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Synthesis of α-sulfonyloxyketones via iodobenzene diacetate (PIDA)-mediated oxysulfonyloxylation of alkynes with sulfonic acids

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General Information.

All the reactions were carried out at room temperature for 24 h in a round-bottom flask equipped with a magnetic stir bar. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in solutions of $CDCl_3$ using tetramethylsilane as the internal standard; δ values are given in ppm, and coupling constants (*J*) in Hz. HR-MS were obtained on a Q-TOF micro spectrometer.

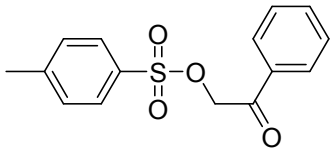
Typical procedure: 1-Oxo-1-phenylethyl 4-Methylbenzenesulfonate (Scheme 2, 3aa).

A mixture of phenylacetylene (**1a**) (204 mg, 2.0 mmol), $TsOH{\cdot}H_2O$ (**2a**) (380 mg, 2.0 mmol), PIDA (837 mg, 2.6 mmol), and CH_3CN (2.0 mL) was added successively in a round-bottom flask, and the resulting solution was stirred for 24 h at room temperature. The mixture was purified by column chromatography on silica gel to afford product **3aa** with PE/ethyl acetate = 10/1 as the eluent.

Procedure for the ^{18}O-labeled control experiment.

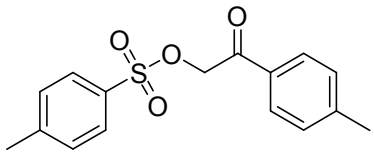
A mixture of phenylacetylene (**1a**) (204 mg, 2.0 mmol), $TsOH{\cdot}H_2O$ (**2a**) (380 mg, 2.0 mmol), PIDA (837 mg, 2.6 mmol), CH_3CN (2.0 mL) and $H_2{}^{18}O$ (0.1 mL, 98% in water) was added successively in a round-bottom flask, and the resulting solution was stirred for 24 h at room temperature. The mixture was purified by column chromatography on silica gel to afford product **3aa** with PE/ethyl acetate = 10/1 as the eluent.

1-Oxo-1-phenylethyl 4-Methylbenzenesulfonate (Scheme 2, 3aa) [1]



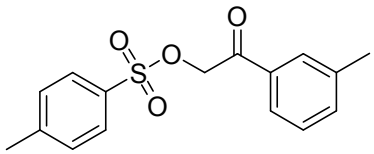
Yield: 79%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.83 (m, 4H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.26 (s, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 190.3, 145.3, 134.2, 133.7, 132.6, 129.9, 128.9, 128.1, 127.9, 69.9, 21.6.

1-Oxo-p-tolylethyl 4-Methylbenzenesulfonate (Scheme 2, 3ba) [2]



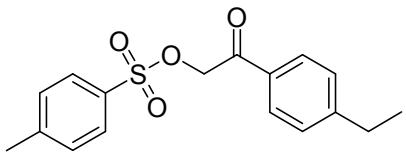
Yield: 79%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 189.8, 145.3, 145.2, 132.7, 131.3, 129.9, 129.6, 128.2, 128.1, 69.9, 21.7, 21.6.

1-Oxo-m-tolylethyl 4-Methylbenzenesulfonate (Scheme 2, 3ca) [3]



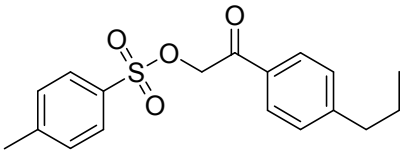
Yield: 73%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34 (m, 3H), 5.26 (s, 2H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 190.4, 145.2, 138.8, 135.0, 133.7, 132.7, 129.9, 128.7, 128.4, 128.1, 125.1, 69.9, 21.6, 21.3.

1-(4-Ethylphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3da)



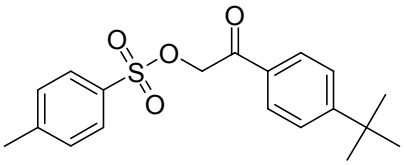
Yield: 80%**;** Orange oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.24 (s, 2H), 2.71 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 189.8, 151.4, 145.2, 132.6, 131.4, 129.8, 128.4, 128.2, 128.1, 69.9, 29.0, 21.6, 15.1; HRMS (ESI): calcd for $C_{17}H_{19}O_4S$: [M+H$^+$] 319.0999, found 319.0994.

1-(4-Propylphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ea)



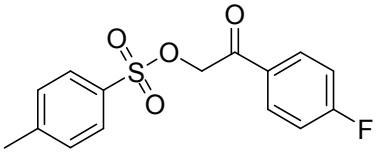
Yield: 84%; Orange oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.24 (s, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.64 (m, *J* = 7.2 Hz, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 189.8, 149.9, 145.2, 132.7, 131.5, 129.9, 129.0, 128.2, 128.1, 69.9, 38.0, 24.1, 21.6, 13.7; HRMS (ESI): calcd for $C_{18}H_{21}O_4S$: [M+H$^+$] 333.1155, found 333.1161.

1-(4-Tert-butylphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3fa)



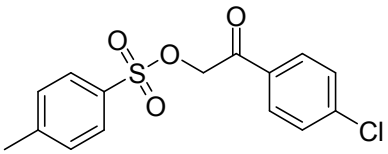
Yield: 81%; Orange oily liquid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 2H), 2.45 (s, 3H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 189.8, 158.2, 145.2, 132.7, 131.2, 129.9, 128.1, 127.9, 125.8, 69.9, 35.2, 30.9, 21.6; HRMS (ESI): calcd for $C_{19}H_{23}O_4S$: [M+H$^+$] 347.1312, found 347.1318.

1-(4-Fluorophenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ga) [4]



Yield: 73%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.87 (dd, *J* = 5.6 Hz, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.14 (m, 2H), 5.21 (s, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 189.0, 166.26 (d, ^{1}J = 255.6 Hz), 145.4, 132.5, 130.8 (d, ^{3}J = 9.5 Hz), 130.2 (d, ^{4}J = 3.1 Hz), 129.9, 128.1, 116.2(d, ^{2}J = 22.0 Hz), 69.8, 21.6.

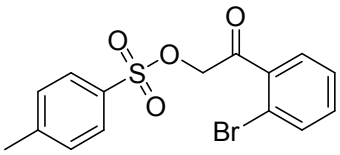
1-(4-Chlorophenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ha) [2]



Yield: 72%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* =

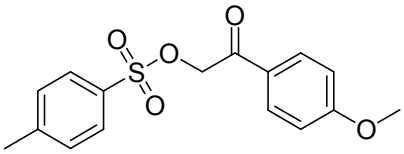
8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 2H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 189.4, 145.4, 140.8, 132.5, 132.1, 129.9, 129.5, 129.3, 128.1, 69.8, 21.7.

1-(2-Bromophenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ia) [5]



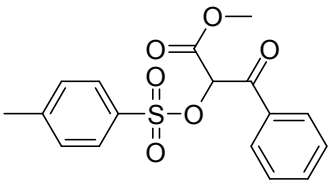
Yield: 59%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.38 (m, 5H), 5.13 (s, 2H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 194.8, 145.3, 133.7, 132.8, 129.9, 129.6, 128.1, 127.5, 119.4, 71.0, 21.7.

1-(4-Methoxyphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ja) [2]



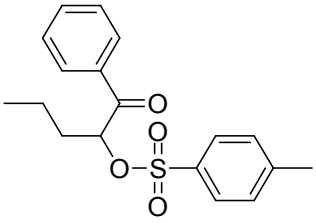
Yield: 86%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 2H), 3.88 (s, 3H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 188.7, 164.3, 145.2, 130.4, 129.8, 128.1, 126.8, 114.1, 69.7, 55.5, 21.6.

1-(Methoxycarbonyl)-2-oxo-2-phenylethyl 4-Methylbenzenesulfonate (Scheme 2, 3ka) [6]



Yield: 85%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.24 (m, 4H), 6.12 (s, 1H), 3.70 (s, 3H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 193.7, 163.8, 155.7, 145.2, 133.0, 130.8, 129.4, 128.5, 128.4, 126.9, 110.4, 51.7, 21.6.

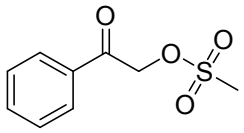
1-Oxo-1-phenylpentan-2-yl 4-Methylbenzenesulfonate (Scheme 2, 3la) [7]



Yield: 83%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.61 (q, *J* = 8.4 Hz, 1H), 2.40 (s, 3H),

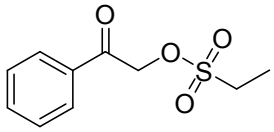
1.85 (m, 2H), 1.41 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H),; ^{13}C NMR ($CDCl_3$, 100 Hz) δ 195.0, 144.9, 133.7, 129.8, 129.6, 128.7, 128.6, 128.1, 128.0, 81.6, 34.7, 21.6, 18.4, 13.3.

1-Oxo-1-phenylethyl Methanesulfonate (Scheme 2, 3ab) [8]



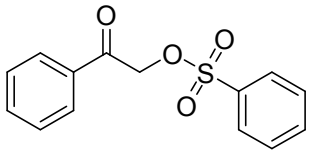
Yield: 87%; . ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.90 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 8.4 Hz, 1H), 7.53 (t, J = 8.4 Hz, 2H), 5.52 (s, 2H), 3.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 190.9, 134.5, 129.7, 129.1, 127.8, 70.1, 39.2.

1-Oxo-1-phenylethyl Ethanesulfonate (Scheme 2, 3ac) [8]



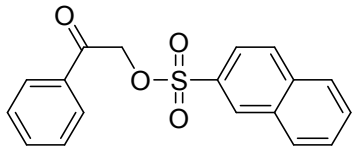
Yield: 85%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.89 (d, J = 8.4 Hz, 2H), 7.64 (t, J = 8.4 Hz, 1H), 7.51 (t, J = 8.4 Hz, 2H), 5.49 (s, 2H), 3.38 (q, J = 7.6 Hz, 2H), 1.52 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 191.3, 134.4, 133.5, 129.0, 127.8, 69.7, 46.5, 8.19.

1-Oxo-1-phenylethyl Benzenesulfonate (Scheme 2, 3ad) [8]



Yield: 82%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.00 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.58 (m, 3H), 7.49 (t, J = 8.0 Hz, 2H), 5.32 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 190.1, 135.7, 134.2, 134.1, 133.7, 129.3, 128.9, 128.1, 128.0, 70.2.

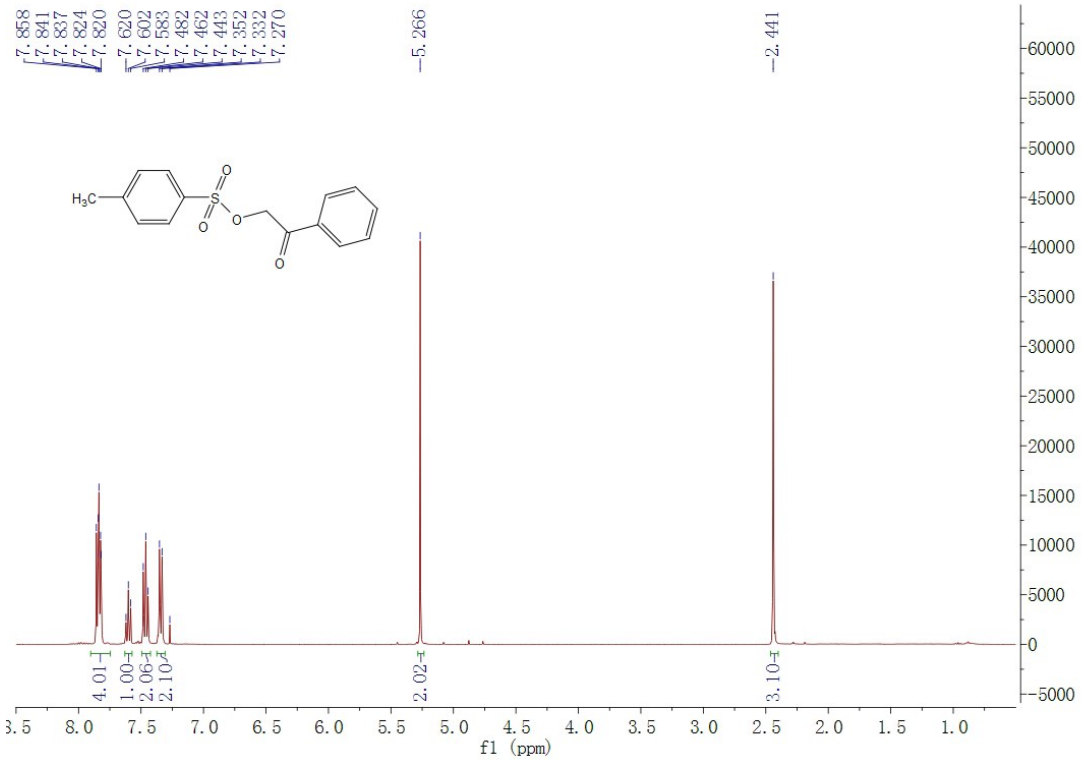
1-Oxo-1-phenylethyl 2-Naphthalenesulfonate (Scheme 2, 3ae) [9]

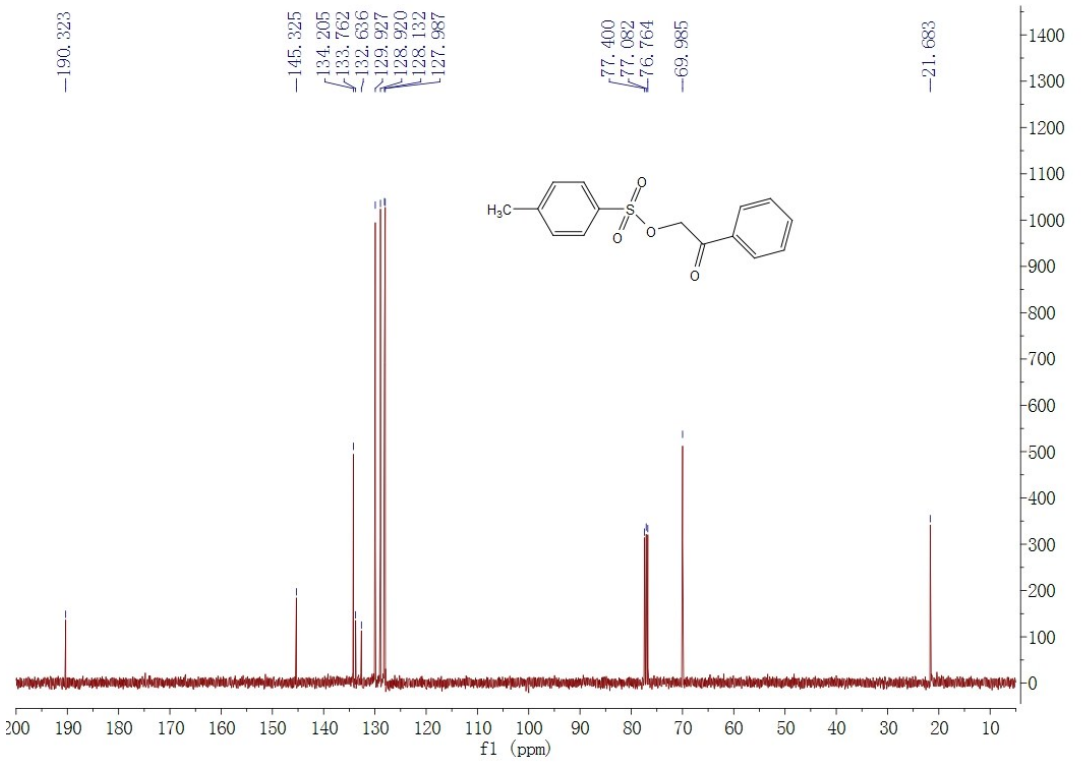


Yield: 81%; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.55 (s, 1H), 8.01 (m, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.63 (m, 3H), 7.45 (m, 4H), 6.12 (t, J = 8.4 Hz, 2H), 5.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 189.3, 135.4, 134.2, 133.7, 132.4, 131.9, 130.3, 129.7, 129.5, 129.4, 128.9, 128.0, 128.0, 127.8, 122.6, 70.1.

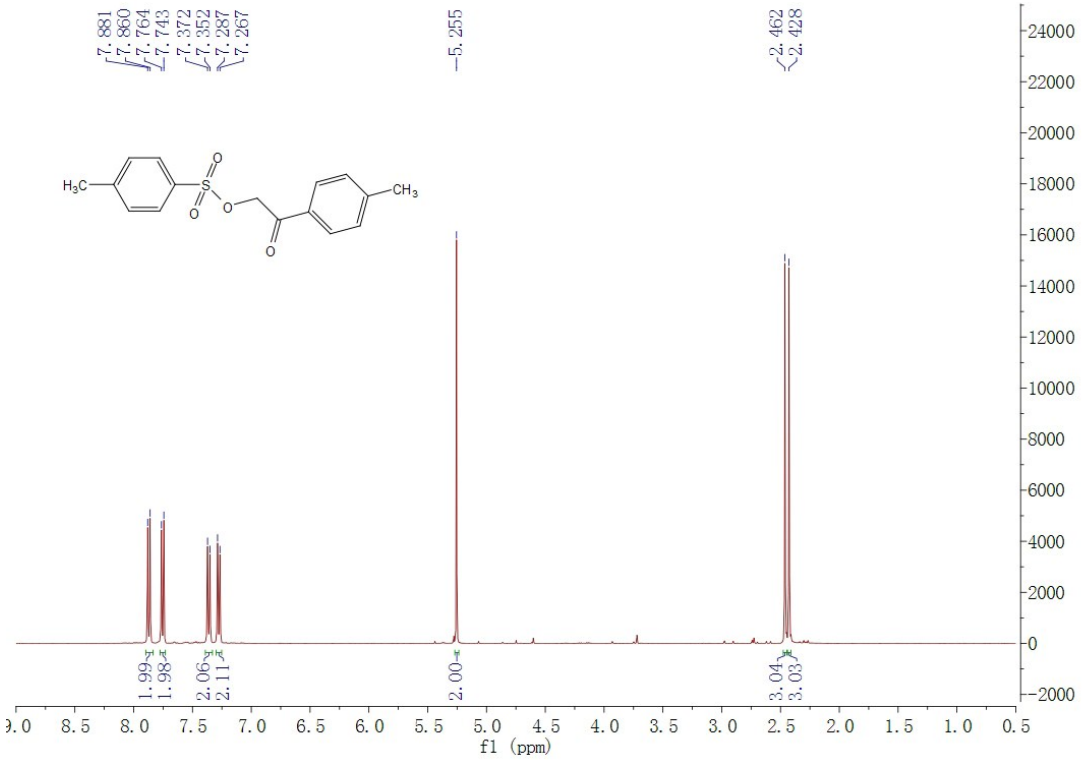
NMR spectra

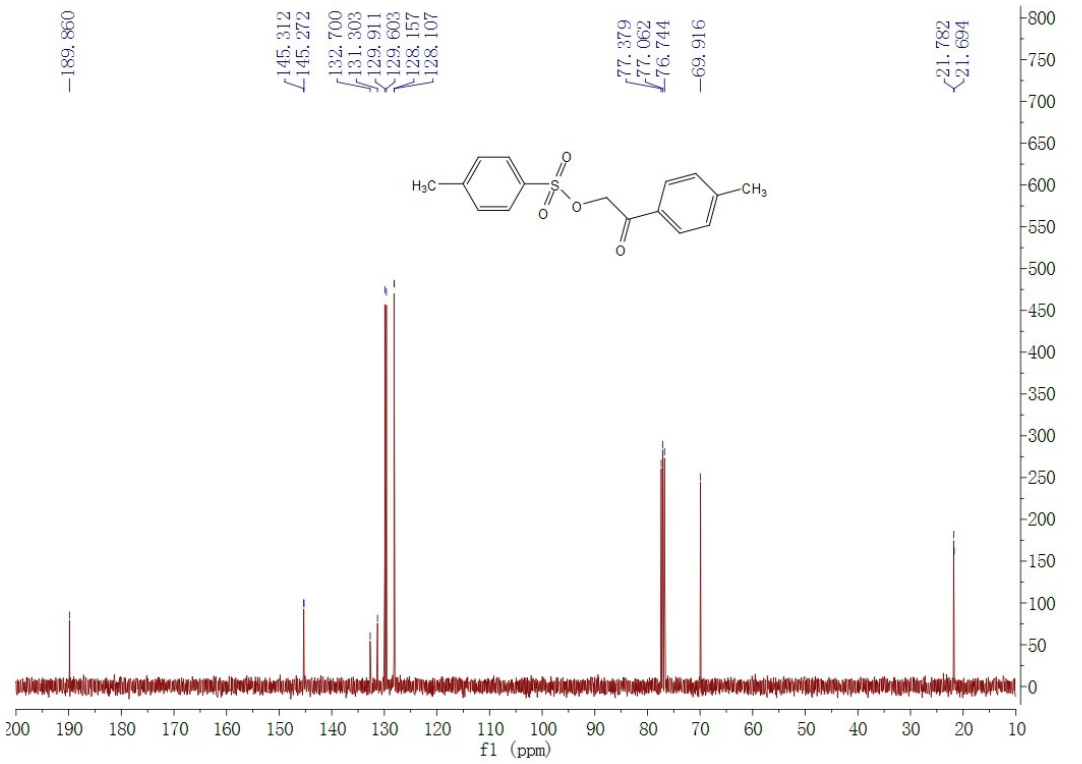
1-Oxo-1-phenylethyl 4-Methylbenzenesulfonate (Scheme 2, 3aa)



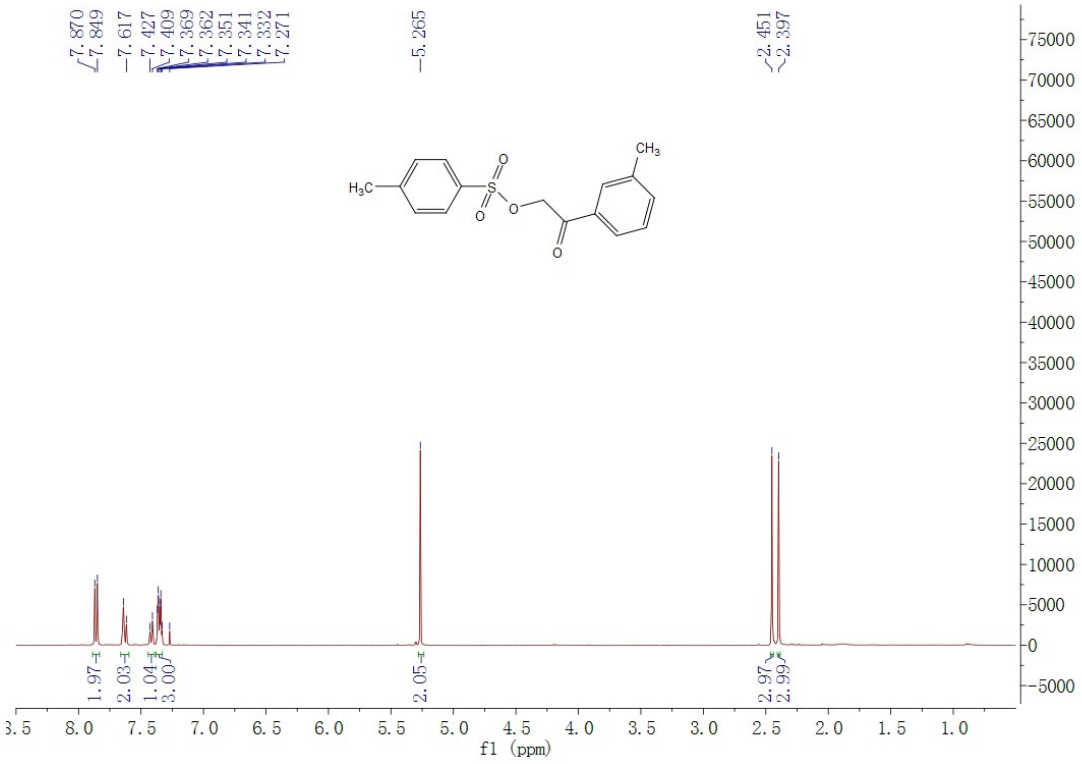


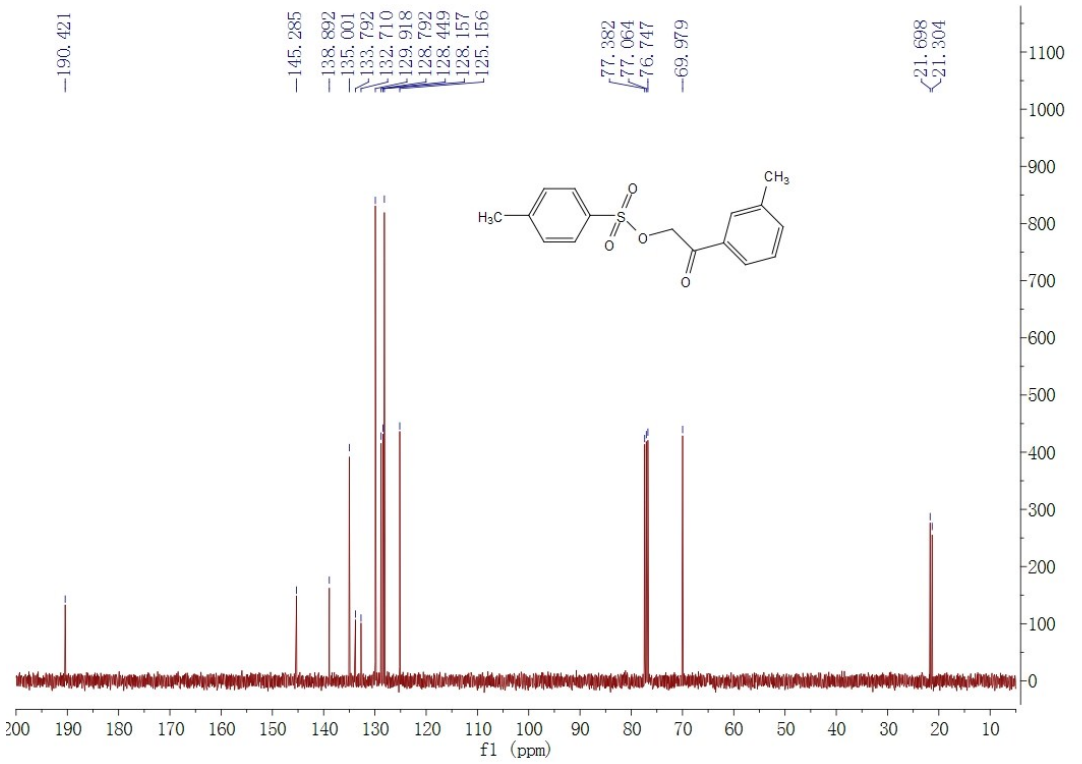
1-Oxo-p-tolylethyl 4-Methylbenzenesulfonate (Scheme 2, 3ba)



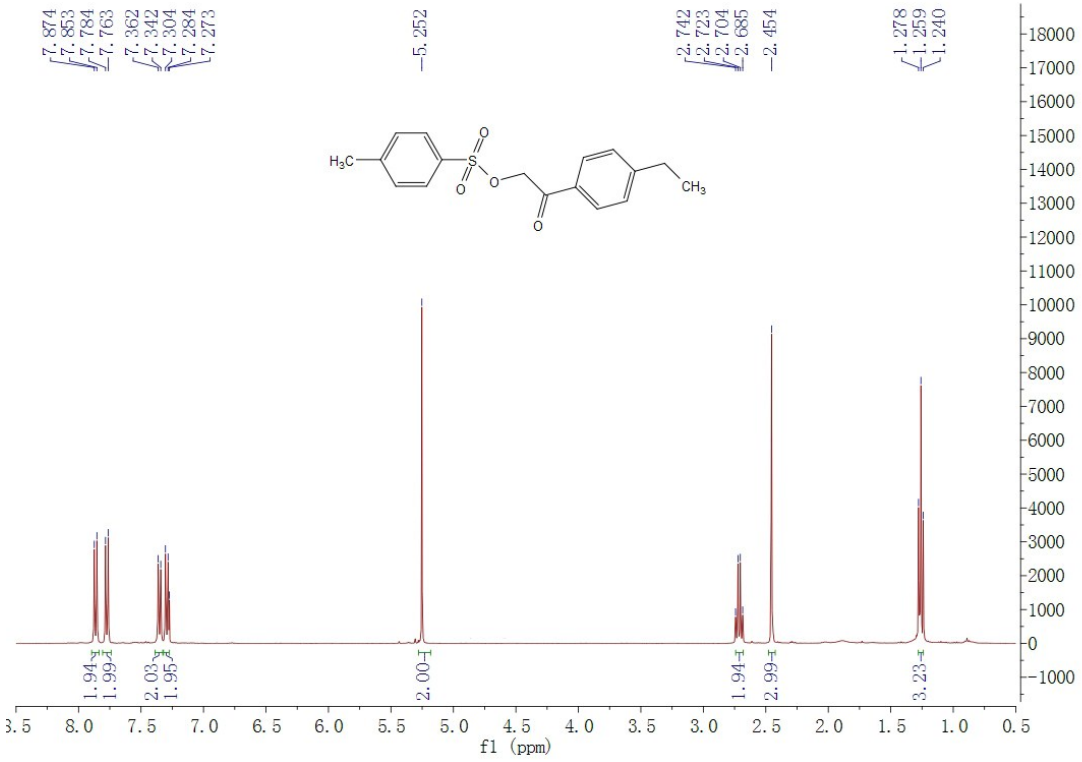


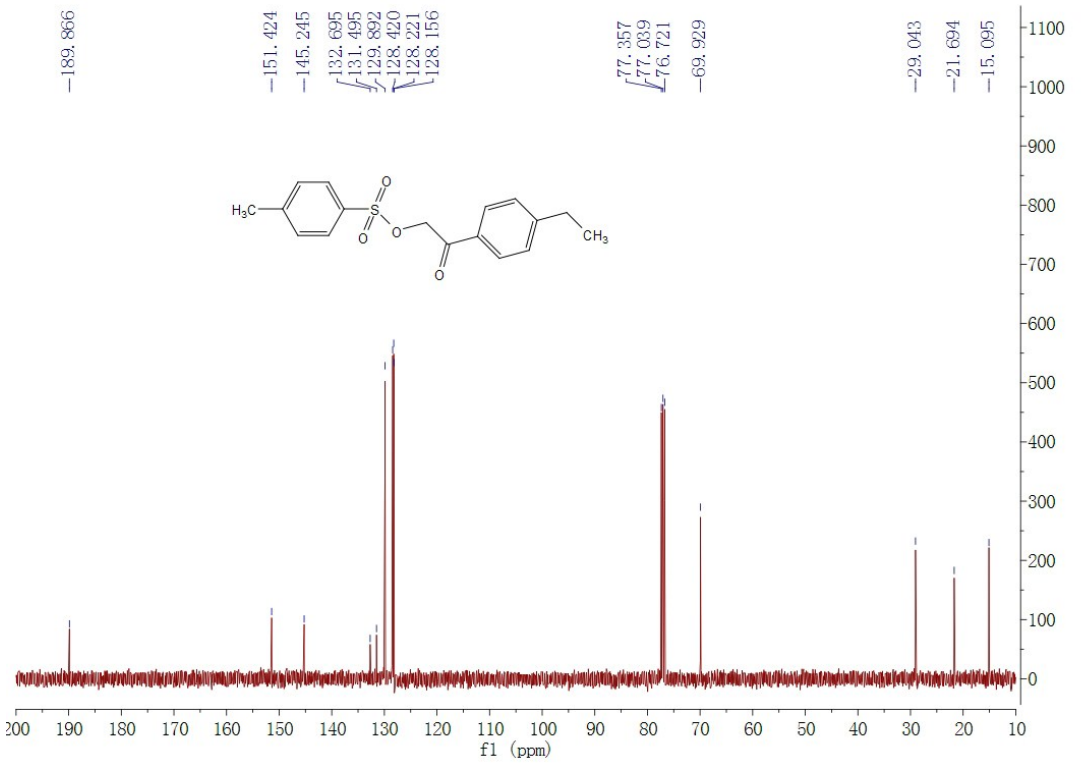
1-Oxo-m-tolylethyl 4-Methylbenzenesulfonate (Scheme 2, 3ca)



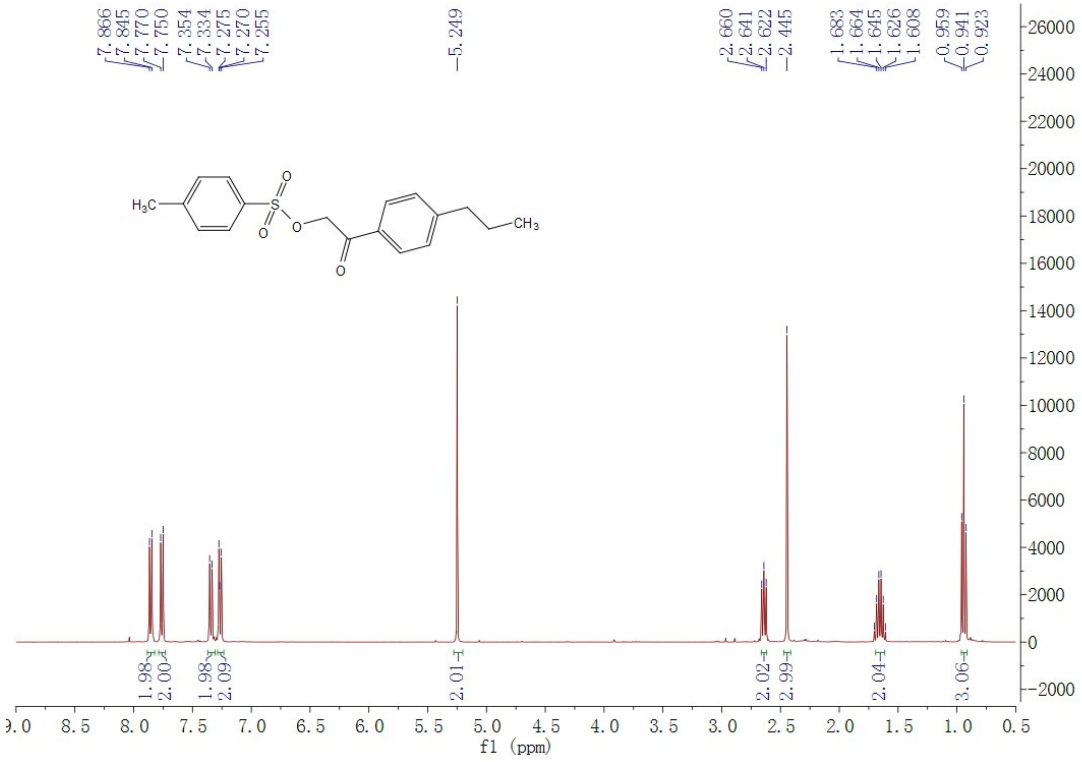


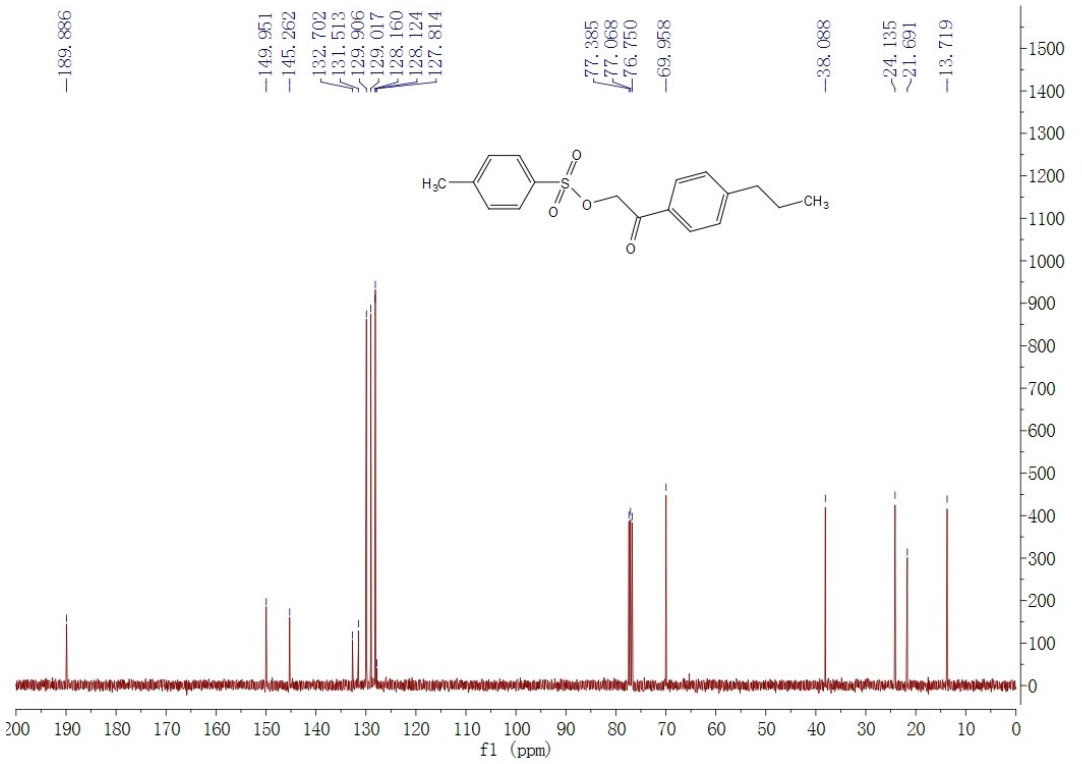
1-(4-Ethylphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3da)



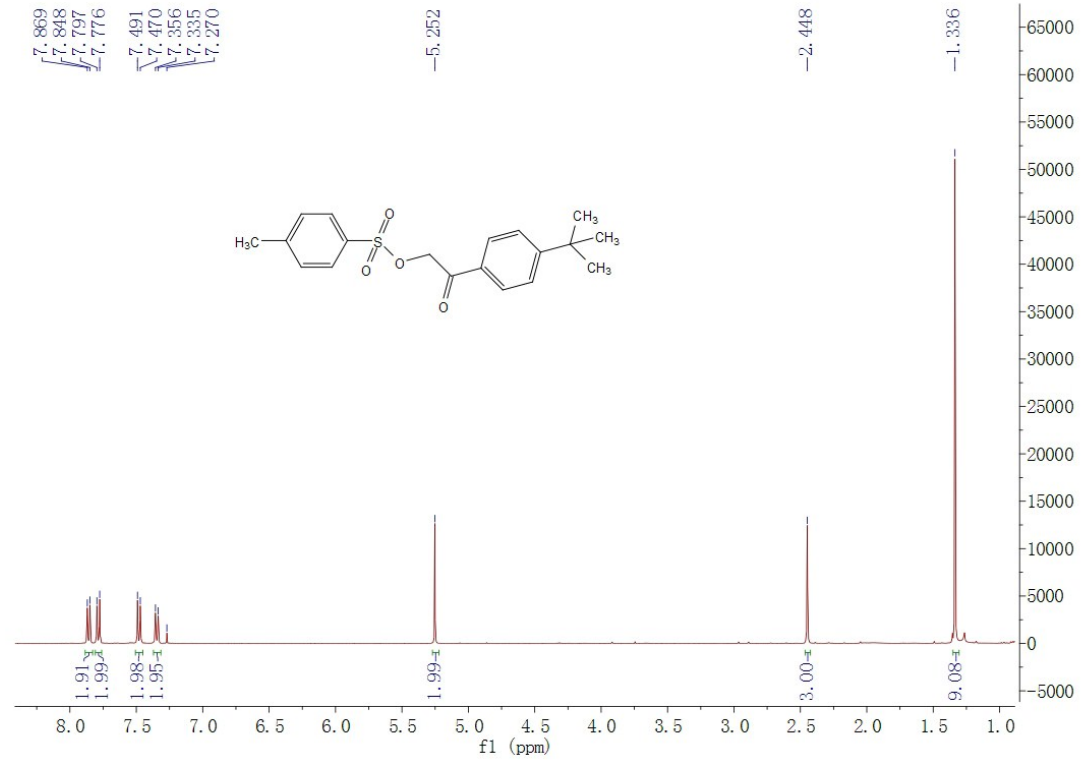


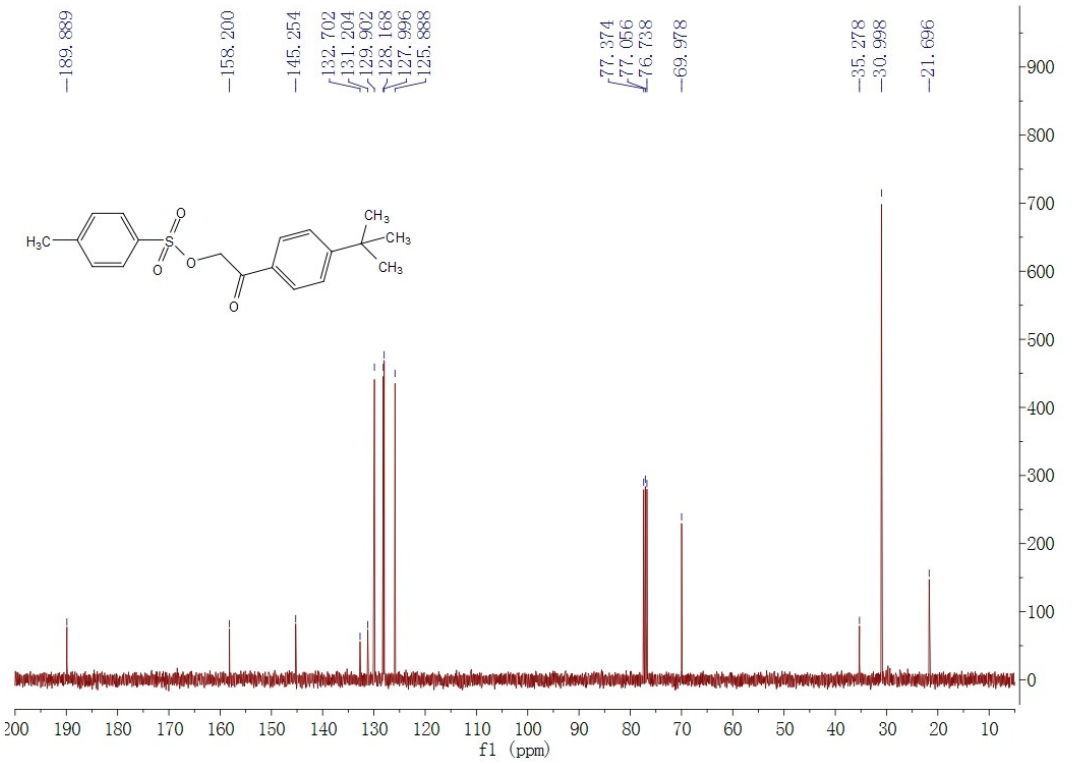
1-(4-Propylphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ea)



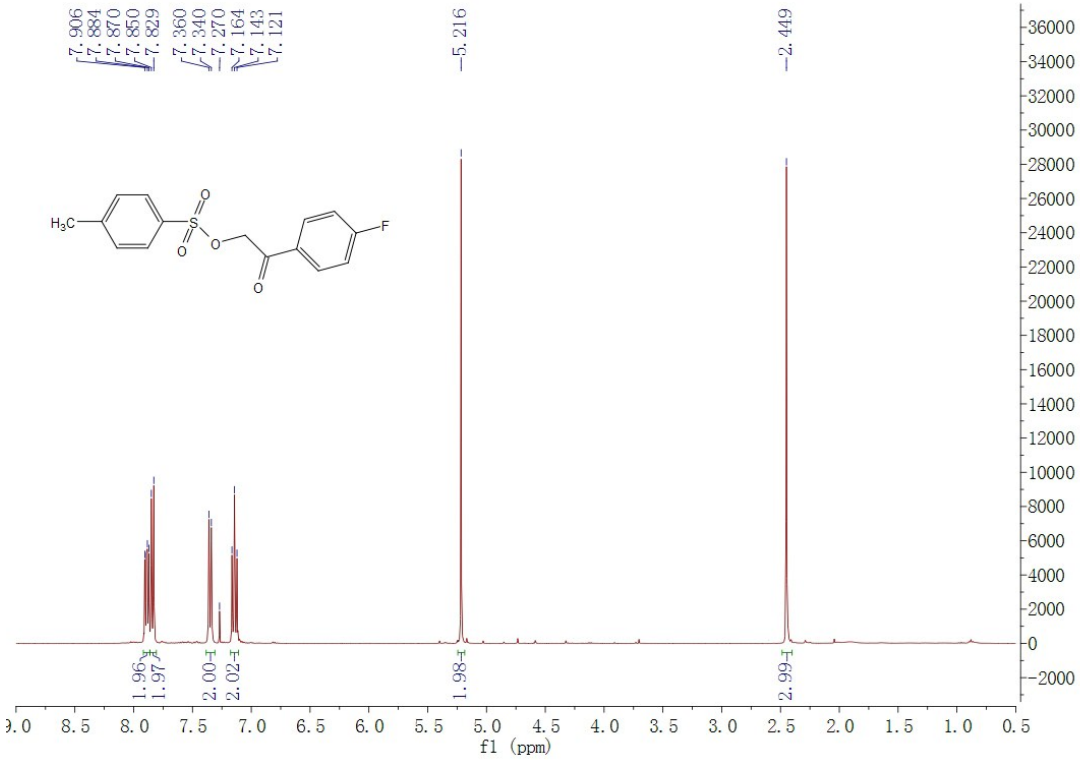


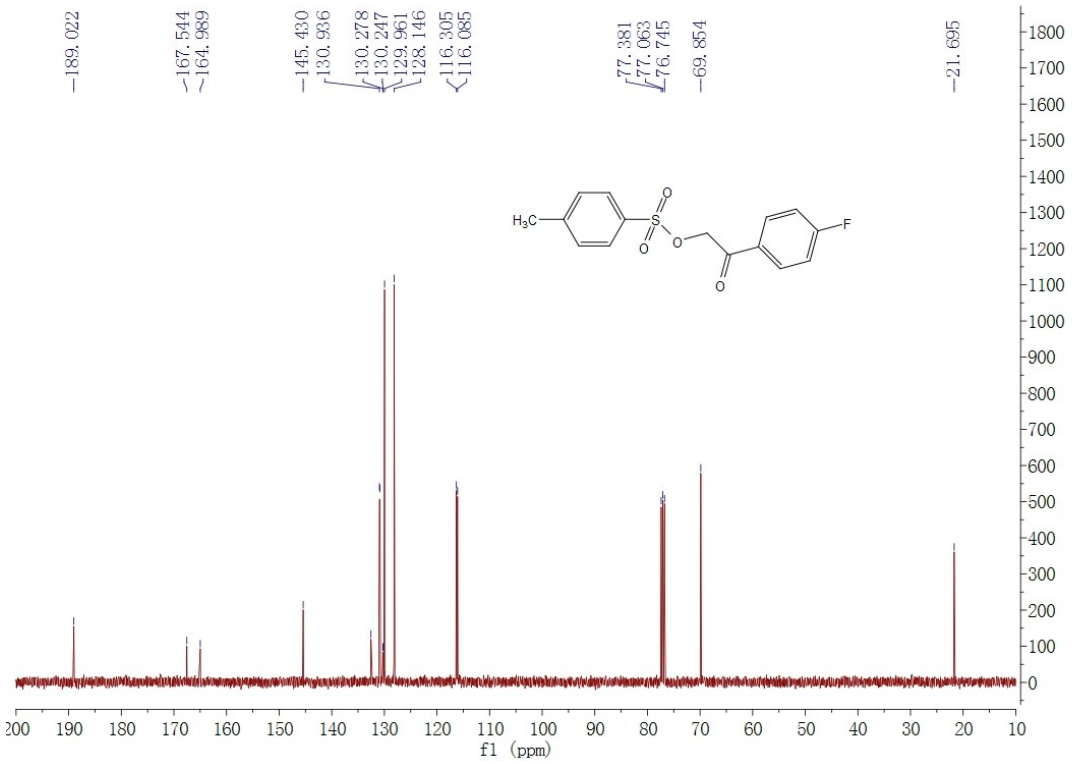
1-(4-Tert-butylphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3fa)



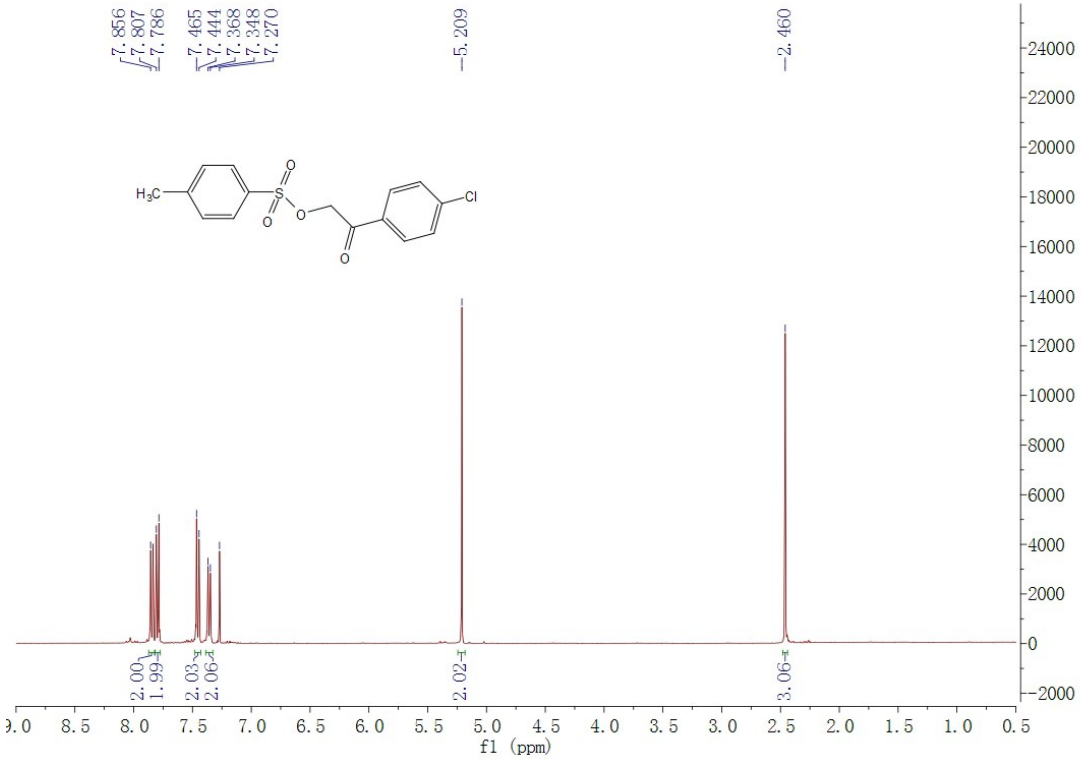


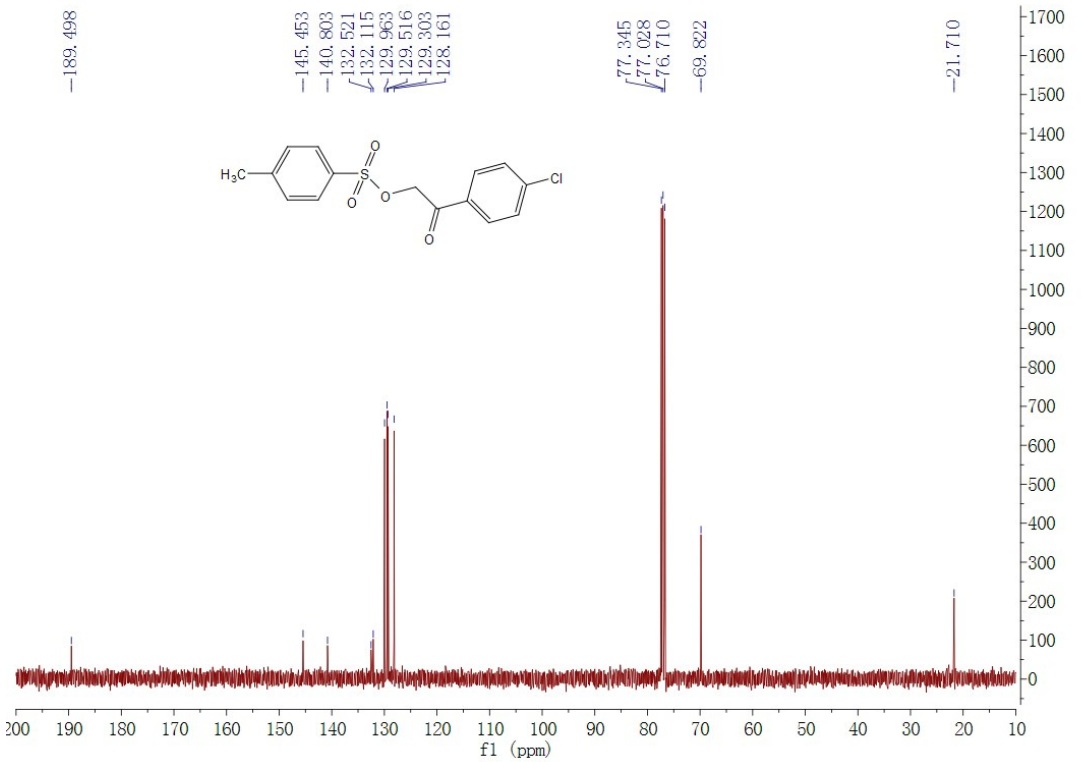
1-(4-Fluorophenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ga)



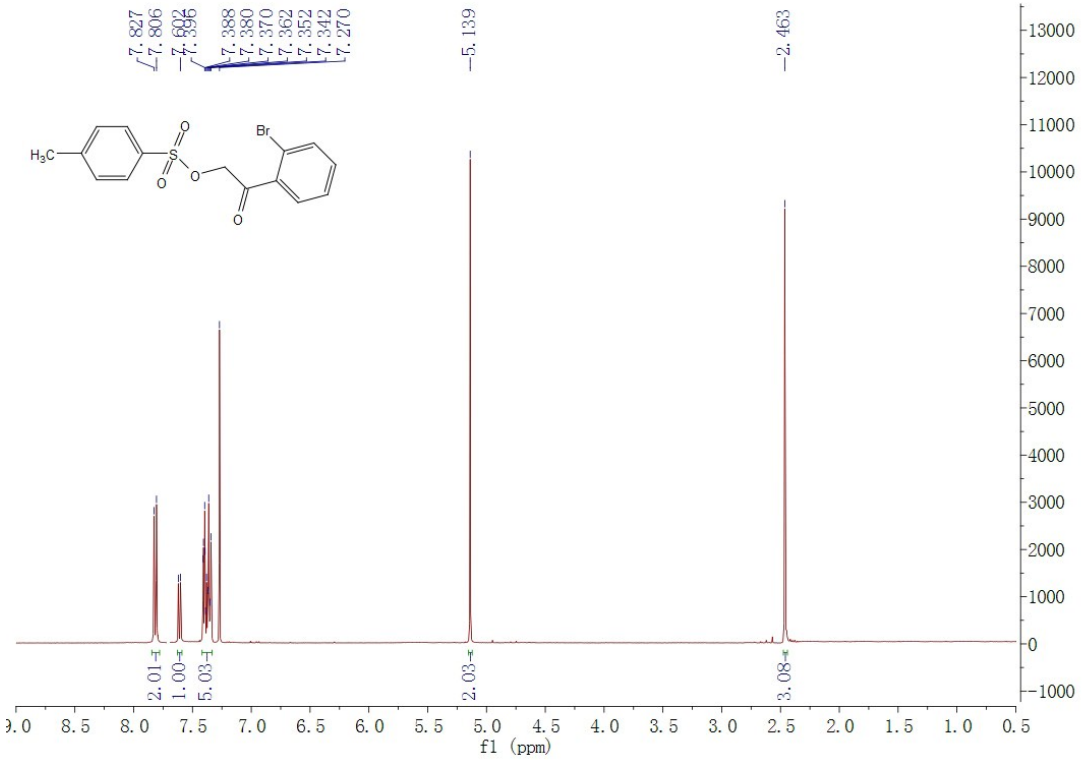


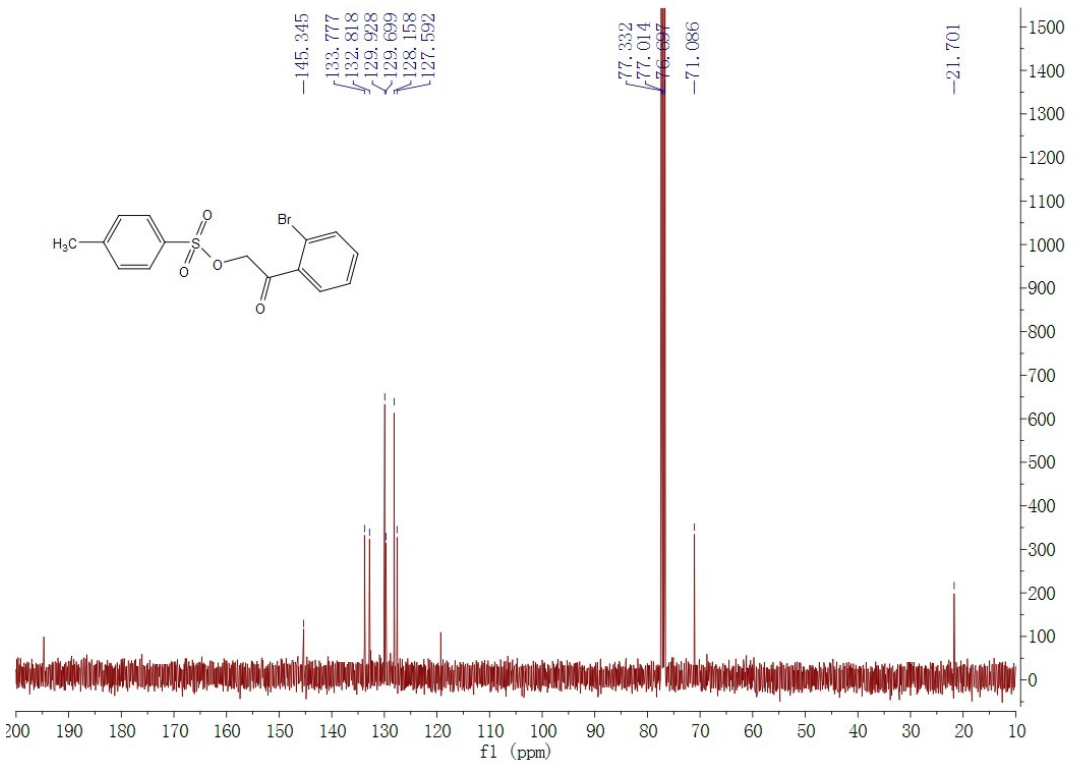
1-(4-Chlorophenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ha)



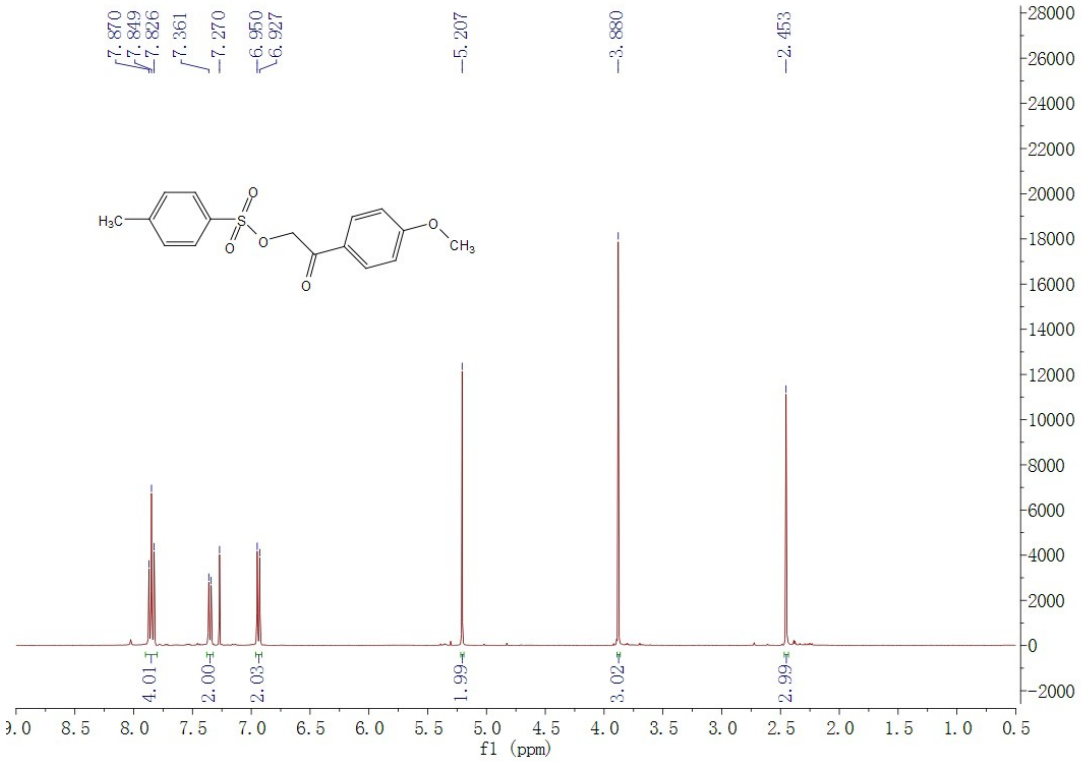


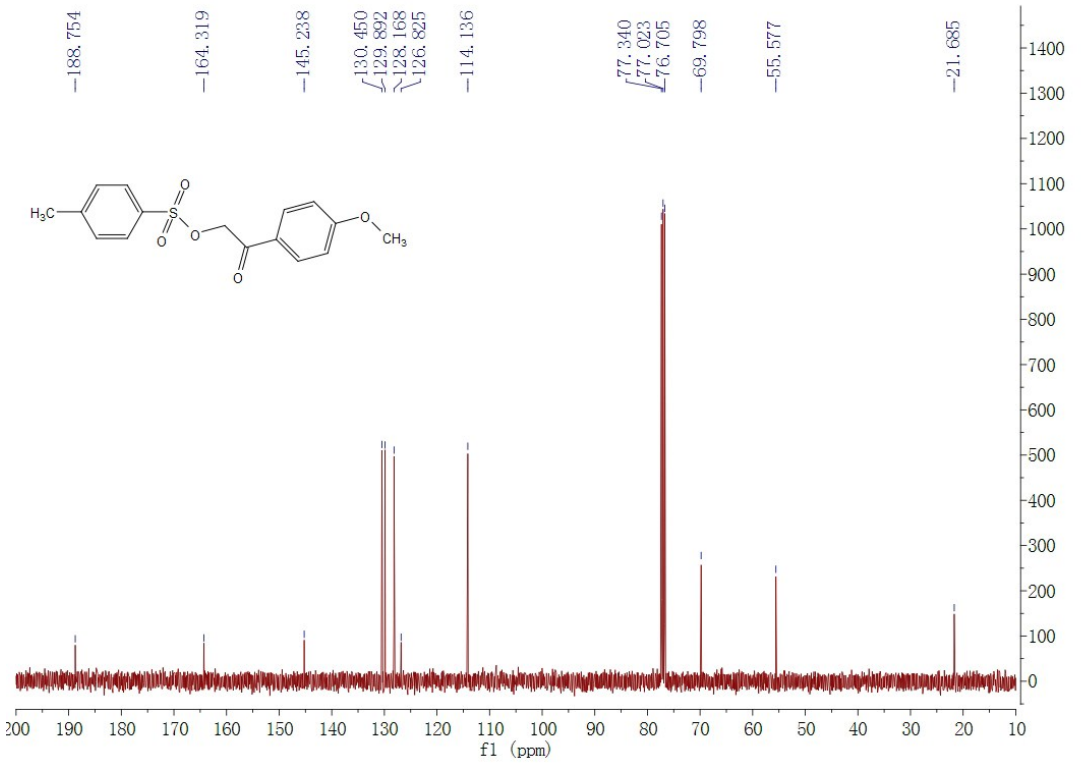
1-(2-Bromophenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ia)



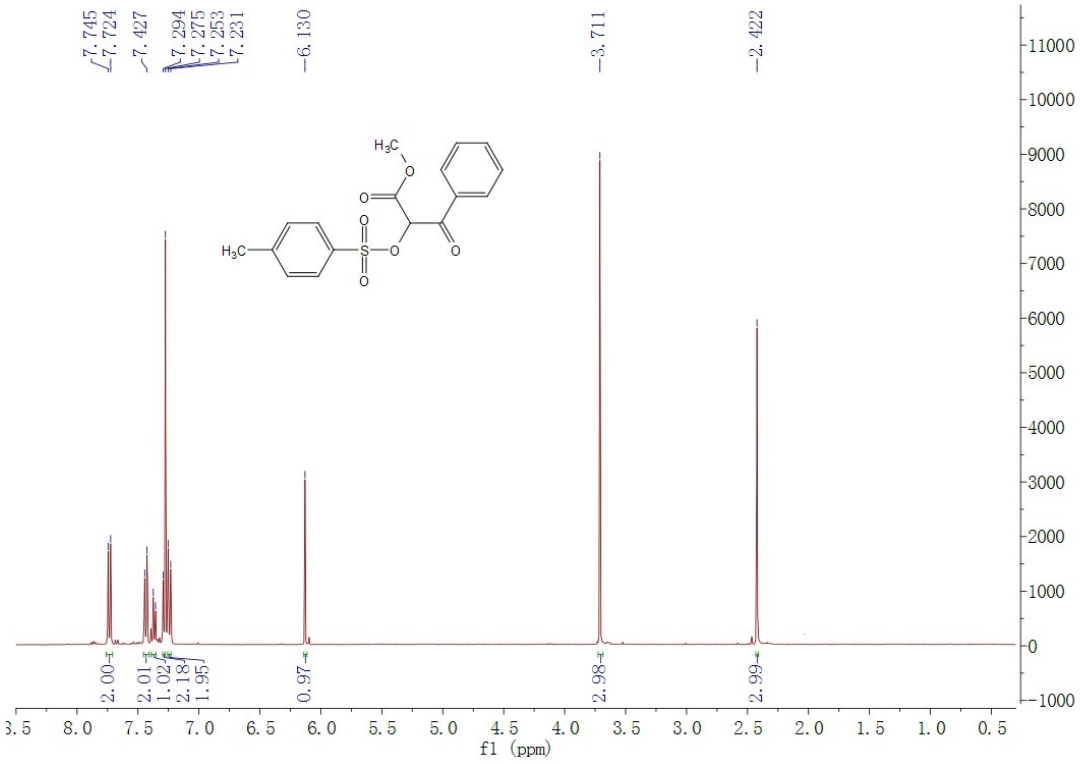


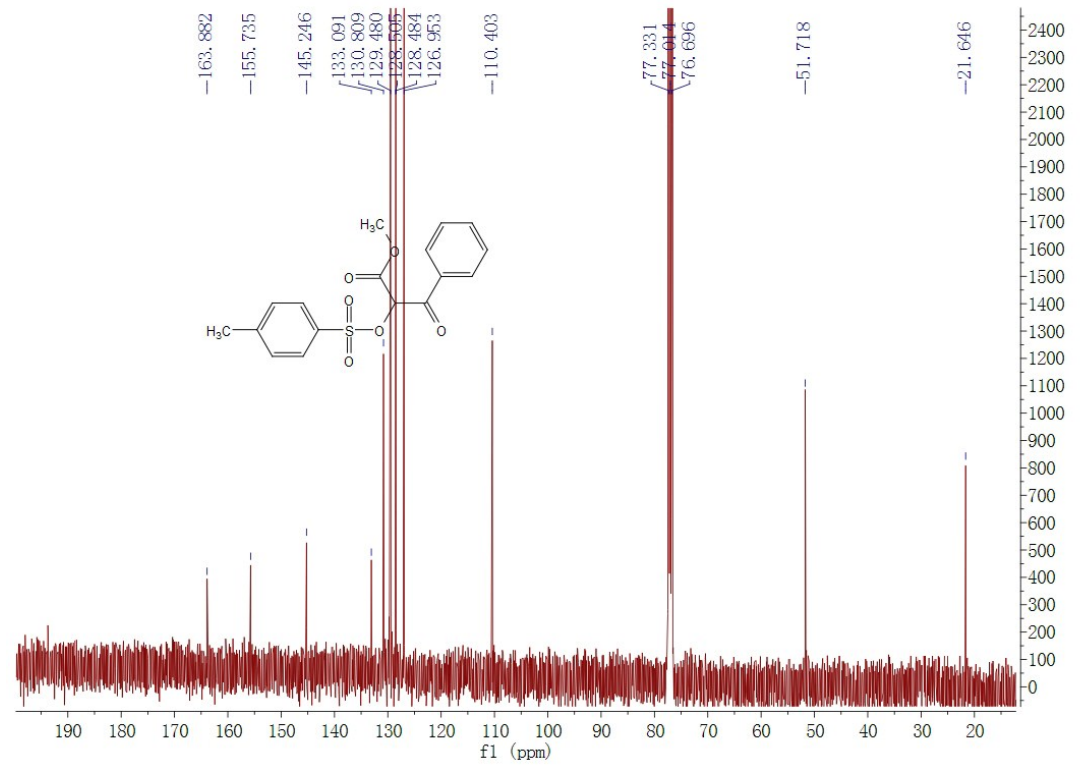
1-(4-Methoxyphenyl)-1-oxoethyl 4-Methylbenzenesulfonate (Scheme 2, 3ja)



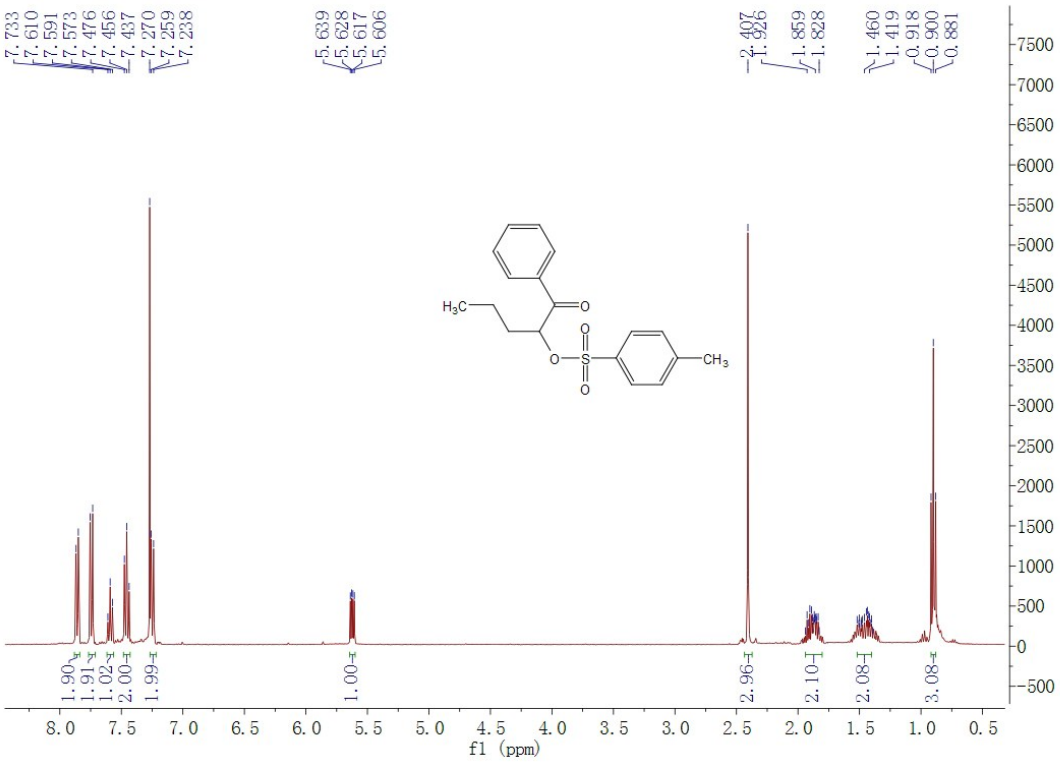


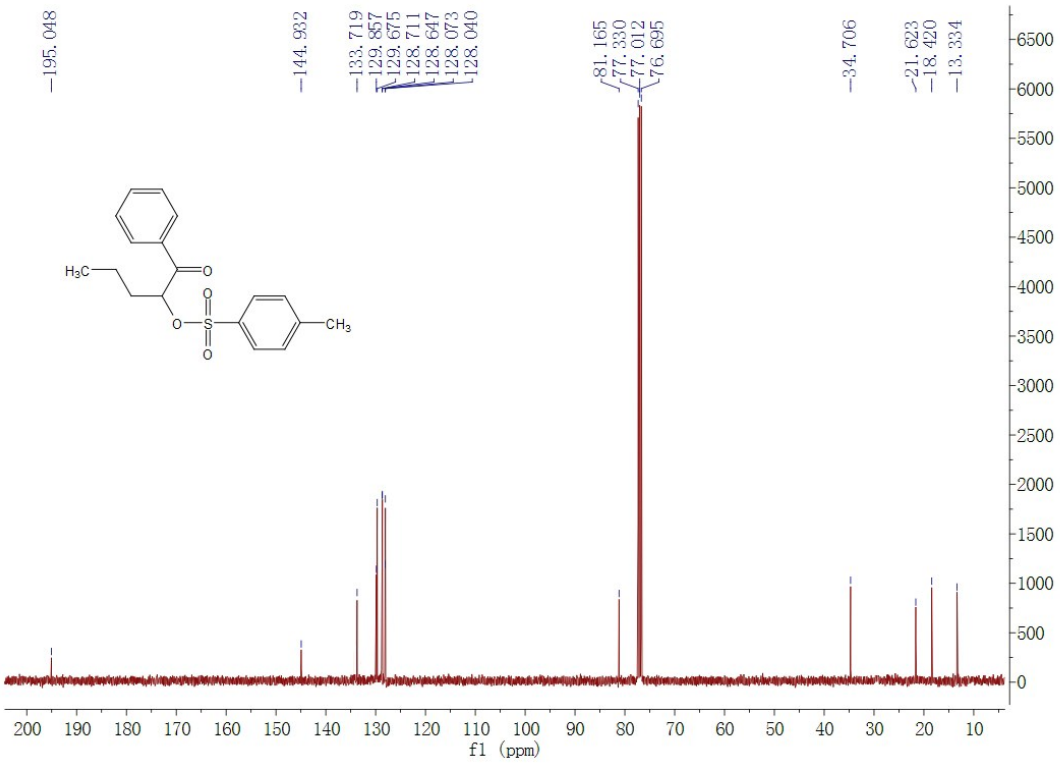
1-(Methoxycarbonyl)-2-oxo-2-phenylethyl 4-Methylbenzenesulfonate (Scheme 2, 3ka)



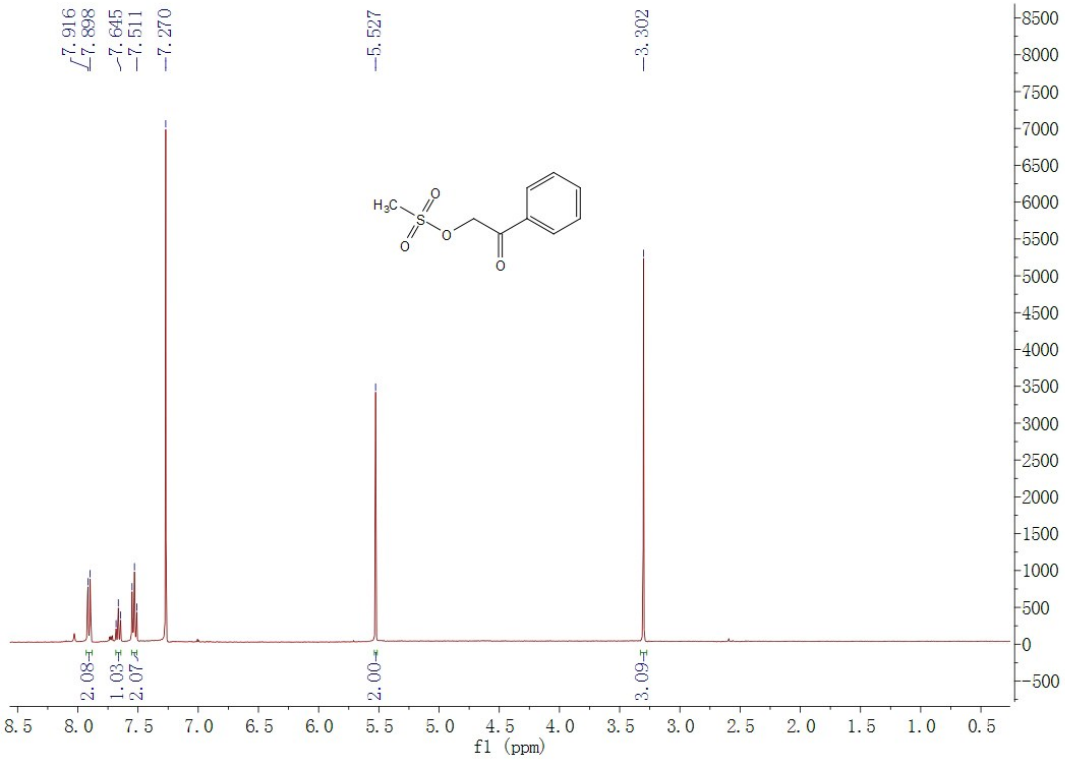


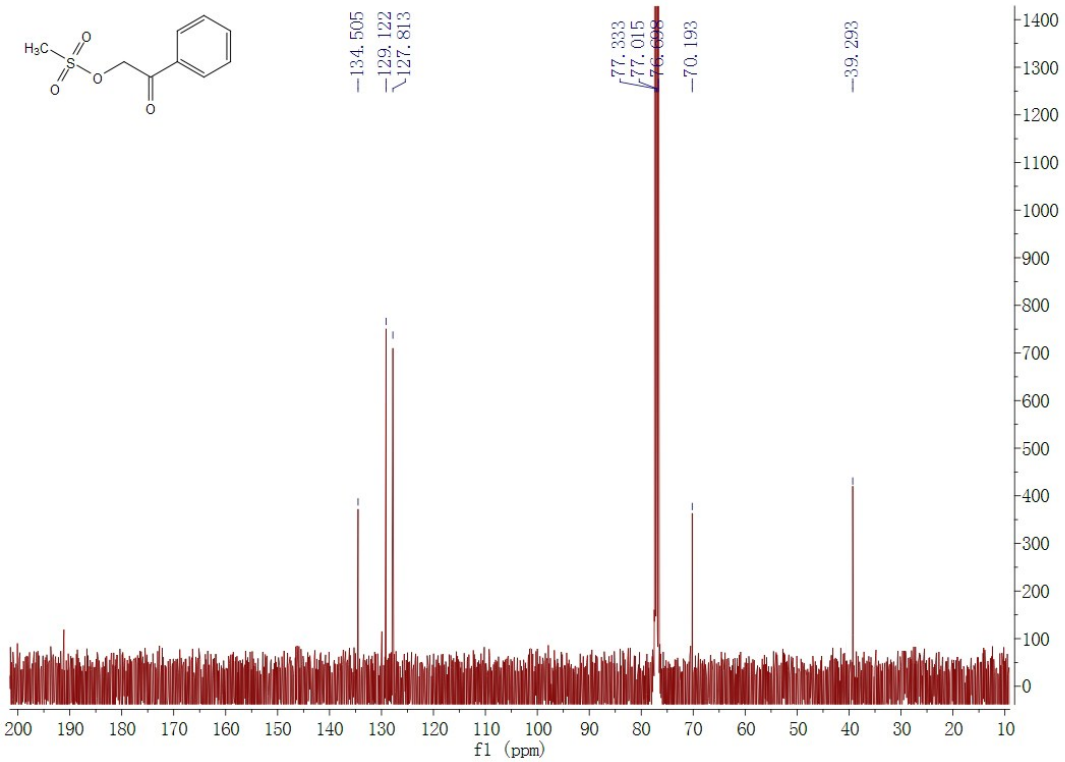
1-Oxo-1-phenylpentan-2-yl 4-Methylbenzenesulfonate (Scheme 2, 3la)



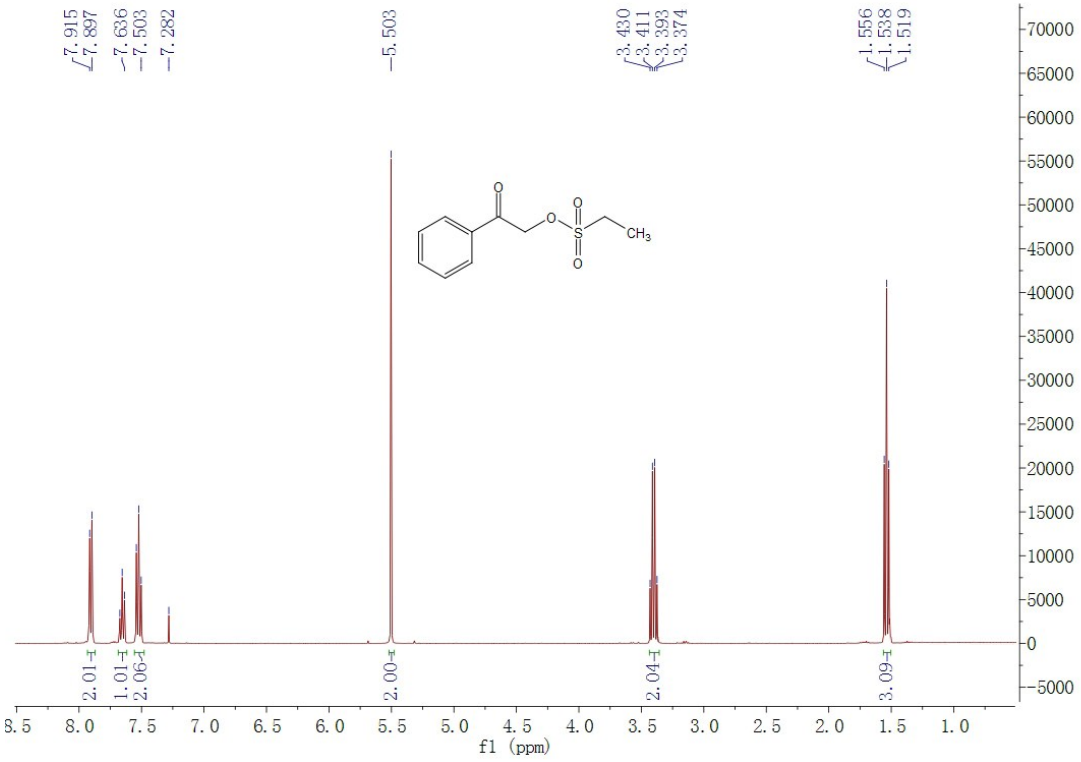


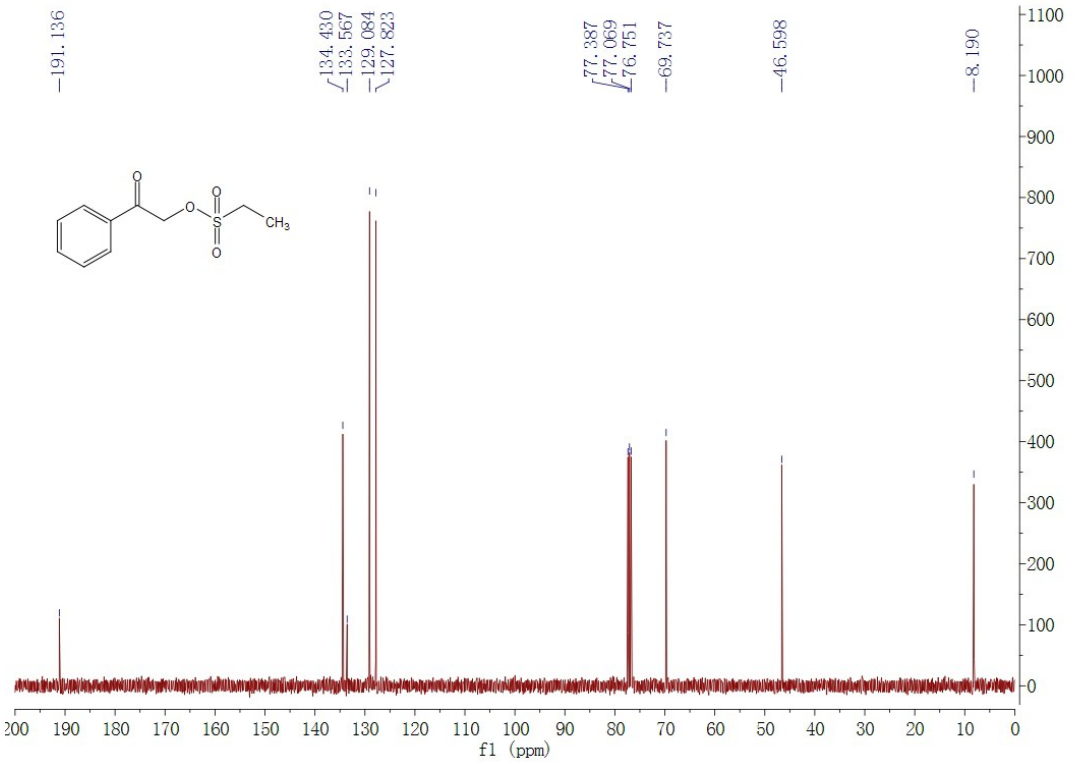
1-Oxo-1-phenylethyl Methanesulfonate (Scheme 2, 3ab)



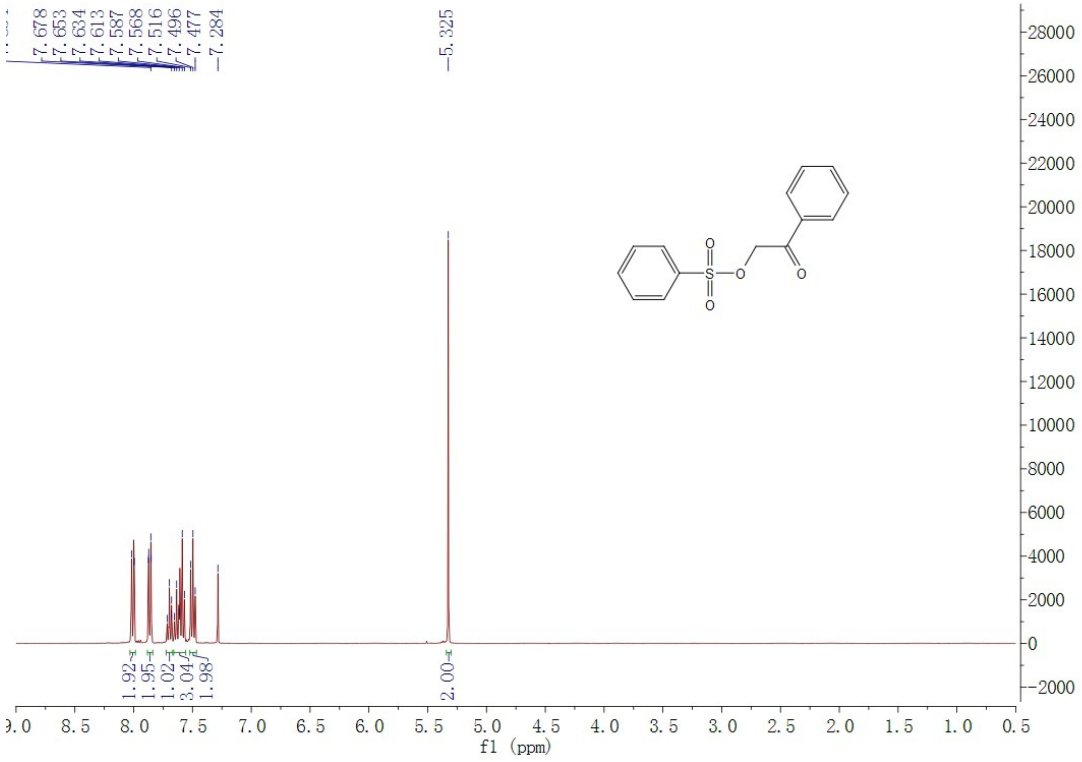


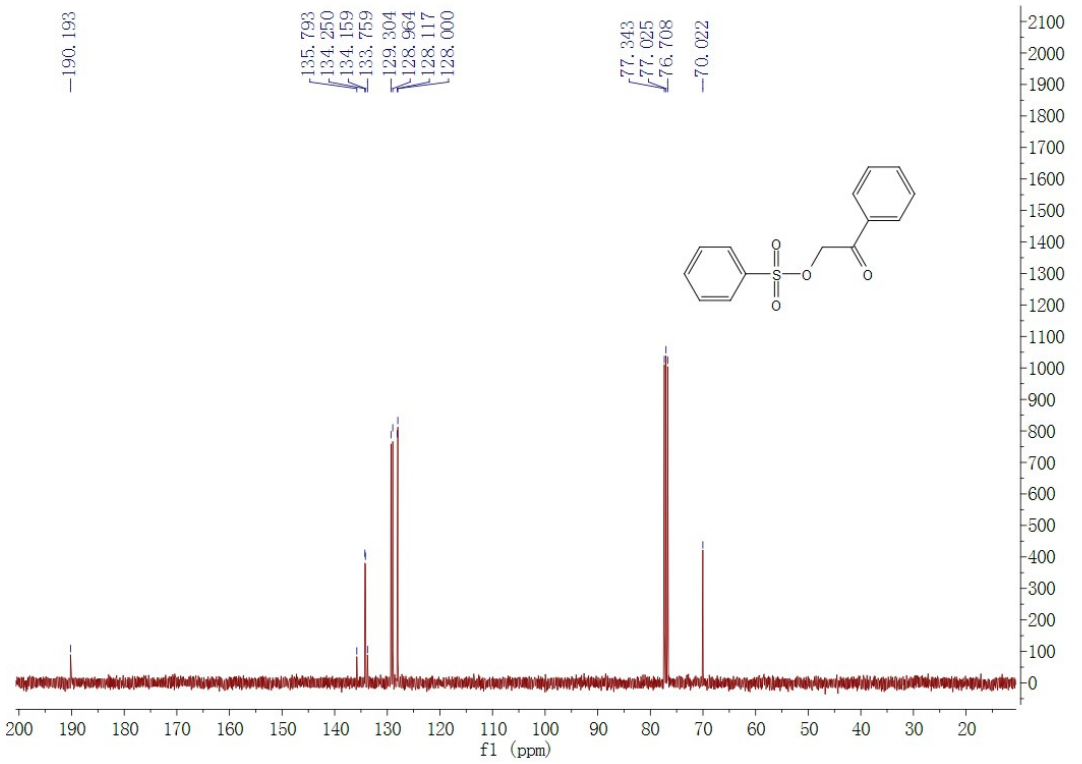
1-Oxo-1-phenylethyl Ethanesulfonate (Scheme 2, 3ac)



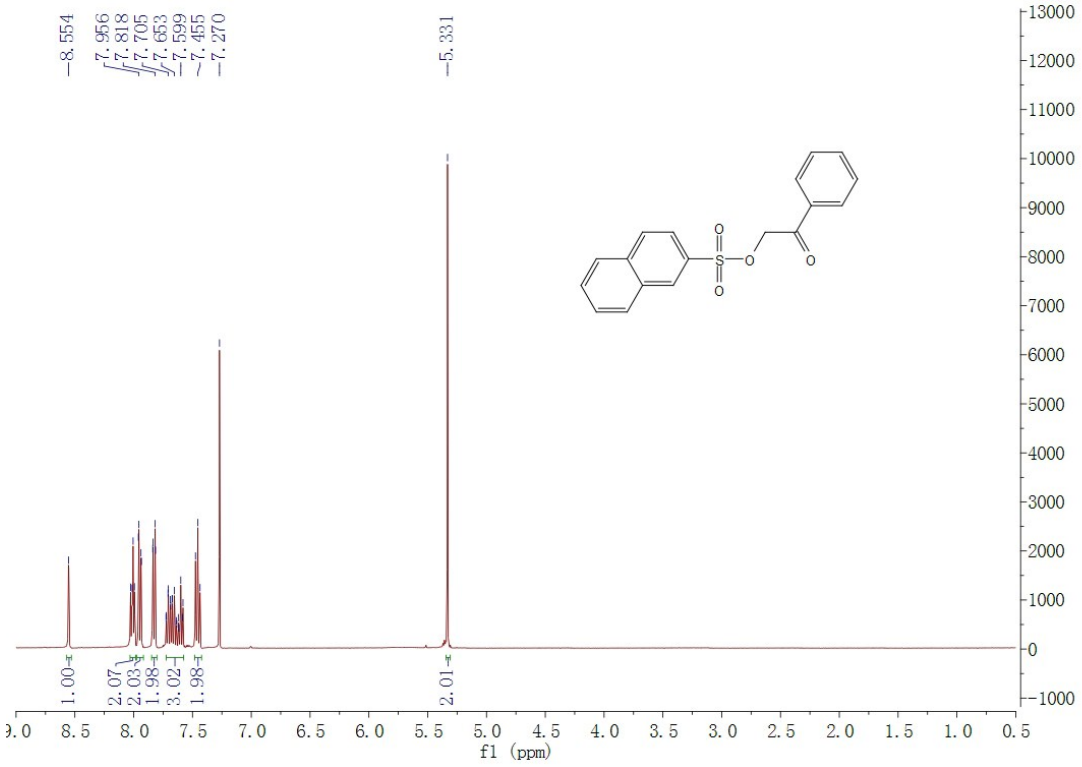


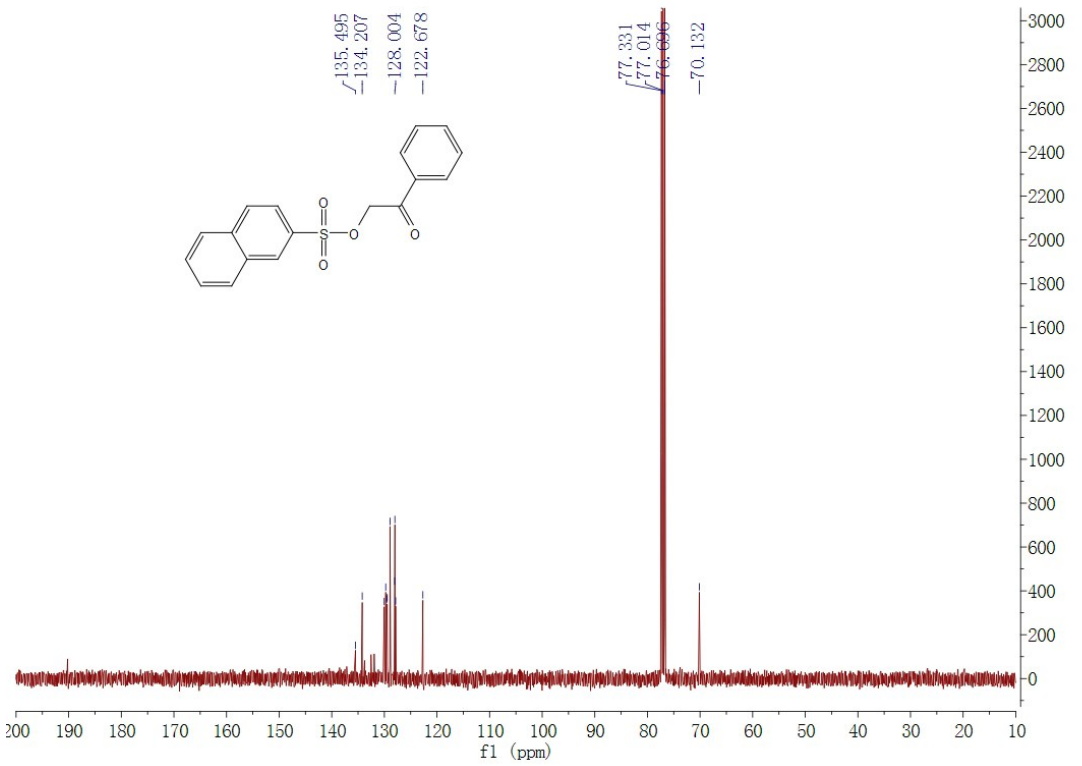
1-Oxo-1-phenylethyl Benzenesulfonate (Scheme 2, 3ad)





1-Oxo-1-phenylethyl 2-Naphthalenesulfonate (Scheme 2, 3ae)





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