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Supporting Information

Iron-catalyzed oxosulfonylation of alkynes with small-ring compounds and $Na_2S_2O_5$ for the synthesis of β-ketone sulfones

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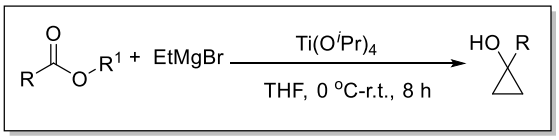
List of Contents

(A) General information

All chemicals were acquired from commercial sources and were employed as received unless otherwise mentioned. The reaction was monitored by TLC with silica gel plates, and the visualization was displayed under UV light (254 nm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker 400 (400, 101, and 376 MHz) or Bruker 500 (500, 126, and 471 MHz) advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and 77.0 ppm) using TMS as internal standard. HRMS spectra were measured on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

(B) Typical experimental procedures

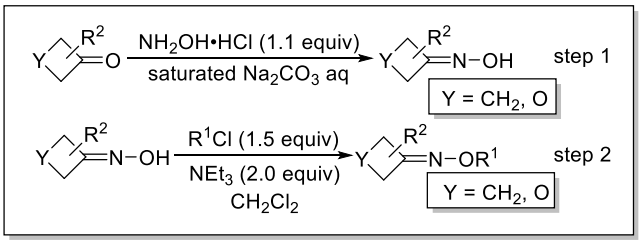
(1) General procedure for the synthesis of cyclopropanol[1].



A dried 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with ester (2.0 mmol, 1.0 equiv) and titanium isopropoxide (2.8 mmol, 1.4 equiv) in THF (20.0 mL) under nitrogen atmosphere. Ethylmagnesium bromide (2.8 mL, 2.8 equiv, 2.0 M in THF) was added to the solution dropwise over 30 min at 0 °C. The resulting reaction mixture was warmed to room temperature and stirred for 12 h. Then the mixture was quenched with water and the precipitate was filtered off. The filtrate was extracted with ethyl acetate (15.0 mL ×3). The combined organic layers was washed with water, and dried over Na_2SO_4. After removal of volatiles under reduced

pressure, the residue was purified by silica gel column chromatography to afford the desired product.

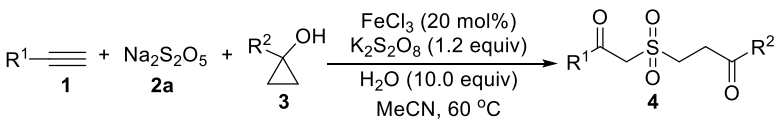
(2) General procedure for the synthesis of oxime esters[2].



Step 1: The ketone (2.0 mmol, 1.0 equiv) and hydroxylamine hydrochloride (2.2 mmol, 1.1 equiv) were placed in a round bottom flask equipped with stirrer. The pH of the solution was held at 7-8 by adding saturated aq. sodium carbonate (5.0 mL). The resulting solution was stirred at 40 ^{o}C. After extraction with ether, the solution was dried over Na_2SO_4 and evaporated to provide crude products which were used in the next step without further purification.

Step 2: To a mixture of cyclobutanone oxime (2.0 mmol, 1.0 equiv), triethylamine (4.0 mmol, 2.0 equiv) and DCM (5.0 mL) in a round bottom flask was slowly added R^1Cl (3.0 mmol, 1.5 equiv) at 0 ^{o}C and then the mixture was stirred at room temperature for 7 h. The organic layer was washed with water and dried over Na_2SO_4. The solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel to give oxime esters.

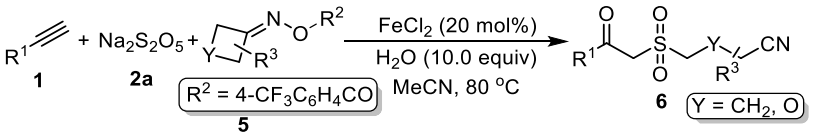
(3) Typical experimental procedures for the synthesis of compounds 4.



To the Schlenk tube was added terminal alkyne **1** (0.2 mmol, 1.0 equiv), sodium pyrosulfite **2a** (0.3mmol, 1.5 equiv), cyclobutanol **3** (0.3 mmol, 1.5 equiv), $FeCl_3$ (0.04

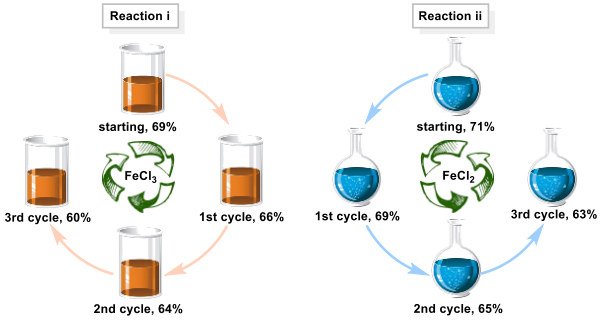
mmol, 20 mol%), $K_2S_2O_8$ (0.24 mmol, 1.2 equiv), H_2O (2.0 mmol, 10.0 equiv) and MeCN (1.5 mL). Then the tube was stirred at 60 °C and until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 2.5:1~1.5:1) to acquire the desired products **4**.

(4) Typical experimental procedures for the synthesis of compounds 6.



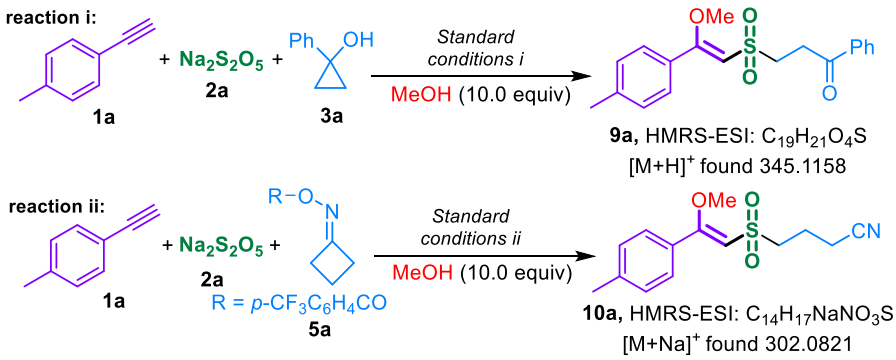
To the Schlenk tube was added terminal alkyne **1** (0.2 mmol, 1.0 equiv), sodium pyrosulfite **2a** (0.3 mmol, 1.5 equiv), oxime esters **5** (0.3 mmol, 1.5 equiv), $FeCl_2$ (0.04 mmol, 20 mol%), H_2O (2.0 mmol, 10.0 equiv) and MeCN (1.5 mL). Then the tube was stirred at 80 °C and until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was concentrated under reduced pressure, and the mixture was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 1.5:1~1.0:1) to acquire the desired products **6**.

(C) Recycling of catalyst.[a]



[a] Reaction conditions for reaction i: **1a** (2.0 mmol), **2a** (1.5 equiv), **3a** (1.5 equiv), $FeCl_3$ (20 mol%), $K_2S_2O_8$ (1.2 equiv), H_2O (10.0 equiv) and MeCN (10.0 mL) at 60 °C under air for 24 h. Reaction conditions for reaction ii: **1a** (2.0 mmol), **2a** (1.5 equiv), **5a** (1.5 equiv), $FeCl_2$ (20 mol%), H_2O (10.0 equiv) and MeCN (10.0 mL) at 80 °C under air for 24 h.

(D) Carbocation capture experiments



Reaction i: To the Schlenk tube was added terminal alkyne **1** (0.2 mmol, 1.0 equiv), sodium pyrosulfite **2a** (0.3 mmol, 1.5 equiv), cyclobutanol **3a** (0.3 mmol, 1.5 equiv), $FeCl_3$ (0.04 mmol, 20 mol%), $K_2S_2O_8$ (0.24 mmol, 1.2 equiv), H_2O (2.0 mmol, 10.0 equiv), MeCN (1.5 mL) and MeOH (2.0 mmol, 10.0 equiv). Then the tube was stirred at 60 °C for 8 h. After the reaction was completed, carbocation adduct **9a** was observed through HMRS-ESI analysis of the reaction solution, shown in **Figure S1**.

Reaction ii: To the Schlenk tube was added terminal alkyne **1** (0.2 mmol, 1.0 equiv), sodium pyrosulfite **2a** (0.3 mmol, 1.5 equiv), oxime esters **5a** (0.3 mmol, 1.5 equiv), $FeCl_2$ (0.04 mmol, 20 mol%), H_2O (2.0 mmol, 10.0 equiv), MeCN (1.5 mL) and MeOH (2.0 mmol, 10.0 equiv). Then the tube was stirred at 80 °C for 8 h. After the reaction was completed, carbocation adduct **10a** was observed through HMRS-ESI analysis of the reaction solution, shown in **Figure S2**.

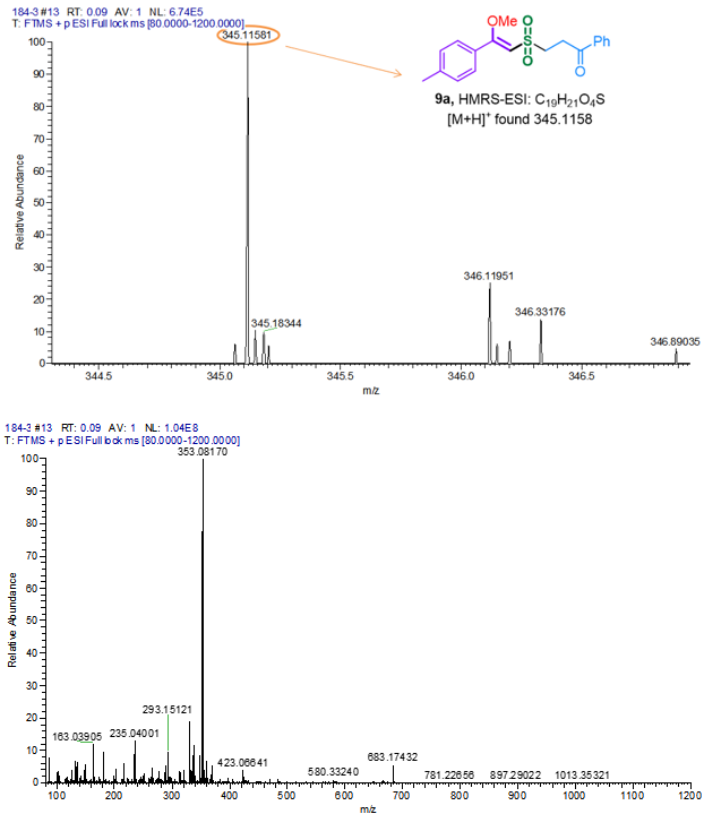


Figure S1 HMRS spectra of **9a**. The reaction mixture was analyzed by Thermo Scientific LTQ Orbitrap XL

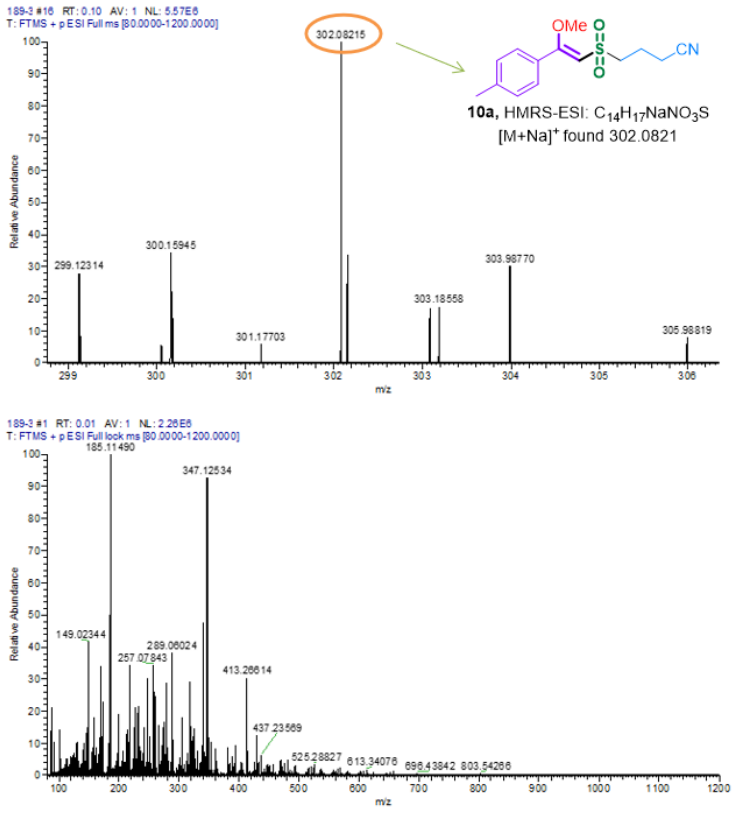
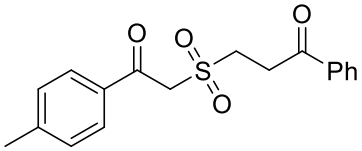
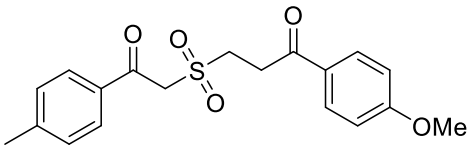


Figure S2 HMRS spectra of **10a**. The reaction mixture was analyzed by Thermo Scientific LTQ Orbitrap XL

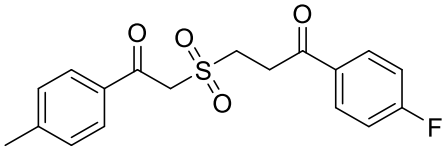
(E) Analytical data



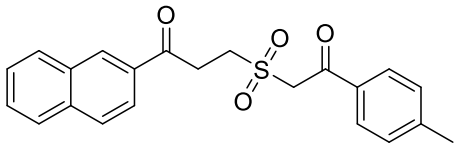
3-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)-1-phenylpropan-1-one (4a). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (58.8 mg, 89% yield), m.p. = 102-105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.67 (s, 2H), 3.78 (t, J = 7.2 Hz, 2H), 3.61 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.5, 188.4, 146.0, 135.8, 133.8, 133.2, 129.7, 129.4, 128.8, 128.2, 60.5, 49.0, 31.1, 21.8; IR (in KBr) v (cm^{-1}): 2919, 2850, 1683, 1605, 1449, 1383, 1318, 1123, 785; HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_4S$ ($[M+H]^+$) 331.0999, found 331.0991.



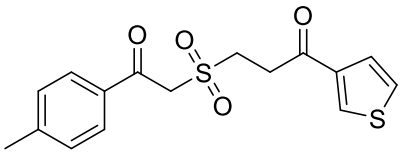
1-(4-Methoxyphenyl)-3-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)propan-1-one (4b). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (64.8 mg, 90% yield), m.p. = 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.61 (s, 2H), 3.79 (s, 3H), 3.67 (t, J = 7.2 Hz, 2H), 3.46 (t, J = 7.6 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 193.9, 188.4, 163.9, 145.8, 133.2, 130.4, 129.6, 129.3, 128.8, 113.8, 60.3, 55.4, 49.1, 30.6, 21.7; IR (in KBr) v (cm^{-1}): 2953, 2933, 2849, 1687, 1598, 1449,1330, 1285, 1148, 997, 801; HRMS *m/z* (ESI) calcd for $C_{19}H_{21}O_5S$ ($[M+H]^+$) 361.1104, found 361.1108.



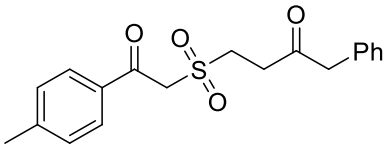
1-(4-Fluorophenyl)-3-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)propan-1-one (4c). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (57.1 mg, 82% yield), m.p. = 112-114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02-7.99 (m, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 8.8 Hz, 2H), 4.68 (s, 2H), 3.76 (t, J = 7.2 Hz, 2H), 3.57 (t, J = 7.6 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.0, 188.4, 166.1 (d, J_{C-F} = 256.9 Hz), 146.0, 133.2, 132.2 (d, J_{C-F} = 3.0 Hz), 130.8 (d, J_{C-F} = 9.5 Hz), 129.7, 129.4, 116.0 (d, J_{C-F} = 22.0 Hz), 60.5, 48.9, 30.9, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -103.7; IR (in KBr) v (cm^{-1}): 2925, 2847, 1683, 1595, 1452, 1328, 1269, 1207, 1149, 1114, 799; HRMS *m/z* (ESI) calcd for $C_{18}H_{18}FO_4S$ ($[M+H]^+$) 349.0904, found 349.0908.



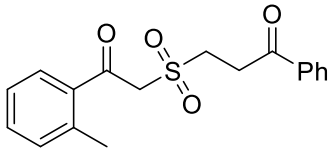
1-(Naphthalen-2-yl)-3-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)propan-1-one (4d). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (61.6 mg, 81% yield), m.p. = 130-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (s, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 5.2 Hz, 1H), 7.36-7.34 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 4.67 (s, 2H), 3.75 (t, J = 7.6 Hz, 2H), 3.51 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.6, 188.4, 146.0, 140.9, 133.2, 132.8, 129.7, 129.4, 126.8, 126.7, 60.4, 48.8, 32.0, 21.8; IR (in KBr) v (cm^{-1}): 2920, 2851, 1689, 1606, 1508, 1470, 1352, 1312, 1290, 1241, 1125, 1006, 789; HRMS *m/z* (ESI) calcd for $C_{22}H_{21}O_4S$ ($[M+H]^+$) 381.1155, found 381.1151.



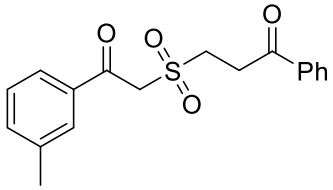
3-((2-Oxo-2-(thiophen-2-yl)ethyl)sulfonyl)-1-phenylpropan-1-one (4e). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). Brown oil (50.9 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (s, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.93-7.87 (m, 4H), 7.63 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 4.71 (s, 2H), 3.83 (t, J = 7.2 Hz, 1H), 3.75 (t, J = 7.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.4, 188.4, 146.0, 135.8, 133.2, 133.1, 132.4, 130.2, 129.7 (2), 129.4, 128.9, 128.7, 127.8, 127.0, 123.5, 60.5, 49.1, 31.1, 21.8; IR (in KBr) ν (cm^{-1}): 3116, 2958, 2918, 1687, 1605, 1520, 1325, 1296, 1139, 999, 803; HRMS *m/z* (ESI) calcd for $C_{15}H_{15}O_4S_2$ ($[M+H]^+$) 323.0406, found 323.0402.



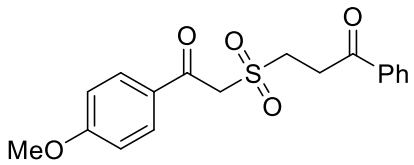
4-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)-1-phenylbutan-2-one (4f). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (48.9 mg, 71% yield), m.p. = 116-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 6.4 Hz, 2H), 7.34-7.31 (m, 3H), 7.29 (d, J = 5.6 Hz, 2H), 7.21 (t, J = 3.6 Hz, 2H), 4.57 (s, 2H), 3.77 (s, 2H), 3.58-3.54 (m, 2H), 3.05 (t, J = 6.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 203.9, 188.3, 146.0, 133.2 (2), 129.7, 129.4, 129.3, 128.9, 127.4, 60.4, 49.9, 48.6, 33.9, 21.8; IR (in KBr) ν (cm^{-1}): 2954, 2923, 2853, 1686, 1599, 1451, 1333, 1279, 1259, 1129, 999, 800; HRMS *m/z* (ESI) calcd for $C_{19}H_{21}O_4S$ ($[M+H]^+$) 345.1155, found 345.1161.



3-((2-Oxo-2-(*o*-tolyl)ethyl)sulfonyl)-1-phenylpropan-1-one (4g). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White oil (57.4 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.43-7.37 (m, 3H), 7.26-7.19 (m, 2H), 4.59 (s, 2H), 3.72 (t, J = 7.2 Hz, 2H), 3.55 (t, J = 7.2 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.5, 191.4, 140.1, 135.7, 135.6, 133.8, 133.1, 132.4, 130.2, 128.8, 128.1, 126.1, 62.6, 49.1, 31.1, 21.6; IR (in KBr) v (cm^{-1}): 2961, 2919, 2848, 1686, 1603, 1453, 1329, 1276, 1260, 1134, 996, 739; HRMS m/z (ESI) calcd for $C_{18}H_{19}O_4S$ ($[M+H]^+$) 331.0999, found 331.0991.

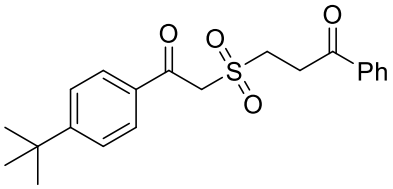


3-((2-Oxo-2-(*m*-tolyl)ethyl)sulfonyl)-1-phenylpropan-1-one (4h). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (56.8 mg, 86% yield), m.p. = 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J = 7.6 Hz, 2H), 7.80 (t, J = 6.4 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.50-7.45 (m, 3H), 7.40 (t, J = 7.6 Hz, 1H), 4.70 (s, 2H), 3.78 (t, J = 7.6 Hz, 2H), 3.60 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.5, 189.1, 138.9, 135.7 (2), 135.4, 133.8, 129.6, 128.8 (2), 128.1, 126.5, 60.5, 49.0, 31.0, 21.3; IR (in KBr) v (cm^{-1}): 2950, 2919, 1676, 1601, 1458, 1319, 1264, 1125, 999, 769, 691; HRMS m/z (ESI) calcd for $C_{18}H_{19}O_4S$ ($[M+H]^+$) 331.0999, found 331.0991.

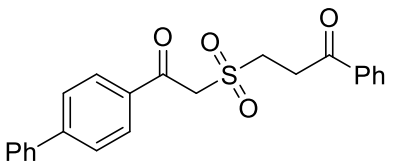


3-((2-(4-Methoxyphenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4i). The product was purified

by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (63.0 mg, 91% yield), m.p. = 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (t, J = 7.6 Hz, 4H), 7.60 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 4.64 (s, 2H), 3.89 (s, 3H), 3.76 (t, J = 7.2 Hz, 2H), 3.60 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.4, 187.0, 164.8, 135.8, 133.8, 131.8, 128.8, 128.7, 128.1, 114.2, 60.4, 55.6, 48.9, 31.1; IR (in KBr) ν (cm^{-1}): 2943, 2845, 1684, 1596, 1517, 1448, 1327, 1306, 1150, 999, 798; HRMS *m/z* (ESI) calcd for $C_{18}H_{19}O_5S$ ($[M+H]^+$) 347.0948, found 347.0954.

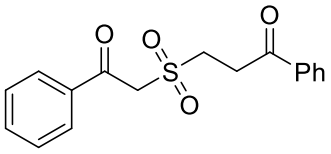


3-((2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4j). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (65.5 mg, 88% yield), m.p. = 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (t, J = 9.2 Hz, 4H), 7.60 (t, J = 7.2 Hz, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 4.69 (s, 2H), 3.78 (t, J = 7.2 Hz, 2H), 3.61 (t, J = 7.2 Hz, 2H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.5, 188.4, 158.8, 135.8, 133.8, 133.2, 129.3, 128.8, 128.2, 126.1, 60.5, 49.0, 35.4, 31.1, 31.0; IR (in KBr) ν (cm^{-1}): 2960, 2924, 1675, 1599, 1516, 1450, 1370, 1330, 1265, 1135, 994, 895, 764; HRMS *m/z* (ESI) calcd for $C_{21}H_{25}O_4S$ ($[M+H]^+$) 373.1468, found 373.1460.

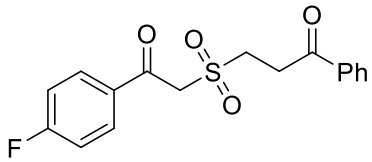


3-((2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4k). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (63.5 mg, 81% yield), m.p. = 125-127 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (d, J = 8.5 Hz, 2H), 7.99-7.97 (m, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.64-7.62 (m, 2H), 7.59 (d, J = 7.5 Hz, 1H), 7.50-7.47 (m, 4H), 7.44-7.42 (m, 1H), 4.74 (s, 2H), 3.80 (t, J = 7.5 Hz, 2H), 3.63 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 195.4, 188.4, 147.3, 139.3, 135.7, 134.3, 133.8, 129.9, 129.0, 128.8, 128.6, 128.1, 127.6, 127.3, 60.6, 49.0, 31.1; IR (in KBr) v (cm^{-1}): 2955, 2920, 1681, 1601, 1581, 1452, 1317, 1280, 1123, 994, 895, 799, 757; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}O_4S$ ($[M+H]^+$) 393.1155, found 393.1153.

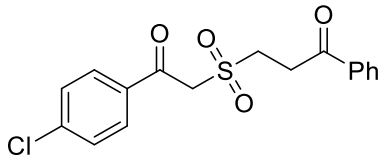


3-((2-Oxo-2-phenylethyl)sulfonyl)-1-phenylpropan-1-one (4l). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (50.6 mg, 80% yield), m.p. = 112-114 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02-7.98 (m, 4H), 7.66 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 4.71 (s, 2H), 3.79 (t, J = 7.5 Hz, 2H), 3.62 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 195.5, 188.9, 135.7, 135.7, 134.7, 133.8, 129.2, 129.0, 128.8, 128.1, 60.5, 49.0, 31.1; IR (in KBr) v (cm^{-1}): 2961, 2920, 1685, 1599, 1449, 1319, 1275, 1124, 997, 901, 760, 699; HRMS *m/z* (ESI) calcd for $C_{17}H_{17}O_4S$ ($[M+H]^+$) 317.0842, found 317.0844.

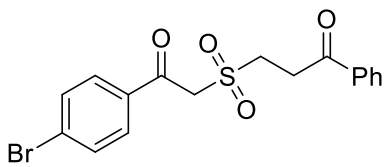


3-((2-(4-Fluorophenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4m). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (43.4 mg, 65% yield), m.p. = 116-118 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.07-8.05 (m, 2H), 7.99-7.97 (m, 2H),

7.62 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 8.5 Hz, 2H), 4.69 (s, 2H), 3.77 (t, J = 7.5 Hz, 2H), 3.62 (t, J = 7.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 195.4, 187.3, 166.6 (d, J_{C-F} = 258.7 Hz), 135.7, 133.9, 132.2 (d, J_{C-F} = 9.8 Hz), 128.8, 128.1, 116.3 (d, J_{C-F} = 22.3 Hz), 60.6, 49.0, 3 1.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -101.8; IR (in KBr) v (cm^{-1}): 2934, 2839, 1682, 1593, 1451, 1333, 1275, 1260, 1135, 1118, 850, 649; HRMS *m/z* (ESI) calcd for $C_{17}H_{16}FO_4S$ ([M+H]$^+$) 335.0748, found 335.0746.

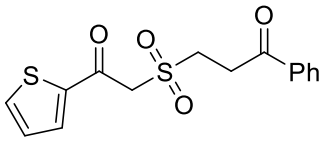


3-((2-(4-Chlorophenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4n). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (44.8 mg, 64% yield), m.p. = 115-117 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (t, J = 9.0 Hz, 4H), 7.62 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 8.5 Hz, 4H), 4.68 (s, 2H), 3.77 (t, J = 7.5 Hz, 2H), 3.62 (t, J = 7.0 Hz, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.4, 187.8, 141.5, 135.7, 134.0, 133.9, 130.6, 129.4, 128.8, 128.1, 60.6, 49.0, 31.1; IR (in KBr) v (cm^{-1}): 2948, 2917, 1681, 1593, 1452, 1326, 1280, 1255, 1122, 763, 705, 501; HRMS *m/z* (ESI) calcd for $C_{17}H_{16}ClO_4S$ ([M+H]$^+$) 351.0452, found 351.0458.

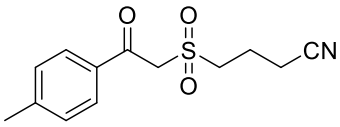


3-((2-(4-Bromophenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4o). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). White solid (49.6 mg, 63% yield), m.p. = 120-122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 4.67 (s, 2H), 3.76

(t, J = 7.2 Hz, 2H), 3.61 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.4, 188.0, 135.7, 134.4, 133.9, 132.4, 130.7, 130.3, 128.8, 128.1, 60.6, 49.0, 31.1; IR (in KBr) v (cm^{-1}): 2931, 2853, 1689, 1587, 1459, 1319, 1277, 1120, 996, 762, 598, 559, 530, 475; HRMS m/z (ESI) calcd for $C_{17}H_{16}BrO_4S$ ($[M+H]^+$) 394.9947, found 394.9941.

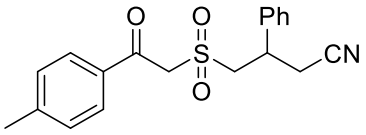


3-((2-Oxo-2-(thiophen-2-yl)ethyl)sulfonyl)-1-phenylpropan-1-one (4p). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2.5:1, v/v). Brown oil (52.8 mg, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, J = 7.5 Hz, 2H), 7.87-7.86 (m, 1H), 7.80-7.79 (m, 1H), 7.60 (t, J = 7.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.21-7.19 (m, 1H), 4.63 (s, 2H), 3.78 (t, J = 7.5 Hz, 2H), 3.60 (t, J = 7.5 Hz, 2H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ: 195.4, 181.0, 143.0, 136.9, 135.7, 135.3, 133.8, 128.8, 128.7, 128.1, 61.3, 49.0, 31.0; IR (in KBr) v (cm^{-1}): 3104, 2919, 2851, 1683, 1596, 1580, 1515, 1451, 1415, 1317, 1290, 1147, 1001, 801, 747, 732; HRMS m/z (ESI) calcd for $C_{15}H_{15}NO_3S$ ($[M+H]^+$) 323.0406, found 323.0402.

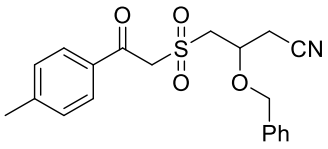


4-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile (6a). A known compound and the characterization data are in accordance with the literature[3]. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). White solid (43.5 mg, 82% yield), m.p. = 90-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.59 (s, 2H), 3.43 (t, J = 7.2 Hz, 2H), 2.61 (t, J = 7.2 Hz, 2H), 2.43 (s, 3H), 2.27 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.4, 146.2, 133.0, 129.7, 129.4, 118.1, 59.9, 51.7, 21.8, 18.3, 16.2; IR (in KBr) v (cm^{-1}): 2953, 2914,

2246, 1682, 1606, 1457, 1318, 1279, 1260, 1121, 1000, 800; HRMS *m/z* (ESI) calcd for $C_{13}H_{15}NNaO_3S$ ($[M+Na]^+$) 288.0665, found 288.0664.

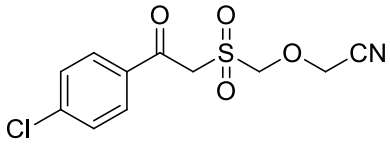


4-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)-3-phenylbutanenitrile (6b). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow oil (48.4 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 4.8 Hz, 2H), 7.24-7.21 (m, 3H), 7.20-7.18 (m, 2H), 4.40 (d, J = 15.2 Hz, 1H), 4.03 (d, J = 15.2 Hz, 1H), 3.87-3.82 (m, 1H), 3.73-3.66 (m, 1H), 3.60-3.55 (m, 1H), 2.89-2.84 (m, 2H), 2.35(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.3, 146.0, 138.4, 132.9, 129.6, 129.3, 129.1, 128.5, 127.3, 117.1, 60.2, 57.1, 36.4, 24.4, 21.7; IR (in KBr) ν (cm^{-1}): 2956, 2918, 2250, 1677, 1602, 1477, 1453, 1320, 1285, 1127, 1008, 789; HRMS *m/z* (ESI) calcd for $C_{19}H_{20}NO_3S$ ($[M+H]^+$) 342.1158, found 342.1156.

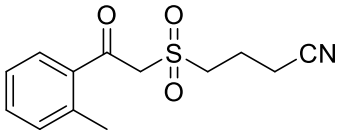


3-(Benzyloxy)-4-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile (6c). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (52.0 mg, 70% yield), m.p. = 117-119 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.26-7.23 (m, 2H), 7.19 (t, J = 2.0 Hz, 1H), 4.68 (s, 2H), 4.64-4.52 (m, 2H), 4.02-3.98 (m, 1H), 3.68-3.62 (m, 1H), 3.40 (t, J = 8.0 Hz, 1H), 2.65 (t, J = 4.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.8, 146.4, 133.0, 129.8, 129.3, 127.8, 125.7 (2), 116.2, 62.9, 60.9 (2), 58.4, 25.6, 21.8; IR (in KBr) ν (cm^{-1}): 2813, 2253, 1674, 1598, 1516, 1399, 1324, 1295, 1137, 1015, 766; HRMS *m/z*

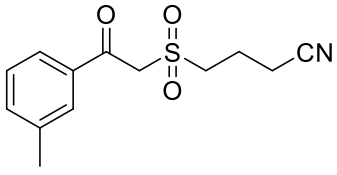
(ESI) calcd for $C_{20}H_{22}NO_4S$ ([M+H]$^+$) 372.1264, found 372.1268.



2-(((2-(4-Chlorophenyl)-2-oxoethyl)sulfonyl)methoxy)acetonitrile (6d). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (33.3 mg, 58% yield), m.p. = 95-97 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 4.83 (s, 2H), 4.70 (s, 2H), 4.65 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 187.2, 141.8, 133.7, 130.4, 129.5, 114.3, 82.3, 57.4, 56.7; IR (in KBr) v (cm^{-1}): 2949, 2910, 2251, 1693, 1610, 1461, 1320, 1285, 1124, 999, 760, 703; HRMS *m/z* (ESI) calcd for $C_{11}H_{11}ClNO_4S$ ([M+H]$^+$) 288.0092, found 288.0094.

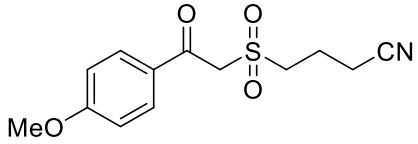


4-((2-Oxo-2-(*o*-tolyl)ethyl)sulfonyl)butanenitrile (6e). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (42.9 mg, 81% yield), m.p. = 91-93 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J = 8.0 Hz 1H), 7.48 (t, J = 7.6 Hz 1H), 7.37-7.30 (m, 2H), 4.58 (s, 2H), 3.47 (t, J = 7.6 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 2.55 (s, 3H), 2.34-2.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.3, 140.3, 135.4, 133.3, 132.5, 130.3, 126.2, 118.1, 62.1, 51.9, 21.7, 18.3, 16.3; IR (in KBr) v (cm^{-1}): 2954, 2914, 2245, 1674, 1602, 1459, 1319, 1259, 1124, 998, 742; HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO_3S$ ([M+H]$^+$) 266.0845, found 266.0847.

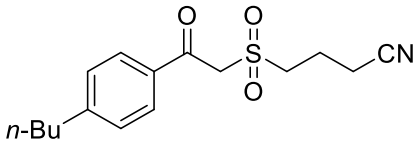


4-((2-Oxo-2-(*m*-tolyl)ethyl)sulfonyl)butanenitrile (6f). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1,

v/v). Yellow solid (42.4 mg, 80% yield), m.p. = 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81-7.76 (m, 2H), 7.48 (d, J = 7.6 Hz 1H), 7.42 (t, J = 7.6 Hz, 1H), 4.60 (s, 2H), 3.45 (t, J = 7.6 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 2.44 (s, 3H), 2.33-2.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.1, 139.1, 135.7, 135.5, 129.6, 129.0, 126.6, 118.0, 60.0, 51.8, 21.3, 18.3, 16.3; IR (in KBr) ν (cm^{-1}): 2953, 2916, 2247, 1678, 1605, 1462, 1315, 1260, 1121, 996, 785, 691; HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO_3S$ ($[M+H]^+$) 266.0845, found 266.0843.

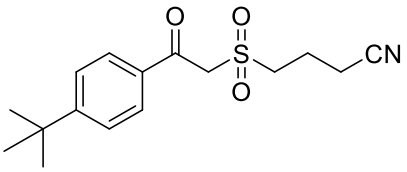


4-((2-(4-Methoxyphenyl)-2-oxoethyl)sulfonyl)butanenitrile (6g). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (44.4 mg, 79% yield), m.p. = 93-95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 4.57 (s, 2H), 3.89 (s, 3H), 3.43 (t, J = 7.5 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.31-2.25 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 187.0, 164.9, 131.8, 128.5, 127.8, 114.3, 59.8, 55.6, 51.7, 18.3, 16.2; IR (in KBr) ν (cm^{-1}): 2964, 2915, 2840, 2246, 1672, 1569, 1514, 1456, 1326, 1273, 1120, 988, 844; HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO_4S$ ($[M+H]^+$) 282.0795, found 282.0797.

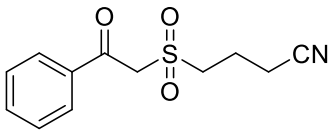


4-((2-(4-Butylphenyl)-2-oxoethyl)sulfonyl)butanenitrile (6h). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow oil (49.1 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ:

7.90 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.59 (s, 2H), 3.44 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 1.62 (t, *J* = 7.6 Hz, 2H), 1.38-1.33 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 188.4, 151.1, 133.2, 129.4, 129.1, 118.1, 60.0, 51.7, 35.8, 33.0, 22.3, 18.3, 16.3, 13.8; IR (in KBr) *v* (cm^{-1}): 2955, 2989, 2856, 2249, 1682, 1503, 1456, 1338, 1267, 1149, 999, 893, 795; HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_3S$ ($[M+H]^+$) 308.1315, found 308.1311.

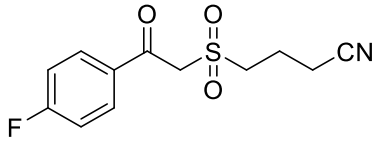


4-((2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)sulfonyl)butanenitrile (6i). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (49.8 mg, 81% yield), m.p. = 94-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.93 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 4.59 (s, 2H), 3.44 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.33-2.26 (m, 2H), 1.35(s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 188.4, 159.1, 132.9, 129.3, 126.1, 118.0, 60.0, 51.7, 35.4, 30.9, 18.3, 16.3; IR (in KBr) *v* (cm^{-1}): 2963, 2921, 2251, 1679, 1599, 1582, 1455, 1324, 1268, 1152, 1110, 994, 895, 799; HRMS *m/z* (ESI) calcd for $C_{16}H_{22}NO_3S$ ($[M+H]^+$) 308.1315, found 308.1319.

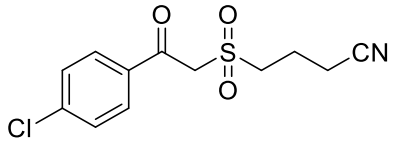


4-((2-Oxo-2-phenylethyl)sulfonyl)butanenitrile (6j). A known compound and the characterization data are in accordance with the literature[3]. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). light yellow solid (39.7 mg, 79% yield), m.p. = 71-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.84 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 4.48 (s,

2H), 3.29 (t, J = 7.2 Hz, 2H), 2.48 (t, J = 7.2 Hz, 2H), 2.17-2.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.0, 135.4, 134.8, 129.2, 129.0, 118.1, 60.0, 51.8, 18.3, 16.3; IR (in KBr) v (cm^{-1}): 2956, 2918, 2247, 1681, 1598, 1450, 1317, 1280, 1123, 994, 895, 757; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}NNaO_3S$ ($[M+Na]^+$) 274.0508, found 274.0508.

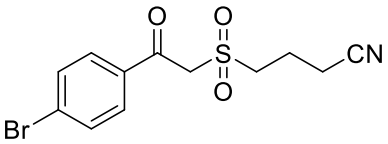


4-((2-(4-Fluorophenyl)-2-oxoethyl)sulfonyl)butanenitrile (6k). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (43.6 mg, 81% yield), m.p. = 95-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ:8.06-8.03 (m, 2H), 7.21 (t, J = 8.4 Hz, 2H), 4.59 (s, 2H), 3.43 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 2.33-2.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 187.3, 166.8 (d, J_{C-F} = 259.8 Hz), 132.2 (d, J_{C-F} = 9.9 Hz), 132.0 (d, J_{C-F} = 2.8 Hz), 118.0, 116.4 (d, J_{C-F} = 22.3 Hz), 60.1, 51.7, 18.3, 16.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -101.3; IR (in KBr) v (cm^{-1}): 2953, 2923, 2251, 1682, 1589, 1453, 1330, 1273, 1209, 1151, 1117, 847, 647; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}FNO_3S$ ($[M+H]^+$) 270.0595, found 270.0599.

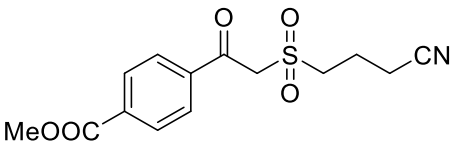


4-((2-(4-Chlorophenyl)-2-oxoethyl)sulfonyl)butanenitrile (6l). A known compound and the characterization data are in accordance with the literature[3]. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v); white solid (45.6 mg, 80% yield), m.p. = 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 4.60 (s, 2H), 3.42 (t, J = 7.2 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H),

2.31-2.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 187.8, 141.7, 133.8, 130.6, 129.4, 118.0, 60.0, 51.7, 18.2, 16.3; IR (in KBr) ν (cm^{-1}): 2949, 2915, 2249, 1683, 1586, 1456, 1325, 1275, 1258, 1125, 764, 704, 499; HRMS *m/z* (ESI) calcd for $C_{12}H_{12}ClNNaO_3S^+$ ($[M+Na]^+$) 308.0119, found 308.0116.

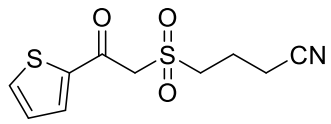


4-((2-(4-Bromophenyl)-2-oxoethyl)sulfonyl)butanenitrile (6m). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (54.0 mg, 82% yield), m.p. = 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 4.58 (s, 2H), 3.42 (t, J = 7.2 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.1, 134.2, 132.4, 130.7, 130.6, 118.0, 60.0, 51.7, 18.2, 16.3; IR (in KBr) ν (cm^{-1}): 2928, 2854, 2248, 1682, 1584, 1456, 1318, 1276, 1119, 994, 761, 507, 471; HRMS *m/z* (ESI) calcd for $C_{12}H_{13}BrNO_3S$ ($[M+H]^+$) 329.9794, found 329.9792.

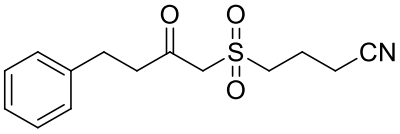


Methyl 4-(2-((3-cyanopropyl)sulfonyl)acetyl)benzoate (6n). A known compound and the characterization data are in accordance with the literature[3].The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v); White solid (51.3 mg, 83% yield), m.p. = 98-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, J = 8.0 Hz, 2H), 8.04 (d, J = 8.0 Hz, 2H), 4.66 (s, 2H), 3.95 (s, 3H), 3.44 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 2.30-2.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.7, 165.7, 138.4,

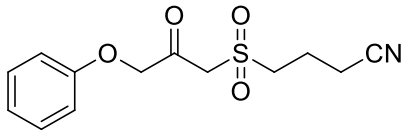
135.3, 130.1, 129.1, 118.0, 60.2, 52.6, 51.8, 18.2, 16.3; IR (in KBr) ν (cm^{-1}): 2254, 1729, 1694, 1575, 1432, 1409, 1281, 1209, 1181, 1112, 995, 762; HRMS *m/z* (ESI) calcd for $C_{14}H_{15}NNaO_5S$ ($[M+Na]^+$) 332.0563, found 332.0566.



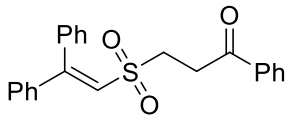
4-((2-Oxo-2-(thiophen-2-yl)ethyl)sulfonyl)butanenitrile (6o). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Brown oil (38.6 g, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.83 (m, 2H), 7.22 (t, J = 4.4 Hz, 1H), 4.52 (s, 2H), 3.44 (t, J = 7.6 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 2.29 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 180.9, 142.8, 137.4, 135.6, 129.0, 118.0, 61.0, 51.7, 18.3, 16.3; IR (in KBr) ν (cm^{-1}): 3110, 3099, 2971, 2941, 2247, 1725, 1518, 1449, 1413, 1307, 1148, 1001, 803, 743; HRMS *m/z* (ESI) calcd for $C_{10}H_{12}NO_3S_2$ ($[M+H]^+$) 258.0253, found 258.0257.



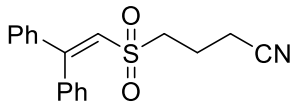
4-((2-Oxo-4-phenylbutyl)sulfonyl)butanenitrile (6p). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow oil (38.0 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29 (t, J = 7.5 Hz, 2H), 7.23-7.18 (m, 3H), 4.01 (s, 2H), 3.22 (t, J = 7.5 Hz, 2H), 3.05 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.21-2.15 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 198.5, 139.7, 128.6, 128.4, 126.4, 117.9, 63.6, 51.5, 46.2, 29.0, 18.1, 16.2; IR (in KBr) ν (cm^{-1}): 2955, 2928, 2849, 2250, 1710, 1601, 1449, 1320, 1276, 1259, 1123, 999, 749, 695; HRMS *m/z* (ESI) calcd for $C_{14}H_{18}NO_3S$ ($[M+H]^+$) 280.1002, found 280.1008.



4-((2-Oxo-3-phenoxypropyl)sulfonyl)butanenitrile (6q). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1.5:1, v/v). Yellow solid (36.5 mg, 65% yield), m.p. = 92-94 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (t, J = 7.6 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 4.75 (s, 2H), 4.30 (s, 2H), 3.35 (t, J = 7.6 Hz, 2H), 2.58 (t, J = 6.8 Hz, 2H), 2.22 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.4, 156.9, 129.8, 122.3, 118.1, 114.5, 72.8, 59.7, 51.9, 18.0, 16.1; IR (in KBr) ν (cm-1): 2938, 2841, 2248, 1714, 1602, 1452, 1320, 1277, 1124, 998, 752, 689; HRMS *m/z* (ESI) calcd for $C_{13}H_{16}NO_4S$ ($[M+H]^+$) 282.0795, found 282.0799.



3-((2,2-Diphenylvinyl)sulfonyl)-1-phenylpropan-1-one (7a). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v). White solid (38.4 mg, 51% yield), m.p. = 114-116 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94-7.92 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.48-7.40 (m, 6H), 7.37-7.34 (m, 4H), 7.27 (t, J = 4.5 Hz, 2H), 6.83 (s, 1H), 3.45-3.42 (m, 2H), 3.30 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 195.7, 156.4, 139.1, 135.8, 135.5, 133.7, 130.5, 129.7, 129.5, 128.8, 128.7, 128.4, 128.1 (2), 125.9, 50.0, 31.1; IR (in KBr) ν (cm^{-1}): 2996, 2921, 2852, 1688, 1596, 1490, 1446, 1310, 1125, 821, 768, 692; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}O_3S$ ($[M+H]^+$) 377.1206, found 377.1204.



4-((2,2-diphenylvinyl)sulfonyl)butanenitrile (8a). A known compound and the characterization data are in accordance

with the literature[4]. The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow oil (28.0 mg, 45% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, J = 7.5 Hz, 2H), 7.45-7.43 (m, 2H), 7.39-7.37 (m, 4H), 7.28 (t, J = 4.5 Hz, 2H), 6.79 (s, 1H), 2.86 (t, J = 7.5 Hz, 2H), 2.47 (t, J = 7.0 Hz, 2H), 2.12-2.08 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.7, 143.8, 138.8, 130.7, 129.8, 129.7, 128.8, 128.7, 128.4, 125.8, 118.1, 52.7, 18.8, 16.2; IR (in KBr) v (cm^{-1}): 2922, 2850, 2249, 1592, 1491, 1444, 1310, 1298, 1124, 821, 801, 700; HRMS (ESI-TOF) m/z: $C_{18}H_{18}NO_2S$ ($[M+H]^+$) calcd for 312.1053, found 312.1058.

(F) References

[1] Q. Zhang, S.-W. Zhou, C.-Y. Shi and L. Yin, Catalytic Asymmetric Allylic Substitution with Copper(I) Homoenolates Generated from Cyclopropanols, *Angew. Chem. Int. Ed.*, 2021, **60**, 26351-26356.

[2] J. Chen, Y.-J. Liang, P.-Z. Wang, G.-Q. Li, B. Zhang, H. Qian, X.-D. Huan, W. Guan, W.-J. Xiao and J.-R. Chen, Photoinduced Copper-Catalyzed Asymmetric C−O Cross-Coupling, *J. Am. Chem. Soc*., 2021, **143**, 13382-13392.

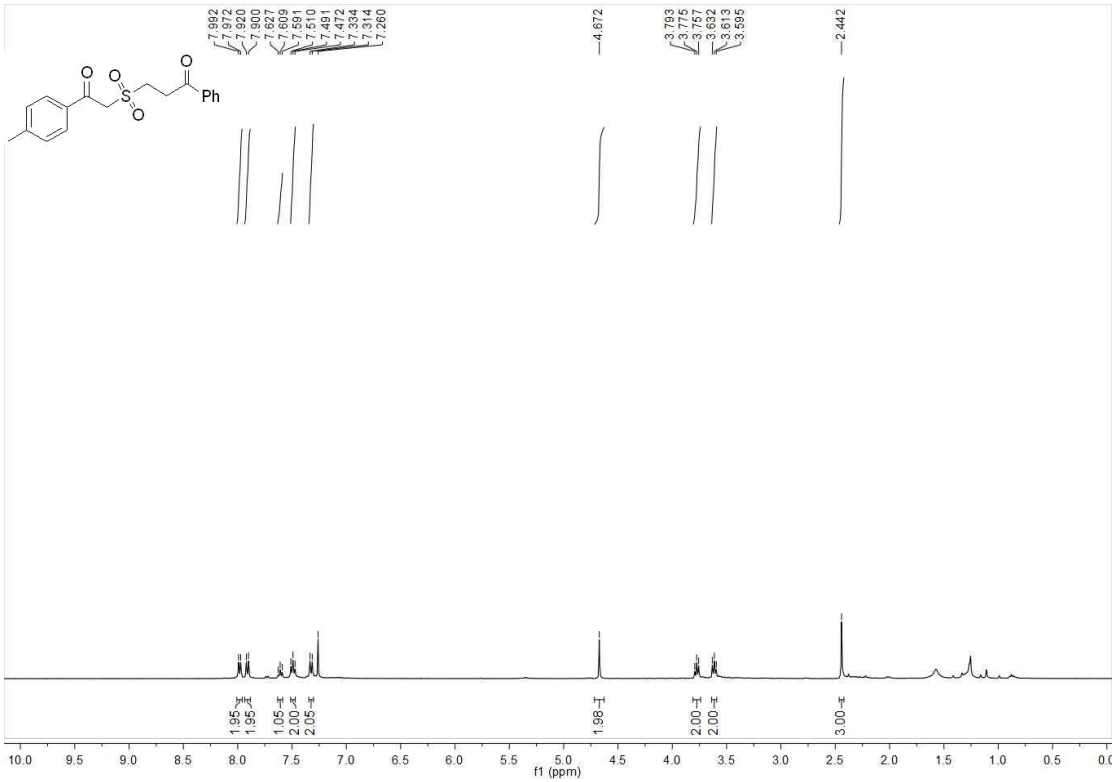
[3] M. Zheng, G. G. Li and H. J. Lu, Photoredox- or Metal-Catalyzed in Situ SO_2-Capture Reactions: Synthesis of β-Ketosulfones and Allylsulfones, *Org. Lett.*, 2019, **21**, 1216-1220.

[4] Y. Liu, L.-Q. Wang, Z. Chen, H. Li, B.-Q. Xiong, P.-L. Zhang and K.-W. Tang, Visible-Light Photoredox-Catalyzed Dual C–C Bond Cleavage: Synthesis of 2-Cyanoalkylsulfonylated 3,4-Dihydronaphthalenes through the Insertion of Sulfur Dioxide. *Chem. Commun*., 2020, **56**, 3011-3014.

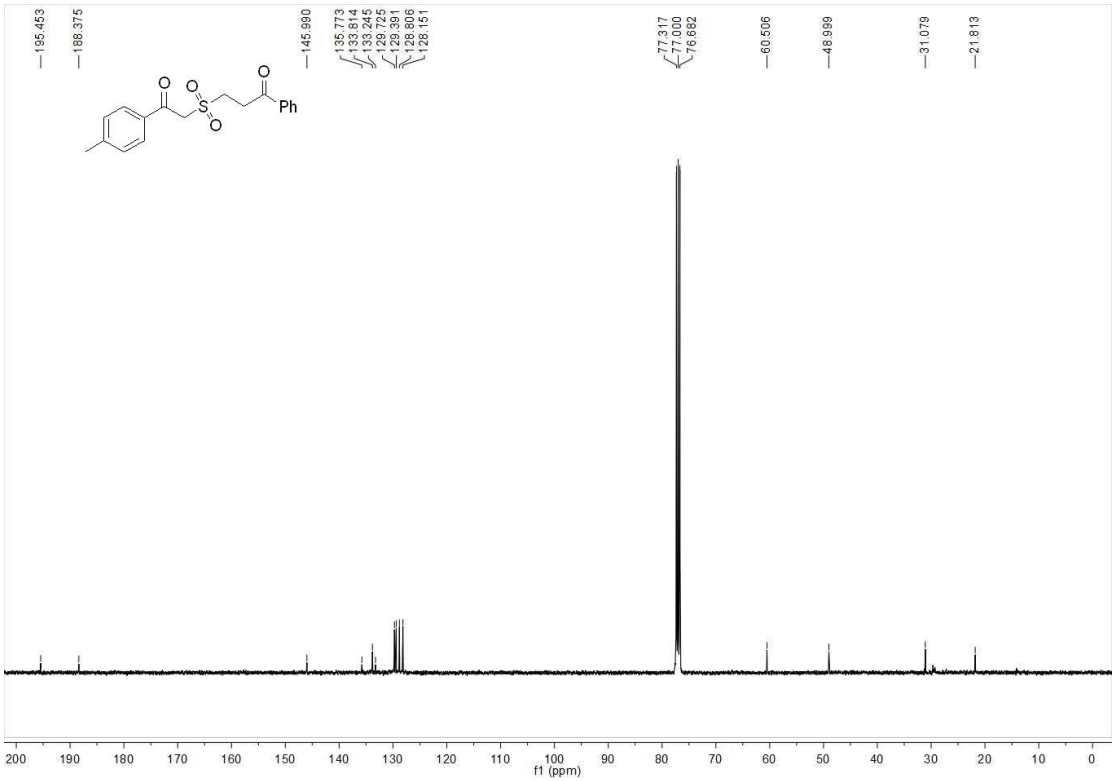
(G) Spectra

3-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)-1-phenylpropan-1-one (4a)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4a**

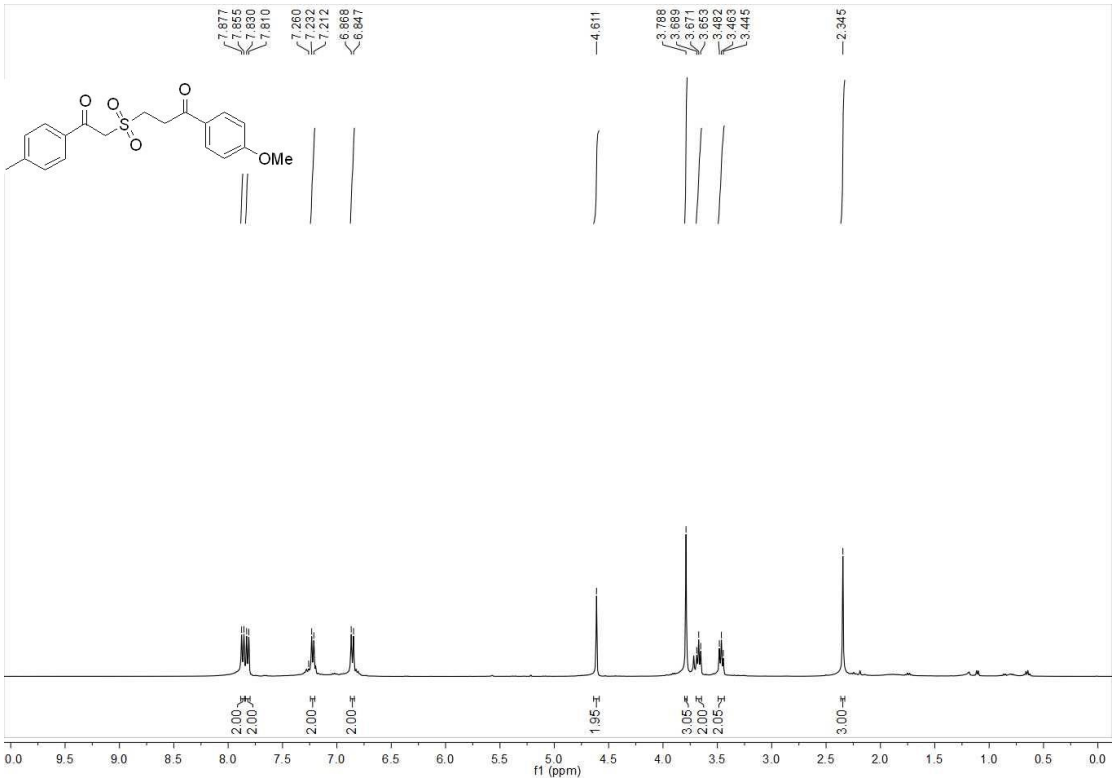


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4a**

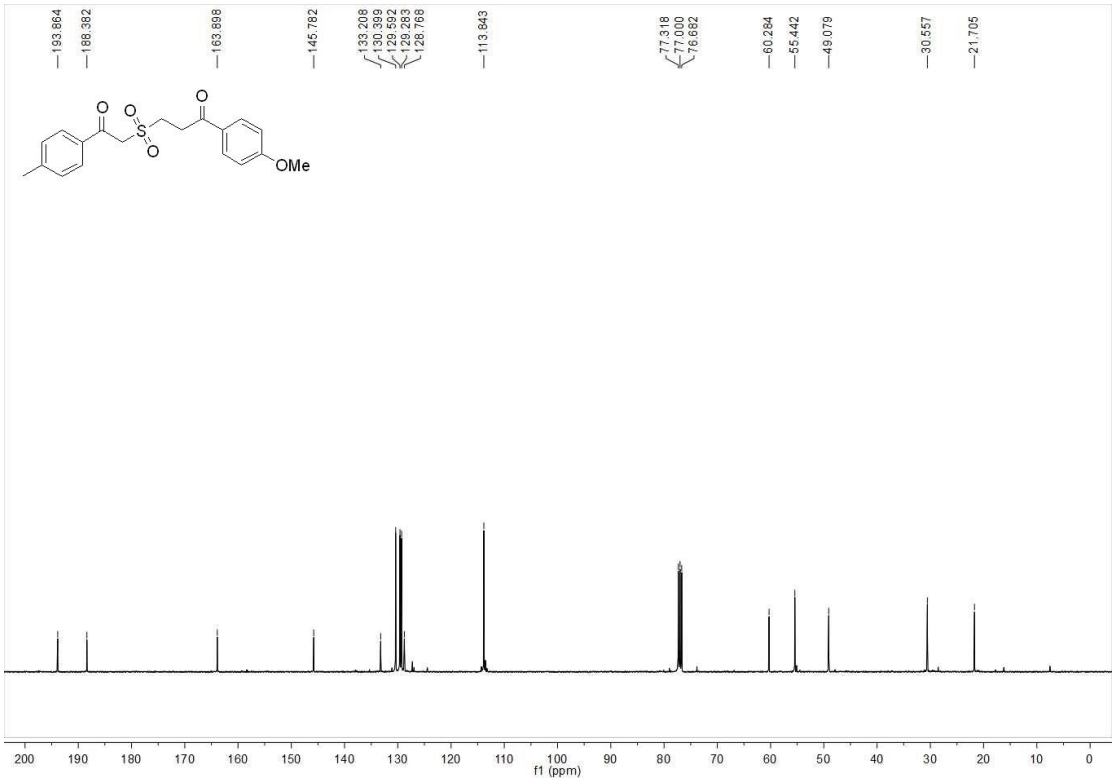


1-(4-Methoxyphenyl)-3-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)propan-1-one (4b)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4b**

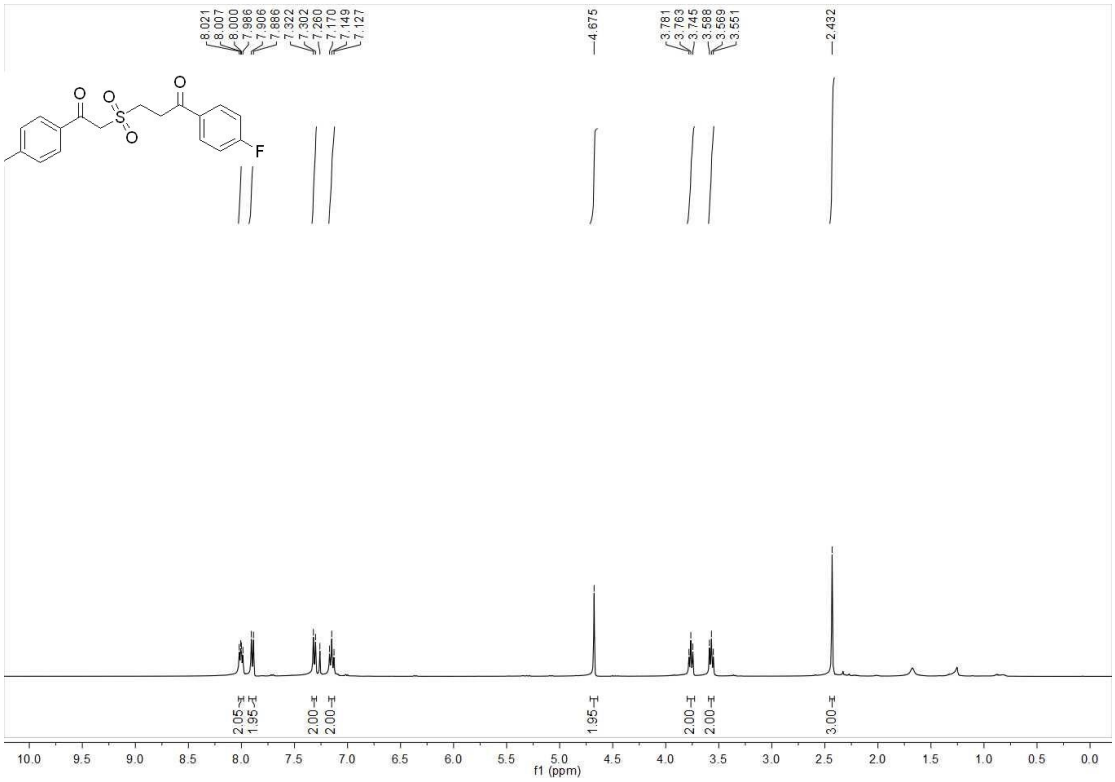


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4b**

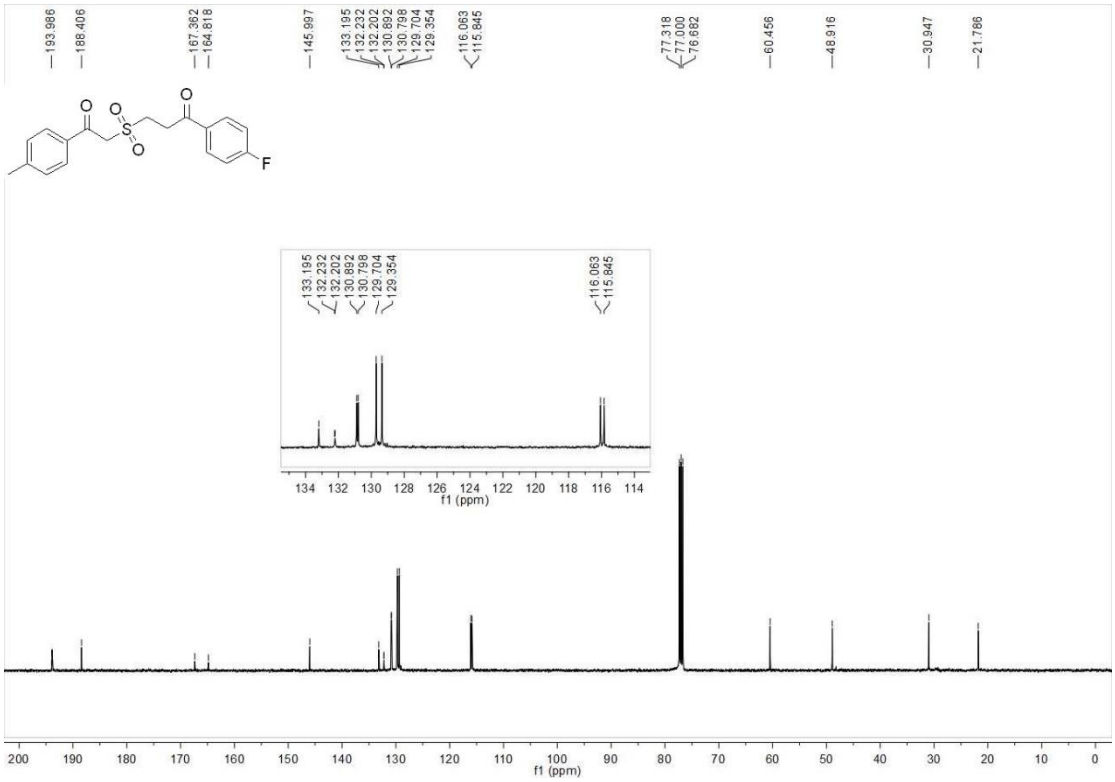


1-(4-Fluorophenyl)-3-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)propan-1-one (4c).

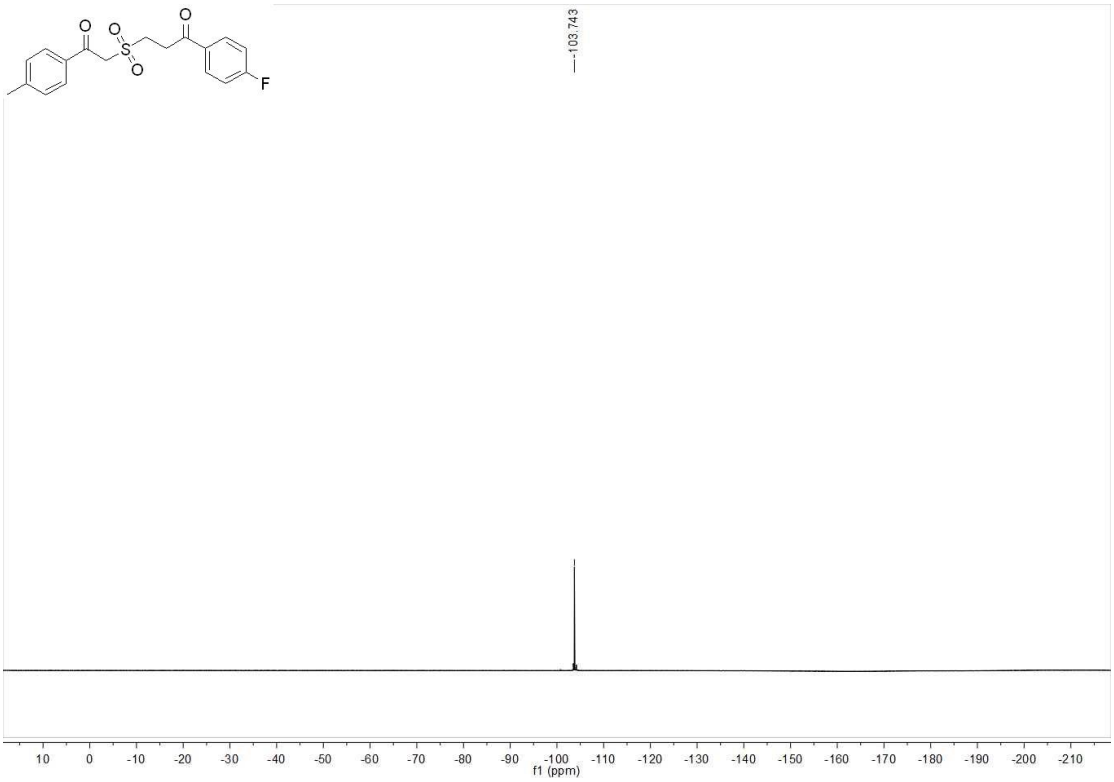
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4c**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4c**

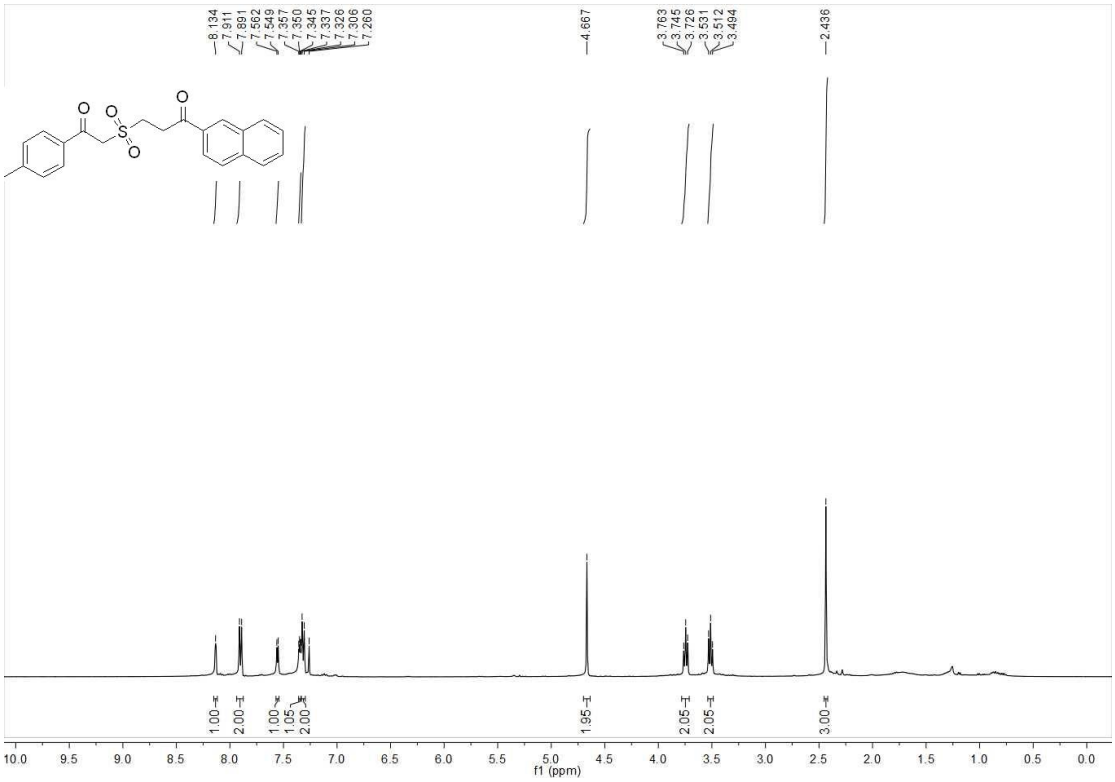


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4c**

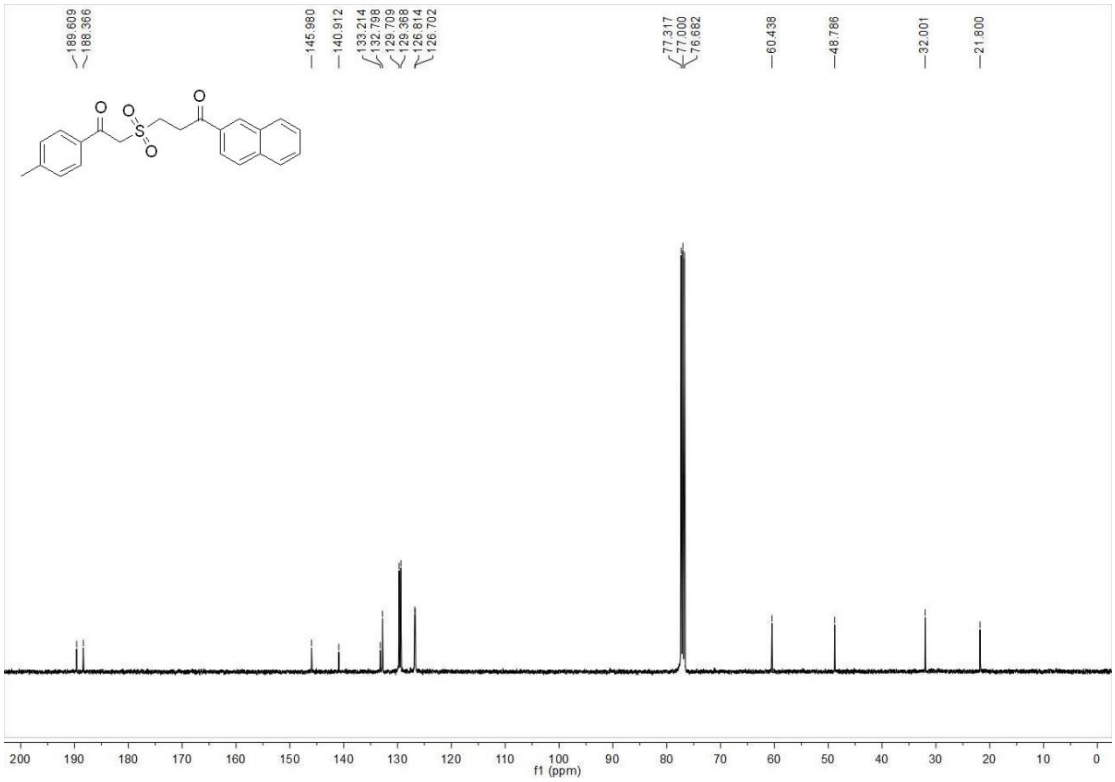


1-(Naphthalen-2-yl)-3-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)propan-1-one (4d)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4d**

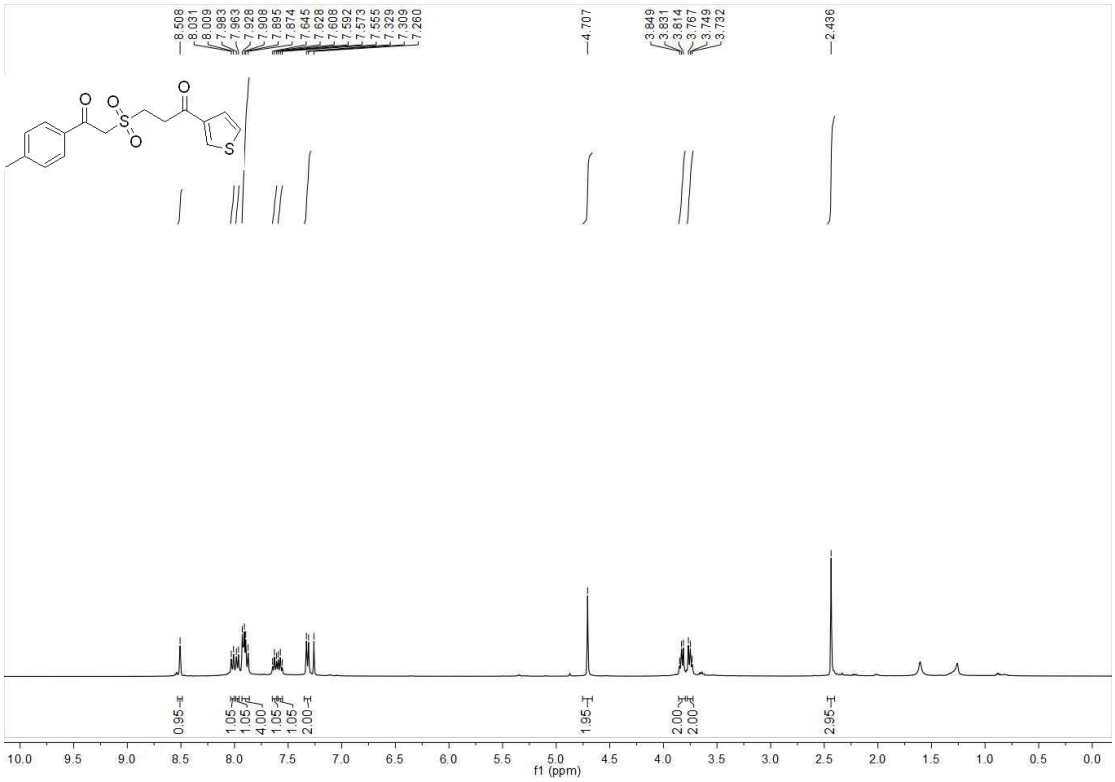


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4d**

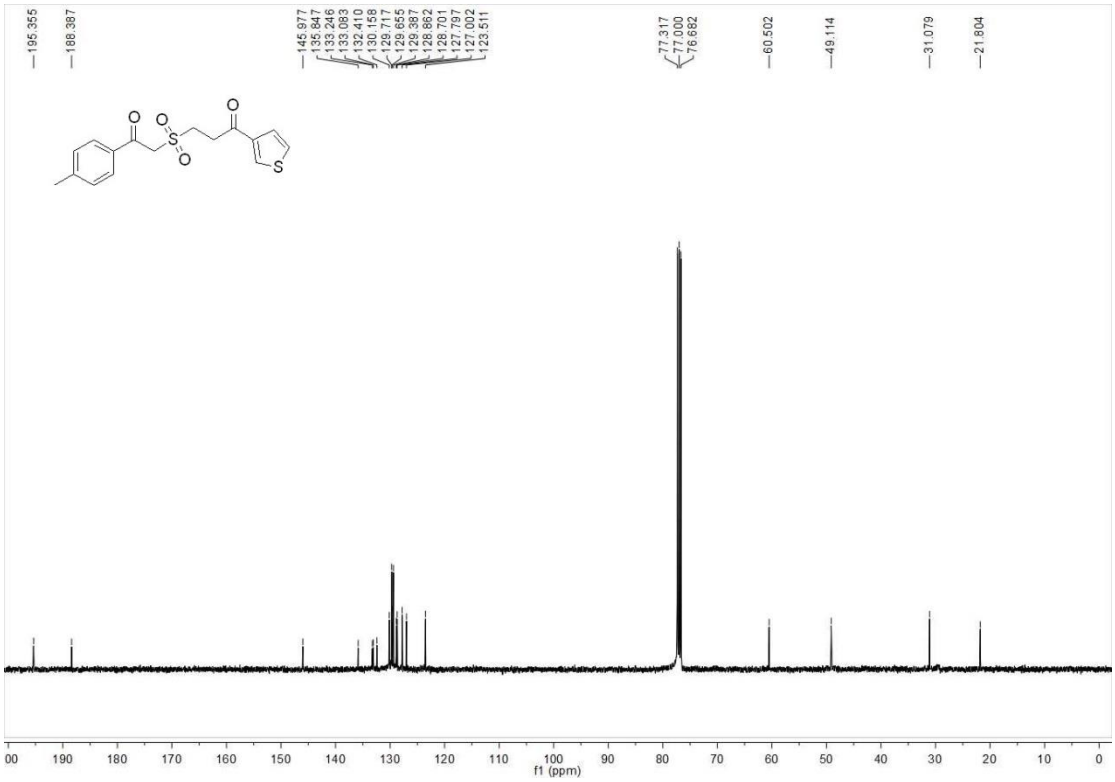


3-((2-Oxo-2-(thiophen-2-yl)ethyl)sulfonyl)-1-phenylpropan-1-one (4e).

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4e**

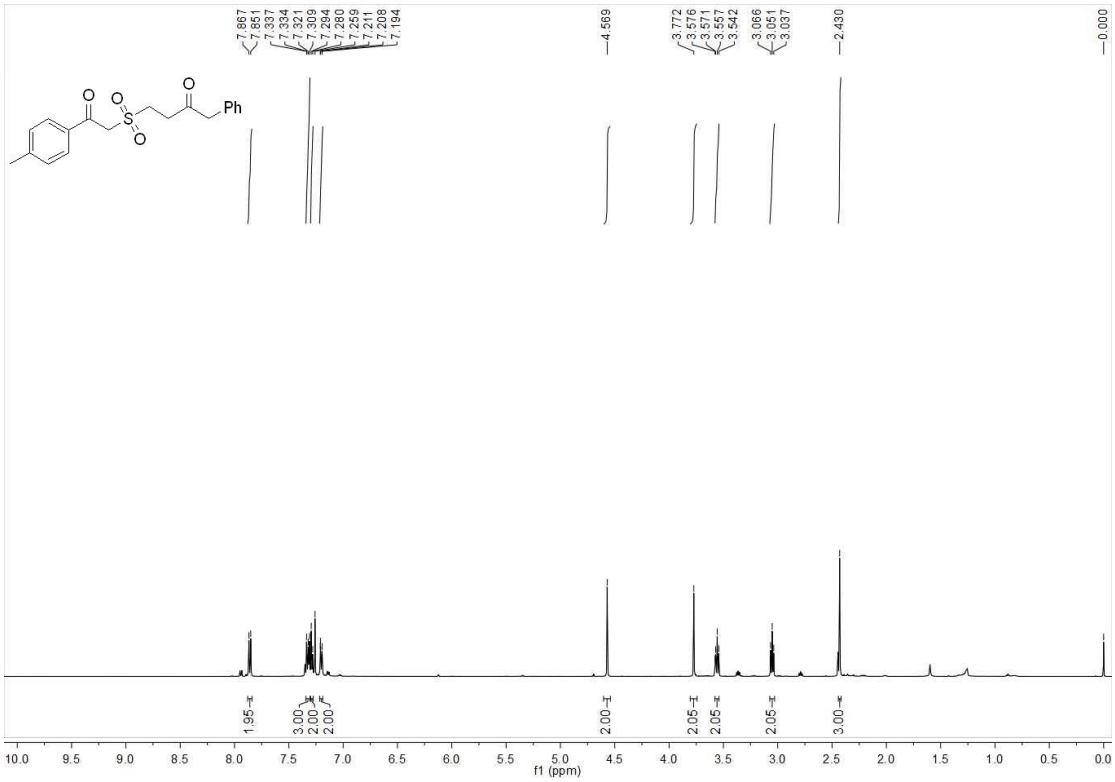


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4e**

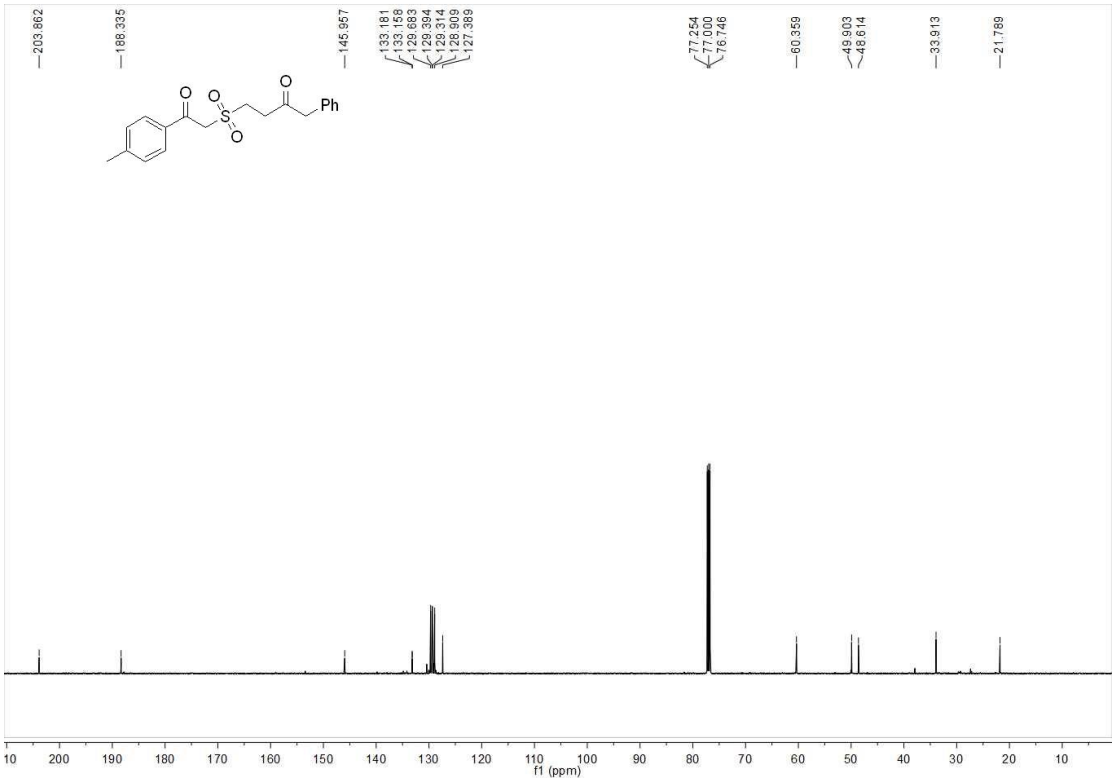


4-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)-1-phenylbutan-2-one (4f)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4f**

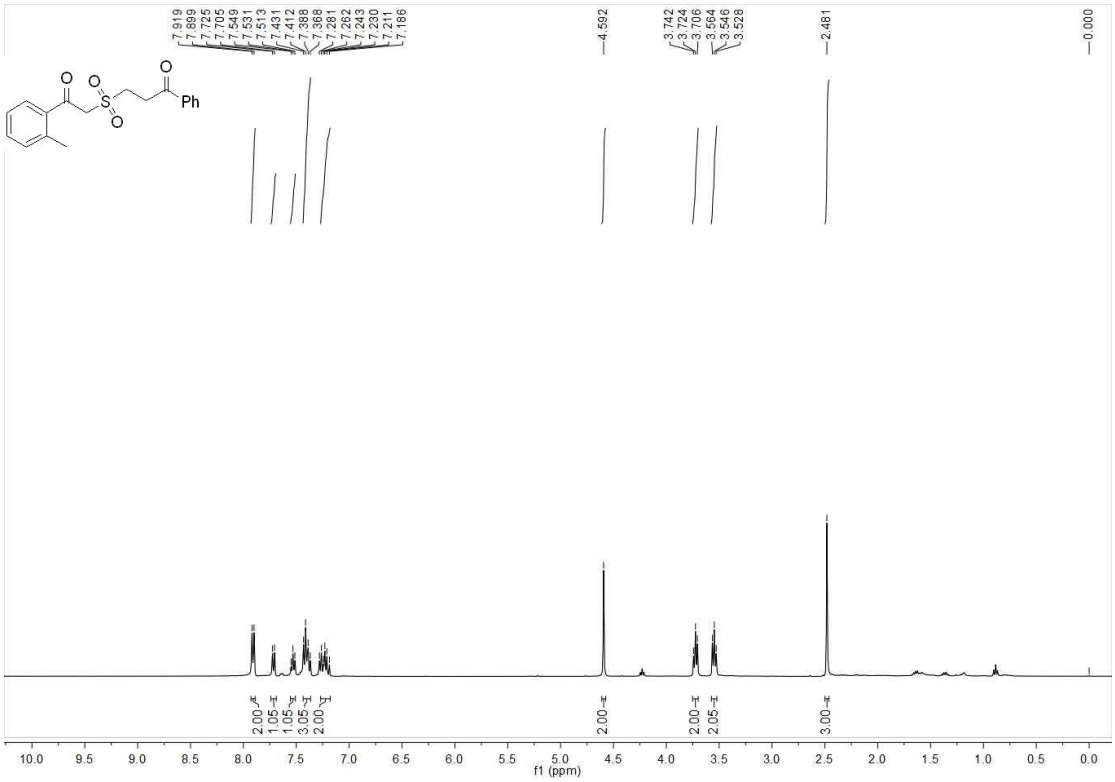


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4f**

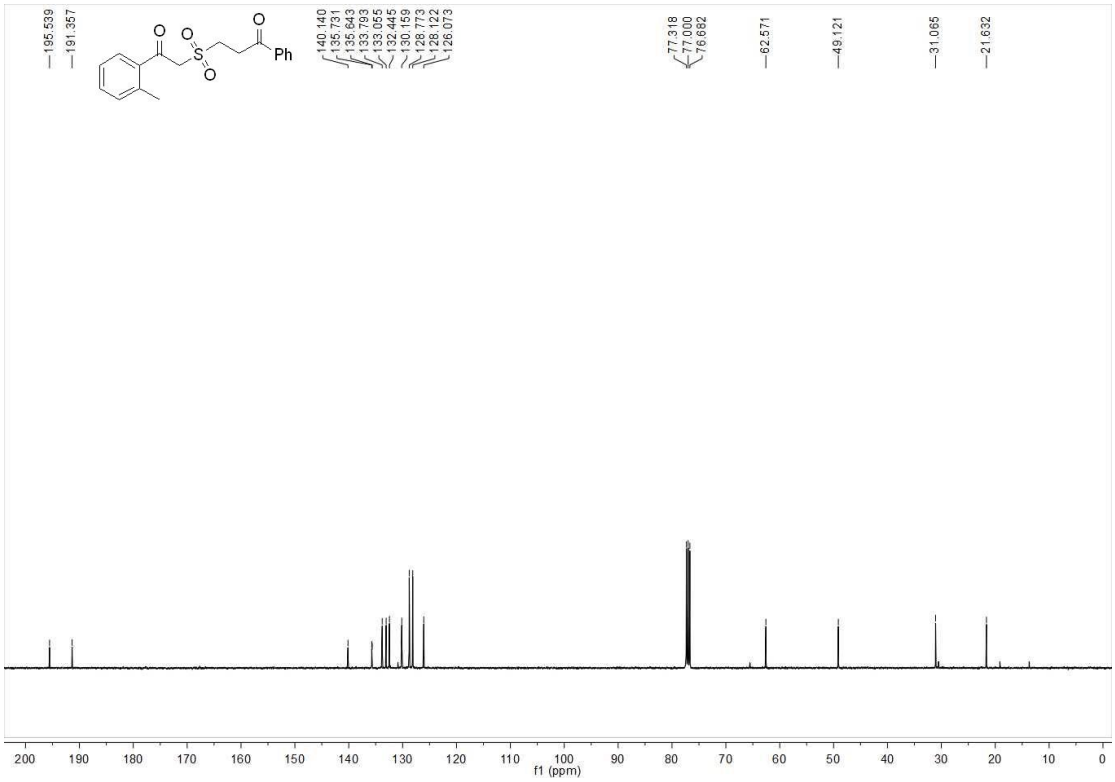


3-((2-Oxo-2-(*o*-tolyl)ethyl)sulfonyl)-1-phenylpropan-1-one (4g)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4g**

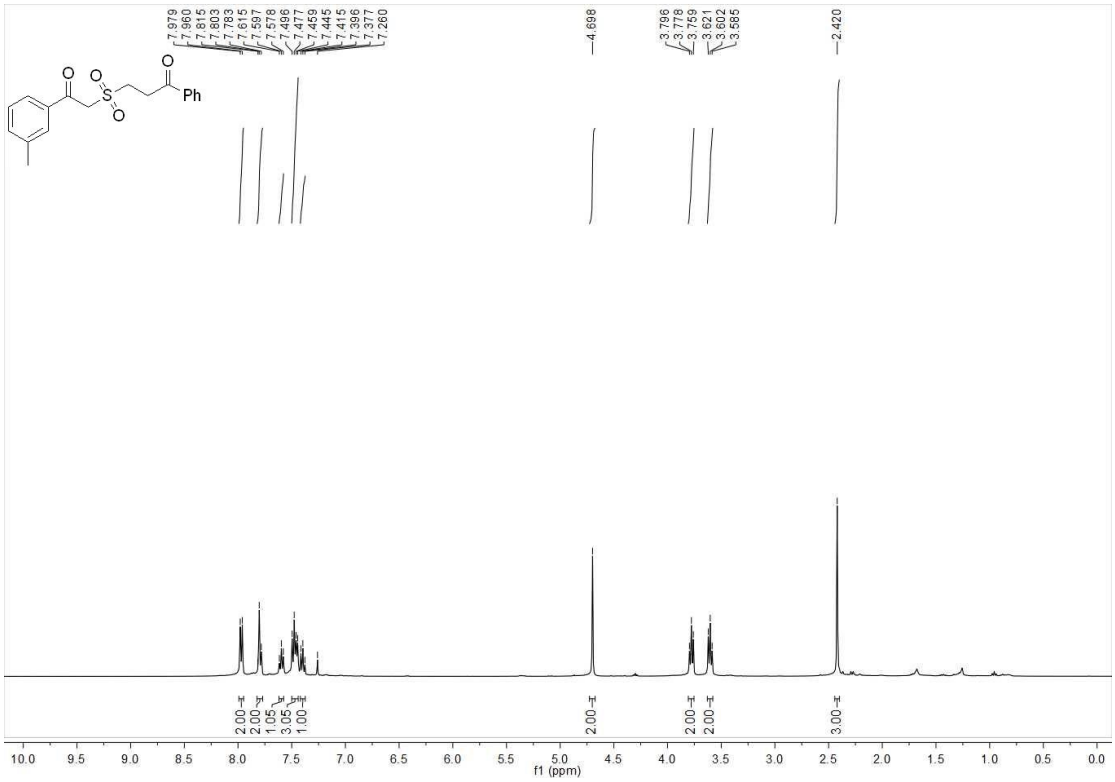


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4g**

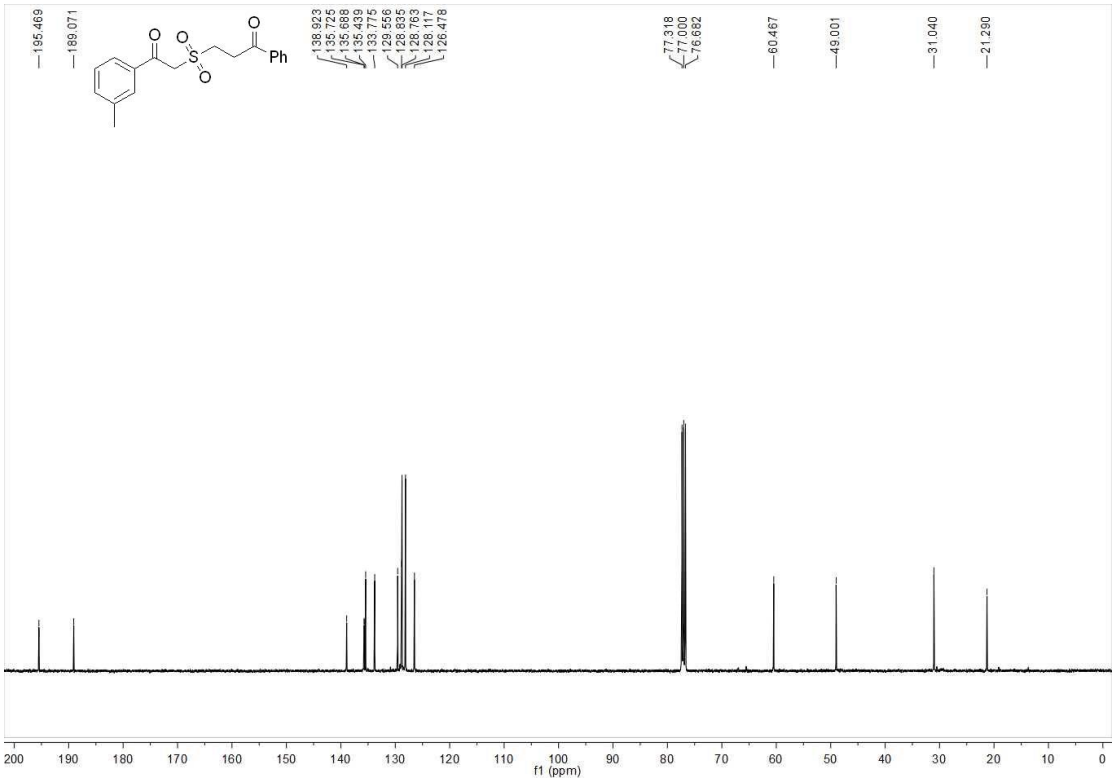


3-((2-Oxo-2-(*m*-tolyl)ethyl)sulfonyl)-1-phenylpropan-1-one (4h)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4h**

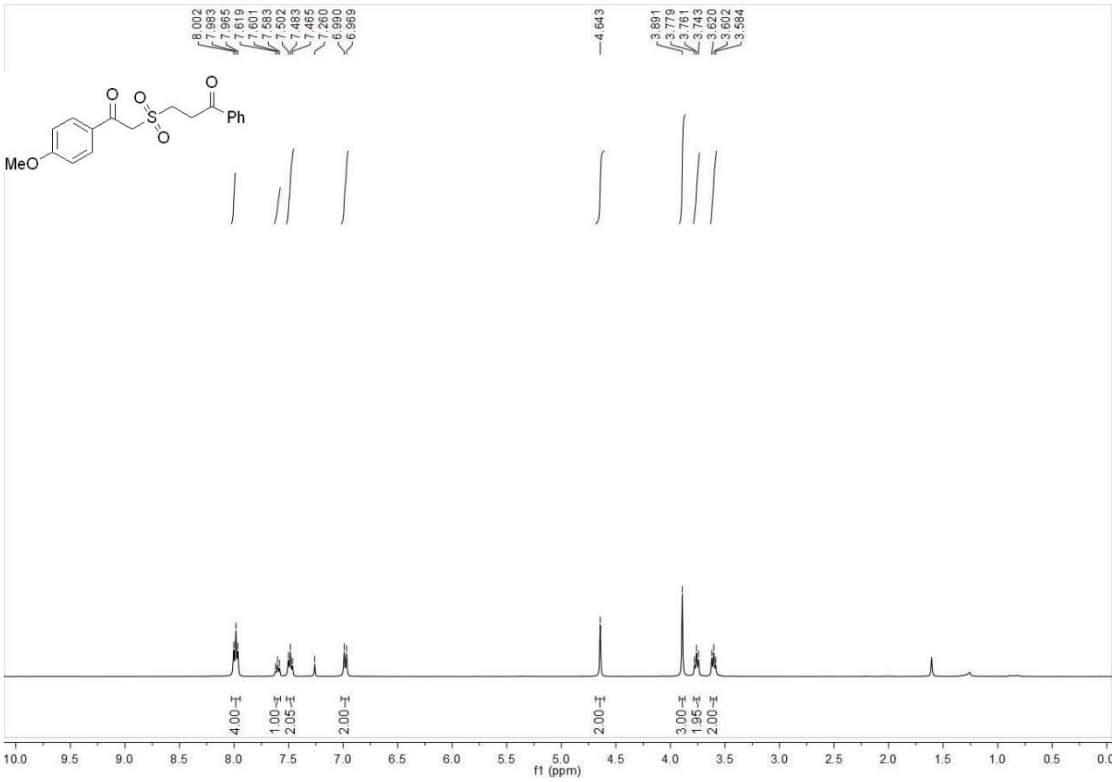


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4h**

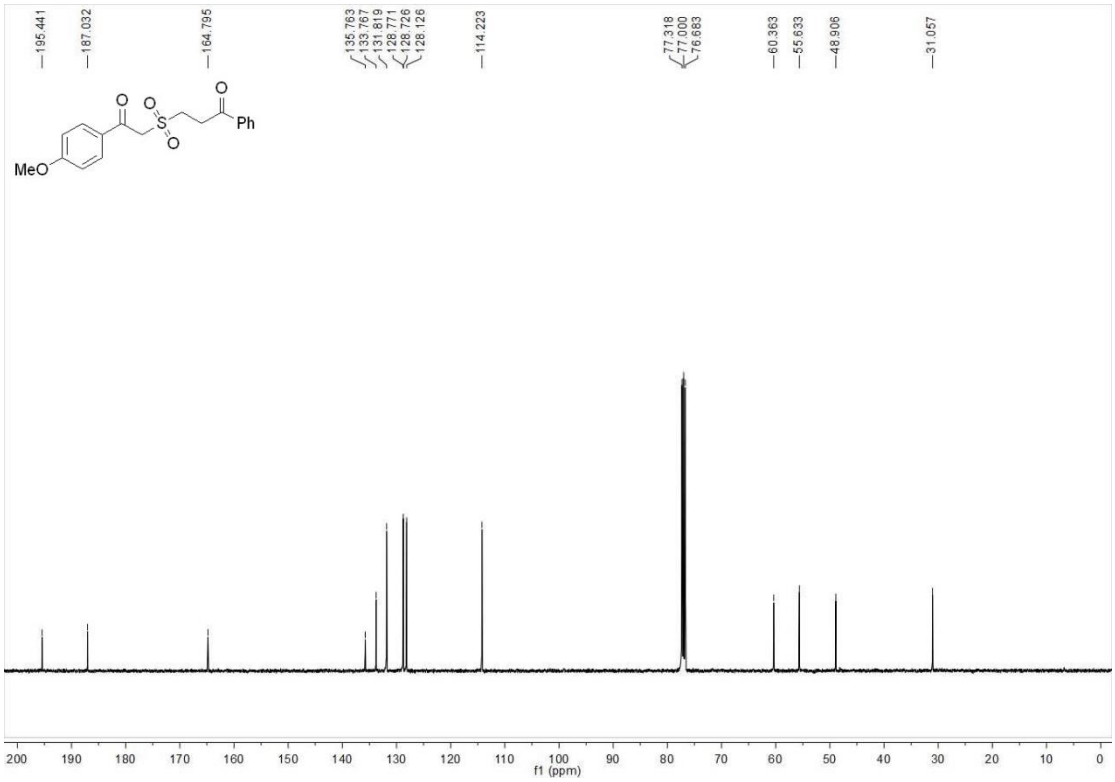


3-((2-(4-Methoxyphenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4i)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4i**

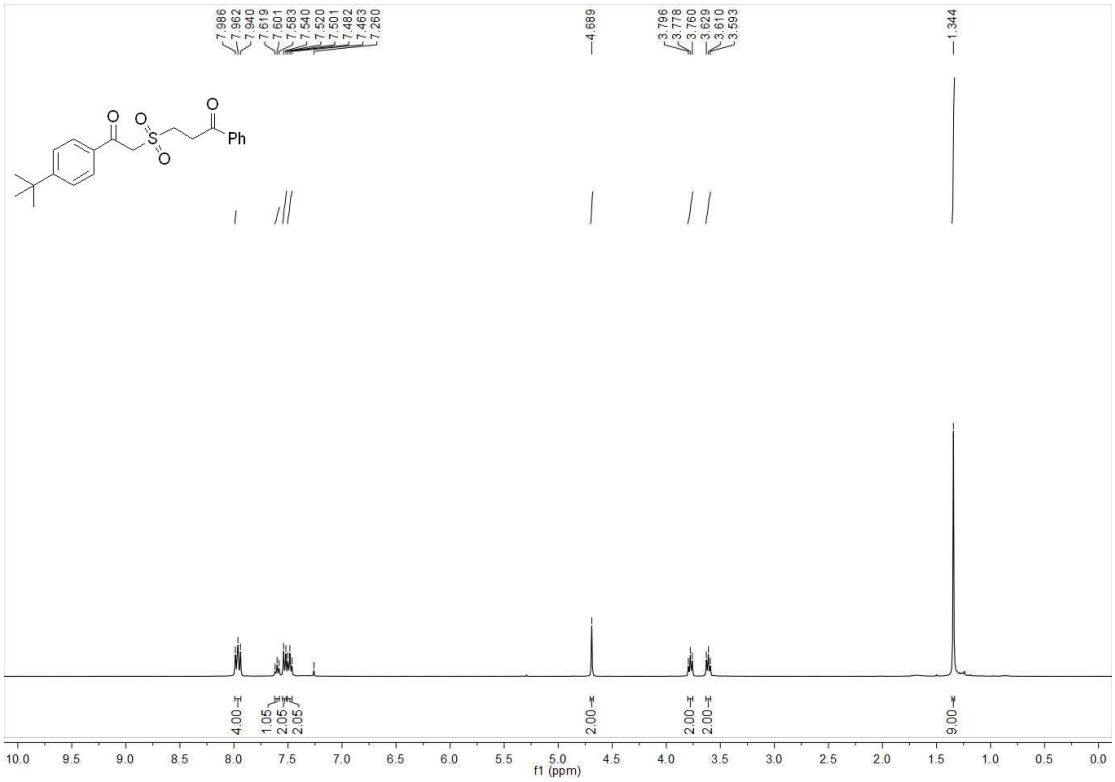


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4i**

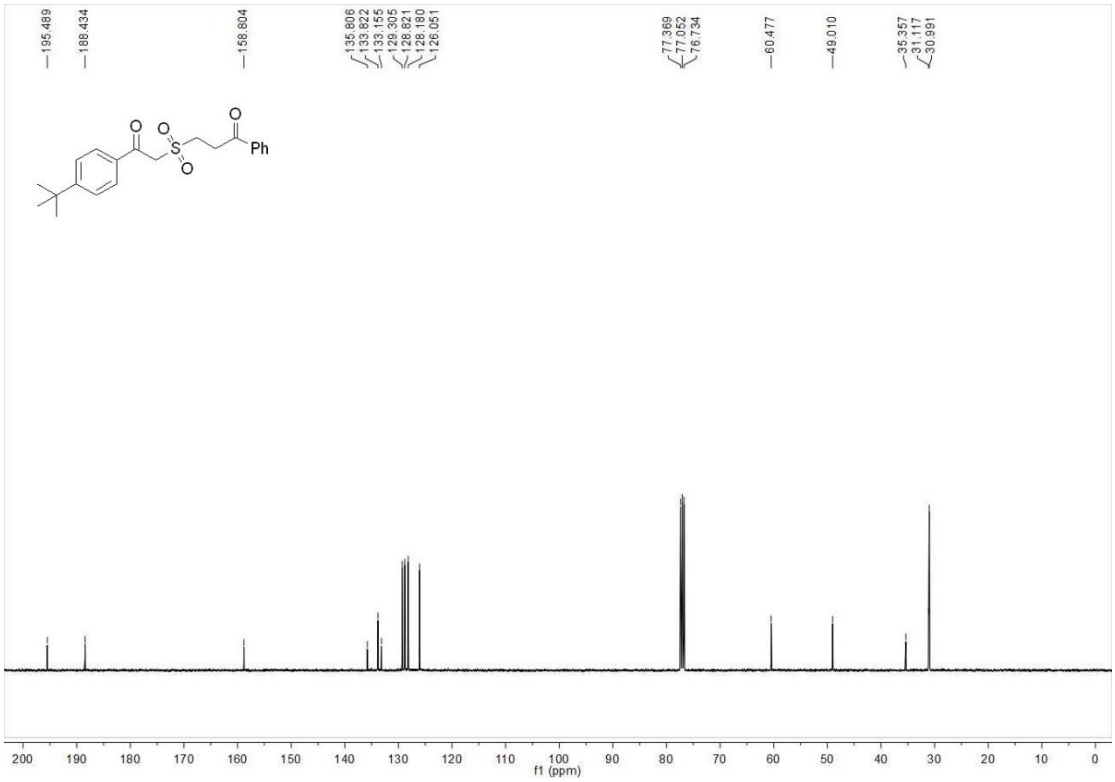


3-((2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4j)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4j**

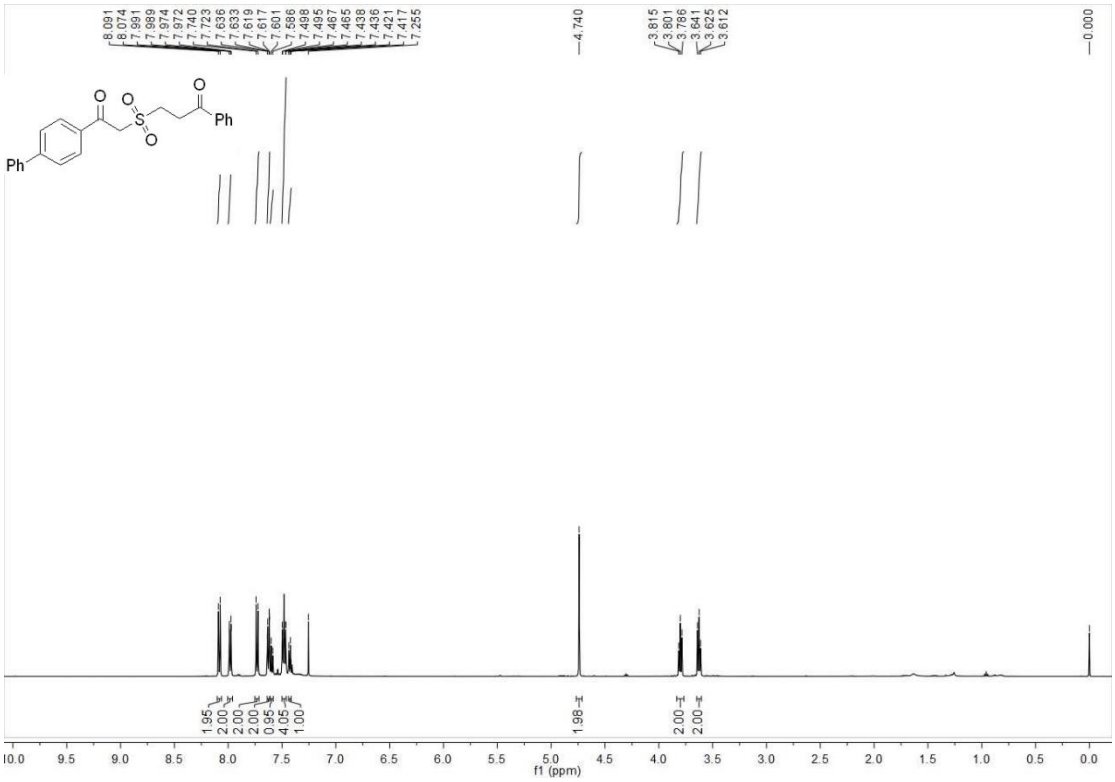


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4j**

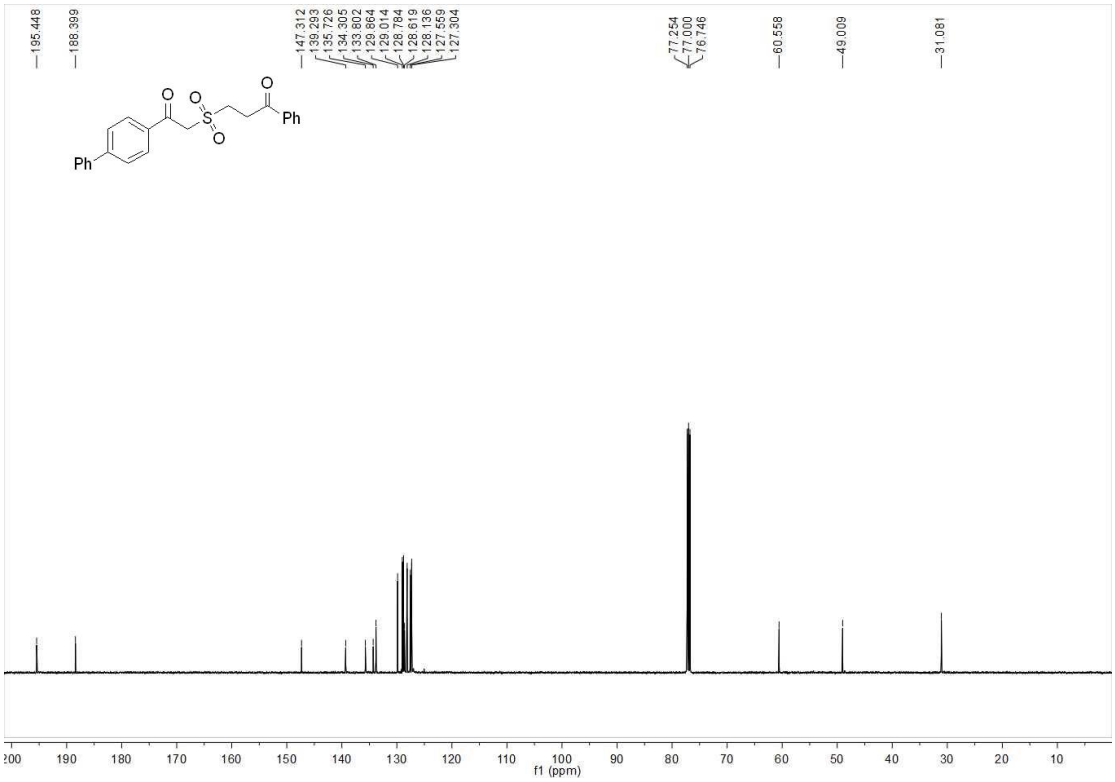


3-((2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4k)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4k**

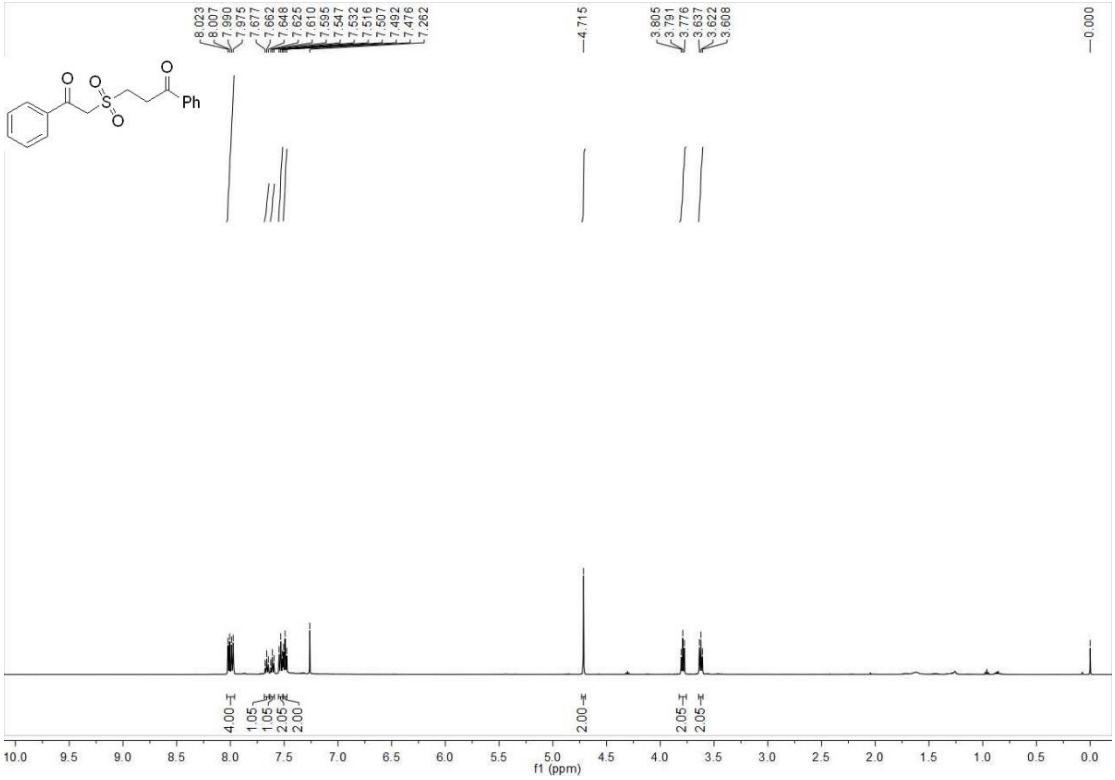


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4k**

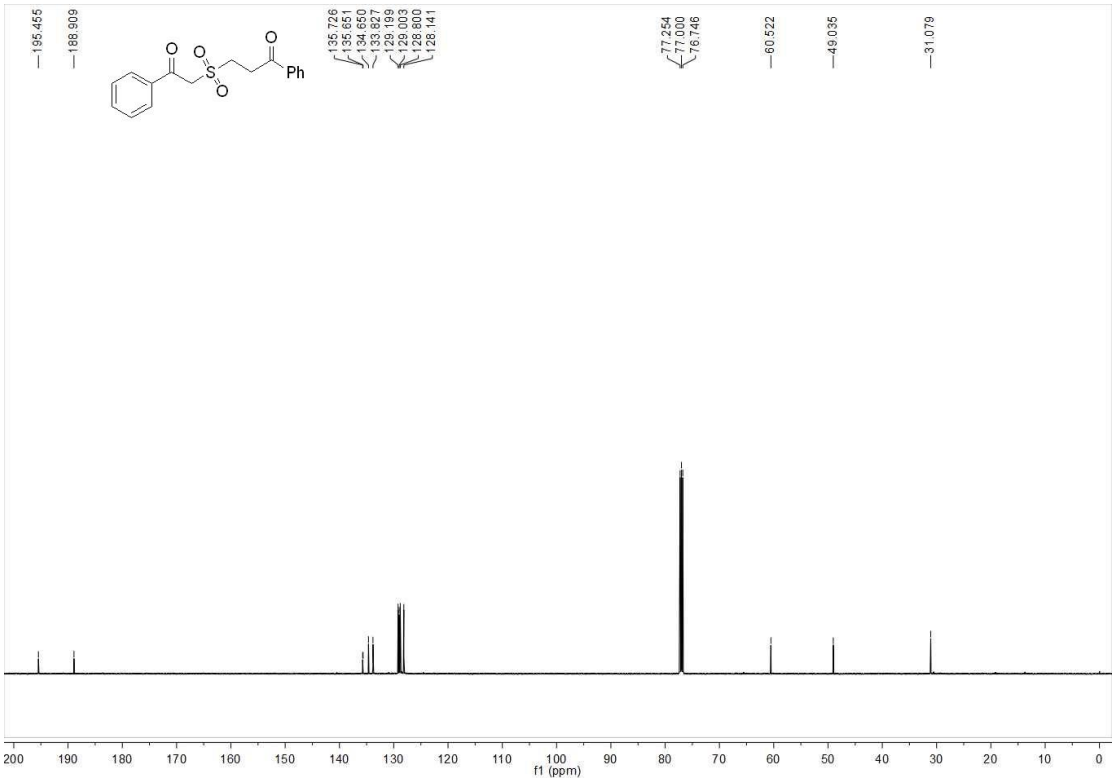


3-((2-Oxo-2-phenylethyl)sulfonyl)-1-phenylpropan-1-one (4l)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4l**

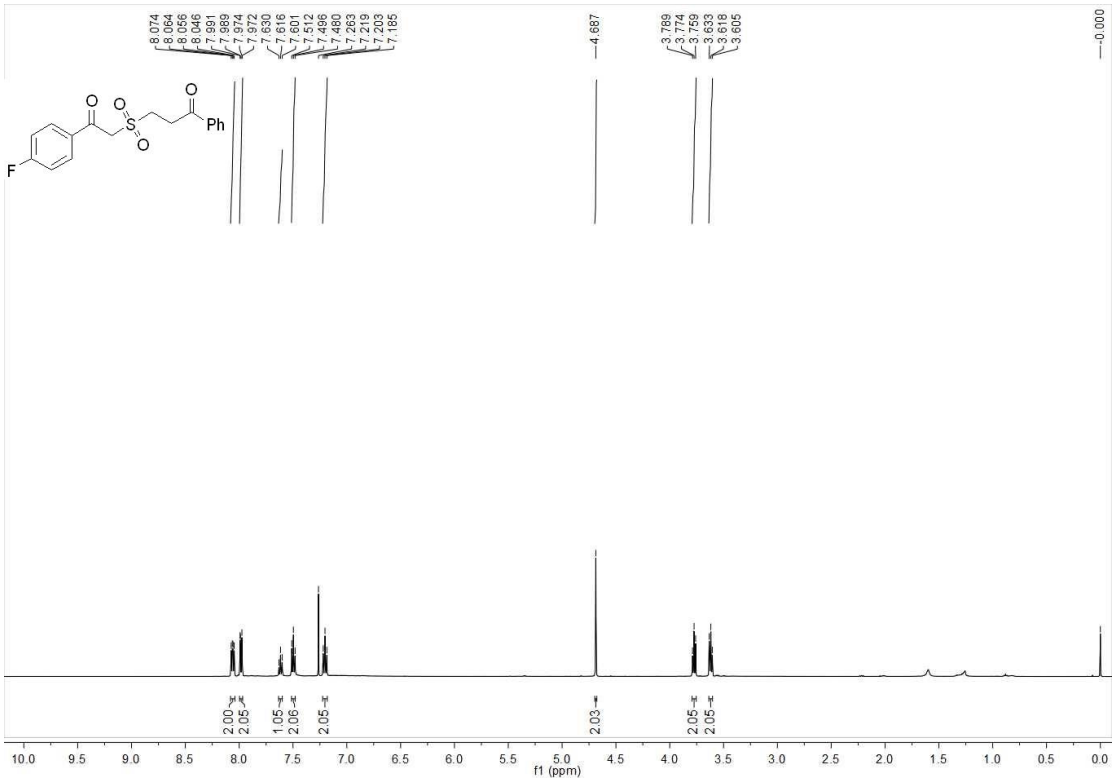


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4l**

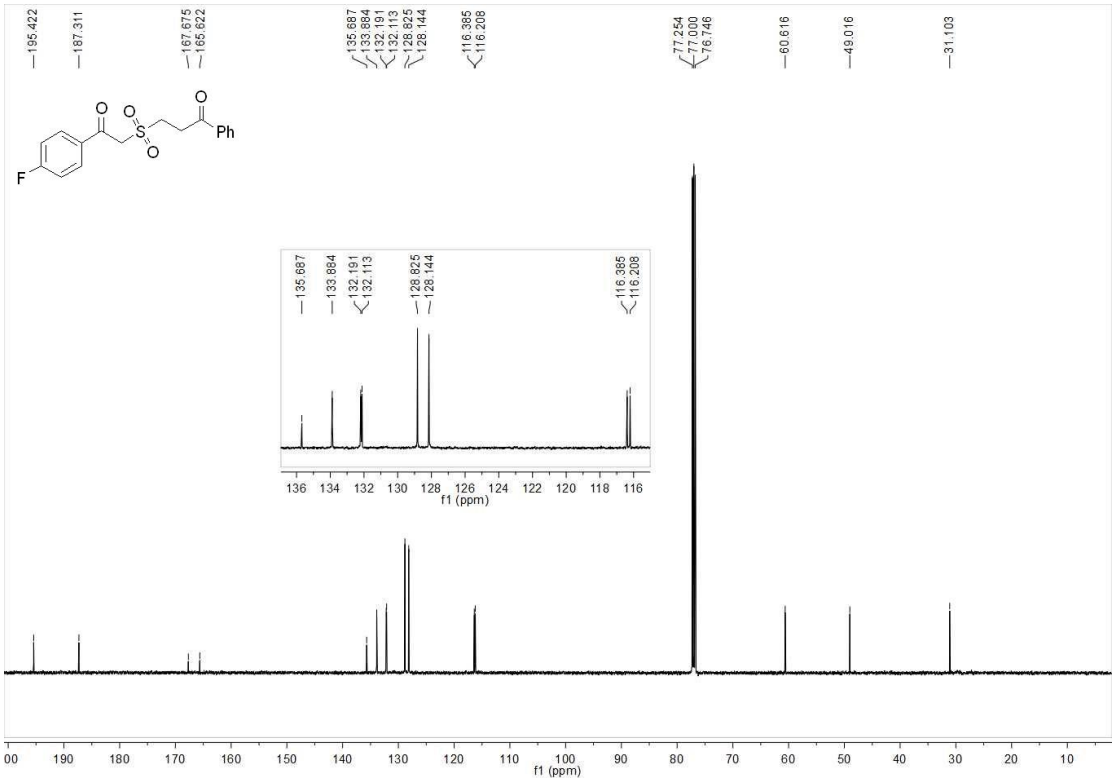


3-((2-(4-Fluorophenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4m)

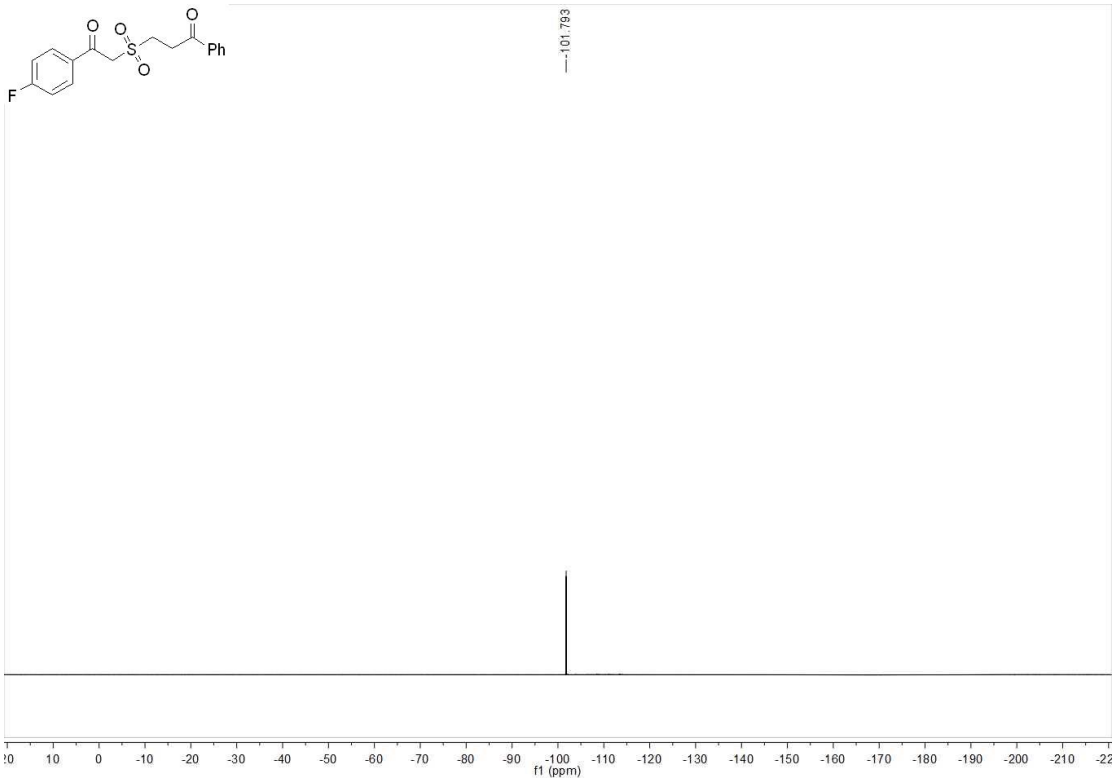
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4m**



^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4m**

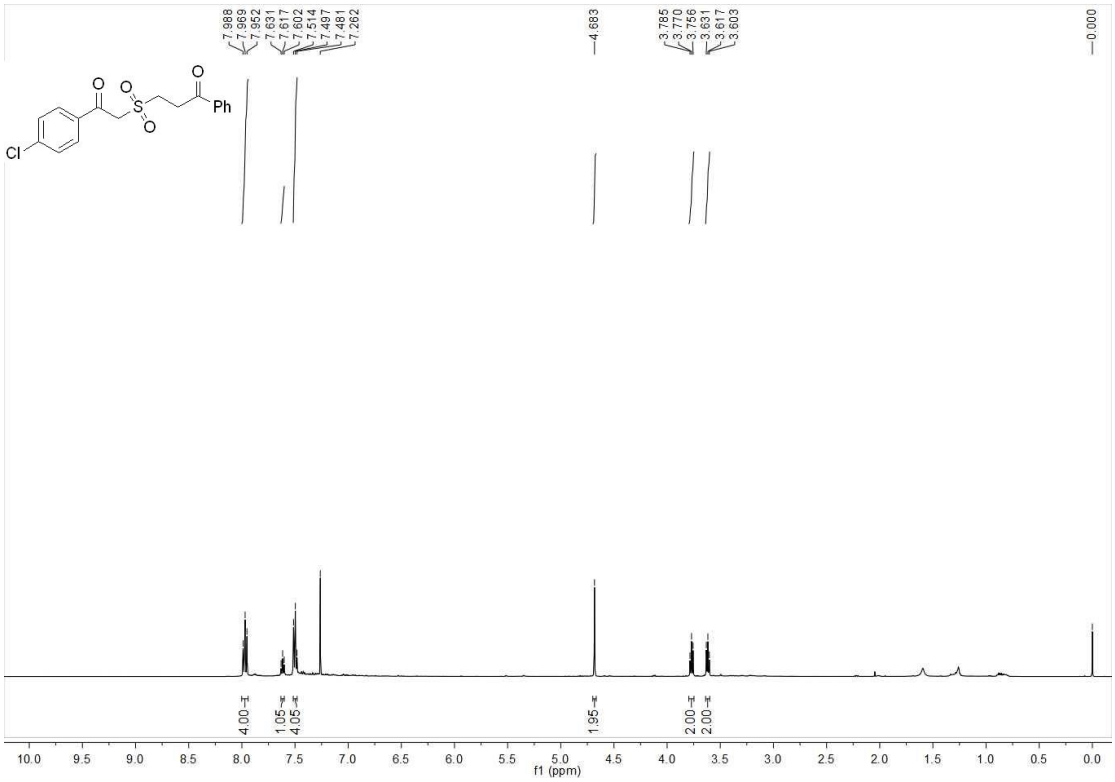


^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **4m**

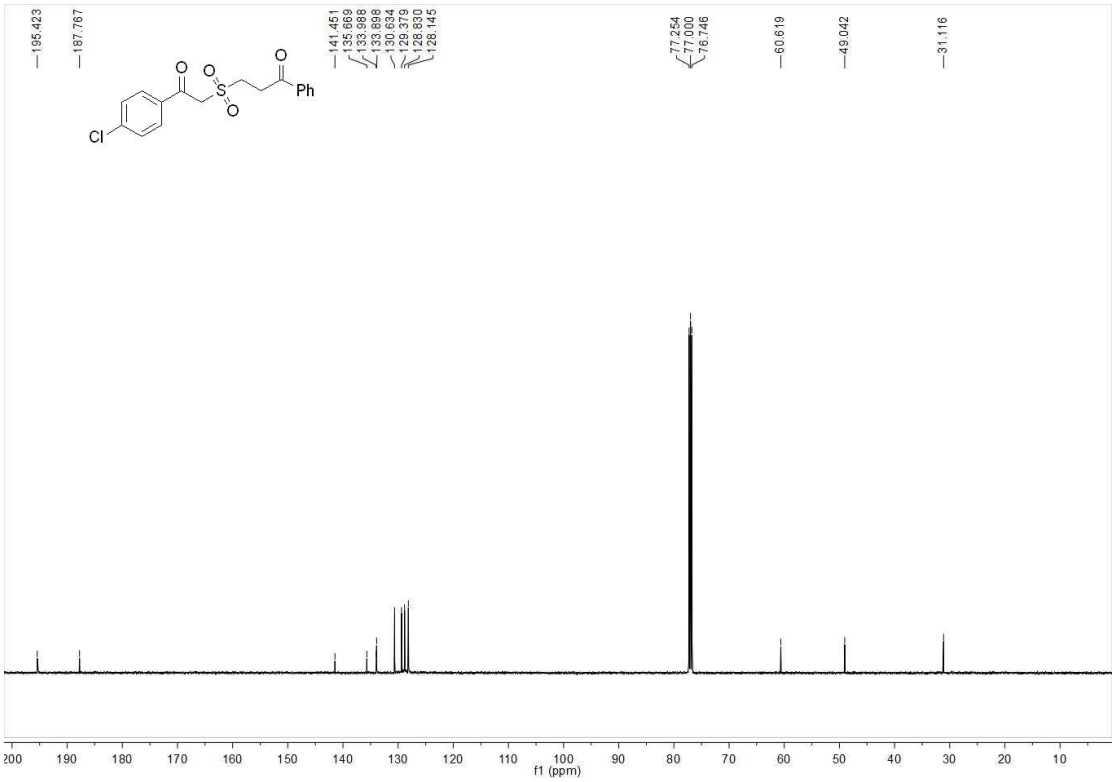


3-((2-(4-Chlorophenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4n)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4n**

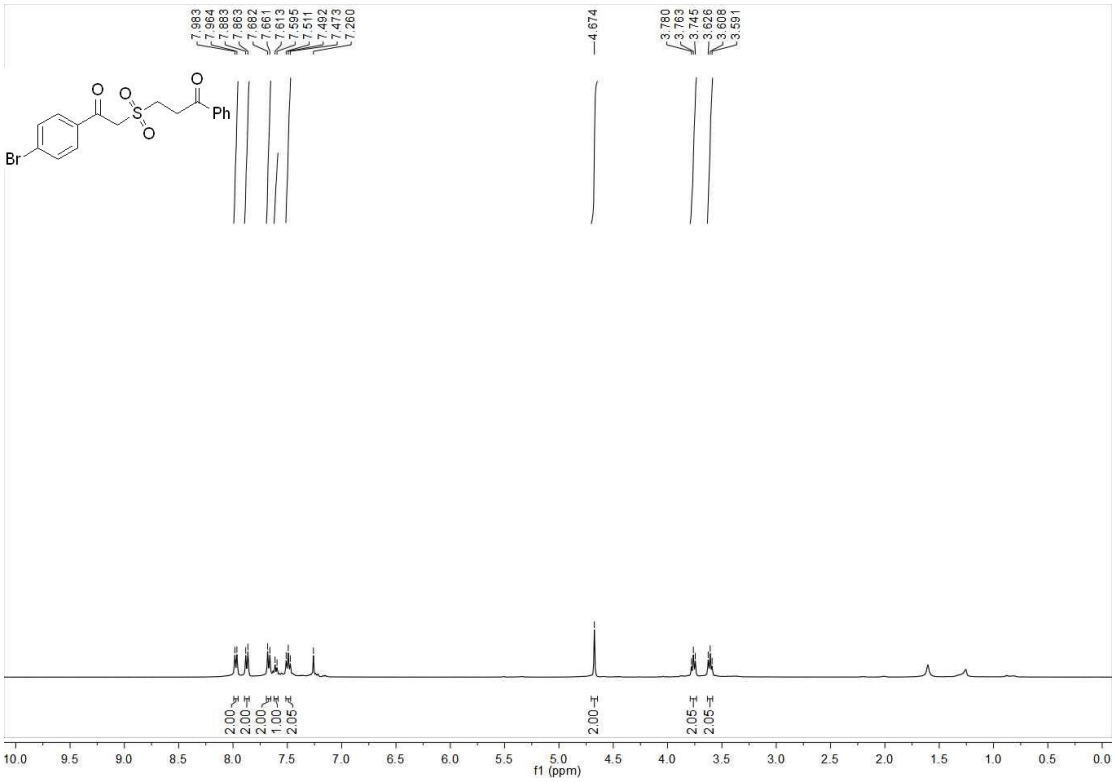


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4n**

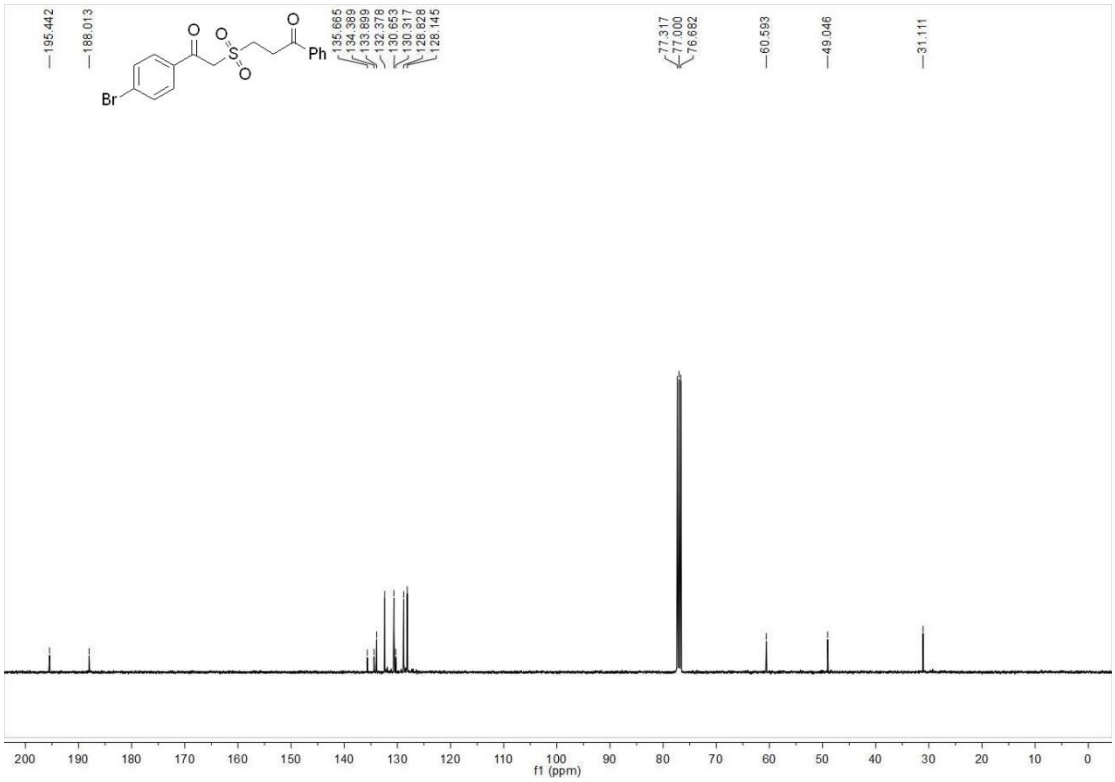


3-((2-(4-Bromophenyl)-2-oxoethyl)sulfonyl)-1-phenylpropan-1-one (4o)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4o**

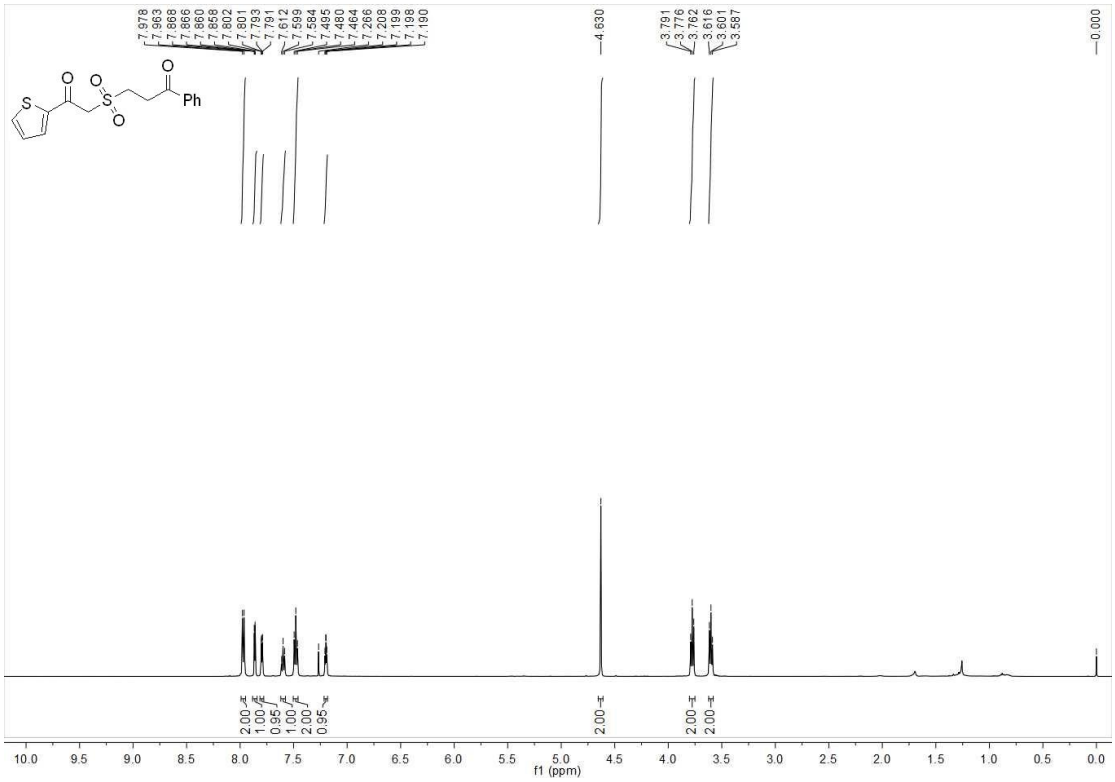


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4o**

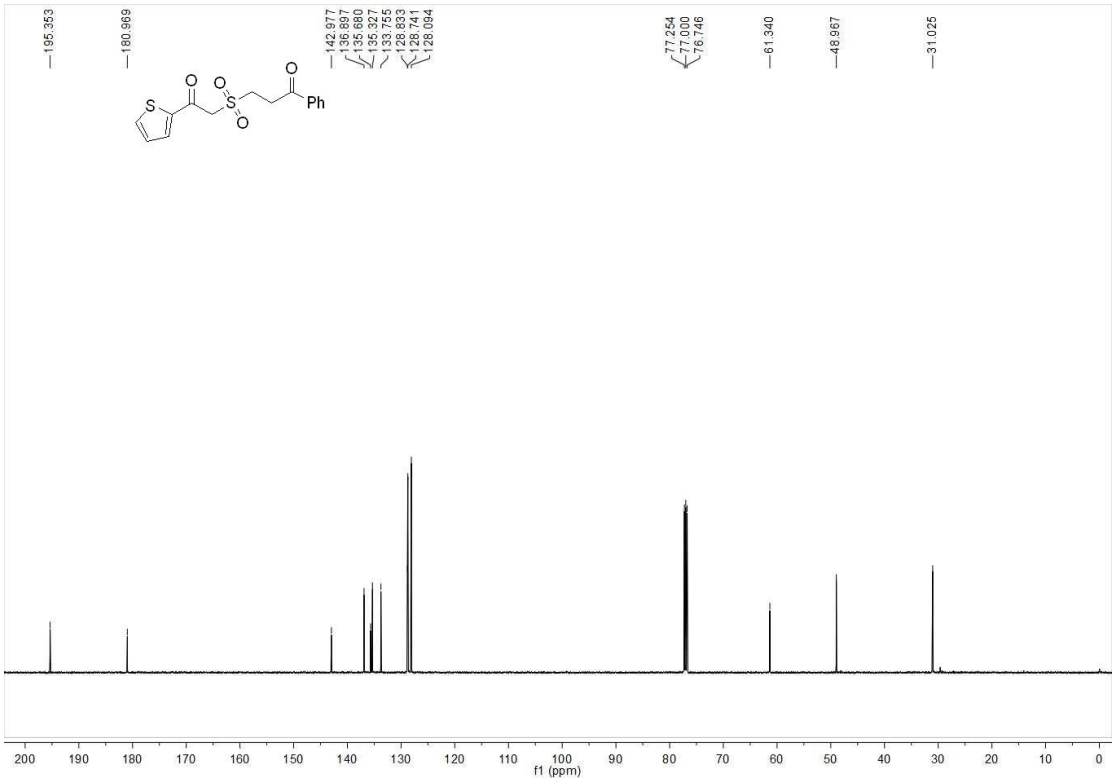


3-((2-Oxo-2-(thiophen-2-yl)ethyl)sulfonyl)-1-phenylpropan-1-one (4p)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4p**

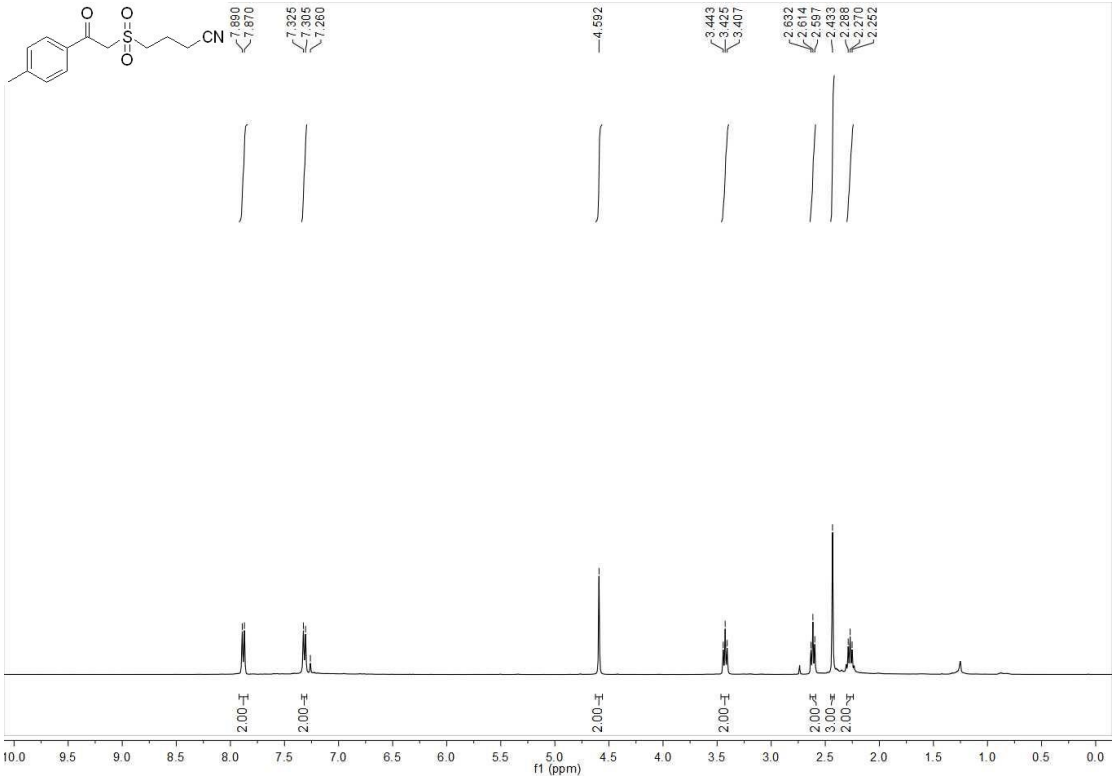


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4p**

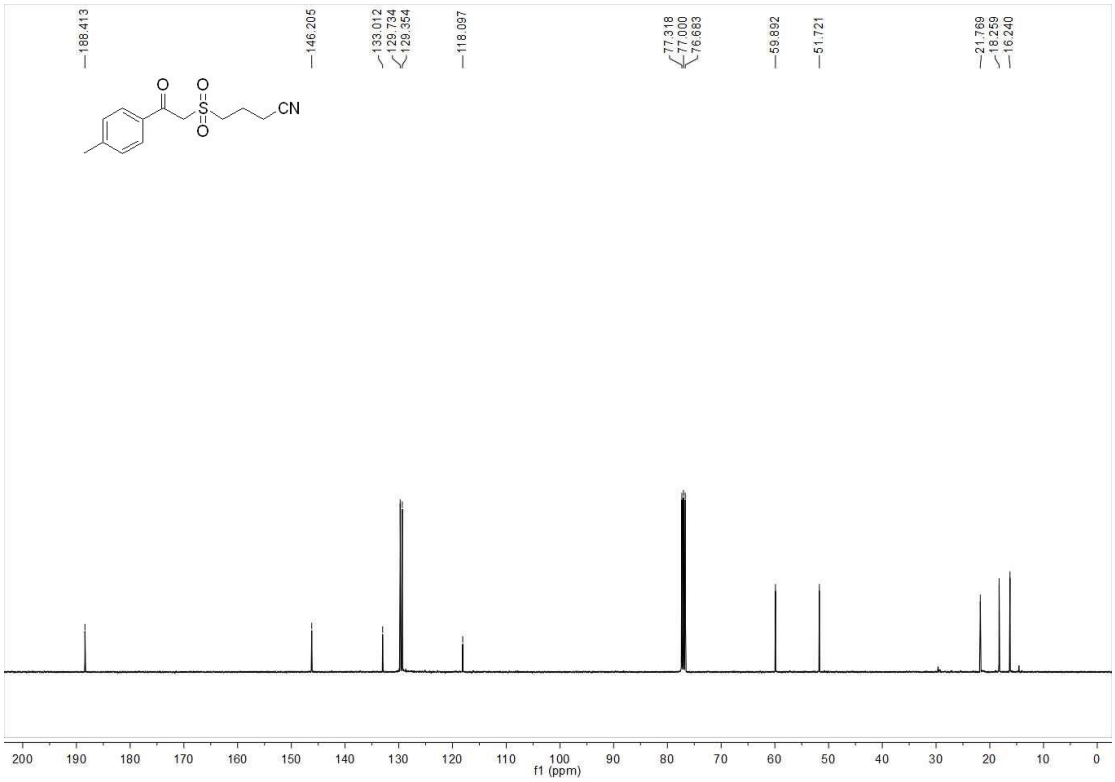


4-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile (6a)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6a**

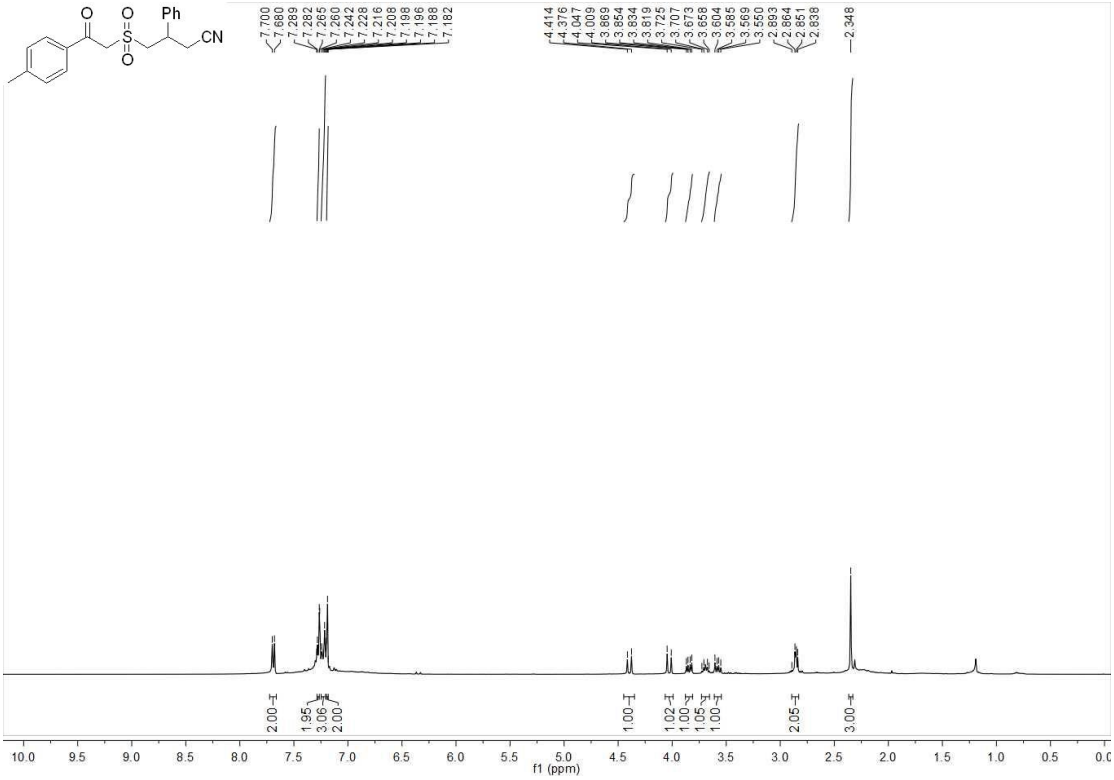


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6a**

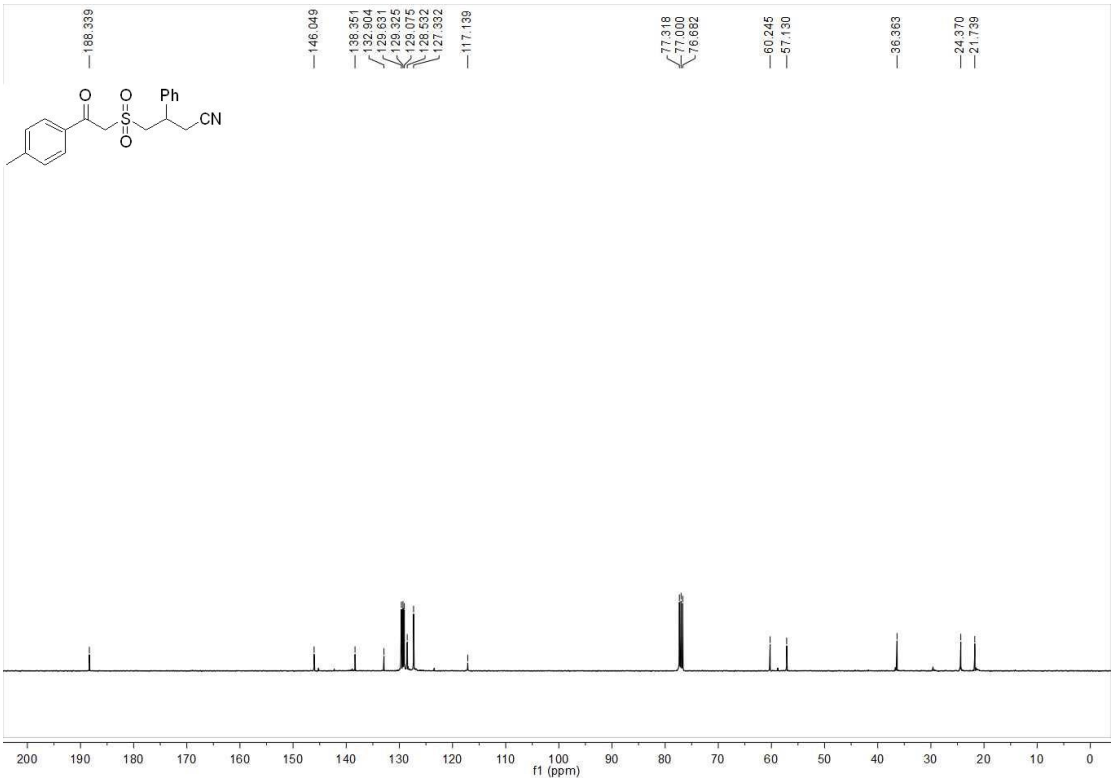


4-((2-Oxo-2-(*p*-tolyl)ethyl)sulfonyl)-3-phenylbutanenitrile (6b)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6b**

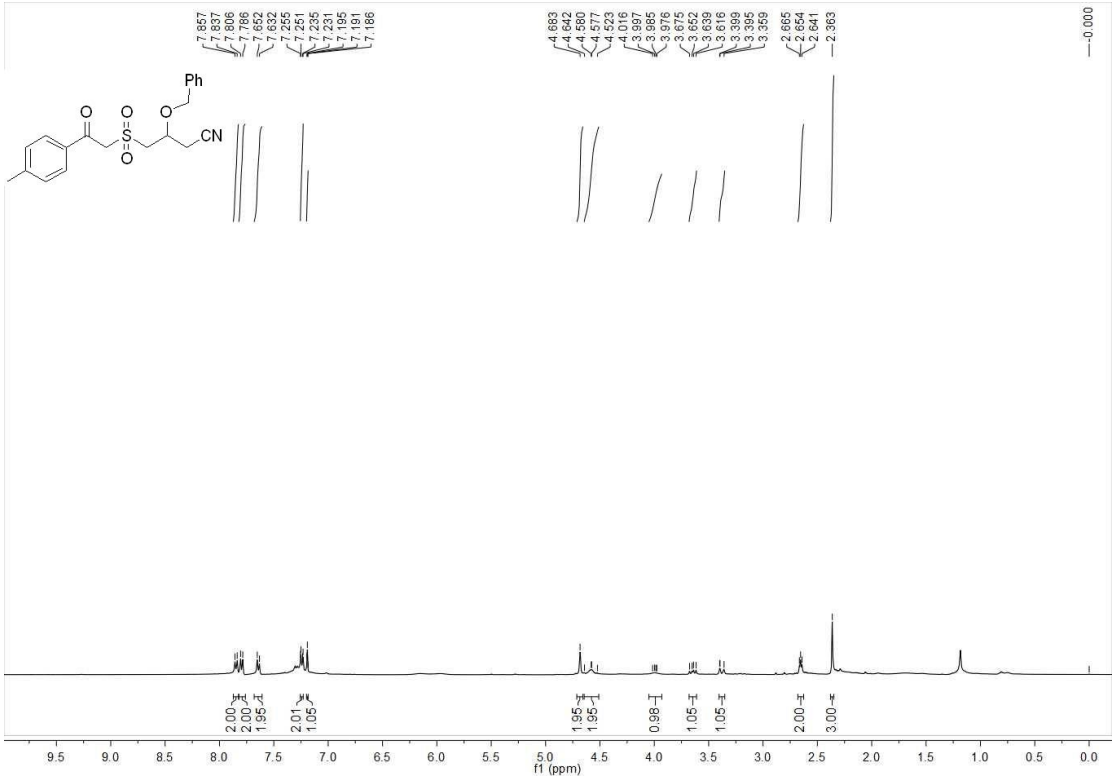


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6b**

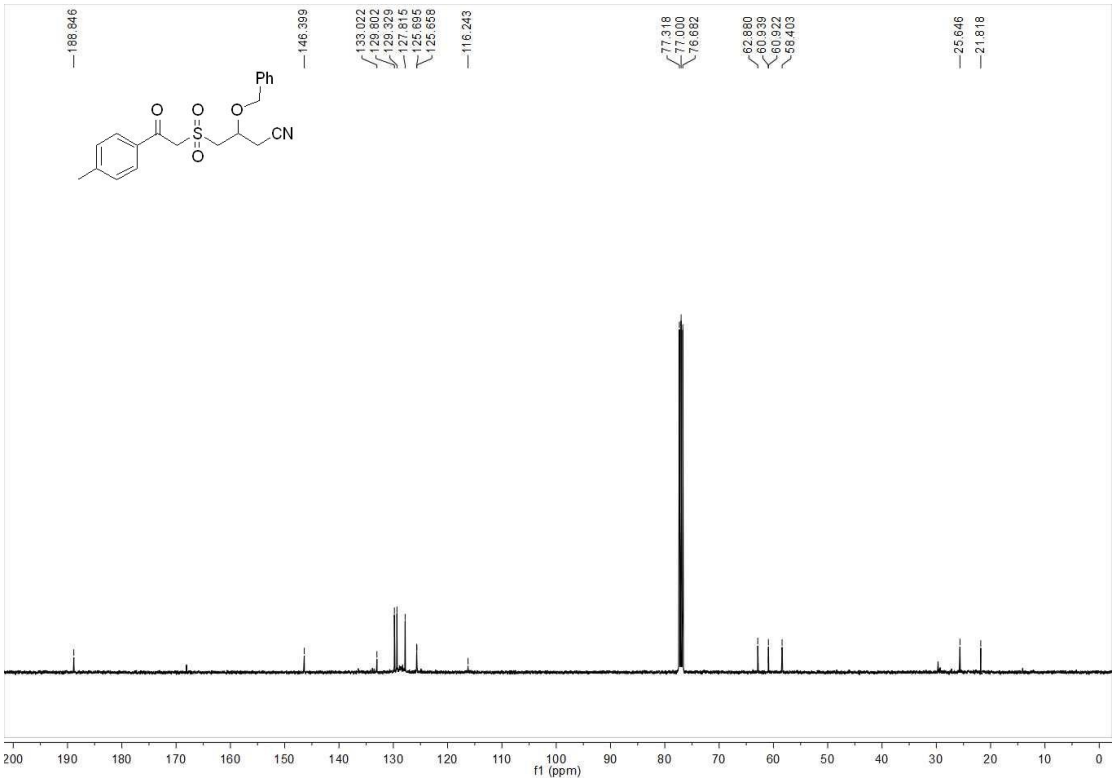


3-(Benzyloxy)-4-((2-oxo-2-(*p*-tolyl)ethyl)sulfonyl)butanenitrile (6c)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6c**

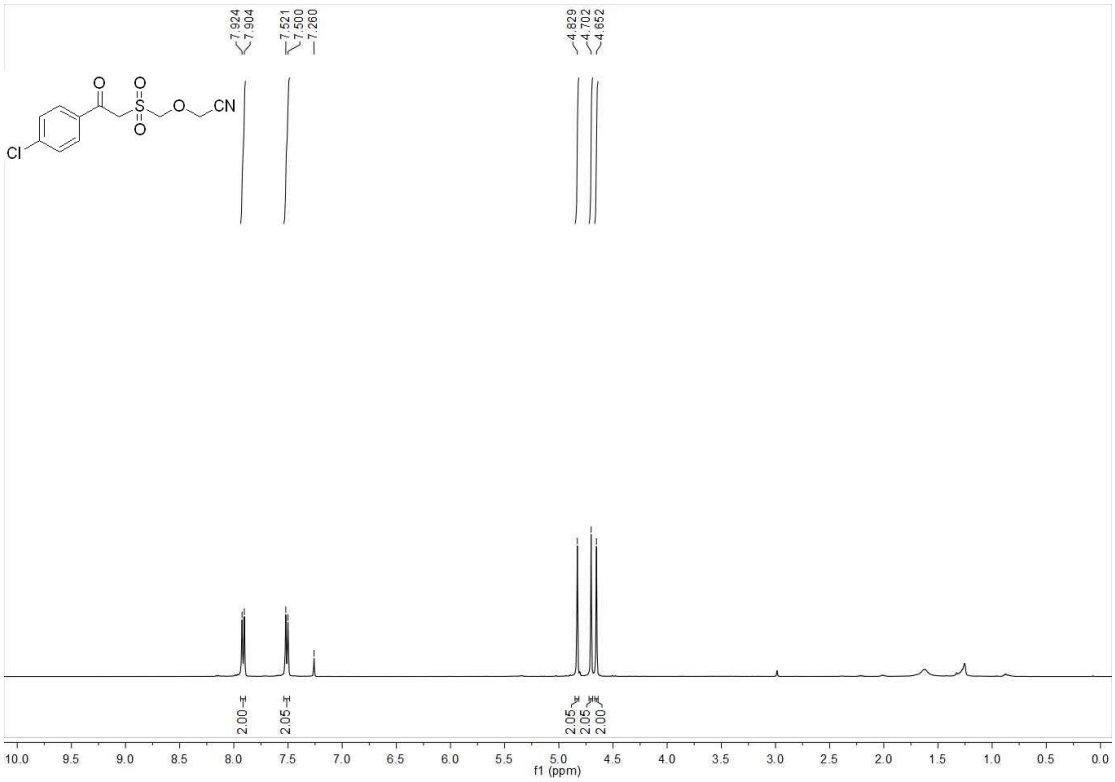


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6c**

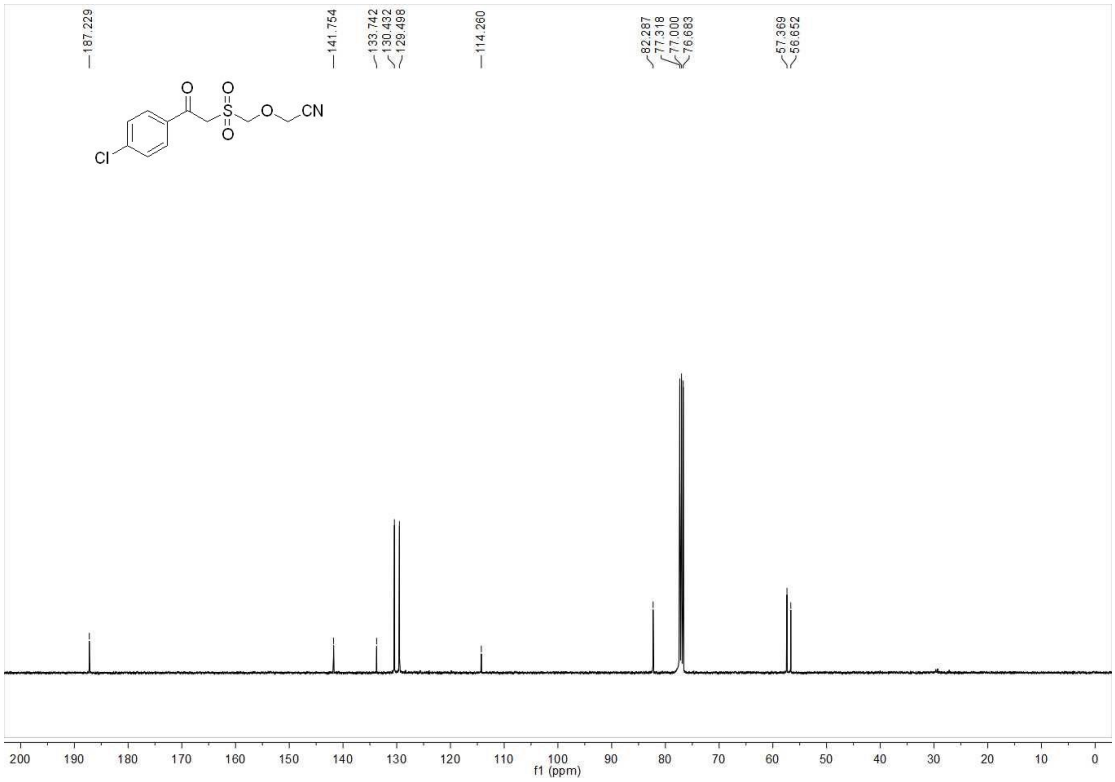


2-(((2-(4-Chlorophenyl)-2-oxoethyl)sulfonyl)methoxy)acetonitrile (6d)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6d**

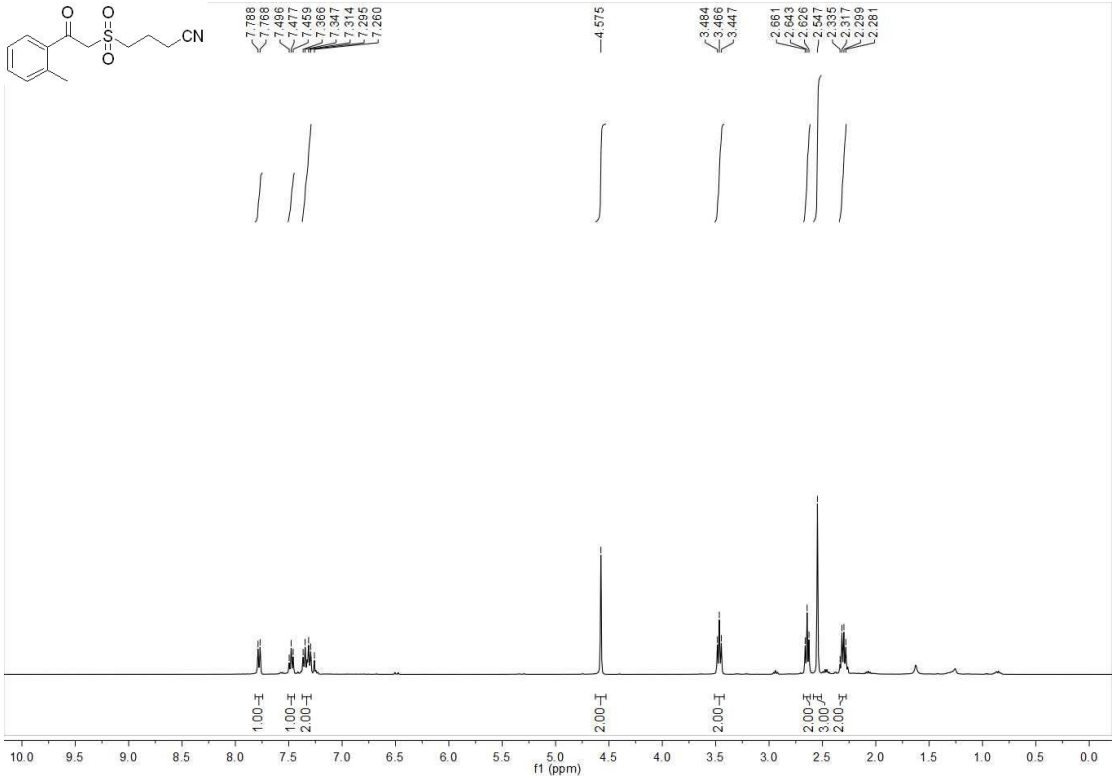


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6d**

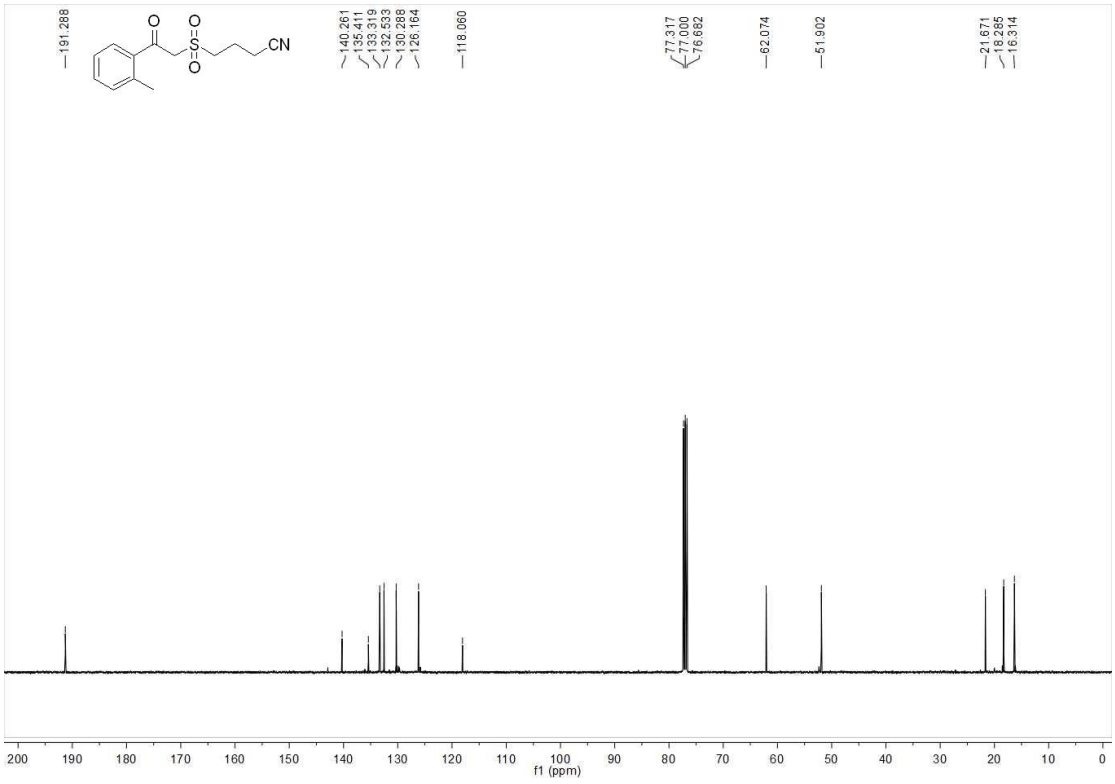


4-((2-Oxo-2-(*o*-tolyl)ethyl)sulfonyl)butanenitrile (6e)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6e**

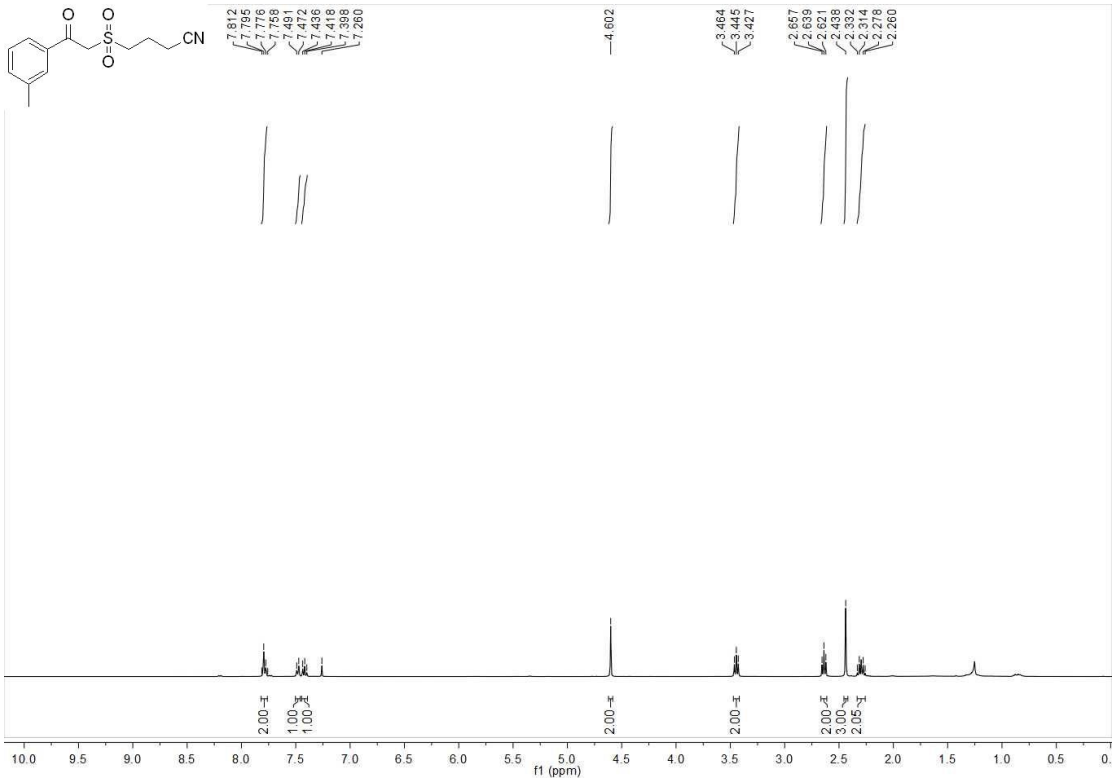


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6e**

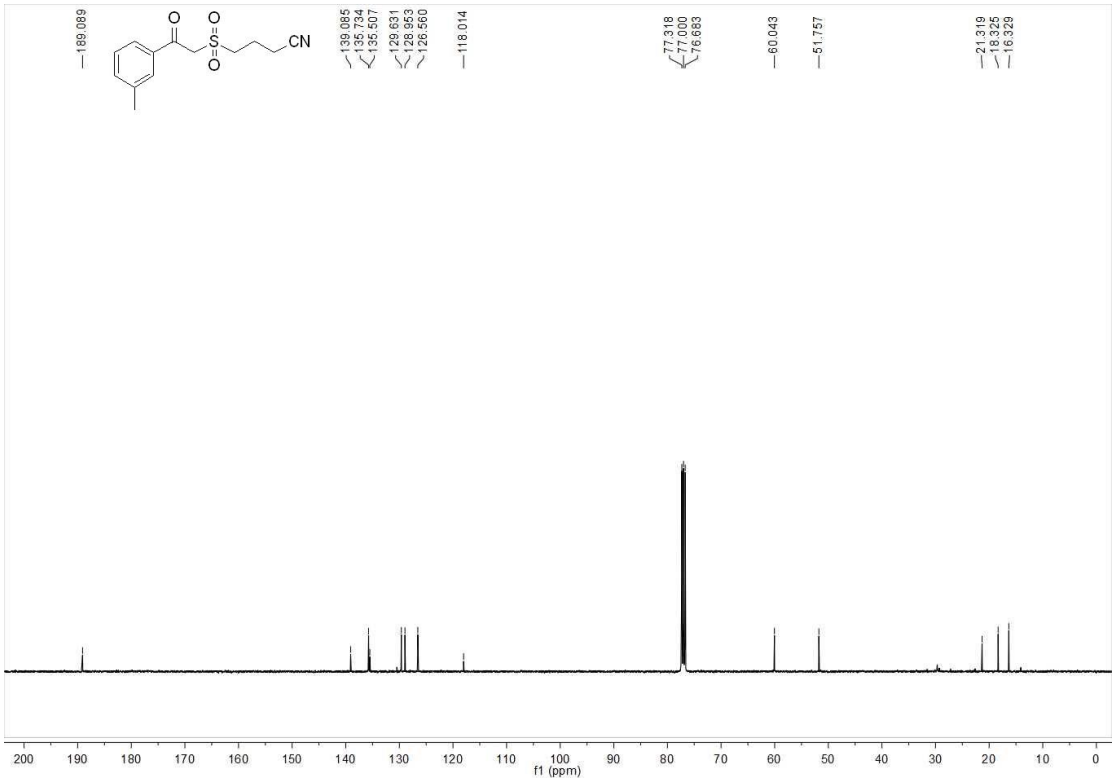


4-((2-Oxo-2-(*m*-tolyl)ethyl)sulfonyl)butanenitrile (6f)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6f**

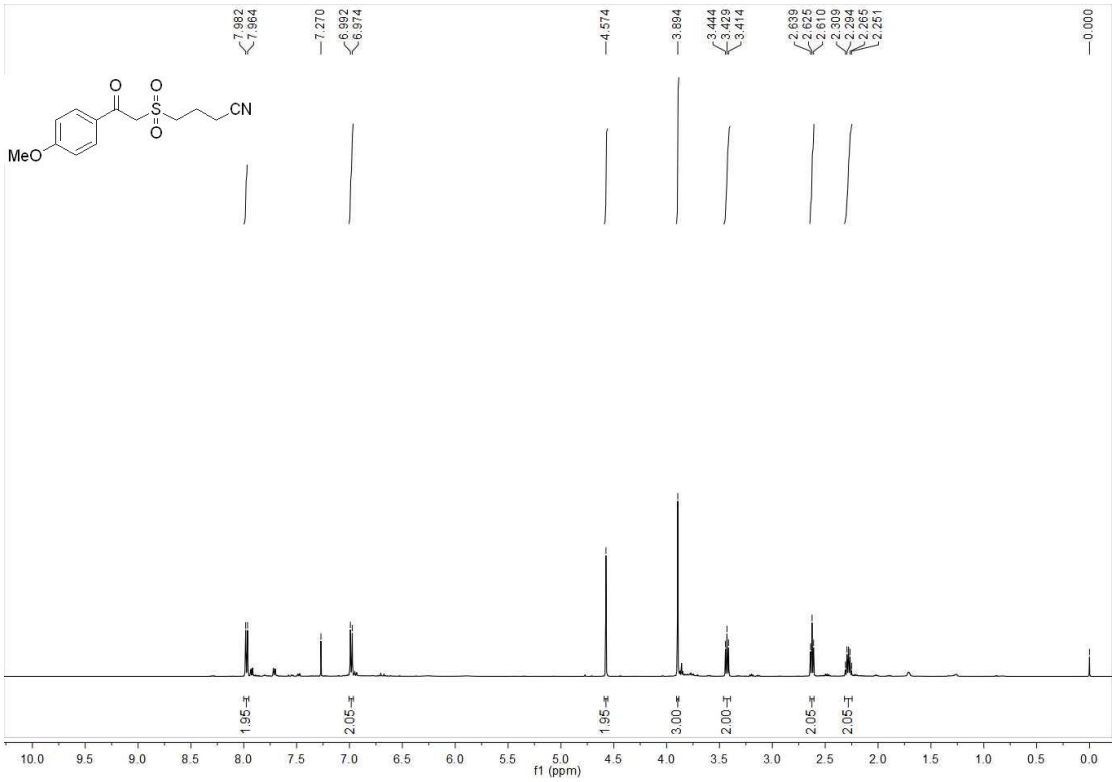


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6f**

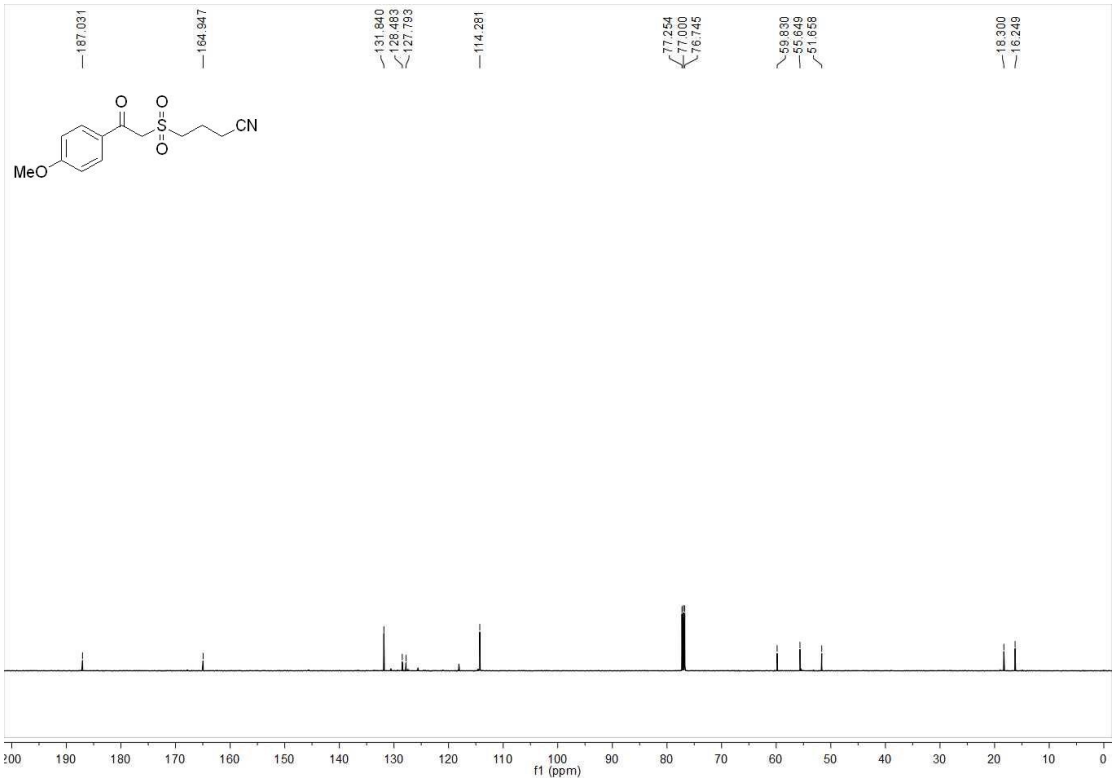


4-((2-(4-Methoxyphenyl)-2-oxoethyl)sulfonyl)butanenitrile (6g)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6g**

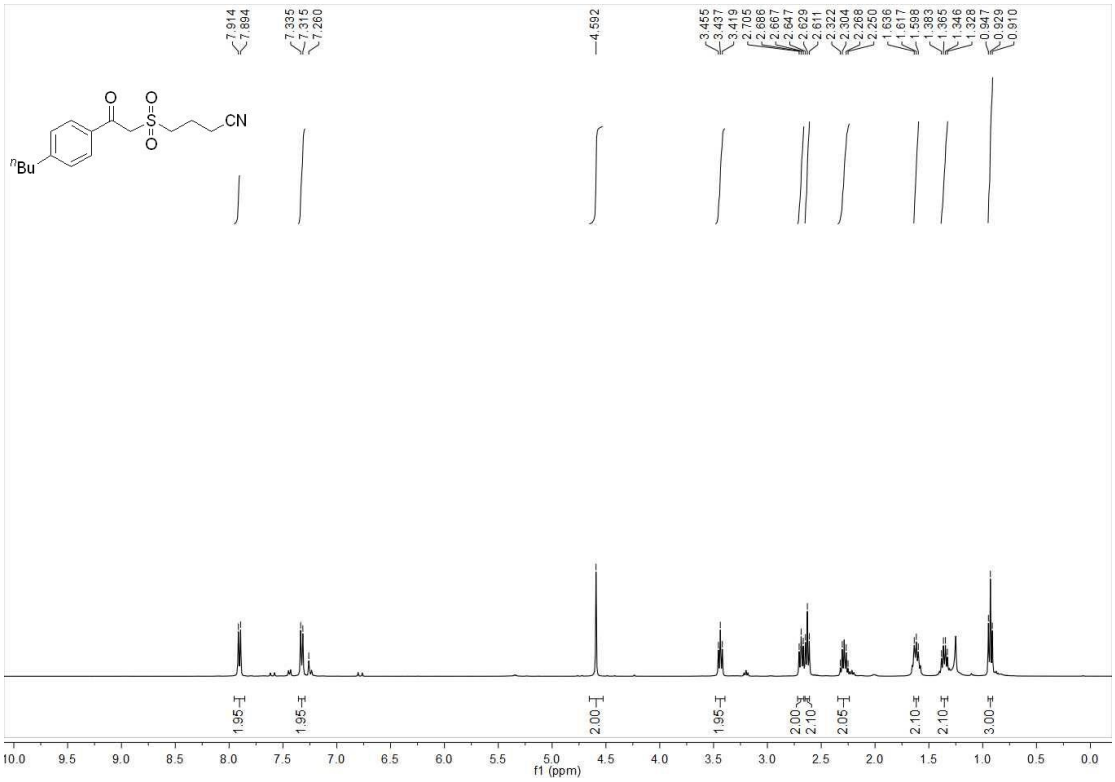


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **6g**

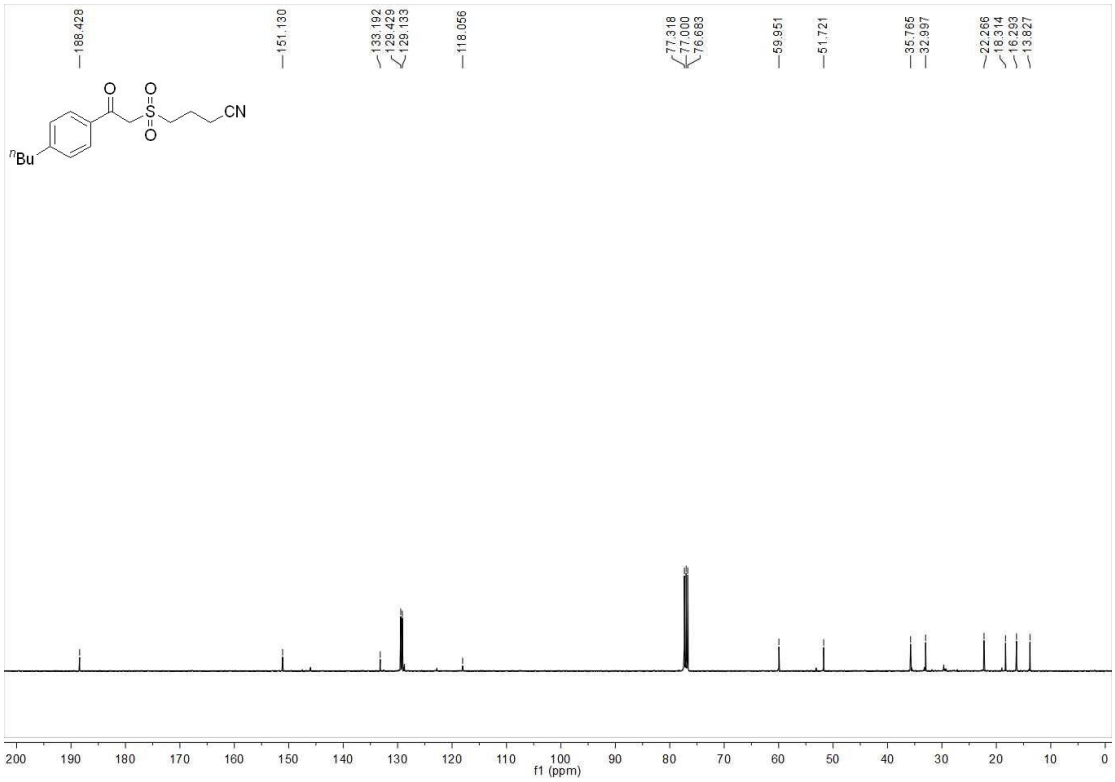


4-((2-(4-Butylphenyl)-2-oxoethyl)sulfonyl)butanenitrile (6h)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6h**

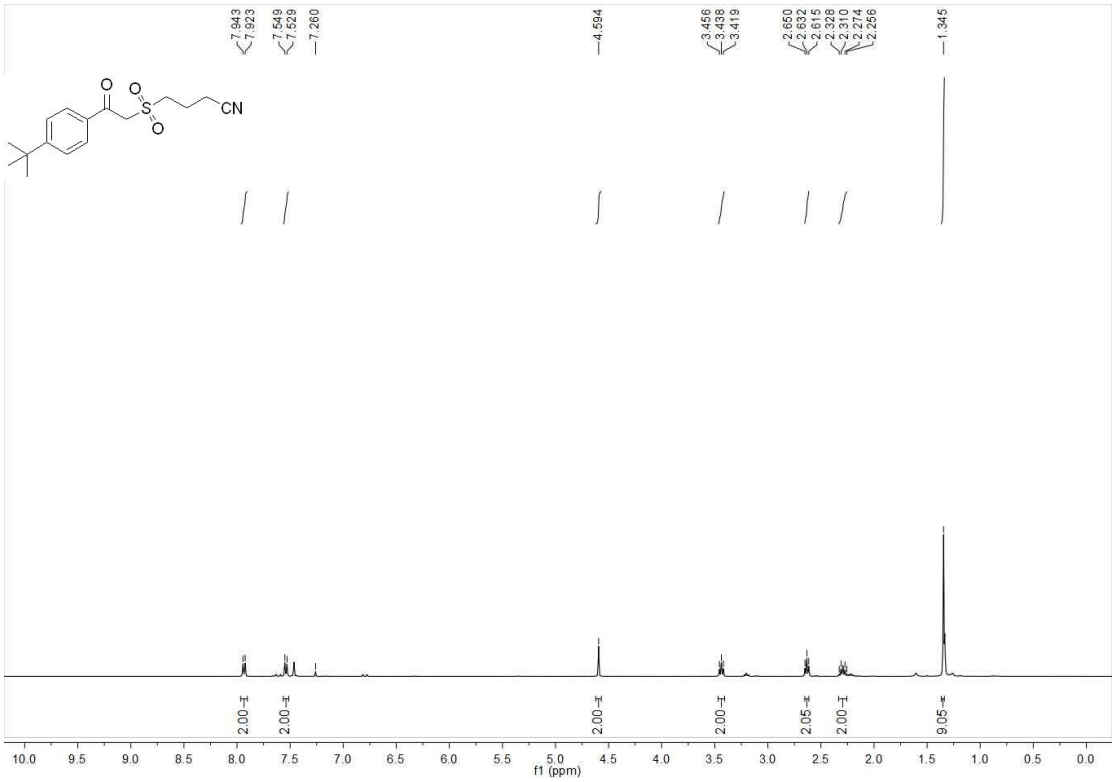


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6h**

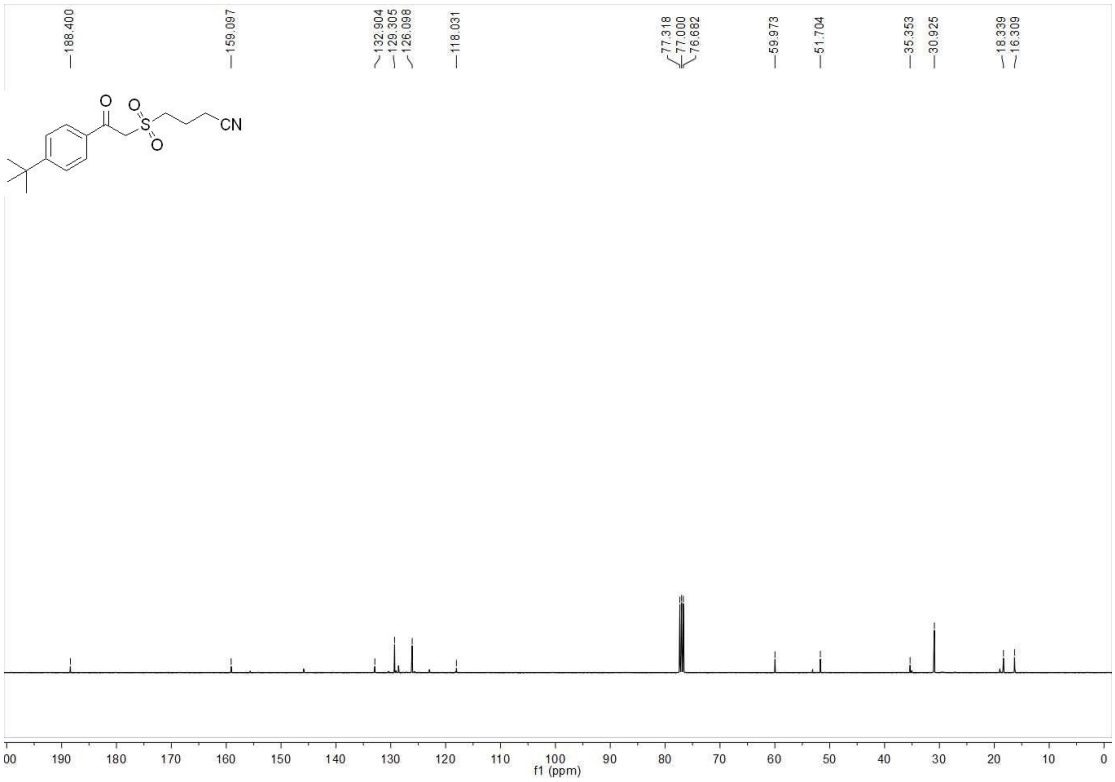


4-((2-(4-(*tert*-Butyl)phenyl)-2-oxoethyl)sulfonyl)butanenitrile (6i)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6i**

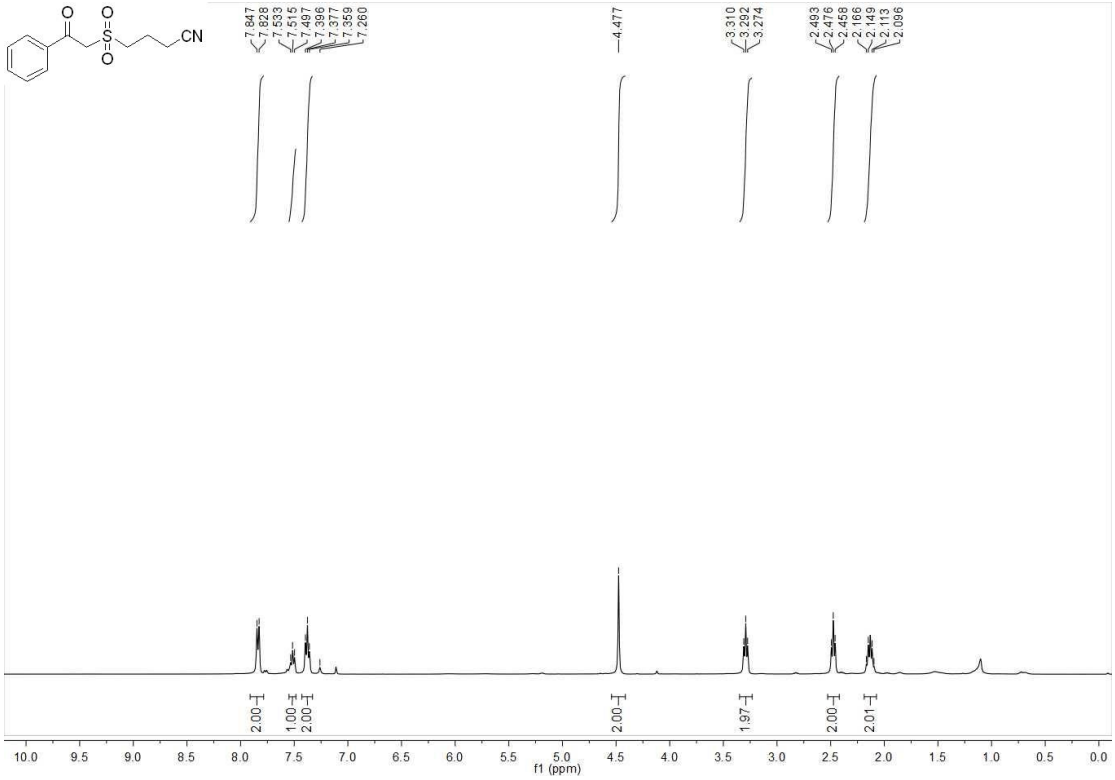


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6i**

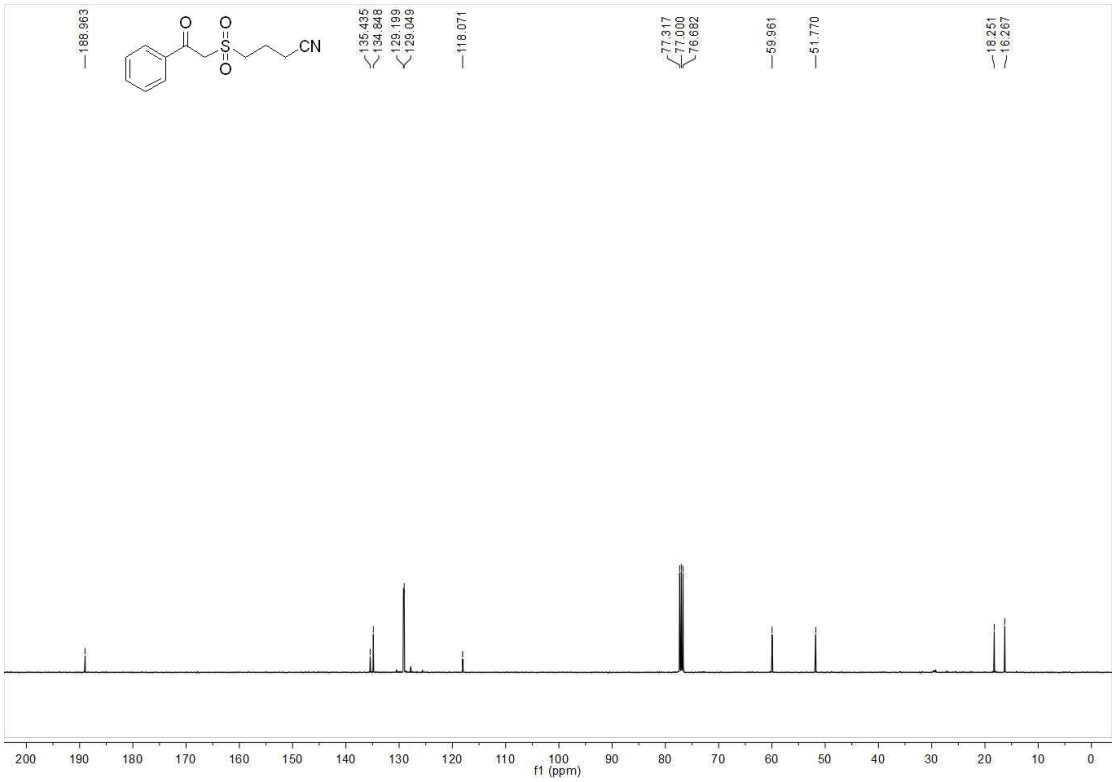


4-((2-Oxo-2-phenylethyl)sulfonyl)butanenitrile (6j)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6j**

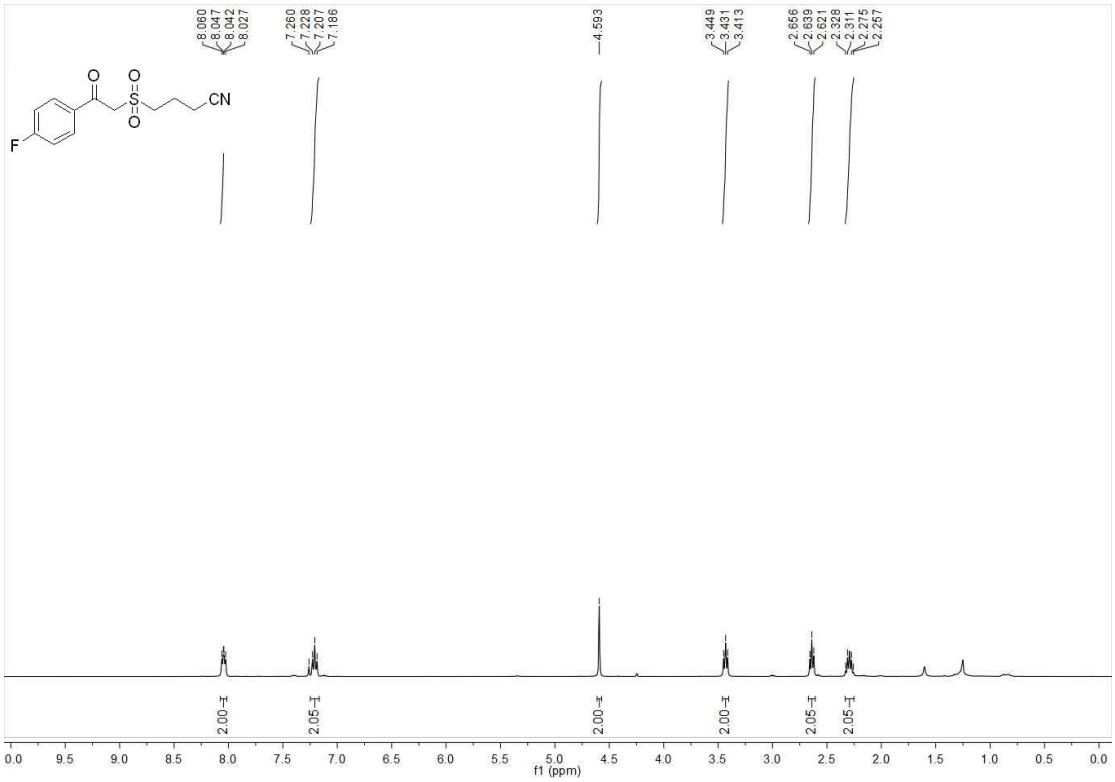


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6j**

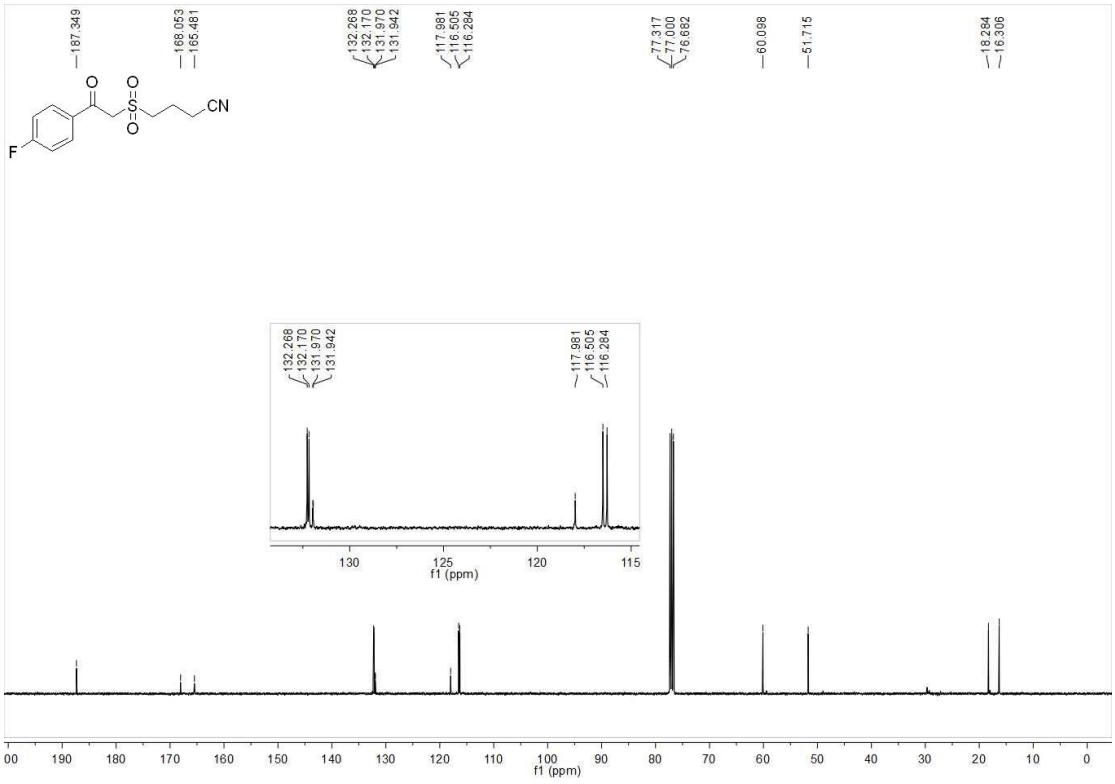


4-((2-(4-Fluorophenyl)-2-oxoethyl)sulfonyl)butanenitrile (6k)

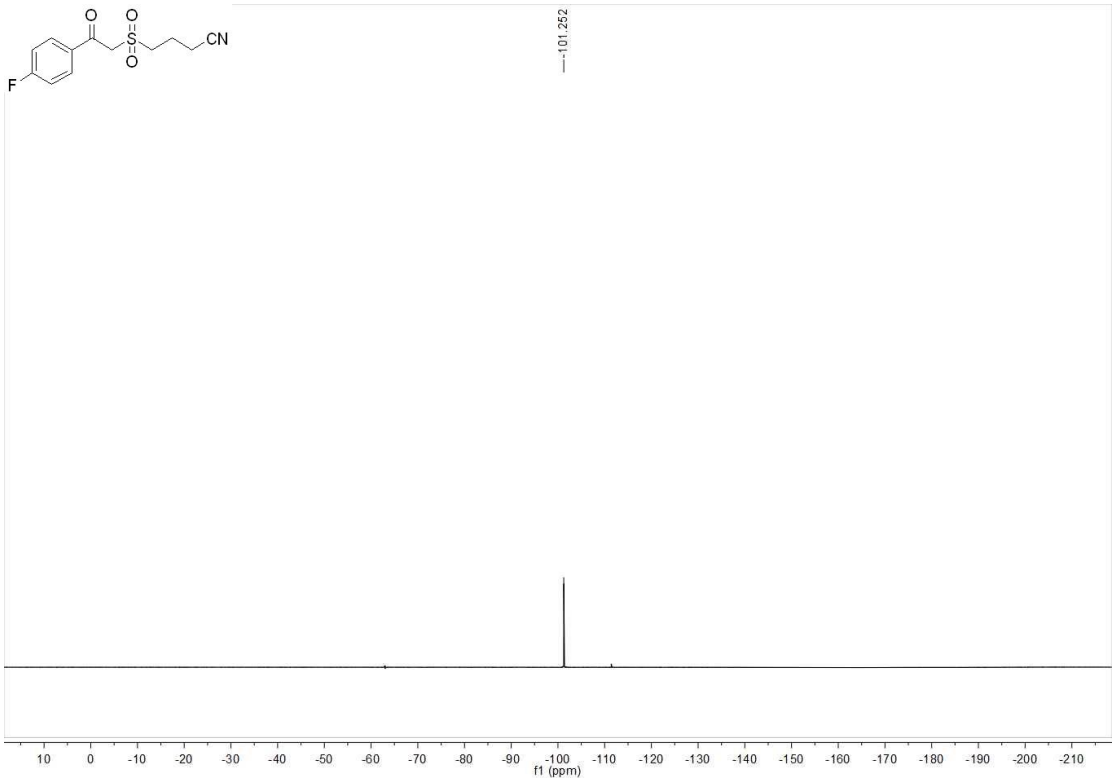
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6k**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6k**

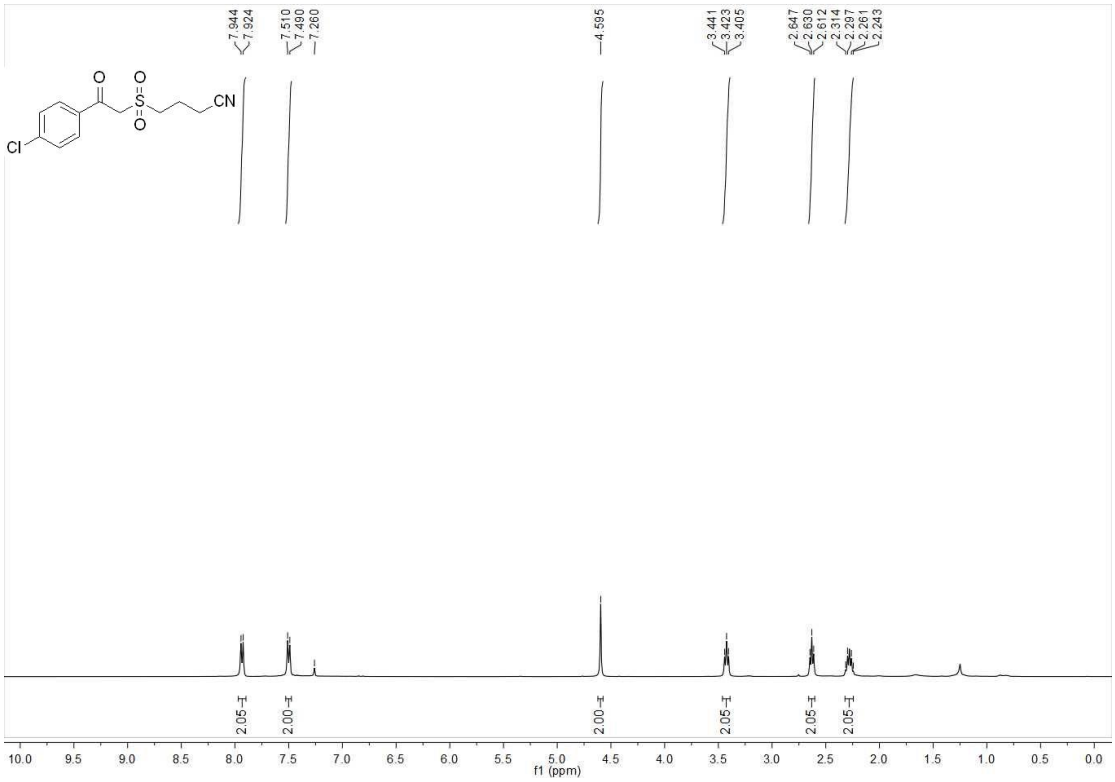


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **6k**

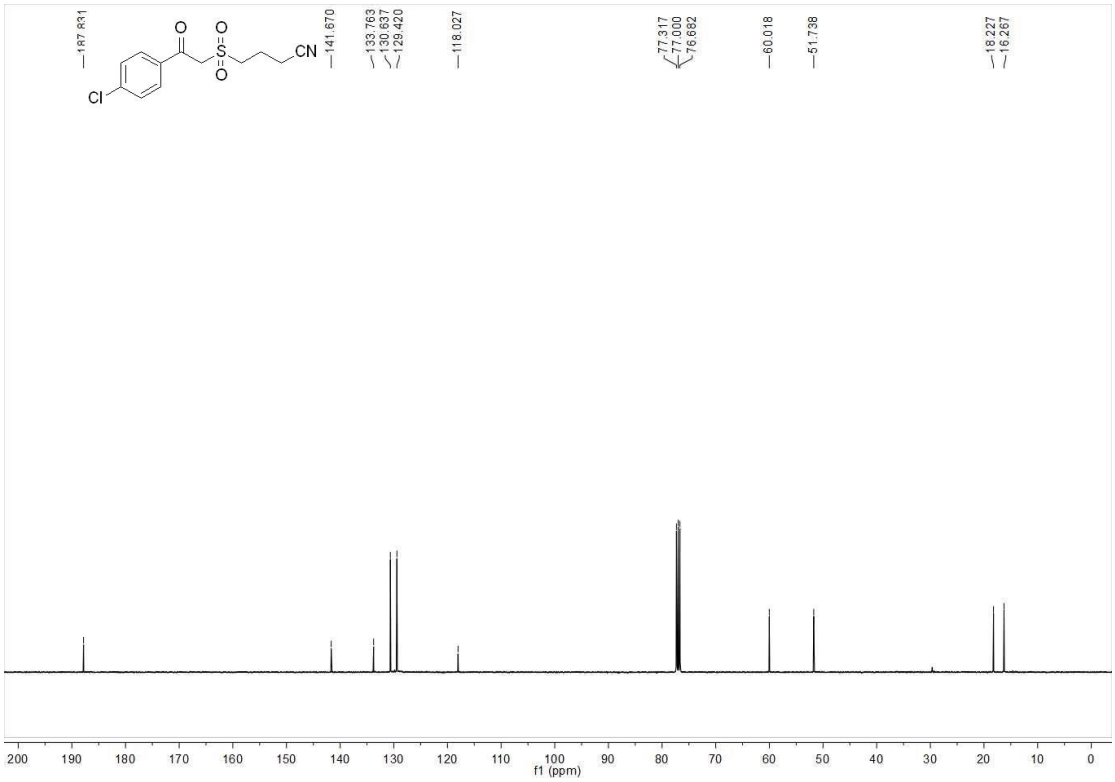


4-((2-(4-Chlorophenyl)-2-oxoethyl)sulfonyl)butanenitrile (6l)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6l**

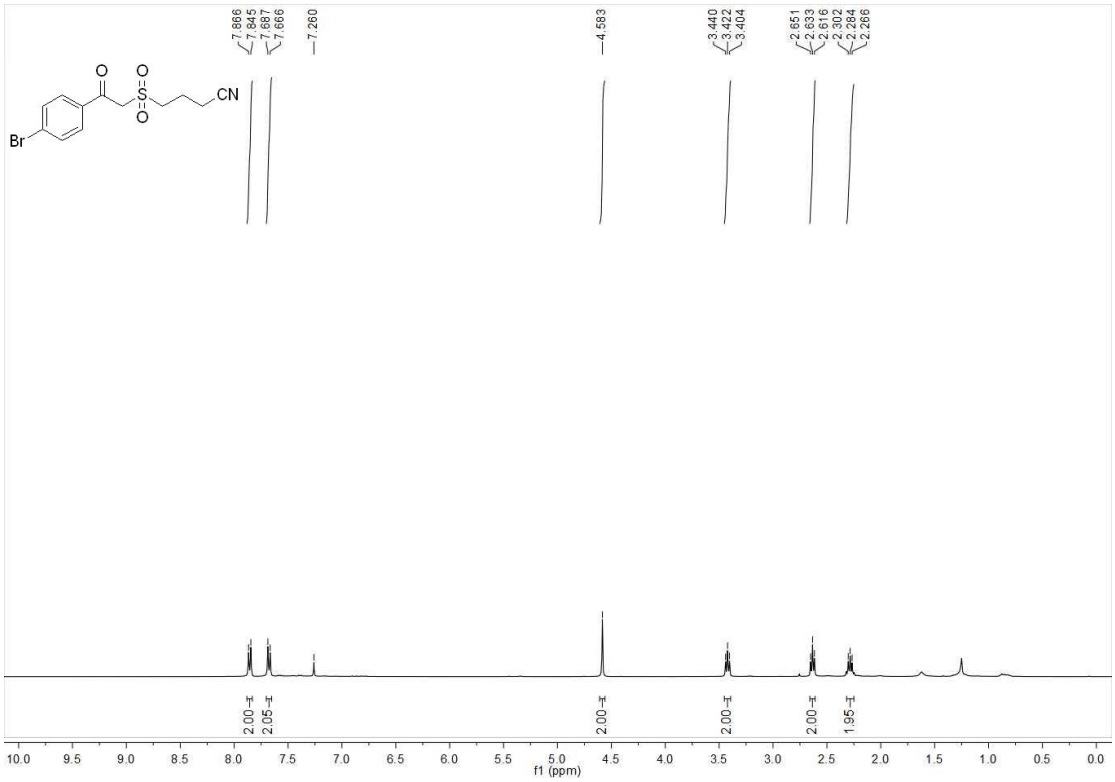


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6l**

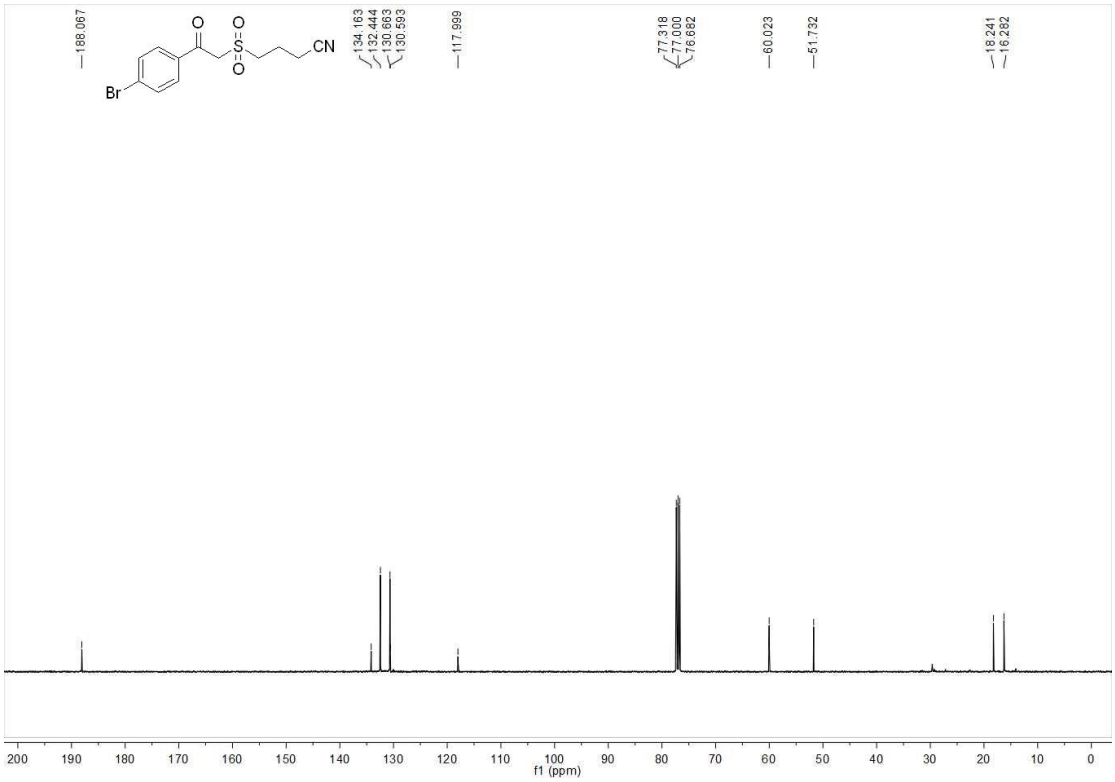


4-((2-(4-Bromophenyl)-2-oxoethyl)sulfonyl)butanenitrile (6m)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6m**

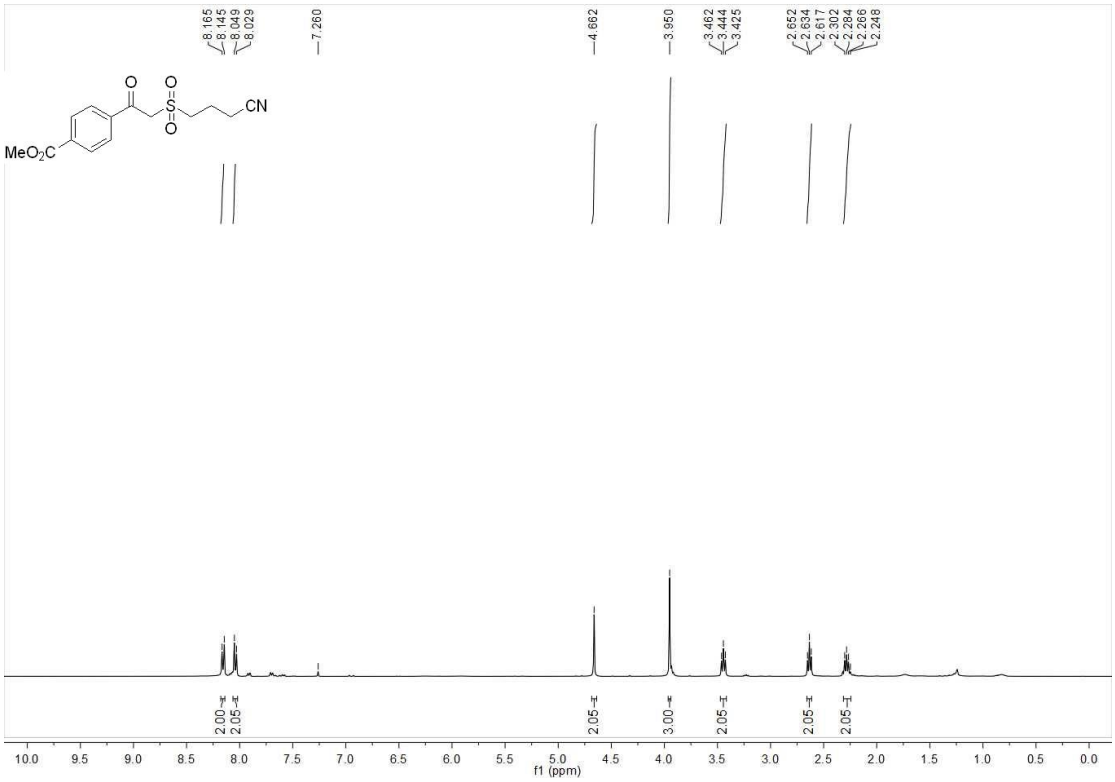


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6m**

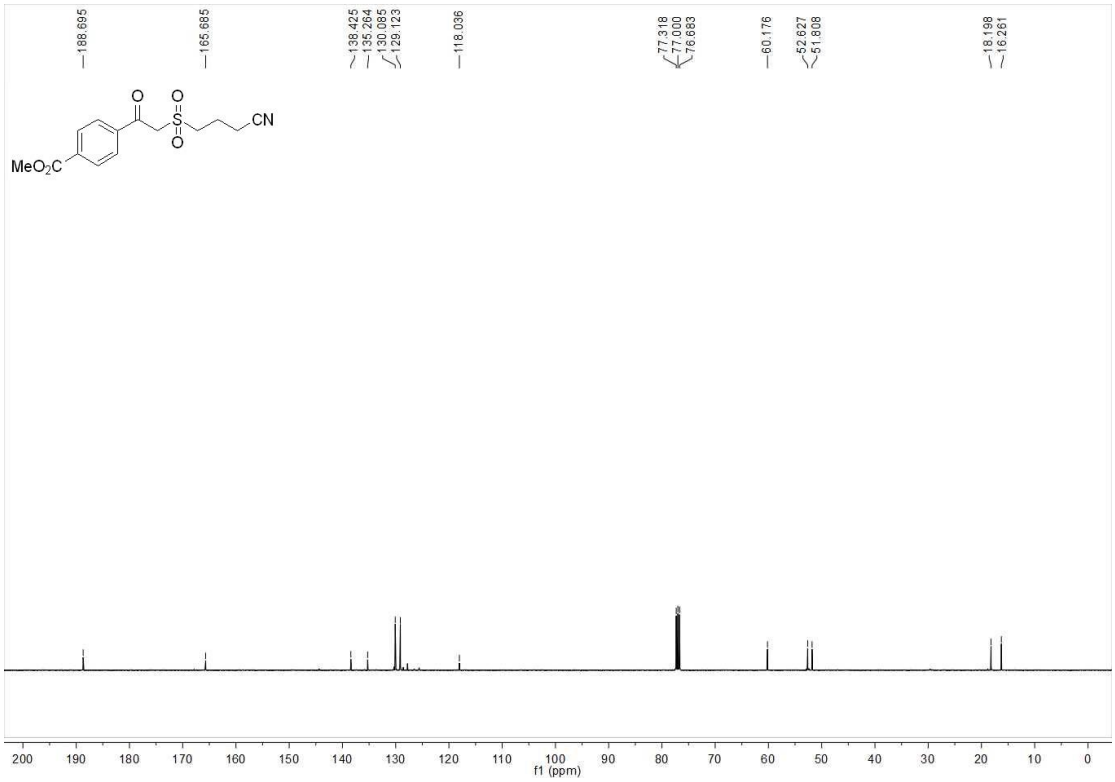


Methyl 4-(2-((3-cyanopropyl)sulfonyl)acetyl)benzoate (6n)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6n**

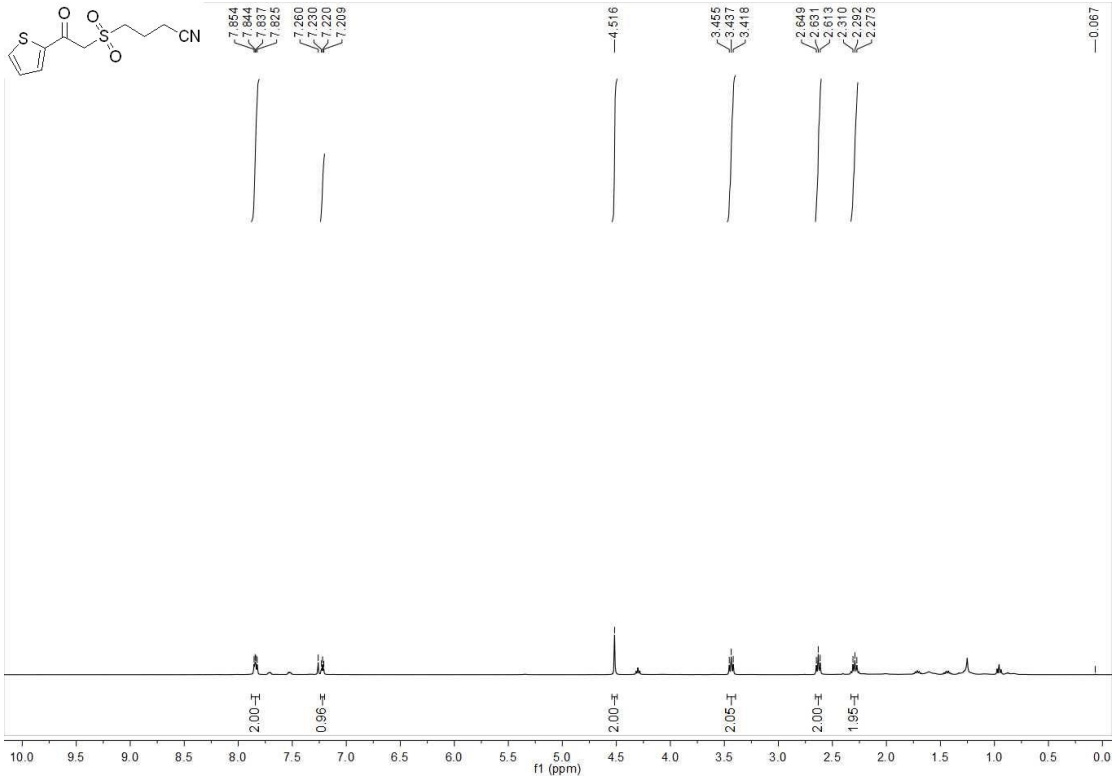


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6n**

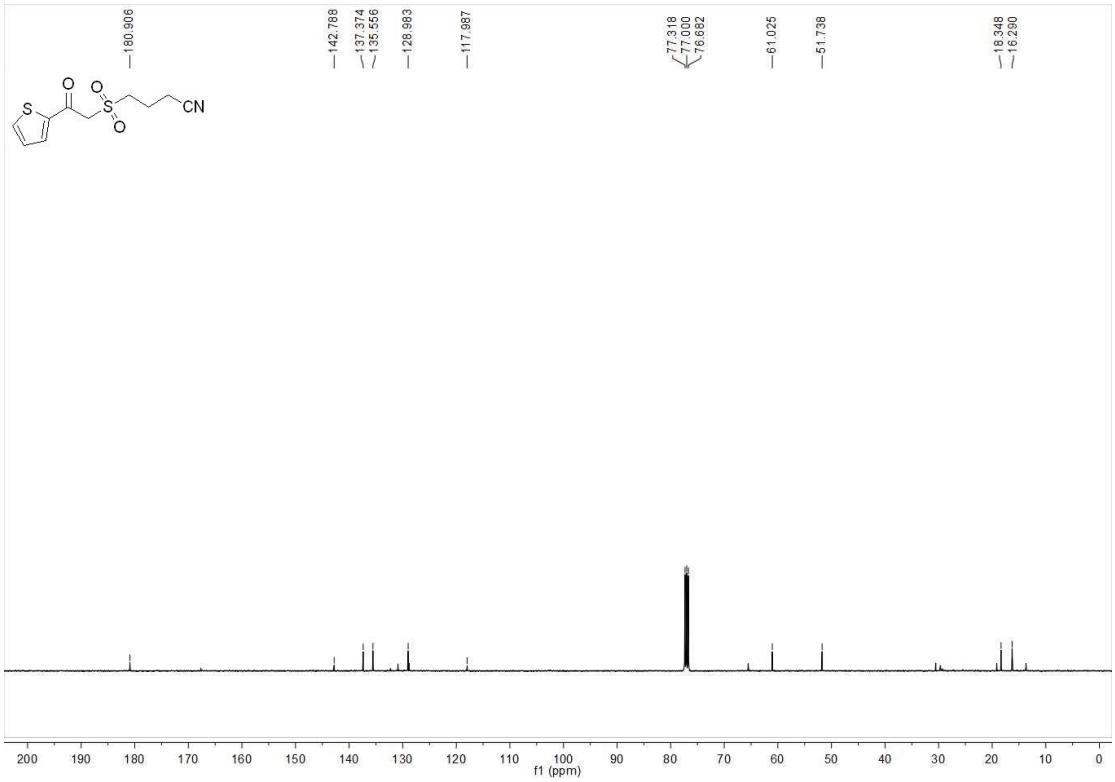


4-((2-Oxo-2-(thiophen-2-yl)ethyl)sulfonyl)butanenitrile (6o)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6o**

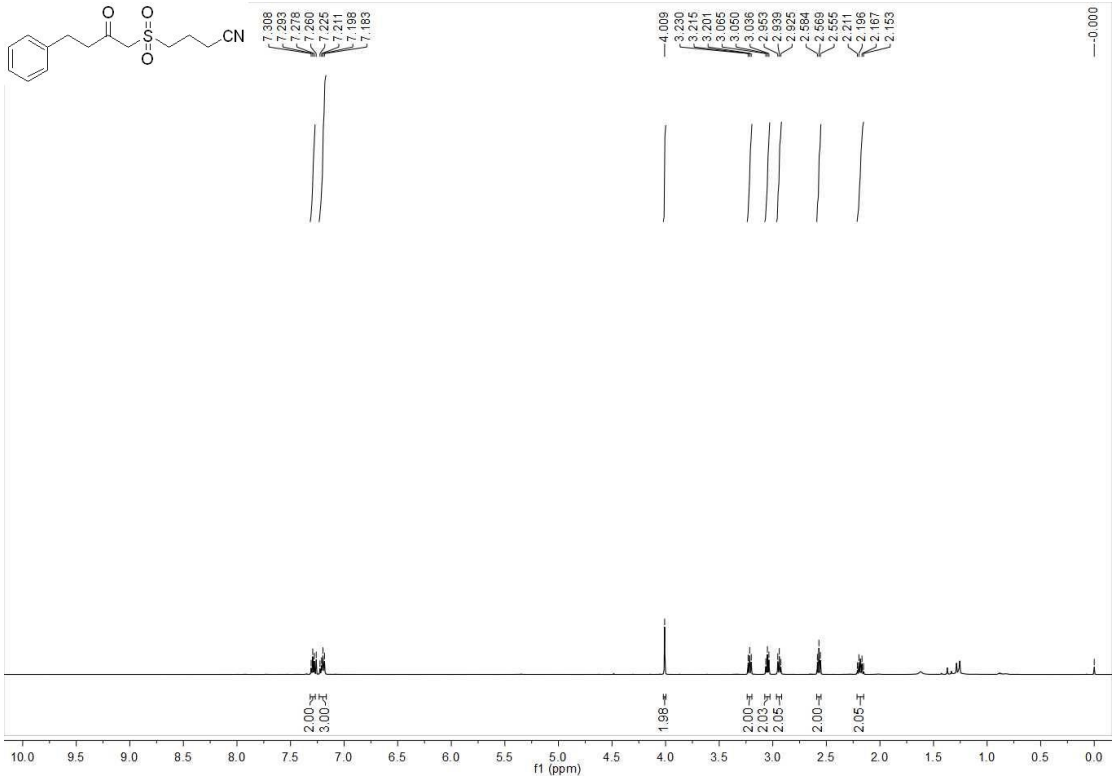


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6o**

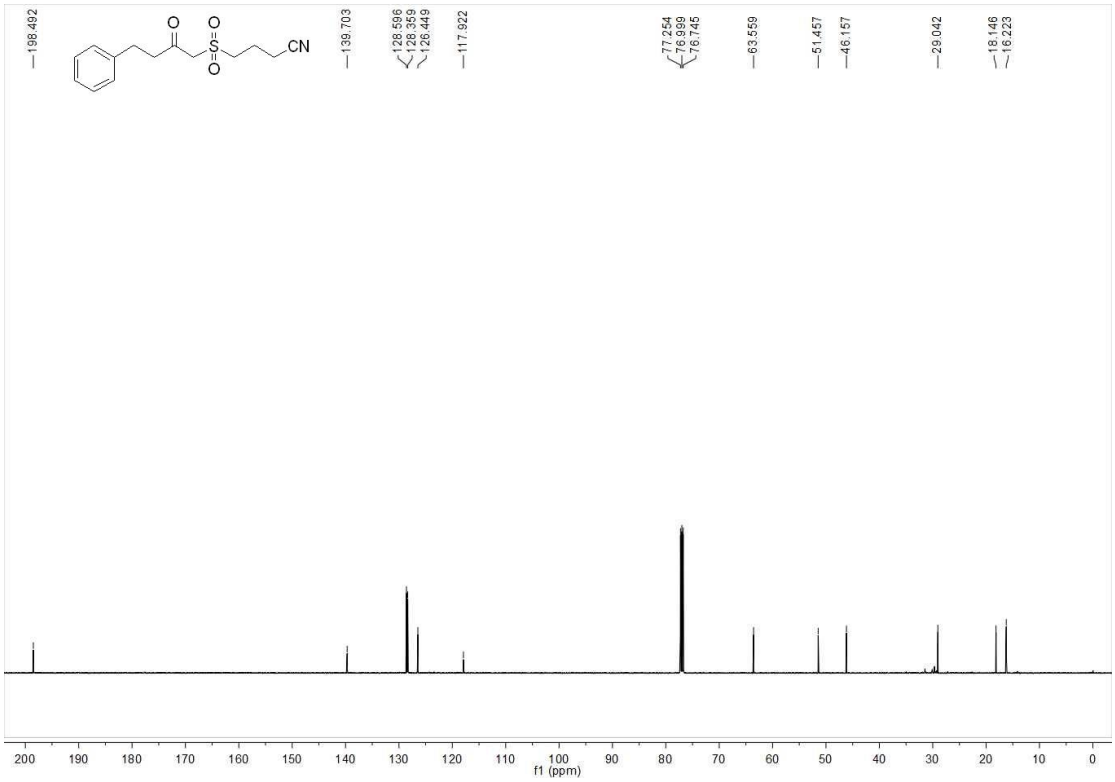


4-((2-Oxo-4-phenylbutyl)sulfonyl)butanenitrile (6p)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **6p**

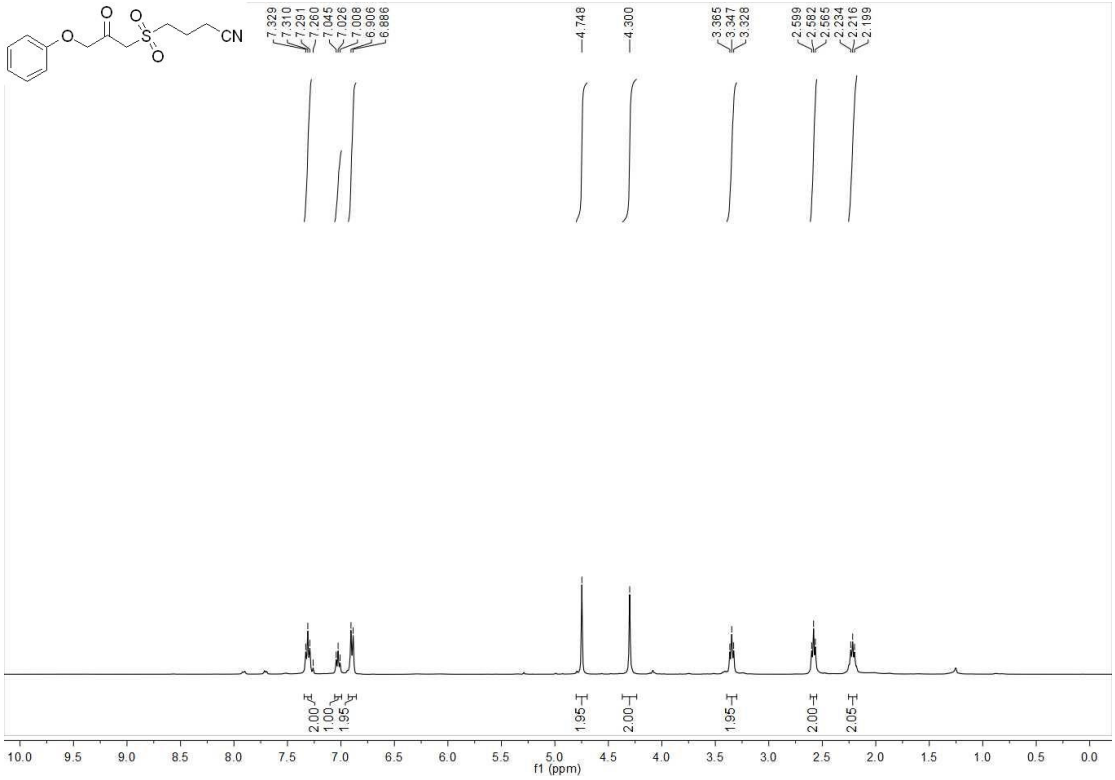


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **6p**

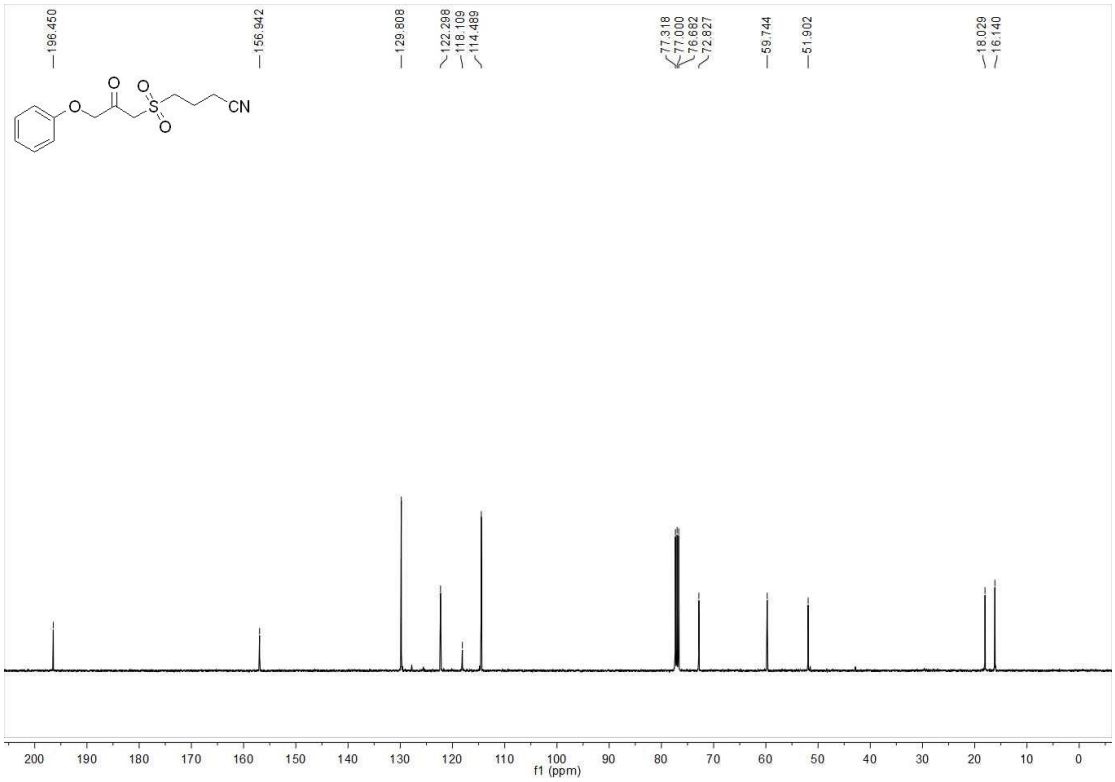


4-((2-Oxo-3-phenoxypropyl)sulfonyl)butanenitrile (6q)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **6q**

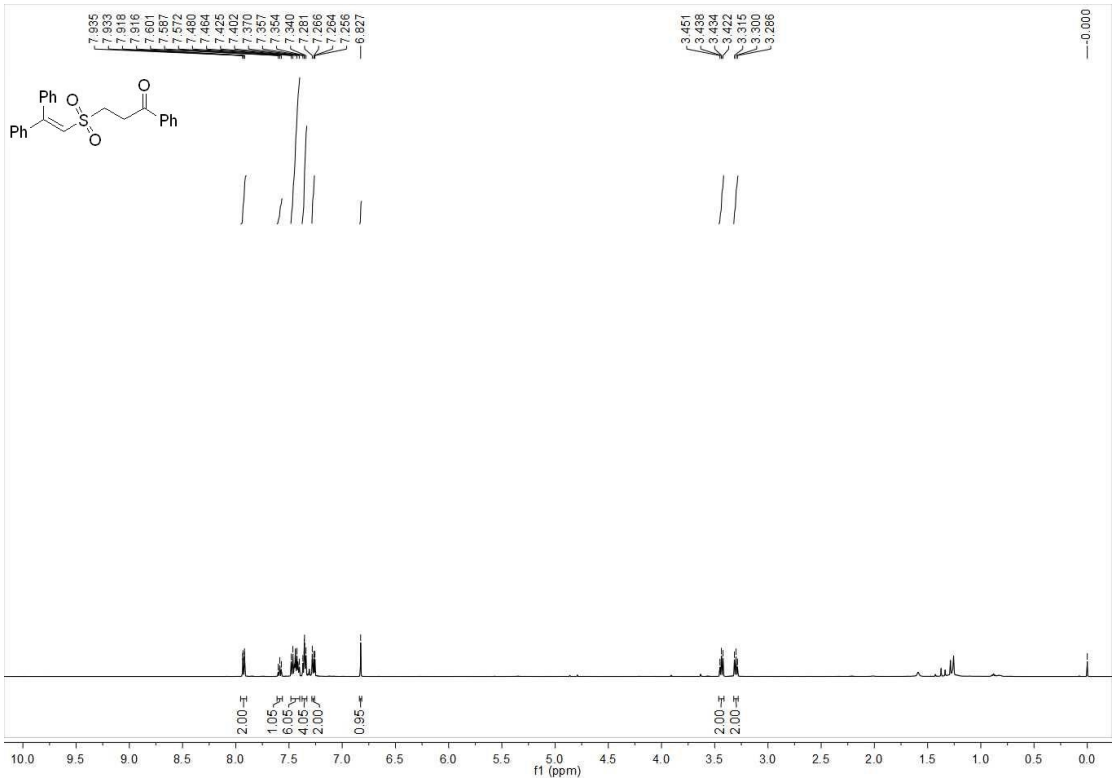


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **6q**

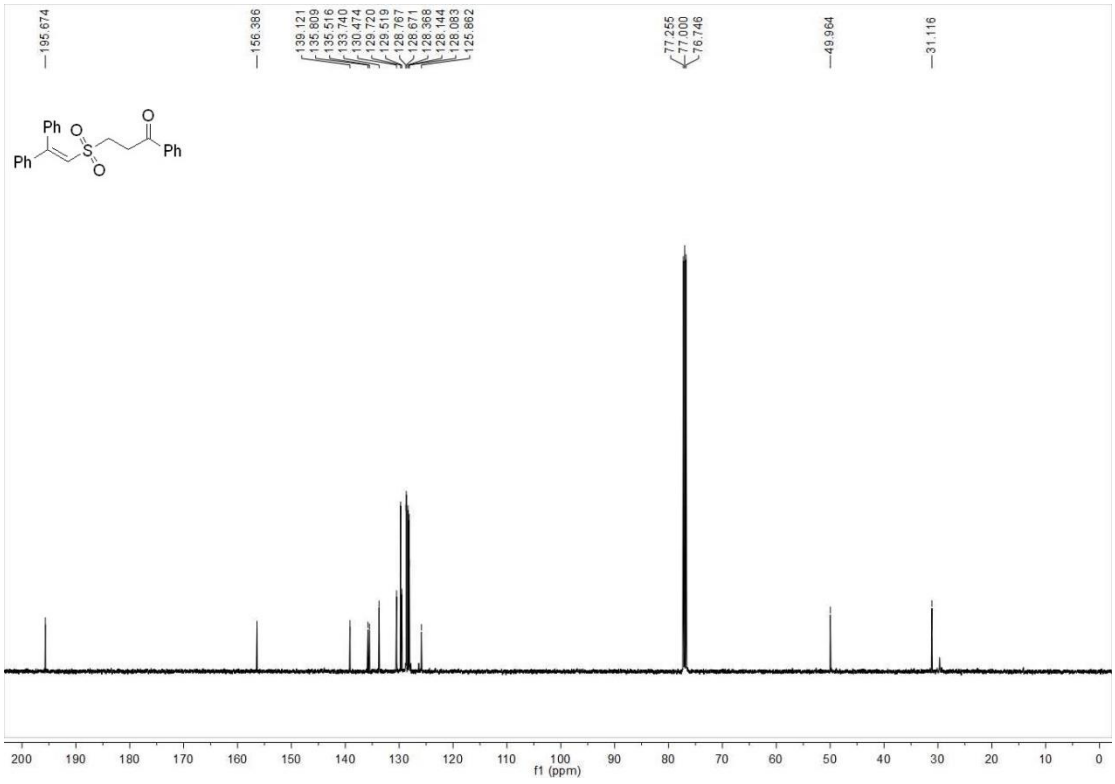


3-((2,2-Diphenylvinyl)sulfonyl)-1-phenylpropan-1-one (7a)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7a**

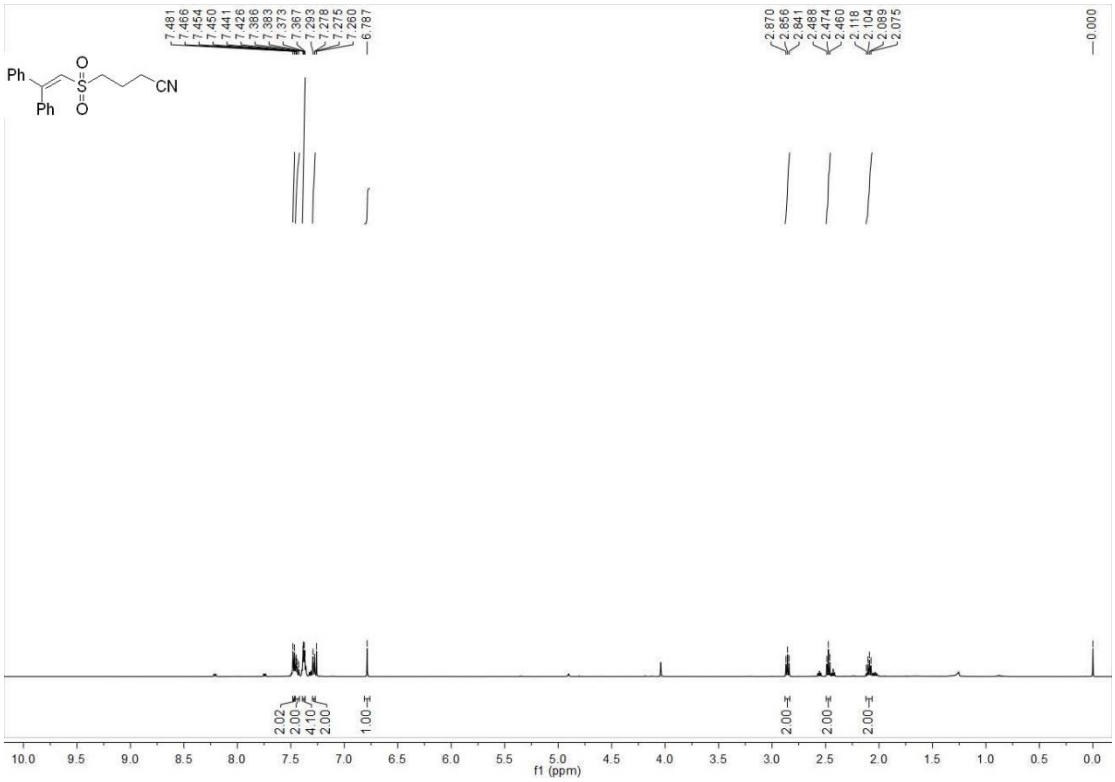


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **7a**



4-((2,2-diphenylvinyl)sulfonyl)butanenitrile (8a)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **8a**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **8a**