Catalyst-free Synthesis of 3-Sulfone Nitrile from Sulfonyl Hydrazides and Acrylonitrile in Water

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Contents:

General Remarks: Unless otherwise indicated, all commercially available reagents and solvents were used directly from the supplier without further purification. ^{1}HNMR and ^{13}CNMR were recorded at ambient temperature in $CDCl_3$ (7.27 ppm). DMSO (2.5 ppm) Chemical shift values are expressed as parts per million (ppm) and J values are in Hertz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, q: quartet or combination, br. s broad singlet or m: multiplet. Infrared samples were

recorded on a Perkin-Elmer 2000FTIR spectrometer. HRMS were recorded on the TOF-HRMS-EI at the Instruments' Center for Physical Science, University of Ji Nan. All reactions were carried out in a thick-walled glass tube (15 mL or 38 mL, purchased from Beijing Synthware Glass (http://www.xinweier.com/), also named 'thick wall pressure pipe') unless otherwise indicated.

Thick-walled glass tube

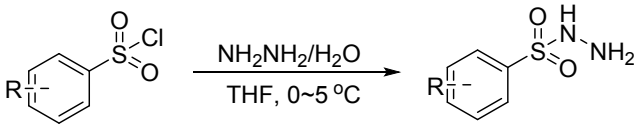
Table S1 Optimization of the reaction solvent[a]

Entry	Solvent	**T**/°C	Yield[b] (%)
1	DMF	80	Trace
2	DMSO	80	-
3	Toluene	80	-
4	CH_3CN	80	Trace
5	THF	80	Trace
6	Dioxane	80	Trace
7	CH_3OH	80	21

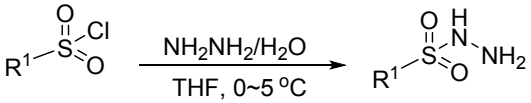
Reaction conditions: [a] The reactions were carried out with **1a** (0.5 mmol，96.1 mg, 1 eq.), **2a** (1 mmol，0.065 mL, 2 eq.), water (1 mL), at 80 °C for 10 h. [b] Yield of isolated product is based on the sulfonyl hydrazine.

Synthesis of substrates 3a-3i and the results of proving experiments

1.1 Synthesis of substrates 1a-1i, control experiment, 3aa-3ai, 3ab-3fc and Characterization data



R= H, CH_3, NO_2, CH_3O, tBu, 2,4,6-triisopropyl, thieyl, fluorine.



R^1= Bn, thieyl.

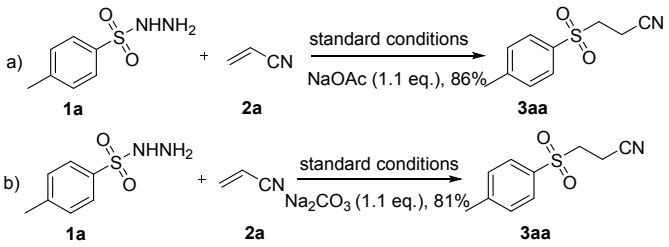
Scheme S1. The synthesizing route of substrates **1a-1i**

References:

(1) C. R. Liu, L. H. Ding, G. Guo, W. W. Liu, Fu-Lai Yang, *Org. Biomol. Chem.*, 2016, **14**, 2824.

(2) J. A. Kishor, J., Nidhi, *Chem. Commu.*, 2016, **52**, 1831.

Control Experiment of base was added into the reaction system



Scheme S2. base was added into the reaction system.

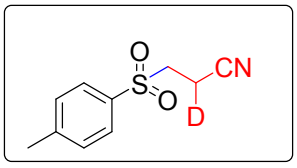


Figure S1. The structure of the **D-3aa.**

Acquired by	: System Administrator
Sample Name	: LCMS62-PH-ZHS-XZ5-1-460-0-1(MCHEN-001E1)1T
Injection Volume	: 1
Data File	: LCMS62-PH-ZHS-XZ5-1-460-0-1(MCHEN-001E1)1T.lcd
Report Format File	: lib format 27June2013.lsr
Date Acquired	: 7/18/2017 3:02:42 PM
Comment	: Mobile Phase A:Water/0.05% TFA ; Mobile phase B:ACN/0.05% TFA

Instrument Name:Shimadzu LCMS-2020

<<Pump>>

Mode	: Binary gradient
Pump A	: LC-20ADXR
Pump B	: LC-20ADXR
Total Flow	: 1.2000 mL/min
B Conc.	: 5.0 %

<<Oven>>

Oven Temperature	: 40 C

<<PDA>>

PDA Model	: SPD-M20A
Lamp	: D2
Start Wavelength	: 190 nm
End Wavelength	: 400 nm

<<Interface>>

Interface	:ESI
DL Temperature	:250 C
Nebulizing Gas Flow	:1.50 L/min
Heat Block	:250 C
Drying Gas	:On
	15.00 L/min

<<MS Parameter>>

--Segment 1 Event 1--	
Start Time	:0.00 min
End Time	:2.00 min
Acquisition Mode	:Scan
Polarity	:Positive
Event Time	:0.50 sec
Detector Voltage	:+1.15 kV
Threshold	:0
Start m/z	:90.00
End m/z	:900.00
Scan Speed	:1667 u/sec
Interface Volt.	:Use the Data in the Tuning File
DL Volt.	:Use the Data in the Tuning File
Qarray DC Voltage	:Use the Data in the Tuning File
Qarray DC Voltage	:Use the Data in the Tuning File

System Configuration

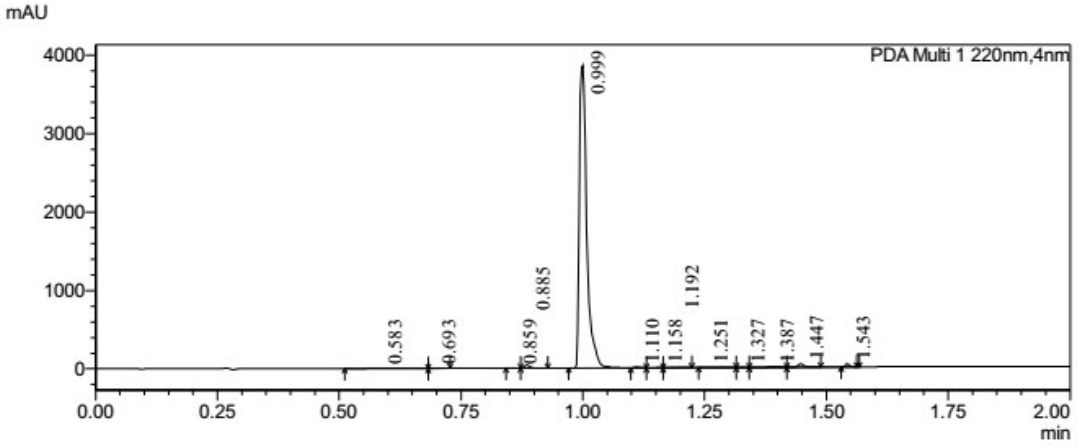
<<Column>>

Column Name	: Shim-pack XR-ODS
Length	: 50 mm
Internal Diameter	: 3.0 mm
Description	: 2.2 um

<<LC Time Program>>

Time	Module	Command	Value
0.01	Pumps	Pump B Conc.	5
1.10	Pumps	Pump B Conc.	100
1.70	Pumps	Pump B Conc.	100
1.75	Pumps	Pump B Conc.	5
2.00	Controller	Stop	

<Chromatogram>



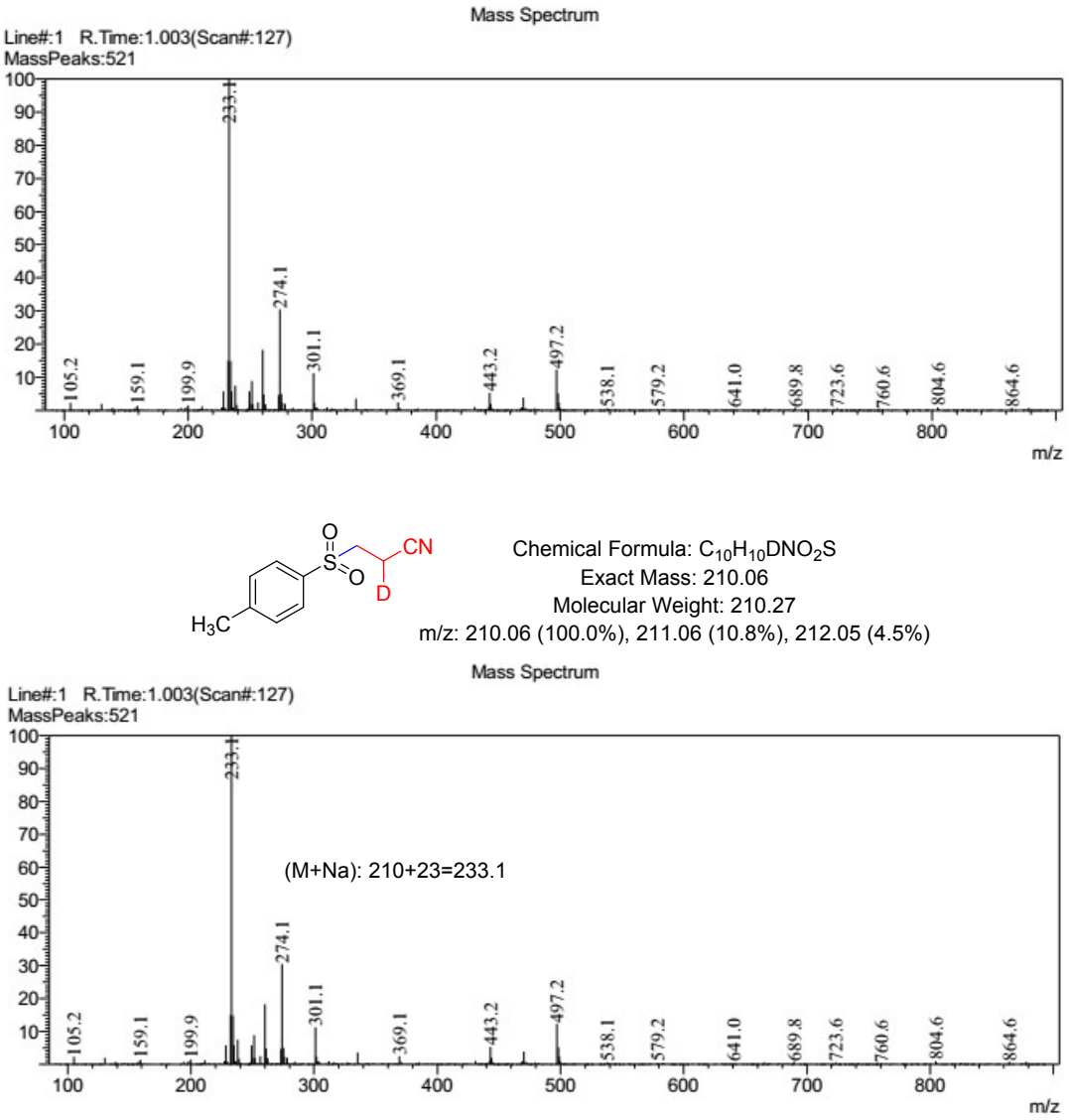
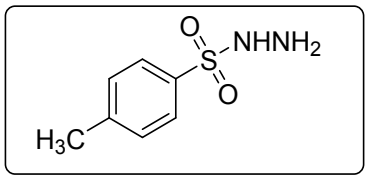


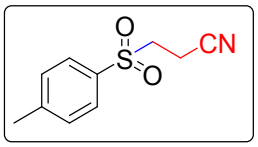
Figure S2. LCMS data of the compound **D-3aa**.

3aa-3ai, 3ab-3fc and Characterization data



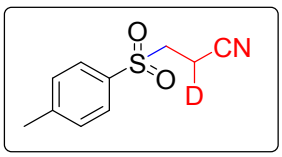
1a, 4-methylbenzenesulfonohydrazide

To a stirred solution of tetrahydrofuran (5 mL) at 0 °C, 0.5 g benzene sulfonyl chloride was added. The resultant mixture was stirred for 2 minutes. Then 2 mL hydrazine hydrate was dropwise added at 0 °C. The solution was stirred for 25 minutes. The mixed solution was extracted. Organic phase was collected and dried with anhydrous sodium sulfate and concentrated under reduced pressure to get white solid. ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.05-7.68 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 5.77 (s, 1H), 3.50 (s, 2H), 2.47 (s, 3H).



3aa, 3-tosylpropanenitrile[lit. (1)]

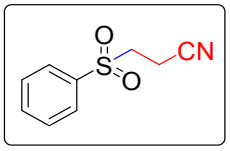
4-methylbenzenesulfo hydrazide (0.5 mmol, 96.1 mg), acrylonitrile (1mmol, 0.065 mL) and water (1 mL) were added in a thick-walled glass tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (99.4 mg, yield of 95%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 3.63-3.23 (m, 2H), 2.92-2.72 (m, 2H), 2.47 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 130.5, 128.3, 116.1, 29.5, 21.5, 12.2. Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.42; H, 5.31; N, 6.67; S, 15.32. Found: C, 57.35; H, 5.21; N, 6.58; S, 15.21. IR (liquidfilm, cm^{-1}): ν= 3421, 2853, 2244, 1594, 1384, 1148, 1302. HRMS (TOF-HRMS-EI): calcd for $C_{10}H_{11}NO_2S$: 209.0508, found 209.0499.



D-3aa, 3-tosylpropanenitrile

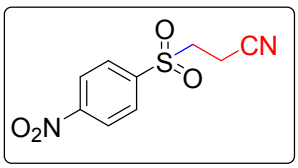
4-methylbenzenesulfo hydrazide (0.5mmol, 96.1 mg), acrylonitrile (1mmol, 0.065 mL) and D_2O (1 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was

extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (98.8 mg, yield of 94%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 3.37-3.35 (m, 2H), 2.80-2.72 (m, 1H), 2.47 (s, 3H). LCMS: calcd for $C_{10}H_{10}DNO_2S$: 210.0, found 210.0+23=233.1.



3ba, 3-(phenylsulfonyl)propanenitrile [lit. (2)]

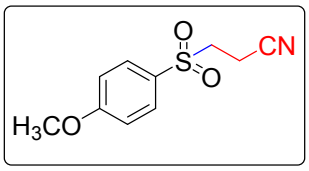
Benzenesulfonylhydrazine (1 mmol, 172.2 mg), acrylonitrile (2 mmol, 0.13 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (175.7 mg, yield of 94%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.3 Hz, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.63 (t, J = 7.7 Hz, 2H), 3.46-3.32 (m, 2H), 2.82 (t, J = 7.7 Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 137.5, 130.1, 128.2, 116.2, 51.2, 29.5, 12.1. Anal. Calcd for $C_9H_9NO_2S$: C, 55.36; H, 4.69; N, 7.18; S, 16.42. Found: C, 55.29; H, 4.57; N, 7.19; S, 16.30. IR (liquid film, cm^{-1}): ν=3411, 2841, 2242, 1581, 1152, 1303. HRMS (TOF-HRMS-EI): calcd for $C_9H_9NO_2S$ 195.0355, found 195.0348.



3ca, 3-((4-nitrophenyl)sulfonyl)propanenitrile [lit. (3)]

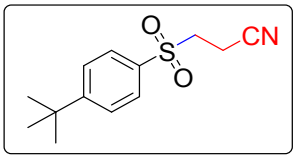
4-nitrobenzenesulfonyl hydrazine (1 mmol, 217.2 mg), acrylonitrile (2 mmol, 0.13 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by

column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (216.2 mg, yield of 93%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.9 Hz, 2H), 8.19 (d, J = 8.9 Hz, 2H), 3.48 (t, J = 7.4 Hz, 2H), 2.92 (t, J = 7.4 Hz, 2H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 151.4, 143.1, 129.8, 124.9, 115.3, 51.0, 29.8 11.9. Anal. Calcd. for $C_9H_8N_2O_4S$: C, 45.09; H, 3.37; N, 11.67; S, 13.35. Found: C, 39.90; H, 3.26; N, 11.59; S, 13.30. IR (liquidfilm, cm^{-1}): ν=3419, 2831, 2254, 1538, 1151, 1306. HRMS (TOF-HRMS-EI): calcd for $C_9H_8N_2O_4S$ 240.2327, found 240.2331.



3da, 3-((4-methoxyphenyl)sulfonyl)propanenitrile

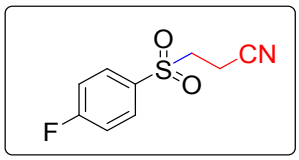
4-methoxy benzenesulfonylhydrazine (0.5 mmol, 101.1 mg), acrylonitrile (1 mmol, 0.065 mL) and water (1 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (219.8 mg, yield of 97%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 9.0 Hz, 2H), 7.06 (d, J = 9.0 Hz, 2H), 3.90 (s, 3H), 3.46-3.26 (m, 2H), 2.90-2.71 (m, 2H). ^{13}CNMR (100MHz, $CDCl_3$) δ 164.4, 130.4, 128.8, 116.0, 114.9, 55.7, 51.3, 12.0. Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22; S, 14.23. Found: C, 53.21; H, 4.80; N, 6.13; S, 14.10. IR (liquid film, cm^{-1}): ν=3430, 2845, 2247, 1573, 2841, 1143, 1300. HRMS (TOF-HRMS-EI): calcd for $C_{10}H_{11}NO_3S$ 225.0455, found 225.0458.



3ea, 3-((4-(tert-butyl)phenyl)sulfonyl)propanenitrile

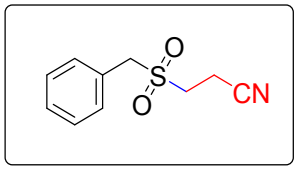
4-tertbutyl benzene sulfonyl hydrazide (2 mmol, 456.6 mg), acrylonitrile (4 mmol, 0.26 mL) and water (4 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by

column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (480 mg, yield of 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 3.72-3.20 (m, 2H), 3.04-2.74 (m, 2H), 1.38 (s, 9H). ^{13}CNMR (100 MHz, $CDCl_3$) δ 158.8, 134.3, 128.1, 126.7, 116.0, 51.0, 35.3, 30.9, 11.9. Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.47; S, 12.66. Found: C, 61.98; H, 6.76; N, 5.29; S, 12.58. IR (liquid film, cm^{-1}): ν=3406, 2837, 2249, 1544, 1448, 1507, 1138, 1311. HRMS (TOF-HRMS-EI): calcd. for $C_{13}H_{17}NO_2S$ 251.0977, found 251.0970.



3fa, 3-((4-fluorophenyl)sulfonyl)propanenitrile [lit. (4)]

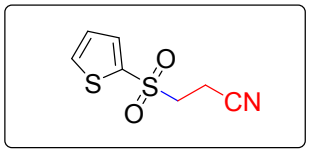
4-monofluoro benzenesulfonylhydrazine (0.5 mmol, 92.2 mg), acrylonitrile (1.5 mmol, 0.19 mL) and water (1 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature.The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (102.3 mg, yield of 92%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.9, 5.0 Hz, 2H), 7.36-7.28 (m, 2H), 3.39 (t, J = 7.6 Hz, 2H), 2.84 (t, J = 7.6 Hz, 2H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 167.6, 165.1, 133.6, 131.2, 117.2, 117.0, 115.8, 51.3, 11.9. Anal. Calcd for $C_9H_8FNO_2S$: C, 50.56; H, 3.68; F, 8.91; N, 6.57; S, 15.04. Found: C, 50.27; H, 3.50; F, 8.89; N, 6.43; S, 15.00. IR (liquid film, cm^{-1}): ν=3390, 2874, 2250, 1599, 1224, 1133, 1301. HRMS (TOF-HRMS-EI): calcd. for $C_9H_8FNO_2S$ 240.2327, found 240.2331.



3ga, 3-(benzylsulfonyl)propanenitrile

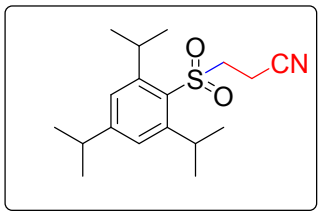
Benzyl benzenesulfonylhydrazine (1 mmol, 262.2 mg), acrylonitrile (2 mmol, 0.13 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered.

The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (256.2 mg, yield of 93%). ^{1}HNMR (400 MHz, DMSO) δ 7.41 (s, 5H), 4.58 (s, 2H), 3.45 (d, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.1 Hz, 2H). ^{13}CNMR (100 MHz, DMSO) δ 131.5, 129.1, 128.3, 118.7, 58.2, 46.7, 11.0. Anal. Calcd for $C_9H_9NO_2S$: C, 57.37; H, 5.25; N, 6.61; S, 15.23. Found: C, 57.11; H, 5.13 N, 6.57; S, 15.14. IR (liquid film, cm^{-1}): ν=3423, 2847, 2249, 1587, 1150, 1307. HRMS (TOF-HRMS-EI): calcd for $C_9H_9NO_2S$ 240.2327, found 240.2331.



3ha, 3-(thiophen-2-ylsulfonyl)propanenitrile

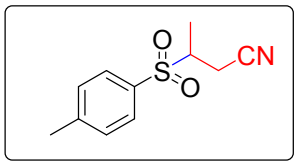
2-thiophene sulfonyl hydrazine (1 mmol, 206.5 mg), acrylonitrile (2 mmol, 0.13 mL) and water (2 mL) were added in a thick-walled glass tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (192.5 mg, yield of 94%). ^{1}HNMR (400 MHz, DMSO) δ 8.05 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.74 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.21 (dd, *J* = 4.9, 3.8 Hz, 1H), 3.68 (t, *J* = 6.8 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H). ^{13}CNMR (101 MHz, DMSO) δ 138.4, 136.3, 135.4, 129.0, 117.7, 51.4, 12.0. Anal. Calcd for $C_7H_7NO_2S_2$: C, 41.59; H, 3.35; N, 6.87; S, 31.76. Found: C, 41.34; H, 3.13; N, 6.80; S, 31.65. IR (liquid film, cm^{-1}): ν=3098, 1531, 2849, 2252, 1137, 1309. HRMS (TOF-HRMS-EI): calcd for $C_7H_7NO_2S_2$ 200.9919, found 200.9923.



3ia, 3-((2,4,6-triisopropylphenyl)sulfonyl)propanenitrile

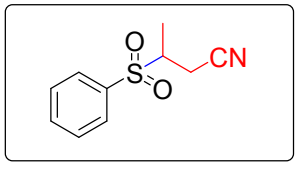
2, 4, 6-three isopropyl benzenesulfonylhydrazide (1 mmol, 321.4 mg), acrylonitrile (2 mmol, 0.13 mL) and water (2 mL) were added in a thick-walled glass tube. The resultant mixture was stirred at 80 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic

extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (192.5 mg, yield of 93%). ^{1}HNMR (400 MHz, CD_3OD) δ 7.10 (s, 2H), 4.47 (dt, *J* = 13.6, 6.8 Hz, 2H), 3.58 (dt, *J* = 13.6, 6.9 Hz, 2H), 3.08-2.74 (m, 3H), 1.24-1.21 (m, 18H). ^{13}CNMR (101 MHz, CD_3OD) δ 151.1, 147.5, 137.9, 123.7, 121.6, 51.9, 33.4, 28.5, 23.3, 22.3, 10.12. Anal. Calcd for $C_{18}H_{27}NO_2S$: C, 67.05; H, 8.58; N, 4.33; S, 9.91. Found: C, 66.78; H, 8.39; N, 4.29; S, 8.89. HRMS (TOF-HRMS-EI): calcd for $C_{18}H_{27}NO_2S$ 321.1753, found 321.1761.



3ab, 3-tosylbutanenitrile

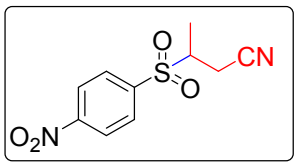
4-methoxybenzenesulfonylhydrazine (1 mmol, 186.2 mg), 2-butenenitrile (2.5 mmol, 0.2 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 120 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (136.2 mg, yield of 85%). ^{1}HNMR (400 MHz, CDCl3) δ 1HNMR (400 MHz, CDCl3) δ 7.76 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.30-3.36 (m, 1H), 2.92 (t, 1H), 2.60 (t, 1H),2.41 (s, 3H), 1.43 (d, 3H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 145.9, 132.68, 130.26, 129.1, 115.8, 56.0, 21.7, 18.9, 13.5. Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.07; H, 5.56; N, 6.19; S, 14.34. Found: C, 58.87; H, 5.40; N, 6.10; S, 14.26. IR (liquid film, cm^{-1}): ν=3438, 3195, 2368, 1161, 1369, 960, 692. HRMS (TOF-HRMS-EI): calcd for $C_{11}H_{13}NO_2S$ 223.0667, found 223.0599.



3bb, 3-(phenylsulfonyl)butanenitrile [lit. (5)]

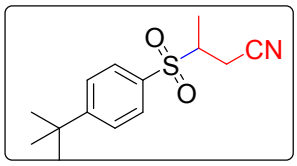
Benzenesulfonylhydrazide (1 mmol, 171.2 mg), 2-butenenitrile (2.5 mmol, 0.2 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 120 °C under magnetic stirring for 10 h. After the reaction was

completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (154.6 mg, yield of 85%). ^{1}HNMR (400 MHz, $CDCl_3$) δ ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.88-7.90 (m 2H), 7.72-7.76 (m, 1H), 7.61-7.65 (m, 2H), 3.32-3.41 (m, 1H), 2.95-3.01 (dd, J = 16.9, 4.3 Hz, 1H), 2.61-2.67 (dd, J = 16.9, 9.9 Hz, 1H), 1.46 (d, J = 6.9 Hz, 3H) ^{13}CNMR (101 MHz, $CDCl_3$) δ, 134.7, 129.6, 129.1, 115.8, 55.9, 29.7, 18.8, 13.5. IR (liquid film, cm^{-1}): ν=3431, 2950, 2243, 1274, 1008, 702. Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 57.40; H, 5.25; N, 6.57; S, 15.19. Found: C, 57.18; H, 5.10; N, 6.51; S, 15.09. HRMS (TOF-HRMS-EI): calcd for $C_{10}H_{11}NO_2S$ 209.0535, found 209.0549.



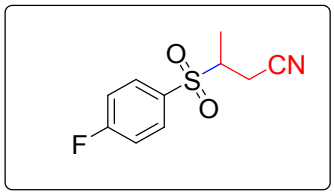
3cb, 3-((4-nitrophenyl)sulfonyl)butanenitrile

4-nitrobenzenesulfonylhydrazide (1 mmol, 217.2 mg), 2-butenenitrile (2.5 mmol, 0.2 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 120 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (179.7 mg, yield of 80%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 3.33 (m, J = 13.9, 6.9, 4.2 Hz, 1H), 2.97 (dd, J = 16.9, 4.2 Hz, 1H), 2.62 (dd, J = 16.9, 10.1 Hz, 1H), 1.46 (d, J = 6.9 Hz, 3H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 151.5, 141.6, 130.6, 124.55, 115.26, 56.1, 18.4, 13.74. IR (liquid film, cm^{-1}): ν= 3423, 2832, 2255, 1536, 1525, 1150, 1309. Anal. Calcd for $C_{10}H_{10}N_2O_4S$: C, 47.24; H, 3.76; N, 11.12; S, 12.61. Found: C, 47.02; H, 3.51; N, 11.04; S, 12.43. HRMS (TOF-HRMS-EI): calcd for $C_{10}H_{10}N_2O_4S$ 254.0355, found 254.0349.



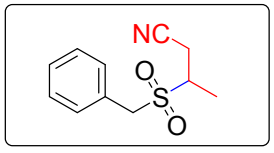
3ed, 3-((4-(tert-butyl)phenyl)sulfonyl)butanenitrile

4-tertbutyl benzene sulfonyl hydrazide (1 mmol, 228.3 mg), 2-butenenitrile (2.5 mmol, 0.2 mL) and water (4 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 120 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (177 mg, yield of 89%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 3.47-3.19 (m, 1H), 2.97 (dd, *J* = 16.9, 4.1 Hz, 1H), 2.61 (dd, *J* = 16.9, 10.1 Hz, 1H), 1.46 (d, *J* = 6.9 Hz, 3H), 1.35 (s, 9H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 159.4, 132.8, 129.27, 126.9, 116.1, 56.2, 36.3, 31.0, 18.9, 13.6. Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.23; H, 7.02; N, 5.19; S, 12.04. Found: C, 63.09; H, 6.89; N, 5.08; S, 11.88. HRMS (TOF-HRMS-EI): calcd for $C_{14}H_{19}NO_2S$ 265.1136, found 266.1170.



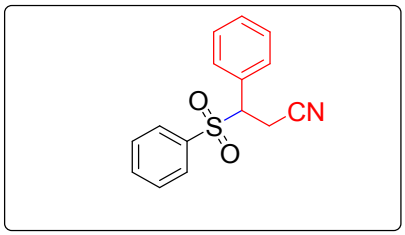
3fb, 3-((4-fluorophenyl)sulfonyl)butanenitrile

4-monofluoro benzenesulfonylhydrazine (1 mmol, 185.8 mg), 2-butenenitrile (2.5 mmol, 0.2 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 120 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (156.8 mg, yield of 75%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.3 Hz, 2H), 7.42 (d, J= 8.0 Hz, 2H), 3.36 (d, J = 7.7 Hz, 2H), 2.76-2.81 (m, 1H), 2.48 (s, 3H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 145.9, 132.68, 130.26, 129.1, 115.8, 56.0, 21.7, 18.9, 13.5. IR (liquid film, cm^{-1}): ν=3558, 3419, 2939, 2252, 1593, 1151, 582. Anal. Calcd for $C_{10}H_{10}FNO_2S$: C, 52.75; H, 4.54; F, 8.29; N, 6.06; S, 14.11. Found: C, 52.57; H, 4.32; F, 8.18; N, 6.01; S, 14.04. HRMS (TOF-HRMS-EI): calcd for $C_{10}H_{10}FNO_2S$ 227.0433, found 227.0426.



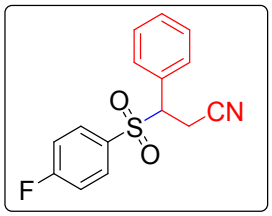
3gb, 3-(benzylsulfonyl)butanenitrile

Phenylmethanesulfonohydrazide (1 mmol, 186.2 mg), 2-butenenitrile (2.5 mmol, 0.2 mL) and water (4 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 120 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (158.5 mg, yield of 87%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.42 (s, 5H), 4.32 (s, 2H), 3.32-3.06 (m, 1H), 2.89 (dd, J = 17.1, 4.7 Hz, 1H), 2.63 (dd, J = 17.1, 9.3 Hz, 1H), 1.54 (d, J = 6.9 Hz, 3H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 130.9, 129.7, 129.6, 127.0, 116.4, 57.8, 52.0, 18.5, 13.96. Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 58.87; H, 5.60; N, 6.27; S, 14.36. Found: C, 58.50; H, 5.45; N, 6.21; S, 14.24. HRMS (TOF-HRMS-EI): calcd for $C_{11}H_{13}NO_2S$ 223.0666, found 223.0716.



3bc,3-phenyl-3-(phenylsulfonyl)propanenitrile

Benzenesulfonylhydrazine (1 mmol, 276.8 mg), cinnamonitrile (1.5 mmol, 0.2 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 130 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (138.4 mg, yield of 50%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.05-7.85 (m, 3H), 7.74 (d, J = 7.2 Hz, 1H), 7.69 -7.56 (m, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.47-7.28 (m, 2H), 4.93 (s, 2H), 3.64 (dt, J = 13.2, 6.6 Hz, 1H). ^{13}CNMR (101 MHz, $CDCl_3$) δ 142.1, 133.0, 129.3, 128.9, 126.5, 125.8, 58.1, 55.7, 29.8. IR (liquid film, cm^{-1}): ν=3429, 2892, 2159, 1543, 1126, 710. Anal. Calcd for $C_{15}H_{13}NO_2S$: C, 66.28; H, 4.43; N, 5.06; S, 11.80. Found: C, 66.00; H, 4.21; N, 4.09; S, 11.69. HRMS (TOF-HRMS-EI): calcd for $C_{15}H_{13}NO_2S$ 271.0657, found 271.0649.



3fc, 3-((4-fluorophenyl)sulfonyl)-3-phenylpropanenitrile

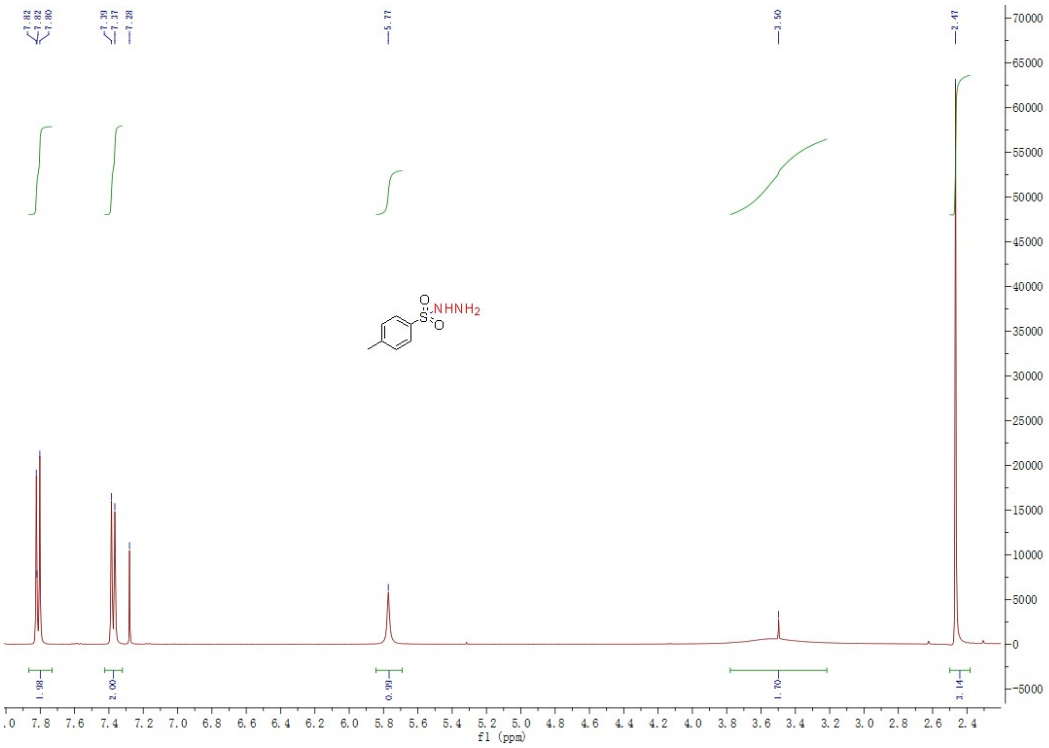
4-monofluoro benzenesulfonylhydrazine (1 mmol, 294.6 mg), cinnamonitrile (1.5 mmol, 0.2 mL) and water (2 mL) were added in a thick-walled pressure tube. The resultant mixture was stirred at 130 °C under magnetic stirring for 10 h. After the reaction was completed, the reaction solution was cooled to room temperature. The mixture was extracted with EtOAc (2 × 50 mL) and then the combined organic extracts were washed with brine for three times (3 × 10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc: petroleum ether =1: 2) a light white solid (153.7 mg, yield of 43%).^{1}HNMR (400 MHz, $CDCl_3$) δ 8.06-7.83 (m, 2H), 7.75 (d, *J* = 7.1 Hz, 2H), 7.53 (dd, *J* = 17.3, 9.4 Hz, 1H), 7.43 (dd, *J* = 12.9, 5.3 Hz, 2H), 7.36 (d, *J* = 6.2 Hz, 1H), 7.24- 7.13 (m, 1H), 4.93 (s, 1H), 2.78 (s, 1H), 2.12 (s, 1H). ^{13}CNMR (101 MHz, $CDCl_3$) δ143.9, 138.9, 129.8, 129.0, 128.9, 128.3, 126.6, 125.8, 125.6, 115.2, 70.4, 32.0, 14.2. Anal. Calcd for $C_{15}H_{12}FNO_2S$: C, 62.24; H, 3.96; F, 6.56; N, 4.74; S, 11.18. Found: C, 62.02; H, 3.67; F, 6.49; N, 4.58; S, 11.02. IR (liquid film, cm^{-1}): ν=3421, 2898, 2238, 1601, 1243, 692. HRMS (TOF-HRMS-EI): calcd for $C_{15}H_{12}FNO_2S$ 289.0572, found 289.0571.

References for the 3-sulfone nitrile:

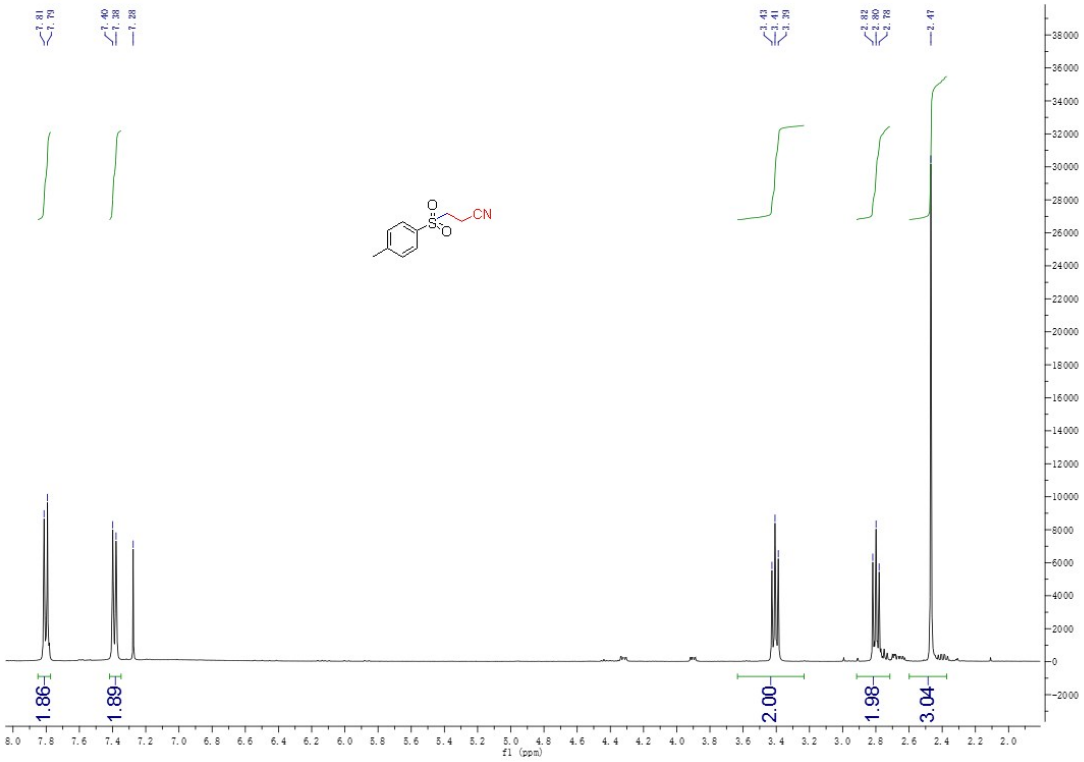
(1) **3aa:** C. D. Hurd, L. L. Gershbein, *J. Am. Chem. Soc.*,1947, **69**, P2328.
(2) **3ba**: J. Y. Lee, Y. T. Hong, S. Sunggak, *Angew. Chem. Int. Edit*., 2006, **45**, 6182.
(3) **3ca**: I. K. Fel'dman, V. N. Mikhailova, *Zhurnal Obshchei Khimii*, 1961, **31**, 2115.
(4) **3fa**: Spectral data were obtained from Wiley Subscription Services, Inc. (US).

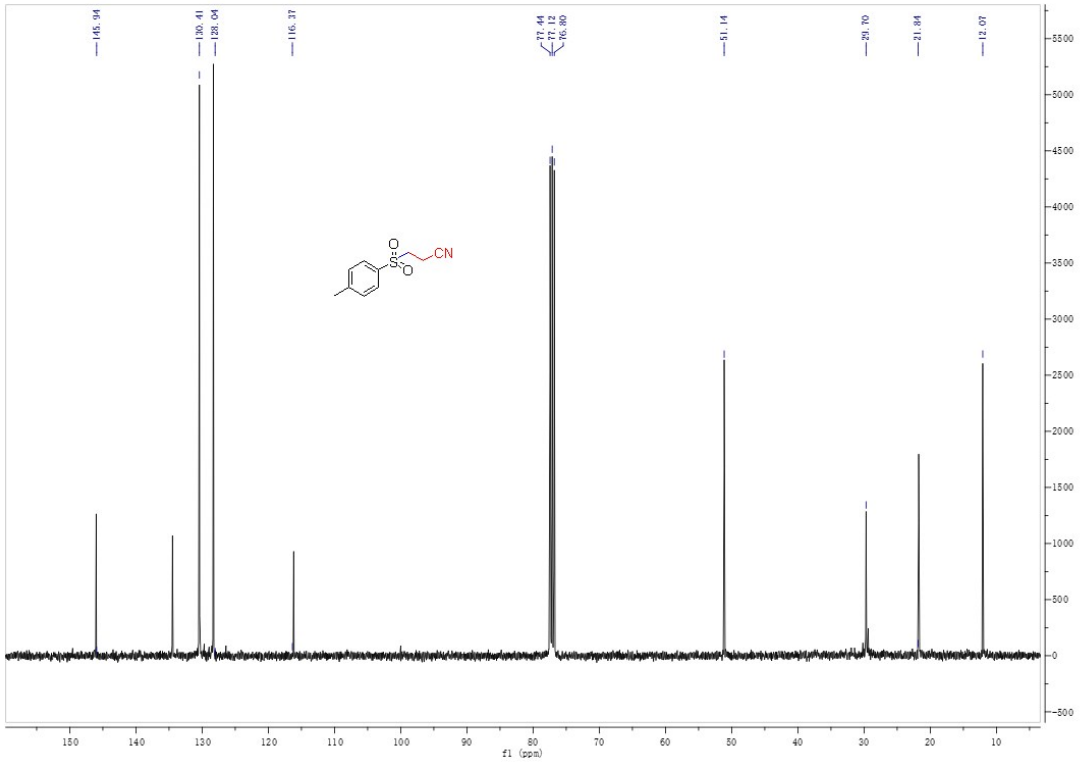
(5) **3bb**: R. M. Ross, *J. Am.* Chem. *Soc.,* 1949, **71**, 3458.

1a 4-methylbenzenesulfonohydrazide



3aa 3-tosylpropanenitrile





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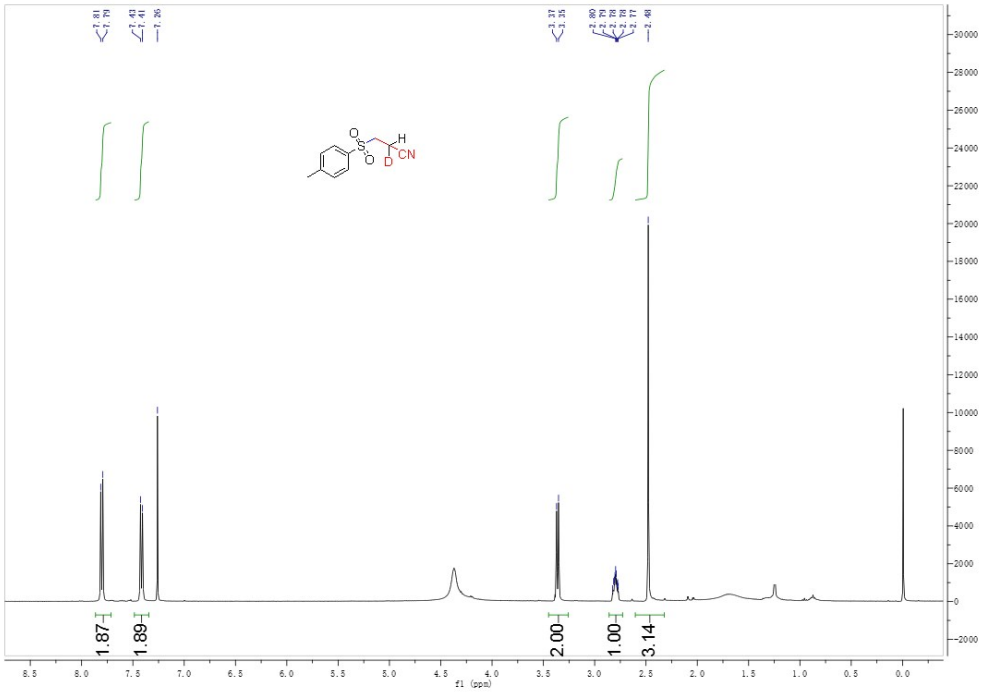
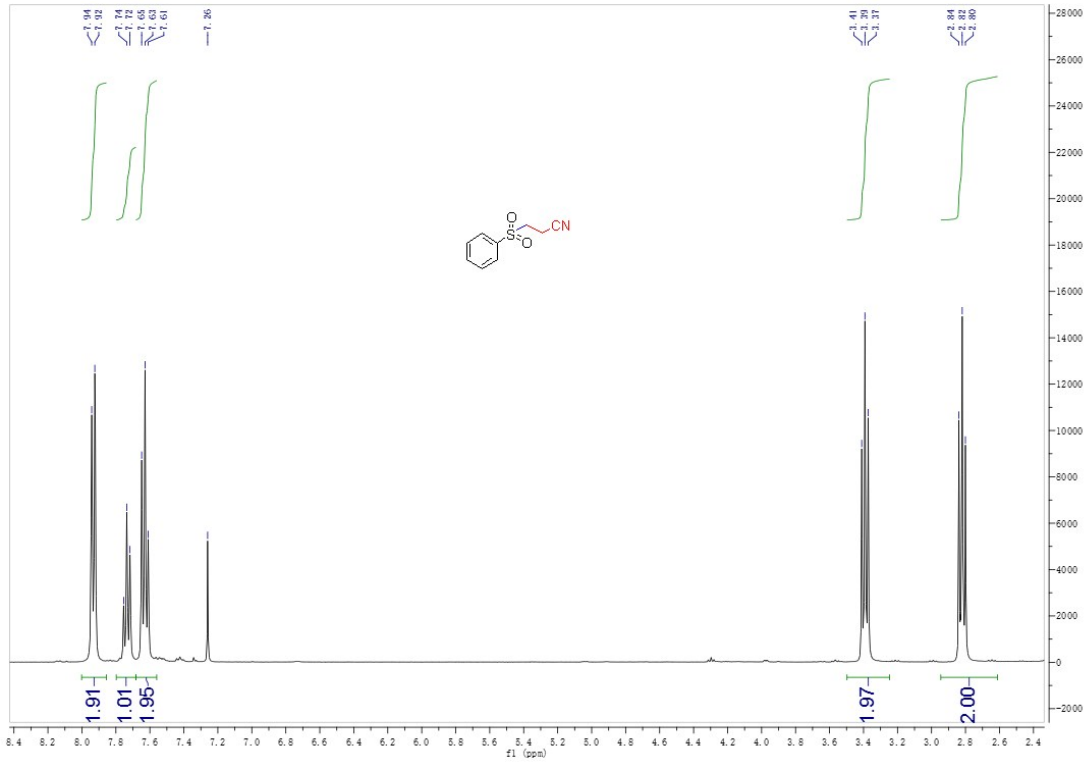
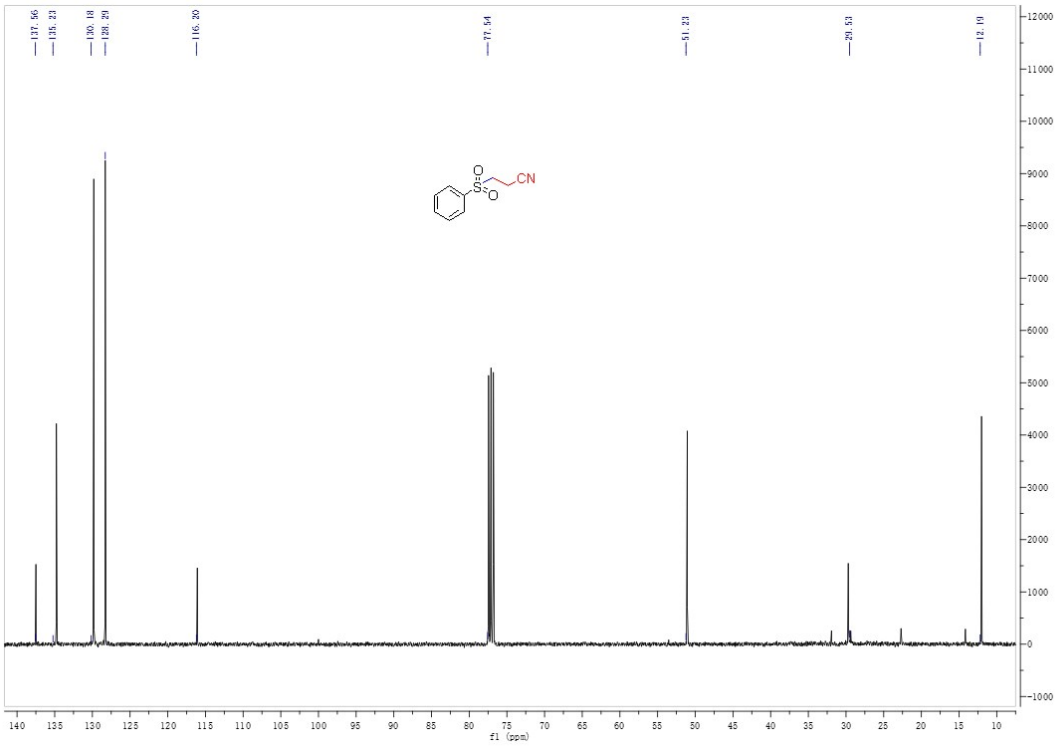


3ba 3-(phenylsulfonyl)propanenitrile

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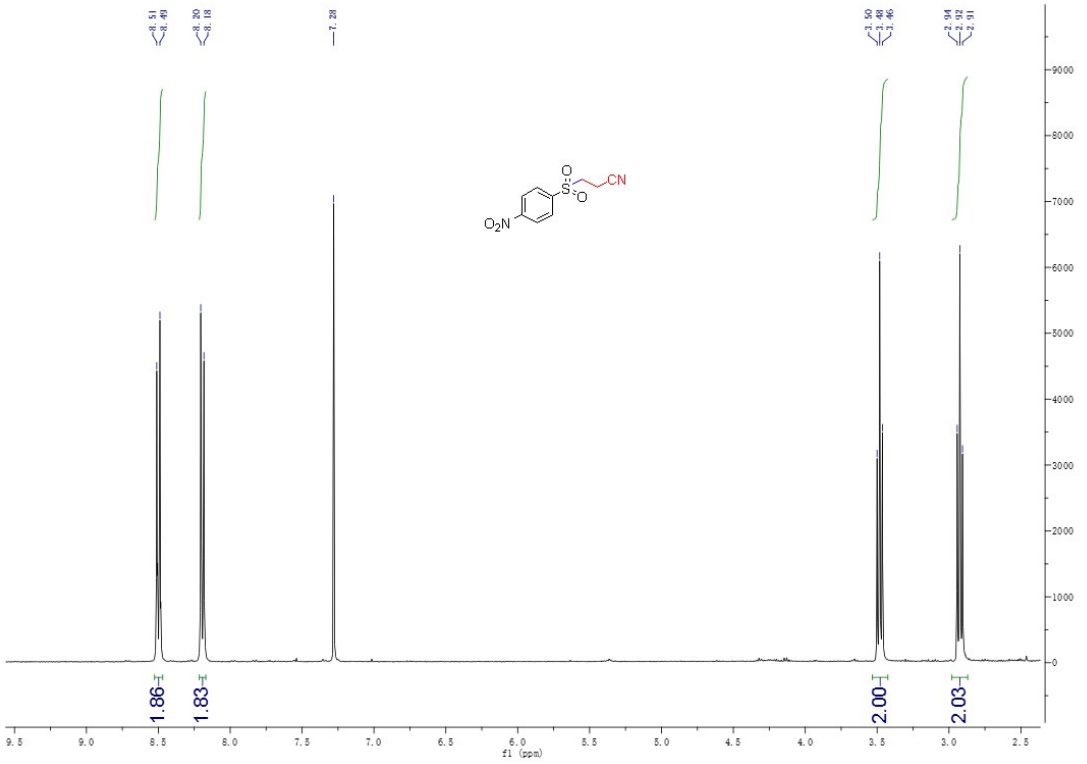
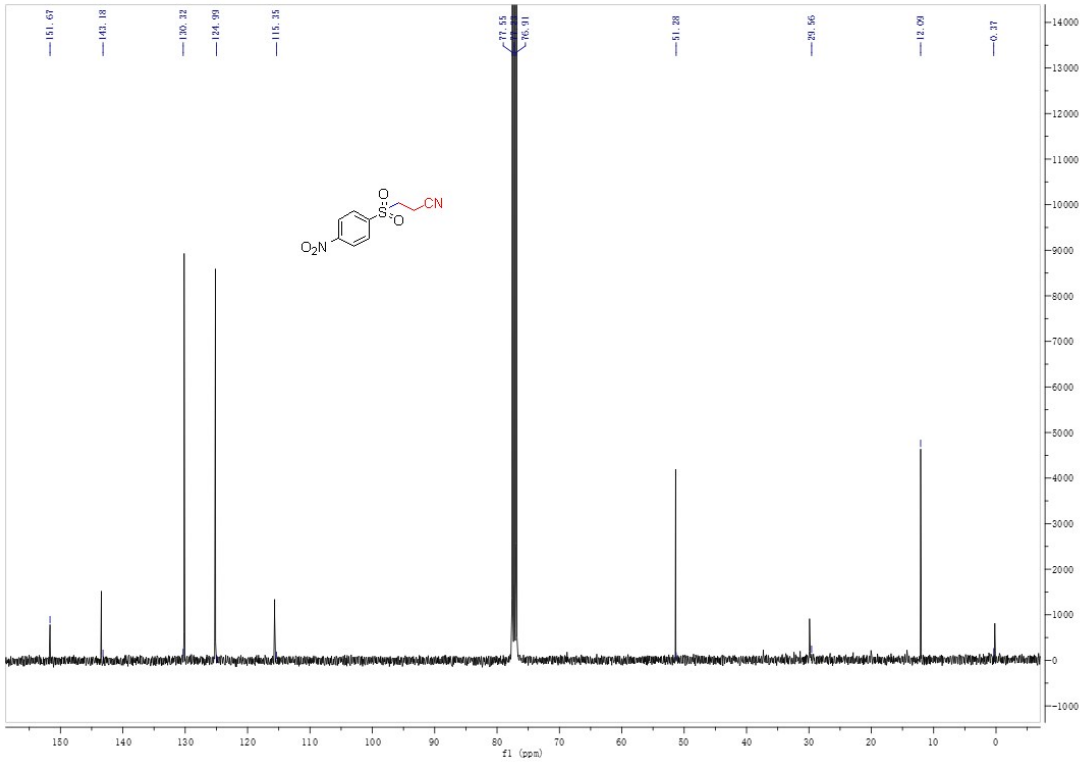
O
S
O
CN
f1 (ppm)

3ca 3-((4-nitrophenyl)sulfonyl)propanenitrile





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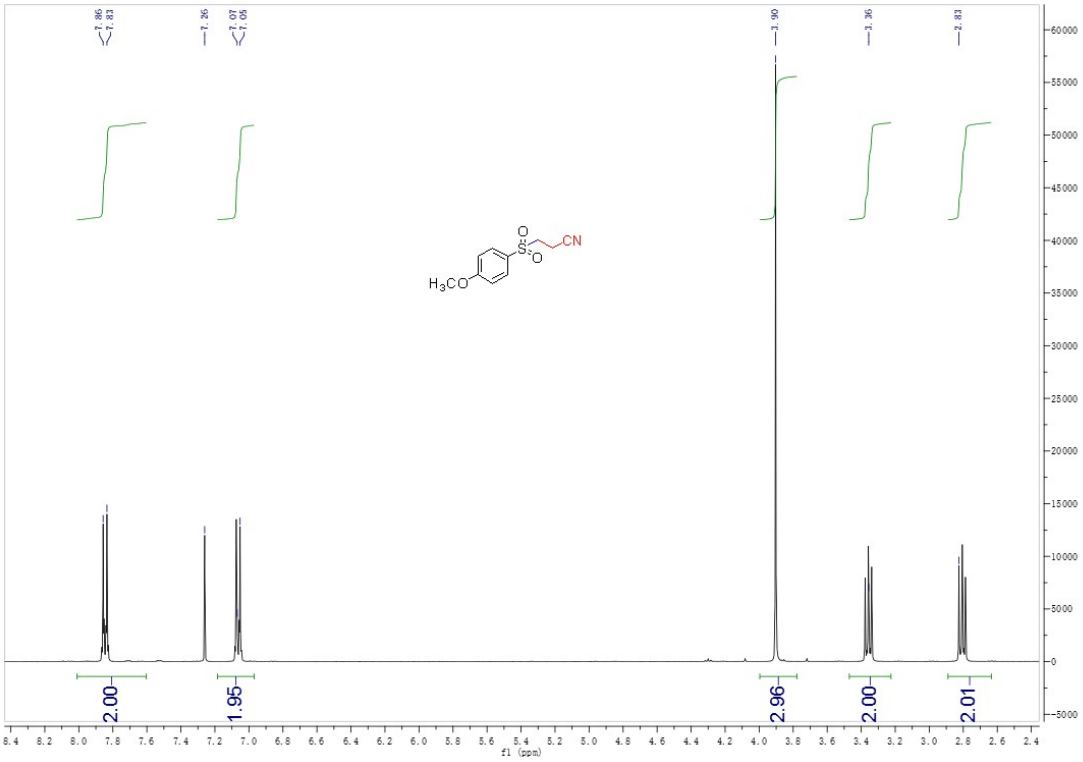

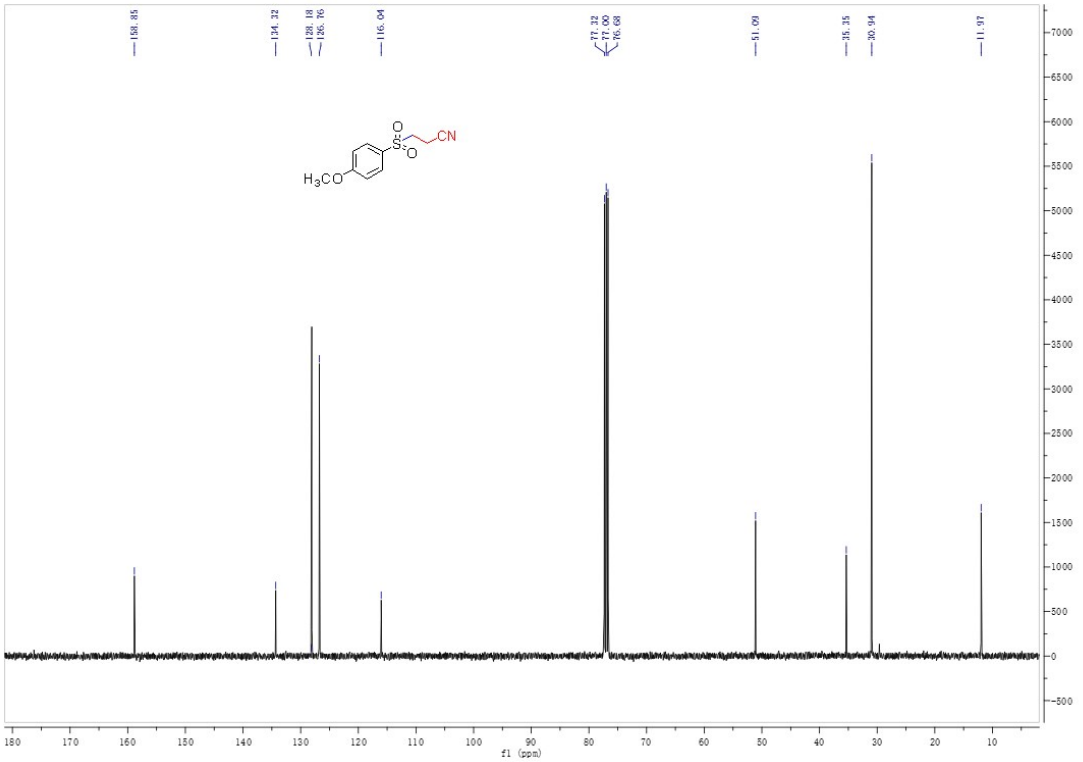

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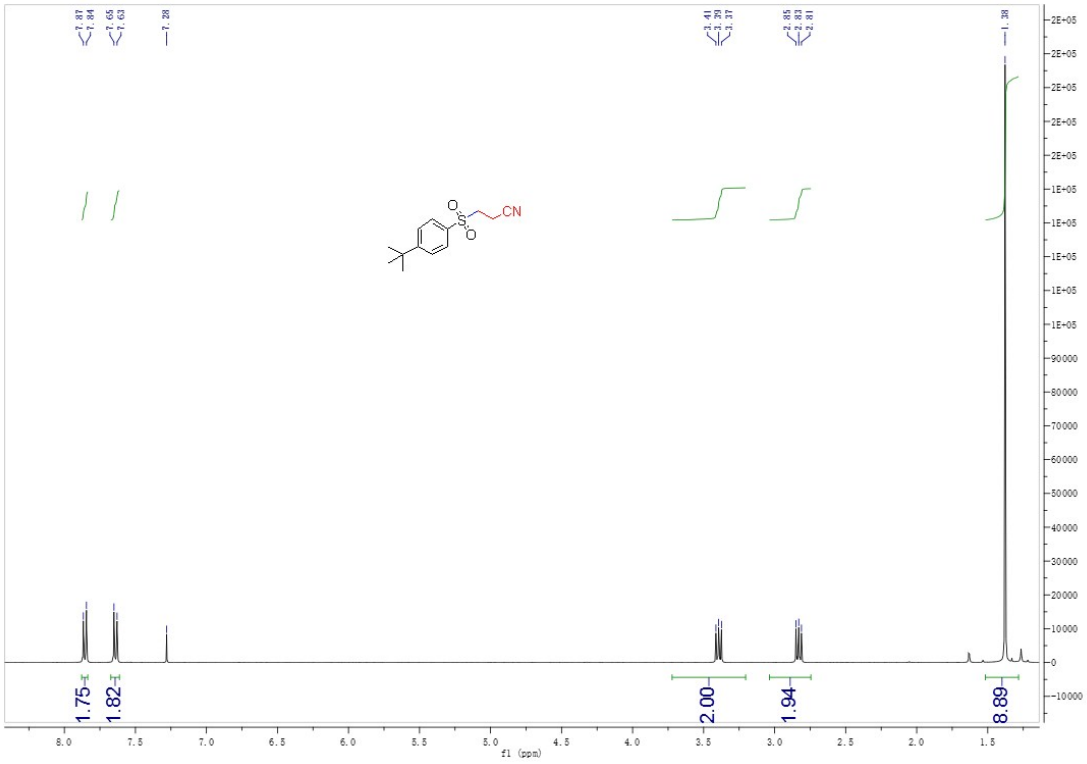
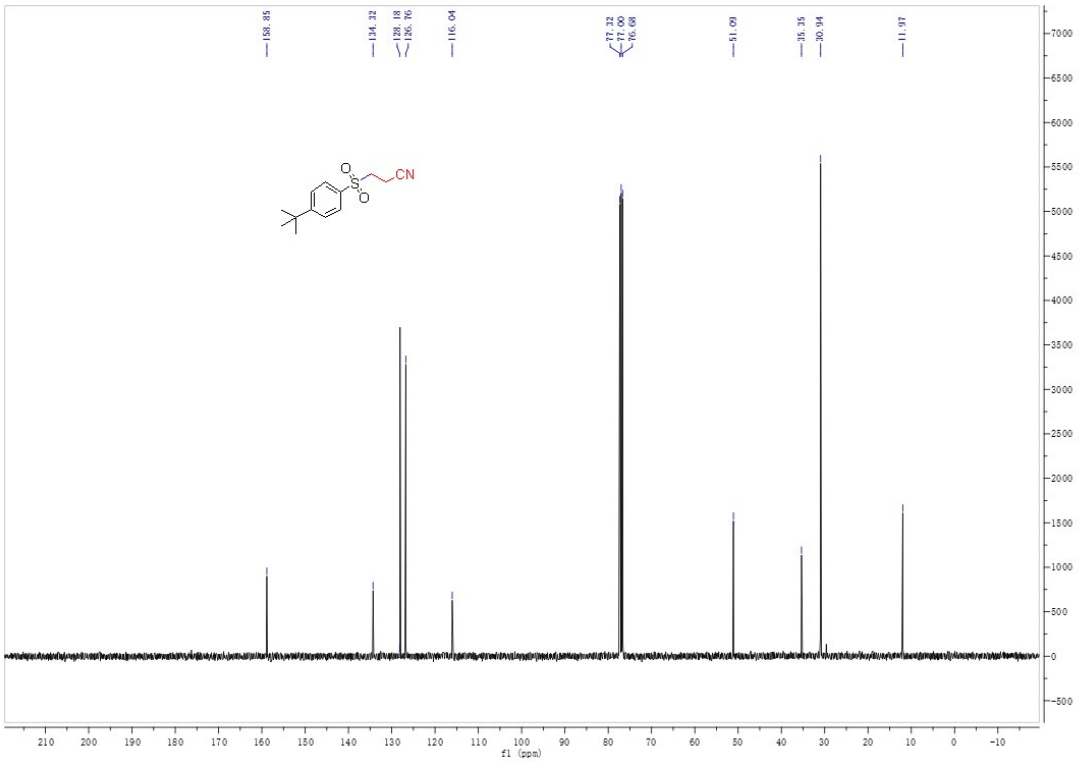
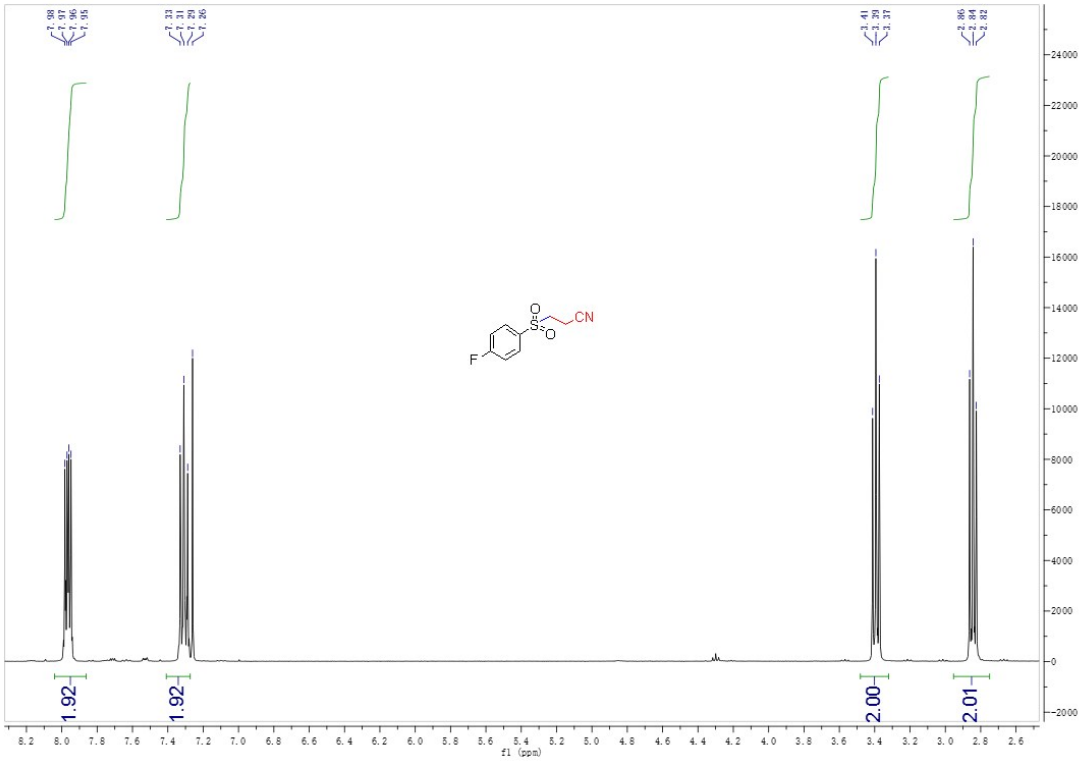
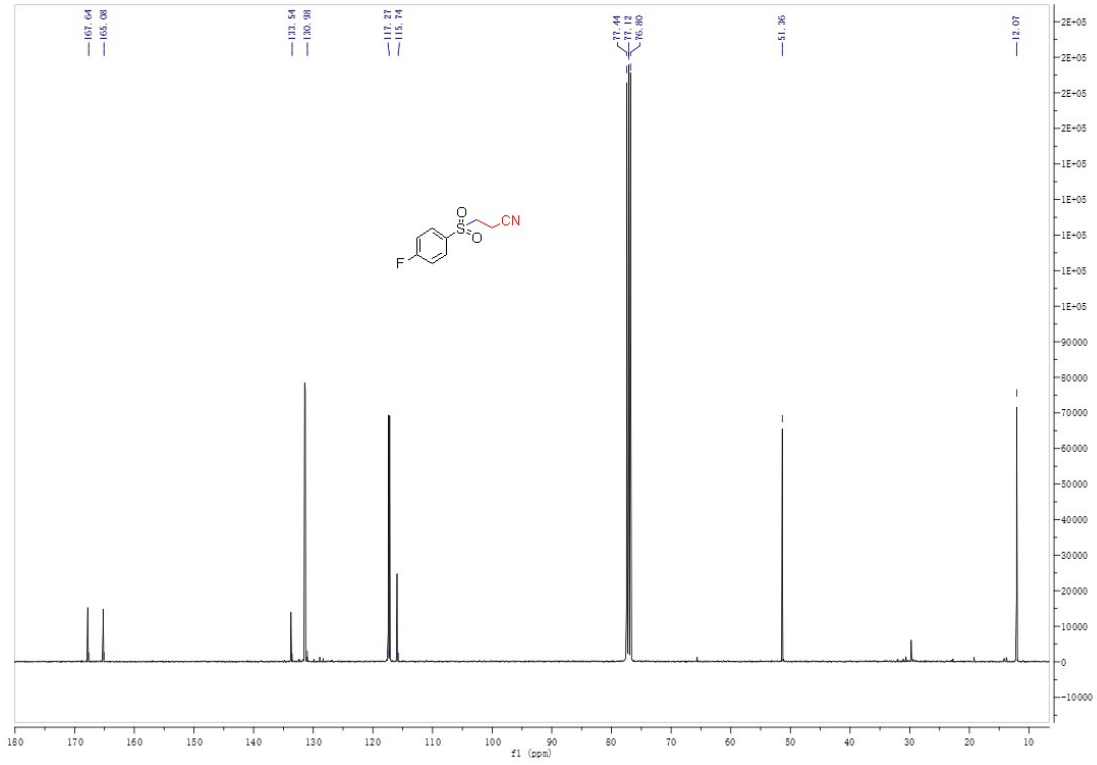


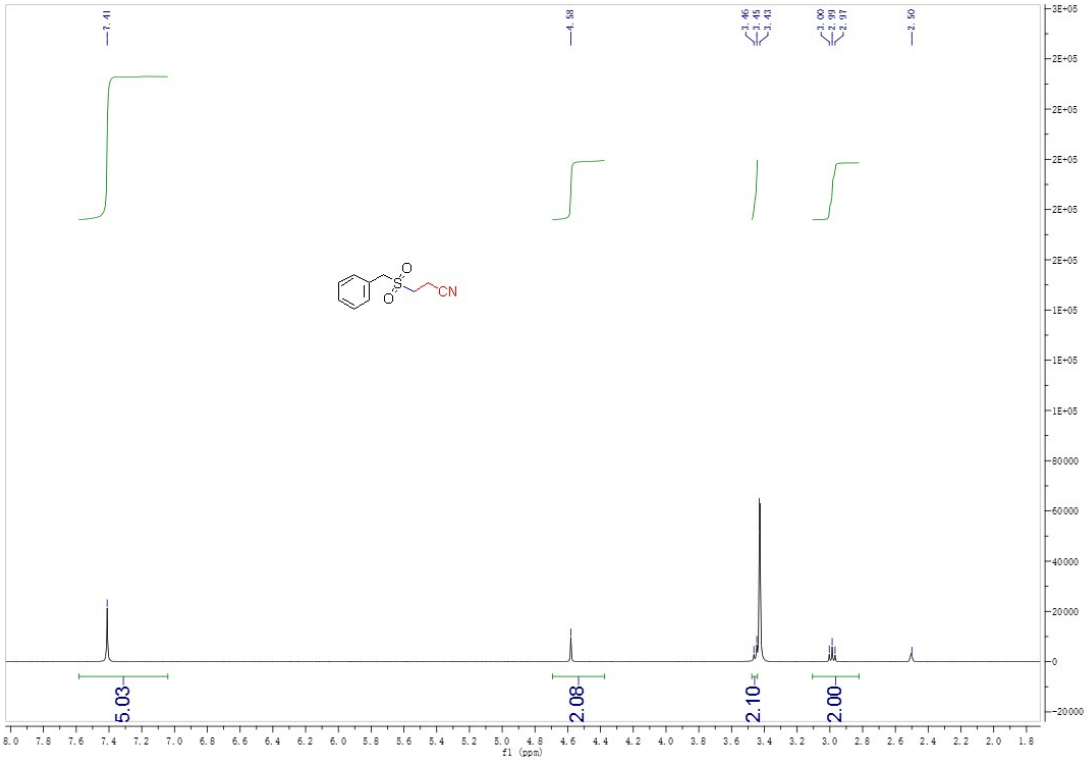


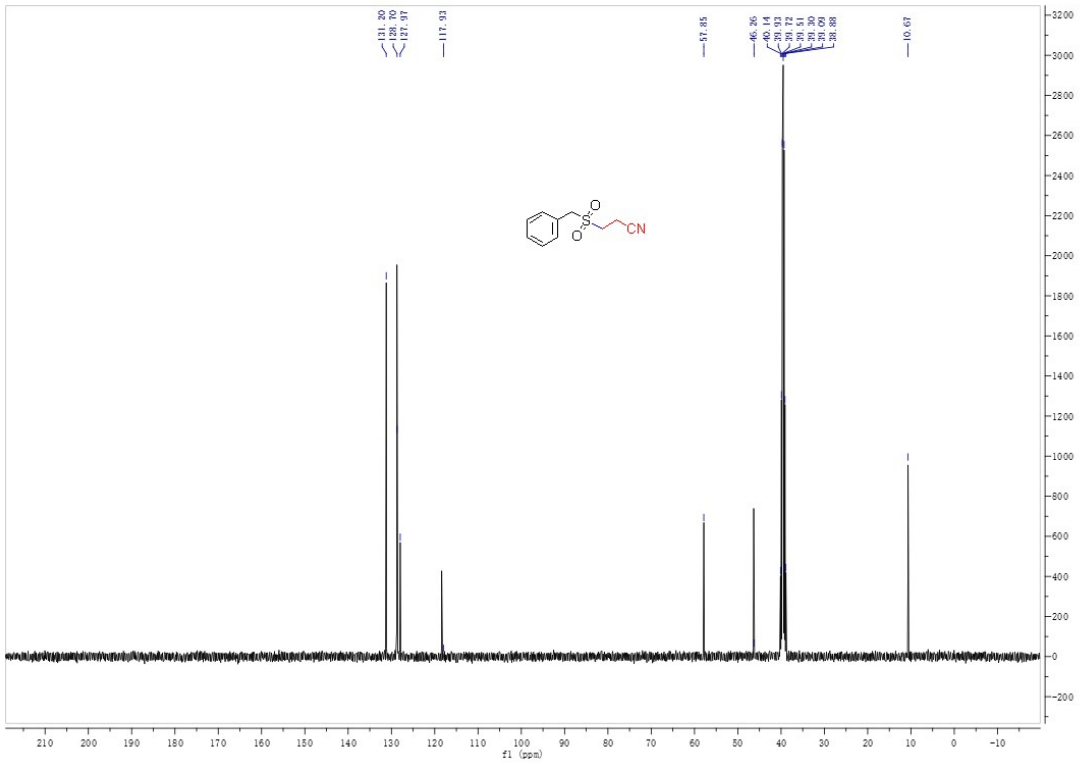
3fa 3-((4-fluorophenyl)sulfonyl)propanenitrile



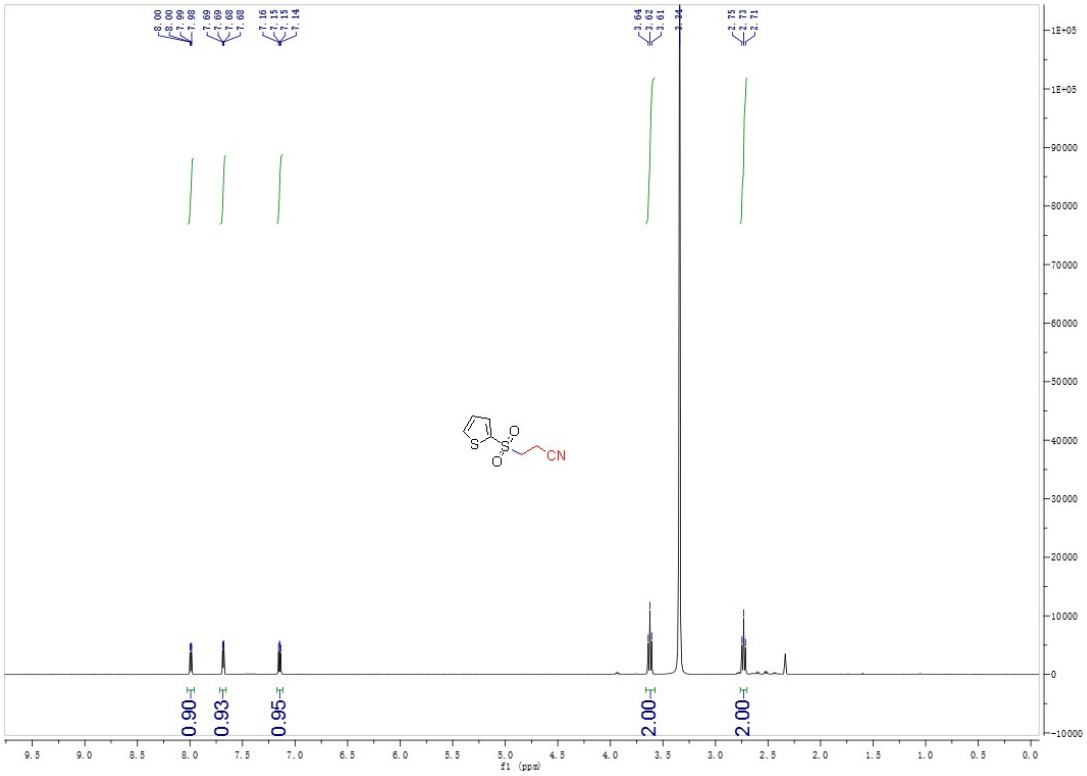


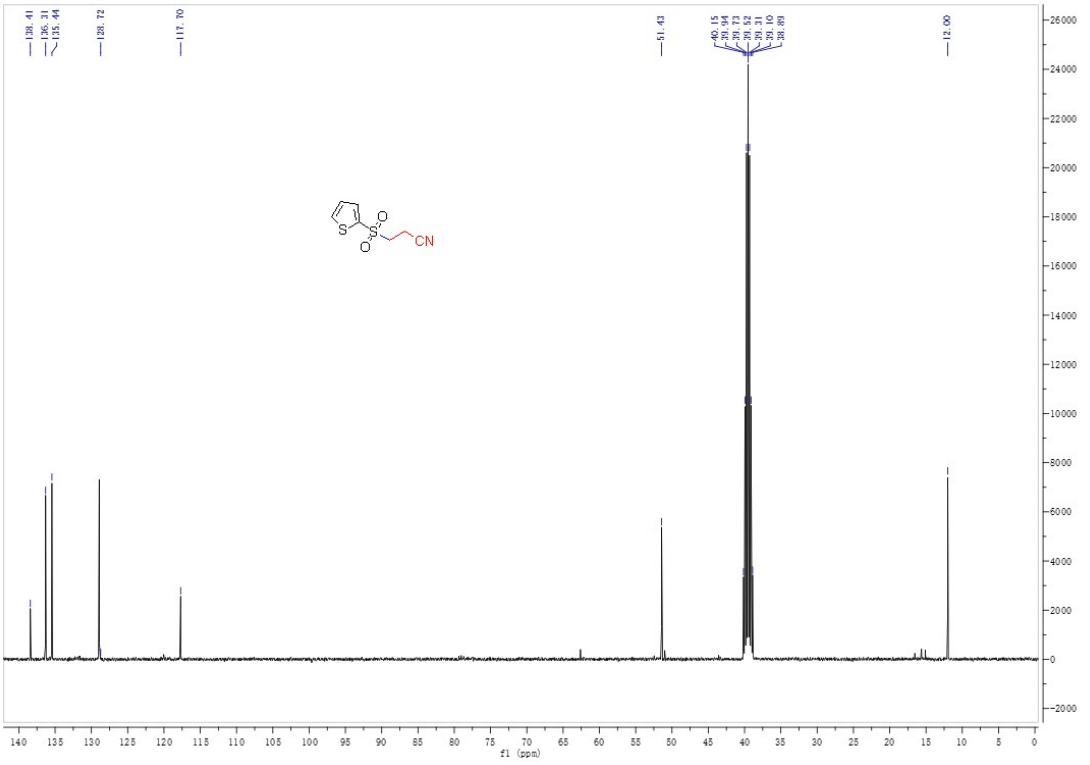
3ga 3-(benzylsulfonyl) propanenitrile



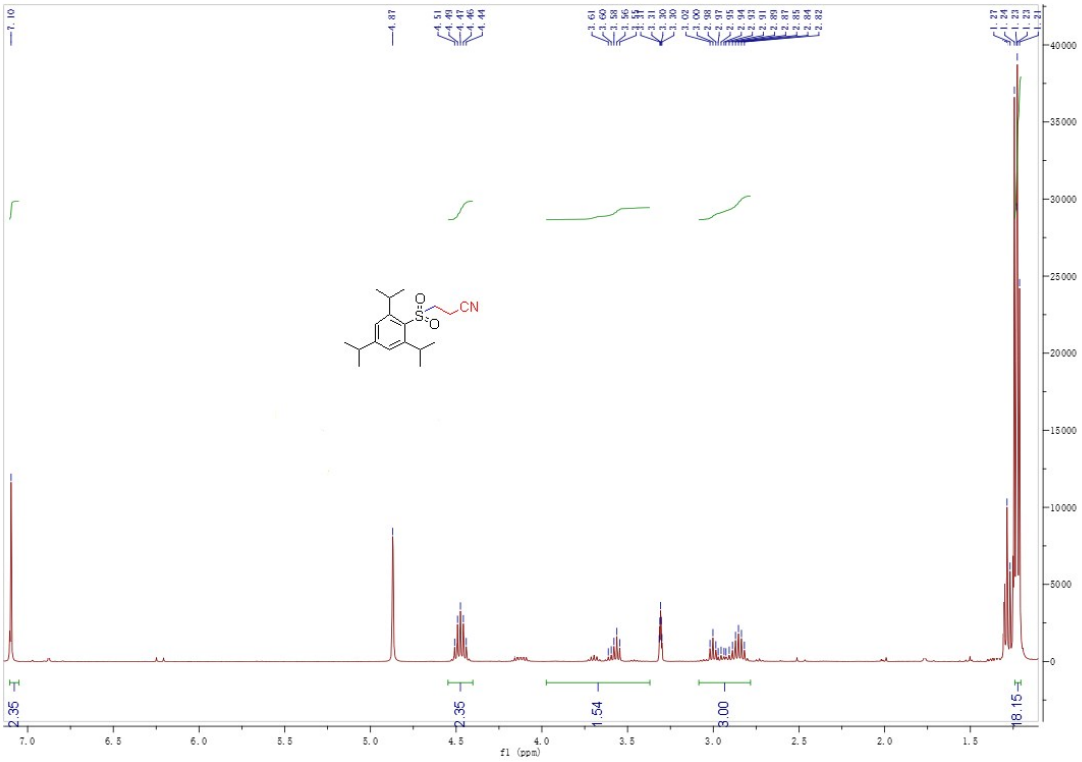


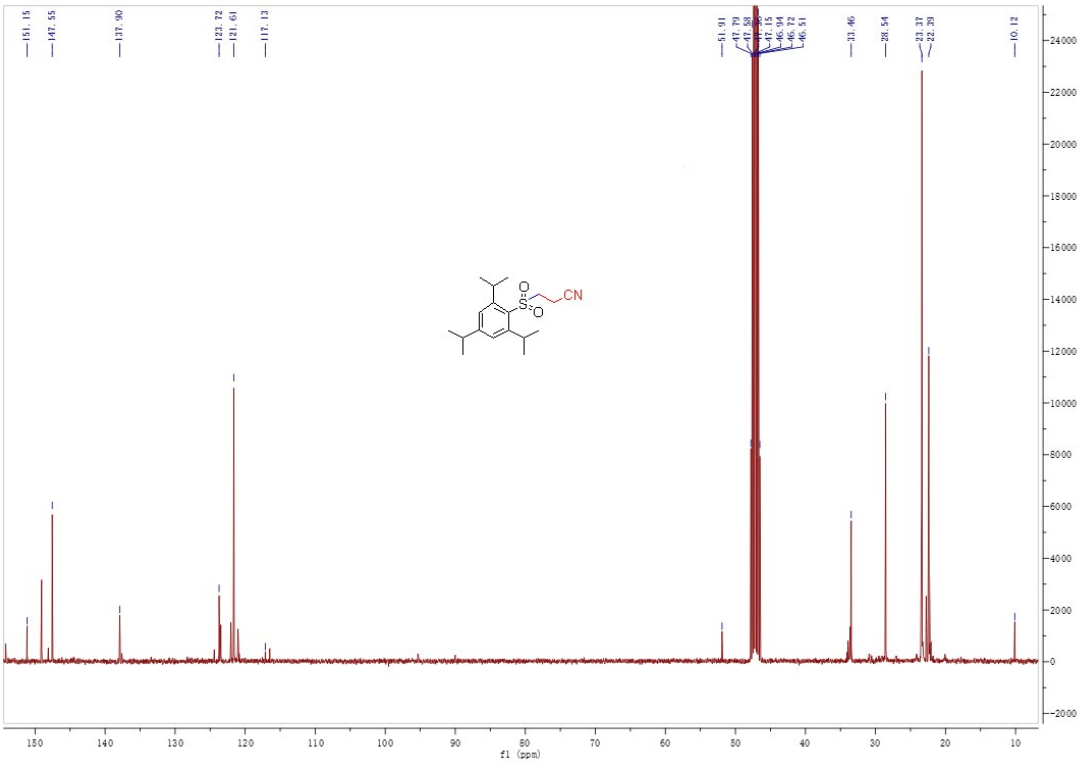
3ha 3-(thiophen-2-ylsulfonyl) propanenitrile



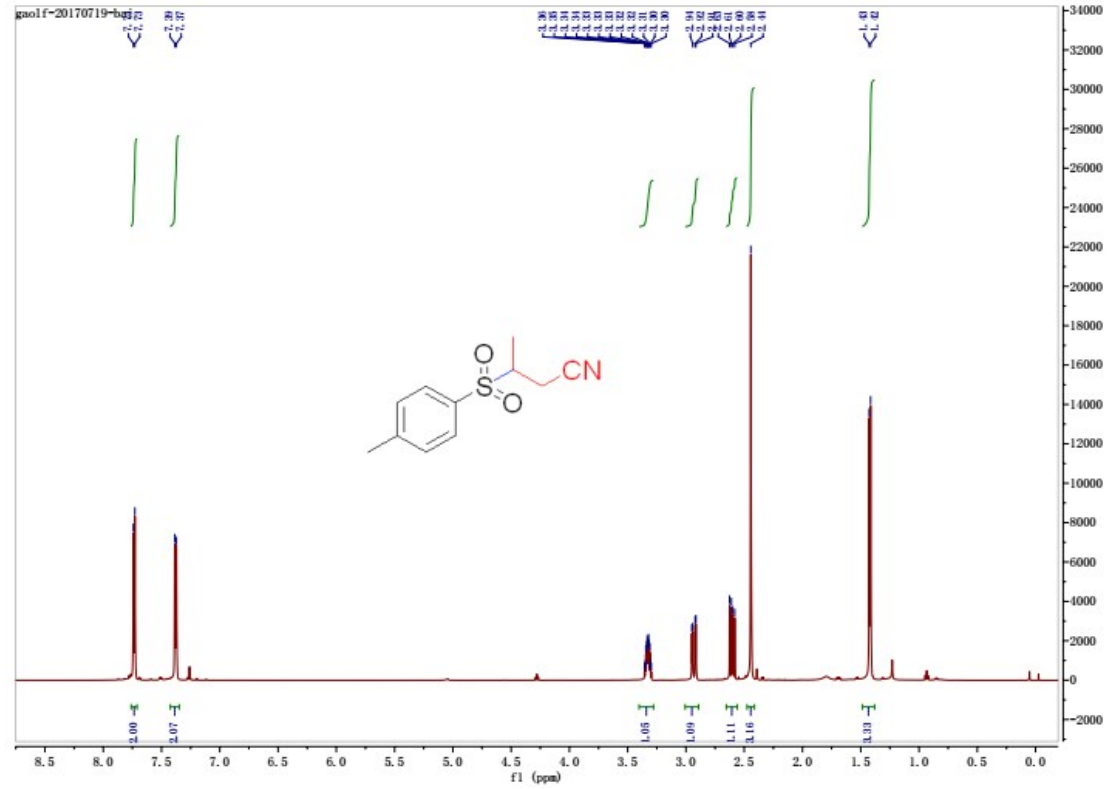


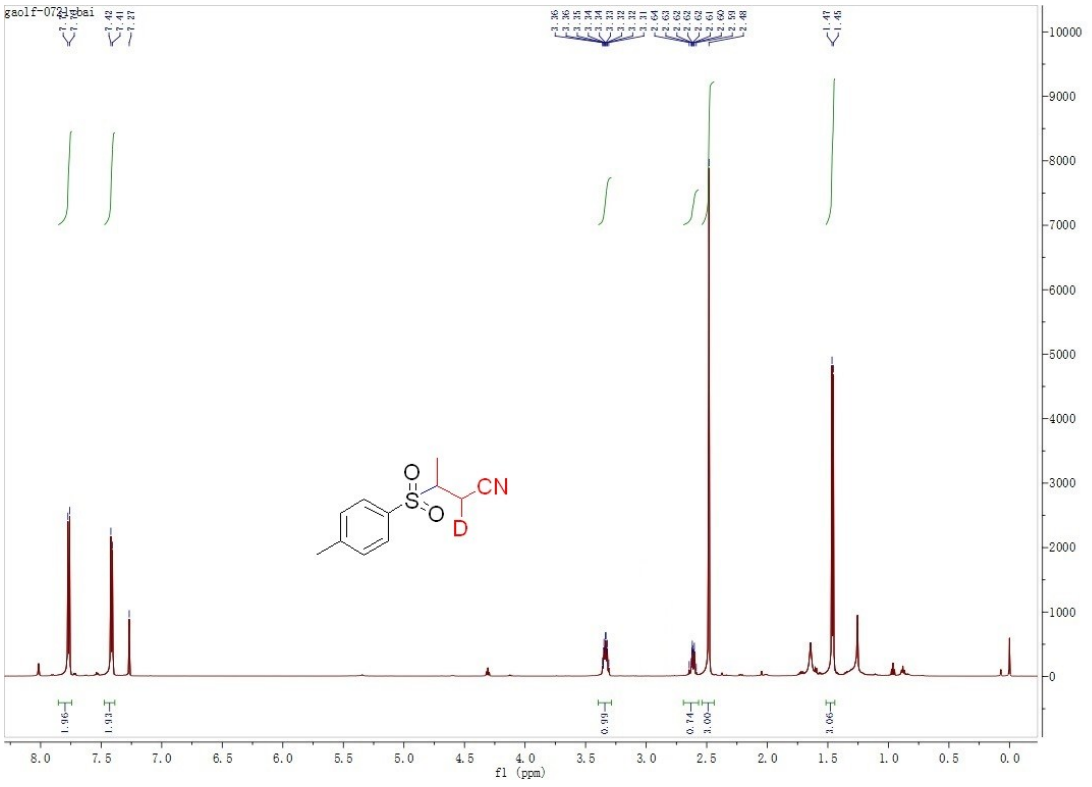
3ia 3-((2,4,6-triisopropylphenyl) sulfonyl) propanenitrile

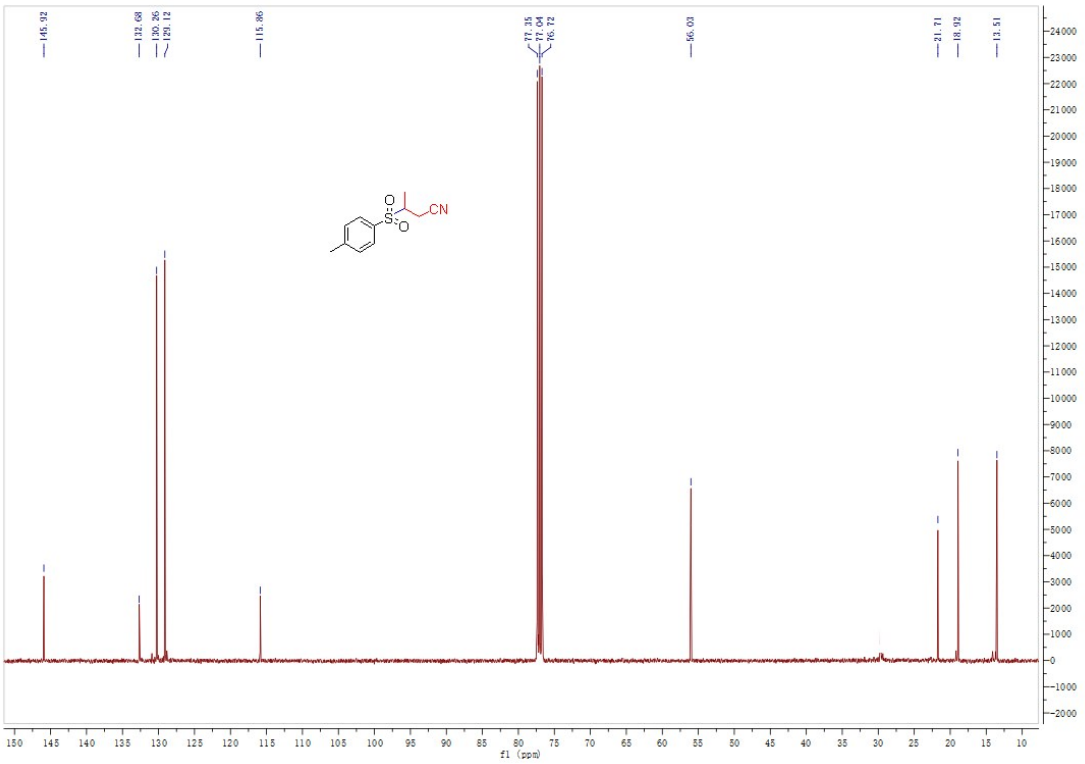




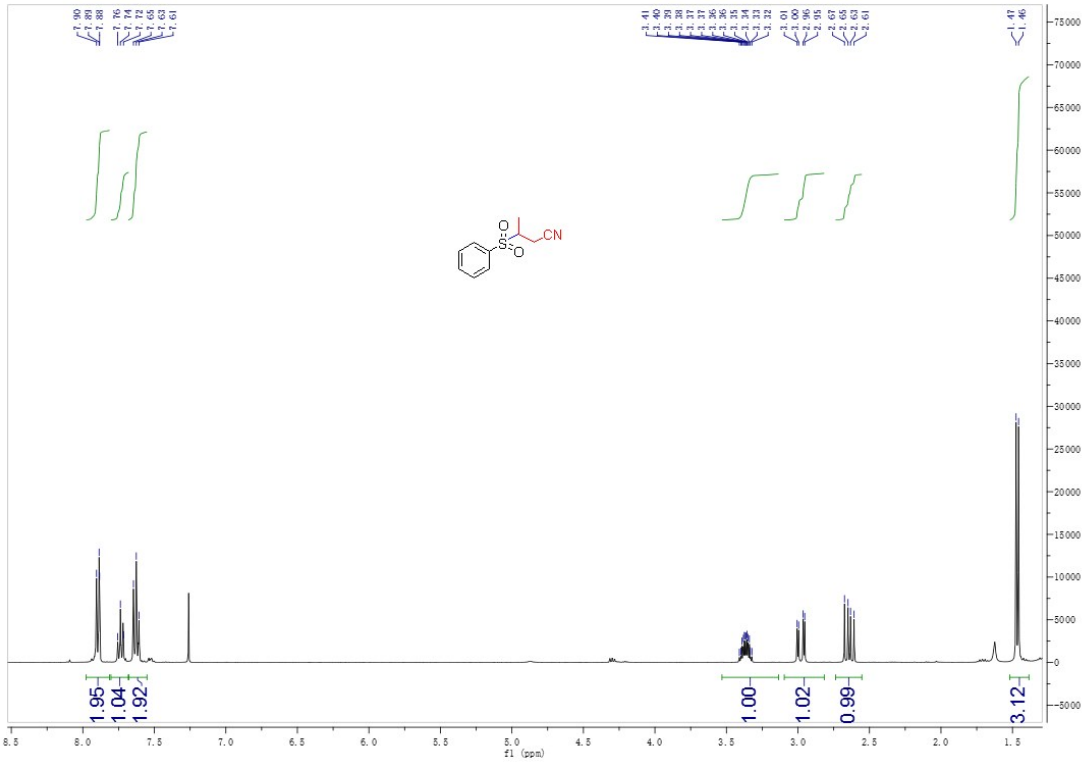
3ab 3-tosylbutanenitrile

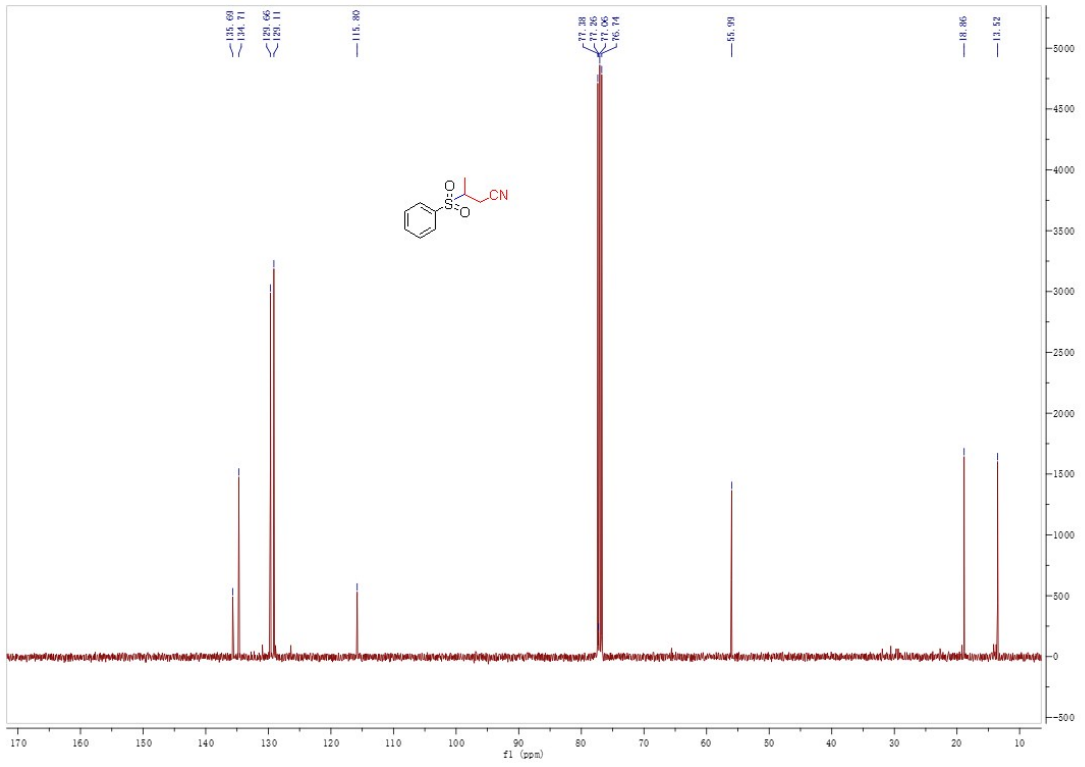




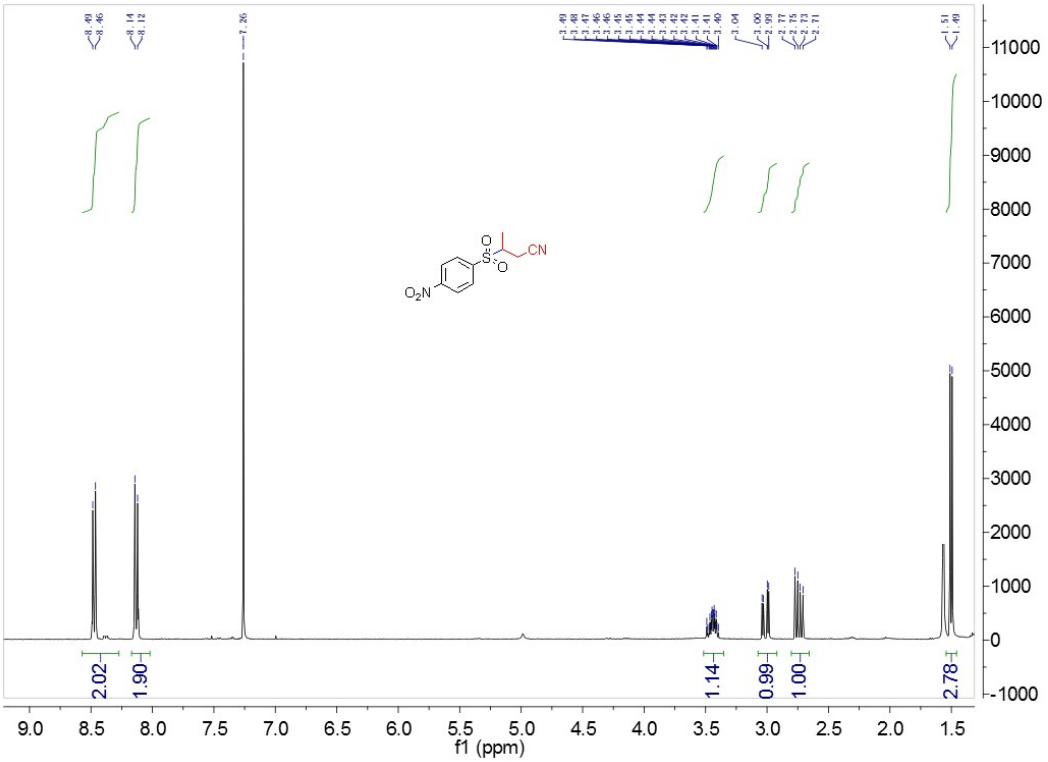

145.92
132.68
130.26
129.12
115.86
77.35
77.04
76.72
56.03
21.71
18.92
13.51
CN
O
S
O
f1 (ppm)

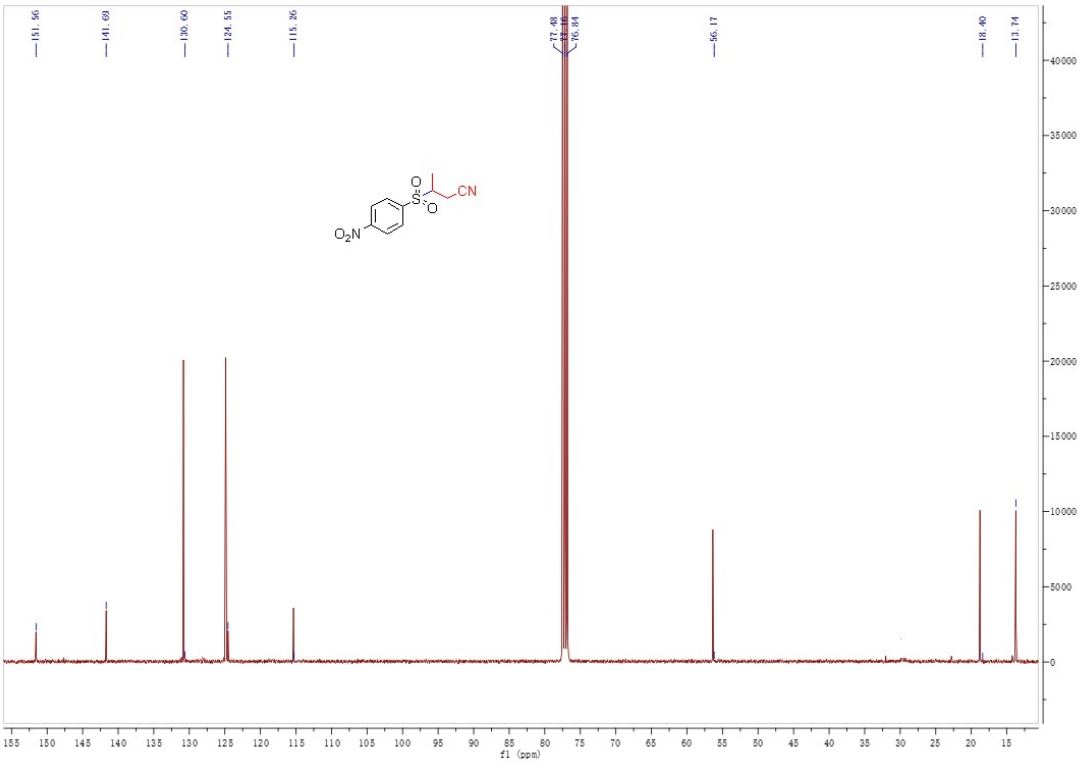
3bb 3-(phenylsulfonyl)butanenitrile



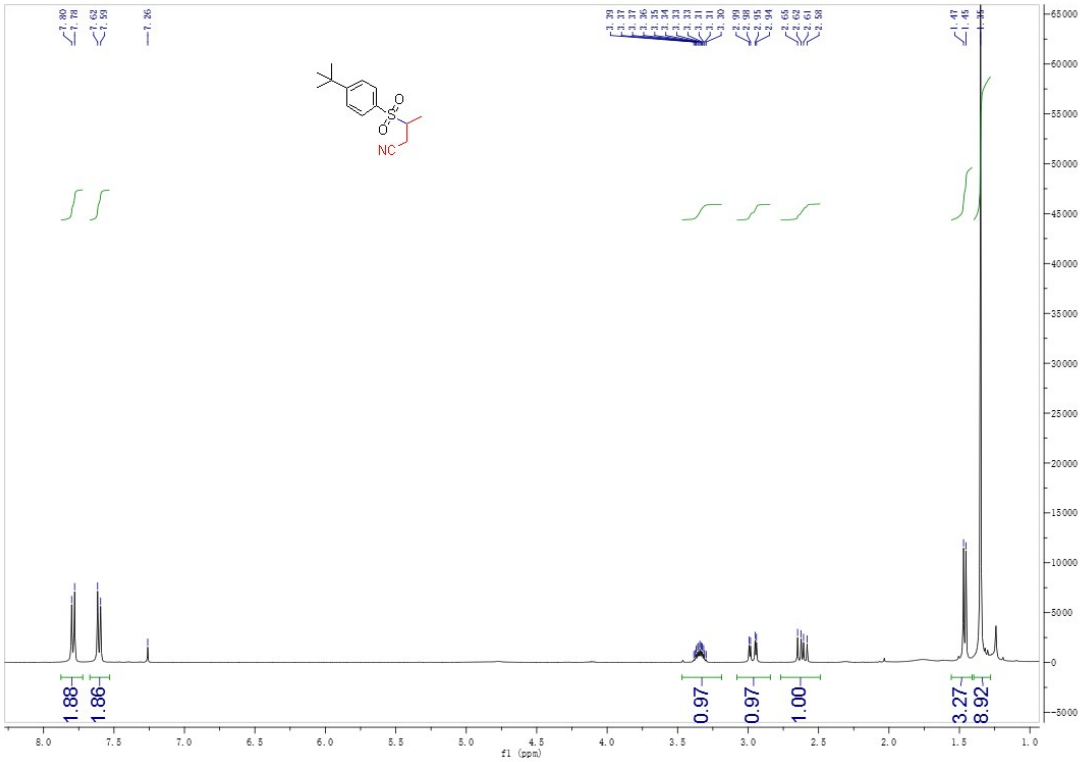


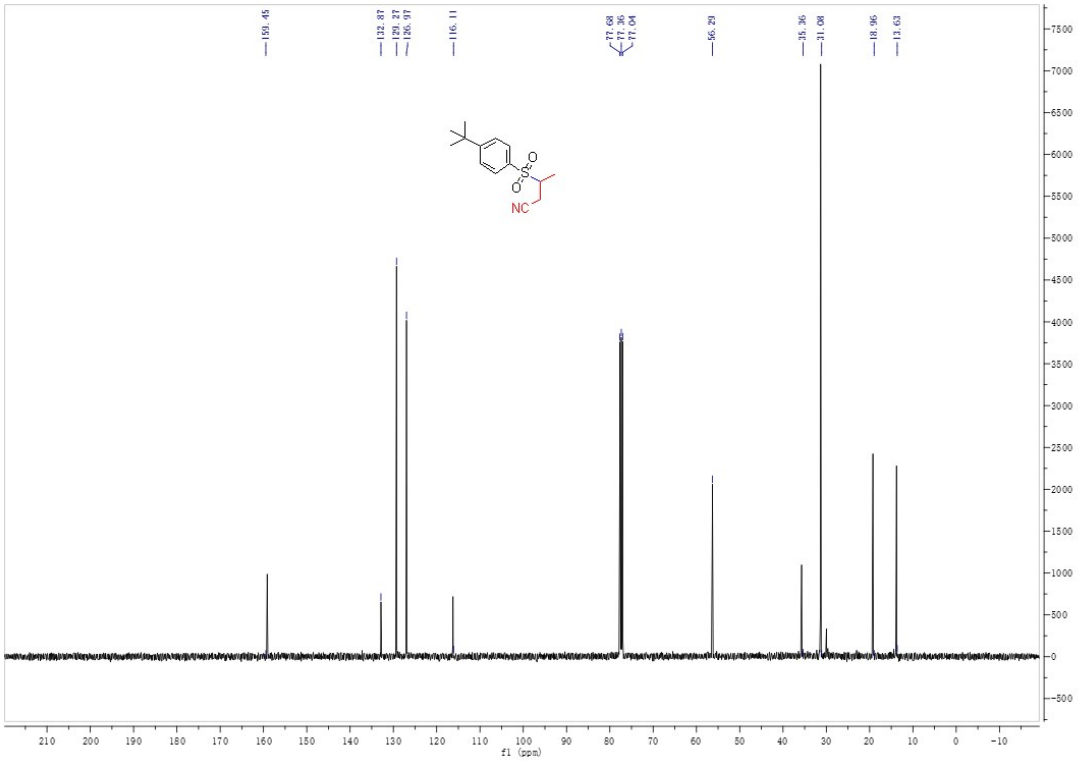
3cb 3-((4-nitrophenyl) sulfonyl) butanenitrile



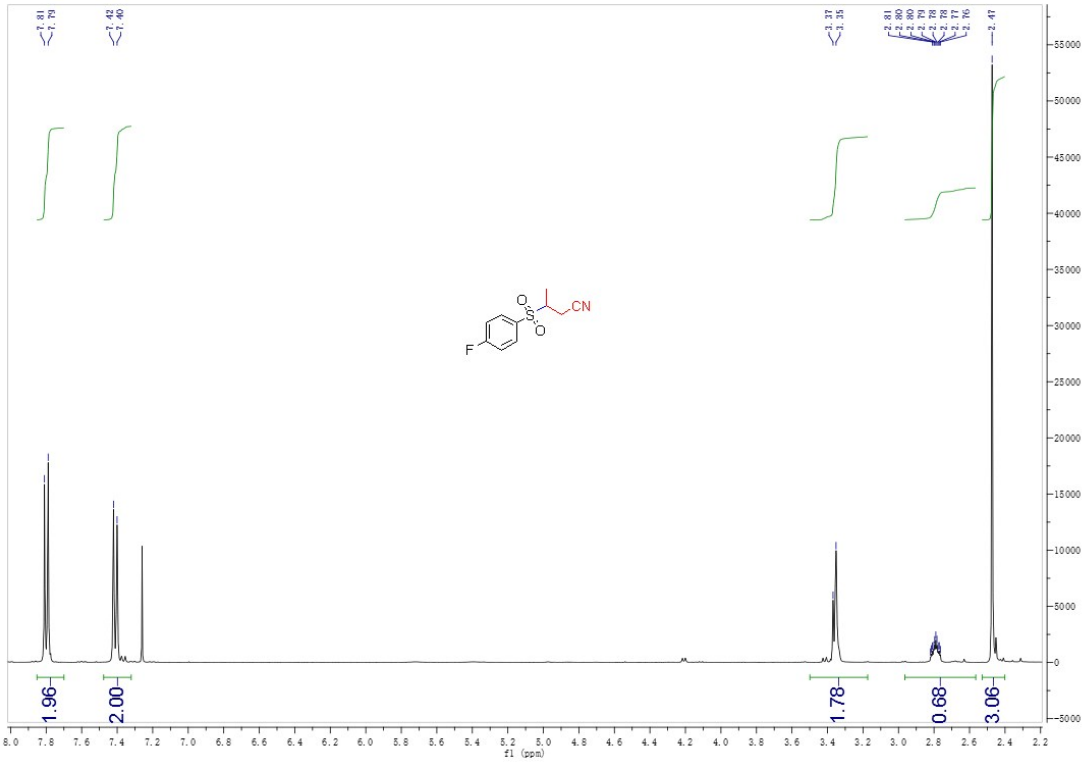


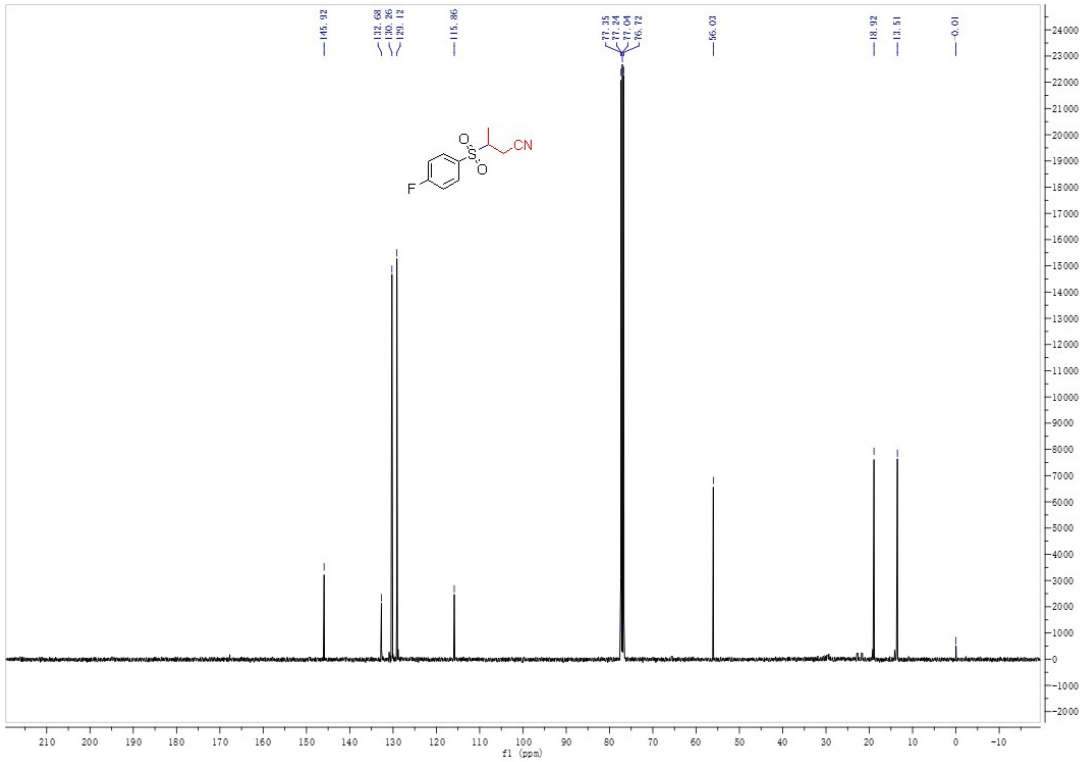
3eb 3-((4-(tert-butyl)phenyl)sulfonyl)butanenitrile



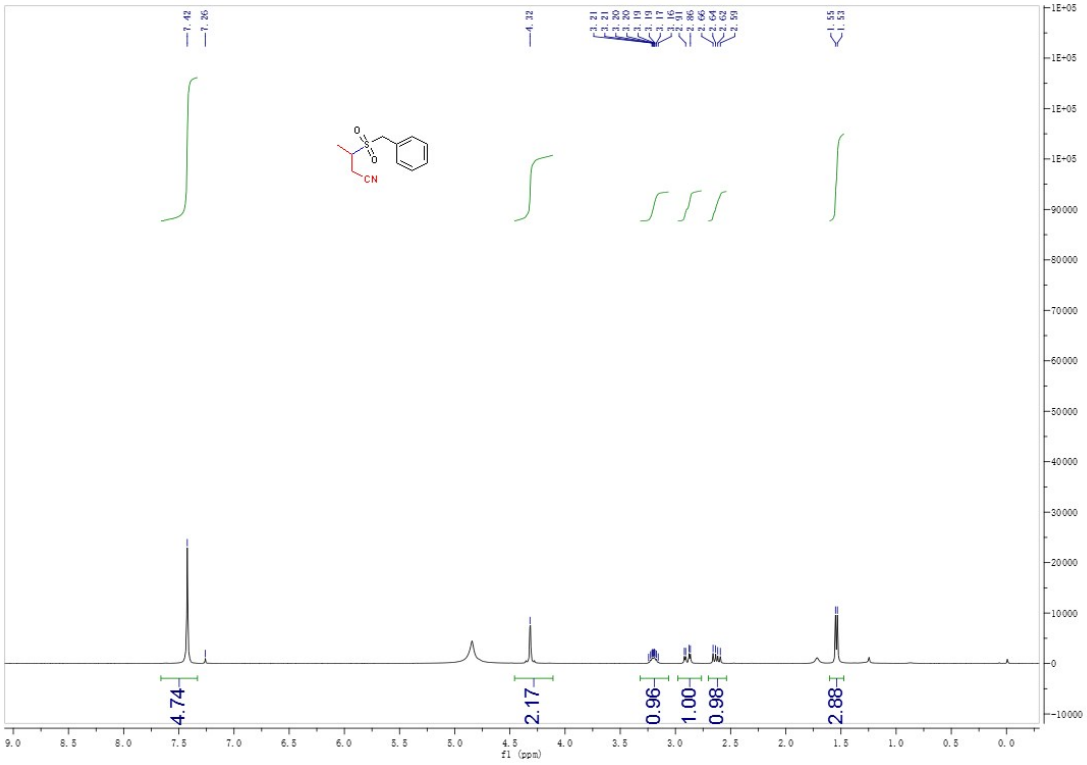


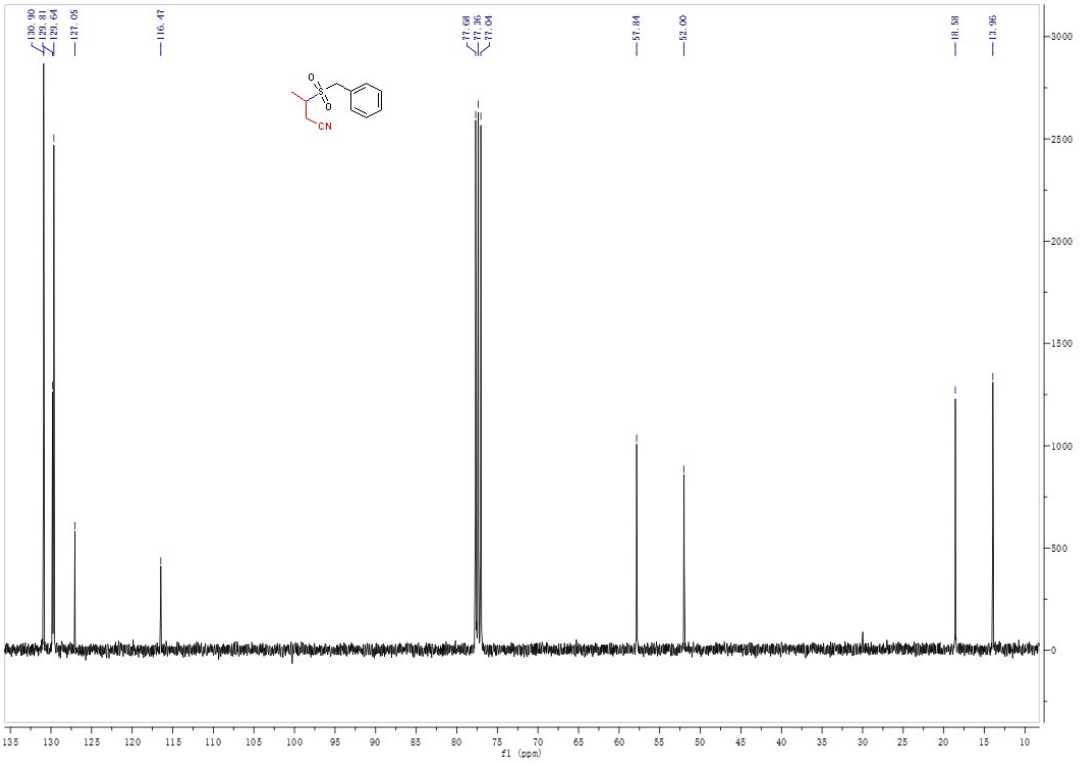
3fb 3-((4-fluorophenyl) sulfonyl)butanenitrile



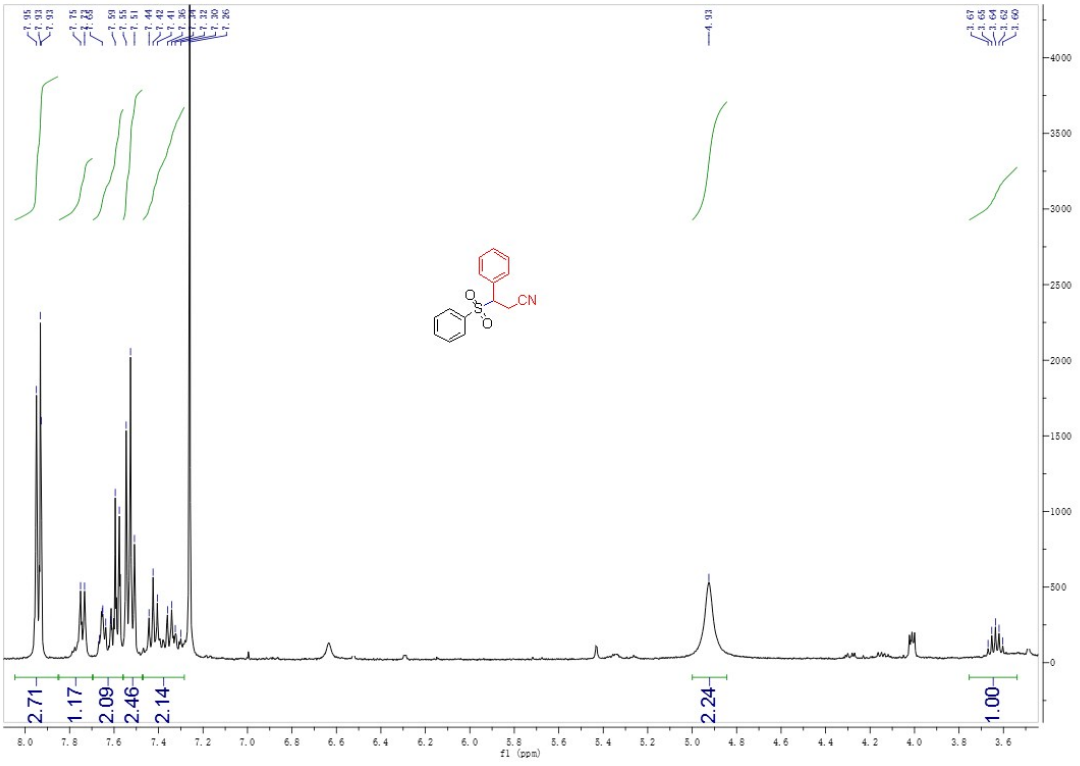


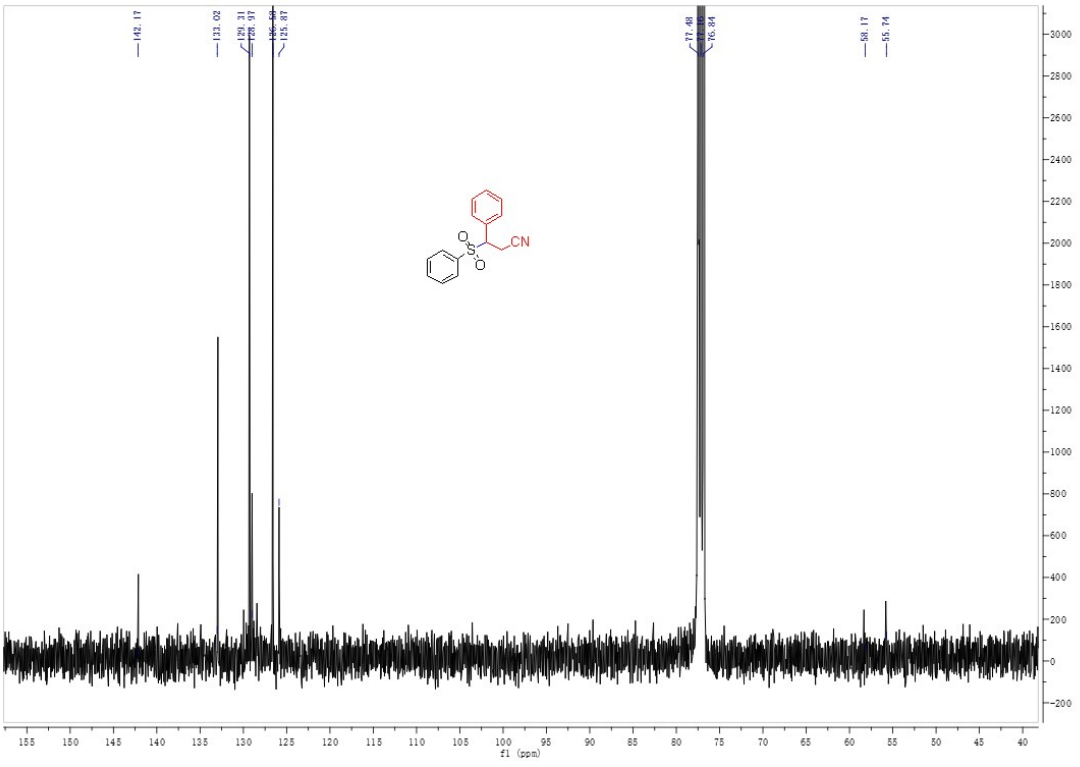
3gb 3-(benzylsulfonyl)butanenitrile





3bc 3-phenyl-3-(phenylsulfonyl)propanenitrile





3fc 3-((4-fluorophenyl)sulfonyl)-3-phenylpropanenitrile