Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Nano rod shaped formation of an ionogel and its high catalytic activity for one-pot synthesis of benzothiazoles

Pankaj Sharma[a], Monika Gupta[a]*, RajniKant[b] and Vivek K. Gupta[b]

[a]Department of Chemistry, University of Jammu, Jammu-180006, India,
E-mail: monika.gupta77@rediffmail.com*
[b]Department of Physics, University of Jammu, Jammu-180006, India.

Table of Contents **Page No.**

Characterization of the Ionogel

TGA-DTA analysis was used to investigate the thermal stability of ionogel, since the observed weight loss is associated with loss of species present. From TGA graph (Fig. S1), the initial weight loss below 100 ^{o}C could be possibly due to loss of some physically adsorbed gases and also may be due to presence of volatile HCl and residual ethanol. The weight loss around 264 ^{o}C may be attributed to loss of chlorine anions associated to IL and the weight loss near 359 ^{o}C can be due to decomposition of alkyl groups of ionic liquid and complete decomposition of ionic liquid occurred near 660 ^{o}C and above 700 ^{o}C the weight loss will be due to decomposition of silica gel.

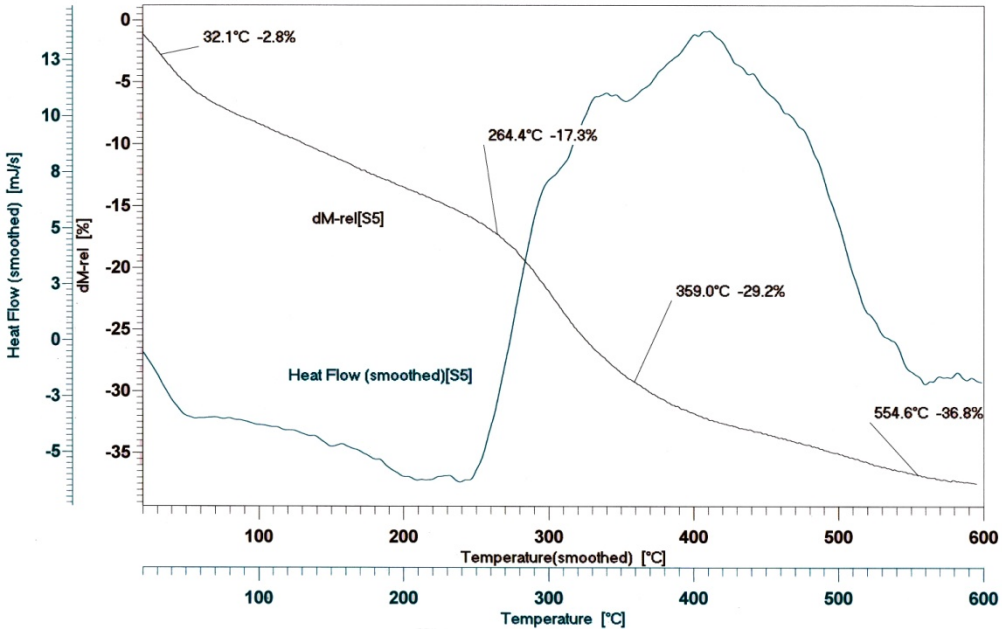


Fig. S1 TGA-DTA graph of ionogel

FTIR spectra (Fig. S2) of ionogel give the number of peaks corresponding to silica and ionic liquid. Silica region can be primarily divided into three peaks centre corresponding to near 453 cm^{-1} due to rocking motion of oxygen atom bridging silicon atoms in siloxane bonds (Si-O-Si), 800 cm^{-1} corresponding to symmetric vibration of silicon atom in silixane and and a larger peak near 1074 cm^{-1} is due to antisymmetric motion of silicon atoms. The strong absorption band at 3302 cm^{-1} which was due to the presence of –NH group and at 2902, 2877, 2281 and 1460 cm^{-1}

shows the presence of –N-C-H, -C-H, N-N and C=N groups respectively corresponding to ionic liquid.

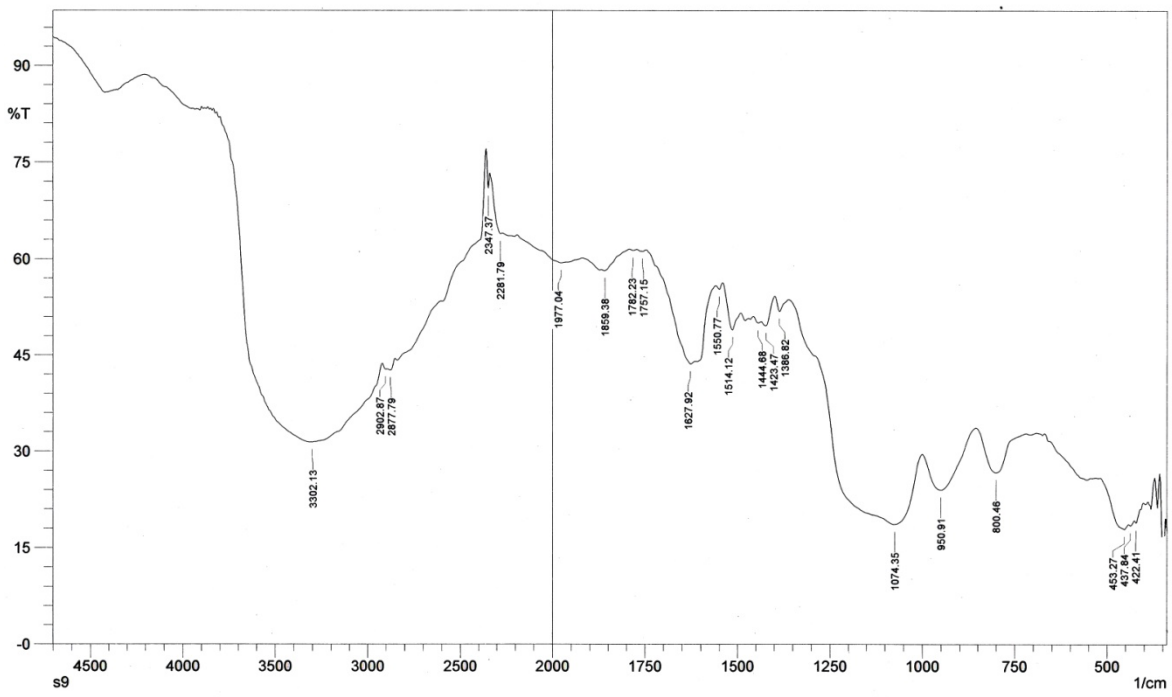


Fig. S2 FTIR spectra of ionogel

Recyclability of the Ionogel

The important feature of ionogel was that it was reusable for several runs with very little loss in activity. To check the recyclability of ionogel 3-nitrobenzaldehyde and 2-aminothiophenol were chosen as test substrates and we tried the ionogel for seven consecutive runs. There was also a little loss of catalyst after every work-up which may be due to human error, so consecutive reactions were performed proportionally with ionogel. So from recyclability graph (Fig S3), it was concluded that the ionogel is reusable in the formation of benzothiazoles with very little loss in activities which is the main feature of heterogeneous catalysis. The little loss in activity may be attributed to reduction of some active sites of ionogel after every use.

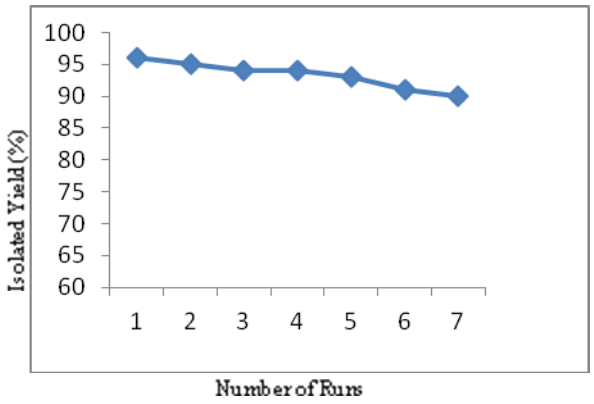


Fig.S3 Recyclability graph of the Ionogel

Spectral data of some products

2-(4-chlorophenyl)benzo[d]thiazole (Table 2, Entry 7, 3g)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.53 (m, 5H, Ar), 7.93 (d, 1H, Ar) 8.05-8.10 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.7, 123.7, 125.4, 126.5, 128.7, 129.3, 132.1, 135.1, 137.1, 154.1, 166.7.

MS (m/z): 246 (M^+)

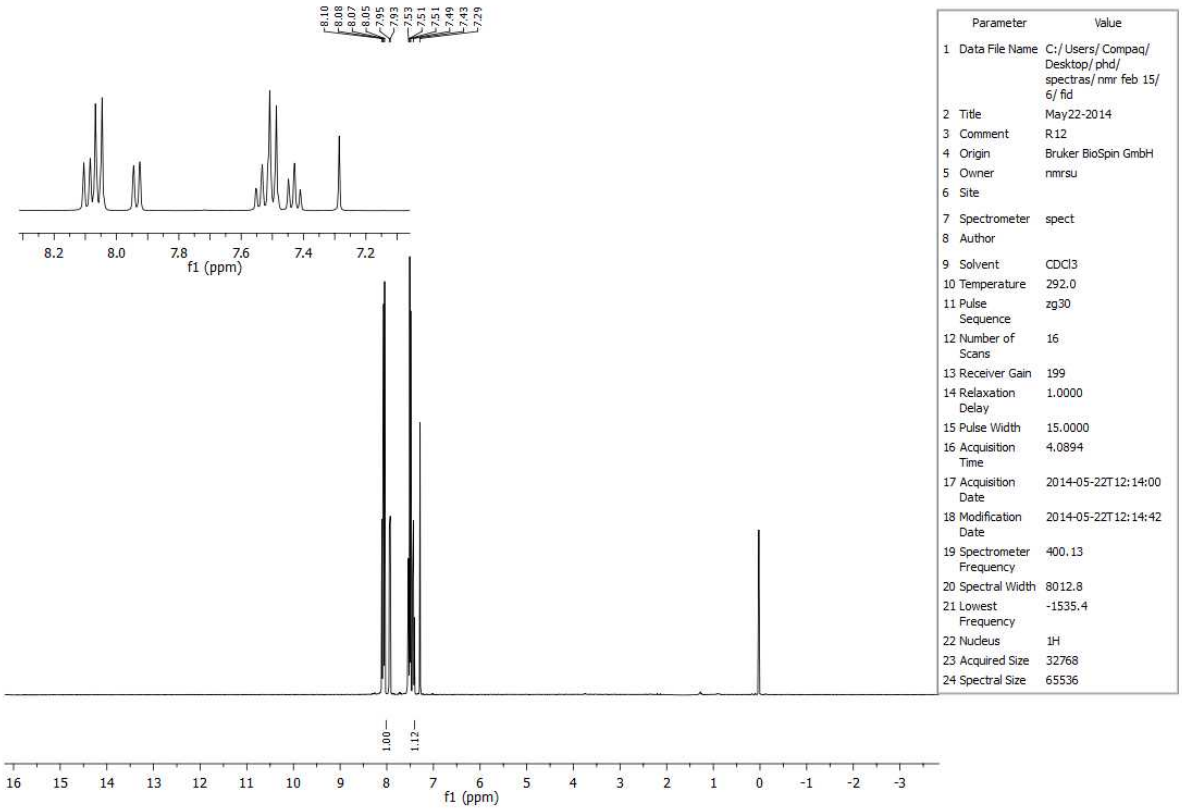


Fig. S4 ^{1}H NMR spectra of 2-(4-chlorophenyl)benzo[d]thiazole

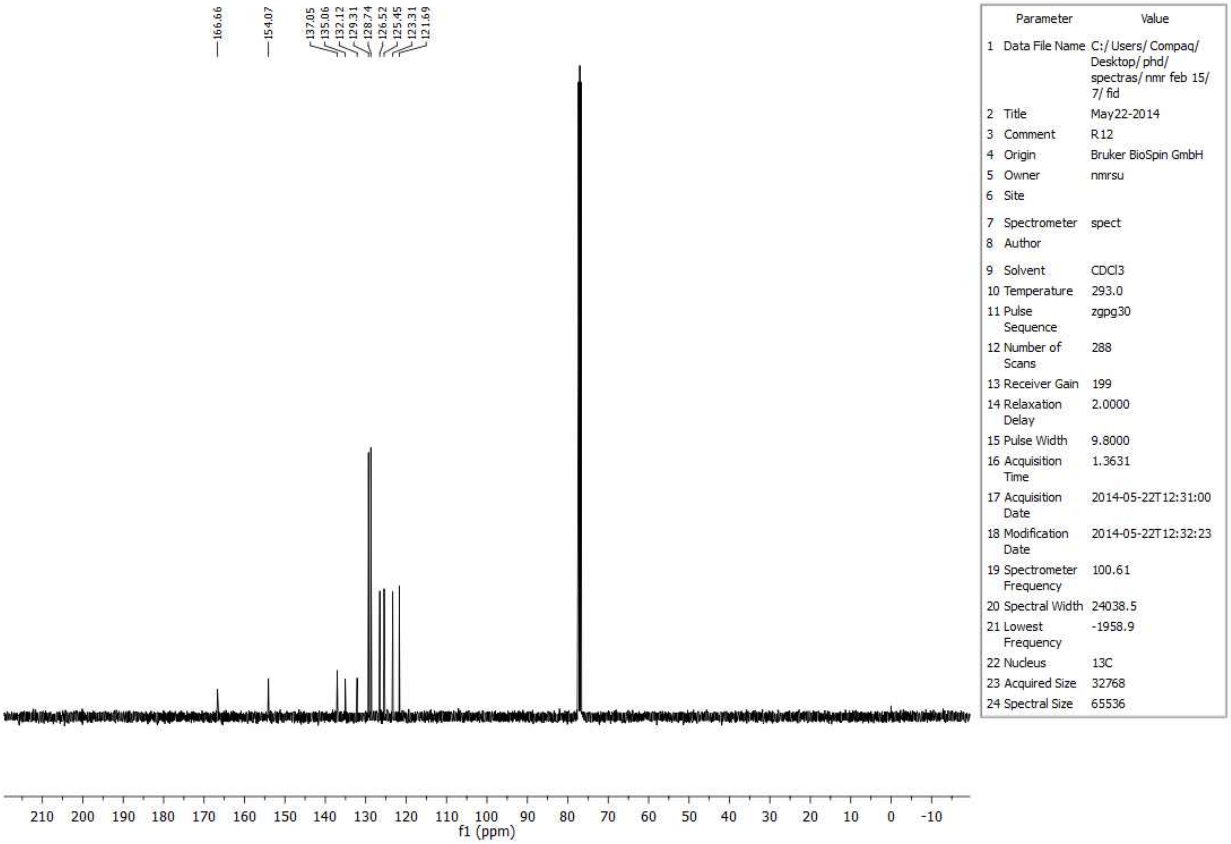


Fig. S5 ^{13}C NMR spectra of 2-(4-chlorophenyl)benzo[d]thiazole

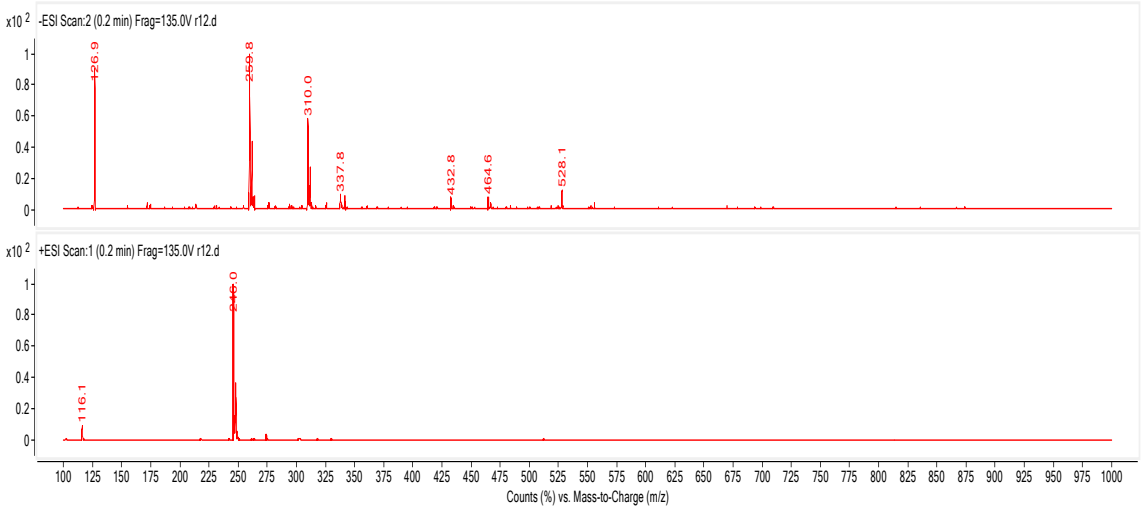


Fig. S6 Mass spectra of 2-(4-chlorophenyl)benzo[d]thiazole

2-(4-methoxyphenyl)benzo[d]thiazole (Table 2, Entry 12, 3l)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3H, -OCH_3), 7.02-7.04 (d, 2H, Ar), 7.36-7.40 (t, 1H, Ar), 7.48-7.52 (t, 1H, Ar), 7.89-7.91(d, 1H, Ar) 8.05-8.07 (m, 3H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 114.4, 121.5, 122.8, 124.8, 126.2, 126.4, 129.1, 134.9, 154.2, 161.9, 167.9.

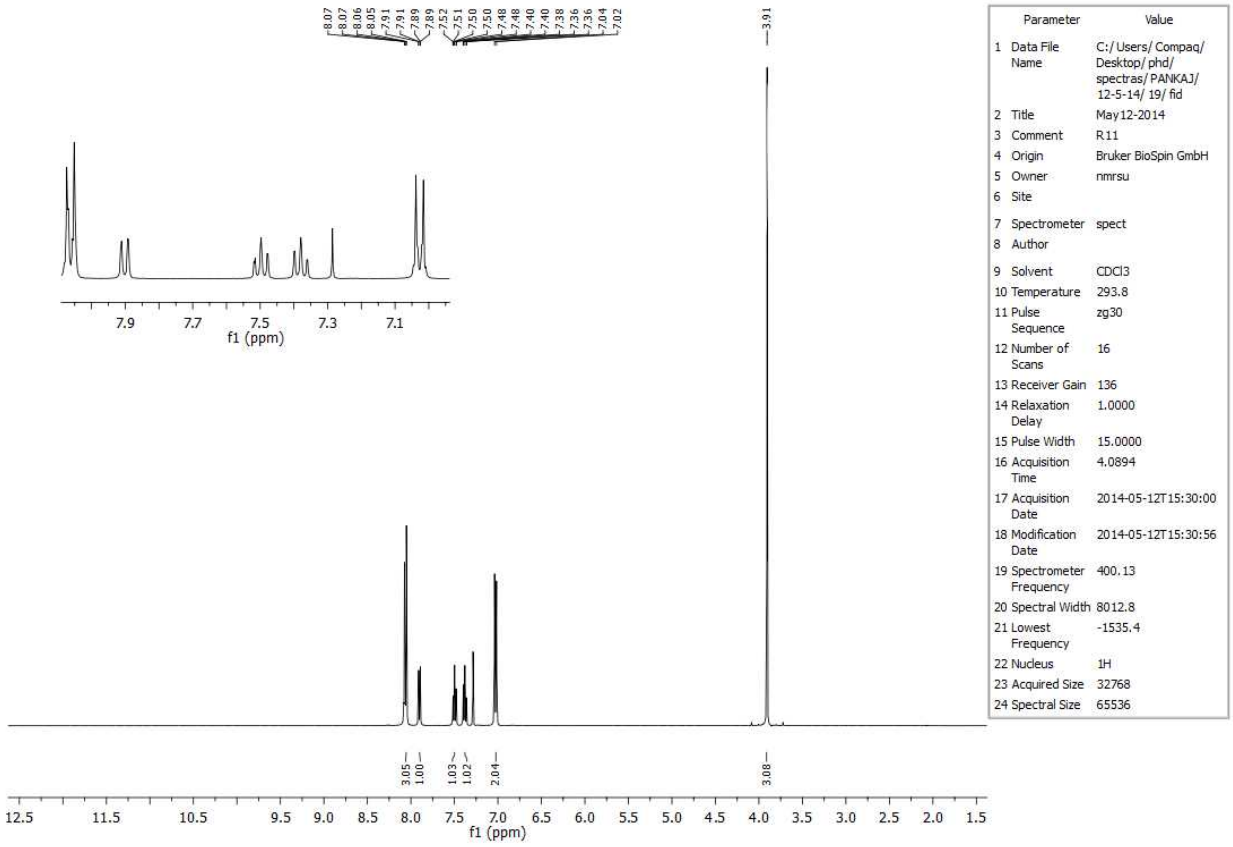
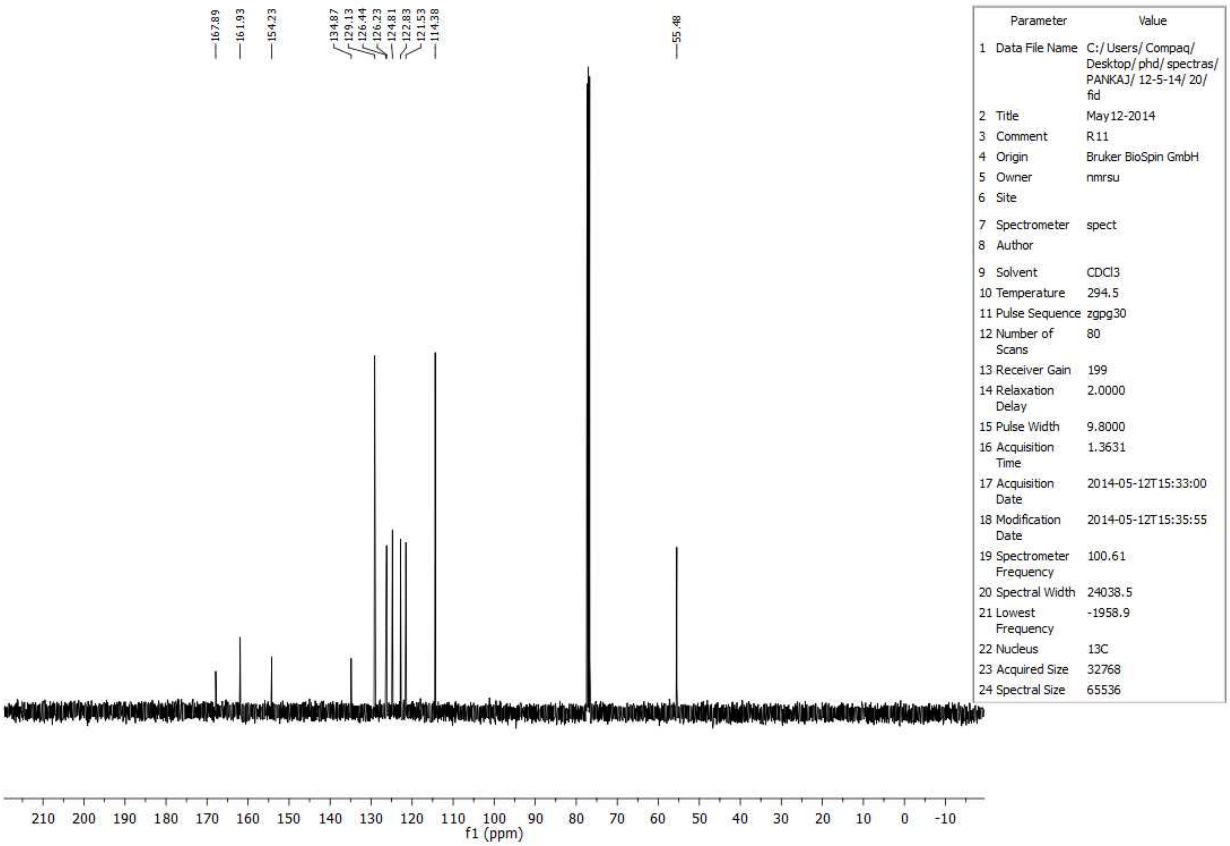


Fig. S7 ^{1}H NMR spectra of 2-(4-methoxyphenyl)benzo[d]thiazole



	Parameter	Value
1	Data File Name	C:/Users/Compaq/Desktop/phd/spectras/PANKAJ/12-5-14/20/fid
2	Title	May12-2014
3	Comment	R11
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.5
11	Pulse Sequence	zgpg30
12	Number of Scans	80
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2014-05-12T15:33:00
18	Modification Date	2014-05-12T15:35:55
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S8 ^{13}C NMR spectra of 2-(4-methoxyphenyl)benzo[d]thiazole

2-(furan-2-yl)benzo[d]thiazole (Table 2, Entry 14, 3n)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (m, 1H, Ar), 7.22 (d, 1H, Ar), 7.40 (t, 1H, Ar), 7.52 (t, 1H, Ar), 7.63 (t, 1H, Ar), 7.90 (d, 1H, Ar), 8.07 (d, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.5, 112.6, 121.6, 123.1, 125.2, 126.5, 134.3, 144.7, 148.8, 153.8, 157.6.

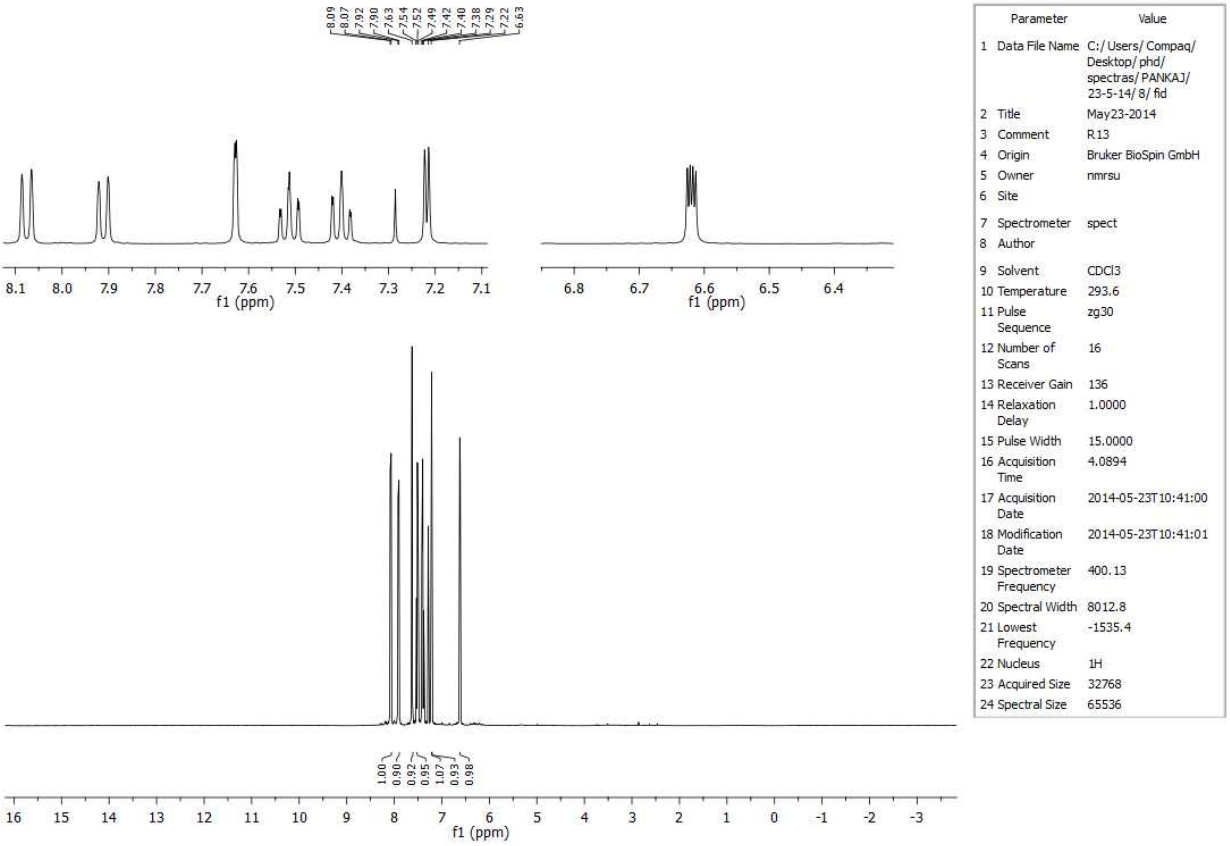


Fig. S9 ^{1}H NMR spectra 2-(furan-2-yl)benzo[d]thiazole

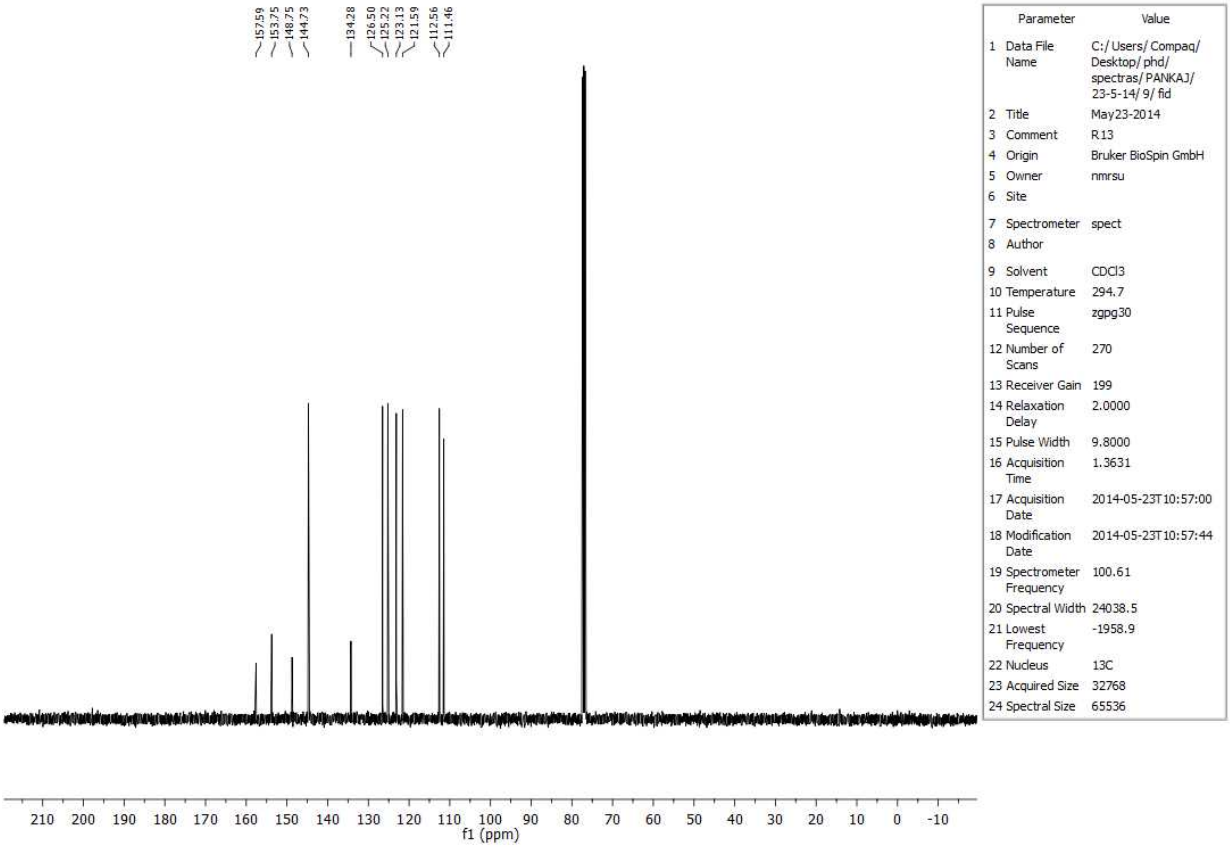


Fig. S10 ^{13}C NMR spectra 2-(furan-2-yl)benzo[d]thiazole

2-(3-methoxyphenyl)benzo[d]thiazole (Table 3, Entry 4, 5a)

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 3H, OCH_3), 7.06 (d, 1H, Ar), 7.29 (s, 1H, Ar), 7.41-7.70 (m, 4H, Ar), 8.09 (d, 1H, Ar), 8.12 (d, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 112.0, 117.4, 120.3, 121.6, 123.3, 125.3, 126.3, 130.1, 134.9, 135.1, 154.1, 160.1, 168.0.

MS (m/z): 242 (M^+).

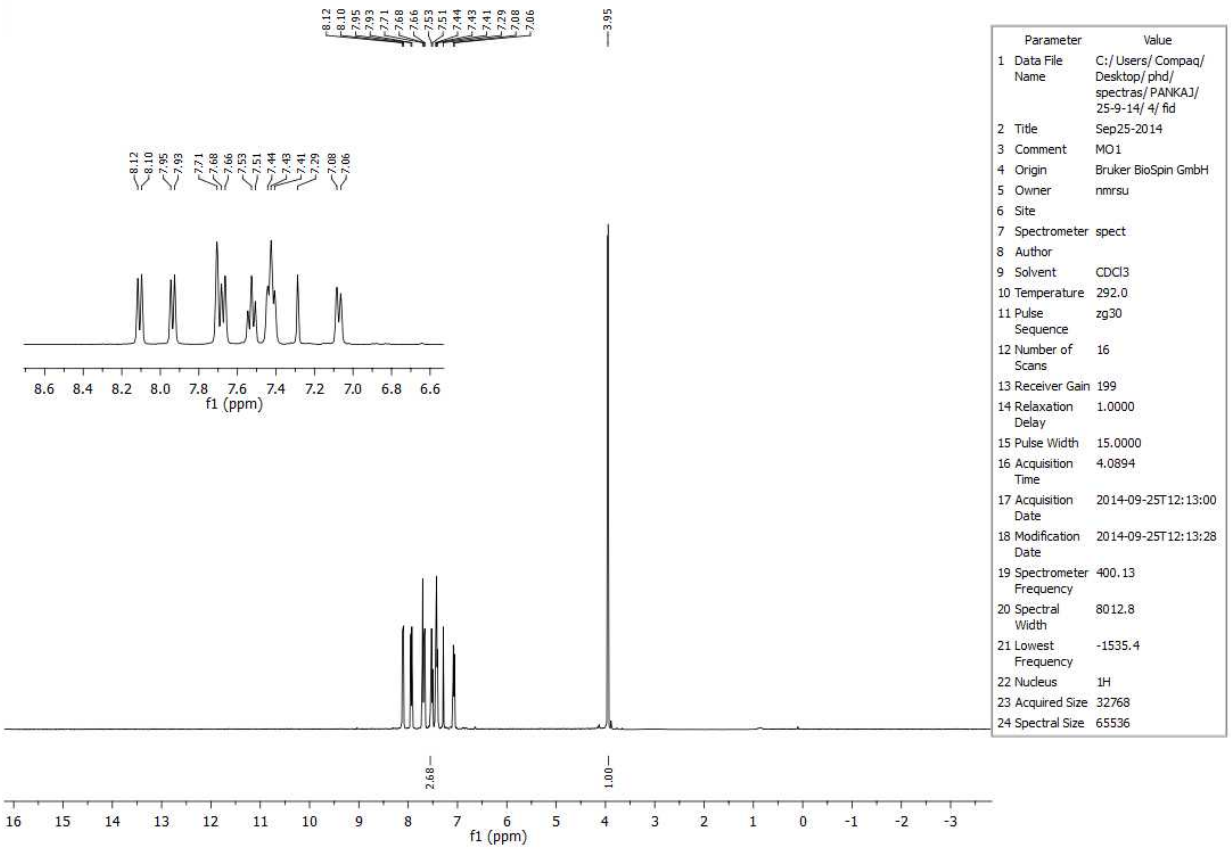
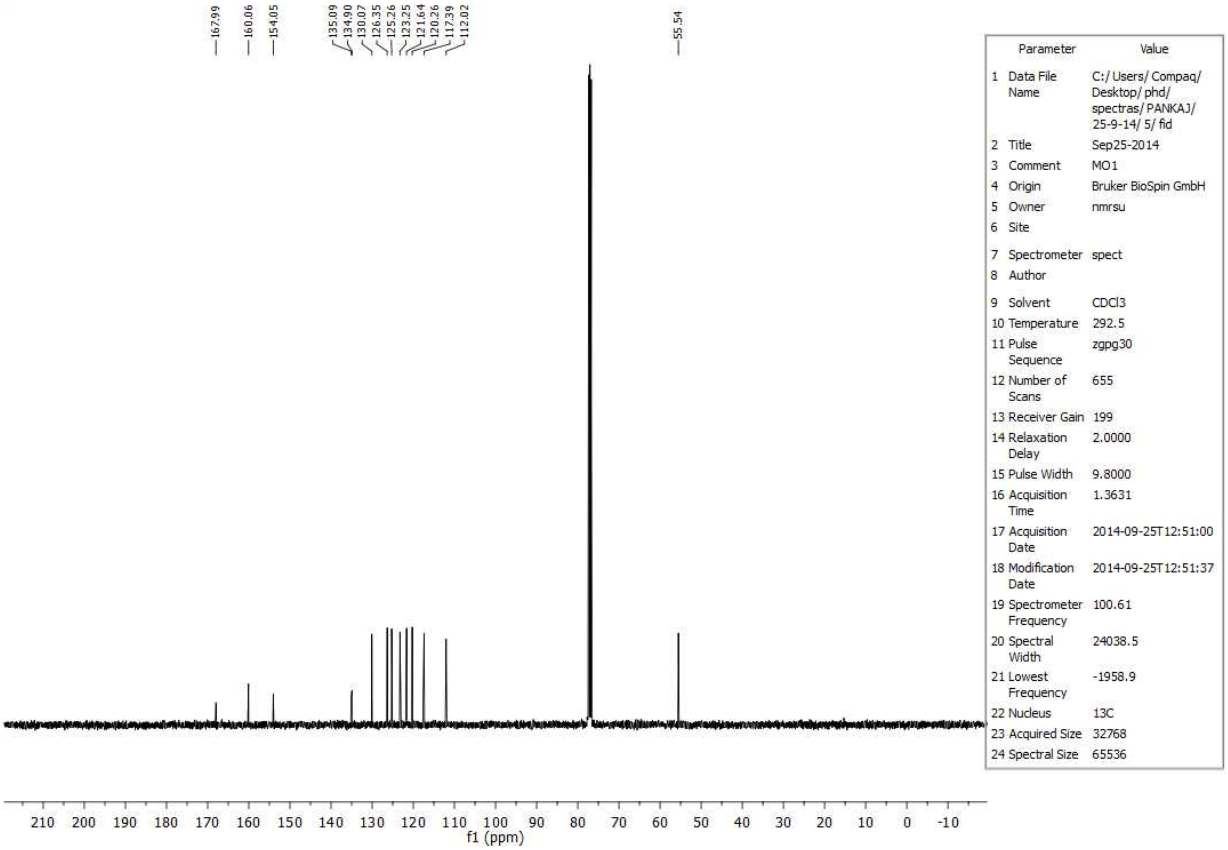


Fig. S11 ^{1}H NMR spectra of 2-(3-methoxyphenyl)benzo[d]thiazole



	Parameter	Value
1	Data File Name	C:/ Users/ Compaq/ Desktop/ phd/ spectras/ PANKAJ/ 25-9-14/ 5/ fid
2	Title	Sep25-2014
3	Comment	MO1
4	Origin	Bruker BioSpin GmbH
5	Owner	nmrsu
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.5
11	Pulse Sequence	zgpg30
12	Number of Scans	655
13	Receiver Gain	199
14	Relaxation Delay	2.0000
15	Pulse Width	9.8000
16	Acquisition Time	1.3631
17	Acquisition Date	2014-09-25T12:51:00
18	Modification Date	2014-09-25T12:51:37
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.9
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

Fig. S12 ^{13}C NMR spectra of 2-(3-methoxyphenyl)benzo[d]thiazole

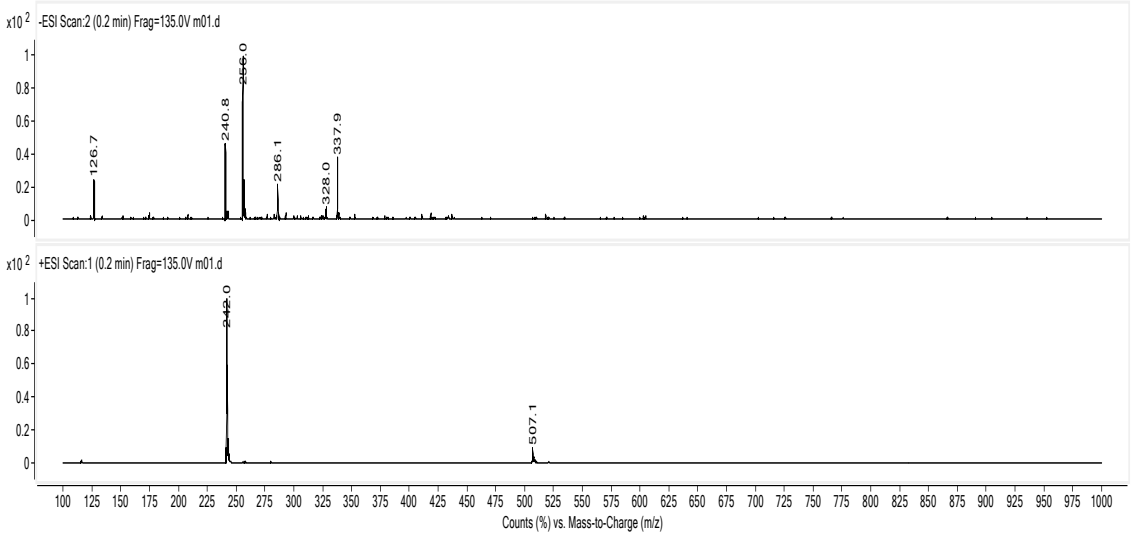


Fig. S13 Mass spectra of 2-(3-methoxyphenyl)benzo[d]thiazole

Crystallography data collection and refinement

X-ray data of complexes were collected on an X'calibur- Oxford Diffraction single crystal diffractometer (Department of Physics and Electronics, University of Jammu, Jammu) with CCD area-detector (graphite-monochromator, Mo-Kα radiations, λ = 0.71073 Å). Data were corrected for Lorentz, polarization and absorption factors. The structures were solved by direct methods using SHELXS97 [1]. All non-H atoms of the molecule were located in the best E-map. Full-matrix least-squares refinement was carried out using SHELXL97 [1]. The geometry of the molecule was calculated using WinGX [2], PARST [3] and PLATON [4]. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). Molecular drawings were obtained using DIAMOND version 2.1 [5]. Crystallographic data, details of the data collection, structure solution and refinements are listed in Table 1.

1. Sheldrick GM (2008) Acta Crystallogr A64:112

2. Farrugia LJ (1999) J Appl Crystallogr 32:837

3. Nardelli M (1995) J Appl Crystallogr 28:659

4. Spek AL (2009) Acta Crystallogr D65:148

5. Brandenburg K (1998) DIAMOND, Version 2.1. Crystal Impact GbR, Bonn, Germany

Table S1 Experimental details

Crystal data	
Chemical formula	$C_{22.40}H_{17.60}N_{1.60}O_{1.60}S_{1.60}$
M_r	386.08
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	14.4054 (13), 6.3686 (5), 25.906 (3)
β (°)	101.775 (10)
V (Å^3)	2326.6 (4)
Z	5
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.26
Crystal size (mm)	0.2 × 0.2 × 0.1
Data collection	
Diffractometer	Xcalibur, Sapphire3 diffractometer
Absorption correction	Multi-scan

	Crys Alis RED
T_{min}, T_{max}	0.919, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8058, 4031, 2090
R_{int}	0.087
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.194, 0.485, 1.06
No. of reflections	4031
No. of parameters	308
No. of restraints	0
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.1505P)^2 + 56.5819P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.66, −0.61

Table S2 Selected geometric parameters (Å º)

S3—C4	1.687 (15)	S22—C21	1.705 (13)
S3—C2	1.802 (14)	S22—C23	1.814 (16)
O16—C14	1.387 (17)	O35—C33	1.388 (17)
O16—C17	1.449 (19)	O35—C36	1.431 (16)
N1—C2	1.265 (17)	N20—C21	1.335 (17)
N1—C5	1.419 (17)	N20—C24	1.350 (17)
C2—C10	1.478 (18)	C21—C29	1.476 (17)
C4—C5	1.41 (2)	C23—C25	1.43 (2)
C4—C9	1.45 (2)	C23—C24	1.43 (2)
C5—C6	1.328 (19)	C24—C28	1.41 (2)
C6—C7	1.38 (2)	C25—C26	1.39 (2)
C6—H6	0.9300	C25—H25	0.9300
C7—C8	1.41 (3)	C26—C27	1.42 (2)
C7—H7	0.9300	C26—H26	0.9300

C8—C9	1.33 (2)	C27—C28	1.30 (2)
C8—H8	0.9300	C27—H27	0.9300
C9—H9	0.9300	C28—H28	0.9300
C10—C11	1.307 (19)	C29—C34	1.375 (18)
C10—C15	1.417 (18)	C29—C30	1.476 (19)
C11—C12	1.40 (2)	C30—C31	1.358 (19)
C11—H11	0.9300	C30—H30	0.9300
C12—C13	1.46 (2)	C31—C32	1.42 (2)
C12—H12	0.9300	C31—H31	0.9300
C13—C14	1.301 (18)	C32—C33	1.44 (2)
C13—H13	0.9300	C32—H32	0.9300
C14—C15	1.374 (18)	C33—C34	1.345 (18)
C15—H15	0.9300	C34—H34	0.9300
C17—H17A	0.9600	C36—H36A	0.9600
C17—H17B	0.9600	C36—H36B	0.9600
C17—H17C	0.9600	C36—H36C	0.9600
C4—S3—C2	92.2 (7)	C21—S22—C23	85.3 (7)
C14—O16—C17	123.7 (11)	C33—O35—C36	114.4 (11)
C2—N1—C5	108.7 (12)	C21—N20—C24	112.6 (12)
N1—C2—C10	121.0 (13)	N20—C21—C29	124.3 (12)
N1—C2—S3	114.1 (11)	N20—C21—S22	119.1 (10)
C10—C2—S3	124.8 (10)	C29—C21—S22	116.5 (10)
C5—C4—C9	127.1 (14)	C25—C23—C24	119.5 (14)
C5—C4—S3	105.7 (10)	C25—C23—S22	128.8 (12)
C9—C4—S3	127.3 (12)	C24—C23—S22	111.7 (10)
C6—C5—C4	114.6 (13)	N20—C24—C28	128.5 (15)
C6—C5—N1	126.1 (14)	N20—C24—C23	111.2 (13)
C4—C5—N1	119.2 (12)	C28—C24—C23	120.3 (14)
C5—C6—C7	120.2 (16)	C26—C25—C23	113.7 (14)
C5—C6—H6	119.9	C26—C25—H25	123.2

C7—C6—H6	119.9	C23—C25—H25	123.2
C6—C7—C8	124.7 (16)	C25—C26—C27	127.1 (16)
C6—C7—H7	117.7	C25—C26—H26	116.4
C8—C7—H7	117.7	C27—C26—H26	116.4
C9—C8—C7	119.1 (16)	C28—C27—C26	116.7 (17)
C9—C8—H8	120.4	C28—C27—H27	121.6
C7—C8—H8	120.4	C26—C27—H27	121.6
C8—C9—C4	114.2 (16)	C27—C28—C24	122.4 (17)
C8—C9—H9	122.9	C27—C28—H28	118.8
C4—C9—H9	122.9	C24—C28—H28	118.8
C11—C10—C15	118.6 (12)	C34—C29—C30	121.7 (12)
C11—C10—C2	119.0 (13)	C34—C29—C21	116.0 (12)
C15—C10—C2	122.3 (11)	C30—C29—C21	122.3 (12)
C10—C11—C12	116.3 (14)	C31—C30—C29	120.4 (14)
C10—C11—H11	121.9	C31—C30—H30	119.8
C12—C11—H11	121.9	C29—C30—H30	119.8
C11—C12—C13	127.0 (14)	C30—C31—C32	116.6 (14)
C11—C12—H12	116.5	C30—C31—H31	121.7
C13—C12—H12	116.5	C32—C31—H31	121.7
C14—C13—C12	111.9 (14)	C31—C32—C33	122.0 (12)
C14—C13—H13	124.1	C31—C32—H32	119.0
C12—C13—H13	124.1	C33—C32—H32	119.0
C13—C14—C15	123.4 (14)	C34—C33—O35	112.1 (12)
C13—C14—O16	117.5 (13)	C34—C33—C32	121.0 (13)
C15—C14—O16	119.1 (12)	O35—C33—C32	126.8 (12)
C14—C15—C10	122.8 (12)	C33—C34—C29	118.2 (13)
C14—C15—H15	118.6	C33—C34—H34	120.9
C10—C15—H15	118.6	C29—C34—H34	120.9
O16—C17—H17A	109.5	O35—C36—H36A	109.5
O16—C17—H17B	109.5	O35—C36—H36B	109.5

H17A—C17—H17B	109.5	H36A—C36—H36B	109.5
O16—C17—H17C	109.5	O35—C36—H36C	109.5
H17A—C17—H17C	109.5	H36A—C36—H36C	109.5
H17B—C17—H17C	109.5	H36B—C36—H36C	109.5

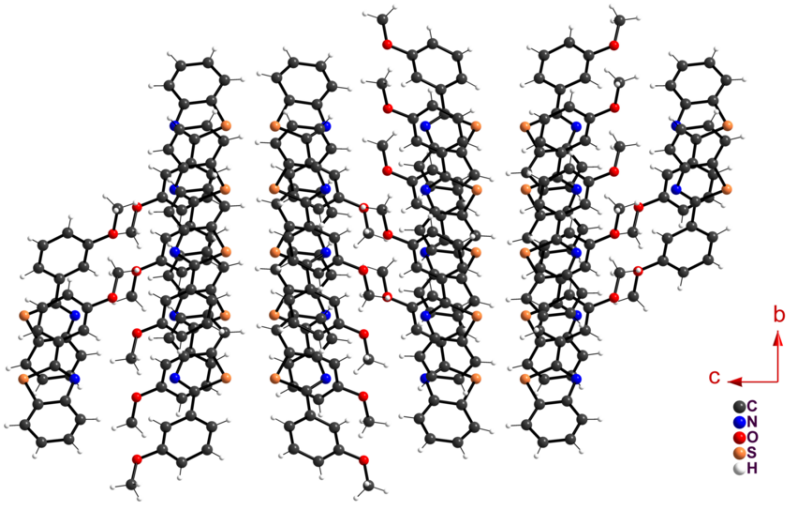


Fig. 14 Packing arrangement of 2-(3-methoxyphenyl)benzo[d]thiazole along *a* axis

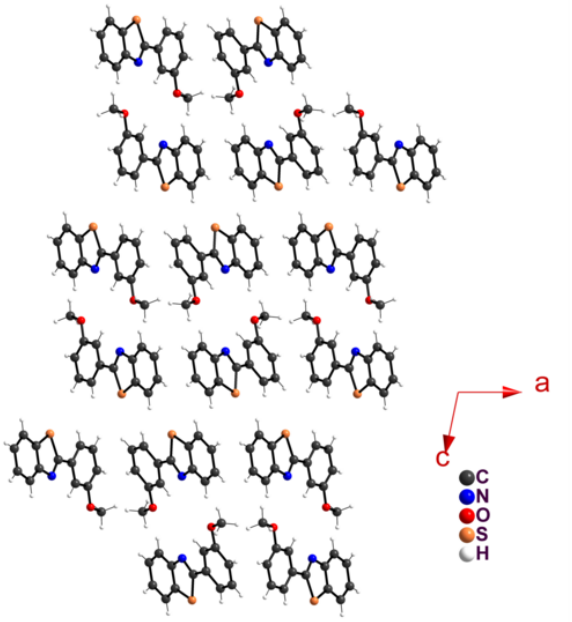


Fig. 15 Packing arrangement of 2-(3-methoxyphenyl)benzo[d]thiazole along *b* axis

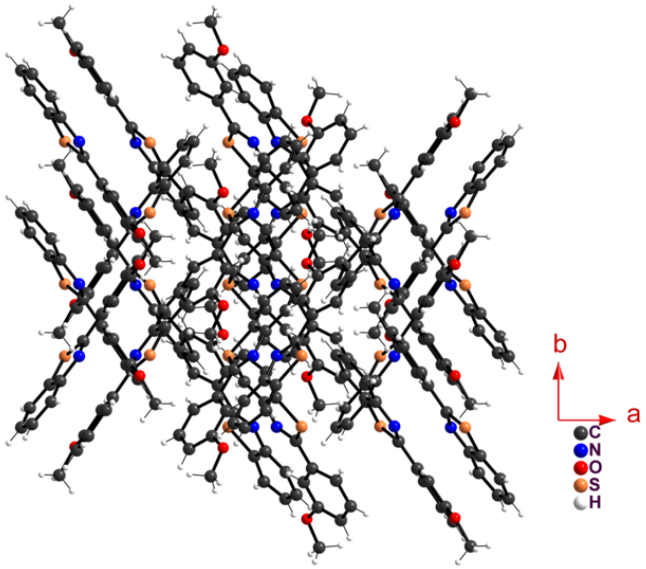


Fig. 16 Packing arrangement of 2-(3-methoxyphenyl)benzo[d]thiazole along *c* axis