Copper Catalyzed Cyano-Sulfonylation of Allenes via the Insertion of Sulfur Dioxide Toward the Synthesis of (*E*)-*α*-Cyanomethyl Vinylsulfones

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content

1. General information

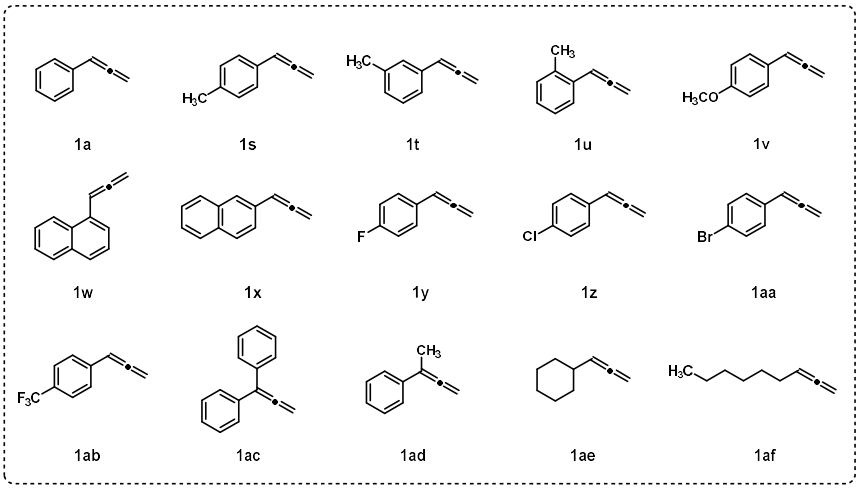
Unless otherwise noted, all reactions or reagents were obtained from commercial suppliers and used as received. Unless otherwise noted, all catalytic reactions were set up in an argon atmosphere glovebox (Vigor, SGI800-750TS-F). The substrates and reagents for catalytic reactions were degassed and stored in the glovebox, unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Thin Layer Chromatography analysis was performed on silica gel coated glass plates (0.25 mm) with fluorescence indicator UV254. For detection of spots, irradiation of UV light at 254 nm or staining reagent using phosphomolybdic acid solution was used. Flash column chromatography was conducted with silica gel 60 (particle size 230–400 mesh, Huanghai) at room temperature and under elevated pressure.

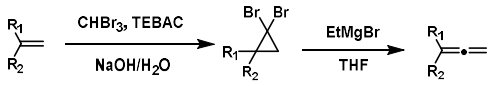
Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2030 instrument equipped with a Rtx-5 column (30 m × 0.25 mm) with dodecane as an internal standard. GC-MS analysis was conducted on a Agilent 5977B GC/MSD instrument equipped with a HP-5MS UI column (30 m × 0.25 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 101 MHz, respectively in $CDCl_3$ (or $(CD_3)_2SO$) at room temperature. ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 7.26 ppm for $CDCl_3$ (or 2.50 ppm for $(CD_3)_2SO$) for ^{1}H NMR. ^{13}C NMR spectra (^{1}H-broadband decoupled) were reported in ppm using the central peak of $CDCl_3$ (77.16 ppm). High-resolution mass spectrometric measurements were provided by the Department of The State Key Laboratory of Biotherapy, Sichuan University. The molecular ion $[M+H]^+$, $[M+K]^+$ and $[M+Na]^+$ are given in m/z units.

2. General procedure for the synthesis of Allenes

Allenes:



Method[1]**:**



Step 1:

To a solution of alkene (1.0 equiv), bromoform (1.5 equiv) and $BnNEt_3Cl$ (1 mol%) was added dropwise a solution of 50% NaOH, and the mixture was stirred at room temperature for 60 min, then heated to 60 °C and further stirred until conversion was complete as observed by TLC analysis. Water and DCM were added and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organic phases were washed with saturated NaCl solution, dried over Na_2SO_4 and the solvent removed under reduced pressure. The reaction mixture was purified by column chromatography afforded dibromocyclopropane derivatives.

Step 2:

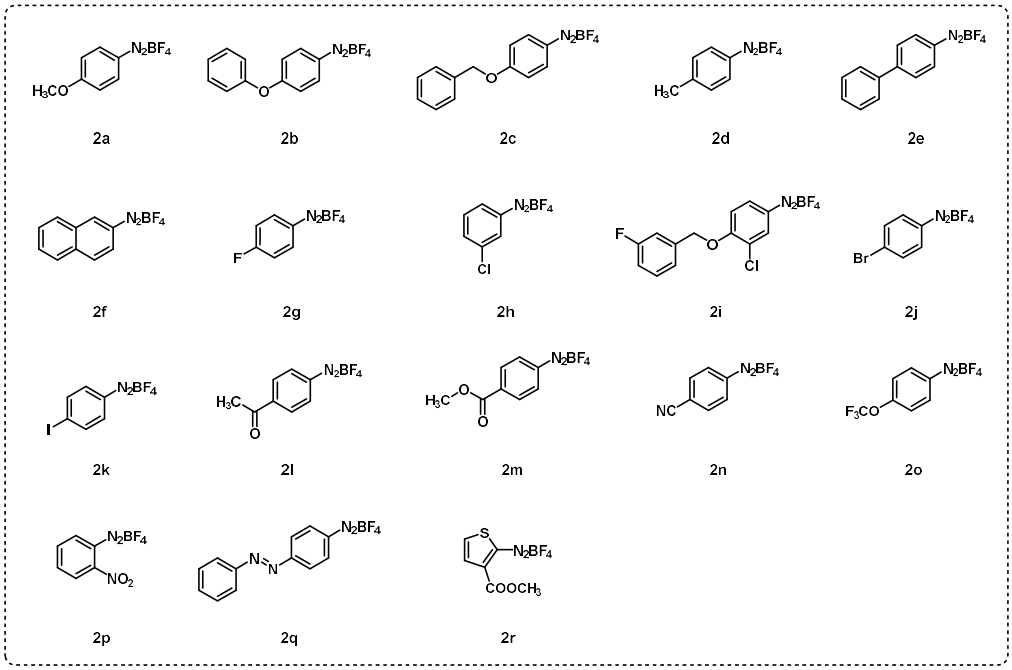
EtMgBr (3.0 M in ether, 1.5 equiv) was added dropwise to a pre-cooled (ice-bath) solution of dibromocyclopropane derivatives (1.0 equiv) in dry THF (1.0 mL/mmol) under nitrogen atmosphere. After EtMgBr was added the mixture was then slowly warmed to room temperature, and stirred at room temperature for an additional 2 hours. Then the reaction was quenched by HCl (0.5 N, 10ml) solution, water was added, and the mixture extracted with ether (3 x 50 mL). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and filtered.

After removing the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to afford allenes.

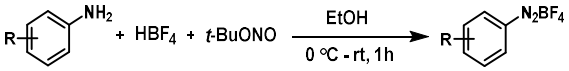
Spectral and physical data of **1a**[1], **1s-1ad**[1], **1ae**[2], **1af**[3]match literature reported values.

3. General procedure for the synthesis of aryldiazonium tetrafluoroborates

Aryldiazonium tetrafluoroborates:



***Method A*:**

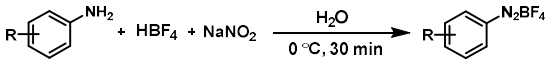


In a 50 mL round-bottom flask, the aniline (10 mmol, 1.0 equiv) was dissolved in a mixture of absolute ethanol (3.0 mL) and an aqueous solution of HBF_4 (48% aq, 2.5 mL, 13.6 mmol, 1.36 equiv), followed by dropwise addition of *t*-BuONO (2.7 mL, 23 mmol, 0.23 equiv) at 0 °C. After stirring at room temperature for 1 h, diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. The solids were filtered off and washed with diethyl ether (3×10 mL), dried in vacuo (10-3 mbar) for 10 minutes, and stored in refrigerator under N_2

atmosphere.

Arenediazonium salts **2a-2f**, **2l-2n**, **2p, 2r** were synthesized in method A. Spectral and physical data of **2a**[4] , **2b-2f**[8], **2m-2n**[7], **2p**[8], **2r**[4]match literature reported values.

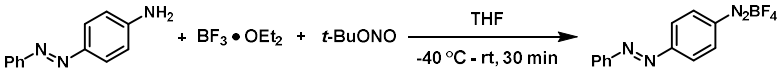
Method B:



In a 100 mL round-bottom flask, the aniline (20 mmol, 1.0 equiv) was dissolved in a mixture of H_2O (10 mL) and HBF_4 (48% aq, 6 mL, 32.7 mmol, 1.64 equiv). After stirring for 15 min, the solution of $NaNO_2$ (1.5 g, 22 mmol, 1.1 equiv., in 4.0 mL H_2O) was added dropwise at 0 ℃. The mixture was stirred for another 30 min at 0 ℃. Then, the arenediazonium tetrafluoroborate was removed by filtration and washed successively twice with Et_2O. The crude product was dried in vacuo for 20 min and was then directly used without further purification.

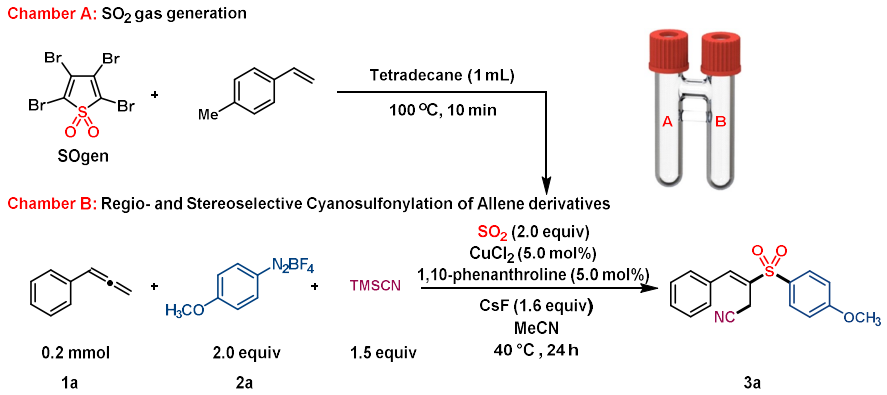
Arenediazonium salts **2g-2k, 2o** were synthesized in method B. Spectral and physical data of **2g**[5], **2h**[5],**2i**[5], **2j**[5], **2k**[5], **2o**[6], match literature reported values.

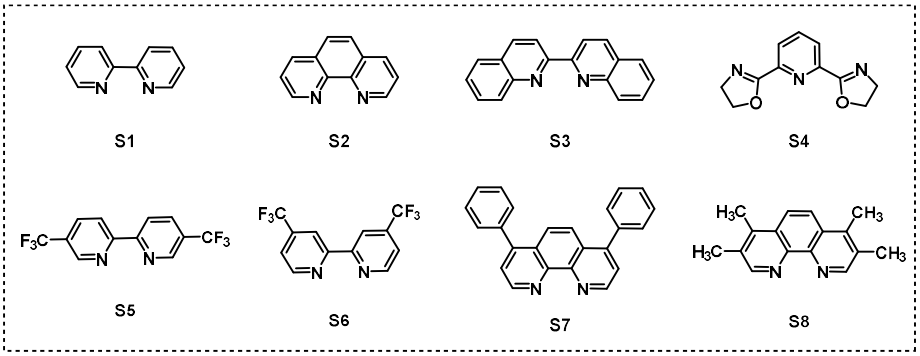
Method C:



To a solution 4-aminoazobenzene (550 mg, 2.8 mmol, 1.0 equiv) in 22 mL of THF was added $BF_3 \cdot OEt_2$ (1.19 g, 7.6 mmol, 2.7 equiv) at -40 ℃. The mixture was stirred for 20 min and then *t*-BuONO (515 mg, 5.0 mmol, 1.8 equiv) was added dropwise. The mixture was stirred for 10 min and then gradually warmed to room temperature. Anhydrous ether was added to precipitate the diazonium salt. The mixture was filtered and the salt washed with ether copiously to give diazonium salt **2q** (385.2 mg, 1.32 mmol, 47% yield). Spectral and physical data of **2q** match literature reported values[9].

4. Optimization of cyano-sulfonylation of allene derivatives

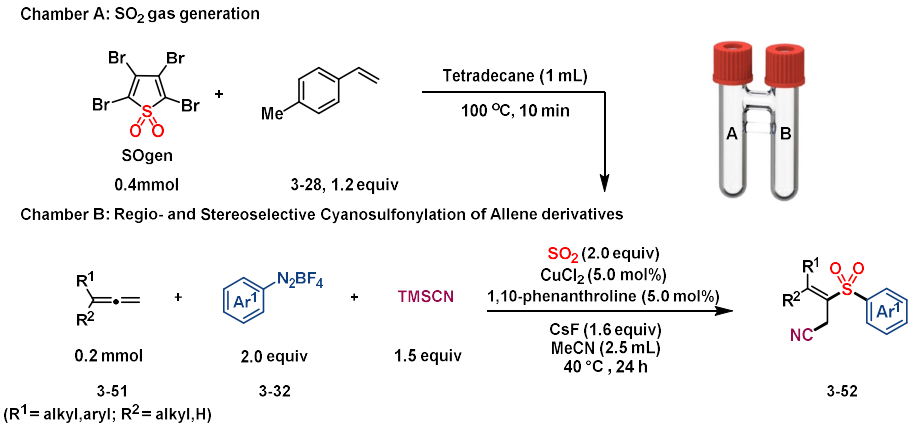




Entry	Deviation from standard conditions	Yield of **3a**[a]
1	**S1** instead of **S2**	**58%**
2	**S2**	**85%**
3	**S3** instead of **S2**	**26%**
4	**S4** instead of **S2**	**67%**
5	**S5** instead of **S2**	**57%**
6	**S6** instead of **S2**	**44%**
7	**S7** instead of **S2**	**36%**
8	**S8** instead of **S2**	**52%**

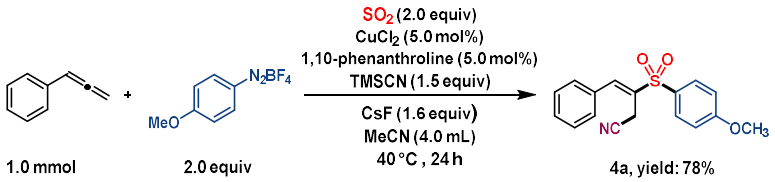
[a]Yields were determined by GC using dodecane as an internal standard.

5. General procedure for the synthesis of (*E*)-*α*- cyanomethyl vinylsulfones compounds



In the glovebox, Allenes (0.2 mmol, 1.0 equiv), aryldiazonium tetrafluoroborates (0.4 mmol, 2.0 equiv), $CuCl_2$ (1.3 mg, 5.0 mol%), 1,10-phenanthroline (1.8 mg, 5.0 mol%), TMSCN (37.5 µl, 0.3 mmol), CsF (48.6 mg, 0.32 mmol) were added to chamber B, followed by addition of MeCN (2.5 mL). Tetrabromothiophene S,S-dioxides (0.4 mmol, 127.7 mg) in tetradecane (1.0 mL) was added to chamber A, followed by addition of 4-methylphenylene (56.6 µl, 0.45 mmol). The two chamber system was sealed and removed out of the glovebox, then chamber A was heated to 100 °C in heat block. About ten minutes later, the sulfur dioxide was completely released since the system in chamber A became clear. Then chamber B was heated to 40 °C in heat block. After 16 hours, two chamber was cooled to room temperature. The mixture in chamber B was passed through a short silica gel pad with ethyl acetate. The filtrate was washed by ethyl acetate and H_2O (15 mL×3), dried by Na_2SO_4, then concentrated and the residue was purified by flash column chromatography to give the desired product.

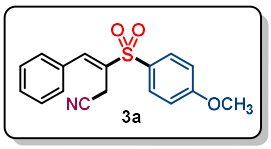
6. The procedure for the 1 mmol scale reaction



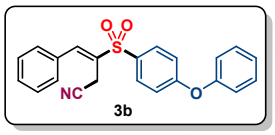
In the glovebox, Allenes (1.0 mmol, 1.0 equiv), aryldiazonium tetrafluoroborates (2.0

mmol, 2.0 equiv), $CuCl_2$ (6.5 mg, 5.0 mol%), 1,10-phenanthroline (9.0 mg, 5.0 mol%), TMSCN (187.5 µl, 1.5 mmol), CsF (243 mg, 1.6 mmol) were added to chamber B, followed by addition of MeCN (4.0 mL). Tetrabromothiophene S,S-dioxides (2.0 mmol, 638.5 mg) in tetradecane (4.0 mL) was added to chamber A, followed by addition of 4-methylphenylene (283.0 µl, 2.25 mmol). The two chamber system was sealed and removed out of the glovebox, then chamber A was heated to 100 °C in heat block. About ten minutes later, the sulfur dioxide was completely released since the system in chamber A became clear. Then chamber B was heated to 40 °C in heat block. After 16 hours, two chamber was cooled to room temperature. The mixture in chamber B was passed through a short silica gel pad with ethyl acetate. The filtrate was washed by ethyl acetate and H_2O (15 mL×3), dried by Na_2SO_4, then concentrated and the residue was purified by flash column chromatography to give the desired product.

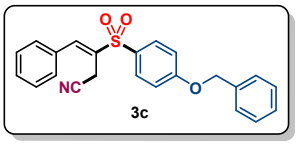
7. Characterization data of products



Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (5:1) as eluent (53.9 mg, 86%). Known compounds[10]. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.0 (s, 1H), 7.8 (d, J = 7.6 Hz, 2H), 7.4 – 7.3 (m, 5H), 7.0 (d, J = 7.6 Hz, 2H), 3.8 (s, 3H), 3.5 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3, 141.9, 132.1, 131.7, 130.7, 130.7, 129.6, 129.4, 129.3, 115.3, 115.0, 55.8, 16.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO_3S$ 336.0665; found: 336.0663.

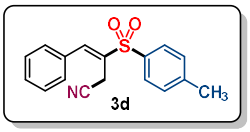


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (63.1mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.56 – 7.39 (m, 7H), 7.29 – 7.22 (m, 1H), 7.18 – 7.08 (m, 4H), 3.62 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.1, 154.9, 142.2, 132.1, 131.50, 131.49, 130.84, 130.78, 130.3, 129.5, 129.4, 125.2, 120.4, 118.2, 115.3, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{17}NNaO_3S$ 398.0821; found: 398.0818.

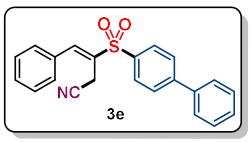


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (67.8 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.32 (m, 10H), 7.14 (d, *J* = 8.9 Hz, 2H), 5.15 (s, 2H), 3.58 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.5, 142.0, 135.6, 132.1,

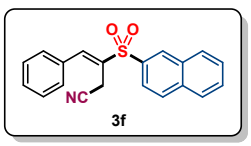
131.7, 130.7, 130.7, 129.8, 129.4, 129.3, 128.8, 128.5, 127.6, 115.8, 115.3, 70.5, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{19}NNaO_3S$ 412.0978; found: 412.0984.



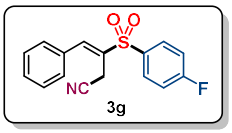
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (7:1) as eluent (44.0 mg, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.51 – 7.38 (m, 7H), 3.58 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.5, 142.4, 135.4, 132.1, 131.4, 130.8, 130.4, 129.5, 129.3, 128.5, 115.3, 21.8, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}NNaO_2S$ 320.0716; found: 320.0713.



Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (56.1mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.54 – 7.39 (m, 8H), 3.63 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 142.9, 139.0, 136.9, 132.0, 131.3, 130.9, 129.5, 129.4, 129.1, 129.0, 128.8, 128.3, 127.5, 115.3, 16.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}NO_2S$ 360.1053; found: 360.1052.

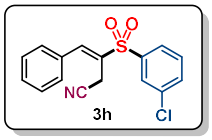


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (42.0mg, 63%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 2.6 Hz, 1H), 7.95 (d, *J* = 2.4 Hz, 1H), 7.84 (dd, *J* = 8.7, 2.8 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.53 – 7.42 (m, 2H), 7.30 – 7.24 (m, 4H), 7.06 (d, *J* = 2.5 Hz, 1H), 3.42 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.1, 135.6, 135.1, 132.3, 132.0, 131.1, 130.9, 130.6, 130.2, 129.7, 129.6, 129.5, 129.4, 128.1, 128.0, 122.6, 115.2, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}NO_2S$ 334.0896; found: 334.0896.

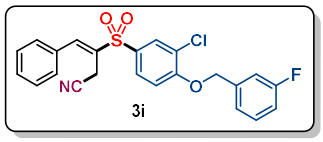


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (5:1) as eluent (45.2 mg, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 8.06 – 8.00 (m, 2H), 7.55 – 7.44 (m, 5H), 7.34 – 7.28 (m, 2H), 3.63 (s, 2H). ^{19}F NMR (376 MHz, Chloroform-d) δ -102.00. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.2 (d, *J* = 257.8 Hz), 143.1, 134.5 (d, *J* = 3.1 Hz), 131.8, 131.4 (d, *J* = 9.8 Hz), 131.0, 131.0, 129.5, 129.4, 117.2 (d, *J* = 22.8

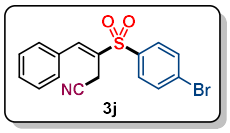
Hz), 115.1, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{12}FNNaO_2S$ 324.0465; found: 324.0461.



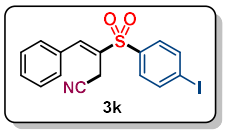
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (58.5mg, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.96 (t, *J* = 1.9 Hz, 1H), 7.88 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.59 – 7.53 (m, 1H), 7.52 – 7.44 (m, 5H), 3.61 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.9, 140.3, 136.0, 134.5, 131.7, 131.1, 131.0, 130.5, 129.6, 129.4, 128.4, 126.6, 115.1, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{12}ClNNaO_2S$ 340.0169; found: 340.0168.



Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (5:1) as eluent (68.1mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.99 (d, *J* = 2.3 Hz, 1H), 7.84 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.53 – 7.42 (m, 5H), 7.41 – 7.34 (m, 1H), 7.24 – 7.15 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.04 (td, *J* = 8.5, 2.5 Hz, 1H), 5.23 (s, 2H), 3.60 (s, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.08. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0 (d, *J* = 246.9 Hz), 158.6, 142.9, 137.6 (d, *J* = 7.5 Hz), 131.9, 131.1 (d, *J* = 4.0 Hz), 130.9, 130.5, 130.4, 129.5, 129.4, 129.0, 124.8, 122.5 (d, *J* = 3.0 Hz), 115.5, 115.3 (d, *J* = 8.7 Hz), 114.1, 113.9, 113.5, 70.3 (d, *J* = 2.1 Hz), 16.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{17}ClFNO_3S$ 442.0674; found: 442.0675.

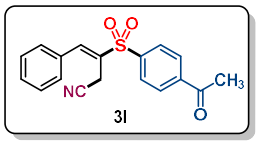


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (57.0 mg, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.88 – 7.82 (m, 2H), 7.78 – 7.73 (m, 2H), 7.54 – 7.41 (m, 5H), 3.61 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 137.6, 133.1, 131.8, 131.1, 130.8, 129.87, 129.86, 129.5, 129.4, 115.1, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{12}BrNNaO_2S$ 383.9664; found: 383.9656.

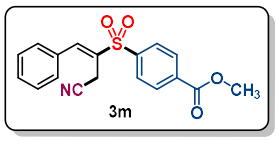


Prepared by the general procedure at the 40 °C; isolated as orange solid using petroleum/ethyl acetate (8:1) as eluent (52.4mg, 64%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.40 (m, 5H), 3.60 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 139.0, 138.3, 131.8, 131.1, 130.8, 129.6, 129.5, 129.4, 115.1,

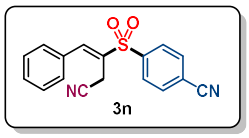
102.5, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{12}INNaO_2S$ 431.9526; found: 431.9525.



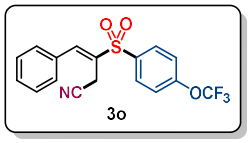
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (5:1) as eluent (58.6 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.14 (m, 3H), 8.13 – 8.08 (m, 2H), 7.55 – 7.50 (m, 3H), 7.49 – 7.44 (m, 2H), 3.65 (s, 2H), 2.69 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 144.2, 142.5, 141.2, 131.7, 131.2, 130.5, 129.6, 129.5, 129.4, 128.8, 115.0, 27.0, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NNaO_3S$ 348.0665; found: 348.0663.



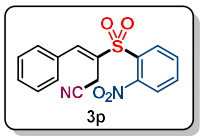
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (3:1) as eluent (48.5 mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (d, J = 8.4 Hz, 2H), 8.12 (s, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.52 – 7.43 (m, 5H), 3.96 (s, 3H), 3.62 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.3, 144.0, 142.5, 135.3, 131.8, 131.1, 130.8, 130.5, 129.6, 129.4, 128.5, 115.0, 52.8, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}NNaO_4S$ 364.0614; found: 364.0611.



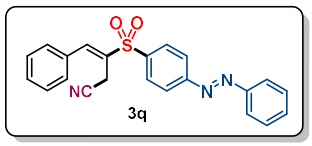
Prepared by the general procedure at the 40 °C; isolated as orange solid using petroleum/ethyl acetate (4:1) as eluent (41.9mg, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.08 (m, 3H), 7.96 – 7.86 (m, 2H), 7.56 – 7.48 (m, 3H), 7.47 – 7.40 (m, 2H), 3.64 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.0, 143.0, 133.4, 131.5, 131.4, 130.0, 129.6, 129.5, 129.1, 118.0, 117.0, 114.9, 16.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{12}N_2NaO_2S$ 331.0512; found: 331.0510.



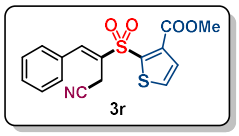
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (62.5mg, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 8.04 (d, J = 8.9 Hz, 2H), 7.54 – 7.39 (m, 7H), 3.61 (s, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.64. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5 (q, J = 2.0 Hz), 143.7, 136.8, 131.8, 131.1, 130.77, 130.75, 129.5, 129.4, 121.3, 120.2 (q, J = 260.1 Hz), 115.1, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{12}F_3NNaO_3S$ 390.0382; found: 390.0378.



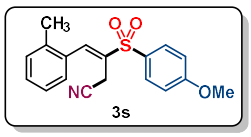
Prepared by the general procedure at the 40 °C; isolated as orange solid using petroleum/ethyl acetate (2:1) as eluent (46.6mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.4 – 8.3 (m, 1H), 8.1 (s, 1H), 7.9 – 7.8 (m, 3H), 7.6 – 7.4 (m, 5H), 3.7 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.9, 145.3, 135.7, 132.8, 132.7, 131.8, 131.8, 131.0, 129.7, 129.5, 129.4, 125.4, 115.1, 16.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}N_2O_4S$ 329.0591; found: 329.0596.



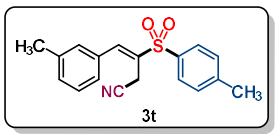
Prepared by the general procedure at the 40 °C; isolated as orange solid using petroleum/ethyl acetate (2:1) as eluent (46.5mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.07 (m, 5H), 7.99 – 7.92 (m, 2H), 7.57 – 7.44 (m, 8H), 3.64 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.7, 152.4, 143.5, 139.7, 132.3, 131.9, 131.0, 130.9, 129.61, 129.56, 129.4, 129.3, 123.9, 123.4, 115.2, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{17}N_3NaO_2S$ 410.0934; found: 410.0930.



Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (3:1) as eluent (45.2mg, 65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.76 (d, *J* = 5.3 Hz, 1H), 7.63 (d, *J* = 5.2 Hz, 1H), 7.54 – 7.42 (m, 5H), 3.87 (s, 3H), 3.67 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3, 145.0, 141.4, 135.9, 132.2, 131.9, 130.7, 130.3, 129.5, 129.4, 129.3, 115.4, 53.1, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{13}NNaO_4S_2$ 370.0178; found: 370.0174.

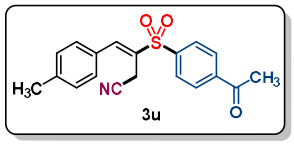


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (10:1) as eluent (51.1 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.31 – 7.11 (m, 4H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.38 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.4, 141.8, 137.6, 133.0, 131.4, 130.9, 130.7, 130.3, 129.6, 127.8, 126.5, 115.3, 115.0, 55.8, 19.9, 16.1. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}NO_3S$ 328.1002; found: 328.1004.

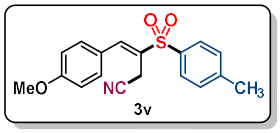


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (56,0 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.77 (d, *J* = 8.3

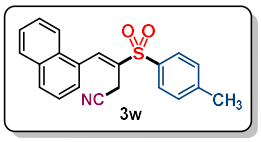
Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 7.9 Hz, 1H), 7.22 – 7.12 (m, 3H), 3.50 (s, 2H), 2.38 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.5, 142.7, 139.2, 135.5, 132.0, 131.6, 131.1, 130.4, 130.2, 129.2, 128.4, 126.4, 115.4, 21.8, 21.4, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO_2S$ 334.0872; found: 334.0878.



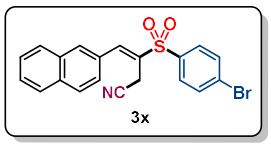
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (5:1) as eluent (59.7mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, J = 8.1 Hz, 2H), 8.06 (d, J = 7.5 Hz, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.63 (s, 2H), 2.65 (d, J = 1.1 Hz, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 196.5, 144.1, 142.6, 142.0, 141.0, 130.1, 129.8, 129.3, 129.1, 128.9, 128.7, 115.1, 26.9, 21.5, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{17}NNaO_3S$ 362.0821; found: 362.0825.



Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (39.3mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.45 – 7.35 (m, 4H), 6.99 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.60 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.7, 145.3, 142.0, 135.8, 131.8, 130.3, 128.3, 128.2, 124.4, 115.4, 114.8, 55.5, 21.7, 16.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}NNaO_3S$ 350.0821; found: 350.0825.

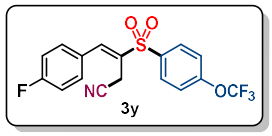


Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (10:1) as eluent (60.5 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.99 – 7.92 (m, 4H), 7.90 – 7.86 (m, 1H), 7.65 – 7.58 (m, 2H), 7.55 (t, J = 7.7 Hz, 1H), 7.48 (t, J = 7.2 Hz, 3H), 3.52 (s, 2H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.7, 141.6, 135.4, 134.1, 133.5, 131.1, 130.9, 130.5, 129.2, 128.9, 128.6, 127.5, 127.0, 126.6, 125.3, 123.9, 115.4, 21.8, 16.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{18}NO_2S$ 348.1053; found: 348.1055.



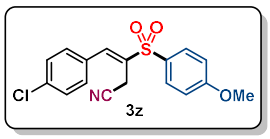
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (77.5 mg, 94%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.78 – 7.70 (m, 3H), 7.62 (d, J = 7.3 Hz, 2H), 7.53 (d, J =

8.1 Hz, 2H), 7.51 – 7.38 (m, 2H), 3.66 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.9, 143.2, 139.5, 137.7, 133.1, 130.6, 130.28, 130.26, 129.9, 129.8, 129.1, 128.4, 128.0, 127.2, 115.2, 16.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}BrNO_2S$ 412.0001; found: 412.0000.



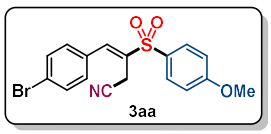
3y

Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (5:1) as eluent (57.1mg, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 8.04 – 8.01 (m, 2H), 7.51 – 7.39 (m, 4H), 7.24 – 7.14 (m, 2H), 3.60 (s, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.66, -107.08. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.06 (d, J = 254.1 Hz), 153.51 (q, J = 1.8 Hz), 142.38, 136.63, 131.86 (d, J = 8.8 Hz), 130.75, 130.55 (d, J = 1.8 Hz), 127.90 (d, J = 3.5 Hz), 121.37, 120.18 (q, J = 260.1 Hz), 116.79 (d, J = 22.0 Hz), 114.93, 16.36. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{11}F_4NO_3S$ 408.0288; found: 408.0285.



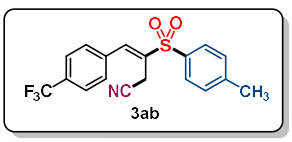
3z

Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (10:1) as eluent (55.0 mg, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.88 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H), 3.55 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.4, 140.4, 137.0, 132.3, 130.8, 130.7, 130.5, 129.7, 129.3, 115.1, 55.8, 16.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{14}ClKNNaO_3S$ 370.0275; found: 370.0271.



3aa

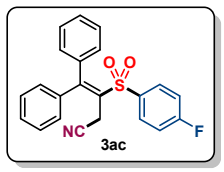
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (10:1) as eluent (44.7 mg, 57%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 3.55 (s, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 140.5, 132.6, 132.5, 130.9, 130.8, 130.8, 129.2, 125.3, 115.1, 55.8, 16.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{14}BrNNaO_3S$ 413.9770; found: 413.9774.



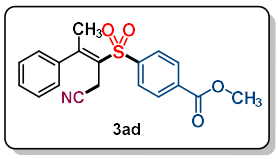
3ab

Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (54.1 mg, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.86 (d, J =

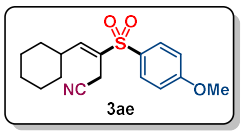
8.0 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 3.54 (s, 2H), 2.48 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.06. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.0, 140.6, 135.5, 134.8, 134.1, 132.3 (q, J = 33.0 Hz), 130.5, 129.5, 128.6, 126.3 (q, J = 3.7 Hz), 123.5 (q, J = 272.5 Hz), 114.8, 21.8, 16.2. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO_2S$ 366.0770; found: 366.0770.



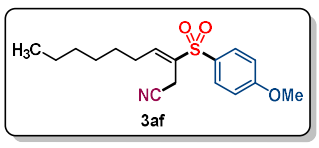
Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (8:1) as eluent (48.3 mg, 64%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.32 (m, 2H), 7.35 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 7.15 – 7.06 (m, 4H), 6.91 – 6.81 (m, 4H), 3.58 (s, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.84. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3 (d, J = 256.3 Hz), 157.6, 138.2 (d, J = 219.1 Hz), 135.7 (d, J = 3.2 Hz), 133.2, 130.6 (d, J = 9.6 Hz), 129.7, 129.3, 129.2, 128.9, 128.0, 127.7, 117.6, 116.0, 115.8, 20.7. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{16}FNNaO_2S$ 400.0778; found: 400.0774.



Prepared by the general procedure at the 40 °C; isolated as white solid using petroleum/ethyl acetate (5:1) as eluent (44.8 mg, 63%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, J = 8.3 Hz, 2H), 8.18 (d, J = 8.5 Hz, 2H), 7.48 – 7.35 (m, 3H), 7.15 (d, J = 6.6 Hz, 2H), 3.98 (s, 3H), 3.44 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 158.0, 144.5, 140.6, 135.0, 130.6, 129.6, 129.4, 129.3, 127.7, 125.8, 116.9, 52.8, 23.5, 20.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{17}NNaO_4S$ 378.0770; found: 378.0777.



Prepared by the general procedure at the 40 °C; isolated as light yellow liquid using petroleum/ethyl acetate (8:1) as eluent (34.5 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 10.4 Hz, 1H), 3.87 (s, 3H), 3.36 (s, 2H), 2.39 – 2.28 (m, 1H), 1.82 – 1.68 (m, 5H), 1.36 – 1.20 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.1, 150.3, 130.4, 129.9, 129.7, 115.3, 114.9, 55.7, 38.5, 31.2, 25.4, 25.1, 14.6. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{17}H_{21}NNaO_3S$ 342.1134; found: 342.1136.

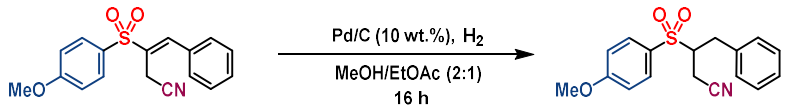


Prepared by the general procedure at the 40 °C; isolated as light yellow liquid using petroleum/ethyl acetate (8:1) as eluent (32.8 mg, 51%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.9 Hz, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.9 Hz,

2H), 3.81 (s, 3H), 3.30 (s, 2H), 2.23 (q, J = 7.5 Hz, 2H), 1.49 (s, 3H), 1.33 – 1.15 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.1, 146.3, 131.7, 130.4, 129.7, 114.9, 114.9, 55.7, 31.5, 29.0, 28.9, 27.9, 22.5, 14.6, 14.0. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{24}NO_3S$ 322.1472; found: 322.1470.

8. Transformations of (*E*)-*α*- cyanomethyl vinylsulfones compounds.

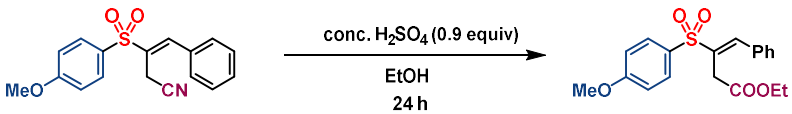
1）[11]



3a, 0.2 mmol　　4, yield: 78%

Compound **3a** (0.2 mmol, 62.7 mg) was dissolved in MeOH (2.5 mL) and EtOAc (1.25 mL) and Pd/C (10 wt. %, 20.9 mg, 0.02 mmol) was added. The reaction mixture was stirred under a hydrogen atmosphere for 12 h at room temperature. The reaction was filtered through celite, and the cake was washed with CH_2Cl_2 (2 × 5 mL). The organic layers were combined and concentrated in vacuo. The crude product was purified by flash column chromatography using petroleum/ethyl acetate (10:1) as eluent to afford **4** as a colorless liquid (49.2 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, J = 8.1 Hz, 2H), 7.38 – 7.26 (m, 3H), 7.20 (d, J = 7.3 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 3.93 (d, J = 1.4 Hz, 3H), 3.54 – 3.37 (m, 2H), 2.90 (dd, J = 13.4, 11.2 Hz, 1H), 2.80 (dd, J = 17.7, 4.2 Hz, 1H), 2.61 (dd, J = 17.7, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.6, 135.1, 131.5, 129.2, 129.0, 127.7, 127.4, 115.4, 114.9, 62.3, 55.8, 33.5, 16.5. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}NNaO_3S$ 338.0821; found: 338.0824.

2）[12]



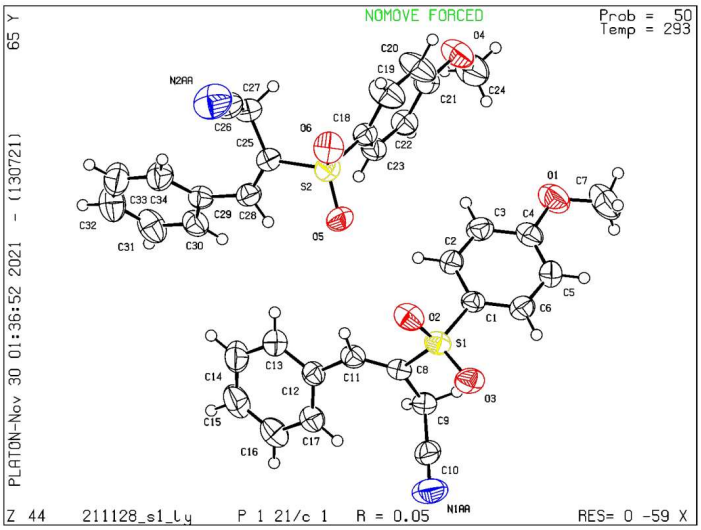
3a, 0.2 mmol　　5, yield: 92%

Compound **3a** (0.2 mmol, 62.7 mg) was dissolved in EtOH (2 ml) and conc. H_2SO_4 (0.18 mmol, 10 μL) was added. The reaction mixture was stirred under a hydrogen atmosphere for 24h at 100 °C. The filtrate was washed by ethyl acetate and H_2O (15 mL×3), dried by Na_2SO_4, then concentrated and the residue was purified by flash column chromatography using petroleum/ethyl acetate (3:1) as eluent to afford **5** as a colorless liquid (66.3 mg, 92%). ^{1}H NMR

(400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.49 – 7.37 (m, 5H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.52 (s, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.9, 163.7, 140.6, 135.5, 133.2, 130.7, 130.4, 129.8, 129.0, 128.8, 114.4, 61.4, 55.7, 33.0, 13.9. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{21}O_5S$ 361.1104; found: 361.1105.

9. Crystal structure and X-ray crystallographic data of 3a.

A view of the molecular structure of compound **3a** (CCDC deposition number: 2158587.)



Compound **3a** was crystallized by slow evaporation of PE:EA=10:1.

Experimental

The crystal was kept at 293.15 K during data collection. Using Olex2[13], the structure was solved with the Superflip[14] structure solution program using Charge Flipping and refined with the ShelXL[15] refinement package using Least Squares minimisation.

Table 1 Crystal data and structure refinement for 3a.

Identification code	211128_s1_ly
Empirical formula	$C_{17}H_{15}NO_3S$

Formula weight	313.36
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.1606(4)
b/Å	42.233(3)
c/Å	14.3998(11)
α/°	90
β/°	97.795(6)
γ/°	90
Volume/Å^3	3109.4(4)
Z	8
ρ_{calc}g/cm^3	1.339
μ/mm^{-1}	0.220
F(000)	1312.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.792 to 52.74
Index ranges	-6 ≤ h ≤ 5, -52 ≤ k ≤ 34, -13 ≤ l ≤ 17
Reflections collected	13163
Independent reflections	6234 [R_{int} = 0.0343, R_{sigma} = 0.0495]
Data/restraints/parameters	6234/0/399
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0492, wR_2 = 0.1108
Final R indexes [all data]	R_1 = 0.0726, wR_2 = 0.1262
Largest diff. peak/hole / e Å^{-3}	0.21/-0.37

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3a. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	9249.1(10)	3156.5(2)	819.2(4)	45.63(17)

O1	2603(4)	3623.1(4)	-2523.7(12)	77.3(5)
O2	10249(3)	3430.6(4)	1335.3(11)	57.8(4)
O3	11064(3)	2928.7(4)	529.3(11)	59.2(4)
C1	7202(4)	3279.3(5)	-188.6(14)	40.4(5)
C2	5202(4)	3493.0(5)	-113.3(15)	48.2(6)
C3	3696(4)	3596.1(5)	-912.8(17)	53.6(6)
C4	4178(5)	3494.3(5)	-1782.1(16)	52.5(6)
C5	6133(5)	3281.7(6)	-1853.4(16)	57.7(6)
C6	7647(5)	3172.3(5)	-1050.4(16)	55.2(6)
C7	3034(6)	3531.3(8)	-3433.5(18)	95.2(11)
C8	7199(4)	2946.8(5)	1483.4(14)	40.0(5)
C9	6329(4)	2630.0(5)	1079.7(15)	46.0(5)
C10	8152(5)	2376.4(6)	1373.4(17)	57.6(6)
C11	6533(4)	3085.1(5)	2244.9(14)	45.7(5)
C12	4926(4)	2962.8(5)	2924.9(14)	45.0(5)
C13	3613(5)	3178.1(6)	3413.8(16)	62.6(7)
C14	2033(6)	3076.7(8)	4059.8(18)	77.9(8)
C15	1778(5)	2761.5(8)	4223.2(18)	73.7(8)
C16	3089(5)	2544.7(7)	3757.1(17)	66.6(7)
C17	4663(5)	2643.7(6)	3117.9(16)	56.2(6)
N1	9572(5)	2177.3(6)	1610.3(19)	96.4(9)
S2	4806.9(10)	4326.0(2)	1801.7(4)	48.22(17)
O4	-2129(4)	4555.6(4)	-1702.9(12)	71.2(5)
O5	5526(3)	3996.5(4)	1837.7(11)	58.8(4)
O6	6819(3)	4562.3(4)	1858.3(11)	61.4(5)
C18	2662(4)	4392.8(5)	770.5(15)	42.9(5)
C19	3001(5)	4650.0(7)	215.7(19)	74.4(8)
C20	1383(5)	4697.7(7)	-605(2)	78.4(9)

C21	-616(4)	4488.8(5)	-879.5(16)	51.0(6)
C22	-987(4)	4233.1(5)	-324.8(16)	50.4(6)
C23	653(4)	4186.0(5)	500.3(15)	47.8(5)
C24	-4048(6)	4330.2(7)	-2071(2)	85.4(9)
C25	2932(4)	4403.5(5)	2713.7(15)	42.6(5)
C26	2361(4)	4748.6(5)	2851.3(17)	50.8(6)
C27	4526(5)	4917.0(6)	3388.2(19)	61.6(7)
C28	2096(4)	4159.9(5)	3165.7(15)	47.4(5)
C29	585(4)	4155.9(5)	3951.7(15)	46.0(5)
C30	-1138(5)	3907.3(6)	4017.1(16)	55.5(6)
C31	-2634(5)	3894.4(7)	4725.5(18)	71.6(8)
C32	-2440(6)	4124.9(7)	5393(2)	77.4(8)
C33	-678(6)	4367.3(7)	5360.6(19)	75.7(8)
C34	824(5)	4383.5(6)	4653.4(18)	62.5(7)
N2	6207(6)	5049.7(6)	3799(2)	96.5(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	39.8(3)	44.6(3)	52.6(3)	7.9(3)	6.6(2)	-2.1(3)
O1	91.0(13)	76.1(13)	59.0(11)	13.0(10)	-10.8(9)	1.2(11)
O2	57.8(9)	51.0(10)	62.1(10)	5.5(8)	-1.0(8)	-18.7(8)
O3	42.6(8)	62.0(10)	75.2(11)	10.7(9)	15.7(8)	13.3(8)
C1	40.7(11)	36.0(11)	45.5(12)	5.6(9)	9.1(9)	0.1(10)
C2	51.5(13)	46.4(13)	48.7(13)	1.1(11)	13.7(10)	3.9(11)
C3	51.1(13)	48.8(14)	60.9(15)	3.7(12)	8.2(11)	10.4(12)
C4	59.6(14)	46.0(14)	49.8(14)	9.5(11)	0.4(11)	-7.5(12)

C5	76.3(16)	54.6(15)	43.9(13)	-2.9(12)	13.9(11)	2.4(14)
C6	62.2(15)	48.3(14)	57.9(15)	2.8(12)	18.7(12)	10.1(12)
C7	127(3)	101(2)	51.5(18)	14.9(17)	-8.3(17)	-22(2)
C8	38.6(11)	35.9(11)	44.1(12)	5.1(9)	0.4(9)	-1.2(10)
C9	51.2(12)	39.6(12)	47.6(13)	2.1(10)	7.7(10)	-0.4(11)
C10	70.0(16)	43.5(14)	64.8(16)	2.9(12)	28.4(13)	3.4(13)
C11	49.8(12)	40.0(12)	45.8(12)	1.3(10)	1.1(10)	-5.6(11)
C12	46.0(12)	49.3(14)	38.3(12)	-0.6(10)	0.8(9)	0.5(11)
C13	80.6(17)	59.5(16)	48.2(14)	-1.3(12)	10.0(12)	10.4(14)
C14	89(2)	98(2)	49.4(16)	0.3(16)	19.9(14)	28.0(19)
C15	62.6(16)	109(2)	52.3(16)	18.7(17)	15.5(12)	8.7(18)
C16	69.4(16)	73.5(18)	57.9(16)	15.7(14)	12.9(13)	-7.2(15)
C17	62.6(14)	56.0(15)	52.5(14)	7.2(12)	16.6(11)	1.2(13)
N1	112(2)	67.0(17)	117(2)	22.3(15)	41.3(17)	37.6(16)
S2	39.6(3)	52.1(4)	52.9(4)	-2.2(3)	6.1(2)	1.5(3)
O4	83.2(12)	62.5(11)	61.5(11)	14.2(9)	-13.0(9)	-15.2(10)
O5	61.4(10)	53.8(10)	61.0(10)	-2.9(8)	7.9(8)	18.2(9)
O6	38.1(8)	73.7(12)	72.0(11)	-4.5(9)	5.9(7)	-13.5(8)
C18	41.6(11)	39.5(12)	48.6(12)	0.6(10)	9.6(9)	-1.8(10)
C19	71.1(18)	66.1(18)	80.3(19)	19.0(15)	-9.8(14)	-33.6(15)
C20	85.2(19)	66.0(18)	77.6(19)	30.2(15)	-12.3(15)	-34.1(16)
C21	55.2(13)	45.9(14)	51.2(14)	2.5(11)	4.9(11)	2.1(12)
C22	49.8(13)	45.7(13)	55.2(14)	0.4(11)	5.2(10)	-10.1(11)
C23	52.7(13)	41.4(12)	49.6(13)	3.8(11)	8.6(10)	-5.4(11)
C24	104(2)	76(2)	66.9(19)	-0.8(15)	-21.7(16)	-19.5(19)
C25	37.7(11)	41.1(12)	47.8(12)	-2.9(10)	1.4(9)	0.1(10)
C26	48.7(13)	41.0(13)	62.6(15)	0.7(11)	6.7(11)	1.0(11)
C27	65.3(16)	46.2(15)	72.5(18)	-6.2(13)	6.9(13)	-6.5(14)

C28	50.2(13)	40.9(13)	50.1(13)	-2.7(11)	3.5(10)	2.8(11)
C29	45.0(12)	44.8(13)	47.0(13)	3.1(10)	2.4(9)	2.5(11)
C30	65.9(15)	51.4(14)	47.0(13)	3.1(11)	-0.2(11)	-8.3(13)
C31	70.8(17)	85(2)	58.5(16)	10.2(15)	7.8(13)	-24.7(16)
C32	75.9(18)	98(2)	62.4(18)	-3.4(17)	23.0(14)	-12.5(18)
C33	95(2)	75(2)	60.8(17)	-14.3(15)	23.3(15)	-7.0(18)
C34	71.4(16)	56.2(16)	61.4(16)	-7.1(13)	14.8(13)	-10.9(14)
N2	96.5(19)	75.5(18)	112(2)	-21.9(16)	-5.9(16)	-22.0(16)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.4334(16)	S2	O5	1.4393(16)
S1	O3	1.4432(15)	S2	O6	1.4344(16)
S1	C1	1.754(2)	S2	C18	1.751(2)
S1	C8	1.759(2)	S2	C25	1.764(2)
O1	C4	1.364(3)	O4	C21	1.358(3)
O1	C7	1.413(3)	O4	C24	1.423(3)
C1	C2	1.386(3)	C18	C19	1.374(3)
C1	C6	1.369(3)	C18	C23	1.371(3)
C2	C3	1.370(3)	C19	C20	1.366(3)
C3	C4	1.378(3)	C20	C21	1.374(3)
C4	C5	1.365(3)	C21	C22	1.372(3)
C5	C6	1.384(3)	C22	C23	1.376(3)
C8	C9	1.503(3)	C25	C26	1.505(3)
C8	C11	1.328(3)	C25	C28	1.321(3)
C9	C10	1.450(3)	C26	C27	1.455(3)
C10	N1	1.137(3)	C27	N2	1.130(3)
C11	C12	1.461(3)	C28	C29	1.459(3)

C12	C13	1.382(3)	C29	C30	1.387(3)
C12	C17	1.387(3)	C29	C34	1.388(3)
C13	C14	1.386(4)	C30	C31	1.361(3)
C14	C15	1.361(4)	C31	C32	1.362(4)
C15	C16	1.367(4)	C32	C33	1.374(4)
C16	C17	1.373(3)	C33	C34	1.363(3)

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	O3	119.08(10)	O5	S2	C18	108.46(10)
O2	S1	C1	108.93(10)	O5	S2	C25	108.50(10)
O2	S1	C8	109.00(10)	O6	S2	O5	119.31(10)
O3	S1	C1	107.42(10)	O6	S2	C18	107.79(10)
O3	S1	C8	106.48(10)	O6	S2	C25	107.12(10)
C1	S1	C8	105.05(9)	C18	S2	C25	104.72(10)
C4	O1	C7	117.7(2)	C21	O4	C24	118.37(18)
C2	C1	S1	119.94(16)	C19	C18	S2	120.32(17)
C6	C1	S1	119.75(16)	C23	C18	S2	120.32(16)
C6	C1	C2	120.3(2)	C23	C18	C19	119.3(2)
C3	C2	C1	119.0(2)	C20	C19	C18	120.5(2)
C2	C3	C4	120.8(2)	C19	C20	C21	120.1(2)
O1	C4	C3	115.1(2)	O4	C21	C20	116.0(2)
O1	C4	C5	124.9(2)	O4	C21	C22	124.2(2)
C5	C4	C3	120.0(2)	C22	C21	C20	119.8(2)
C4	C5	C6	119.8(2)	C21	C22	C23	119.9(2)
C1	C6	C5	120.1(2)	C18	C23	C22	120.4(2)
C9	C8	S1	114.08(15)	C26	C25	S2	114.49(16)
C11	C8	S1	118.01(16)	C28	C25	S2	118.12(17)
C11	C8	C9	127.87(19)	C28	C25	C26	127.3(2)
C10	C9	C8	113.38(18)	C27	C26	C25	113.16(19)
N1	C10	C9	179.4(3)	N2	C27	C26	179.4(3)
C8	C11	C12	129.2(2)	C25	C28	C29	129.5(2)
C13	C12	C11	118.1(2)	C30	C29	C28	118.4(2)

C13	C12	C17	118.0(2)	C30	C29	C34	118.0(2)
C17	C12	C11	123.9(2)	C34	C29	C28	123.5(2)
C12	C13	C14	120.8(3)	C31	C30	C29	121.0(2)
C15	C14	C13	119.9(3)	C30	C31	C32	120.4(3)
C14	C15	C16	120.3(3)	C31	C32	C33	119.6(3)
C15	C16	C17	120.2(3)	C34	C33	C32	120.6(3)
C16	C17	C12	120.9(2)	C33	C34	C29	120.4(2)

Table 6 Torsion Angles for 3a.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
S1	C1	C2	C3	177.27(17)	S2	C18	C19	C20	177.9(2)
S1	C1	C6	C5	-176.38(17)	S2	C18	C23	C22	-178.02(17)
S1	C8	C9	C10	86.9(2)	S2	C25	C26	C27	-80.7(2)
S1	C8	C11	C12	-178.44(17)	S2	C25	C28	C29	178.39(18)
O1	C4	C5	C6	178.5(2)	O4	C21	C22	C23	-179.9(2)
O2	S1	C1	C2	-51.63(19)	O5	S2	C18	C19	-134.4(2)
O2	S1	C1	C6	125.99(18)	O5	S2	C18	C23	44.5(2)
O2	S1	C8	C9	-171.75(14)	O5	S2	C25	C26	171.67(15)
O2	S1	C8	C11	10.45(19)	O5	S2	C25	C28	-11.2(2)
O3	S1	C1	C2	178.11(16)	O6	S2	C18	C19	-3.9(2)
O3	S1	C1	C6	-4.3(2)	O6	S2	C18	C23	174.95(17)
O3	S1	C8	C9	-42.11(17)	O6	S2	C25	C26	41.64(18)
O3	S1	C8	C11	140.09(17)	O6	S2	C25	C28	-141.28(17)
C1	S1	C8	C9	71.64(16)	C18	S2	C25	C26	-72.66(17)
C1	S1	C8	C11	-106.16(18)	C18	S2	C25	C28	104.43(19)
C1	C2	C3	C4	-1.1(3)	C18	C19	C20	C21	0.4(5)
C2	C1	C6	C5	1.2(3)	C19	C18	C23	C22	0.9(3)
C2	C3	C4	O1	-177.7(2)	C19	C20	C21	O4	179.8(3)
C2	C3	C4	C5	1.7(4)	C19	C20	C21	C22	0.3(4)

C3	C4	C5	C6	-0.8(4)	C20	C21	C22	C23	-0.4(4)
C4	C5	C6	C1	-0.6(4)	C21	C22	C23	C18	-0.2(3)
C6	C1	C2	C3	-0.3(3)	C23	C18	C19	C20	-1.0(4)
C7	O1	C4	C3	179.0(2)	C24	O4	C21	C20	173.4(3)
C7	O1	C4	C5	-0.3(4)	C24	O4	C21	C22	-7.1(4)
C8	S1	C1	C2	65.03(19)	C25	S2	C18	C19	109.9(2)
C8	S1	C1	C6	-117.35(18)	C25	S2	C18	C23	-71.22(19)
C8	C11	C12	C13	-153.5(2)	C25	C28	C29	C30	148.0(2)
C8	C11	C12	C17	27.3(4)	C25	C28	C29	C34	-33.7(4)
C9	C8	C11	C12	4.1(4)	C26	C25	C28	C29	-5.0(4)
C11	C8	C9	C10	-95.6(3)	C28	C25	C26	C27	102.6(3)
C11	C12	C13	C14	179.2(2)	C28	C29	C30	C31	-178.8(2)
C11	C12	C17	C16	-179.1(2)	C28	C29	C34	C33	179.1(2)
C12	C13	C14	C15	0.5(4)	C29	C30	C31	C32	-0.8(4)
C13	C12	C17	C16	1.7(4)	C30	C29	C34	C33	-2.6(4)
C13	C14	C15	C16	0.4(4)	C30	C31	C32	C33	-1.5(4)
C14	C15	C16	C17	-0.3(4)	C31	C32	C33	C34	1.7(4)
C15	C16	C17	C12	-0.8(4)	C32	C33	C34	C29	0.4(4)
C17	C12	C13	C14	-1.6(4)	C34	C29	C30	C31	2.9(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a.

Atom	***x***	***y***	***z***	**U(eq)**
H2	4888.57	3565.34	471.16	58
H3	2330.42	3736.62	-868.18	64
H5	6446.51	3210.69	-2439.21	69
H6	8969.56	3025.8	-1096.45	66
H7A	1911.89	3651.57	-3889.75	143

H7B	2655.05	3309.85	-3520.27	143
H7C	4826.21	3569.98	-3508.95	143
H9A	4643.05	2578.5	1267.41	55
H9B	6102.35	2644.1	401.13	55
H11	7182.83	3288.71	2361.89	55
H13	3792.54	3393.73	3307.71	75
H14	1147.89	3223.59	4381.07	93
H15	707.81	2693.36	4653.54	88
H16	2914.56	2329.73	3873.45	80
H17	5565.23	2494.67	2810.25	67
H19	4344.23	4792.9	400.2	89
H20	1634.23	4871.74	-978.09	94
H22	-2344.05	4091.85	-505.93	60
H23	396.44	4012.96	876.68	57
H24A	-4880.58	4400.45	-2672.76	128
H24B	-5334	4309.01	-1652.02	128
H24C	-3224.32	4129.22	-2137.73	128
H26A	1952	4848.51	2242.55	61
H26B	831.31	4766.48	3171.98	61
H28	2534.15	3961.87	2951.44	57
H30	-1273.25	3746.97	3570.33	67
H31	-3794.76	3727.4	4753.74	86
H32	-3493.07	4118.2	5868.54	93
H33	-509.57	4521.7	5825.32	91
H34	2017.4	4547.96	4641.01	75

10. References

[1] Zhao, Z.; Racicot, L.; Murphy, G. K. Fluorinative Rearrangements of Substituted Phenylallenes Mediated by (Difluoroiodo)toluene: Synthesis of α-(Difluoromethyl)styrenes. *Angew. Chem., Int. Ed.* **2017**, *56*, 11620–11623.

[2] Deng, H.; Meng, Z.; Wang, S.; Zhang, Z.; Zhang, Y.; Shangguan, Y.; Yang, F.; Yuan, D.; Guo, H.; Zhang, C. Enantioselective Copper-Catalyzed Three-Component Carboboronation of Allenes: Access to Functionalized Dibenzo[b, *f*][1,4]oxazepine Derivatives. *Adv. Synth. Catal.* **2019**, *361*, 1–7.

[3] Hasenbeck, M.; Ahles, S.; Averdunk, A.; Becker, J.; Gellrich, U. Formation of Nucleophilic Allylboranes from Molecular Hydrogen and Allenes Catalyzed by a Pyridonate Borane that Displays Frustrated Lewis Pair Reactivity. *Angew. Chem., Int. Ed.* **2020**, *59*, 23885–23891.

[4] Liu, Y.; Pan, Q.; Hu, X.; Guo, Y.; Chen, Q-Y; Liu, C. Rapid Access to N-Protected Sulfonimidoyl Fluorides: Divergent Synthesis of Sulfonamides and Sulfonimidamides. *Org. Lett.* **2021**, *23*, 3975–3980.

[5] Singh, A. K.; Kandasamy, J. Palladium catalyzed stereocontrolled synthesis of C-aryl glycosides using glycals and arenediazonium salts at room temperature. *Org. Biomol. Chem.* **2018**, *16*, 5107–5112.

[6] Liu, S.; Huang, Y.; Xu, X-H; Qing, F-L. Fluorosulfonylation of arenediazonium tetrafluoroborates with $Na_2S_2O_5$ and N-fluorobenzenesulfonimide. *J. Fluorine Chem.* **2020**, *240*, 109653.

[7] Ramanathan, M.; Liu, S.-T. Cascade annulations of aryldiazonium salts, nitriles and halo-alkynes leading to 3-haloquinolines. *Tetrahedron* **2017**, *73*, 4317–4322.

[8] Xing, B.; Li, L.; Ni, C.; Hu, J. Pentafluoroethylation of Arenediazonium Tetrafluoroborates Using On-Site Generated Tetrafluoroethylene. *Chin. J. Chem.* **2019**, *37*, 1131–1136.

[9] Min, M.; Bang, G. S.; Lee, H.; Yu, B-C. A photoswitchable methylene-spaced fluorinated aryl azobenzene monolayer grafted on silicon. *Chem. Commun.*, **2010**, *46*, 5232–5234.

[10] Cheng, C.Y.; Isobe, M. Three types of products by carbon nu-cleophiles toward methoxyphenylacetylenic sulfones. *Tetrahedron* **2011**, *67*, 9957–9965.

[11] Yu, R. -R; Xing, Y. -D; Fang, X. -J. Regio-, Chemo-, and Enanti-oselective Ni-Catalyzed Hydrocyanation of 1,3-Dienes. *Org. Lett*. **2021**, *23*, 930–935.

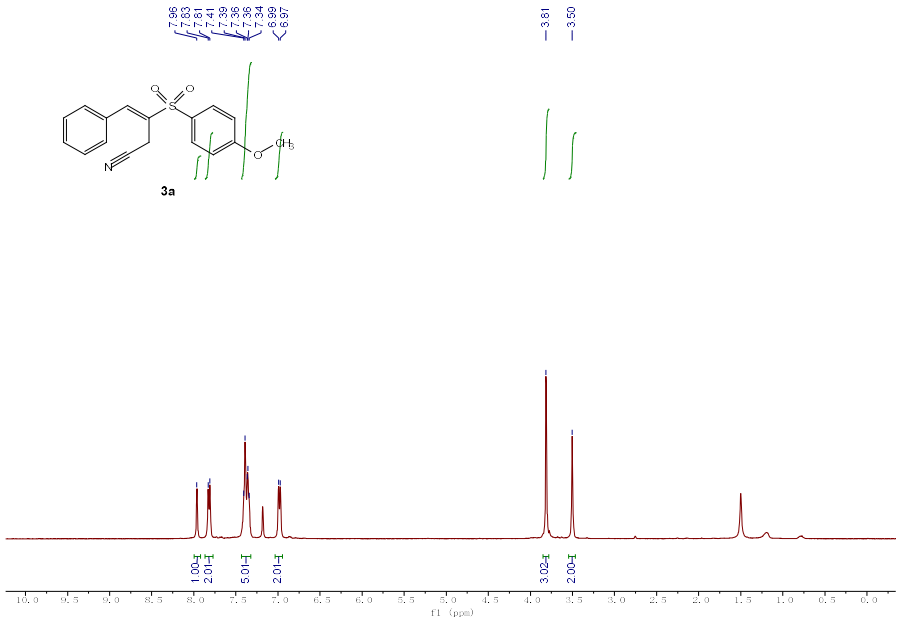
[12] Beck, H.; Jeske, M.; Thede, K.; Stoll, F.; Flamme, I.; Akbaba, M.; Ergeden, J. -K.; Karig, G.; Keldenich, J.; Oehme, F.; Militzer, H. -C.; Hartung, I. -V.; Thuss, U. Discovery of Molidustat (BAY 85-3934): A Small-Molecule Oral HIF-Prolyl Hydroxylase (HIF-PH) Inhibitor for the Treatment of Renal Anemia. *ChemMedChem* **2018**, *13*, 988–1003.

[13] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.

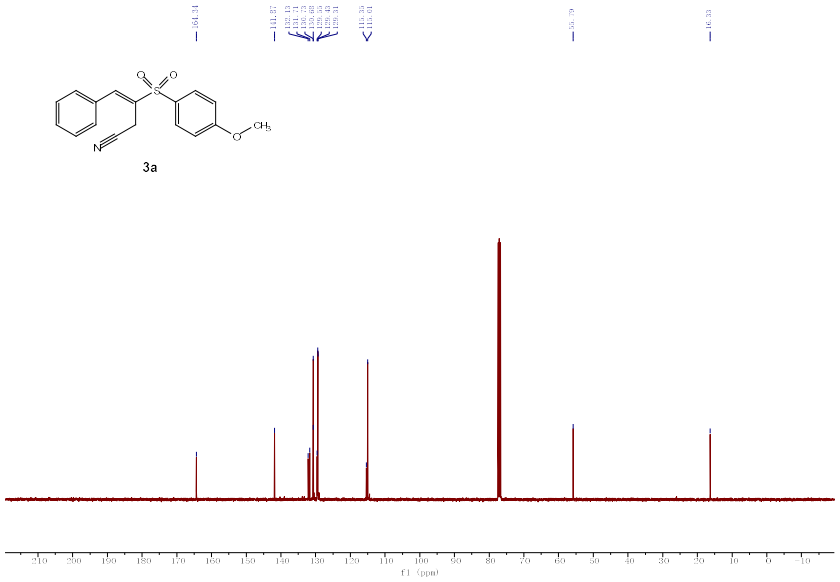
[14] (a) Palatinus, L.; Chapuis, G. SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Cryst.* **2007**, *40*, 786–790; (b) Palatinus, L.; van der Lee, A. Symmetry determination following structure solution in P1. *J. Appl. Cryst.* **2008**, *41*, 975–984; (c) Palatinus, L.; Prathapa, S. J.; van Smaalen, S. EDMA: a computer program for topological analysis of discrete electron densities. *J. Appl. Cryst.* **2012**, 45, 575–580.

[15] Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.

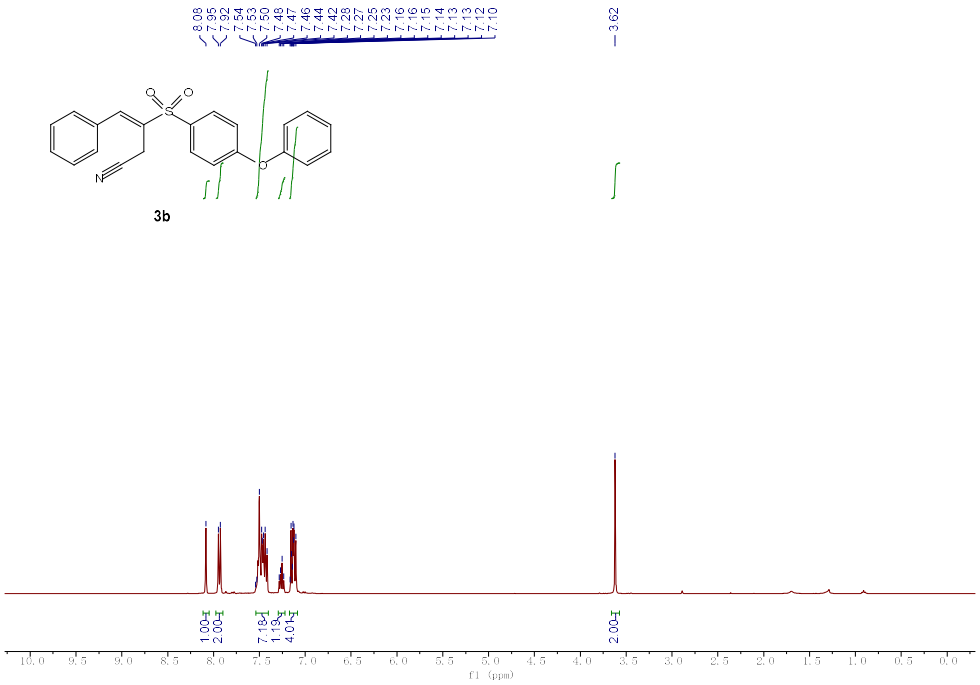
11. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra



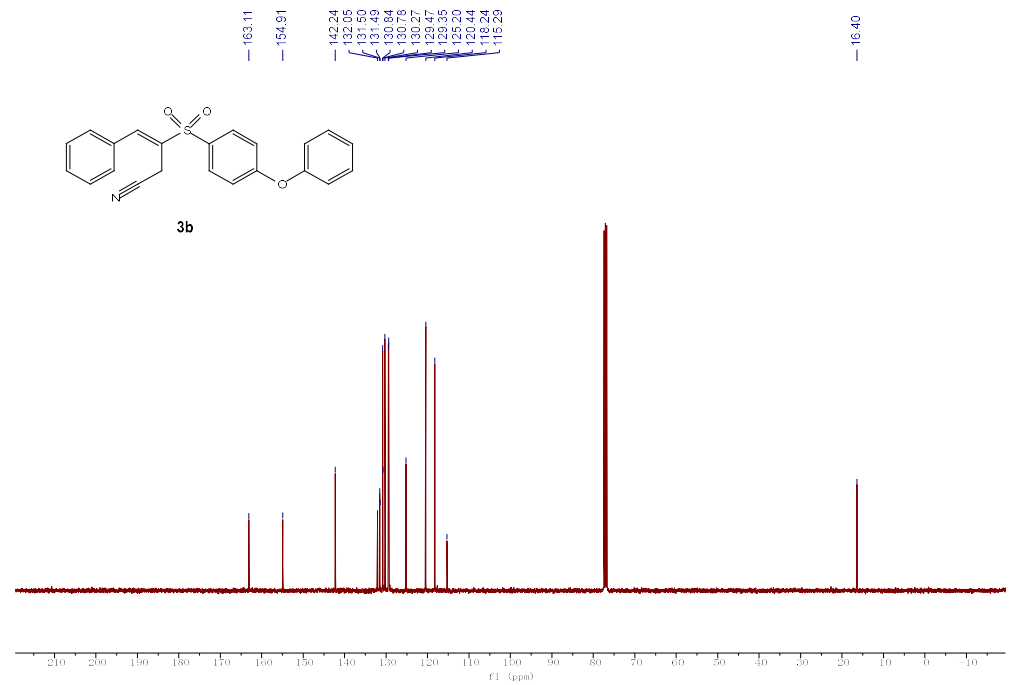
^{1}H NMR Spectrum of 3a ($CDCl_3$, 400 MHz)



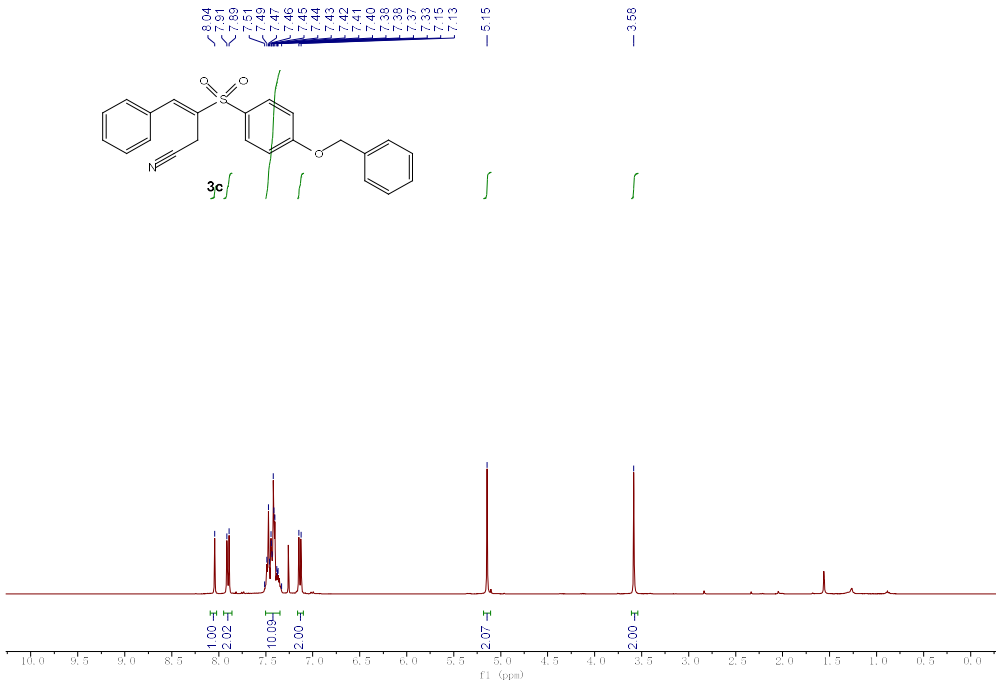
^{13}C NMR Spectrum of 3a ($CDCl_3$, 101MHz)



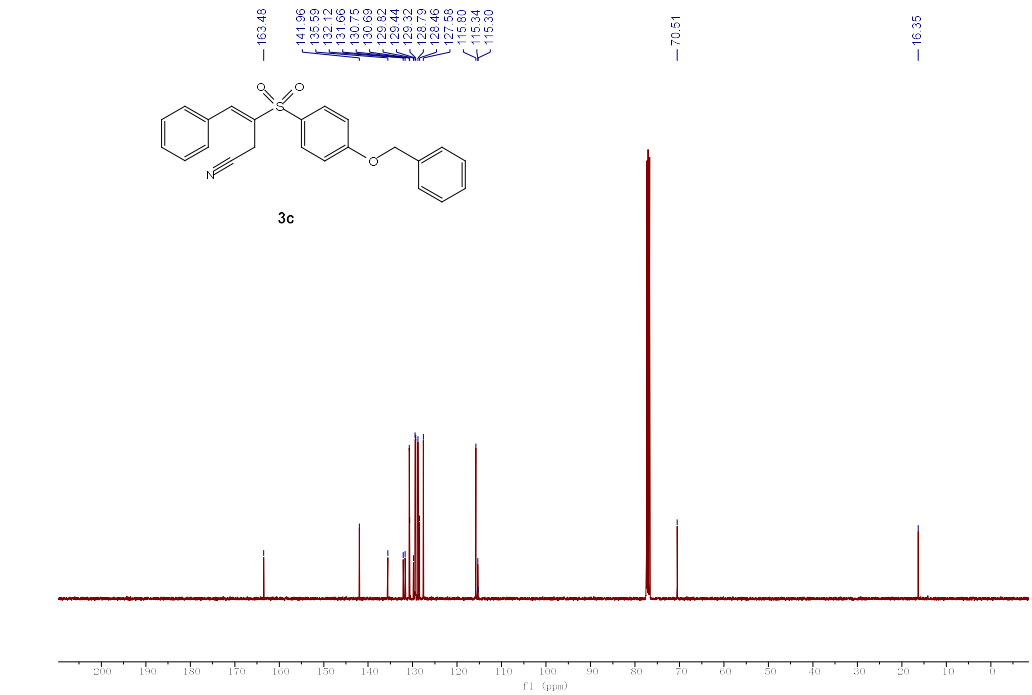
^{1}H NMR Spectrum of 3b ($CDCl_3$, 400 MHz)



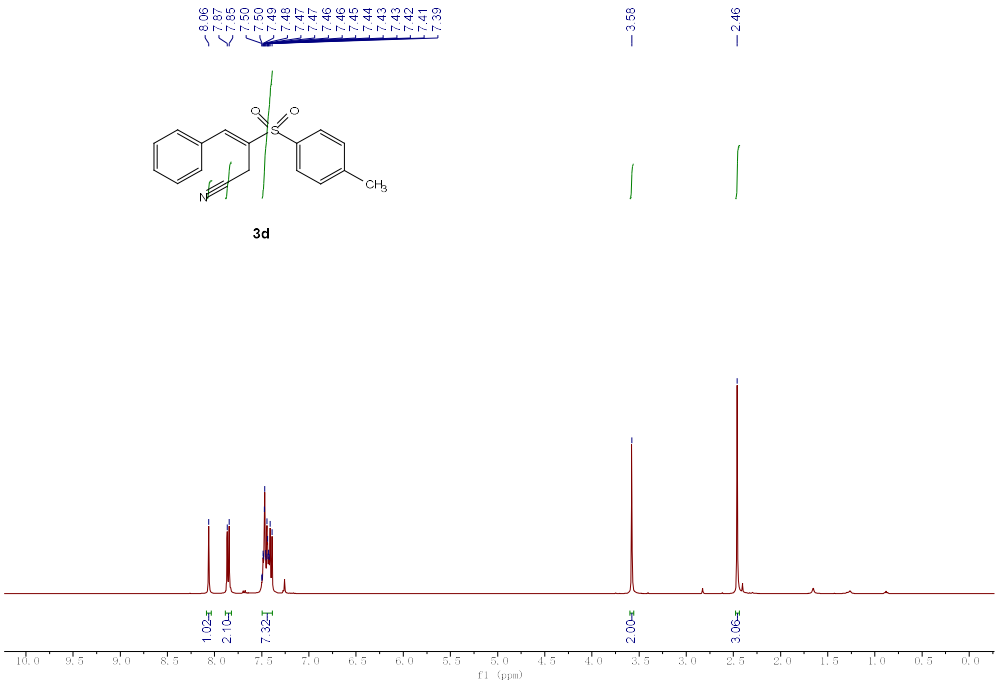
^{13}C NMR Spectrum of 3b ($CDCl_3$, 101MHz)



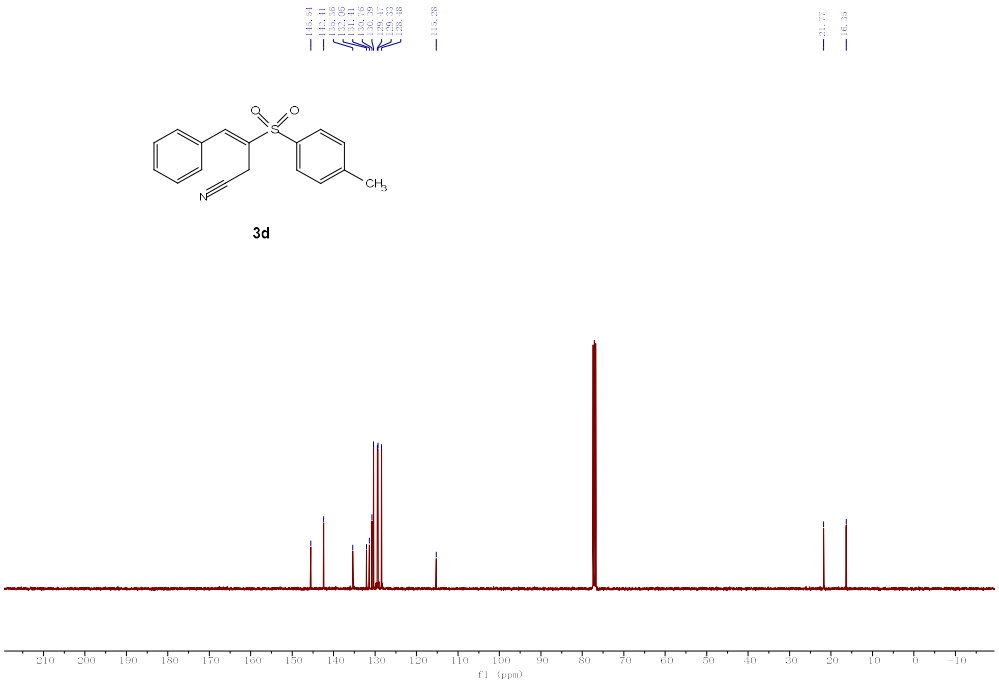
^{1}H NMR Spectrum of 3c ($CDCl_3$, 400 MHz)



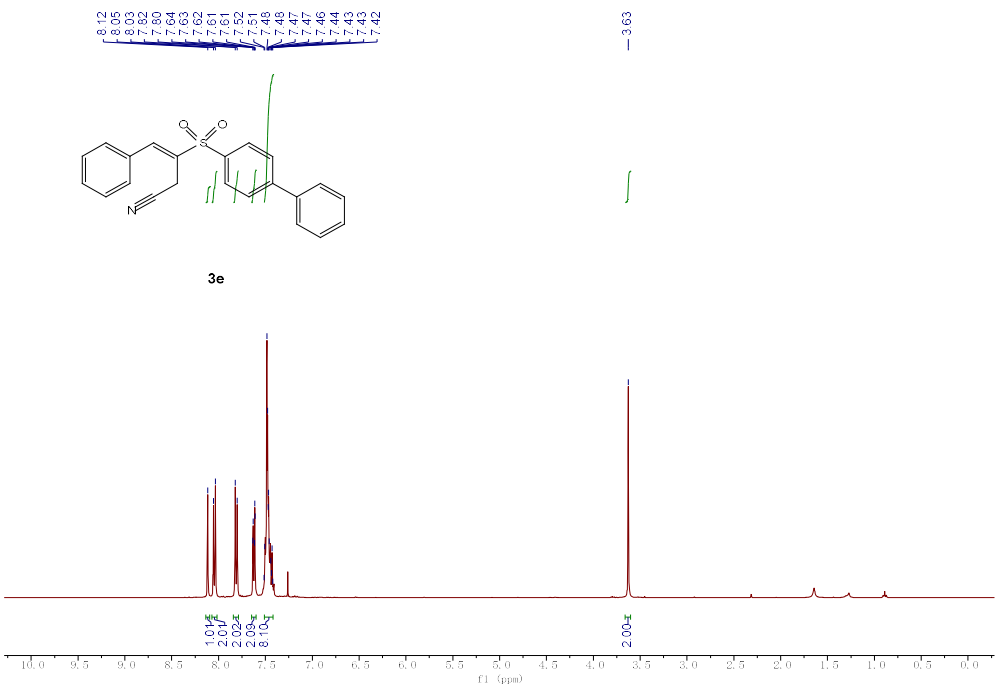
^{13}C NMR Spectrum of 3c ($CDCl_3$, 101MHz)



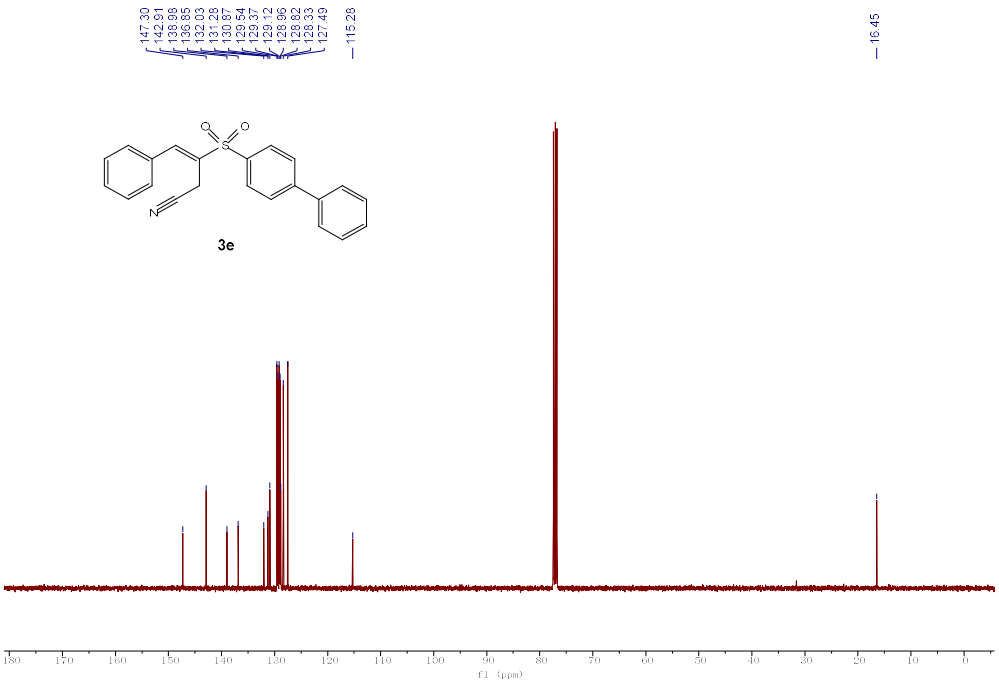
^{1}H NMR Spectrum of 3d ($CDCl_3$, 400 MHz)



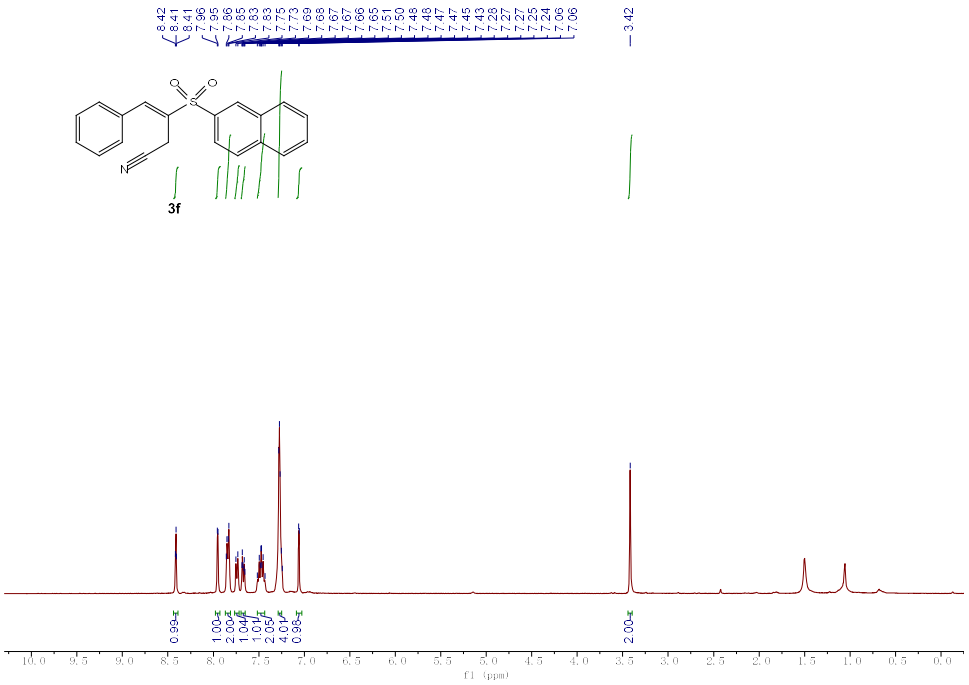
^{13}C NMR Spectrum of 3d ($CDCl_3$, 101MHz)



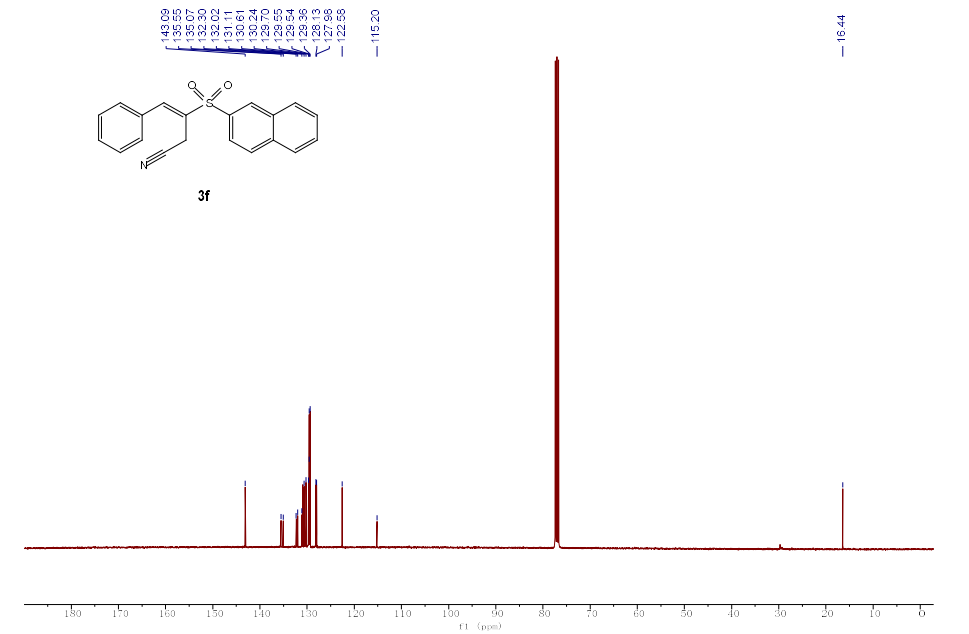
^{1}H NMR Spectrum of 3e ($CDCl_3$, 400 MHz)



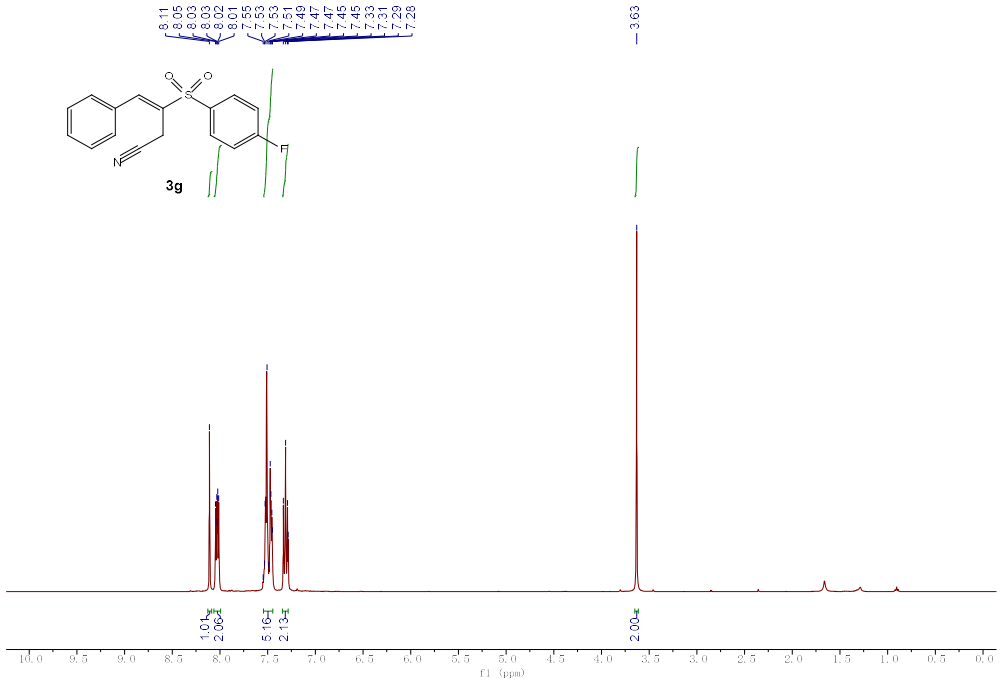
^{13}C NMR Spectrum of 3e ($CDCl_3$, 101MHz)



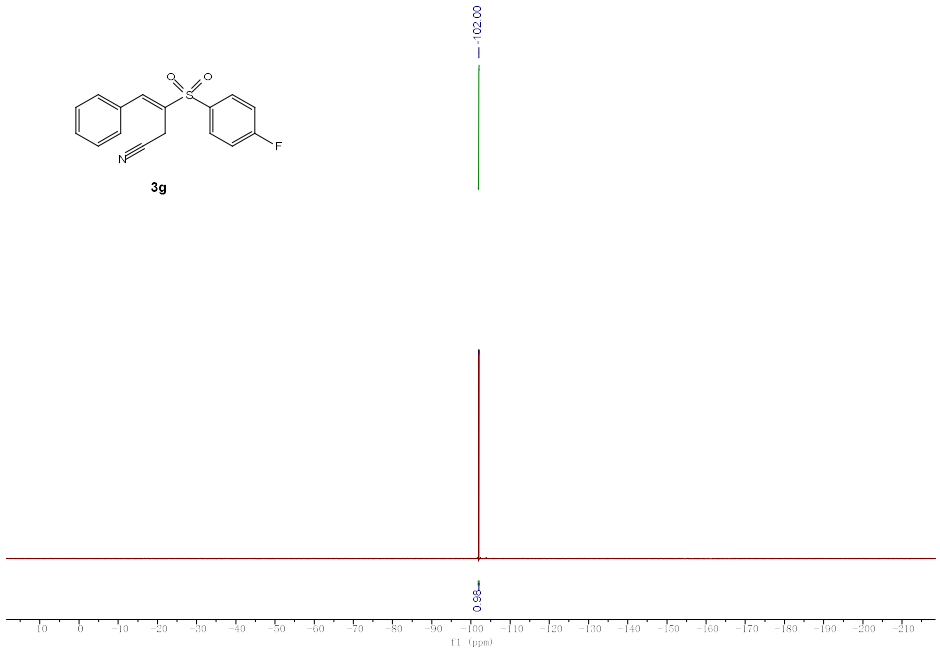
^{1}H NMR Spectrum of 3f ($CDCl_3$, 400 MHz)



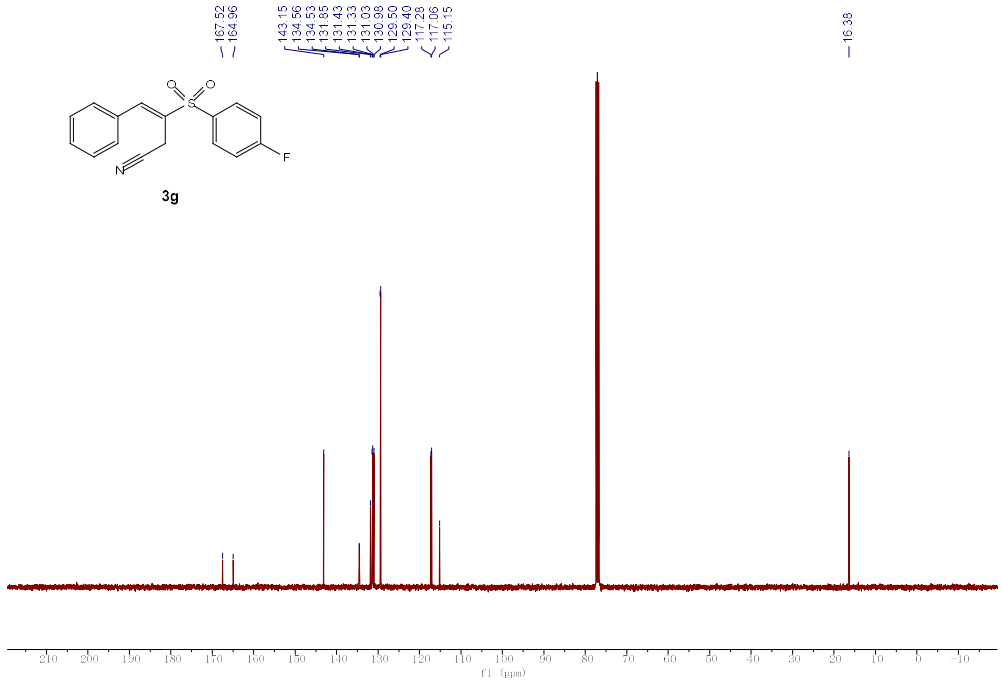
^{13}C NMR Spectrum of 3f ($CDCl_3$, 101MHz)



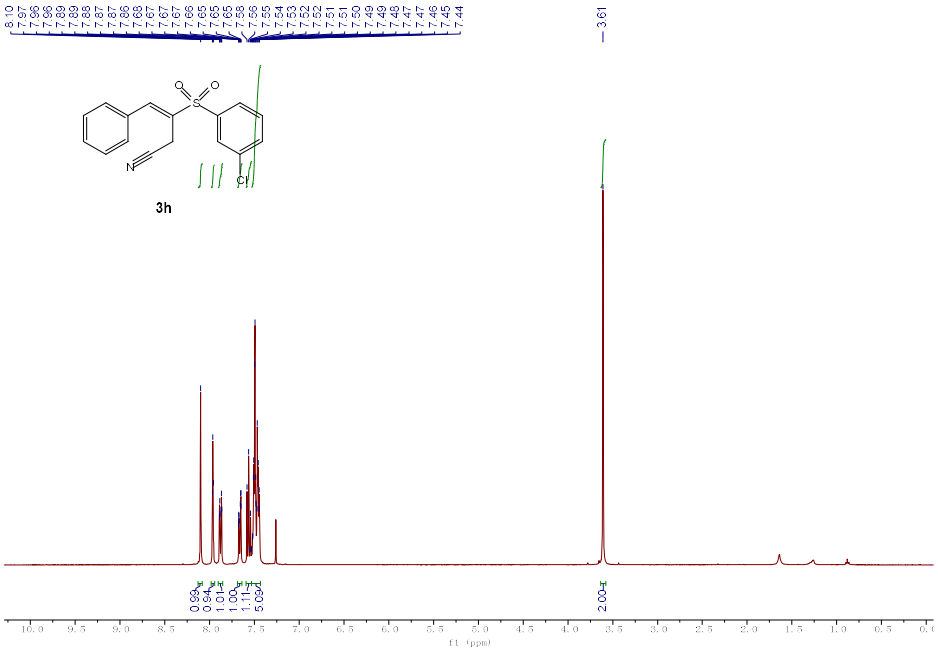
^{1}H NMR Spectrum of 3g ($CDCl_3$, 400 MHz)



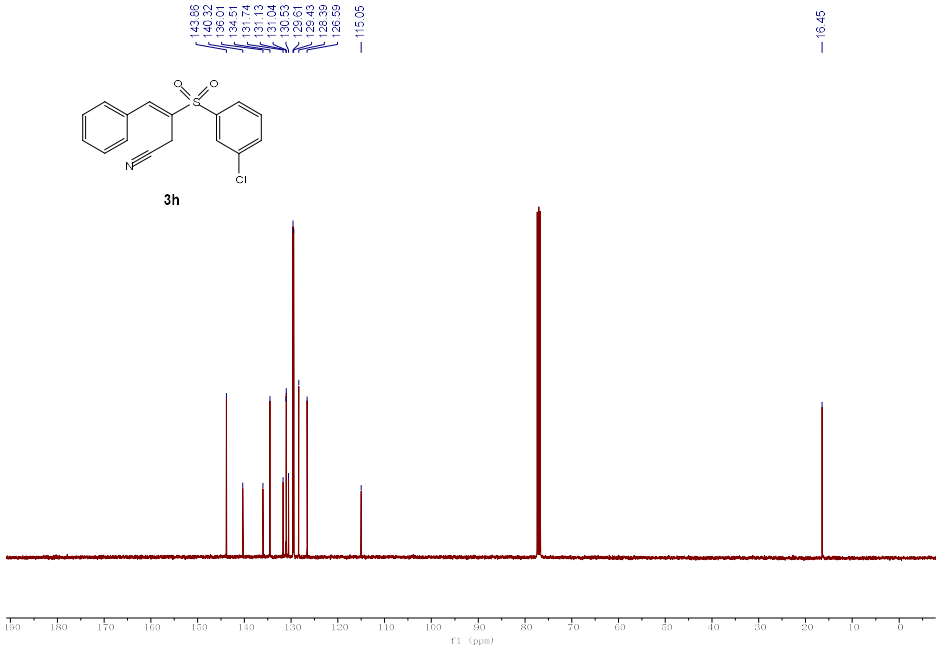
^{19}F NMR Spectrum of 3g ($CDCl_3$, 376 MHz)



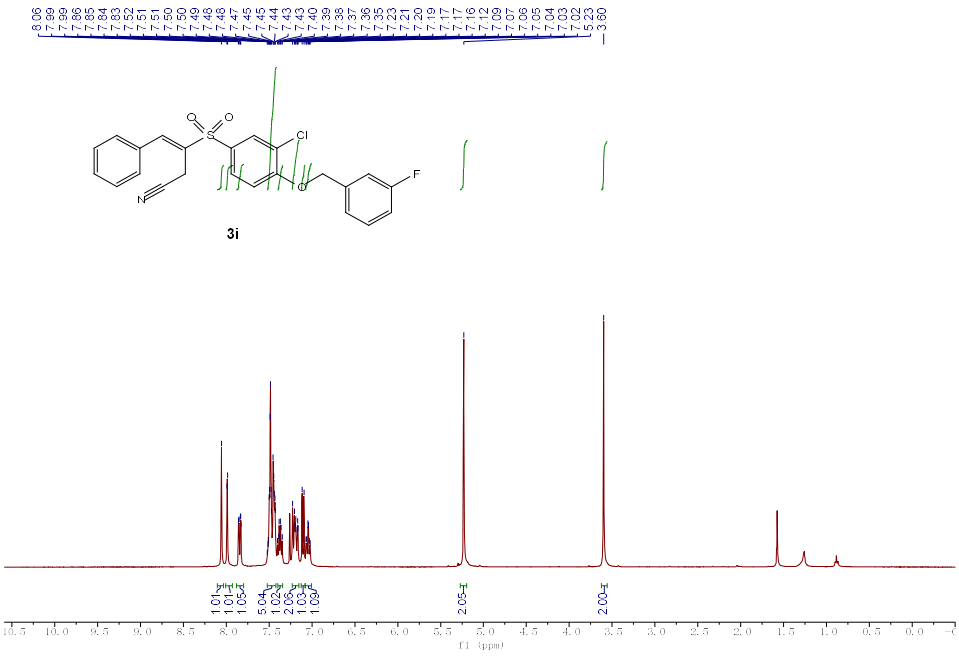
^{13}C NMR Spectrum of 3g ($CDCl_3$, 101MHz)



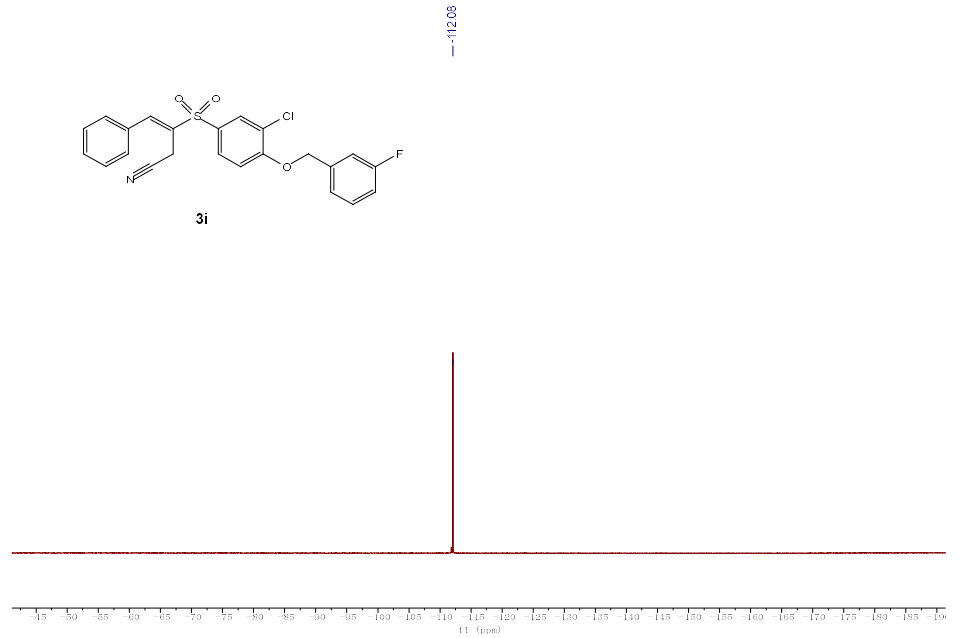
^{1}H NMR Spectrum of 3h ($CDCl_3$, 400 MHz)



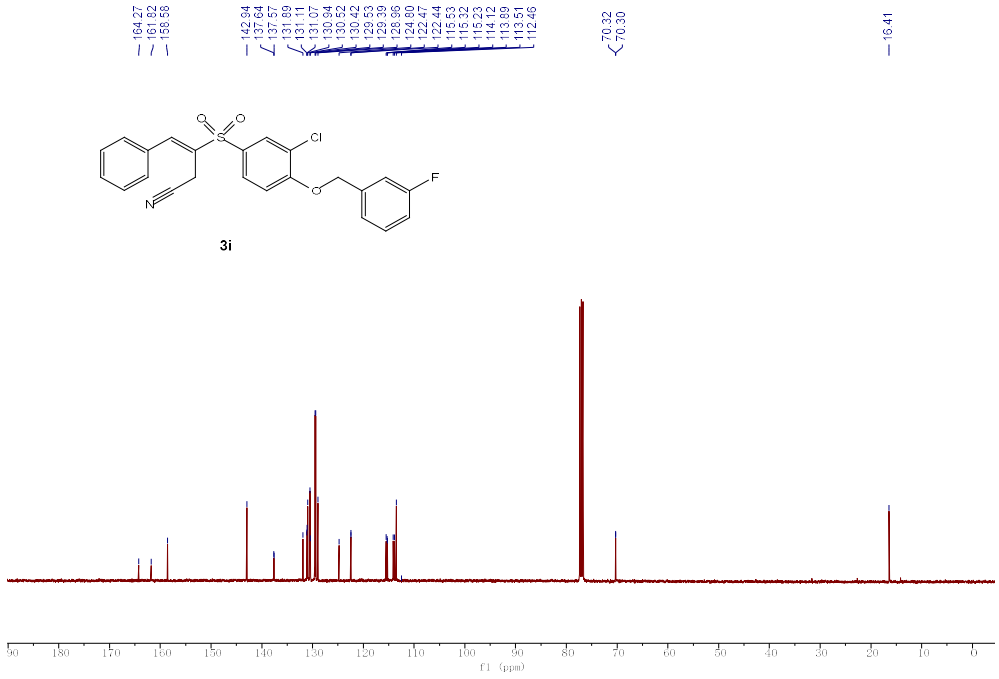
^{13}C NMR Spectrum of 3h ($CDCl_3$, 101MHz)



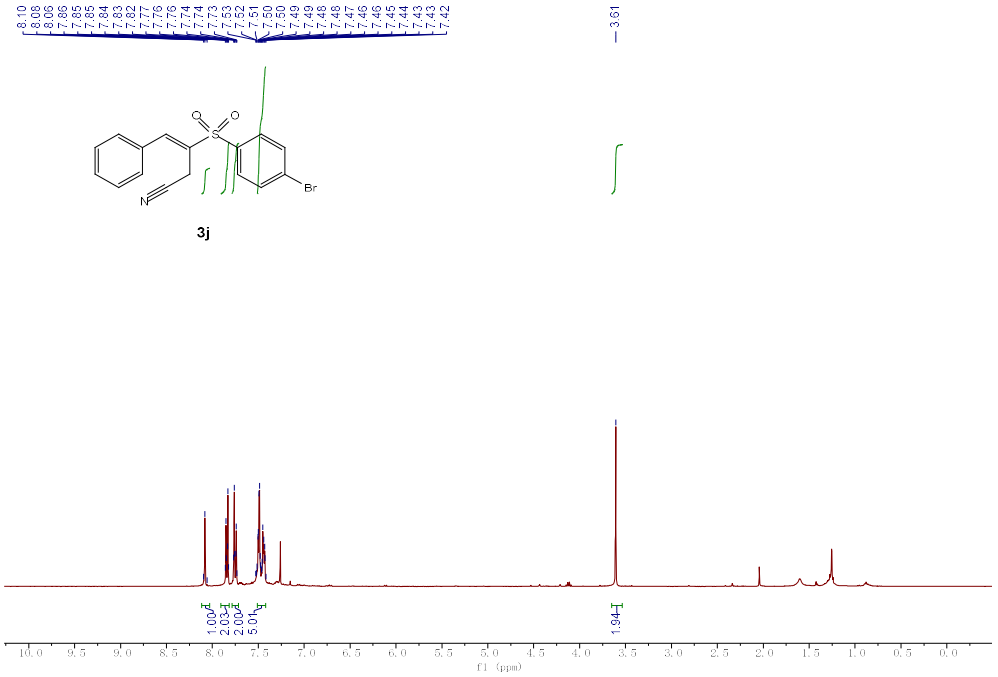
^{1}H NMR Spectrum of 3i ($CDCl_3$, 400 MHz)



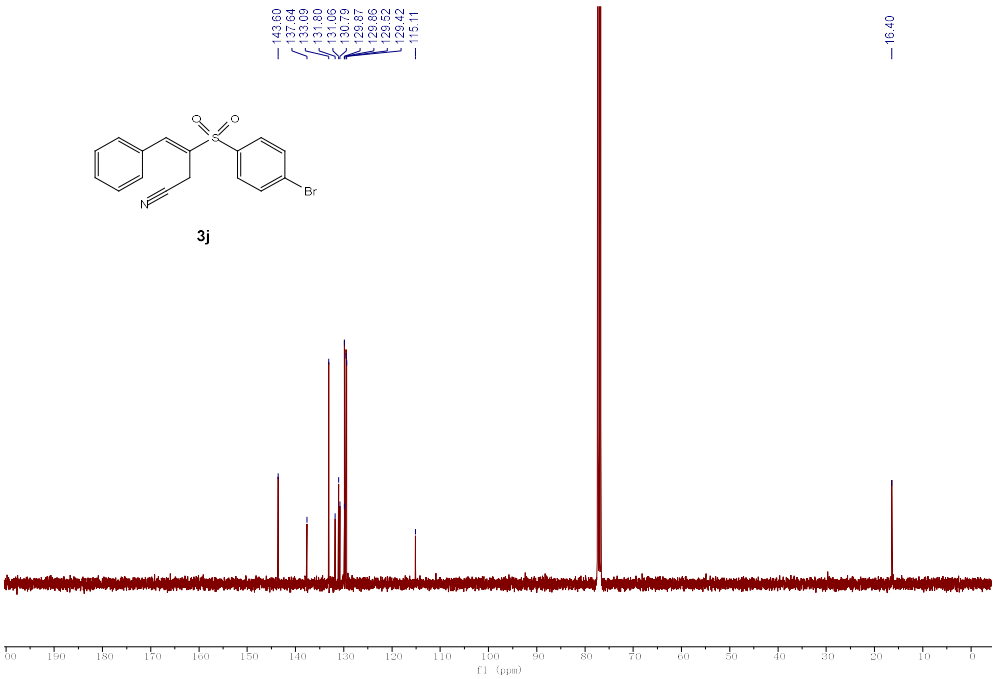
^{19}F NMR Spectrum of 3i ($CDCl_3$, 376 MHz)



^{13}C NMR Spectrum of 3i ($CDCl_3$, 101MHz)



^{1}H NMR Spectrum of 3j ($CDCl_3$, 400 MHz)



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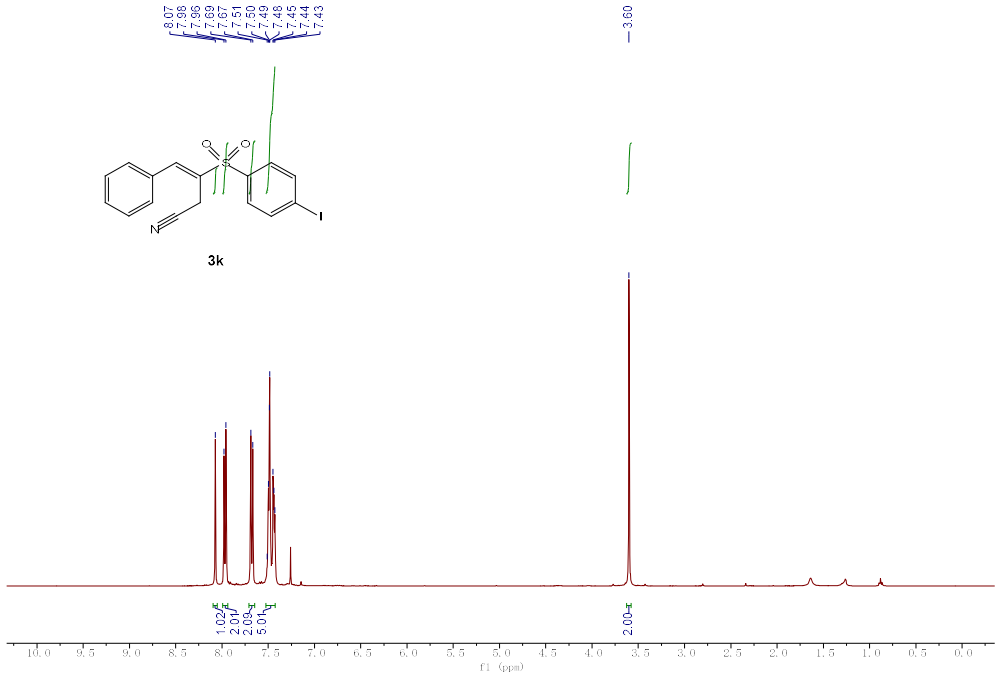
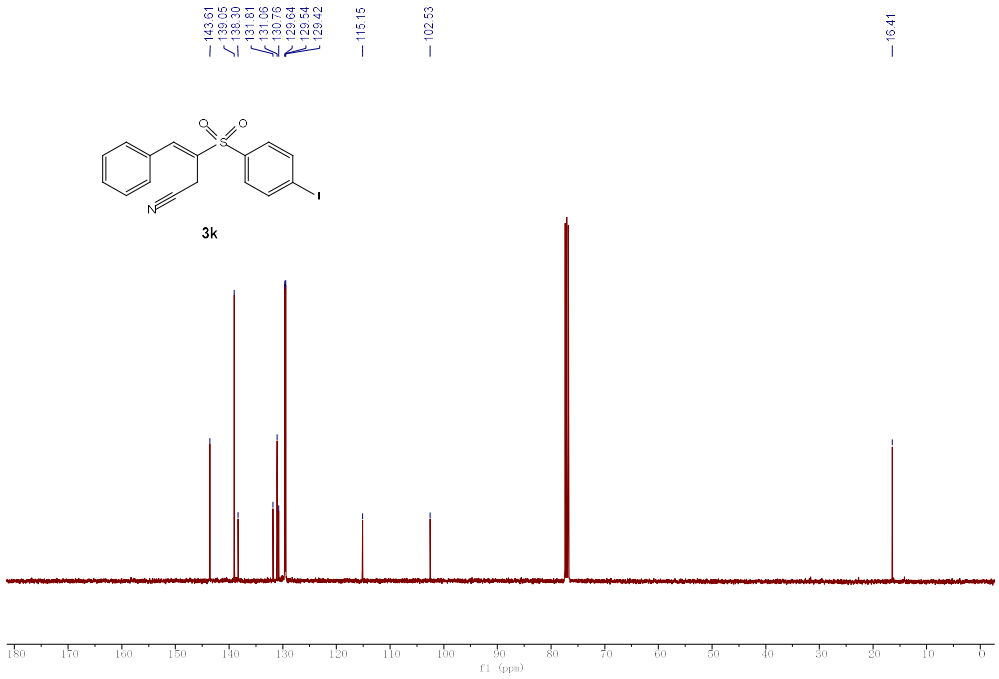
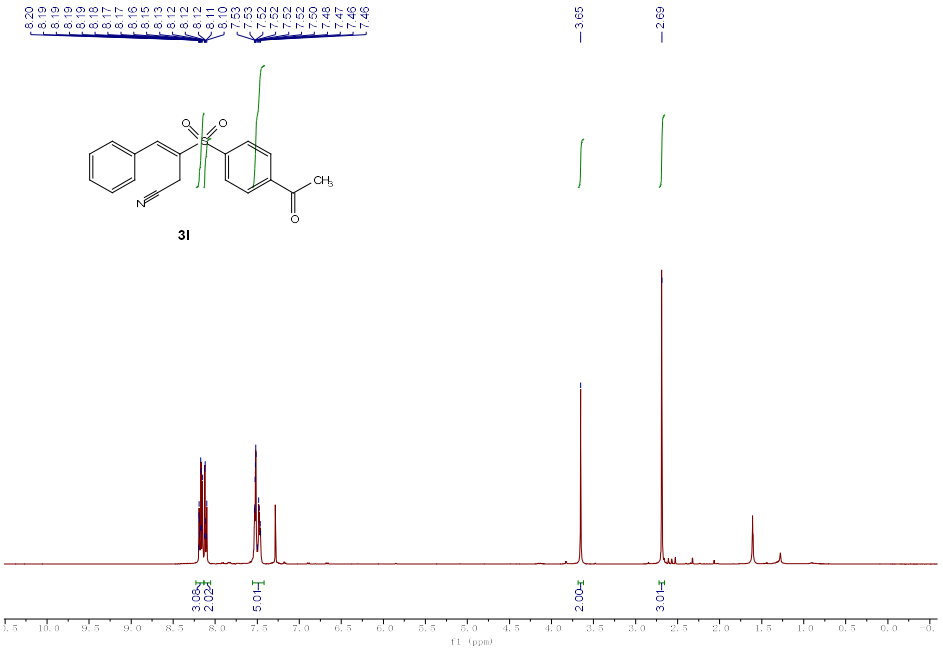


^{1}H NMR Spectrum of 3k ($CDCl_3$, 400 MHz)

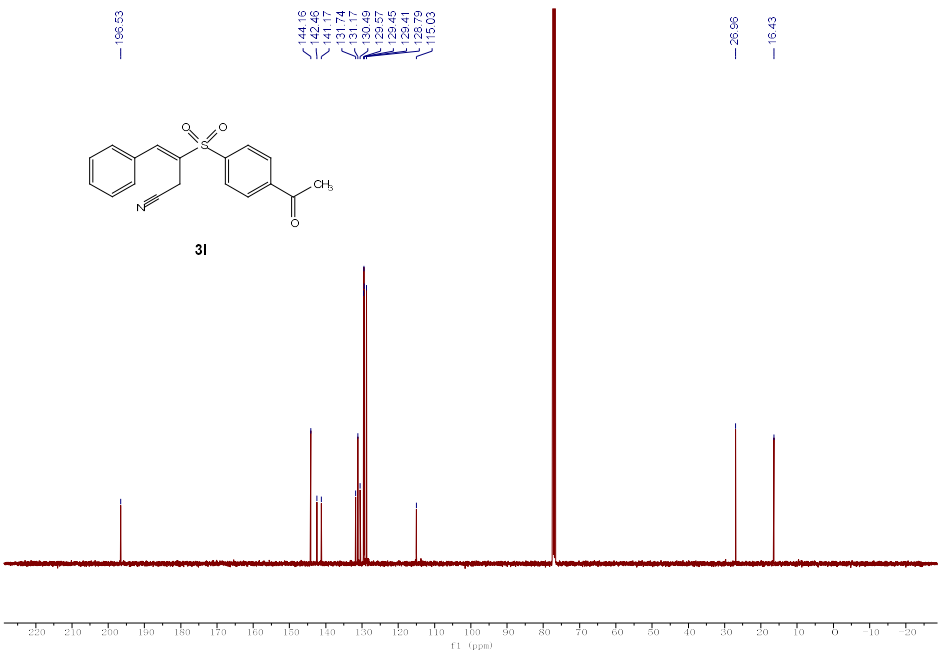


^{13}C NMR Spectrum of 3k ($CDCl_3$, 101MHz)



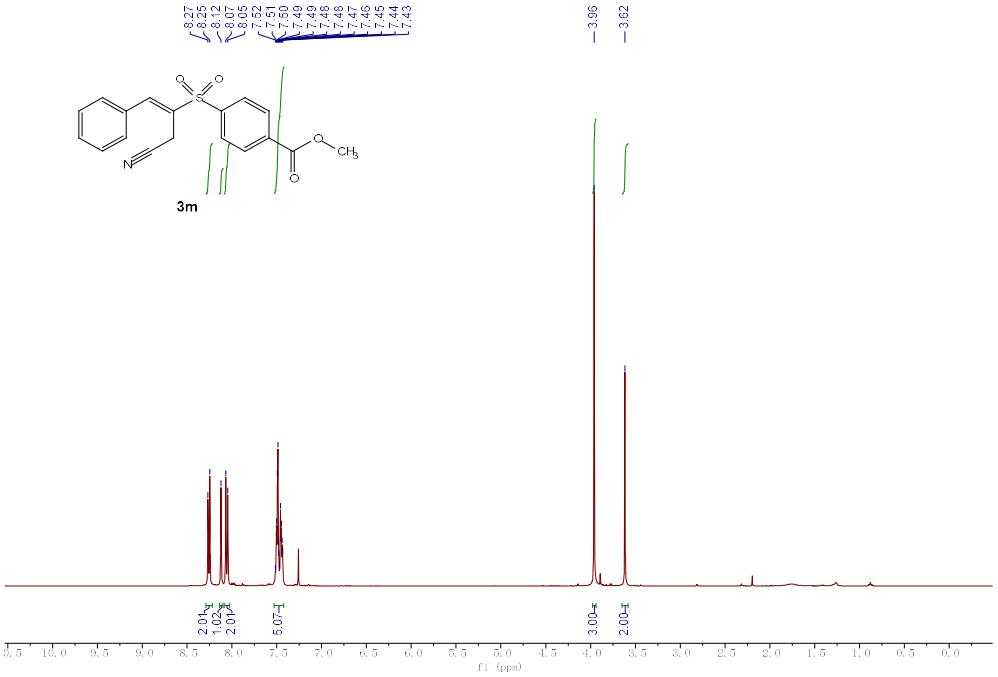
3l

^{1}H NMR Spectrum of 3l ($CDCl_3$, 400 MHz)

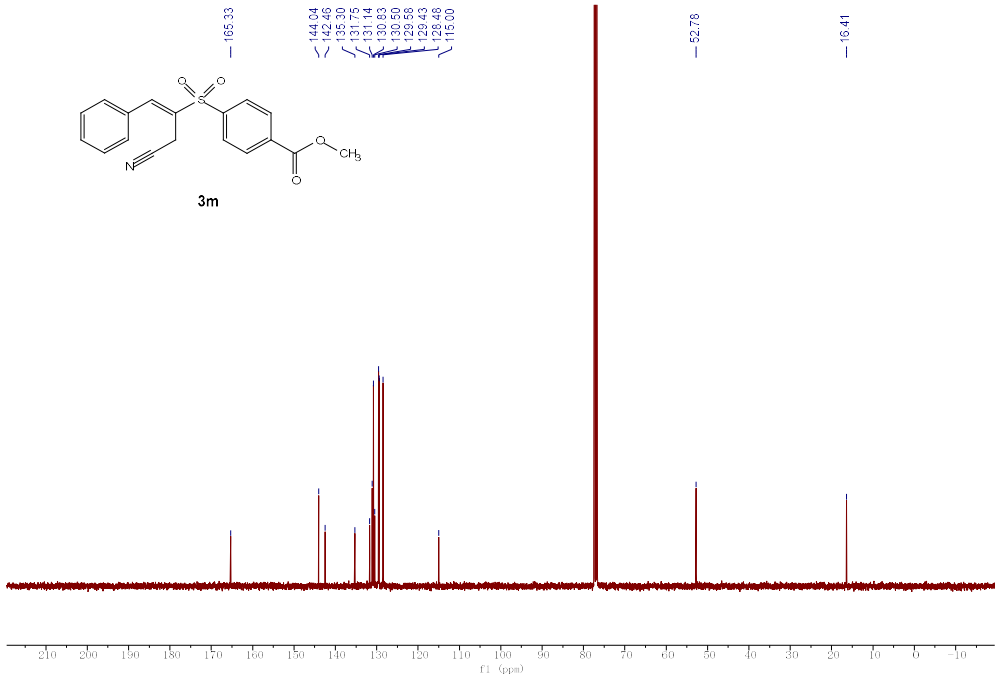


3l

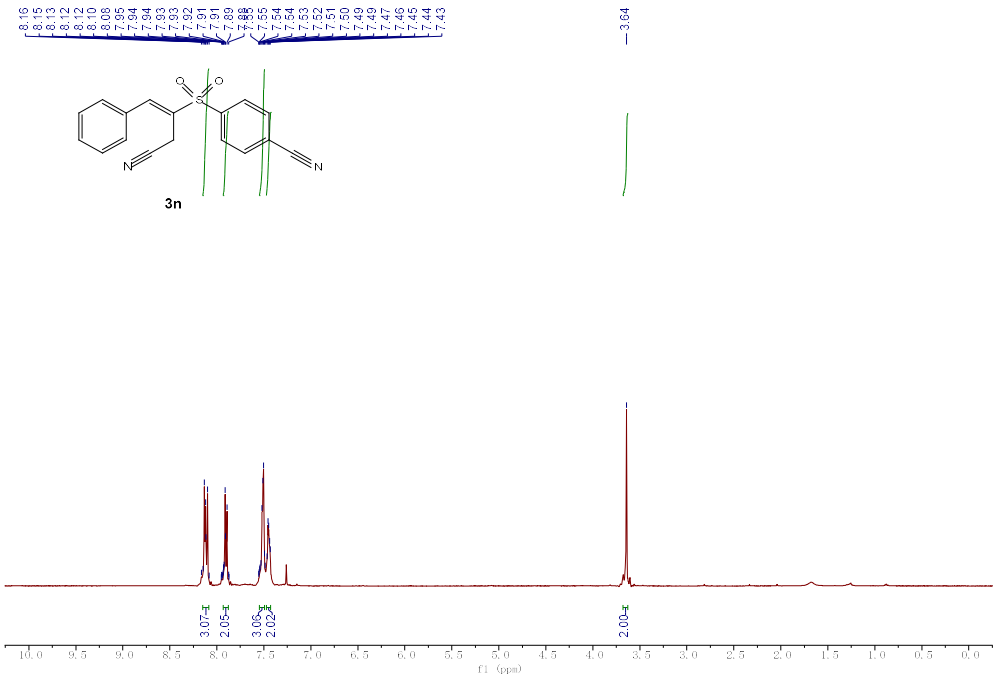
^{13}C NMR Spectrum of 3l ($CDCl_3$, 101MHz)



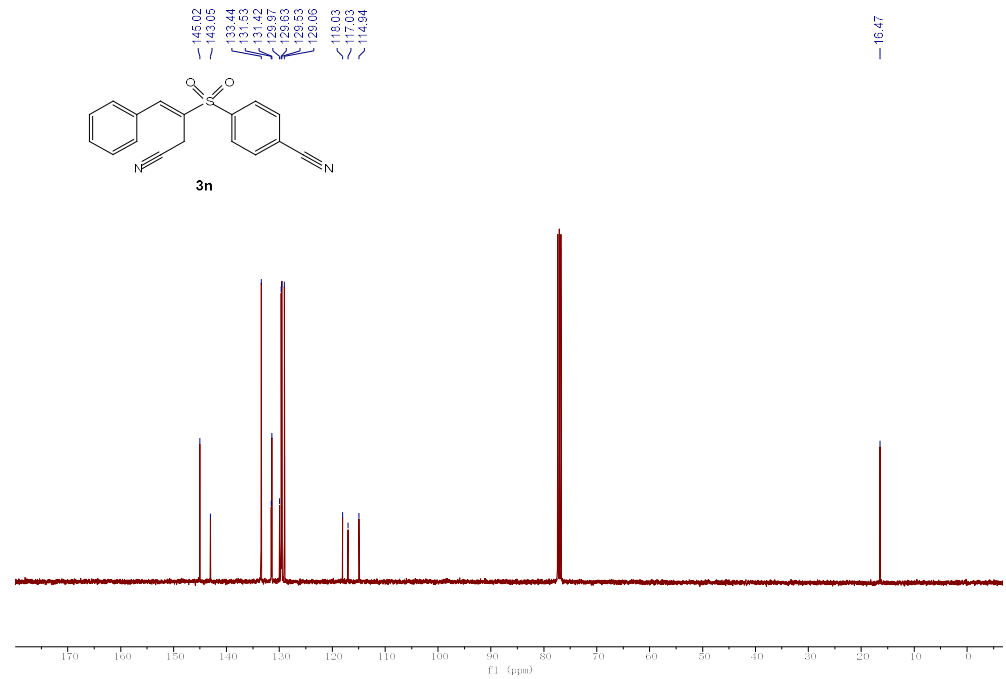
^{1}H NMR Spectrum of 3m ($CDCl_3$, 400 MHz)



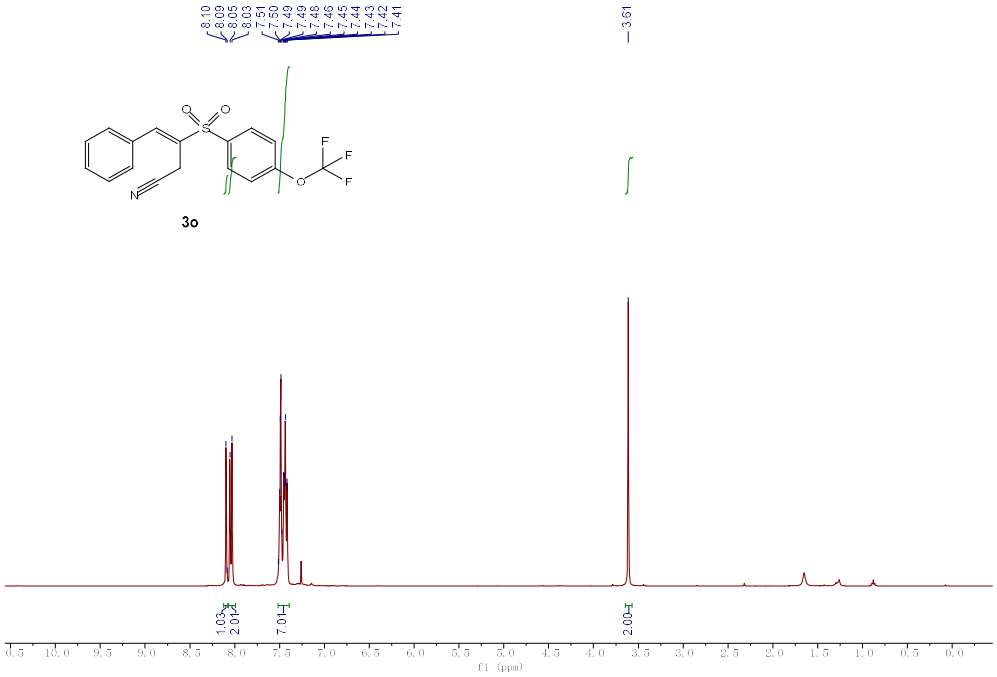
^{13}C NMR Spectrum of 3m ($CDCl_3$, 101MHz)



^{1}H NMR Spectrum of 3n ($CDCl_3$, 400 MHz)

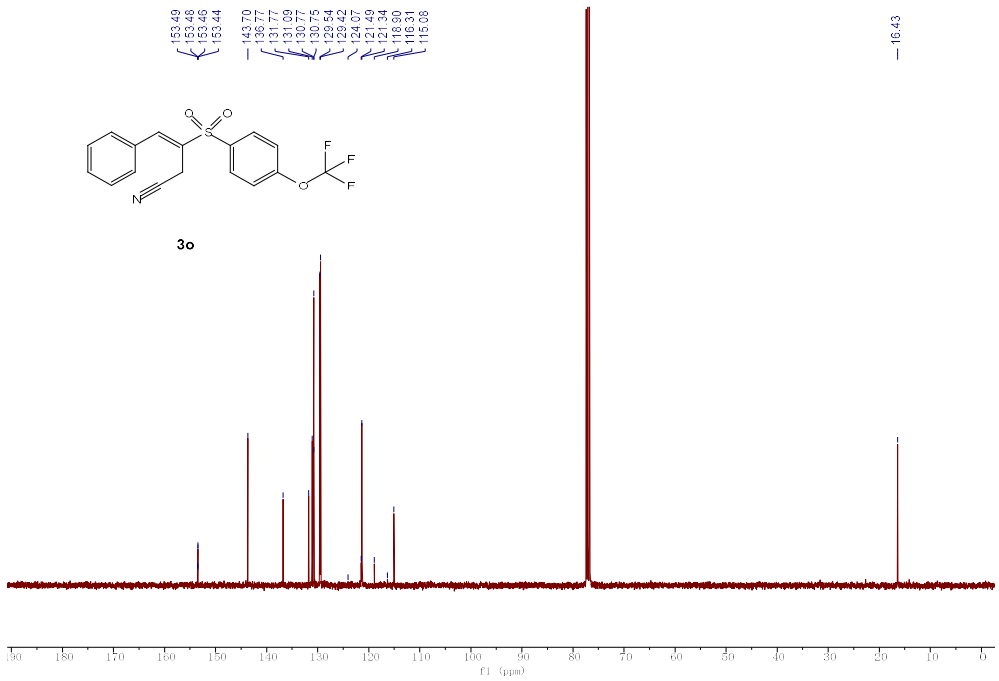


^{13}C NMR Spectrum of 3n ($CDCl_3$, 101MHz)

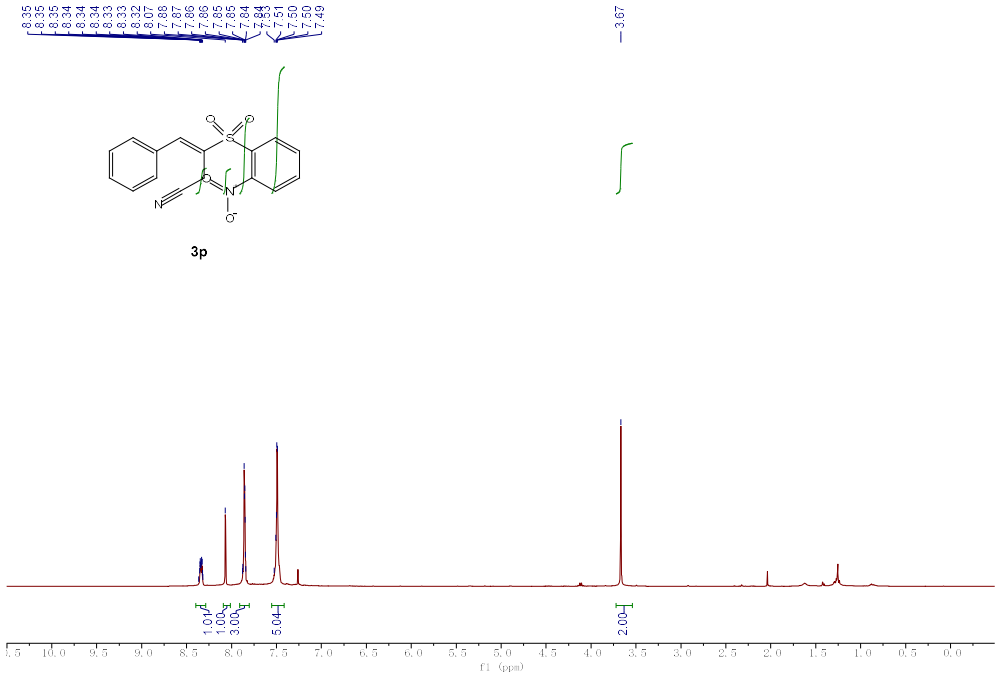


^{1}H NMR Spectrum of 3o ($CDCl_3$, 400 MHz)

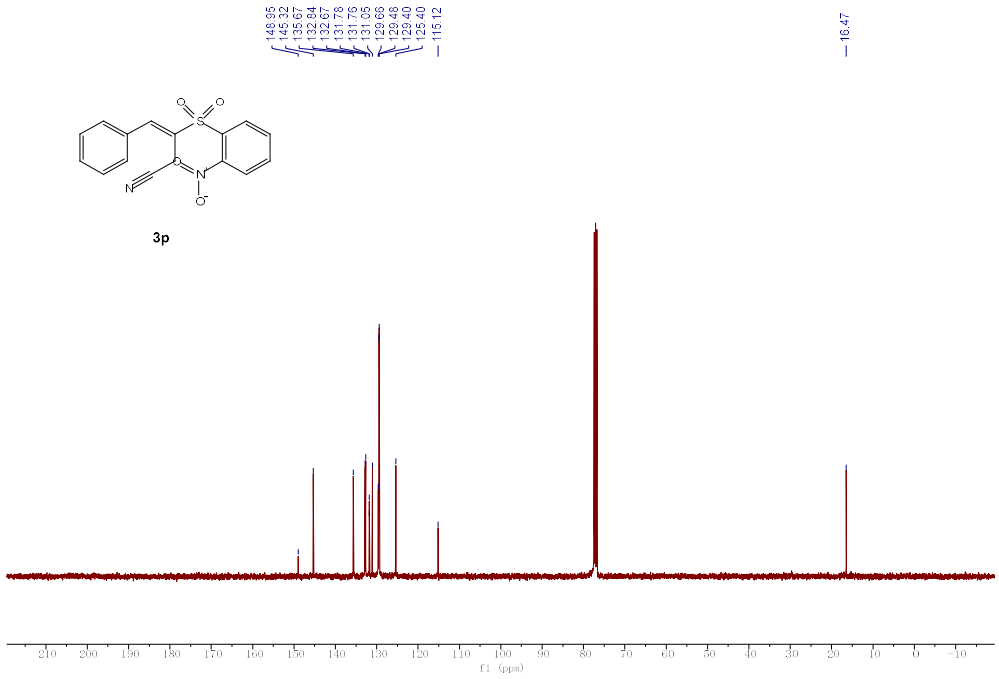
^{19}F NMR Spectrum of 3o ($CDCl_3$, 376 MHz)



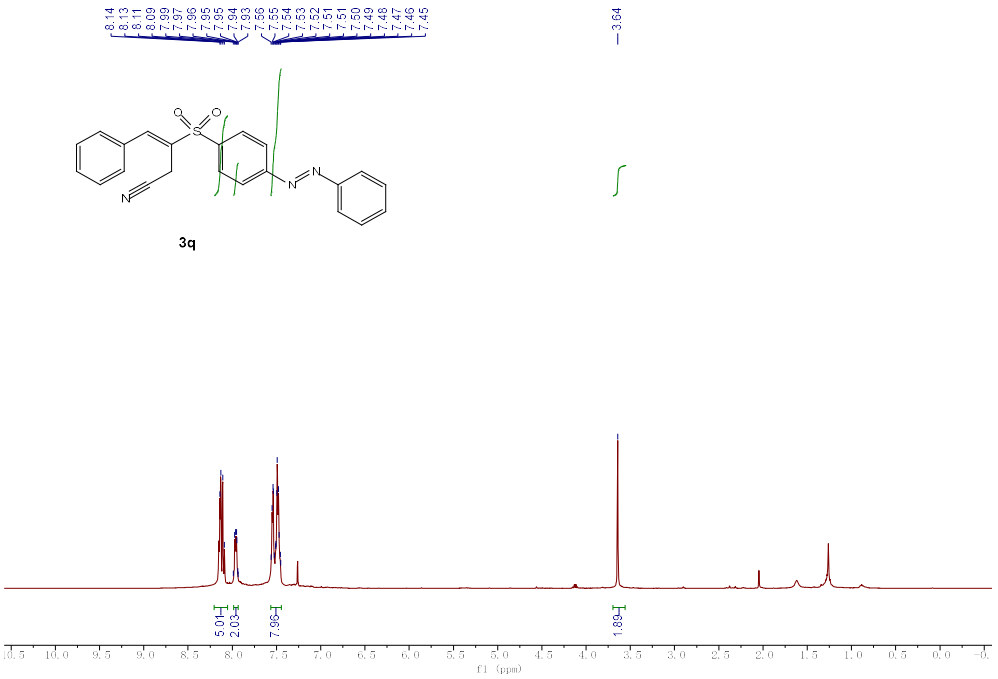
^{13}C NMR Spectrum of 3o ($CDCl_3$, 101MHz)



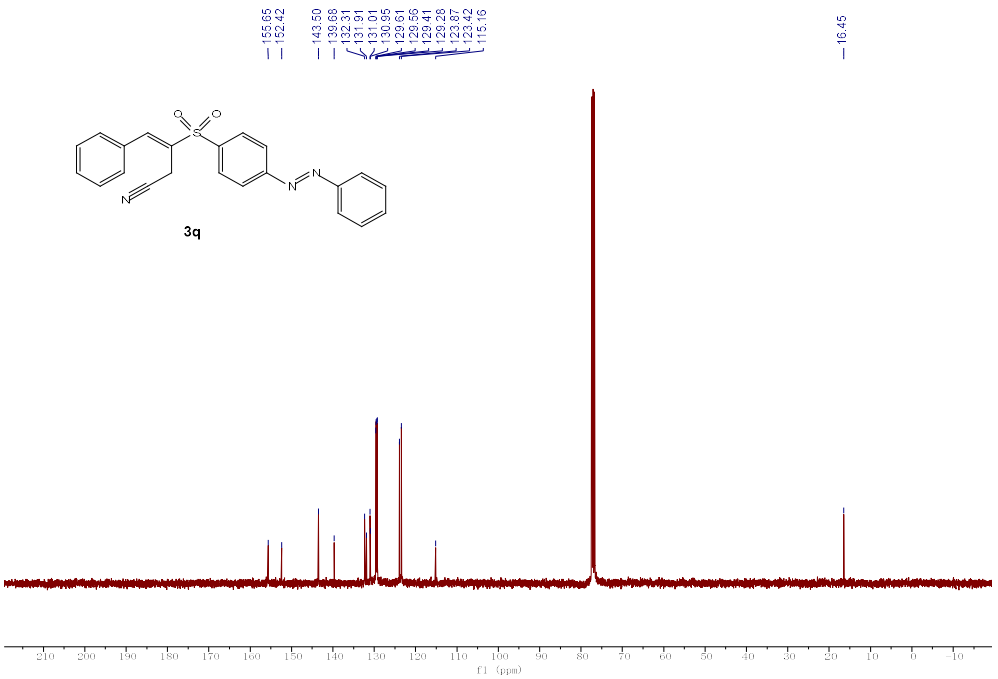
^{1}H NMR Spectrum of 3p ($CDCl_3$, 400 MHz)



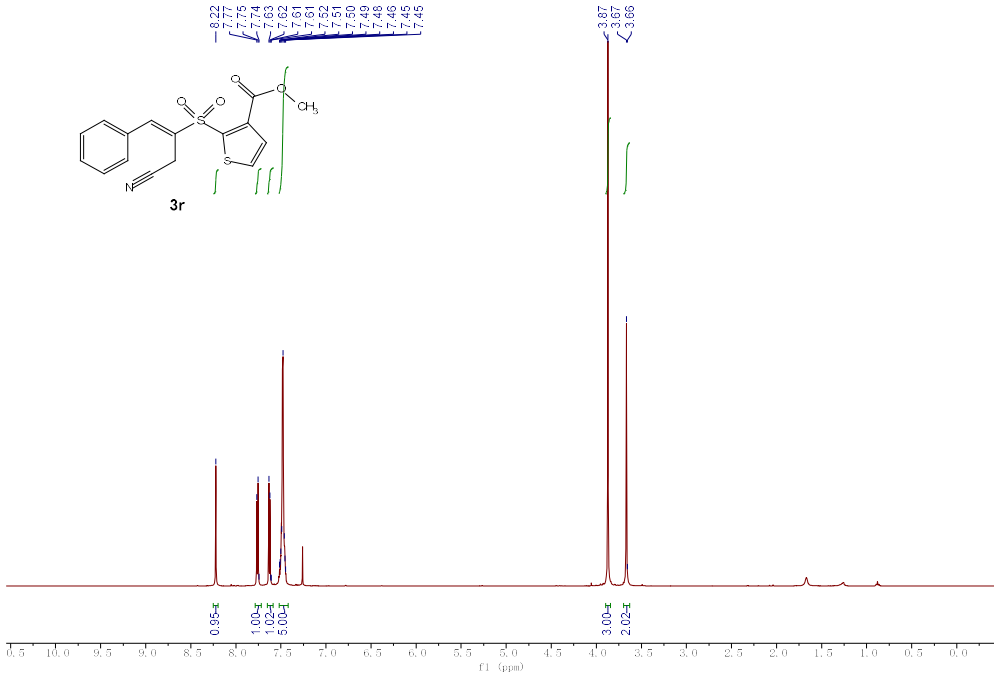
^{13}C NMR Spectrum of 3p ($CDCl_3$, 101MHz)



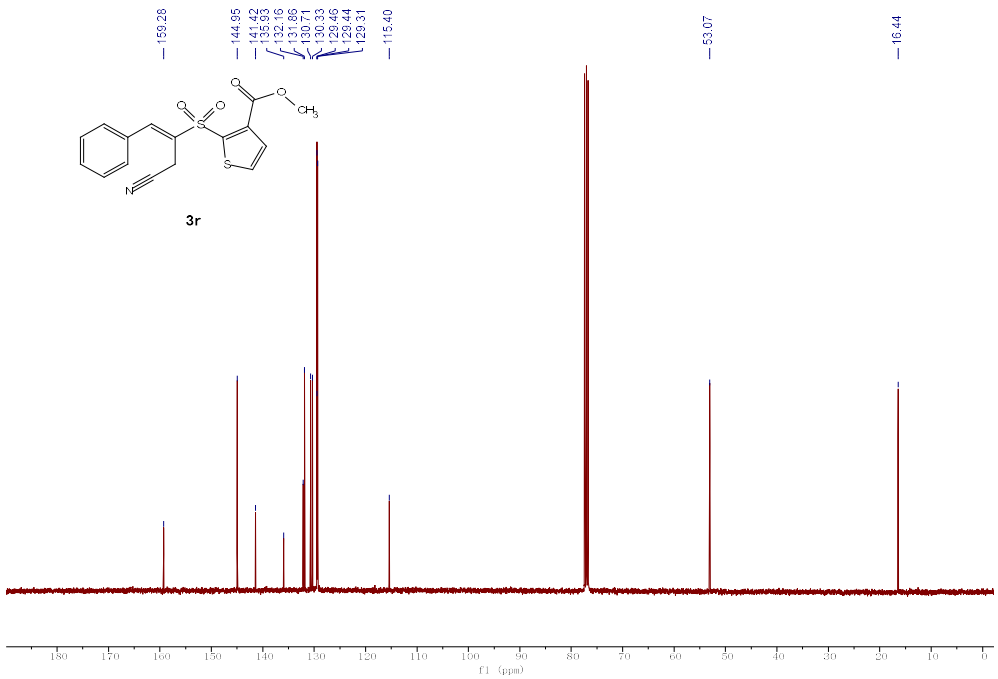
^{1}H NMR Spectrum of 3q ($CDCl_3$, 400 MHz)



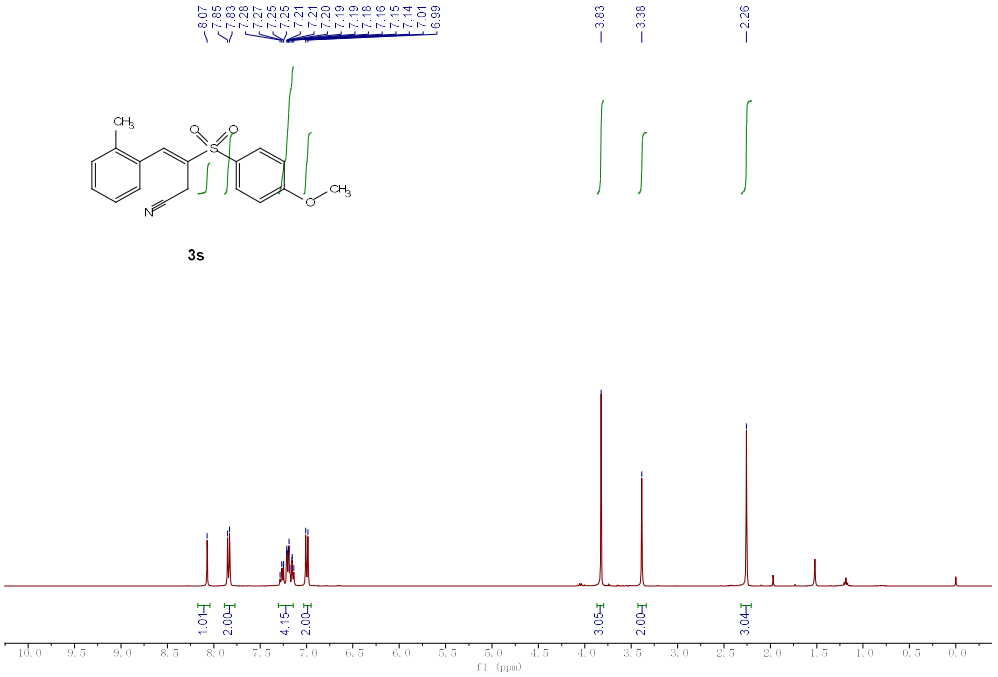
^{13}C NMR Spectrum of 3q ($CDCl_3$, 101MHz)



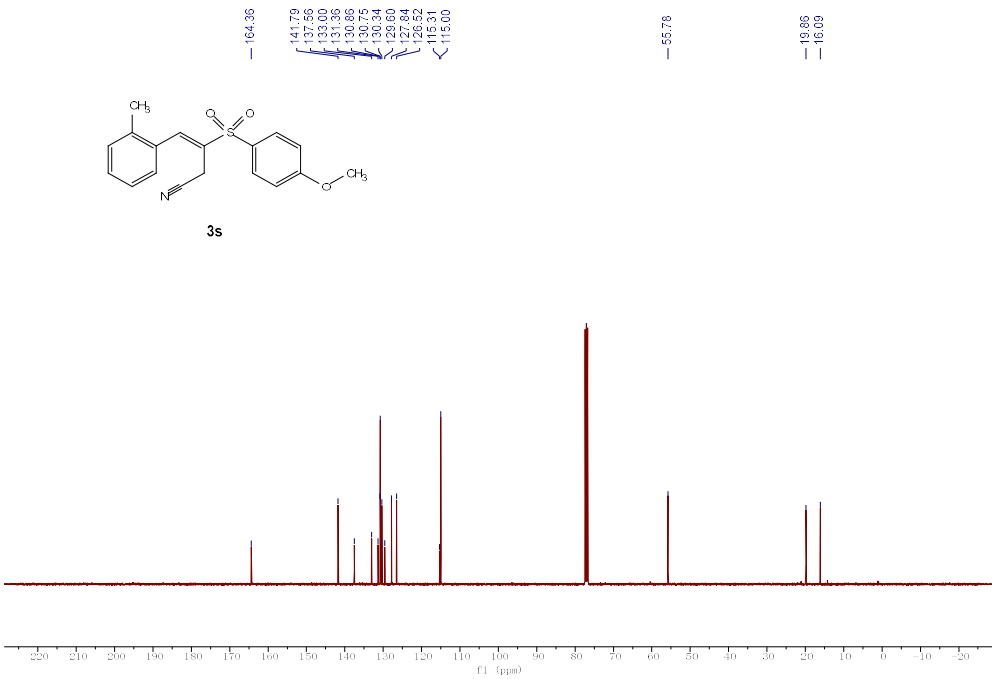
^{1}H NMR Spectrum of 3r ($CDCl_3$, 400 MHz)



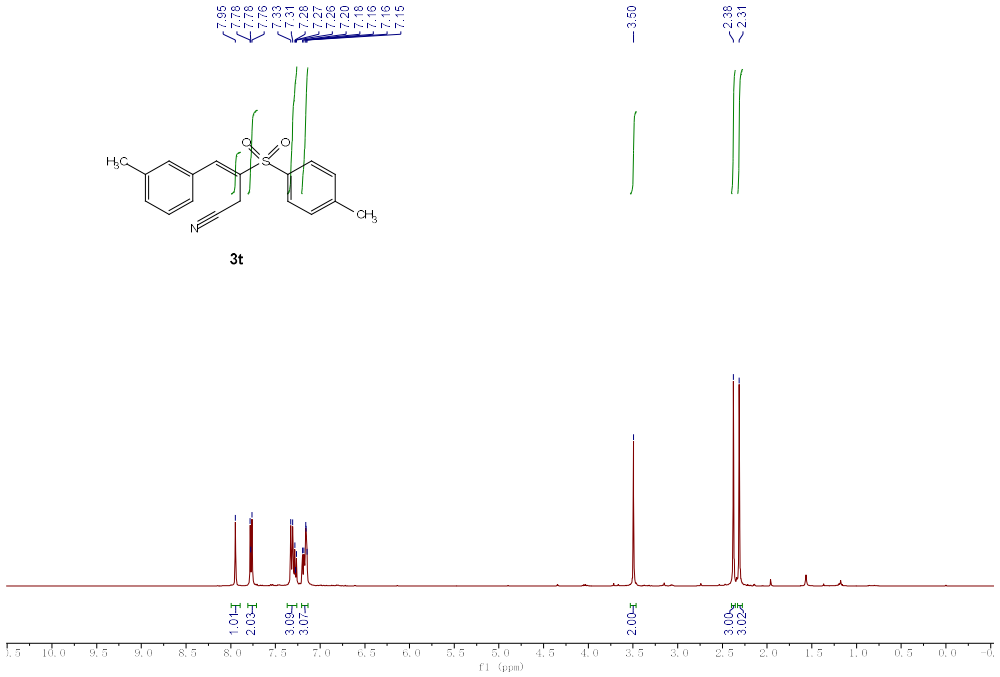
^{13}C NMR Spectrum of 3r ($CDCl_3$, 101MHz)



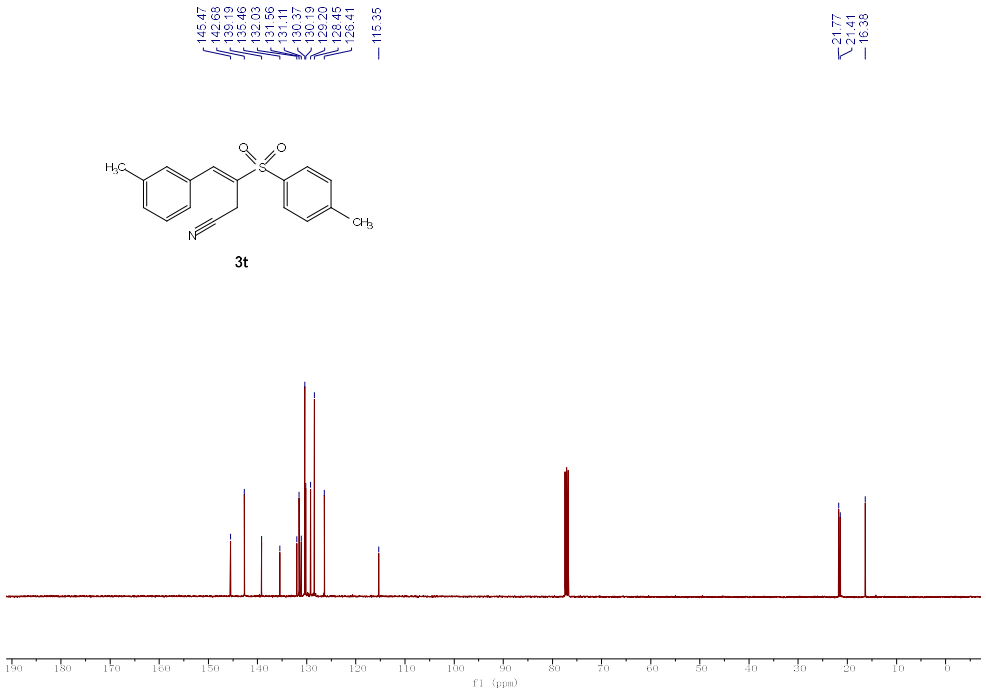
^{1}H NMR Spectrum of 3s ($CDCl_3$, 400 MHz)



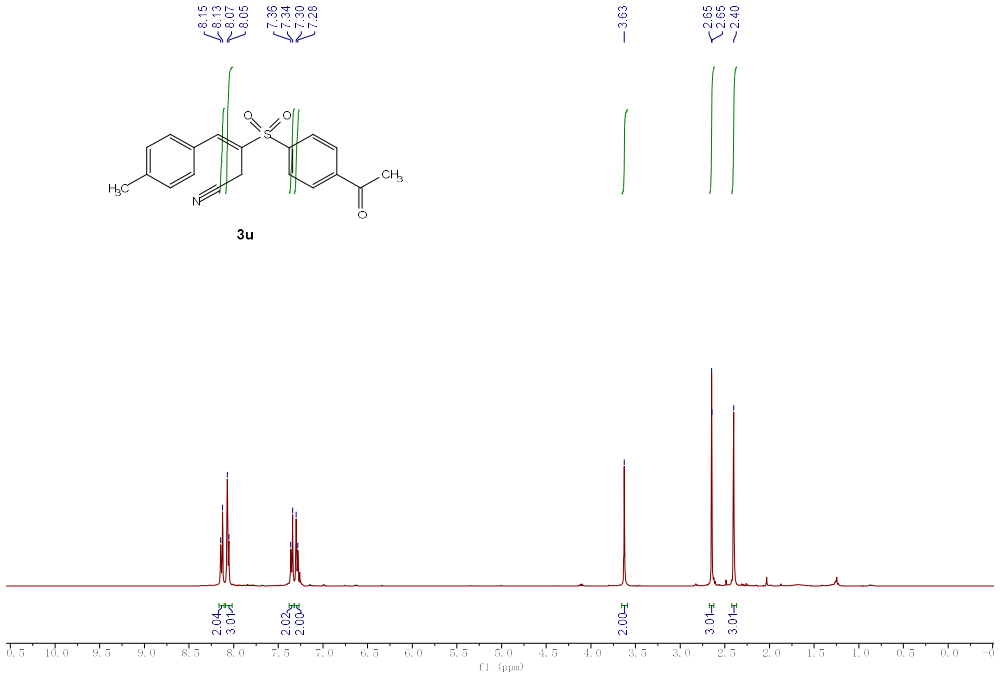
^{13}C NMR Spectrum of 3s ($CDCl_3$, 101MHz)



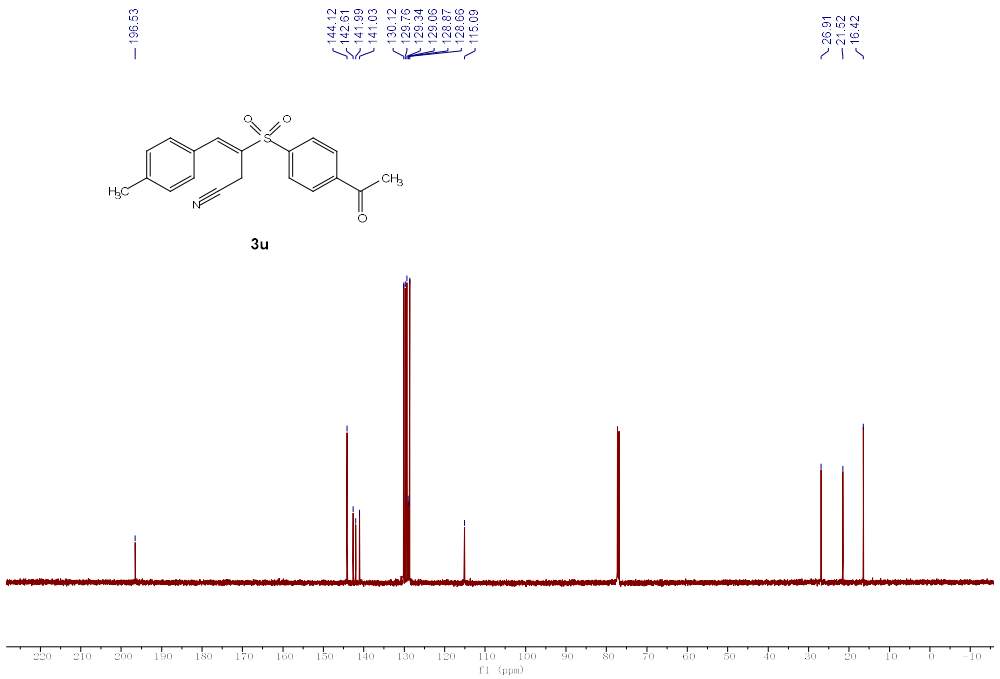
^{1}H NMR Spectrum of 3t ($CDCl_3$, 400 MHz)



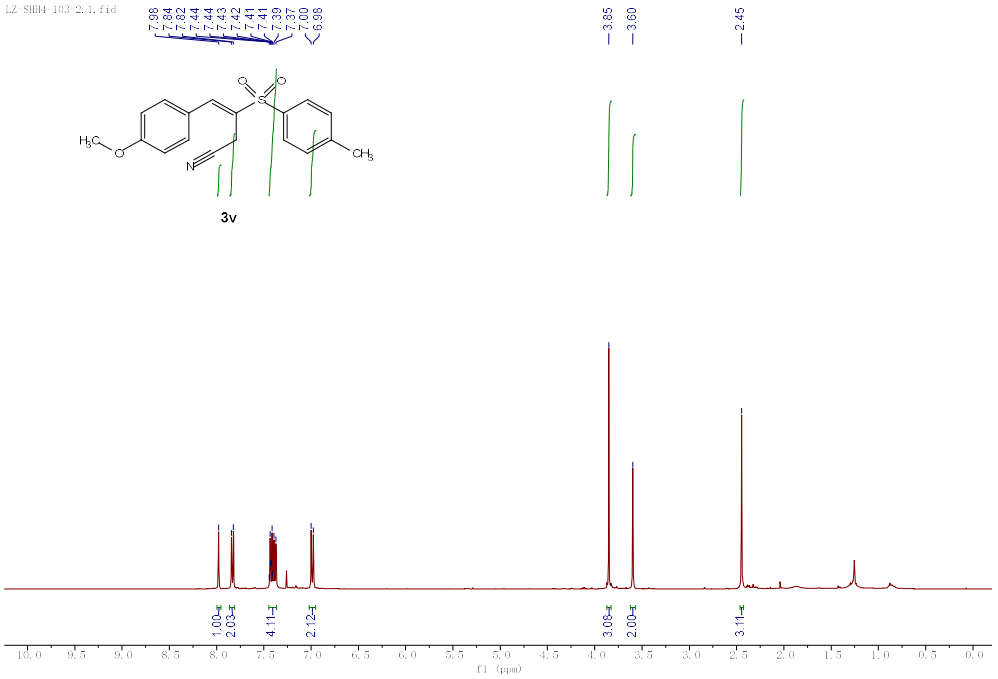
^{13}C NMR Spectrum of 3t ($CDCl_3$, 101MHz)



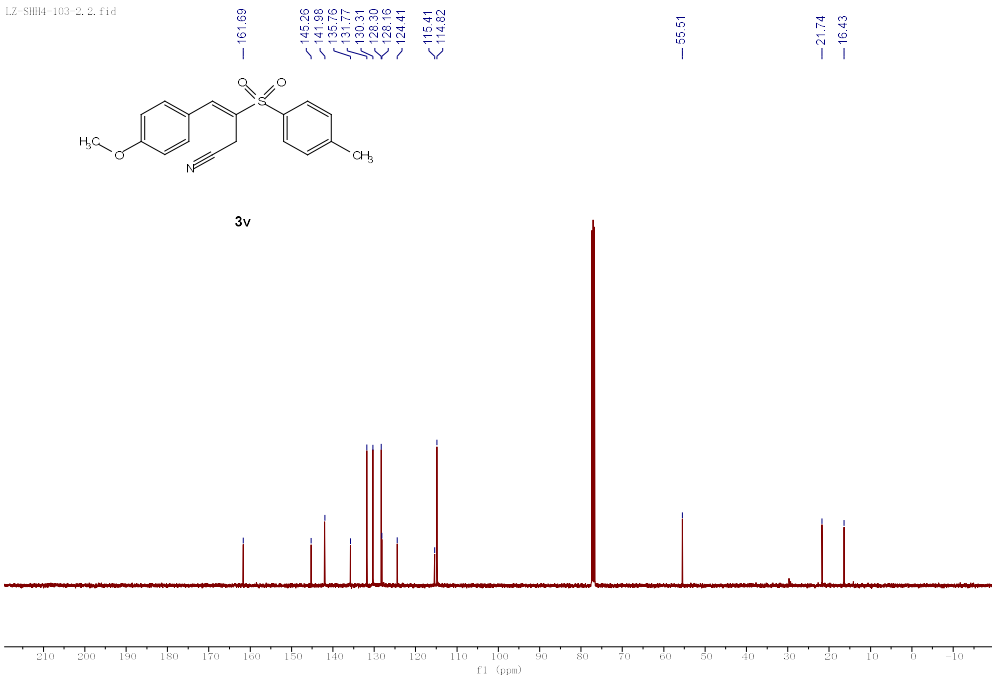
^{1}H NMR Spectrum of 3u ($CDCl_3$, 400 MHz)



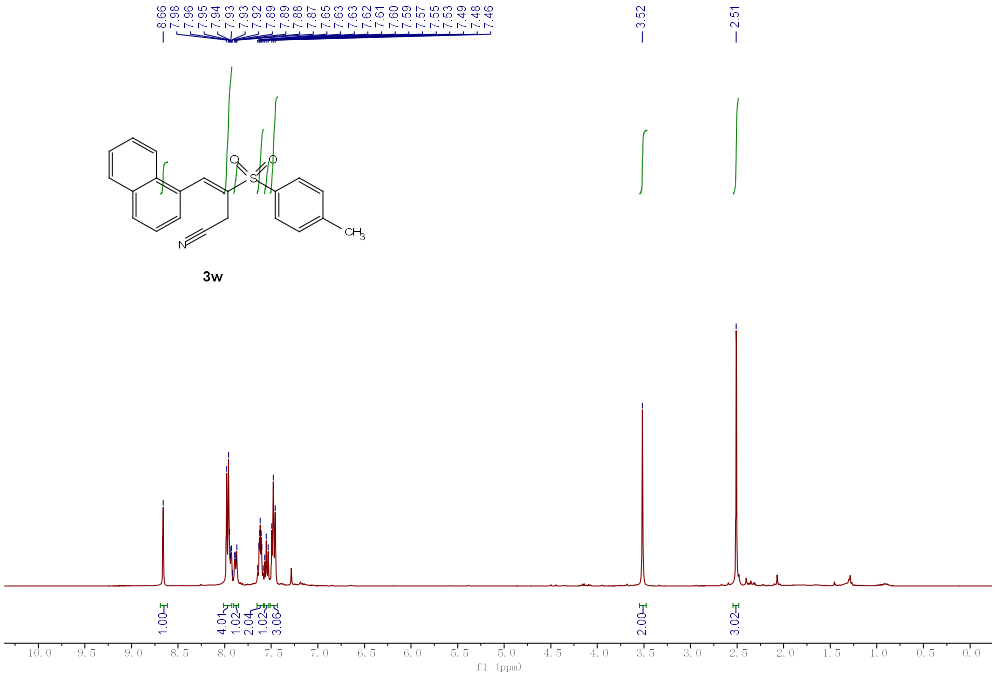
^{13}C NMR Spectrum of 3u ($CDCl_3$, 101MHz)



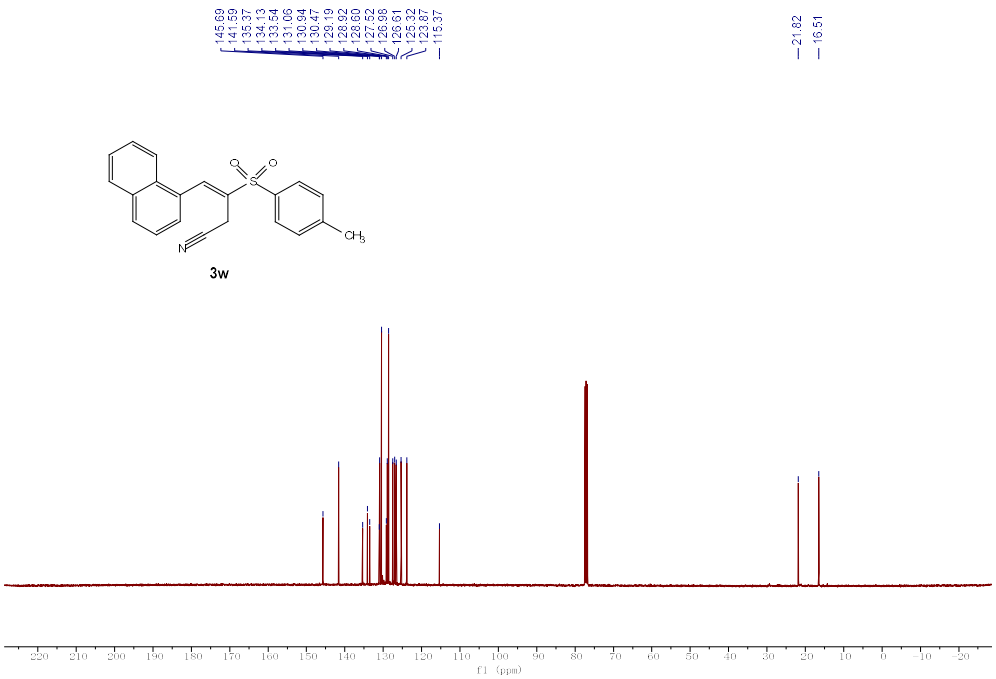
^{1}H NMR Spectrum of 3v ($CDCl_3$, 400 MHz)



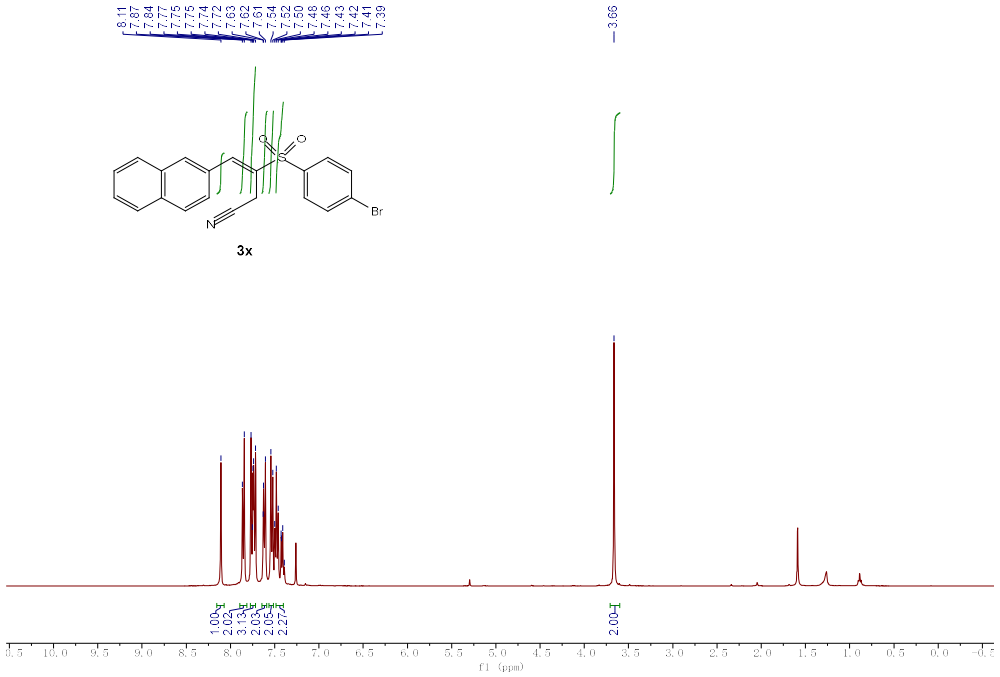
^{13}C NMR Spectrum of 3v ($CDCl_3$, 101MHz)



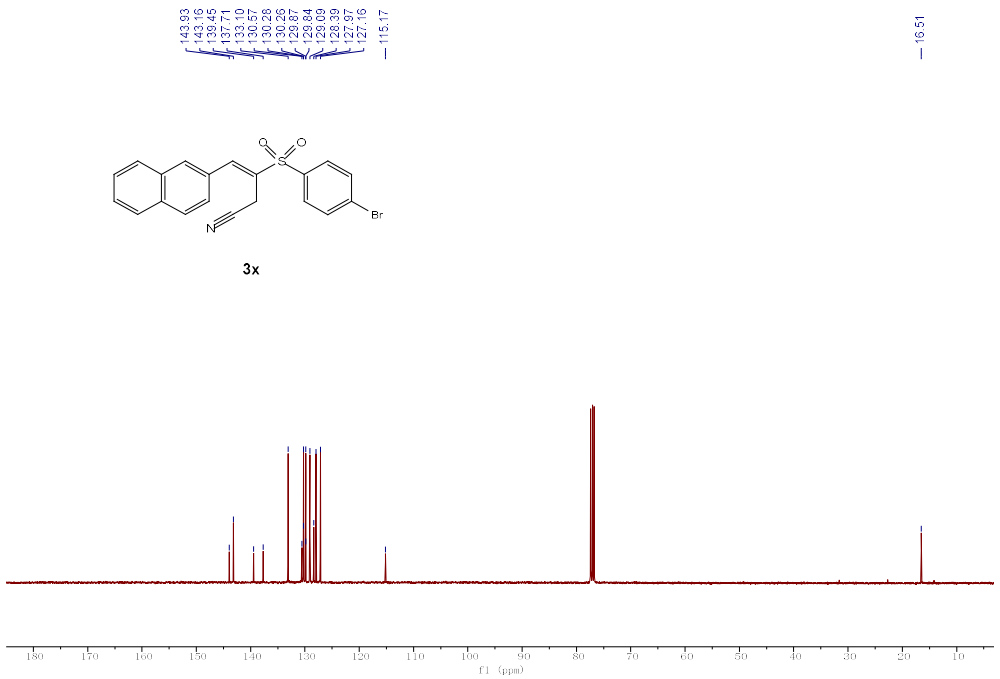
^{1}H NMR Spectrum of 3w ($CDCl_3$, 400 MHz)



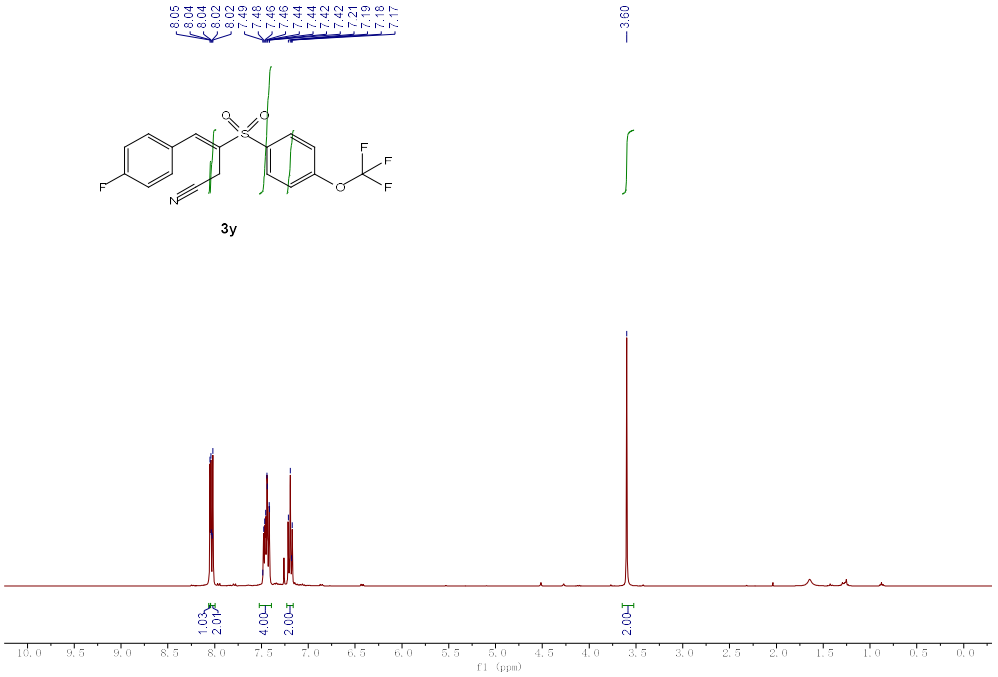
^{13}C NMR Spectrum of 3w ($CDCl_3$, 101MHz)



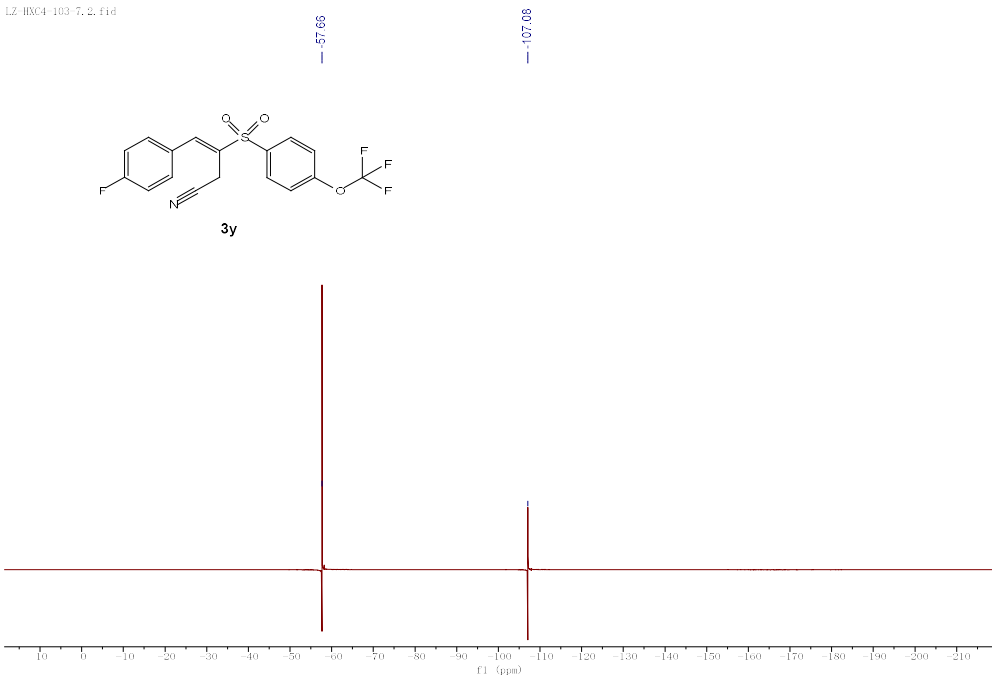
^{1}H NMR Spectrum of 3x ($CDCl_3$, 400 MHz)



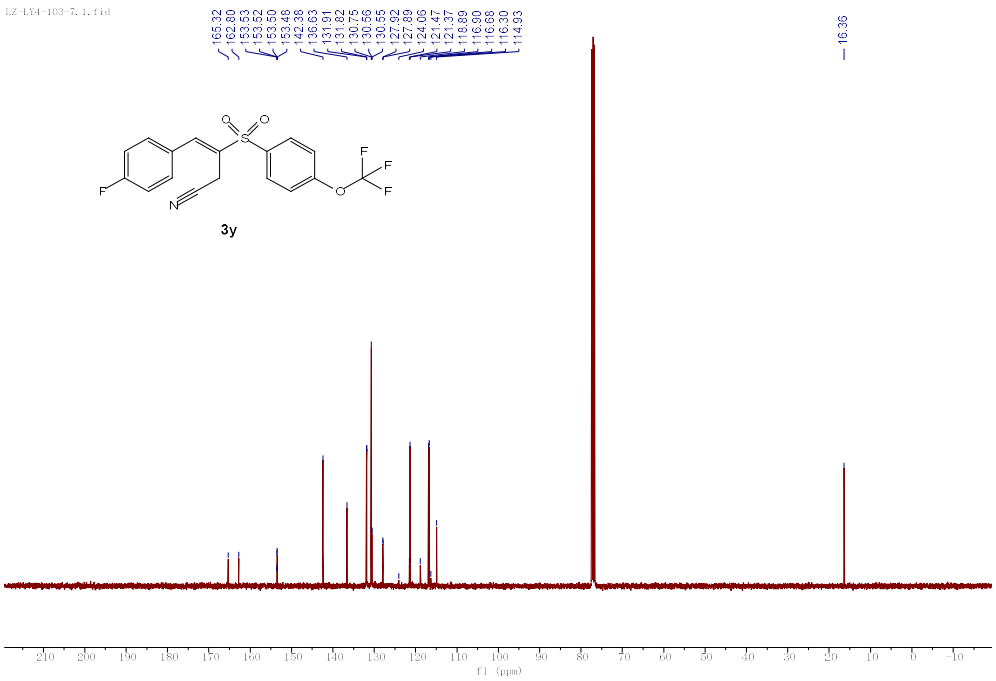
^{13}C NMR Spectrum of 3x ($CDCl_3$, 101MHz)



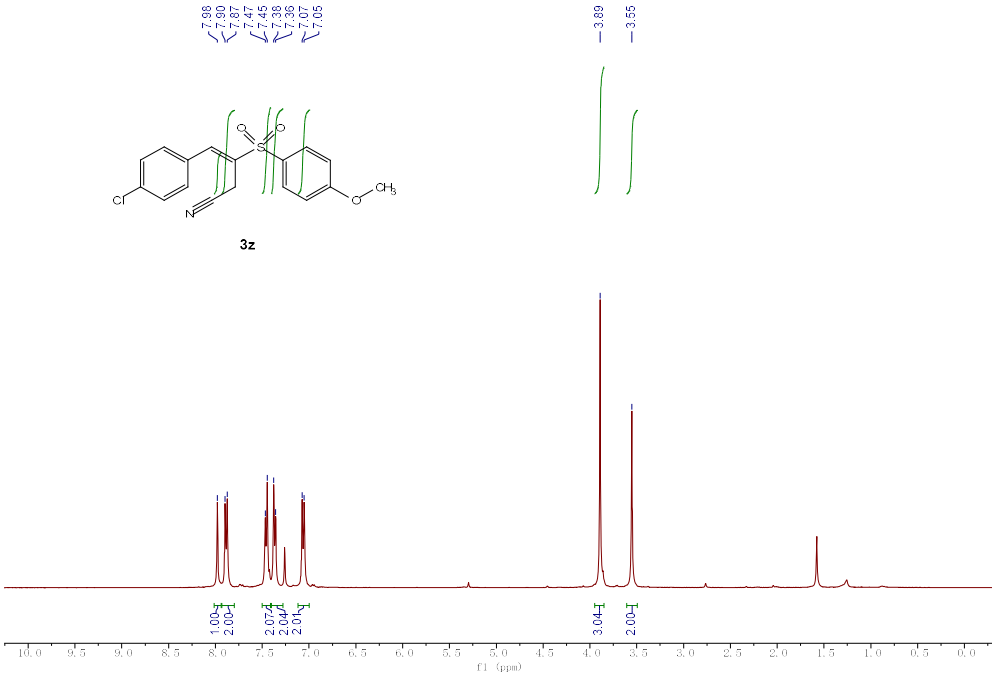
^{1}H NMR Spectrum of 3y ($CDCl_3$, 400 MHz)



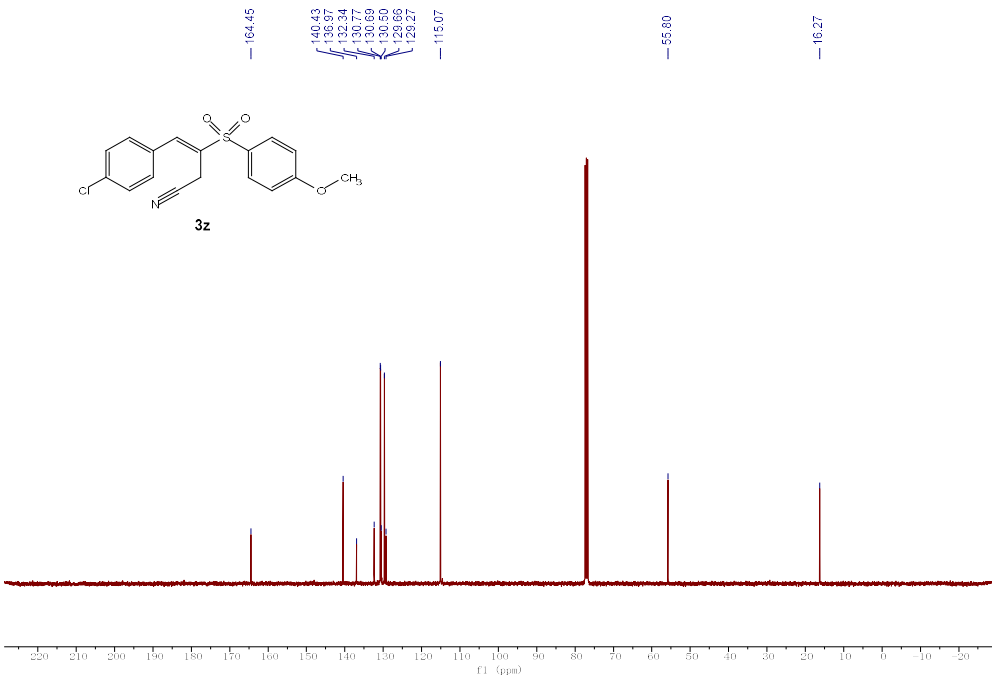
^{19}F NMR Spectrum of 3y ($CDCl_3$, 376 MHz)



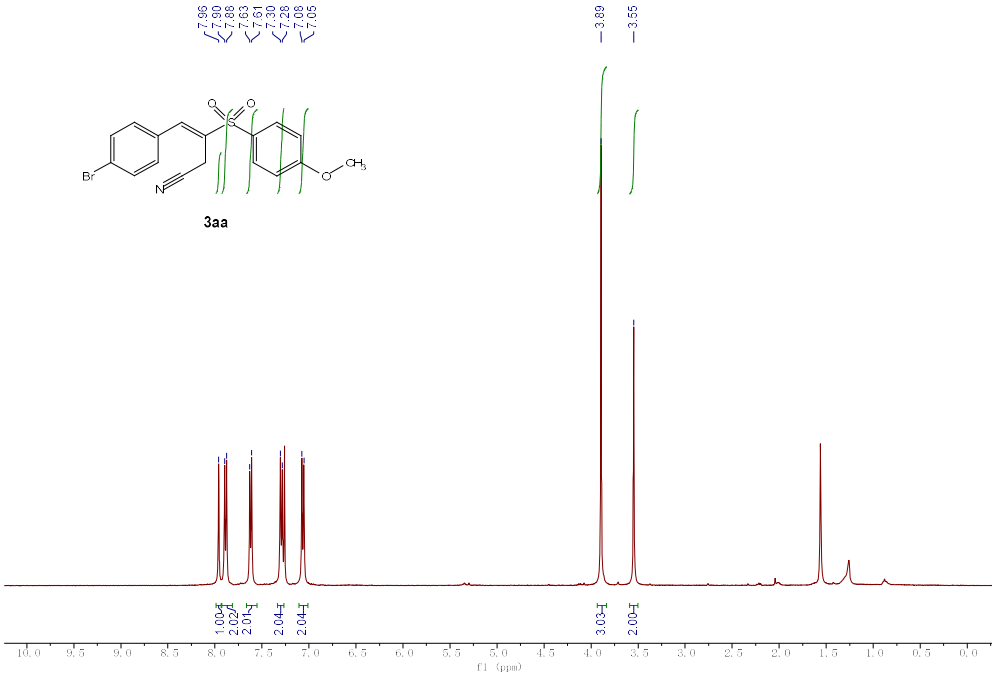
^{13}C NMR Spectrum of 3y ($CDCl_3$, 101MHz)



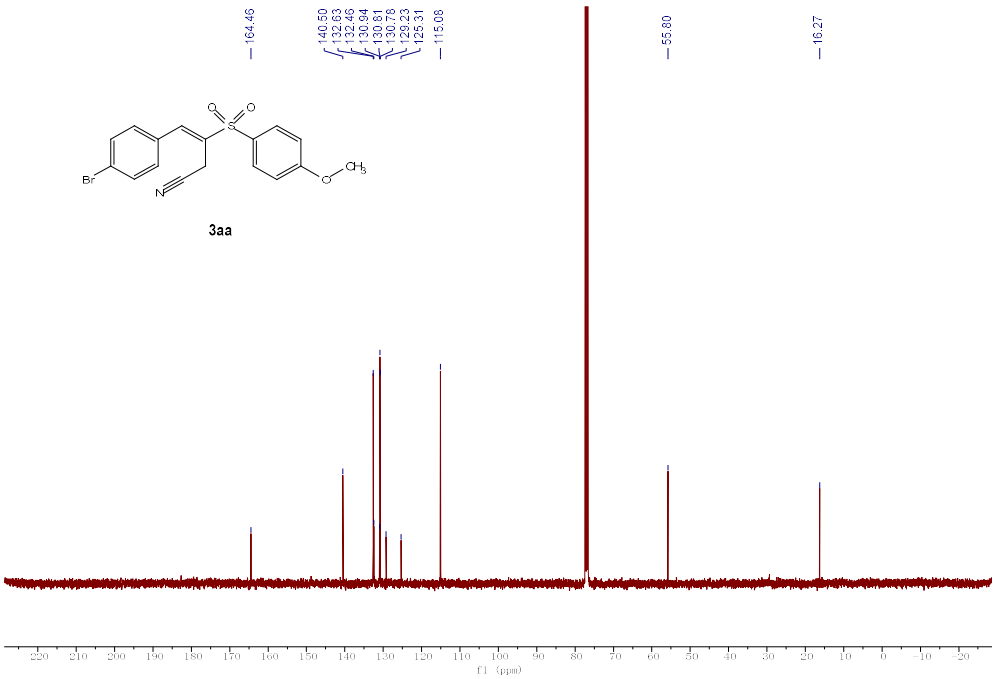
^{1}H NMR Spectrum of 3z ($CDCl_3$, 400 MHz)



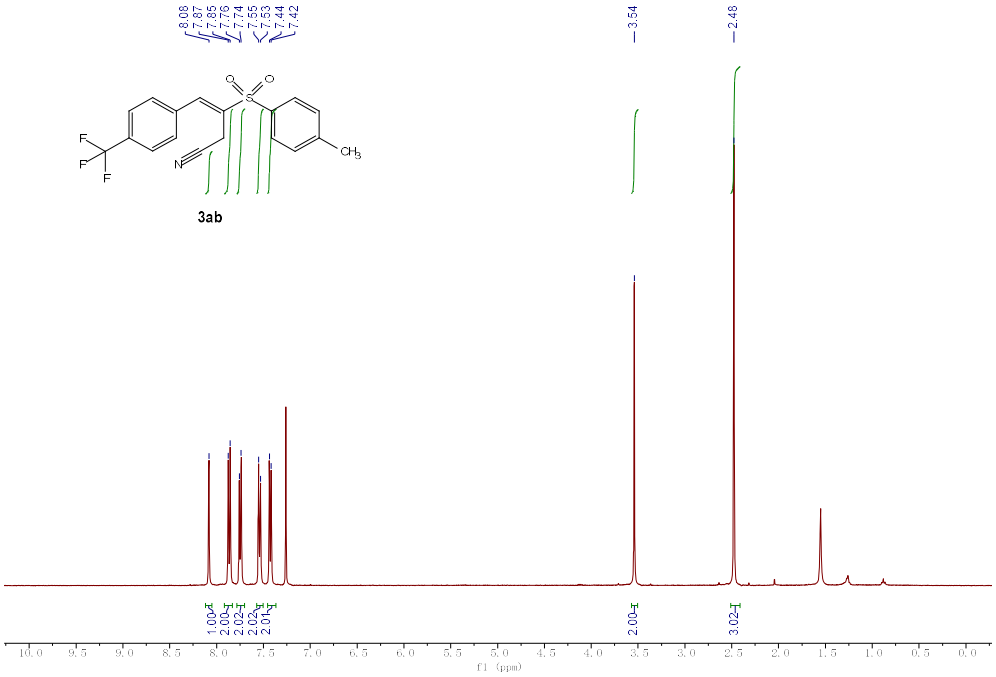
^{13}C NMR Spectrum of 3z ($CDCl_3$, 101MHz)



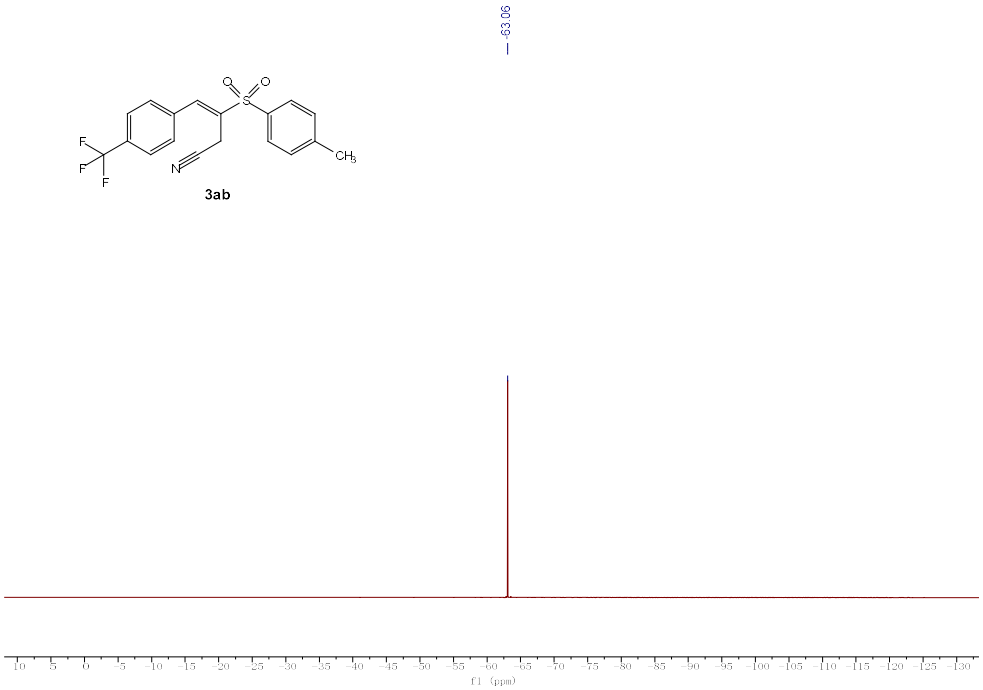
^{1}H NMR Spectrum of 3aa ($CDCl_3$, 400 MHz)



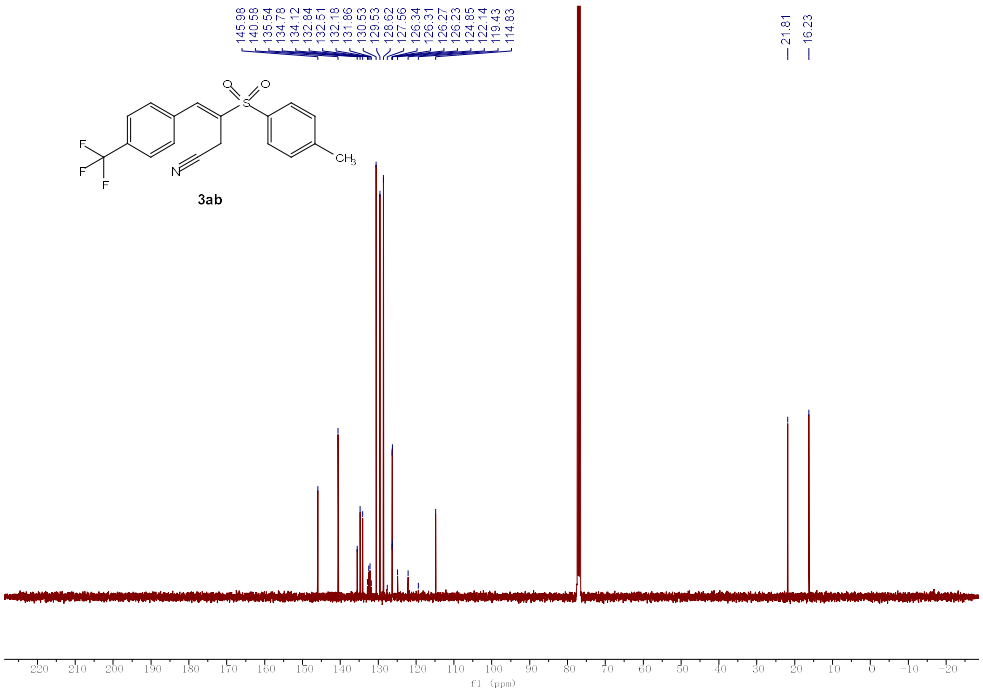
^{13}C NMR Spectrum of 3aa ($CDCl_3$, 101MHz)



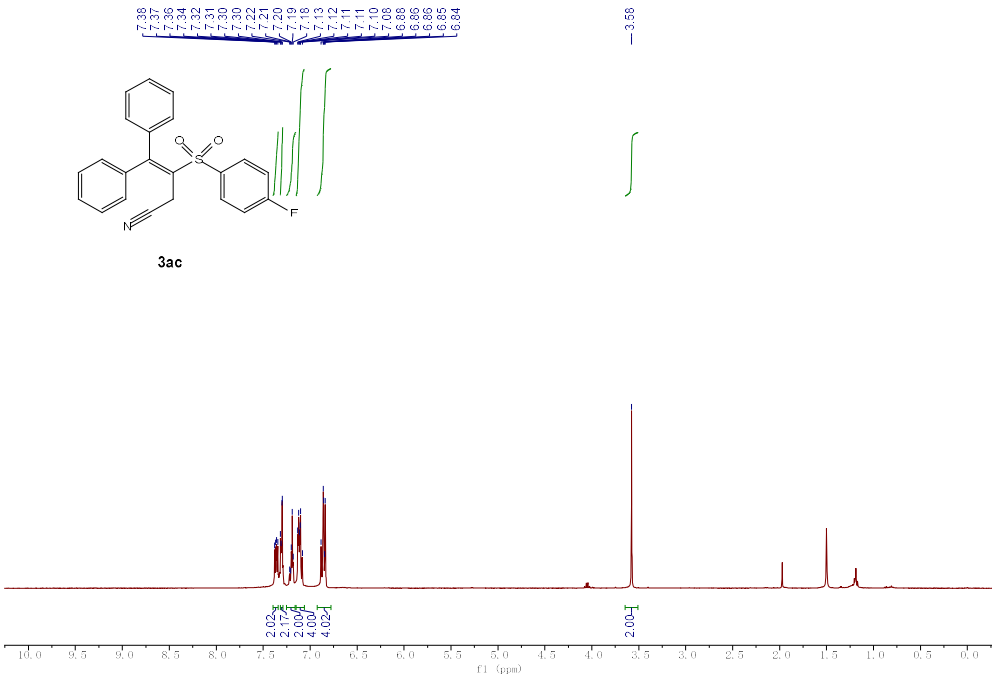
^{1}H NMR Spectrum of 3ab ($CDCl_3$, 400 MHz)



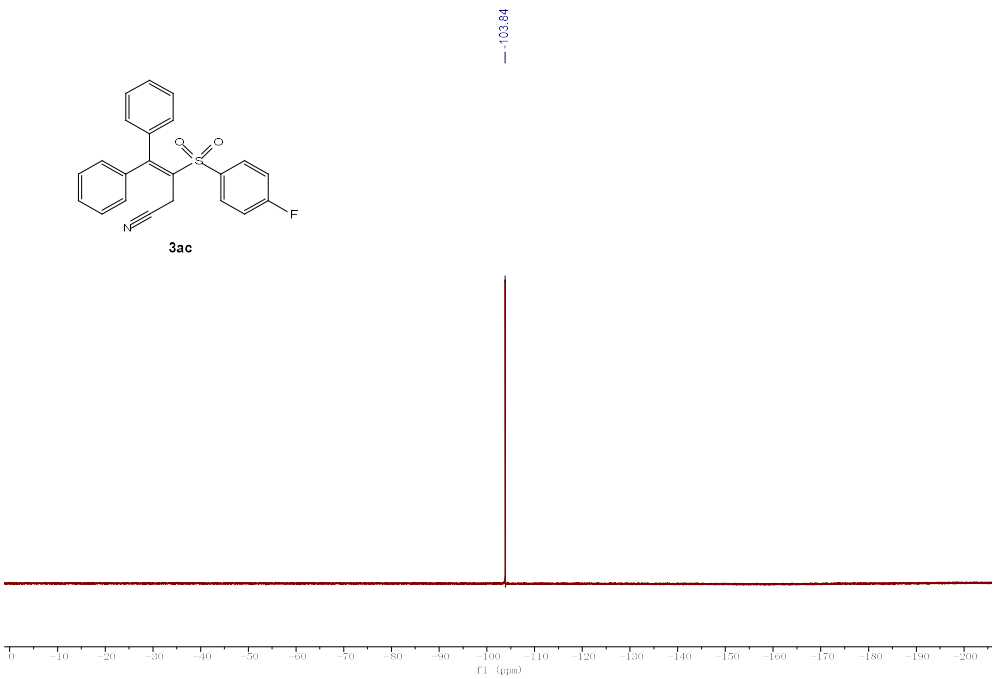
^{19}F NMR Spectrum of 3ab ($CDCl_3$, 376 MHz)



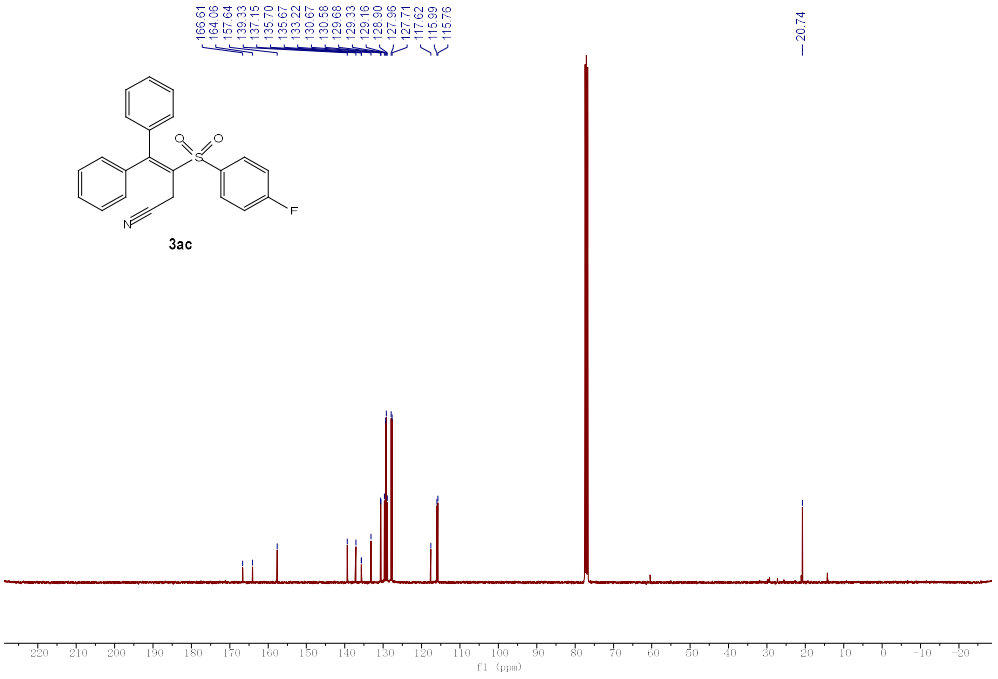
^{13}C NMR Spectrum of 3ab ($CDCl_3$, 101MHz)



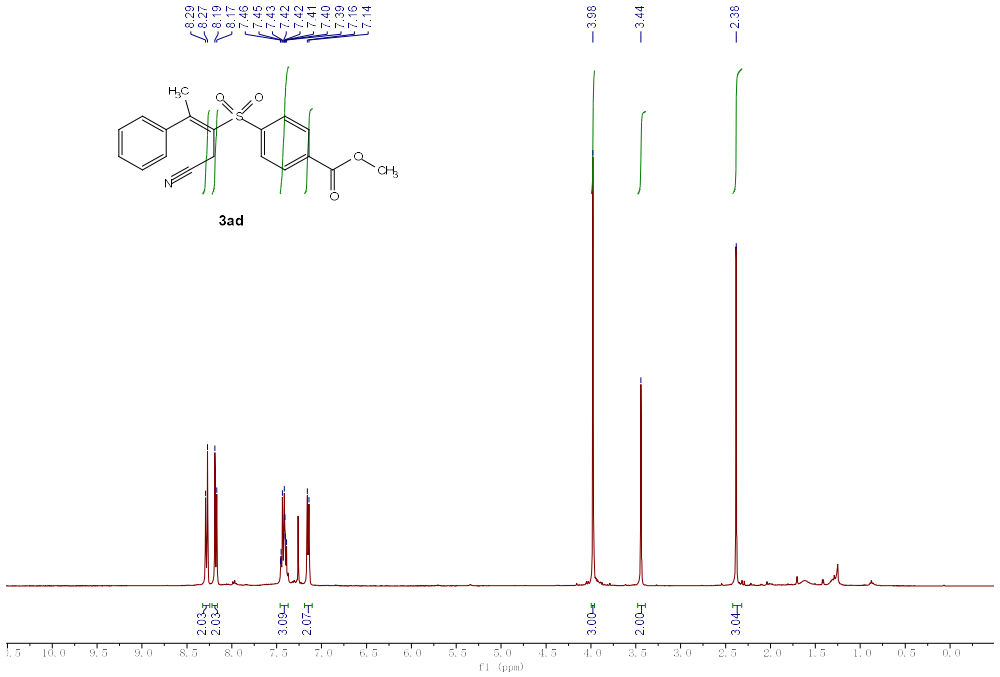
^{1}H NMR Spectrum of 3ac ($CDCl_3$, 400 MHz)



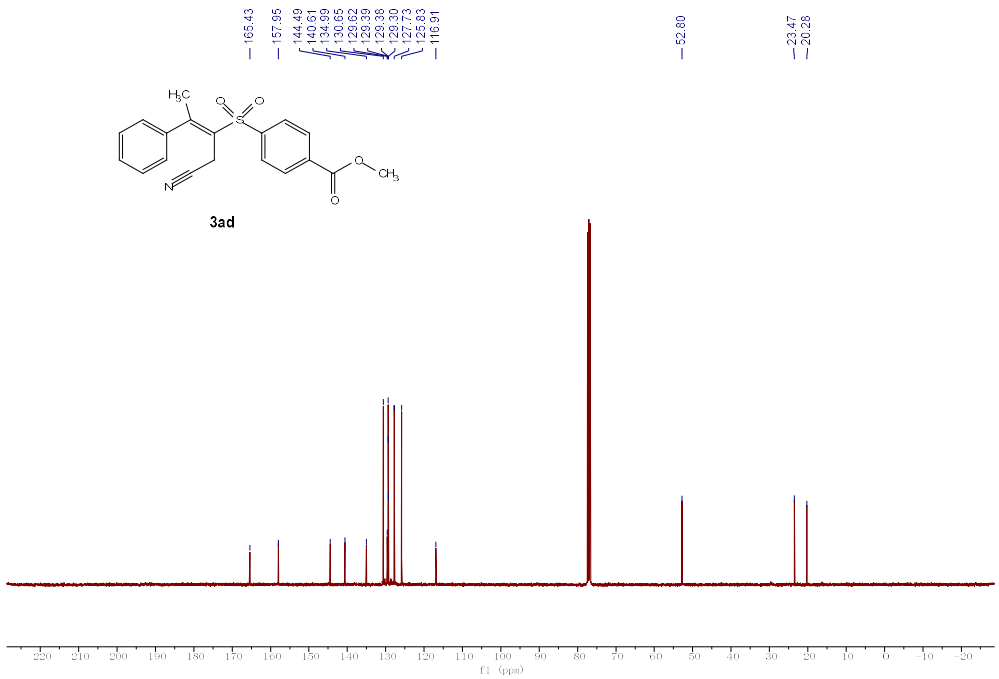
^{19}F NMR Spectrum of 3ac ($CDCl_3$, 376 MHz)



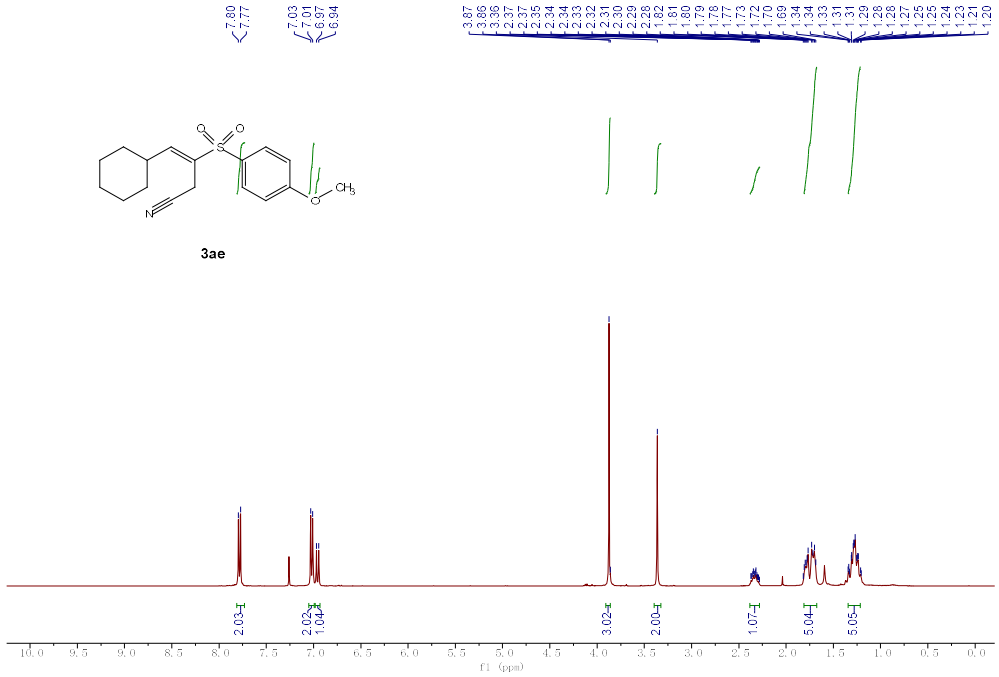
^{13}C NMR Spectrum of 3ac ($CDCl_3$, 101MHz)



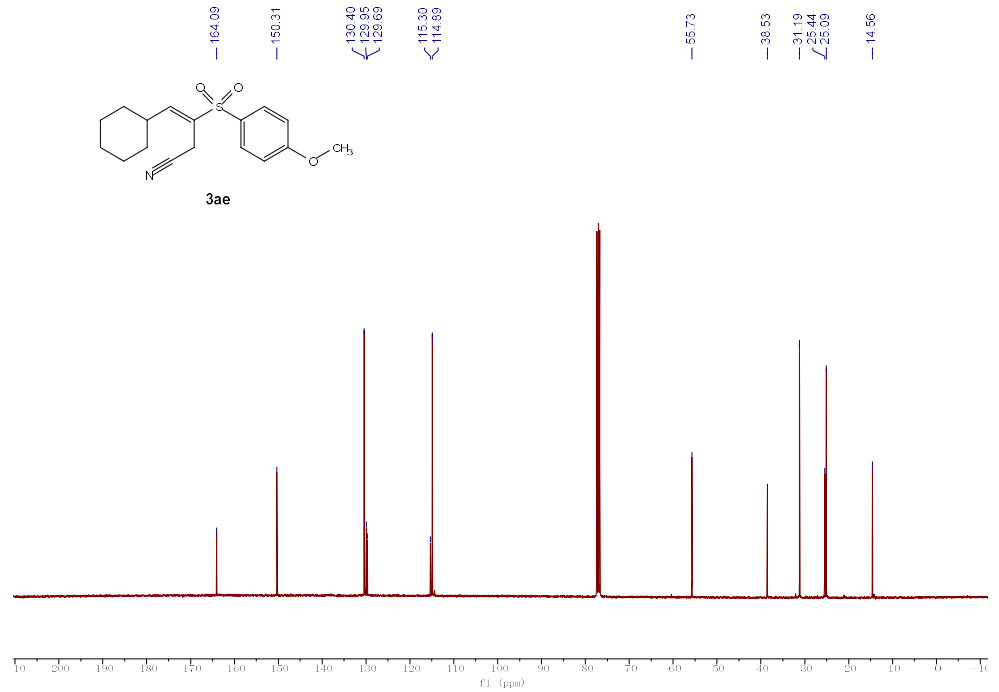
^{1}H NMR Spectrum of 3ad ($CDCl_3$, 400 MHz)



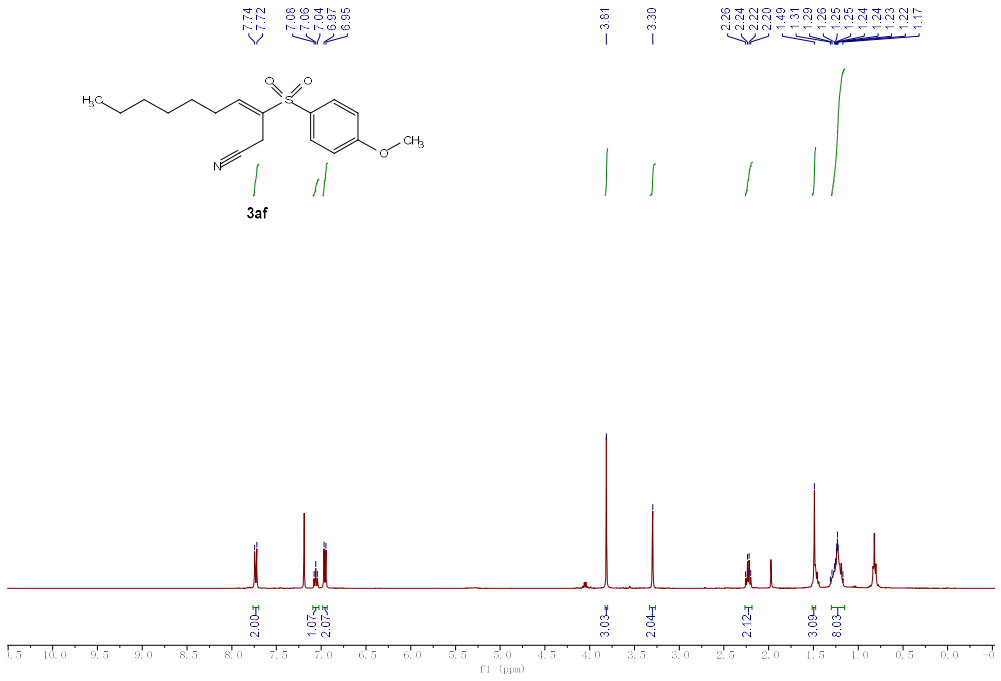
^{13}C NMR Spectrum of 3ad ($CDCl_3$, 101MHz)



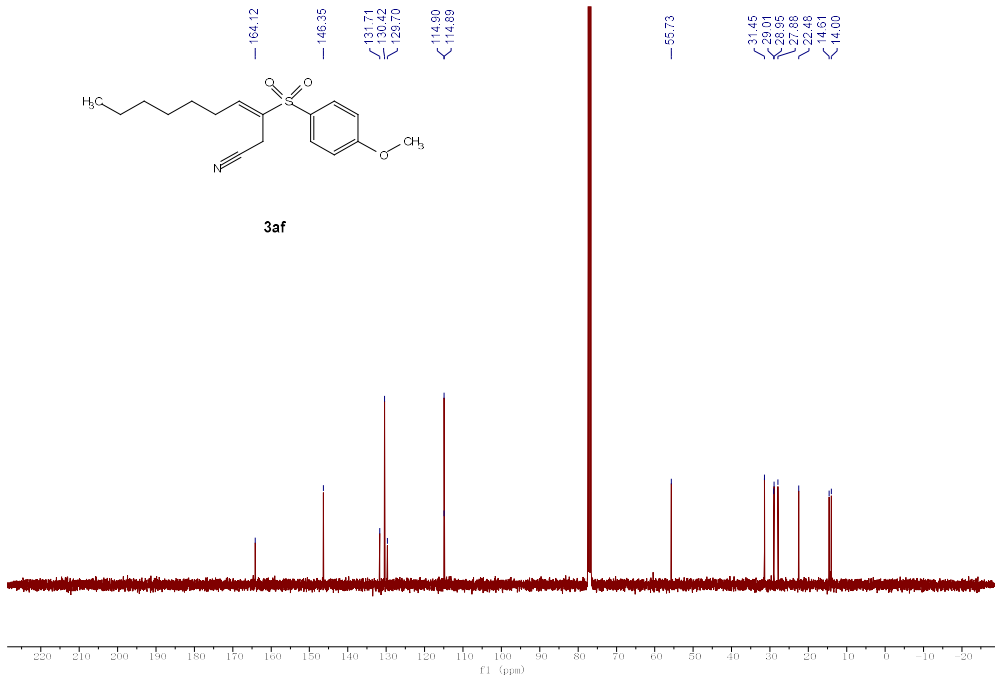
^{1}H NMR Spectrum of 3ae ($CDCl_3$, 400 MHz)



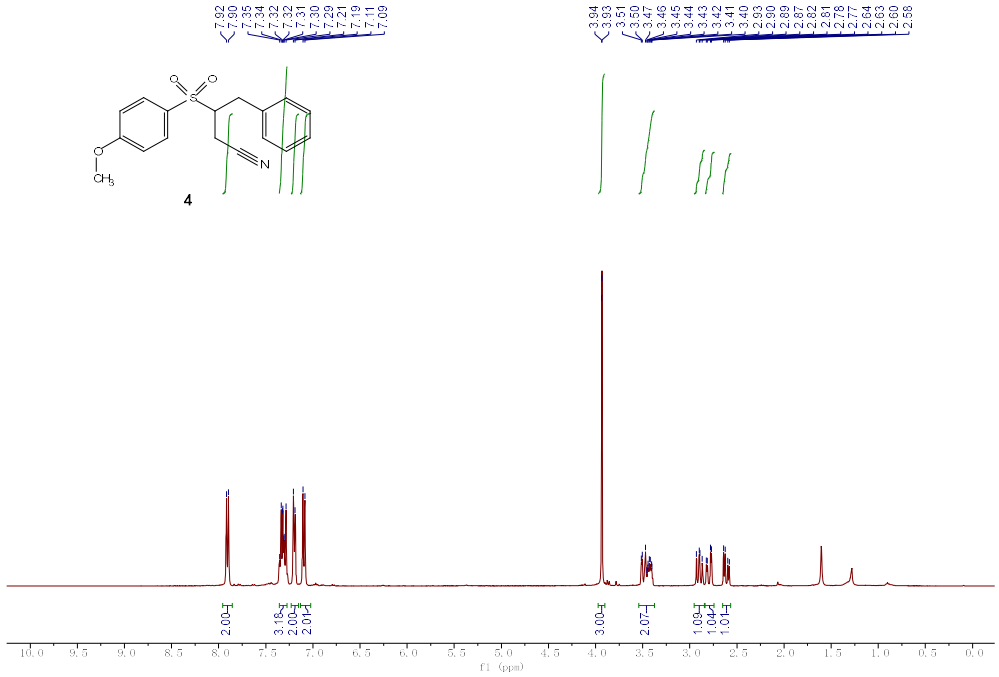
^{13}C NMR Spectrum of 3ae ($CDCl_3$, 101MHz)



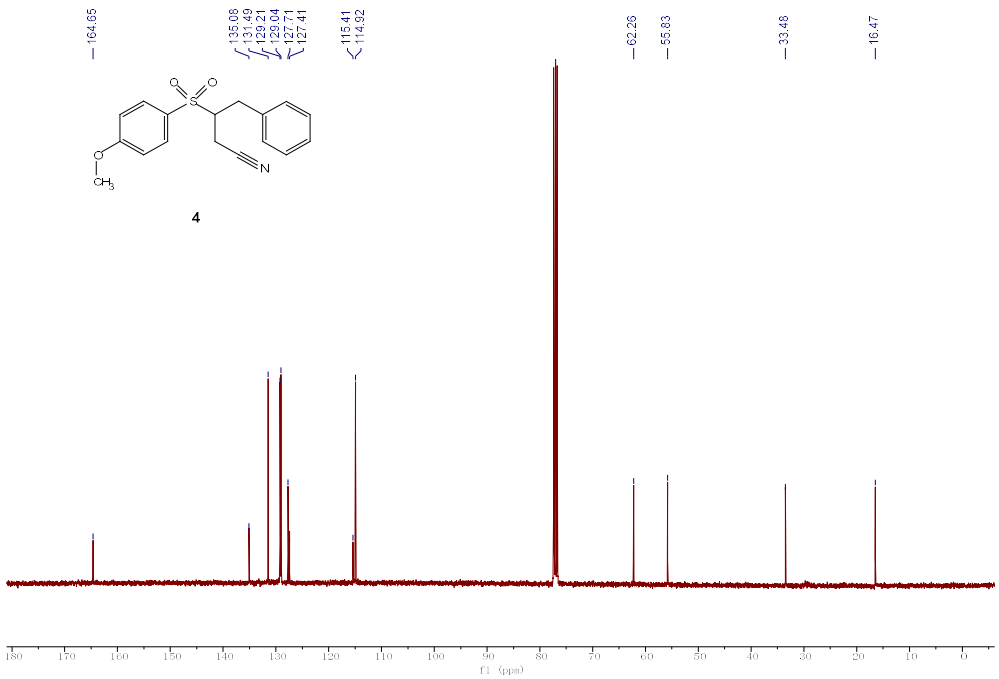
^{1}H NMR Spectrum of 3af ($CDCl_3$, 400 MHz)



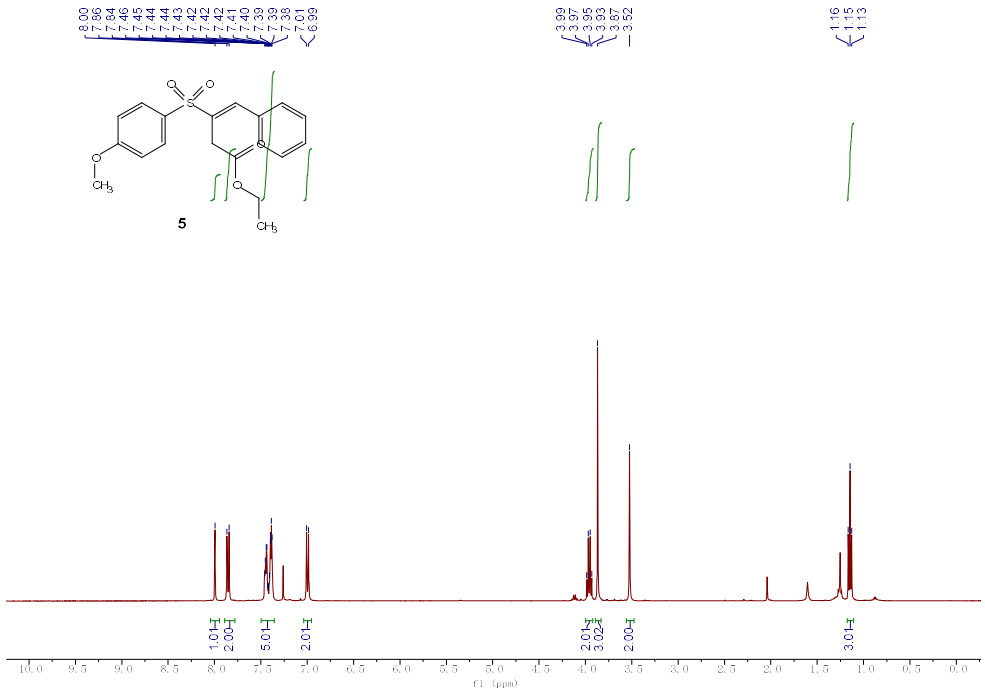
^{13}C NMR Spectrum of 3af ($CDCl_3$, 101MHz)



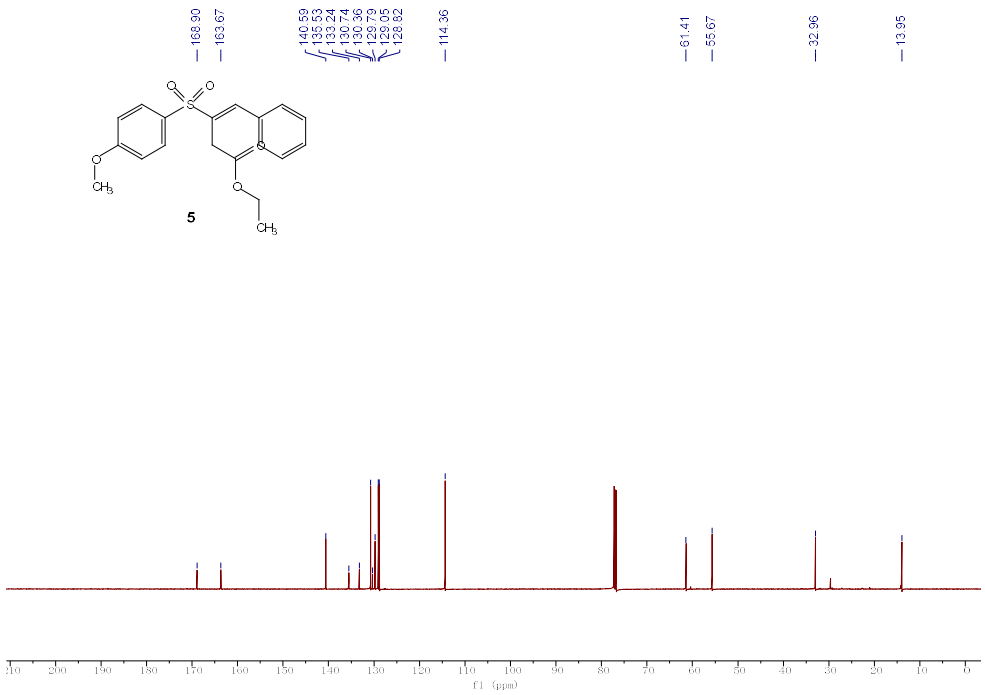
^{1}H NMR Spectrum of 4 ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of 4 ($CDCl_3$, 101MHz)



^{1}H NMR Spectrum of 5 ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of 5 ($CDCl_3$, 101MHz)