http://dx.doi.org/10.5935/0103-5053.20130218

J. Braz. Chem. Soc., Vol. 24, No. 11, 1739-1743, 2013.
Printed in Brazil - ©2013 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Hydrocyanation of Sulfonylimines Using Potassium Hexacyanoferrate(II) as an Eco-Friendly Cyanide Source

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Um método eficiente e ecologicamente amigável de hidrocianação de sulfoniliminas por um procedimento de duas etapas em uma única operação usando hexacianoferrato(II) de potássio como fonte de cianeto, cloreto de benzoíla como promotor e carbonato de potássio como uma base é descrito. Este método tem como característica o uso de fonte de cianeto atóxica, não volátil e barata, alto rendimento e um procedimento simples.

An efficient and eco-friendly method for hydrocyanation of sulfonylimines via one-pot two-step procedure using potassium hexacyanoferrate(II) as a cyanide source, benzoyl chloride as a promoter, and potassium carbonate as a base is described. This protocol has the features of using nontoxic, nonvolatile and inexpensive cyanide source, high yield, and simple work-up procedure.

Keywords: sulfonylimine, hydrocyanation, potassium hexacyanoferrate(II), Strecker-type reaction, green chemistry

Introduction

The Strecker reaction, nucleophilic addition of cyanide ion to imines, is of great importance to modern organic chemistry as it offers one of the most direct and viable methods for the synthesis of α-aminonitriles.[1] α-Aminonitriles are significantly important intermediates for the synthesis of a wide variety of amino acids, amides, diamines, and nitrogen-containing heterocycles.[2] The recent advance of Strecker reaction has been reviewed by Feng and coworkers.[3] The hydrocyanation of sulfonylimines to synthesize α-sulfonylimidonitriles is one of the most important Strecker-type reactions. Ooi[4] reported the Strecker reaction of sulfonylimines using aqueous potassium cyanide as a cyanide source. Kim[5] studied the hydrocyanation of sulfonylimines using ethyl cyanoformate as a cyanide source. Nakamura,[6] Feng[7] and Kantam[8] investigated the Strecker-type reaction of sulfonylimines using trimethylsilane cyanide as a cyanide source. In addition, the reported Strecker reactions also utilize HCN,[9] $Zn(CN)_2$,[10] $(EtO)_2P(O)CN$,[11] Et_2AlCN,[12] Bu_3SnCN,[13] MeCOCN,[14] and acetone cyanohydrin[15] as cyanide sources. However, some problems including toxicity, volatility or high cost are still associated with these cyanating agents. To overcome these problems, attention has been given to the development of alternative cyanide sources that are relative cheap, less toxic, and easier to handle.

Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$, is mainly used as carburizing agent in the iron and steel industry. And it is also used in the food industry for metal precipitation. In addition, it has been described as an anti-agglutinating auxiliary for table salt (NaCl). $K_4[Fe(CN)_6]$ is a by-product of the coal chemical industry and commercially available on a ton scale, and it is even cheaper than KCN. Recently, $K_4[Fe(CN)_6]$ has been used as a cyanide source for some substitution reactions to synthesize benzonitriles,[16] aroyl cyanides,[17] benzyl cyanides,[18] cinnamonitriles,[19] dihaloacrylonitriles[20] and cyano substituted heterocycles.[21] Our recent research interests focused on the cyanation of unsaturated compounds by nucleophilic addition reactions using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source, which included the cyanation of aldehydes and ketones to cyanohydrins,[22] the cyanation of aldimines and ketimines to α-aminonitriles,[23] and the cyanation of α,β-unsaturated ketones to β-cyano ketones.[24] In this work, we report an efficient method for the hydrocyanation of sulfonylimines to α-sulfonylimidonitriles using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source.

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Results and Discussion

Initially, *N*-benzylidene-4-methylbenzenesulfonamide (**1a**) was selected as a substrate to investigate the feasibility of hydrocyanation of sulfonylimines using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source (Scheme 1). The reaction was attempted under different conditions such as using Lewis acids, Lewis bases, and organometallic compounds as catalysts at different temperature in various solvents. However, no product could be obtained for this reaction, the possible reason is that $K_4[Fe(CN)_6]$ is too stable to release cyanide ions in the studied conditions. In the later study, it was found that benzoyl chloride could efficiently promote the reaction to yield corresponding hydrocyanation product through an intermediate, benzoyl cyanide, which could be isolated and identified from the reaction system. Actually, the hydrocyanation reaction for **1a** directly utilized benzoyl cyanide as a cyanating agent could effectively give the same product by a similar way in high yield. This further demonstrated the fact of benzoyl cyanide as a reaction intermediate. It was also found that only 0.2 equiv of $K_4[Fe(CN)_6]$ was needed for 1 equiv of **1a**, which indicated that six CN^- of $K_4[Fe(CN)_6]$ could be fully utilized in this reaction. In addition, no by-products were observed in this reaction, which implied the high chemoselectivity of the reaction.

It was found that bases played a key role in the studied reaction. The reaction gave very low yield in the absence of a base (Table 1, entry 1). However, the reaction could be proceeded smoothly in the presence of some bases, such as Et_3N, DMAP, K_2CO_3, KOH, and NaOH (Table 1, entries 2-6). Among them, K_2CO_3 gave the highest yield within the shortest reaction time (Table 1, entry 4).

Table 1. The effect of bases on the yield of hydrocyanation of **1a** using $K_4[Fe(CN)_6]$[a]

Entry	Base	Reaction time / h	Yield / %[b]
1	none	24	10
2	Et_3N	24	90
3	DMAP	1	91
4	K_2CO_3	1	93
5	KOH	2	92
6	NaOH	10	75

[a]Reaction condition: **1a** (0.5 mmol), potassium hexacyanoferrate(II) (0.1 mmol), benzoyl chloride (0.6 mmol) and base (0.1 mmol) in ethanol (8 mL); [b]isolated yields.

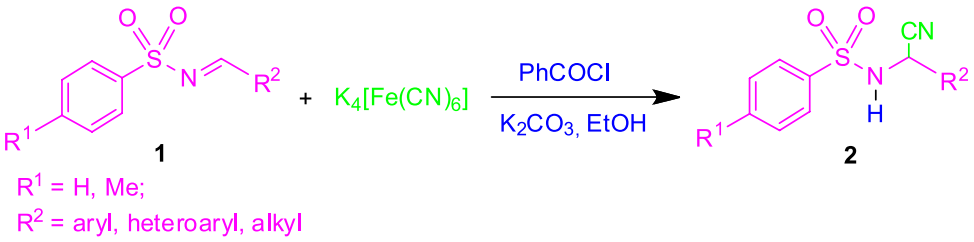
The solvents also played an important role in the hydrocyanation of **1a** using $K_4[Fe(CN)_6]$ as an eco-friendly cyanide source, benzoyl chloride as a promoter, and potassium carbonate as a base (Table 2). A set of anhydrous solvents was tested for the reaction. Polar solvents such as MeOH, EtOH, MeCN, THF, and CH_2Cl_2 gave the desired product **2a** in moderate to high yields (Table 2, entries 1-5). Especially the reaction in EtOH afforded **2a** in the highest yield (Table 2, entry 2). However, it was found that the reaction in polar aprotic solvents such as DMSO and DMF gave unidentified by-products (Table 2, entries 6-7). In addition, no product was observed in nonpolar solvents such as toluene and n-hexane.

Table 2. The effect of solvents on the yield of hydrocyanation of **1a** using $K_4[Fe(CN)_6]$[a]

Entry	Solvent	Reaction time / h	Yield / %[b]
1	MeOH	5	80
2	EtOH	1	93
3	CH_3CN	12	50
4	THF	3.5	30
5	CH_2Cl_2	12	55
6	DMSO	24	0[c]
7	DMF	24	0[c]

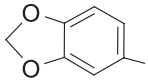
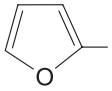
[a]Reaction condition: **1a** (0.5 mmol), potassium hexacyanoferrate(II) (0.1 mmol), benzoyl chloride (0.6 mmol) and potassium carbonate (0.1 mmol) in solvent (8 mL); [b]isolated yields; [c]unidentified by-products were observed.

Based on the above promising findings, a series of sulfonylimines formed from aldehydes and sulfonamides were examined for the hydrocyanation in EtOH using $K_4[Fe(CN)_6]$ as a cyanating agent, benzoyl chloride as a promoter, and K_2CO_3 as a base (Table 3, Scheme 1). It was found that sulfonylimines including electron-donating groups on aromatic rings of R^2 gave the corresponding products in very high yields (Table 3, entries 1-5). In contrast, sulfonylimines including electron-withdrawing groups on aromatic rings of R^2 gave slightly lower yields (Table 3, entries 6-10). In addition, *ortho*-substituted sulfonylimines exhibited large sterical hindrance and gave lower yields than the *para*-ones (Table 3, entries 7-8). Sulfonylimines with aliphatic R^2, such as ethyl and isopropyl, could also participate in the hydrocyanation reactions to give the corresponding products in high yields although they needed more reaction time (Table 3, entries 12-13). Sulfonylimines including heterocycle, such as furan-2-yl, could also smoothly react with $K_4[Fe(CN)_6]$ (Table 3, entry 11). R^1 groups on sulfonylimines had no obvious effect on the yields of products. In addition, the sulfonylimines formed from



Scheme 1. The hydrocyanation of sulfonylimines using $K_4[Fe(CN)_6]$.

Table 3. Optimized hydrocyanation of sulfonylimines using $K_4[Fe(CN)_6]$[a]

Entry	R^1	R^2	Product	time / h	Yield / %[b]	mp (lit.) / °C
1	4-CH_3	C_6H_5	**2a**	1	93	152-154 (152-154)[26]
2	4-CH_3	4-$CH_3C_6H_4$	**2b**	0.5	95	149-150 (155-156)[27]
3	4-CH_3	4-$CH_3OC_6H_4$	**2c**	0.5	96	124-125 (128-129)[26]
4	4-CH_3	4-$(CH_3)_2NC_6H_4$	**2d**	1.5	82	158-160
5	4-CH_3		**2e**	1	90	166-168 (124-126)[28]
6	4-CH_3	4-FC_6H_4	**2f**	1	60	122-124 (100-104)[28]
7	4-CH_3	2-ClC_6H_4	**2g**	1	65	112-114 (118-119)[27]
8	4-CH_3	4-ClC_6H_4	**2h**	1	74	130-132 (134-135)[27]
9	4-CH_3	2,4-$2ClC_6H_3$	**2i**	1	54	136-137
10	4-CH_3	4-BrC_6H_4	**2j**	1	66	150-151 (150-151)[27]
11	4-CH_3		**2k**	3	63	98-100 (98-100)[26]
12	4-CH_3	CH_3CH_2	**2l**	4	86	52-54
13	4-CH_3	$(CH_3)_2CH$	**2m**	4	65	78-79 (74-76)[28]
14	H	C_6H_5	**2n**	1	93	98-100 (100-102)[28]
15	H	4-$CH_3C_6H_4$	**2o**	1	95	100-102
16	H	4-ClC_6H_4	**2p**	1	90	122-124
17	H	4-BrC_6H_4	**2q**	1	72	130-132

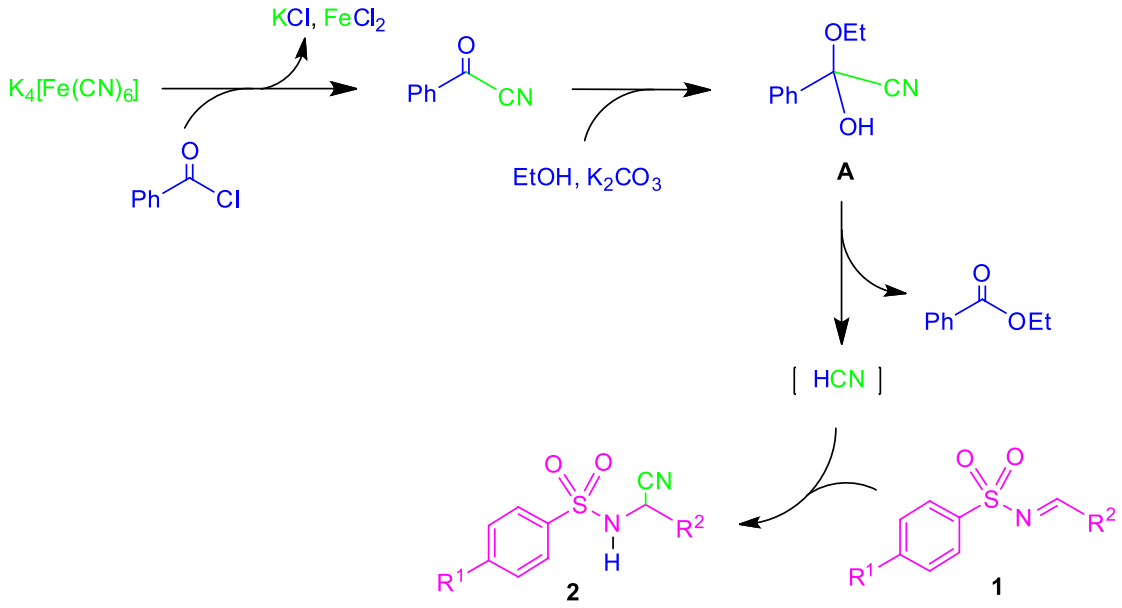
[a]Reaction condition: sulfonylimines (0.5 mmol), potassium hexacyanoferrate(II) (0.1 mmol), benzoyl chloride (0.6 mmol) and potassium carbonate (0.1 mmol) in ethanol (8 mL); [b]isolated yields.

ketones and *p*-toluenesulfonamide were also attempted for the hydrocyanation reactions using $K_4[Fe(CN)_6]$. However, very low isolated yields were obtained under the similar conditions. The possible reason is the large sterical hindrance of the substrates.

A plausible mechanism for the hydrocyanation of sulfonylimines to synthesize α-sulfonylimidonitriles using $K_4[Fe(CN)_6]$ as a cyanide source, according to Hunig's review,[25] is shown in Scheme 2. Firstly $K_4[Fe(CN)_6]$ reacts with benzoyl chloride to form benzoyl cyanide as an intermediate. Then benzoyl cyanide is attacked by ethanol in the presence of potassium carbonate to yield nucleophilic additional intermediate **A**. Intermediate **A** undergoes the loss of ethyl benzoate to produce hydrogen cyanide *in situ*. Then the nucleophilic additions of hydrogen cyanide to sulfonylimines **1** yield α-sulfonylimidonitriles **2** as products.

Conclusions

In summary, an efficient method has been developed for the hydrocyanation of sulfonylimines to synthesize α-sulfonylimidonitriles by one-pot two-step procedure using $K_4[Fe(CN)]_6$ as an original eco-friendly cyanide source, benzoyl chloride as a promoter, and potassium carbonate as a base. The protocol compared with literature methods has advantages of using non-toxic, nonvolatile and inexpensive cyanide source, high yield, and simple work-up procedure.



Scheme 2. The proposed mechanism for hydrocyanation of sulfonylimines using $K_4[Fe(CN)]_6$.

Experimental

IR spectra were recorded using KBr pellets on an Alpha Centauri FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury-400BB instrument using $CDCl_3$ as solvent and Me_4Si as internal standard. Melting points were observed in an electrothermal melting point apparatus. Potassium hexacyanoferrate(II) was dried at 80 °C under vacuum for 24 h and finely powdered prior to use. Sulfonylimines were generally prepared according to modified literature methods by refluxing of 4-methylbenzenesulfonamide or benzenesulfonamide with various aldehydes in toluene using anhydrous magnesium sulfate as a dehydrating agent and acetic acid as a catalyst.[29]

The general procedure for the hydrocyanation of sulfonylimines

The mixture of $K_4[Fe(CN)_6]$ (0.1 mmol) and benzoyl chloride (0.6 mmol) was stirred at 160 °C for 3 h, then the reaction system was cooled to room temperature, and sulfonylimines (0.5 mmol) and potassium carbonate (0.1 mmol) in ethanol (8 mL) were added. The mixture was further stirred at room temperature for appropriate time indicated in Table 3. After completion of the reaction monitored by TLC, the resulting mixture was filtered to remove the solids. The liquor was concentrated, and the residues were isolated by column chromatography using petroleum ether and ethyl acetate (6:1) as eluent to give pure product.

Supplementary Information

Full set of characterization data (IR, ^{1}H and ^{13}C NMR spectra) are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

The authors thank the National Natural Science Foundation of China (21162024) and Provincial Natural Science Foundation of Gansu (1107RJZA189) for the financial support of this work.

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Submitted: July 5, 2013
Published online: September 4, 2013

J. Braz. Chem. Soc., Vol. 24, No. 11, S1-S29, 2013.
Printed in Brazil - ©2013 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

Hydrocyanation of Sulfonylimines Using Potassium Hexacyanoferrate(II) as an Eco-Friendly Cyanide Source

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The general procedure for the preparation of sulfonylimines

The mixture of 4-methylbenzenesulfonamide or benzenesulfonamide (20 mmol), aldehyde (22 mmol), anhydrous magnesium sulfate (5 mmol) and acetic acid (4 mmol) in 20 mL of toluene was refluxed at 110 °C for 15 h. The progress of the reaction was monitored by TLC. After the completion, the system was cooled to room temperature, and the solvent was removed under reduced pressure. The resulting solid was recrystallized from diethyl ether to give pure product. The analytical data for representative products are given below.

N-Benzylidene-4-methylbenzenesulfonamide (**1a**)

White solid; mp: 109-110 °C (lit. 112-113 °C).[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H, CH_3), 7.24 (d, 2H, *J* 8.4 Hz, Ar-H), 7.48 (t, 2H, *J* 7.8 Hz, Ar-H), 7.50 (t, 1H, *J* 6.4 Hz, Ar-H), 7.80-7.83 (m, 4H, Ar-H), 8.98 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 128.3, 129.8, 130.2, 131.5, 135.3, 140.1, 145.1, 170.6.

N-(4-Methylbenzylidene)-4-methylbenzenesulfonamide (**1b**)

White solid; mp: 111-113 °C (lit. 112-114 °C).[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 6H, CH_3), 7.27 (d, 2H, *J* 7.6 Hz, Ar-H), 7.35 (d, 2H, *J* 7.8 Hz, Ar-H), 7.83 (d, 2H, *J* 7.6 Hz, Ar-H), 7.91 (d, 2H, *J* 7.6 Hz, Ar-H), 8.97 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 126.9, 128.5, 129.9, 130.3, 130.4, 131.9, 135.8, 144.9, 170.5.

N-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide (**1c**)

White solid; mp: 128-130 °C (lit. 128-129 °C).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 6.92 (d, 2H, *J* 8.6 Hz, Ar-H), 7.28 (d, 2H, *J* 7.8 Hz, Ar-H), 7.80 (d, 2H, *J* 7.6 Hz, Ar-H), 7.84 (d, 2H, *J* 7.6 Hz, Ar-H), 8.90 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) *d* 22.3, 56.7, 115.4, 125.8, 128.6, 130.3, 134.4, 136.5, 145.1, 166.1, 170.0.

N-(2-Chlorobenzylidene)-4-methylbenzenesulfonamide (**1g**)

White solid; mp: 115-116 °C (lit. 114-116 °C).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H, CH_3), 7.28-7.91 (m, 8H, Ar-H), 9.12 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 126.8, 128.6, 129.2, 129.6, 131.3, 131.8, 134.4, 137.2, 168.2.

N-(Furan-2-ylmethylene)-4-methylbenzenesulfonamide (**1k**)

Brown solid; mp: 100-102 °C (lit. 101-102 °C).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 1H, CH_3), 6.78–7.77 (m, 7H, Ar-H), 8.85 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 112.8, 115.6, 126.8, 128.8, 131.1, 148.6, 151.8, 154.5, 157.2.

The general procedure for the hydrocyanation of sulfonylimines

The mixture of $K_4[Fe(CN)_6]$ (0.1 mmol) and benzoyl chloride (0.6 mmol) was stirred at 160 °C for 3 h, then the reaction system was cooled to room temperature, and sulfonylimines (0.5 mmol) and potassium carbonate (0.1 mmol) in ethanol (8 mL) were added. The mixture was further stirred at room temperature for appropriate time indicated in Table 3. After completion of the reaction monitored by TLC, the resulting mixture was filtered to remove the solids. The liquor was concentrated, and the residues were isolated by column chromatography using petroleum ether and ethyl acetate (6:1) as eluent to give pure product. The analytical data for products are given below.

N-(Cyanophenylmethyl)-4-methylbenzenesulfonamide (**2a**)

White solid; mp 152-154 °C; IR (KBr) ν_{max}/cm^{-1} 3254 (NH), 2245 (CN), 1334 (S=O asym), 1157 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H, CH_3), 5.10 (d,

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1H, *J* 8.4 Hz, NH), 5.48 (d, 1H, *J* 8.4 Hz, CH), 7.36-7.46 (m, 7H, ArH), 7.82 (t, 2H, *J* 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 48.2, 116.2, 127.0, 127.3, 129.4, 129.9, 130.0, 132.0, 135.9, 144.7. Anal. calcd. for $C_{15}H_{14}N_2O_2S$: C, 62.92; H, 4.93; N, 9.78; found: C, 62.81; H, 4.95; N, 9.81.

N-[Cyano(4-tolyl)methyl]-4-methylbenzenesulfonamide (**2b**)

White solid; mp 149-150 °C; IR (KBr) ν_{max}/cm^{-1} 3270 (NH), 2248 (CN), 1336 (S=O asym), 1160 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 5.09 (d, 1H, *J* 8.4 Hz, NH), 5.34 (d, 1H, *J* 8.4 Hz, CH), 7.12 (d, 2H, *J* 8.0 Hz, ArH), 7.23 (d, 2H, *J* 8.0 Hz, ArH), 7.28 (d, 2H, *J* 8.0 Hz, ArH), 7.72 (d, 2H, *J* 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.6, 47.9, 116.4, 127.0, 127.3, 129.1, 130.0, 136.1, 140.0, 144.6. Anal. calcd. for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33; found: C, 64.09; H, 5.36; N, 9.35.

N-[Cyano(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide (**2c**)

White solid; mp 124-125 °C; IR (KBr) ν_{max}/cm^{-1} 3271 (NH), 2248 (CN), 1337 (S=O asym), 1160 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 3.71 (s, 3H, OCH_3), 5.25 (d, 1H, *J* 8.4 Hz, NH), 5.32 (d, 1H, *J* 8.4 Hz, CH), 6.77-6.82 (m, 2H, ArH), 7.18-7.28 (m, 4H, ArH), 7.68-7.73 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 48.0, 55.8, 115.0, 116.8, 124.4, 127.5, 128.8, 130.3, 136.4, 144.9, 160.9. Anal. calcd. for $C_{16}H_{16}N_2O_3S$: C, 60.74; H, 5.10; N, 8.85; found: C, 60.83; H, 5.09; N, 8.82.

N-{Cyano[4-(dimethylamino)phenyl]methyl}-4-methylbenzenesulfonamide (**2d**)

White solid; mp 158-160 °C; IR (KBr) ν_{max}/cm^{-1} 3297 (NH), 2247 (CN), 1335 (S=O asym), 1164 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H, CH_3), 2.99 (s, 6H, $N(CH_3)_2$), 4.95 (d, 1H, *J* 8.0 MHz, NH), 5.37 (d, 1H, *J* 8.0 Hz, CH), 6.69 (d, 2H, *J* 8.0 Hz, ArH), 7.27 (d, 2H, *J* 8.0 Hz, ArH), 7.38 (d, 2H, *J* 8.0 Hz, ArH), 7.84 (d, 2H, *J* 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 40.3, 47.9, 112.6, 117.0, 127.2, 128.3, 129.9, 136.2, 144.9. Anal. calcd. for $C_{17}H_{19}N_3O_2S$: C, 61.98; H, 5.81; N, 12.76; found: C, 62.21; H, 5.83; N, 12.73.

N-{Benzo[*d*][1,3]dioxol-5-yl(cyano)methyl}-4-methylbenzenesulfonamide (**2e**)

White solid; mp 166-168 °C; IR (KBr) ν_{max}/cm^{-1} 3212 (NH), 2244 (CN), 1338 (S=O asym), 1159 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H, CH_3), 5.10 (d, 1H, *J* 8.4 Hz, NH), 5.39 (d, 1H, *J* 8.4 Hz, CH), 6.03 (s, 2H, CH_2), 6.81 (d, 1H, *J* 8.4 Hz, ArH), 6.89 (s, 1H, CH, ArH), 6.95 (d, 1H, *J* 8.4 Hz, ArH), 7.39 (d, 2H, *J* 7.6 Hz, ArH), 7.83 (d, 2H, *J* 7.6 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 48.0, 101.8, 107.5, 108.7, 116.3, 121.0, 125.6, 126.5, 127.3, 129.7, 130.1, 136.0, 144.7, 148.6, 149.0. Anal. calcd. for $C_{16}H_{14}N_2O_4S$: C, 58.17; H, 4.27; N, 8.48; found: C, 58.09; H, 4.26; N, 8.50.

N-[Cyano(4-fluorophenyl)methyl]-4-methylbenzenesulfonamide (**2f**)

White solid; mp 122-124 °C; IR (KBr) ν_{max}/cm^{-1} 3256 (NH), 2243 (CN), 1332 (S=O asym), 1156 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H, CH_3), 5.43 (d, 1H, *J* 9.6 Hz, CH), 5.59 (bs, 1H, NH), 7.03-7.07 (m, 2H, ArH), 7.33-7.42 (m, 4H, ArH), 7.76 (d, 2H, *J* 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 47.5, 116.3, 127.2, 128.0, 129.1, 129.2, 130.0, 135.9, 144.8, 162.1, 164.6. Anal. calcd. for $C_{15}H_{13}FN_2O_2S$: C, 59.20; H, 4.31; N, 9.20; found: C, 59.14; H, 4.30; N, 9.16.

N-[(2-Chlorophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2g**)

White solid; mp 112-114 °C; IR (KBr) ν_{max}/cm^{-1} 3248 (NH), 2241 (CN), 1340 (S=O asym), 1159 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), 5.67-5.70 (m, 2H, NH and CH), 7.24-7.34 (m, 5H, ArH), 7.49 (d, 1H, *J* 7.2 Hz, ArH), 7.72-7.74 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 46.3, 115.8, 127.4, 127.9, 129.4, 130.0, 130.3, 130.7, 131.4, 133.1, 135.9, 144.6. Anal. calcd. for $C_{15}H_{13}ClN_2O_2S$: C, 56.16; H, 4.08; N, 8.73; found: C, 56.00; H, 4.09; N, 8.75.

N-[4-Chlorophenyl(cyano)methyl]-4-methylbenzenesulfonamide (**2h**)

White solid; mp 130-132 °C; IR (KBr) ν_{max}/cm^{-1} 3262 (NH), 2249 (CN), 1342 (S=O asym), 1160 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H, CH_3), 5.30 (d, 1H, *J* 9.2 Hz, NH), 5.45 (d, 1H, *J* 9.2 Hz, CH), 7.35-7.39 (m, 6H, ArH), 7.77 (d, 2H, *J* 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 47.5, 116.0, 127.2, 128.5, 129.5, 130.0, 130.6, 135.8, 136.0, 144.8. Anal. calcd. for $C_{15}H_{13}ClN_2O_2S$: C, 56.16; H, 4.08; N, 8.73; found: C, 56.22; H, 4.08; N, 8.72.

N-[Cyano(2,4-dichlorophenyl)methyl]-4-methylbenzenesulfonamide (**2i**)

White solid; mp 136-137 °C; IR (KBr) ν_{max}/cm^{-1} 3248 (NH), 2248 (CN), 1343 (S=O asym), 1158 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H, CH_3), 5.51 (bs, 1H, NH), 5.64 (d, 1H, *J* 8.8 Hz, CH), 7.28-7.32 (m, 3H, ArH), 7.37 (s, 1H, ArH), 7.44 (d, 1H, *J* 8.4 Hz, ArH), 7.72 (d, 2H, *J* 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 45.7, 115.5, 127.3, 128.1, 128.4, 130.0, 130.3, 130.4, 133.9,

135.7, 137.0, 144.8. Anal. calcd. for $C_{15}H_{12}Cl_2N_2O_2S$: C, 50.72; H, 3.41; N, 7.89; found: C, 50.64; H, 3.42; N, 7.91.

N-[4-(Bromophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2j**)

White solid; mp 150-151 °C; IR (KBr) ν_{max}/cm^{-1} 3262 (NH), 2248 (CN), 1343 (S=O asym), 1160 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H, CH_3), 5.40 (d, 1H, *J* 9.6 Hz, NH), 5.51 (d, 1H, *J* 9.6 Hz, CH), 7.29 (d, 2H, *J* 8.4 Hz, ArH), 7.34 (d, 2H, *J* 8.4 Hz, ArH), 7.50 (d, 2H, *J* 8.4 Hz, ArH), 7.75 (d, 2H, *J* 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 47.7, 115.9, 124.2, 127.3, 127.8, 128.8, 130.1, 130.6, 131.2, 132.6, 135.8, 144.9. Anal. calcd. for $C_{15}H_{13}BrN_2O_2S$: C, 49.33; H, 3.59; N, 7.67; found: C, 49.26; H, 3.60; N, 7.70.

N-[Cyano(furan-2-yl)methyl]-4-methylbenzenesulfonamide (**2k**)

White solid; mp 98-100 °C; IR (KBr) ν_{max}/cm^{-1} 3277 (NH), 2251 (CN), 1337 (S=O asym), 1161 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H, CH_3), 5.37 (d, 1H, *J* 9.2 Hz, NH), 5.53 (d, 1H, *J* 9.2 Hz, CH), 6.34-6.35 (m, 1H, Fu-H), 6.47 (d, 1H, *J* 3.6 Hz, Fu-H), 7.34 (d, 2H, *J* 8.4 Hz, ArH), 7.38 (s, 1H, Fu-H), 7.77 (d, 2H, *J* 8.4 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 42.4, 110.6, 111.0, 114.7, 127.3, 131.2, 135.9, 143.9, 144.5, 144.8. Anal. calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14; found: C, 56.66; H, 4.39; N, 10.13.

N-(1-Cyanopropyl)-4-methylbenzenesulfonamide (**2l**)

White solid; mp 52-54 °C; IR (KBr) ν_{max}/cm^{-1} 3283 (NH), 2249 (CN), 1333 (S=O asym), 1161 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95-0.96 (m, 3H, CH_3), 2.01-2.04 (m, 2H, CH_2), 2.44 (s, 3H, CH_3), 4.69 (d, 1H, *J* 9.2 Hz, CH), 5.12 (bs, 1H, NH), 7.26-7.36 (m, 2H, ArH), 7.77-7.79 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 21.3, 21.6, 51.2, 116.0, 126.0, 127.3, 129.9, 134.2, 136.2, 144.5. Anal. calcd. for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92; N, 11.76; found: C, 55.58; H, 5.94; N, 11.80.

N-(1-Cyano-2-methylpropyl)-4-methylbenzenesulfonamide (**2m**)

White solid; mp 78-79 °C; IR (KBr) ν_{max}/cm^{-1} 3281 (NH), 2240 (CN), 1339 (S=O asym), 1162 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, 6H, *J* 6.8 Hz, CH_3), 1.99-2.07 (m, 1H, CH), 2.44 (s, 3H, CH_3), 4.01-4.05 (m, 1H, CH), 5.53 (bs, 1H, NH), 7.35 (d, 2H, *J* 7.6 Hz, ArH), 7.78 (d, 2H, *J* 7.6 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 18.5, 21.7, 32.4, 50.6, 116.8, 127.2, 130.1, 136.0, 144.6. Anal. calcd. for $C_{12}H_{16}N_2O_2S$: C, 57.12; H, 6.39; N, 11.10; found: C, 57.04; H, 6.41; N, 11.06.

N-[Cyano(phenyl)methyl]benzenesulfonamide (**2n**)

White solid; mp 98-100 °C; IR (KBr) ν_{max}/cm^{-1} 3261 (NH), 2248 (CN), 1341 (S=O asym), 1169 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (d, 1H, *J* 9.2 Hz, NH), 5.79 (d, 1H, *J* 9.2 Hz, CH), 7.28-7.91 (m, 10H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.2, 116.3, 127.1, 127.3, 129.4, 129.5, 129.9, 132.0, 133.7, 138.9. Anal. calcd. for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29; found: C, 61.66; H, 4.45; N, 10.25.

N-[Cyano(4-tolyl)methyl]benzenesulfonamide (**2o**)

White solid; mp 100-102 °C; IR (KBr) ν_{max}/cm^{-1} 3278 (NH), 2245 (CN), 1336 (S=O asym), 1163(S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H, CH_3), 5.43 (d, 1H, *J* 8.0 Hz, NH), 5.59 (d, 1H, *J* 8.0 Hz, CH), 7.18-7.31 (m, 4H, ArH), 7.55-7.93 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 48.0, 116.4, 127.0, 127.3, 129.0, 129.5, 130.0, 133.7, 139.0, 140.1. Anal. calcd. for $C_{15}H_{14}N_2O_2S$: C, 62.92; H, 4.93; N, 9.78; found: C, 62.99; H, 4.92; N, 9.76.

N-[(4-Chlorophenyl)(cyano)methyl]benzenesulfonamide (**2p**)

White solid; mp 122-124 °C; IR (KBr) ν_{max}/cm^{-1} 3229 (NH), 2238 (CN), 1333 (S=O asym), 1170 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (bs, 1H, NH), 5.50 (d, 1H, *J* 8.0 Hz, CH), 7.40 (s, 4H, ArH), 7.58-7.62 (m, 2H, ArH), 7.68-7.72 (m, 1H, ArH), 7.93 (d, 2H, *J* 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.7, 115.8, 127.3, 128.5, 129.6, 129.6, 130.5, 133.9, 136.2, 138.8. Anal. calcd. for $C_{14}H_{11}ClN_2O_2S$: C, 54.82; H, 3.61; N, 9.13; found: C, 54.77; H, 3.60; N, 9.16.

N-[(4-Bromophenyl)(cyano)methyl]benzenesulfonamide (**2q**)

White solid; mp 130-132 °C; IR (KBr) ν_{max}/cm^{-1} 3233 (NH), 2239 (CN), 1332 (S=O asym), 1169 (S=O sym); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (d, 1H, *J* 9.2 Hz, NH), 5.50 (d, 1H, *J* 9.2 Hz, CH), 7.33-7.55 (m, 2H, ArH), 7.56-7.74 (m, 5H, ArH), 7.92-7.96 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.7, 115.7, 124.4, 127.2, 128.7, 129.6, 130.9, 132.6, 133.9, 138.8. Anal. calcd. for $C_{14}H_{11}BrN_2O_2S$: C, 47.88; H, 3.16; N, 7.98; found: C, 47.74; H, 3.17; N, 7.95.

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1. Lu, K.; Kwon, O.; Brummond, K. M.; Davis, M. M.; *Org. Synth.* **2009**, *86*, 212.
2. Hasaninejad, A.; Zare, A.; *J. Sulfur Chem.* **2007**, *28*, 357.
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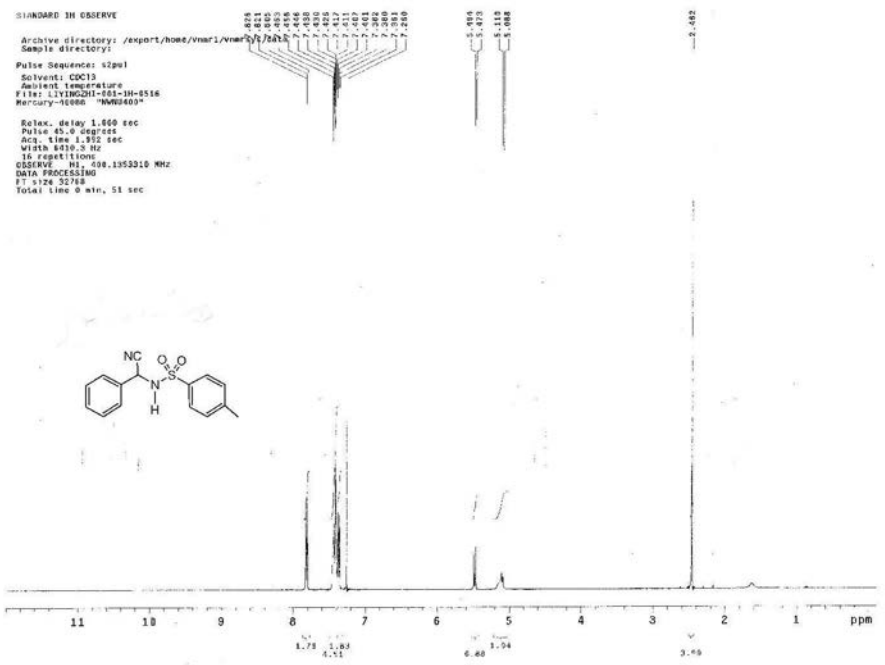

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-(cyanophenylmethyl)-4-methylbenzenesulfonamide (**2a**).

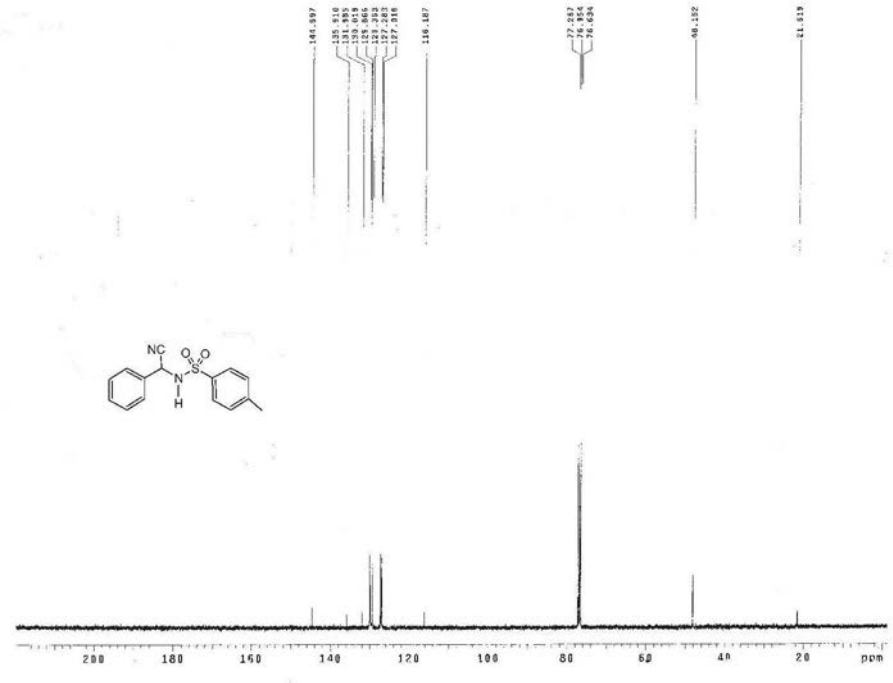

Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-(cyanophenylmethyl)-4-methylbenzenesulfonamide (**2a**).

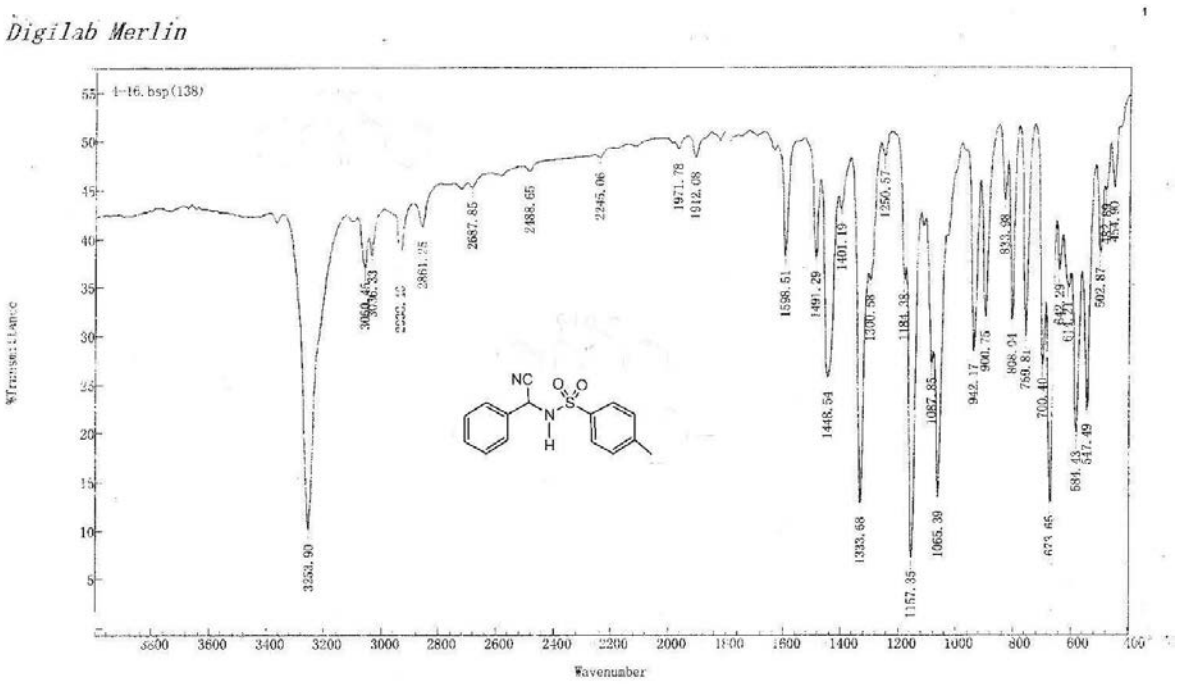

Figure S3. IR of *N*-(cyanophenylmethyl)-4-methylbenzenesulfonamide (**2a**).

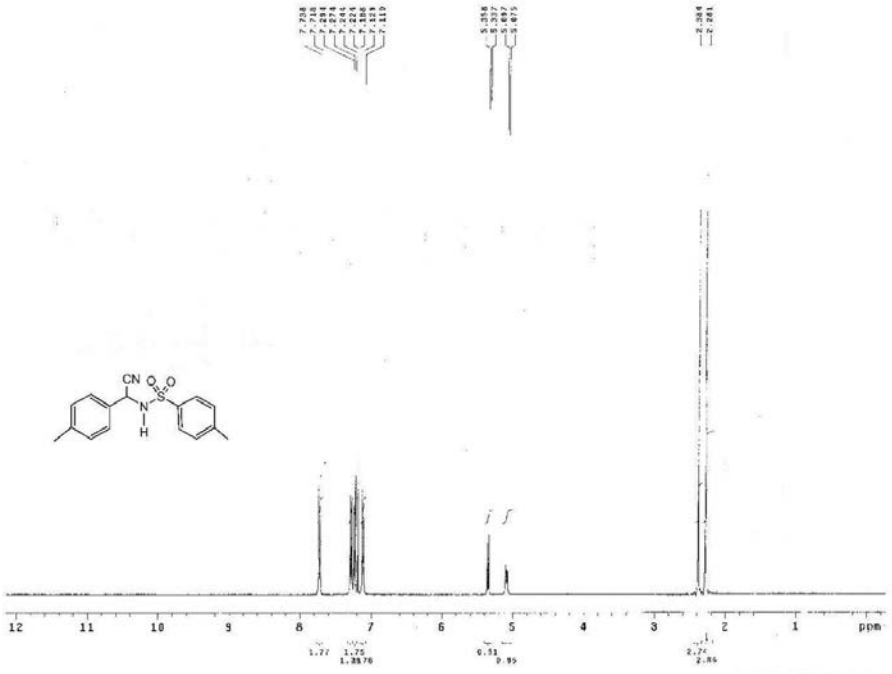

Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[cyano(4-tolyl)methyl]-4-methylbenzenesulfonamide (**2b**).

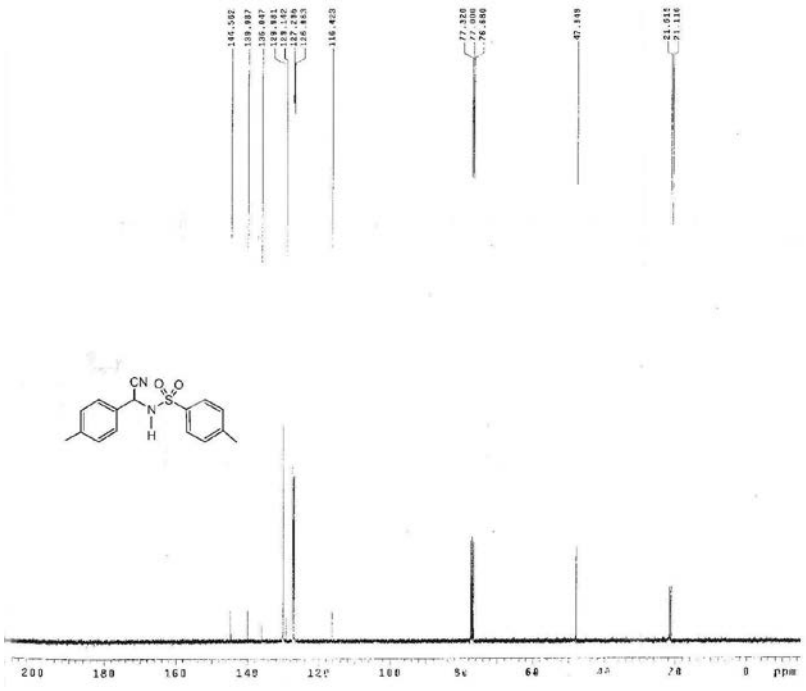

Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[cyano(4-tolyl)methyl]-4-methylbenzenesulfonamide (**2b**).

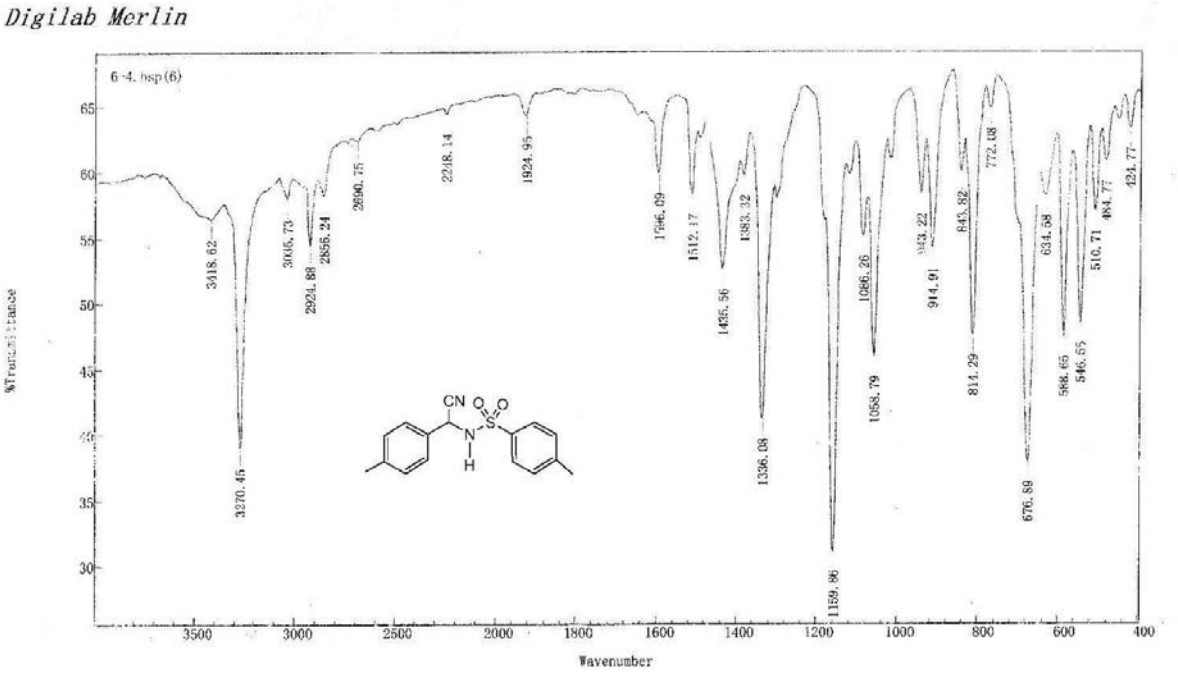

Figure S6. IR of *N*-[cyano(4-tolyl)methyl]-4-methylbenzenesulfonamide (**2b**).

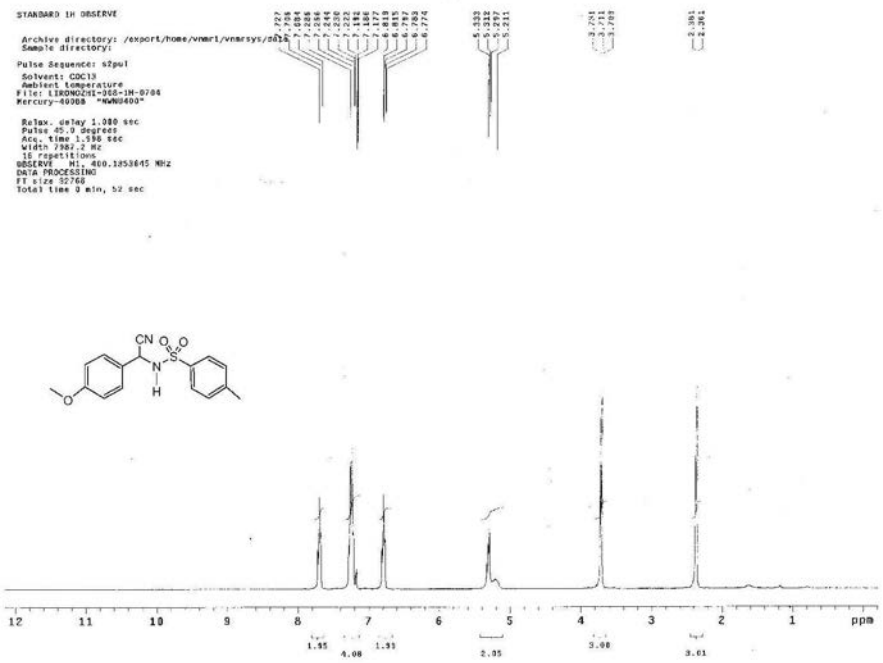

Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[cyano(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide (**2c**).

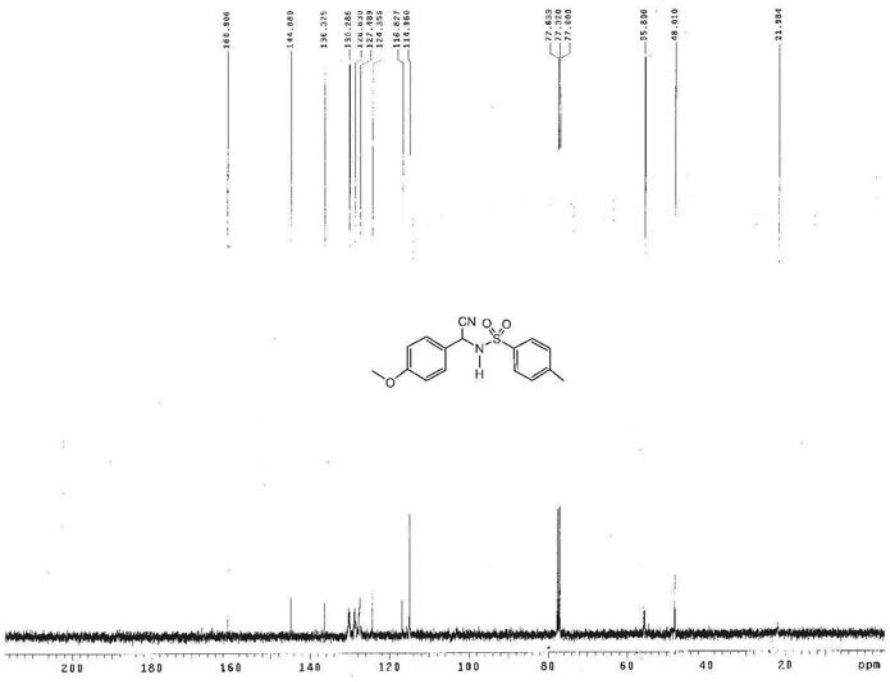

Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[cyano(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide (**2c**).

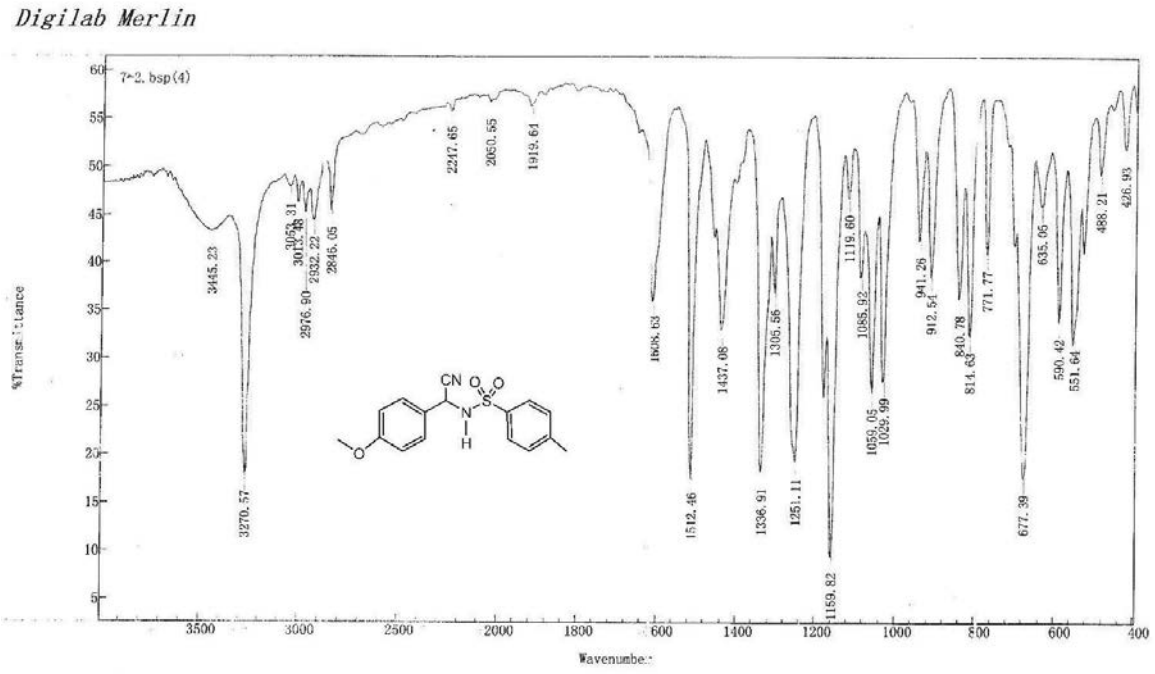

Figure S9. IR of *N*-[cyano(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide (**2c**).

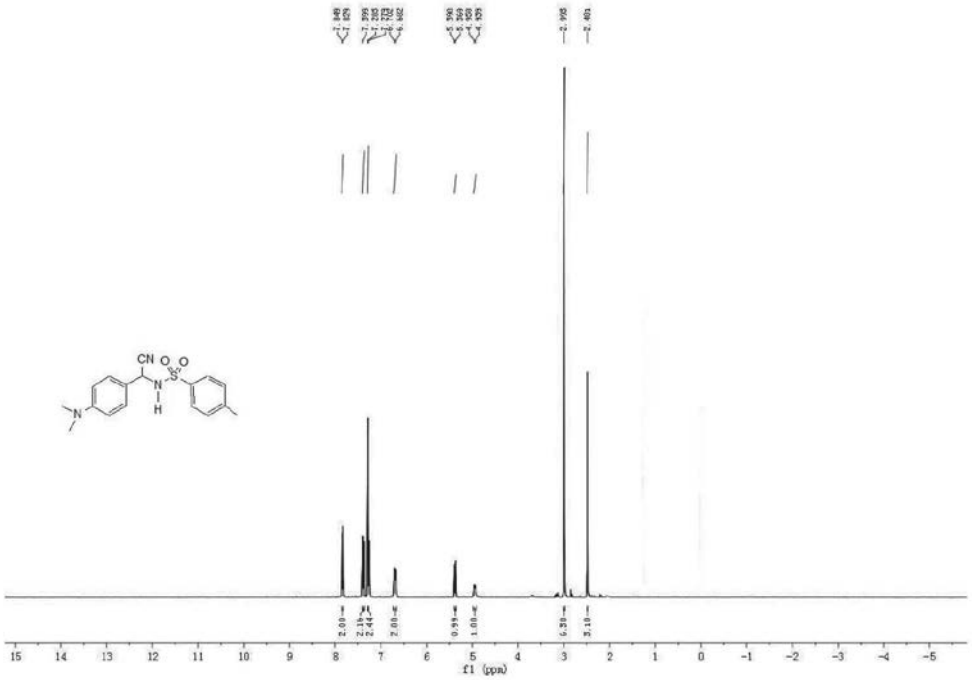

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-{cyano[4-(dimethylamino)phenyl]methyl}-4-methylbenzenesulfonamide (**2d**).

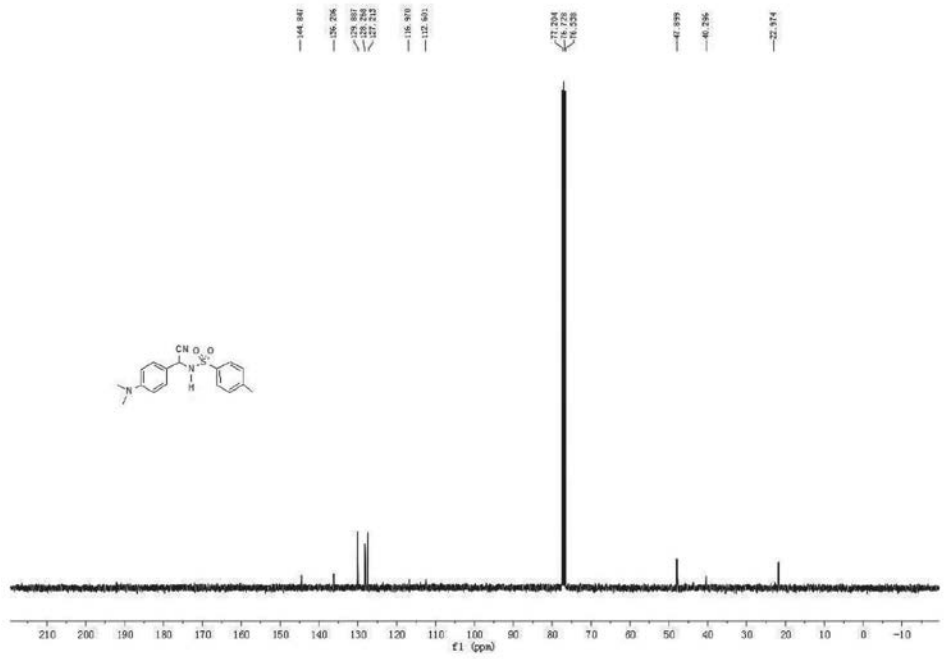

Figure S11. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-{cyano[4-(dimethylamino)phenyl]methyl}-4-methylbenzenesulfonamide (**2d**).

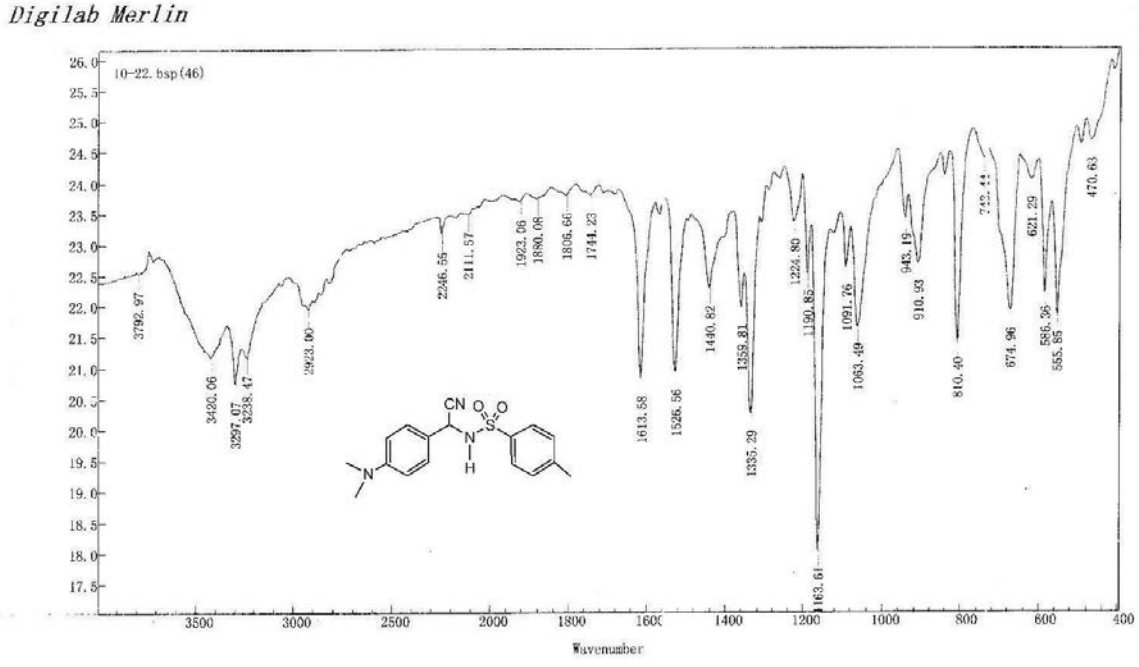

Figure S12. IR of *N*-{cyano[4-(dimethylamino)phenyl]methyl}-4-methylbenzenesulfonamide (**2d**).

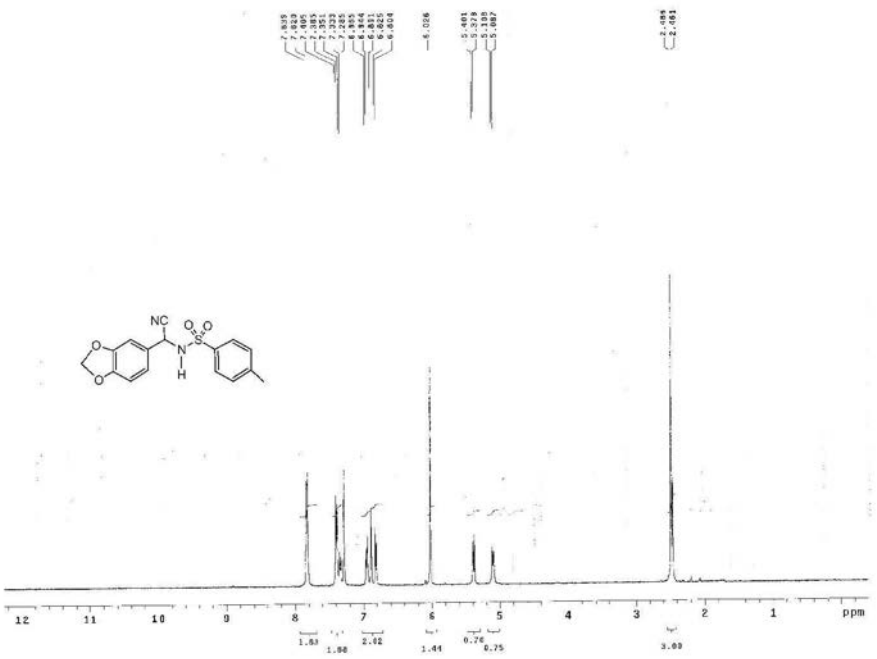

Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-{benzo[*d*][1,3]dioxol-5-yl(cyano)methyl}-4-methylbenzenesulfonamide (**2e**).

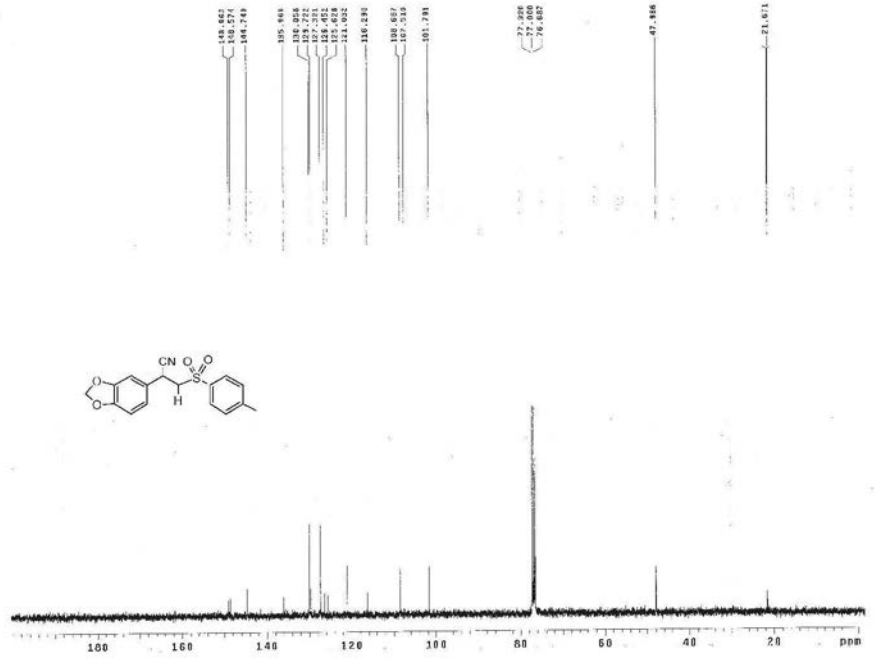

Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-{benzo[*d*][1,3]dioxol-5-yl(cyano)methyl}-4-methylbenzenesulfonamide (**2e**).

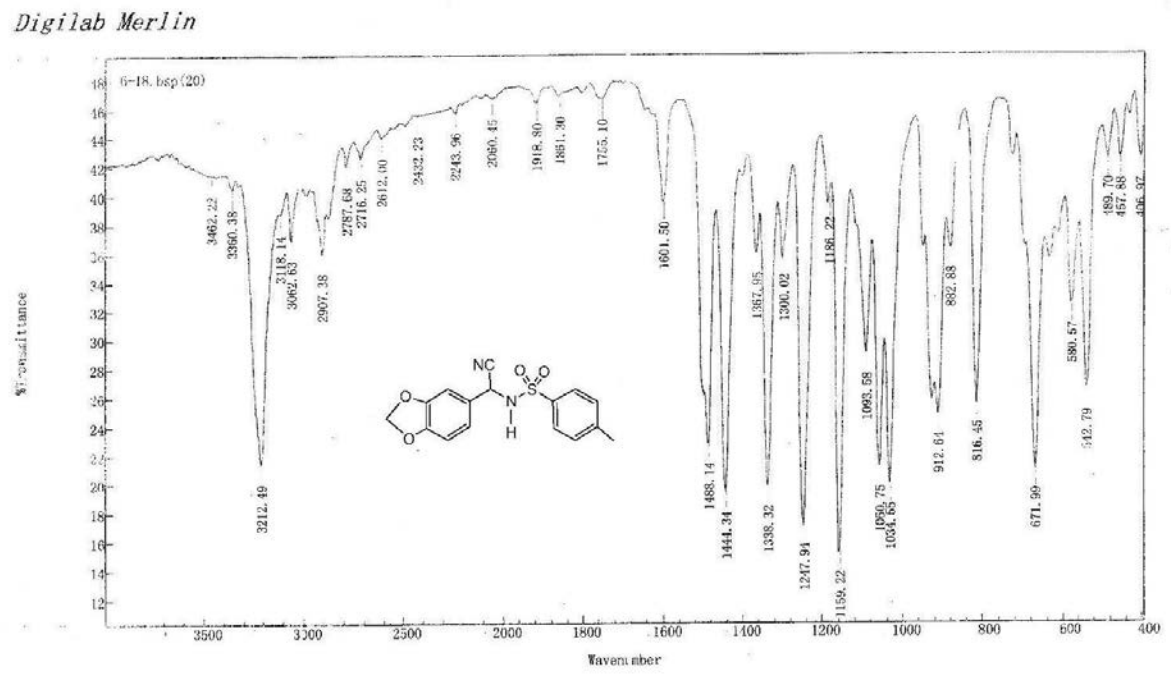

Figure S15. IR of *N*-{benzo[*d*][1,3]dioxol-5-yl(cyano)methyl}-4-methylbenzenesulfonamide (**2e**).

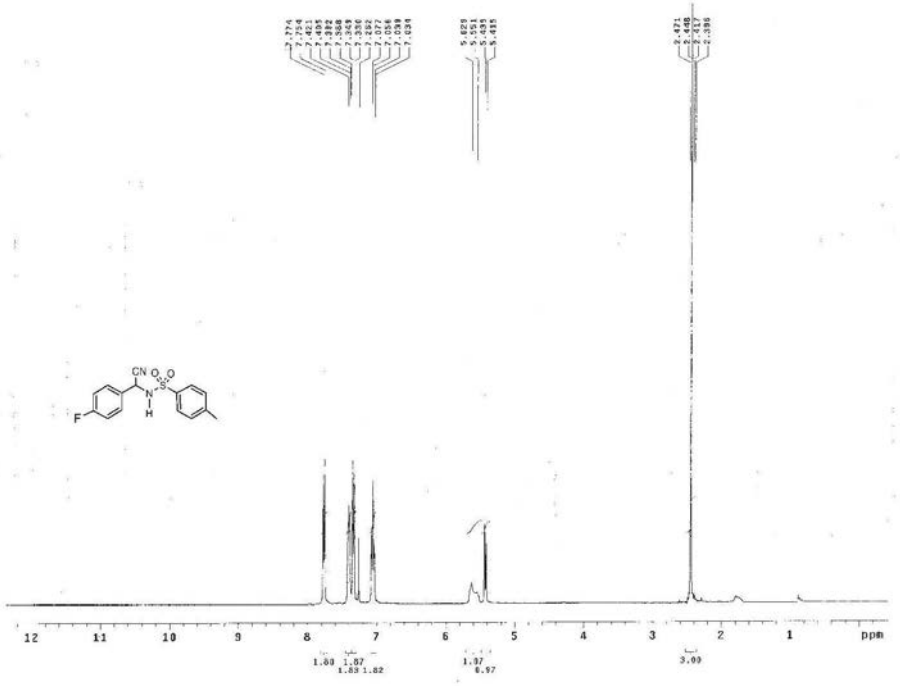

Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[cyano(4-fluorophenyl)methyl]-4-methylbenzenesulfonamide (**2f**).

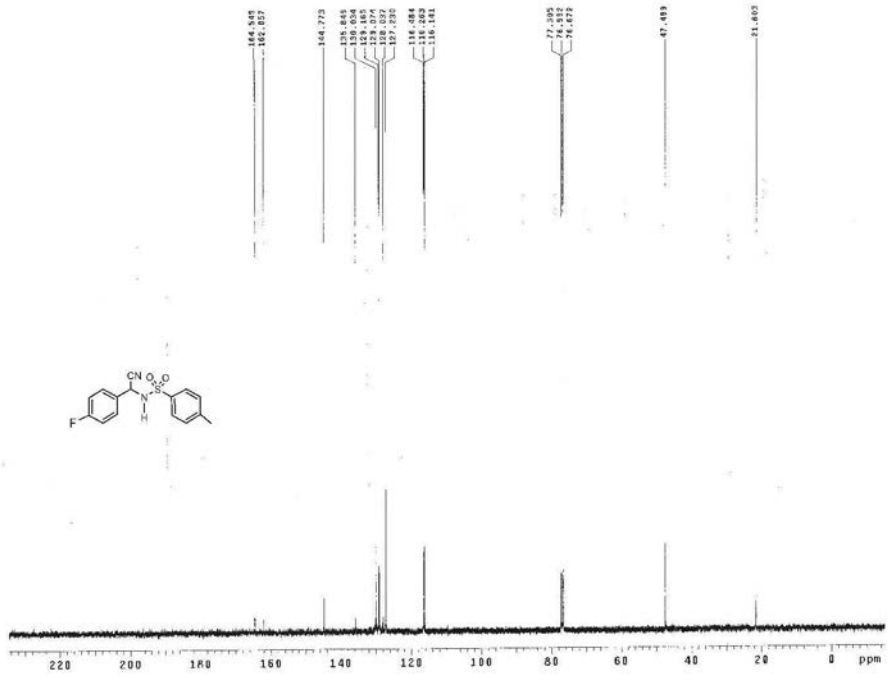

Figure S17. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[cyano(4-fluorophenyl)methyl]-4-methylbenzenesulfonamide (**2f**).

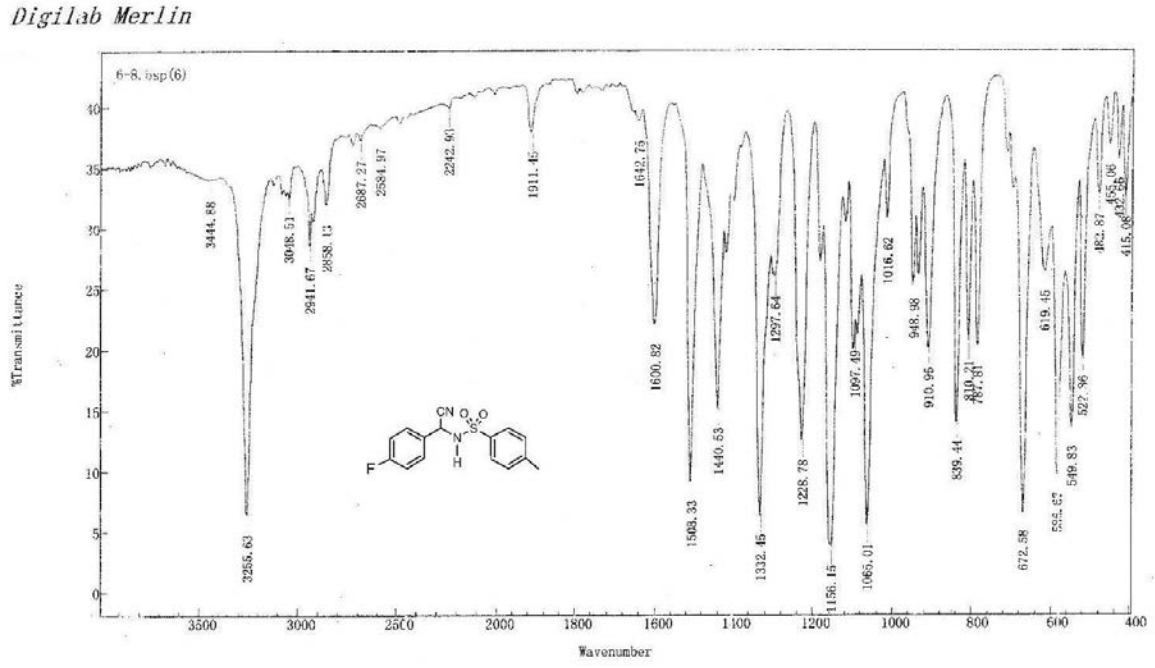

Figure S18. IR of *N*-[cyano(4-fluorophenyl)methyl]-4-methylbenzenesulfonamide (**2f**).

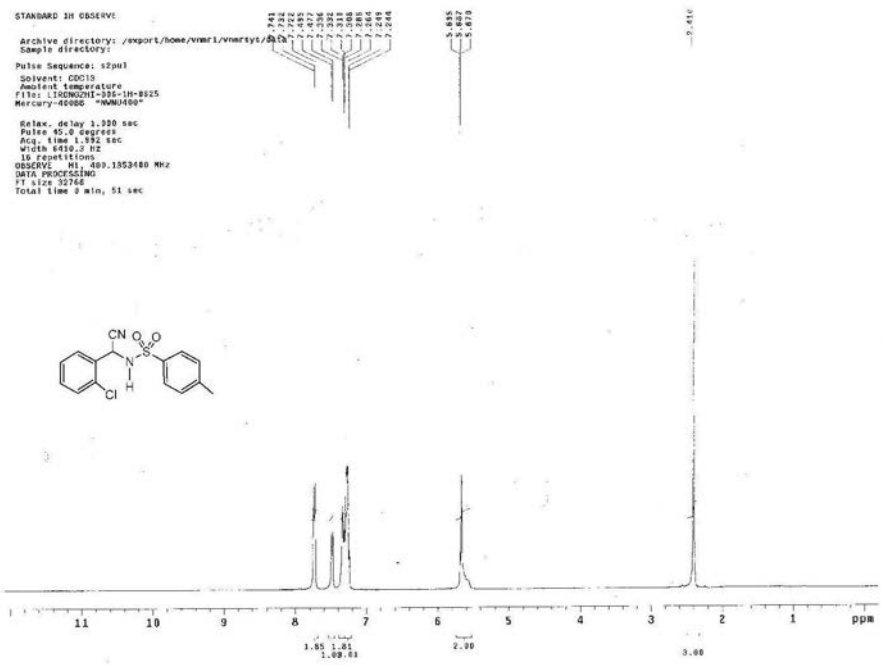

Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[(2-chlorophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2g**).

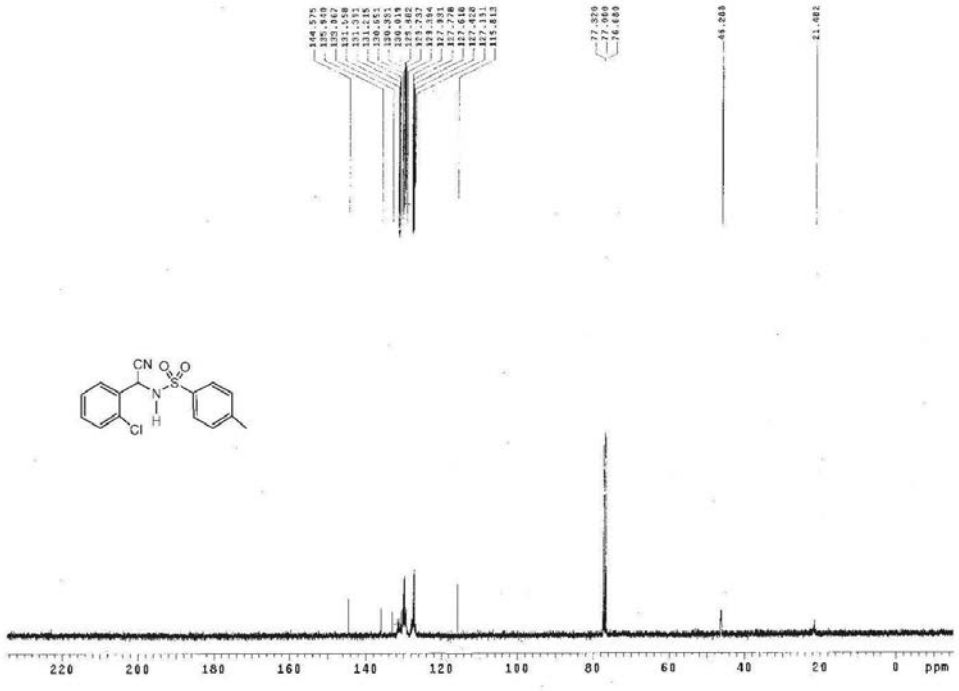

Figure S20. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[(2-chlorophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2g**).

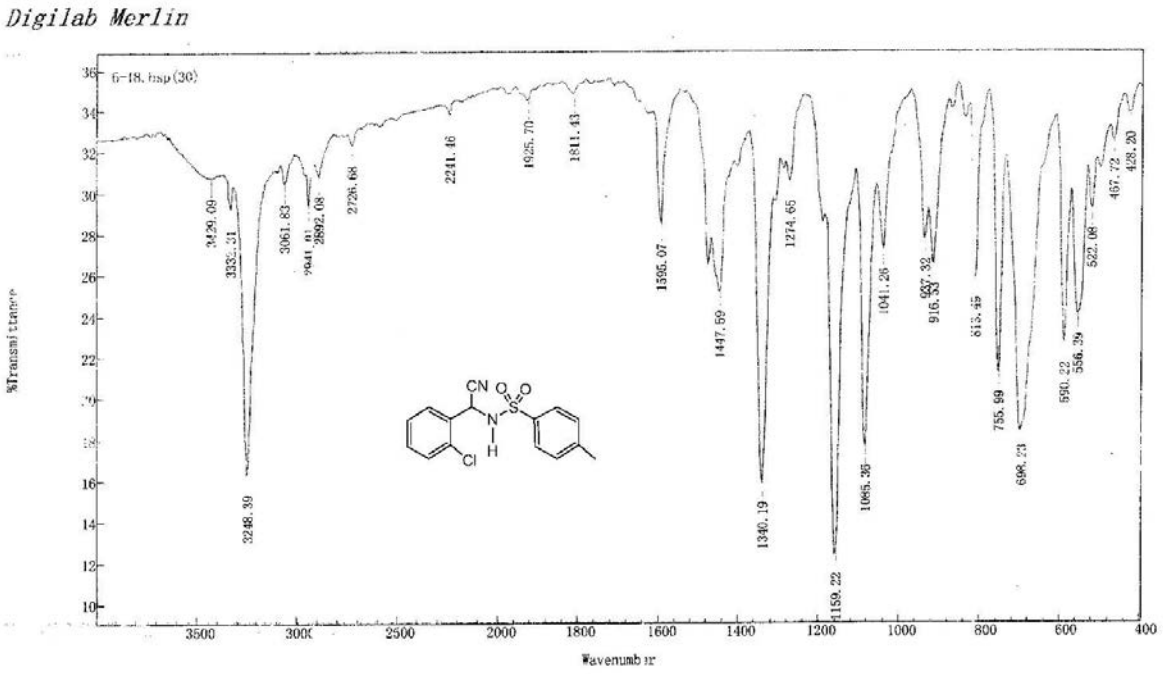

Figure S21. IR of *N*-[(2-chlorophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2g**).

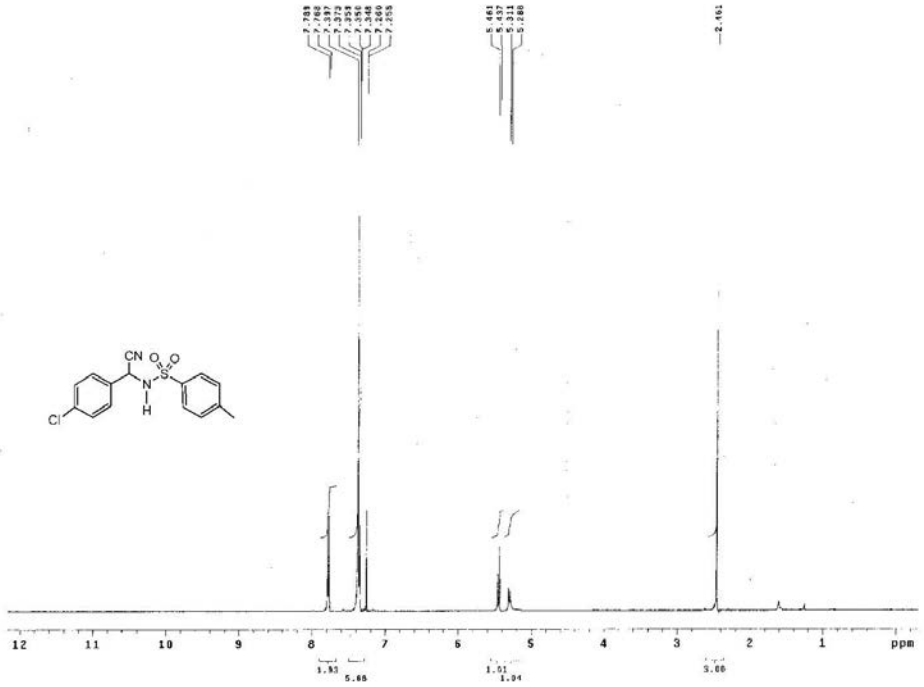

Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[4-chlorophenyl(cyano)methyl]-4-methylbenzenesulfonamide (**2h**).

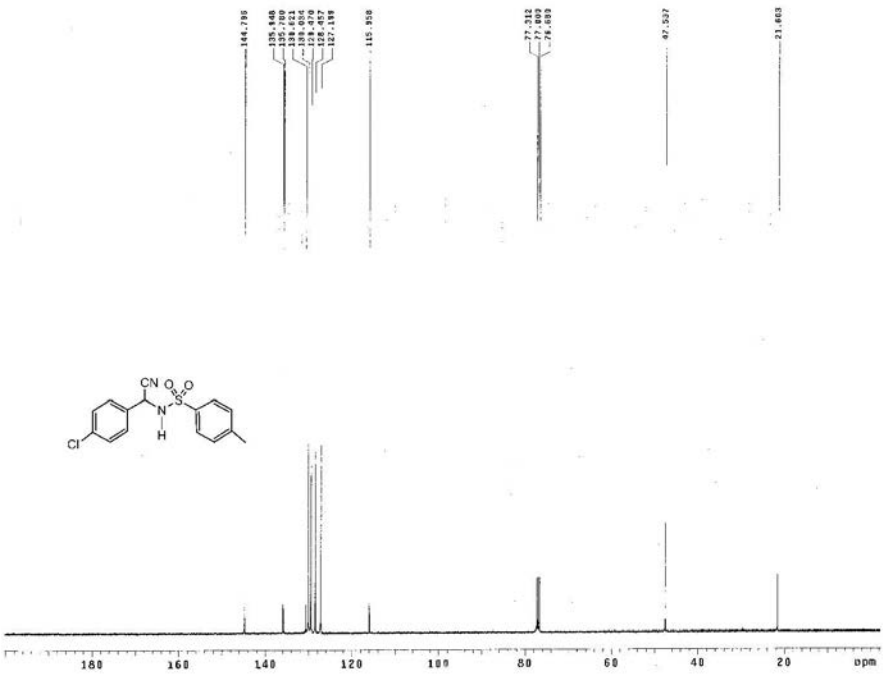

Figure S23. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[4-chlorophenyl(cyano)methyl]-4-methylbenzenesulfonamide (**2h**).

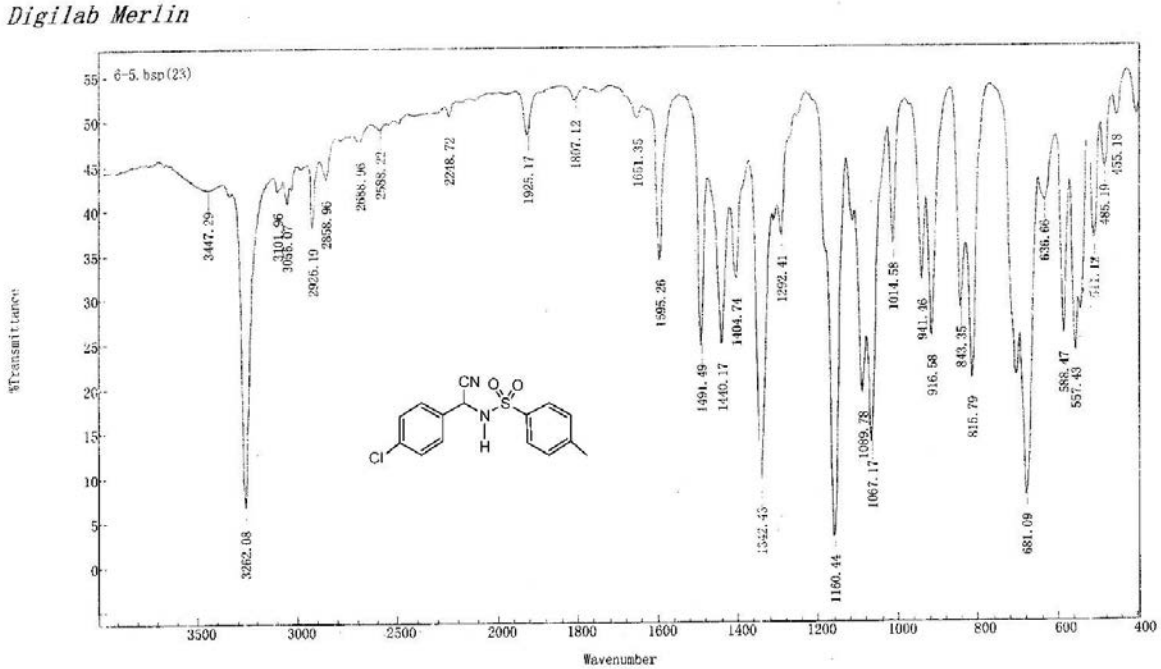

Figure S24. IR of *N*-[4-chlorophenyl(cyano)methyl]-4-methylbenzenesulfonamide (**2h**).

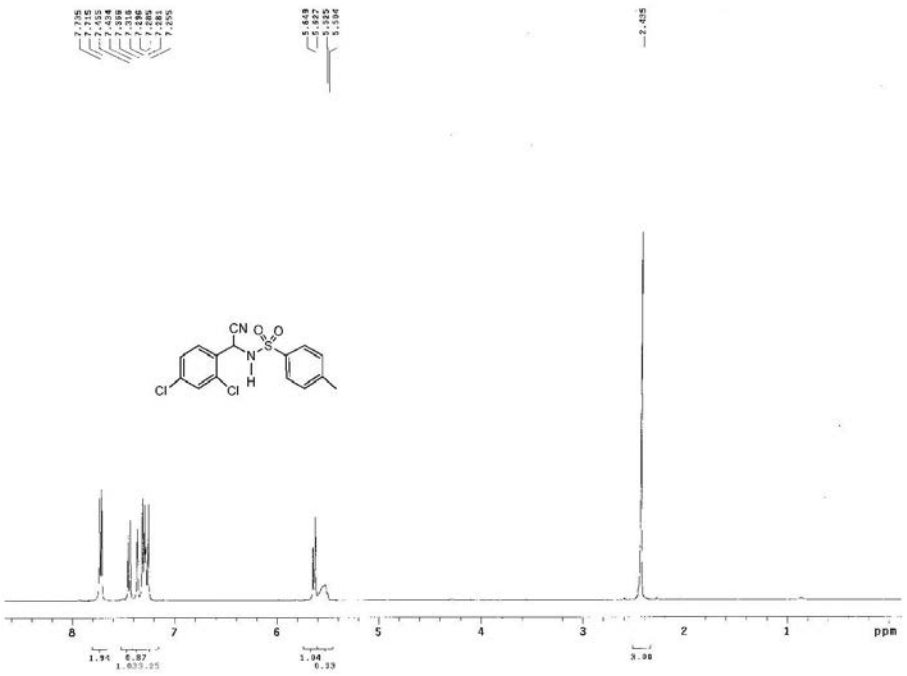

Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[cyano(2,4-dichlorophenyl)methyl]-4-methylbenzenesulfonamide (**2i**).

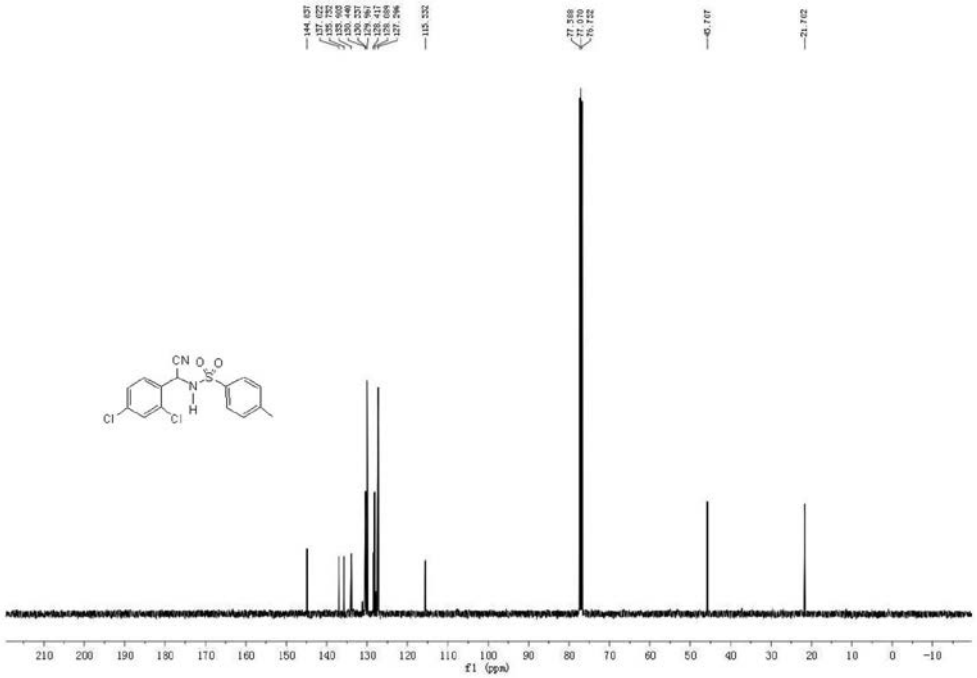

Figure S26. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[cyano(2,4-dichlorophenyl)methyl]-4-methylbenzenesulfonamide (**2i**).

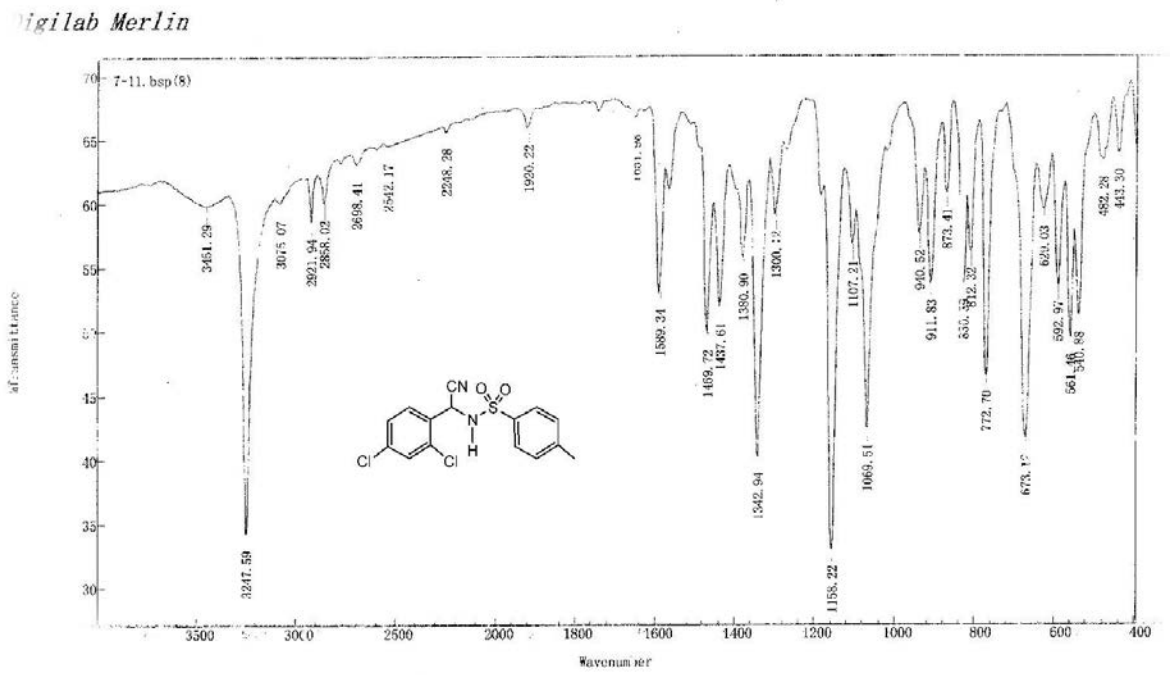

Figure S27. IR of *N*-[cyano(2,4-dichlorophenyl)methyl]-4-methylbenzenesulfonamide (**2i**).

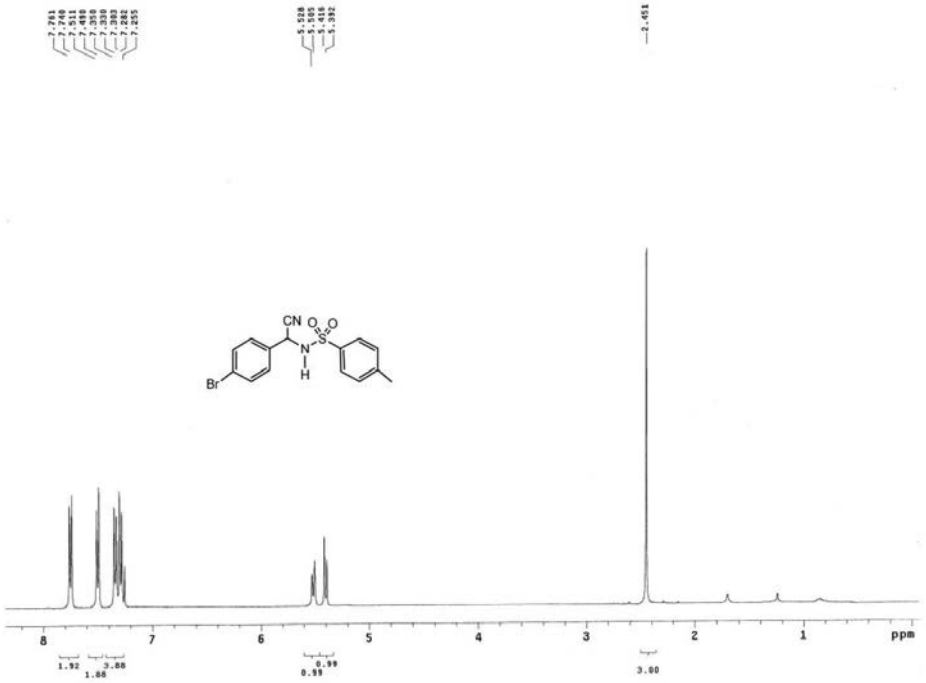

Figure S28. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[4-(bromophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2j**).

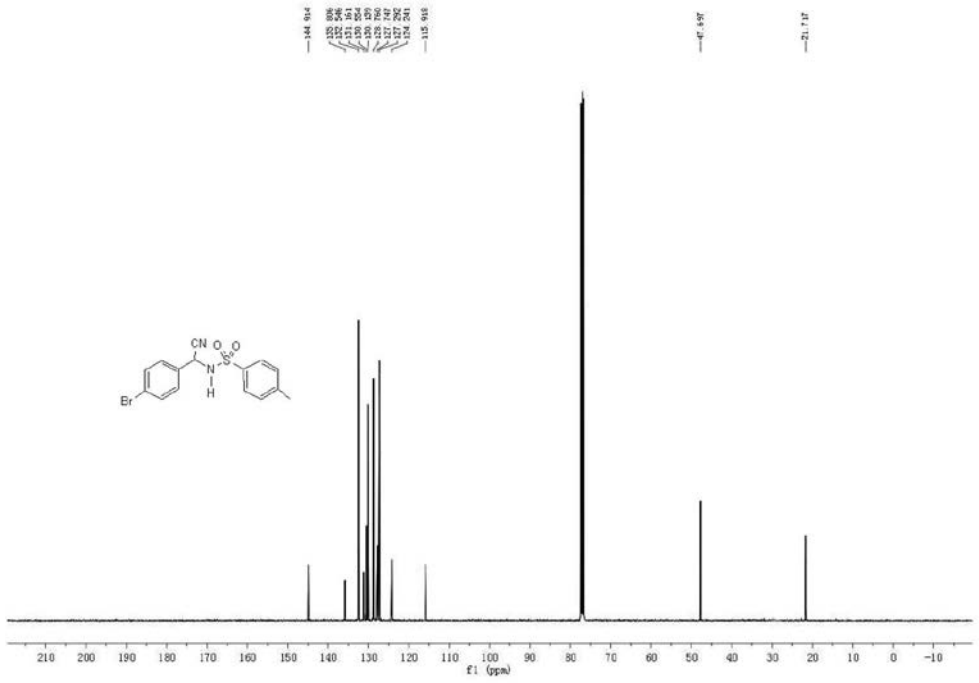

Figure S29. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[4-(bromophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2j**).

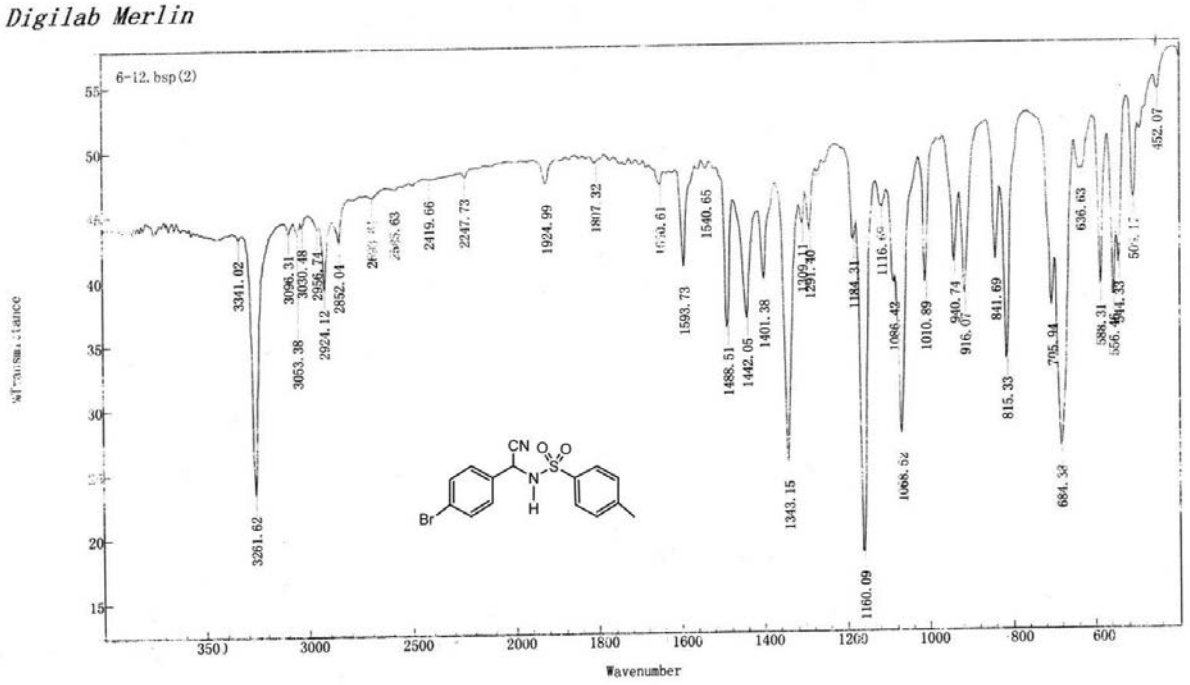

Figure S30. IR of *N*-[4-(bromophenyl)(cyano)methyl]-4-methylbenzenesulfonamide (**2j**).

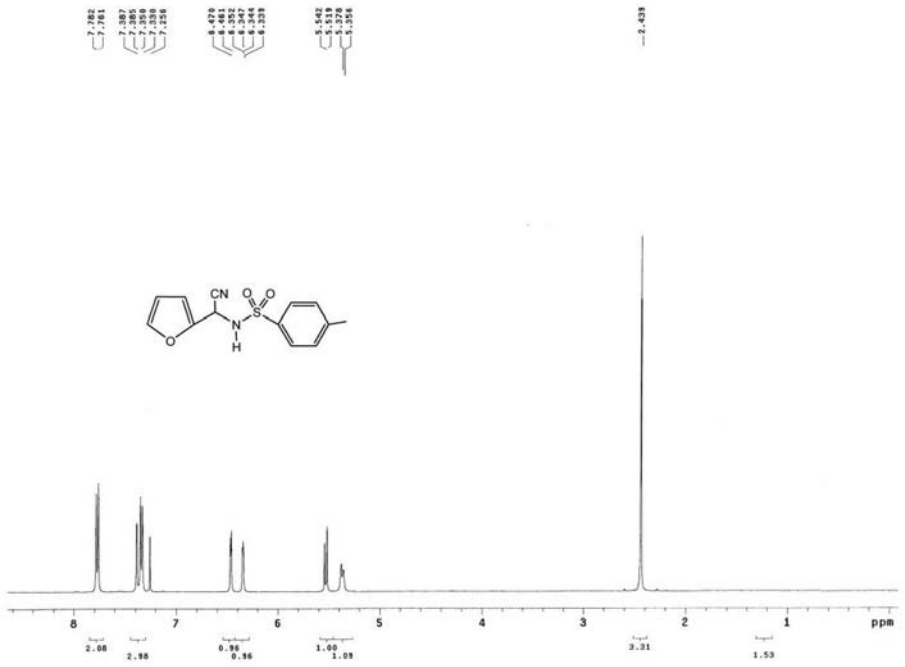

Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[cyano(furan-2-yl)methyl]-4-methylbenzenesulfonamide (**2k**).

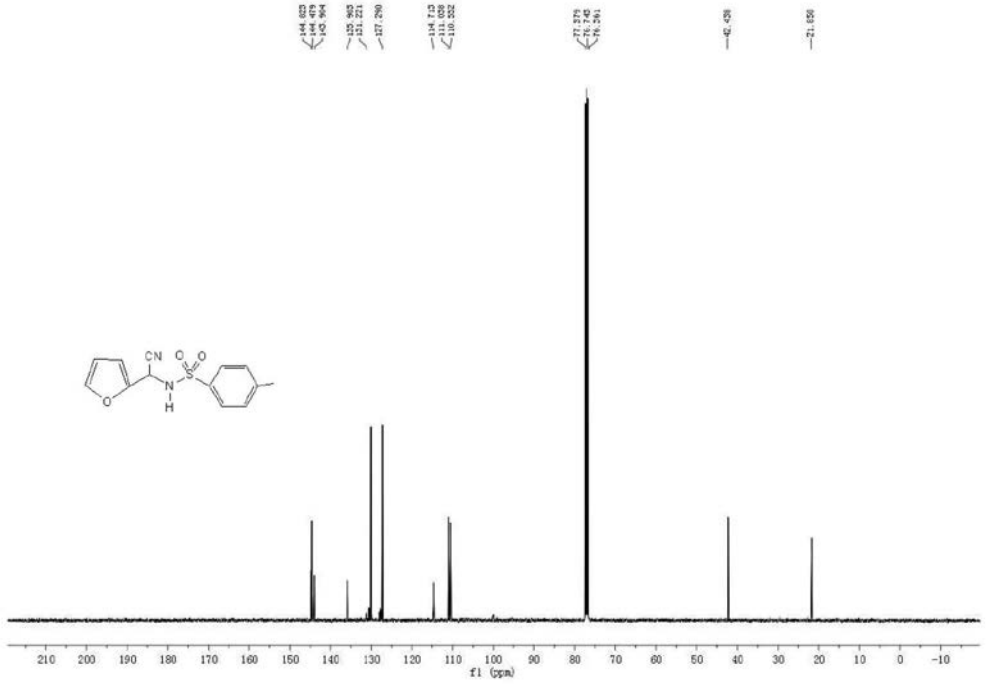

Figure S32. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[cyano(furan-2-yl)methyl]-4-methylbenzenesulfonamide (**2k**).

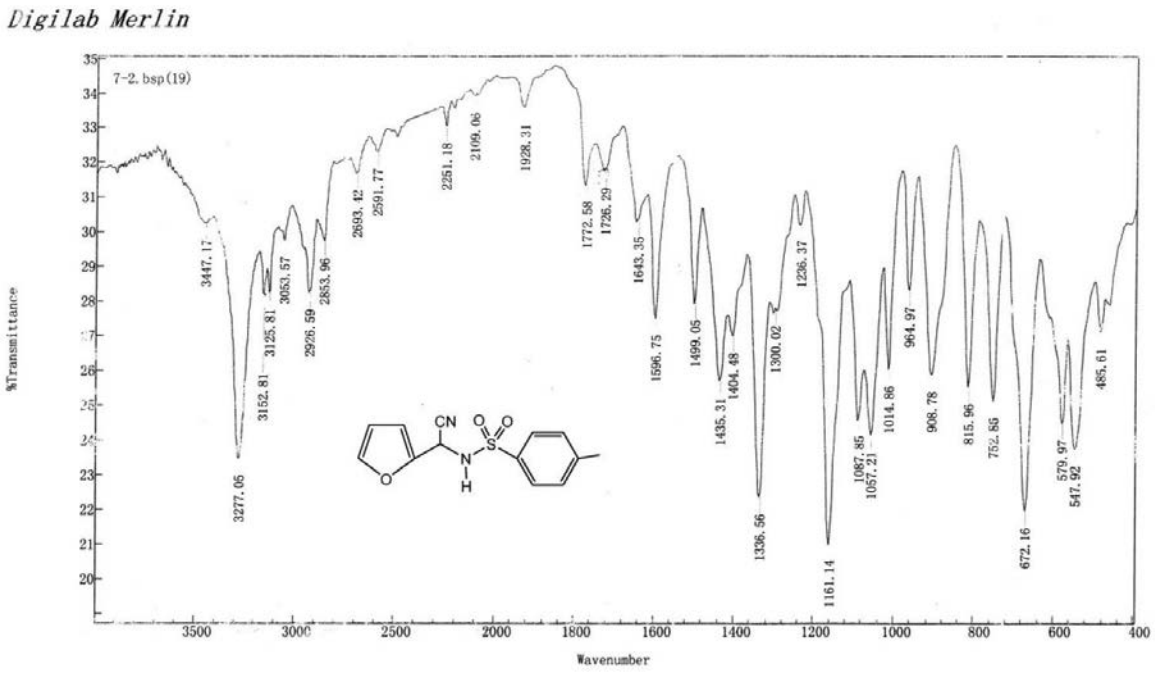

Figure S33. IR of *N*-[cyano(furan-2-yl)methyl]-4-methylbenzenesulfonamide (**2k**).

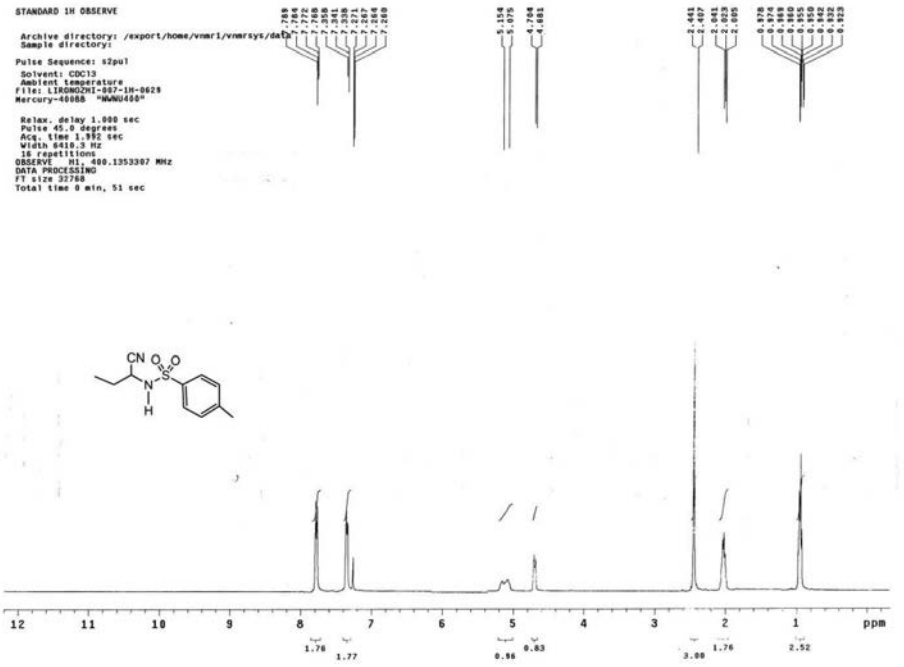

Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) *N*-(1-cyanopropyl)-4-methylbenzenesulfonamide (**2l**).

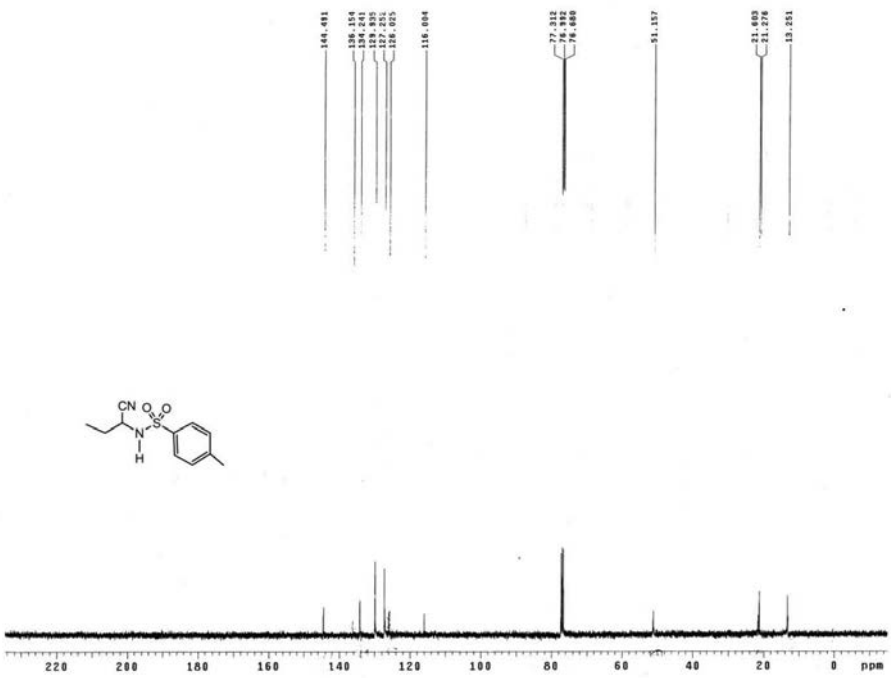

Figure S35. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-(1-cyanopropyl)-4-methylbenzenesulfonamide (**2l**).

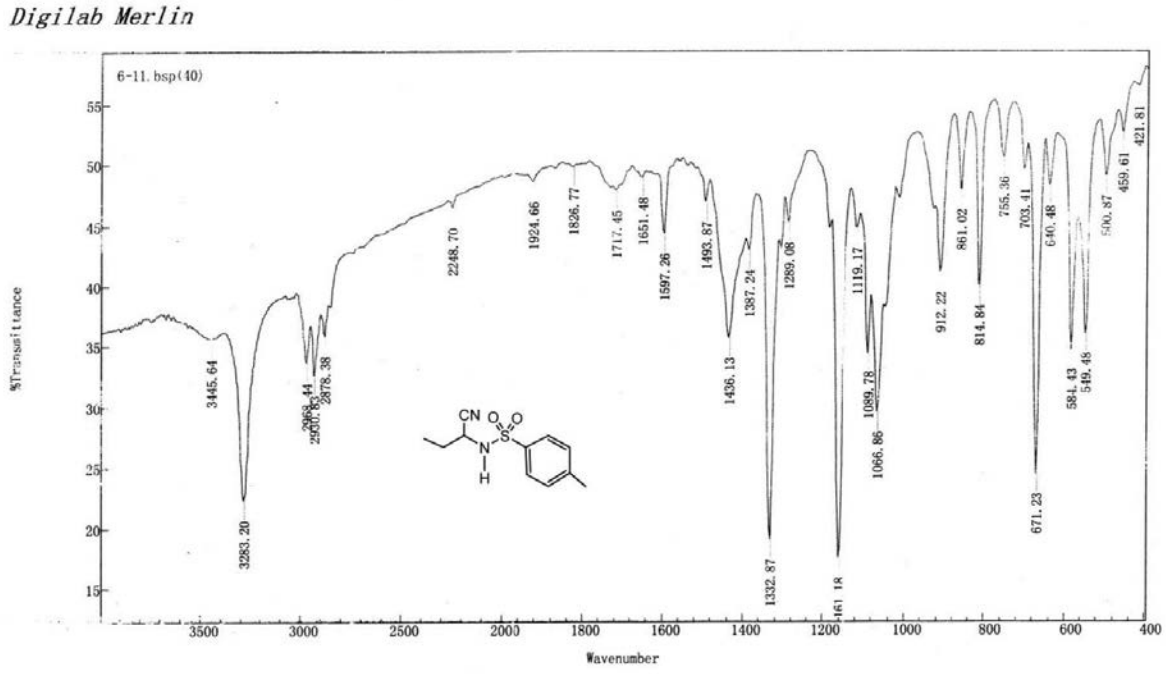

Figure S36. IR of *N*-(1-cyanopropyl)-4-methylbenzenesulfonamide (**2l**).

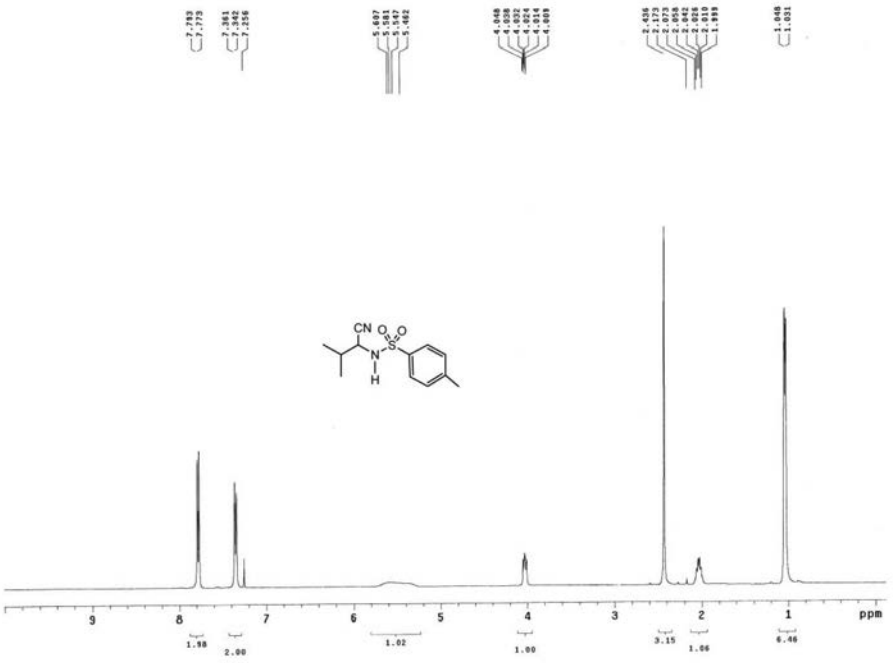

Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-(1-cyano-2-methylpropyl)-4-methylbenzenesulfonamide (**2m**).

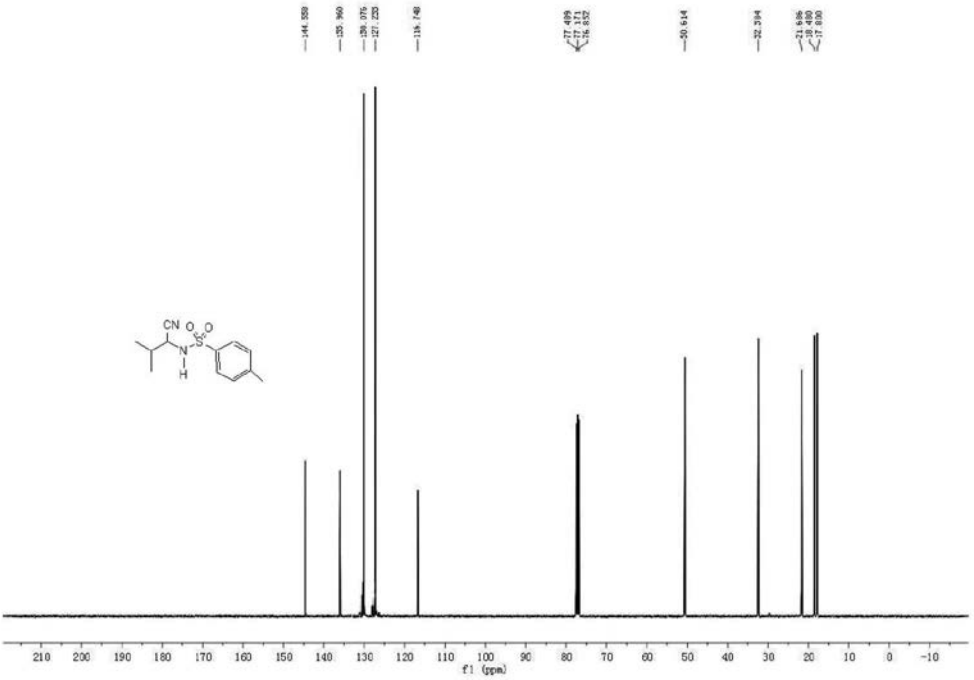

Figure S38. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-(1-cyano-2-methylpropyl)-4-methylbenzenesulfonamide (**2m**).

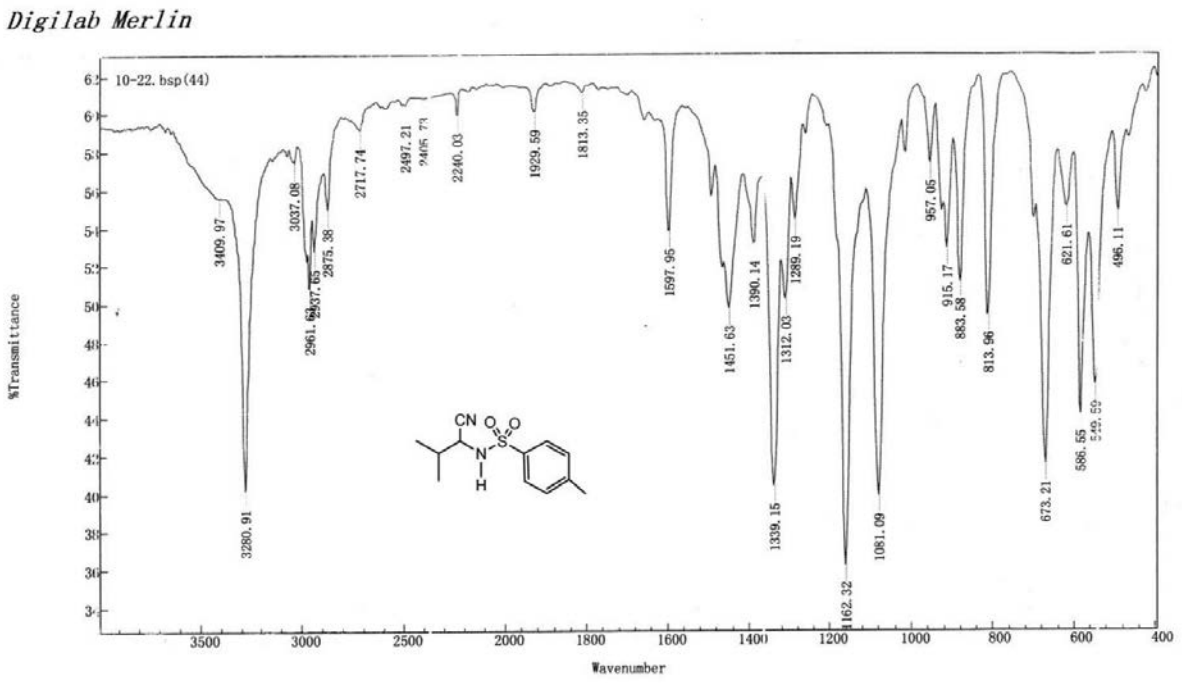

Figure S39. IR of *N*-(1-cyano-2-methylpropyl)-4-methylbenzenesulfonamide (**2m**).

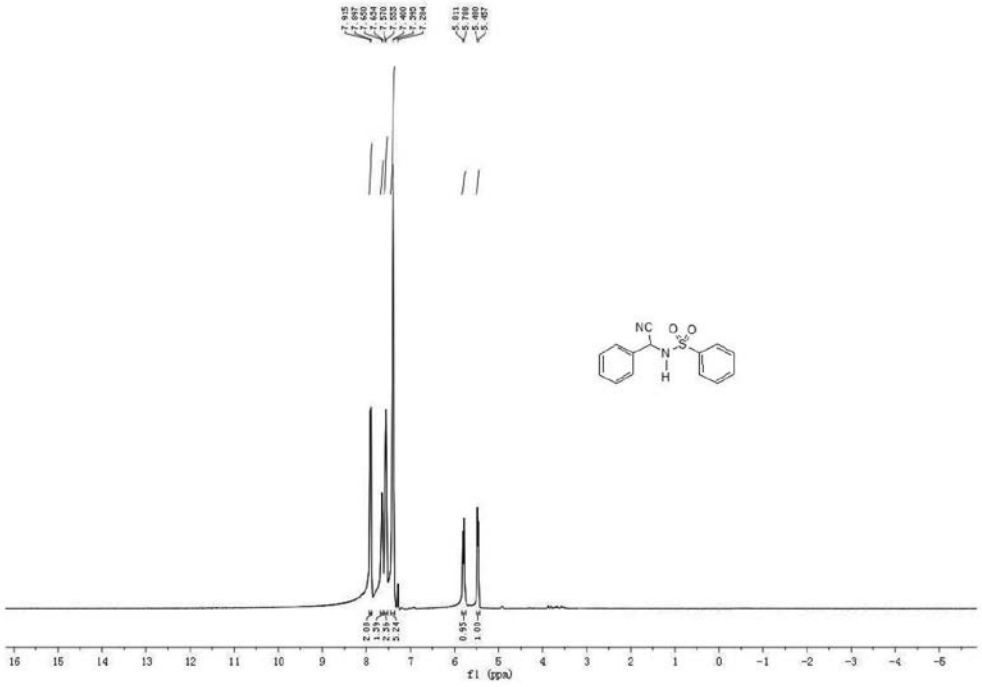

Figure S40. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[cyano(phenyl)methyl]benzenesulfonamide (**2n**).

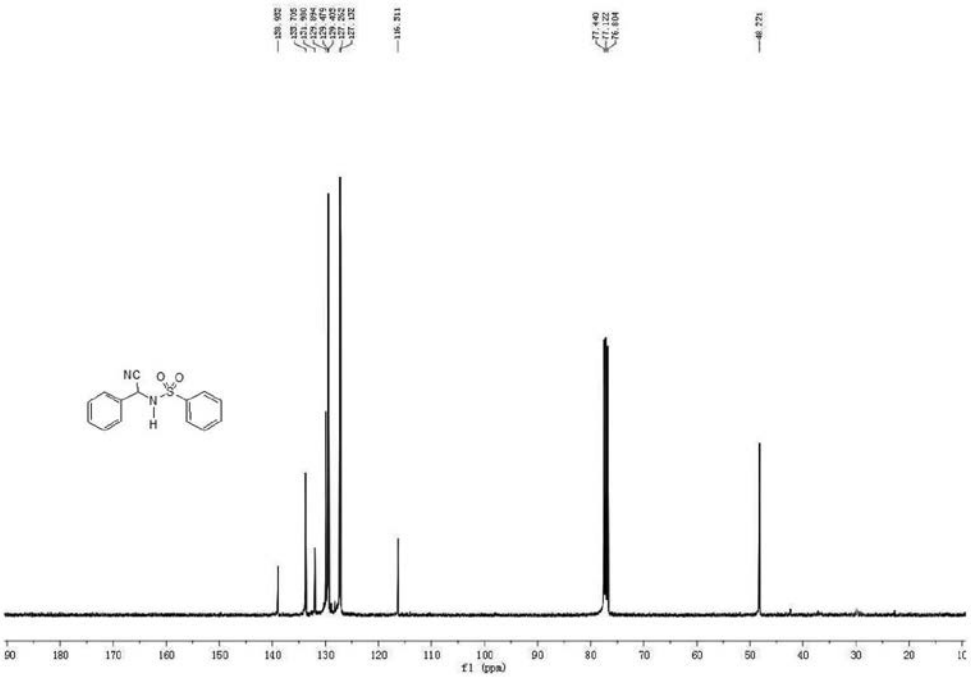

Figure S41. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[cyano(phenyl)methyl]benzenesulfonamide (**2n**).

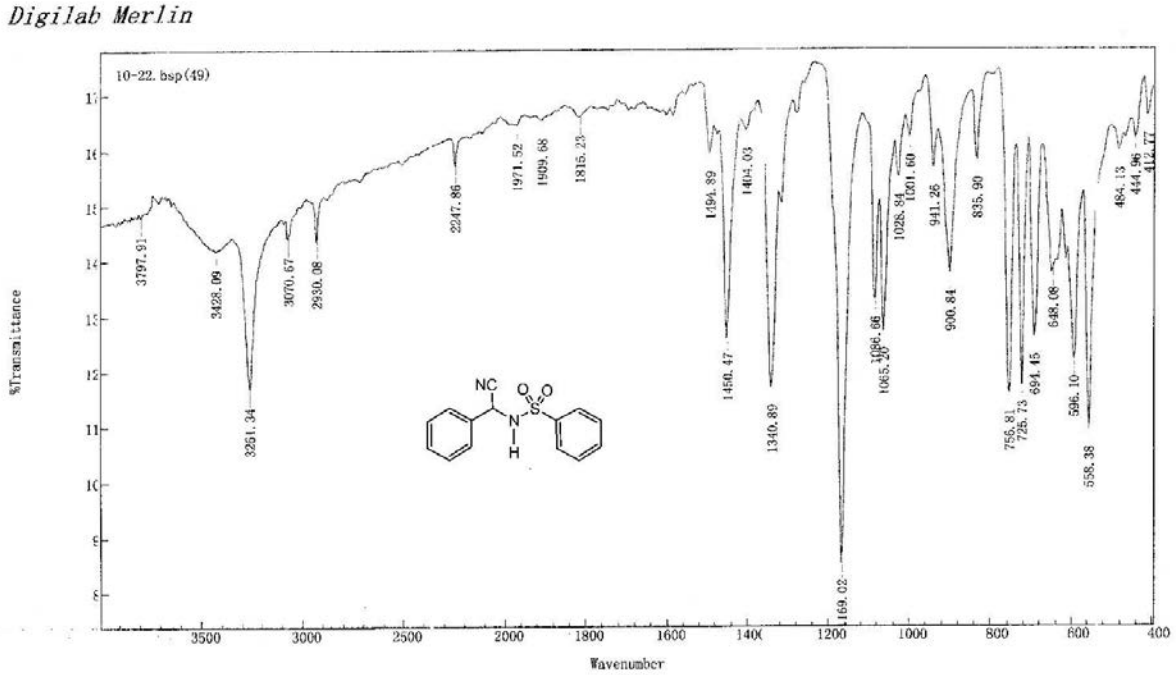

Figure S42. IR of *N*-[cyano(phenyl)methyl]benzenesulfonamide (**2n**).

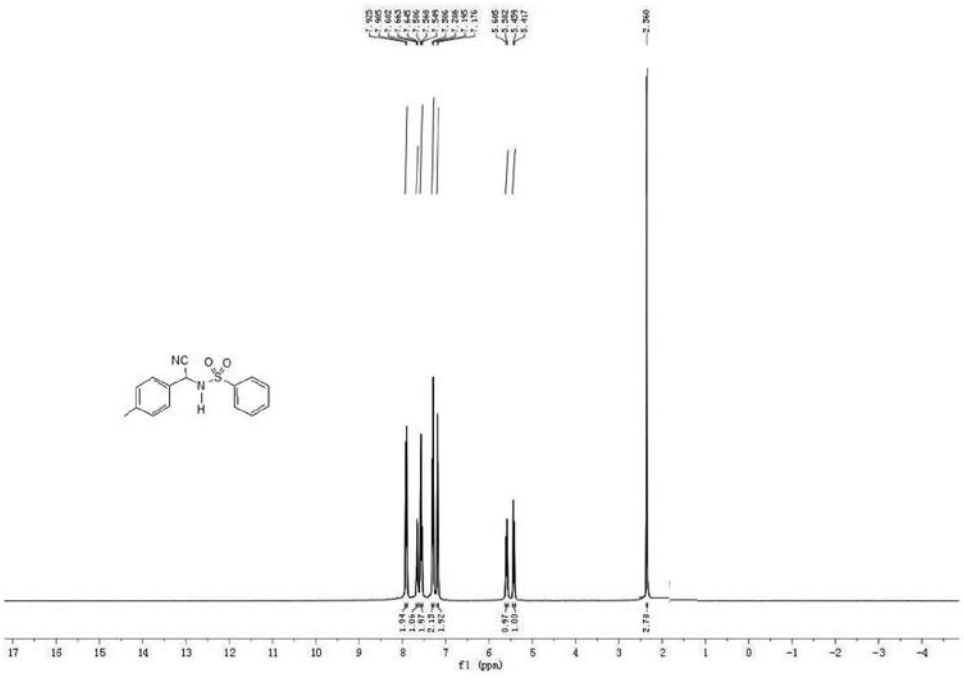

Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[cyano(4-tolyl)methyl]benzenesulfonamide (**2o**).

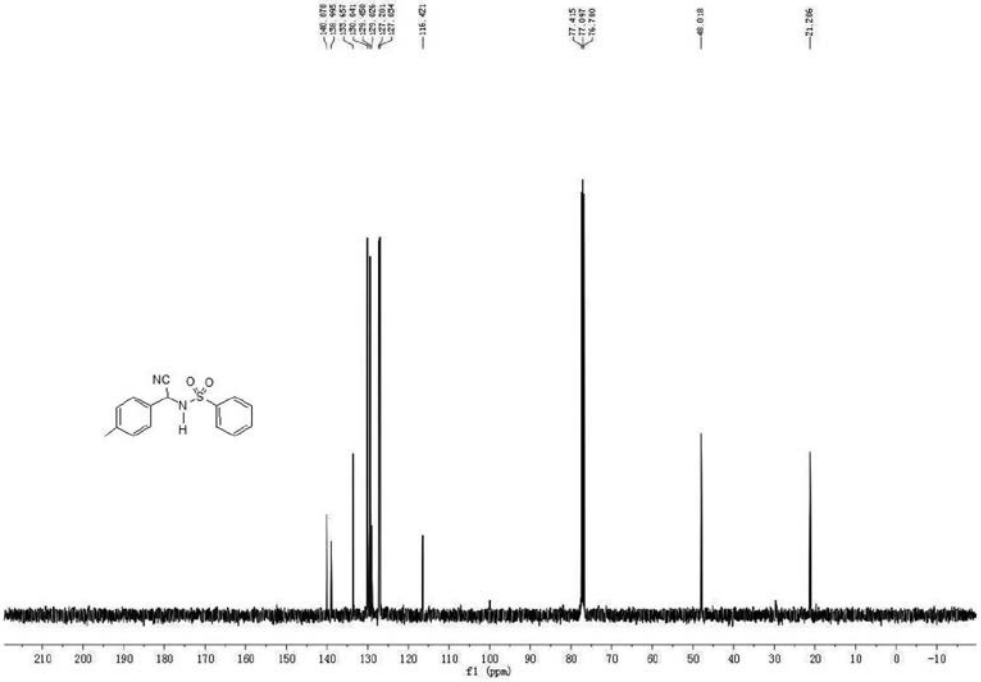

Figure S44. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[cyano(4-tolyl)methyl]benzenesulfonamide (**2o**).

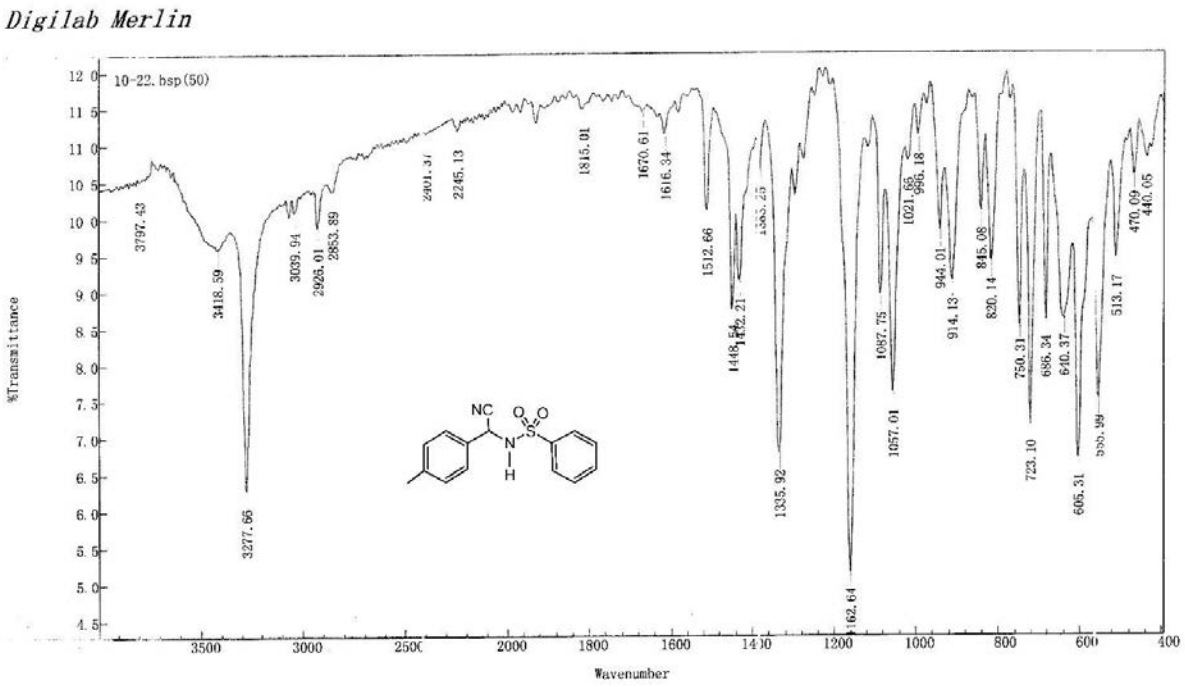

Figure S45. IR of *N*-[cyano(4-tolyl)methyl]benzenesulfonamide (**2o**).

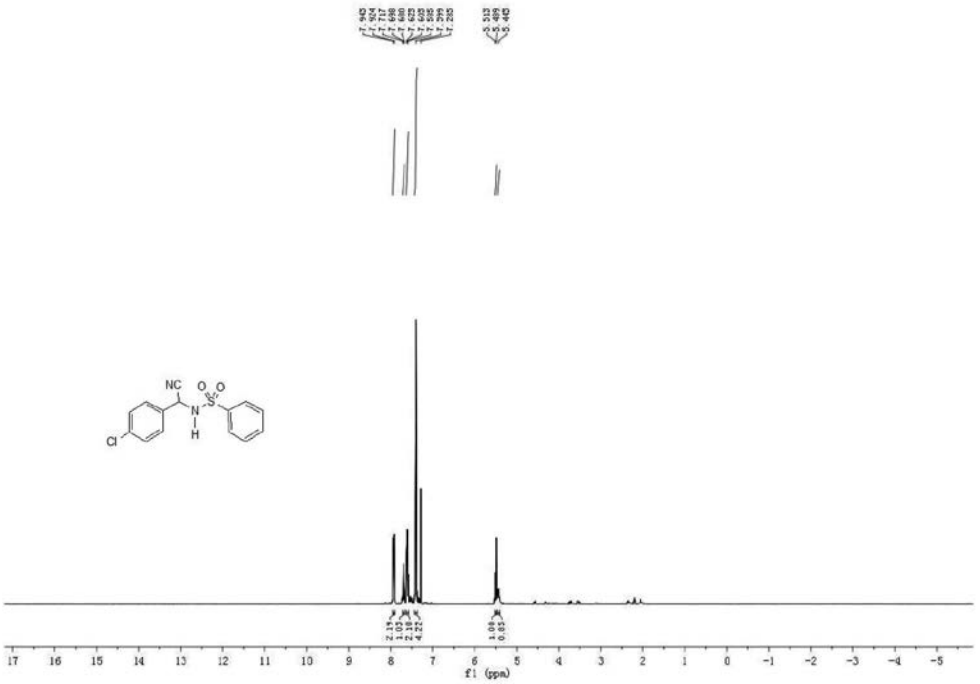

Figure S46. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[(4-chlorophenyl)(cyano)methyl]benzenesulfonamide (**2p**).

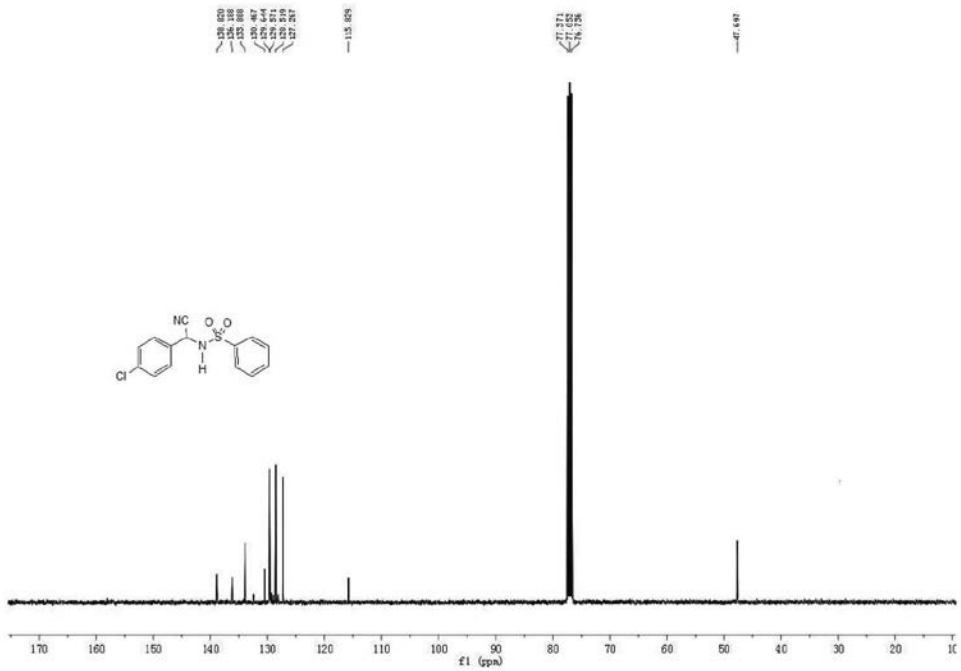

Figure S47. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[(4-chlorophenyl)(cyano)methyl]benzenesulfonamide (**2p**).

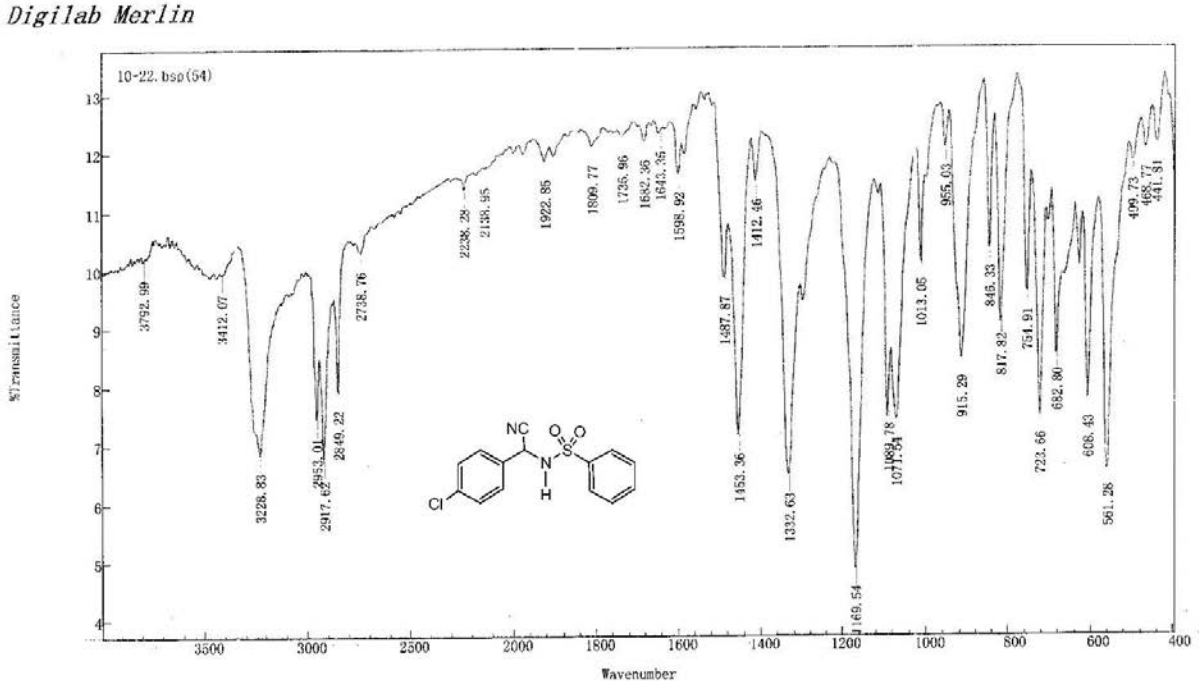

Figure S48. IR of *N*-[(4-chlorophenyl)(cyano)methyl]benzenesulfonamide (**2p**).

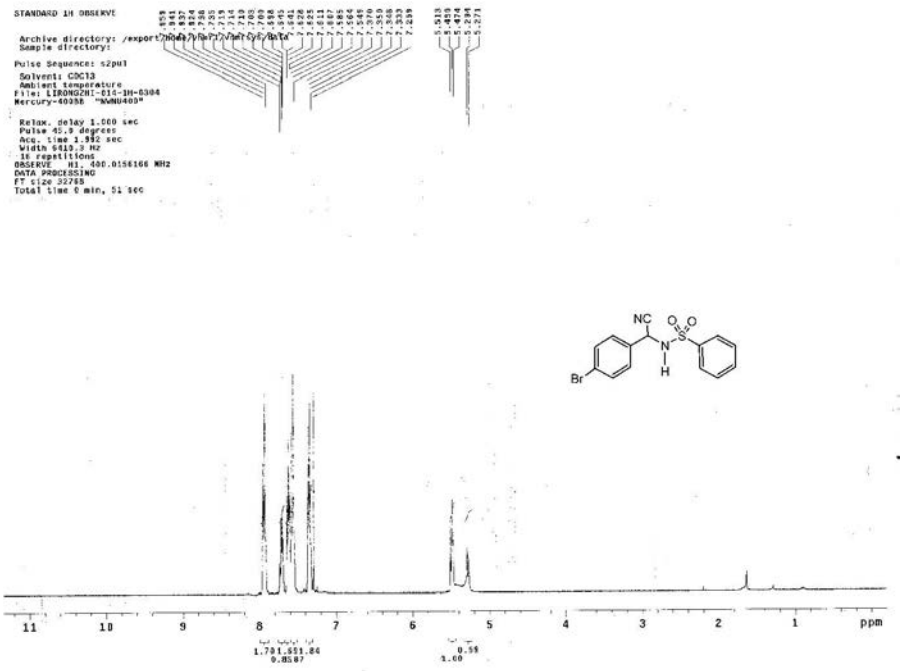

Figure S49. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N*-[(4-bromophenyl)(cyano)methyl]benzenesulfonamide (**2q**).

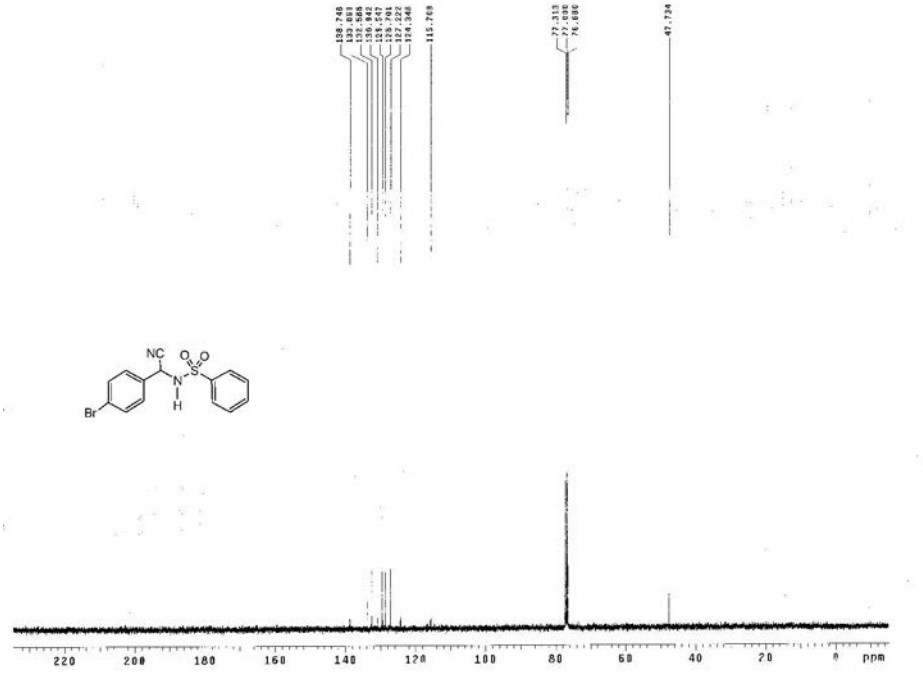

Figure S50. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of *N*-[(4-bromophenyl)(cyano)methyl]benzenesulfonamide (**2q**).

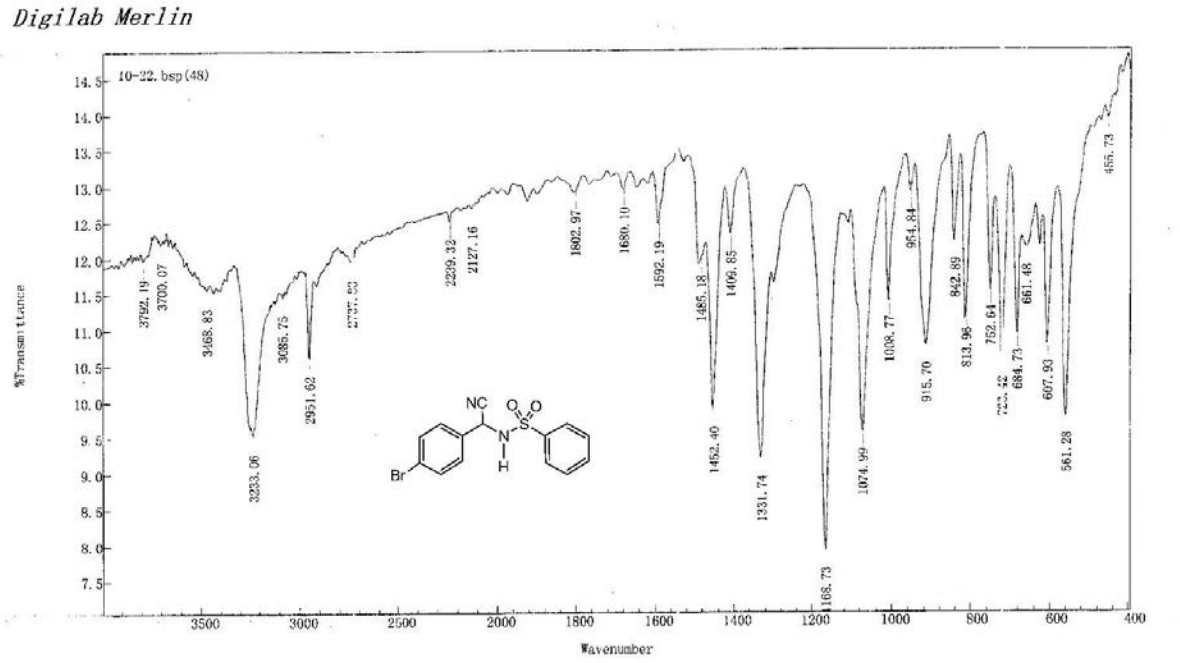

Figure S51. IR of *N*-[(4-bromophenyl)(cyano)methyl]benzenesulfonamide (**2q**).