituent	σ	log(conv.X/conv.H)
1	4-MeO	-0.27	-0.0792
2	4-*t*-Bu	-0.2	-0.0827
3	3,5-$(CH_3)_2$	-0.07	-0.0029
4	H	0	0
5	4-Br	0.23	0.0864
6	3-F	0.34	0.0792
7	4-CF_3	0.54	0.1461



An argon-flushed 2 mL vial was charged with quinoline *N*-oxide (29 mg, 0.2 mmol), palladium acetate (2.2 mg, 0.01 mmol, 5 mol %) silver phosphate (41 mg, 0.10 mmol, 50 mol %), a degassed mixture of glacial acetic acid (0.36 mL, 6.0 mmol, 30 equiv.) and degassed and deionized water (0.145 mL, 8.0 mmol, 40 equiv), and a substituted iodoarene (0.60 mmol, 3 equiv.). The vial was sealed, and the reaction mixture was stirred under microwave irradiation (180 ^oC) for 10 min. Work up was

performed according to the general procedure GP2. Each experiment was carried out in triplicate. log(conv.X/conv.H) Values are derived from the average of three runs for each substituted iodoarene and reported in Table S4.

Table S5. Hammett correlation study for the C8-C–H arylation of 5- and 6-substituted quinoline *N*-oxides with 4-iodobenzotrifluoride (4).



entry	Substituent	σ	log(conv.X/conv.H)
1	*m*-(6)-CH_3	-0.07	0.125
2	H	0	0
3	*m*-(6)-CH_3O	0.12	-0.0987
4	*p*-(5)-Br	0.23	-0.4486
5	*m*-(6)-Br	0.39	-0.7570

An argon-flushed 2 mL vial was charged with the respective 5- or 6-substituted quinoline *N*-oxide (0.2 mmol), palladium acetate (2.2 mg, 0.01 mmol, 5 mol %) silver phosphate (41 mg, 0.10 mmol, 50 mol %), a degassed mixture of glacial acetic acid (0.36 mL, 6.0 mmol, 30 equiv.) and degassed and deionized water (0.020 mL, 1.1 mmol, 5.5 equiv), and 4-iodobenzotrifluoride (88 μL, 0.60 mmol, 3 equiv.). The vial was sealed, and the reaction mixture was stirred under microwave irradiation (180 ^{o}C) for 10 min. Work up was performed according to the general procedure GP2. Each experiment was carried out in triplicate. Values of log(conv.X/conv.H) are derived from the average of three runs for each substituted quinoline *N*-oxide and reported in Table S5.

Table S6. Single Crystal X-Ray Crystallographic Data for 8-(4-(Trifluoromethyl)phenyl)quinoline *N*-oxide (2)

CCDC Nr: CCDC 1018649

Bond precision:	C-C = 0.0035 A	Wavelength=0.71073	
Cell:	a=5.7026(14)	b=24.817(6)	c=9.363(2)
	alpha=90	beta=104.841(3)	gamma=90
Temperature:	98 K		

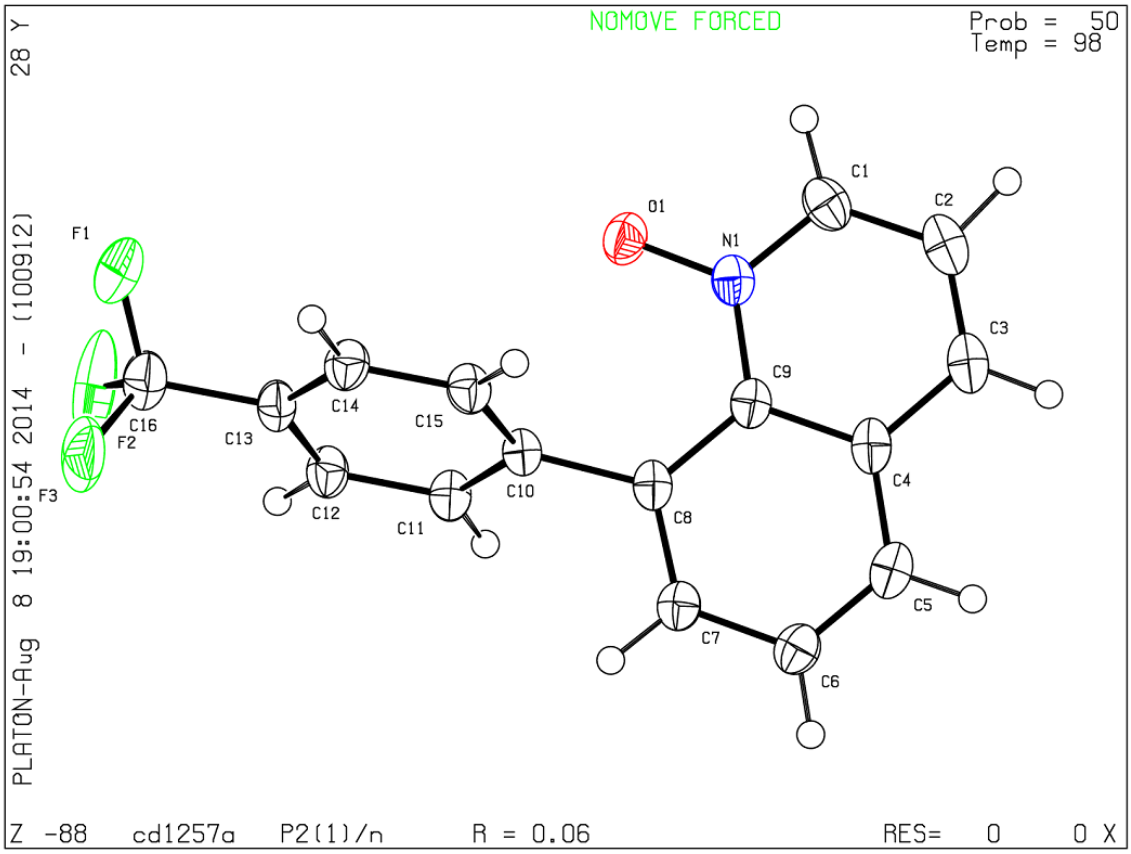
	Calculated	Reported
Volume	1280.9(5)	1280.9(5)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C16 H10 F3 N O	C16 H10 F3 N O
Sum formula	C16 H10 F3 N O	C16 H10 F3 N O
Mr	289.25	289.25
Dx,g cm^{-3}	1.500	1.500
Z	4	4
Mu (mm^{-1})	0.124	0.124
F000	592.0	592.0
F000'	592.40	
h,k,lmax	6,29,11	6,29,11
Nref	2270	2265
Tmin,Tmax	0.971,0.982	0.697,1.000
Tmin'	0.962	

Correction method= MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.040

R(reflections)= 0.0583(1989) wR2(reflections)= 0.1320(2265)

S = 1.007 Npar= 220



Computational Details

All computations were performed using Gaussian 09[7] suite of programs. Gas-phase structures were fully optimized in redundant internal coordinates without any symmetry constraints,[8] with density-functional theory (DFT) and a wave function incorporating Becke's three-parameter hybrid functional (B3),[9] along with the Lee-Yang-Parr correlation functional (LYP).[10] The Pd and P atoms were represented with the effective core pseudopotentials of the Stuttgart group and the associated basis sets improved with a set of f-polarization functions for Pd (α = 1.472)[11] and a set of d-polarization functions for P (α = 0.387).[12] The remaining atoms (C, H, N and O) were represented with the 6-31G(d,p)[13] basis sets. Frequency calculations were performed on the optimized geometries using the same basis sets to confirm that each optimized ground state has no imaginary frequencies and each optimized transition state has a single imaginary

frequency. For each transition state structure, the intrinsic reaction coordinate (IRC) routes were followed ten points in both directions. In order to reach the energy minima on the potential energy surface, geometry optimizations were carried out as a continuation of the IRC path starting from the last points in the forward and the reverse directions of the IRC calculations. Zero-point energy, thermal corrections, and entropic corrections were calculated from the frequency calculations. Solvent effects on the relative stabilities of the structures were evaluated by computing the single-point solvation-corrected energies at the stationary points with the Pd and P basis detailed above and the 6-311+G(d,p) basis set for all other atoms using SMD solvation model.[14] The energies discussed throughout the text are solvation Gibbs free energies calculated in *N*,*N*-dimethylformamide and acetic acid at 298.15 K and 1 atm. Single-point energies for the transition state structures were also calculated with the M06-L[15] functional for comparison purposes. Optimized structures are illustrated using GausView 5.[16] The electronic structure of the transition states where studied by using Natural Bond Analysis (NBO)[17]

Complete Reference for *Gaussian 09*

Gaussian 09, Revision **D.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.;

Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

Table S7. Charge Distribution on Pd and C Atoms in the Transition State Structures Leading to C–H Bond Activation in M1a, M1b and M1c.

	Natural Charges			
Mechanism	**Pd**	**C2**	**Pd**	**C8**
M1a	0.615	-0.204	0.638	-0.443
M1b	0.685	-0.102	0.645	-0.383
M1c	0.655	-0.084	0.620	-0.350

Table S8. Single-Point Energies in Hartree/Particle Computed with B3LYP and M06-L Functionals of the C2–H and C8–H Activation Transition States.

Method	$TS2^{M1a}$	$TS8^{M1a}$	$TS2^{M1b}$	$TS8^{M1b}$	$TS2^{M1c}$	$TS8^{M1c}$	$TS2^{M2}$	$TS8^{M2}$
B3LYP	-1292.08356	-1292.11726	-1062.65251	-1062.66663	-1062.25177	-1062.25740	-1191.77417	-1191.76627
M06-L	-1291.97798	-1292.00810	-1062.57710	-1062.59212	-1062.17650	-1062.18481	-1191.66625	-1191.66207

Table S9. Solvation-Corrected Single-Point Energies and Thermochemical Corrections at 298.15K of Stationary Points in Mechanism 1a.

Compound	ZPE[a]	Total E[a]	H[a]	S[b]	G[a]	E[a]	E_{sol} (DMF) [a]	E_{sol} (AA) [a]
$S2^{M1a}$	-1291.50841	-1291.48213	-1291.48118	185.497	-1291.56932	-1292.15144	-1292.38829	-1292.35635
$TS2^{M1a}$	-1291.44879	-1291.42215	-1291.42121	188.743	-1291.51089	-1292.08356	-1292.32468	-1292.29167
$P2^{M1a}$	-1291.48835	-1291.46143	-1291.46048	191.766	-1291.55160	-1292.12757	-1292.36597	-1292.33465
$S8^{M1a}$	-1291.51928	-1291.49317	-1291.49223	186.318	-1291.58075	-1292.16218	-1292.39817	-1292.36475
$I8^{M1a}$	-1291.48088	-1291.45383	-1291.45289	194.804	-1291.54544	-1292.12247	-1292.36197	-1292.32544
$TS8^{M1a}$	-1291.54544	-1291.45474	-1291.45380	187.978	-1291.54311	-1292.11726	-1292.35448	-1292.31811
$P8^{M1a}$	-1291.49304	-1291.46635	-1291.46540	191.06	-1291.55618	-1292.13579	-1292.37426	-1292.34030

[a]Hartree/Particle, [b]cal/mol.K

Table S10. Solvation-Corrected Single-Point Energies and Thermochemical Corrections at 298.15K of Stationary Points in Mechanism 1b.

Compound	ZPE[a]	Total E[a]	H[a]	S[b]	G[a]	E[a]	E_{sol} (DMF) [a]	E_{sol} (AA) [a]
$S2^{M1b}$	-1062.20056	-1062.18024	-1062.17930	158.918	-1062.25480	-1062.69923	-1062.77891	-1062.76058
$TS2^{M1b}$	-1062.15700	-1062.13730	-1062.13636	151.372	-1062.20828	-1062.65251	-1062.7324	-1062.71400
$P2^{M1b}$	-1062.18570	-1062.16505	-1062.16411	157.514	-1062.23894	-1062.68841	-1062.77055	-1062.75399
$S8^{M1b}$	-1062.19779	-1062.17755	-1062.17660	159.311	-1062.25230	-1062.69671	-1062.77730	-1062.75880
$I8^{M1b}$	-1062.17455	-1062.15458	-1062.15363	151.084	-1062.22542	-1062.67455	-1062.76076	-1062.74143
$TS8^{M1b}$	-1062.17124	-1062.15186	-1062.15091	146.948	-1062.22073	-1062.66663	-1062.74981	-1062.73000
$P8^{M1b}$	-1062.20438	-1062.18404	-1062.18309	153.729	-1062.25613	-1062.70697	-1062.78893	-1062.77229

[a]Hartree/Particle, [b]cal/mol.K

Table S11. Solvation-Corrected Single-Point Energies and Thermochemical Corrections at 298.15K of Stationary Points in Mechanism 1c.

Compound	ZPE[a]	Total E[a]	H[a]	S[b]	G[a]	E[a]	E_{sol} (DMF) [a]	E_{sol} (AA) [a]
$S2^{M1c}$	-1061.80878	-1061.78870	-1061.78776	155.595	-1061.86169	-1062.30266	-1062.33462	-1062.31978
$TS2^{M1c}$	-1061.76200	-1061.74227	-1061.7413	151.822	-1061.81346	-1062.25177	-1062.28555	-1062.27220
$P2^{M1c}$	-1061.82046	-1061.80051	-1061.79956	153.698	-1061.87259	-1062.31653	-1062.34219	-1062.32709
$S8^{M1c}$	-1061.80880	-1061.78878	-1061.78783	154.592	-1061.86128	-1062.30270	-1062.33467	-1062.31972
$TS8^{M1c}$	-1061.76793	-1061.74856	-1061.74762	147.204	-1061.81756	-1062.25740	-1062.29689	-1062.28333
$P8^{M1c}$	-1061.83381	-1061.81405	-1061.81311	152.103	-1061.88538	-1062.32943	-1062.35700	-1062.34173

[a]Hartree/Particle, [b]cal/mol.K

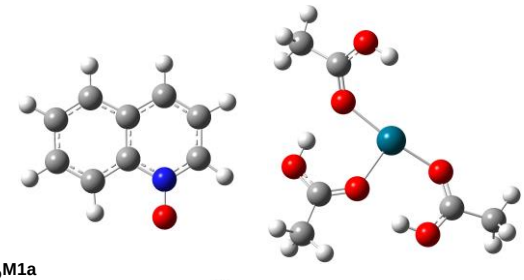
Table S12. Solvation-Corrected Single-Point Energies and Thermochemical Corrections at 298.15K of Stationary Points in Mechanism 2.

Compound	ZPE[a]	Total E[a]	H[a]	S[b]	G[a]	E[a]	E_{sol} (DMF) [a]	E_{sol} (Tol) [a]
Quinoline *N*-oxide	-476.96559	-476.95808	-476.95714	85.688	-476.99785	-477.22063	-477.23660	-477.23495
(PMe_3)PdPh(κ-acetate)	-714.17578	-714.15643	-714.15549	149.784	-714.22665	-714.59837	-714.60399	-714.59810
$S8^{M2}$	-1191.14340	-1191.11469	-1191.11375	197.176	-1191.20743	-1191.81220	-1191.84381	-1191.83826
$TS8^{M2}$	-1191.10370	-1191.07542	-1191.07448	190.566	-1191.16502	-1191.76627	-1191.79338	-1191.78955
$P8^{M2}$	-1191.11021	-1191.08124	-1191.08029	195.955	-1191.1734	-1191.77840	-1191.80432	-1191.80114
$I2^{M2}$	-1191.14594	-1191.11728	-1191.11634	195.416	-1191.2091	-1191.80881	-1191.84013	-1191.83514
$S2^{M2}$	-1191.12097	-1191.09196	-1191.09101	196.794	-1191.18452	-1191.79083	-1191.82259	-1191.81622
$TS2^{M2}$	-1191.11063	-1191.08234	-1191.08139	191.316	-1191.17229	-1191.77417	-1191.80183	-1191.79787
$P2^{M2}$	-1191.11766	-1191.08877	-1191.08782	198.605	-1191.18219	-1191.78713	-1191.81491	-1191.81108

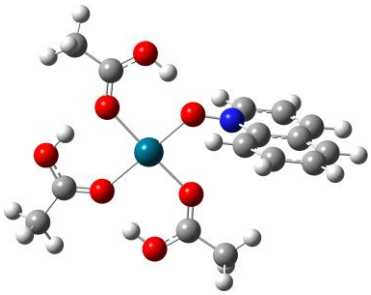
[a]Hartree/Particle, [b]cal/mol.K

Scheme S13. Optimized Geometries of Stationary Points on the Potential Energy Surface on the C–H bond Cleavage Pathway in Mechanism 1a. S2, TS2 and P2 are the structures along the C2–H bond cleavage pathway. S8, I8, TS8 and P8 are the structures along the C8–H bond cleavage pathway.

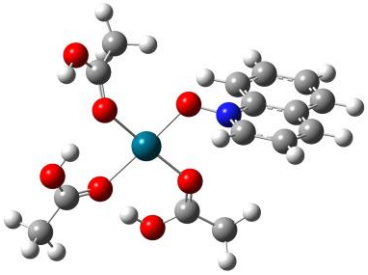
Quinoline *N*-oxide and $Pd(HOAc)_3^{2+}$



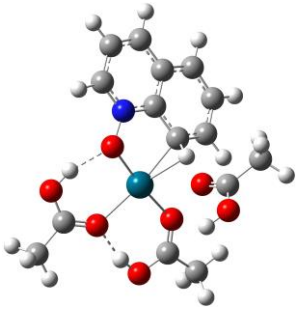
$S8^{M1a}$



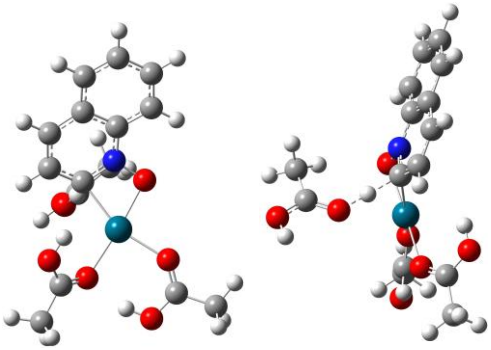
$S2^{M1a}$



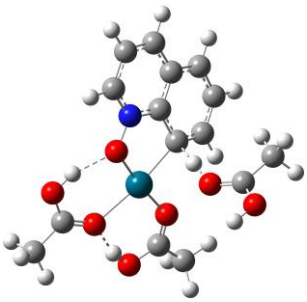
$I8^{M1a}$



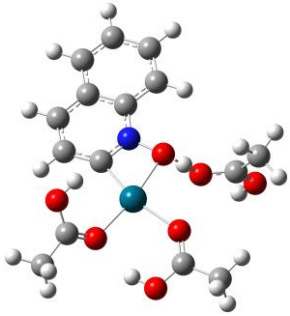
$TS2^{M1a}$ (From two different views)



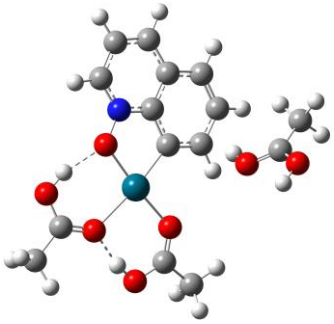
$TS8^{M1a}$



$P2^{M1a}$

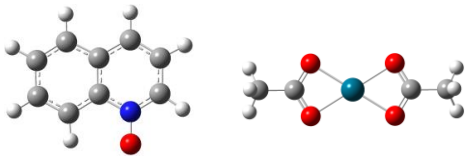


$P8^{M1a}$

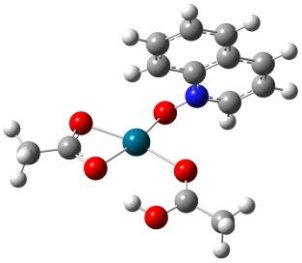


Scheme S14. Optimized Geometries of Stationary Points on the Potential Energy Surface on the C–H bond Cleavage Pathway in Mechanism 1b. S2, TS2 and P2 are the structures along the C2–H bond cleavage pathway. S8, I8, TS8 and P8 are the structures along the C8–H bond cleavage pathway.

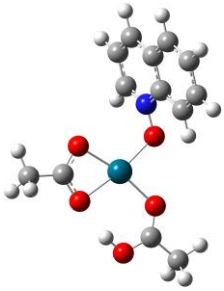
Quinoline *N*-oxide and Pd(κ-acetate)$_2$



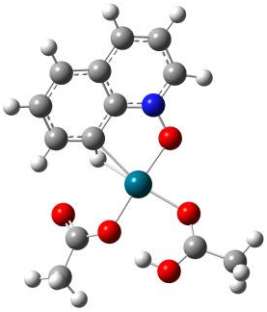
S8^{M1b}



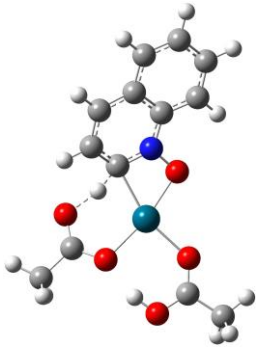
S2^{M1b}



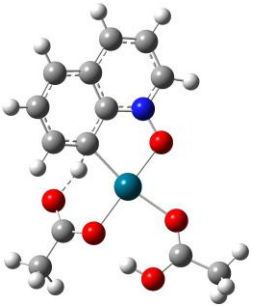
I8^{M1b}



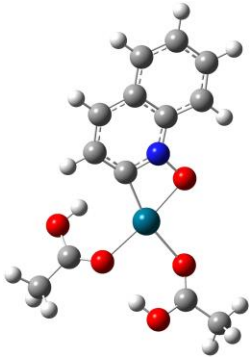
TS2^{M1b}



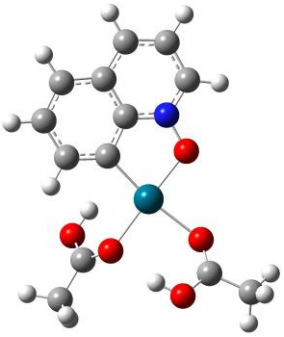
TS8^{M1b}



P2^{M1b}

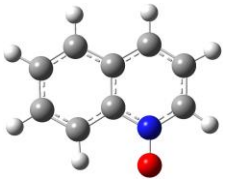


P8^{M1b}

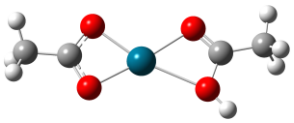


Scheme S15. Optimized Geometries of Stationary Points on the Potential Energy Surface on the C–H bond Cleavage Pathway in Mechanism 1c. S2, TS2 and P2 are the structures along the C2–H bond cleavage pathway. S8, TS8 and P8 are the structures along the C8–H bond cleavage pathway.

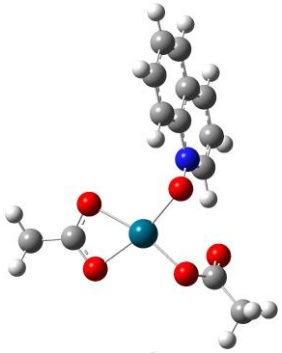
Quinoline *N*-oxide



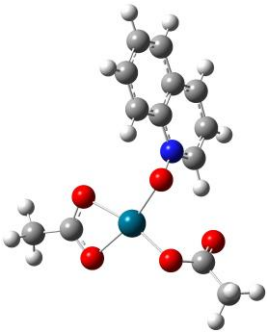
Pd(κ-acetate)$_2$



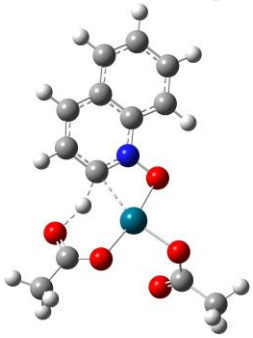
S2^{M1c}



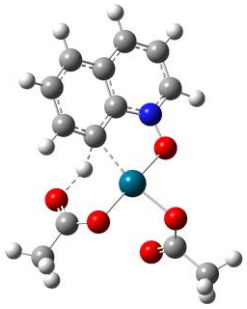
S8^{M1c}



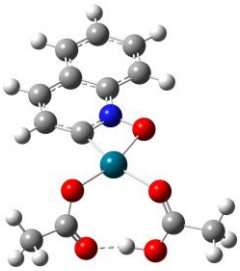
TS2^{M1c}



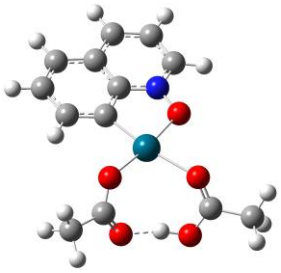
TS8^{M1c}



P2^{M1c}

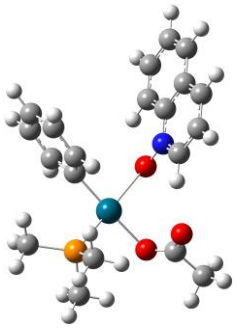


P8^{M1c}

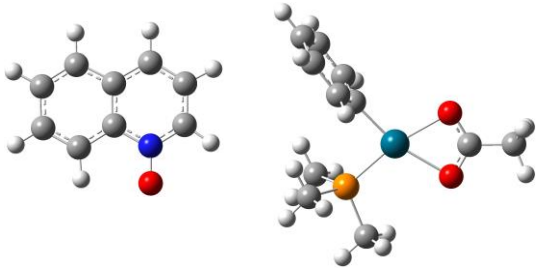


Scheme S16. Optimized Geometries of Stationary Points on the Potential Energy Surface on the C–H bond Cleavage Pathway in Mechanism 2. I2, S2, TS2 and P2 are the structures along the C2–H bond cleavage pathway. S8, TS8 and P8 are the structures along the C8–H bond cleavage pathway.

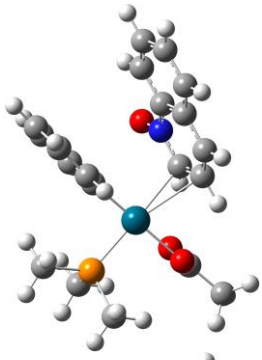
I2^{M2}



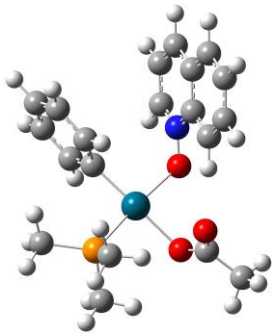
Quinoline *N*-oxide and $(PMe_3)(Ph)Pd(\kappa$-acetate)



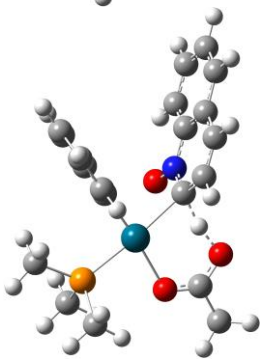
S2^{M2}



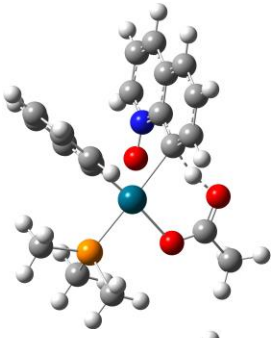
S8^{M2}



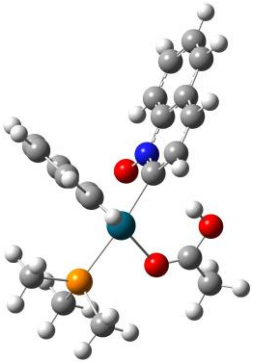
TS2^{M2}



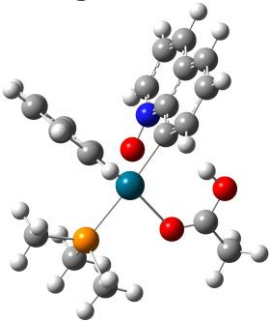
TS8^{M2}



P2^{M2}



P8^{M2}



Cartesian Coordinates of Optimized Complexes in Mechanism 1a

Quinoline *N*-oxide

C	-1.533549	-1.541164	-1.595985
H	-0.945338	-1.382164	-2.494197
C	-2.779366	-2.205912	-1.680889
H	-3.138752	-2.552308	-2.645222
C	-1.833910	-1.305683	0.777750
C	-3.090185	-1.971719	0.722343
C	-3.537702	-2.415720	-0.550457
H	-4.494328	-2.926390	-0.613307
C	-2.069716	-1.039552	3.130917
H	-1.609989	-0.650521	4.028955
C	-3.831798	-2.162289	1.916807
H	-4.789969	-2.669720	1.883571
O	-0.208621	-0.243386	2.057791
N	-1.335686	-0.840377	2.012091
C	-3.308620	-1.692933	3.099861
H	-3.839854	-1.815874	4.037666
C	-1.062150	-1.093811	-0.379709
H	-0.115602	-0.580555	-0.267884

$Pd(HOAc)_3^{2+}$

Pd	0.374527	-1.359282	-0.940920
O	2.010099	-1.887676	0.178027
O	2.825058	0.028260	1.073833
H	2.280364	0.526305	0.438460
C	2.787039	-1.265599	0.973067
C	3.730977	-2.002670	1.852817
H	4.751077	-1.851213	1.475213
H	3.698727	-1.569803	2.858168
H	3.499537	-3.066483	1.885389
O	0.843111	-2.662684	-2.461303
O	2.369200	-4.012914	-1.481060
H	2.301879	-3.403583	-0.708342
C	1.625814	-3.675006	-2.477953
C	1.696685	-4.533132	-3.692067
H	1.164550	-4.092192	-4.533886
H	2.748400	-4.699818	-3.947923

$S8^{M1a}$

Pd	0.576570	-1.083915	-0.486228
C	-0.764708	2.138862	1.182908
C	-1.942523	2.818838	1.636922
C	-2.052845	4.213009	1.381929
C	-1.048012	4.881414	0.720212
C	0.106598	4.185379	0.287264
C	0.259276	2.828890	0.510914
H	-2.938197	4.737659	1.726964
H	-1.132503	5.946535	0.533093
H	0.893499	4.729458	-0.225347
H	1.149886	2.304930	0.191215
O	2.310750	-1.914719	0.307926
O	2.473939	-0.964163	2.339789
H	1.659205	-0.461623	2.051594
C	2.900763	-1.770475	1.426561
C	4.152281	-2.520562	1.729378
H	5.006981	-1.874128	1.492275
H	4.198422	-2.751002	2.795651
H	4.225106	-3.430716	1.133657
O	0.747883	-2.323007	-2.163557
O	2.640978	-3.480208	-1.805719
H	2.672268	-2.952063	-0.965023
C	1.606528	-3.186111	-2.524365
C	1.479885	-3.902310	-3.824828
H	0.477335	-3.803989	-4.239769
H	2.206122	-3.475264	-4.527556
H	1.739589	-4.955410	-3.690704
O	-1.139534	-0.243500	-1.194791
O	-1.412900	-1.217426	-3.217440
H	-0.594337	-1.722804	-2.977695
C	-1.770203	-0.395483	-2.278762
C	-3.009548	0.391586	-2.545965
H	-2.883144	0.949595	-3.479329
H	-3.845400	-0.299701	-2.696203
H	-3.224524	1.071721	-1.724275

H	1.261809	-5.511016	-3.446925
O	-1.323217	-0.783755	-1.734386
O	-1.463861	-1.752454	-3.764604
H	-0.605190	-2.168205	-3.529317
C	-1.931920	-0.982557	-2.836122
C	-3.234834	-0.315630	-3.082329
H	-3.167786	0.253621	-4.016881
H	-3.999344	-1.089423	-3.225495
H	-3.508116	0.335949	-2.253502

S2^{M1a}

Pd	0.165451	-0.341850	-1.171037
C	-1.016737	1.898573	1.678638
C	-1.950547	2.017571	2.758598
C	-3.292998	1.628680	2.554985
C	-3.705401	1.144201	1.323327
C	-2.780061	1.047031	0.287917
H	-4.002999	1.722641	3.371384
H	-4.732636	0.852971	1.139135
H	-3.024224	0.704132	-0.709767
O	-0.134555	-1.108851	0.700942
O	1.155552	-2.967354	0.703804
H	1.292601	-2.762458	-0.253852
C	0.353548	-2.118556	1.277010
C	0.020057	-2.411843	2.701861
H	-0.531687	-3.356974	2.749660
H	0.946304	-2.552292	3.267254
H	-0.575095	-1.609789	3.133813
O	1.087019	-2.123754	-1.827228
O	0.784654	-2.050851	-4.051074
H	0.459100	-1.141344	-3.861978
C	1.185367	-2.653964	-2.969670
C	1.785610	-4.003248	-3.164127
H	1.918600	-4.520105	-2.214800
H	1.155862	-4.590365	-3.838464
H	2.759395	-3.885325	-3.654497
O	0.290914	0.481065	-3.102569
O	0.477527	2.005340	-4.704906
C	-1.623242	0.097058	2.121369
H	-1.416640	-0.953942	2.281454
C	-2.777524	0.734090	2.567059
H	-3.521605	0.157669	3.103770
C	-2.936198	2.090760	2.326587
H	-3.825827	2.606619	2.675863
O	0.468772	0.135210	1.112107
N	-0.675651	0.782456	1.460131

I8^{M1a}

Pd	0.200756	-0.764420	0.083532
C	-0.822808	1.711756	1.051301
C	-1.737191	2.677162	1.533355
C	-3.039326	2.681814	0.947115
C	-3.394068	1.765802	-0.028406
C	-2.444306	0.853117	-0.528333
C	-1.121081	0.844724	-0.055784
H	-3.762846	3.413374	1.295648
H	-4.400156	1.771899	-0.434359
H	-2.709427	0.189455	-1.345989
H	-0.366427	0.948917	-0.968249
O	1.542344	-2.363780	0.512458
O	2.692697	-1.524645	2.251810
H	2.164438	-0.707391	2.086717
C	2.410338	-2.485315	1.421907
C	3.167405	-3.753936	1.620916
H	4.229149	-3.530731	1.755405
H	2.817262	-4.228280	2.545506
H	3.022352	-4.436013	0.784347
O	-0.923444	-1.903242	-1.191552
O	0.147942	-3.894954	-1.168976
H	0.771221	-3.456125	-0.538008
C	-0.804631	-3.101895	-1.563228
C	-1.792828	-3.705269	-2.505317
H	-2.497245	-2.956917	-2.863385
H	-1.261083	-4.165561	-3.343225
H	-2.330806	-4.506295	-1.986409

H	-0.029601	1.352617	-5.223598
C	0.688256	1.619956	-3.478085
C	1.417295	2.596325	-2.622891
H	0.784662	2.859356	-1.770066
H	2.326786	2.124407	-2.236255
H	1.674156	3.488358	-3.192524
O	-0.667342	1.375441	-0.595271
N	-1.497014	1.402477	0.474041
C	0.730713	2.798932	3.055362
H	1.761616	3.113704	3.182774
C	0.323350	2.294506	1.833768
H	1.010699	2.214095	1.002834
C	-1.484543	2.539995	3.995930
H	-2.186781	2.639005	4.817671
C	-0.170287	2.922840	4.140260
H	0.179665	3.327860	5.083742

TS2[M1a]

Pd	0.075165	-1.190615	-1.434594
C	-1.591786	1.563179	0.451907
C	-2.993046	1.759014	0.187900
C	-3.565233	1.186753	-0.977822
C	-2.791287	0.472368	-1.873977
C	-1.395300	0.342177	-1.660121
H	-4.626258	1.326620	-1.163497
H	-3.223330	0.078301	-2.788029
H	-0.657363	0.603687	-2.769811
O	1.693922	-2.222623	-0.620143
O	2.281028	-3.698945	-2.225834
H	1.456225	-3.397710	-2.658669
C	2.455780	-3.110580	-1.065306
C	3.640065	-3.577510	-0.287429
H	3.500064	-4.631502	-0.023905
H	4.533909	-3.518939	-0.915863
H	3.763435	-2.980357	0.614131
O	-0.322033	-2.760435	-2.754059
O	-2.510810	-3.087313	-2.353344
H	-2.376277	-2.395620	-1.678223
O	0.601911	1.389232	-2.149929
O	1.350226	2.393981	-3.989317
H	2.130005	1.841565	-3.800104
C	0.420026	2.188261	-3.078084
C	-0.817307	3.002890	-3.312344
H	-0.547642	4.058483	-3.406895
H	-1.268717	2.704853	-4.264009
H	-1.536653	2.870703	-2.505770
C	0.803530	2.403915	2.640330
H	1.789990	2.208128	3.043789
C	-0.047277	3.416259	3.099798
H	0.305994	4.064992	3.893036
C	-1.321409	3.544197	2.573708
H	-2.004039	4.295249	2.958994
O	1.170669	0.524022	1.305081
N	0.387505	1.577870	1.669899

TS8[M1a]

Pd	0.064927	-1.193220	-1.346202
C	-0.943886	1.275665	-0.389463
C	-1.861743	2.241263	0.090466
C	-3.160899	2.243038	-0.499692
C	-3.500810	1.328885	-1.480376
C	-2.546726	0.407929	-1.966920
C	-1.224296	0.397925	-1.494395
H	-3.891693	2.966401	-0.149593
H	-4.505387	1.326267	-1.890597
H	-2.821740	-0.278150	-2.763050
H	-0.434928	0.624116	-2.528722
O	1.408334	-2.806423	-0.912085
O	2.556908	-1.962972	0.825102
H	2.025643	-1.147761	0.657239
C	2.275244	-2.926458	-0.003641
C	3.035366	-4.193018	0.199370
H	4.096314	-3.967943	0.336099
H	2.684096	-4.667895	1.123103
H	2.893331	-4.875954	-0.637058
O	-1.061670	-2.336658	-2.625995

C	-1.395177	-3.374466	-2.977624
C	-1.482934	-4.489781	-3.961019
H	-0.615967	-4.494678	-4.620316
H	-1.527408	-5.437123	-3.409253
H	-2.409224	-4.408703	-4.535335
O	-0.215686	0.916508	-3.924242
O	0.991655	2.134868	-5.324272
H	0.532338	1.581305	-5.984154
C	0.615504	1.840821	-4.110029
C	1.226447	2.688215	-3.043596
H	1.258794	2.158732	-2.090404
H	2.227509	3.002464	-3.343773
H	0.618534	3.594879	-2.933439
O	0.367087	0.445031	-0.291368
N	-0.896603	0.869774	-0.496722
C	-1.751189	2.733239	2.530821
H	-1.302095	3.115486	3.441678
C	-0.973630	2.039210	1.628428
H	0.081760	1.861265	1.795889
C	-3.741451	2.489186	1.143004
H	-4.797939	2.662508	0.965381
C	-3.131670	2.963909	2.286337
H	-3.712068	3.519923	3.015400

P2^{M1a}

Pd	0.075838	-1.029247	-0.295062
C	-1.723949	2.076870	1.171586
C	-3.153838	2.006813	1.097194
C	-3.760766	0.866896	0.513886
C	-3.007744	-0.192215	0.026071
C	-1.611197	-0.105109	0.103824
H	-4.845074	0.824130	0.459596
H	-3.484389	-1.062939	-0.407378
H	0.881271	1.742388	-0.221620
O	2.128331	-1.546370	-0.541876
O	2.126766	-3.243008	-2.028618
H	1.154764	-3.137871	-1.985415
C	2.734666	-2.395818	-1.228185
O	0.011237	-4.328316	-2.592456
H	0.632533	-3.887679	-1.959665
C	-0.942029	-3.536356	-2.990301
C	-1.928365	-4.147233	-3.930505
H	-2.634612	-3.402136	-4.291838
H	-1.395985	-4.610466	-4.766281
H	-2.465206	-4.946957	-3.408657
O	0.430672	0.948769	-3.531474
O	1.197613	1.928395	-5.367060
H	1.975082	1.373768	-5.169005
C	0.254760	1.749480	-4.475616
C	-0.971552	2.566231	-4.723683
H	-0.690147	3.618501	-4.824983
H	-1.412836	2.263694	-5.679184
H	-1.700917	2.445989	-3.924656
C	0.667567	1.960844	1.221543
H	1.649067	1.760809	1.634757
C	-0.185430	2.974501	1.675449
H	0.161030	3.620255	2.474030
C	-1.453881	3.104583	1.137782
H	-2.139989	3.854424	1.519255
O	1.046074	0.091734	-0.126060
N	0.260141	1.140634	0.244025

P8^{M1a}

Pd	0.197043	-0.752202	0.078929
C	-0.811990	1.708755	1.033451
C	-1.729993	2.681753	1.510817
C	-3.028265	2.683074	0.926355
C	-3.356280	1.776108	-0.060660
C	-2.399106	0.840553	-0.539863
C	-1.107824	0.791048	-0.019140
H	-3.763958	3.395921	1.286063
H	-4.360695	1.765673	-0.472225
H	-2.695257	0.121663	-1.299084
H	-0.157633	1.215647	-1.421436
O	1.545760	-2.372900	0.513437
O	2.690885	-1.525192	2.250178

C	4.221562	-2.529926	-1.199066
H	4.484001	-3.531623	-0.843003
H	4.617434	-2.439669	-2.215261
H	4.661277	-1.777833	-0.546789
O	-0.522149	-2.817541	-1.150040
O	-1.948456	-3.522068	0.441937
H	-1.648843	-2.718405	0.910250
C	-1.337243	-3.667120	-0.705360
C	-1.657386	-4.916307	-1.451100
H	-1.335130	-4.841506	-2.488824
H	-1.140659	-5.753680	-0.965721
H	-2.729164	-5.121426	-1.389929
O	1.333937	2.463560	-0.957405
O	2.973216	3.809784	-1.563538
H	2.392258	3.942419	-2.337776
C	2.459412	2.980888	-0.707423
C	3.276445	2.727527	0.511557
H	2.791534	2.017238	1.180257
H	4.259197	2.351078	0.209532
H	3.451003	3.678072	1.026951
O	0.331513	0.874324	0.587436
N	-1.071247	1.001941	0.623513
C	-1.833766	4.189578	2.286476
H	-1.344897	5.031862	2.765441
C	-1.064511	3.162697	1.771139
H	0.015330	3.174220	1.849472
C	-3.896158	3.092460	1.633058
H	-4.980022	3.060560	1.584053
C	-3.247737	4.161084	2.211952
H	-3.819517	4.985415	2.624212
H	2.153531	-0.712612	2.081707
C	2.409708	-2.490827	1.421369
C	3.170975	-3.756407	1.626418
H	4.231920	-3.532413	1.763864
H	2.819747	-4.231802	2.549727
H	3.028563	-4.439131	0.789944
O	-0.928664	-1.900026	-1.204733
O	0.146046	-3.891038	-1.166605
H	0.763534	-3.449031	-0.529766
C	-0.808839	-3.098308	-1.564844
C	-1.794152	-3.711881	-2.505061
H	-2.501006	-2.966903	-2.865518
H	-1.262981	-4.176369	-3.340772
H	-2.331760	-4.511110	-1.983538
O	0.584261	1.382446	-2.114026
O	1.328327	2.358436	-3.928569
H	2.114067	1.806936	-3.741501
C	0.382330	2.202974	-3.067584
C	-0.842860	3.003789	-3.294906
H	-0.558833	4.056325	-3.399644
H	-1.280663	2.701009	-4.253619
H	-1.570808	2.879315	-2.494996
C	0.801237	2.395180	2.648088
H	1.781773	2.195062	3.063110
C	-0.052242	3.411741	3.100504
H	0.293842	4.057057	3.899441
C	-1.318282	3.542065	2.561037
H	-2.004650	4.291358	2.943162
O	1.183810	0.531592	1.297003
N	0.394993	1.576416	1.673848

Cartesian Coordinates of Optimized Complexes in Mechanism 1b

Quinoline *N*-oxide

C	-1.533549	-1.541164	-1.595985
H	-0.945338	-1.382164	-2.494197
C	-2.779366	-2.205912	-1.680889
H	-3.138752	-2.552308	-2.645222
C	-1.833910	-1.305683	0.777750
C	-3.090185	-1.971719	0.722343
C	-3.537702	-2.415720	-0.550457
H	-4.494328	-2.926390	-0.613307
C	-2.069716	-1.039552	3.130917
H	-1.609989	-0.650521	4.028955
C	-3.831798	-2.162289	1.916807
H	-4.789969	-2.669720	1.883571
O	-0.208621	-0.243386	2.057791
N	-1.335686	-0.840377	2.012091
C	-3.308620	-1.692933	3.099861
H	-3.839854	-1.815874	4.037666
C	-1.062150	-1.093811	-0.379709
H	-0.115602	-0.580555	-0.267884

Pd(κ-acetate)(HOAc)$^+$

Pd	1.019756	2.727233	0.080735
O	-0.157723	4.791521	0.397282
O	-1.075436	2.870053	0.060225
O	1.583561	0.824662	-0.217145
O	2.996711	2.416096	0.073623
C	-1.290679	4.069803	0.255061
C	-2.627221	4.713045	0.336076
H	-2.756028	5.186293	1.316346
H	-3.400596	3.959521	0.189147
H	-2.717556	5.488886	-0.432803
C	2.828133	1.157314	-0.141155
C	3.936628	0.194172	-0.310238
H	4.812190	0.533469	0.247827
H	4.198961	0.142649	-1.373865
H	3.623589	-0.799613	0.017634

S8^{M1b}

Pd	0.468442	-1.391546	-1.135781
C	-0.555170	1.937562	-0.063668
C	-0.687459	2.840761	1.035025
C	-1.966222	3.405243	1.286327
C	-3.037695	3.089531	0.481998
C	-2.875160	2.203746	-0.610091
C	-1.651664	1.628025	-0.891611
H	-2.078150	4.092372	2.119153
H	-4.011558	3.525998	0.677073
H	-3.726317	1.978155	-1.244453
H	-1.517175	0.967101	-1.737817
O	-0.754103	-1.750353	-2.762134
O	-0.114376	-3.344268	-1.426767
C	-0.772914	-2.994741	-2.487781
C	-1.480590	-3.998004	-3.328305
H	-0.739325	-4.573788	-3.893515
H	-2.030246	-4.695927	-2.691698
H	-2.154145	-3.498905	-4.025690
H	0.972524	-3.726586	-0.021943
O	1.561128	-3.737243	0.766621
O	1.649737	-1.481969	0.560375
C	1.962126	-2.547879	1.138212
C	2.856418	-2.543403	2.336701
H	3.775272	-3.088269	2.097245
H	3.094577	-1.523188	2.631652
H	2.368595	-3.076002	3.157873
C	0.453350	3.146848	1.814584
C	1.674957	2.580134	1.510131
H	2.567795	2.809314	2.079354
C	1.771086	1.690233	0.435725
H	2.686972	1.205718	0.125367
H	0.358013	3.838033	2.646372
O	0.859748	0.572937	-1.363282
N	0.696063	1.381239	-0.298826

H	-0.260099	5.745493	0.555011

S2^{M1b}

Pd	0.509868	-1.039370	-0.511600
C	-1.667566	3.246494	0.401754
C	-1.920432	3.669086	-0.924427
C	-1.188604	3.145586	-1.972287
C	-0.203052	2.190160	-1.710472
H	-2.690749	4.411928	-1.107326
H	-1.354501	3.456701	-2.996582
H	0.418685	1.735514	-2.471198
O	-1.416355	-1.067294	-1.252572
O	-0.296725	-2.898949	-0.900225
C	-1.393988	-2.344972	-1.296650
C	-2.552111	-3.156248	-1.762271
H	-2.229169	-3.832041	-2.559582
H	-2.915492	-3.773570	-0.934335
H	-3.352453	-2.507189	-2.118189
H	1.382281	-3.545673	-0.384464
O	2.298561	-3.689514	-0.063788
O	2.400797	-1.439729	0.196101
C	2.910059	-2.577569	0.273819
C	4.306447	-2.762233	0.773919
H	4.907323	-3.237892	-0.007409
H	4.738292	-1.801792	1.049098
H	4.297143	-3.438673	1.633713
O	1.032500	0.888745	-0.251271
N	0.036298	1.773327	-0.461040
C	-0.651870	2.269782	0.636785
C	-1.061098	2.354940	2.997896
H	-0.833518	2.027632	4.007291
C	-2.079236	3.317349	2.792639
H	-2.621957	3.712114	3.645027
C	-0.346733	1.830342	1.939304
H	0.444621	1.107426	2.084744
C	-2.375986	3.756129	1.522353
H	-3.149546	4.499175	1.355977

TS2^{M1b}

I8^{M1b}

Pd	0.401265	-0.527854	-0.284466
C	-0.260449	2.270379	0.203948
C	-0.969863	3.399700	0.690916
C	-2.360115	3.483180	0.392210
C	-2.989936	2.503879	-0.345389
C	-2.251661	1.424397	-0.881425
C	-0.890837	1.300982	-0.629540
H	-2.917536	4.339503	0.759496
H	-4.050414	2.581757	-0.559223
H	-2.716829	0.712751	-1.553611
H	-0.336200	0.743610	-1.444320
O	-1.384872	-0.902007	-2.690879
O	-0.766961	-2.047967	-0.861045
C	-1.396599	-1.935545	-2.041172
C	-2.113217	-3.198786	-2.457327
H	-1.383588	-3.991872	-2.651435
H	-2.773555	-3.546198	-1.657993
H	-2.686635	-3.008413	-3.364023
H	0.037758	-3.251186	-0.273720
O	0.754194	-3.828987	0.149004
O	1.808324	-1.850192	0.426934
C	1.759487	-3.103361	0.531758
C	2.915935	-3.842422	1.127971
H	3.326281	-4.525687	0.377851
H	3.683918	-3.146607	1.461075
H	2.561065	-4.451370	1.964526
C	-0.267599	4.368623	1.449056
C	1.075540	4.187171	1.711641
H	1.646392	4.912080	2.279559
C	1.718981	3.018007	1.287500
H	2.745284	2.762273	1.519503
H	-0.793009	5.241971	1.821296
O	1.665707	0.929571	0.318315
N	1.046149	2.091996	0.593630

TS8^{M1b}

Pd	-0.789975	-0.219213	0.053905
C	-2.977454	3.775448	1.097613
C	-3.887578	3.024538	0.312898
C	-3.481152	1.869489	-0.324759
C	-2.137964	1.451729	-0.230117
H	-4.910312	3.373927	0.209677
H	-4.152502	1.305407	-0.960709
H	-1.908937	0.700638	-1.271840
O	-2.304776	-0.105657	-2.387516
O	-1.599227	-1.737668	-1.027347
C	-2.169238	-1.323245	-2.127154
C	-2.645234	-2.383204	-3.080505
H	-1.779353	-2.786159	-3.617600
H	-3.113683	-3.205199	-2.535292
H	-3.337807	-1.952758	-3.802851
H	-0.534483	-2.934490	-0.517393
O	0.218787	-3.418288	-0.085828
O	0.735594	-1.399533	0.794805
C	0.955449	-2.623820	0.642874
C	2.121776	-3.272603	1.317361
H	2.748038	-3.761216	0.565199
H	2.698389	-2.534473	1.871784
H	1.756022	-4.052407	1.992711
O	-0.123561	1.538566	0.802630
N	-1.301554	2.156375	0.569227
C	-1.637523	3.300533	1.251503
C	-1.095261	5.110407	2.718123
H	-0.387980	5.639777	3.348064
C	-2.410820	5.619079	2.568556
H	-2.690330	6.530206	3.087087
C	-0.698916	3.958717	2.072359
H	0.302554	3.558583	2.168297
C	-3.332696	4.968452	1.778804
H	-4.341617	5.353128	1.669144

P2^{M1b}

Pd	0.401507	-0.707567	-0.112919
C	-1.721146	3.281007	0.901868

Pd	-0.786063	-0.183184	0.030177
C	-1.407540	2.595074	0.279344
C	-2.052728	3.840382	0.506984
C	-3.461993	3.894893	0.316084
C	-4.163036	2.766376	-0.044573
C	-3.485205	1.556360	-0.322379
C	-2.098189	1.446718	-0.226207
H	-3.975009	4.837806	0.478082
H	-5.240834	2.807721	-0.160339
H	-4.054652	0.717131	-0.706054
H	-1.828493	0.737571	-1.286908
O	-2.246120	-0.105707	-2.454001
O	-1.908259	-1.637411	-0.861452
C	-2.328710	-1.283692	-2.049689
C	-2.918256	-2.373279	-2.904219
H	-2.111406	-3.028245	-3.250520
H	-3.610796	-2.982105	-2.318269
H	-3.421452	-1.941333	-3.768207
H	-1.011187	-2.941747	-0.336955
O	-0.297111	-3.523093	0.042264
O	0.662793	-1.560676	0.621969
C	0.661870	-2.810352	0.573357
C	1.800037	-3.597646	1.141956
H	2.225275	-4.235264	0.361343
H	2.560196	-2.929426	1.542430
H	1.422220	-4.256700	1.929729
C	-1.277803	4.939822	0.948958
C	0.071443	4.772101	1.192316
H	0.694865	5.592132	1.528087
C	0.649928	3.505023	1.060479
H	1.675356	3.266139	1.313141
H	-1.754583	5.901501	1.108071
O	0.460648	1.241987	0.683699
N	-0.092150	2.468011	0.650859

P8^{M1b}

Pd	0.297883	-0.462832	0.010861
C	-0.331691	2.228557	0.514620

C	-2.543345	2.532032	0.021701	C	-0.986879	3.481354	0.647741
C	-2.141012	1.298311	-0.465912	C	-2.339732	3.545598	0.219304
C	-0.885526	0.799062	-0.080643	C	-2.957743	2.421316	-0.282762
H	-3.507616	2.939981	-0.267367	C	-2.268872	1.182646	-0.402253
H	-2.779451	0.729004	-1.131430	C	-0.944305	1.066464	-0.023121
H	-0.593496	-0.159921	-2.407906	H	-2.877391	4.484678	0.301351
O	-1.006242	-0.822597	-3.003163	H	-3.995867	2.473612	-0.595851
O	-0.439429	-2.204001	-1.328851	H	-2.813941	0.327678	-0.790269
C	-0.940652	-2.014697	-2.458952	H	-0.555797	-0.177335	-2.353857
C	-1.493186	-3.125600	-3.287963	O	-1.047414	-0.866263	-2.854288
H	-0.811681	-3.311212	-4.125832	O	-0.938109	-1.916828	-0.873104
H	-1.597133	-4.031919	-2.693353	C	-1.297436	-1.888159	-2.071283
H	-2.455853	-2.829144	-3.711601	C	-2.034137	-3.017071	-2.712898
H	0.540589	-3.586768	-0.484435	H	-1.367894	-3.510559	-3.429260
O	1.302431	-4.068859	-0.103166	H	-2.362295	-3.734662	-1.962493
O	2.072612	-1.986086	0.299728	H	-2.886963	-2.631018	-3.276855
C	2.214740	-3.217678	0.334174	H	-0.084499	-3.309544	0.164536
C	3.445052	-3.864716	0.886076	O	0.647078	-3.877257	0.479361
H	3.868577	-4.547504	0.144271	O	1.842212	-1.974238	0.273784
H	4.172393	-3.105443	1.167643	C	1.773948	-3.181860	0.536020
H	3.171929	-4.464305	1.760426	C	2.965133	-3.985390	0.954540
O	1.017698	0.843886	1.034781	H	3.055268	-4.874773	0.325166
N	-0.143207	1.528006	0.753795	H	3.865664	-3.377050	0.892064
C	-0.454541	2.744994	1.292317	H	2.819093	-4.329409	1.983728
C	0.009450	4.645692	2.662349	C	-0.253226	4.559522	1.203143
H	0.658461	5.188817	3.341653	C	1.054362	4.366454	1.604701
C	-1.238560	5.209661	2.293587	H	1.637829	5.171945	2.034466
H	-1.524463	6.175501	2.696663	C	1.658502	3.106723	1.471523
C	0.412359	3.420980	2.172283	H	2.671119	2.872679	1.774613
H	1.361328	2.972635	2.440365	H	-0.726496	5.529804	1.314592
C	-2.085794	4.546197	1.434379	O	1.536454	0.880602	0.833201
H	-3.041591	4.977399	1.153292	N	0.962890	2.097102	0.944674

Cartesian Coordinates of Optimized Complexes in Mechanism 1c

Quinoline *N*-oxide

C	-1.533549	-1.541164	-1.595985

Pd(κ-acetate)$_2$

Pd	3.667302	1.895074	0.249431

H	-0.945338	-1.382164	-2.494197
C	-2.779366	-2.205912	-1.680889
H	-3.138752	-2.552308	-2.645222
C	-1.833910	-1.305683	0.777750
C	-3.090185	-1.971719	0.722343
C	-3.537702	-2.415720	-0.550457
H	-4.494328	-2.926390	-0.613307
C	-2.069716	-1.039552	3.130917
H	-1.609989	-0.650521	4.028955
C	-3.831798	-2.162289	1.916807
H	-4.789969	-2.669720	1.883571
O	-0.208621	-0.243386	2.057791
N	-1.335686	-0.840377	2.012091
C	-3.308620	-1.692933	3.099861
H	-3.839854	-1.815874	4.037666
C	-1.062150	-1.093811	-0.379709
H	-0.115602	-0.580555	-0.267884
O	3.317854	3.898765	0.599476
O	1.726759	2.547716	-0.010614
O	4.016374	-0.108933	-0.099011
O	5.607504	1.242088	0.511082
C	5.253747	0.056558	0.183290
C	6.237787	-1.066540	0.104092
H	7.053932	-0.900524	0.809552
H	6.656535	-1.101147	-0.907575
H	5.739328	-2.016787	0.303755
C	2.082895	3.735731	0.305405
C	1.116058	4.876421	0.300689
H	0.109470	4.515831	0.519942
H	1.110787	5.333323	-0.694920
H	1.424099	5.632255	1.025347

S2[M1c]

Pd	0.313891	-1.604315	-0.211673
C	-0.654968	1.993541	1.155952
C	-1.157279	3.232252	0.661881
C	-0.800921	3.644320	-0.646212
C	0.022573	2.847728	-1.409602
C	0.515251	1.637860	-0.896603
H	-1.183772	4.584465	-1.031401
H	0.316665	3.130575	-2.413721
H	1.183964	0.956046	-1.430260
O	-1.781188	-1.747202	-0.213337
O	-0.509599	-3.284859	-1.110965
C	-1.683935	-2.860054	-0.837146
C	-2.899593	-3.629977	-1.260061
H	-3.097003	-3.432610	-2.319204
H	-2.720784	-4.701336	-1.145829
H	-3.766820	-3.319753	-0.675212
O	2.480683	-0.364929	-1.996435
O	2.273270	-1.939905	-0.383684
C	2.936540	-1.263428	-1.279724

S8[M1c]

Pd	-0.181854	-1.811500	-0.108333
C	-1.008124	2.054464	0.277949
C	-0.531917	3.304762	-0.212551
C	-1.477078	4.347630	-0.401314
C	-2.809128	4.146212	-0.118676
C	-3.256745	2.892582	0.362838
C	-2.374134	1.852219	0.563350
H	-1.125850	5.305665	-0.773077
H	-3.523502	4.949967	-0.266872
H	-4.311025	2.746814	0.576168
H	-2.690812	0.885388	0.930387
O	-1.129726	-1.436042	-1.939755
O	-0.137079	-3.338931	-1.516483
C	-0.808413	-2.613075	-2.326375
C	-1.232283	-3.137892	-3.665746
H	-0.496596	-3.852484	-4.039544
H	-2.190578	-3.657437	-3.557327
H	-1.363384	-2.313815	-4.369307
O	2.585476	-1.348196	1.136218

C	4.388537	-1.707601	-1.394692
H	4.943477	-1.006704	-2.019529
H	4.845300	-1.778326	-0.404164
H	4.427445	-2.704519	-1.845313
O	0.688918	0.117454	0.850659
N	0.179279	1.241869	0.336617
C	-2.324830	3.536782	2.770506
H	-2.973359	4.125094	3.412077
C	-1.816631	2.299898	3.234980
H	-2.083595	1.950582	4.227435
C	-0.988972	1.530043	2.445058
H	-0.587802	0.581902	2.776538
C	-2.003380	3.992423	1.512040
H	-2.391024	4.939045	1.147302

TS2^{M1c}

Pd	-0.930339	-0.291655	0.172400
C	-1.640859	3.405307	1.092543
C	-2.902055	4.004145	0.812112
C	-3.837211	3.289744	0.020101
C	-3.509166	2.051485	-0.484245
C	-2.239986	1.480614	-0.241710
H	-4.806163	3.733781	-0.187342
H	-4.191775	1.496062	-1.116556
H	-2.088257	0.550528	-1.152501
O	-2.520769	-0.294505	-2.205530
O	-1.780692	-1.866186	-0.776848
C	-2.371628	-1.502275	-1.853251
C	-2.882291	-2.603478	-2.749578
H	-2.092312	-2.851498	-3.466607
H	-3.110632	-3.497974	-2.168883
H	-3.756871	-2.263736	-3.306346
O	1.510691	-1.439036	-0.955334
O	0.409195	-1.495901	1.016058
C	1.391824	-1.828729	0.200216
C	2.384883	-2.777152	0.858993
H	3.223814	-2.952926	0.184794
H	2.742641	-2.357759	1.803410
O	0.746164	-2.629933	1.456339
C	1.961734	-2.239393	1.723794
C	2.590598	-3.022433	2.868486
H	3.557880	-2.590183	3.127240
H	1.928805	-3.016614	3.738876
H	2.724337	-4.066052	2.567196
O	-0.558098	-0.114416	0.993006
C	0.849160	3.450255	-0.494732
H	1.218266	4.398192	-0.874204
C	1.701548	2.389628	-0.284821
H	2.763686	2.464486	-0.487288
C	1.211136	1.171846	0.211462
H	1.821408	0.289378	0.424391
N	-0.093058	1.026738	0.473630

TS8^{M1c}

Pd	-0.913128	-0.231358	0.133041
C	-1.432892	2.610197	0.234961
C	-2.014710	3.899216	0.417143
C	-3.414864	4.028217	0.212925
C	-4.167347	2.931089	-0.134424
C	-3.549121	1.681487	-0.373409
C	-2.179416	1.484982	-0.233601
H	-3.873945	5.002829	0.348150
H	-5.240316	3.027037	-0.268769
H	-4.150713	0.862474	-0.751469
H	-1.938752	0.607293	-1.188580
O	-2.407153	-0.260944	-2.294344
O	-2.112778	-1.700090	-0.597166
C	-2.516732	-1.408340	-1.780279
C	-3.132615	-2.534561	-2.575289
H	-2.320016	-3.079109	-3.067766
H	-3.654932	-3.230253	-1.916567
H	-3.803132	-2.140599	-3.339969
O	1.017743	-1.987986	-1.243957
O	0.321924	-1.622522	0.874464
C	1.040623	-2.235421	-0.042212
C	1.927662	-3.322873	0.552344

H	1.890542	-3.726163	1.088127
O	-0.253892	1.521910	0.883720
N	-1.379457	2.163286	0.545343
C	-2.217459	5.910775	2.152489
H	-2.425069	6.890463	2.571161
C	-0.977328	5.283674	2.426489
H	-0.248946	5.789187	3.052547
C	-0.682256	4.040372	1.908912
H	0.257149	3.538916	2.102766
C	-3.159035	5.285839	1.365443
H	-4.113446	5.760168	1.157408

P2^{M1c}

Pd	-0.034779	-0.871679	0.110761
C	-0.536144	2.758850	1.260419
C	-1.744589	3.370048	0.812726
C	-2.641641	2.613338	0.009048
C	-2.353331	1.308277	-0.338797
C	-1.153426	0.724734	0.110607
H	-3.562184	3.082061	-0.328069
H	-3.028867	0.720573	-0.949385
H	1.489260	-2.327962	-1.962899
O	0.224573	-2.316789	-2.682957
O	-1.248903	-2.075221	-0.983229
C	-0.899691	-2.473497	-2.153882
C	-1.971742	-3.212871	-2.934590
H	-1.697177	-4.270929	-2.996085
H	-2.948941	-3.122089	-2.459814
H	-2.005872	-2.825855	-3.956122
O	2.433620	-2.552261	-1.568068
O	1.508258	-2.311536	0.478117
C	2.441350	-2.656022	-0.274380
C	3.702546	-3.244882	0.302813
H	3.867117	-4.242095	-0.115133
H	4.555243	-2.625132	0.009606
H	3.634774	-3.296056	1.388602
O	0.768019	0.735802	1.210932
N	-0.333949	1.461317	0.868244
H	2.569145	-3.740538	-0.224619
H	2.537025	-2.914929	1.363717
H	1.303240	-4.114036	0.979028
O	0.411317	1.220253	0.662172
C	-1.192836	4.980113	0.818294
H	-1.629939	5.966061	0.938989
C	0.146066	4.762790	1.066270
H	0.806934	5.565821	1.370836
C	0.668579	3.468912	0.975381
H	1.684472	3.195385	1.228124
N	-0.109972	2.440745	0.607865

P8^{M1c}

Pd	-0.050201	-0.584759	0.226672
C	-0.434614	2.175330	0.596831
C	-0.978540	3.490257	0.630022
C	-2.300581	3.646364	0.139519
C	-2.992138	2.549641	-0.334029
C	-2.416569	1.253037	-0.351629
C	-1.128258	1.039082	0.107180
H	-2.753772	4.633024	0.145778
H	-4.005727	2.678804	-0.704161
H	-2.991112	0.411707	-0.725096
H	0.985246	-2.480674	-1.814489
O	-0.374370	-2.397971	-2.350196
O	-1.560171	-1.709843	-0.548260
C	-1.426253	-2.308153	-1.677827
C	-2.698167	-2.924771	-2.235192
H	-2.468342	-3.881771	-2.708158
H	-3.452346	-3.051279	-1.457587
H	-3.097842	-2.261658	-3.010574
O	1.946000	-2.777955	-1.531173
O	1.356246	-2.198767	0.569140
C	2.127665	-2.739076	-0.244625
C	3.386984	-3.418536	0.230586
H	3.378970	-4.467439	-0.079251
H	4.252103	-2.946445	-0.244736
H	3.470851	-3.344795	1.314032

C	-1.063051	5.388423	1.983798
H	-1.253169	6.416660	2.275246
C	0.127673	4.751596	2.411992
H	0.835475	5.299655	3.026281
C	0.399292	3.446275	2.059198
H	1.300578	2.932812	2.371053
C	-1.977489	4.714424	1.203472
H	-2.890932	5.201800	0.874670
O	1.323796	0.715019	1.034411
C	-0.173839	4.536185	1.146883
H	-0.565817	5.547971	1.181986
C	1.099264	4.258089	1.602237
H	1.737888	5.036477	2.003651
C	1.599757	2.947986	1.557490
H	2.583032	2.652167	1.898401
N	0.843261	1.959604	1.069134

Cartesian Coordinates of Optimized Complexes in Mechanism 2

Quinoline *N*-oxide

C	-1.533549	-1.541164	-1.595985
H	-0.945338	-1.382164	-2.494197
C	-2.779366	-2.205912	-1.680889
H	-3.138752	-2.552308	-2.645222
C	-1.833910	-1.305683	0.777750
C	-3.090185	-1.971719	0.722343
C	-3.537702	-2.415720	-0.550457
H	-4.494328	-2.926390	-0.613307
C	-2.069716	-1.039552	3.130917
H	-1.609989	-0.650521	4.028955
C	-3.831798	-2.162289	1.916807
H	-4.789969	-2.669720	1.883571
O	-0.208621	-0.243386	2.057791
N	-1.335686	-0.840377	2.012091
C	-3.308620	-1.692933	3.099861
H	-3.839854	-1.815874	4.037666
C	-1.062150	-1.093811	-0.379709
H	-0.115602	-0.580555	-0.267884

(PMe_3)(Ph)Pd(κ-acetate)

Pd	1.901812	0.258164	-0.641798
C	0.724242	2.639858	-3.997058
C	1.479083	1.975665	-3.023810
C	0.856980	1.394175	-1.907205
C	-0.537447	1.505336	-1.784065
C	-1.290115	2.169993	-2.758739

$I2^{M2}$

Pd	1.122385	0.573175	0.621723
C	-1.582167	2.808150	-1.873406
C	-0.538970	1.988234	-1.423137
C	-0.232861	1.884036	-0.055346
C	-0.997485	2.648140	0.847367
C	-2.039495	3.464530	0.399659
C	-2.335368	3.550302	-0.963402
H	0.029461	1.417631	-2.155204
H	-2.620001	4.039085	1.118253
H	-3.142618	4.190525	-1.308646
H	-1.801359	2.863018	-2.937307
H	-0.790992	2.594868	1.914656
P	2.797534	1.948518	0.046874
C	2.542270	3.772779	-0.091488
C	3.459802	1.462362	-1.610128
C	4.238385	1.776258	1.191550
H	3.471045	4.268016	-0.388375
H	1.758104	3.965016	-0.825330
H	2.211198	4.157991	0.875711
H	4.347713	2.046669	-1.874136
H	3.697152	0.396727	-1.584453
H	2.681286	1.626108	-2.358061
H	5.141754	2.225433	0.767612
H	3.998819	2.265917	2.139132
H	4.381094	0.712631	1.388337

C	-0.661888	2.741661	-3.866516
H	2.556149	1.897658	-3.150407
H	-2.370098	2.236086	-2.650406
H	-1.246992	3.258194	-4.622259
H	1.223714	3.074383	-4.859712
H	-1.047694	1.057427	-0.934799
P	2.241429	2.091521	0.625169
C	0.736986	2.904427	1.331096
C	3.160323	3.490433	-0.162984
C	3.259479	1.679705	2.115192
H	1.011360	3.766765	1.946194
H	0.089753	3.223830	0.511856
H	0.193360	2.180171	1.942761
H	3.290552	4.317872	0.541033
H	4.140277	3.134622	-0.490560
H	2.603494	3.831567	-1.037989
H	3.427401	2.564639	2.736735
H	2.744612	0.911380	2.696376
H	4.217793	1.269383	1.788914
O	2.908527	-1.421848	0.351290
C	2.510010	-2.187200	-0.588038
O	1.815298	-1.709562	-1.545502
C	2.835515	-3.659935	-0.566136
H	1.925474	-4.224888	-0.338690
H	3.181219	-3.978594	-1.552777
H	3.591129	-3.876938	0.190047
O	2.470041	-0.861389	1.406913
C	2.715565	-1.888957	0.663175
O	2.326745	-2.034106	-0.516974
C	3.539610	-2.981877	1.335466
H	2.899467	-3.522224	2.042167
H	3.923705	-3.684849	0.594697
H	4.361263	-2.550472	1.914440
H	0.337426	-1.904892	-0.802359
C	-0.747038	-2.024107	-0.794839
C	-1.459782	-2.684758	-1.808416
H	-0.894417	-3.055827	-2.656018
N	-1.376927	-1.540459	0.287605
O	-0.728828	-0.946721	1.256991
C	-2.821316	-2.859044	-1.720097
H	-3.377395	-3.371717	-2.498429
C	-3.504004	-2.359382	-0.582990
C	-2.763436	-1.683298	0.428191
C	-4.905318	-2.494579	-0.396851
H	-5.481980	-3.008276	-1.160686
C	-3.400346	-1.160349	1.571717
H	-2.794331	-0.649943	2.307878
C	-5.521274	-1.985142	0.724261
H	-6.593770	-2.096960	0.852143
C	-4.763994	-1.312251	1.711224
H	-5.261983	-0.907303	2.586860

S2^{M2}

Pd	0.932825	-0.028749	-0.156731
C	-2.237459	2.686530	-1.160393
C	-1.172133	1.782153	-1.228835
C	-0.513718	1.354519	-0.062802
C	-0.937435	1.873273	1.171891
C	-2.000702	2.781195	1.237918
C	-2.651442	3.192908	0.073225
H	-0.862232	1.402087	-2.199974
H	-2.319494	3.163329	2.204741
H	-3.474138	3.900818	0.126232

S8^{M2}

Pd	0.987463	0.502355	0.727464
C	-2.257592	2.623556	-1.164526
C	-1.168131	1.777942	-0.923939
C	-0.473061	1.808214	0.299536
C	-0.907234	2.734040	1.268104
C	-1.996774	3.579819	1.031307
C	-2.677021	3.528508	-0.187375
H	-0.861358	1.082209	-1.702393
H	-2.309972	4.283697	1.799641
H	-3.519645	4.188734	-0.374871

H	-2.740118	2.996747	-2.073608	H	-2.776661	2.575068	-2.119435
H	-0.461550	1.547779	2.093373	H	-0.390553	2.796283	2.223913
P	2.484977	1.616262	-0.360239	P	2.537393	1.771439	-0.309741
C	2.010111	3.352612	-0.777071	C	2.192221	3.539574	-0.732758
C	3.759235	1.182416	-1.626517	C	3.016419	1.008717	-1.925771
C	3.420142	1.771566	1.226552	C	4.118849	1.857249	0.644413
H	2.900656	3.987585	-0.814560	H	3.047981	3.986007	-1.248645
H	1.504314	3.370314	-1.744574	H	1.306347	3.592665	-1.368305
H	1.316240	3.726988	-0.022545	H	1.986361	4.096404	0.184324
H	4.620675	1.854180	-1.561813	H	3.919643	1.474332	-2.332828
H	4.059857	0.147284	-1.457394	H	3.162686	-0.061953	-1.763635
H	3.312445	1.255337	-2.621223	H	2.191776	1.136107	-2.631901
H	4.308001	2.398955	1.098327	H	4.914960	2.314534	0.048931
H	2.761779	2.218012	1.975883	H	3.956584	2.445329	1.551254
H	3.694190	0.772244	1.571701	H	4.388467	0.841556	0.937061
O	2.467065	-1.509061	-0.400264	O	2.526295	-0.834226	1.327309
C	2.998979	-1.952446	0.701672	C	2.743495	-1.865689	0.578214
O	2.692377	-1.566214	1.838553	O	2.251140	-2.058778	-0.548145
C	4.068891	-3.022773	0.500736	C	3.675818	-2.907034	1.194944
H	4.886820	-2.627400	-0.110608	H	3.116977	-3.486507	1.938288
H	4.458395	-3.356883	1.463141	H	4.049881	-3.587968	0.428240
H	3.648617	-3.874625	-0.043210	H	4.507764	-2.427174	1.717386
H	0.332802	-1.927056	1.500253	H	0.093431	-2.255767	-0.310876
C	-0.493633	-1.818697	0.803157	C	-0.949818	-2.389428	-0.580637
C	-0.491743	-2.316506	-0.521820	C	-1.305054	-3.155588	-1.672848
H	0.437517	-2.732056	-0.893785	H	-0.522941	-3.638424	-2.250259
N	-1.644133	-1.343730	1.373311	C	-2.659406	-3.315848	-2.049528
O	-1.653285	-0.948966	2.579970	H	-2.909599	-3.927316	-2.911353
C	-1.635524	-2.286226	-1.293673	C	-1.971504	-1.756762	0.157625
H	-1.635699	-2.666634	-2.309674	C	-3.344796	-1.892479	-0.204915
C	-2.824622	-1.759498	-0.734674	C	-3.658325	-2.696576	-1.332232
C	-2.820274	-1.282878	0.608343	H	-4.700771	-2.808914	-1.616050
C	-4.051619	-1.688297	-1.449626	C	-2.596691	-0.346908	1.971854
H	-4.073824	-2.047789	-2.474412	H	-2.223482	0.237944	2.800678
C	-3.984931	-0.761370	1.206590	C	-4.333508	-1.225008	0.559919
H	-3.918026	-0.414033	2.229211	H	-5.378944	-1.324786	0.284942
C	-5.185303	-1.177649	-0.859765	O	-0.390596	-0.889536	1.657431

H	-6.113788	-1.131347	-1.421193
C	-5.152155	-0.709968	0.476800
H	-6.053564	-0.307006	0.927924

TS2^{M2}

Pd	0.556021	-0.118317	0.064234
C	-1.995188	2.542620	-2.160977
C	-1.010999	1.613486	-1.804569
C	-0.856534	1.201205	-0.470404
C	-1.718501	1.743603	0.496897
C	-2.700398	2.674681	0.139217
C	-2.840663	3.081002	-1.189286
H	-0.364535	1.207214	-2.579490
H	-3.360423	3.077947	0.903917
H	-3.602907	3.804711	-1.464924
H	-2.098701	2.844012	-3.201045
H	-1.641575	1.415811	1.530860
P	2.129546	1.568323	0.149261
C	1.657154	3.325629	-0.174630
C	3.553841	1.274253	-0.998793
C	2.935543	1.630726	1.814950
H	2.524744	3.983979	-0.069658
H	1.243925	3.410993	-1.181421
H	0.878609	3.621535	0.531768
H	4.348772	2.010384	-0.842815
H	3.937543	0.268857	-0.813137
H	3.204283	1.331311	-2.032574
H	3.766568	2.342956	1.829029
H	2.192498	1.920621	2.561836
H	3.295648	0.627880	2.052543
O	2.211471	-1.422060	0.647548
C	2.000398	-2.660868	0.800157
O	0.882124	-3.230561	0.592534
C	3.137752	-3.534589	1.287980
H	3.008946	-3.705755	2.362112
H	3.107372	-4.506602	0.791600
H	4.099211	-3.047231	1.121555
H	0.002044	-2.333564	0.302314

N	-1.648188	-0.976143	1.268208
C	-3.953314	-0.456917	1.636241
H	-4.678113	0.075975	2.240688

TS8^{M2}

Pd	0.624419	-0.092644	0.175335
C	-2.199292	2.480917	-1.823621
C	-1.198785	1.538625	-1.559999
C	-0.811647	1.242661	-0.242419
C	-1.458500	1.922916	0.803521
C	-2.458772	2.865727	0.539841
C	-2.832160	3.151097	-0.774874
H	-0.724359	1.025824	-2.393338
H	-2.946751	3.376533	1.367162
H	-3.607797	3.884087	-0.979726
H	-2.483615	2.689044	-2.852850
H	-1.184778	1.707586	1.833569
P	2.209116	1.570900	0.019198
C	1.731928	3.304028	-0.414083
C	3.541915	1.170628	-1.204699
C	3.144177	1.762931	1.607099
H	2.612363	3.953323	-0.436150
H	1.240206	3.308946	-1.388871
H	1.015004	3.672901	0.322259
H	4.353645	1.904049	-1.164701
H	3.926624	0.175362	-0.973009
H	3.114522	1.156373	-2.210375
H	3.962413	2.483233	1.506916
H	2.456674	2.095526	2.388577
H	3.539838	0.784663	1.887746
O	2.325758	-1.390895	0.630363
C	2.112050	-2.607129	0.893204
O	0.970163	-3.168382	0.815559
C	3.268007	-3.467518	1.357344
H	3.237139	-3.528543	2.450565
H	3.169935	-4.481215	0.964027
H	4.220491	-3.028496	1.057548
H	0.114960	-2.313365	0.502125

C	-1.088607	-1.633864	0.011079
C	-1.709644	-2.004620	-1.214184
H	-1.057927	-2.112802	-2.076118
N	-1.883100	-1.507353	1.122274
O	-1.376786	-1.151067	2.242865
C	-3.055775	-2.233465	-1.330955
H	-3.507066	-2.511793	-2.278410
C	-3.870256	-2.111922	-0.172953
C	-3.266937	-1.752280	1.063314
C	-5.270719	-2.339371	-0.179733
H	-5.745834	-2.614161	-1.117300
C	-4.032625	-1.624709	2.239587
H	-3.519925	-1.346728	3.151082
C	-6.014573	-2.215866	0.974319
H	-7.085789	-2.393661	0.950176
C	-5.391550	-1.857037	2.192020
H	-5.987271	-1.762942	3.094922

P2^{M2}

Pd	0.876065	0.389231	-0.221886
C	-1.038669	3.262294	-2.785302
C	-0.243772	2.215104	-2.303794
C	-0.299683	1.829838	-0.954200
C	-1.187244	2.510721	-0.104207
C	-1.977734	3.559193	-0.586636
C	-1.905513	3.941821	-1.927953
H	0.424118	1.700004	-2.990476
H	-2.658290	4.071920	0.089335
H	-2.522237	4.754594	-2.301771
H	-0.978059	3.544027	-3.834297
H	-1.271339	2.210301	0.937055
P	2.711974	1.884757	-0.040983
C	2.431535	3.694671	-0.314503
C	4.142486	1.518182	-1.169994
C	3.505550	1.839443	1.636184
H	3.359651	4.261250	-0.193135
H	2.027661	3.848998	-1.317273
H	1.686732	4.049479	0.401630

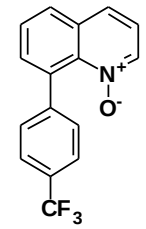
C	-1.031836	-1.652499	0.132236
C	-1.490437	-2.068752	-1.117520
H	-0.768520	-2.211083	-1.918480
C	-2.851800	-2.330766	-1.386373
H	-3.158836	-2.643475	-2.380733
C	-2.020889	-1.527008	1.147594
C	-3.400340	-1.806089	0.923482
C	-3.787661	-2.202095	-0.384857
H	-4.837498	-2.410186	-0.573017
C	-2.530860	-1.023821	3.427768
H	-2.113841	-0.705769	4.373794
C	-4.335031	-1.694217	1.983879
H	-5.382446	-1.914639	1.803882
O	-0.388569	-0.818258	2.668618
N	-1.619931	-1.116010	2.435078
C	-3.885939	-1.310182	3.226161
H	-4.560920	-1.213831	4.069892

P8^{M2}

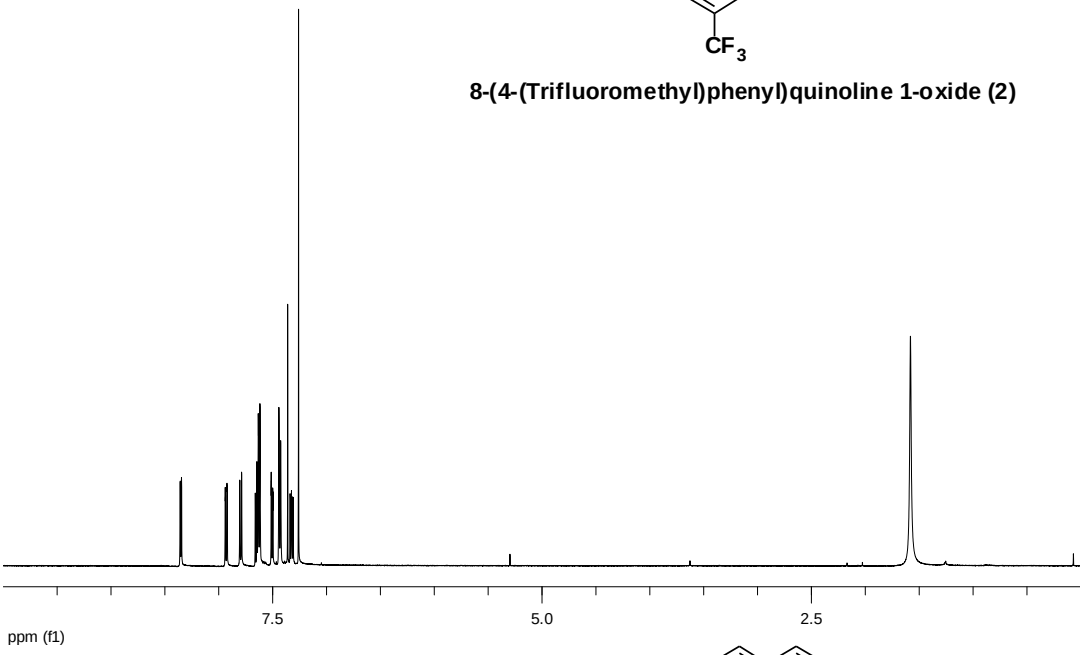
Pd	0.644191	0.225654	-0.362100
C	-1.727942	2.967281	-2.689780
C	-0.856508	1.940735	-2.307754
C	-0.652779	1.630932	-0.952829
C	-1.361377	2.373361	0.007472
C	-2.232136	3.399682	-0.374978
C	-2.418195	3.703550	-1.725236
H	-0.334871	1.377794	-3.078050
H	-2.769528	3.959586	0.387495
H	-3.095470	4.499955	-2.021842
H	-1.867310	3.188087	-3.745977
H	-1.234219	2.144301	1.062551
P	2.425692	1.781891	-0.379454
C	2.089740	3.556916	-0.790127
C	3.821193	1.356522	-1.531021
C	3.289128	1.899078	1.260813
H	3.004128	4.155869	-0.740010
H	1.659599	3.618545	-1.792220
H	1.350524	3.949853	-0.088531

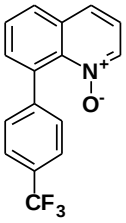
H	4.987152	2.188003	-0.979873	H	4.664240	2.046000	-1.419531
H	4.458247	0.483455	-1.015916	H	4.149793	0.337261	-1.315469
H	3.820459	1.630649	-2.208505	H	3.458779	1.392691	-2.561676
H	4.397926	2.471720	1.679839	H	4.151718	2.571904	1.220945
H	2.781084	2.180509	2.380172	H	2.578824	2.258453	2.009613
H	3.770494	0.805276	1.865847	H	3.614120	0.897808	1.552368
O	2.317539	-1.157014	0.612177	O	2.298355	-1.269532	0.201142
C	2.126333	-2.375042	0.642566	C	2.149105	-2.474408	0.407676
O	1.076799	-2.962601	0.100270	O	1.013330	-3.116696	0.200617
C	3.072706	-3.329860	1.315844	C	3.250760	-3.355160	0.931770
H	2.608973	-3.689094	2.240338	H	3.017129	-3.638663	1.963136
H	3.253519	-4.198261	0.677925	H	3.313504	-4.274060	0.343672
H	4.008206	-2.824882	1.553230	H	4.199259	-2.819973	0.908977
H	0.463793	-2.254207	-0.233194	H	0.333260	-2.457316	-0.098389
C	-0.839717	-0.777853	-0.344443	C	-1.027353	-1.032777	-0.399080
C	-1.545669	-1.180140	-1.507888	C	-1.549991	-1.535597	-1.591537
H	-1.084710	-0.951586	-2.463814	H	-1.009119	-1.355940	-2.517117
N	-1.420181	-1.028728	0.865178	C	-2.774292	-2.239738	-1.666396
O	-0.823164	-0.677229	1.958910	H	-3.125040	-2.608970	-2.626787
C	-2.760548	-1.825646	-1.466980	C	-1.810798	-1.286188	0.766188
H	-3.273580	-2.125595	-2.376140	C	-3.073989	-1.957842	0.721420
C	-3.352256	-2.086262	-0.205365	C	-3.531507	-2.433162	-0.534754
C	-2.664299	-1.676308	0.969709	H	-4.485196	-2.951822	-0.578429
C	-4.603900	-2.738042	-0.046301	C	-2.083923	-1.048590	3.137364
H	-5.138699	-3.055394	-0.937463	H	-1.618258	-0.683399	4.042722
C	-3.210357	-1.907779	2.248719	C	-3.832689	-2.142214	1.905496
H	-2.644363	-1.571802	3.107653	H	-4.791364	-2.648820	1.852893
C	-5.131499	-2.962665	1.206523	O	-0.163158	-0.334204	2.149941
H	-6.090623	-3.461744	1.310682	N	-1.330401	-0.872163	2.031416
C	-4.429322	-2.544089	2.361230	C	-3.334663	-1.674378	3.098363
H	-4.854205	-2.724914	3.344267	H	-3.881874	-1.787561	4.028205

^{1}H and ^{13}C NMR Spectral Data

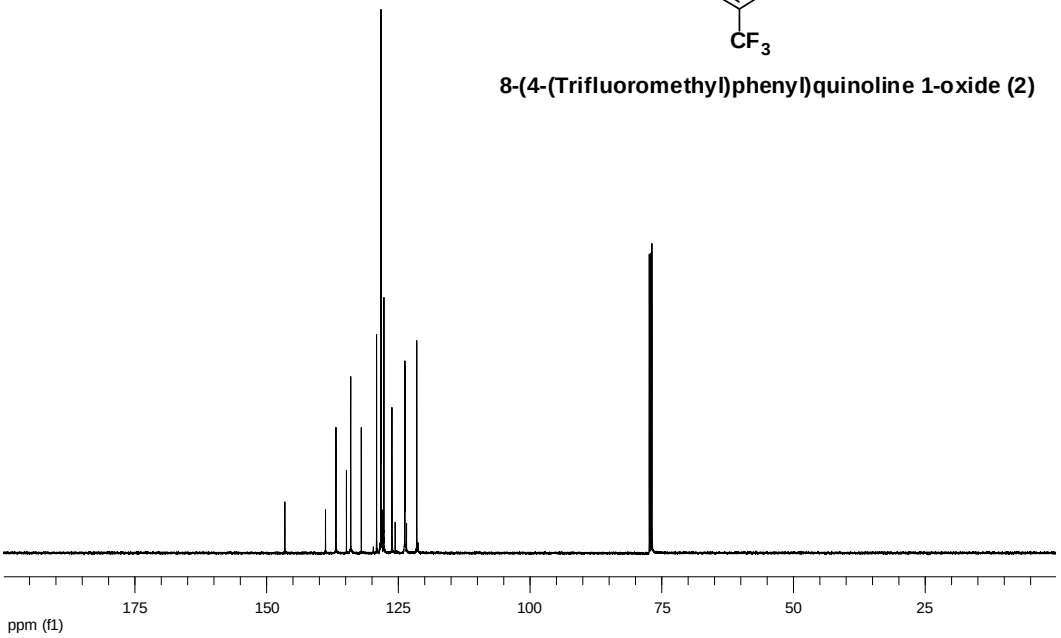


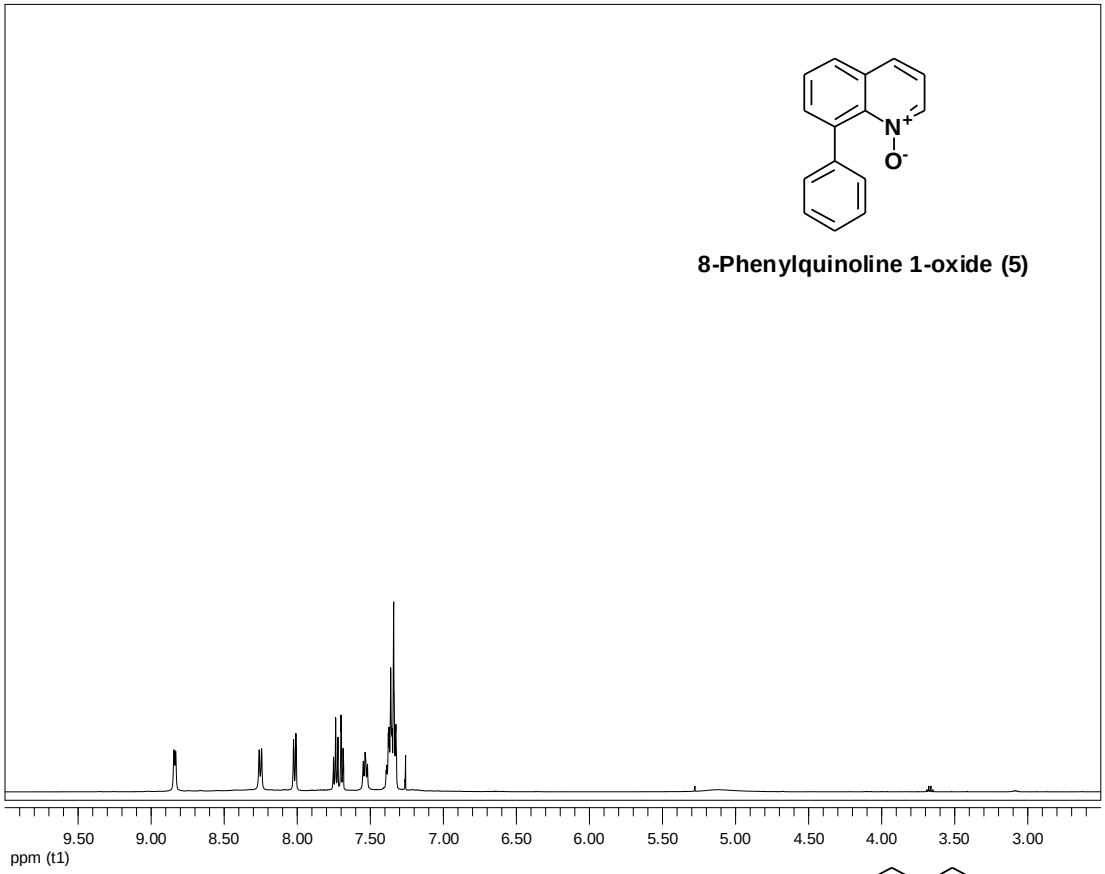
8-(4-(Trifluoromethyl)phenyl)quinoline 1-oxide (2)



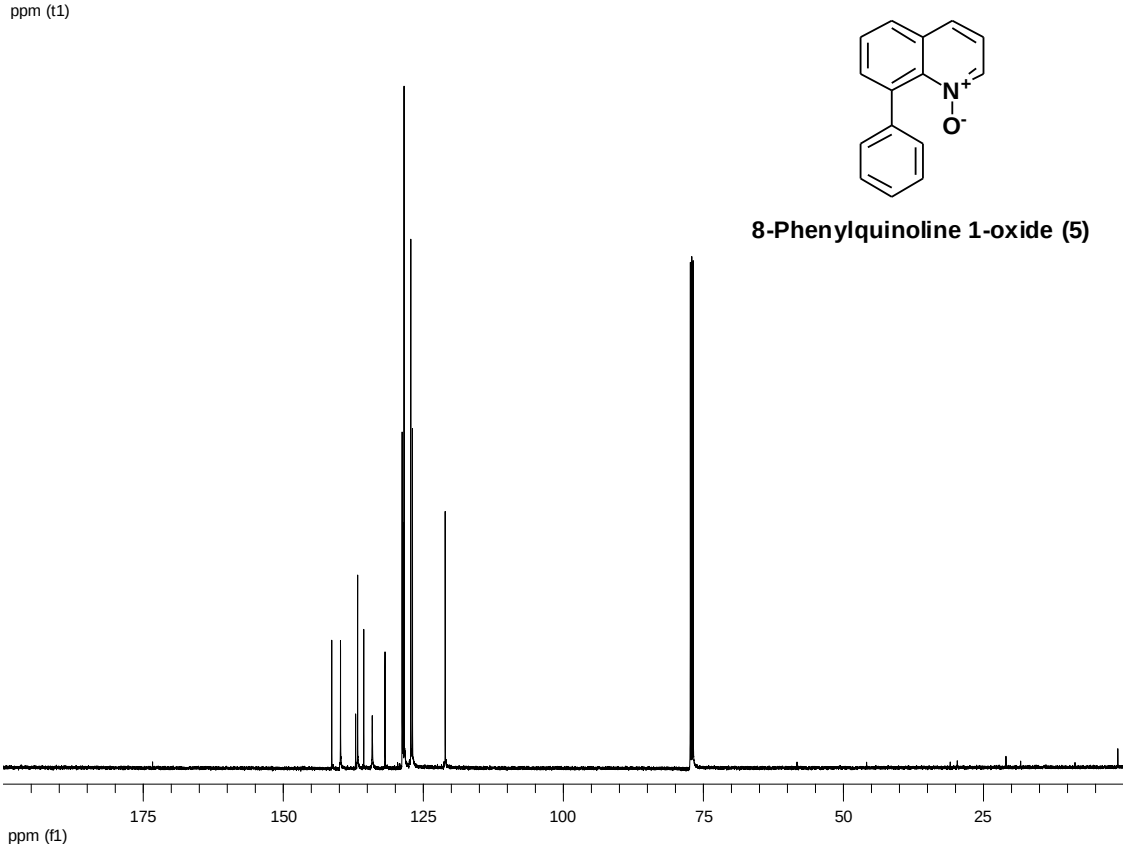


8-(4-(Trifluoromethyl)phenyl)quinoline 1-oxide (2)

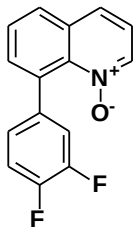




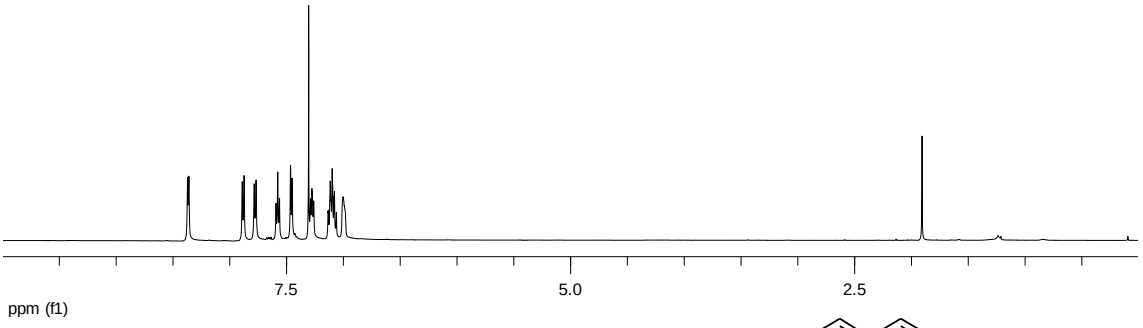
8-Phenylquinoline 1-oxide (5)

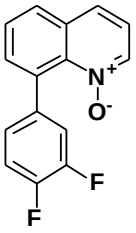


8-Phenylquinoline 1-oxide (5)

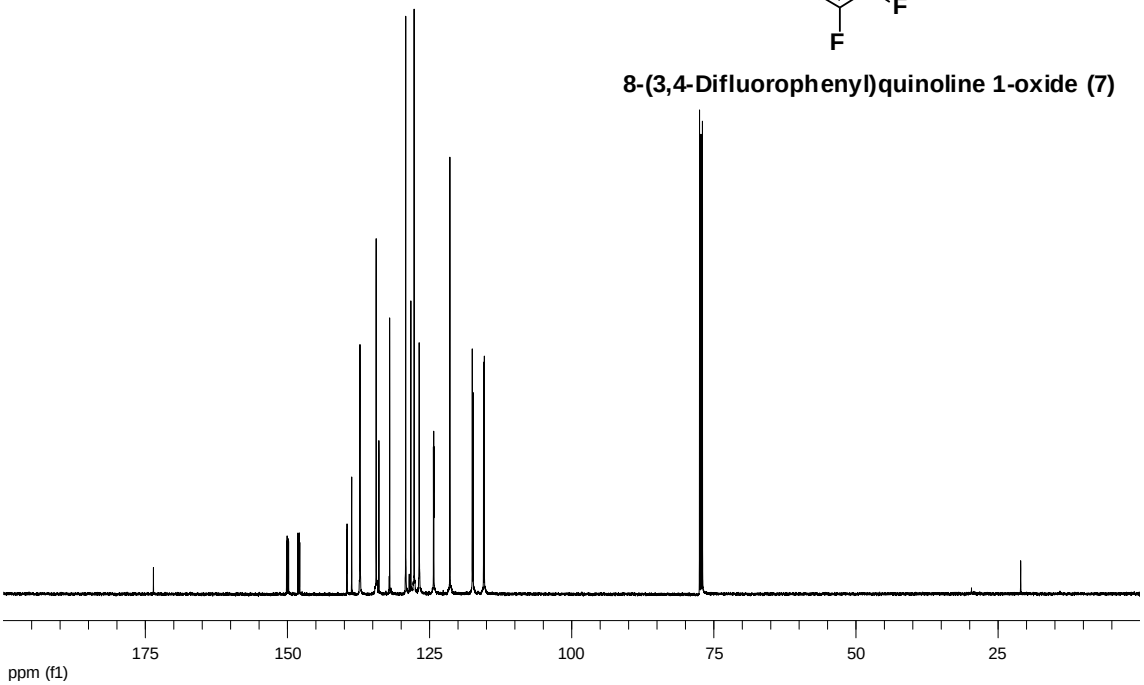


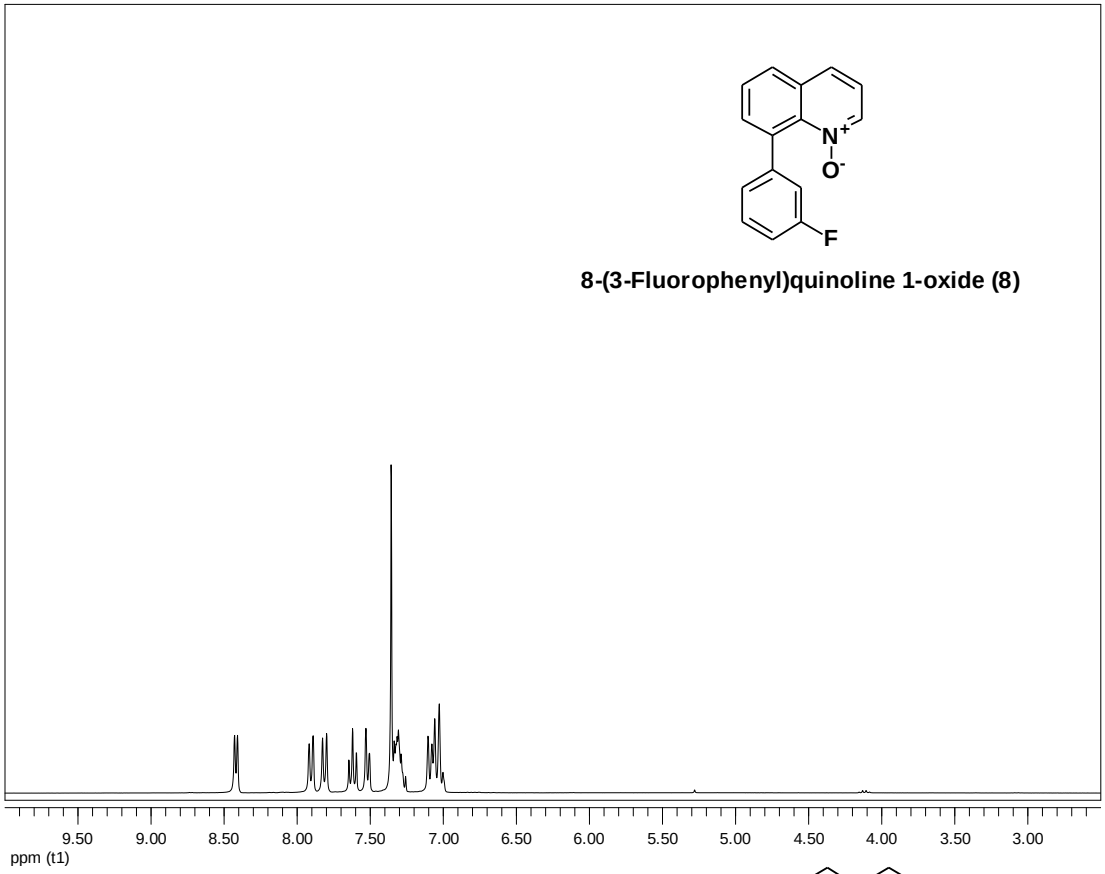
8-(3,4-Difluorophenyl)quinoline 1-oxide (7)



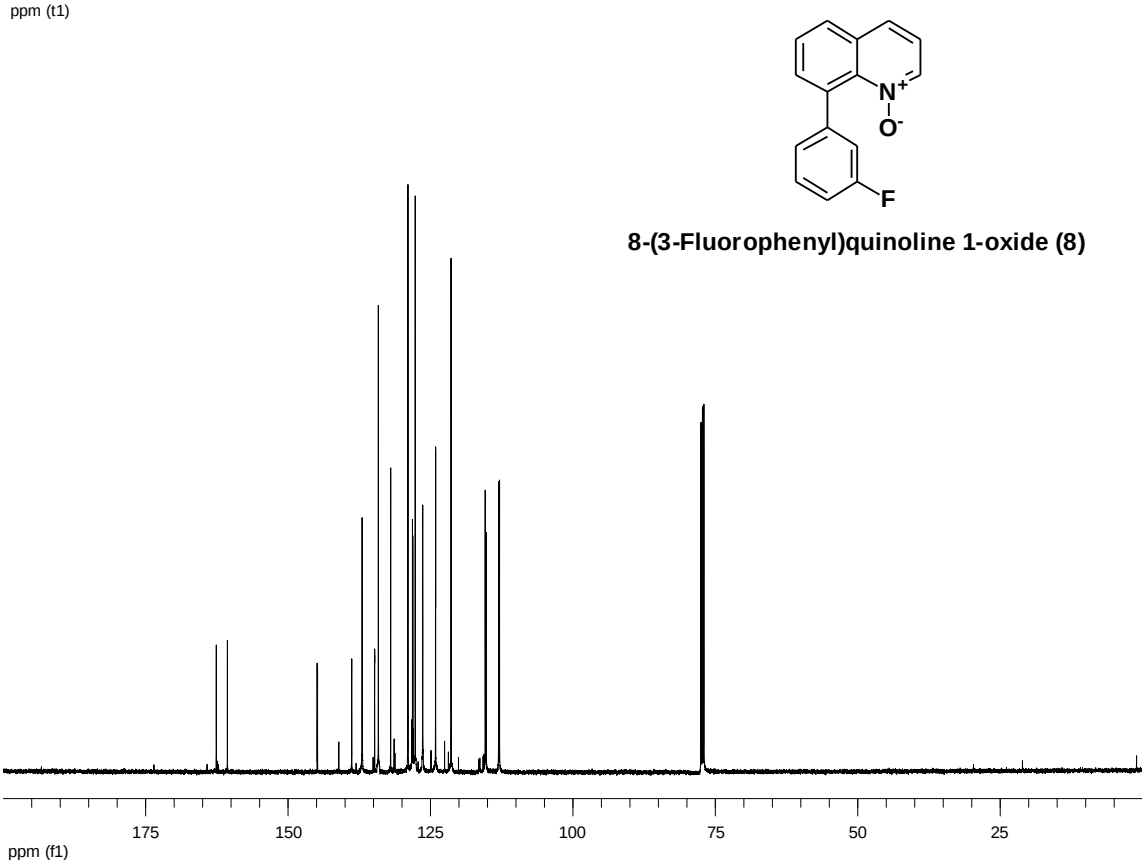


8-(3,4-Difluorophenyl)quinoline 1-oxide (7)

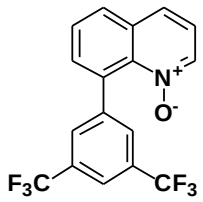




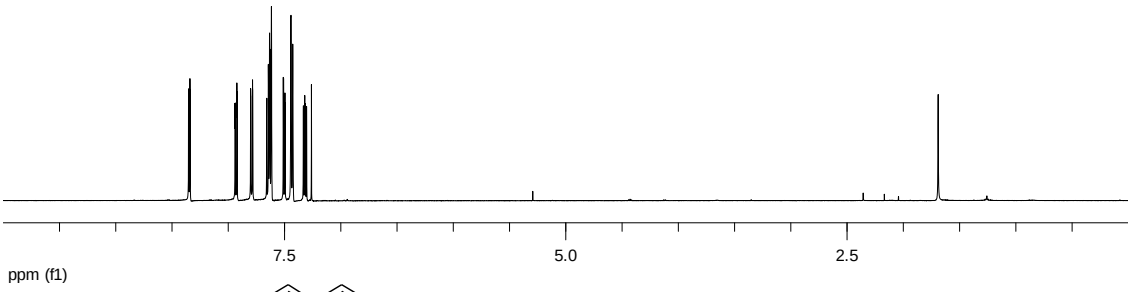
8-(3-Fluorophenyl)quinoline 1-oxide (8)

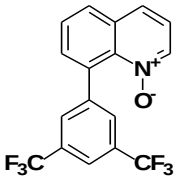


8-(3-Fluorophenyl)quinoline 1-oxide (8)

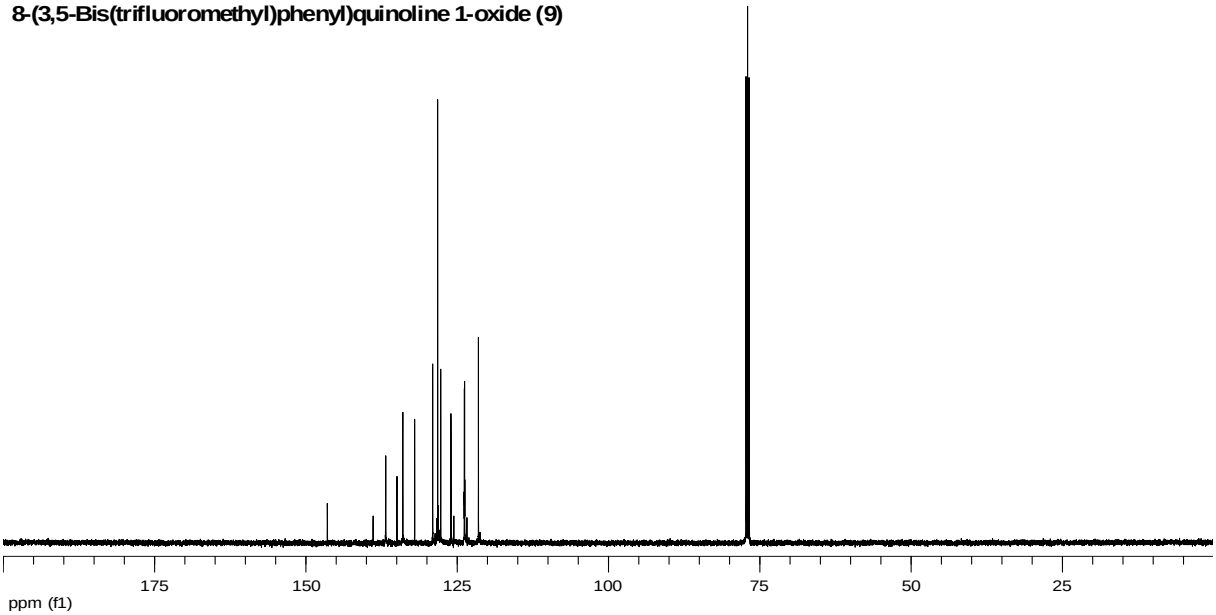


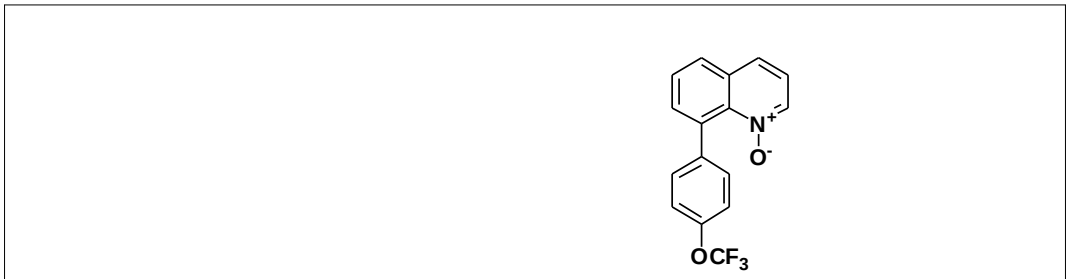
8-(3,5-Bis(trifluoromethyl)phenyl)quinoline 1-oxide (9)



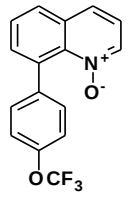


8-(3,5-Bis(trifluoromethyl)phenyl)quinoline 1-oxide (9)

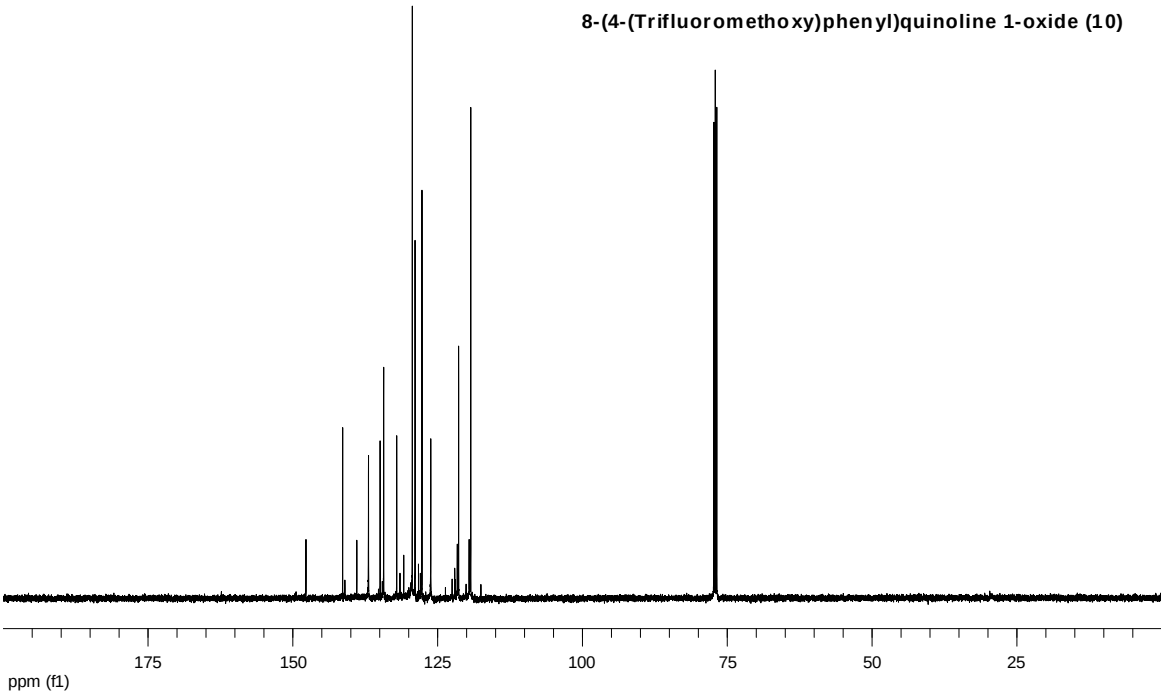


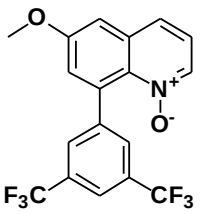


8-(4-(Trifluoromethoxy)phenyl)quinoline 1-oxide (10)

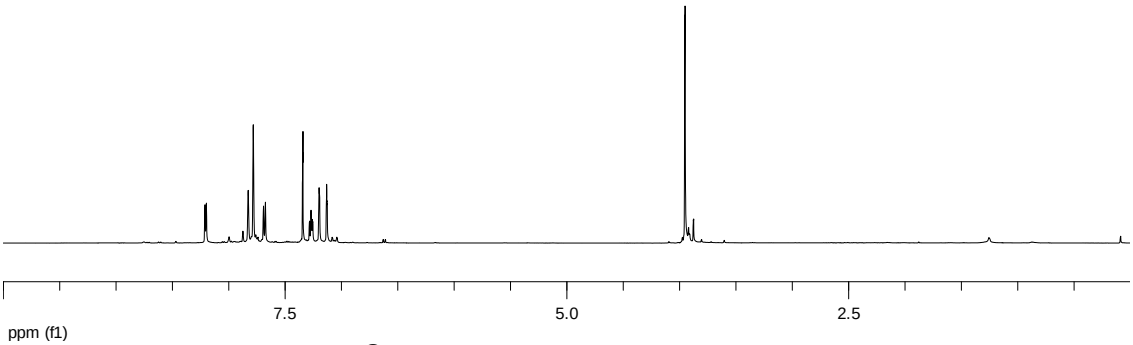


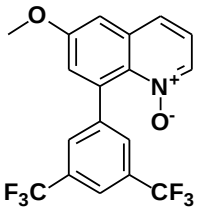
8-(4-(Trifluoromethoxy)phenyl)quinoline 1-oxide (10)



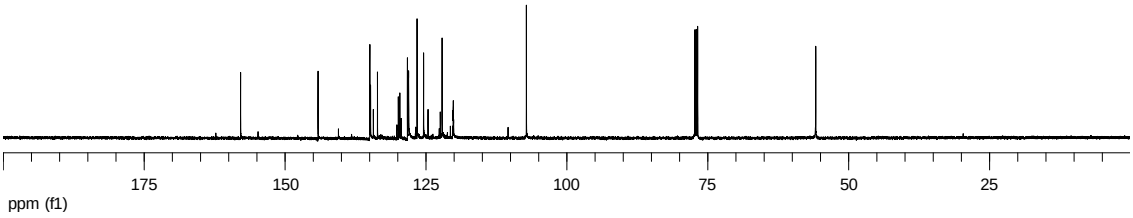


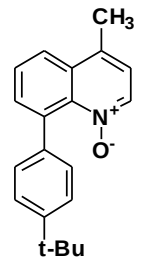
8-(3,5-Bis(trifluoromethyl)phenyl)-6-methoxyquinoline 1-oxide (11)



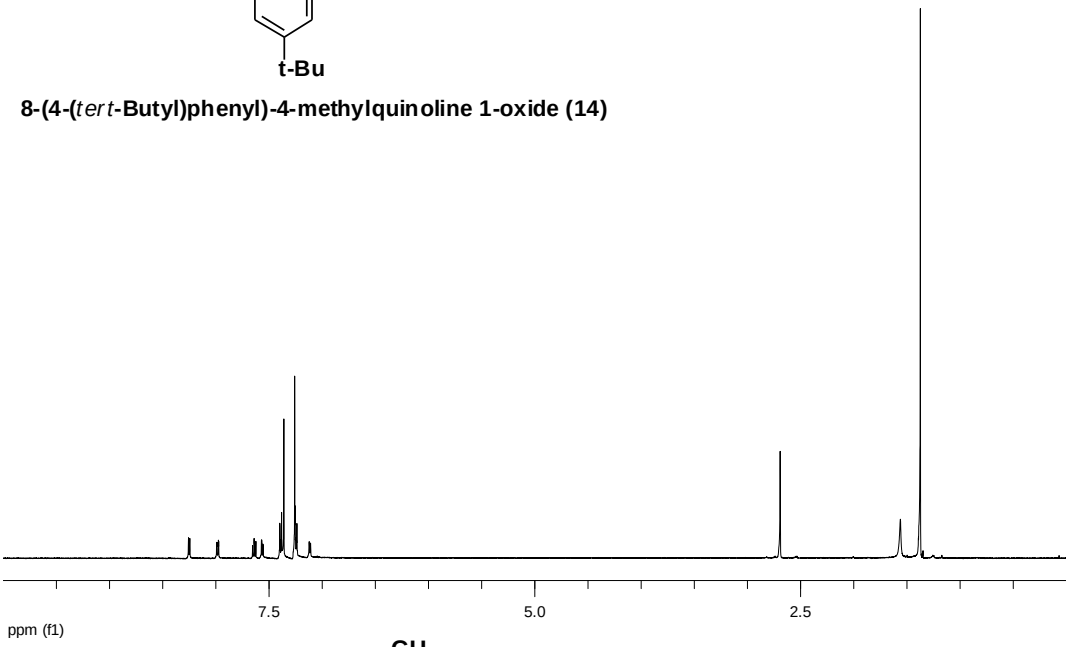


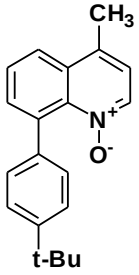
8-(3,5-Bis(trifluoromethyl)phenyl)-6-methoxyquinoline 1-oxide (11)



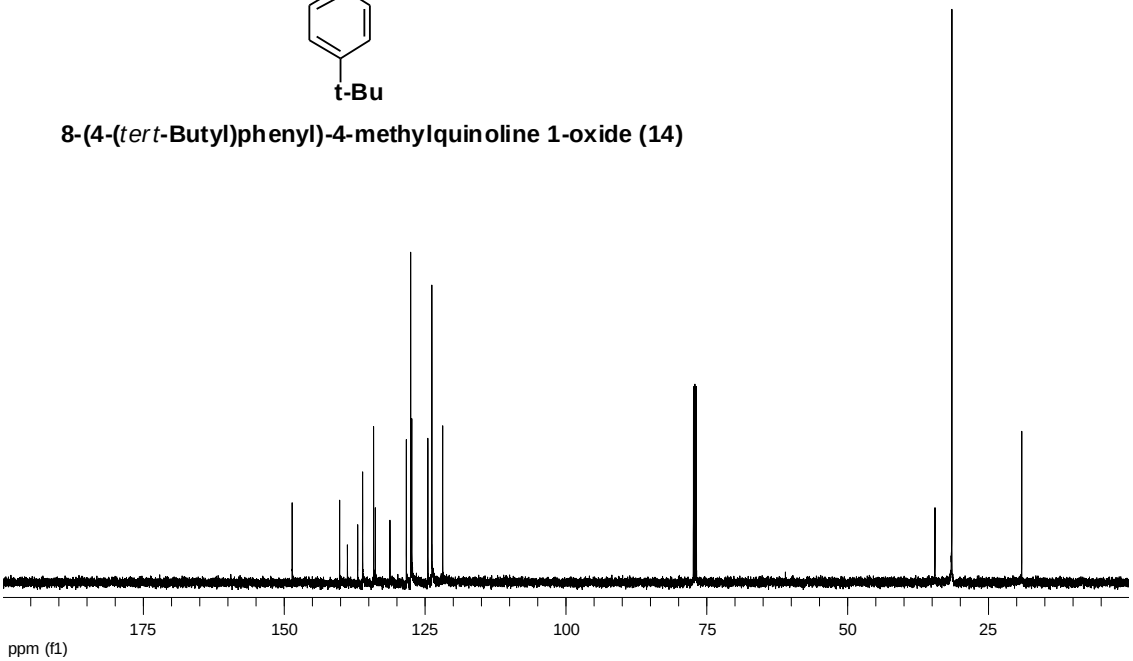


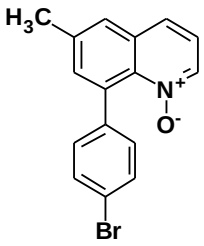
8-(4-(*tert*-Butyl)phenyl)-4-methylquinoline 1-oxide (14)



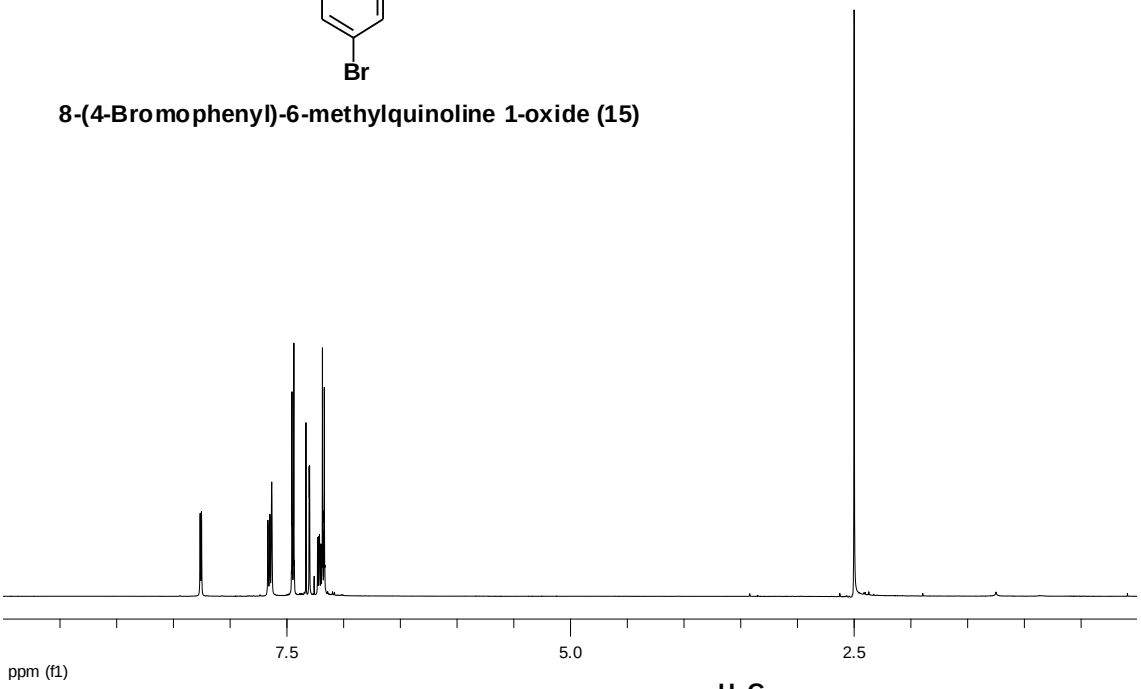


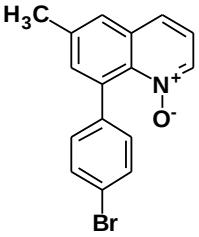
8-(4-(*tert*-Butyl)phenyl)-4-methylquinoline 1-oxide (14)



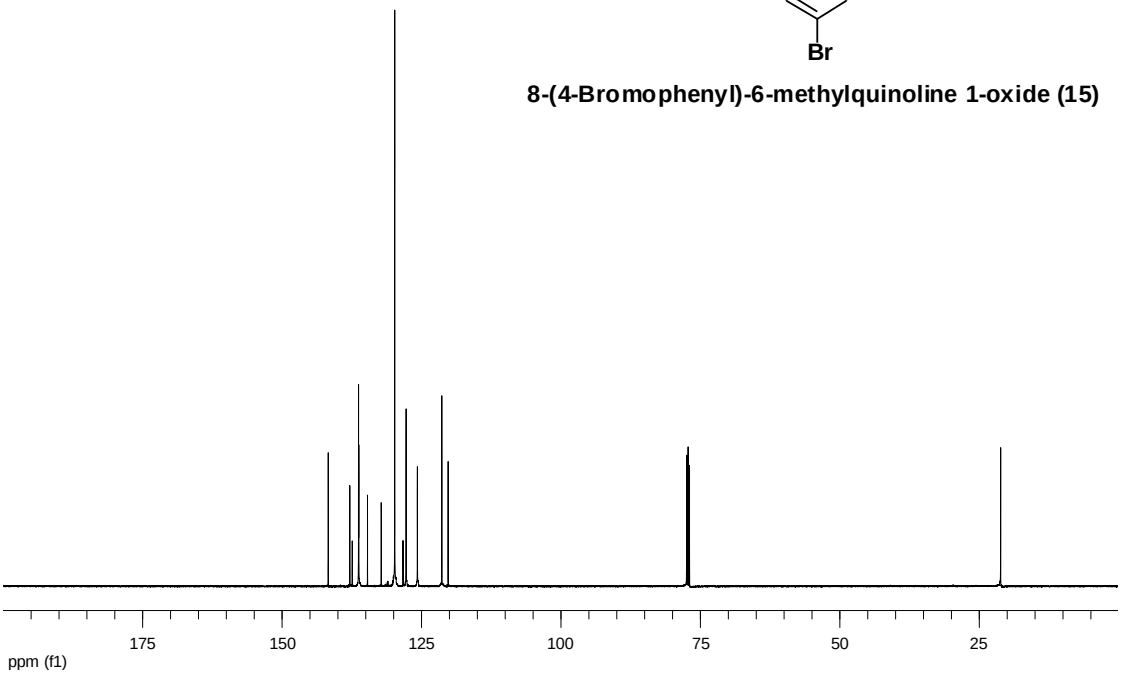


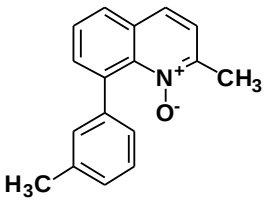
8-(4-Bromophenyl)-6-methylquinoline 1-oxide (15)



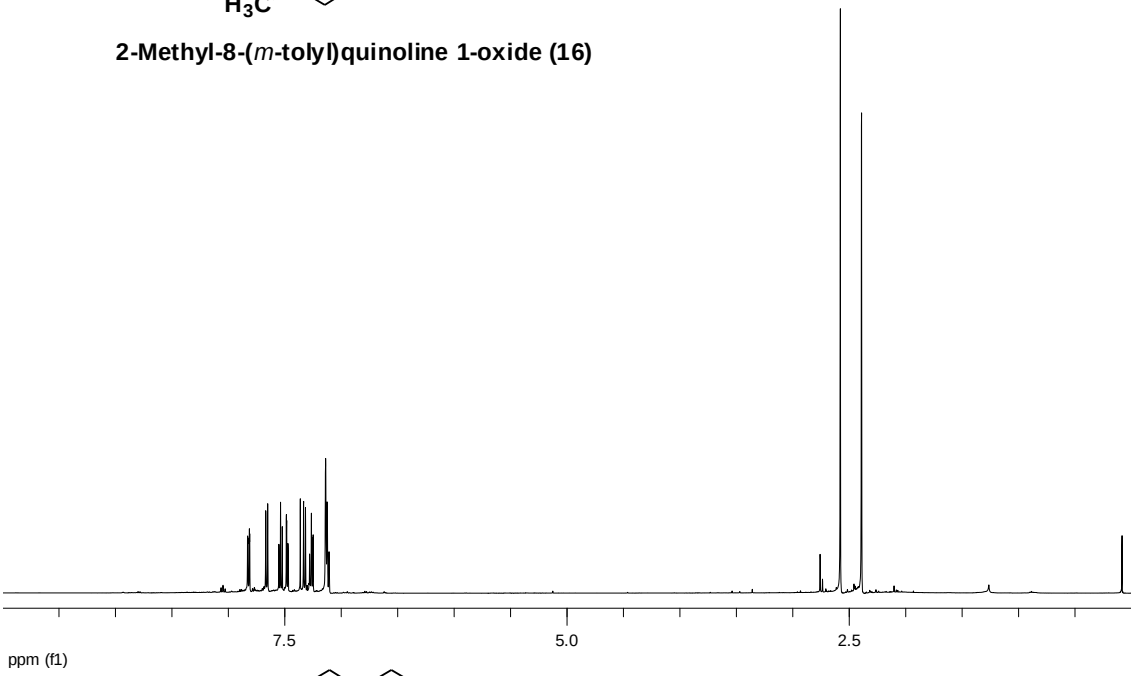


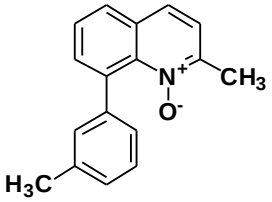
8-(4-Bromophenyl)-6-methylquinoline 1-oxide (15)



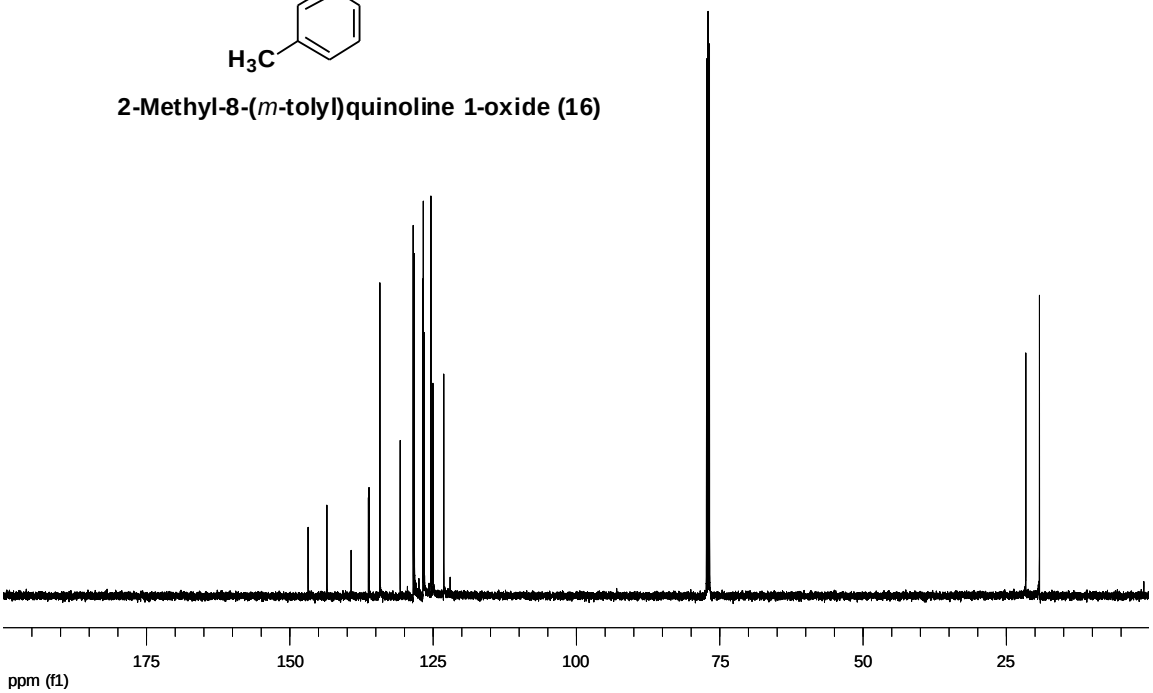


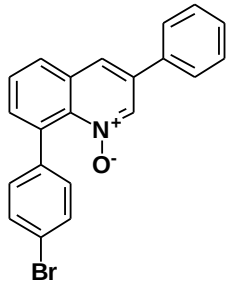
2-Methyl-8-(*m*-tolyl)quinoline 1-oxide (16)



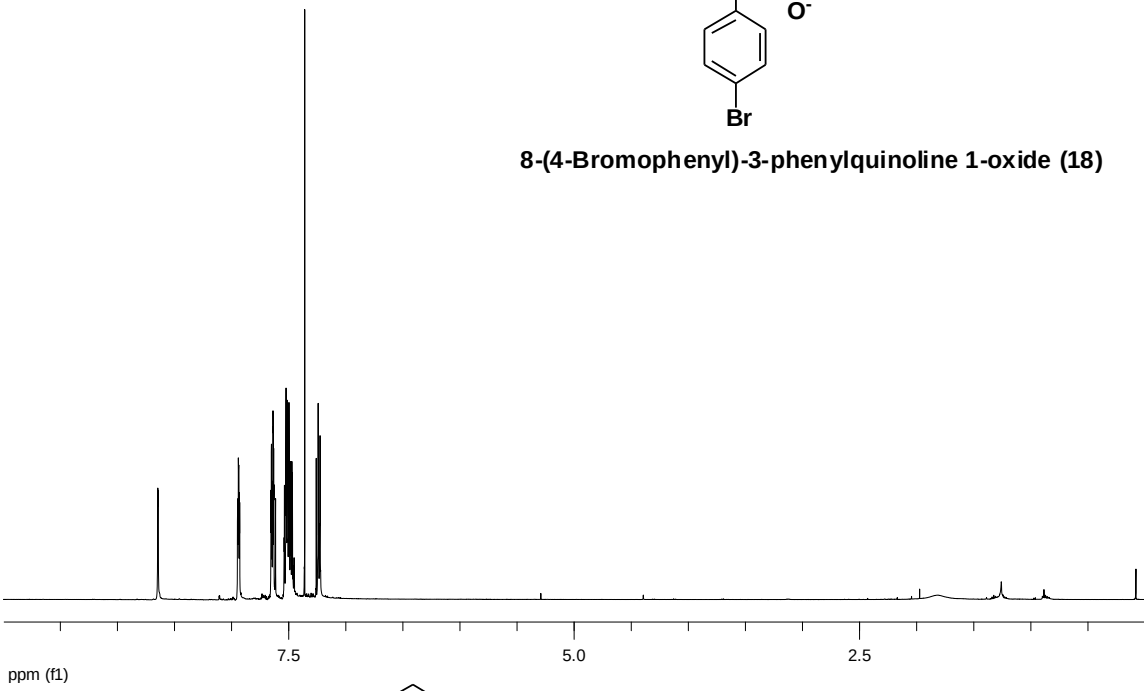


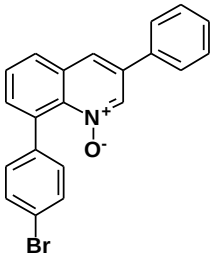
2-Methyl-8-(*m*-tolyl)quinoline 1-oxide (16)



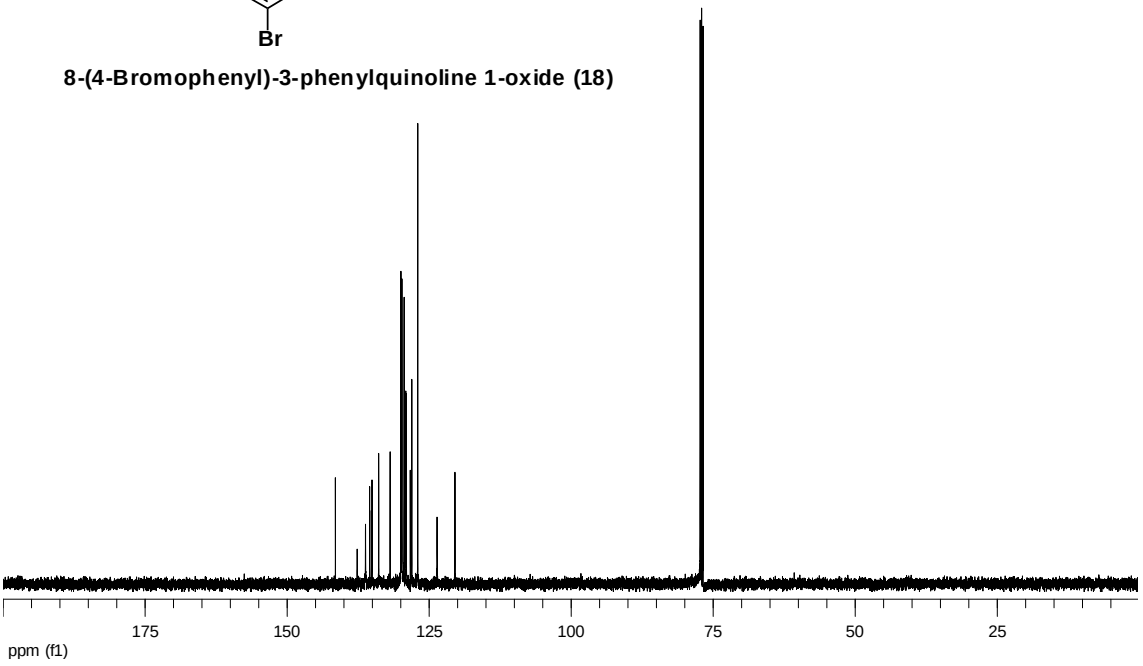


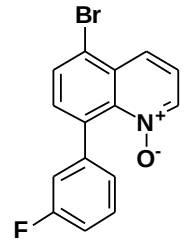
8-(4-Bromophenyl)-3-phenylquinoline 1-oxide (18)



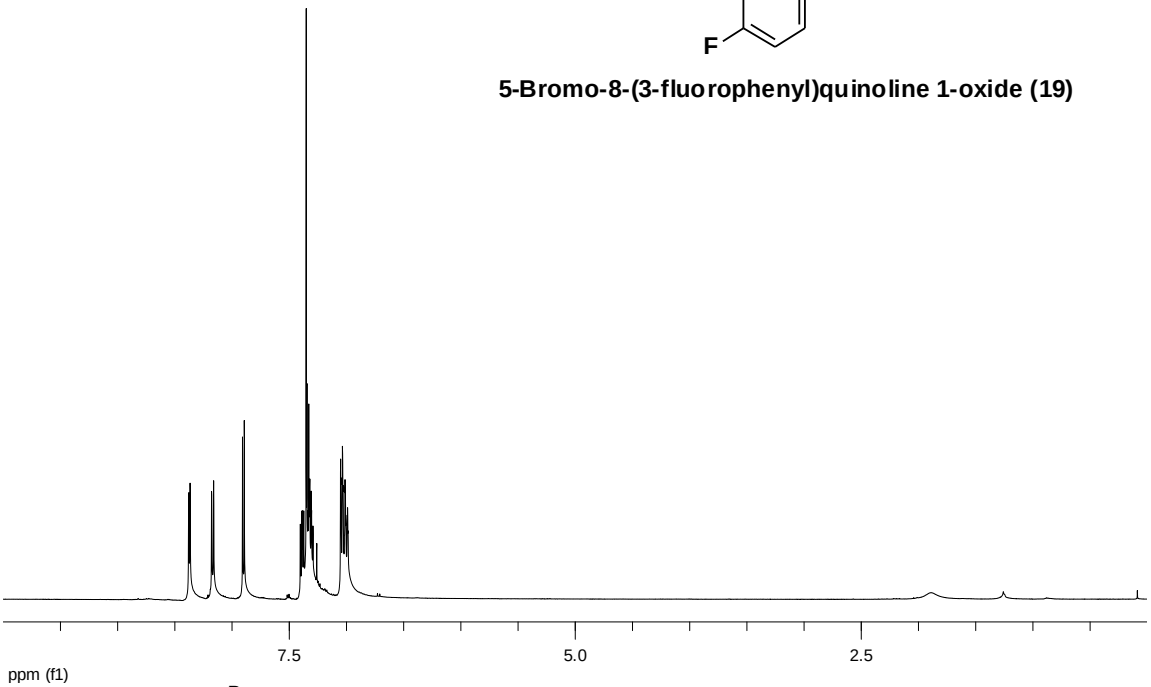


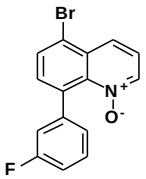
8-(4-Bromophenyl)-3-phenylquinoline 1-oxide (18)



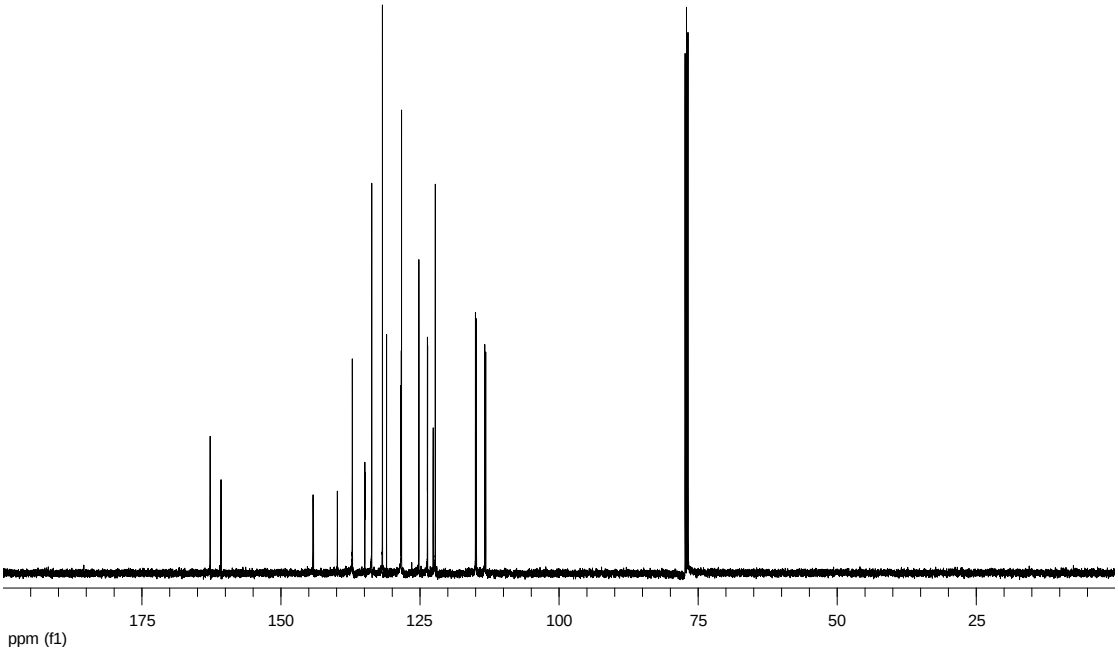


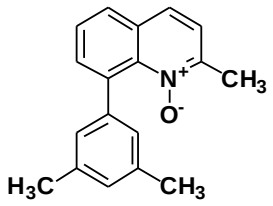
5-Bromo-8-(3-fluorophenyl)quinoline 1-oxide (19)



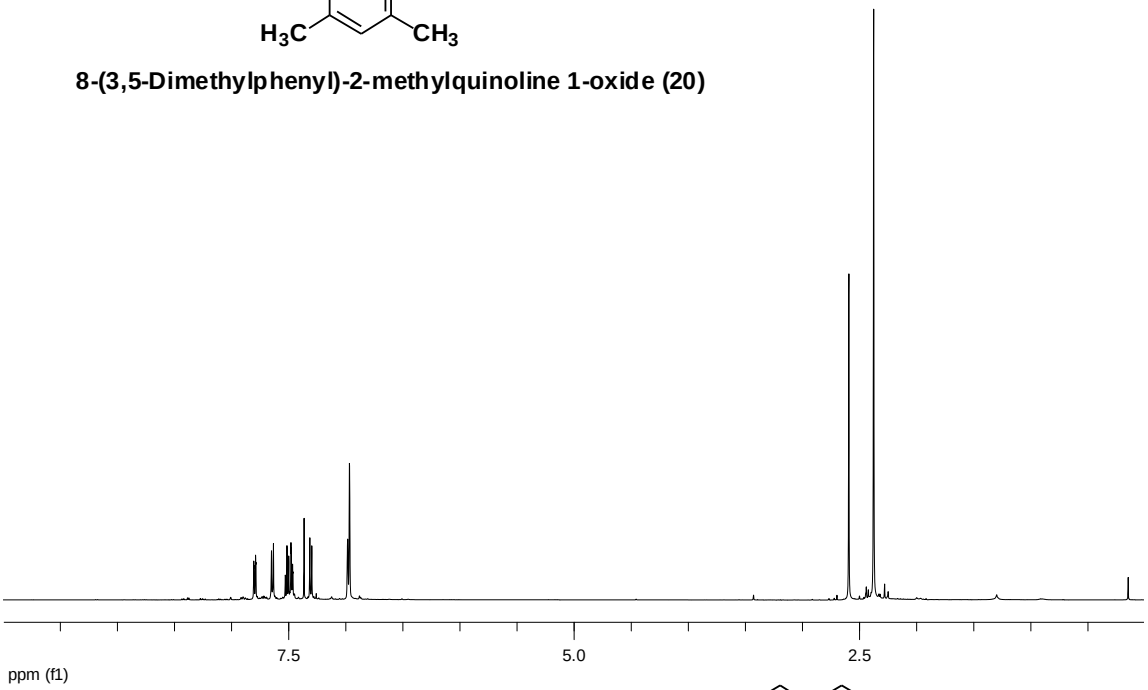


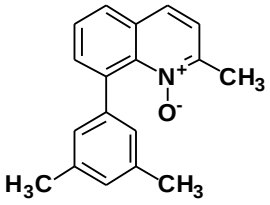
5-Bromo-8-(3-fluorophenyl)quinoline 1-oxide (19)



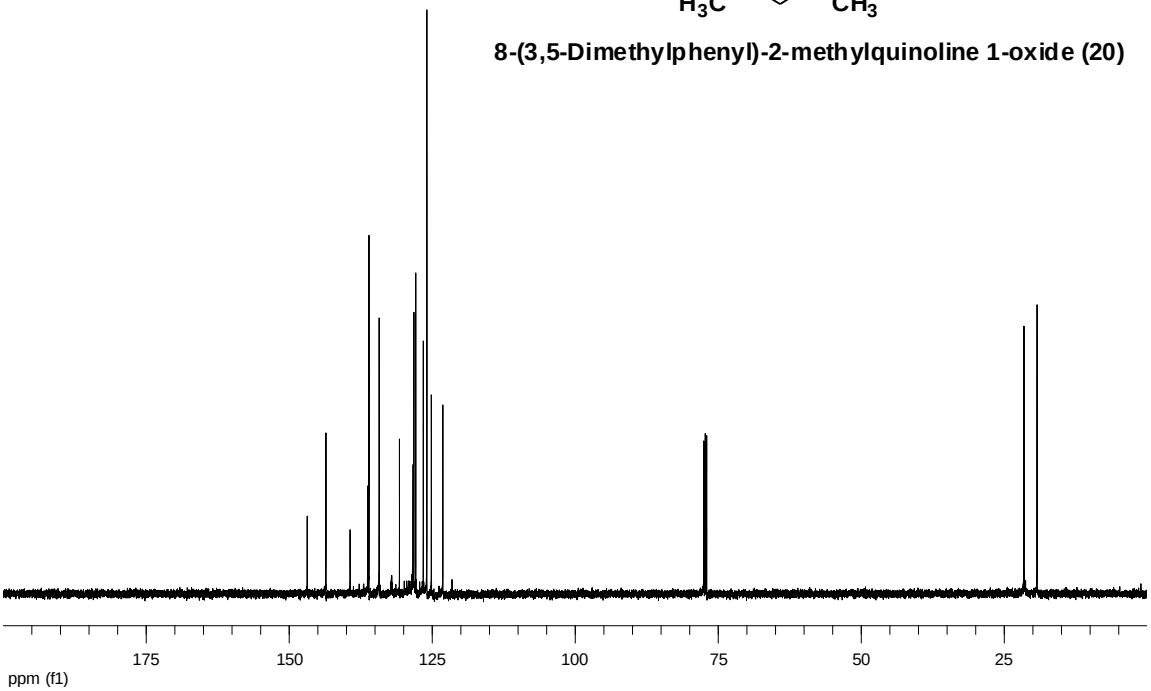


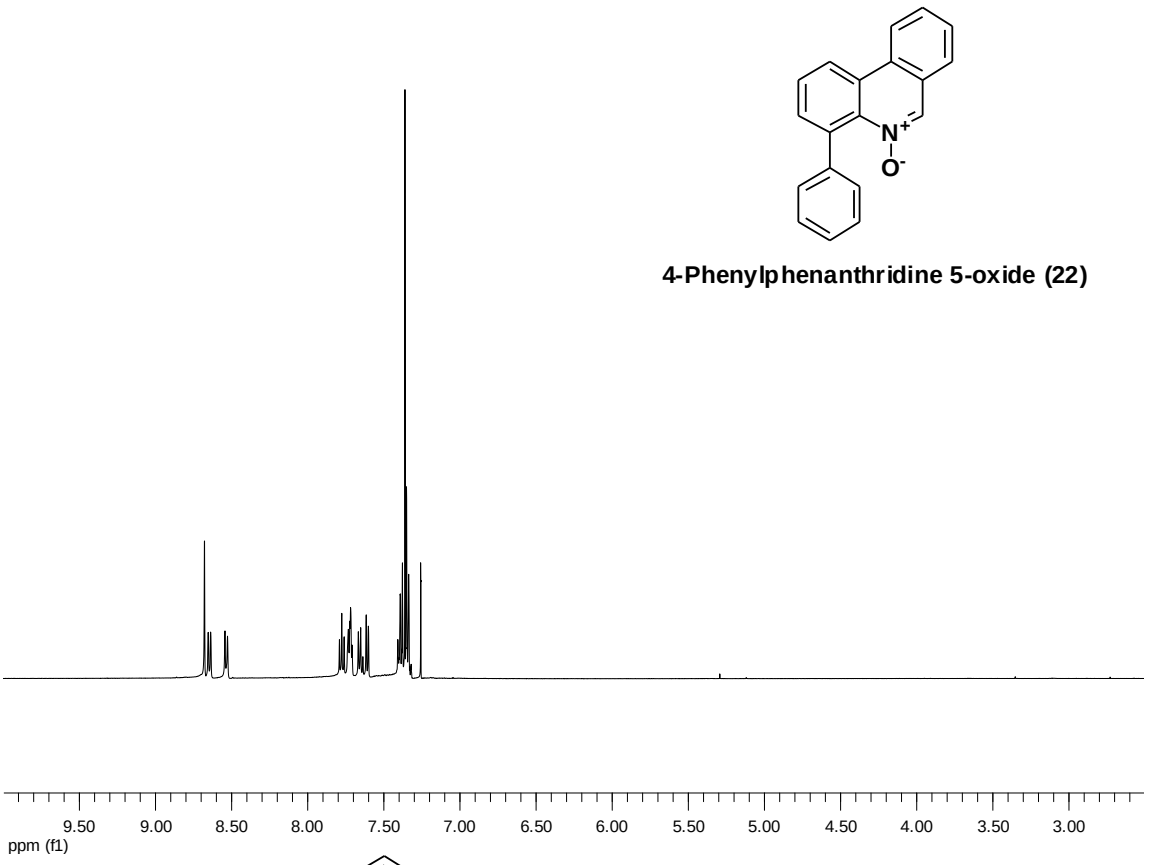
8-(3,5-Dimethylphenyl)-2-methylquinoline 1-oxide (20)



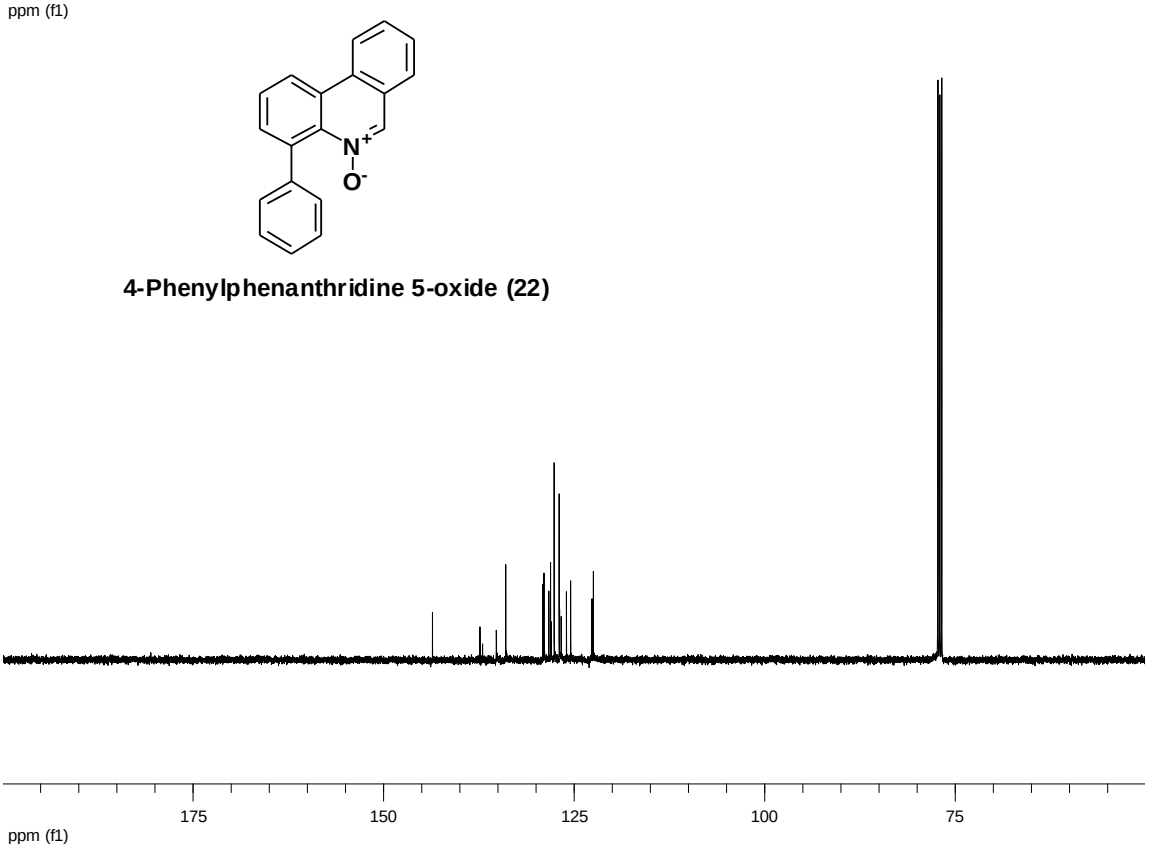


8-(3,5-Dimethylphenyl)-2-methylquinoline 1-oxide (20)

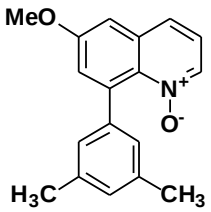




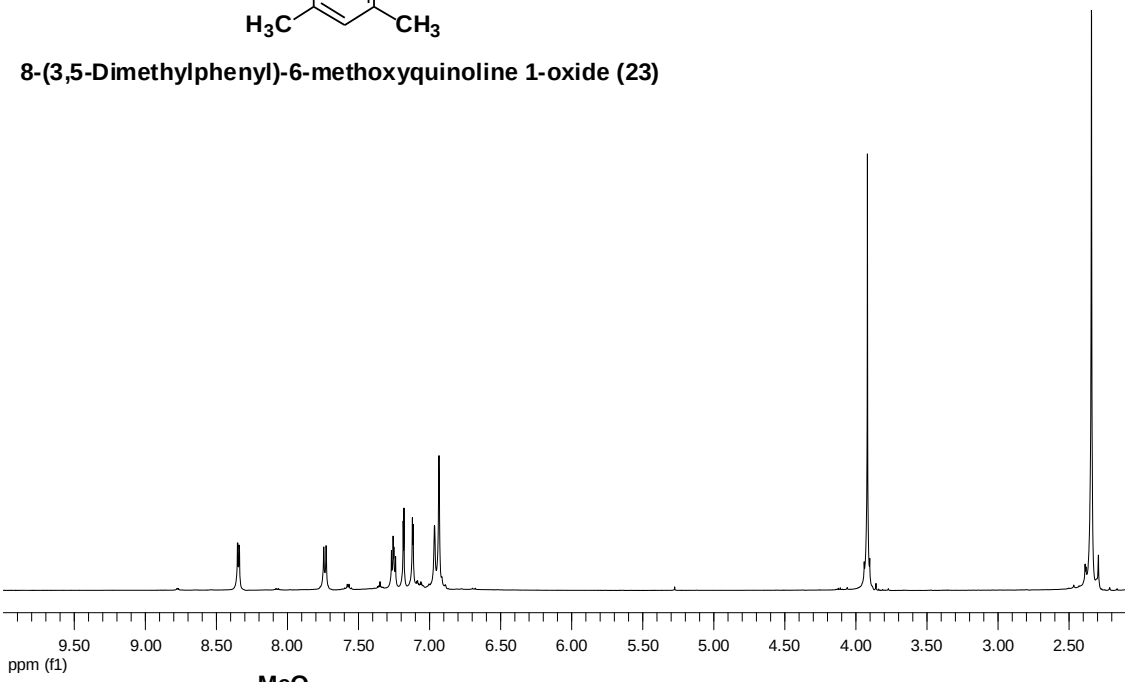
4-Phenylphenanthridine 5-oxide (22)

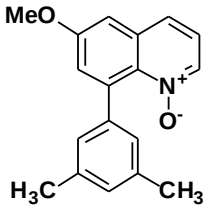


4-Phenylphenanthridine 5-oxide (22)

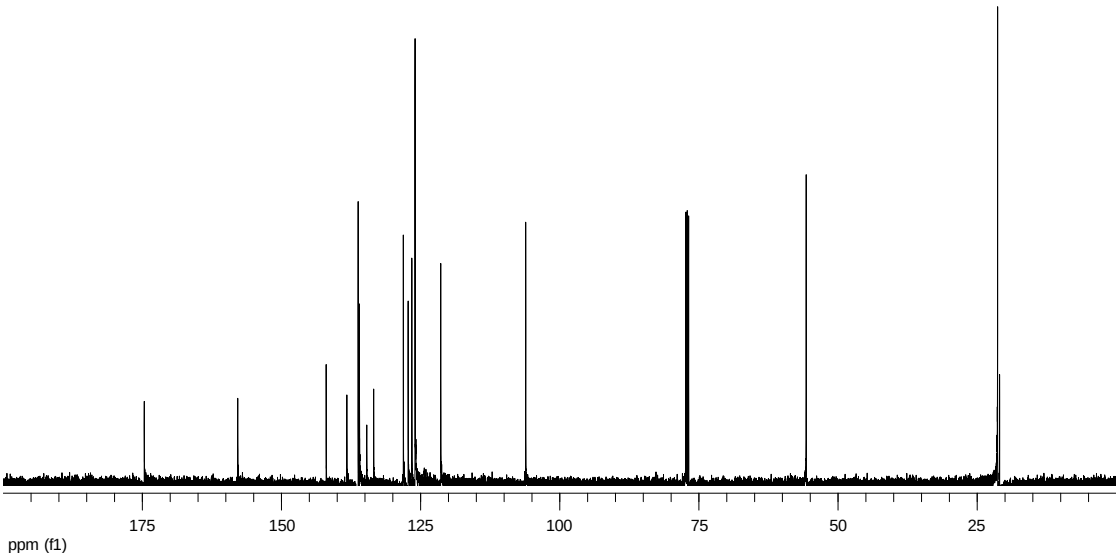


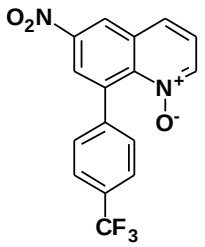
8-(3,5-Dimethylphenyl)-6-methoxyquinoline 1-oxide (23)



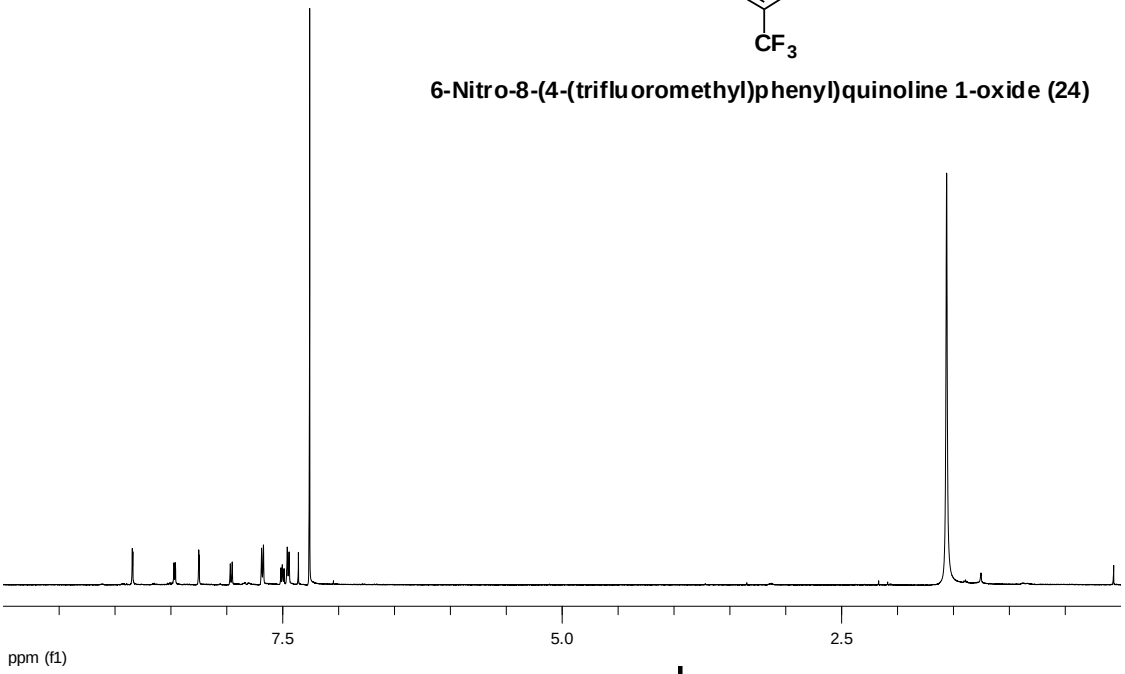


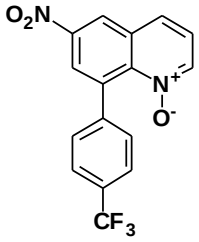
8-(3,5-Dimethylphenyl)-6-methoxyquinoline 1-oxide (23)



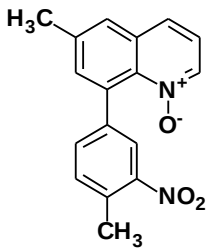


6-Nitro-8-(4-(trifluoromethyl)phenyl)quinoline 1-oxide (24)

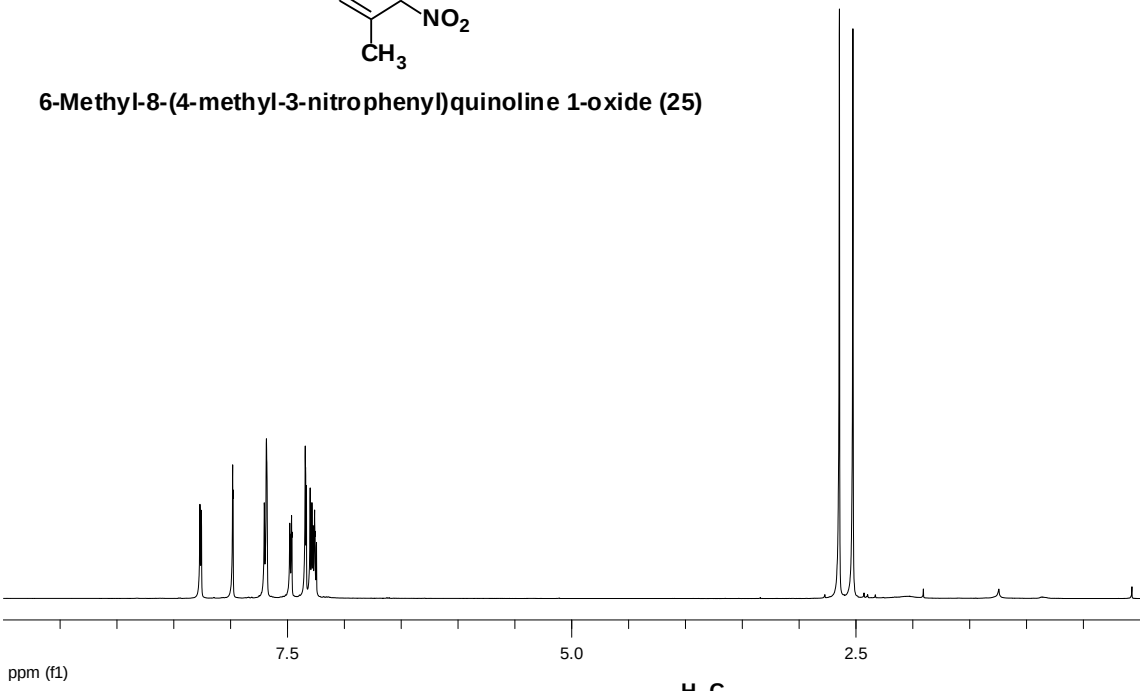


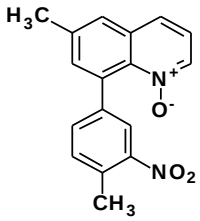


6-Nitro-8-(4-(trifluoromethyl)phenyl)quinoline 1-oxide (24)

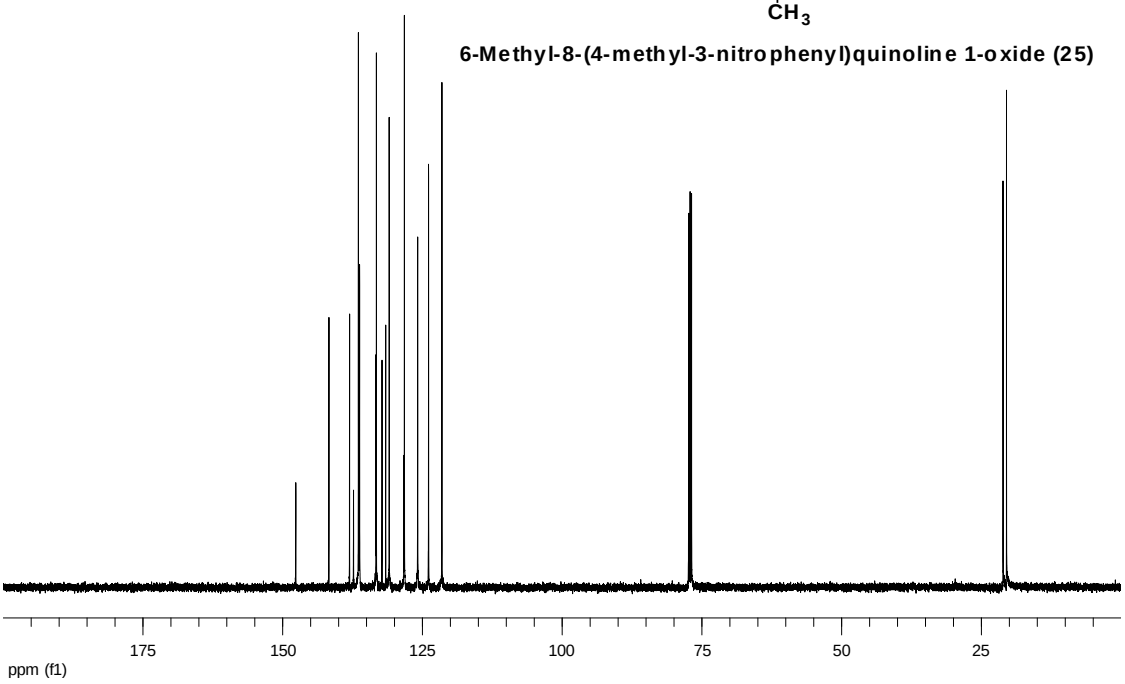


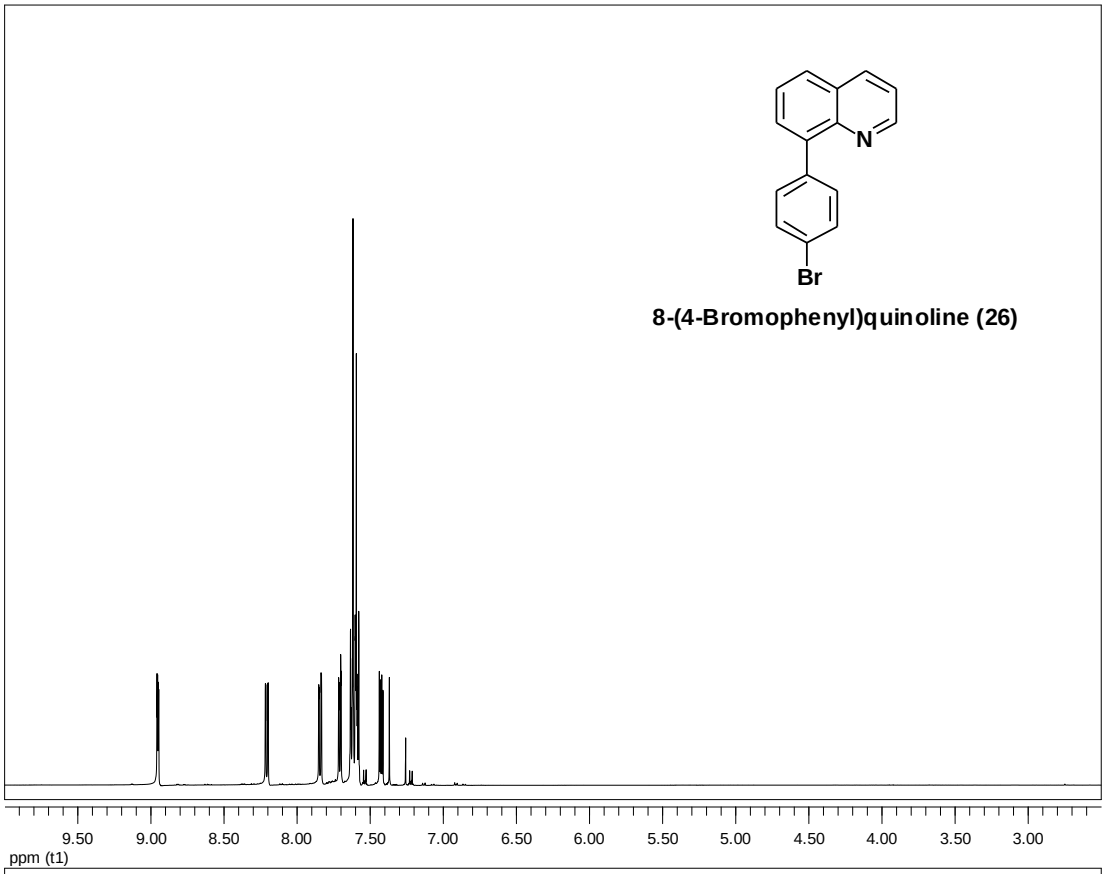
6-Methyl-8-(4-methyl-3-nitrophenyl)quinoline 1-oxide (25)

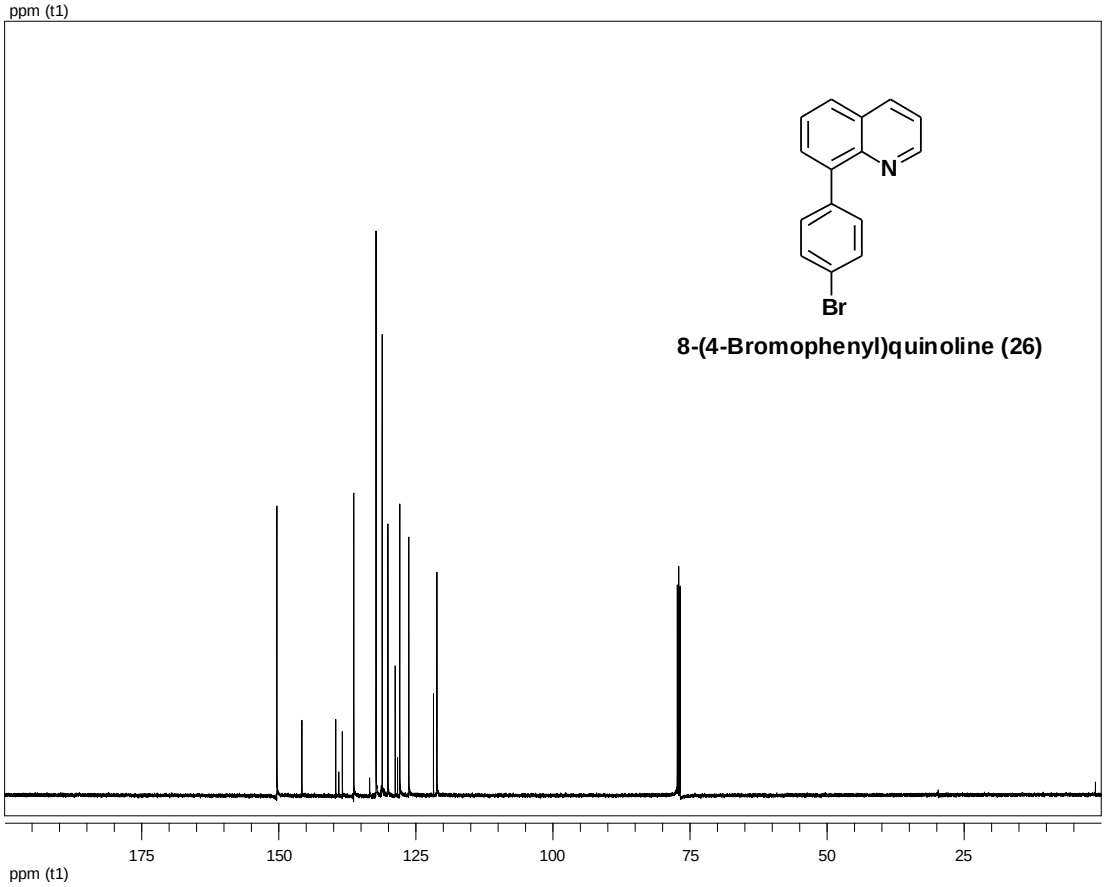


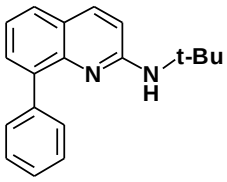


6-Methyl-8-(4-methyl-3-nitrophenyl)quinoline 1-oxide (25)

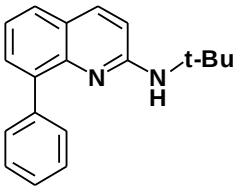



N
Br
8-(4-Bromophenyl)quinoline (26)
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
ppm (t1)

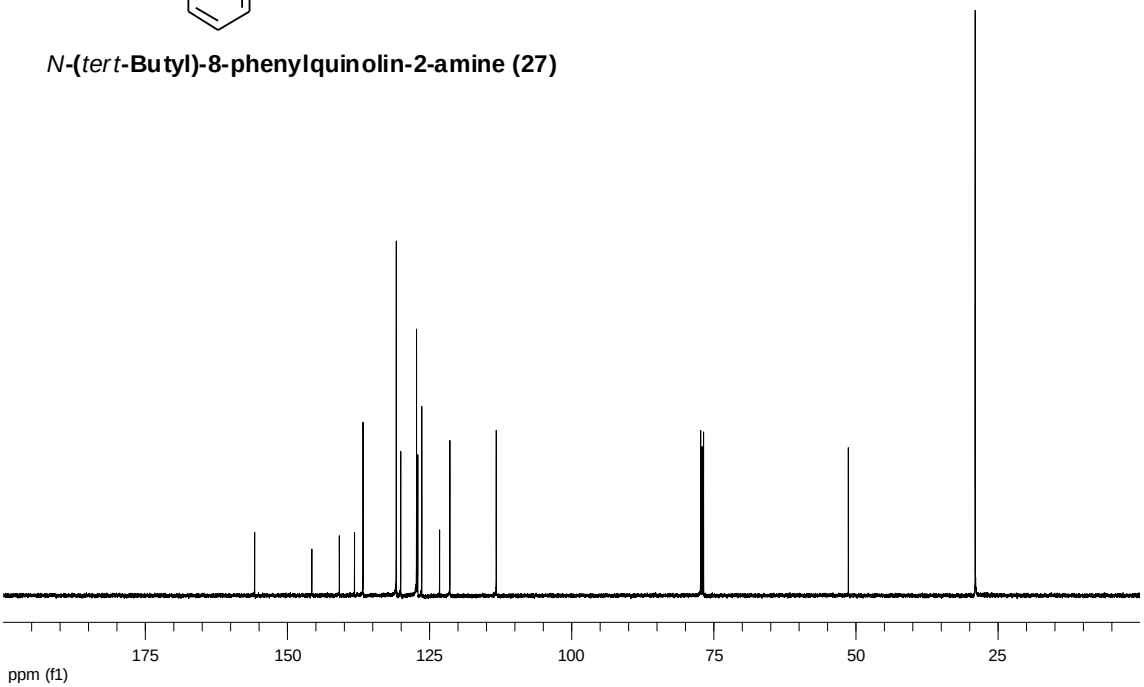

N
Br
8-(4-Bromophenyl)quinoline (26)
175
150
125
100
75
50
25
ppm (t1)

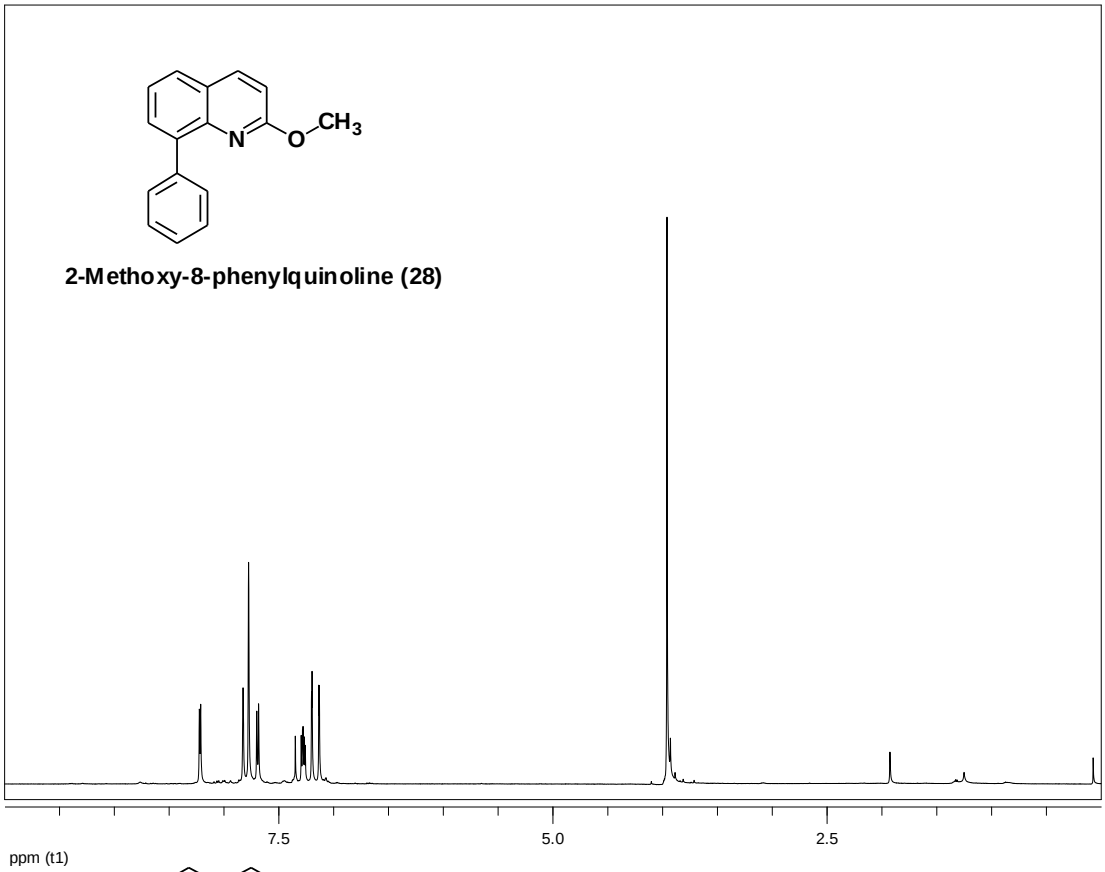


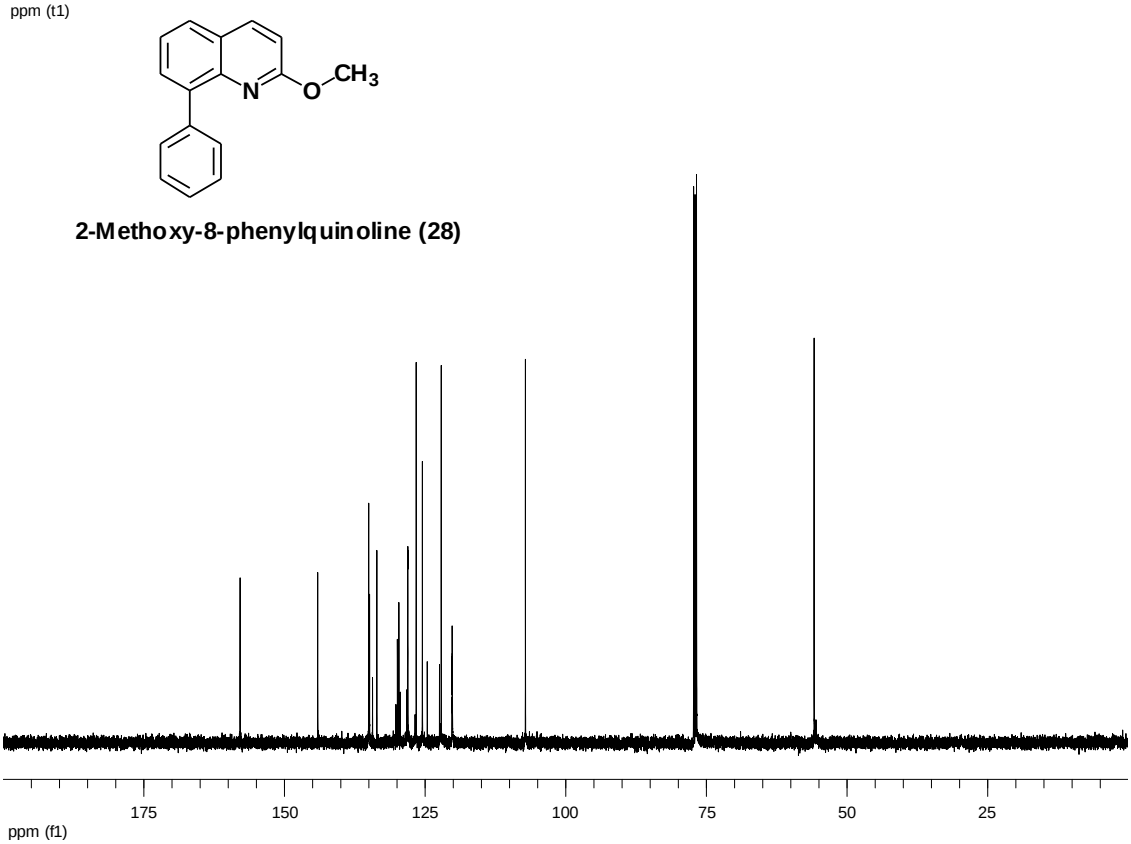
N-(*tert*-Butyl)-8-phenylquinolin-2-amine (27)

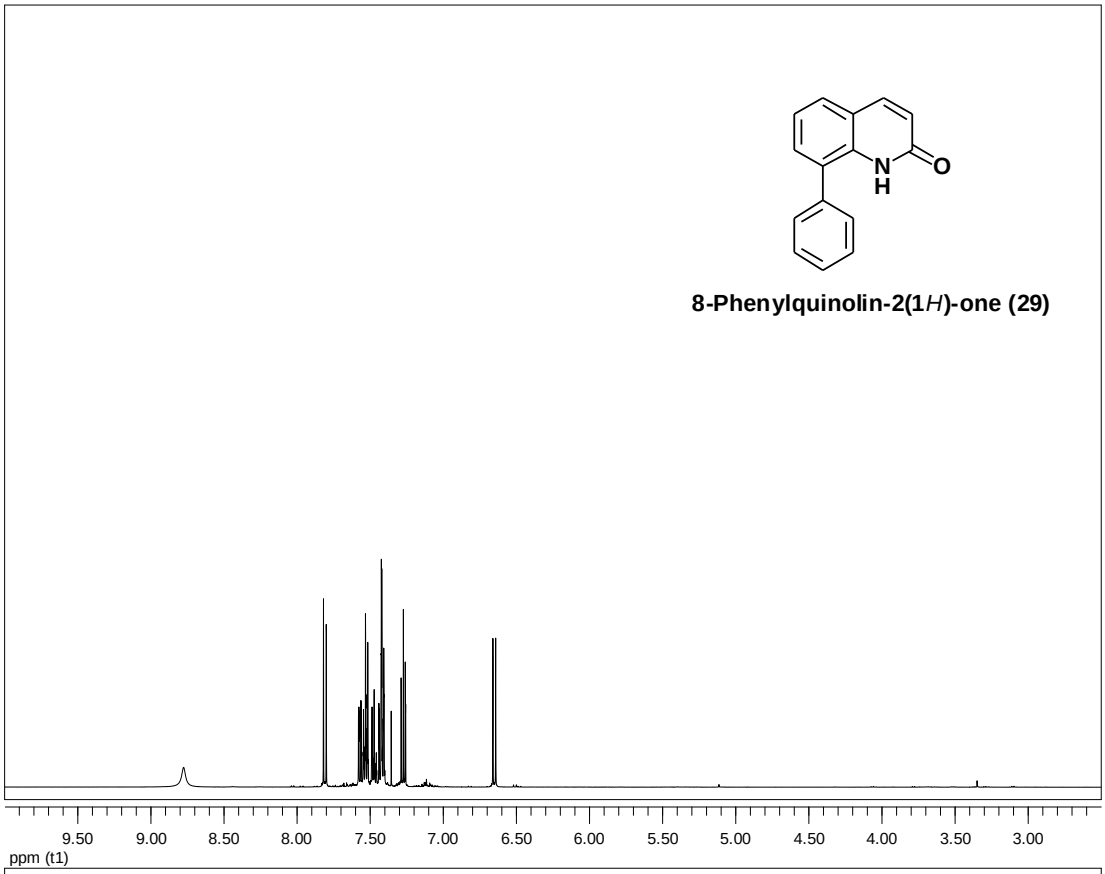


N-(*tert*-Butyl)-8-phenylquinolin-2-amine (27)

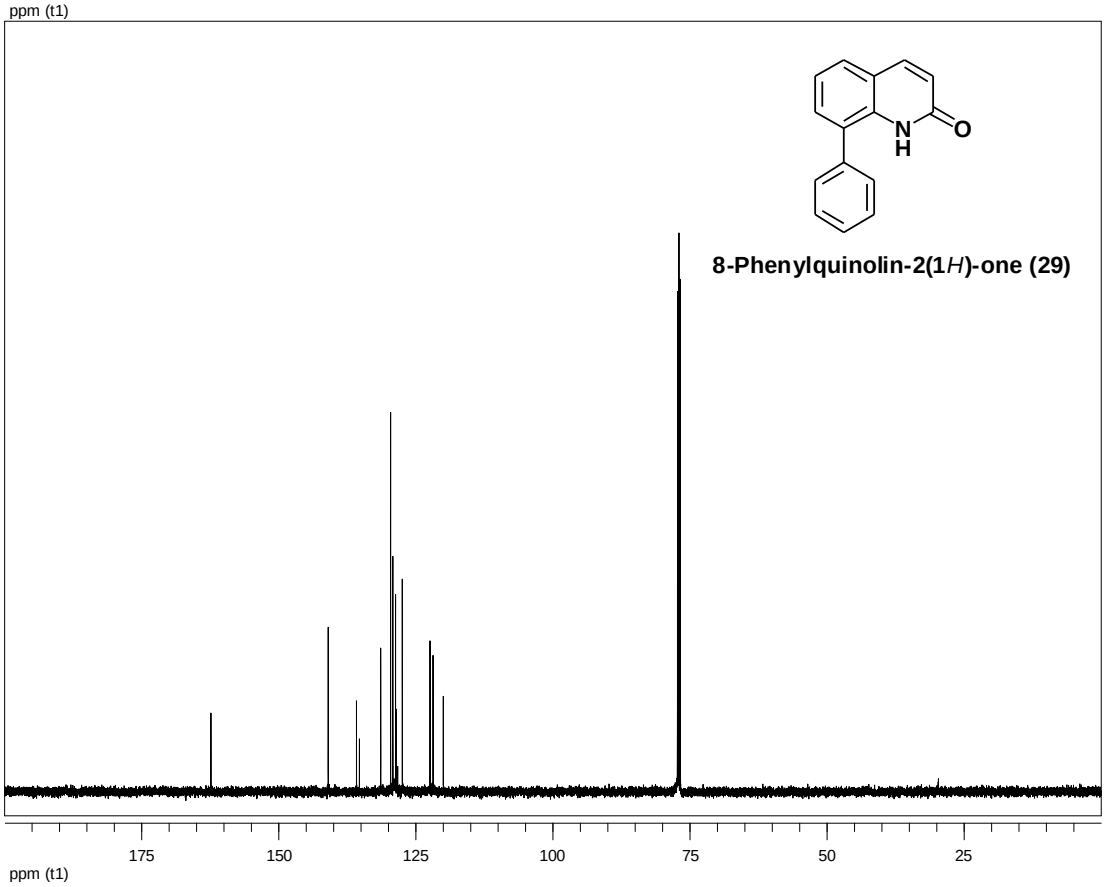



N
O
CH3
2-Methoxy-8-phenylquinoline (28)
7.5
5.0
2.5
ppm (t1)

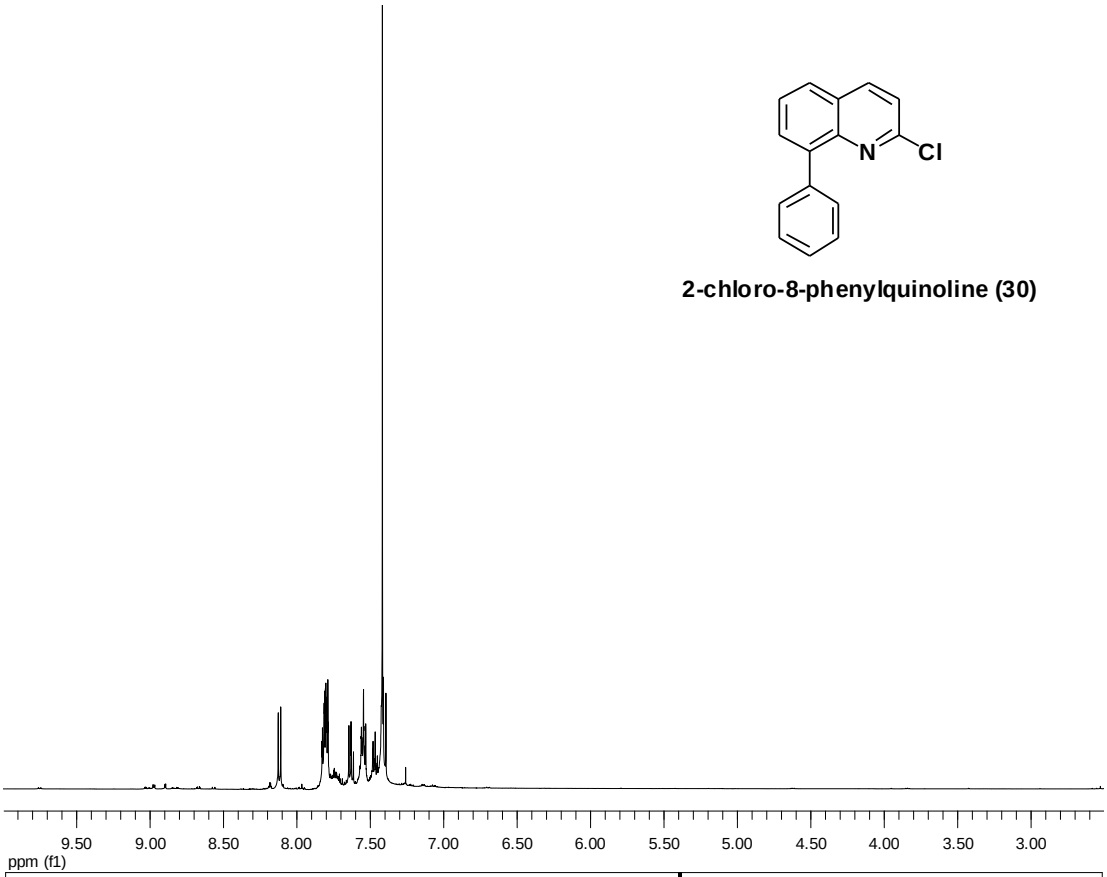

N
O
CH3
2-Methoxy-8-phenylquinoline (28)
175
150
125
100
75
50
25
ppm (f1)



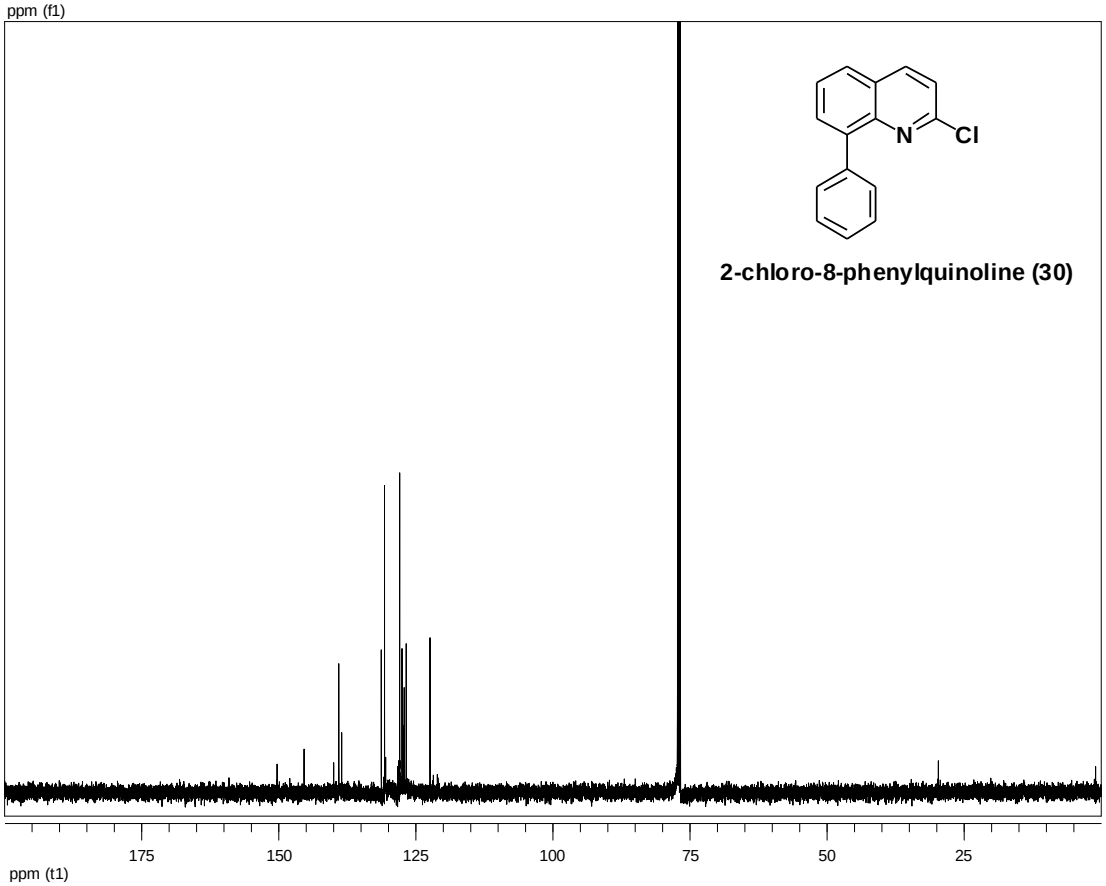
8-Phenylquinolin-2(1*H*)-one (29)



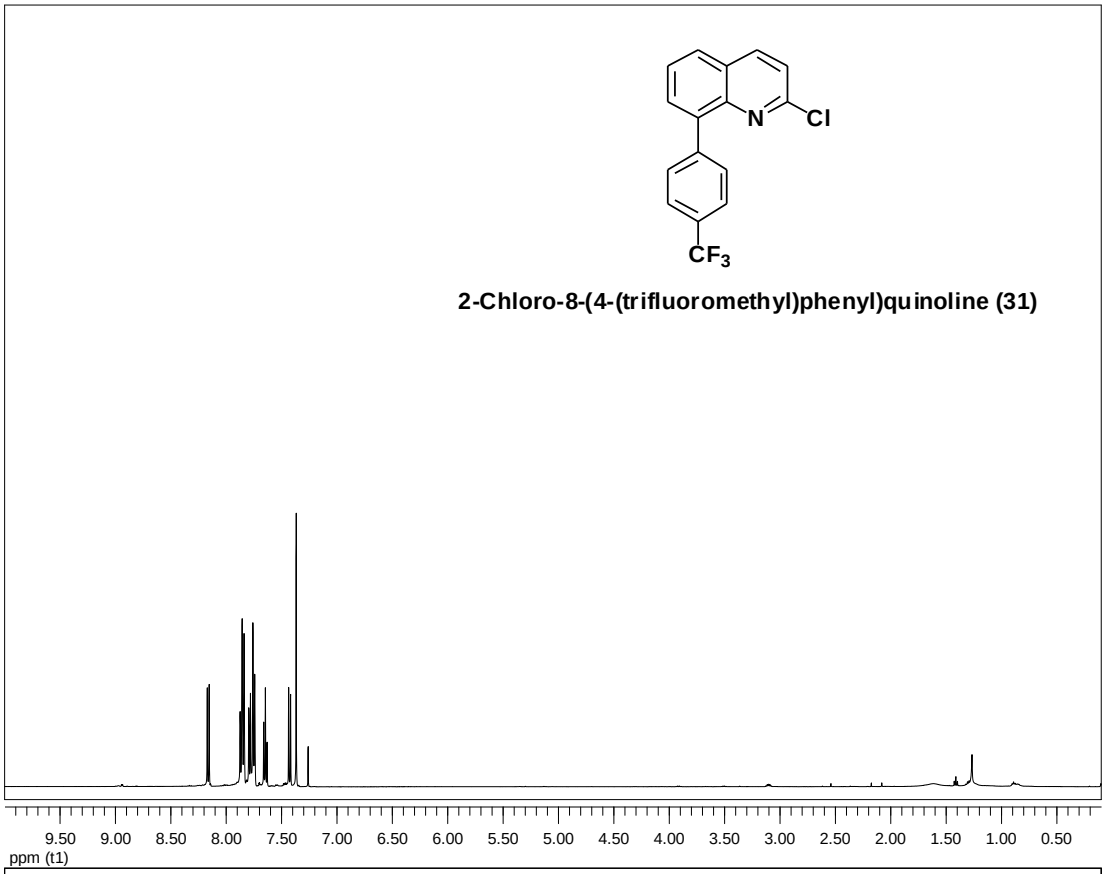
8-Phenylquinolin-2(1*H*)-one (29)

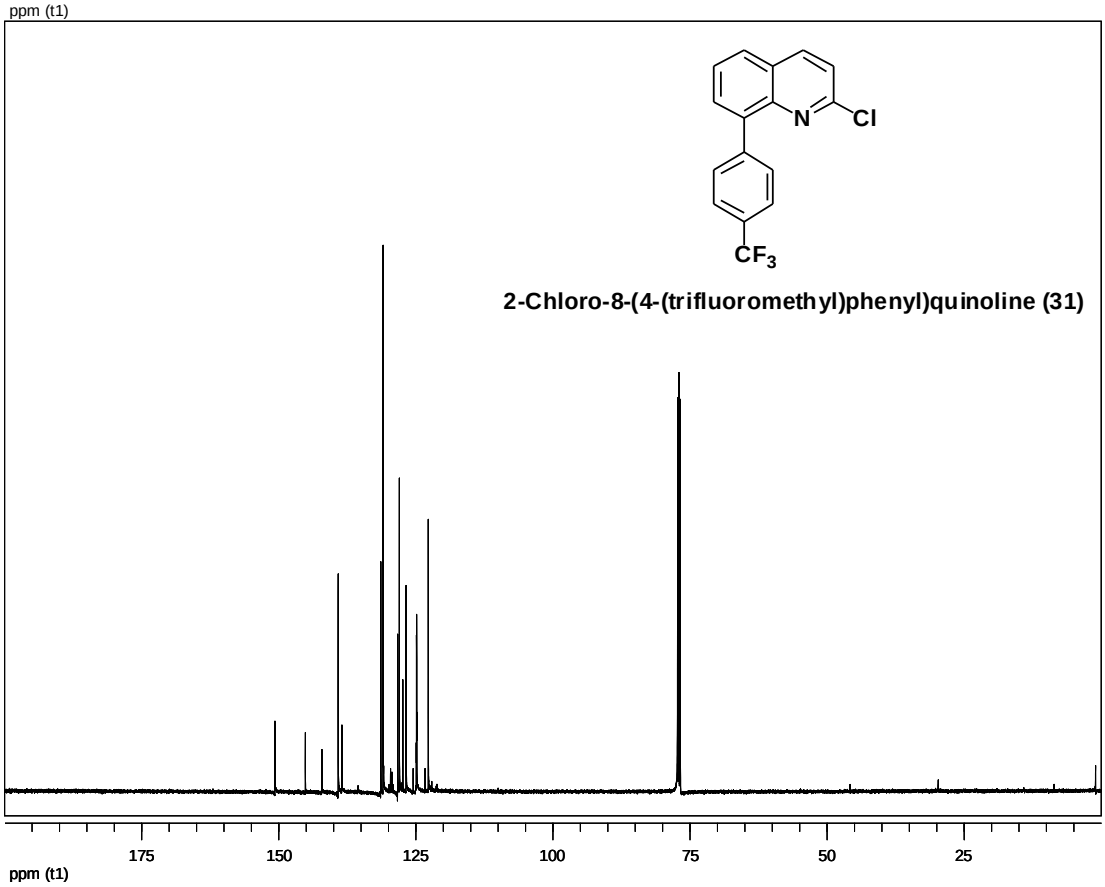


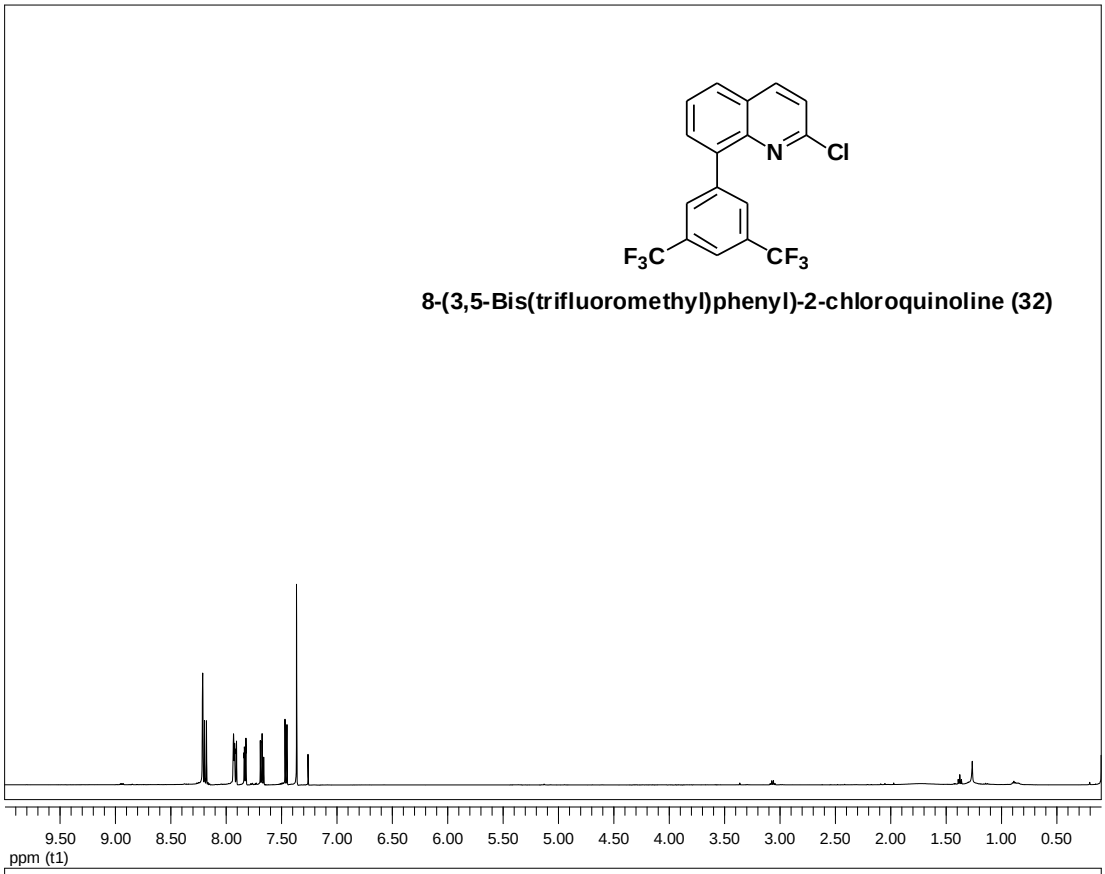
2-chloro-8-phenylquinoline (30)

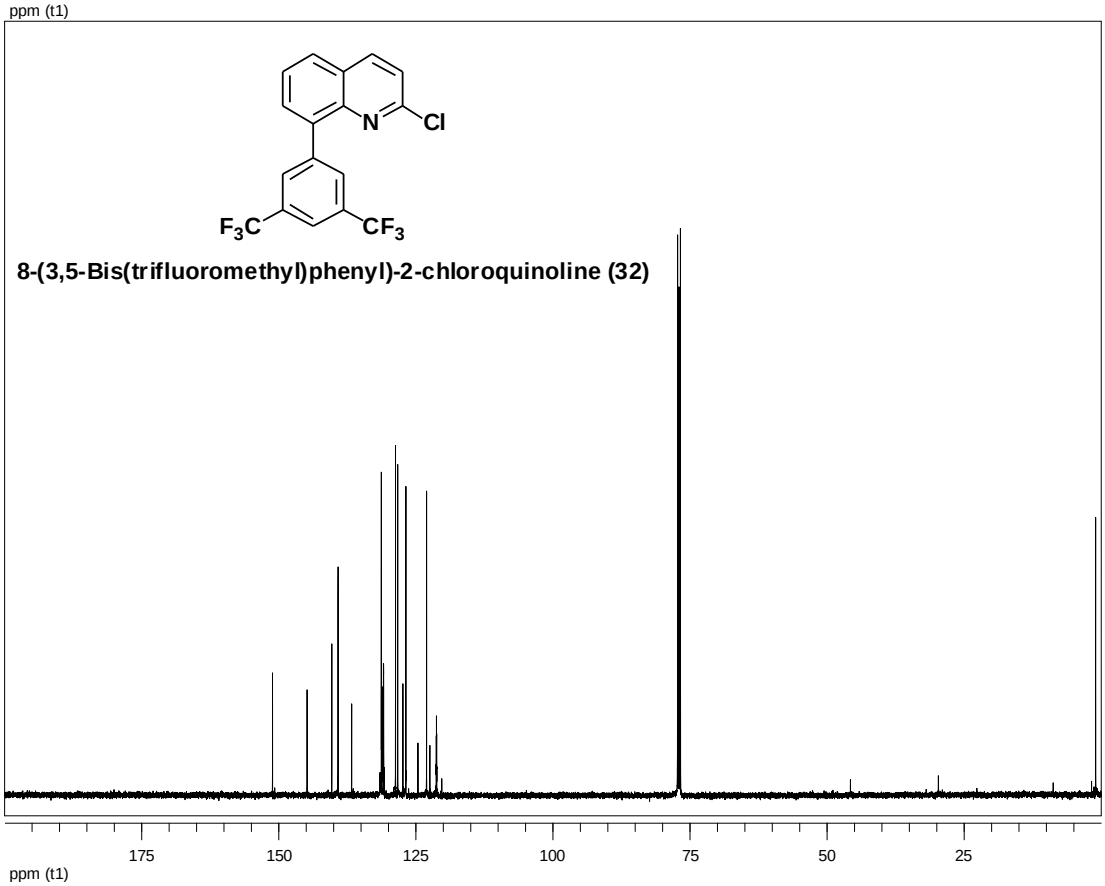


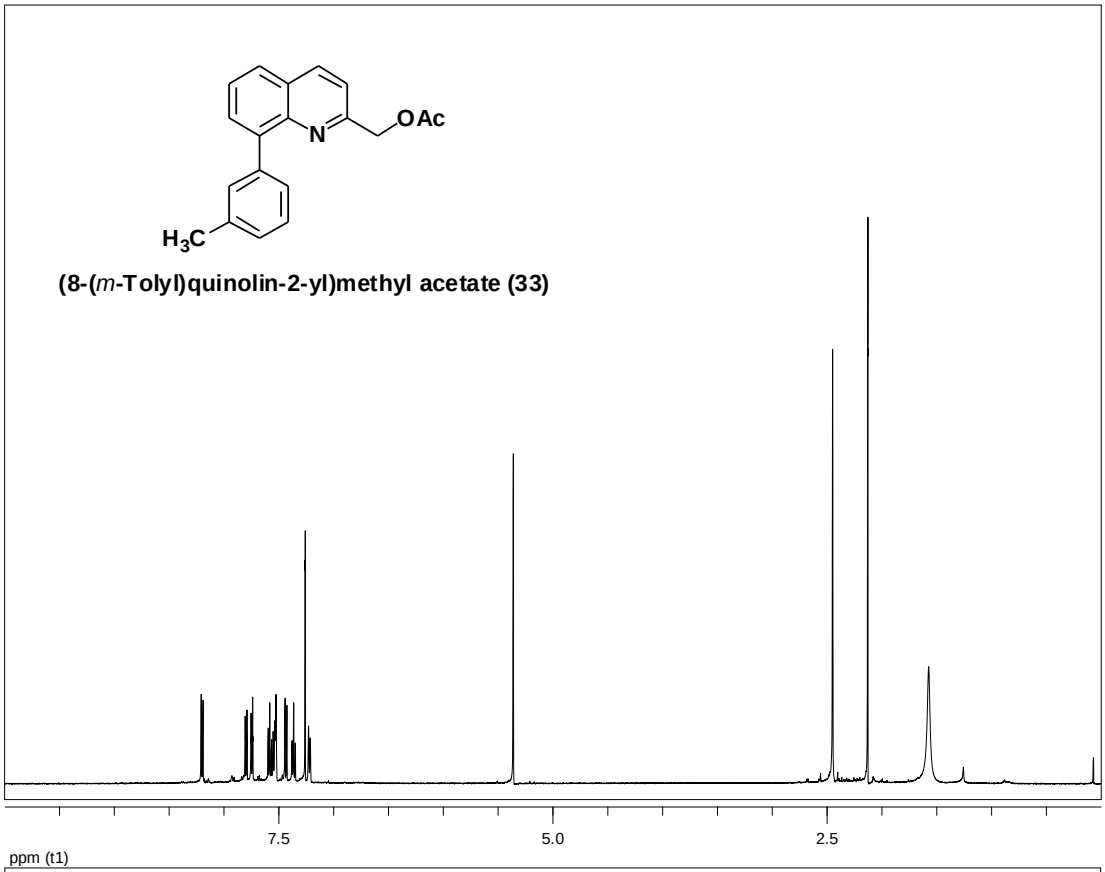
2-chloro-8-phenylquinoline (30)

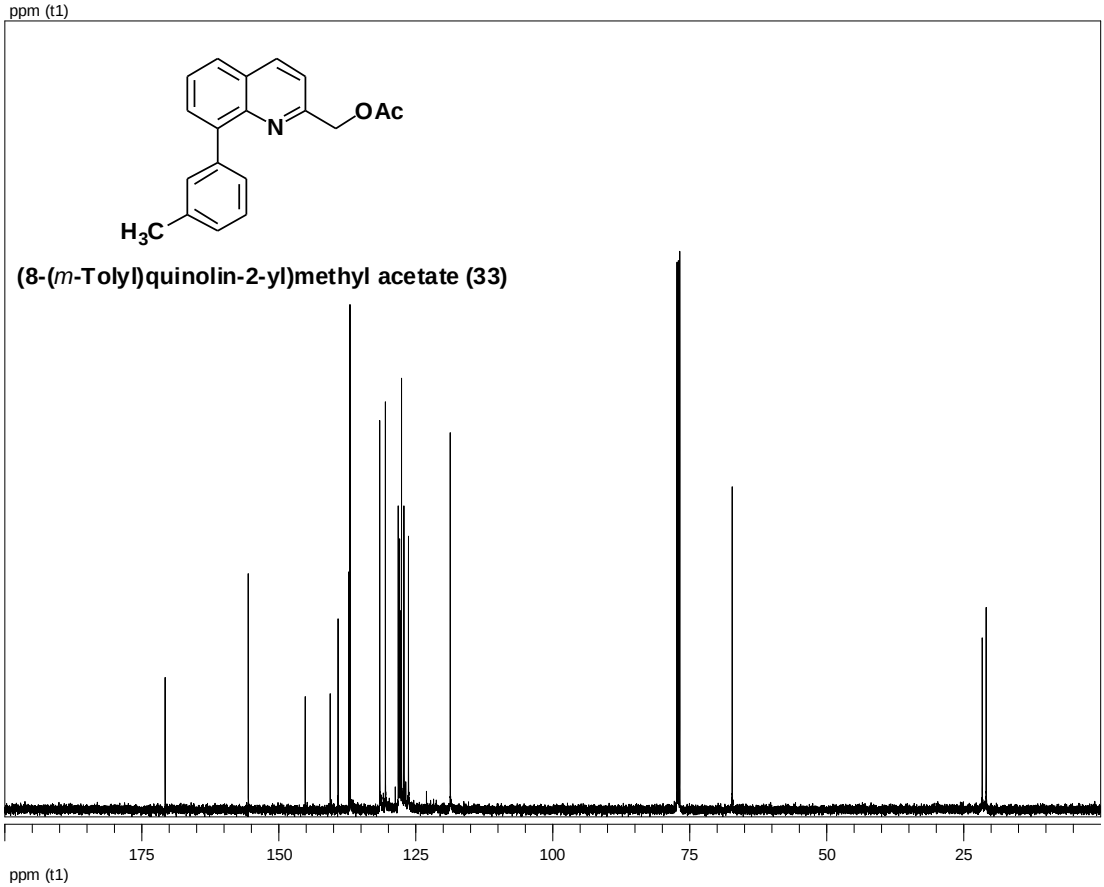

N
Cl
CF3
2-Chloro-8-(4-(trifluoromethyl)phenyl)quinoline (31)
9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50
ppm (t1)

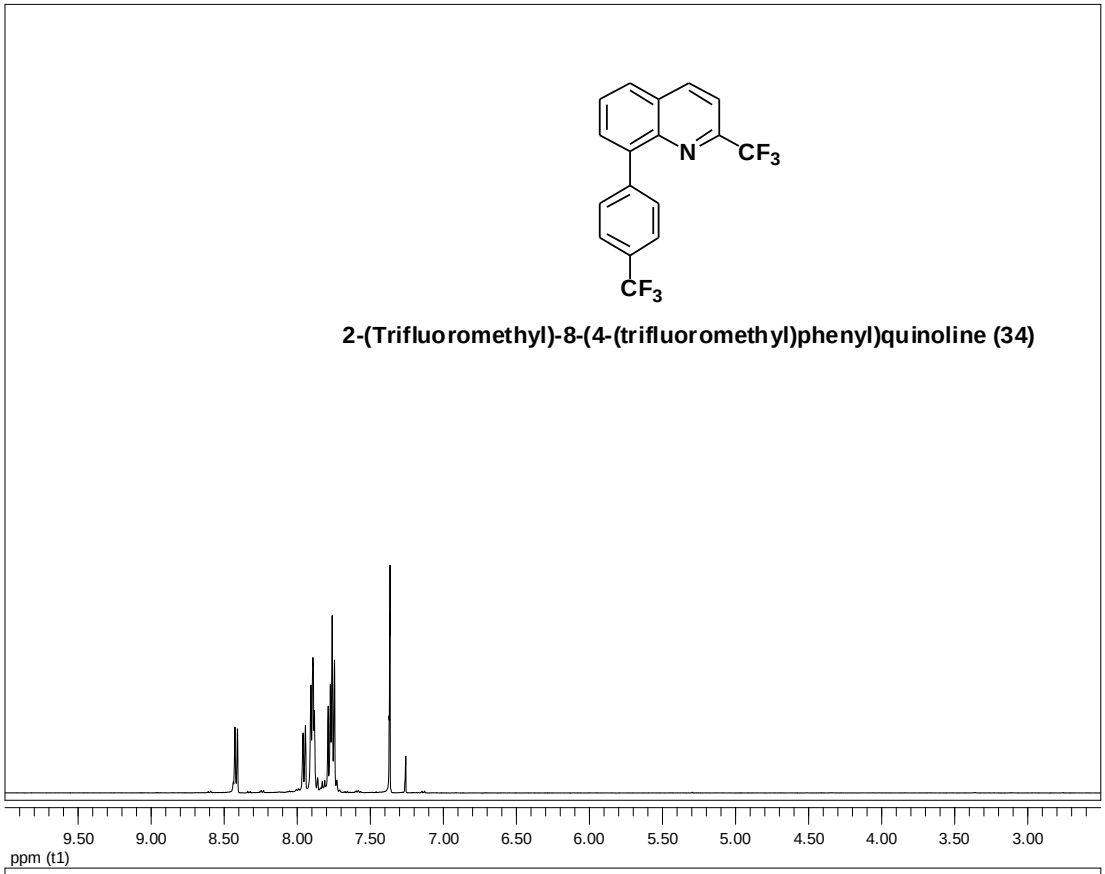

N
Cl
CF3
2-Chloro-8-(4-(trifluoromethyl)phenyl)quinoline (31)
175 150 125 100 75 50 25
ppm (t1)


N
Cl
F3C
CF3
8-(3,5-Bis(trifluoromethyl)phenyl)-2-chloroquinoline (32)
9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50
ppm (t1)

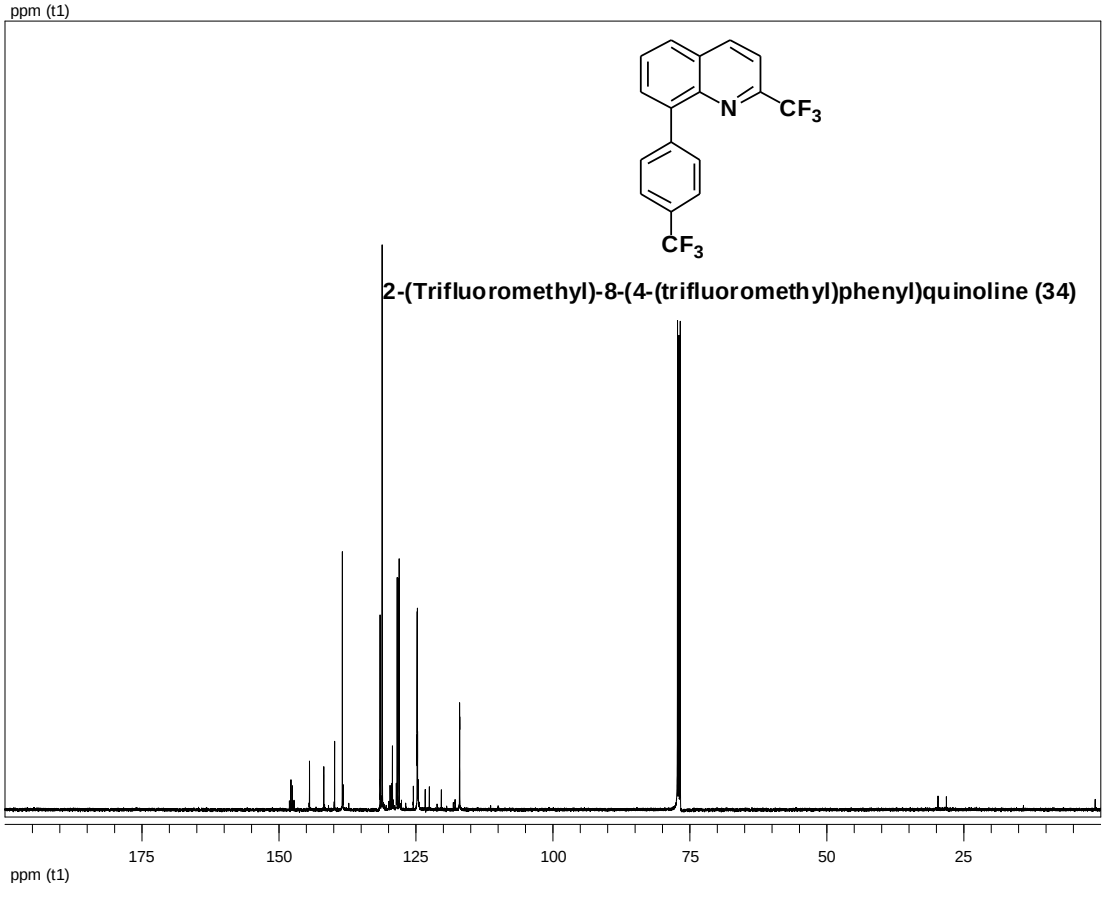

N
Cl
F3C
CF3
8-(3,5-Bis(trifluoromethyl)phenyl)-2-chloroquinoline (32)
175 150 125 100 75 50 25
ppm (t1)


OAc
N
H3C
(8-(m-Tolyl)quinolin-2-yl)methyl acetate (33)
7.5
5.0
2.5
ppm (t1)

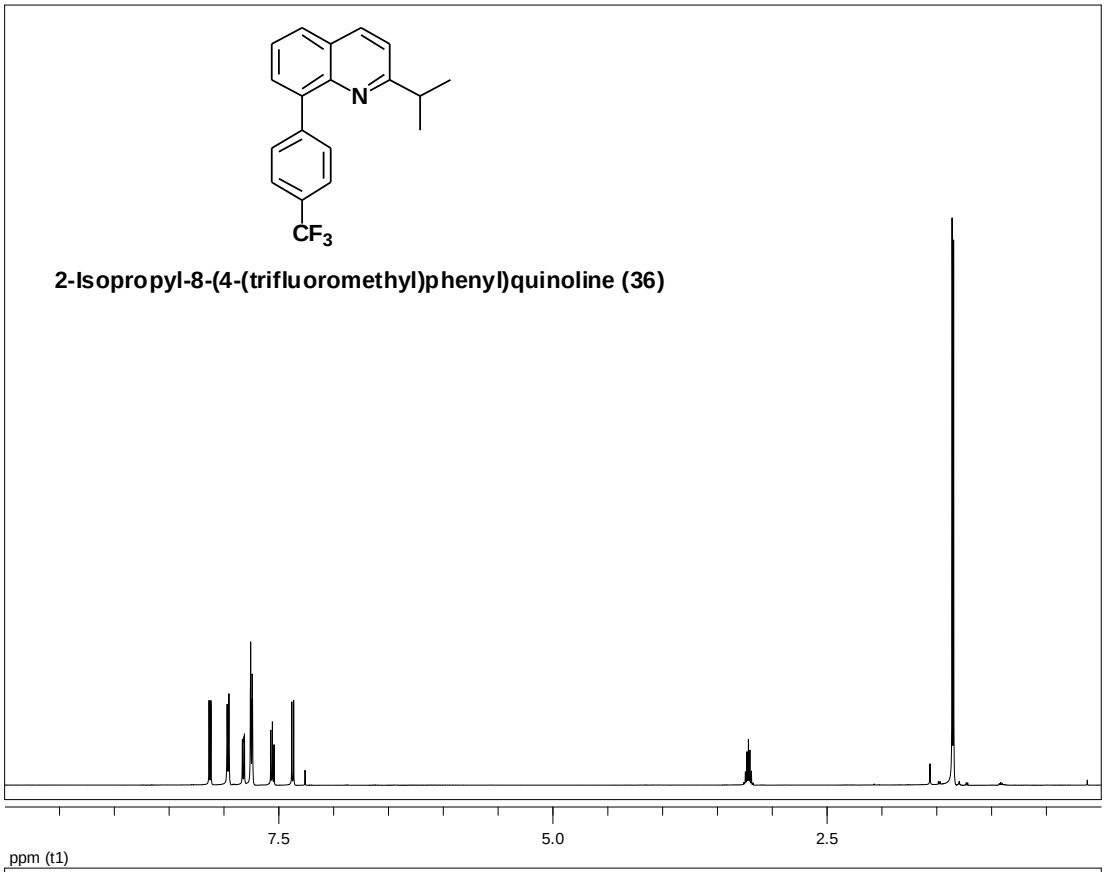

OAc
N
H3C
(8-(m-Tolyl)quinolin-2-yl)methyl acetate (33)
175
150
125
100
75
50
25
ppm (t1)

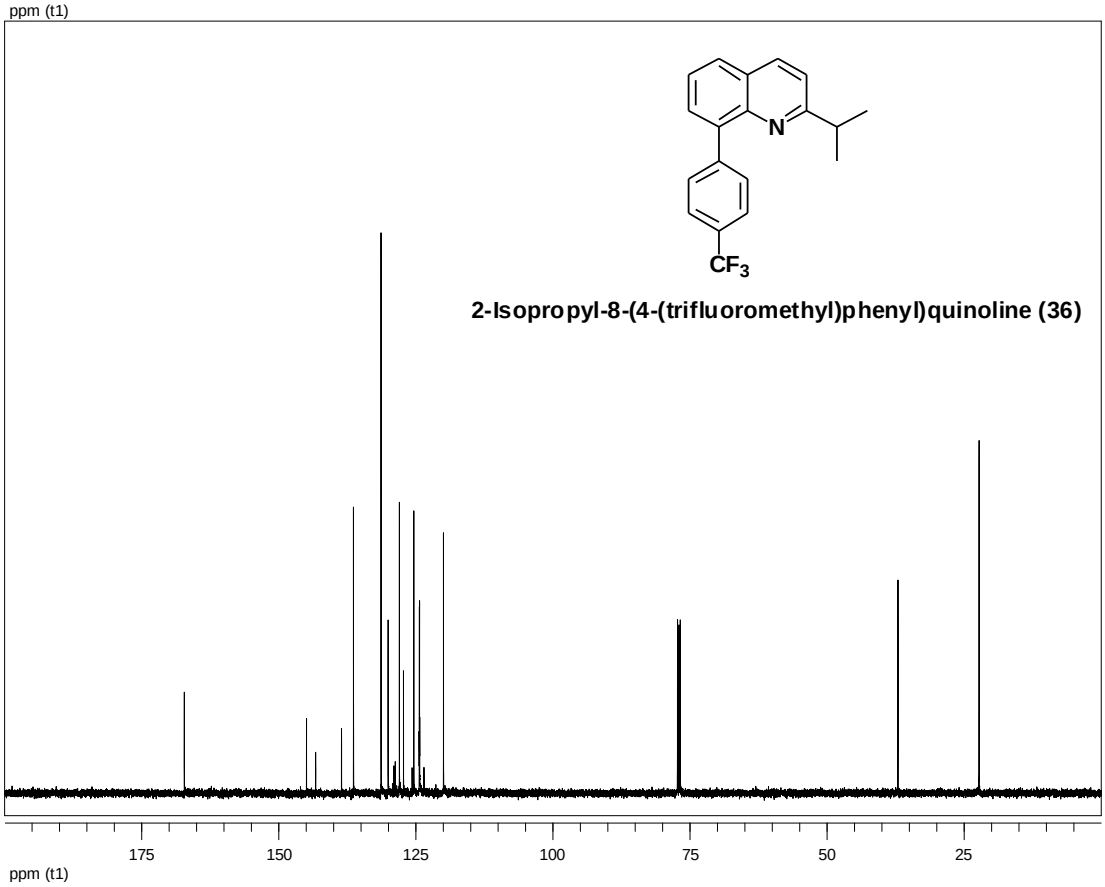


2-(Trifluoromethyl)-8-(4-(trifluoromethyl)phenyl)quinoline (34)



2-(Trifluoromethyl)-8-(4-(trifluoromethyl)phenyl)quinoline (34)


N
CF3
2-Isopropyl-8-(4-(trifluoromethyl)phenyl)quinoline (36)
7.5
5.0
2.5
ppm (t1)


N
CF3
2-Isopropyl-8-(4-(trifluoromethyl)phenyl)quinoline (36)
175
150
125
100
75
50
25
ppm (t1)

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