Supporting Information

Visible-light-catalyzed sulfonylation reaction of aryl selenonium salt via electron donor-acceptor complex

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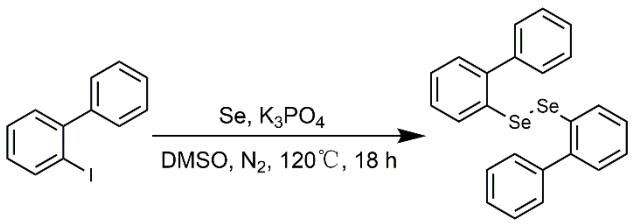
Contents

1 General Experimental Information

All reagents unless otherwise noted were obtained from commercial sources and used without further purification. Photoredox reactions were subjected to irradiation from a blue LED with an input power of 34 W and a maximum wavelength of 456 nm. The reaction tube is placed about 5 cm away from the bulb. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates and visualization of the plates was performed under UV light (254 nm and 365 nm). Further flash column chromatography was performed on silica gel (200-300 mesh). NMR spectra (^{1}H, ^{19}F, ^{13}C) were obtained using Bruker 400MHz, 500MHz or 600 MHz instruments, using TMS (Me_4Si) as an internal standard. Chemical shifts (δ) and coupling constants (J) are reported in units of ppm and Hz, respectively. The following abbreviations are used to set multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet and dt = double triplet. Low-resolution and high-resolution mass spectra were obtained using either positive and/or negative electrospray ionization (ES), or atmospheric-pressure chemical ionization (APCI) techniques.

2 Synthesis of Substrates

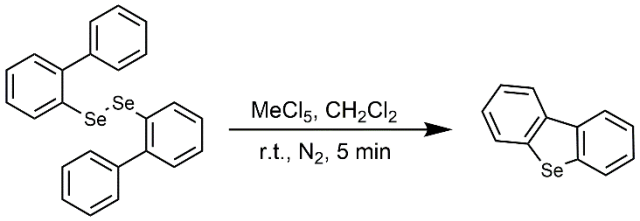
2.1.1 Preparation of 2-Biphenylyl diselenide[1]



A flame-dried test tube containing a magnetic stirring bar was charged with CuI (0.1 eq., 0.5 mmol, 0.1 g), K_3PO_4 (3.0 eq., 15 mmol, 3.2 g), Se (3.0 eq.,

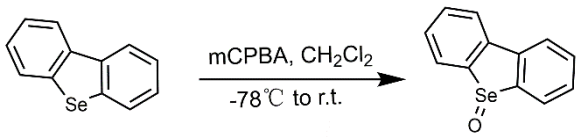
15 mmol, 1.2 g), 2-iodobiphenyl (1.0 eq., 5 mmol, 1.4 g), and DMSO (10 mL) under N_2. The mixture was heated at the indicated temperature for 18 h and allowed to cool to room temperature. The resulting mixture was extracted with ethyl acetate (30 mL×3). The combined organic layers were dried with Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel with an eluent consisting of petroleum ether and ethyl acetate to give an orange solid (0.966 g, 83%). All the physical data for known compounds were consistent with those reported in the literature.

2.1.2 Preparation of dibenzoselenophene[2]



Bis-(biphenyl-2-yl)diselenide (1.0 eq., 0.43 mmol, 200 mg) was treated with $MoCl_5$ (2.0 eq., 0.86 mmol, 235 mg) in CH_2Cl_2 (10 mL) and stirred for 5 minutes. The crude product was purified by flash column chromatography (cyclohexane:ethyl acetate, 99:1) to yield compound dibenzoselenophene as a colorless solid (190 mg, 88.4%).

2.1.3 Preparation of dibenzoselenophene oxide[3]

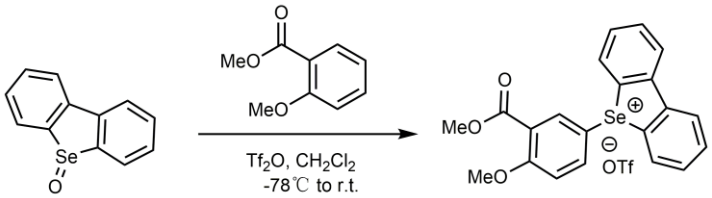


mCPBA (234 mg, 1.04 mmol, dissolved in 10 mL CH_2Cl_2) was added dropwise a solution of dibenzoselenophene (200 mg, 0.87 mmol) in CH_2Cl_2 (50 mL) at -78˚C. The mixture was stirred while it was allowed to slowly warm to 0˚C. An aqueous solution of saturated aqueous $NaHCO_3$ (10 mL)

was added into the reaction mixture the combined organic layers were washed with saturated brine and dried over Na_2SO_4 and then concentrated under reduced pressure. The crystals were purified by recrystallizations from CH_2Cl_2 to produce 0.190 g of white crystal (84% yield).

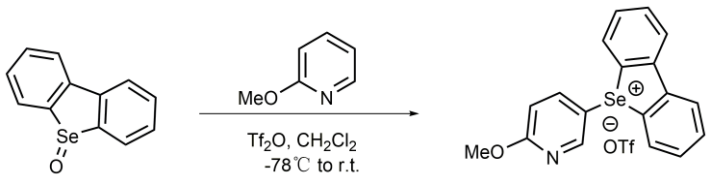
2.1.4 Preparation of aryl and heterocyclic selenonium salts

methyl 2-methoxybenzoate derived selenonium salt **1a**[4]



Tf_2O (1.2 eq., 0.24 mmol, 40 μL) was added dropwise a solution of methyl 2-methoxybenzoate (1.0 eq., 0.2 mmol, 29 μL) and dibenzoselenophene oxide (1.1 eq, 0.22 mmol, 55 mg) in CH_2Cl_2 (0.1 M) at -78°C under N_2. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 1 h, TLC showed the arene starting material was consumed completely, at which point the solvent was removed in vacuo. The crude product was purified by recrystallization from CH_2Cl_2/Et_2O to produce 88 mg of off-white solid **1a** (81% yield).

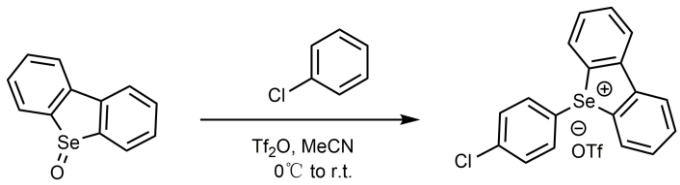
2-methoxypyridine derived selenonium salt **1b**



The heterocyclic selenonium salt were synthesized as follows. Tf_2O (1.2 eq., 0.72 mmol, 120 μL) was added dropwise a solution of 2-methoxypyridine (1.0 eq., 0.6 mmol, 64 μL) and dibenzoselenophene oxide (1.1 eq, 0.66 mmol, 165 mg) in CH_2Cl_2 (0.1 M) at -78°C under N_2. The resulting solution

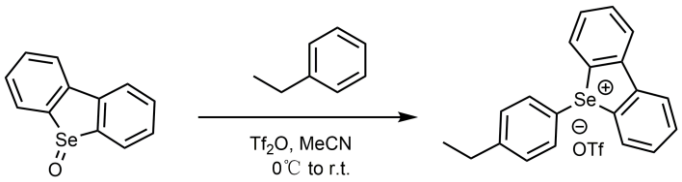
was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 12 h, color changes from dark green to pale yellow. The solution was diluted with 10ml DCM then removed in vacuo. The crude product was dissolved in 3 ml DCM and washed with 20 ml Et_2O. During the washing a precipitate formed, which was collected by filtration. The solid was washed with DCM (15 ml×3). The solid was dried in vacuo to afford 106 mg (36 % yield) as a colorless solid **1b**.

chlorobenzene derived selenonium salt **1c**



Tf_2O (1.2 eq., 0.72 mmol, 120 μL) was added dropwise a solution of chlorobenzene (1.0 eq., 0.6 mmol, 98.2 mg) and dibenzoselenophene oxide (1.1 eq, 0.66 mmol, 165 mg) in MeCN (0.1 M) at 0°C under N_2. The resulting solution was stirred at this temperature for 15 minutes before warming to room temperature. After stirring for 1 h, TLC showed the arene starting material was consumed completely, at which point the solvent was removed in vacuo. The crude product was purified by recrystallization from CH_2Cl_2/Et_2O to produce 230 mg of off-white solid **1c** (78% yield).

ethylbenzene derived selenonium salt **1d**



Tf_2O (1.2 eq., 0.72 mmol, 120 μL) was added dropwise a solution of ethylbenzene (1.0 eq., 0.6 mmol, 97.2 mg) and dibenzoselenophene oxide (1.1 eq, 0.66 mmol, 165 mg) in MeCN (0.1 M) at 0°C under N_2. The resulting solution was stirred at this temperature for 15 minutes before

warming to room temperature. After stirring for 1 h, TLC showed the arene starting material was consumed completely, at which point the solvent was removed in vacuo. The crude product was purified by recrystallization from CH_2Cl_2/Et_2O to produce 256.6 mg of off-white solid **1d** (88% yield).

2.2 Preparation of sodium sulfonates

The sodium sulfinate salts (2c-2e, 2g-2k, 2n-2s) were prepared according to previously described methods[5][6]. Sulfinates 2a, 2b, 2f, 2l, 2m, and 2t are commercially available.

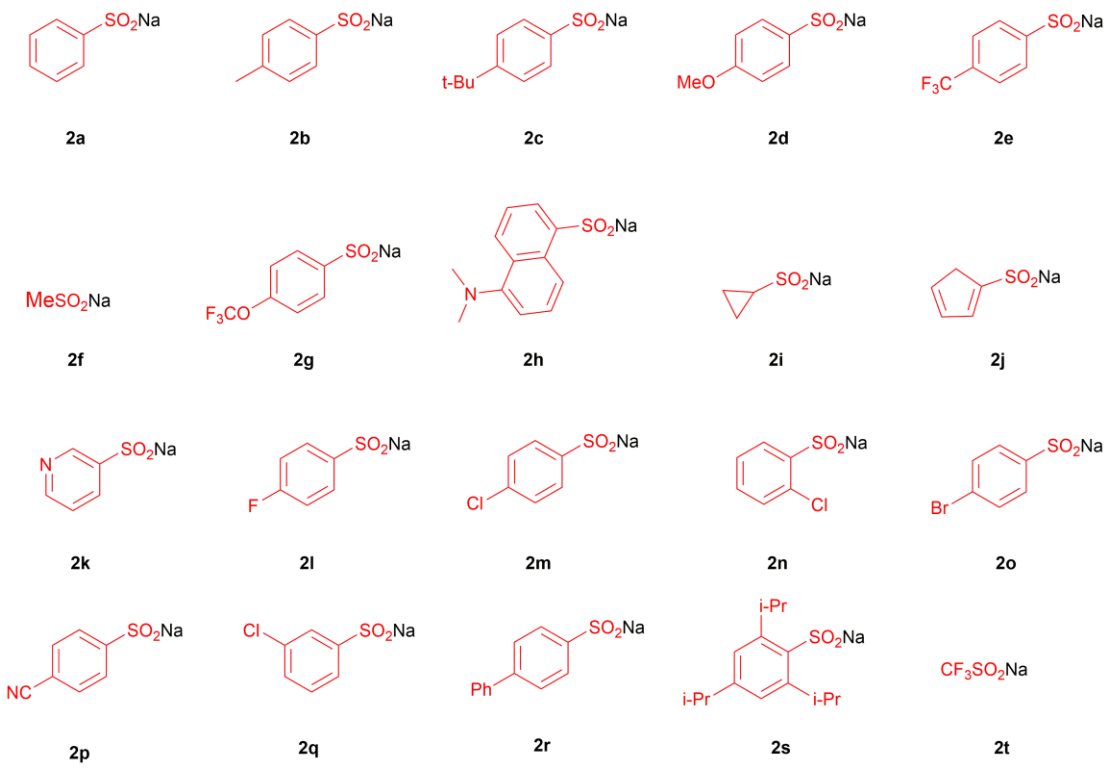
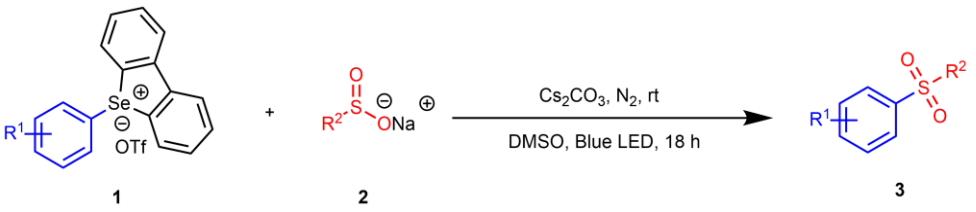


Figure S1. Sodium sulfinates purchased and synthesized

3 General method for photo-induced sulfonylation with selenonium salts



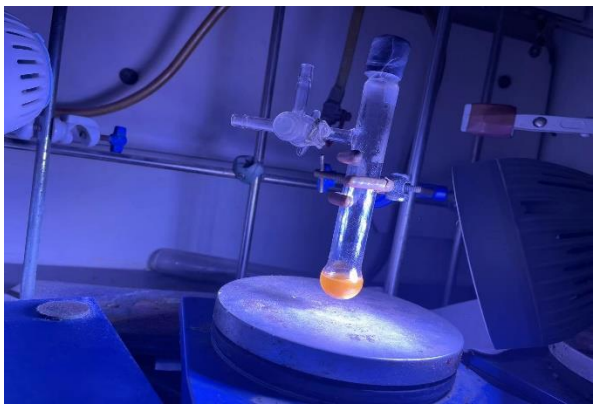


Figure S2. Reaction setup for the sulfonylation reactions

To a solution of selenonium salt (1.0 eq., 0.2 mmol, 110 mg), sodium sulfite (6 eq., 1.2 mmol, 196 mg), Cs_2CO_3(3 eq., 0.6 mmol, 196 mg) were added to DMSO (0.15 M) under N_2. The reaction solution was reacted under a blue LED irradiation for 18 h. Then it was quenched with saturated $NaHCO_3$ solution and the reaction solution was diluted with DCM. The separated organic layer was washed with saturated brine, dried over Na_2SO_4 and evaporated to dryness, the crude product was purified by silica gel column chromatography.

4 Mechanism Studies

4.1 UV/vis studies

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a UV/vis spectrophotometer from Agilent. Absorption spectra of individual reaction components

and mixtures thereof were recorded[7].

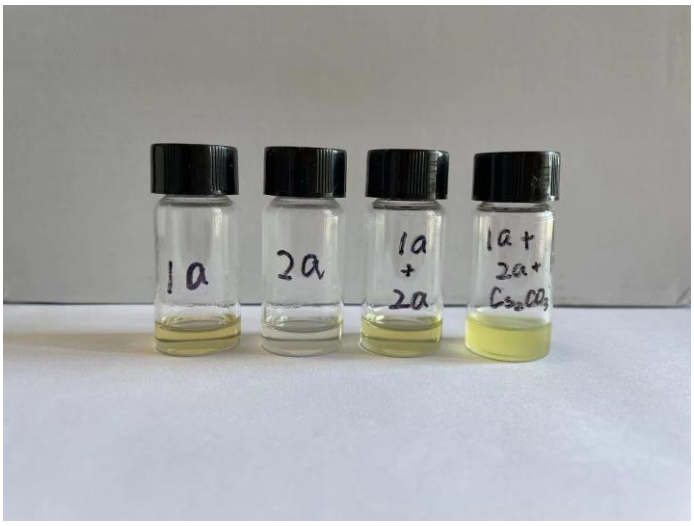


Figure S3. Visual appearance of reaction components and mixtures thereof

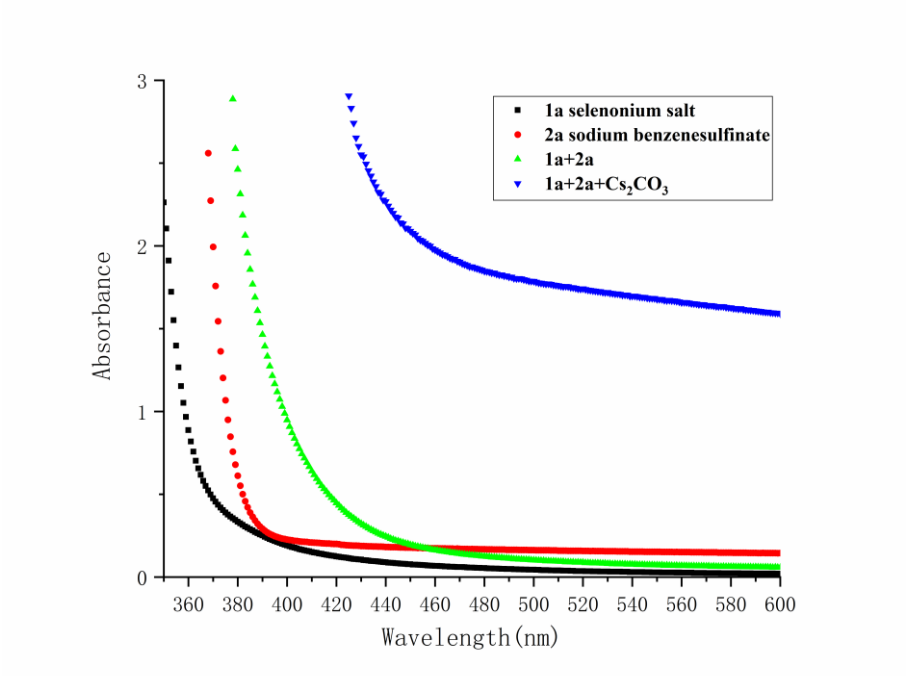
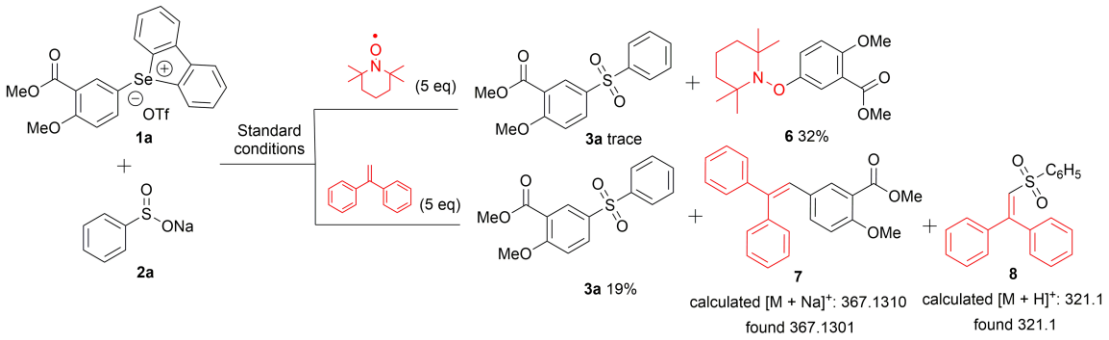


Figure S4. UV/vis absorption spectra of individual reaction components and a combination thereof. All spectra were measured in DMSO and with a concentration of: 0.15 M biphenyl sulfonium salt, 0.45 M sodium benzenesulfinate and 0.45 M Cs_2CO_3.

4.2 radical trapping experiments



To a solution of selenonium salt **1a** (1.0 eq., 0.2 mmol, 110 mg), sodium sulfonate **2a** (6 eq., 1.2 mmol, 197 mg), TEMPO/1,1-diphenylethylene (5.0 eq., 1.0 mmol), Cs_2CO_3 (3 eq., 0.6 mmol, 196 mg) were added to DMSO (0.15 M) under N_2. The reaction solution was reacted under a blue LED irradiation for 18 h. Then it was quenched with saturated $NaHCO_3$ solution and the reaction solution was diluted with DCM. The separated organic layer was washed with saturated brine, dried over Na_2SO_4 and evaporated to dryness, the crude product was purified by silica gel column chromatography.

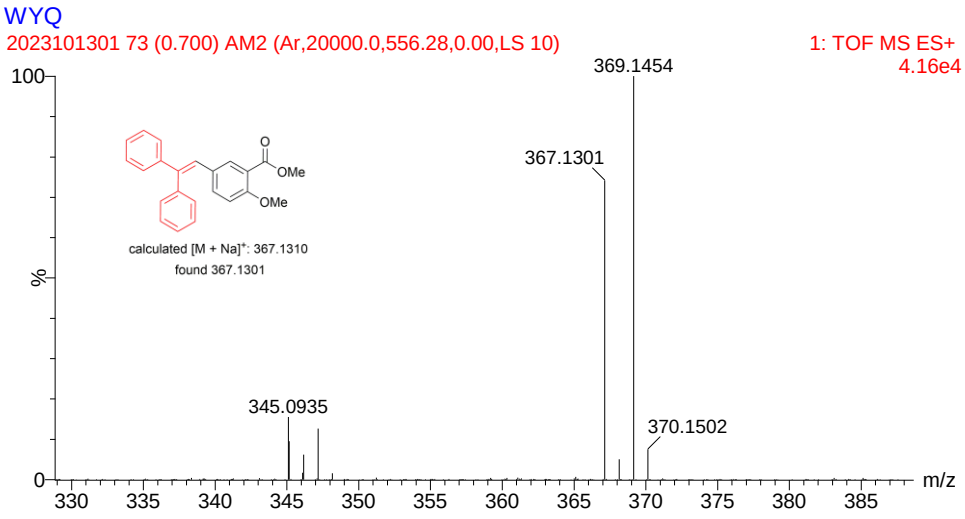


Figure S4. Mass spectrum of product of **7**

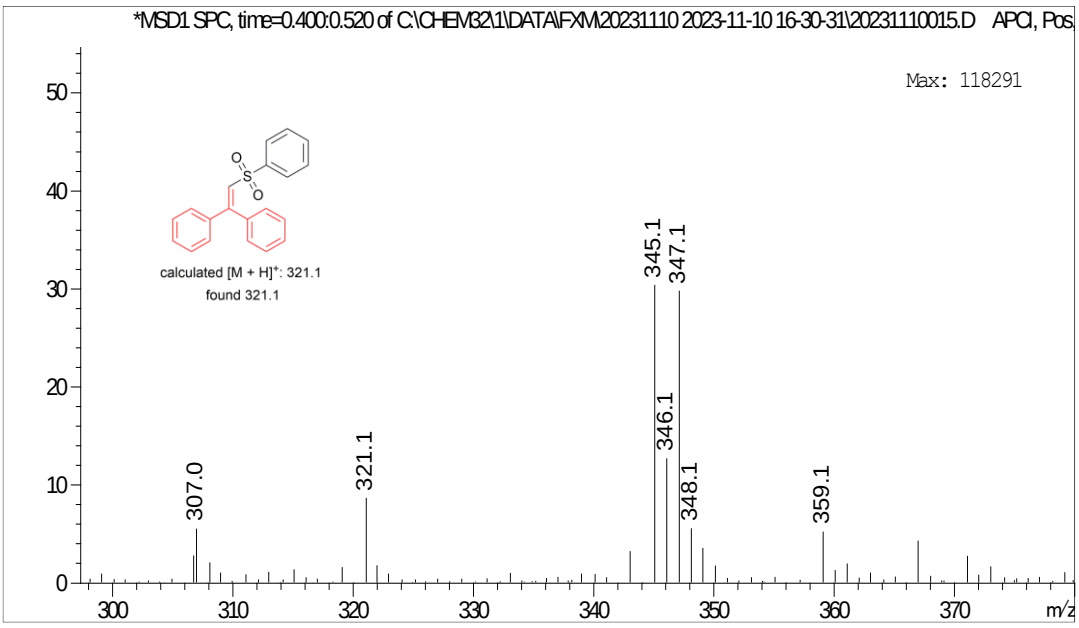


Figure S5. Mass spectrum of product of **8**

4.3 Emission spectrum of light source

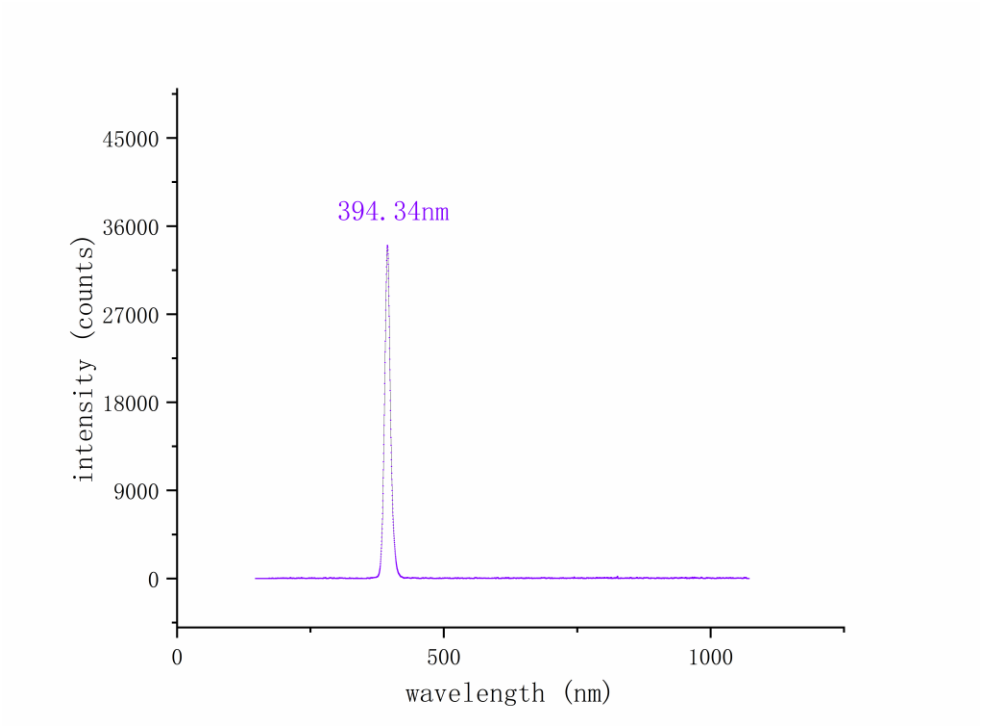


Figure S6. Purple lamp emission spectrum

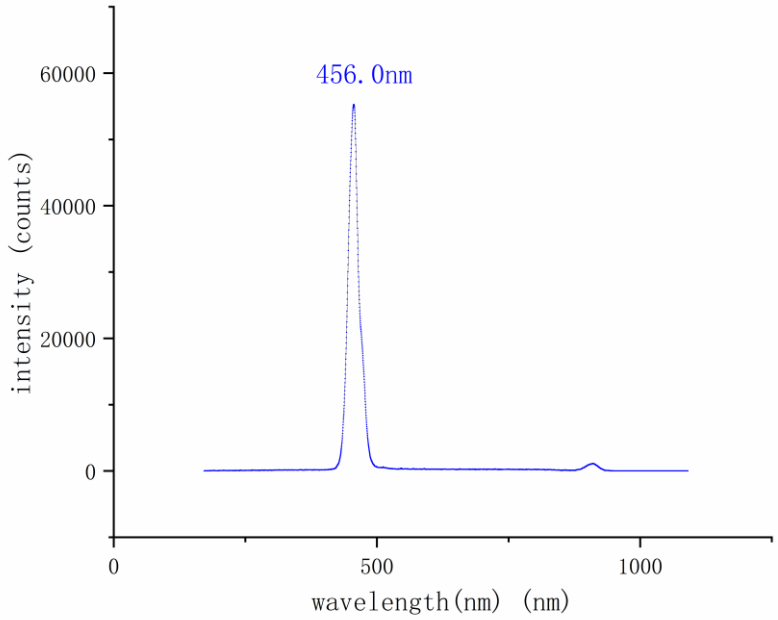


Figure S7. Blue lamp emission spectrum

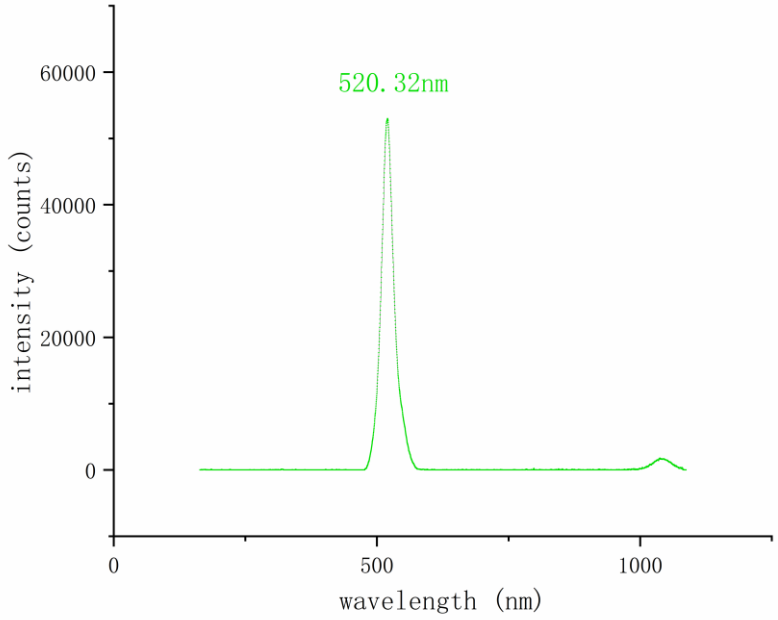
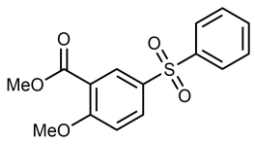
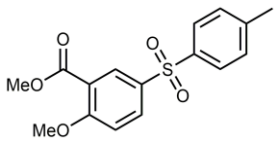


Figure S8. Green lamp emission spectrum

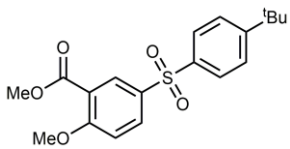
5 Characterization data of products



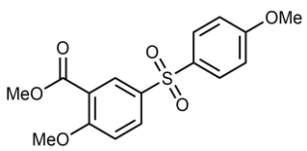
Methyl 2-methoxy-5-(phenylsulfonyl)benzoate (**3a**) was a white solid (68% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.34 (d, J = 2.4 Hz, 1H), 8.02 (dd, J = 8.9, 2.5 Hz, 1H), 7.93 – 7.89 (m, 2H), 7.57 – 7.52 (m, 1H), 7.49 (dd, J = 8.4, 6.8 Hz, 2H), 7.05 (d, J = 8.9 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.90, 162.54, 141.76, 133.20, 133.11, 132.98, 131.74, 129.38, 127.43, 120.85, 112.56, 56.53, 52.42; **MS(ESI)** calculated *m/z* for $C_{15}H_{14}O_5S$ $[M + H]^+$: 307.0641, found 307.0633.



Methyl 2-methoxy-5-tosylbenzoate (**3b**) was a white solid (63% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.34 (d, J = 2.5 Hz, 1H), 8.02 (dd, J = 8.8, 2.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.9 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.94, 162.41, 144.18, 138.83, 133.44, 132.95, 131.63, 130.01, 127.52, 120.79, 112.45, 56.51, 52.42, 21.57; **MS(ESI)** calculated *m/z* for $C_{16}H_{16}O_5S$ $[M + H]^+$: 321.0797, found 321.0793.

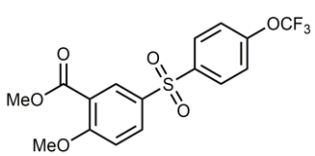


Methyl 5-((4-(tert-butyl)phenyl)sulfonyl)-2-methoxybenzoate (**3c**) was a white solid (65% yield). Rf=0.4 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.35 (d, J = 2.5 Hz, 1H), 8.03 (dd, J = 8.8, 2.5 Hz, 1H), 7.85 – 7.81 (m, 2H), 7.52 – 7.47 (m, 2H), 7.05 (d, J = 8.9 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H), 1.29 (s, 9H).**^{13}C NMR** (151 MHz, Chloroform-d) δ 164.98, 162.40, 157.08, 138.74, 133.42, 133.04, 131.67, 127.32, 126.40, 120.83, 112.45, 56.50, 52.41, 35.18, 31.02; **MS(ESI)** calculated *m/z* for $C_{19}H_{22}O_5S$ $[M + H]^+$: 363.1267, found. 363.1257.



Methyl 2-methoxy-5-((4-methoxyphenyl)sulfonyl)benzoate (**3d**) was a white solid (66% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.32 (d, J = 2.5 Hz, 1H), 8.00 (dd, J = 8.9, 2.5 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.04 (d, J = 8.9 Hz, 1H), 6.97 – 6.93 (m, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.97, 163.37, 162.28, 133.84, 133.29, 132.76, 131.42, 129.68, 120.75, 114.59, 112.45, 56.51, 55.67, 52.40; **MS(ESI)** calculated *m/z* for $C_{16}H_{16}O_6S$ $[M + H]^+$: 337.0747, found 337.0733.

Methyl2-methoxy-5-((4- (trifluoromethoxy)phenyl)sulfonyl)benzoate (**3e**) was a white



solid (71% yield). Rf=0.4 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.34 (d, J = 2.5 Hz, 1H), 8.03 (dd, J = 9.0, 2.5 Hz, 1H), 7.97 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 8.9 Hz, 1H), 3.95 (s, 3H), 3.89 (s,

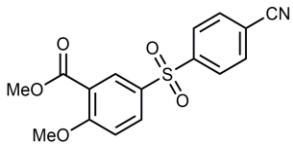
3H); **^{19}F NMR** (565 MHz, Chloroform-d) δ -57.69; **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.80, 162.79, 152.51, 140.12, 133.16, 132.40, 131.85, 129.70, 121.19, 121.05, 119.31, 112.70, 56.58, 52.49; **MS(ESI)** calculated *m/z* for $C_{16}H_{13}F_3O_6S$ $[M + H]^+$: 391.0464, found 391.0459.

Methyl 2-methoxy-5-((4-(trifluoromethyl)phenyl)sulfonyl)benzoate (**3f**) was a white solid (59% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.36 (d, J = 2.5 Hz, 1H), 8.07 – 8.02 (m, 3H), 7.76 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 9.0 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.71, 162.98, 145.36, 134.81 (d, J = 32.8 Hz), 133.34, 131.94 (d, J = 30.8 Hz), 128.03, 126.55 (q, J = 3.5 Hz), 124.01, 122.20, 121.13, 112.79, 56.61, 52.52; **^{19}F NMR** (565 MHz, Chloroform-d) δ -63.19; **MS(ESI)** calculated *m/z* for $C_{16}H_{13}F_3O_5S$ $[M + H]^+$: 375.0515, found 375.0509.

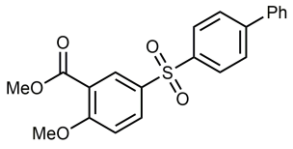
Methyl 5-((4-fluorophenyl)sulfonyl)-2-methoxybenzoate (**3g**) was a white solid (76% yield). Rf=0.4 (pentane/EtOAc, 2.5:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.32 (d, J = 2.5 Hz, 1H), 8.01 (dd, J = 8.9, 2.5 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.16 (t, J = 8.5 Hz, 2H), 7.06 (d, J = 8.9 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H); **^{19}F NMR** (565 MHz, Chloroform-d) δ -104.18 (d, J = 7.1 Hz).**^{13}C NMR** (151 MHz, Chloroform-d) δ 166.26, 164.84, 164.56, 162.62, 137.87 (d, J = 3.1 Hz), 132.92 (d, J = 26.2 Hz), 131.69, 130.29 (d, J = 9.0 Hz), 120.95, 116.69 (d, J = 22.8 Hz), 112.63, 56.56, 52.47; **MS(ESI)** calculated *m/z* for $C_{15}H_{13}FO_5S$ $[M + H]^+$: 325.0547, found 325.0546.

Methyl 5-((4-chlorophenyl)sulfonyl)-2-methoxybenzoate (**3h**) was a white solid (77% yield). Rf=0.4 (pentane/EtOAc, 2.5:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.33 (d, J = 2.5 Hz, 1H), 8.01 (dd, J = 8.8, 2.5 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.9 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.79, 162.72, 140.30, 139.88, 133.07, 132.55, 131.78, 129.70, 128.93, 120.99, 112.64, 56.57, 52.47; **MS(ESI)** calculated *m/z* for $C_{15}H_{13}ClO_5S$ $[M + H]^+$: 341.0251, found 341.0248.

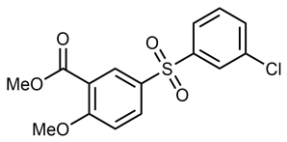
Methyl 5-((4-bromophenyl)sulfonyl)-2-methoxybenzoate (**3i**) was a white solid (64% yield). Rf=0.3 (pentane/EtOAc, 2.5:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.34 (d, J = 2.4 Hz, 1H), 8.04 – 7.99 (m, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.9 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.79, 162.75, 140.84, 133.10, 132.71, 132.51, 131.83, 129.02, 128.46, 121.00, 112.63, 56.58, 52.50; **MS(ESI)** calculated *m/z* for $C_{15}H_{13}BrO_5S$ $[M + H]^+$: 384.9746, found 384.9737.



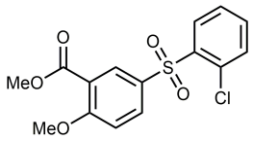
Methyl 5-((4-cyanophenyl)sulfonyl)-2-methoxybenzoate(**3j**) was a white solid (50% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.33 (d, J = 2.5 Hz, 1H), 8.02 (d, J = 8.6 Hz, 3H), 7.79 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.9 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.66, 163.13, 146.00, 133.39, 133.19, 132.13, 131.36, 128.11, 121.28, 117.16,116.90, 112.89, 56.66, 52.56; **MS(ESI)** calculated *m/z* for $C_{16}H_{13}NO_5S$ $[M + H]^+$: 332.0593, found 332.0589.



Methyl 5-([1,1'-biphenyl]-4-ylsulfonyl)-2-methoxybenzoate (**3k**) was a white solid (42% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.39 (d, J = 2.4 Hz, 1H), 8.07 (dd, J = 8.9, 2.4 Hz, 1H), 8.01 – 7.95 (m, 2H), 7.82 – 7.67 (m, 2H), 7.58 – 7.53 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.43 – 7.34 (m, 1H), 7.08 (d, J = 8.9 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-d) δ 164.91, 162.54, 146.20, 140.35, 139.18, 133.24, 133.04, 131.74, 129.06, 128.59, 128.00, 127.34, 121.01, 112.54, 56.50, 52.38; **MS(ESI)** calculated *m/z* for $C_{21}H_{18}O_5S$ $[M + H]^+$: 383.0954, found 383.0951.

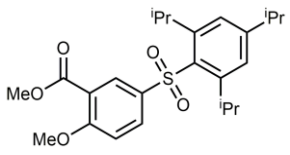


Methyl 5-((3-chlorophenyl)sulfonyl)-2-methoxybenzoate (**3l**) was a white solid (50% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.34 (d, J = 2.5 Hz, 1H), 8.03 (dd, J = 8.8, 2.5 Hz, 1H), 7.89 (t, J = 1.9 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.51 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.44 (t, J = 7.9 Hz, 1H), 7.08 (d, J = 8.9 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-d) δ 164.77, 162.82, 143.61, 135.56, 133.31, 133.22, 132.26, 131.88, 130.68, 127.48, 125.59, 121.14, 112.70, 56.56, 52.44; **MS(ESI)** calculated *m/z* for $C_{15}H_{13}ClO_5S$ $[M + Na]^+$: 363.0064, found 363.0058.



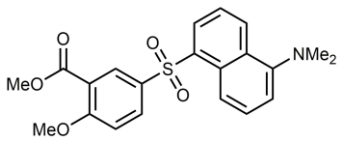
Methyl 5-((2-chlorophenyl)sulfonyl)-2-methoxybenzoate (**3m**) was a white solid (43% yield). Rf=0.4 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.33 (dt, J = 5.2, 2.1 Hz, 2H), 8.09 (dd, J = 8.9, 2.5 Hz, 1H), 7.50 (ddd, J = 15.6, 7.6, 1.6 Hz, 2H), 7.42 (dd, J = 7.6, 1.4 Hz, 1H), 7.07 (d, J = 8.8 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.88, 162.79, 138.54, 134.69, 134.33, 132.82, 132.08, 131.29, 130.91, 129.38, 127.43, 120.54, 112.01, 56.56, 52.43; **MS(ESI)** calculated *m/z* for $C_{15}H_{13}ClO_5S$ $[M + H]^+$: 341.0251, found 341.0246.

Methyl 2-methoxy-5-((2,4,6-triisopropylphenyl)sulfonyl)benzoate (**3n**) was a white

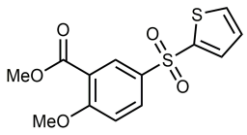


solid (33% yield). Rf=0.4 (pentane/EtOAc, 1:1); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 2.5 Hz, 1H), 7.87 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.16 (s, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 4.20 (hept, *J* = 6.8 Hz, 2H), 3.95 (s, 3H), 3.88 (s, 3H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.15 (d, *J* = 6.7 Hz, 12H).; **^{13}C**

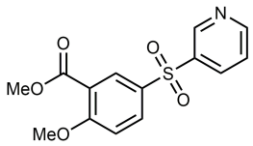
NMR (126 MHz, Chloroform-d) δ 164.95, 161.79, 153.89, 151.21, 136.82, 132.59, 131.22, 130.06, 124.15, 120.39, 112.10, 56.44, 52.29, 34.19, 29.48, 24.65, 23.50; **MS(ESI)** calculated *m/z* for $C_{24}H_{32}O_5S$ $[M + H]^+$: 433.2049, found 433.2047.



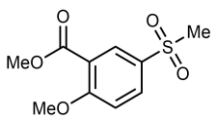
Methyl 5-((5-(dimethylamino)naphthalen-1-yl)sulfonyl)-2-methoxybenzoate (**3o**) was a yellow solid (26% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.57 (d, J = 8.5 Hz, 1H), 8.51 – 8.46 (m, 1H), 8.38 (d, J = 2.5 Hz, 1H), 8.25 (d, J = 8.7 Hz, 1H), 8.06 (dd, J = 8.9, 2.5 Hz, 1H), 7.60 (t, J = 7.9 Hz, 1H), 7.48 (t, J = 8.1 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 8.9 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 2.85 (s, 6H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.94, 162.31, 151.97, 135.98, 133.33, 132.90, 131.63, 131.44, 129.90, 129.81, 129.76, 128.46, 123.47, 120.63, 118.67, 115.29, 112.20, 56.45, 52.40, 45.40; **MS(ESI)** calculated *m/z* for $C_{21}H_{21}NO_5S$ $[M + H]^+$: 400.1219, found 400.1216.



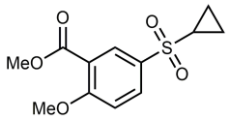
Methyl 2-methoxy-5-(thiophen-2-ylsulfonyl)benzoate (**3p**) was a white solid (64% yield). Rf=0.4 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.38 (d, J = 2.4 Hz, 1H), 8.07 (dd, J = 8.9, 2.5 Hz, 1H), 7.67 (dd, J = 3.7, 1.5 Hz, 1H), 7.63 (dd, J = 5.0, 1.4 Hz, 1H), 7.09 – 7.05 (m, 2H), 3.95 (s, 3H), 3.89 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.85, 162.61, 143.23, 133.83, 133.48, 133.19, 132.80, 131.48, 127.93, 120.87, 112.55, 56.57, 52.46; **HRMS**(ESI, *m/z*): $[M+Na]^+$ calcd for $C_{13}H_{12}O_5S_2$,335.0018, found 335.0022.



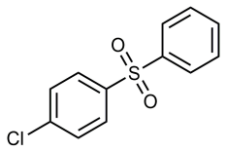
Methyl 2-methoxy-5-(pyridin-3-ylsulfonyl)benzoate (**3q**) was a white solid (59% yield). Rf=0.4 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 9.11 (d, J = 2.3 Hz, 1H), 8.76 (dd, J = 4.9, 1.6 Hz, 1H), 8.35 (d, J = 2.5 Hz, 1H), 8.18 (dt, J = 8.1, 2.0 Hz, 1H), 8.04 (dd, J = 8.9, 2.5 Hz, 1H), 7.44 (dd, J = 8.1, 4.8 Hz, 1H), 7.08 (d, J = 8.9 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.67, 162.99, 153.68, 148.51, 138.45, 135.08, 133.21, 132.04, 131.91, 123.94, 121.17, 112.82, 56.63, 52.51; **MS(ESI)** calculated *m/z* for $C_{14}H_{13}NO_5S$ $[M + H]^+$: 308.0593, found 308.0589.



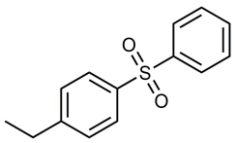
Methyl 2-methoxy-5-(methylsulfonyl)benzoate (**3r**) was a white solid (47% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.36 (d, J = 2.4 Hz, 1H), 8.04 (dd, J = 8.8, 2.4 Hz, 1H), 7.12 (d, J = 8.8 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 3.05 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.82, 162.89, 132.84, 132.07, 131.60, 120.92, 112.47, 56.61, 52.48, 44.78; **MS(ESI)** calculated *m/z* for $C_{10}H_{12}O_5S$ $[M + H]^+$: 245.0484, found 245.0488.



Methyl 5-(cyclopropylsulfonyl)-2-methoxybenzoate (**3s**) was a white solid (49% yield). Rf=0.3 (pentane/EtOAc, 2:1); **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.30 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 8.9 Hz, 1H), 3.98 (s, 3H), 3.90 (s, 3H), 2.45 (t, J = 6.3 Hz, 1H), 1.34 – 1.31 (m, 2H), 1.02 (d, J = 7.7 Hz, 2H); **^{13}C NMR** (151 MHz, Chloroform-d) δ 164.97, 162.66, 133.00, 132.22, 131.67, 120.78, 112.41, 56.56, 52.45, 33.20, 6.04; **MS(ESI)** calculated *m/z* for $C_{12}H_{14}O_5S$ $[M + H]^+$: 271.0641, found 271.0638.

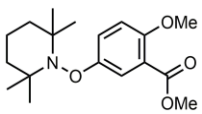


1-chloro-4-(phenylsulfonyl)benzene (**3ca**) was a white solid (52% yield). Rf=0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 2H), 7.90 – 7.86 (m, 2H), 7.61 – 7.56 (m, 1H), 7.54 – 7.50 (m, 2H), 7.49 – 7.45 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.25, 140.18, 139.93, 133.47, 129.65, 129.44, 129.16, 127.68; **MS(ESI)** calculated *m/z* for $C_{12}H_9ClO_2S$ $[M + Na]^+$: 274.9904, found 274.9907.

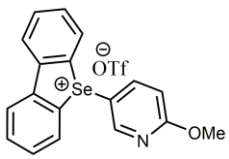


1-ethyl-4-(phenylsulfonyl)benzene (**3da**) was a white solid (63% yield). Rf=0.3 (pentane/EtOAc, 8:1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.91 (m, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.52 – 7.46 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.28, 142.02, 138.84, 133.01, 129.24, 128.80, 127.84, 127.56, 28.84, 15.07; **MS(ESI)** calculated *m/z* for $C_{14}H_{14}O_2S$ $[M + Na]^+$: 269.0607, found 269.0610.

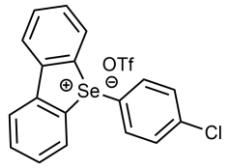
Methyl 2-methoxy-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzoate (**6**) was a pale



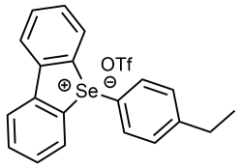
yellow solid (32% yield). Rf=0.4 (pentane/EtOAc, 6:1); **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.53 (d, J = 3.1 Hz, 1H), 7.33 (dd, J = 9.1, 3.2 Hz, 1H), 6.84 (d, J = 8.9 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 1.70 (s, 2H), 1.58 (s, 4H), 1.21 (s, 6H), 0.99 (s, 6H); **^{13}C NMR** (126 MHz, Chloroform-d) δ 166.88, 156.99, 152.75, 120.03, 118.62, 116.34, 113.04, 60.41, 56.75, 52.03, 39.72, 35.27, 32.58, 27.72, 20.40, 16.99; **MS(ESI)** calculated *m/z* for $C_{18}H_{27}NO_4$ $[M + H]^+$: 322.2019, found 322.2014.



5-(6-methoxypyridin-3-yl)-5H-dibenzo[b,d]selenophen-5-ium trifluoromethanesulfonate (**1b**) was a off-white solid (36% yield); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.62 – 7.95 (m, 6H), 7.71 (d, *J* = 72.4 Hz, 3H), 7.23 (s, 2H), 3.99 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 142.40, 141.13, 133.57, 130.38, 129.28, 124.02, 121.97, 119.41, 117.78, 116.84, 110.78, 55.71; **MS(ESI)** calculated *m/z* for $C_{18}H_{14}NOSe^+$ $[M\text{-}OTf]^+$: 340.0235, found 340.0232.



5-(4-chlorophenyl)-5H-dibenzo[b,d]selenophen-5-ium trifluoromethanesulfonate (**1c**) was a off-white solid (78% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.41 (d, J = 7.8 Hz, 2H), 8.35 (t, J = 6.8 Hz, 2H), 7.86 (t, J = 7.6 Hz, 2H), 7.70 (t, J = 7.7 Hz, 2H), 7.56 (dd, J = 9.1, 2.9 Hz, 2H), 7.50 (dd, J = 9.0, 4.3 Hz, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 141.60, 137.46, 137.38, 133.36, 132.38, 131.48, 131.38, 131.03, 130.20, 125.40; **MS(ESI)** calculated *m/z* for $C_{18}H_{12}ClSe^+$ $[M\text{-}OTf]^+$: 342.9787, found 342.9792.



5-(4-ethylphenyl)-5H-dibenzo[b,d]selenophen-5-ium trifluoromethanesulfonate (**1d**) was a off-white solid (88% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.41 (d, J = 7.8 Hz, 2H), 8.34 (d, J = 7.9 Hz, 2H), 7.86 (t, J = 7.6 Hz, 2H), 7.69 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 2.56 (q, J = 8.0 Hz, 2H), 1.09 (t, J = 7.4 Hz, 4H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 148.85, 141.57, 137.51, 133.19, 131.27, 130.52, 130.27, 130.18, 129.59, 125.30, 28.22, 15.60; **MS(ESI)** calculated *m/z* for $C_{20}H_{17}Se^+$ $[M\text{-}OTf]^+$: 337.0490, found 337.0497.

6 Reference

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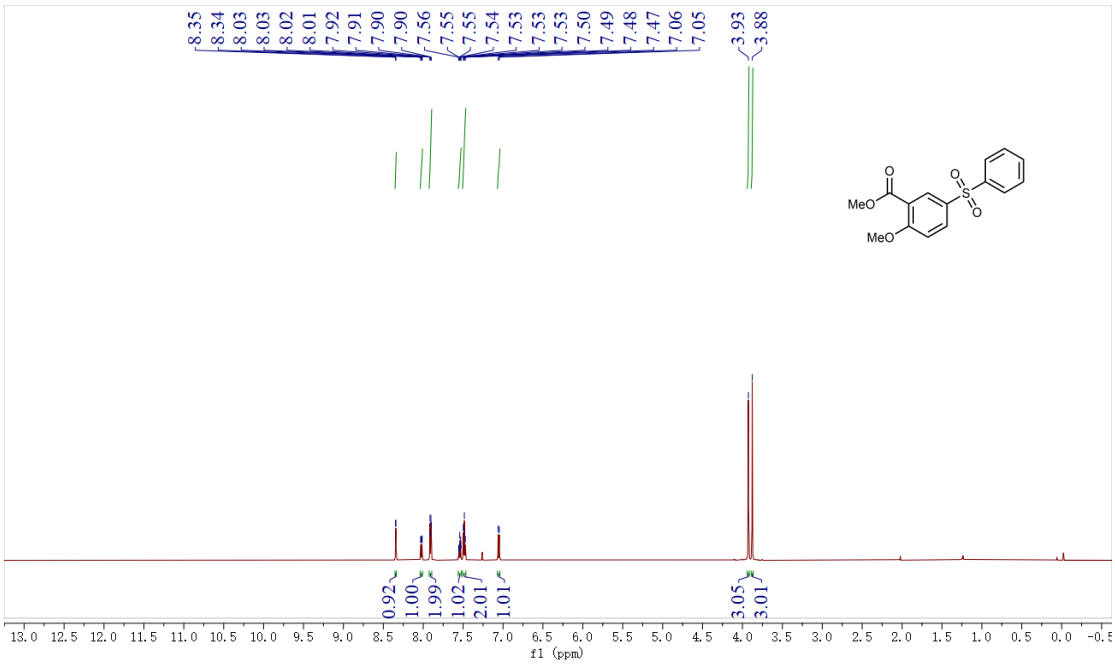
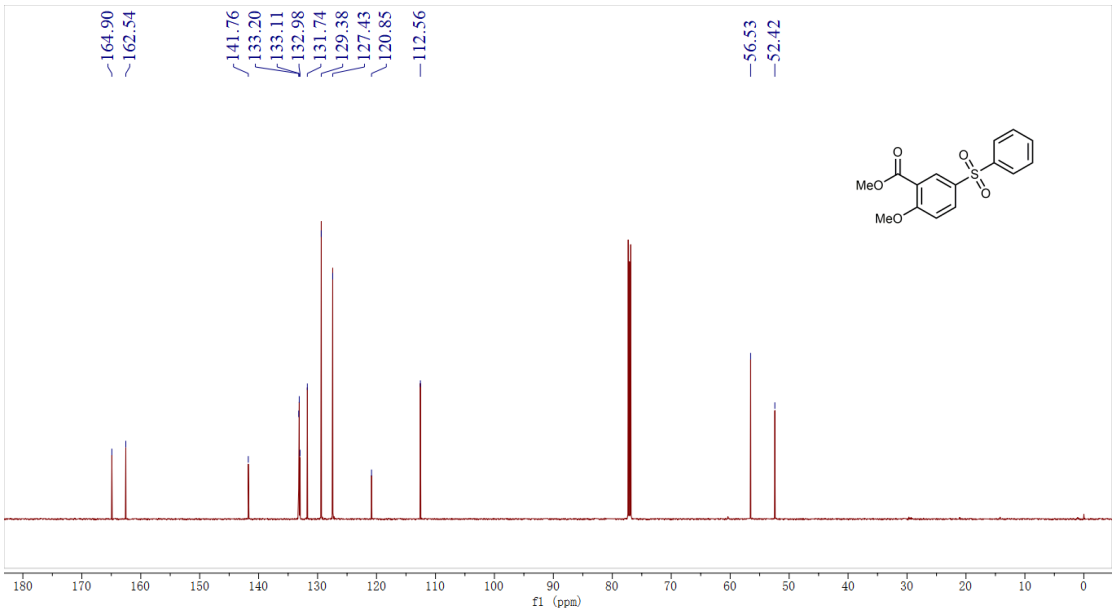
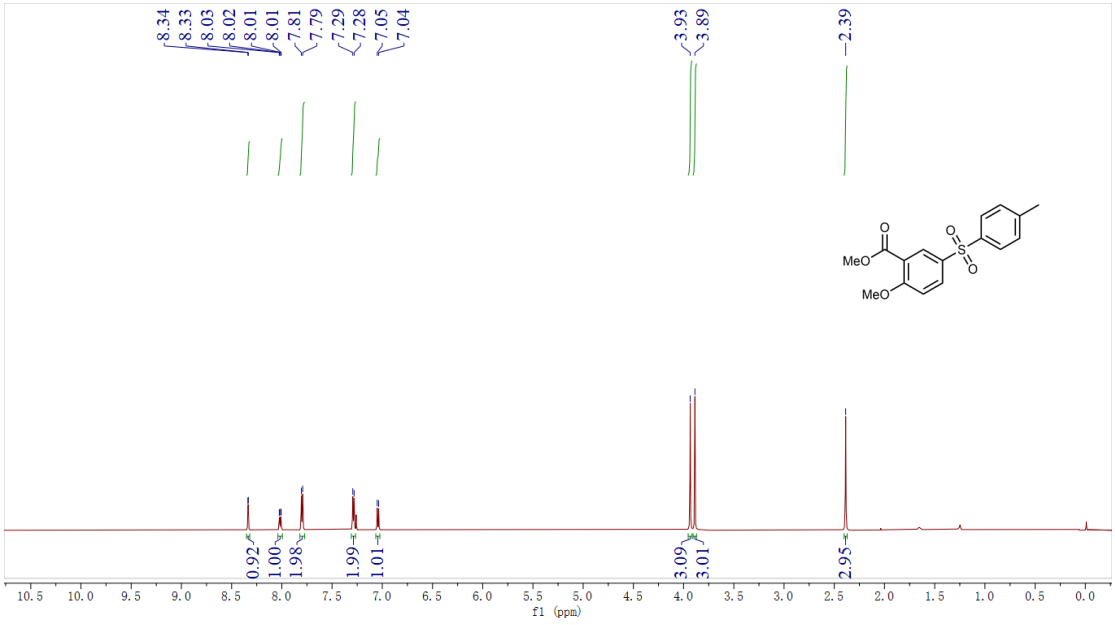
7 NMR spectra

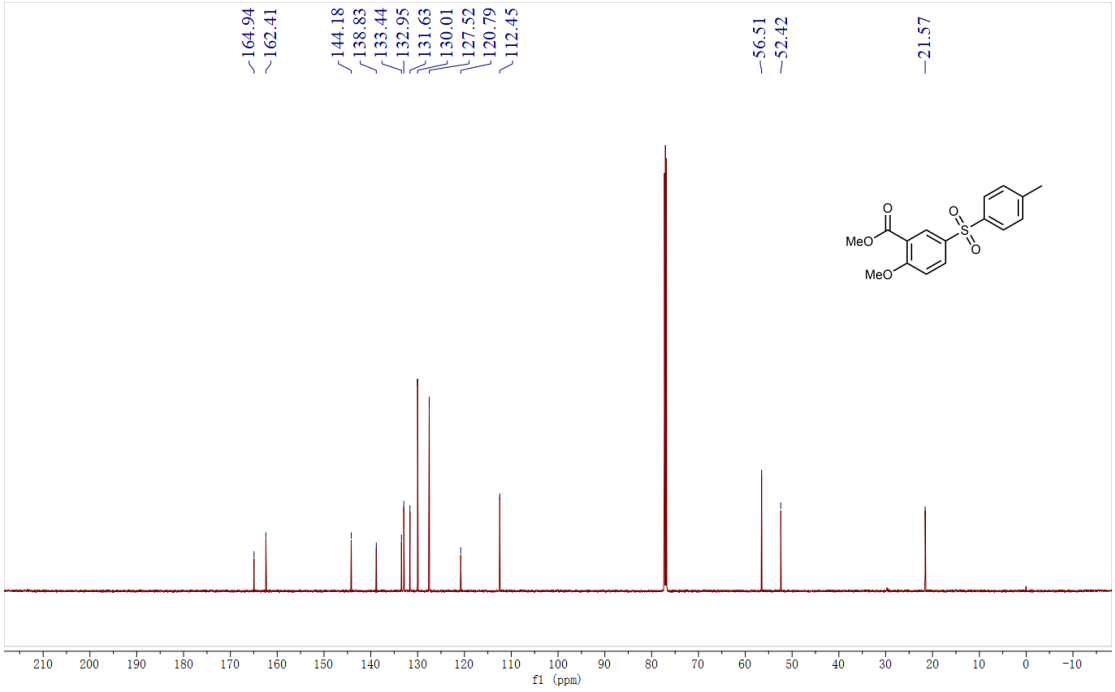
Methyl 2-methoxy-5-(phenylsulfonyl)benzoate (**3a**)



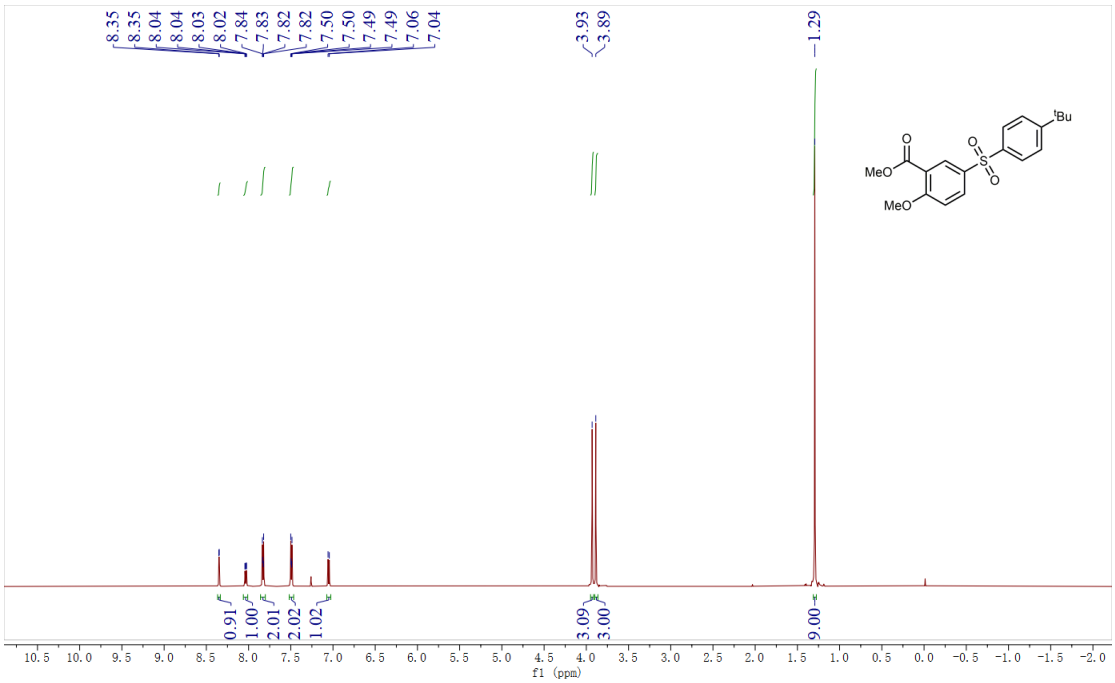


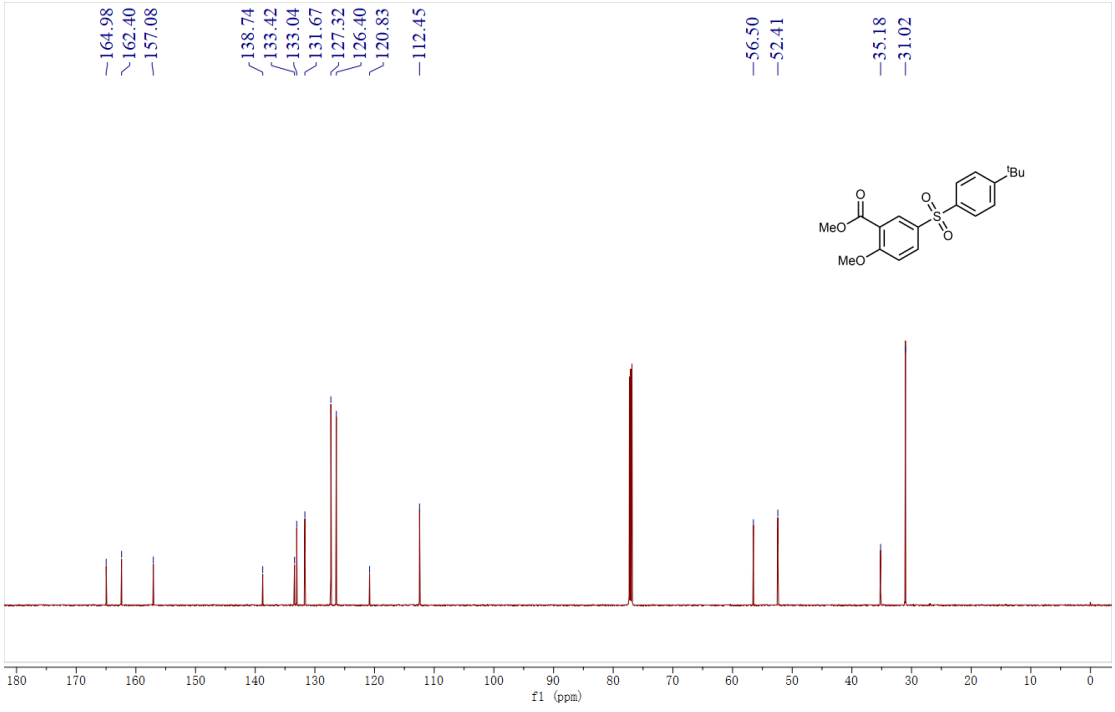
Methyl 2-methoxy-5-tosylbenzoate (**3b**)



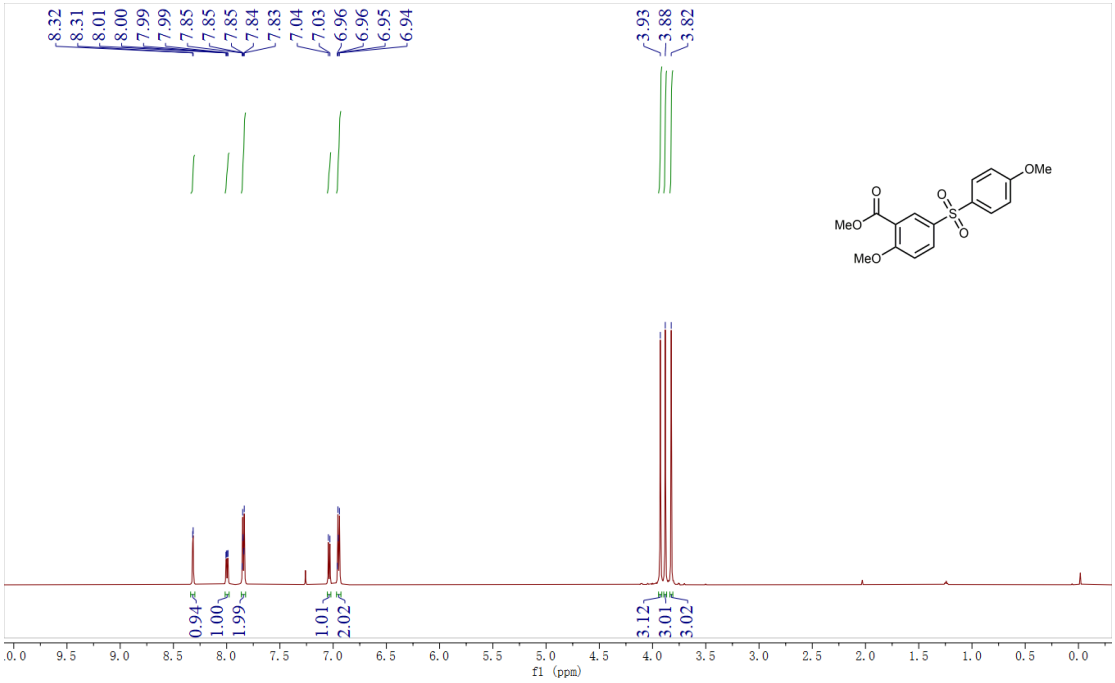


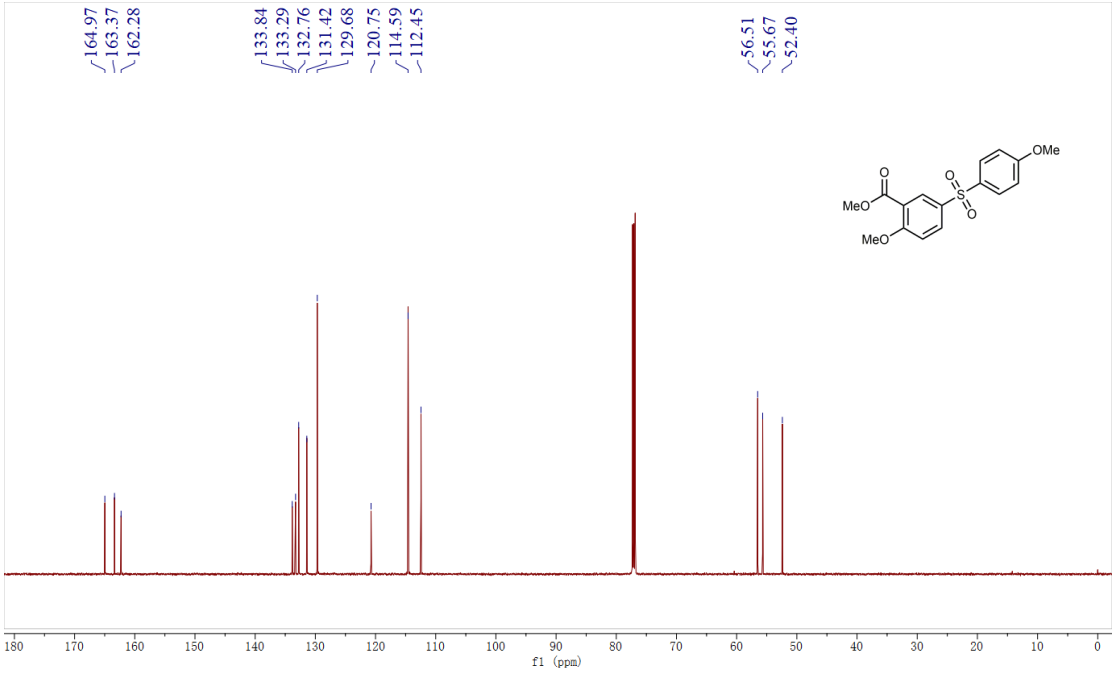
Methyl 5-((4-(tert-butyl)phenyl)sulfonyl)-2-methoxybenzoate (**3c**)



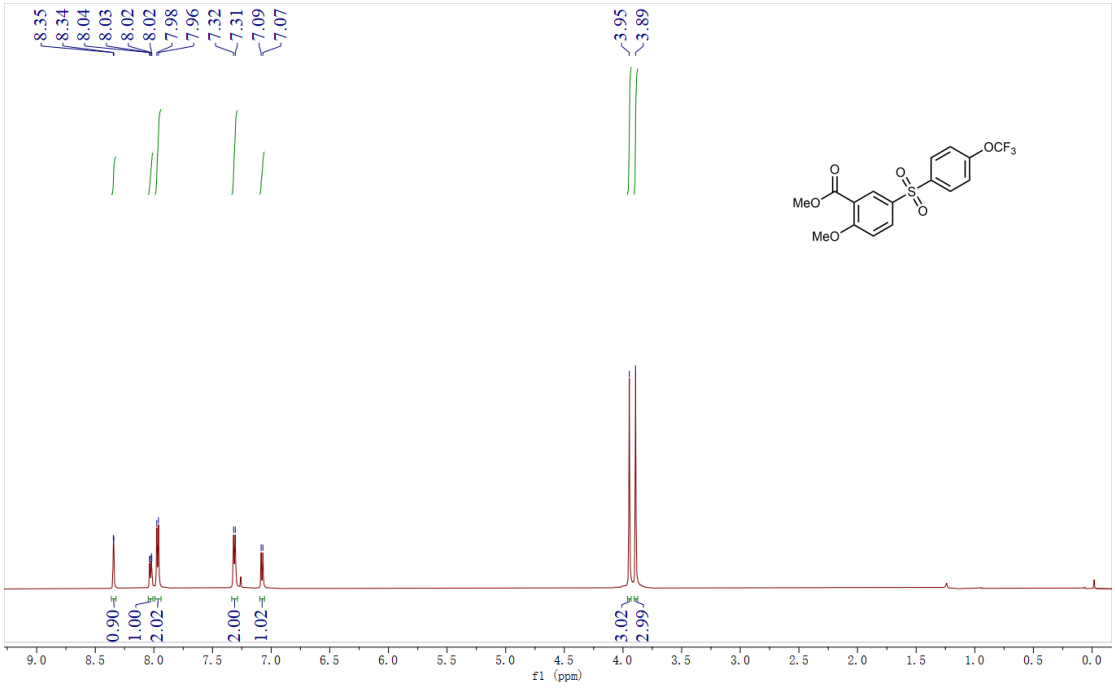


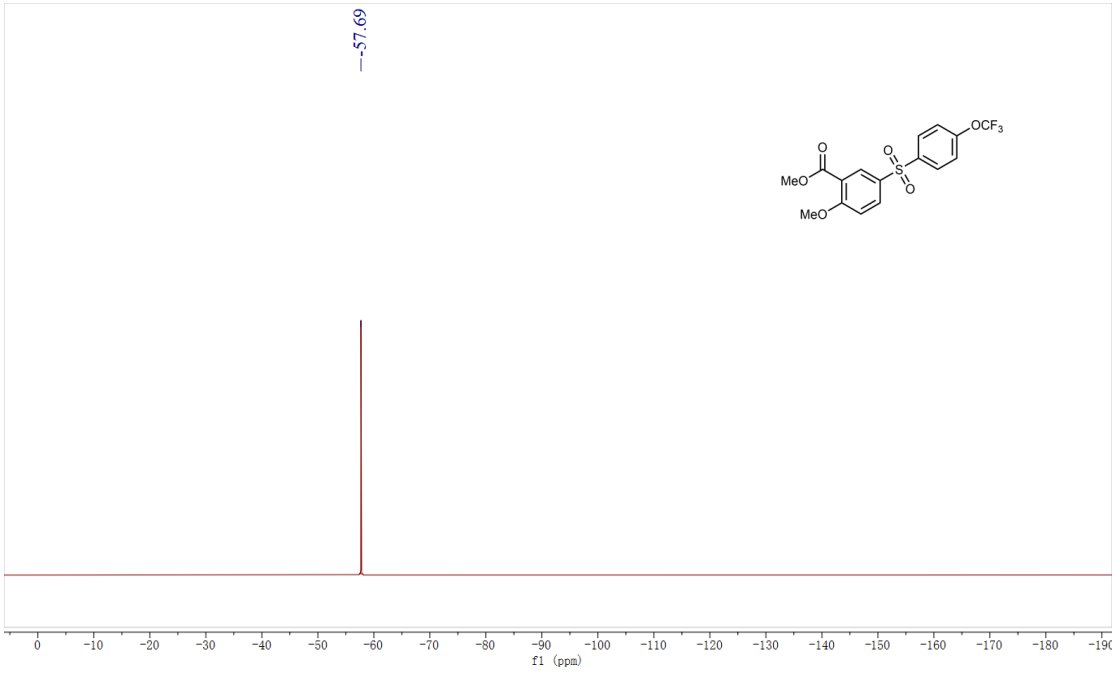
Methyl 2-methoxy-5-((4-methoxyphenyl)sulfonyl)benzoate (**3d**)



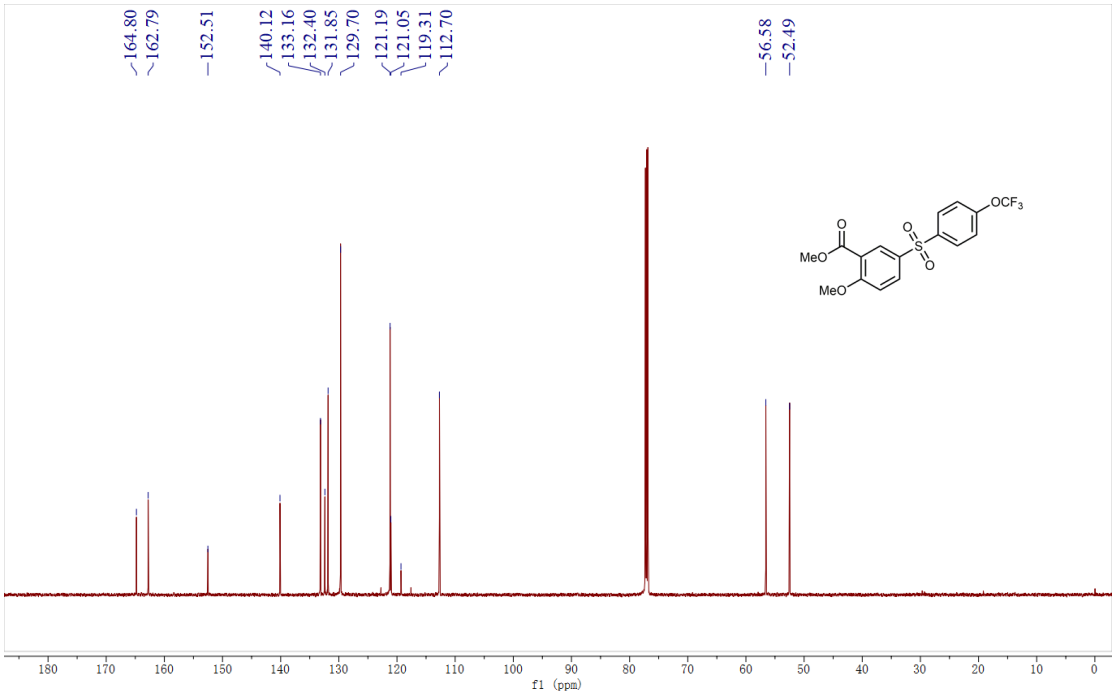


Methyl2-methoxy-5-((4- (trifluoromethoxy)phenyl)sulfonyl)benzoate (**3e**)

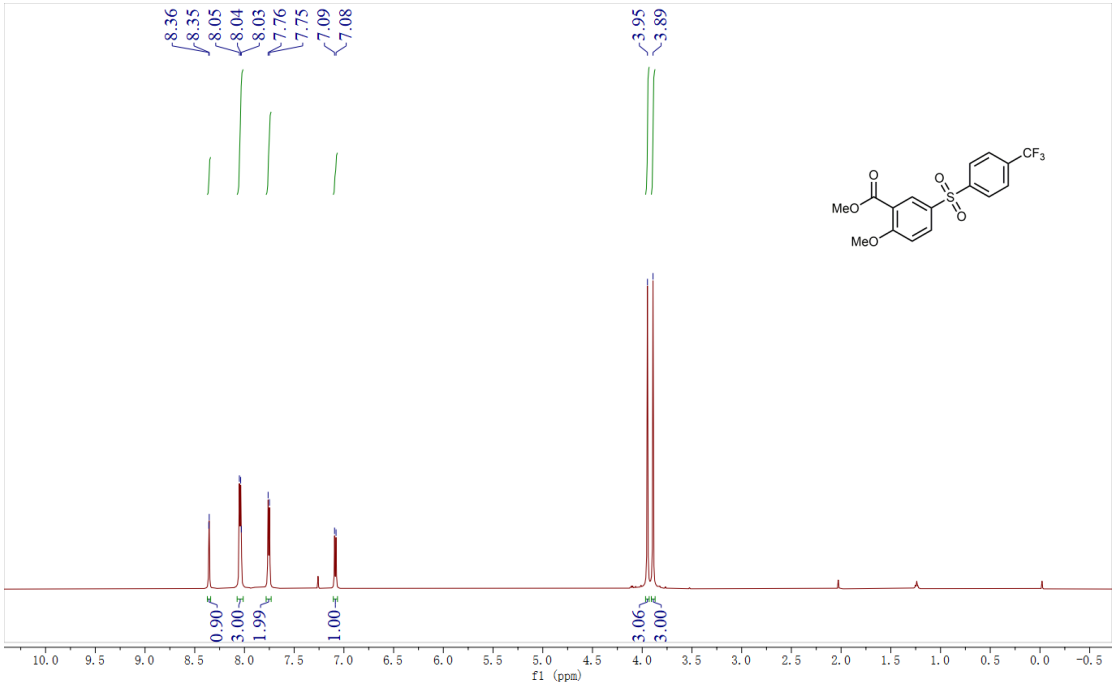




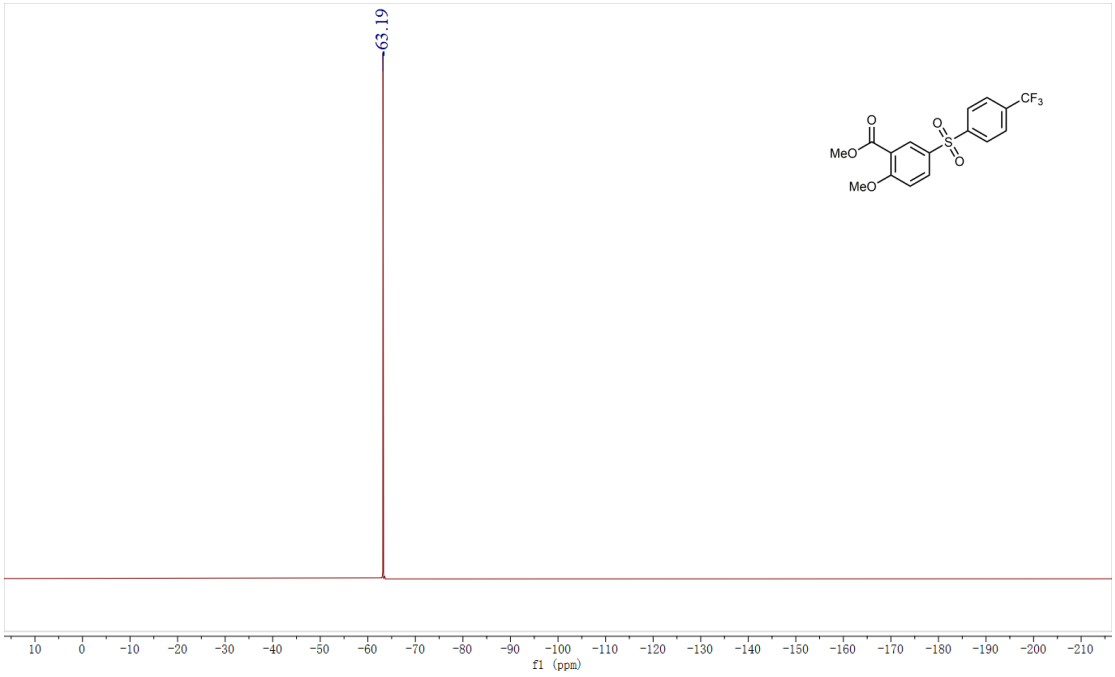
Methyl2-methoxy-5-((4- (trifluoromethoxy)phenyl)sulfonyl)benzoate (**3e**)

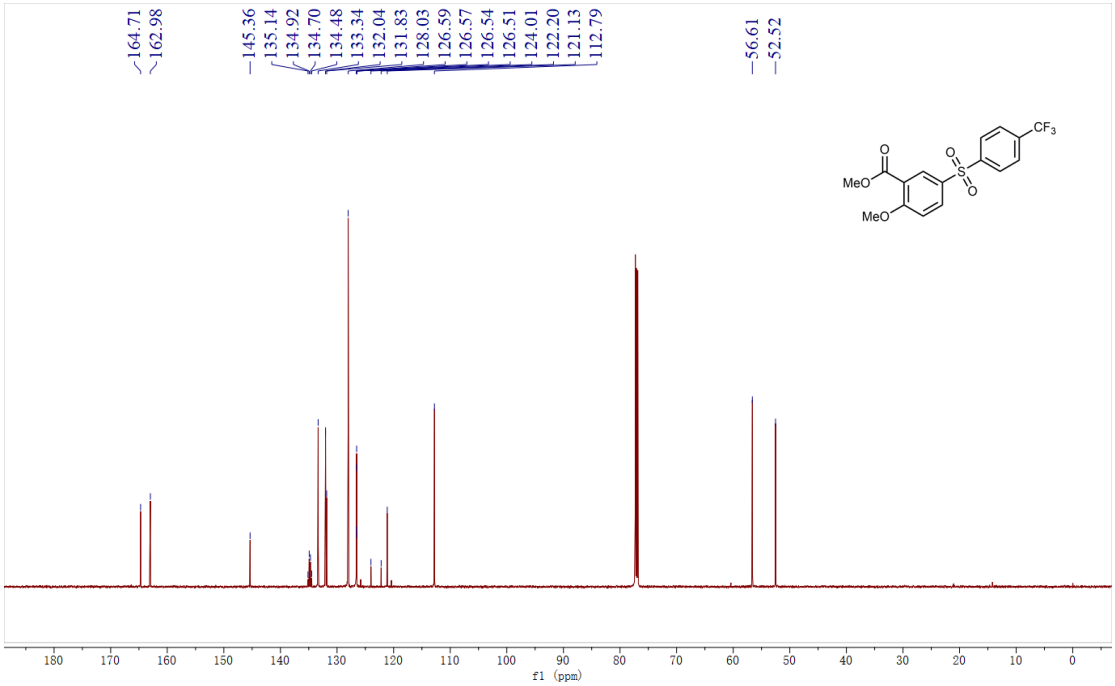


Methyl 2-methoxy-5-((4-(trifluoromethyl)phenyl)sulfonyl)benzoate (**3f**)

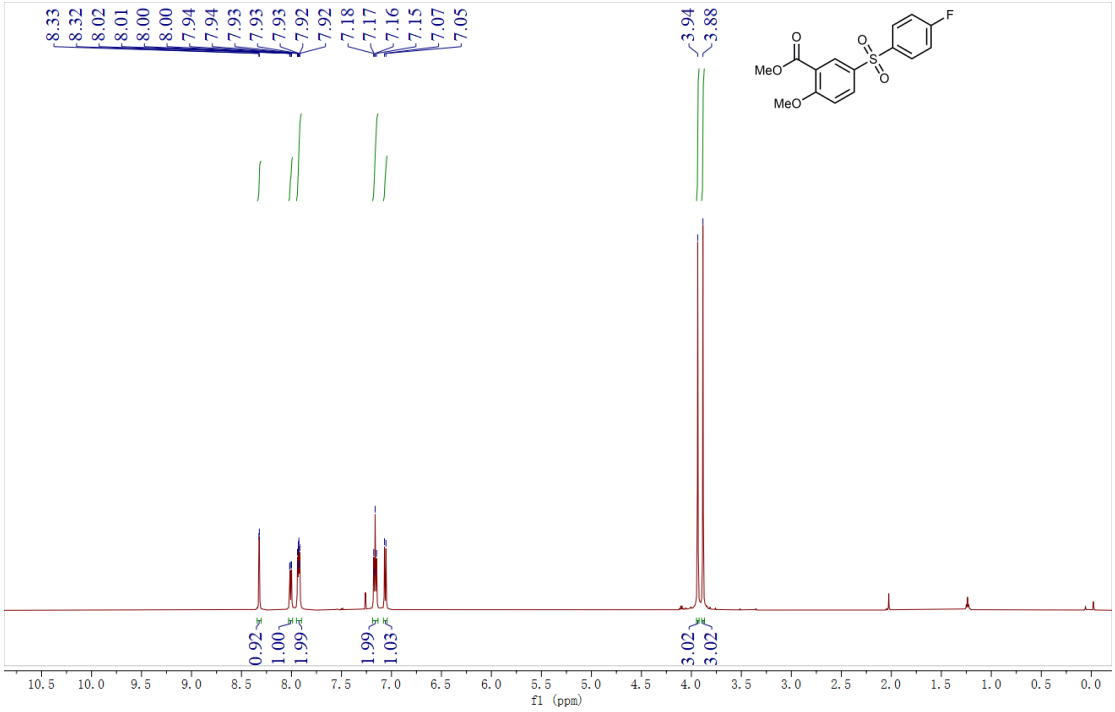


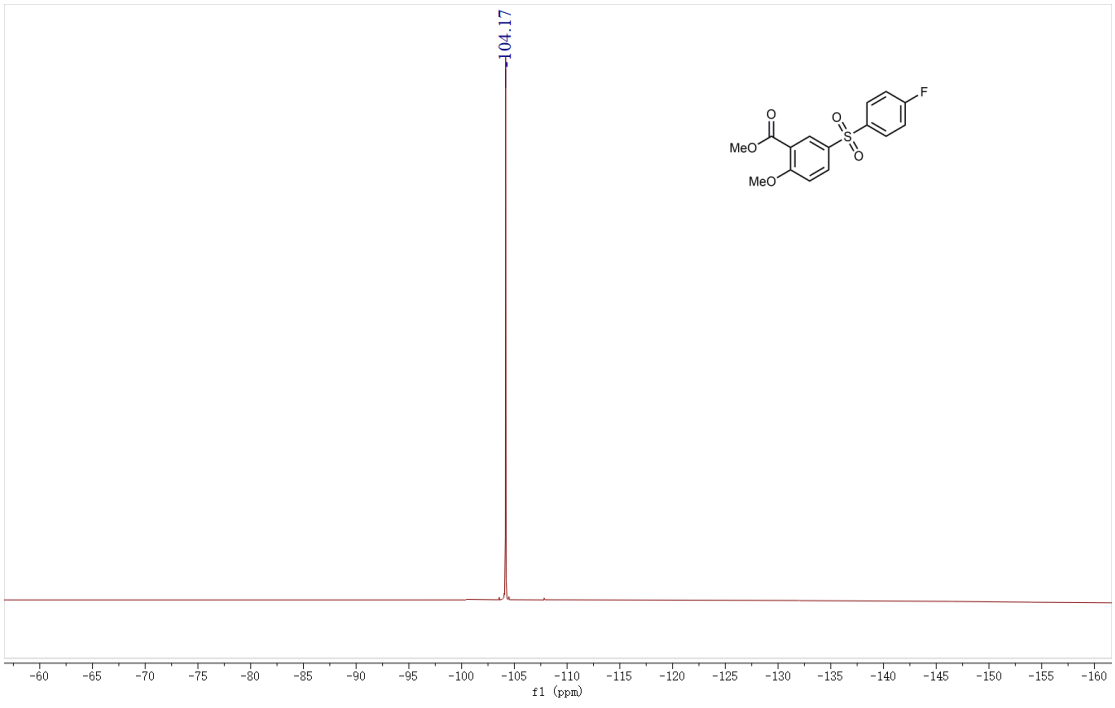
Methyl 2-methoxy-5-((4-(trifluoromethyl)phenyl)sulfonyl)benzoate (**3f**)



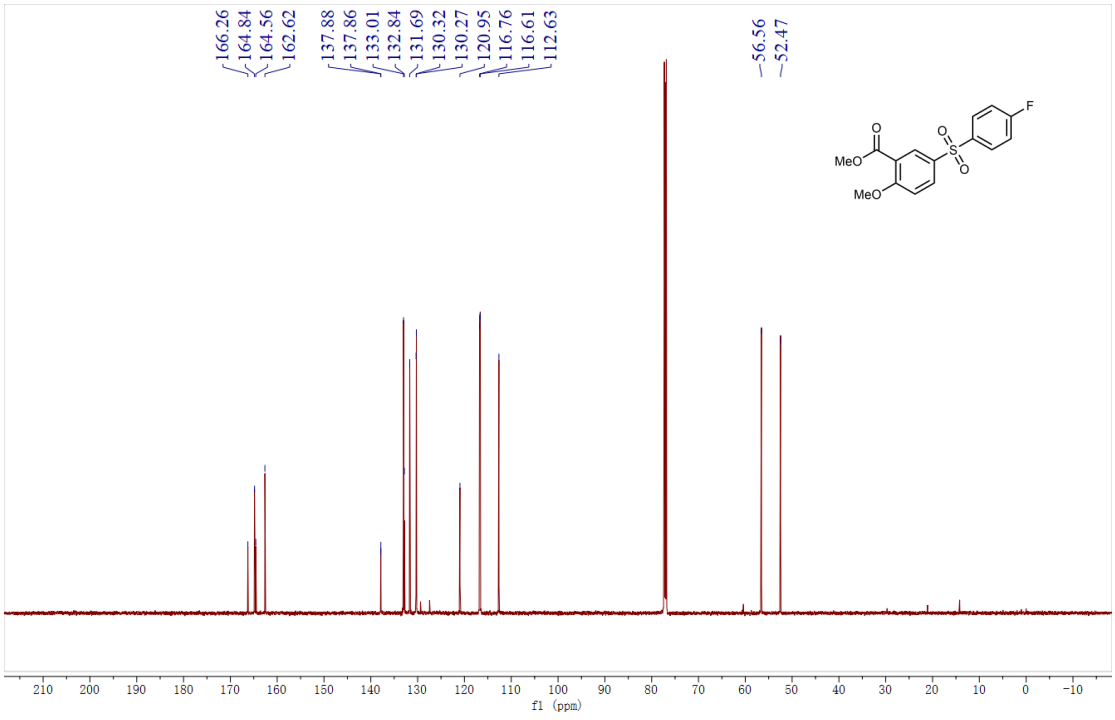


Methyl 5-((4-fluorophenyl)sulfonyl)-2-methoxybenzoate (**3g**)

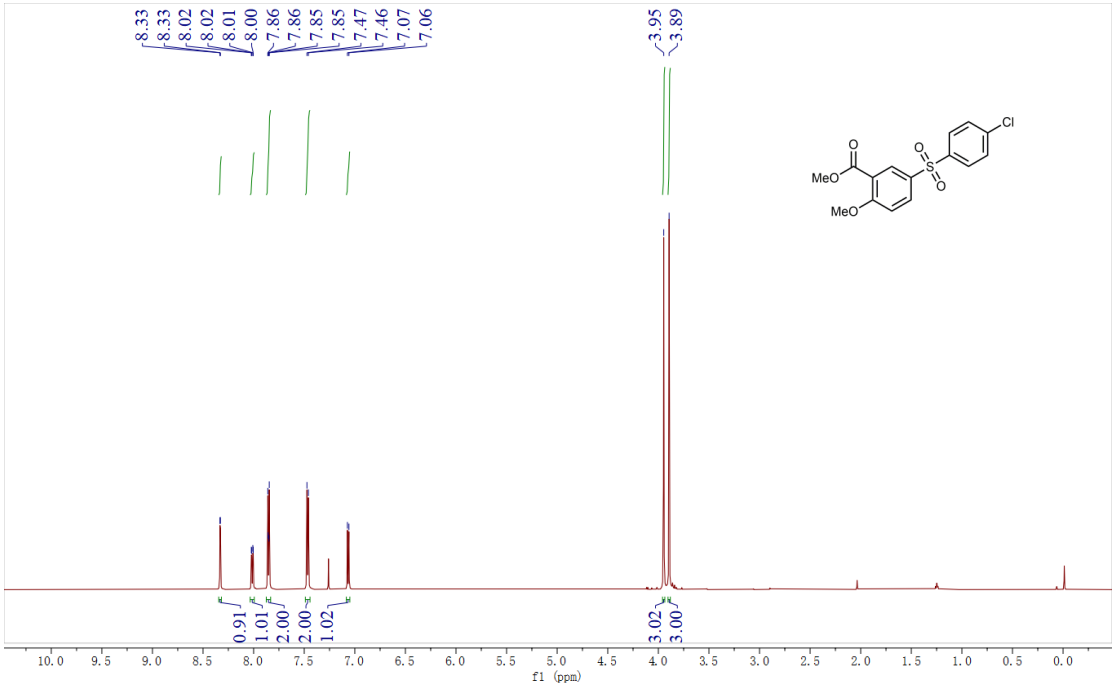


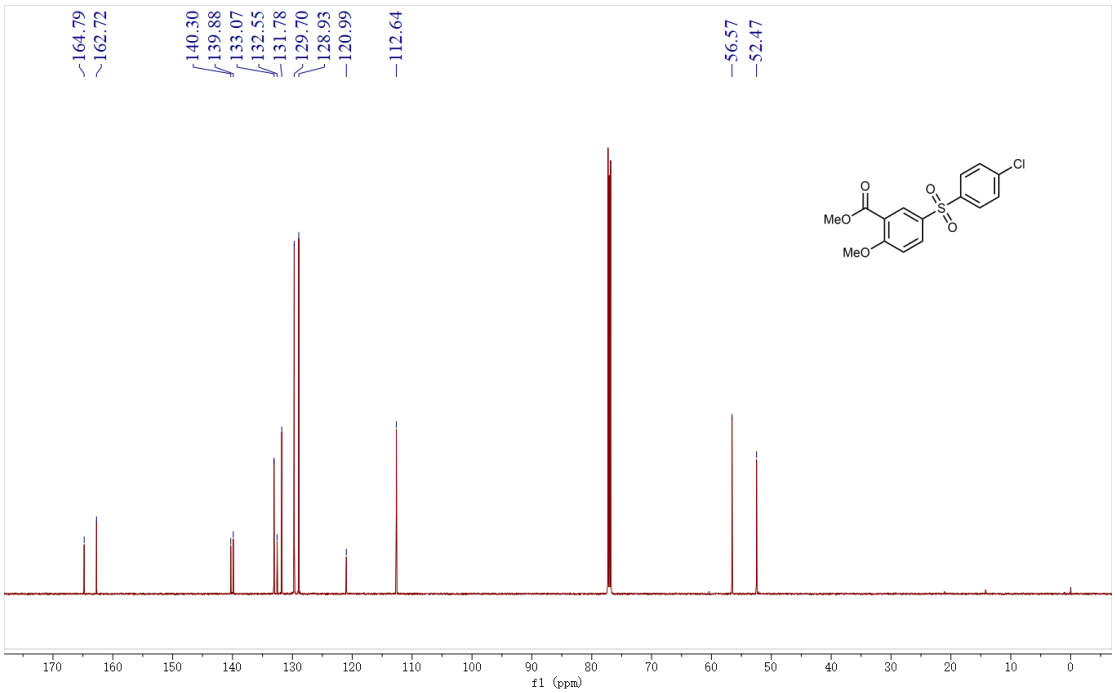


Methyl 5-((4-fluorophenyl)sulfonyl)-2-methoxybenzoate (**3g**)

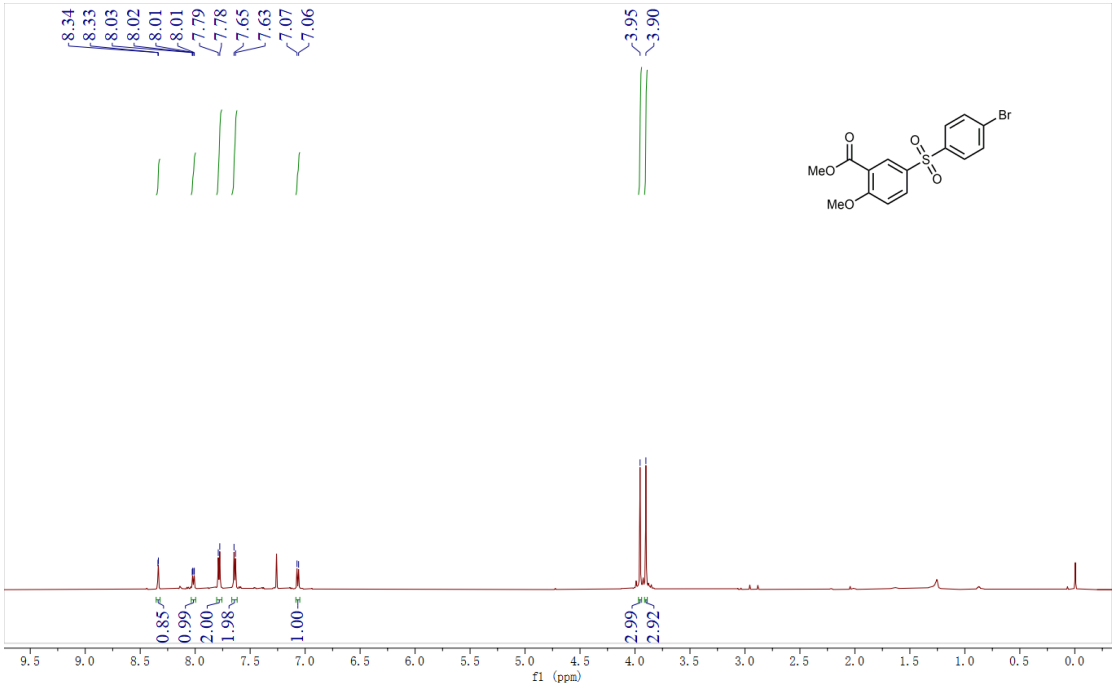


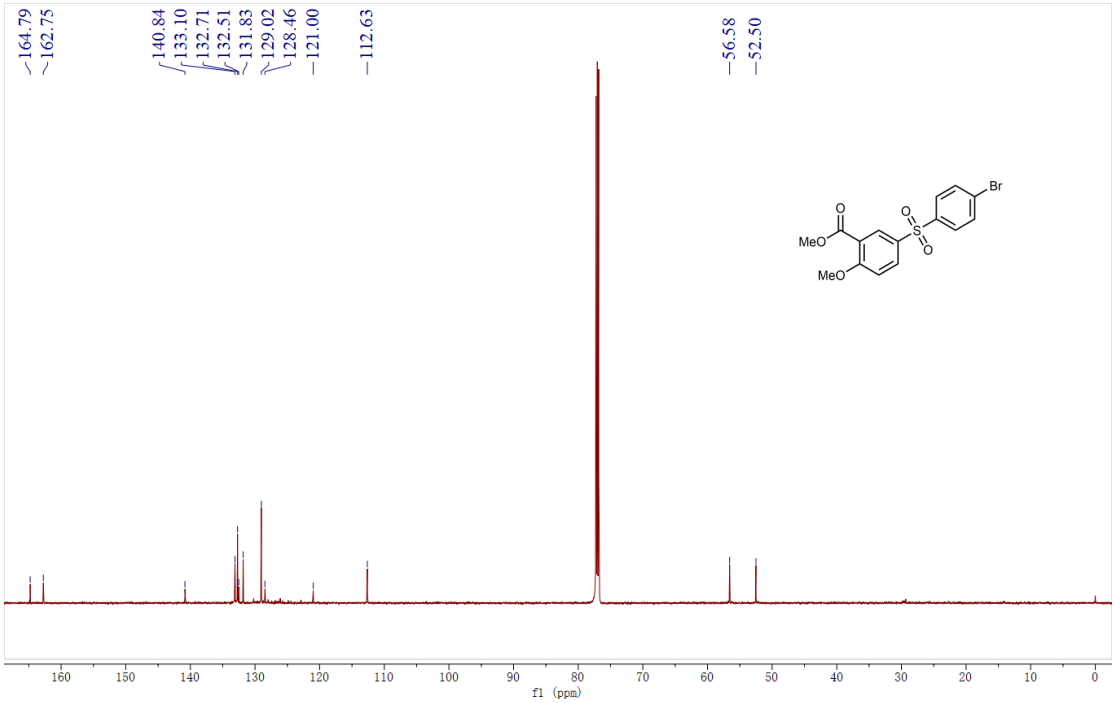
Methyl 5-((4-chlorophenyl)sulfonyl)-2-methoxybenzoate (**3h**)



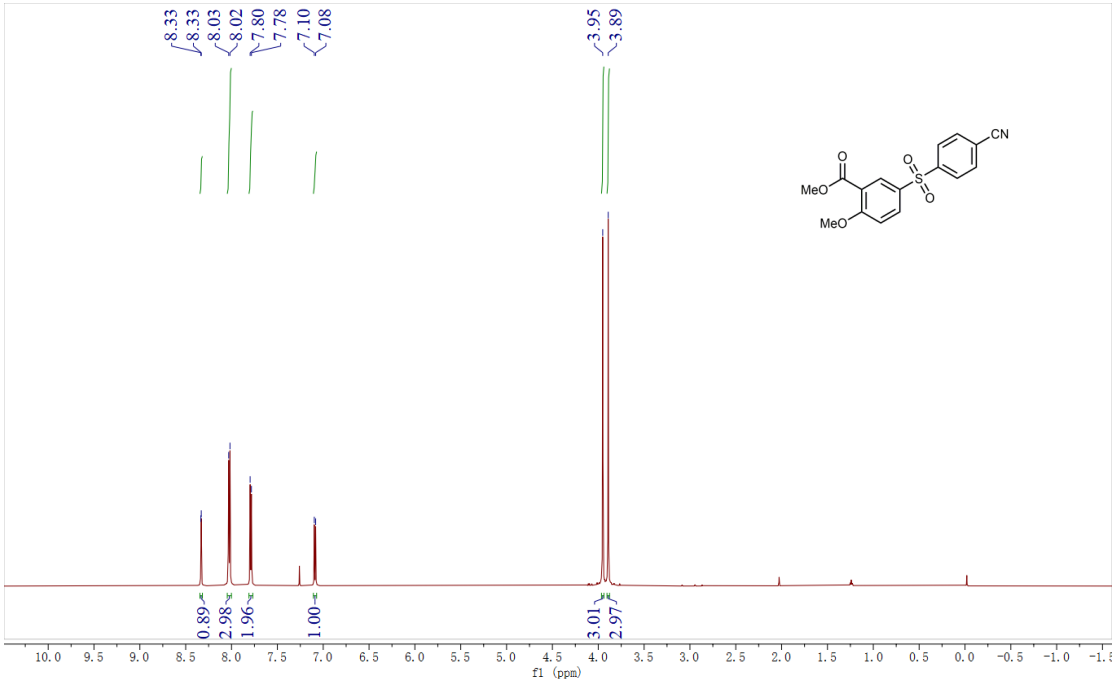


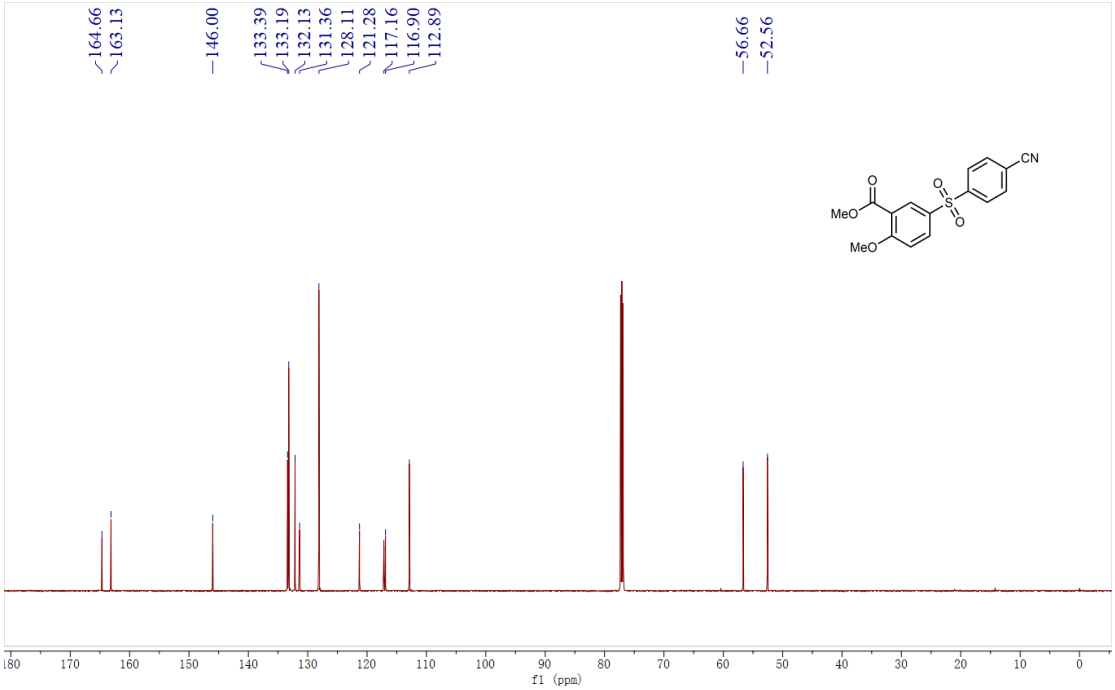
Methyl 5-((4-bromophenyl)sulfonyl)-2-methoxybenzoate (**3i**)



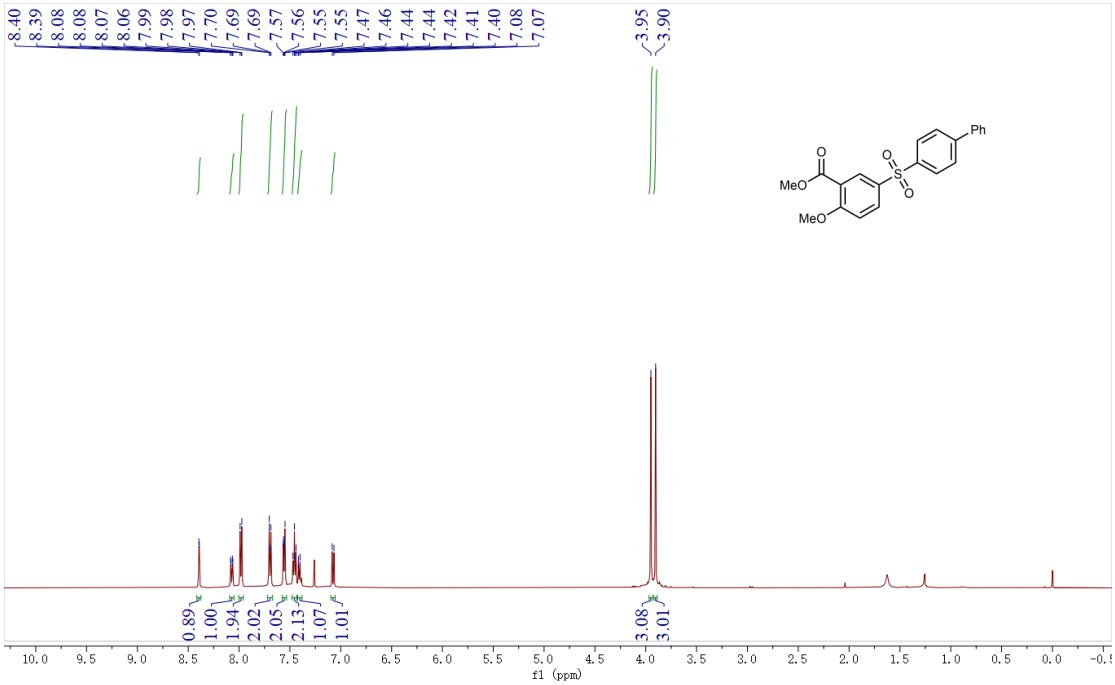


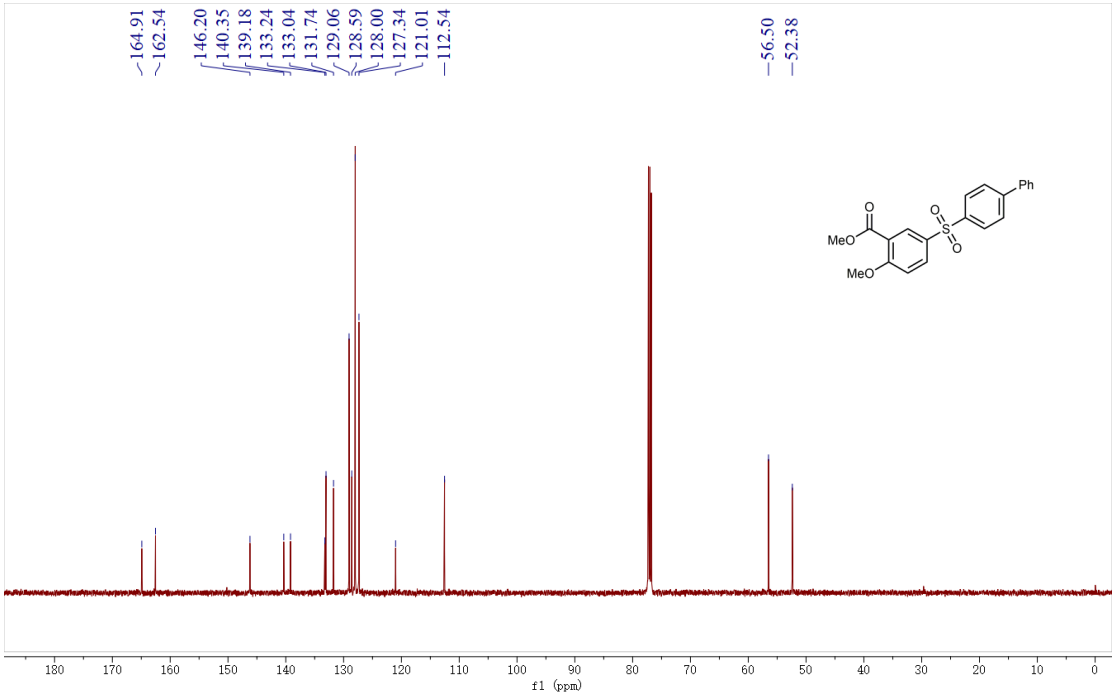
Methyl 5-((4-cyanophenyl)sulfonyl)-2-methoxybenzoate(**3j**)



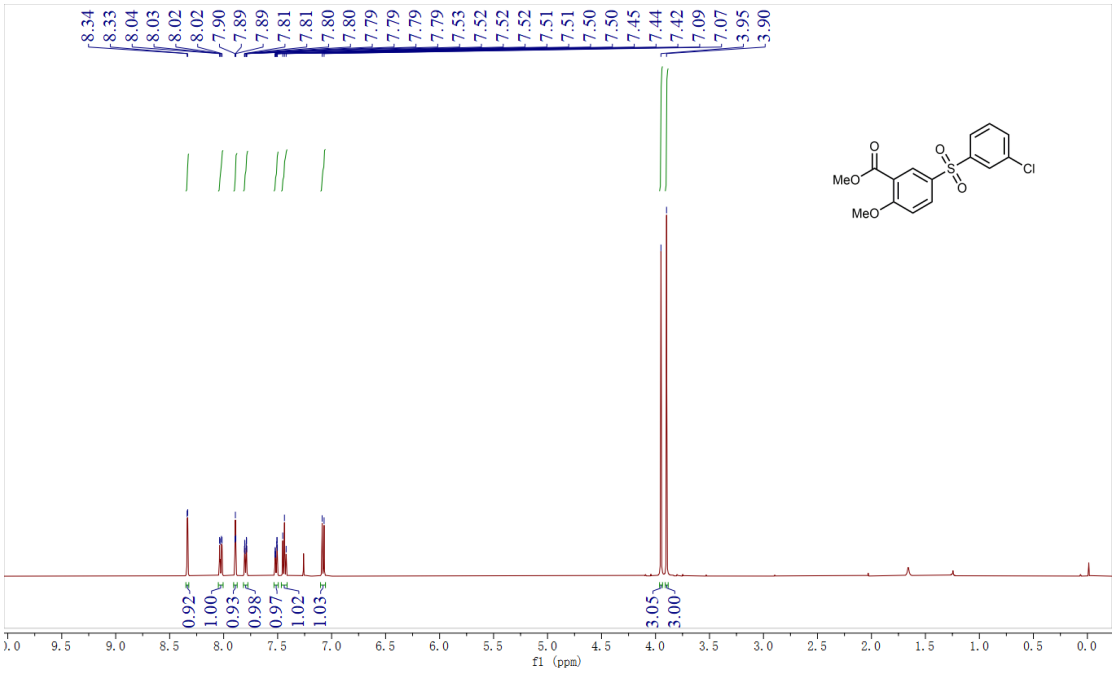


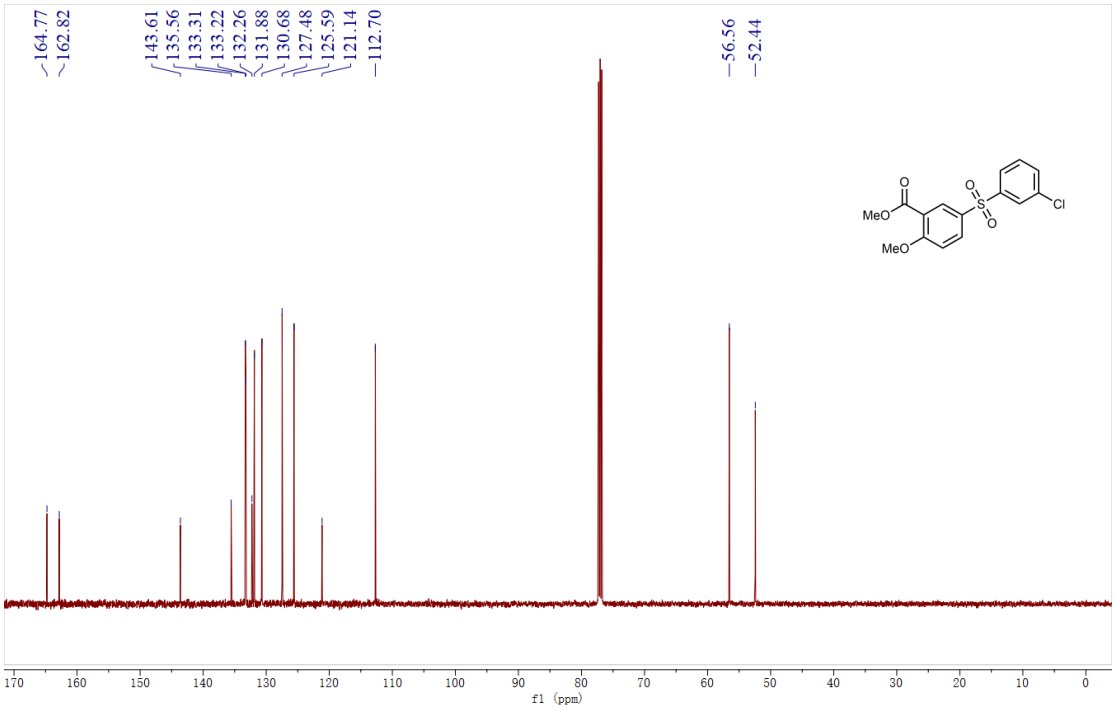
Methyl 5-([1,1'-biphenyl]-4-ylsulfonyl)-2-methoxybenzoate (**3k**)



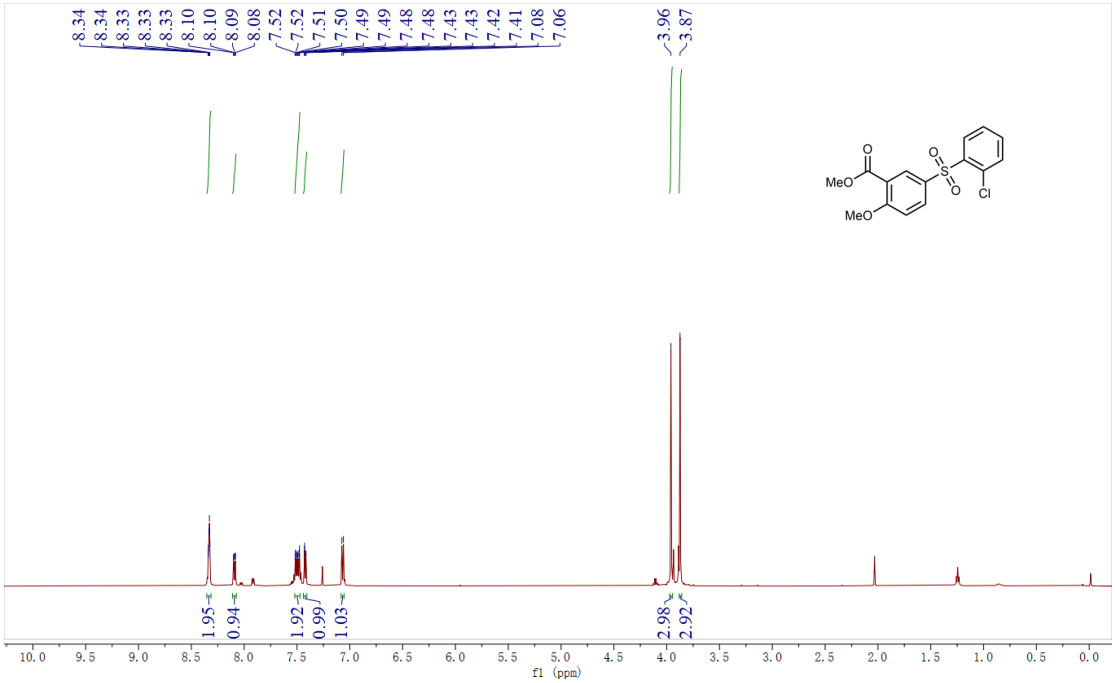


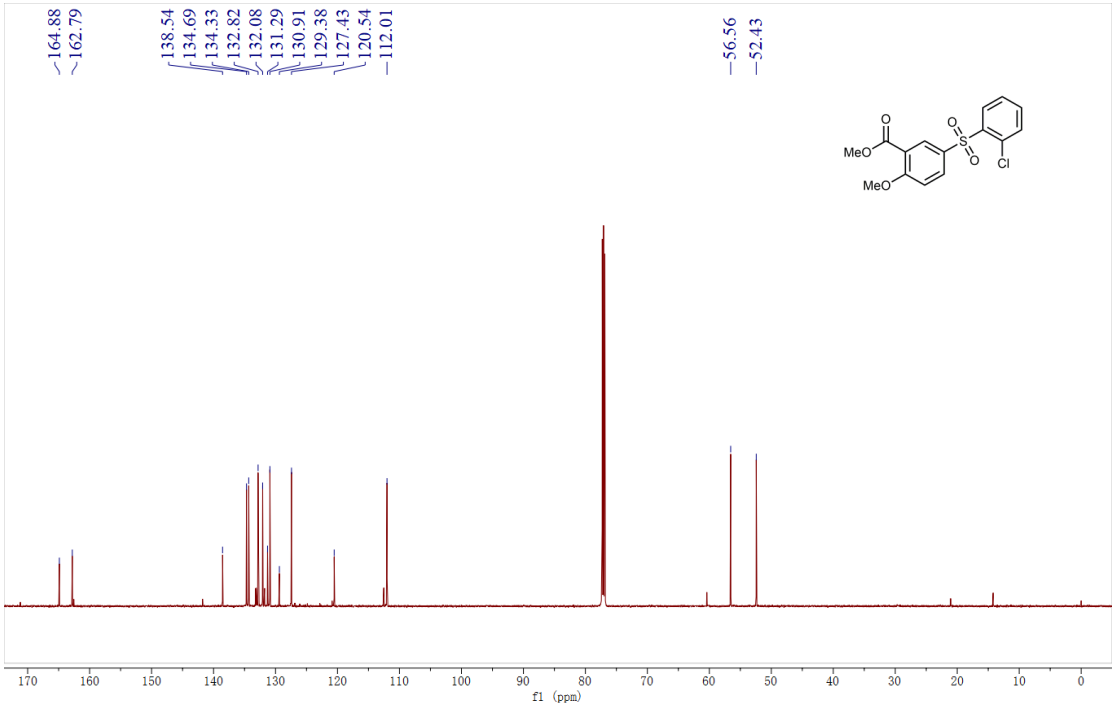
Methyl 5-((3-chlorophenyl)sulfonyl)-2-methoxybenzoate (**3l**)



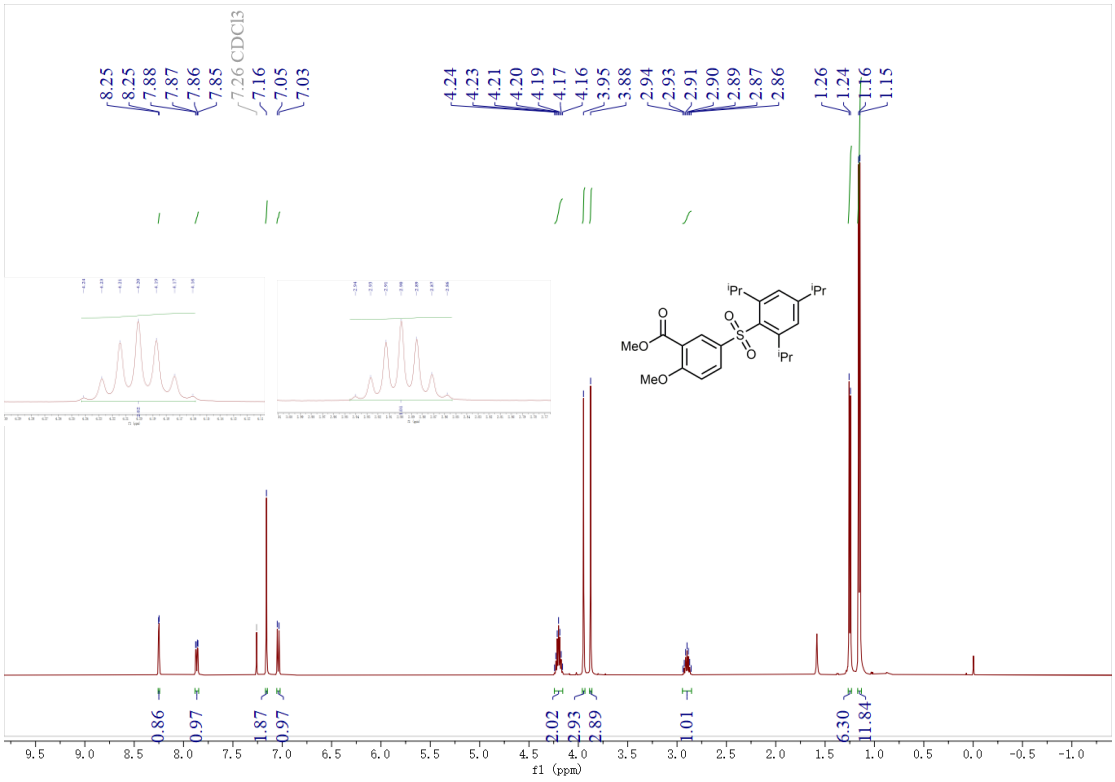


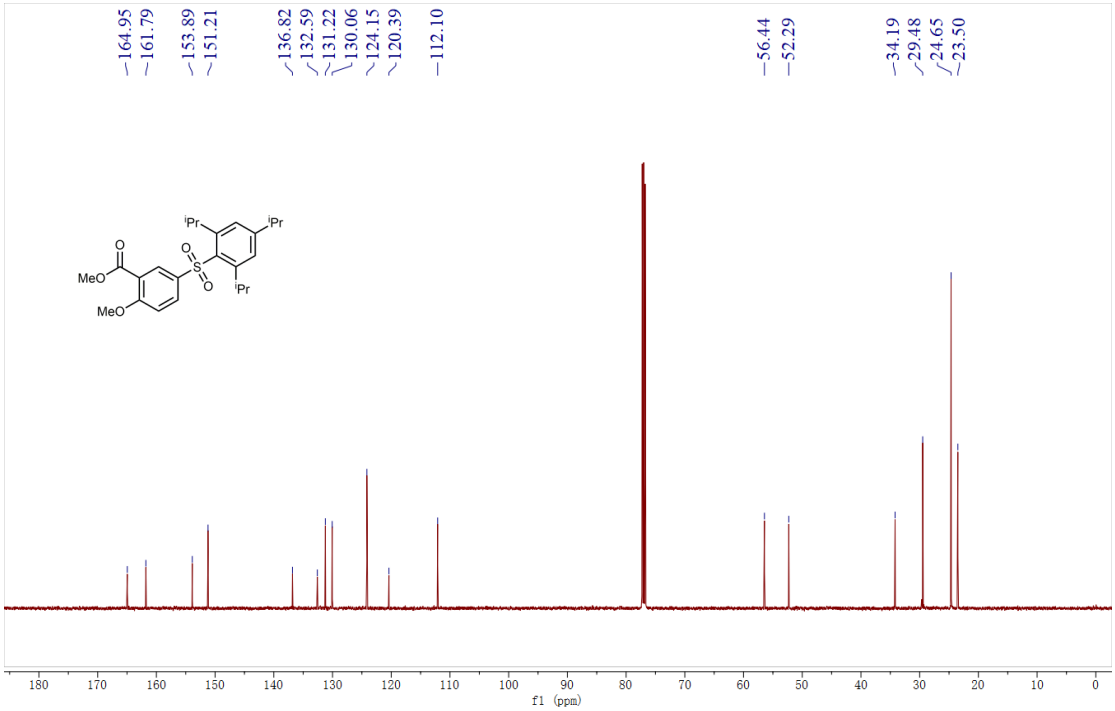
Methyl 5-((2-chlorophenyl)sulfonyl)-2-methoxybenzoate (**3m**)



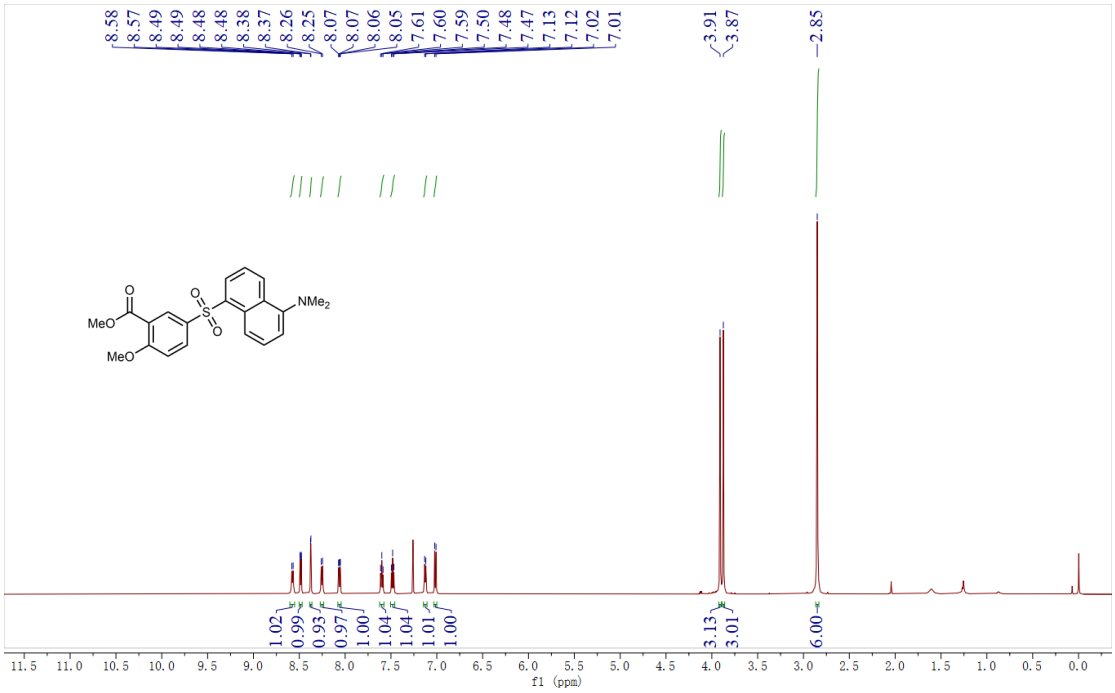


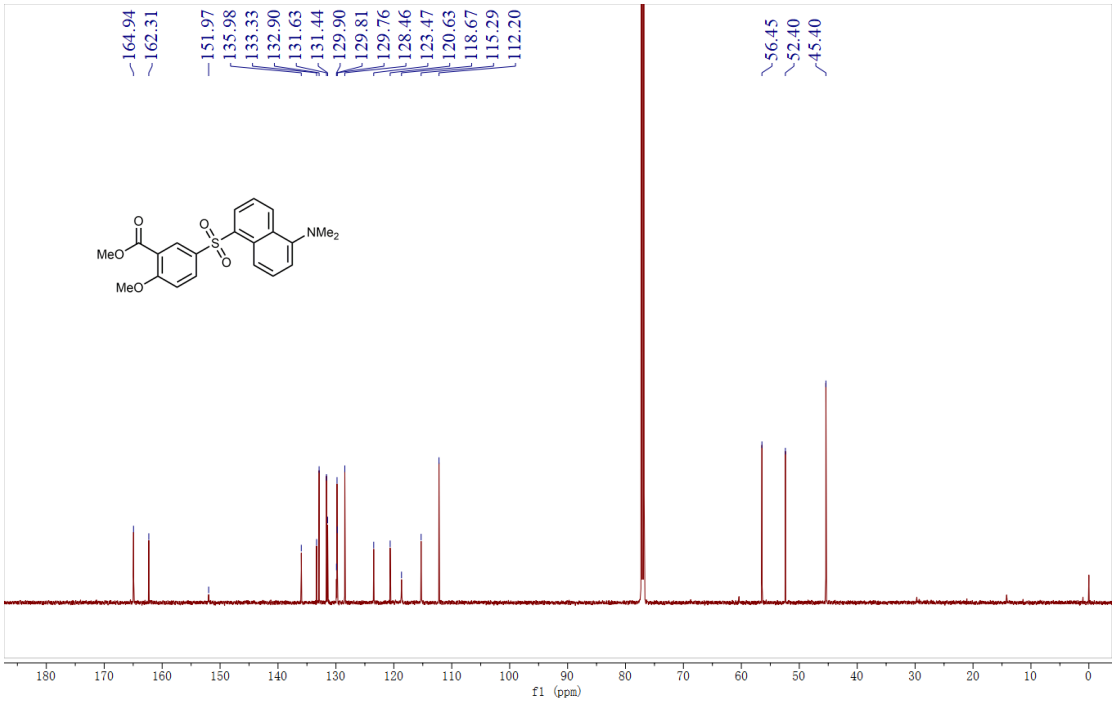
Methyl 2-methoxy-5-((2,4,6-triisopropylphenyl)sulfonyl)benzoate (**3n**)



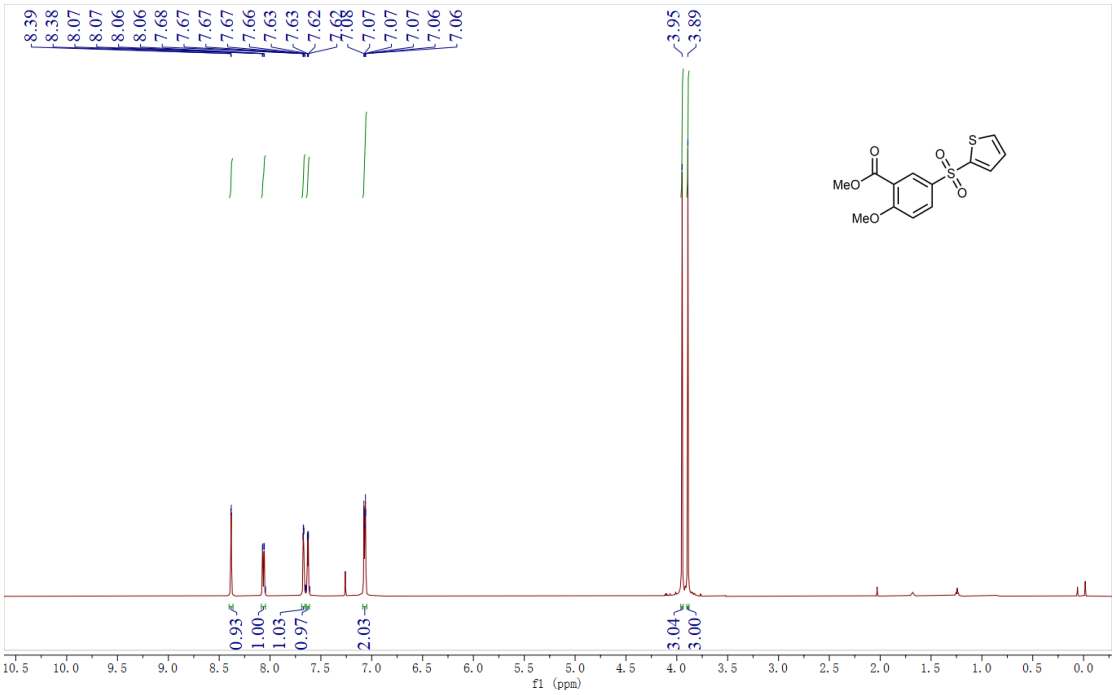


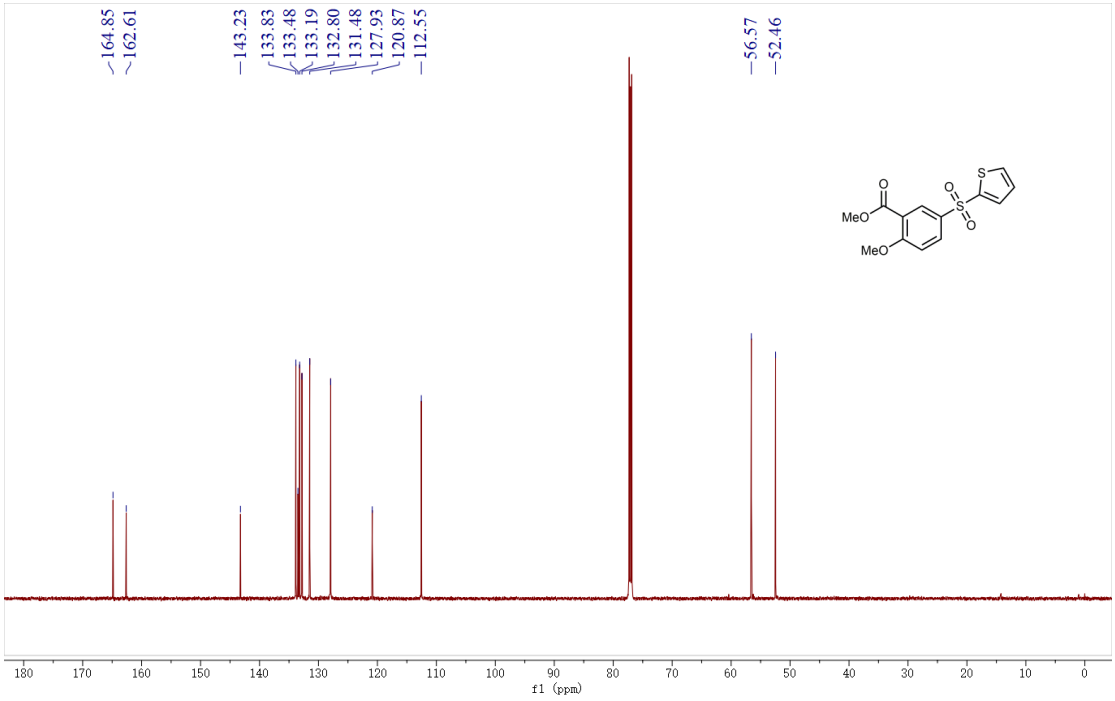
Methyl 5-((5-(dimethylamino)naphthalen-1-yl)sulfonyl)-2-methoxybenzoate (**3o**)



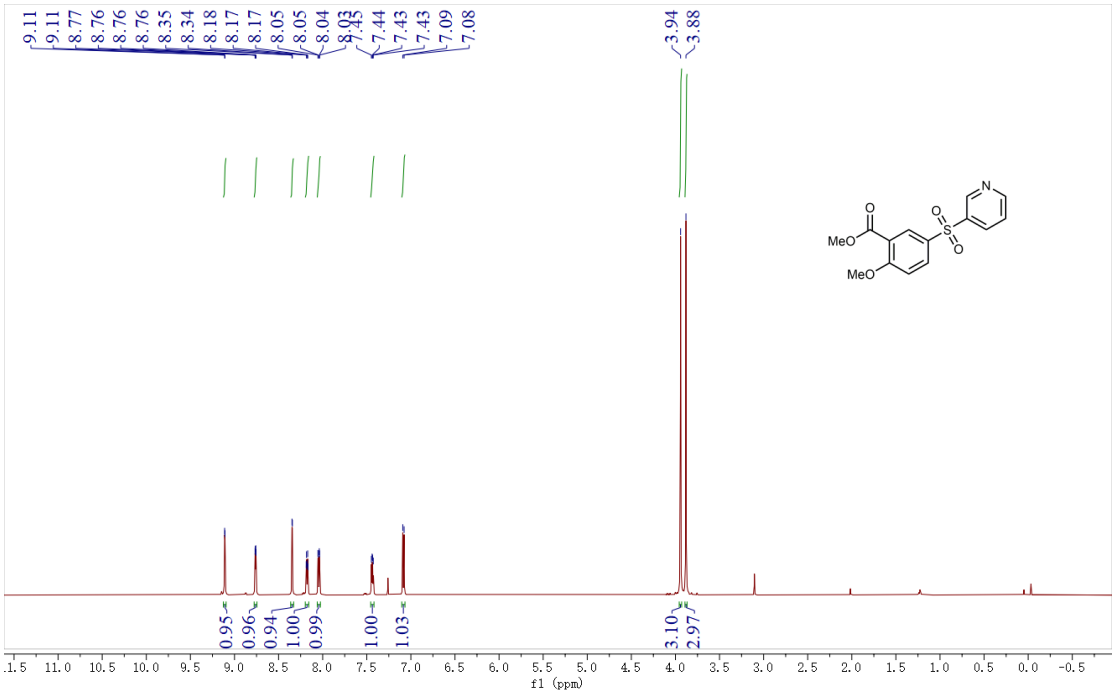


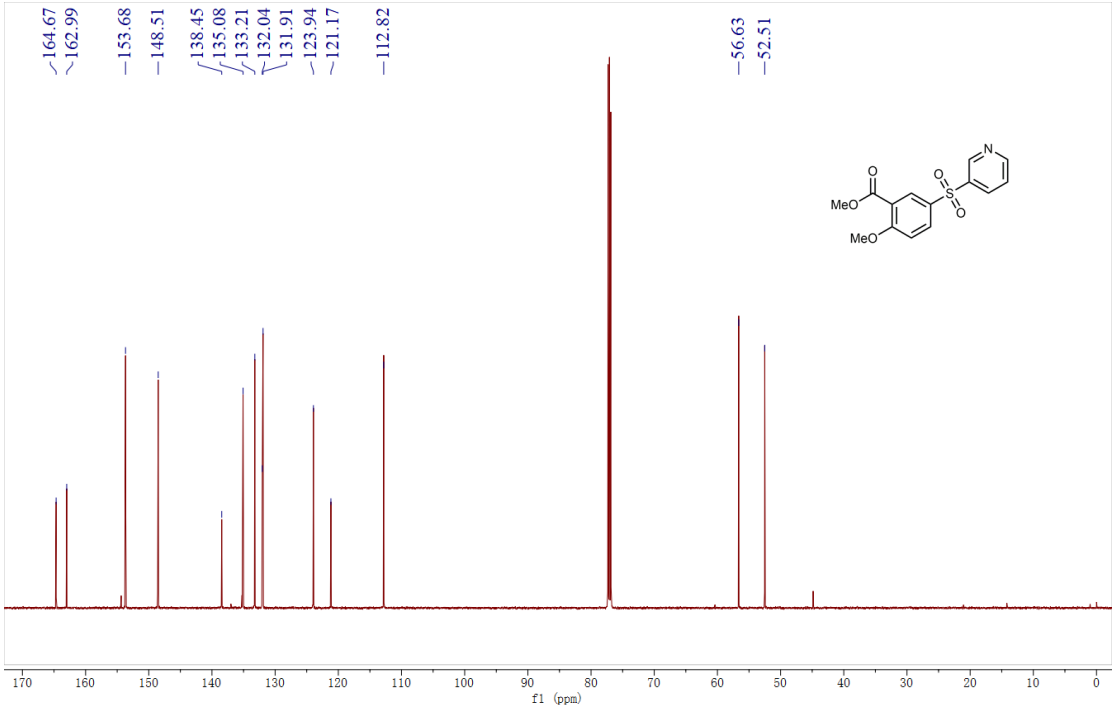
Methyl 2-methoxy-5-(thiophen-2-ylsulfonyl)benzoate (**3p**)



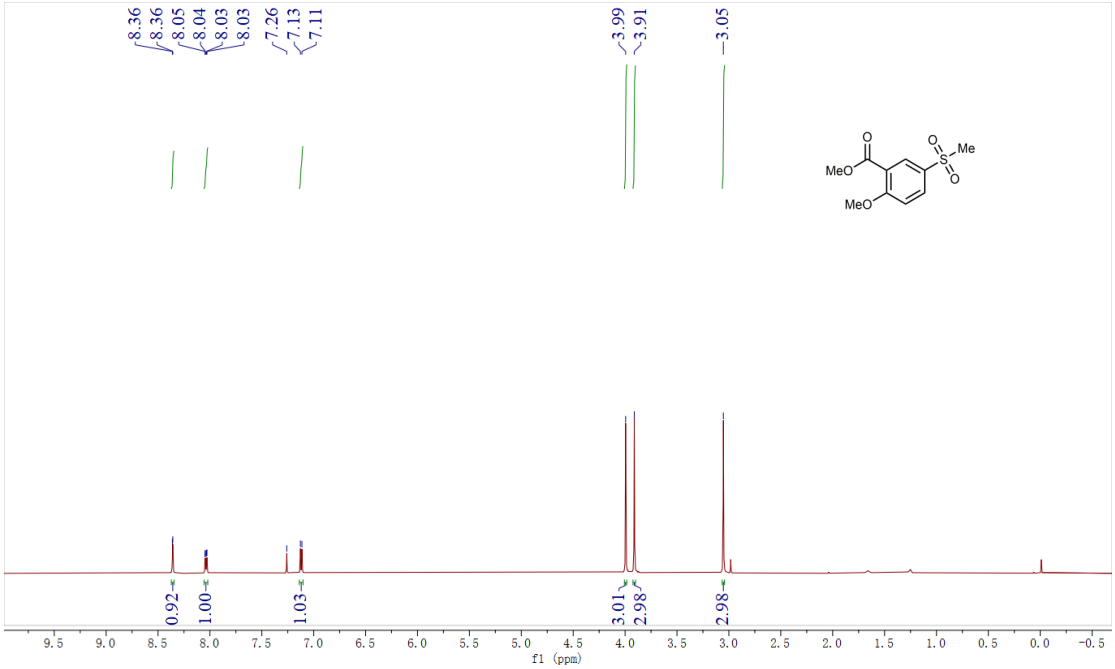


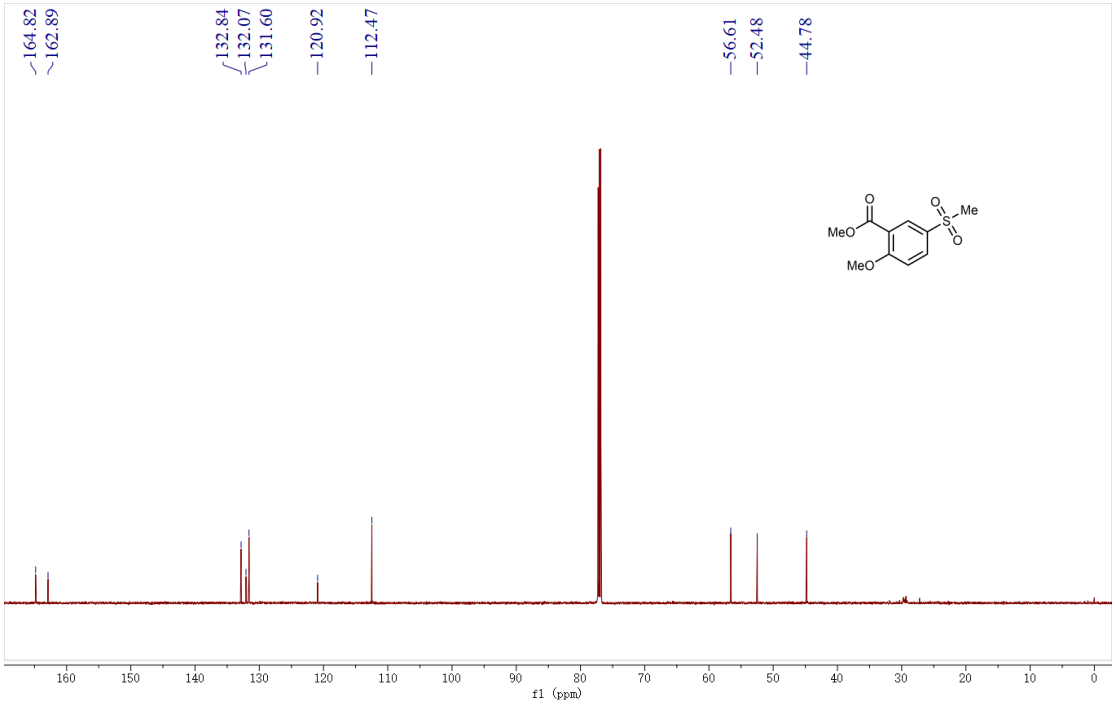
Methyl 2-methoxy-5-(pyridin-3-ylsulfonyl)benzoate (**3q**)



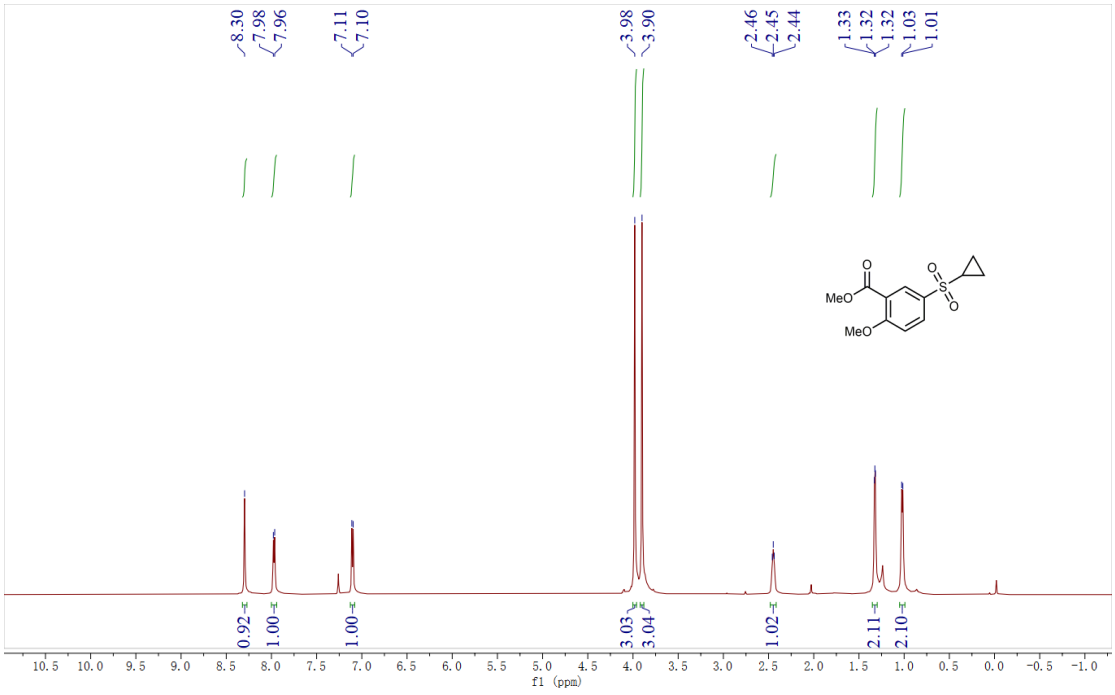


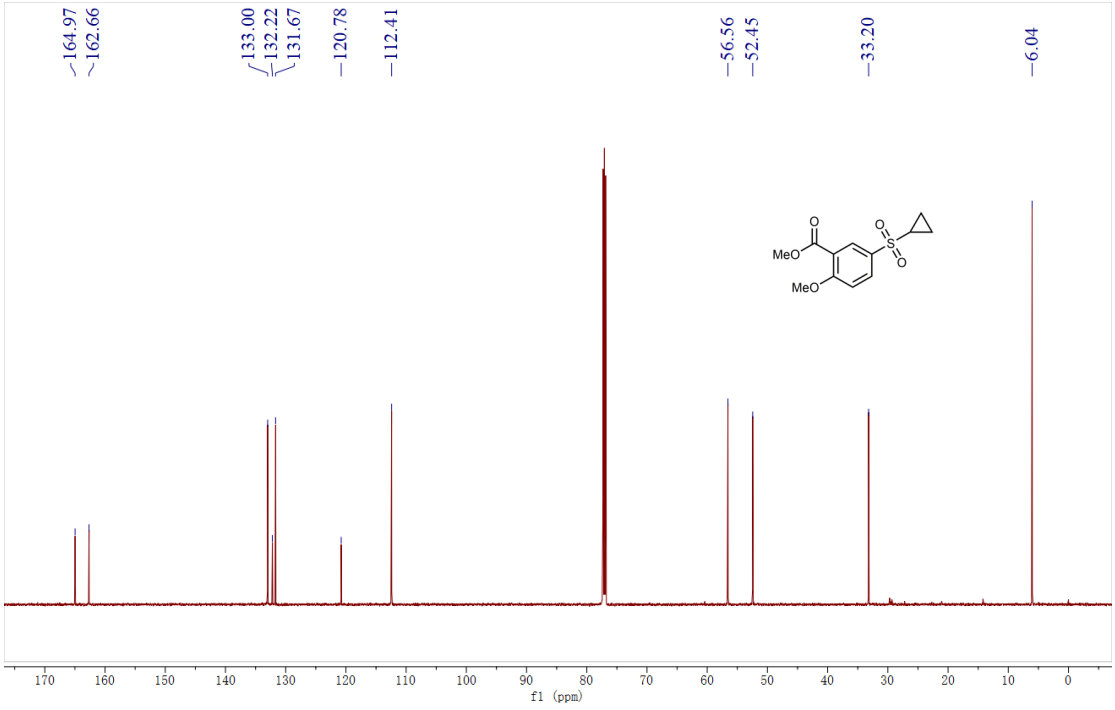
Methyl 2-methoxy-5-(methylsulfonyl)benzoate (**3r**)



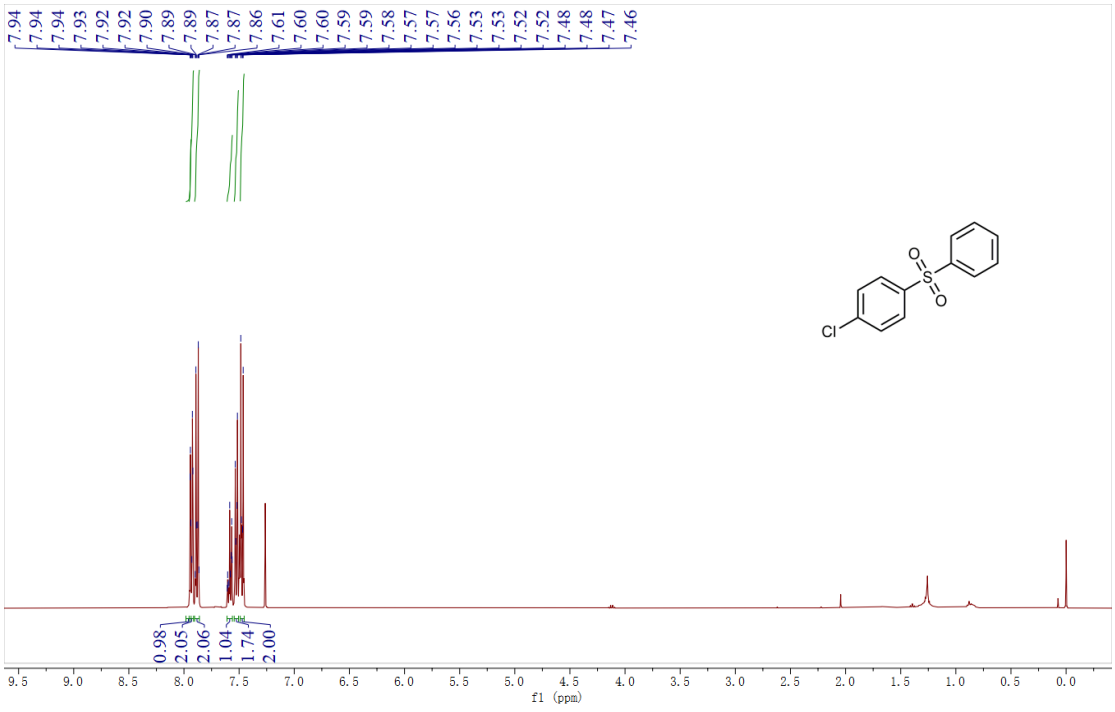


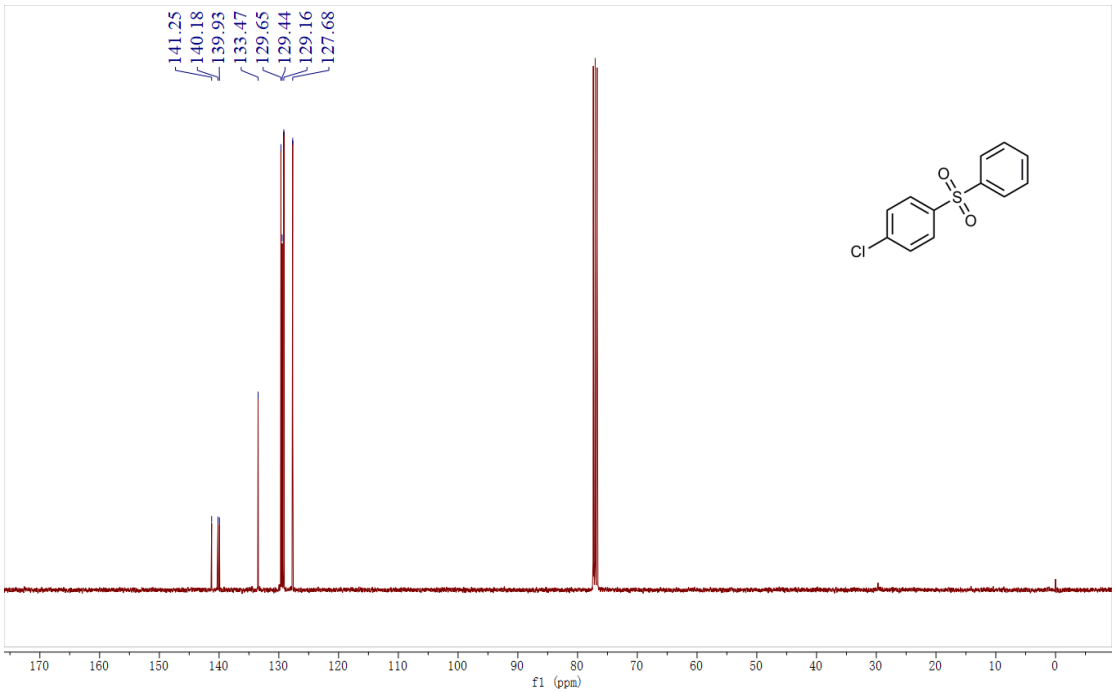
Methyl 5-(cyclopropylsulfonyl)-2-methoxybenzoate (**3s**)



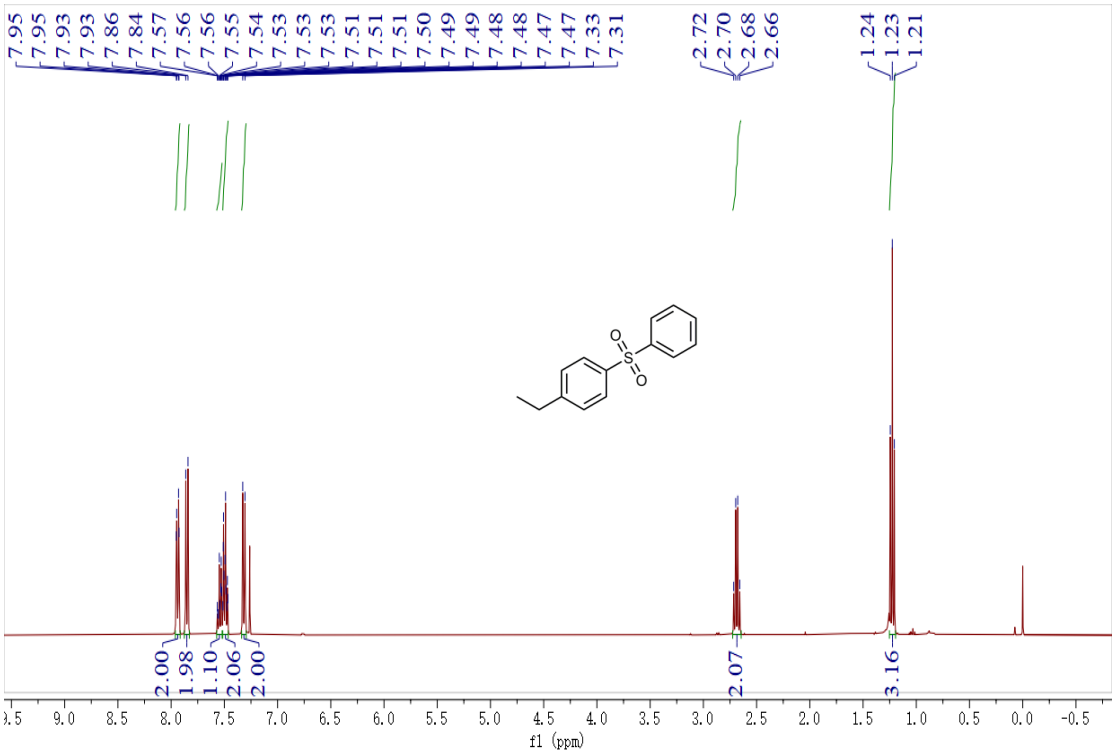


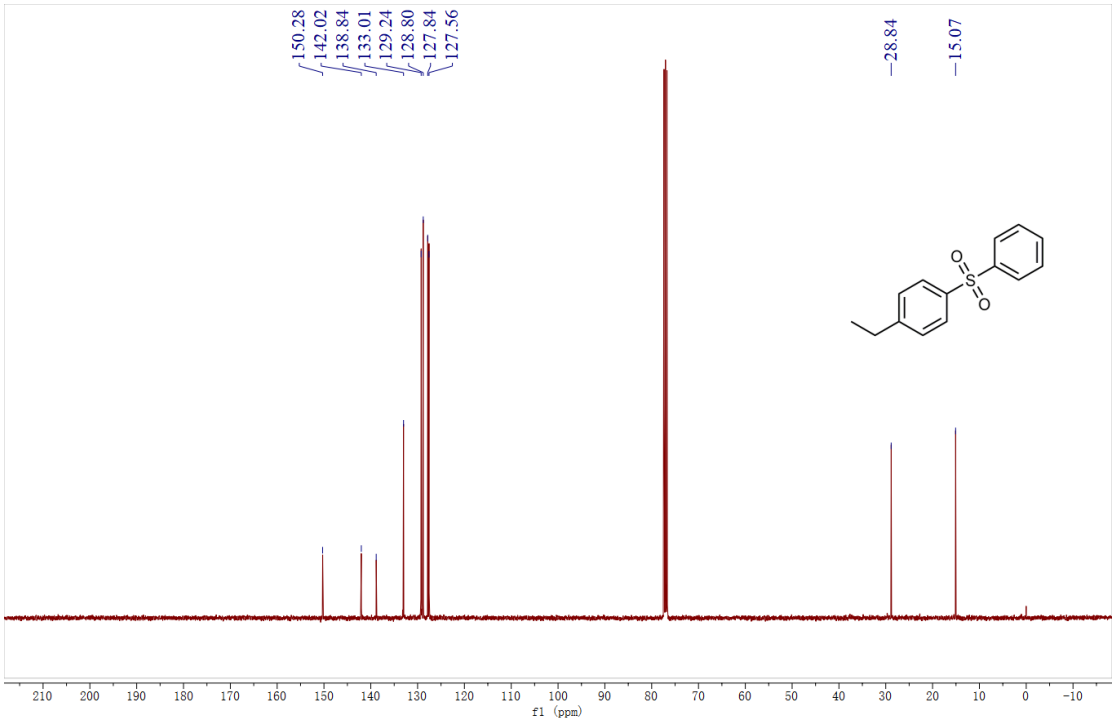
1-chloro-4-(phenylsulfonyl)benzene



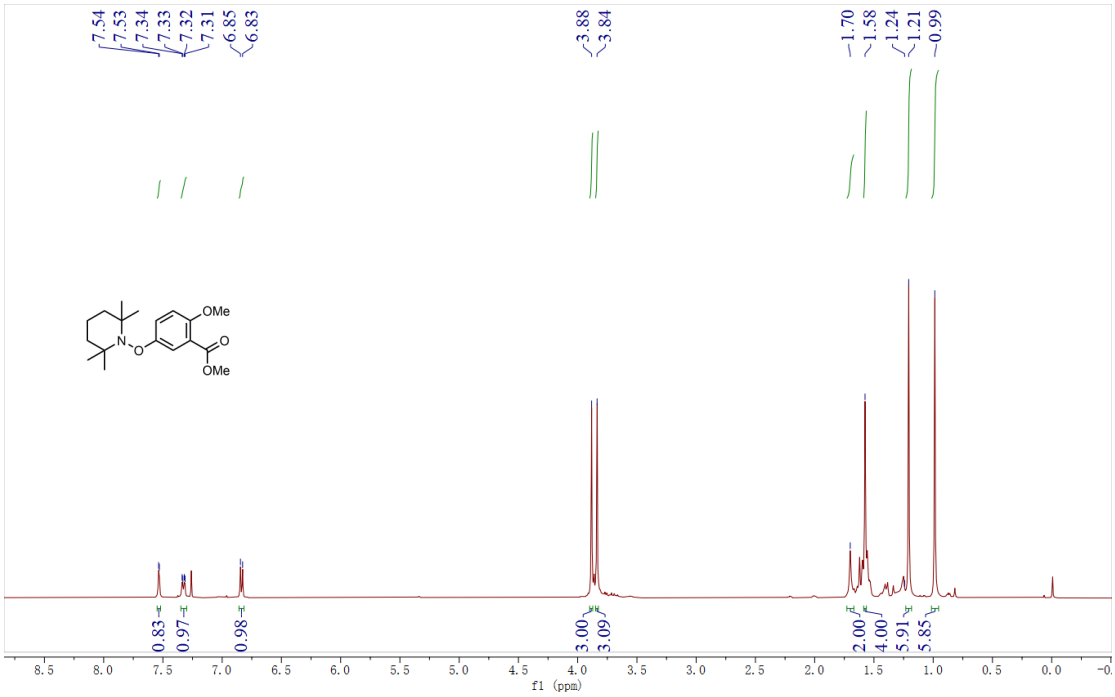


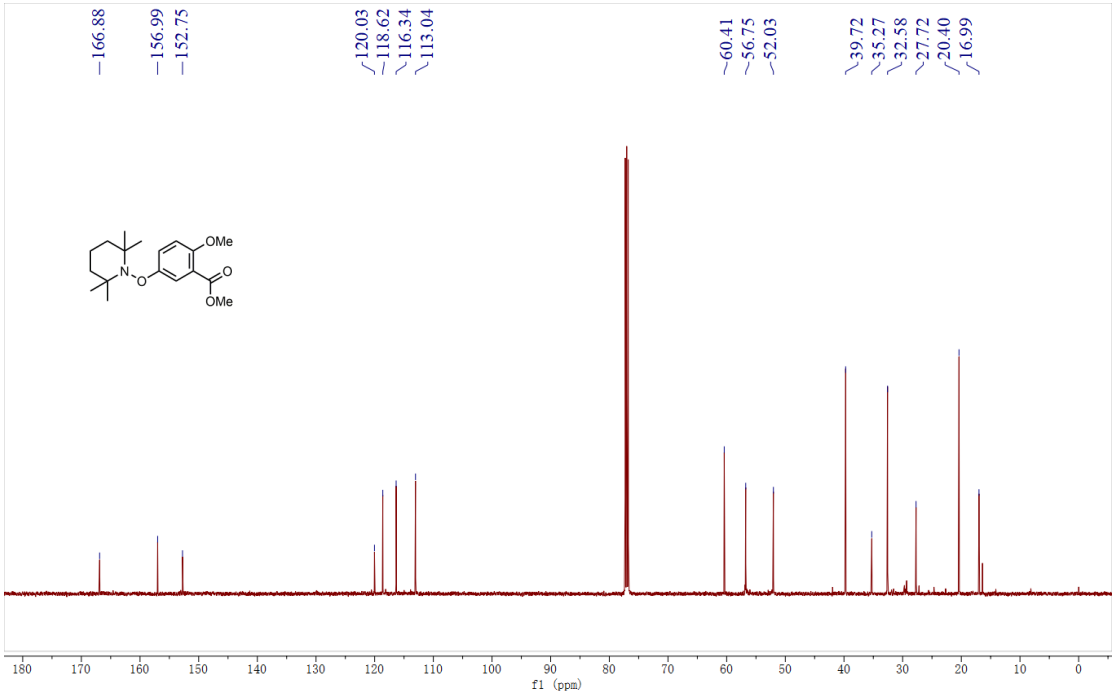
ethyl-4-(phenylsulfonyl)benzene



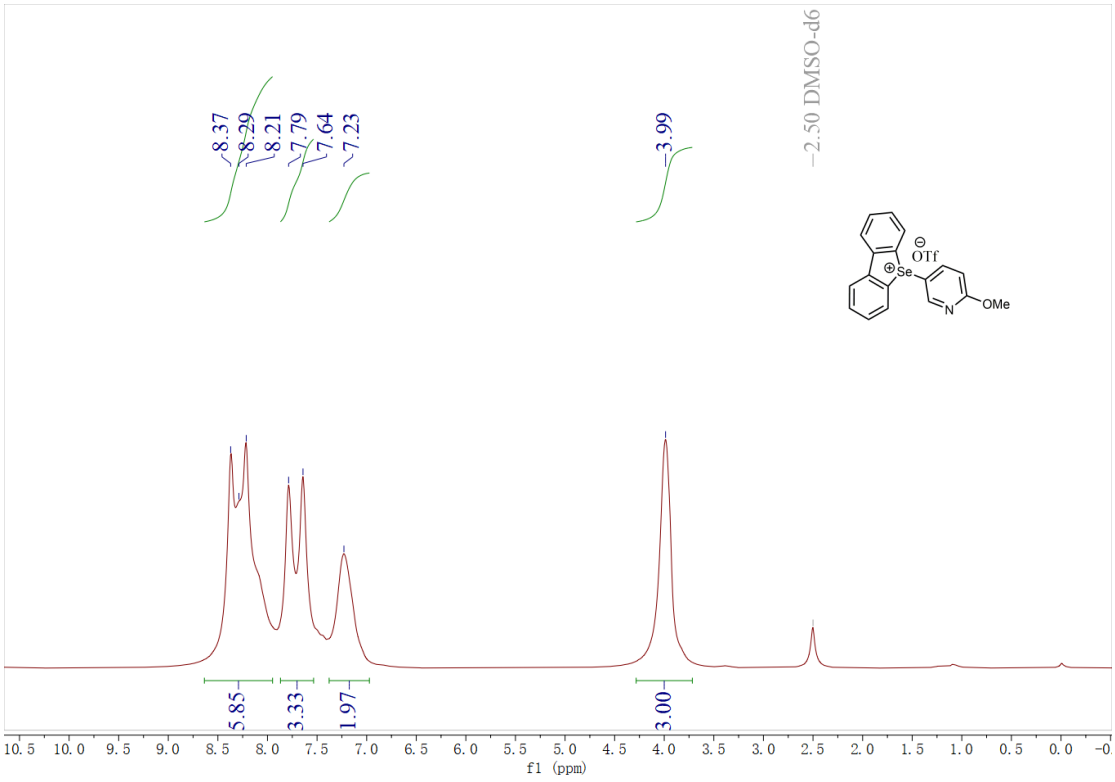


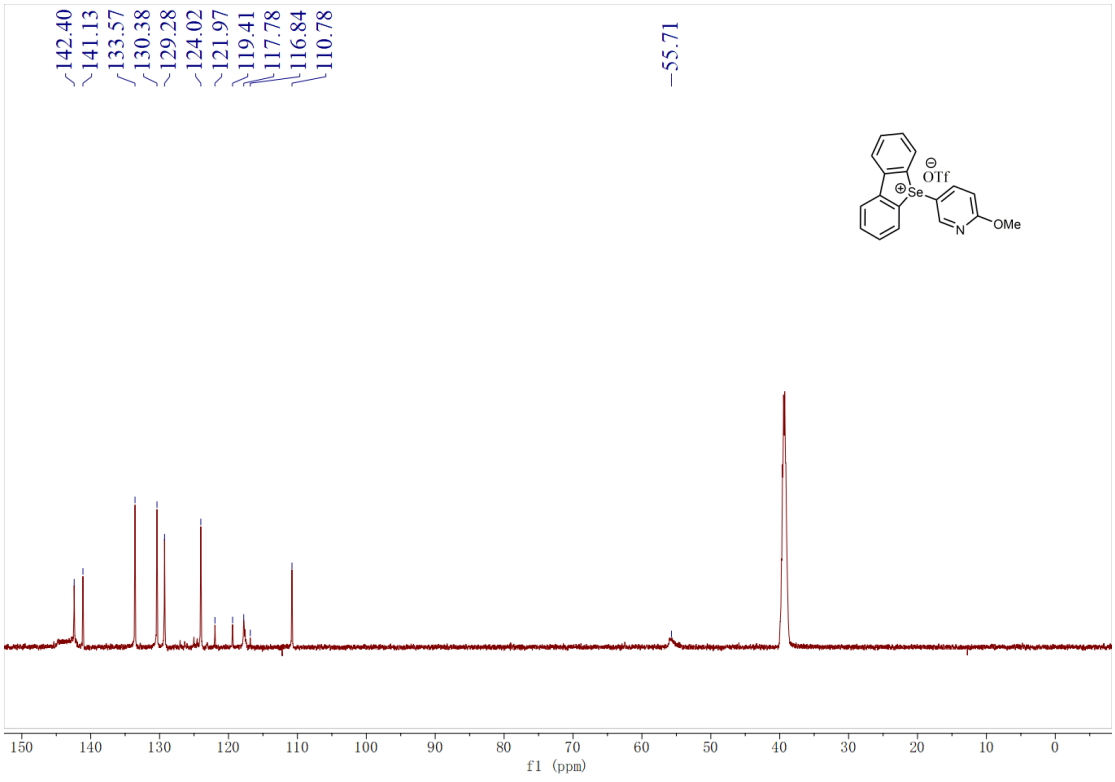
Methyl 2-methoxy-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)benzoate (**6**)



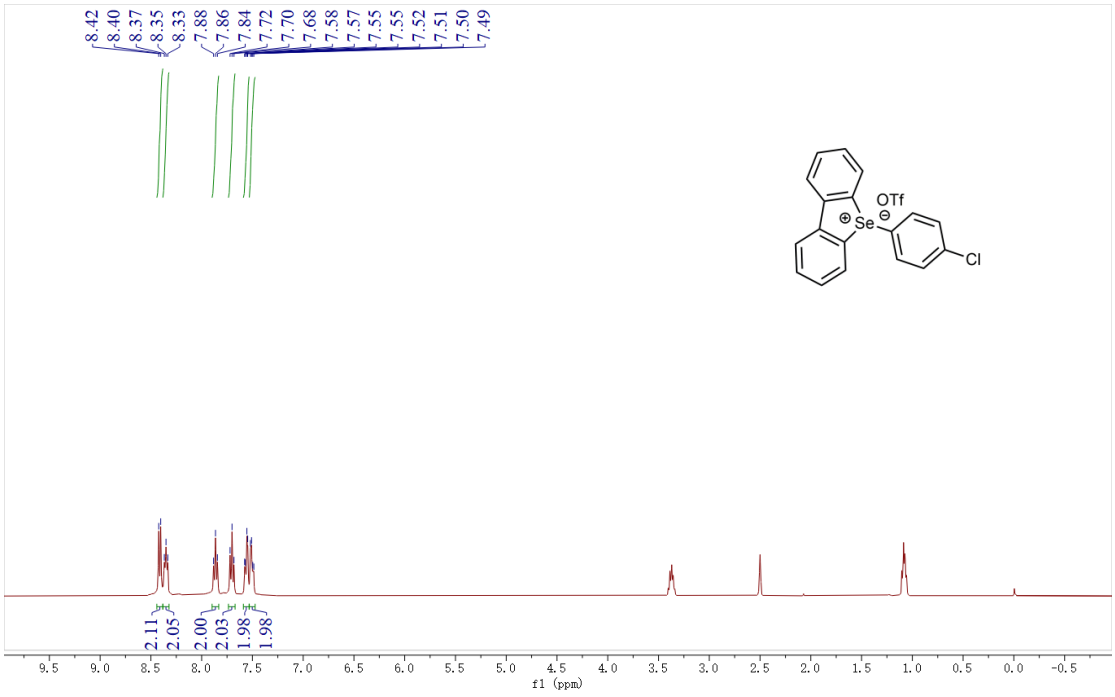


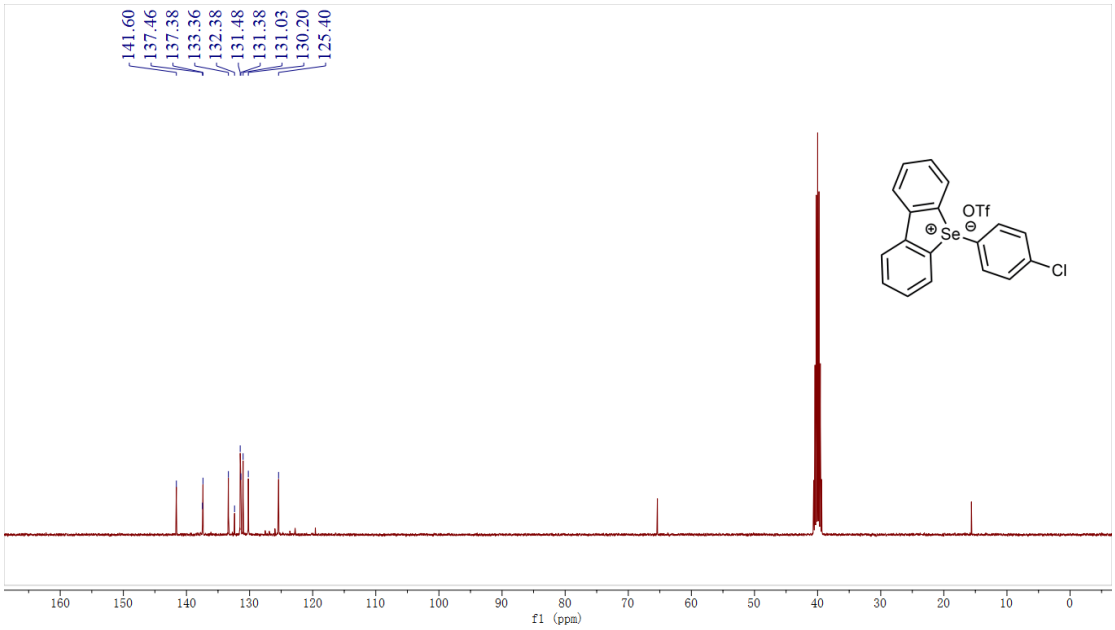
5-(6-methoxypyridin-3-yl)-5H-dibenzo[b,d]selenophen-5-ium trifluoromethanesulfonate



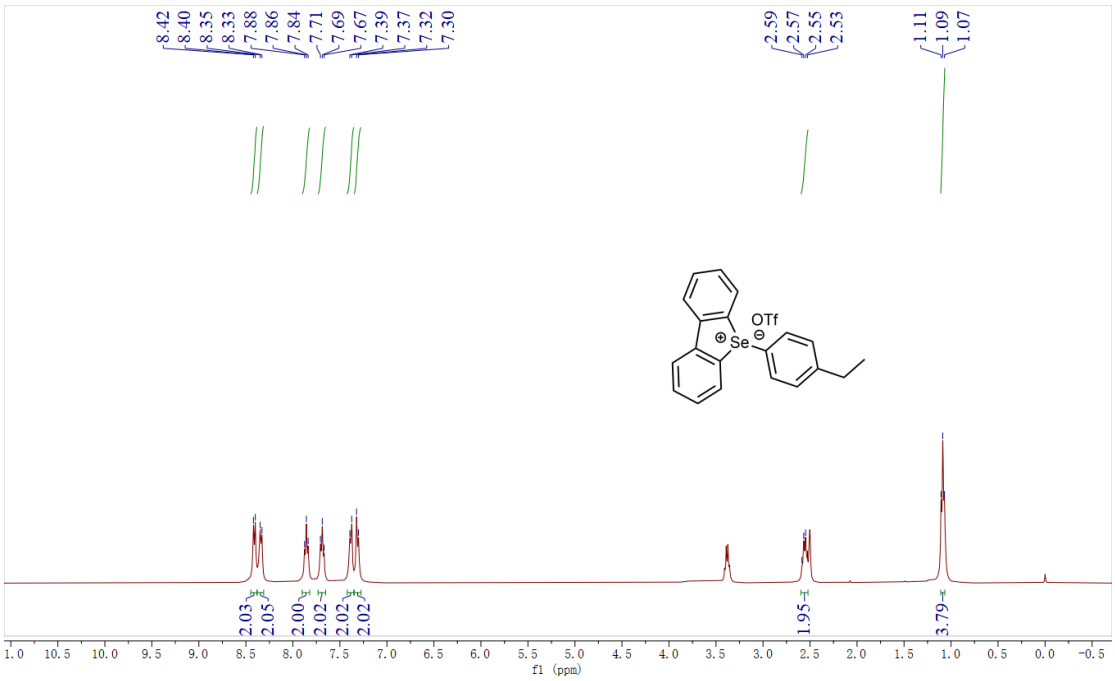


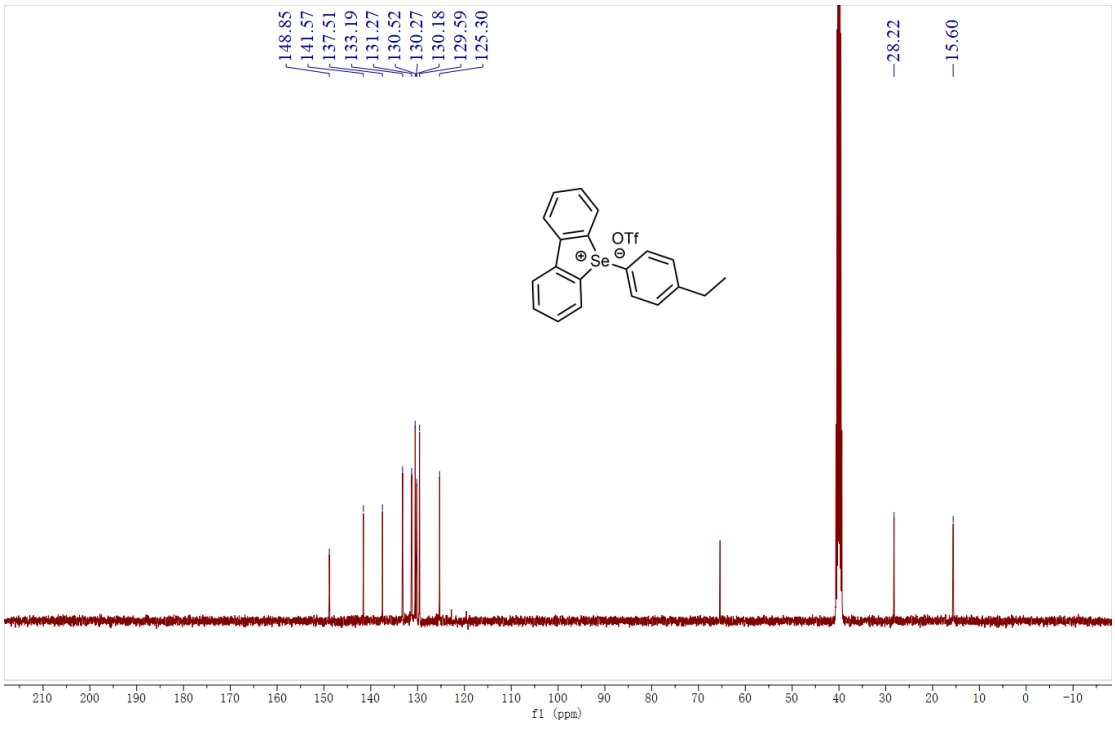
5-(4-chlorophenyl)-5H-dibenzo[b,d]selenophen-5-ium trifluoromethanesulfonate





5-(4-ethylphenyl)-5H-dibenzo[b,d]selenophen-5-ium trifluoromethanesulfonate





2-methoxy-5-(phenylsulfonyl)pyridine (**3ba**)

Instrument model： Synapt G2-*Si*

MS(ESI) calculated *m/z* for $C_{12}H_{11}NO_3S$ $[M + H]^+$: 250.0539, found 250.0535.