Supporting Information

Palladium-Catalyzed 1,2-Amino Carbonylation of 1,3-Dienes with (*N*-SO_2Py)-2-Iodoanilines: 2,3-Dihydroquinolin-4(1*H*)-ones Synthesis

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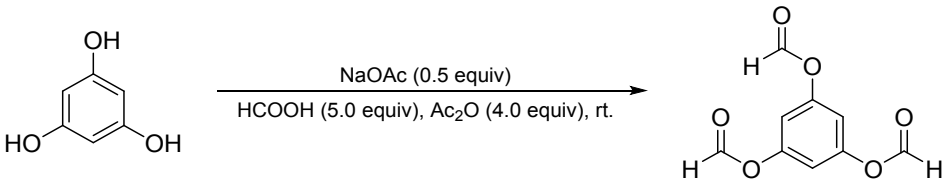
Table of Contents

1. General experimental information

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (100 MHz) chemical shifts were reported in ppm (δ) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer.

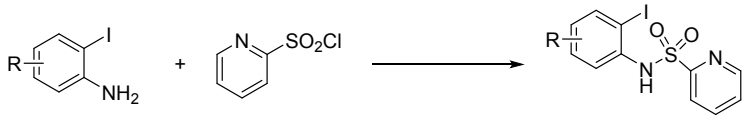
2. Preparation of benzene-1,3,5-triyl triformate (TFBen)[1]



Formic acid (8.4 mL, 222.8 mmol, 5.0 equiv) was added to acetic anhydride (16.8 mL, 178.2 mmol, 4.0 equiv) at rt. The mixture was stirred at 60 °C for 1 h and cooled to rt. The resulting solution was poured into a flask containing 1,3,5-trihydroxybenzene (5.62 g, 44.6 mmol, 1.0 equiv) and AcONa (1.83 g, 22.3 mmol, 0.5 equiv). The mixture was stirred for 4 h in a water bath and then diluted with toluene (100.0 mL), washed with H_2O (50.0 mL) twice. Keep the organic phase in fridge (2-8 °C) for overnight. Then filtered and dried in vacuo to afford the desired product benzene-1,3,5-triyl triformate (TFBen) as a white solid (5.1 g, 55%).

3. General procedure for the synthesis of *N*-(2-iodophenyl) pyridine-2-sulfonamides (1a–k)

The (*N*-SO_2Py)-2-iodoanilines **1a-d** and **1j-k** were prepared according to a general procedure reported by Carretero.[2]



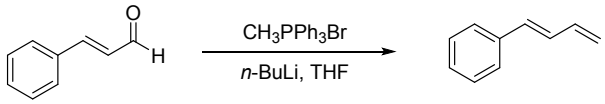
To a solution of 2-iodoaniline (4.0 mmol, 1.0 equiv) in THF (40.0 mL), pyridine (379.7 mg, 4.8 mmol, 1.2 equiv) and 2-pyridylsulfonyl chloride (852.5 mg, 4.8 mmol, 1.2 equiv) were successively added dropwise at 0 ºC and under N_2 atmosphere. The mixture was warmed to room temperature and stirred overnight. During this time, a gradual formation of a precipitate was observed. The resulting mixture was then suction filtered through a 6-cm fritted glass funnel (coarse) into a round-bottomed flask, and the filter cake was rinsed with THF (3 × 10.0 mL). To the resulting filtrate and the washes, water (20.0 mL) was added and the THF was removed by evaporation at reduced pressure, yielding a suspension of a white solid in the aqueous medium. This solid was collected by filtration, washed sequentially with toluene (2 × 5.0 mL) and diethyl ether (2 × 5.0 mL). Then it was transferred to a round-bottomed flask, and dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude mixture was purified by silica gel column chromatography (petroleum ether / dichloromethane = 1:2) to obtain *N*-(2-iodophenyl) pyridine-2-sulfonamide **1a-d** and **1j-k**.

The (*N*-SO_2Py)-2-iodoanilines **1e-i** were prepared according to a general procedure reported by Chan.[3]

To a solution of 2-iodoaniline (5.0 mmol, 1.0 equiv) in pyridine (5.0 mL) was added pyridine-2-sulfonyl chloride (1.33 g, 7.5 mmol, 1.5 equiv) at 0 °C under N_2 atmosphere and the resulting reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with the addition of DCM (30.0 mL) followed by HCl (50.0 mL, 1M). The organic layer was extracted and washed with water (10.0 mL × 2), brine (10.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography to obtain the (*N*-SO_2Py)-2-iodoanilines **1e-i**.

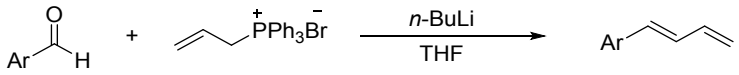
4. General procedure for the synthesis of 1,3-dienes (2a–q)

The 1,3-diene **2a** was prepared according to a general procedure reported by Sawama.[4]



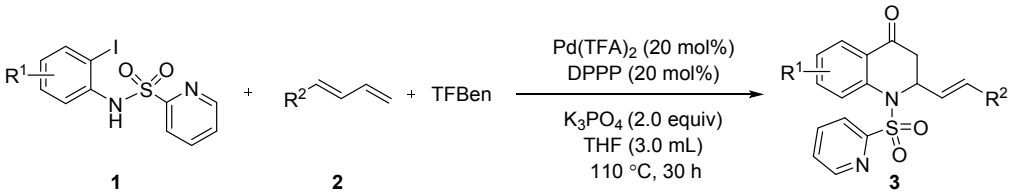
To a suspension of methyltriphenylphosphonium bromide (6.0 mmol) in THF (30.0 mL) was added *n*-BuLi (2.3 mL, 2.6 M in *n*-hexane, 3.6 mmol) at 0 °C under argon. After stirring for 15 min, a cinnamaldehyde (6.0 mmol) was added. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with sat. NH_4Cl aq. (10.0 mL) and extracted with EtOAc (10.0 mL × 2). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding (*E*)-buta-1,3-dien-1-ylbenzene (**2a**).

The 1,3-dienes **2b-q** were prepared according to a general procedure reported by Sawama.[4]



To a suspension of allyltriphenylphosphonium bromide (2.30 g, 6.0 mmol) in THF (30.0 mL) was added *n*-BuLi (2.3 mL, 2.6 M in *n*-hexane, 6.0 mmol) at 0 °C under argon. After stirring for 15 min, a benzaldehyde derivative (5.0 mmol) was added. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with sat. NH_4Cl aq. (10.0 mL) and extracted with EtOAc (10.0 mL × 2). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1-aryl-1,3-butadiene derivative (**2b-q**)

5. General procedure for the synthesis of (*E*)-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-ones (3aa–ka and 3ab–aq)

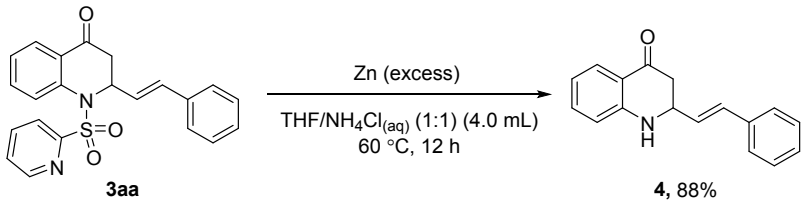


1 **2** **3**

The (*N*-SO_2Py)-2-iodoanilines **1** (0.5 mmol, 1.0 equiv), $Pd(TFA)_2$ (33.2 mg, 0.1 mmol, 20 mol%), dppp (41.2 mg, 0.1 mmol, 20 mol%), K_3PO_4 (212.3 mg, 1.0 mmol, 2.0 equiv) and a 2.5 mL vial containing TFBen (420.3 mg, 2.0 mmol, 4.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. The 1,3-dienes **2** (1.5 mmol, 3.0 equiv) and THF (3.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 110 °C for 30 h. Upon the reaction was completed, the resulting mixture was concentrated under vacuum and purified by silica gel column using chromatography (petroleum ether / dichloromethane = 2:1) to obtain the products **3**.

6. Removal of the *N*-SO_2Py directing group of 3aa

Compound **4** was prepared according to a general procedure reported by Carretero.[5]

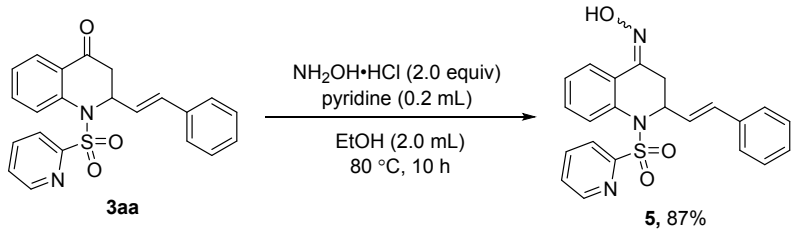


3aa **4,** 88%

A suspension of **3aa** (39.0 mg, 0.1 mmol, 1.0 equiv) and Zn powder (326.9 mg, 5.0 mmol, 50.0 equiv) in a 1:1 mixture of THF and sat aq. NH_4Cl solution (4.0 mL) was stirred at 60 °C until consumption of the starting material. The mixture was diluted with EtOAc (5.0 mL) and filtered over a pad of Celite to remove the Zn. The filtrate was washed with brine (5.0 mL) and the combined organic phase was dried ($NaSO_4$) and concentrated to dryness. The residue was purified by flash chromatography (petroleum ether / EtOAc = 9:1) to afford the product **4** (21.9 mg, 88% yield).

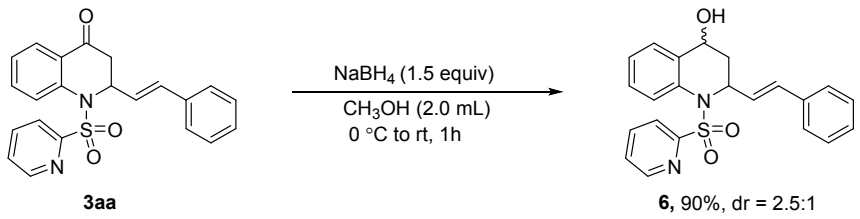
7. Transformation 3aa into compounds 5-6

Compound **5** was prepared according to a general procedure reported by Chiba.[6]



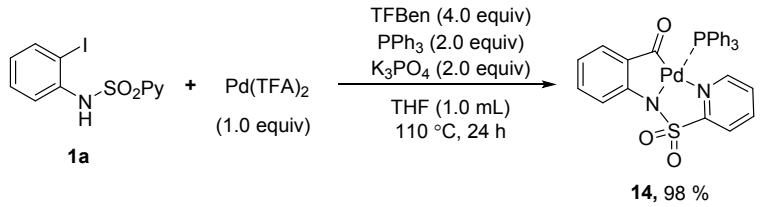
To a solution of **3aa** (39.0 mg, 0.1 mmol, 1.0 equiv) in EtOH (2.0 mL) and pyridine (0.2 mL) was added hydroxylamine hydrochloride (13.9 mg, 0.2 mmol, 2.0 equiv) and the solution was stirred at 80 °C. Upon completion of the reaction, the solution was cooled to room temperature. EtOH and pyridine were removed under reduced pressure and the resulting crude material was dissolved in ethyl acetate (5.0 mL) and washed with water and brine. After drying with $MgSO_4$ and removal of the solvents under reduced pressure, the resulting crude material was purified by flash column chromatography (petroleum ether / EtOAc = 5:1) to afford the product **5** (35.3 mg, 87% yield).

Compound **6** was prepared according to a general procedure reported by Wu.[7]

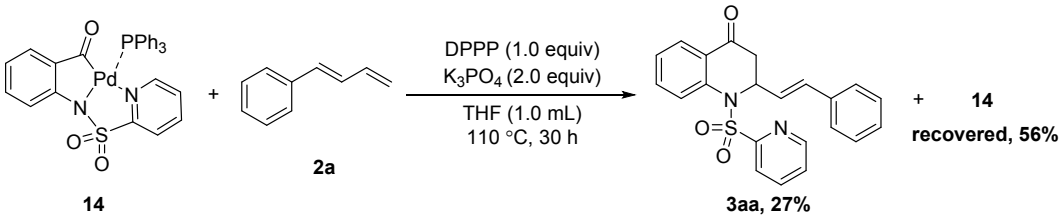


To a solution of **3aa** (39.0 mmol, 0.1 mmol, 1.0 equiv) in CH_3OH (2.0 mL) was added portionwise $NaBH_4$ (5.7 mg, 0.15 mmol, 1.5 equiv). The reaction was stirred at 0 °C for 10 min. The mixture was warmed to room temperature and stirred for 1 h. After completion of the reaction (as indicated by TLC), the solution poured into a saturated aqueous sodium hydrogencarbonate solution (5.0 mL), then extracted with ethyl acetate (5.0 mL × 3), the combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuum, the crude residue was purified by silica-gel column chromatography (petroleum ether/EtOAc = 2:1) to afford the product **6** (35.3 mg, 90% yield).

8. Control experiments

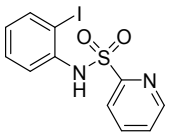


The (*N*-SO_2Py)-2-iodoaniline **1a** (36.0 mg, 0.1 mmol, 1.0 equiv), $Pd(TFA)_2$ (33.2 mg, 0.1 mmol, 1.0 equiv), PPh_3 (52.5 mg, 0.2 mmol, 2.0 equiv), K_3PO_4 (212.3 mg, 1.0 mmol, 2.0 equiv) and a 2.5 mL vial containing TFBen (84.1 mg, 0.4 mmol, 4.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. THF (1.0 mL) was added into the tube via syringe. The tube was sealed and stirred at 110 °C for 24 h. Upon the reaction was completed, the resulting mixture was concentrated under vacuum and purified by silica gel column using chromatography (petroleum ether/EtOAc = 2:1) to obtain the product **14** (61.6 mg, 98% yield).

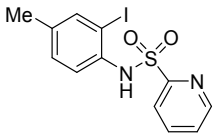


Compound **14** (62.9 mg, 0.1 mmol, 1.0 equiv), DPPP (41.2 mg, 0.1 mmol, 1.0 equiv), K_3PO_4 (42.5 mg, 0.2 mmol, 2.0 equiv) were added to an oven-dried tube (15.0 mL) which was then placed under vacuum and refilled with nitrogen three times. (*E*)-buta-1,3-dien-1-ylbenzene **2a** (39.1 mg, 0.3 mmol, 3.0 equiv) and THF (1.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 110 °C for 30 h. Upon the reaction was completed, the resulting mixture was concentrated under vacuum and purified by silica gel column using chromatography (petroleum ether / dichloromethane = 2:1) to obtain the product **3aa** (10.5 mg, 27% yield).

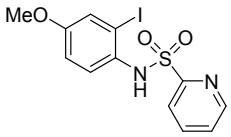
9. Characterization data of compounds 1a-k and 2a-q



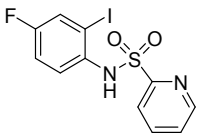
***N*-(2-iodophenyl)pyridine-2-sulfonamide (1a).** White solid in 75% yield, mp 178.9 – 180.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.2 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.85 (td, J = 7.7, 1.7 Hz, 1H), 7.67 (dd, J = 8.1, 1.1 Hz, 2H), 7.48 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.09 (s, 1H), 6.82 (td, J = 7.9, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 150.5, 139.4, 138.1, 137.6, 129.6, 127.3, 127.0, 122.8, 122.5, 92.0.



***N*-(2-iodo-4-methylphenyl)pyridine-2-sulfonamide (1b).** White solid in 70% yield, mp 144.3 – 145.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 4.6 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.50 – 7.45 (m, 3H), 7.07 (d, J = 10.3 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.4, 139.6, 138.1, 137.5, 134.9, 130.3, 127.3, 123.2, 122.8, 92.8, 20.4.

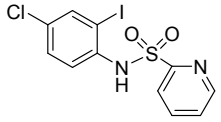


***N*-(2-iodo-4-methoxyphenyl)pyridine-2-sulfonamide (1c).** White solid in 69% yield, mp 155.4 – 156.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 4.6 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.50 – 7.47 (m, 2H), 7.18 (d, J = 2.8 Hz, 1H), 6.94 (s, 1H), 6.84 (dd, J = 8.9, 2.8 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 156.6, 150.4, 138.1, 130.5, 127.2, 125.8, 124.3, 122.9, 115.1, 94.8, 55.8.

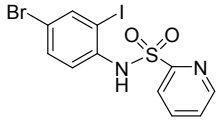


***N*-(4-fluoro-2-iodophenyl)pyridine-2-sulfonamide (1d).** White solid in 73% yield, mp 143.8 –

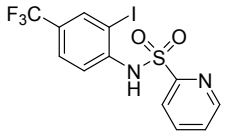
145.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dt, J = 4.7, 1.2 Hz, 1H), 7.86 (dd, J = 4.9, 1.2 Hz, 2H), 7.61 (dd, J = 9.0, 5.3 Hz, 1H), 7.50 (dd, J = 8.8, 4.7 Hz, 1H), 7.39 (dd, J = 7.6, 2.9 Hz, 1H), 7.09 (s, 1H), 7.03 (ddd, J = 9.0, 7.8, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 157.5 (d, J = 222.8 Hz, 1C), 150.4, 138.2, 134.0, 127.4, 126.0 (d, J = 24.8 Hz, 1C), 124.9 (d, J = 8.0 Hz, 1C), 122.8, 116.5 (d, J = 22.1 Hz, 1C), 93.0 (d, J = 8.0 Hz, 1C).



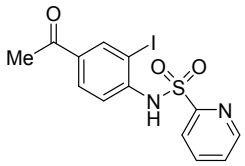
***N*-(4-chloro-2-iodophenyl)pyridine-2-sulfonamide (1e)** White solid in 86% yield, mp 119.2 – 121.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.6 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.70 (d, J = 2.3 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.32 – 7.30 (m, 1H), 7.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.5, 138.5, 138.3, 136.4, 131.6, 129.7, 127.5, 123.4, 122.8, 92.3.



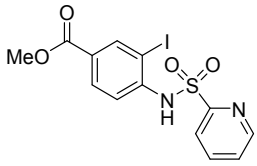
***N*-(4-bromo-2-iodophenyl)pyridine-2-sulfonamide (1f)** White solid in 64% yield, mp 123.5 – 125.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 4.1, 0.9 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.79 (d, J = 2.2 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.50 (ddd, J = 7.1, 4.7, 1.5 Hz, 1H), 7.39 (dd, J = 8.7, 2.2 Hz, 1H), 7.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 150.5, 141.1, 138.3, 136.9, 132.5, 127.5, 123.7, 122.8, 119.1, 92.7.



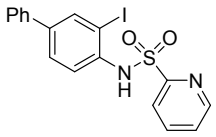
***N*-(2-iodo-4-(trifluoromethyl)phenyl)pyridine-2-sulfonamide (1g).** White solid in 81% yield, mp 118.7 – 120.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.5 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.80 (d, J = 8.6 Hz, 1H), 7.51 (dd, J = 7.2, 5.4 Hz, 2H), 7.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.5, 140.9, 138.4, 136.3 (q, J = 3.7 Hz, 1C), 128.2 (q, J = 33.4 Hz, 1C), 127.7, 126.7 (q, J = 3.4 Hz, 1C), 122.8 (q, J = 272.4 Hz, 1C), 122.7, 120.7, 90.1.



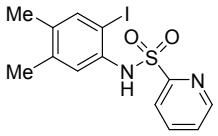
***N*-(4-acetyl-2-iodophenyl)pyridine-2-sulfonamide (1h).** White solid in 86% yield, mp 164.3 – 166.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.5 Hz, 1H), 8.28 (d, J = 1.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.90 (td, J = 7.8, 1.5 Hz, 1H), 7.83 (dd, J = 8.6, 1.7 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.50 (dd, J = 7.3, 4.9 Hz, 1H), 7.37 (s, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 156.2, 150.6, 141.7, 139.6, 138.3, 134.7, 129.8, 127.6, 122.8, 119.8, 90.3, 26.5.



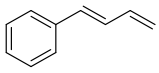
methyl 3-iodo-4-(pyridine-2-sulfonamido)benzoate (1i). White solid in 71% yield, mp 152.8 – 154.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.5 Hz, 1H), 8.35 (s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.89 (dd, J = 15.4, 8.1 Hz, 2H), 7.74 (d, J = 8.2 Hz, 1H), 7.49 (dd, J = 7.6, 4.7 Hz, 1H), 7.35 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 156.1, 150.4, 141.5, 140.6, 138.1, 130.8, 127.7, 127.5, 122.7, 119.6, 89.6, 52.4.



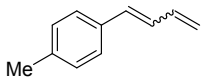
***N*-(3-iodo-[1,1'-biphenyl]-4-yl)pyridine-2-sulfonamide (1j).** White solid in 77% yield, mp 133.8 – 135.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 4.2 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 2.0 Hz, 1H), 7.87 (td, J = 7.8, 1.6 Hz, 1H), 7.72 (d, J = 8.5 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.48 – 7.46 (m, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.35 – 7.32 (m, 1H), 7.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.5, 140.1, 138.6, 138.2, 137.7, 136.6, 129.0, 128.2, 128.0, 127.4, 126.9, 122.8, 122.7, 92.7.



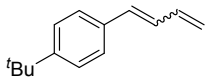
***N*-(2-iodo-4,5-dimethylphenyl)pyridine-2-sulfonamide (1k).** White solid in 76% yield, mp 209.8 – 211.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, 1H), 8.75 (d, J = 4.0 Hz, 1H), 8.06 – 8.03 (m, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.68 (dd, J = 6.9, 4.9 Hz, 1H), 7.58 (s, 1H), 6.83 (s, 1H), 2.12 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.5, 150.0, 139.6, 138.6, 137.6, 137.1, 135.7, 129.5, 127.2, 122.2, 95.8, 19.0, 18.2.



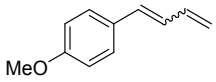
(*E*)-buta-1,3-dien-1-ylbenzene (2a). Colorless oil in 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 6.89 (dd, J = 15.6, 10.5 Hz, 1H), 6.67 – 6.56 (m, 2H), 5.43 (d, J = 16.8 Hz, 1H), 5.27 (d, J = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 137.2, 133.0, 129.7, 128.7, 127.7, 126.5, 117.7.



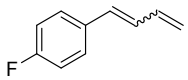
1-(buta-1,3-dien-1-yl)-4-methylbenzene (2b). Colorless oil in 90% yield, *E/Z* mixture was obtained. *E/Z* ratio = 41/59 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 6.6 Hz, 1H), 7.19 (dd, J = 10.1, 8.3 Hz, 2H), 6.98 – 6.77 (m, 1H), 6.61 – 6.53 (m, 2H), 5.44 – 5.34 (m, 1H), 5.23 (dd, J = 25.7, 9.9 Hz, 1H), 2.39 (s, 3H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 6.6 Hz, 1H), 7.19 (dd, J = 10.1, 8.3 Hz, 2H), 6.61 – 6.53 (m, 1H), 6.49 (d, J = 11.6 Hz, 1H), 6.28 (t, J = 11.3 Hz, 1H), 5.44 – 5.34 (m, 1H), 5.23 (dd, J = 25.7, 9.9 Hz, 1H), 2.41 (s, 3H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.4, 136.9, 134.6, 134.4, 133.5, 132.9, 130.5, 130.3, 129.4, 129.1, 128.8, 126.5, 119.3, 117.1, 21.4, 21.3.



1-(buta-1,3-dien-1-yl)-4-(tert-butyl)benzene (2c). Colorless oil in 60% yield, *E/Z* mixture was obtained. *E/Z* ratio = 38/62 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 3H), 7.36 (d, J = 8.1 Hz, 1H), 7.07 – 6.82 (m, 1H), 6.65 – 6.56 (m, 2H), 5.42 (t, J = 18.1 Hz, 1H), 5.26 (dd, J = 25.8, 10.1 Hz, 1H), 1.40 (s, 9H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 3H), 7.36 (d, J = 8.1 Hz, 1H), 7.07 – 6.82 (m, 1H), 6.52 (d, J = 11.9 Hz, 1H), 6.32 (t, J = 11.3 Hz, 1H), 5.42 (t, J = 18.1 Hz, 1H), 5.26 (dd, J = 25.8, 10.1 Hz, 1H), 1.42 (s, 9H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.4, 136.9, 134.6, 134.4, 133.5, 132.9, 130.5, 130.3, 129.4, 129.1, 128.8, 126.5, 119.3, 117.1, 21.4, 21.3.

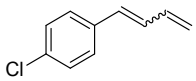


1-(buta-1,3-dien-1-yl)-4-methoxybenzene (2d). Colorless oil in 85% yield, *E/Z* mixture was obtained. *E/Z* ratio = 36/64 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.7 Hz, 2H), 6.96 (dd, J = 15.8, 5.5 Hz, 1H), 6.92 – 6.90 (m, 2H), 6.56 – 6.47 (m, 2H), 5.41 – 5.29 (m, 1H), 5.19 (dd, J = 34.0, 9.6 Hz, 1H), 3.83 (s, 3H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.6 Hz, 2H), 6.96 (dd, J = 15.8, 5.5 Hz, 1H), 6.92 – 6.90 (m, 2H), 6.43 (d, J = 11.5 Hz, 1H), 6.22 (t, J = 11.3 Hz, 1H), 5.41 – 5.29 (m, 1H), 5.19 (dd, J = 34.0, 9.6 Hz, 1H), 3.84 (s, 3H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 137.4, 136.9, 134.6, 134.4, 133.5, 132.9, 130.5, 130.3, 129.4, 129.1, 128.8, 126.5, 119.3, 117.1, 21.4, 21.3.

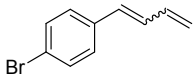


1-(buta-1,3-dien-1-yl)-4-fluorobenzene (2e). Colorless oil in 74% yield, *E/Z* mixture was obtained. *E/Z* ratio = 42/58 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.3, 5.6 Hz, 2H), 7.08 – 7.01 (m, 2H), 6.91 – 6.70 (m, 1H), 6.57 – 6.48 (m, 2H), 5.39 (dd, J = 22.9, 16.8 Hz, 1H), 5.24 (dd, J = 24.6, 10.0 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 8.1, 5.7 Hz, 2H), 7.08 – 7.01 (m, 2H), 6.91 – 6.70 (m, 1H), 6.44 (d, J = 11.5 Hz, 1H), 6.28 (t, J = 11.3 Hz, 1H), 5.39 (dd, J = 22.9, 16.8 Hz, 1H), 5.24 (dd, J = 24.6, 10.0 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, J =

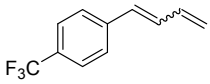
49.7 Hz, 1C), 161.0 (d, J = 49.2 Hz, 1C), 137.1, 133.5 (d, J = 3.3 Hz, 1C), 133.4 (d, J = 3.3 Hz, 1C), 132.9, 131.7, 130.8, 130.73, 130.65, 129.5 (d, J = 2.1 Hz, 1C), 129.3, 128.0 (d, J = 7.9 Hz, 1C), 120.0, 117.8, 115.7 (d, J = 21.7 Hz, 1C), 115.3 (d, J = 21.4 Hz, 1C).



1-(buta-1,3-dien-1-yl)-4-chlorobenzene (2f). Colorless oil in 88% yield, *E/Z* mixture was obtained. *E/Z* ratio = 42/58 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 4H), 6.94 – 6.77 (m, 1H), 6.59 – 6.50 (m, 2H), 5.44 (dd, J = 19.7, 17.6 Hz, 1H), 5.33 – 5.26 (m, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 4H), 6.94 – 6.77 (m, 1H), 6.44 (d, J = 11.6 Hz, 1H), 6.33 (t, J = 11.3 Hz, 1H), 5.44 (dd, J = 19.7, 17.6 Hz, 1H), 5.33 – 5.26 (m, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 135.8, 135.7, 133.2, 132.9, 132.8, 131.5, 131.4, 130.3, 130.2, 129.1, 128.8, 128.5, 127.6, 120.4, 118.3.

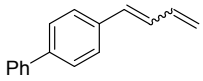


1-bromo-4-(buta-1,3-dien-1-yl)benzene (2g). Colorless oil in 60% yield, *E/Z* mixture was obtained. *E/Z* ratio = 37/63 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.27 (d, J = 8.3 Hz, 2H), 6.88 – 6.75 (m, 1H), 6.55 – 6.46 (m, 2H), 5.40 (t, J = 17.4 Hz, 1H), 5.26 (dd, J = 19.6, 10.0 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.20 (d, J = 8.3 Hz, 2H), 6.88 – 6.75 (m, 1H), 6.39 (d, J = 11.5 Hz, 1H), 6.30 (t, J = 11.2 Hz, 1H), 5.40 (t, J = 17.4 Hz, 1H), 5.26 (dd, J = 19.6, 10.0 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 136.3, 136.1, 132.8, 131.8, 131.6, 131.5, 131.49, 131.46 130.7, 130.4, 129.2, 128.0, 121.4, 121.1, 120.5, 118.5.

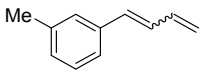


1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (2h). Colorless oil in 65% yield, *E/Z* mixture was obtained. *E/Z* ratio = 54/46 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 13.9, 8.2 Hz, 2H), 7.50 (d, J = 8.3 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 6.92 – 6.81 (m, 1H), 6.61 – 6.53 (m, 2H), 5.46 (dd, J = 16.8, 11.8 Hz, 1H), 5.32 (t, J = 11.2 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz,

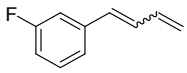
$CDCl_3$) δ 7.61 (dd, J = 13.9, 8.2 Hz, 2H), 7.50 (d, J = 8.3 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 6.92 – 6.81 (m, 1H), 6.48 (d, J = 12.3 Hz, 1H), 6.38 (t, J = 11.3 Hz, 1H), 5.46 (dd, J = 16.8, 11.8 Hz, 1H), 5.32 (t, J = 11.2 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.7, 136.8, 134.0, 133.8, 132.7, 132.6, 132.1, 131.3, 129.4 (q, J = 32.6 Hz, 1C), 129.3, 128.9, 128.7 (q, J = 7.0 Hz, 1C), 126.6, 125.7 (q, J = 7.5 Hz, 1C), 125.3 (q, J = 7.4, 3.6 Hz, 1C), 124.1 (q, J = 271.8 Hz, 1C), 121.3, 119.5.



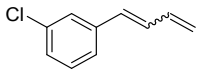
4-(buta-1,3-dien-1-yl)-1,1'-biphenyl (2i). Colorless oil in 82% yield, *E/Z* mixture was obtained. *E/Z* ratio = 40/60 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.52 – 7.43 (m, 4H), 7.40 – 7.37 (m, 1H), 6.87 (dd, J = 15.6, 10.5 Hz, 1H), 6.65 – 6.50 (m, 2H), 5.46 – 5.37 (m, 1H), 5.26 (dd, J = 26.6, 10.1 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.52 – 7.43 (m, 4H), 7.40 – 7.37 (m, 1H), 7.04 – 6.94 (m, 1H), 6.65 – 6.50 (m, 1H), 6.33 (t, J = 11.4 Hz, 1H), 5.46 – 5.37 (m, 1H), 5.26 (dd, J = 26.6, 10.1 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.80, 140.75, 140.4, 139.9, 137.3, 136.5, 136.3, 133.4, 132.5, 131.0, 130.1, 129.8, 129.6, 128.9, 127.5, 127.4, 127.1, 127.04, 127.03, 127.00, 120.0, 117.9.



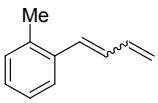
1-(buta-1,3-dien-1-yl)-3-methylbenzene (2j). Colorless oil in 60% yield, *E/Z* mixture was obtained. *E/Z* ratio = 42/58 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.25 (s, 1H), 7.18 – 7.14 (m, 1H), 7.08 – 6.87 (m, 1H), 6.66 – 6.59 (m, 2H), 5.50 – 5.42 (m, 1H), 5.30 (dd, J = 22.5, 9.9 Hz, 1H), 2.45 (s, 3H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.25 (s, 1H), 7.18 – 7.14 (m, 1H), 7.08 – 6.87 (m, 1H), 6.55 (d, J = 11.8 Hz, 1H), 6.36 (t, J = 11.3 Hz, 1H), 5.47 (dd, J = 25.5, 8.7 Hz, 1H), 5.30 (dd, J = 22.5, 9.9 Hz, 1H), 2.46 (s, 3H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.8, 137.4, 137.1, 133.4, 133.1, 130.7, 130.6, 129.8, 129.5, 128.59, 128.56, 128.2, 127.9, 127.3, 126.2, 123.7, 119.5, 117.5, 21.51, 21.49.



1-(buta-1,3-dien-1-yl)-3-fluorobenzene (2k). Colorless oil in 75% yield, *E/Z* mixture was obtained. *E/Z* ratio = 53/47 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 1H), 7.11 (t, J = 8.5 Hz, 1H), 7.04 (d, J = 10.0 Hz, 1H), 6.95 (dd, J = 18.0, 8.9 Hz, 1H), 6.89 – 6.76 (m, 1H), 6.56 – 6.47 (m, 2H), 5.41 (t, J = 16.1 Hz, 1H), 5.26 (dd, J = 19.7, 10.2 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.11 (t, J = 8.5 Hz, 1H), 6.95 (dd, J = 18.0, 8.9 Hz, 1H), 6.89 – 6.76 (m, 1H), 6.42 (d, J = 11.5 Hz, 1H), 6.30 (t, J = 11.2 Hz, 1H), 5.41 (t, J = 16.1 Hz, 1H), 5.26 (dd, J = 19.7, 10.2 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, J = 42.2 Hz, 1C), 161.8 (d, J = 42.6 Hz, 1C), 139.6 (d, J = 7.8 Hz, 1C), 136.8, 132.9, 131.9, 131.7 (d, J = 2.4 Hz, 1C), 131.0, 130.1 (d, J = 8.4 Hz, 1C), 129.8 (d, J = 8.5 Hz, 1C), 129.1, 124.9 (d, J = 2.6 Hz, 1C), 122.5 (d, J = 2.4 Hz, 1C), 120.7, 118.8, 115.8 (d, J = 21.5 Hz, 1C), 114.5 (d, J = 21.5 Hz, 1C), 114.0 (d, J = 21.2 Hz, 1C), 112.8 (d, J = 21.8 Hz, 1C).

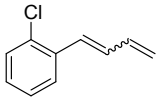


1-(buta-1,3-dien-1-yl)-3-chlorobenzene (2l). Colorless oil in 80% yield, *E/Z* mixture was obtained. *E/Z* ratio = 49/51 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.30 – 7.22 (m, 3H), 6.93 – 6.79 (m, 1H), 6.58 – 6.49 (m, 2H), 5.45 (dd, J = 25.6, 9.2 Hz, 1H), 5.30 (dd, J = 20.1, 10.3 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.30 – 7.22 (m, 3H), 6.93 – 6.79 (m, 1H), 6.42 (d, J = 11.6 Hz, 1H), 6.33 (t, J = 11.2 Hz, 1H), 5.45 (dd, J = 25.6, 9.2 Hz, 1H), 5.30 (dd, J = 20.1, 10.3 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 139.1, 136.8, 134.6, 134.2, 132.7, 132.0, 131.4, 131.0, 129.9, 129.5, 129.0, 128.9, 127.6, 127.2, 127.1, 126.3, 124.7, 120.8, 118.8.

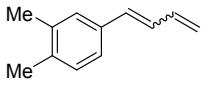


1-(buta-1,3-dien-1-yl)-2-methylbenzene (2m). Colorless oil in 55% yield, *E/Z* mixture was obtained. *E/Z* ratio = 27/73 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.62 (d, J = 6.7 Hz, 1H), 7.30 – 7.26 (m, 3H), 6.93 – 6.77 (m, 1H), 6.76 – 6.66 (m, 2H), 5.47 (d, J = 16.9 Hz, 1H), 5.28 (d, J =

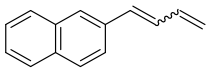
10.0 Hz, 1H), 2.48 (s, 3H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.37 (d, J = 2.2 Hz, 1H), 7.30 – 7.26 (m, 3H), 6.93 – 6.77 (m, 1H), 6.62 (d, J = 11.8 Hz, 1H), 6.43 (t, J = 11.2 Hz, 1H), 5.47 (d, J = 16.9 Hz, 1H), 5.28 (d, J = 10.0 Hz, 1H), 2.39 (s, 3H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.5, 136.1, 135.8, 133.6, 131.0, 130.9, 130.6, 130.5, 130.0, 129.9, 129.7, 127.7, 127.4, 126.2, 125.5, 125.3, 119.1, 117.6, 20.1, 19.9.



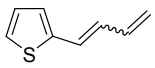
1-(buta-1,3-dien-1-yl)-2-chlorobenzene (2n). Colorless oil in 45% yield, *E/Z* mixture was obtained. *E/Z* ratio = 34/66 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.7, 1.3 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.02 (d, J = 15.6 Hz, 1H), 6.84 – 6.68 (m, 1H), 6.65 – 6.56 (m, 1H), 5.43 (dd, J = 16.8, 10.2 Hz, 1H), 5.28 (d, J = 10.1 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.25 (ddd, J = 9.1, 7.3, 3.9 Hz, 2H), 6.84 – 6.68 (m, 1H), 6.62 (d, J = 11.7 Hz, 1H), 6.41 (t, J = 11.3 Hz, 1H), 5.43 (dd, J = 16.8, 10.2 Hz, 1H), 5.28 (d, J = 10.1 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.5, 135.2, 133.7, 133.4, 132.9, 132.11, 132.07, 131.2, 129.9, 129.6, 128.7, 128.61, 128.57, 127.6, 126.9, 126.42, 126.36, 120.5, 118.9.



4-(buta-1,3-dien-1-yl)-1,2-dimethylbenzene (2o). Colorless oil in 75% yield, *E/Z* mixture was obtained. *E/Z* ratio = 42/58 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 2H), 7.10 (s, 1H), 7.00 – 6.75 (m, 1H), 6.58 – 6.48 (m, 2H), 5.41 – 5.31 (m, 1H), 5.20 (dd, J = 27.0, 9.7 Hz, 1H), 2.28 (s, 6H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.13 (d, J = 4.8 Hz, 2H), 7.00 – 6.75 (m, 1H), 6.44 (d, J = 11.5 Hz, 1H), 6.25 (t, J = 11.3 Hz, 1H), 5.41 – 5.31 (m, 1H), 5.20 (dd, J = 27.0, 9.7 Hz, 1H), 2.30 (s, 6H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.8, 136.5, 136.4, 135.7, 135.1, 134.9, 133.6, 133.1, 130.6, 130.4, 130.1, 130.0, 129.6, 128.7, 127.8, 126.6, 124.1, 119.2, 117.0, 19.9, 19.71, 19.65.

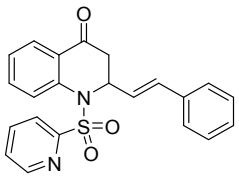


2-(buta-1,3-dien-1-yl)naphthalene (2p). Colorless oil in 70% yield, *E/Z* mixture was obtained. *E/Z* ratio = 24/76 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 4H), 7.51 – 7.48 (m, 3H), 7.07 – 6.92 (m, 1H), 6.78 – 6.56 (m, 2H), 5.45 (t, J = 17.6 Hz, 1H), 5.25 (d, J = 10.0 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 15.6, 11.5 Hz, 4H), 7.51 – 7.48 (m, 3H), 7.07 – 6.92 (m, 1H), 6.64 (d, J = 11.5 Hz, 1H), 6.39 (t, J = 11.3 Hz, 1H), 5.45 (t, J = 17.6 Hz, 1H), 5.31 (d, J = 10.1 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 135.0, 134.7, 133.7, 133.4, 133.1, 132.5, 131.3, 130.5, 130.1, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.3, 126.7, 126.4, 126.3, 126.1, 126.0, 123.6, 120.1, 118.0.

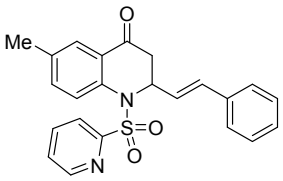


2-(buta-1,3-dien-1-yl)thiophene (2q). Colorless oil in 92% yield, *E/Z* mixture was obtained. *E/Z* ratio = 51/49 ^{1}H NMR of *E* isomer (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 1H), 7.06 – 7.00 (m, 2H), 6.75 – 6.61 (m, 2H), 6.50 – 6.43 (m, 1H), 5.35 (dd, J = 8.7, 6.6 Hz, 1H), 5.19 (d, J = 10.0 Hz, 1H); ^{1}H NMR of *Z* isomer (400 MHz, $CDCl_3$) δ 7.31 (d, J = 4.9 Hz, 1H), 7.20 – 7.14 (m, 1H), 7.06 – 7.00 (m, 2H), 6.53 (d, J = 11.2 Hz, 1H), 6.18 (t, J = 11.5 Hz, 1H), 5.45 (d, J = 16.6 Hz, 1H), 5.35 (dd, J = 8.7, 6.6 Hz, 1H); Spectroscopic data of ^{1}H NMR was identical to that of the reference 4. ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.3, 136.8, 133.3, 129.4, 128.5, 128.4, 127.7, 127.0, 126.2, 126.1, 125.8, 124.6, 122.6, 120.2, 117.6.

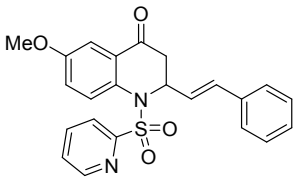
10. Characterization data of products 3aa–ka and 3ab–aq



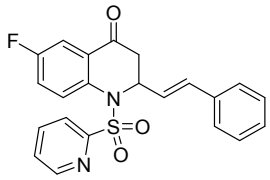
(*E*)-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3aa). Yellow oil, 164.0 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.64 (m, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 7.9, 1.6 Hz, 1H), 7.85 (td, J = 7.8, 1.7 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.47 – 7.44 (m, 1H), 7.24 – 7.19 (m, 5H), 7.17 – 7.13 (m, 1H), 6.51 (dd, J = 16.1, 1.7 Hz, 1H), 6.18 (dd, J = 16.1, 5.0 Hz, 1H), 5.79 – 5.75 (m, 1H), 3.49 (dd, J = 17.7, 6.0 Hz, 1H), 2.90 (dd, J = 17.7, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 156.8, 150.4, 140.1, 138.3, 135.9, 135.0, 133.5, 128.7, 128.3, 127.6, 127.4, 126.7, 126.3, 125.7, 125.4, 124.3, 123.5, 58.0, 41.9; HRMS (ESI-TOF) Calcd. for $C_{22}H_{19}N_2O_3S^+$ $[M+H]^+$: 391.1111; found: 391.1112.



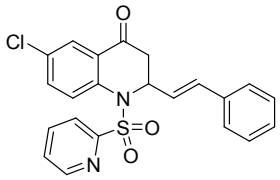
(*E*)-6-methyl-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3ba). Yellow oil, 163.8 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, J = 4.6, 0.6 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.85 (dd, J = 7.7, 1.7 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 1.7 Hz, 1H), 7.45 (ddd, J = 7.6, 4.7, 1.0 Hz, 1H), 7.29 (dd, J = 8.4, 2.0 Hz, 1H), 7.24 – 7.17 (m, 5H), 6.50 (dd, J = 16.1, 1.7 Hz, 1H), 6.18 (dd, J = 16.1, 4.9 Hz, 1H), 5.76 – 5.73 (m, 1H), 3.45 (dd, J = 17.8, 6.0 Hz, 1H), 2.87 (dd, J = 17.8, 1.7 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 156.7, 150.4, 138.3, 137.6, 135.93, 135.91, 135.4, 133.3, 128.6, 128.2, 127.6, 127.4, 126.7, 126.5, 125.6, 124.5, 123.5, 57.9, 41.7, 20.8; HRMS (ESI-TOF) Calcd. for $C_{23}H_{21}N_2O_3S^+$ $[M+H]^+$: 405.1267; found: 405.1279.



(*E*)-6-methoxy-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3ca). Yellow oil, 170.3 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.64 (m, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.85 – 7.81 (m, 2H), 7.45 (ddd, J = 7.6, 4.7, 1.1 Hz, 1H), 7.32 (d, J = 3.1 Hz, 1H), 7.25 – 7.20 (m, 5H), 7.06 (dd, J = 9.1, 3.2 Hz, 1H), 6.50 (dd, J = 16.1, 1.8 Hz, 1H), 6.18 (dd, J = 16.1, 4.8 Hz, 1H), 5.74 – 5.71 (m, 1H), 3.76 (s, 3H), 3.46 (dd, J = 17.9, 6.0 Hz, 1H), 2.86 (dd, J = 17.9, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 157.2, 156.7, 150.4, 138.3, 135.9, 133.4, 133.3, 128.7, 128.3, 127.4, 127.0, 126.7, 126.63, 126.61, 123.6, 122.7, 109.5, 57.9, 55.7, 41.5; HRMS (ESI-TOF) Calcd. for $C_{23}H_{21}N_2O_4S^+$ $[M+H]^+$: 421.1217; found: 421.1213.

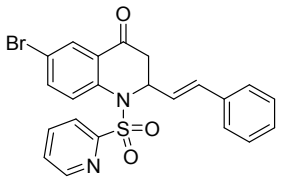


(*E*)-6-fluoro-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3da). Yellow oil, 175.6 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.6 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.87 (td, J = 7.7, 1.5 Hz, 1H), 7.55 (dd, J = 8.3, 3.1 Hz, 1H), 7.48 (ddd, J = 7.5, 4.7, 0.6 Hz, 1H), 7.25 – 7.18 (m, 6H), 6.48 (dd, J = 16.1, 1.6 Hz, 1H), 6.15 (dd, J = 16.1, 4.8 Hz, 1H), 5.75 – 5.73 (m, 1H), 3.47 (dd, J = 17.9, 6.0 Hz, 1H), 2.91 (dd, J = 17.9, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 160.0 (d, J = 247.8 Hz, 1C), 156.6, 150.5, 138.5, 136.2 (d, J = 2.5 Hz, 1C), 135.7, 133.7, 128.7, 128.4, 127.6, 127.4 (d, J = 6.4 Hz, 1C), 126.9 (d, J = 7.4 Hz, 1C), 126.7, 126.0, 123.5, 122.2 (d, J = 23.2 Hz, 1C), 113.5 (d, J = 23.5 Hz, 1C), 57.9, 41.4; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}FN_2O_3S^+$ $[M+H]^+$: 409.1017; found: 409.1007.

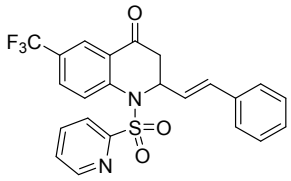


(*E*)-6-chloro-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3ea). Yellow oil, 170.0 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.6 Hz, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.89 (td, J = 8.0, 1.5 Hz, 1H), 7.85 (d, J = 2.6 Hz, 1H), 7.49 (dd, J = 7.5, 4.7 Hz, 1H), 7.43 (dd, J = 8.9, 2.5 Hz, 1H), 7.25 – 7.21 (m, 5H), 6.48 (dd, J = 16.1, 1.2 Hz, 1H), 6.15 (dd, J = 16.1, 4.9 Hz, 1H), 5.77 – 5.74 (m, 1H), 3.47 (dd, J = 17.7, 5.9 Hz, 1H), 2.92 (dd,

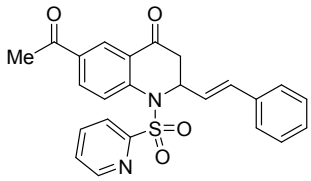
J = 17.7, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 156.5, 150.5, 138.6, 138.5, 135.6, 134.8, 133.8, 131.5, 128.7, 128.4, 127.6, 127.3, 126.69, 126.65, 125.9, 125.8, 123.5, 57.9, 41.5; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}ClN_2O_3S^+$ $[M+H]^+$: 425.0721; found: 425.0726.



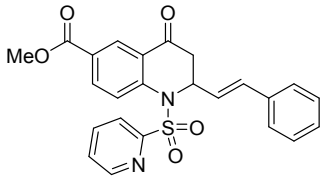
(*E*)-6-bromo-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3fa). Yellow oil, 194.8 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.1 Hz, 1H), 8.01 – 7.99 (m, 2H), 7.88 (dd, J = 13.3, 8.3 Hz, 2H), 7.57 (dd, J = 8.9, 2.4 Hz, 1H), 7.49 (dd, J = 7.4, 4.8 Hz, 1H), 7.25 – 7.21 (m, 5H), 6.48 (d, J = 16.1 Hz, 1H), 6.15 (dd, J = 16.1, 4.9 Hz, 1H), 5.77 – 5.74 (m, 1H), 3.47 (dd, J = 17.7, 5.9 Hz, 1H), 2.92 (d, J = 17.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 156.5, 150.5, 139.1, 138.5, 137.7, 135.6, 133.8, 130.3, 128.7, 128.4, 127.7, 126.8, 126.7, 126.1, 125.8, 123.5, 119.1, 57.9, 41.5; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}BrN_2O_3S^+$ $[M+H]^+$: 469.0216; found: 469.0220.



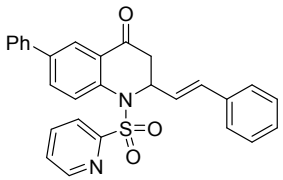
(*E*)-1-(pyridin-2-ylsulfonyl)-2-styryl-6-(trifluoromethyl)-2,3-dihydroquinolin-4(1*H*)-one (3ga). Yellow oil, 171.9 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, J = 4.6, 0.7 Hz, 1H), 8.20 (d, J = 1.9 Hz, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.92 (td, J = 7.8, 1.7 Hz, 1H), 7.71 (dd, J = 8.8, 2.2 Hz, 1H), 7.51 (ddd, J = 7.7, 4.7, 0.9 Hz, 1H), 7.25 – 7.20 (m, 5H), 6.48 (dd, J = 16.1, 1.6 Hz, 1H), 6.15 (dd, J = 16.1, 5.0 Hz, 1H), 5.81 – 5.79 (m, 1H), 3.49 (dd, J = 17.6, 5.9 Hz, 1H), 3.00 (dd, J = 17.5, 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 156.5, 150.6, 143.0, 138.6, 135.5, 134.0, 131.3 (q, J = 3.2 Hz, 1C), 128.7, 128.5, 127.8, 127.2 (d, J = 33.8 Hz, 1C), 126.7, 125.1 (d, J = 3.8 Hz, 1C), 125.0, 124.2, 123.51 (q, J = 272.2 Hz, 1C), 123.47, 58.1, 41.7; HRMS (ESI-TOF) Calcd. for $C_{23}H_{18}F_3N_2O_3S^+$ $[M+H]^+$: 459.0985; found: 459.0984.



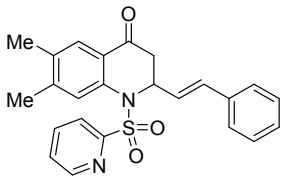
(*E*)-6-acetyl-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3ha). Yellow oil, 170.8 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.6, 0.7 Hz, 1H), 8.46 (d, J = 1.0 Hz, 1H), 8.07 (t, J = 4.0 Hz, 3H), 7.91 (td, J = 7.8, 1.7 Hz, 1H), 7.49 (ddd, J = 7.6, 4.7, 0.9 Hz, 1H), 7.24 – 7.19 (m, 5H), 6.48 (dd, J = 16.1, 1.6 Hz, 1H), 6.16 (dd, J = 16.1, 4.9 Hz, 1H), 5.83 – 5.81 (m, 1H), 3.52 (dd, J = 17.5, 5.8 Hz, 1H), 3.00 (dd, J = 17.5, 1.9 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 191.8, 156.4, 150.5, 144.1, 138.5, 135.6, 134.1, 133.8, 133.4, 128.7, 128.5, 128.4, 127.8, 126.7, 125.5, 124.6, 123.6, 123.5, 58.1, 41.8, 26.6; HRMS (ESI-TOF) Calcd. for $C_{24}H_{21}N_2O_4S^+$ $[M+H]^+$: 433.1217; found: 433.1223.



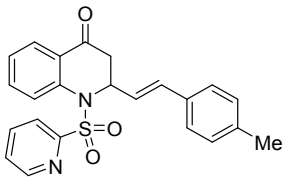
methyl (*E*)-4-oxo-1-(pyridin-2-ylsulfonyl)-2-styryl-1,2,3,4-tetrahydroquinoline-6-carboxylate (3ia). Yellow oil, 190.6 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.6, 0.7 Hz, 1H), 8.57 (d, J = 2.0 Hz, 1H), 8.12 (dd, J = 8.8, 2.1 Hz, 1H), 8.05 (d, J = 3.3 Hz, 1H), 8.03 (d, J = 4.2 Hz, 1H), 7.89 (td, J = 7.8, 1.7 Hz, 1H), 7.49 (ddd, J = 7.7, 4.7, 1.0 Hz, 1H), 7.23 – 7.18 (m, 5H), 6.48 (dd, J = 16.1, 1.5 Hz, 1H), 6.15 (dd, J = 16.1, 5.0 Hz, 1H), 5.82 – 5.80 (m, 1H), 3.87 (s, 3H), 3.51 (dd, J = 17.5, 5.8 Hz, 1H), 2.98 (dd, J = 17.5, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 165.8, 156.4, 150.5, 143.8, 138.5, 135.59, 135.56, 133.8, 129.4, 128.7, 128.4, 127.7, 126.8, 126.7, 125.6, 124.9, 123.6, 123.5, 58.1, 52.4, 41.8; HRMS (ESI-TOF) Calcd. for $C_{24}H_{21}N_2O_5S^+$ $[M+H]^+$: 449.1166; found: 449.1170.



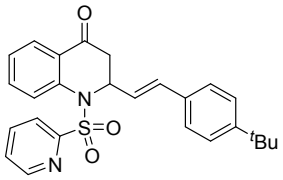
(*E*)-6-phenyl-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3ja). Yellow oil, 179.6 mg, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.4 Hz, 1H), 8.16 (d, J = 1.9 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.87 (t, J = 7.7 Hz, 1H), 7.74 (dd, J = 8.6, 2.0 Hz, 1H), 7.55 (d, J = 7.6 Hz, 2H), 7.47 (dd, J = 7.6, 4.7 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 4.1 Hz, 4H), 7.20 (dd, J = 9.1, 4.0 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 6.23 (dd, J = 16.1, 4.9 Hz, 1H), 5.82 – 5.79 (m, 1H), 3.50 (dd, J = 17.6, 5.9 Hz, 1H), 2.95 (d, J = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 156.7, 150.5, 139.2, 139.0, 138.4, 138.1, 135.8, 133.5, 133.4, 129.0, 128.7, 128.3, 127.9, 127.5, 126.9, 126.7, 126.3, 125.7, 124.7, 123.5, 58.0, 41.8; HRMS (ESI-TOF) Calcd. for $C_{28}H_{23}N_2O_3S^+$ $[M+H]^+$: 467.1424; found: 467.1413.



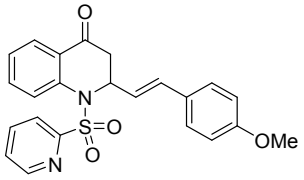
(*E*)-6,7-dimethyl-1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (3ka). Yellow oil, 180.0 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, J = 4.7, 0.7 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.84 (td, J = 7.7, 1.7 Hz, 1H), 7.65 (d, J = 19.3 Hz, 2H), 7.45 (ddd, J = 7.6, 4.7, 1.0 Hz, 1H), 7.24 – 7.23 (m, 4H), 7.22 – 7.18 (m, 1H), 6.51 (dd, J = 16.1, 1.7 Hz, 1H), 6.18 (dd, J = 16.1, 5.0 Hz, 1H), 5.72 – 5.69 (m, 1H), 3.37 (dd, J = 17.8, 6.0 Hz, 1H), 2.81 (dd, J = 17.8, 1.6 Hz, 1H), 2.27 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 156.9, 150.4, 145.2, 138.3, 137.8, 136.0, 134.5, 133.3, 128.6, 128.2, 128.0, 127.4, 126.7, 125.6, 123.9, 123.5, 58.0, 41.6, 20.8, 19.2; HRMS (ESI-TOF) Calcd. for $C_{24}H_{23}N_2O_3S^+$ $[M+H]^+$: 419.1424; found: 419.1429.



(*E*)-2-(4-methylstyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ab). Yellow oil, 147.6 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.5 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.91 (dd, J = 11.9, 8.2 Hz, 2H), 7.85 (t, J = 7.7 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.15 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 6.47 (d, J = 16.1 Hz, 1H), 6.12 (dd, J = 16.1, 5.0 Hz, 1H), 5.76 – 5.74 (t, J = 4.7 Hz, 1H), 3.47 (dd, J = 17.7, 5.9 Hz, 1H), 2.89 (d, J = 17.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 156.7, 150.5, 140.1, 138.3, 138.2, 135.0, 133.4, 133.1, 129.4, 127.6, 127.5, 126.6, 125.7, 125.4, 125.2, 124.4, 123.5, 58.1, 41.9, 21.3; HRMS (ESI-TOF) Calcd. for $C_{23}H_{21}N_2O_3S^+$ $[M+H]^+$: 405.1267; found: 405.1272.

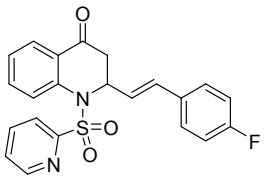


(*E*)-2-(4-(tert-butyl)styryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ac). Yellow oil, 160.8 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.6 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.50 – 7.45 (m, 2H), 7.28 – 7.26 (m, 2H), 7.17 – 7.12 (m, 3H), 6.48 (d, J = 15.7 Hz, 1H), 6.15 (dd, J = 16.1, 4.8 Hz, 1H), 5.77 – 5.75 (m, 1H), 3.47 (dd, J = 17.7, 6.0 Hz, 1H), 2.91 (dd, J = 17.7, 0.9 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 156.7, 151.5, 150.5, 140.1, 138.3, 135.0, 133.2, 133.1, 127.6, 127.4, 126.4, 125.8, 125.60, 125.57, 125.4, 124.4, 123.5, 57.9, 41.8, 34.7, 31.3; HRMS (ESI-TOF) Calcd. for $C_{26}H_{27}N_2O_3S^+$ $[M+H]^+$: 447.1737; found: 447.1746.

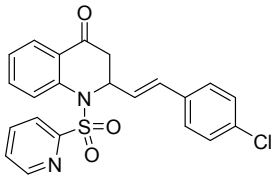


(*E*)-2-(4-methoxystyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ad). Yellow oil, 159.8 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.64 (m, 1H), 7.94 (dd, J =

18.4, 8.1 Hz, 2H), 7.91 – 7.82 (m, 2H), 7.51 – 7.44 (m, 2H), 7.17 – 7.13 (dt, *J* = 7.2, 1.9 Hz, 3H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.45 (dd, *J* = 16.1, 1.4 Hz, 1H), 6.04 (dd, *J* = 16.0, 5.1 Hz, 1H), 5.75 – 5.73 (m, 1H), 3.76 (s, 3H), 3.46 (dd, *J* = 17.7, 5.9 Hz, 1H), 2.88 (dd, *J* = 17.7, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 159.7, 156.8, 150.4, 140.1, 138.3, 135.0, 133.0, 128.6, 127.9, 127.6, 127.4, 125.7, 125.4, 124.4, 123.9, 123.5, 114.0, 58.1, 55.4, 41.9; HRMS (ESI-TOF) Calcd. for $C_{23}H_{21}N_2O_4S^+$ $[M+H]^+$: 421.1217; found: 421.1230.

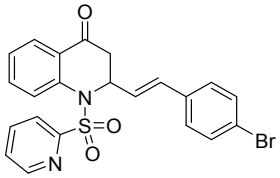


(*E*)-2-(4-fluorostyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ae). Yellow oil, 157.3 mg, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.6, 0.7 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.85 (td, *J* = 7.8, 1.7 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.20 – 7.14 (m, 3H), 6.93 (t, *J* = 8.7 Hz, 2H), 6.48 (dd, *J* = 16.1, 1.4 Hz, 1H), 6.10 (dd, *J* = 16.1, 5.0 Hz, 1H), 5.78 – 5.75 (m, 1H), 3.50 (dd, *J* = 17.7, 6.0 Hz, 1H), 2.88 (dd, *J* = 17.7, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 162.7 (d, *J* = 248.1 Hz, 1C), 156.6, 150.5, 140.1, 138.4, 135.1, 132.3, 132.0 (d, *J* = 3.3 Hz, 1C), 128.3, 128.2, 127.7, 127.5, 126.1 (d, *J* = 1.8 Hz, 1C), 125.6, 125.5, 124.2, 123.6, 115.6 (d, *J* = 21.6 Hz, 1C), 58.0, 41.8; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}FN_2O_3S^+$ $[M+H]^+$: 409.1017; found: 409.1022.

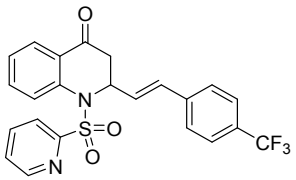


(*E*)-2-(4-chlorostyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3af). Yellow oil, 182.7 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.5 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.90 (dd, *J* = 13.5, 5.1 Hz, 2H), 7.85 (td, *J* = 7.8, 1.4 Hz, 1H), 7.48 (ddd, *J* = 11.4, 8.5, 3.1 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.18 – 7.13 (m, 3H), 6.47 (dd, *J* = 16.0, 1.1 Hz, 1H), 6.16 (dd, *J* = 16.1, 5.0 Hz, 1H), 5.78 – 5.76 (t, *J* = 5.4 Hz, 1H), 3.51 (dd, *J* = 17.7, 6.0 Hz, 1H), 2.88 (dd, *J* = 17.7, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 156.6, 150.5, 140.0, 138.4, 135.1, 134.4,

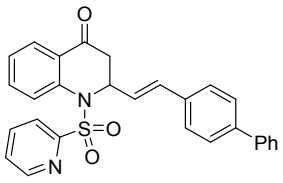
134.0, 132.3, 128.8, 127.9, 127.7, 127.5, 127.0, 125.6, 125.5, 124.2, 123.6, 58.0, 41.8; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}ClN_2O_3S^+$ $[M+H]^+$: 425.0721; found: 425.0721.



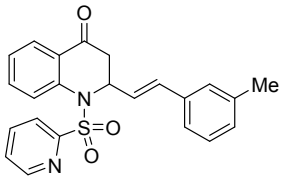
(*E*)-2-(4-bromostyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ag). Yellow oil, 176.0 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.64 (m, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.93 – 7.84 (m, 3H), 7.51 – 7.45 (m, 2H), 7.37 – 7.35 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.09 – 7.07 (m, 2H), 6.46 (d, J = 16.1 Hz, 1H), 6.21 – 6.15 (m, 1H), 5.77 (s, 1H), 3.51 (dd, J = 17.6, 5.9 Hz, 1H), 2.88 (d, J = 17.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 156.6, 150.5, 140.0, 138.4, 135.1, 134.8, 132.3, 131.8, 128.2, 127.7, 127.5, 127.2, 125.6, 125.5, 124.2, 123.6, 122.1, 57.9, 41.8; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}BrN_2O_3S^+$ $[M+H]^+$: 469.0216; found: 469.0219.



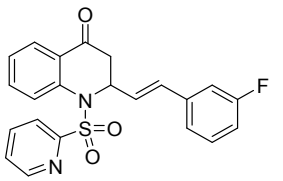
(*E*)-1-(pyridin-2-ylsulfonyl)-2-(4-(trifluoromethyl)styryl)-2,3-dihydroquinolin-4(1*H*)-one (3ah). Yellow oil, 160.5 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 4.0 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.90 (dd, J = 8.0, 1.6 Hz, 1H), 7.86 (td, J = 7.8, 1.7 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.31 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 7.3 Hz, 1H), 6.55 (dd, J = 16.1, 1.1 Hz, 1H), 6.29 (dd, J = 16.1, 4.8 Hz, 1H), 5.83 – 5.80 (m, 1H), 3.55 (dd, J = 17.7, 6.0 Hz, 1H), 2.91 (dd, J = 17.7, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 156.6, 150.5, 140.0, 139.3, 138.4, 135.2, 132.1, 130.0 (q, J = 32.5 Hz, 1C), 129.2, 127.7, 127.6, 126.9, 125.6 (q, J = 3.8 Hz, 1C), 125.5 (q, J = 4.5 Hz, 1C), 125.4, 124.14, 124.10 (q, J = 272.1 Hz, 1C), 123.6, 57.8, 41.7; HRMS (ESI-TOF) Calcd. for $C_{23}H_{18}F_3N_2O_3S^+$ $[M+H]^+$: 459.0985; found: 459.0987.



(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ai). Yellow oil, 196.0 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.1 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.86 (t, J = 7.8 Hz, 1H), 7.56 – 7.45 (m, 6H), 7.41 (t, J = 7.5 Hz, 2H), 7.35 – 7.26 (m, 3H), 7.16 (t, J = 7.6 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 6.24 (dd, J = 16.1, 4.9 Hz, 1H), 5.81 – 5.77 (m, 1H), 3.51 (dd, J = 17.7, 5.9 Hz, 1H), 2.93 (d, J = 17.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 156.7, 150.5, 141.1, 140.6, 140.1, 138.3, 135.1, 134.9, 133.0, 128.9, 127.64, 127.56, 127.5, 127.4, 127.12, 127.05, 126.4, 125.7, 125.5, 124.3, 123.5, 58.0, 41.8; HRMS (ESI-TOF) Calcd. for $C_{28}H_{23}N_2O_3S^+$ $[M+H]^+$: 467.1424; found: 467.1420.

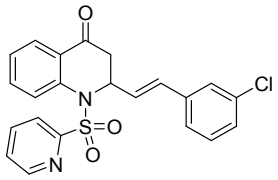


(*E*)-2-(3-methylstyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3aj). Yellow oil, 141.6 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.7, 0.7 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 7.8, 1.6 Hz, 1H), 7.85 (td, J = 7.8, 1.7 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.17 – 7.11 (m, 2H), 7.03 – 7.00 (m, 3H), 6.47 (dd, J = 16.1, 1.6 Hz, 1H), 6.17 (dd, J = 16.1, 4.9 Hz, 1H), 5.78 – 5.75 (m, 1H), 3.48 (dd, J = 17.7, 6.0 Hz, 1H), 2.90 (dd, J = 17.7, 1.7 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 156.7, 150.5, 140.1, 138.3, 135.8, 135.0, 133.6, 129.1, 128.6, 127.6, 127.5, 127.4, 126.1, 125.7, 125.4, 124.3, 123.8, 123.5, 58.0, 41.8, 21.4; HRMS (ESI-TOF) Calcd. for $C_{23}H_{21}N_2O_3S^+$ $[M+H]^+$: 405.1267; found: 405.1270.

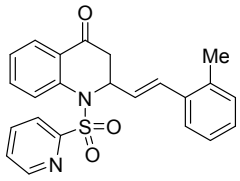


(*E*)-2-(3-fluorostyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ak). Yellow oil, 165.4 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.64 (m, 1H), 7.98 (d, J = 7.9 Hz,

1H), 7.93 – 7.84 (m, 3H), 7.52 – 7.45 (m, 2H), 7.23 – 7.14 (m, 2H), 6.98 (d, J = 7.7 Hz, 1H), 6.89 (t, J = 9.4 Hz, 2H), 6.48 (d, J = 16.1 Hz, 1H), 6.20 (dd, J = 16.0, 4.8 Hz, 1H), 5.79 – 5.78 (m, 1H), 3.52 (dd, J = 17.7, 5.9 Hz, 1H), 2.89 (d, J = 17.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 163.0 (d, J = 245.8 Hz, 1C), 156.6, 150.5, 140.0, 138.4, 138.2 (d, J = 7.8 Hz, 1C), 135.1, 132.4 (d, J = 2.1 Hz, 1C), 130.1 (d, J = 8.5 Hz, 1C), 127.8, 127.7, 127.5, 125.6, 125.5, 124.2, 123.6, 122.6 (d, J = 2.5 Hz, 1C), 115.1 (d, J = 21.4 Hz, 1C), 113.1 (d, J = 21.9 Hz, 1C), 57.8, 41.8; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}FN_2O_3S^+$ $[M+H]^+$: 409.1017; found: 409.1022.

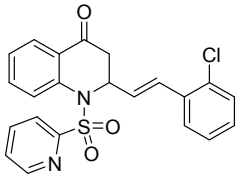


(*E*)-2-(3-chlorostyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3al). Yellow oil, 178.5 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.7, 0.7 Hz, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.86 (td, J = 7.8, 1.7 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.19 – 7.14 (m, 4H), 7.09 – 7.07 (m, 1H), 6.46 (dd, J = 16.1, 1.7 Hz, 1H), 6.20 (dd, J = 16.1, 4.9 Hz, 1H), 5.79 – 5.77 (m, 1H), 3.51 (dd, J = 17.7, 6.0 Hz, 1H), 2.89 (dd, J = 17.7, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 156.6, 150.5, 140.0, 138.4, 137.7, 135.2, 134.6, 132.1, 129.9, 128.2, 128.0, 127.7, 127.5, 126.5, 125.6, 125.5, 125.0, 124.2, 123.6, 57.9, 41.8; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}ClN_2O_3S^+$ $[M+H]^+$: 425.0721; found: 425.0726.

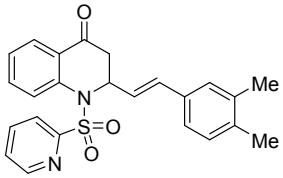


(*E*)-2-(2-methylstyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3am). Yellow oil, 163.8 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.0 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 7.9, 1.4 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.52 – 7.45 (m, 2H), 7.22 – 7.20 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.07 (m, 3H), 6.70 (dd, J = 15.9, 1.4 Hz, 1H), 6.01 (dd, J = 15.9, 4.5 Hz, 1H), 5.79 – 5.77 (m, 1H), 3.49 (dd, J = 17.7, 5.9 Hz, 1H), 2.91 (dd, J = 17.6, 1.6 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 156.7, 150.5, 140.2, 138.4,

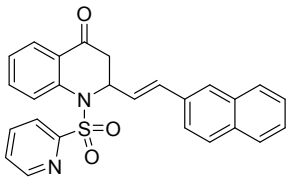
135.8, 135.2, 135.0, 131.6, 130.3, 128.1, 127.7, 127.54, 127.47, 126.2, 125.9, 125.7, 125.4, 124.4, 123.5, 58.1, 42.0, 19.6; HRMS (ESI-TOF) Calcd. for $C_{23}H_{21}N_2O_3S^+$ $[M+H]^+$: 405.1267; found: 405.1286.



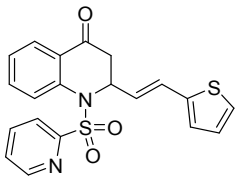
(*E*)-2-(2-chlorostyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3an). Yellow oil, 138.1 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.6 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.86 (t, J = 7.8 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.30 – 7.25 (m, 1H), 7.19 – 7.11 (m, 4H), 6.88 (d, J = 16.1 Hz, 1H), 6.12 (dd, J = 16.0, 3.5 Hz, 1H), 5.81 – 5.80 (m, 1H), 3.51 (dd, J = 17.7, 4.8 Hz, 1H), 2.92 (d, J = 17.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 156.7, 150.5, 140.1, 138.4, 135.1, 134.2, 133.4, 130.0, 129.7, 129.2, 129.0, 127.6, 127.5, 127.0, 126.9, 125.8, 125.5, 124.4, 123.5, 58.0, 42.1; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}ClN_2O_3S^+$ $[M+H]^+$: 425.0721; found: 425.0733.



(*E*)-2-(3,4-dimethylstyryl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ao). Yellow oil, 180.0 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.0 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 7.8, 1.5 Hz, 1H), 7.85 (td, J = 7.8, 1.6 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.14 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.2 Hz, 2H), 6.95 (d, J = 7.8 Hz, 1H), 6.44 (dd, J = 16.1, 1.3 Hz, 1H), 6.12 (dd, J = 16.1, 5.0 Hz, 1H), 5.76 – 5.73 (m, 1H), 3.46 (dd, J = 17.7, 5.9 Hz, 1H), 2.89 (dd, J = 17.7, 1.6 Hz, 1H), 2.19 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 156.7, 150.4, 140.1, 138.3, 137.0, 136.8, 135.0, 133.5, 129.9, 127.9, 127.6, 127.4, 125.8, 125.4, 125.0, 124.4, 124.1, 123.5, 58.0, 41.8, 19.8, 19.6; HRMS (ESI-TOF) Calcd. for $C_{24}H_{23}N_2O_3S^+$ $[M+H]^+$: 419.1424; found: 419.1431.

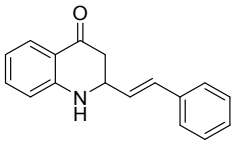


(*E*)-2-(2-(naphthalen-2-yl)vinyl)-1-(pyridin-2-ylsulfonyl)-2,3-dihydroquinolin-4(1*H*)-one (3ap). Yellow oil, 193.8 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.0 Hz, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.92 (dd, J = 7.8, 1.5 Hz, 1H), 7.86 (td, J = 7.8, 1.6 Hz, 1H), 7.74 (dd, J = 6.3, 2.9 Hz, 2H), 7.70 (d, J = 8.6 Hz, 1H), 7.60 (s, 1H), 7.53 – 7.45 (m, 3H), 7.44 – 7.40 (m, 3H), 7.16 (t, J = 7.2 Hz, 1H), 6.68 (dd, J = 16.1, 1.2 Hz, 1H), 6.31 (dd, J = 16.1, 5.0 Hz, 1H), 5.85 – 5.82 (m, 1H), 3.53 (dd, J = 17.7, 6.0 Hz, 1H), 2.95 (dd, J = 17.7, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 156.7, 150.5, 140.1, 138.3, 135.1, 133.6, 133.5, 133.3, 133.2, 128.3, 128.1, 127.74, 127.66, 127.5, 127.1, 126.6, 126.5, 126.3, 125.7, 125.5, 124.3, 123.6, 123.4, 58.1, 41.9; HRMS (ESI-TOF) Calcd. for $C_{26}H_{21}N_2O_3S^+$ $[M+H]^+$: 441.1267; found: 441.1274.

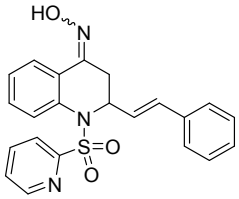


(*E*)-1-(pyridin-2-ylsulfonyl)-2-(2-(thiophen-2-yl)vinyl)-2,3-dihydroquinolin-4(1*H*)-one (3aq). Yellow oil, 158.6 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.6 Hz, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.86 (t, J = 7.8 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 4.9 Hz, 1H), 6.90 – 6.88 (m, 1H), 6.86 (d, J = 3.3 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 6.02 (dd, J = 15.9, 4.9 Hz, 1H), 5.76 – 5.74 (m, 1H), 3.48 (dd, J = 17.7, 6.0 Hz, 1H), 2.87 (d, J = 17.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 156.6, 150.5, 140.9, 140.0, 138.4, 135.1, 127.7, 127.5, 126.9, 126.6, 125.7, 125.6, 125.5, 125.1, 124.2, 123.5, 57.8, 41.7; HRMS (ESI-TOF) Calcd. for $C_{20}H_{17}N_2O_3S_2^+$ $[M+H]^+$: 397.0675; found: 397.0679.

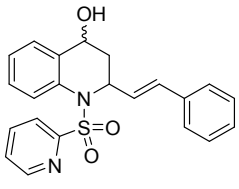
11. Characterization data of compounds 4-6, 11 and 14



(*E*)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one (4). White solid, 21.9 mg, 88% yield, mp 132.8 – 134.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.4 Hz, 3H), 7.29 (d, J = 7.0 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 6.67 (d, J = 15.8 Hz, 1H), 6.30 (dd, J = 15.8, 7.6 Hz, 1H), 4.42 (s, 1H), 4.36 (ddd, J = 11.9, 7.5, 4.7 Hz, 1H), 2.80 (dd, J = 16.2, 4.4 Hz, 1H), 2.72 (dd, J = 16.2, 11.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 151.2, 136.1, 135.5, 132.7, 128.8, 128.6, 128.4, 127.7, 126.7, 119.3, 118.5, 116.1, 56.4, 44.4.

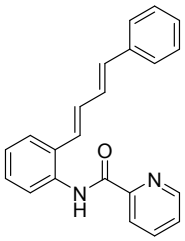


1-(pyridin-2-ylsulfonyl)-2-styryl-2,3-dihydroquinolin-4(1*H*)-one oxime (5). White solid, 35.3 mg, 87% yield, mp 155.7 – 157.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.2 Hz, 1H), 8.46 (s, 1H), 7.85 – 7.75 (m, 4H), 7.41 (ddd, J = 7.3, 4.7, 1.0 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.24 – 7.18 (m, 5H), 7.12 – 7.08 (m, 1H), 6.48 (dd, J = 16.0, 1.3 Hz, 1H), 6.04 (dd, J = 16.0, 5.2 Hz, 1H), 5.58 – 5.55 (t, J = 5.9 Hz, 1H), 3.35 (dd, J = 18.4, 1.0 Hz, 1H), 3.09 (dd, J = 18.5, 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 150.3, 150.2, 138.1, 136.2, 135.3, 132.9, 130.5, 128.6, 128.0, 127.21, 127.17, 126.6, 126.1, 126.0, 125.1, 124.0, 123.3, 55.3, 28.1.

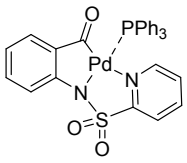


(*E*)-1-(pyridin-2-ylsulfonyl)-2-styryl-1,2,3,4-tetrahydroquinolin-4-ol (6). Yellow oil, 35.3 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 4.3 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.83 (dd, J = 7.0, 5.5 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.29 (t, J = 7.5 Hz, 2H), 7.24 – 7.15 (m, 4H), 7.02 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 15.8 Hz, 1H), 6.29 (dd, J = 15.8, 6.4 Hz, 1H), 5.50 (dd, J = 15.6, 6.7

Hz, 1H), 4.72 (s, 1H), 2.65 – 2.58 (m, 1H), 2.04 – 1.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 149.5, 138.7, 136.6, 135.1, 133.1, 131.0, 129.9, 129.2, 128.6, 128.4, 127.8, 127.3, 126.7, 125.4, 124.4, 123.7, 66.4, 56.6, 39.0.



***N*-(2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)phenyl)picolinamide (11).** Yellow oi1, 76.7 mg, 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.67 (d, J = 4.0 Hz, 1H), 8.34 (d, J = 7.9 Hz, 1H), 8.22 (d, J = 8.1 Hz, 1H), 7.93 (t, J = 7.7 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.35 (t, J = 6.9 Hz, 3H), 7.26 (t, J = 6.8 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.93 (dd, J = 24.2, 12.1 Hz, 2H), 6.72 (d, J = 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 150.0, 148.3, 137.8, 137.2, 134.5, 133.8, 132.8, 129.6, 129.4, 129.2, 128.8, 128.4, 127.9, 127.0, 126.7, 126.6, 125.2, 122.9, 122.6, 119.8.



Compound 14. Yellow so1id, 61.6 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.9 Hz, 1H), 7.92 (td, J = 7.9, 1.4 Hz, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.78 – 7.73 (m, 6H), 7.52 – 7.48 (m, 3H), 7.43 (td, J = 7.4, 1.7 Hz, 6H), 7.38 – 7.34 (m, 1H), 7.30 – 7.28 (m, 1H), 6.99 (dd, J = 9.2, 3.6 Hz, 1H), 6.72 (t, J = 7.4 Hz, 1H), 6.58 (d, J = 5.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1, 162.5, 151.2, 149.1, 140.4, 140.11, 140.07, 134.8, 134.7, 131.3, 131.12, 131.11, 130.8, 129.0, 128.9, 126.4, 125.9, 122.5, 120.4, 118.28, 118.25.

12. References

1. Jiang, L.-B.; Qi, X.; Wu, X.-F. Benzene-1,3,5-triyl triformate (TFBen): a convenient, efficient, and non-reacting CO source in carbonylation reactions. *Tetrahedron Lett.* **2016**, *57*, 3368-3370.

2. Hernando, E.; Castillo, R. R.; Rodriguez, N.; Arrayas, R. G.; Carretero, J. C. Copper-catalyzed mild nitration of protected anilines. *Chem. Eur. J.* **2014**, *20*, 13854-13859.

3. Chen, X.; Baratay, C. A.; Mark, M. E.; Xu, X.; Chan, P. W. H. Gold and brønsted acid catalyzed spirocyclization of 2- and 3-indolyl-tethered 1,4-enyne acetates to spiro[4,*n*]alkyl[*b*]indoles. *Org. Lett.* **2020**, *22*, 2849–2853.

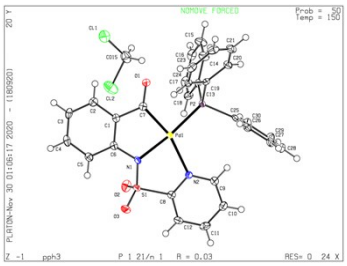
4. (a) Yasukawa, N.; Yokoyama, H.; Masuda, M.; Monguchi, Y.; Sajiki, H.; Sawama, Y. Highly-functionalized arene synthesis based on palladium on carbon-catalyzed aqueous dehydrogenation of cyclohexadienes and cyclohexenes. *Green Chem.* **2018**, *20*, 1213-1217; (b) Tortajada, A.; Ninokata, R.; Martin, R. Ni-catalyzed site-selective dicarboxylation of 1,3-dienes with CO_2. *J. Am. Chem. Soc.* **2018**, *140*, 2050-2053.

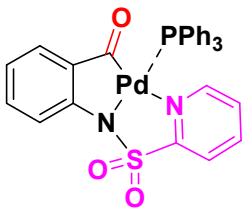
5. Garcia-Rubia, A.; Urones, B.; Arrayas, R. G.; Carretero, J. C. Pd^{II}-catalyzed C-H olefination of *N*-(2-Pyridyl)sulfonyl anilines and arylalkylamines. *Angew. Chem. Int. Ed.* **2011**, *50*, 10927-10931.

6. Peng, X. G.; Meng, B.; Tong, K.; Hirao, H.; Chiba, S.; Inorganic-base-mediated hydroamination of alkenyl oximes for the synthesis of cyclic nitrones. *Angew. Chem. Int. Ed.* **2014**, 5*3*, 1959-1962.

7. Liang, J. Q.; Huang, G. Z;. Peng, P.; Zhang, T. Y.; Wu, J. J.; Wu, F. H. Palladium-catalyzed benzodifluoroalkylation of alkynes: a route to fluorine-containing 1,1-diarylethylenes. *Adv. Synth. Catal*. **2018**, *360*, 2221-2227.

13. X-ray crystal data for compound 14 (CCDC: 2058728)

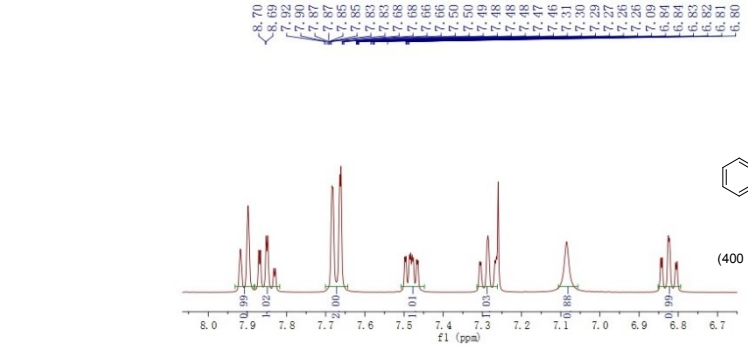


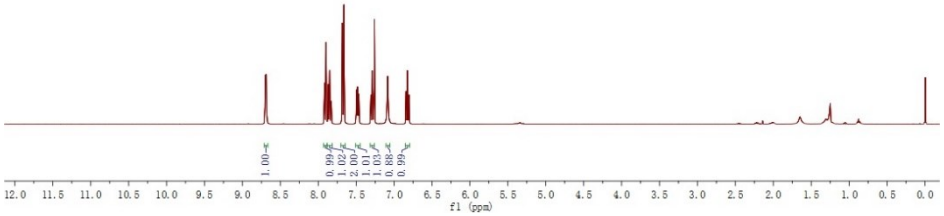


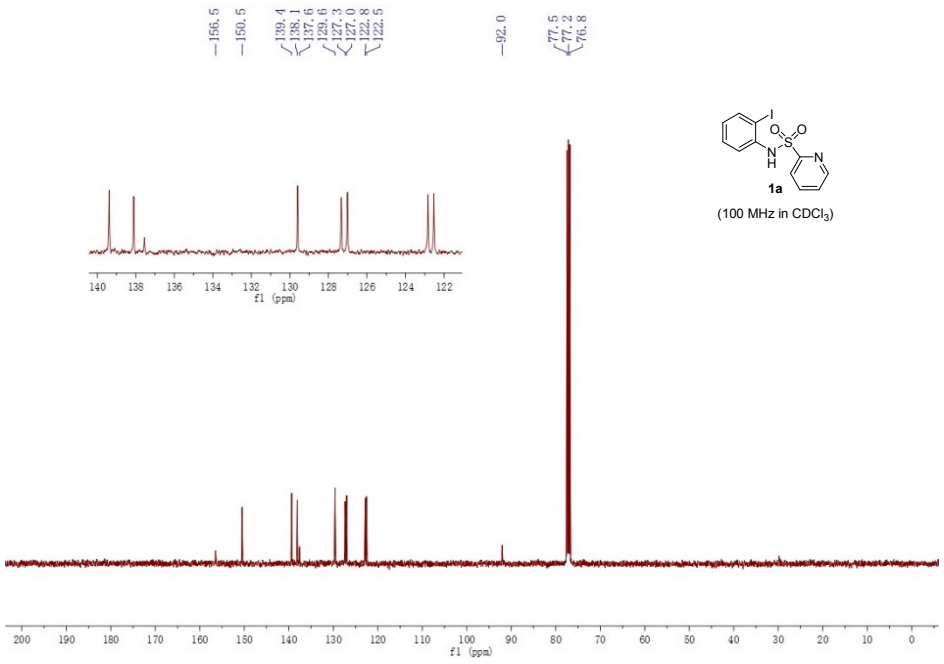
·CH_2Cl_2

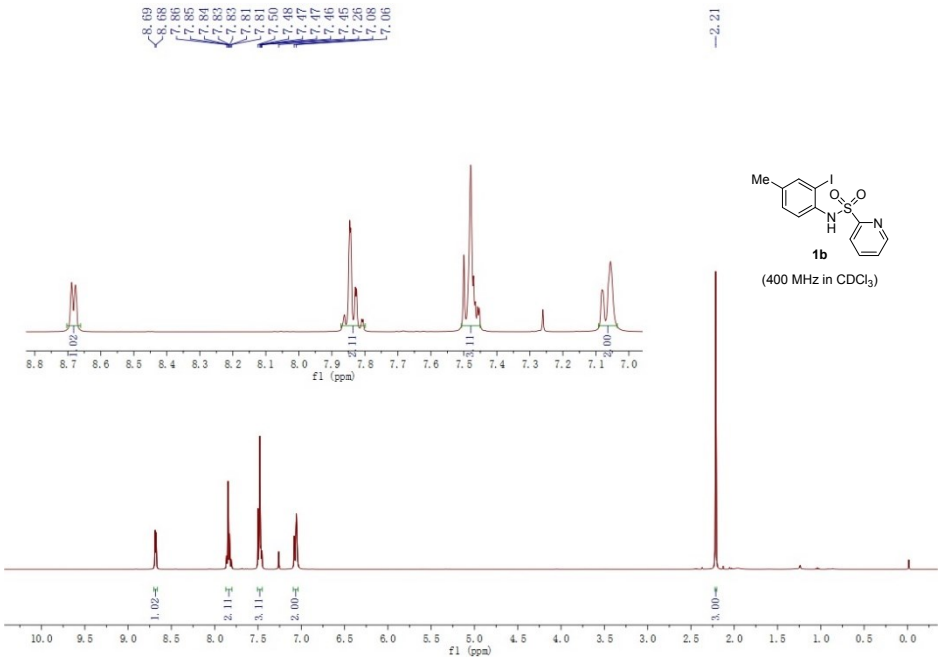
Compound	**14**
Empirical formula	$C_{31}H_{25}Cl_2N_2O_3PPdS$
Formula weight	713.86
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.5079(6)
b/Å	16.5743(11)
c/Å	16.2395(11)
α/°	90
β/°	93.771(5)
γ/°	90
Volume/Å^3	2822.2(3)
Z	4
ρ_{calc}g/cm^3	1.680
μ/mm^{-1}	1.016
F(000)	1440.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection /°	4.486 to 49.994
Index ranges	$-12 \le h \le 10$, $-19 \le k \le 15$, $-16 \le l \le 19$
Reflections collected	13057
Independent reflections	4981 [R_{int} = 0.0287, R_{sigma} = 0.0374]
Data/restraints/parameters	4981/1/370
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0272, wR_2 = 0.0603
Final R indexes [all data]	R_1 = 0.0316, wR_2 = 0.0625
Largest diff. peak/hole / e Å^{-3}	0.36/-0.50

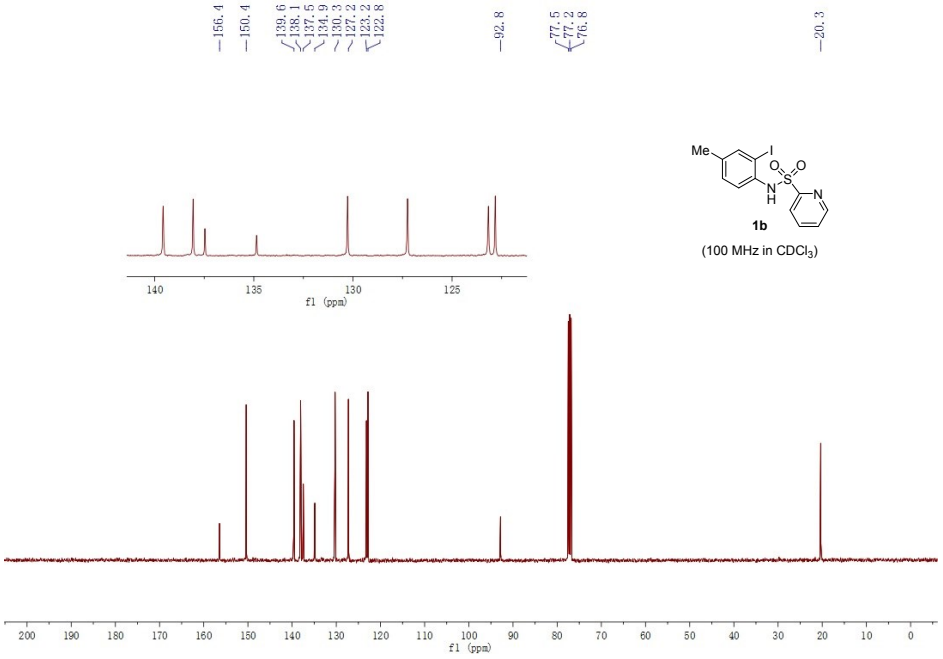
14. ^{1}H, ^{13}C spectra of 1a–k, 2a–q, 3aa–ka, 3ab–aq, 4–6, 11and 14

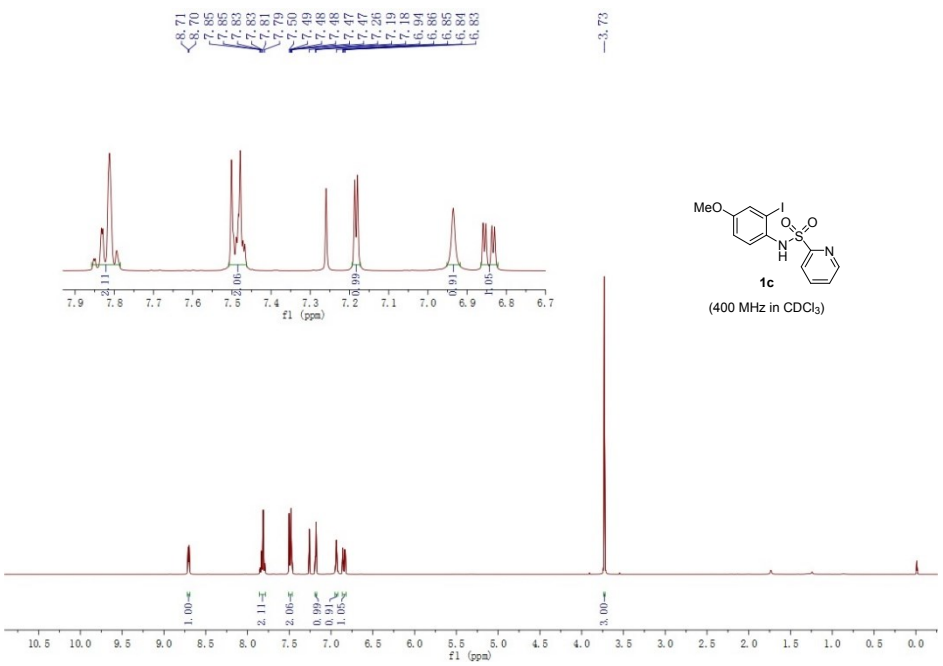


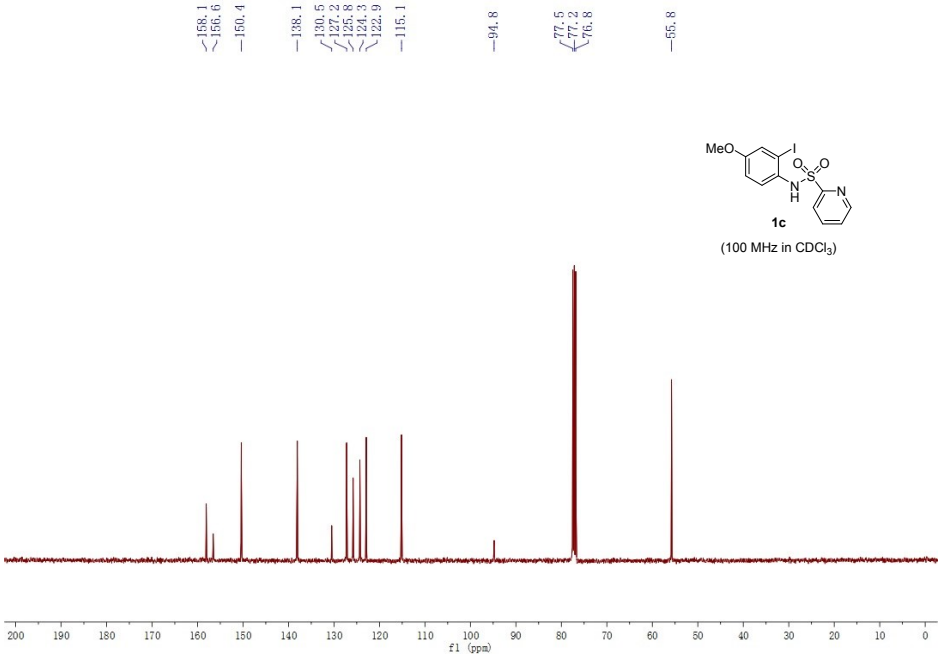


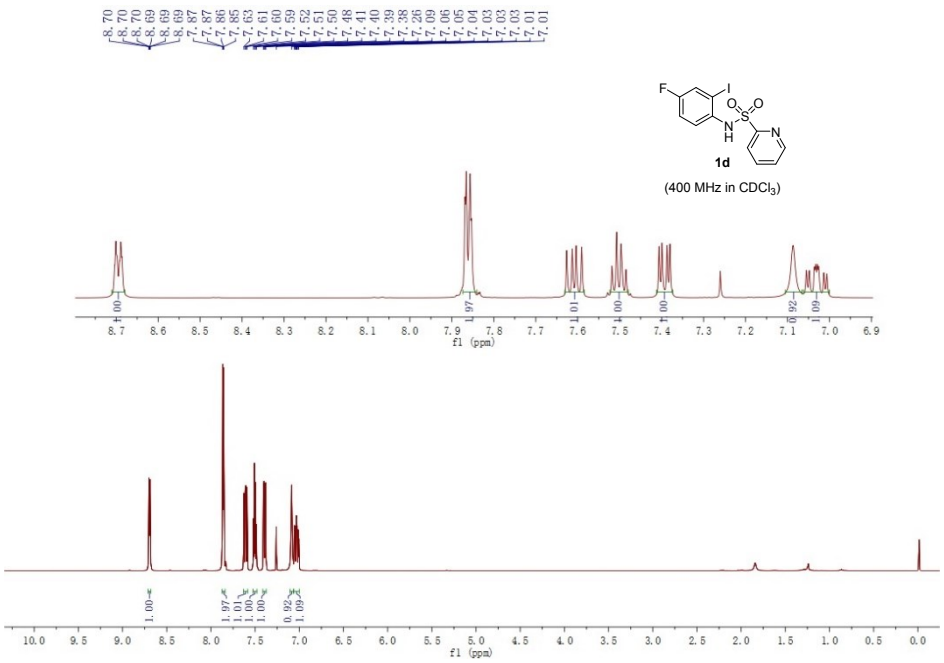


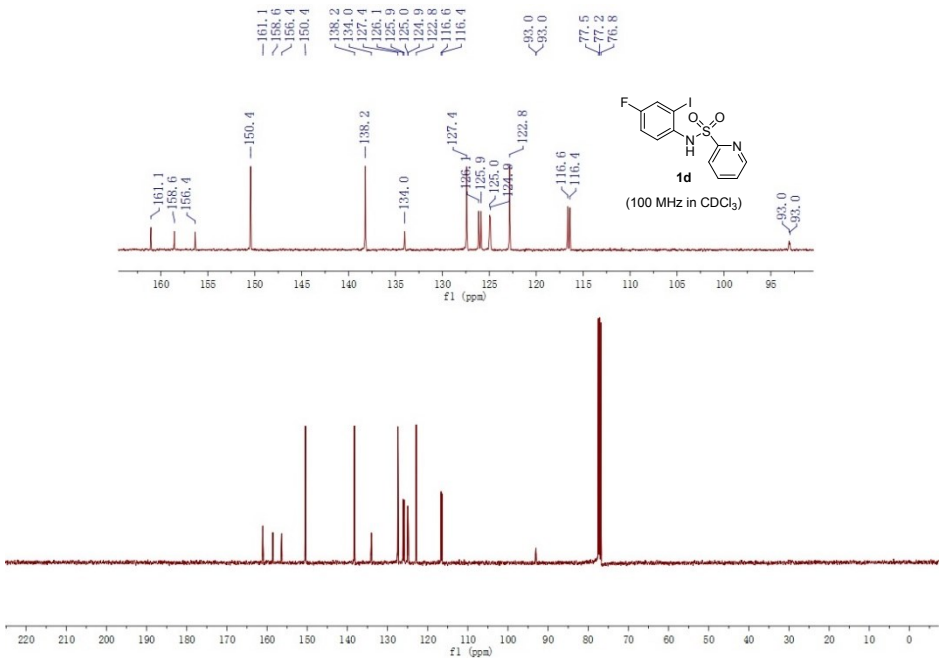

8.69
8.68
7.86
7.85
7.84
7.83
7.83
7.81
7.81
7.50
7.48
7.47
7.47
7.46
7.45
7.26
7.08
7.06
2.21
Me
I
O
S
O
N
H
N
1b
(400 MHz in CDCl3)
1.02
2.11
3.11
2.00
3.00
f1 (ppm)

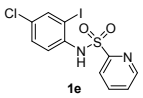

156.4
150.4
139.6
138.1
137.5
134.9
130.3
127.2
123.2
122.8
92.8
77.5
77.2
76.8
20.3
Me
I
O
S
O
N
H
N
1b
(100 MHz in CDCl3)
f1 (ppm)


8.71
8.70
7.85
7.85
7.83
7.83
7.81
7.79
7.50
7.49
7.48
7.48
7.47
7.47
7.26
7.19
7.18
6.94
6.86
6.85
6.84
6.83
3.73
2.11
2.06
0.99
0.91
1.05
f1 (ppm)
MeO
I
O
S
N
H
N
1c
(400 MHz in CDCl3)
1.00
2.11
2.06
0.99
0.91
1.05
3.00
f1 (ppm)


158.1
156.6
150.4
138.1
130.5
127.2
125.8
124.3
122.9
115.1
94.8
77.5
77.2
76.8
55.8
MeO
I
O
S
N
H
N
1c
(100 MHz in CDCl3)
f1 (ppm)

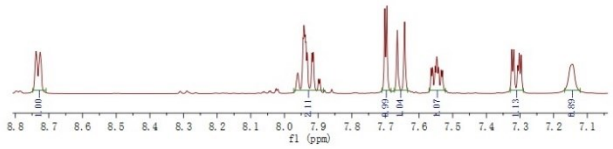

1d
(400 MHz in CDCl3)
f1 (ppm)

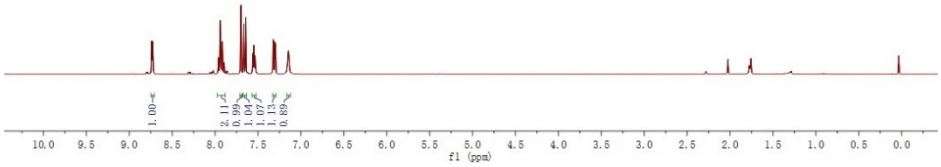

1d
(100 MHz in CDCl3)
f1 (ppm)

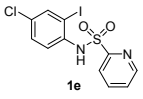


1e

(400 MHz in $CDCl_3$)

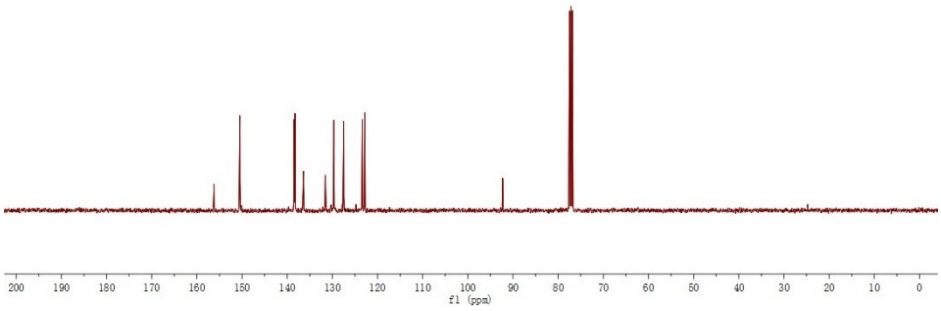


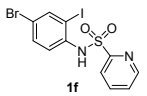




1e

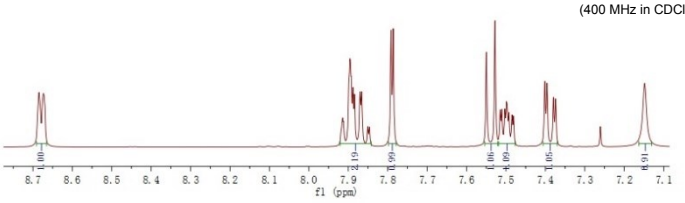
(100 MHz in $CDCl_3$)

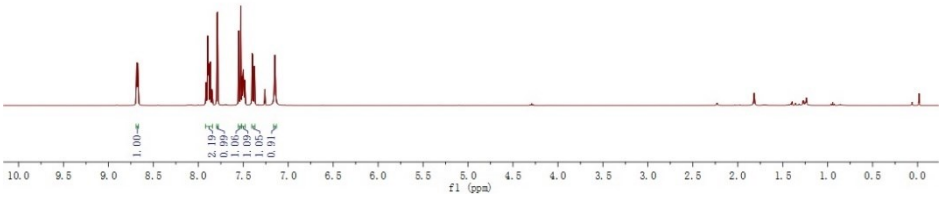


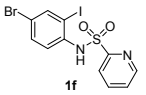


1f

(400 MHz in $CDCl_3$)

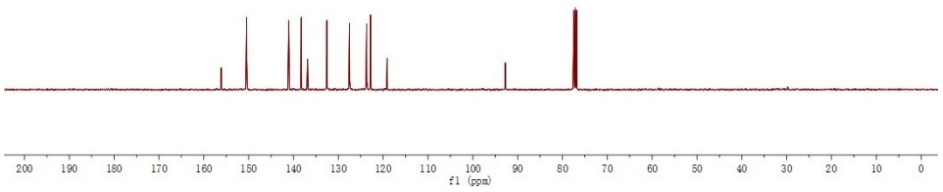


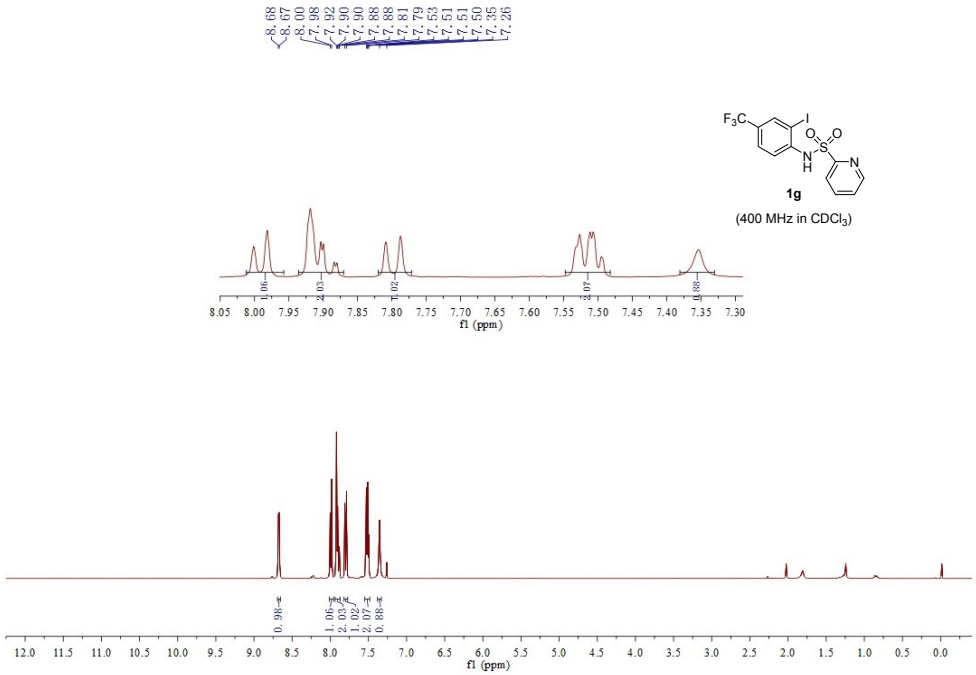


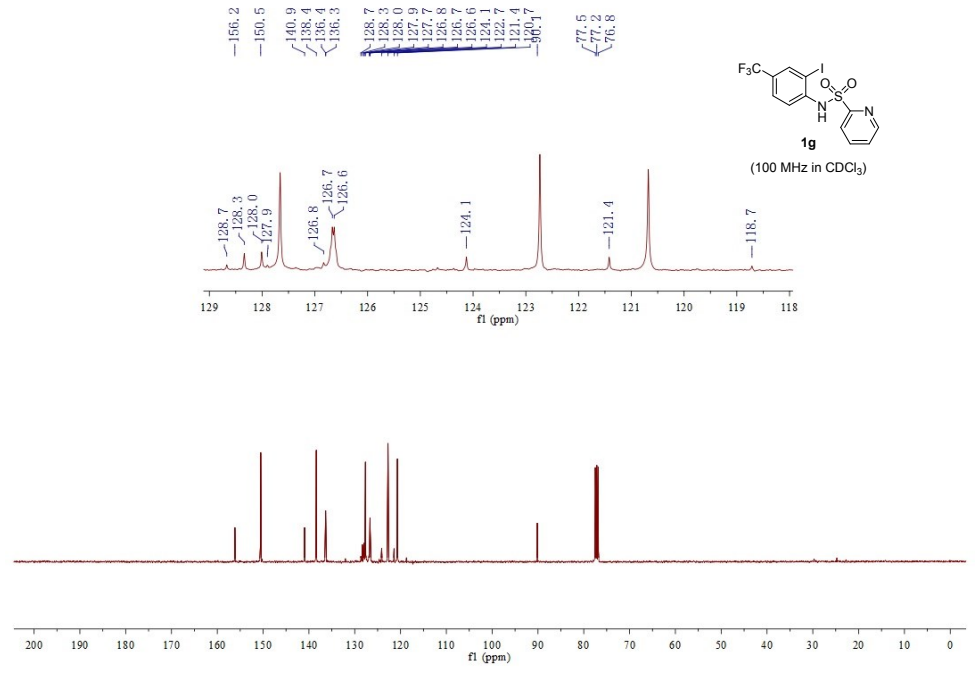


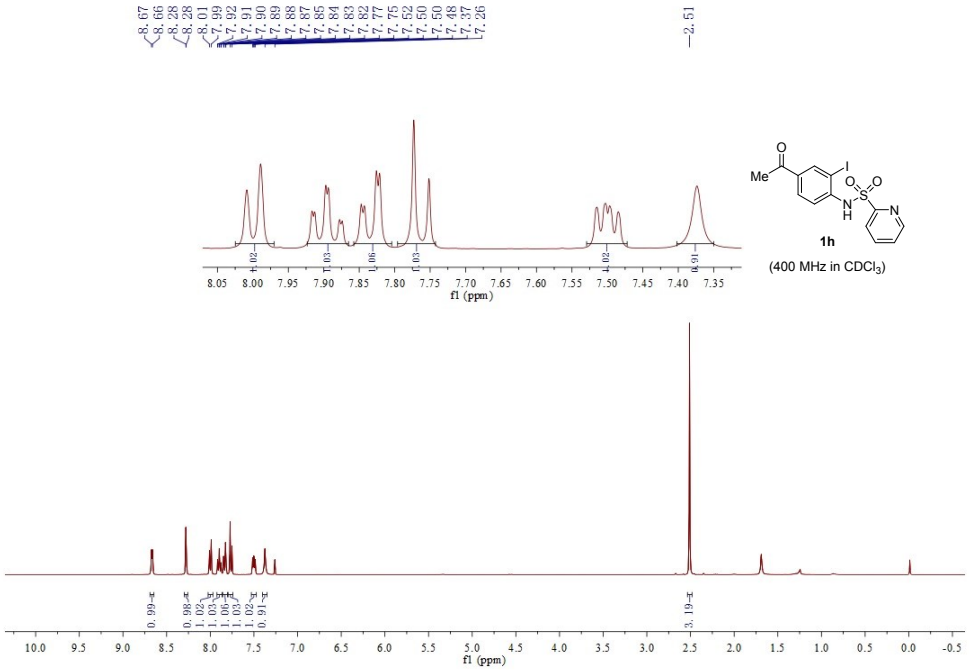
1f

(100 MHz in $CDCl_3$)

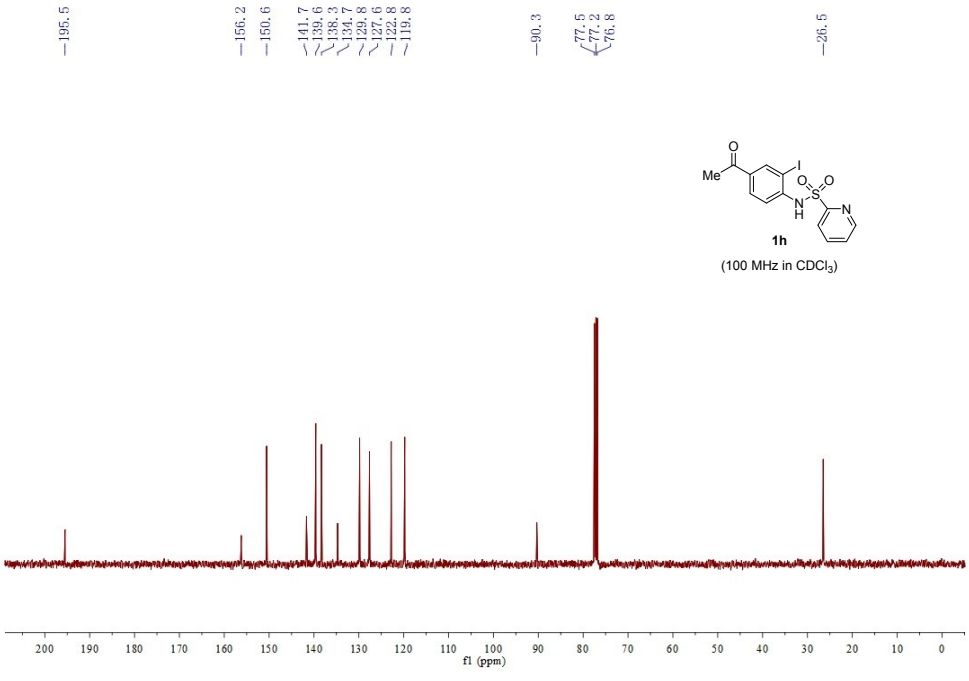


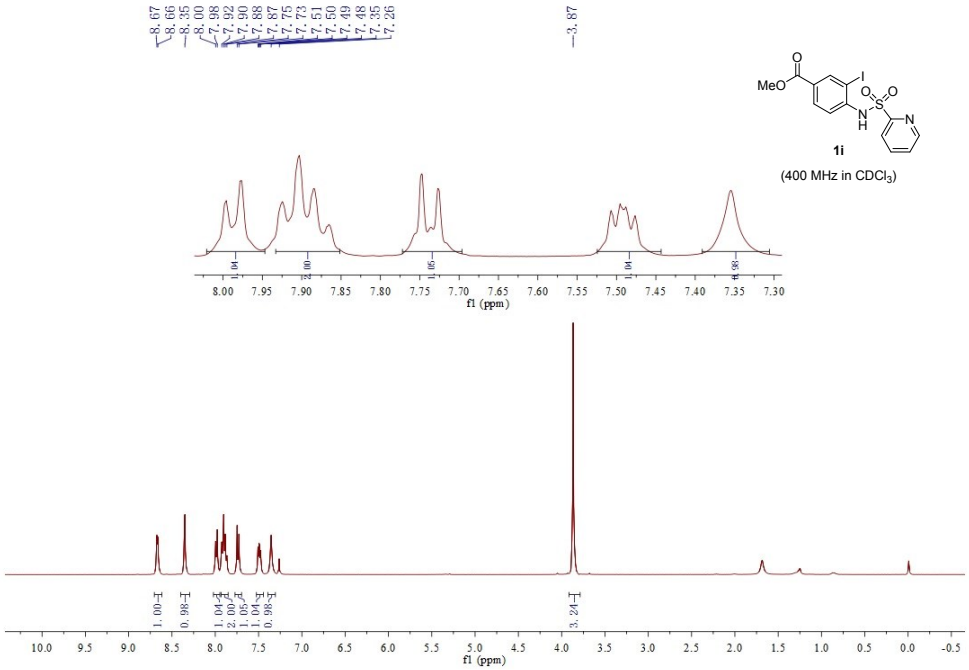

8.68
8.67
8.00
7.98
7.92
7.90
7.90
7.88
7.88
7.81
7.79
7.53
7.51
7.51
7.50
7.35
7.26
F3C
I
O
O
S
N
H
N
1g
(400 MHz in CDCl3)
1.06
2.03
1.02
2.07
0.88
8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
0.98
1.06
2.03
1.02
2.07
0.88
12.0 11.5 11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)

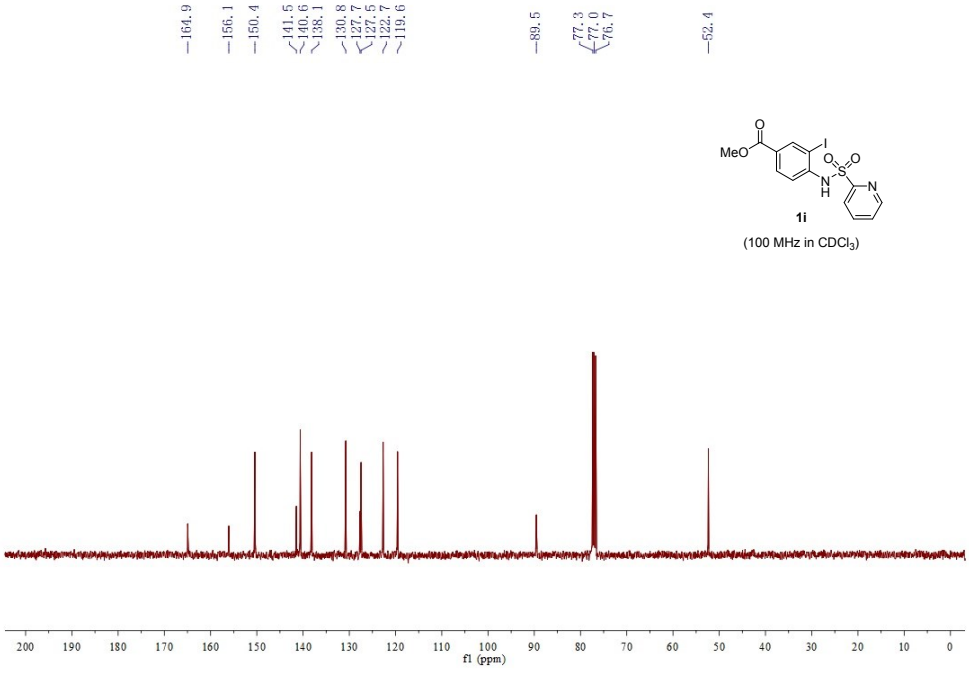

156.2
150.5
140.9
138.4
136.4
136.3
128.7
128.3
128.3
128.0
127.9
127.7
126.8
126.7
126.6
124.1
122.7
121.4
120.7
90.1
77.5
77.2
76.8
F3C
I
O
O
S
N
H
N
1g
(100 MHz in CDCl3)
128.7
128.3
128.0
127.9
126.8
126.7
126.6
124.1
121.4
118.7
129 128 127 126 125 124 123 122 121 120 119 118
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

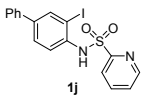

8.67
8.66
8.28
8.28
8.01
7.99
7.92
7.91
7.90
7.89
7.88
7.87
7.85
7.84
7.83
7.82
7.77
7.75
7.52
7.50
7.50
7.48
7.37
7.26
2.51
Me
O
I
O
S
N
H
N
1h
(400 MHz in CDCl3)
f1 (ppm)

0.99
0.98
1.02
1.03
1.06
1.02
1.02
0.91
3.19
f1 (ppm)


195.5
156.2
150.6
141.7
139.6
138.3
134.7
129.8
127.6
122.8
119.8
90.3
77.5
77.2
76.8
26.5
Me
O
I
O
S
N
H
N
1h
(100 MHz in CDCl3)
f1 (ppm)

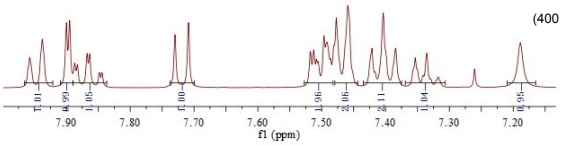

8.67
8.66
8.35
8.00
7.98
7.92
7.90
7.88
7.87
7.75
7.73
7.51
7.50
7.49
7.48
7.35
7.26
3.87
MeO
O
I
O
S
O
N
H
N
1i
(400 MHz in CDCl3)
f1 (ppm)
f1 (ppm)

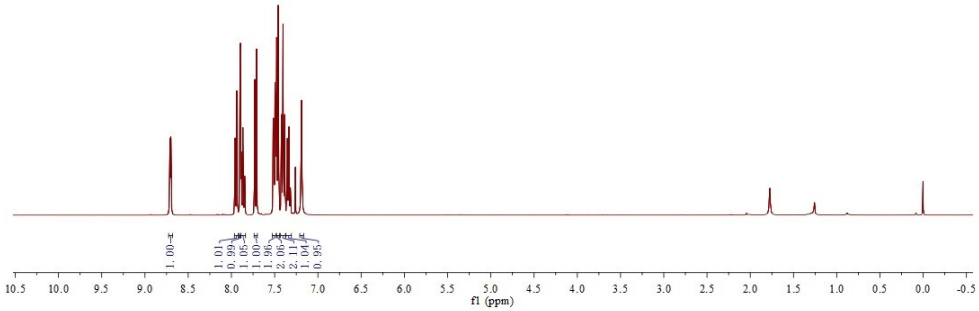

164.9
156.1
150.4
141.5
140.6
138.1
130.8
127.7
127.5
122.7
119.6
89.5
77.3
77.0
76.7
52.4
MeO
O
I
O
S
O
N
H
N
1i
(100 MHz in CDCl3)
f1 (ppm)

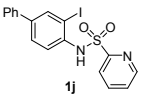


1j

(400 MHz in $CDCl_3$)

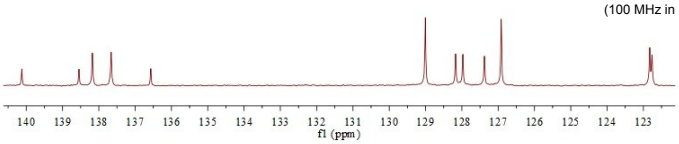


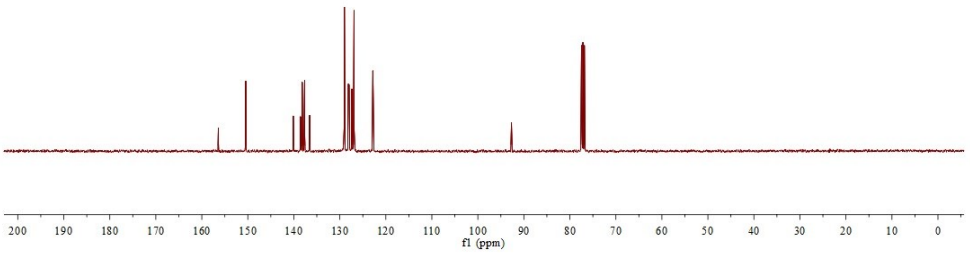


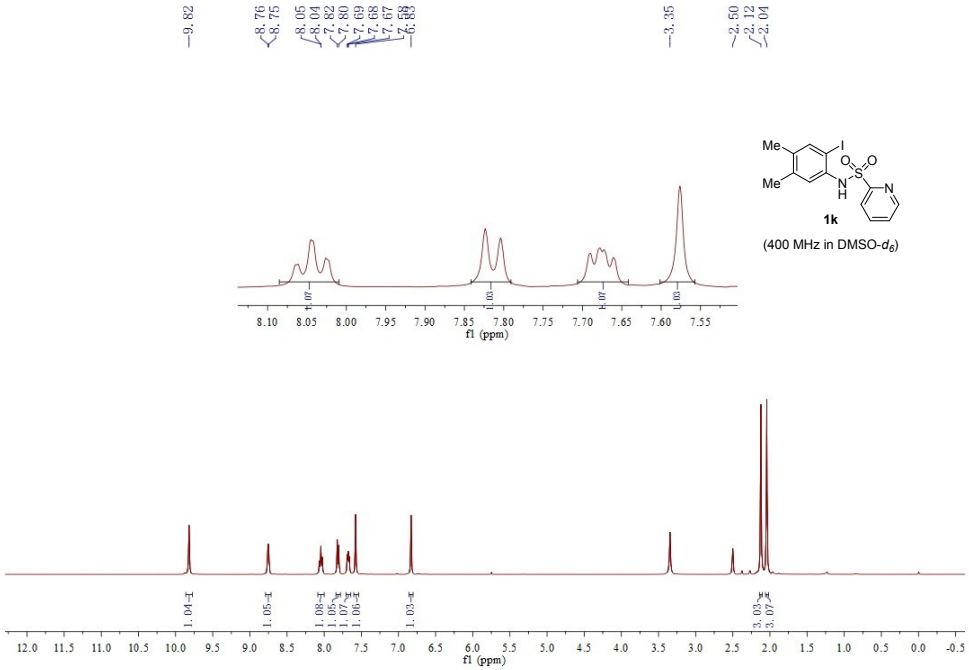


1j

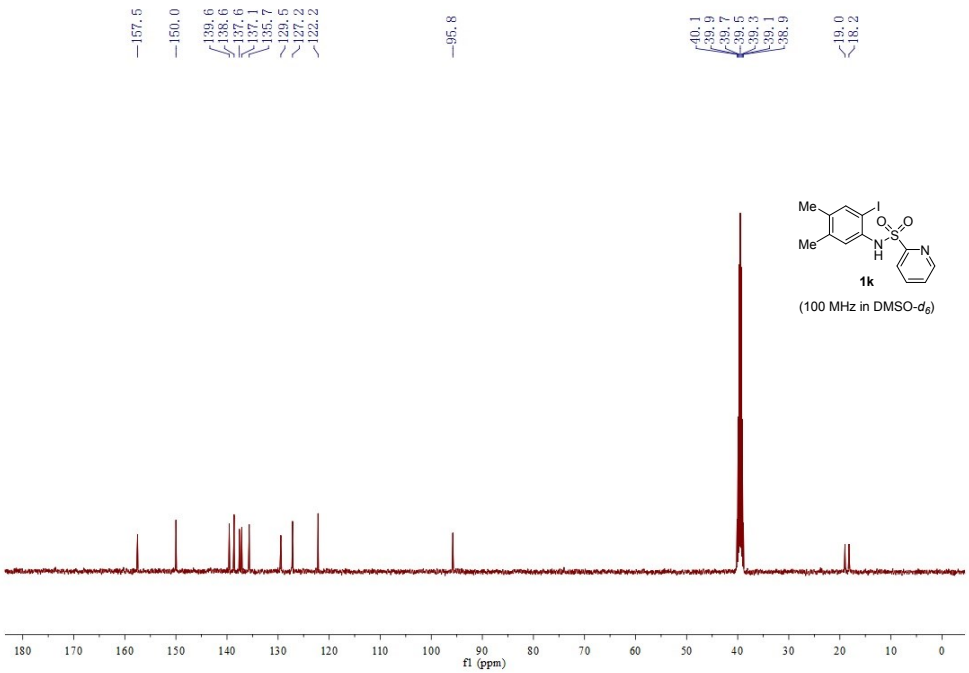
(100 MHz in $CDCl_3$)

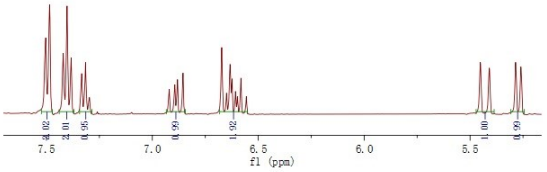


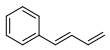



9.82
8.76
8.75
8.05
8.04
7.82
7.80
7.69
7.68
7.67
7.58
7.55
3.35
2.50
2.12
2.04
Me
Me
I
O
O
S
N
H
N
1k
(400 MHz in DMSO-d_6)
f1 (ppm)

f1 (ppm)

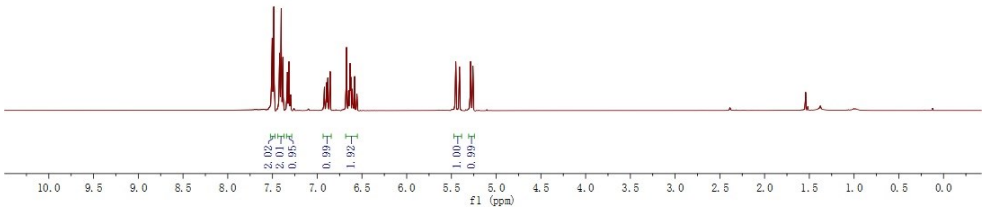

157.5
150.0
139.6
138.6
137.6
137.1
135.7
129.5
127.2
122.2
95.8
40.1
39.9
39.7
39.5
39.3
39.1
38.9
19.0
18.2
Me
Me
I
O
O
S
N
H
N
1k
(100 MHz in DMSO-d_6)
f1 (ppm)

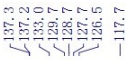


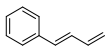


2a

(400 MHz in $CDCl_3$)

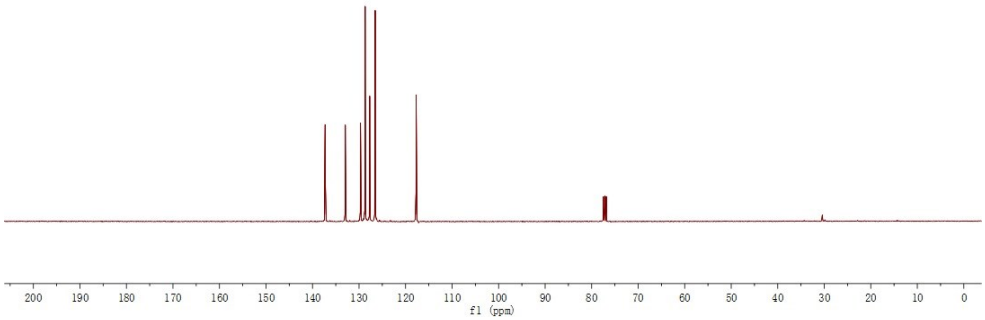


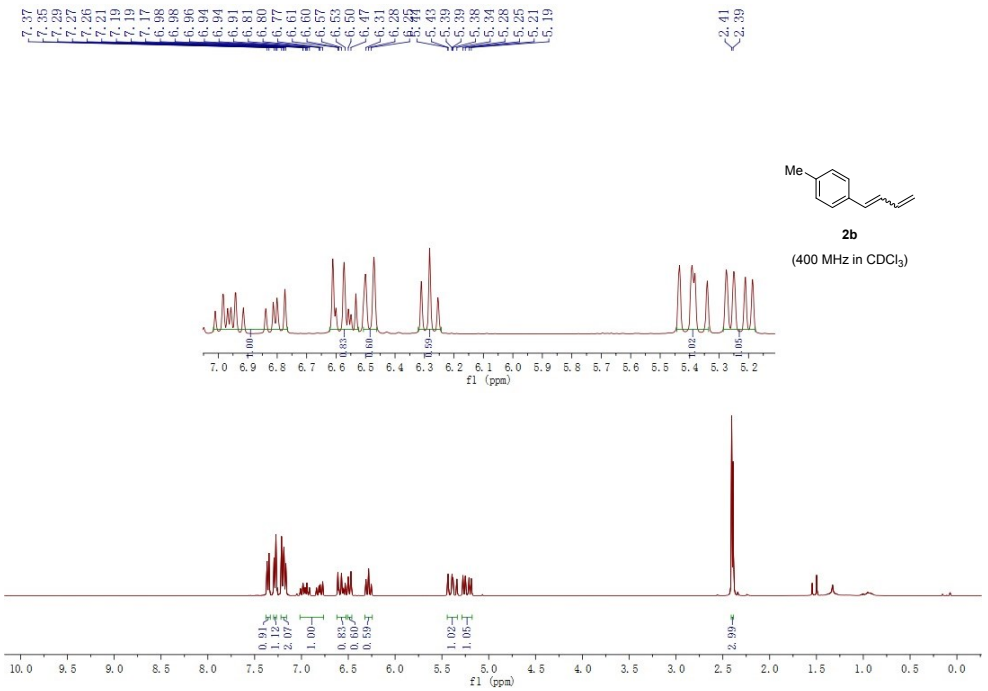


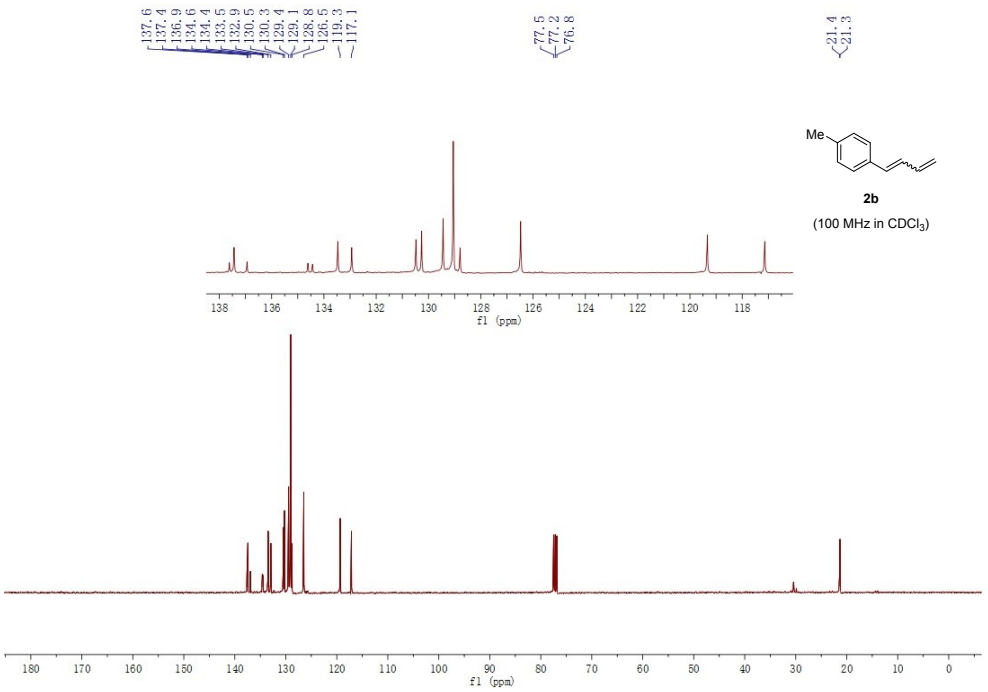


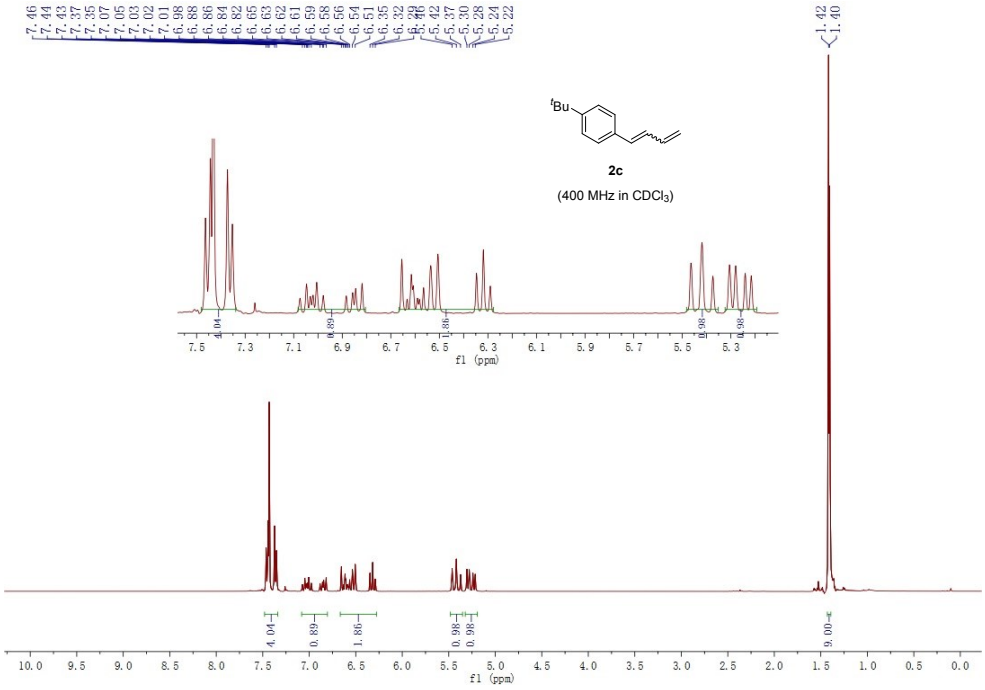
2a

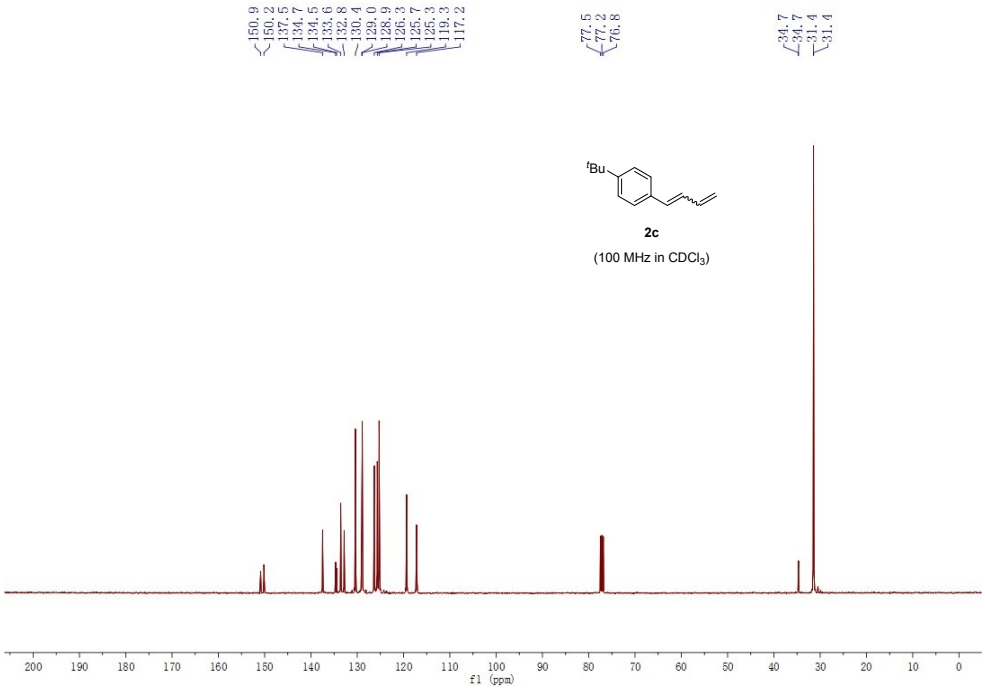
(100 MHz in $CDCl_3$)

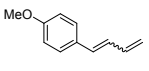



Me
2b
(400 MHz in CDCl3)
f1 (ppm)


Me
2b
(100 MHz in CDCl3)
f1 (ppm)

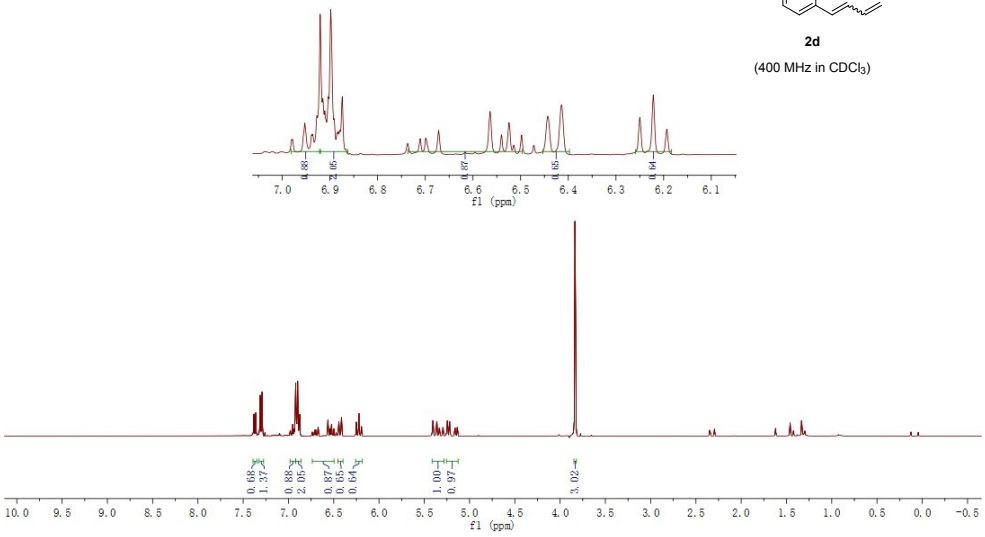

7.46
7.44
7.43
7.37
7.35
7.07
7.05
7.03
7.02
7.01
6.98
6.88
6.86
6.84
6.82
6.65
6.63
6.62
6.61
6.59
6.58
6.56
6.54
6.51
6.35
6.32
5.42
5.37
5.30
5.28
5.24
5.22
1.42
1.40
tBu
2c
(400 MHz in CDCl3)
4.04
0.89
1.86
0.98
0.98
9.00
f1 (ppm)

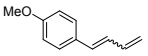

150.9
150.2
137.5
134.7
134.5
133.6
132.8
130.4
129.0
128.9
126.3
125.7
125.3
119.3
117.2
77.5
77.2
76.8
34.7
34.7
31.4
31.4
tBu
2c
(100 MHz in CDCl3)
f1 (ppm)



2d

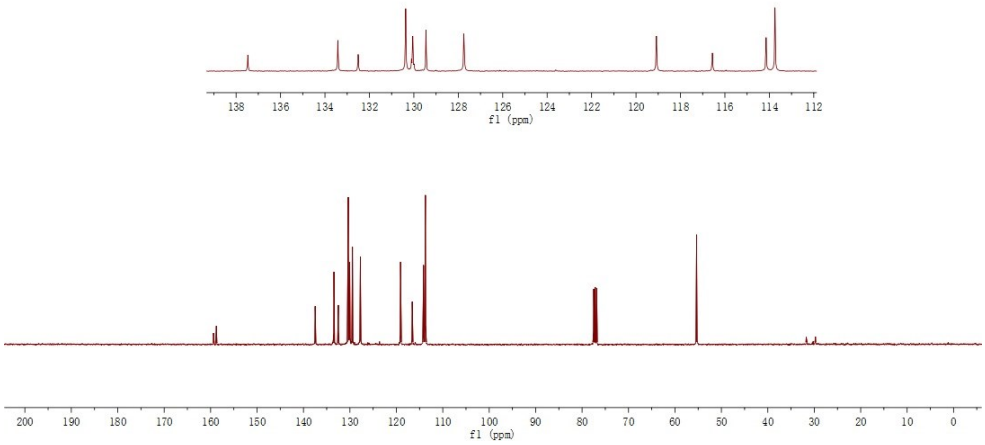
(400 MHz in $CDCl_3$)

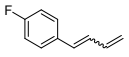




2d

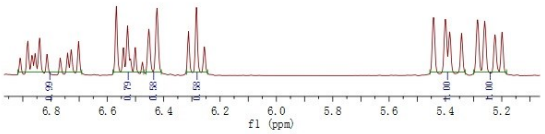
(100 MHz in $CDCl_3$)

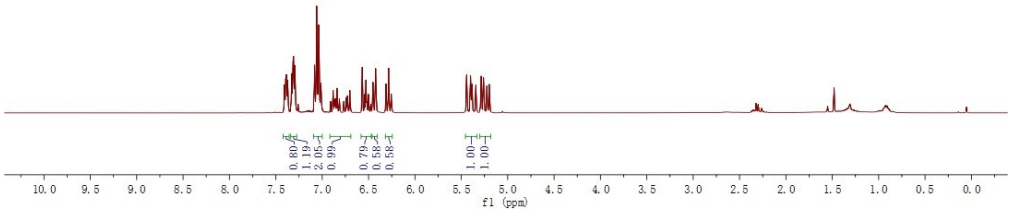


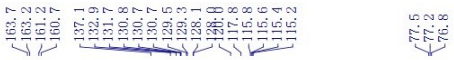


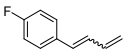
2e

(400 MHz in $CDCl_3$)



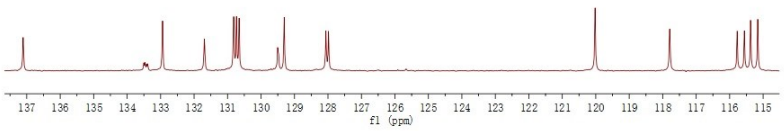


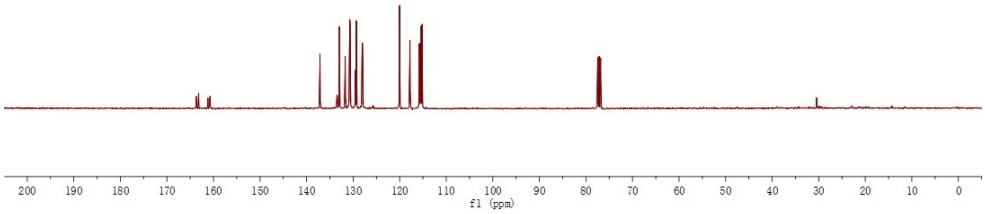


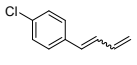


2e

(100 MHz in $CDCl_3$)

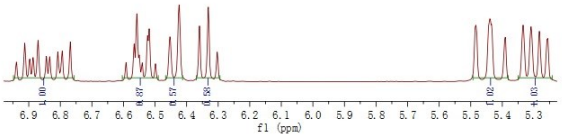


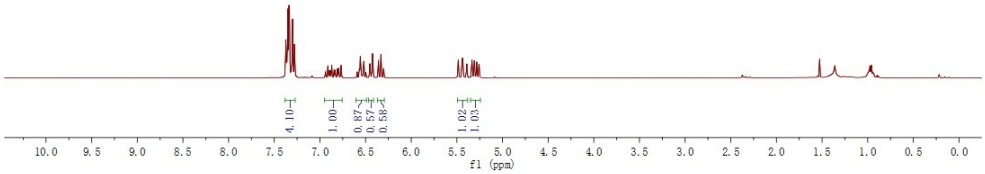


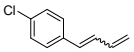


2f

(400 MHz in $CDCl_3$)

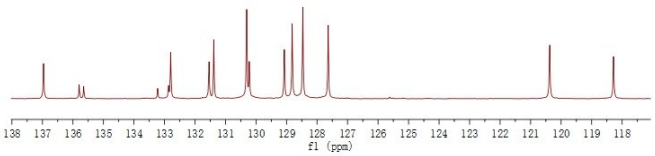


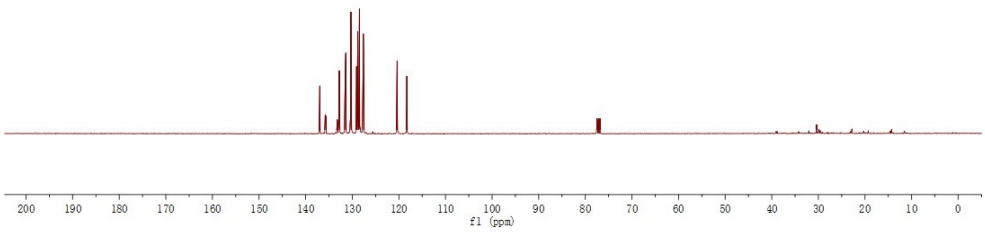


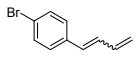


2f

(100 MHz in $CDCl_3$)

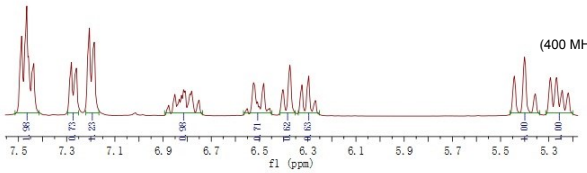


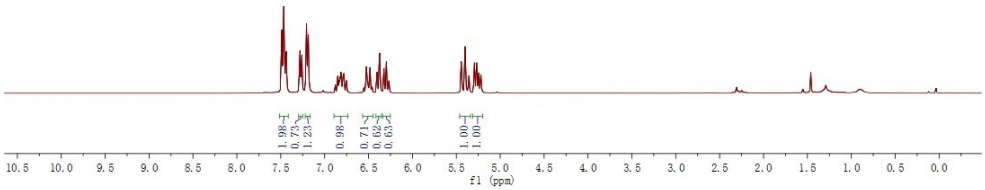


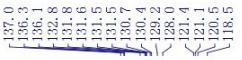


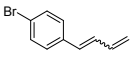
2g

(400 MHz in $CDCl_3$)



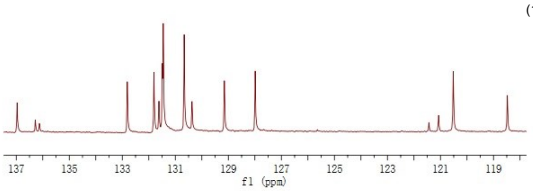


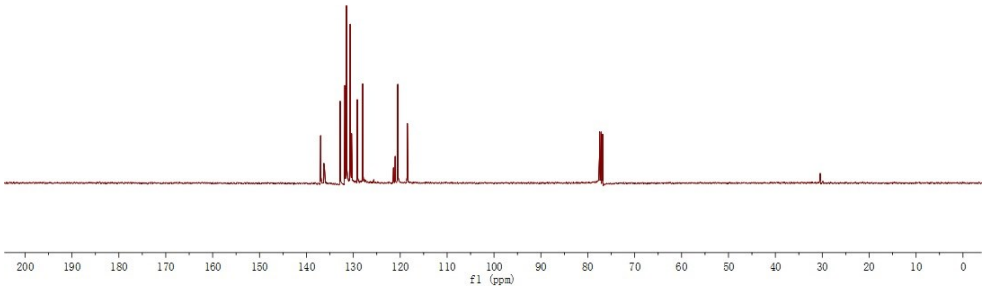


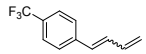


2g

(100 MHz in $CDCl_3$)

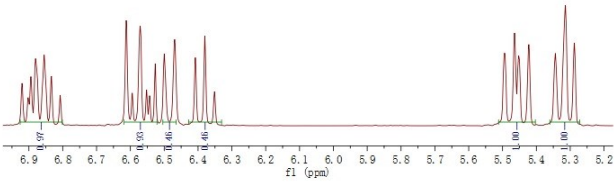


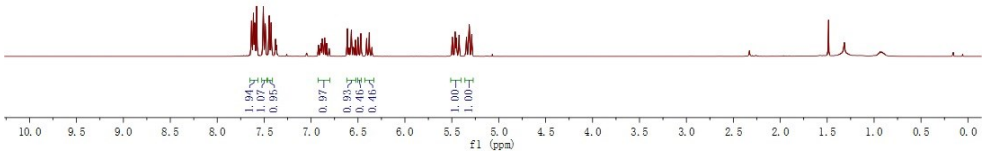


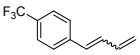


2h

(400 MHz in $CDCl_3$)

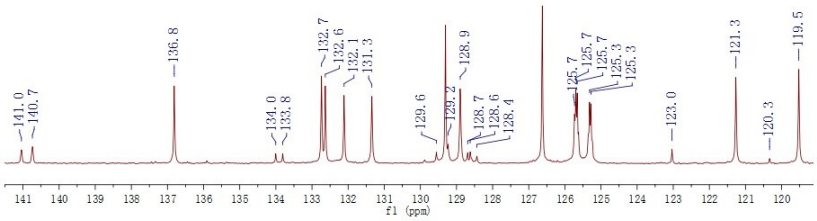


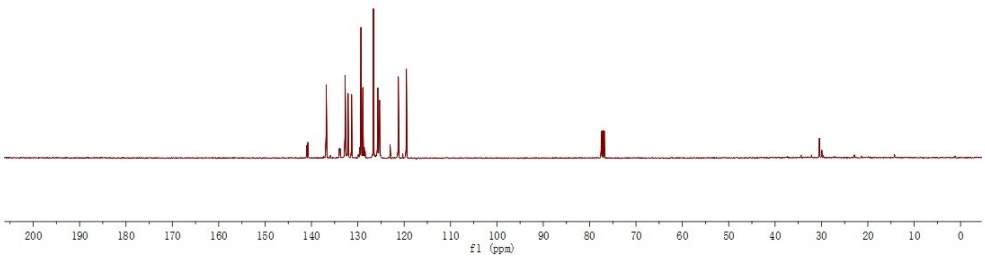


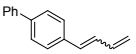


2h

(100 MHz in $CDCl_3$)

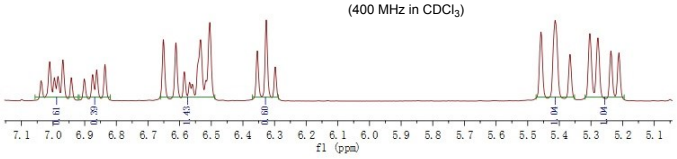


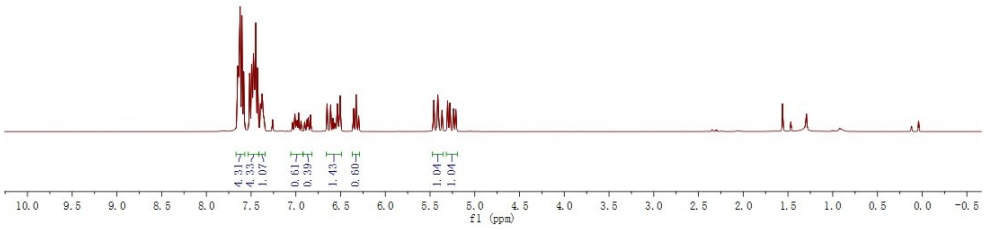


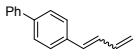


2i

(400 MHz in $CDCl_3$)

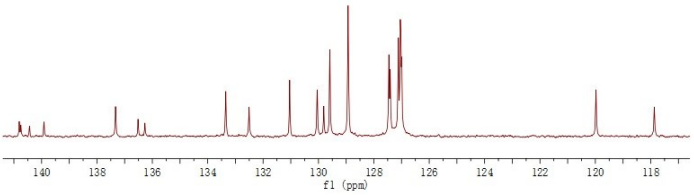


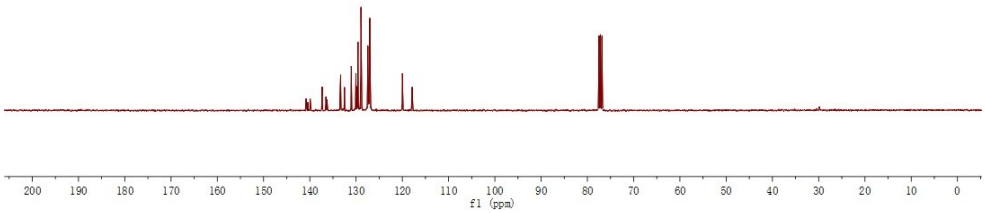


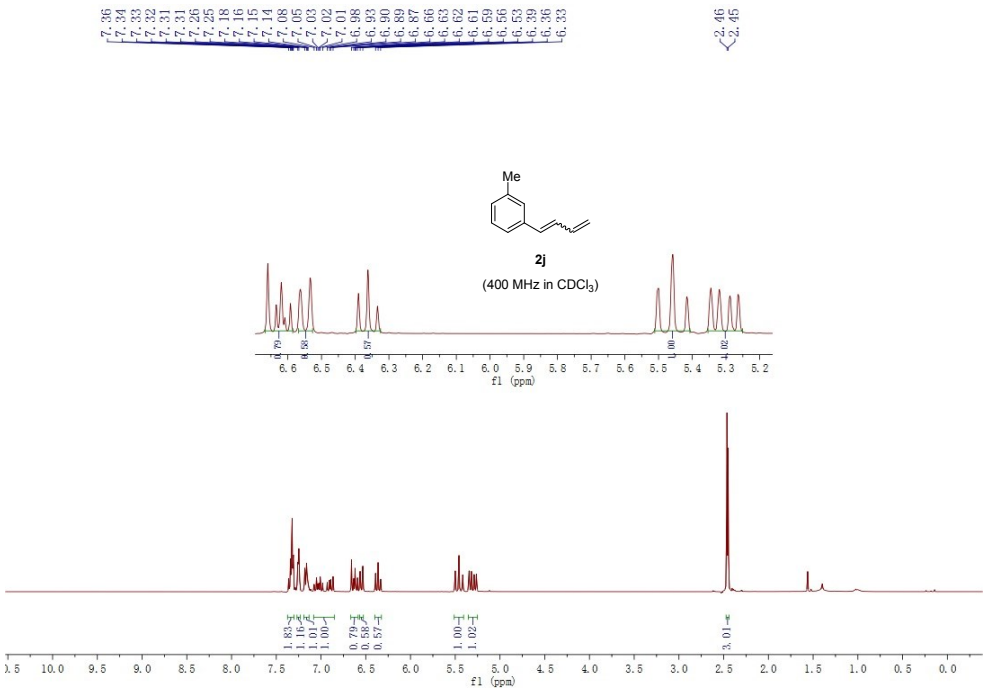


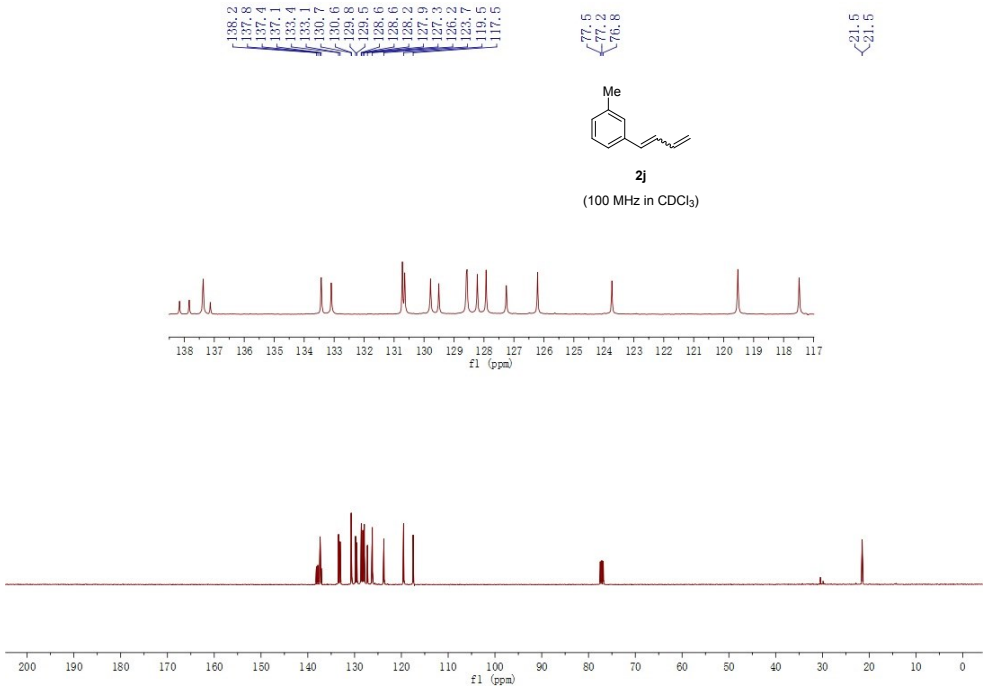
2i

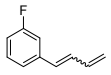
(100 MHz in $CDCl_3$)





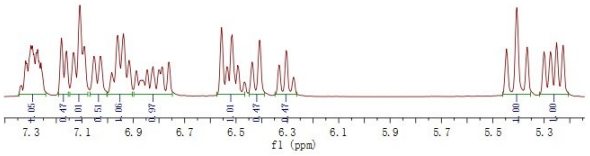

Me
2j
(400 MHz in CDCl3)
f1 (ppm)

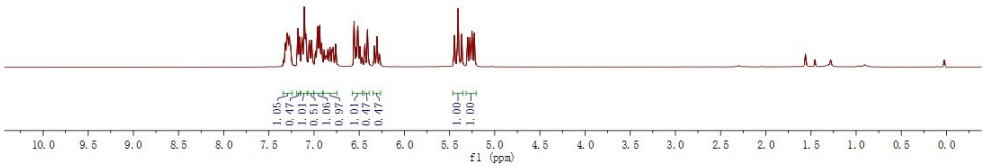

Me
2j
(100 MHz in CDCl3)
f1 (ppm)

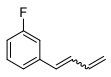


2k

(400 MHz in $CDCl_3$)

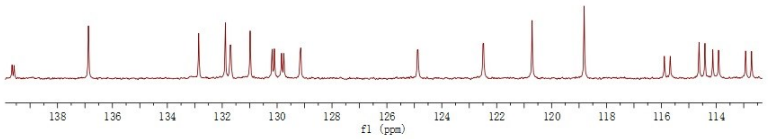


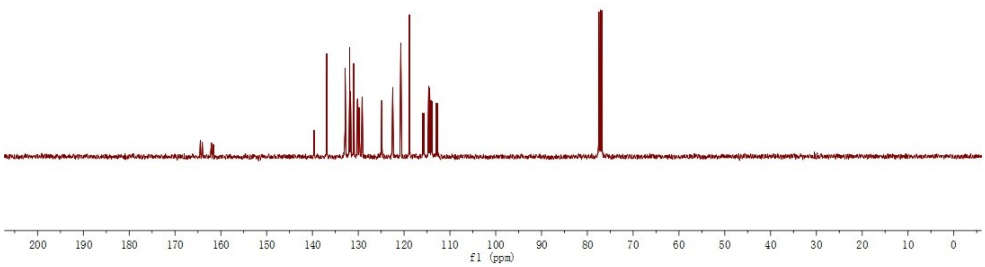


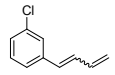


2k

(100 MHz in $CDCl_3$)

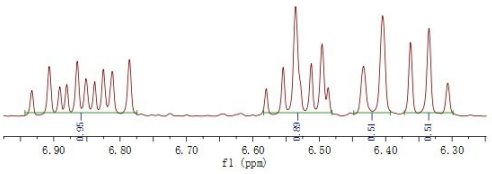


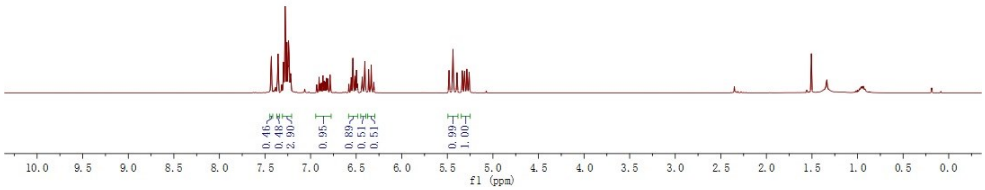


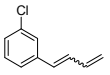


2l

(400 MHz in $CDCl_3$)

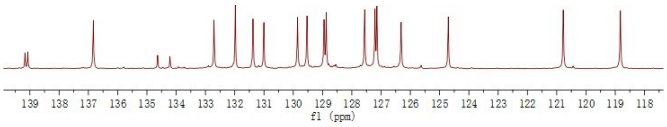


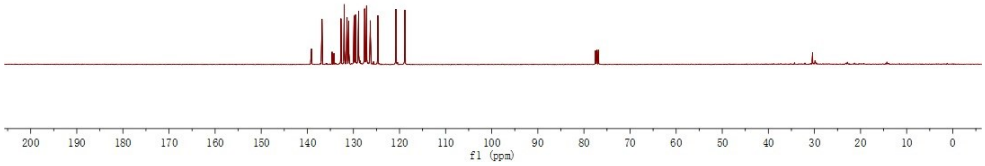


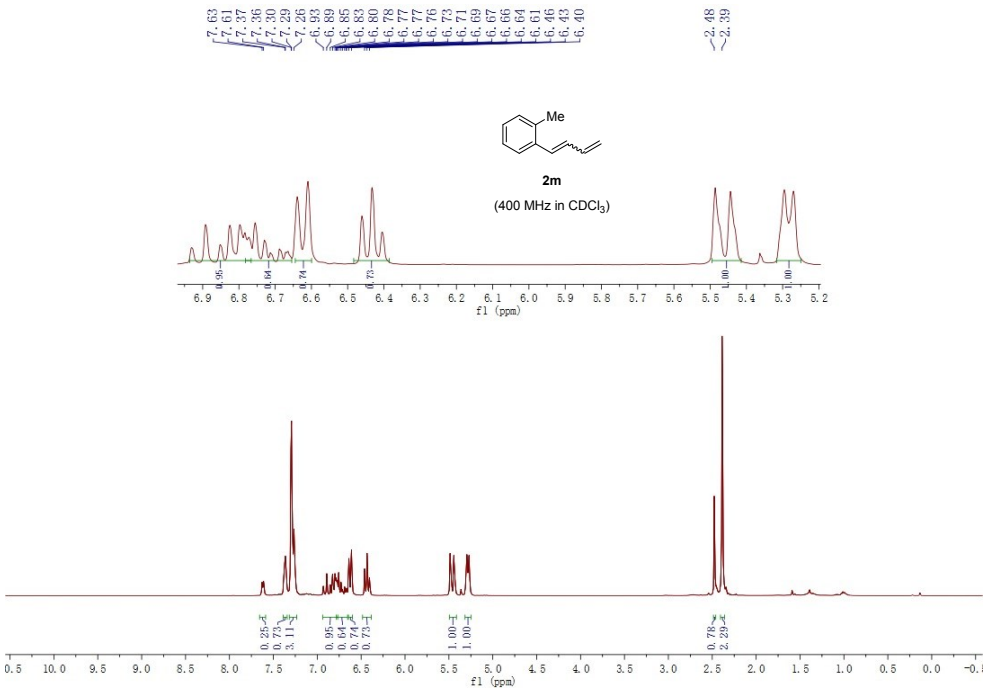


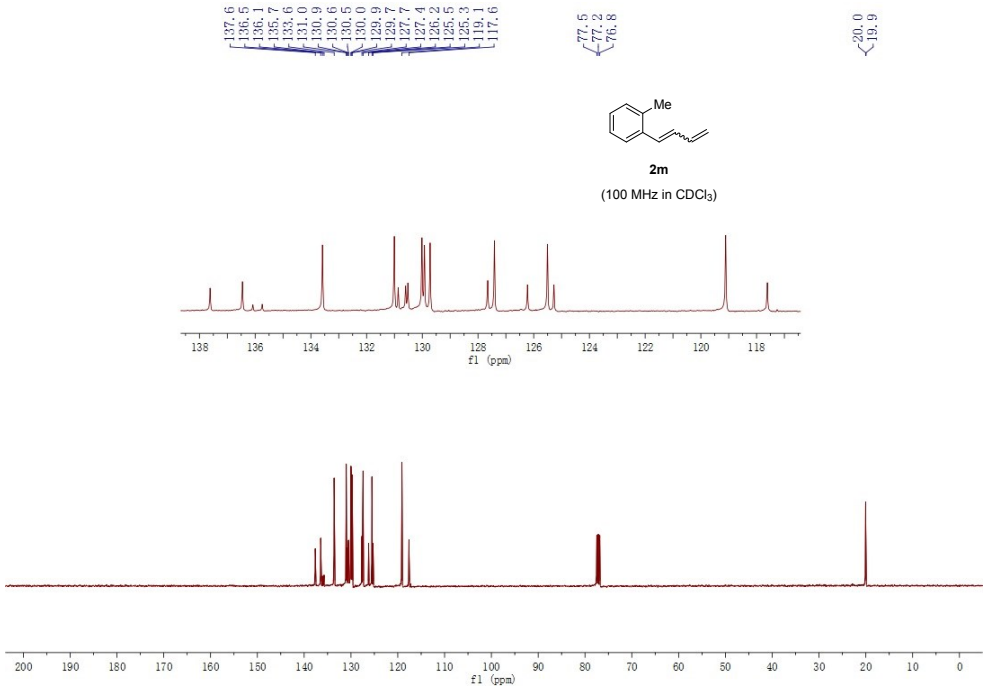
2l

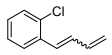
(100 MHz in $CDCl_3$)





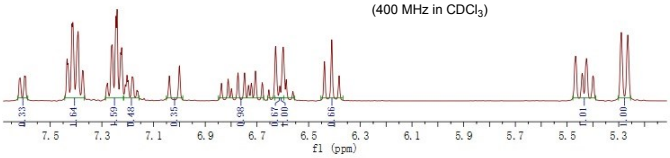

Me
2m
(400 MHz in CDCl3)
f1 (ppm)

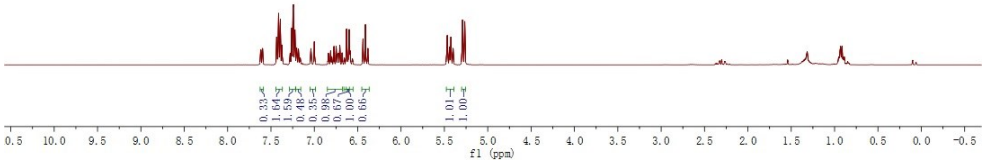

Me
2m
(100 MHz in CDCl3)
f1 (ppm)

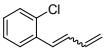


2n

(400 MHz in $CDCl_3$)

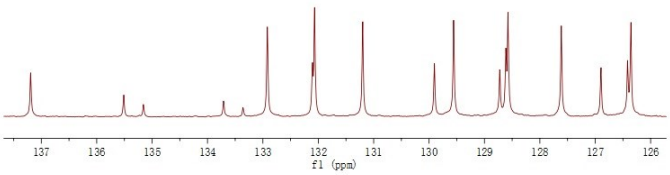


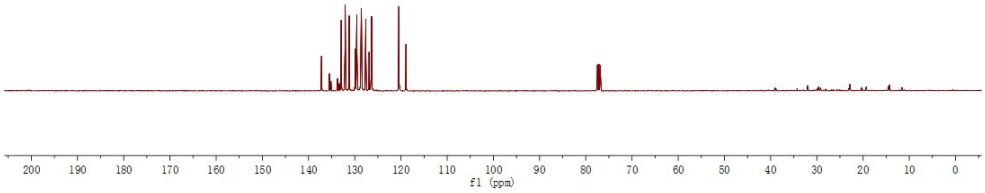


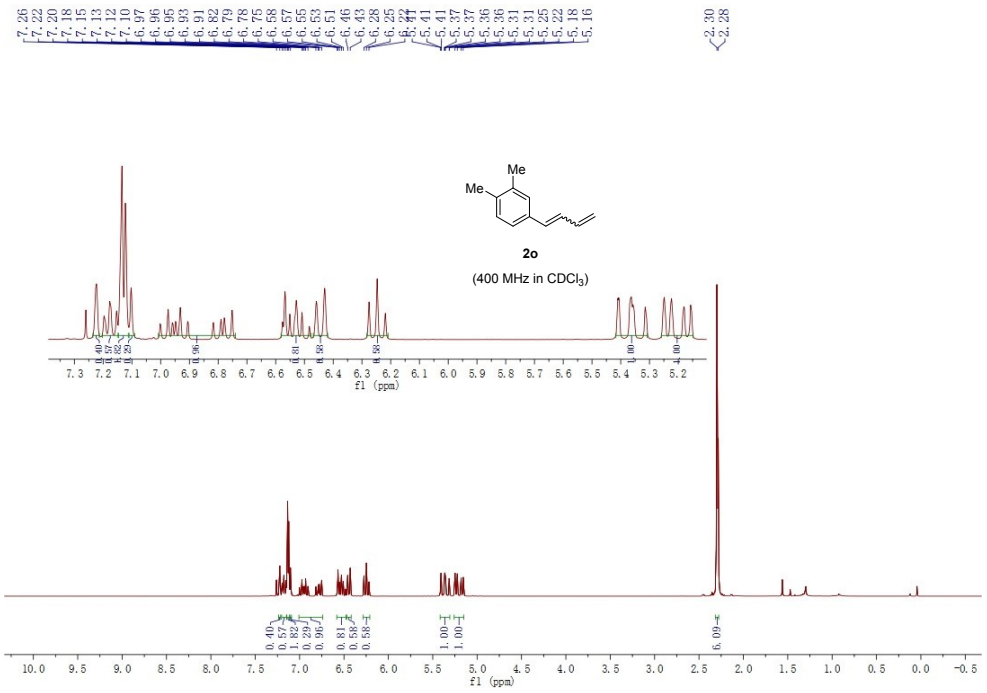


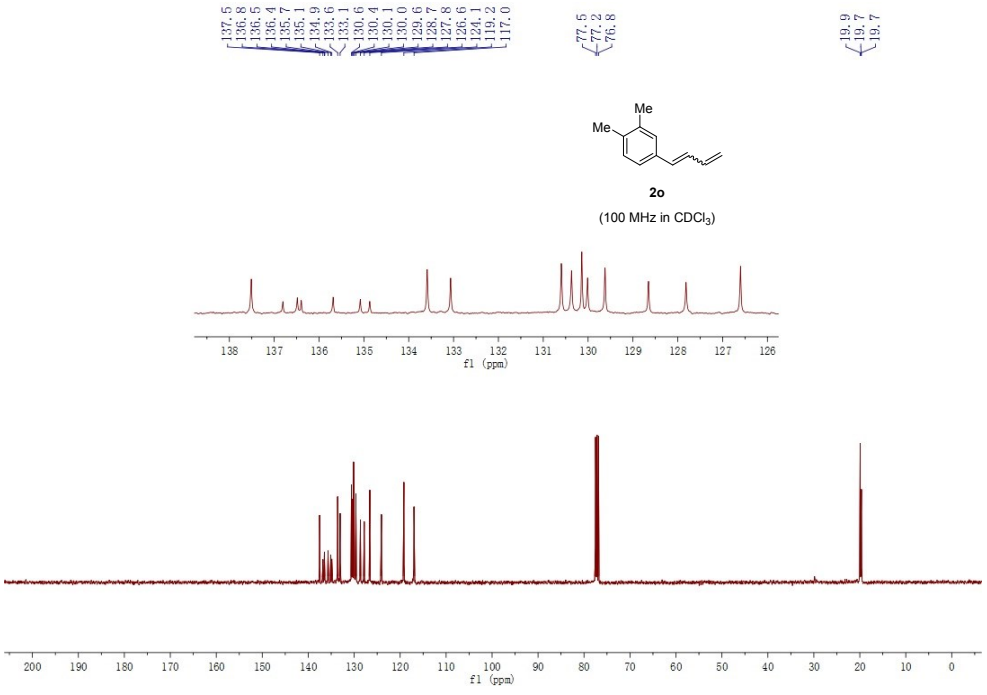
2n

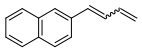
(100 MHz in $CDCl_3$)





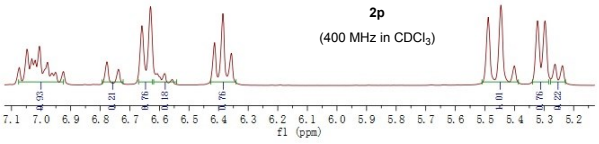

Me
Me
2o
(400 MHz in CDCl3)
f1 (ppm)

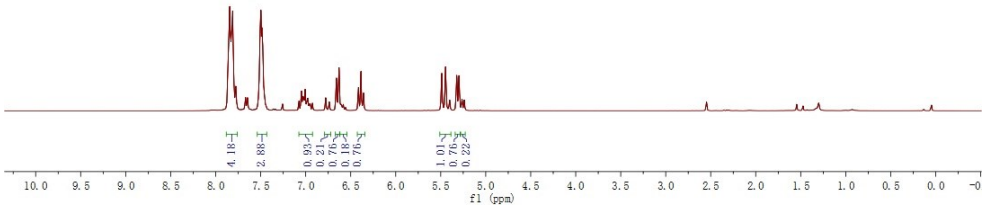

Me
Me
2o
(100 MHz in CDCl3)
f1 (ppm)

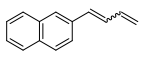


2p

(400 MHz in $CDCl_3$)

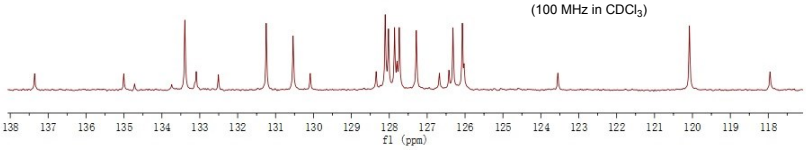


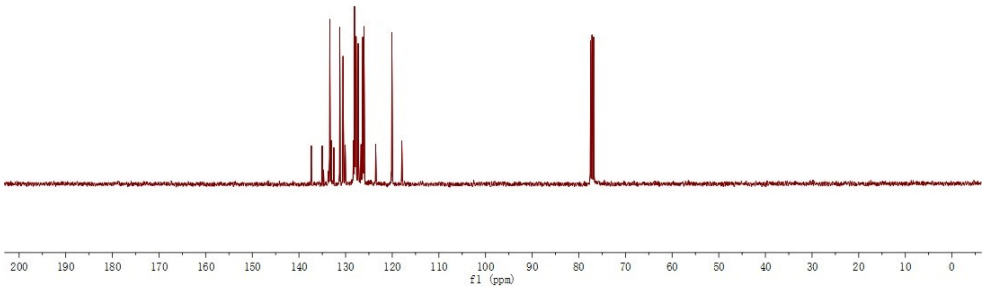


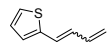


2p

(100 MHz in $CDCl_3$)

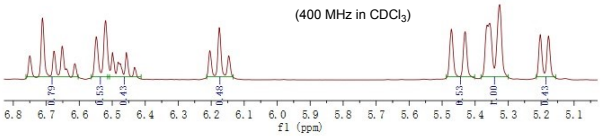


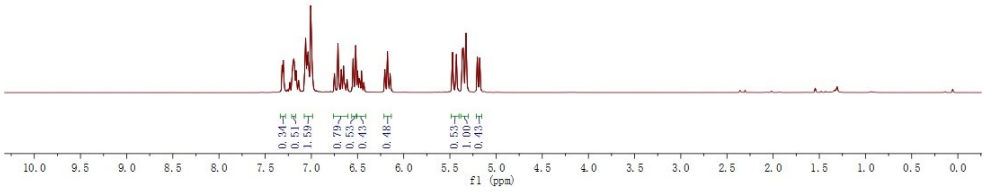


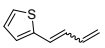


2q

(400 MHz in $CDCl_3$)

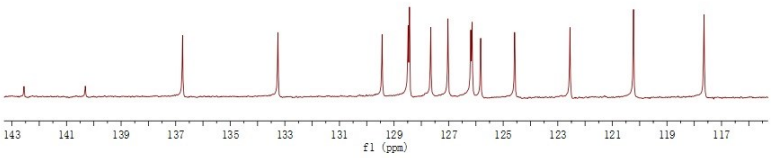


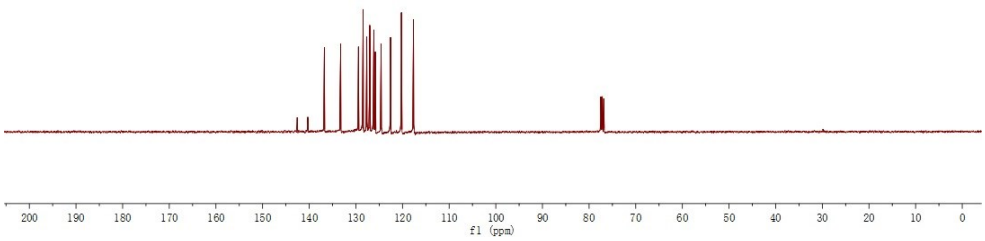


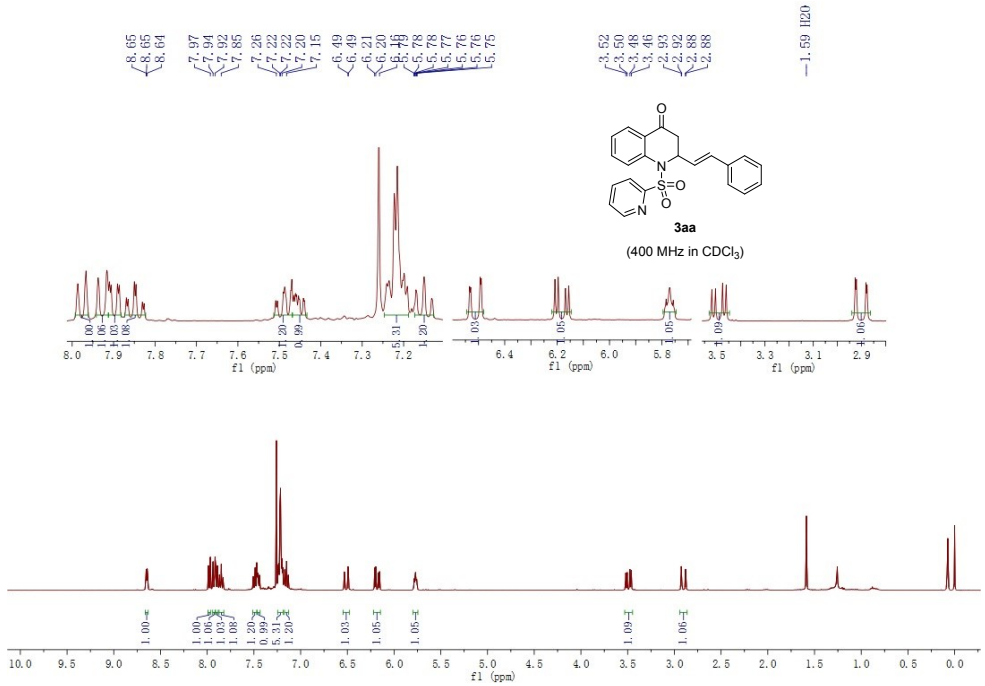


2q

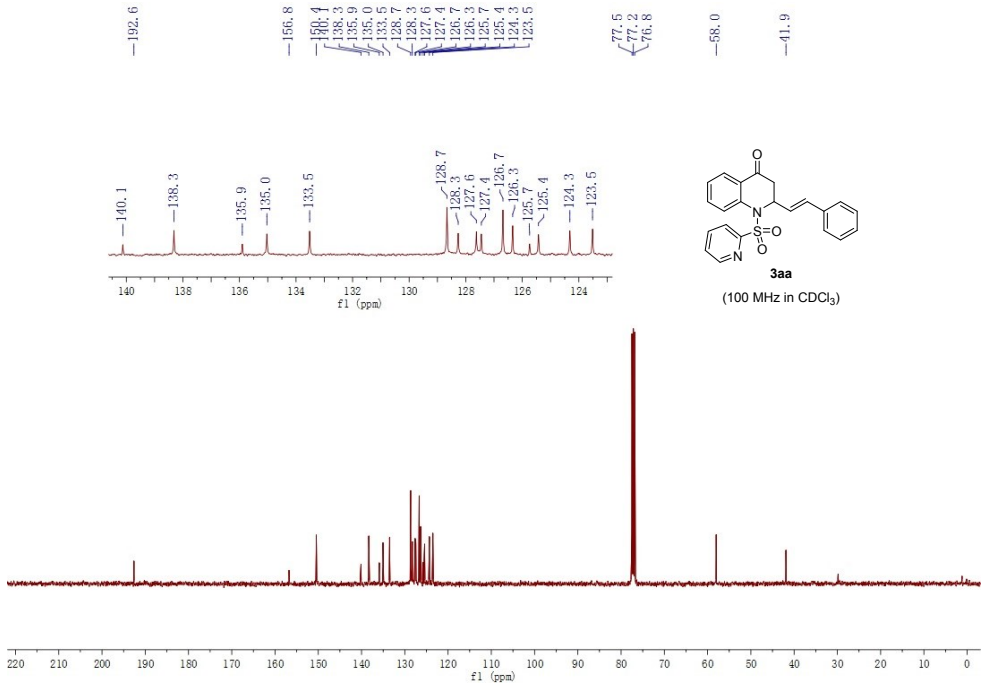
(100 MHz in $CDCl_3$)

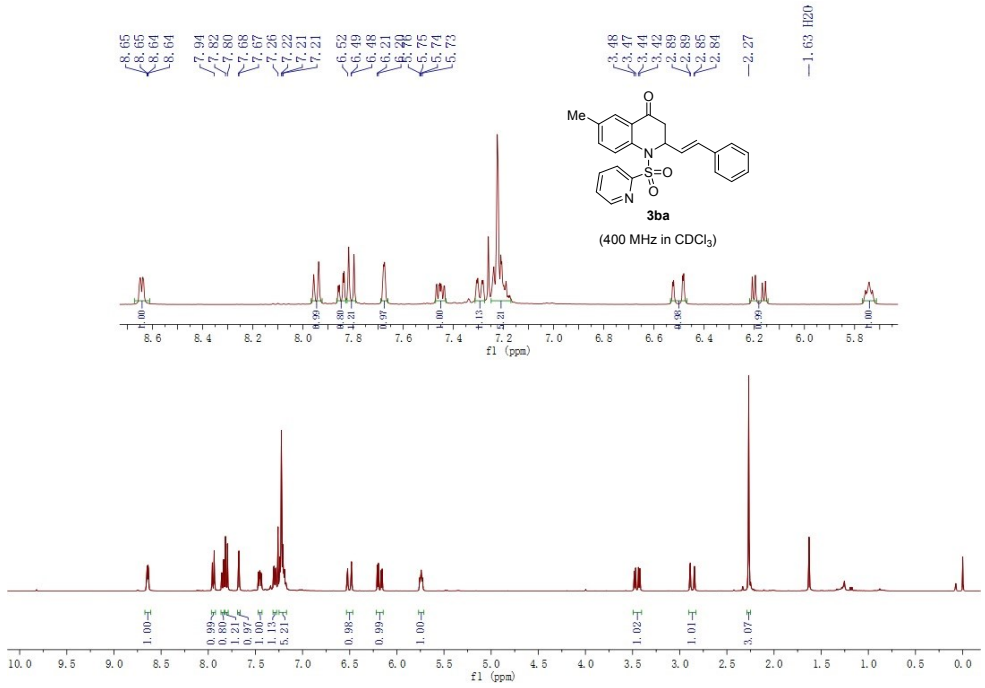


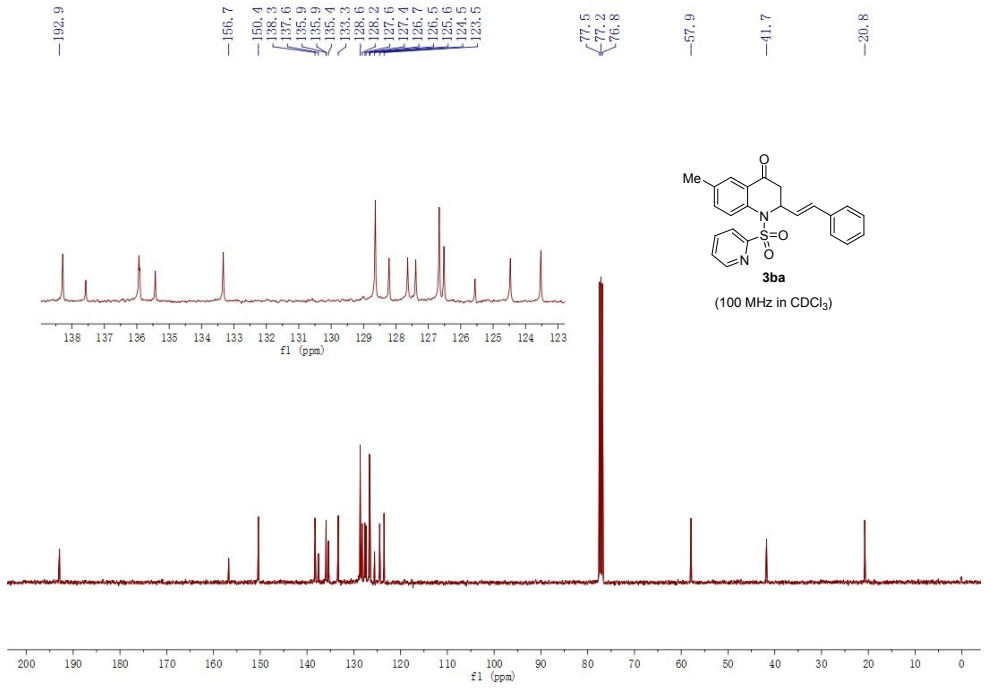


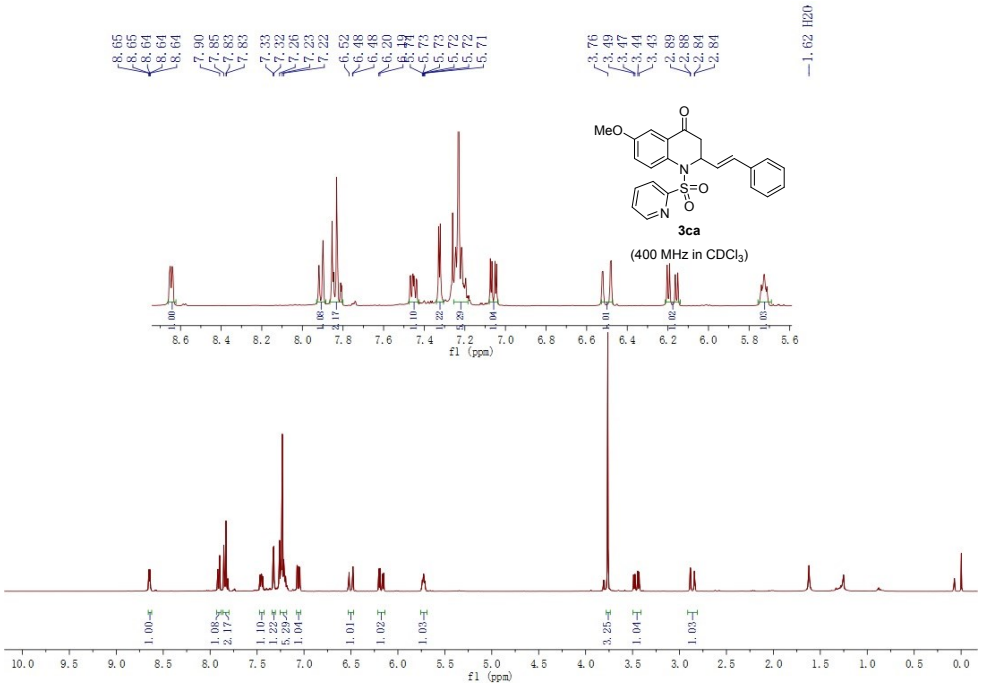

8.65
8.65
8.64
7.97
7.94
7.92
7.85
7.26
7.22
7.22
7.20
7.15
6.49
6.49
6.21
6.20
5.78
5.78
5.77
5.76
5.76
5.75
3.52
3.50
3.48
3.46
2.93
2.92
2.88
2.88
1.59
H2O
3aa
(400 MHz in CDCl3)
f1 (ppm)

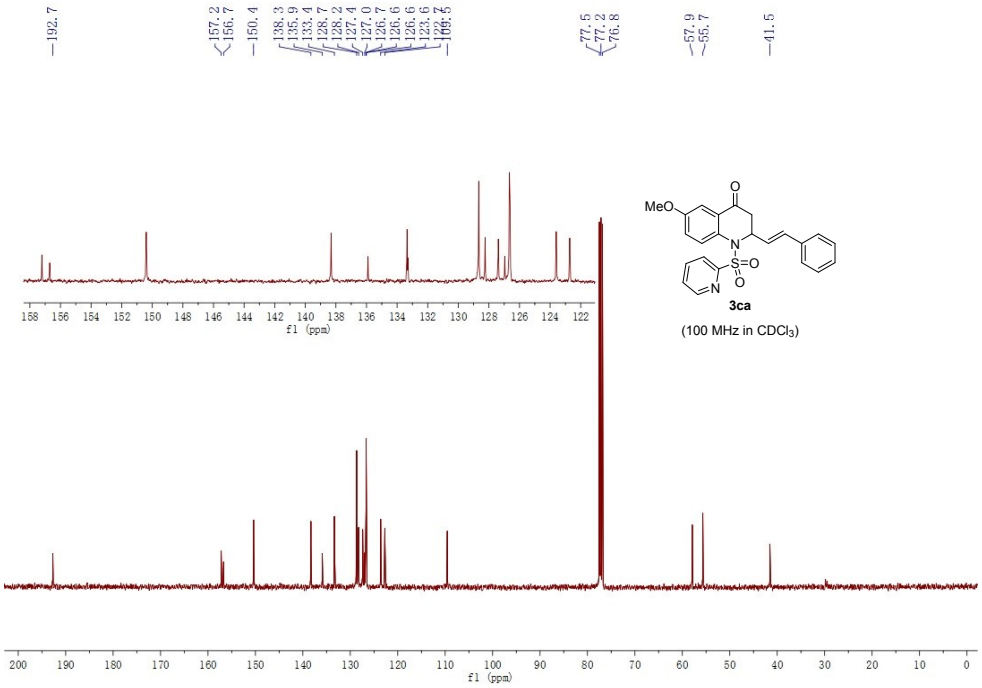
f1 (ppm)

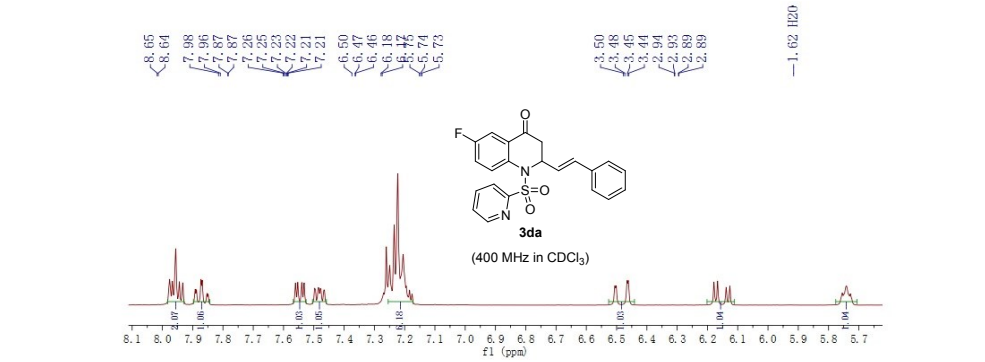

192.6
166.8
150.4
140.1
138.3
135.9
135.0
133.5
128.7
128.3
127.6
127.4
126.7
126.3
125.7
125.4
124.3
123.5
77.5
77.2
76.8
58.0
41.9
3aa
(100 MHz in CDCl3)
f1 (ppm)

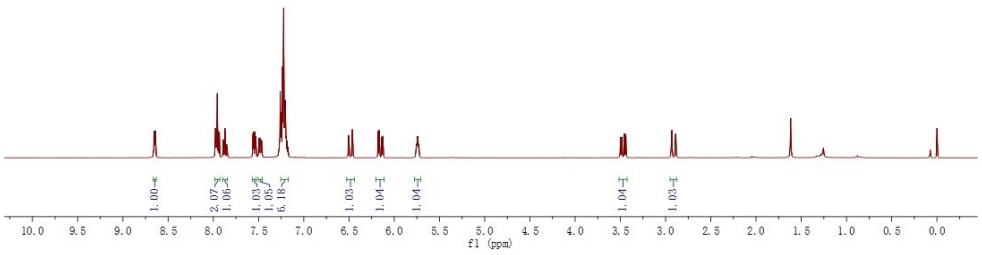

8.65
8.65
8.64
8.64
7.94
7.82
7.80
7.68
7.67
7.26
7.22
7.21
7.21
6.52
6.49
6.48
6.21
5.75
5.74
5.73
3.48
3.47
3.44
3.42
2.89
2.89
2.85
2.84
2.27
1.63 H2O
Me
O
N
S=O
O
N
3ba
(400 MHz in CDCl3)
f1 (ppm)
f1 (ppm)

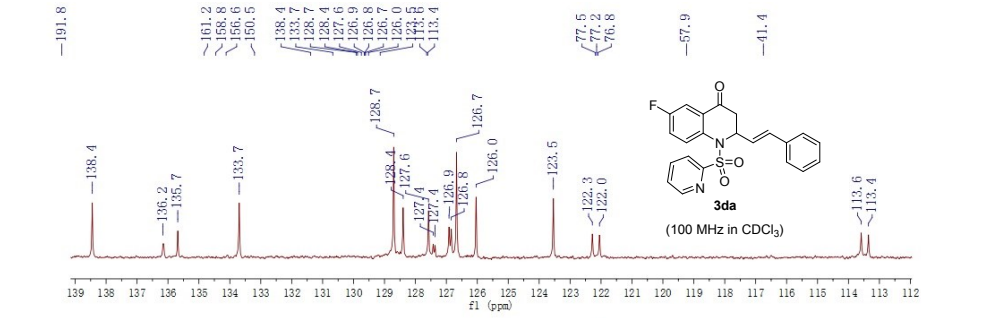

192.9
156.7
150.4
138.3
137.6
135.9
135.9
135.4
133.3
128.6
128.2
127.6
127.4
126.7
126.5
125.6
124.5
123.5
77.5
77.2
76.8
57.9
41.7
20.8
Me
O
N
S=O
O
N
3ba
(100 MHz in CDCl3)
f1 (ppm)
f1 (ppm)

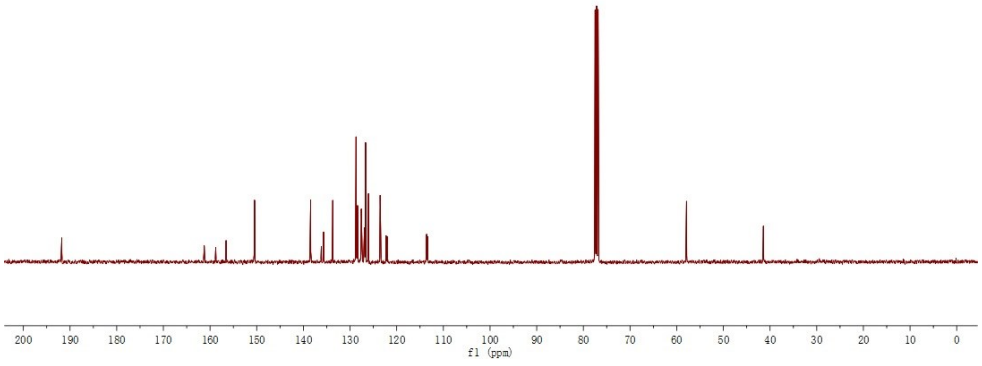

8.65
8.65
8.64
8.64
8.64
7.90
7.85
7.83
7.83
7.33
7.32
7.26
7.23
7.22
6.52
6.48
6.48
6.20
5.73
5.73
5.72
5.72
5.71
3.76
3.49
3.47
3.44
3.43
2.89
2.88
2.84
2.84
1.62 H2O
MeO
O
N
S
O
O
N
3ca
(400 MHz in CDCl3)
f1 (ppm)

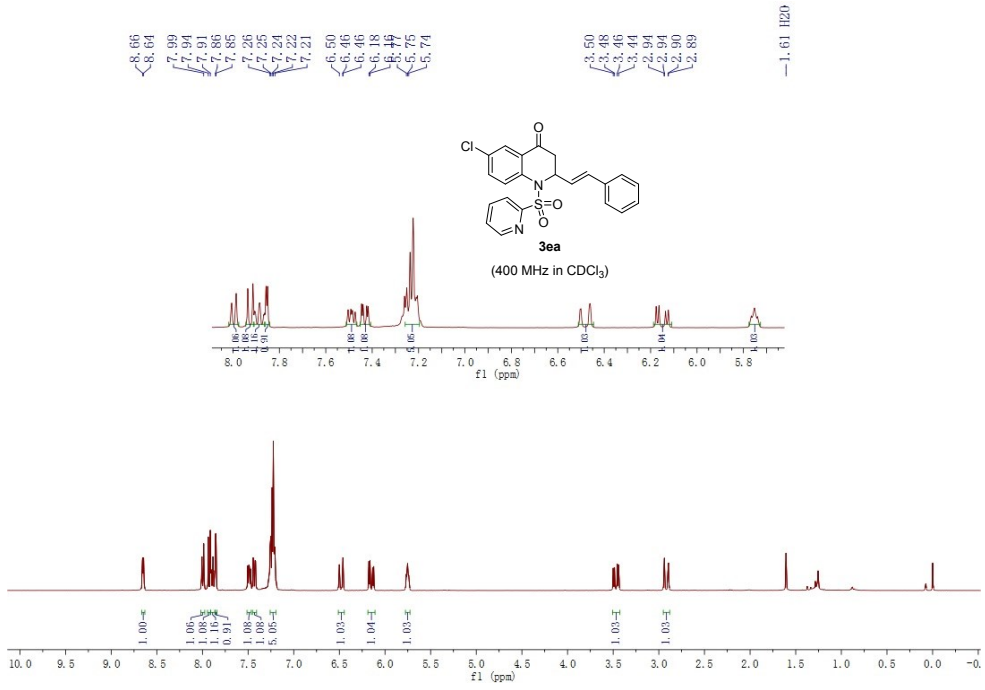

192.7
157.2
156.7
150.4
138.3
135.9
133.4
128.7
128.2
127.4
127.0
126.7
126.6
126.6
123.6
122.7
116.5
77.5
77.2
76.8
57.9
55.7
41.5
MeO
O
N
S
O
O
N
3ca
(100 MHz in CDCl3)
f1 (ppm)


8.65
8.64
7.98
7.96
7.87
7.87
7.26
7.25
7.23
7.22
7.21
7.21
6.50
6.47
6.46
6.18
5.74
5.73
3.50
3.48
3.45
3.44
2.94
2.93
2.89
2.89
1.62 H2O
F
O
N
S=O
O
N
3da
(400 MHz in CDCl3)
f1 (ppm)

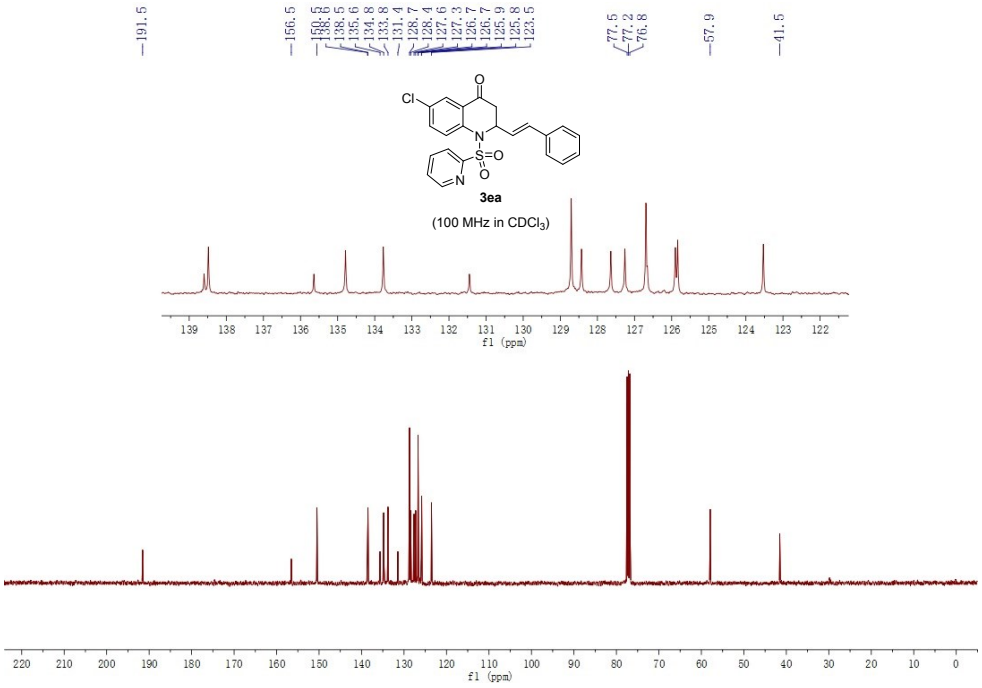

1.00
2.07
1.06
1.03
1.05
6.18
1.03
1.04
1.04
1.04
1.03
f1 (ppm)

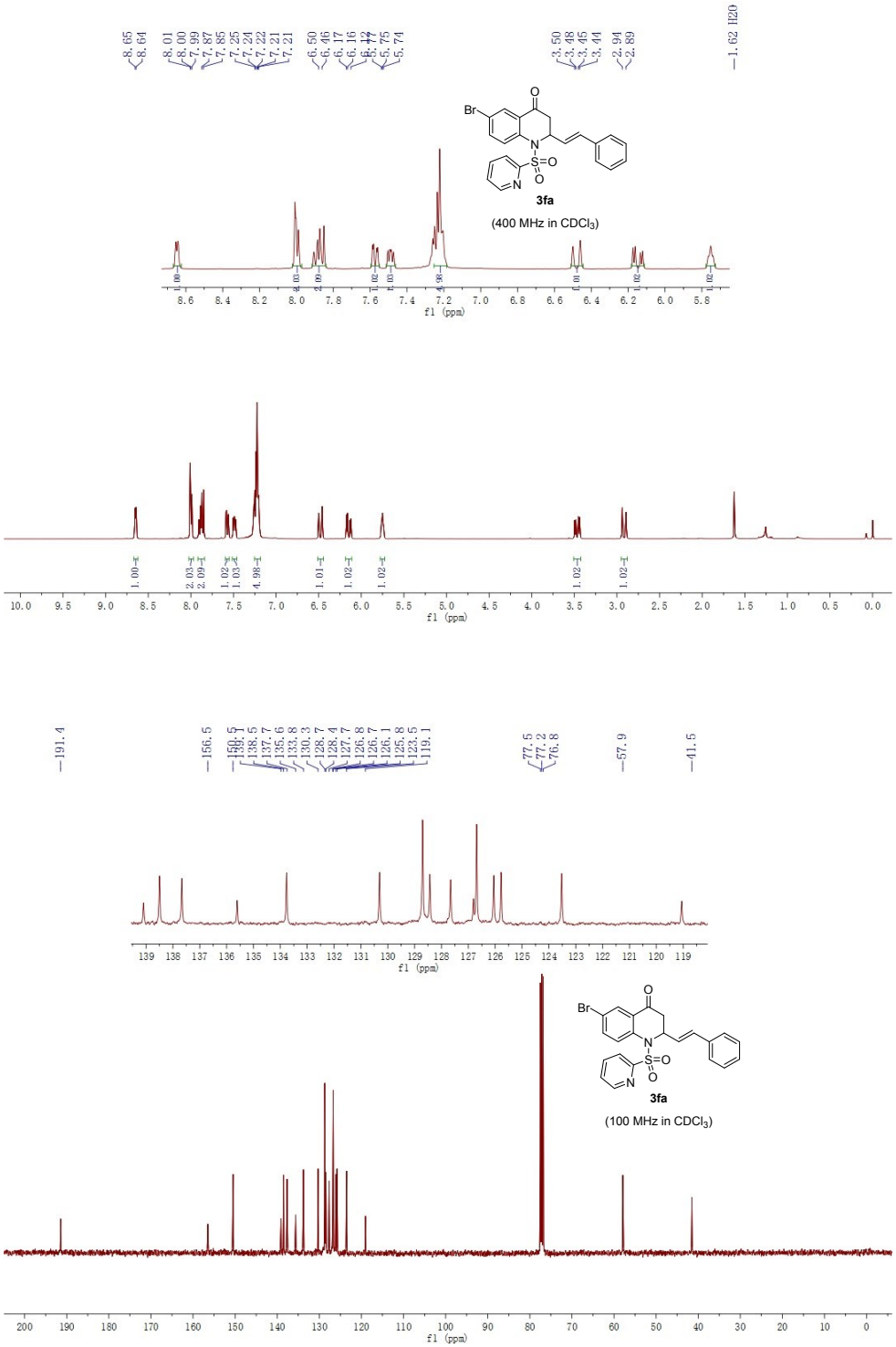

191.8
161.2
158.8
156.6
150.5
138.4
133.7
128.7
128.4
127.6
126.9
126.8
126.7
126.0
123.5
113.4
77.5
77.2
76.8
67.9
41.4
F
O
N
S=O
O
N
3da
(100 MHz in CDCl3)
f1 (ppm)

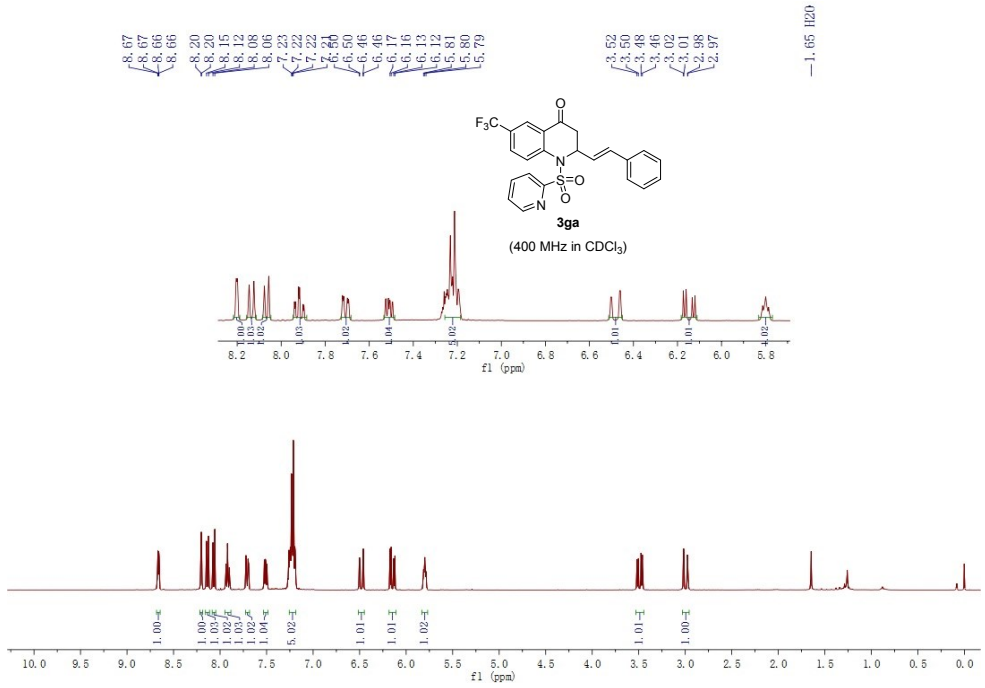

f1 (ppm)

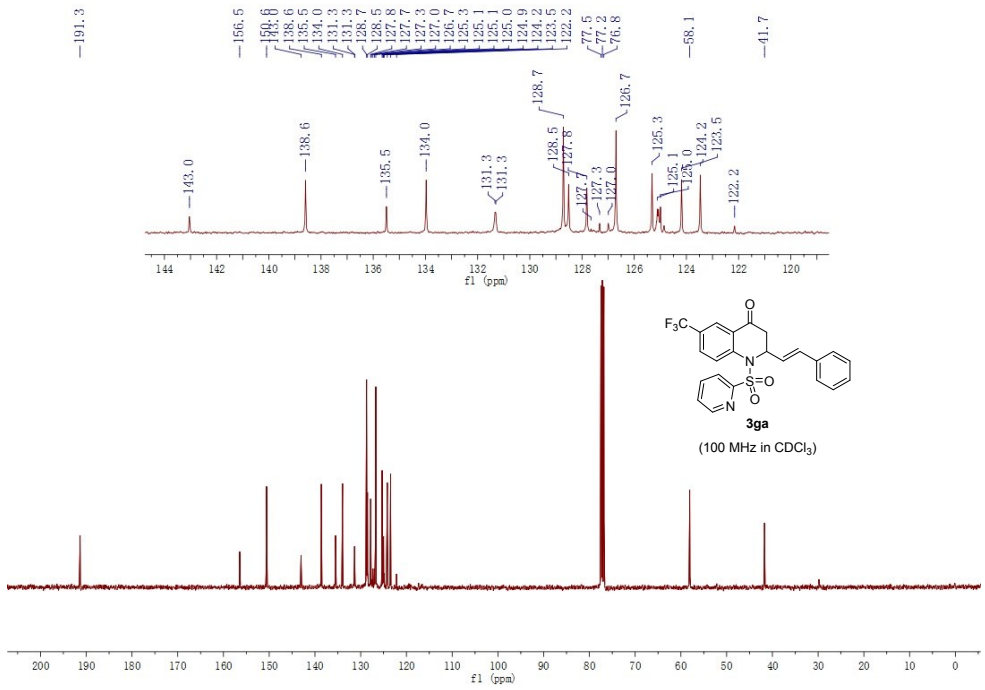

8.66
8.64
7.99
7.94
7.91
7.86
7.85
7.26
7.25
7.24
7.22
7.21
6.50
6.46
6.46
6.18
5.75
5.74
3.50
3.48
3.46
3.44
2.94
2.94
2.90
2.89
1.61 H2O
Cl
O
N
S
O
O
N
3ea
(400 MHz in CDCl3)
f1 (ppm)

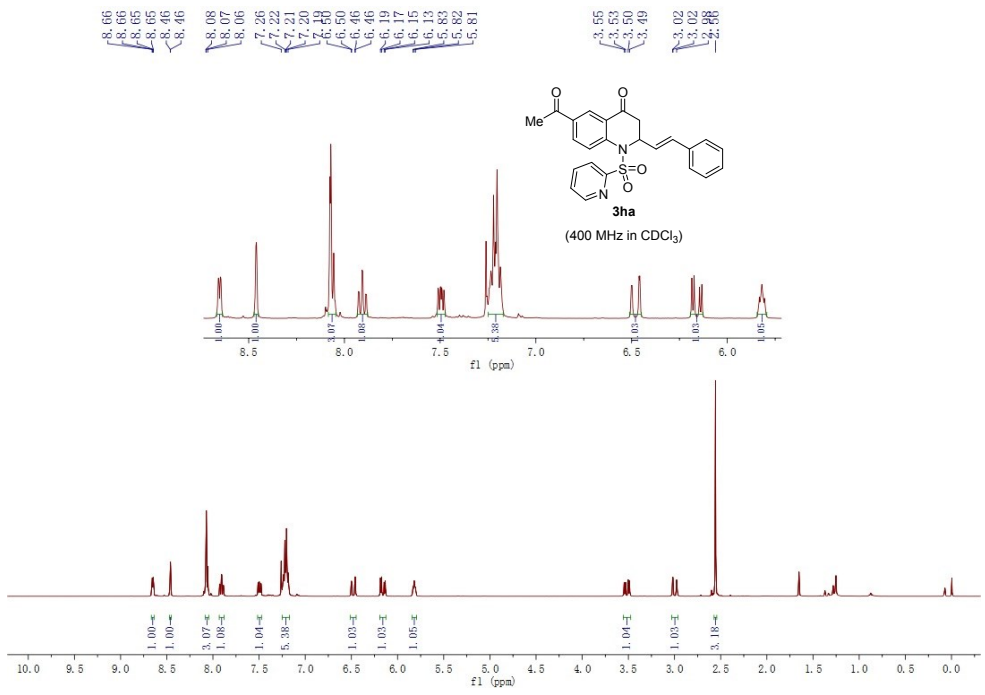
1.00
1.06
1.08
1.16
0.91
1.08
1.08
5.05
1.03
1.04
1.03
1.03
1.03
f1 (ppm)

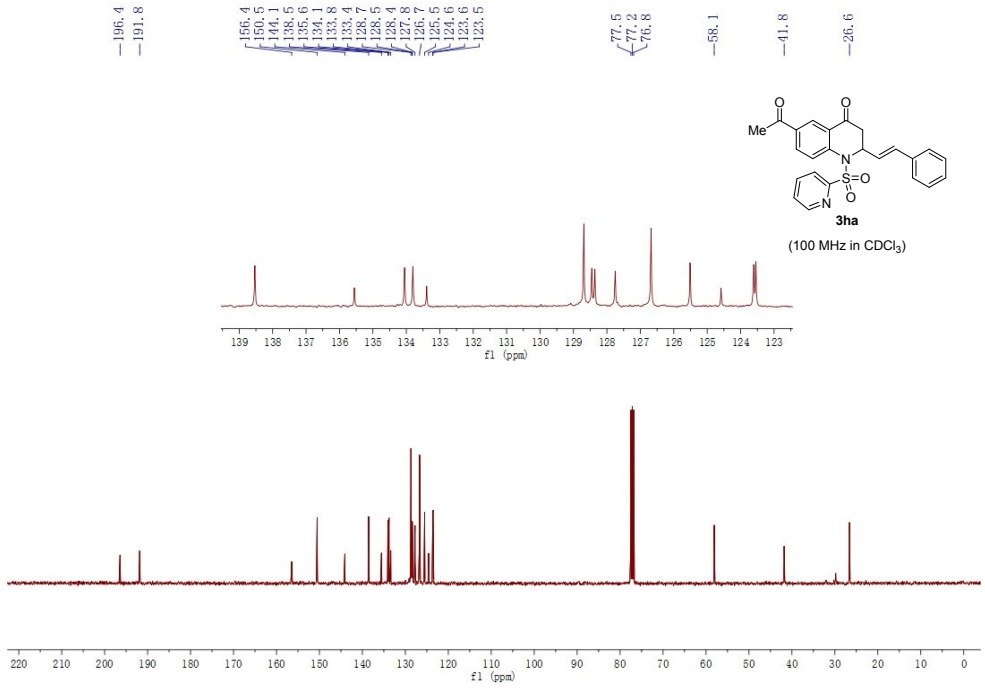

191.5
156.5
150.6
138.5
135.6
134.8
133.8
131.4
128.7
128.4
127.6
127.3
126.7
126.7
125.9
125.8
123.5
77.5
77.2
76.8
57.9
41.5
Cl
O
N
S
O
O
N
3ea
(100 MHz in CDCl3)
f1 (ppm)

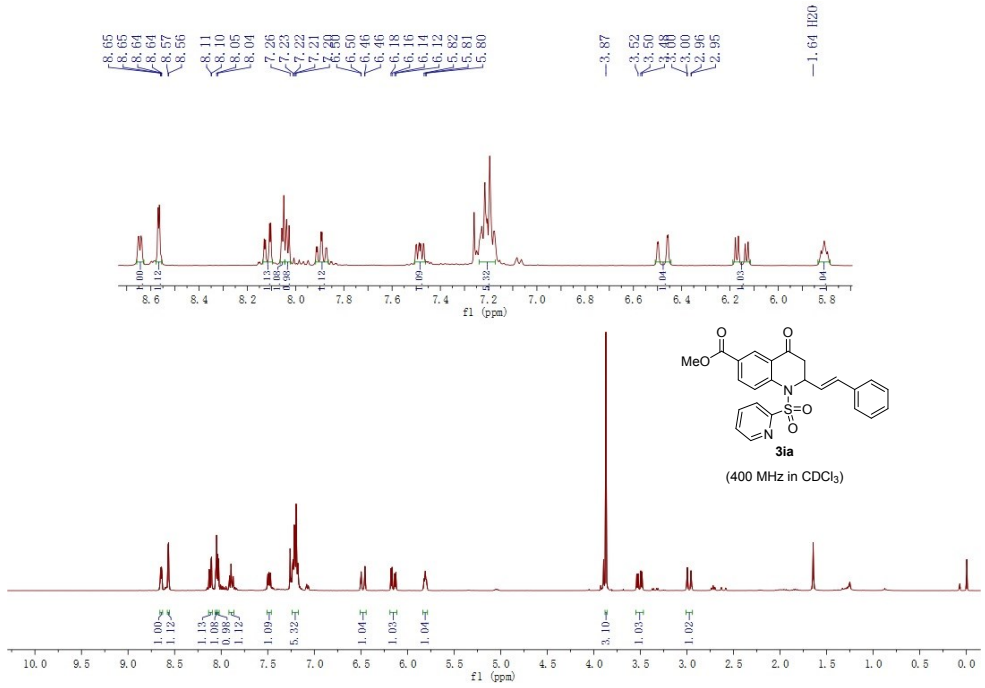

3fa
(400 MHz in CDCl3)
f1 (ppm)
3fa
(100 MHz in CDCl3)
f1 (ppm)

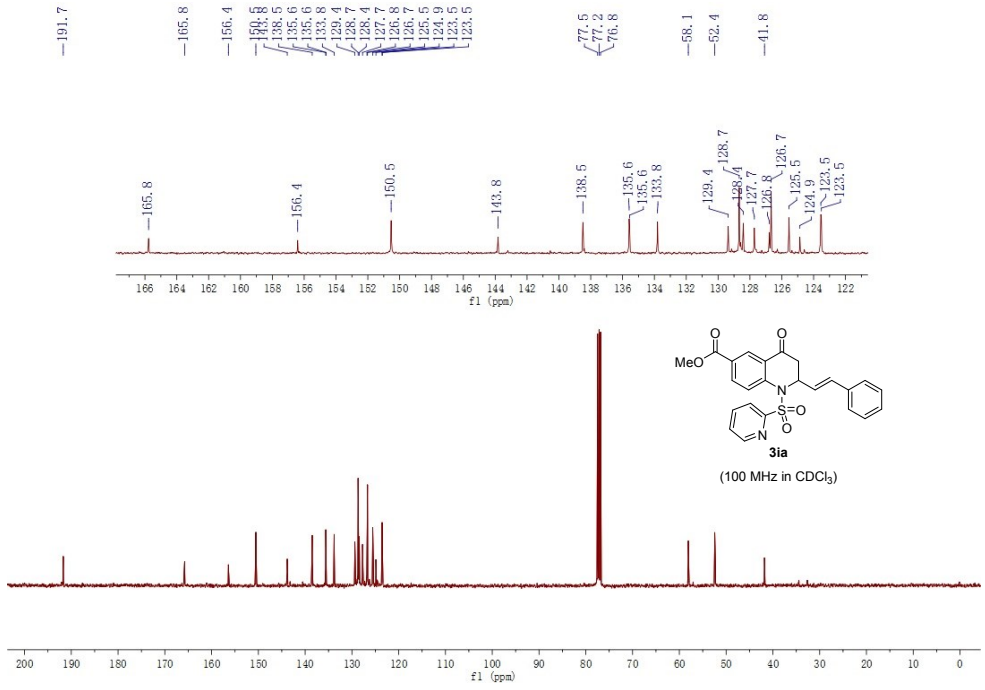

3ga
(400 MHz in CDCl3)
f1 (ppm)

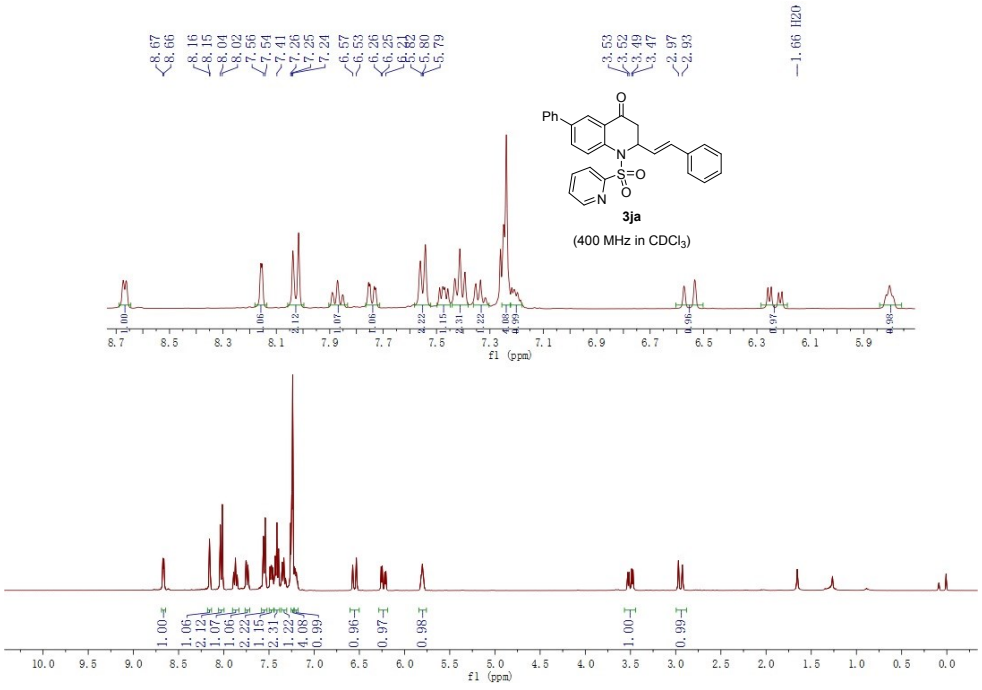

3ga
(100 MHz in CDCl3)
f1 (ppm)

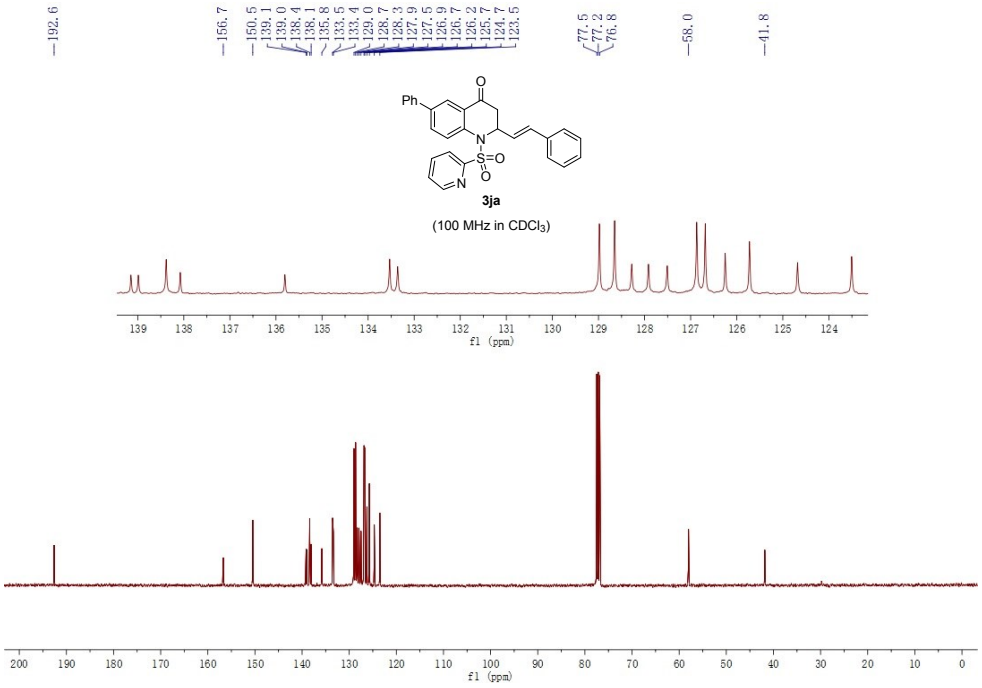

8.66
8.66
8.65
8.65
8.46
8.46
8.08
8.07
8.06
7.26
7.22
7.21
7.20
6.50
6.46
6.46
6.19
6.17
6.15
6.13
5.83
5.82
5.81
3.55
3.53
3.50
3.49
3.02
3.02
2.98
2.68
Me
O
O
N
S
O
O
N
3ha
(400 MHz in CDCl3)
1.00
1.00
3.07
1.08
4.04
5.38
1.03
1.03
1.05
8.5
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
1.00
1.00
3.07
1.08
1.04
5.38
1.03
1.03
1.05
1.04
1.03
3.18
10.0
9.5
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
f1 (ppm)

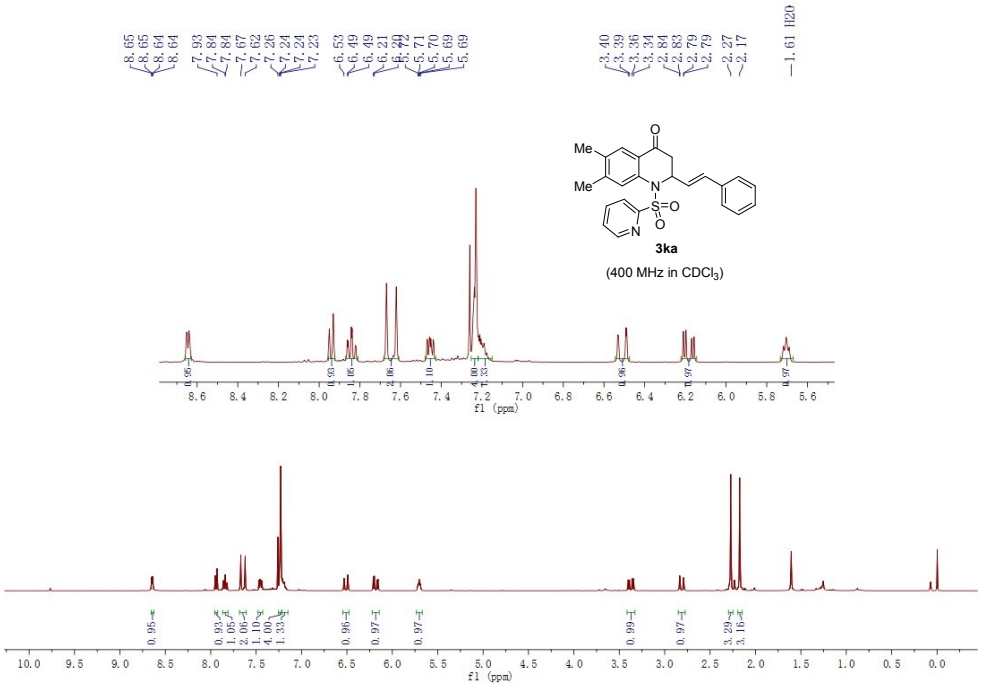

196.4
191.8
156.4
150.5
144.1
138.5
135.6
134.1
133.8
133.4
128.7
128.5
128.4
127.8
126.7
125.5
124.6
123.6
123.5
77.5
77.2
76.8
58.1
41.8
26.6
Me
O
O
N
S
O
O
N
3ha
(100 MHz in CDCl3)
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
3ia
(400 MHz in CDCl3)


MeO
3ia
(100 MHz in CDCl3)


8.67
8.66
8.16
8.15
8.04
8.02
7.56
7.54
7.41
7.26
7.25
7.24
6.57
6.53
6.26
6.25
5.82
5.80
5.79
3.53
3.52
3.49
3.47
2.97
2.93
1.66 H2O
Ph
O
N
S
O
O
N
3ja
(400 MHz in CDCl3)
f1 (ppm)
1.00
1.06
2.12
1.07
1.06
2.22
1.15
2.31
1.22
4.08
0.99
0.96
0.97
0.98
1.00
0.99


192.6
156.7
150.5
139.1
139.0
138.4
138.1
135.8
133.5
133.4
129.0
128.7
128.3
127.9
127.5
126.9
126.7
126.2
125.7
124.7
123.5
77.5
77.2
76.8
58.0
41.8
Ph
O
N
S
O
O
N
3ja
(100 MHz in CDCl3)
f1 (ppm)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8.64
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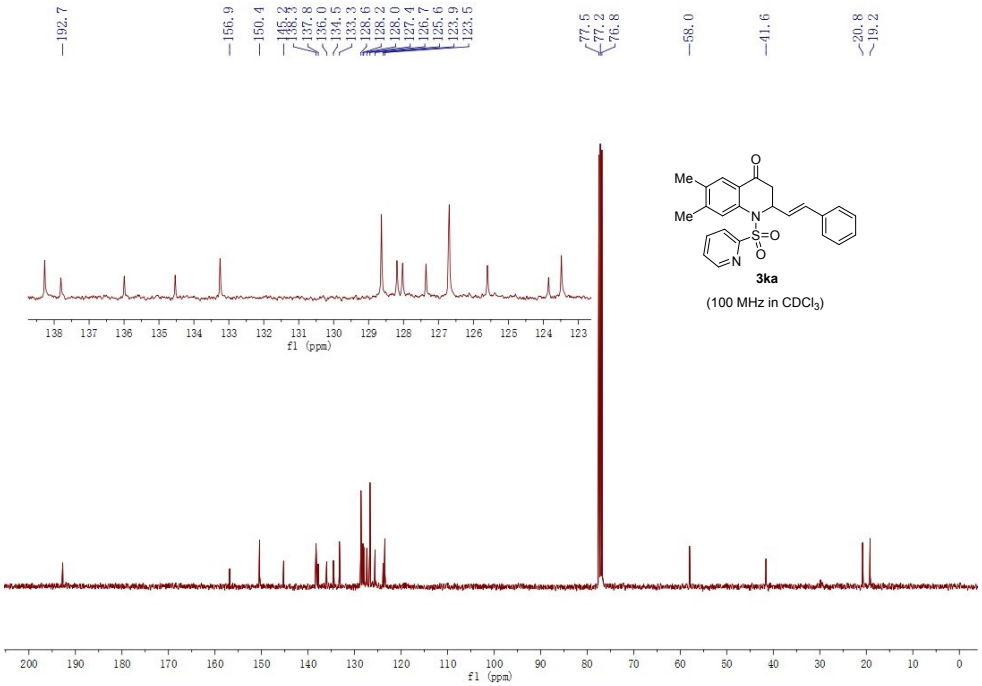
7.84
7.67
7.62
7.26
7.24
7.24
7.23
6.53
6.49
6.49
6.21
5.71
5.70
5.69
5.69
3.40
3.39
3.36
3.34
2.84
2.83
2.79
2.79
2.27
2.17
1.61 H2O
Me
Me
O
N
S=O
O
N
3ka
(400 MHz in CDCl3)
f1 (ppm)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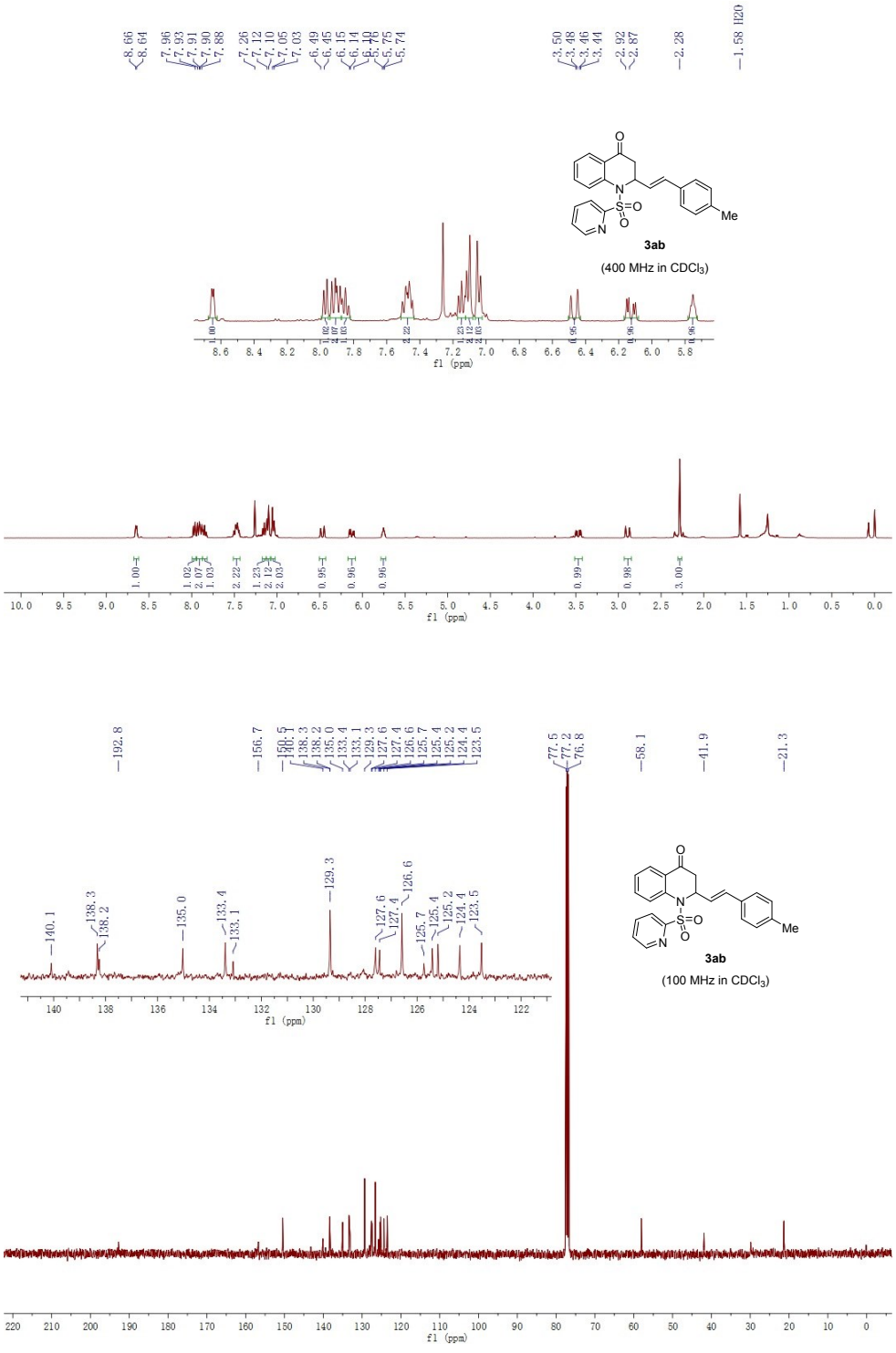
150.4
145.2
138.3
137.8
136.0
134.5
133.3
128.6
128.2
128.0
127.4
126.7
125.6
123.9
123.5
77.5
77.2
76.8
58.0
41.6
20.8
19.2
Me
Me
O
N
S=O
O
N
3ka
(100 MHz in CDCl3)
f1 (ppm)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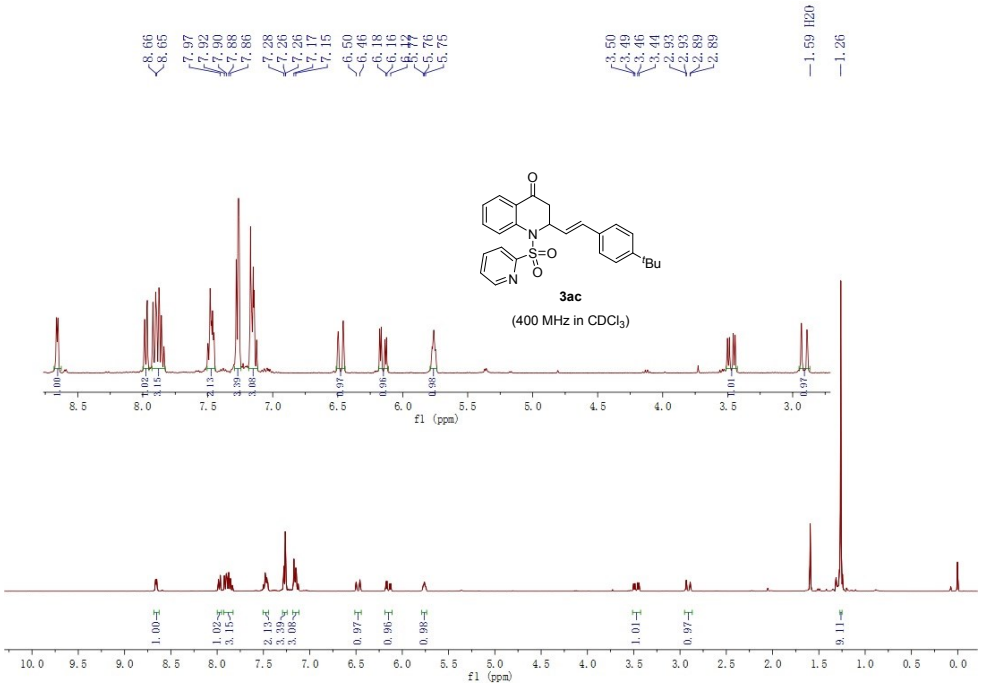
7.91
7.90
7.88
7.26
7.12
7.10
7.05
7.03
6.49
6.45
6.15
6.14
5.76
5.75
5.74
3.50
3.48
3.46
3.44
2.92
2.87
2.28
1.58 H2O
Me
3ab
(400 MHz in CDCl3)
f1 (ppm)
f1 (ppm)
192.8
156.7
150.5
140.1
138.3
138.2
135.0
133.4
133.1
129.3
127.6
127.4
126.6
125.7
125.4
125.2
124.4
123.5
77.5
77.2
76.8
58.1
41.9
21.3
Me
3ab
(100 MHz in CDCl3)
f1 (ppm)
f1 (ppm)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7.88
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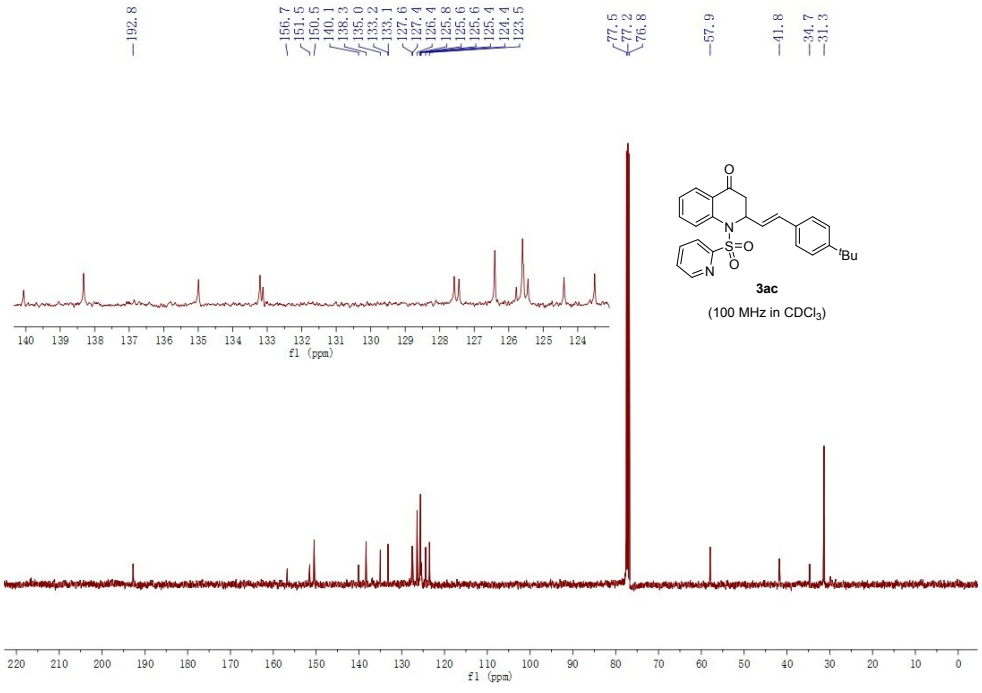
7.28
7.26
7.26
7.17
7.15
6.50
6.46
6.18
6.16
5.77
5.76
5.75
3.50
3.49
3.46
3.44
2.93
2.89
2.89
1.59 H2O
1.26
O
N
S=O
O
N
tBu
3ac
(400 MHz in CDCl3)
1.00
1.02
1.15
2.13
3.39
3.08
0.97
0.96
0.98
1.01
0.97
9.11
f1 (ppm)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140.1
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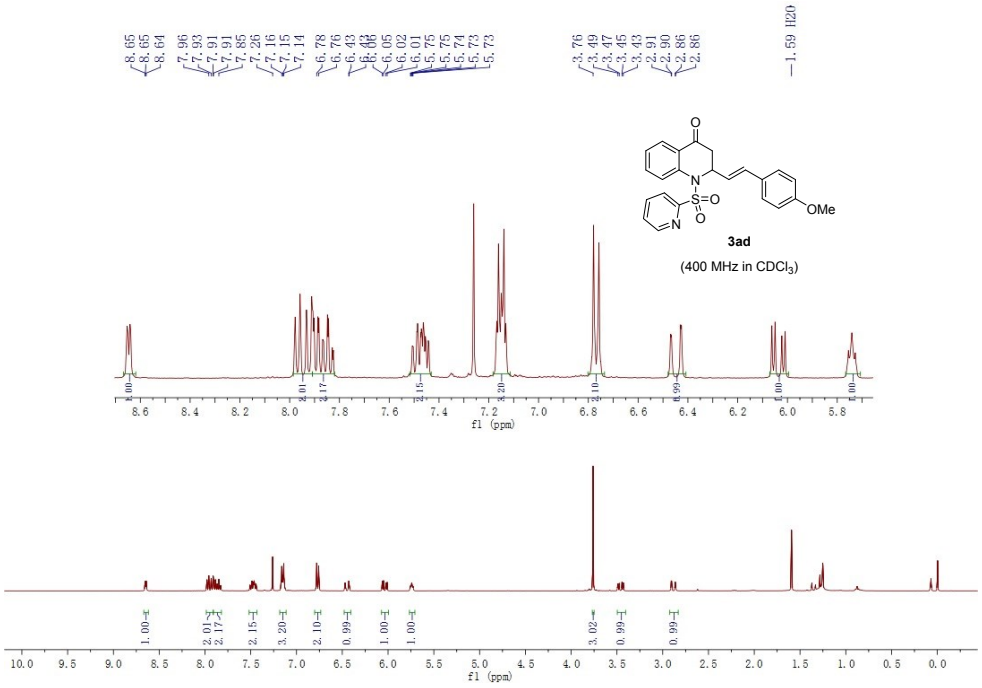
135.0
133.2
133.1
127.6
127.4
126.4
125.8
125.6
125.6
125.4
124.4
123.5
77.5
77.2
76.8
57.9
41.8
34.7
31.3
O
N
S=O
O
N
tBu
3ac
(100 MHz in CDCl3)
f1 (ppm)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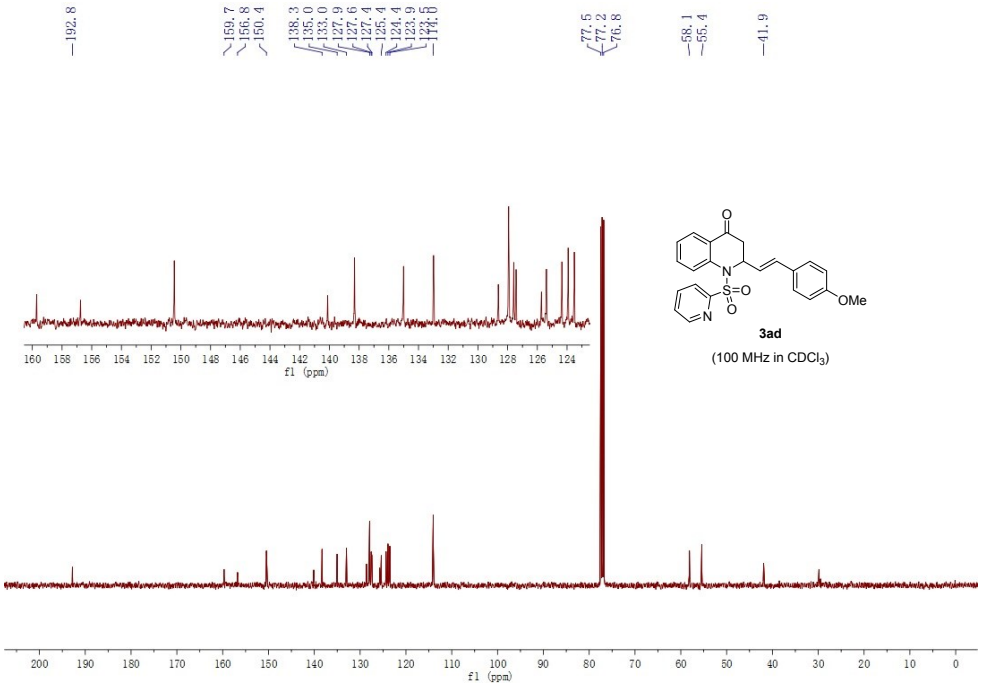
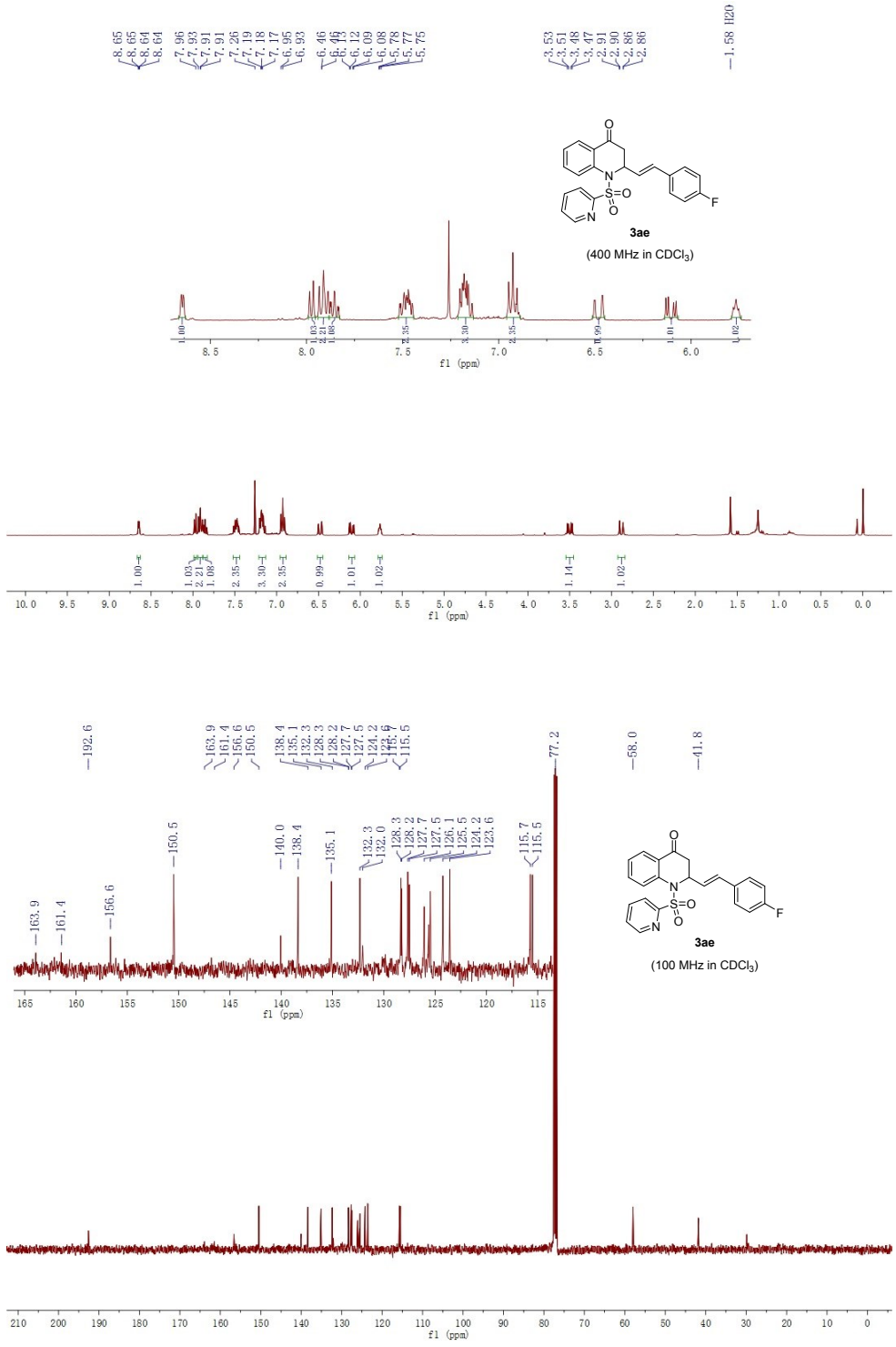
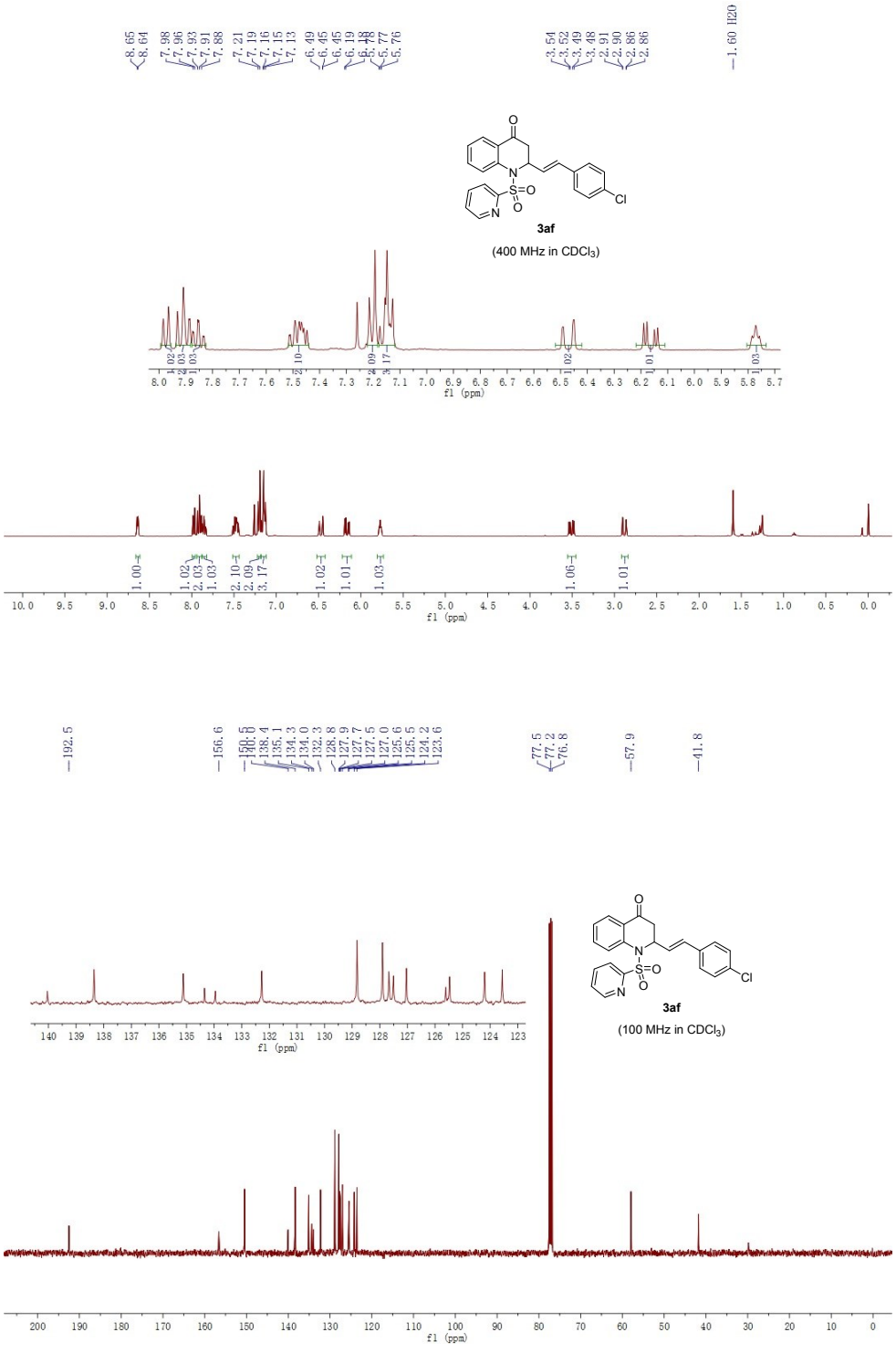
8.64
7.96
7.93
7.91
7.91
7.85
7.26
7.16
7.15
7.14
6.78
6.76
6.43
6.06
6.05
6.02
6.01
5.75
5.75
5.74
5.73
5.73
3.76
3.49
3.47
3.45
3.43
2.91
2.90
2.86
2.86
1.59 H2O
OMe
3ad
(400 MHz in CDCl3)
f1 (ppm)

1.00
2.01
2.17
2.15
3.20
2.10
0.99
1.00
1.00
3.02
0.99
0.99
f1 (ppm)


192.8
159.7
156.8
150.4
138.3
135.0
133.0
127.9
127.6
127.4
125.4
124.4
123.9
121.5
77.5
77.2
76.8
58.1
55.4
41.9
OMe
3ad
(100 MHz in CDCl3)
f1 (ppm)


3ae
(400 MHz in CDCl3)
f1 (ppm)
3ae
(100 MHz in CDCl3)
f1 (ppm)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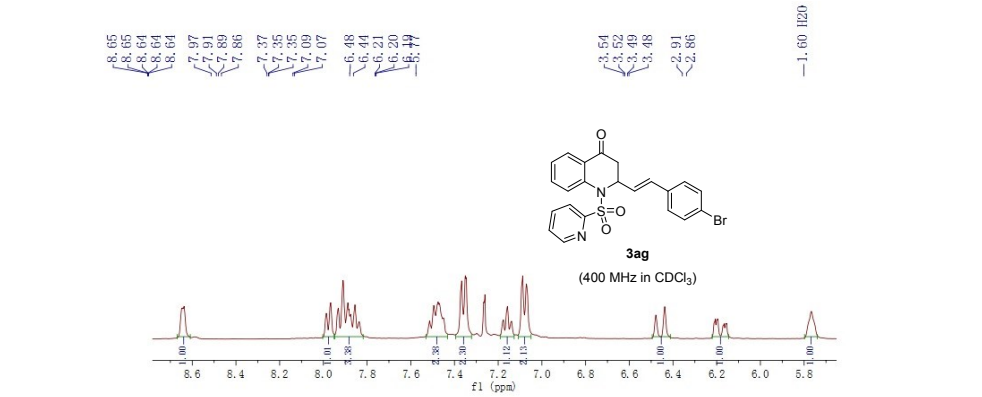
7.96
7.93
7.91
7.88
7.21
7.19
7.16
7.15
7.13
6.49
6.45
6.19
5.77
5.76
3.54
3.52
3.49
3.48
2.91
2.90
2.86
2.86
1.60
H2O
3af
(400 MHz in CDCl3)
f1 (ppm)
f1 (ppm)
192.5
156.6
150.5
140.0
138.4
135.1
134.3
134.0
132.3
128.8
127.9
127.7
127.5
127.0
125.6
125.5
124.2
123.6
77.5
77.2
76.8
57.9
41.8
3af
(100 MHz in CDCl3)
f1 (ppm)
f1 (ppm)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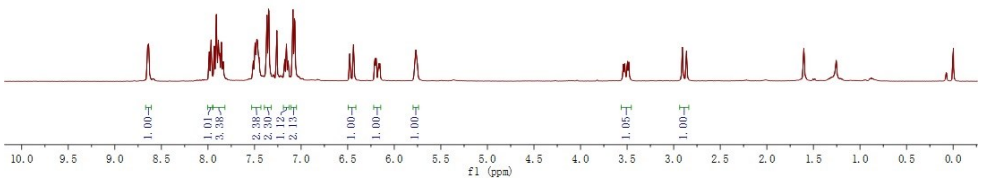
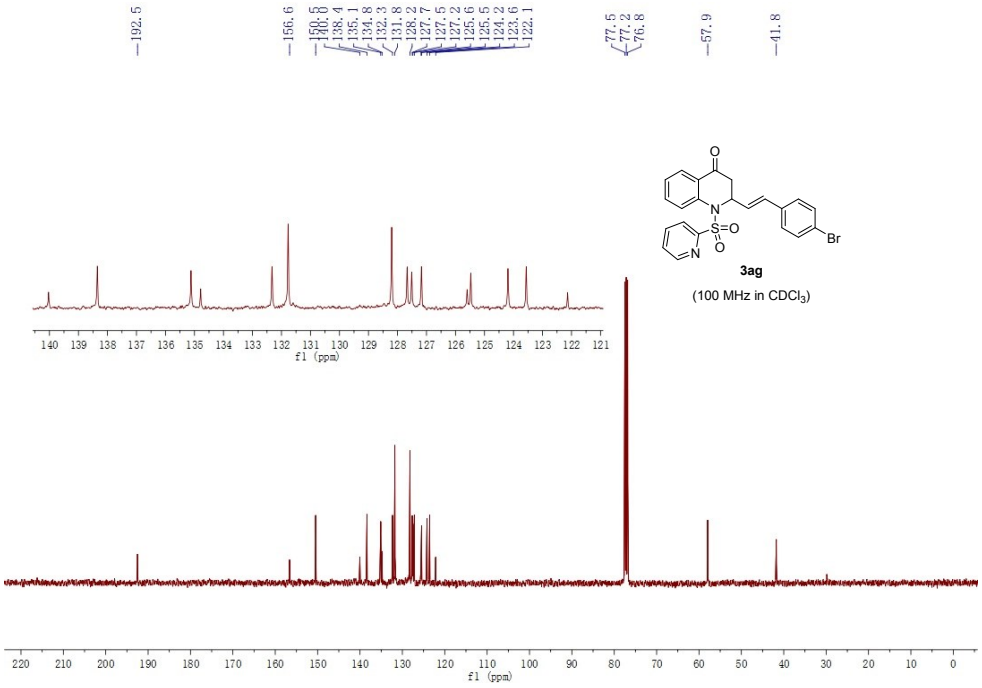
8.64
8.64
8.64
7.97
7.91
7.89
7.86
7.37
7.35
7.35
7.09
7.07
6.48
6.44
6.21
6.20
3.54
3.52
3.49
3.48
2.91
2.86
1.60
H2O
3ag
(400 MHz in CDCl3)
f1 (ppm)


f1 (ppm)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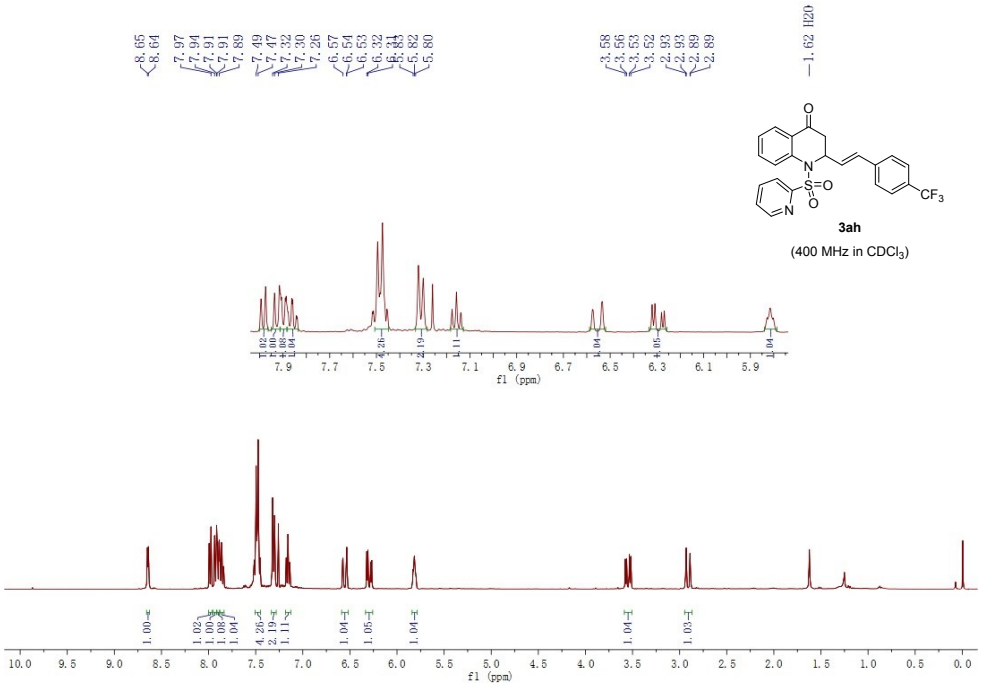
150.5
140.0
138.4
135.1
134.8
132.3
131.8
128.2
127.7
127.5
127.2
125.6
125.5
124.2
123.6
122.1
77.5
77.2
76.8
57.9
41.8
3ag
(100 MHz in CDCl3)
f1 (ppm)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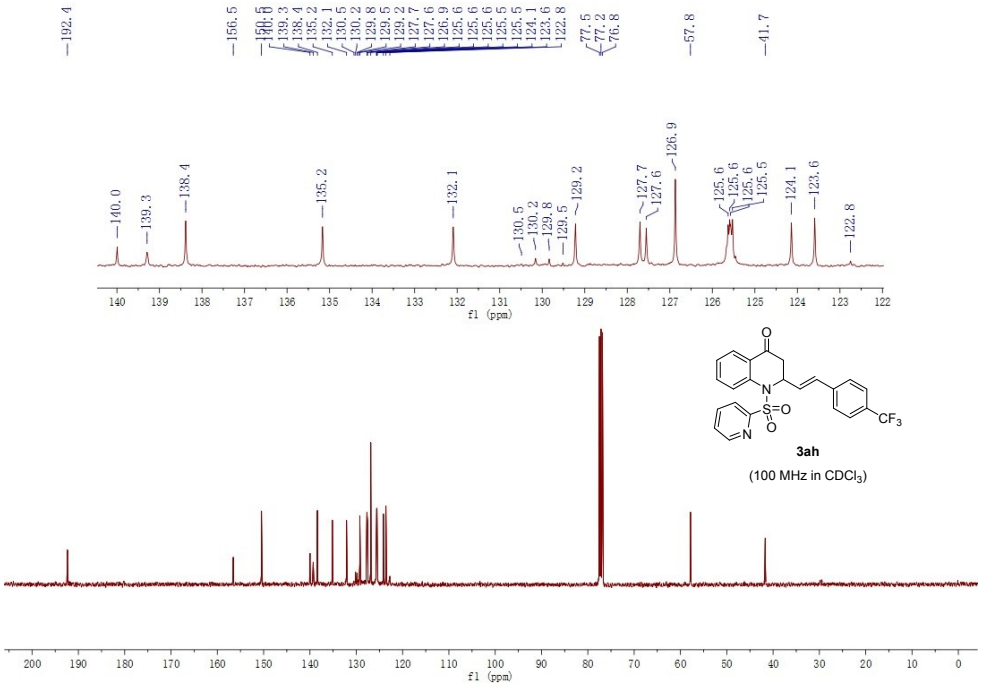
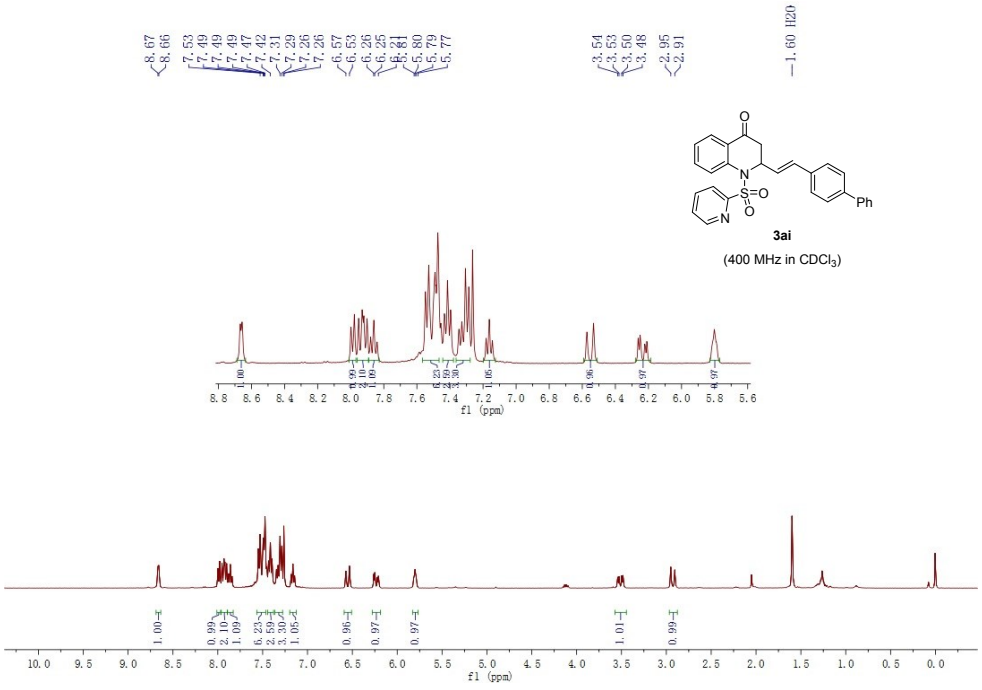
(400 MHz in CDCl3)
f1 (ppm)


3ah
(100 MHz in CDCl3)
f1 (ppm)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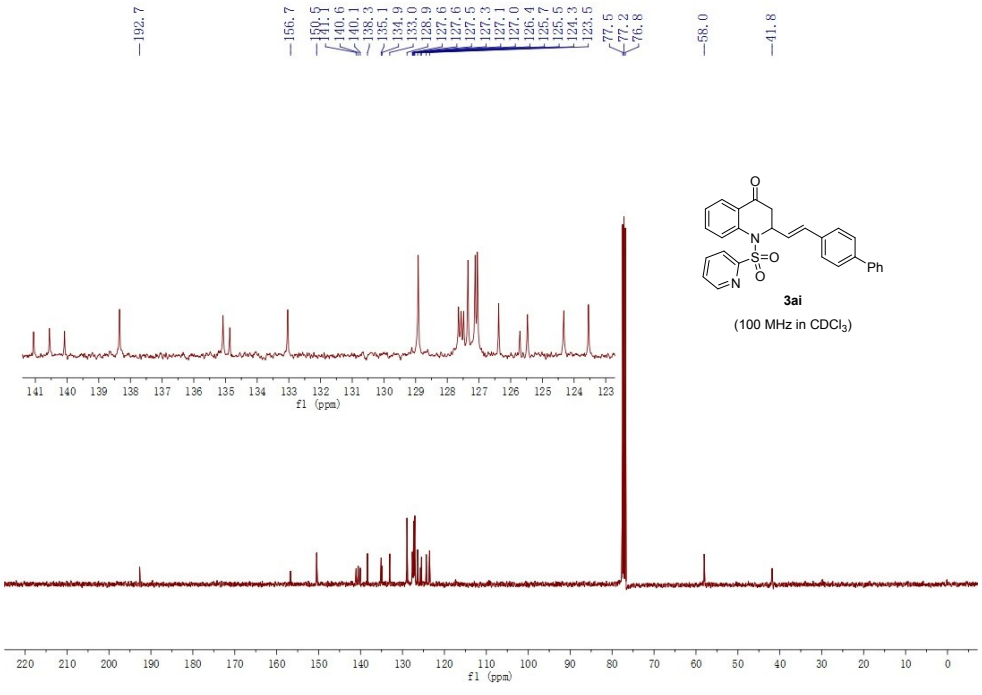
7.26
7.26
6.57
6.53
6.26
6.25
6.21
6.21
5.80
5.79
5.77
3.54
3.53
3.50
3.48
2.95
2.91
1.60 H2O
Ph
3ai
(400 MHz in CDCl3)
f1 (ppm)

f1 (ppm)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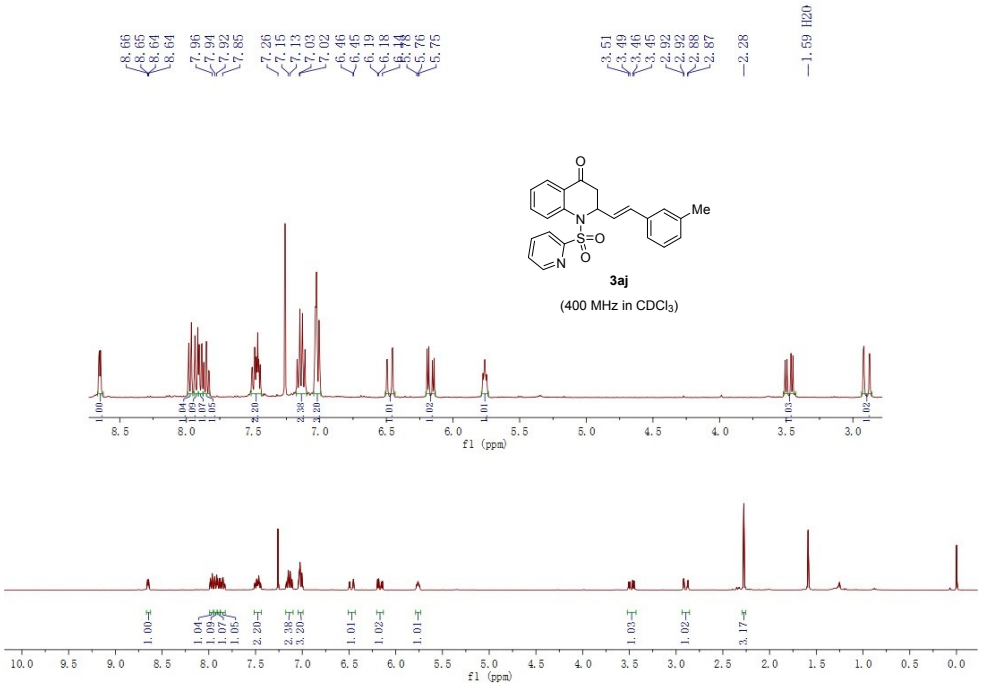
135.1
134.9
133.0
128.9
127.6
127.6
127.5
127.3
127.1
127.0
126.4
125.7
125.5
124.3
123.5
77.5
77.2
76.8
58.0
41.8
Ph
3ai
(100 MHz in CDCl3)
f1 (ppm)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8.64
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7.85
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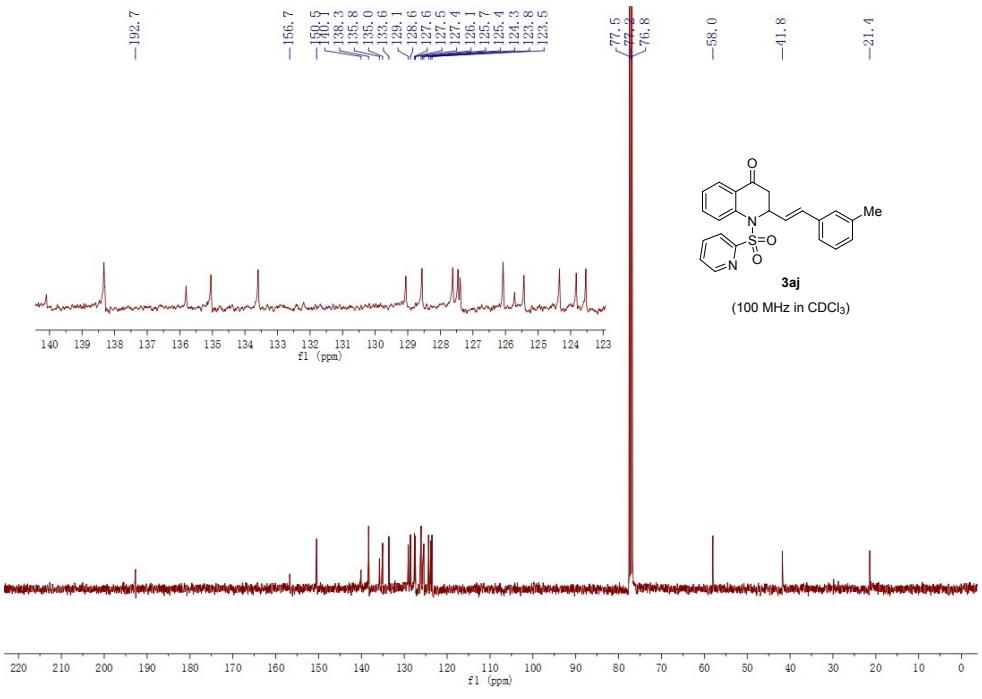
7.15
7.13
7.03
7.02
6.46
6.45
6.19
6.18
5.76
5.75
3.51
3.49
3.46
3.45
2.92
2.92
2.88
2.87
2.28
1.59 H2O
Me
3aj
(400 MHz in CDCl3)
f1 (ppm)

f1 (ppm)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133.6
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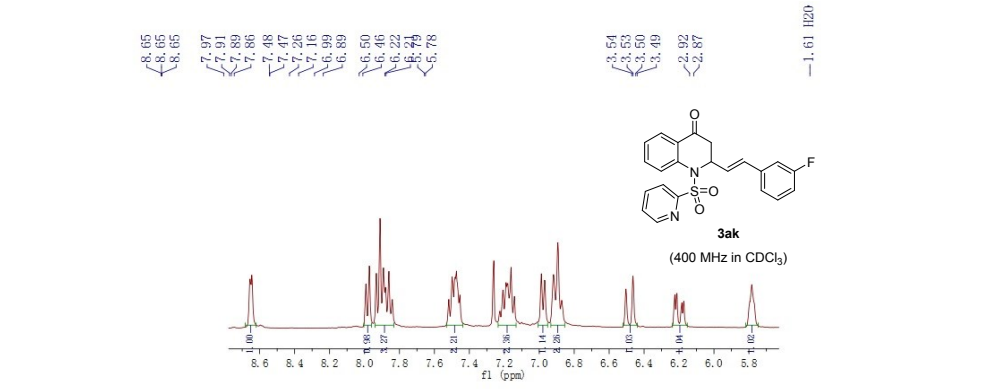
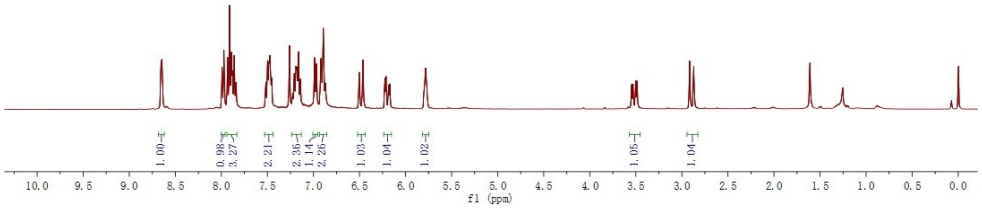
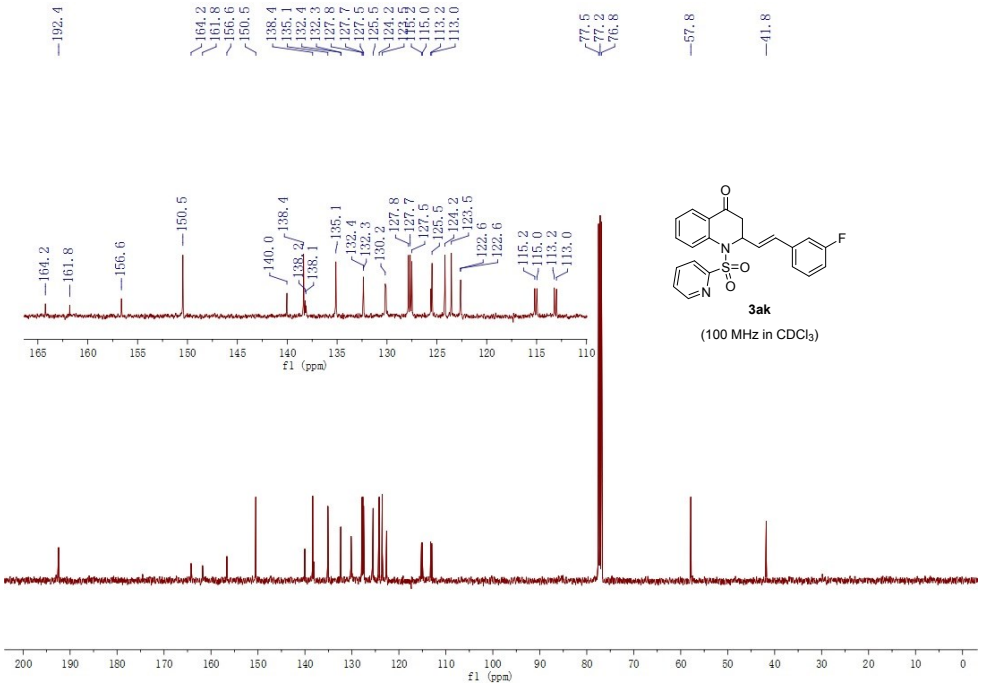
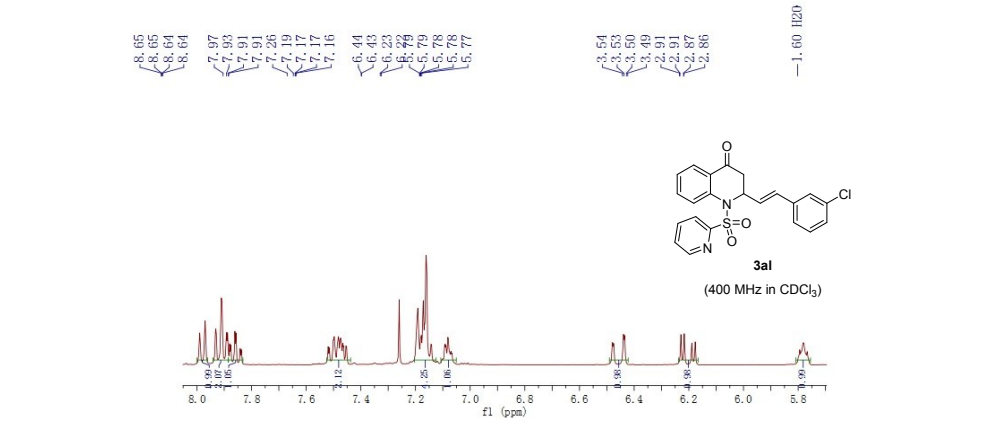
128.6
127.6
127.5
127.4
126.1
125.7
125.4
124.3
123.8
123.5
77.5
76.8
58.0
41.8
21.4
Me
3aj
(100 MHz in CDCl3)
f1 (ppm)


3ak
(400 MHz in CDCl3)
f1 (ppm)


f1 (ppm)


3ak
(100 MHz in CDCl3)
f1 (ppm)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8.64
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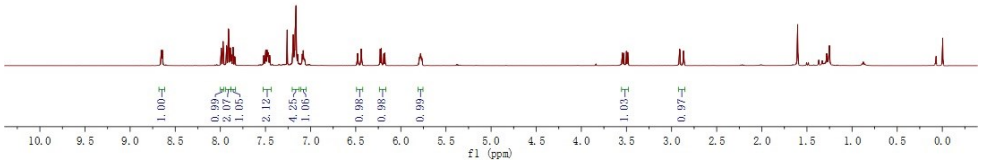
7.93
7.91
7.91
7.26
7.19
7.17
7.17
7.16
6.44
6.43
6.23
5.79
5.78
5.77
3.54
3.53
3.50
3.49
2.91
2.91
2.87
2.86
1.60 H2O
Cl
3al
(400 MHz in CDCl3)
f1 (ppm)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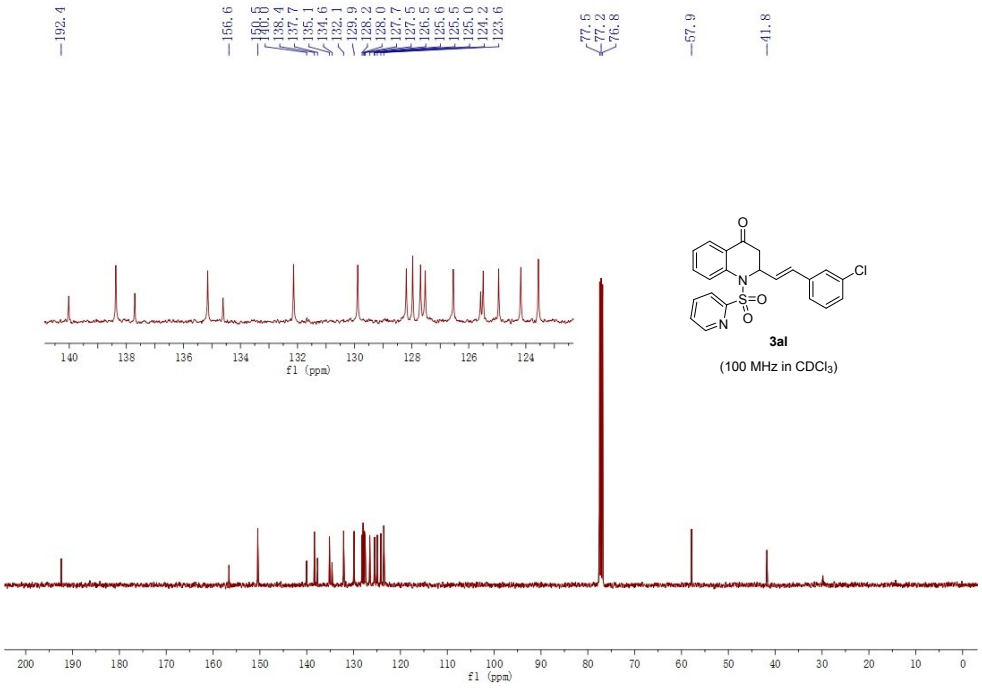
4.25
1.06
0.98
0.98
0.99
1.03
0.97
f1 (ppm)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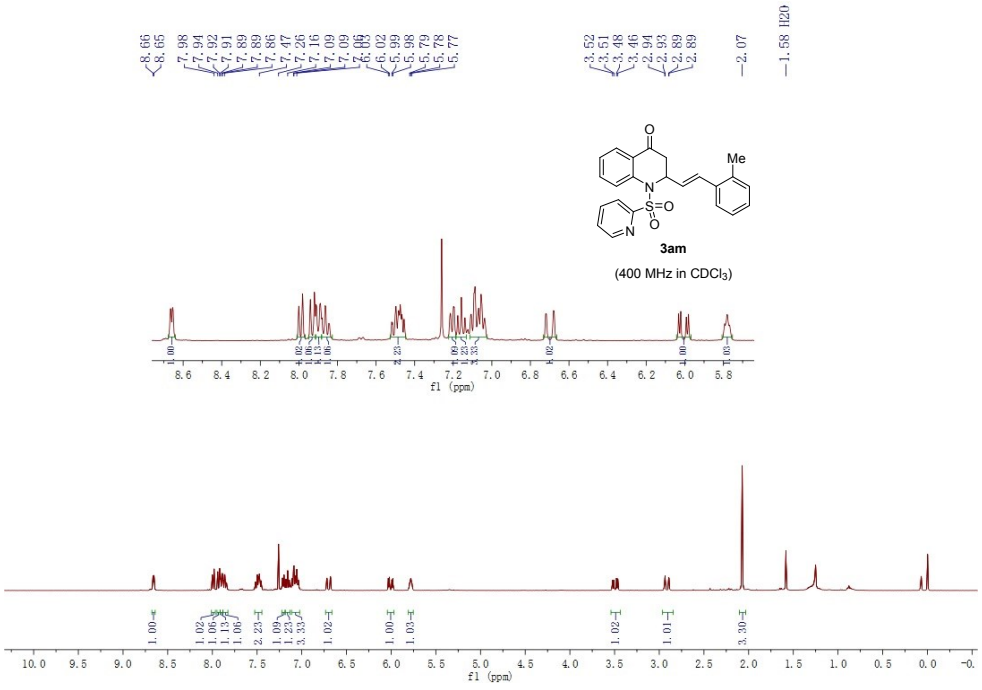
140.0
138.4
137.7
135.1
134.6
132.1
129.9
128.2
128.0
127.7
127.5
126.5
125.6
125.5
125.0
124.2
123.6
77.5
77.2
76.8
57.9
41.8
Cl
3al
(100 MHz in CDCl3)
f1 (ppm)


8.66
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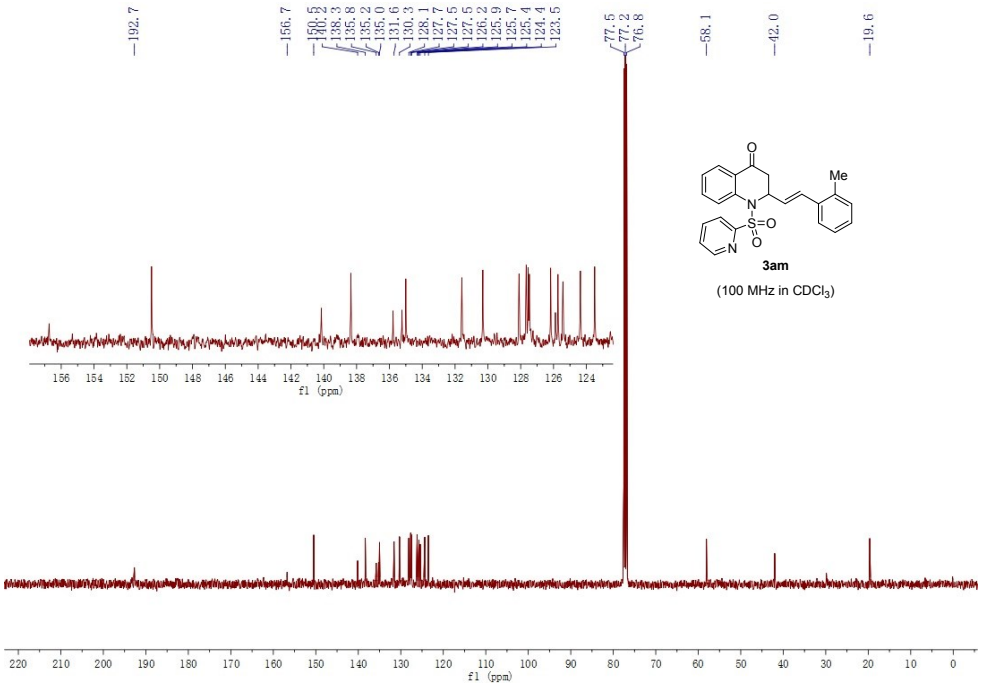
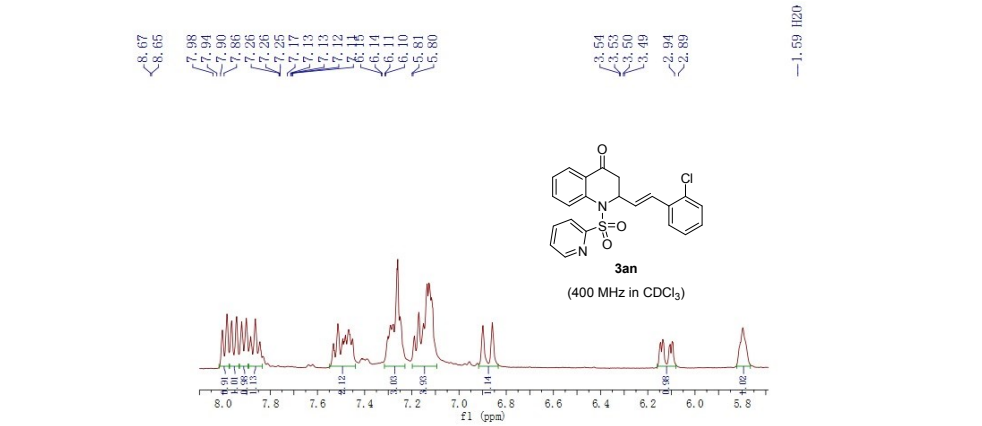
7.92
7.91
7.89
7.89
7.86
7.47
7.26
7.16
7.09
7.09
6.02
5.99
5.98
5.79
5.78
5.77
3.52
3.51
3.48
3.46
2.94
2.93
2.89
2.89
2.07
1.58
H20
Me
3am
(400 MHz in CDCl3)
f1 (ppm)

f1 (ppm)


192.7
156.7
150.5
140.2
138.3
135.8
135.2
135.0
131.6
130.3
128.1
127.7
127.5
127.5
126.2
125.9
125.7
125.4
124.4
123.5
77.5
77.2
76.8
58.1
42.0
19.6
Me
3am
(100 MHz in CDCl3)
f1 (ppm)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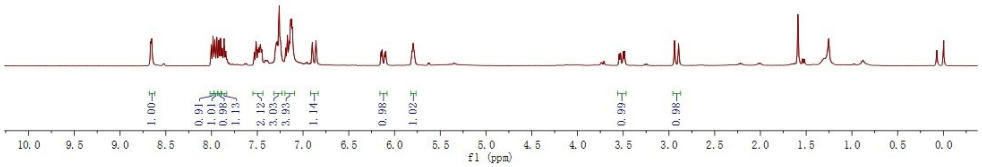
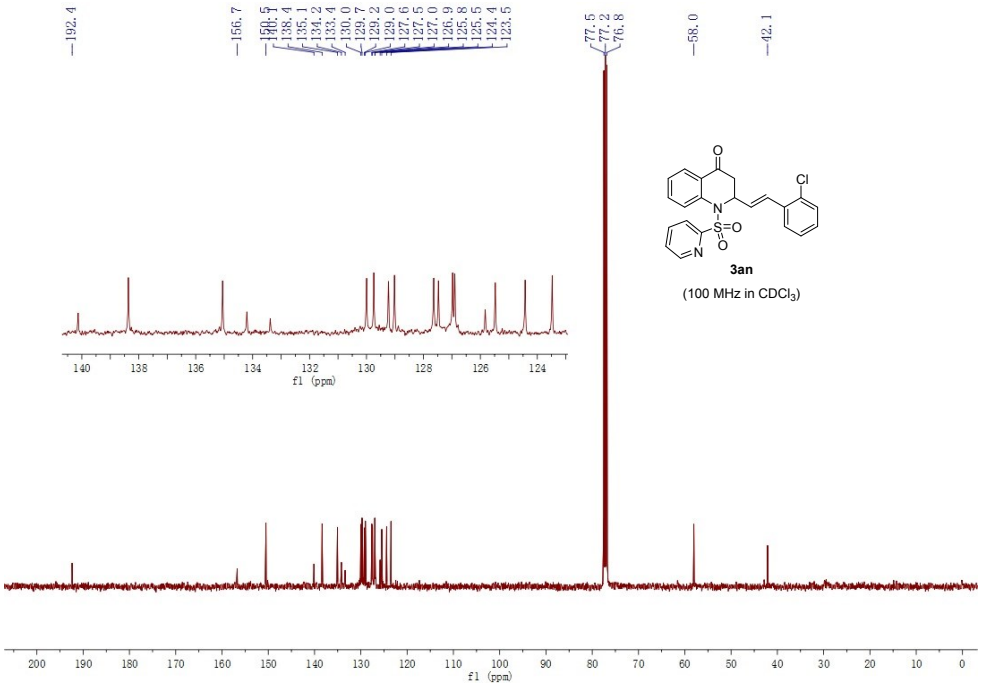
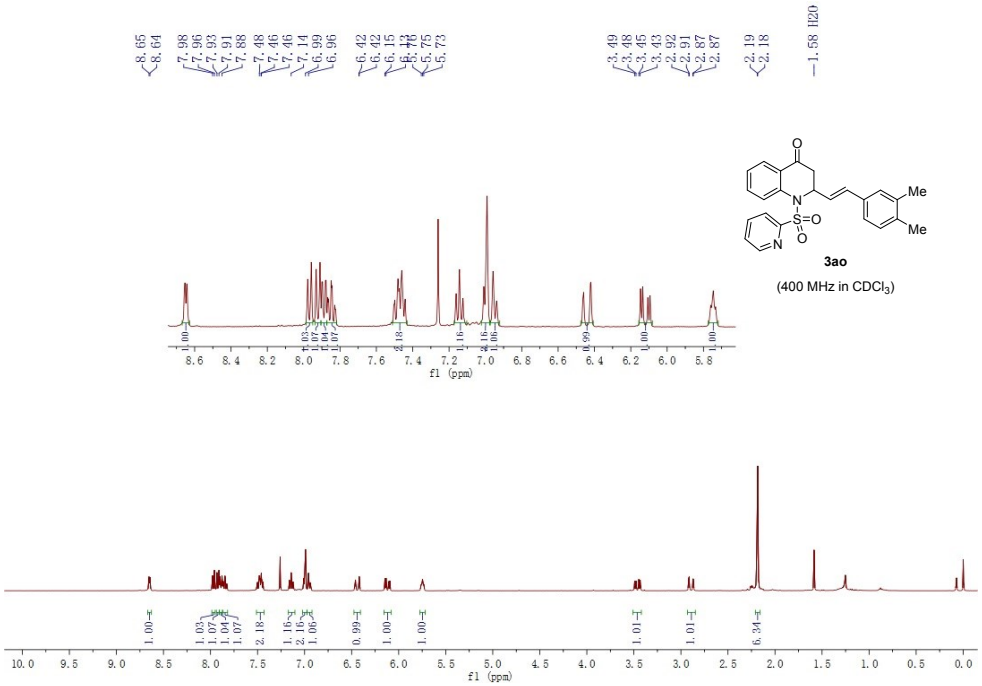
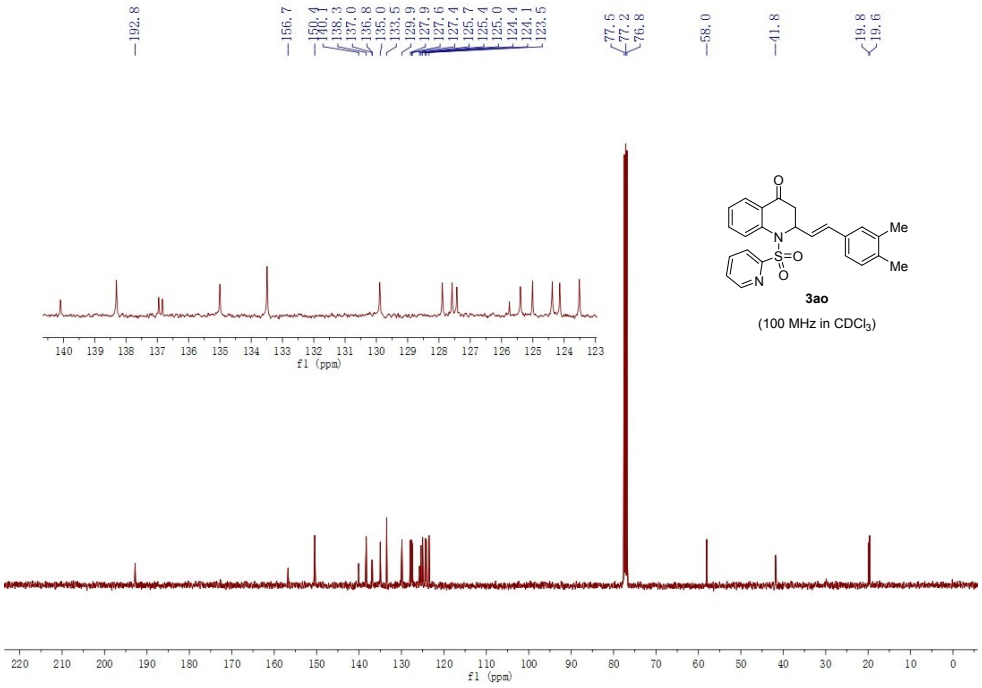
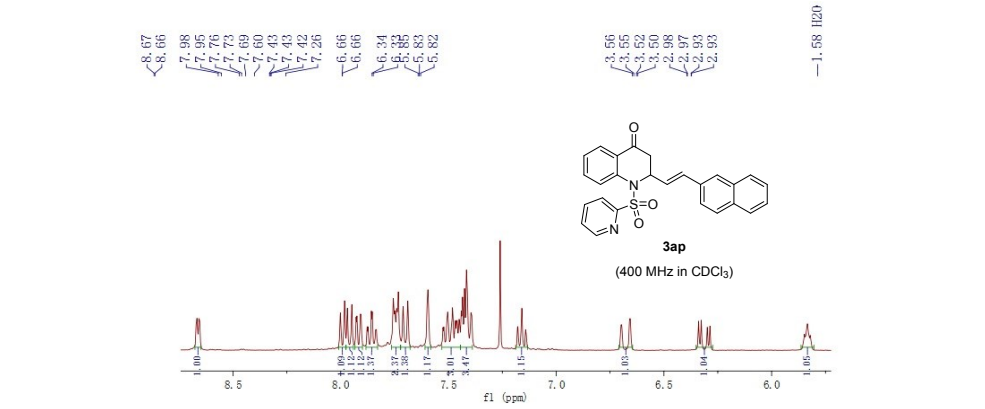
7.26
7.25
7.17
7.13
7.12
6.15
6.14
6.11
6.10
5.81
5.80
3.54
3.53
3.50
3.49
2.94
2.89
1.59 H2O
Cl
O
N
S
O
O
N
3an
(400 MHz in CDCl3)
f1 (ppm)

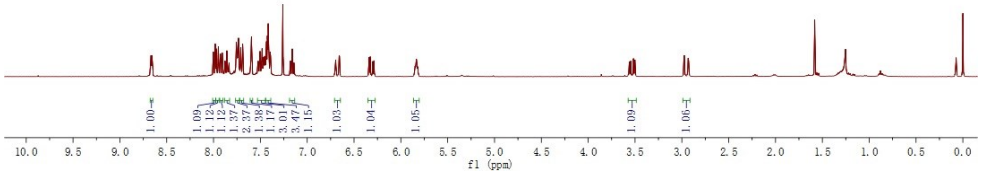

1.00
0.91
1.01
0.98
1.13
2.12
3.03
3.93
1.14
0.98
1.02
0.99
0.98
f1 (ppm)

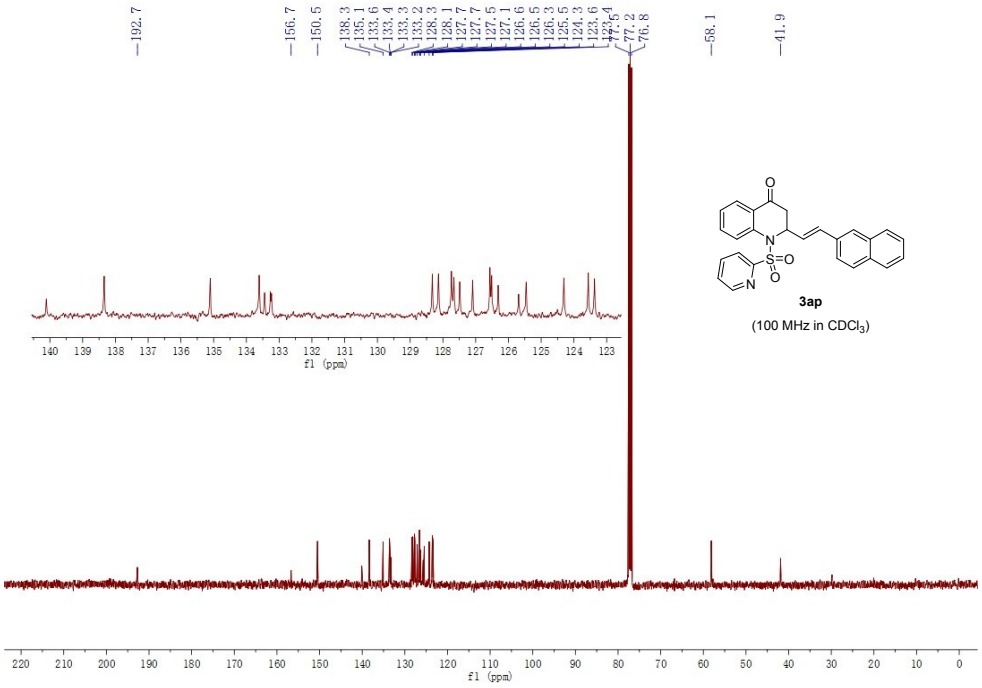

192.4
156.7
150.5
140.1
138.4
135.1
134.2
133.4
130.0
129.7
129.2
129.0
127.6
127.5
127.0
126.9
125.8
125.5
124.4
123.5
77.5
77.2
76.8
58.0
42.1
Cl
O
N
S
O
O
N
3an
(100 MHz in CDCl3)
f1 (ppm)

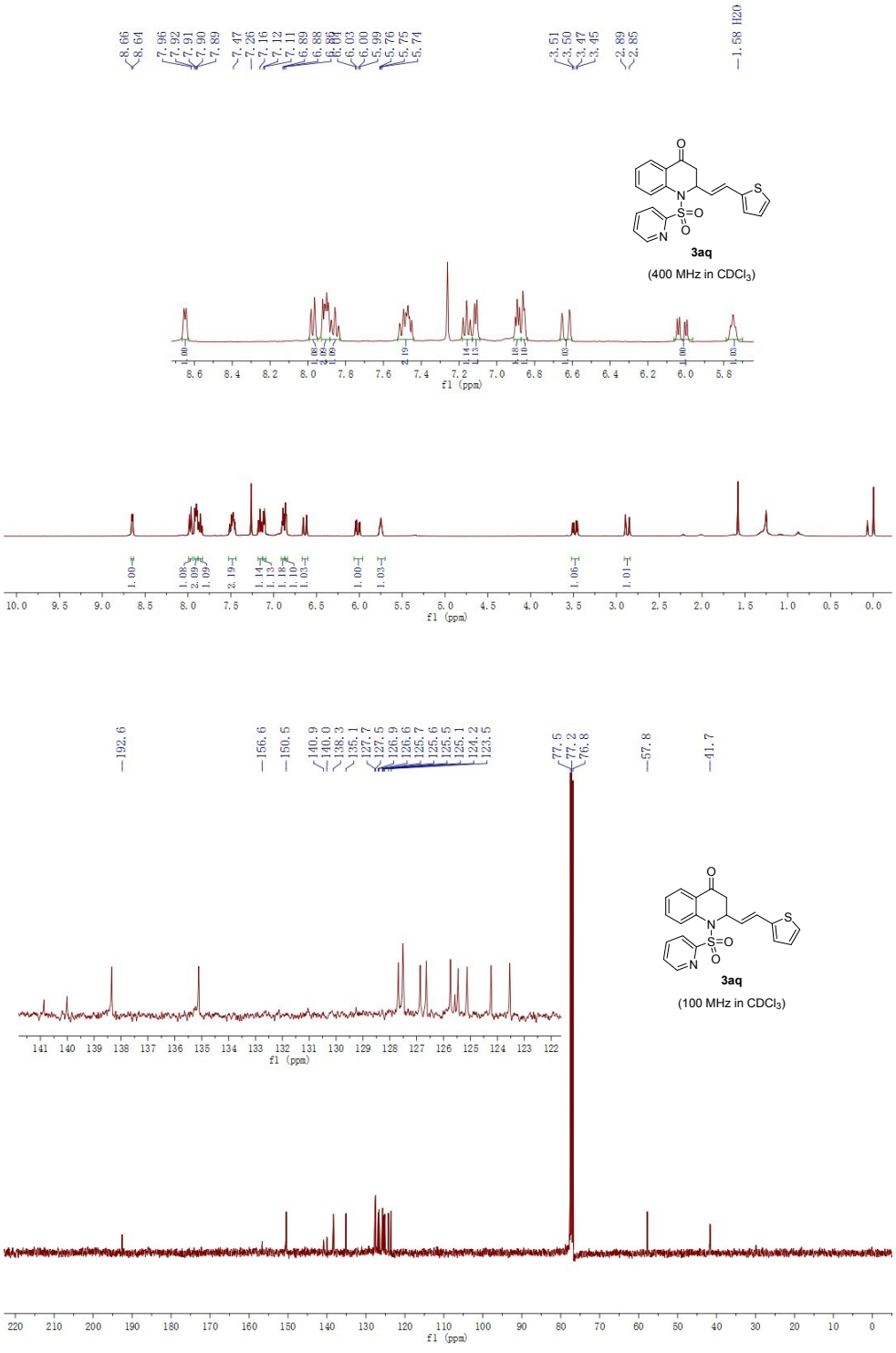

3ao
(400 MHz in CDCl3)
f1 (ppm)

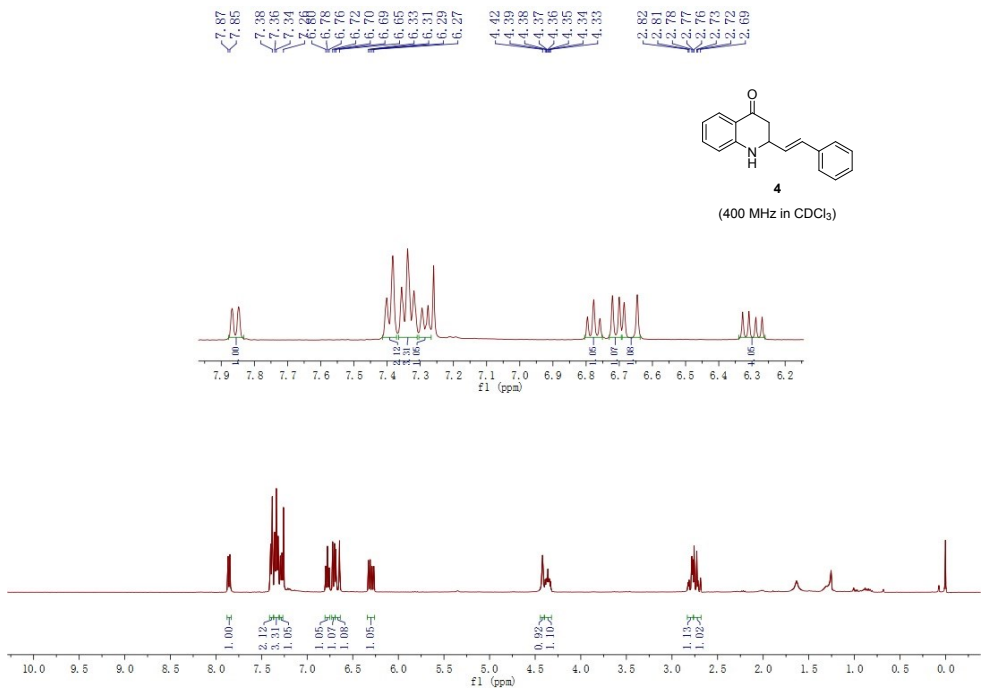

3ao
(100 MHz in CDCl3)
f1 (ppm)

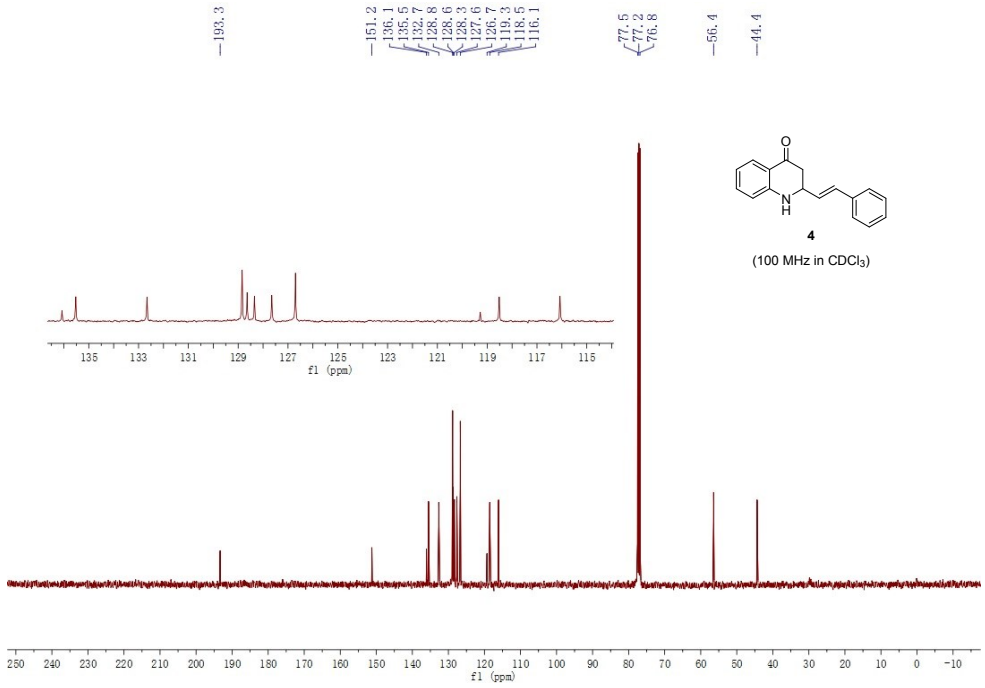

8.67
8.66
7.98
7.95
7.76
7.73
7.69
7.60
7.43
7.43
7.42
7.26
6.66
6.66
6.34
6.33
5.85
5.83
5.82
3.56
3.55
3.52
3.50
2.98
2.97
2.93
2.93
1.58 H2O
3ap
(400 MHz in CDCl3)
f1 (ppm)

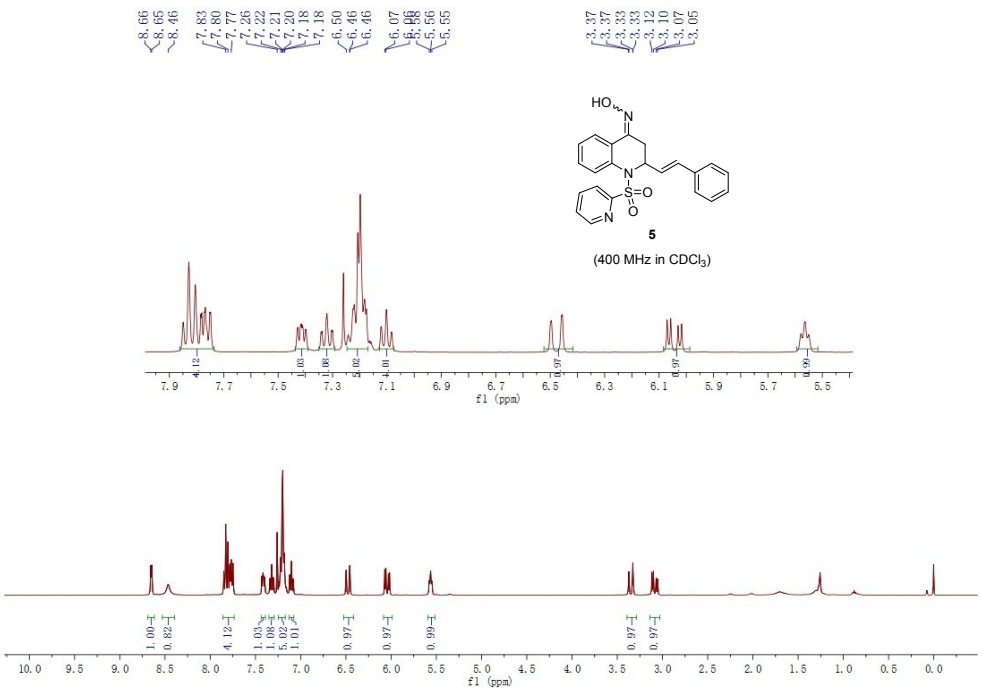

f1 (ppm)

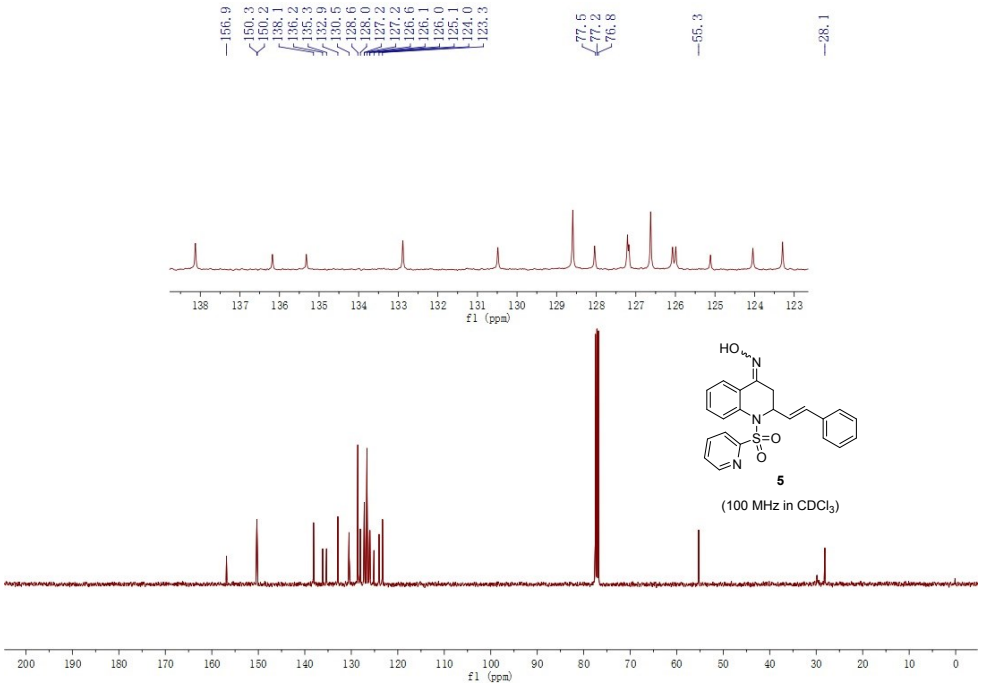

192.7
156.7
150.5
138.3
135.1
133.6
133.4
133.3
133.2
128.3
128.1
127.7
127.7
127.5
127.1
126.6
126.5
126.3
125.5
124.3
123.6
77.2
76.8
58.1
41.9
3ap
(100 MHz in CDCl3)
f1 (ppm)

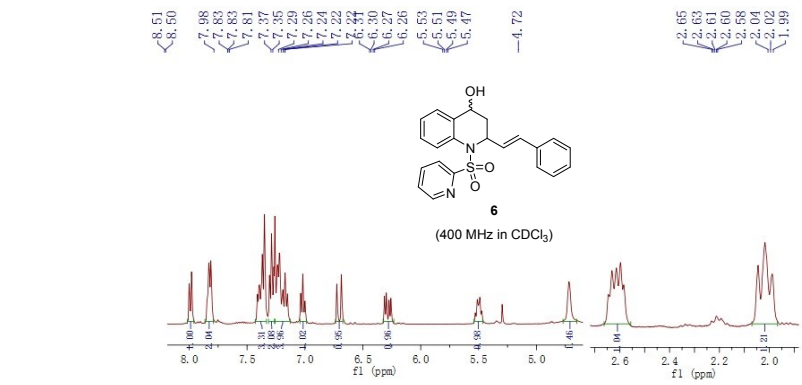

8.66
8.64
7.96
7.92
7.91
7.90
7.89
7.47
7.26
7.16
7.12
7.11
6.89
6.88
6.84
6.03
6.00
5.99
5.76
5.75
5.74
3.51
3.50
3.47
3.45
2.89
2.85
1.58 H2O
3aq
(400 MHz in CDCl3)
f1 (ppm)
f1 (ppm)
192.6
156.6
150.5
140.9
140.0
138.3
135.1
127.7
127.5
126.9
126.6
125.7
125.6
125.5
125.1
124.2
123.5
77.5
77.2
76.8
57.8
41.7
3aq
(100 MHz in CDCl3)
f1 (ppm)
f1 (ppm)

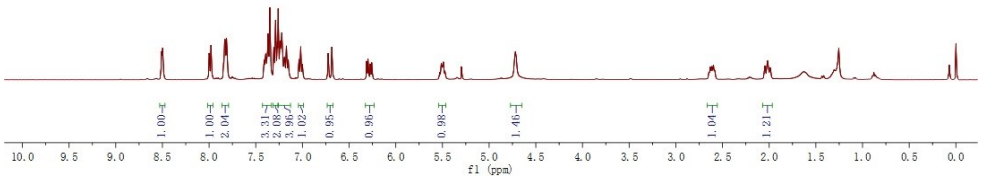

7.87
7.85
7.38
7.36
7.34
6.78
6.76
6.72
6.70
6.69
6.65
6.33
6.31
6.29
6.27
4.42
4.39
4.38
4.37
4.36
4.35
4.34
4.33
2.82
2.81
2.78
2.77
2.76
2.73
2.72
2.69
O
N
H
4
(400 MHz in CDCl3)
f1 (ppm)

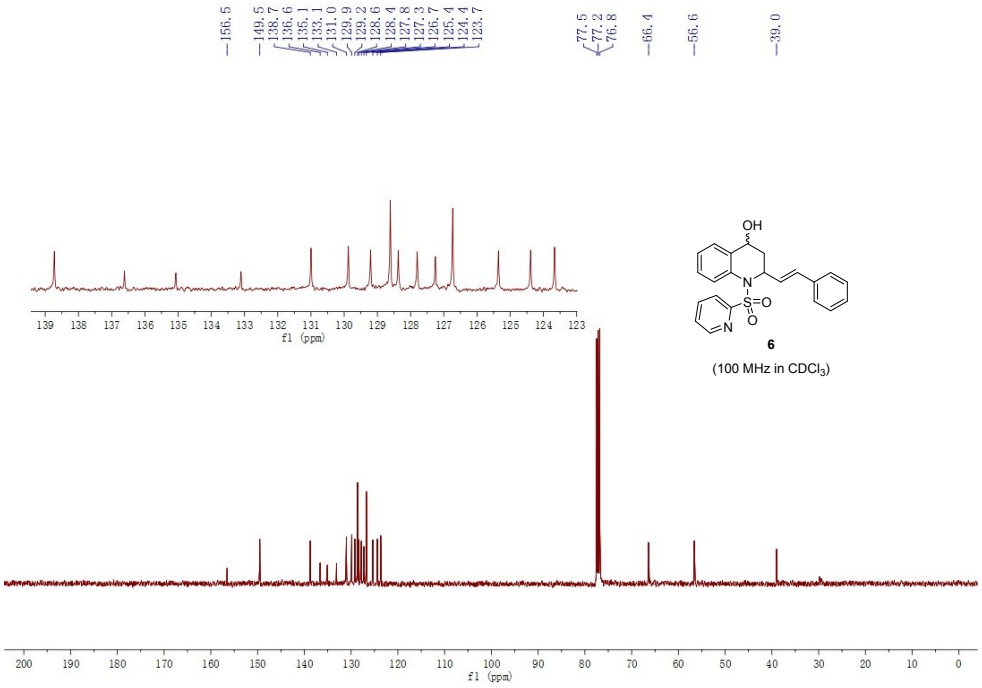

193.3
151.2
136.1
135.5
132.7
128.8
128.6
128.3
127.6
126.7
119.3
118.5
116.1
77.5
77.2
76.8
56.4
44.4
O
N
H
4
(100 MHz in CDCl3)
f1 (ppm)


8.66
8.65
8.46
7.83
7.80
7.77
7.26
7.22
7.21
7.20
7.18
6.50
6.46
6.46
6.07
5.56
5.55
3.37
3.37
3.33
3.33
3.12
3.10
3.07
3.05
HO
N
N
S=O
O
N
5
(400 MHz in CDCl3)
f1 (ppm)
f1 (ppm)

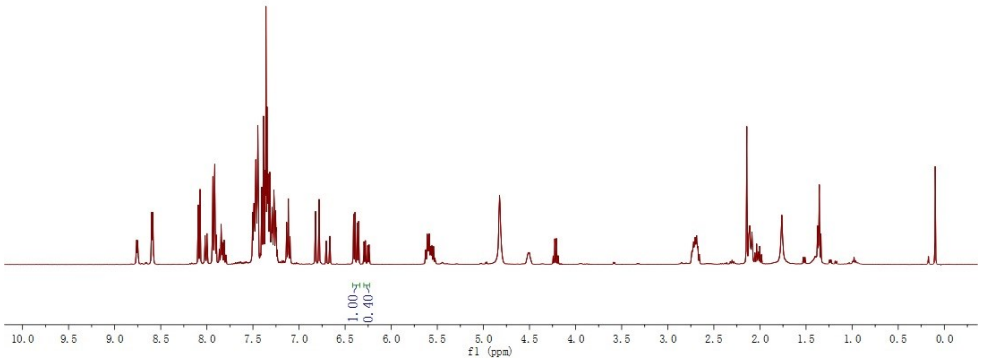

156.9
150.3
150.2
138.1
136.2
135.3
132.9
130.5
128.6
128.0
127.2
127.2
126.6
126.1
126.0
125.1
124.0
123.3
77.5
77.2
76.8
55.3
28.1
f1 (ppm)
HO
N
N
S=O
O
N
5
(100 MHz in CDCl3)
f1 (ppm)

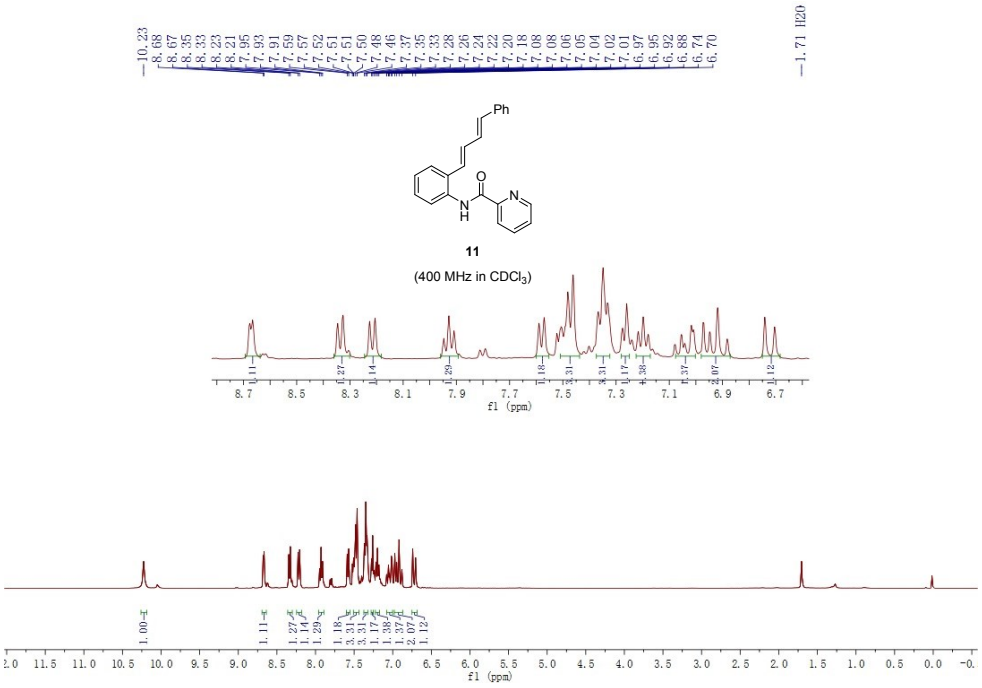

8.51
8.50
7.98
7.83
7.83
7.81
7.37
7.35
7.29
7.26
7.24
7.22
6.31
6.30
6.27
6.26
5.53
5.51
5.49
5.47
4.72
2.65
2.63
2.61
2.60
2.58
2.04
2.02
1.99
OH
N
S
O
O
N
6
(400 MHz in CDCl3)
f1 (ppm)
f1 (ppm)


1.00
1.00
2.04
3.31
2.08
3.96
1.02
0.95
0.96
0.98
1.46
1.04
1.21
f1 (ppm)

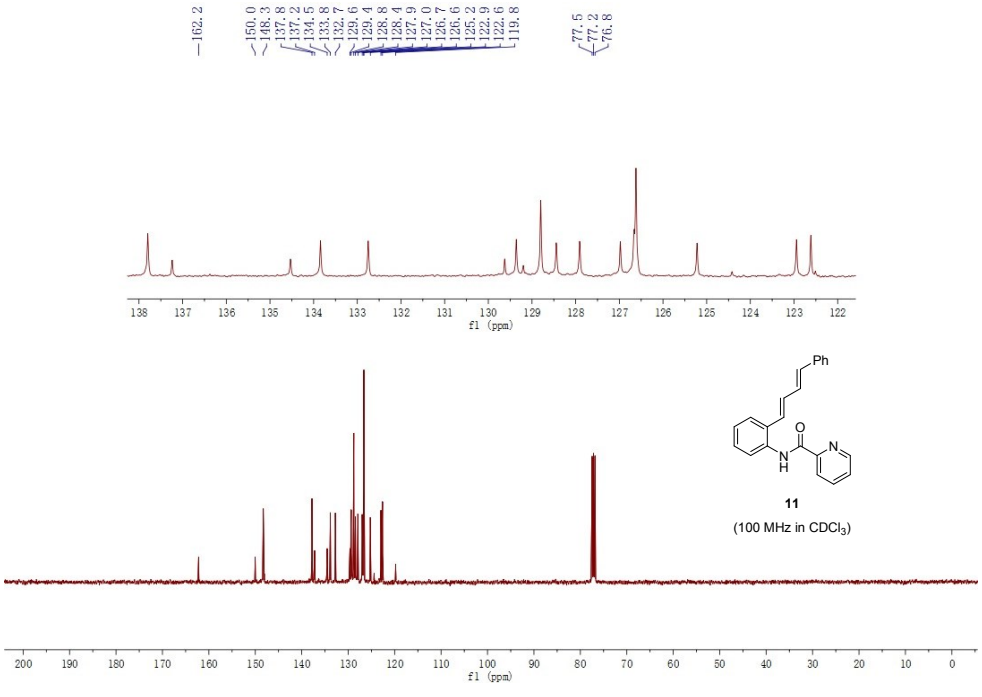

156.5
149.5
138.7
136.6
135.1
133.1
131.0
129.9
129.2
128.6
128.4
127.8
127.3
126.7
125.4
124.4
123.7
77.5
77.2
76.8
66.4
56.6
39.0
OH
N
S
O
O
N
6
(100 MHz in CDCl3)
f1 (ppm)
f1 (ppm)

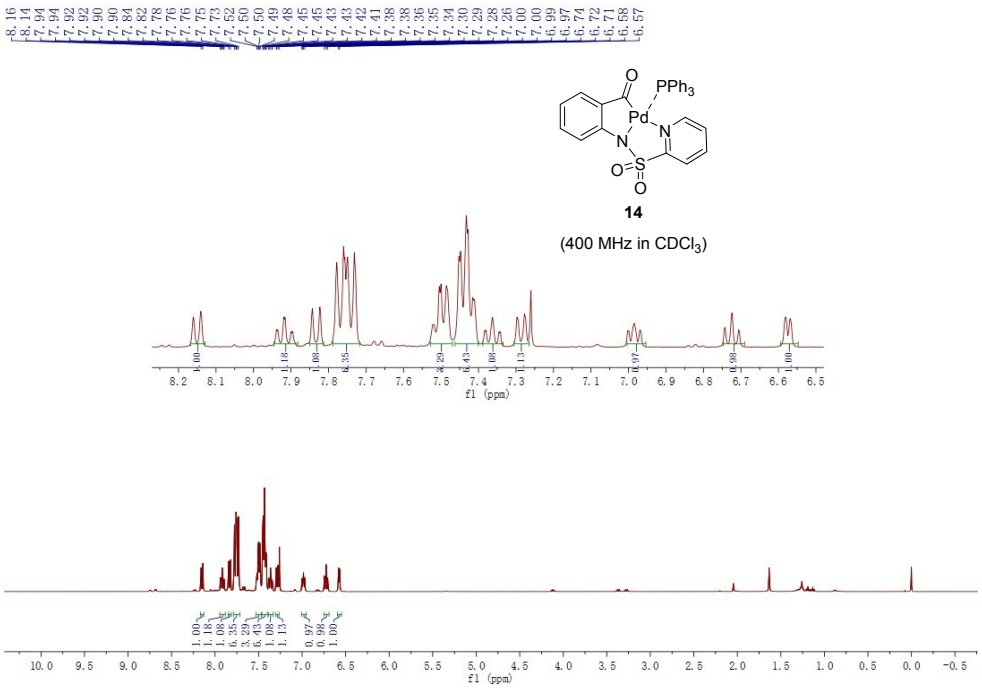
Diastereomeric ratio of compound **6**

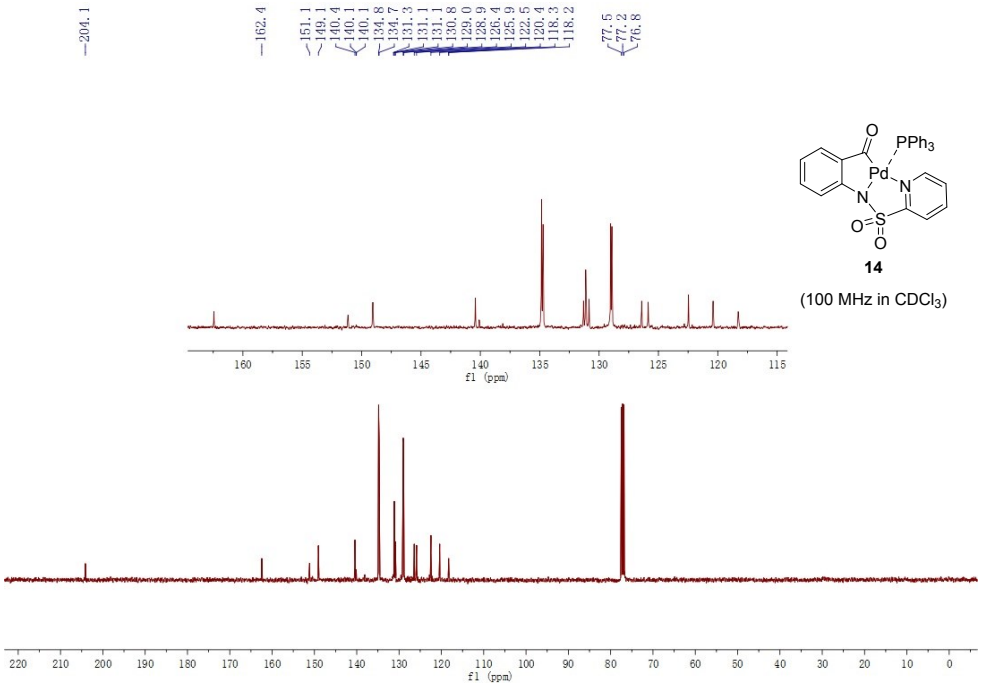



Ph
O
N
H
N
11
(400 MHz in CDCl3)
f1 (ppm)

f1 (ppm)


Ph
O
N
H
N
11
(100 MHz in CDCl3)
f1 (ppm)


PPh3
Pd
N
N
O
S
O
O
14
(400 MHz in CDCl3)
f1 (ppm)


PPh3
Pd
N
N
O
S
O
O
14
(100 MHz in CDCl3)
f1 (ppm)