Electronic Supplementary Material (ESI) for RSC Advances.

Cobalt(II)-Catalyzed Remote C5-Selective C-H Sulfonylation of Quinolines via Insertion of Sulfur Dioxide

Kai Wang, Guodong Wang, Guiyun Duan and Chengcai Xia*

Pharmacy College, Taishan Medical University, Taian 271016 (China).

E-mail: xiachc@163.com

Supporting Information

Table of contents

1. General Information

All the chemicals were obtained commercially and used without any prior purification. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90°C) and ethyl acetate. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Advance 500 spectrometer at ambient temperature with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. The small-angle X-ray diffraction(SAXRD) data was taken on a German Bruker D4 X-ray diffractometer. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates.

2. Experimental Section

General procedure for the preparation of aryl diazonium tetrafluoroborates

The appropriate aniline (10.0 mmol) was dissolved in a mixture of 4.0 mL of distilled water and 3.4 mL of 50% hydrofluoroboric acid. After the reaction mixture was cooling to 0 °C using ice bath and the sodium nitrite (690 mg in 1.5 mL H_2O) was added dropwise in 5 min interval of time. The resulting mixture was stirred for 40 min and the precipitate was collected by filtration and re-dissolved in minimum amount of acetone. Diethyl ether was added until precipitation of diazonium tetrafluoroborate, it was filtered and washed with diethyl ether and dried under vacuum.

General procedure for the synthesis of compounds 3

A mixture of **1** (49.6 mg, 0.2 mmol), DABCO•$(SO_2)_2$ (57.6 mg, 1.2 eq.), **2** (1.2 eq.), $Co(acac)_2$ (5.0 mg, 10 mol%) in 1,2-dichloroethane (1.0 mL) was stirred at 50 ^{o}C under N_2 atmosphere for 12 h. Then the mixture was cooled to room temperature and poured into water (5.0 mL), extracted with EtOAc (5.0 mL x 3), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The products **3** were purified by flash column chromatography using PE/AcOEt as an eluent.

General procedure for gram-scale synthesis of compound 3a

A mixture of **1a** (1.2 g, 5.0 mmol), DABCO•$(SO_2)_2$ (1.4 g, 1.2 eq.), **2a** (1.2 g, 1.2 eq.), $Co(acac)_2$ (129.0 mg, 10 mol%) in 1,2-dichloroethane (20.0 mL) was stirred at 50 ^{o}C under N_2 atmosphere for 12 h. Then the mixture was cooled to room temperature and poured into water (100.0 mL), extracted with EtOAc (50.0 mL x 3), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The products **3a** were

purified by flash column chromatography using PE/AcOEt as an eluent.

General procedure for synthesis of compounds 4a

A mixture of **3a** (402 mg, 1.0 mmol), concentrated hydrochloric acid (2.5 mL) and EtOH (5.0 mL) was stirred at 100 ^{o}C for 12 h. After completion, the mixture was cooled to room temperature and neutralized with NaOH aqoeous solution. Then extracted with EtOAc (10.0 mL). The collected organic layer was washed with brine (10.0 mL), dried with $MgSO_4$, and filtered through a pad of Celite gradually. The solvent was removed under reduced pressure, and the gathered residue was then purified by silica gel column chromatography using PE/AcOEt as an eluent.

General procedure for the synthesis of compounds 3 by using anilines as the starting materials

^{t}BuONO (0.48 mmol) was added dropwise to a solution of arylamine **5** (0.4 mmol) and $BF_3 \cdot Et_2O$ (0.36 mmol) in 1,2-dichloroethane (1.0 mL) under 0 ^{o}C. After 10 min, the above mixture was added to a solution of quinoline amides **1** (0.2 mmol), $Co(acac)_2$ (5.0 mg, 10 mol%) and DABCO•$(SO_2)_2$ (57.6 mg, 0.24 mmol) in 1,2-dichloroethane (1.0 mL) under N_2 protection. The reaction was heated to 50 ^{o}C for 12 h. Then the mixture was cooled to room temperature and poured into water (5.0 mL), extracted with EtOAc (5.0 mL x 3), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The products **3** were purified by flash column chromatography using PE/AcOEt as an eluent.

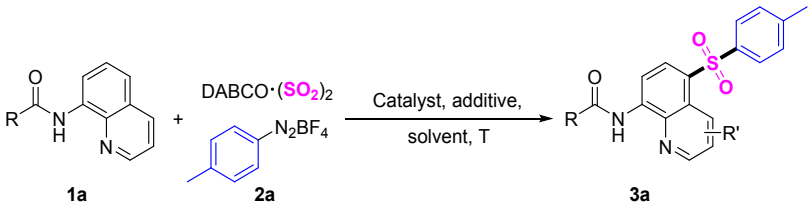
General procedure for synthesis of compounds 1a-D2

To a 50 mL schlenk tube with 8-aminoquinoline (288.0 mg, 2.0 mmol) was added conc. DCl in D_2O (1 equiv, 2.0 mL). Then the tube was capped and sealed. Upon completion of the reaction for 12 h at 150 ^{o}C, the mixture was cooled to room temperature and diluted with water (25 mL). After extracting with EtOAc (10 mL x 3), the combined organic layer was gradually washed with 1 M $NaHCO_3$ aqueous solution (3 x 15 mL) and brine (50 mL), dried with Na_2SO_4, and filtered through a pad of Celite. The solvent was removed under reduced pressure to afford the deuterated 8-aminoquinoline. Note that the deuterated 8-aminoquinoline was used without any purification in the following step.

To a 100 mL single-neck flask charged with CH_2Cl_2 (6 mL) were added deuterated 8-

aminoquinoline (2 mmol) and triethylamine (3 mmol). After stirring at room temperature for 5 min, the reaction solution was cooled in an ice bath. Benzoyl chloride (2.1 mmol) was added dropwise. Then the reaction solution was stirred overnight to improve the yield. The mixture was filtered through a pad of Celite, and the residue was washed with CH_2Cl_2 (5 mL) subsequently. The collected CH_2Cl_2 solution was washed with 1 M $NaHCO_3$ aqueous solution for three times. After that, the organic layer was collected and dried over Na_2SO_4. The solvent was removed by rotary-evaporation. The raw product was then purified by silica gel column with a mixture solvent of PE/EtOAc (v/v; 20:1) as the eluent.

3. Screening of reaction conditions for sulfonylationa



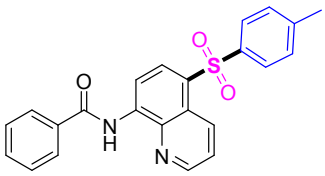
1a 2a 3a

Entry	Catalyst	Additive	Solvent	Yield [%][b]
1	$Cu(OTf)_2$	Na_2CO_3	DCE	31
2	$Cu(acac)_2$	Na_2CO_3	DCE	69
3	-	Na_2CO_3	DCE	0
4	$Cu(acac)_2$	K_2CO_3	DCE	62
5	$Cu(acac)_2$	$NaHCO_3$	DCE	65
6	$Cu(acac)_2$	*t*-BuOK	DCE	trace
7	$Cu(acac)_2$	AcOH	DCE	50
8	**$Cu(acac)_2$**	**-**	**DCE**	**83**(40)[c]
9	$Cu(acac)_2$	-	dioxane	41
10	$Cu(acac)_2$	-	MeCN	31
11	$Cu(acac)_2$	-	toluene	trace
12	$Cu(acac)_2$	-	DMF	trace
13	$Cu(acac)_2$	-	NMP	trace
14[d]	$Cu(acac)_2$	-	DCE	48
15[e]	$Cu(acac)_2$	-	DCE	58
16[f]	$Cu(acac)_2$	-	DCE	82

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (10 mol%), DABCO·$(SO_2)_2$ (1.2 eq.), **2a** (1.2 eq.), DCE (1.0 mL), stirred at 50 °C, under N_2, 12 h. [b] Isolated yields. [c] DABCO·$(SO_2)_2$ (0.6 eq.), [d] Under air. [e] Stirred at rt. [f] Stirred at 80 °C.

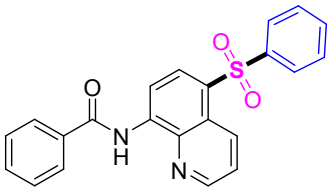
4. Characterization of the products

***N*-(5-tosylquinolin-8-yl)benzamide (3a)**



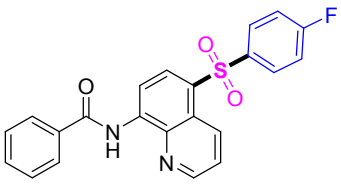
This compound is known;[1] white solid, 64 mg (80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 9.10 (d, *J* = 8.7 Hz, 1H), 9.04 (d, *J* = 8.4 Hz, 1H), 8.88 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.1 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 9.8, 5.7 Hz, 2H), 7.57 (t, *J* = 6.8 Hz, 2H), 7.28 (s, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.69, 148.72, 144.15, 139.94, 139.11, 138.50, 134.41, 133.64, 132.44, 132.08, 129.91, 129.48, 128.97, 127.43, 127.32, 124.34, 123.31, 114.34, 21.52.

***N*-(5-(phenylsulfonyl)quinolin-8-yl)benzamide (3b)**



This compound is known;[2] white solid, 60 mg (77%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 9.07 (dd, *J* = 16.1, 8.5 Hz, 2H), 8.88 (s, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.64 – 7.52 (m, 5H), 7.50 – 7.46 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.68, 148.79, 142.07, 140.13, 138.50, 134.36, 133.50, 133.14, 132.45, 132.34, 129.28, 128.99, 128.97, 127.42, 127.21, 124.37, 123.39, 114.27.

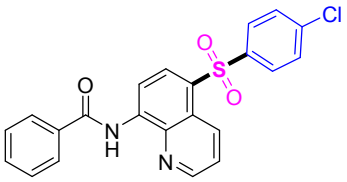
***N*-[5-(4-Fluoro-benzenesulfonyl)-quinolin-8-yl]-benzamide (3c)**



This compound is known;[2] white solid, 59 mg (73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.05 (d, *J* = 8.5 Hz, 2H), 8.90 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 2H), 7.98 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.61 (dd, *J* = 8.0, 3.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.33, 165.51 (d. *J* = 257.0 Hz), 148.87,

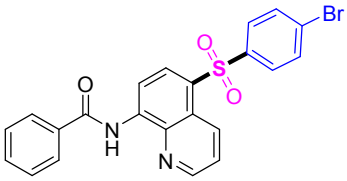
140.25, 138.49, 138.04 (d. J = 2.5 Hz), 134.26, 133.29, 132.54, 132.38, 130.05 (d. J = 10.1 Hz), 129.00, 128.70, 127.43, 124.23, 123.52, 116.64 (d. J = 22.7 Hz), 114.26.

***N*-(5-((4-chlorophenyl)sulfonyl)quinolin-8-yl)benzamide (3d)**



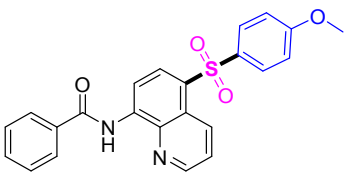
This compound is known;[2] white solid, 60 mg (71%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.05 (d, J = 8.4 Hz, 1H), 9.03 (dd, J = 8.7, 1.4 Hz, 1H), 8.89 (dd, J = 4.1, 1.3 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.2 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.56 (t, J = 7.4 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.79, 148.98, 146.63, 140.59, 140.44, 139.91, 138.54, 134.32, 133.33, 132.62, 129.71, 129.08, 128.76, 128.46, 127.51, 124.33, 123.65, 114.34.

***N*-[5-(4-Bromo-benzenesulfonyl)-quinolin-8-yl]-benzamide (3e)**



This compound is known;[3] white solid, 70 mg (75%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.97 (s, 1H), 9.04 (t, J = 9.4 Hz, 2H), 8.89 (dd, J = 4.2, 1.4 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H), 8.08 – 8.05 (m, 2H), 7.81 (d, J = 8.7 Hz, 2H), 7.61 (dd, J = 8.7, 3.2 Hz, 4H), 7.56 (t, J = 7.3 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.68, 148.88, 141.14, 140.39, 138.49, 134.28, 133.26, 132.59, 132.56, 132.51, 128.98, 128.72, 128.37, 128.34, 127.42, 124.29, 123.53, 114.27.

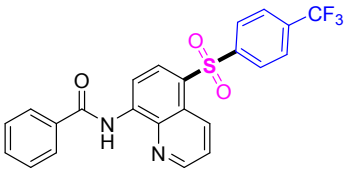
***N*-(5-((4-methoxyphenyl)sulfonyl)quinolin-8-yl)benzamide (3f)**



This compound is known;[3] white solid, 68 mg (81%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 9.09 (dd, J = 8.7, 1.6 Hz, 1H), 9.02 (d, J = 8.4 Hz, 1H), 8.87 (dd, J = 4.2, 1.5 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 8.08 – 8.05 (m, 2H), 7.90 – 7.88 (m, 2H), 7.62 – 7.55 (m, 4H), 6.95 – 6.92 (m, 2H), 3.81 (s, 3H).

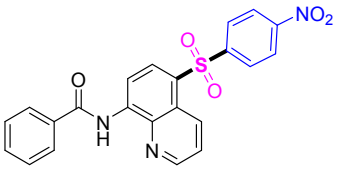
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.69, 163.31, 148.75, 139.79, 138.51, 134.36, 133.56, 133.42, 132.46, 131.75, 129.83, 129.53, 128.98, 127.42, 124.19, 123.34, 114.53, 114.26, 55.67.

***N*-(5-((4-(trifluoromethyl)phenyl)sulfonyl)quinolin-8-yl) benzamide (3g)**



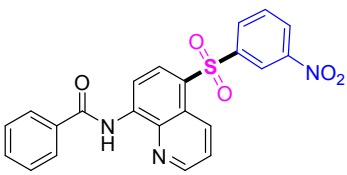
This compound is known;[2] white solid, 60 mg (65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.08 (d, J = 8.4 Hz, 1H), 9.04 (d, J = 7.9 Hz, 1H), 8.90 (dd, J = 4.2, 1.4 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.08 (t, J = 8.6 Hz, 4H), 7.74 (d, J = 8.3 Hz, 2H), 7.62 (dt, J = 10.7, 4.6 Hz, 2H), 7.57 (t, J = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.72, 148.99, 145.58, 140.68, 138.44, 134.78 (q, J = 33.0 Hz), 134.17, 133.11, 133.03, 132.59, 129.01, 127.72, 127.62, 127.43, 126.48 (q, J = 3.6 Hz), 124.34, 123.72, 123.03 (q, J = 271.4 Hz), 114.27.

***N*-(5-((4-nitrophenyl)sulfonyl)quinolin-8-yl)benzamide (3h)**



This compound is known;[4] yellow solid, 64 mg (62%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.00 (s, 1H), 9.10 (d, J = 8.5 Hz, 1H), 9.03 (dd, J = 8.7, 1.4 Hz, 1H), 8.92 (dd, J = 4.2, 1.4 Hz, 1H), 8.63 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.9 Hz, 2H), 8.13 (d, J = 8.9 Hz, 2H), 8.07 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 6.4 Hz, 2H), 7.58 (d, J = 7.7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.73, 150.30, 149.07, 147.81, 141.05, 138.49, 134.17, 133.43, 132.97, 132.63, 129.04, 128.46, 127.45, 127.05, 124.53, 124.41, 123.81, 114.36.

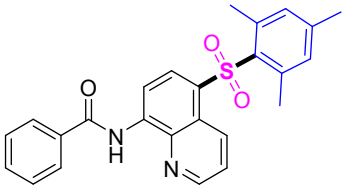
***N*-(5-((3-nitrophenyl)sulfonyl)quinolin-8-yl)benzamide (3i)**



This compound is known;[2] yellow solid, 60 mg (69%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.99 (s, 1H), 9.09 (d, J = 8.5 Hz, 1H), 9.07 (dd, J = 8.8,

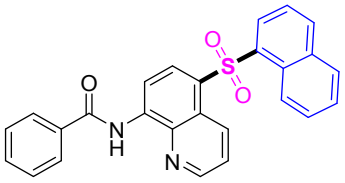
1.4 Hz, 1H), 8.92 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.80 (t, *J* = 1.8 Hz, 1H), 8.63 (d, *J* = 8.5 Hz, 1H), 8.37 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 2H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.64 (dd, *J* = 11.4, 6.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.71, 149.08, 148.42, 144.44, 141.00, 138.48, 134.18, 133.38, 132.95, 132.64, 132.61, 130.76, 129.02, 127.61, 127.44, 127.18, 124.36, 123.88, 122.33, 114.36.

***N*-(5-(mesitylsulfonyl)quinolin-8-yl)benzamide (3j)**



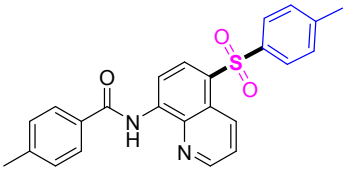
This compound is known;[4] white solid, 27 mg (31%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.95 (s, 1H), 8.94 (d, *J* = 8.4 Hz, 1H), 8.88 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.84 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 3H), 7.63 – 7.59 (m, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.55 – 7.53 (m, 1H), 6.97 (s, 2H), 2.57 (s, 6H), 2.31 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.69, 148.80, 143.58, 140.02, 139.04, 138.44, 134.45, 134.30, 133.31, 132.45, 132.38, 132.08, 129.35, 128.94, 127.39, 124.04, 123.10, 113.78, 22.80, 21.04.

***N*-(5-(naphthalen-1-ylsulfonyl)quinolin-8-yl)benzamide (3k)**



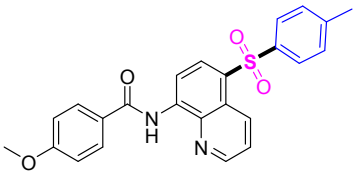
White solid, 55 mg (63%); m.p. 168-169 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.95 (s, 1H), 9.14 (dd, *J* = 8.7, 1.3 Hz, 1H), 9.06 (d, *J* = 8.4 Hz, 1H), 8.83 (dd, *J* = 4.2, 1.3 Hz, 1H), 8.65 – 8.60 (m, 2H), 8.05 (d, *J* = 7.3 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.56 (m, 3H), 7.56 – 7.53 (m, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.65, 148.80, 140.15, 138.92, 138.47, 134.95, 134.32, 133.48, 132.46, 132.42, 132.14, 129.68, 129.37, 129.20, 128.97, 128.50, 127.94, 127.72, 127.65, 127.42, 124.37, 123.44, 122.32, 114.27.

4-methyl-*N*-(5-tosylquinolin-8-yl)benzamide (3l)



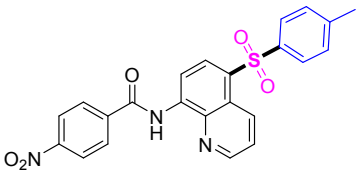
This compound is known;[5] white solid, 68 mg (81%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 9.08 (dd, *J* = 8.7, 1.3 Hz, 1H), 9.03 (d, *J* = 8.4 Hz, 1H), 8.87 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.57 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 5.7 Hz, 2H), 2.45 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.67, 148.69, 144.11, 143.12, 140.09, 139.16, 138.53, 133.57, 132.11, 131.61, 129.90, 129.63, 129.24, 127.46, 127.30, 124.33, 123.28, 114.20, 21.58, 21.52.

4-methoxy-*N*-(5-tosylquinolin-8-yl)benzamide (3m)



This compound is known;[1] white solid, 74 mg (85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.88 (s, 1H), 9.07 (dd, *J* = 8.7, 1.4 Hz, 1H), 9.00 (d, *J* = 8.4 Hz, 1H), 8.85 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.14, 163.03, 148.65, 144.09, 140.18, 139.17, 138.48, 133.51, 132.10, 129.88, 129.37, 129.02, 127.27, 126.60, 124.31, 123.27, 114.18, 114.02, 55.52, 21.50.

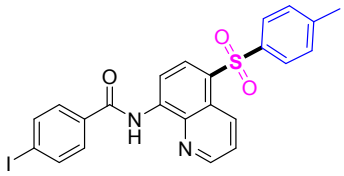
4-nitro-*N*-(5-tosylquinolin-8-yl)benzamide(3n)



This compound is known;[1] yellow solid, 63 mg (70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.03 (s, 1H), 9.12 (dd, *J* = 8.7, 1.4 Hz, 1H), 9.01 (d, *J* = 8.4 Hz, 1H), 8.89 (dd, *J* = 4.2, 1.4 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.84 (s, 2H), 7.62 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.30 (s, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.53, 150.17, 149.01,

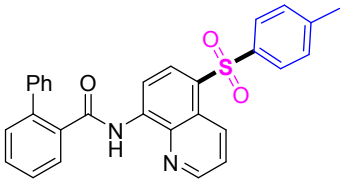
144.36, 139.80, 139.13, 138.89, 138.45, 133.80, 131.82, 130.54, 129.98, 128.64, 127.39, 124.32, 124.21, 123.54, 114.70, 21.55.

4-iodo-*N*-(5-tosylquinolin-8-yl)benzamide (3o)



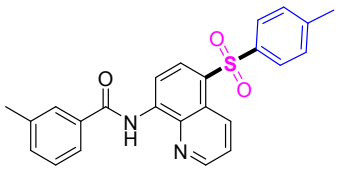
This compound is known;[4] white solid, 76 mg (72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 9.09 (dd, *J* = 8.7, 1.5 Hz, 1H), 9.00 (d, *J* = 8.4 Hz, 1H), 8.87 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.59 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.28 (s, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.95, 148.80, 144.23, 139.60, 138.93, 138.43, 138.25, 133.78, 133.67, 131.99, 129.94, 129.71, 128.92, 127.33, 124.29, 123.41, 114.41, 99.77, 21.56.

***N*-(5-tosylquinolin-8-yl)-[1,1'-biphenyl]-2-carboxamide (3p)**



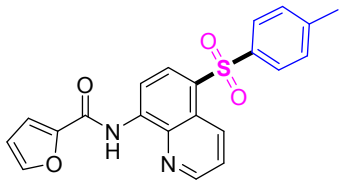
This compound is known;[4] white solid, 75 mg (79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.93 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.89 (d, *J* = 8.4 Hz, 1H), 8.47 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.56 (t, *J* = 6.8 Hz, 1H), 7.49 (d, *J* = 6.4 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 3H), 7.41 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.24 (t, *J* = 6.1 Hz, 4H), 7.13 (t, *J* = 7.5 Hz, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.12, 148.10, 144.13, 140.43, 139.78, 139.74, 139.04, 138.07, 135.23, 133.09, 131.87, 131.09, 130.87, 129.88, 129.56, 129.17, 129.04, 128.49, 127.85, 127.79, 127.31, 123.98, 123.01, 113.91, 21.52.

3-methyl-*N*-(5-tosylquinolin-8-yl)benzamide (3q)



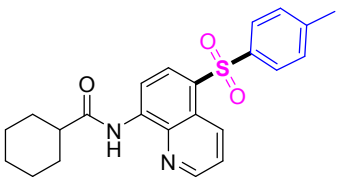
This compound is known;[2] white solid, 67 mg (80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.91 (s, 1H), 9.07 (dd, *J* = 8.7, 1.3 Hz, 1H), 9.02 (d, *J* = 8.4 Hz, 1H), 8.86 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 7.87 – 7.81 (m, 4H), 7.56 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 2.47 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.89, 148.74, 144.13, 140.02, 139.13, 138.91, 138.52, 134.38, 133.54, 133.20, 132.05, 129.90, 129.80, 129.36, 128.80, 128.18, 127.30, 124.32, 123.30, 114.25, 21.51, 21.46.

***N*-(5-tosylquinolin-8-yl)furan-2-carboxamide (3r)**



This compound is known;[5] white solid, 53 mg (68%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.96 (s, 1H), 9.05 (d, *J* = 8.7 Hz, 1H), 8.95 (d, *J* = 8.4 Hz, 1H), 8.87 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.62 (s, 1H), 7.56 (dd, *J* = 8.7, 4.1 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.59 (dd, *J* = 3.4, 1.7 Hz, 1H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.46, 148.84, 147.76, 145.05, 144.17, 139.60, 139.04, 138.36, 133.43, 131.89, 129.91, 129.53, 127.31, 124.29, 123.33, 116.17, 114.28, 112.73, 21.51.

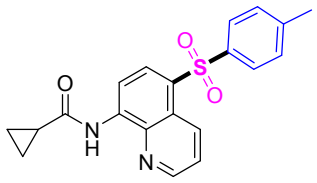
***N*-(5-tosylquinolin-8-yl)cyclohexanecarboxamide (3s)**



This compound is known;[3] white solid, 65 mg (79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 9.03 (dd, *J* = 8.7, 1.3 Hz, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.81 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.53 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.48 (t, *J* = 11.6 Hz, 1H), 2.33 (s, 3H), 2.05 (d, *J* = 13.3 Hz, 2H), 1.86 (d, *J* = 13.2 Hz, 2H), 1.65 – 1.57 (m,

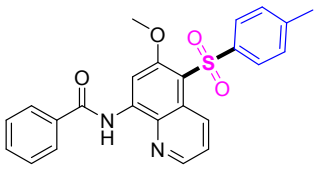
2H), 1.43 – 1.34 (m, 2H), 1.34 – 1.22 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 175.26, 148.56, 144.07, 140.03, 139.13, 138.18, 133.44, 132.05, 129.86, 128.91, 127.22, 124.23, 123.20, 114.09, 46.84, 29.61, 25.70, 25.63, 21.49.

***N*-(5-tosylquinolin-8-yl)cyclopropanecarboxamide (3t)**



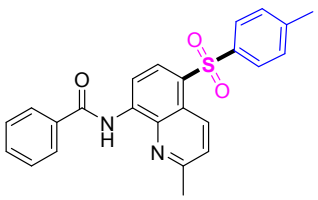
This compound is known;[6] white solid, 54 mg (74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 9.01 (dd, J = 8.7, 1.6 Hz, 1H), 8.83 – 8.81 (m, 2H), 8.46 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.53 (dd, J = 8.7, 4.2 Hz, 1H), 7.23 (d, J = 6.4 Hz, 2H), 2.34 (s, 3H), 1.82 – 1.80 (m, 1H), 1.17 – 1.15 (m, 2H), 0.96 – 0.94 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 172.85, 148.54, 144.10, 139.94, 139.02, 137.89, 133.37, 132.05, 129.87, 128.22, 127.22, 124.21, 123.24, 113.99, 21.53, 16.45, 8.84.

***N*-(6-methoxy-5-tosylquinolin-8-yl)benzamide (3u)**



This compound is known;[2] white solid, 75 mg (87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.10 (s, 1H), 9.94 (dd, J = 9.0, 1.4 Hz, 1H), 8.79 (s, 1H), 8.75 (dd, J = 4.1, 1.4 Hz, 1H), 8.04 (d, J = 7.0 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.55 (t, J = 7.3 Hz, 2H), 7.28 – 7.24 (m, 2H), 3.87 (s, 3H), 2.39 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 164.44, 159.10, 148.73, 144.16, 139.95, 138.51, 133.65, 132.45, 132.09, 129.92, 129.49, 128.98, 127.44, 127.33, 124.35, 123.32, 114.35, 102.71, 54.98, 21.53.

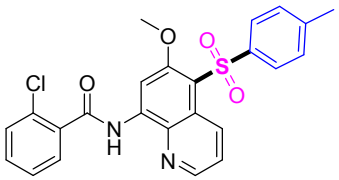
***N*-(2-methyl-5-tosylquinolin-8-yl)benzamide (3v)**



This compound is known;[2] white solid, 59 mg (71%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.03 (s, 1H), 9.00 (d, J = 8.4 Hz, 1H), 8.94 (d, J = 8.8 Hz,

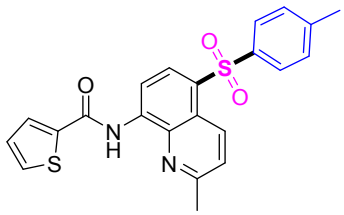
1H), 8.48 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 6.9 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.58 (dd, *J* = 13.9, 6.4 Hz, 3H), 7.46 – 7.43 (m, 1H), 7.25 (s, 2H), 2.76 (s, 3H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.65, 158.05, 144.08, 139.31, 139.11, 137.98, 134.49, 133.48, 132.37, 130.92, 129.86, 129.26, 128.99, 127.36, 127.27, 124.21, 122.44, 114.26, 25.25, 21.54.

2-chloro-*N*-(5-tosylquinolin-8-yl)benzamide (3w)



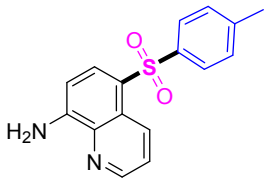
White solid, 73 mg (79%); m.p. 192-193 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.89 (s, 1H), 9.94 (dd, *J* = 9.0, 1.4 Hz, 1H), 8.80 (s, 1H), 8.70 (dd, *J* = 4.1, 1.4 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.78 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.60 (dd, *J* = 9.0, 4.1 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 164.38, 158.15, 145.27, 142.43, 139.99, 139.96, 133.75, 132.57, 132.03, 131.13, 130.17, 129.70, 129.11, 127.99, 126.29, 126.27, 126.12, 122.85, 114.00, 102.71, 55.81, 20.53. HRMS (ESI+): Calculated for $C_{24}H_{19}ClN_2O_4S$, $[M+H]^+$ 467.0827, Found 467.0825.

***N*-(2-methyl-5-tosylquinolin-8-yl)thiophene-2-carboxamide (3x)**



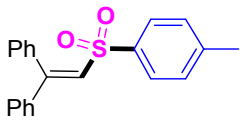
White solid, 63 mg (75%); m.p. 205-206 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.87 (s, 1H), 8.93 (d, *J* = 8.8 Hz, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 3H), 7.62 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.20 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.76 (s, 3H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 159.05, 157.02, 143.02, 138.30, 138.07, 137.94, 136.65, 132.43, 130.69, 129.82, 128.83, 128.17, 128.04, 127.06, 126.23, 123.21, 121.34, 113.09, 24.18, 20.50. HRMS (ESI+): Calculated for $C_{22}H_{18}N_2O_3S_2$, $[M+H]^+$ 423.0832, Found 423.0839.

5-tosylquinolin-8-amine (4a)



This compound is known;[7] yellow solid, 265 mg (89%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (dd, *J* = 8.7, 1.3 Hz, 1H), 8.69 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 8.7, 4.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.76 (s, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.81, 147.35, 143.42, 140.18, 137.05, 133.08, 132.91, 129.69, 126.86, 125.48, 123.15, 121.47, 106.74, 21.44.

(2-tosylethene-1,1-diyl)dibenzene (7)



This compound is known.[1] white solid, 18 mg (32%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 4H), 7.23 – 7.20 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.13 – 7.08 (m, 2H), 7.01 (s, 1H), 2.38 (s, 3H).

References:

(1) J. Wei, J. Jiang, X. Xiao, D. Lin, Y. Deng, Z. Ke, H. Jiang, W. Zeng, *J. Org. Chem.*, 2016, **81**, 946.

(2) H. Qiao, S. Sun, F. Yang, Y. Zhu, W. Zhu, Y. Dong, Y. Wu, X. Kong, L. Jiang, Y. Wu, *Org. Lett.*, 2015, **17**, 6086.

(3) H.-W. Liang, K. Jiang, W. Ding, Y. Yuan, L. Shuai, Y.-C. Chen, Y. Wei, *Chem. Commun.,* 2015, **51**, 16928.

(4) J. Xu, C. Shen, X. Zhu, P. Zhang, M. J. Ajitha, K.-W. Huang, Z. An, X. Liu, *Chem. Asian J.*, 2016, **11**, 882.

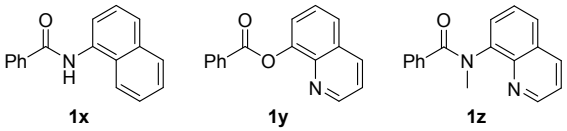
(5) S. Liang, G. Manolikakes, *Adv. Synth. Catal.*, 2016, **358**, 2371.

(6) Y. Wang, Y. Wang, Q. Zhang, D. Li, *Org. Chem. Front.*, 2017, **4**, 514.

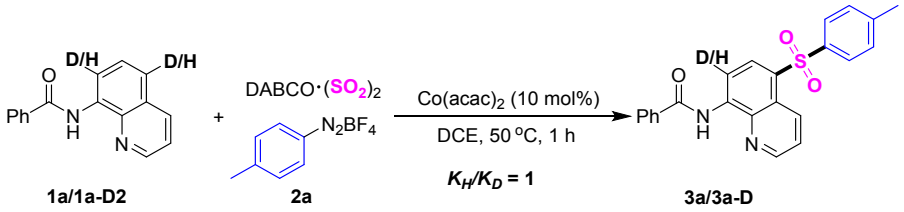
(7) J.-M. Li, J. Weng, Gui Lu, A. S. C. Chan, *Tetrahedron Lett.*, 2016, **57**, 2121.

5. Investigation into the mechanism of reaction

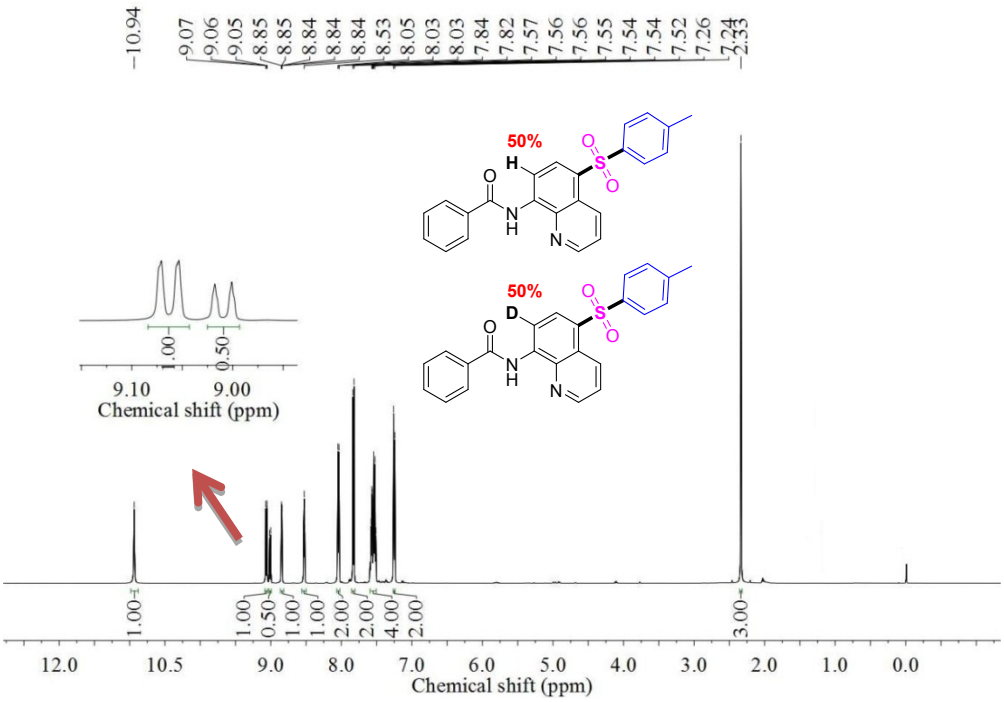
The exploration of the analogous substrates



KIE experiment

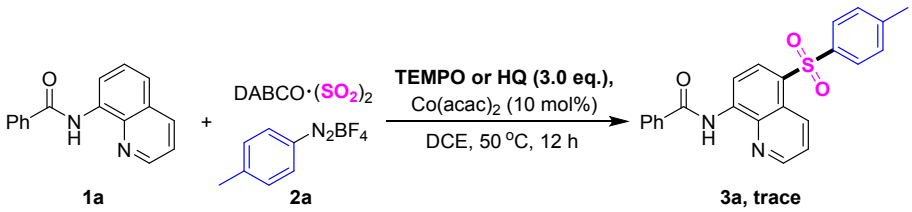


A mixture of **1a** (24.8 mg, 0.1 mmol), **1a-D2** (25.0 mg, 0.1 mmol), DABCO•$(SO2)_2$ (57.6 mg, 1.2 eq.), **2a** (49.0 mg, 1.2 eq.), $Co(acac)_2$ (5.0 mg, 10 mol%) in 1,2-dichloroethane (1.0 mL) was stirred at 50 °C under N_2 atmosphere for 1 h. Then the mixture was cooled to room temperature and poured into water (5.0 mL). The mixture was extracted with EtOAc (5.0 mL x 3) and the combined organic layer was washed with brine (10.0 mL), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The products **3a/3a-D** was obtained in 22% yield by flash column chromatography using PE/AcOEt as an eluent. This result indicated that the turnover-limiting step does not involve C-H activation.



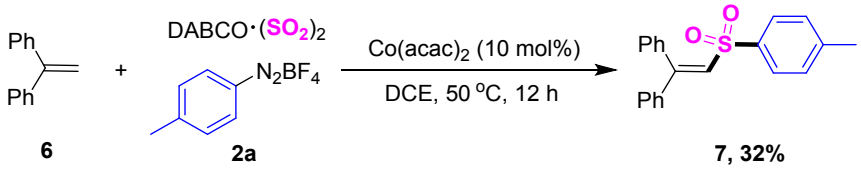
Radical inhibition experiment

The reaction was inhibited in the presence of the radical inhibitor TEMPO or HQ, which showed that a radical pathway should be involved.



Radical capture experiment

A mixture of **6** (36.0 mg, 0.2 mmol), DABCO•$(SO_2)_2$ (57.6 mg, 1.2 eq.), **2a** (1.2 eq.), $Co(acac)_2$ (5.0 mg, 10 mol%) in 1,2-dichloroethane (1.0 mL) was stirred at 50 °C under N_2 atmosphere for 12 h. Then the mixture was cooled to room temperature and poured into water (5.0 mL). The mixture was extracted with EtOAc (5.0 mL x 3) and the combined organic layer was washed with brine (10.0 mL), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The products **7** were purified by flash column chromatography using PE/AcOEt as an eluent.



6. X-ray Crystal Data for 3f

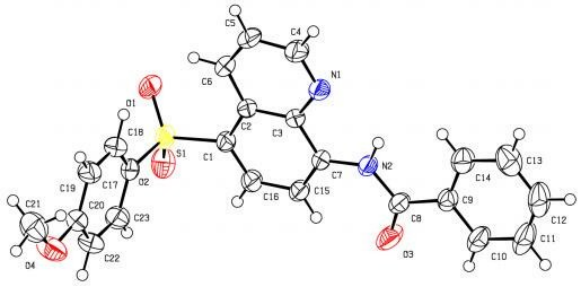


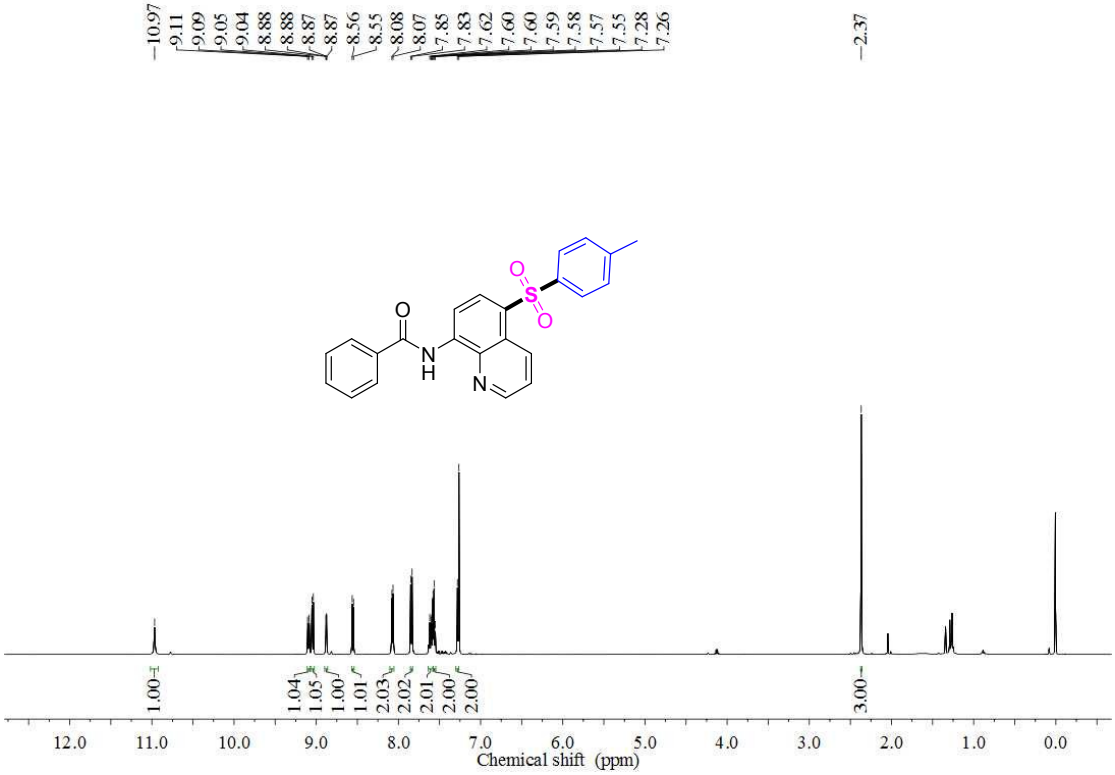
Figure 1 Single-crystal X-ray structure of **3f**. Ellipsoids are represented at 30% probability.

Table S1. Crystallographic data and structure refinement for **3f**

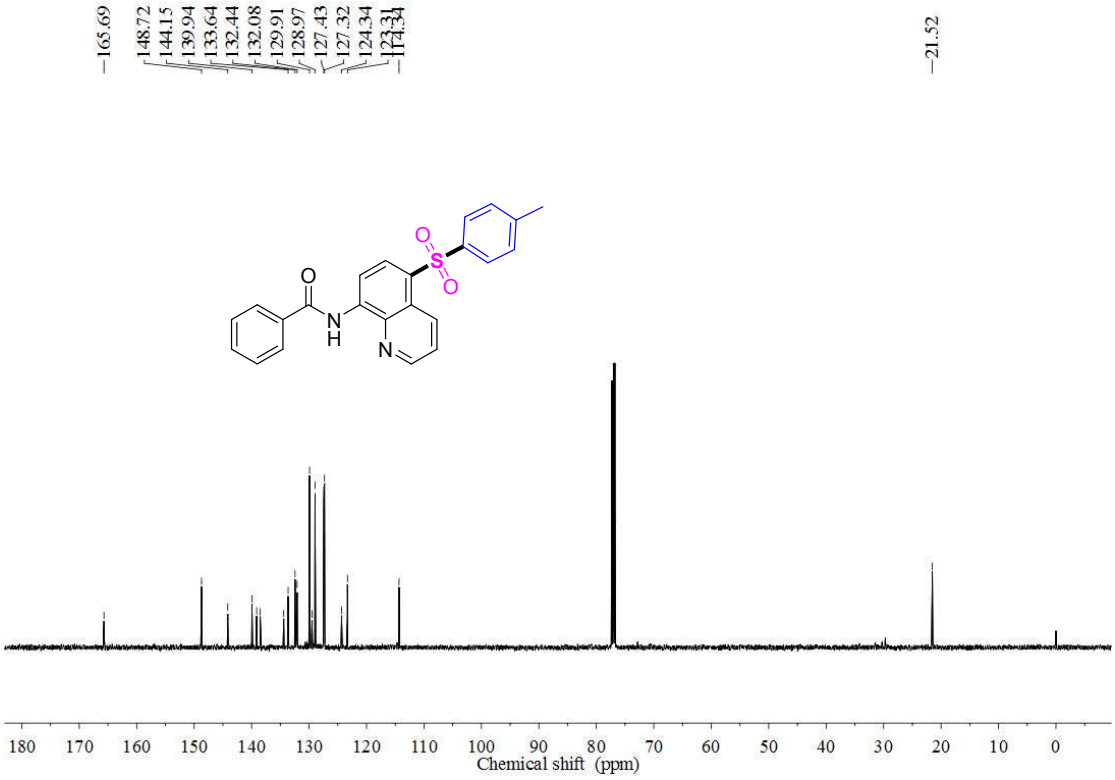
CCDC	1565132
Empirical formula	$C_{23}H_{18}N_2O_4S$
Formula weight	418.45
Temperature, K	296.15
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	P-1
a, *b*, *c*, Å	10.136 (3), 10.173 (3), 11.012 (3)
α, β, γ, °	104.003 (3), 97.178 (3), 111.781 (3)
Volume, Å^3	993.6 (5)
Z	2
Calculated density, Mg/m^3	1.399
Absorption coefficient, mm^{-1}	0.197
F (000)	365
Crystal size, mm	0.20 x 0.20 x 0.20
Theta range for data collection, °	2.228 to 27.801
Limiting indices	-13<=h<=13, -12<=k<=12, -14<=l<=13
Reflections collected / unique	7906 / 4238 [R(int) = 0.0478]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4238 / 0 / 272
Goodness of fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1388
R indices (all data)	R1 = 0.0607, wR2 = 0.1499

7. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra

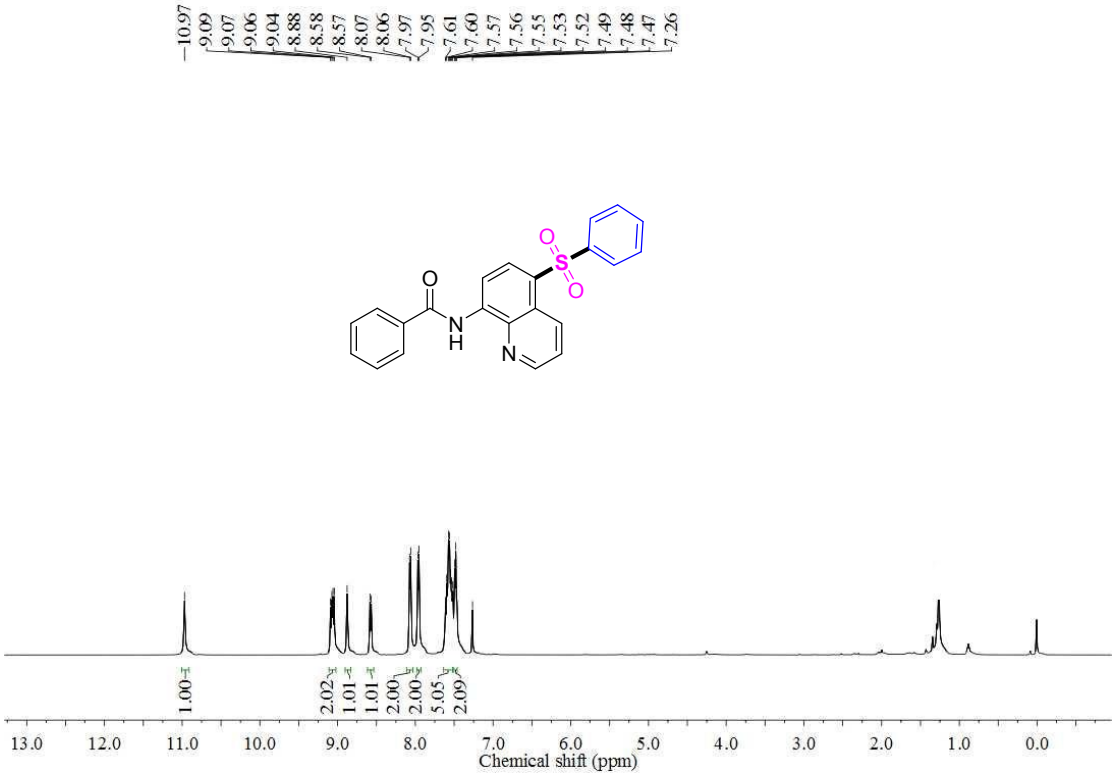
3a ^{1}H NMR



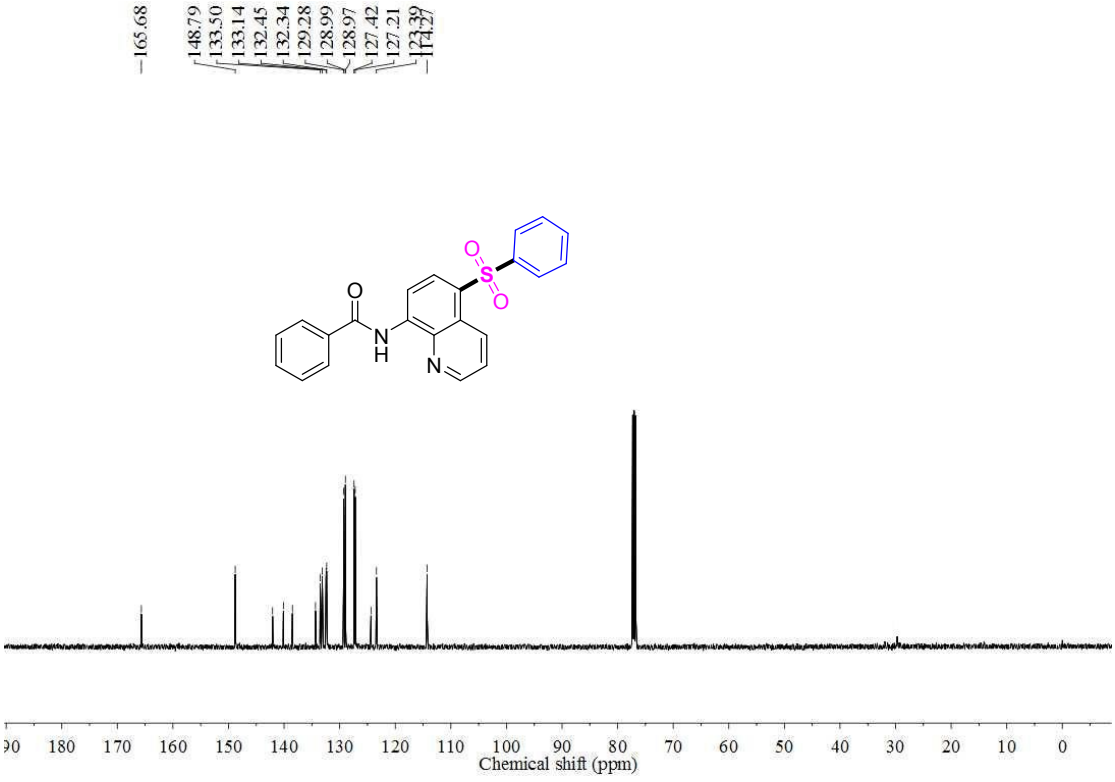
3a $^{13}C\{^{1}H\}$ NMR



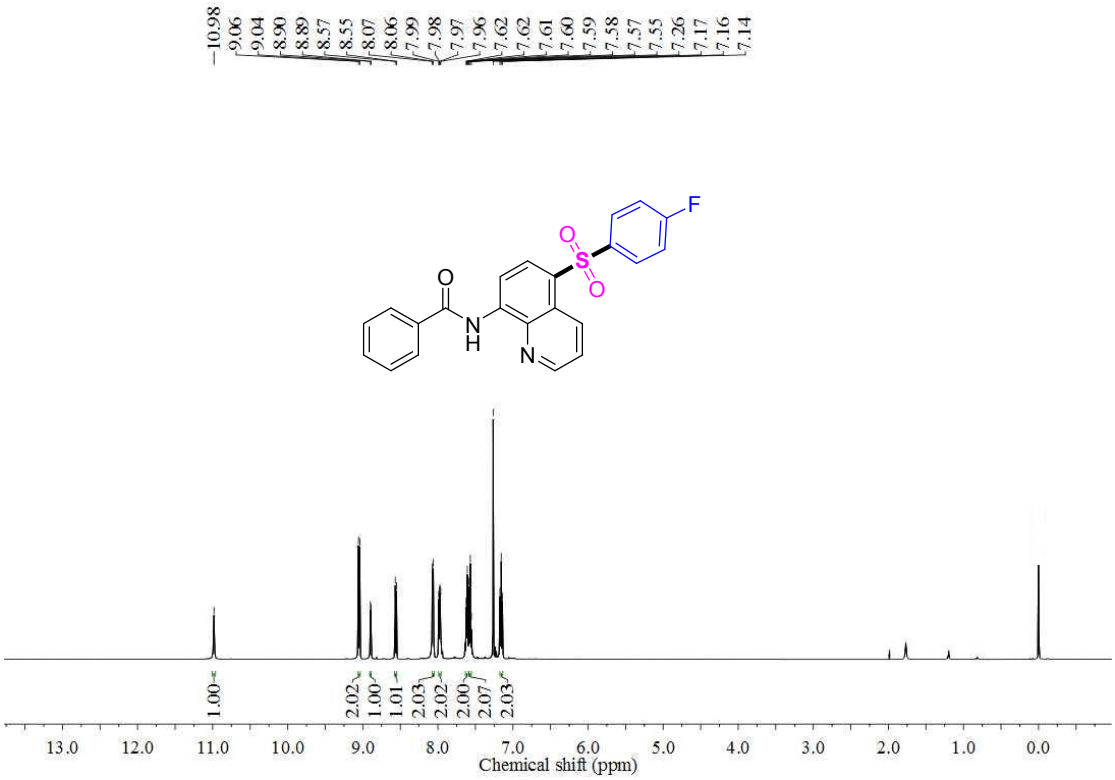
3b ^{1}H NMR



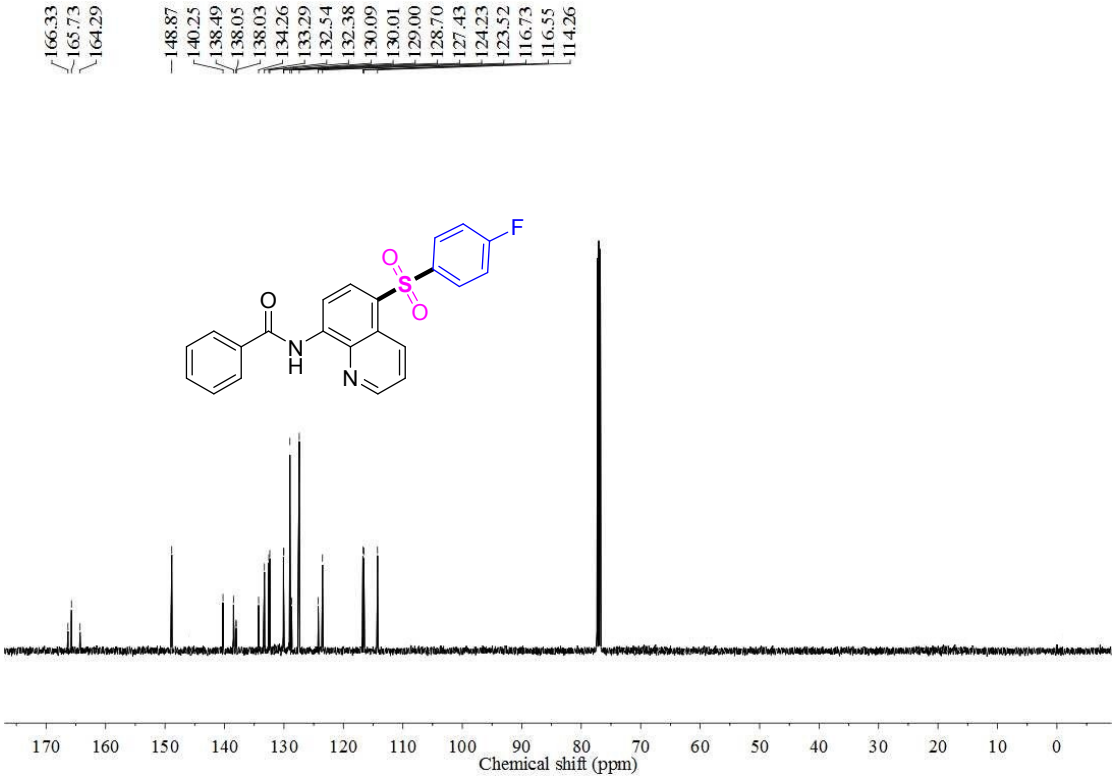
3b ^{13}C{^{1}H} NMR



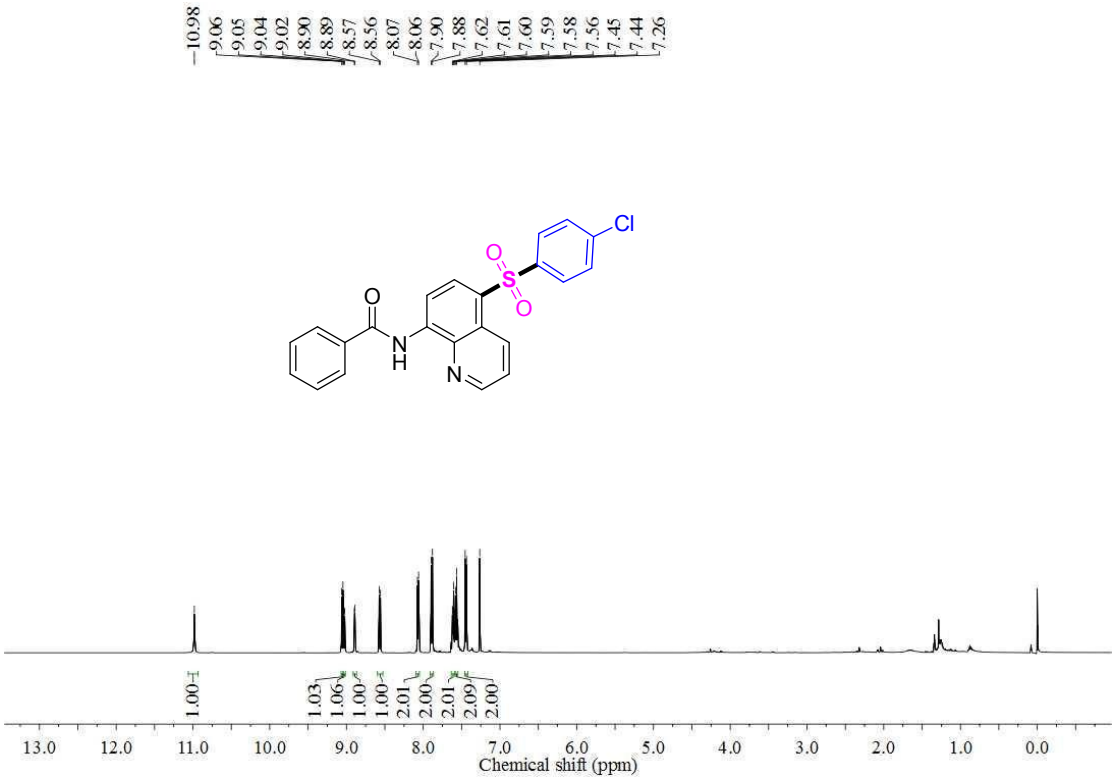
3c ^{1}H NMR



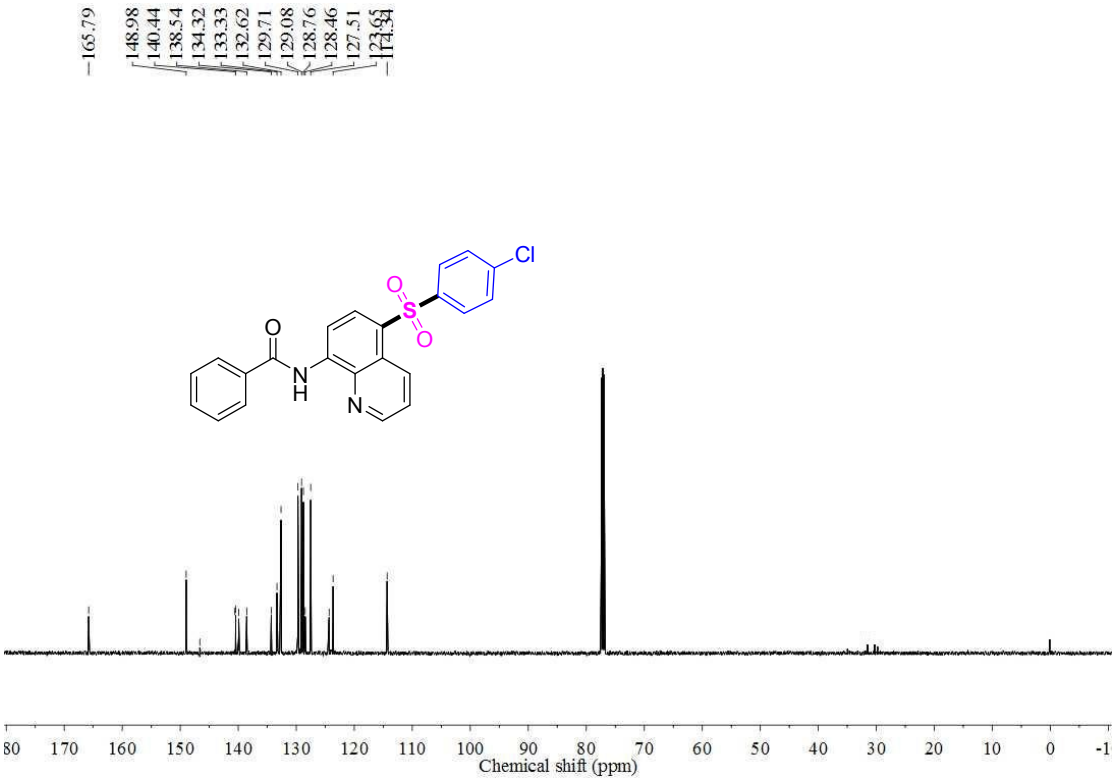
3c ^{13}C{^{1}H} NMR



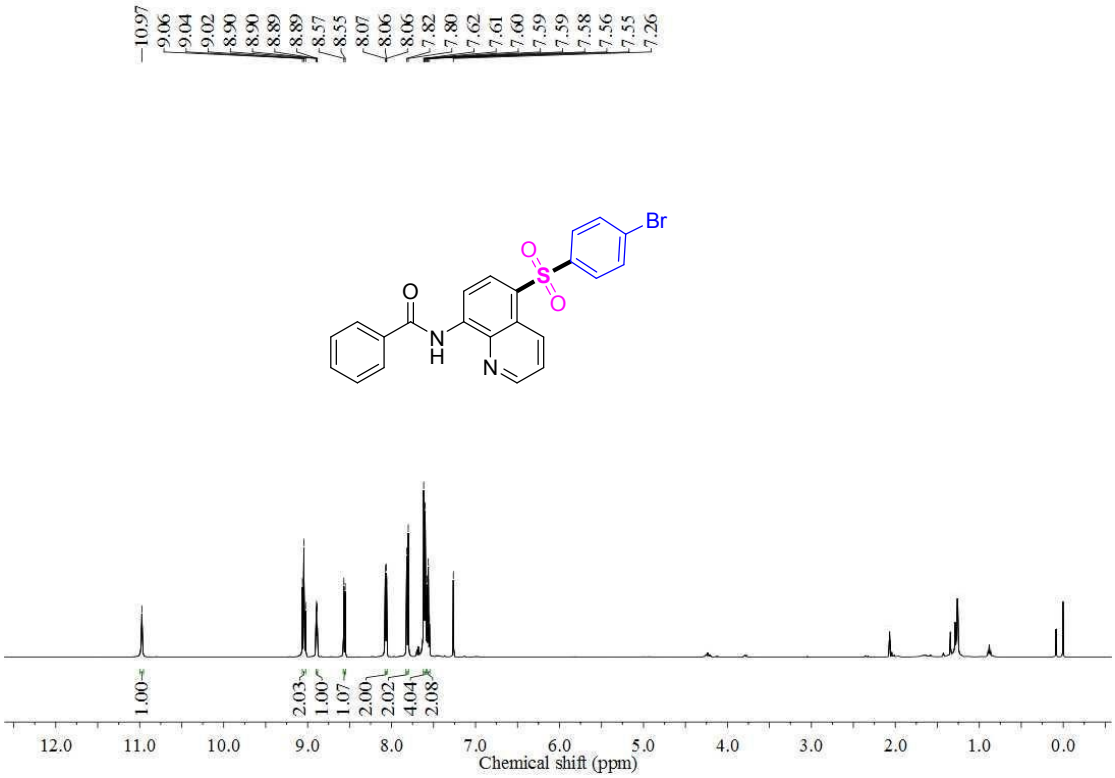
3d ^{1}H NMR



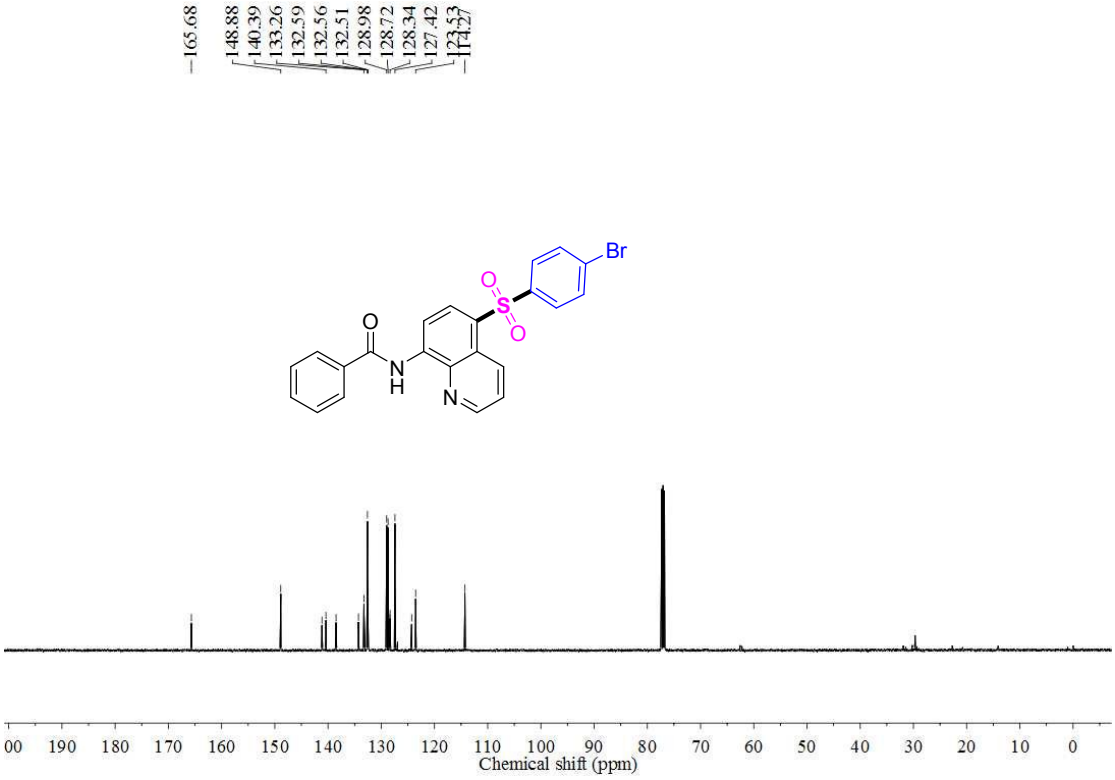
3d ^{13}C{^{1}H} NMR



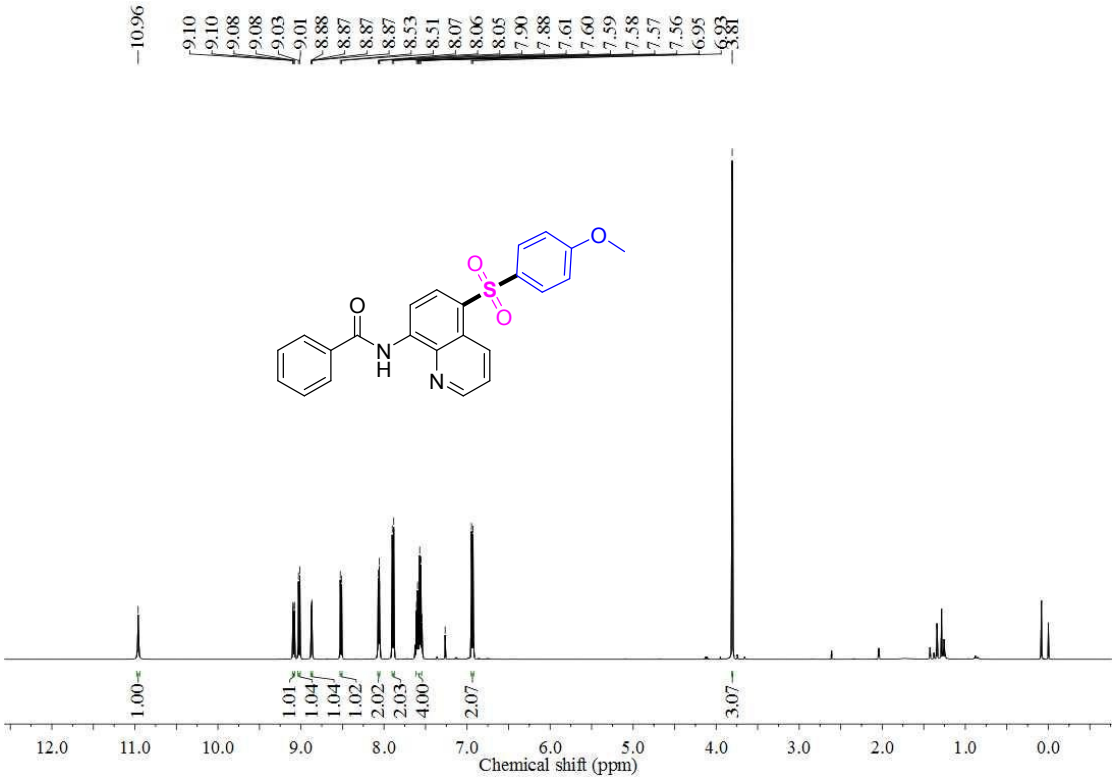
3e ^{1}H NMR



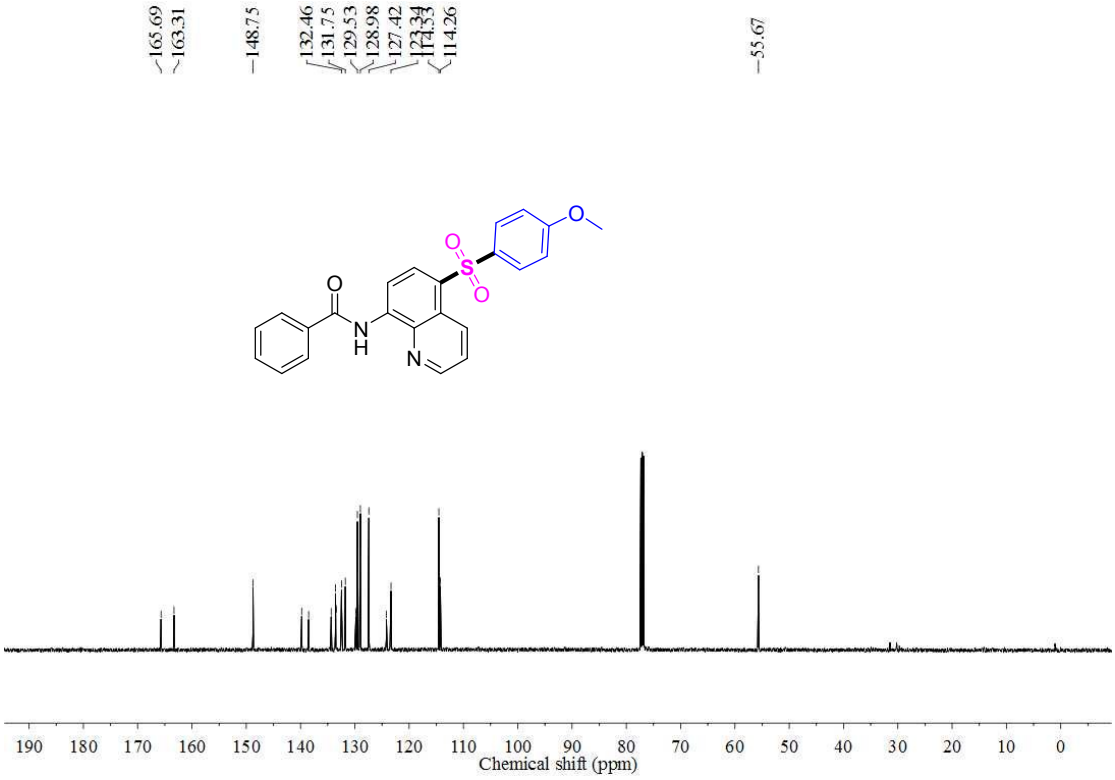
3e ^{13}C{^{1}H} NMR



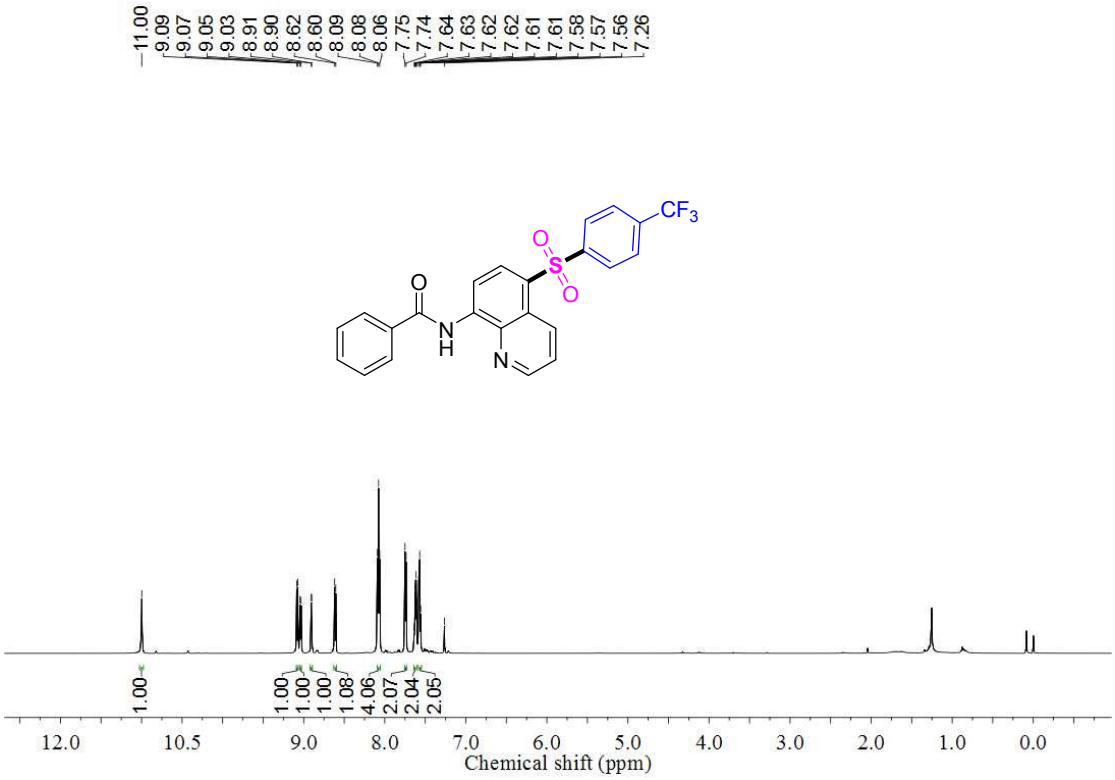
3f ^{1}H NMR



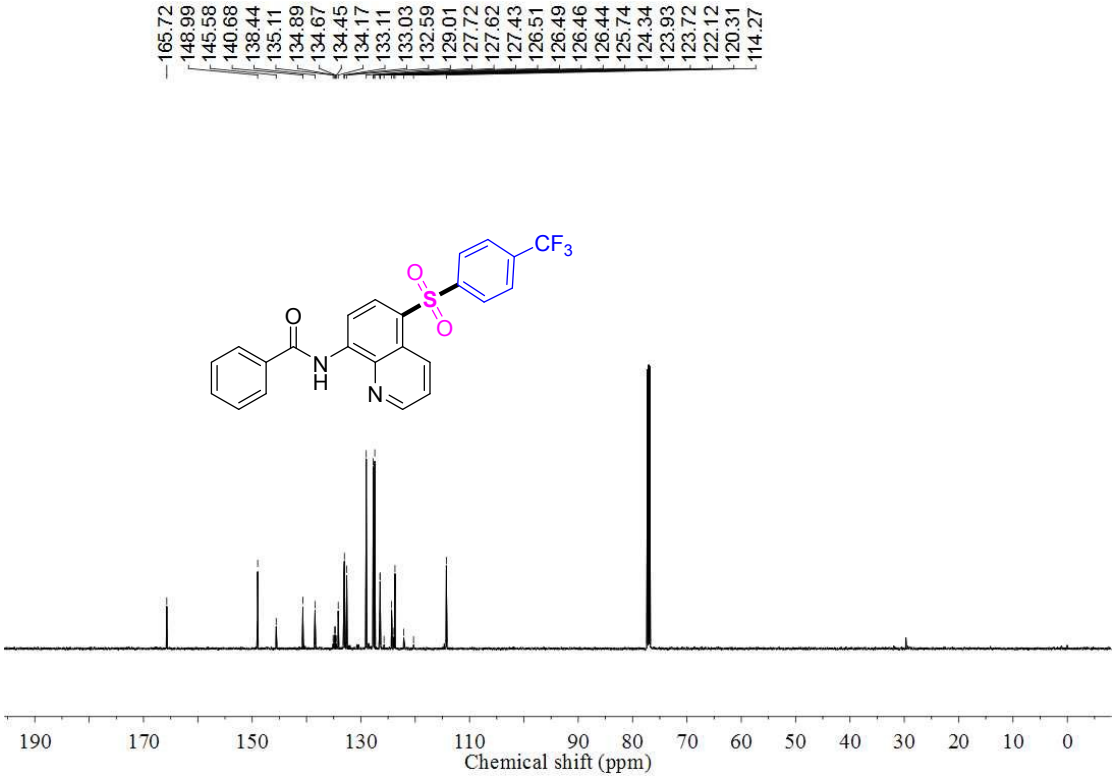
3f ^{13}C{^{1}H} NMR



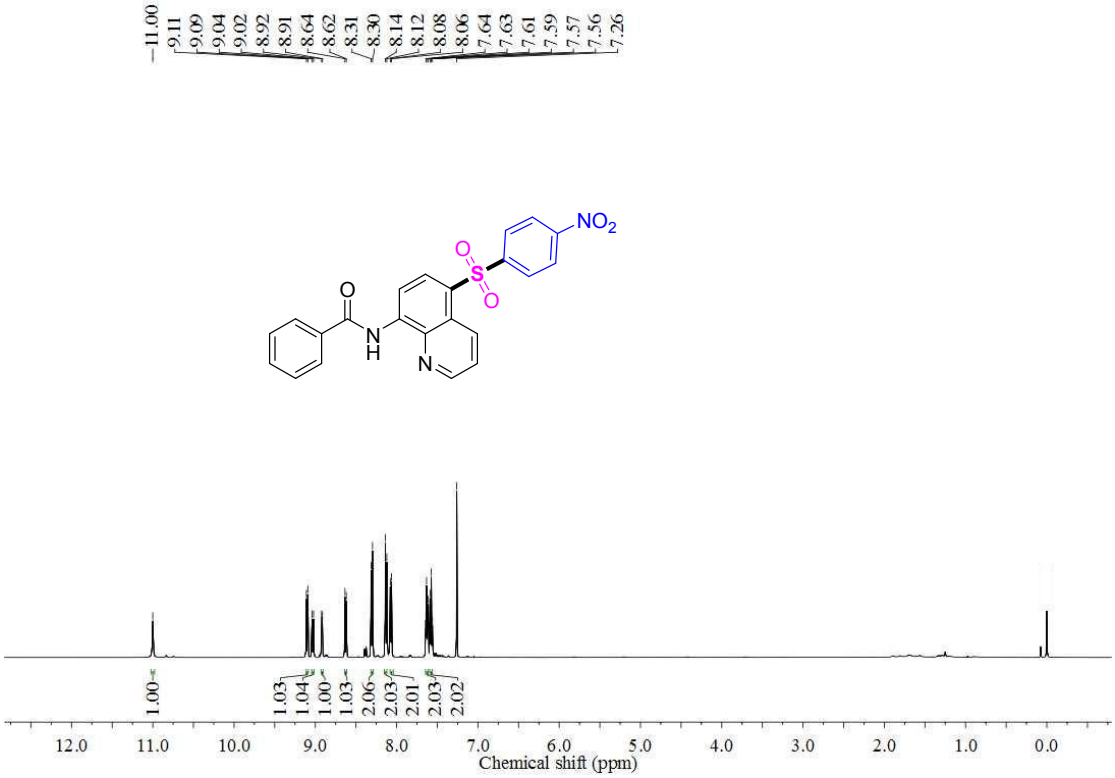
3g ^{1}H NMR



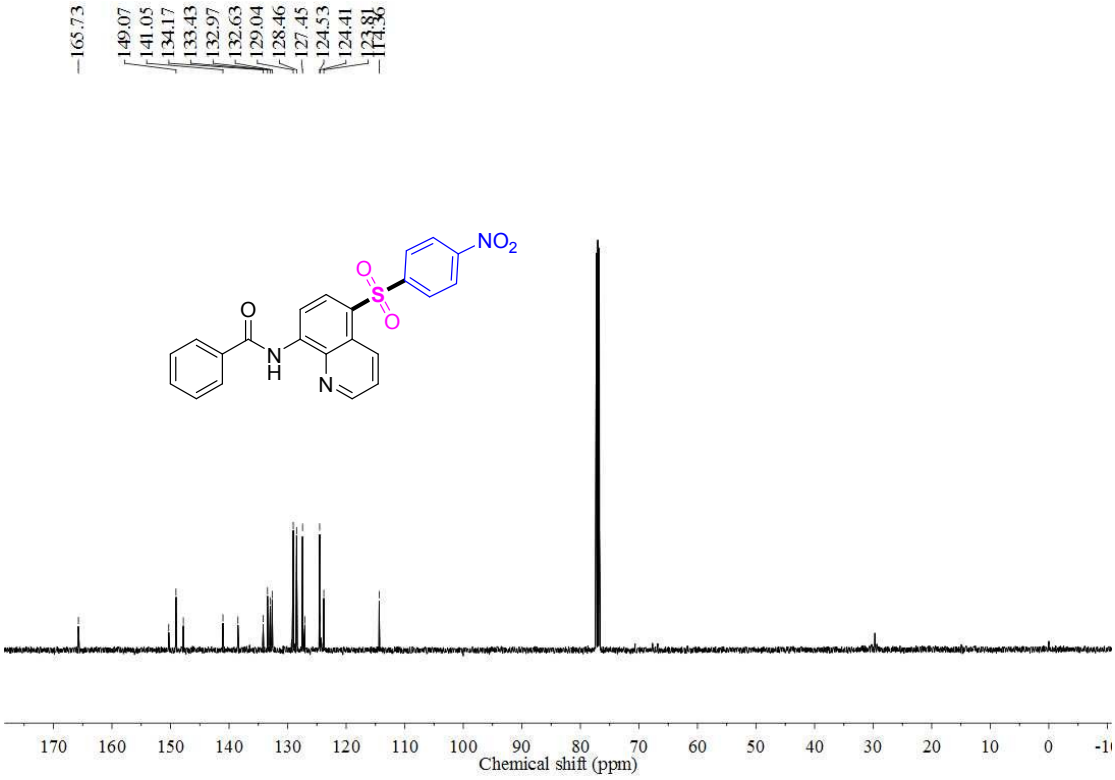
3g ^{13}C{^{1}H} NMR



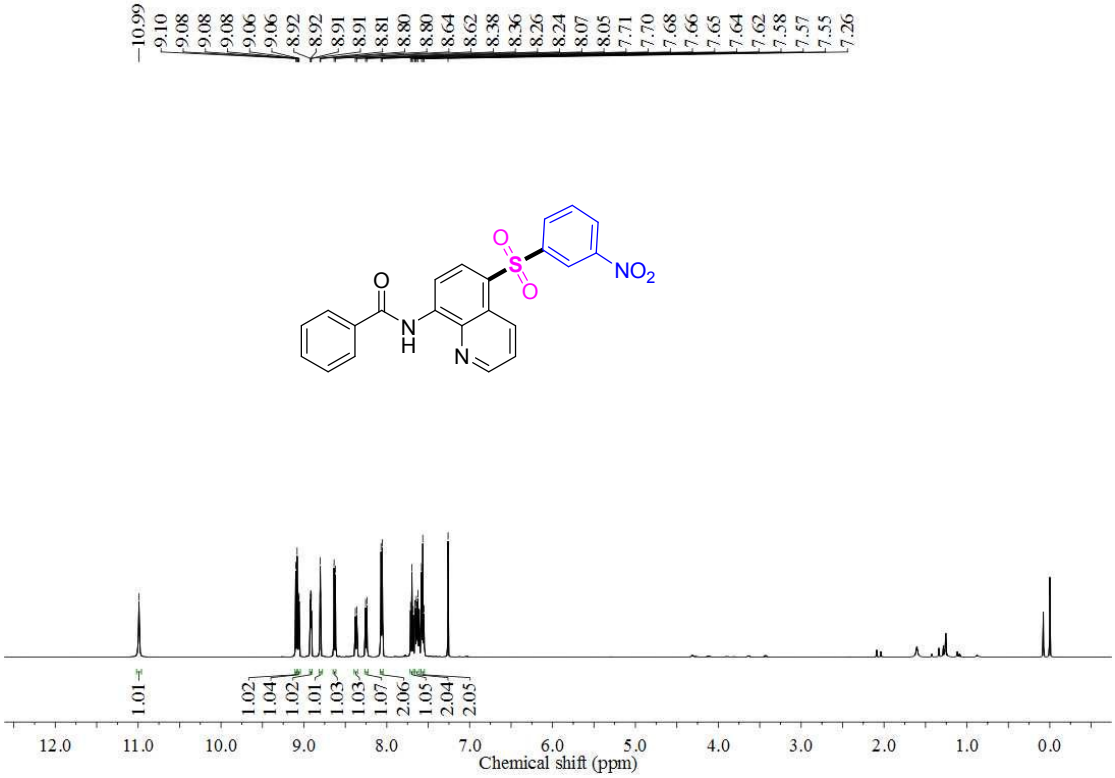
3h ^{1}H NMR



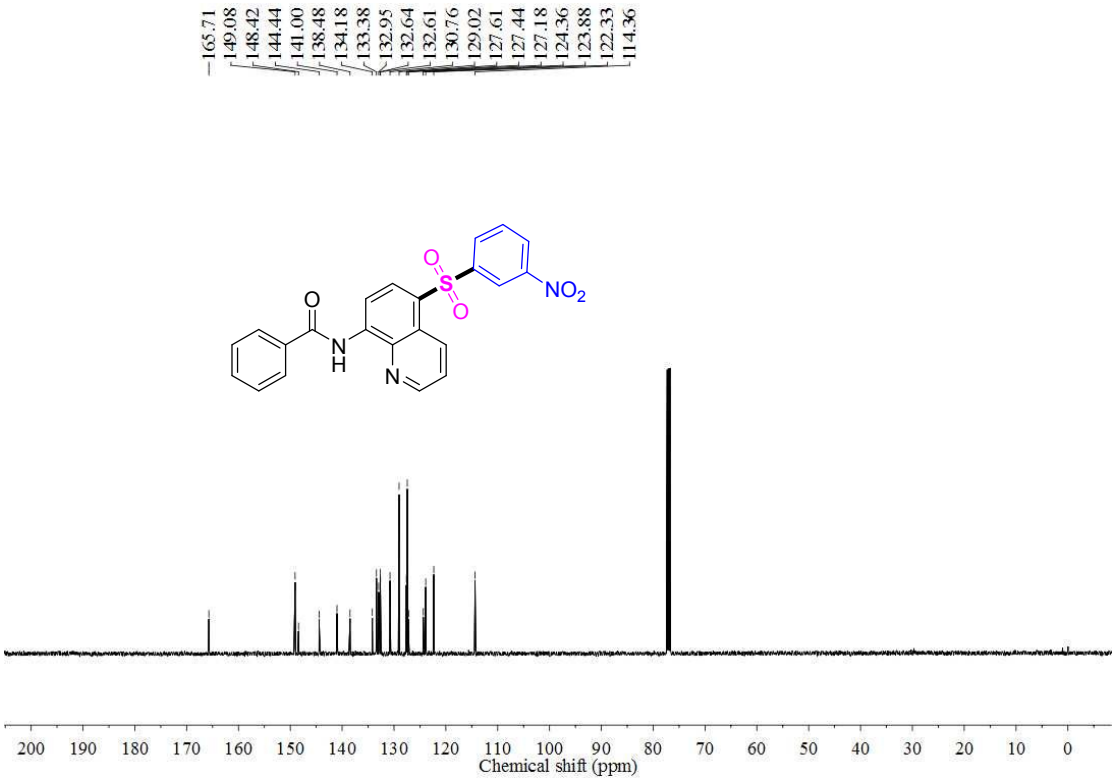
3h ^{13}C{^{1}H} NMR



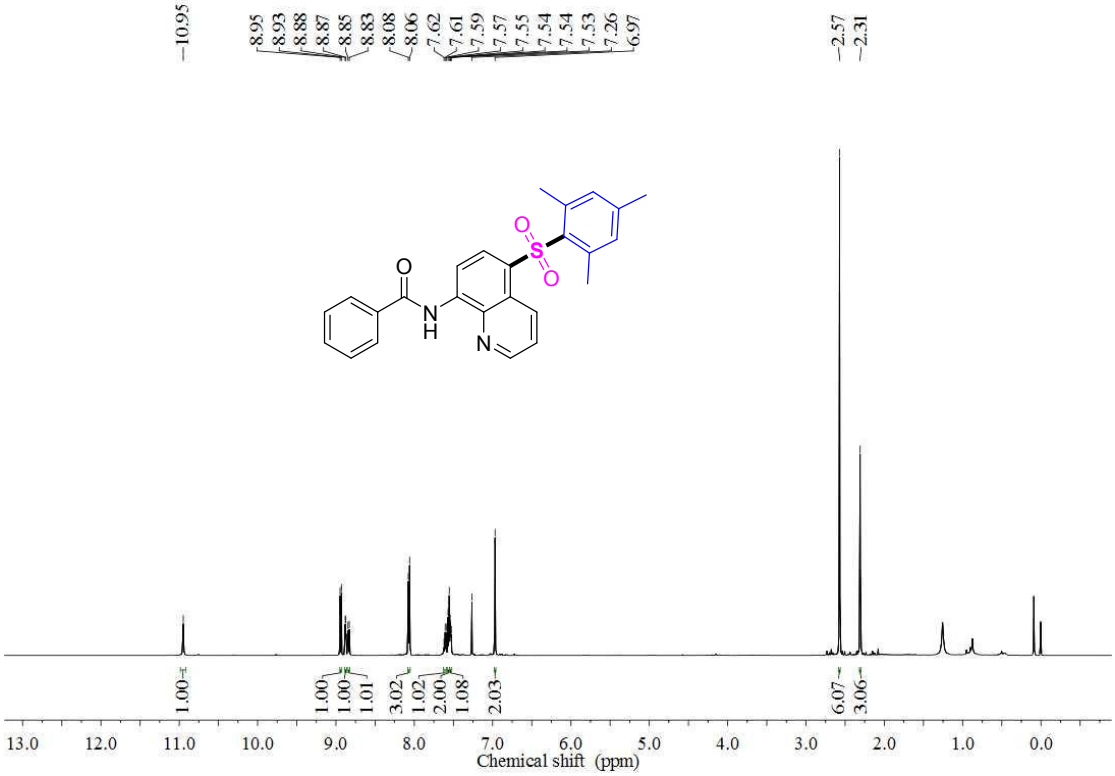
3i ^{1}H NMR



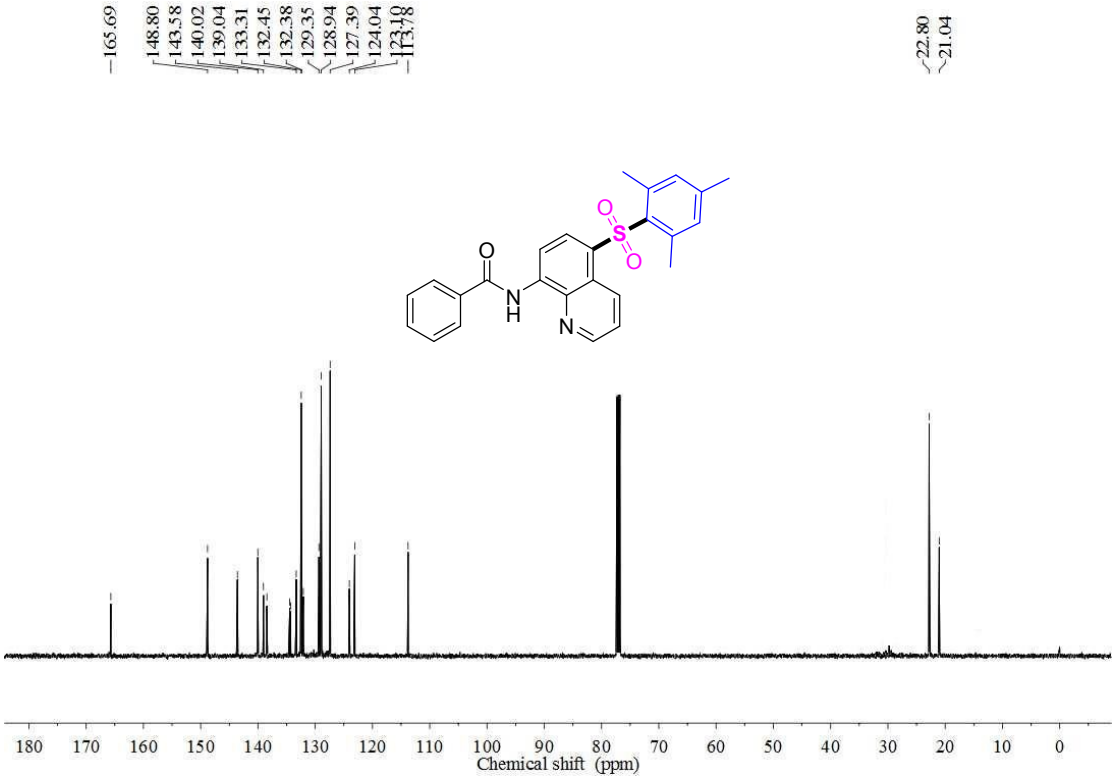
3i ^{13}C{^{1}H} NMR



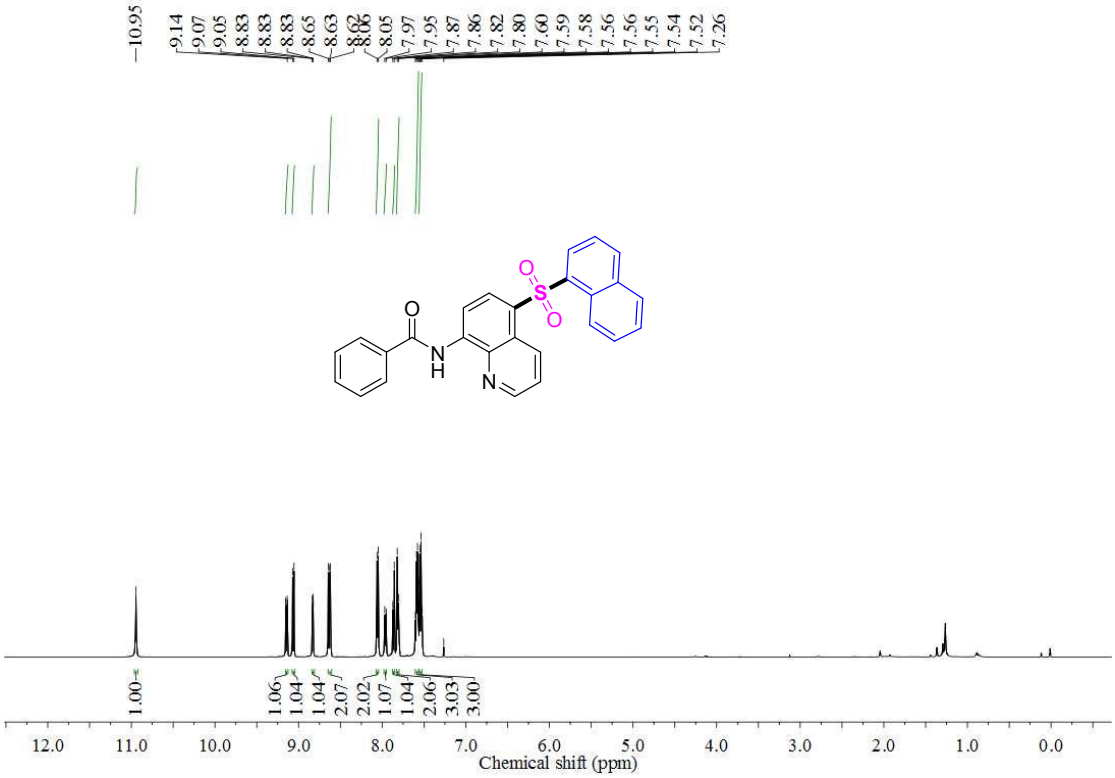
3j ^{1}H NMR



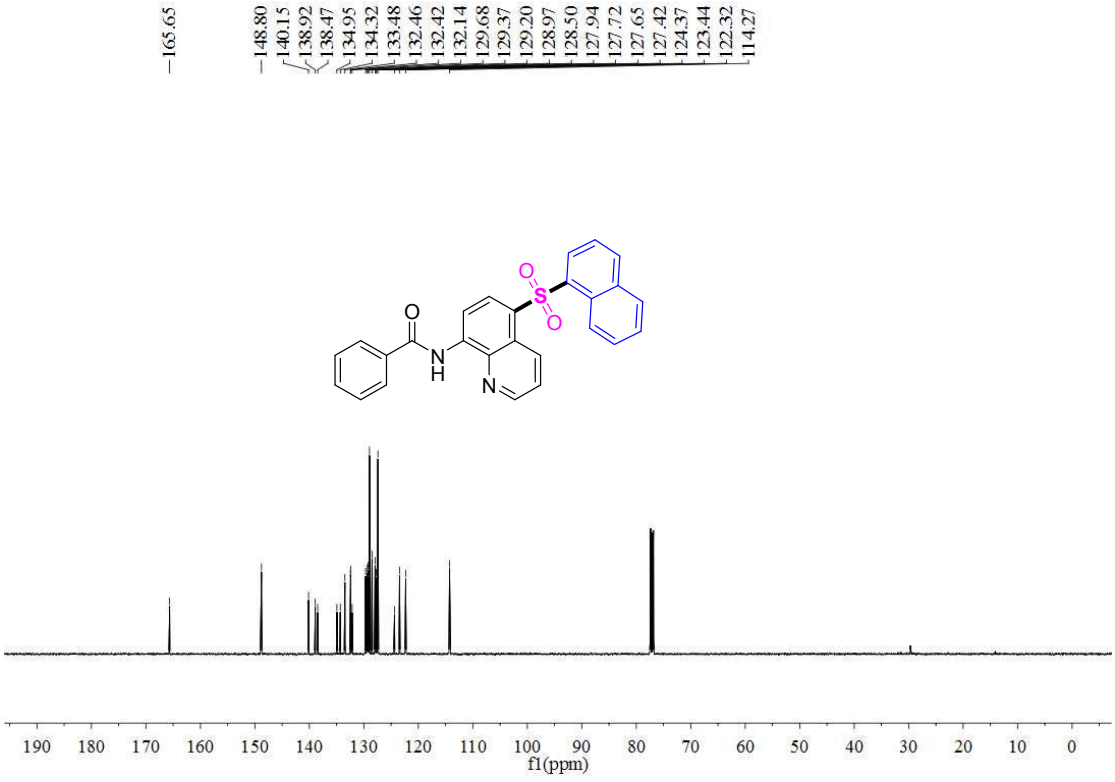
3j ^{13}C{^{1}H} NMR



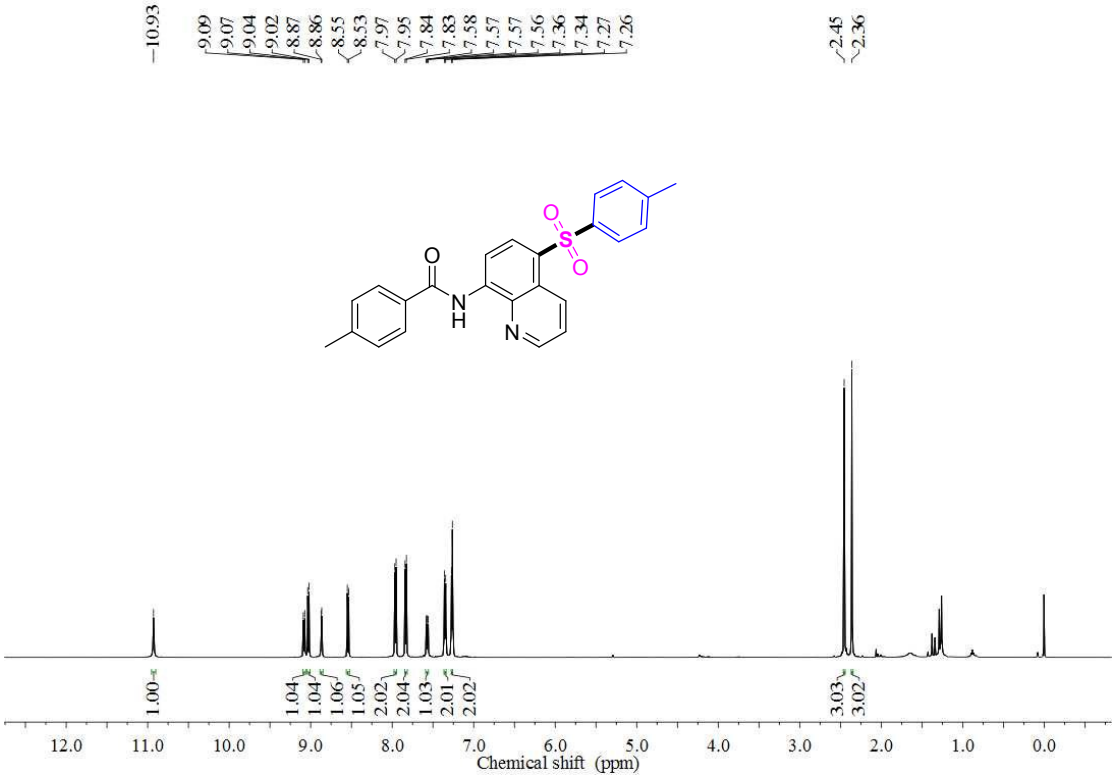
3k ^{1}H NMR



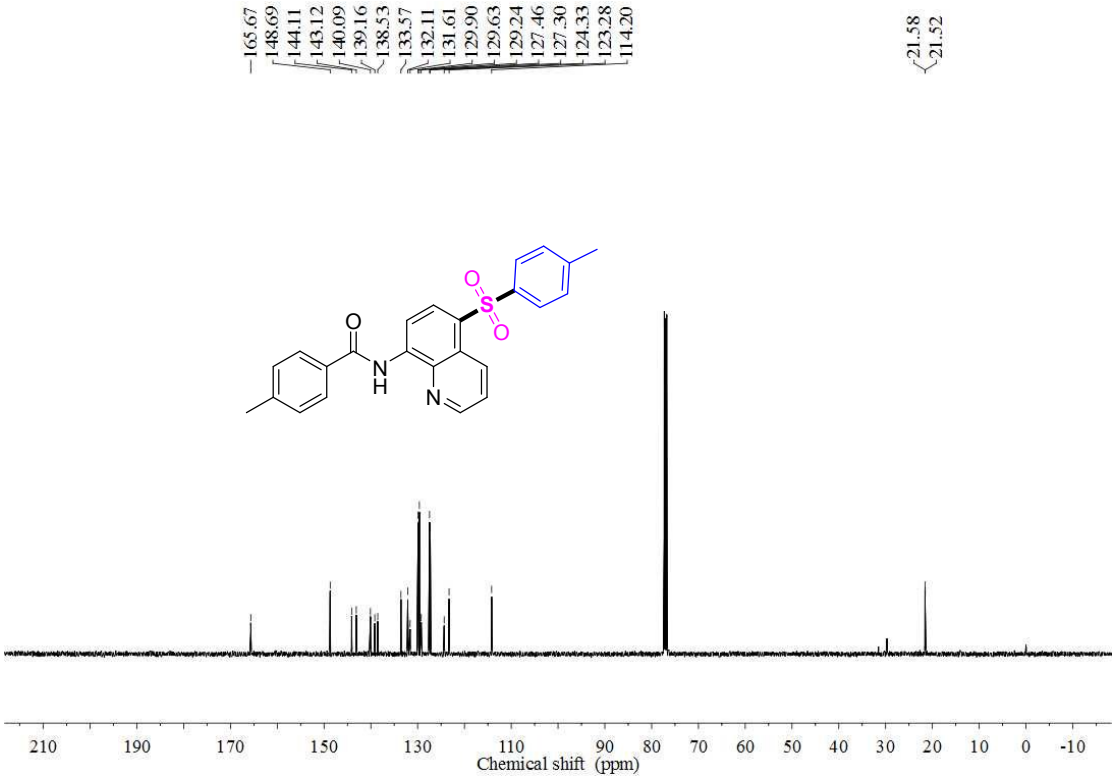
3k ^{13}C{^{1}H} NMR



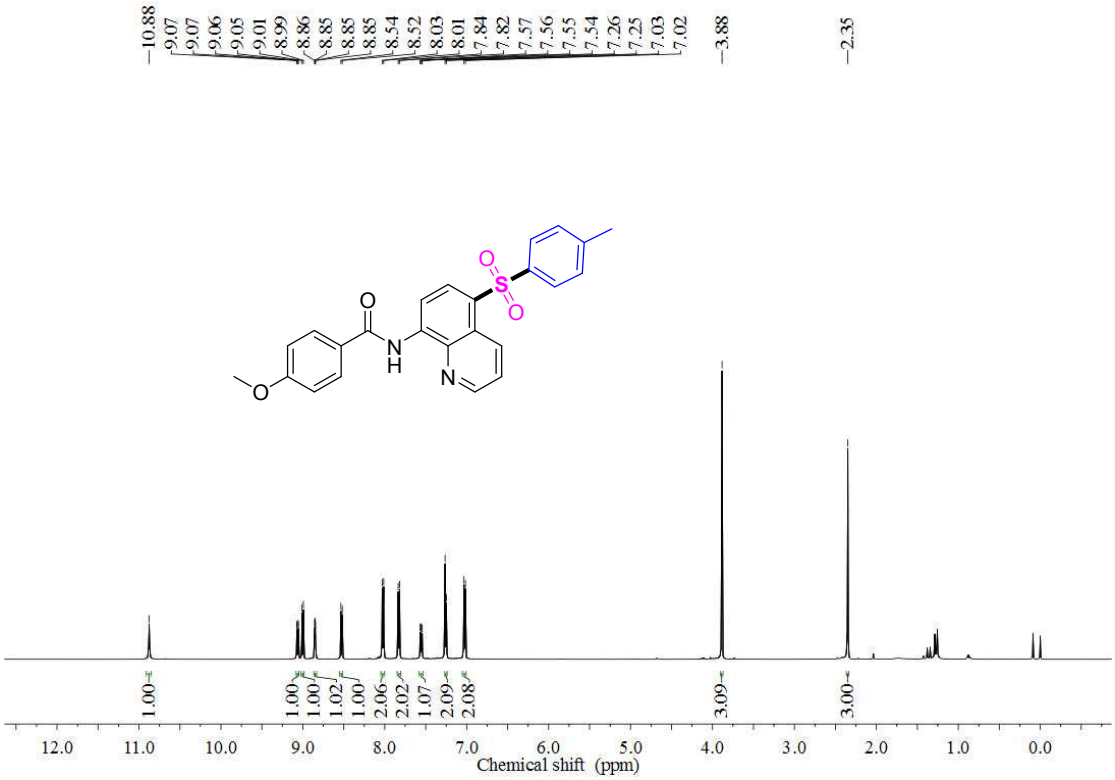
3l ^{1}H NMR



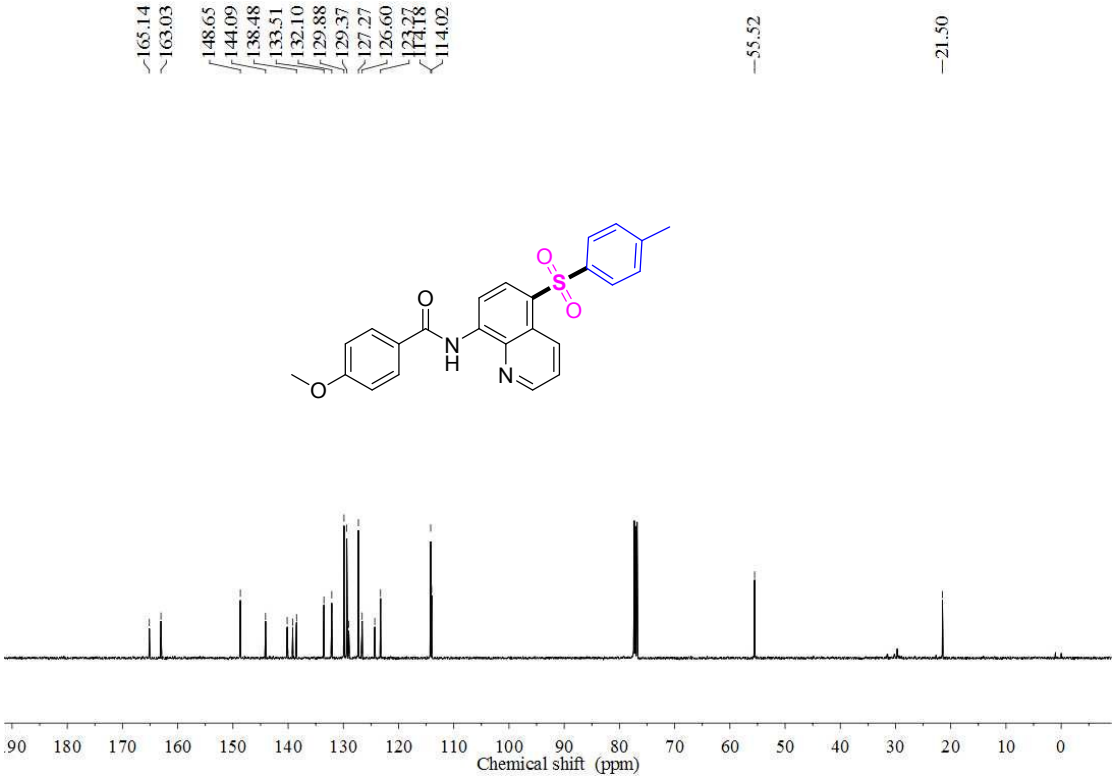
3l ^{13}C{^{1}H} NMR



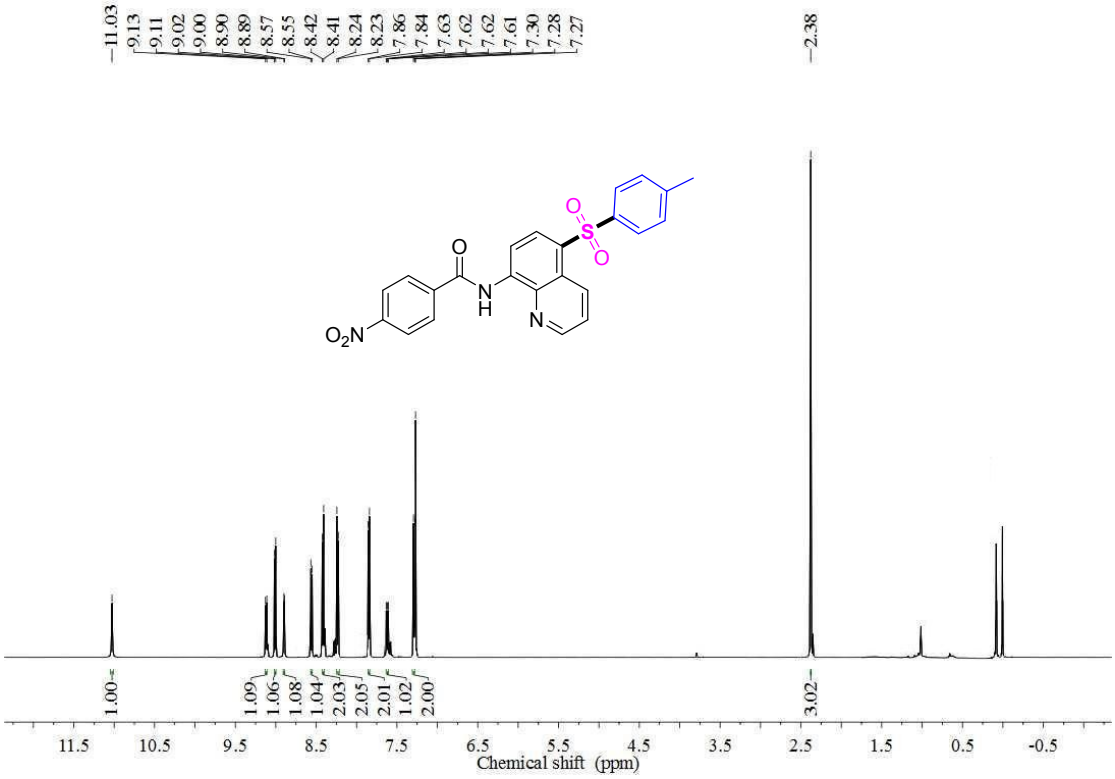
3m ^{1}H NMR



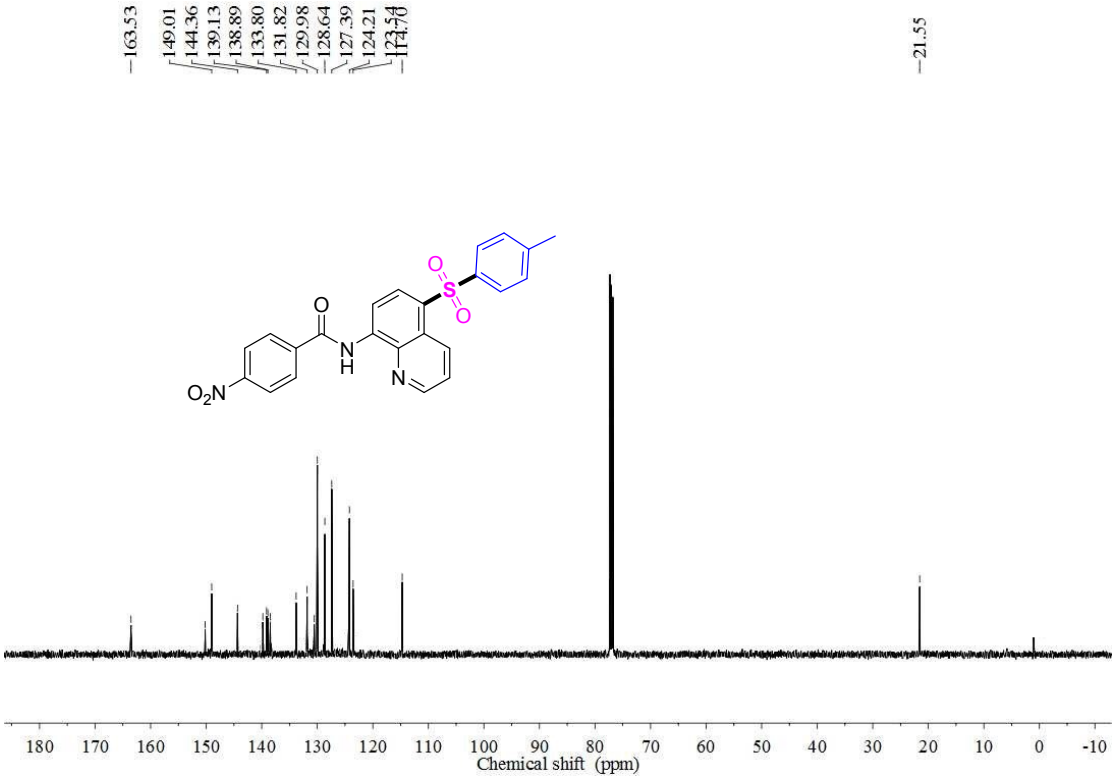
3m ^{13}C{^{1}H} NMR



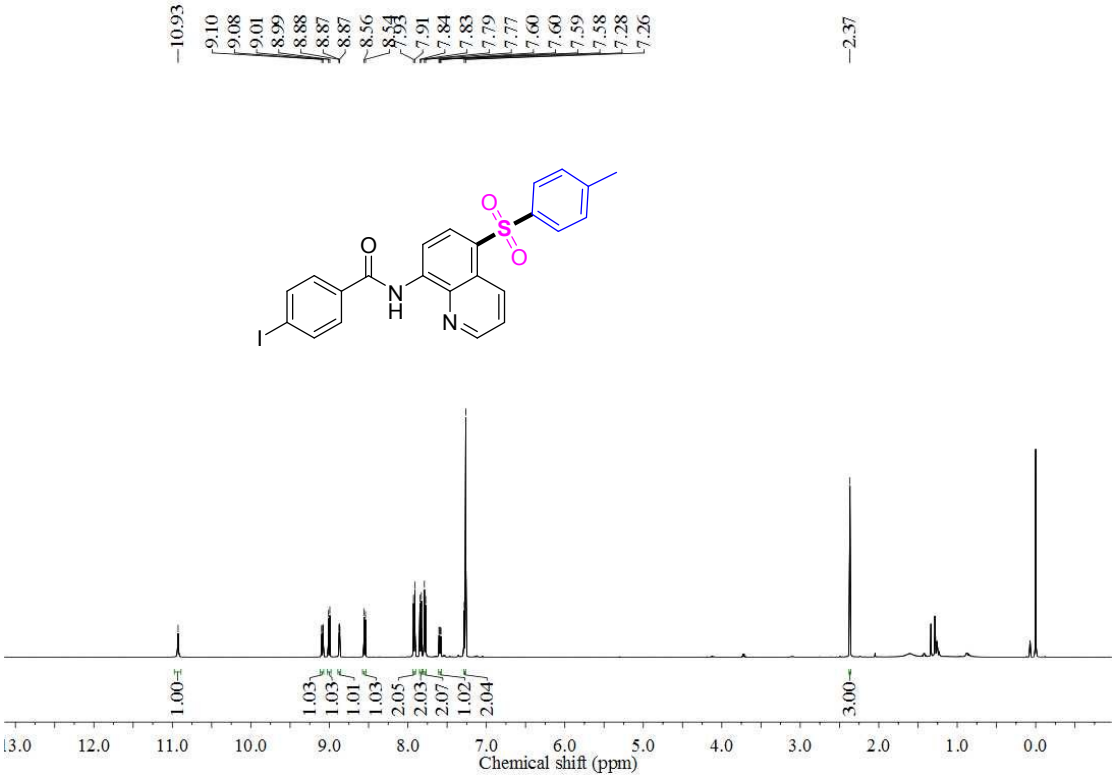
3n ^{1}H NMR



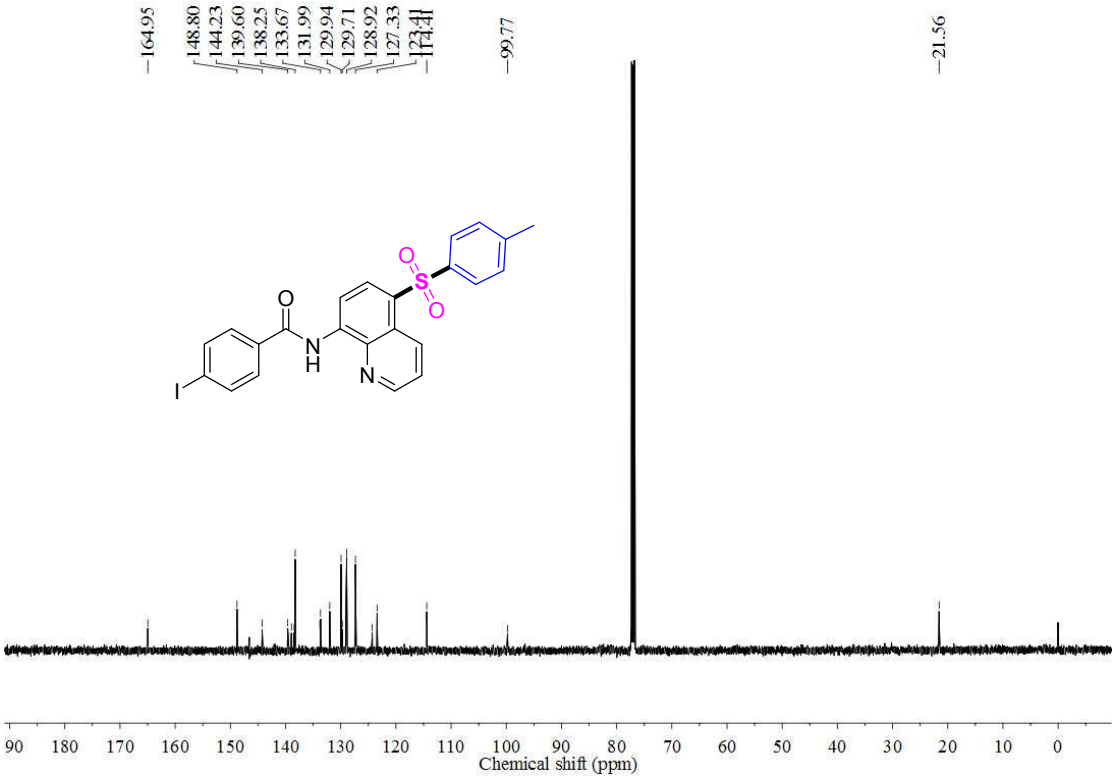
3n ^{13}C{^{1}H} NMR



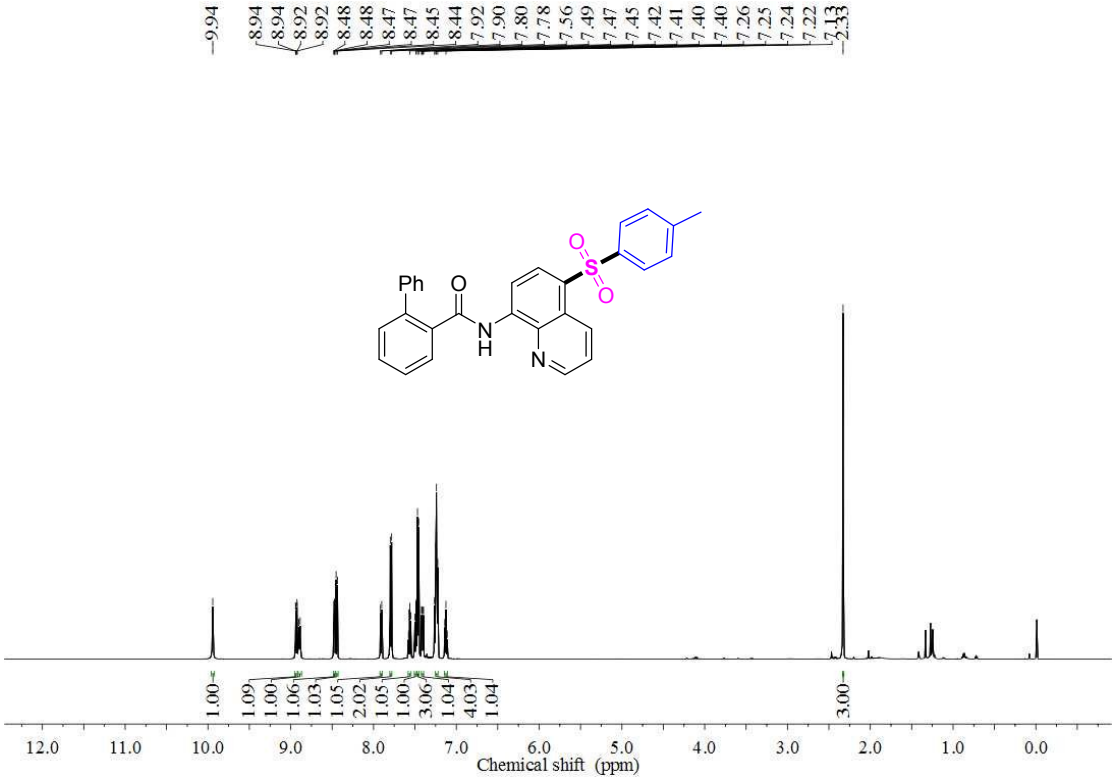
3o ^{1}H NMR



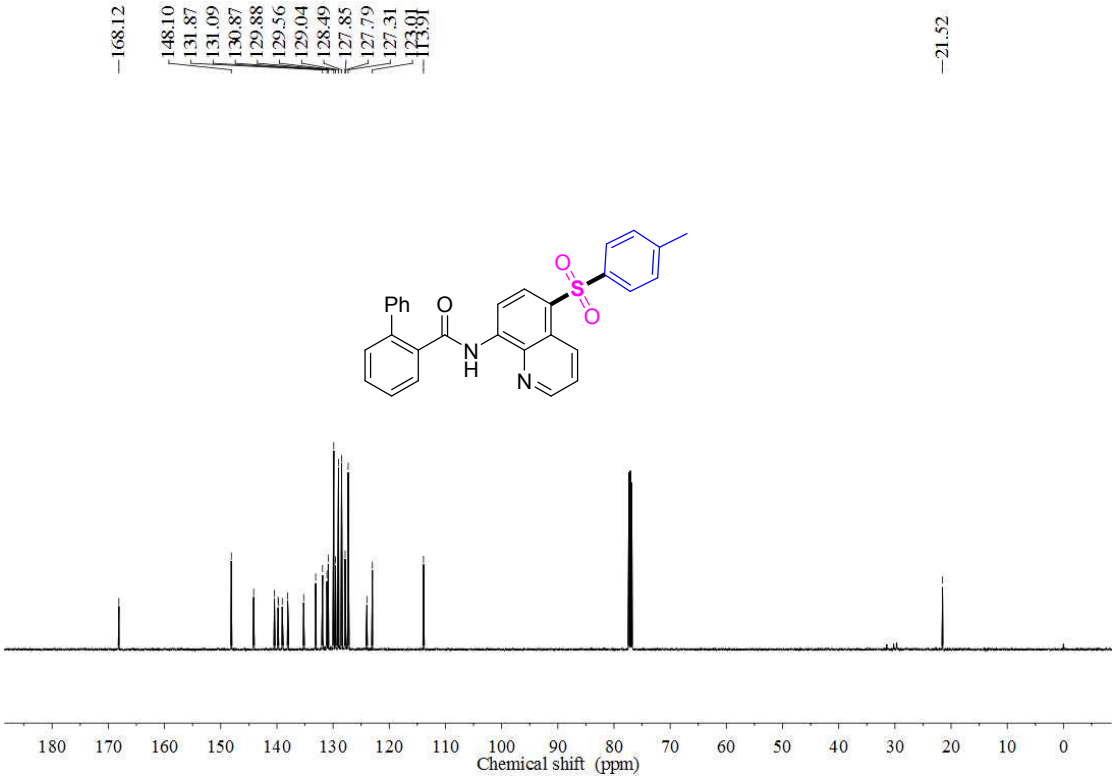
3o ^{13}C{^{1}H} NMR



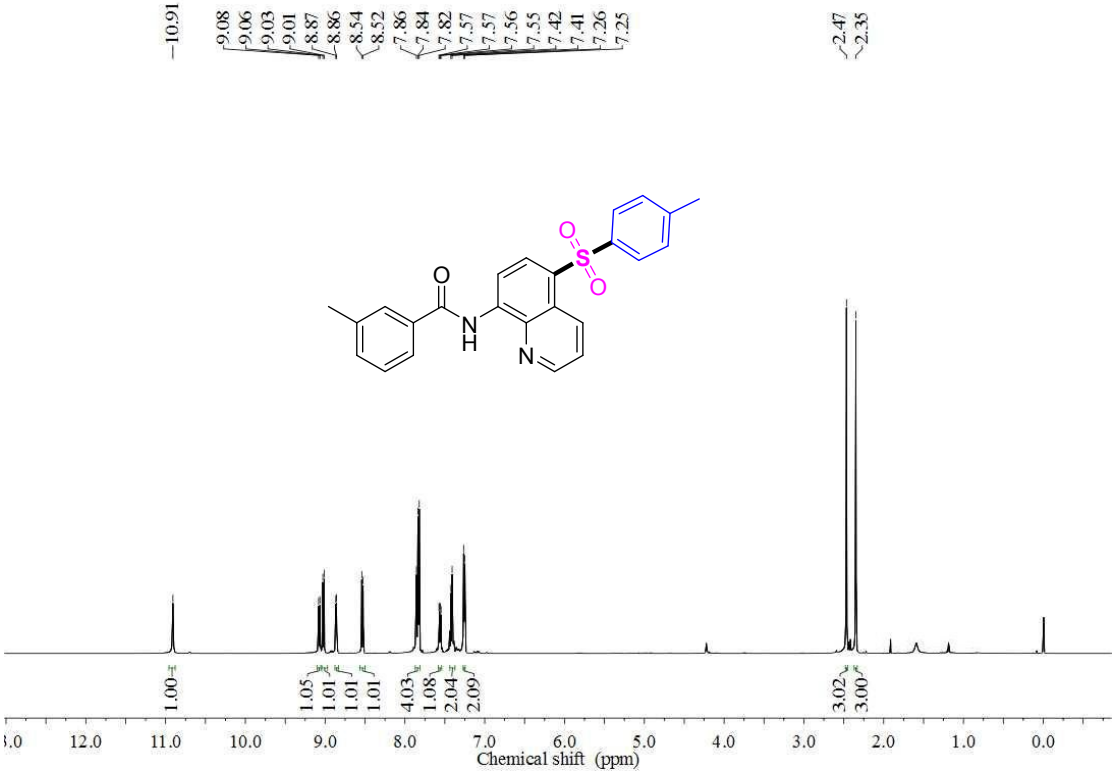
3p ^{1}H NMR



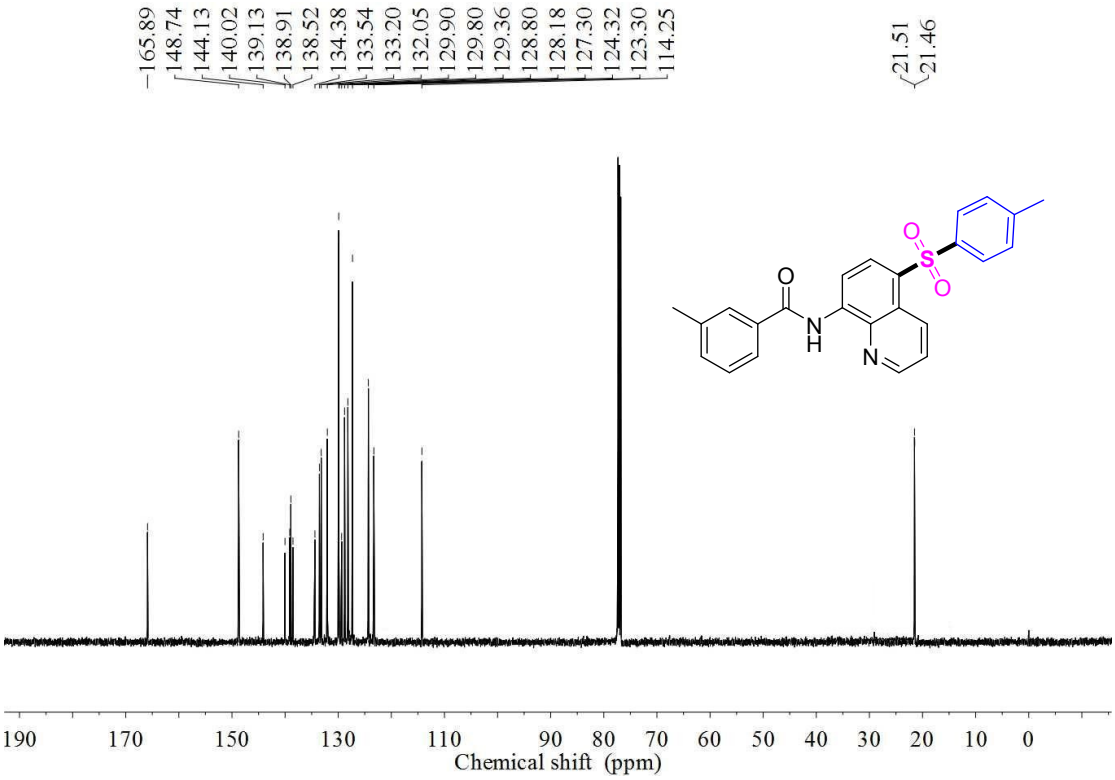
3p ^{13}C{^{1}H} NMR



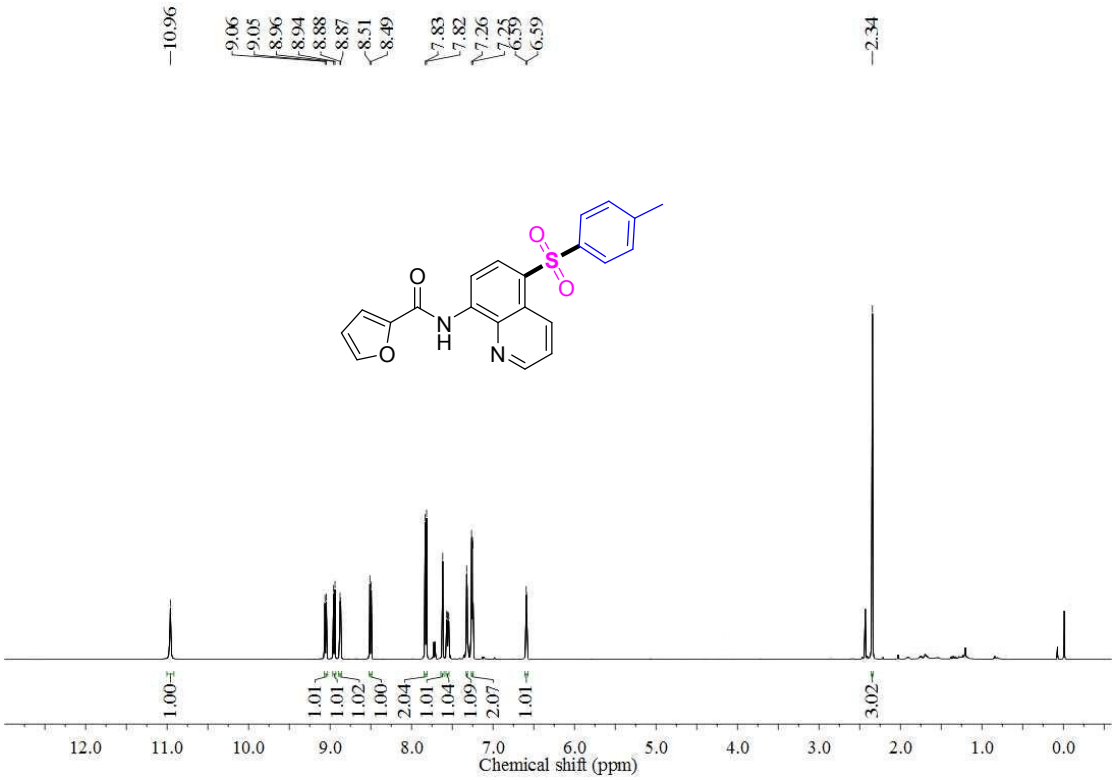
3q ^{1}H NMR



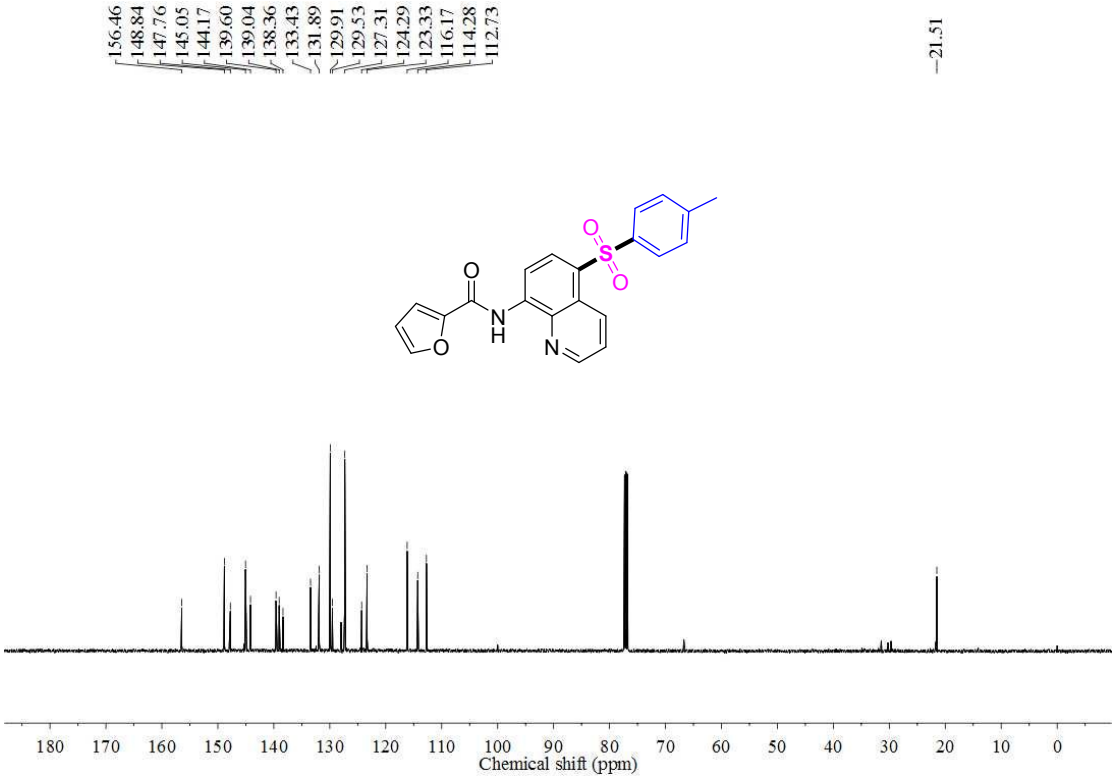
3q ^{13}C{^{1}H} NMR



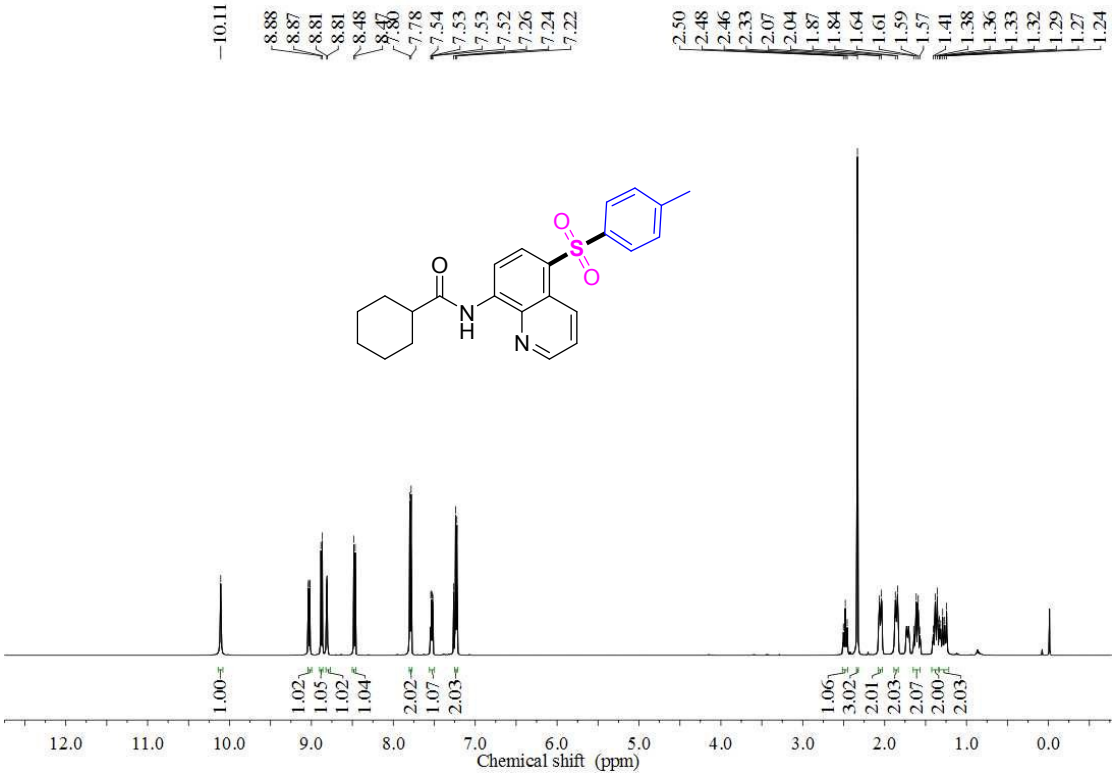
3r ^{1}H NMR



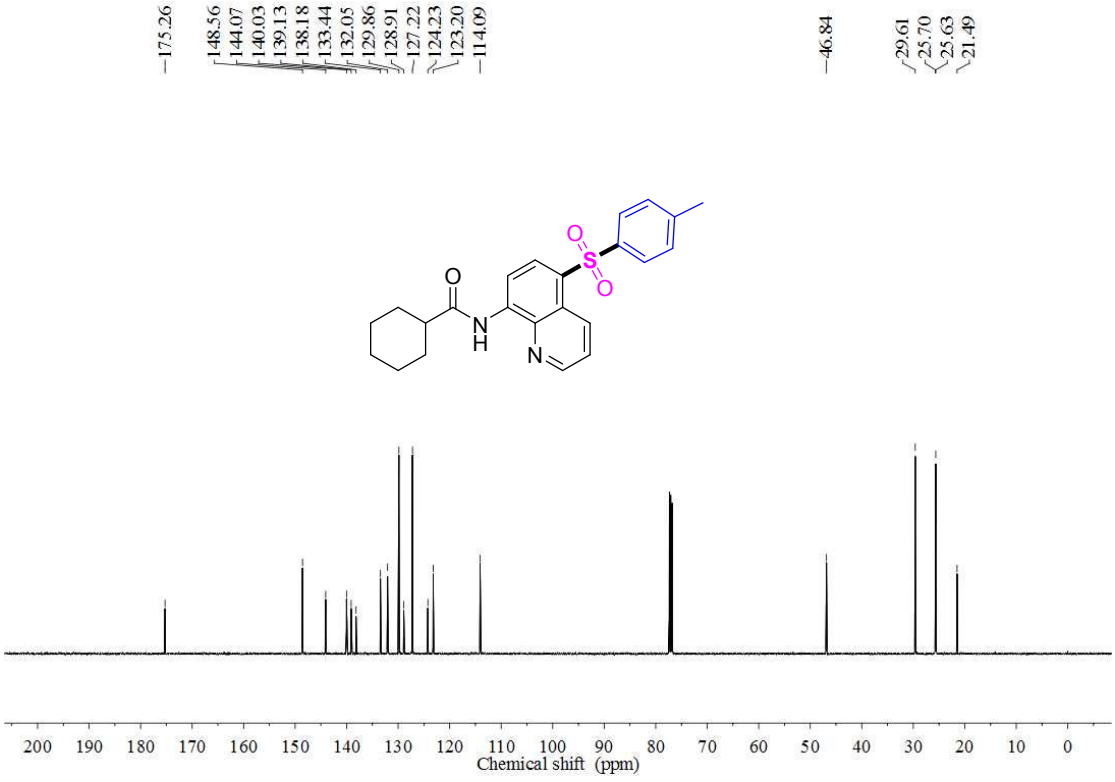
3r ^{13}C{^{1}H} NMR



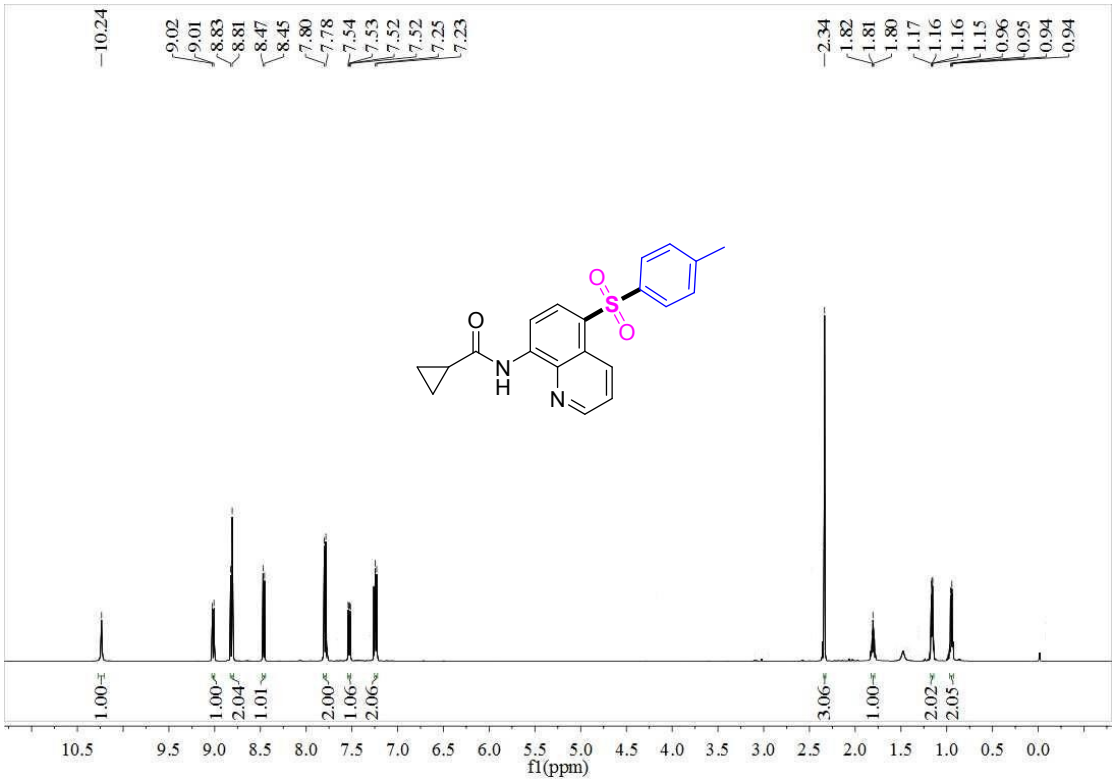
3s ^{1}H NMR



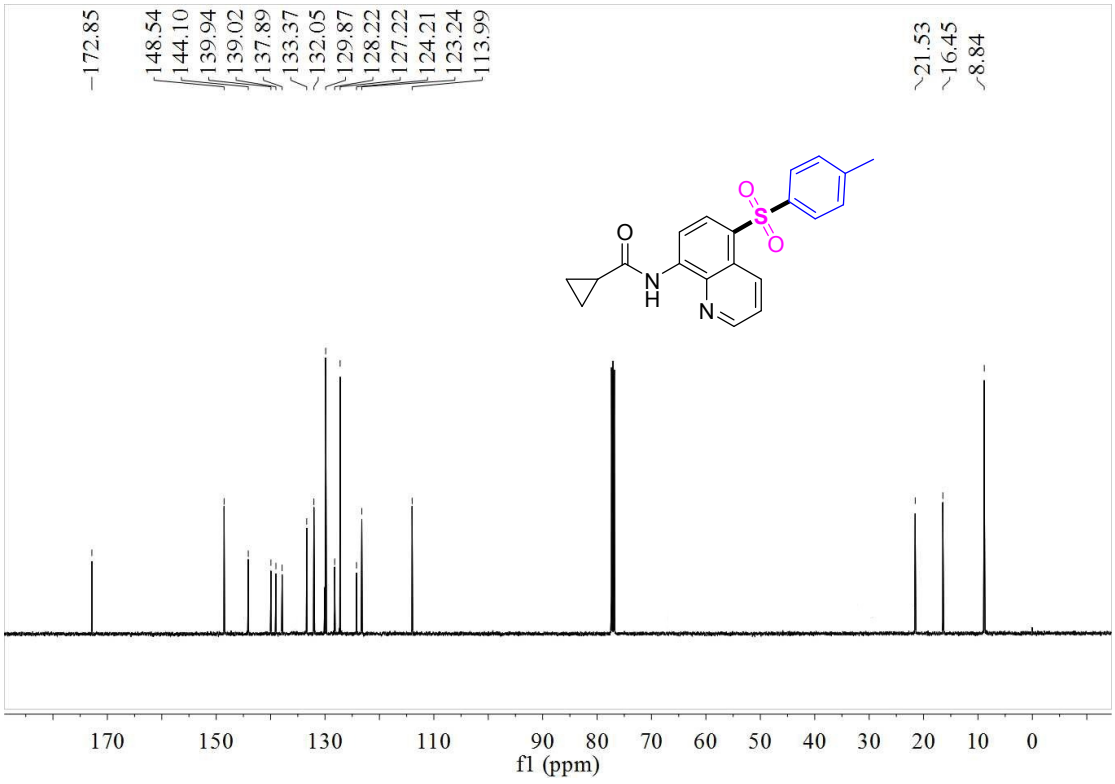
3s ^{13}C{^{1}H} NMR



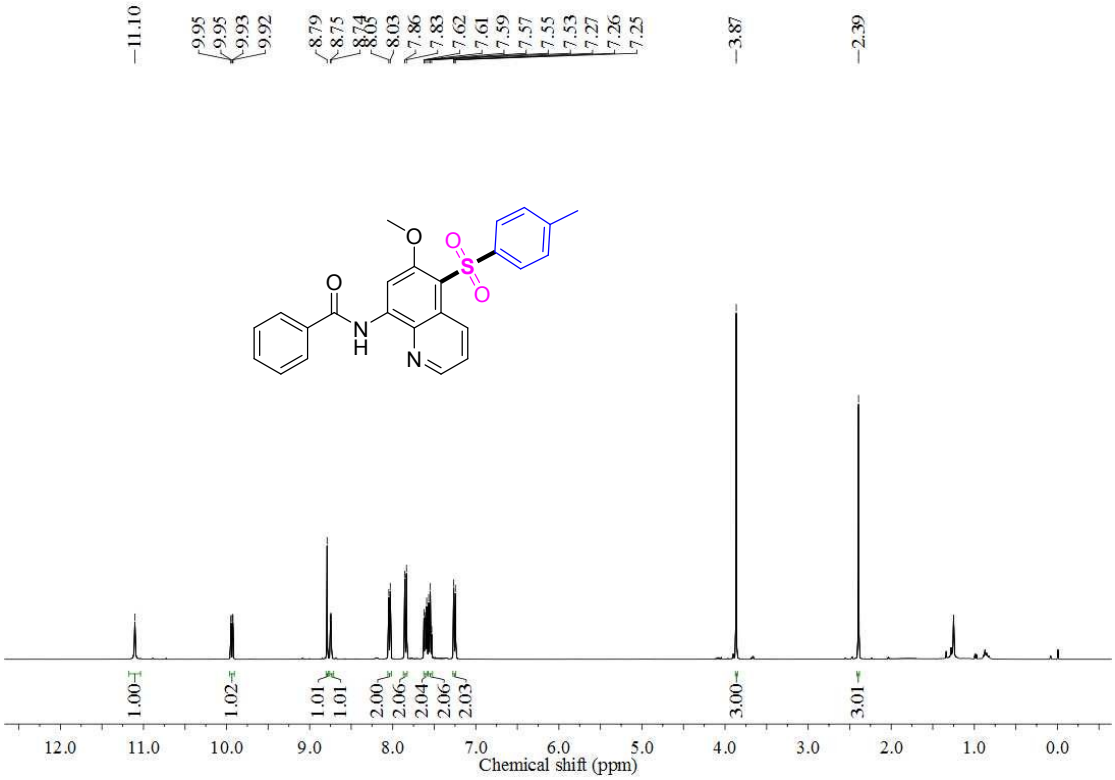
3t ^{1}H NMR



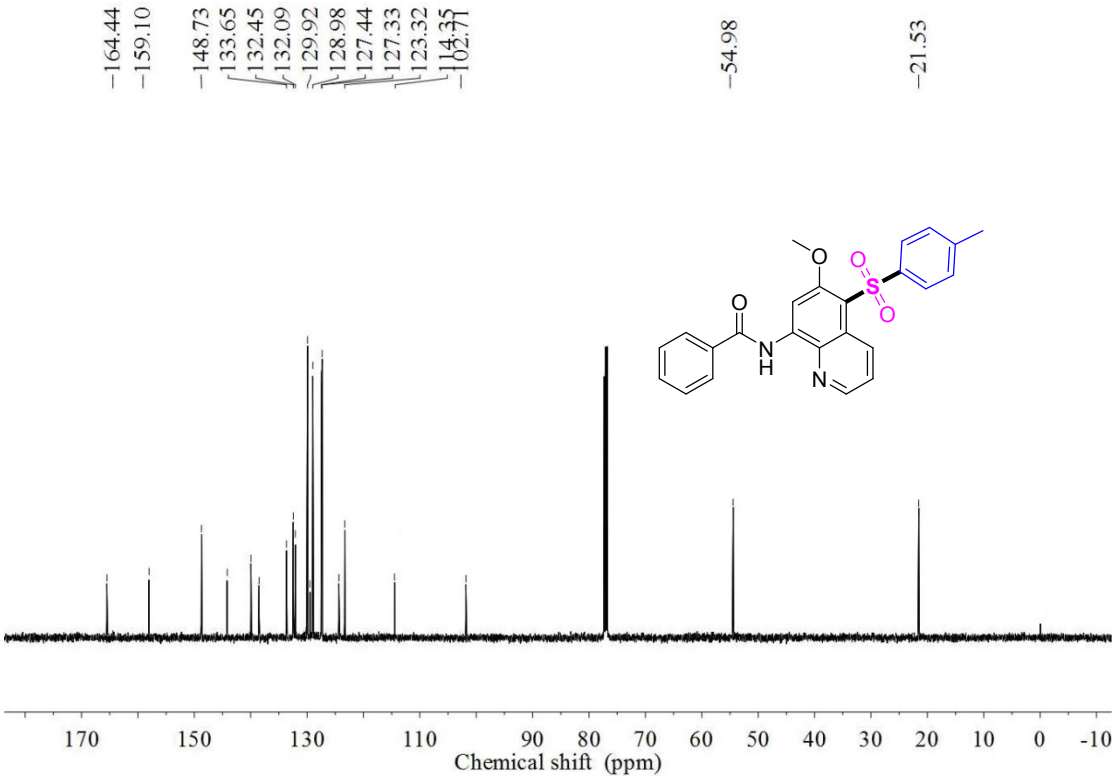
3t ^{13}C{^{1}H} NMR



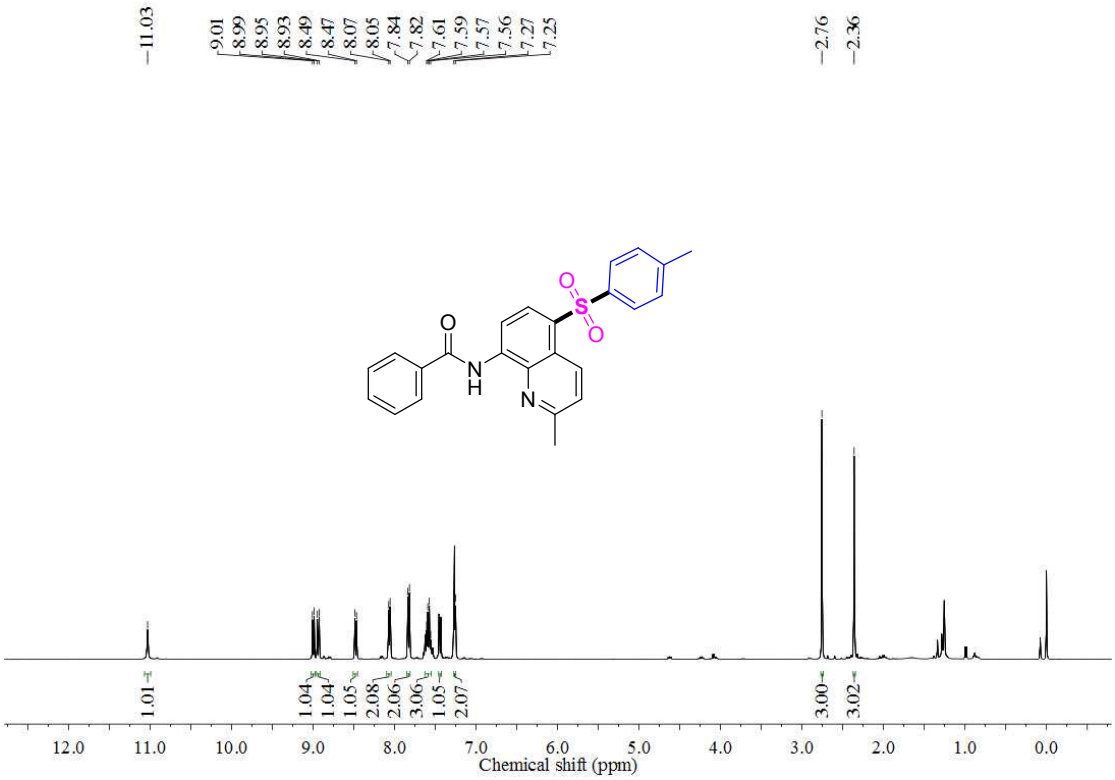
3u ^{1}H NMR



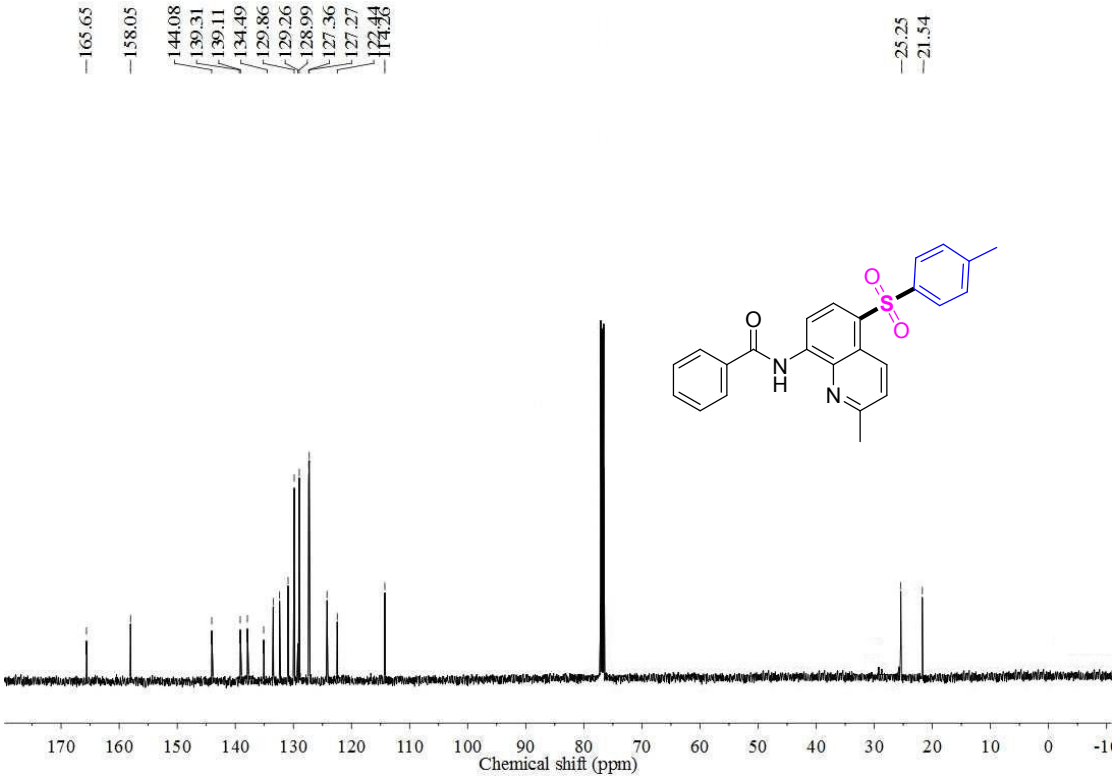
3u ^{13}C{^{1}H} NMR



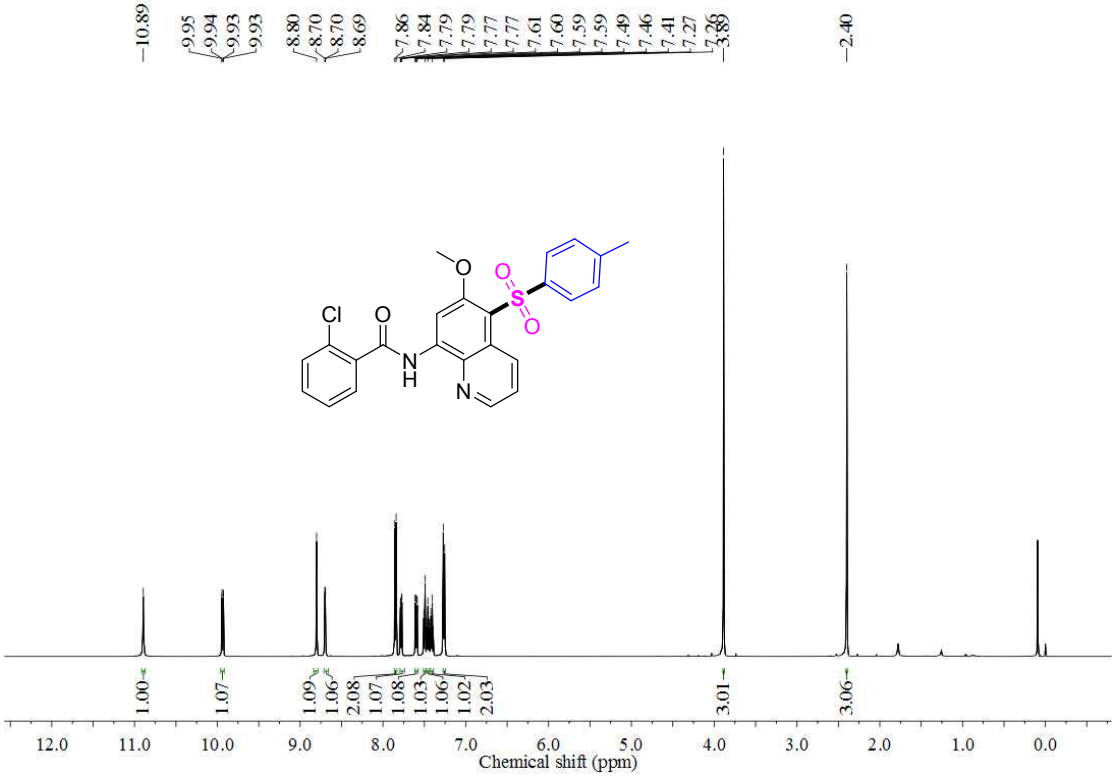
3v ^{1}H NMR



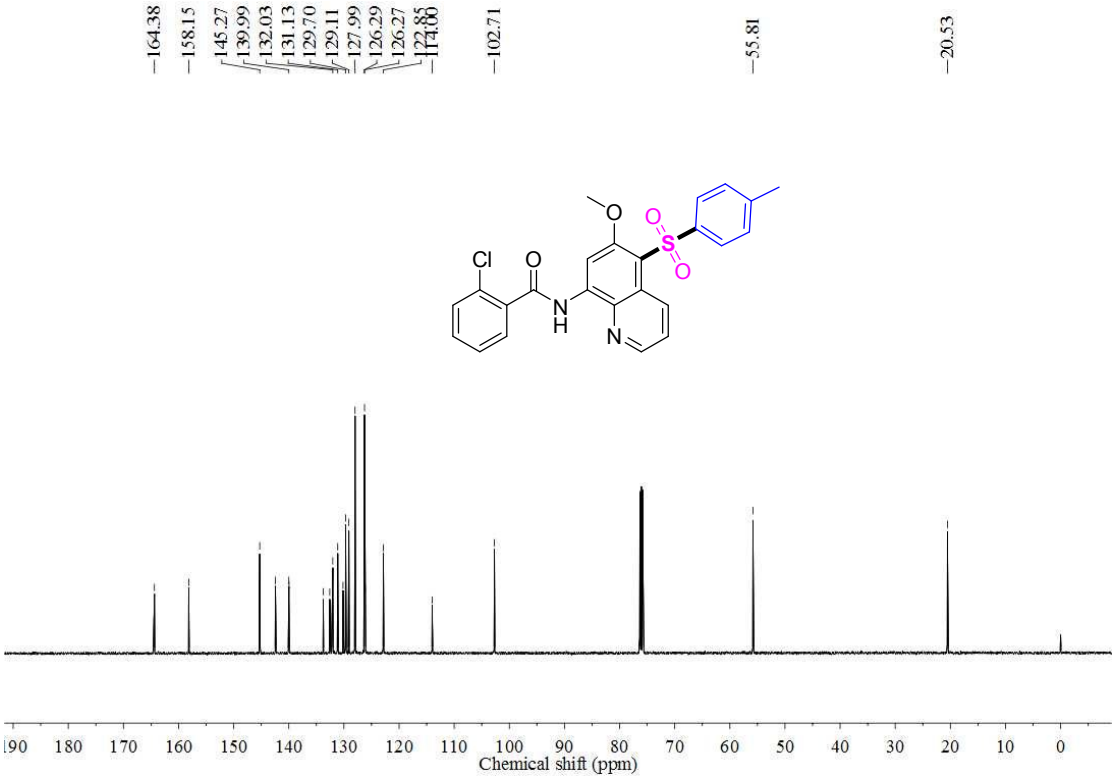
3v ^{13}C{^{1}H} NMR



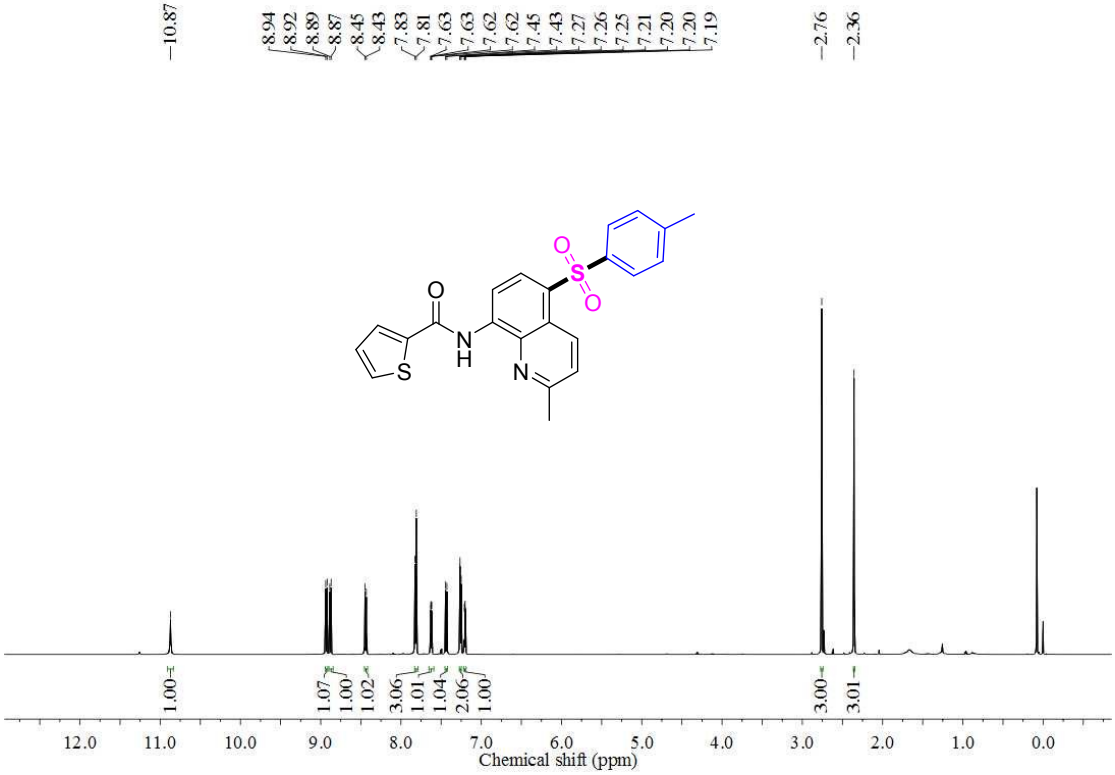
3w ^{1}H NMR



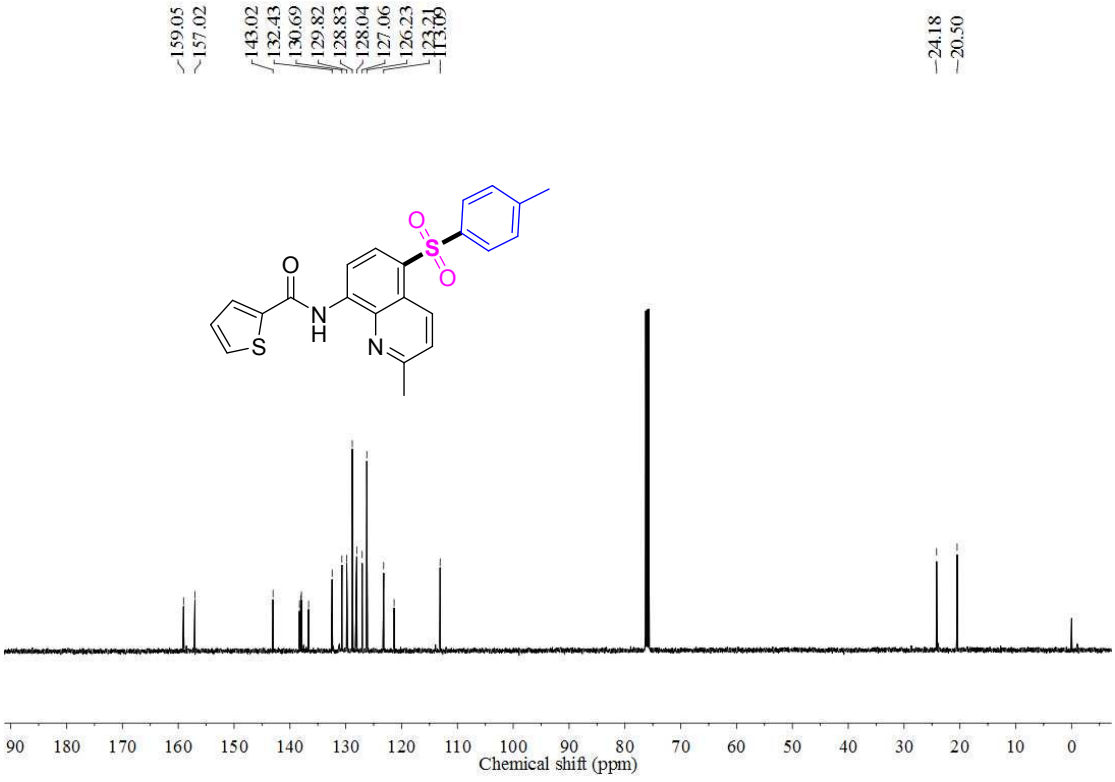
3w ^{13}C{^{1}H} NMR



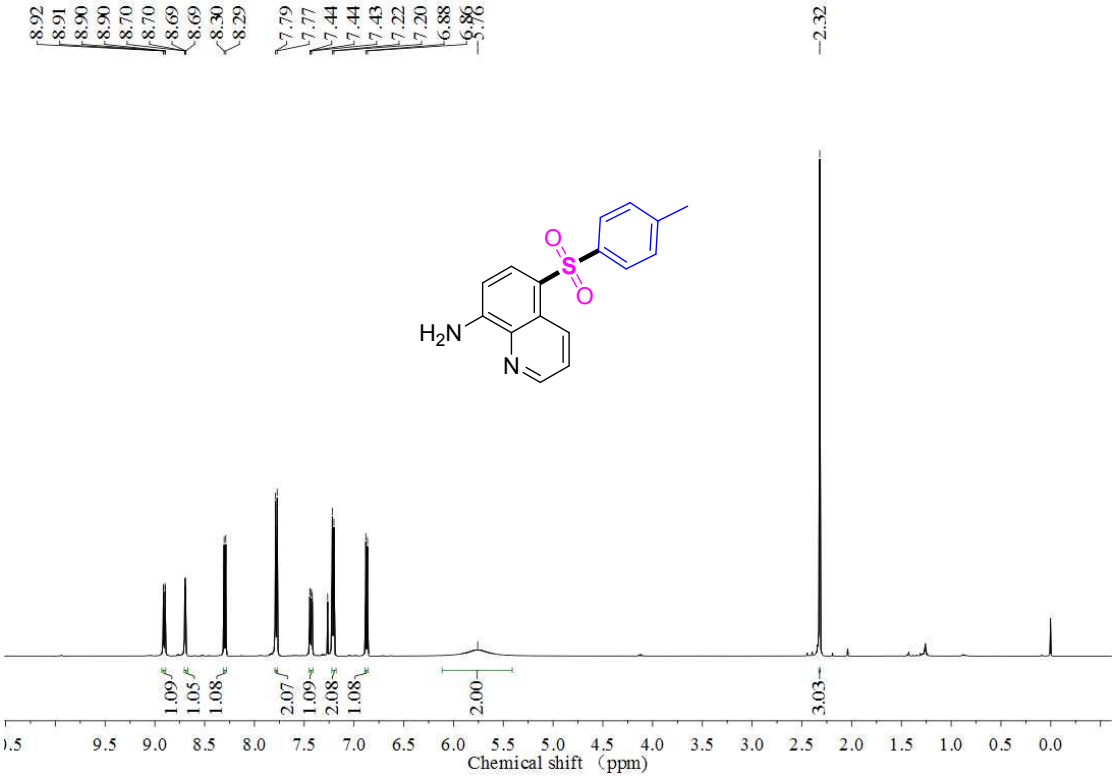
3x ^{1}H NMR



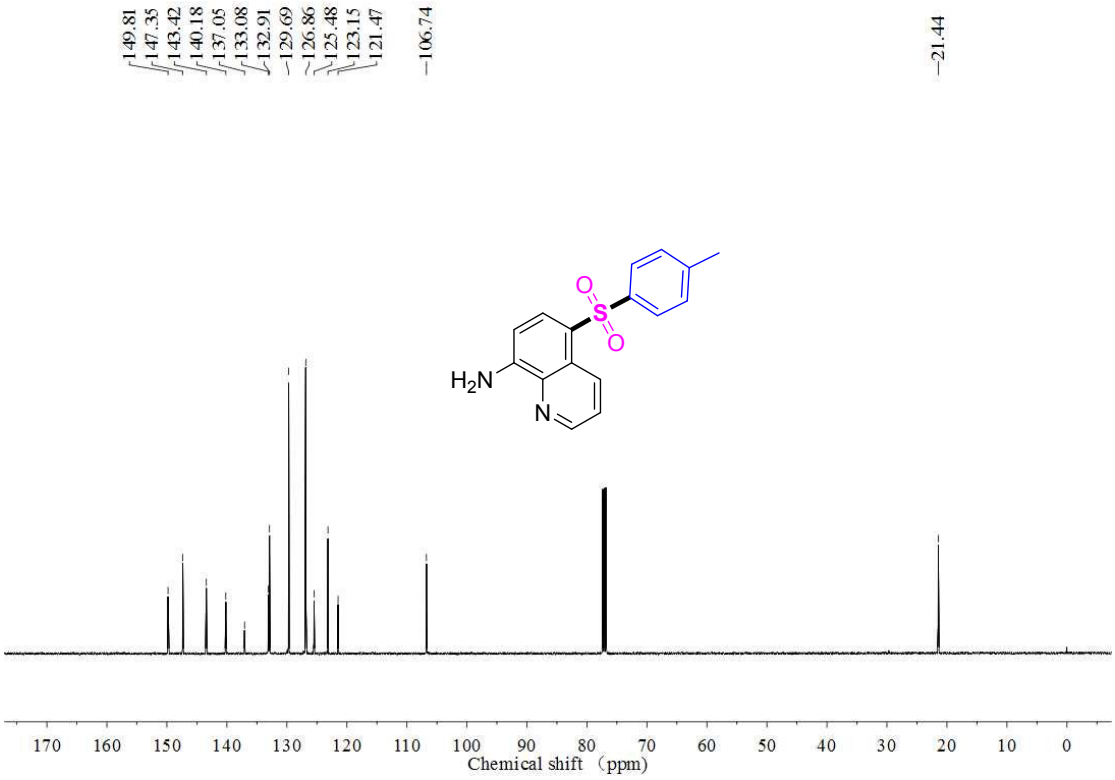
3x ^{13}C{^{1}H} NMR



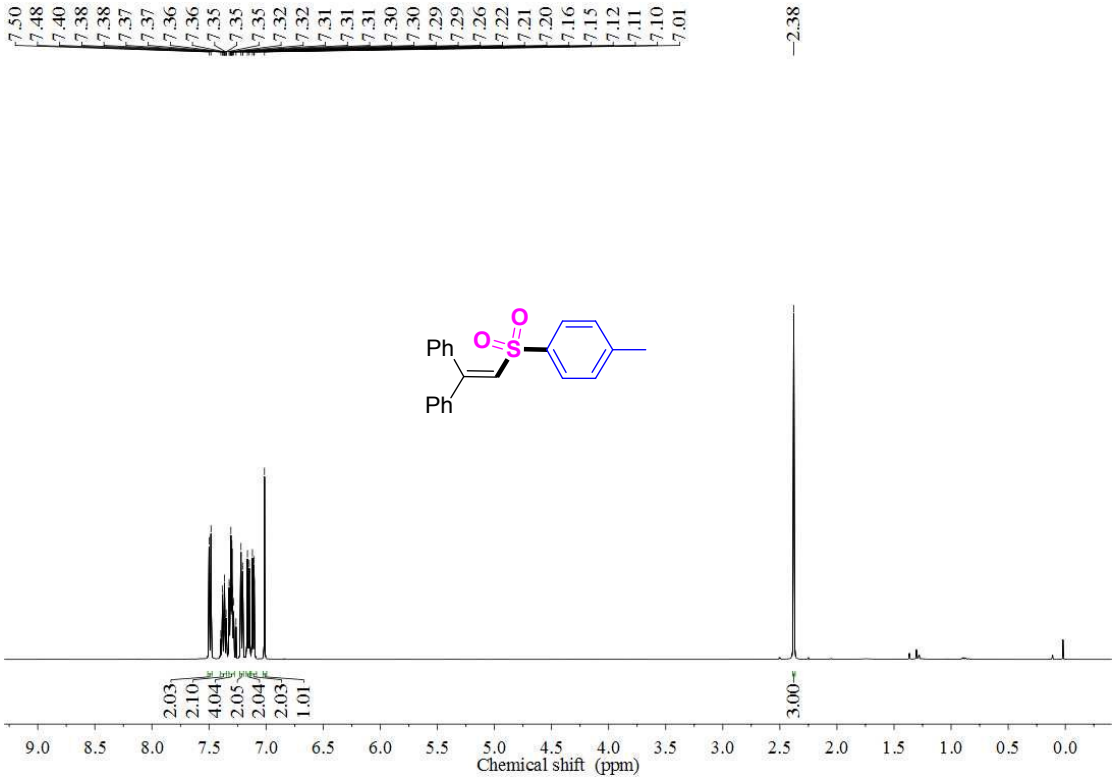
4a ^{1}H NMR



4a ^{13}C{^{1}H} NMR



7 ^{1}H NMR


7.50
7.48
7.40
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.26
7.22
7.21
7.20
7.16
7.15
7.12
7.11
7.10
7.01
2.38
Ph
Ph
O
O
S
2.03
2.10
4.04
2.05
2.04
2.03
1.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Chemical shift (ppm)