Supporting information

L. Wan,[a,c] K. Qiao,[a] X. N. Sun,[a] Z. C. Di,[a] Z. Fang,[a] Z. J. Li[a] and K. Guo*[a,b,c]

[a] *College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, 30 Puzhu South Road, Nanjing (P. R. China)*

[b] *State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, 5 Xinmofan Road, Nanjing (P. R. China)*

[c] *Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), 30 Puzhu South Road, Nanjing (P. R. China)*

E-mail: guok@njtech.edu.cn

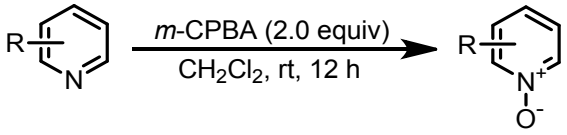
Table of Contents

1.General Information

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All solvents before used were dried and distilled under standard methods. All other commercially available reagents were used as received. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: TMS = 0.00 ppm, for ^{13}C NMR: $CDCl_3$ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on precoated silica gel plates. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

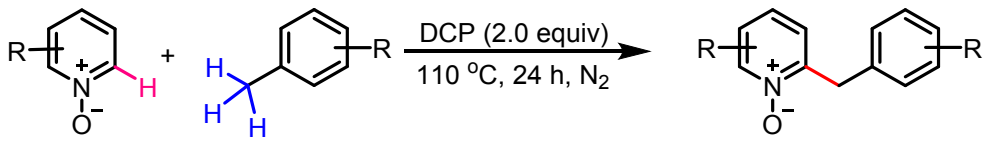
2. Experimental Section

2.1 General Procedure for the synthesis of starting materials

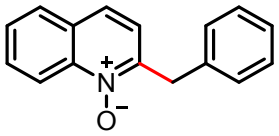


To a solution of the corresponding *N*-heterocycles (10.0 mmol) in CH_2Cl_2 (20 mL), *m*-chloroperoxybenzoic acid (*m*-CPBA, 20.0 mmol, 2.0 equiv) was added at 0 °C. The reaction mixture was allowed to stir at room temperature for 12 h. Then saturated aqueous $NaHCO_3$ (20 mL) was added. The aqueous was extracted with CH_2Cl_2 (10 mL × 3) and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc/*n*-hexene or EtOAc/MeOH to afford desired *N*-oxides.

2.2 General procedure for the benzylation of heterocyclic *N*-oxides

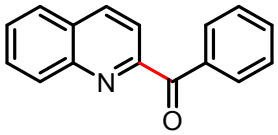


In a 25 mL tube, the corresponding heterocyclic *N*-oxides(0.5 mmol, 1.0 equiv), DCP (1.0 mmol, 2.0 equiv) and toluene or toluene derivatives (2 mL) were added under N_2 atmosphere. The tube was sealed and the resulting solution was heated in a 110 °C oil bath with vigorous stirring for 24 h. Then the reaction mixture was cooled to room temperature. The mixture was extracted with ethyl acetate (20 mL × 3), and the combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under vacuum. The residue was purified by flash chromatography using EtOAc/*n*-hexene (1:2) as eluent to afford the products.



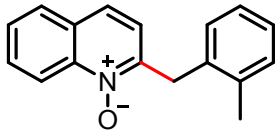
2-benzylquinoline 1-oxide (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.53 – 7.46 (m, 2H), 7.30 – 7.16 (m, 5H), 6.97 (d, *J* = 8.7 Hz, 1H), 4.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.09, 141.41, 136.44, 130.30, 129.59, 128.98, 128.75, 127.91, 127.86, 126.90, 125.10, 121.83, 119.64, 37.31; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1070, found: 236.1089.



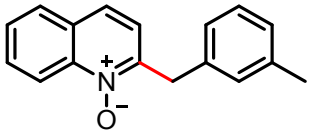
phenyl(quinolin-2-yl)methanone (3a')

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.5 Hz, 1H), 8.30 – 8.16 (m, 3H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.73 – 7.58 (m, 2H), 7.58 – 7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.82, 154.65, 146.70, 137.11, 136.09, 133.07, 131.44, 130.53, 130.09, 128.88, 128.41, 128.14, 127.63, 120.80; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{11}NO$ $[M+H]^+$: 234.0913, found: 234.0923.



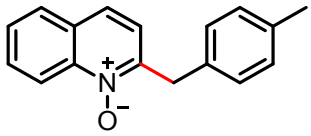
2-(2-methylbenzyl)quinoline 1-oxide (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.55 – 7.46 (m, 2H), 7.21 – 7.09 (m, 4H), 6.74 (d, *J* = 8.7 Hz, 1H), 4.39 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.70, 141.45, 137.18, 134.67, 130.55, 130.34, 128.90, 127.93, 127.85, 127.40, 126.44, 125.15, 121.04, 119.58, 35.22, 19.39; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1231.



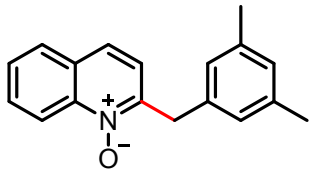
2-(3-methylbenzyl)quinoline 1-oxide (3c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.57 – 7.47 (m, 2H), 7.19 – 7.14 (m, 1H), 7.07 – 6.97 (m, 4H), 4.37 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.41, 141.41, 138.46, 136.34, 130.38, 130.36, 129.00, 128.67, 127.93, 127.89, 127.71, 126.65, 125.33, 121.94, 119.69, 37.25, 21.34; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1226.



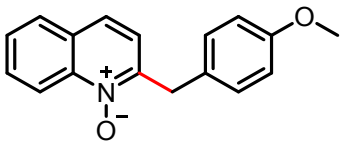
2-(4-methylbenzyl)quinoline 1-oxide (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.54 – 7.47 (m, 2H), 7.17 – 7.06 (m, 4H), 6.98 (d, *J* = 8.7 Hz, 1H), 4.37 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.44, 141.48, 136.54, 133.36, 130.30, 129.55, 129.49, 128.99, 127.93, 127.85, 125.08, 121.85, 119.71, 36.94, 21.04; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1231.



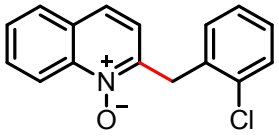
2-(3,5-dimethylbenzyl)quinoline 1-oxide (3e)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.63 – 7.56 (m, 2H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.93 (s, 3H), 4.41 (s, 2H), 2.31 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.45, 141.49, 138.37, 136.36, 130.31, 129.03, 128.62, 127.94, 127.87, 127.45, 125.08, 122.03, 119.79, 37.16, 21.25; HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{17}NO$ $[M+H]^+$: 264.1383, found: 264.1350.



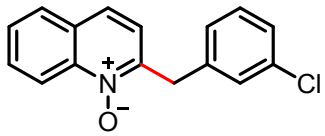
2-(4-methoxybenzyl)quinoline 1-oxide (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.64 – 7.55 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.46 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.77, 145.57, 141.24, 130.93, 130.54, 130.13, 129.21, 128.32, 128.15, 125.91, 119.08, 119.05, 114.51, 64.96, 20.46; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO_2$ $[M+H]^+$: 266.1176, found: 266.1192.



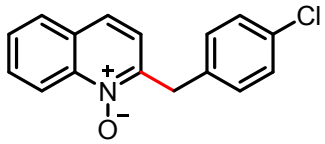
2-(2-chlorobenzyl)quinoline 1-oxide (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.38 – 7.30 (m, 2H), 7.22 – 7.16 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 4.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.57, 141.51, 134.77, 134.34, 132.02, 130.38, 129.73, 129.09, 128.70, 127.98, 127.21, 125.17, 121.57, 119.63, 35.49; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}ClNO$ $[M+H]^+$: 270.0680, found: 270.0676.



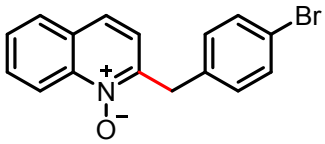
2-(3-chlorobenzyl)quinoline 1-oxide (3h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.32 (s, 1H), 7.30 – 7.22 (m, 3H), 7.12 (d, *J* = 8.6 Hz, 1H), 4.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.12, 141.57, 138.58, 134.54, 130.51, 130.03, 129.53, 129.21, 128.12, 128.03, 127.80, 127.22, 125.23, 121.89, 119.75, 37.06; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}ClNO$ $[M+H]^+$: 270.0680, found: 270.0687.



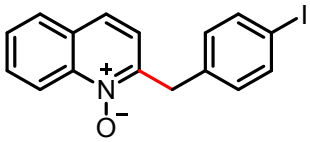
2-(4-chlorobenzyl)quinoline 1-oxide (3i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.66 – 7.58 (m, 2H), 7.34 – 7.24 (m, 4H), 7.10 (d, *J* = 8.6 Hz, 1H), 4.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.42, 141.58, 135.05, 132.87, 130.91, 130.52, 129.18, 128.94, 128.11, 128.03, 125.22, 121.84, 119.74, 36.83; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}ClNO[M+H]^+$: 270.0680, found: 270.0696.



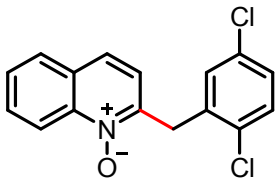
2-(4-bromobenzyl)quinoline 1-oxide (3j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.17 – 7.13 (m, 2H), 7.04 (d, *J* = 8.6 Hz, 1H), 4.38 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.74, 141.47, 135.46, 131.89, 131.29, 130.70, 129.13, 128.16, 128.03, 125.92, 121.82, 120.97, 119.69, 36.90; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}BrNO$ $[M+H]^+$: 314.0175, found: 314.0189.



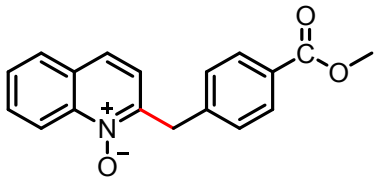
2-(4-iodobenzyl)quinoline 1-oxide (3k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.70 – 7.57 (m, 4H), 7.14 – 7.05 (m, 3H), 4.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.22, 141.53, 137.82, 136.23, 131.54, 130.47, 129.15, 128.07, 128.00, 125.17, 121.83, 119.70, 92.37, 36.98; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}INO$ $[M+H]^+$: 362.0036, found: 362.0021.



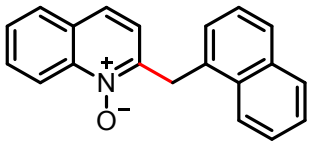
2-(2,5-dichlorobenzyl)quinoline 1-oxide (3l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.33 – 7.26 (m, 2H), 7.19 – 7.14 (m, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 4.48 (s, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 145.62, 141.59, 136.15, 133.03, 132.94, 131.64, 130.75, 130.53, 129.24, 128.76, 128.19, 128.05, 125.25, 121.62, 119.68, 35.38; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{11}Cl_2NO$ $[M+H]^+$: 304.0290, found: 304.0306.



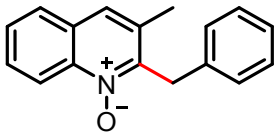
2-(4-(methoxycarbonyl)benzyl)quinoline 1-oxide (3m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.46 – 7.38 (m, 2H), 7.11 (d, *J* = 8.6 Hz, 1H), 4.54 (s, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.86, 147.08, 141.97, 141.59, 130.56, 130.10, 129.56, 129.23, 128.93, 128.16, 128.04, 125.27, 121.92, 119.76, 52.08, 37.43; HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}NO_3$ $[M+H]^+$: 294.1125, found: 294.1133.



2-(naphthalen-1-ylmethyl)quinoline 1-oxide (3n)

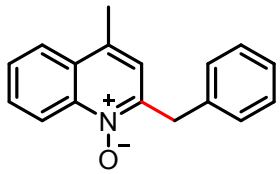
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J*= 8.1 Hz, 1H), 7.87 – 7.84 (m, 1H), 7.81 – 7.73 (m, 3H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.37 (m, 5H), 6.71 (d, *J* = 8.7 Hz, 1H), 4.94 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.04, 141.40, 133.91, 132.61, 132.20, 130.40, 128.89, 128.73, 128.44, 128.12, 127.96, 127.91, 126.50, 125.91, 125.66, 125.17, 124.01, 121.49, 119.69, 34.68; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{15}NO$ $[M+H]^+$: 286.1226, found: 286.1241.



2-benzyl-3-methylquinoline 1-oxide (4a)

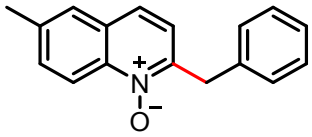
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.53 (s, 1H), 7.31 – 7.16 (m, 5H), 4.63 (s, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.99, 140.18, 136.73, 131.36, 129.39, 128.60, 128.32, 128.09,

127.17, 126.48, 125.57, 120.10, 33.68, 19.91; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO[M+H]^+$: 250.1226, found: 250.1223.



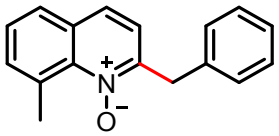
2-benzyl-4-methylquinoline 1-oxide (4b)

^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.67 – 7.59 (m, 1H), 7.39 – 7.27 (m, 5H), 6.90 (s, 1H), 4.48 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.38, 140.98, 136.71, 133.56, 130.05, 129.64, 128.79, 128.56, 127.68, 126.91, 124.56, 122.39, 120.31, 37.23, 18.29; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1224.



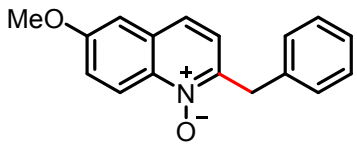
2-benzyl-6-methylquinoline 1-oxide (4c)

^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.39 – 7.26 (m, 5H), 7.02 (d, *J* = 8.7 Hz, 1H), 4.48 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.52, 139.99, 138.09, 136.65, 132.61, 129.69, 129.18, 128.80, 126.93, 126.89, 124.99, 121.88, 119.54, 37.30, 21.31; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1213.



2-benzyl-8-methylquinoline 1-oxide (4d)

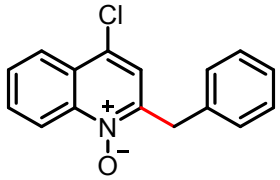
^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.25 (m, 7H), 6.90 (d, *J* = 8.6 Hz, 1H), 4.38 (s, 2H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.30, 141.43, 136.79, 133.55, 133.34, 130.96, 129.83, 128.85, 127.35, 126.94, 126.80, 125.39, 121.47, 37.59, 25.34; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1224.



2-benzyl-6-methoxyquinoline 1-oxide (4e)

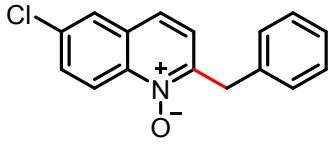
^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 9.5 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.28 (m, 6H), 7.06 (d, *J* = 2.6 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 4.45 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.88, 146.17, 137.20, 136.77, 130.39, 129.64, 128.78, 126.89, 124.25, 122.45,

122.41, 121.45, 105.84,55.62, 37.12; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO_2$ $[M+H]^+$: 266.1176, found: 266.1191.



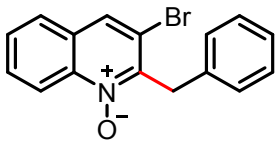
2-benzyl-4-chloroquinoline 1-oxide (4f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 9.2 Hz,1H), 7.86 – 7.79 (m, 1H), 7.73 – 7.67 (m, 1H), 7.41 – 7.28 (m, 5H), 7.13 (s, 1H), 4.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.20, 142.14, 135.81, 131.16, 129.67, 129.41, 128.99, 128.79, 127.26, 126.72, 125.03, 121.72, 120.28, 37.24; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}ClNO$ $[M+H]^+$: 270.0680, found: 270.0696.



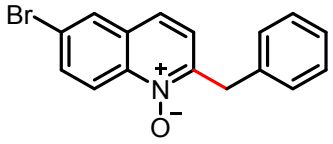
2-benzyl-6-chloroquinoline 1-oxide (4g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 9.3 Hz, 1H), 7.79 (d, *J* = 2.1 Hz, 1H), 7.67 (dd, *J* = 9.3, 2.1 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.41 – 7.27 (m, 5H), 7.08 (d, *J* = 8.7 Hz, 1H), 4.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.36, 140.01, 136.18, 134.12, 130.99, 129.77, 129.63, 128.87, 127.08, 126.61, 123.77, 123.12, 121.71, 37.30; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}ClNO$ $[M+H]^+$: 270.0680, found: 270.0663.



2-benzyl-3-bromoquinoline 1-oxide (4h)

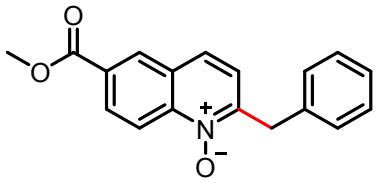
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.8 Hz, 1H), 7.99 (s, 1H), 7.78 – 7.70 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.31 – 7.24 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 4.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.47, 141.06, 136.05, 130.52, 129.04, 128.91, 128.67, 128.48, 128.13, 127.08, 126.76, 120.28, 117.80, 36.65; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}BrNO$ $[M+H]^+$: 314.0175, found: 314.0180.



2-benzyl-6-bromoquinoline 1-oxide (4i)

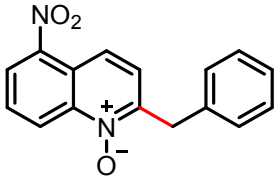
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 9.3 Hz, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.80 (dd, *J* = 9.3, 2.0 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.26 (m, 5H), 7.07 (d, *J* = 8.7 Hz, 1H), 4.44 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.42, 140.28, 136.13, 133.53, 130.16, 129.89, 129.62, 128.86, 127.07, 123.61, 123.07, 122.24, 121.74, 37.32; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}BrNO$ $[M+H]^+$: 314.0175, found: 314.0187.



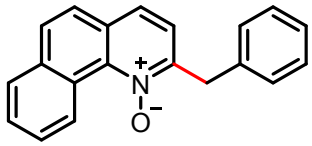
2-benzyl-6-(methoxycarbonyl)quinoline 1-oxide (4j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 9.1 Hz, 1H), 8.57 (d, *J* = 1.6 Hz, 1H), 8.34 (dd, *J* = 9.1, 1.8 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.42 – 7.28 (m, 5H), 7.14 (d, *J* = 8.7 Hz, 1H), 4.50 (s, 2H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.91, 150.25, 143.17, 136.04, 130.88, 129.91, 129.72, 129.67, 128.93, 128.47, 127.17, 125.82, 122.78, 120.34, 52.59, 37.54; HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}NO_3$ $[M+H]^+$: 294.1125, found: 294.1137.



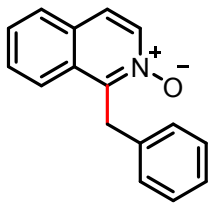
2-benzyl-5-nitroquinoline 1-oxide (4k)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.8 Hz, 1H), 8.40 (dd, *J* = 7.7, 1.0 Hz, 1H), 8.37 (d, *J* = 9.3 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.43 – 7.24 (m, 6H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.33, 145.94, 142.32, 135.50, 129.66, 129.03, 128.35, 127.36, 126.44, 125.81, 124.94, 122.49, 120.11, 37.36;HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}N_2O_3$ $[M+H]^+$: 281.0921, found: 281.0949.



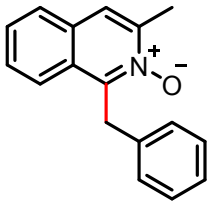
2-benzylbenzo[h]quinoline 1-oxide (4l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.01 – 10.89 (m, 1H), 8.01 – 7.90 (m, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.69 – 7.60 (m, 2H), 7.44 – 7.29 (m, 5H), 7.15 (d, *J* = 8.3 Hz, 1H), 4.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.27, 138.46, 136.94, 134.38, 129.92, 129.83, 129.52, 128.87, 128.80, 128.39, 128.08, 127.59, 126.96, 126.32, 125.13, 124.81, 121.91, 37.98; HRMS (ESI-TOF) m/z Calcd for $C_{20}H_{15}NO$ $[M+H]^+$: 286.1226, found: 286.1227.



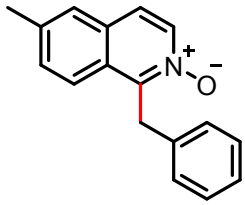
1-benzylisoquinoline 2-oxide (4m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.1 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.49 (m, 3H), 7.37 – 7.13 (m, 5H), 4.82 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.88, 136.94, 136.84, 129.34, 128.91, 128.87, 128.61, 128.58, 128.17, 127.38, 126.54, 123.98, 122.54, 31.70; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{13}NO$ $[M+H]^+$: 236.1070, found: 236.1078.



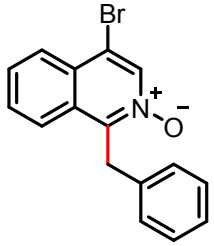
1-benzyl-3-methylisoquinoline 2-oxide (4n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.47 (m, 3H), 7.35 – 7.30 (m, 2H), 7.27 – 7.21 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 4.83 (s,2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.78, 145.62, 137.20, 128.64, 128.52, 128.10, 127.84, 127.77, 126.54, 126.40, 123.74, 121.57, 32.23, 18.43; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1242.



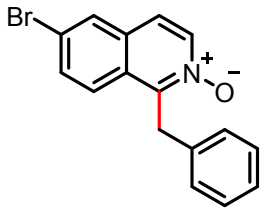
1-benzyl-6-methylisoquinoline 2-oxide (4o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.39 (m, 3H), 7.36 – 7.10 (m, 5H), 4.81 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.81, 138.74, 137.05, 136.75, 131.45, 129.35, 128.55, 126.94, 126.47, 123.94, 121.92, 31.65, 21.43; HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{15}NO$ $[M+H]^+$: 250.1226, found: 250.1235.



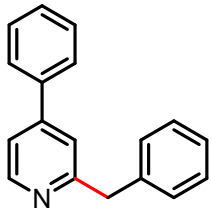
1-benzyl-4-bromoisoquinoline 2-oxide (4p)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.15 – 8.09 (m, 1H), 8.05 – 7.97 (m, 1H), 7.70 – 7.63 (m, 2H), 7.34 – 7.16 (m, 5H), 4.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.59, 138.20, 136.53, 130.21, 129.23, 128.76, 128.74, 128.54, 128.45, 126.94, 126.75, 124.46, 118.79, 31.67; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}BrNO$ $[M+H]^+$: 314.0175, found: 314.0169.



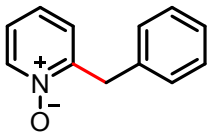
1-benzyl-6-bromoisoquinoline 2-oxide (4q)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 4.0 Hz1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.67 (dd, *J* = 9.0, 1.7 Hz, 1H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.34 – 7.15 (m, 5H), 4.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.13, 137.89, 136.56, 132.81, 129.87, 129.56, 128.71, 128.48, 127.48, 126.73, 125.57, 122.67, 121.50, 31.68; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{12}BrNO$ $[M+H]^+$: 314.0175, found: 314.0164.



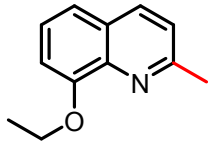
2-benzyl-4-phenylpyridine (4r)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.6 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.49 – 7.40 (m, 3H), 7.36 – 7.29 (m, 6H), 7.25 – 7.20 (m, 1H), 4.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.43, 149.76, 149.00, 139.44, 138.34, 129.08, 129.00, 128.92, 128.60, 127.02, 126.40, 121.09, 119.41, 44.78; HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{15}N$ $[M+H]^+$: 246.1277, found: 246.1274.



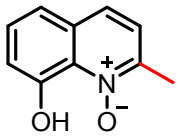
2-benzylpyridine 1-oxide (4s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.26 (m, 1H), 7.42 – 7.33 (m, 2H), 7.33 – 7.24 (m, 3H), 7.19 – 7.10 (m, 2H), 6.98 – 6.88 (m, 1H), 4.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.98, 139.37, 136.24, 129.71, 128.84, 127.03, 125.74, 125.42, 123.50, 36.51; HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{11}NO$ $[M+H]^+$: 186.0913, found: 186.0920.



8-ethoxy-2-methylquinoline (6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.20 (m, 3H), 7.04 (d, *J* = 7.3 Hz, 1H), 4.34 (q, *J* = 6.9 Hz, 2H), 2.80 (s, 3H), 1.63 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.09, 154.04, 139.75, 136.11, 127.66, 125.68, 122.47, 119.23, 108.66, 64.28, 25.74, 14.55; HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{13}NO$ $[M+H]^+$: 188.1070, found: 188.1079.

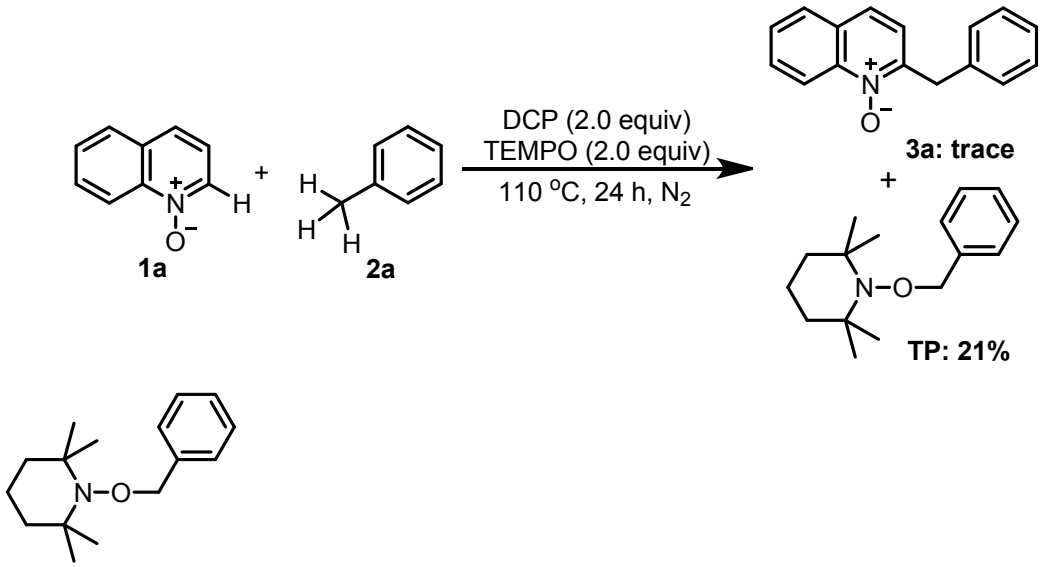


8-hydroxy-2-methylquinoline 1-oxide (8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 15.46 (s, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.04 (dd, *J* = 7.9, 1.0 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.71, 144.51, 130.93, 129.88, 129.53, 128.74, 122.61, 116.58, 114.79, 17.86; HRMS (ESI-TOF) m/z Calcd for $C_{10}H_9NO_2$ $[M+H]^+$: 176.0706, found: 176.0719.

2.3 Trapping of radical intermediates with radical scavenger TEMPO

In a 25 mL tube, quinoline *N*-oxide (0.5 mmol, 1.0 equiv), DCP (1.0 mmol, 2.0 equiv), TEMPO (1.0 mmol, 2.0 equiv) and toluene (2.0 mL) were added under N_2 atmosphere. The tube was sealed and the resulting solution was heated in a 110 °C oil bath with vigorous stirring for 24 h. Then the reaction mixture was cooled to room temperature. The mixture was extracted with ethyl acetate (20 mL × 3), and the combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated under vacuum. The residue was purified by flash chromatography using EtOAc/*n*-hexene as eluent (1:40). The TEMPO product **TP** was isolated in 21% yield along with a trace of **3a**.



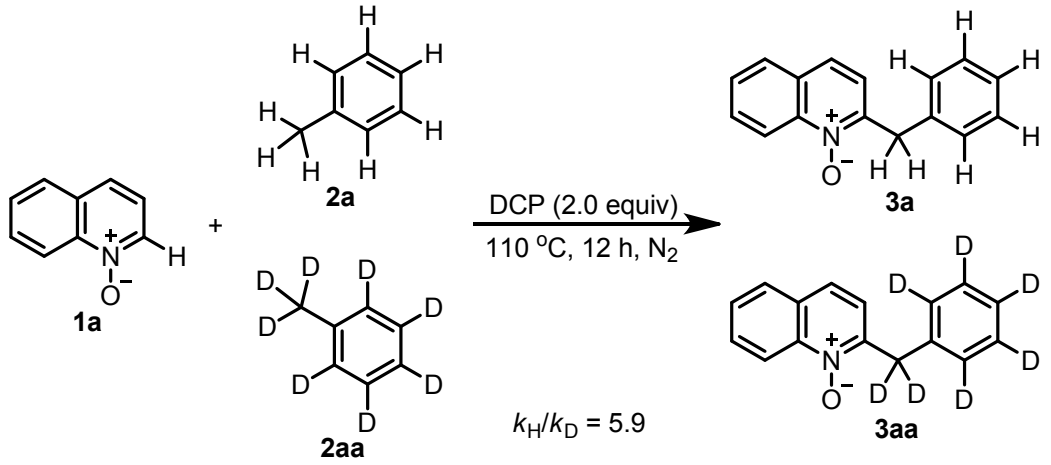
1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (TP)

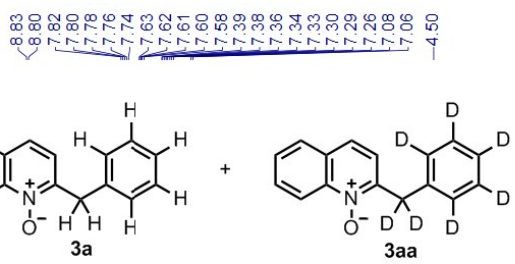
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 4H), 7.18 (t, *J* = 6.8 Hz, 1H), 4.75 (s, 2H), 1.55 – 1.34 (m, 5H), 1.32 – 1.22 (m, 1H), 1.18 (s, 6H), 1.07 (s, 6H);^{13}C NMR (100 MHz, $CDCl_3$) δ 138.24, 128.17, 127.37, 127.23, 78.71, 59.94, 39.69, 33.07, 20.27, 17.10; HRMS (ESI-TOF) m/z Calcd for $C_{16}H_{25}NO$ $[M+H]^+$: 248.2009, found: 248.2015.

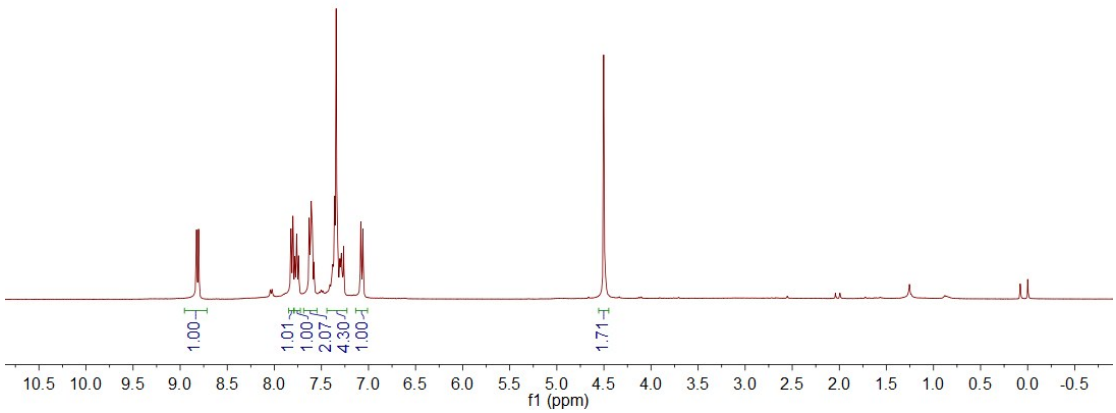
2.4 Kinetic isotope effect studies

To a mixture of quinoline *N*-oxide (0.5 mmol, 1.0 equiv) and DCP (1.0 mmol, 2.0 equiv) was added an equivalent of toluene (1.0 mL) and d_8-toluene (1.0 mL) under N_2 atmosphere. The

resultant mixture was heated in a preheated oil bath at 110 °C for 12 h. Then the reaction mixture was cooled to room temperature. The mixture was extracted with ethyl acetate (20 mL × 3), and the combined organic layer was dried over Na_2SO_4, filtered and the solvent was evaporated under vacuum. The crude product was obtained by purifying over a column of silica gel and eluted with EtOAc/*n*-hexene (1:2) to give the expected product in 38% yield (**3a** and **3aa**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.66 – 7.55 (m, 2H), 7.46 – 7.21 (m, 4.3H), 7.07 (d, J = 8.6 Hz, 1H), 4.50 (s, 1.71H). The KIE value was calculated as k_H/k_D = 5.9.

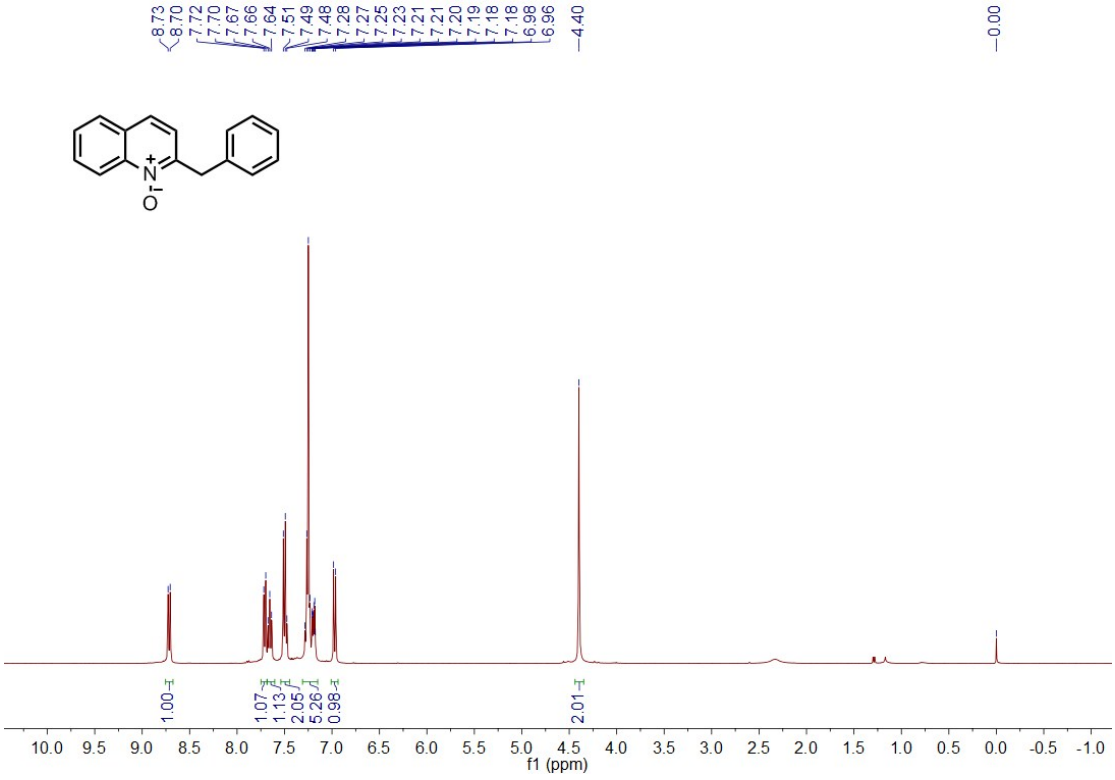


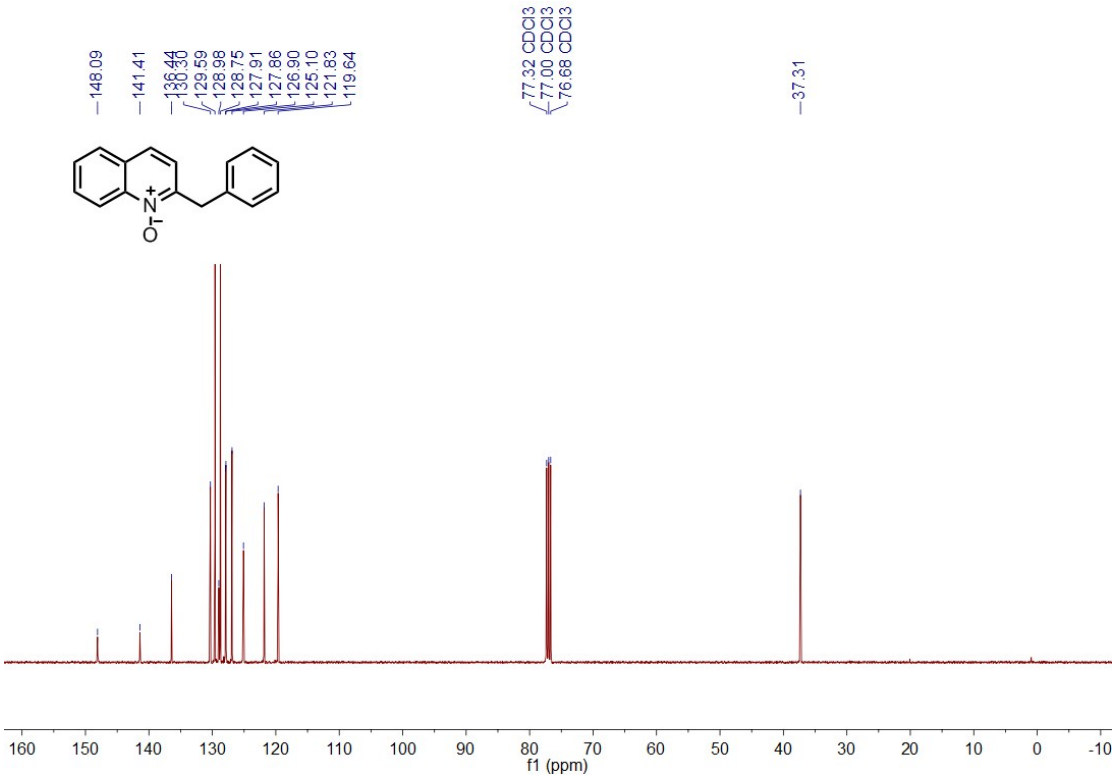




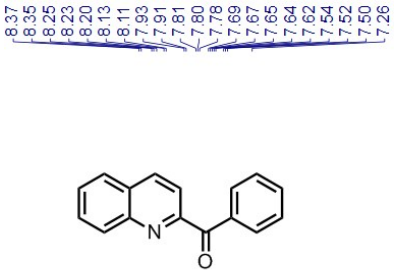
3. ^{1}H and ^{13}C NMR spectra

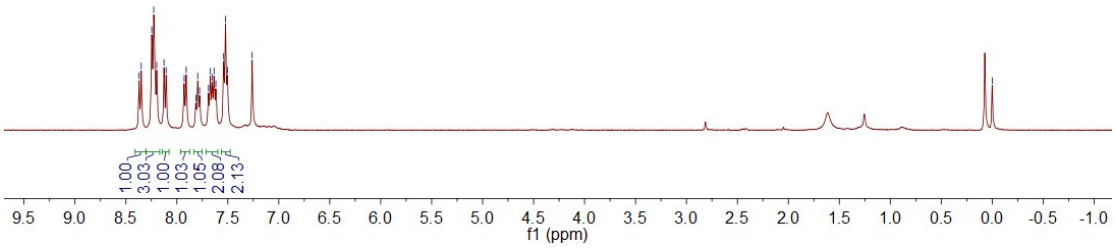
2-benzylquinoline 1-oxide (3a)

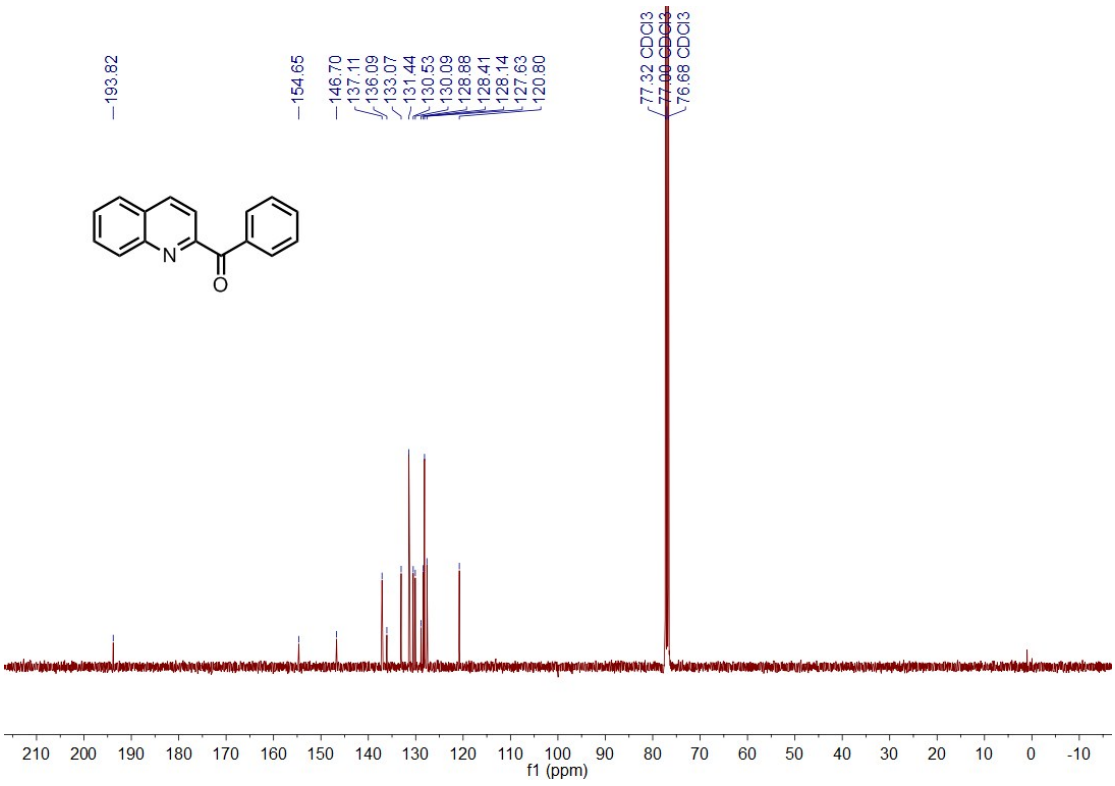




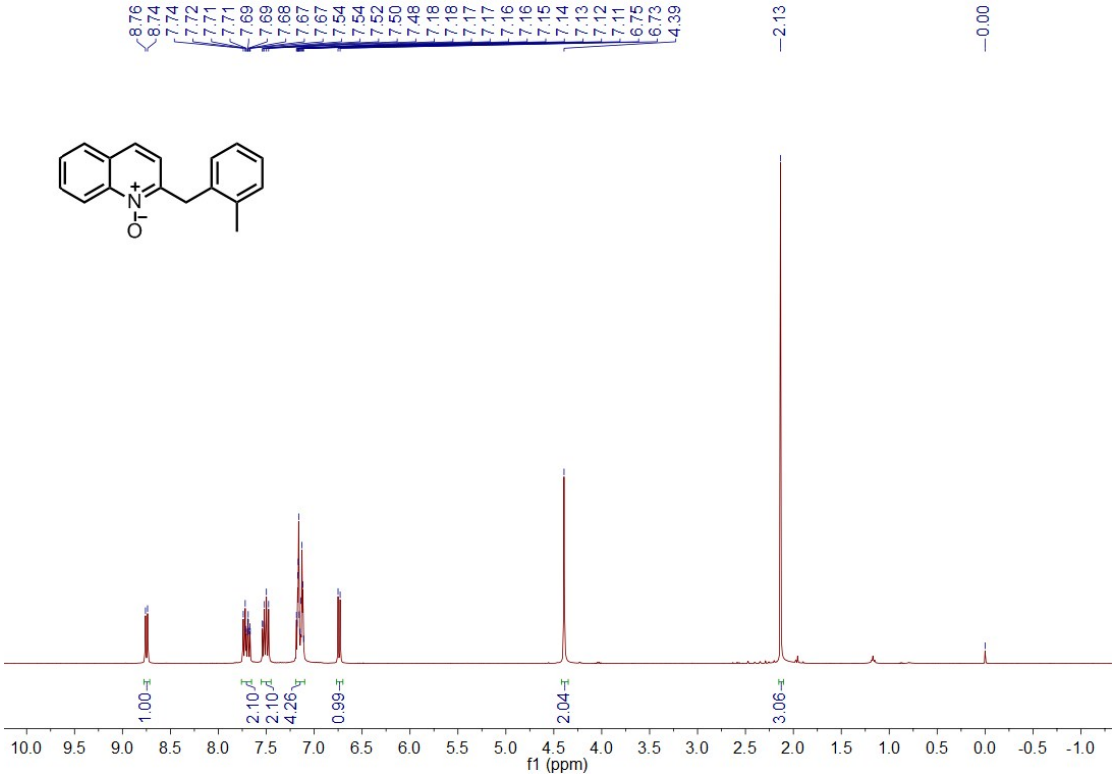
phenyl(quinolin-2-yl)methanone (3a')

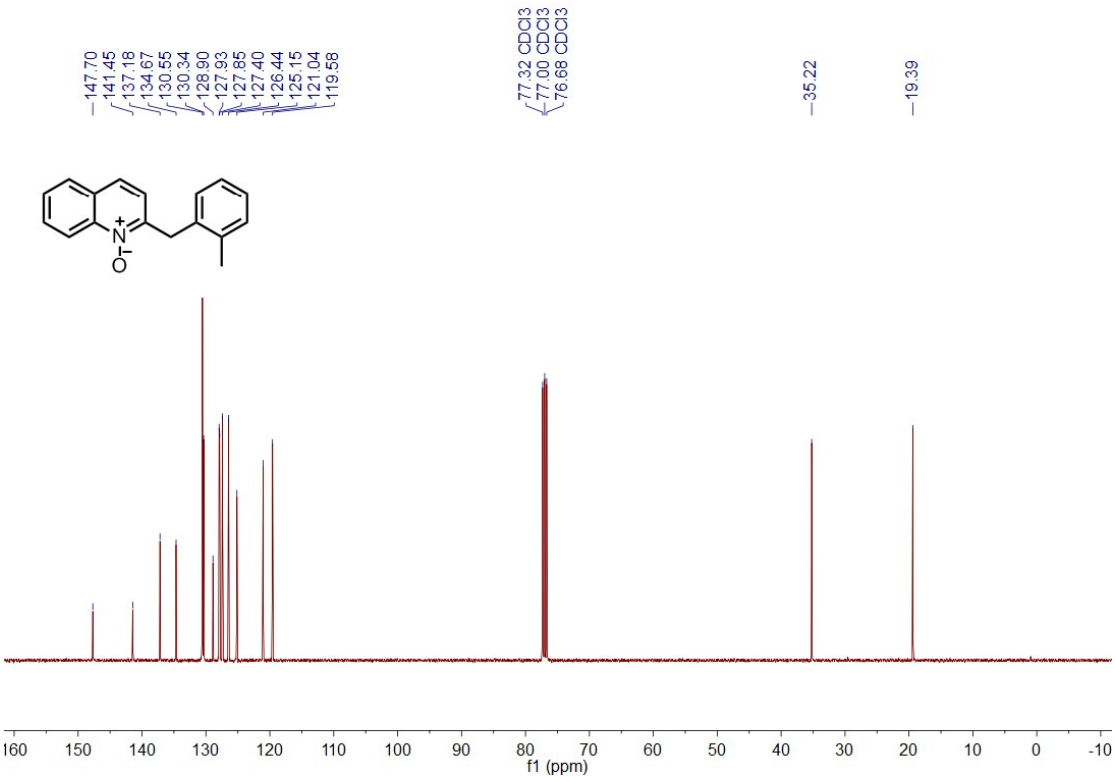




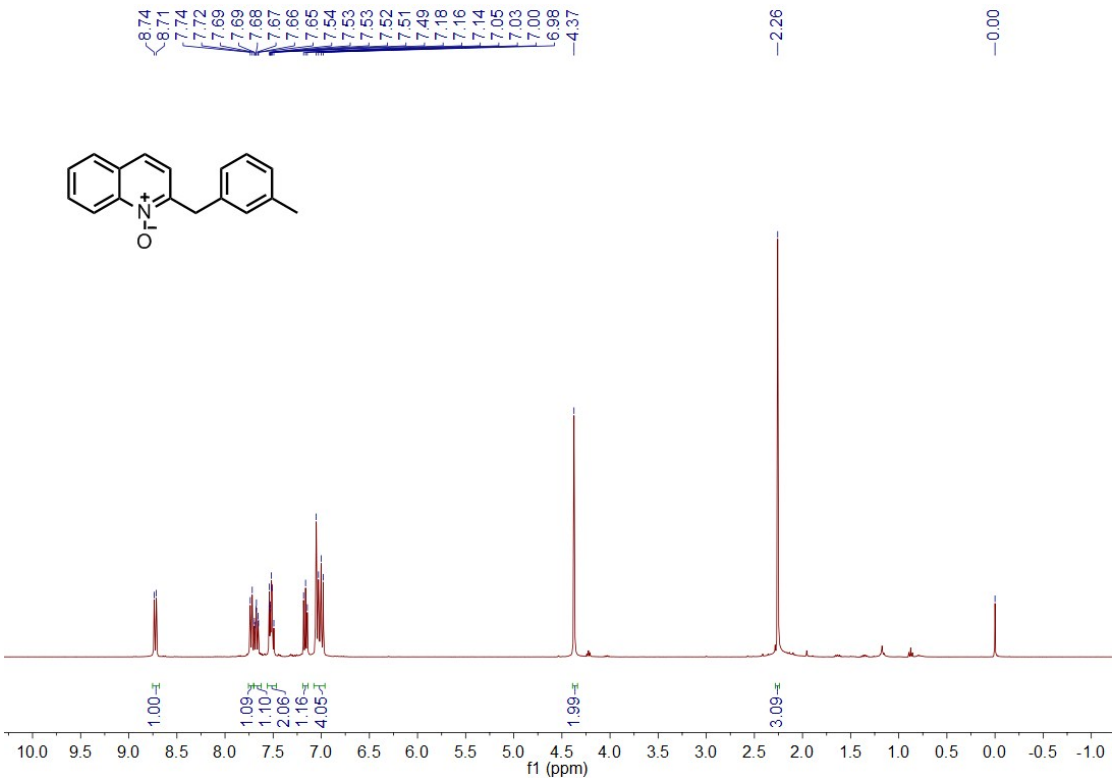


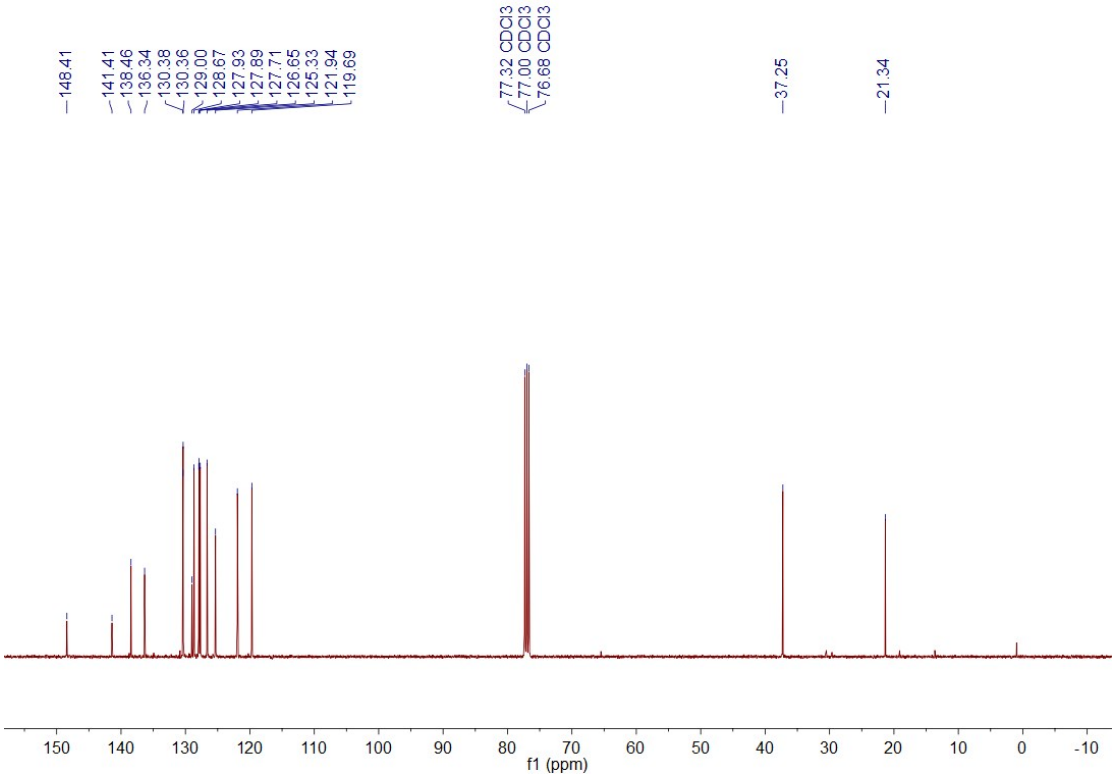
2-(2-methylbenzyl)quinoline 1-oxide (3b)



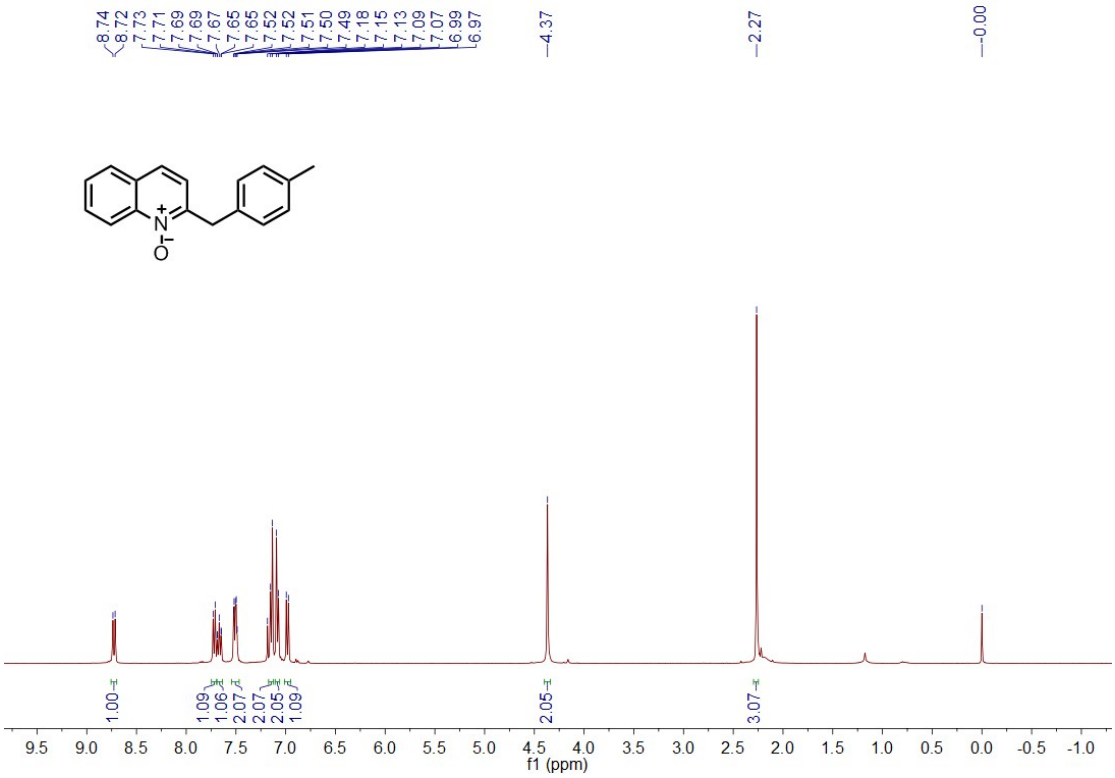


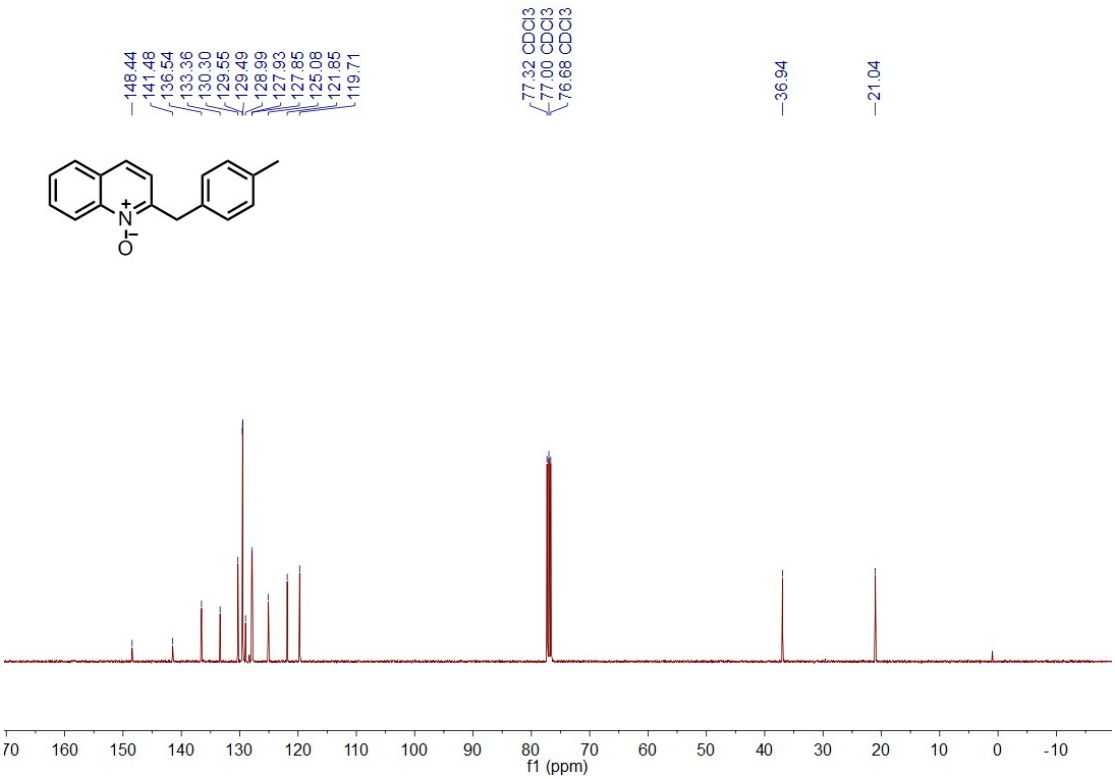
2-(3-methylbenzyl)quinoline 1-oxide (3c)



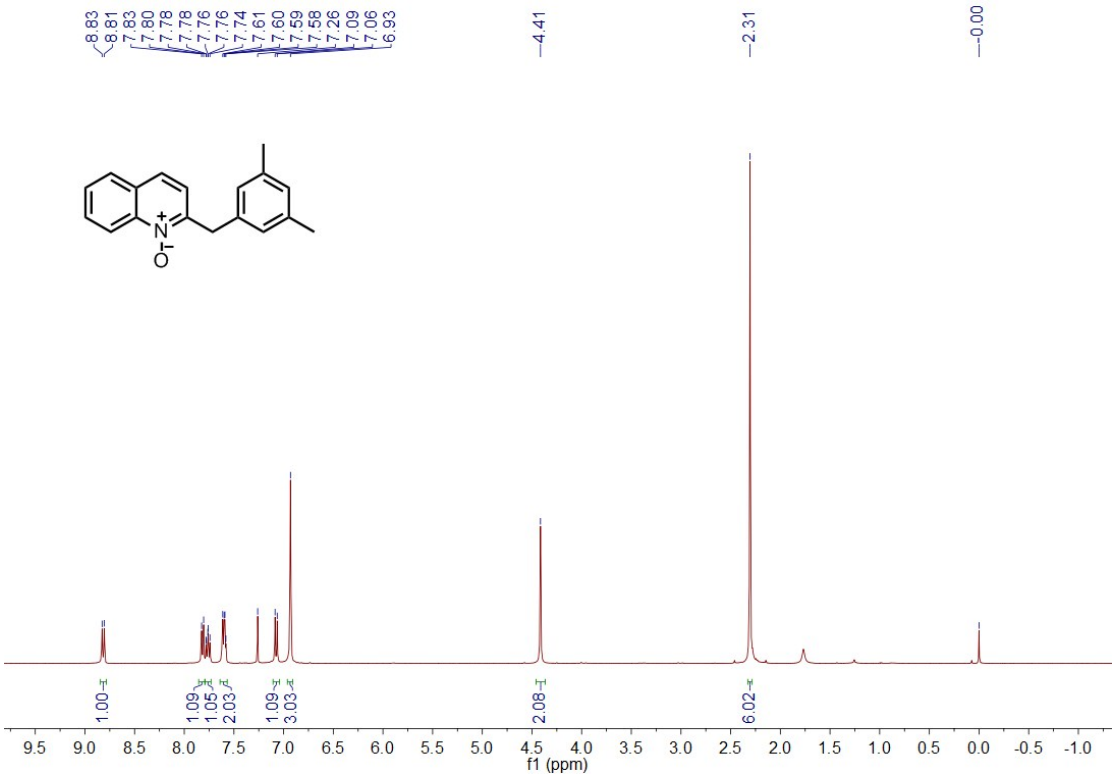


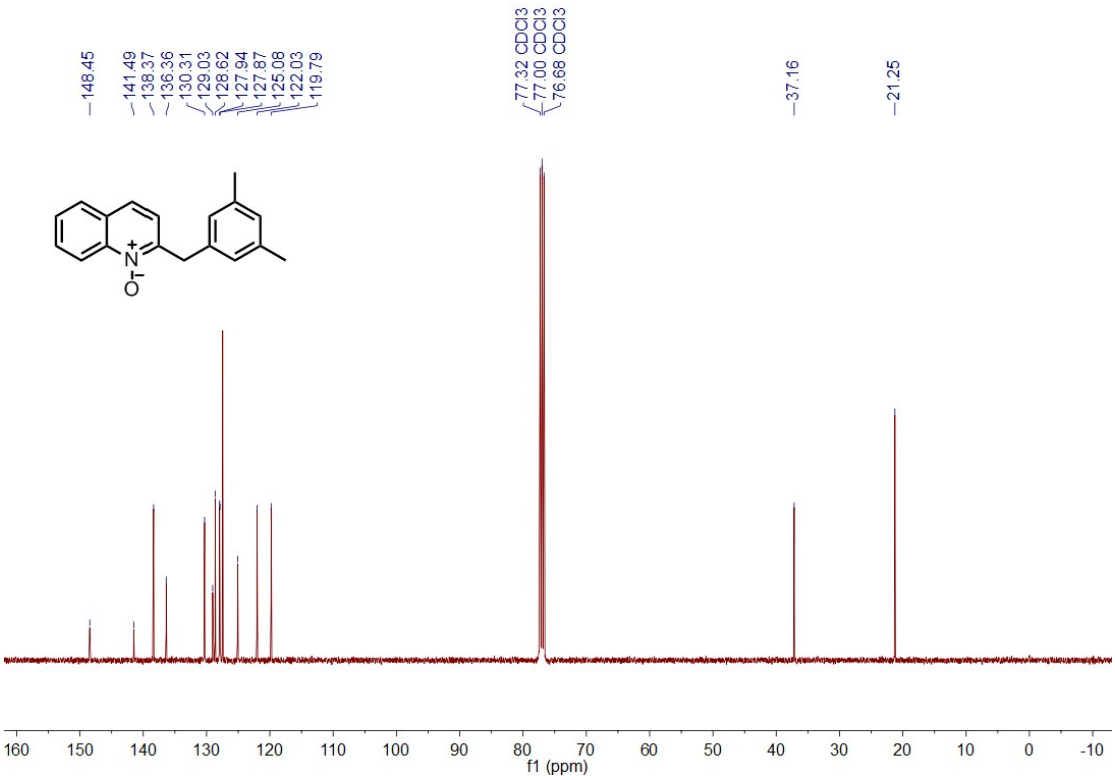
2-(4-methylbenzyl)quinoline 1-oxide (3d)



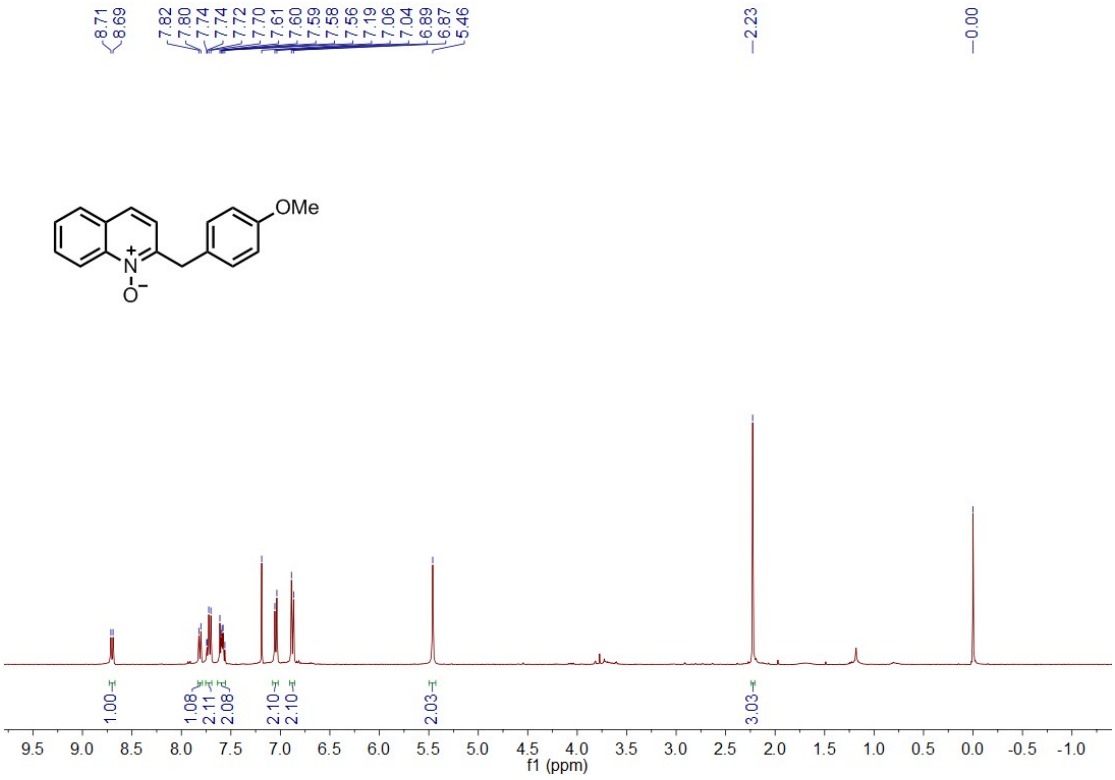


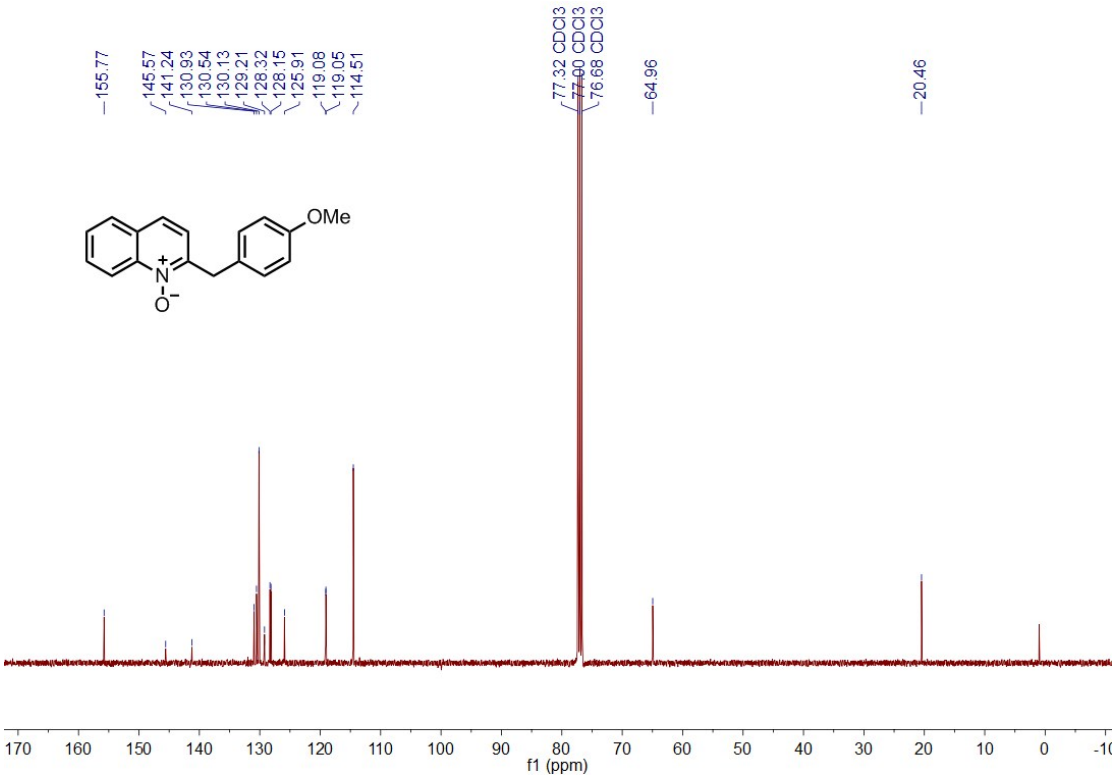
2-(3,5-dimethylbenzyl)quinoline 1-oxide (3e)



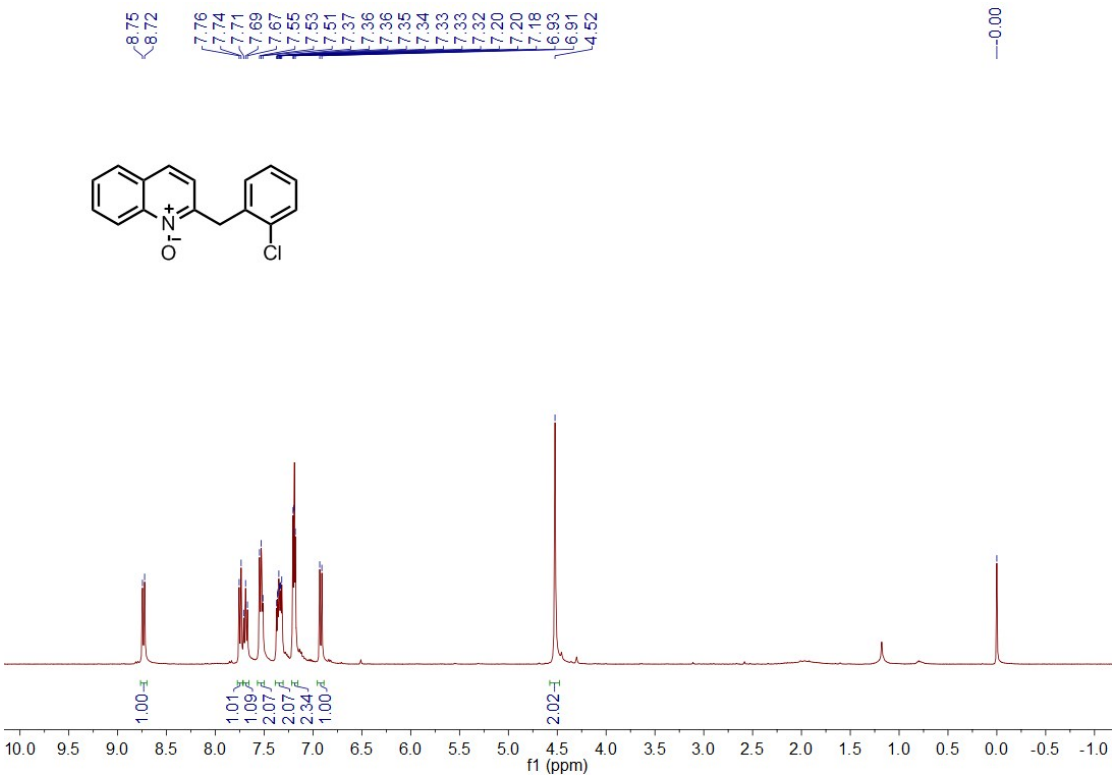


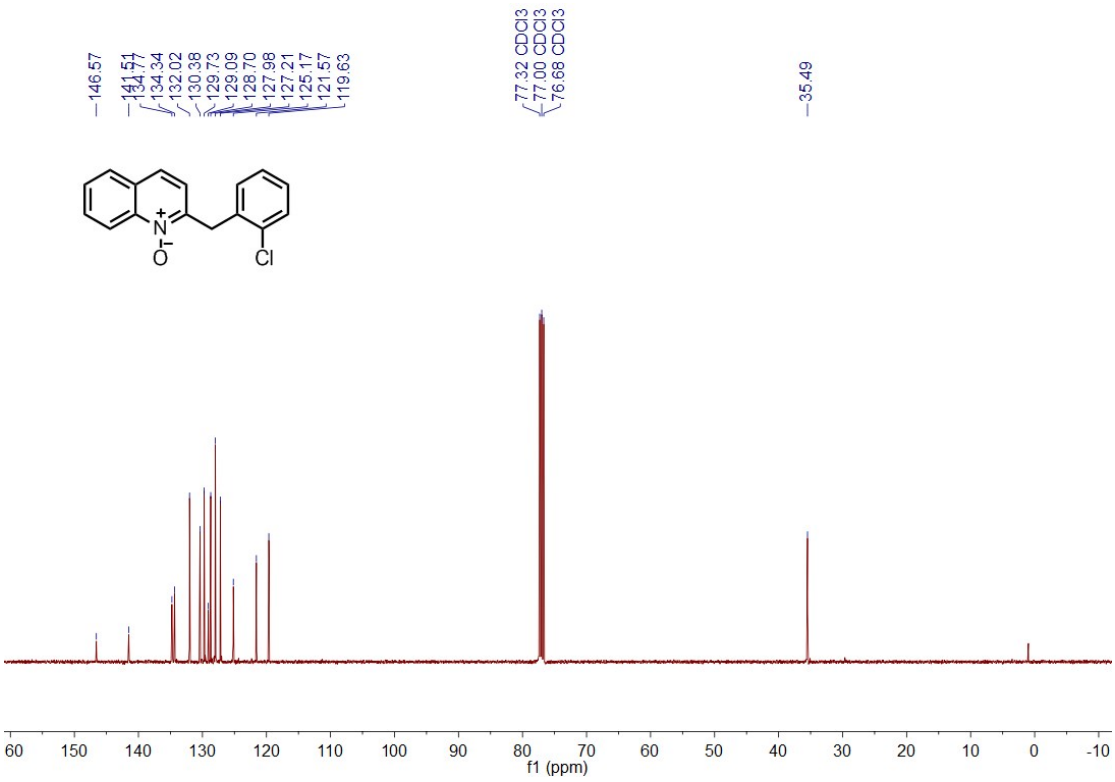
2-(4-methoxybenzyl)quinoline 1-oxide (3f)



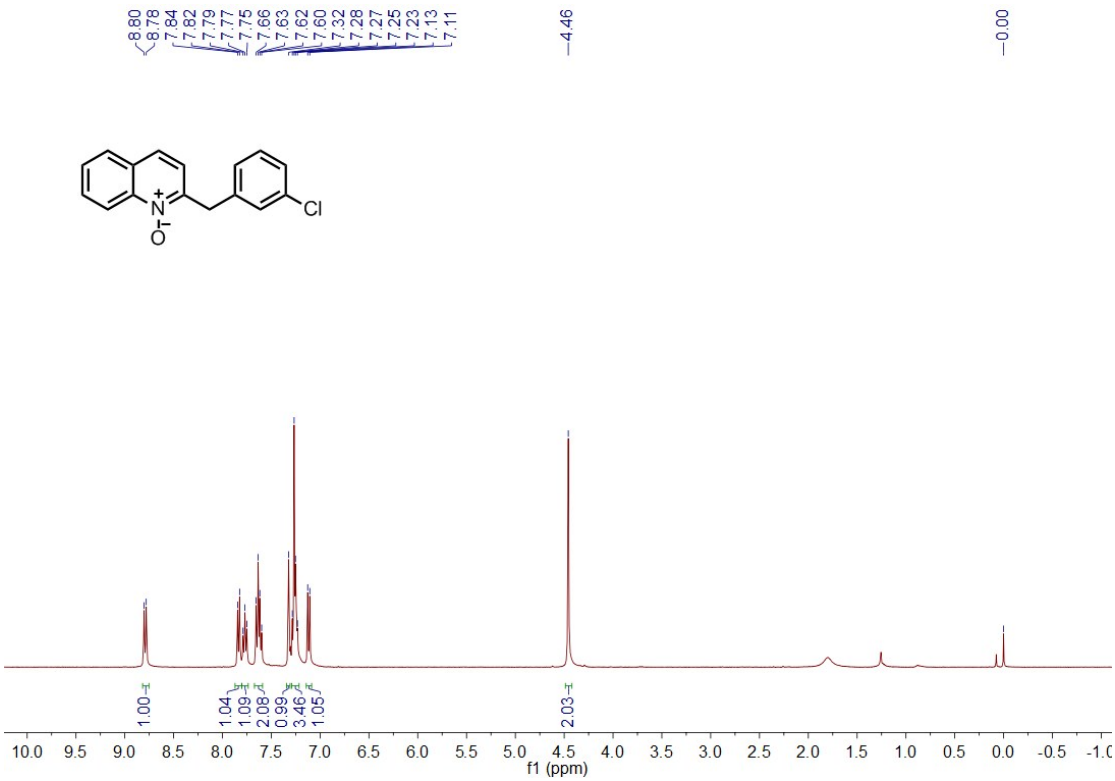


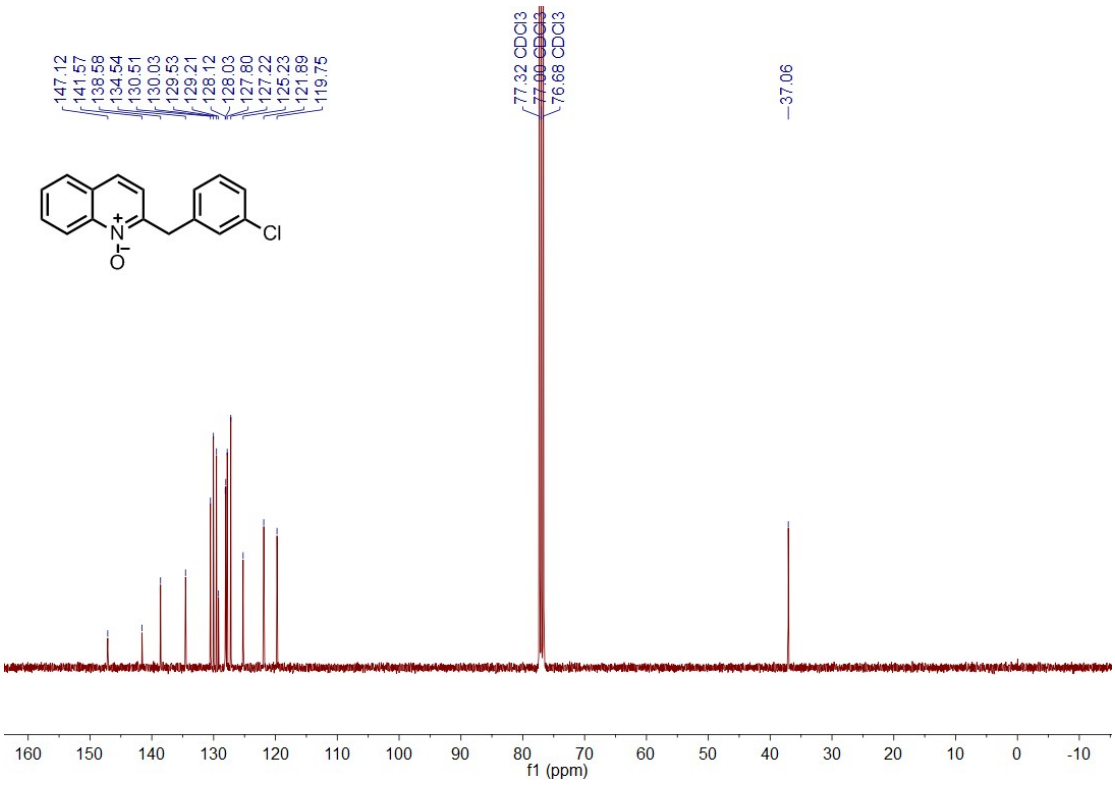
2-(2-chlorobenzyl)quinoline 1-oxide (3g)



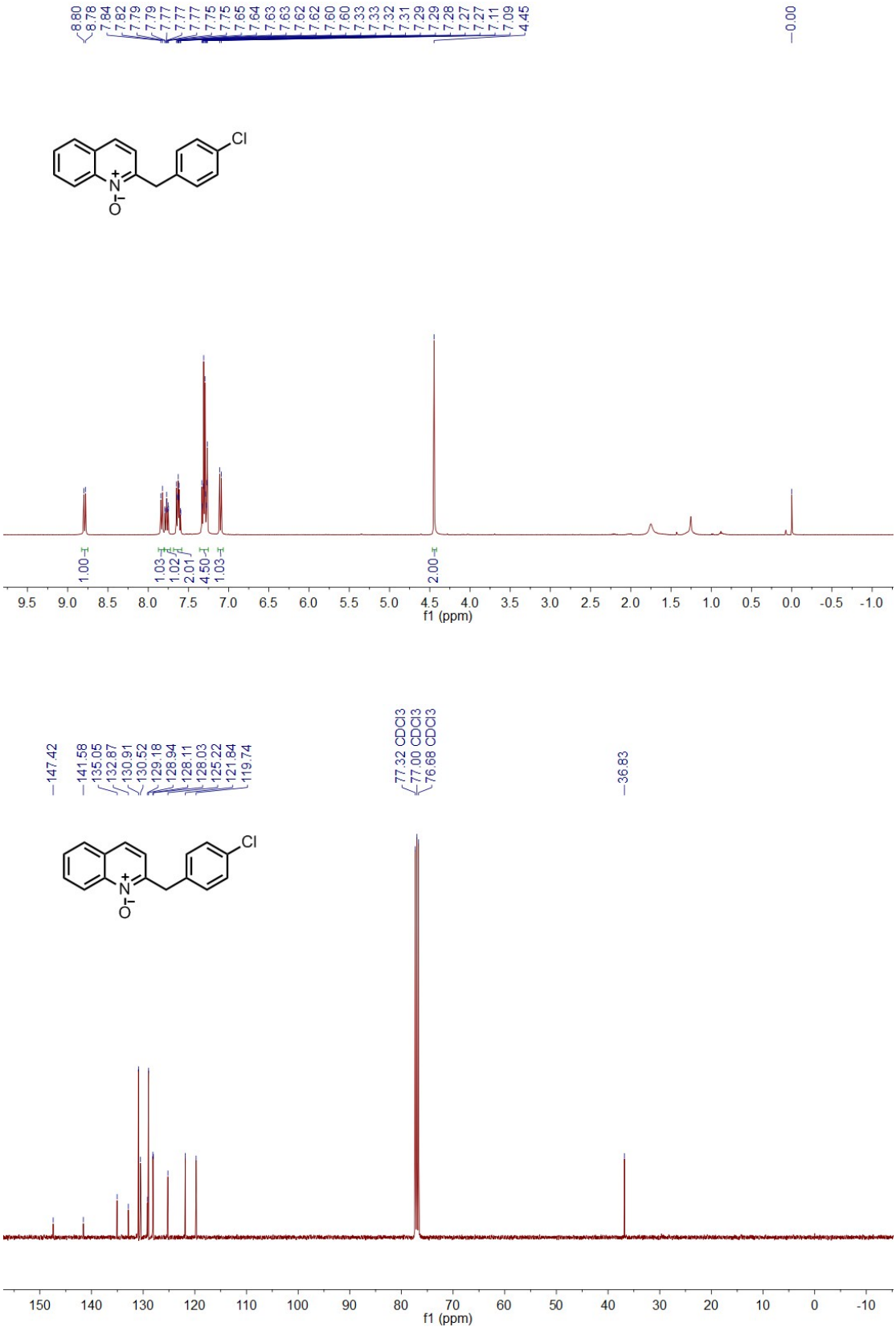


2-(3-chlorobenzyl)quinoline 1-oxide (3h)

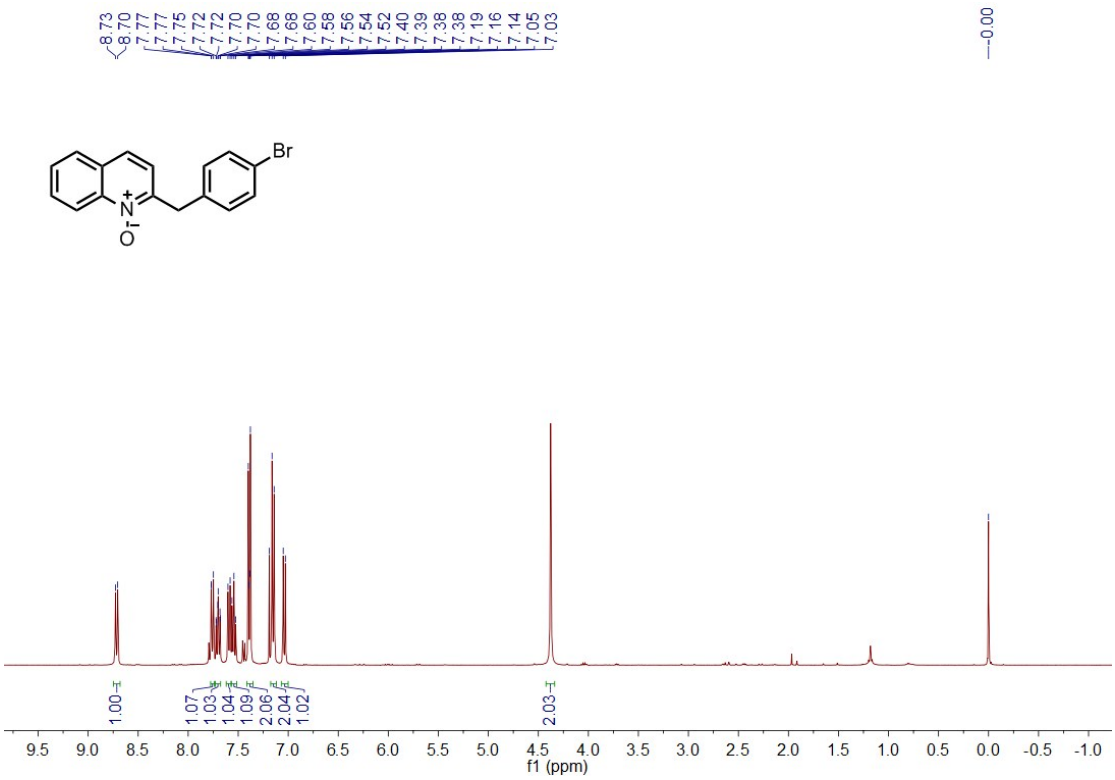


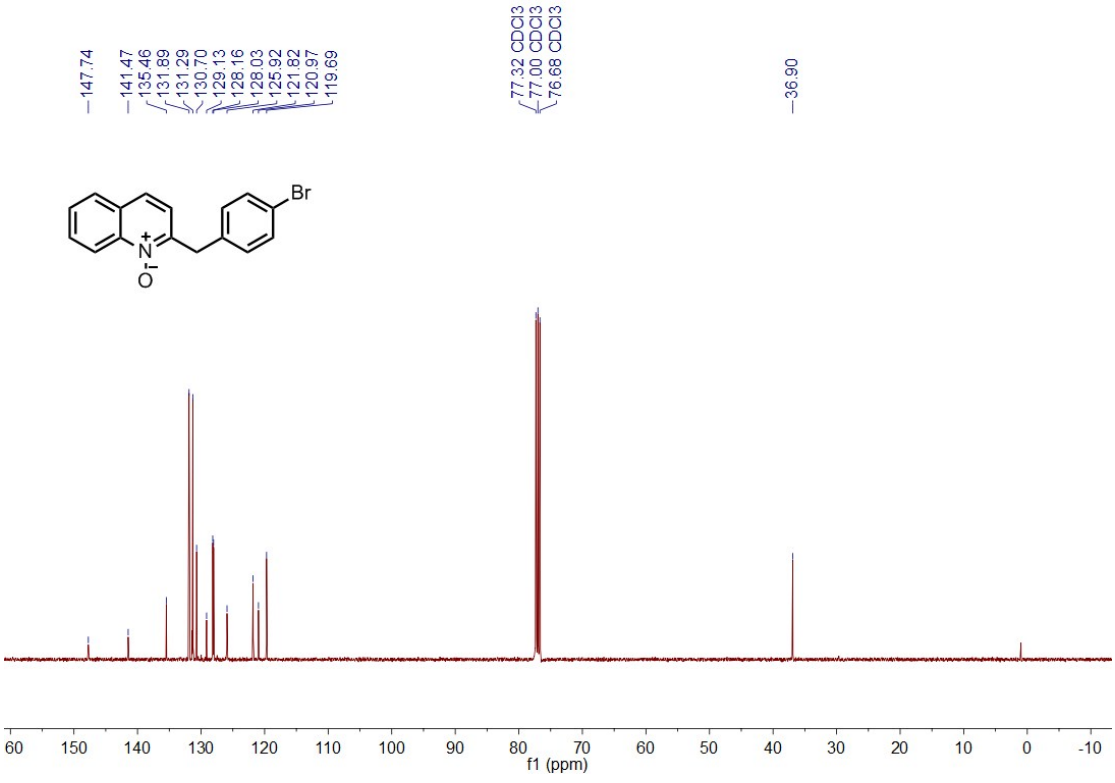


2-(4-chlorobenzyl)quinoline 1-oxide (3i)

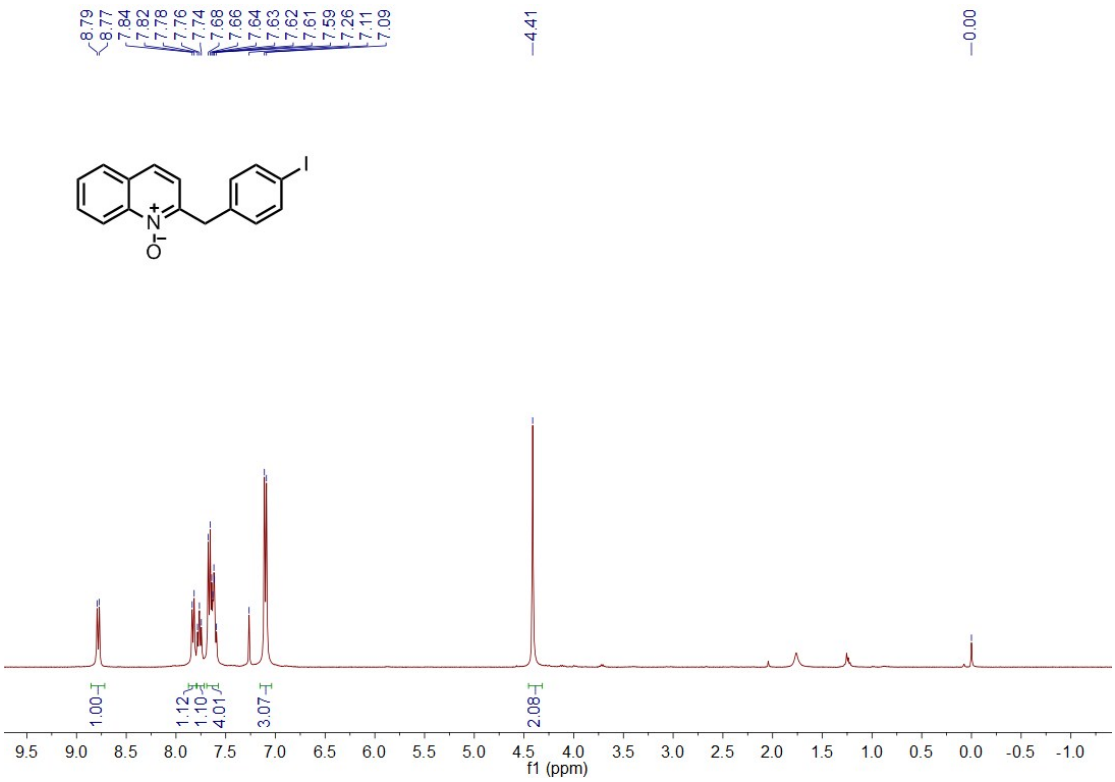


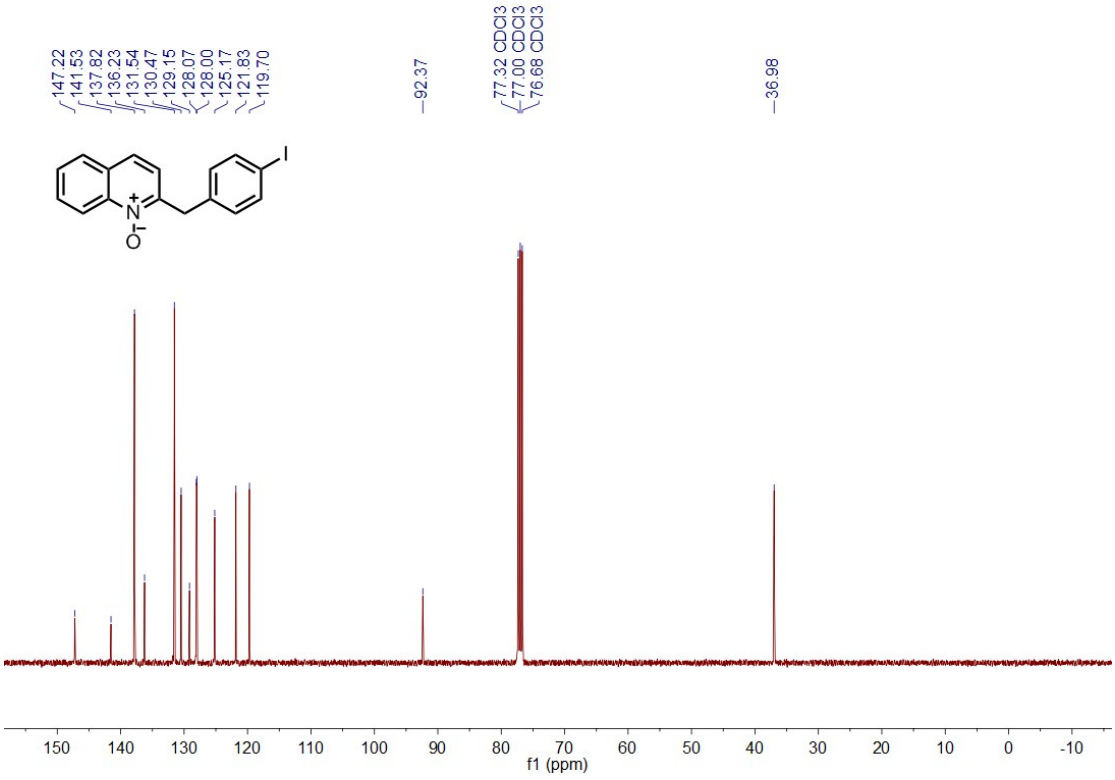
2-(4-bromobenzyl)quinoline 1-oxide (3j)



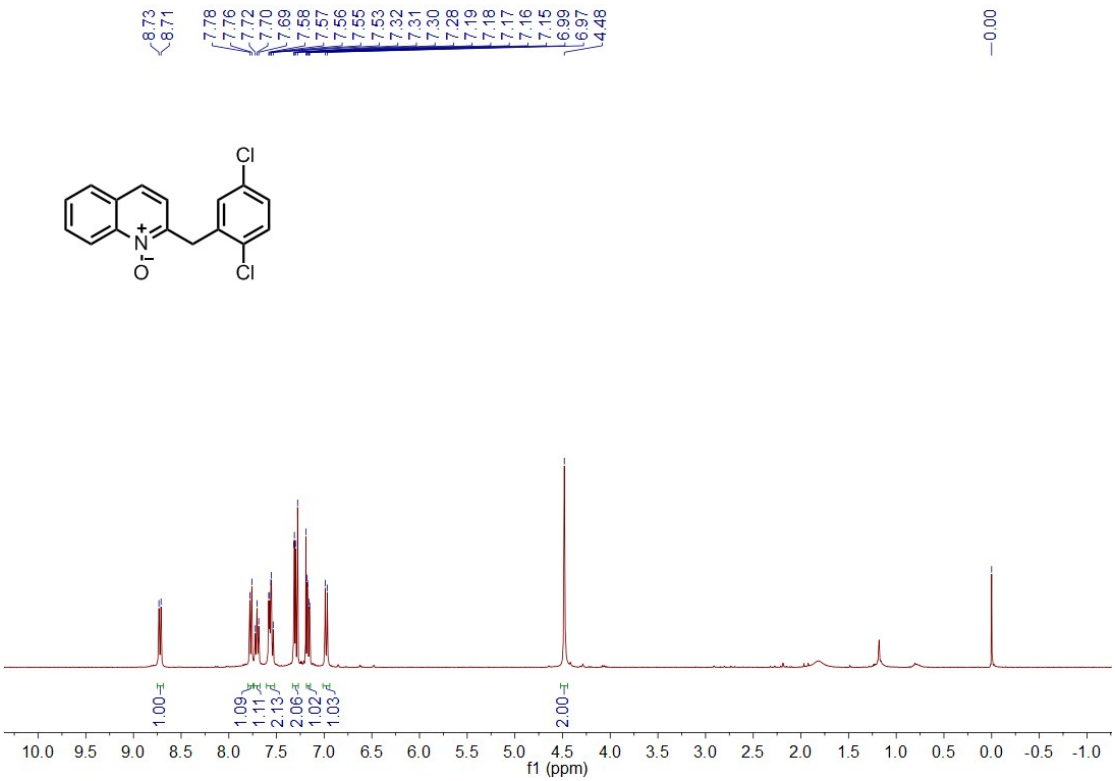


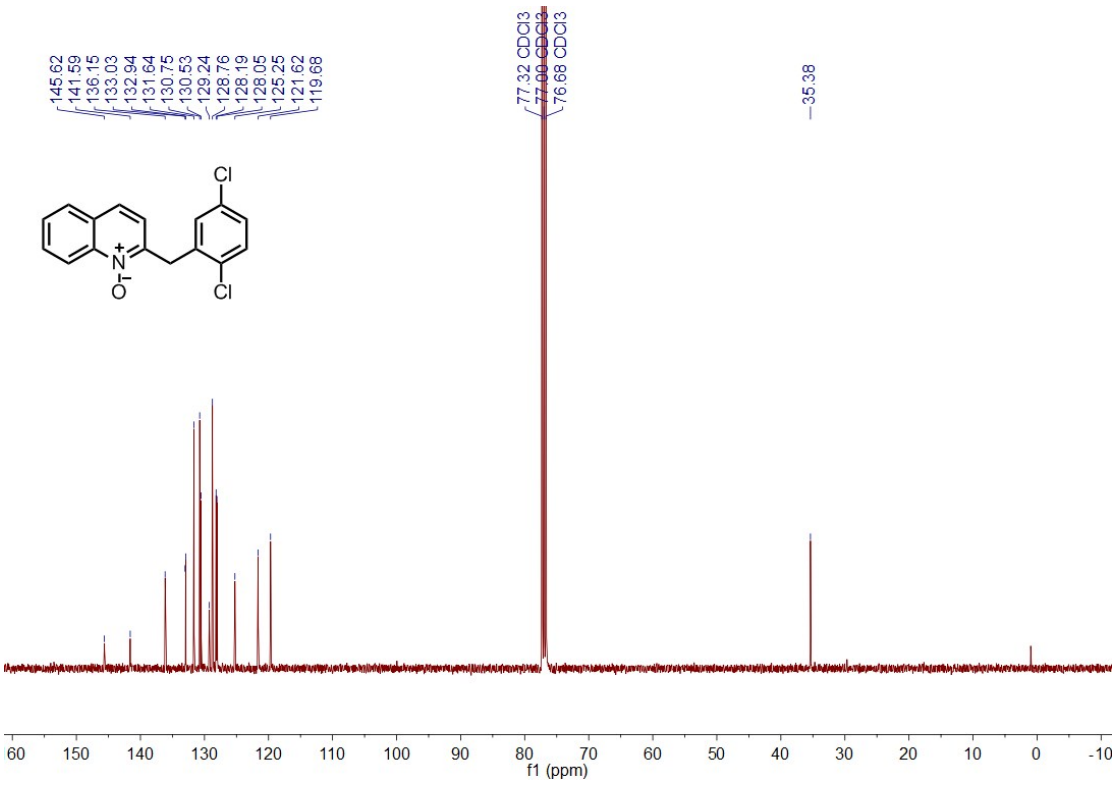
2-(4-iodobenzyl)quinoline 1-oxide (3k)



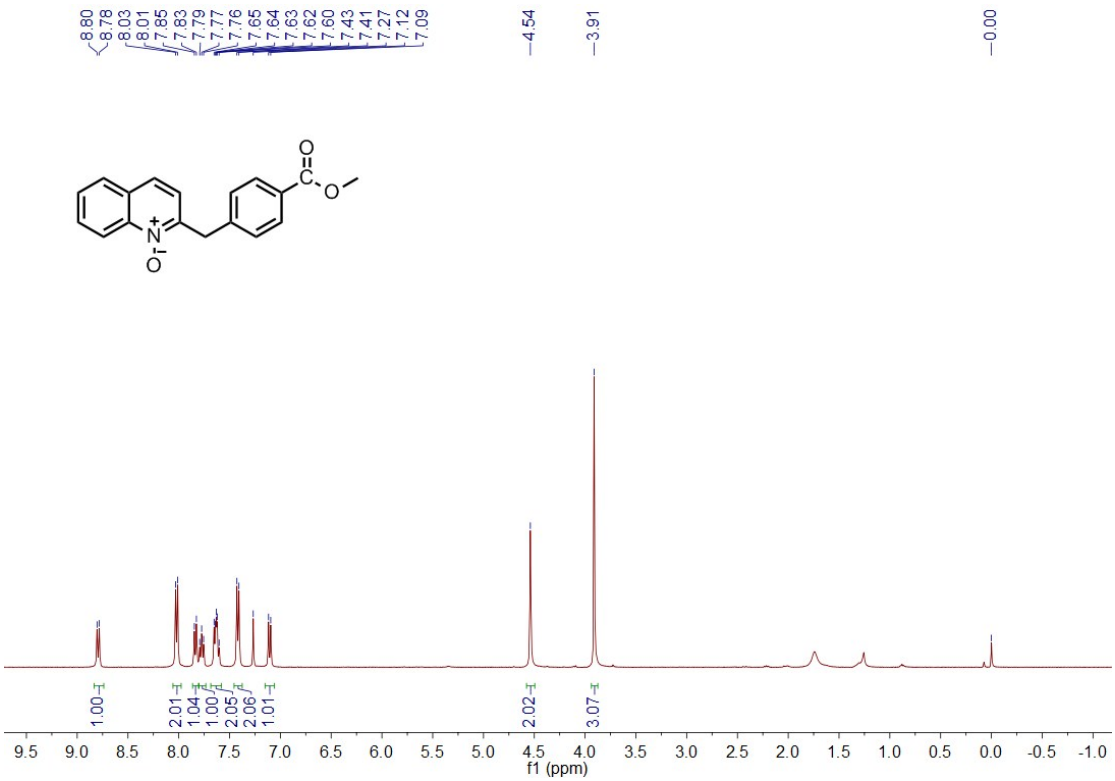


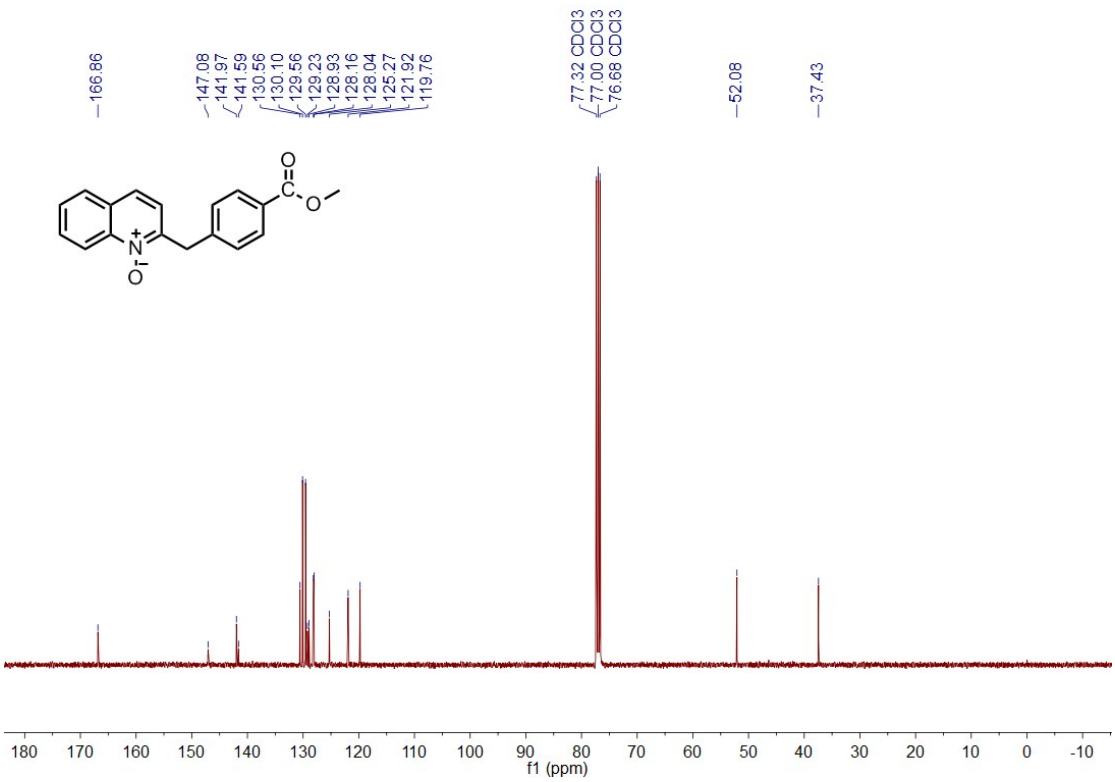
2-(2,5-dichlorobenzyl)quinoline 1-oxide (3l)



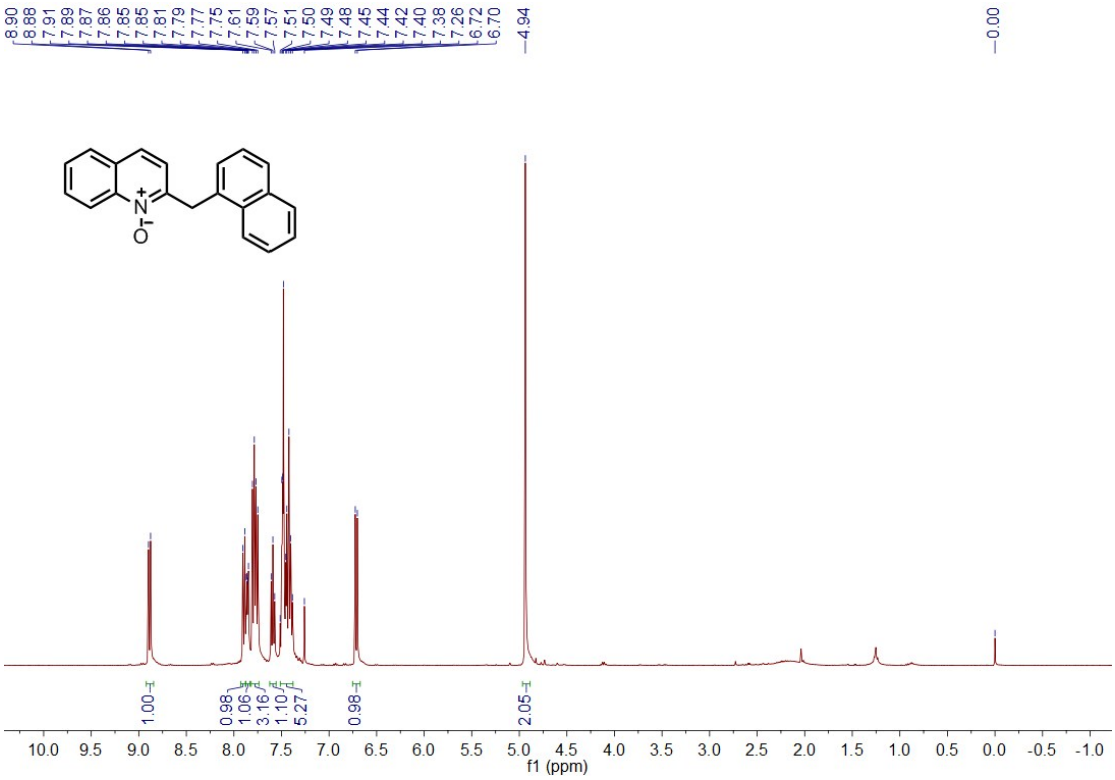


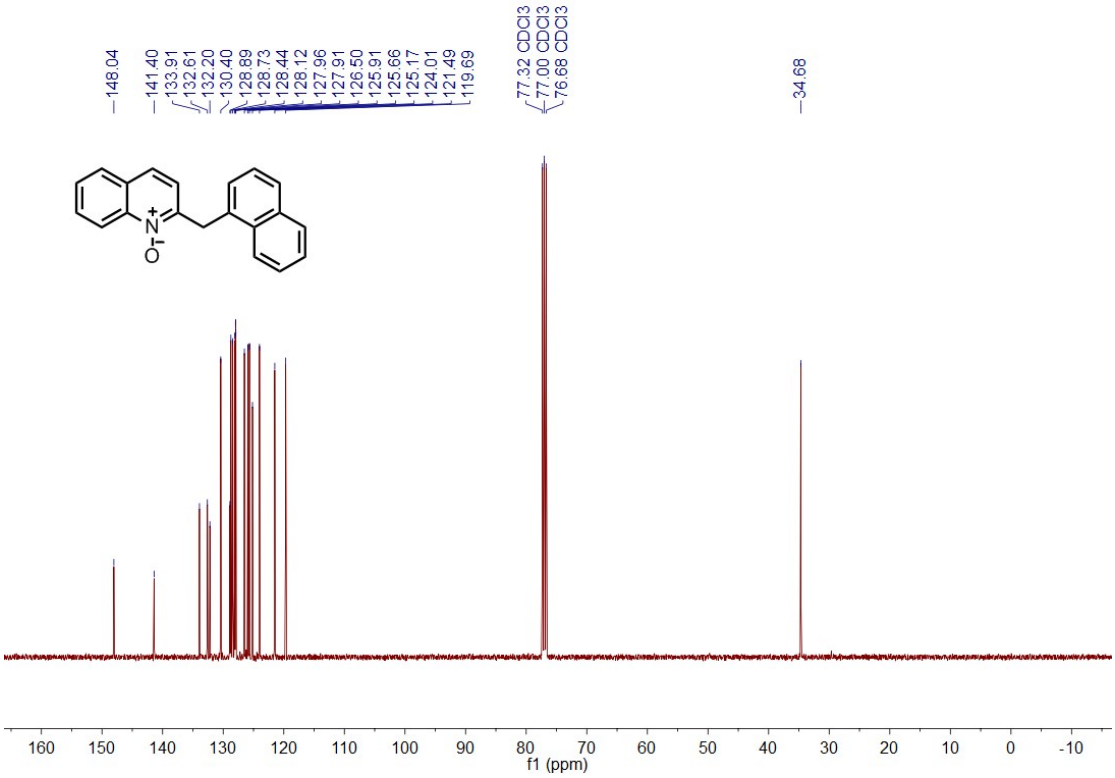
2-(4-(methoxycarbonyl)benzyl)quinoline 1-oxide (3m)



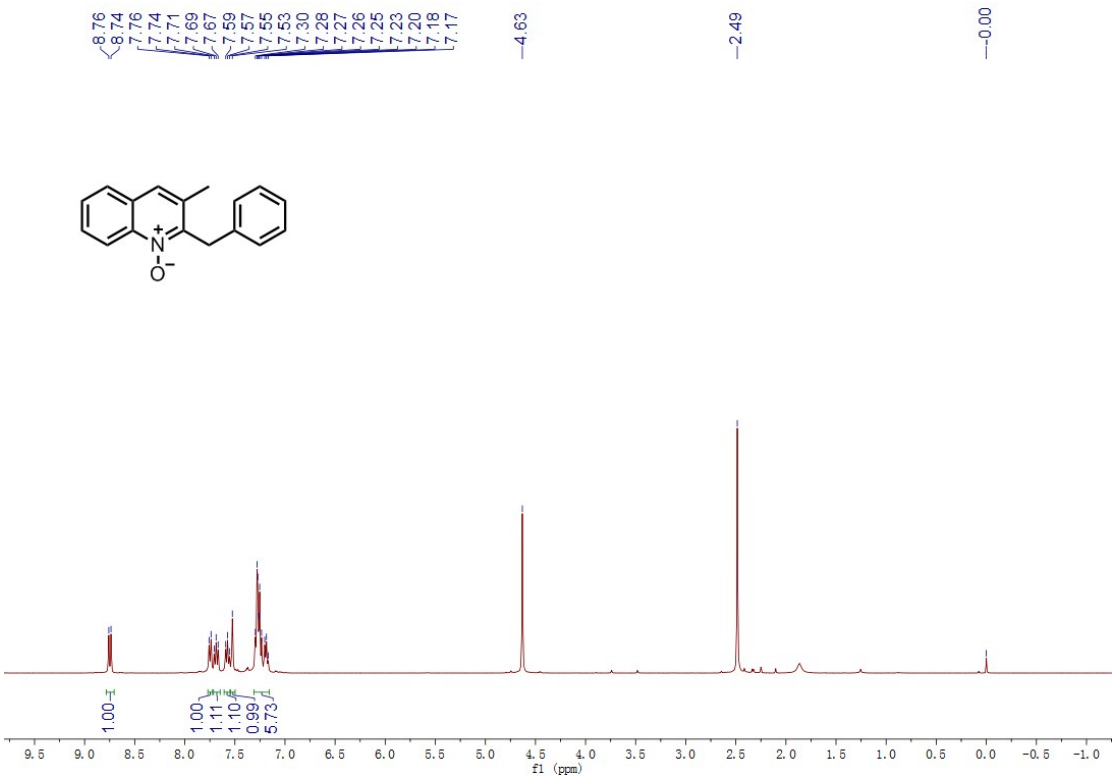


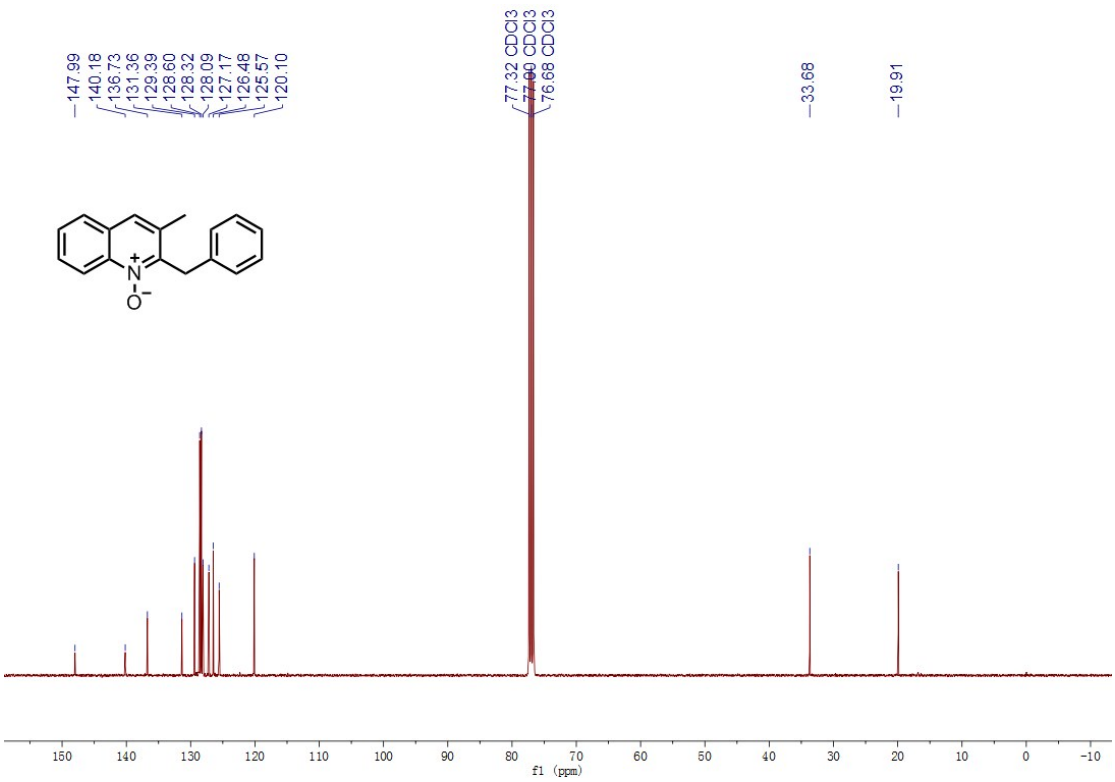
2-(naphthalen-1-ylmethyl)quinoline 1-oxide (3n)



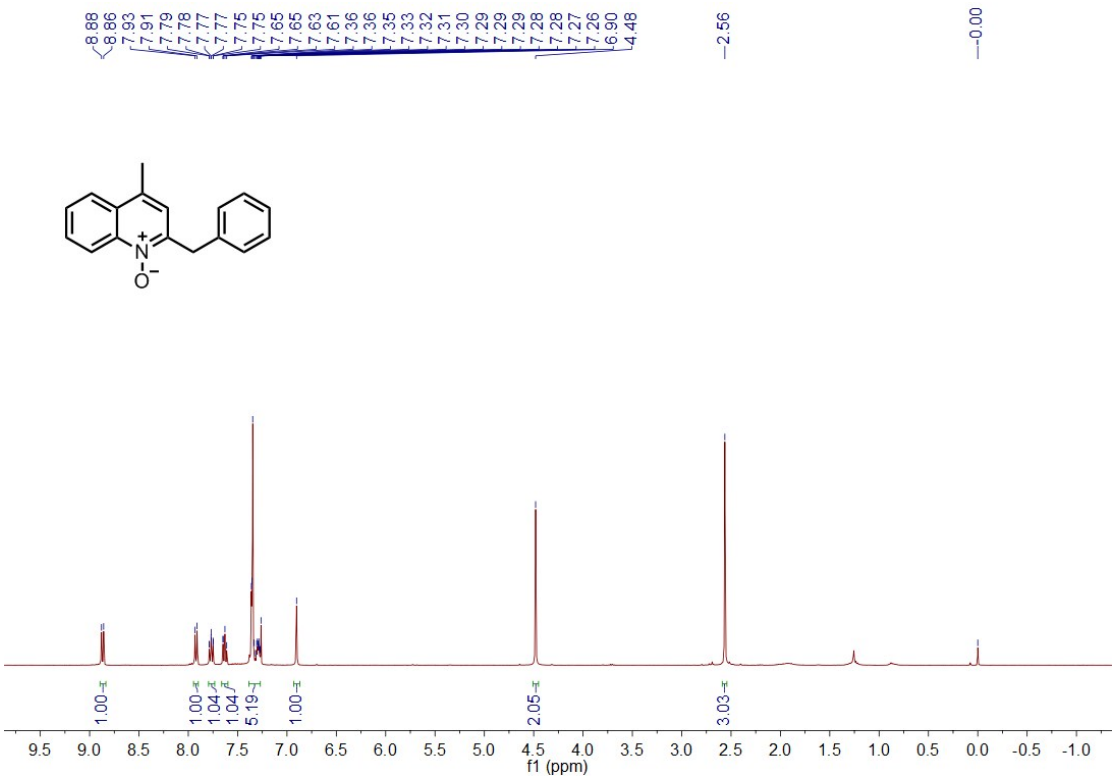


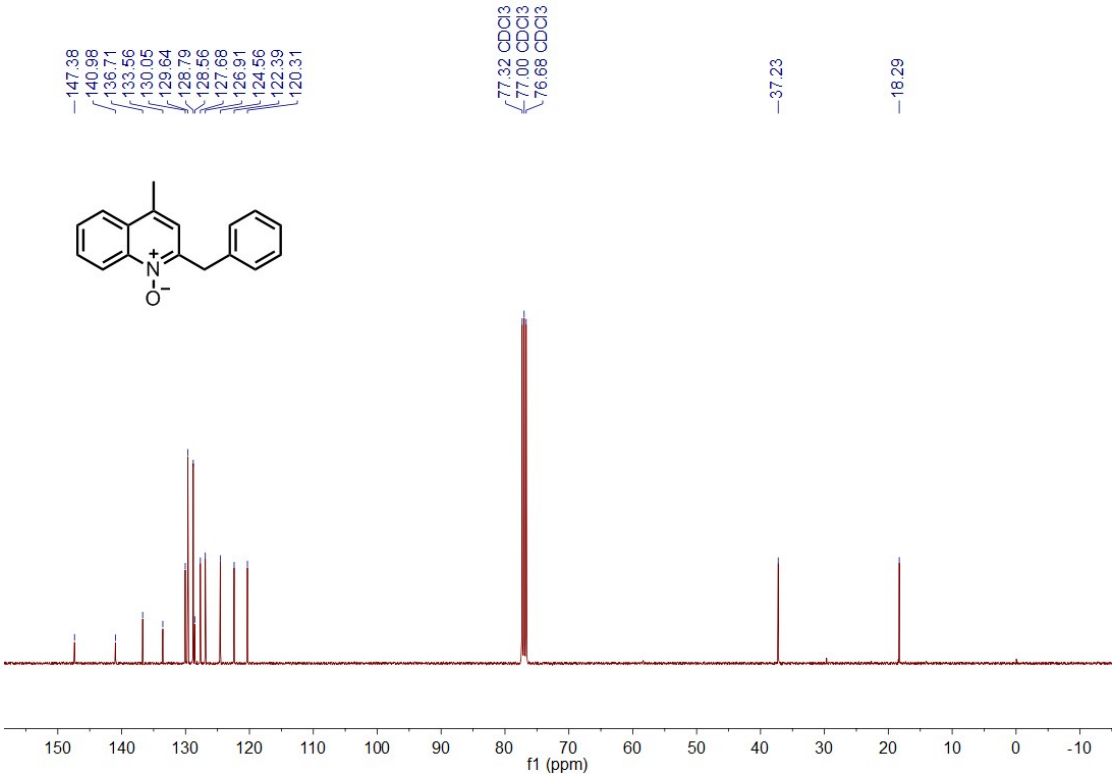
2-benzyl-3-methylquinoline 1-oxide (4a)



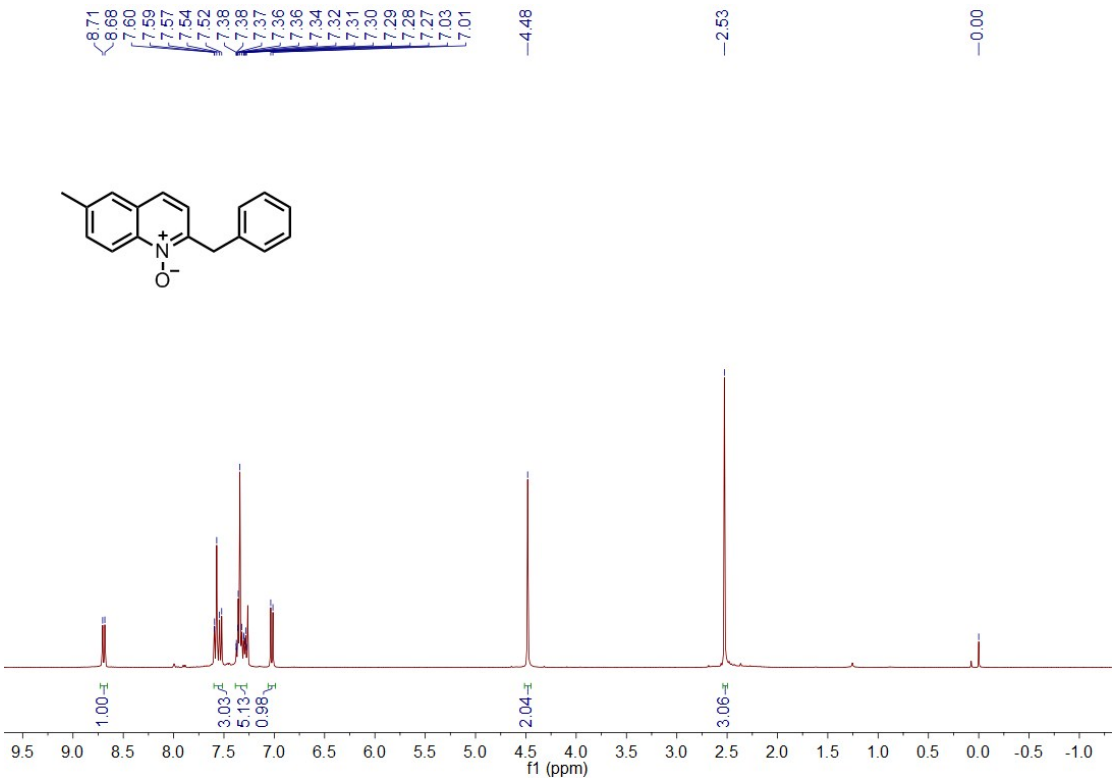


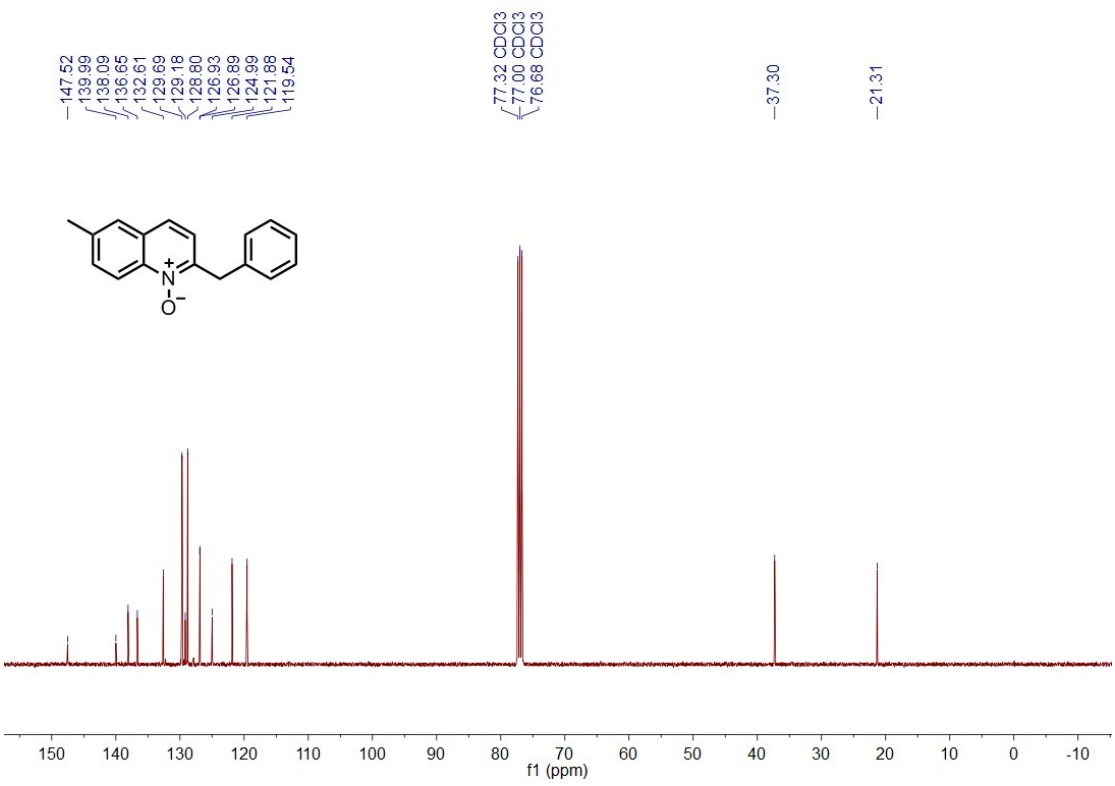
2-benzyl-4-methylquinoline 1-oxide (4b)



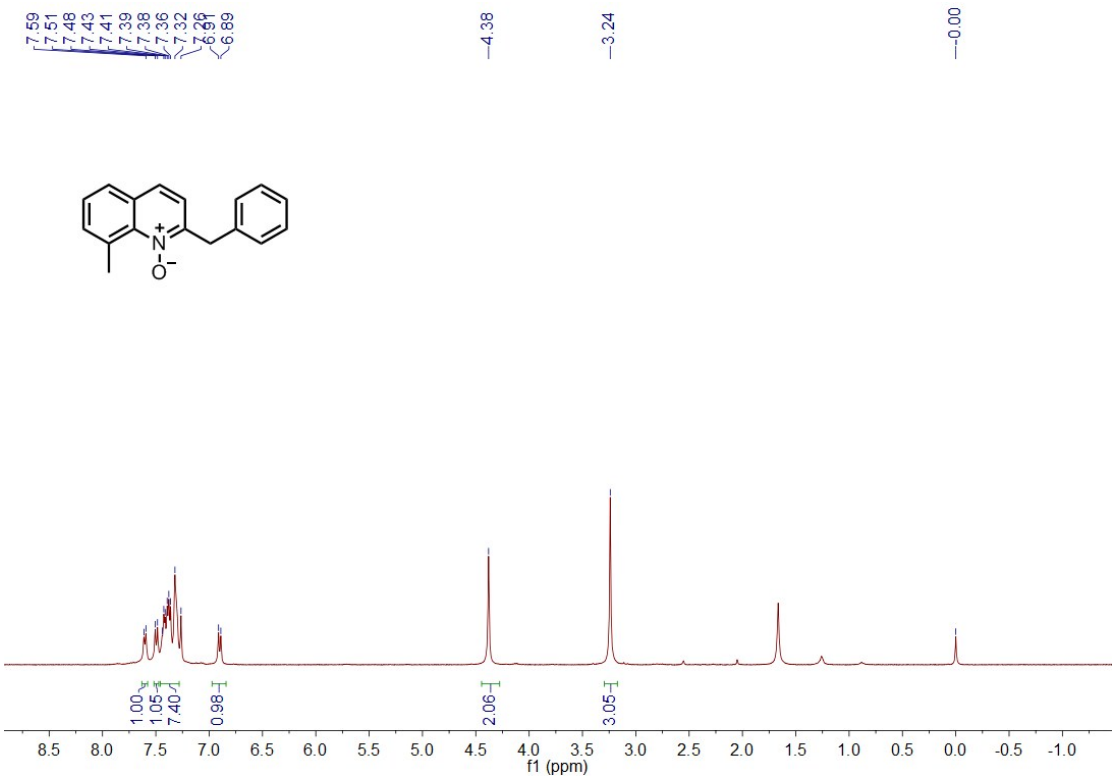


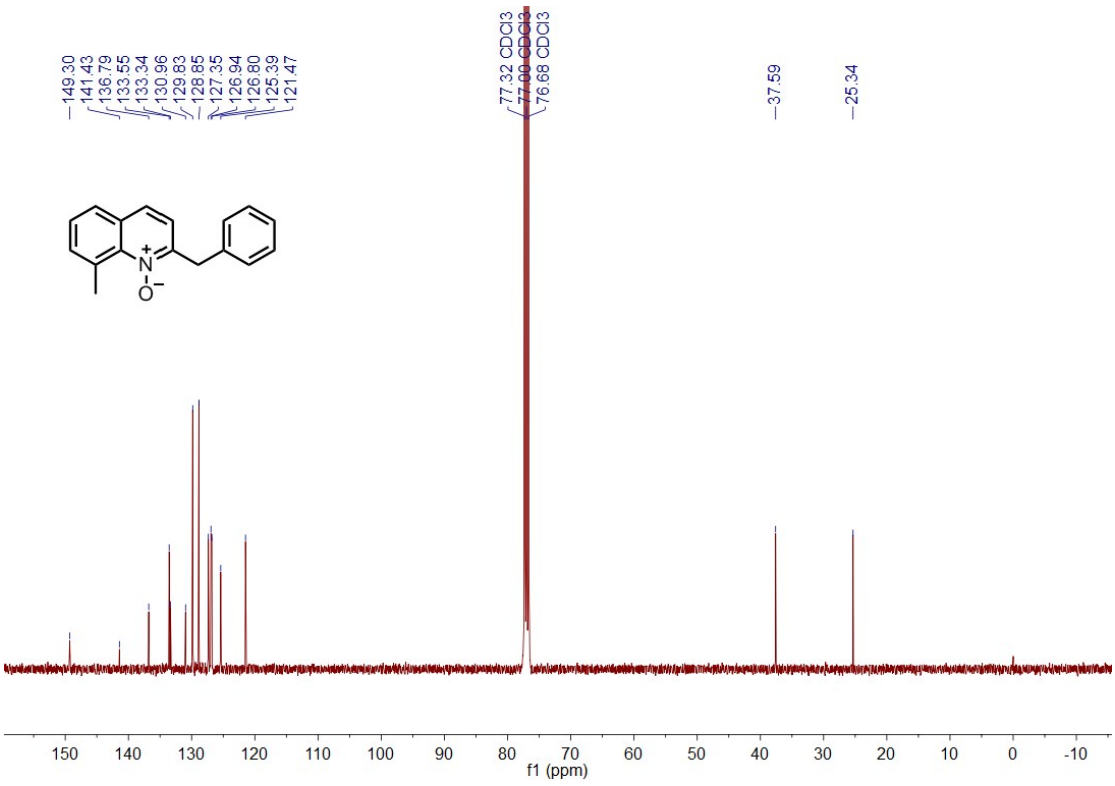
2-benzyl-6-methylquinoline 1-oxide (4c)



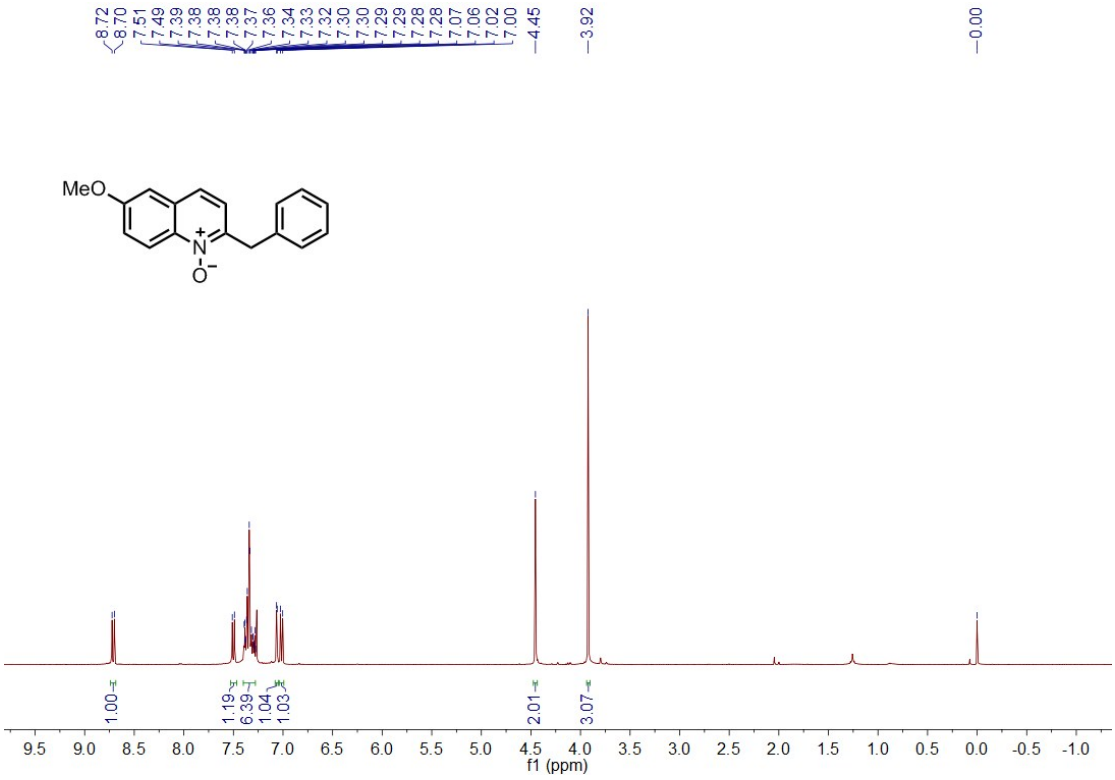


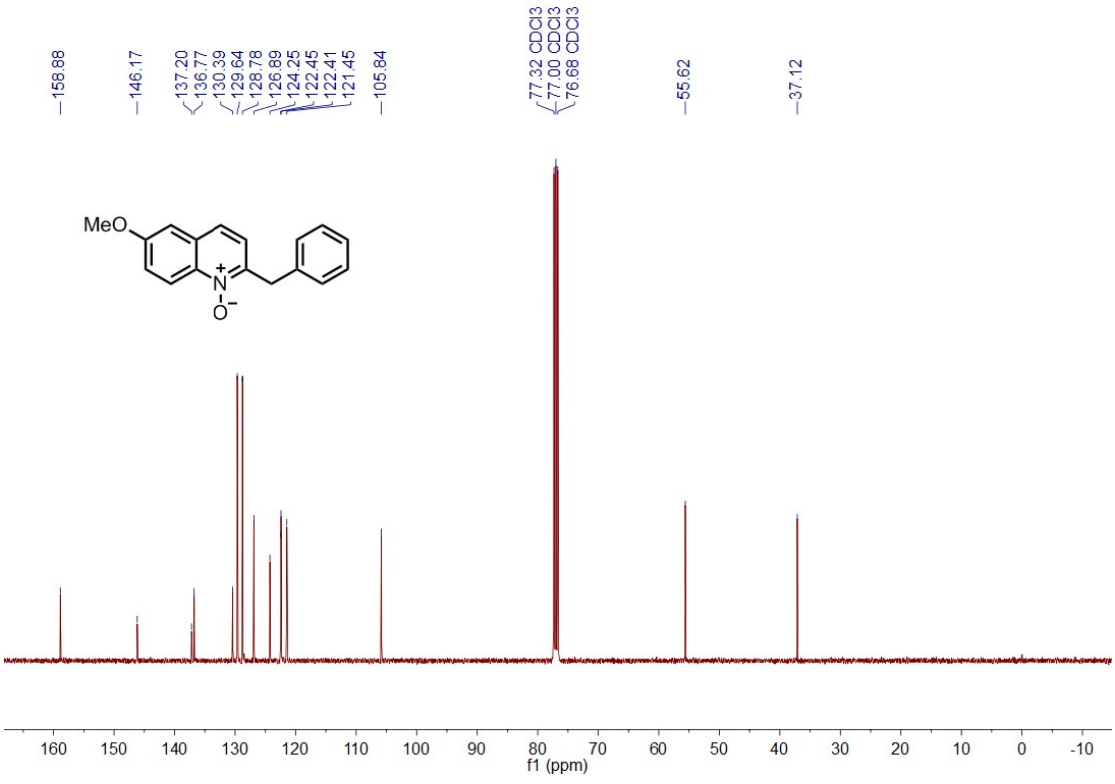
2-benzyl-8-methylquinoline 1-oxide (4d)



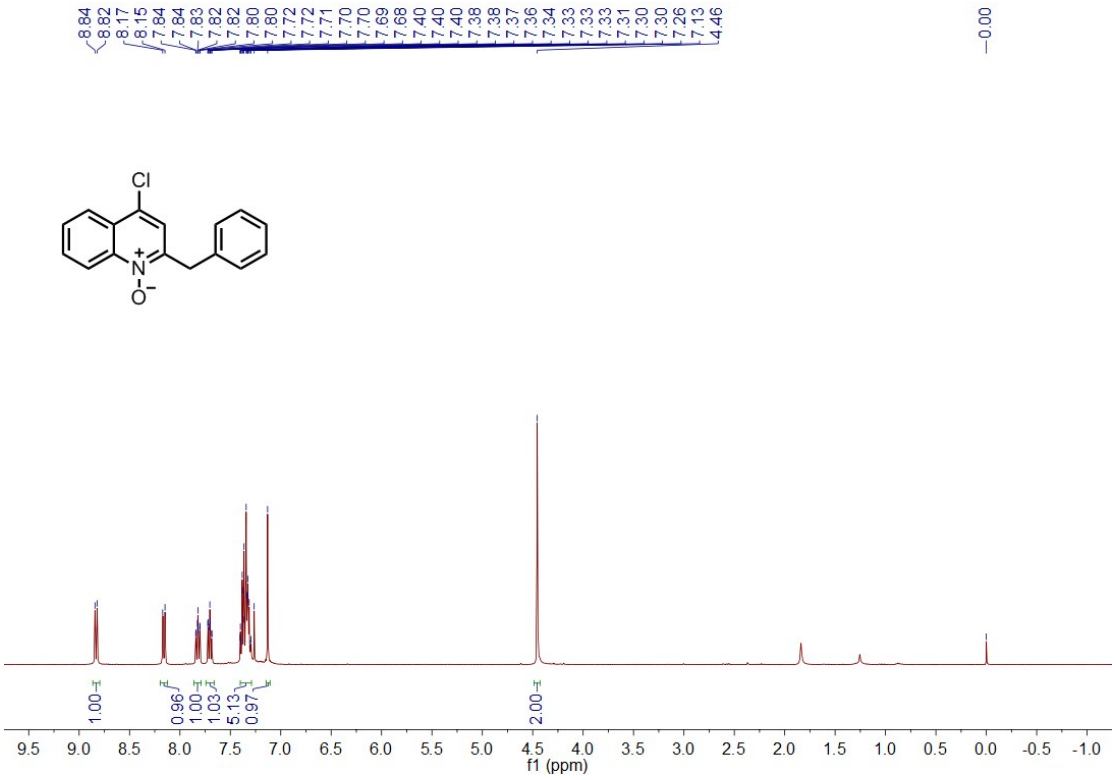


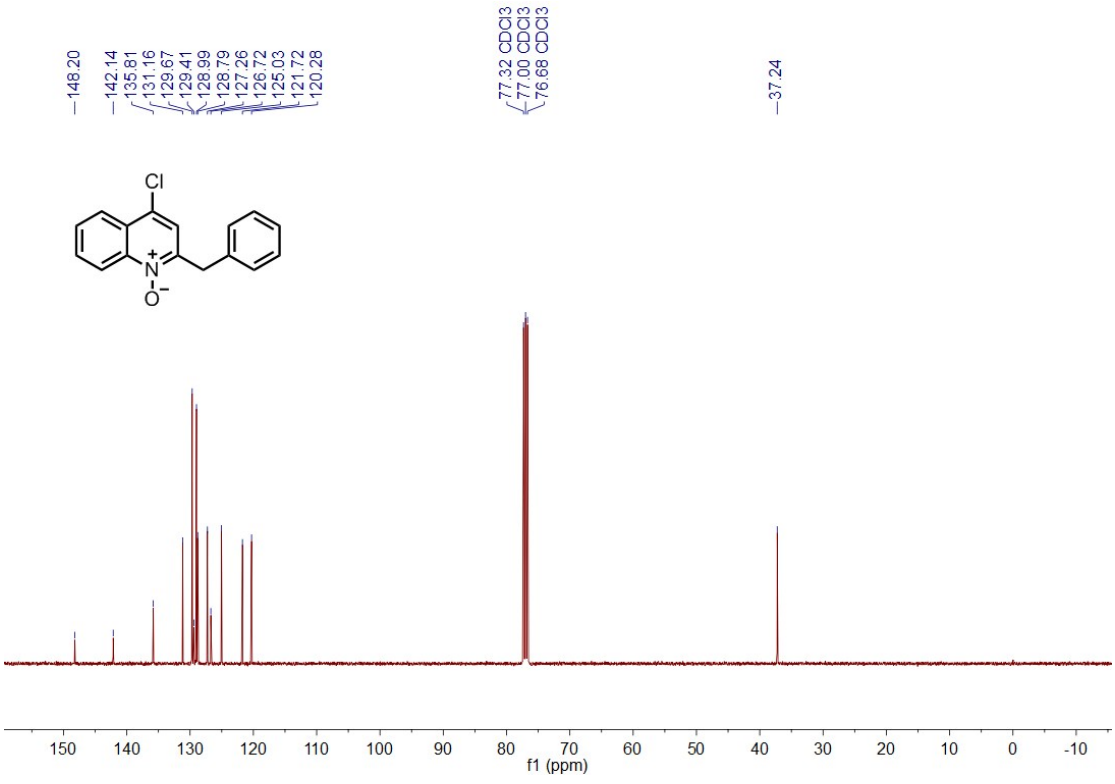
2-benzyl-6-methoxyquinoline 1-oxide (4e)



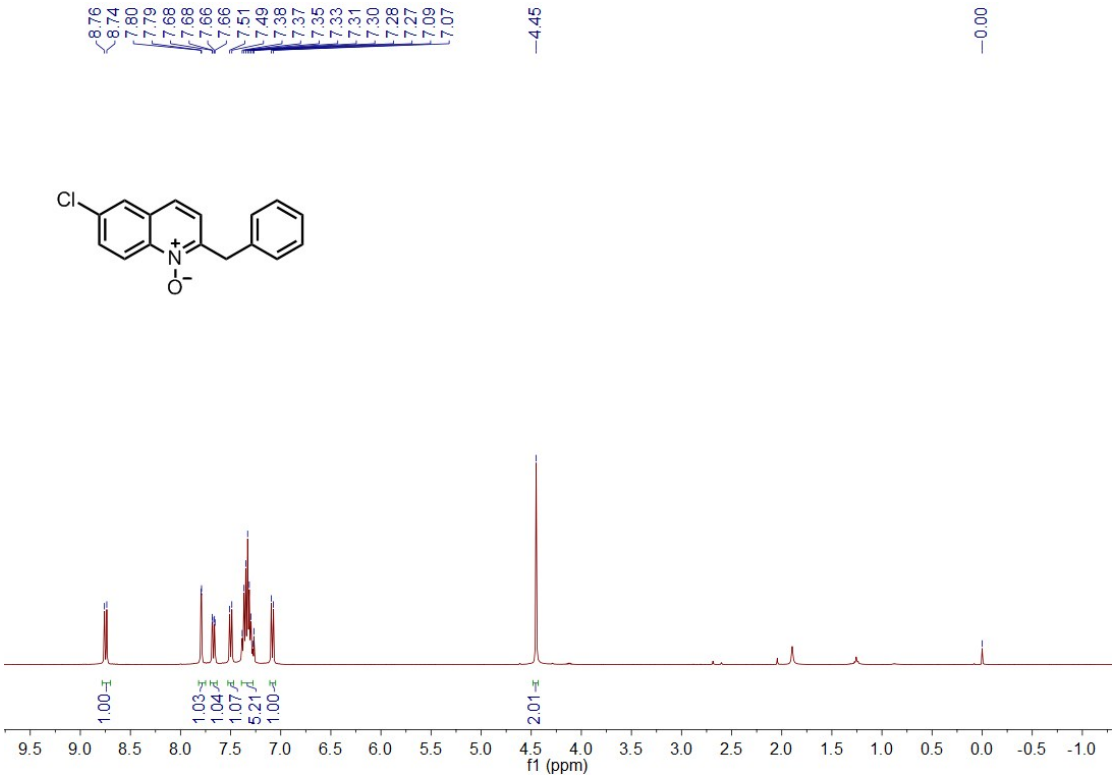


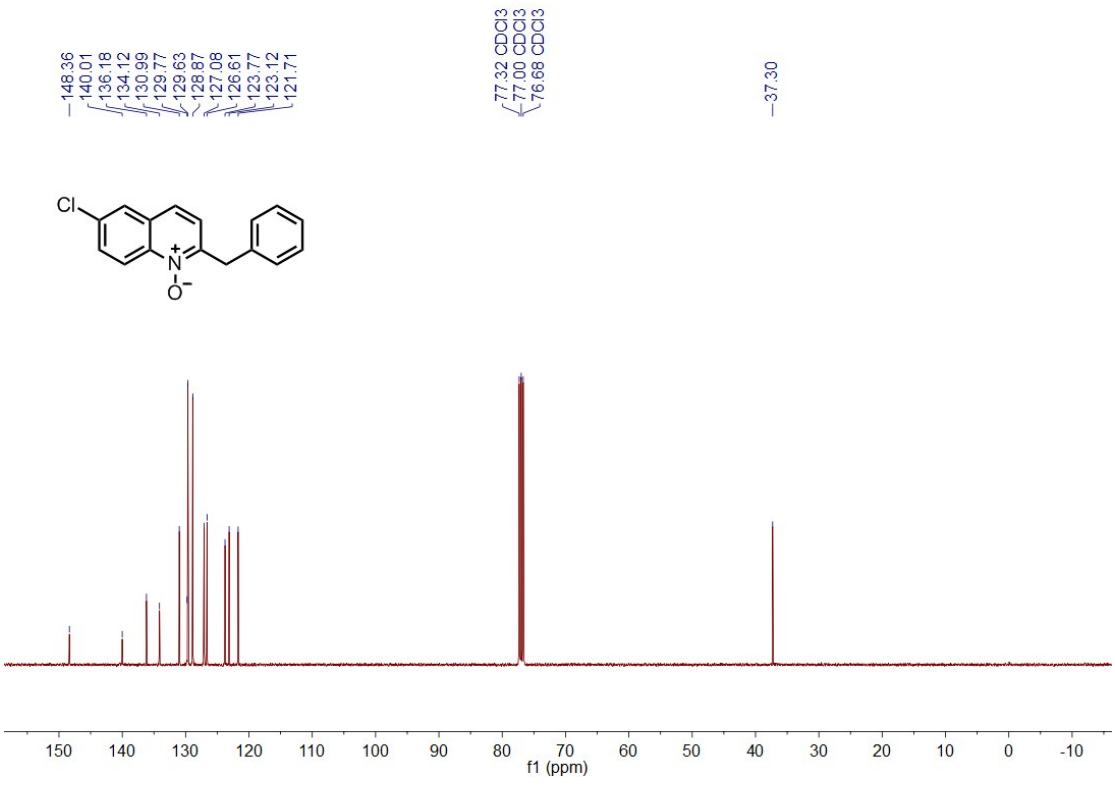
2-benzyl-4-chloroquinoline 1-oxide (4f)



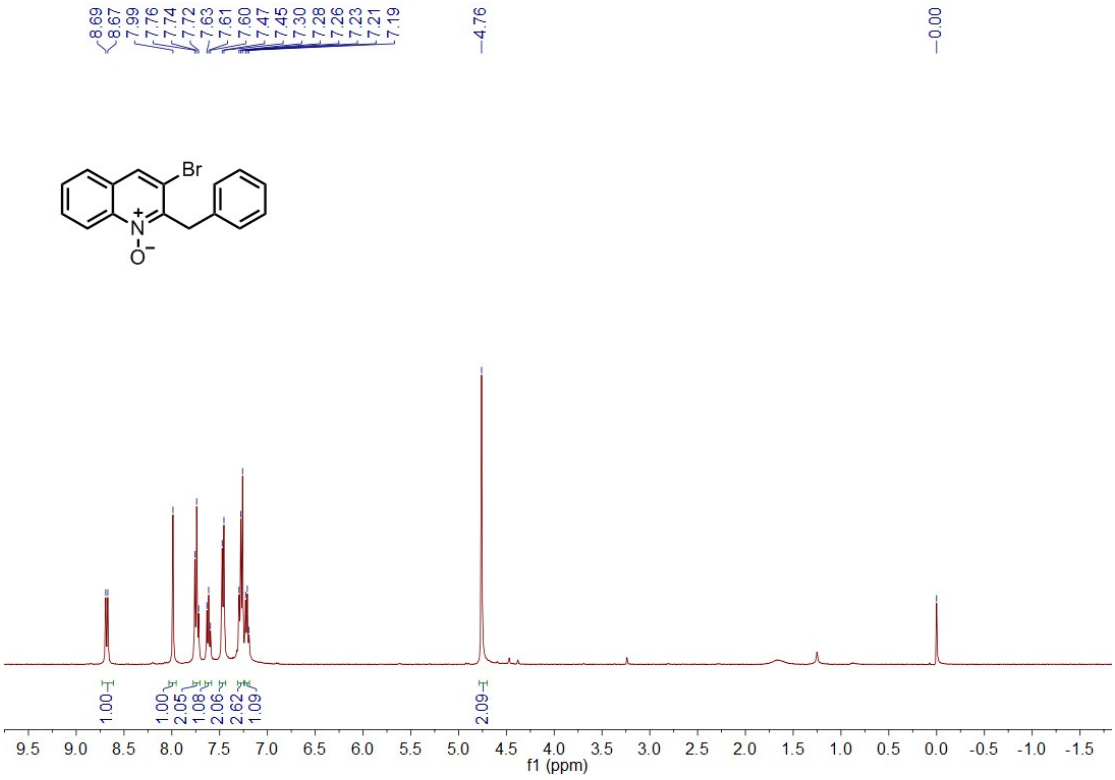


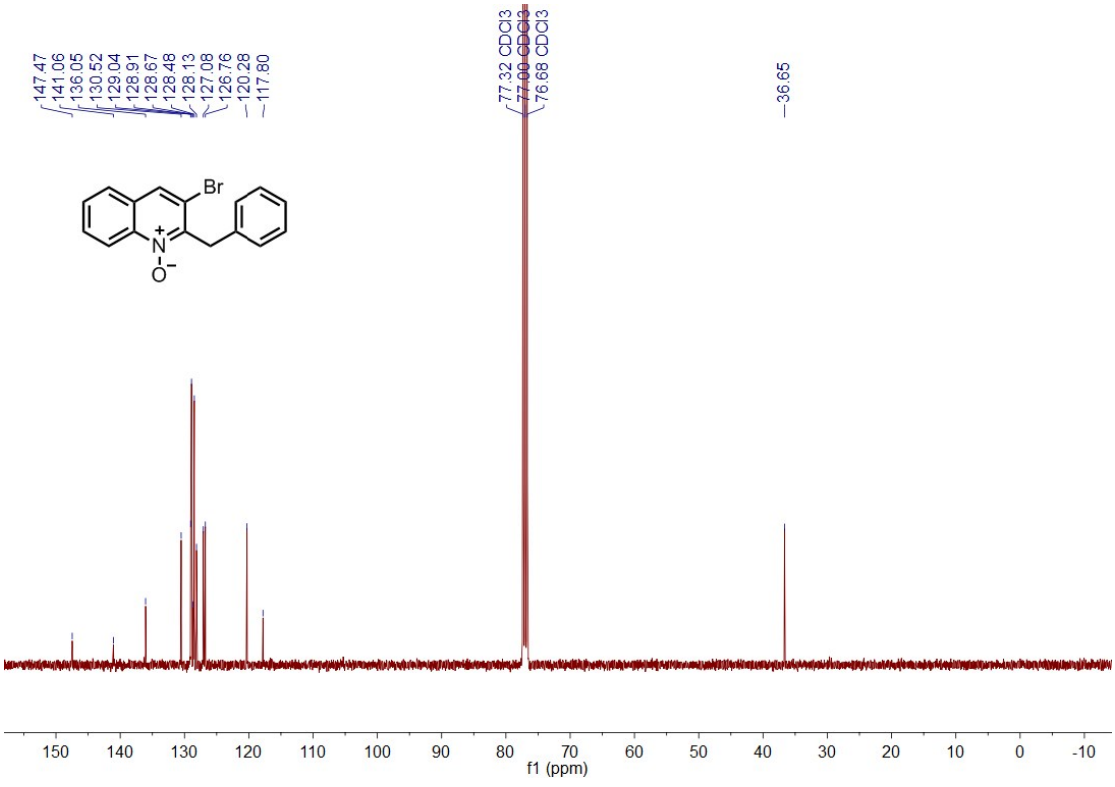
2-benzyl-6-chloroquinoline 1-oxide (4g)



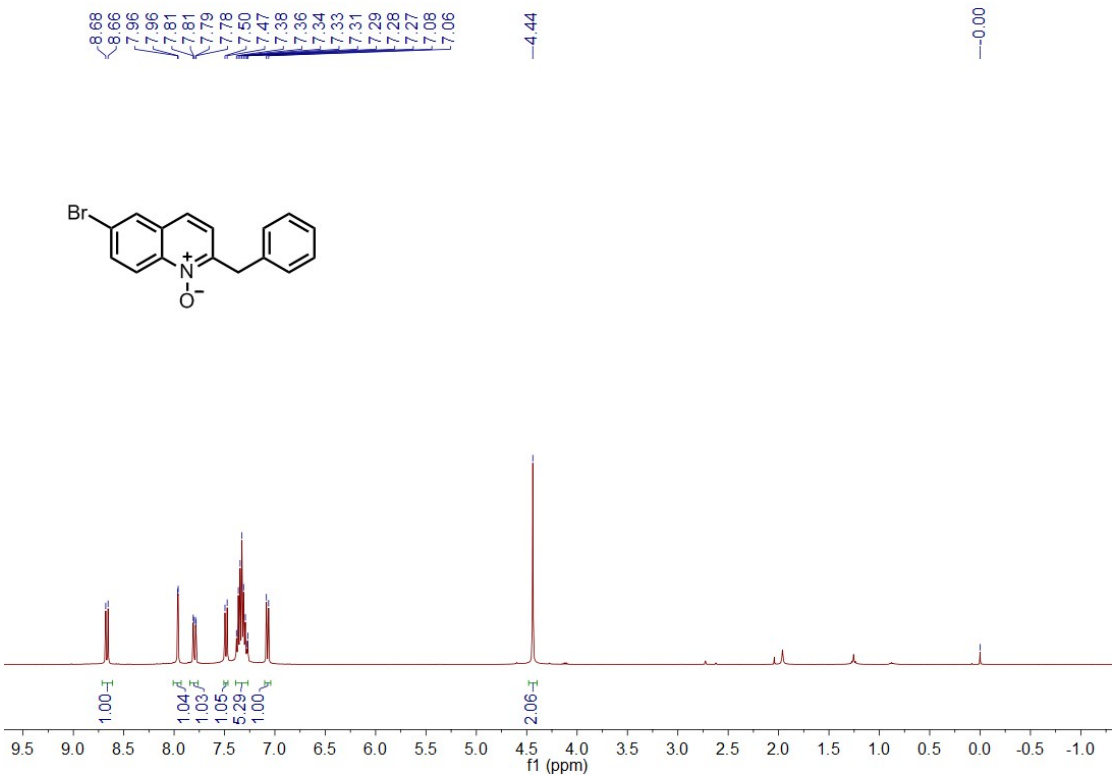


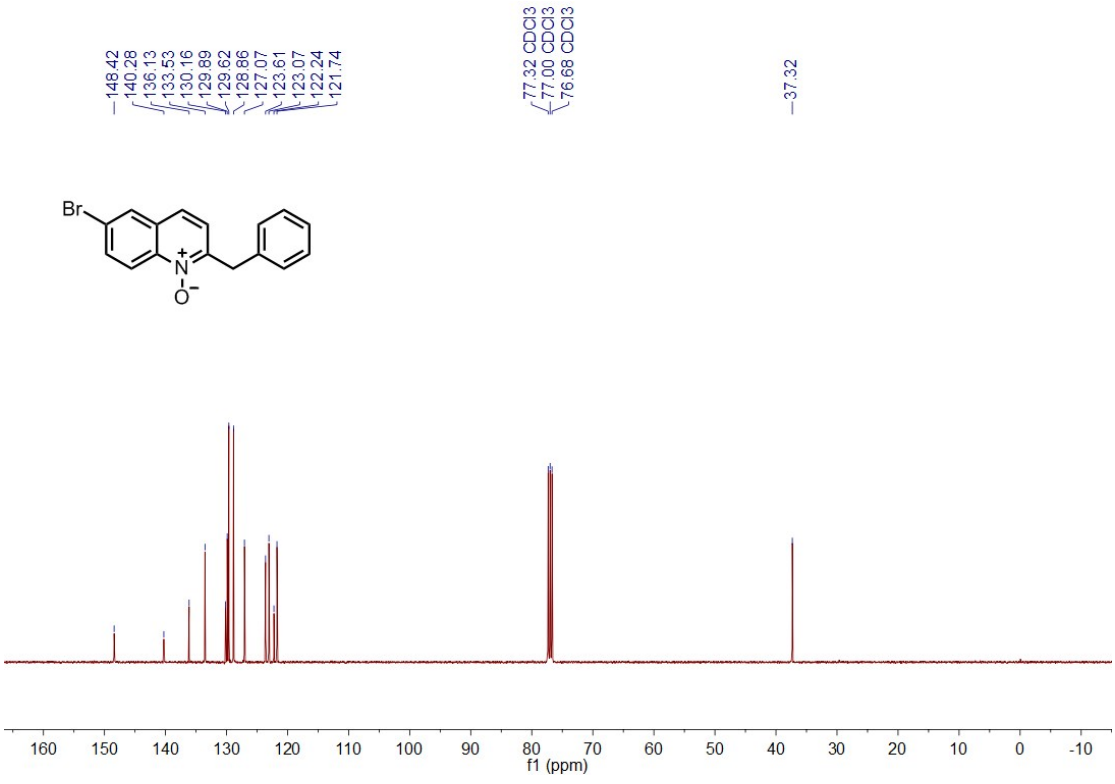
2-benzyl-3-bromoquinoline 1-oxide (4h)



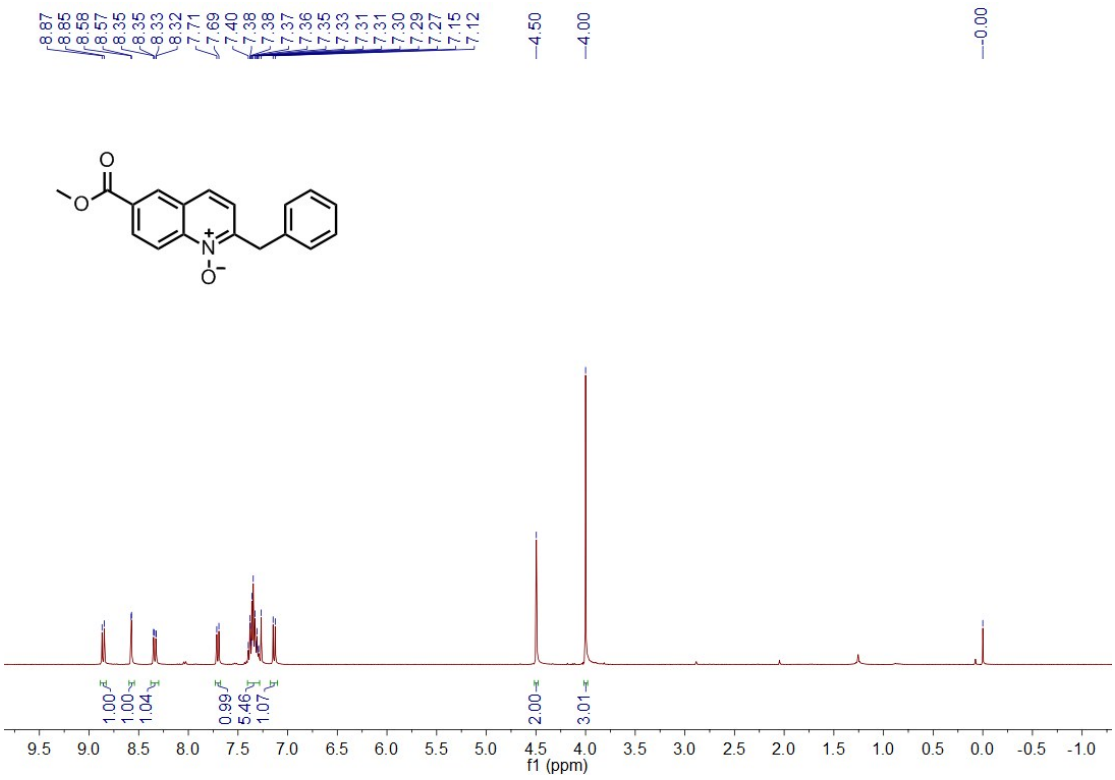


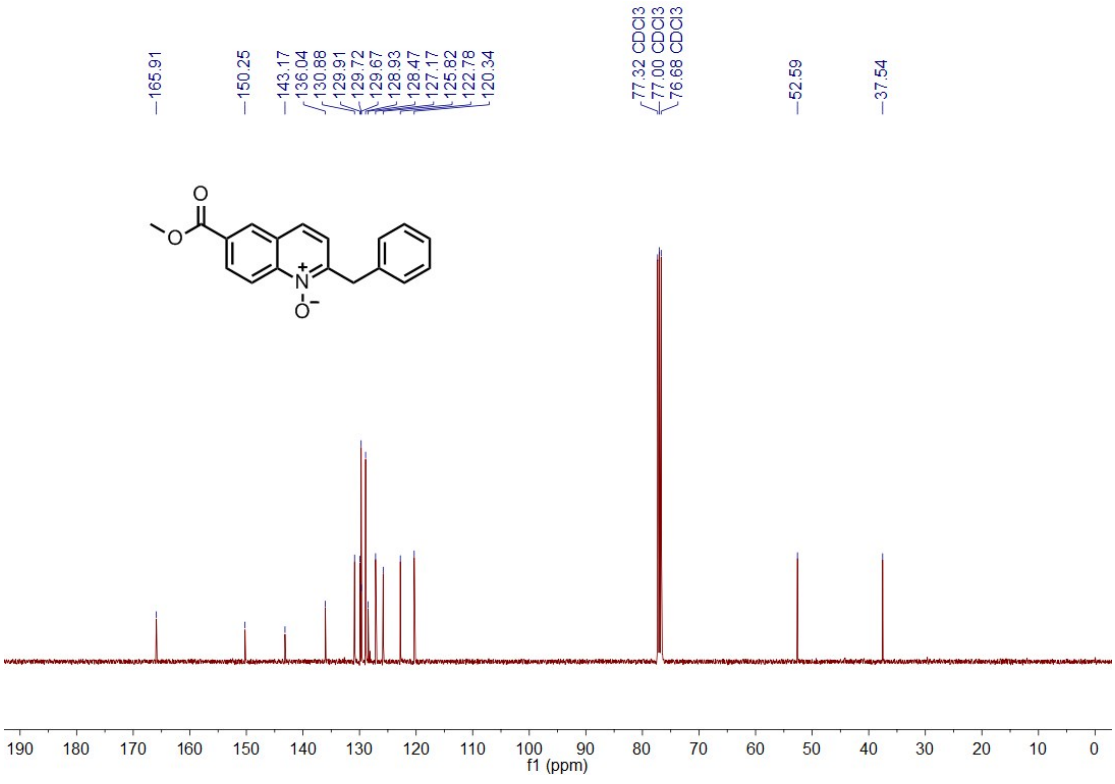
2-benzyl-6-bromoquinoline 1-oxide (4i)



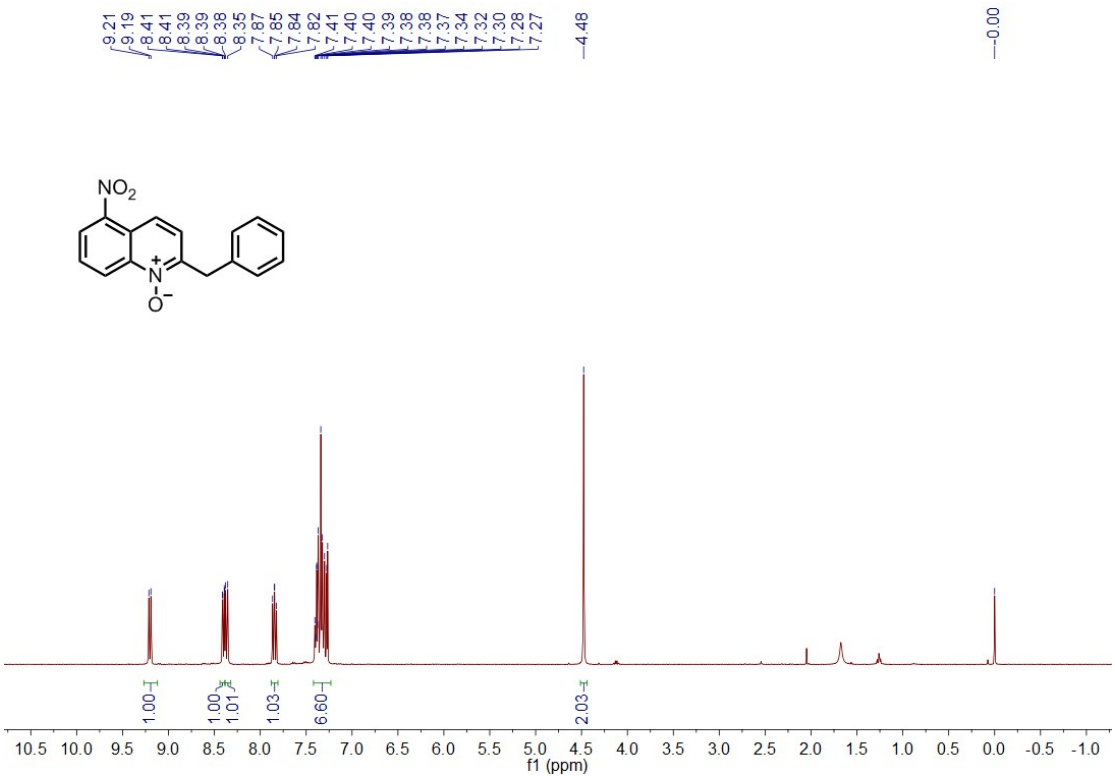


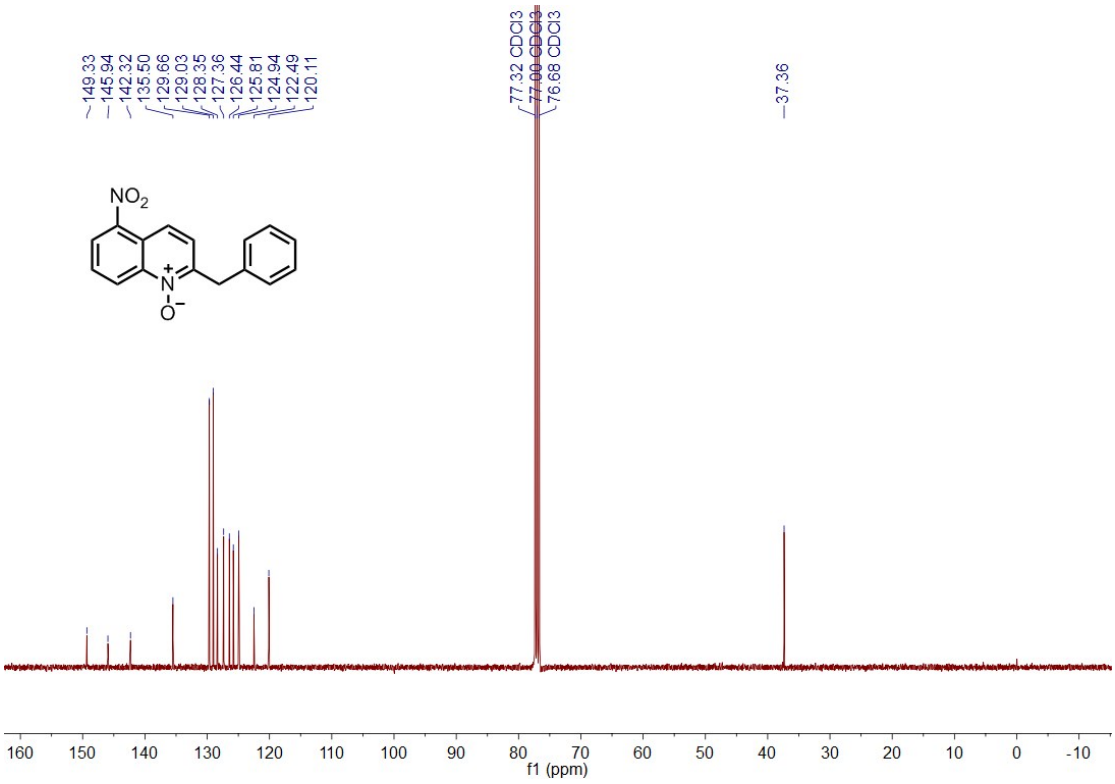
2-benzyl-6-(methoxycarbonyl)quinoline 1-oxide (4j)



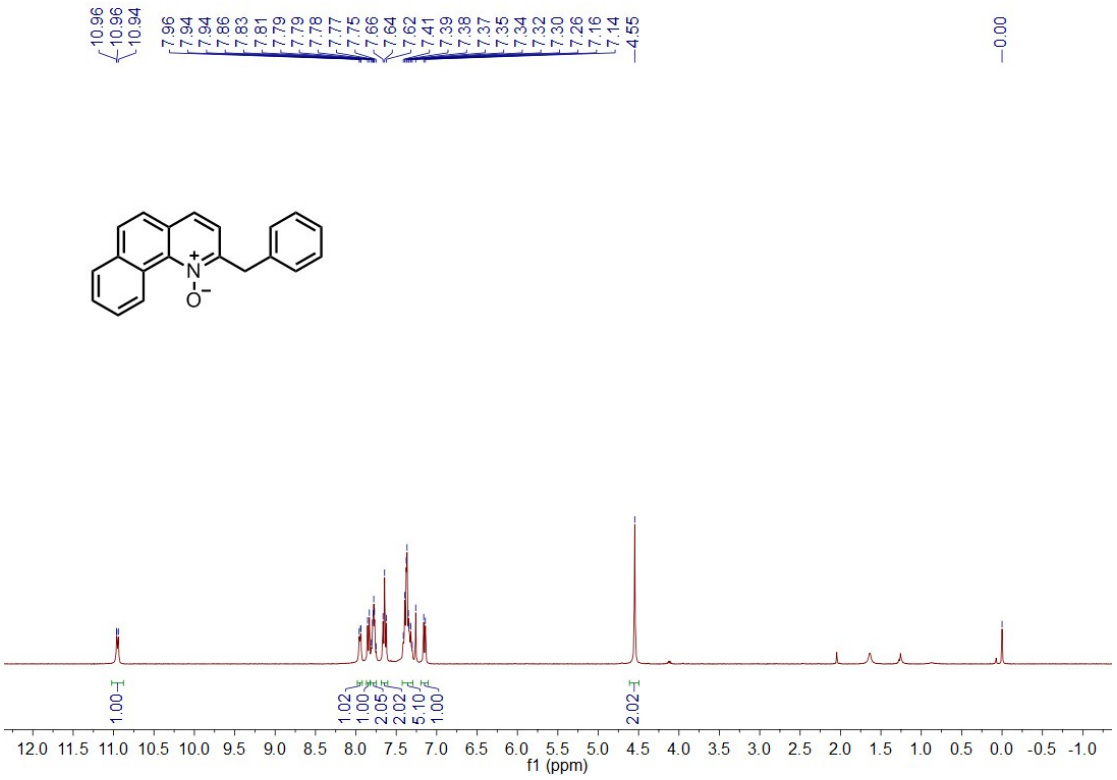


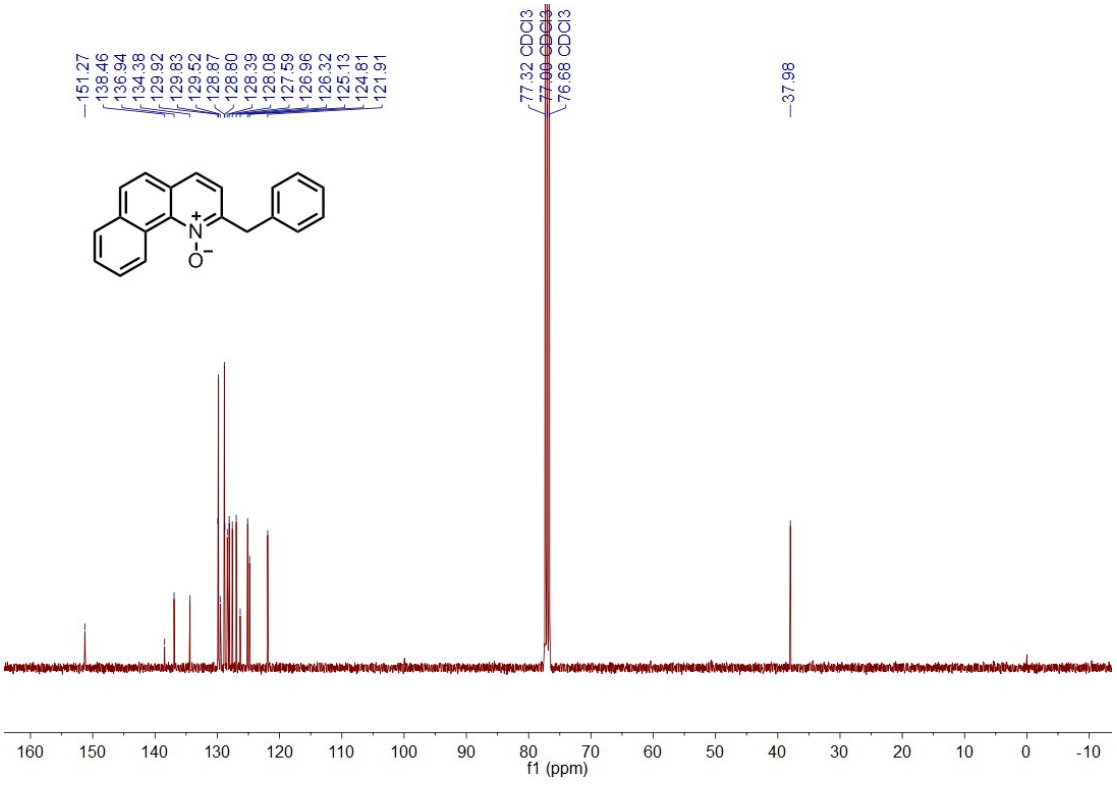
2-benzyl-5-nitroquinoline 1-oxide (4k)



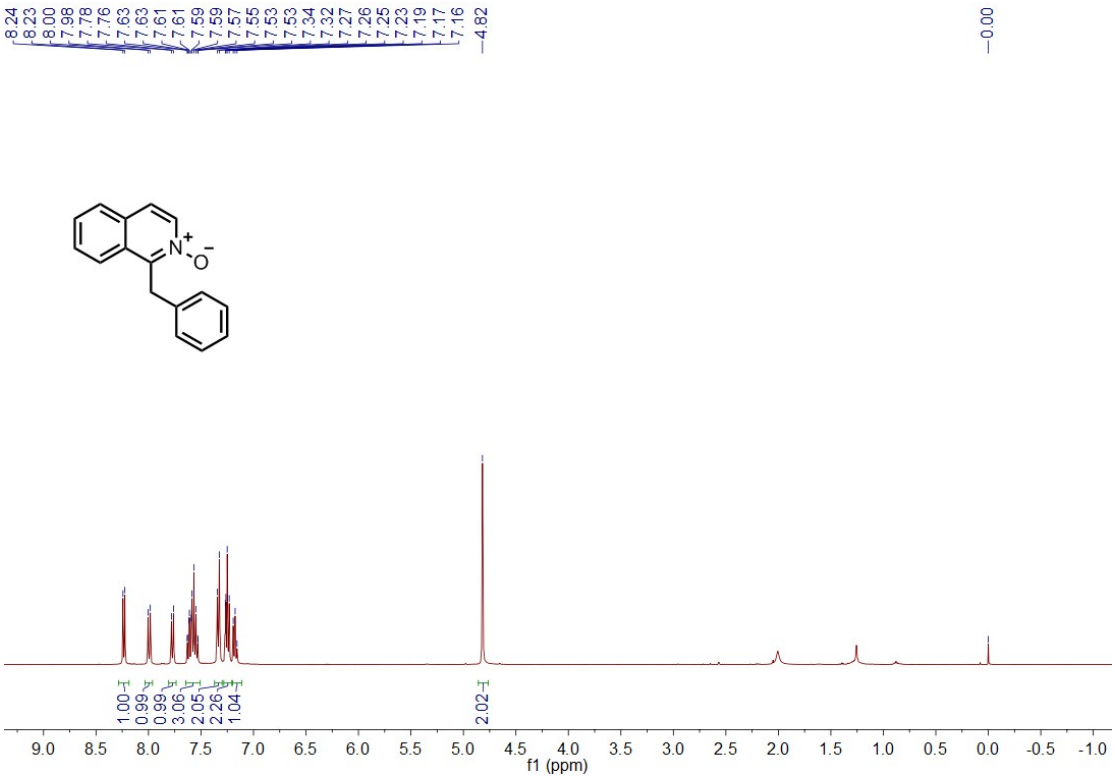


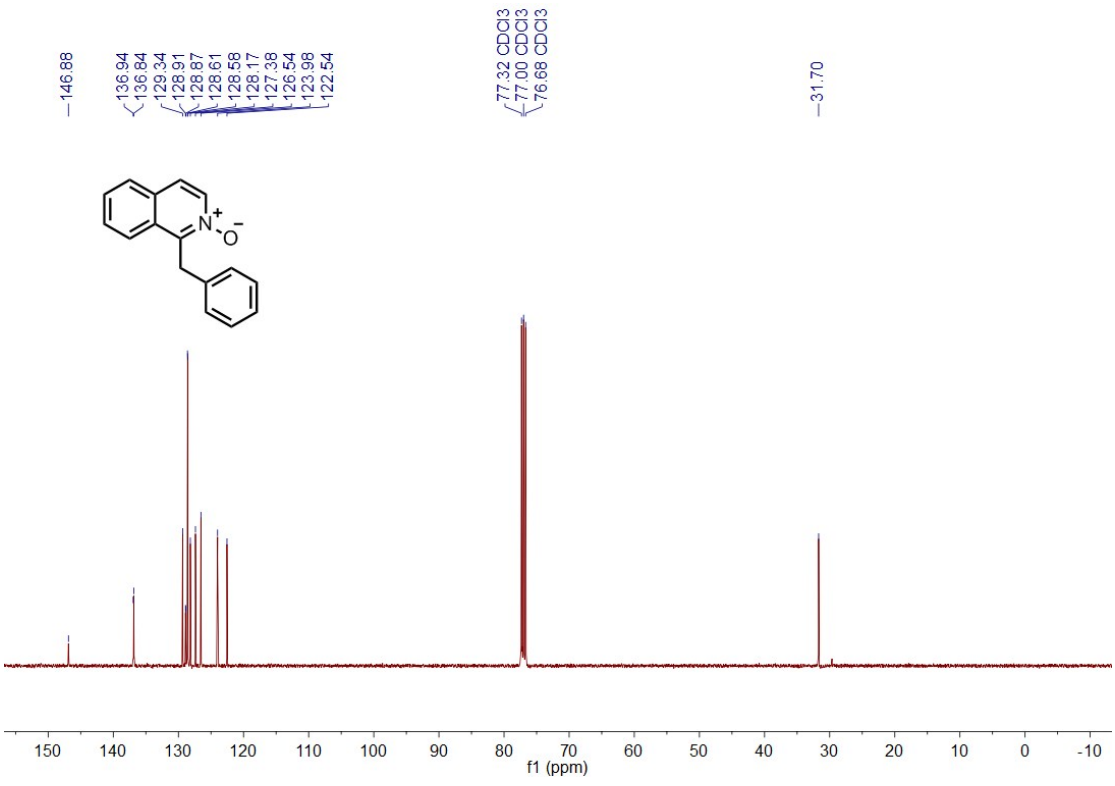
2-benzylbenzo[h]quinoline 1-oxide (4l)



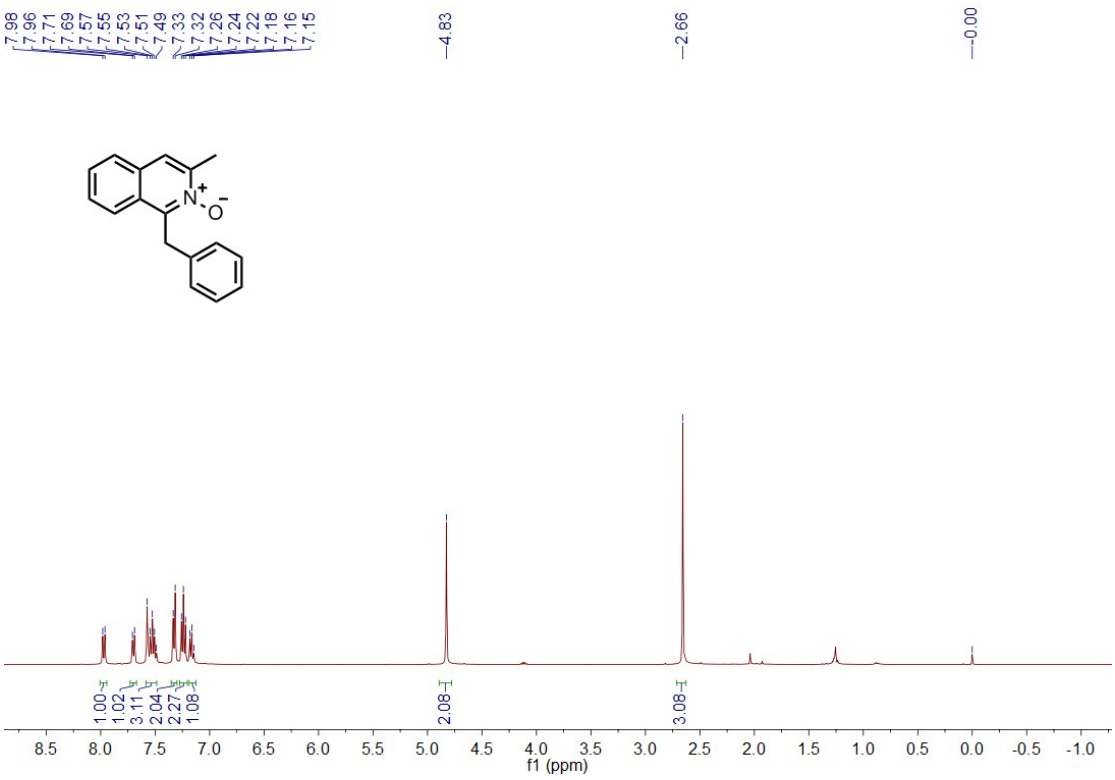


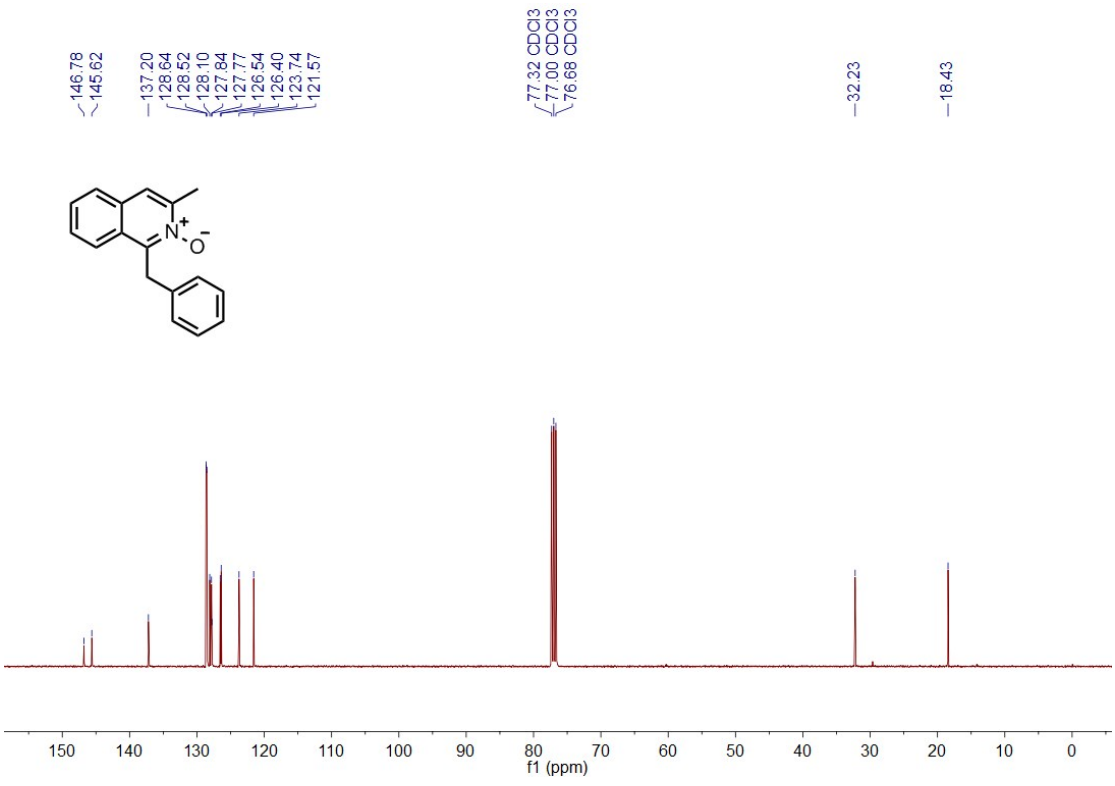
1-benzylisoquinoline 2-oxide (4m)



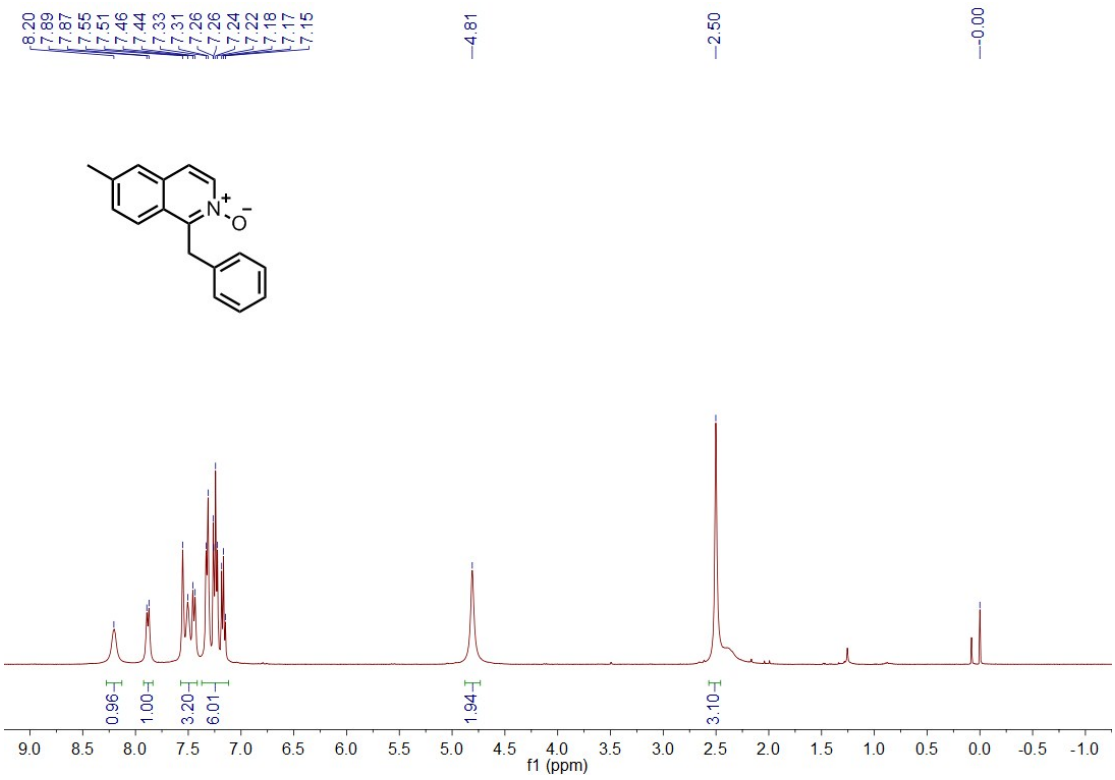


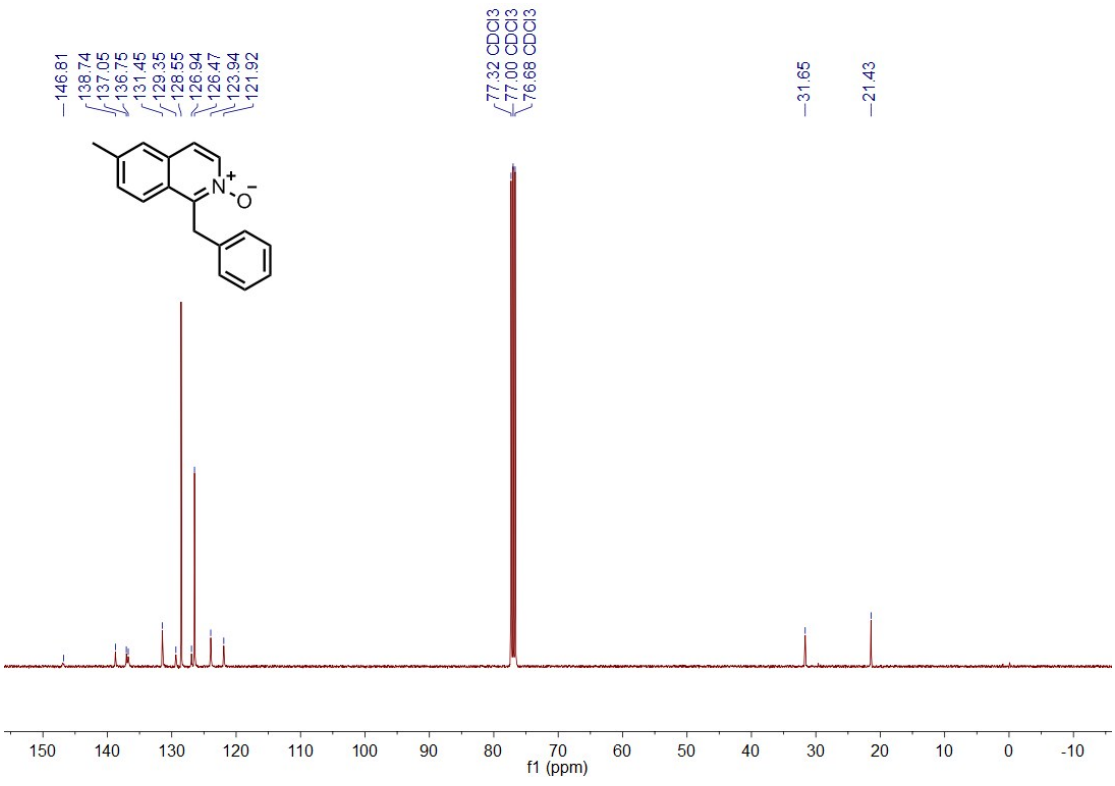
1-benzyl-3-methylisoquinoline 2-oxide (4n)



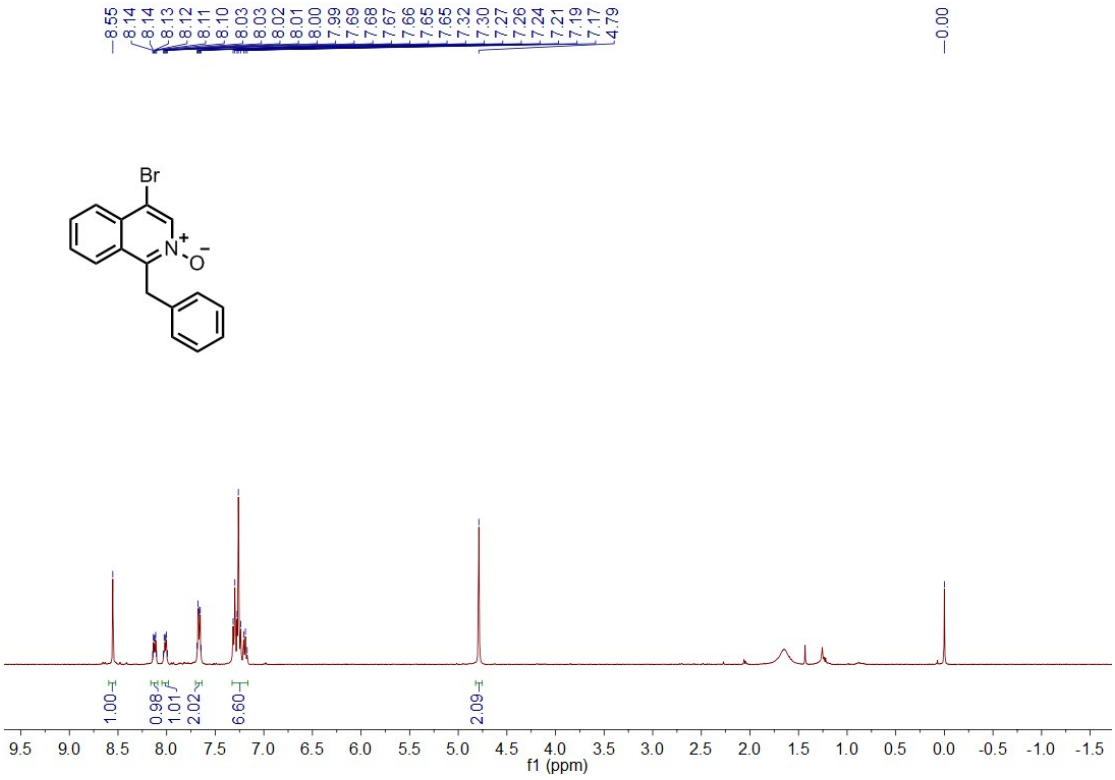


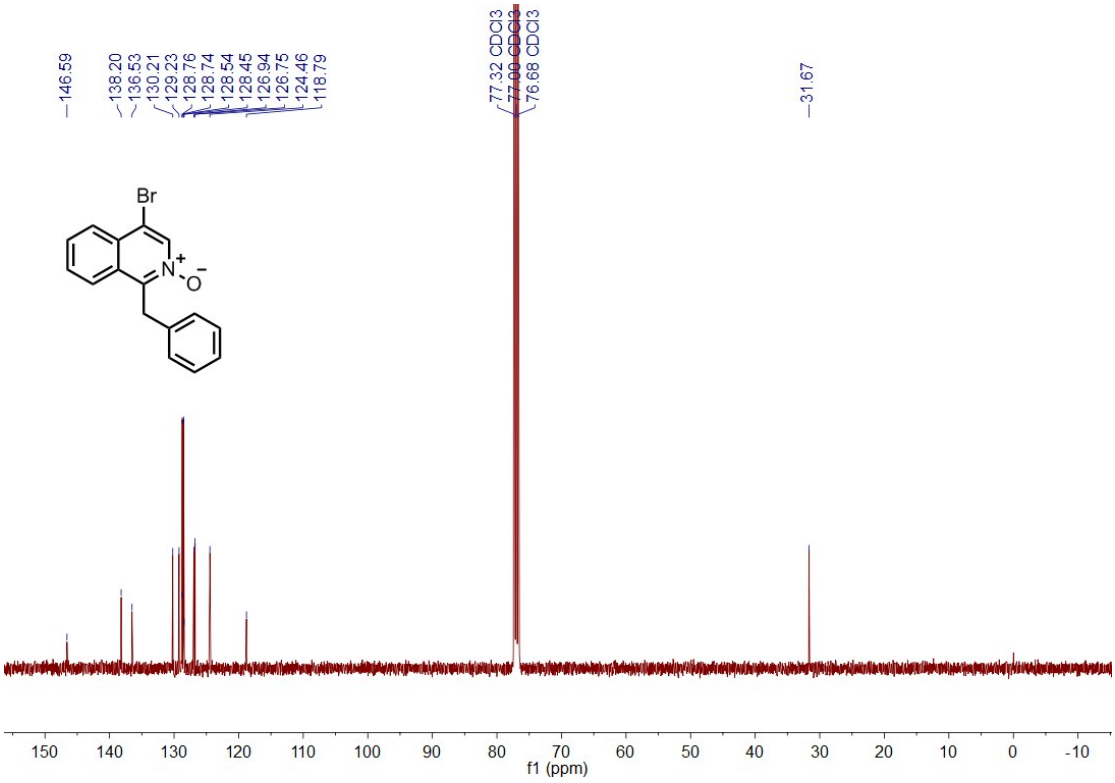
1-benzyl-6-methylisoquinoline 2-oxide (4o)



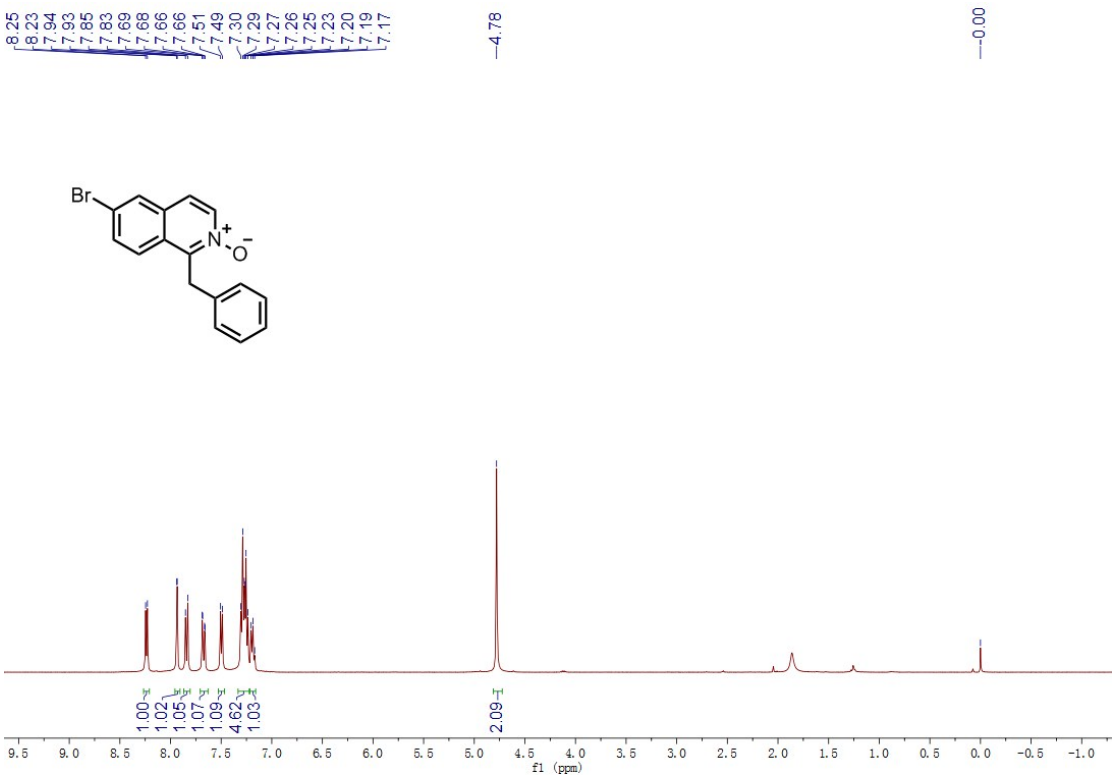


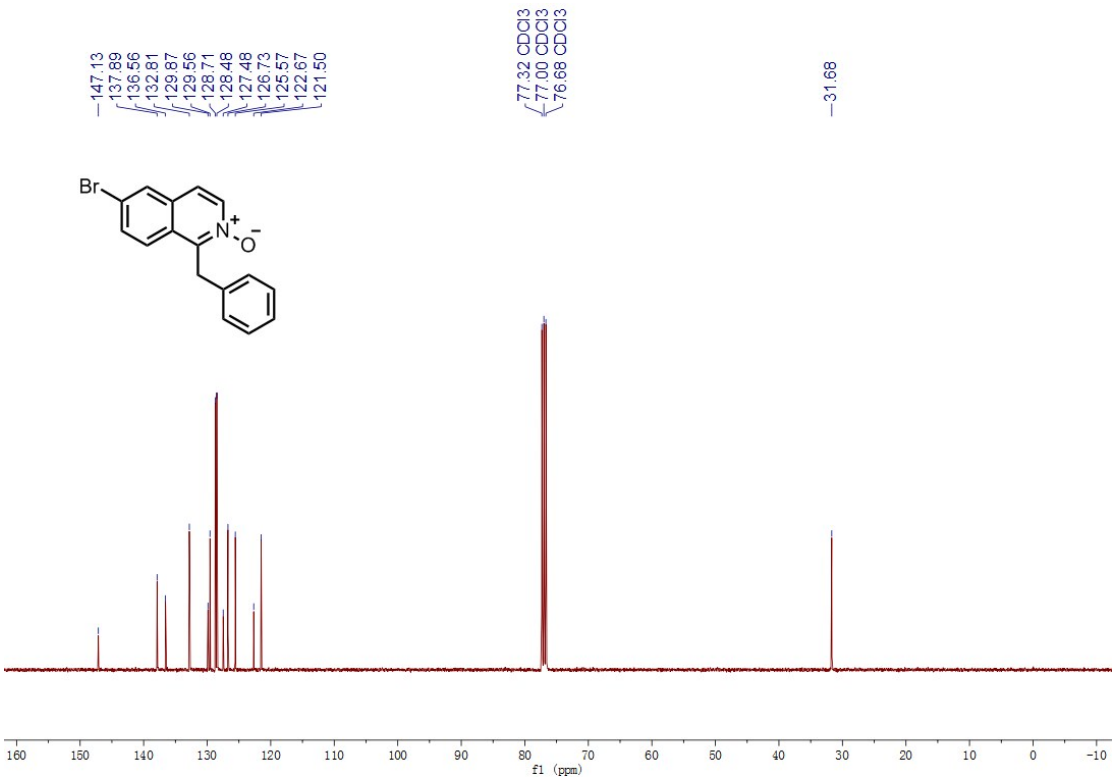
1-benzyl-4-bromoisoquinoline 2-oxide (4p)



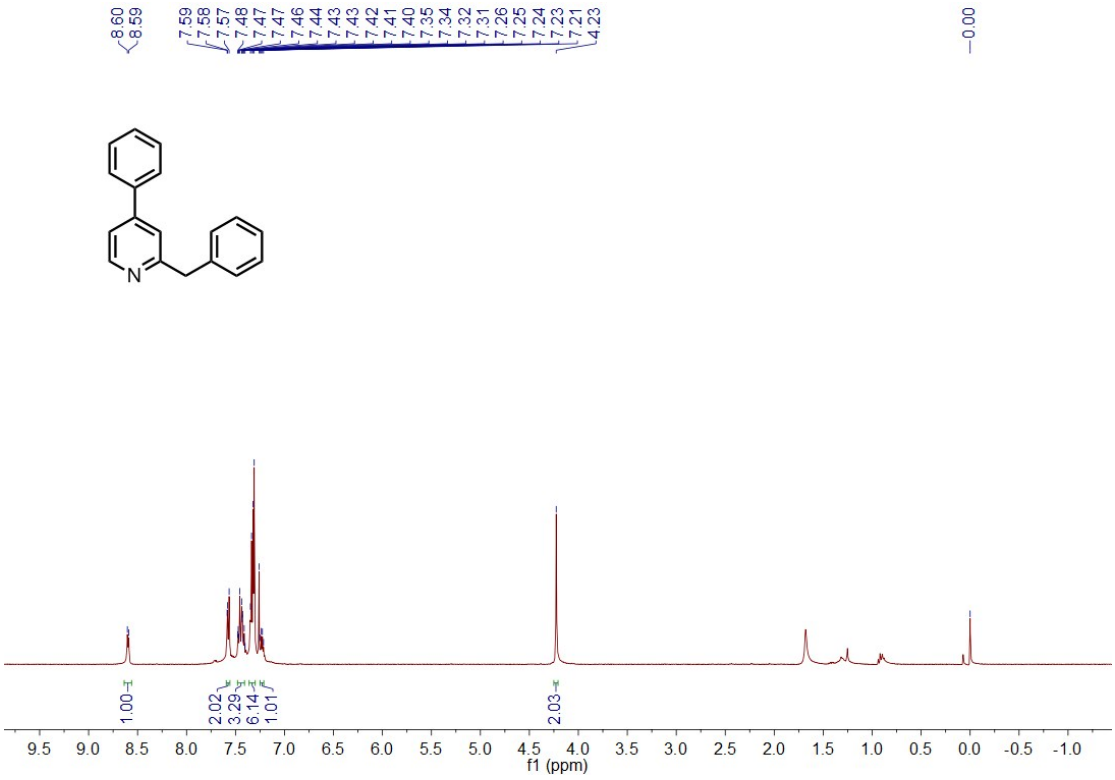


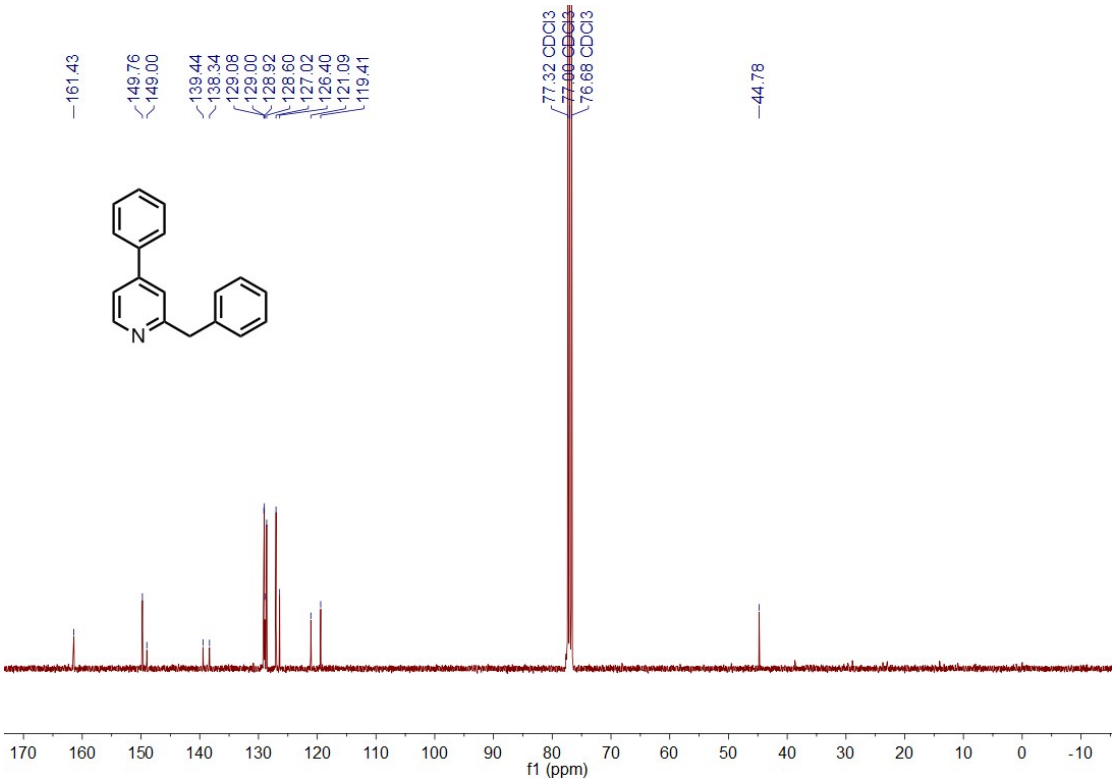
1-benzyl-6-bromoisoquinoline 2-oxide (4q)



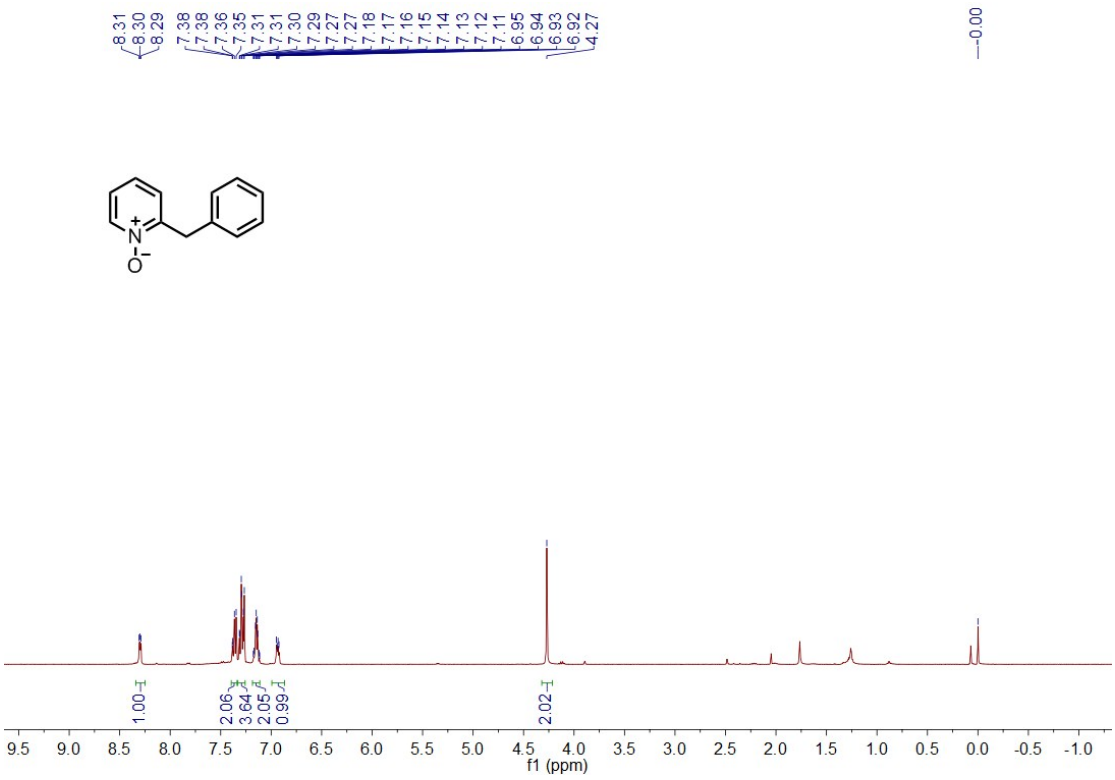


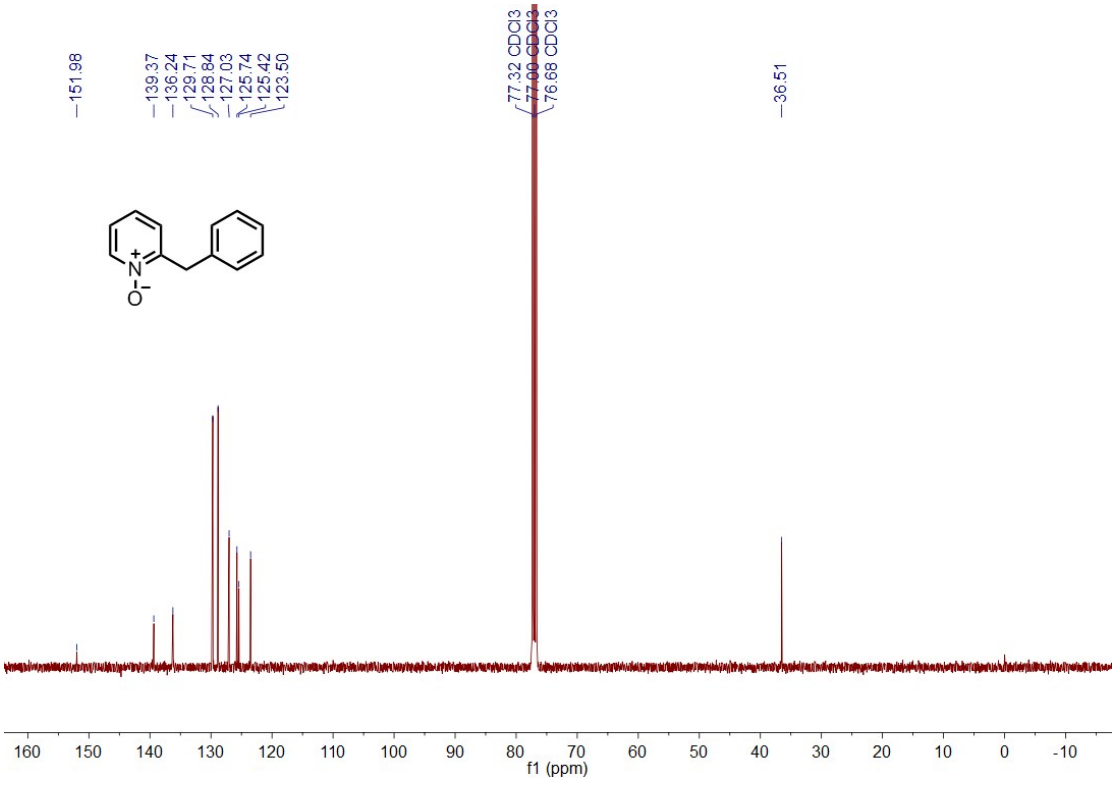
2-benzyl-4-phenylpyridine (4r)



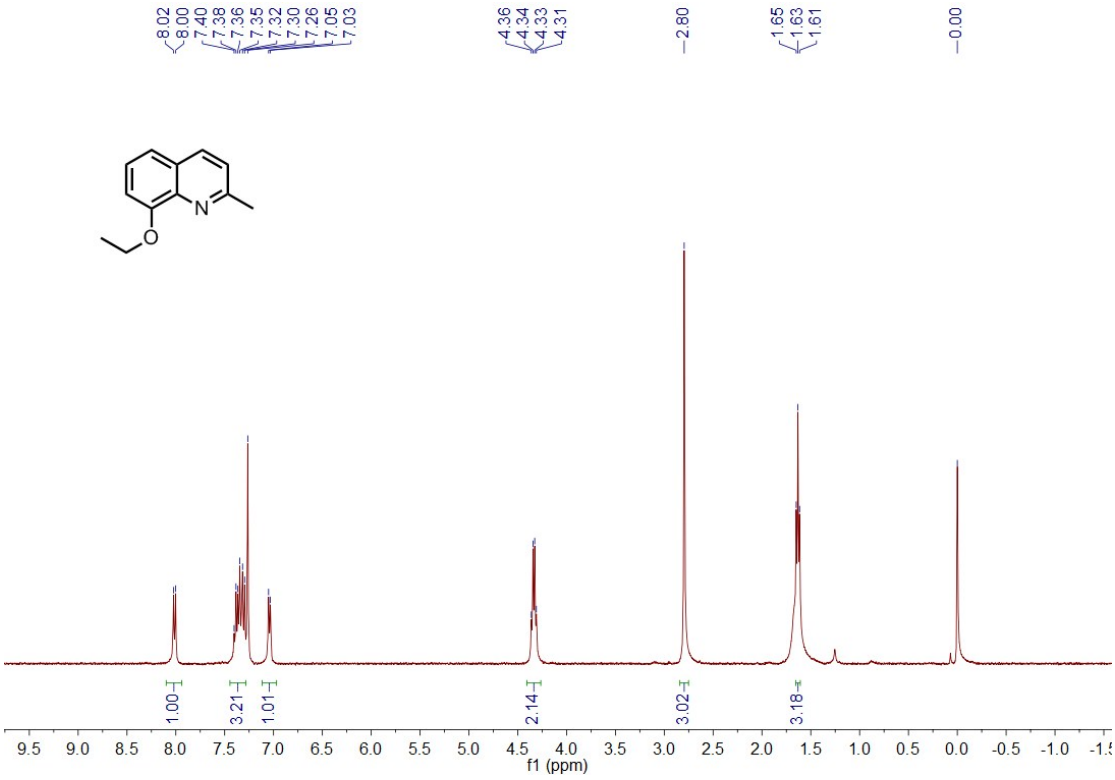


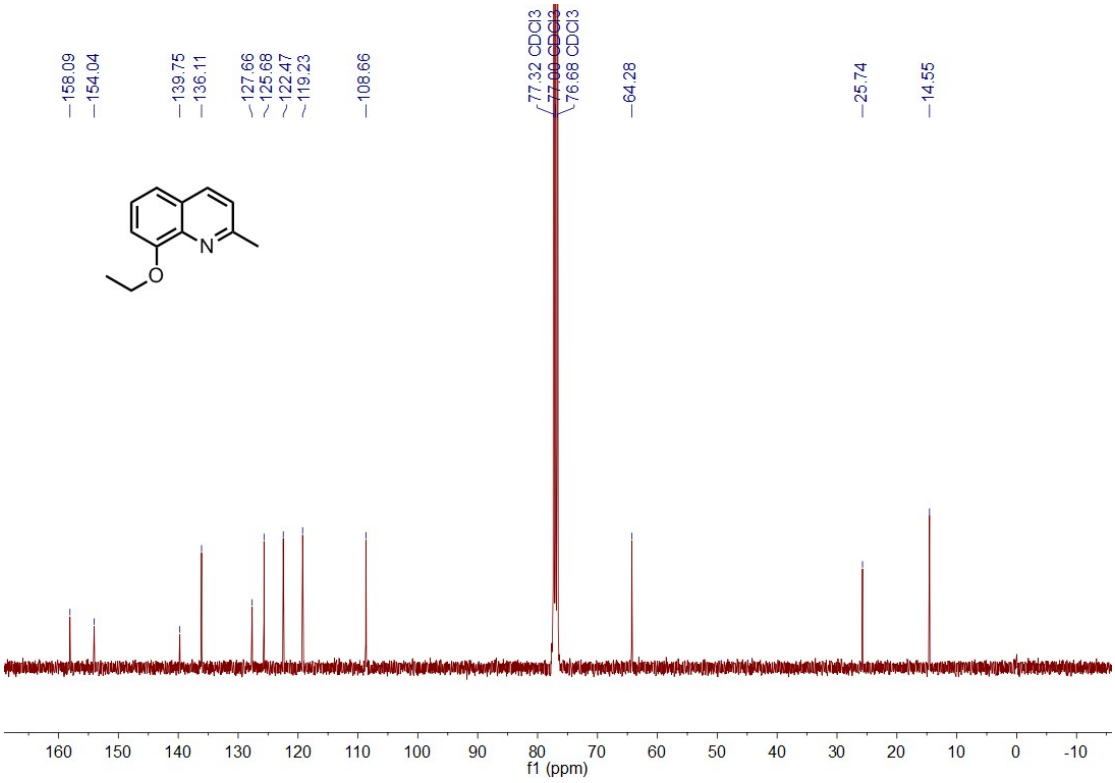
2-benzylpyridine 1-oxide (4s)



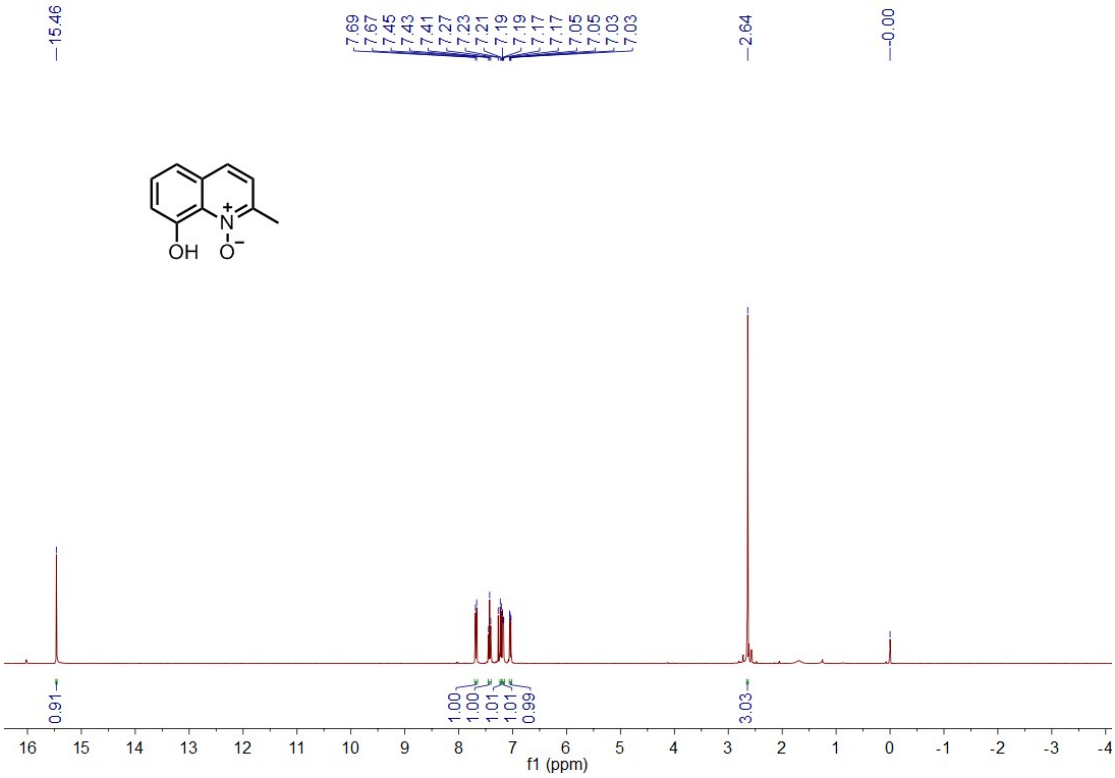


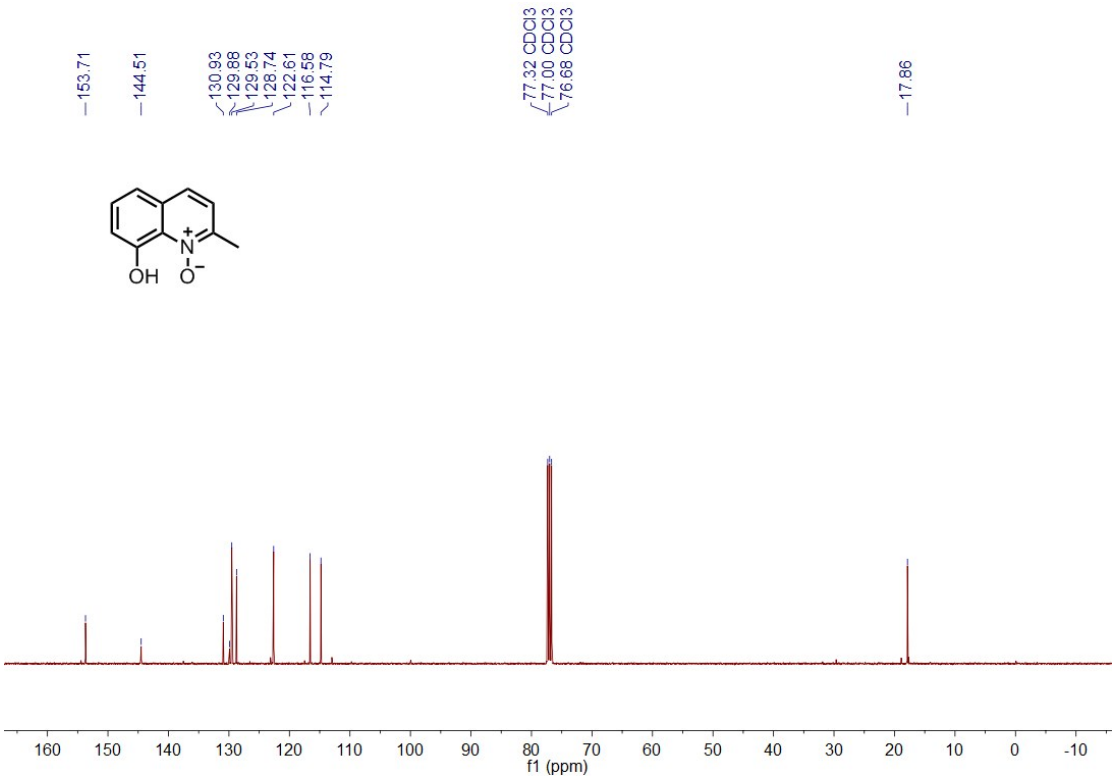
8-ethoxy-2-methylquinoline (6)





8-hydroxy-2-methylquinoline 1-oxide (8)





1-(benzyloxy)-2,2,6,6-tetramethylpiperidine (TP)