Electronic Supplementary Material (ESI) for ChemComm.

Rhodium(III)-catalyzed sulfonamide directed *ortho* C–H carbenoid functionalization *via* metal carbene migratory insertion

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General methods

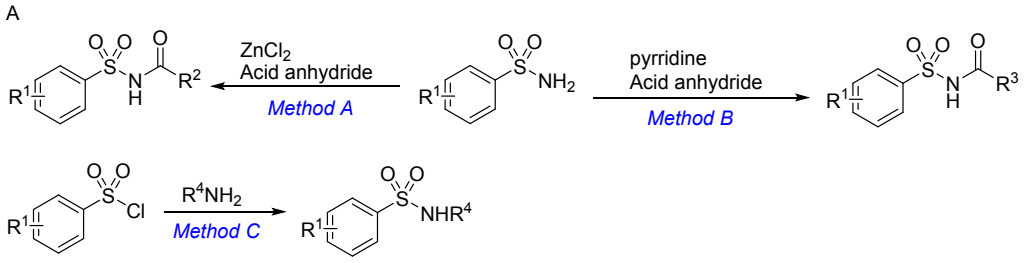
Dried solvent, such as DCE, MeOH and toluene were purchased from domestic corporations and used without purification. Analytical thin layer chromatography (TLC) plates, preparative TLC and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd.

High-resolution LC-MS was carried out by Agilent LC/MSD TOF using a column of Agilent ZORBAX SB-C18 (rapid resolution, 3.5 μm, 2.1 × 30 mm) at a flow of 0.40 mL/min. The solvent was MeOH/water (75:25 (v/v)), containing 5 mmol/L ammonium formate. The ion source is electrospray ionization (ESI).

Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on Bruker Advance 400M NMR and 600M NMR spectrometers. Chemical shifts of ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from SiMe4 (δ 0.0) and relative to the signal of chloroform-*d* (δ = 7.260, singlet) and DMSO-*d6* (δ = 2.500, quintet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as in units of parts per million (ppm) downfield from SiMe4 (δ 0.0) and relative to the signal of chloroform-*d* (δ = 77.230, triplet) and DMSO-*d6* (δ = 39.510, septet).

Acetylation of sulfonamide derivatives:

General procedure for synthesis of sulfonamide derivertives:



General procedure for synthesis of diazo compounds

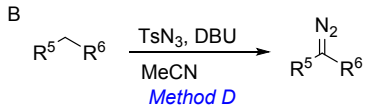


Figure S1. General procedure for synthesis of sulfonamide derivertives and diazo compounds

Method A:

Sulfonamide (5 mmol) was dissolved in 5 mL acid anhydride, 0.1eq~1eq anhydrous $ZnCl_2$ was added, the reaction mixture was stirred at room temperature and monitored by TLC until the free sulfonamide was consumed completely, then poured into a mixture of EtOAc and water (100mL, *v*/*v* =

1:1). The organic layer was separated and the aqueous phase was extracted by EtOAc (50 mL). The organic layers were combined and washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, concentrated in *vacuo* to afford solid powder and washed with cold toluene to give the acetyl or propionyl sulfonamide without further purification, the purity was detected by ^{1}HNMR.

Method B:

Sulfonamide (5 mmol) and DMAP (61 mg, 0.5 mmol) were dissolved in 5 mL pyridine, then Ac_2O (4.7 mL, 50 mmol, 10 equiv) was added. The reaction mixture was stirred at room temperature overnight, and concentrated. The residue was dissolved in EtOAc (50 mL) and washed with saturated NH_4Cl (50 mL). The organic layer was dried over Na_2SO_4, concentrated again in *vacu*o, the residue was purified by silica gel chromatography.

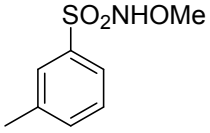
Method C:

Amine (5 mmol) was dissolved in 20 mL DCM, the mixture was cooled to 0°C, then sulfonyl chloride (5 mmol) was added. The reaction mixture was warmed to room temperature and stirred overhight, and concentrated. The residue was dissolved in EtOAc (50 mL) and washed with saturated NH_4Cl (50 mL). The organic layer was dried over Na_2SO_4, concentrated again in *vacu*o, the residue was purified by silica gel chromatography.

Method D:

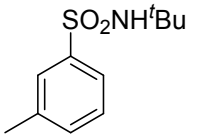
1,3-dicarbonyl compound (50 mmol) and tosyl azide (55 mmol) were dissolved in acetonitrile (100 mL), the mixture was cooled to 0°C. DBU (55 mmol) was added dropwise, and the reaction mixture was stirred for 3h. Solvent was removed and the residue was dissolved in DCM, washed with water, the aqueous layer was extracted by DCM, and the organic layers were combined and washed with brine, and dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography.

***N*-methoxy-3-methylbenzenesulfonamide (1c)**



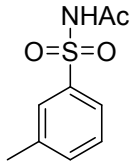
Method C, (94%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 79 – 80°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 10.48 (s, 1H), 7.68 – 7.63 (m, 2H), 7.54 – 7.50 (m, 2H), 3.65 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 138.8, 137.2, 134.1, 129.0, 128.1, 125.2, 64.3, 20.8. **MS** (ESI): m/z (M + H^+) 202.2.

***N*-(tert-butyl)-3-methylbenzenesulfonamide (1d)**



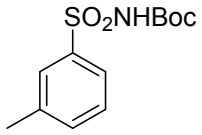
Method C, (92%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 82 – 83°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.47 – 7.36 (m, 2H), 2.37 (s, 3H), 1.08 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 144.2, 138.5, 132.4, 128.8, 126.4, 123.4, 53.2, 29.7, 20.9. **MS** (ESI): m/z (M + H^+) 228.2.

***N*-(*m*-tolylsulfonyl)acetamide (1e)**



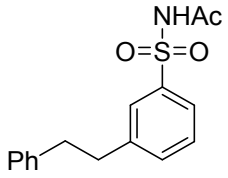
Method A, (95%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 95 – 96°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.04 (s, 1H), 7.73 – 7.67 (m, 2H), 7.53 – 7.49 (m, 2H), 2.40 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.7, 139.4, 138.8, 134.2, 129.0, 127.5, 124.6, 23.2, 20.8. **MS** (ESI): m/z (M + H^+) 214.2.

***tert*-butyl (m-tolylsulfonyl)carbamate (1f)**



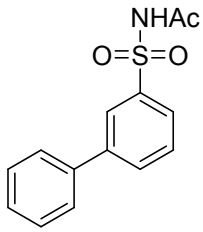
Method B, (70%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 105 – 107°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.56 (s, 1H), 7.71 – 7.65 (m, 2H), 7.54 – 7.50 (m, 2H), 2.40 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 149.8, 139.6, 138.7, 134.0, 129.0, 127.3, 124.4, 82.1, 27.5, 20.8. **MS** (ESI): m/z (M + H^+) 272.2.

***N*-((3-phenethylphenyl)sulfonyl)acetamide (1g)**



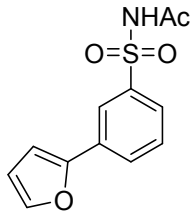
(*E*)-*N*-((3-styrylphenyl)sulfonyl)acetamide (3.87 mmol, 1.165 g), $NiCl_2{\cdot}6H_2O$ (7.75 mmol, 1.84 g) and $NaBH_4$ (19.36 mmol, 732 mg) were dissolved in a mixture of 15 mL dry THF and 10 mL MeOH, and the reaction mixture was stirred at room temperature overnight. 50 mL H_2O was added and the mixture was extracted by ethyl acetate. Organic layer was washed by sat. NaCl solution and dried over anhydrous Na_2SO_4. Solvent was removed, and the residue was purified by silica gel chromatography (50% yield, white powder, R_f = 0.4 (EtOAc/Petroleum ether = 1:2). **m.p.**: 77–78°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.01 (s, 1H), 7.76 – 7.71 (m, 2H), 7.58 – 7.49 (m, 2H), 7.30 – 7.15 (m, 5H), 3.02 – 2.95 (m, 2H), 2.93 – 2.87 (m, 2H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.69, 142.69, 140.92, 139.33, 133.73, 128.99, 128.41, 128.23, 127.00, 125.94, 125.08, 36.61, 36.55, 23.24. **MS** (ESI): m/z (M + H^+) 304.2.

***N*-([1,1'-biphenyl]-3-ylsulfonyl)acetamide (1h)**



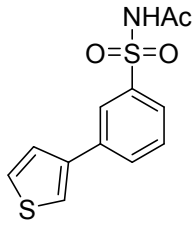
Method A, (90%, light yellow powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 118 – 119°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.18 (s, 1H), 8.18 (s, 1H), 8.00 – 7.96 (m, 2H), 7.75 – 7.65 (m, 3H), 7.55 – 7.37 (m, 3H), 1.96 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 141.0, 140.2, 138.5, 131.9, 129.9, 129.2, 128.4, 126.9, 126.3, 125.6, 23.3. **MS** (ESI): m/z (M + H^+) 276.2.

***N*-((3-(furan-2-yl)phenyl)sulfonyl)acetamide (1i)**



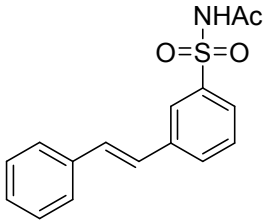
Method B, (90%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 146 – 147°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.17 (s, 1H), 8.18 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.83 (s, 2H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 6.64 (s, 1H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.9, 151.2, 144.0, 140.3, 131.0, 129.9, 128.3, 126.0, 121.8, 112.4, 107.8, 23.3. **MS** (ESI): m/z (M + H^+) 266.2.

***N*-((3-(thiophen-3-yl)phenyl)sulfonyl)acetamide (1j)**



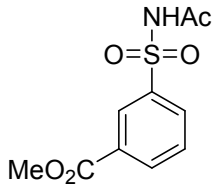
Method B, (85%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 126 – 127°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.13 (s, 1H), 8.15 (t, *J* = 1.7 Hz, 1H), 8.07 – 8.02 (m, 1H), 8.00 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.72 – 7.65 (m, 2H), 7.57 (dd, *J* = 5.0, 1.4 Hz, 1H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 140.2, 139.6, 136.0, 131.1, 129.9, 127.9, 126.0, 125.9, 124.7, 122.8, 23.3. **MS** (ESI): m/z (M + H$^+$) 282.1.

(E)-*N*-((3-styrylphenyl)sulfonyl)acetamide (1k)



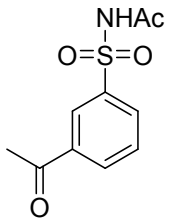
Method A, (82%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 158 – 160°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.13 (s, 1H), 8.08 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 9.1 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.59 (m, 3H), 7.46 – 7.25 (m, 5H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 140.0, 138.1, 136.5, 130.8, 130.7, 129.6, 128.7, 128.2, 126.8, 126.7, 126.2, 125.3, 23.3. **MS** (ESI): m/z (M + H$^+$) 302.2.

Methyl 3-(*N*-acetylsulfamoyl)benzoate (1l)



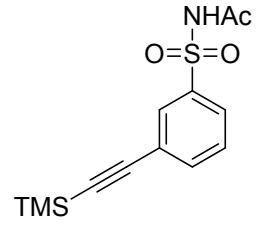
Method A, (85%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 122 – 123°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.76 (s, 1H), 7.41 (dd, *J* = 17.0, 7.9 Hz, 2H), 6.88 (t, *J* = 7.8 Hz, 1H), 3.12 (s, 3H), 1.16 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 161.4, 157.2, 131.9, 125.8, 123.8, 122.7, 121.0, 120.5, 43.6, 13.8. **MS** (ESI): m/z (M + H$^+$) 258.1.

***N*-((3-acetylphenyl)sulfonyl)acetamide (1m)**



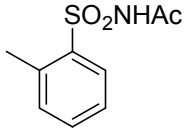
Method A, (88%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 2:1). **m.p.**: 146 – 147°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.23 (s, 1H), 8.37 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 2.65 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 196.7, 169.0, 140.1, 137.2, 133.4, 131.6, 129.9, 126.5, 26.8, 23.3. **MS** (ESI): m/z (M + H$^+$) 242.2.

***N*-((3-((trimethylsilyl)ethynyl)phenyl)sulfonyl)acetamide (1n)**



Method A, (92%, white powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 136 – 137°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.18 (s, 1H), 7.94 – 7.90 (m, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 8.1 Hz, 1H), 1.94 (s, 3H), 0.24 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-*d6*)) δ 168.9, 139.8, 136.2, 130.4, 129.8, 127.7, 123.0, 103.0, 96.6, 23.2, -0.3. **MS** (ESI): m/z (M + H$^+$) 296.2.

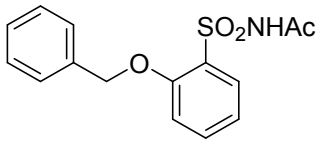
***N*-(o-tolylsulfonyl)acetamide (1o)**



Method A, (94%, white powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 124 – 125°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.18 (**s,** 1H**),** 7.94 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 2.62 – 2.54 (m, 3H), 1.97 – 1.92 (m, 3H).

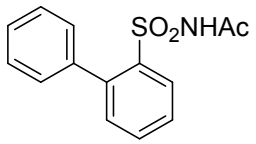
^{13}C NMR (101 MHz, DMSO-*d6*) δ 168.6, 137.4, 136.9, 133.5, 132.4, 130.2, 126.2, 23.1, 19.5. **MS** (ESI): m/z (M + H$^+$) 214.2.

<u>*N*-((2-(benzyloxy)phenyl)sulfonyl)acetamide (1p)</u>



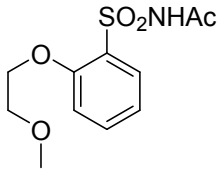
Method A, (92%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 140 – 141°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.15 (d, *J* = 7.9 Hz, 1H), 6.74 – 6.64 (m, 3H), 6.58 – 6.46 (m, 3H), 6.34 (d, *J* = 8.4 Hz, 1H), 6.24 (t, *J* = 7.6 Hz, 1H), 4.52 (s, 2H), 1.12 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 161.6, 147.8, 128.2, 127.1, 123.2, 120.2, 119.6, 119.0, 118.6, 111.8, 105.6, 61.9, 13.8. **MS** (ESI): m/z (M + H$^+$) 306.2.

<u>*N*-([1,1'-biphenyl]-2-ylsulfonyl)acetamide (1q)</u>



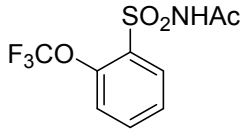
Method A, (91%, white powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 180 – 182°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.50 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.38 – 7.32 (m, 3H), 1.72 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.5, 140.5, 138.7, 137.4, 133.0, 132.5, 129.6, 128.9, 127.9, 127.8, 127.7, 23.0. **MS** (ESI): m/z (M + H$^+$) 276.2.

<u>*N*-((2-(2-methoxyethoxy)phenyl)sulfonyl)acetamide(1r)</u>



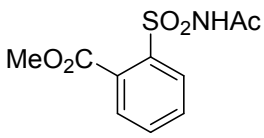
Method A, (95%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 2:1). **m.p.**: 95 – 96°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.77 (s, 1H), 7.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.13 – 7.07 (m, 1H), 4.32 – 4.25 (m, 2H), 3.78 – 3.70 (m, 2H), 3.31 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 155.8, 135.5, 130.8, 126.9, 120.2, 114.0, 70.1, 68.3, 58.2, 23.1. **MS** (ESI): m/z (M + H+) 274.2.

<u>*N*-((2-(trifluoromethoxy)phenyl)sulfonyl)acetamide (1s)</u>



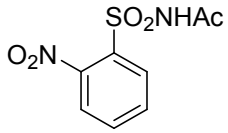
Method A, (91%, white powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 166 – 168°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.49 (s, 1H), 8.06 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.65 – 7.58 (m, 2H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 145.2, 136.1, 132.3, 131.2, 127.4, 120.9, 120.0 (q, *J* = 260.6 Hz), 23.0. **MS** (ESI): m/z (M + H$^+$) 284.1.

<u>Methyl 2-(*N*-acetylsulfamoyl)benzoate (1t)</u>



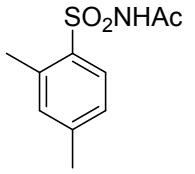
Method A, (75%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 146 – 147°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.10 (s, 1H), 8.11 – 8.06 (m, 1H), 7.77 (pd, *J* = 7.5, 1.6 Hz, 2H), 7.70 – 7.66 (m, 1H), 3.87 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 167.0, 136.4, 133.7, 132.1, 130.75, 130.74, 129.0, 53.2, 23.2. **MS** (ESI): m/z (M + H$^+$) 258.2.

<u>*N*-((2-nitrophenyl)sulfonyl)acetamide (1u)</u>



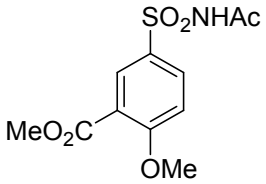
Method A, (75%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 166 – 167°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.62 (d, *J* = 38.3 Hz, 1H), 8.15 (dd, *J* = 7.5, 1.7 Hz, 1H), 8.00 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.94 – 7.84 (m, 2H), 1.97 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.1, 147.6, 135.5, 132.4, 132.2, 130.7, 124.6, 23.1. **MS** (ESI): m/z (M + H^+) 215.2.

<u>*N*-((2,4-dimethylphenyl)sulfonyl)acetamide (1v)</u>



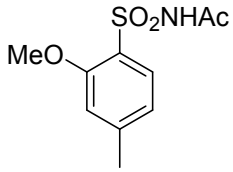
Method A, (95%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 137 – 138°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.07 (s, 1H), 7.88 – 7.79 (m, 1H), 7.25 – 7.18 (m, 2H), 2.53 (s, 3H), 2.34 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.5, 143.9, 136.7, 134.5, 132.8, 130.4, 126.6, 23.1, 20.8, 19.4. **MS** (ESI): m/z (M + H^+) 228.2.

<u>Methyl 5-(*N*-acetylsulfamoyl)-2-methoxybenzoate (1w)</u>



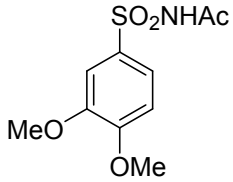
Method A, (77%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 2:1). **m.p.**: 169 – 171°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.06 (s, 1H), 8.16 (d, *J* = 2.5 Hz, 1H), 8.05 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 3.93 (s, 3H), 3.83 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.9, 164.7, 161.8, 133.4, 130.8, 130.4, 119.8, 113.2, 56.6, 52.4, 23.2. **MS** (ESI): m/z (M + H^+) 288.2.

<u>*N*-((2-methoxy-4-methylphenyl)sulfonyl)acetamide (1x)</u>



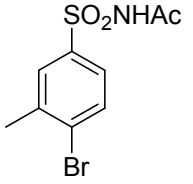
Method A, (95%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 2:1). **m.p.**: 202 – 204°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.87 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H), 2.37 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.7, 156.5, 146.4, 130.8, 123.8, 120.7, 113.6, 56.2, 23.1, 21.4. **MS** (ESI): m/z (M + H^+) 244.1.

<u>*N*-((3,4-dimethoxyphenyl)sulfonyl)acetamide (1y)</u>



Method A, (95%, white powder), R_f = 0.2 (EtOAc/Petroleum ether = 1:1). **m.p.**: 125 – 126°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.89 (s, 1H), 7.51 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.7, 152.9, 148.3, 130.8, 121.6, 111.1, 110.1, 55.9, 55.8, 23.2. **MS** (ESI): m/z (M + H^+) 260.2.

<u>*N*-((4-bromo-3-methylphenyl)sulfonyl)acetamide (1z)</u>



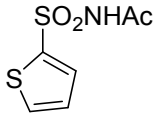
Method A, (87%, brown powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 166 – 167°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.14 (s, 1H), 7.86 – 7.83 (m, 2H), 7.63 (ddd, *J* = 8.5, 2.4, 0.6 Hz, 1H), 2.43 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ

168.9, 138.7, 138.7, 132.9, 130.0, 129.4, 126.7, 23.3, 22.4. **MS** (ESI): m/z (M + H^+) 292.1.

<u>*N*-((2,5-dimethoxyphenyl)sulfonyl)acetamide (1aa)</u>

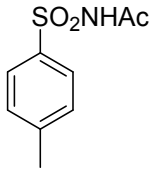
Method A, (92%, white powder), R_f = 0.2 (EtOAc/Petroleum ether = 1:1). **m.p.**: 164 – 165℃. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.00 (s, 1H), 7.31 (s, 1H), 7.24 (d, *J* = 9.1 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 152.2, 150.6, 127.2, 120.7, 115.5, 114.7, 56.7, 55.8, 23.1. **MS** (ESI): m/z (M + H^+) 260.1.

<u>*N*-(thiophen-2-ylsulfonyl)acetamide (1ab)</u>



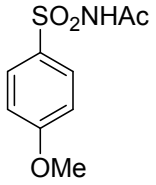
Method A, (85%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 90 – 91°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.24 (s, 1H), 8.02 (d, *J* = 4.9 Hz, 1H), 7.78 (d, *J* = 3.2 Hz, 1H), 7.19 (t, *J* = 4.2 Hz, 1H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 139.7, 134.6, 134.1, 127.5, 23.3. **MS** (ESI): m/z (M + H^+) 206.1

<u>*N*-tosylacetamide (1ac)</u>



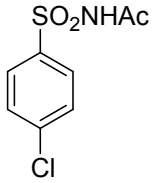
Method A (95%, white powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 133 – 135°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.03 (s, 1H), 7.80 – 7.77 (m, 2H), 7.44 – 7.41 (m, 2H), 2.39 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.7, 144.2, 136.5, 129.5, 127.6, 23.2, 21.1. **MS** (ESI): m/z (M + H^+) 214.2.

<u>*N*-((4-methoxyphenyl)sulfonyl)acetamide (1ad)</u>



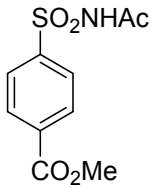
Method A, (97%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 2:1). **m.p.**: 142 – 143°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.94 (s, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 163.2, 130.9, 130.0, 114.3, 55.8, 23.2. **MS** (ESI): m/z (M + H^+) 230.2.

<u>*N*-((4-chlorophenyl)sulfonyl)acetamide (1ae)</u>



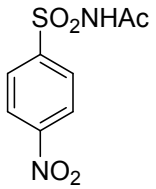
Method A, (88%, white powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 192 – 193°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.21 (s, 1H), 7.94 – 7.89 (m, 2H), 7.74 – 7.69 (m, 2H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 138.7, 138.1, 129.5, 129.3, 23.2. **MS** (ESI): m/z (M + H^+) 234.1.

<u>Methyl 4-(*N*-acetylsulfamoyl)benzoate (1af)</u>



Method A, (77%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 193 – 195°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.27 (s, 1H), 8.15 – 8.10 (m, 2H), 8.03 – 7.98 (m, 2H), 3.86 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 165.0, 143.2, 133.9, 129.9, 128.0, 52.7, 23.2. **MS** (ESI): m/z (M + H^+) 258.2.

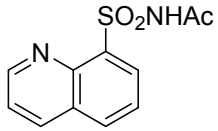
<u>*N*-((4-nitrophenyl)sulfonyl)acetamide (1ag)</u>



Method A, (75%, white powder), R_f = 0.2 (EtOAc/Petroleum ether = 1:1). **m.p.**: 196 – 198°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.43 (s, 1H), 8.42 – 8.37 (m, 2H), 8.15 – 8.11

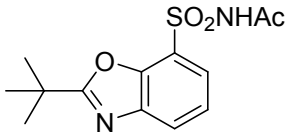
(m, 2H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.1, 150.3, 144.5, 129.2, 124.5, 23.3. **MS** (ESI): m/z (M + H^+) 215.2.

***N*-(quinolin-8-ylsulfonyl)acetamide (1ah)**



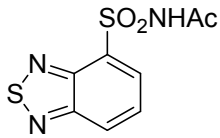
Method B, (77%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 200 – 201°C.**^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.30 (s, 1H), 9.09 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.56 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.46 (dd, *J* = 7.4, 1.4 Hz, 1H), 8.35 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.72 (dd, *J* = 8.3, 4.2 Hz, 1H), 1.88 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 151.5, 142.8, 137.1, 135.2, 134.7, 133.1, 128.4, 125.6, 122.6, 23.1. **MS** (ESI): m/z (M + H^+) 250.2.

***N*-((2-(tert-butyl)benzo[d]oxazol-7-yl)sulfonyl)acetamide (1ai)**



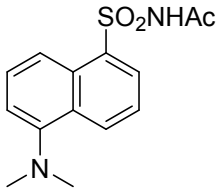
Method A, (89%, gray powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 178 – 179°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.64 (s, 1H), 8.06 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 1H), 1.95 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 174.2, 169.0, 145.2, 142.3, 125.2, 124.9, 124.4, 122.9, 34.0, 27.9, 23.1. **MS** (ESI): m/z (M + H^+) 297.2.

***N*-(benzo[c][1,2,5]thiadiazol-4-ylsulfonyl)acetamide (1aj)**



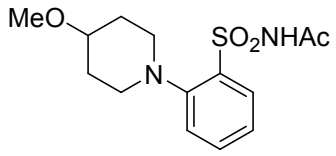
Method B, (85%, red powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:2). **m.p.**: 209-211°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.38 (s, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 8.33 (d, *J* = 7.0 Hz, 1H), 7.88 (dd, *J* = 8.5, 7.3 Hz, 1H), 1.88 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.0, 154.9, 148.4, 132.5, 131.3, 128.7, 126.5, 23.6. **HRMS** (ESI): m/z (M + H^+) calcd for $C_8H_8O_3N_3S_2$, 258.0001, found: 258.0003.

***N*-((5-(dimethylamino)naphthalen-1-yl)sulfonyl)acetamide (1ak)**



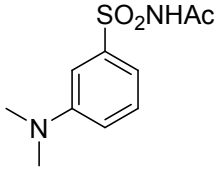
Method B, (87%, yellow powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 216 – 218°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.38 (s, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 7.3 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 7.65 (dt, *J* = 16.1, 8.0 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 2.82 (s, 6H), 1.89 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.5, 151.6, 134.2, 130.9, 130.7, 128.8, 128.8, 128.4, 123.5, 117.9, 115.2, 45.0, 23.2. **MS** (ESI): m/z (M + H^+) 293.2.

***N*-((2-(4-methoxypiperidin-1-yl)phenyl)sulfonyl)acetamide (1ah)**



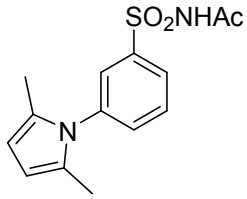
Method A, (85%, yellow powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 125 – 127℃. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.67 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.38 – 3.30 (m, 1H), 3.28 (s, 3H), 2.98 – 2.91 (m, 2H), 2.74 – 2.68 (m, 2H), 2.02 – 1.94 (m, 2H), 1.92 (s, 3H), 1.85 – 1.74 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.3, 152.7, 135.4, 134.7, 131.1, 125.1, 124.6, 75.3, 54.9, 51.1, 30.3, 22.9. **MS** (ESI): m/z (M + H^+) 313.2.

***N*-((3-(dimethylamino)phenyl)sulfonyl)acetamide (1ai)**



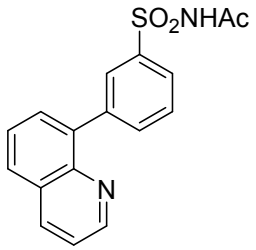
Method B, (83%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 112 – 113℃. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.92 (s, 1H), 7.42 – 7.35 (m, 1H), 7.16 – 7.11 (m, 2H), 7.01 – 6.96 (m, 1H), 2.95 (s, 6H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.64 150.1, 140.2, 129.6, 116.6, 114.0, 109.7, 39.8, 23.3. **MS** (ESI): m/z (M + H^+) 243.2.

***N*-((3-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide (1aj)**



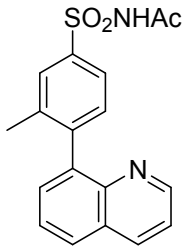
Method B, (88%, brown powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 193 – 194°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.22 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.78 (t, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 2H), 1.98 (s, 6H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 167.0, 140.2, 138.6, 133.1, 130.4, 127.7, 127.0, 126.3, 106.7, 23.2, 12.7. **MS** (ESI): m/z (M + H^+) 293.2.

***N*-((3-(quinolin-8-yl)phenyl)sulfonyl)acetamide (1ak)**



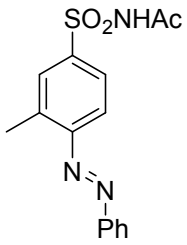
Method B, (82%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 173°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.13 (s, 1H), 8.92 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.48 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.21 (t, *J* = 1.7 Hz, 1H), 8.08 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.03 – 8.00 (m, 1H), 7.97 (ddd, *J* = 7.9, 1.7, 1.1 Hz, 1H), 7.84 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.61 (dd, *J* = 8.3, 4.1 Hz, 1H), 1.96 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.9, 150.6, 144.8, 139.8, 139.0, 137.8, 136.6, 135.7, 130.3, 129.3, 128.8, 128.6, 128.4, 126.5, 126.1, 121.7, 23.3. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{17}H_{15}O_3N_2S$, 327.0798, found: 327.0786.

***N*-((3-methyl-4-(quinolin-8-yl)phenyl)sulfonyl)acetamide (1al)**



Method B, (80%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**:215℃.**^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.14 (s, 1H), 8.83 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.46 (dd, *J* = 8.3, 1.8 Hz, 1H), 8.07 (dt, *J* = 7.5, 3.7 Hz, 1H), 7.84 (d, *J* = 1.4 Hz, 1H), 7.81 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.65 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.57 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 2.02 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.9, 150.5, 145.5, 145.3, 138.8, 138.3, 137.8, 136.5, 130.9, 130.0, 128.6, 128.0, 127.9, 126.3, 124.4, 121.6, 23.4, 20.1. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{18}H_{17}O_3N_2S$, 341.0954, found: 341.0945.

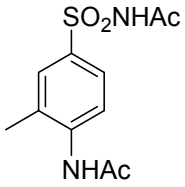
***(E)*-*N*-((3-methyl-4-(phenyldiazenyl)phenyl)sulfonyl)acetamide (1am)**



Method B, (85%, red powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:2). **m.p.**: 137-138°C. **^{1}H NMR** (400 MHz, DMSO–*d6*) δ 12.17 (s, 1H), 7.97 – 7.93 (m, 3H), 7.86 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.61 (m, 3H), 2.73 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 168.9, 152.6, 152.2, 140.7, 137.9, 132.4, 130.4,

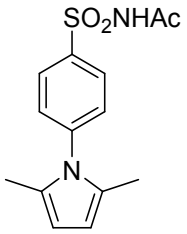
129.6, 126.2, 123.0, 116.2, 23.3, 17.1. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{15}H_{16}O_3N_3S$, 318.0907, found: 318.0897

***N*-((4-acetamido-3-methylphenyl)sulfonyl)acetamide (1an)**



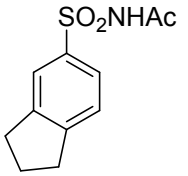
Method B, (82%, light yellow powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 238-240°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.98 (s, 1H), 9.46 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.73 – 7.67 (m, 2H), 2.30 (s, 3H), 2.12 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 168.7, 141.4, 134.4, 130.7, 129.4, 125.7, 123.6, 23.6, 23.2, 17.9. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{11}H_{15}O_4N_2S$, 271. 0747, found: 271.0737.

***N*-((4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide (1ao)**



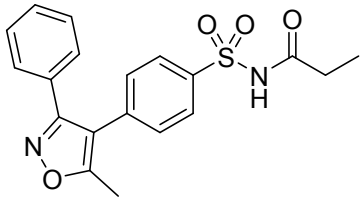
Method B, (81%, gray powder), R_f = 0.5 (EtOAc/Petroleum ether = 1:1). **m.p.**: 204 – 206℃. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.22 (s, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 10.8 Hz, 2H), 5.85 (s, 2H), 1.99 (s, 6H), 1.97 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 142.7, 138.1, 128.7, 128.5, 127.7, 107.0, 23.3, 12.9. **MS** (ESI): m/z (M + H^+) 293.2.

***N*-((2,3-dihydro-1H-inden-5-yl)sulfonyl)acetamide (1ap)**



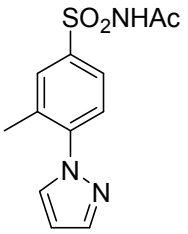
Method A, (95%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 136 – 137°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.97 (s, 1H), 7.73 (s, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 2.93 (td, *J* = 7.3, 2.6 Hz, 4H), 2.06 (p, *J* = 7.5 Hz, 2H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.6, 150.4, 144.9, 137.3, 125.9, 124.6, 123.2, 32.4, 32.1, 25.0, 23.2. **MS** (ESI): m/z (M + H^+) 240.2.

***N*-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)propionamide (1aq)**



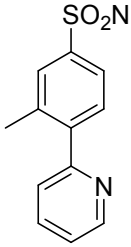
Method A, (89%, white powder), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **m.p.**: 142 – 143℃. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.09 (s, 1H), 7.95 – 7.89 (m, 2H), 7.50 – 7.39 (m, 5H), 7.36 – 7.31 (m, 2H), 2.49 (s, 3H), 2.24 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 172.4, 167.8, 160.7, 137.8, 130.1, 129.8, 128.8, 128.3, 128.2, 127.9, 114.0, 28.8, 11.5, 8.3. **MS** (ESI): m/z (M + H^+) 371.2.

***N*-((3-methyl-4-(1H-pyrazol-1-yl)phenyl)sulfonyl)acetamide (1ar)**



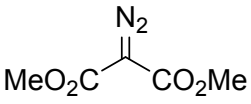
Method B, (77%, light yellow powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 148-149°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.21 (s, 1H), 8.19 (d, *J* = 2.4 Hz, 1H), 7.91 (d, *J* = 1.8 Hz, 1H), 7.85 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.80 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 6.57 – 6.52 (m, 1H), 2.35 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 143.3, 141.2, 138.3, 133.2, 131.8, 130.5, 126.3, 126.1, 107.3, 23.4, 18.5. **MS** (ESI): m/z (M + H^+) 280.1.

N-((3-methyl-4-(pyridin-2-yl)phenyl)sulfonyl)acetamide (1as)



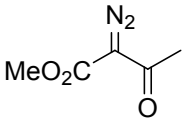
Method B, (86%, white powder), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **m.p.**: 187 – 189°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.17 (s, 1H), 8.68 (ddd, *J* = 4.7, 1.6, 0.9 Hz, 1H), 7.95 (td, *J* = 7.6, 1.7 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.62 (ddd, *J* = 7.7, 2.5, 1.3 Hz, 2H), 7.45 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H), 2.40 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.3, 157.5, 149.4, 144.8, 139.2, 137.0, 136.7, 130.5, 129.2, 125.1, 124.3, 122.9, 23.5, 20.2. **MS** (ESI): m/z (M + H$^+$) 291.1.

Dimethyl 2-diazomalonate (2a)



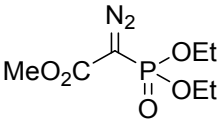
Method C, (78%, yellow oil), R_f = 0.4 (EtOAc/Petroleum ether = 1:4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.79 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6, 52.6. **MS** (ESI): m/z (M + H$^+$) 159.2.

Methyl 2-diazo-3-oxobutanoate (2b)



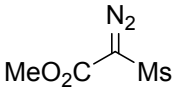
Method C, (76%, yellow oil), R_f = 0.4 (EtOAc/Petroleum ether = 1:4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.9, 161.7, 52.1, 28.0. **MS** (ESI): m/z (M + H$^+$) 143.2.

Methyl 2-diazo-2-(diethoxyphosphoryl)acetate (2c)



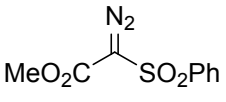
Method C, (76%, yellow oil), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.28 – 4.05 (m, 4H), 3.77 (s, 3H), 1.35 – 1.30 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 63.5, 63.4, 52.3, 15.9, 15.8. **MS** (ESI): m/z (M + H$^+$) 237.2.

Methyl 2-diazo-2-(methylsulfonyl)acetate (2d)



Method C, (75%, white thick solid), R_f = 0.3 (EtOAc/Petroleum ether = 1:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 53.3, 45.0. **MS** (ESI): m/z (M + H$^+$) 179.1.

Methyl 2-diazo-2-tosylacetate (2e)

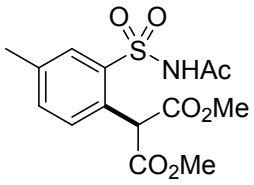


Method C, (75%, yellow powder, R_f = 0.3 (EtOAc/Petroleum ether = 1:2). **m.p.**: 68 – 69°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.67 – 7.61 (m, 1H), 7.57 – 7.52 (m, 2H), 3.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 141.8, 134.3, 129.4, 128.0, 53.0. **MS** (ESI): m/z (M + H$^+$) 254.1.

General procedure for the Rh-catalyzed C-H bond carbenoid founctionalization: A 10 mL tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (2.5 ~ 5.0 mol%), AgOAc (10 ~ 20 mol%), *N*-Ac substituted sulfonamide (0.25 mmol) and 2.5 mL DCE, then diazo compound (1.1 ~ 2.0 equivlent) was added. The tube was sealed, and the reaction mixture was stirred at 60°C for 5h. DCE was removed under vacuo, and 10 mL DCM was added. The mixture was then filtered, the filtrate was concentrated,

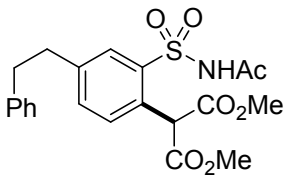
and the residue was purified by preparative TLC on silica gel to afford desired compound.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-methylphenyl)malonate (3)



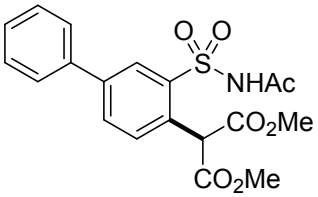
A 10 mL tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), **1a** (53.3 mg, 0.25 mmol) and 2.5 mL DCE, then **2a** (79 mg, 0.5 mmol) was added. The tube was sealed, and the reaction mixture was stirred at 60°C for 5h. DCE was removed under vacuo, and 10 mL DCM was added. The mixture was then filtered, the filtrate was concentrated, and the residue was purified by preparative TLC on silica gel (EAOAc/ Petroleum ether = 1:1, R_f = 0.4) to afford **3** (80 mg) which was dissolved in 2 mL toluene and followed by adding a small amount of petroleum ether under ultrasonic condition to 71.5 mg white powder (83% yield). **m.p.**: 157 – 159°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.40 (s, 1H), 7.83 (d, *J* = 1.3 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 5.73 (s, 1H), 3.69 (s, 6H), 2.40 (s, 3H), 1.89 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 168.0, 138.4, 137.4, 134.5, 130.8, 130.8, 128.4, 53.0, 52.2, 23.1, 20.5. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{14}H_{18}O_7NS$, 344.0798, found: 344.0792.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-phenethylphenyl)malonate (4)



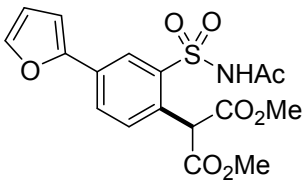
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-phenethylphenyl)sulfonyl)acetamide** (75.7 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 85.2 mg **4** was obtained (79% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.3). **m.p.**: 101 – 102°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.81 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.31 – 7.28 (m, 4H), 7.26 – 7.15 (m, 2H), 6.03 (s, 1H), 3.65 (s, 6H), 3.01 – 2.80 (m, 4H), 1.69 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 173.4, 168.6, 142.5, 141.3, 141.0, 131.2, 129.9, 128.7, 128.3, 128.3, 126.0, 125.3, 52.6 (X2), 36.7, 36.6, 25.4. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{21}H_{24}O_7NS$, 434.1268, found: 434.1269.

Dimethyl 2-(3-(*N*-acetylsulfamoyl)-[1,1'-biphenyl]-4-yl)malonate (5)



$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-([1,1'-biphenyl]-3-ylsulfonyl)acetamide** (68.7 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 89 mg **5** was obtained (88% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.4). **m.p.**: 97–98℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.46 (d, *J* = 2.0 Hz, 1H), 7.87 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.38 (m, 1H), 5.96 (s, 1H), 3.79 (s, 6H), 2.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 168.6, 142.1, 138.5, 137.8, 132.6, 132.2, 130.3, 130.2, 129.3, 128.7, 127.4, 23.5. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{19}H_{20}O_7NS$, 406.0955, found: 406.0949.

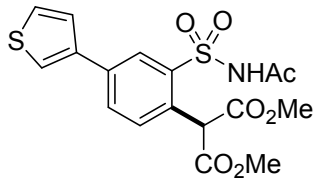
Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-(furan-2-yl)phenyl)malonate (6)



$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-(furan-**

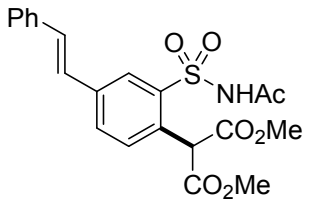
2-yl)phenyl)sulfonyl)acetamide (66.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 86 mg **6** was obtained (87% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4). **m.p.**: 155 – 156°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.13 (d, *J* = 2.0 Hz, 1H), 7.79 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.73 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 6.97 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.63 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.19 (s, 1H), 3.64 (s, 6H), 1.59 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 175.7, 168.8, 152.2, 145.7, 143.5, 130.2, 129.3, 129.1, 124.8, 123.3, 112.3, 106.7, 52.9, 52.5, 26.5. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{17}H_{18}O_8NS$, 396.0748, found: 396.0744.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-(thiophen-3-yl)phenyl)malonate (7)



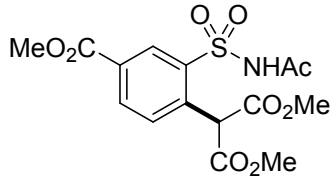
[RhCp*Cl$_2$]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-(thiophen-3-yl)phenyl)sulfonyl)acetamide** (70.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 87.7 mg **7** was obtained (85% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4). **m.p.**: 144 – 145°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.09 (d, *J* = 2.0 Hz, 1H), 7.87 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.75 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.68 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.51 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 6.18 (s, 1H), 3.65 (s, 6H), 1.61 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 175.2, 168.8, 145.3, 140.4, 134.0, 130.1, 129.1, 127.6, 127.5, 126.1, 125.9, 121.8, 52.8, 52.5, 26.3. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{17}H_{18}O_7NS_2$, 412.0519, found: 412.0514.

Dimethyl (E)-2-(2-(*N*-acetylsulfamoyl)-4-styrylphenyl)malonate (8)



[RhCp*Cl$_2$]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***(E)-N*-((3-styrylphenyl)sulfonyl)acetamide** (75.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 94 mg **8** was obtained (87% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.5). **m.p.**: 211 – 212°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.02 (d, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 3H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.22 (m, 4H), 6.19 (s, 1H), 3.64 (s, 6H), 1.59 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 175.3, 168.8, 145.6, 136.8, 135.8, 129.8, 129.5, 129.3, 128.7, 127.9, 127.5, 127.4, 126.7, 126.4, 52.8, 52.4, 26.5. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{21}H_{22}O_7NS$, 432.1111, found: 432.1109.

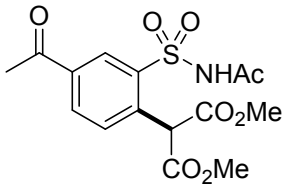
Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-(methoxycarbonyl)phenyl)malonate (9)



[RhCp*Cl$_2$]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***methyl 3-(N-acetylsulfamoyl)benzoate*** (64.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 67.3 mg **9** was obtained (69% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.5). **m.p.**: 171 – 172°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.66 (s, 1H), 8.54 (d, *J* = 1.5 Hz, 1H), 8.25 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 5.89 (s, 1H), 3.92 (s, 3H), 3.71 (s, 6H),

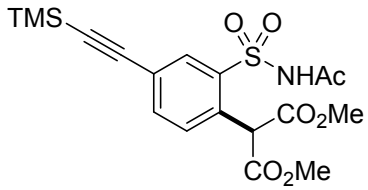
1.87 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*)) δ 169.8, 167.4, 164.7, 135.9, 133.6, 131.7, 131.1, 129.6, 53.2, 52.7, 52.6, 23.4. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{15}H_{18}O_9NS$, 388.0697, found: 388.0685.

Dimethyl 2-(4-acetyl-2-(*N*-acetylsulfamoyl)phenyl)malonate (10)



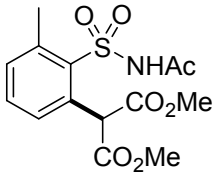
[RhCp*Cl_2]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-acetylphenyl)sulfonyl)acetamide** (60.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 70 mg **10** was obtained (71% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.5). **m.p.**: 125 – 126°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.48 (s, 1H), 8.27 (d, *J* = 6.0 Hz, 1H), 7.63 (d, *J* = 6.7 Hz, 1H), 5.92 (s, 1H), 3.70 (s, 6H), 2.64 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 196.5, 169.9, 167.5, 139.2, 136.2, 135.6, 133.1, 131.6, 129.6, 53.2, 52.6, 26.8, 23.5. **HRMS** (ESI): m/z (M + Na^+) calcd for $C_{15}H_{17}O_8NNaS$, 394.0567, found: 394.0555.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-((trimethylsilyl)ethynyl)phenyl)malonate (11)



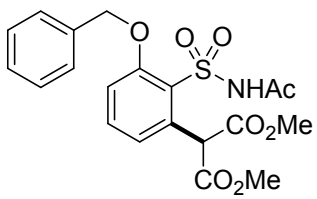
[RhCp*Cl_2]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-((trimethylsilyl)ethynyl)phenyl)sulfonyl)acetamide** (73.7 mg, 0.25 mmol), **2a** (59.2 mg, 0.375 mmol), 2.5 mL DCE, 60°C for 5h. 44.5 mg **11** was obtained (42% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.5). **m.p.:** 88 – 89°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 5.83 (s, 1H), 3.75 (s, 6H), 2.02 (s, 3H), 0.22 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 168.2, 137.5, 137.1, 134.8, 131.8, 131.4, 124.6, 102.3, 98.5, 53.6, 53.2, 23.6, -0.1. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{18}H_{24}O_7NSSi$, 426.1037, found: 426.1028.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-methylphenyl)malonate (12)



[RhCp*Cl_2]$_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-(*o*-tolylsulfonyl)acetamide** (53.2 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 78 mg **12** was obtained (91% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.4), **m.p.**: 160 – 161°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.46 (s, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 6.10 (s, 1H), 3.67 (s, 6H), 2.66 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.0, 168.8, 140.2, 136.3, 134.2, 133.2, 132.8, 128.7, 54.3, 52.7, 23.1, 22.2. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{14}H_{18}O_7NS$, 344.0798, found: 344.0795.

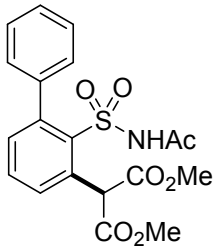
Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-(benzyloxy)phenyl)malonate (13)



[RhCp*Cl_2]$_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2-(benzyloxy)phenyl)sulfonyl)acetamide** (76.2 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 100 mg **13** was obtained (92% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 178

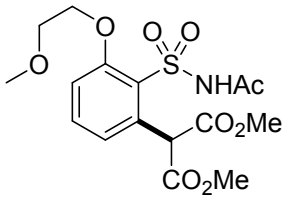
– 179°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.24 (s, 1H), 7.55 – 7.48 (m, 3H), 7.41 – 7.35 (m, 2H), 7.30 (ddd, *J* = 7.2, 3.8, 1.3 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.77 (dd, *J* = 7.9, 0.8 Hz, 1H), 6.08 (s, 1H), 5.42 (s, 2H), 3.67 (s, 6H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.7, 168.7, 157.0, 136.4, 135.4, 134.2, 128.5, 127.9, 127.2, 125.8, 121.6, 114.5, 69.8, 54.2, 52.6, 23.1. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{20}H_{22}O_8NS$, 436.1061, found: 436.1054.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-[1,1'-biphenyl]-3-yl)malonate (14)



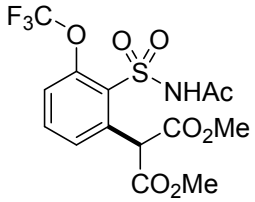
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-([1,1'-biphenyl]-2-ylsulfonyl)acetamide** (68.7 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 89.4 mg **14** was obtained (88% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.3), **m.p.**: 147 – 148°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.92 (s, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.15 (s, 1H), 3.70 (s, 6H), 1.76 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.2, 168.6, 143.3, 141.1, 137.5, 133.2, 133.1, 131.7, 130.3, 128.9, 127.2, 126.9, 54.1, 52.8, 23.5. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{19}H_{20}O_7NS$, 406.0955, found: 406.0947.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-(2-methoxyethoxy)phenyl)malonate (15)



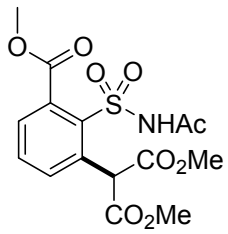
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2-(2-methoxyethoxy)phenyl)sulfonyl)acetamide** (68.2 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 93.7 mg **15** was obtained (93% yield, white powder, EAOAc/ Petroleum ether = 3:1, R_f = 0.4), **m.p.**: 159 – 160°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.80 (s, 1H), 7.60 (t, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.03 (s, 1H), 4.37 – 4.26 (m, 2H), 3.77 – 3.74 (m, 2H), 3.68 (s, 6H), 3.32 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.6, 168.7, 157.8, 135.1, 134.4, 126.1, 121.8, 115.0, 70.1, 69.0, 58.3, 54.3, 52.7, 23.0. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{16}H_{22}O_9NS$, 404.1010, found: 404.1002.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-(trifluoromethoxy)phenyl)malonate (16)



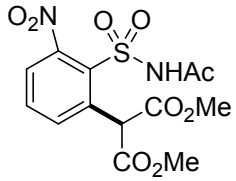
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2-(trifluoromethoxy)phenyl)sulfonyl)acetamide** (70.7 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 93 mg **16** was obtained (90% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.3), **m.p.**: 153 – 154°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.70 (s, 1H), 7.83 (t, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 6.12 (s, 1H), 3.71 (s, 6H), 1.94 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.2, 168.3, 146.9, 146.9, 136.3, 135.1, 130.6, 129.2, 121.5, 119.9 (q, *J* = 260.5), 53.8, 52.9, 23.0. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{14}H_{15}O_8NF_3S$, 414.0465, found: 414.0456.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-(methoxycarbonyl)phenyl)malonate (17)



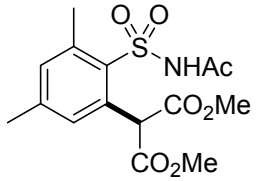
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), **methyl 2-(*N*-acetylsulfamoyl)benzoate** (64.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 74 mg **17** was obtained (76% yield, yellow powder, DCM/ MeOH = 25:1, R_f = 0.3), **m.p.**: 177 – 178°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.46 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.35 (s, 1H), 3.70 (s, 3H), 3.63 (s, 6H), 1.59 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 175.7, 169.8, 168.7, 142.0, 133.7, 131.8, 131.2, 129.6, 126.5, 53.2, 52.5, 52.3, 26.3. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{15}H_{18}O_9NS$, 388.0697, found: 388.0689.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-nitrophenyl)malonate (18)



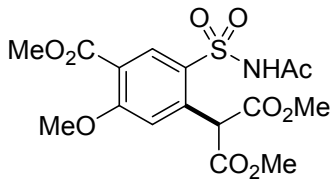
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((2-nitrophenyl)sulfonyl)acetamide** (61 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 31 mg **18** was obtained (33% yield, white powder, DCM/ MeOH = 20:1, R_f = 0.3), **m.p.**: 168 – 169°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.67 – 7.50 (m, 2H), 7.45 (d, *J* = 6.8 Hz, 1H), 6.47 (d, *J* = 45.7 Hz, 1H), 3.65 (s, 6H), 1.61 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 175.5, 168.5, 149.7, 136.6, 133.4, 132.3, 130.7, 122.7, 53.2, 52.7, 26.1. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{13}H_{15}O_9N_2S$, 375.0493, found: 375.0476.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3,5-dimethylphenyl)malonate (19)



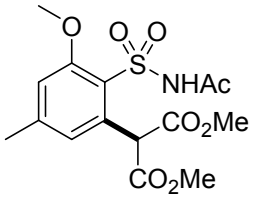
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2,4-dimethylphenyl)sulfonyl)acetamide** (56.7 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 81.2 mg **19** was obtained (91% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.5), **m.p.**: 175 – 176°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.38 (s, 1H), 7.24 (s, 1H), 6.95 (s, 1H), 6.05 (s, 1H), 3.68 (s, 6H), 2.62 (s, 3H), 2.32 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.6, 168.7, 143.1, 140.1, 134.2, 133.7, 133.4, 129.0, 54.1, 52.7, 22.9, 22.1, 20.7. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{15}H_{20}O_7NS$, 358.0955, found: 358.0942.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-5-methoxy-4-(methoxycarbonyl)phenyl)malonate (20)



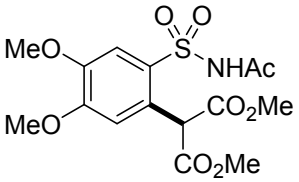
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), **methyl 5-(*N*-acetylsulfamoyl)-2-methoxybenzoate** (71.7 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 74 mg **20** was obtained (71% yield, white powder, EAOAc/ Petroleum ether = 3:1, R_f = 0.4, **m.p.**: 178 – 179°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.24 (s, 1H), 7.05 (s, 1H), 5.96 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.71 (s, 6H), 1.77 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 171.3, 167.7, 164.6, 160.3, 136.6, 133.3, 132.1, 118.8, 114.0, 56.4, 53.1, 52.7, 52.4, 24.3. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{16}H_{20}O_{10}NS$, 418.0802, found: 418.0792.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-methoxy-5-methylphenyl)malonate (21)



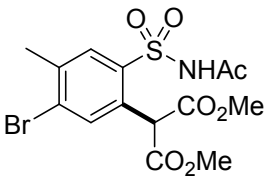
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2-methoxy-4-methylphenyl)sulfonyl)acetamide** (60.7 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 88.6 mg **21** was obtained (95% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 167 – 168°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.03 (s, 1H), 7.13 (s, 1H), 6.59 (s, 1H), 6.02 (s, 1H), 3.90 (s, 3H), 3.68 (s, 6H), 2.35 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.6, 168.7, 158.4, 145.2, 134.8, 123.0, 122.2, 114.3, 56.9, 54.0, 52.6, 23.0, 21.4. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{15}H_{20}O_8NS$, 374.0904, found: 374.0895.

Dimethyl 2-(2-(N-acetylsulfamoyl)-4,5-dimethoxyphenyl)malonate (22)



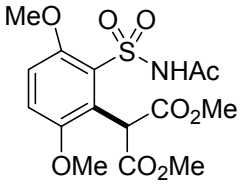
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3,4-dimethoxyphenyl)sulfonyl)acetamide** (64.7 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 1h. 78.8 mg **22** was obtained (81% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.3), **m.p.**: 171 – 172°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.31 (s, 1H), 7.47 (s, 1H), 6.92 (s, 1H), 5.76 (s, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.70 (s, 6H), 1.87 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.9, 168.0, 152.2, 147.5, 129.8, 124.8, 113.5, 112.8, 55.9, 53.0, 52.0, 23.1. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{15}H_{20}O_9NS$, 390.0853, found: 390.0843.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-5-bromo-4-methylphenyl)malonate (23)



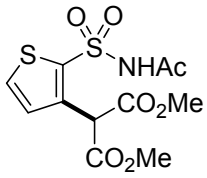
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((4-bromo-3-methylphenyl)sulfonyl)acetamide** (73 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C for 5h. 74 mg **23** was obtained (70% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 141 – 142°C. **^{1}H NMR** (400 MHz, DMSO -*d6*) δ 7.79 (s, 1H), 7.41 (s, 1H), 6.11 (s, 1H), 3.65 (s, 6H), 2.37 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (101 MHz, DMSO -*d6*) δ 175.31, 168.47, 143.98, 136.58, 132.75, 130.88, 129.71, 125.71, 52.75, 52.24, 26.18, 22.09. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{14}H_{17}O_7NBrS$, 421.9904, found: 421.9894.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3,6-dimethoxyphenyl)malonate (24)



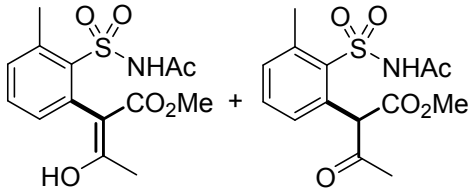
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2,5-dimethoxyphenyl)sulfonyl)acetamide** (64.7 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 92.4 mg **24** was obtained (95% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 195 – 196°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.10 (s, 1H), 7.40 (d, *J* = 9.2 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 6.13 (s, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 3.61 (s, 6H), 1.93 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.5, 167.9, 152.3, 152.1, 126.5, 125.1, 119.1, 114.7, 57.4, 57.2, 52.1, 49.5, 23.1. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{15}H_{20}O_9NS$, 390.0853, found: 390.0843.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)thiophen-3-yl)malonate (25)



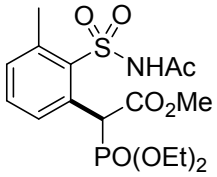
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-(thiophen-2-ylsulfonyl)acetamide** (51.2 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 68 mg **25** was obtained (81% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 121 – 122°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.44 (s, 1H), 8.02 (d, *J* = 5.2 Hz, 1H), 7.16 (d, *J* = 5.2 Hz, 1H), 5.65 (s, 1H), 3.70 (s, 6H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.1, 167.2, 137.0, 136.7, 133.0, 129.5, 53.2, 50.1, 23.2. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{11}H_{14}O_7NS_2$, 336.0206, found: 336.0198.

Methyl (E)-2-(2-(*N*-acetylsulfamoyl)-3-methylphenyl)-3-hydroxybut-2-enoate and methyl 2-(2-(N-acetylsulfamoyl)-3-methylphenyl)-3-oxobutanoate (26 + 26')



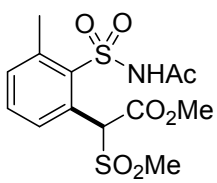
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-(*o*-tolylsulfonyl)acetamide** (53.2 mg, 0.25 mmol), **2b** (35.5 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 71 mg **26** and **26'** were obtained (87% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.5), **m.p.**: 195 – 197°C. **26**: **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.75 (s, 1H), 12.03 (s, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.12 (m, 1H), 3.54 (s, 3H), 2.66 (s, 3H), 1.90 (s, 3H), 1.73 (s, 3H). **26'**:**^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.48 (s, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 3.65 (s, 3H), 2.67 (s, 3H), 2.16 (s, 3H), 1.96 (s, 3H). **26+26'**: **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 202.1, 172.0, 171.1, 170.1, 169.2, 168.9, 140.3, 139.2, 137.2, 136.3, 135.9, 134.3, 133.1, 132.9, 132.8, 132.6, 132.3, 129.2, 103.1, 61.2, 52.4, 51.5, 29.5, 23.1, 22.9, 22.2, 21.8, 19.8. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{14}H_{18}O_6NS$, 328.0849, found: 328.0841.

Methyl 2-(2-(*N*-acetylsulfamoyl)-3-methylphenyl)-2-(diethoxyphosphoryl)acetate (27)



$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-(*o*-tolylsulfonyl)acetamide** (53.2 mg, 0.25 mmol), **2c** (59 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 95 mg **27** was obtained (90% yield, white powder, DCM/ MeOH = 30:1, R_f = 0.3), **m.p.**: 163 – 164°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.44 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 6.07 (d, *J* = 28.2 Hz, 1H), 4.16 – 4.02 (m, 2H), 3.92 – 3.77 (m, 1H), 3.76 – 3.66 (m, 1H), 3.65 (s, 3H), 2.65 (s, 3H), 1.83 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.7, 167.5 (d, *J* = 4.4 Hz), 139.5, 137.8, 132.6 (d, *J* = 4.7 Hz), 132.4, 131.1, 130.9 (d, *J* = 5.8 Hz), 62.6 (t, *J* = 6.1 Hz), 52.5, 47.2, 46.0, 23.7, 22.7, 16.2 (d, *J* = 5.9 Hz), 15.8 (d, *J* = 5.8 Hz). **HRMS** (ESI): m/z (M + H^+) calcd for $C_{16}H_{25}O_8NPS$, 422.1033, found: 422.1023.

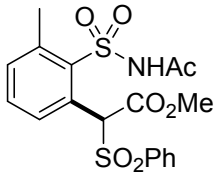
Methyl 2-(2-(*N*-acetylsulfamoyl)-3-methylphenyl)-2-(methylsulfonyl)acetate (28)



$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-(*o*-tolylsulfonyl)acetamide** (53.2 mg, 0.25 mmol), **2d** (44.5 mg, 0.25 mmol), 2.5 mL

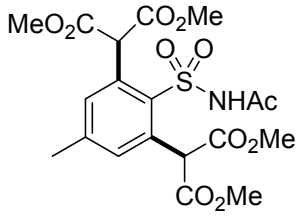
DCE, 60°C for 5h. 82.5 mg **28** was obtained (91% yield, white powder, EAOAc/ Petroleum ether = 3:1, R_f = 0.4), **m.p.**: 204 – 205°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.63 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.27 (s, 1H), 3.74 (s, 3H), 3.18 (s, 3H), 2.65 (s, 3H), 1.79 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 172.8, 165.1, 140.5, 139.4, 133.4, 130.4, 129.7, 128.7, 68.1, 53.2, 42.2, 24.6, 22.6. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{13}H_{18}O_7NS_2$, 364.0519, found: 364.0511.

Methyl 2-(2-(*N*-acetylsulfamoyl)-3-methylphenyl)-2-(phenylsulfonyl)acetate (29)



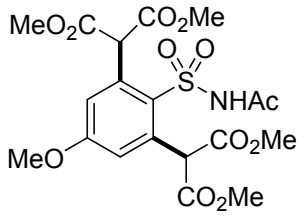
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-(*o*-tolylsulfonyl)acetamide** (53.2 mg, 0.25 mmol), **2e** (60 mg, 0.25 mmol), 2.5 mL DCE, 60°C for 5h. 94.7 mg **29** was obtained (89% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 171 – 172°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.54 (s, 1H), 7.94 – 7.90 (m, 2H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.79 (ddd, *J* = 8.5, 2.2, 1.1 Hz, 1H), 7.71 – 7.60 (m, 3H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.38 (s, 1H), 3.56 (s, 3H), 2.66 (s, 3H), 1.86 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.8, 164.7, 139.8, 139.3, 138.2, 134.3, 134.1, 131.6, 130.5, 129.2, 129.1, 128.7, 68.7, 52.8, 23.5, 22.5. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{18}H_{20}O_7NS_2$, 426.0676, found: 426.0663.

Tetramethyl 2,2'-(2-(*N*-acetylsulfamoyl)-5-methyl-1,3-phenylene)dimalonate (30)



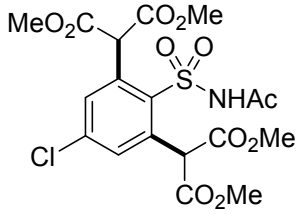
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-tosylacetamide** (53.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 98 mg **30** was obtained (83% yield, white powder, EAOAc/ Petroleum ether = 3:1, R_f = 0.4, **m.p.**: 173 – 174°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.77 (s, 1H), 7.15 (s, 2H), 6.03 (s, 2H), 3.69 (s, 12H), 2.37 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 171.12, 169.01, 143.85, 134.83, 132.01, 120.00, 54.53, 53.36, 23.61, 21.38. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{19}H_{24}O_{11}NS$, 474.1065, found: 474.1059.

Tetramethyl 2,2'-(2-(*N*-acetylsulfamoyl)-5-methoxy-1,3-phenylene)dimalonate (31)



$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((4-methoxyphenyl)sulfonyl)acetamide** (57.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 104.2 mg **31** was obtained (85% yield, white powder, EAOAc/ Petroleum ether = 3:1, R_f = 0.3, **m.p.**: 183 – 184°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.69 (s, 1H), 6.85 (s, 2H), 6.05 (s, 2H), 3.82 (s, 3H), 3.70 (s, 12H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*)) δ 170.3, 168.3, 161.2, 136.7, 130.0, 116.1, 55.8, 54.1, 53.0, 23.0. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{19}H_{24}O_{12}NS$, 490.1014, found: 490.0997.

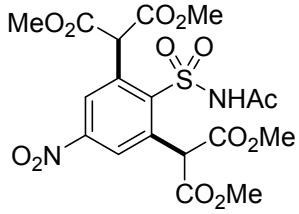
Tetramethyl 2,2'-(2-(*N*-acetylsulfamoyl)-5-chloro-1,3-



phenylene)dimalonate (32)

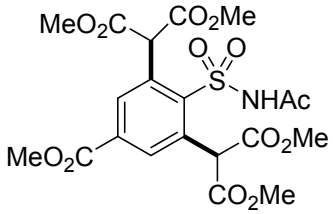
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((4-chlorophenyl)sulfonyl)acetamide** (58 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 96.5 mg **32** was obtained (78% yield, white powder, DCM/ MeOH = 25:1, R_f = 0.3, **m.p.**: 193 – 194°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.16 (s, 2H), 6.61 (s, 2H), 3.65 (s, 12H), 1.61 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 171.8, 168.5, 137.4, 136.7, 131.1, 125.8, 54.1, 53.66, 23.8. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{18}H_{21}O_{11}NClS$, 494.0518, found: 494.0516.

Tetramethyl 2,2'-(2-(*N*-acetylsulfamoyl)-5-nitro-1,3-phenylene)dimalonate (33)



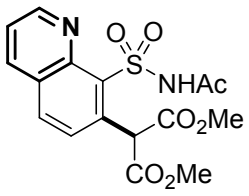
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((4-nitrophenyl)sulfonyl)acetamide** (61 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 44 mg **33** was obtained (35% yield, white powder, DCM/ MeOH = 20:1, R_f = 0.3, **m.p.**: 217 – 218°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 8.01 (s, 2H), 6.69 (s, 2H), 3.67 (s, 12H), 1.64 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 177.1, 168.8, 150.9, 146.4, 134.9, 124.0, 53.8, 52.76, 26.0. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{18}H_{21}O_{13}N_2S$, 505.0759, found: 505.0756.

Tetramethyl 2,2'-(2-(*N*-acetylsulfamoyl)-5-(methoxycarbonyl)-1,3-phenylene)dimalonate (34)



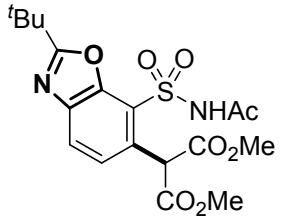
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), **methyl 4-(*N*-acetylsulfamoyl)benzoate** (64.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 92 mg **34** was obtained (71% yield, white powder, DCM/ MeOH = 20:1, R_f = 0.3, **m.p.**: 161 – 162°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.75 (s, 1H), 6.64 (s, 1H), 3.87 (s, 2H), 3.64 (s, 7H), 1.62 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 176.9, 169.3, 165.1, 149.2, 133.6, 130.0, 129.4, 54.0, 52.7, 52.5, 26.1. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{20}H_{24}O_{13}NS$, 518.0963, found: 518.0961.

Dimethyl 2-(8-(*N*-acetylsulfamoyl)quinolin-7-yl)malonate (35)



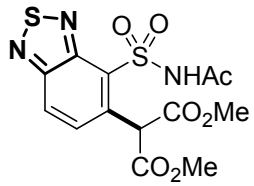
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-(quinolin-8-ylsulfonyl)acetamide** (62.5 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 73 mg **35** was obtained (77% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 235 – 237°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.47 (s, 1H), 9.09 (dd, *J* = 4.1, 1.7 Hz, 1H), 8.53 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 7.72 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 6.56 (s, 1H), 3.71 (s, 6H), 1.86 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.2, 168.4, 151.1, 143.9, 137.1, 136.7, 134.2, 133.7, 127.8, 127.7, 122.6, 54.2, 52.8, 23.2. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{16}H_{17}O_7N_2S$, 381.0750, found: 381.0747.

Dimethyl 2-(7-(*N*-acetylsulfamoyl)-2-(tert-butyl)benzo[d]oxazol-6-yl)malonate (36)



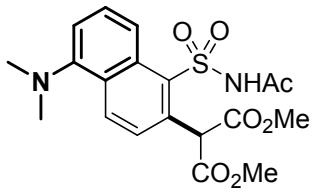
$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2-(tert-butyl)benzo[d]oxazol-7-yl)sulfonyl)acetamide** (74 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C ovenight. 89.1 mg **36** was obtained (84% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 171 – 172°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.79 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 6.02 (s, 1H), 3.70 (s, 6H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 175.0, 169.6, 168.1, 147.4, 142.1, 128.9, 126.2, 124.4, 122.3, 53.0, 52.4, 34.0, 27.8, 23.1. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{18}H_{23}O_8N_2S$, 427.1170, found: 427.1163.

Dimethyl 2-(4-(*N*-acetylsulfamoyl)benzo[c][1,2,5]thiadiazol-5-yl)malonate (37)



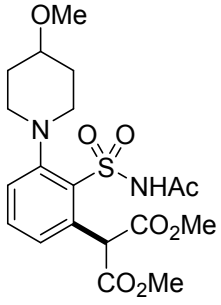
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-(benzo[c][1,2,5]thiadiazol-4-ylsulfonyl)acetamide** (64.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C ovenight. 63 mg **37** was obtained (65% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.3), **m.p.**: 202 – 203°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.86 (s, 1H), 8.44 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 6.57 (s, 1H), 3.73 (s, 6H), 1.89 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 170.2, 167.7, 153.9, 149.6, 137.0, 131.5, 125.9, 53.1, 52.6, 23.1. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{13}H_{14}O_7N_3S_2$, 388.068, found: 388.0265.

Dimethyl 2-(1-(*N*-acetylsulfamoyl)-5-(dimethylamino)naphthalen-2-yl)malonate (38)



$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((5-(dimethylamino)naphthalen-1-yl)sulfonyl)acetamide** (73 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C ovenight. 93 mg **38** was obtained (88% yield, yellow powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 108 – 109°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.71 (s, 1H), 8.52 (d, *J* = 9.0 Hz, 1H), 8.39 (d, *J* = 8.9 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.50 (s, 1H), 3.70 (s, 6H), 2.82 (s, 6H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.0, 168.8, 151.3, 135.0, 133.2, 130.6, 130.2, 128.6, 128.3, 126.0, 119.6, 115.3, 54.8, 52.7, 45.1, 23.1. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{19}H_{23}O_7N_2S$, 423.1220, found: 423.1216.

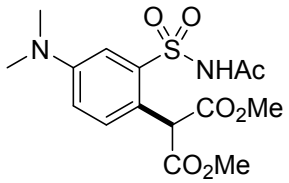
Dimethyl 2-(2-(*N*-acetylsulfamoyl)-3-(4-methoxypiperidin-1-yl)phenyl)malonate (39)



$[RhCp^*Cl_2]_2$ (3.9 mg, 2.5 mol%), AgOAc (4.2 mg, 10 mol%), ***N*-((2-(4-methoxypiperidin-1-yl)phenyl)sulfonyl)acetamide** (40 mg, 0.25 mmol), **2a** (40 mg, 0.25 mmol), 2.5 mL DCE, 60°Covenight. 98.3 mg **39** was obtained (89% yield, brown powder, DCE/MeOH = 20:1, R_f = 0.5), **m.p.**: 172 – 174°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 11.75 (s, 1H), 7.69 – 7.63 (m, 2H), 7.13 (dd, *J* = 6.0, 2.5 Hz, 1H), 6.05 (s, 1H), 3.68 (s, 6H), 3.32 (s, 1H), 3.29 (s, 3H), 3.14 – 2.63 (m, 4H), 2.08 – 1.94

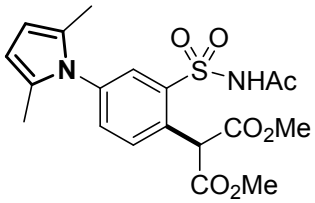
(m, 2H), 1.90 (s, 3H), 1.88 – 1.74 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.7, 169.1, 153.9, 135.8, 135.4, 134.3, 128.5, 126.0, 77.1, 55.4, 55.0, 53.1, 49.6, 31.1, 23.5. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{19}H_{27}O_8N_2S$, 443.1483, found: 443.1480.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-(dimethylamino)phenyl)malonate (40)



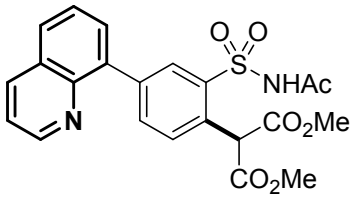
[RhCp*Cl$_2$]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-(dimethylamino)phenyl)sulfonyl)acetamide** (60.5 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 78.1 mg **40** was obtained (84% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4). **m.p.**: 148 – 149°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.21 (d, *J* = 2.9 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.87 (dd, *J* = 8.7, 2.8 Hz, 1H), 5.81 (s, 1H), 3.63 (s, 6H), 2.94 (s, 6H), 1.74 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 171.9, 169.0, 149.1, 141.6, 130.8, 117.2, 114.9, 112.4, 52.5, 51.9, 39.9, 24.7. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{15}H_{21}O_7N_2S$, 373.1064, found: 373.1061.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)malonate (41)



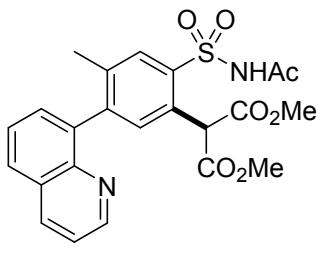
[RhCp*Cl$_2$]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide** (73 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 85.8 mg **41** was obtained (81% yield, white powder, EAOAc/ Petroleum ether = 3:1, R_f = 0.5). **m.p.**: 243 – 244°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.64 (s, 1H), 7.48 – 7.32 (m, 2H), 6.15 (s, 1H), 5.82 (s, 2H), 3.68 (s, 6H), 2.00 (s, 6H), 1.63 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 175.5, 168.6, 145.5, 136.8, 130.4, 129.4, 129.2, 128.1, 127.7, 106.3, 52.7, 52.5, 26.3, 13.0. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{19}H_{23}O_7N_2S$, 423.1220, found: 423.1216.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-(quinolin-8-yl)phenyl)malonate (42)



[RhCp*Cl$_2$]$_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((3-(quinolin-8-yl)phenyl)sulfonyl)acetamide** (81.4 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 82 mg **42** was obtained (72% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.3), **m.p.**: 233 – 235°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.48 (s, 1H), 8.94 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.49 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.31 (d, *J* = 1.9 Hz, 1H), 8.13 – 8.04 (m, 2H), 7.86 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.66 – 7.58 (m, 2H), 5.88 (s, 1H), 3.75 (s, 6H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.0, 167.9, 150.7, 144.7, 139.1, 137.2, 137.2, 136.7, 135.8, 132.5, 130.3, 129.9, 129.0, 128.4, 126.6, 125.3, 121.8, 53.1, 52.4, 23.1. **HRMS** (ESI): m/z (M + H$^+$) calcd for $C_{22}H_{21}O_7N_2S$, 457.1064, found: 457.1051.

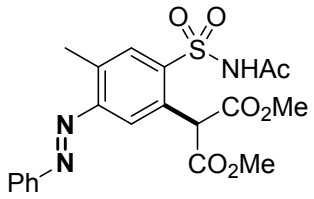
Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-methyl-5-(quinolin-8-yl)phenyl)malonate (43)



[RhCp*Cl$_2$]$_2$ (3.9 mg, 5 mol%), AgOAc (4.2 mg, 20 mol%), ***N*-((3-methyl-4-(quinolin-8-yl)phenyl)sulfonyl)acetamide** (42.5 mg, 0.125 mmol), **2a**

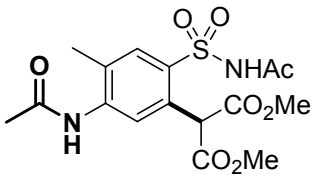
(22 mg, 1.1 equiv), 12.5 mL toluene, 60°C overnight. 53 mg **43** was obtained (91% yield, white powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.3), **m.p.**: 143 – 145°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 8.17 (s, 1H), 8.02 – 7.99 (m, 1H), 7.73 (d, *J* = 4.7 Hz, 2H), 7.63 – 7.56 (m, 2H), 6.26 (s, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 2.24 (s, 3H), 1.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.7, 169.0, 149.8, 144.8, 143.9, 139.2, 139.0, 137.7, 136.8, 133.7, 132.4, 132.0, 130.5, 129.1, 128.9, 127.4, 121.9, 53.3, 53.0, 23.5, 20.6. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{23}H_{23}O_7N_2S$, 471.1220, found: 471.1225.

Dimethyl (E)-2-(2-(*N*-acetylsulfamoyl)-4-methyl-5-(phenyldiazenyl)phenyl)malonate (44)



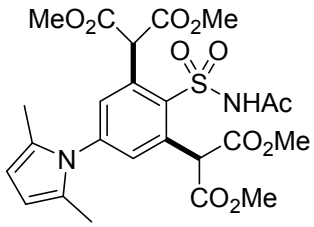
$[RhCp^*Cl_2]_2$ (7.8 mg, 5 mol%), AgOAc (8.3 mg, 20 mol%), ***(E)-N-((3-methyl-4-(phenyldiazenyl)phenyl)sulfonyl)acetamide*** (79.2 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 95 mg **44** was obtained (85% yield, red powder, EAOAc/ Petroleum ether = 2:1, R_f = 0.4), **m.p.**: 211 – 212°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.55 (s, 1H), 8.10 (s, 1H), 7.99 – 7.93 (m, 2H), 7.66 – 7.62 (m, 3H), 7.60 (s, 1H), 5.79 (s, 1H), 3.71 (s, 6H), 2.73 (s, 3H), 1.92 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.1, 167.8, 152.2, 152.0, 137.3, 133.8, 132.5, 129.8, 129.6, 123.2, 119.9, 117.5, 53.2, 52.2, 23.2, 16.8. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{20}H_{22}O_7N_3S$, 448.1773, found: 448.1158.

Dimethyl 2-(5-acetamido-2-(*N*-acetylsulfamoyl)-4-methylphenyl)malonate (45)



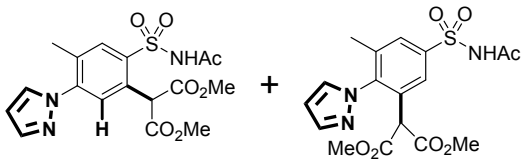
$[RhCp^*Cl_2]_2$ (7.8 mg, 5 mol%), AgOAc (8.3 mg, 20 mol%), ***N-((4-acetamido-3-methylphenyl)sulfonyl)acetamide*** (67.4 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 92 mg **45** was obtained (92% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.3), **m.p.**: 219 – 221°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.32 (s, 1H), 9.48 (s, 1H), 7.86 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 5.68 (s, 1H), 3.68 (s, 6H), 2.31 (s, 3H), 2.12 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 168.9, 168.7, 167.9, 141.5, 132.7, 132.1, 129.6, 129.4, 124.5, 52.9, 52.5, 23.7, 23.0, 17.7. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{16}H_{21}O_8N_2S$, 401.1013, found: 401.0997.

Tetramethyl 2,2'-(2-(*N*-acetylsulfamoyl)-5-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-phenylene)dimalonate (46)



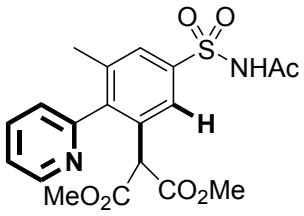
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((4-(2,5-dimethyl-1H-pyrrol-1-yl)phenyl)sulfonyl)acetamide** (73 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL DCE, 60°C overnight. 100.8 mg **46** was obtained (73% yield, white powder, DCM/MeOH = 20:1, R_f = 0.3, **m.p.**: 267 – 268°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.01 (s, 2H), 6.66 (s, 2H), 5.84 (s, 2H), 3.63 (s, 12H), 1.99 (s, 6H), 1.67 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 176.8, 169.2, 143.7, 137.6, 133.8, 128.4, 127.5, 107.0, 53.7, 52.4, 26.3, 12.9. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{24}H_{29}O_{11}N_2S$, 553.1487, found: 553.1492.

Dimethyl 2-(2-(*N*-acetylsulfamoyl)-4-methyl-5-(1H-pyrazol-1-yl)phenyl)malonate (47) and Dimethyl 2-(5-(*N*-acetylsulfamoyl)-3-methyl-2-(1H-pyrazol-1-yl)phenyl)malonate (47')



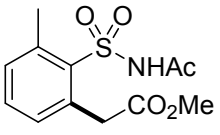
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.4 mg, 20 mol%), ***N-((3-methyl-4-(1H-pyrazol-1-yl)phenyl) sulfonyl)acetamide*** (69.4 mg, 0.25 mmol), **2a** (44 mg, 1.1 equiv), 2.5 mL DCE, 60°C overnight. 15.6 mg **47** was obtained (15% yield, white powder, DCM/MeOH = 20:1, R_f = 0.3), **m.p.**: 83 – 85°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.60 (s, 1H), 8.18 (s, 1H), 8.00 (s, 1H), 7.80 (s, 1H), 7.46 (s, 1H), 6.57 (s, 1H), 5.89 (s, 1H), 3.69 (s, 6H), 2.37 (s, 3H), 1.85 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 170.3, 167.8, 142.4, 141.1, 136.9, 133.4, 132.2, 131.8, 131.6, 129.6, 126.9, 107.3, 53.0, 52.0, 23.8, 18.2. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{17}H_{20}O_7N_3S$, 410.1016, found: 410.1007; 67 mg **47'** was obtained (66% yield, white powder, DCM/MeOH = 20:1, R_f = 0.4), **m.p.**: 157 – 159°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.31 (br s, 1H), 8.01 (d, *J* = 1.8 Hz, 1H), 7.96 (s, 1H), 7.90 (s, 1H), 7.82 (s, 1H), 6.59 (s, 1H), 4.24 (s, 1H), 3.66 (s, 6H), 2.07 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.1, 167.0, 142.6, 141.3, 140.0, 137.5, 132.7, 131.8, 129.2, 126.2, 107.1, 53.1, 51.9, 23.4, 17.3. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{17}H_{20}O_7N_3S$, 410.1016, found: 410.1011.

Dimethyl 2-(5-(*N*-acetylsulfamoyl)-3-methyl-2-(pyridin-2-yl)phenyl)malonate (48')



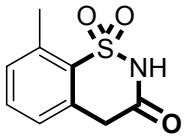
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.4 mg, 20 mol%), ***N-((3-methyl-4-(pyridin-2-yl)phenyl)sulfonyl)acetamide*** (72.4 mg, 0.25 mmol), **2a** (44 mg, 1.1 equiv), 2.5 mL DCE, 60°C overnight. 80 mg **48'** was obtained (76% yield, white powder, DCM/MeOH = 20:1, R_f = 0.4, **m.p.**: 187 – 188°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.18 (s, 1H), 8.71 (d, J = 4.7 Hz, 1H), 7.96 (t, *J* = 7.7 Hz, 1H), 7.86 (s, 1H), 7.81 (s, 1H), 7.50 – 7.45 (m, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 4.41 (s, 1H), 3.63 (s, 6H), 2.10 (s, 3H), 1.95 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.2, 167.5, 155.5, 149.9, 145.0, 139.4, 137.4, 137.1, 132.1, 128.2, 125.3, 124.7, 123.2, 54.1, 52.9, 23.5, 20.2. **HRMS** (ESI): m/z (M + H+) calcd for $C_{19}H_{21}O_7N_2S$, 421.1064, found: 421.1055.

Methyl 2-(2-(*N*-acetylsulfamoyl)-3-methylphenyl)acetate (49)



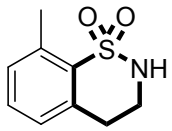
The mixture of **12** (2.803 g, 8.17 mmol), LiCl (520 mg, 12.26 mmol), H_2O (1.634 mL) in 65 mL DMSO was refluxed at 150°C for 3.5 h, then poured into 100 mL sat. NaCl solution and extracted by ethyl acetate. The organic layers were dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography to afford **49** as yellow solid (1.304 g, 56% yield, EAOAc/ Petroleum ether = 1:2, R_f = 0.5). **m.p.**: 152 – 153°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.23 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 4.18 (s, 2H), 3.57 (s, 3H), 2.64 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 171.5, 169.4, 139.1, 136.5, 136.2, 132.7, 132.3, 132.0, 51.4, 40.1, 23.0, 21.7. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{12}H_{16}O_5NS$, 286.0744, found: 286.0732.

8-Methyl-2H-benzo[e][1,2]thiazin-3(4H)-one 1,1-dioxide (50)



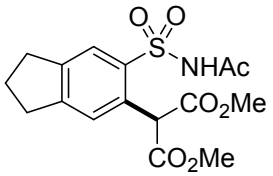
The mixture of **49** (163 mg, 0.57 mmol) and *p*-TsOH (11 mg, 0.057 mmol) in 20 mL toluene was refluxed at 150°C overnight, then poured into 30 mL sat. NaCl solution and extracted by ethyl acetate. The organic layers were dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography to afford **50** as light yellow solid (115.5 mg, 96% yield, EAOAc/ Petroleum ether = 1:2, R_f = 0.2). **m.p.**: 213 – 215°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.51 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 2H), 4.01 (s, 2H), 2.60 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 169.6, 134.3, 134.1, 132.2, 132.1, 131.0, 127.1, 37.3, 19.4. **HRMS** (ESI): m/z (M + H^+) calcd for $C_9H_{10}O_3NS$, 212.0375, found: 212.0371.

8-Methyl-3,4-dihydro-2H-benzo[e][1,2]thiazine 1,1-dioxide (51)



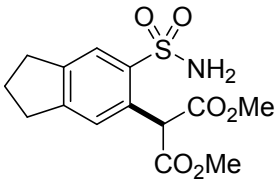
The mixture of **50** (32 mg, 0.15 mmol) and $LiAlH_4$ (12 mg, 0.3 mmol) in 5 mL dry THF was stirred at room temperature for 1h. Solvent was removed in *vacuo*, and the residue was purified by silica gel chromatography to afford **51** as light yellow solid (26.5 mg, 90% yield, EAOAc/ Petroleum ether = 1:2, R_f = 0.3). **m.p.**: 163 – 164°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.6 Hz, 1H), 7.12 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 3.71 (s, 2H), 2.94 (t, *J* = 5.9 Hz, 2H), 2.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.2, 137.1, 136.08, 131.5, 131.0, 127.5, 41.9, 30.2, 20.4. **HRMS** (ESI): m/z (M + H^+) calcd for $C_9H_{12}O_2NS$, 198.0583, found: 198.0580.

Dimethyl 2-(6-(*N*-acetylsulfamoyl)-2,3-dihydro-1H-inden-5-yl)malonate (52)



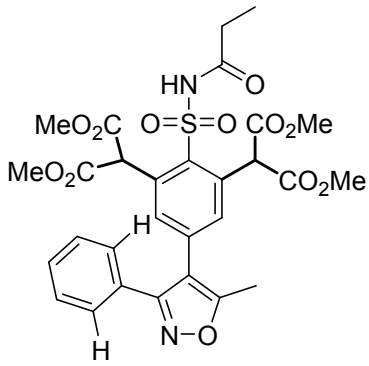
$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((2,3-dihydro-1H-inden-5-yl)sulfonyl)acetamide** (59.7 mg, 0.25 mmol), **2a** (79 mg, 0. 5 mmol), 2.5 mL DCE, 60°C for 1h. 56.1 mg **52** was obtained (61% yield, white powder, EAOAc/ Petroleum ether = 1:1, R_f = 0.3), **m.p.**: 165 – 166°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.78 (s, 1H), 7.18 (s, 1H), 5.96 (s, 1H), 3.65 (s, 6H), 2.94 –2.86 (s, 4H), 2.14 – 2.00 (m, 2H), 1.73 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-*d6*) δ 172.0, 168.6, 148.2, 143.5, 139.3, 129.0, 125.6, 125.4, 52.7, 52.6, 32.3, 32.0, 25.0, 24.7. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{16}H_{20}O_7NS$, 370.0955, found: 370.0950.

Dimethyl 2-(6-sulfamoyl-2,3-dihydro-1H-inden-5-yl)malonate (53)



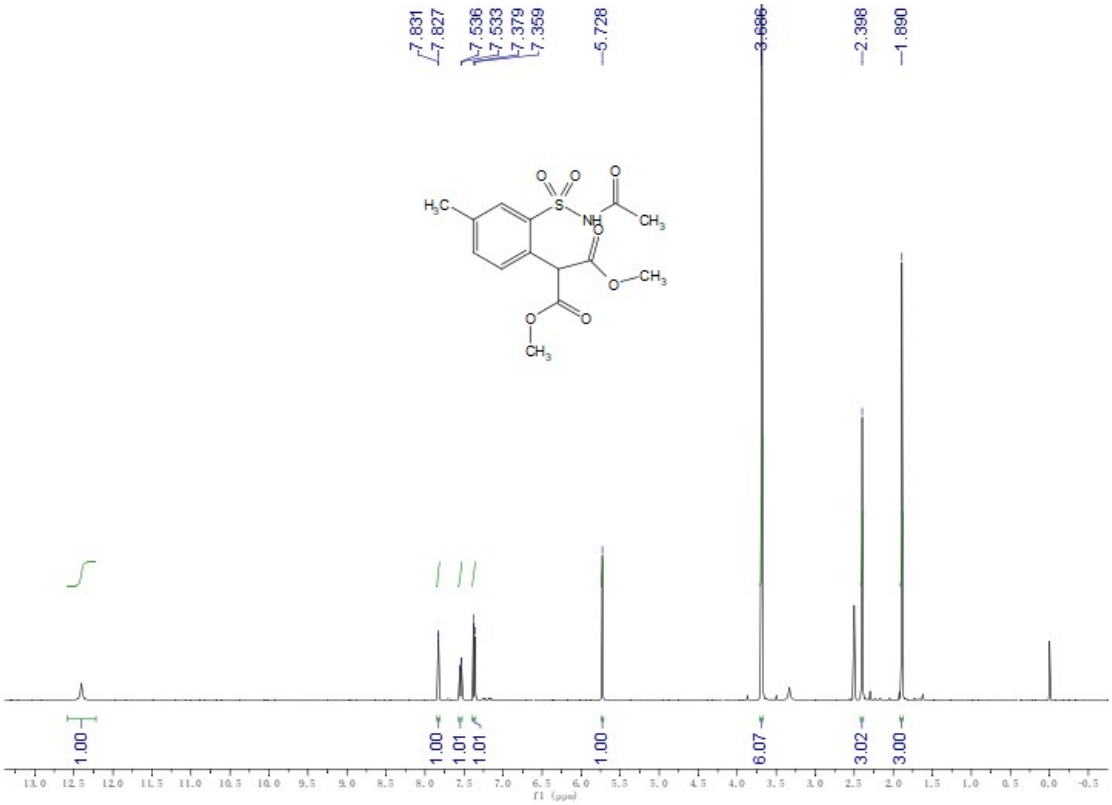
52 (55mg, 0.15 mmol) was dissolved in 3.0 mL MeOH, and 2 drops con. H_2SO_4 was added, the reaction mixture was stirred at room temperature for 4h. 47.5 mg **53** was obtained (97% yield, white solid, EAOAc/ Petroleum ether = 1:1, R_f = 0.3), **m.p.**: 174 – 176°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 7.77 (s, 1H), 7.56 (s, 2H), 7.21 (s, 1H), 5.72 (s, 1H), 3.67 (s, 6H), 2.92 (t, *J* = 7.4 Hz, 4H), 2.06 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 168.4, 148.3, 144.2, 140.5, 128.5, 126.1, 123.2, 53.2, 52.7, 32.3, 32.0, 25.0. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{14}H_{18}O_6NS$, 328.0849, found: 328.0843.

Tetramethyl 2,2'-(5-(5-methyl-3-phenylisoxazol-4-yl)-2-(*N*-propionylsulfamoyl)-1,3-phenylene) dimalonate (54)

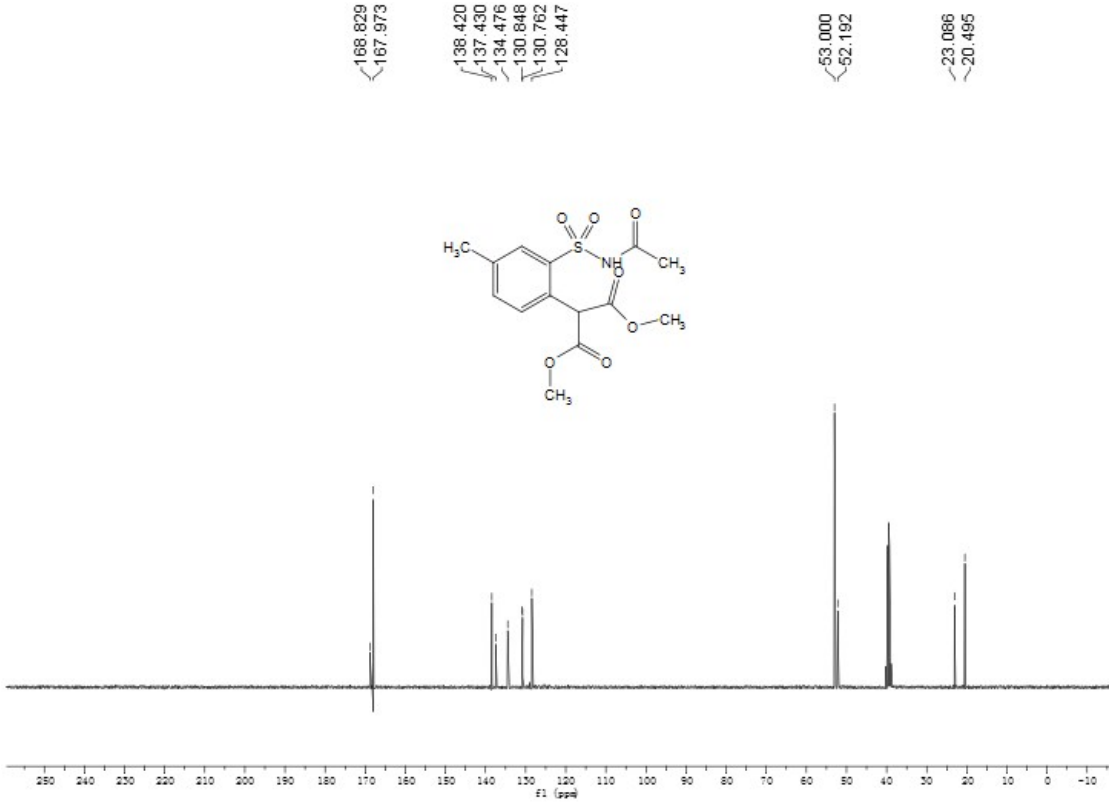


$[RhCp^*Cl_2]_2$ (7.8 mg, 5.0 mol%), AgOAc (8.3 mg, 20 mol%), ***N*-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)propionamide** (92.5 mg, 0.25 mmol), **2a** (79 mg, 0.5 mmol), 2.5 mL toluene, 60°C overnight. 127.6 mg **54** was obtained (81% yield, white powder, EAOAc/ Petroleum ether = 3:1, R_f = 0.3, **m.p.**: 215 – 216°C. **^{1}H NMR** (400 MHz, DMSO-*d6*) δ 12.86 (s, 1H), 7.53 – 7.49 (m, 1H), 7.48 – 7.43 (m, 2H), 7.38 – 7.35 (m, 2H), 7.24 (s, 2H), 6.05 (s, 2H), 3.60 (s, 12H), 2.28 – 2.20 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (151 MHz, DMSO-*d6*) δ 174.7, 170.8, 169.1, 168.6, 160.8, 135.0, 134.0, 131.8, 130.3, 129.5, 128.6, 128.4, 113.5, 54.3, 53.3, 29.5, 12.0, 9.0. **HRMS** (ESI): m/z (M + H^+) calcd for $C_{29}H_{31}O_{12}N_2S$, 631.1592, found: 631.1578.

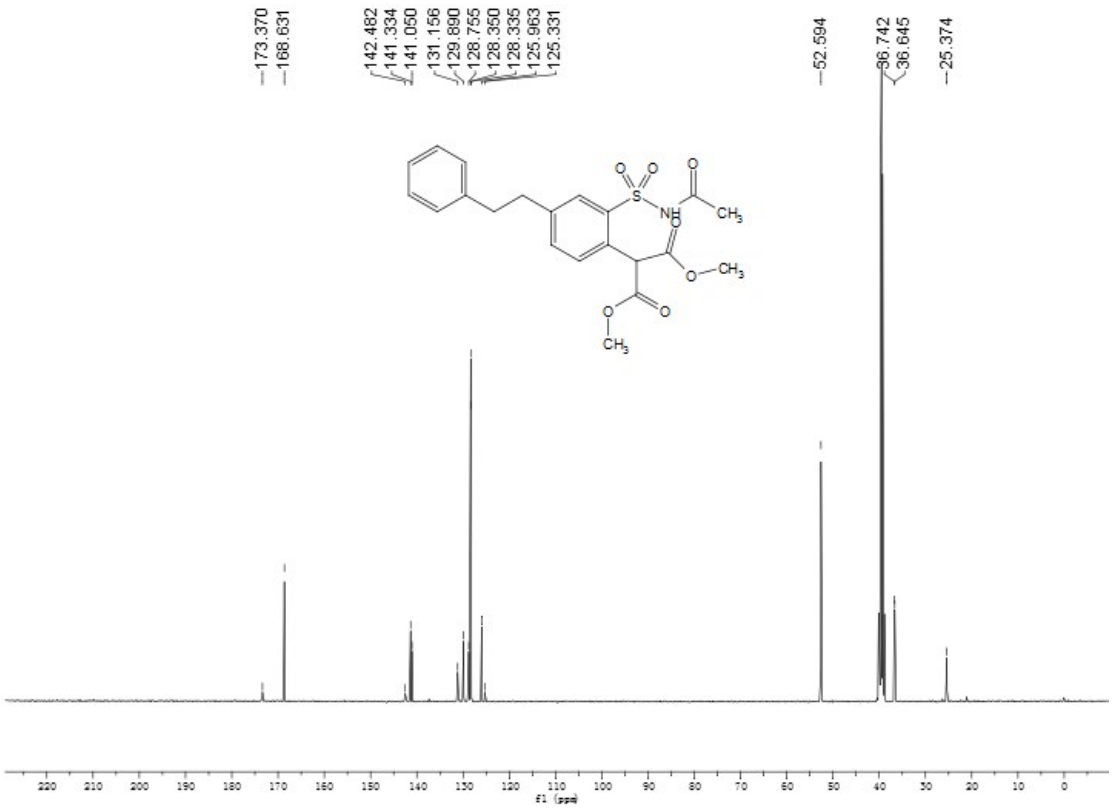
^{1}H NMR of compound **3**



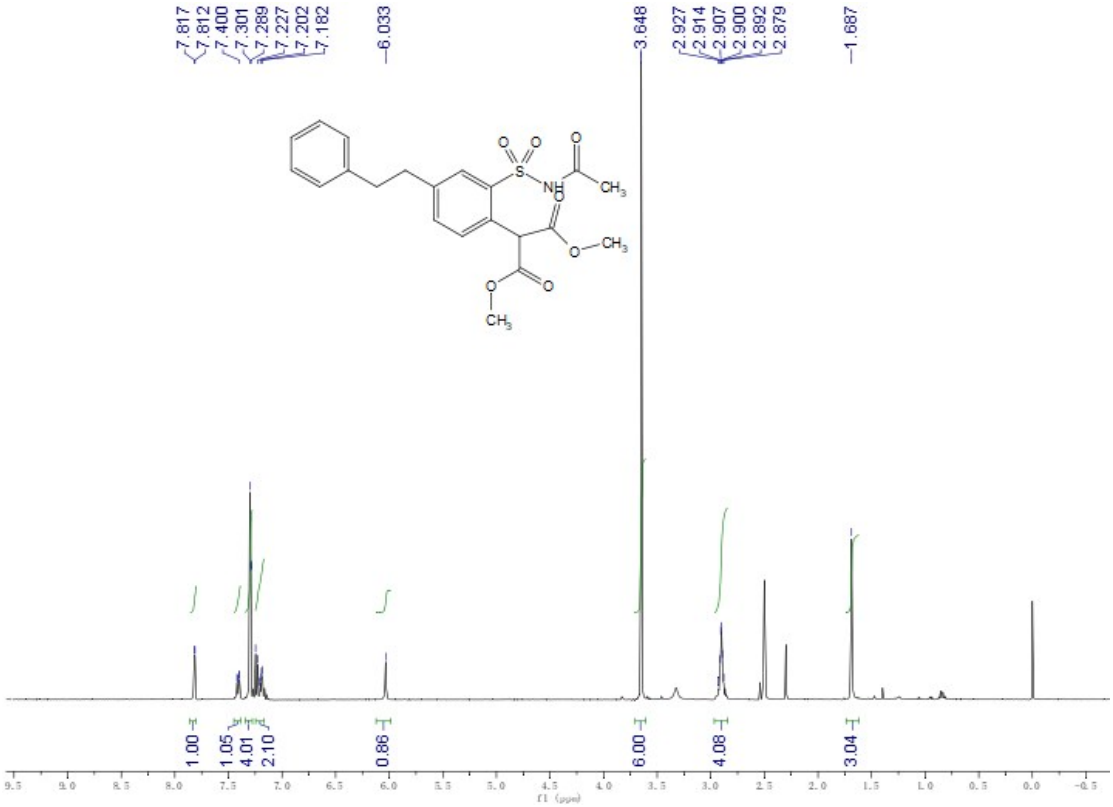
^{13}C NMR of compound **3**



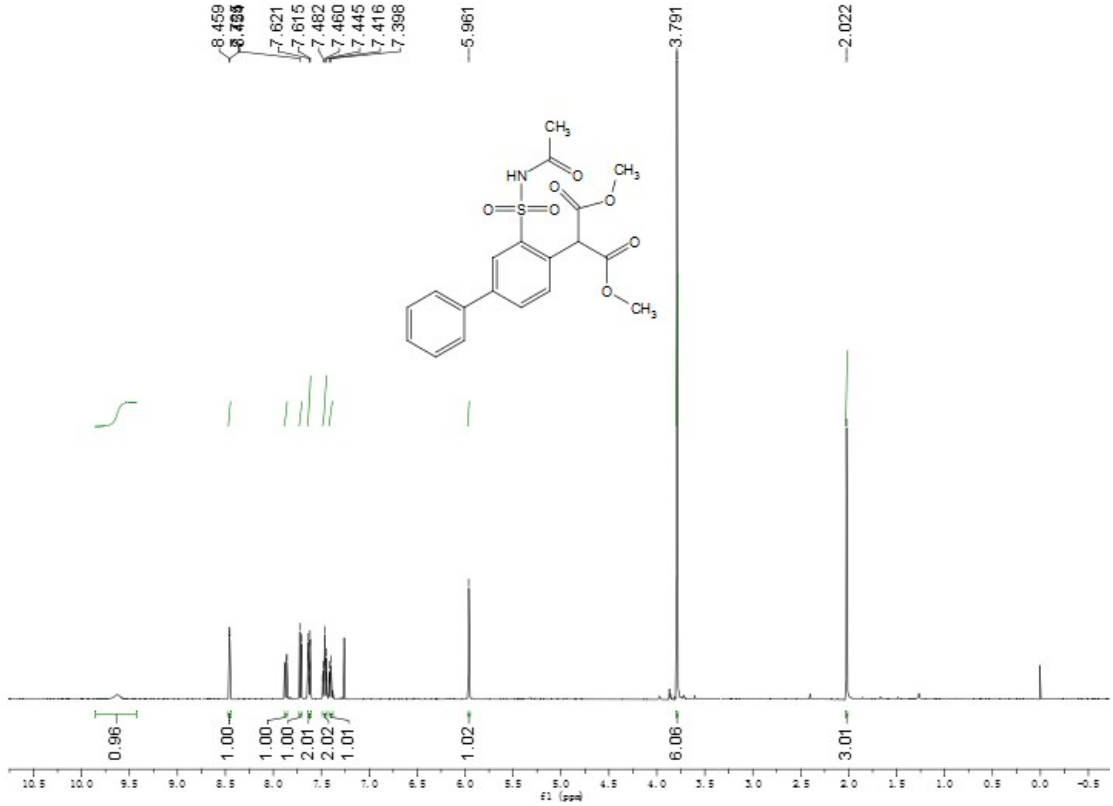
^{1}H NMR of compound **4**



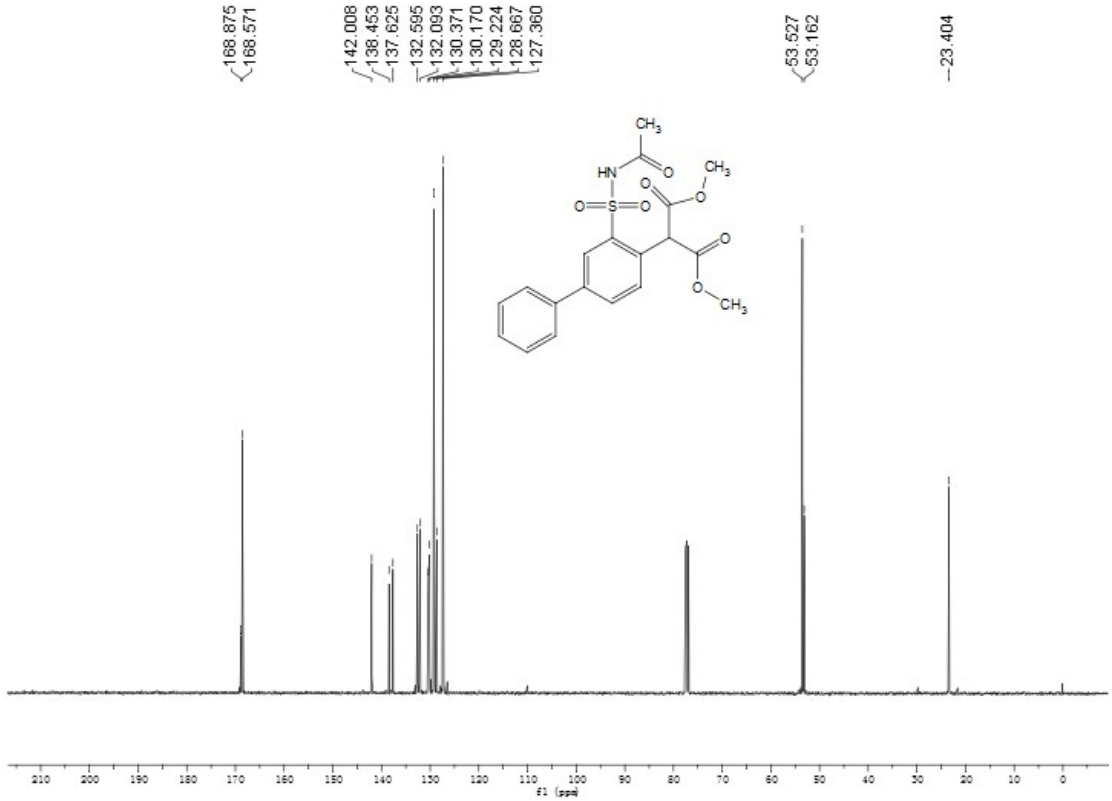
^{13}C NMR of compound **4**



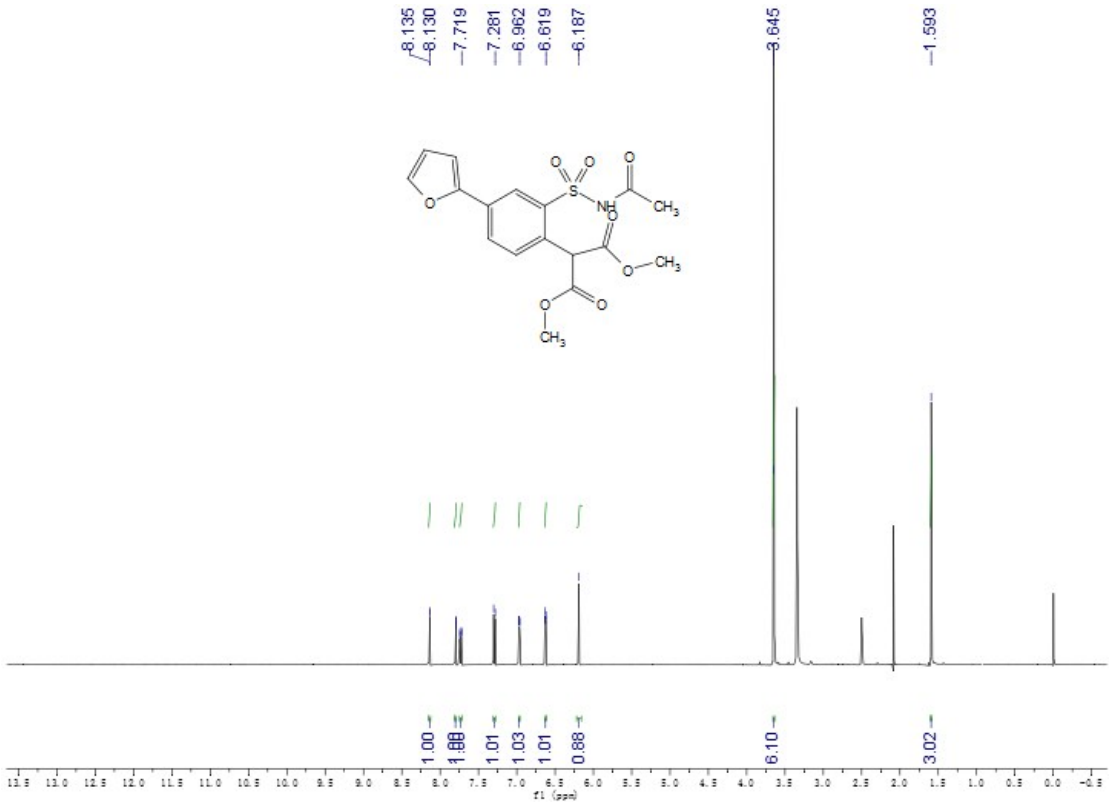
^{1}H NMR of compound **5**



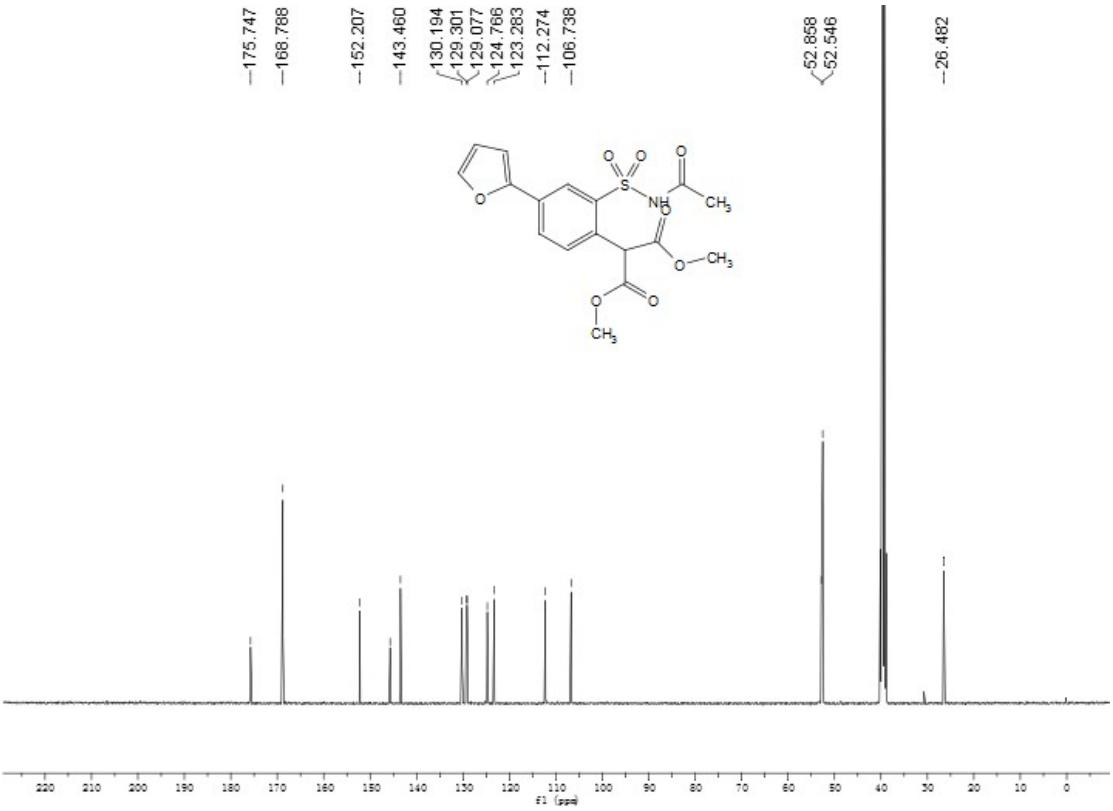
^{13}C NMR of compound **5**



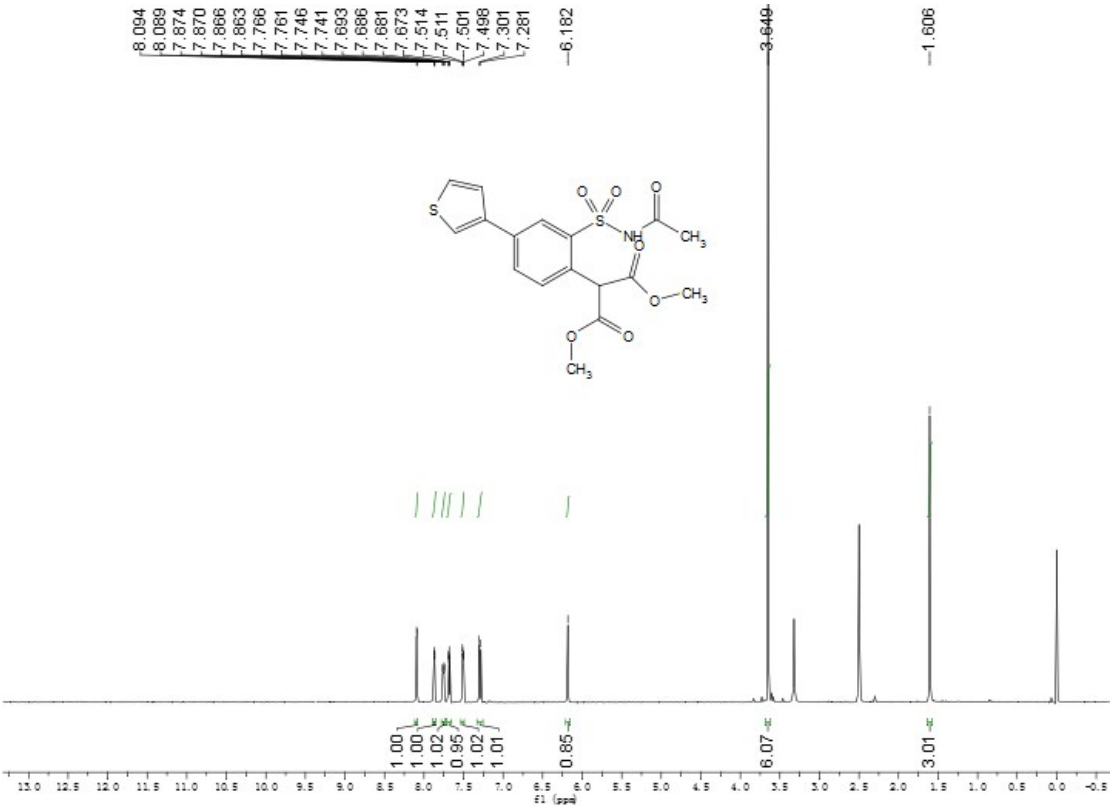
^{1}H NMR of compound **6**



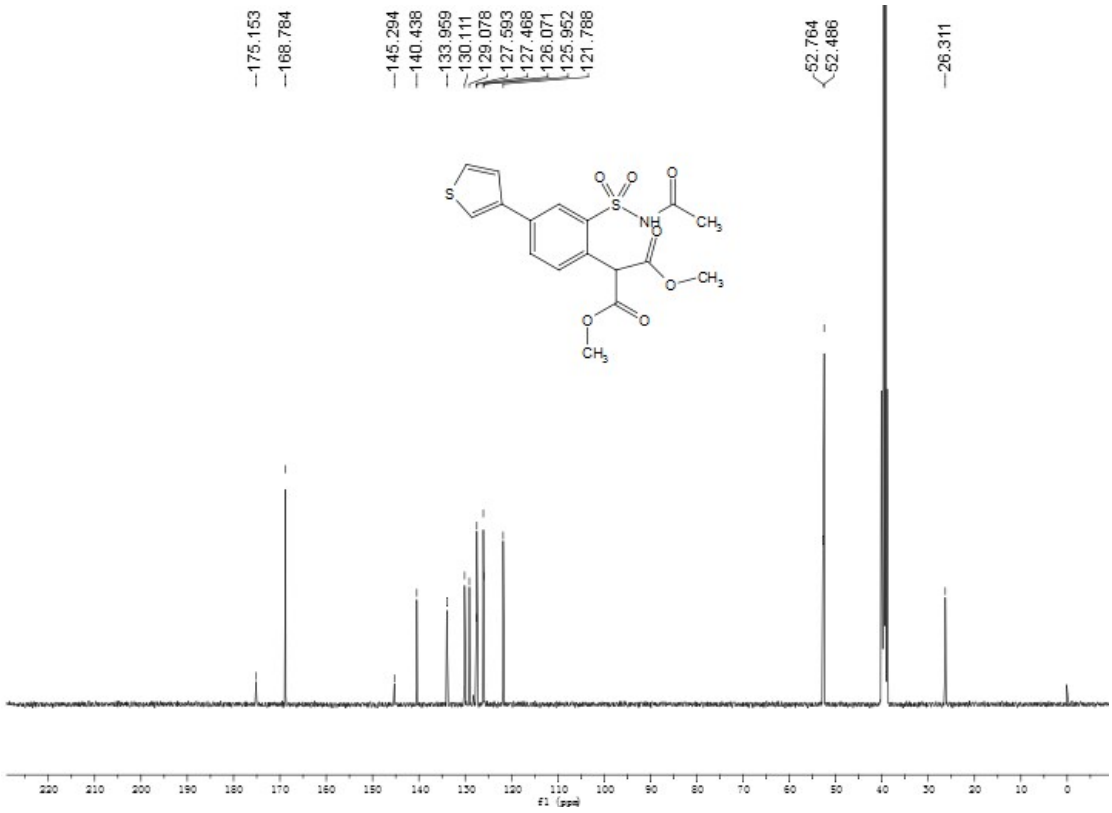
^{13}C NMR of compound **6**



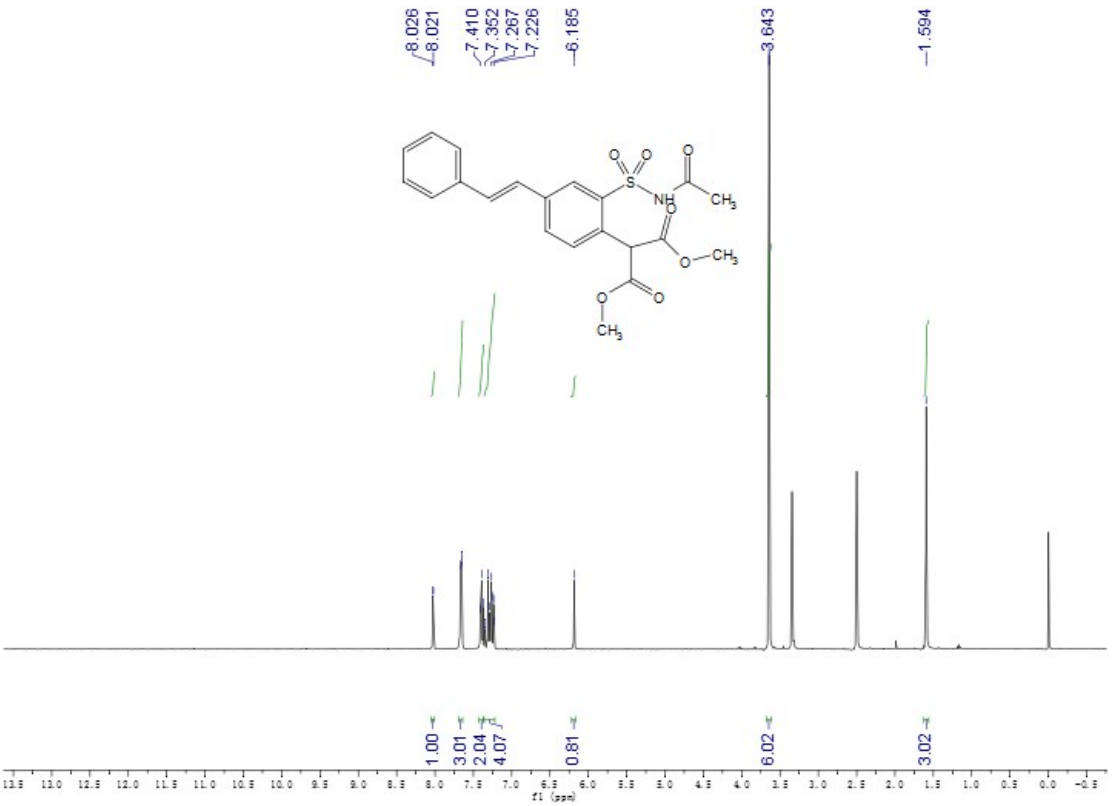
^{1}H NMR of compound **7**



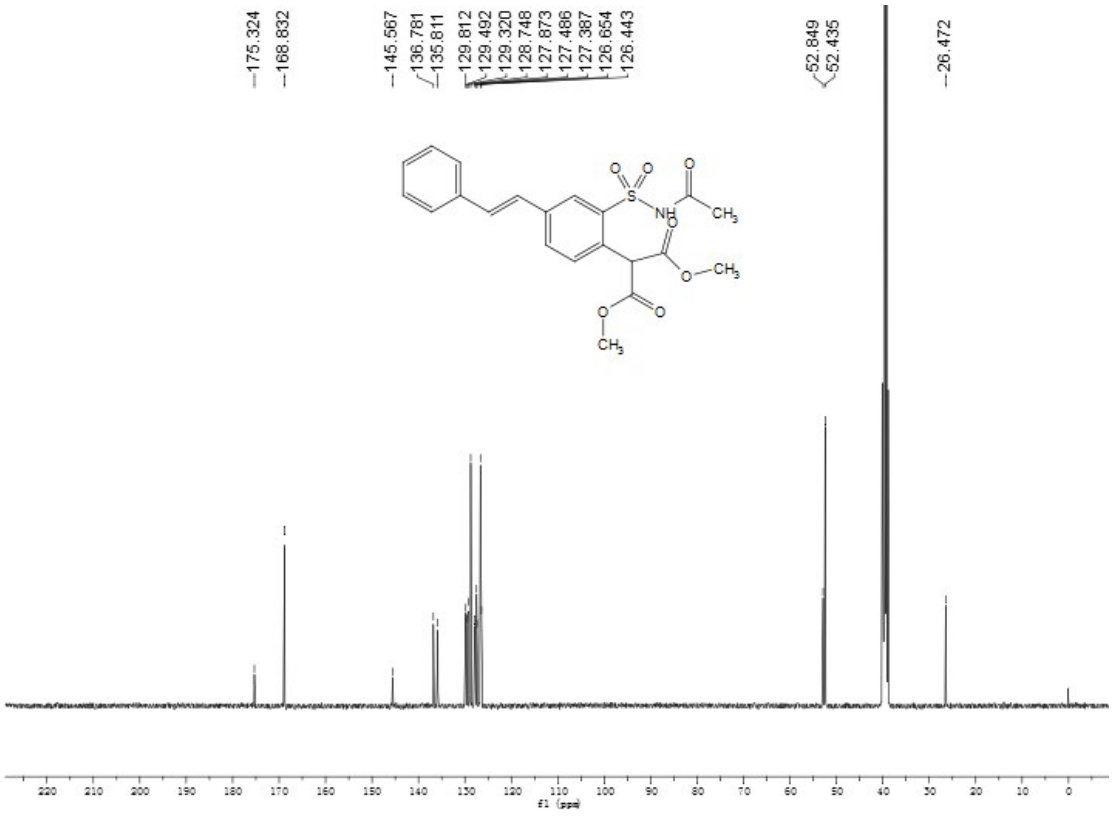
^{13}C NMR of compound **7**



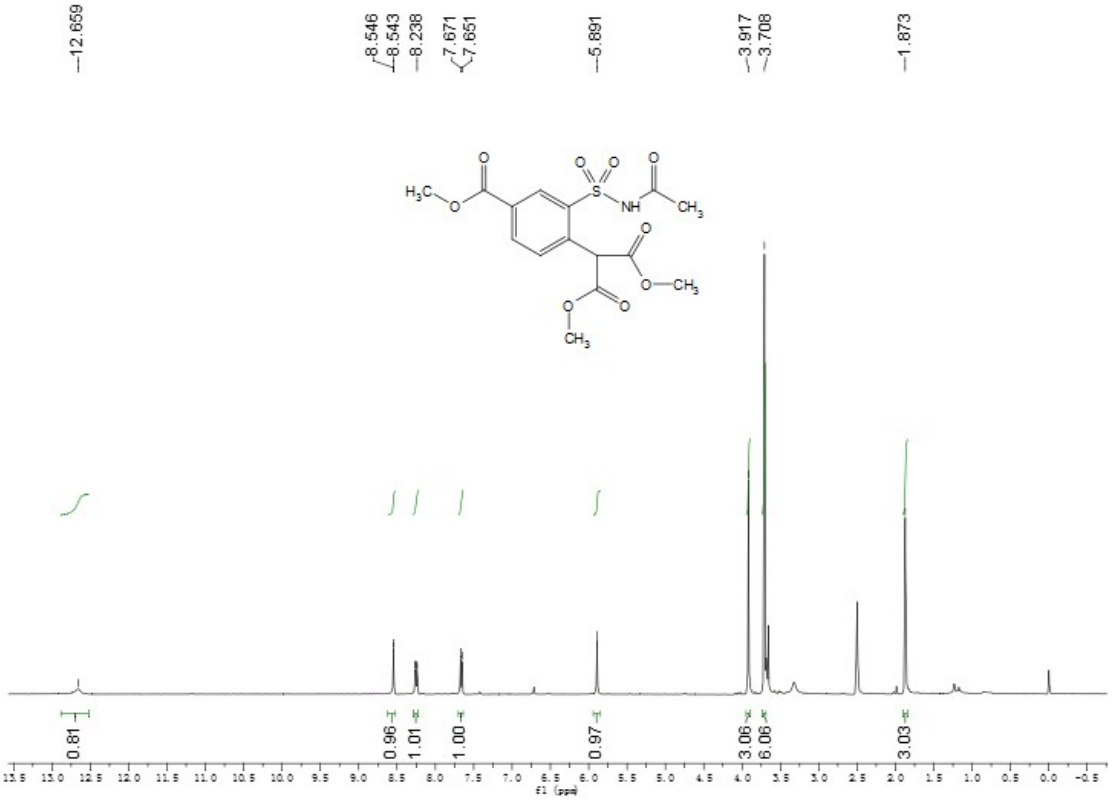
^{1}H NMR of compound **8**



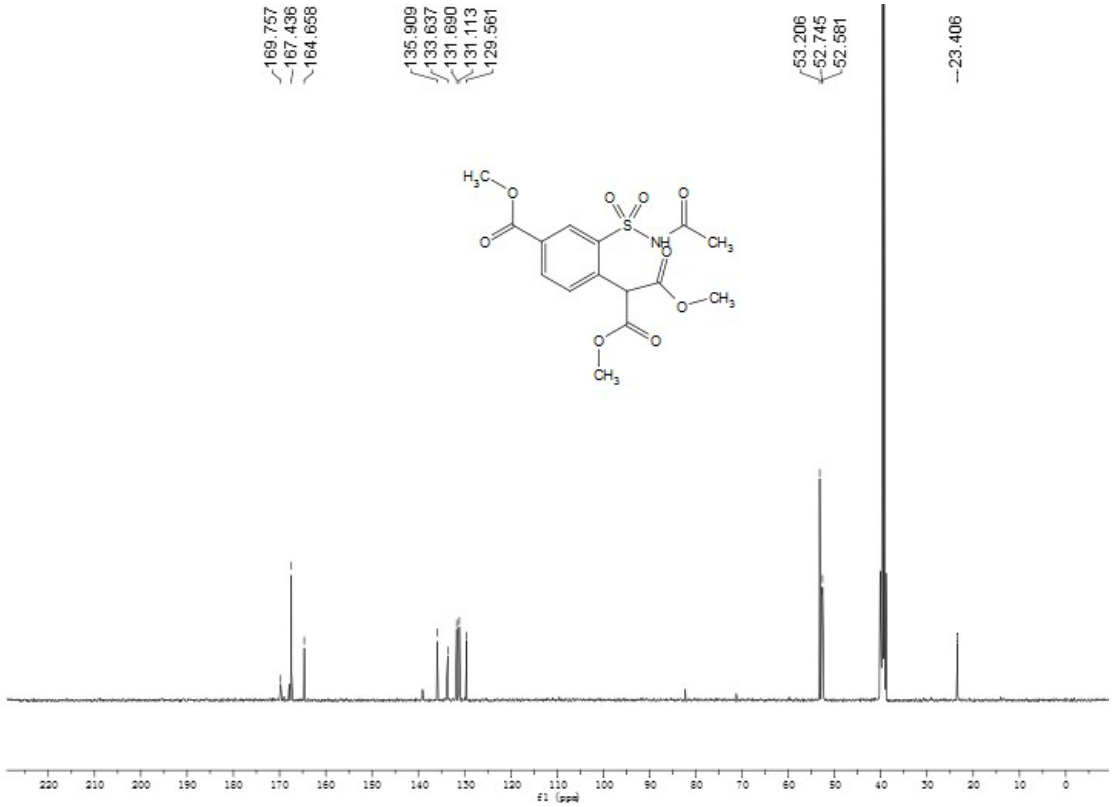
^{13}C NMR of compound **8**



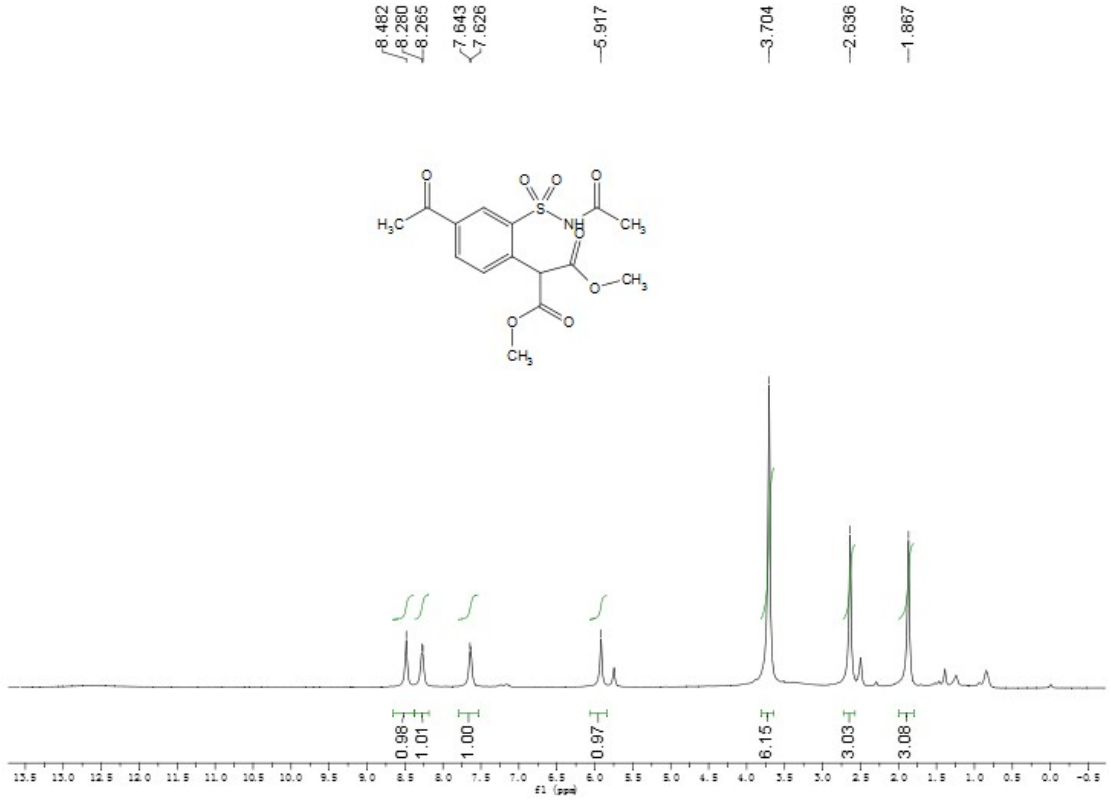
^{1}H NMR of compound **9**



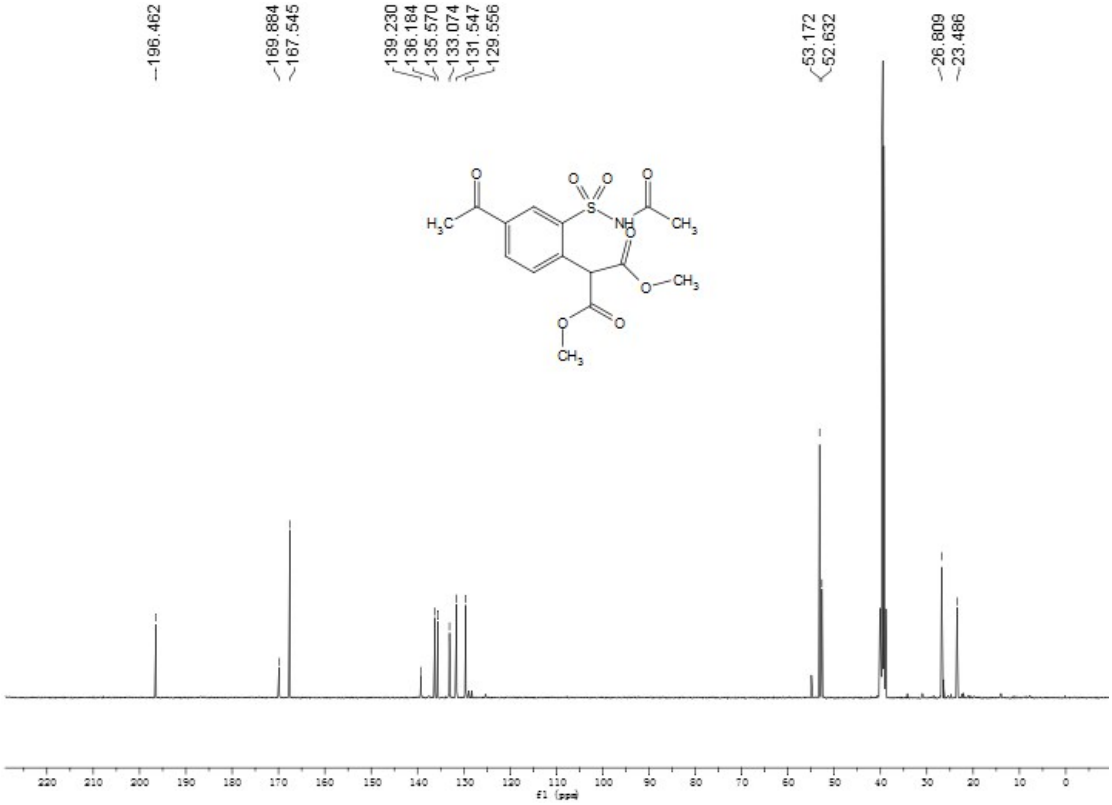
^{13}C NMR of compound **9**



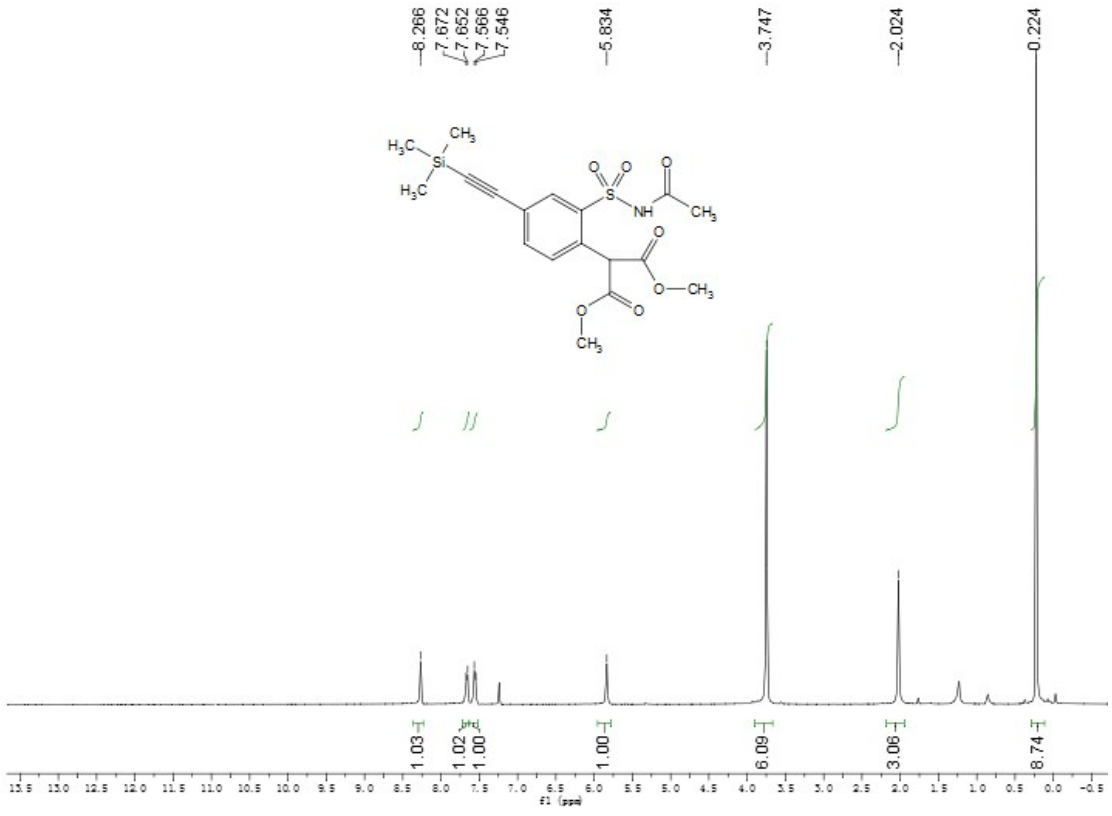
^{1}H NMR of compound **10**



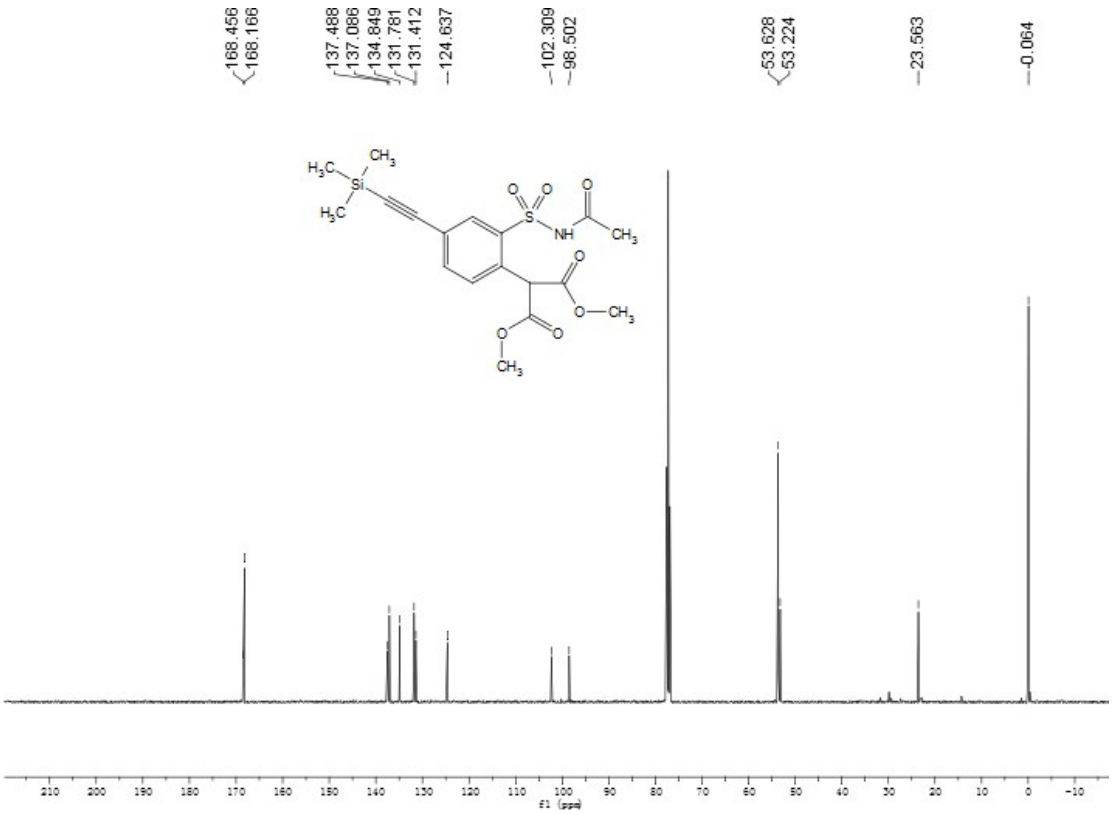
^{13}C NMR of compound **10**



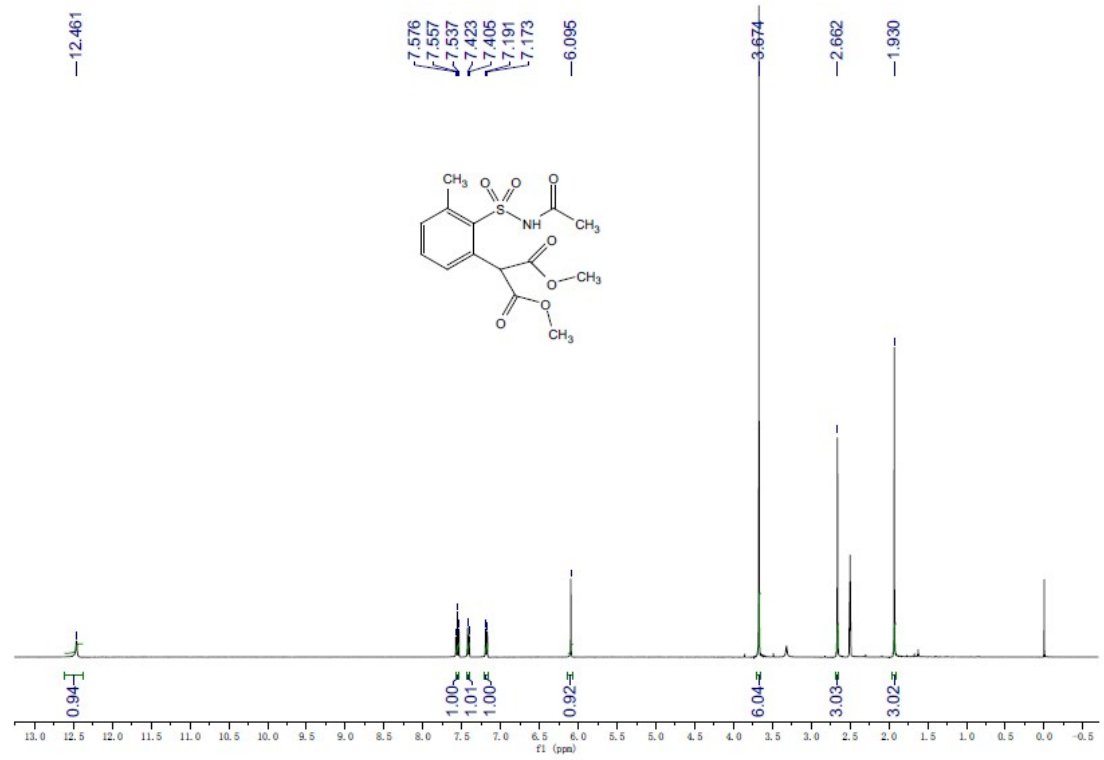
^{1}H NMR of compound **11**



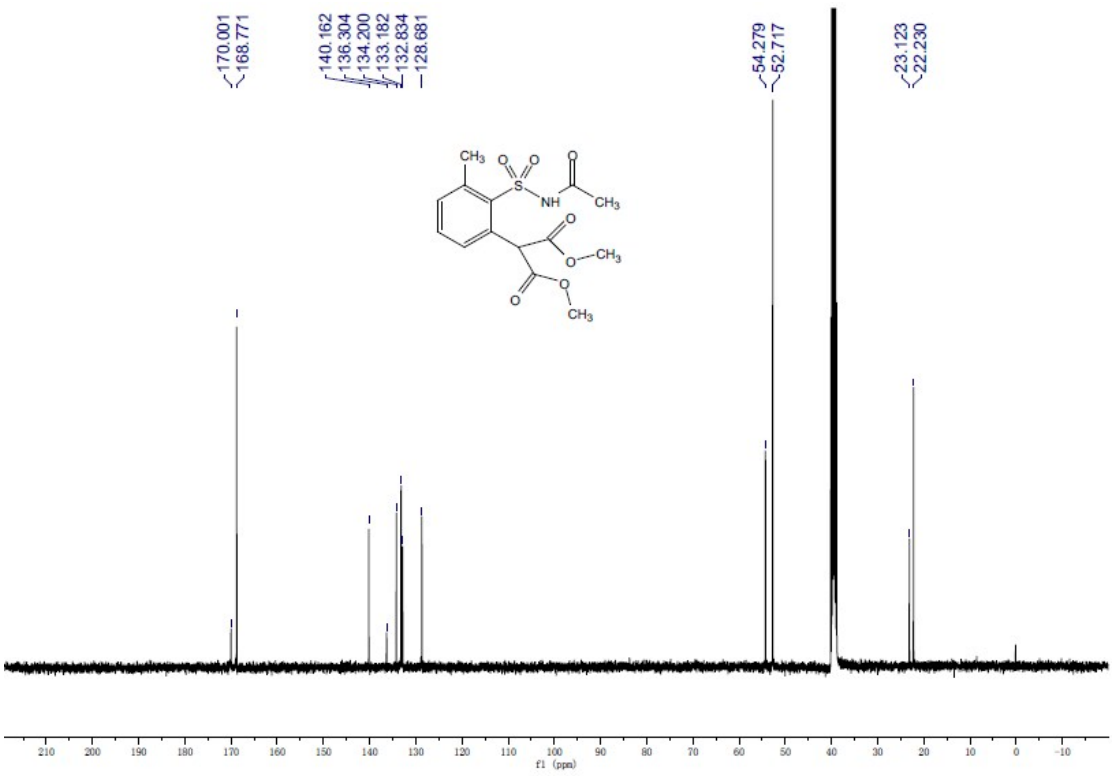
^{13}C NMR of compound **11**



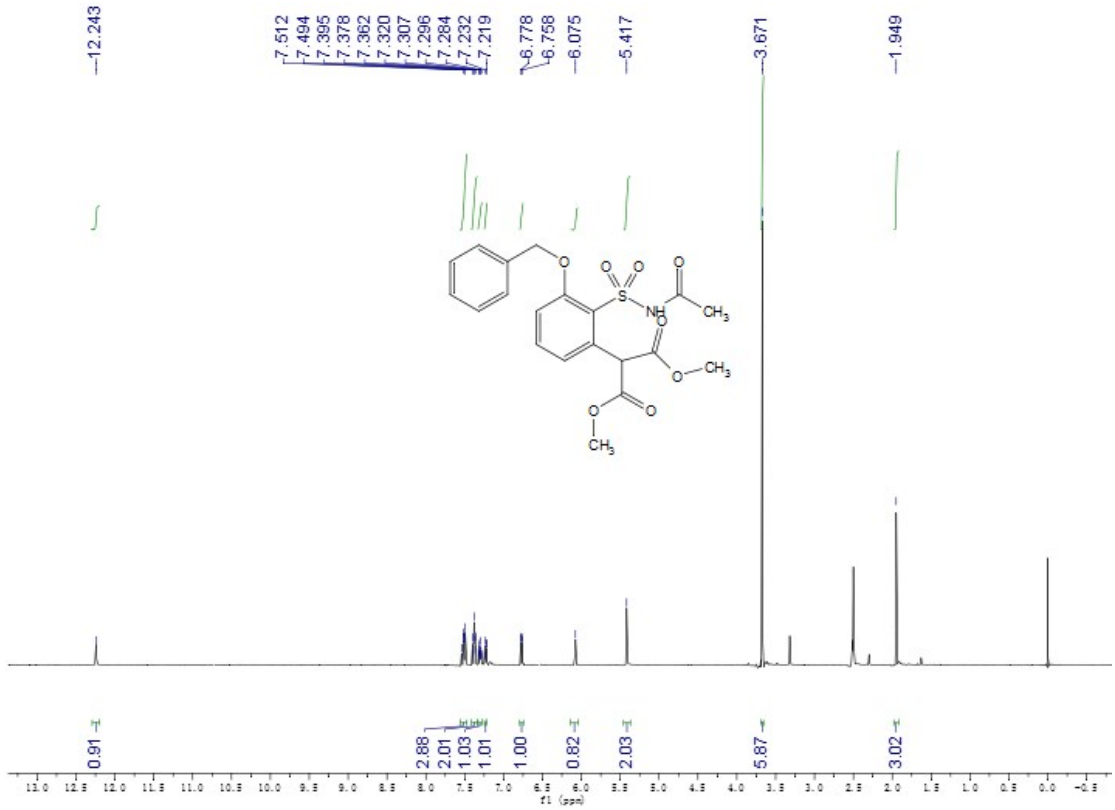
^{1}H NMR of compound **12**



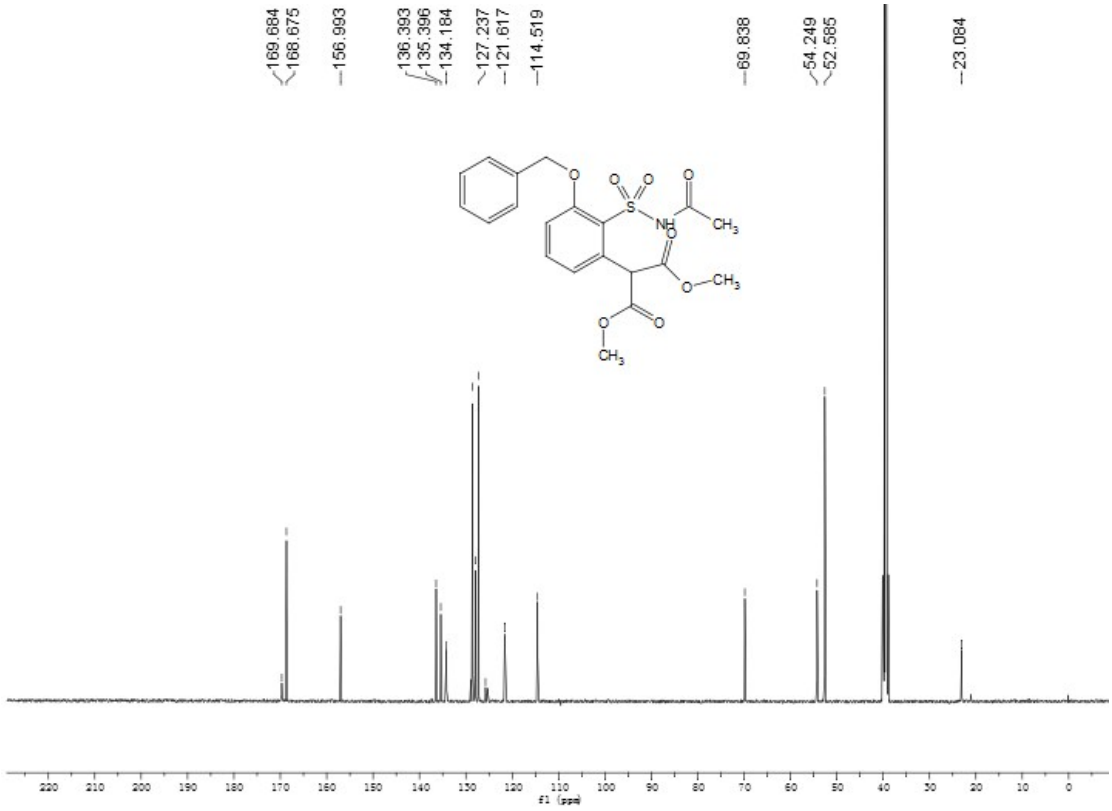
^{13}C NMR of compound **12**



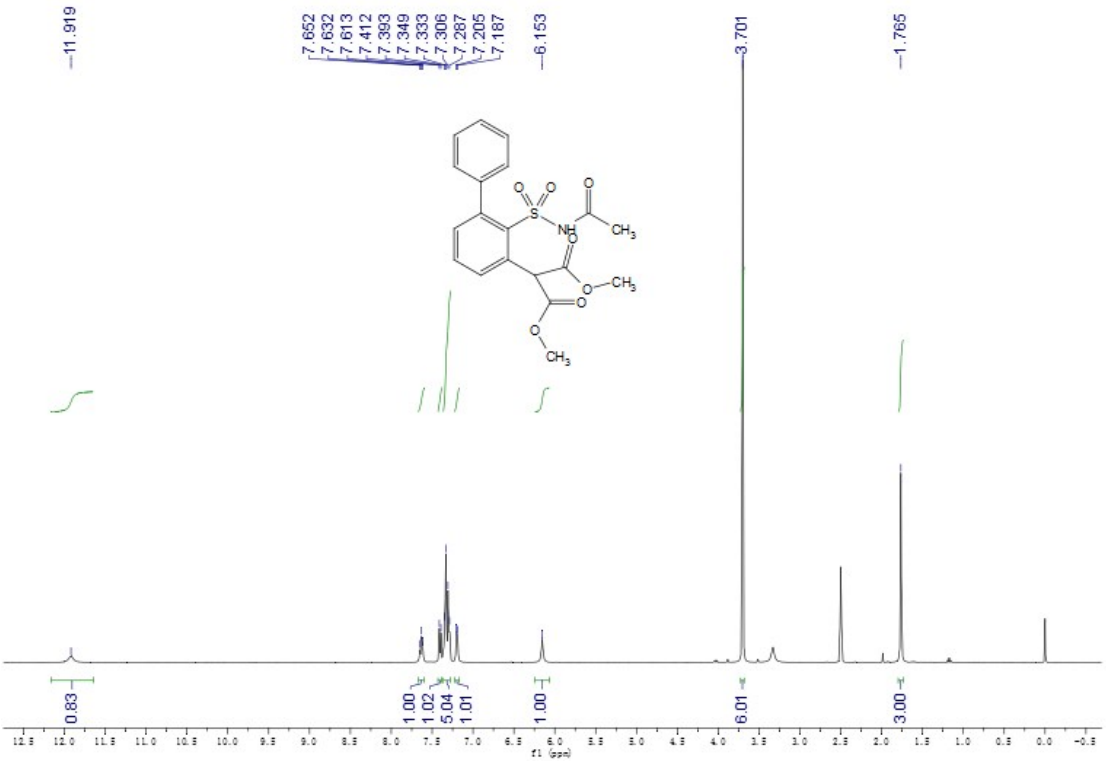
^{1}H NMR of compound **13**



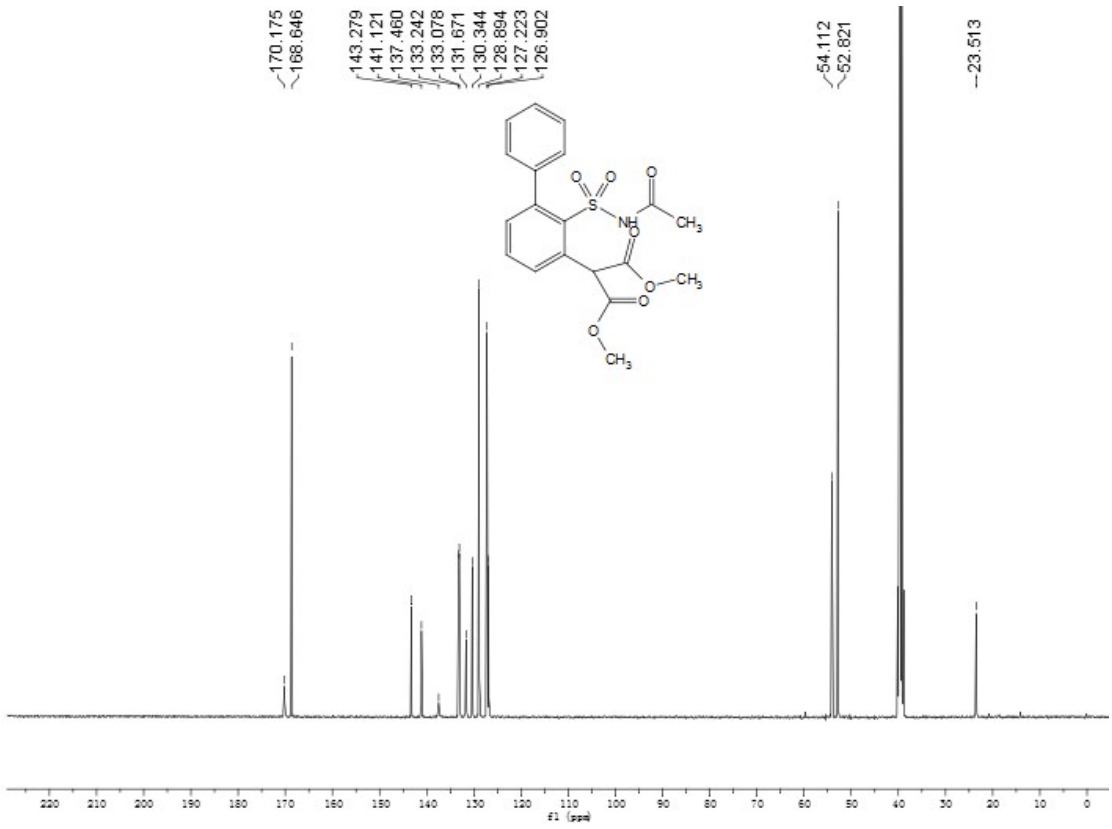
^{13}C NMR of compound **13**



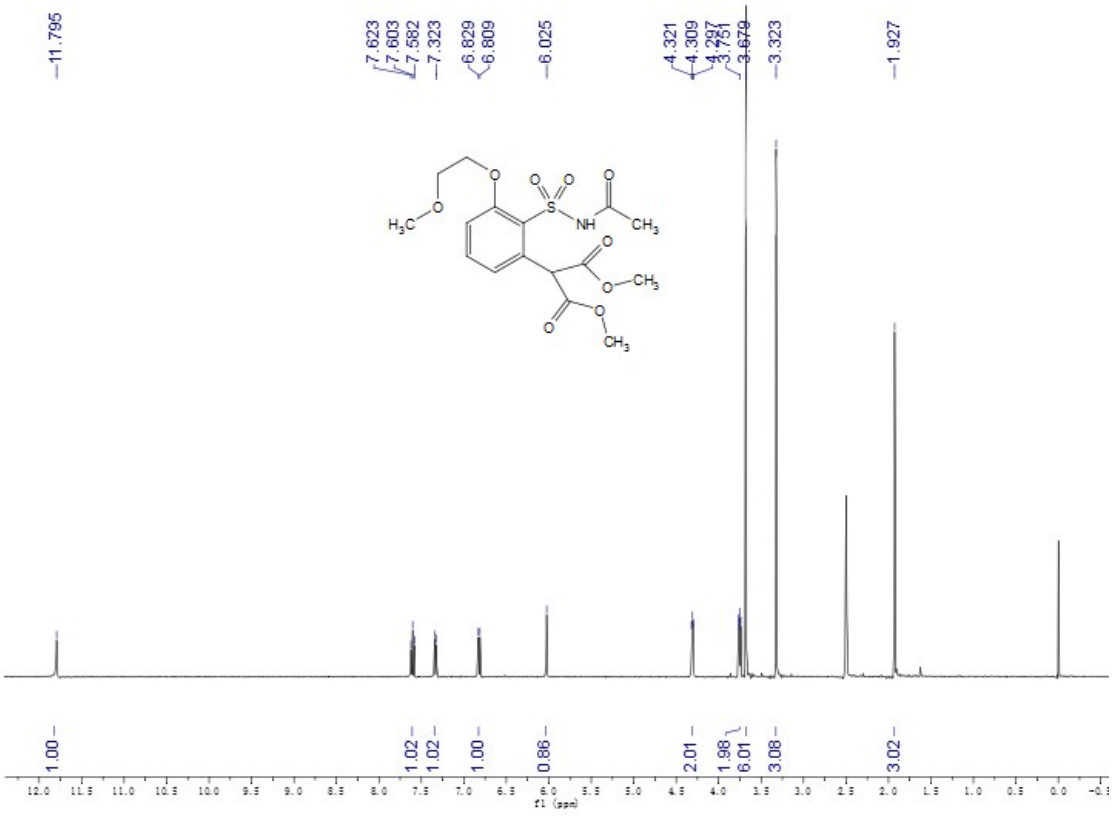
^{1}H NMR of compound **14**



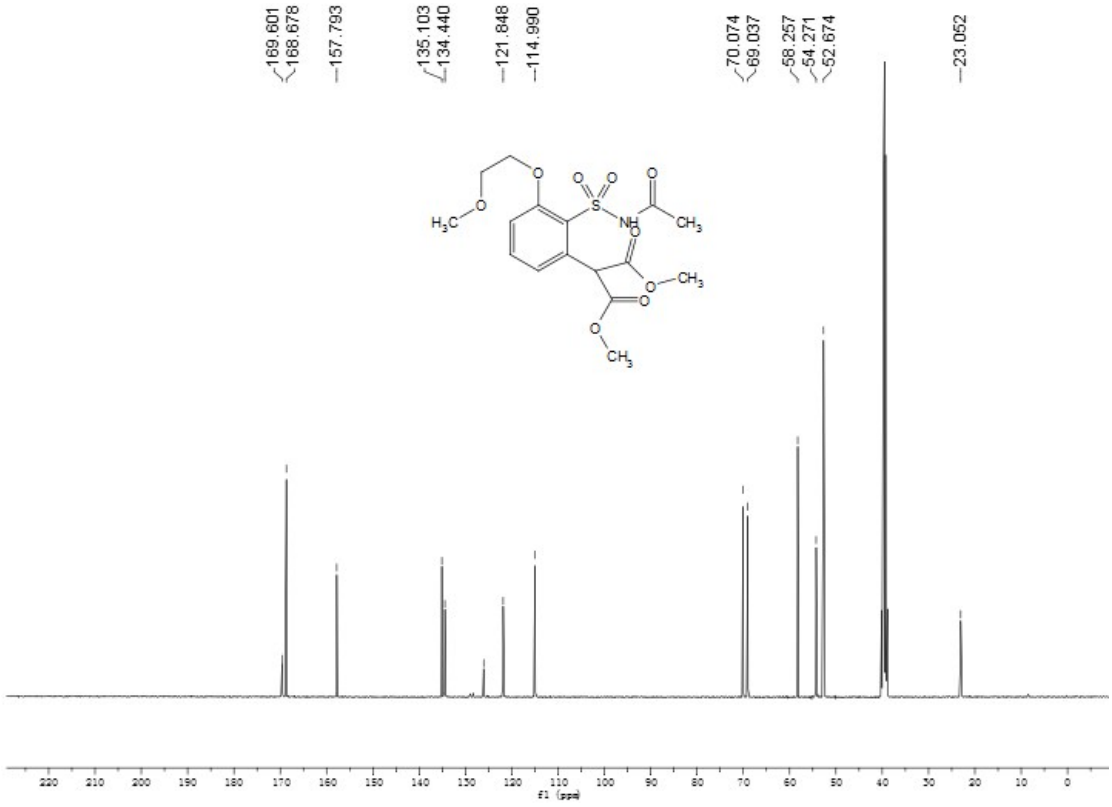
^{13}C NMR of compound **14**



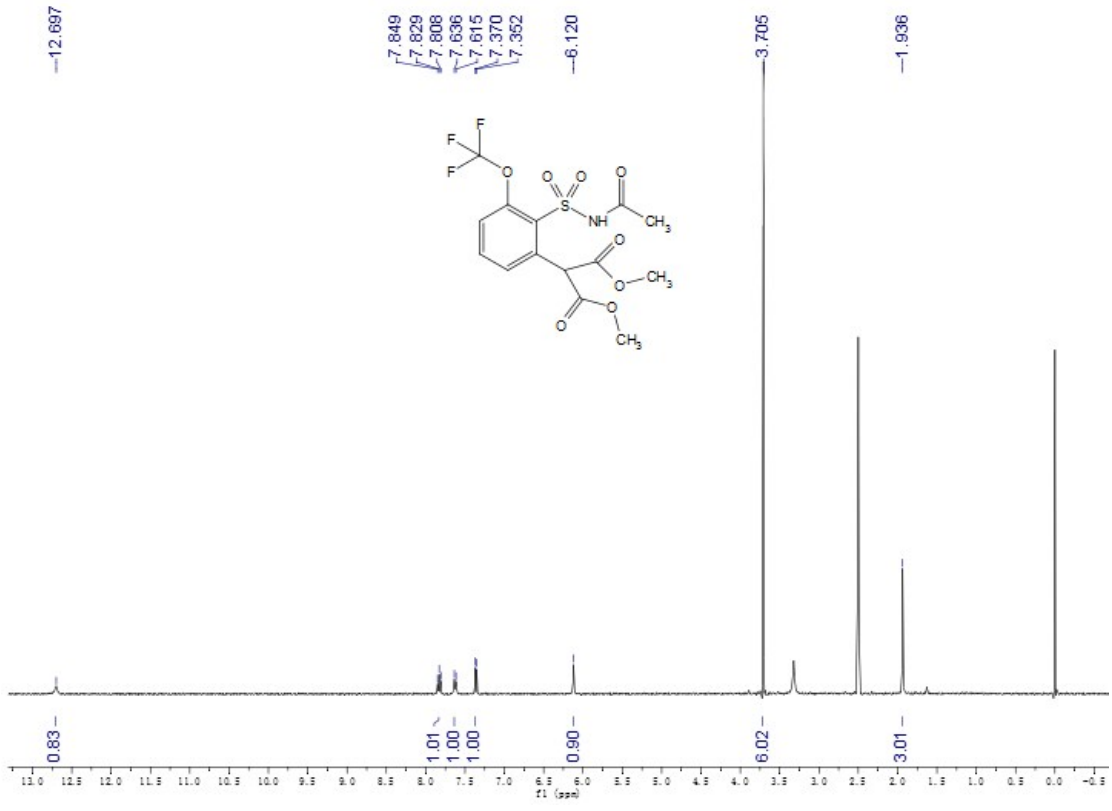
^{1}H NMR of compound **15**



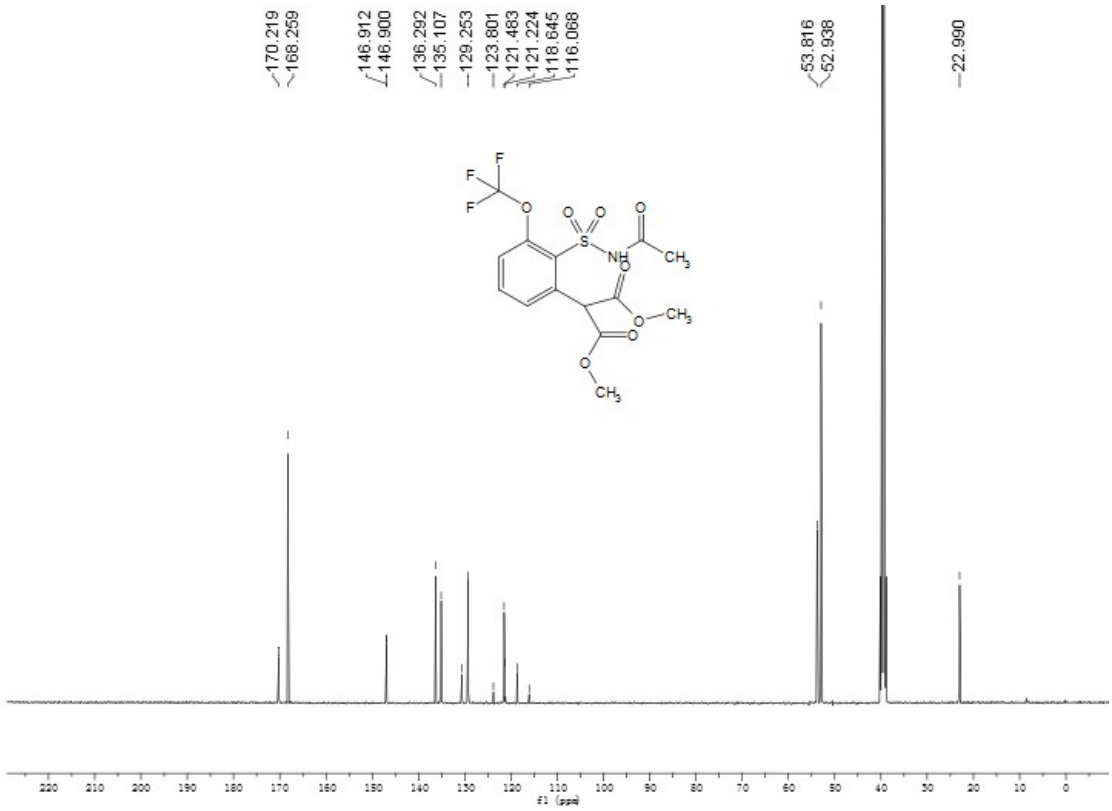
^{13}C NMR of compound **15**



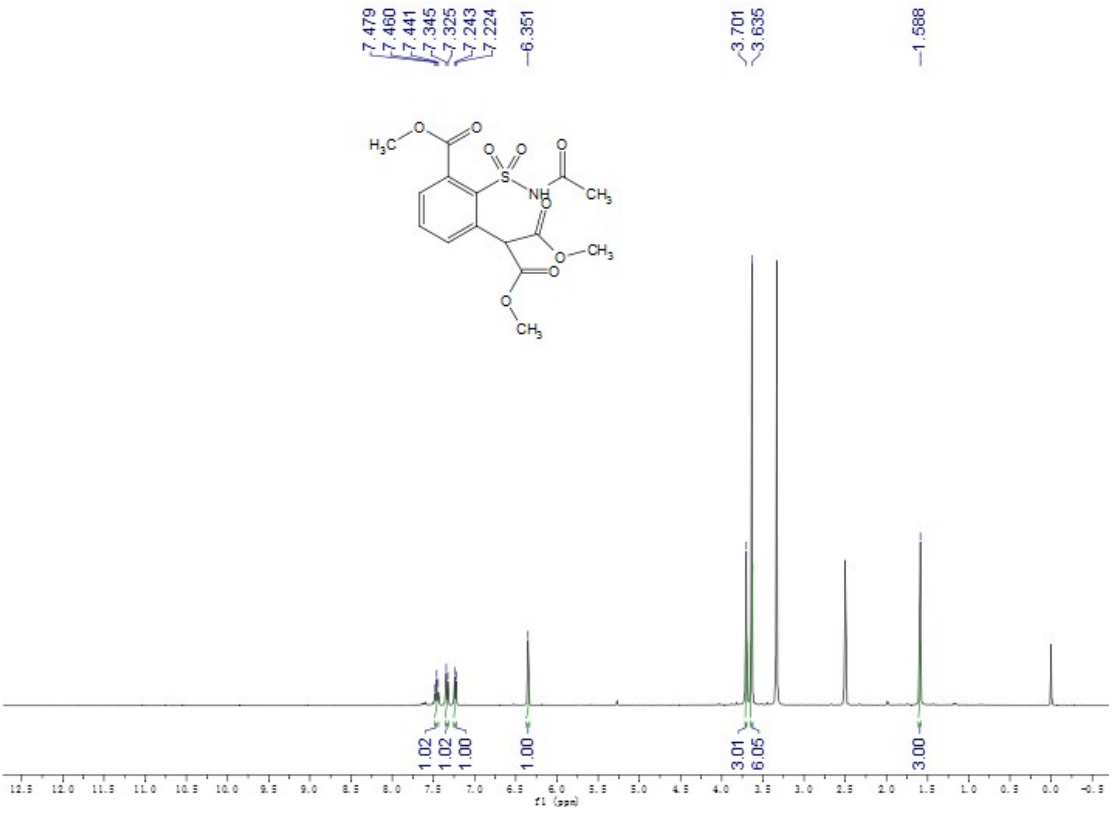
^{1}H NMR of compound **16**



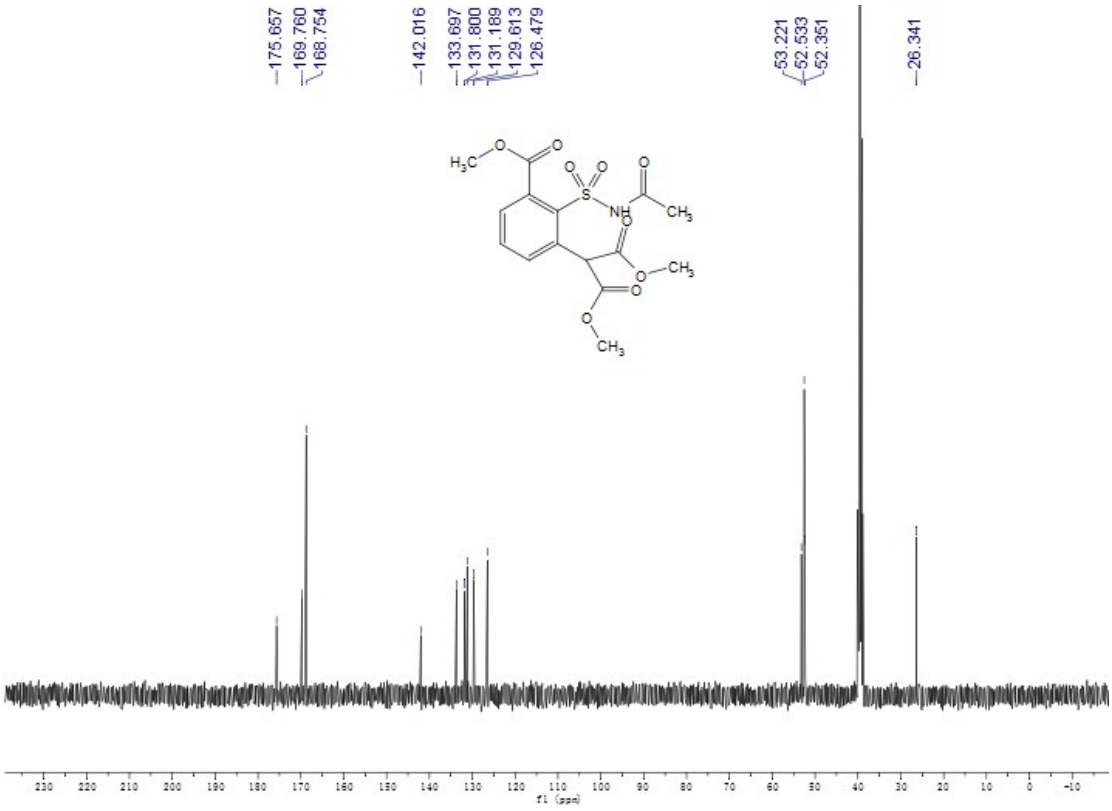
^{13}C NMR of compound **16**



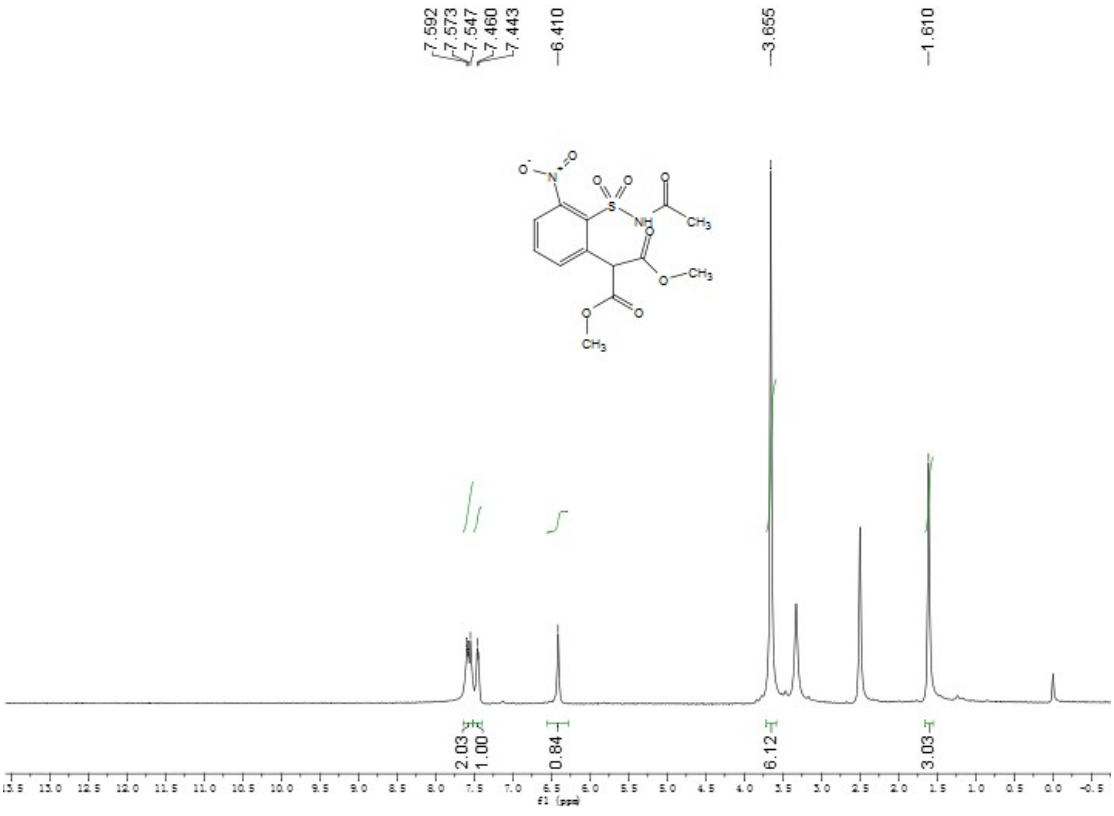
^{1}H NMR of compound **17**



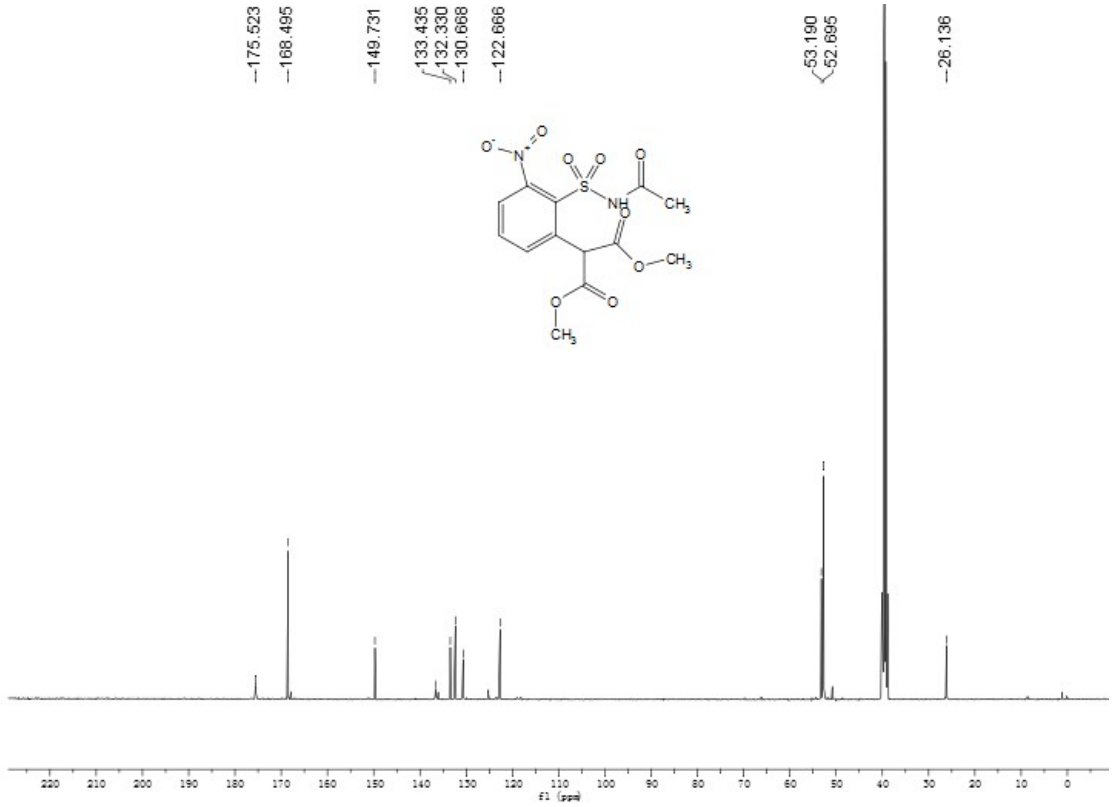
^{13}C NMR of compound **17**



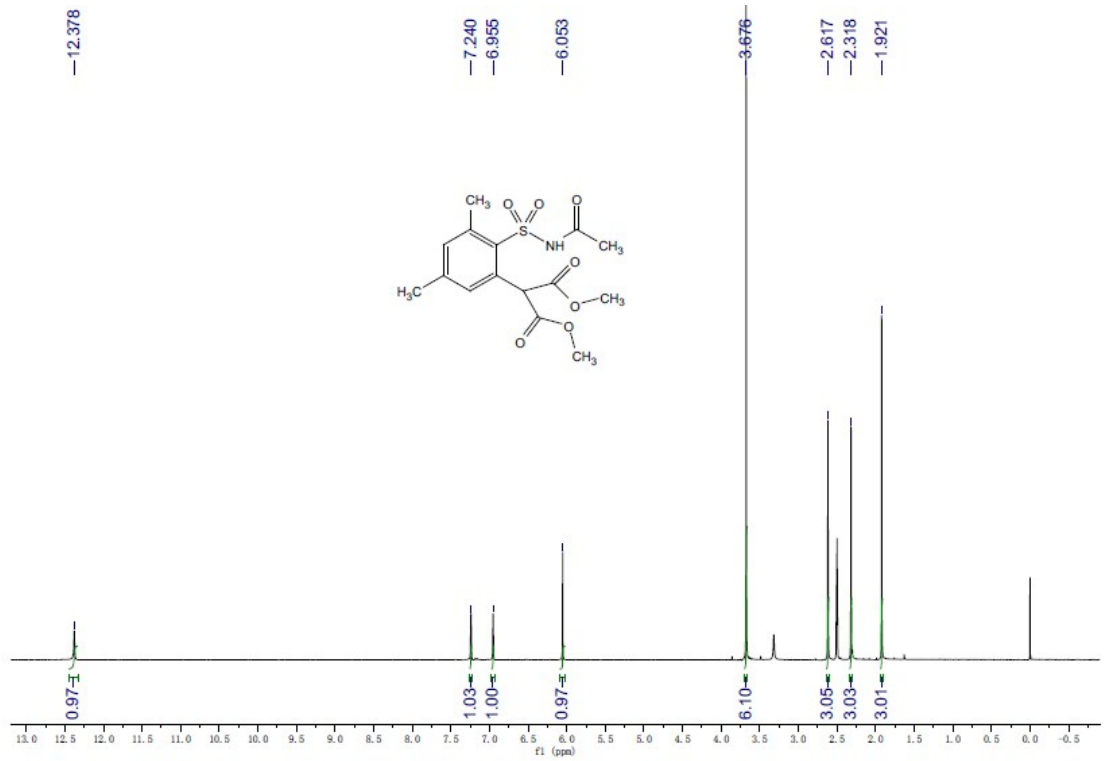
^{1}H NMR of compound **18**



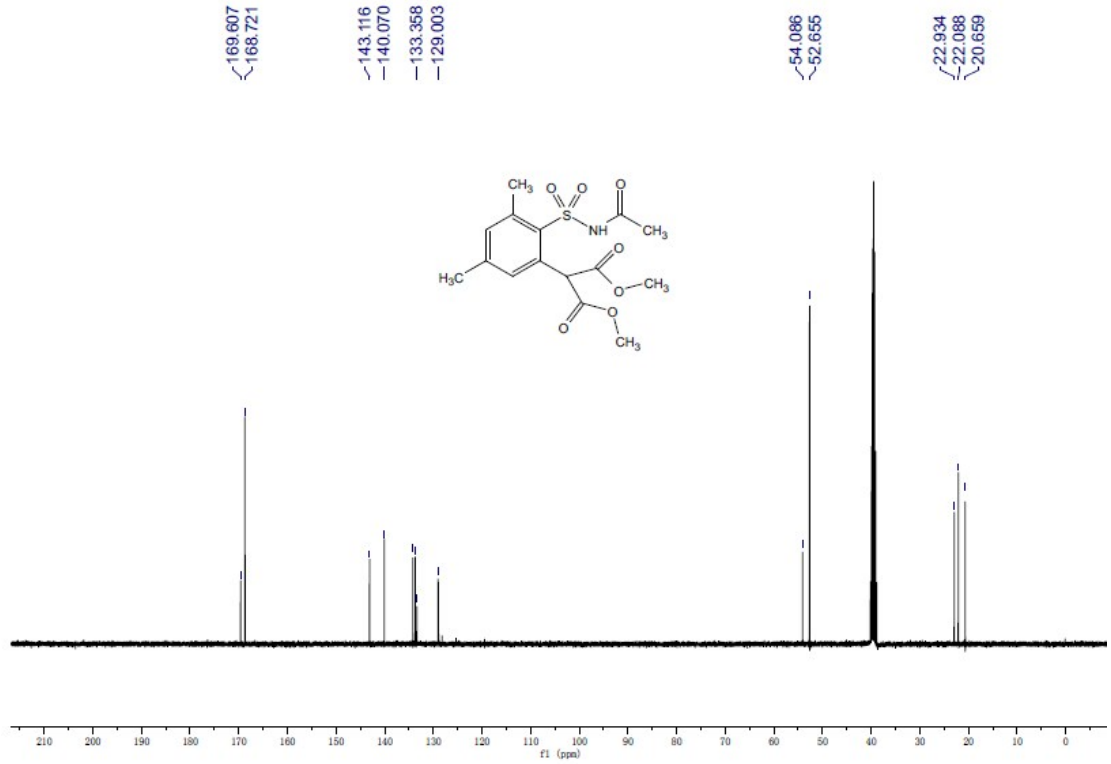
^{13}C NMR of compound **18**



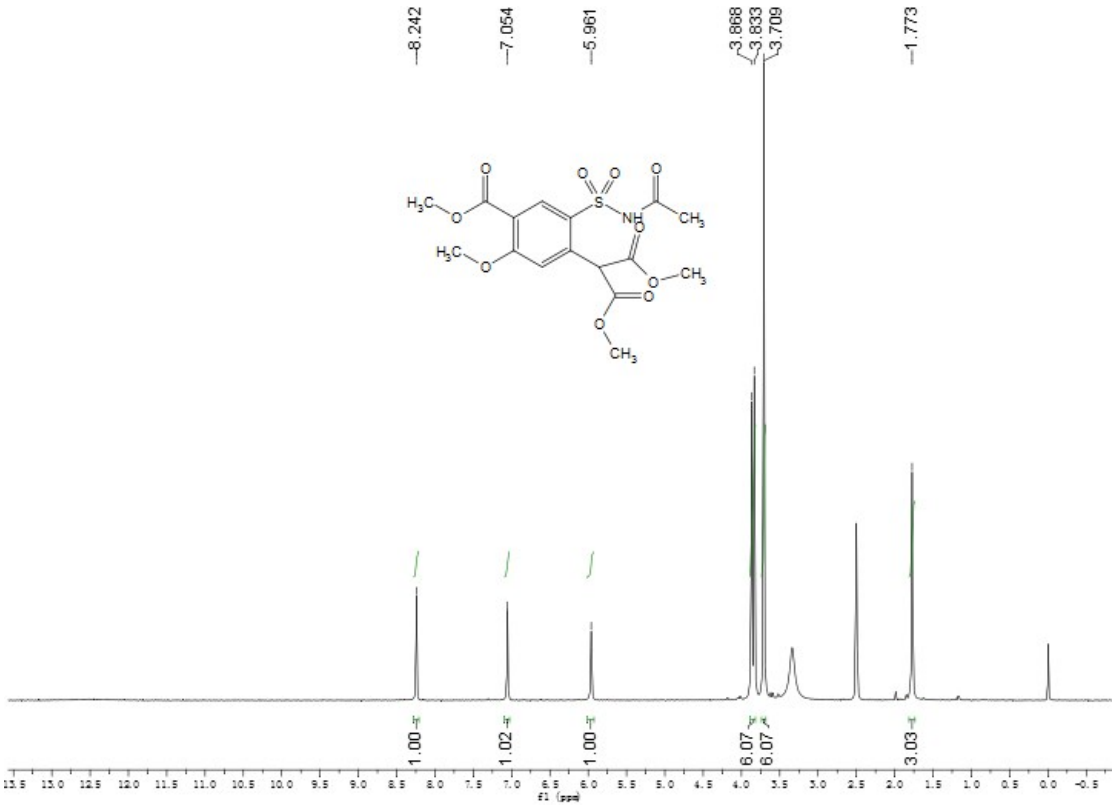
^{1}H NMR of compound **19**



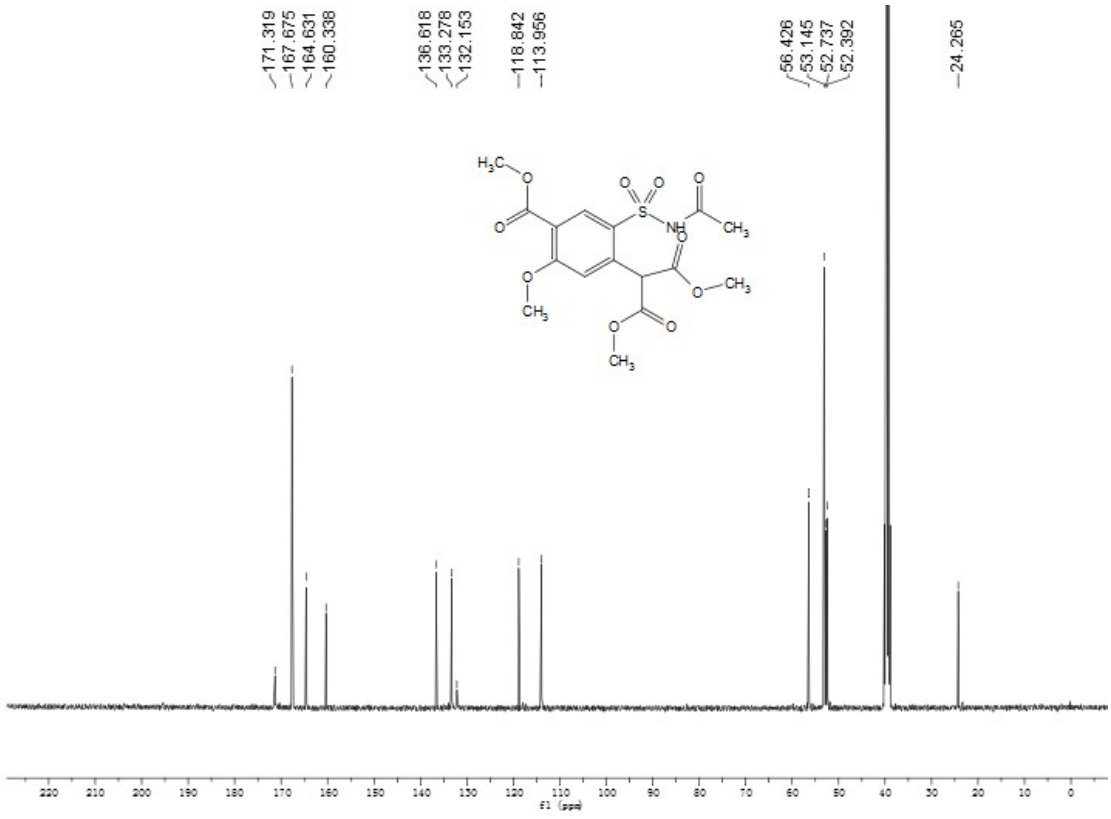
^{13}C NMR of compound **19**



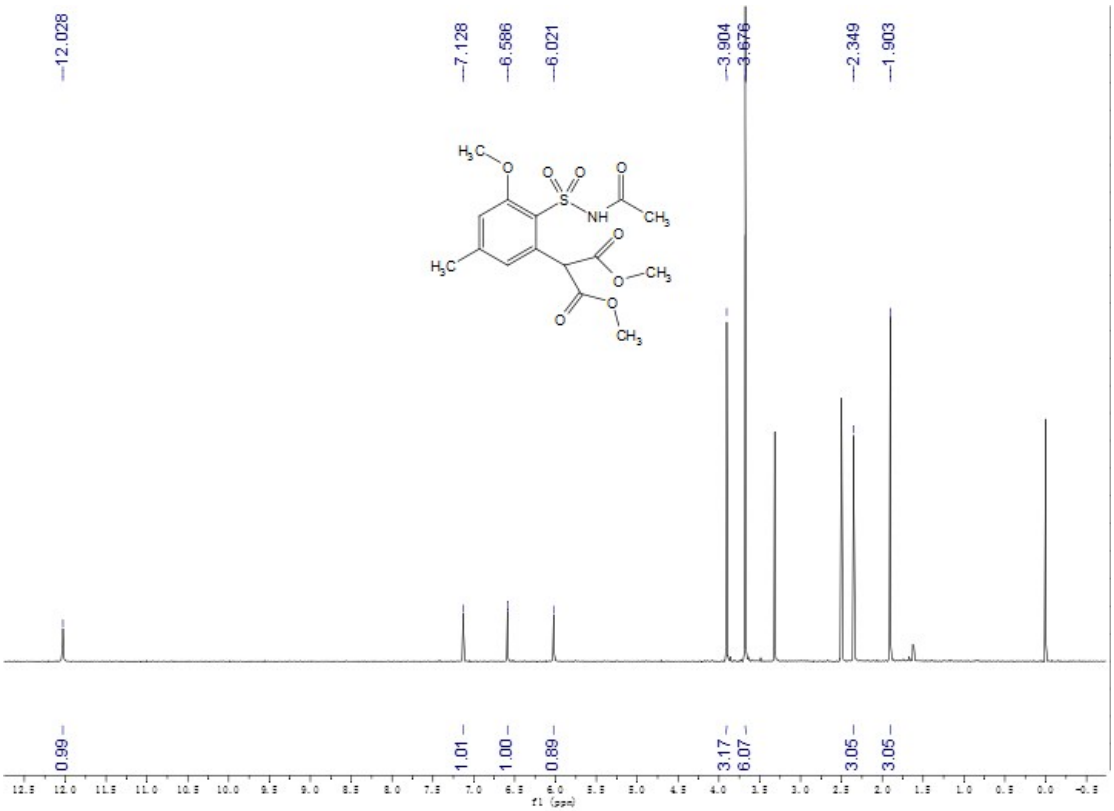
^{1}H NMR of compound **20**



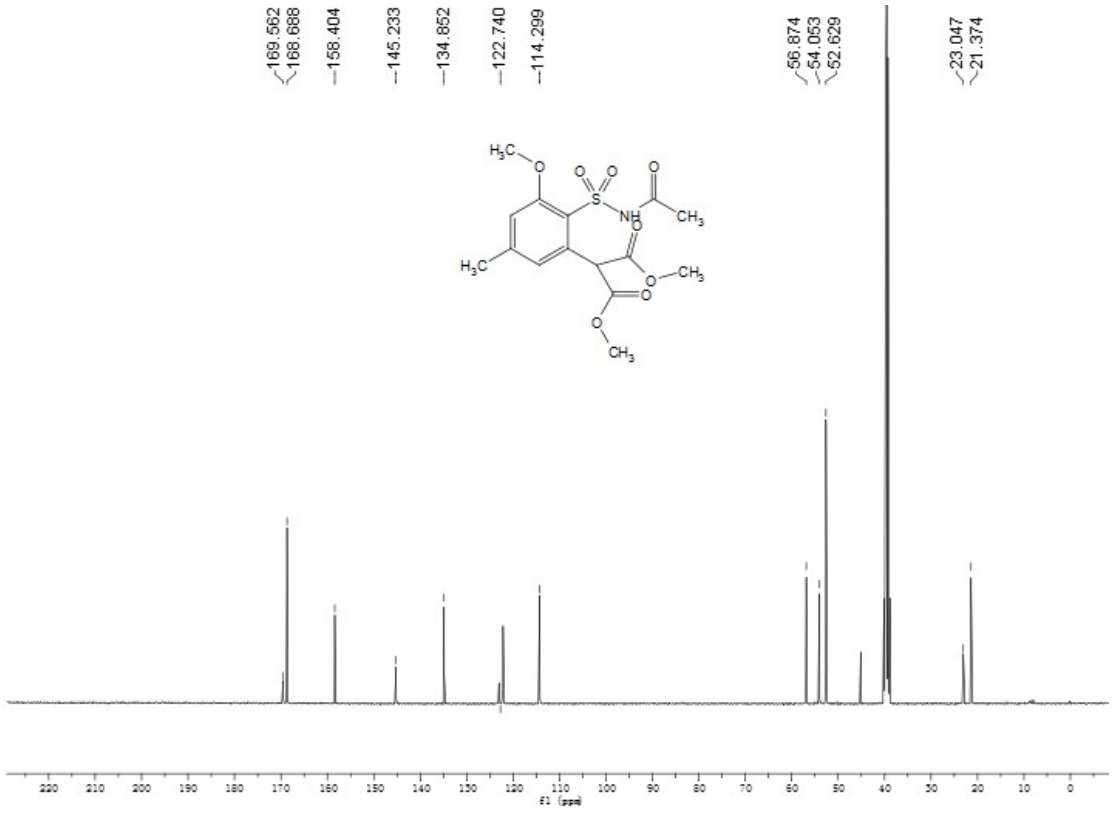
^{13}C NMR of compound **20**



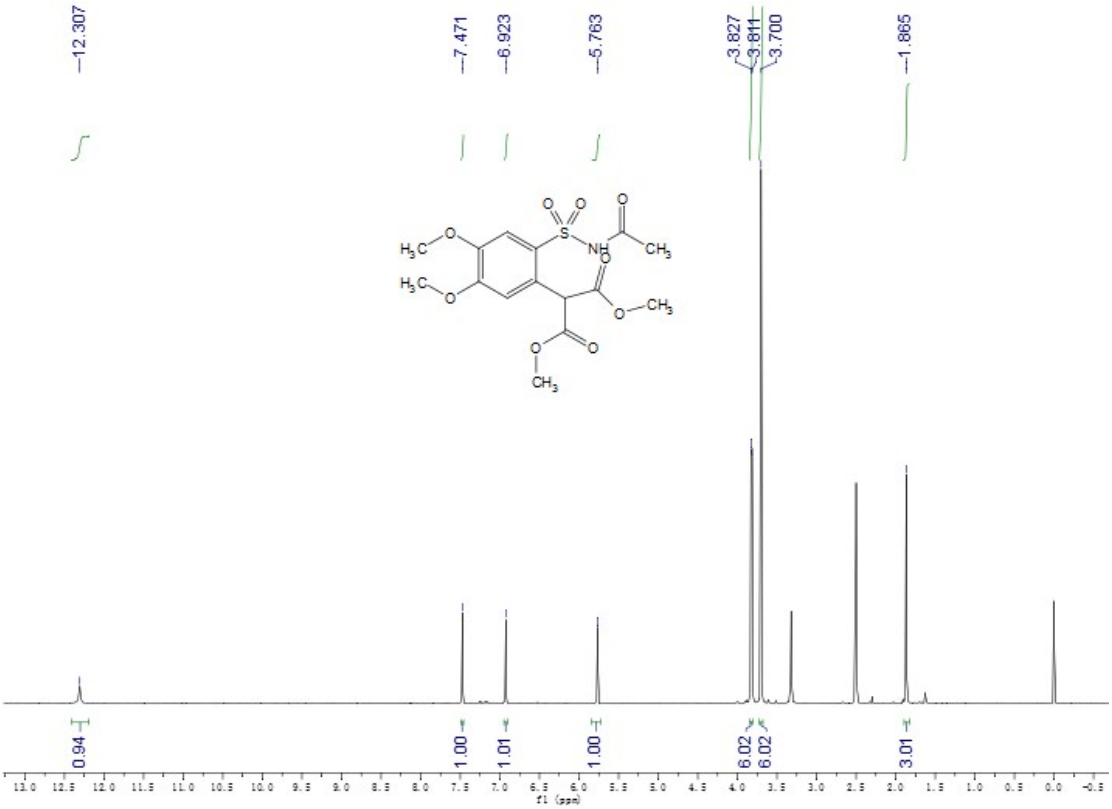
^{1}H NMR of compound **21**



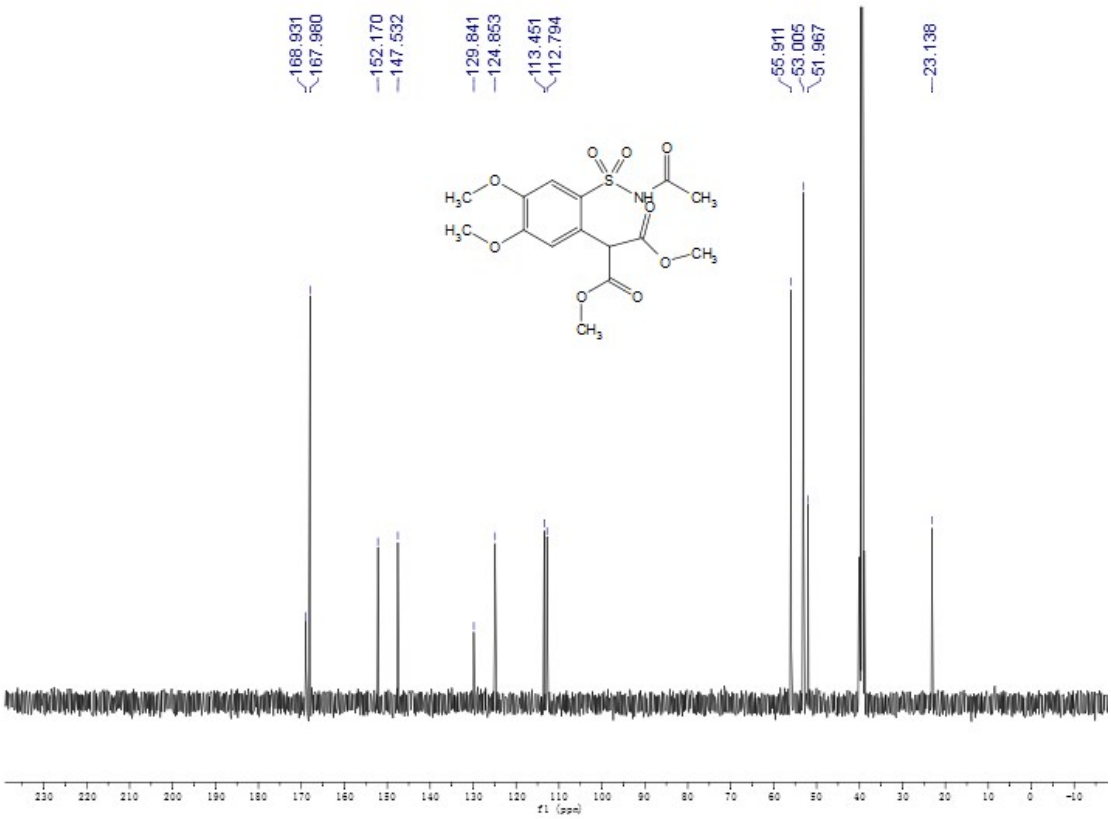
^{13}C NMR of compound **21**



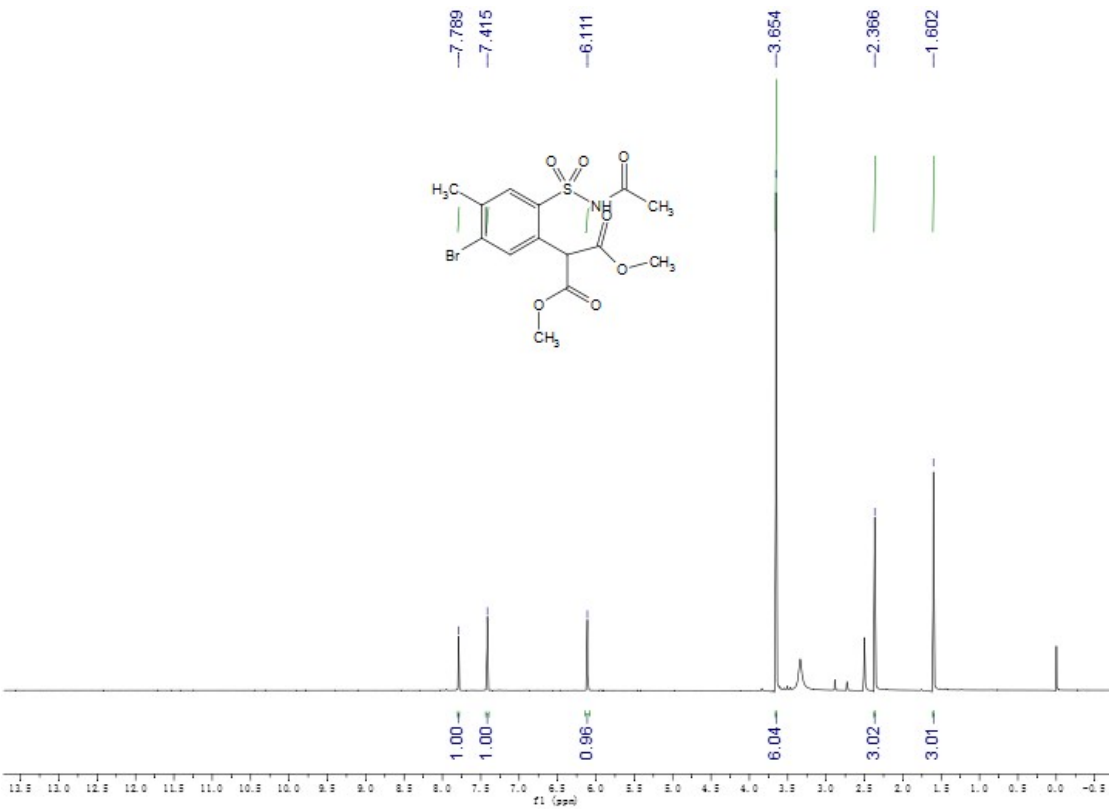
^{1}H NMR of compound **22**



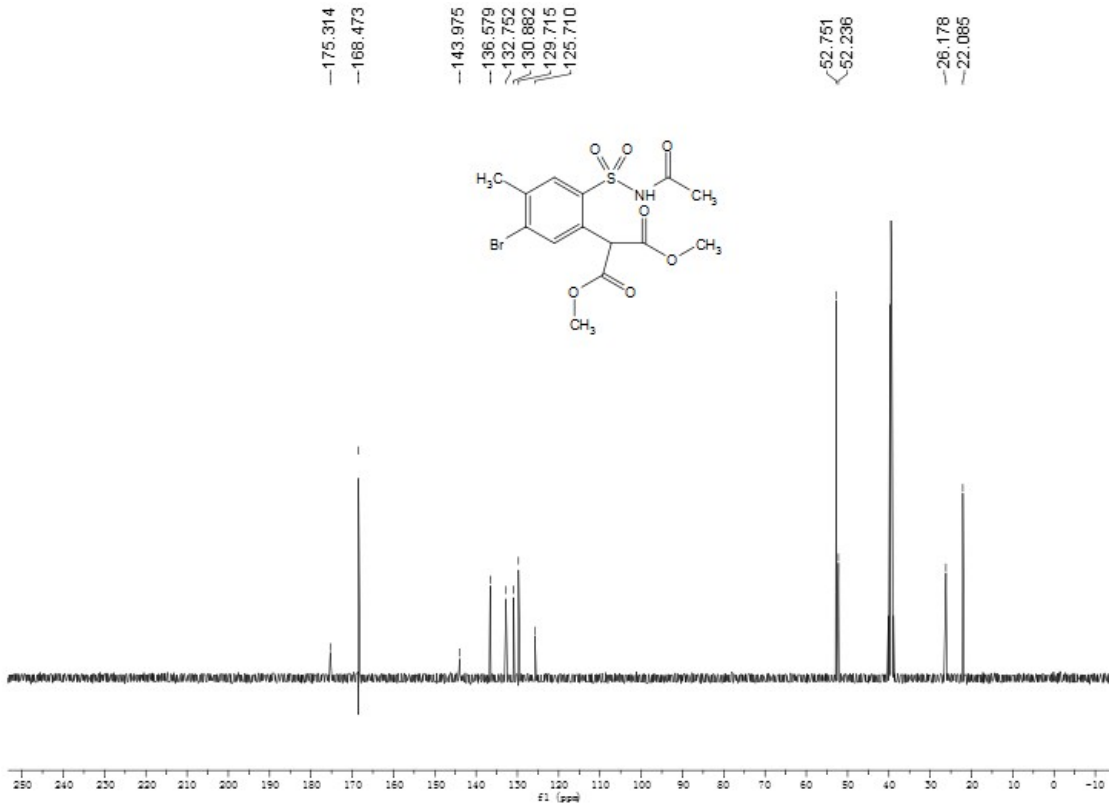
^{13}C NMR of compound **22**



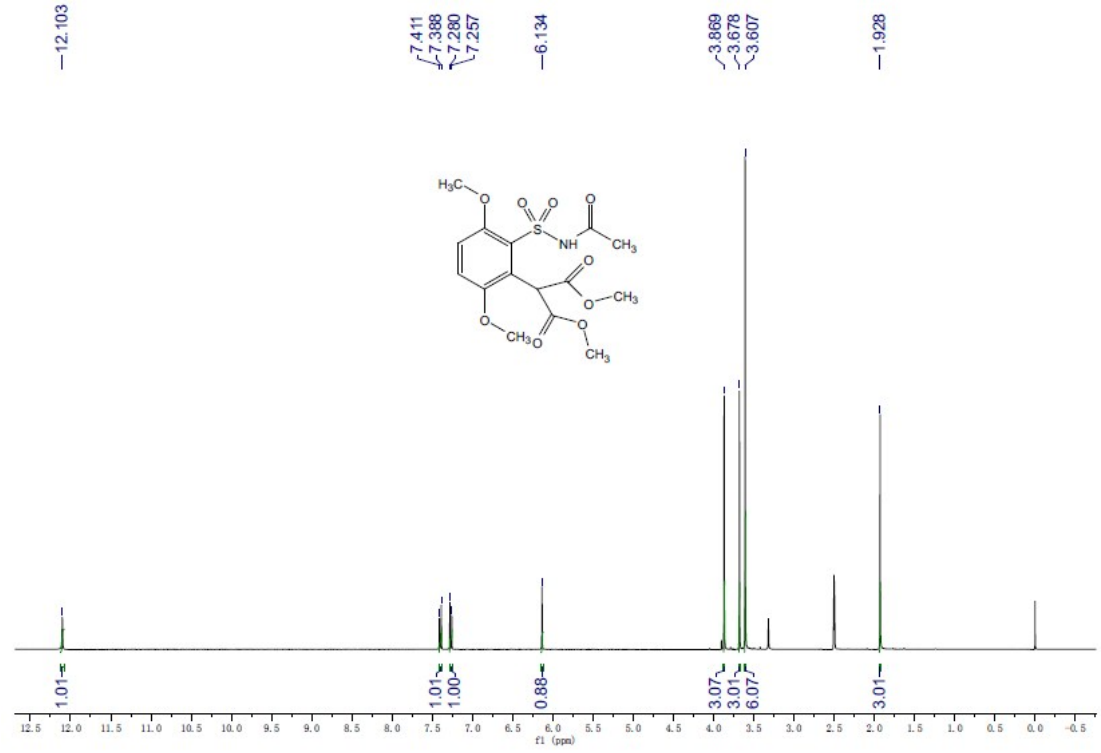
^{1}H NMR of compound **23**



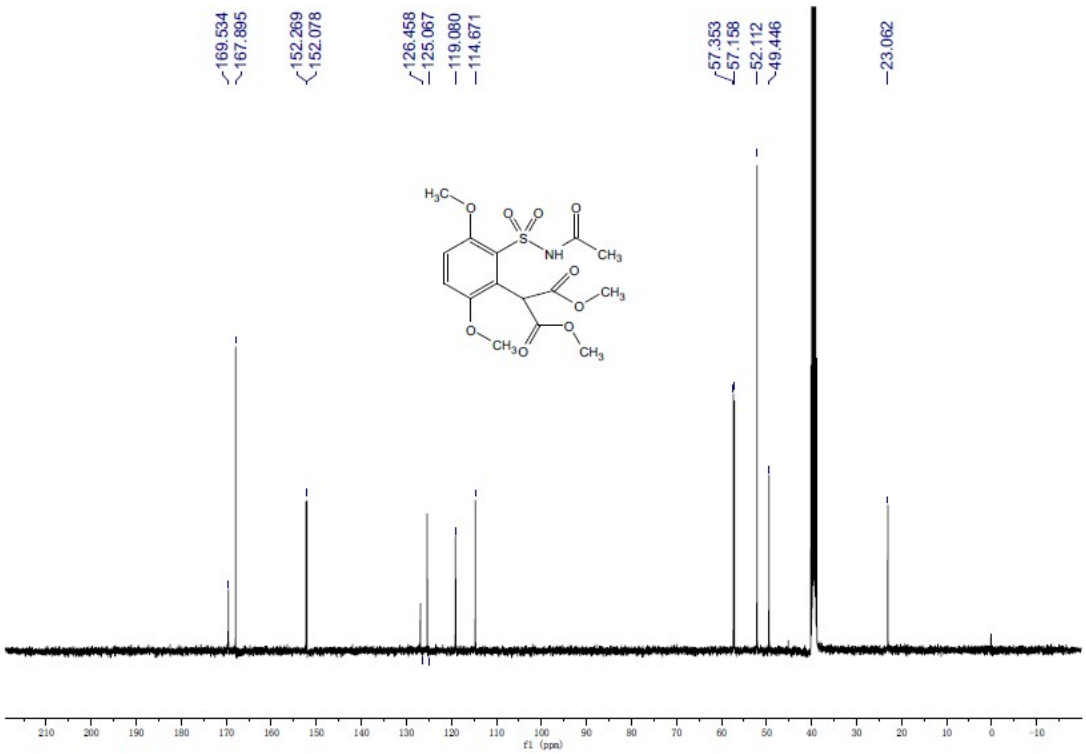
^{13}C NMR of compound **23**



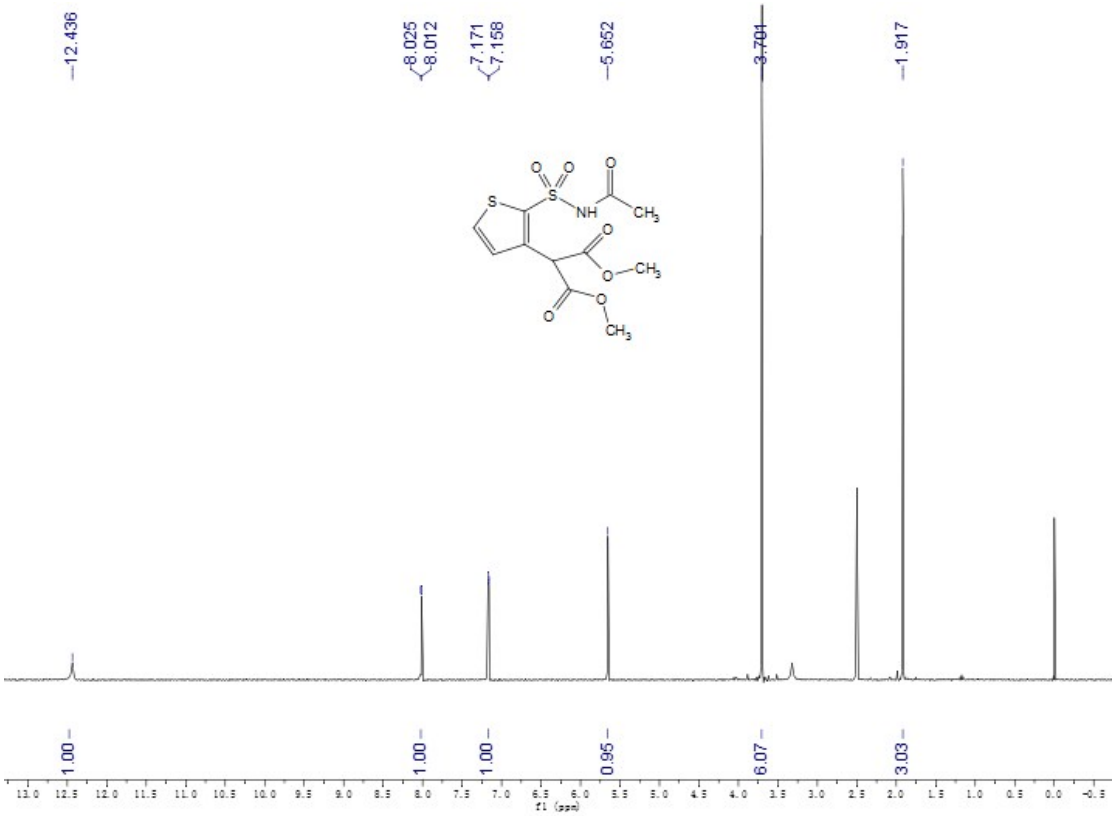
^{1}H NMR of compound **24**



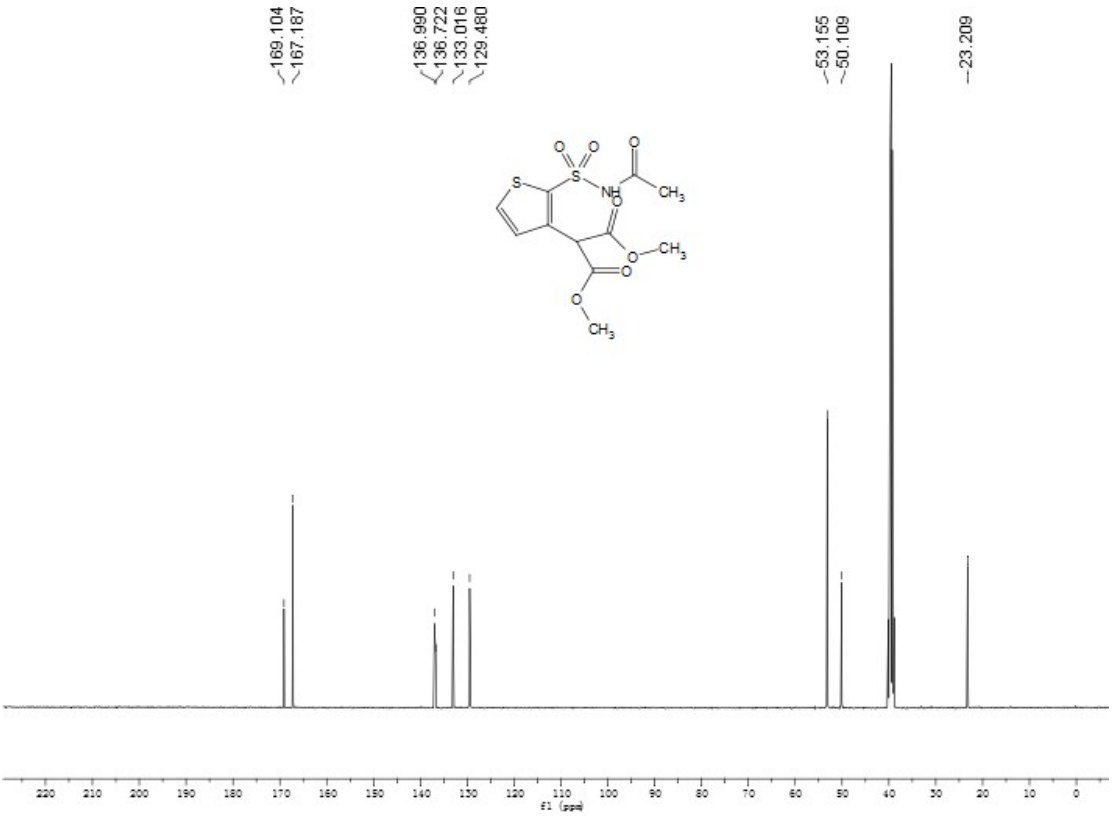
^{13}C NMR of compound **24**



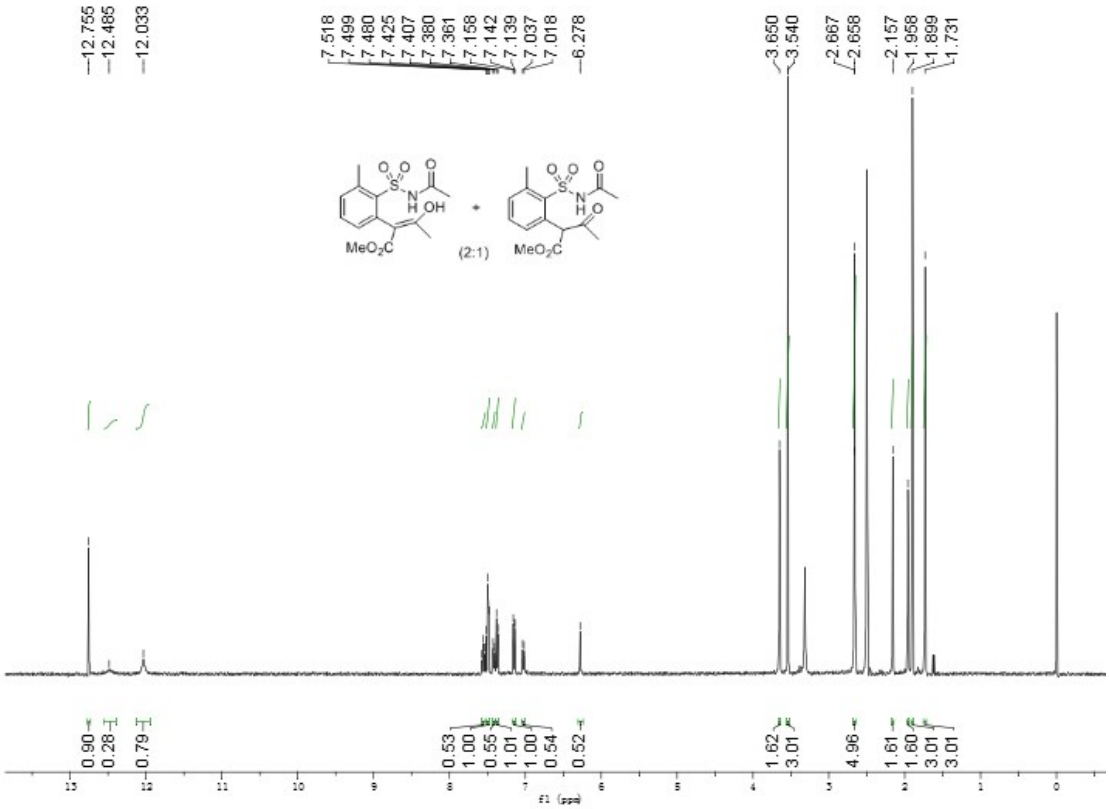
^{1}H NMR of compound **25**



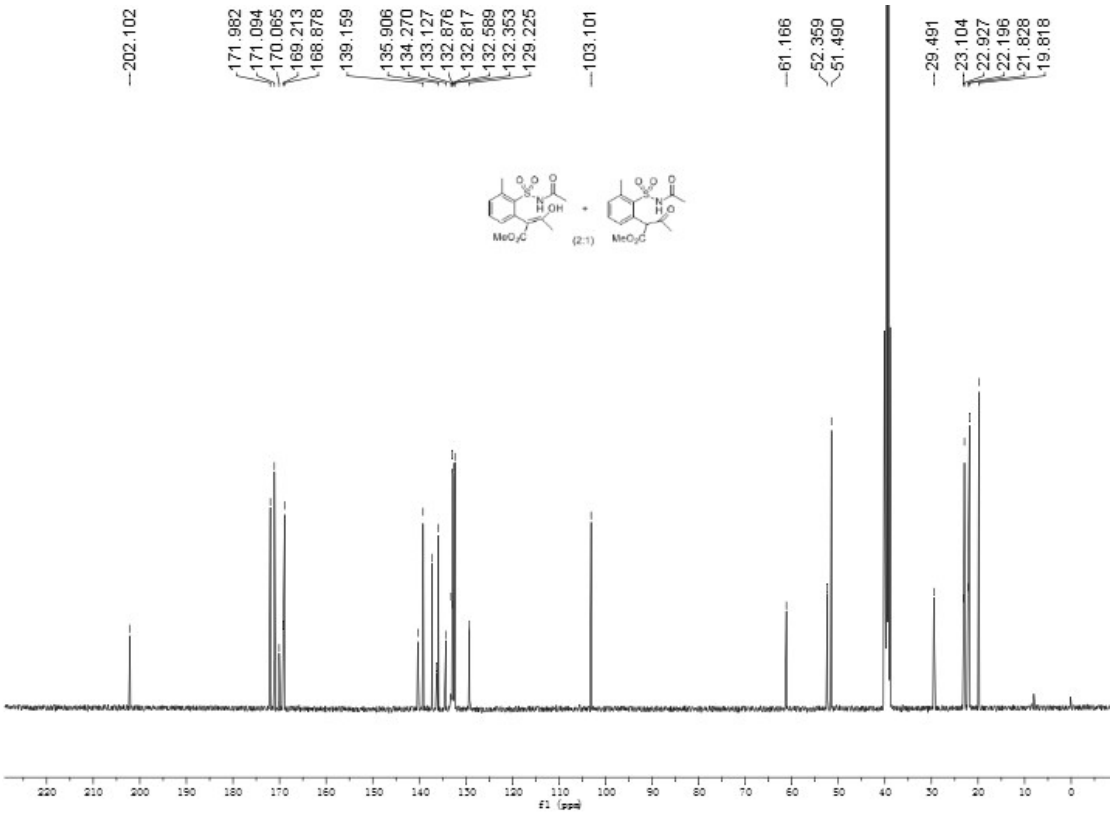
^{13}C NMR of compound **25**



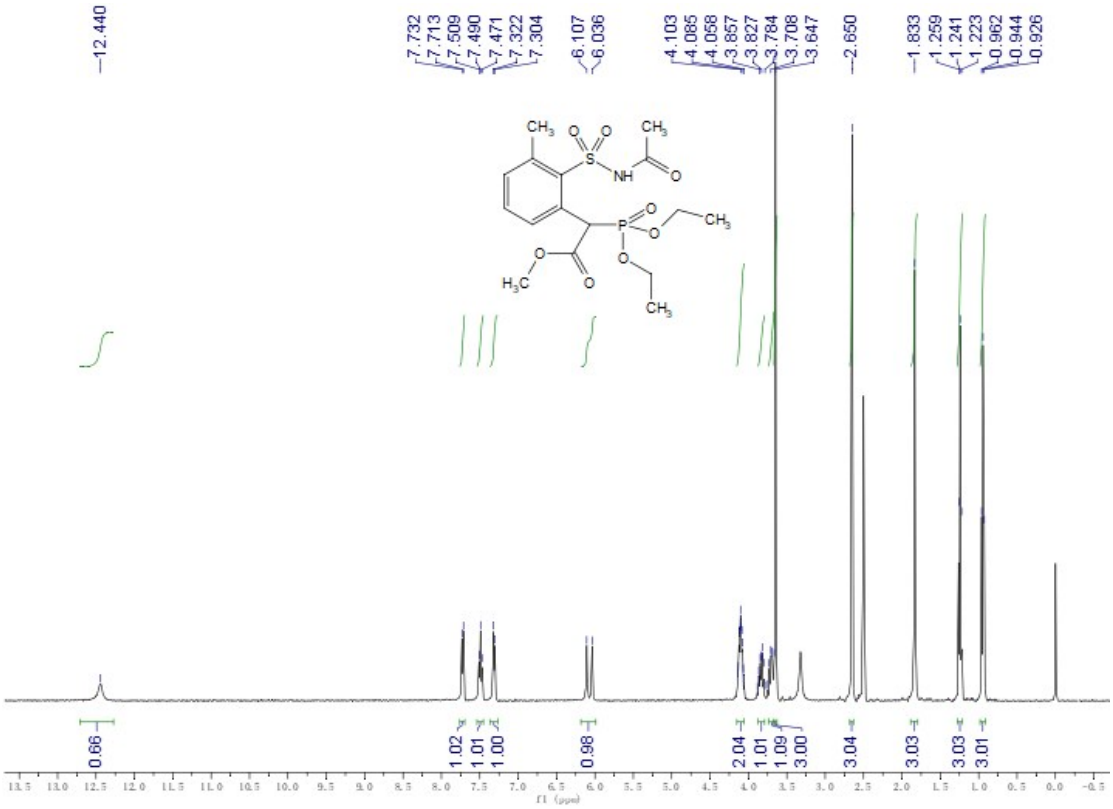
^{1}H NMR of compound **26**



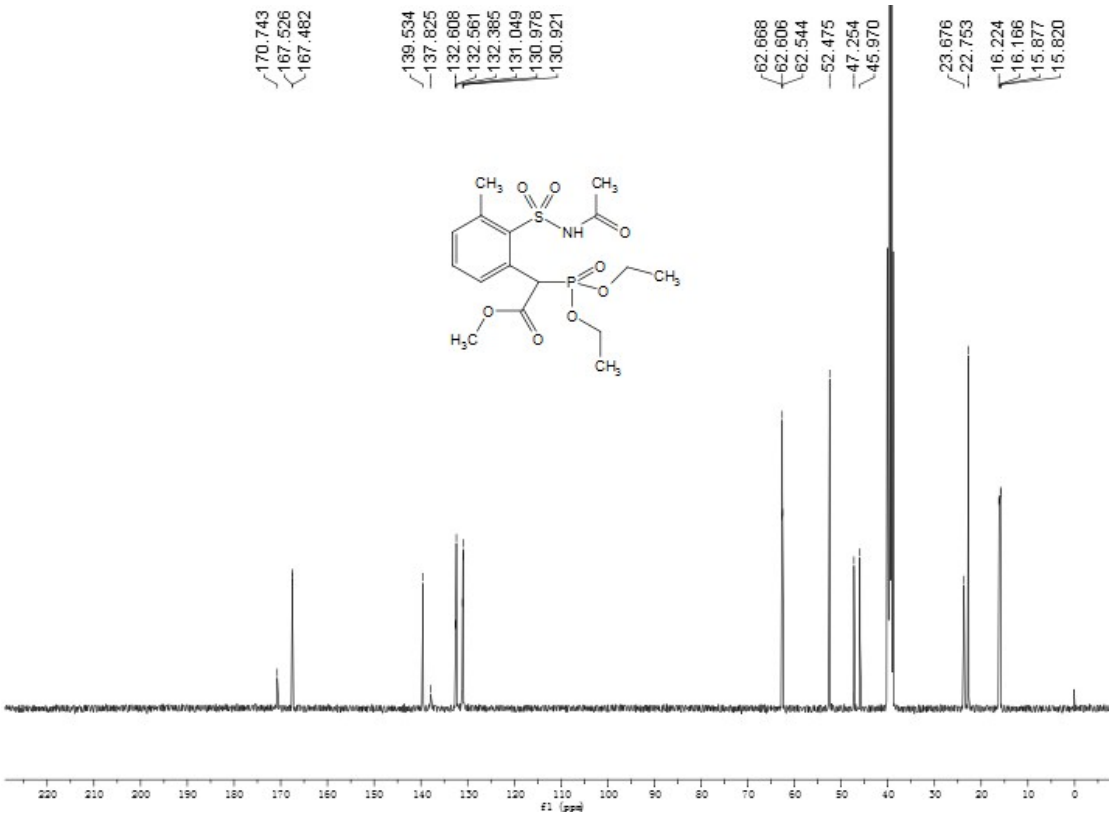
^{13}C NMR of compound **26**



^{1}H NMR of compound **27**



^{13}C NMR of compound **27**



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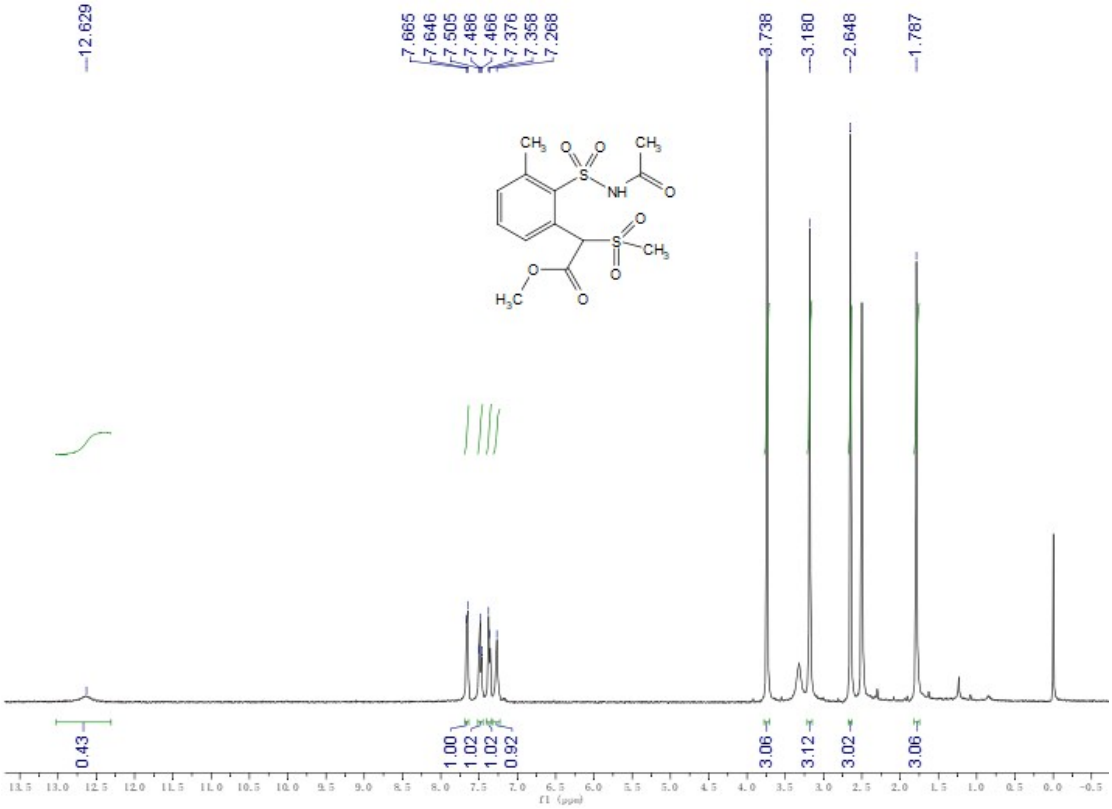
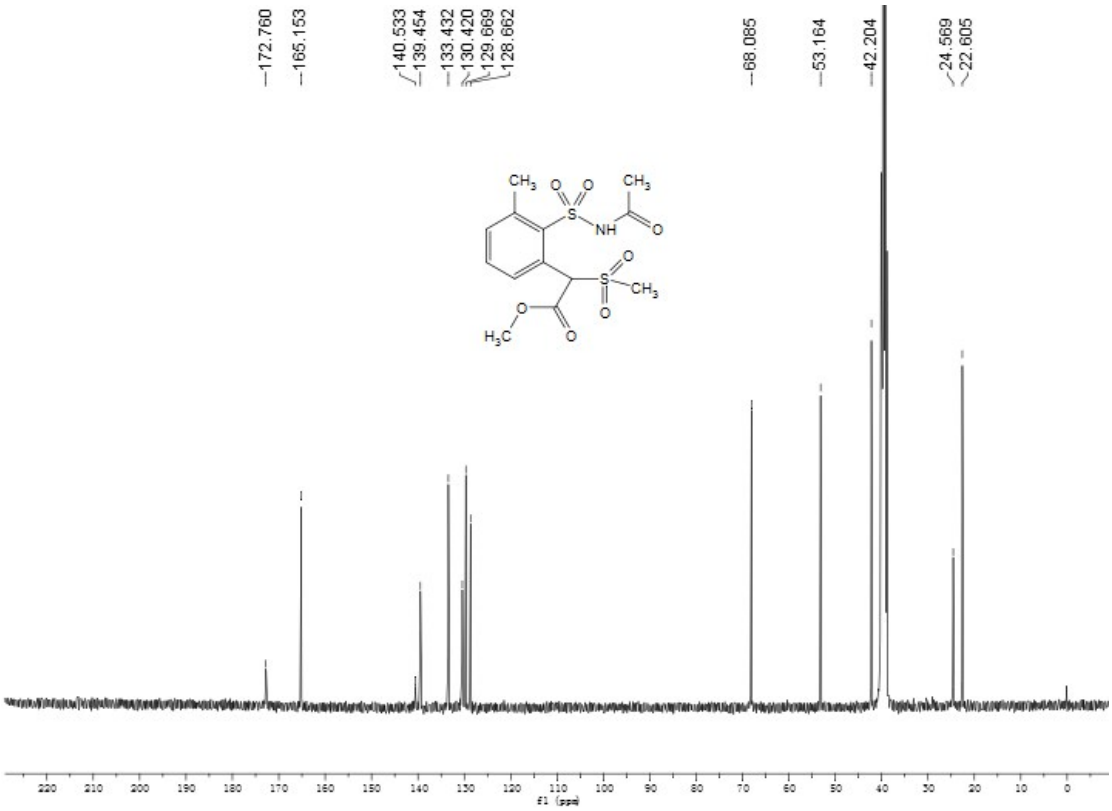


^{13}C NMR of compound **28**



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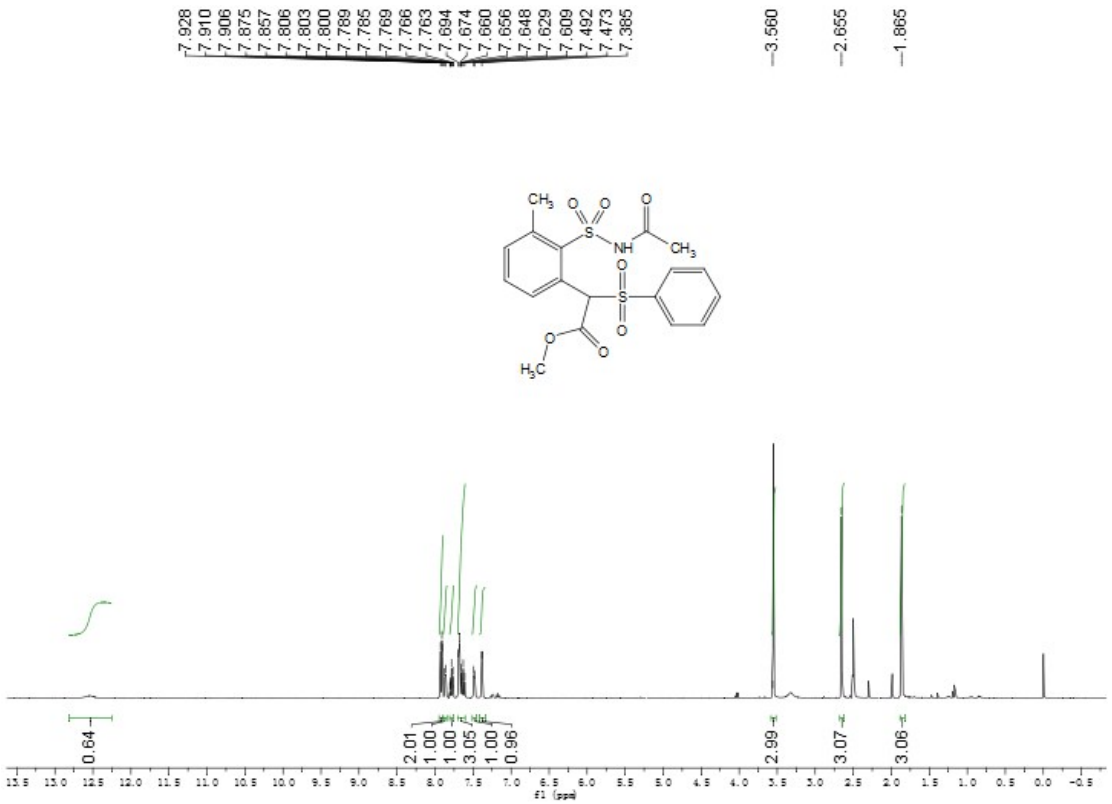
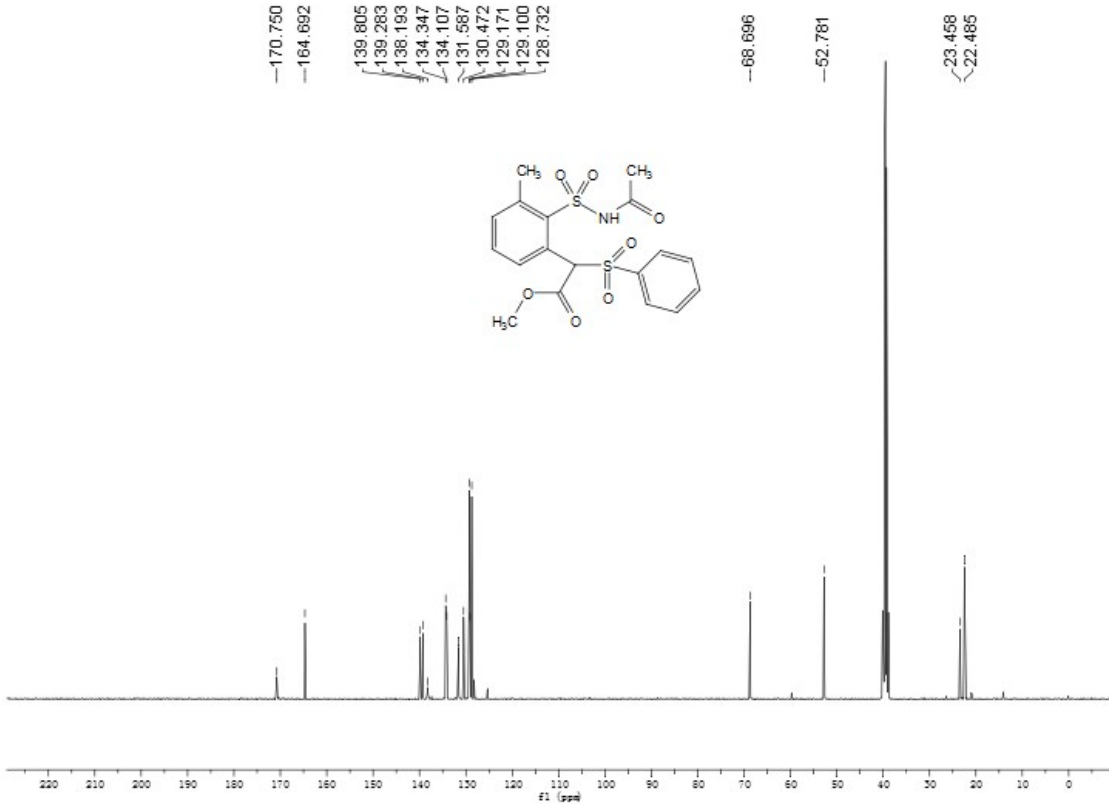
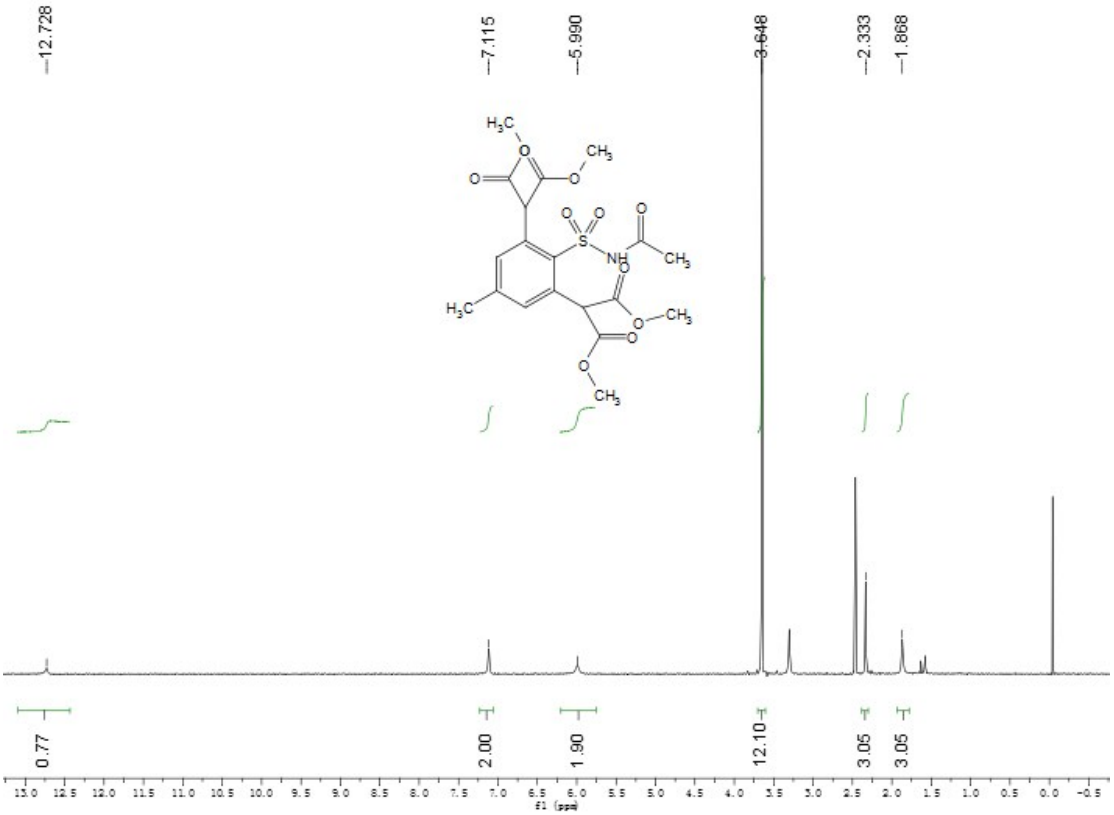


^{13}C NMR of compound **29**



^{1}H NMR of compound **30**



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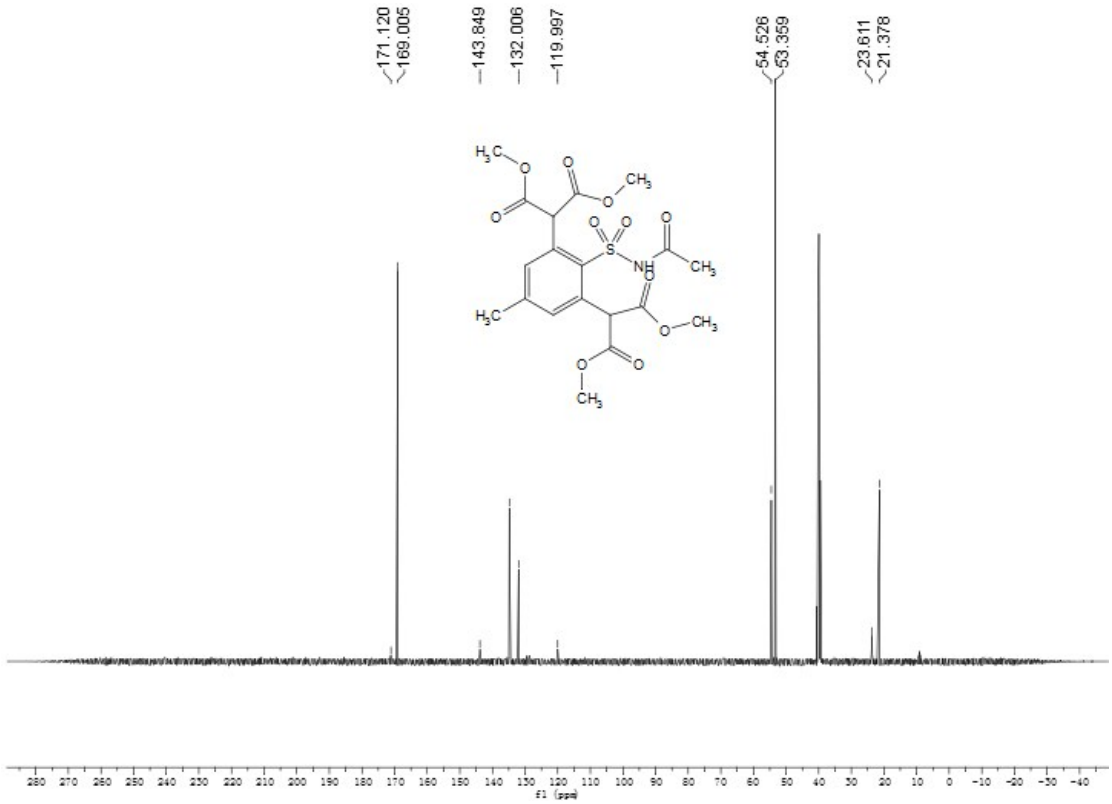
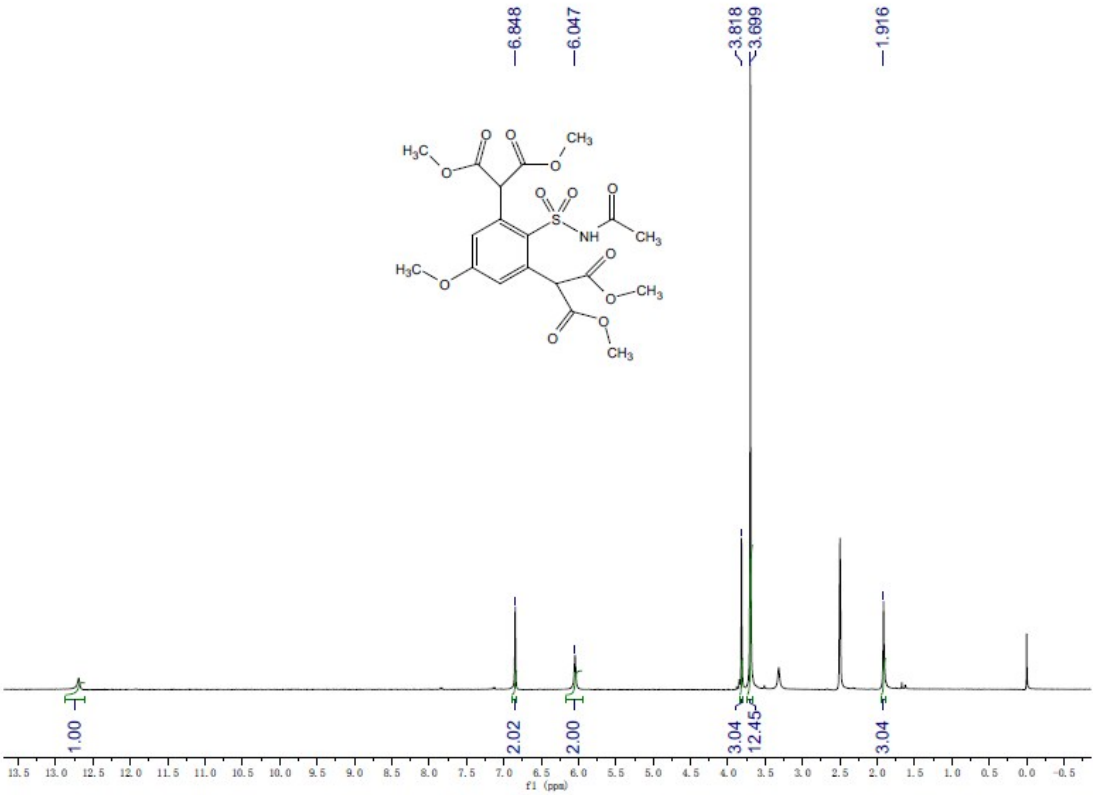


^{1}H NMR of compound **31**



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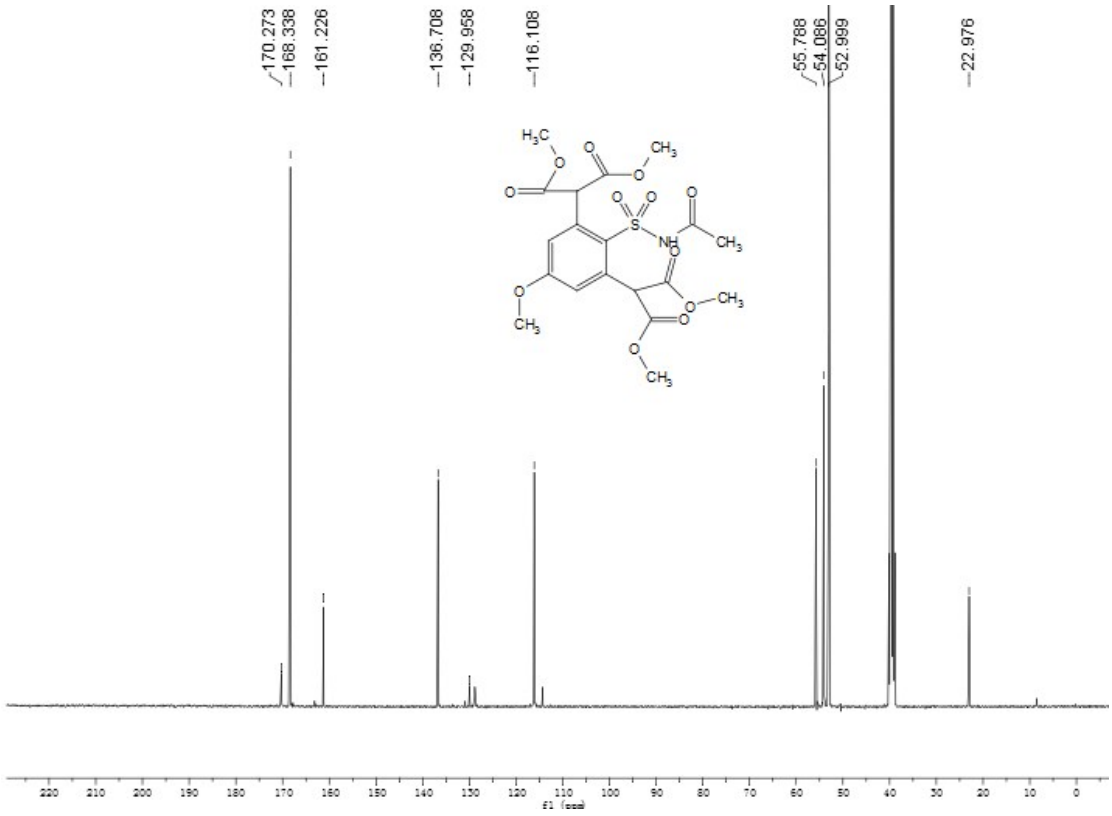

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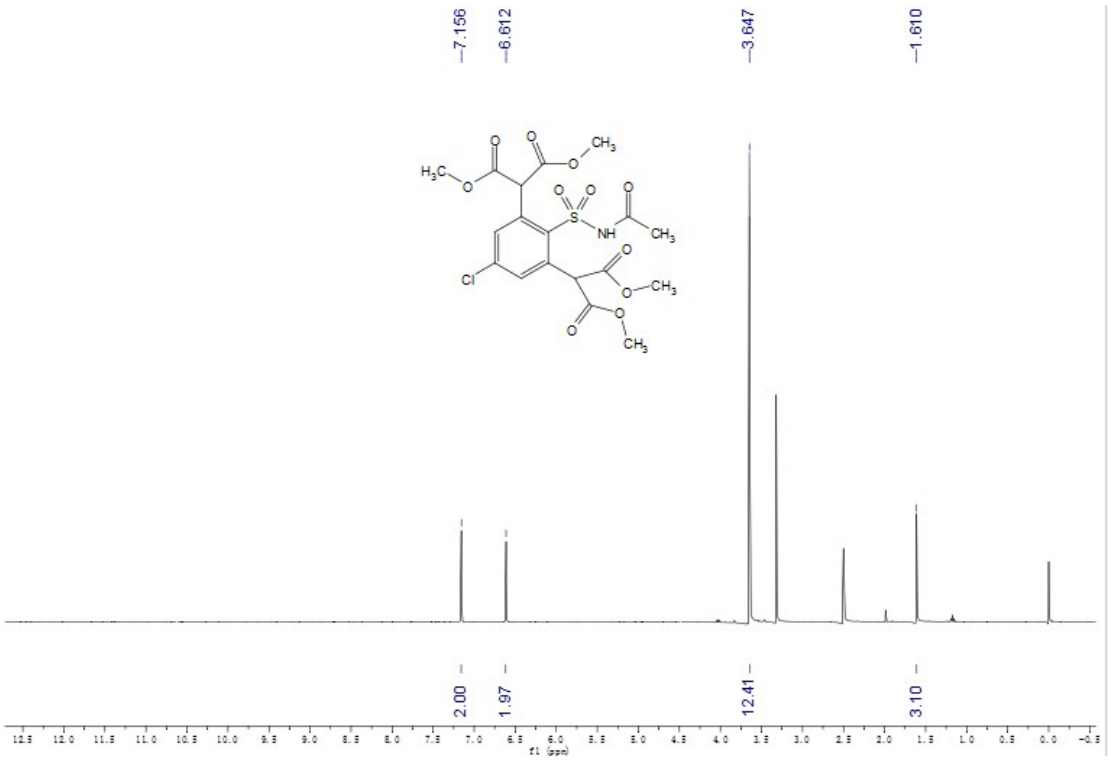

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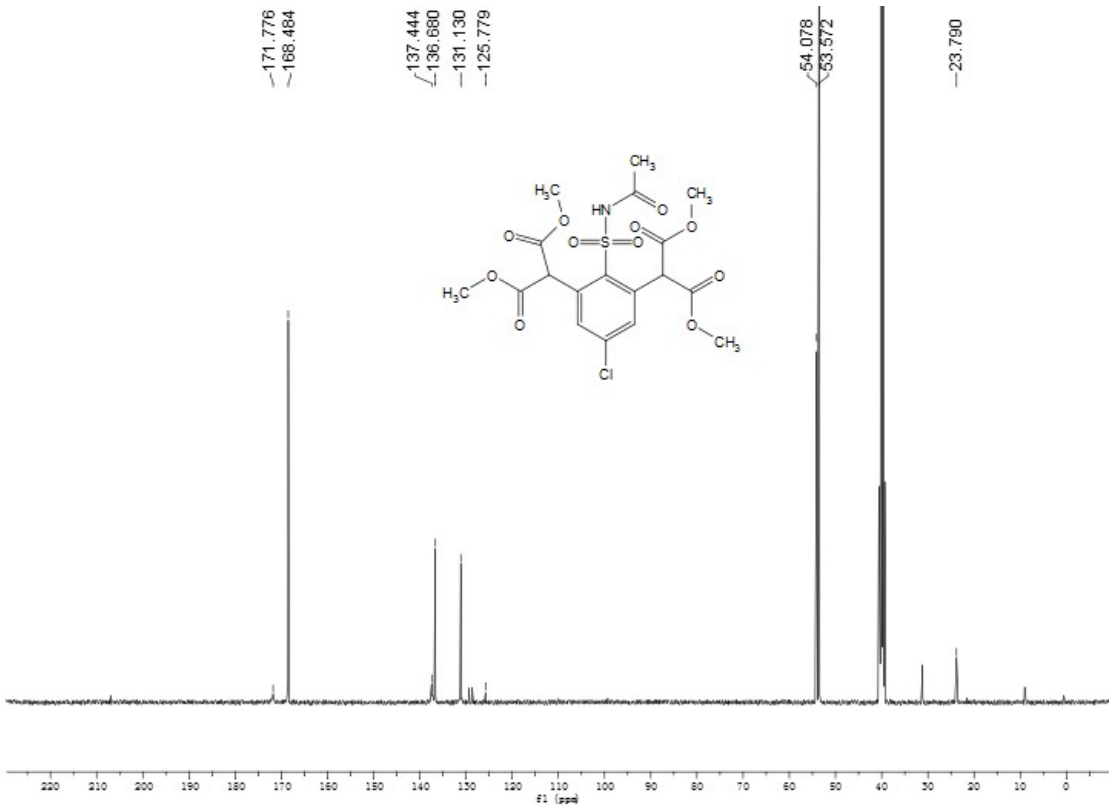

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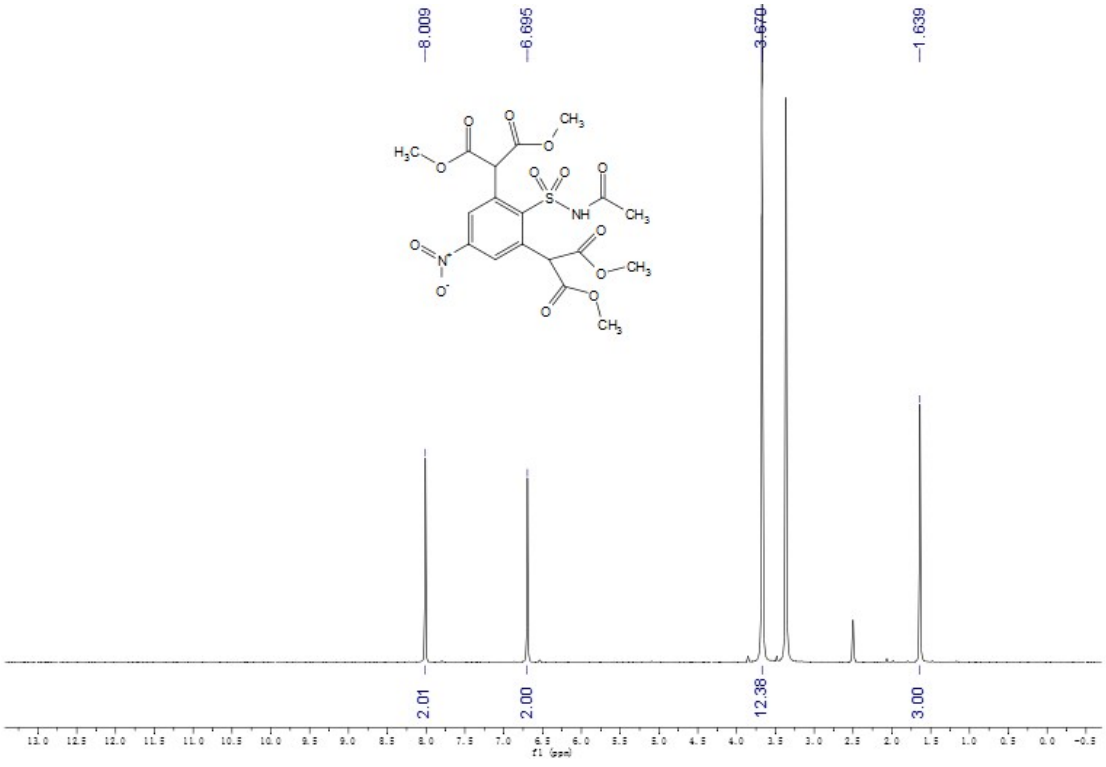
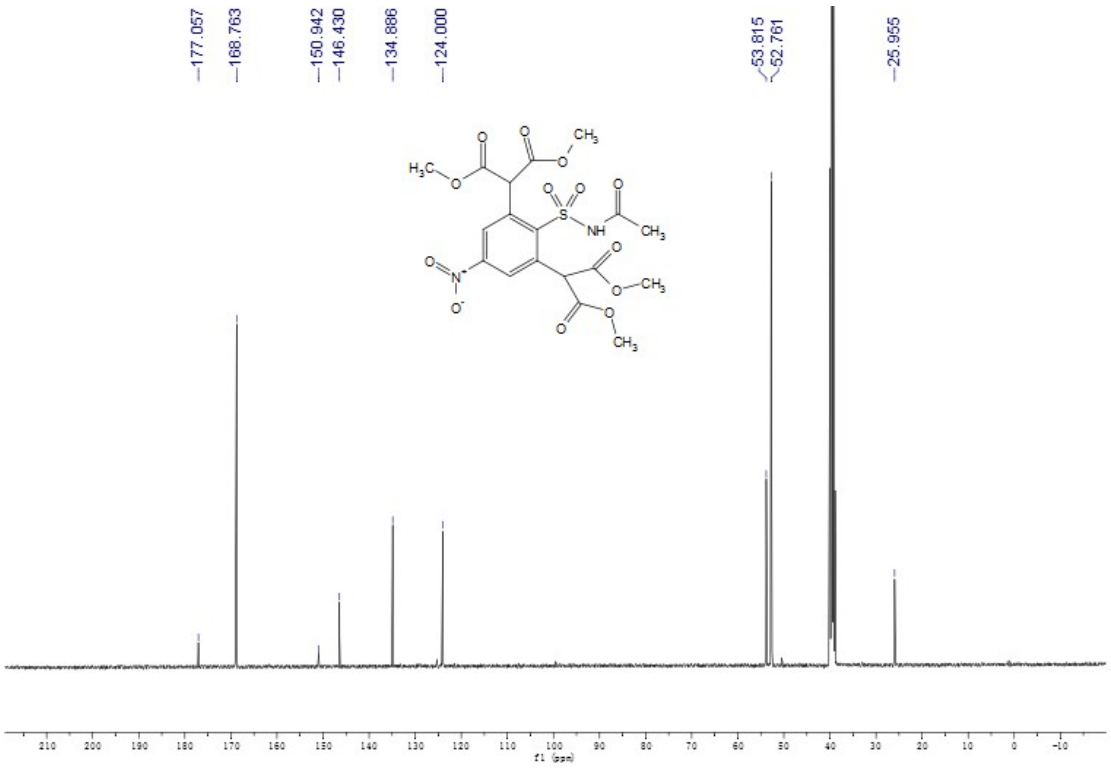


^{13}C NMR of compound **33**



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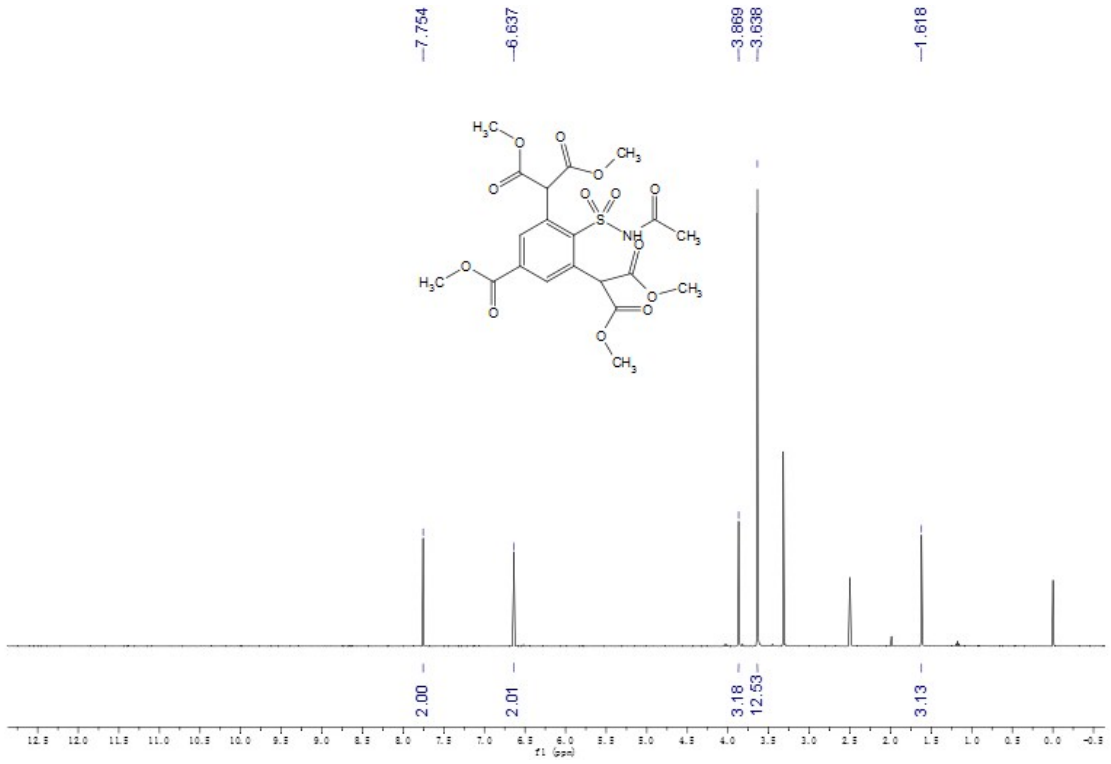

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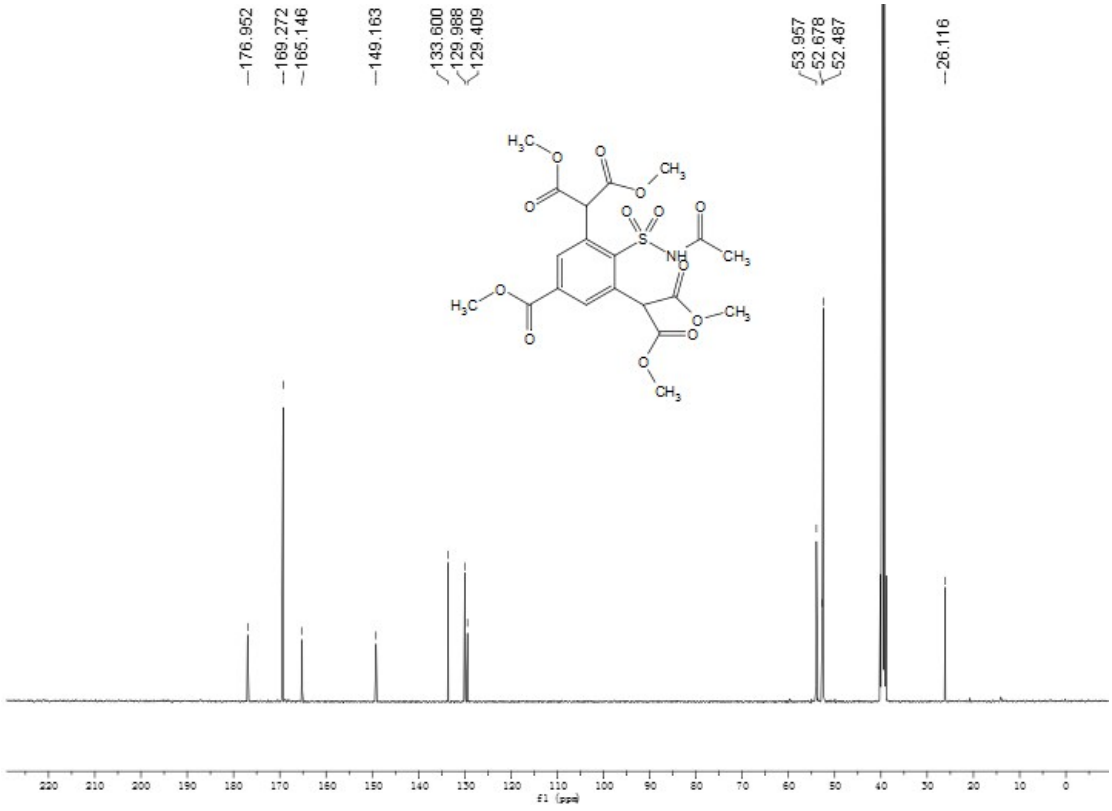

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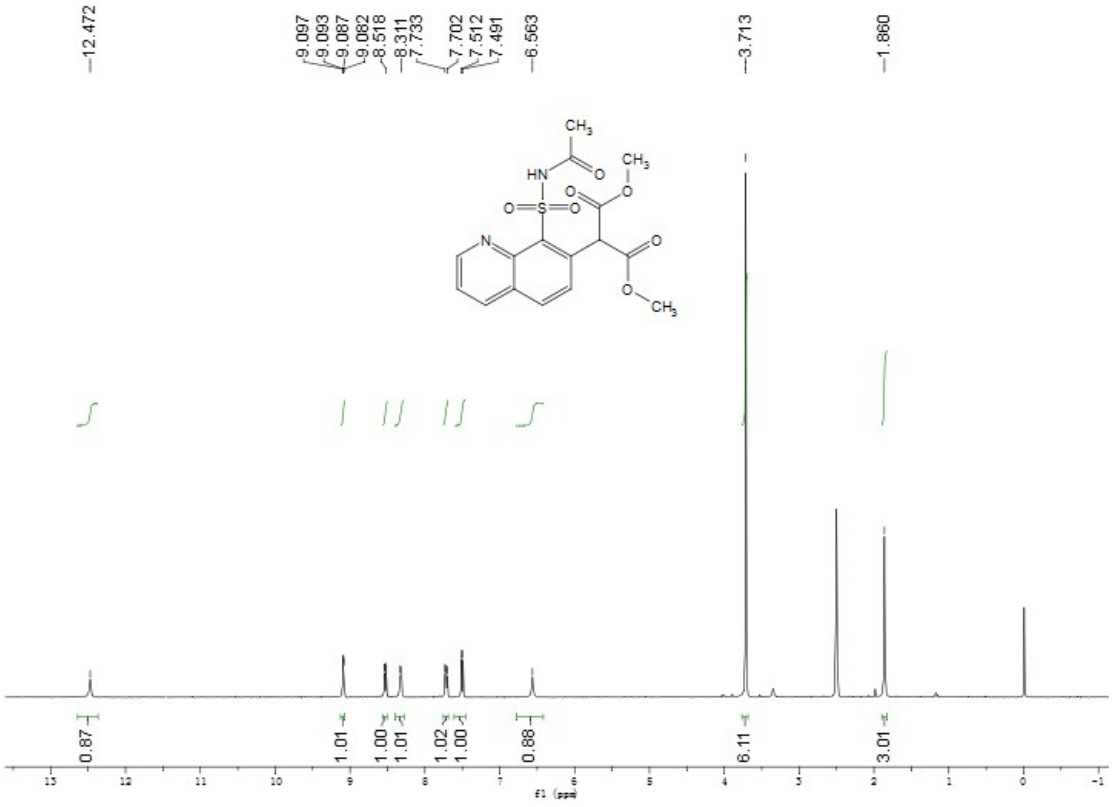
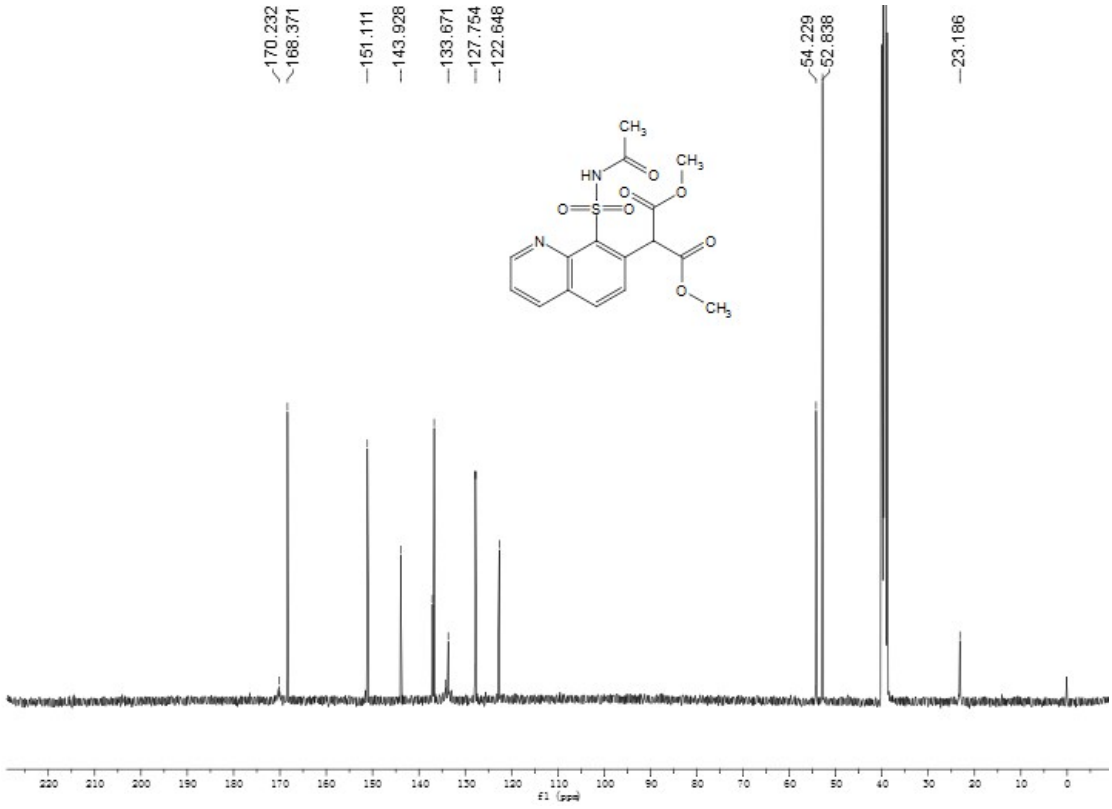
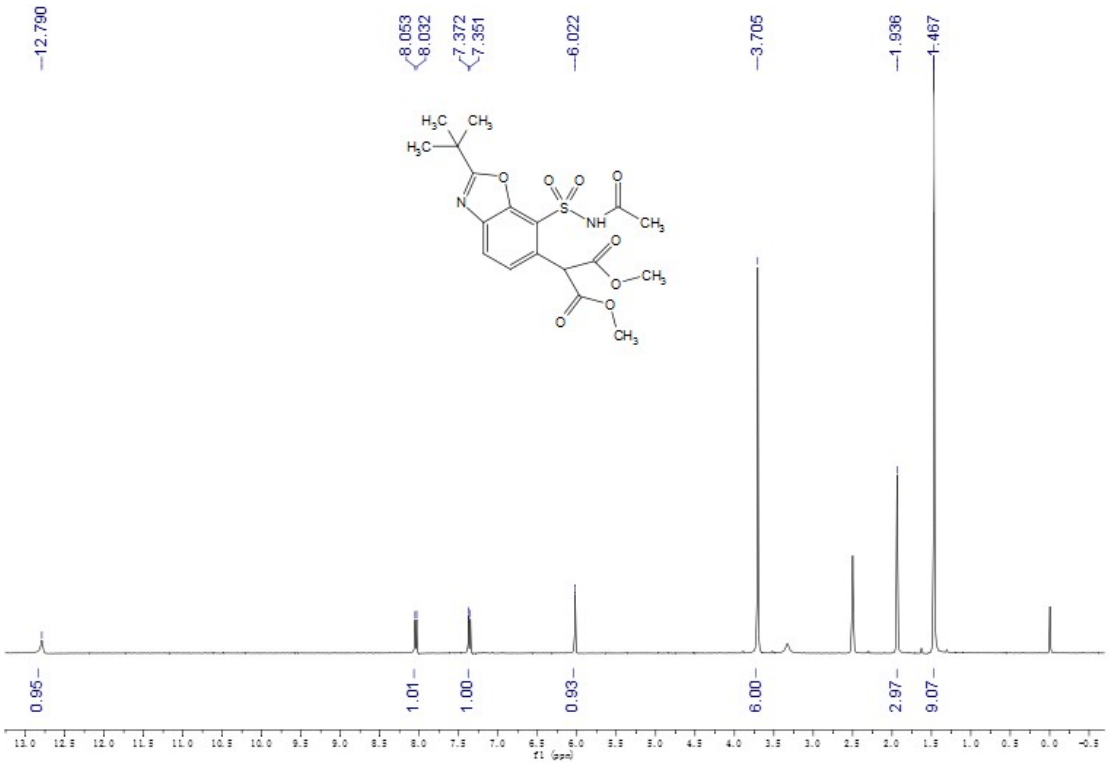


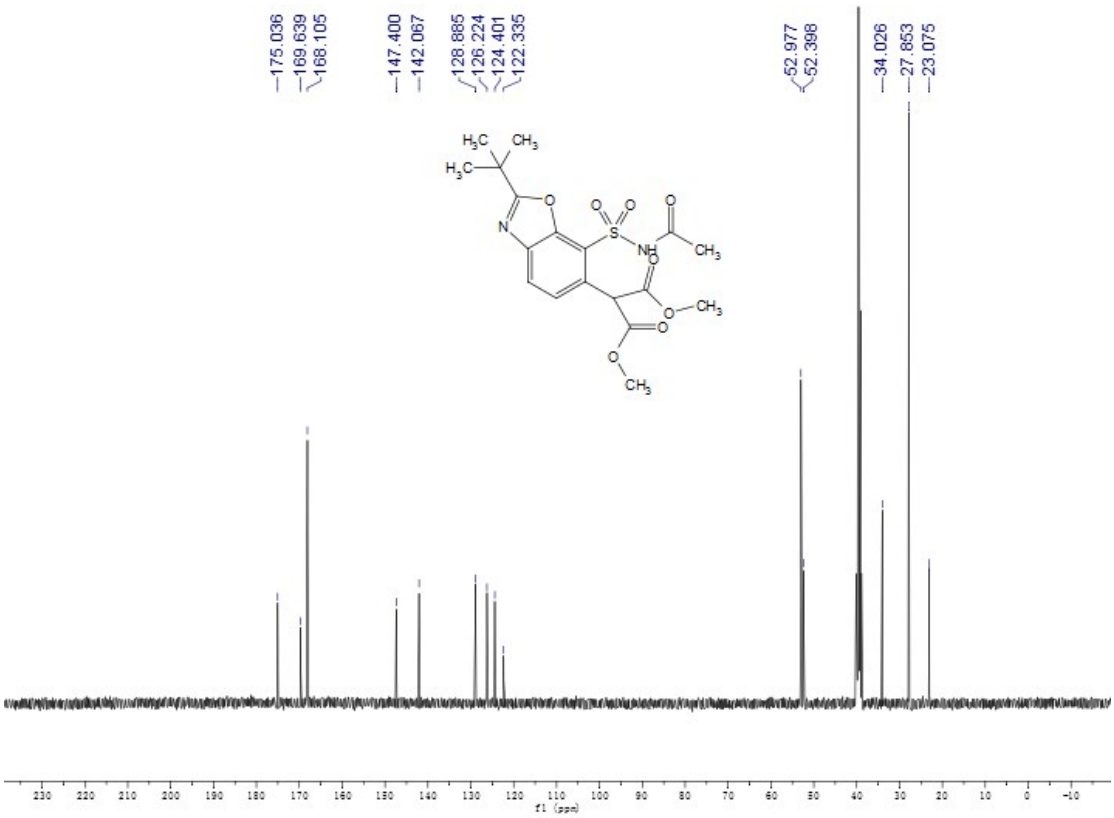
^{13}C NMR of compound **35**



^{1}H NMR of compound **36**

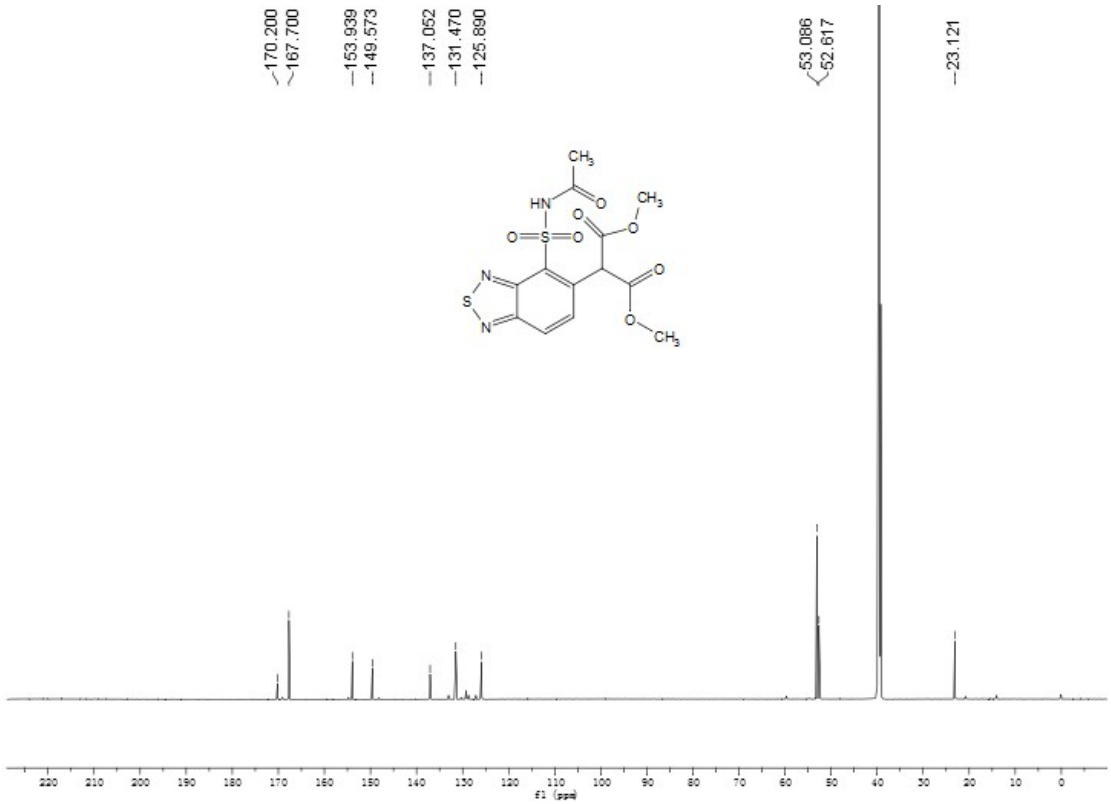


^{13}C NMR of compound **36**

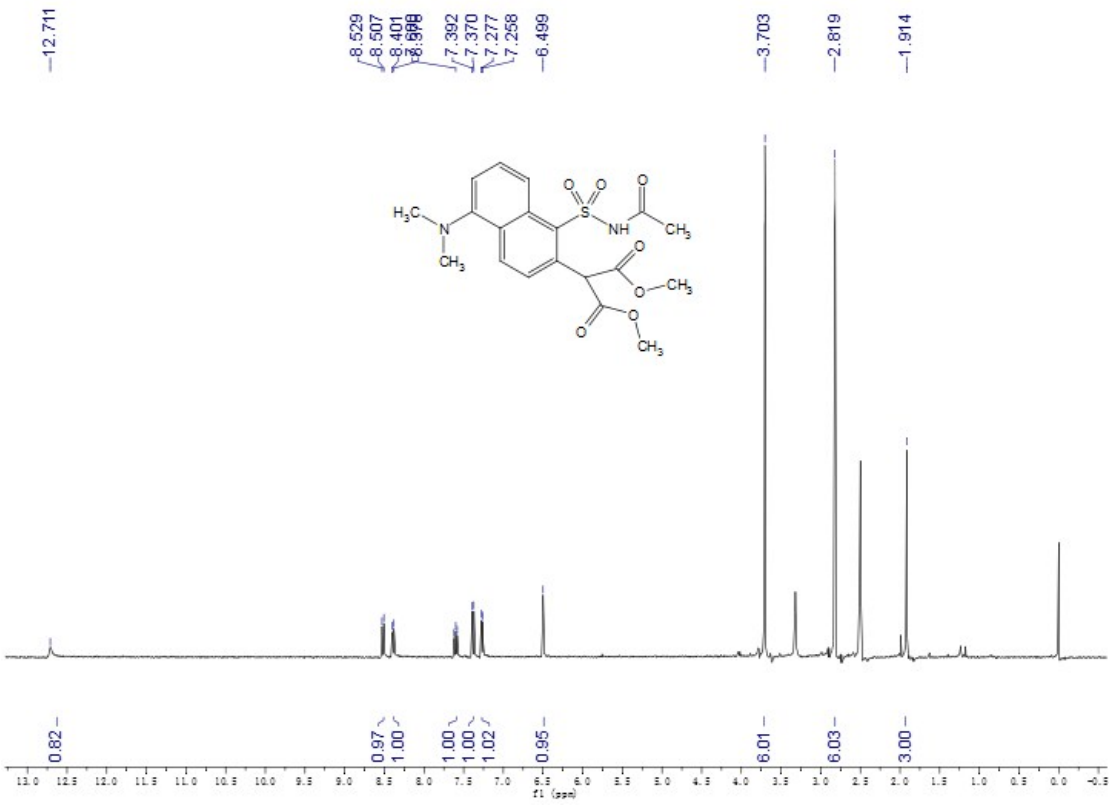


^{1}H NMR of compound **37**

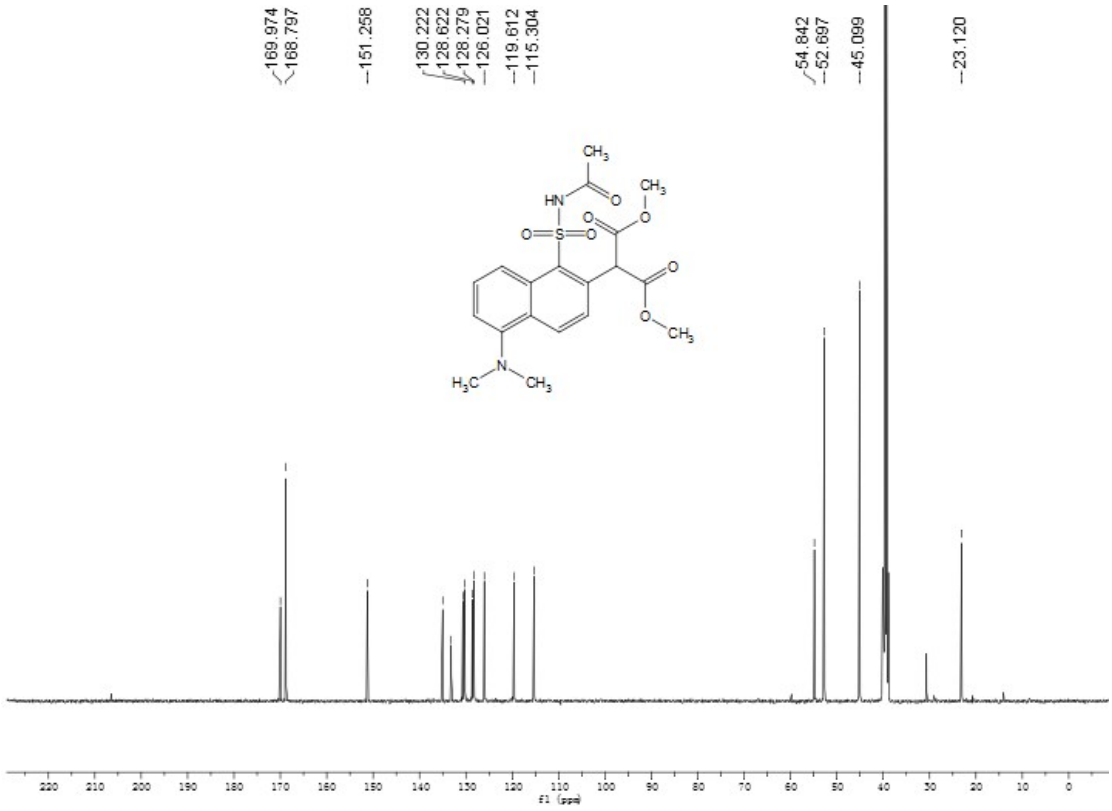
^{13}C NMR of compound **37**



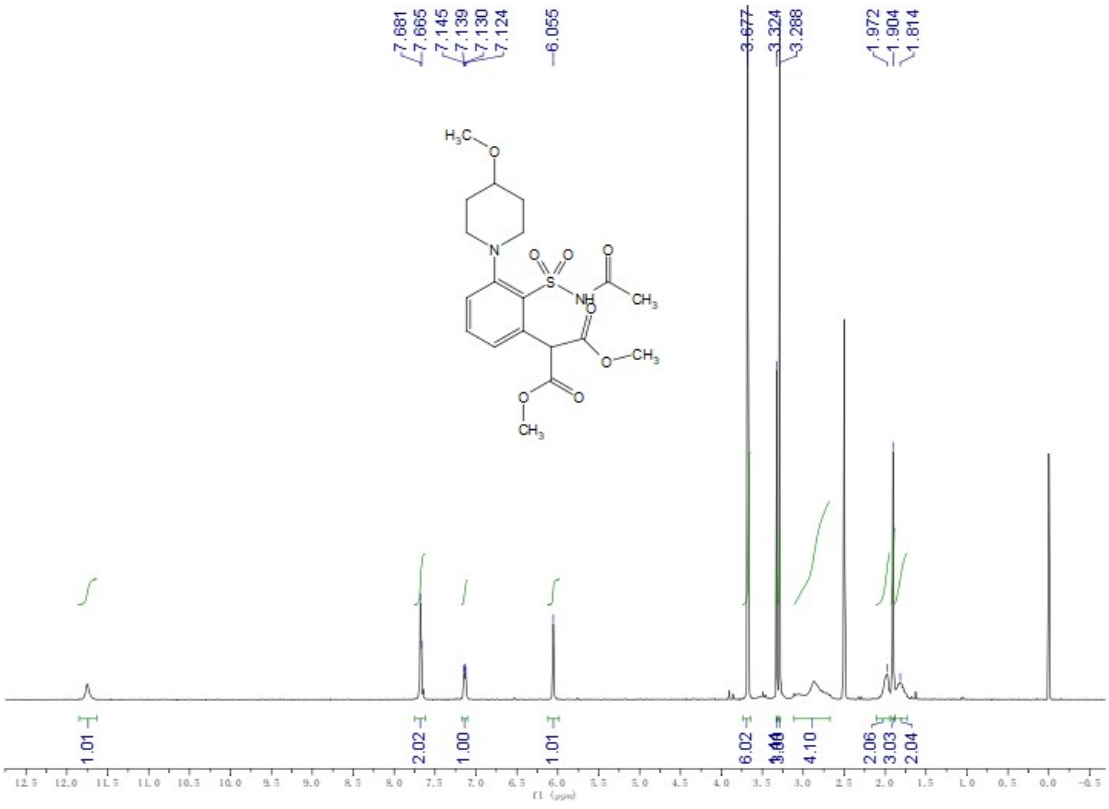
^{1}H NMR of compound **38**



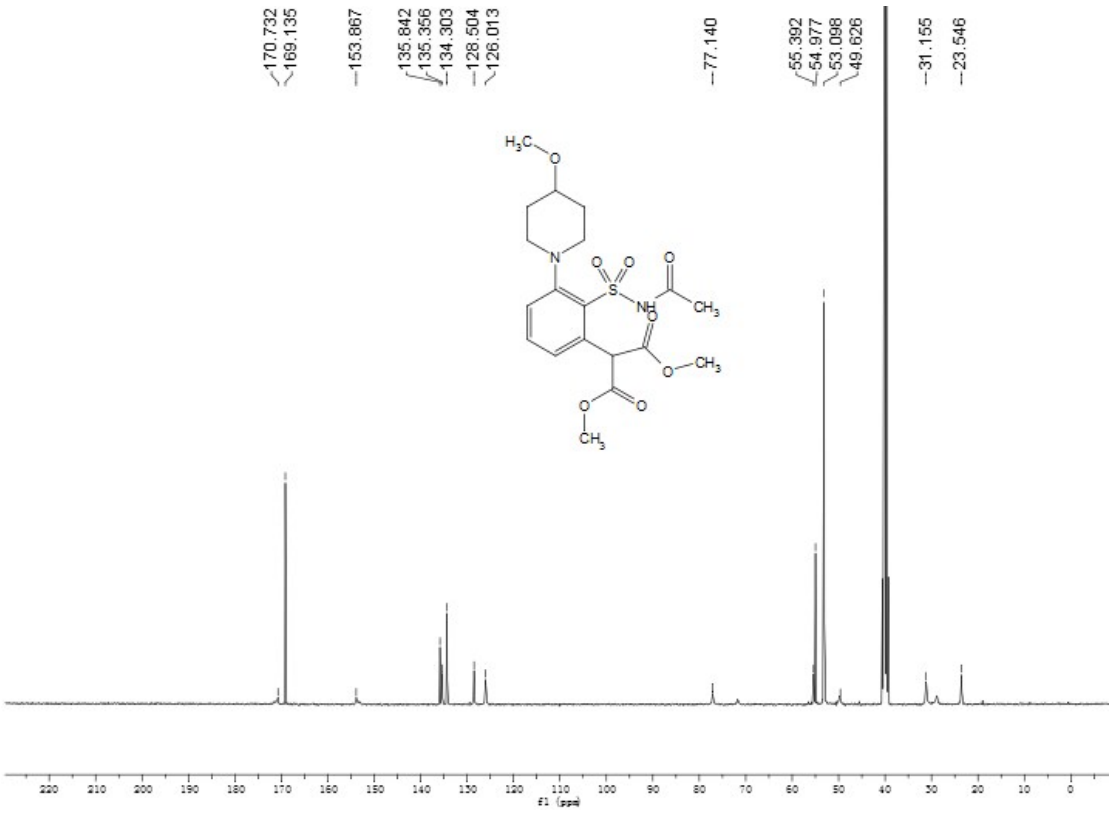
^{13}C NMR of compound **38**



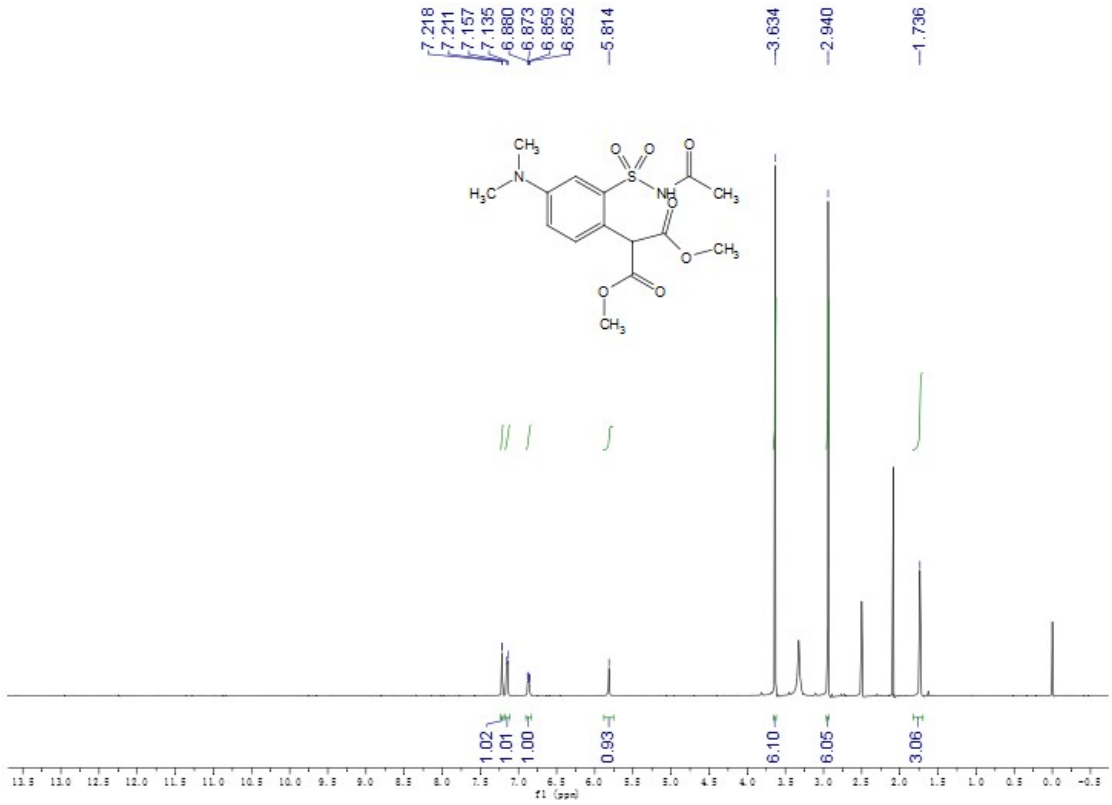
^{1}H NMR of compound **39**



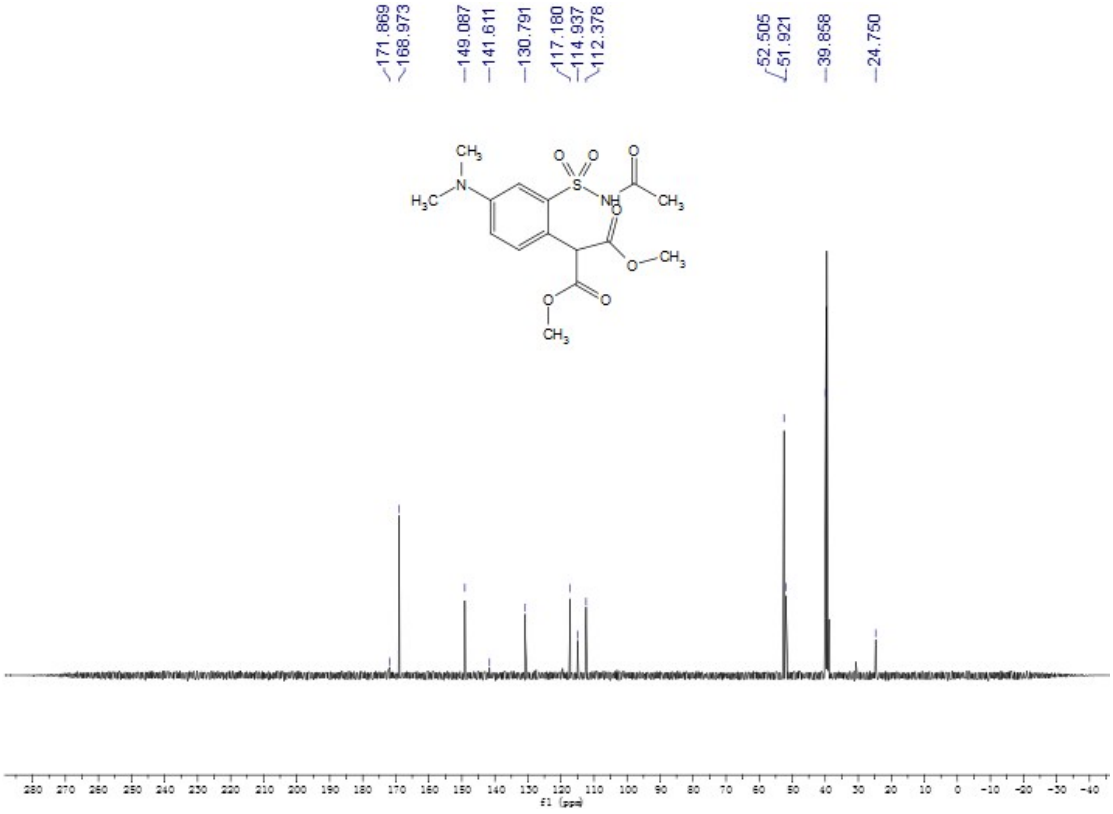
^{13}C NMR of compound **39**



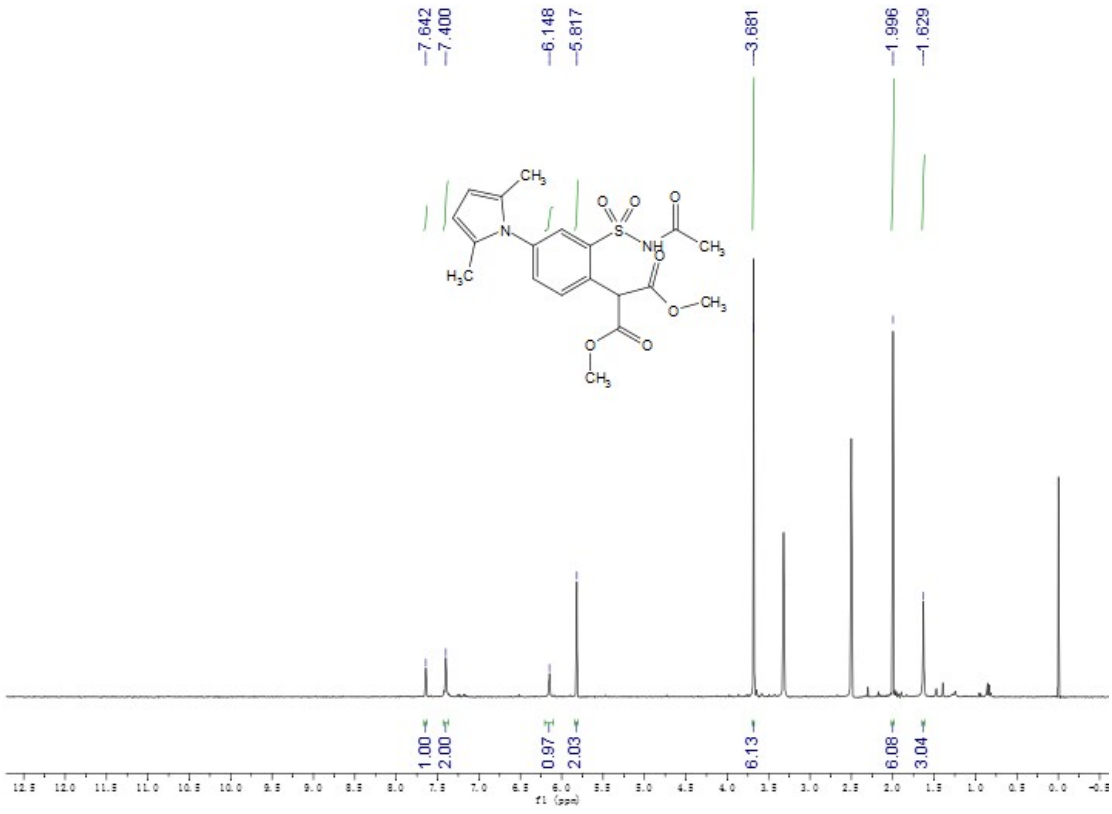
^{1}H NMR of compound **40**



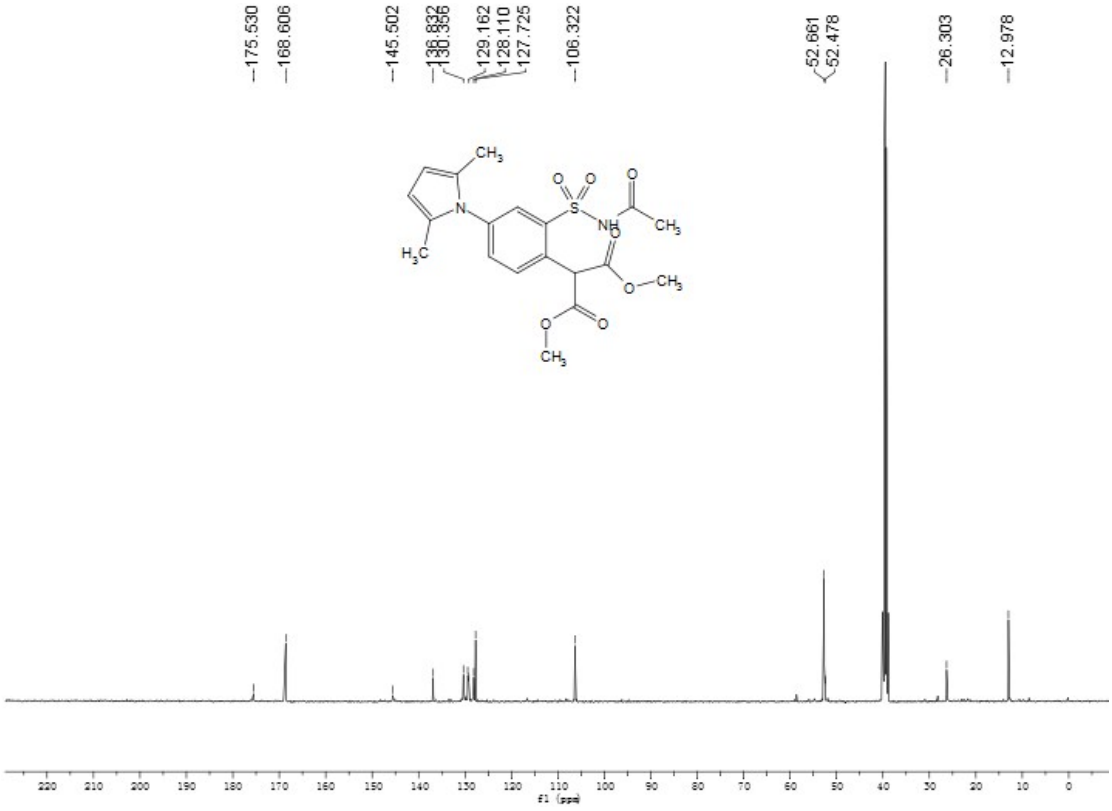
^{13}C NMR of compound **40**



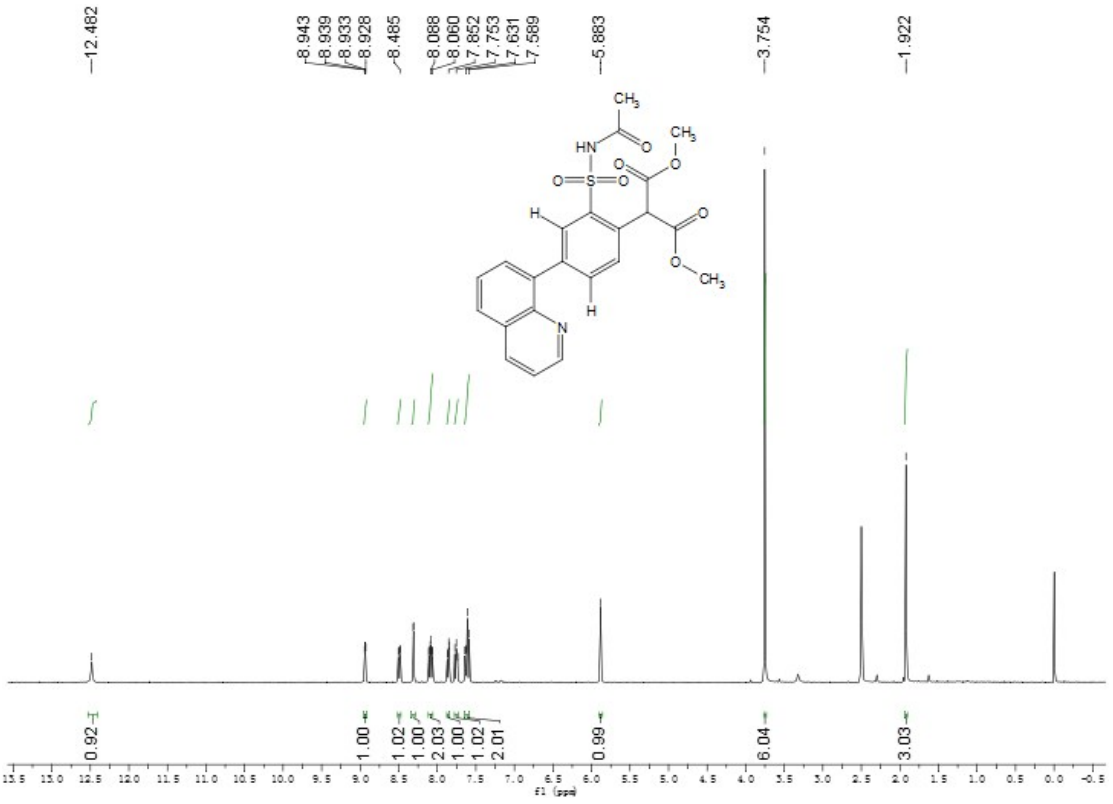
^{1}H NMR of compound **41**



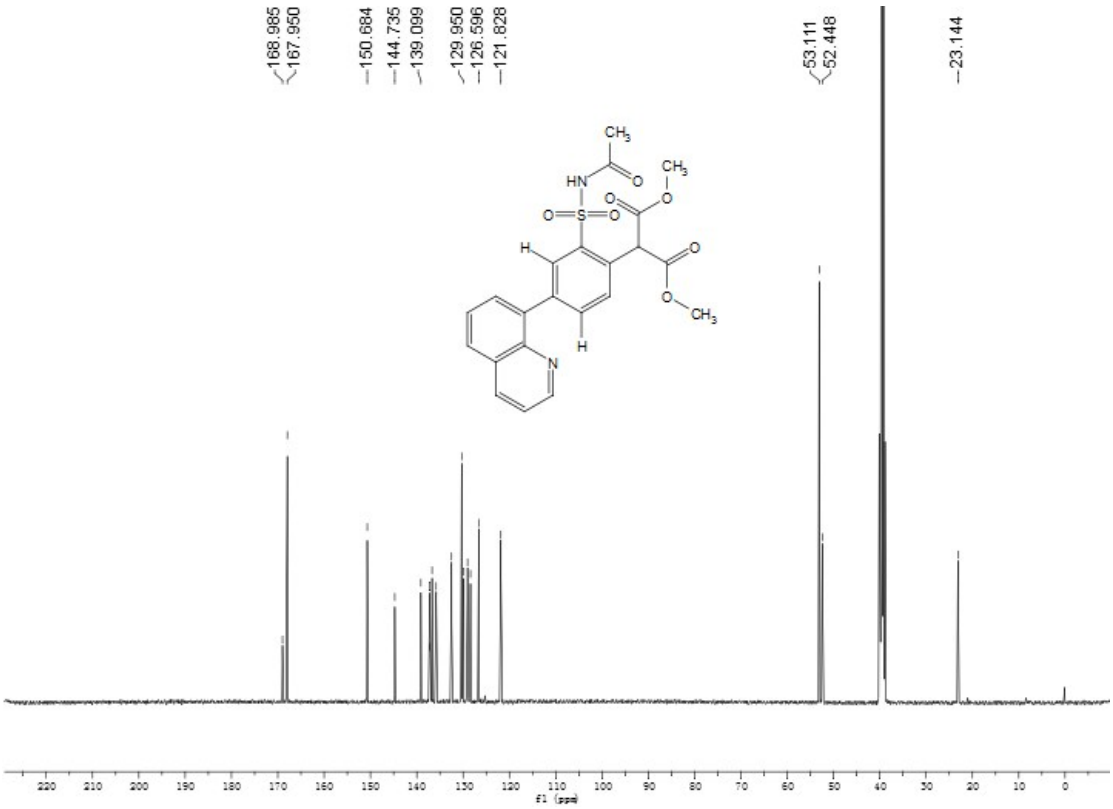
^{13}C NMR of compound **41**



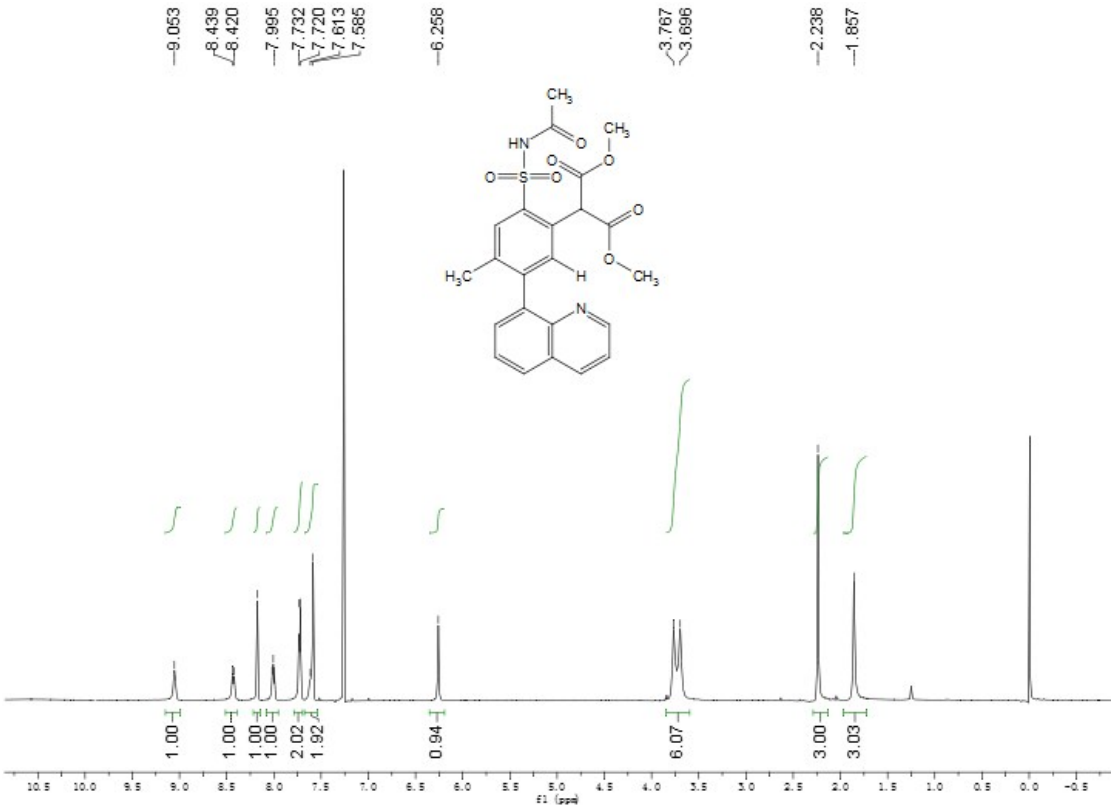
^{1}H NMR of compound **42**



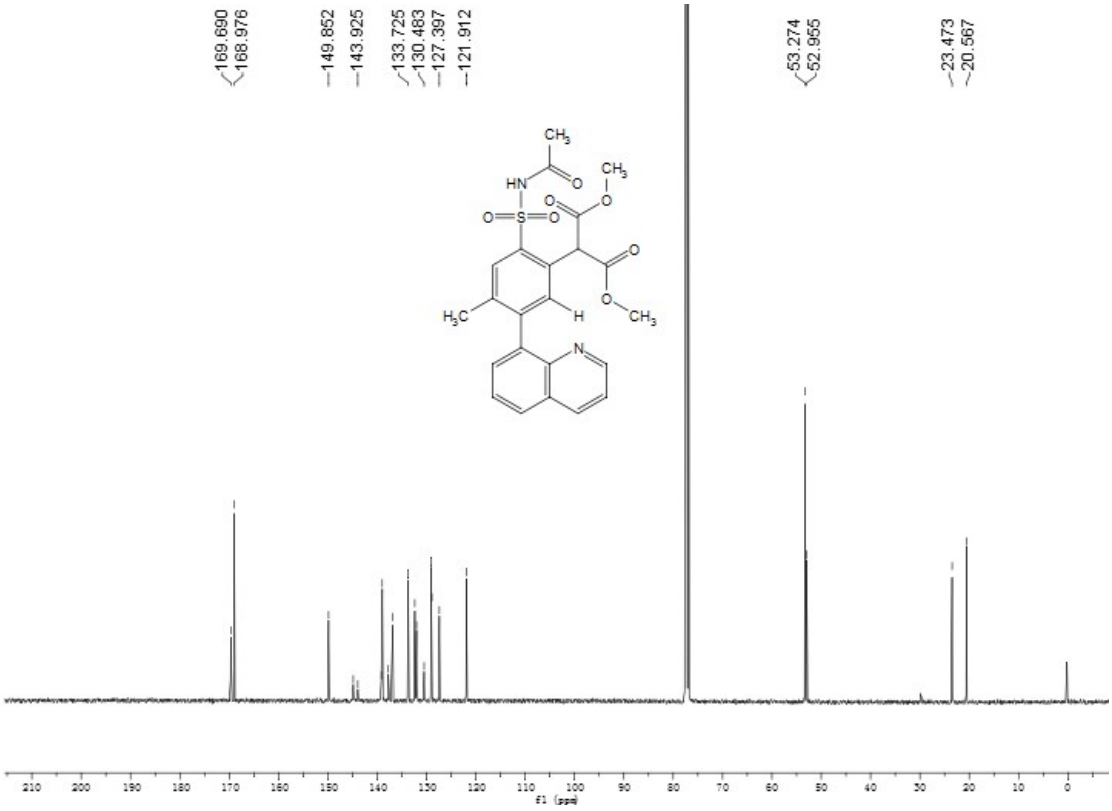
^{13}C NMR of compound **42**



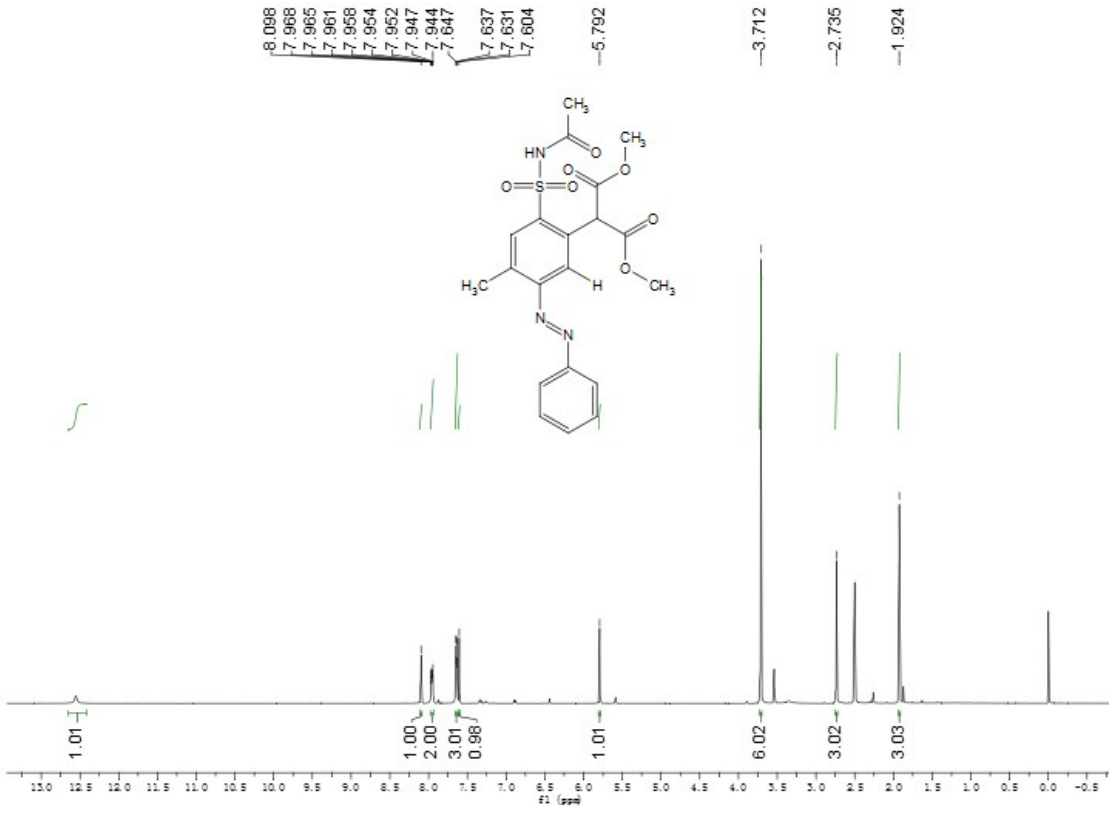
^{1}H NMR of compound **43**



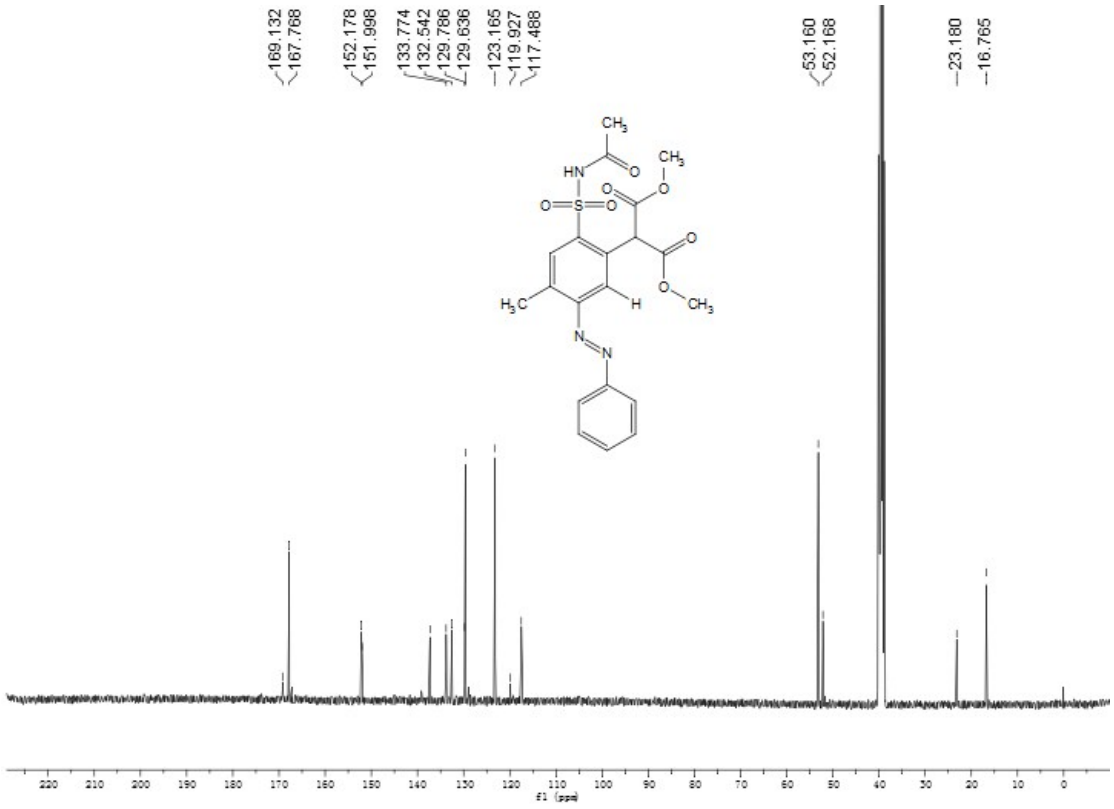
^{13}C NMR of compound **43**



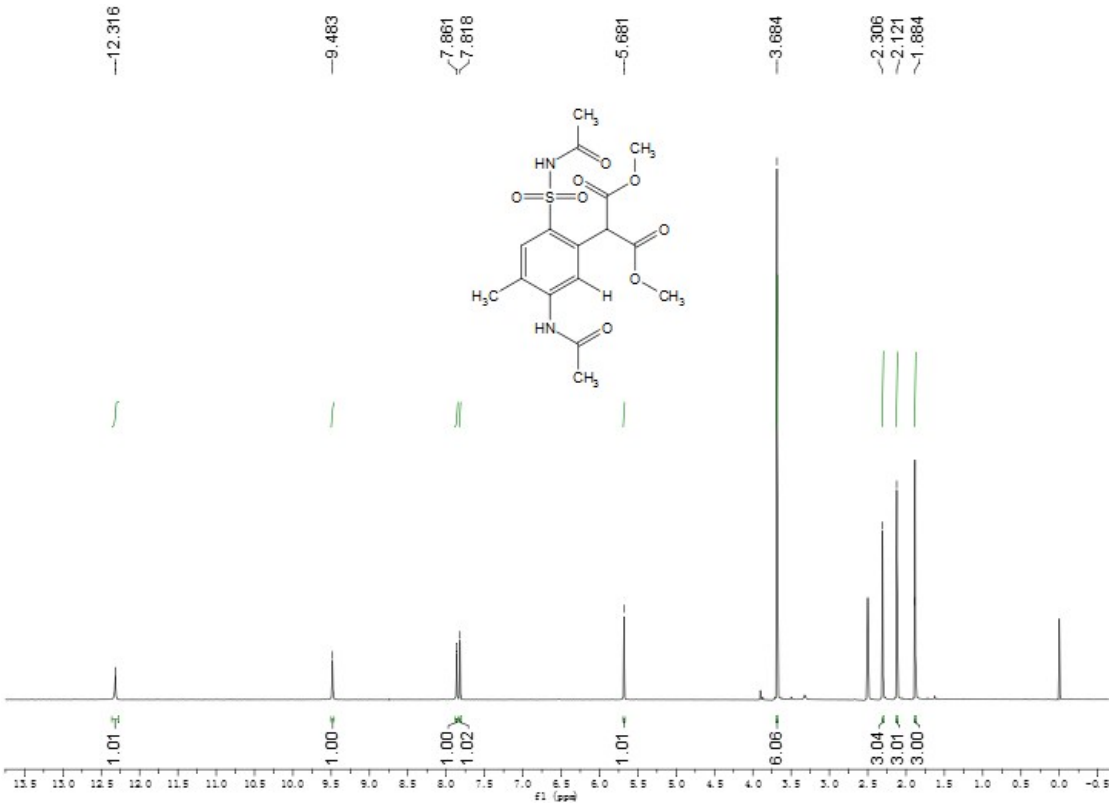
^{1}H NMR of compound **44**



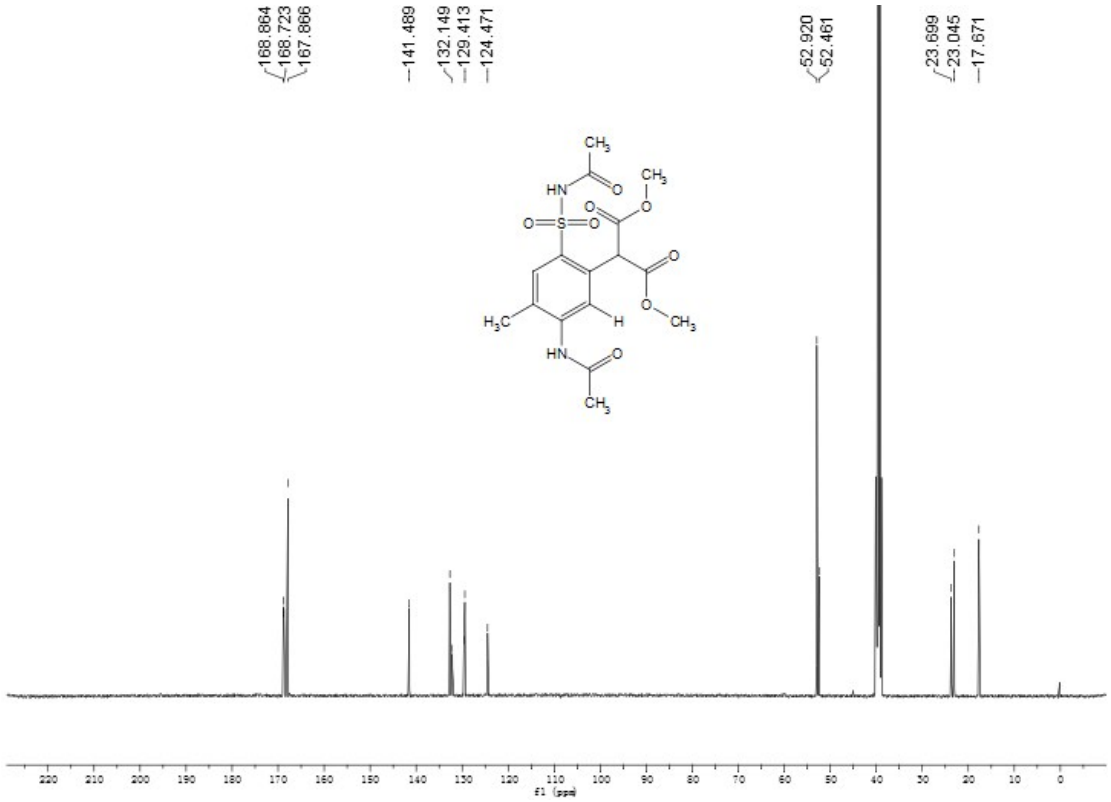
^{13}C NMR of compound **44**



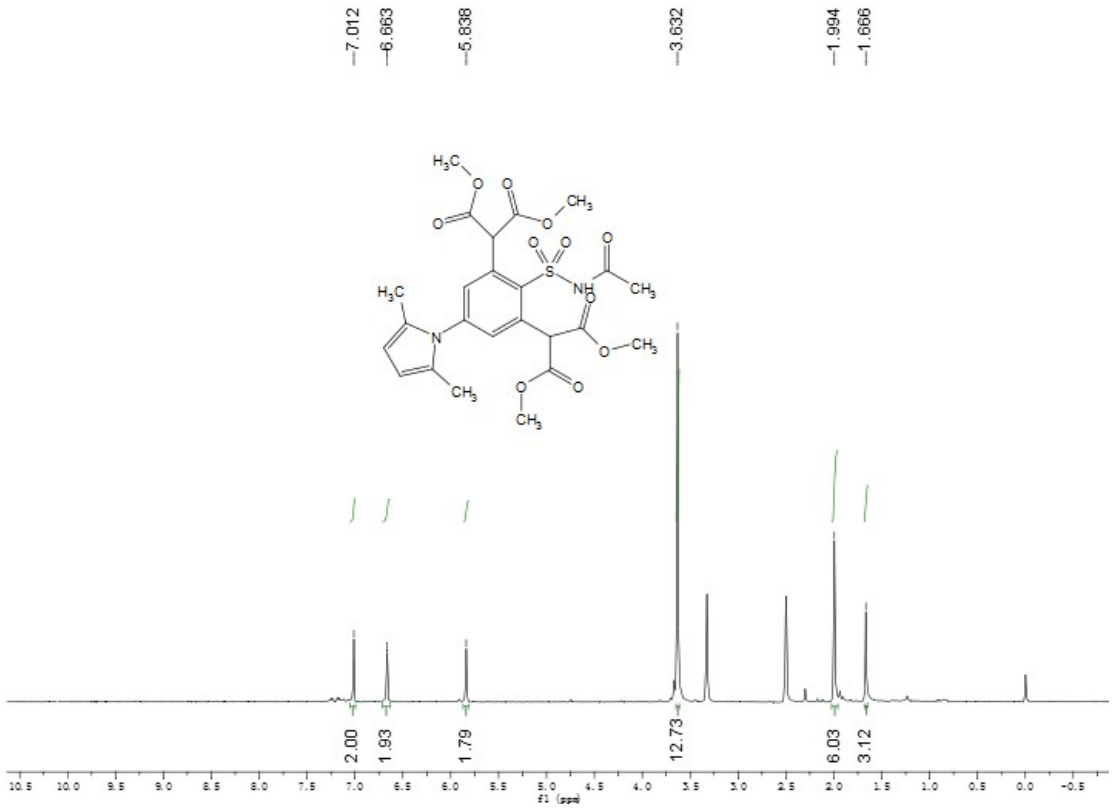
^{1}H NMR of compound **45**



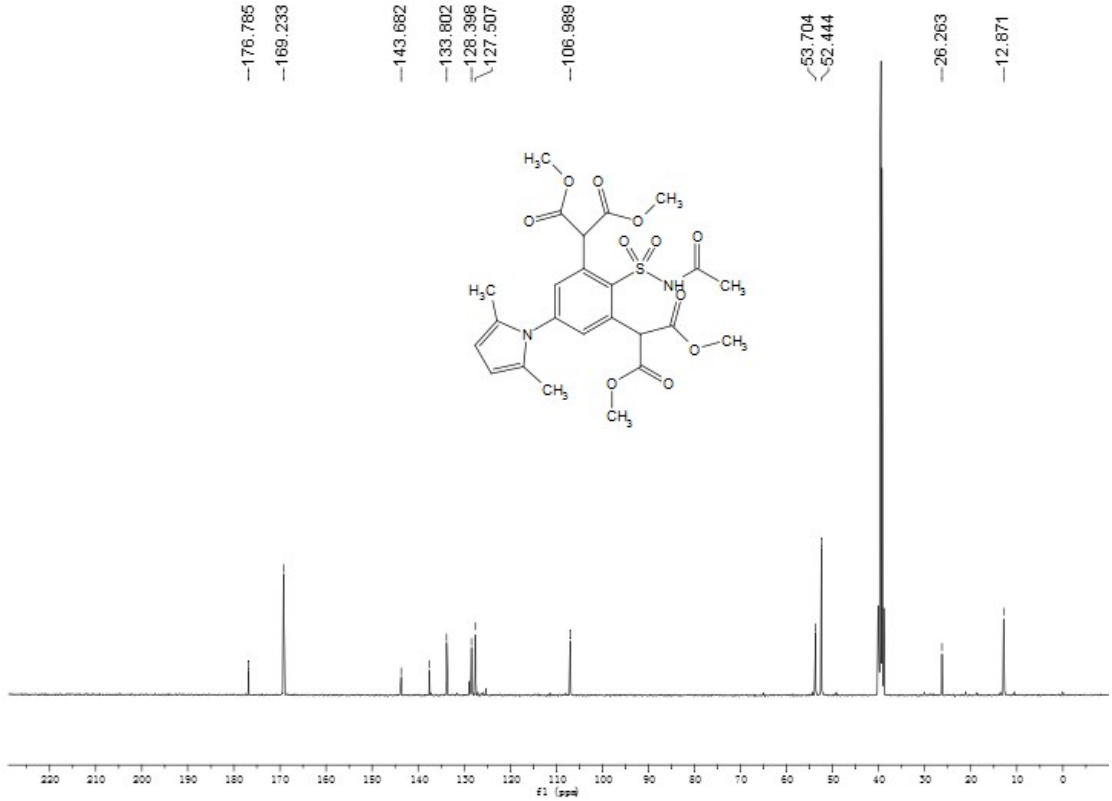
^{13}C NMR of compound **45**



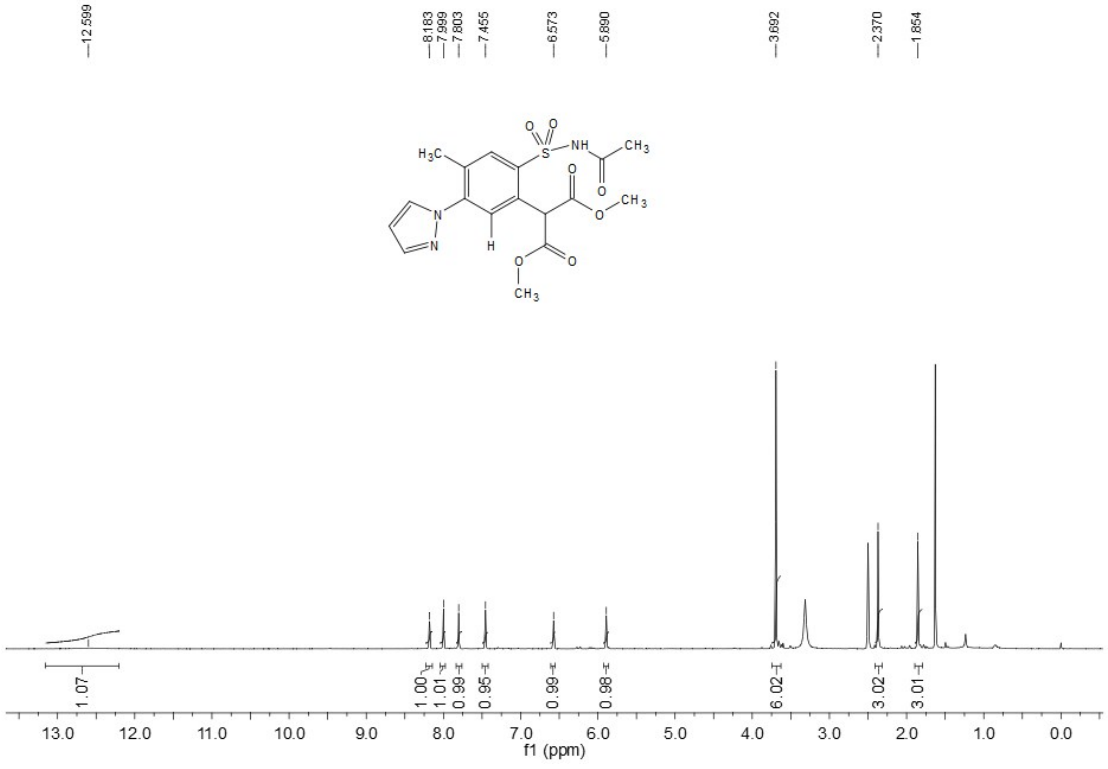
^{1}H NMR of compound **46**



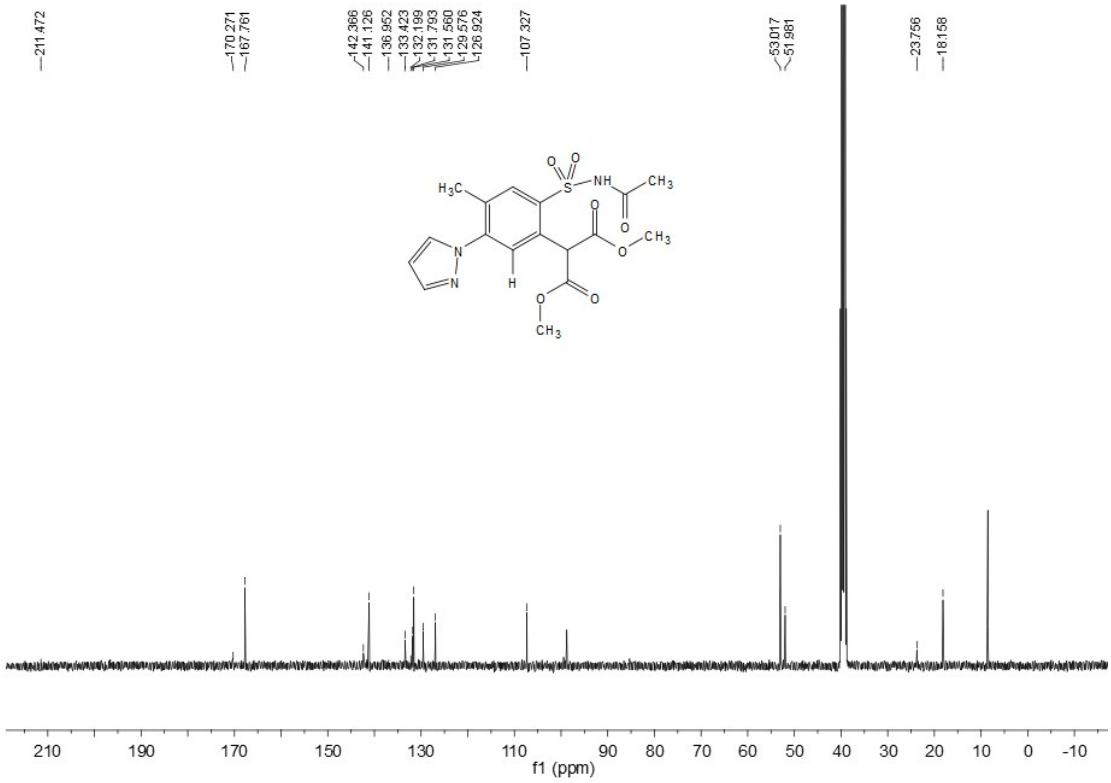
^{13}C NMR of compound **46**



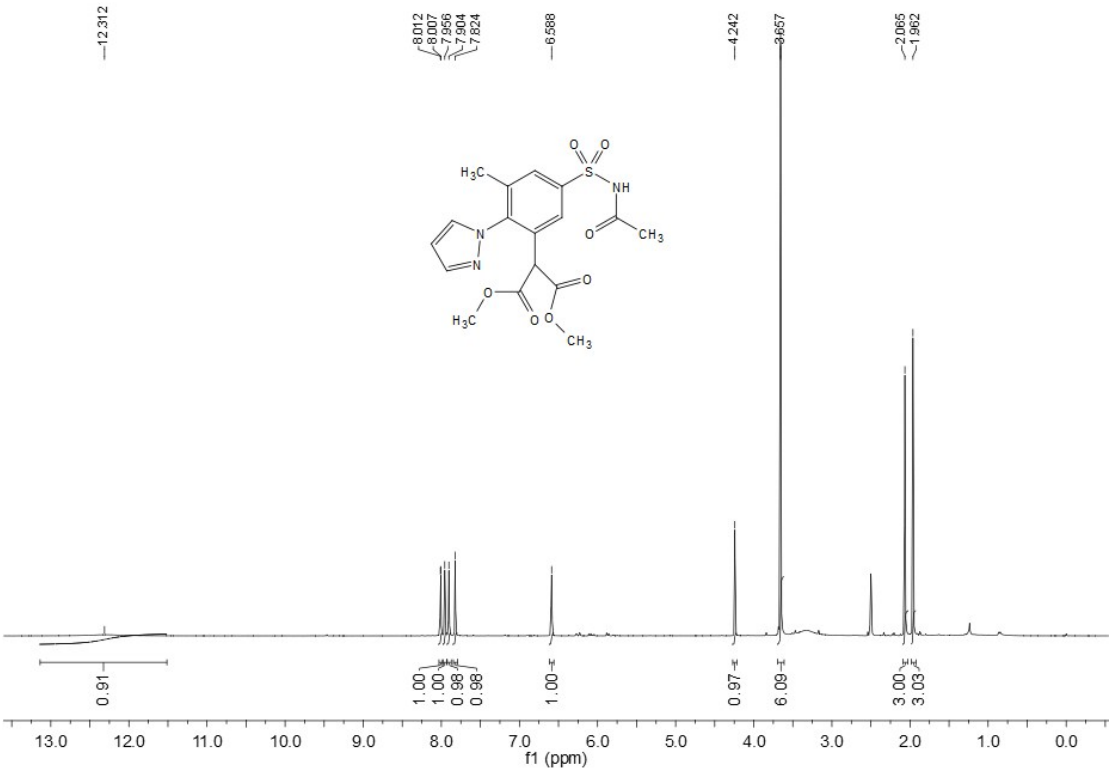
^{1}H NMR of compound **47**



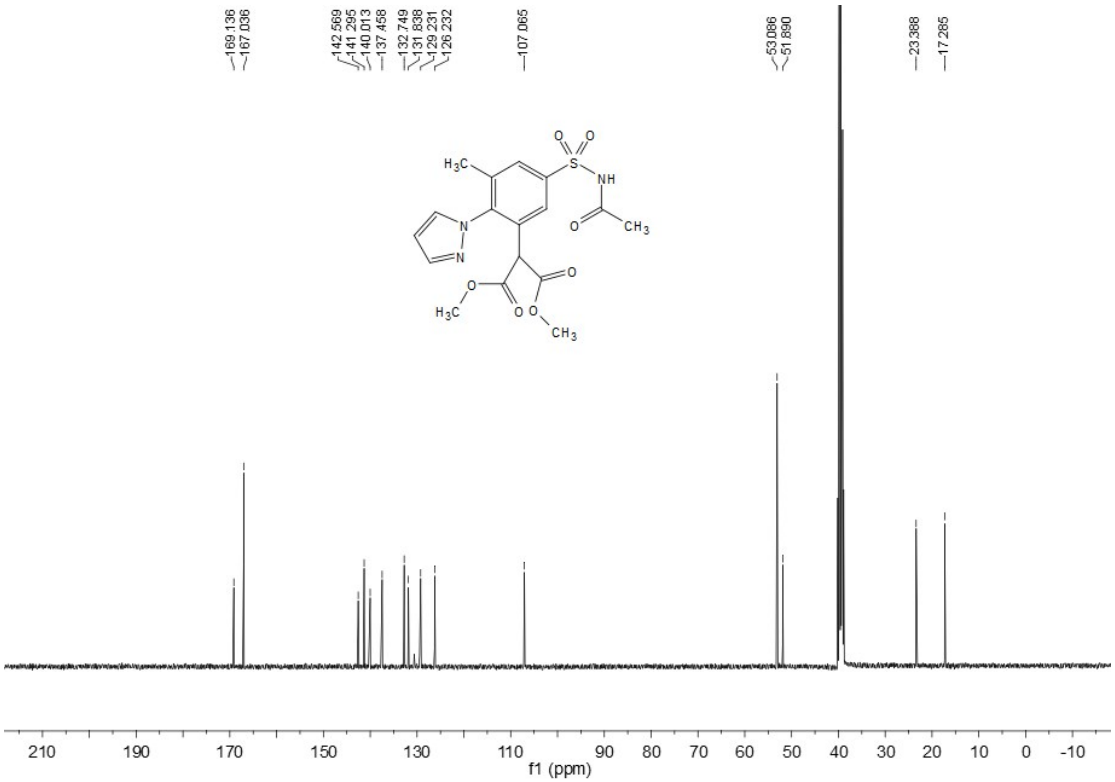
^{13}C NMR of compound **47**



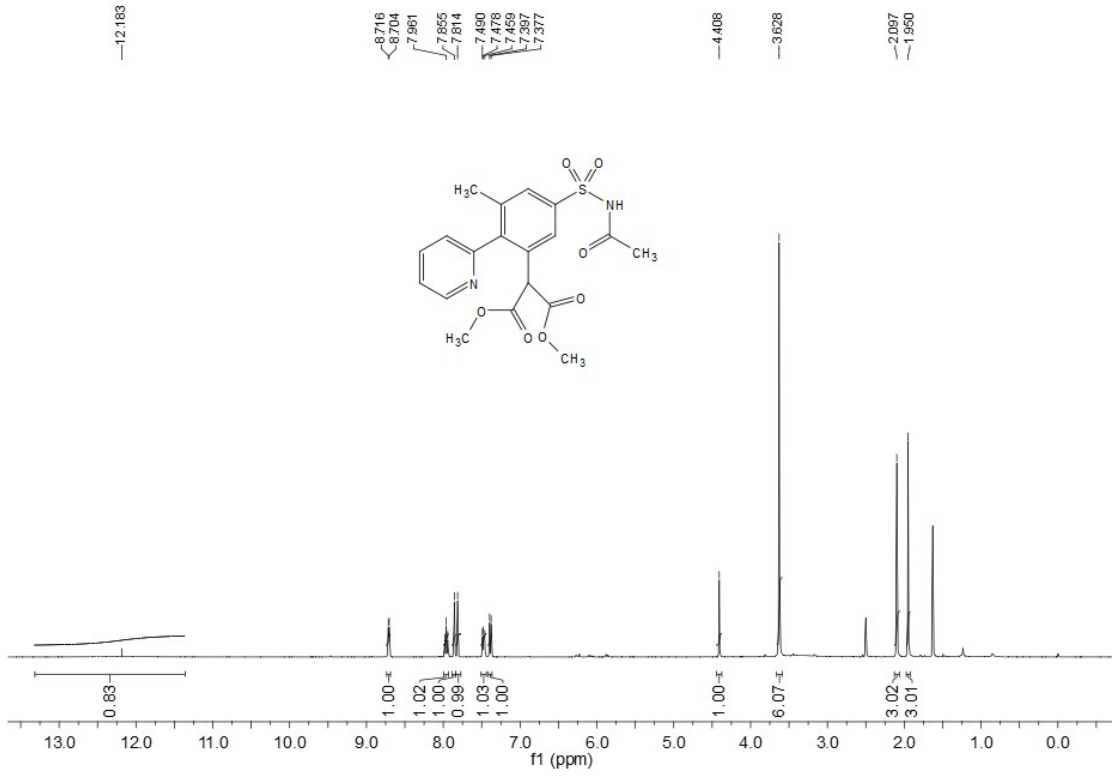
^{1}H NMR of compound **47'**



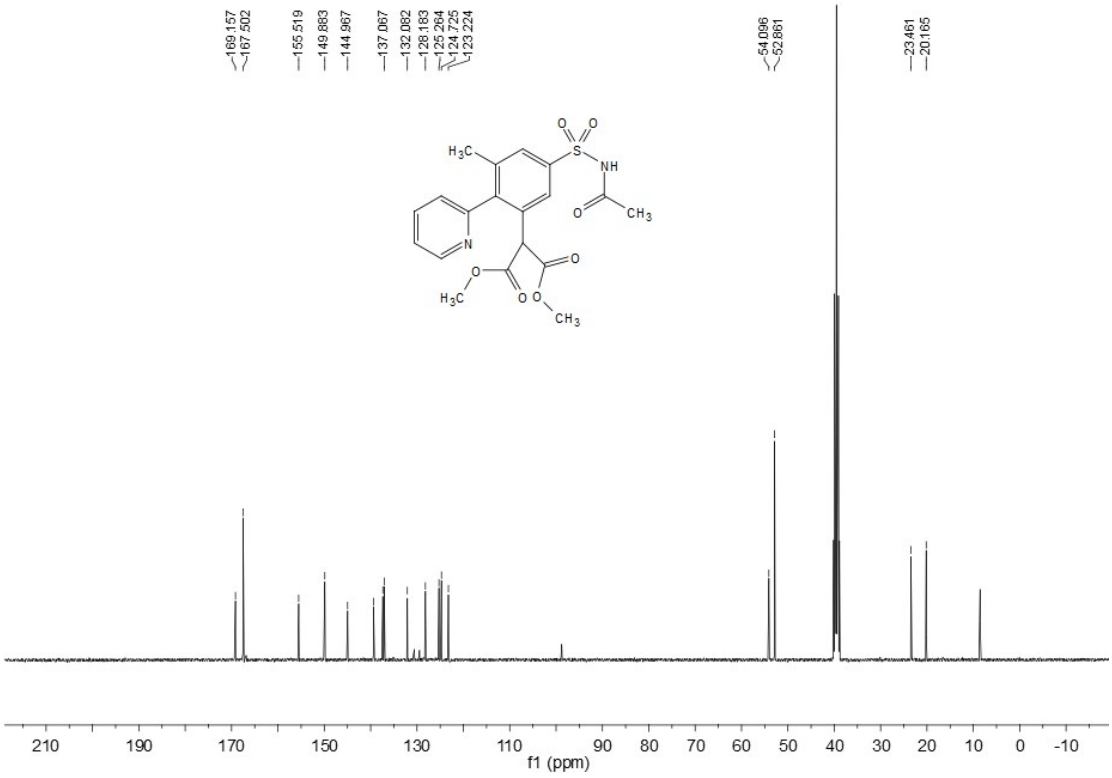
^{13}C NMR of compound **47'**



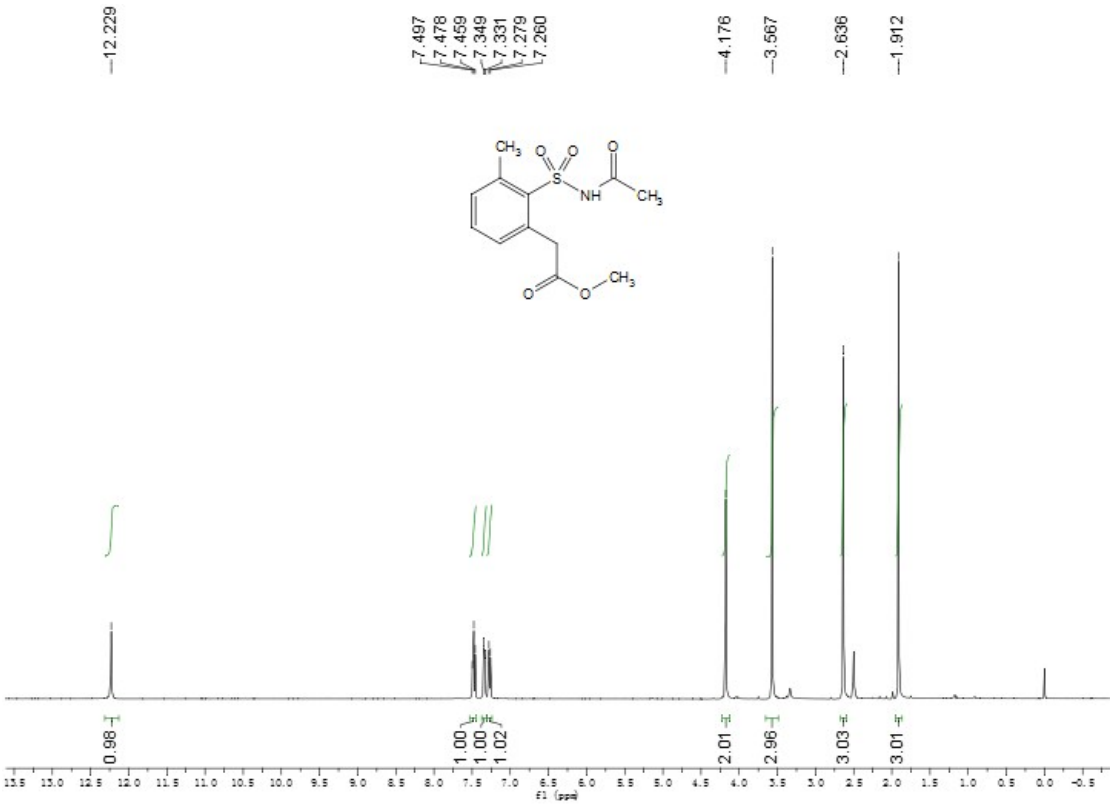
^{1}H NMR of compound **48'**



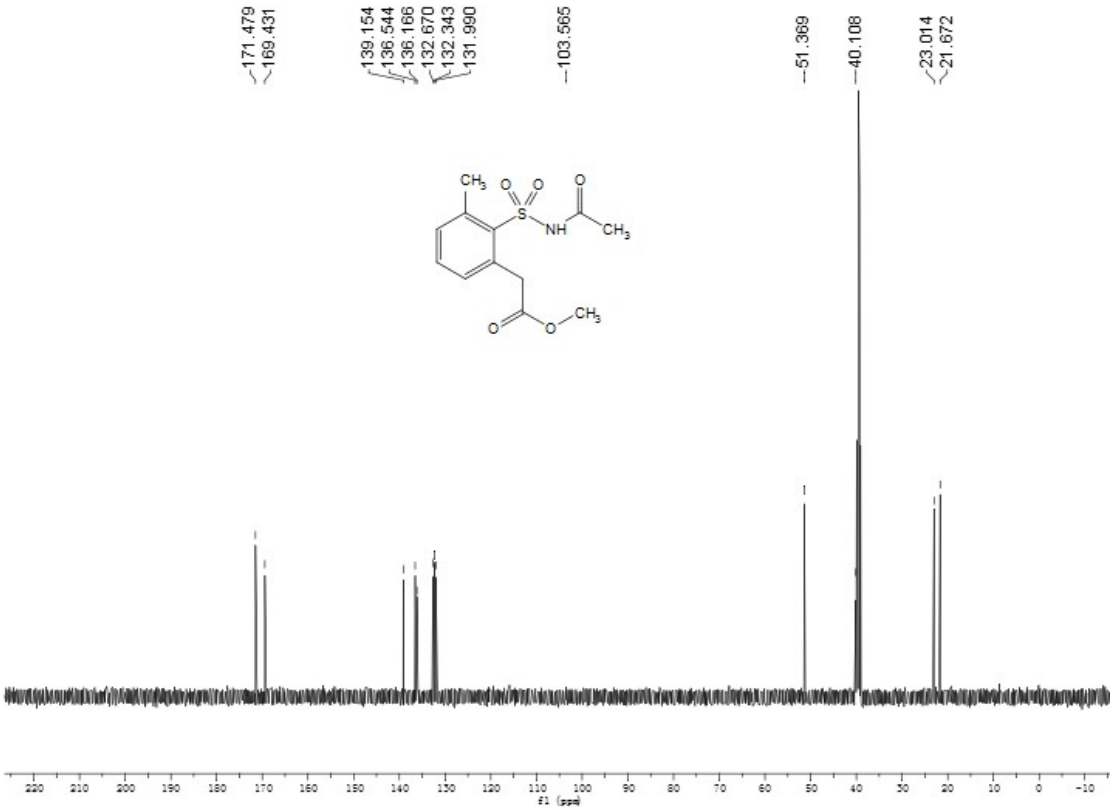
^{13}C NMR of compound **48'**



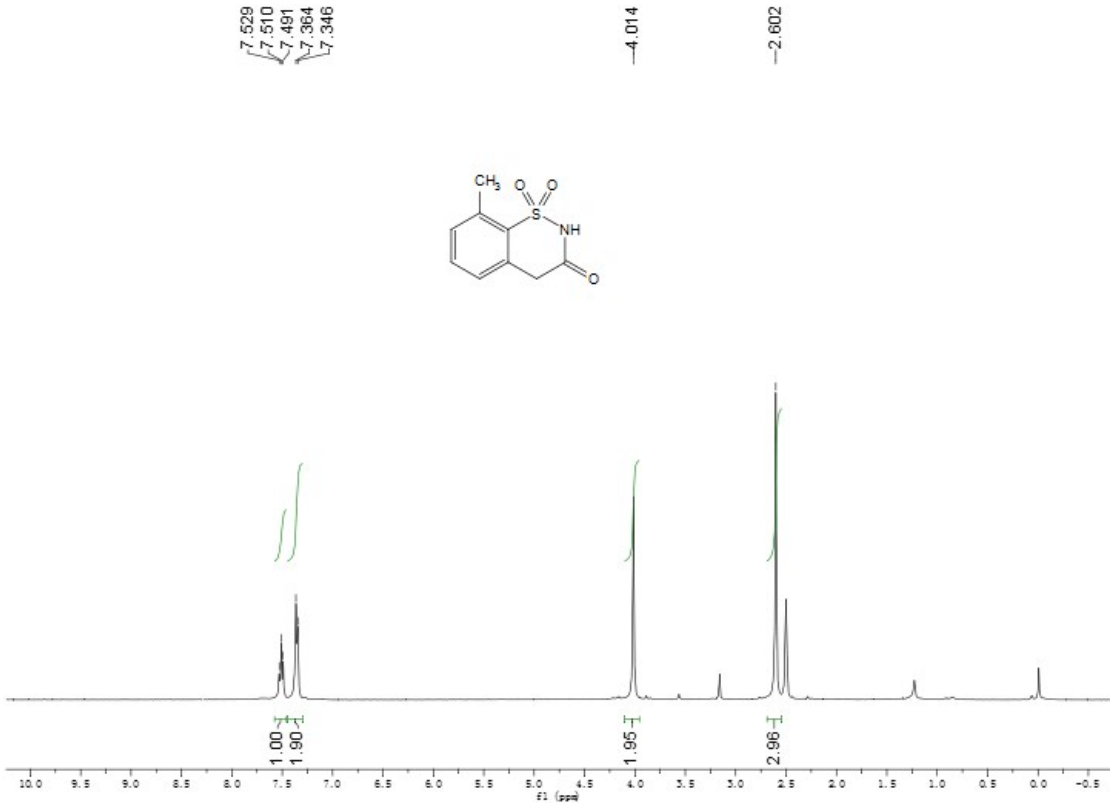
^{1}H NMR of compound **49**



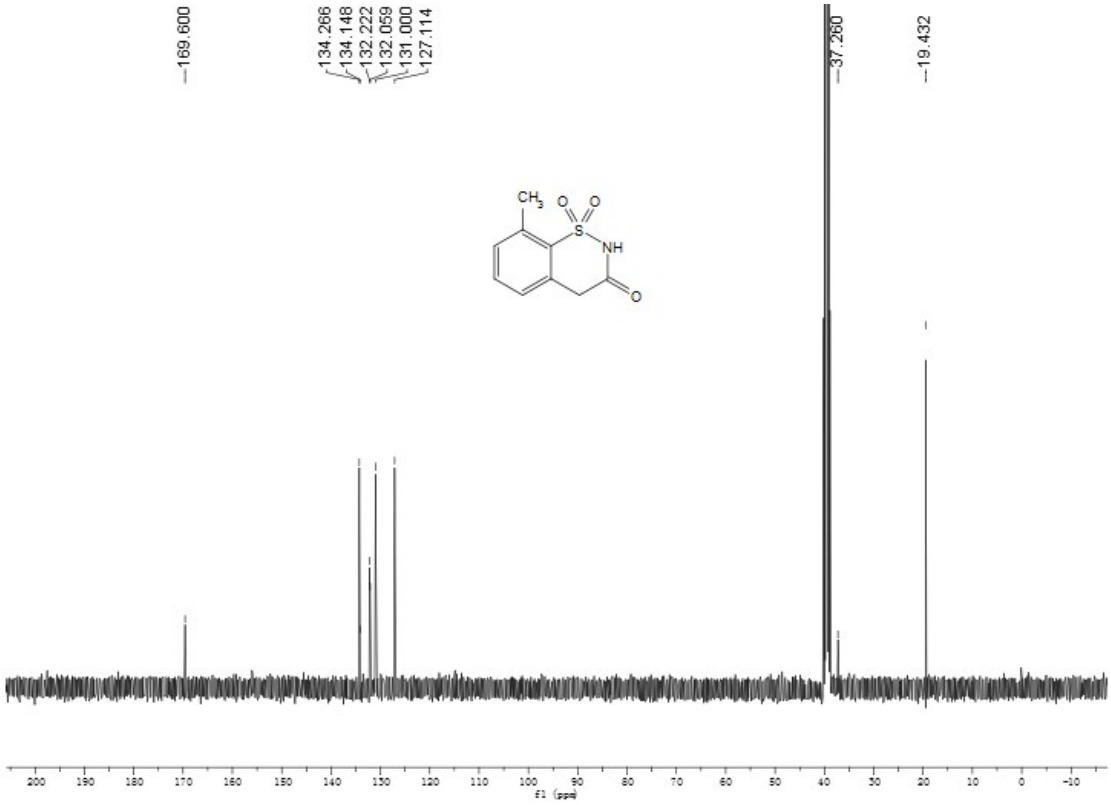
^{13}C NMR of compound **49**



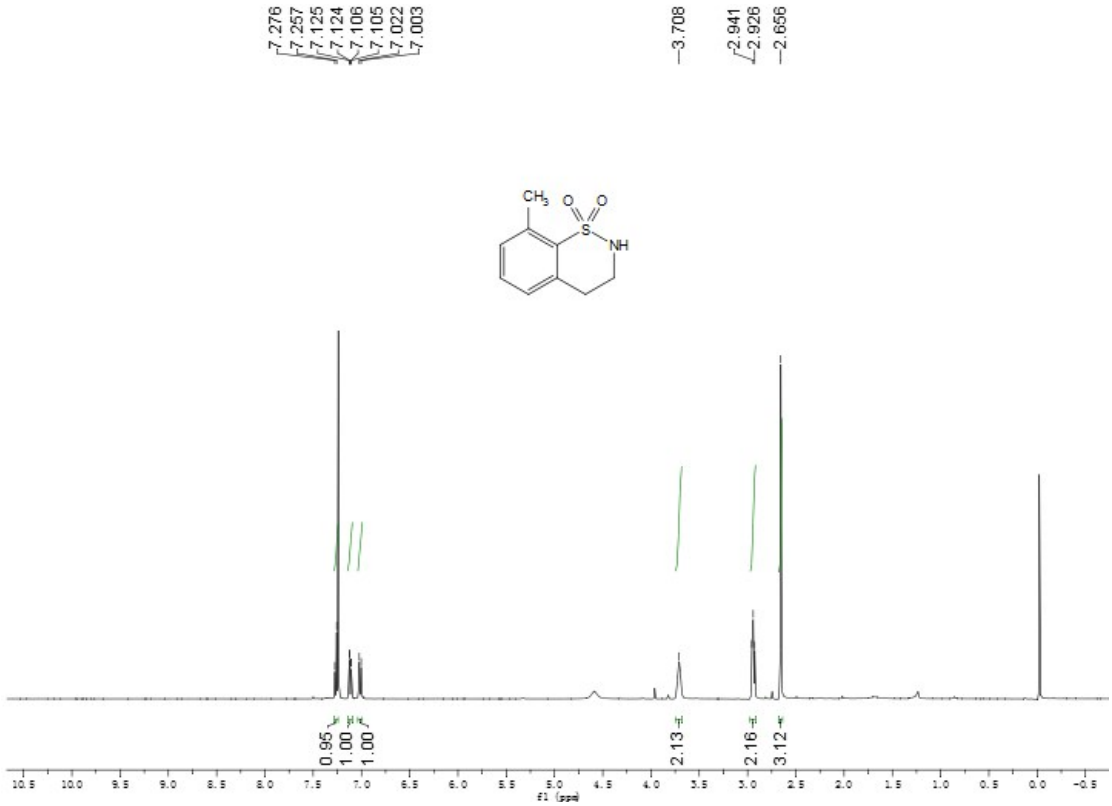
^{1}H NMR of compound **50**



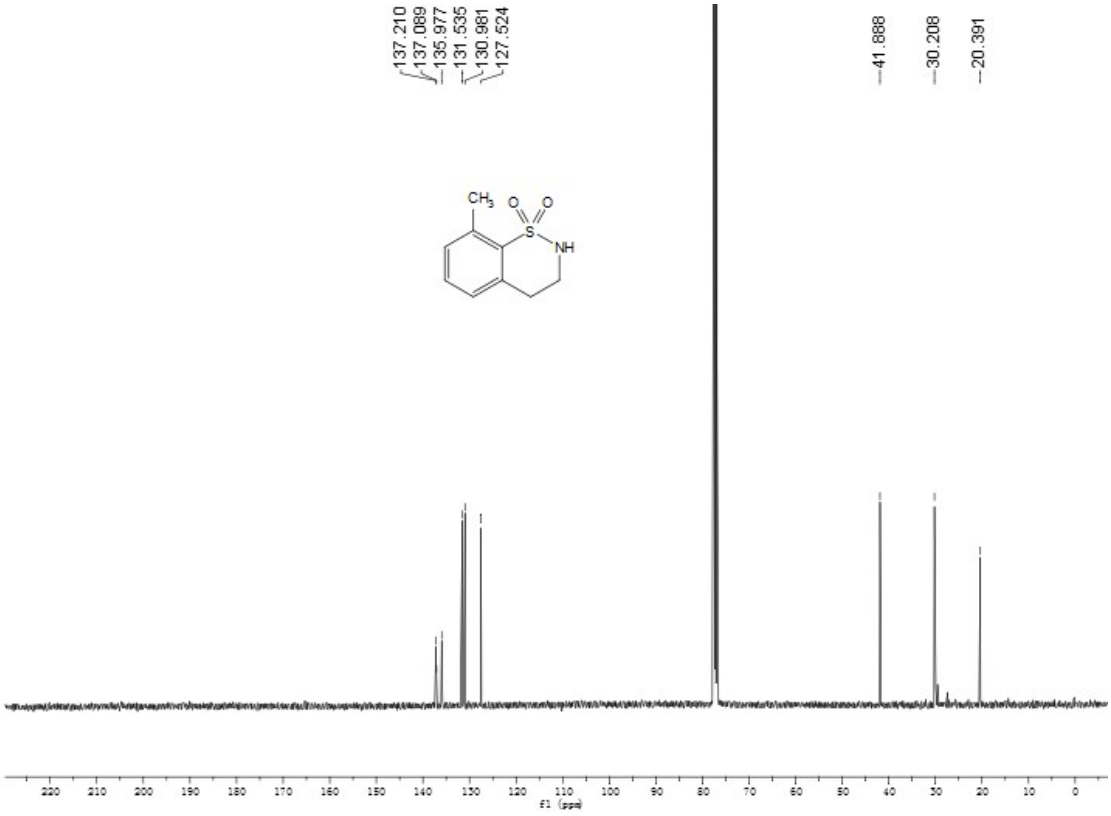
^{13}C NMR of compound **50**



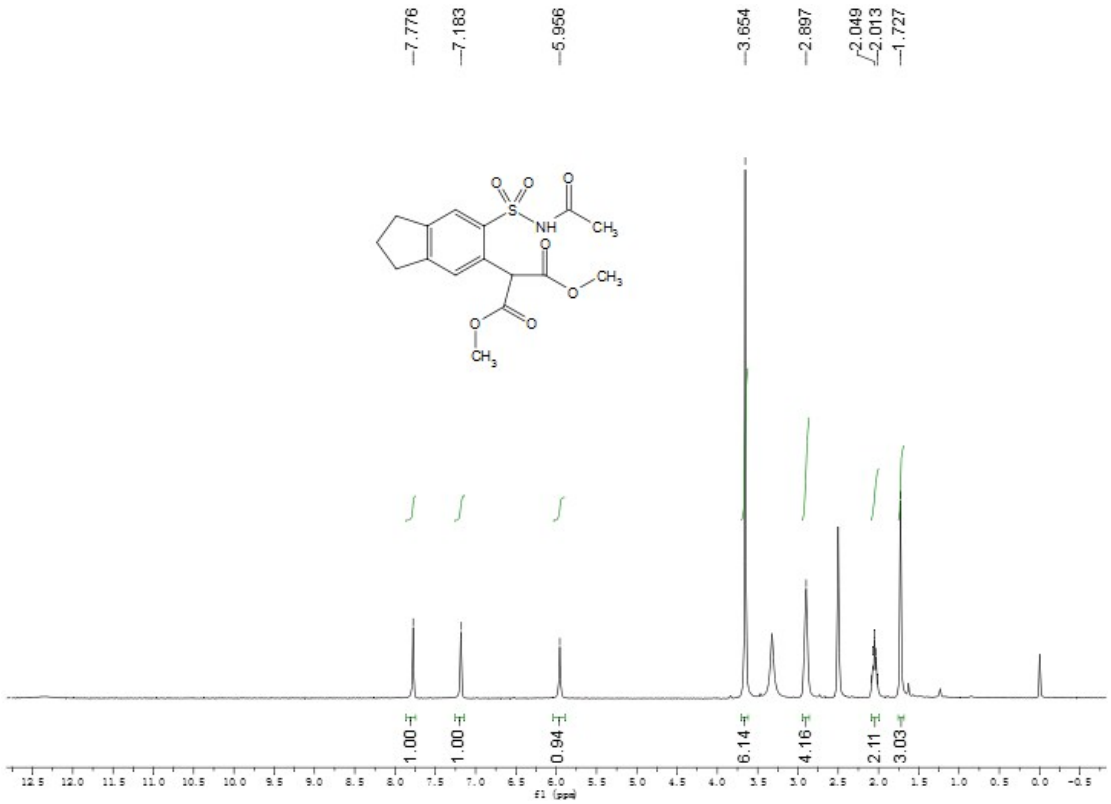
^{1}H NMR of compound **51**



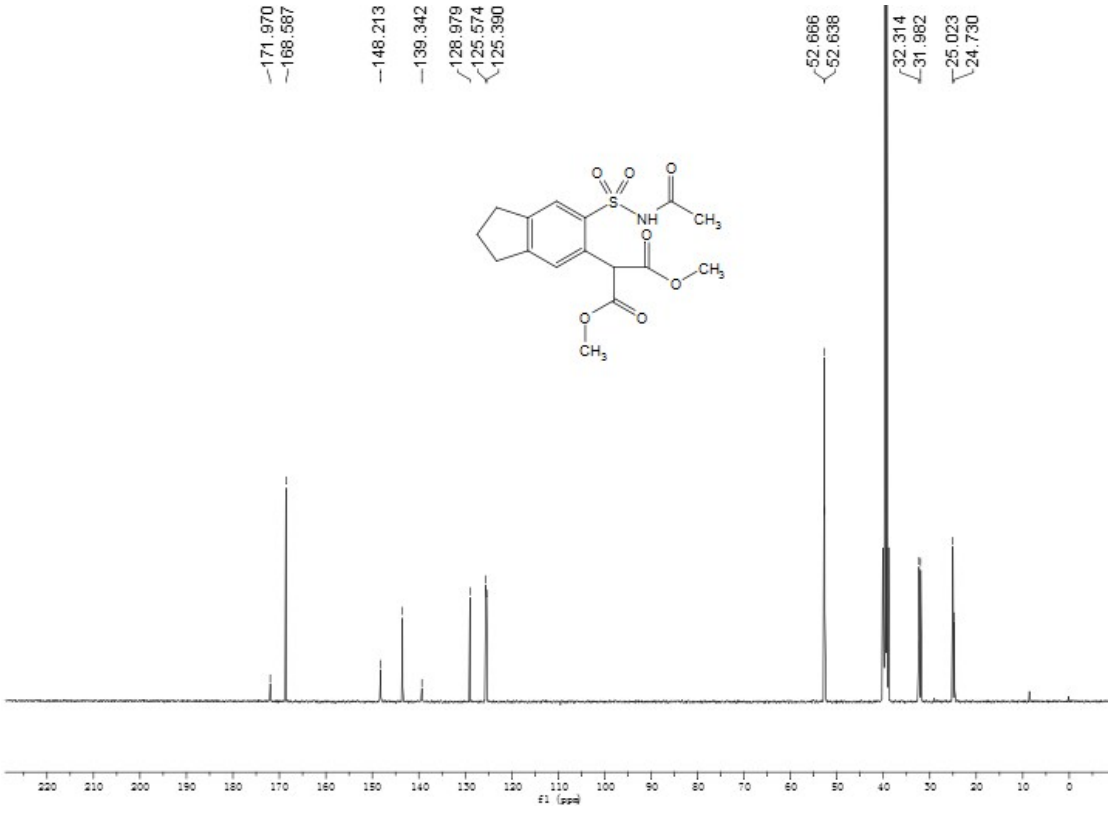
^{13}C NMR of compound **51**



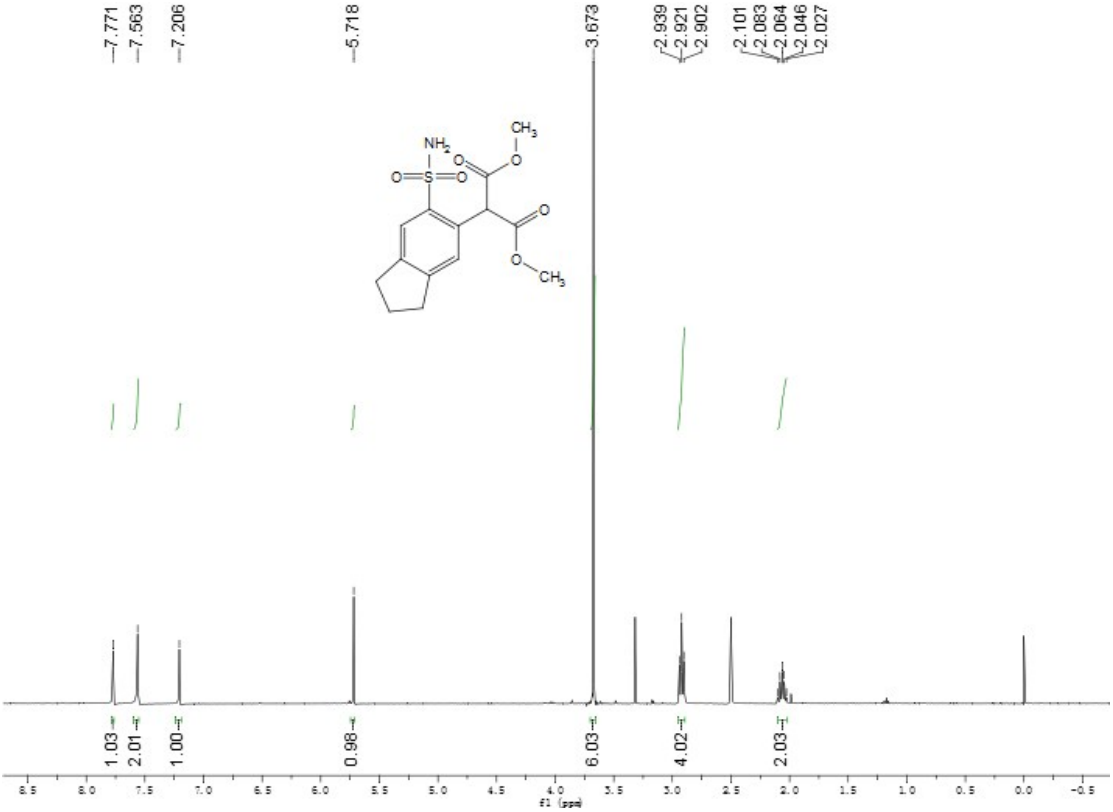
^{1}H NMR of compound **52**



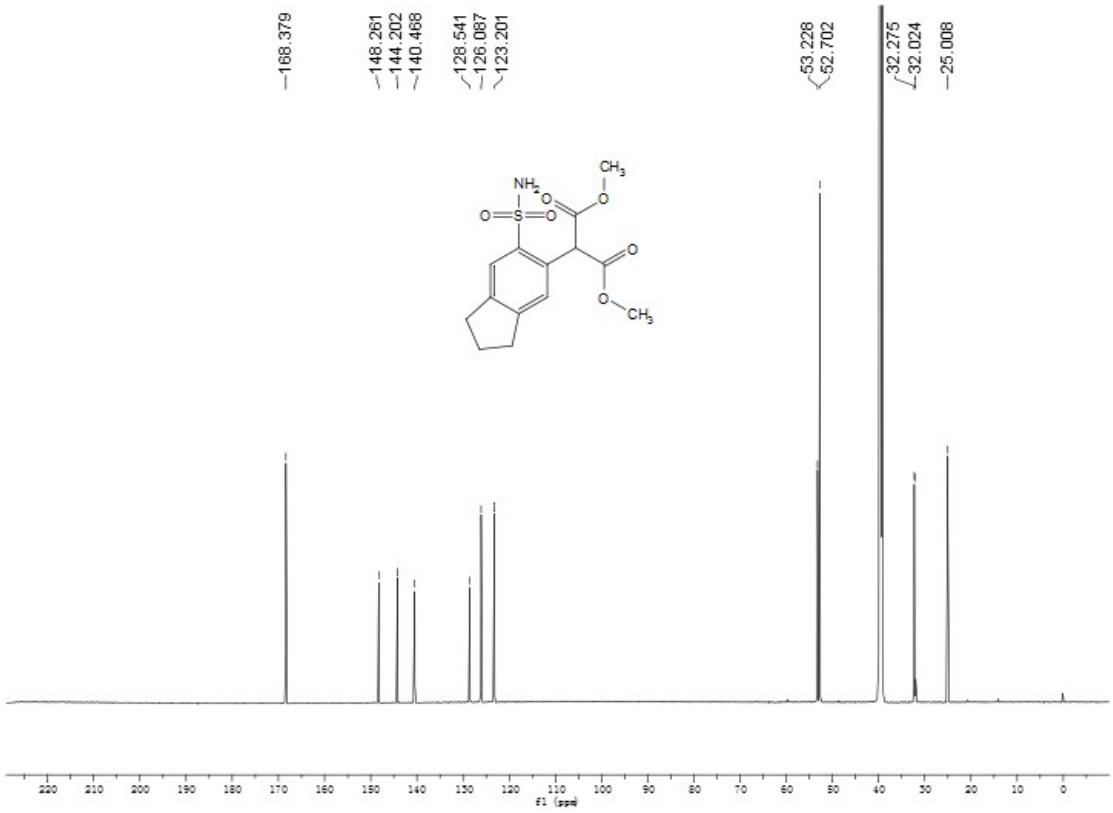
^{13}C NMR of compound **52**



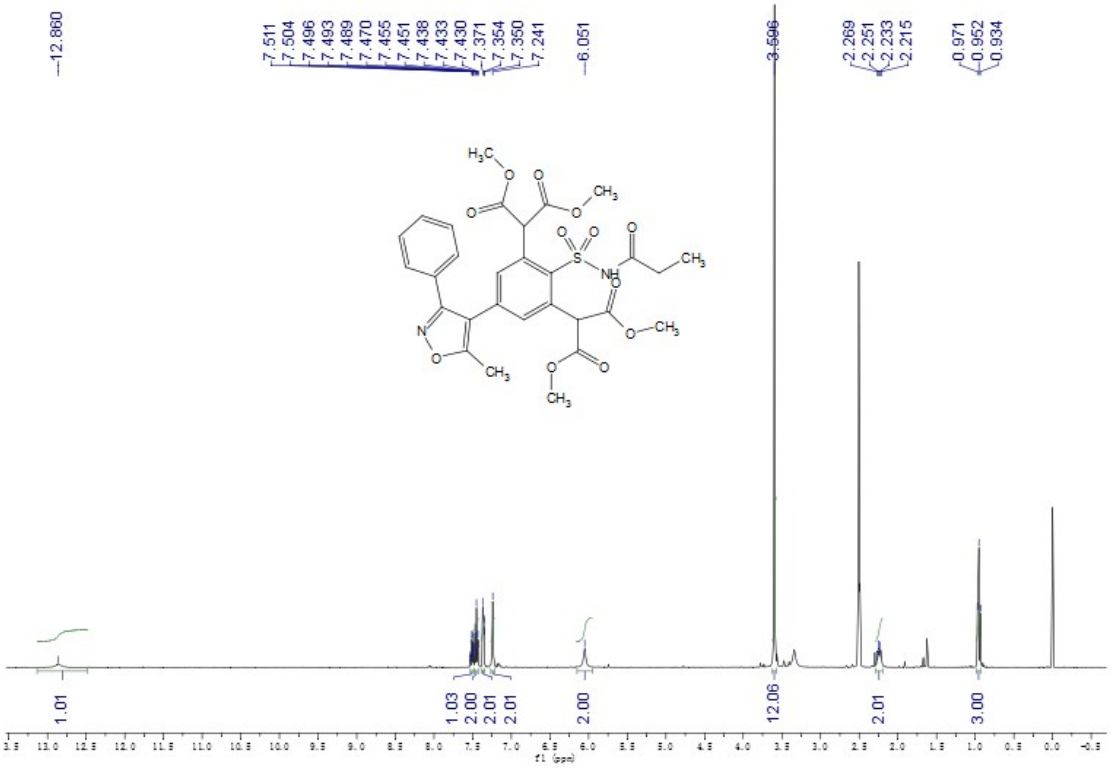
^{1}H NMR of compound **53**



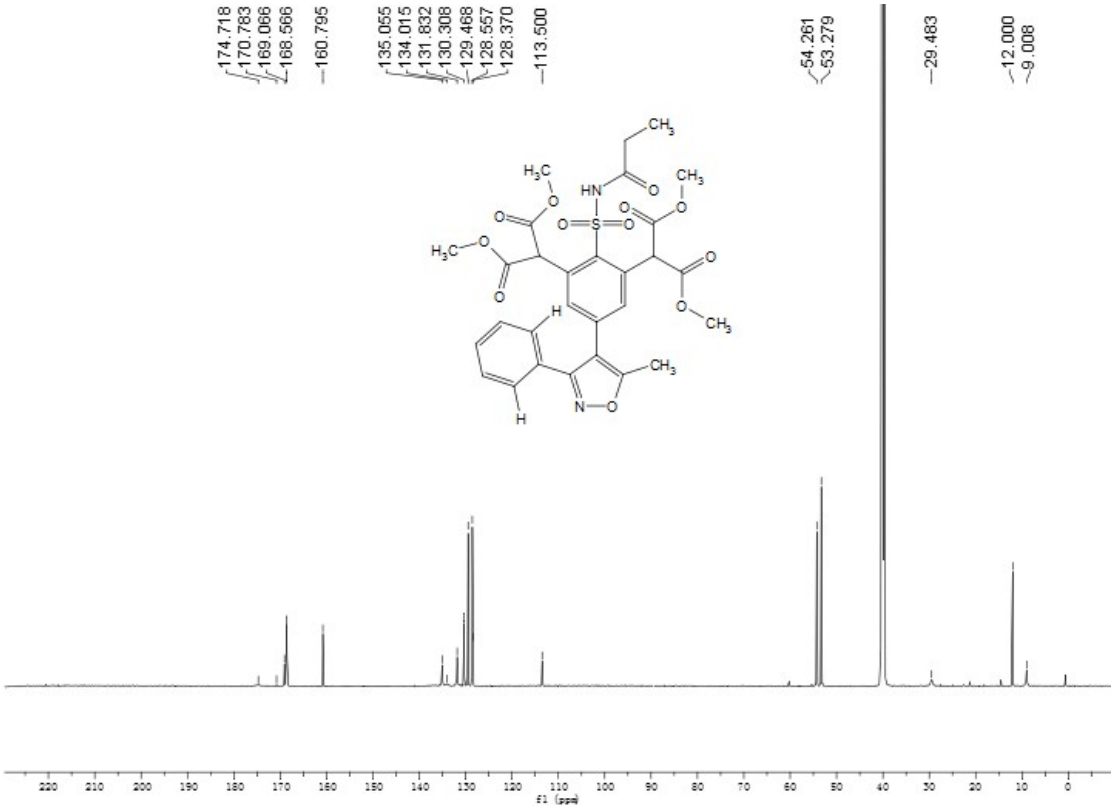
^{13}C NMR of compound **53**



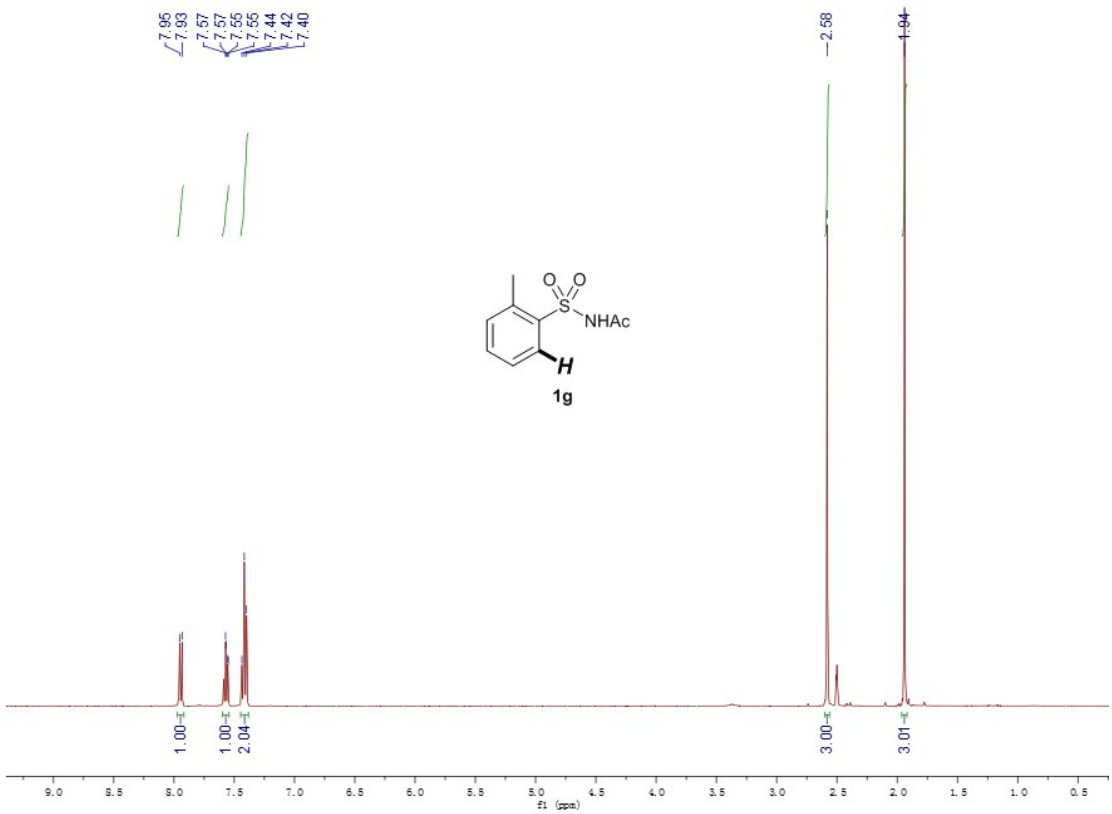
^{1}H NMR of compound **54**



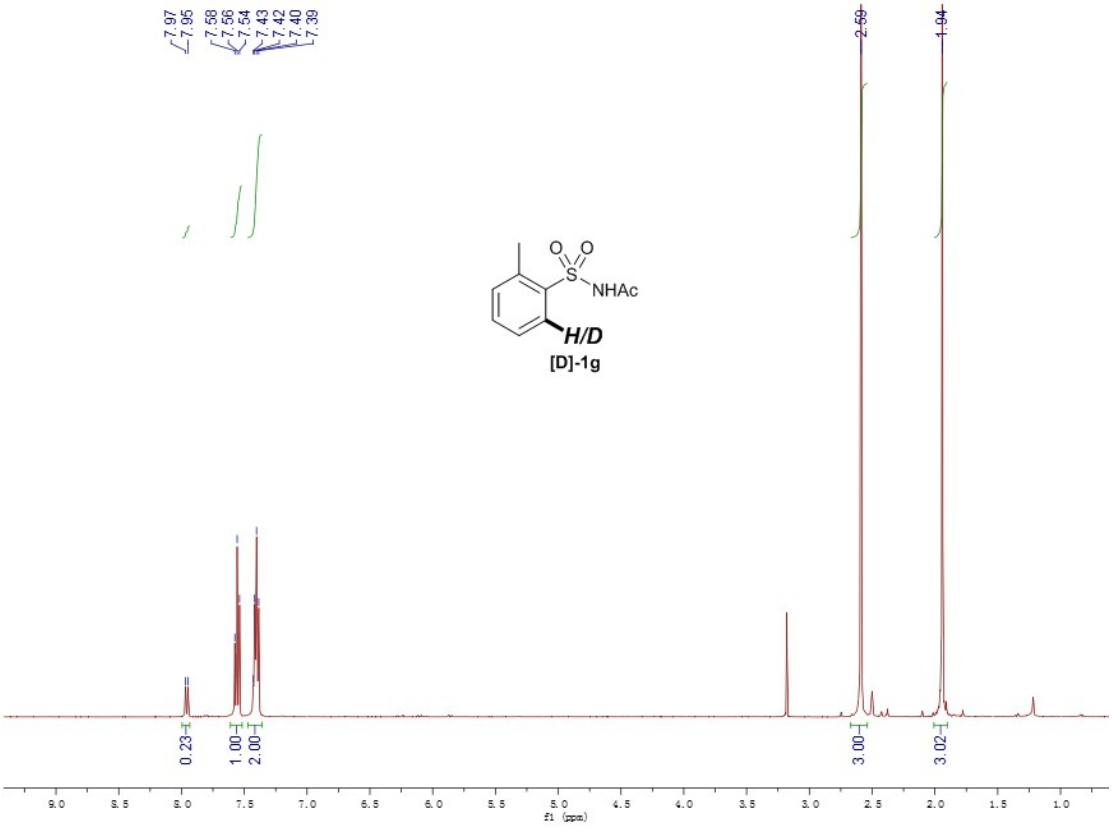
^{13}C NMR of compound **54**



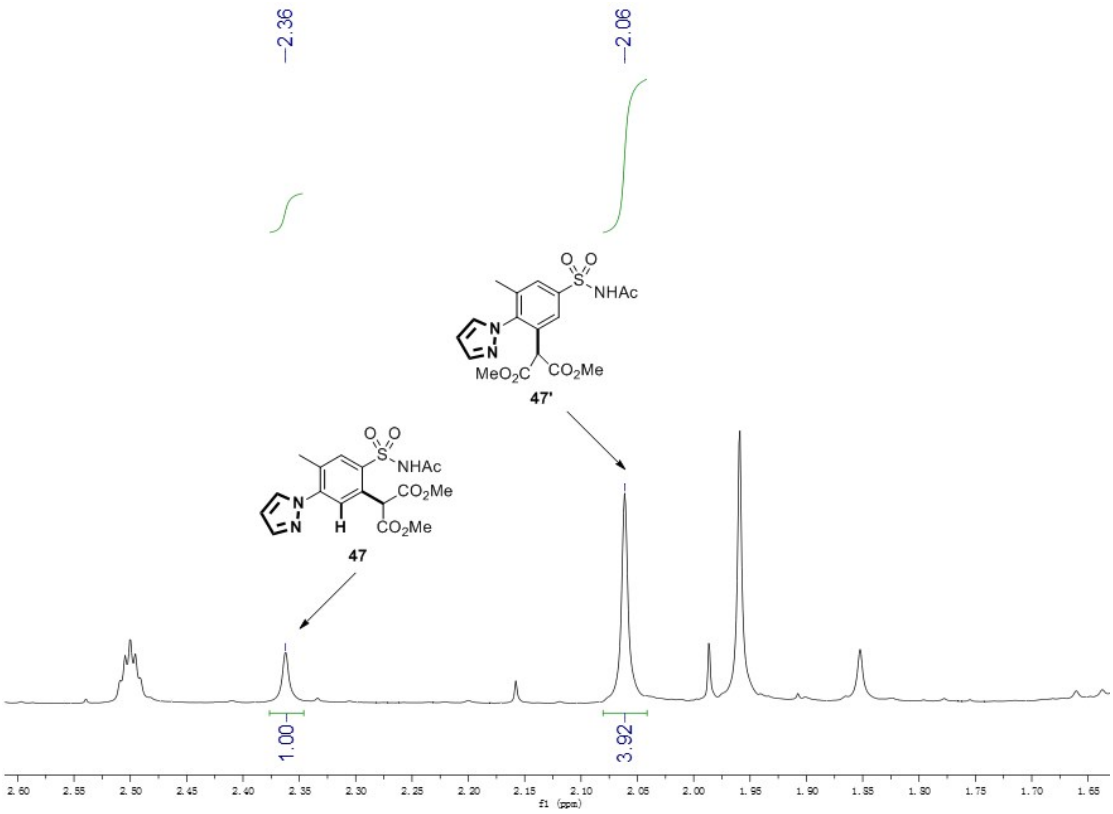
^{1}H NMR of **1g**



^{1}H NMR of **[D]-1g**



Analysis for the ratio of **47**:**47'**



Analysis for the ratio of **48**:**48'**