Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Metal-free Deoxygenative Sulfonylation of Quinoline *N*-oxides with Sodium Sulfinates via a Dual Radical Coupling Process

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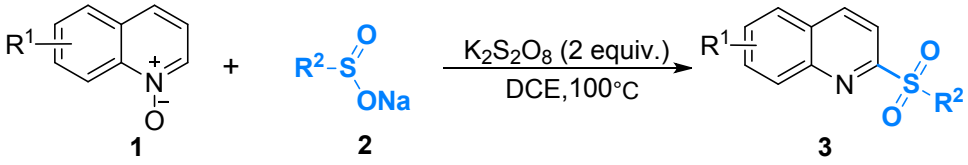
1. General information

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

2. Experimental Section

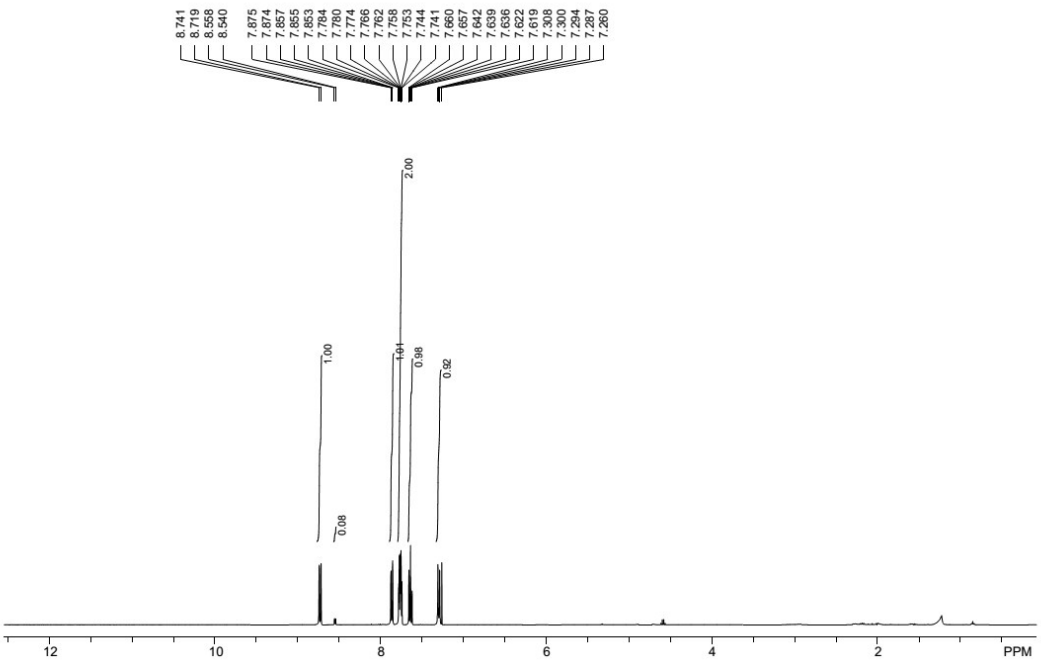
(a) General procedure for the synthesis of *2-Sulfonylquinolines*



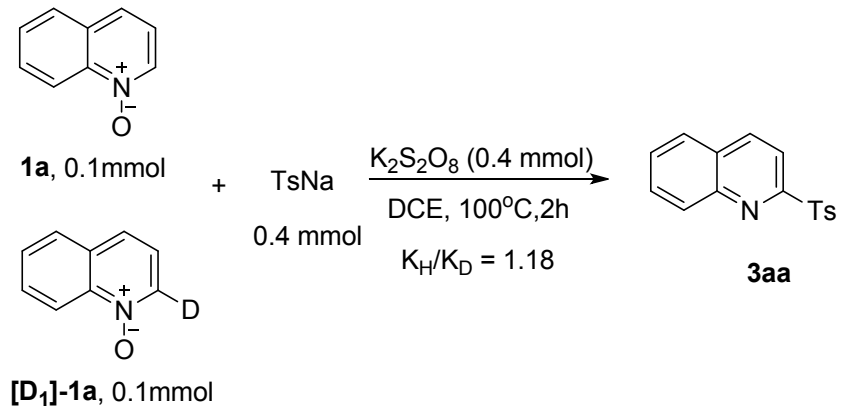
In a pressure tube was consecutively placed quinoline *N*-oxide (0.3 mmol), CH_2ClCH_2Cl (1.2mL), Sodium Sulfinates (0.6 mmol) and $K_2S_2O_8$ (0.6mmol), then the mixtures were heated to 100 °C, The progress of the reaction was monitored by TLC. The reaction typically took 8h -12h. Upon completion, the reaction was cooled to room temperature, then water (5mL) was added to the reaction mixtue, it was extracted with CH_2Cl_2 (5 mL x 3) and the organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1 - 4:1) to obtain 2-Sulfonylquinolines.

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

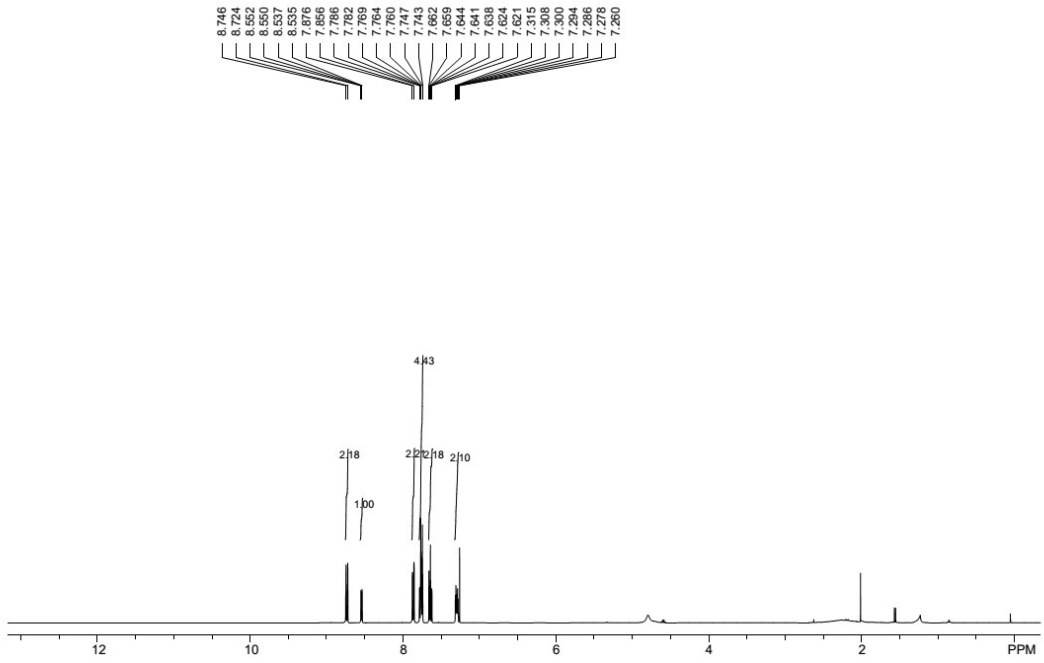
D_2O (1.5 mL), NaOH (200 mg, 5 mmol), quinoline-*N*-oxide (258 mg, 2.0 mmol)were weighed into 30-mL pressure tube sealed with rubber plugs. The reaction mixture was stirred at 100 ℃ for overnight. After cooling to room temperature, the mixture was then extracted with EtOAc (3 x 10 mL). The combined organic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



(c) KIE Experiment

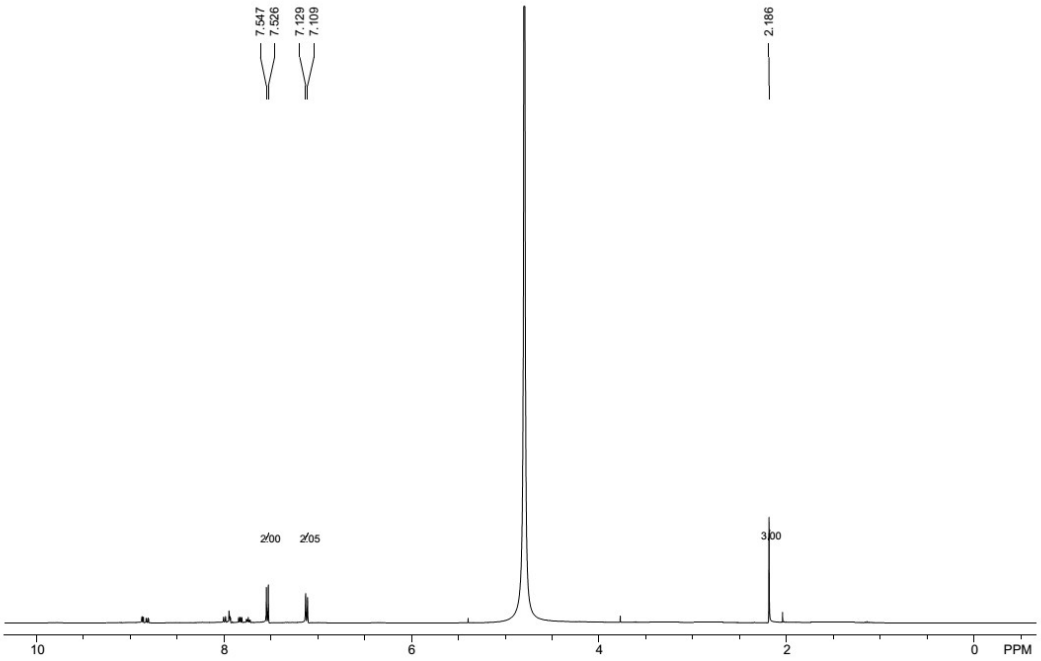


In a pressure tube was consecutively placed Quinoline *N*-oxide **1a** and 2-d_1-quinoline *N*-oxide **[D_1]-1a** (1:1，totally 0.2 mmol, deuteration ratio has been calculated), CH_2ClCH_2Cl (0.8 mL), sodium 4-methylbenzenesulfinate (71.2 mg, 0.4mmol) and $K_2S_2O_8$ (108 mg, 0.4 mmol), then the mixture was heated to 100 °C for 2h, After cooling to room temperature, residual starting material (mixture of 2-d_1-quinoline-*N*-oxide and quinolone -*N*-oxide) was recovered by column chromatography on silica gel (200-300 mesh), which was characterized by ^{1}H NMR spectroscopy. The k_H/k_D= 1.18 was calculated by ^{1}H NMR of the isolated mixture of *N*‐oxides **1a** and **[D_1]-1a.**

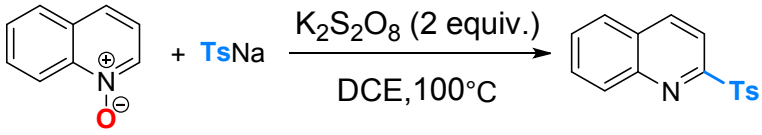


(d) Experimental procedure of TsOH detection by ^{1}H NMR

In a pressure tube was consecutively placed quinoline *N*-oxide **1a** (72.5 mg, 0.5 mmol), CH_2ClCH_2Cl (2 mL), sodium 4-methylbenzenesulfinate **2a** (178 mg, 1 mmol) and $K_2S_2O_8$ (270 mg, 1 mmol), then the mixtures were heated to 100 °C for about 8h, after completion, the reaction was cooled to room temperature, then D_2O (2mL)was added to the mixture, the component of aqueous phase was detected by ^{1}H NMR. Analysis of ^{1}H NMR spectrum showed that TsOH generated after reaction completion.



(e) Large scale experiment of preparation of 3aa



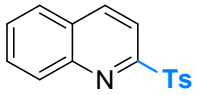
1a, 10mmol
1.45g

3aa, 2.21 g
yield 78%

In a round-bottom flask was consecutively placed quinoline *N*-oxide **1a** (1.45 g, 10 mmol), CH_2ClCH_2Cl (40 mL), sodium 4-methylbenzenesulfinate **2a** (3.56 g, 20 mmol) and $K_2S_2O_8$ (5.4 g, 20 mmol), then the mixtures were heated to 100 °C for about 12 h, after completion, the reaction was cooled to room temperature, then water (20 mL) was added to the reaction mixtue, it was extracted with CH_2Cl_2 (20 mL x 3) and the organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 10:1 - 4:1) to obtain 2.21gram of 2-Sulfonylquinoline **3aa** ,yield 78%. Note: The yield of **3aa** was decreased (72%) when the amount of DCE was reduced to 30 ml.

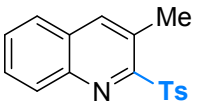
3. Characterization data of products

2-tosylquinoline (3aa)[1]



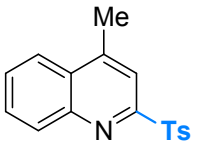
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.4 Hz , 1 H), 8.20 (d, *J* = 8.4 Hz , 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.80 – 7.76 (m, 1 H), 7.64 (t, *J* = 7.2 Hz , 1 H), 7.33 (d, *J* = 8.4 Hz , 2 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 147.2, 144.7, 138.6, 135.9, 130.8, 130.1, 129.6, 129.0, 128.8, 128.6, 127.6, 117.5, 21.5.

3-methyl-2-tosylquinoline (3ba)[2]



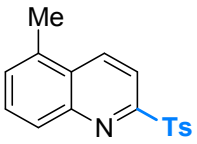
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.94 – 7.92 (m, 3 H), 7.73 (d, *J* = 6.8 Hz, 1 H), 7.63 – 7.56 (m, 2 H), 7.34 (d, *J* = 6.8 Hz, 2 H), 2.84 (s, 3 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 144.6, 144.4, 139.8, 135.7, 129.8, 129.6, 129.3 (2 C), 129.0, 128.9, 128.5, 126.6, 21.6, 18.8;

4-methyl-2-tosylquinoline (3ca)[3]



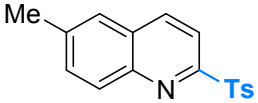
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 1 H), 8.03 – 8.00 (m, 4 H), 7.77 – 7.73 (m, 1 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 2.78 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 147.9, 147.2, 144.7, 136.2, 131.0, 130.5, 129.7, 129.0, 128.8, 128.7, 123.8, 118.0, 21.6, 19.1.

5-methyl-2-tosylquinoline (3da)[4]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (dd, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1 H), 8.19 (d, *J* = 8.8 Hz, 1 H), 8.02 – 8.00 (m, 3 H), 7.66 – 7.62 (m, 1 H), 7.46 – 7.44 (m, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 2.67 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 147.8, 144.7, 136.1, 135.1, 134.7, 130.6, 129.7, 129.4, 128.9, 128.5, 128.2, 117.2, 21.6, 18.6.

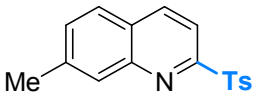
6-methyl-2-tosylquinoline (3ea)[5]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.4 Hz, 1 H), 8.14 (d, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 8.8 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 2.54 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 146.1, 144.7, 139.6, 137.8, 136.3, 133.3, 130.0, 129.7, 128.9, 128.9, 126.4, 117.7, 21.8,

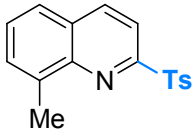
21.6.

7-methyl-2-tosylquinoline (3fa)[6]



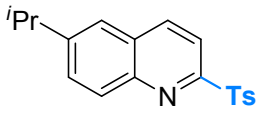
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 8.4 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.95 (s, 1 H), 7.75 (d, *J* = 8.4 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 2.54 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 147.7, 144.7, 141.6, 138.2, 136.2, 131.5, 129.7, 129.2, 129.0, 127.2, 126.9, 116.8, 21.8, 21.6.

8-methyl-2-tosylquinoline (3ga) [1]



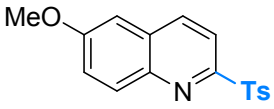
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.4 Hz, 1 H), 8.19 (d, *J* = 8.4 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.67 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 146.3, 144.6, 138.6, 138.3, 135.9, 130.8, 129.4, 129.3, 128.8, 128.7, 125.5, 116.6, 21.6, 17.4.

6-isopropyl-2-tosylquinoline (3ha)[4]



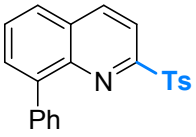
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 7.99 (d, *J* = 8.8 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.58 – 7.53 (m, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 3.01 – 2.94 (m, 1 H), 2.25 (s, 3 H), 1.20 (d, *J* = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 150.0, 146.2, 144.5, 138.1, 136.3, 130.9, 130.0, 129.6, 128.8, 128.7, 123.6, 117.6, 34.1, 23.5, 21.5.

6-methoxy-2-tosylquinoline (3ia)[2]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.4 Hz, 1 H), 8.13 (d, *J* = 8.8 Hz, 1 H), 8.05 (d, *J* = 9.2 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 2 H), 7.41 (dd, *J* = 9.2 Hz, 2.8 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.08 (d, *J* = 2.4 Hz, 1 H), 3.93 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 155.6, 144.6, 143.6, 136.8, 136.4, 131.8, 130.3, 129.7, 128.8, 124.2, 118.2, 104.5, 55.7, 21.6.

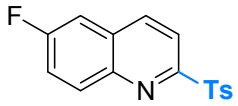
8-phenyl-2-tosylquinoline (3ja)[4]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 1 H), 7.80 (d, *J* = 8.4 Hz, 2 H), 7.76 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1 H), 7.71 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.37 – 7.32

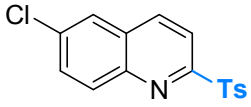
(m, 5 H), 7.15 (d, J = 8.4 Hz, 2 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 144.7, 144.5, 141.2, 138.8, 137.9, 135.1, 131.4, 130.7, 129.6, 129.3, 129.1, 128.8, 127.6, 127.3, 127.2, 116.5, 21.6.

6-fluoro-2-tosylquinoline (3ka)[2]



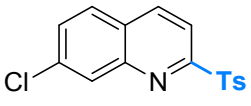
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.8 Hz, 1 H), 8.17 (d, J = 8.8 Hz, 1 H), 8.14 – 8.11 (m, 1 H), 7.98 (d, J = 8.0 Hz, 2 H), 7.52 – 7.44 (m, 2 H), 7.29 (d, J = 8.4 Hz, 2 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 160.4, 157.7, 157.7, 144.8, 144.3, 138.0, 138.0, 135.8, 132.9, 132.8, 129.7, 129.6, 129.5, 128.9, 121.5, 121.3, 118.3, 110.8, 110.6, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 108.3.

6-chloro-2-tosylquinoline (3la)[1]



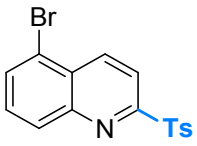
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.4 Hz, 1 H), 8.08 (d, J = 9.2 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 2 H), 7.84 (d, J = 2.4 Hz, 1 H), 7.70 (dd, J = 9.2 Hz, 2.0 Hz, 1 H), 7.33 (d, J = 8.0 Hz, 2 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 145.7, 145.0, 137.7, 135.7, 135.1, 132.0, 131.8, 129.8, 129.3, 129.0, 126.3, 118.6, 21.6.

7-chloro-2-tosylquinoline (3ma)



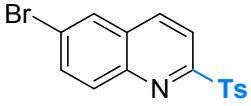
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.8 Hz, 1 H), 8.16 – 8.15 (m, 1 H), 8.00 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.8 Hz, 1 H), 7.59 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H), 7.34 (d, J = 8.4 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 147.6, 145.0, 138.6, 137.1, 135.6, 130.2, 129.8, 129.2, 128.8, 128.0, 127.1, 117.7, 21.7; HRMS (ESI) *m/z* calcd. for $C_{16}H_{13}ClNO_2S[M+H]^+$: 318.0350, found 318.0347.

5-bromo-2-tosylquinoline (3na)



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 8.8 Hz, 1 H), 8.27 (d, J = 8.8 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 1 H), 8.01 (d, J = 8.0 Hz, 2 H), 7.91 (d, J = 6.8 Hz, 1 H), 7.62 (t, J = 8.0 Hz, 1 H), 7.33 (d, J = 8.4 Hz, 2 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 148.1, 145.0, 138.5, 135.5, 132.7, 131.1, 130.2, 129.8, 129.1, 128.2, 121.8, 118.8, 21.6; HRMS (ESI) *m/z* calcd. for $C_{16}H_{13}BrNO_2S[M+H]^+$: 361.9845, found 361.9843.

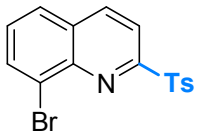
6-bromo-2-tosylquinoline (3oa)[2]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.8 Hz, 1 H), 8.04 – 7.99 (m, 4 H), 7.83 (dd,

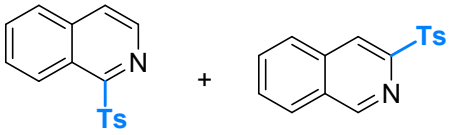
J = 9.2 Hz, 2.0 Hz, 1 H), 7.33 (d, J = 8.0 Hz, 2 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 145.9, 144.9, 137.6, 135.6, 134.5, 131.8, 129.8, 129.6, 129.0, 123.5, 118.5, 21.6.

8-bromo-2-tosylquinoline (3pa)



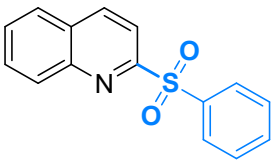
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.4 Hz, 1 H), 8.21 (d, J = 8.4 Hz, 1 H), 8.04 – 7.99 (m, 4 H), 7.84 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1 H), 7.34 (d, J = 8.8 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 146.0, 145.0, 137.6, 135.8, 134.6, 131.9, 129.8, 129.7, 129.1, 123.5, 118.6, 21.7; HRMS (ESI) *m/z* calcd. for $C_{16}H_{13}BrNO_2S[M+H]^+$: 361.9845, found 361.9841.

Mixture of 1-tosylisoquinoline and 3-tosylisoquinoline (3qa)[2]



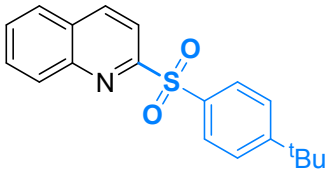
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.23 (s, 1 H), 9.14 (s, 0.91 H), 8.65 (s, 0.97 H), 8.09 (s, 1.09 H), 8.01 – 7.99 (m,,6.62 H), 7.80 – 7.70 (m, 5.86 H), 7.66 – 7.63 (m, 1.14 H), 7.34 – 7.31 (m, 4.47 H), 2.45 (s, 3.33 H), 2.39 (s, 3.07 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 152.3, 151.2, 145.9, 144.6, 136.3, 135.8, 135.3, 132.0, 131.2, 130.5, 130.2, 130.0, 129.7, 129.4, 128.8, 128.6, 128.2, 128.2, 127.8, 127.2, 121.1, 121.0, 21.7, 21.6.

2-(phenylsulfonyl)quinoline (3ab)[3]



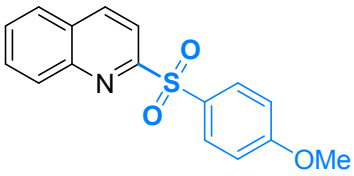
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, J = 8.4 Hz, 1 H), 8.23 – 8.14 (m, 4 H), 7.88 (d, J = 8.4 Hz, 1 H), 7.79 (t, J = 7.2 Hz, 1 H), 7.67 (d, J = 7.6 Hz, 1 H), 7.60 (d, J = 7.6 Hz, 1 H), 7.54 (t, J = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 147.5, 138.7, 133.7, 131.0, 130.4, 129.6, 129.2, 129.1, 129.0, 128.8, 127.7, 117.7.

2-((4-(tert-butyl)phenyl)sulfonyl)quinoline (3ac)[3]



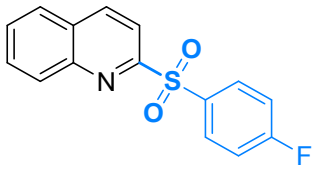
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, J = 8.8 Hz, 1 H), 8.21 (d, J = 8.4 Hz, 2 H), 8.06 (d, J = 8.4 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 1 H), 7.81 – 7.77 (m, 1 H), 7.67 – 7.64 (m, 1 H), 7.54 (d, J = 8.4 Hz, 2 H), 1.30 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 157.6, 147.5, 138.7, 136.1, 130.9, 130.4, 129.1, 128.8, 127.7, 126.2, 117.8, 35.2, 31.0.

2-((4-methoxyphenyl)sulfonyl)quinoline (3ad)[5]



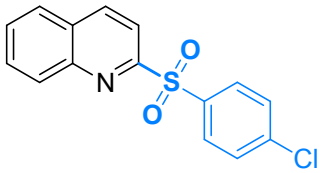
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.8 Hz, 1 H), 8.19 – 8.15 (m, 2 H), 8.06 (d, *J* = 8.8 Hz, 2 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.79 – 7.75 (m, 1 H), 7.64 (t, *J* = 8.0 Hz, 1 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 158.5, 147.4, 138.6, 131.2, 130.9, 130.4, 130.3, 129.0, 128.7, 127.6, 117.5, 114.3, 55.6.

2-((4-fluorophenyl)sulfonyl)quinoline (3ae)[2]



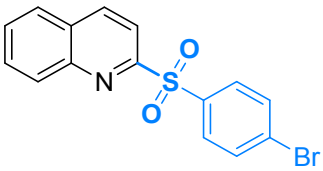
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.4 Hz, 1 H), 8.22 – 8.15 (m, 4 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.82 - 7.79 (m, 1 H), 7.77 – 7.66 (m, 1 H), 7.22 (t, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 164.7, 157.9, 147.4, 138.8, 135.0, 132.0, 131.9, 131.1, 130.3, 129.3, 128.8, 128.5, 127.7, 117.5, 116.5, 116.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 103.3.

2-((4-chlorophenyl)sulfonyl)quinoline (3af)[7]



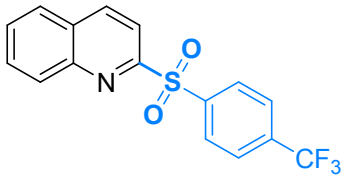
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.4 Hz, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.82 – 7.78 (m, 1 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.51 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 147.4, 140.6, 138.9, 137.5, 131.1, 130.6, 130.3, 129.4 (2 C), 128.9, 127.7, 117.5.

2-((4-bromophenyl)sulfonyl)quinoline (3ag)[5]



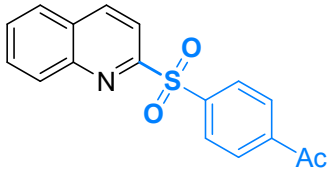
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.4 Hz, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.81 (t, *J* = 8.0 Hz, 1 H), 7.70 – 7.67 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 147.4, 138.9, 138.0, 132.4, 131.1, 130.6, 130.3, 129.4, 129.2, 128.9, 127.7, 117.5.

2-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (3ah)[2]



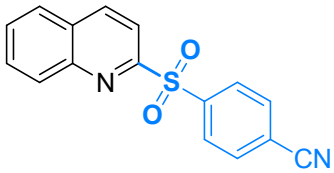
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.4 Hz, 1 H), 8.29 (d, *J* = 8.4 Hz, 2 H), 8.24 (d, *J* = 8.8 Hz, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.81 – 7.79 (m, 3 H), 7.70 – 7.67 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 147.4, 142.6, 139.0, 135.4, 135.1, 131.3, 130.3, 129.7, 129.5, 128.9, 127.8, 126.2, 126.1, 126.1, 126.1, 124.5, 121.7, 117.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 63.2.

1-(4-(quinolin-2-ylsulfonyl)phenyl)ethanone (3ai)[4]



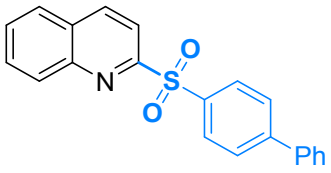
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.8 Hz, 1 H), 8.24 – 8.21 (m, 3 H), 8.14 (d, *J* = 8.4 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.81 – 7.77 (m, 1 H), 7.69 – 7.65 (m, 1 H), 2.62 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 157.4, 147.4, 142.8, 138.9, 131.1, 130.2, 129.4, 129.4, 128.8, 128.8, 128.7, 127.7, 117.5, 26.8.

4-(quinolin-2-ylsulfonyl)benzonitrile (3aj)[5]



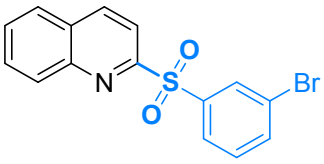
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.4 Hz, 1 H), 8.27 (d, *J* = 8.4 Hz, 2 H), 8.23 (d, *J* = 8.8 Hz, 1 H), 8.13 (d, *J* = 8.8 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.85 – 7.81 (m, 3 H), 7.70 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 147.5, 143.2, 139.1, 132.7, 131.4, 130.3, 129.8, 129.7, 129.0, 127.8, 117.5, 117.4, 117.2.

2-([1,1'-biphenyl]-4-ylsulfonyl)quinolone (3ak)[2]



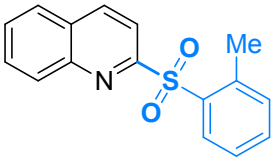
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.8 Hz, 1 H), 8.25 (d, *J* = 8.8 Hz, 1 H), 8.21 – 8.19 (m, 3 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.80 (t, *J* = 7.2 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.69 – 7.65 (m, 1 H), 7.59 – 7.56 (m, 2 H), 7.47 – 7.40 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 147.5, 146.7, 139.2, 138.8, 137.6, 131.0, 130.4, 129.6, 129.2, 129.0, 128.6, 127.7, 127.7, 127.4, 117.7.

2-((3-bromophenyl)sulfonyl)quinoline (3al)[8]



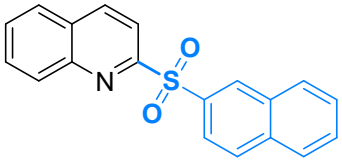
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.4 Hz, 1 H), 8.27 (s, 1 H), 8.20 (d, *J* = 8.8 Hz, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.81 – 7.77 (m, 1 H), 7.71 – 7.65 (m, 2 H), 7.40 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 147.4, 140.9, 138.9, 136.7, 131.7, 131.2, 130.5, 130.3, 129.4, 128.9, 127.7, 127.6, 123.0, 117.6.

2-(o-tolylsulfonyl)quinoline (3am)[5]



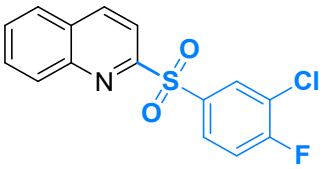
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.8 Hz, 1 H), 8.30 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 8.8 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.78 – 7.74 (m, 1 H), 7.66 – 7.63 (m, 1 H), 7.51 – 7.47 (m, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.24 (d, *J* = 7.6 Hz, 1 H), 2.55 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 147.1, 139.0, 138.6, 137.0, 133.9, 132.4, 130.9, 130.5, 130.3, 129.1, 128.8, 127.7, 126.3, 117.7, 20.6.

2-(naphthalen-2-ylsulfonyl)quinoline (3an)[3]



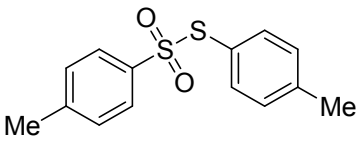
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (s, 1 H), 8.38 (d, *J* = 8.4 Hz, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 1 H), 8.08 (dd, *J* = 8.4 Hz, 1.6 Hz, 1 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 7.95 (d, *J* = 8.8 Hz, 1 H), 7.88 – 7.85 (m, 2 H), 7.78 – 7.74 (m, 1 H), 7.66 – 7.57 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 147.4, 138.7, 135.9, 135.3, 132.1, 131.0, 130.8, 130.3, 129.5, 129.3 (2 C), 129.2, 128.8, 127.9, 127.7, 127.5, 123.7, 117.8.

2-((3-chloro-4-fluorophenyl)sulfonyl)quinoline (3ao)[4]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.8 Hz, 1 H), 8.24 – 8.20 (m, 2 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 8.08 – 8.04 (m, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.84 – 7.80 (m, 1 H), 7.71 – 7.67 (m, 1 H), 7.30 (t, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7, 160.1, 157.4, 147.4, 139.0, 135.9 (2 C), 132.1, 131.2, 130.3, 129.8, 129.7, 129.5, 128.9, 127.7, 122.6, 122.4, 117.5, 117.4, 117.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 105.5.

S-p-tolyl 4-methylbenzenesulfonothioate (5a)[9]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.4 Hz, 2 H), 7.27 – 7.21 (m, 4 H), 7.15 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 142.0, 140.5, 136.5, 130.2, 129.3, 127.6, 124.6, 21.6, 21.5.

4. References

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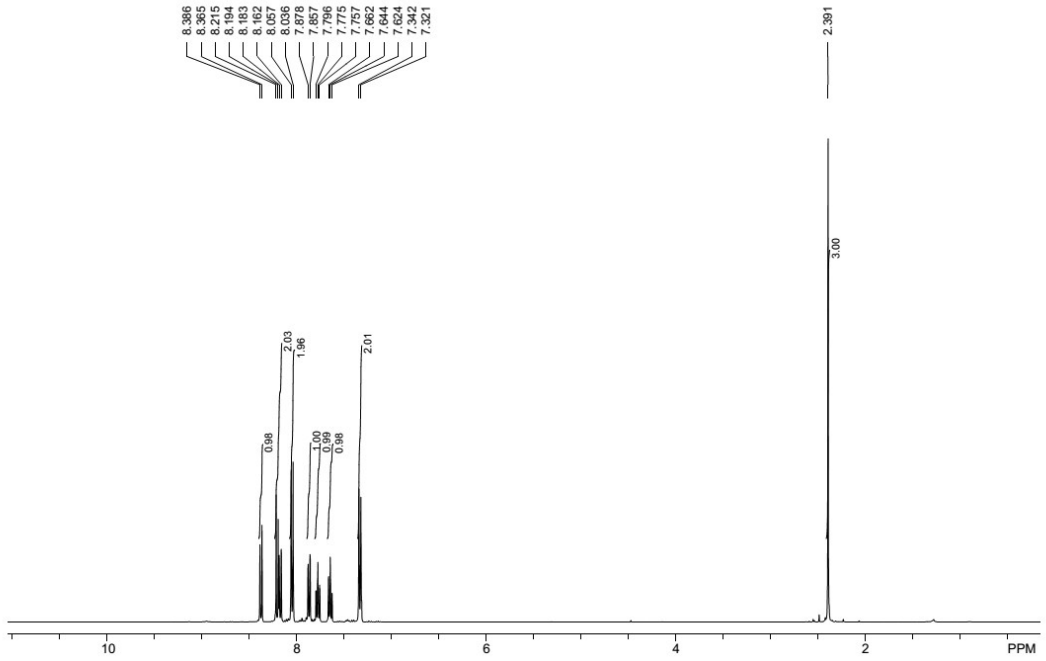
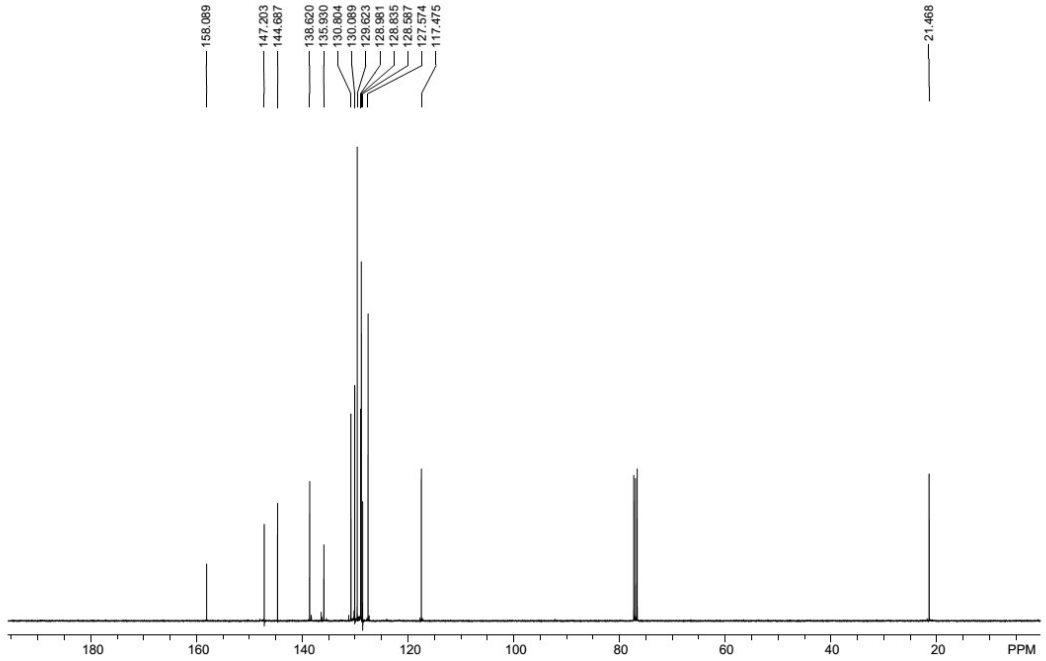
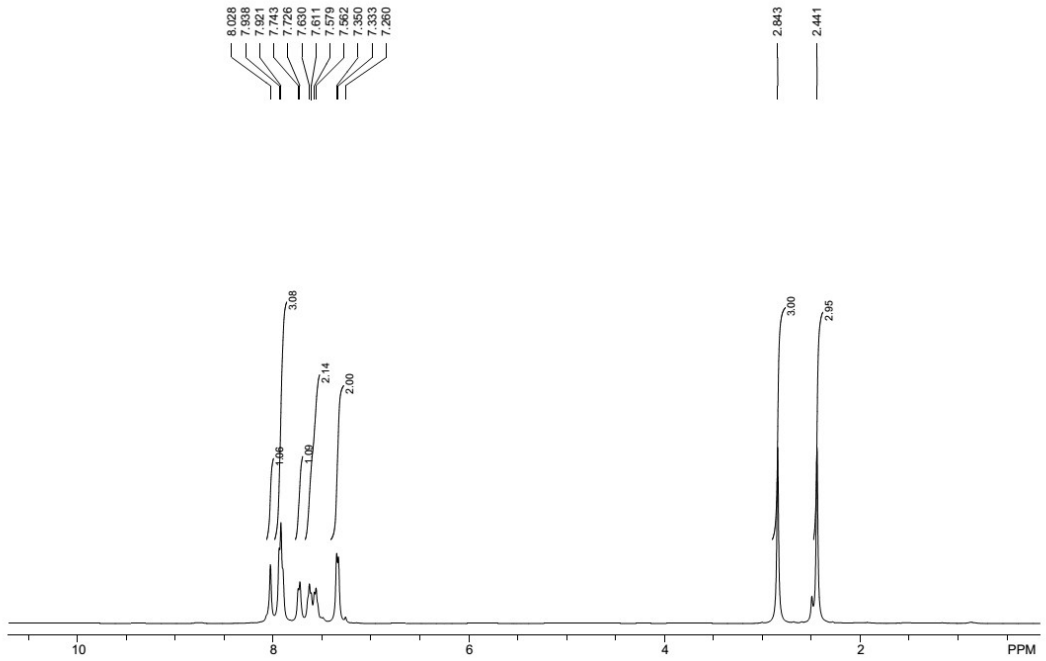
5. ^{1}H and ^{13}C NMR spectra of products

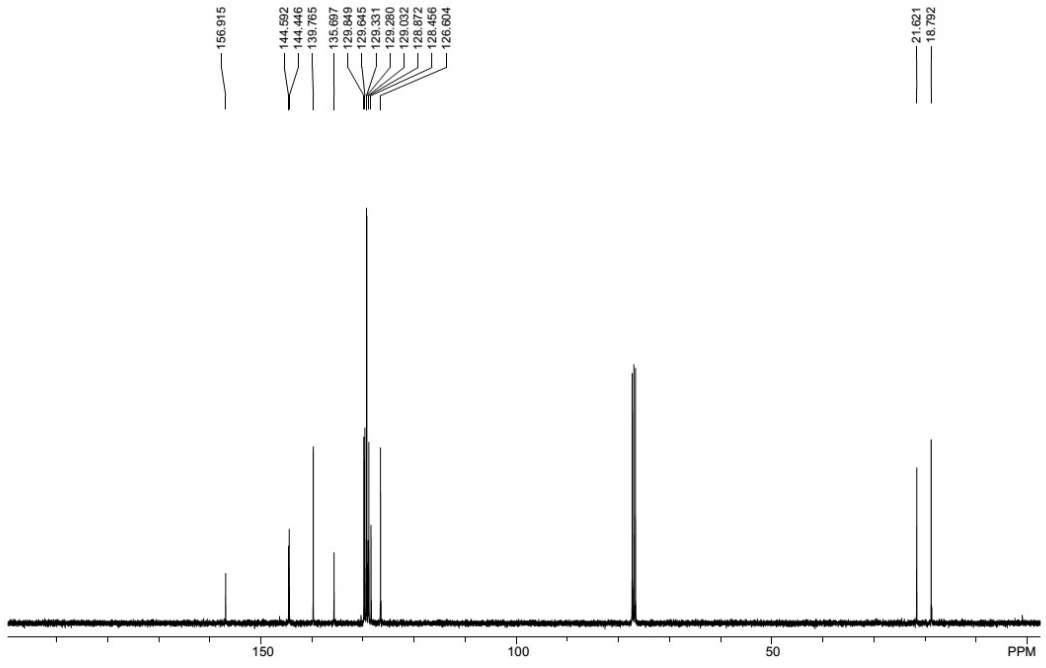
2-tosylquinoline (3aa)



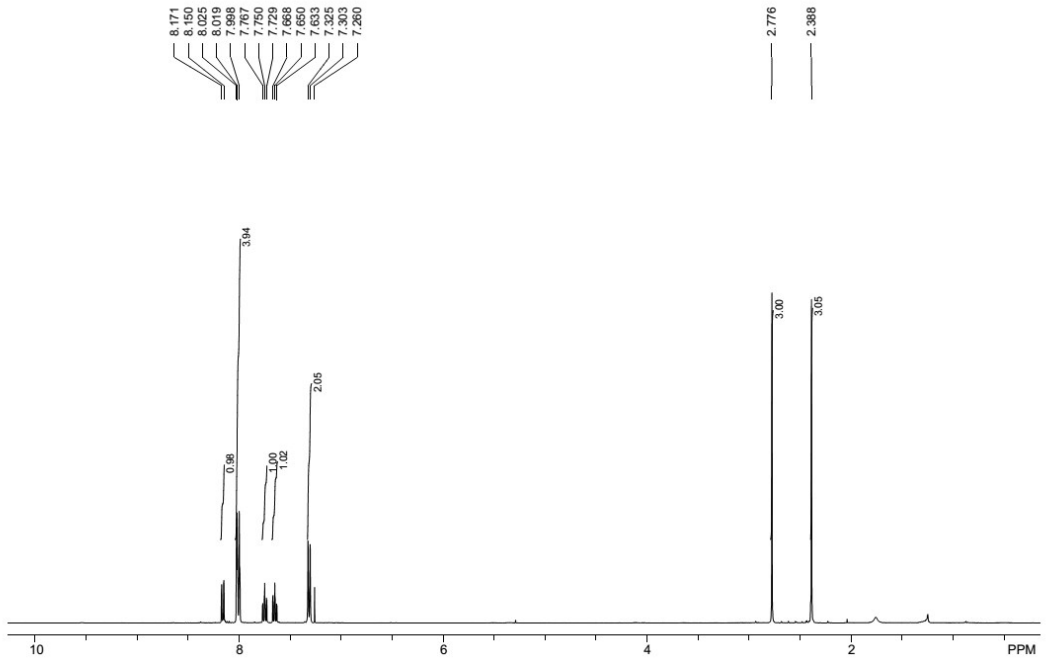


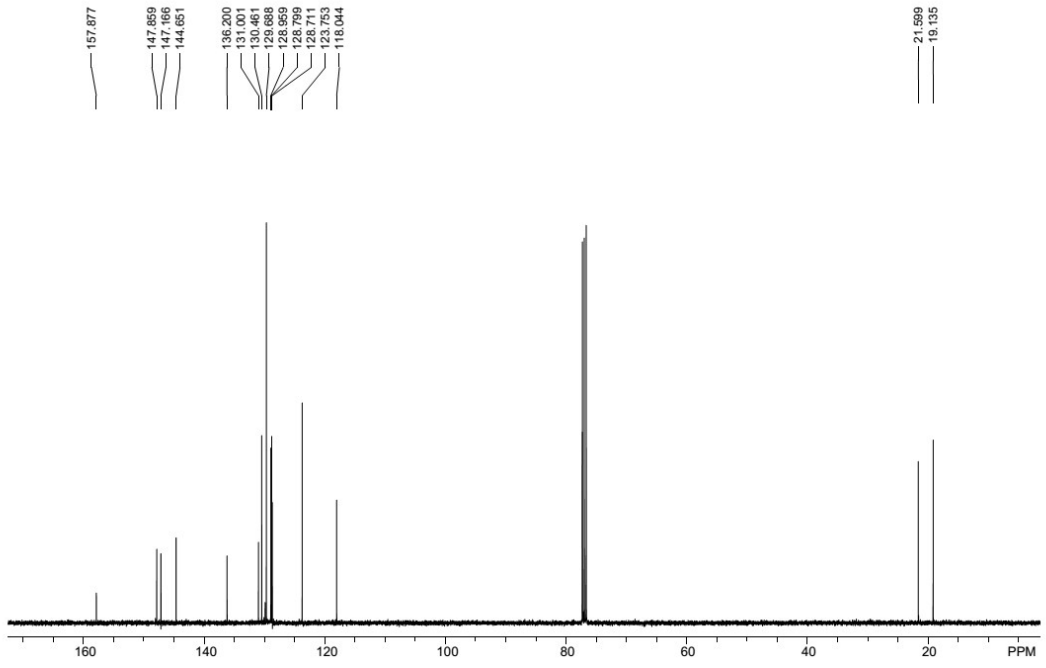
3-methyl-2-tosylquinoline (3ba)





4-methyl-2-tosylquinoline (3ca)





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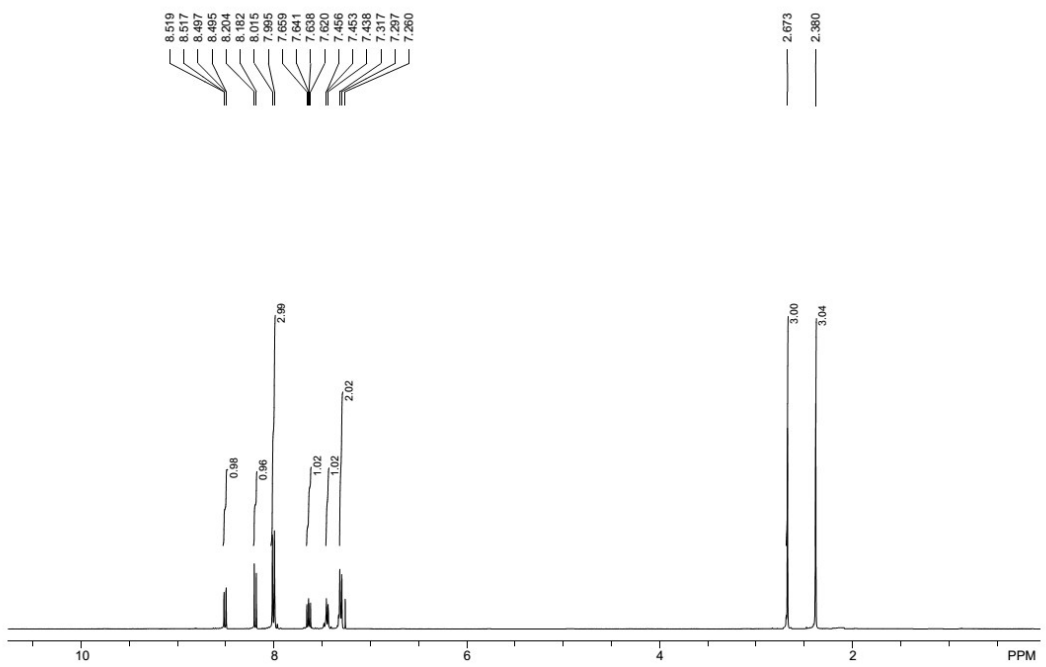

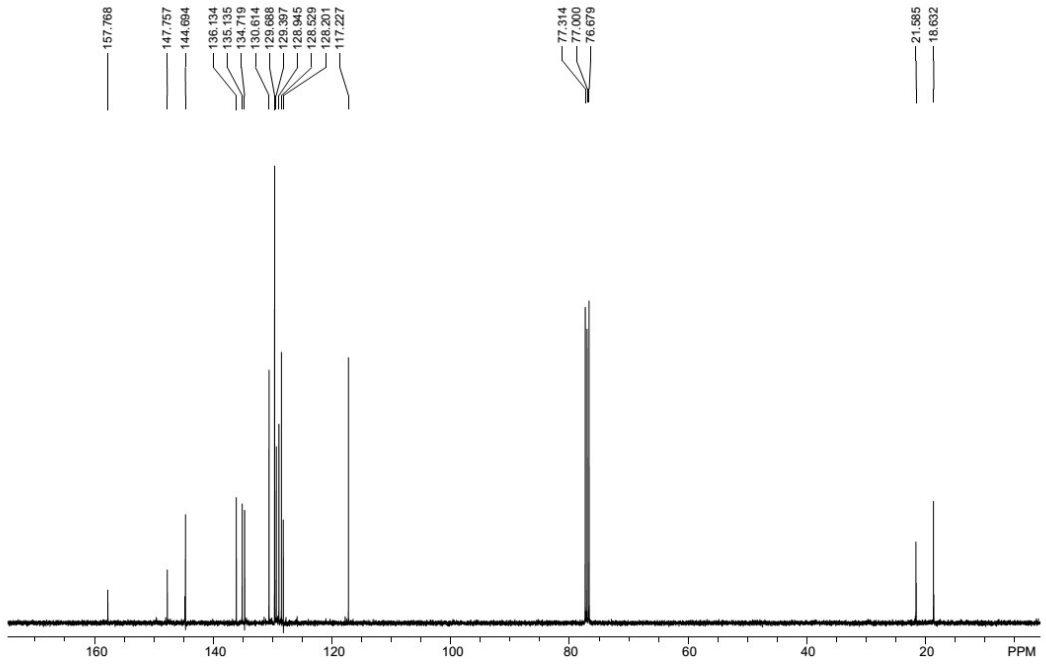

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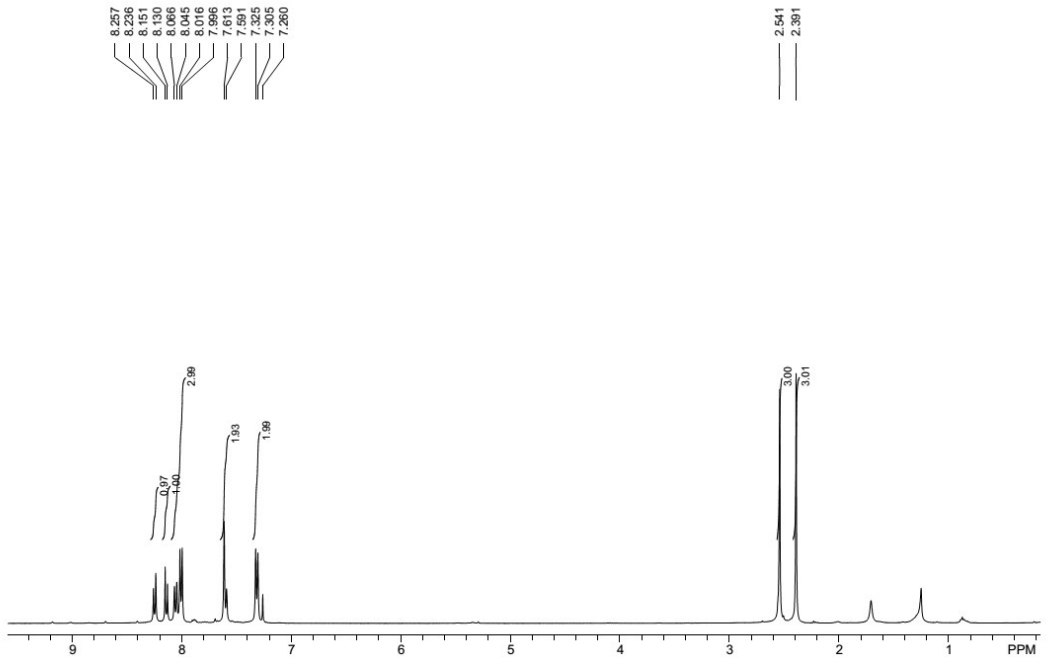

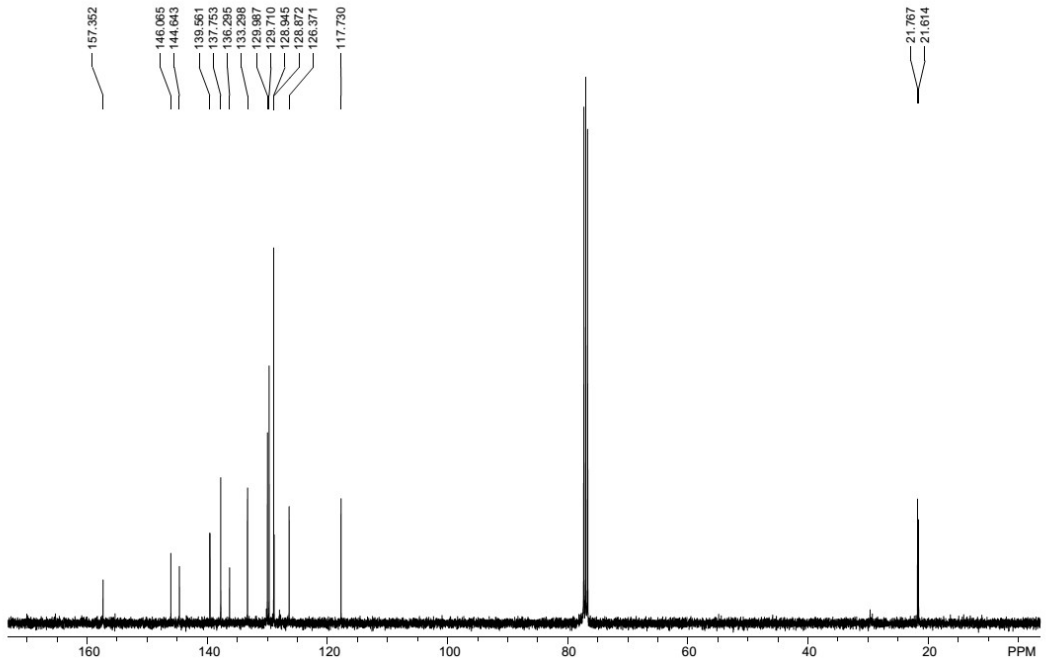

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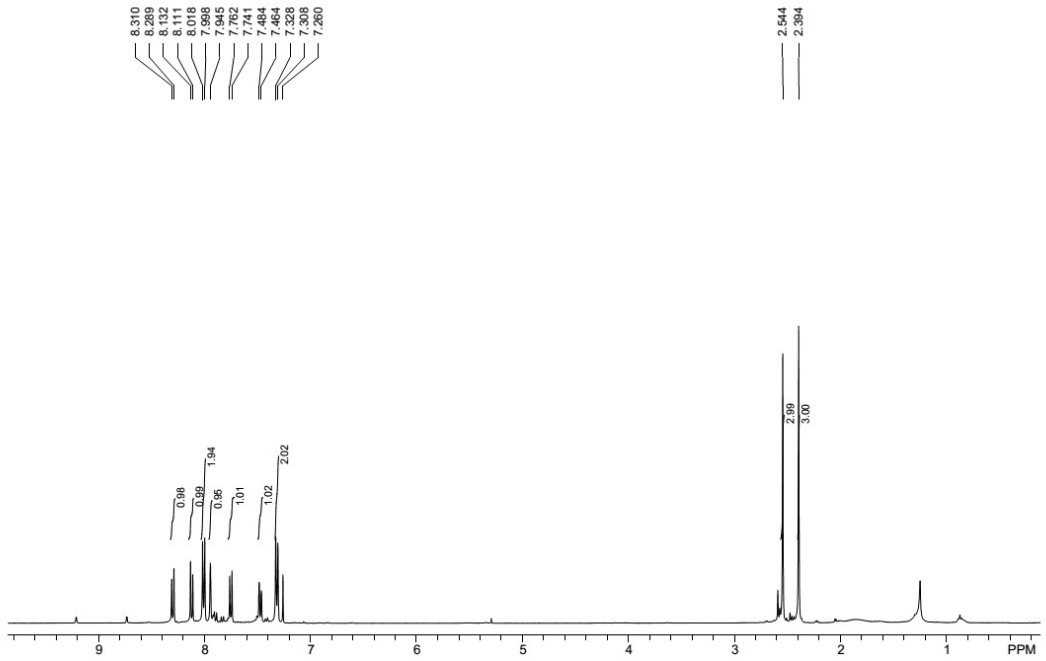
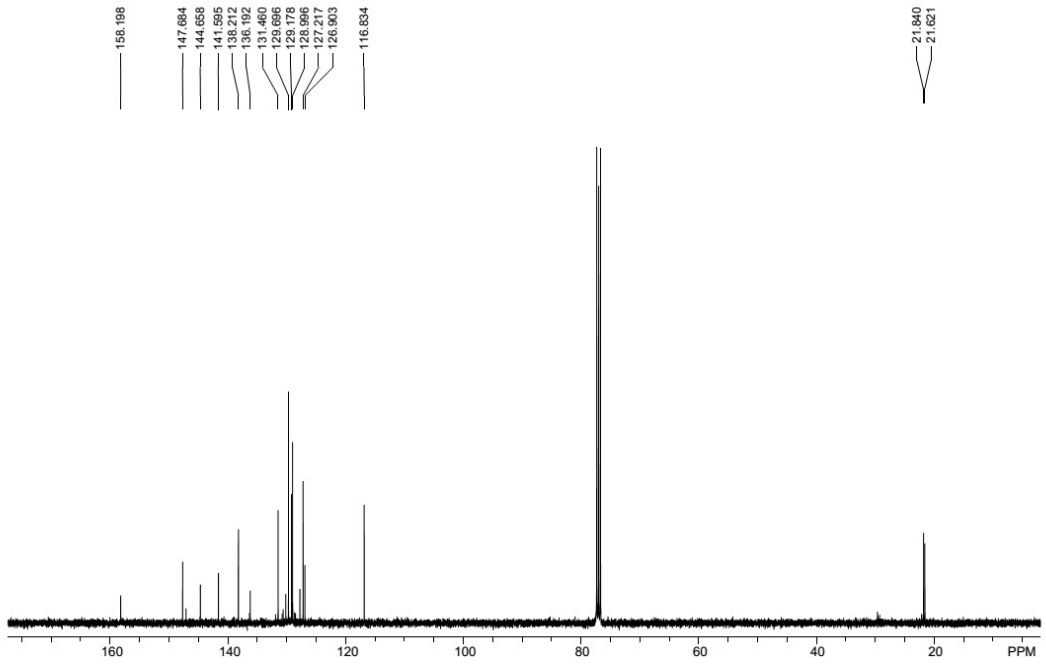
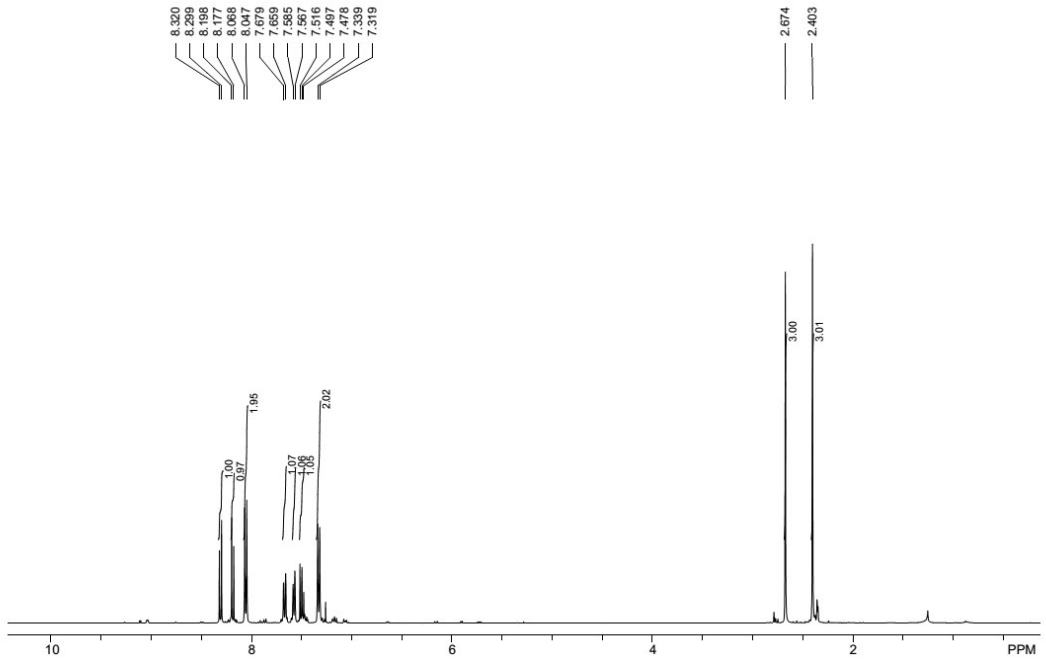
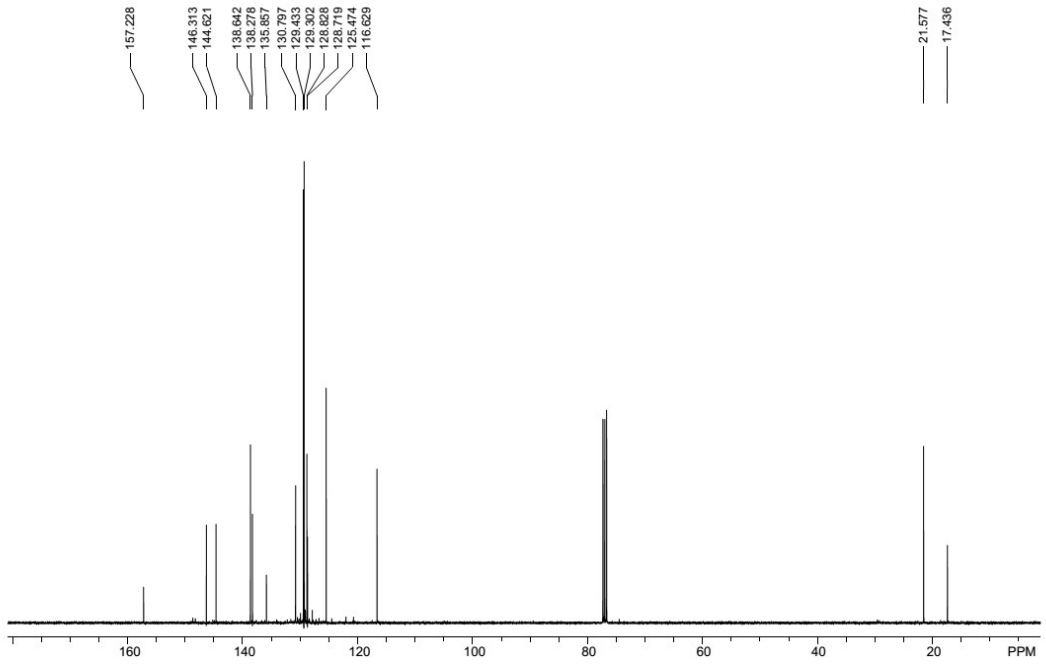


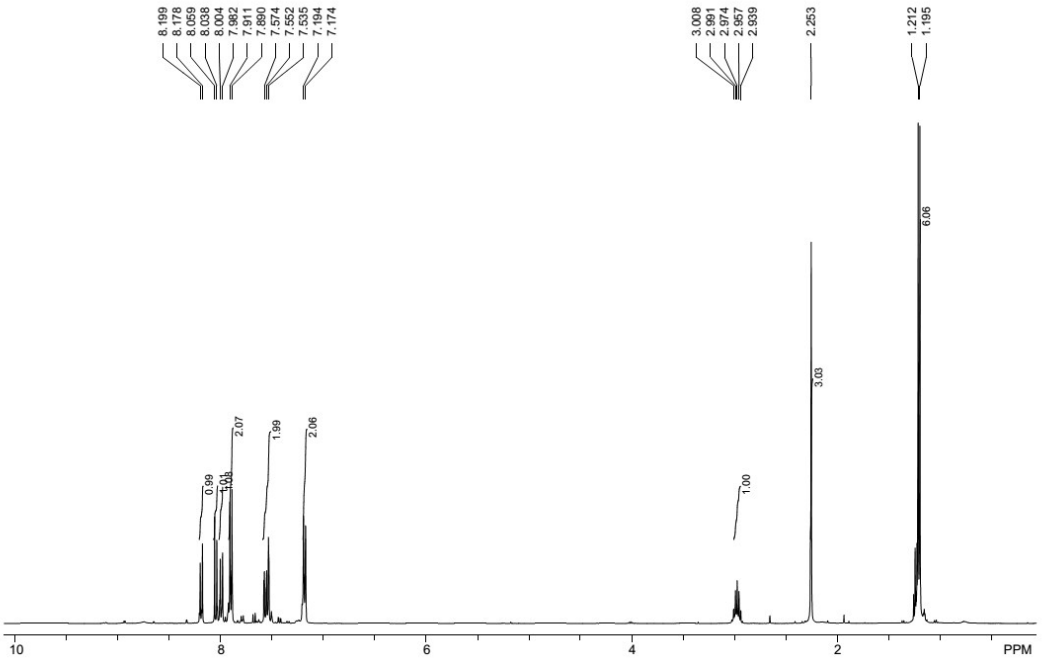


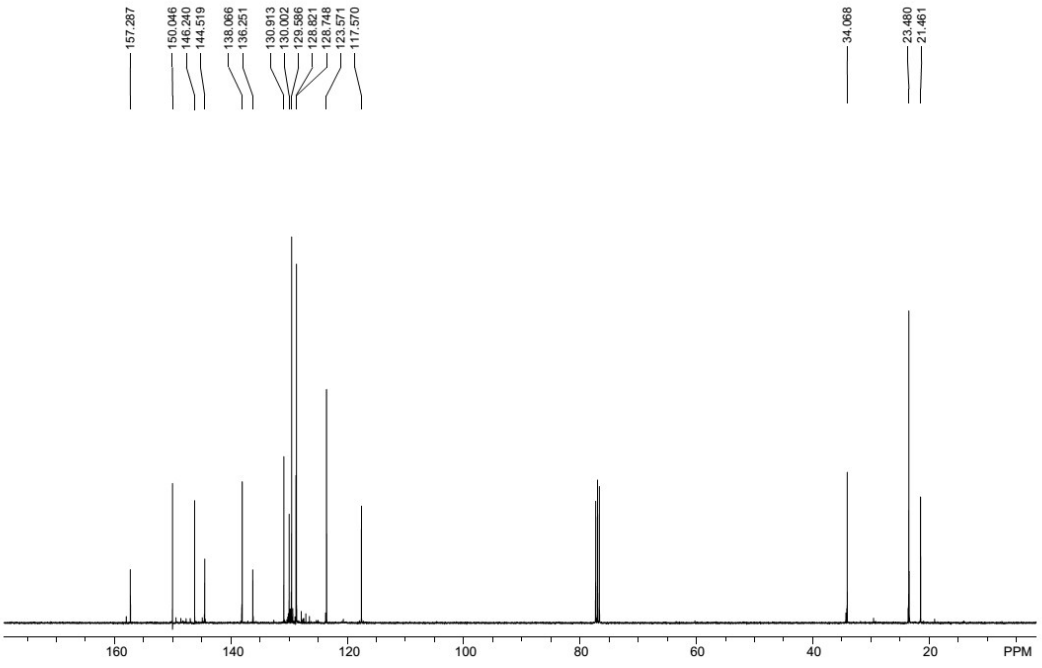
8-methyl-2-tosylquinoline (3ga)



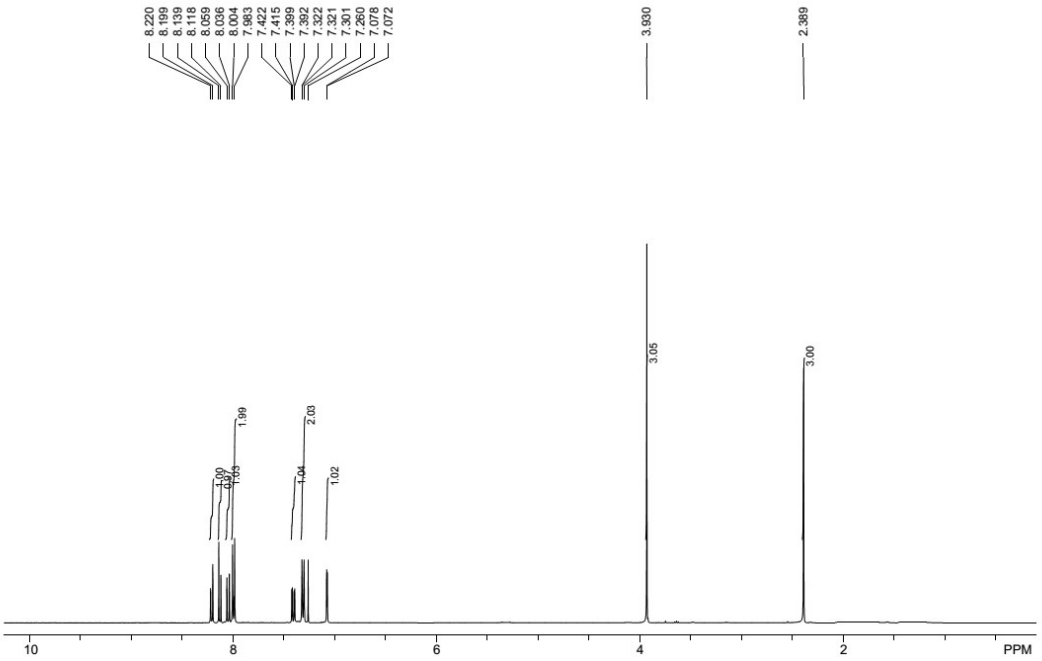


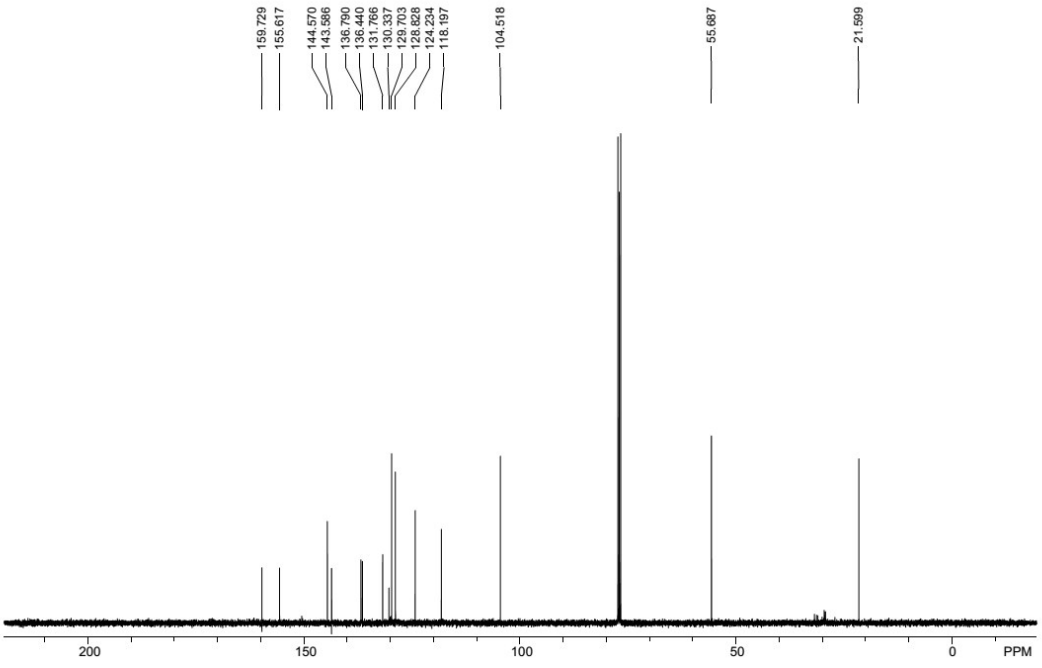
6-isopropyl-2-tosylquinoline (3ha)



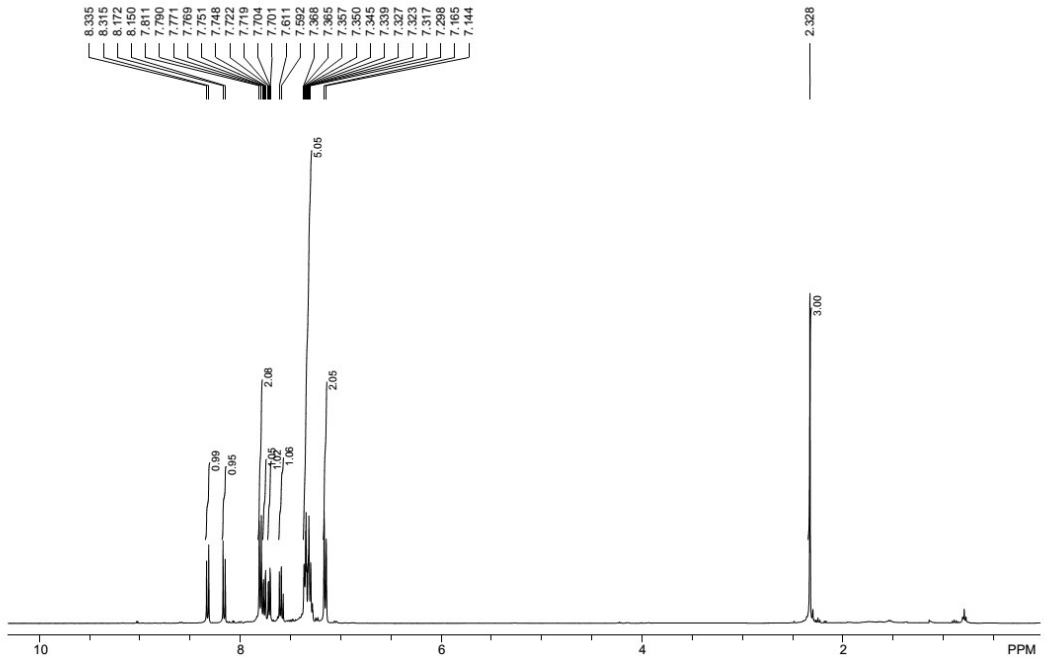


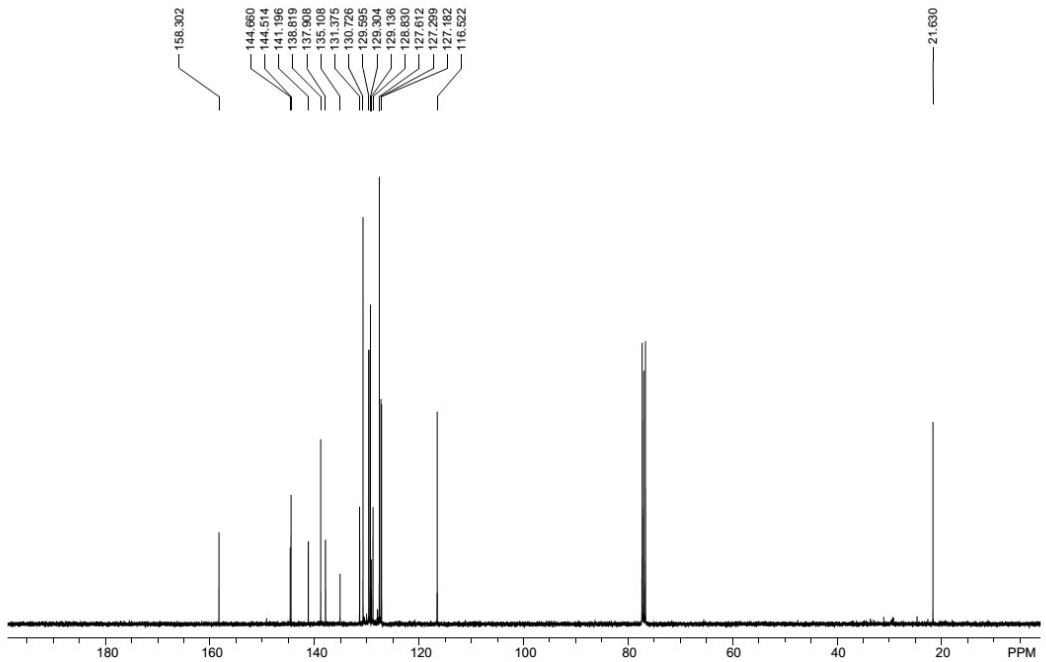
6-methoxy-2-tosylquinoline (3ia)



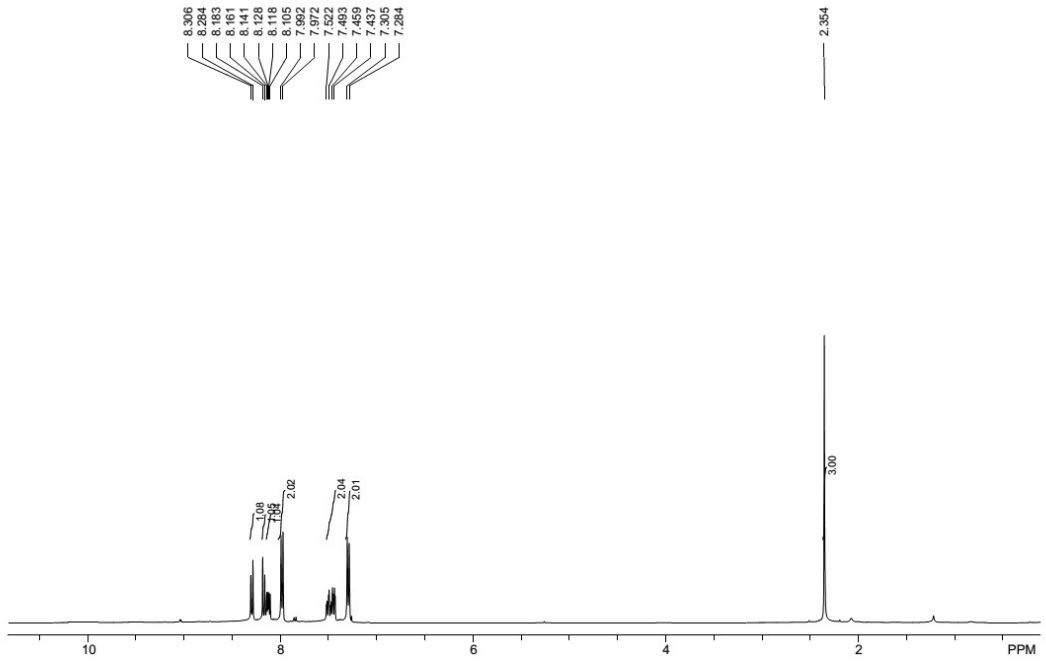


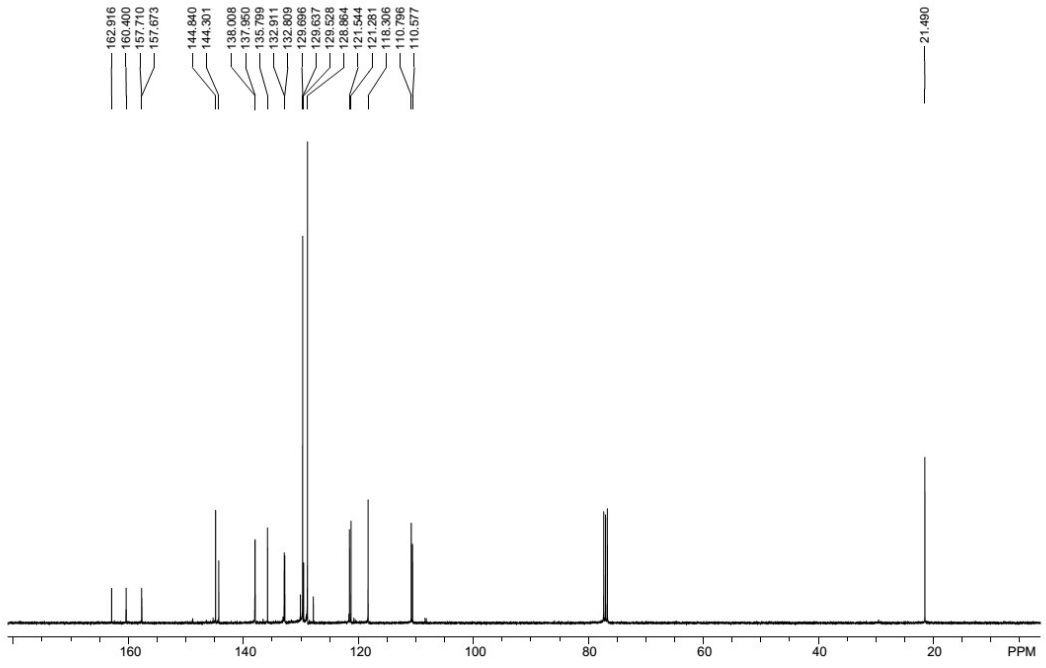
8-phenyl-2-tosylquinoline (3ja)



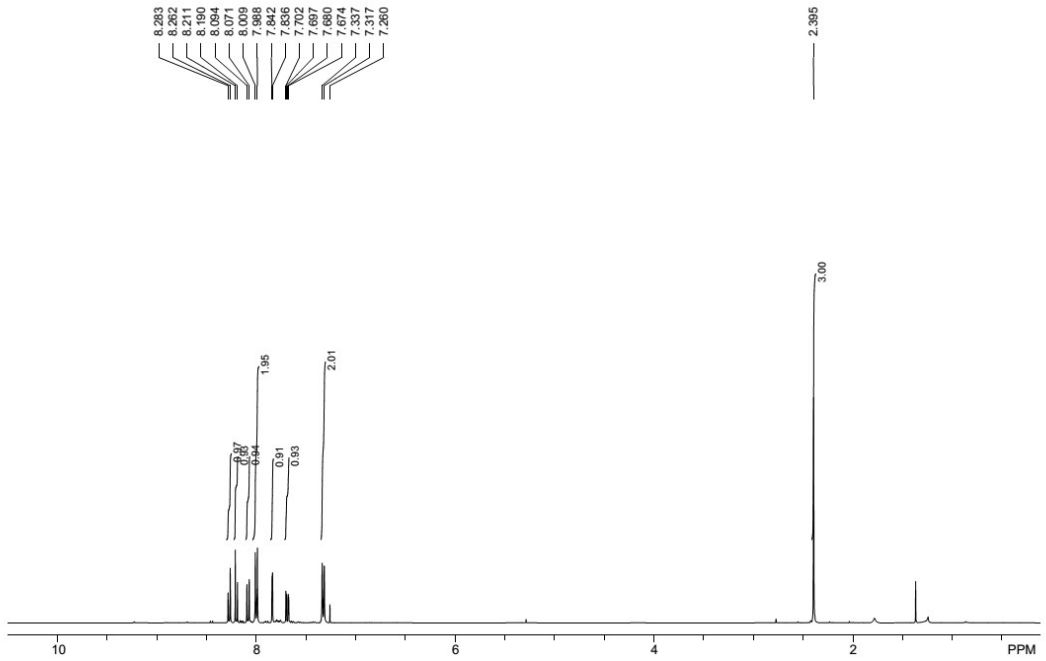


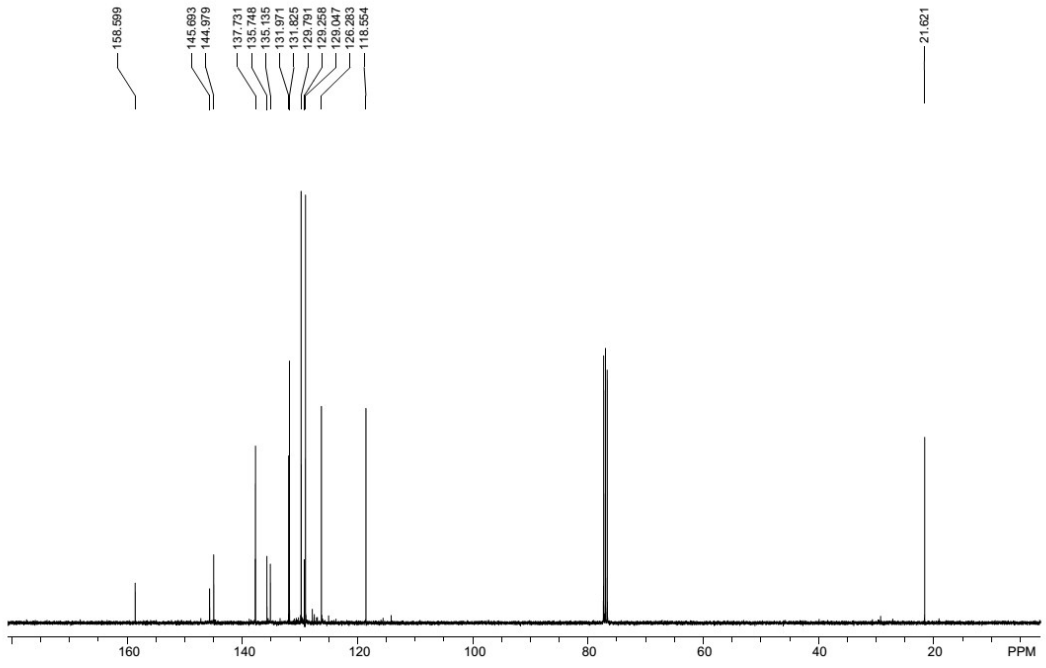
6-fluoro-2-tosylquinoline (3ka)



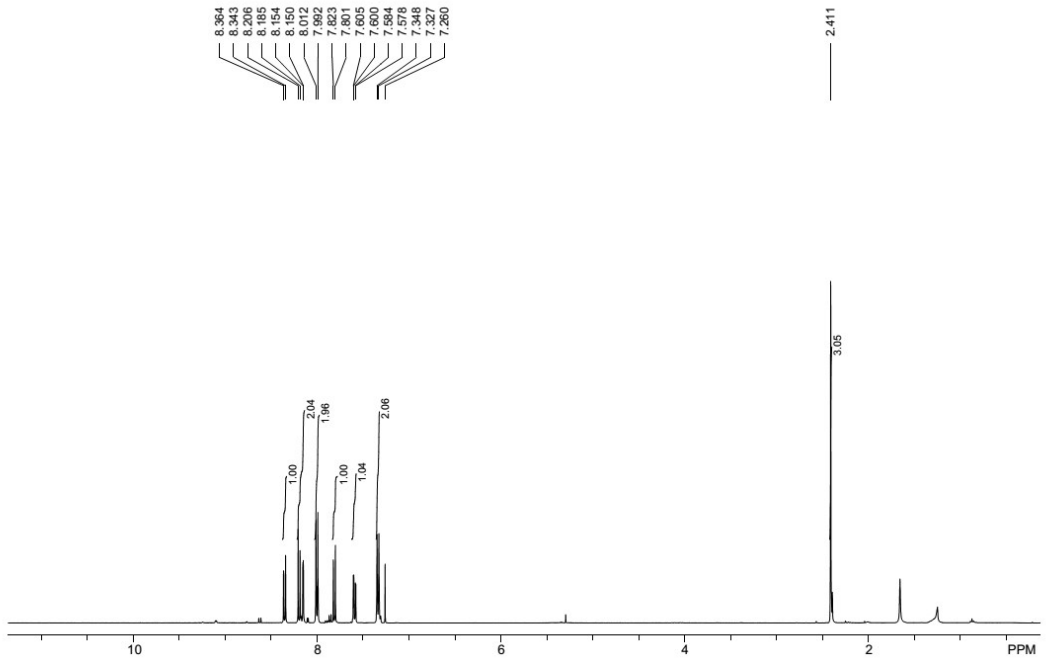


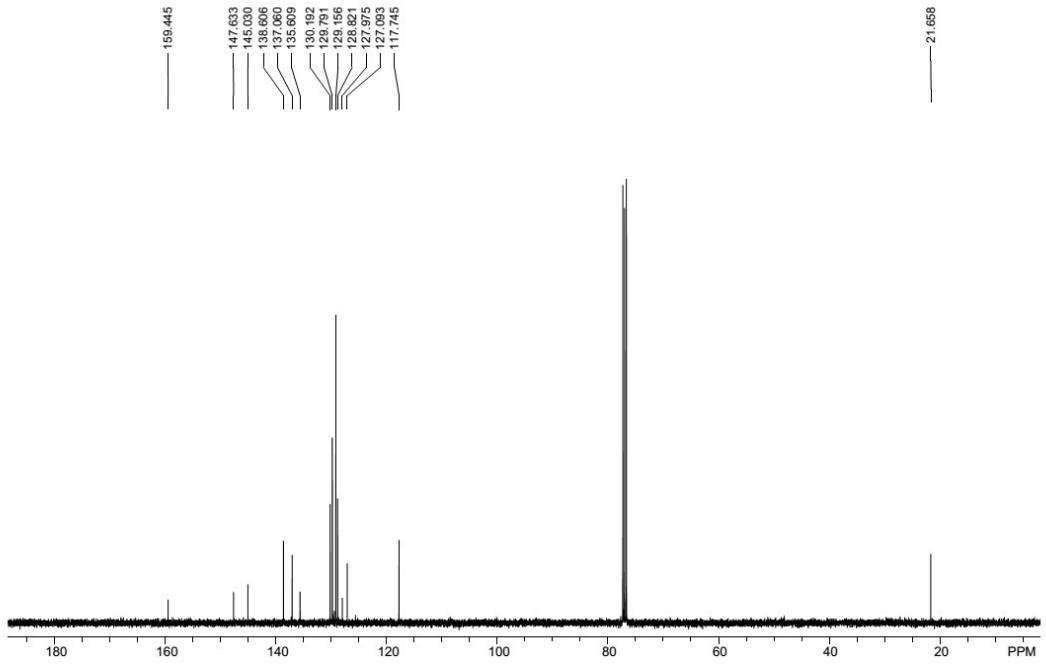
6-chloro-2-tosylquinoline (3la)



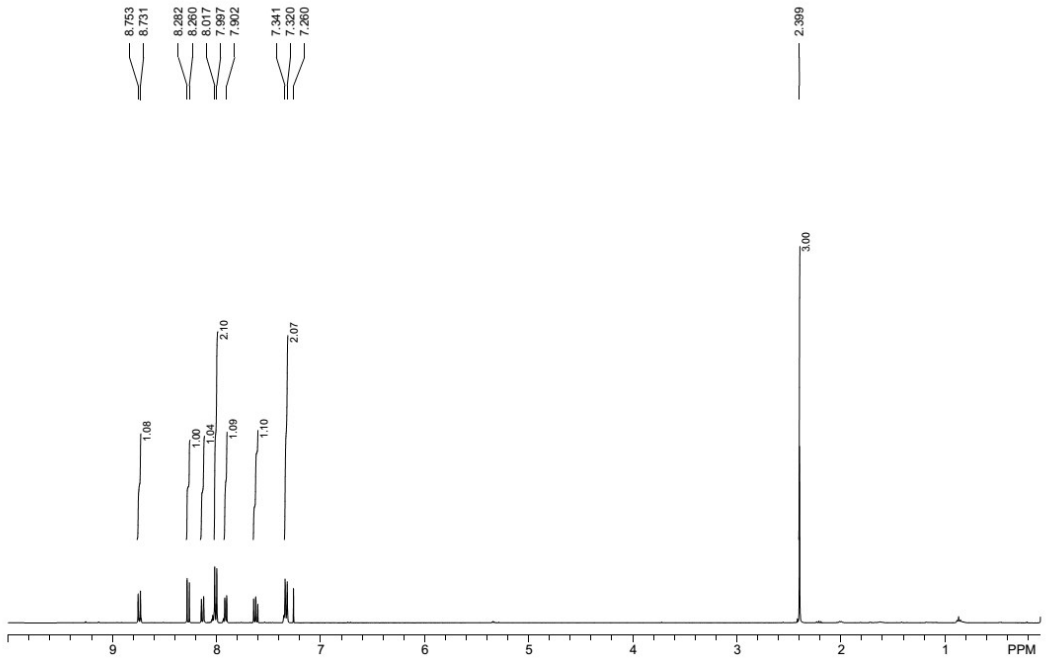


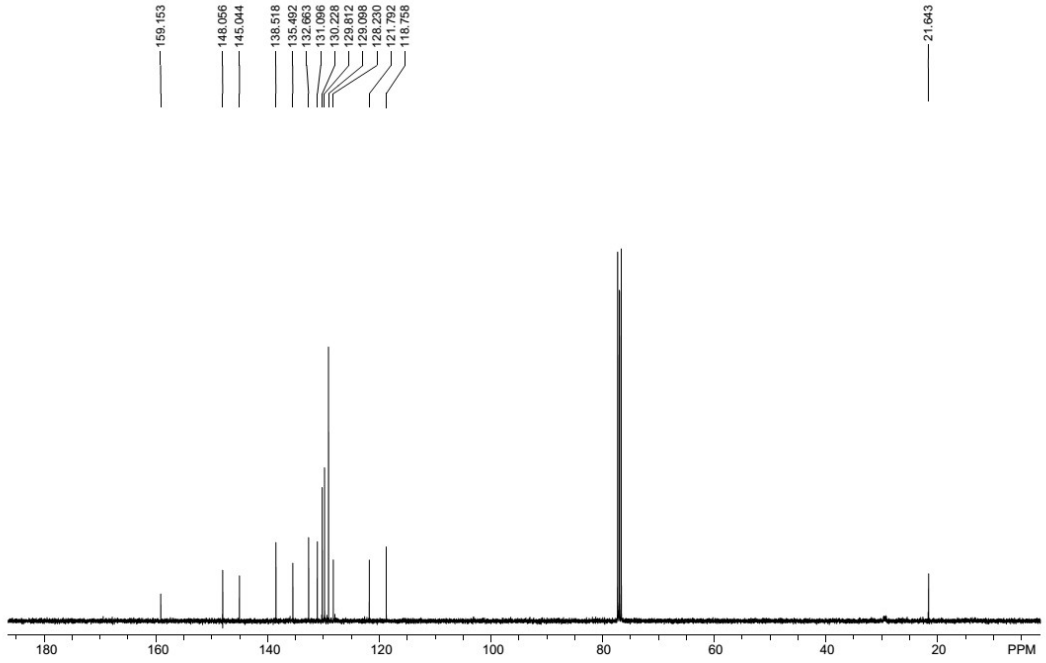
7-chloro-2-tosylquinoline (3ma)



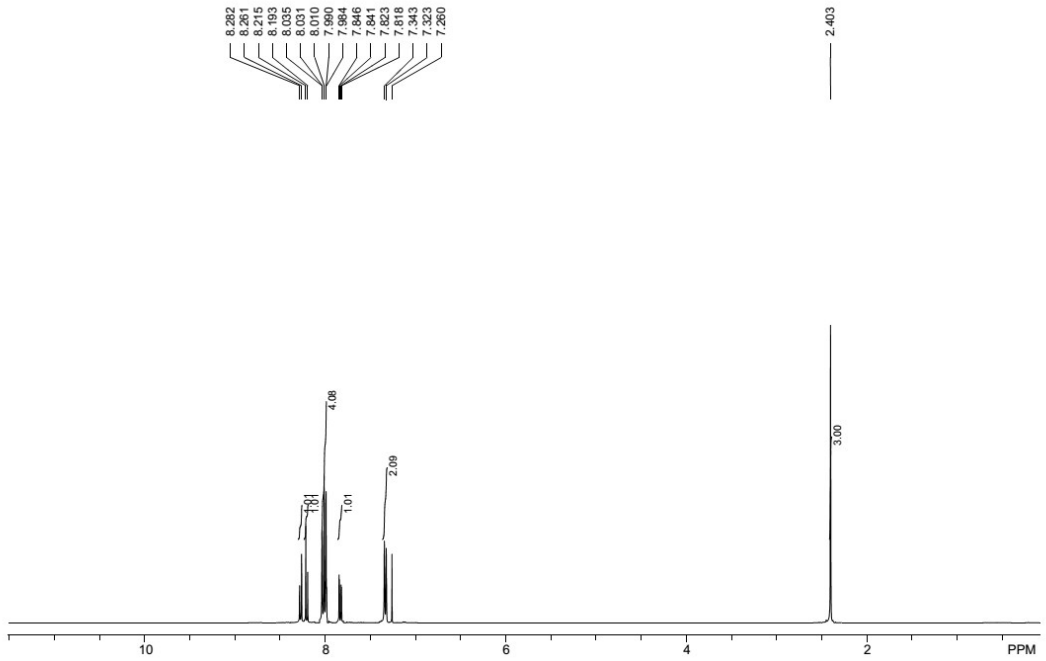


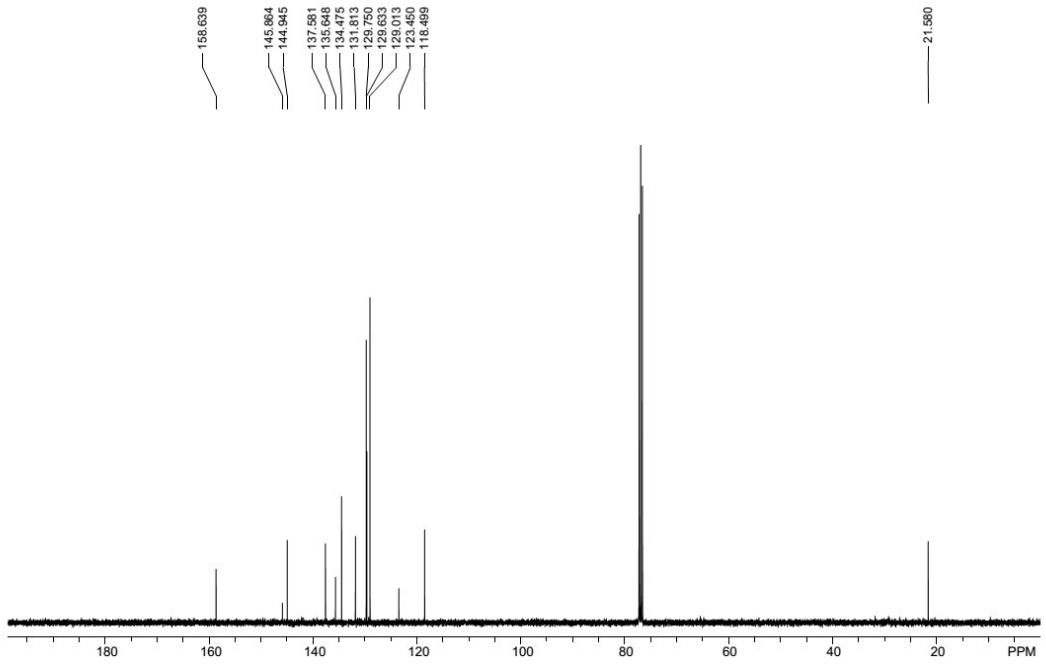
5-bromo-2-tosylquinoline (3na)



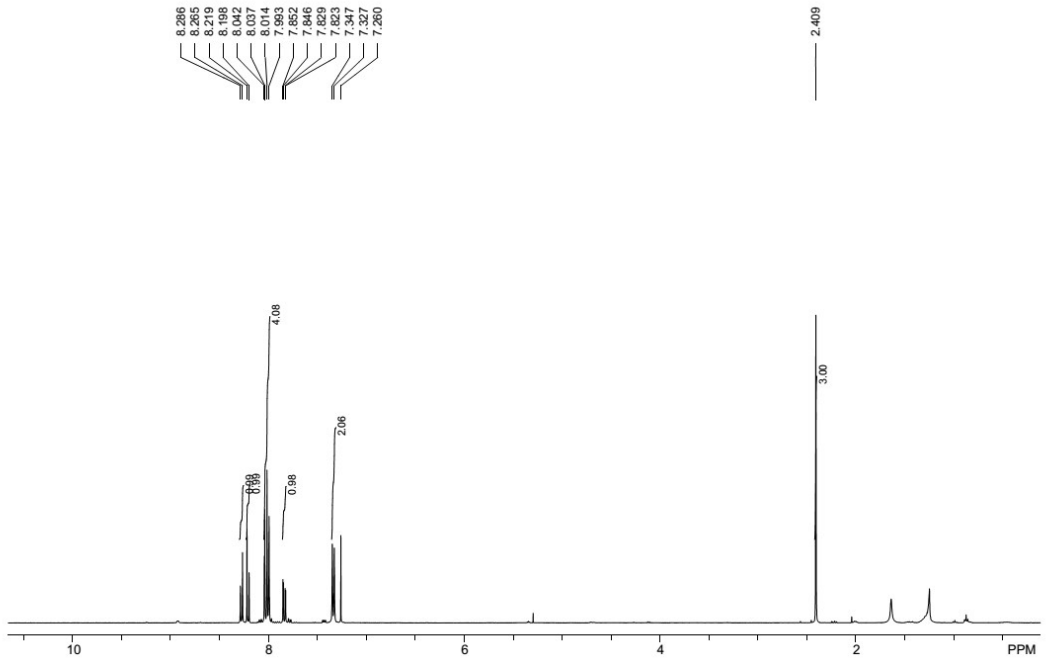


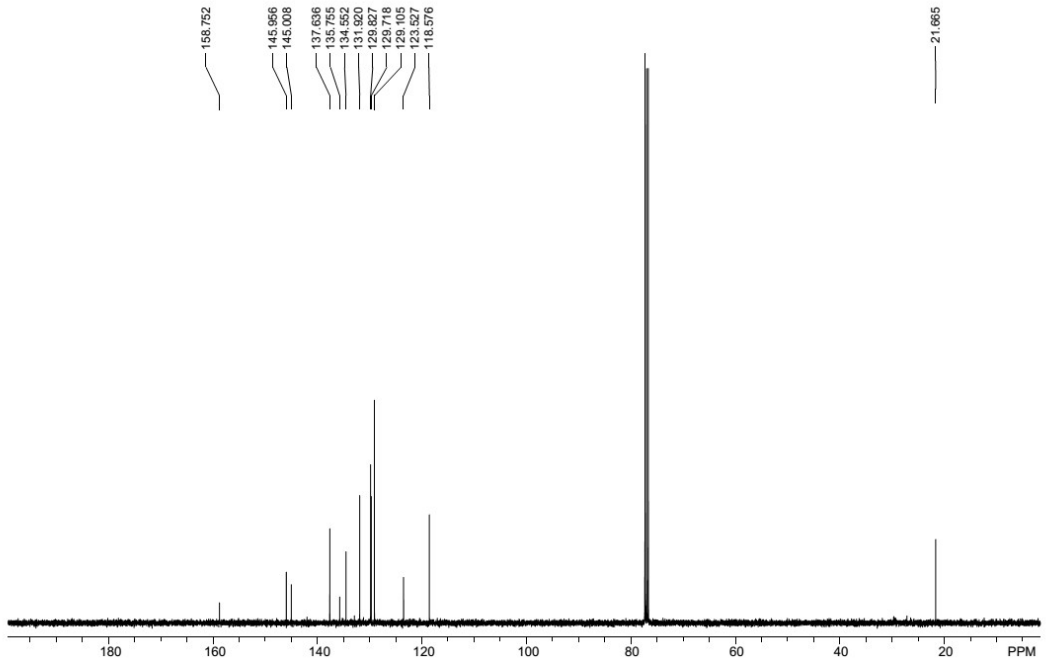
6-bromo-2-tosylquinoline (3oa)



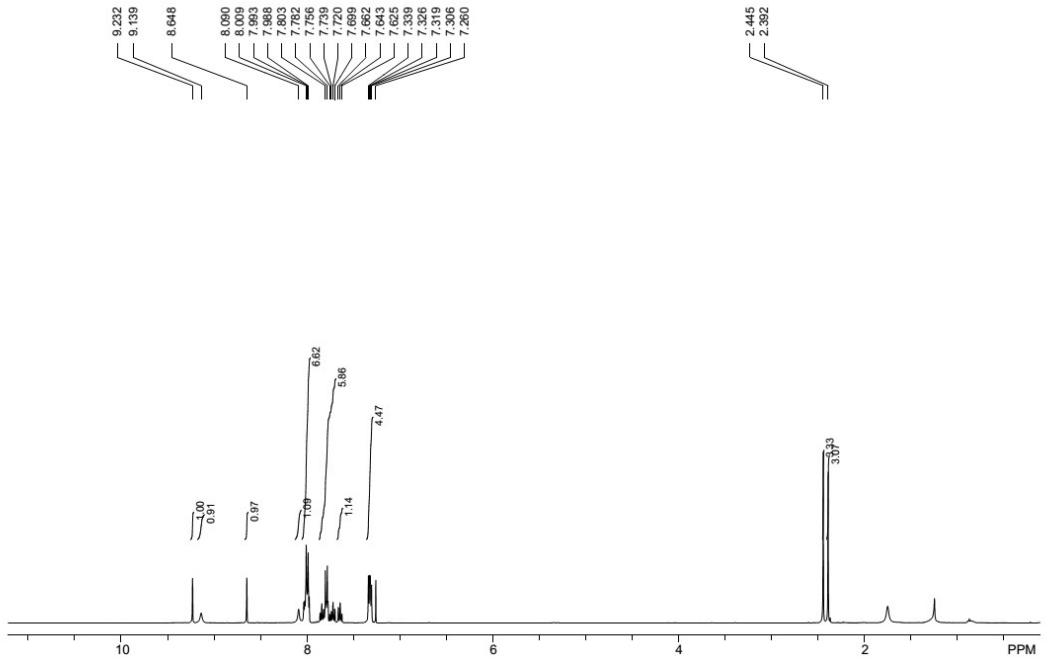


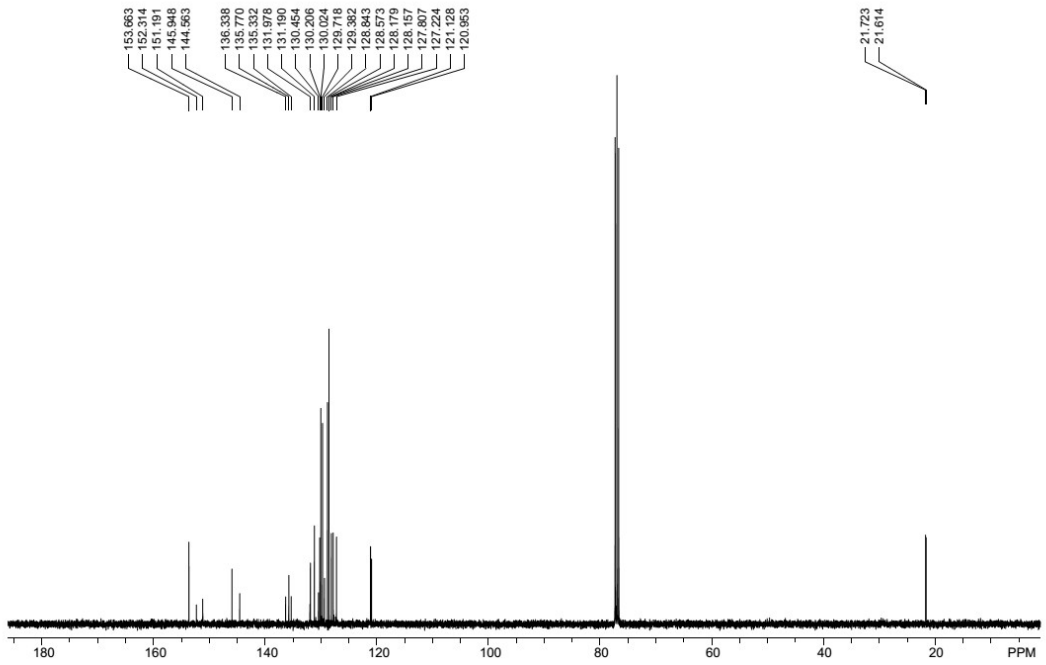
8-bromo-2-tosylquinoline (3pa)



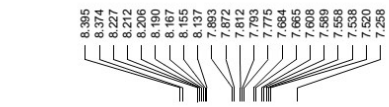


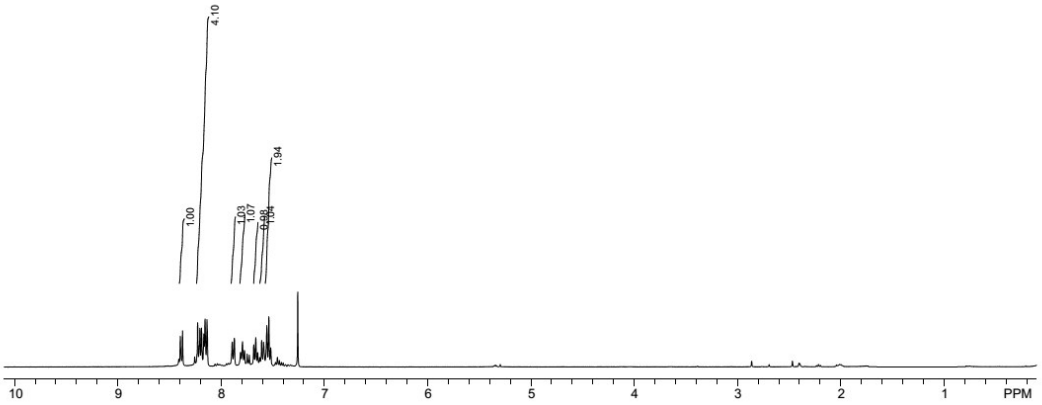
Mixture of 1-tosylisoquinoline and 3-tosylisoquinoline (3qa)

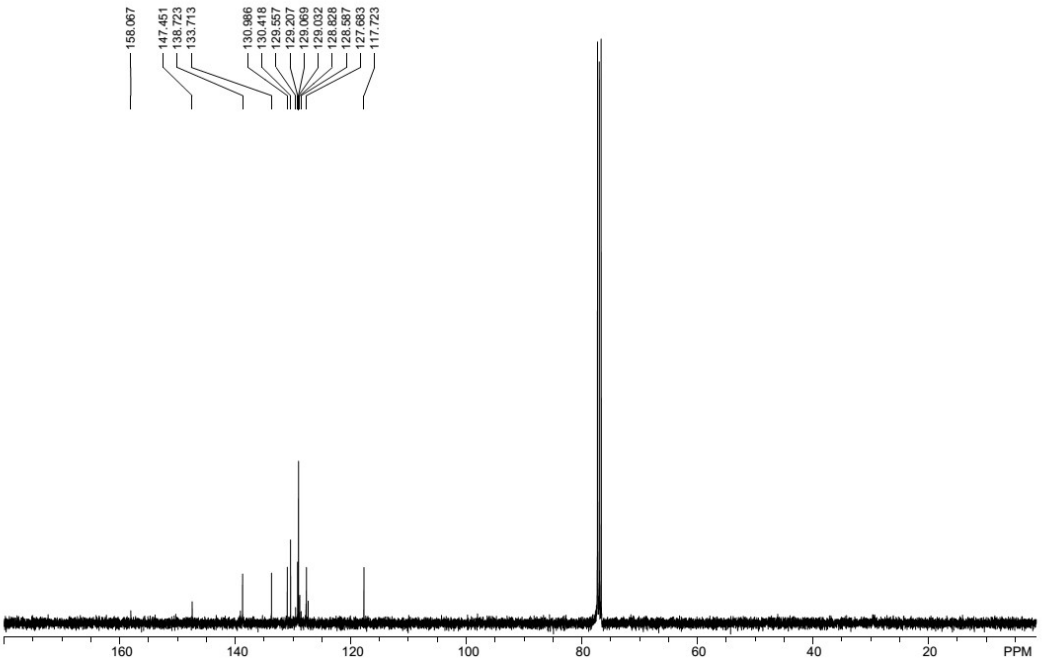




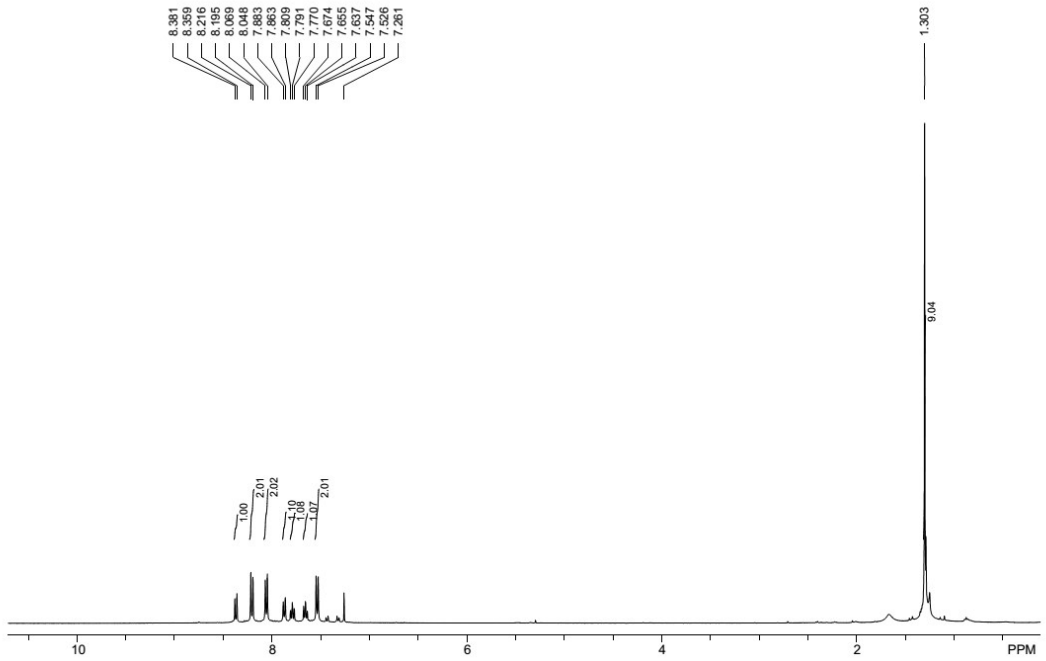
2-(phenylsulfonyl)quinoline (3ab)

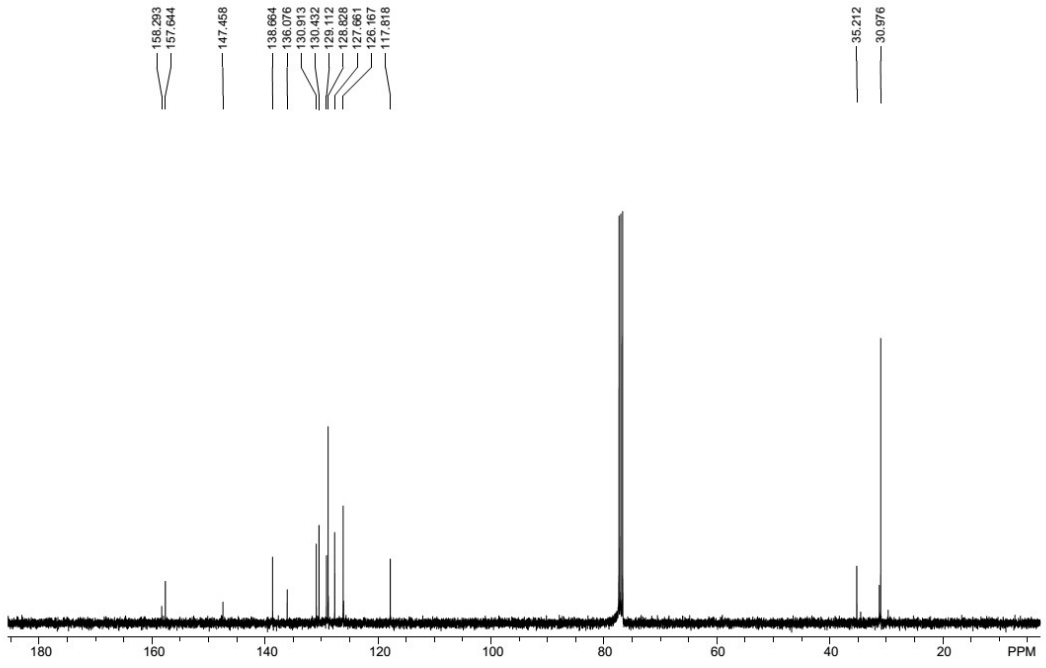




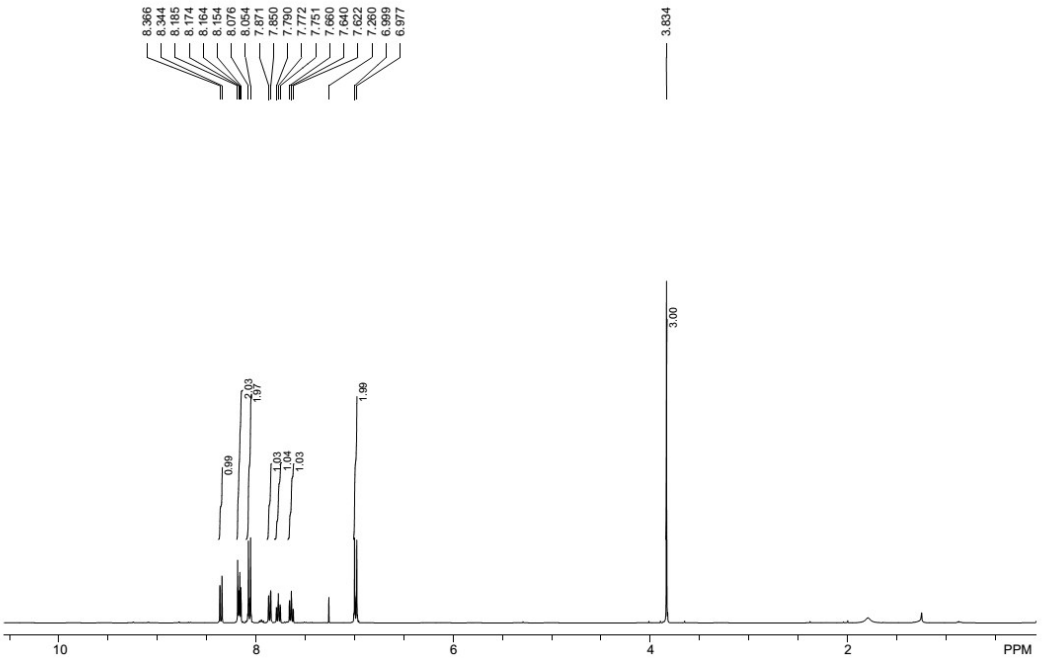


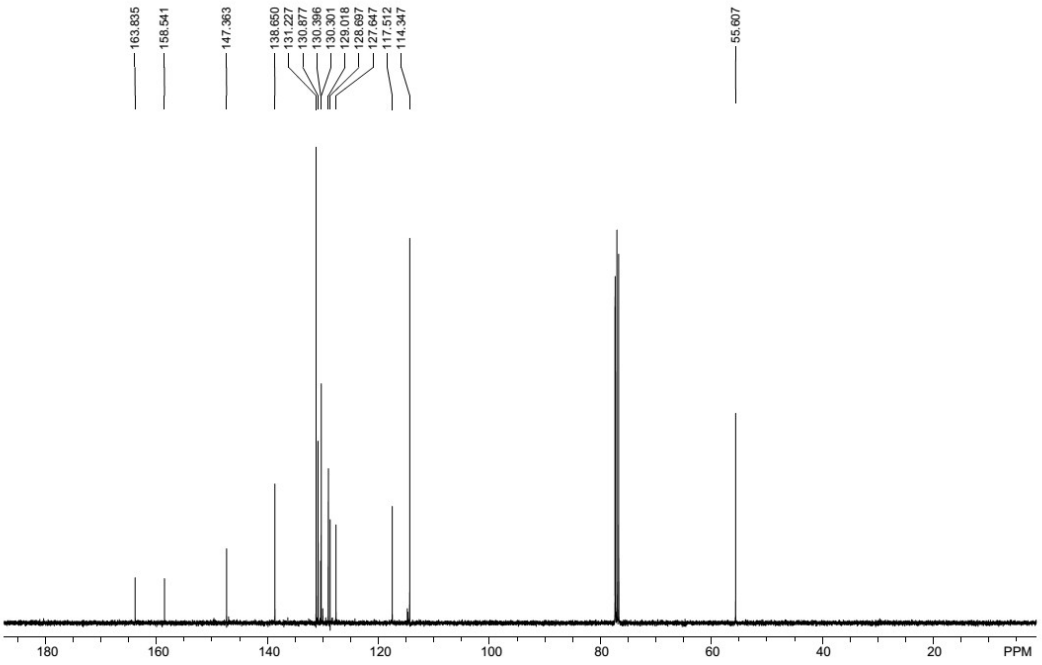
2-((4-(tert-butyl)phenyl)sulfonyl)quinoline (3ac)



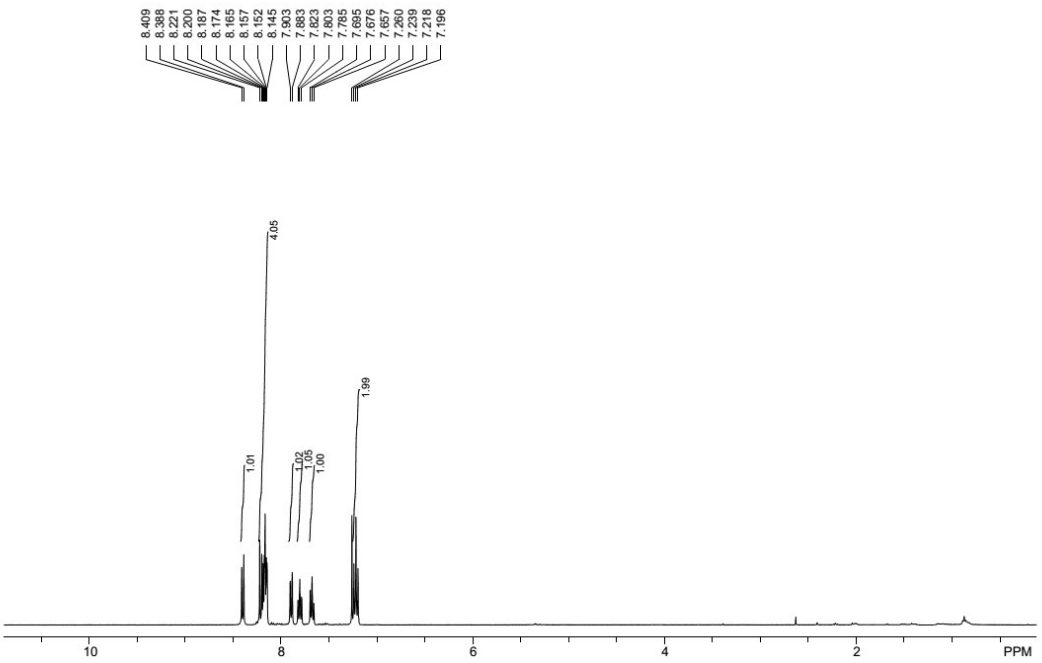


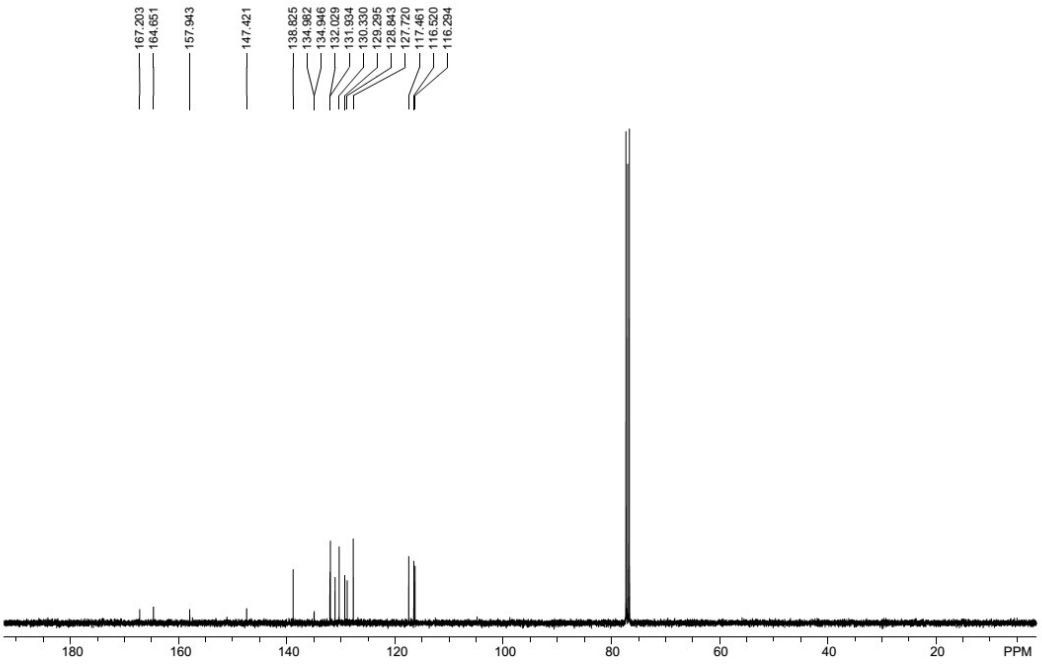
2-((4-methoxyphenyl)sulfonyl)quinoline (3ad)



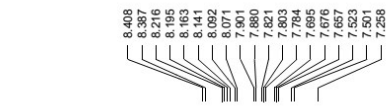


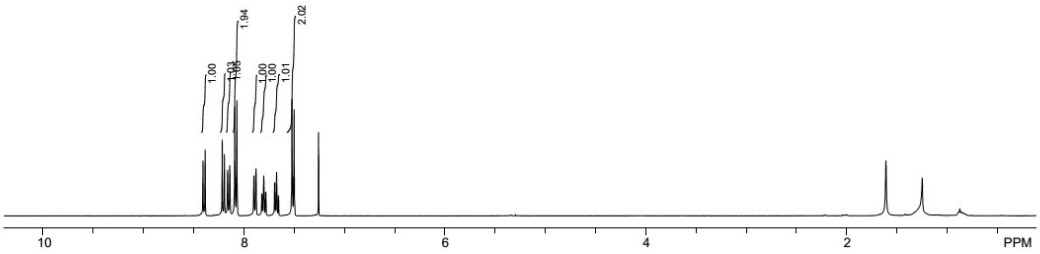
2-((4-fluorophenyl)sulfonyl)quinoline (3ae)

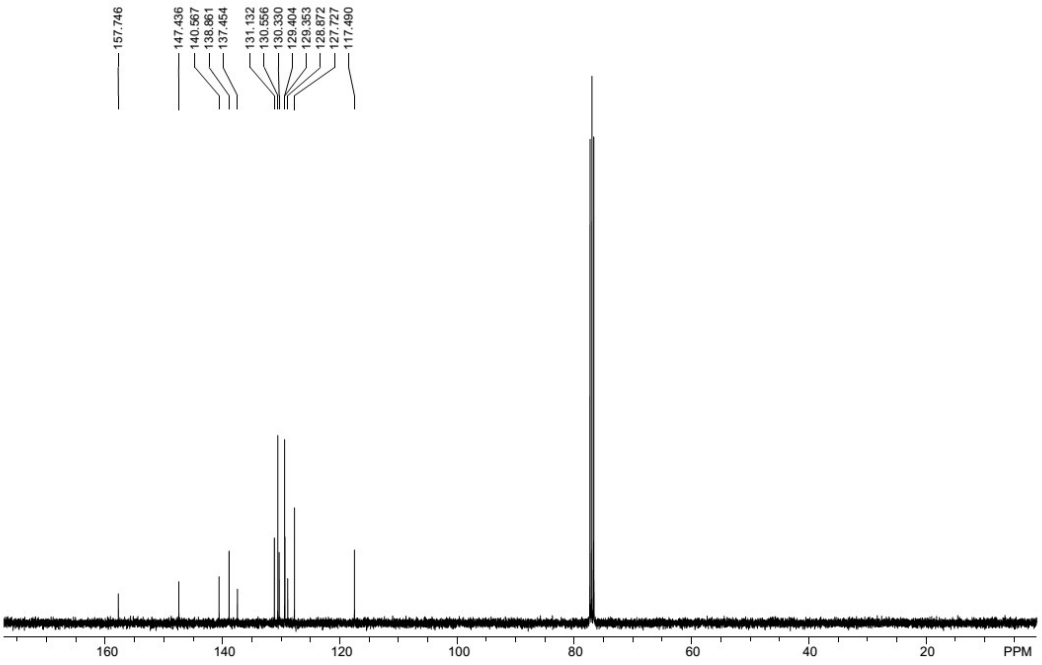




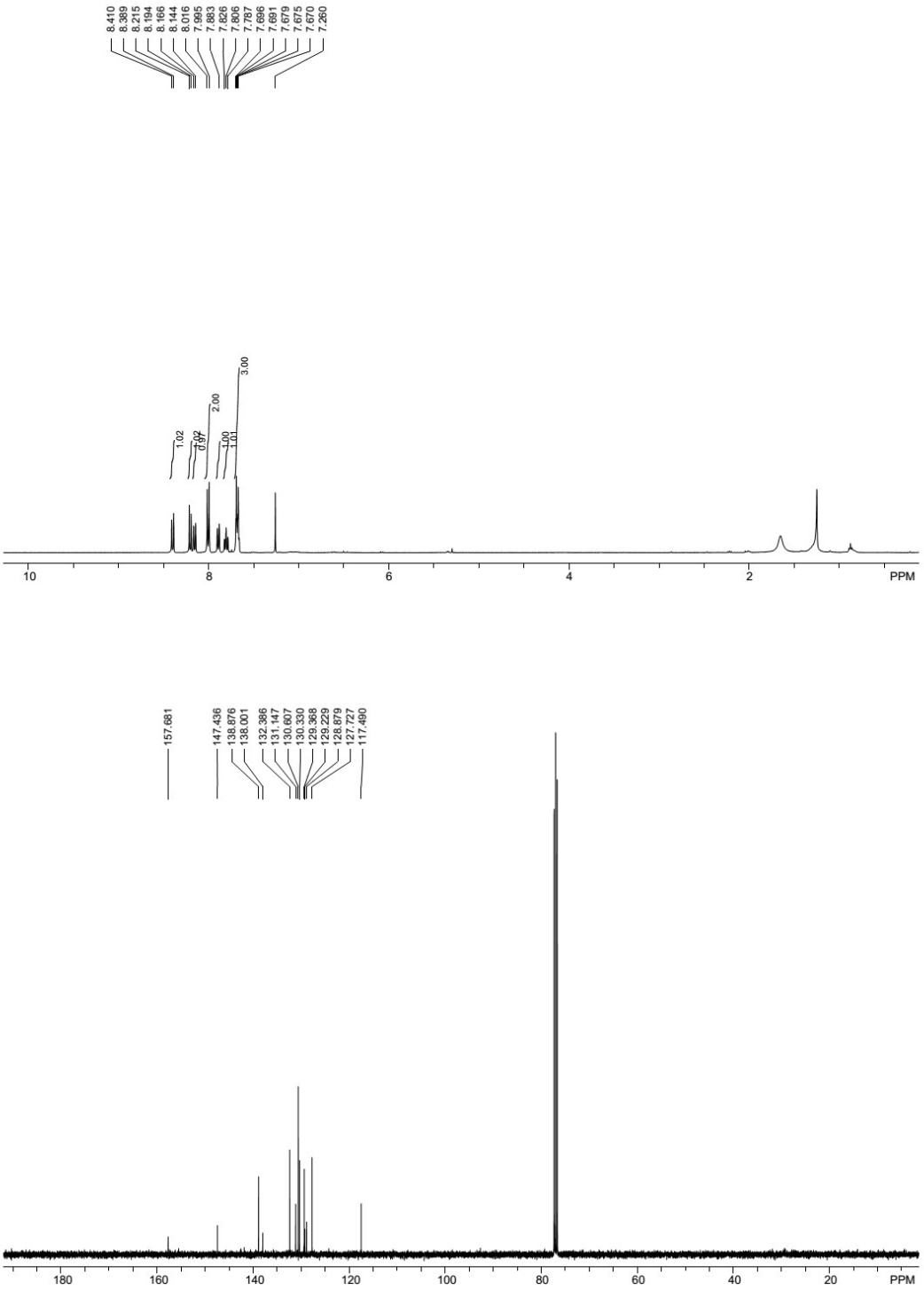
2-((4-chlorophenyl)sulfonyl)quinoline (3af)



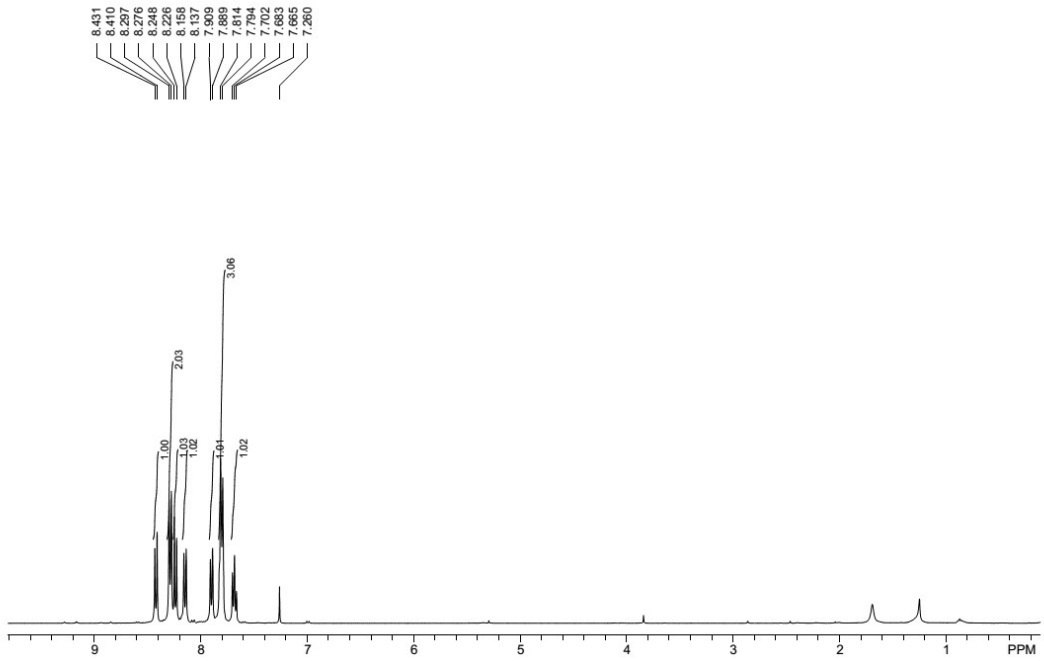


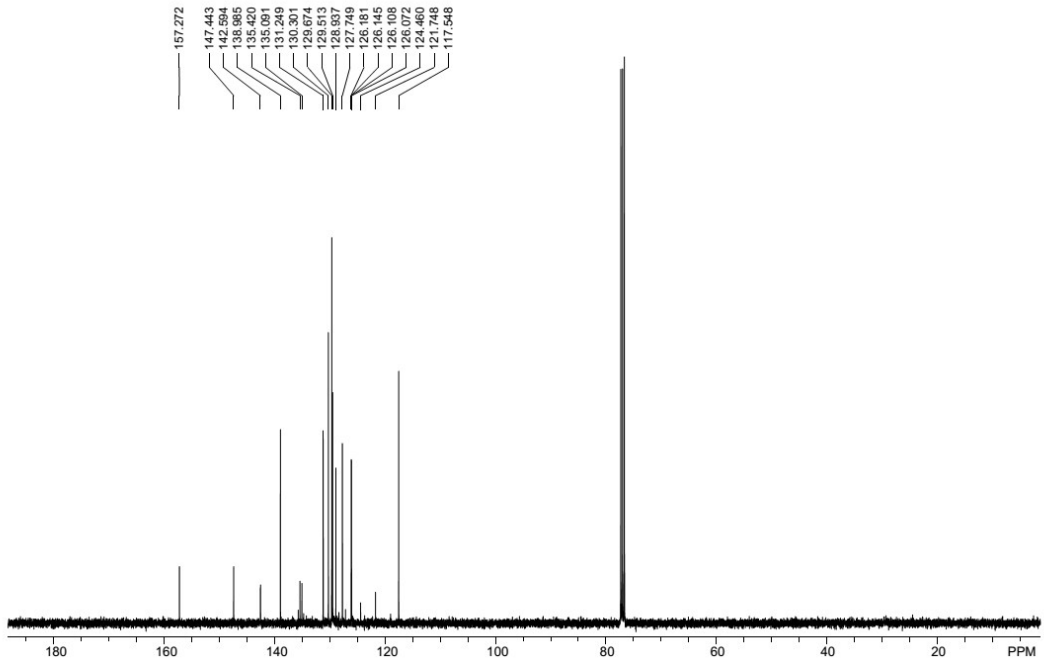


2-((4-bromophenyl)sulfonyl)quinoline (3ag)

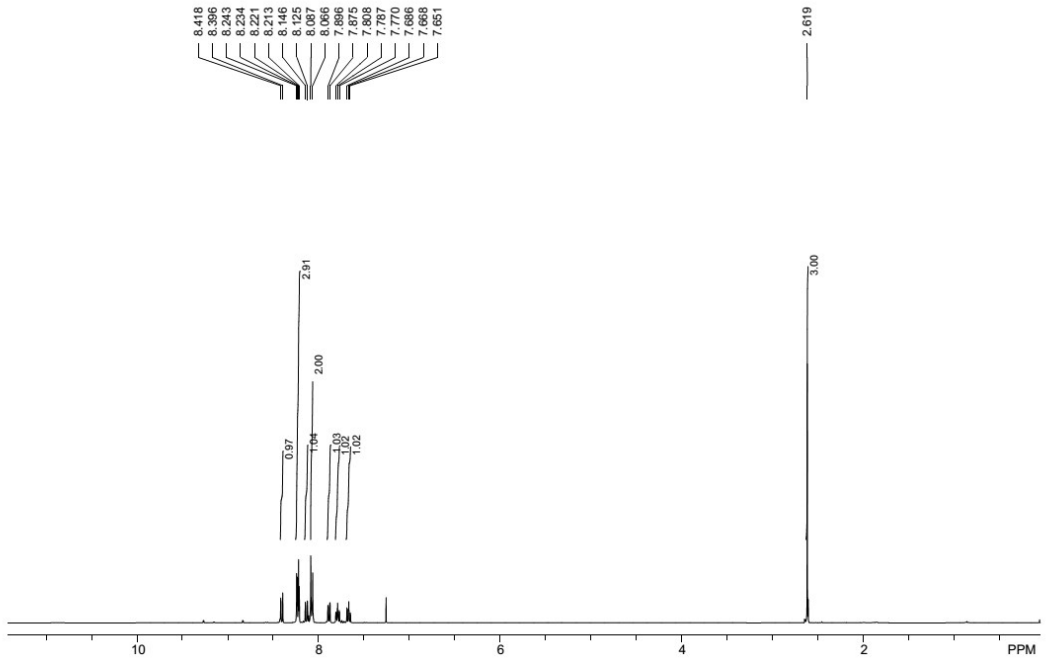


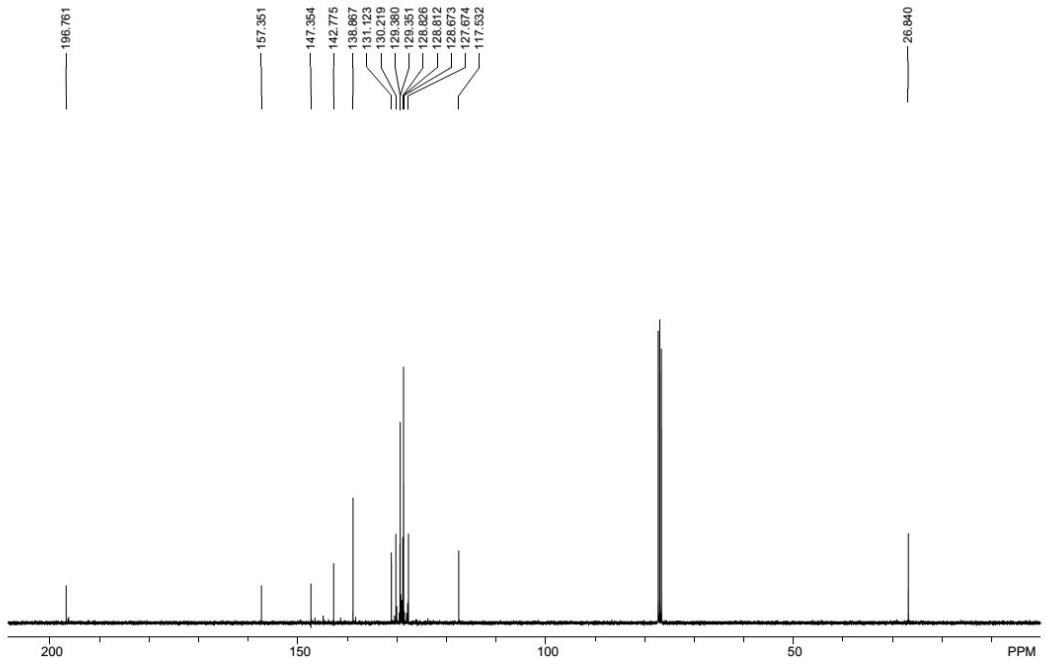
2-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (3ah)



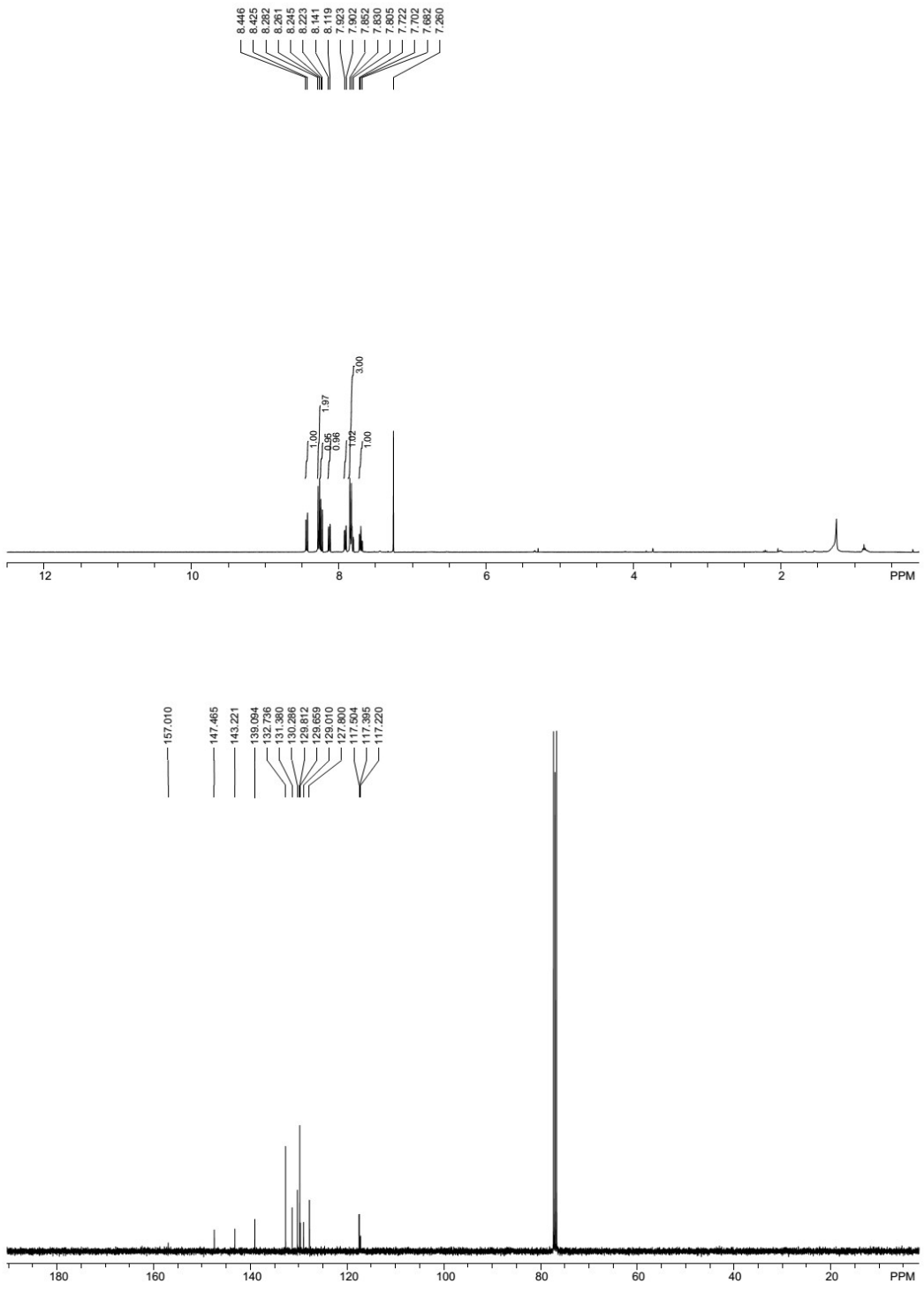


1-(4-(quinolin-2-ylsulfonyl)phenyl)ethanone (3ai)

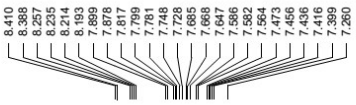


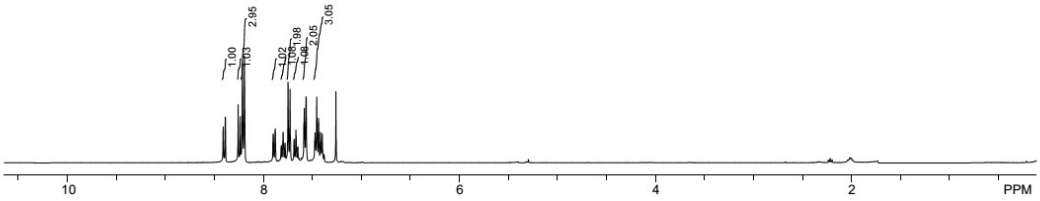


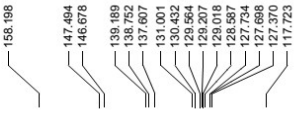
4-(quinolin-2-ylsulfonyl)benzonitrile (3aj)

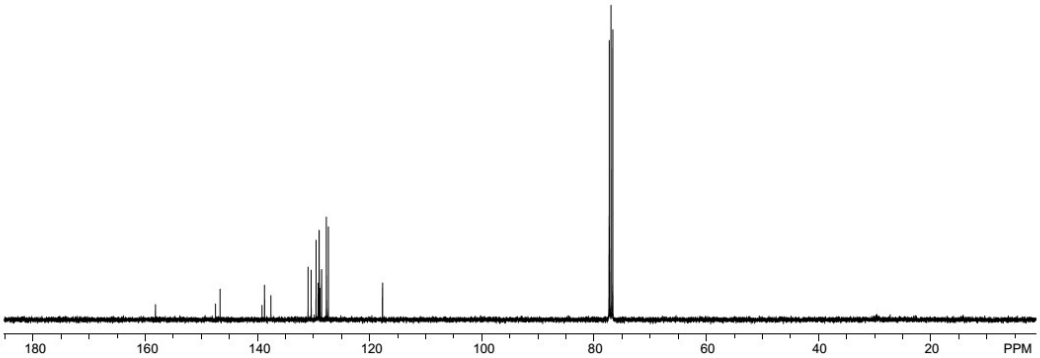


2-([1,1'-biphenyl]-4-ylsulfonyl)quinolone (3ak)

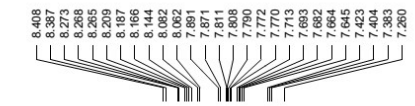


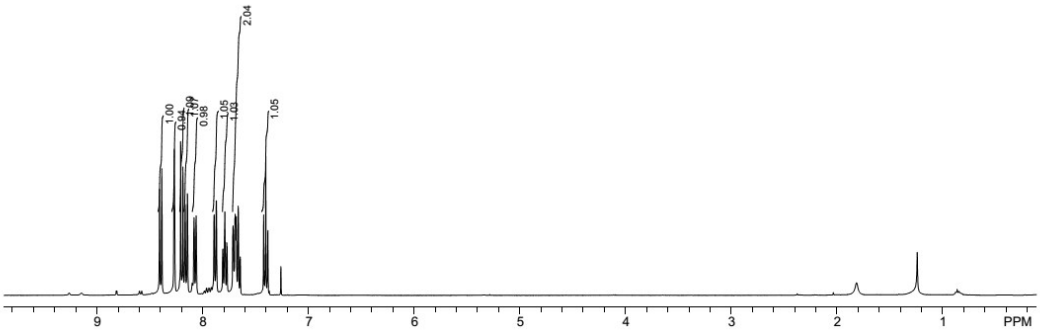


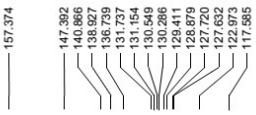


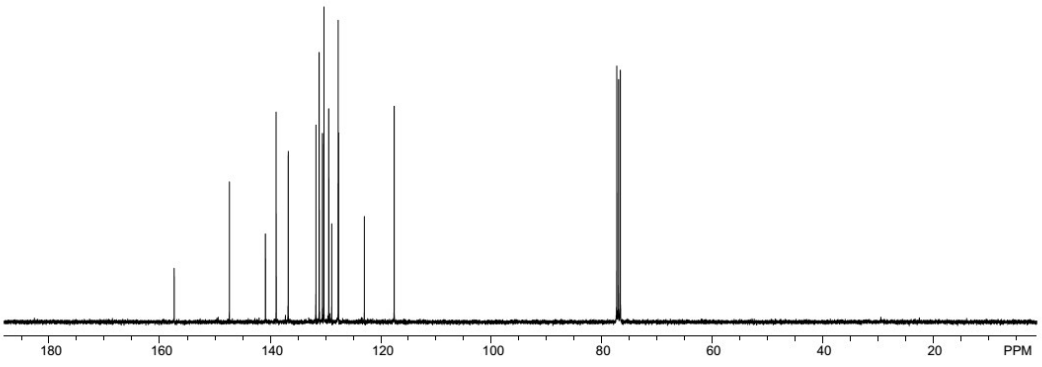


2-((3-bromophenyl)sulfonyl)quinoline (3al)

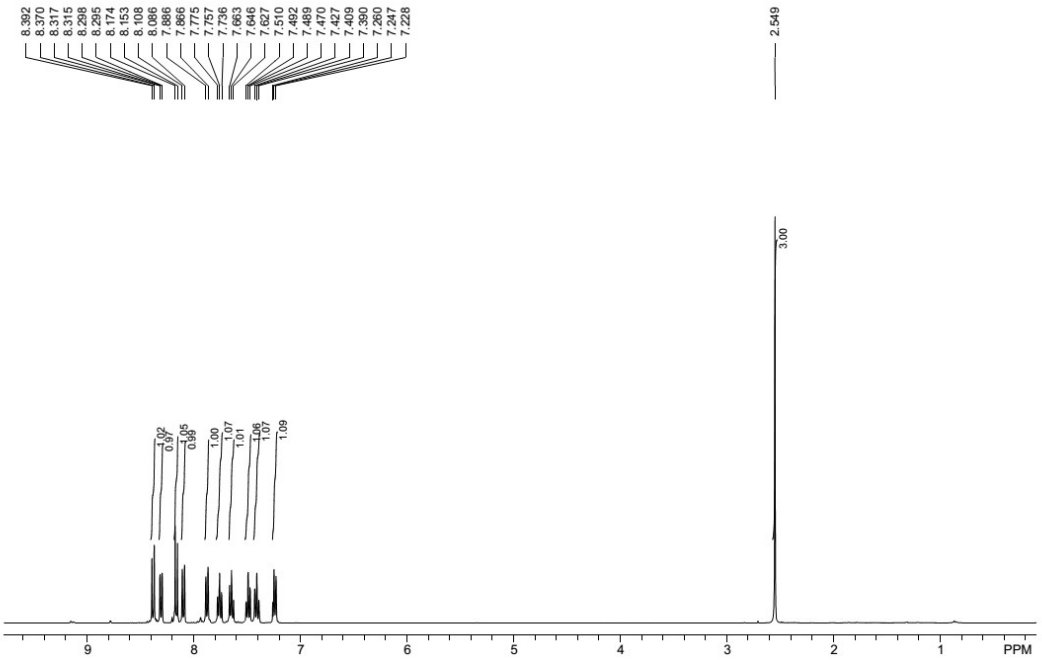


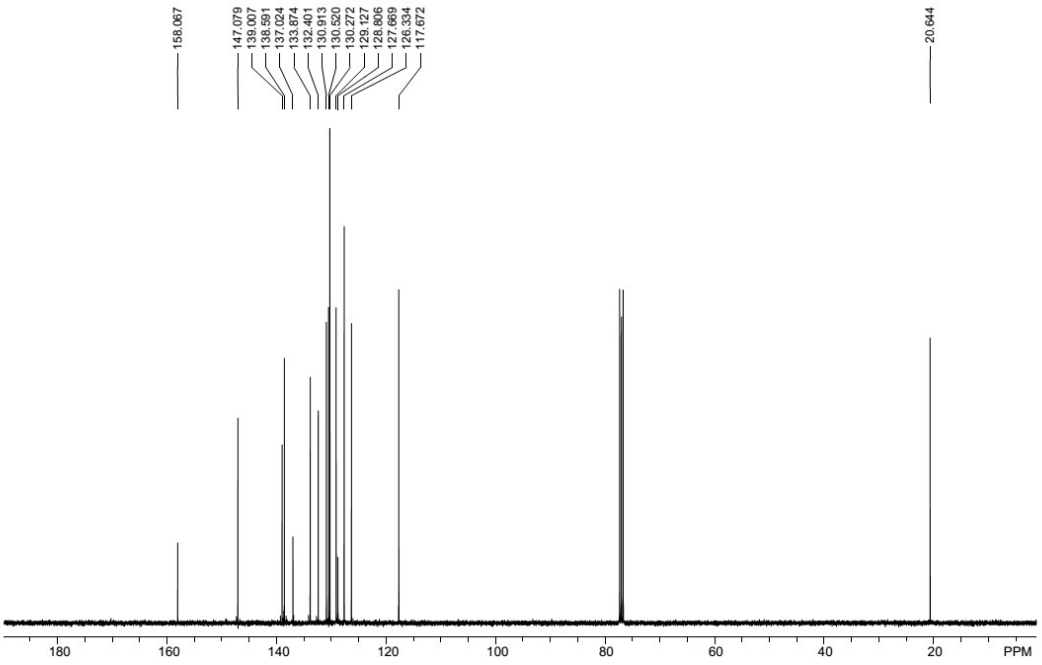




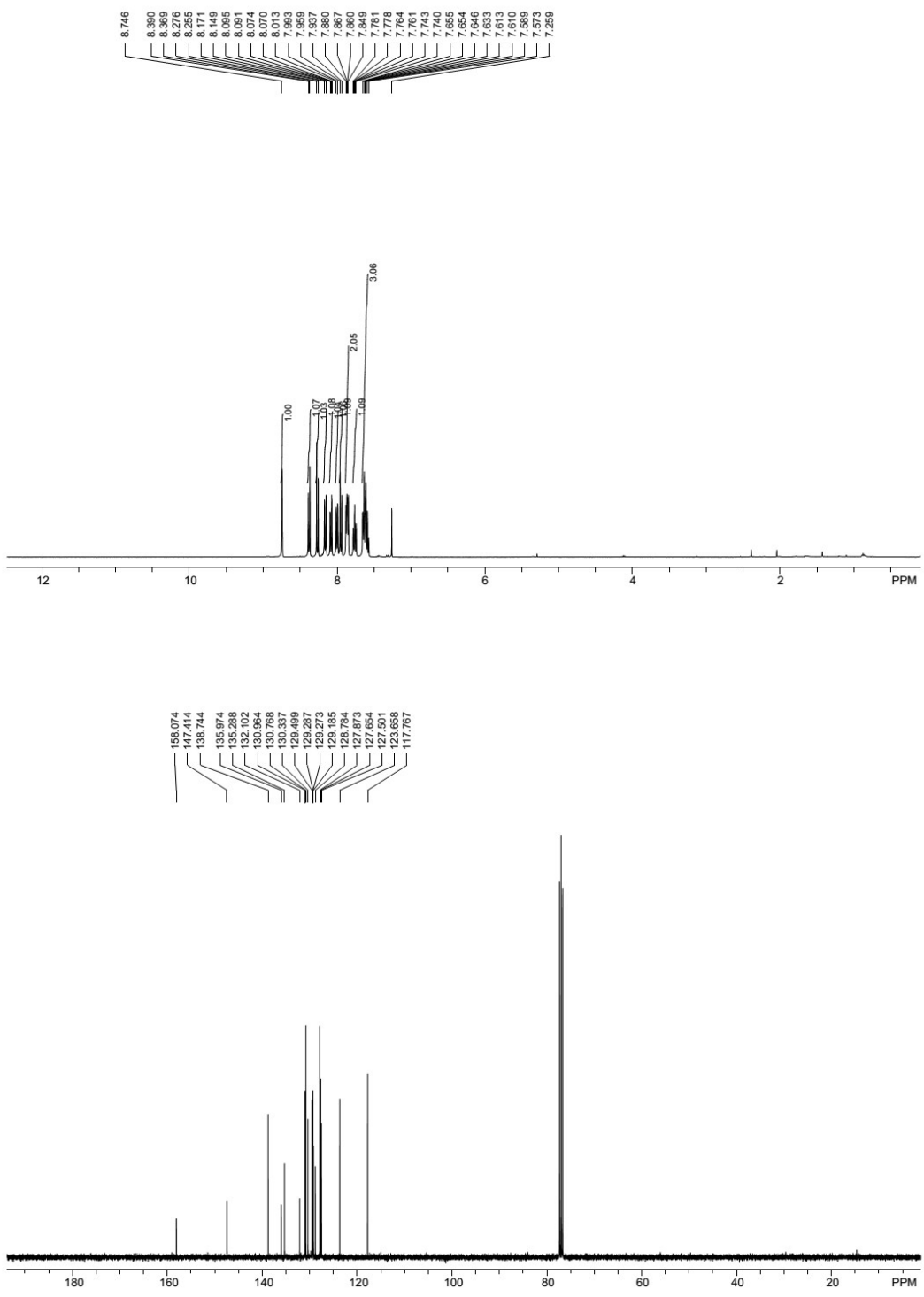


2-(o-tolylsulfonyl)quinoline (3am)

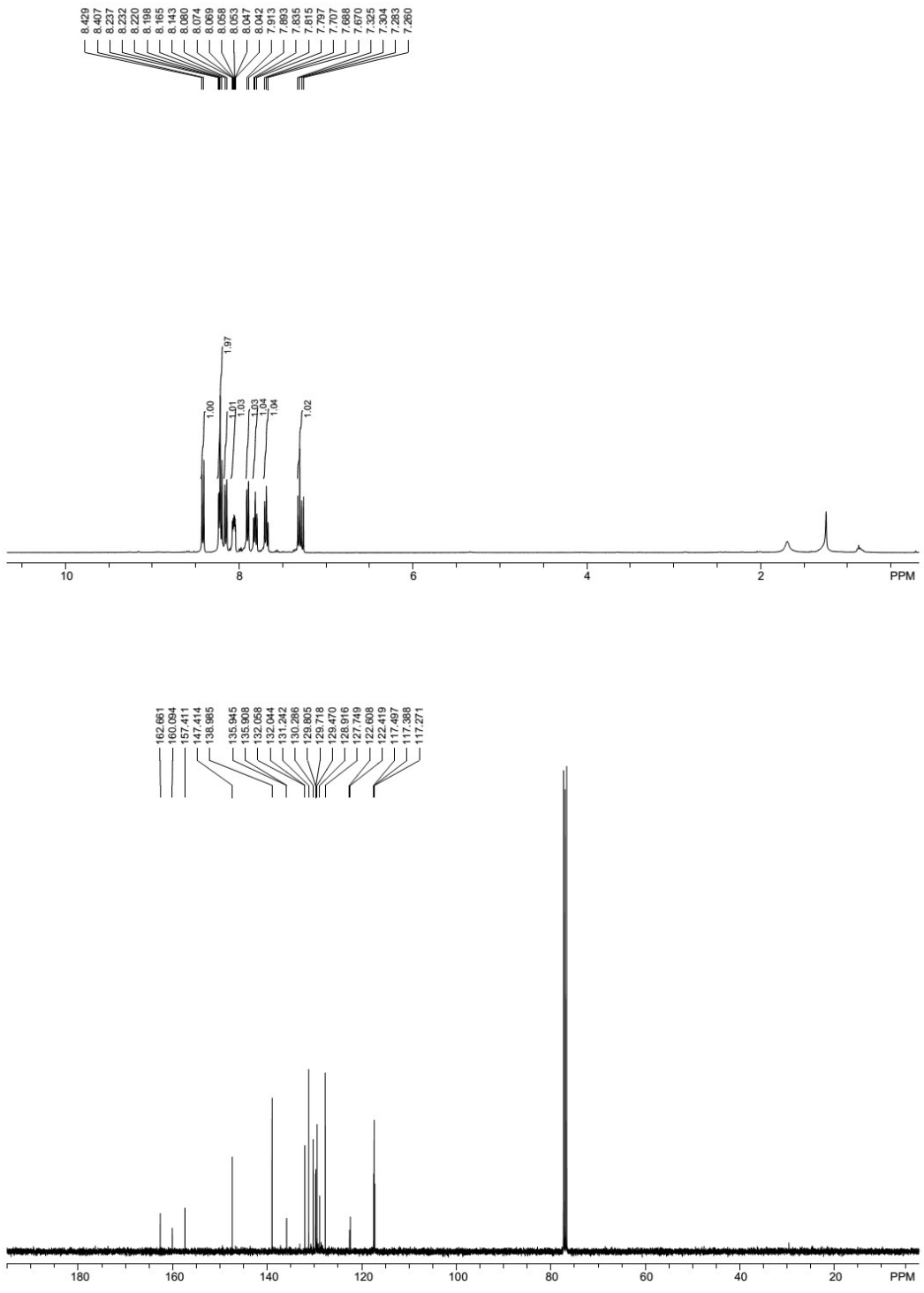




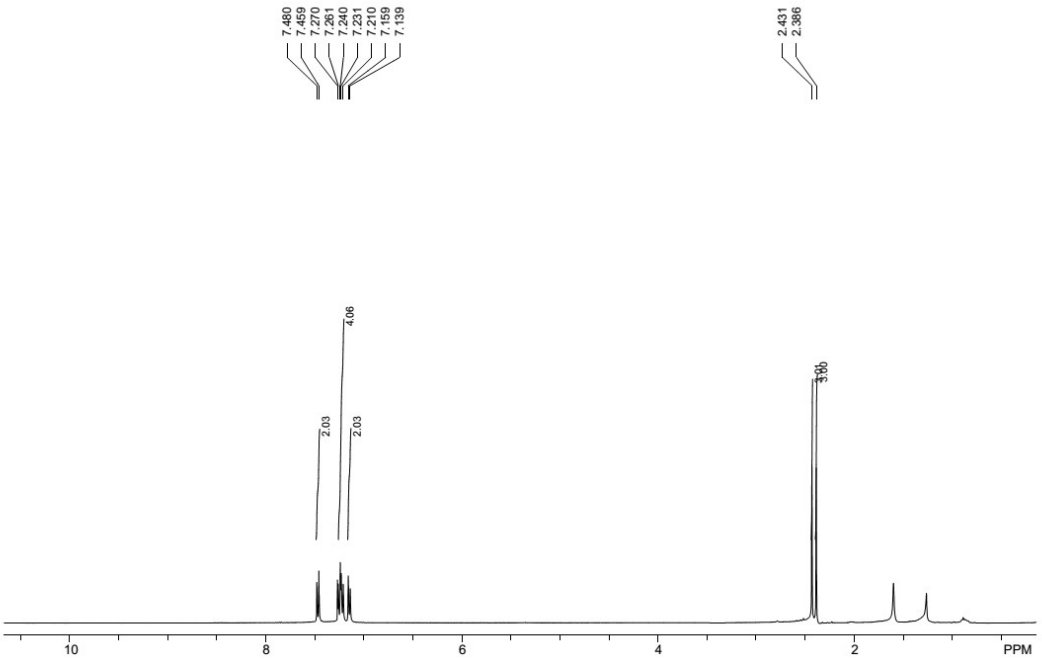
2-(naphthalen-2-ylsulfonyl)quinoline (3an)



2-((3-chloro-4-fluorophenyl)sulfonyl)quinoline (3ao)



S-p-tolyl 4-methylbenzenesulfonothioate (5a)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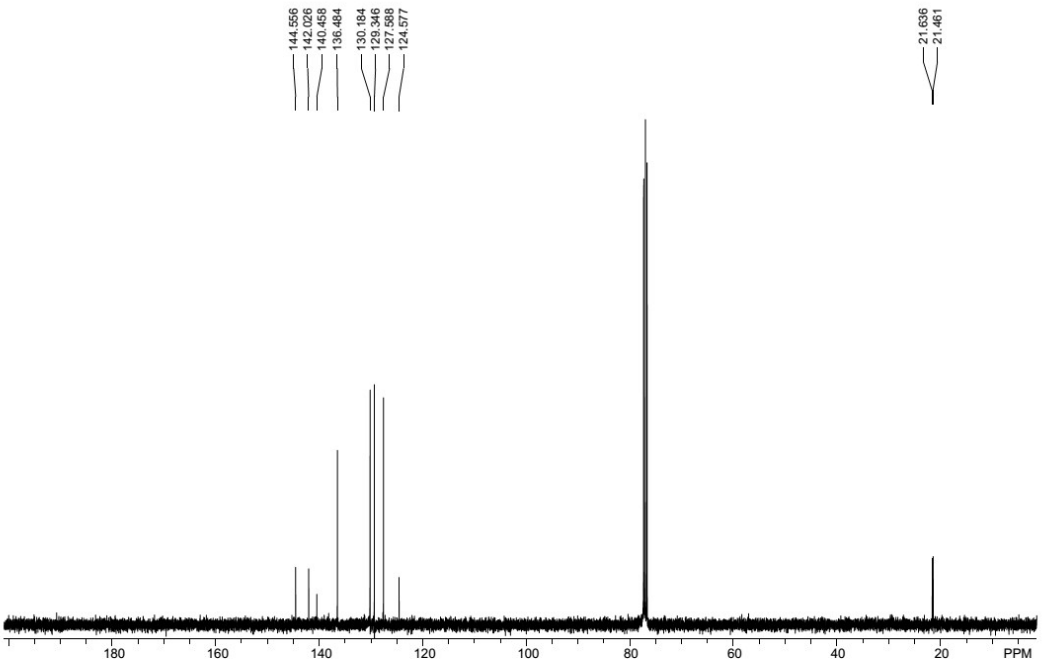
7.270
7.261
7.240
7.231
7.210
7.159
7.139
2.431
2.386
4.06
2.03
2.03
3.00
3.00
10
8
6
4
2
PPM


144.556
142.026
140.458
136.484
130.184
129.346
127.588
124.577
21.636
21.461
180
160
140
120
100
80
60
40
20
PPM