Supporting information for

Strong Lewis Base $Ga_4B_2O_9$: Ga-O Connectivity Enhanced Basicity and Its Applications in the Strecker Reaction and Catalytic Conversion of n-propanol

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Table S1 Operation conditions, some characteristics of the laboratory-scale apparatus and the catalyst used in this study

Micro-reactor parameters		**GC parameters**	
Pressure of Carrier gas N_2 (Mpa)	1	Pressure of Carrier gas N_2 (Mpa)	0.4
Flow rates of Carrier gas N_2 (mL/min)	40	Flow rates of Carrier gas N_2 (mL/min)	30
Temperature of the catalyst bed (°C)	350	Flow rates of Hydrogen (mL/min)	30
Liquid weight hourly space velocity (h^{-1})	2.36	Flow rates of air (mL/min)	300
Catalyst parameters		Temperature of injector (°C)	150
Catalyst weight (g)	0.2	Temperature of FID (°C)	250
Catalyst particle size (mesh)	40-60	Temperature of column (°C)	100

Table S2 Surrounding environments and Bader charge distribution for oxygen atoms in $Ga_4B_2O_9$ with the structural mode shown in Figure 5 in the main text. The oxygen with red numbers means that they are surficial atoms and exposed to vacuum.

Oxygen No.		**Surrounding environment**	**Bader Charge distribution**
O1	39	1Ga(5)+2Ga(6)	-0.91|e|
	41	2Ga(5)+2Ga(6)	-0.86|e|
	50	2Ga(5)+2Ga(6)	-0.88|e|
	52	1Ga(5)+2Ga(6)	-0.91|e|
	61	1Ga(5)+2Ga(6)	-0.88|e|
	63	2Ga(5)+2Ga(6)	-0.88|e|
	72	2Ga(5)+2Ga(6)	-0.88|e|
	74	1Ga(5)+2Ga(6)	-0.91|e|
O2	33	2Ga(5)+2Ga(6)	-0.89|e|
	37	2Ga(5)+2Ga(6)	-0.89|e|

	44	2Ga(5)+2Ga(6)	-0.88|e|
	46	2Ga(5)+2Ga(6)	-0.9|e|
	55	2Ga(5)+2Ga(6)	-0.91|e|
	59	2Ga(5)+2Ga(6)	-0.89|e|
	66	2Ga(5)+2Ga(6)	-0.89|e|
	68	2Ga(5)+2Ga(6)	-0.91|e|
O3	34	2Ga(6)+1B	-0.85|e|
	38	2Ga(6)+1B	-0.66|e|
	45	2Ga(6)+1B	-0.79|e|
	47	2Ga(6)+1B	-0.79|e|
	56	2Ga(6)+1B	-0.83|e|
	60	2Ga(6)+1B	-0.84|e|
	67	2Ga(6)+1B	-0.83|e|
	69	2Ga(6)+1B	-0.83|e|
O4	40	2Ga(6)+1B	-0.82|e|
	42	2Ga(6)+1B	-0.81|e|
	51	2Ga(6)+1B	-0.8|e|
	53	2Ga(6)+1B	-0.82|e|
	62	2Ga(6)+1B	-0.83|e|
	64	2Ga(6)+1B	-0.8|e|
	73	2Ga(6)+1B	-0.8|e|
	75	2Ga(6)+1B	-0.82|e|
O5	1	1Ga(5)+1Ga(6)+1B	-0.82|e|
	3	1Ga(5)+1Ga(6)+1B	-0.77|e|
	5	1Ga(5)+1Ga(6)+1B	-0.82|e|
	7	1Ga(5)+1Ga(6)+1B	-0.84|e|
	9	1Ga(5)+1Ga(6)+1B	-0.83|e|
	11	1Ga(5)+1Ga(6)+1B	-0.82|e|
	13	1Ga(5)+1Ga(6)+1B	-0.82|e|

	15	1Ga(5)+1Ga(6)+1B	-0.77|e|
	17	1Ga(5)+1Ga(6)+1B	-0.82|e|
	19	1Ga(5)+1Ga(6)+1B	-0.77|e|
	21	1Ga(5)+1Ga(6)+1B	-0.82|e|
	23	1Ga(5)+1Ga(6)+1B	-0.84|e|
	25	1Ga(5)+1Ga(6)+1B	-0.83|e|
	27	1Ga(5)+1Ga(6)+1B	-0.82|e|
	29	1Ga(5)+1Ga(6)+1B	-0.82|e|
	31	1Ga(5)+1Ga(6)+1B	-0.77|e|
O6	2	1Ga(5)+1Ga(6)+1B	-0.81|e|
	4	1Ga(5)+1Ga(6)+1B	-0.82|e|
	6	1Ga(5)+1Ga(6)+1B	-0.83|e|
	8	1Ga(5)+1Ga(6)+1B	-0.82|e|
	10	1Ga(5)+1Ga(6)+1B	-0.81|e|
	12	1Ga(5)+1Ga(6)+1B	-0.82|e|
	14	1Ga(5)+1Ga(6)+1B	-0.81|e|
	16	1Ga(5)+1Ga(6)+1B	-0.82|e|
	18	1Ga(5)+1Ga(6)+1B	-0.81|e|
	20	1Ga(5)+1Ga(6)+1B	-0.82|e|
	22	1Ga(5)+1Ga(6)+1B	-0.83|e|
	24	1Ga(5)+1Ga(6)+1B	-0.82|e|
	26	1Ga(5)+1Ga(6)+1B	-0.81|e|
	28	1Ga(5)+1Ga(6)+1B	-0.82|e|
	30	1Ga(5)+1Ga(6)+1B	-0.81|e|
	32	1Ga(5)+1Ga(6)+1B	-0.82|e|
O7	35	3Ga(5)	-0.92|e|
	48	3Ga(5)	-0.95|e|
	57	3Ga(5)	-0.92|e|
	65	3Ga(5)	-0.9|e|

	70	3Ga(5)	-0.92|e|
O8	36	2Ga(5) +1B	-0.8|e|
	43	2Ga(5) +1B	-0.68|e|
	49	2Ga(5) +1B	-0.82|e|
	54	2Ga(5) +1B	-0.71|e|
	58	2Ga(5) +1B	-0.82|e|
	71	2Ga(5) +1B	-0.81|e|

Table S3. Strecker reactions catalyzed over three gallium borates, $Ga_4B_2O_9$, Ga-PKU-1 and $GaBO_3$ [a)]

Entry	Catalyst	Imine	Yield/%	TOF/(h^{-1})
1	$Ga_4B_2O_9$	1a	81.0	0.68
2		1b	64.1	0.55
3		1c	35.5	0.30
4		1d	53.5	0.46
5		1e	58.5	0.50
6	Ga-PKU-1	1a	12.0	0.10
7		1b	18.0	0.15
8		1c	12.9	0.11
9		1d	12.6	0.11
10		1e	21.3	0.18
11	$GaBO_3$	1a	7.0	0.06
12		1b	9.9	0.08
13		1c	9.5	0.08
14		1d	11.8	0.10
15		1e	13	0.11

[a)] Reaction conditions: 0.2 mmol imines, 1 mL chloroform solvent, 0.3 equiv. catalyst, 2.0 equiv. TMSCN, 45 ^{o}C, N_2 atmosphere, 4 h.

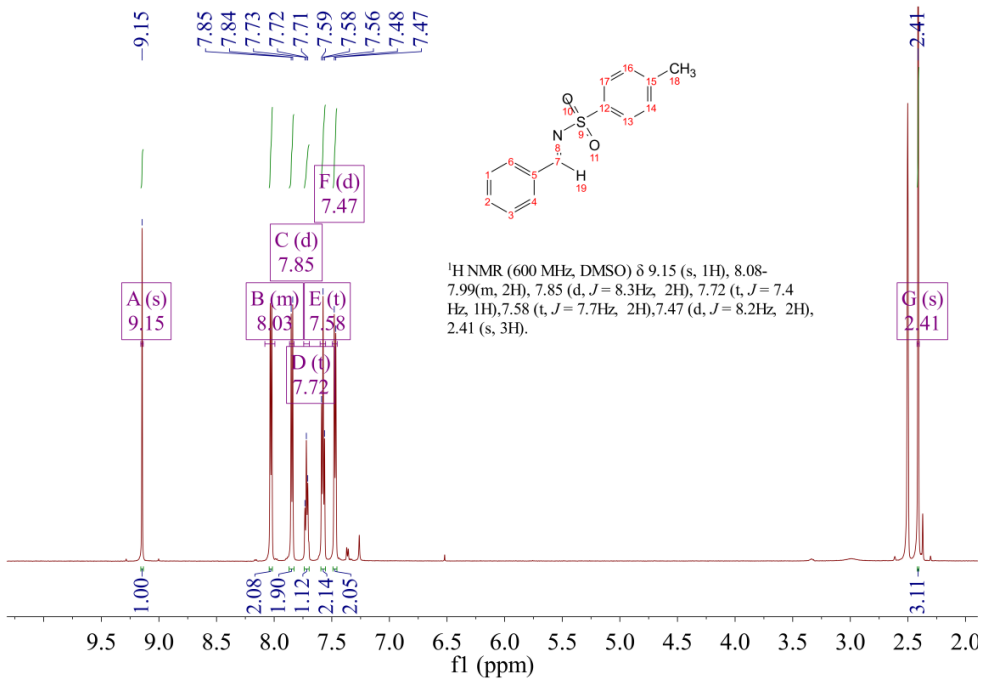


Figure S1 ^{1}H NMR spectrum of 4-methyl-*N*-phenylmethylene-benzenesulfonamide (**1a**): δ 9.15 (s, 1H), 8.08-7.99(m, 2H), 7.85 (d, J = 8.3Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H),7.58 (t, J = 7.7Hz, 2H),7.47 (d, J = 8.2Hz, 2H), 2.41 (s, 3H).

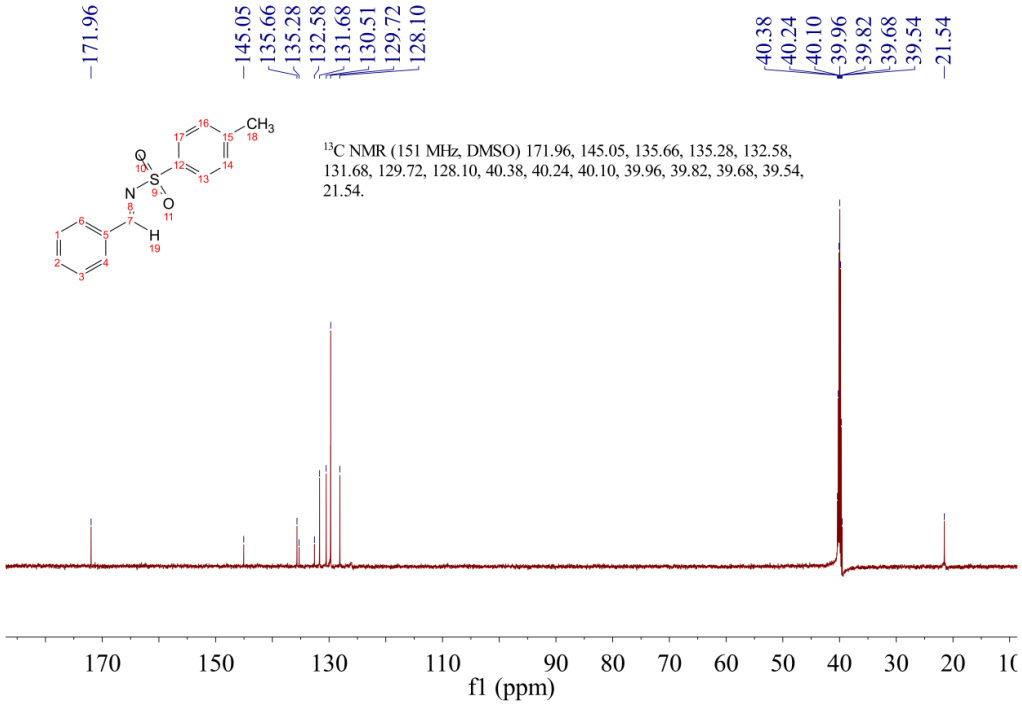


Figure S2 ^{13}C NMR spectrum of 4-methyl-*N*-phenylmethylene-benzenesulfonamide (**1a**): δ 171.96, 145.05, 135.66, 135.28, 132.58, 131.68, 130.51, 129.72, 128.10, 40.38, 40.24, 40.10, 39.96, 39.82, 39.68, 39.54, 21.54.

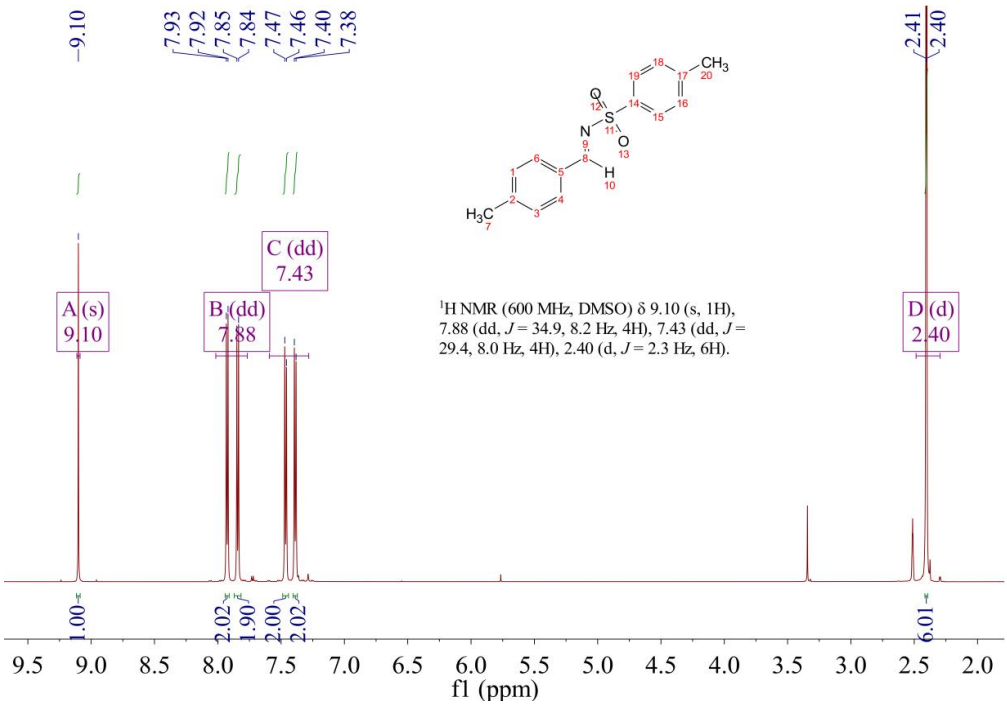


Figure S3 ^{1}H NMR spectrum of 4-methyl-*N*-[(4-methylphenyl)methylene]-benzenesulfonamide (**1b**): δ 9.10 (s, 1H), 7.88 (dd, J = 34.9, 8.2 Hz, 4H), 7.43 (dd, J = 29.4, 8.0 Hz, 4H), 2.40 (d, J = 2.3 Hz, 6H).

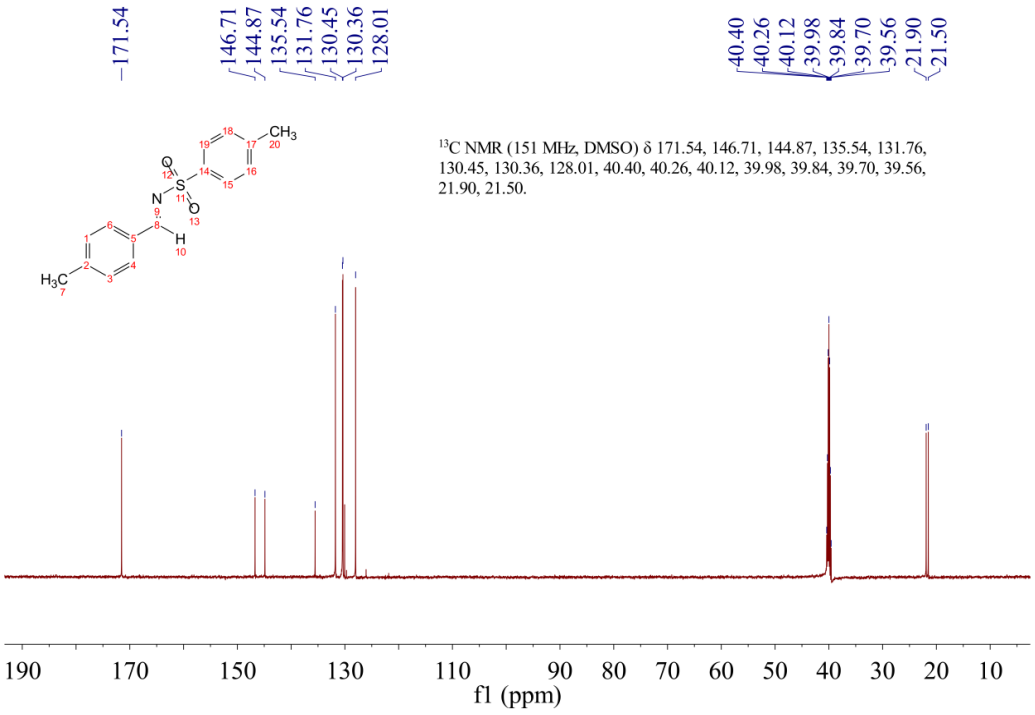


Figure S4 ^{13}C NMR spectrum of 4-methyl-*N*-[(4-methylphenyl)methylene]-benzenesulfonamide (**1b**): δ 171.54, 146.71, 144.87, 135.54, 131.76,130.45, 130.36, 128.01, 40.40, 40.26, 40.12, 39.98,

39.84, 39.70, 39.56, 21.90, 21.50.

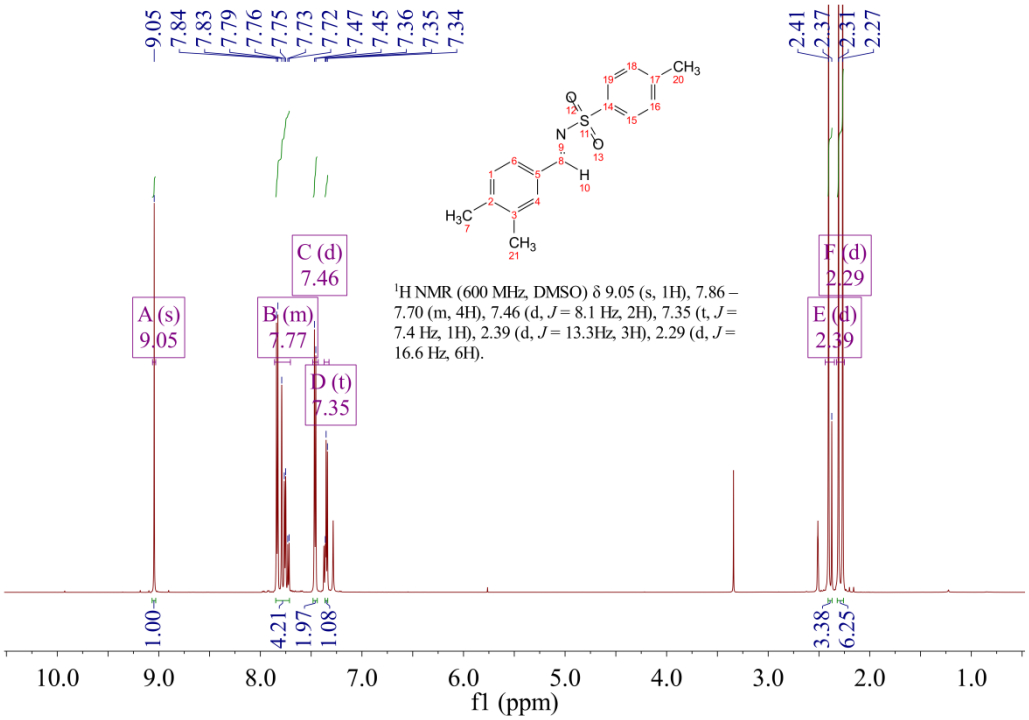


Figure S5 ^{1}H NMR spectrum of 4-methyl-*N*-[(3,4-dimethylphenyl)methylene]-benzenesulfonamid (**1c**): δ 9.05 (s, 1H), 7.86 – 7.70 (m, 4H), 7.46 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 2.39 (d, J = 13.3Hz, 3H), 2.29 (d, J = 16.6 Hz, 6H).

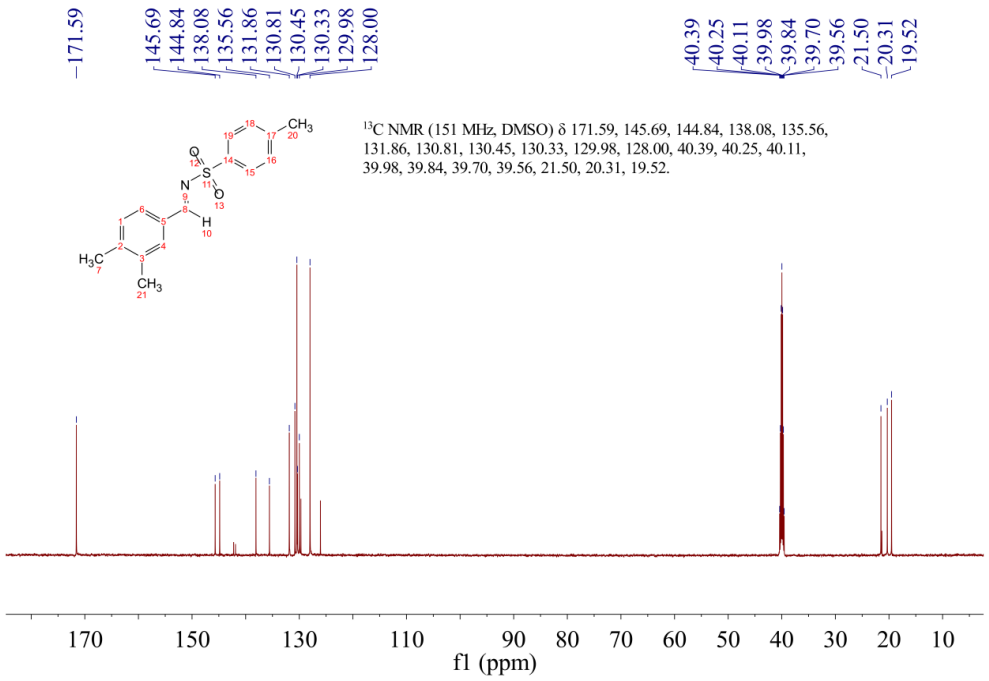


Figure S6 ^{13}C NMR spectrum of 4-methyl-*N*-[(3,4-dimethylphenyl)methylene]-benzenesulfonamide (**1c**): δ 171.59, 145.69, 144.84, 138.08, 135.56, 131.86, 130.81, 130.45, 130.33, 129.98, 128.00,

40.39, 40.25, 40.11, 39.98, 39.84, 39.70, 39.56, 21.50, 20.31, 19.52.

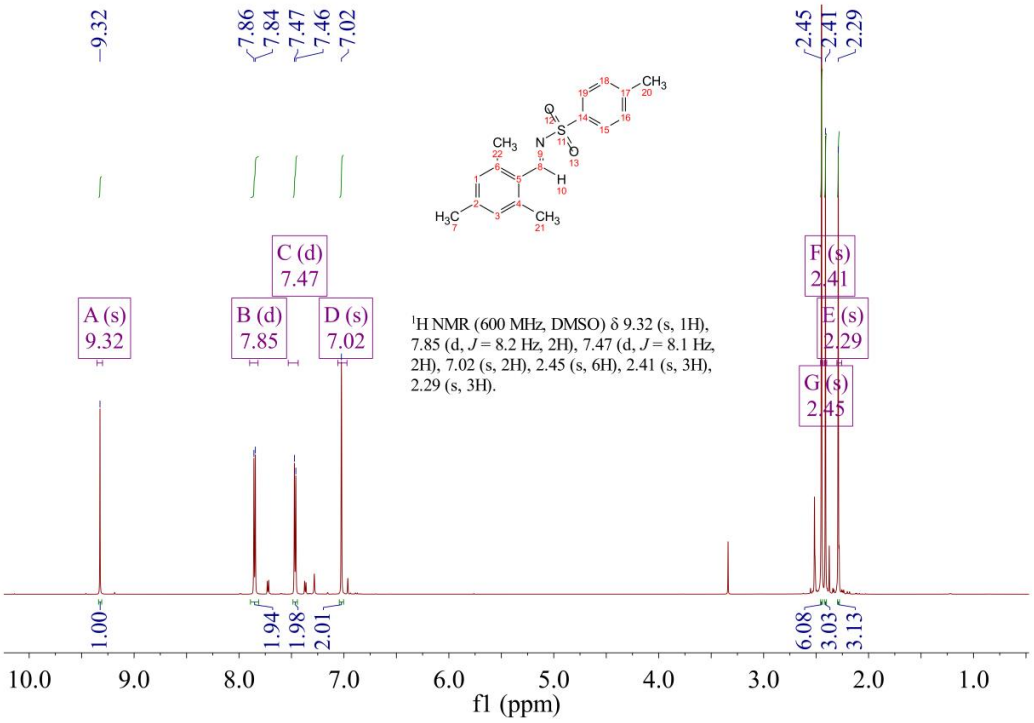


Figure S7 ^{1}H NMR spectrum of 4-methyl-*N*-[(2,4,6-trimethylphenyl)methylene]-benzenesulfonamide (**1d**): δ 9.32 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.02 (s, 2H), 2.45 (s, 6H), 2.41 (s, 3H), 2.29 (s, 3H).

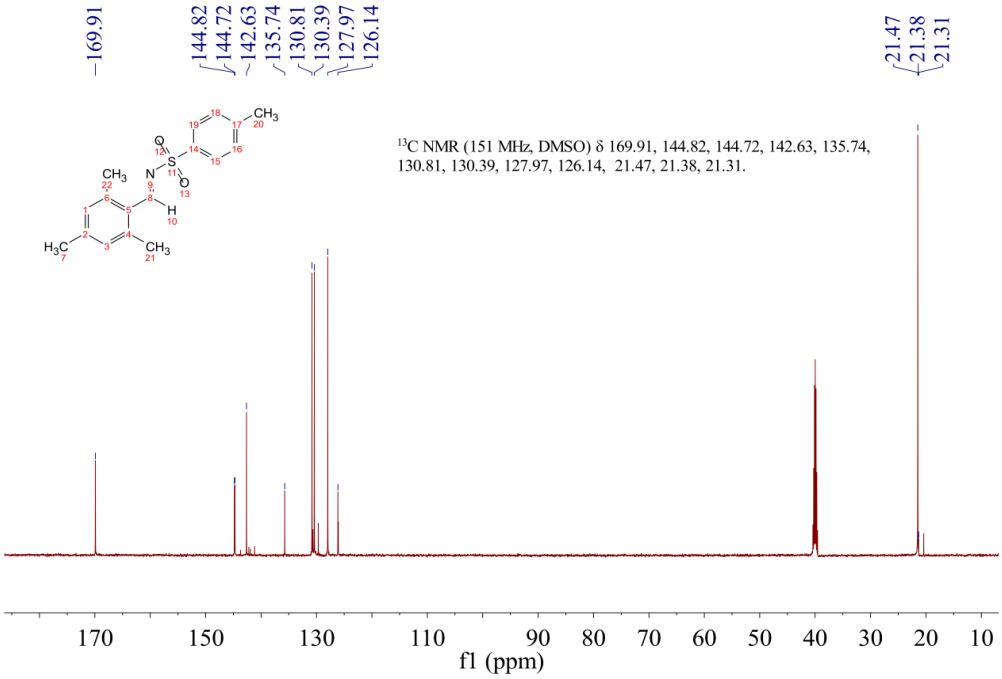
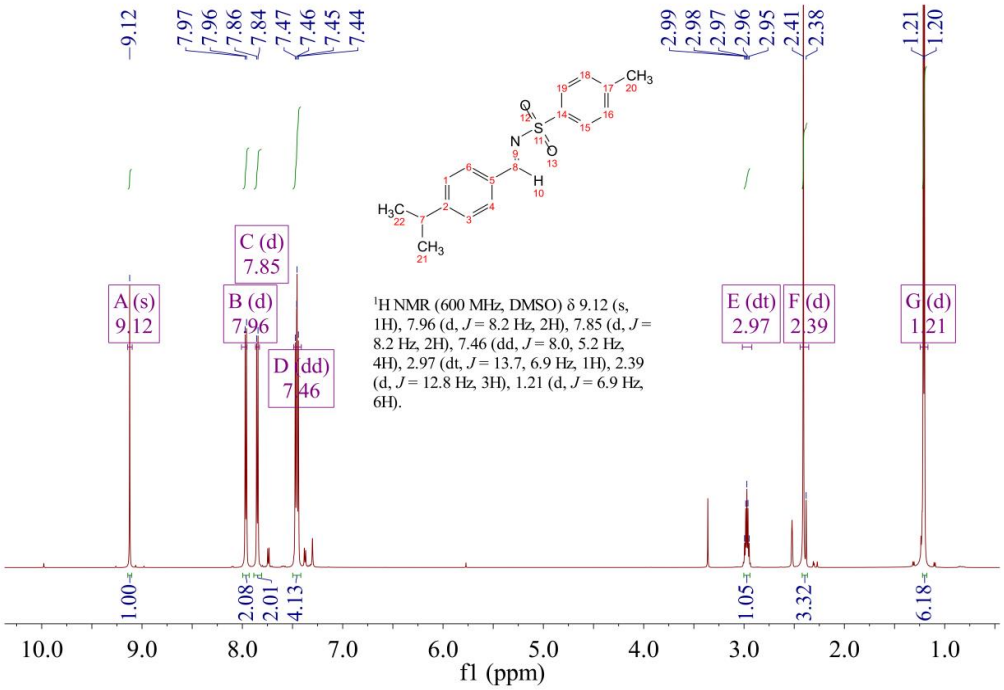


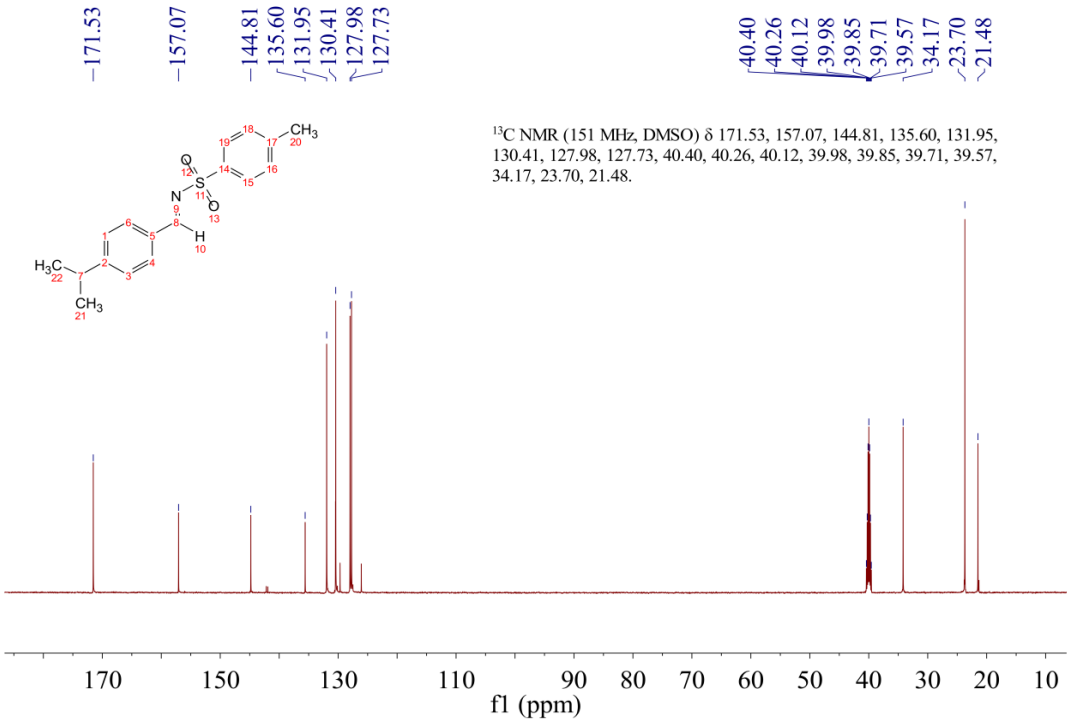
Figure S8 ^{13}C NMR spectrum of 4-methyl-*N*-[(2,4,6-trimethylphenyl)methylene]-benzenesulfonamide (**1d**): δ 169.91, 144.82, 144.72,

142.63, 135.74, 130.81, 130.39, 127.97, 126.14, 21.47, 21.38, 21.31.



^{1}H NMR (600 MHz, DMSO) δ 9.12 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 8.0, 5.2 Hz, 4H), 2.97 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.39 (d, *J* = 12.8 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 6H).

Figure S9 ^{1}H NMR spectrum of 4-methyl-*N*-{[4-(1-methylethyl)phenyl]methylene}-benzenesulfonamide (**1e**): δ 9.12 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H), 7.46 (dd, J = 8.0, 5.2 Hz, 4H), 2.97 (dt, J = 13.7, 6.9 Hz, 1H), 2.39 (d, J = 12.8 Hz, 3H), 1.21 (d, J = 6.9 Hz, 6H).



^{13}C NMR (151 MHz, DMSO) δ 171.53, 157.07, 144.81, 135.60, 131.95, 130.41, 127.98, 127.73, 40.40, 40.26, 40.12, 39.98, 39.85, 39.71, 39.57, 34.17, 23.70, 21.48.

Figure S10 ^{13}C NMR spectrum of

4-methyl-*N*-{[4-(1-methylethyl)phenyl]methylene}-benzenesulfonamide (**1e**): δ 171.53, 157.07, 144.81, 135.60, 131.95, 130.41, 127.98,127.73, 40.40, 40.26, 40.12, 39.98, 39.85, 39.71, 39.57, 34.17, 23.70, 21.48.

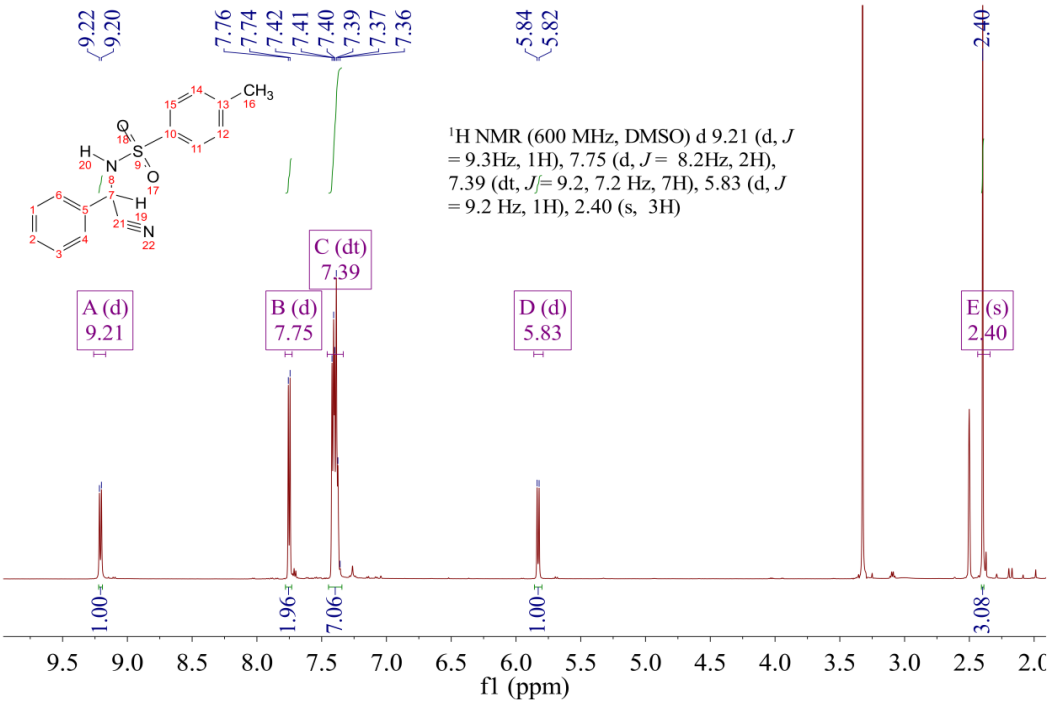


Figure S11 ^{1}H NMR spectrum of *N*-[cyano(phenyl)methyl]-4-methyl-benzenesulfonamide (**2a**): δ 9.21 (d, J = 9.3Hz, 1H), 7.75 (d, J = 8.2Hz, 2H), 7.39 (dt, J = 9.2, 7.2 Hz, 7H), 5.83 (d, J = 9.2 Hz, 1H), 2.40 (s, 3H).

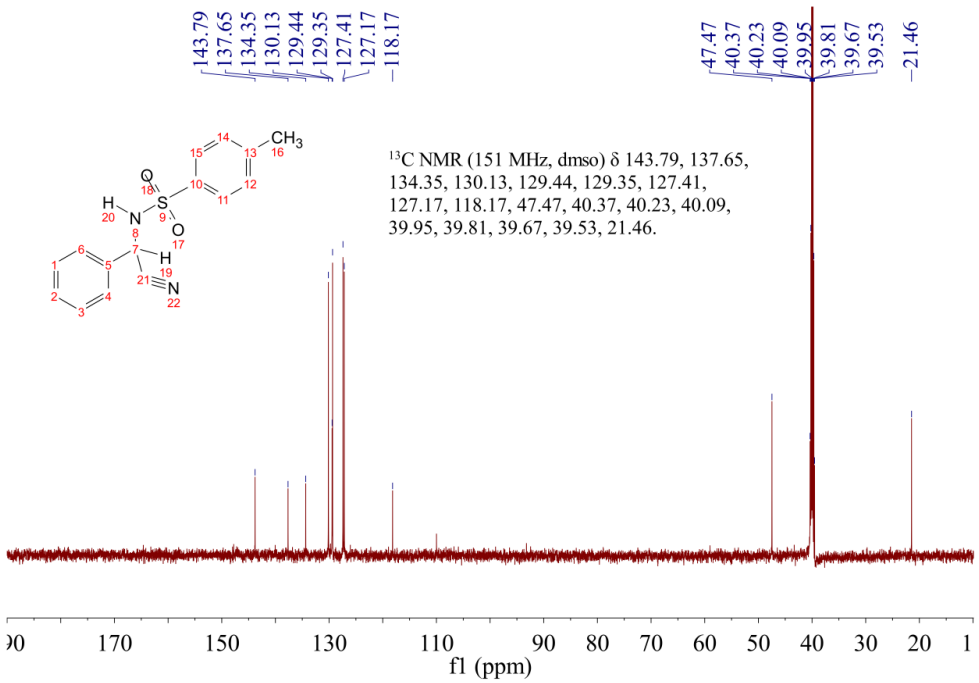


Figure S12 ^{13}C NMR spectrum of *N*-[cyano(phenyl)methyl]-4-methyl-benzenesulfonamide (**2a**): δ 143.79, 137.65, 134.35, 130.13, 129.44, 129.35, 127.41, 127.17, 118.17, 47.47, 40.37, 40.23, 40.09, 39.95, 39.81, 39.67, 39.53, 21.46.

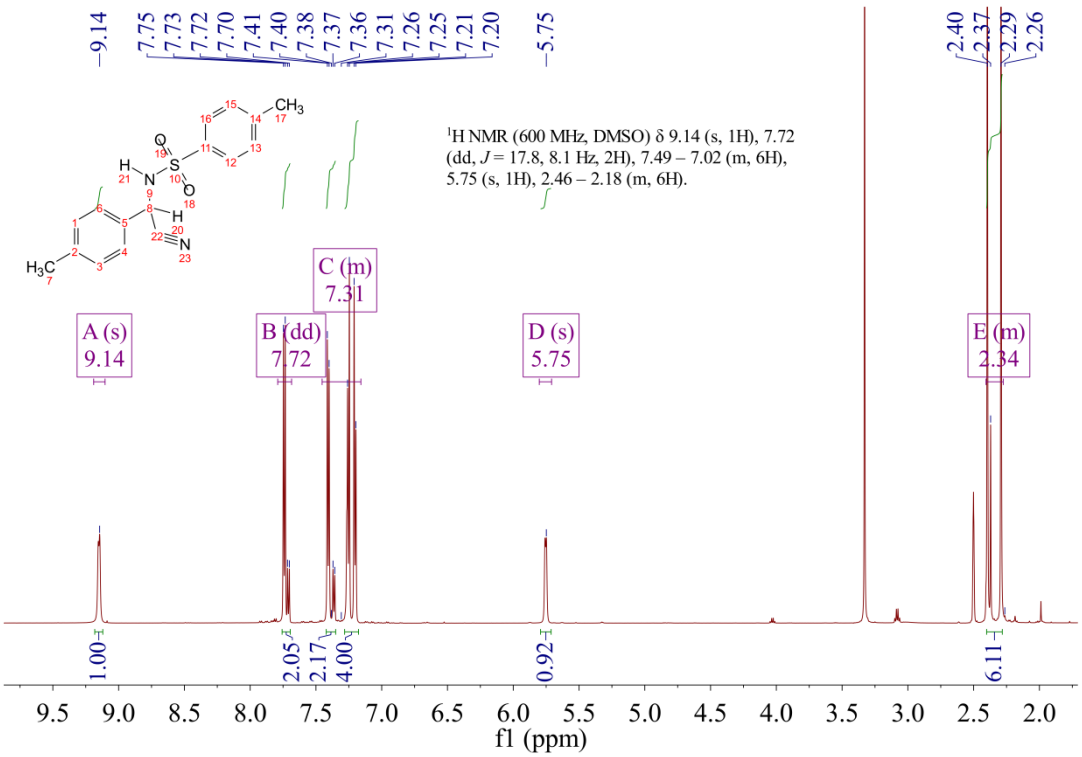


Figure S13 ^{1}H NMR spectrum of *N*-[cyano(p-tolyl)methyl]-4-methyl-benzenesulfonamide (**2b**): δ 9.14 (s, 1H), 7.72 (dd, J = 17.8, 8.1 Hz, 2H), 7.49 – 7.02 (m, 6H), 5.75 (s, 1H), 2.46 – 2.18 (m, 6H).

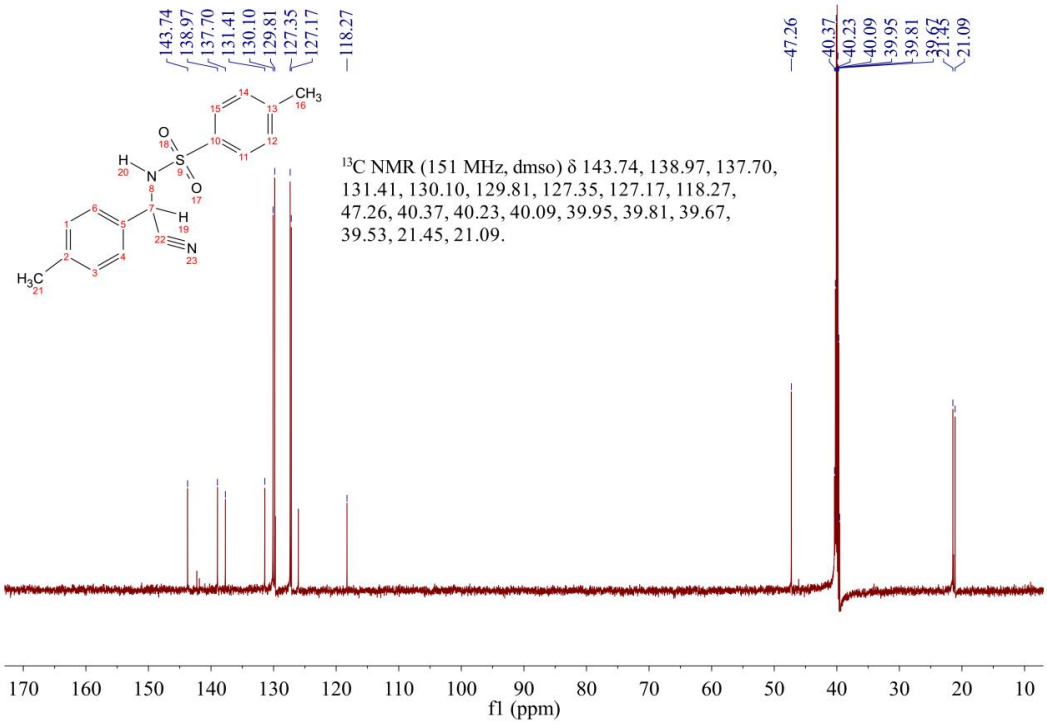


Figure S14 ^{13}C NMR spectrum of *N*-[cyano(p-tolyl)methyl]-4-methyl-benzenesulfonamide (**2b**): δ 143.74, 138.97, 137.70, 131.41, 130.10, 129.81, 127.35, 127.17, 118.27, 47.26, 40.37, 40.23, 40.09, 39.95, 39.81, 39.67, 39.53, 21.45, 21.09.

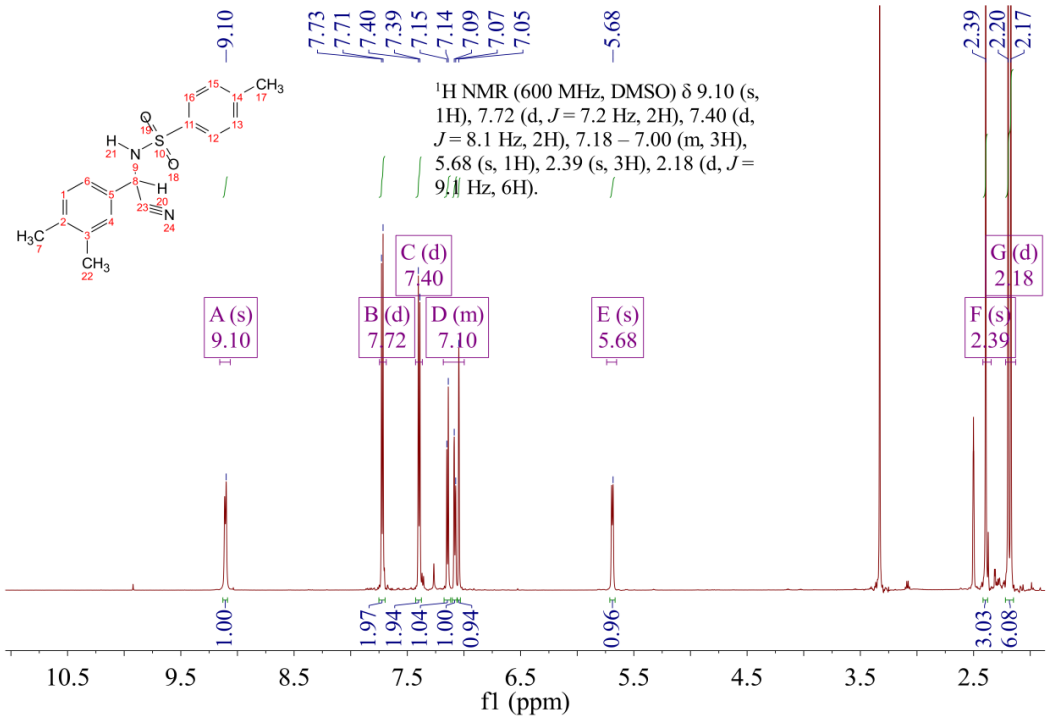


Figure S15 ^{1}H NMR spectrum of *N*-[cyano(3,4-dimethylphenyl)methyl]-4-methyl-benzenesulfonamide (**2c**): δ 9.10 (s, 1H), 7.72 (d, J = 7.2 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.18 – 7.00 (m, 3H), 5.68 (s, 1H), 2.39 (s, 3H), 2.18 (d, J = 9.1 Hz, 6H).

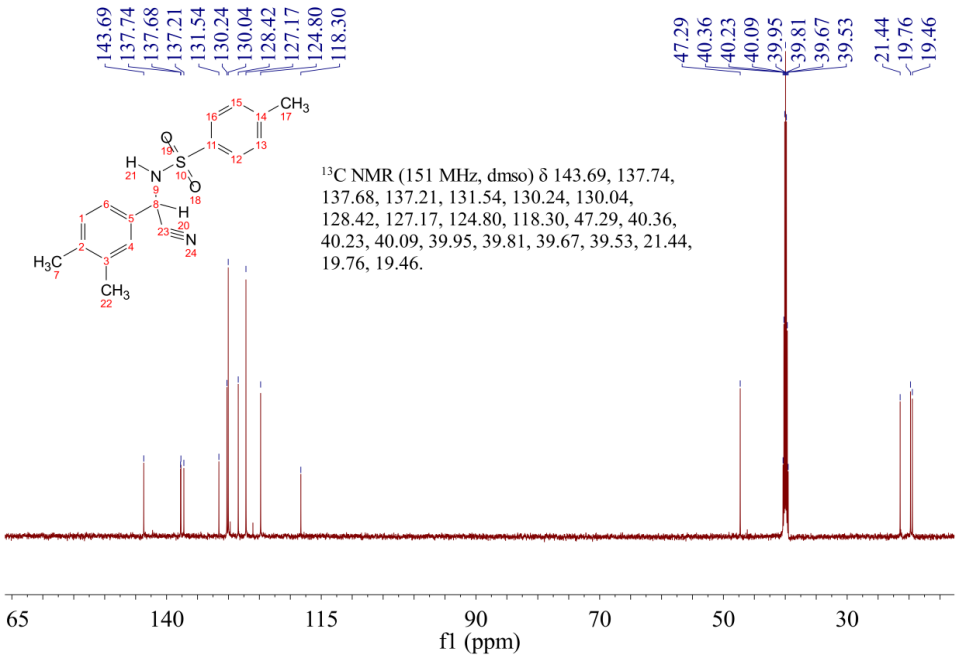


Figure S16 ^{13}C NMR spectrum of *N*-[cyano(3,4-dimethylphenyl)methyl]-4-methyl-benzenesulfonamide (**2c**): δ 143.69, 137.74, 137.68, 137.21, 131.54, 130.24, 130.04, 128.42, 127.17, 124.80, 118.30, 47.29, 40.36, 40.23, 40.09, 39.95, 39.81, 39.67, 39.53, 21.44, 19.76, 19.46.

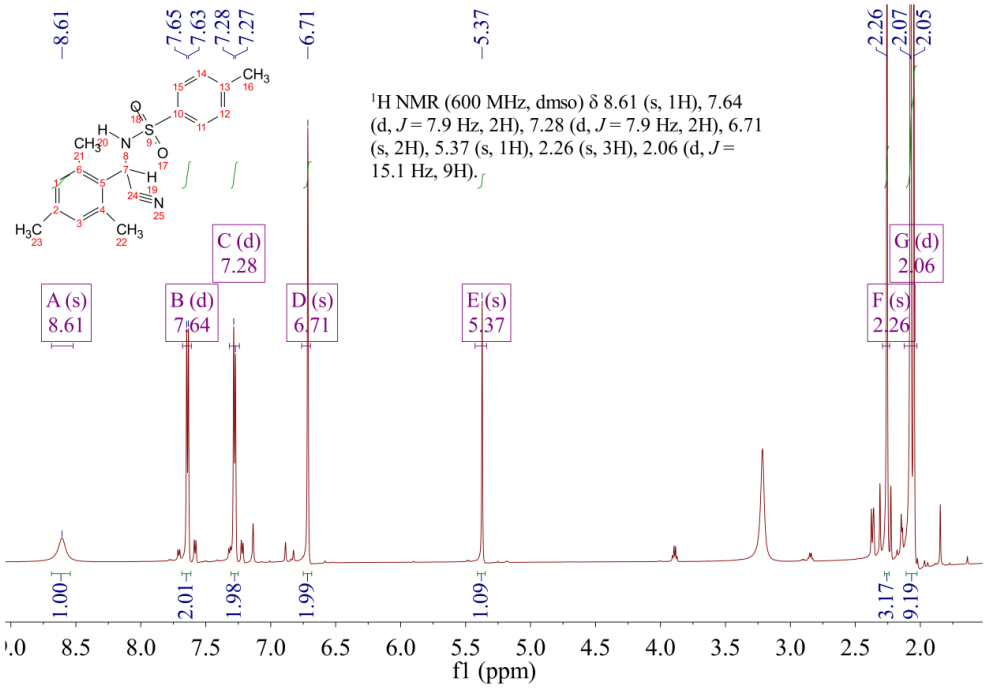


Figure S17 ^{1}H NMR spectrum of *N*-[cyano(mesityl)methyl]-4-methyl-benzenesulfonamide (**2d**): δ 9.14 (s, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.26 (q, J = 8.4 Hz, 2H), 5.76 (d, J = 3.1 Hz, 1H), 2.87 (dt, J = 13.8, 6.9 Hz, 1H), 2.39 (s, 3H), 1.17 (d, J = 6.9 Hz, 6H).

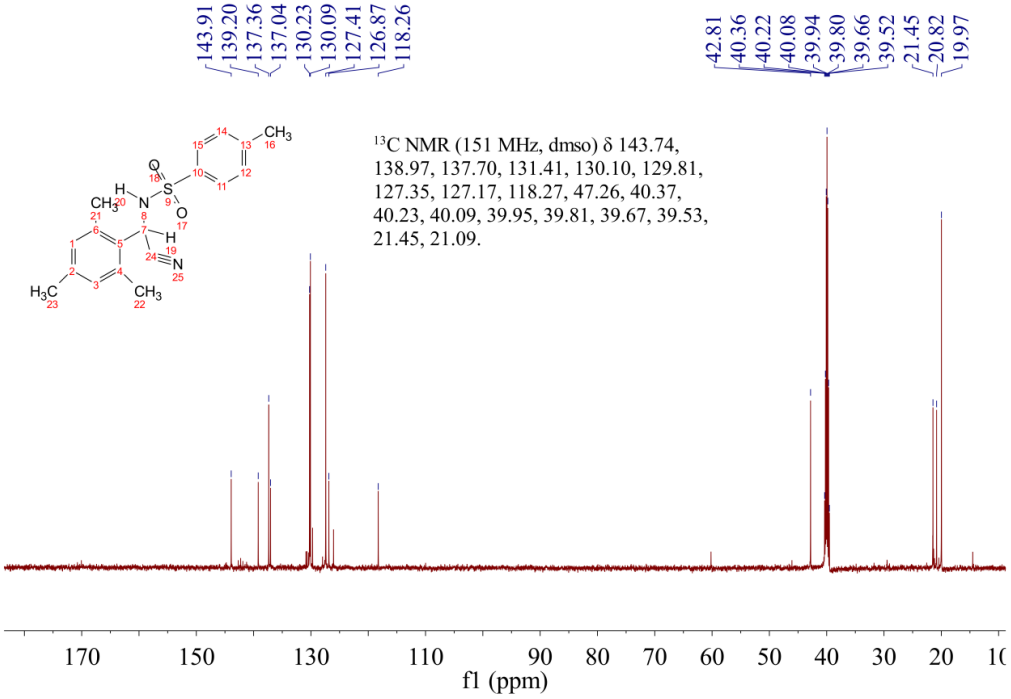


Figure S18 ^{13}C NMR spectrum of *N*-[cyano(mesityl)methyl]-4-methyl-benzenesulfonamide (**2d**): δ 143.74, 138.97, 137.70, 131.41, 130.10, 129.81, 127.35, 127.17, 118.27, 47.26, 40.37, 40.23, 40.09, 39.95, 39.81, 39.67, 39.53, 21.45, 21.0.

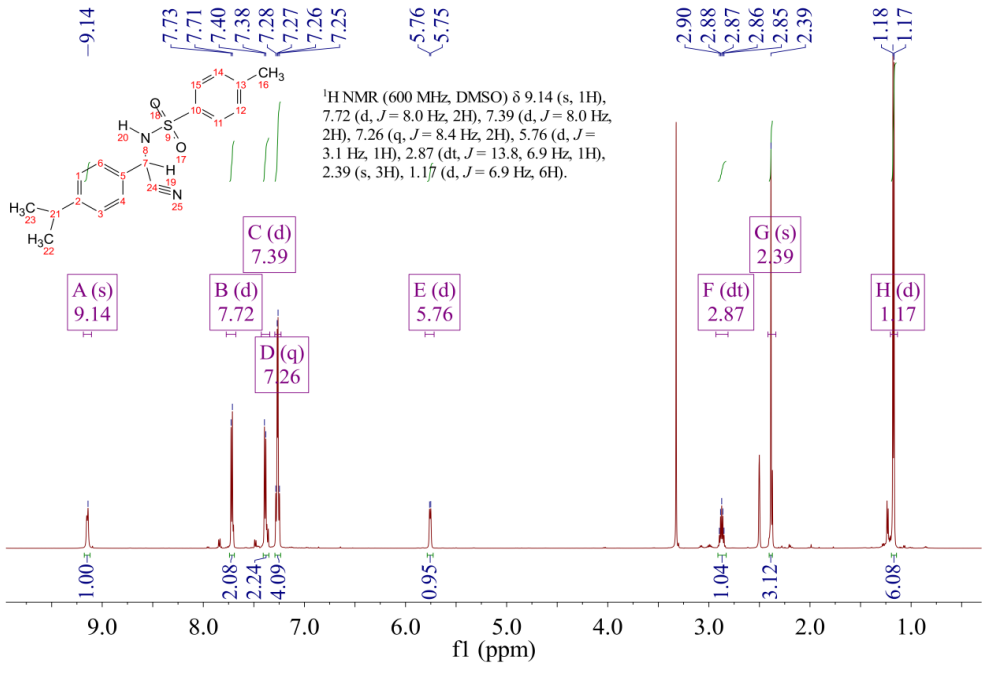


Figure S19 ^{1}H NMR spectrum of *N*-[cyano(4-isopropylphenyl)methyl]-4-methyl-benzenesulfonamide (**2e**): δ 9.14 (s, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.26 (q, J = 8.4 Hz, 2H), 5.76 (d, J = 3.1 Hz, 1H), 2.87 (dt, J =

13.8, 6.9 Hz, 1H), 2.39 (s, 3H), 1.17 (d, J = 6.9 Hz, 6H).

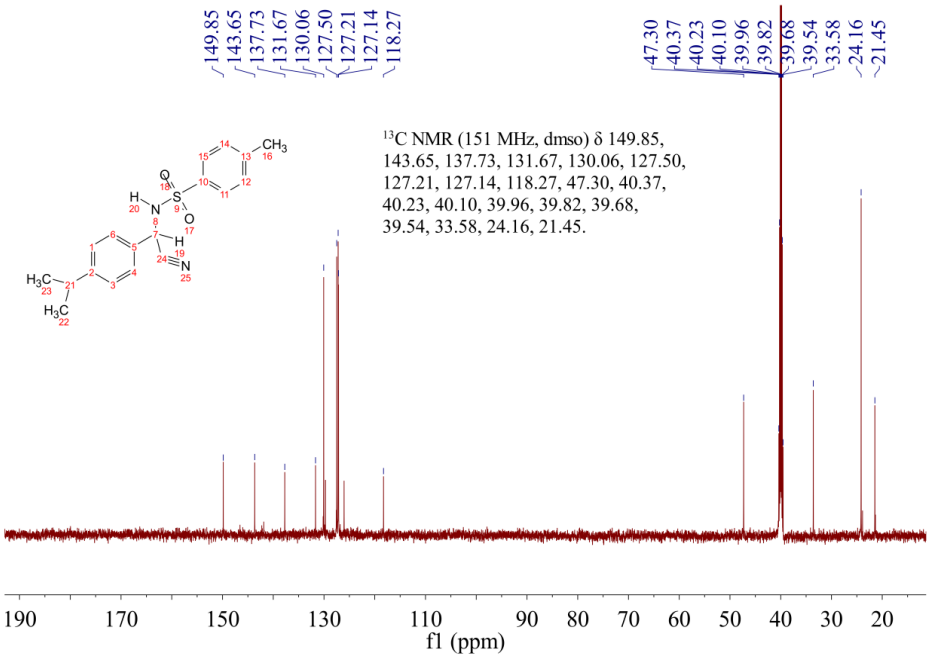


Figure S20 ^{13}C NMR spectrum of *N*-[cyano(4-isopropylphenyl)methyl]-4-methyl-benzenesulfonamide (**2e**): δ 149.85, 143.65, 137.73, 131.67, 130.06, 127.50, 127.21, 127.14, 118.27, 47.30, 40.37, 40.23, 40.10, 39.96, 39.82, 39.68, 39.54, 33.58, 24.16, 21.45.