Supporting information for

Ga1-xAlx)4B2O9-The controlled surface acid-base properties, and the catalytic behavior towards Strecker reaction

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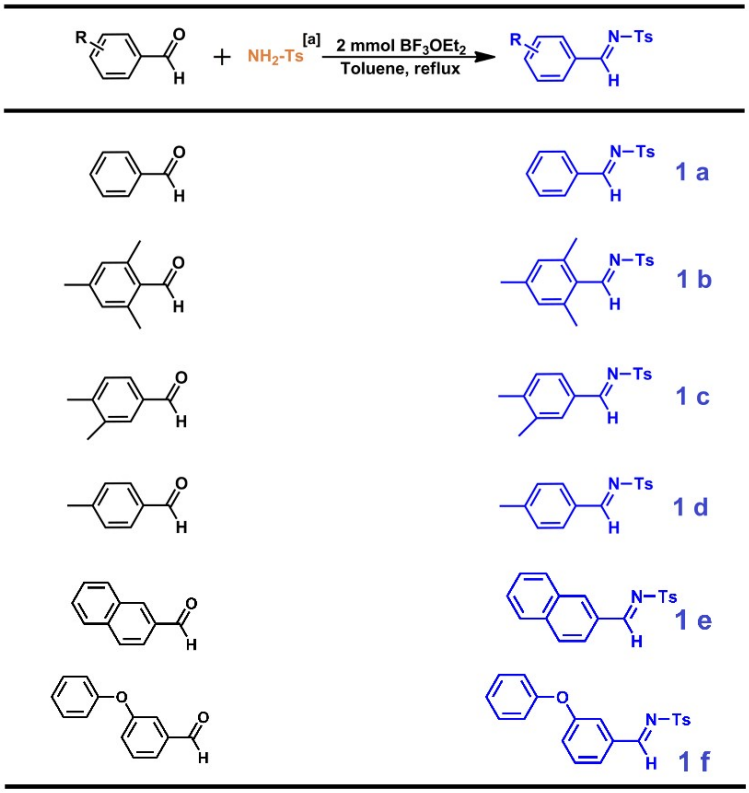
1. Synthesis procedure for six substrates：

All the solvents were purified by distillation method. Other reagents were used as received. Thin layer chromatography (TLC) was carries out using Merck 0.2 mm silica gel 60 F-254 Al-plaes (200-300 mesh). Taking 4-methyl-*N*-phenylmethylene-benzenesulfonamide as an example, 4-methylbenzenesulfonamide (12 mmol) was added to a mixture of benzaldehzyde (10 mmol) and TOL (25 mL) in a 50 mL flask. After refluxing for 1 h, BF_3OET_2 (2 mmol) was added into the reaction mixture. The reaction solution should be quenched with NaOH solution (1 M) and extracted with ethyl acetate for three times when the reaction ends (monitored by TLC). By washing with brine, drying over anhydrous Na_2SO_4, then concentrating under reduced atmosphere, the primary product was obtained. In some cases, this primary product was purified using flash column chromatography to afford pure product.

If using 2,4,6-Trimethylbenzaldehyde, 3,4-Dimethylbenzaldehyde, 4-Methylbenzaldehyde, 2-Naphthaldehyde, and 3-Phenoxybenzaldehyde, as the starting materials, the corresponding substrates are noted as **1b**, **1c**, **1d, 1e, and 1f**.

Scheme S1. Procedure for the synthesis of six imines precursors[a]



[a]Ts = *p*-toluenesulfonyl

2. ^{1}H NMR spectra of six imine substrates and six products

1 a ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.15 (s, 1H), 8.03 (d, J = 7.4 Hz, 2H), 7.85 (d, J = 8.1 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H).

1 b ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 6.99 (s, 2H), 2.42 (s, 6H), 2.39 (s, 3H), 2.26 (s, 3H).

1 c ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.76 (s, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.8 Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H).

1 d ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.10 (s, 1H), 7.93 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H).

1 e ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 8.68 (s, 1H), 8.08 (d, J = 8.1 Hz, 1H), 8.04 – 7.96 (m, 3H), 7.89 (d, J = 8.2 Hz, 2H), 7.73 – 7.67 (m, 1H), 7.66 – 7.60 (m, 1H), 7.46 (d, J = 8.1 Hz, 2H), 2.39 (s, 3H).

1 f ^{1}H NMR (400 MHz, DMSO-*d*6) δ 9.14 (s, 1H), 7.81 (dd, *J* = 12.3, 7.9 Hz, 3H), 7.63 – 7.53 (m, 2H), 7.48 – 7.38 (m, 4H), 7.34 (dd, *J* = 7.9, 2.6 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.08 – 7.01 (m, 2H), 2.38 (s, 3H).

2 a ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.21 (d, *J* = 9.3 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.40 (dd, *J* = 12.4, 7.6 Hz, 6H), 5.83 (d, *J* = 9.2 Hz, 1H), 2.40 (s, 3H).

2 b ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.77 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 2H), 5.68 (d, *J* = 6.1 Hz, 1H), 5.22 (d, *J* = 6.2 Hz, 1H), 2.44 (s, 3H), 2.33 (s, 6H), 2.24 (s, 3H).

2 c ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.08 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 5.69 (d, *J* = 7.6 Hz, 1H), 2.39 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H).

2 d ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.86 – 7.77 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.43 (d, *J* = 8.9 Hz, 1H), 5.13 (d, *J* = 8.9 Hz, 1H), 2.46 (s, 3H), 2.36 (s, 3H)..

2 e ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 9.31 (d, *J* = 9.1 Hz, 1H), 7.98 – 7.87 (m, 4H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.57 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.46 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.02 (d, *J* = 9.1 Hz, 1H), 2.36 (s, 3H).

2 f ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.77 (d, *J* = 8.3 Hz, 2H), 7.33 (ddd, *J* = 12.0, 8.3, 5.8 Hz, 5H), 7.15 (ddd, *J* = 7.3, 4.2, 2.8 Hz, 2H), 7.04 (t, *J* = 2.1 Hz, 1H), 7.01 – 6.94 (m, 3H), 5.69 (d, *J* = 9.1 Hz, 1H), 5.40 (d, *J* = 9.1 Hz, 1H), 2.43 (s, 3H).

3. ^{13}C NMR spectra of six imine substrates and six products

1 a ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.96, 145.05, 135.28, 131.68, 130.51(2C), 129.72(2C), 128.10(2C), 126.05(2C), 21.54.

1 b ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.51, 144.38, 144.28, 142.19, 135.27, 130.37(2C), 129.95(2C), 127.51(2C), 125.70, 21.02(4C)

1 c ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.12, 145.22, 144.38, 137.61, 135.11, 131.40, 130.34, 129.98(2C),129.87, 129.51, 127.54(2C), 21.04, 19.84, 19.05.

1 d ^{13}C NMR (151 MHz, DMSO-d_6) δ 171.54, 146.71, 144.87, 135.54, 131.76(2C), 130.45(2C), 130.36(2C), 130.05,128.01(2C), 21.90, 21.50

1 e ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.13 , 144.57 , 136.53 , 135.95 , 132.22 , 130.06 (2C), 129.76 , 129.63 , 129.56 , 129.05 , 127.96 , 127.71(2C) , 127.37 , 123.62 , 21.07.

1 f ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.03, 157.42, 155.78, 144.66, 134.59, 133.98, 131.05, 130.23(2C), 130.05(2C), 127.70(2C), 126.39, 125.05, 124.18, 119.45, 119.13(2C), 21.07.

2 a ^{13}C NMR (151 MHz, DMSO-d_6) δ 143.79, 137.65, 134.35, 130.13(2C), 129.44, 129.35(2C), 127.41(2C), 127.17(2C), 118.17, 47.52, 21.46.

2 b ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.64, 140.00, 136.74, 136.13, 130.55(2C), 130.03(2C), 127.46(2C), 126.25, 116.79, 42.82, 21.76, 21.01, 20.15(4C).

2 c ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.25, 137.31, 137.25, 136.77, 131.11, 129.81, 129.60(2C), 127.99, 126.74(2C), 124.37, 117.86, 46.86, 21.01, 19.32, 19.03.

2 d ^{13}C NMR (101 MHz, Chloroform-*d*) δ144.71, 140.12, 136.20, 130.12(4C), 129.30, 127.48, 127.41, 127.11(2C), 116.60, 48.10, 21.76, 21.27.

2 e ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.36, 137.21, 132.72, 132.35, 131.19, 129.66(2C), 128.83, 128.03, 127.60, 127.01, 126.89, 126.76(2C), 126.02, 124.46, 117.66, 47.29, 20.98.

2 f ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.34 , 156.30 , 144.81 , 136.05 , 134.11 , 130.87 , 130.16(2C) , 130.09(2C) , 127.40 (2C), 124.17 , 121.58 , 119.74 , 119.37(2C) , 117.31 , 116.29 , 48.02 , 21.75.

Fig. S1 ^{1}H NMR spectrum of substrate **1a**: 4-methyl-*N*-phenylmethylene-benzenesulfonamide

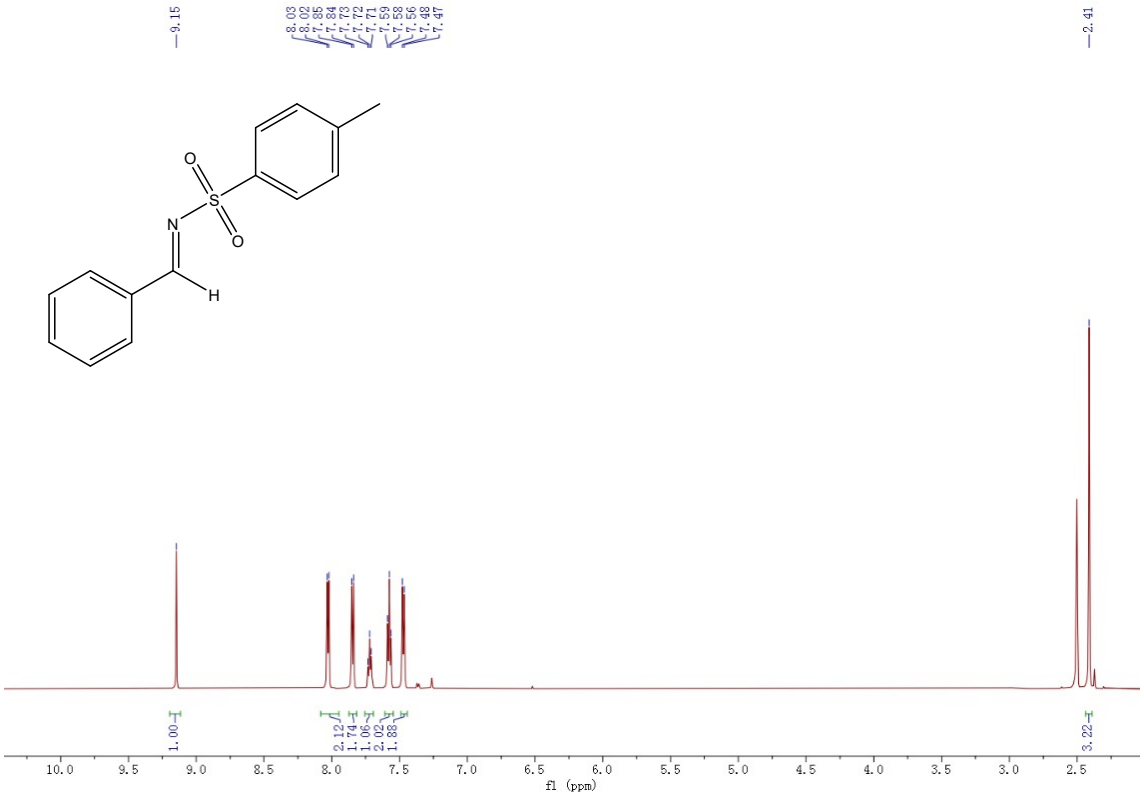


Fig. S2 ^{1}H NMR spectrum of substrate **1b**: 4-methyl-*N*-[(2,4,6-trimethylphenyl)methylene]-Benzenesulfonamide

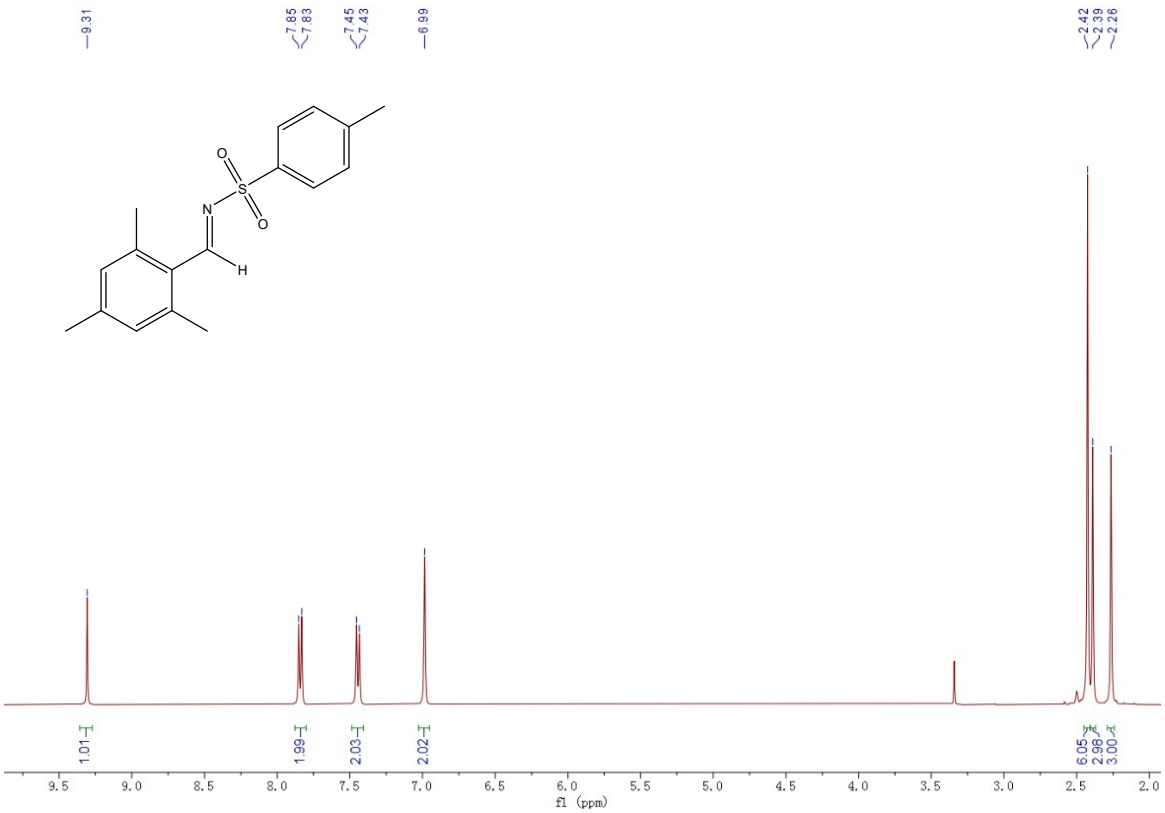


Fig. S3 ^{1}H NMR spectrum of substrate **1c**: 4-methyl-*N*-[(3,4-dimethylphenyl)methylene]-

Benzenesulfonamide

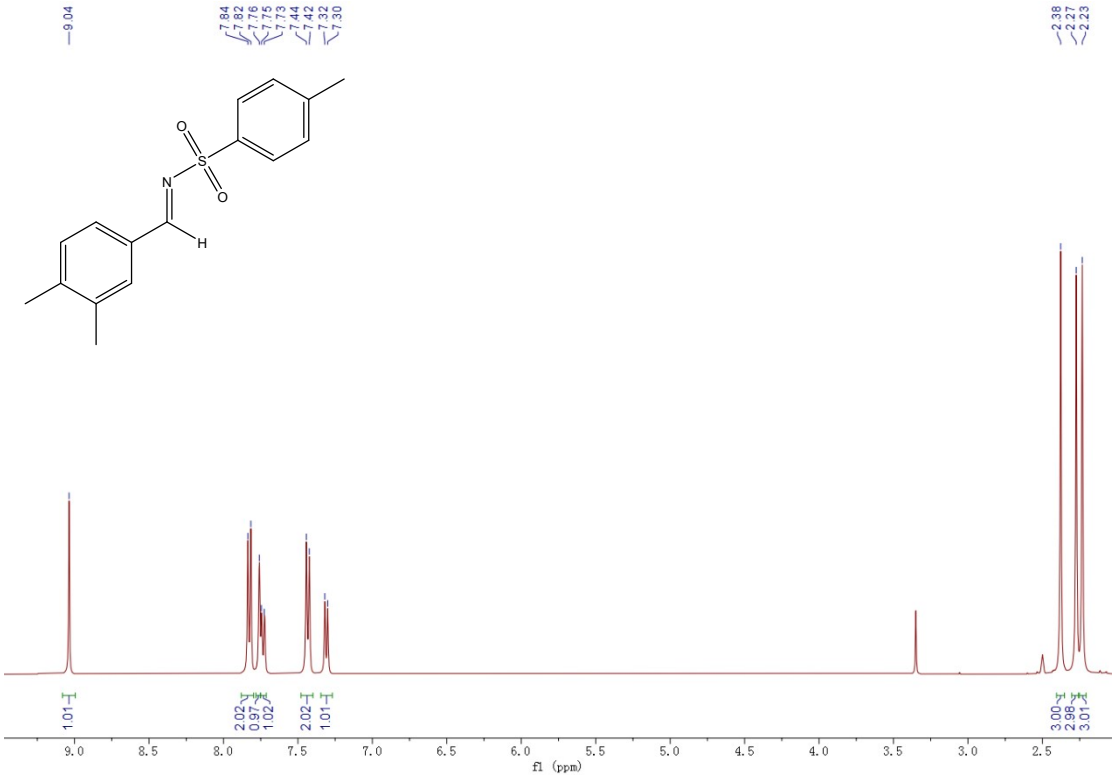


Fig. S4 ^{1}H NMR spectrum of substrate **1d**: 4-methyl-*N*-[(4-methylphenyl)methylene]-

Benzenesulfonamide

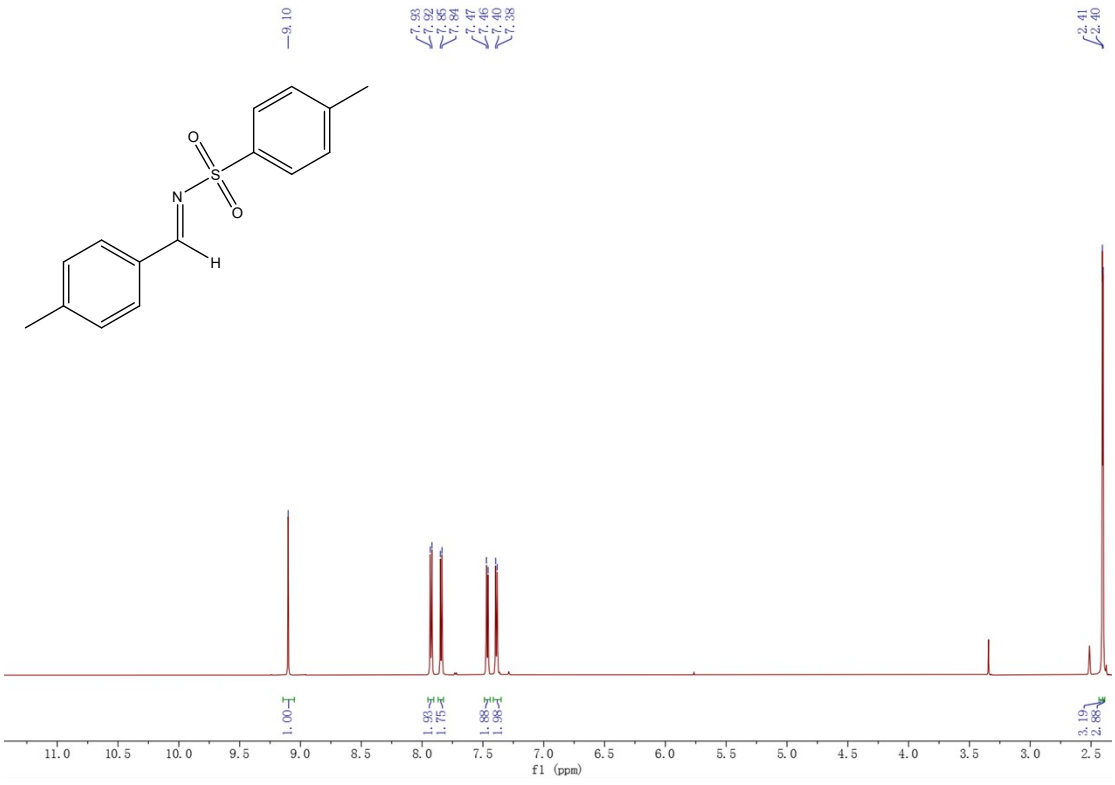


Fig. S5 ^{1}H NMR spectrum of substrate **1e**: 4-methyl-*N*-(2-naphthalenylmethylene)-benzenesulfonamide

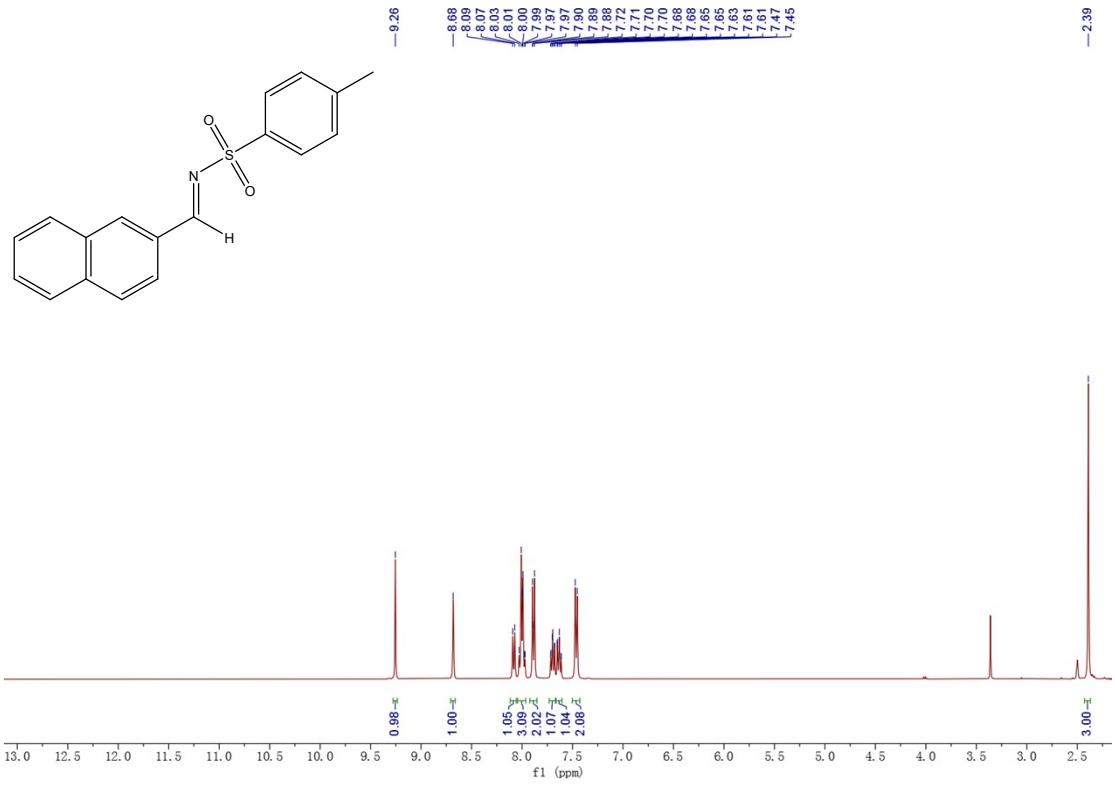


Fig. S6 ^{1}H NMR spectrum of substrate **1f**: 4-methyl-*N*-[(3-phenoxyphenyl)methylene]-benzenesulfonamide

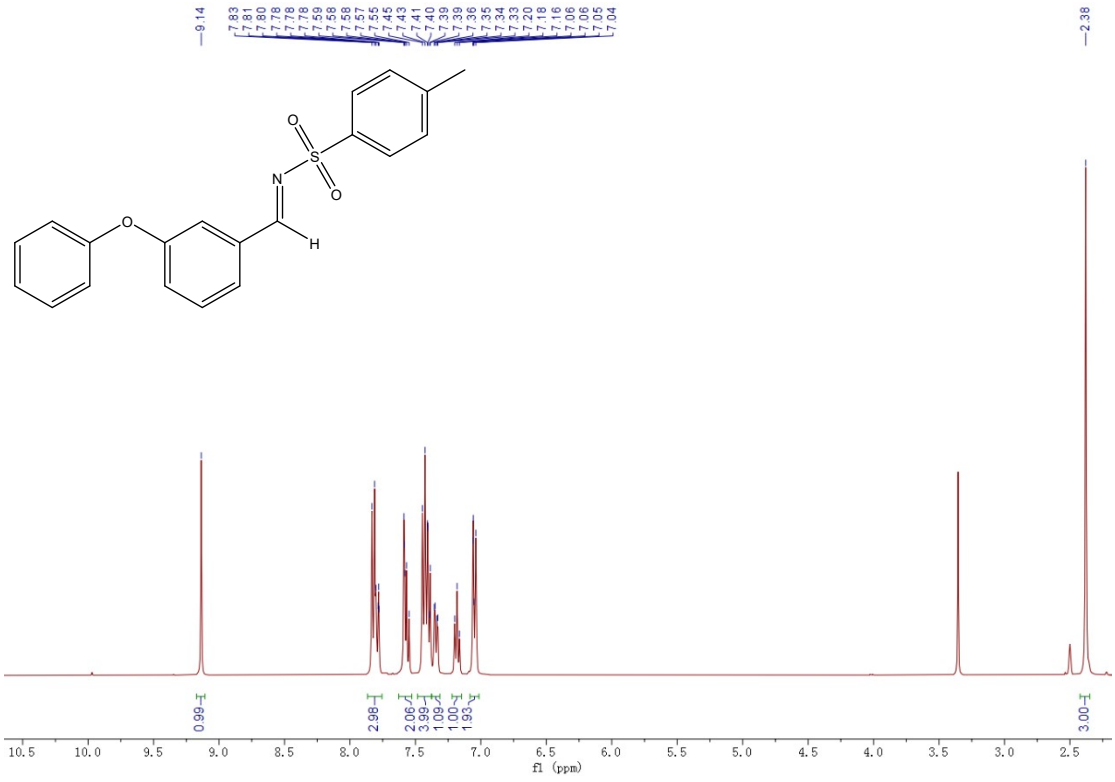


Fig. S7 ^{1}H NMR spectrum of substrate **2a**: *N*-[cyano(phenyl)methyl]-4-methyl-benzenesulfonamide

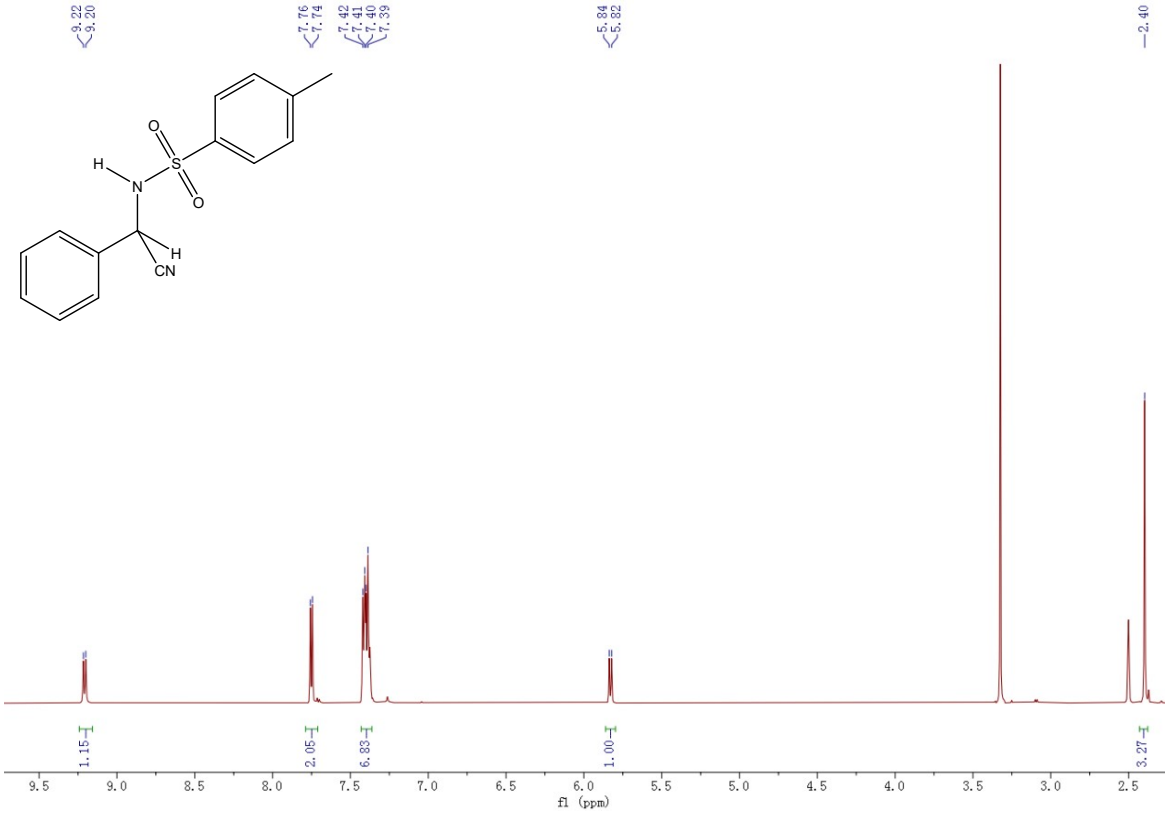


Fig. S8 ^{1}H NMR spectrum of substrate **2b**: *N*-[cyano(2,4,6-trimethylphenyl)methyl]-4-methylbenzenesulfonamide

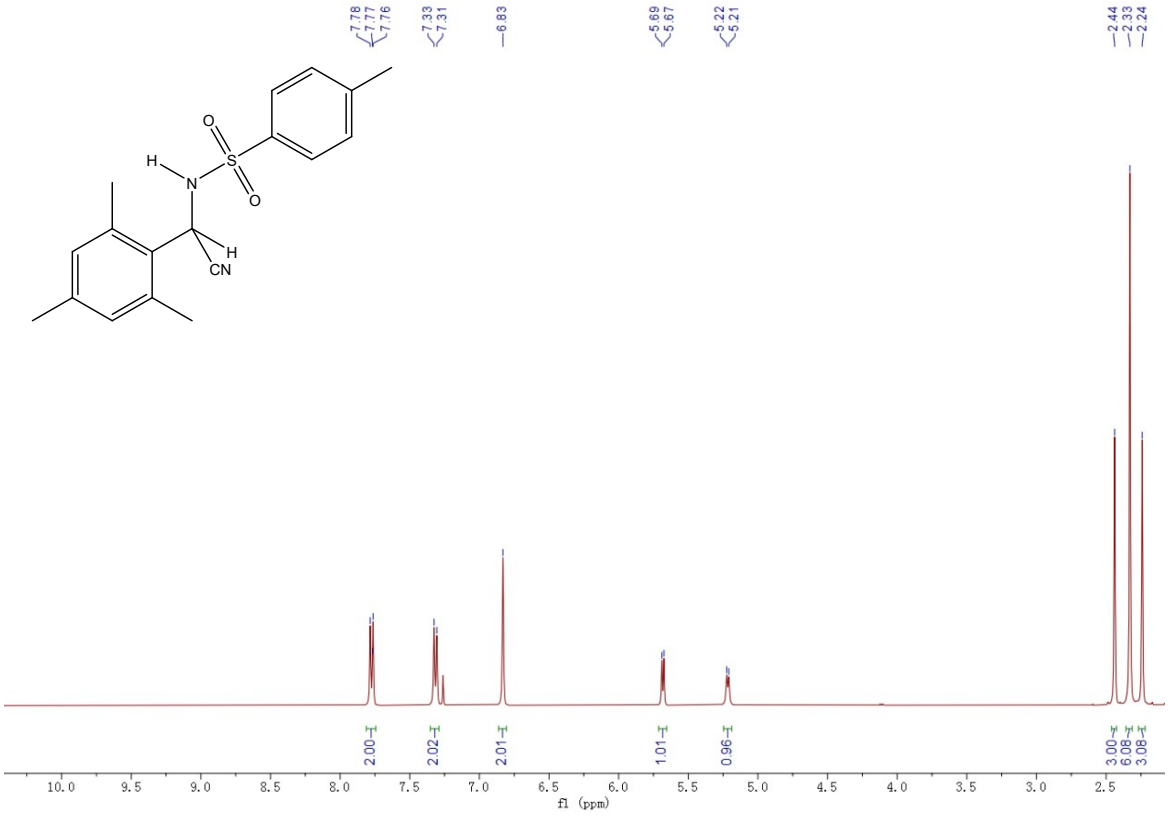


Fig. S9 ^{1}H NMR spectrum of substrate **2c**: *N*-[cyano(3,4-dimethylphenyl)methyl]-4-methylbenzenesulfonamid

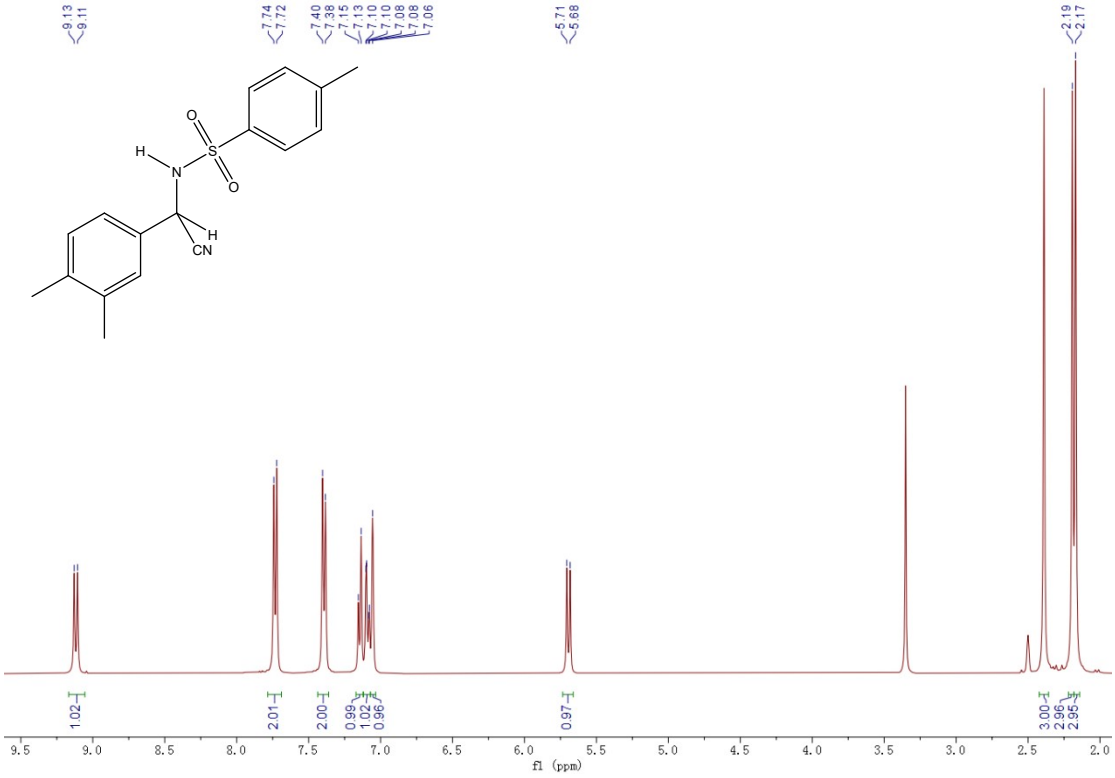


Fig. S10 ^{1}H NMR spectrum of substrate **2d**: *N*-[cyano(p-tolyl)methyl]-4-methyl-benzenesulfonamide

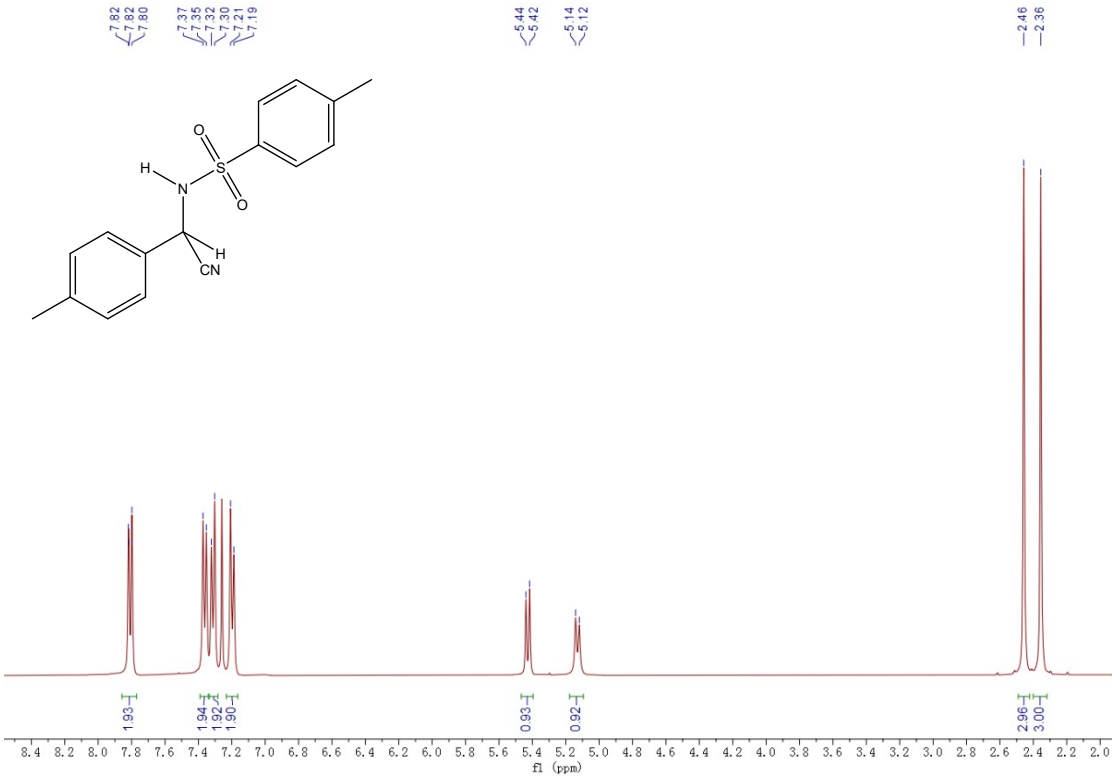


Fig. S11 ^{1}H NMR spectrum of substrate **2e**: *N*-(cyano-2-naphthalenylmethyl)-4-methyl-benzenesulfonamide

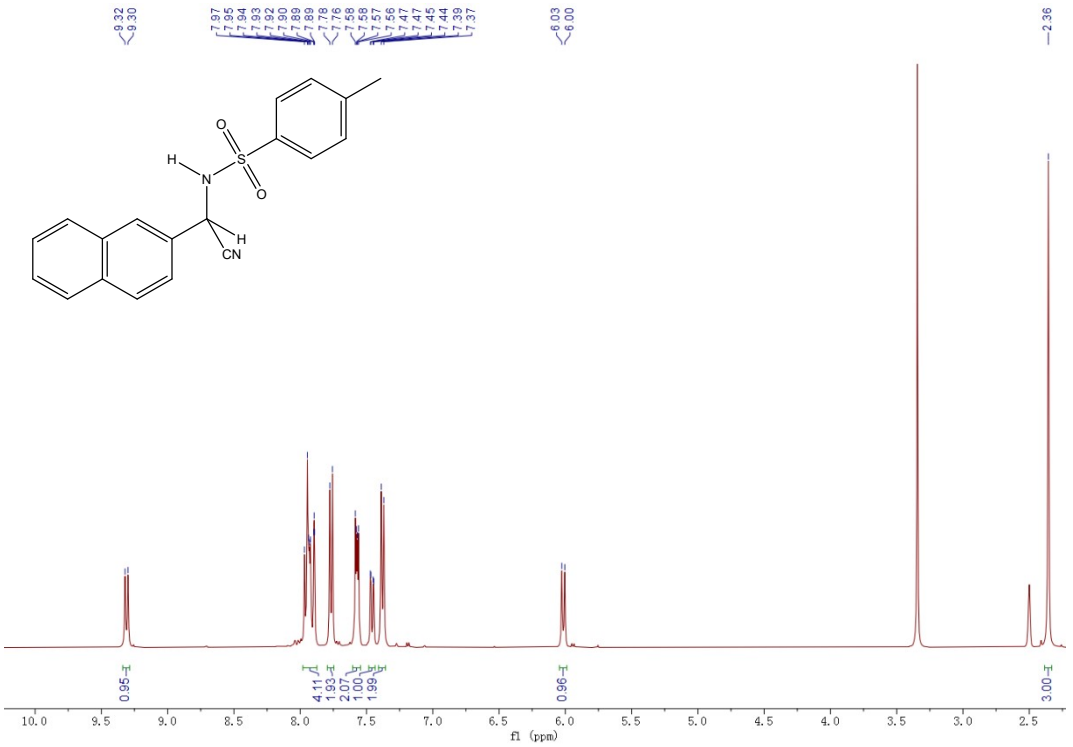


Fig. S12 ^{1}H NMR spectrum of substrate **2f**: *N*-{cyano[(3-phenoxyphenyl)methylene]methyl}-4-methyl-benzenesulfonamide

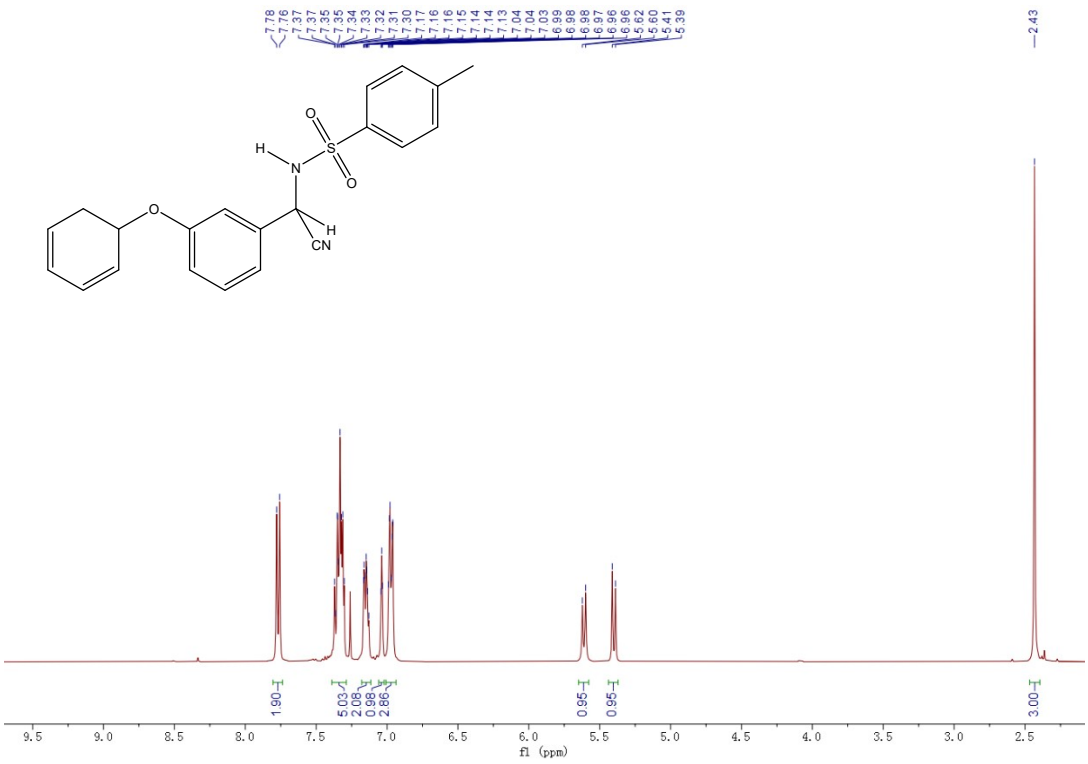


Fig. S13 ^{13}C NMR spectrum of substrate **1a**: 4-methyl-*N*-phenylmethylene-benzenesulfonamide

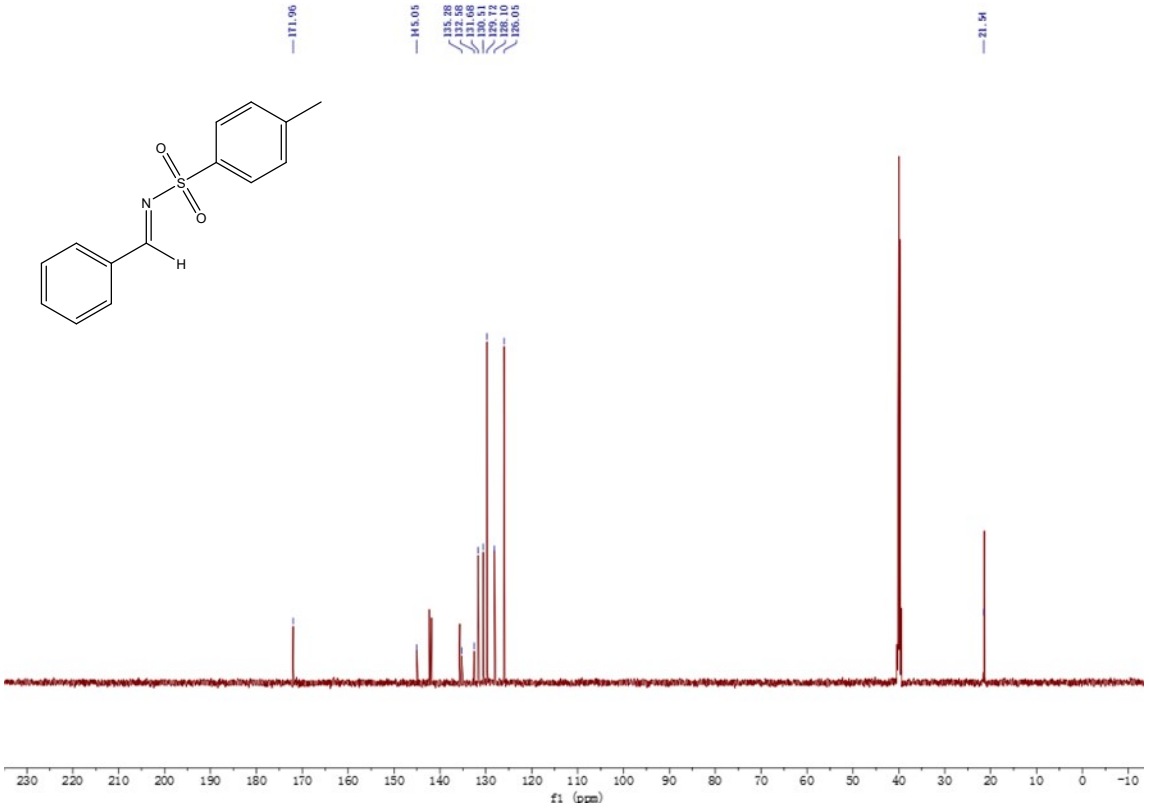


Fig. S14 ^{13}C NMR spectrum of substrate **1b**: 4-methyl-*N*-[(2,4,6-trimethylphenyl)methylene]-Benzenesulfonamide

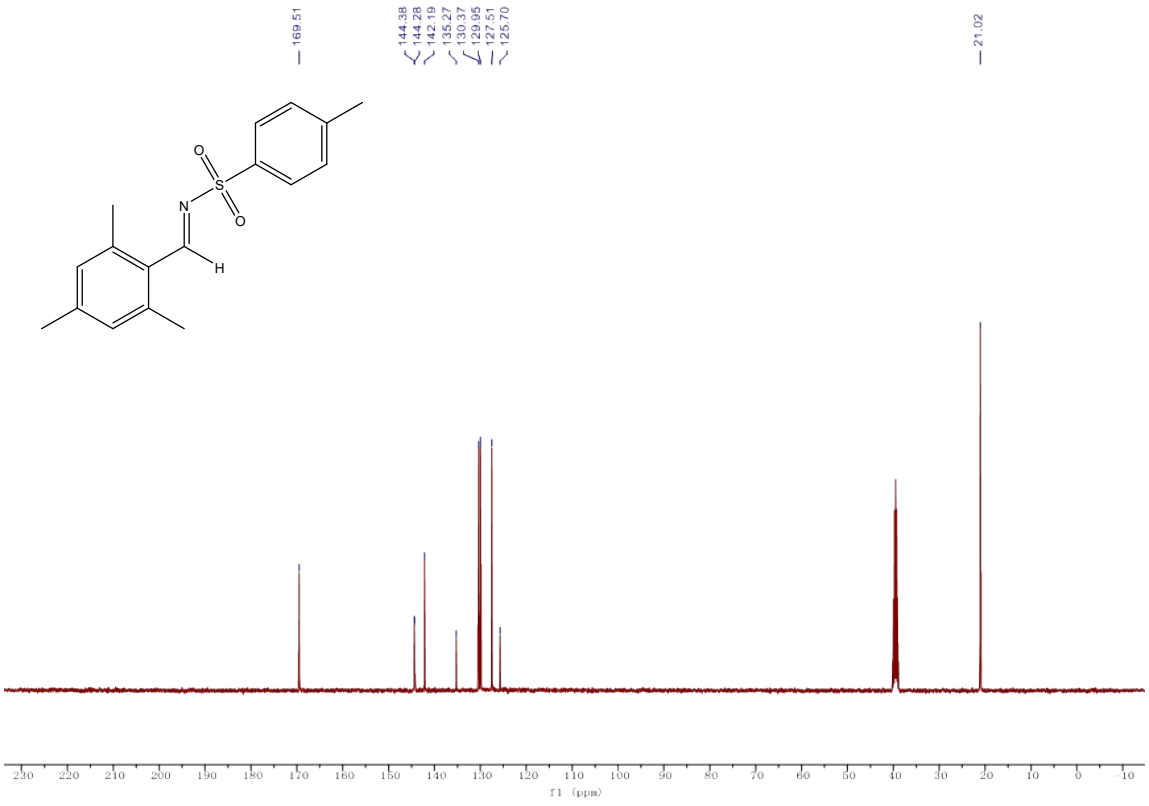


Fig. S15 ^{13}C NMR spectrum of substrate **1c**: 4-methyl-*N*-[(3,4-dimethylphenyl)methylene]-Benzenesulfonamide

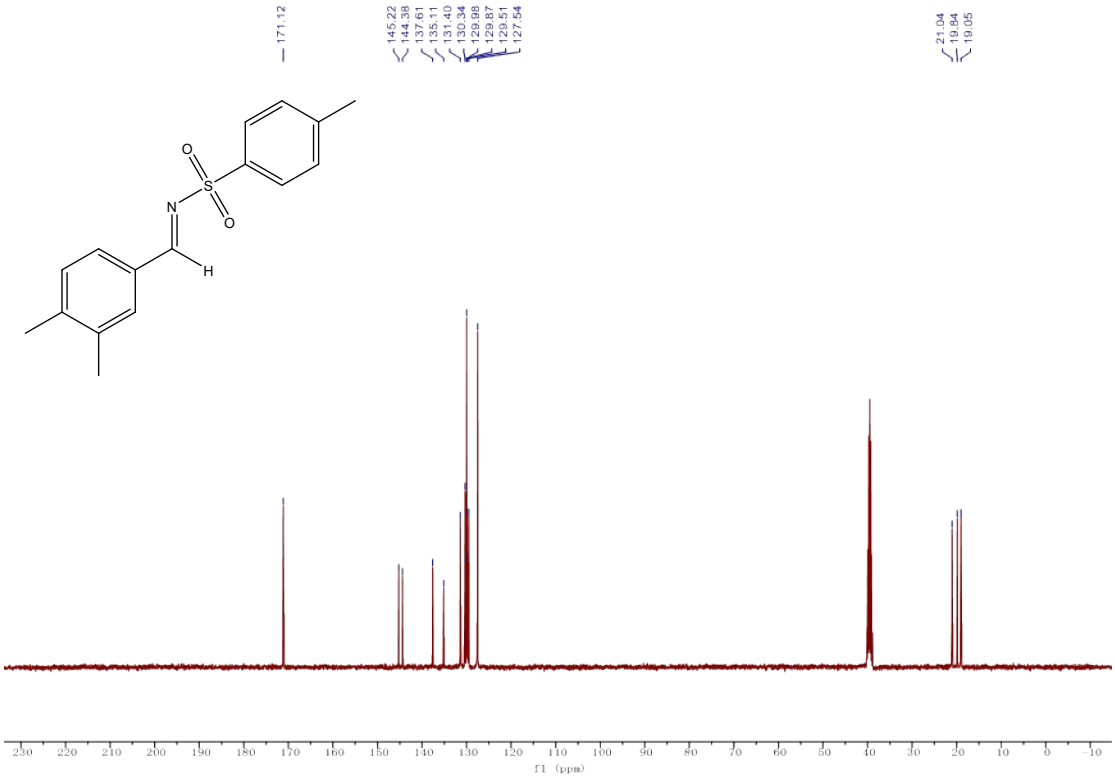


Fig. S16 ^{13}C NMR spectrum of substrate **1d**: 4-methyl-*N*-[(4-methylphenyl)methylene]-Benzenesulfonamide

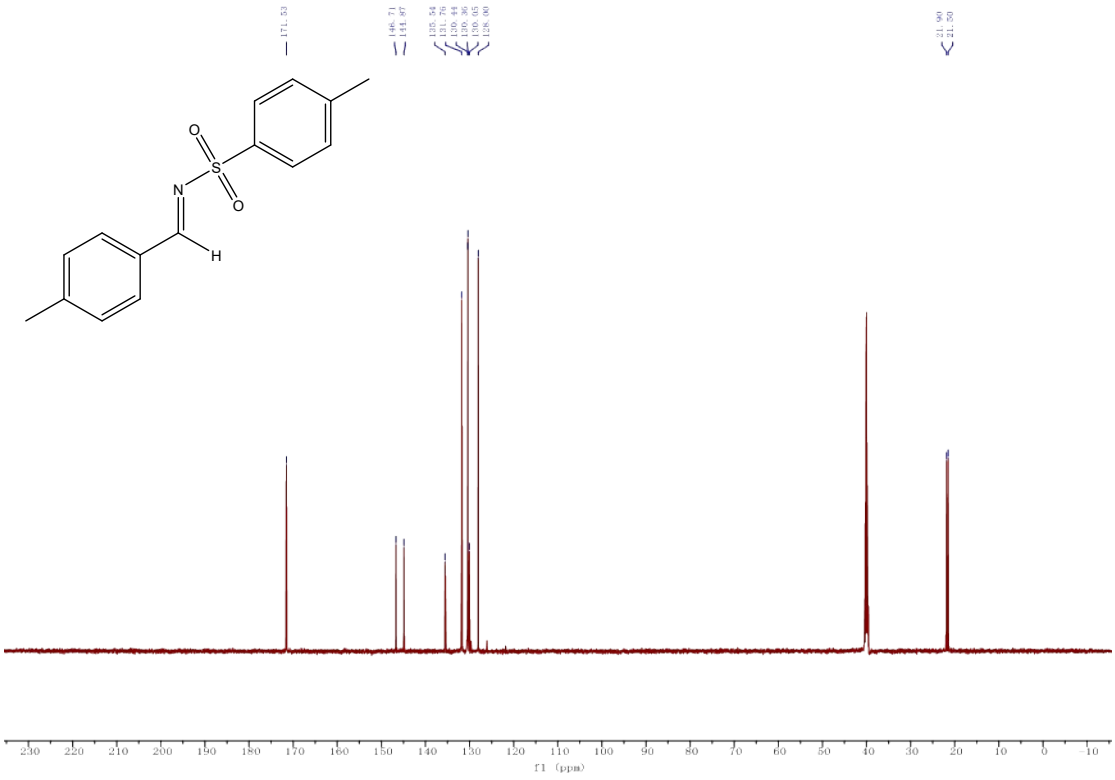


Fig. S17 ^{13}C NMR spectrum of substrate **1e**: 4-methyl-*N*-(2-naphthalenylmethylene)-benzenesulfonamide

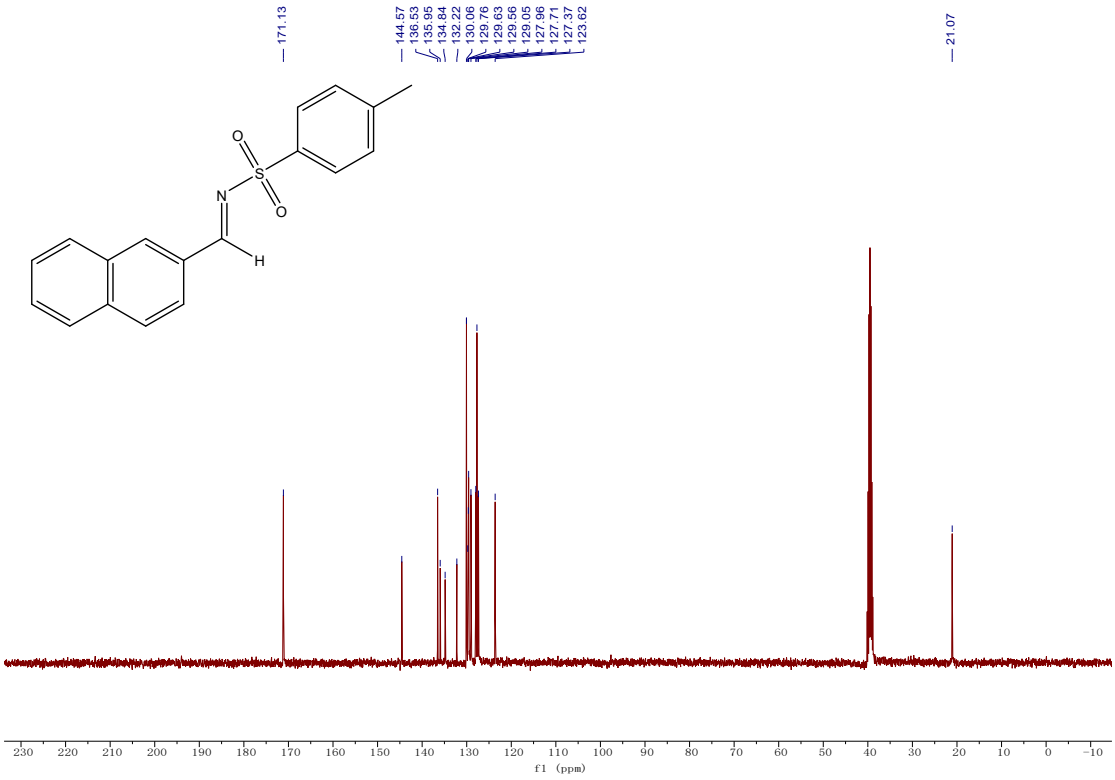


Fig. S18 ^{13}C NMR spectrum of substrate **1f**: 4-methyl-*N*-[(3-phenoxyphenyl)methylene]-benzenesulfonamide

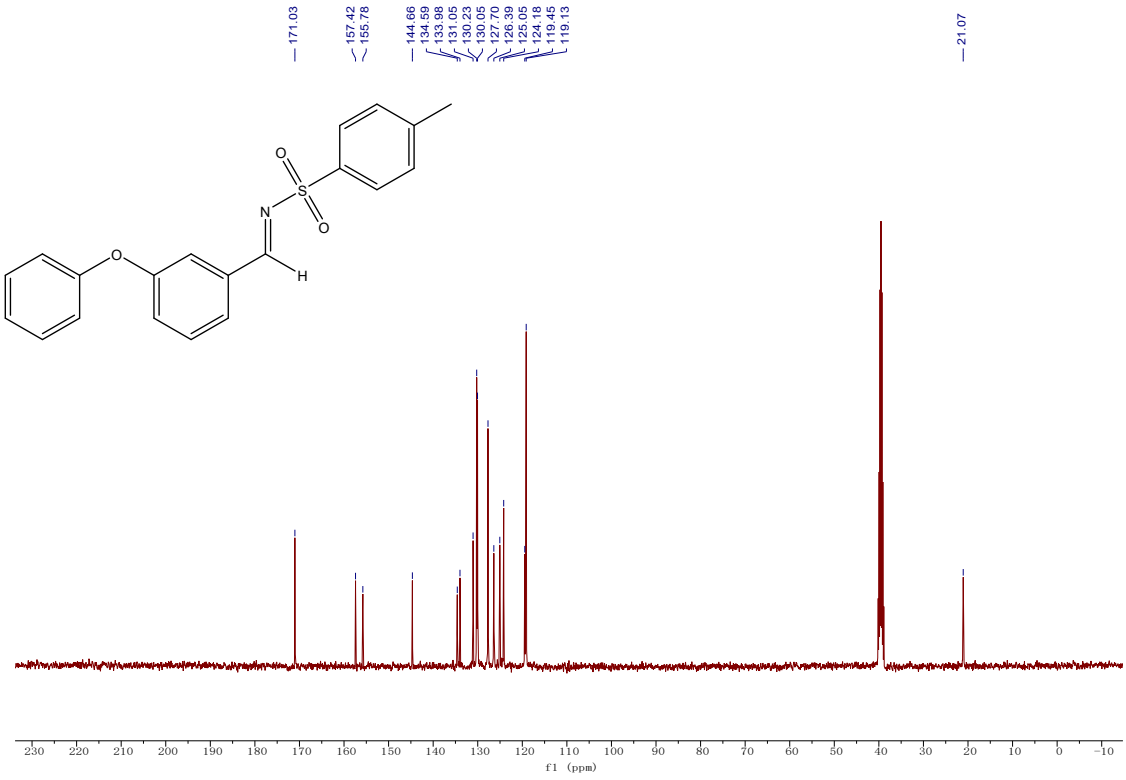


Fig. S19 ^{13}C NMR spectrum of substrate **2a**: *N*-[cyano(phenyl)methyl]-4-methyl-benzenesulfonamide

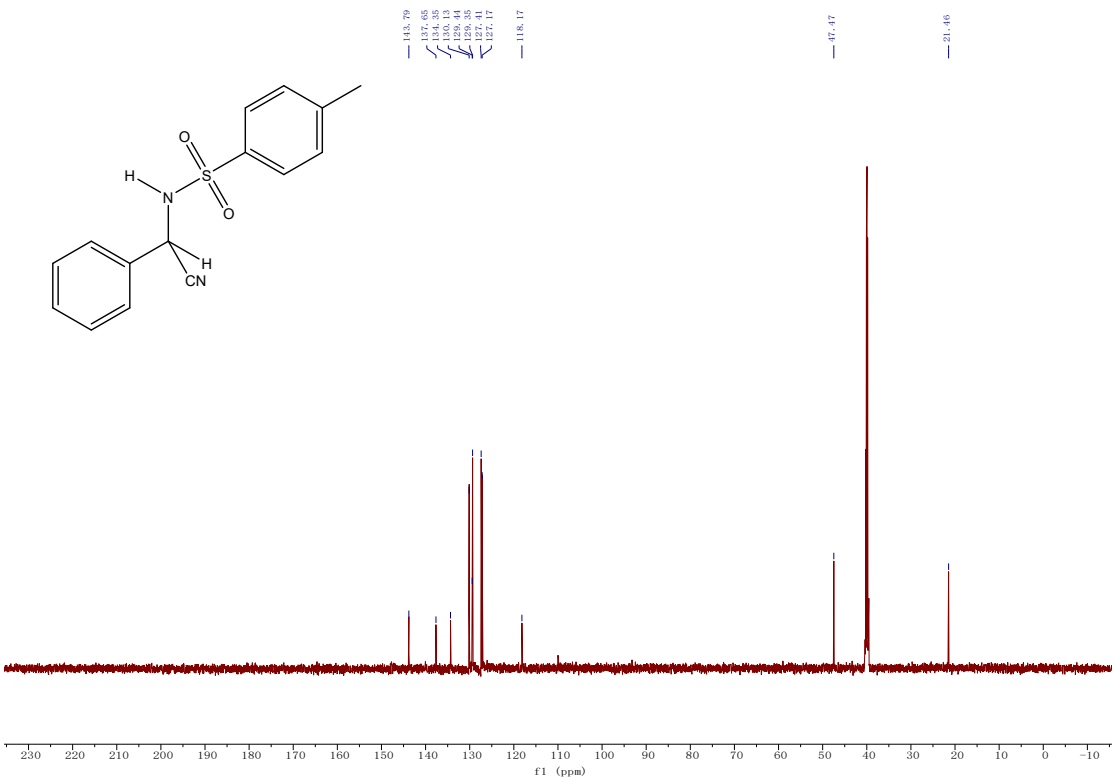


Fig. S20 ^{13}C NMR spectrum of substrate **2b**: *N*-[cyano(2,4,6-trimethylphenyl)methyl]-4-methylbenzenesulfonamide

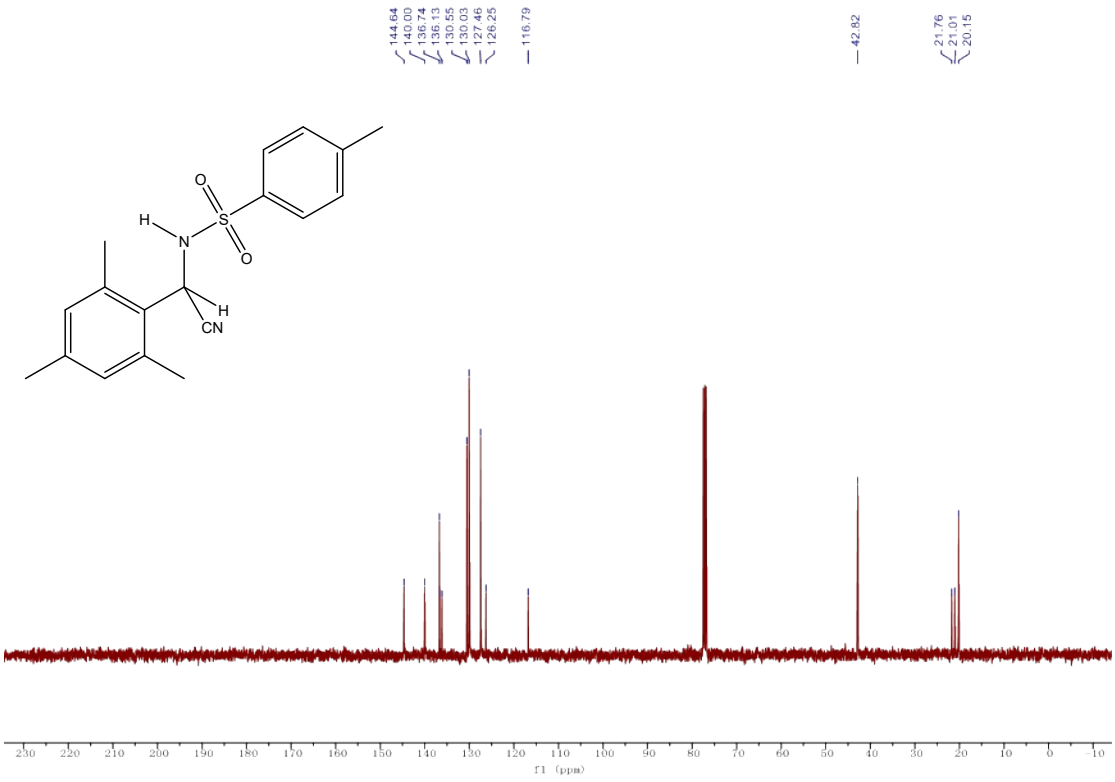


Fig. S21 ^{13}C NMR spectrum of substrate **2c**: *N*-[cyano(3,4-dimethylphenyl)methyl]-4-methylbenzenesulfonamid

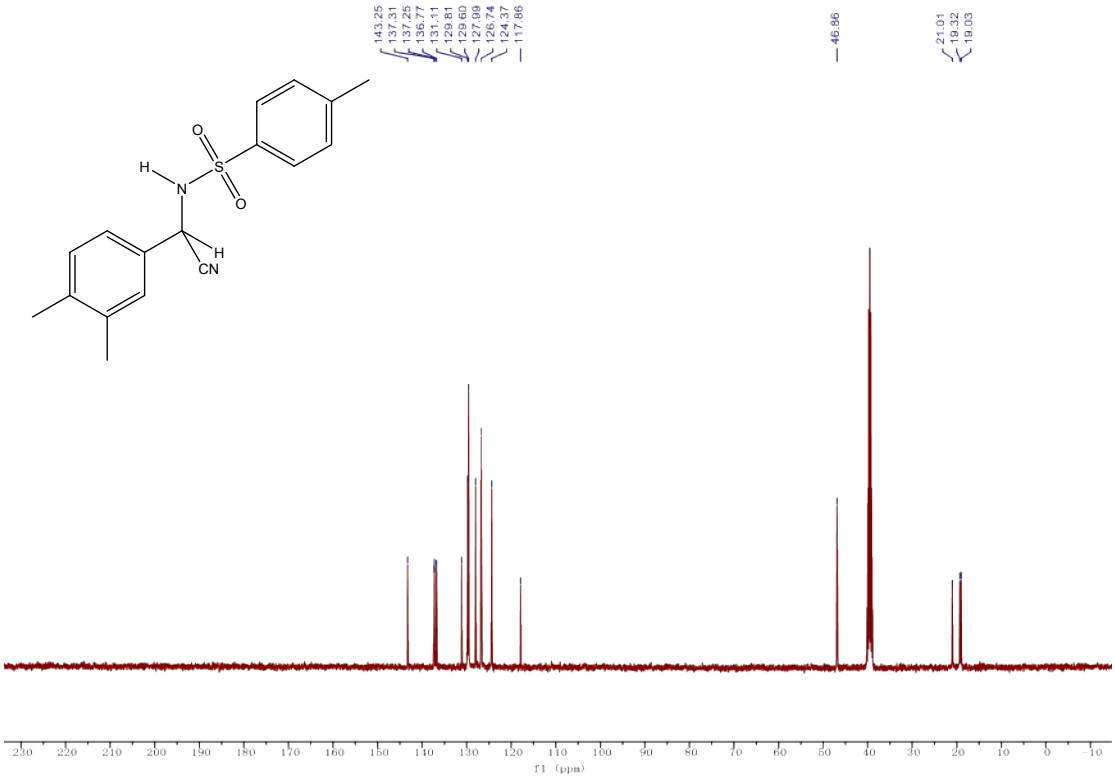


Fig. S22 ^{13}C NMR spectrum of substrate **2d**: *N*-[cyano(p-tolyl)methyl]-4-methyl-benzenesulfonamide

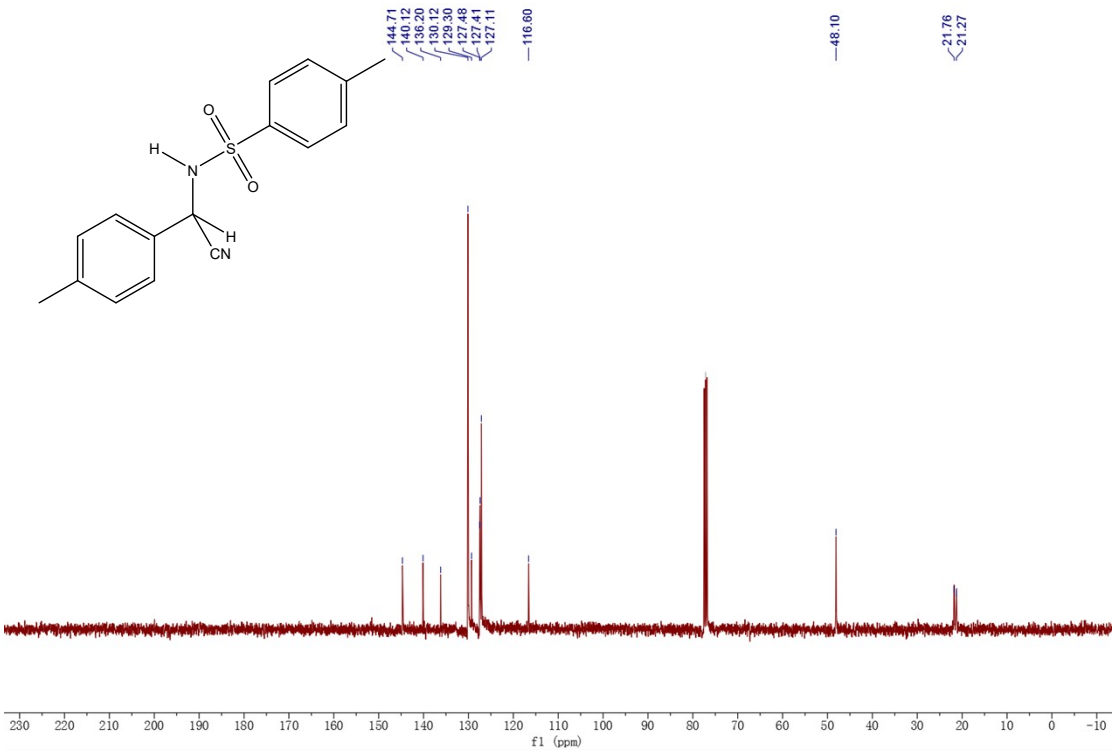


Fig. S23 ^{13}C NMR spectrum of substrate **2e**: *N*-(cyano-2-naphthalenylmethyl)-4-methyl-benzenesulfonamide

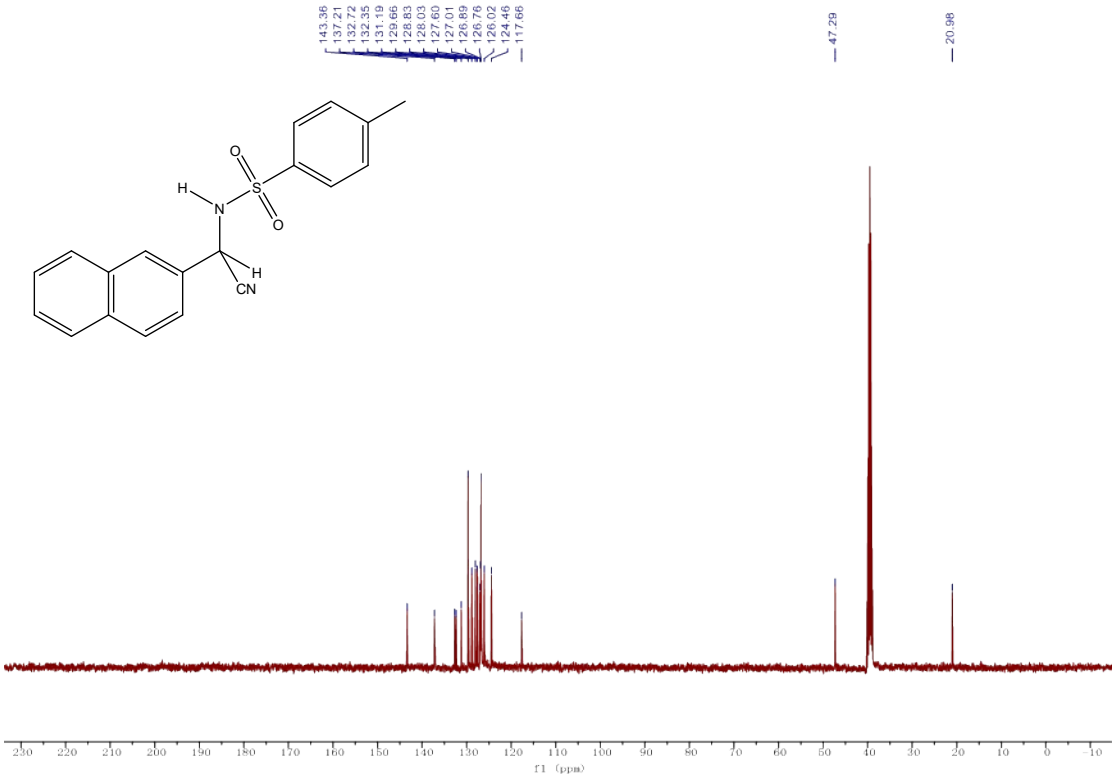
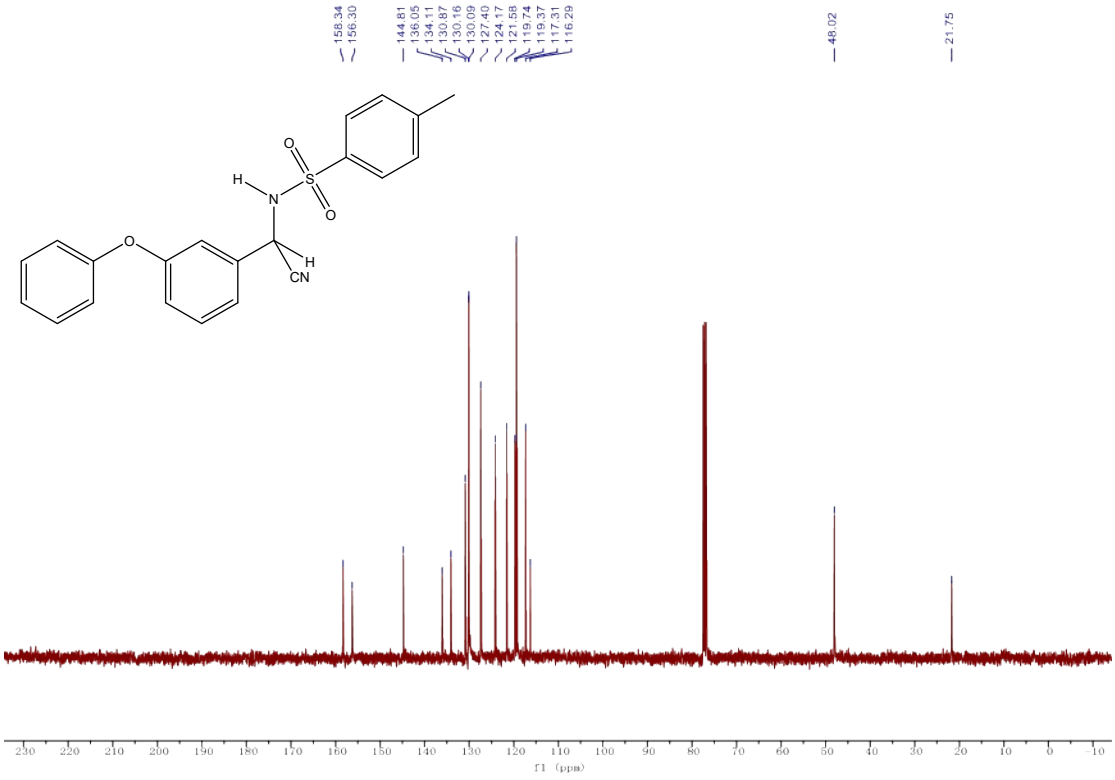


Fig. S24 13C NMR spectrum of substrate **2f**: *N*-{cyano[(3-phenoxyphenyl)methylene] methyl}-4-methyl-benzenesulfonamide



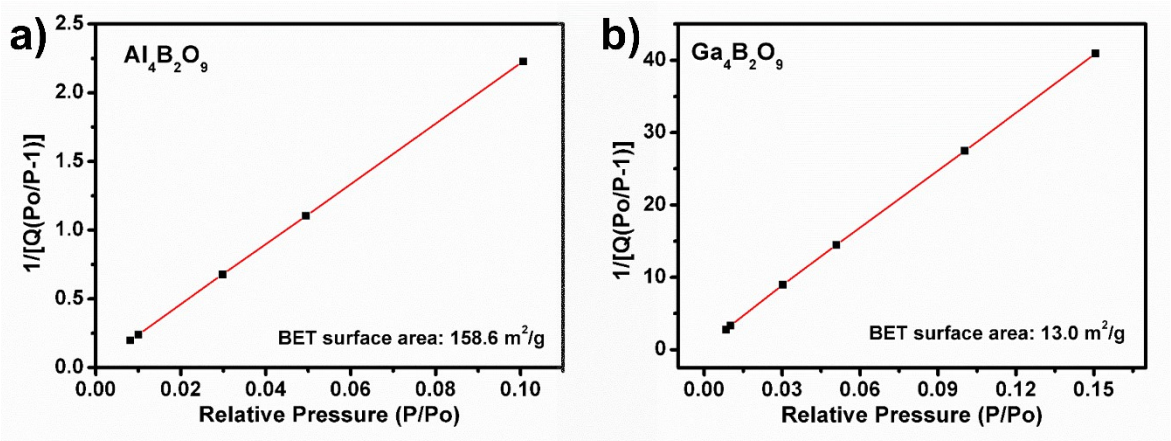


Fig. S25 BET surface areas of a) $Al_4B_2O_9$ and b) $Ga_4B_2O_9$.