Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

D-glucosamine as a green ligand for copper catalyzed synthesis of aryl sulfones from aryl halides and sulfinic acid salts

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1. General Information

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90^{o}C) and ethyl acetate. Melting points were determined on an X-5 Data microscopic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature with $CDCl_3$ or DMSO-d_6 as solvent unless otherwise noted and tetramethylsilane (TMS) as the internal standard. ^{1}H NMR data were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, m = multiplet and br = broad), coupling constant (*J* values, Hz). ^{13}C NMR data were reported in terms of chemical shift (δ ppm). Mass spectra (EI-MS) were acquired on an Agilent 5975 spectrometer. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates.

2. Experimental Section

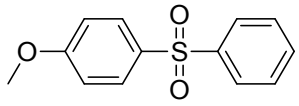
General Procedure for CuI-Catalyzed Coupling of Aryl Halides and Sodium Benzenesulfonate. A mixture of aryl halide (1 mmol), sodium benzenesulfonate (1.2 mmol), copper iodide (0.1 mmol), D-glucosamine(0.2 mmol), and 4 mL of DMSO-H_2O (1:1) in a sealed tube was heated to 100 °C under air. The cooled mixture was partitioned between ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyacetate twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. After drying with anhydrous $MgSO_4$ overnight, the liquid was analyzed by GC-MS. The residue was concentrated under reduced pressure to afford the desired product without further purification. All compounds were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy, which are consistent with those reported in the literature.

General procedure for the catalyst recycling experiment.

To check if the catalyst is recyclable, the C-S coupling reaction was repeated five times with the same catalyst sample, which was recovered after each reaction. After completion of the reaction under the optimal conditions reaction, a simple filtration was sufficient to separate the catalyst solution from the products when the reaction was cool down. The catalyst was washed with ethyl acetate twice and was dried for 6 h at 75 °C. Then the separated catalyst was recharged with fresh substrate for the next run under the same reaction conditions.

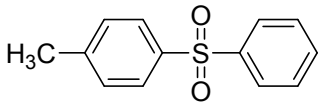
3. Characterization of the Products

1-(4-Methoxyphenylsulfonyl)benzene 3a[1]:



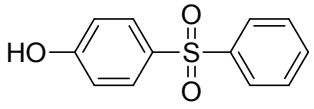
white solid; mp 90-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.80 (m, 4H), 7.47-7.41 (m, 3H), 6.90-6.88 (m, 2H), 3.77 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.37, 141.35, 132.09, 128.89, 128.19, 126.31, 113.51, 54.64. GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O_3S$: 248.0, found: 248.

1-(*p*-Tolylsulfonyl)benzene 3b[2]:



white solid; mp 125-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 2H), 7.77-7.75 (m, 2H), 7.48-7.42 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 143.15, 140.90, 137.56, 131.98, 128.89, 128.20, 126.68, 126.46, 20.55. GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O_2S$: 232.0, found: 232.

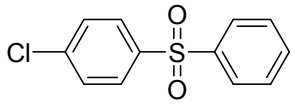
4-(Benzenesulfonyl)phenol 3c[3]:



brown solid; mp 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51 (br s, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 7.56-7.47 (m, 3H), 7.82 (d, *J* = 8.0 Hz, 2H),

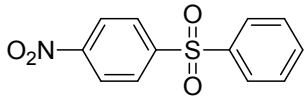
7.91 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.27, 131.84, 129.13, 128.18, 126.28, 115.08. GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_{10}O_3S$: 234.0, found: 234.

1-(4-Chlorophenylsulfonyl)benzene 3d[1]:



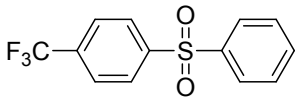
white solid; mp 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.88 (m, 4H), 7.58-7.46 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.09, 140.05, 139.85, 133.47, 129.60, 129.42, 129.10, 127.60. GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9ClO_2S$: 252.0, found: 252.

1-(4-Nitrophenylsulfonyl)benzene 3e[1]:



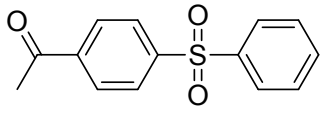
yellow solid; mp 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36-8.34 (m, 2H), 8.15-8.13 (m, 2H), 7.99-7.97 (m, 2H), 7.67-7.63 (m, 1H), 7.58-7.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.33, 147.36, 139.87, 134.15, 129.71, 128.99, 128.05, 124.55. GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9NO_4S$: 263.0, found: 263.

1-(Trifluoromethyl)-4-(phenylsulfonyl)benzene 3f[1]:



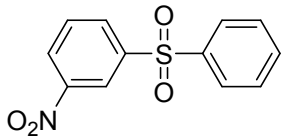
white solid; mp 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 4 Hz, 2H), 7.97-7.96(m, 2H), 7.76 (d, J = 4 Hz, 2H), 7.62-7.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.30, 140.65, 135.00, 134.70, 133.70, 129.53, 128.21, 127.91, 126.45, 126.42. GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_9F_3O_2S$: 286.0, found: 286.

1-(4-(phenylsulfonyl)phenyl)ethanone 3g[3]:



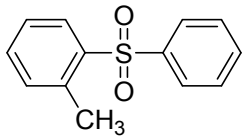
white solid; mp 90-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.04 (m, 4H), 7.98-7.96 (m, 2H), 7.61 (dd , *J* = 8.3 , 6.5Hz, 1H), 7.54 (m, 2H), 2.64(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 145.4, 140.7, 140.3, 133.6, 130.9, 129.4, 129.0, 128.0, 127.8, 115.3, 26.8. GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O_3S$: 260.0, found: 260.

3-Nitrol-(phenylsulfonyl)benzene 3h[1]:



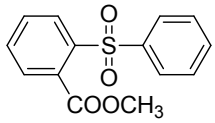
yellow solid; mp 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.35 (d, *J* = 8.2Hz, 1H), 8.22 (d, *J* = 7.8Hz, 1H), 7.93 (d, *J* = 7.5Hz, 2H), 7.67 (t, *J* = 8.0Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.5Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 142.9, 139.0, 133.0, 132.0, 129.7, 128.7, 126.9, 126.6, 121.9. GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_9NO_4S$: 263.0, found: 263.

1-Methyl-2-(phenylsulfonyl)benzene 3i[1]:



white solid; mp 73-75 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (dd, *J* = 1, 1 Hz, 1H), 7.87-7.85 (m, 2H), 7.58-7.55 (m, 1H), 7.51-7.46（m, 3H), 7.41-7.38 (m, 1H), 7.26-7.22 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.41, 138.92, 138.01, 133.57, 132.97, 132.66, 129.45, 129.00, 127.65, 126.46, 20.16. GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O_2S$: 232.0, found: 232.

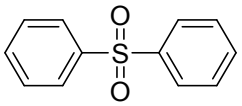
Methyl 2-(phenylsulfonyl)benzoate 3j[1]:



white solid; mp 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18-8.16 (m, 1H), 8.00-7.98 (m, 2H), 7.66-7.52 (m, 6H), 3.94 (s, 3H).^{13}C NMR (100 MHz,

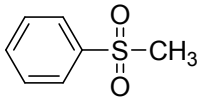
$CDCl_3$): δ 167.72, 141.41, 138.90, 133.40, 133.32, 133.19, 131.00, 130.23, 129.26, 129.00, 127.79, 53.11. GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}O_4S$: 276.0, found: 276.

1-(Phenylsulfonyl)benzene 3k[4]:



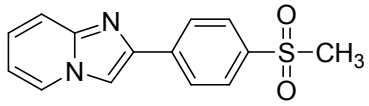
white solid; mp 122-124 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.6Hz, 4H), 7.56 (t, *J* = 7.4Hz, 2H), 7.50 (t, J = 7.6Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.69, 133.15, 129.26, 127.67. GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_{10}O_2S$: 218.0, found: 218.

4-(methanesulfonyl)benzene 3l[4]:



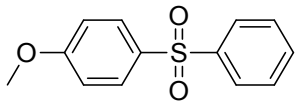
white solid; mp 90-91 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.95-7.94 (m, 2H), 7.67-7.65 (m, 1H), 7.59-7.56 (m, 2H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.65, 133.68, 129.36, 127.28, 44.45. GC-MS (EI) [M]+: m/z calcd. for $C_7H_8O_2S$: 156.0, found: 156.

Zolimidine[5]:

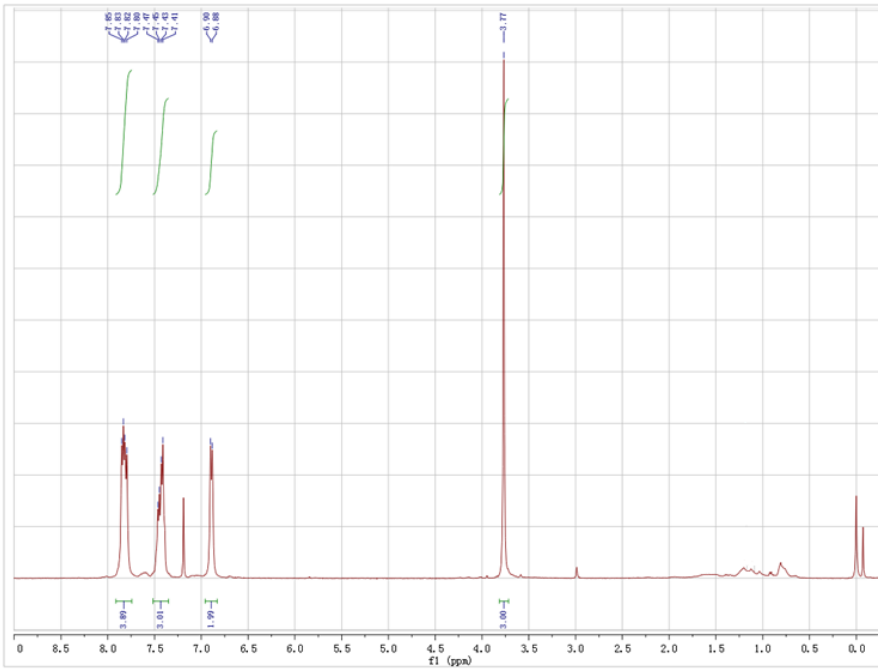


yellowish white solid ; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.8 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 2H), 8.02 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 9.1 Hz, 1H), 7.31 – 7.28 (m, 1H), 6.90-6.87 (m, 1H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.42, 142.68, 139.65, 138.65,127.93, 126.75, 126.34, 126.04, 117.42, 113.58, 109.83, 44.57. GC-MS (EI) [M]+: m/z calcd. for $C_{14}H_{12}N_2O_2S$: 272.0, found: 272.

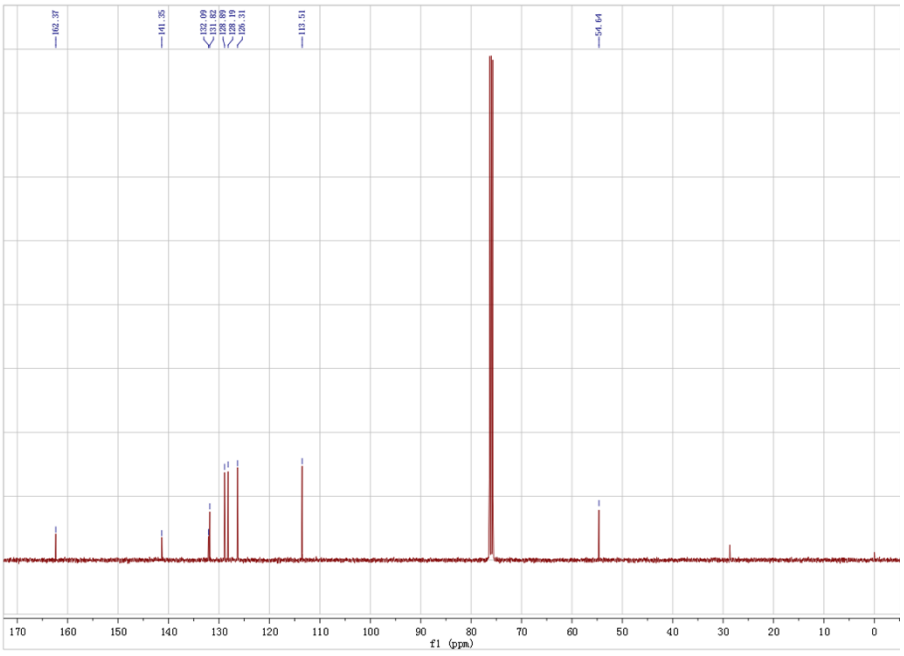
1-(4-Methoxyphenylsulfonyl)benzene 3a:



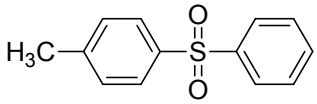
^{1}H NMR:



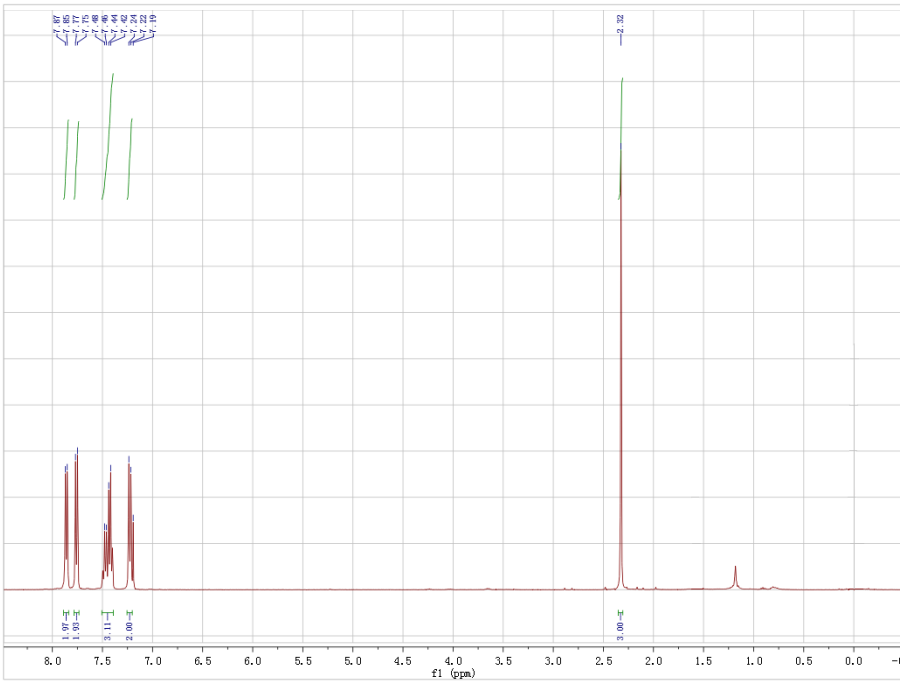
^{13}C NMR:



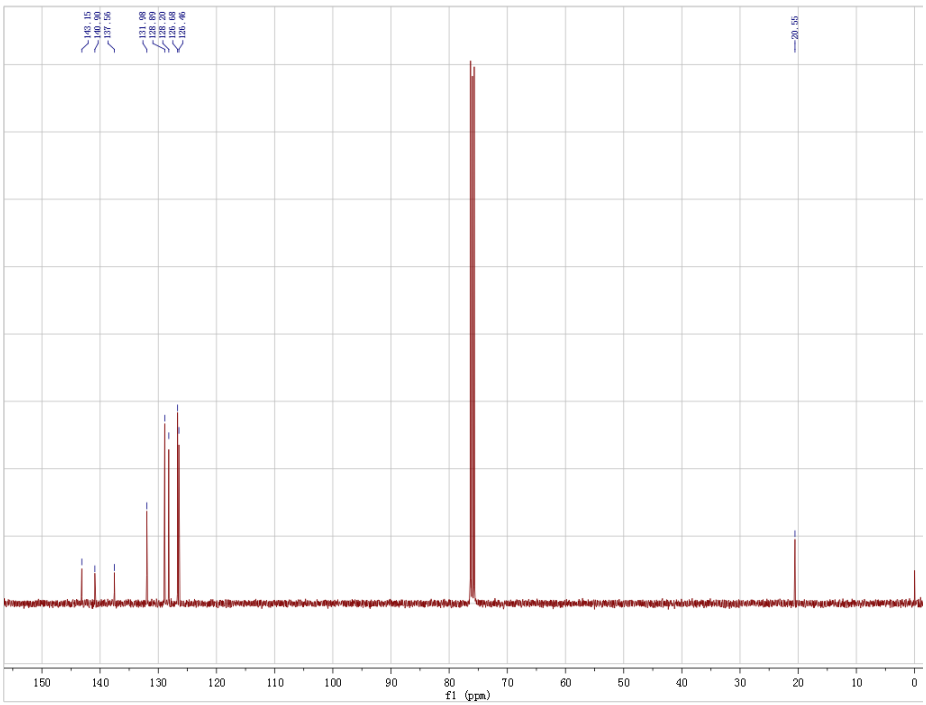
1-(*p*-Tolylsulfonyl)benzene 3b:



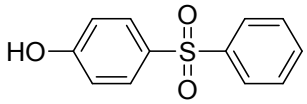
[1]HNMR:



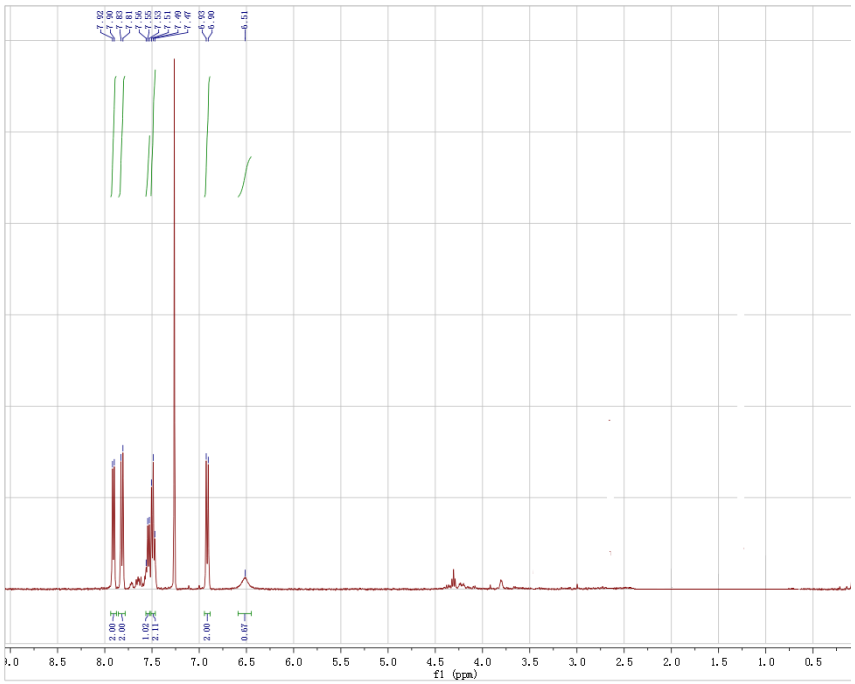
[13] C NMR:



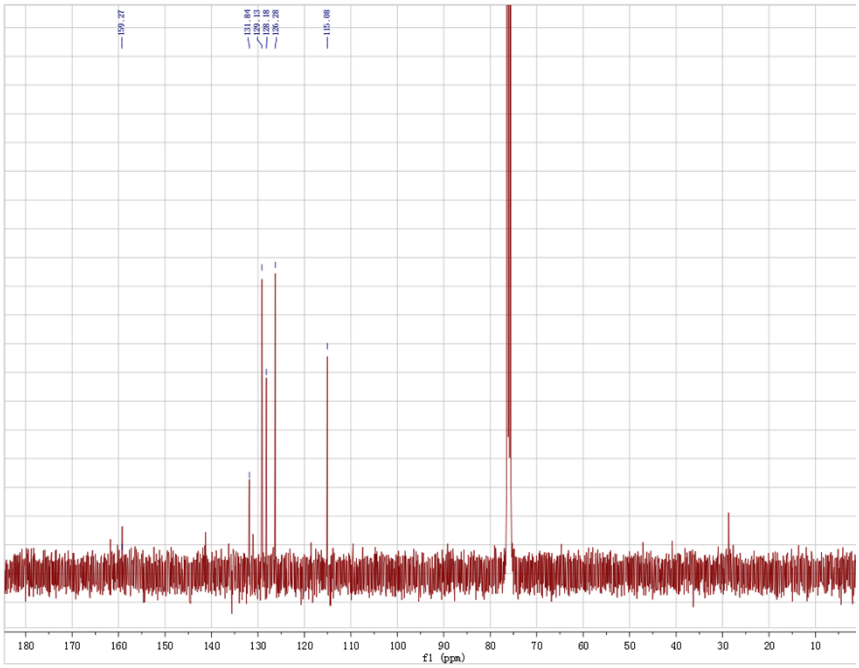
4-(Benzenesulfonyl)phenol 3c:



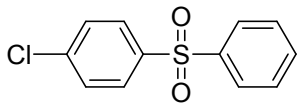
^{1}H NMR



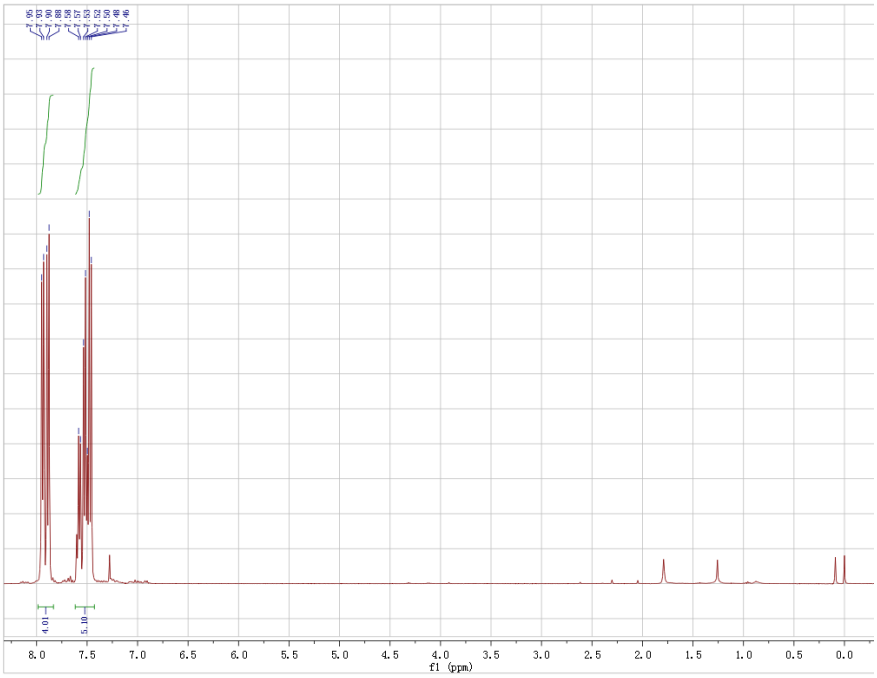
^{13}C NMR



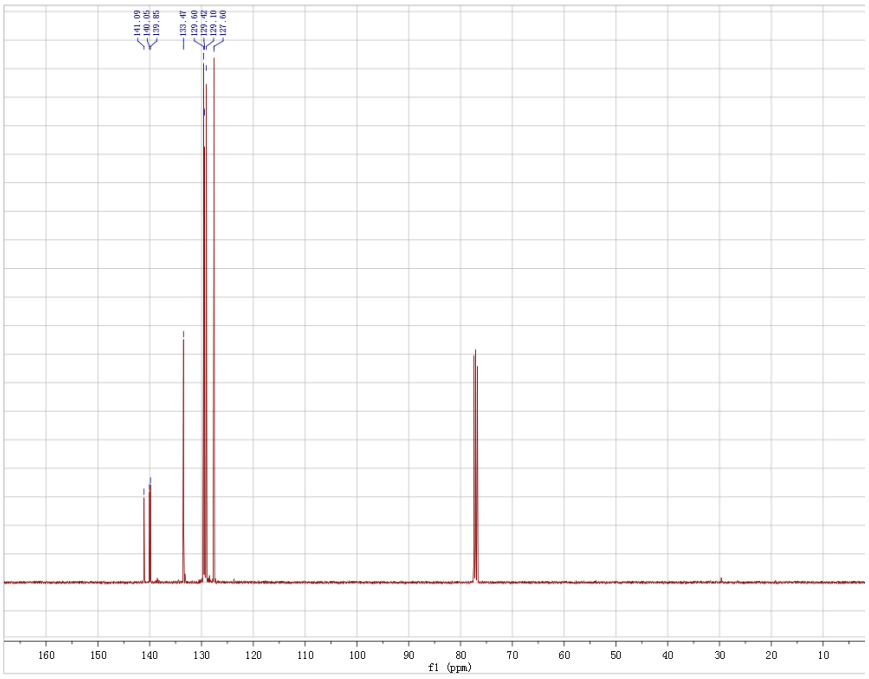
1-(4-Chlorophenylsulfonyl)benzene 3d:



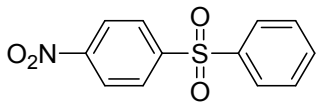
^{1}H NMR



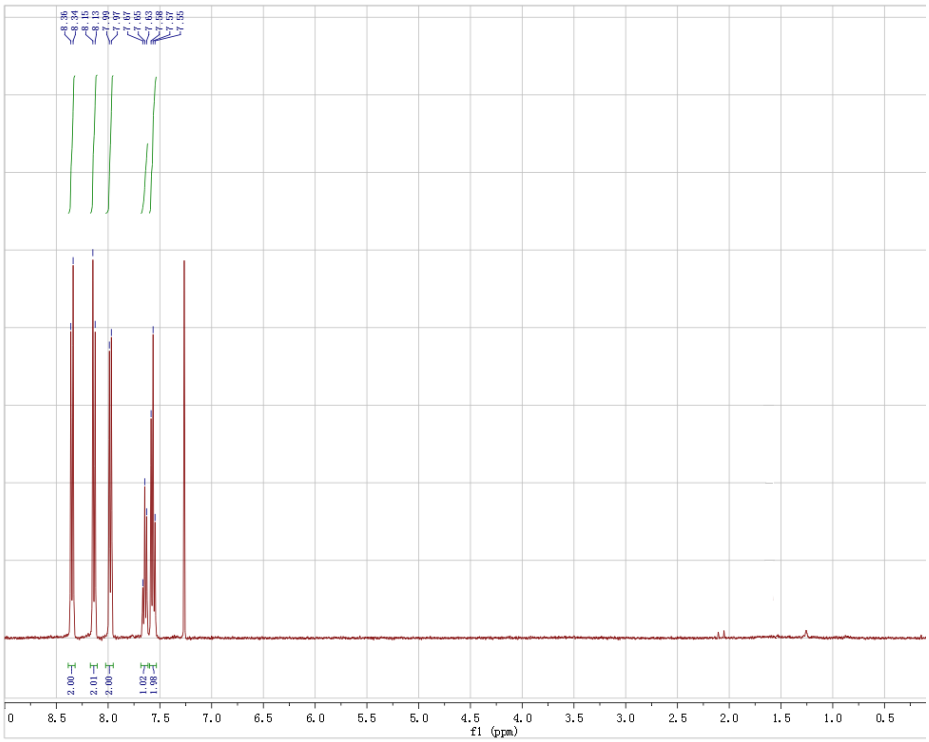
^{13}C NMR



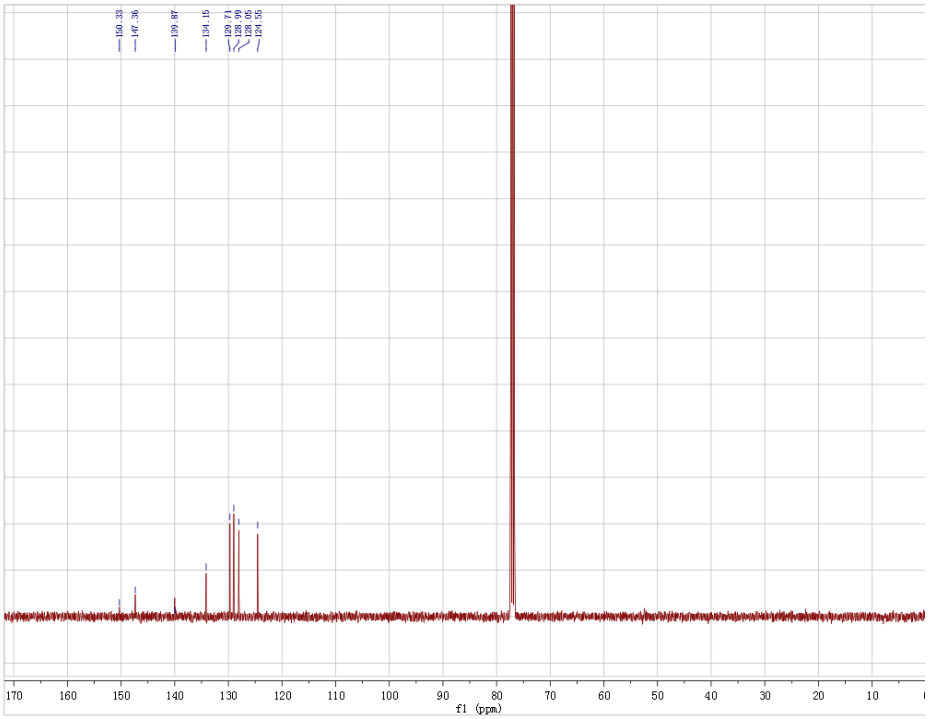
1-(4-Nitrophenylsulfonyl)benzene 3e:



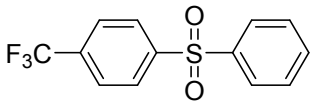
^{1}H NMR



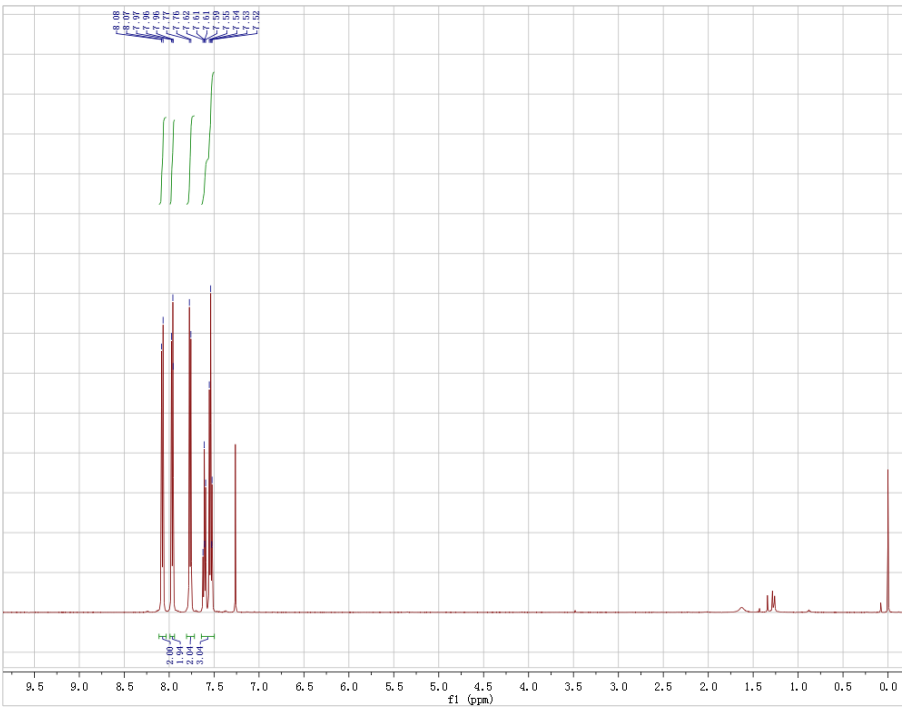
^{13}C NMR



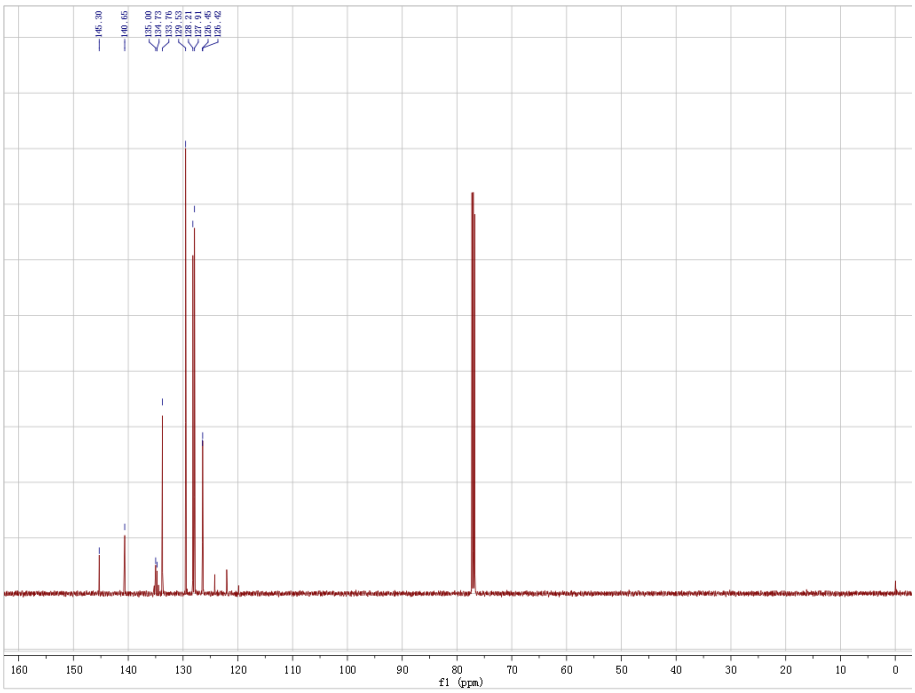
1-(Trifluoromethyl)-4-(phenylsulfonyl)benzene 3f



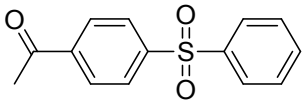
^{1}H NMR



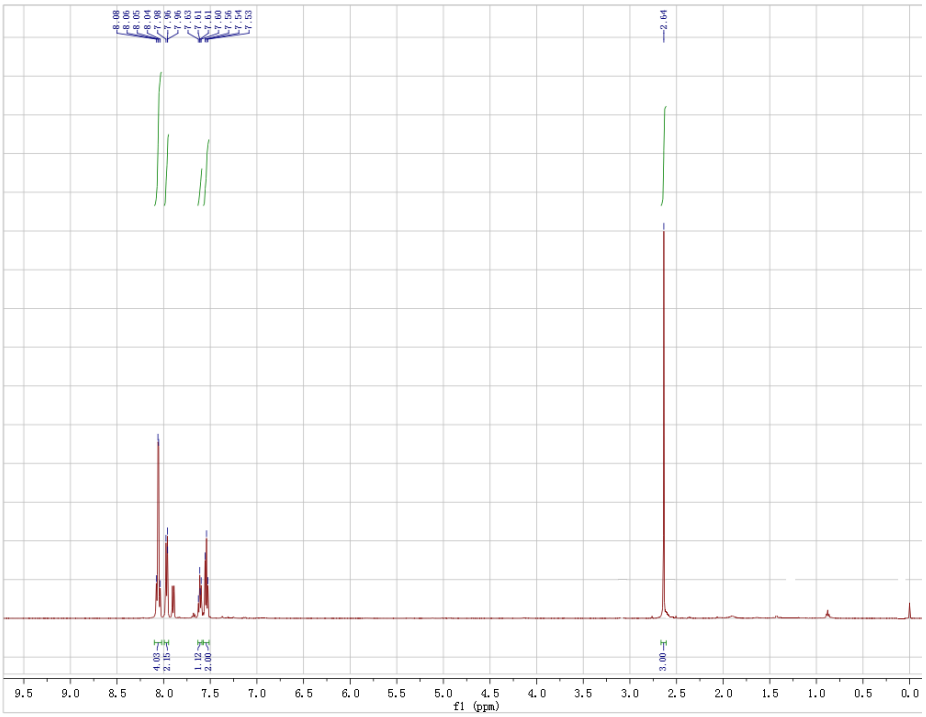
^{13}C NMR



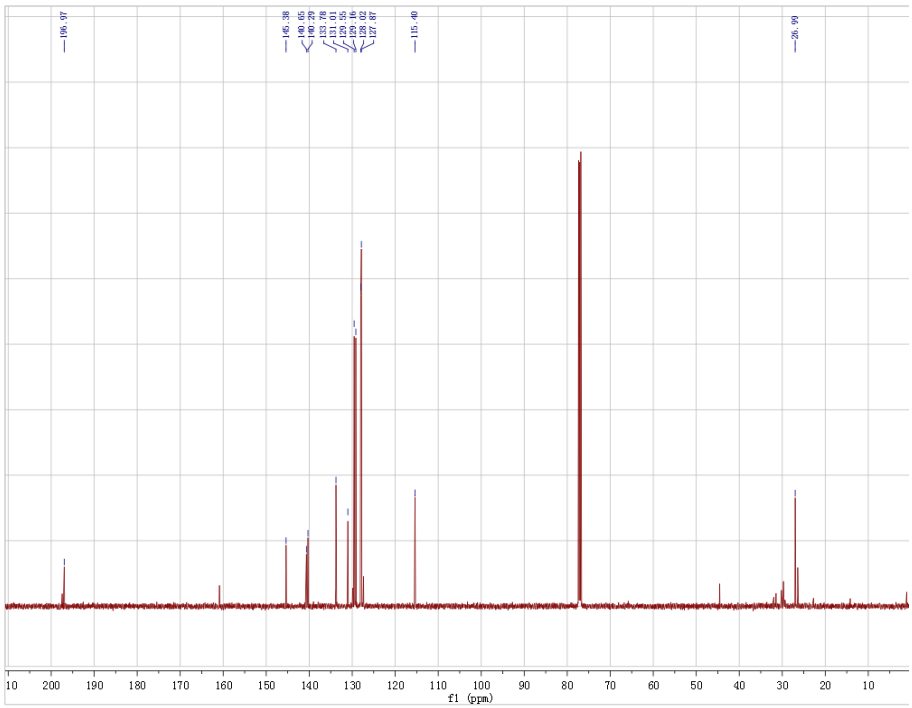
1-(4-(phenylsulfonyl)phenyl)ethanone 3g:



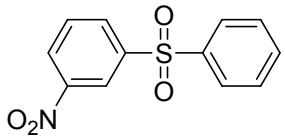
^{1}H NMR



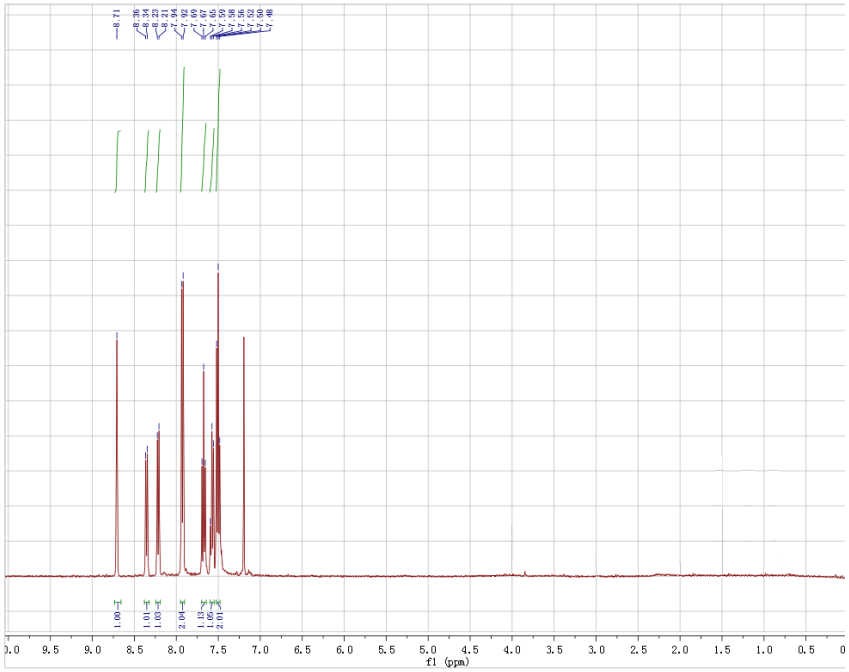
^{13}C NMR



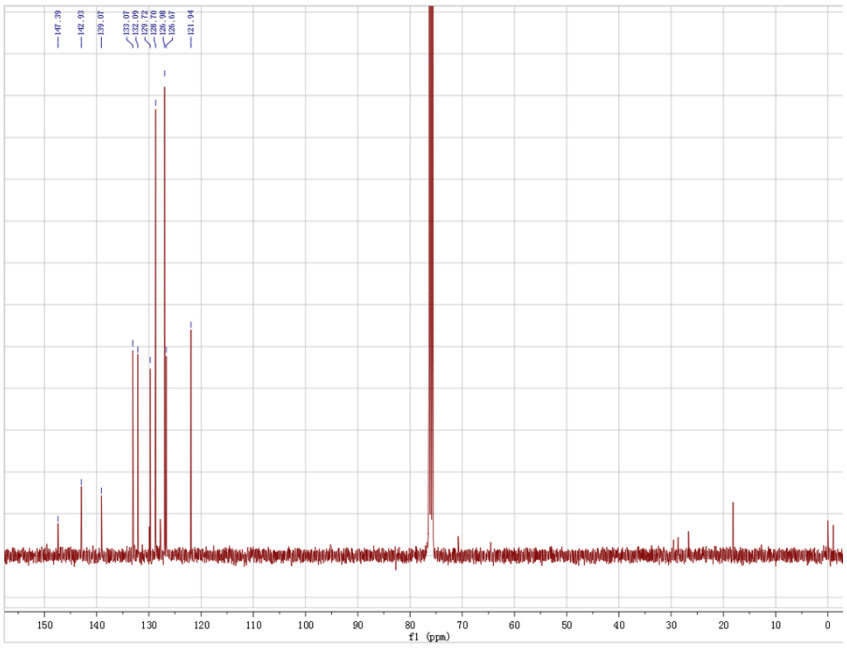
3-Nitrol-(phenylsulfonyl)benzene 3h:



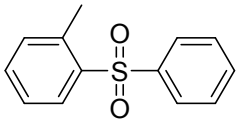
^{1}H NMR



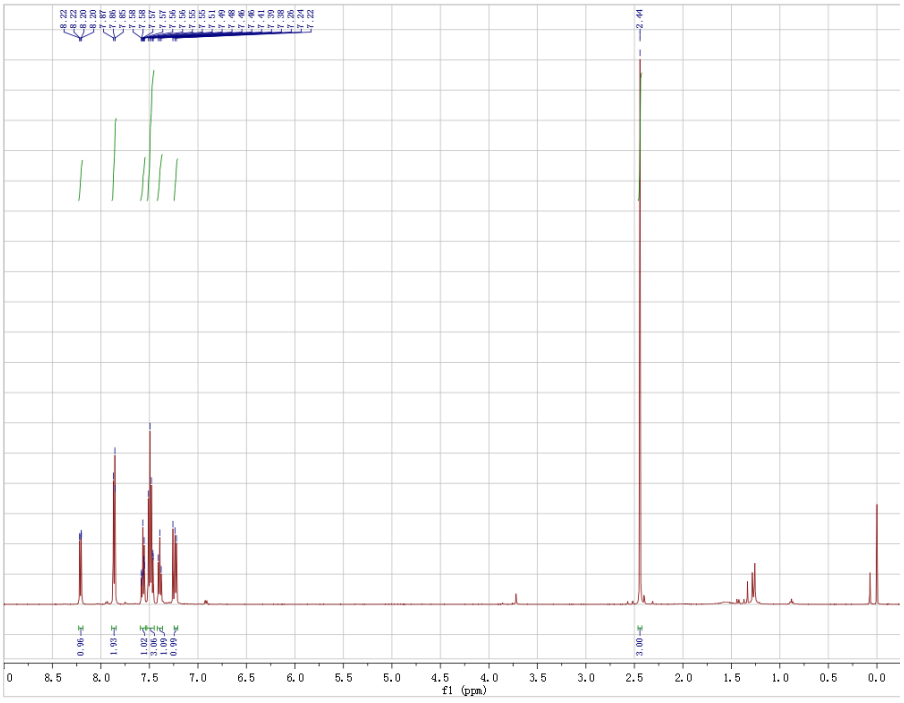
^{13}C NMR



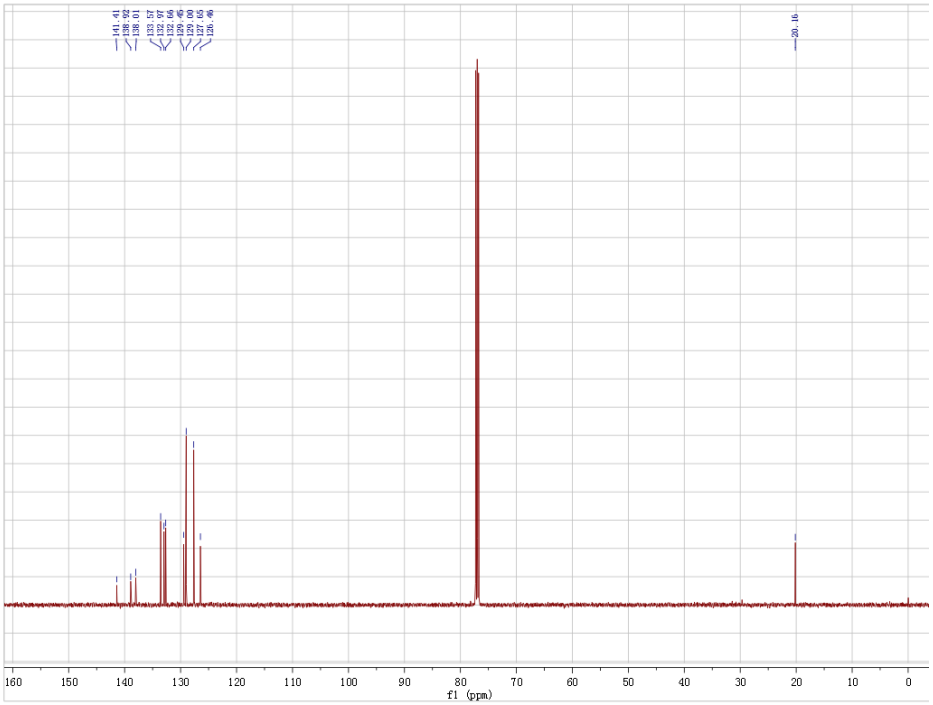
1-methyl-2-(phenylsulfonyl)benzene 3i:



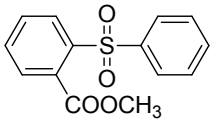
^{1}H NMR



^{13}C NMR

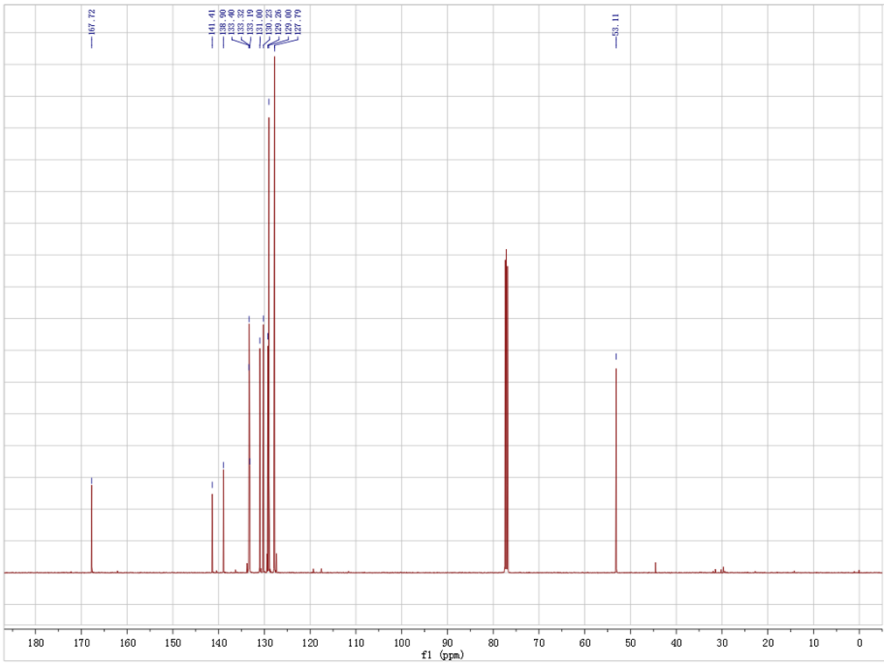


Methyl 2-(phenylsulfonyl)benzoate 3j:

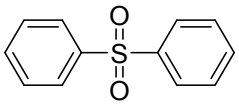


^{1}H NMR

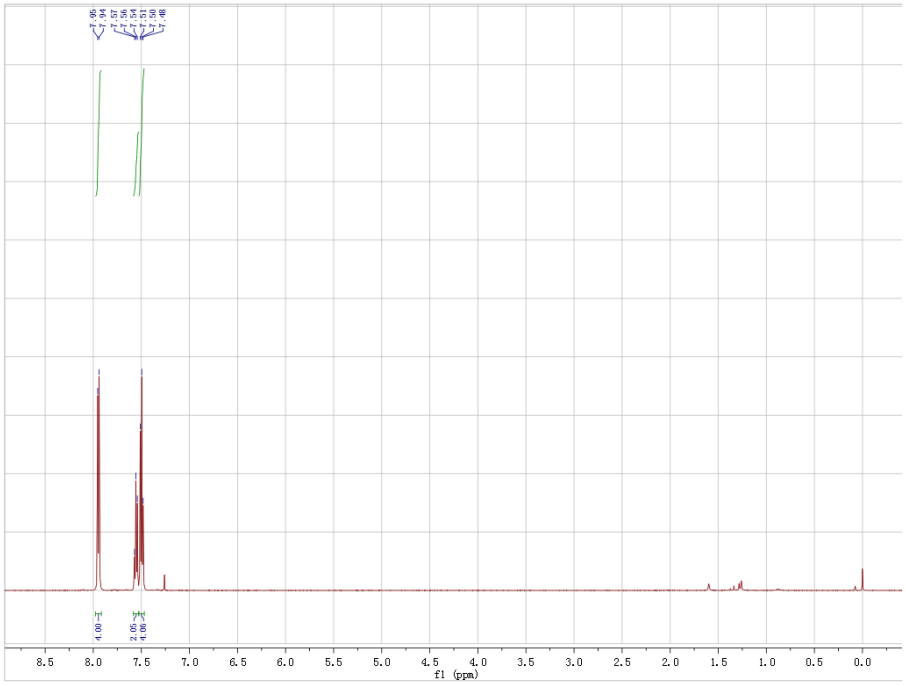
^{13}C NMR



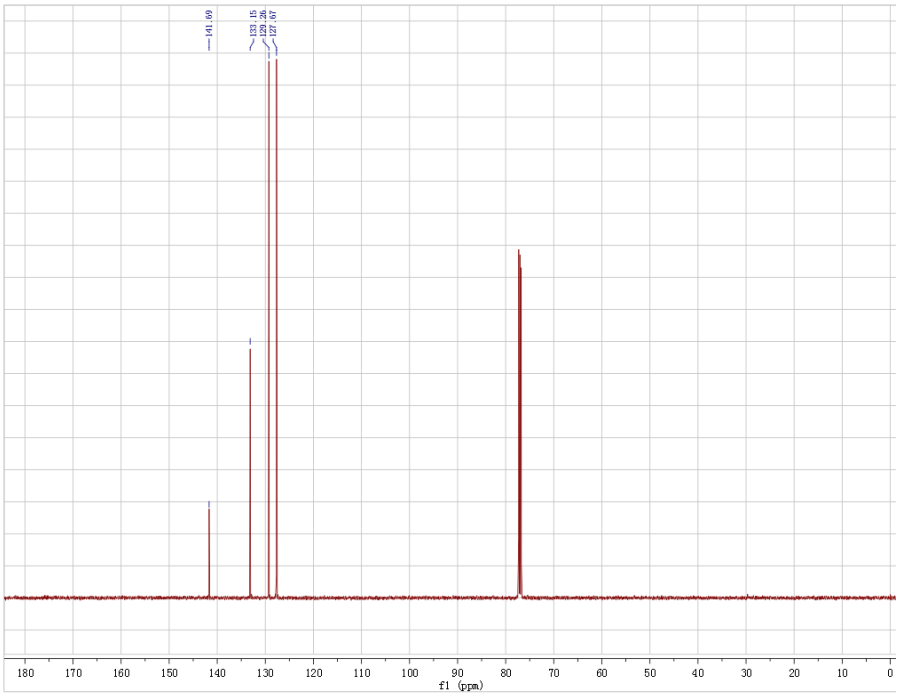
1-(Phenylsulfonyl)benzene 3k:



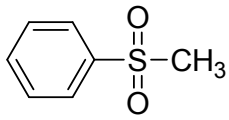
^{1}H NMR



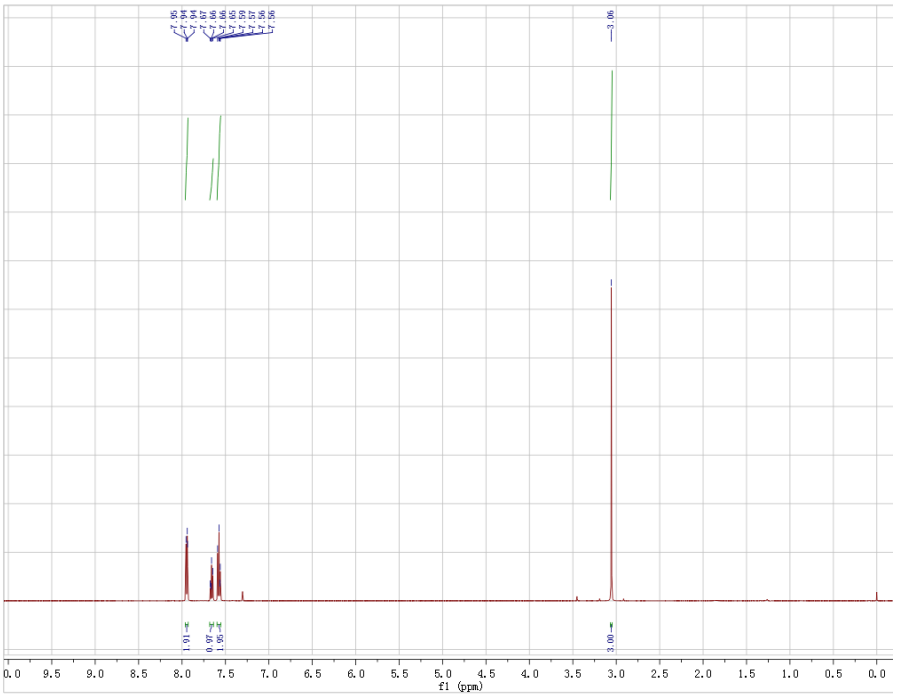
^{13}C NMR



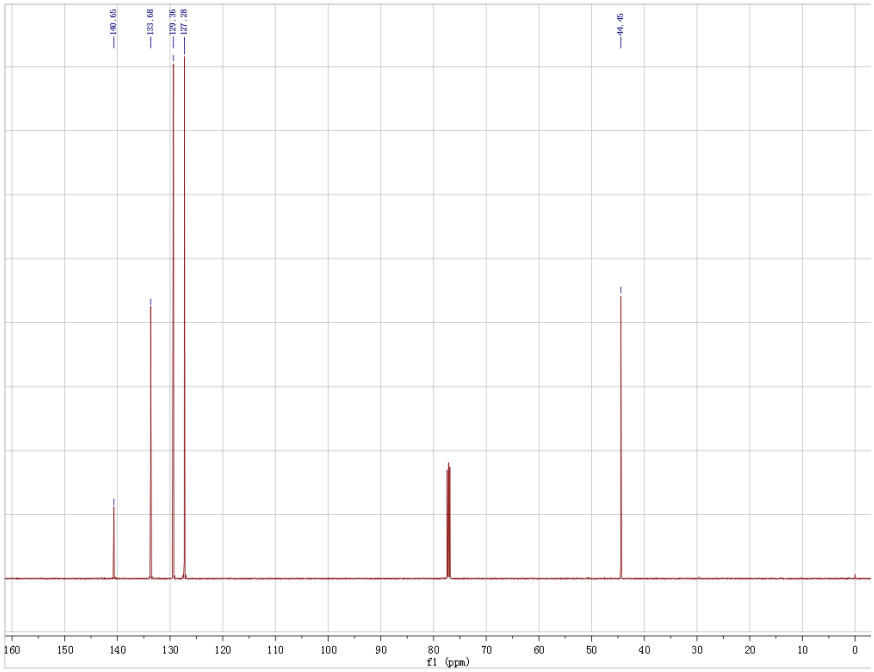
4-(methanesulfonyl)benzene 3l:



^{1}H NMR

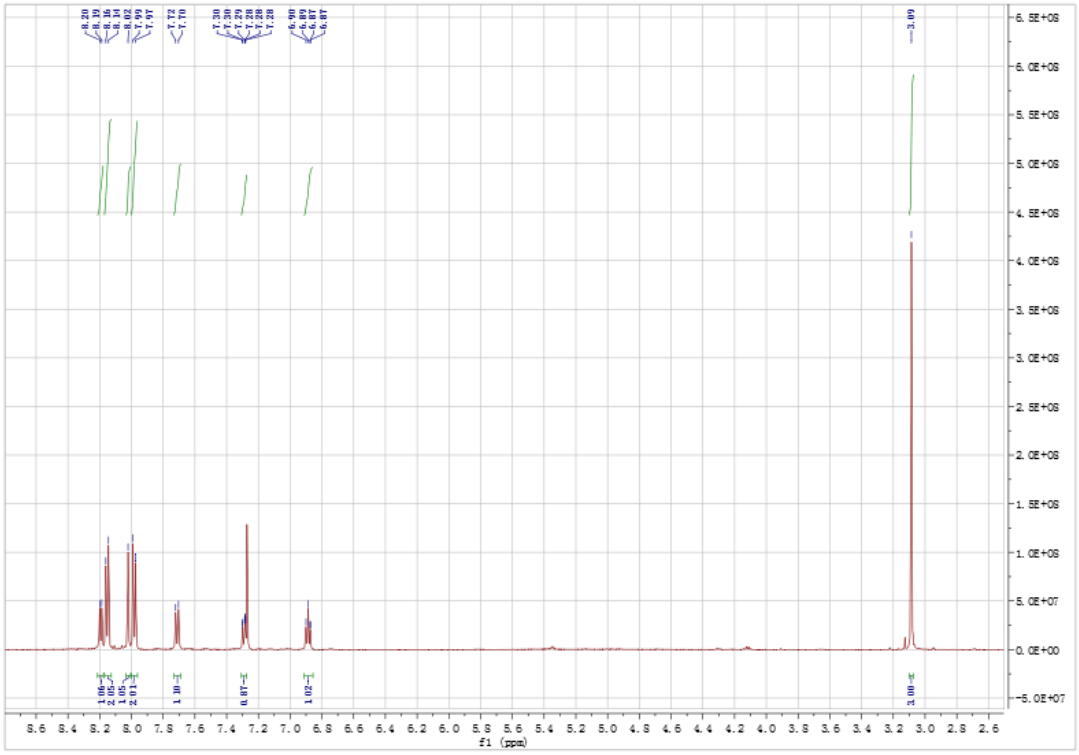


^{13}C NMR

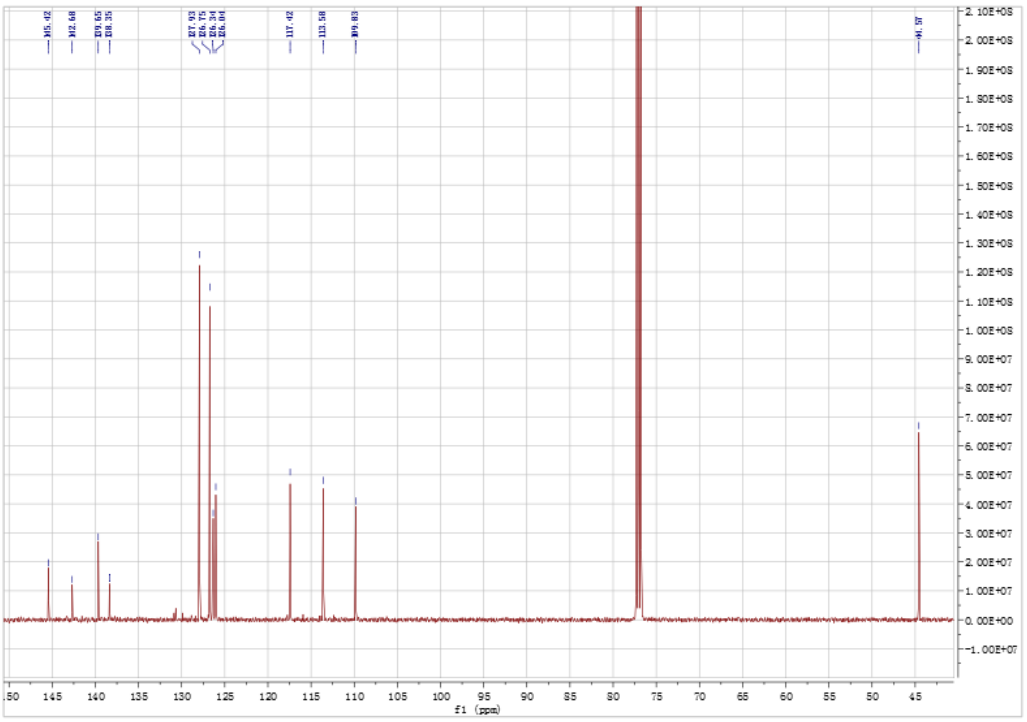


Zolimidine:

^{1}H NMR

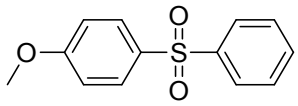


^{13}C NMR

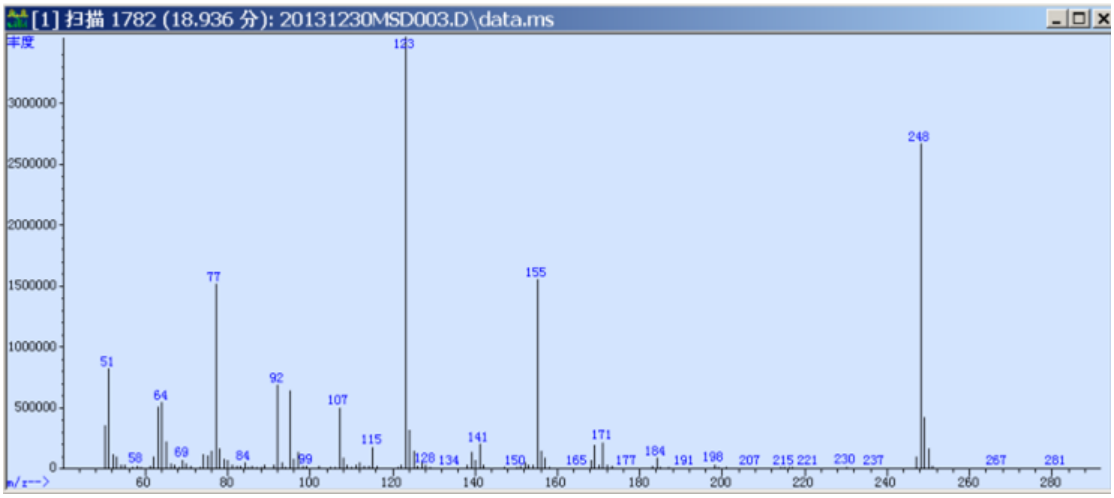


The selected GC-MS chromatogram of products:

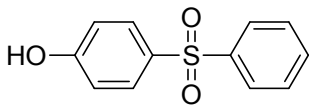
1-(4-Methoxyphenylsulfonyl)benzene 3a:



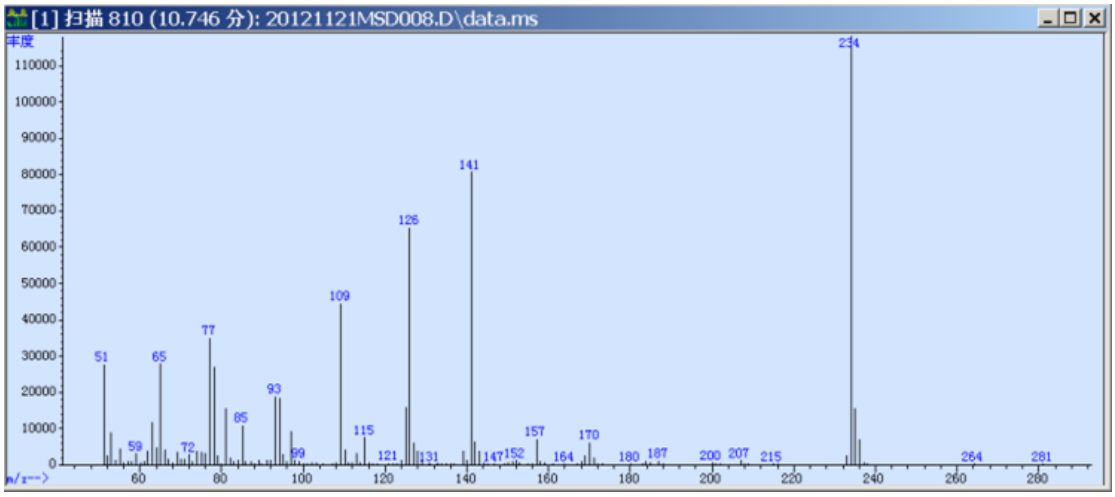
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O_3S$: 248.0, found: 248.



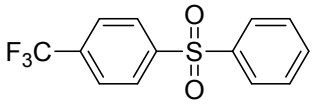
4-(Benzenesulfonyl)phenol 3c:



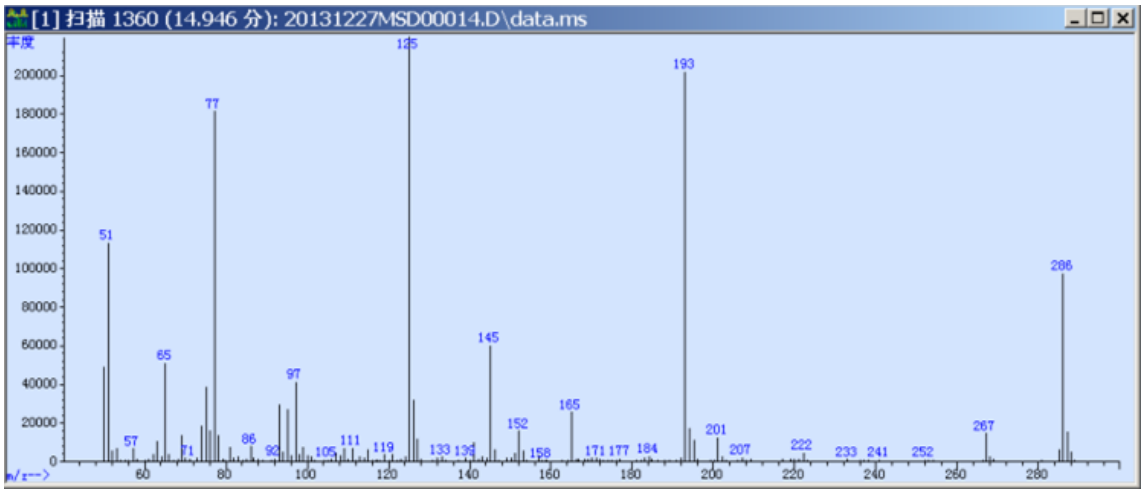
GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_{10}O_3S$: 234.0, found: 234.



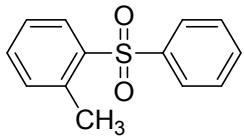
1-(Trifluoromethyl)-4-(phenylsulfonyl)benzene 3f:



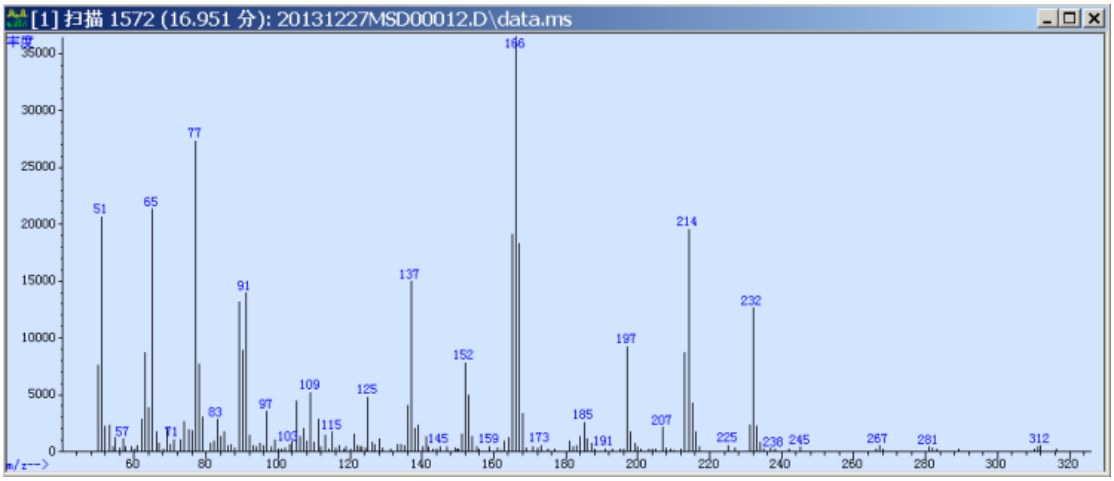
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_9F_3O_2S$: 286.0, found: 286.



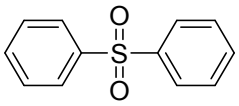
1-Methyl-2-(phenylsulfonyl)benzene 3i:



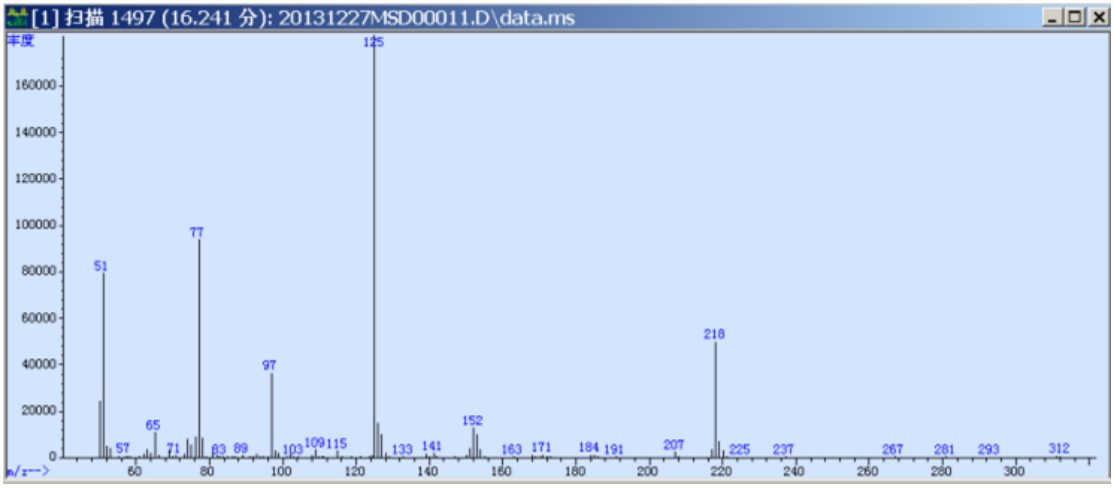
GC-MS (EI) [M]+: m/z calcd. for $C_{13}H_{12}O_2S$: 232.0, found: 232.



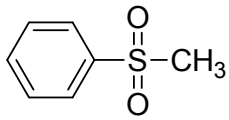
1-(Phenylsulfonyl)benzene 3k:



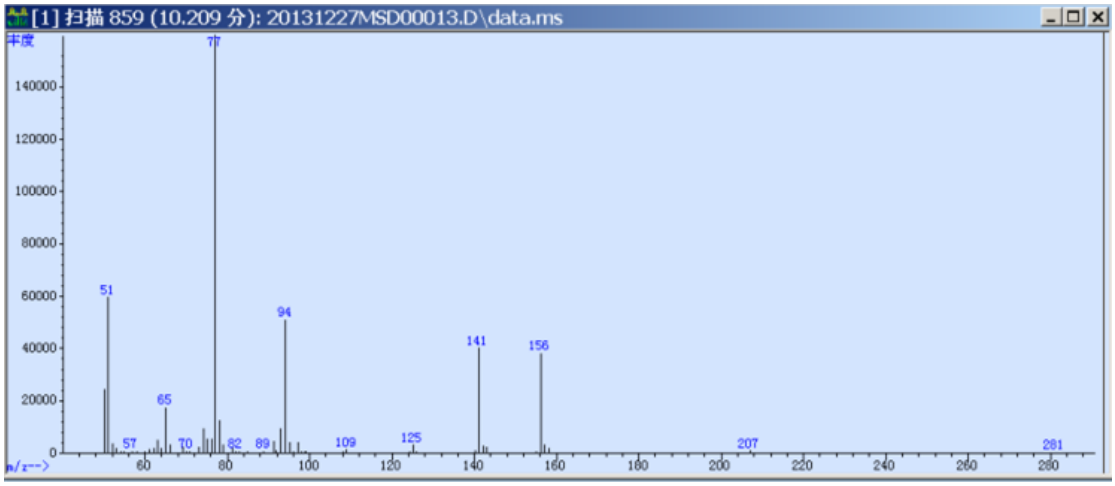
GC-MS (EI) [M]+: m/z calcd. for $C_{12}H_{10}O_2S$: 218.0, found: 218.



4-(Methanesulfonyl)benzene 3l：



GC-MS (EI) [M]+: m/z calcd. for $C_7H_8O_2S$: 156.0, found: 156.



4. References:

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3 W. Zhu and D. Ma, *J. Org. Chem.* 2013, **70**, 2696.

4 B. Yu, A. H. Liu, L. N. He, B. Li, Z. F. Diao and Y. N. Li, *Green Chem*., 2012, **14**, 957.

5 C. He, J. Hao, H. Xu, Y.-P. Mo, H.-Y. Liu, J.-J. Han, A. Lei, *Chem. Commun*. 2012, **48**, 11073;