

Supporting Information

Electrooxidative tandem cyclization of *N*-propargylanilines with sulfinic acids for rapid access to 3-arylsulfonylquinoline derivatives

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1. General considerations

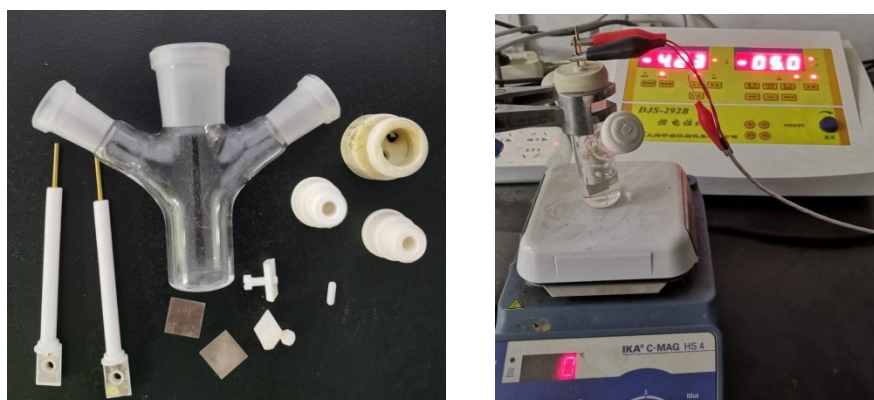
All ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a 600 MHz

Bruker FT-NMR spectrometer (600 MHz or 150 MHz or 564 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as internal reference. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purification. The starting material propargylamines (**1a–1u**) were prepared according to the reported method (L. Zhang, S. Chen, Y. Gao, P. Zhang, Y. Wu, G. Tang and Y. Zhao, *Org. Lett.*, 2016, **18**, 1286). The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purification. All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography packed with 200–300 mesh silica gels, SiO₂.

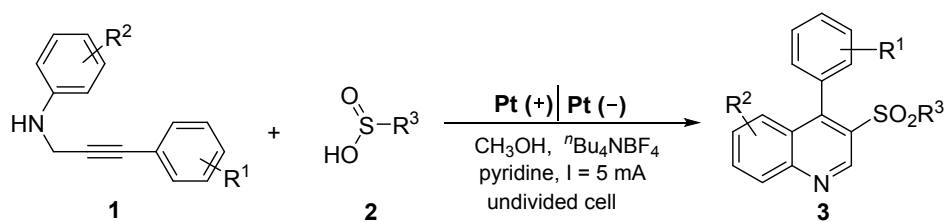
2. General procedure for the reaction

2.1 Graphical guide for the set-up

As experimental set-up, two platinum plate electrodes (15 mm×15 mm×0.3 mm), rubber plugs, an undivided three-necked bottle, a dual display potentiostat (DJS-292B) (Made in China) and a magnetic whisk were used.

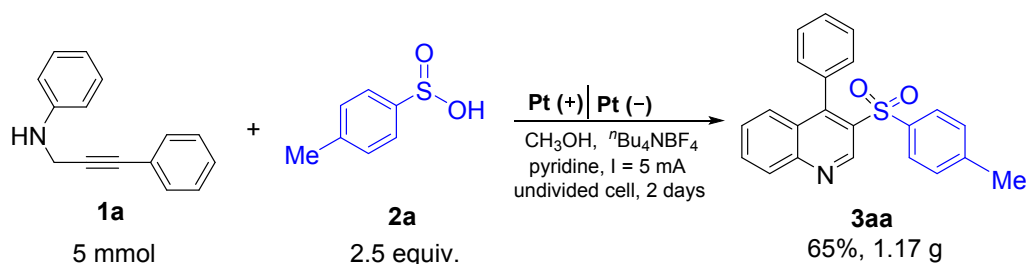


2.2 Experimental procedures



N-(3-Phenyl-2-propynyl)aniline derivative (**1**, 0.20 mmol), sulfinic acid (**2**, 0.50 mmol), pyridine (0.40 mmol), ⁿBu₄NBF₄ (0.30 mmol) and CH₃OH (5.0 mL) were sequentially added to a 15.0 mL oven-dried undivided three necked bottle that equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. The bottle was equipped with two platinum electrodes (1.5 cm×1.5 cm×0.3 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under air at room temperature for 5 h. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1 to 5:1) to give the desired product (**3**).

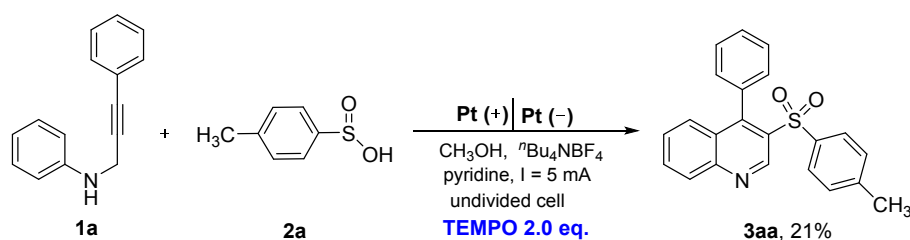
2.3 Gram scale synthesis



N-(3-Phenylprop-2-yn-1-yl)aniline (**1a**, 5.0 mmol), 4-methylbenzenesulfinic acid (**2a**, 12.5 mmol), pyridine (10.0 mmol), ⁿBu₄NBF₄ (7.5 mmol) and CH₃OH (125 mL) were sequentially added to a 250 mL oven-dried undivided electrolytic cell that equipped with a magnetic stirrer bar and sealed with PTFE plug under air atmosphere. The bottle was equipped with two platinum electrodes (5 cm×5 cm×0.3 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at room temperature for 2 days. When the reaction was complete, the reaction solution was concentrated in vacuum. The resulting crude mixture was purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1) to give the desired product (**3aa**) in 65% yield.

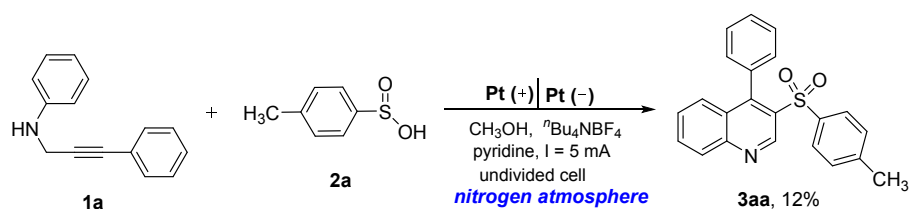
3. Preliminary mechanistic study

3.1 Free radical-inhibiting experiment



N-(3-Phenylprop-2-yn-1-yl)aniline (**1a**, 0.20 mmol), 4-methylbenzenesulfonic acid (**2a**, 0.50 mmol), pyridine (0.40 mmol), ⁿBu₄NBF₄ (0.30 mmol), 2,2,6,6-tetramethyl-1-oxypiperidine (TEMPO, 0.40 mmol) and CH₃OH (5.0 mL) were sequentially added to a 15.0 mL oven-dried undivided three necked bottle equipped with a magnetic stirrer bar and sealed with rubber plugs under air atmosphere. The bottle was equipped with two platinum electrodes (1.5 cm×1.5 cm×0.3 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under air at room temperature for 5 h. After the reaction was completed, the product **3aa** was isolated in 21% yield, indicating that radical process might be involved under the standard conditions.

3.2 The model reaction under nitrogen atmosphere



Under nitrogen atmosphere, *N*-(3-phenylprop-2-yn-1-yl) aniline (**1a**, 0.20 mmol), 4-methylbenzenesulfonic acid (**2a**, 0.50 mmol), pyridine (0.40 mmol), ⁿBu₄NBF₄ (0.3 mmol), 2,2,6,6-tetramethyl-1-oxypiperidine (TEMPO, 0.40 mmol) and CH₃OH (5.0 mL) were sequentially added to a 15.0 mL oven-dried undivided three necked flask, which equipped with a magnetic stirrer bar. The bottle was equipped with two platinum electrodes (1.5 cm×1.5 cm×0.3 mm) as both the anode and cathode and flushed with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 5 h. After the reaction was completed, the product **3aa** was isolated in 12% yield, indicating oxygen is necessary in the process.

3.3 The cyclic voltammetry (CV) determination

3.3.1 The cyclic voltammetry determination for **1a**, **2a** and **3aa**

Cyclic voltammetry was performed in a three electrode cell connected to a Schlenk line at room temperature. The working electrode was a platinum wire; the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode. A 5.0 mL of MeOH containing 0.30 mmol *n*-Bu₄NBF₄ and 0.40 mmol pyridine was added into the electrochemical cell in all experiments. The applied potential range is 4.0 to -1.0 V at a sweep rate of 100 mV/s using a CHI760E electrochemical workstation under ambient conditions. The cyclic voltammeteries (CVs) of **1a**, **2a** and **3aa** were listed in Figure S1.

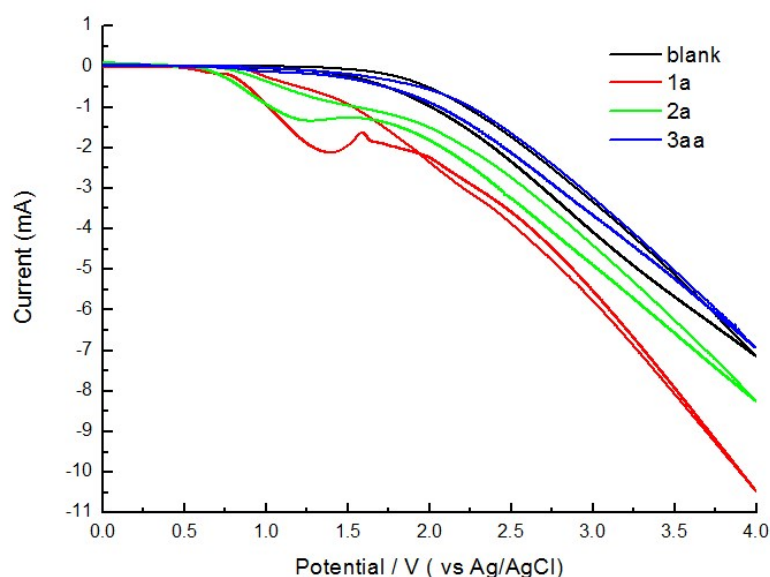


Figure S1. The cyclic voltammeteries (CVs) of **1a**, **2a**, and **3aa** in the presence of pyridine (0.40 mmol) in CH₃OH (5.0 mL) with *n*-Bu₄NBF₄ (0.30 mmol) using a platinum wire as the working electrode, and a Pt wire as the counter electrode, and an Ag/AgCl as the reference electrode

Black line, blank; Red line, *N*-(3-phenylprop-2-yn-1-yl)aniline (**1a**, 0.20 mmol)

Green line, 4-methylbenzenesulfinic acid (**2a**, 0.50 mmol)

Blue line, 4-phenyl-3-tosylquinoline (**3aa**, 0.17 mmol)

An oxidation potential peak of substrate *N*-(3-phenylprop-2-yn-1-yl) aniline (**1a**) (Ag/AgCl in CH₃OH) was found at 1.39 V (Figure S1, red line). The oxidation peak of 4-methylbenzenesulfinic acid (**2a**) (Ag/AgCl in CH₃OH) was observed at 1.28 V (Figure S1, green line). The results indicated that 4-methylbenzenesulfinic acid (**2a**) was probably oxidized at the surface of anode before **1a** in the presence of pyridine.

3.3.2 The cyclic voltammeteries of mixtures **1a/2a** in different molar ratios

Cyclic voltammetry was performed in a three electrode cell connected to a Schlenk line at room temperature. The working electrode was a platinum wire; the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode. A 5.0 mL of MeOH containing 0.30 mmol *n*-Bu₄NBF₄ and 0.40 mmol pyridine was added into the electrochemical cell in all experiments. The applied potential range is 4.0 to -1.0 V at a sweep rate of 100 mV/s using a CHI760E electrochemical workstation under ambient conditions. The cyclic voltammeteries (CVs) of mixtures **1a/2a** in different molar ratios were listed in Figure S2. From Figure 2, it can be seen obviously that 4-methylbenzenesulfinate (**2a**) is easier to be oxidized than that of **1a** under the present reaction conditions.

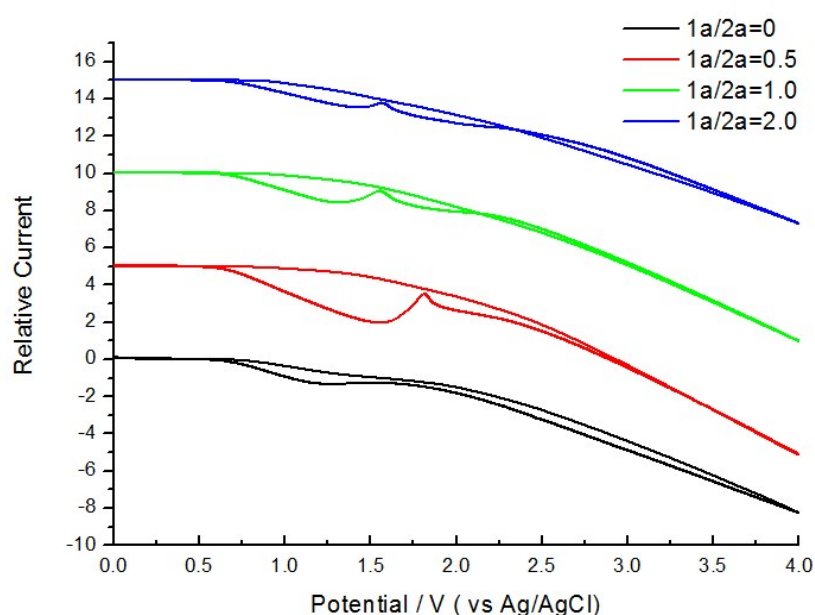


Figure S2. The cyclic voltammetry of mixtures of **1a** and **2a** in the presence of pyridine (0.40 mmol) in CH₃OH (5.0 mL) with *n*Bu₄NBF₄ (0.3 mmol) a platinum wire as the working electrode, and a Pt wire and Ag/AgCl as the counter and reference electrodes

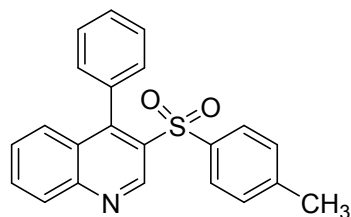
Black line, **1a/2a** = 0; Red line, **1a/2a** = 0.50; Green line, **1a/2a** = 1.0; Blue line, **1a/2a** = 2.0

4. Faradaic efficiency

$$\eta = \frac{\text{moles of product (measured by isolated)}}{It/nF} \times 100\%$$

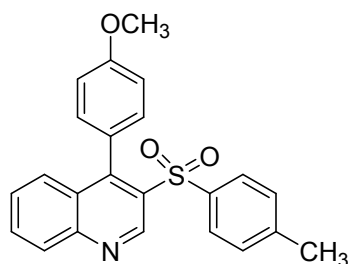
The current efficiency c.e. (coulombic yield) for the products were given according to the following Faraday efficiency formula. They were presented in Schemes 3 and 4 in the revised main text.

5. Characterization data for the products



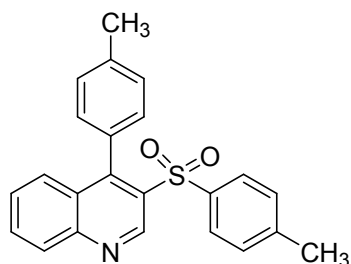
4-Phenyl-3-tosylquinoline (3aa)¹

Yield: 64.0 mg (89%). ¹H NMR (600 MHz, CDCl₃): δ = 9.79 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.83–7.80 (m, 1H), 7.48–7.44 (m, 2H), 7.35–7.33 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.7, 149.6, 147.7, 144.0, 137.9, 132.6, 132.1, 129.9, 129.6, 129.2, 128.6, 127.8, 127.7, 127.6, 127.4, 127.4, 21.5.



4-(4-Methoxyphenyl)-3-tosylquinoline (3ba)¹

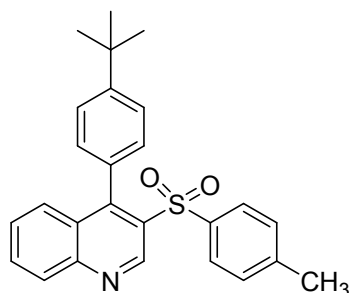
Yield: 72.4 mg (93%). ¹H NMR (400 MHz, CDCl₃): δ = 9.55 (s, 1H), 8.02 (d, *J* = 9.6 Hz, 1H), 7.39–7.37 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.43 (d, *J* = 2.4 Hz, 1H), 3.52 (s, 3H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 158.5, 148.0, 146.0, 145.3, 143.9, 137.9, 132.8, 132.8, 130.9, 129.9, 129.2, 128.8, 128.6, 127.8, 127.7, 124.8, 104.7, 55.3, 21.5.



4-(*p*-Tolyl)-3-tosylquinoline (3ca)¹

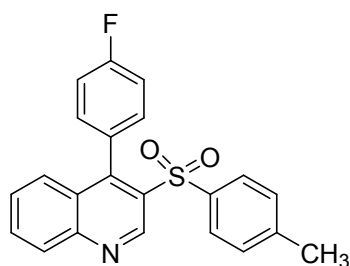
Yield: 65.0 mg (87%). ¹H NMR (600 MHz, CDCl₃): δ = 9.77 (s, 1H), 8.20 (d, *J* = 8.4

Hz, 1H), 7.82–7.80 (m, 1H), 7.46–7.44(m, 1H), 7.38–7.37 (m, 1H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 7.2$ Hz, 2H), 7.06 (d, $J = 7.8$ Hz, 2H), 6.86 (d, $J = 7.2$ Hz, 2H), 2.48 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 150.1, 149.6, 147.8, 144.0, 138.6, 138.0, 132.8, 132.0, 129.9, 129.7, 129.6, 129.1, 128.3, 128.0, 127.7, 127.5, 21.5, 21.4$.



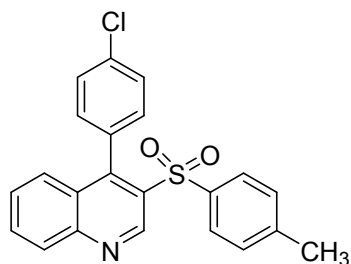
4-(4-(*tert*-Butyl)phenyl)-3-tosylquinoline (3da)¹

Yield: 73.1 mg (88%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.81$ (s, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.81 (td, $J_1 = 7.2$ Hz, $J_2 = 1.2$ Hz, 1H), 7.47–7.45 (m, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 7.8$ Hz, 2H), 6.87 (d, $J = 7.8$ Hz, 2H), 2.34 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 151.7, 150.1, 149.7, 147.6, 143.7, 137.8, 132.8, 132.0, 129.8, 129.6, 129.4, 129.0, 127.8, 127.6, 127.6, 127.5, 124.5, 34.7, 31.4, 21.5$.



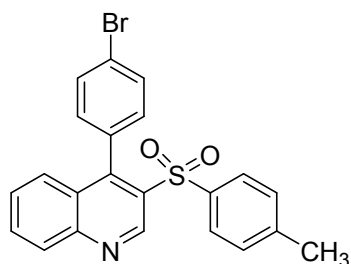
4-(4-Fluorophenyl)-3-tosylquinoline (3ea)³

Yield: 59.6 mg (79%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.78$ (s, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.84–7.82 (m, 1H), 7.50–7.48 (m, 1H), 7.35–7.33 (m, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.06 (t, $J = 8.4$ Hz, 2H), 6.97–6.95 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 162.8$ (d, $J = 247.5$ Hz), 149.6, 148.6, 147.5, 144.2, 137.8, 132.7, 132.1, 131.8 (d, $J = 8.4$ Hz), 129.6, 129.2, 128.3 (d, $J = 3.0$ Hz), 127.9, 127.6, 127.3, 127.0, 114.7 (d, $J = 21.0$ Hz), 21.4. ^{19}F NMR (564 MHz, CDCl_3) $\delta = -112.14$.



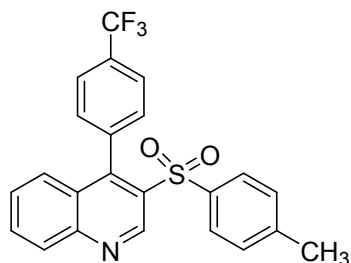
4-(4-Chlorophenyl)-3-tosylquinoline (3fa)³

Yield: 63.1 mg (80%). ¹H NMR (600 MHz, CDCl₃): δ = 9.76 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.85–7.82 (m, 1H), 7.50–7.47 (m, 1H), 7.34–7.32 (m, 3H), 7.28–7.26 (m, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.7, 148.3, 147.7, 144.3, 137.9, 135.0, 132.8, 132.2, 131.4, 131.1, 129.8, 129.3, 128.0, 127.9, 127.8, 127.1, 127.0, 21.5.



4-(4-Bromophenyl)-3-tosylquinoline (3ga)³

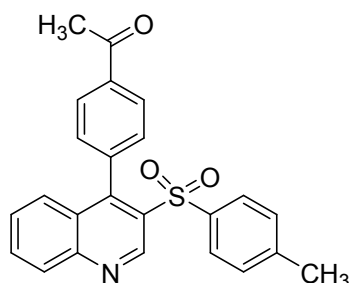
Yield: 73.6 mg (84%). ¹H NMR (600 MHz, CDCl₃): δ = 9.77 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.85–7.82 (m, 1H), 7.49–7.48 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 2.38 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.7, 148.3, 147.7, 144.4, 137.9, 132.7, 132.3, 131.6, 131.6, 130.9, 129.8, 129.3, 128.0, 127.9, 127.1, 127.0, 123.2, 21.6.



3-Tosyl-4-(4-(trifluoromethyl)phenyl)quinolone (3ha)¹

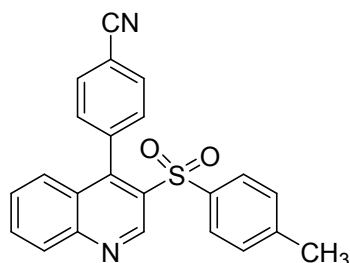
Yield: 66.7 mg (78%). ¹H NMR (600 MHz, CDCl₃): δ = 9.79 (s, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.87–7.84 (m, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.52–7.49 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz,

2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 149.7, 147.7, 147.5, 144.4, 137.6, 136.5, 132.6, 132.4, 130.8$ (q, $J = 33.0$ Hz), $130.4, 129.8, 129.3, 128.2, 127.7, 126.8, 126.7, 124.5$ (q, $J = 4.5$ Hz), 123.8 (q, $J = 271.5$ Hz), 21.4 . ^{19}F NMR (564 MHz, CDCl_3): $\delta = -62.72$.



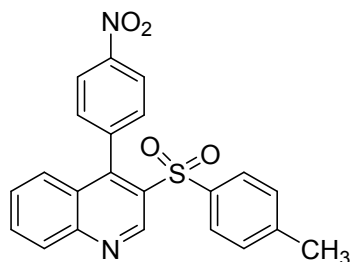
1-(4-(3-Tosylquinolin-4-yl)phenyl)ethan-1-one (3ia)³

Yield: 59.4 mg (74%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.75$ (s, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 2H), 7.85 (t, $J = 7.8$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 1H), 7.29 – 7.27 (m, 3H), 7.14 – 7.10 (m, 4H), 2.74 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 197.2, 149.4, 148.1, 147.4, 144.3, 137.6, 137.5, 136.8, 132.2, 130.1, 129.6, 129.2, 128.0, 127.6, 127.3, 126.8, 126.6, 26.6, 21.4$.



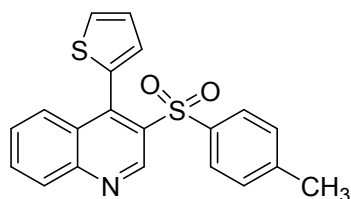
4-(3-Tosylquinolin-4-yl)benzonitrile (3ja)¹

Yield: 59.2 mg (77%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.75$ (s, 1H), 8.25 (d, $J = 8.4$ Hz, 1H), 7.88 – 7.86 (m, 1H), 7.67 (d, $J = 7.8$ Hz, 2H), 7.53 – 7.50 (m, 1H), 7.28 – 7.27 (m, 2H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.15 – 7.14 (m, 4H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 149.7, 147.7, 147.1, 144.8, 137.8, 137.8, 132.5, 132.4, 131.4, 130.8, 130.0, 129.5, 128.4, 127.8, 126.6, 126.5, 118.2, 112.8, 21.6$.



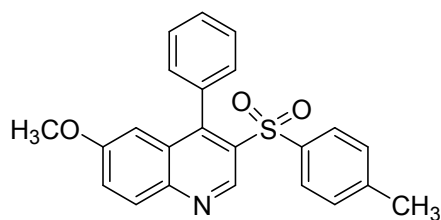
4-(4-Nitrophenyl)-3-tosylquinoline (3ka)¹

Yield: 60.7 mg (75%). ¹H NMR (600 MHz, CDCl₃): δ = 9.66 (s, 1H), 8.19–8.15 (m, 3H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 9.0 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.15–7.13 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.6, 148.1, 147.8, 146.9, 144.9, 139.7, 137.9, 132.6, 132.6, 131.1, 130.0, 129.6, 128.5, 127.8, 126.6, 126.4, 122.8, 21.6.



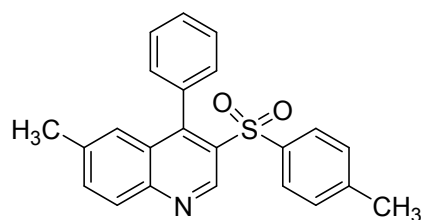
4-(Thiophen-2-yl)-3-tosylquinoline (3la)³

Yield: 57.8 mg (79%). ¹H NMR (600 MHz, CDCl₃): δ = 9.78 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.83–7.80 (m, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.51–7.49 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.13–7.09 (m, 3H), 7.00–6.99 (m, 1H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.5, 147.7, 144.1, 143.0, 137.5, 134.3, 132.3, 131.7, 131.4, 129.5, 129.3, 128.6, 128.4, 128.1, 127.8, 127.1, 126.7, 21.5.



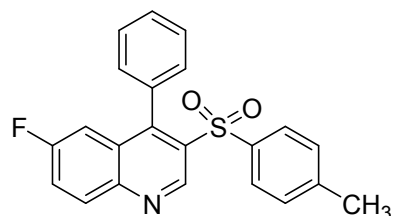
6-Methoxy-4-phenyl-3-tosylquinoline (3ma)¹

Yield: 69.3 mg (89%). ¹H NMR (600 MHz, CDCl₃): δ = 9.78 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.47–7.45 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.89–6.86 (m, 4H), 3.91 (s, 3H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 159.8, 149.9, 149.5, 147.6, 143.9, 137.8, 132.9, 132.0, 131.3, 129.4, 129.0, 127.8, 127.7, 127.6, 127.3, 124.4, 113.0, 55.3, 21.4.



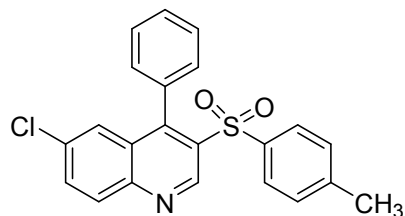
6-Methyl-4-phenyl-3-tosylquinoline (3na)¹

Yield: 64.9 mg (87%). ¹H NMR (600 MHz, CDCl₃): δ = 9.71 (s, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.64 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.35–7.32 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.05–7.04 (m, 3H), 6.94 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.0, 148.4, 146.8, 143.9, 138.1, 134.5, 132.8, 132.6, 130.0, 129.3, 129.2, 128.5, 127.9, 127.6, 127.5, 125.9, 21.7, 21.5.



6-Fluoro-4-phenyl-3-tosylquinoline (3oa)¹

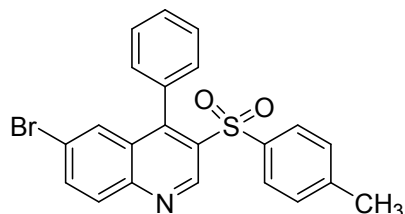
Yield: 52.8mg (70%). ¹H NMR (600 MHz, CDCl₃): δ = 9.66 (s, 1H), 8.13 (dd, *J*₁ = 9.6 Hz, *J*₂ = 5.4 Hz, 1H), 7.51–7.48 (m, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.87–6.83 (m, 3H), 2.27 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 161.0 (d, *J* = 249.3 Hz), 149.1 (d, *J* = 6.0 Hz), 147.1 (d, *J* = 1.5 Hz), 146.8, 144.2, 137.6, 133.4, 132.2, 132.2, 129.8, 129.2, 128.9, 128.6 (d, *J* = 10.5 Hz), 127.9, 127.8, 122.4 (d, *J* = 27.0 Hz), 110.6 (d, *J* = 24.0 Hz), 21.5. ¹⁹F NMR (564 MHz, CDCl₃): δ = -109.67.



6-Chloro-4-phenyl-3-tosylquinoline (3pa)¹

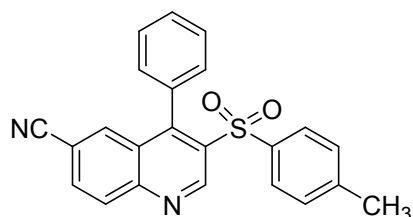
Yield: 55.2 mg (70%). ¹H NMR (600 MHz, CDCl₃): δ = 9.77 (s, 1H), 8.15 (d, *J* = 9.0 Hz, 1H), 7.74 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.8 Hz,

2H), 6.96–6.94 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 148.9, 148.1, 148.0, 144.2, 137.7, 134.0, 133.6, 132.9, 132.0, 131.3, 129.9, 129.3, 128.9, 128.3, 127.9, 127.8, 126.0, 21.5.



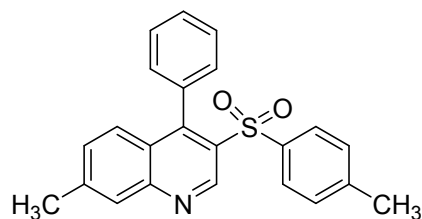
6-Bromo-4-phenyl-3-tosylquinoline (3qa)¹

Yield: 71.0 mg (81%). ^1H NMR (600 MHz, CDCl_3): δ = 9.78 (s, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.87 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.2 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 148.8, 148.3, 148.1, 144.2, 137.6, 135.5, 133.5, 131.8, 131.3, 129.9, 129.3, 129.0, 128.7, 127.9, 127.8, 122.2, 21.5.



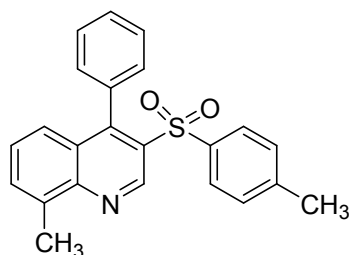
4-Phenyl-3-tosylquinoline-6-carbonitrile (3ra)¹

Yield: 60.8 mg (79%). ^1H NMR (600 MHz, CDCl_3): δ = 9.89 (s, 1H), 8.31 (d, J = 9.0 Hz, 1H), 7.95 (dd, J_1 = 9.0 Hz, J_2 = 1.8 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.2 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ = 150.5, 150.3, 150.2, 144.5, 137.1, 134.4, 133.7, 132.3, 131.3, 131.1, 129.8, 129.3, 128.0, 127.9, 127.2, 117.8, 111.6, 21.5.



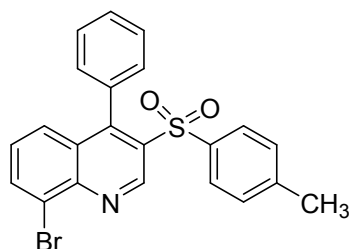
7-Methyl-4-phenyl-3-tosylquinoline (3sa)³

Yield: 61.3 mg (82%). ¹H NMR (600 MHz, CDCl₃): δ = 9.80 (s, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.82–7.80 (m, 1H), 7.46–7.44 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.28–7.25 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 6.6 Hz, 1H), 6.54 (s, 1H), 2.36 (s, 3H), 2.24 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 150.0, 149.6, 147.5, 143.8, 137.9, 137.1, 132.5, 132.4, 132.0, 130.1, 129.5, 129.2, 129.0, 127.9, 127.7, 127.6, 127.4, 127.2, 21.4, 21.2.



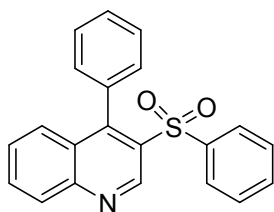
8-Methyl-4-phenyl-3-tosylquinoline (3ta)¹

Yield: 52.3 mg (70%). ¹H NMR (600 MHz, CDCl₃): δ = 9.79 (s, 1H), 7.64 (d, *J* = 6.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.33–7.30 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 7.2 Hz, 2H), 2.86 (s, 3H), 2.34 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.7, 148.7, 146.5, 143.9, 138.1, 137.5, 133.0, 132.3, 132.1, 130.0, 129.1, 128.4, 127.8, 127.5, 127.4, 125.3, 21.4, 18.1.



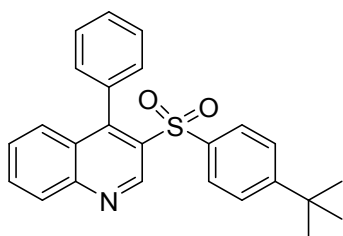
8-Bromo-4-phenyl-3-tosylquinoline (3ua)³

Yield: 65.7 mg (75%). ¹H NMR (600 MHz, CDCl₃): δ = 9.87 (s, 1H), 8.13 (dd, *J*₁ = 6.6 Hz, *J*₂ = 1.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.33–7.29 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 7.2 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 150.3, 148.5, 146.6, 144.2, 137.6, 135.6, 133.6, 132.3, 129.9, 129.3, 129.0, 128.8, 128.0, 127.9, 127.7, 127.3, 125.2, 21.5.



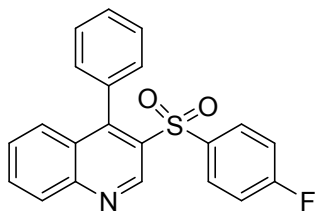
4-Phenyl-3-(phenylsulfonyl)quinolone (3ab)¹

Yield: 57.3 mg (83%). ¹H NMR (600 MHz, CDCl₃): δ = 9.82 (s, 1H), 8.22 (d, *J* = 9.0 Hz, 1H), 7.84–7.82 (m, 1H), 7.47–7.44 (m, 3H), 7.35–7.31 (m, 5H), 7.27–7.25 (m, 2H), 6.94 (d, *J* = 7.8 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 150.0, 149.8, 147.7, 140.8, 133.0, 132.5, 132.3, 132.2, 130.0, 129.7, 128.6, 128.6, 127.8, 127.8, 127.7, 127.5, 127.4.



3-((4-(*tert*-Butyl)phenyl)sulfonyl)-4-phenylquinoline (3ac)

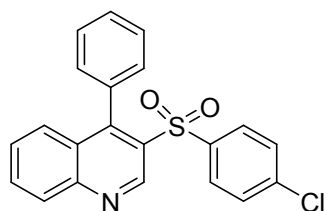
Yield: 69.9 mg (87%). ¹H NMR (600 MHz, CDCl₃): δ = 9.80 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.34–7.29 (m, 3H), 7.27–7.25 (m, 4H), 6.95 (d, *J* = 7.2 Hz, 2H), 1.29 (s, 9H); ¹³C NMR (150 MHz, CDCl₃): δ = 156.9, 149.7, 147.6, 137.7, 132.7, 132.6, 132.1, 130.0, 129.6, 128.5, 127.7, 127.7, 127.6, 127.4, 127.3, 125.6, 35.1, 31.0. HRMS (ESI) ([*M*+*H*]⁺) Calcd. For C₂₅H₂₃NO₂S: 402.1522, Found: 402.1523.



3-((4-Fluorophenyl)sulfonyl)-4-phenylquinoline (3ad)¹

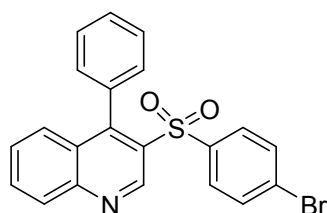
Yield: 59.6 mg (82%). ¹H NMR (600 MHz, CDCl₃): δ = 9.80 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.86–7.83 (m, 1H), 7.50–7.47 (m, 2H), 7.38–7.34 (m, 3H), 7.33–7.30 (m, 2H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 8.4 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 165.2 (d, *J* = 255.0 Hz), 149.8 (d, *J* = 13.5 Hz), 147.4, 136.7 (d, *J* = 3.0 Hz), 132.4,

132.3, 132.2, 130.7 (d, $J = 9.0$ Hz), 130.0, 129.7, 129.3, 128.8, 128.0, 127.8, 127.3, 122.0, 115.8 (d, $J = 22.5$ Hz). ^{19}F NMR (564 MHz, CDCl_3): $\delta = -103.89$.



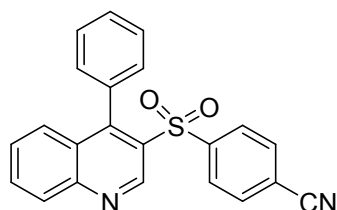
3-((4-Chlorophenyl)sulfonyl)-4-phenylquinoline (3ae)¹

Yield: 60.8 mg (80%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.79$ (s, 1H), 8.23 (d, $J = 8.4$ Hz, 1H), 7.84 (t, $J = 7.8$ Hz, 1H), 7.50–7.47 (m, 2H), 7.38–7.34 (m, 3H), 7.24–7.21 (m, 4H), 6.97 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 149.9$, 149.9, 147.4, 139.7, 139.3, 132.4, 132.0, 130.1, 129.7, 129.3, 128.8, 128.0, 127.8, 127.4, 127.3.



3-((4-Bromophenyl)sulfonyl)-4-phenylquinoline (3af)¹

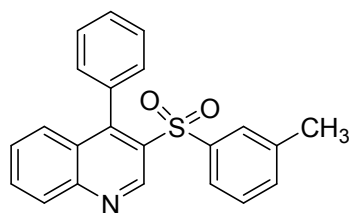
Yield: 66.2 mg (78%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.79$ (s, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 7.84 (t, $J = 7.8$ Hz, 1H), 7.50–7.46 (m, 2H), 7.39–7.34 (m, 5H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 149.9$, 149.8, 147.4, 139.8, 132.4, 132.0, 131.8, 130.0, 129.7, 129.3, 128.8, 128.3, 128.0, 127.8, 127.3, 127.3.



4-((4-Phenylquinolin-3-yl)sulfonyl)benzonitrile (3ag)²

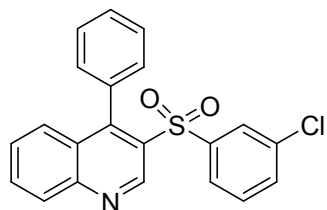
Yield: 56.3 mg (76%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.80$ (s, 1H), 8.25 (d, $J = 8.4$ Hz, 1H), 7.87 (t, $J = 7.2$ Hz, 1H), 7.55–7.53 (m, 2H), 7.50–7.49 (m, 2H), 7.41–7.40 (m, 2H), 7.35–7.34 (m, 3H), 6.95–6.94 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta =$

150.2, 150.1, 147.2, 144.8, 132.8, 132.2, 132.2, 131.2, 130.1, 129.8, 129.1, 128.4, 128.2, 127.9, 127.4, 127.2, 117.1, 116.5.



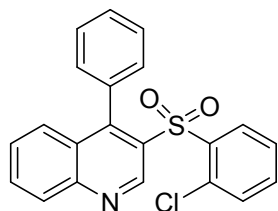
4-Phenyl-3-(*m*-tolylsulfonyl)quinolone (3ah)³

Yield: 57.5 mg (80%). ¹H NMR (600 MHz, CDCl₃): δ = 9.82 (s, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.48–7.44 (m, 2H), 7.35–7.32 (m, 3H), 7.26–7.25 (m, 1H), 7.16–7.15 (m, 2H), 7.05 (s, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 2.23 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 149.8, 149.6, 147.4, 140.3, 138.6, 133.8, 132.4, 132.3, 132.1, 129.9, 129.5, 128.5, 128.4, 128.2, 127.7, 127.5, 127.3, 127.3, 124.8, 21.0.



3-((3-Chlorophenyl)sulfonyl)-4-phenylquinoline (3ai)³

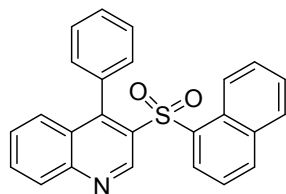
Yield: 60.0 mg (79%). ¹H NMR (600 MHz, CDCl₃): δ = 9.80 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.86–7.83 (m, 1H), 7.53–7.47 (m, 2H), 7.43–7.41 (m, 1H), 7.38–7.36 (m, 3H), 7.27–7.21 (m, 2H), 7.16–7.15 (m, 1H), 6.97–6.95 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 150.0, 149.8, 147.2, 142.2, 134.6, 133.1, 132.4, 131.9, 131.8, 129.9, 129.9, 129.6, 129.0, 128.0, 127.9, 127.7, 127.3, 127.2, 125.8.



3-((2-Chlorophenyl)sulfonyl)-4-phenylquinoline (3aj)³

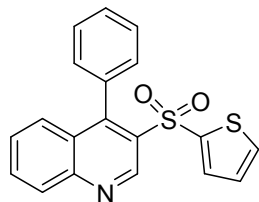
Yield: 55.5 mg (73%). ¹H NMR (600 MHz, CDCl₃): δ = 9.85 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.38–7.36 (m, 1H), 7.33–7.31 (m, 2H), 7.30–7.26 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 1H),

6.91 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 149.7, 149.4, 148.6, 138.0, 134.2, 132.3, 132.0, 131.8, 131.5, 131.1, 131.0, 129.8, 129.7, 128.7, 127.9, 127.6, 127.4, 127.2, 126.8$.



3-(Naphthalen-2-ylsulfonyl)-4-phenylquinoline (3ak)¹

Yield: 61.7 mg (78%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.80$ (s, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.74–7.71 (m, 2H), 7.65–7.62 (m, 2H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.53–7.51 (m, 1H), 7.48–7.45 (m, 1H), 7.35–7.32 (m, 2H), 7.30–7.27 (m, 1H), 7.22–7.21 (m, 1H), 7.09 (t, $J = 7.8$ Hz, 2H), 6.78 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.3$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 150.2, 149.8, 147.8, 137.3, 134.8, 132.4, 132.3, 132.2, 131.7, 130.2, 130.0, 129.7, 129.5, 129.2, 129.0, 128.9, 127.9, 127.8, 127.6, 127.5, 127.5, 127.4, 122.4$.



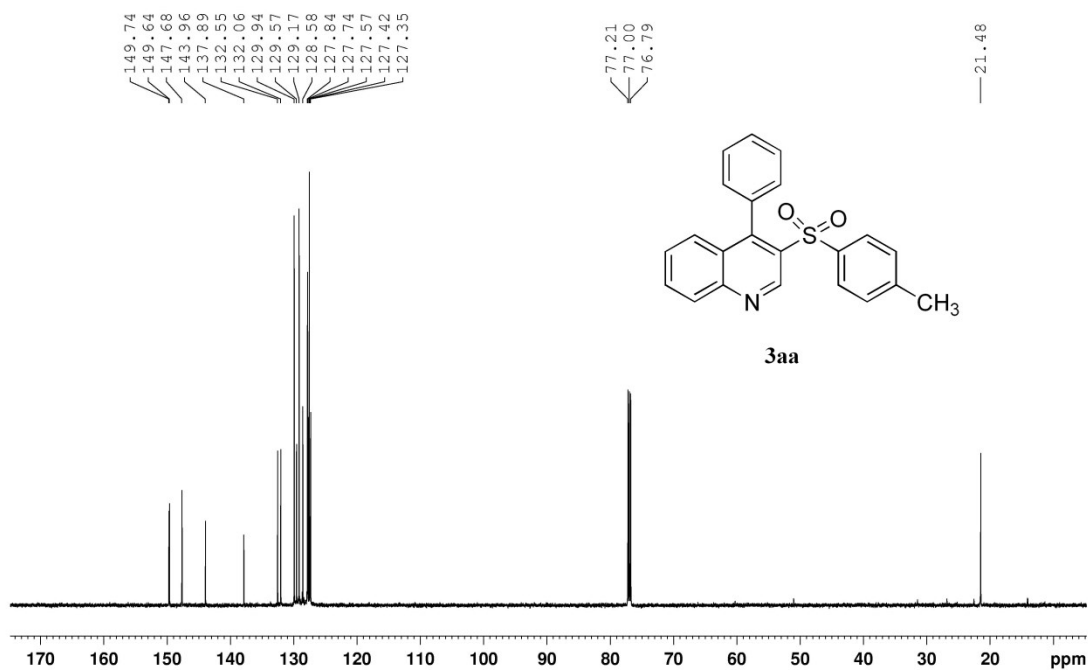
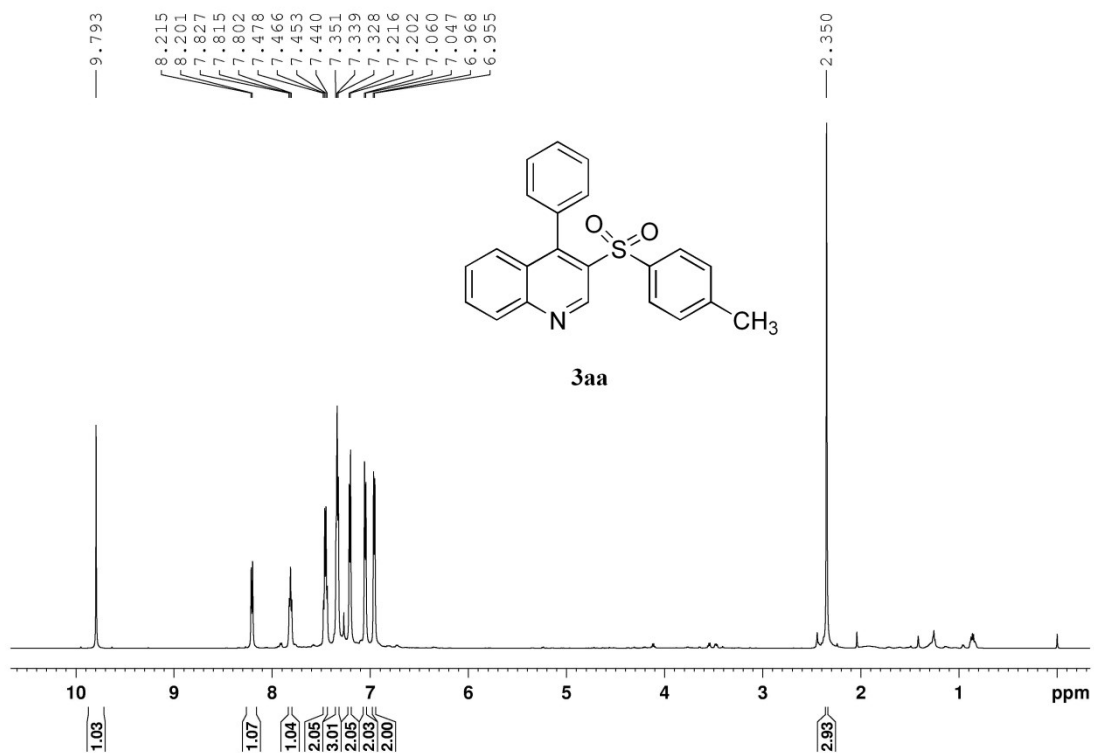
4-Phenyl-3-(thiophen-2-ylsulfonyl)quinolone (3al)³

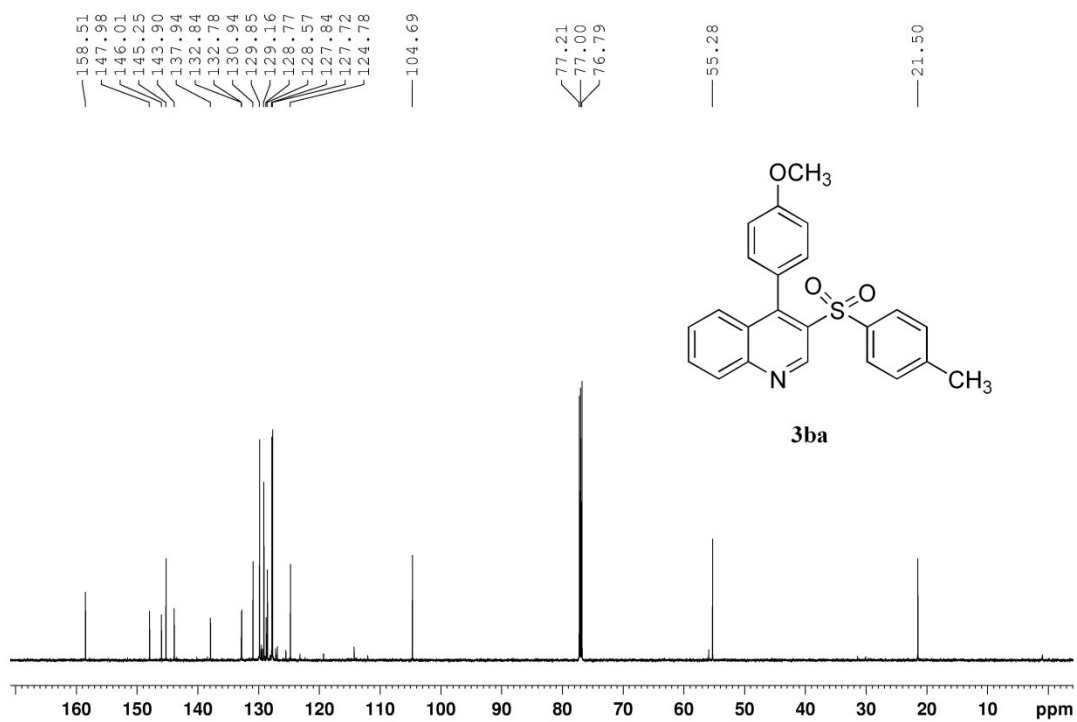
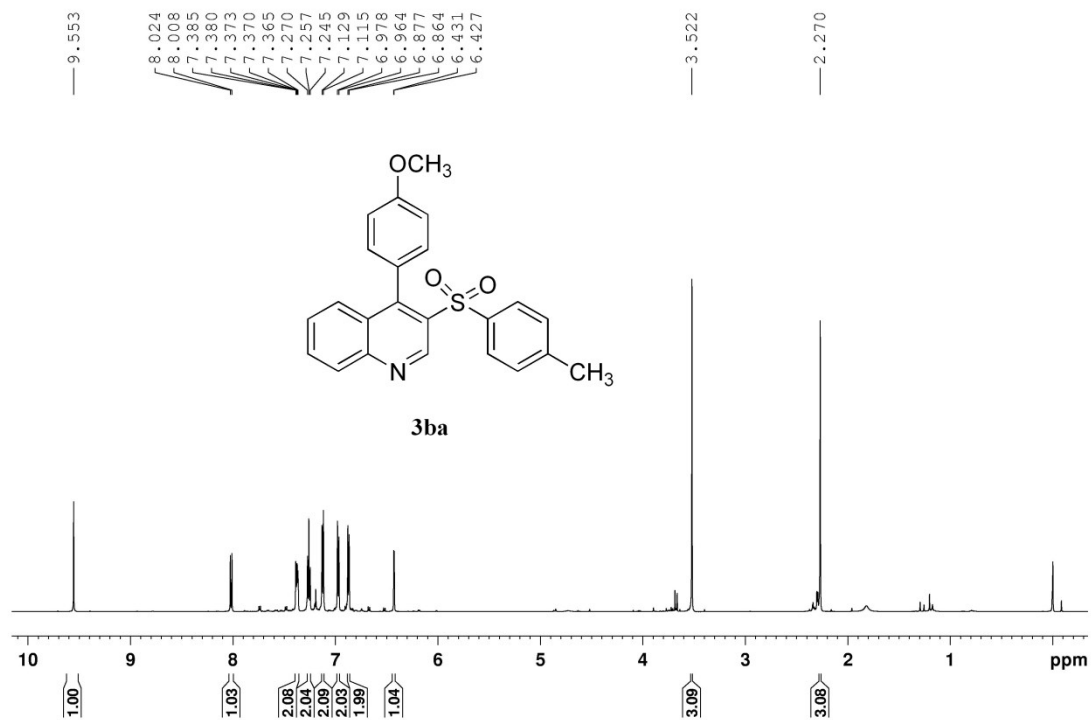
Yield: 52.7 mg (75%). ^1H NMR (600 MHz, CDCl_3): $\delta = 9.74$ (s, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 7.84 (t, $J = 7.8$ Hz, 1H), 7.55–7.54 (m, 1H), 7.51–7.43 (m, 2H), 7.43–7.37 (m, 3H), 7.10 (d, $J = 7.2$ Hz, 2H), 6.99–6.98 (m, 1H), 6.87–6.85 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 149.9, 149.7, 147.4, 142.0, 134.5, 134.2, 132.8, 132.6, 132.3, 129.8, 129.6, 128.8, 127.9, 127.8, 127.5, 127.4, 127.2$.

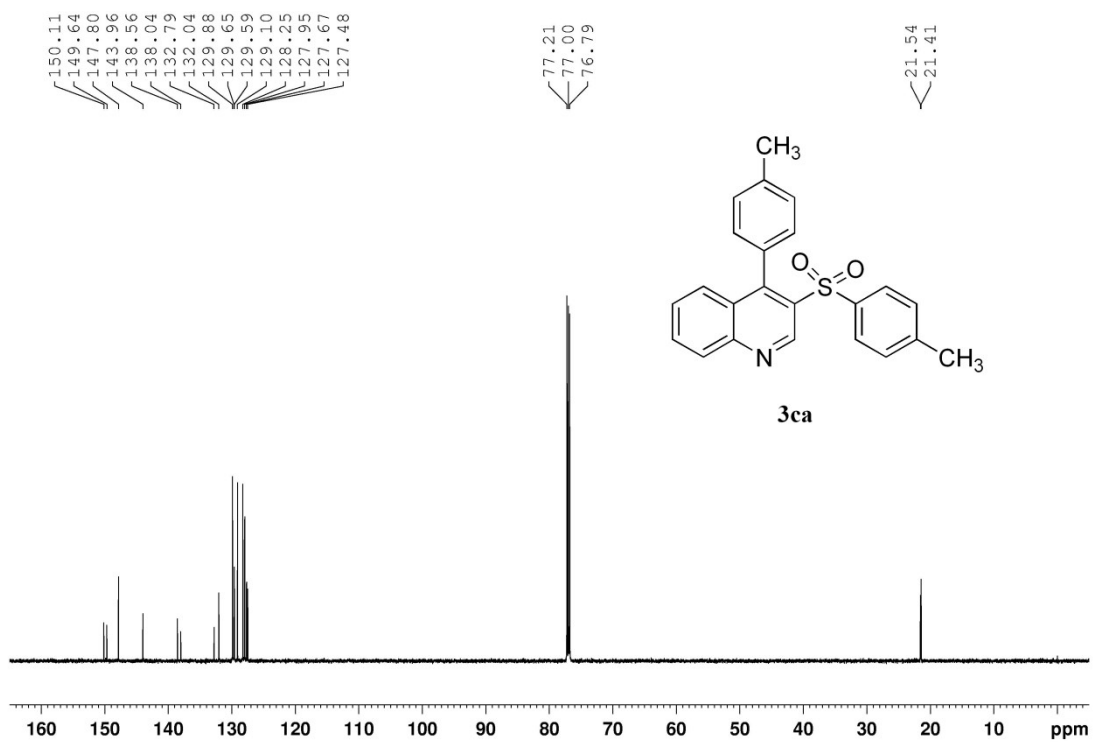
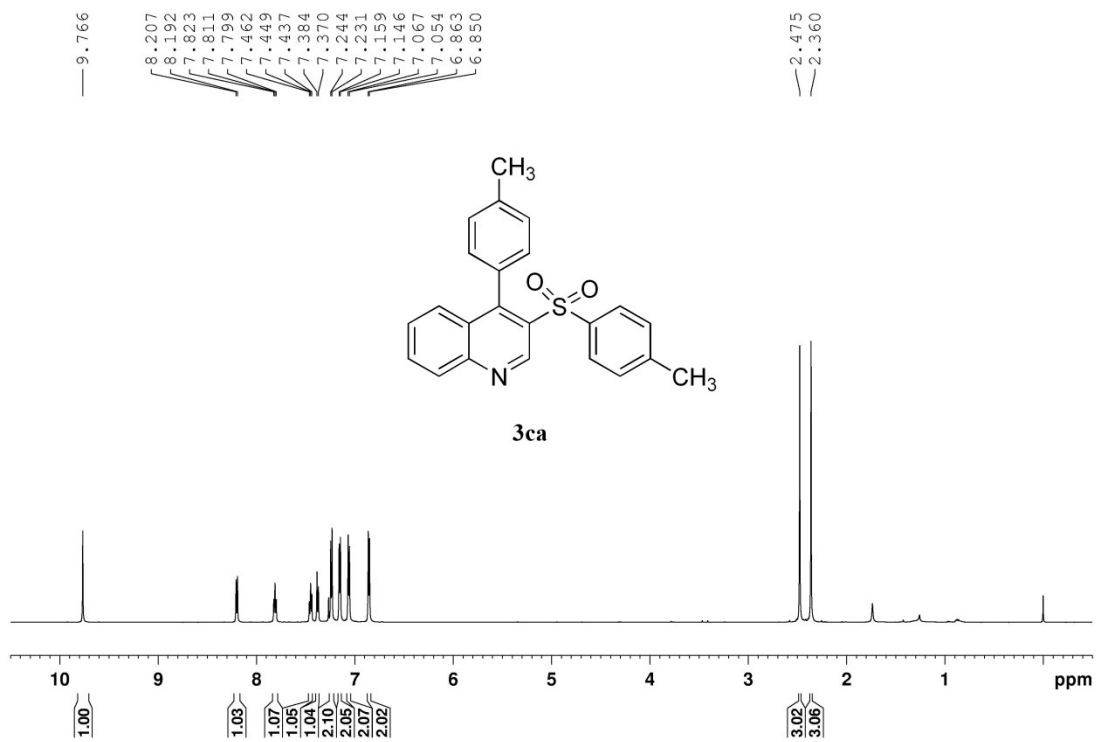
6. References

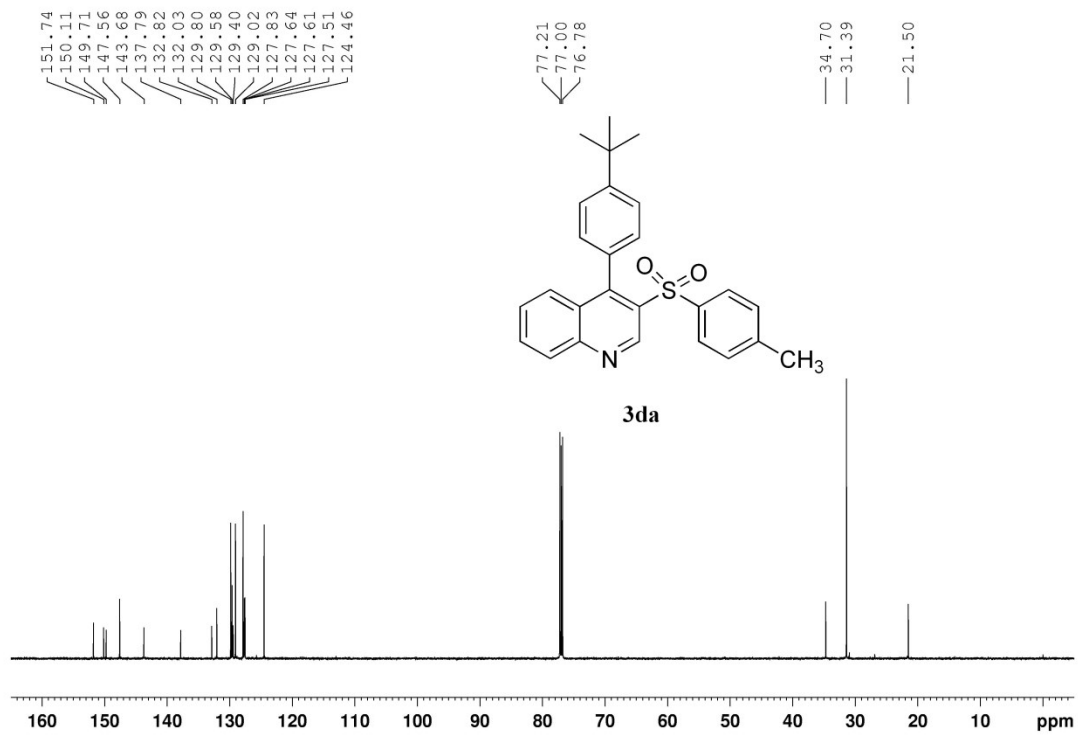
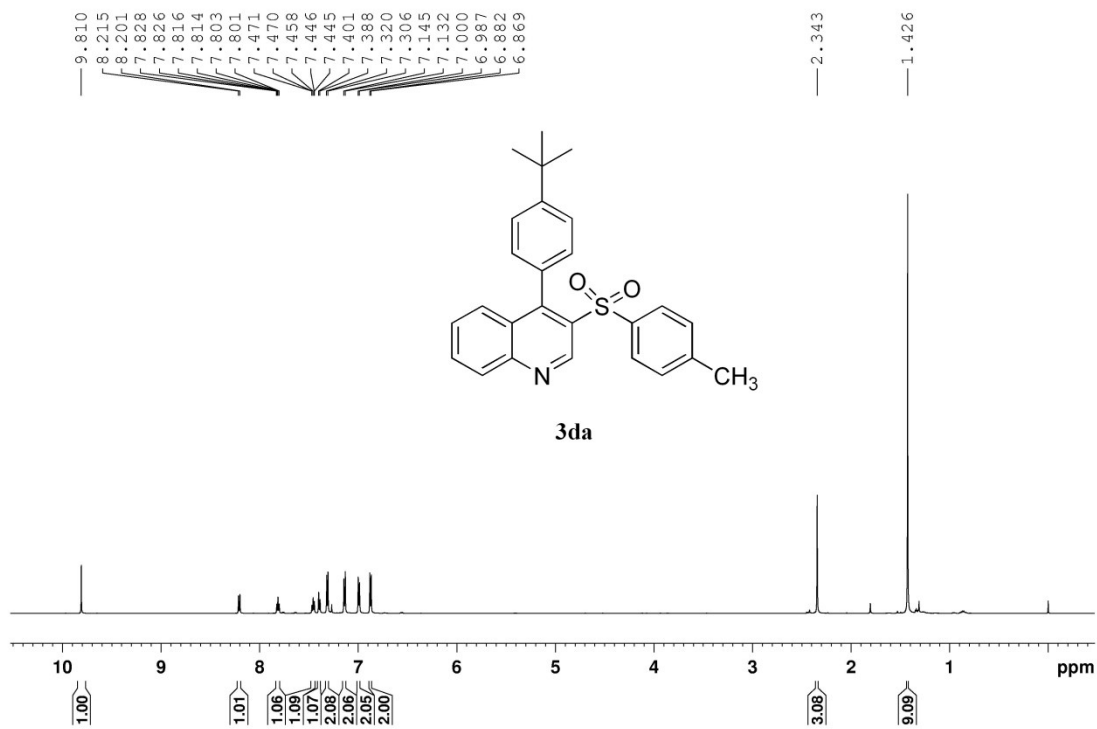
- [1] L. Zhang, S. Chen, Y. Gao, P. Zhang, Y. Wu, G. Tang and Y. Zhao, *Org. Lett.*, **2016**, *18*, 1286–1289.
- [2] D. Sun, K. Yin and R. Zhang, *Chem. Commun.*, **2018**, *54*, 1335–1338.
- [3] Y. Zhang, W. Chen, X. Jia, L. Wang and P. Li, *Chem. Commun.*, **2019**, *55*, 2785–2788.

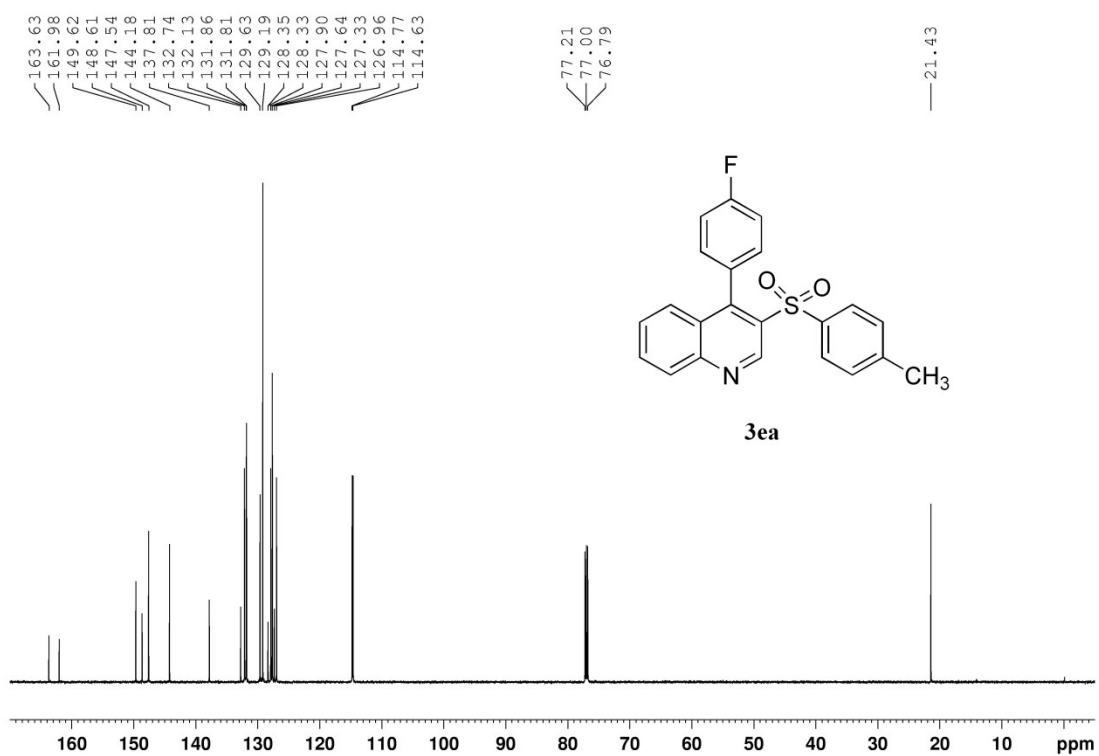
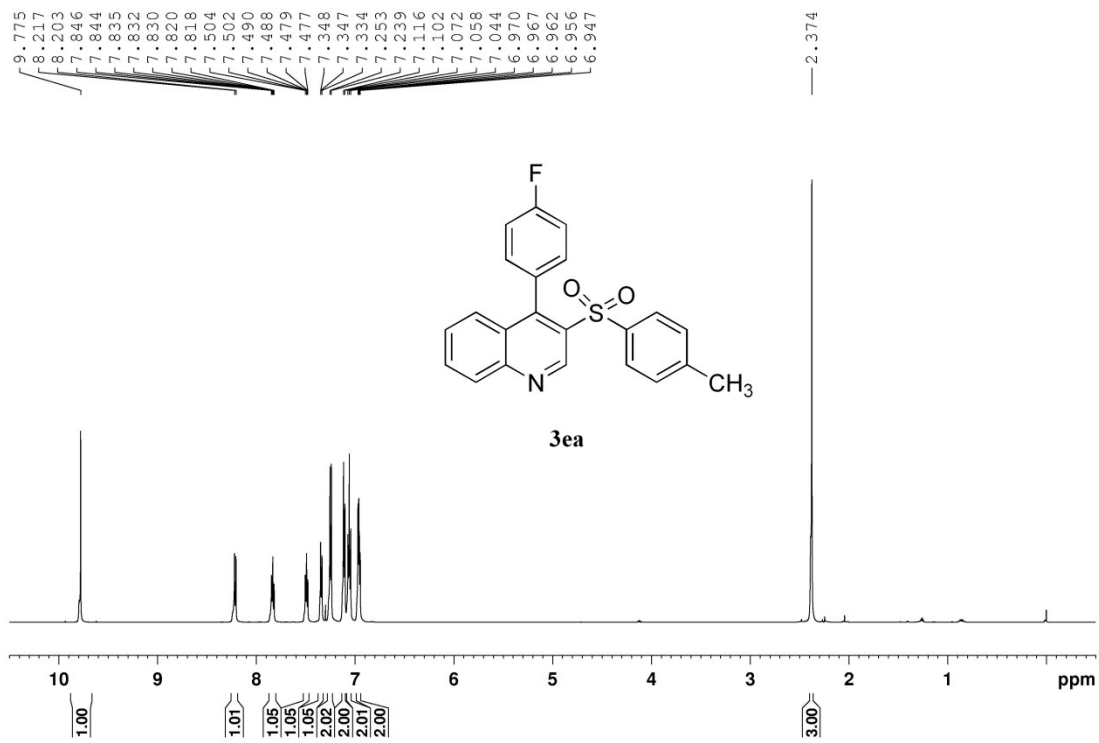
7. ^1H and ^{13}C NMR spectra of the products

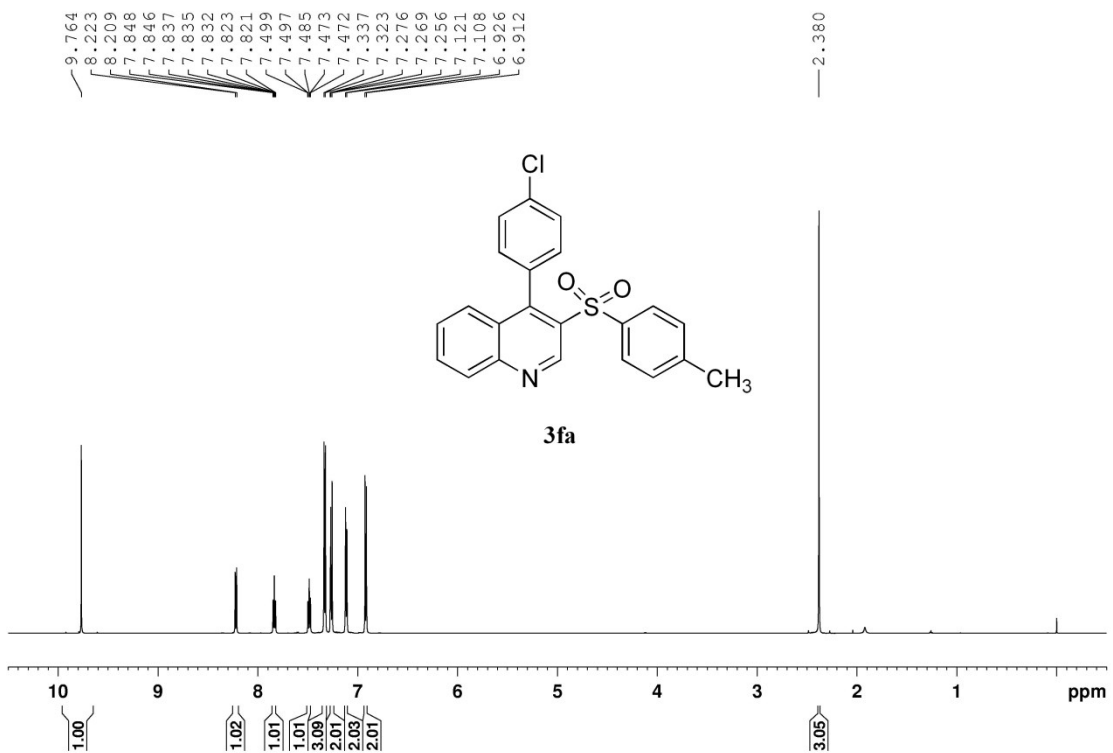
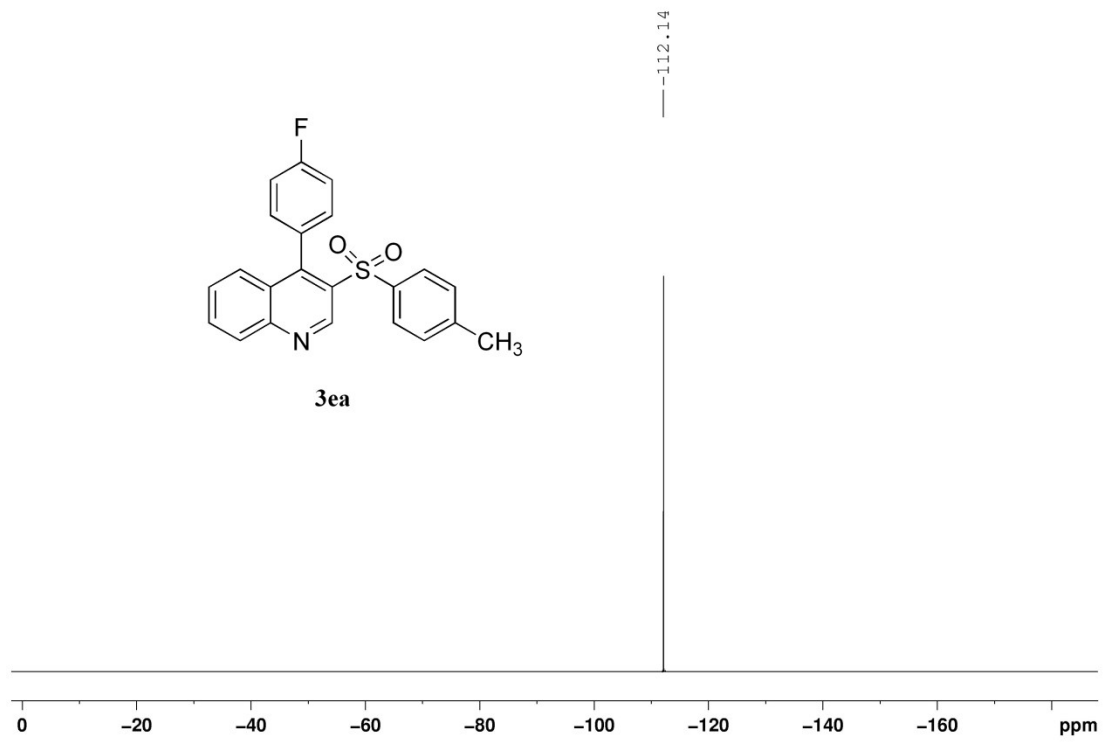


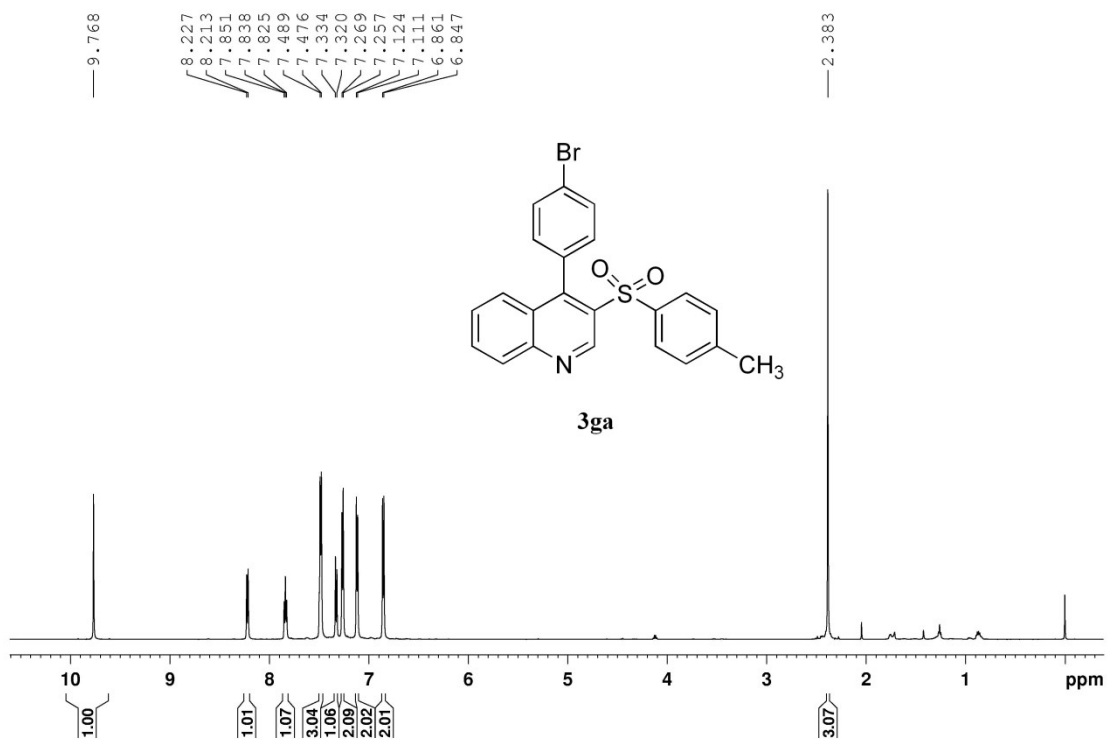
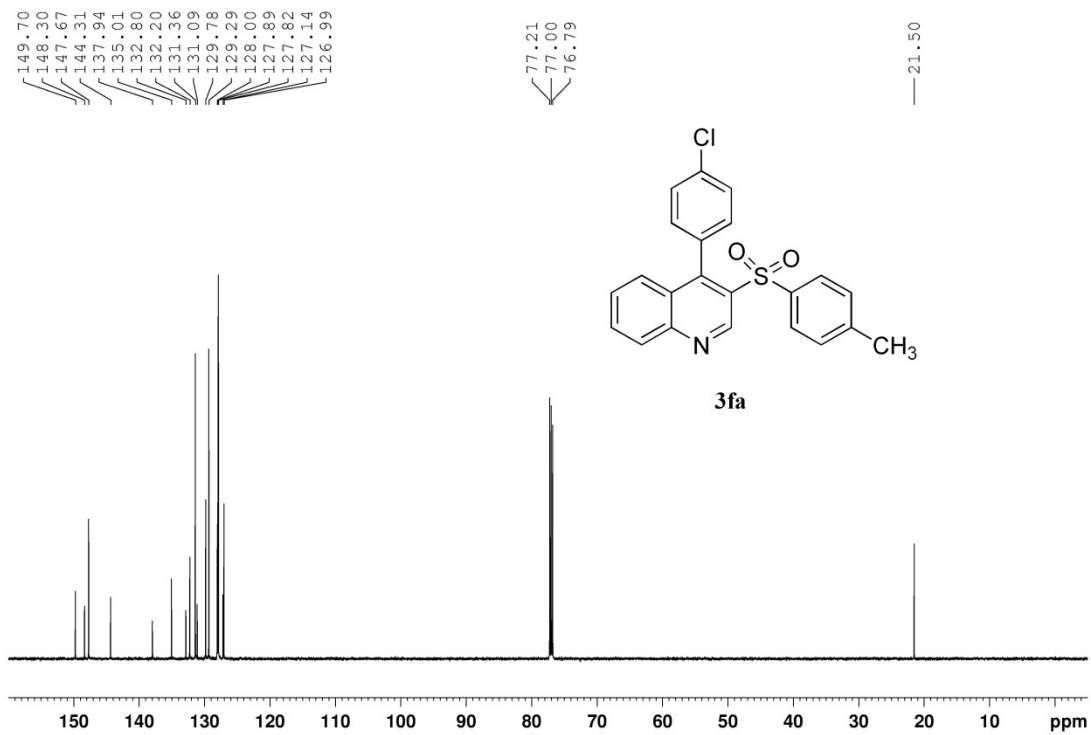


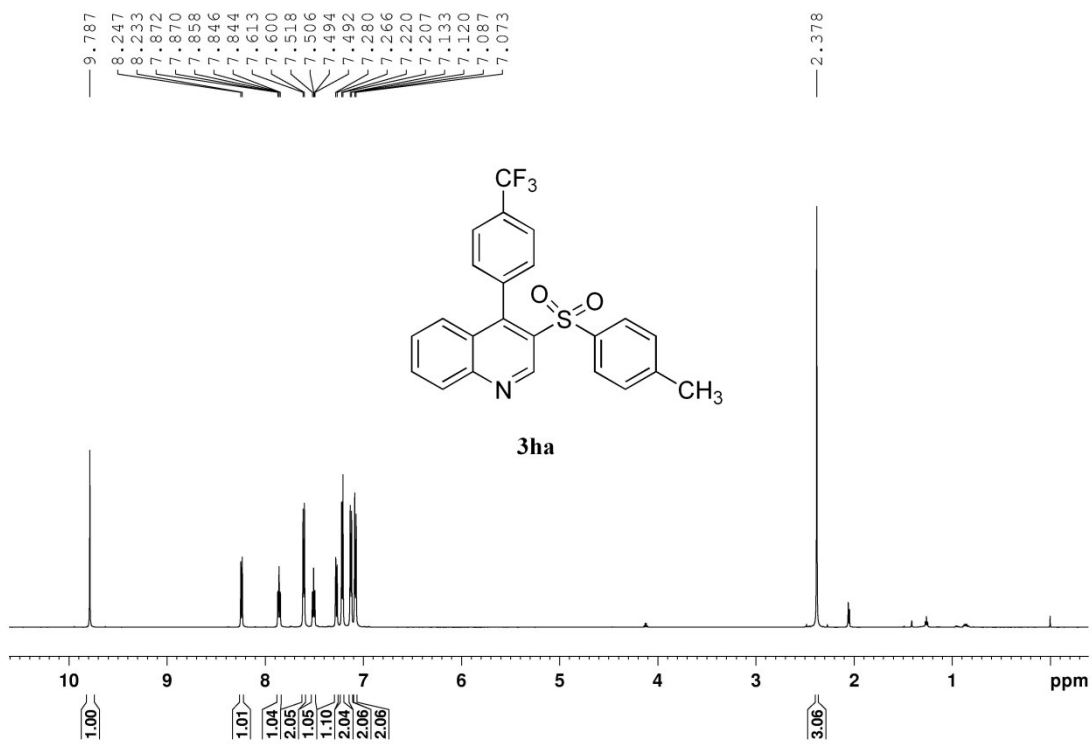
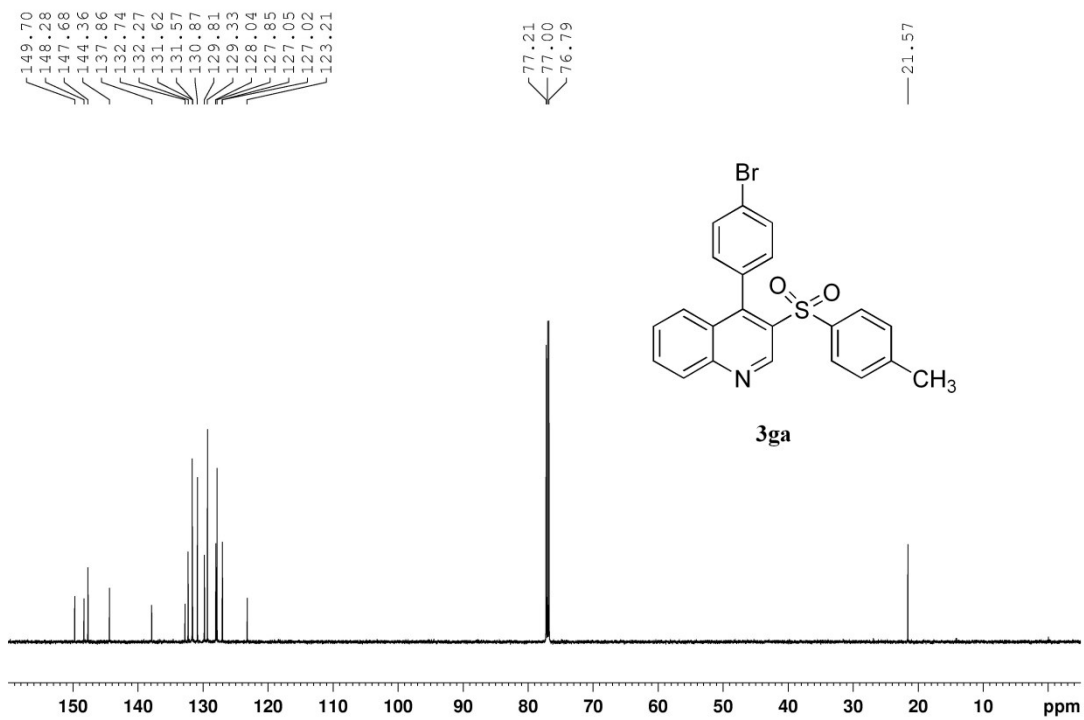


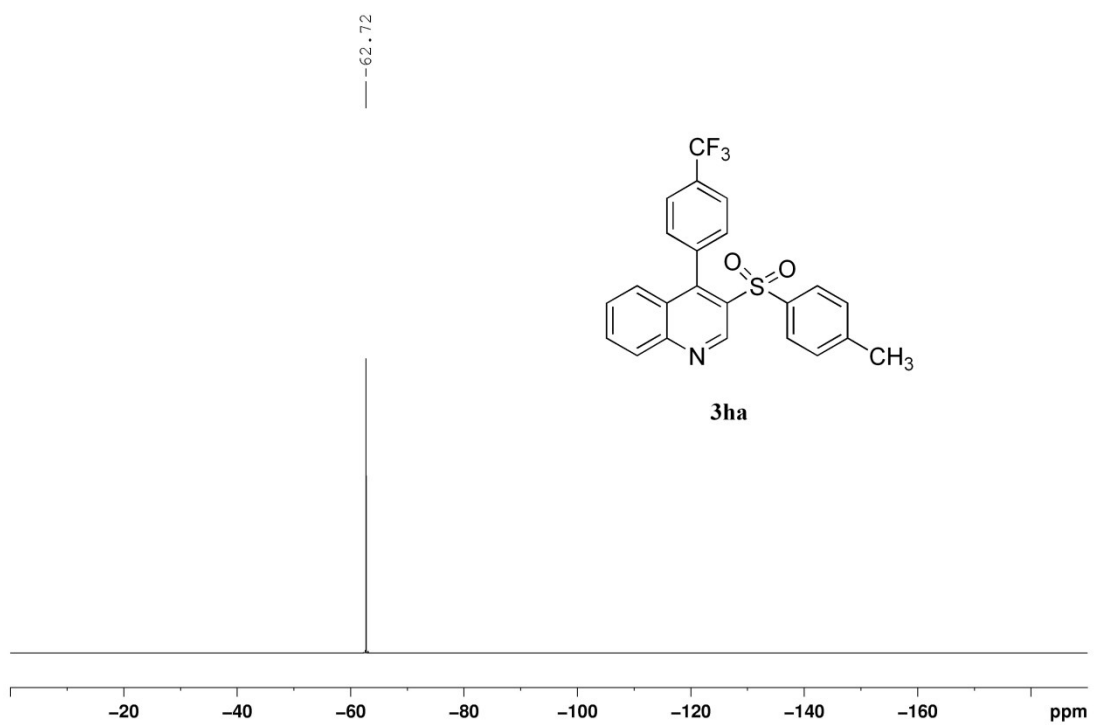
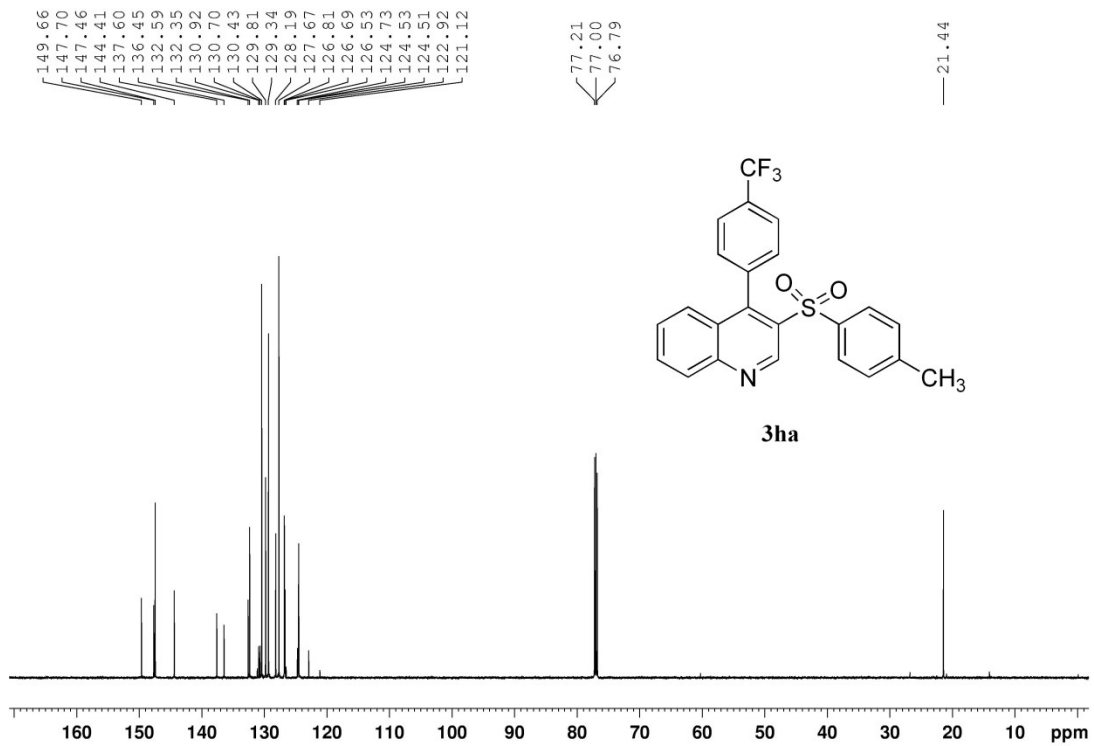


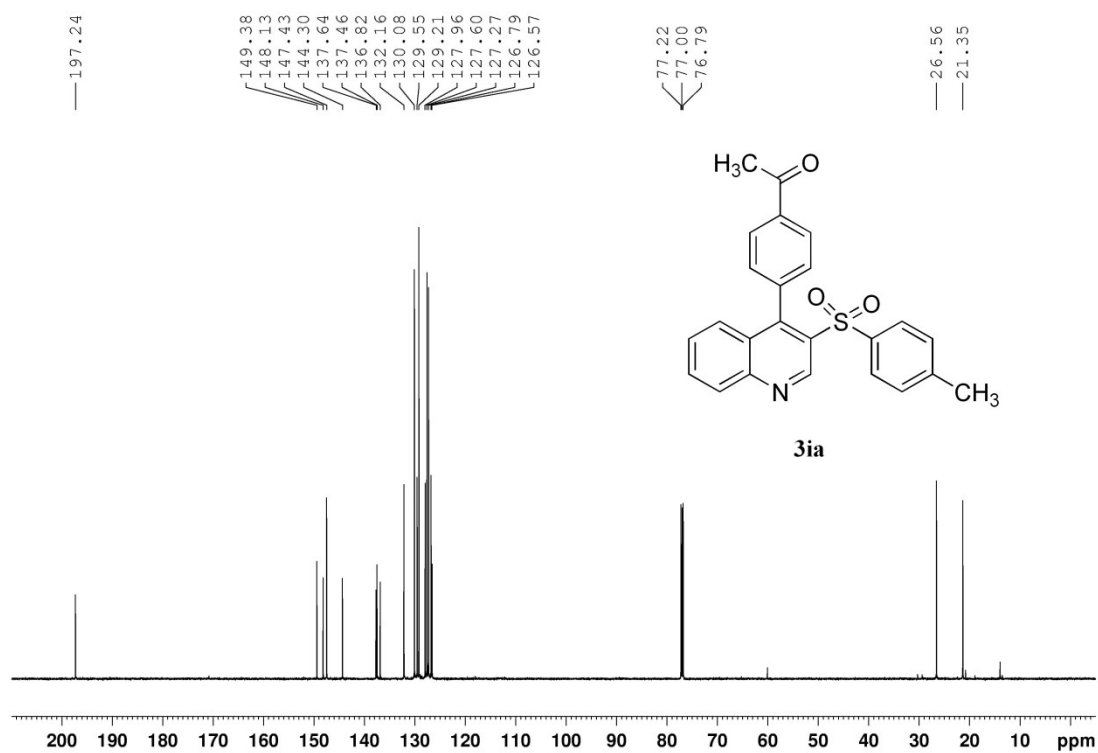
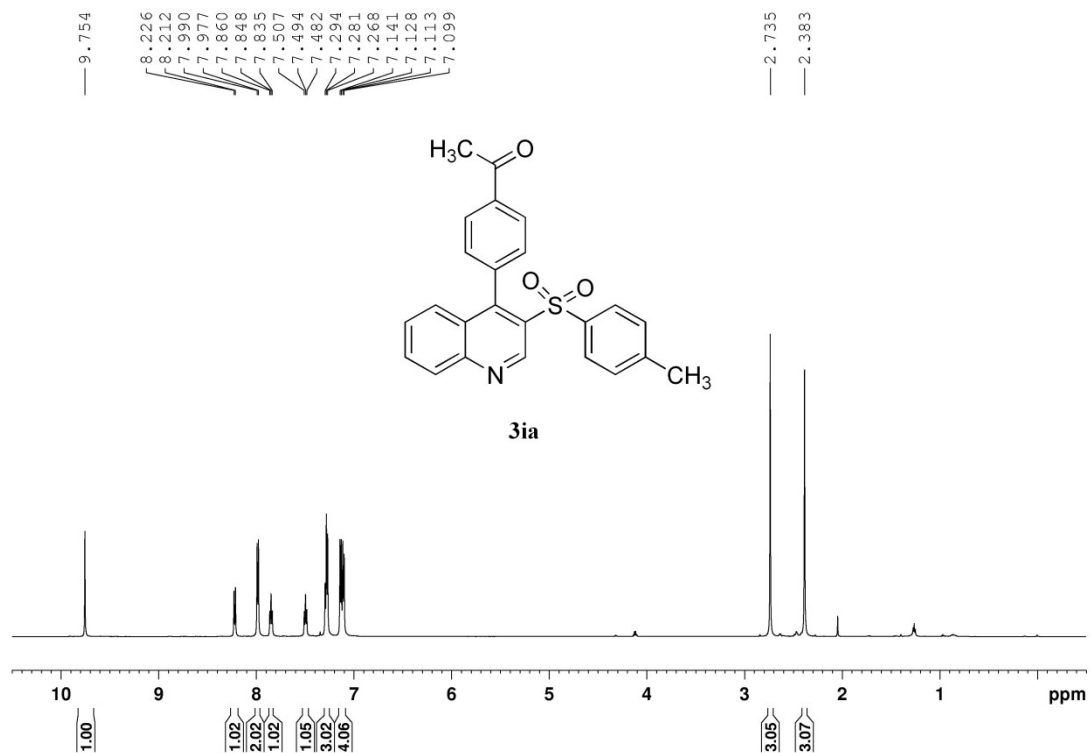


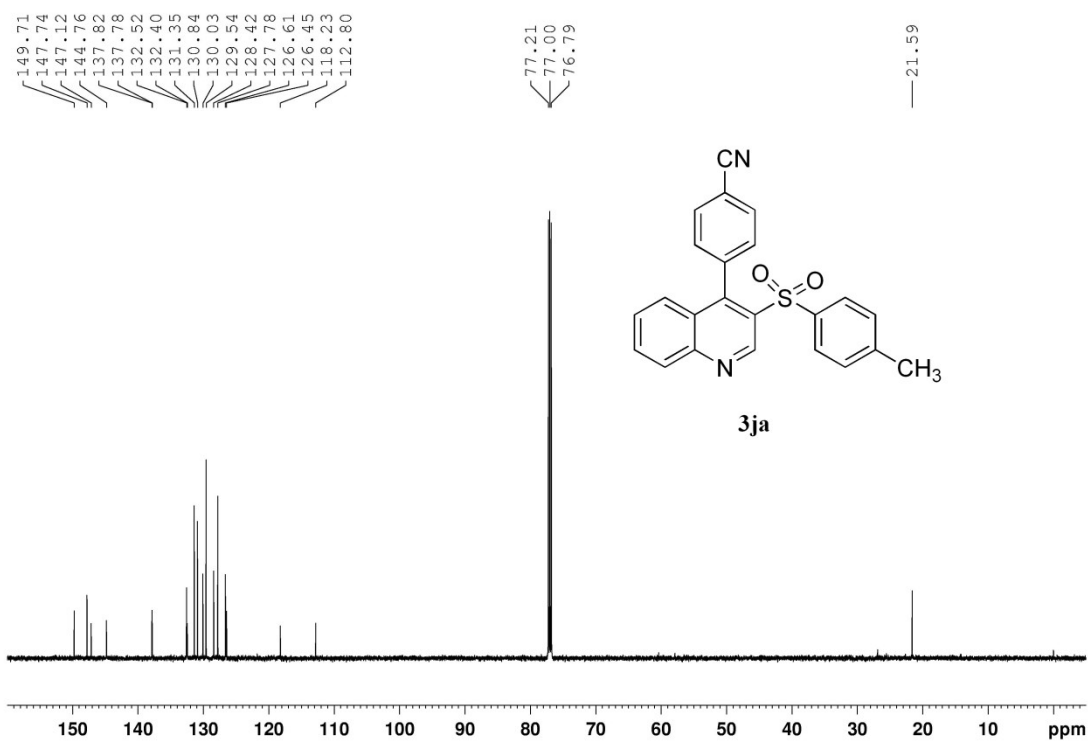
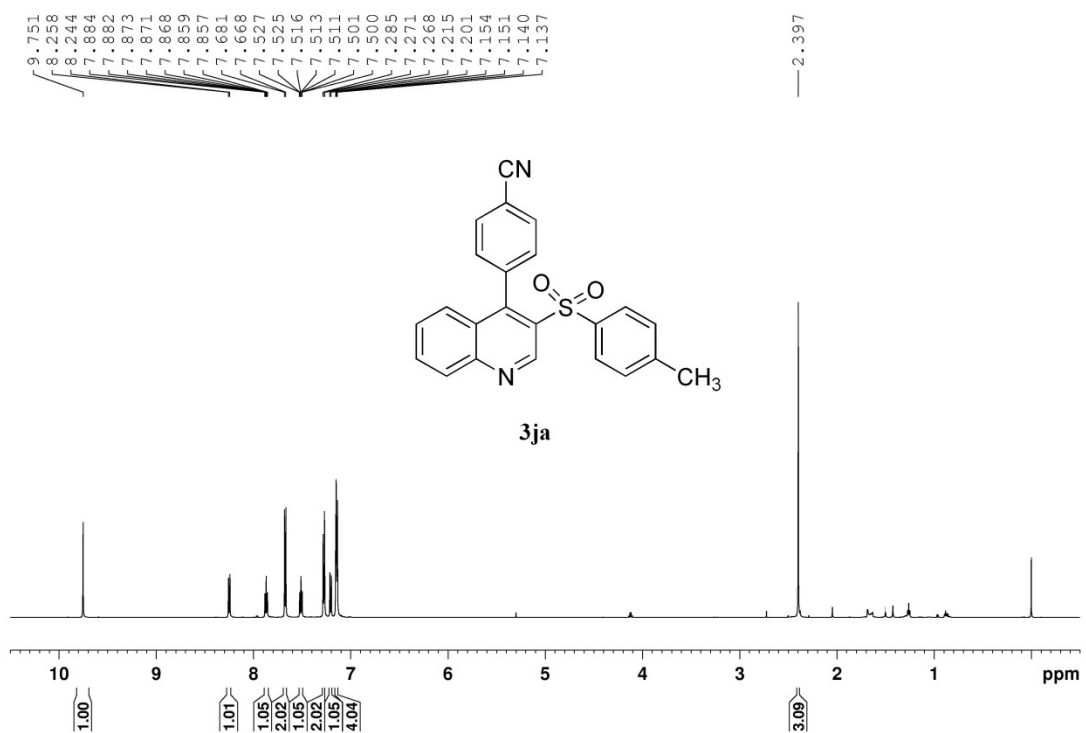


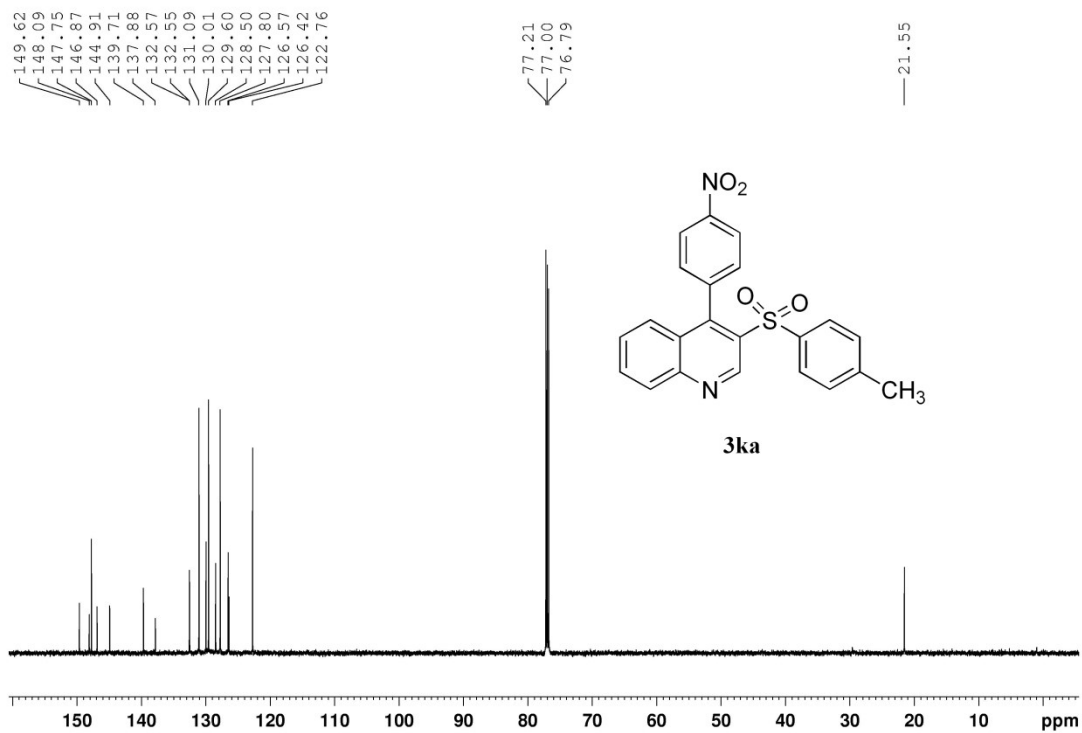
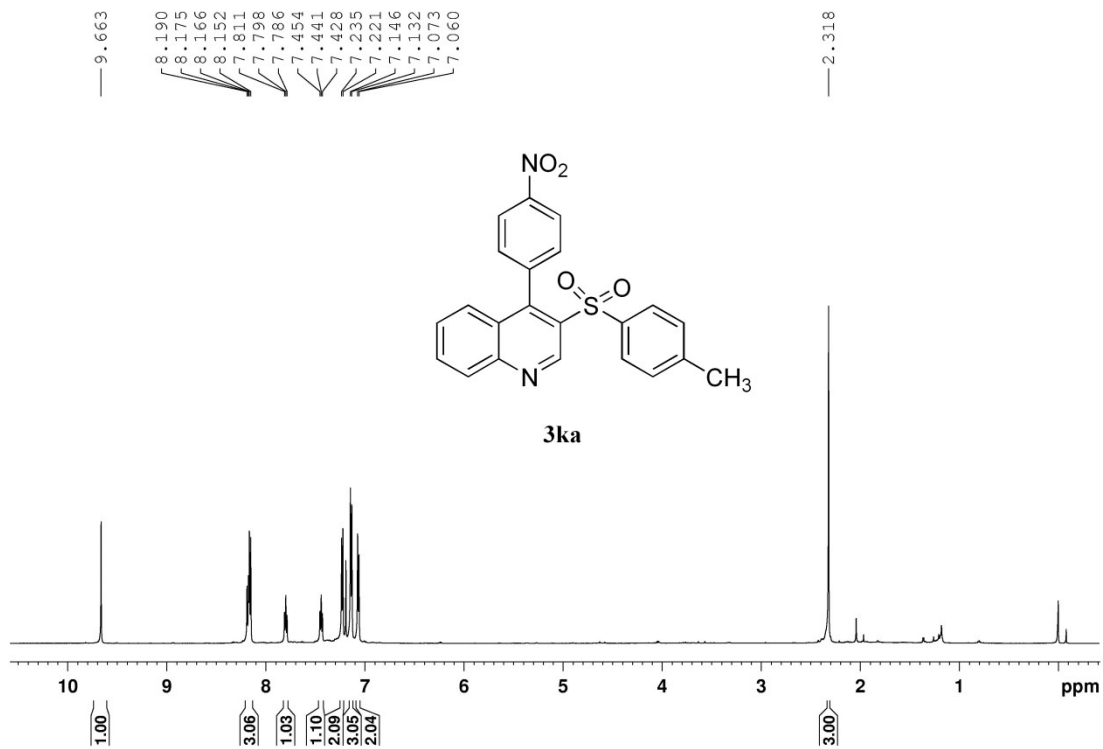


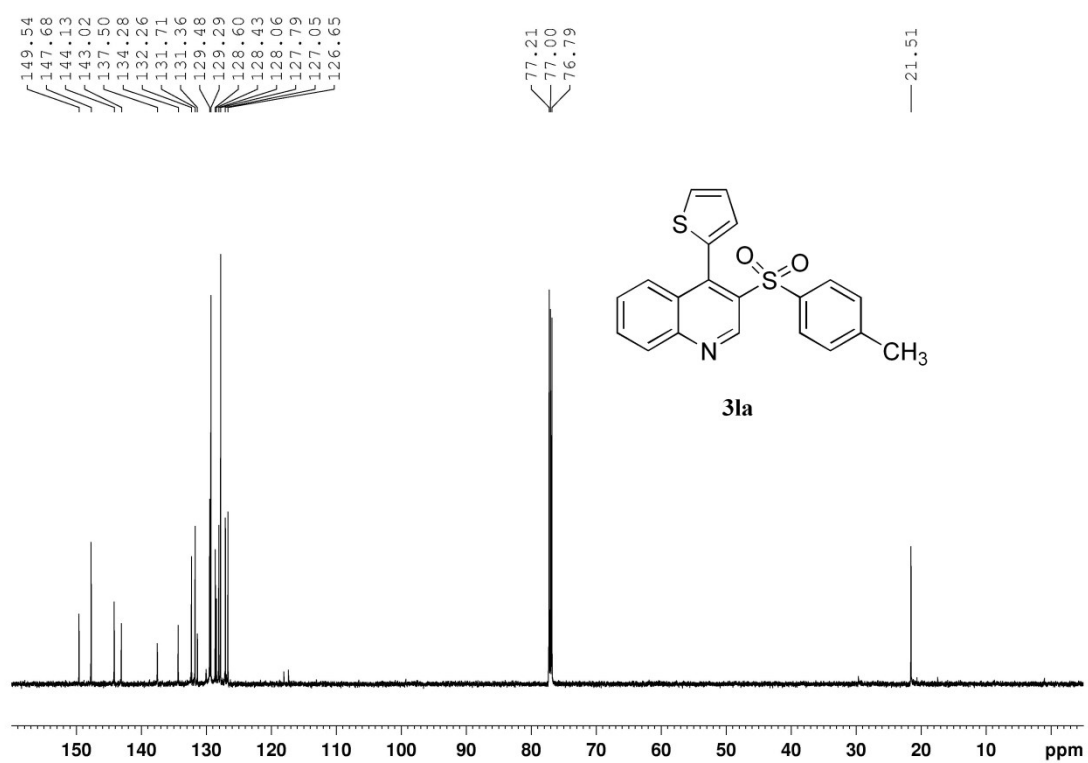
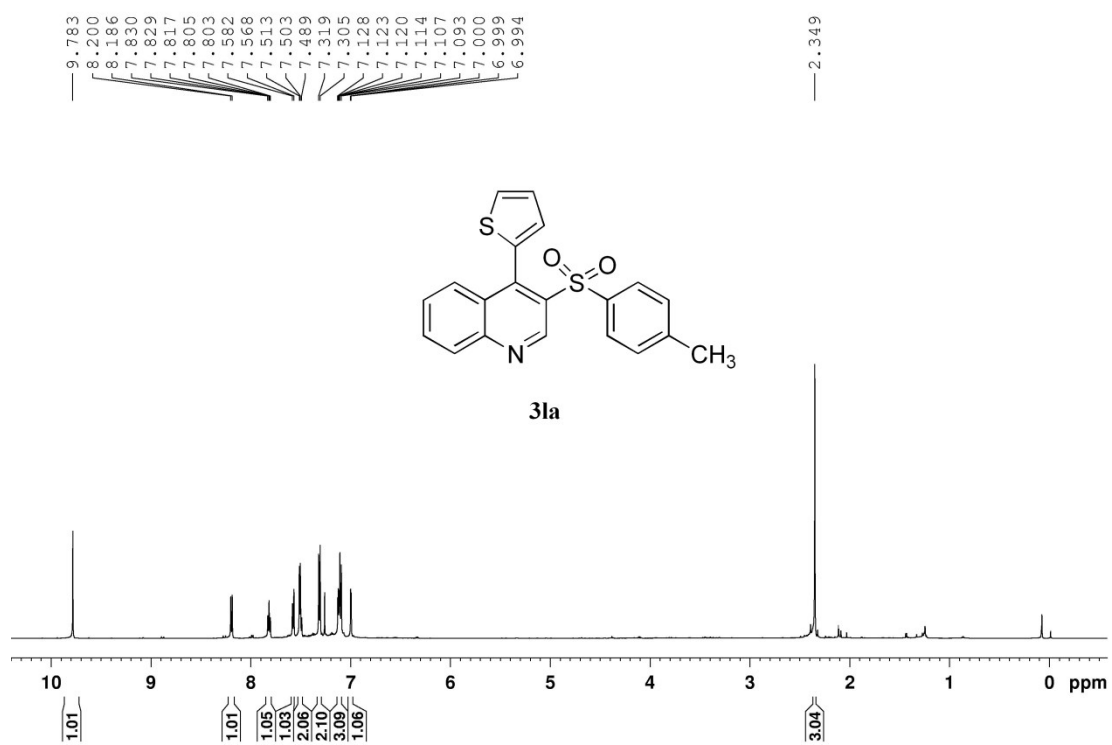


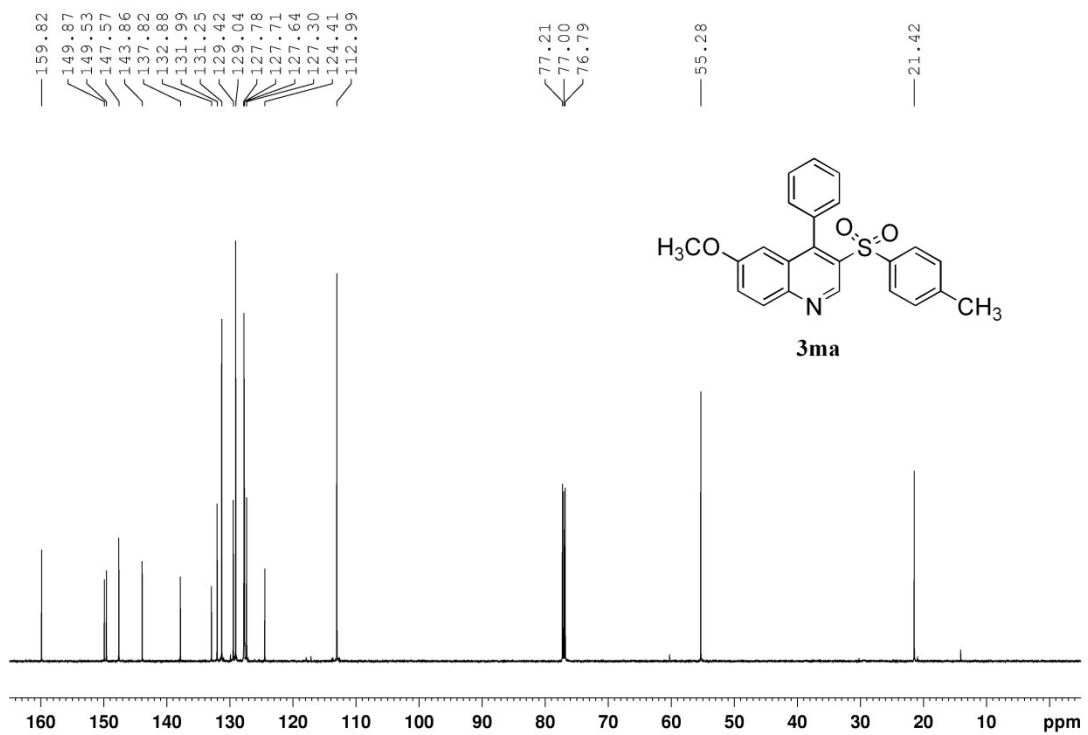
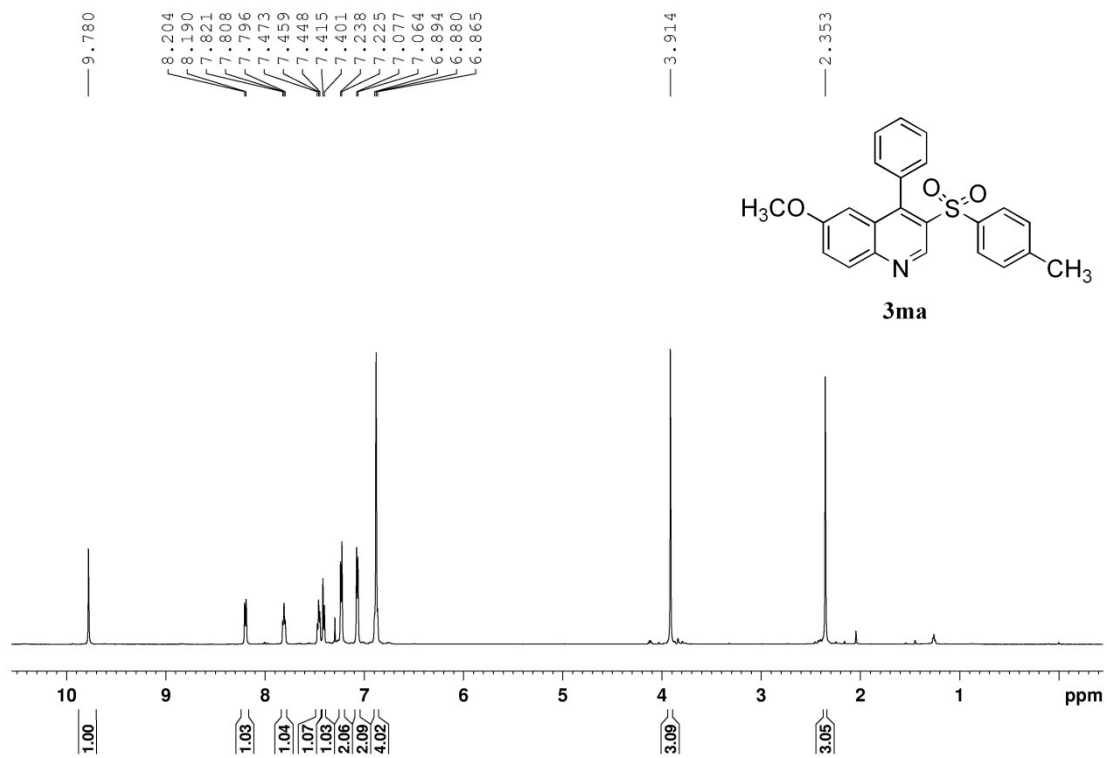


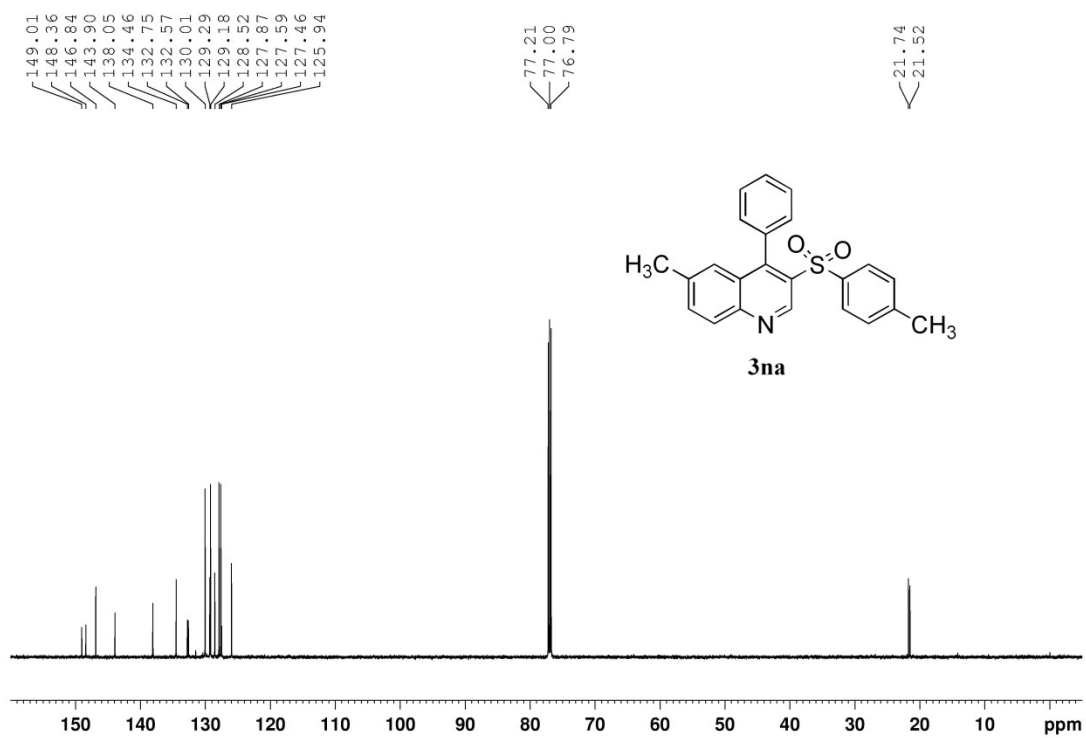
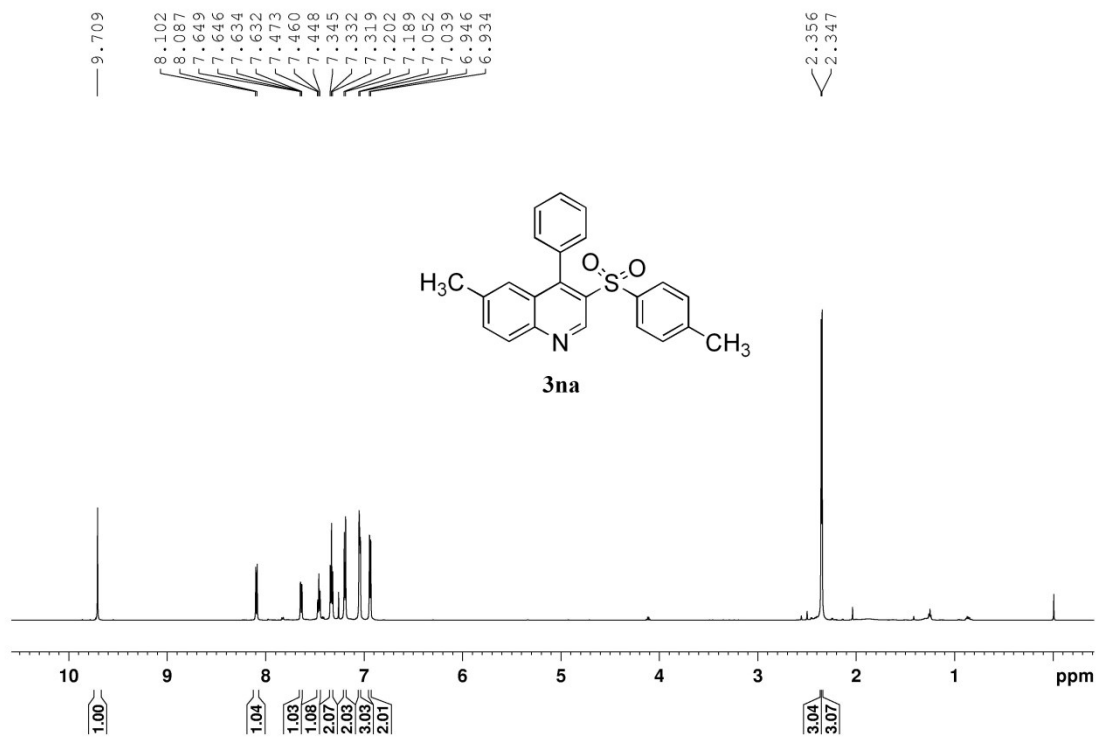


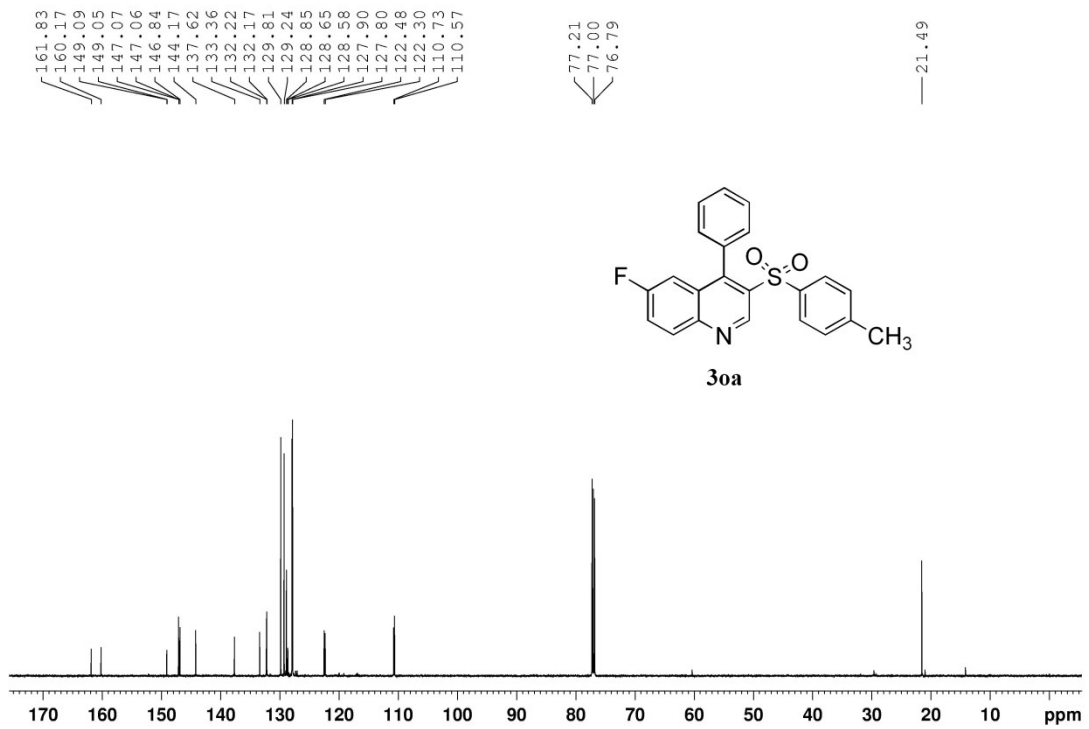
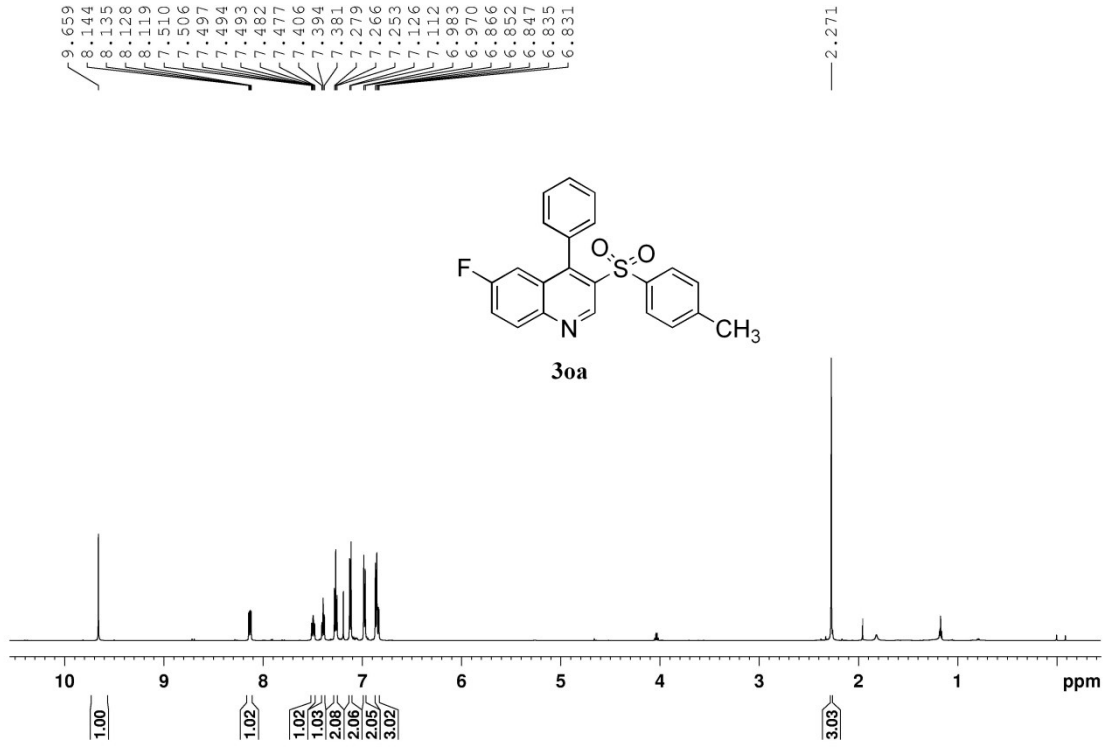


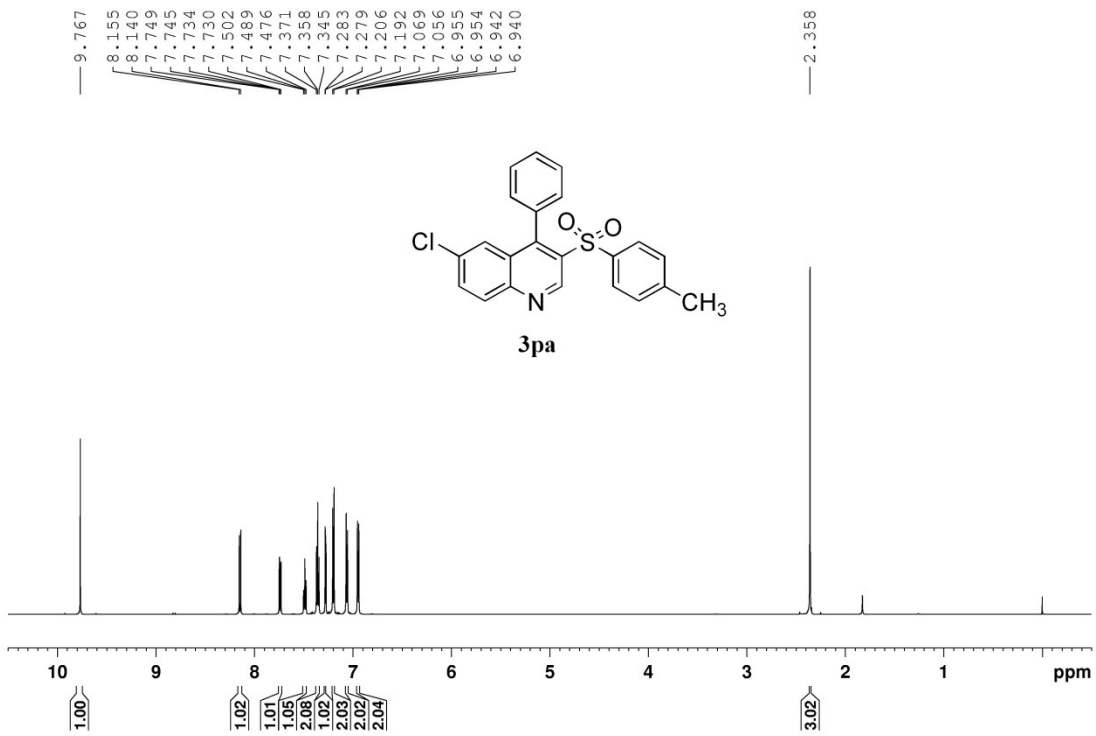
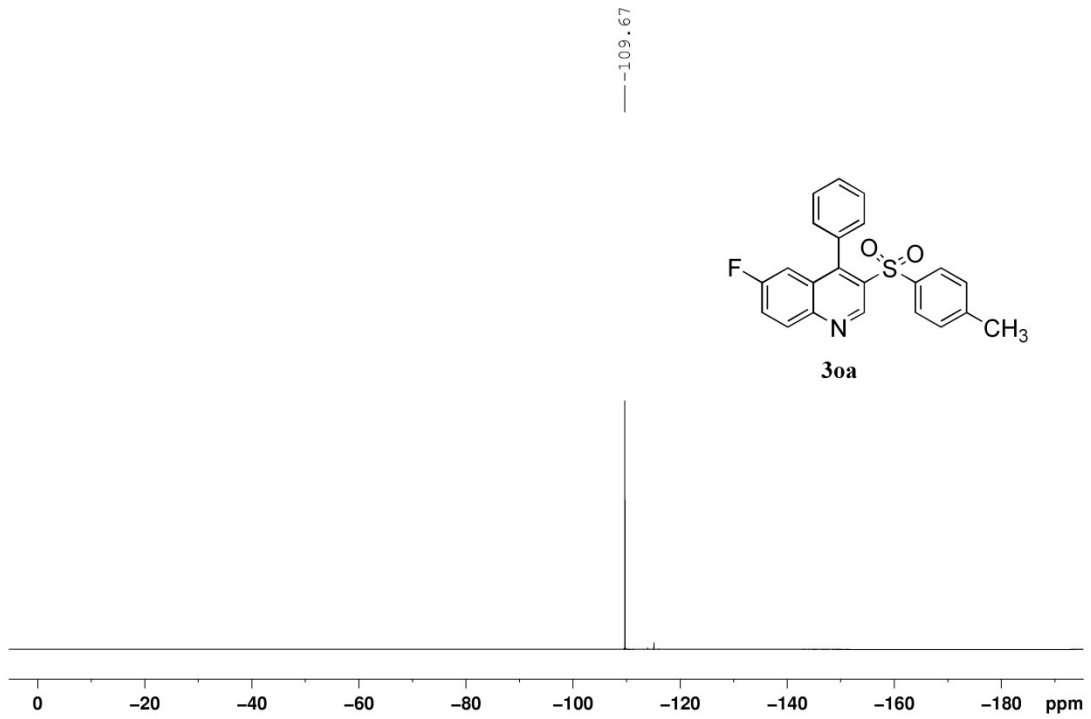


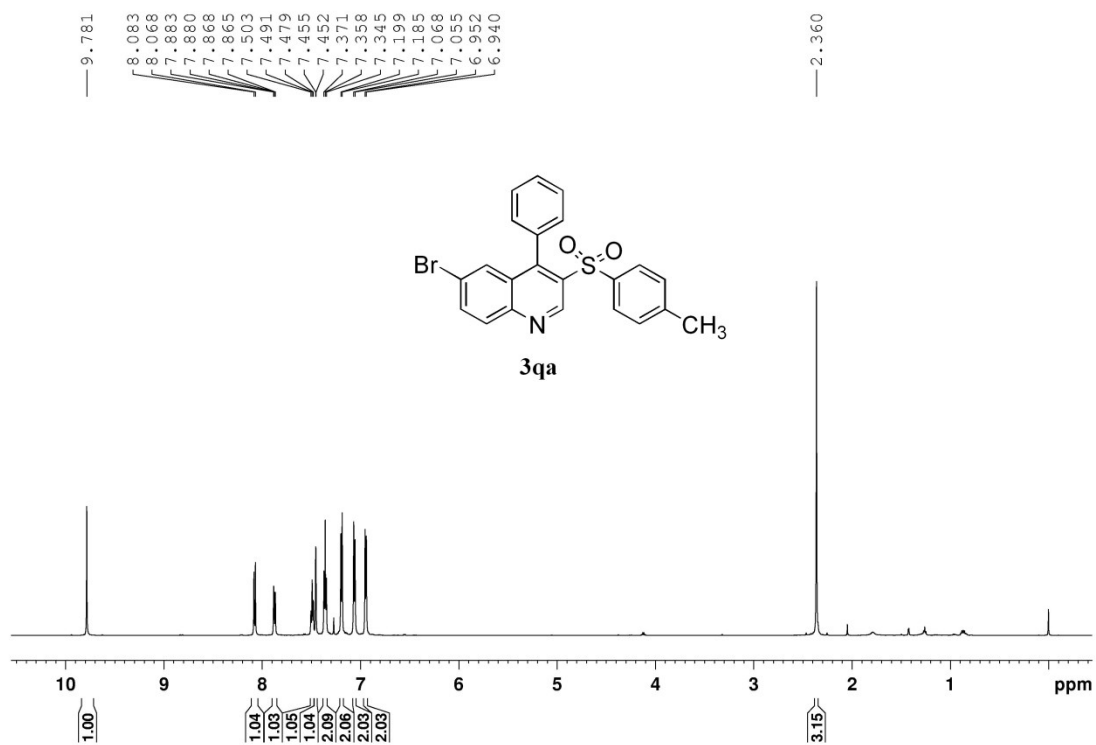
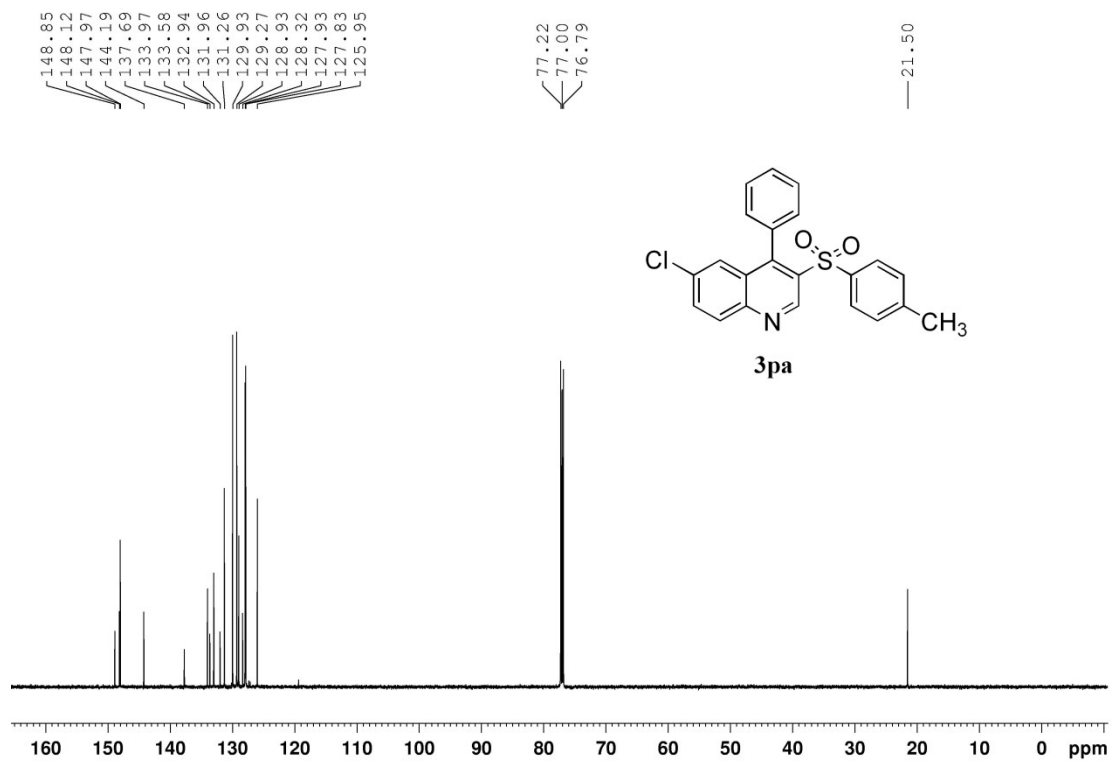


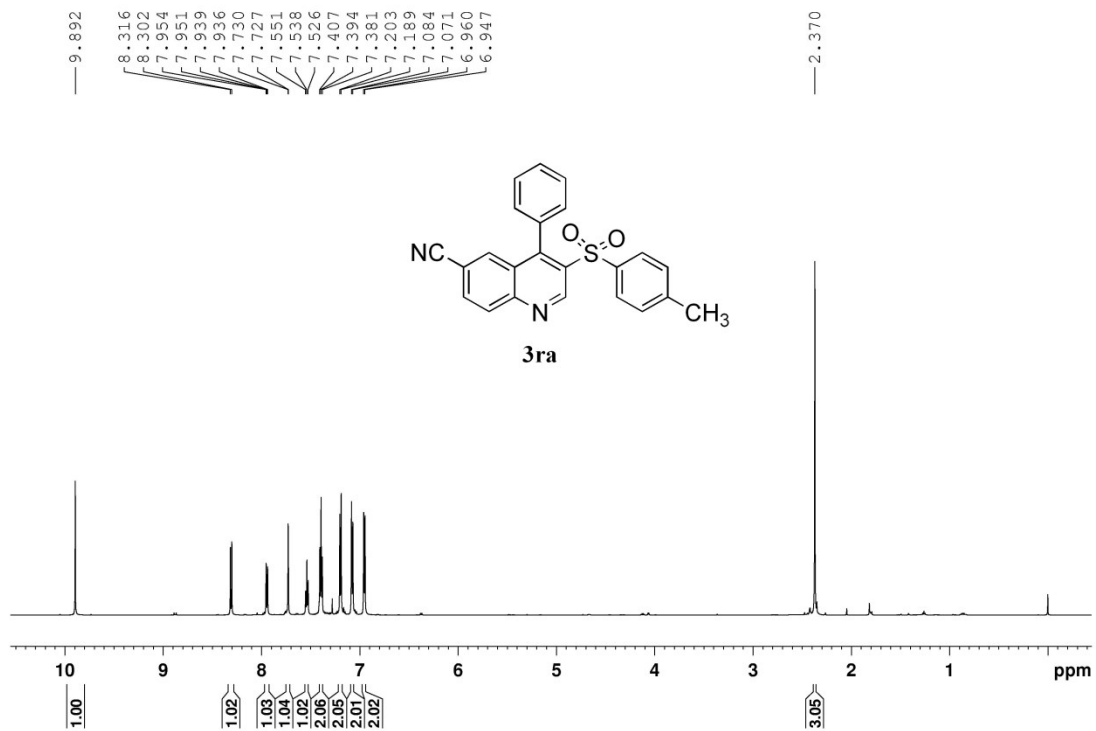
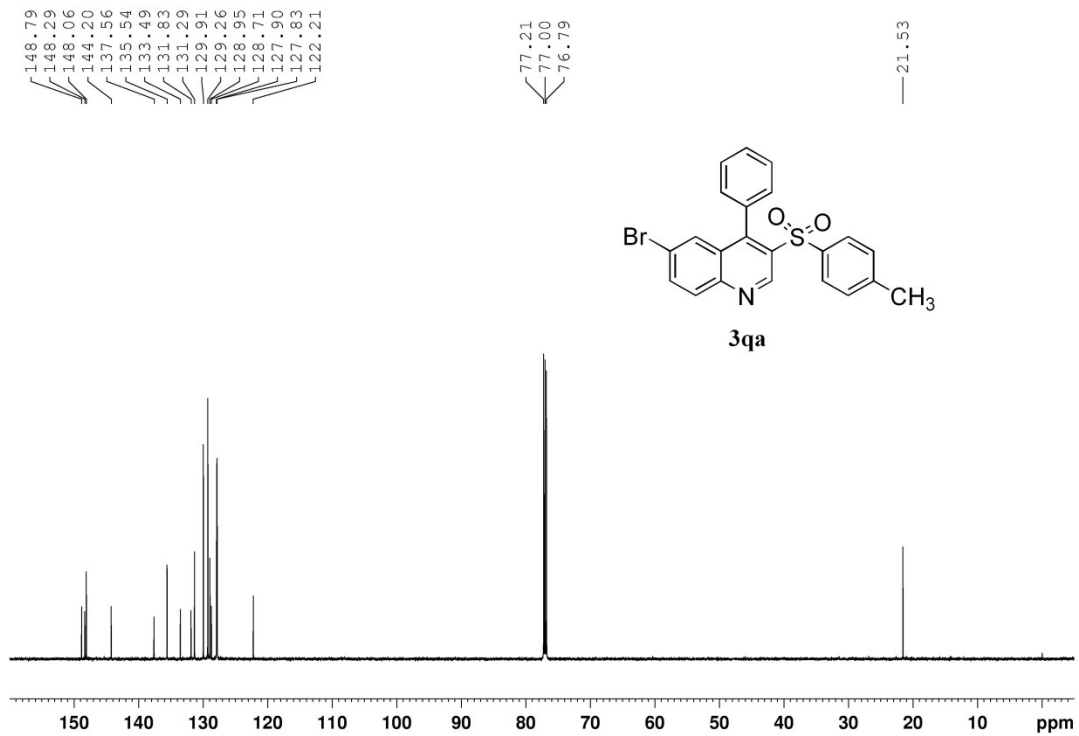


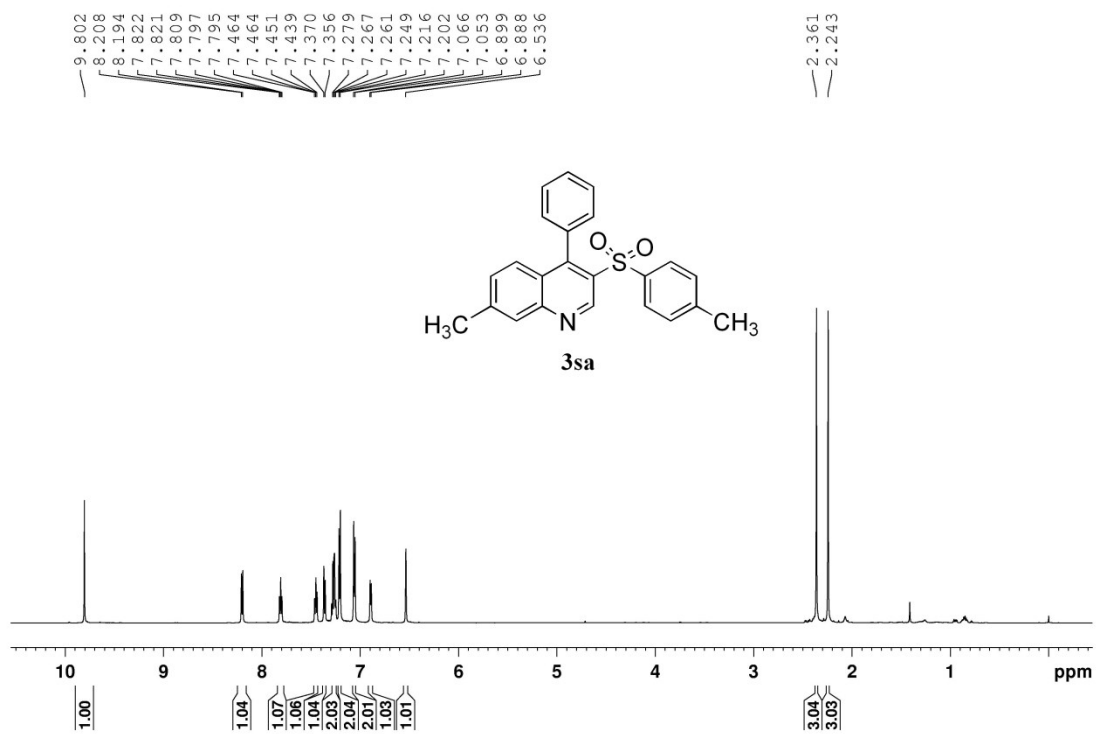
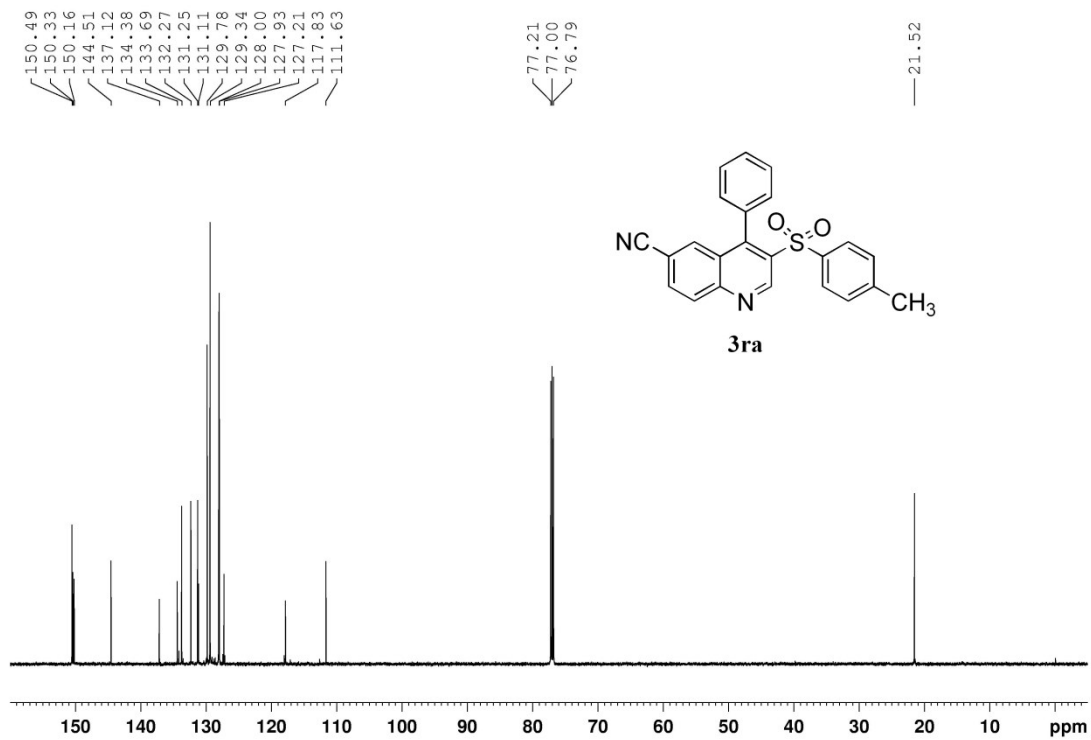


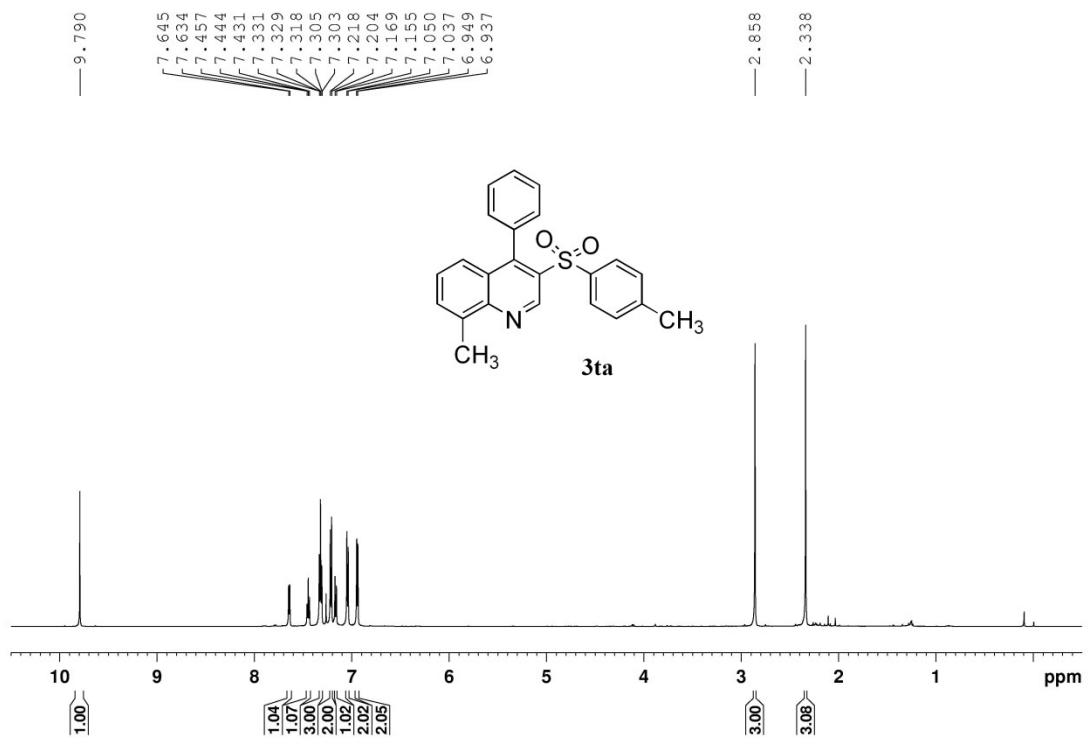
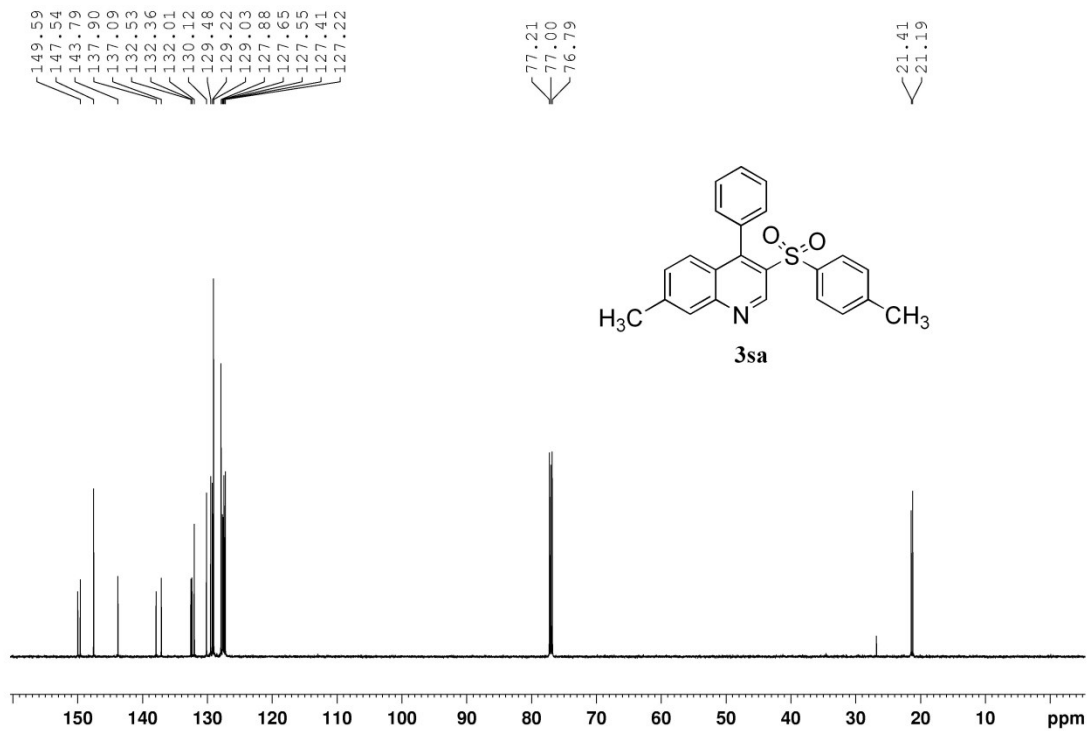


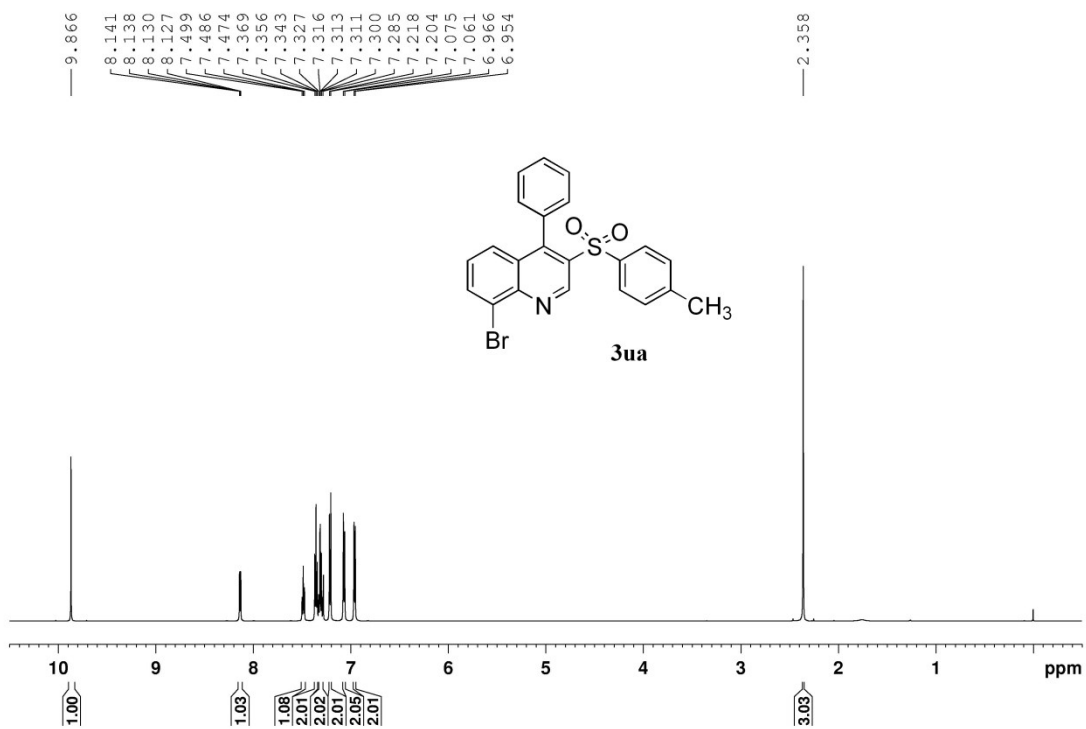
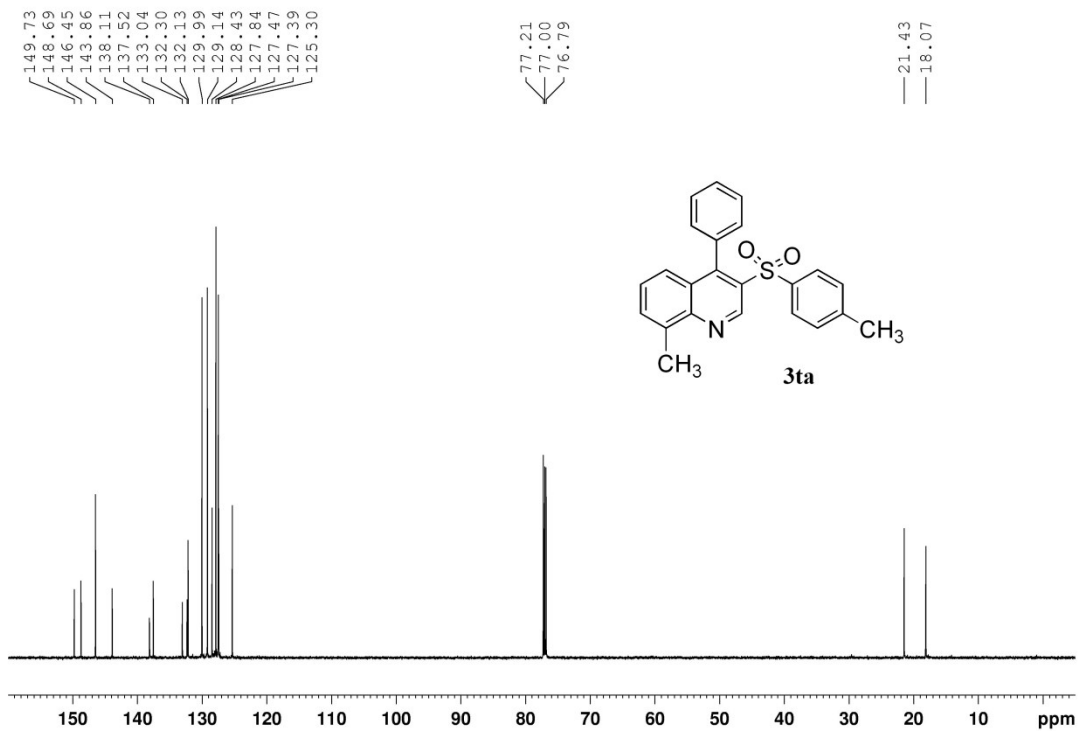


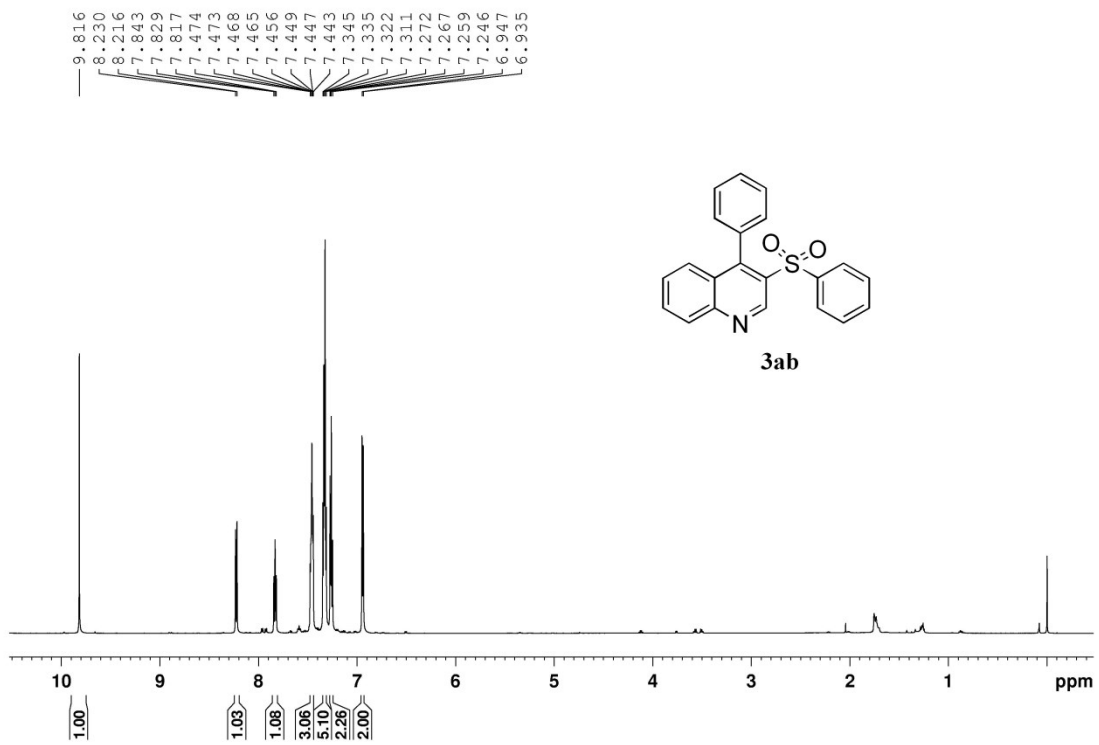
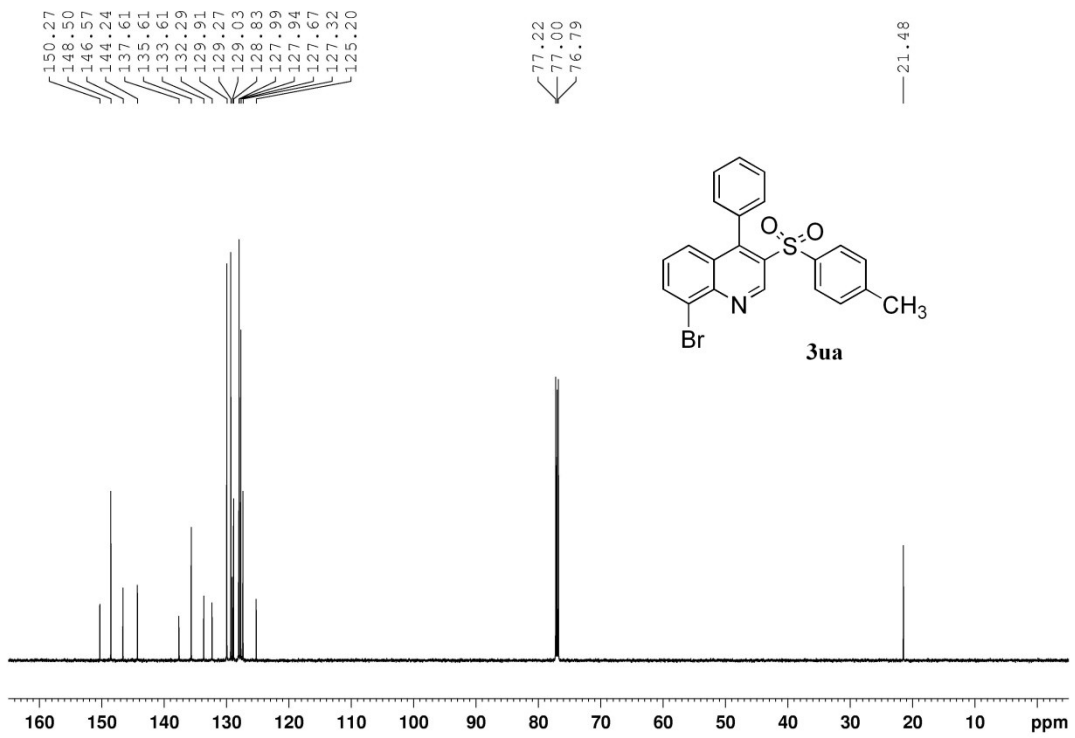


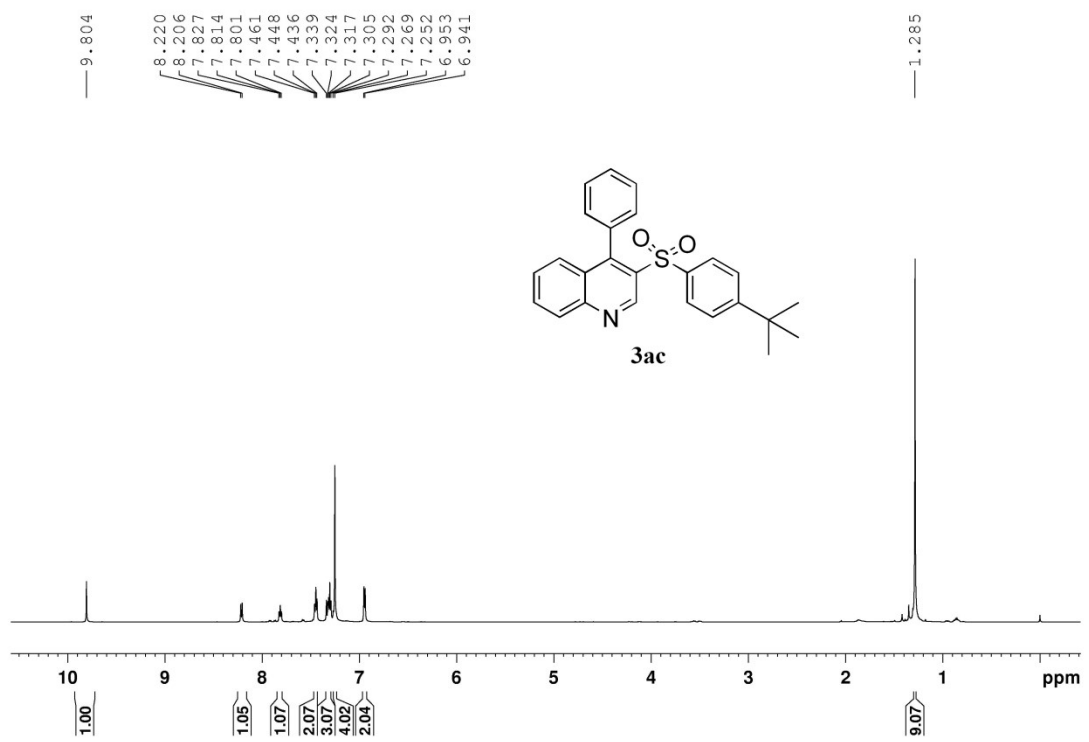
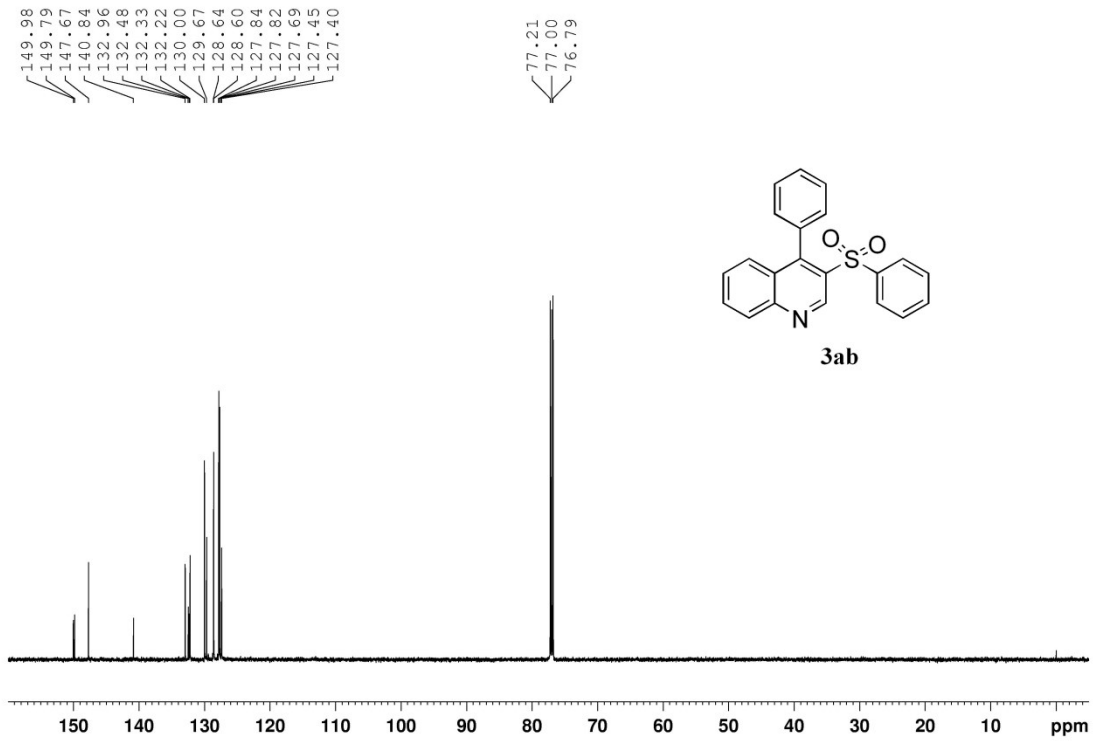


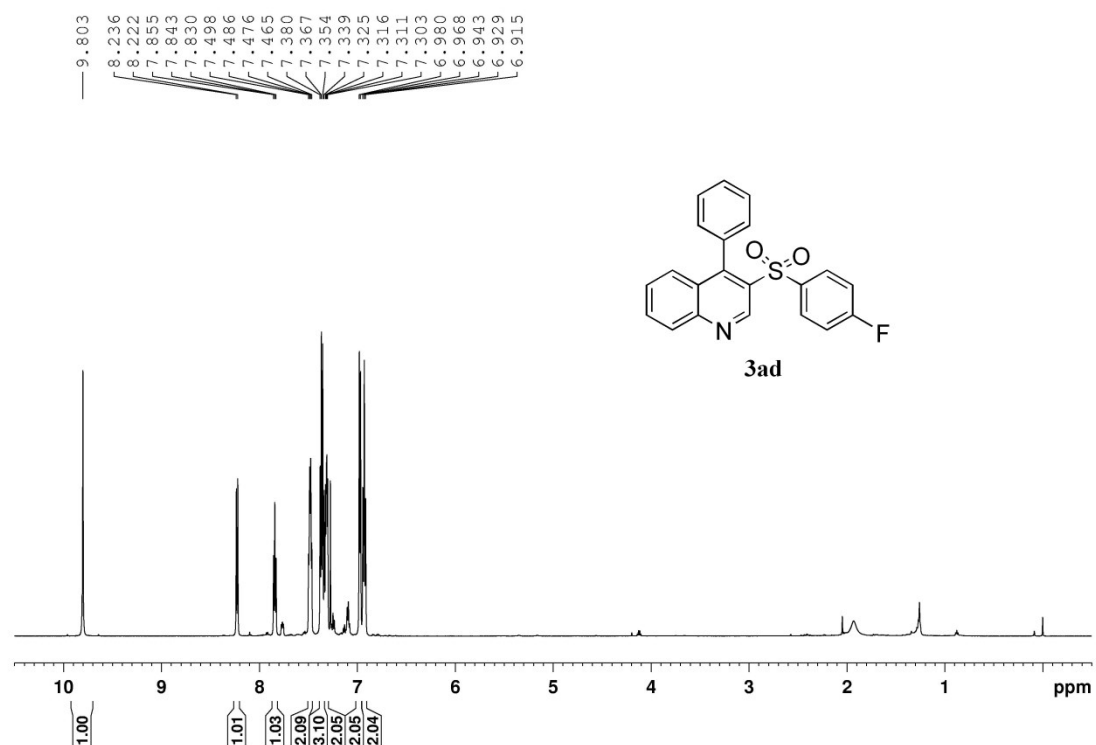
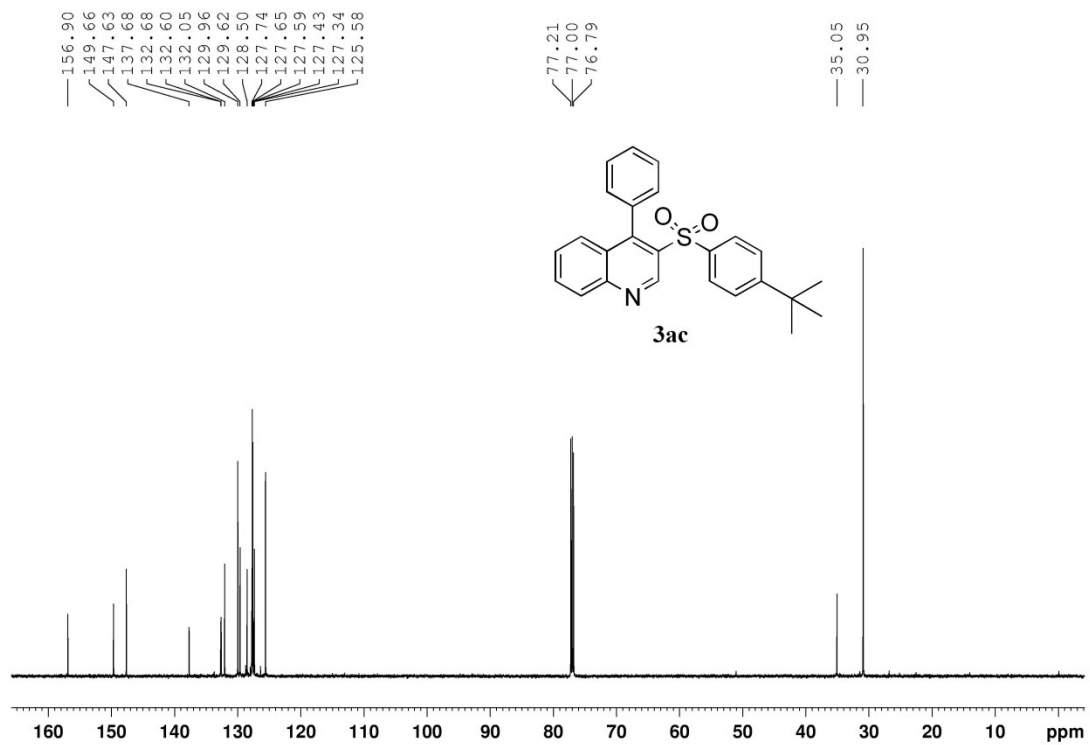


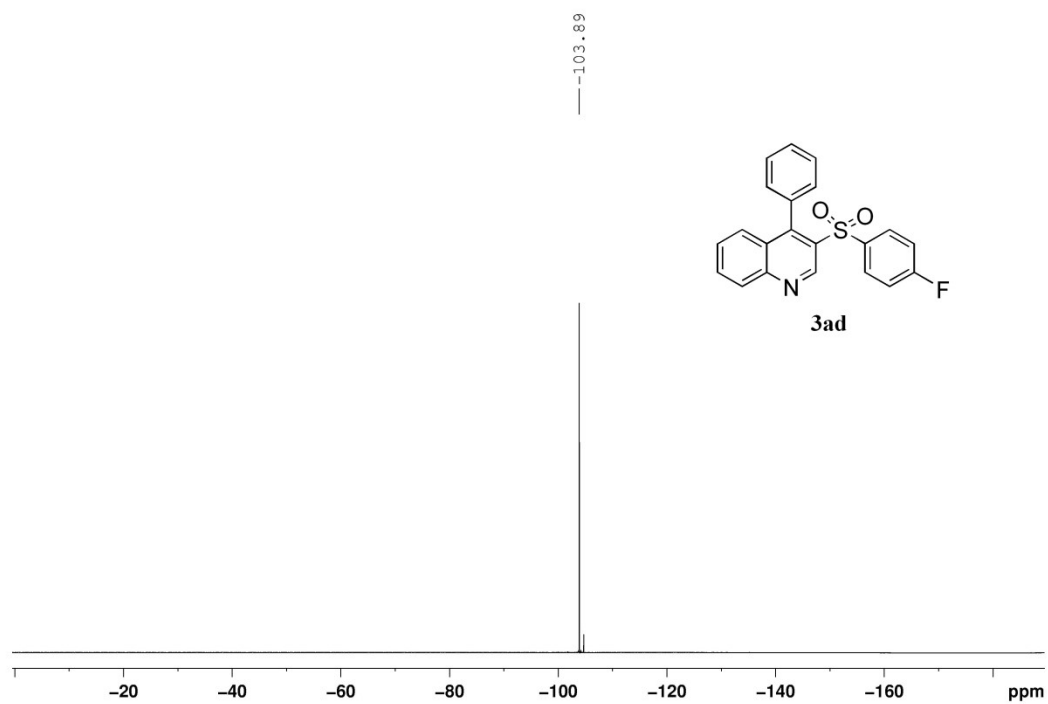
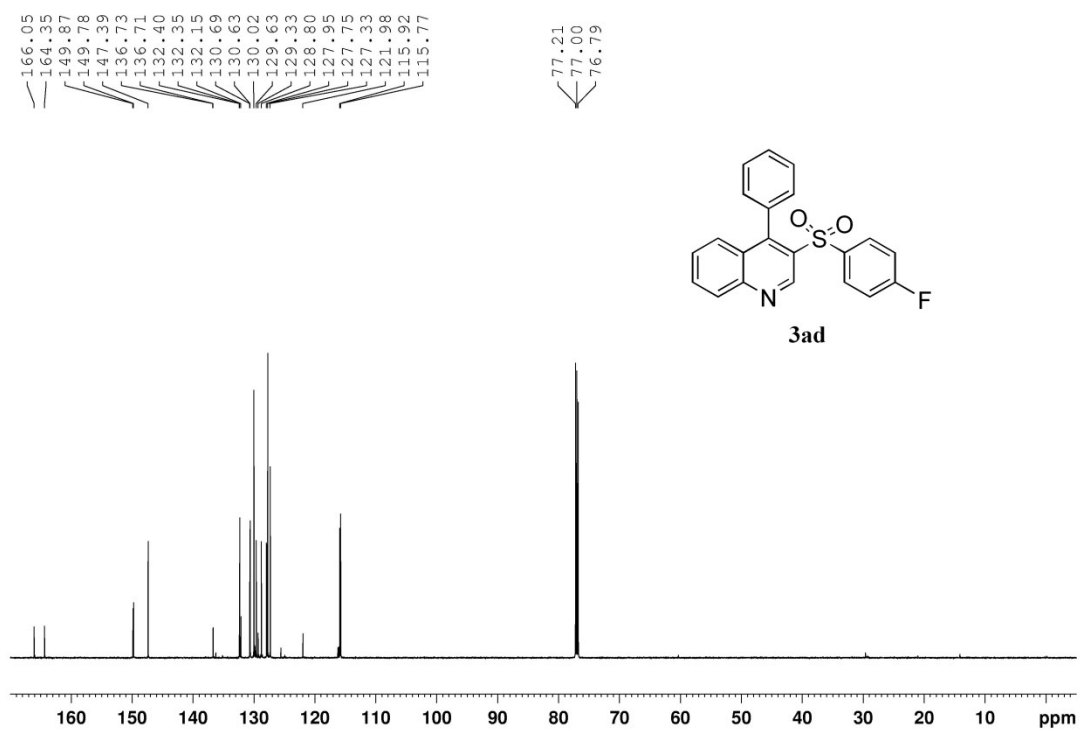


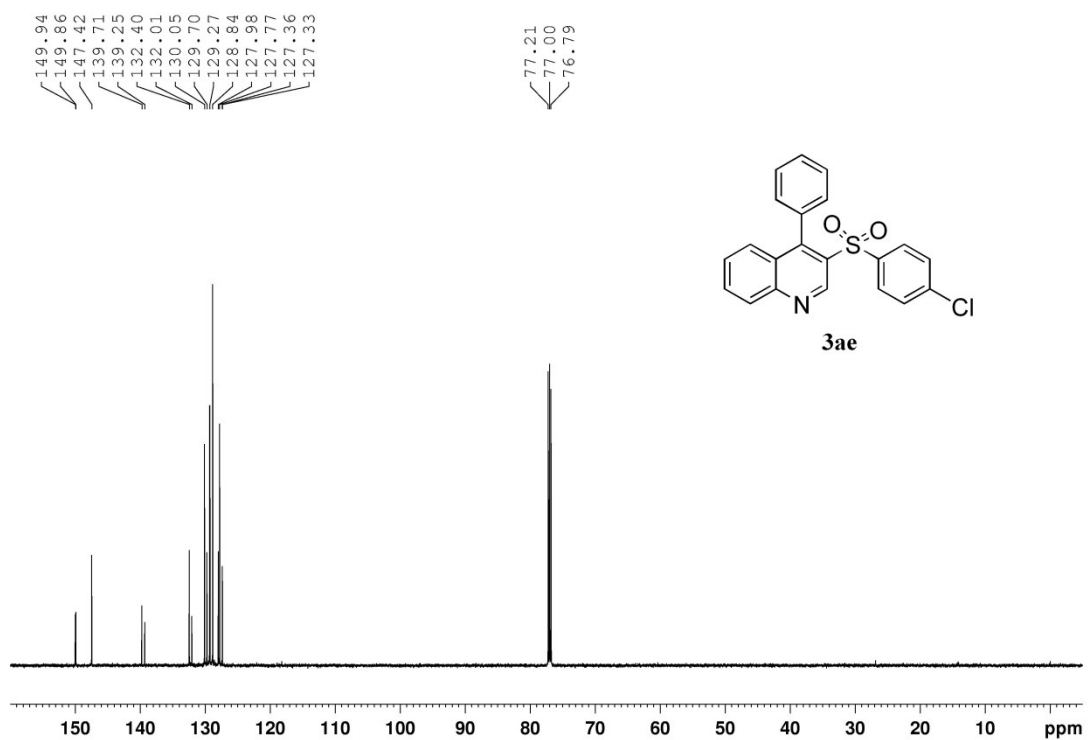
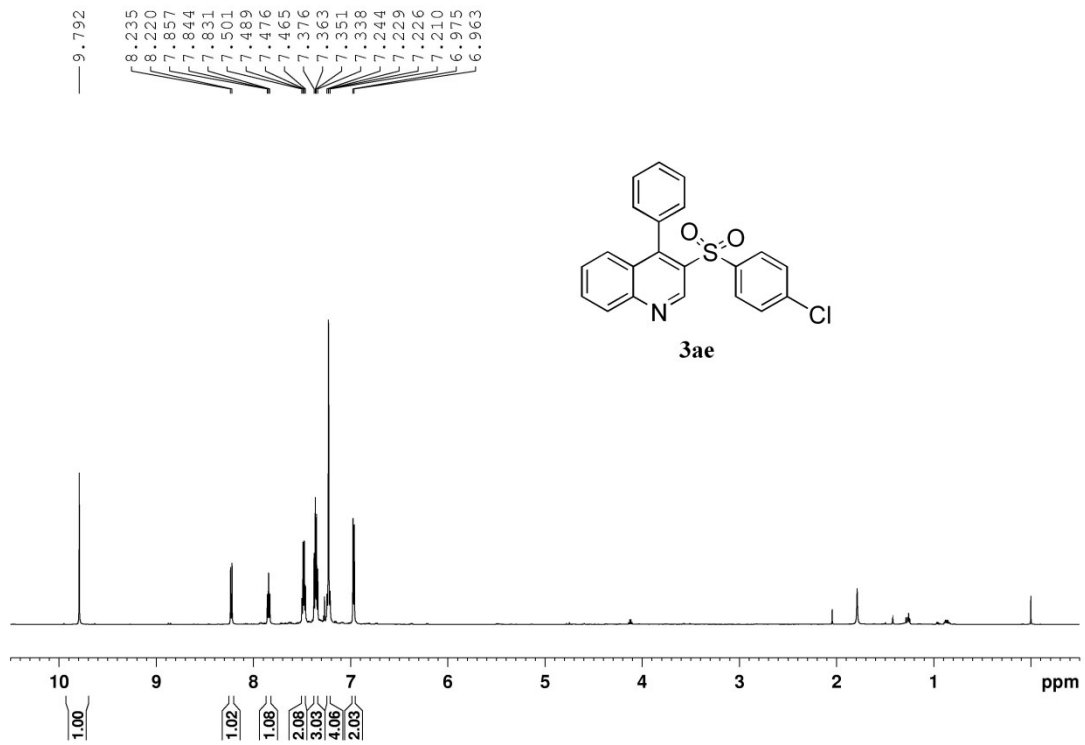


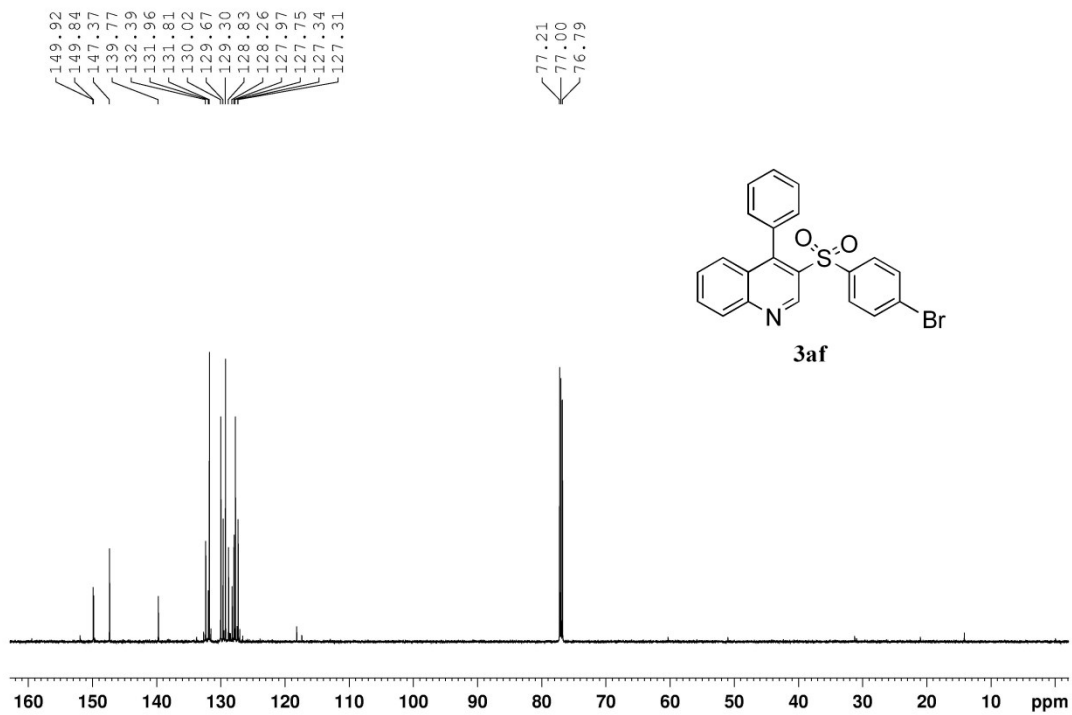
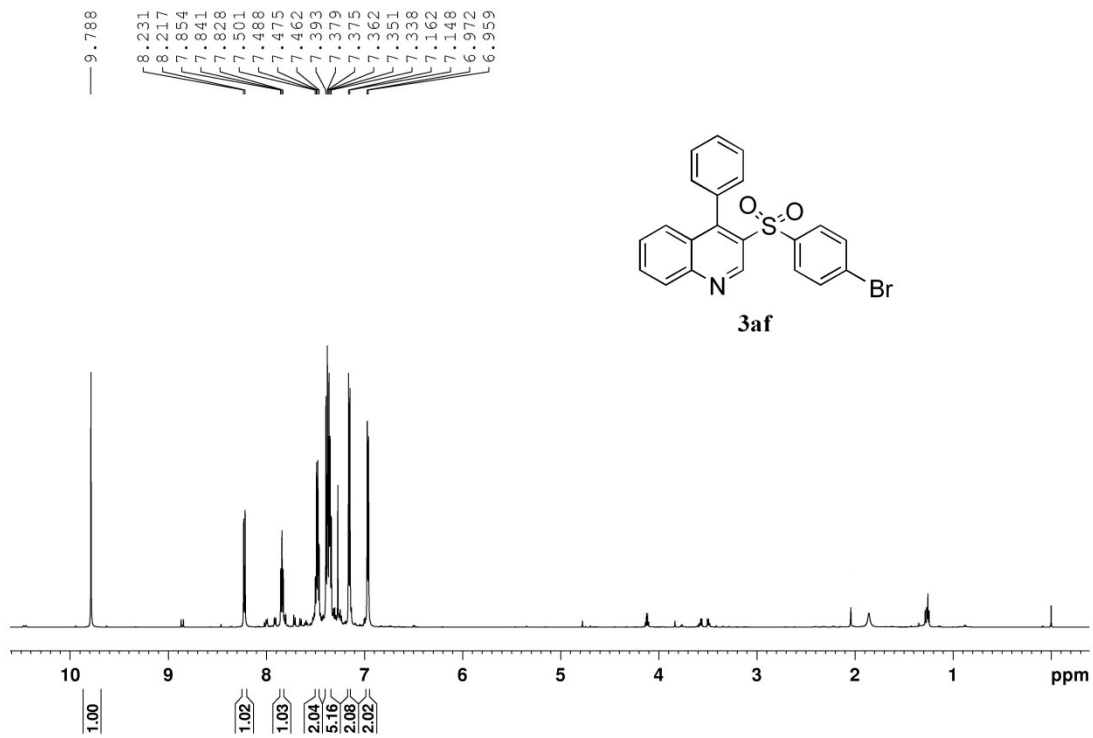


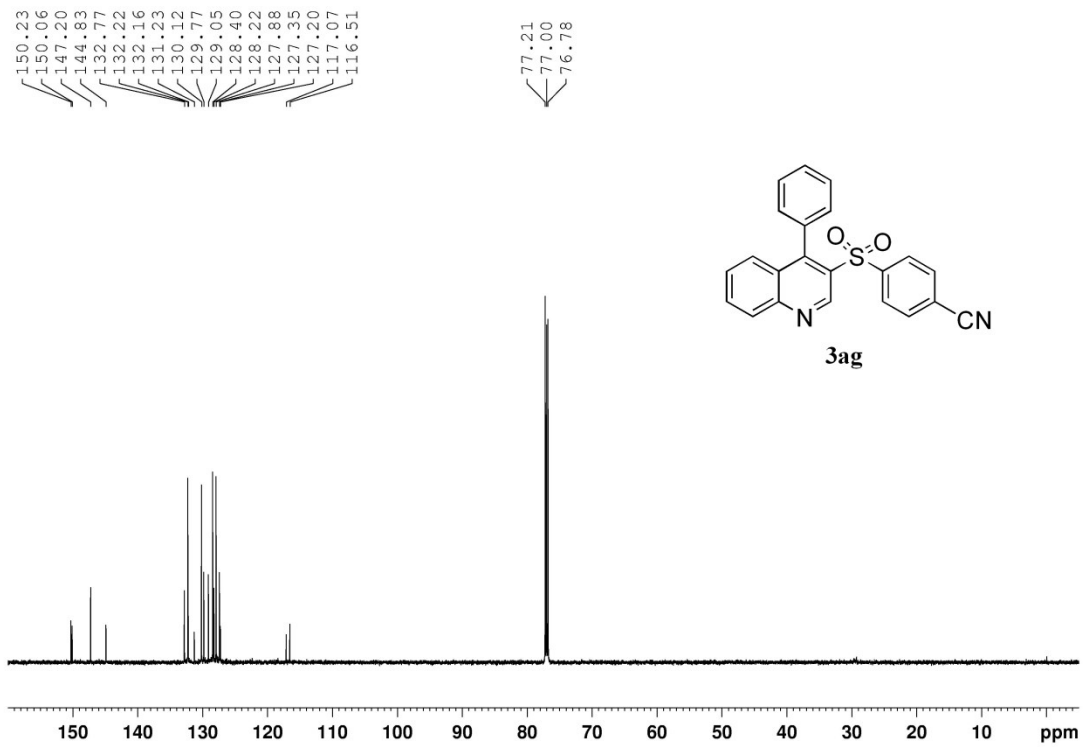
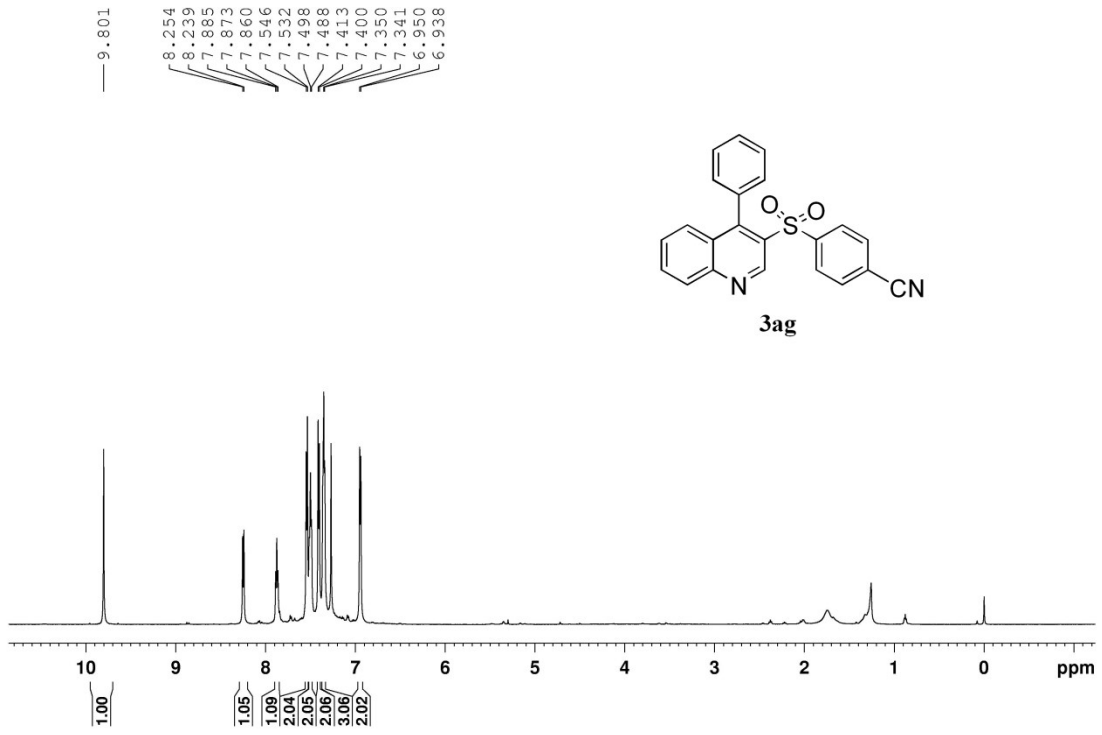


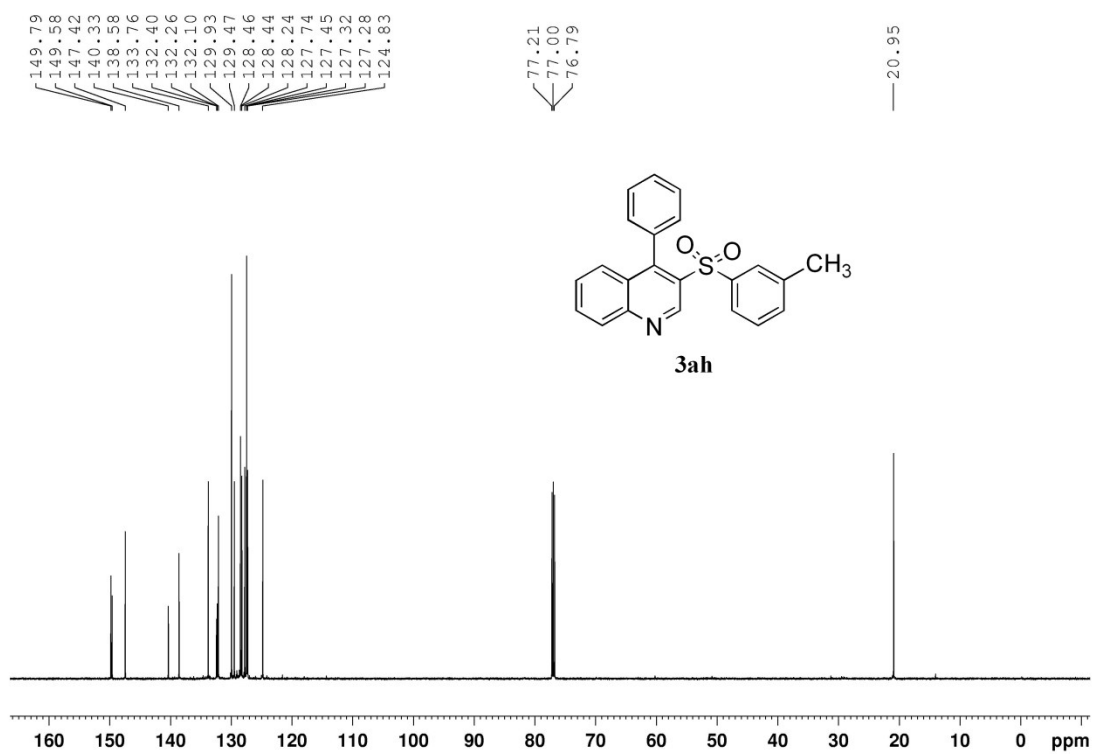
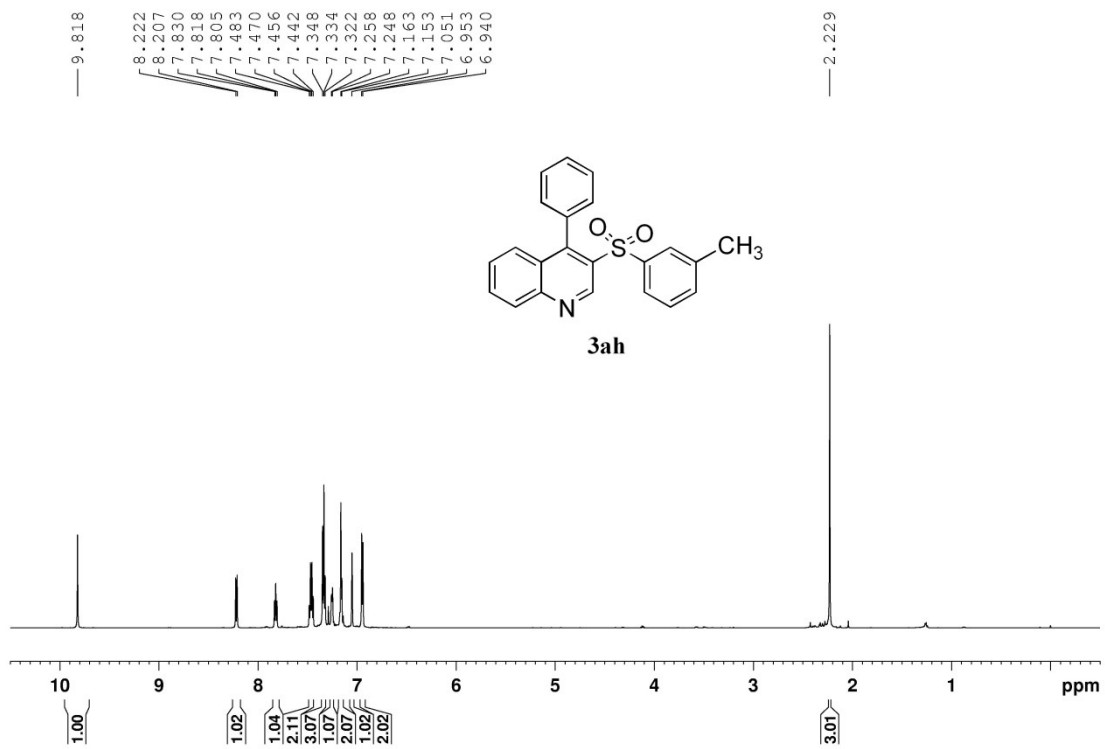


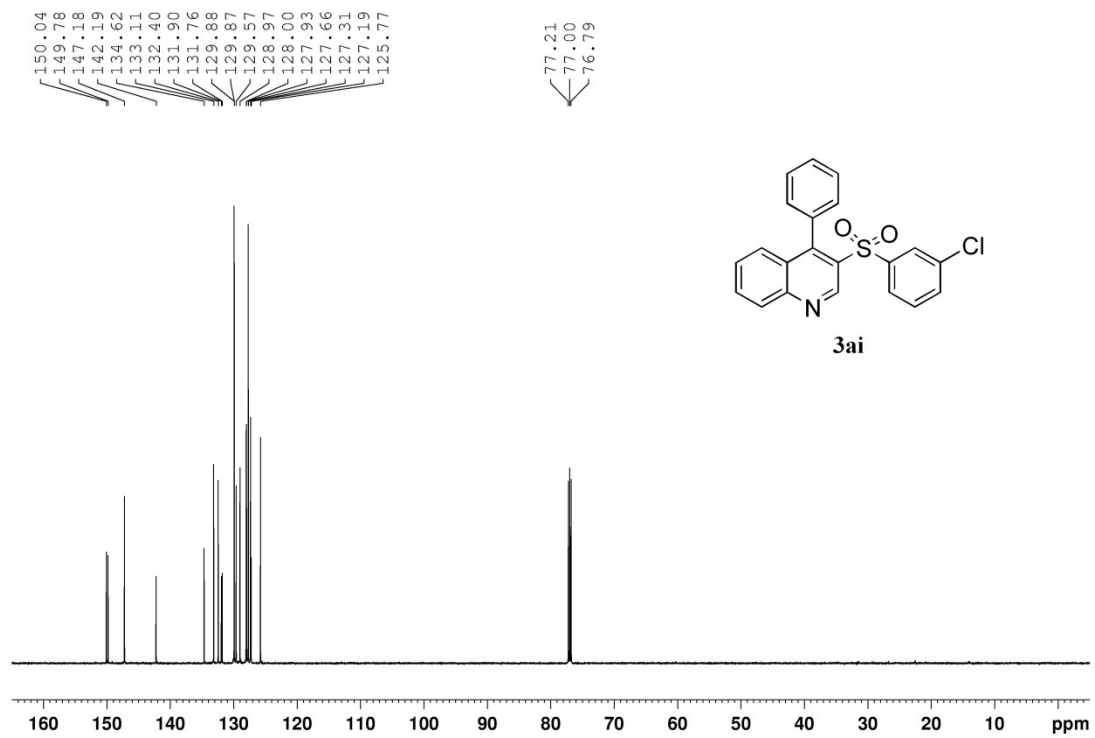
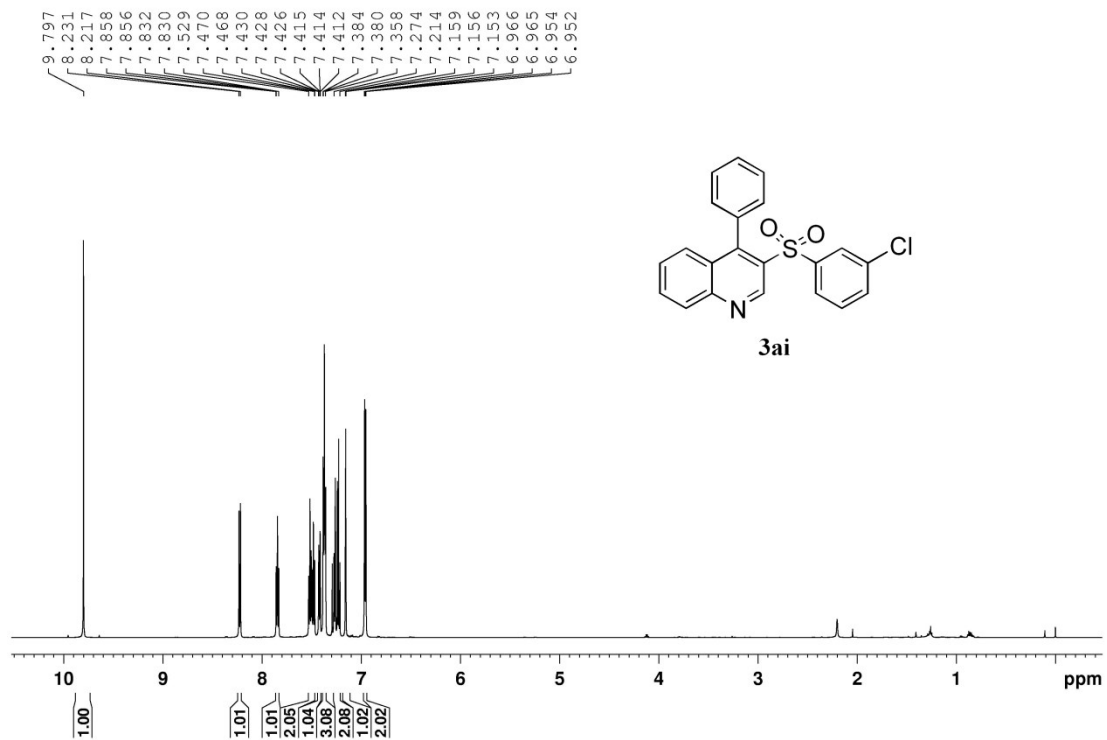


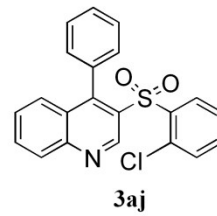
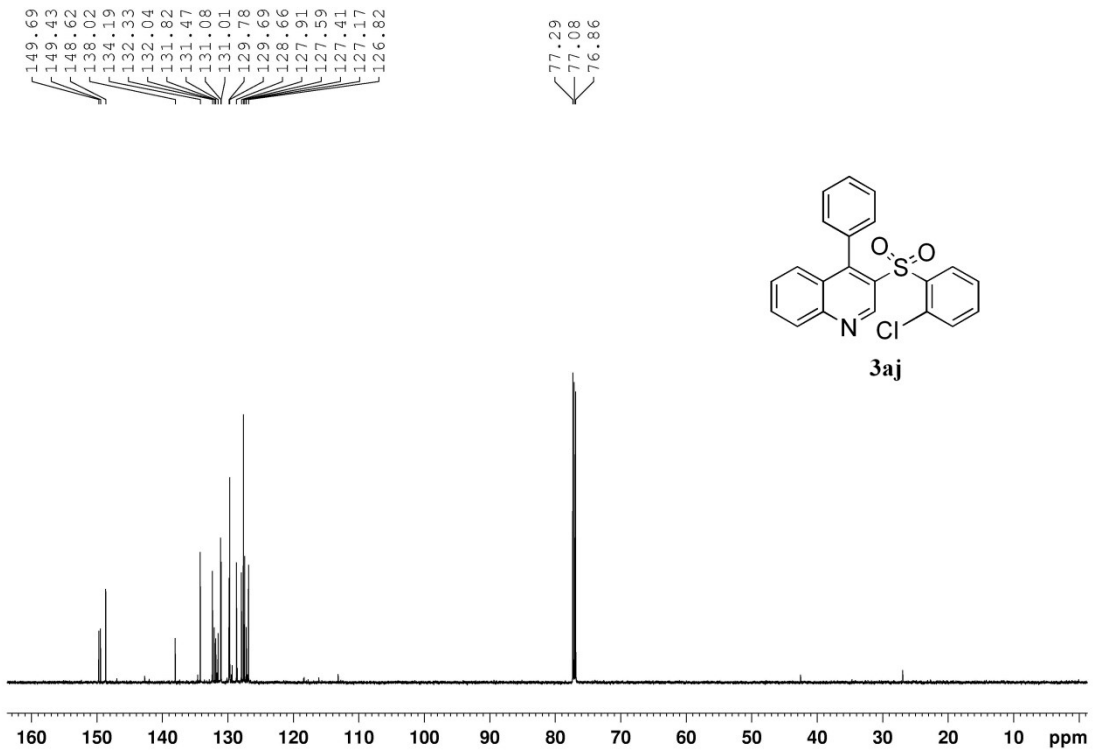
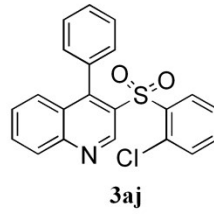
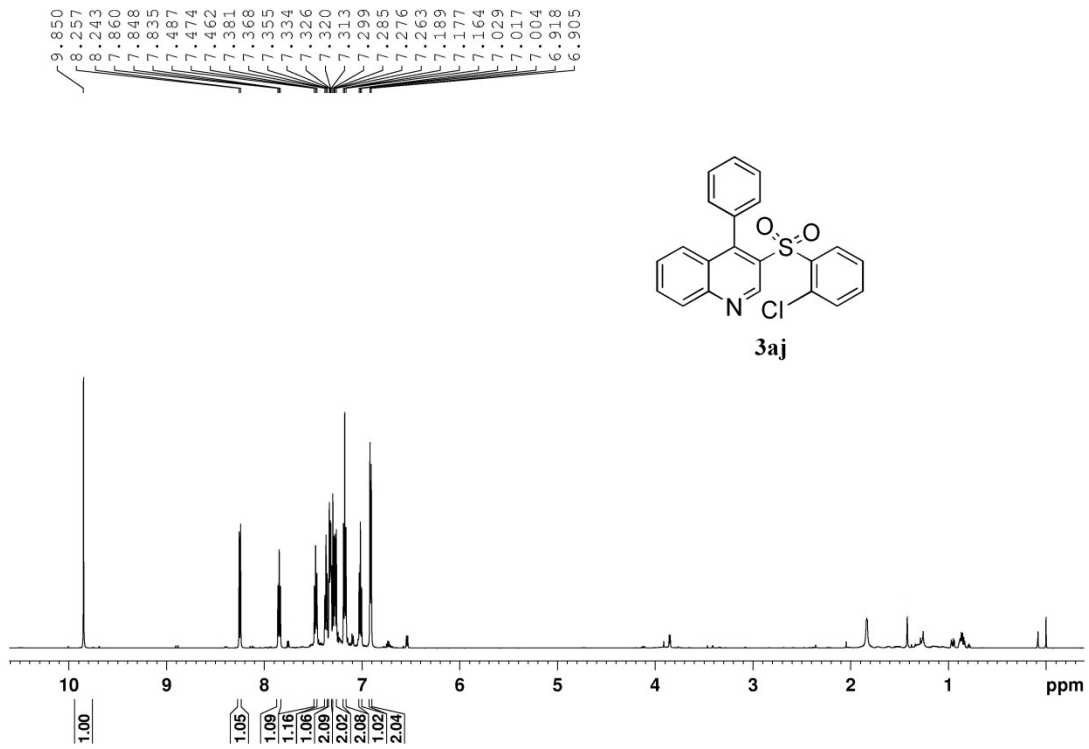


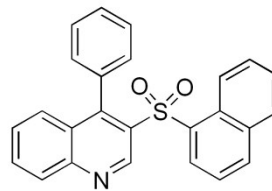
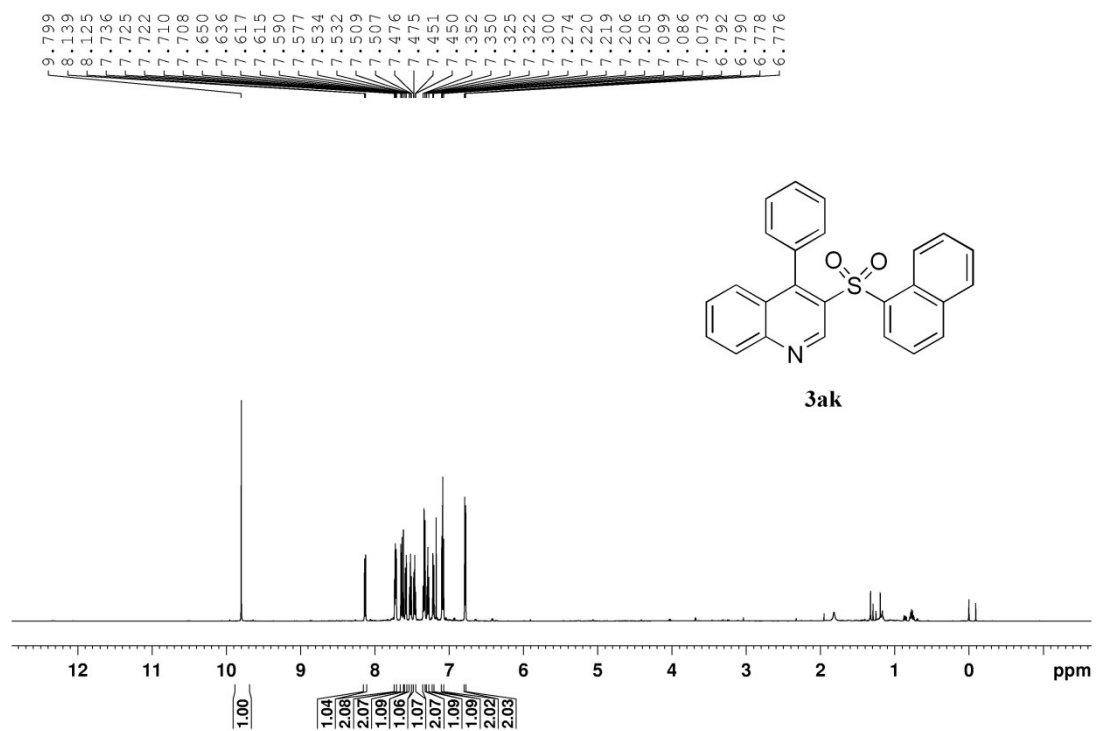




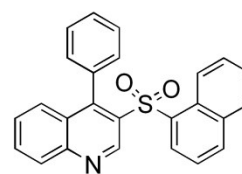
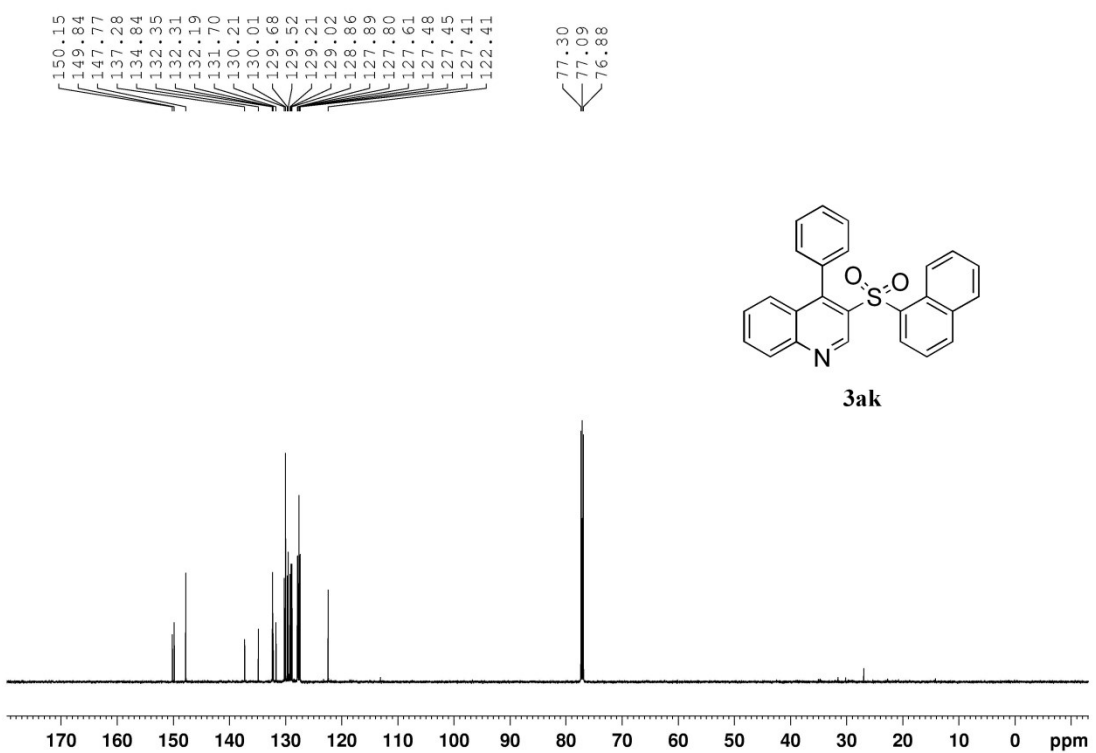








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