Electronic Supplementary Material (ESI) for Green Chemistry.

Base-free, ultrasound accelerated one-pot synthesis of 2-sulfonylquinolines on water

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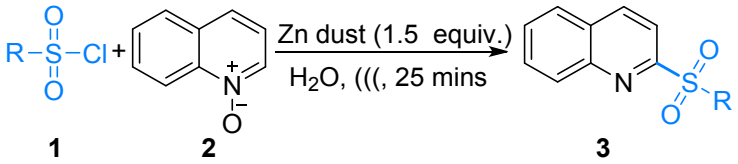
1. General information

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, $CDCl_3$ 77.0 ppm). HRMS data were obtained on a Bruker micrOTOF Focus II (ESI Mode). Sonication was performed by K1000E-type sonicator (with a frequency of 40 kHz and ultrasonic peak max. 40 W).

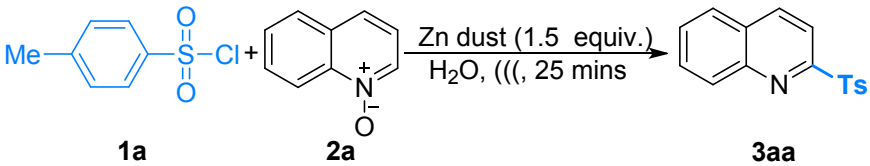
2. Experimental Section

(a) Typical procedure for the synthesis of 2-sulfonylquinolines



In a vail were placed sulfonyl chloride (0.3 mmol), H_2O (3 mL) and Zn dust (19.5 mg, 0.3mmol), then the contents were shaken at room temperature under ultrasound conditions for 20 mins. Next, quinoline *N*-oxide (0.2 mmol) was added to the aqueous solution, The progress of the reaction was monitored by TLC. The total reaction time typically took 25 - 30 mins. Upon completion, H_2O (10ml) was added to the mixture and it was extracted with CH_2Cl_2 (10 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 to obtain the pure 2-sulfonylquinolines.

(b) Large scale experiments of preparation of 3aa

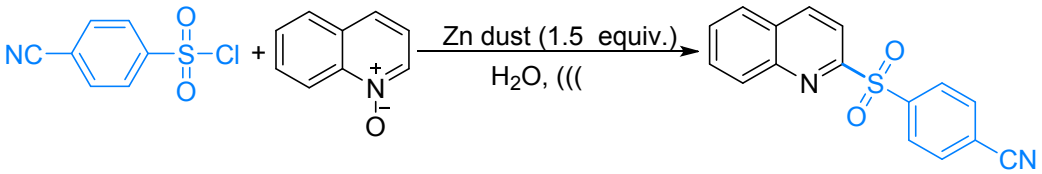


Method A (purify via column chromatography): In a vail were placed TsCl (2.85g, 15mmol), H_2O (50 mL) and Zn dust (0.98g, 15mmol), then the contents were stirred at room temperature under ultrasound conditons for 20 mins. Next, quinoline *N*-oxide (1.45 g, 10 mmol) was added to the aqueous solution,

The progress of the reaction was monitored by TLC. Upon completion, it was extracted with CH_2Cl_2 (30mL 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 to give 2.37g of 2-sulfonylquinoline in 84% yield.

Method B (purify via recrystallization): In a vail were placed TsCl (2.85g, 15mmol), H_2O (50 mL) and Zn dust (0.98g, 15mmol), then the contents were stirred at room temperature under ultrasound conditons for 20 mins. Next, quinoline *N*-oxide (1.45 g, 10 mmol) was added to the aqueous solution, The progress of the reaction was monitored by TLC. Upon completion, it was extracted with EtOAc (15mL x 3) and the organic extracts were concentrated under reduced pressure (small amount of water from organic extracts was removed via azeotropic disstillation with EtOAc). The crude product was purified via recrystallization with 90% ethanol aqueous solution (6 ml) to give 2.09 g of 3ga in 74% yield.

(c) Large scale experiment of preparation of 3ga



1g 9.05 g, 45mmol

2a 4.35 g, 30mmol

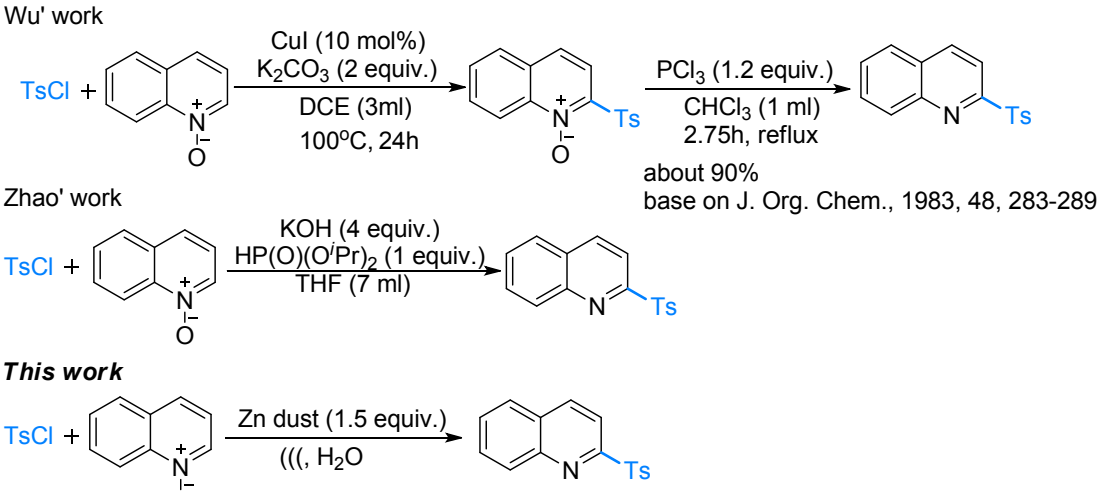
3ga

Method A (purify via column chromatography): In a vail were placed **1g** (9.05g, 45mmol), H_2O (150 mL) and Zn dust (2.93g, 45mmol), then the contents were stirred at room temperature under ultrasound conditons for 20mins. Next, quinoline *N*-oxide (4.35 g, 30 mmol) was added to the aqueous solution, The progress of the reaction was monitored by TLC. Upon completion, it was extracted with CH_2Cl_2 (40mL 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 to give 7.23 g of **3ga** in 82% yield.

Method B (purify via recrystallization): In a vail were placed **1g** (9.05g, 45mmol), H_2O (150 mL) and Zn dust (2.93g, 45mmol), then the contents were stirred at room temperature under ultrasound conditons for 20mins. Next, quinoline *N*-oxide (4.35 g, 30 mmol) was added to the aqueous solution, The progress of the reaction was monitored by TLC. Upon completion, it was extracted with EtOAc (50 mL x 3) and the organic extracts were concentrated under reduced pressure (small amount of water

from organic extracts was removed via azeotropic disstillation with EtOAc). The crude product was purified via recrystallization with 80% ethanol aqueous solution (20 ml) to give 6.61 g of 3ga in 75% yield.

(d) Calculation of green chemistry metrics



Entry	steps	Reagent 1	Reagent 2	Reagent 3	Reagent 4	Reagent 5	Solvent	Time	Yield	Product
Wu' work	1	TsCl 0.8 mmol MW190.6 152.4mg	Quinoline *N*-oxide 0.2 mmol MW 145.2 29mg	CuI 0.02 mmol MW 190.5 3.81mg	K_2CO_3 0.4 mmol MW138.2 55.3mg	PCl_3 0.22 mmol MW137.3 30mg	DCE 3ml 3705mg $CHCl_3$ 1ml 1500mg	>24h	81%	**3aa** 0.162 mmol MW283.3 45.8mg
Zhao' work	2	TsCl 0.4 mmol MW190.6 76.2 mg	Quinoline *N*-oxide 0.2 mmol MW 145.2 29mg	$HP(O)(OiPr)_2$ 0.2 mmol MW 166.2 33.2mg	KOH 0.8 mmol MW56.1 44.9mg		THF 7ml 6224mg	1h	85%	**3aa** 0.17 mmol MW283.3 48.1mg
This work										
Ultrasonic Radiation	1	TsCl 0.3 mmol MW190.6 57.2 mg	Quinoline *N*-oxide 0.2 mmol MW 145.2 29mg	Zn 0.3 mmol MW 65 19.5 mg	-	-	Water 3ml	25 min	86%	**3aa** 0.172 mmol MW283.3 48.7mg
Traditional Heating	1	TsCl 0.3 mmol MW190.6 57.2 mg	Quinoline *N*-oxide 0.2 mmol MW 145.2 29mg	Zn 0.3 mmol MW 65 19.5 mg	-	-	Water 3ml	8h	67%	**3aa** 0.134 mmol MW283.3 37.9mg

$$\text{Atom Economy} = \frac{\text{MW of desired product}}{\Sigma \text{ of MW of stoichiometric reactants}} \times 100\%$$

$$\frac{283.3}{190.6+145.2+190.5+138.2+137.3} \times 100\% = 35.3\%$$

$$\frac{283.3}{190.6+145.2+166.2+56.1} \times 100\% = 50.7\%$$

$$\frac{283.3}{190.6+145.2+65} \times 100\% = 70.7\%$$

$$\frac{283.3}{190.6+145.2+65} \times 100\% = 70.7\%$$

$$\text{E-factor} = \frac{\Sigma \text{ of mass of inputs - mass yield of desired product}}{\text{mass yield of desired product}}$$

$$\frac{152.4+29+3.81+55.3+30+3705+1500-45.8}{45.8} = 118.5$$

$$\frac{76.2+29+33.2+110.6+6224.4-48.1}{48.1} = 133.6$$

$$\frac{57.2+29+19.5-48.7}{48.7} = 1.17$$

$$\frac{57.2+29+19.5-37.9}{37.9} = 1.79$$

Wu' work

Parameter	Detail of parameters	Penalty points
1. Yield	81%	9.5
2. Cost of reactants to obtain	10 mmol of product	
	Quinoline *N*-oxide	0
	TsCl	0
	CuI	0
	H_2O	0
	K_2CO_3	0
	DCE	0
3. Safety	TsCl	10 (N,T)
	PCl_3	35 (N,T+, E, F+)
	DCE	20 (N,T,F, E)
4. Technical setup	Common setup	0
5. Temperature/time	Heating > 24 h	3
6. Workup and purification	Classical chromatography	10
Eco-scale score		12.5

Zhao' work

Parameter	Detail of parameters	Penalty points
1. Yield	85%	7.5
2. Cost of reactants to obtain	10 mmol of product	
	Quinoline *N*-oxide	0
	TsCl	0
	$HP(O)(OiPr)_2$	0
	KOH	0
3. Safety	TsCl	10 (N,T)
	$HP(O)(OiPr)_2$	10 (N,T)
	KOH	10 (N,T)
	THF	30 (N,T,F+, E)
4. Technical setup	Common setup	0
5. Temperature/time	Room temperature, < 24 h	1
6. Workup and purification	Classical chromatography	10
Eco-scale score		21.5

This work

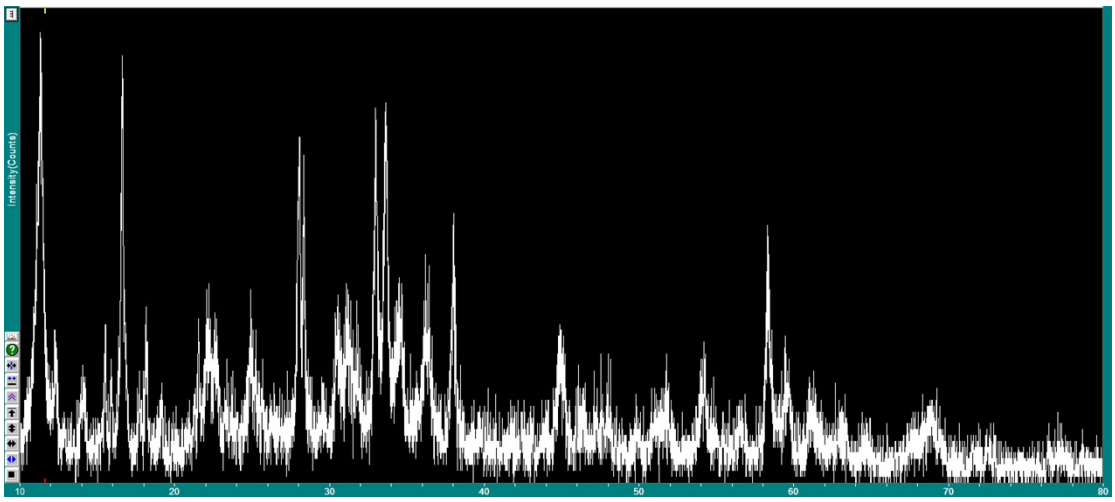
Ultrasonic Radiation

Parameter	Detail of parameters	Penalty points
1. Yield	86%	7
2. Cost of reactants to obtain	10 mmol of product	
	Quinoline *N*-oxide	0
	TsCl	0
	Zn	0
	H_2O	0
3. Safety	TsCl	10 (N,T)
4. Technical setup	ultrasound	2
5. Temperature/time	Room temperature, < 1 h	0
6. Workup and purification	Classical chromatography	10
Eco-scale score		71

Traditional Heating

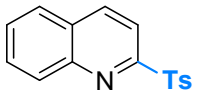
Parameter	Detail of parameters	Penalty points
1. Yield	67%	16.5
2. Cost of reactants to obtain	10 mmol of product	
	Quinoline *N*-oxide	0
	TsCl	0
	Zn	0
	H_2O	0
3. Safety	TsCl	10 (N,T)
4. Technical setup	Common steup	0
5. Temperature/time	heating, 8h	3
6. Workup and purification	Classical chromatography	10
Eco-scale score		60.5

(e) XRD spectra of the gray solid mixture [Zn, $Zn(OH)_2$ and $(p\text{-}TolSO_2)_2Zn$]



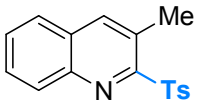
3. Characterization data of products

2-tosylquinoline (3aa)[1]



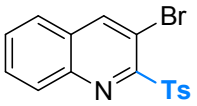
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.8 Hz , 1 H), 8.20 – 8.16 (m, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.79 – 7.75 (m, 1 H), 7.66 -7.62 (m, 1 H), 7.32 (d, *J* = 8.4 Hz , 2 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 147.4, 144.8, 138.7, 136.0, 130.9, 130.3, 129.7, 129.1, 129.0, 128.7, 127.6, 117.6, 21.6.

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



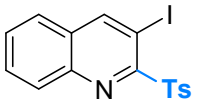
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H), 7.94 – 7.91 (m, 3 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.66 – 7.55 (m, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 2.84 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 144.6, 144.5, 139.8, 135.7, 129.9, 129.7, 129.3 (2 C), 129.0, 128.9, 128.5, 126.6, 21.6, 18.8;

3-bromo-2-tosylquinoline (3ac)[3]



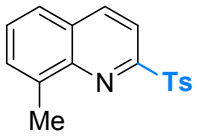
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1 H), 7.80 – 7.96 (m, 3 H), 7.79 – 7.76 (m, 2 H), 7.69 – 7.65 (m, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 144.9, 144.4, 142.9, 134.9, 131.0, 130.2, 130.0 , 129.8, 129.7, 129.4, 126.5, 111.4, 21.7.

3-iodo-2-tosylquinoline (3ad)[4]



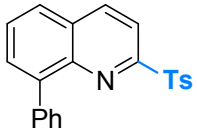
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.85 (s, 1 H), 7.97 (d, *J* = 6.4 Hz, 2 H), 7.89 (d, *J* = 7.6 Hz, 1 H), 7.74 – 7.71 (m, 2 H), 7.64 (t, *J* = 6.4 Hz, 1 H), 7.36 (d, *J* = 6.4 Hz, 2 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.3, 150.5, 144.8, 135.4, 134.5, 131.2, 130.1, 130.0 , 129.8 (2 C), 129.3, 126.3, 79.9, 21.7.

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



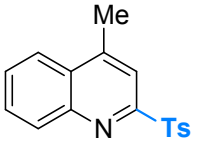
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 8.4 Hz, 1 H), 8.19 (d, *J* = 8.8 Hz, 1 H), 8.06 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.68 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 146.3, 144.7, 138.7, 138.3, 135.9, 130.8, 129.5, 129.3, 128.9, 128.7, 125.5, 116.7, 21.6, 17.5.

8-phenyl-2-tosylquinoline (3af)



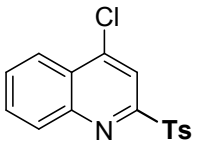
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 8.0 Hz, 1 H), 8.16 (d, *J* = 8.8 Hz, 1 H), 7.81 – 7.70 (m, 4 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.37 – 7.30 (m, 5 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 144.7, 144.5, 141.2, 138.8, 137.9, 135.1, 131.4, 130.7, 129.6, 129.3, 129.2, 128.9, 127.6, 127.3, 127.2, 116.5, 21.7; HRESIMS Calcd for $[C_{22}H_{17}NNaO_2S]^+$ (M + Na^+) 382.0872, found 380.0876.

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



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.4 Hz, 1 H), 8.03 – 8.00 (m, 4 H), 7.76 (t, *J* = 8.0 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.32 (d, *J* = 8.4 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, 118.1, 21.6, 19.2.

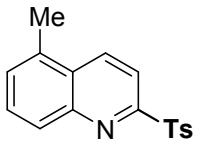
4-chloro-2-tosylquinoline ***(3ah)***



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (s, 1 H), 8.26 – 8.24 (m, 1 H), 8.19 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 8.4 Hz,

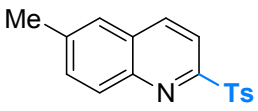
2 H), 7.85 – 7.81 (m, 1 H), 7.77 – 7.73 (m, 1 H), 7.34 (d, J = 8.4 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 148.1, 145.2, 145.2, 135.6, 131.7, 130.8, 130.1, 129.9, 129.1, 127.0, 124.2, 117.9, 21.7; HRESIMS Calcd for $[C_{16}H_{12}ClNNaO_2S]^+$ (M + Na^+) 340.0169, found 340.0166.

5-methyl-2-tosylquinoline (3ai)



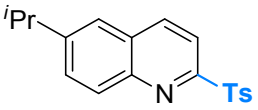
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, J = 8.4 Hz, 1 H), 8.19 (d, J = 8.8 Hz, 1 H), 8.02 – 8.00 (m, 3 H), 7.66 – 7.62 (m, 1 H), 7.46 – 7.44 (m, 1 H), 7.31 (d, J = 8.0 Hz, 2 H), 2.67 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 147.8, 144.7, 136.1, 135.1, 134.7, 130.6, 129.7, 129.4, 128.9, 128.5, 128.2, 117.2, 21.6, 18.6; HRESIMS Calcd for $[C_{17}H_{15}NNaO_2S]^+$ (M + Na^+) 320.0716, found 320.0720.

6-methyl-2-tosylquinoline (3aj)[3]



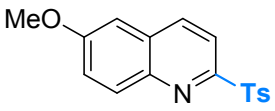
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, J = 8.4 Hz, 1 H), 8.13 (d, J = 8.4 Hz, 1 H), 8.05 (d, J = 8.8 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 2 H), 7.60 (d, J = 8.8 Hz, 2 H), 7.31 (d, J = 8.8 Hz, 2 H), 2.54 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 146.0, 144.7, 139.6, 137.8, 136.2, 133.3, 130.0, 129.7, 128.9, 128.9, 126.4, 117.7, 21.8, 21.6.

6-isopropyl-2-tosylquinoline (3ak)[5]



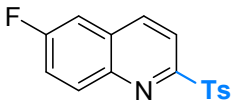
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.4 Hz, 1 H), 8.05 (d, J = 8.4 Hz, 1 H), 8.00 (d, J = 8.8 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 2 H), 7.59 – 7.54 (m, 2 H), 7.19 (q, J = 8.0 Hz, 2 H), 2.98 (q, J = 6.8 Hz, 1 H), 2.26 (s, 3 H), 1.21 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 150.1, 146.2, 144.5, 138.1, 136.2, 130.9, 130.0, 129.6, 128.8 (2 C), 123.6, 117.6, 34.1, 23.5, 21.4.

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



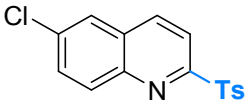
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.8 Hz, 1 H), 8.13 (d, *J* = 8.8 Hz, 1 H), 8.04 (d, *J* = 9.2 Hz, 1 H), 8.01 – 7.99 (m, 2 H), 7.41 (dd, *J* = 9.2 Hz, 2.8 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.07 (d, *J* = 2.4 Hz, 1 H), 3.93 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 155.7, 144.5, 143.6, 136.8, 136.5, 131.8, 130.3, 129.7, 128.9, 124.2, 118.2, 104.6, 55.7, 21.6.

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



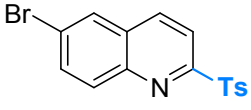
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 8.8 Hz, 1 H), 8.21 – 8.15 (m, 2 H), 8.00 (d, *J* = 8.0 Hz, 2 H), 7.57 – 7.52 (m, 1 H), 7.49 – 7.46 (m ,1 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 160.5, 157.9, 157.8, 144.9, 144.4, 138.1, 138.0, 135.9, 133.1, 133.0, 129.8, 129.7, 129.0, 121.7, 121.4, 118.4, 110.8, 110.6, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 108.3.

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



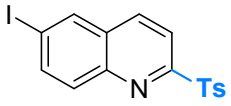
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 8.8 Hz, 1 H), 8.21 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 9.2 Hz, 1 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.85 (d, *J* = 2.0 Hz, 1 H), 7.71 (dd, *J* = 9.2 Hz, 2.4 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 145.8, 145.0, 137.7, 135.8, 135.2, 132.0, 131.9, 129.8, 129.3, 129.1, 126.3, 118.6, 21.6.

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



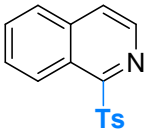
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.4 Hz, 1 H), 8.20 (d, *J* = 8.8 Hz, 1 H), 8.04 – 7.98 (m, 4 H), 7.83 (dd, *J* = 9.2 Hz, 2.0 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 145.9, 145.0, 137.7, 135.7, 134.5, 131.9, 129.8 (2 C), 129.7, 129.1, 123.5, 118.6, 21.7.

6-iodo-2-tosylquinoline (3ap)[5]



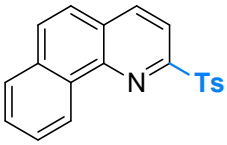
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 – 8.18 (m, 3 H), 8.01 – 7.99 (m, 3 H), 7.87 (d, *J* = 8.8 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 146.3, 145.0, 139.8, 137.4, 136.4, 135.7, 131.7, 130.1, 129.8, 129.5, 118.4, 95.6, 21.7.

1-tosylisoquinoline (3aq)[1]



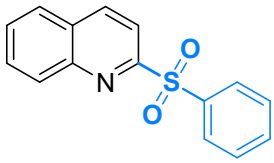
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (d, *J* = 9.6 Hz, 1 H), 8.43 (d, *J* = 5.6 Hz, 1 H), 7.97 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 9.2 Hz, 1 H), 7.79 – 7.75 (m, 3 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 144.7, 140.5, 137.8, 136.1, 131.1, 129.6, 129.2 (2 C), 127.5, 125.4, 124.9, 124.3, 21.7.

2-tosylbenzo[h]quinoline (3ar)



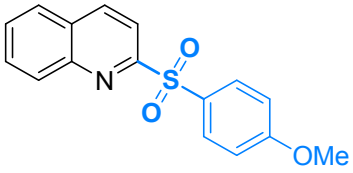
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 8.0 Hz, 1 H), 8.24 (d, *J* = 8.8 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 2 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.80 (d, *J* = 8.8 Hz, 1 H), 7.70 – 7.62 (m, 3 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.8 Hz, 1 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 145.1, 144.6, 140.3, 134.5, 133.8, 130.6, 129.6, 128.8, 128.6, 127.9, 127.7, 126.8, 125.2, 124.7, 124.4, 114.4, 21.7; HRESIMS Calcd for $[C_{20}H_{15}NNaO_2S]^+$ (M + Na^+) 356.0716, found 356.0723.

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



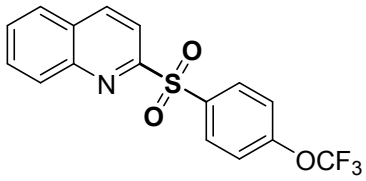
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.4 Hz, 1 H), 8.21 – 8.13 (m, 4 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.77 (t, *J* = 8.0 Hz, 1 H), 7.66 – 7.51 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 147.4, 139.1, 138.7, 133.7, 131.0, 130.3, 129.2, 129.0 (2 C), 128.8, 127.7, 117.7.

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



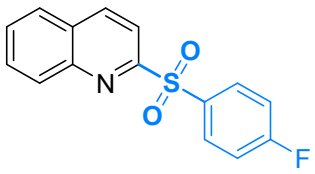
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.4 Hz, 1 H), 8.20 – 8.17 (m, 2 H), 8.07 (d, *J* = 9.2 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.80 – 7.77 (m, 1 H), 7.65 (t, *J* = 8.4 Hz, 1 H), 7.00 (d, *J* = 9.2 Hz, 2 H), 3.85 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.9, 158.6, 147.4, 138.7, 131.3, 130.9, 130.4 (2 C), 129.0, 128.7, 127.7, 117.6, 114.4, 55.6.

2-((4-(trifluoromethoxy)phenyl)sulfonyl)quinolone (3da)



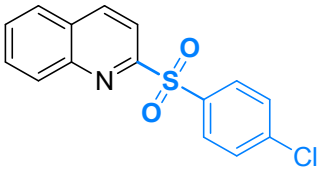
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.8 Hz, 1 H), 8.22 – 8.19 (m, 3 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.81 – 7.77 (m, 1 H), 7.68 – 7.64 (m, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 153.0, 147.4, 138.9, 137.2, 131.3, 131.1, 130.2, 130.0, 129.4, 128.8, 127.7, 120.7, 117.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 57.6; HRESIMS Calcd for $[C_{16}H_{10}F_3NNaO_3S]^+$ (M + Na^+) 376.0226, found 376.0234.

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



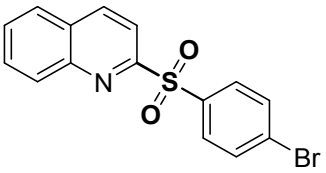
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.4 Hz, 1 H), 8.21 – 8.13 (m, 4 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.81 - 7.76 (m, 1 H), 7.68 – 7.64 (m, 1 H), 7.20 (t, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 164.6, 157.8, 147.3, 138.8, 132.0, 131.9, 131.1, 130.2, 129.3, 128.8, 127.7, 117.4, 116.5, 116.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 103.3.

2-((4-chlorophenyl)sulfonyl)quinoline (3fa)[3]



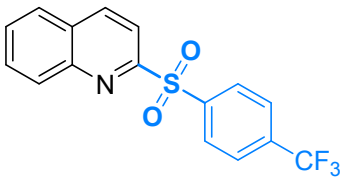
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.8 Hz, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 8.15 (d, *J* = 8.0 Hz, 1 H), 8.10 - 8.07 (m, 2 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.82 – 7.78 (m, 1 H), 7.70 - 7.66 (m, 1 H), 7.51 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 147.4, 140.6, 138.9, 137.4, 131.1, 130.5, 130.3, 129.4 (2 C), 128.9, 127.7, 117.5.

2-((4-bromophenyl)sulfonyl)quinolone (3ga)[2]



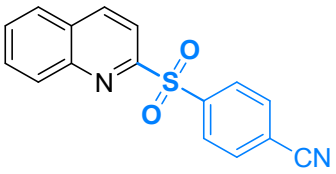
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (d, *J* = 8.8 Hz, 1 H), 8.19 (d, *J* = 8.8 Hz, 1 H), 8.14 (d, *J* = 8.4 Hz, 1 H), 8.01 – 7.98 (m, 2 H), 7.87 (d, *J* = 8.4 Hz, 1 H), 7.81 – 7.77 (m, 1 H), 7.68 – 7.64 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.6, 147.4, 138.9, 138.0, 132.3, 131.1, 130.5, 130.2, 129.3, 129.2, 128.8, 127.7, 117.4.

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



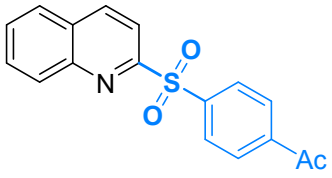
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 8.4 Hz, 1 H), 8.29 (d, *J* = 8.4 Hz, 2 H), 8.24 (d, *J* = 8.4 Hz, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 7.90 (d, *J* = 8.4 Hz, 1 H), 7.83 – 7.80 (m, 3 H), 7.70 – 7.67 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 147.5, 142.6, 139.0, 131.2, 130.3, 129.7, 129.5, 129.0, 127.8, 126.2, 126.2, 126.1, 126.1, 124.5, 121.8, 117.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 63.2.

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



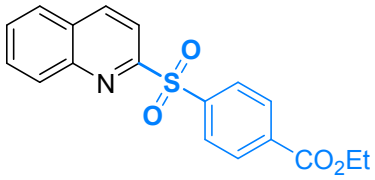
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.4 Hz, 1 H), 8.28 – 8.22 (m, 3 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.85 – 7.80 (m, 3 H), 7.70 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 147.4, 143.2, 139.1, 132.7, 131.4, 130.2, 129.8, 129.6, 129.0, 127.8, 117.5, 117.4, 117.2.

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



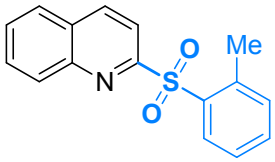
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.8 Hz, 1 H), 8.25 – 8.22 (m, 3 H), 8.14 (d, *J* = 8.8 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.82 – 7.77 (m, 1 H), 7.69 – 7.65 (m, 1 H), 2.62 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 157.4, 147.4, 142.8, 138.9, 131.2, 130.3, 129.4, 129.4, 128.9, 128.7, 127.7, 117.6, 26.9; HRESIMS Calcd for $[C_{17}H_{13}NNaO_3S]^+$ (M + Na^+) 334.0508, found 334.0510.

ethyl 4-(quinolin-2-ylsulfonyl)benzoate (3ka)[1]



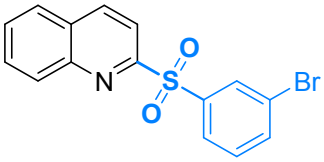
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.4 Hz, 1 H), 8.24 – 8.19 (m, 5 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 1 H), 7.82 – 7.77 (m, 1 H), 7.69 – 7.65 (m, 1 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 1.38 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 156.5, 146.4, 141.7, 137.9, 134.0, 130.2, 129.3, 129.1, 128.4, 128.1, 126.7, 116.6, 60.7, 13.2.

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



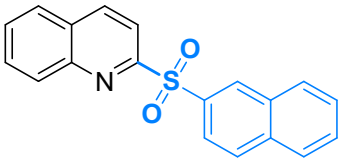
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37 (d, *J* = 8.8 Hz, 1 H), 8.30 (d, *J* = 8.0 Hz, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.74 (t, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.47 (t, *J* = 7.2 Hz, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.22 (d, *J* = 7.6 Hz, 1 H), 2.54 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 147.1, 139.1, 138.6, 137.1, 133.9, 132.4, 131.0, 130.6, 130.4, 129.2, 128.9, 127.7, 126.4, 117.7, 20.7.

2-((3-bromophenyl)sulfonyl)quinoline (3ma)[6]



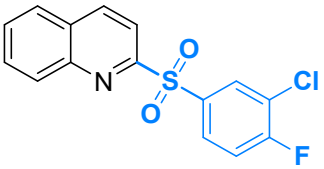
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 8.8 Hz, 1 H), 8.27 (s, 1 H), 8.20 (d, *J* = 8.4 Hz, 1 H), 8.16 (d, *J* = 9.2 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.82 – 7.78 (m, 1 H), 7.72 – 7.65 (m, 2 H), 7.41 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 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-(naphthalen-2-ylsulfonyl)quinoline (3na)[3]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1 H), 8.37 (d, *J* = 8.4 Hz, 1 H), 8.26 (d, *J* = 8.4 Hz, 1 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 8.08 (dd, *J* = 8.8 Hz, 2.0 Hz, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.94 (d, *J* = 8.8 Hz, 1 H), 7.86 – 7.83 (m, 2 H), 7.77 – 7.72 (m, 1 H), 7.66 – 7.55 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 147.4, 135.9, 138.7, 135.2, 132.0, 130.9, 130.7, 130.3, 129.4, 129.3 (2 C), 129.2, 128.7, 127.8, 127.6, 127.5, 123.6, 117.7.

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



^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.8 Hz, 1 H), 8.23 – 8.19 (m, 2 H), 8.15 (d, *J* = 8.4 Hz, 1 H), 8.08 – 8.04 (m, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.83 – 7.79 (m, 1 H), 7.70 – 7.66 (m, 1 H), 7.30 (t, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 160.1, 157.3, 147.4, 139.0, 135.9 (2 C), 132.0, 131.2, 130.2, 129.8, 129.5, 128.9, 127.7, 122.6, 117.5, 117.4, 117.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ = - 105.5, HRESIMS Calcd for $[C_{15}H_9ClFNNaO_2S]^+$ (M + Na^+) 343.9919, found 343.9924.

4. References

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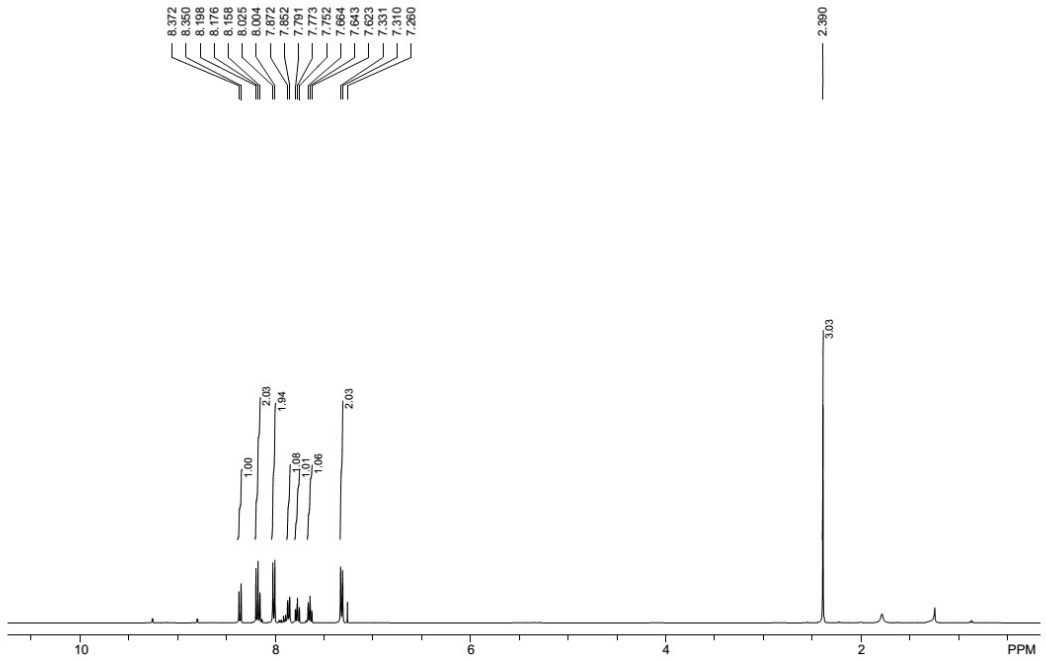
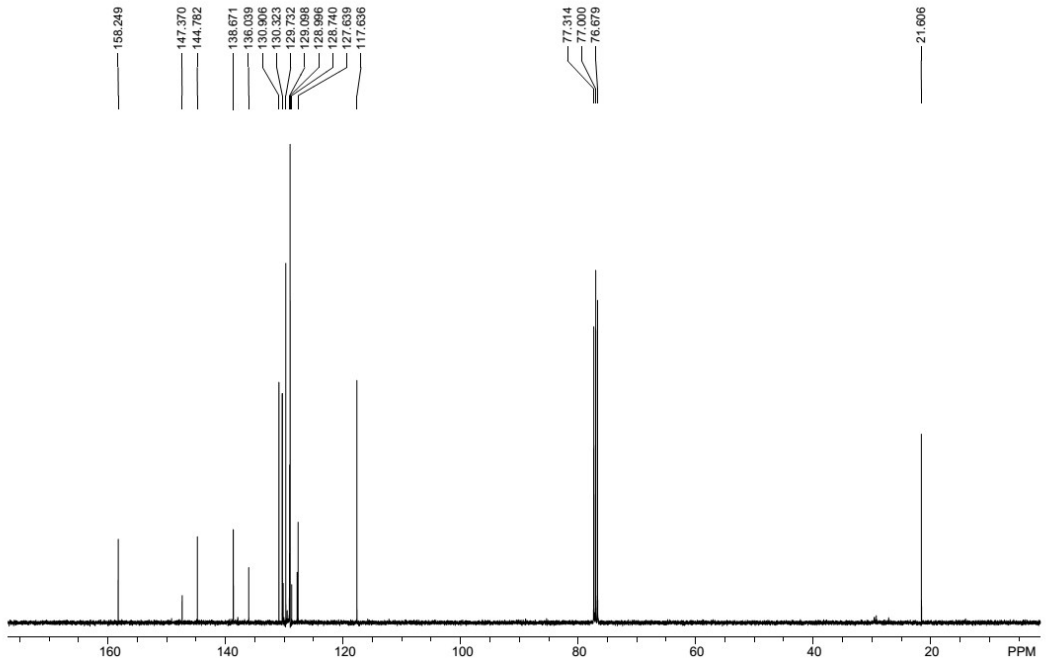
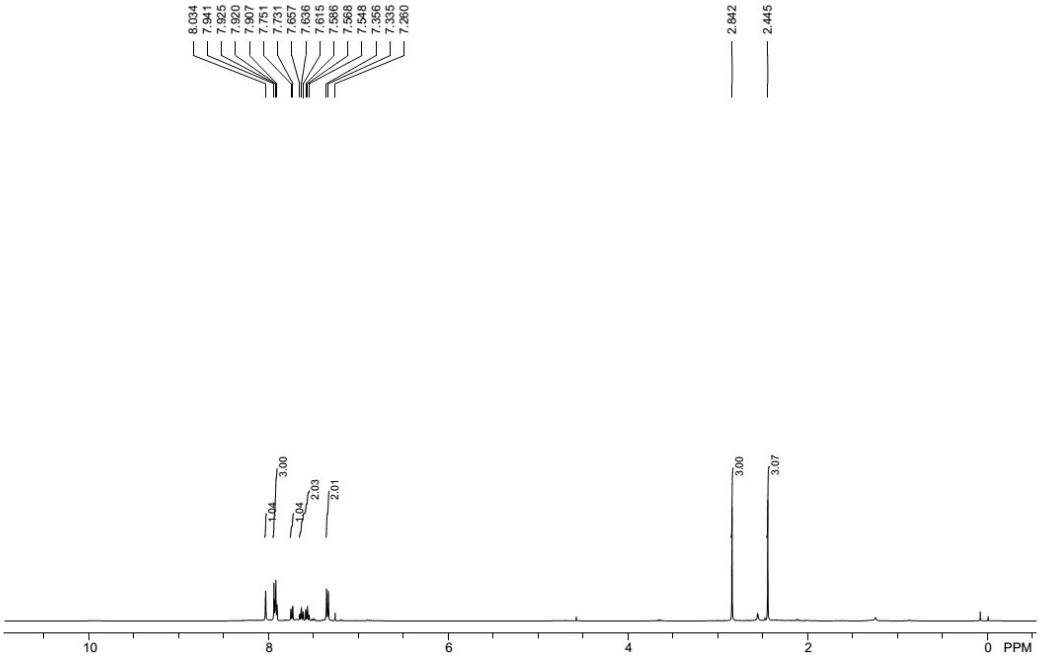
5. ^{1}H and ^{13}C NMR spectra of products

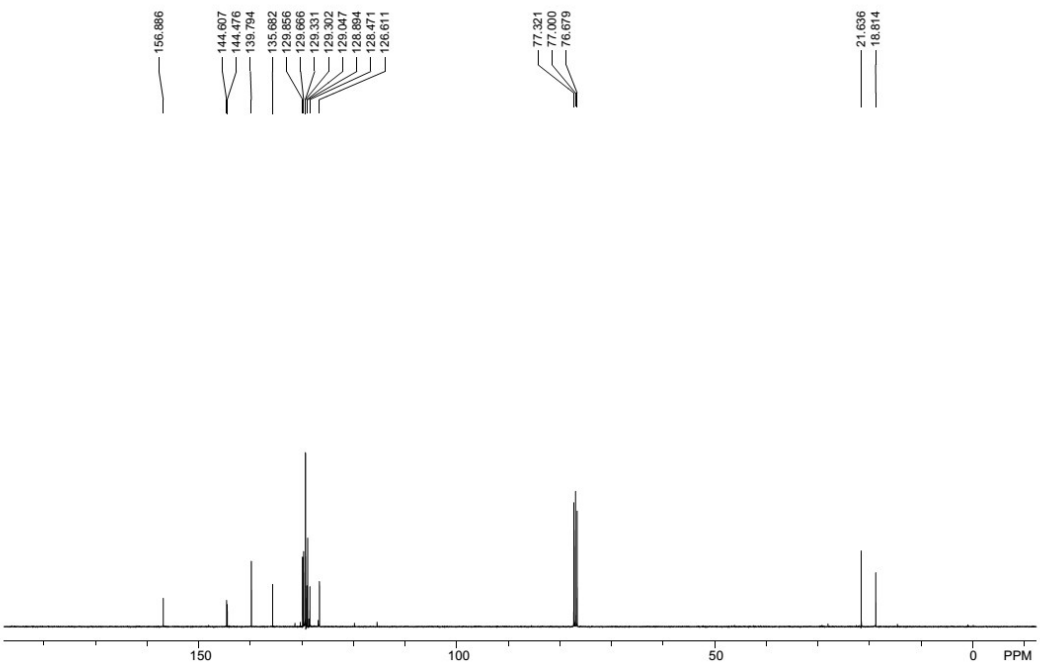
2-tosylquinoline (3aa)



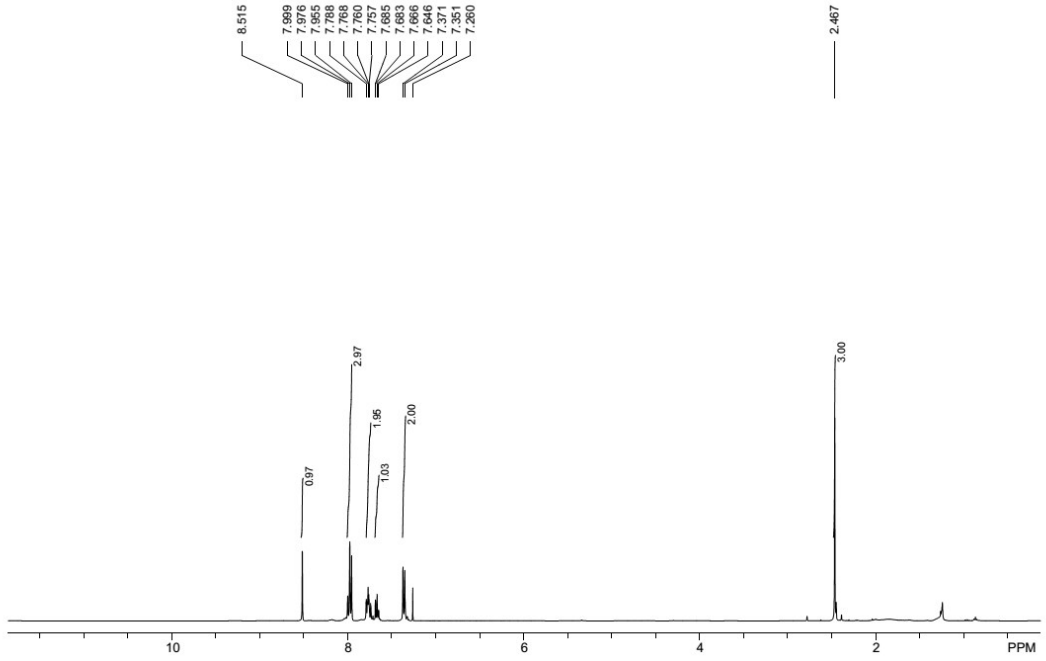


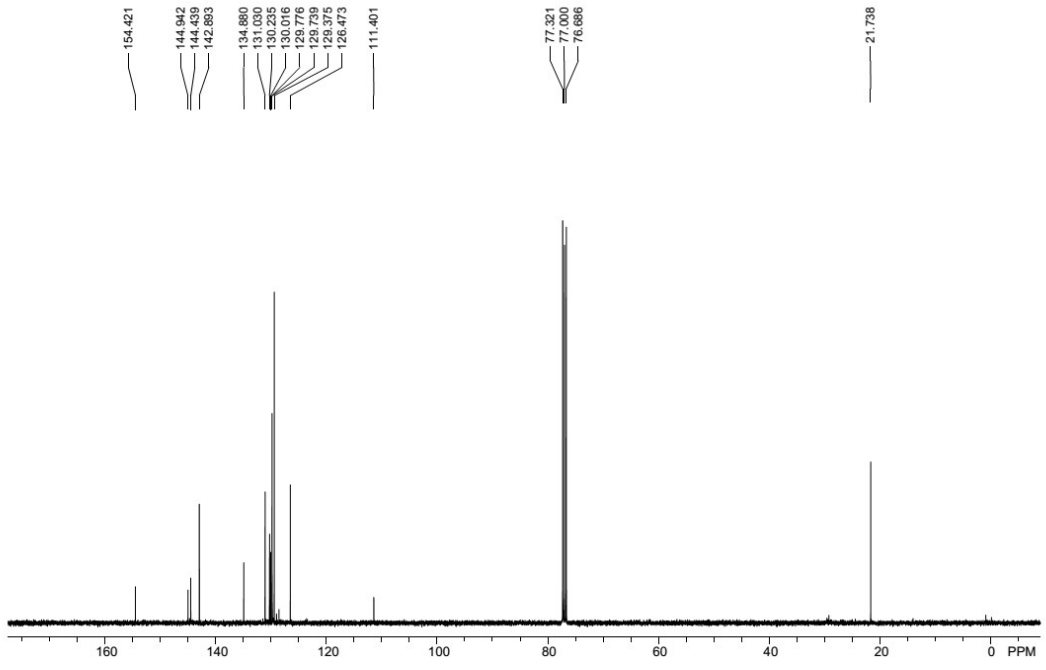
3-methyl-2-tosylquinoline (3ab)



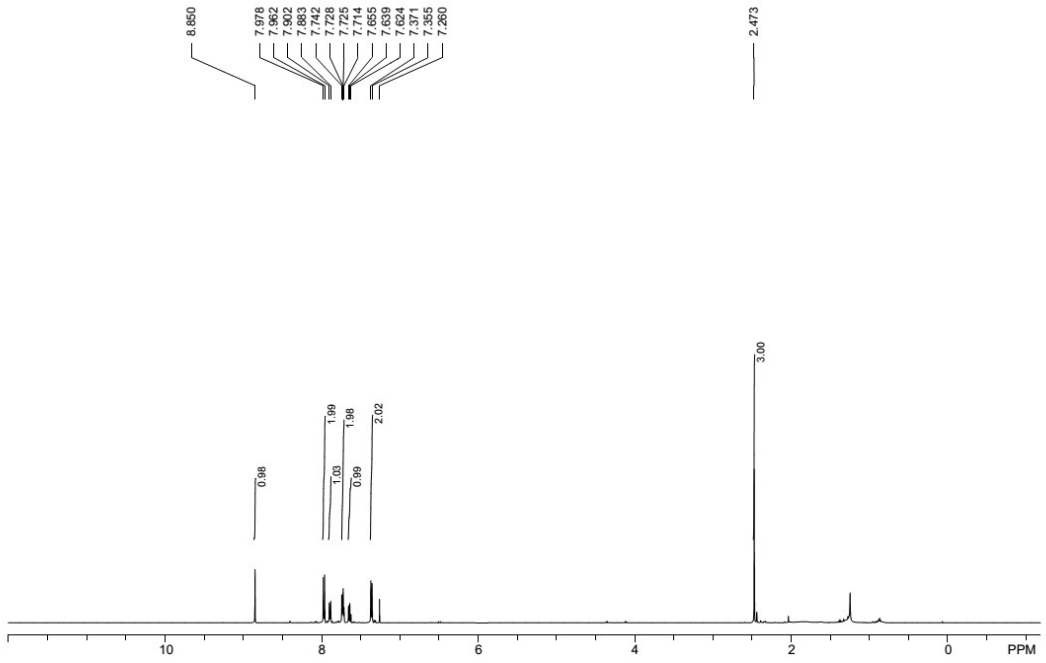


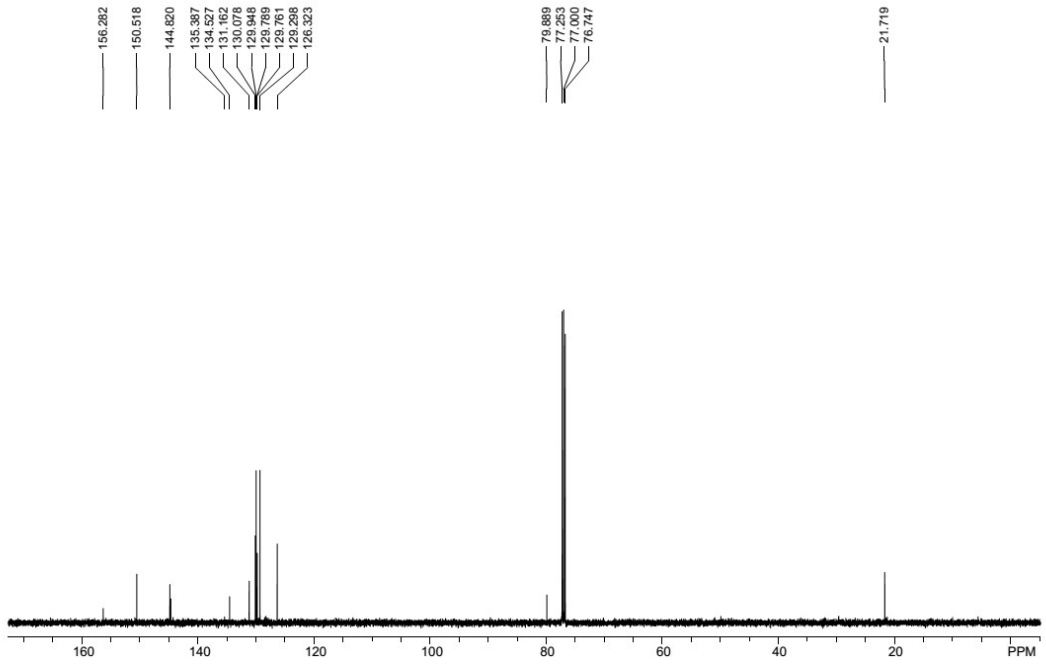
3-bromo-2-tosylquinoline (3ac)



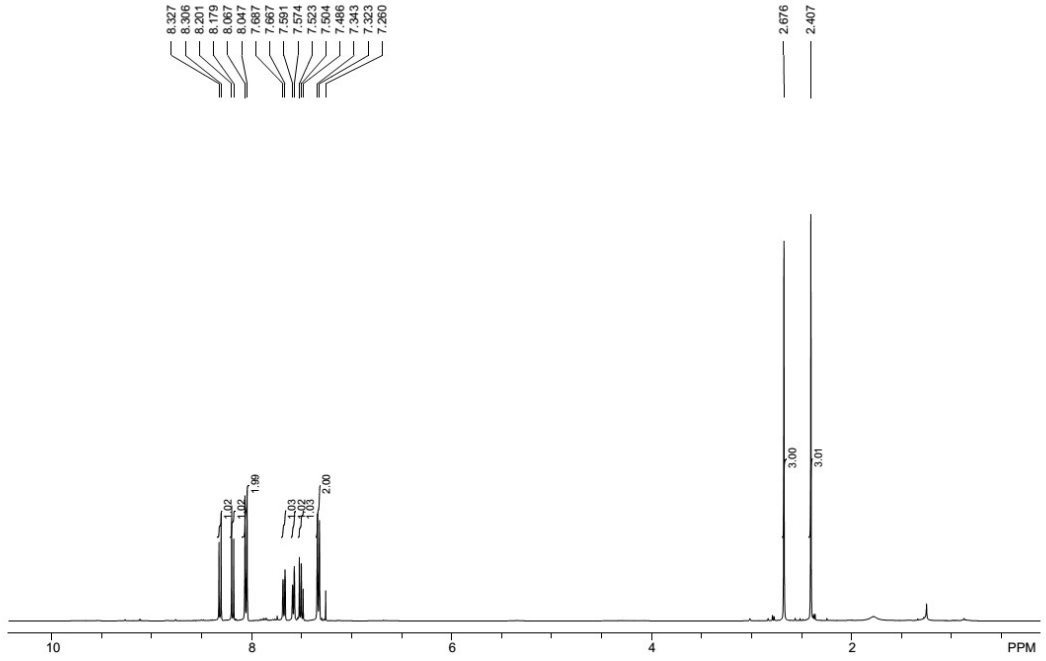


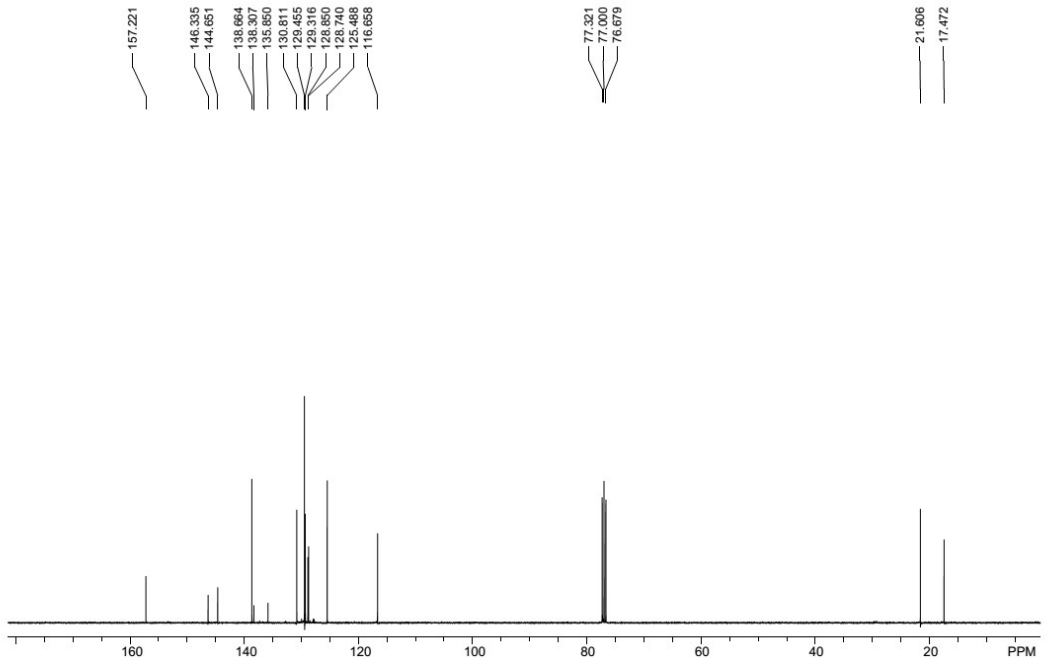
3-iodo-2-tosylquinoline (3ad)



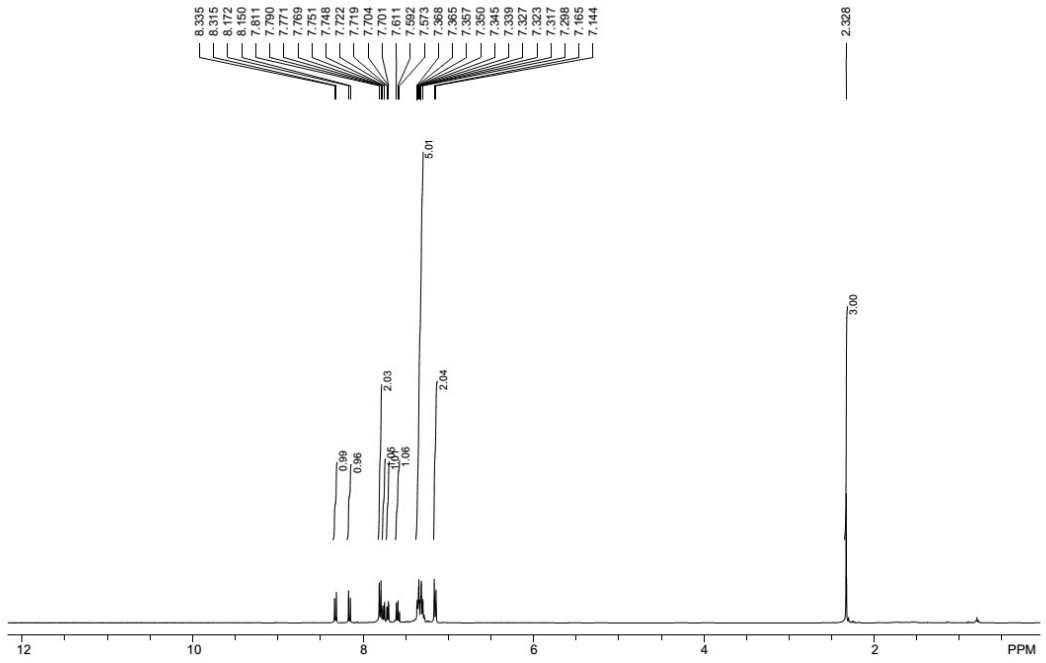


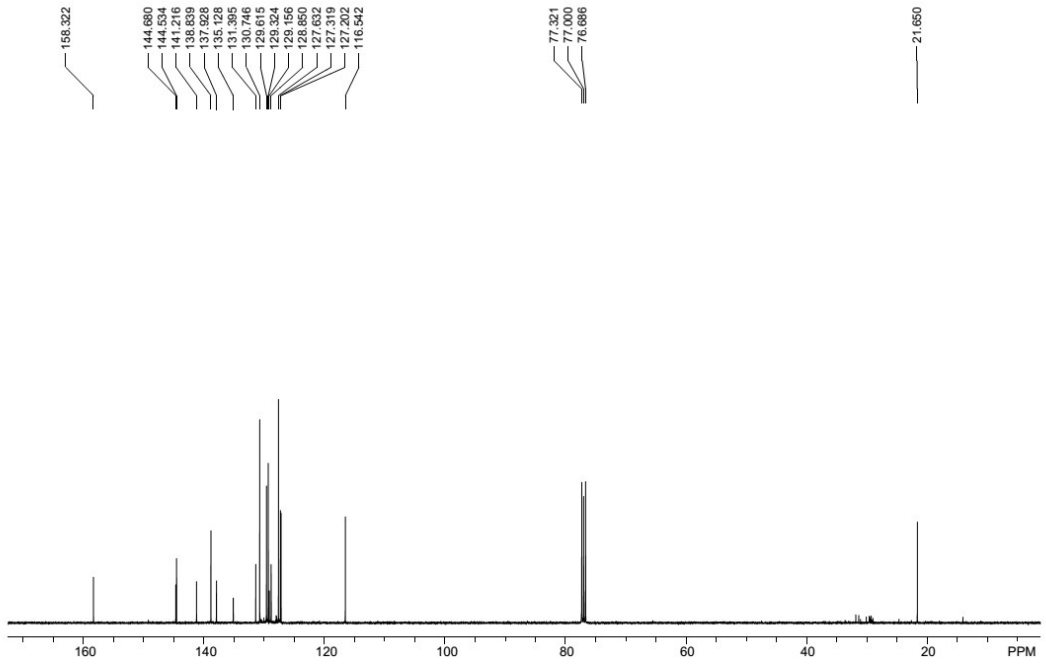
8-methyl-2-tosylquinoline (3ae)



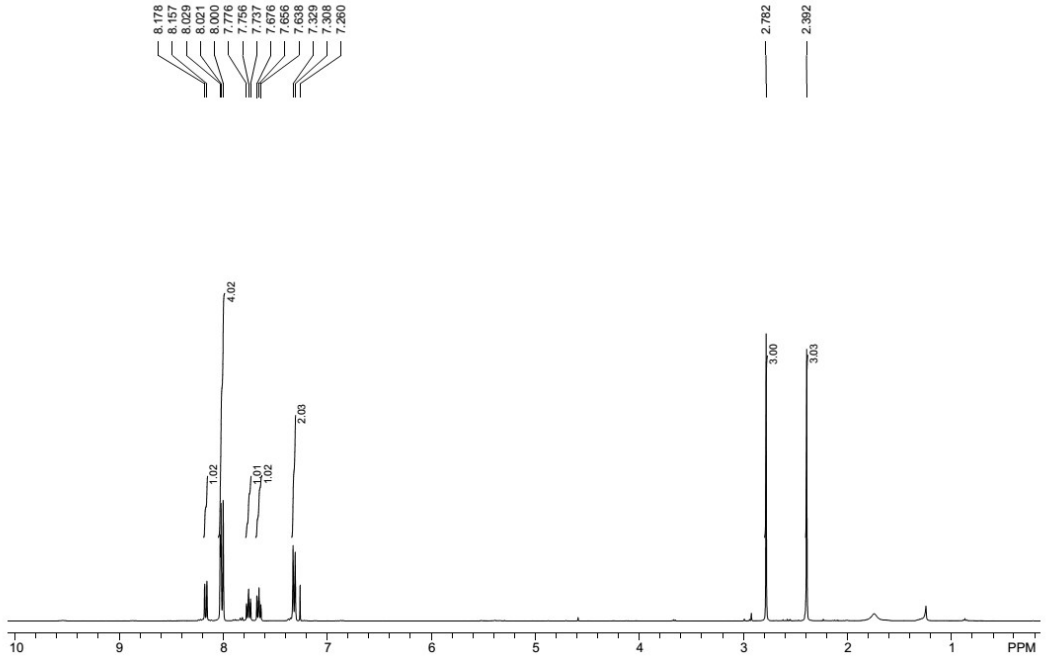


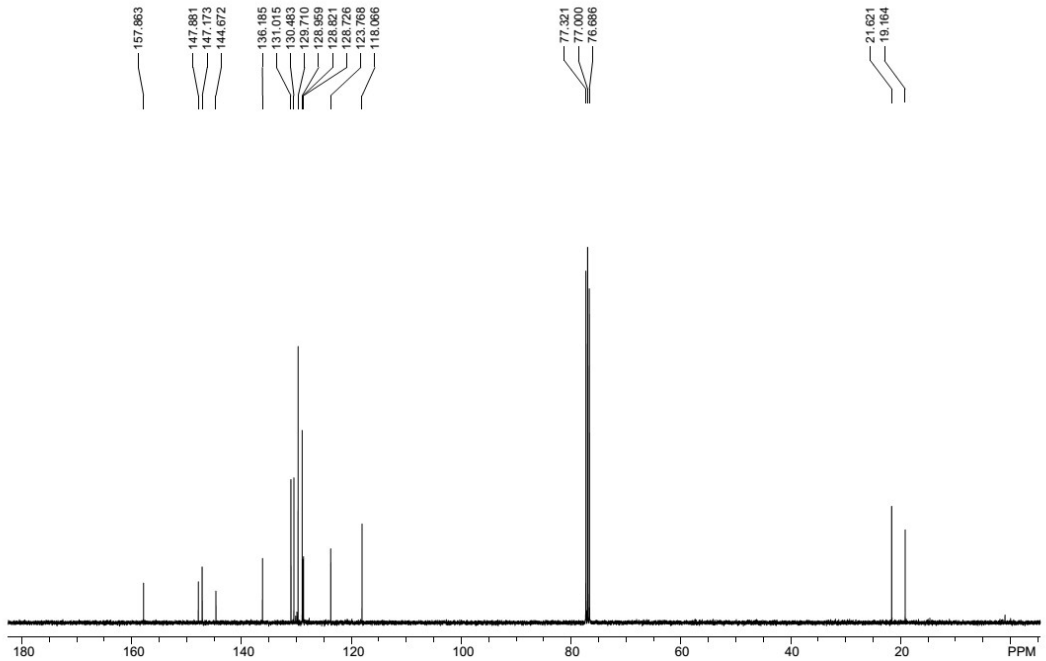
8-phenyl-2-tosylquinoline (3af)



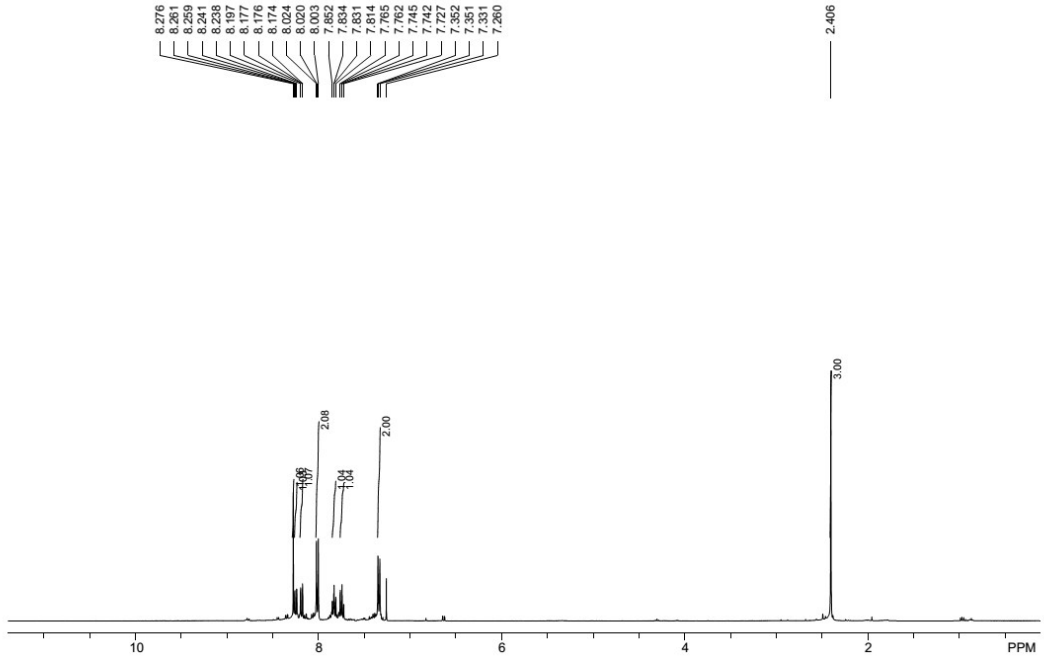


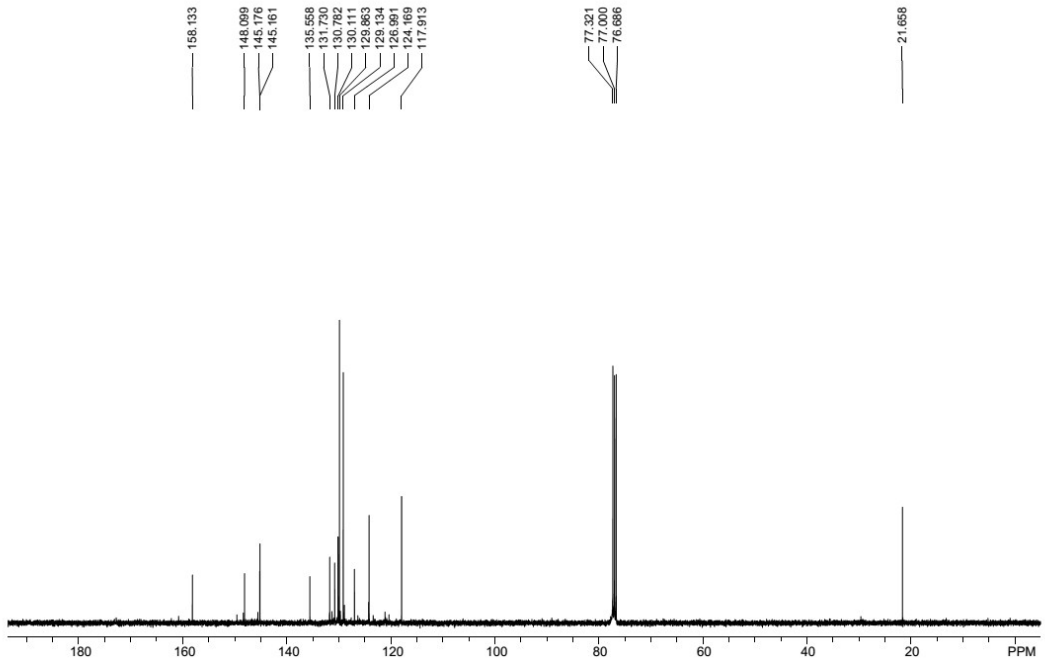
4-methyl-2-tosylquinoline (3ag)



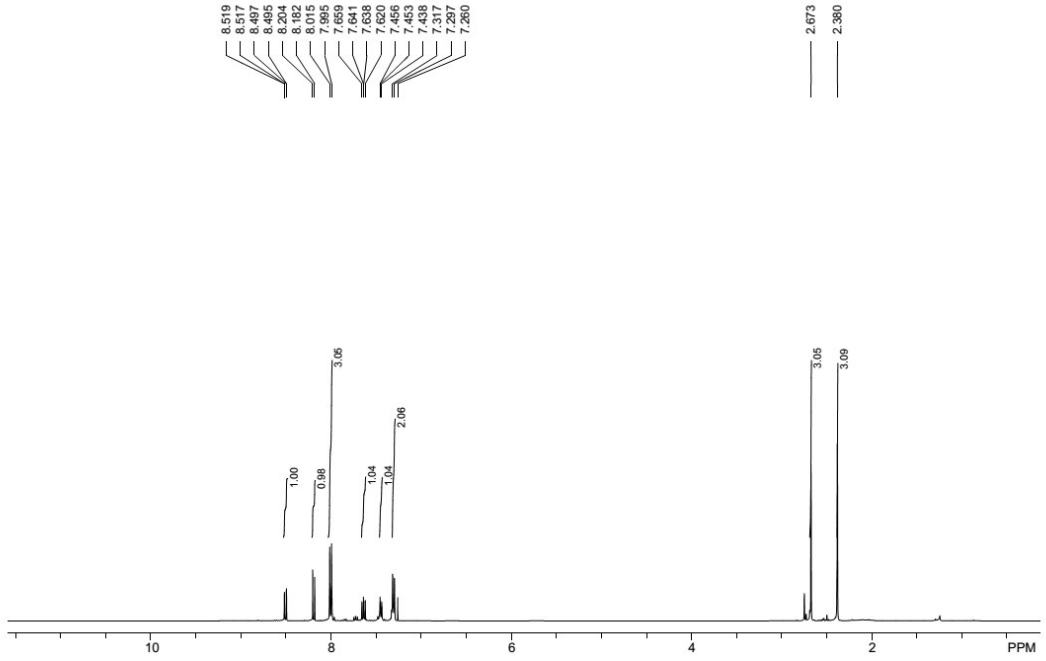


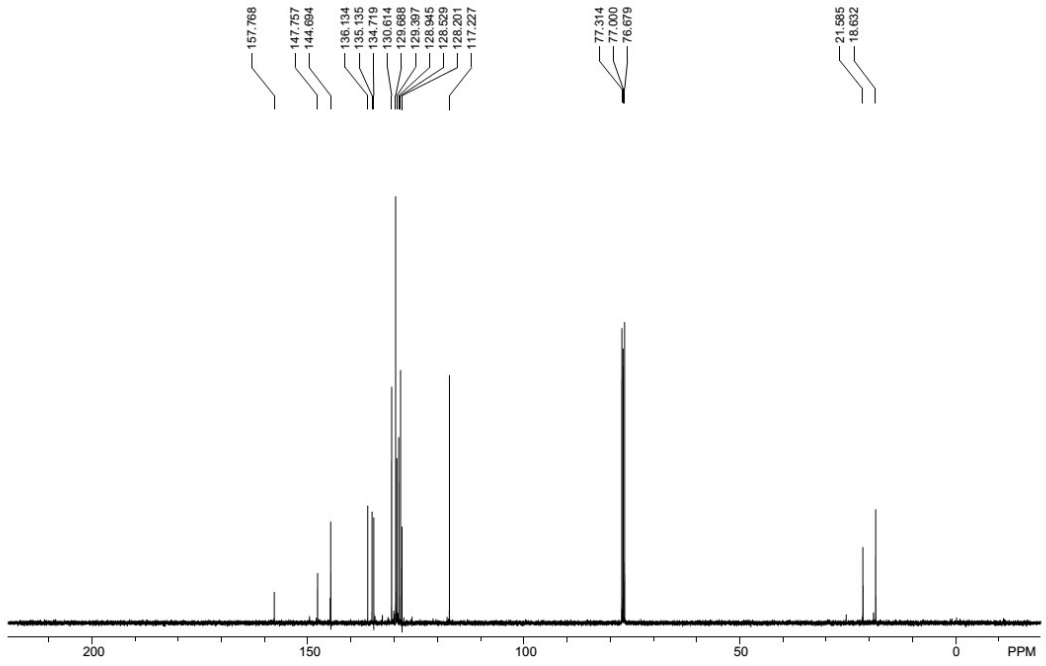
4-chloro-2-tosylquinoline ***(3ah)***



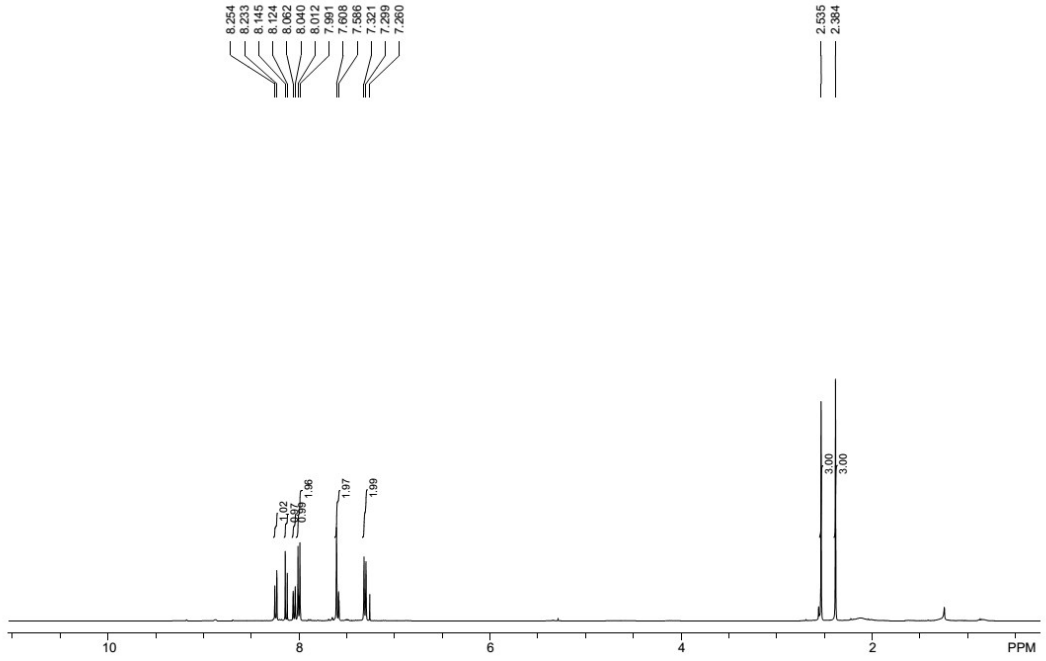


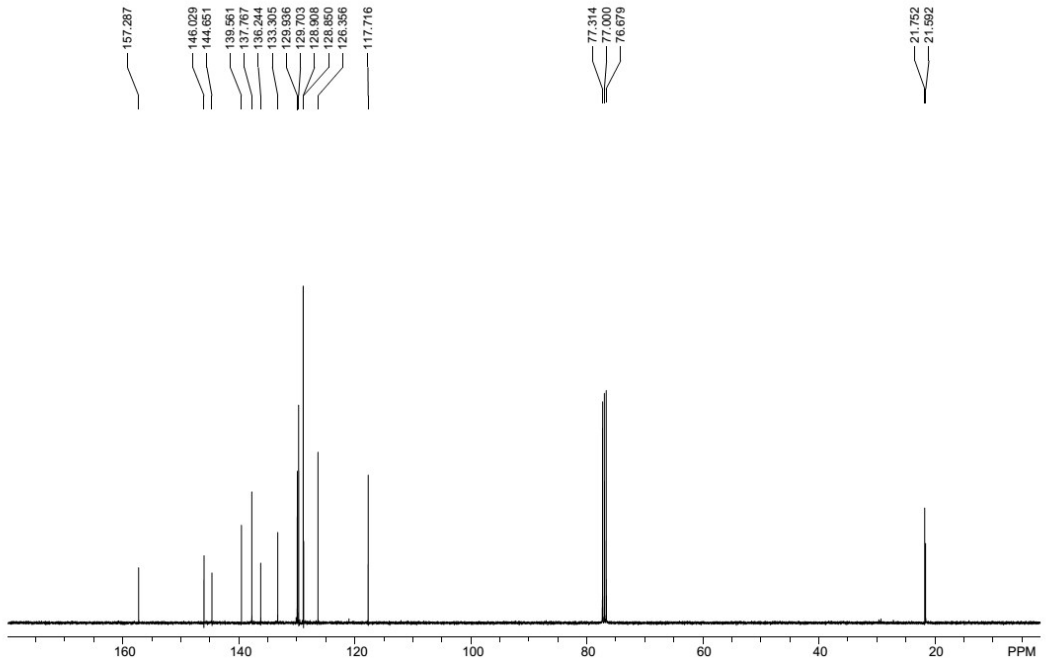
5-methyl-2-tosylquinoline (3ai)



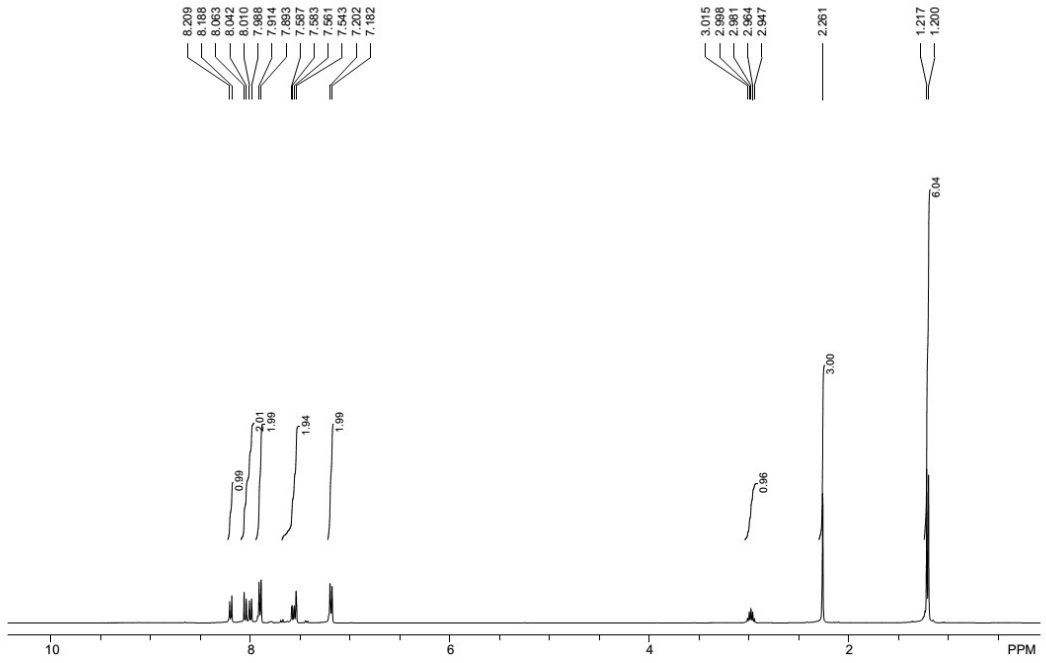


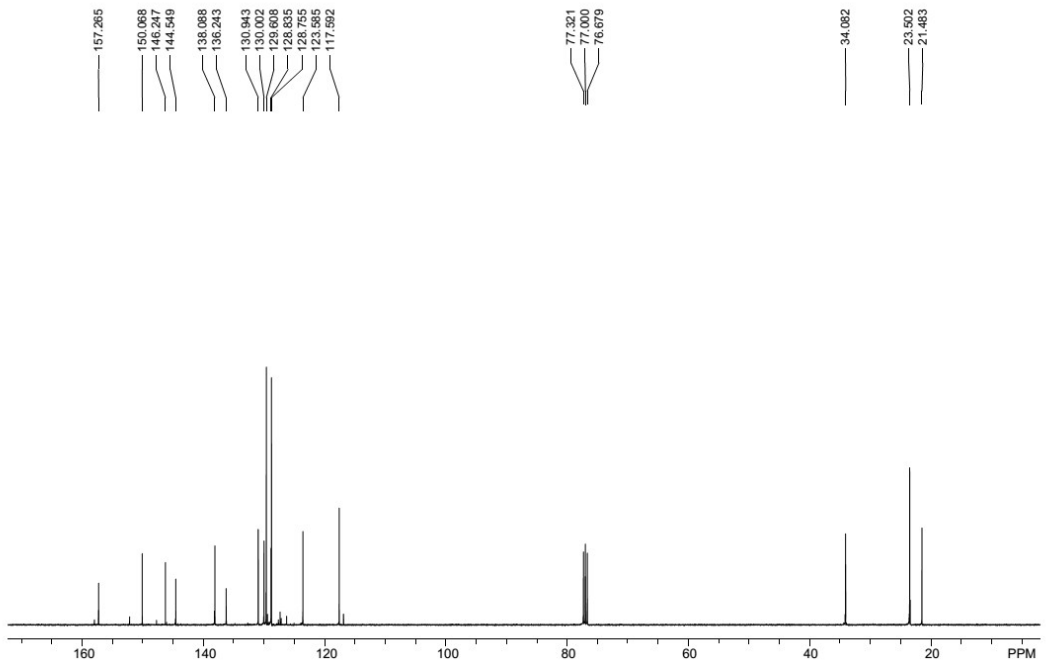
6-methyl-2-tosylquinoline (3aj)



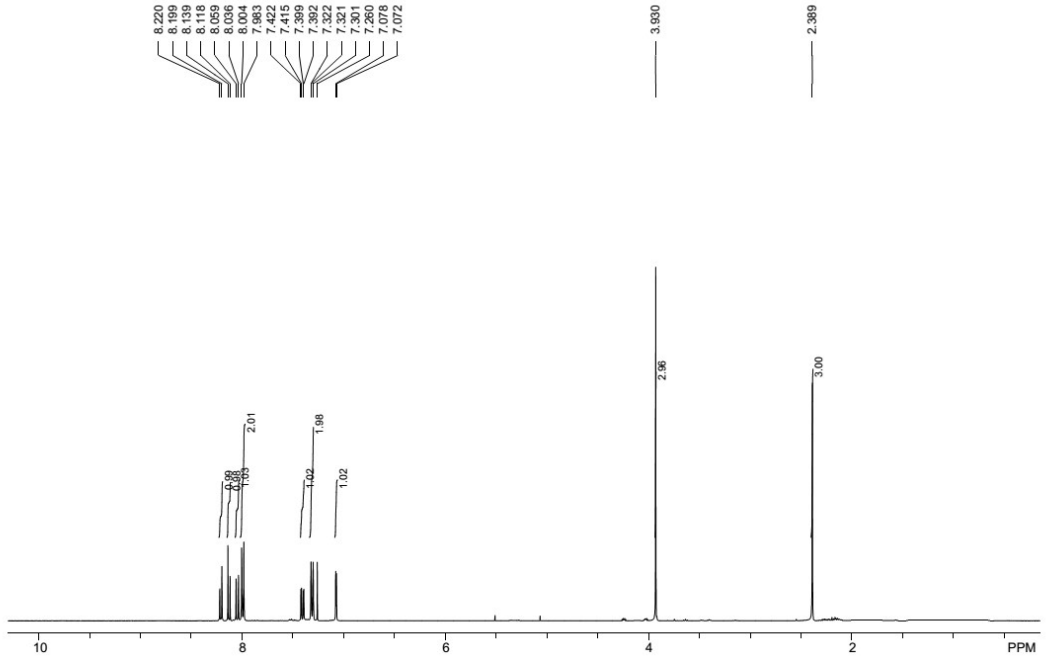


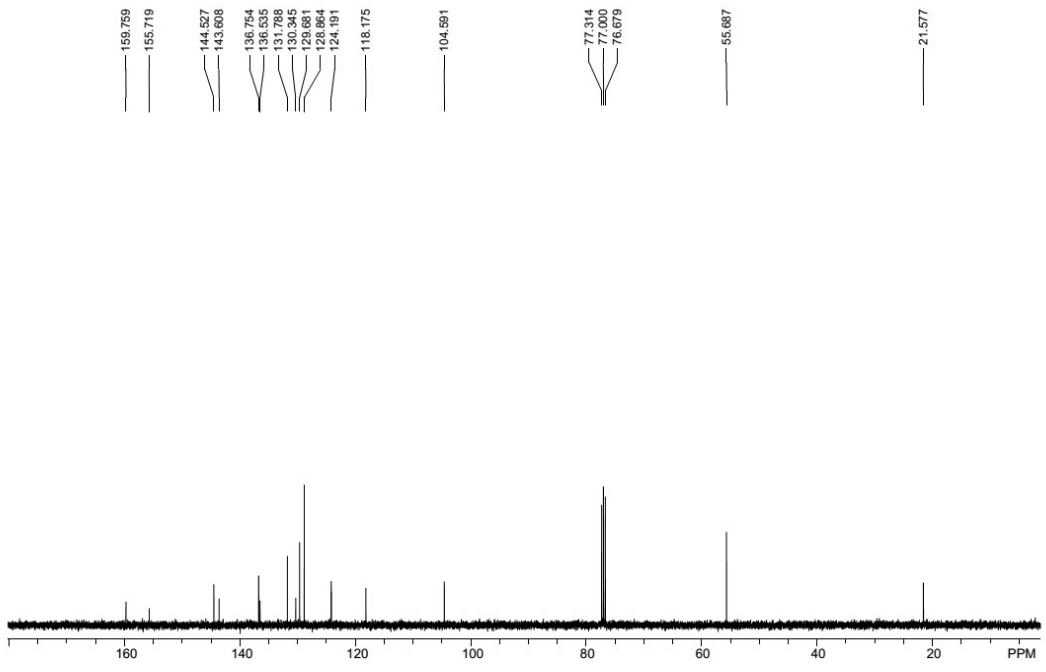
6-isopropyl-2-tosylquinoline (3ak)



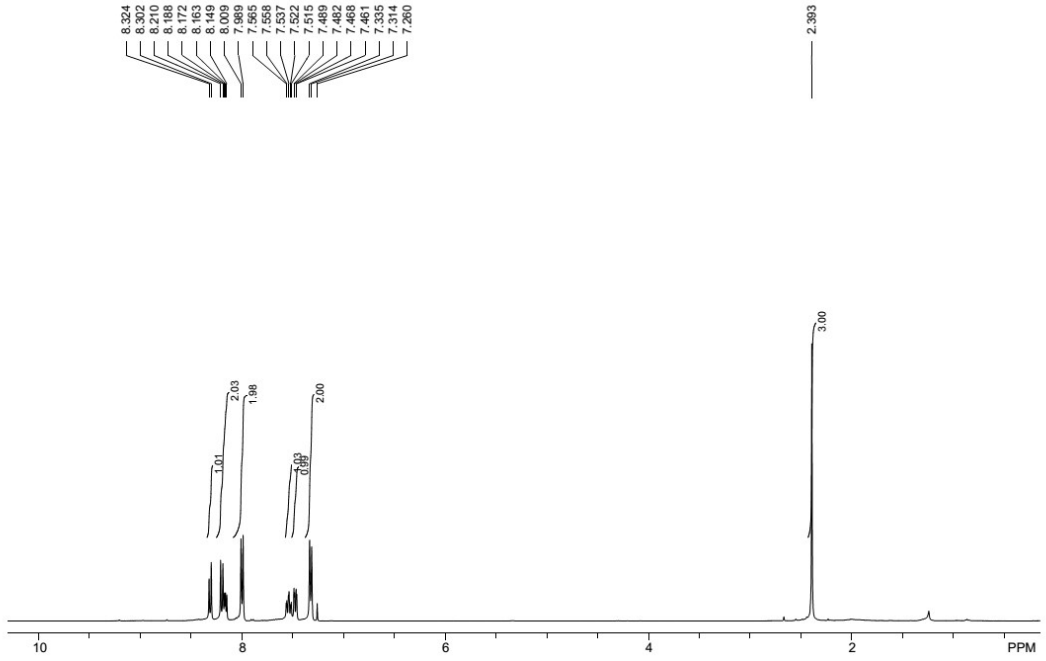


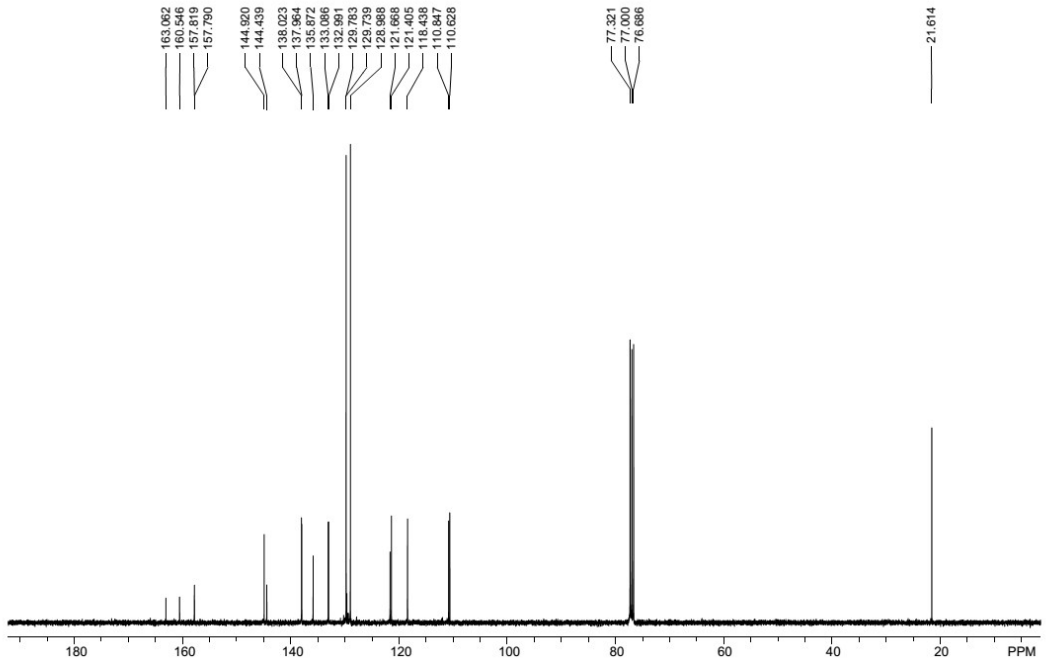
6-methoxy-2-tosylquinoline (3al)



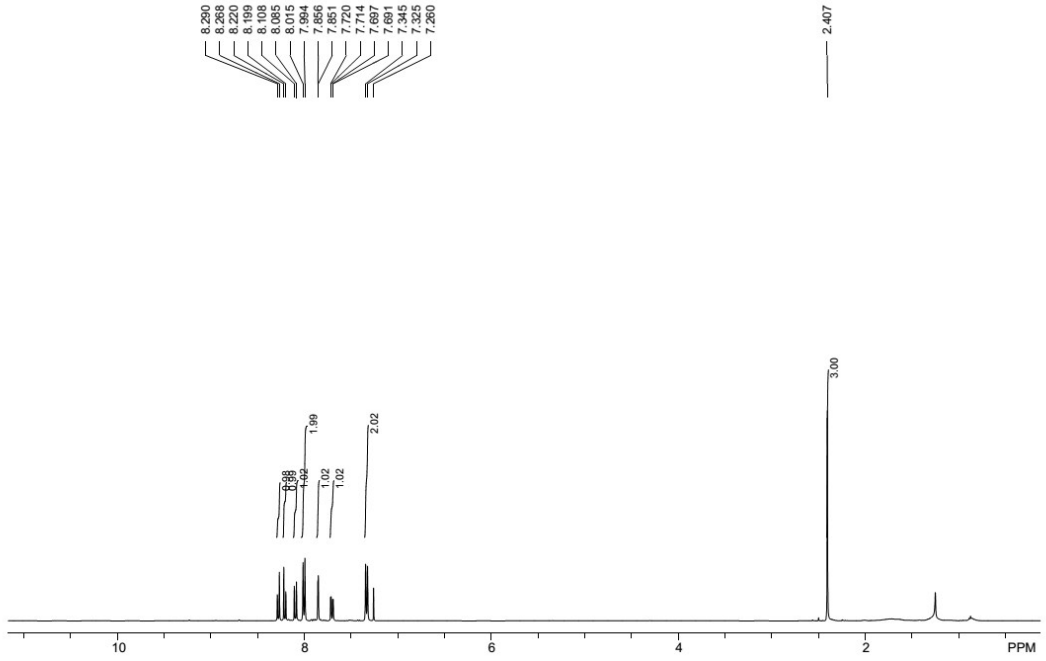


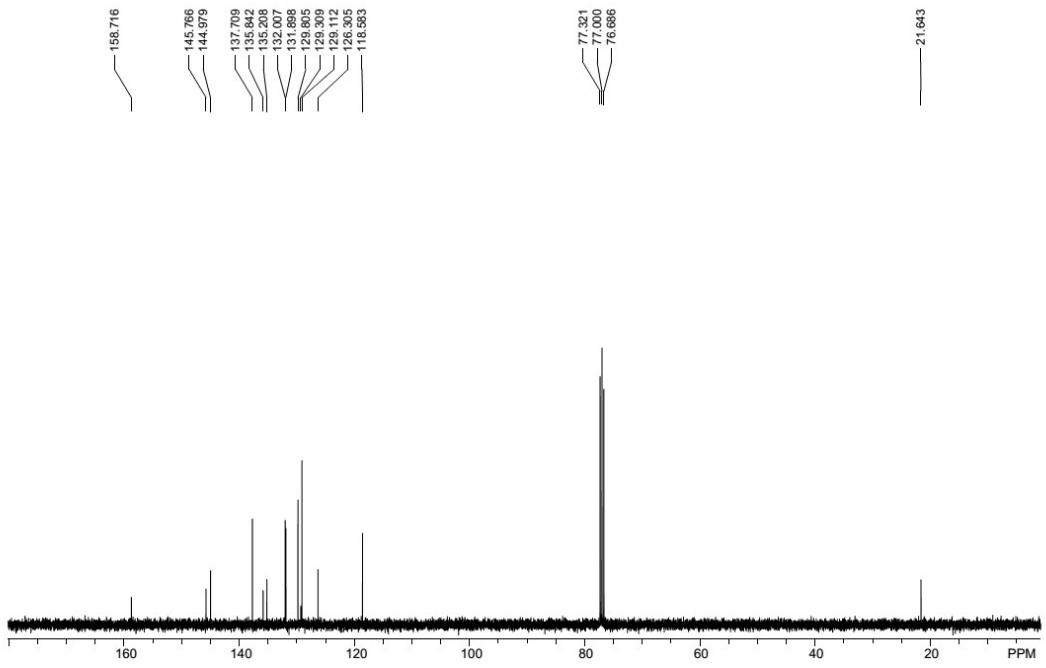
6-fluoro-2-tosylquinoline (3am)



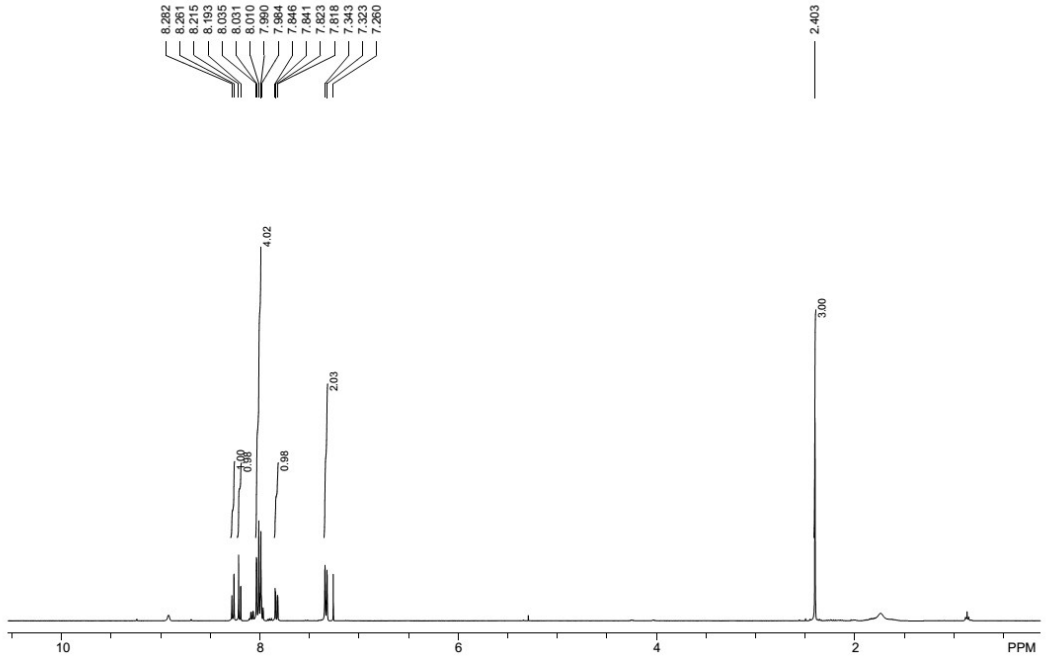


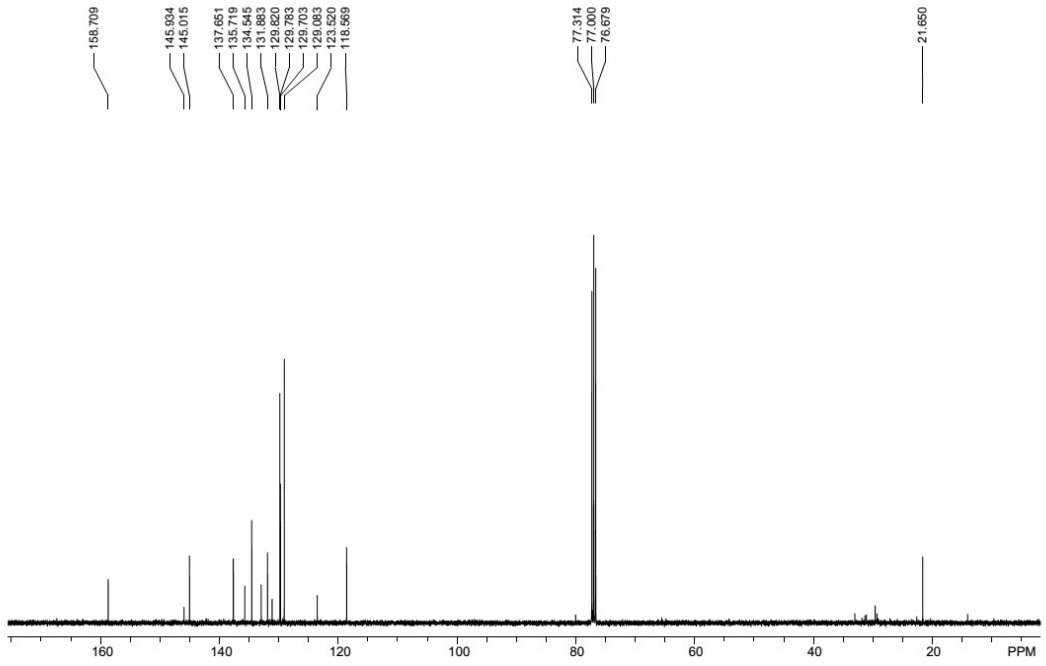
6-chloro-2-tosylquinoline (3an)



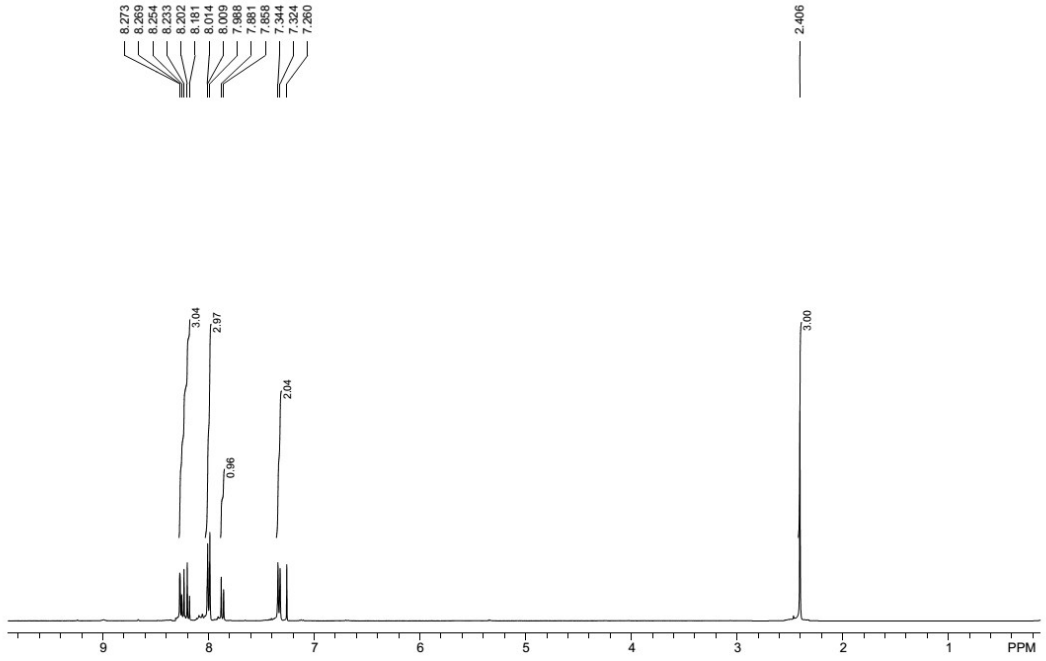


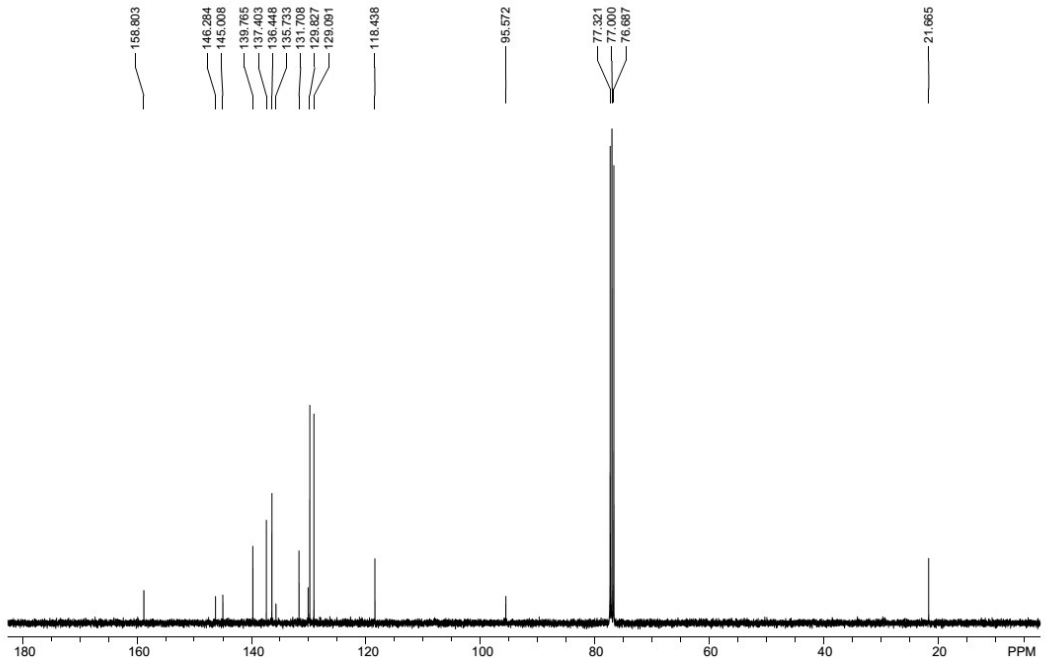
6-bromo-2-tosylquinoline (3ao)



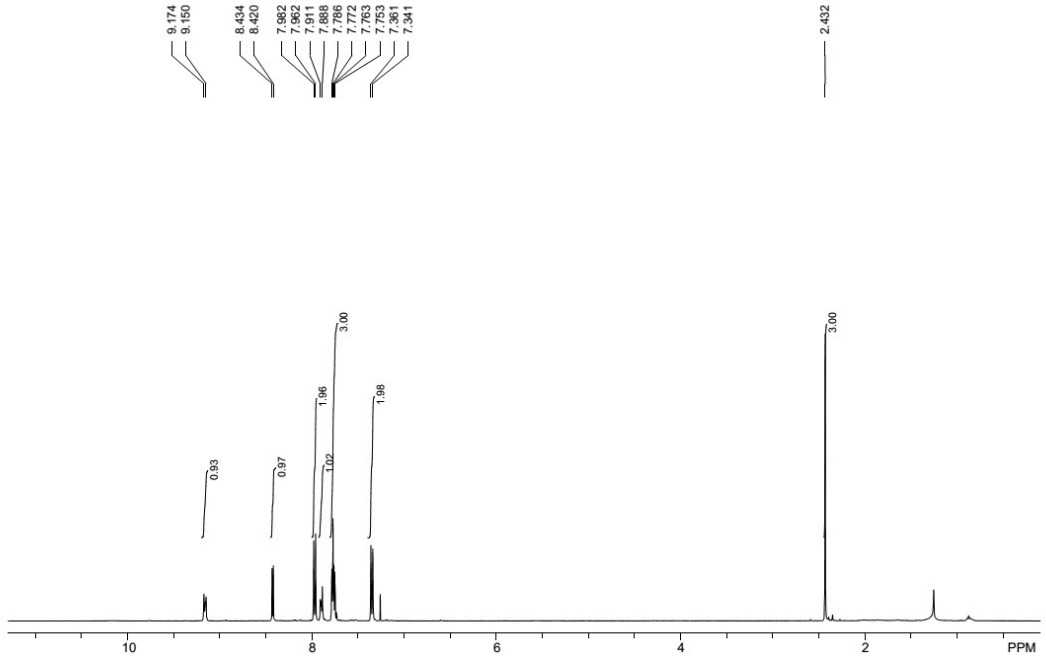


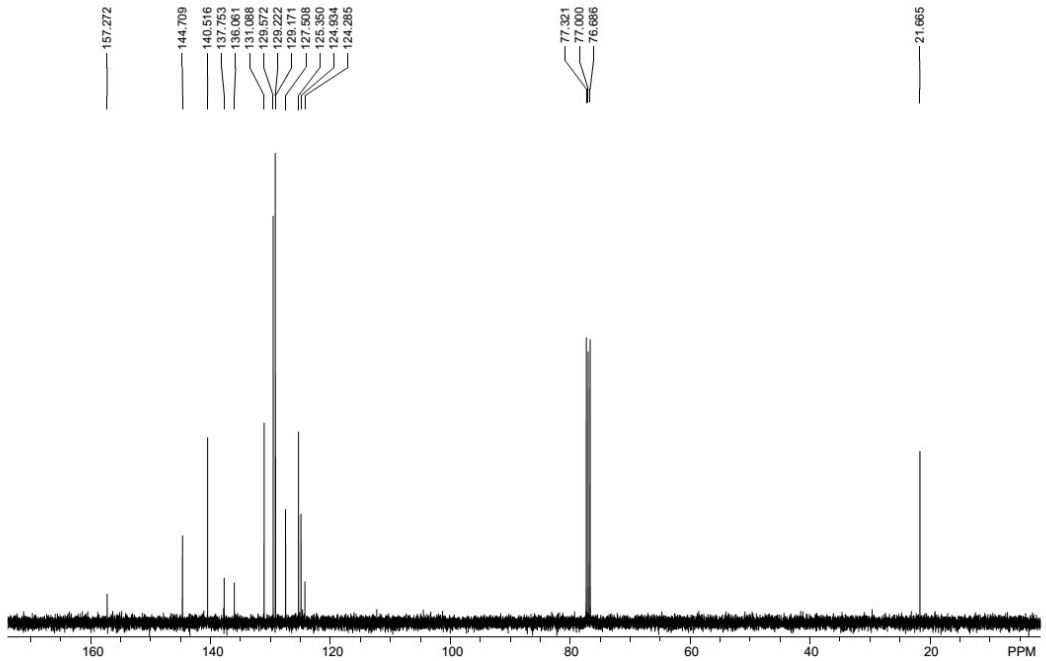
6-iodo-2-tosylquinoline (3ap)



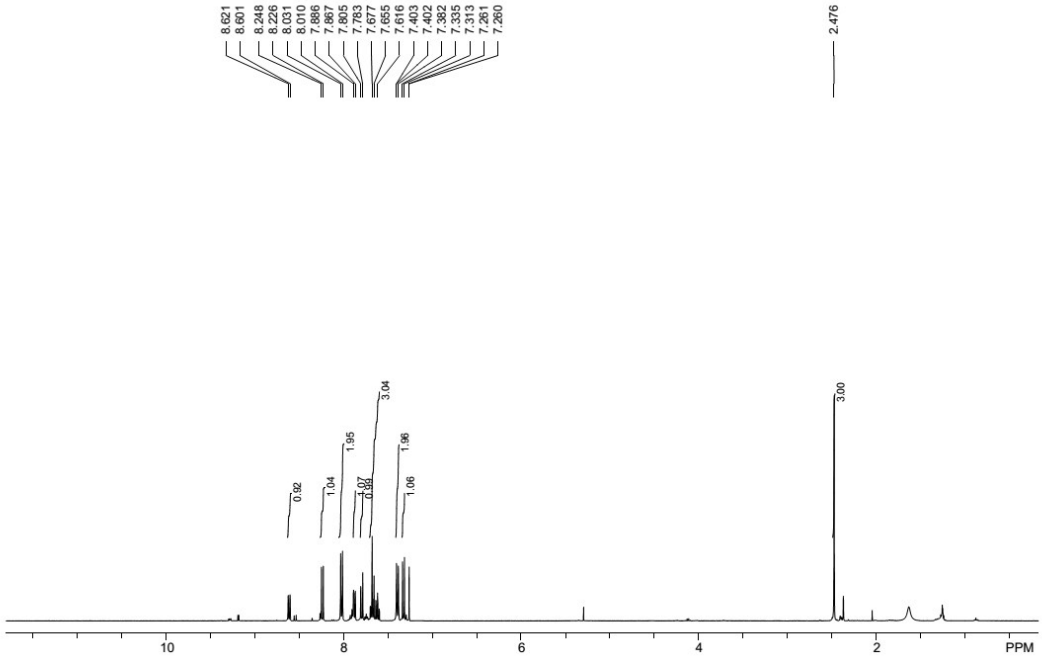


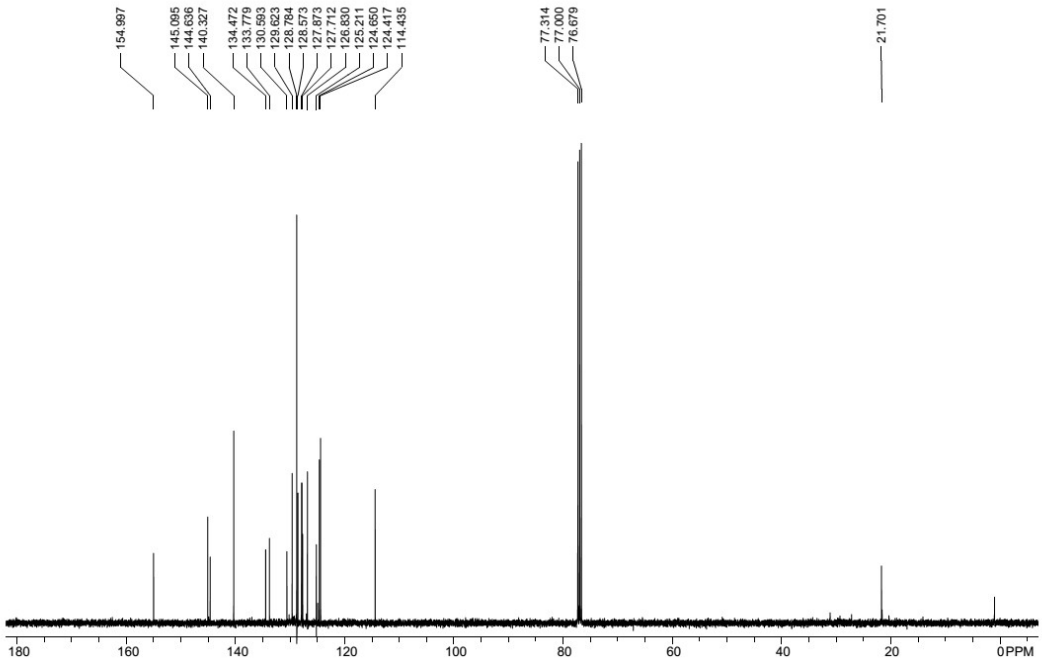
1-tosylisoquinoline (3aq)



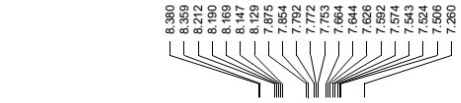


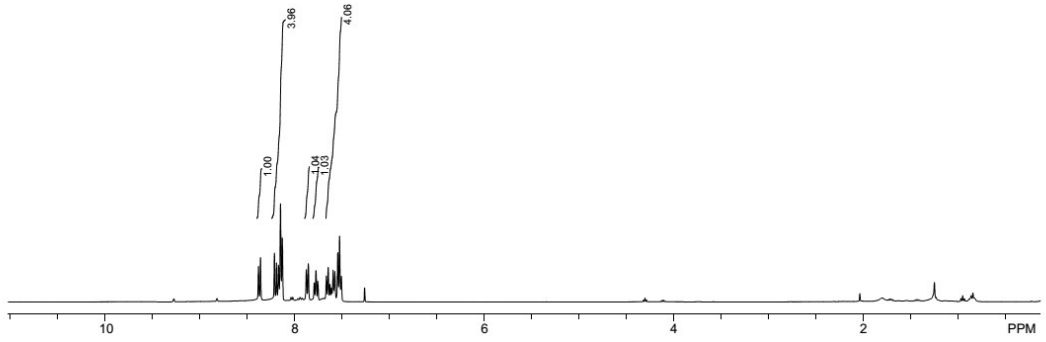
2-tosylbenzo[h]quinoline (3ar)

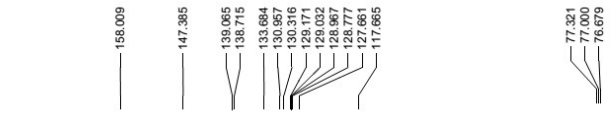


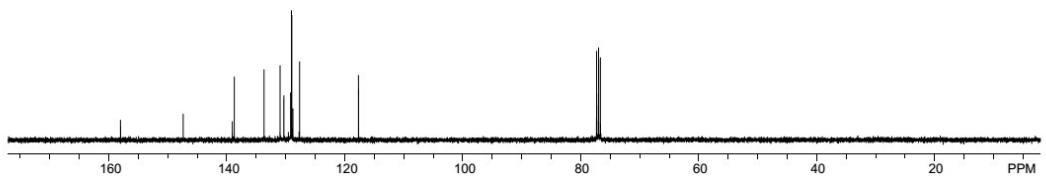


2-(phenylsulfonyl)quinoline (3ba)

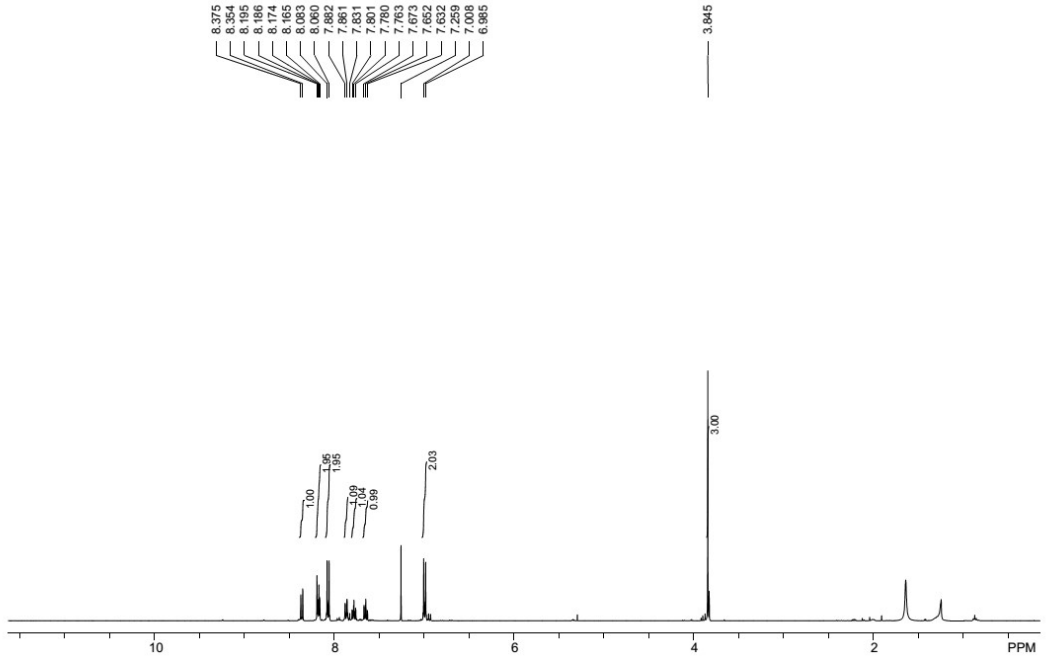


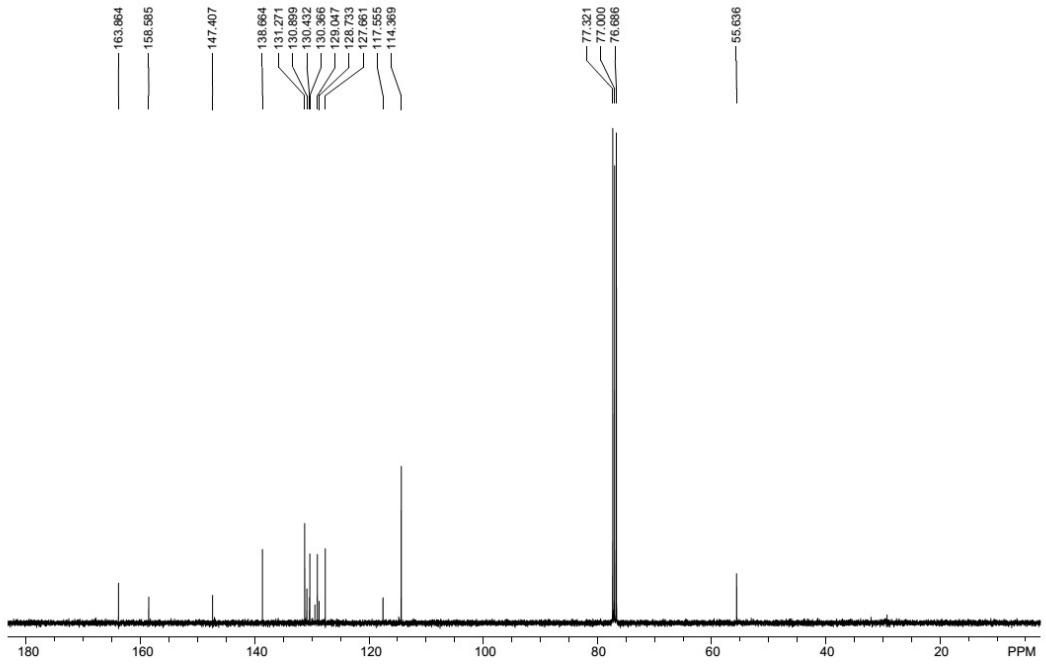




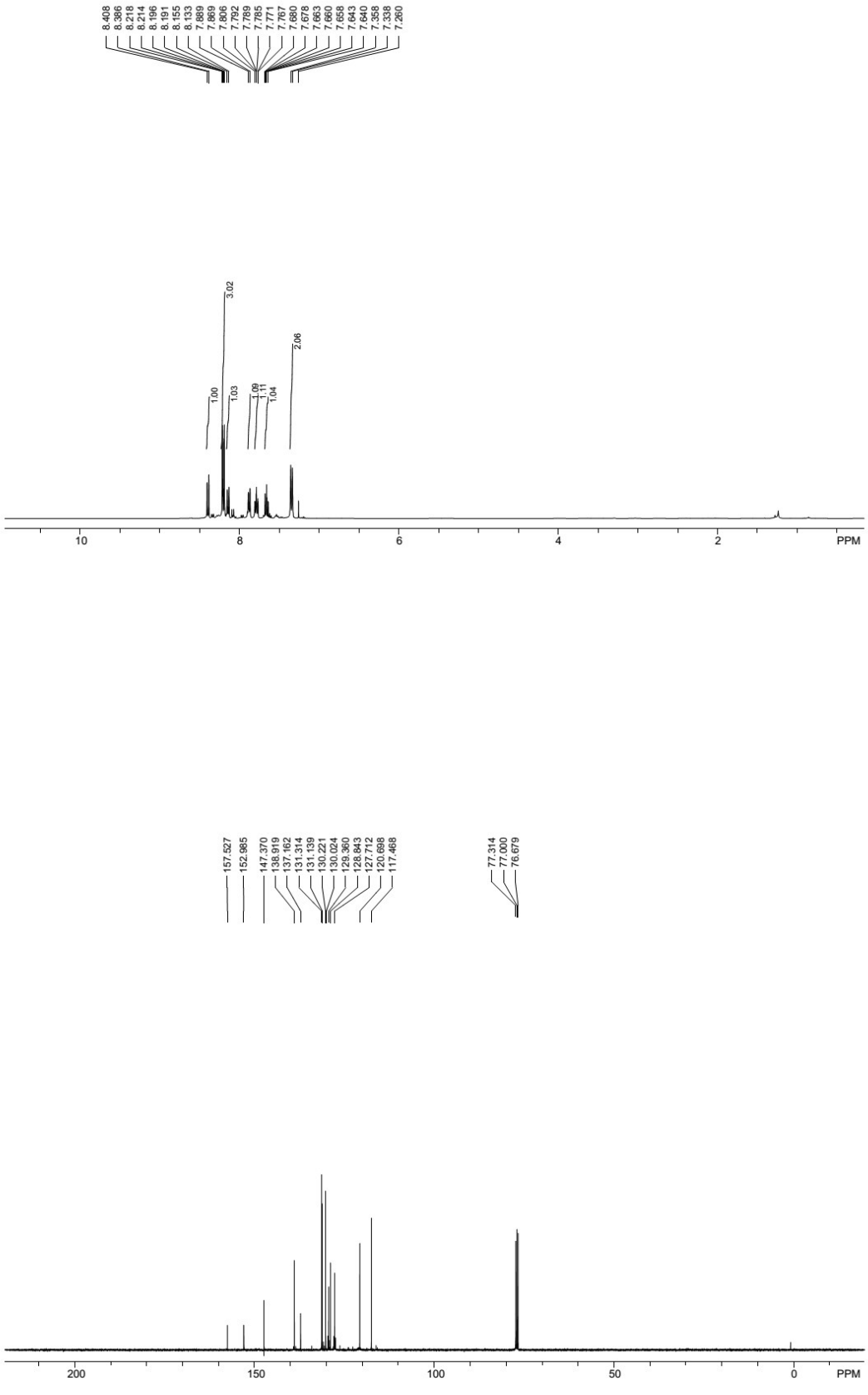


2-((4-methoxyphenyl)sulfonyl)quinoline (3ca)

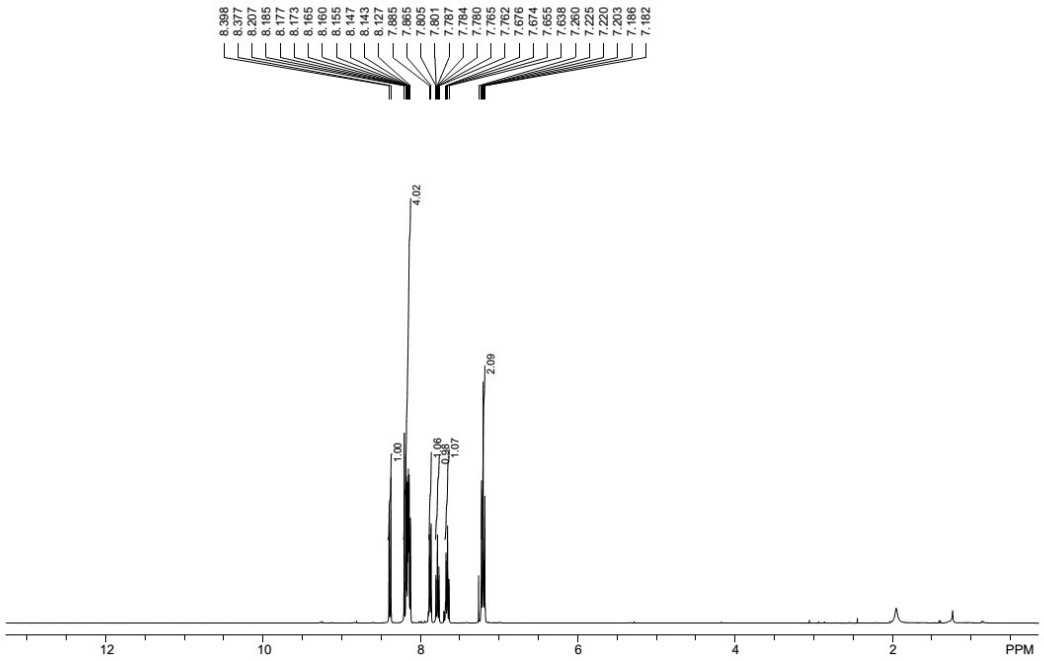


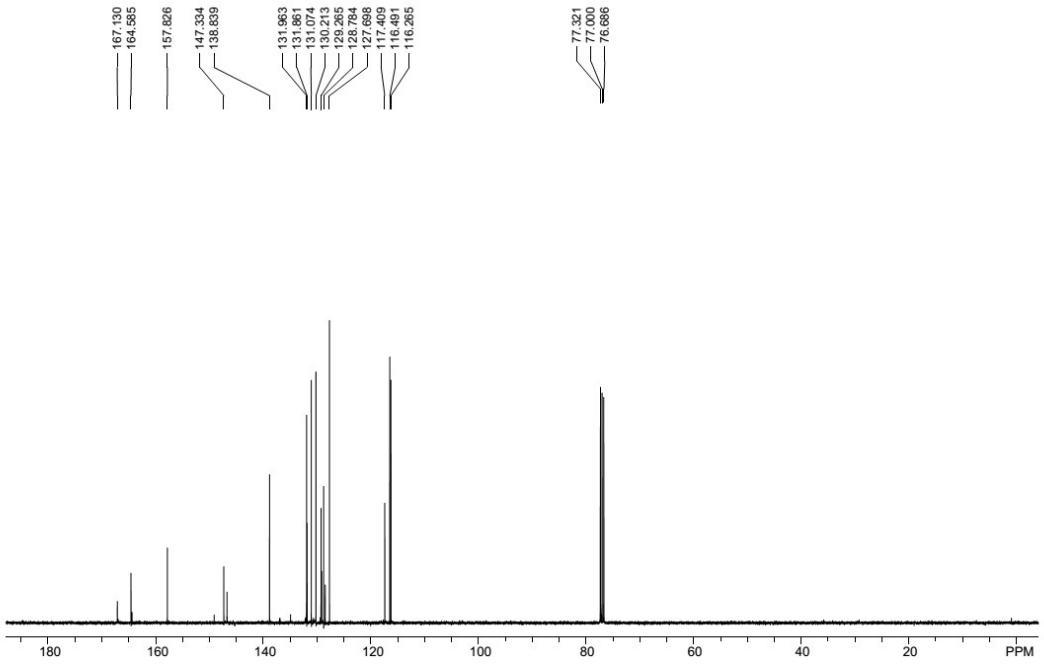


2-((4-(trifluoromethoxy)phenyl)sulfonyl)quinolone (3da)

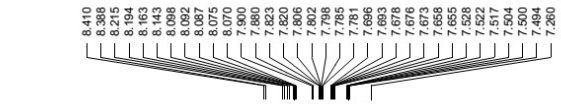


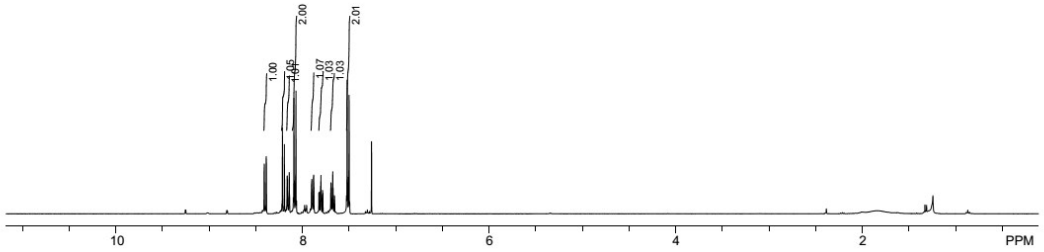
2-((4-fluorophenyl)sulfonyl)quinoline (3ea)

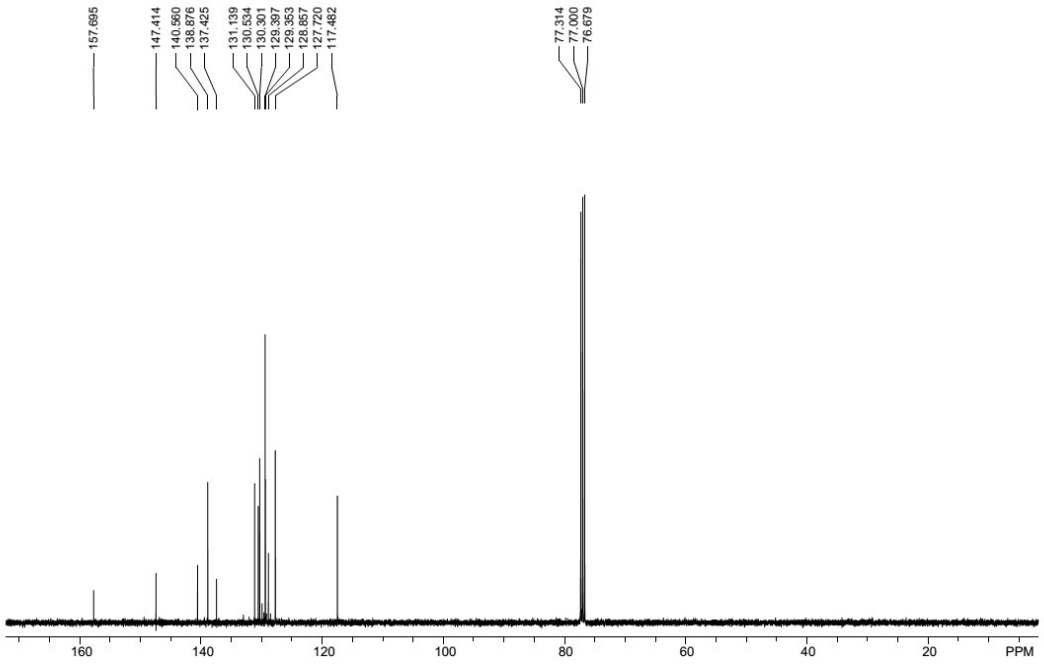




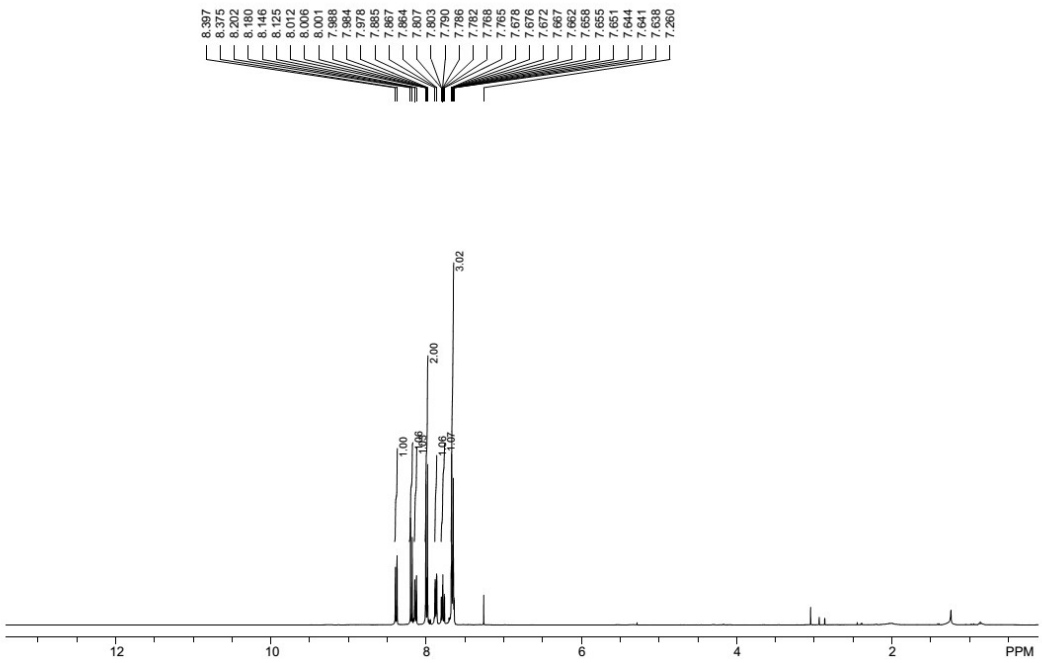
2-((4-chlorophenyl)sulfonyl)quinoline (3fa)

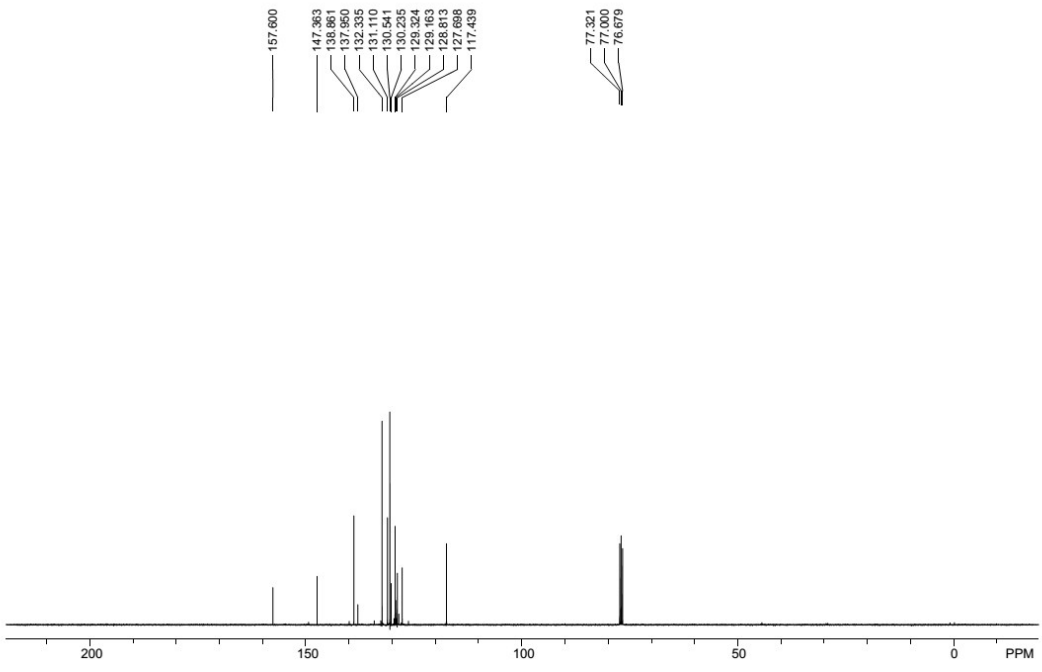




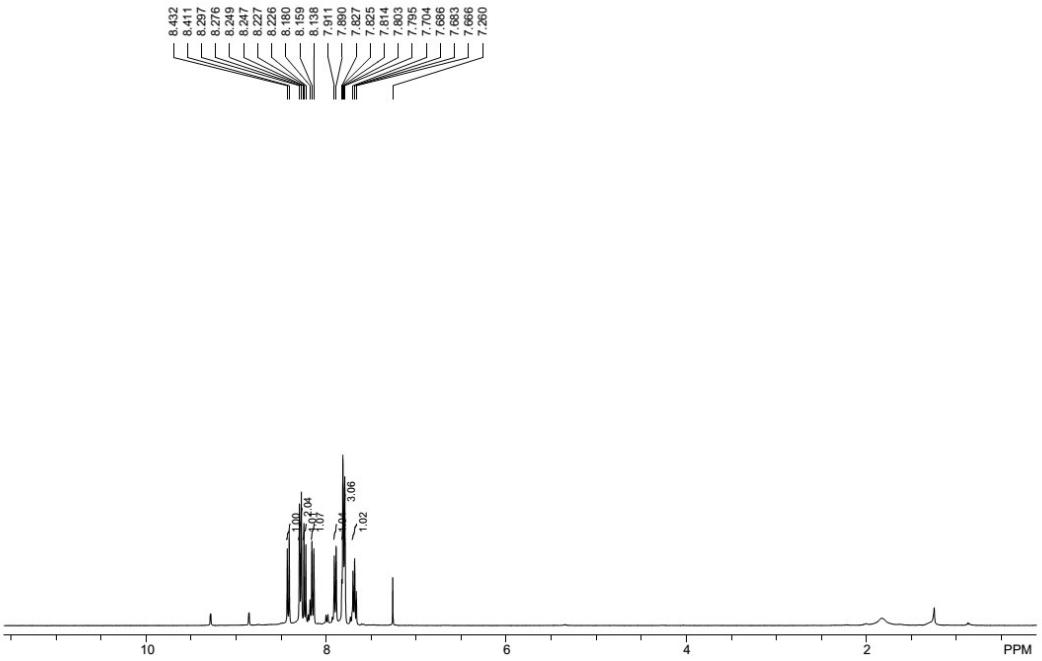


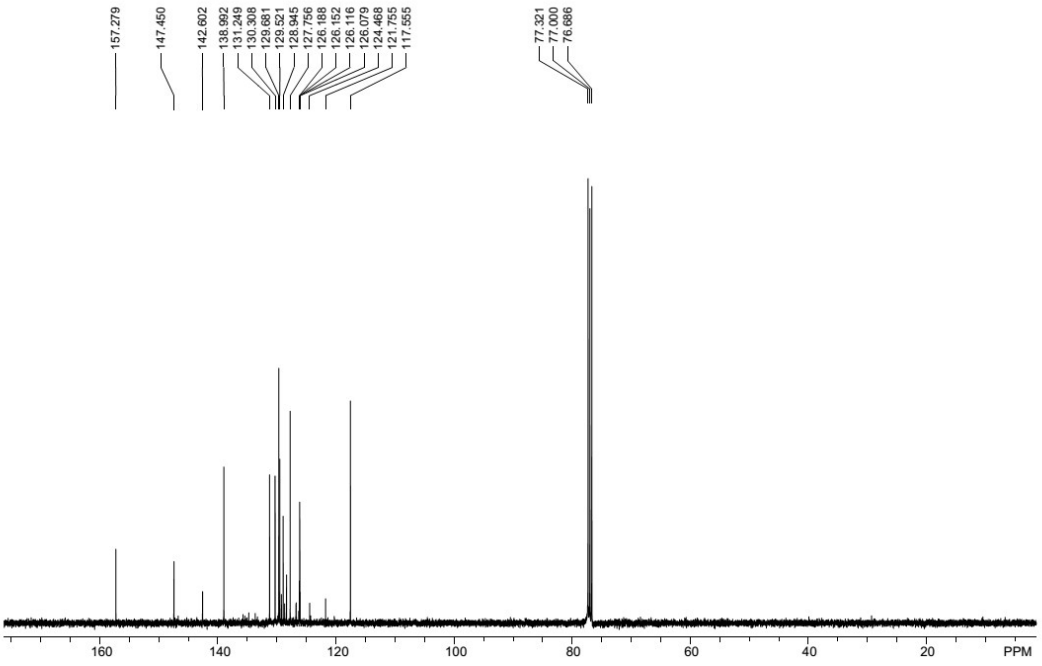
2-((4-bromophenyl)sulfonyl)quinolone (3ga)



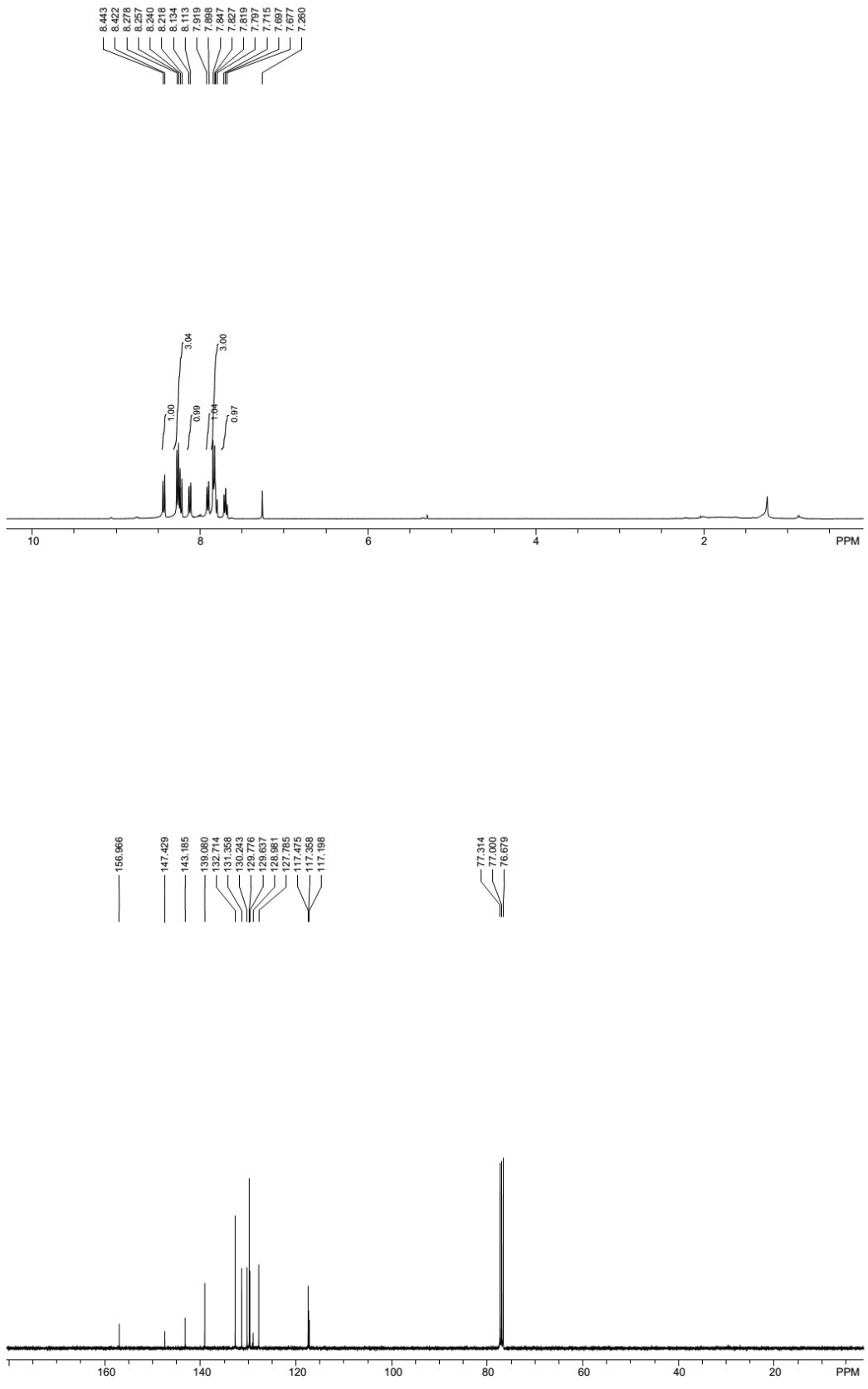


2-((4-(trifluoromethyl)phenyl)sulfonyl)quinoline (3ha)

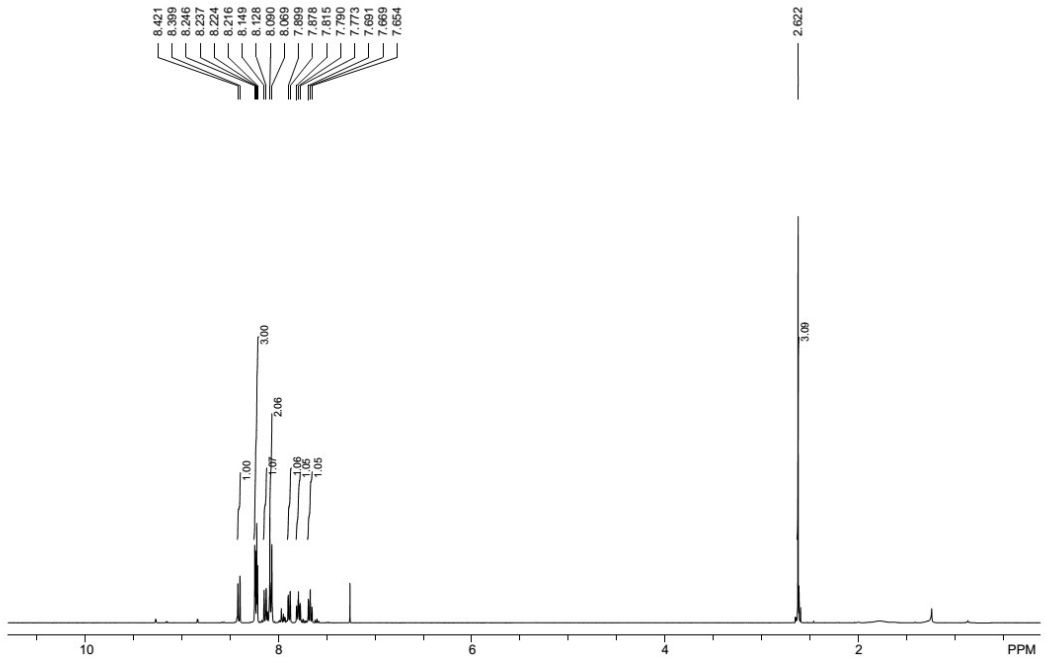


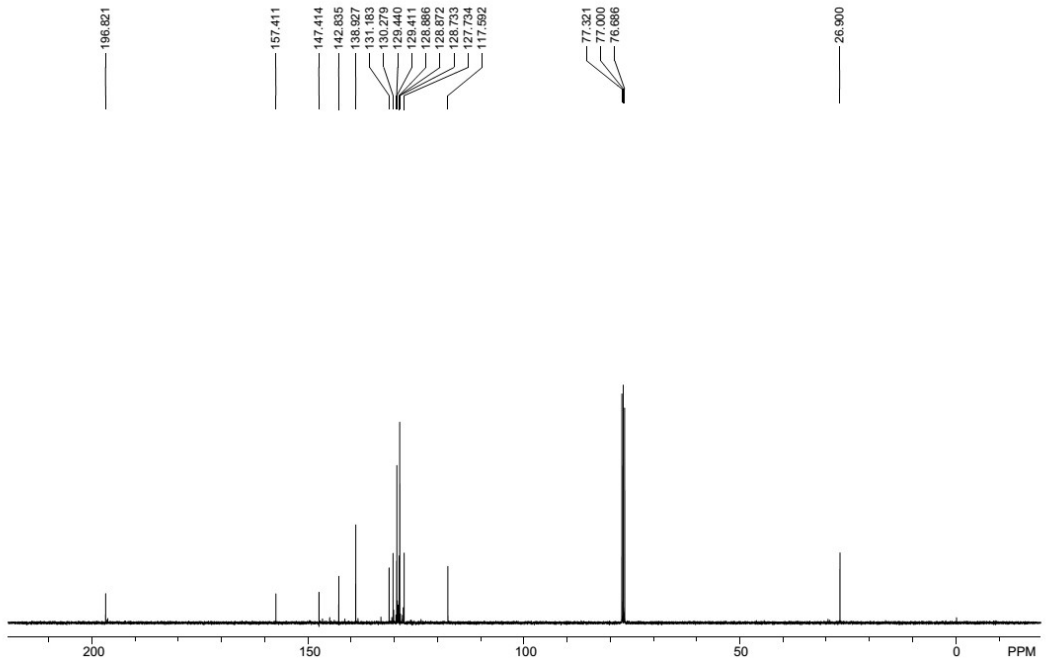


4-(quinolin-2-ylsulfonyl)benzonitrile (3ia)

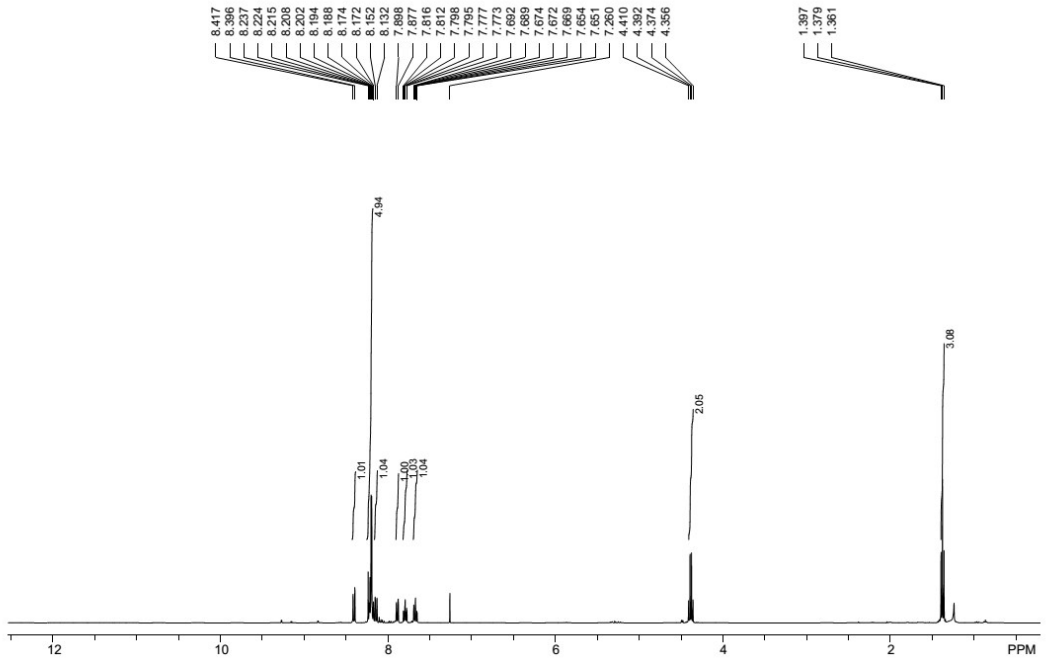


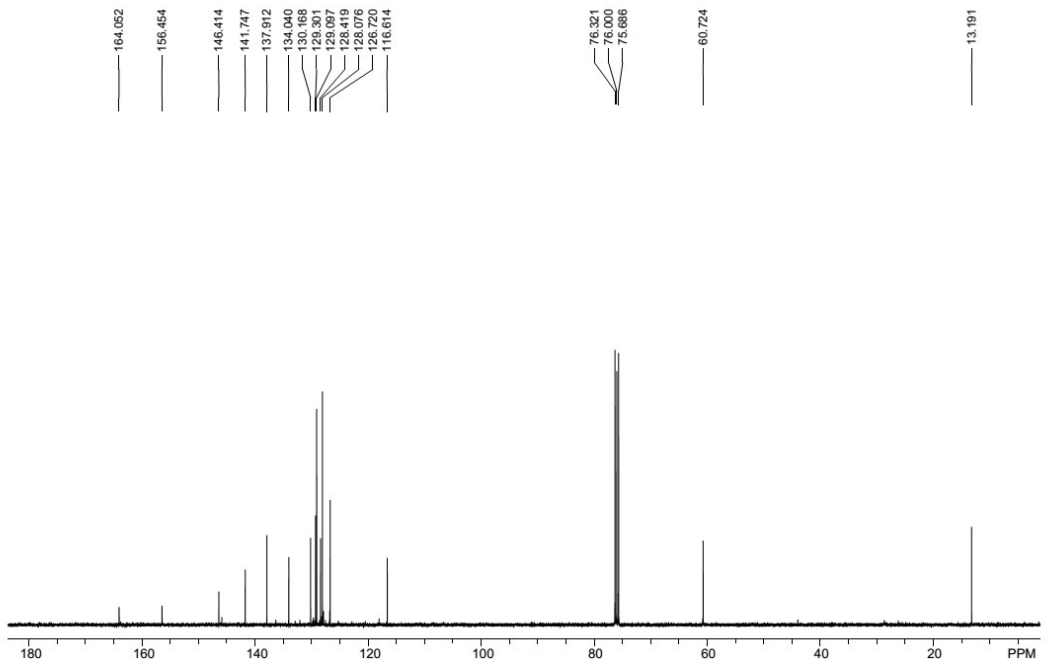
1-(4-(quinolin-2-ylsulfonyl)phenyl)ethanone (3ja)



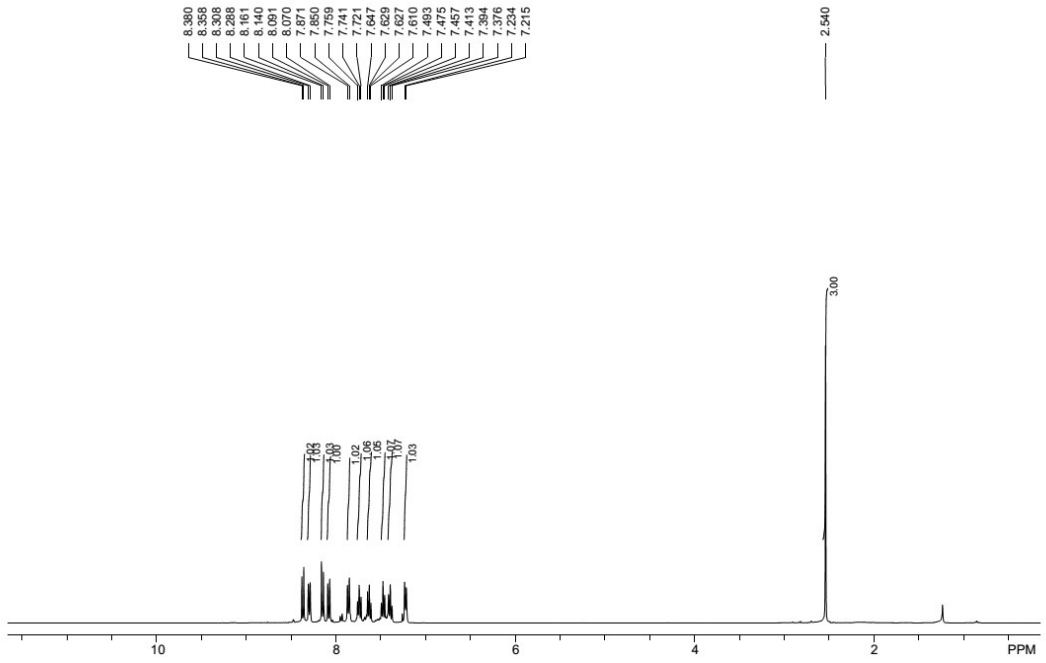


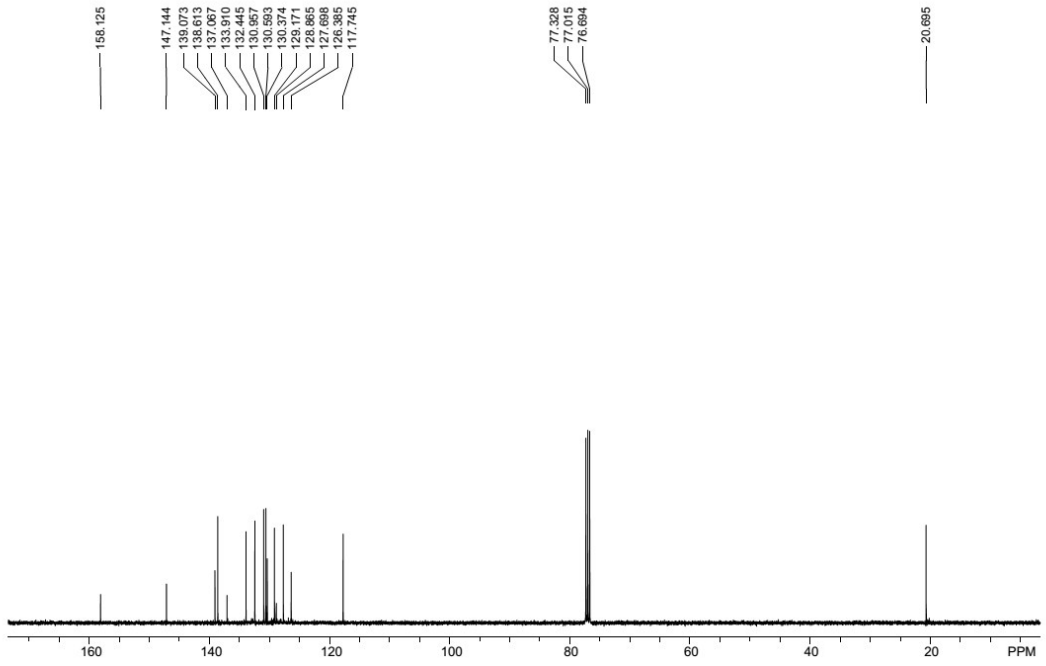
ethyl 4-(quinolin-2-ylsulfonyl)benzoate (3ka)



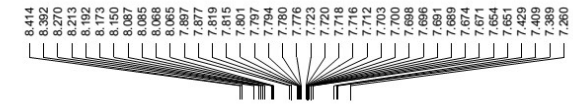


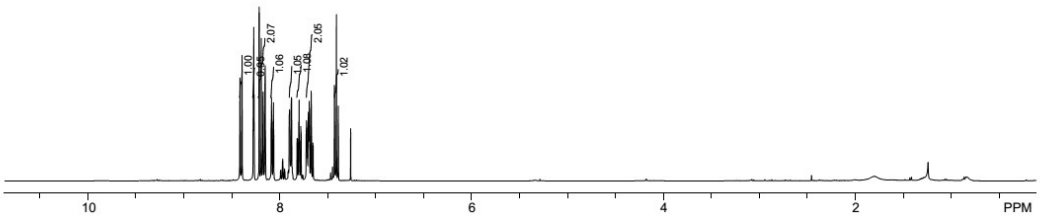
2-(o-tolylsulfonyl)quinoline (3la)

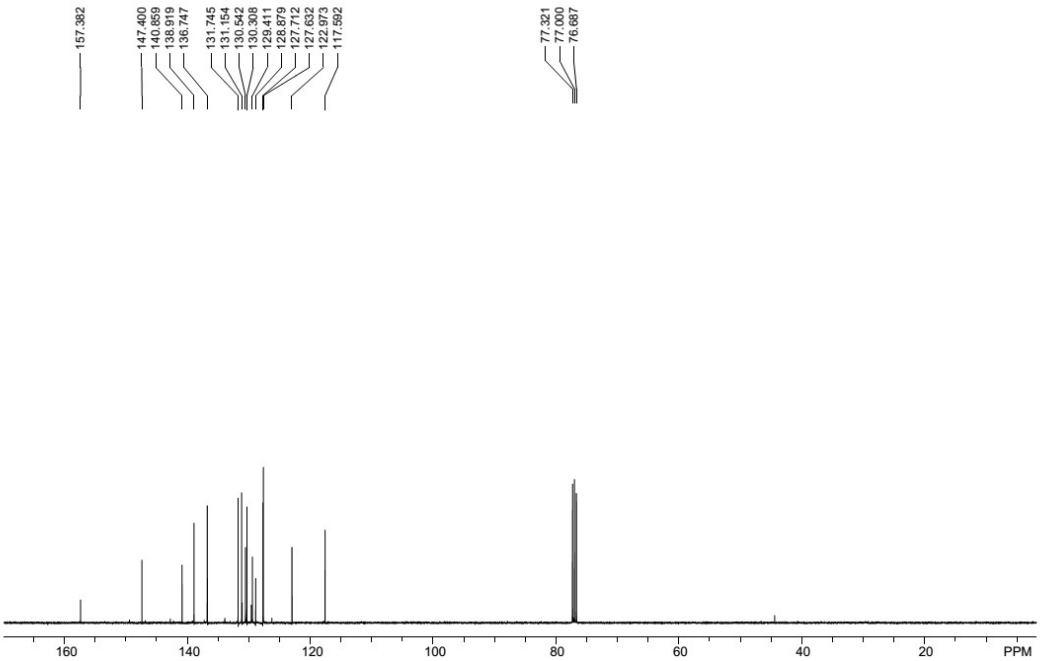




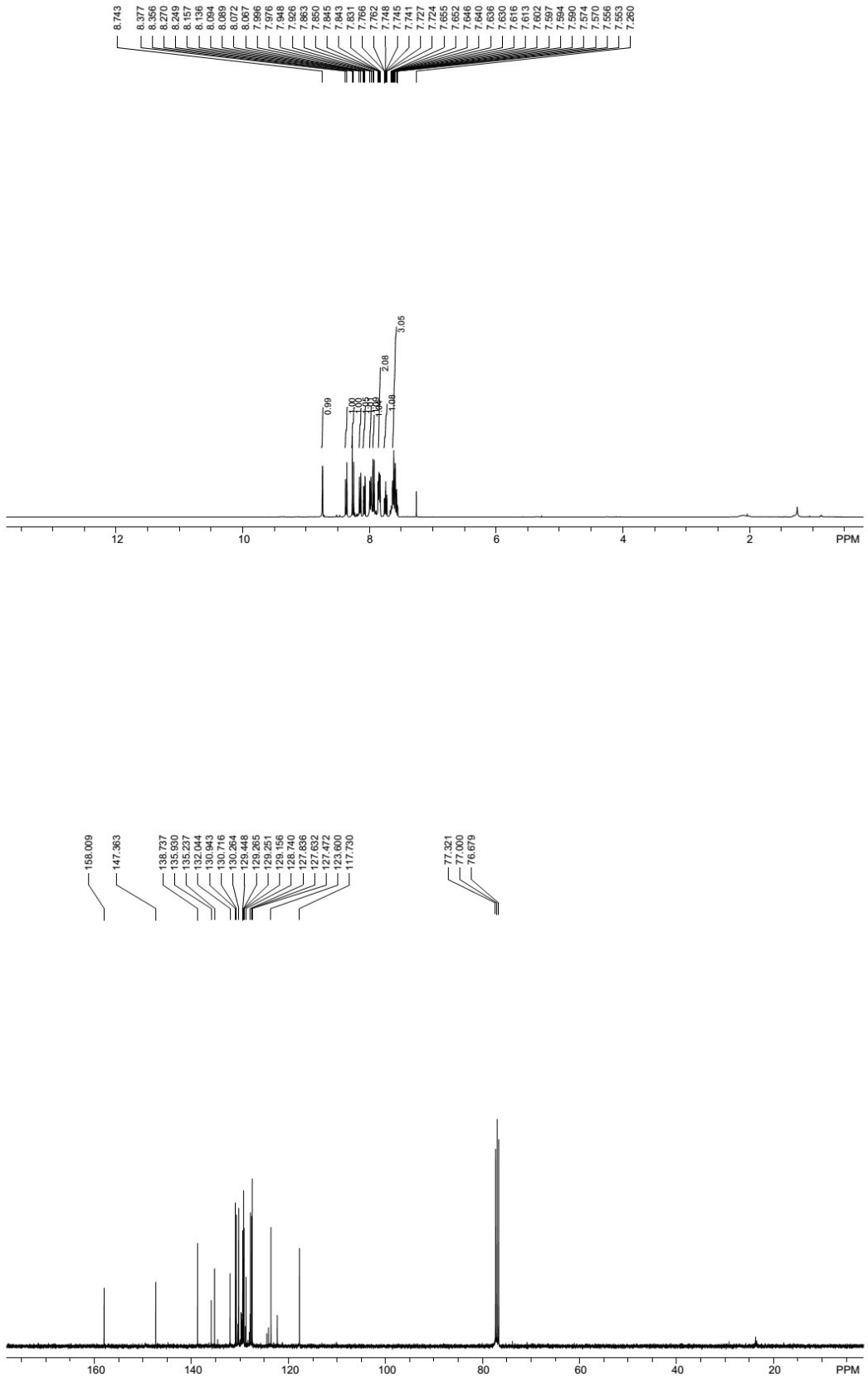
2-((3-bromophenyl)sulfonyl)quinoline (3ma)







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



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