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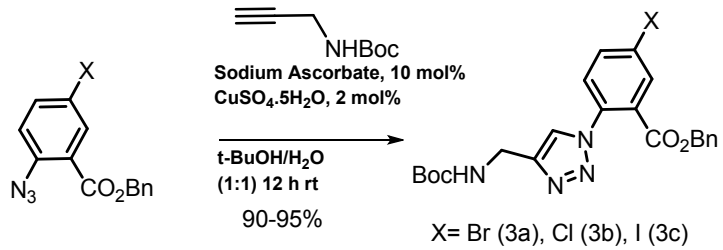
General experimental information:

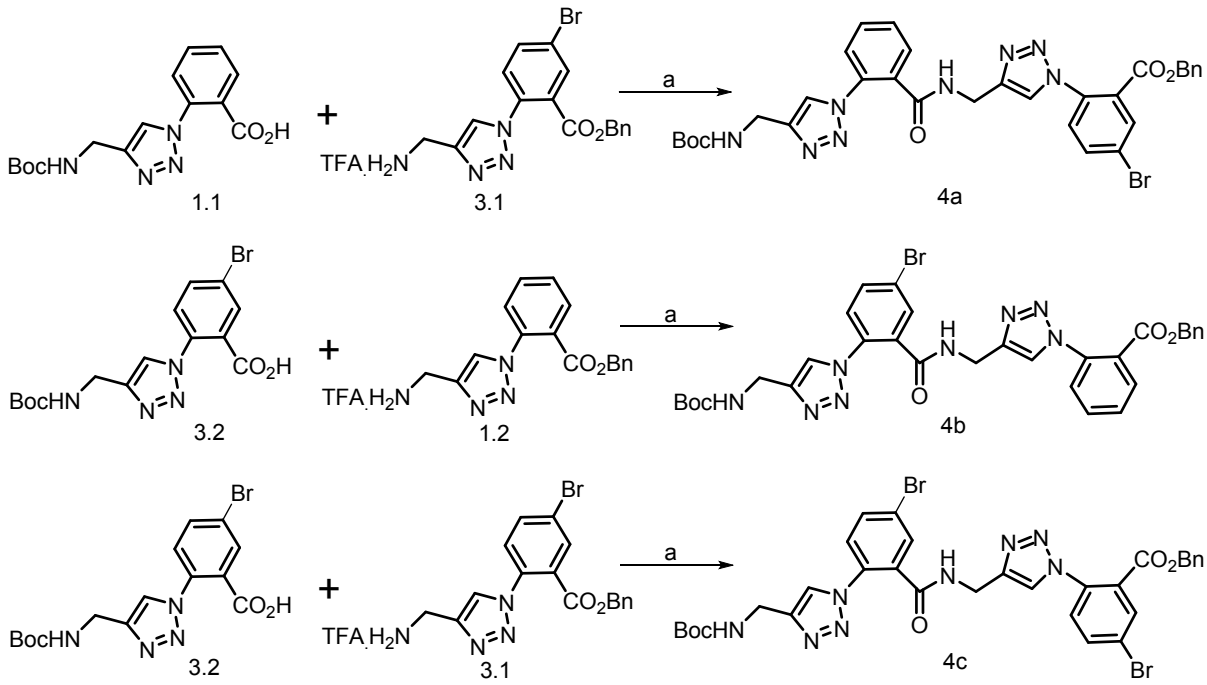
Experiments which required anhydrous conditions were carried out under nitrogen atmosphere in dry dichloromethane (DCM). Thin-layer chromatography (TLC) was performed on 0.25 mm silica gel plates (60 F254 grade) from Merck, and were analyzed using 254 nm UV light. Chromatographic separation was carried out on 100-200 mesh silica gel in gravity mode. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz and 500 MHz instruments, and the chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) with coupling constant (*J*) values in Hertz (Hz). The splitting patterns in ^{1}H NMR spectra are reported as follows: s = singlet; d = doublet; t = triplet; dd = doublet of doublet; m = multiplet, bs = broad singlet. ^{13}C NMR data are reported with the solvent peak ($CDCl_3$, δ = 77.0 ppm) as the internal standard. High resolution mass spectra (HRMS) were recorded on a Waters Q-Tof micro™ spectrometer with lock spray source**.** Infrared spectra were recorded using a Nicolet 6700 FT-IR spectrophotometer. Powder X-Ray diffraction data was obtained on BRUKER D8-Advance diffractometer using CuKα radiation (λ=1.5418 Å) over the range of $0.5° < 2\theta < 30°$ at room temperature. Samples for SEM imaging were coated with Au-Pd (Gatan precision etching coating system (model No. 682) operating at 5 KeV) and analyzed by FEI Quanta FEG 200 High Resolution Scanning Electron Microscope operating at 10-30 kV. Rheological measurements were performed with a stress-controlled rheometer (MCR 301) equipped with steel-coated parallel-plate geometry (25 mm diameter). The gap distance was fixed at 1 mm and a solvent-trapping device was placed above the plate to prevent solvent evaporation. All measurements were done at 25°C. The intensity data collection during X-ray crystallographic analysis was carried out on a Bruker AXS (kappa apex II) diffractometer equipped with graphite monochromated M_o (K_α) radiation. The data were collected for θ up to 25_o for M_o (K_α) radiation. ω and ϕ scans were employed to collect the data. The frame width for ω was set to 0.5 deg for data collection. The frames were integrated and data were reduced for Lorentz and polarization correction using SAINT- Plus. The multi-scan absorption correction was applied to the data. All structures were solved using SIR-92 and refined using SHELXL-97. The molecular and packing diagrams were drawn using Mercury 3.1. The non-hydrogen atoms were refined with anisotropic displacement parameter. All hydrogen atoms could be located in the difference Fourier map. However, the hydrogen atoms bonded to carbons were fixed at chemically meaningful positions and were allowed to ride with parent atom during the refinement. The synthetic strategy adopted to access

various compounds reported here is presented in Schemes 1 and 2. Detailed experimental procedures are given subsequently.

Synthesis of aryl-triazole peptides



Scheme 1. Synthesis of Building-block **3a-c.**



Scheme 2. Syntheses of compounds **4a-c**; a) EDCI (1equiv.), HOBt (1 equiv.), DIPEA (3 equiv.), 24 h, 0°C to rt, 70-80%.

General reaction procedures:

Synthesis of aryl triazolyl amino acids 3a-c and dipeptides 4a-c:

Aryl-triazolyl amino acid **1** and other intermediates needed for the synthesis of 4a-c were prepared according to the literature protocol published by us.[1]

General procedure for 3a-c:

Azido benzyl ester (1 eq.) was taken in a round bottom flask and Boc-protected propargyl amine (1 eq.) and ^{t}BuOH (20 mL for 1g) were added to it. This mixture was stirred until homogeneous and then admixed with sodium ascorbate in water (10 mL), followed by a solution of copper sulphate pentahydrate in water so as to maintain the overall ratio of tert-butanol to water 1:1. After completion of the reaction (TLC), precipitation/gelation was observed. The reaction mixture was subjected to rotary evaporation to reduce the volume by half and then extracted with Ethyl acetate (3 x 25 mL), dried (Na_2SO_4), filtered and dried under vacuum to get a solid which was purified by column chromatography to get the product in ~90 to 95 % yield.

Benzyl 2-(4-(((tert-butoxycarbonyl) amino) methyl)-1H-1,2,3-triazol-1-yl)-5-bromobenzoate (3a):

5-bromo-2-azido-benzylester (3.0 mmol, 1g) was reacted with Boc-protected propargyl amine (3.0 mmol, 0.5 g) according to the general procedure described above using 1.5 mmol (0.3 g) of sodium ascorbate and 0.15 mmol (0.04 g) of copper sulphate pentahydrate. Purification of crude product was done by column chromatography using 50% Ethyl acetate-hexane solvent system in a gradient mode and the product was obtained as off-white solid (1.38 g, 94 %). Analytical data: R_f: 0.57 (30 % Ethyl acetate-Hexane); m.p. 102-104 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.13 (d, 1H, *J* = 1.5 Hz), 7.8 (dd, 1H, *J* = 2.2 Hz, *J* = 8.5 Hz) 7.67 (s, 1H), 7.39-7.33 (m, 3H), 7.32 (d, 1H, *J* = 8.5 Hz), 7.24-7.18 (m, 2H), 5.12 (s, 2H), 5.0 (s, 1H) 4.34 (d, 2H, *J* = 5.9 Hz), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 163.7, 155.8, 145.4, 135.7, 135, 134.5, 134.2, 128.9, 128.7 (2C), 128.66, 128.56 (2C), 128.1, 123.8, 123.6, 79.7, 67.9, 36, 28.34 (3C) IR (neat): 3330, 3144, 2973, 1710, 1508, 1258 cm^{-1} ; HRMS (ESI) exact mass calcd. for $C_{22}H_{23}N_4O_4BrNa$ $[M+Na]^+$ 509.0800, found $[M+Na]^+$ 509.0810.

Benzyl 2-(4-(((tert-butoxycarbonyl) amino) methyl)-1H-1,2,3-triazol-1-yl)-5-chlorobenzoate (3b):

5-chloro-2-azido-benzylester (3.48 mmol, 1g) was reacted with Boc-protected propargyl amine (3.48 mmol, 0.54 g) according the general procedure described above using 1.74 mmol (0.34 g) of sodium ascorbate and 0.18 mmol (0.04 g) of copper sulphate pentahydrate. Purification of crude product was done by column chromatography using 50% Ethyl acetate-hexane solvent system in a gradient mode and the product was obtained as off-white solid (1.35 g, 88 %). Analytical data: R_f: 0.52 (30 % Ethyl acetate- Hexane); m.p. 96-98 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, 1H, *J* = 1.8 Hz), 7.67 (s, 1H), 7.62 (dd, 1H, *J* = 2.4 Hz, *J* = 8.3 Hz), 7.40 (d, 1H, *J* = 8.5 Hz), 7.37-7.32 (m, 3H), 7.24-7.19 (m, 2H), 5.13 (s, 2H), 4.98 (s, 1H) 4.34 (d, 2H, *J* = 5.95 Hz), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 163.8, 155.8, 145.4, 136.0, 134.51, 134.48, 132.7, 131.3, 128.75, 128.7 (2C), 128.6, 128.5 (2C), 127.98, 123.7, 79.7, 67.9, 35.9, 28.32 (3C); HRMS (ESI) exact mass calcd. for $C_{22}H_{24}N_4O_4Cl$ $[M+H]^+$ 443.1486, found $[M+H]^+$ 443.1479.

Benzyl 2-(4-(((tert-butoxycarbonyl) amino) methyl)-1H-1,2,3-triazol-1-yl)-5-iodobenzoate:

5-Iodo-2-azido-benzylester (2.64 mmol, 1g) was reacted with Boc-protected propargyl amine (3.69 mmol, 0.41 g) according the general procedure described above using 1.32 mmol (0.26 g) of sodium ascorbate and 0.13 mmol (0.03 g) of copper sulphate pentahydrate. Purification of crude product was done by column chromatography using 50% Ethyl acetate-hexane solvent system in a gradient mode and the product was obtained as pale yellow solid (1.2 g, 85 %). Analytical data: R_f: 0.48 (30 % Ethyl acetate- Hexane); m.p. 120-124 ^oC; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.32 (d, 1H, *J* = 2.0 Hz), 7.97 (dd, 1H, *J* = 2.0 Hz, *J* = 8.3 Hz), 7.66 (s, 1H), 7.39-7.30 (m, 3H), 7.24-7.19 (m, 2H), 7.17 (d, 1H, *J* = 8.3 Hz), 5.12 (s, 2H), 4.98 (brs, 1H) 4.33 (d, 2H, *J* = 5.85 Hz), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): 163.7, 155.8, 145.5, 141.7, 140.0, 135.7, 134.5, 128.9, 128.7 (2C), 128.65, 128.57 (2C), 128.0, 123.6, 94.94, 79.8, 68, 36, 28.35 (3C); HRMS (ESI) exact mass calcd. for $C_{22}H_{24}N_4O_4I$ $[M+H]^+$ 535.0842, found $[M+H]^+$ 535.0829.

Syntheses of compounds 4a-c:

Benzyl 5-bromo-2-(4-((2-(4-(((tert-butoxycarbonyl) amino)methyl)-1H-1,2,3-triazol-1-yl)benzamido)methyl)-1H-1,2,3-triazol-1-yl)benzoate (4a):

To a stirred mixture of the acid **1.1** (0.5 g, 1.57 mmol; Scheme 2), HOBt (0.25 g, 1.88 mmol) and EDCI (0.36 g, 1.88 mmol) in dry dichloromethane (10 mL) at 0^{o}C was added DIPEA (0.81 mL, 4.71 mmol). After stirring for 1 h, the amine trifluoroacetate salt **3.1** (0.83 g, 1.73 mmol) in 10 mL of dry dichloromethane was added, and stirring was continued for ~24 h at room temperature (TLC was checked for completion of reaction). All the volatiles were then removed under reduced pressure, the residue dissolved in ethyl acetate and washed successively with 5% HCl (3 x 10 mL) and saturated $NaHCO_3$ (3 x 10 mL). After drying with sodium sulphate, the organic layer was evaporated under reduced pressure to get a residue which was purified by column chromatography using 90 % ethyl acetate/hexane system to get the product as a glassy solid (0.85 g, 80 %). Analytical data: R_f:, 0.3 (80 % Ethyl acetate-Hexane); m.p. 124-126 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): 8.13 (d, 1H, *J* = 2.2 Hz), 7.80 (s, 1H), 7.79 (dd, 1H, *J* = 8Hz, *J* = 2.2 Hz), 7.77 (s, 1H), 7.65 (dd, *J* = 7.5 Hz, *J* = 2Hz), 7.6-7.5 (m, 2H), 7.63-7.53 (m, 3H), 7.46-7.40 (m, 1H), 7.29-7.24 (m, 3H), 7.20-7.12 (m, 2H) 6.58 (bs NH^2, 1H), 5.33 (bs, 1H, NH^1), 5.09 (s, 2H), 4.45 (d, 2H, *J* = 5.9 Hz), 4.37 (d, 2H, *J* = 5.9 Hz), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): 166.5, 163.8, 155.8, 146.0, 144, 135.7, 135, 134.58, 134.3, 134.16, 132.3, 131.1, 129.8, 129.0, 128.8, 128.6 (2C), 128.5, 128.46 (2C), 128.4, 125.6, 124.5, 123.8, 123.5, 79.7, 67.9, 36.0, 35.2, 28.3 (3C); IR(neat): 3290, 3144, 2973, 1710, 1660, 1504, 1265 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{32}H_{31}N_8O_5BrNa$ $[M+Na]^+$ 709.1498, found $[M+Na]^+$ 709.1509.

Benzyl 2-(4-((5-bromo-2-(4-(((tert-butoxycarbonyl) amino)methyl)-1H-1,2,3-triazol-1-yl)benzamido)methyl)-1H-1,2,3-triazol-1-yl)benzoate (4b):

To a stirred mixture of the acid **3.2** (0.5 g, 1.26 mmol), HOBt (0.20 g, 1.51 mmol) and EDCI (0.29 g, 1.51 mmol) in dry dichloromethane (10 mL) at 0^{o}C was added DIPEA (0.65 mL, 3.78 mmol). After stirring for 1 h, the amine trifluoroacetate salt **1.2** (0.56 g, 1.38 mmol) in 10 mL of dry dichloromethane was added, and stirring continued for ~24 h at room temperature (TLC was checked for completion of reaction). All the volatiles were then removed under reduced pressure, the residue dissolved in ethyl acetate and washed successively with 5% HCl (3 x 10 mL) and saturated $NaHCO_3$ (3 x 10 mL). After drying with sodium sulphate, the organic layer was evaporated under reduced pressure to get a residue

which was purified by column chromatography using 90 % ethyl acetate/hexane system to get the product as a white fluffy solid (0.6 g, 70 %). Analytical data: R_f:, 0.5 (80 % Ethyl acetate- Hexane); m.p. 68-72 ^oC; ^1H NMR ($CDCl_3$, 500 MHz): 8.06 (dd, 1H, *J* = 7.8 Hz, *J* =1.4 Hz), 7.79 (d, 1H, *J* = 2.0 Hz), 7.77 (s, 1H), 7.76 (s, 1H), 7.72-7.66 (m, 2H), 7.63- 7.55 (m, 2H), 7.34 (d, 1H, *J* = 8.5 Hz), 7.29-7.25 (m, 3H), 7.20-7.15 (m, 2H) 6.53 (bs NH^2, 1H), 5.34 (bs, 1H, NH^1), 5.11 (s, 2H), 4.46 (d, 2H, *J* = 5.8 Hz), 4.37 (d, 2H, *J* = 5.9 Hz), 1.41 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): 165 (2C), 155.8, 146.3, 143.3, 136.13, 134.9, 134.1, 133.68, 133.2, 132.9, 132.1, 131.5, 130.0, 128.5 (2C), 128.44 (2C), 128.4, 127.3, 127.14, 127.0, 124.62, 123.7, 123.6, 79.7, 67.5, 36.0, 35.3, 28.3 (3C); IR(neat): 3300, 3148, 2973, 1718, 1655, 1508, 1269 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{32}H_{32}N_8O_5Br$ $[M+H]^+$ 687.1679, found $[M+H]^+$ 687.1696.

Benzyl 5-bromo-2-(4-((5-bromo-2-(4-(((tert-butoxycarbonyl) amino)methyl)-1H-1,2,3-triazol-1-yl)benzamido)methyl)-1H-1,2,3-triazol-1-yl)benzoate (4c):

To a stirred mixture of the acid **3.2** (0.5 g, 1.26 mmol), HOBt (0.20 g, 1.51 mmol) and EDCI (0.29 g, 1.51 mmol) in dry dichloromethane (10 mL) at 0^{o}C was added DIPEA (0.65, 3.78 mmol). After stirring for 1 h, the amine trifluoroacetate salt **3.1** (0.67 g, 1.38 mmol) in 10 mL of dry dichloromethane was added, and stirring continued for ~24 h at room temperature (TLC was checked for completion of reaction). All the volatiles were then removed under reduced pressure, the residue dissolved in ethyl acetate and washed successively with 5% HCl (3 x 10 mL) and saturated $NaHCO_3$ (3 x 10 mL). After drying with sodium sulphate, the organic layer was evaporated under reduced pressure to get a residue which was purified by column chromatography using 80 % ethyl acetate/hexane system to get the product as a white solid (0.7 g, 72 %). Analytical data: R_f: 0.6 (80 % Ethyl acetate- Hexane); m.p. 118-120 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): 8.14 (s, 1H), 7.84-7.72 (m, 2H), 7.78 (s, 1H), 7.76 (s, 1H), 7.66 (d, 1H, 8.0 Hz), 7.51 (d, 1H, 8.4 Hz), 7.34-7.26 (m, 4H), 7.20-7.13 (m, 2H) 6.8 (bs NH^2, 1H), 5.35 (bs, 1H, NH^1), 5.09 (s, 2H), 4.44 (d, 2H, 5.6 Hz), 4.35 (d, 2H, 5.7 Hz), 1.41 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): 165, 163.7, 155.8, 146.2, 143.7, 135.8, 134.9, 134.6, 134.2, 134.1, 133.6, 133.16, 132.08, 128.69, 128.55 (2C), 128.52, 128.48 (2C), 128.46, 126.91, 124.62, 123.85, 123.61, 123.46, 79.7, 67.9, 36.0, 35.2, 28.3 (3C); IR(neat): 3291, 3140, 2974, 1717, 1654, 1508, 1261 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{32}H_{31}N_8O_5Br2$ $[M+H]^+$ 765.0784, found $[M+H]^+$ 765.0784.

Gelation studies

Gelation study was carried out according to our previous report.[1] In a typical experiment 25 mg of the gelator was added to a 5 mL glass vial and 500 µL of solvent was added to it. The mixture was gently heated to yield a transparent solution, further cooling to room temperature yield immobilised gel, which was stable on vial inversion.

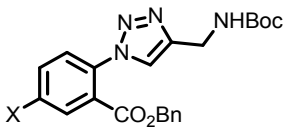
Table 1A. Gelation test for compound **1** and **3a** (maximum concentration tested was 5 wt%) in different organic solvents; G: gel, S: solution, P: precipitate, I: insoluble.

Solvents	1	3a
Methanol	S	G
Ethanol	S	G
Isopropanol	S	G
n-heptanol	S	G
n-dodecanol	S	G
t-butanol	S	G
Benzene	S	S
Toluene	S	G
Mesitylene	S	G
Bromobenzene	S	S
Chlorobenzene	S	S
Iodobenzene	S	S
Nitrobenzene	S	S
Dichloro benzene	S	S

Solvents	1	3a
Acetone	S	S
Isobutyl methyl ketone	S	S
cyclohexanone	S	S
Ethylacetate	S	S
n-butylacetate	S	S
1,2 DME	S	S
THF	S	S
Chloroform	S	S
Dichloromethane	S	S
Carbontetrachloride	P	G
n- Heptane	I	G
n- Dodecane	I	G
Pump oil	I	G
Diesel oil	I	G

Solvents	1	3a
DMSO	S	S
DMF	S	S
EtOH-water(1:1)	P	G
IPA- water (1:1)	P	G
Ethylacetate-hexane(1:1)	S	G
Chloroform-hexane (1:1)	S	G
Petrol oil	I	G
Type 3 oil	I	G
Coconut oil	I	G
Groundnut oil	I	G
Gingelli oil	I	G
Mixture of oil	I	G

Table **1B**. CLogP values calculated from the tools available in molinspiration.com.



Compound	X	CLogP
1	H	3.55
3a	Br	4.34
3b	Cl	4.20
3c	I	4.61

Compounds	CLogP
2a	3.73
4a	4.52
4b	4.52
4c	5.30

Table 2. Kamlet-Taft parameters π* (dipolarity), β (H-bond acceptor), α (H- bond donor) for different solvents. Colour code: Black ($\pi^* \neq 0, \beta = 0, \alpha = 0$); Green ($\pi^* \neq 0, \beta \neq 0, \alpha = 0$); Blue ($\pi^* \neq 0, \beta = 0, \alpha \neq 0$); Red ($\pi^* \neq 0, \beta \neq 0, \alpha \neq 0$).[a]

S no.	Solvent	π*	β (HBA)	α (HBD)	**3a**	**4a**
1	Acetone	0.71	0.48	0.08	S	S
2	Acetonitrile	0.75	0.31	0.19	S	S
3	Benzene	0.59	0.1	0	S	G
4	Bromo benzene	0.79	0.06	0	S	G
5	2-butanone	0.67	0.48	0.06	S	S
6	CCl_4	0.28	0	0	G	G
7	Chlorobenzene	0.71	0.07	0	S	G
8	Chloroform	0.58	0	0.44	S	S
9	Dichloroethane	0.81	0	0	S	S
10	Dibromoethane	0.75	0	0	S	S
11	DMF	0.88	0.69	0	S	S
12	DMSO	1	0.76	0	S	S
13	DCM	0.82	0	0.3	S	S
14	1,4 Dioxane	0.55	0.37	0	S	S
15	dimethoxyethane	0.53	0.41	0	S	S
16	Ethylacetate	0.55	0.45	0	S	S
17	Ethanol	0.54	0.77	0.83	G	G
18	Ethylene glycol	0.92	0.52	0.9	G	G
19	Isopropanol	0.48	0.95	0.76	G	G
20	Methanol	0.6	0.62	0.93	G	G
21	Nitrobenzene	1.01	0.39	0	S	S
22	THF	0.58	0.55	0	S	S
23	t-butanol	0.41	1.01	0.68	G	G
24	Toulene	0.54	0.11	0	G	G
25	Water	1.09	0.18	1.17	I	I
26	Dodecane	0.05	0	0	G	G

[a] Gel forming ability of **3a and 4a** was correlated with solvatochromic parameters of solvents to understand the relative influences of hydrogen bond donation ability (α), hydrogen bond acceptor ability (β) and dipolarity (π^*). To know whether any pattern would emerge, the solvents under study were grouped into four categories and represented in different colours: i) Black ($\pi^* \neq 0, \beta = 0, \alpha = 0$); ii) Green ($\pi^* \neq 0, \beta \neq 0, \alpha = 0$); iii) Blue ($\pi^* \neq 0, \beta = 0, \alpha \neq 0$); iv) Red ($\pi^* \neq 0, \beta \neq 0, \alpha \neq 0$).

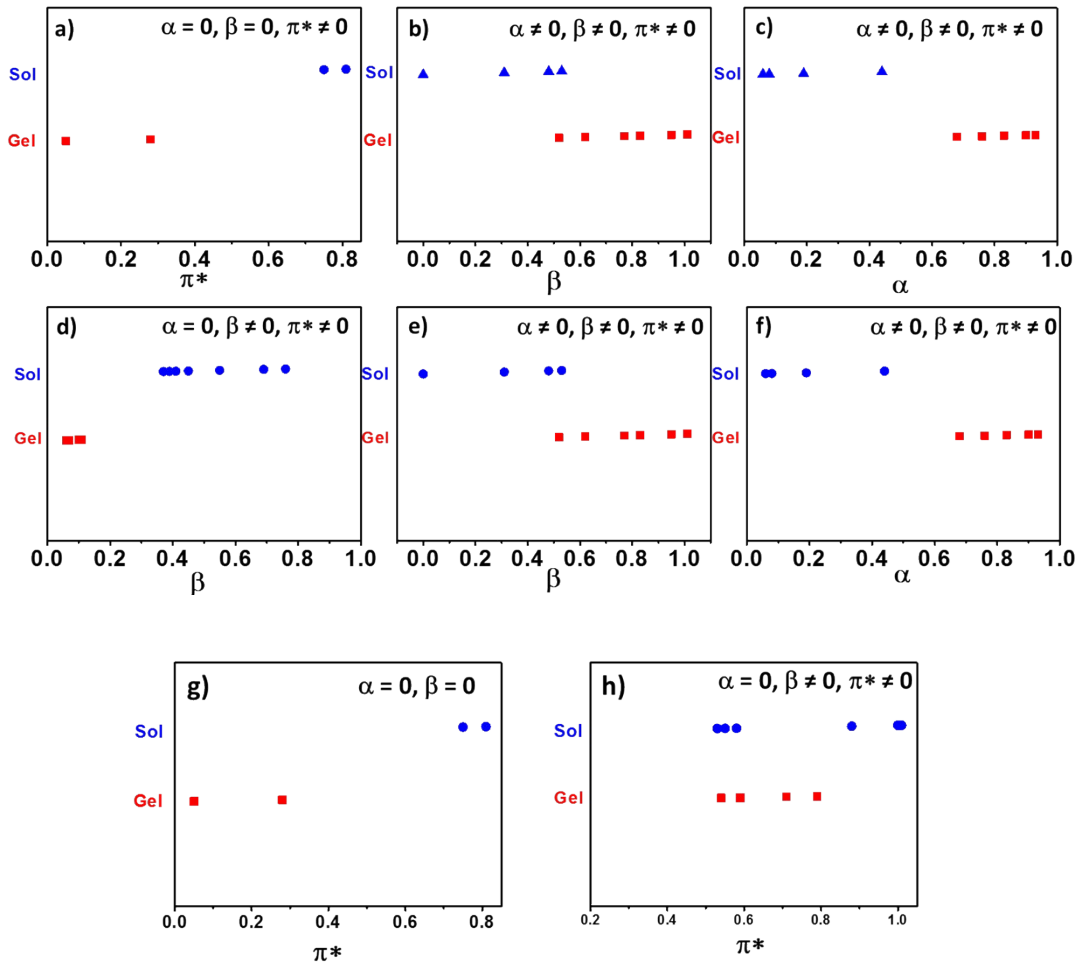


Figure 1. Dependence of gelation of **3a** (a-c) and **4a** (d-f) to solvatochromic parameters; comparison of (b) vs. (e) and (c) vs. (f) show that they have similar solvent preference g) Gelation profile of **4a** in different solvents having $\alpha = 0$, $\beta = 0$ but vary in π^*; h) gelation preferences of **4a** in solvents having positive π^* and β but with $\alpha = 0$.

Table 3. Comparison of gelation profile of **1**, **2a**, **2b**, **3a-c**, **4a-c**; cgc values are also shown in appropriate cases

Solvents	Gelators (cgc wt%)								
	1	**2a***	**2b***	**3a**	**3b**	**3c**	**4a**	**4b**	**4c**
Methanol	S	S	S	G (5.0)	S	P	G(3)	S	P
Ethanol	S	S	S	G(3.5)	S	G(2.5)	G(2)	S	P
Isopropanol	S	G(2.5)	S	G(3.0)	G(3.3)	G(2.0)	G(1.5)	S	S
DMSO	S	S	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S	S	S
Mesitylene	S	G(0.1)	G(0.5)	G(5.0)	G(4.2)	G(4.5)	G(0.5)	S	G(2.0)
Toluene	S	G(0.6)	G(1.0)	G(4.0)	S	G	G(1.0)	S	G(2.5)
PhCl	S	G(2.0)	S	S	S	S	G(1.5)	S	S
PhBr	S	G(2.0)	S	S	S	S	G(2.0)	S	S
Acetone	S	S	S	S	S	S	S	S	S
$CHCl_3$	S	S	S	S	S	S	S	S	S
CCl_4	P	G(0.08)	G(1.5)	G(3.5)	G(4.0)	P	G(0.8)	G (2.5)	I
Dodecane	I	P	G(1.0)	G(0.06)	G(0.08)	G(0.067)	G(0.25)	P	I
Diesel oil	I	I	G(0.3)	G(0.1)	G(0.15)	G(0.1)	G(0.3)	P	P
Mineral oil (Type 3)	P	I	G(1.0)	G(0.3)	G(0.5)	G(0.5)	G(0.4)	P	I
Ethanol/ Water(1:1)	P	P	S	G(0.5)	P	G(1.0)	G(2.0)	P	P
IPA/Water (1:1)	P	P	S	G(0.3)	G(0.5)	G(0.5)	G(2.0)	P	P

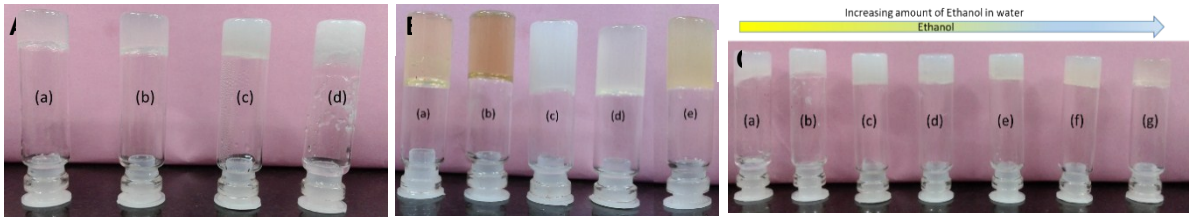


Figure 2. A) Gels of **3a** in a) ^{t}BuOH-H_2O/1:1, b) IPA-H_2O/1:1, c) EtOH-H_2O/1:1, d) MeOH-H_2O/1:1 *(weak gel)* at 1 wt% concentration. **B**) Gels of **3a** in a) Commercial Almond oil (Type 3 oil)/ 0.5wt% , b) Crude Pump oil/ 1wt%, c) Dodecane/ 0.5wt%, d) Diesel/ 0.5 wt% e) Mixture of oil (almond oil: diesel: dodecane: pump oil/ 1:1:1:1)/ 1wt%. **C**) Gels of **3a** in a) EtOH:H_2O/3:7 (0.5wt%, *weak gel*), b) EtOH:H_2O/4:6 (0.5wt%), c) EtOH:H_2O/5:5 (0.5wt%), d) EtOH:H_2O/6:4 (0.5wt%), e) EtOH:H_2O/7:3 (3wt%), f) EtOH:H_2O/8:2 (4wt%), g) EtOH:H_2O/9:1 (5wt%).

Procedure of making gel blocks with specific shapes:

For making gel block shown in Figure 5g of the manuscript, 1.5g of **3a** was dissolved in 50 mL of type-3 oil in a 100 mL beaker with gentle heating and then it was allowed to reach room temperature (25^{o}C) to get the corresponding gel (3 wt%). Being very stable, it was possible to take out the gel without deformation and it retained the shape of the container. It was also possible to cut it into any desired shape with the help of a blade.

To dope the oil gel with rhodamine B, a small amount of this dye in IPA was added to the oil and gelation was performed with **3a** as discussed earlier.

For making gels from IPA-water mixture, 1g of **3a** was taken in 100 mL of IPA-Water (1:1) in a 500 mL beaker and dissolved by gentle heating. It was allowed to come to room temperature (25^{o}C) to get the gel shown in Figure 5 below.

Shape persistency, flexibility and Bulk properties of 3a gels:

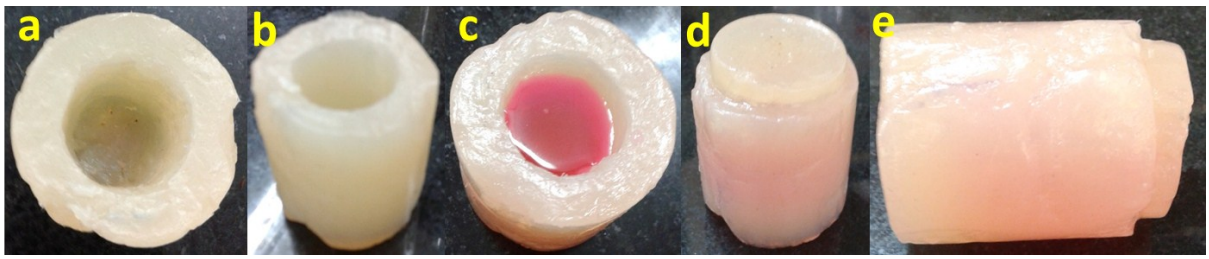


Figure 3. a & b) top- and side views of a hollow container prepared from 50 mL of 3 wt% oil gel of **3a**, c) 10 mL of rhodamine B aqueous solution was poured into it, d) container was closed with a disc and heat was applied from hot gun so that gel-sol transition followed by self-healing eventually seals it, e) after reaching to room temperature the entire block was stable and no leakage of rhodamine B was observed even after 2 months.

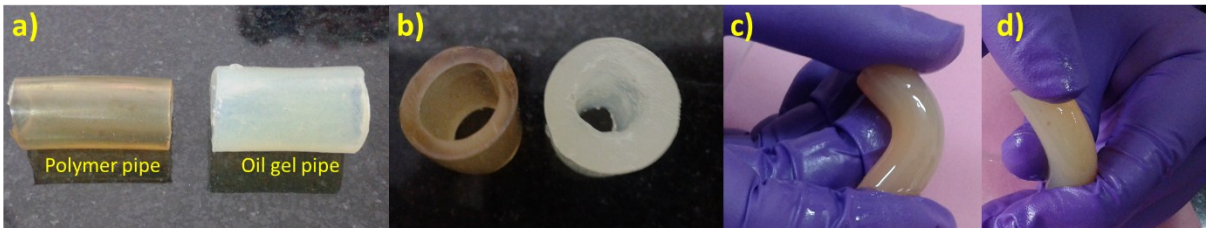


Figure 4. a) Comparison of a polymer pipe with a hollow-pipe prepared from oil gel of **3a;** b) top view of the same, c & d) flexible solid cylinders made from oil gel of **3a** showing high flexibility.

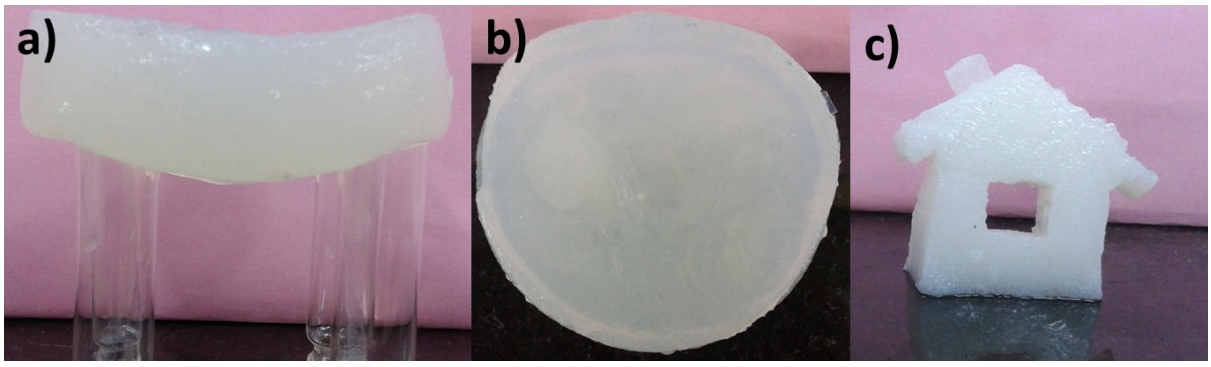


Figure 5. Scale-up and gel formation in bulk. a) side view of a solid cylinder of **3a** gel (1 wt%) from 100 ml of IPA/H_2O (1:1); b) top view of the same. c) Shape persistent property of 1 wt% IPA/H_2O (1:1) gel of **3a**.

[1]H NMR experiments:

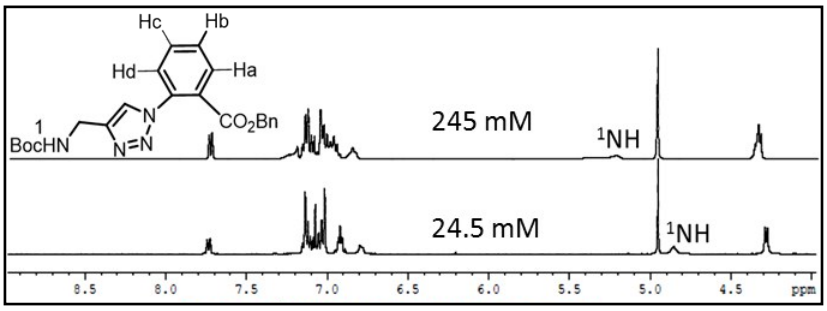


Figure 6. Selected region from [1]HNMR spectra of **1** in Toluene-d8 at different concentrations

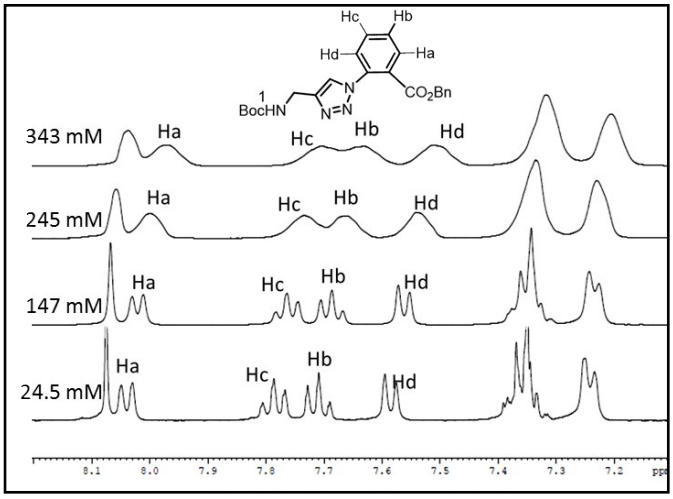


Figure 7. Selected region from [1]HNMR spectra of **1** in Methanol-d4 at different concentrations

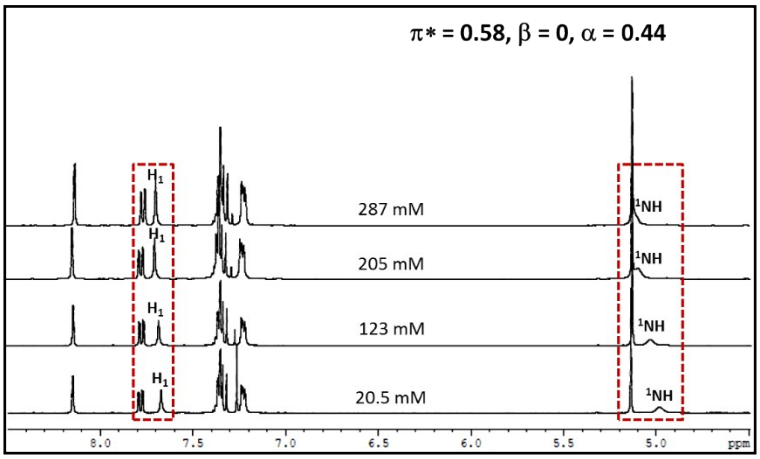


Figure 8. Selected region from [1]HNMR spectra of **3a** in $CDCl_3$ at different concentrations

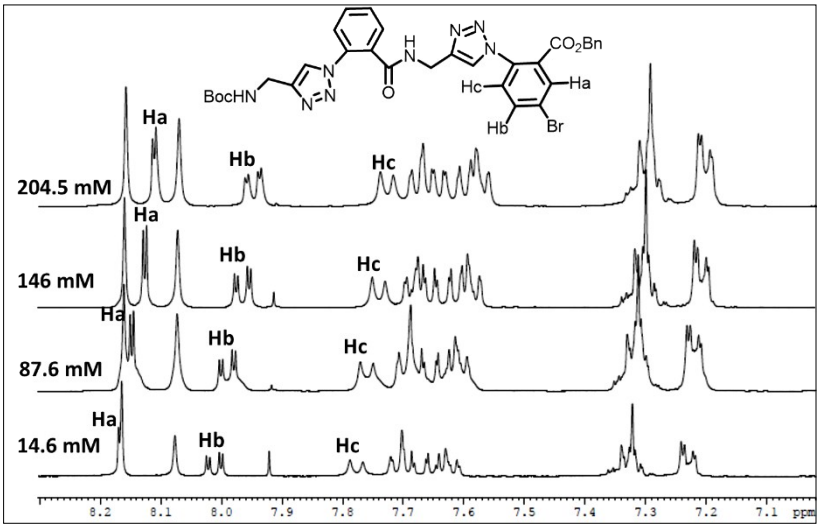


Figure 9. Selected regions from ^{1}HNMR spectra of **4a** in Methanol-d4 at different concentrations

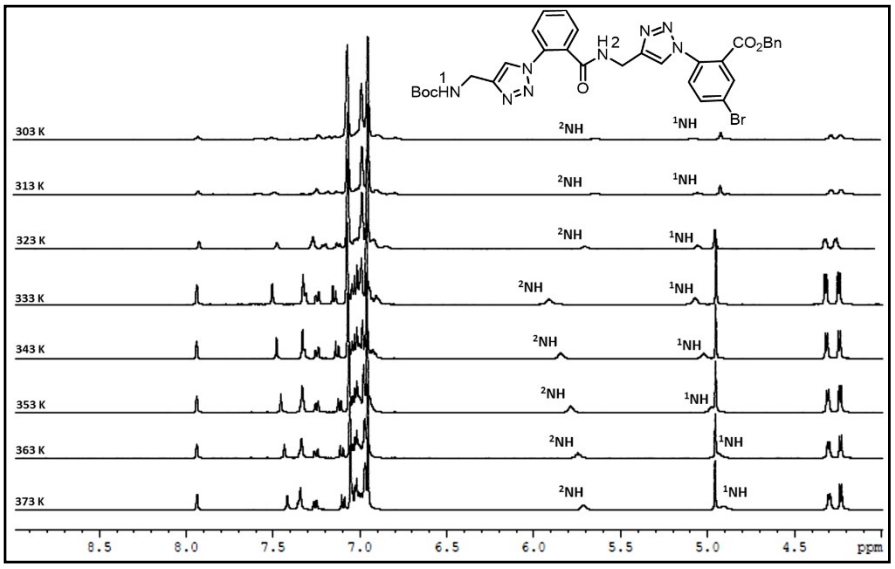


Figure 10. Variable temperature ^{1}HNMR (500 MHz) spectra of **4a** in Toluene-d_8

On cooling the sample from 373K to 333K, we can see down-field shifting of both 1NH and 2NH indicating of H-bonding effects. On further cooling to 303K, 1NH signal was found to reach ~5.1 ppm whereas 2NH signal showed a slight upfield shift. This could be due to the population of a different conformation in unbound molecules at lower temperature that exposes it to the anisotropic effect from adjacent aromatic ring.

IR experiments:

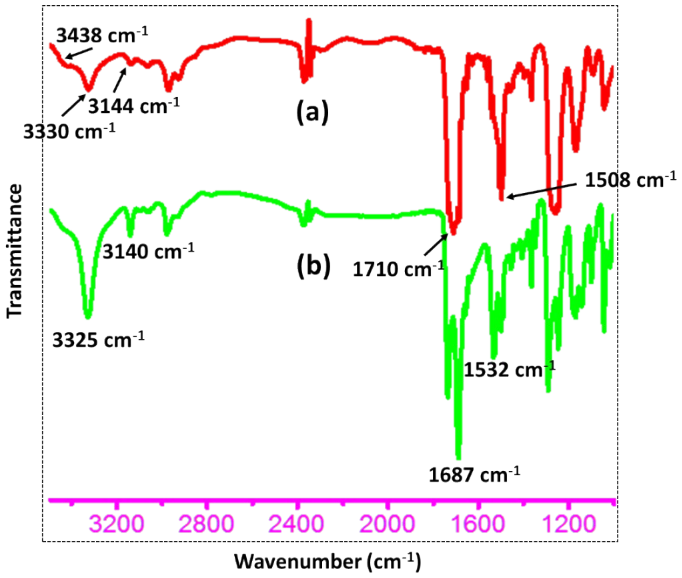


Figure 11. a) IR spectrum of **3a** (neat) from $CHCl_3$, b) IR spectrum of the of **3a** from its Toluene gel (5 wt%)

FT-IR is useful for understanding the hydrogen bonding pattern in self-assembled systems. The FT-IR spectrum of **3a** drop-casted from chloroform solution showed transmission bands at 3330, 1710, and 1508 cm^{-1} (Figure 11a) which are characteristic of nonhydrogen bonded NH (stretching), carbonyl (stretching), and NH (bending) whereas its toluene gel had these bands at 3325, 1687, and 1532 cm^{-1} (Figure 11b). Lowering of stretching frequencies of NH and amide carbonyl and a slight increase in NH bending frequency are clear indications of hydrogen bonding effects. In addition to this Triazole C-H also showed lowering in its stretching frequency in the gel state from 3144 to 3140 cm^{-1} evidencing its hydrogen bonding with triazole nitrogens.[2]

Rheology experiments (Flow behaviour of gels) for 3a:

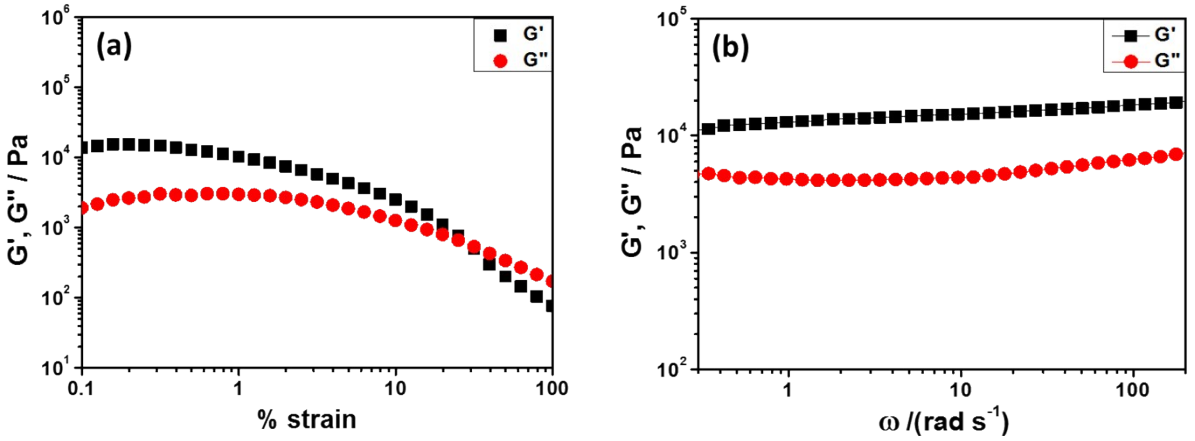


Figure 12. a) Results from strain sweep experiment of EtOH/H_2O gel (1 wt%) of **3a**; b) Results from frequency sweep experiment EtOH/H_2O gel (1 wt%) of **3a**.

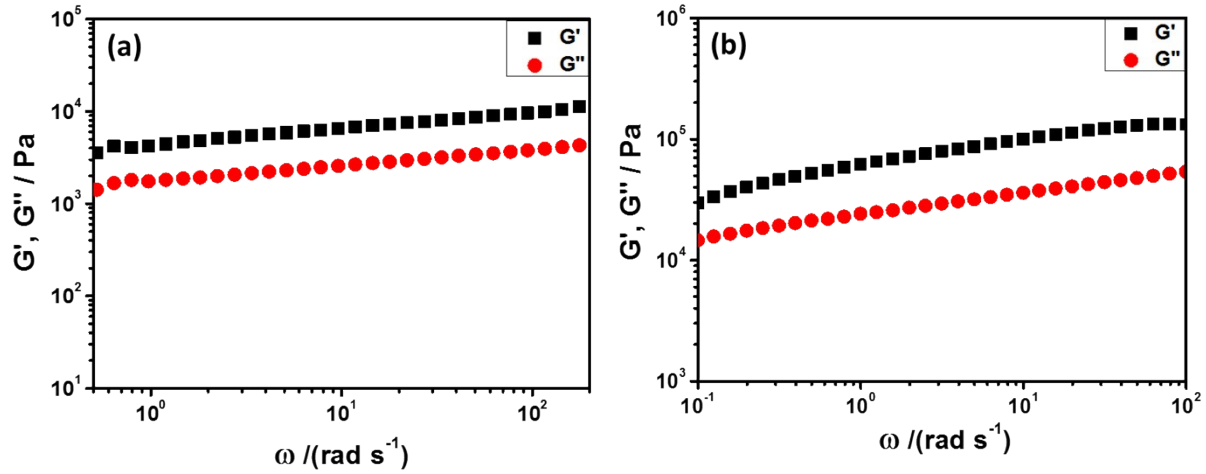


Figure 13. a) Results from frequency sweep experiment of type 3 oil gel (1 wt%) of **3a**; b) Results from frequency sweep experiment of IPA gel (5 wt%) of **3a**.

Powder XRD details and proposed self-assembly pattern for 3a:

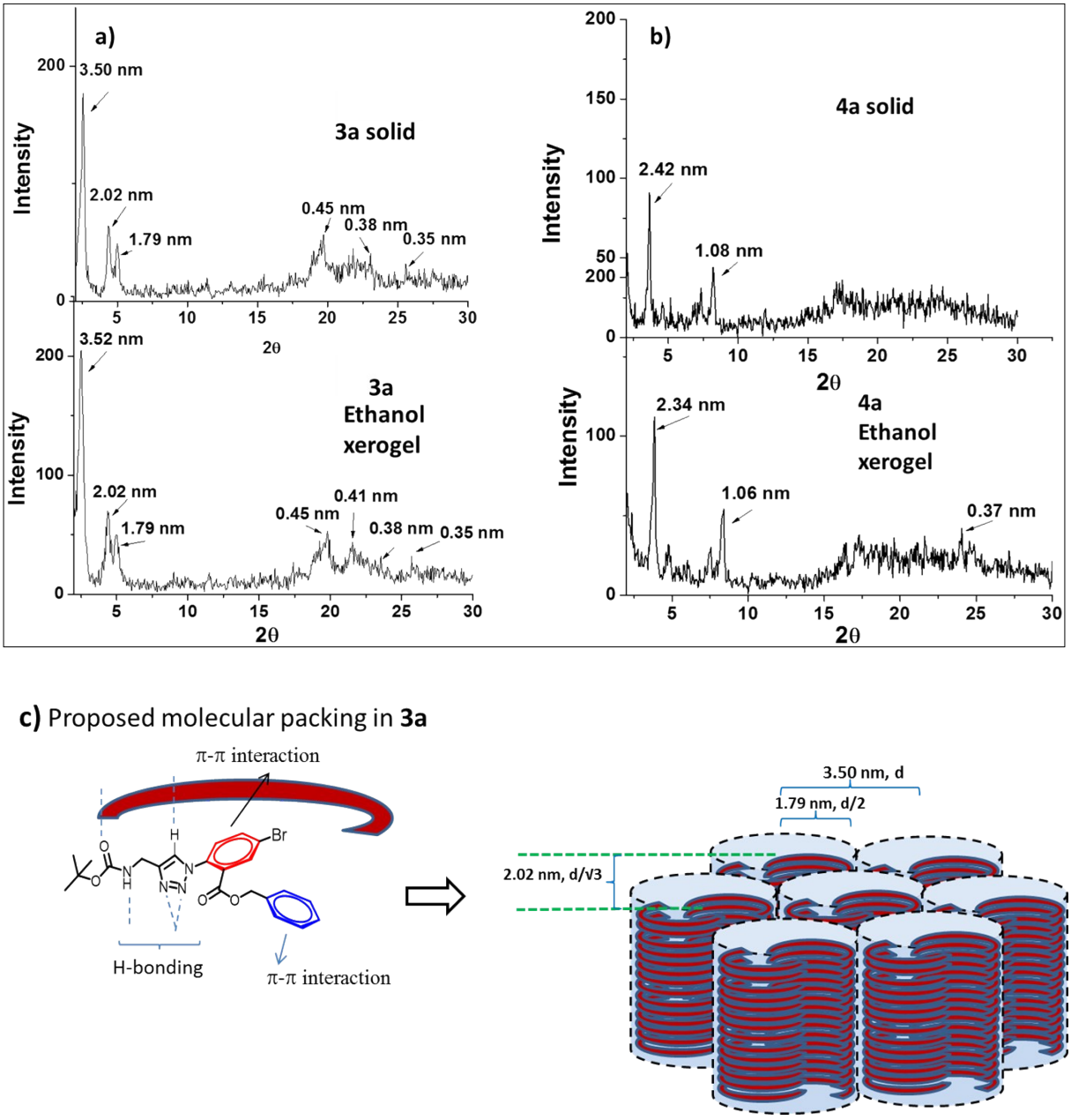


Figure 14: a) comparison of PXRD pattern of solid **3a** and Ethanol xerogel of **3a**; b) comparison of PXRD pattern of solid **4a** and Ethanol xerogel of **4a**; c) proposal of the self-assembly pattern of **3a** based on its PXRD spectrum shown in figure 14a.

Scanning Electron Microscopic images:

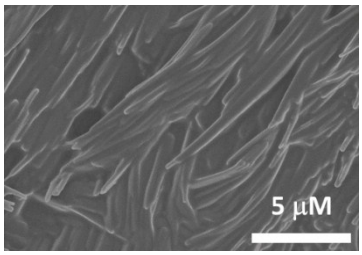


Figure 15. SEM image of **1** from its 5wt% solution in IPA (after one day of self-assembly)

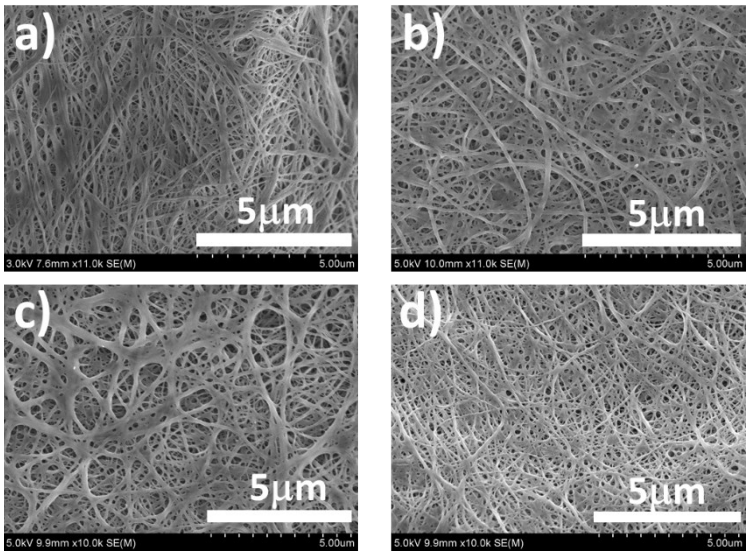


Figure 16. SEM image of xerogels of **3a** from various solvent systems a) Ethanol xerogel (3.5 wt%), b) Ethanol-Water xerogel (1 wt%), c) IPA-Water xerogel (1 wt%), d) ^{t}BuOH-Water xerogel (1 wt%)

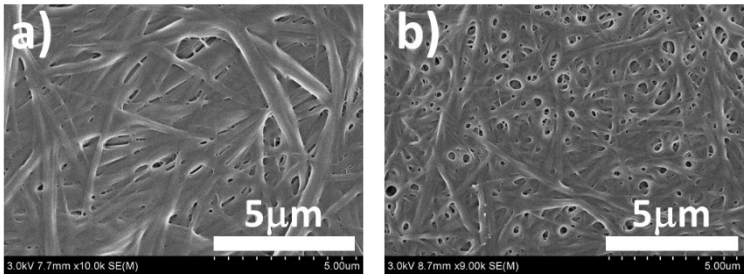


Figure 17. SEM images of xerogels from mesitylene a) **3b** (5 wt%), b) **3c** (5 wt%).

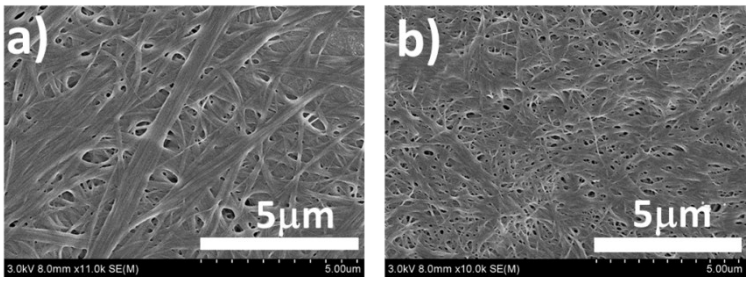


Figure 18. SEM images of xerogels of **4a** from a) Mesitylene (1 wt%), b) Dodecane (2 wt%).

Table 4. Crystallographic summary for compound **1**

Compound	**1**
Chemical formula	C22 H24 N4 O4
Formula weight	408.45
Crystal system	Triclinic
a (Å)	5.31640(10)
b (Å)	11.5830(3)
c (Å)	17.1059(4)
α	84.2779(12)
β	82.5641(12)
γ	85.7426(12)
Temperature	296(2) K
V (A^3)	1037.31(4)
Space group	P-1
Z	2
Reflections collected	13176
Unique reflections	3647
Final R	R1 = 0.0408
CCDC Number	1528029

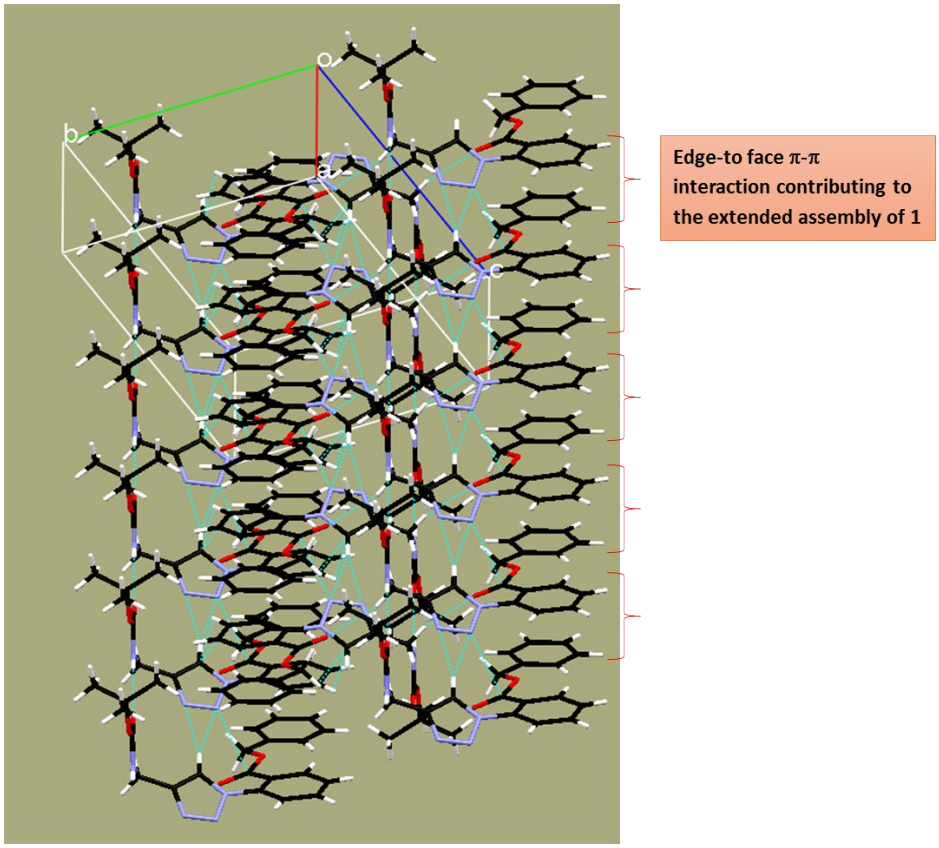


Figure 19. Arrangement of molecules in the lattice of **1**.

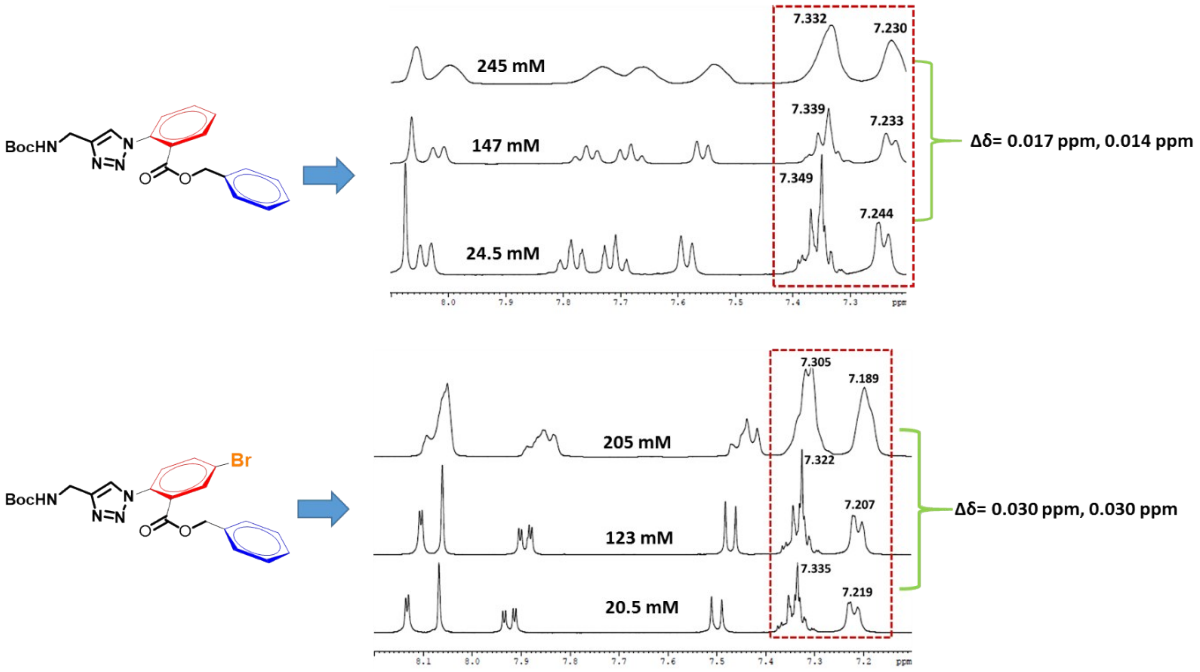


Figure 20. Concentration-dependant ^{1}HNMR spectra of **1** and **3a** in Methanol-d_4 showing relative differences in upfield shifting of benzyl aromatic signals

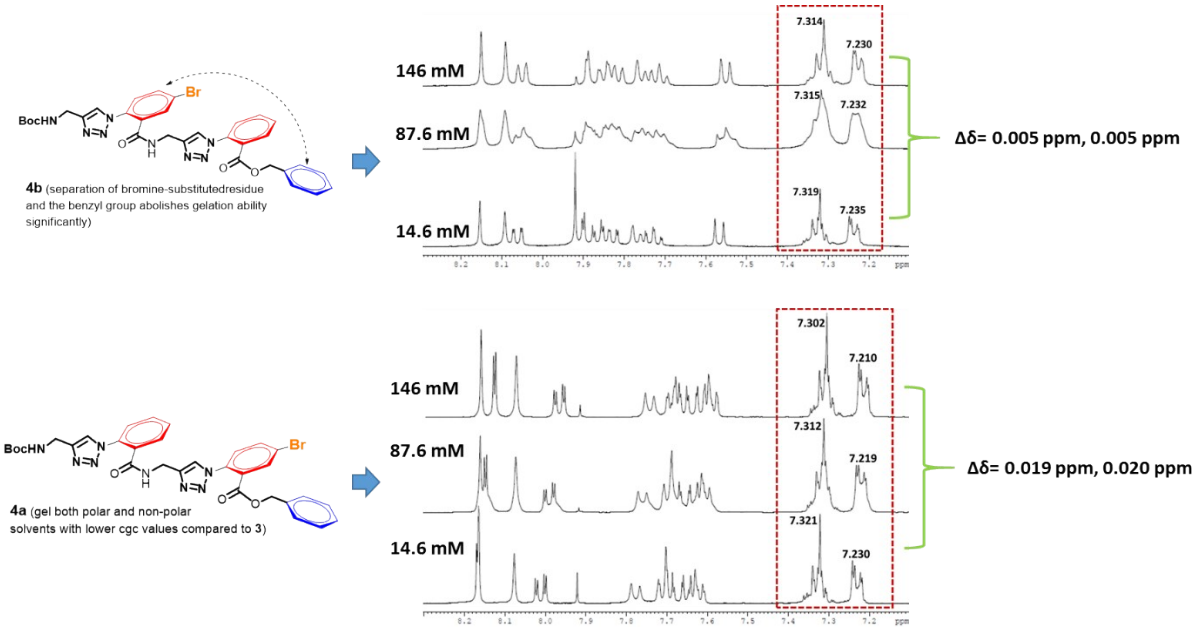


Figure 21. Concentration-dependant ^{1}HNMR spectra of **4b** and **4a** in Methanol-d_4 showing relative differences in upfield shifting of benzyl aromatic signals

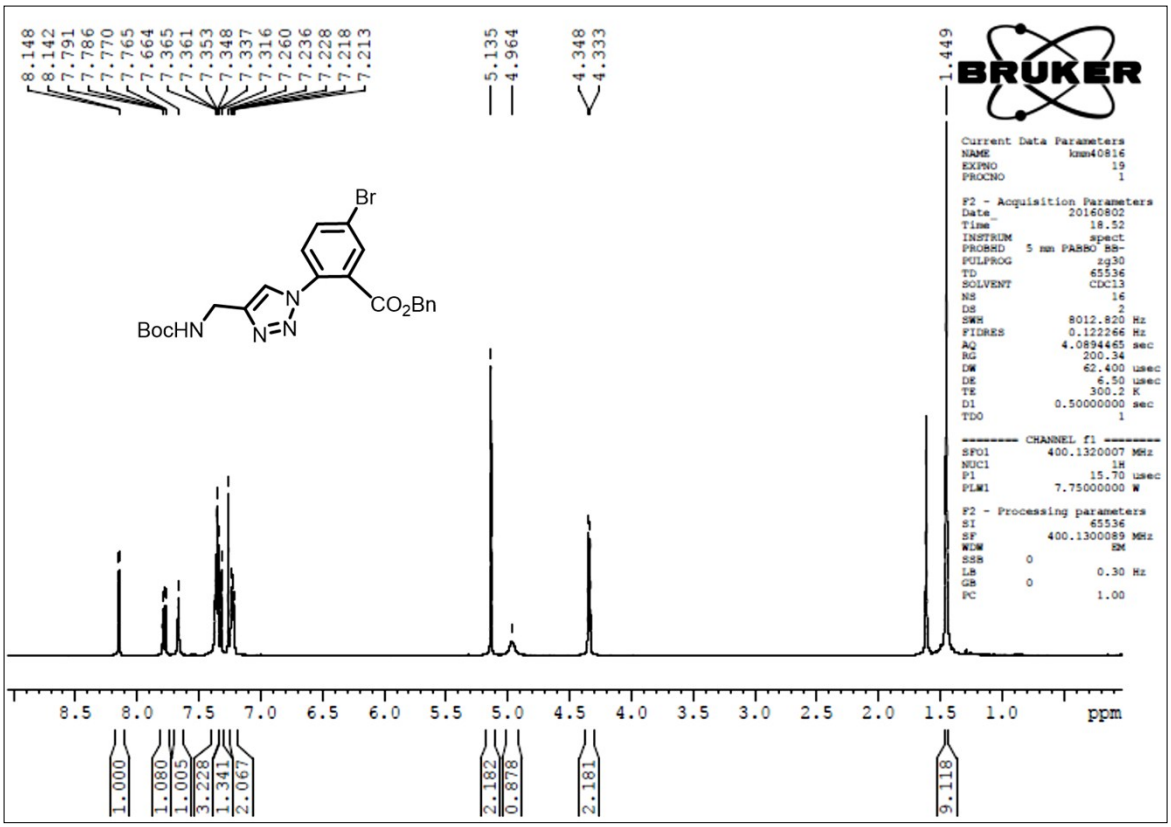


Figure 22. [1]HNMR of **3a** (400 MHz)

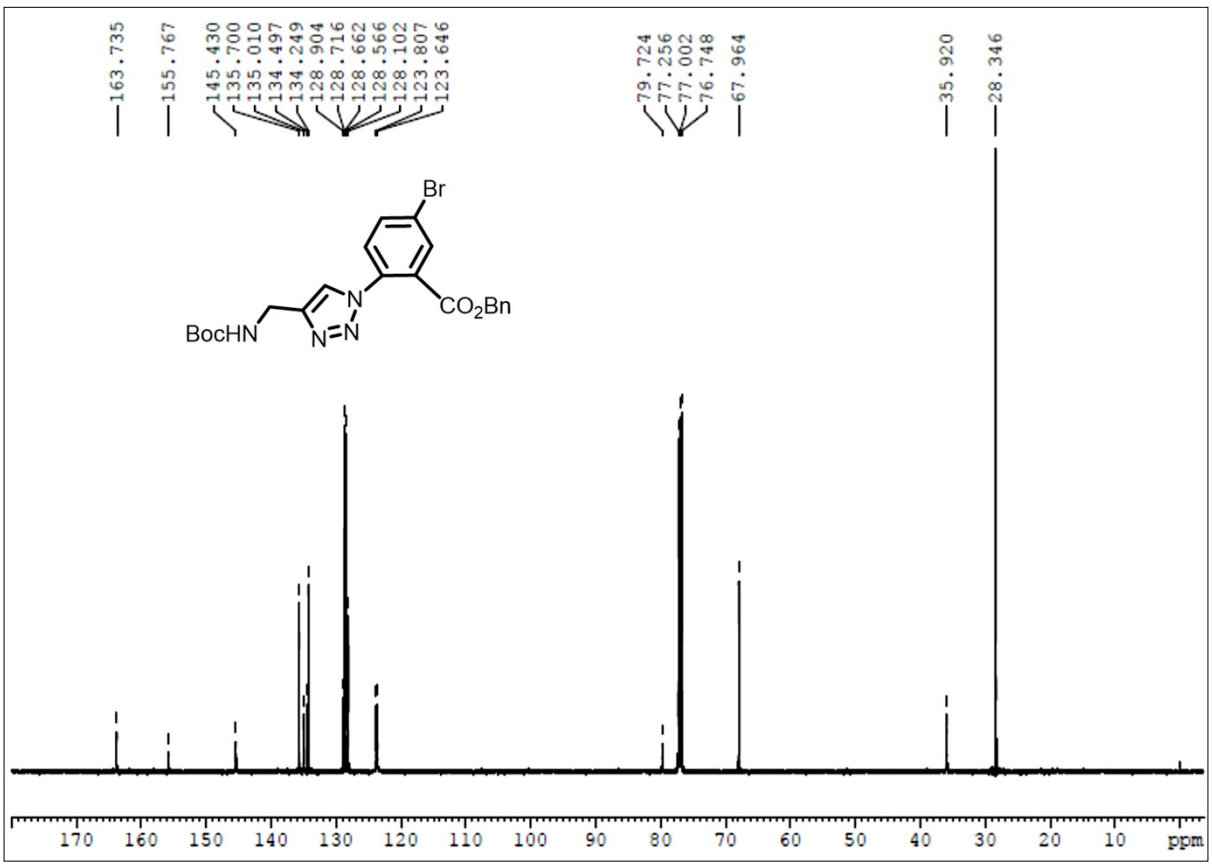


Figure 23. [13]C NMR of **3a** (125 MHz)

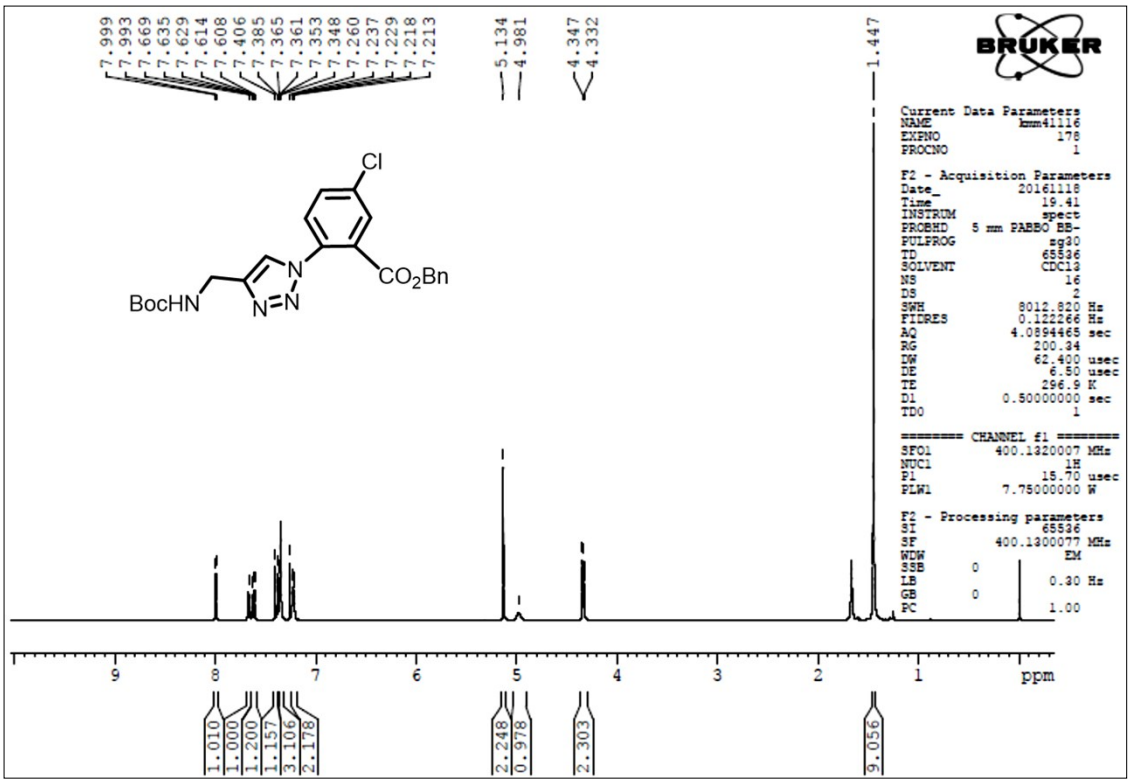


Figure 24. [1]HNMR of **3b** (400 MHz)

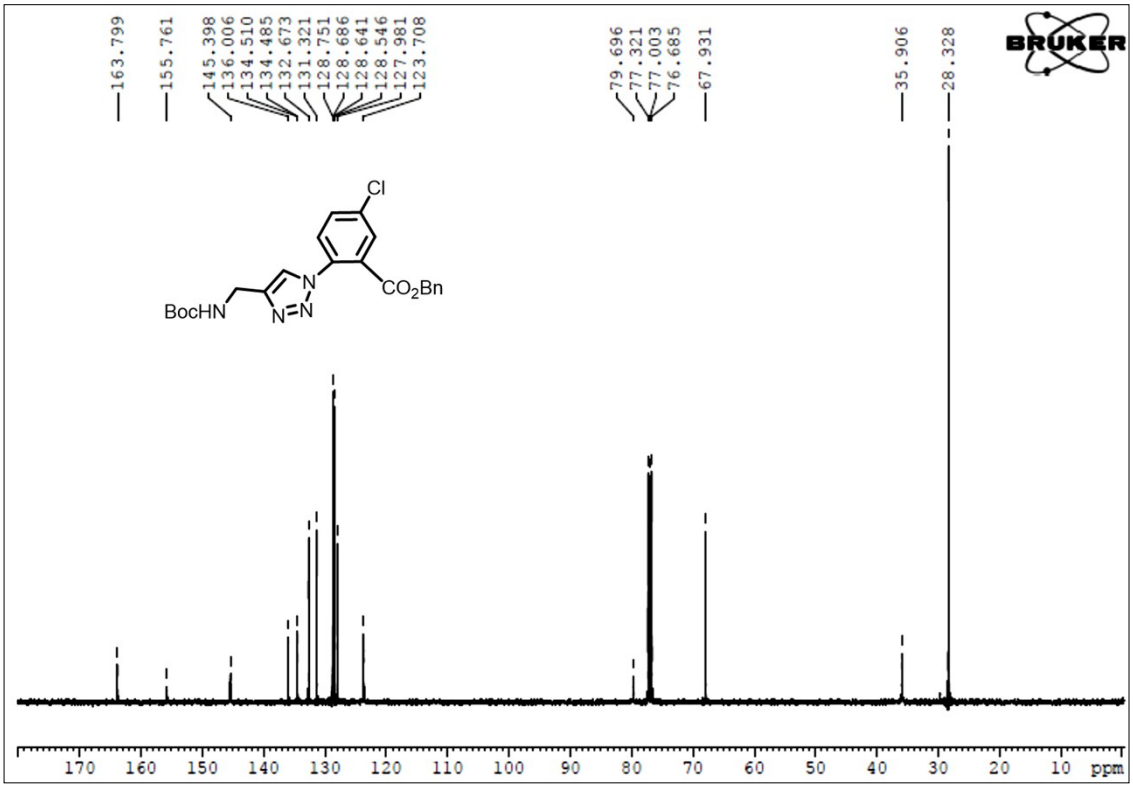


Figure 25. [13]C NMR of **3b** (400 MHz)

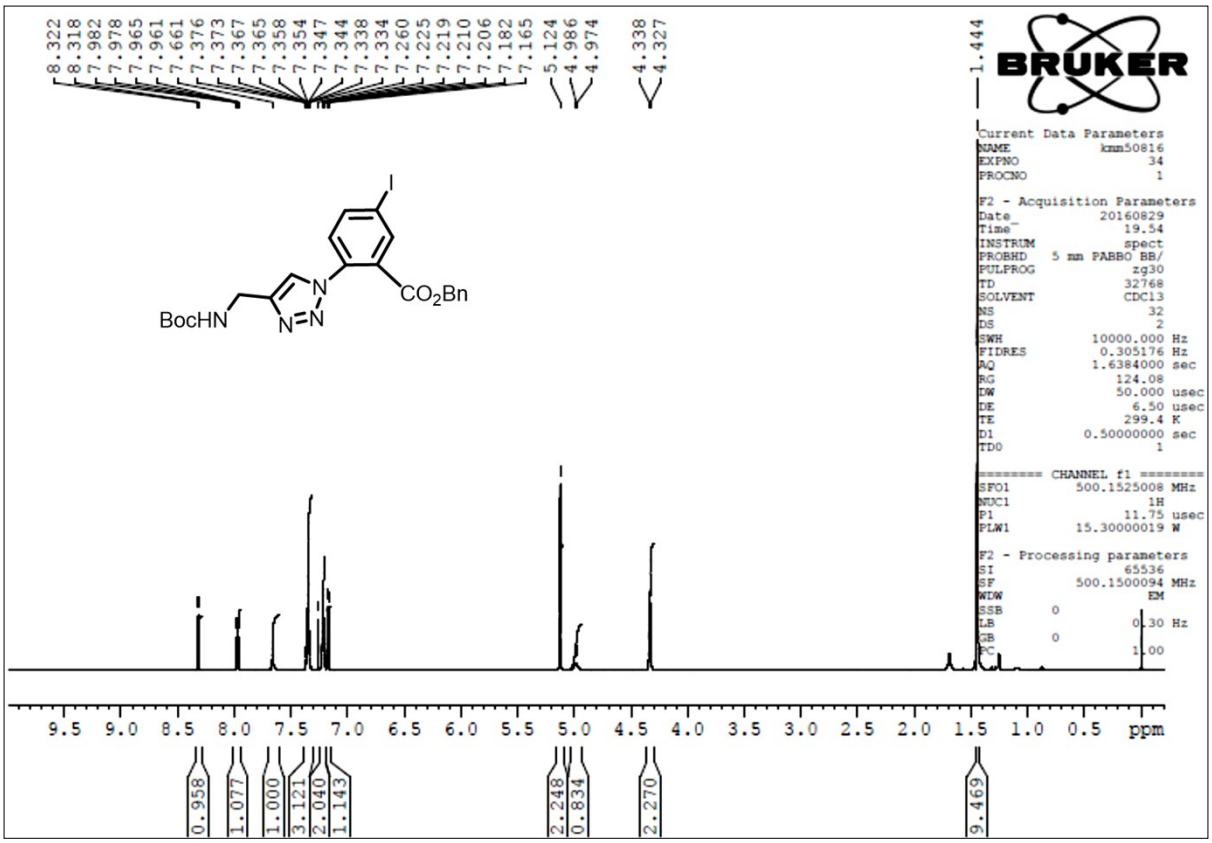


Figure 26. [1]HNMR of **3c** (500 MHz)

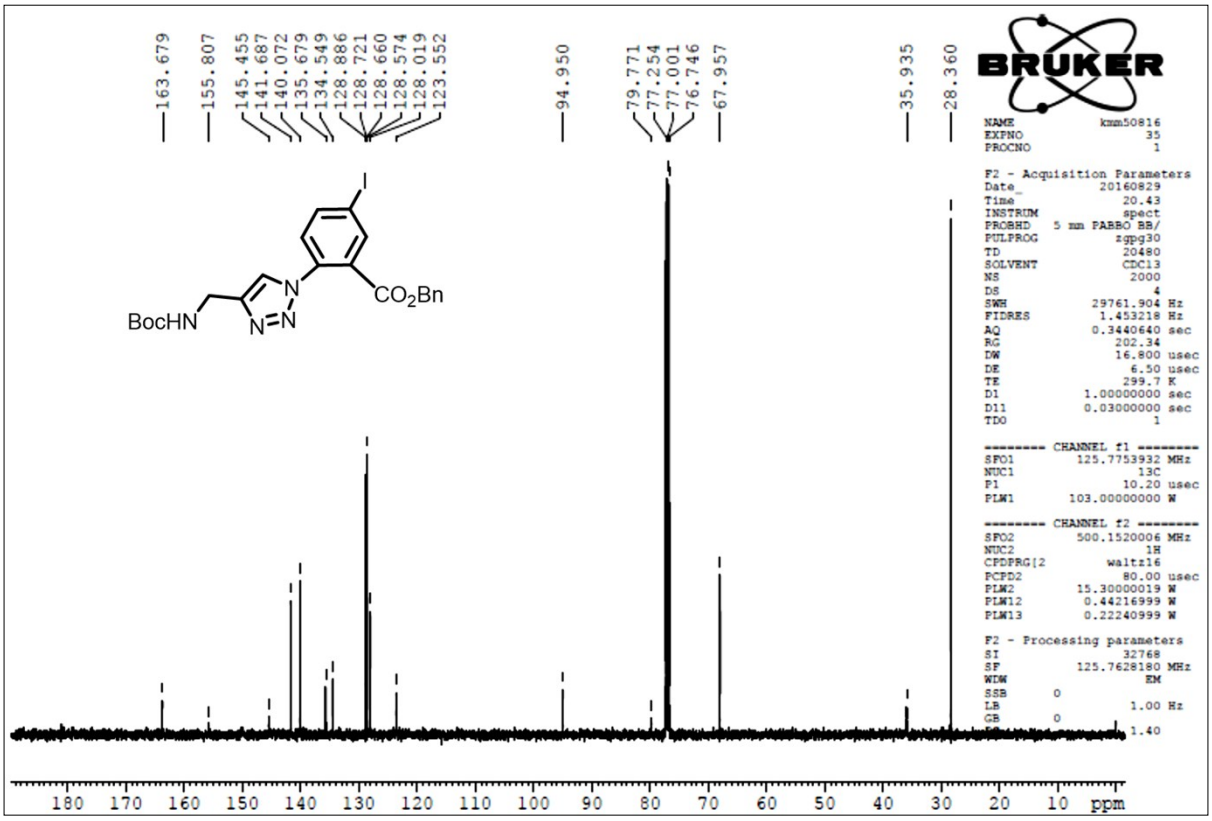


Figure 27. [13]C NMR of **3c** (125 MHz)

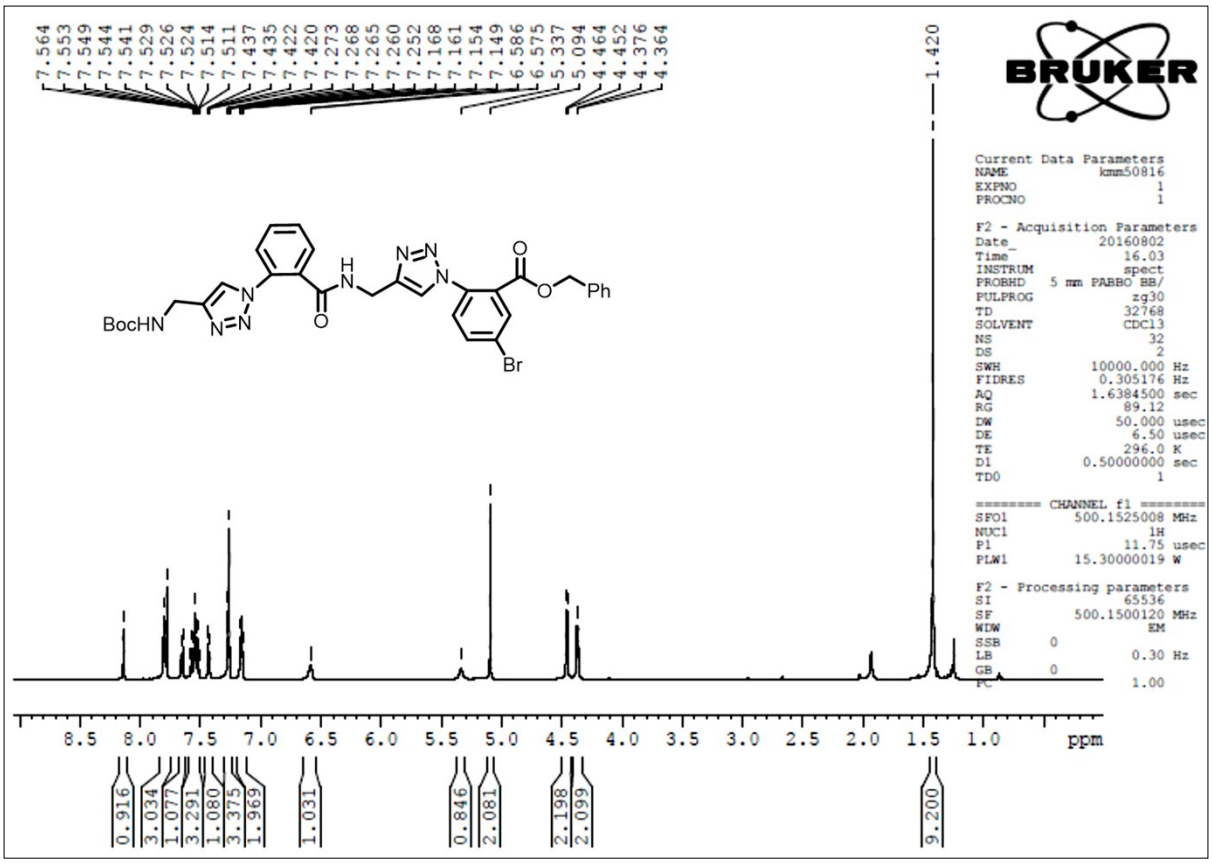


Figure 28. [1]HNMR of **4a** (500 MHz)

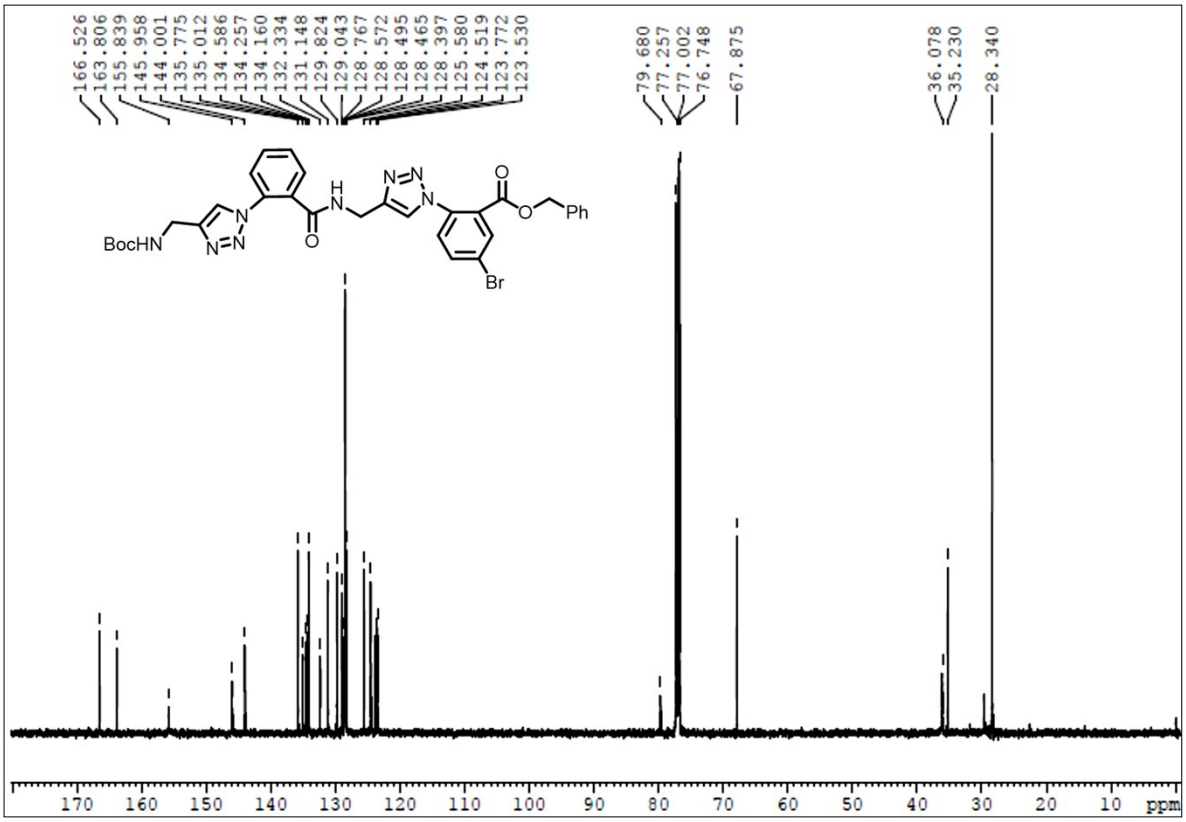


Figure 29. [13]C NMR of **4a** (125 MHz)

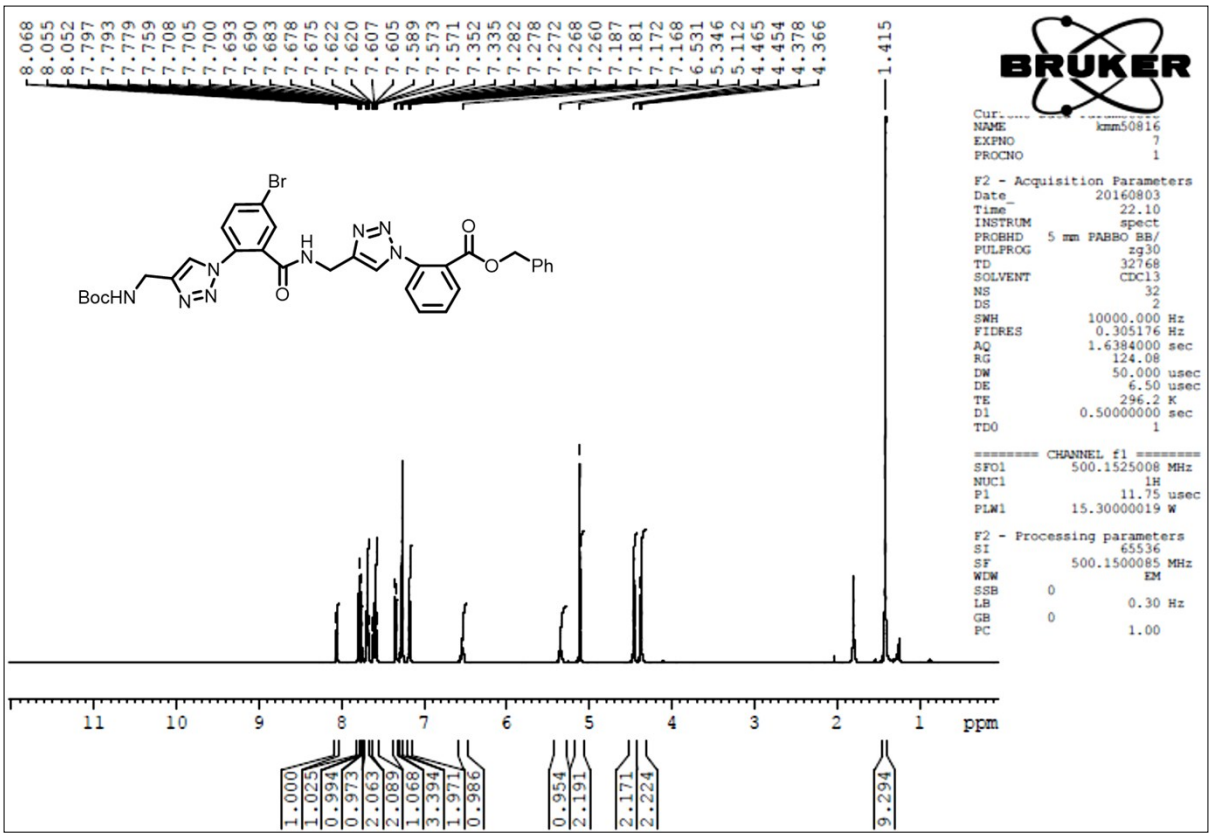


Figure 30. [1]HNMR of **4b** (500 MHz)

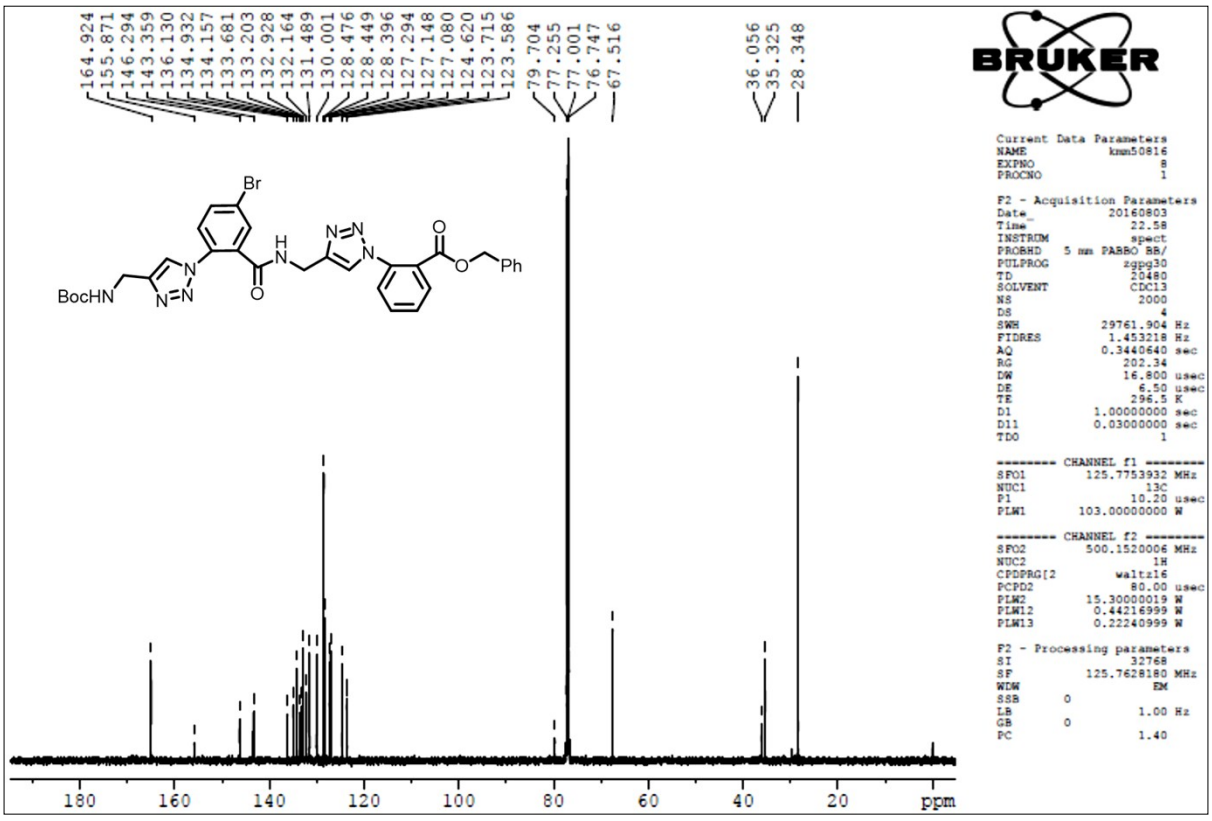


Figure 31. [13]C NMR **4b** (125 MHz)

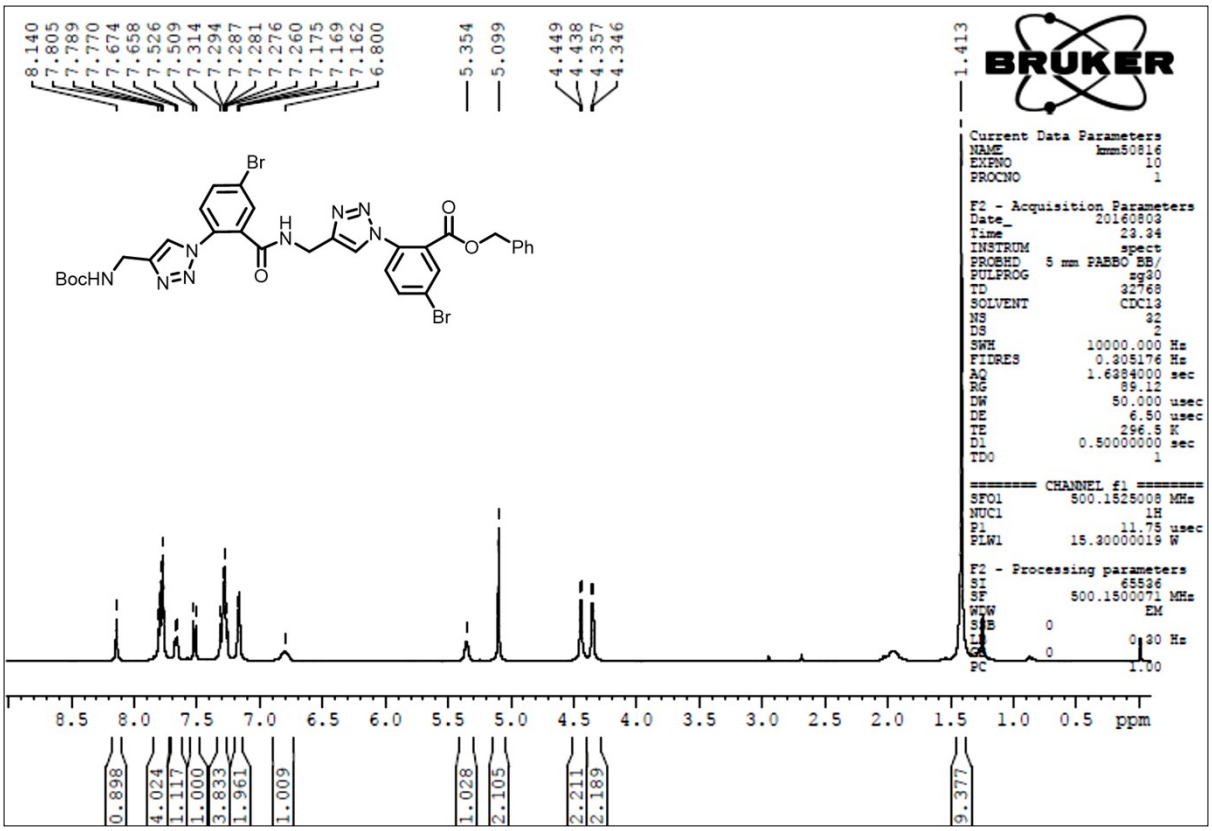


Figure 32. [1]HNMR of **4c** (500 MHz)

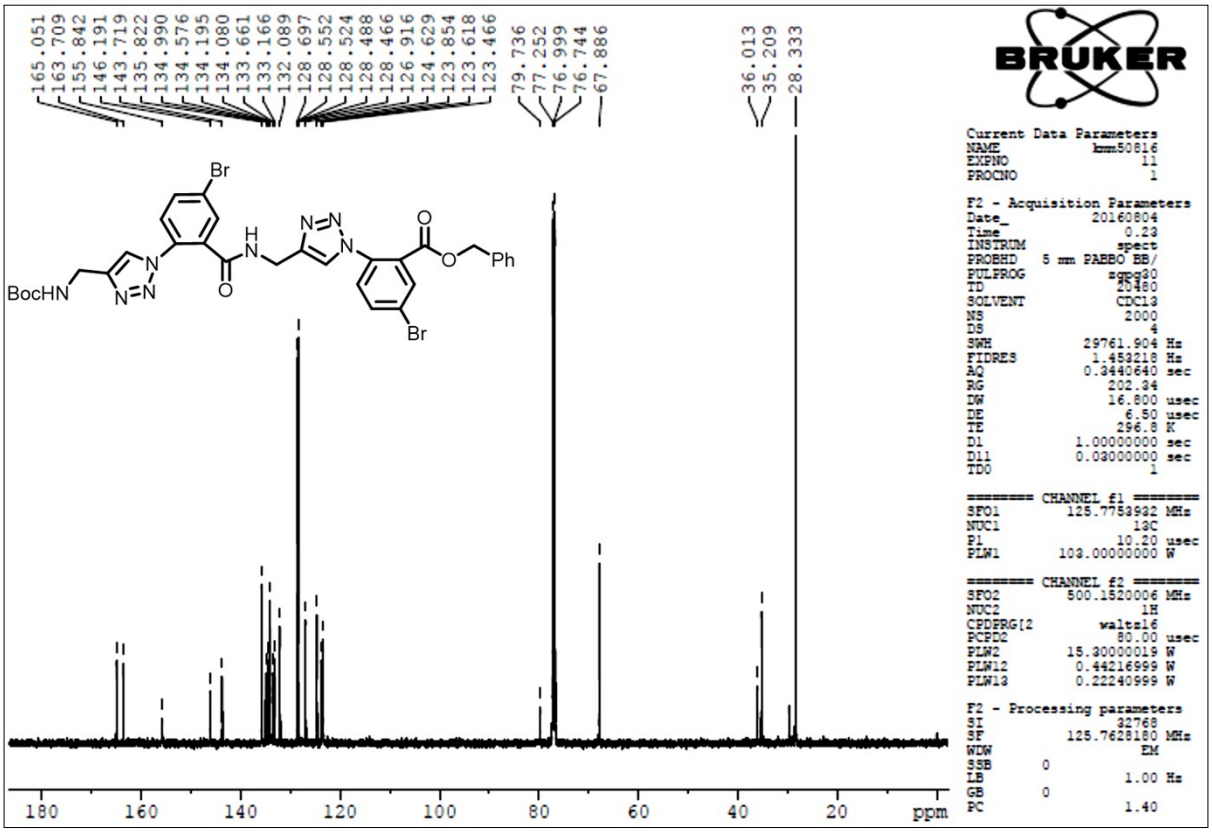


Figure 33. [13]C NMR of **4c** (125 MHz)

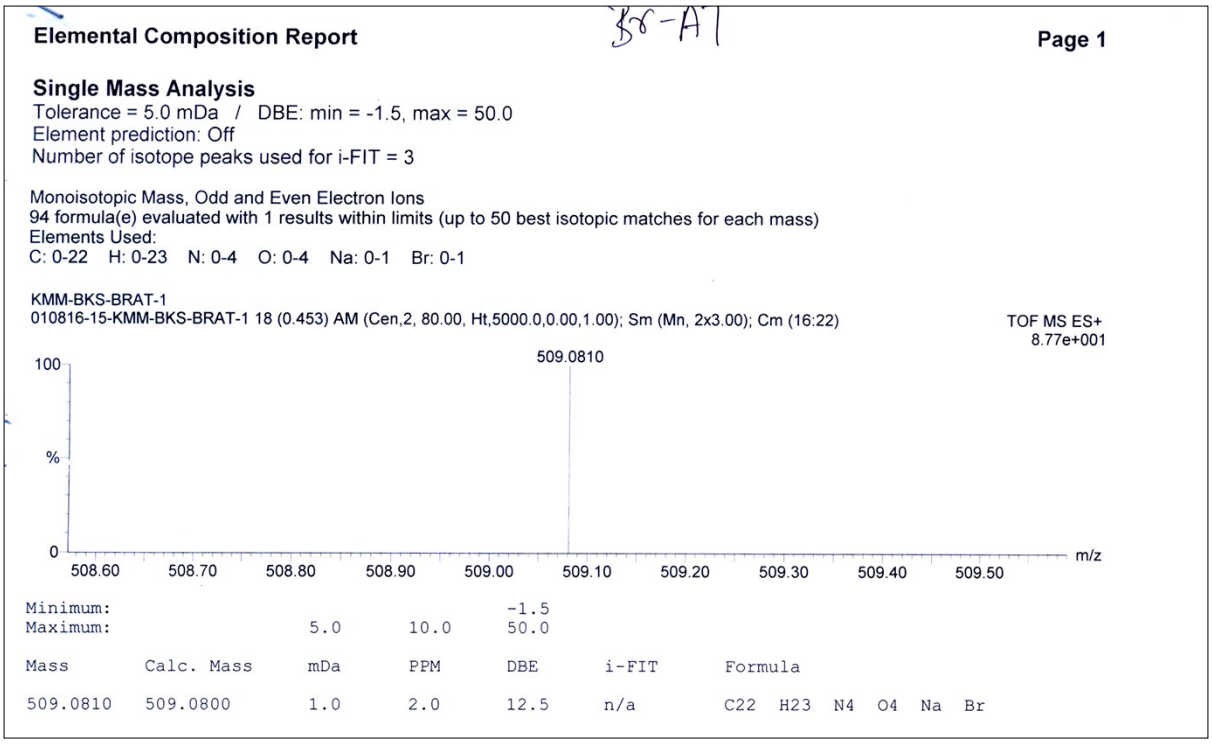


Figure 34. HRMS spectrum of **3a** showing [**M+Na**]$^+$ peak

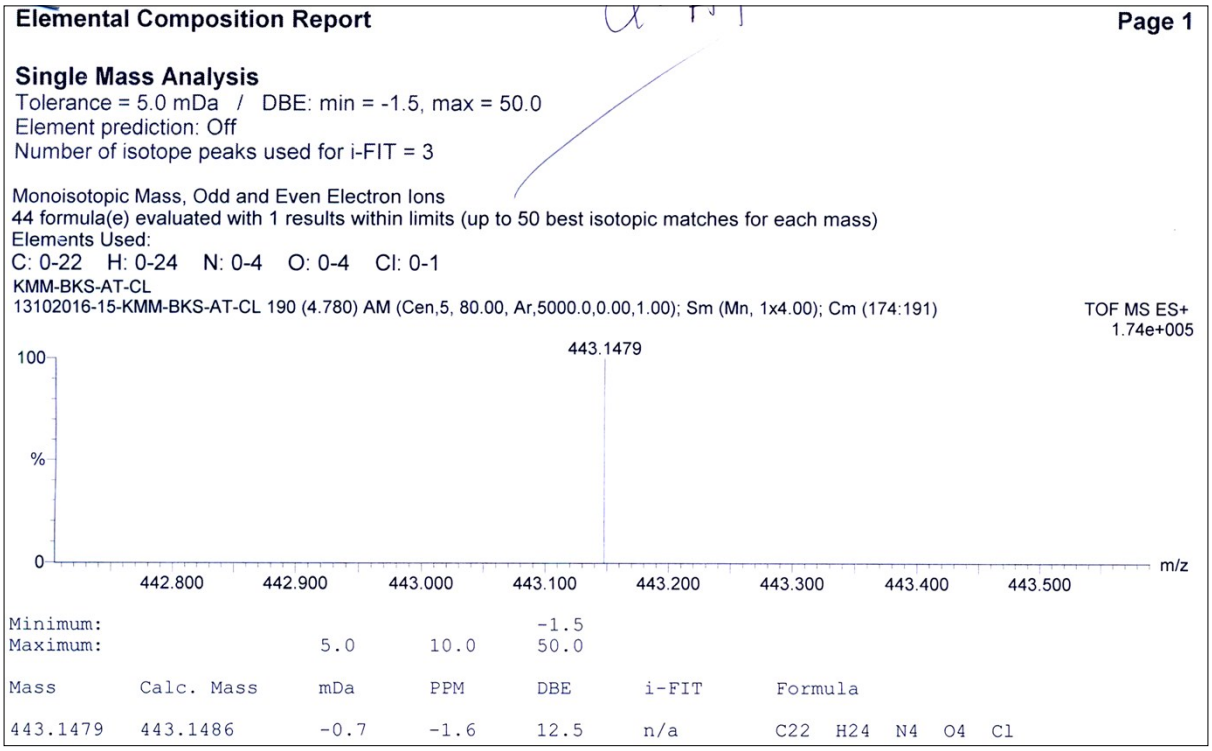


Figure 35. HRMS spectrum of **3b** showing [**M+H**]$^+$ peak

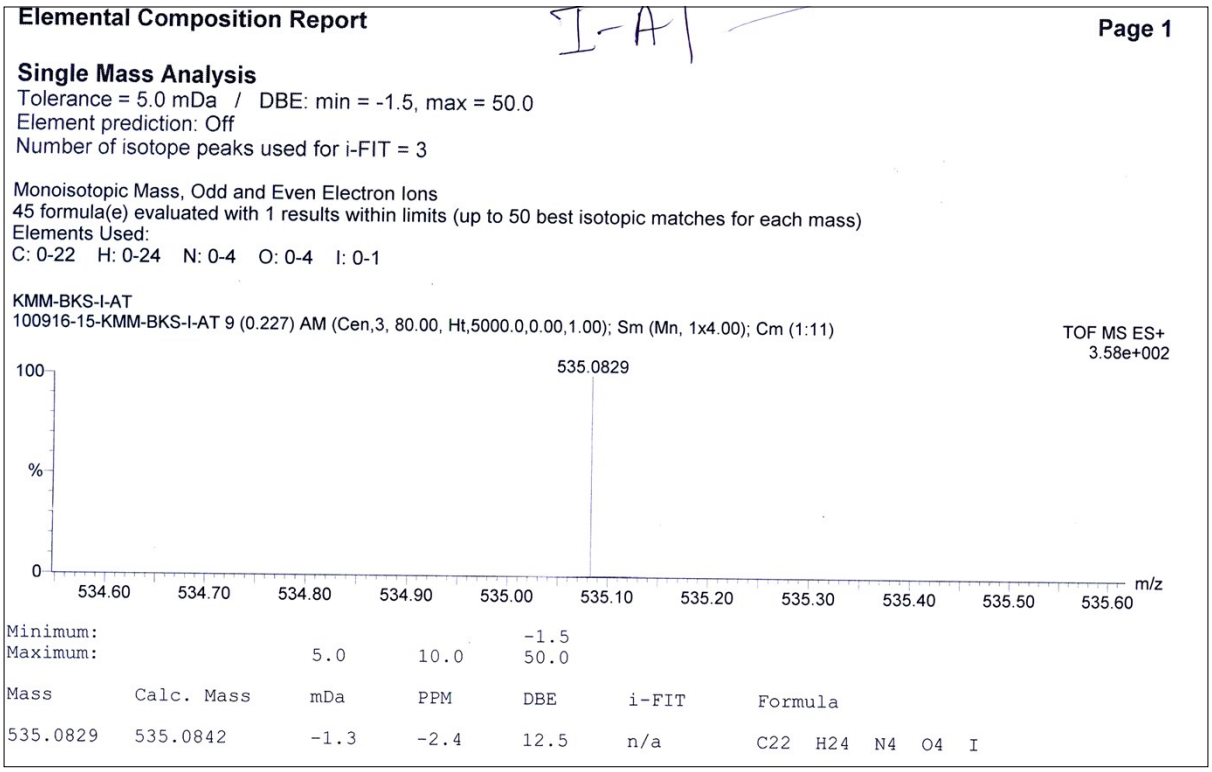


Figure 36. HRMS spectrum of **3c** showing [**M+H**]$^+$ peak

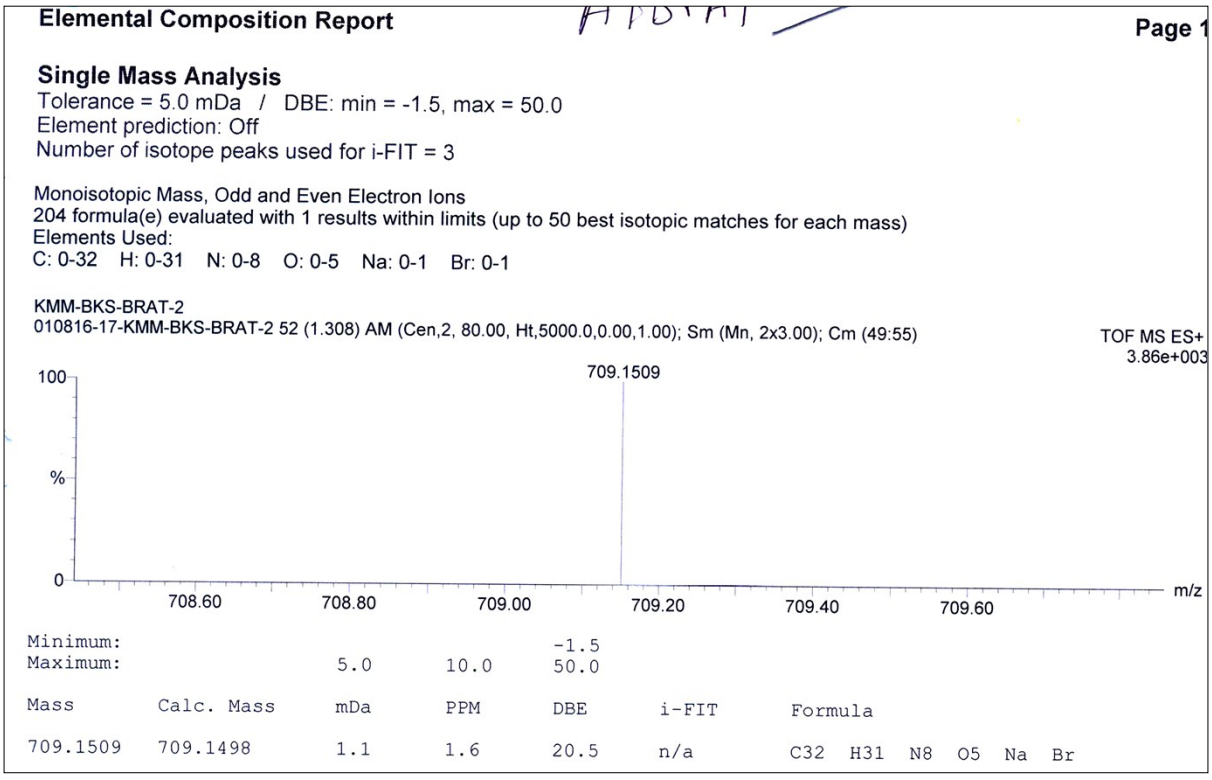
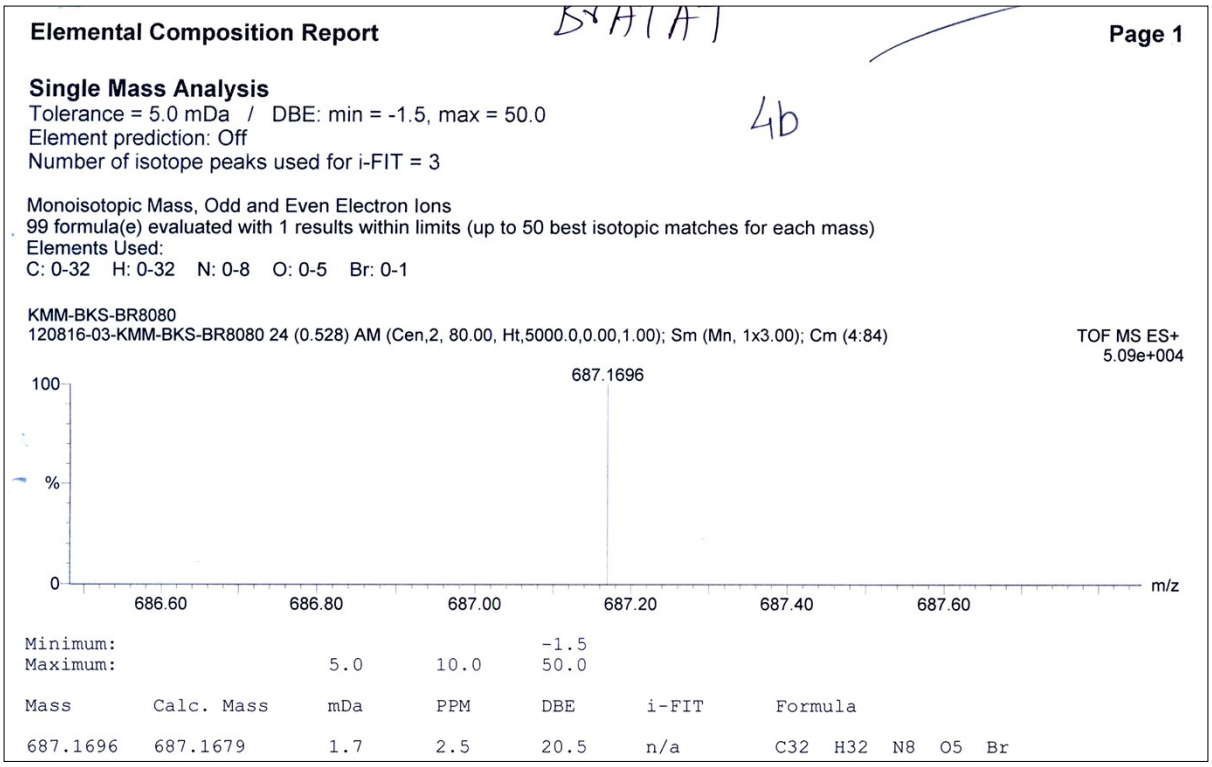


Figure 37. HRMS spectrum of **4a** showing [**M+Na**]$^+$ peak



Elemental Composition Report Page 1

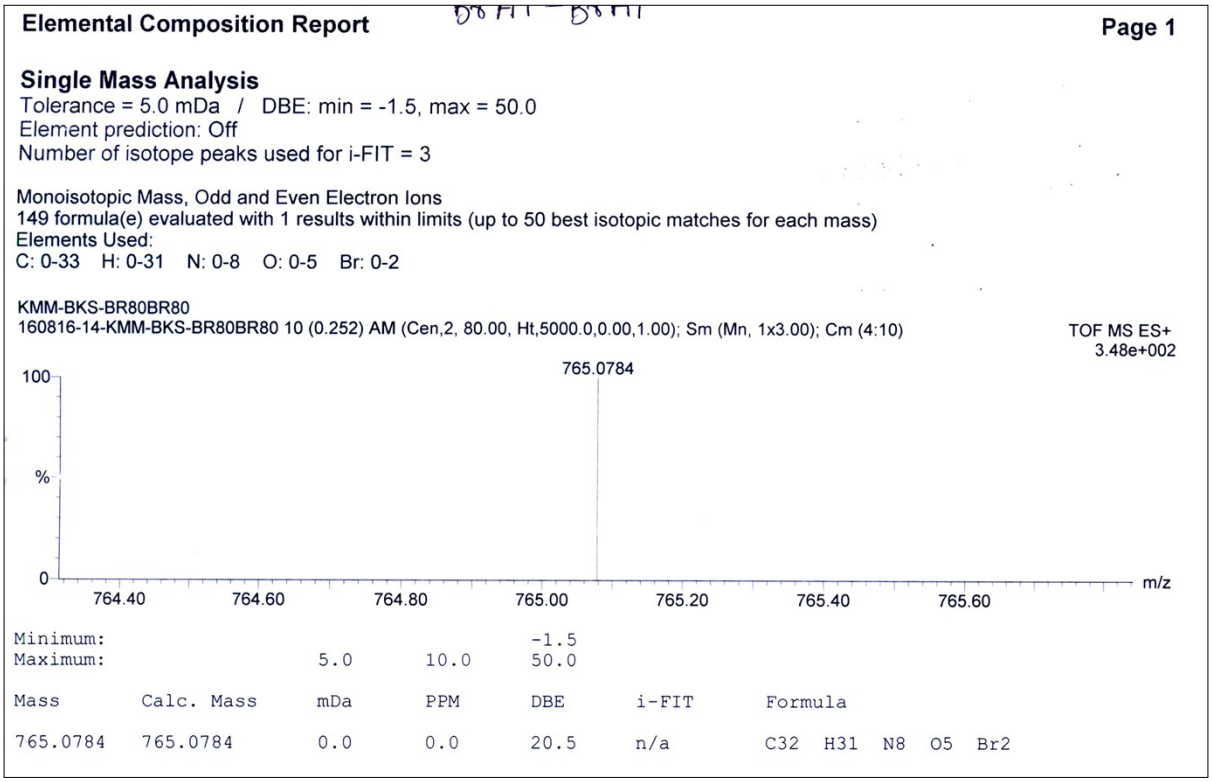
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
99 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-32 H: 0-32 N: 0-8 O: 0-5 Br: 0-1

KMM-BKS-BR8080
120816-03-KMM-BKS-BR8080 24 (0.528) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 1x3.00); Cm (4:84)
TOF MS ES+
5.09e+004

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
687.1696	687.1679	1.7	2.5	20.5	n/a	C32 H32 N8 O5 Br

Figure 38. HRMS spectrum of **4b** showing [**M+H**]$^+$ peak



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
149 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-33 H: 0-31 N: 0-8 O: 0-5 Br: 0-2

KMM-BKS-BR80BR80
160816-14-KMM-BKS-BR80BR80 10 (0.252) AM (Cen,2, 80.00, Ht,5000.0,0.00,1.00); Sm (Mn, 1x3.00); Cm (4:10)
TOF MS ES+
3.48e+002

Minimum:				-1.5		
Maximum:		5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
765.0784	765.0784	0.0	0.0	20.5	n/a	C32 H31 N8 O5 Br2

Figure 39. HRMS spectrum of **4c** showing [**M+H**]$^+$ peak

Supporting video:

1) Supporting video 1 is included which shows the effect of mechanical force on thermal stimuli healing property of type 3 oil gel of **3a**.
2) Supporting video 2 is included which shows the effect of mechanical disturbance on shape persistence of a self-healed material made from Isopropanol gel of **3a**.

Refrences:

1) B. K. Srivastava and M. K. Manheri, *RSC. Adv.*, 2016, **6**, 29197-29201.
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