Tetra-Coordinated Organoboron Complexes with Triaminoguanidine-Salicylidene based Ligands: Aggregation Induced Enhanced Emission and Mechanoresponsive Features

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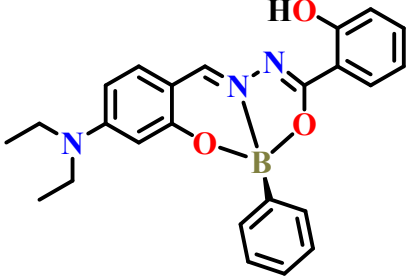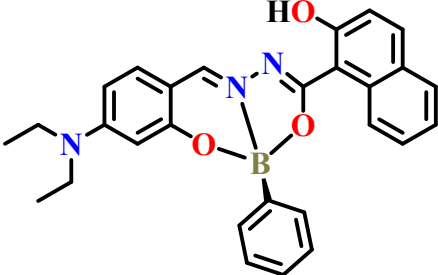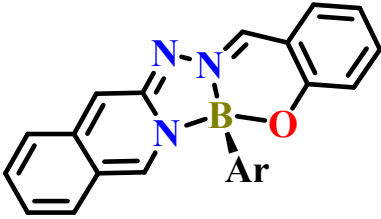
Stock solution preparation for spectroscopic measurements
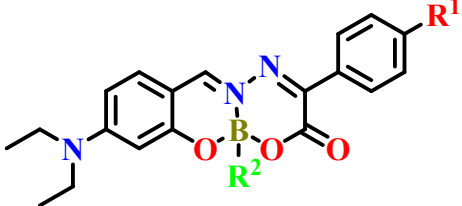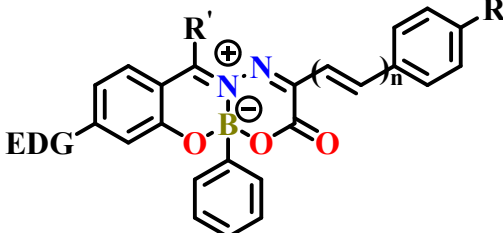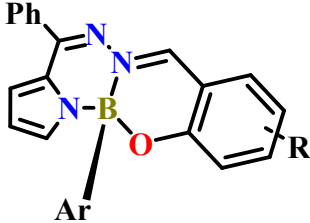
Stock solutions of 1×10^{-5} were prepared for the solvent effect studies of boron compounds 6-10. For aggregation studies, stock solutions of 1×10^{-4} were made using double-distilled ultrapure water and THF as solvents.

Computation Details

DFT calculations were performed by using the Gaussian 16 package.[1] The ground state geometries were optimized using DFT at the B3LYP/6-31G(d). The electronic excited state energies of the compounds were calculated by time-dependent DFT (TDDFT) with B3LYP functional and 6-31G(d) basis set based on the optimized ground state geometry.

Table S1. Comparative table between previously reported organoboron AIE gen bearing ESIPT unit

S.No.	Compound	AIE with ESIPT	Reference
1. (a)	DPDP	AIE Only	2
(b)	DPDN	AIE Only	
2.		AIE Only	3

3.	R^1 - H, CF$_3$, CN, NO$_2$ R^2-C$_6$H$_5$	-	4
4.	R$'$ = H, Me, Et, iPr R = H, CF$_3$	-	5
5.		AIE Only	6
6.	**This work**	**AIE with ESIPT unit**	
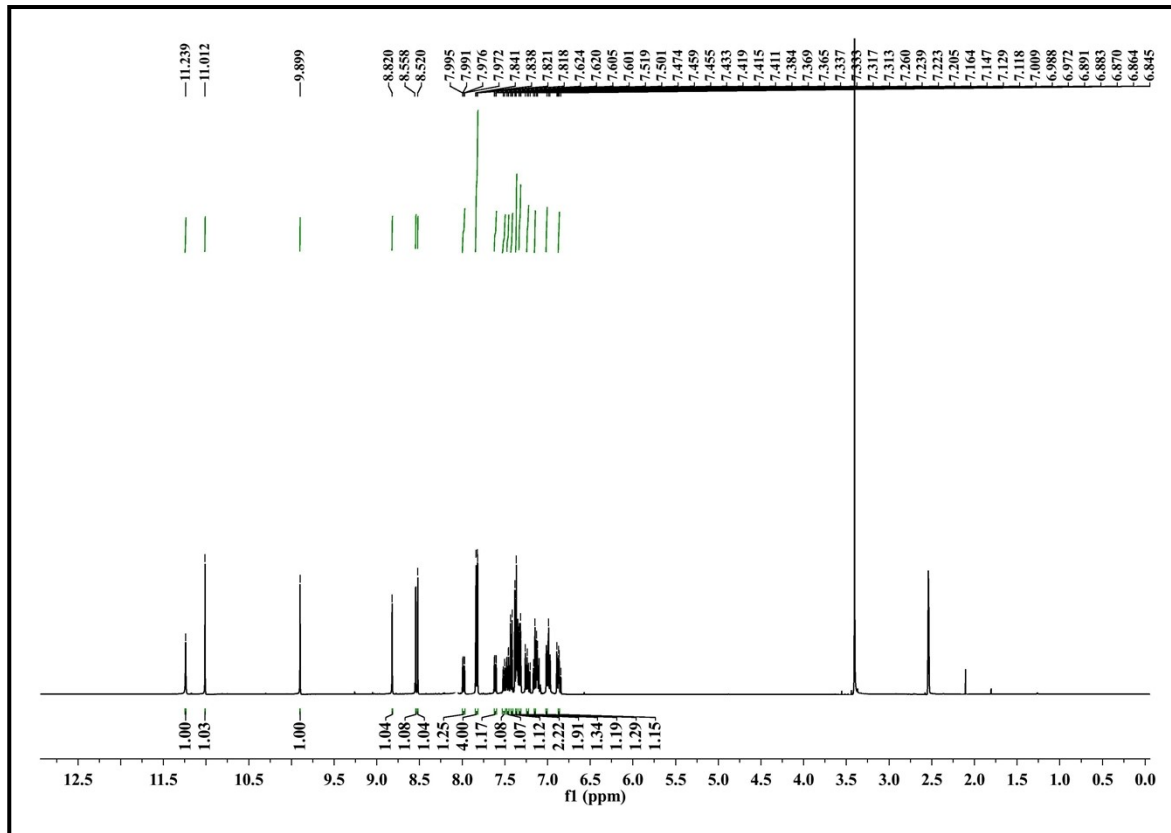
Fig. S1. ^{1}H NMR Spectrum of **6** in DMSO-d_6
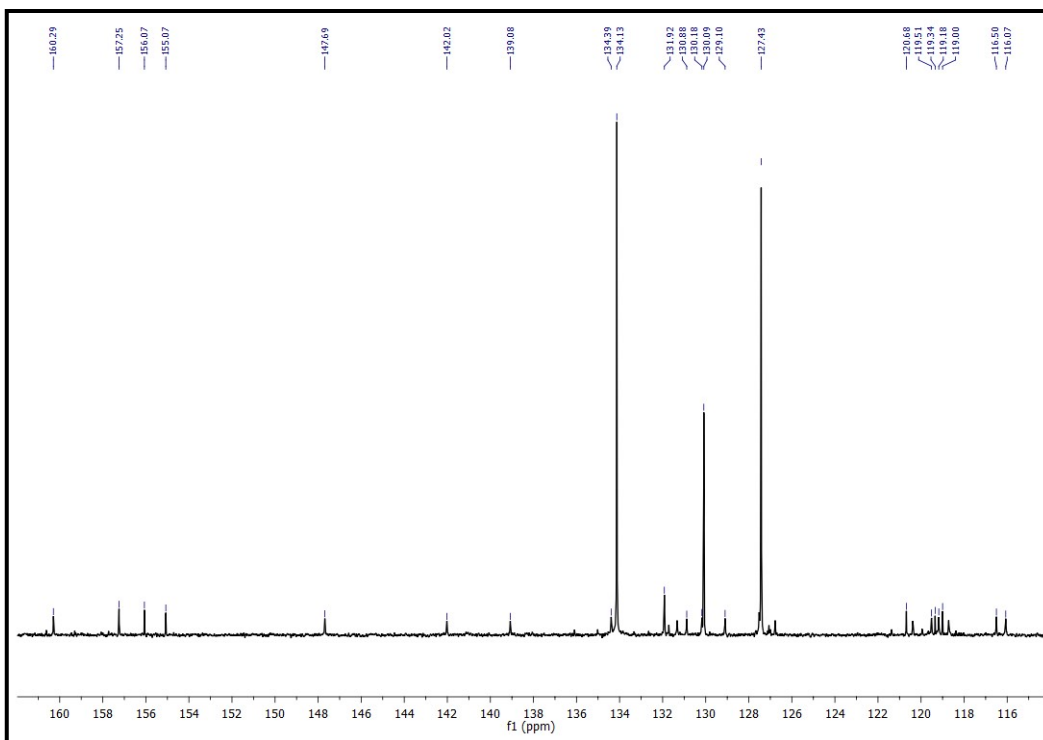
Fig. S2. ^{13}C NMR Spectrum of **6** in DMSO-d_6.
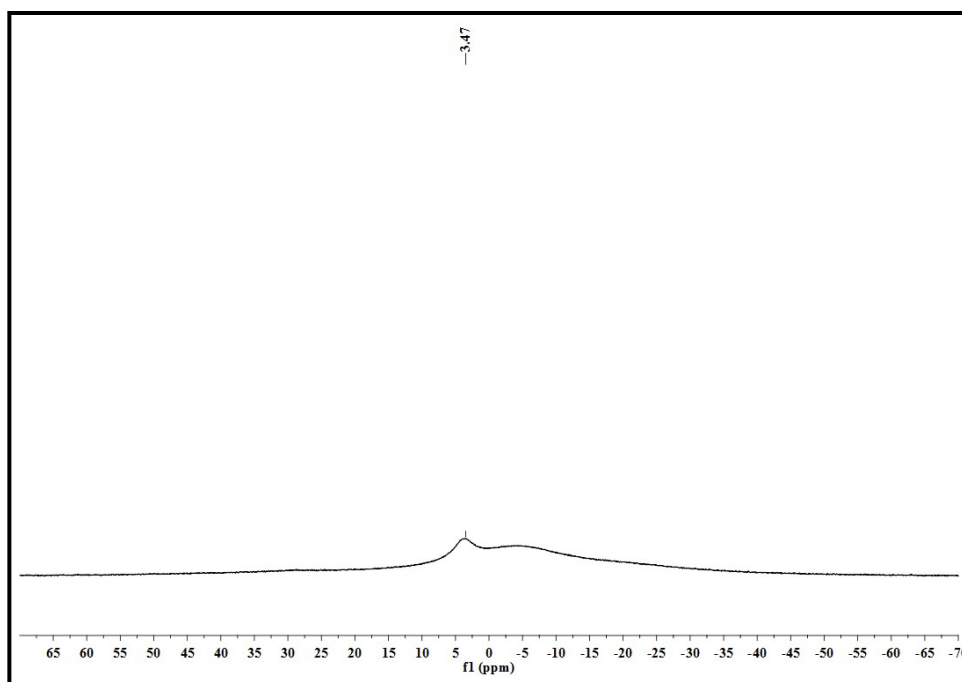
Fig. S3. ^{11}B NMR Spectrum of **6** in DMSO-d_6.
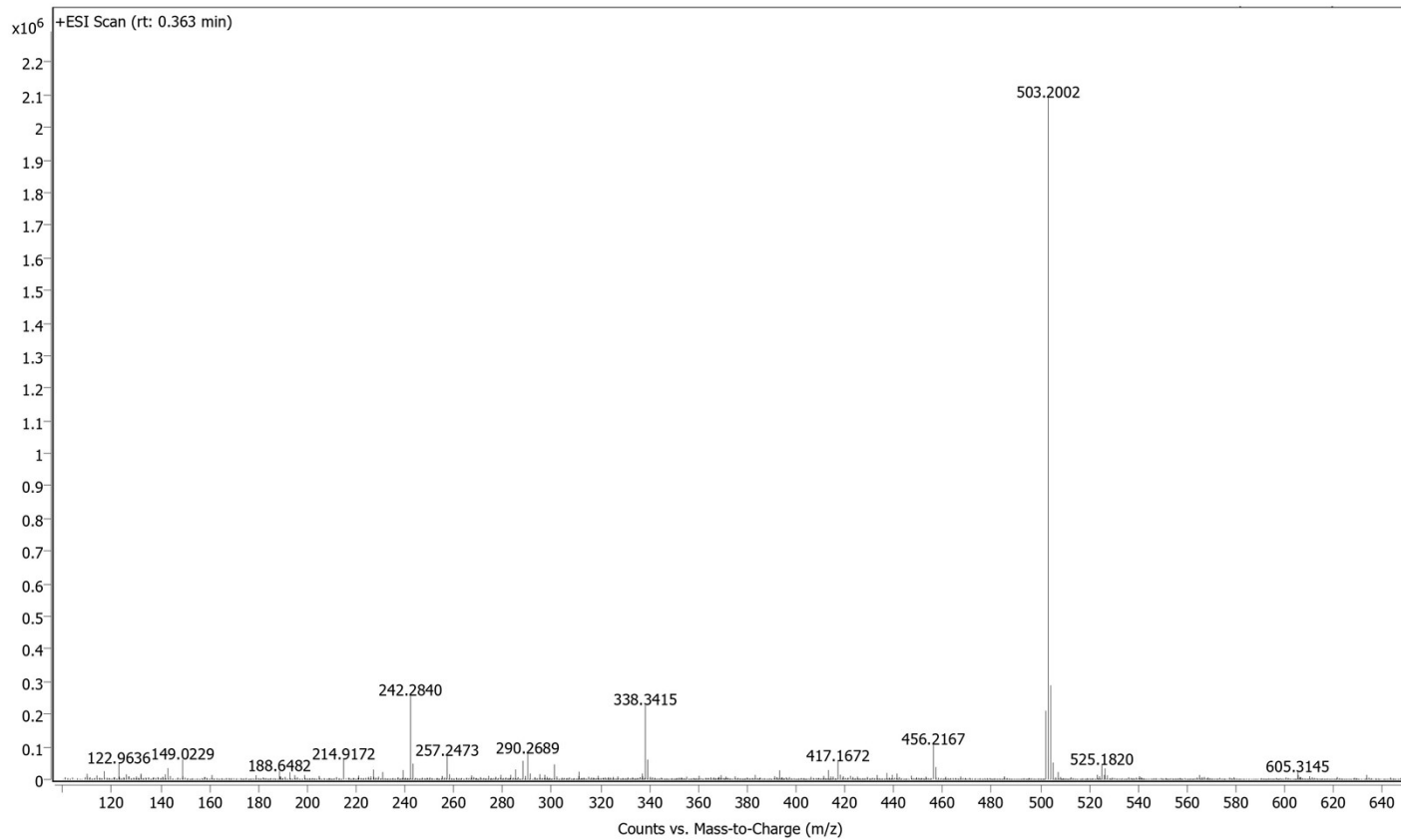
Fig. S4. The HRMS of compound 6.
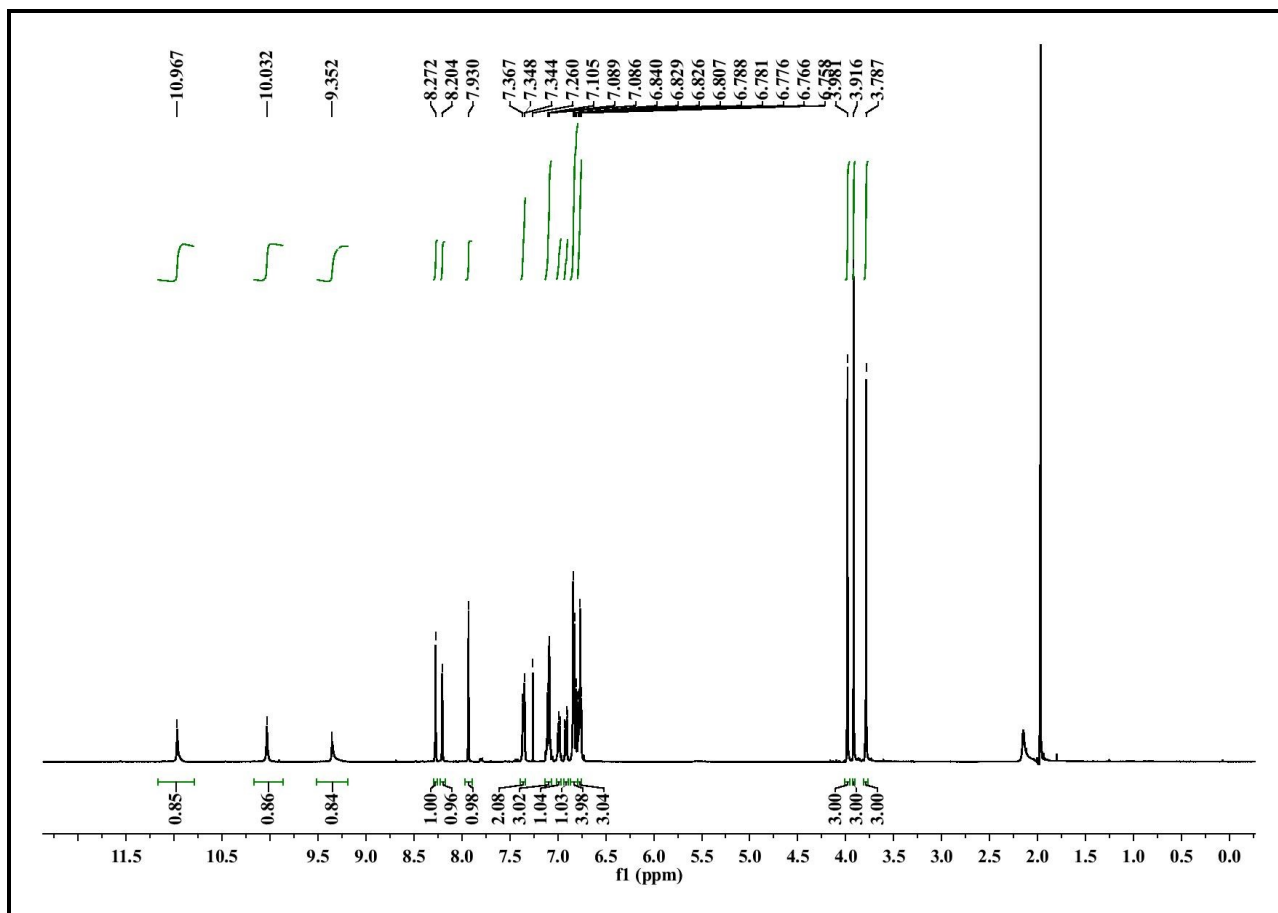
Fig. S5. ^{1}H NMR Spectrum of **7** in CDCl$_3$.
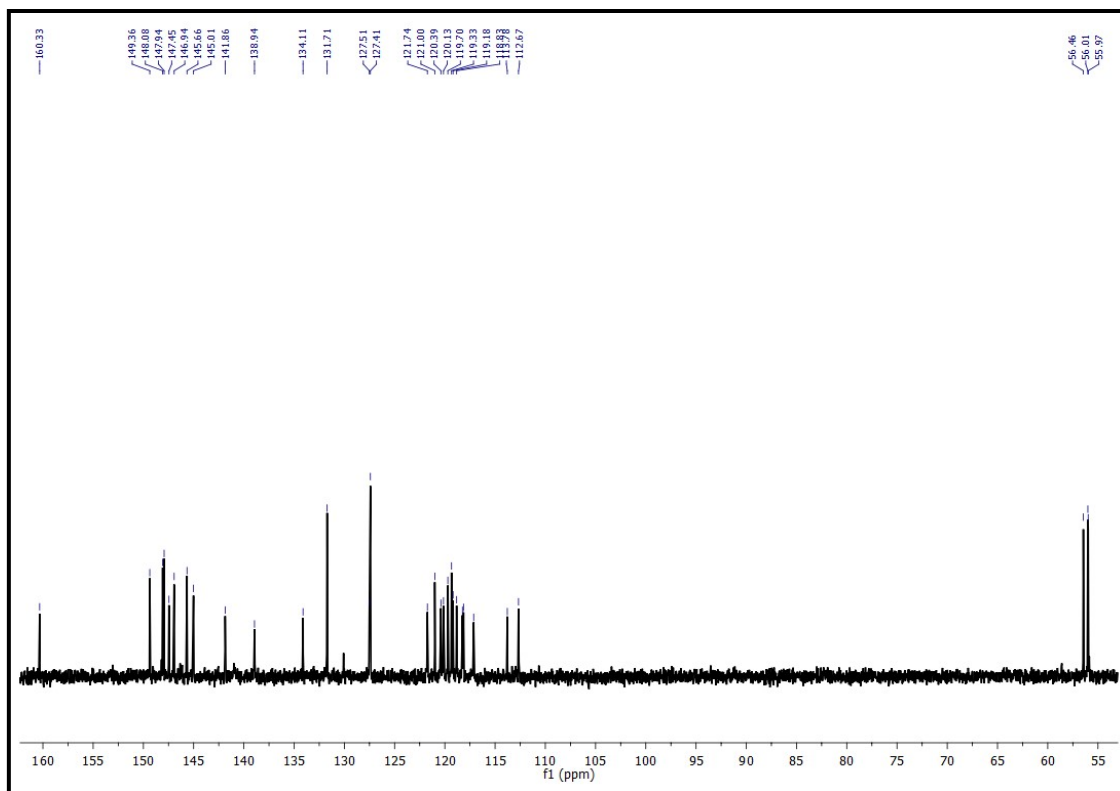
Fig. S6. ^{13}C NMR Spectrum of **7** in DMSO-d$_6$.
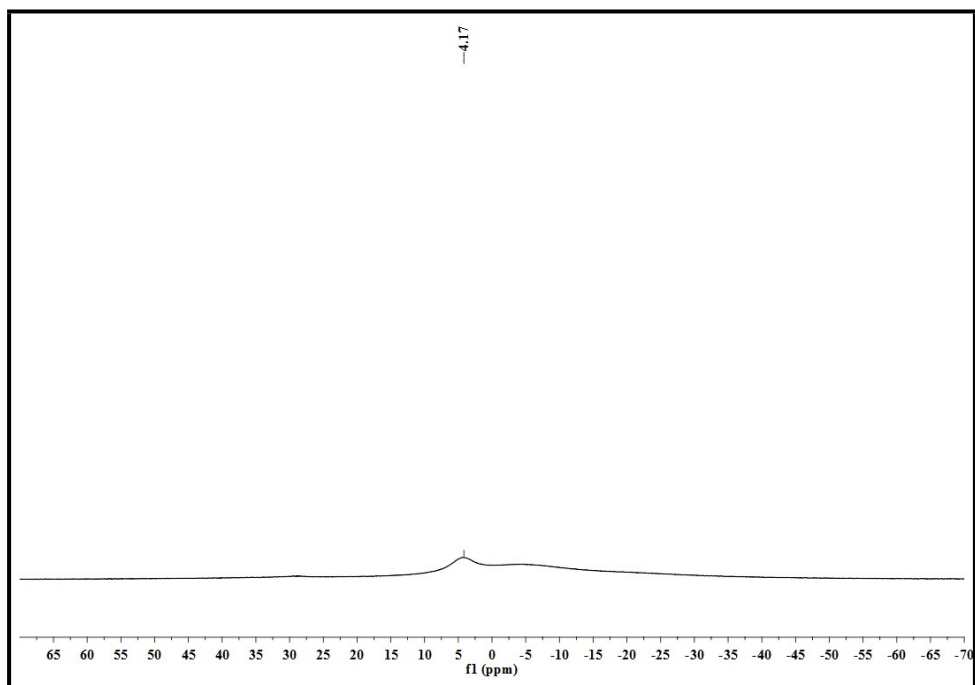
Fig. S7. ^{11}B NMR Spectrum of **7** in CDCl$_3$.
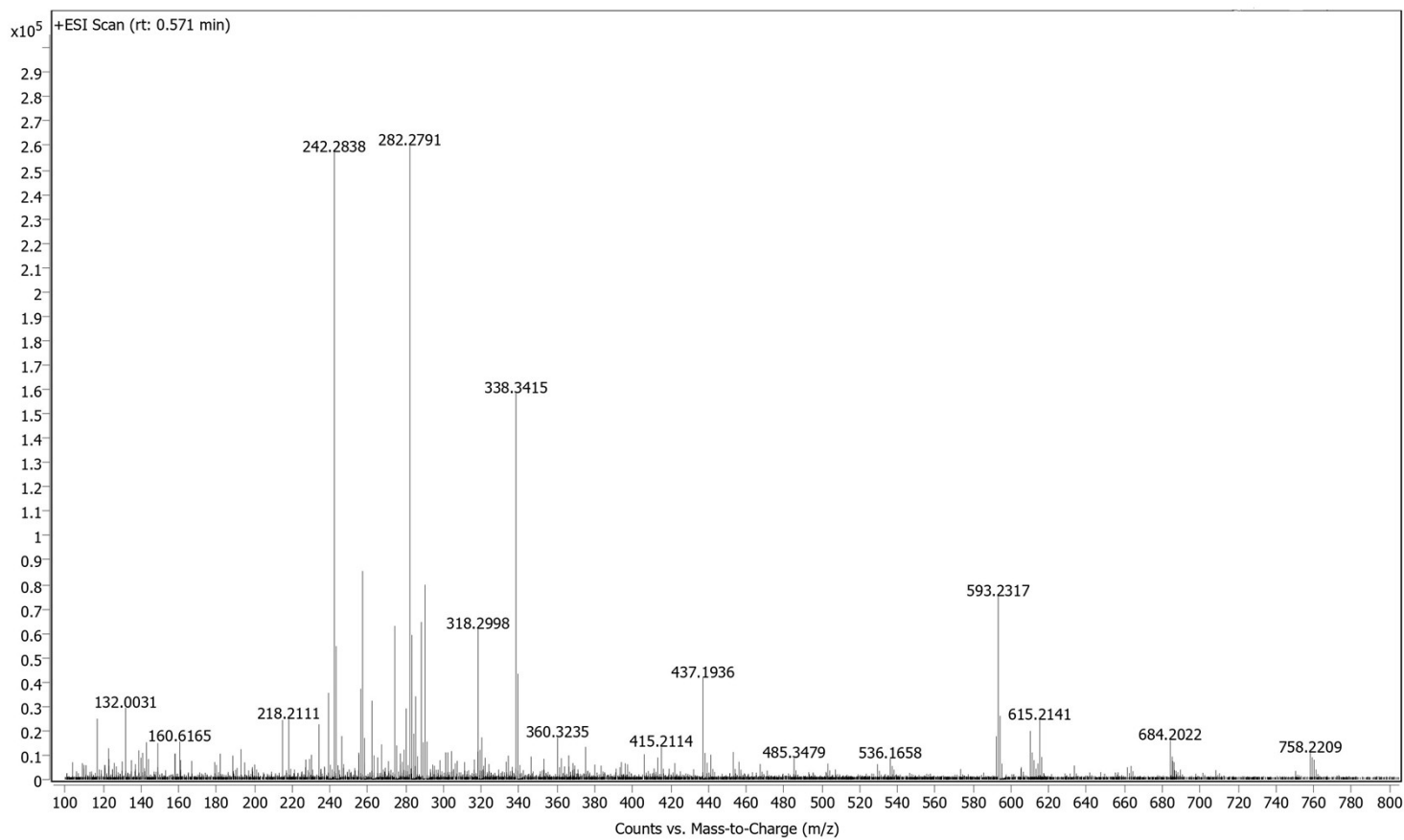
Fig. S8. The HRMS of compound 7.
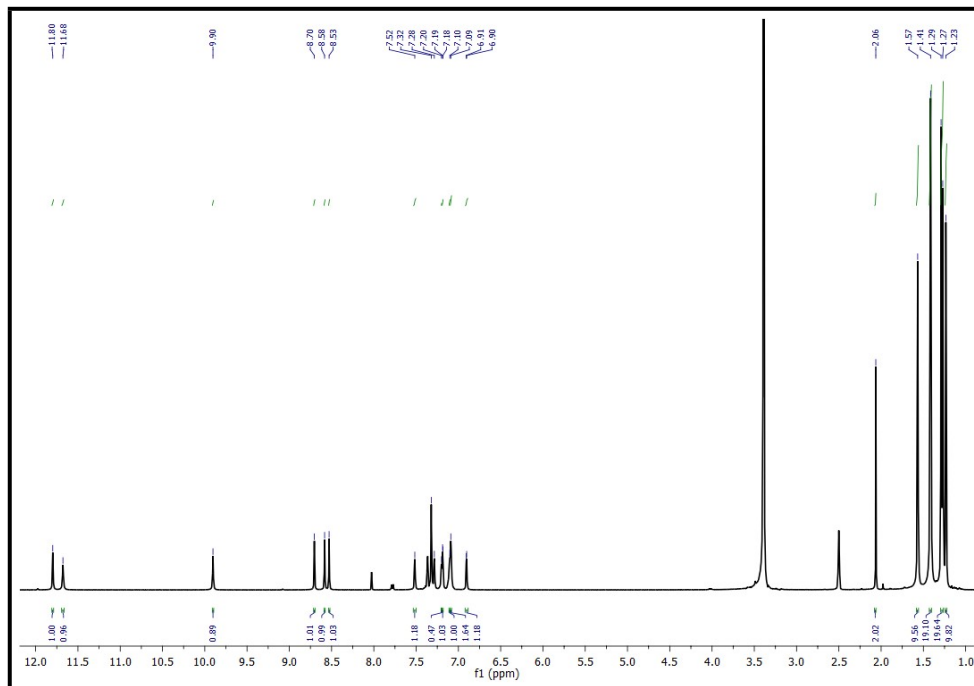
Fig. S9. ^{1}H NMR Spectrum of **8** in DMSO-d$_{6}$.
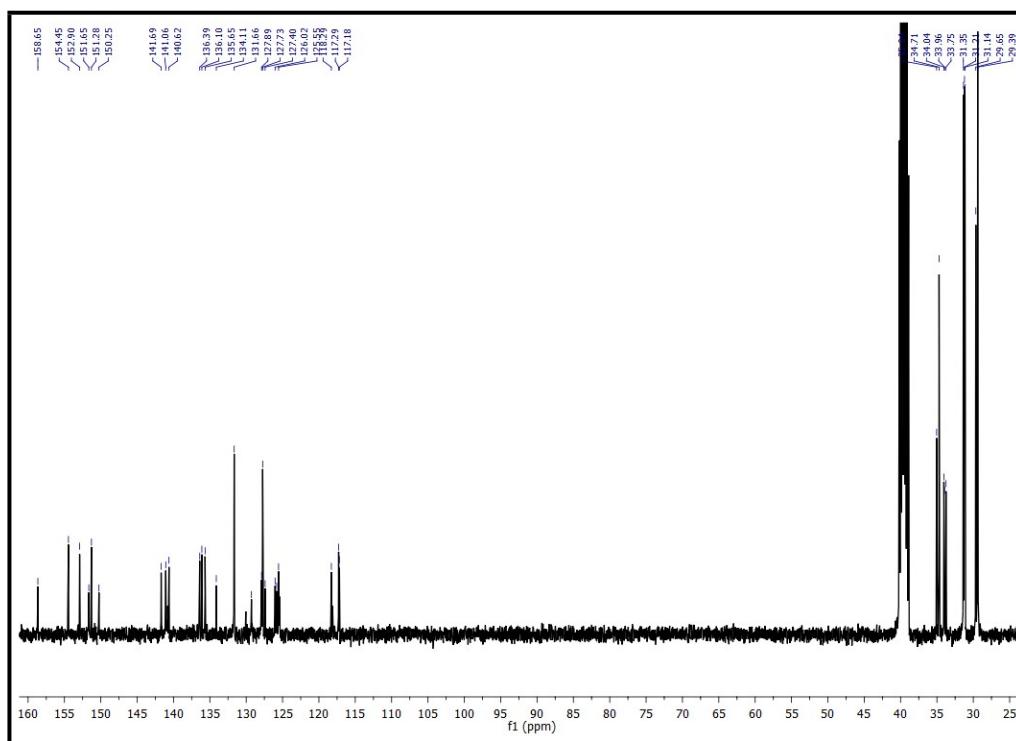
Fig. S10. ^{13}C NMR Spectrum of **8** in DMSO-d$_{6}$.

13
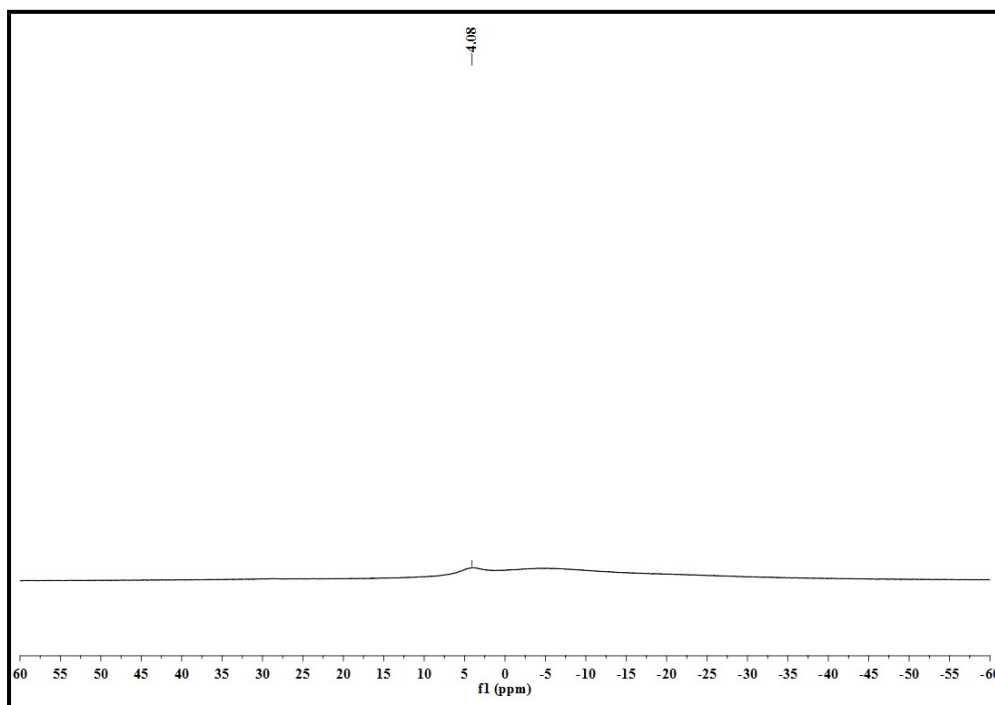
Fig. S11. ^{11}B NMR Spectrum of **8** in CDCl$_3$.

LN-01 #83   RT: 0.84   AV: 1   NL: 1.39E7
T: FTMS + p ESI Full ms [150.0000-1000.0000]
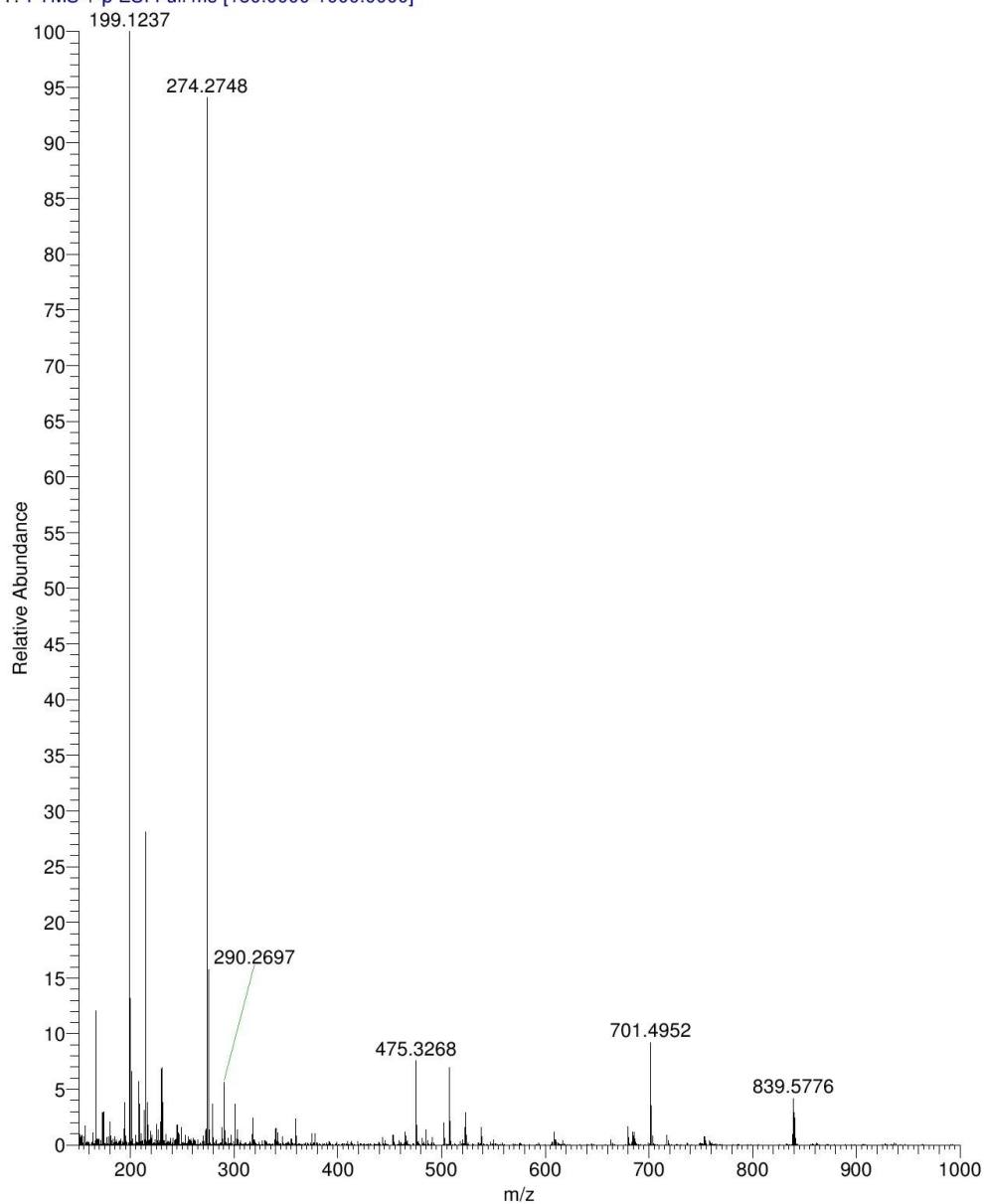
Fig. S12. The HRMS of compound 8.
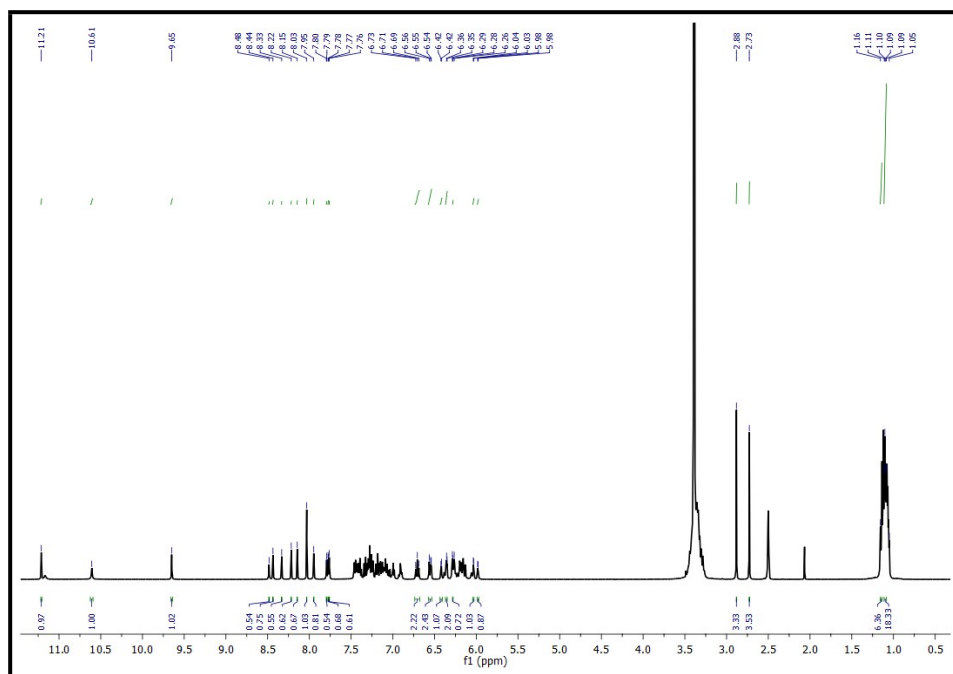
Fig. S13. ¹H NMR Spectrum of **9** in DMSO-d*₆*.
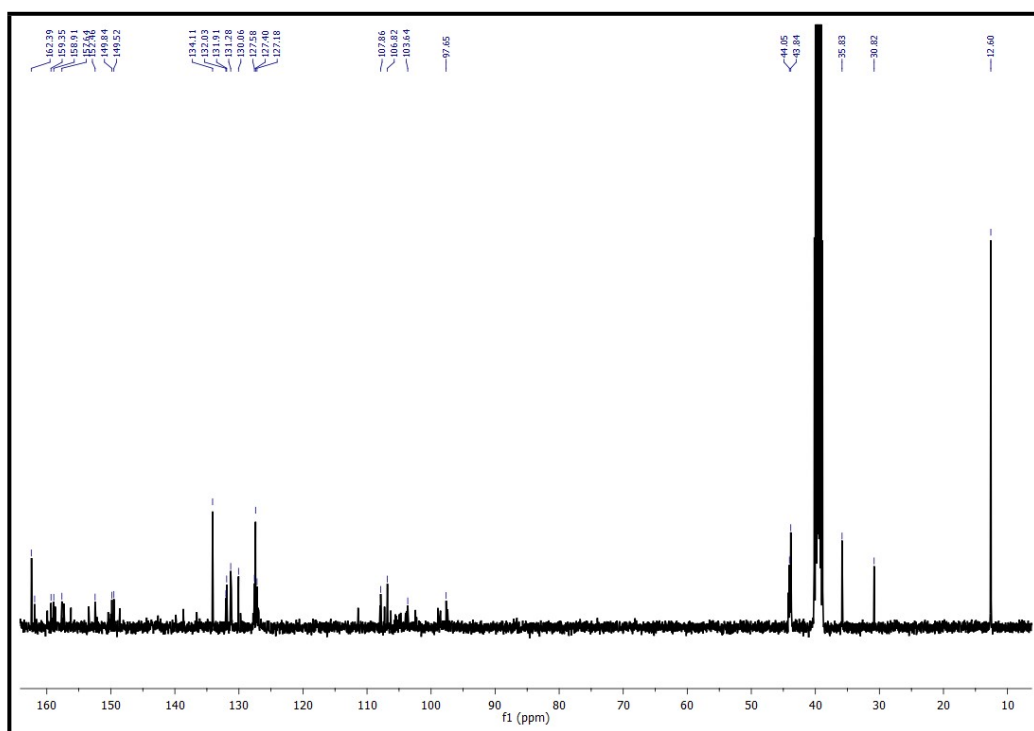
Fig. S14. ¹³C NMR Spectrum of **9** in DMSO-d*₆*.
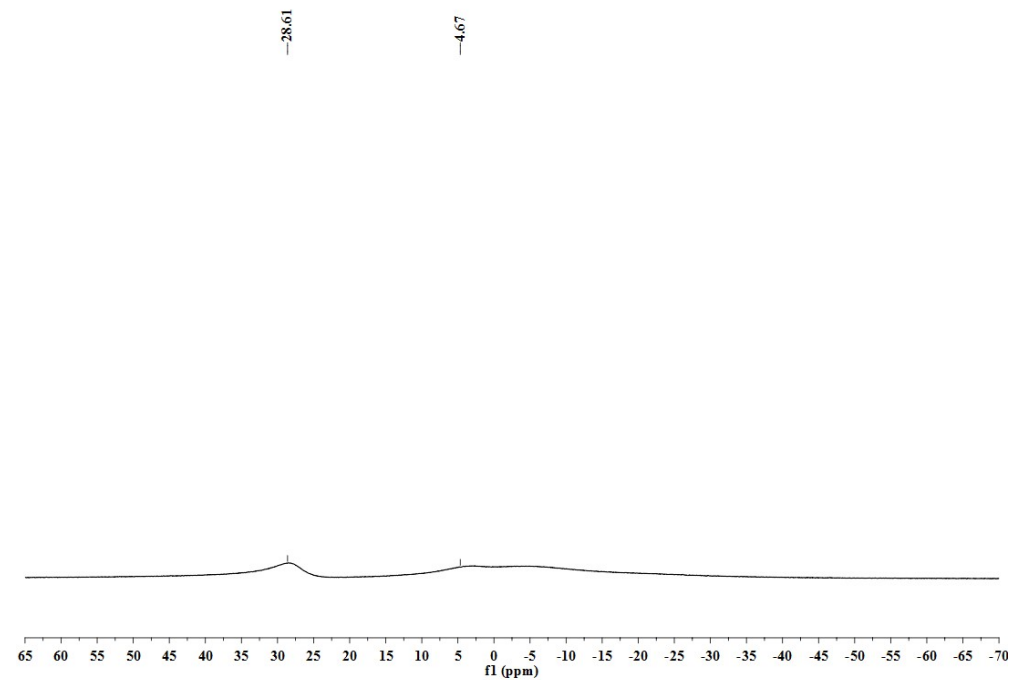
Fig. S15 ^{11}B NMR Spectrum of **9** in CDCl$_3$.

LN-04 #45 RT: 0.46 AV: 1 NL: 4.62E8
T: FTMS + p ESI Full ms [150.0000-1000.0000]
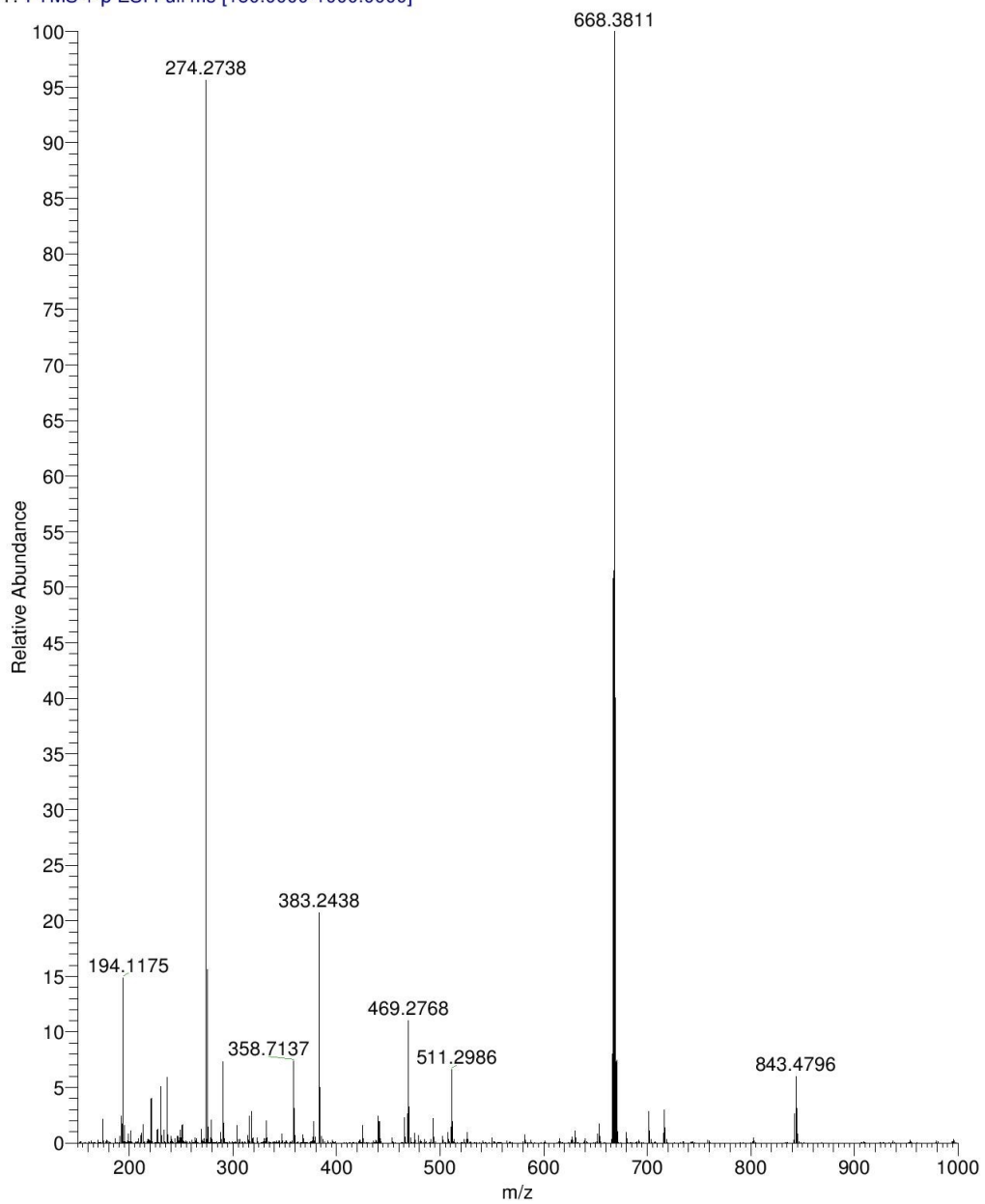
Fig. S16. The HRMS of compound **9**.
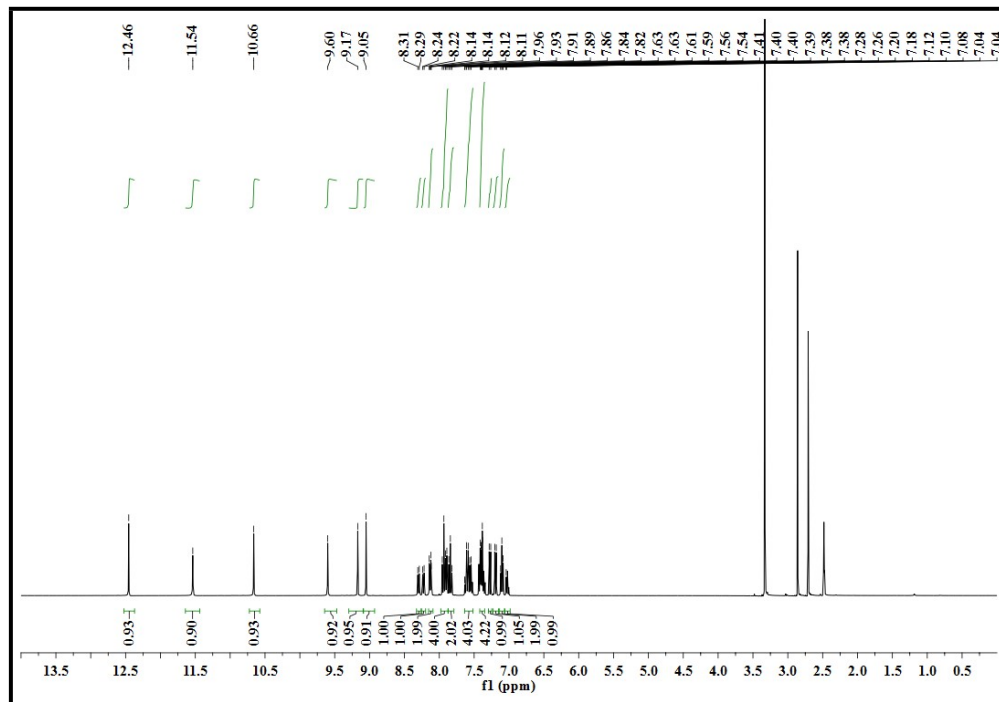
Fig. S17. ^{1}H NMR Spectrum of **10** in DMSO-d_6.
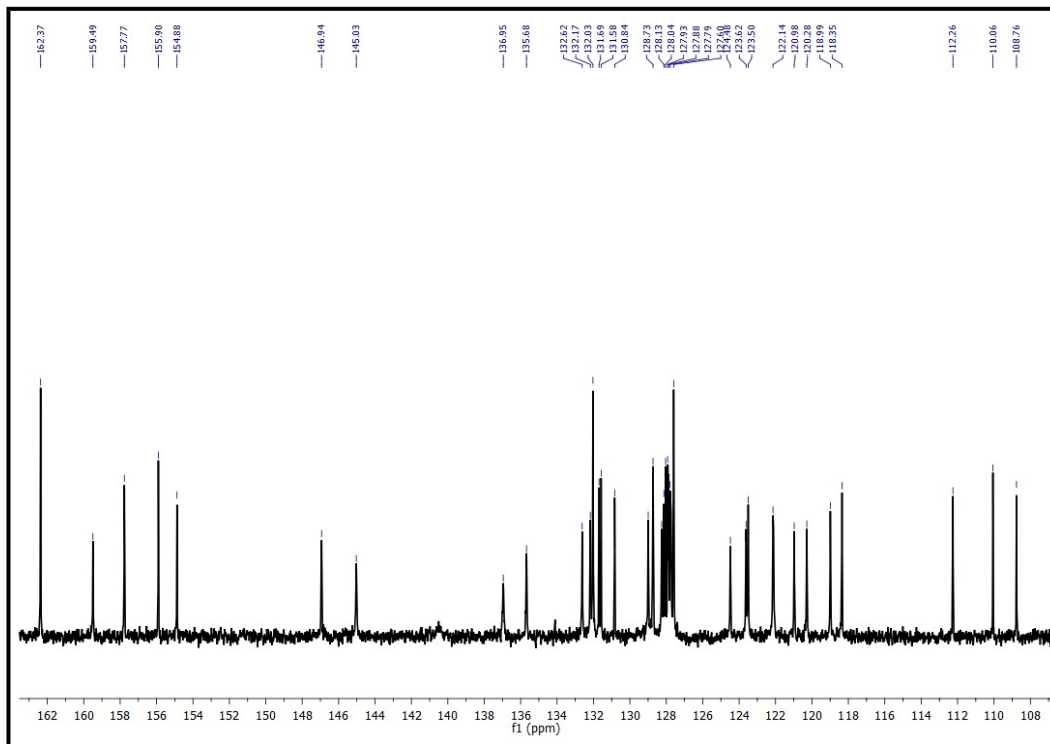
Fig. S18. ^{13}C NMR Spectrum of **10** in DMSO-d_6.
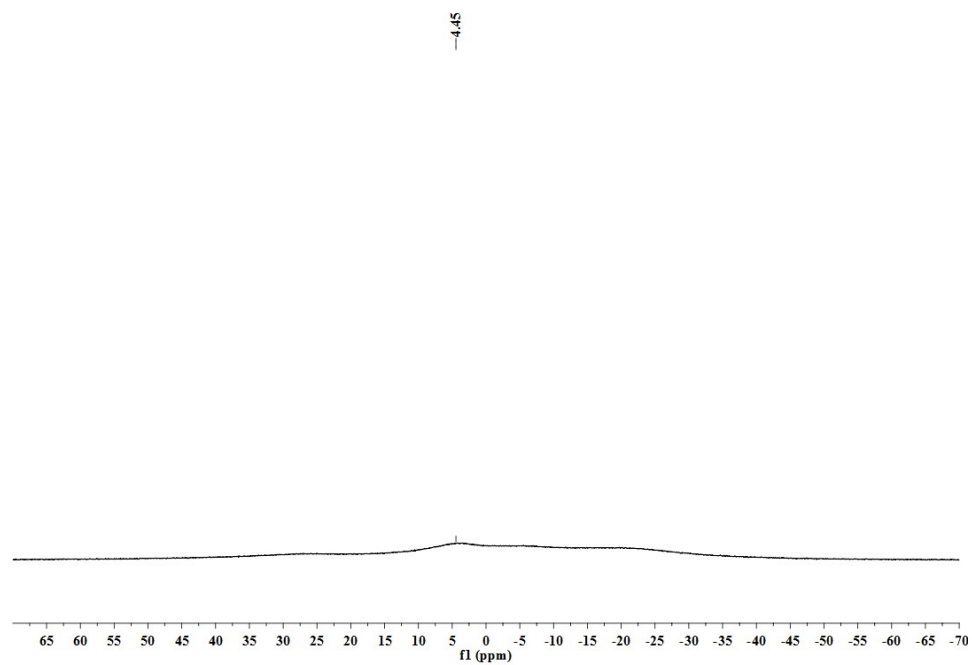
Fig. S19. ^{11}B NMR Spectrum of **10** in DMSO-d_6.
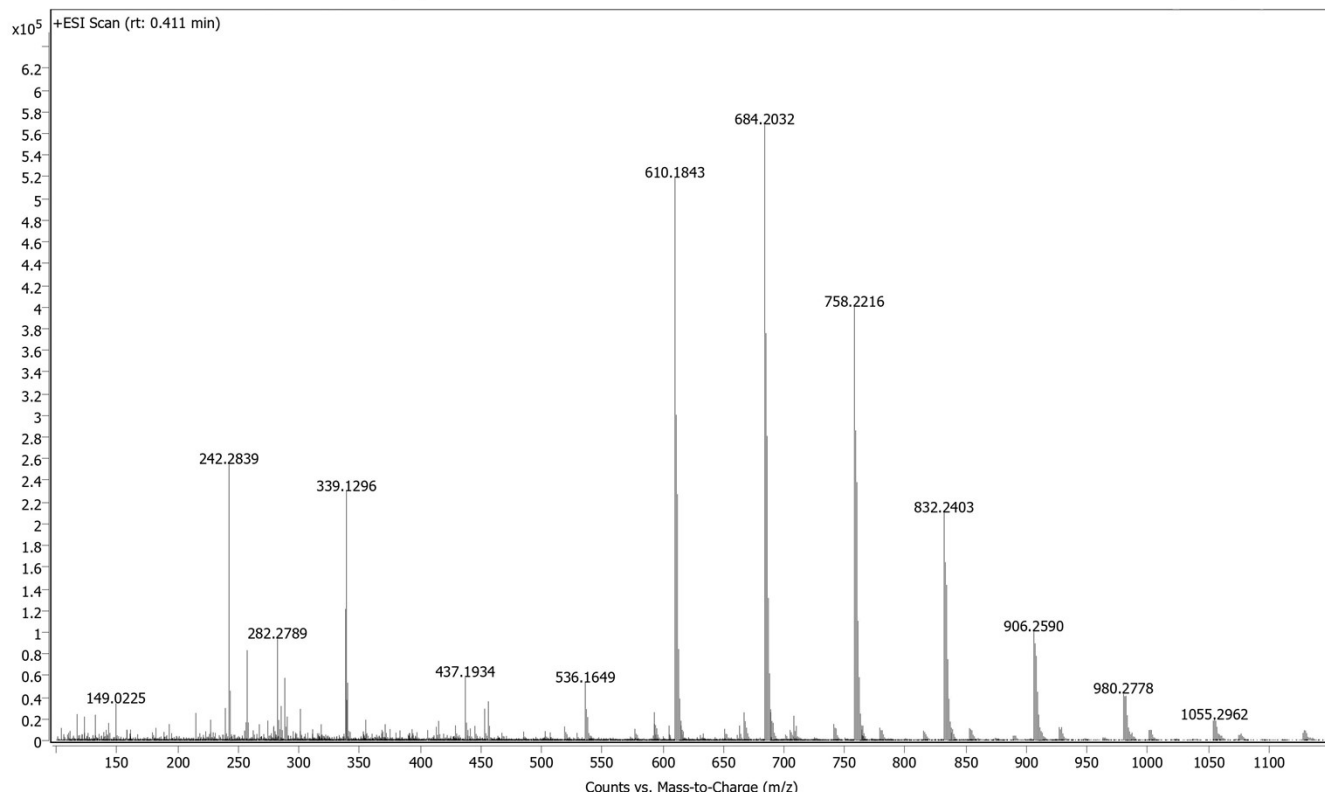
Fig. S20. The HRMS of compound 10.
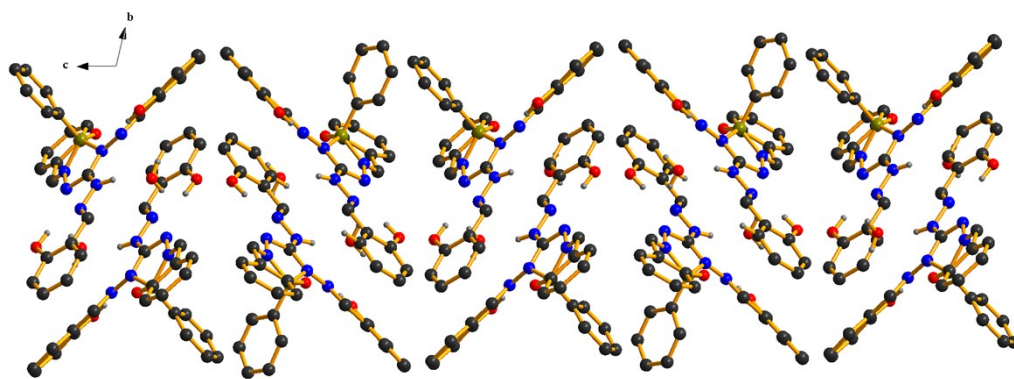
Fig. **S21** Two-dimensional chain like supramolecular network of **6**.
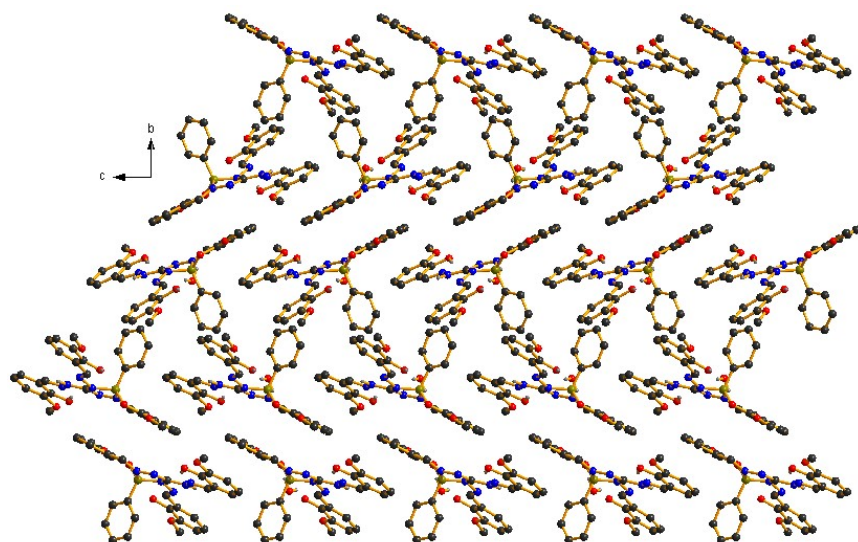
Fig. S22 Two-dimensional polymeric supramolecular network of **7**.
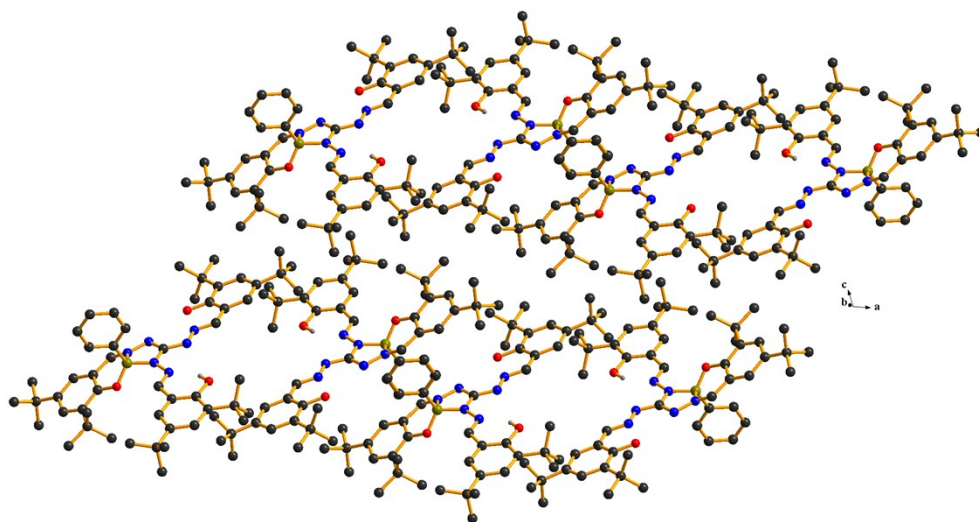
Fig. S23 Two-dimensional polymeric supramolecular network of **8**.
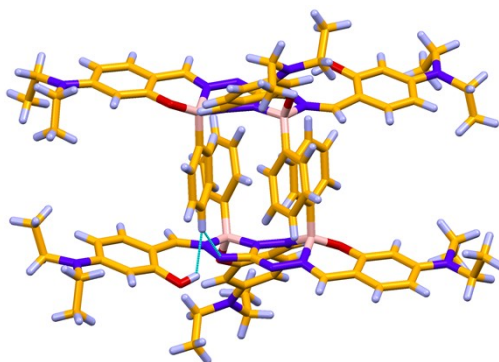
Fig. S24 Dimeric structure of compound **9**.
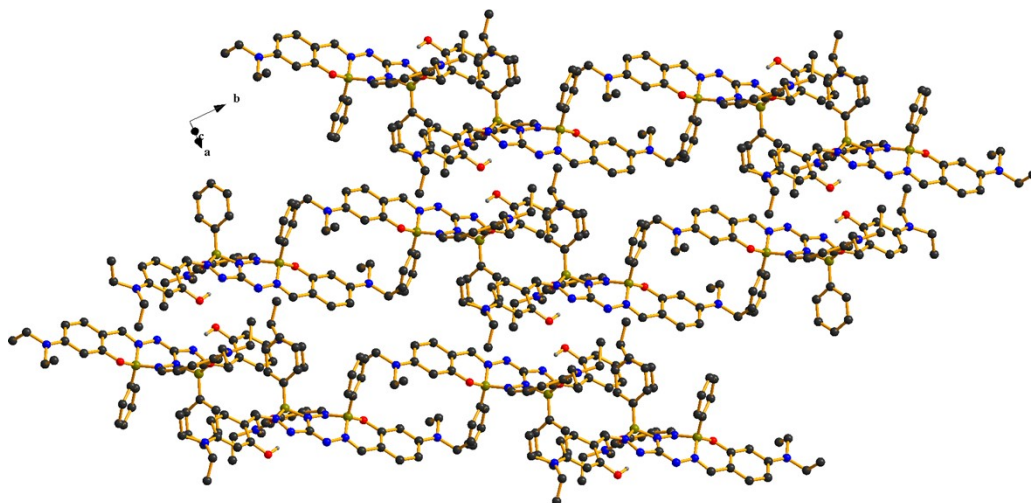
Fig. S25 Two-dimensional supramolecular network of **9**.
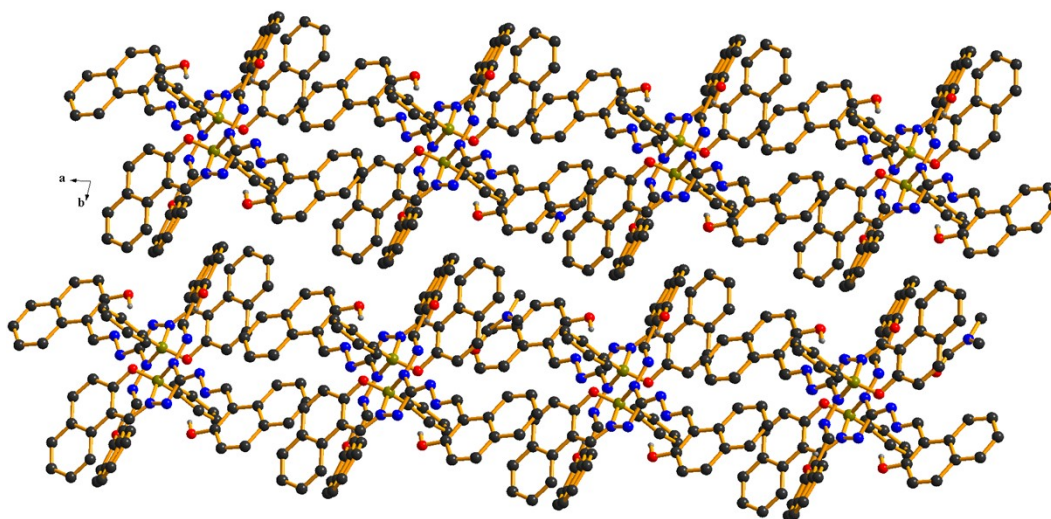
Fig. S26 Two-dimensional chain like supramolecular network of **10**.
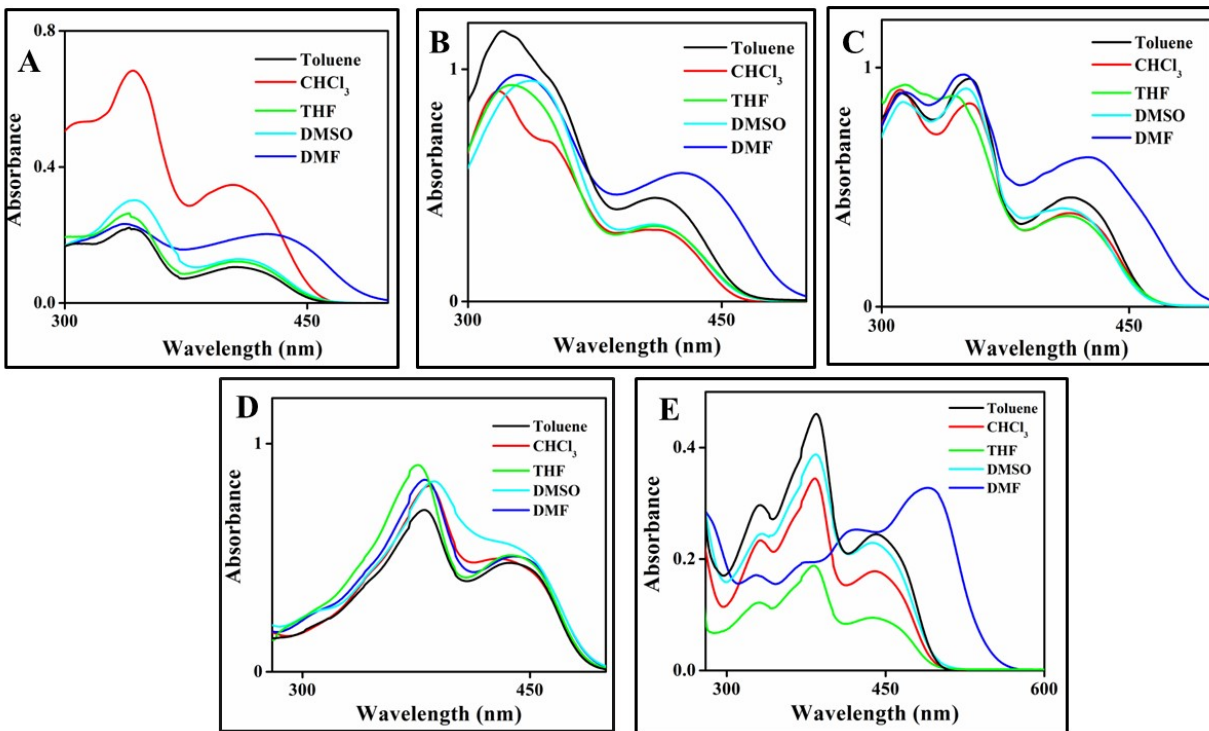
Fig. S27. Absorption spectra of boron compounds **6-10 (A - E)** in various solvents with different polarities at room temperature.
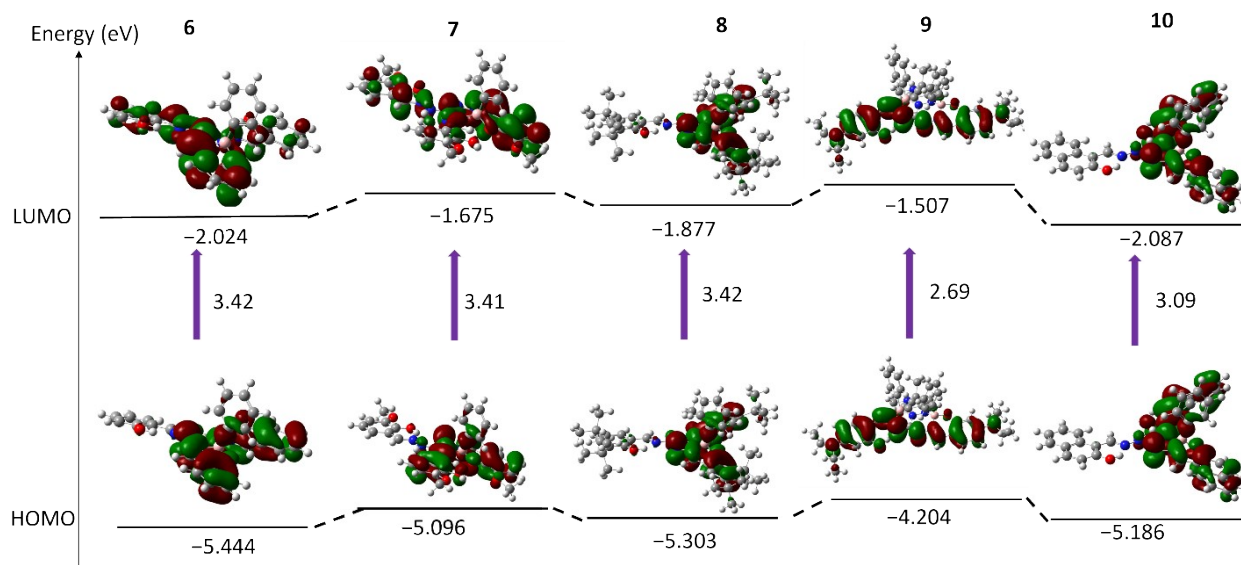
Fig. S28. Enol form of selected frontier molecular orbital of organoboron complexes **6-10** based on optimized ground state geometry. Calculation was performed at B3LYP/6-31G(d) level with Gaussian 16.
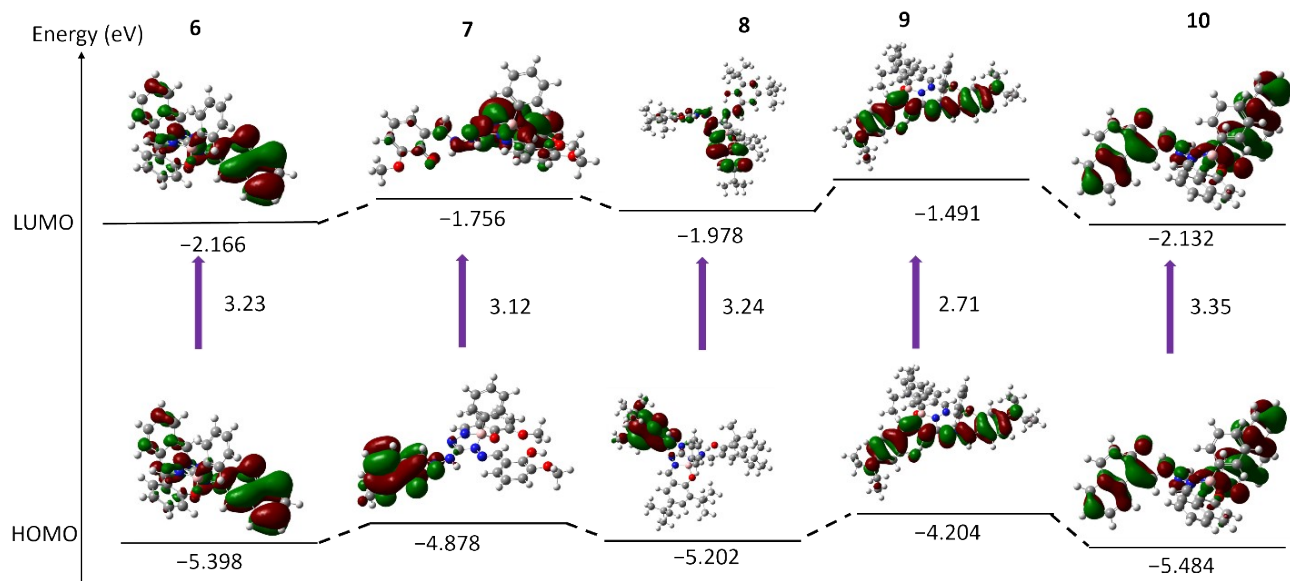
Fig. S29. Keto form of selected frontier molecular orbital of organoboron complexes **6-10** based on optimized ground state geometry. Calculation was performed at B3LYP/6-31G(d) level with Gaussian 16.

Table S2. Selected bond lengths (A˚) for [6-10] from X-ray and calculated structures using the B3LYP 6-31G method.

	6	6 cal.	7	7 cal	8	8cal	9	9 cal	10	10cal
B1-N2	1.583(4)	1.582	1.574(2)	1.586	1.567(5)	1.578	1.520(3)	1.534	1.564(3)	1.574
B1-N3	1.566(4)	1.568	1.561(3)	1.566	1.542(3)	1.567	1.571(5)	1.593	1.561(1)	1.565
B1-O1	1.450(4)	1.468	1.459(3)	1.465	1.454(3)	1.469	1.462(4)	1.478	1.463(1)	1.472
B1-C23	1.597(3)	1.612	1.611(3)	1.566	1.605(5)	1.616	1.592(1)	1.593	1.607(2)	1.614
B1-N2							1.573(3)	1.587		
B1-N3							1.566(2)	1.579		
B1-O1							1.444(3)	1.462		
B1-C23							1.599(2)	1.612		

Table S3. Electronic transition for organoboron complexes 6-10 calculated using the B3LYP 6-31G method.

Complexes	Transition	MO Contribution	Energy gap		Oscillator Strength (f)
			ev	nm	
6	S_0-S_1	HOMO ⟶ LUMO	3.42	371	0.4242
7	S_0-S_1	HOMO ⟶ LUMO	3.41	377	0.3129
8	S_0-S_1	HOMO ⟶ LUMO	3.42	374	0.3617
9	S_0-S_1	HOMO ⟶ LUMO	2.69	416	0.4507
10	S_0-S_1	HOMO ⟶ LUMO	3.09	400	0.5116

Table S4. UV-visible absorption and emission spectra of **6-10** in different solvents at room temperature.

Solvents		Toluene	CHCl$_3$	THF	DMSO	DMF
6	λ_{abs} (nm)	342, 409	343, 405	341, 409	342, 409	338, 432
	λ_{em} (nm)	485, 507	487, 505	485, 502	479, 518	481, 515
	Φ_F	0.006	0.010	0.001	0.016	0.020
7	λ_{abs} (nm)	320,414	317,415	327,415	338,415	330,428
	λ_{em} (nm)	500,535	499	510	496,544	498,463
	Φ_F	0.008	0.007	0.004	0.009	0.014
8	λ_{abs} (nm)	353, 416	354, 416	344, 415	352, 413	350, 428
	λ_{em} (nm)	482, 522	481, 499	480, 501	482, 518	478, 533
	Φ_F	0.016	0.017	0.006	0.004	0.040
9	λ_{abs} (nm)	379, 439	380, 436	376, 441	386, 443	382, 440
	λ_{em} (nm)	541	509, 560	503, 556	478,573	574
	Φ_F	0.012	0.046	0.005	0.012	0.088
10	λ_{abs} (nm)	330, 383, 441	331, 383, 441	329, 382, 441	332, 384, 437	329, 371, 492
	λ_{em} (nm)	507, 533	501, 529	503,530	507,539	550
	Φ_F	0.052	0.026	0.004	0.006	0.031
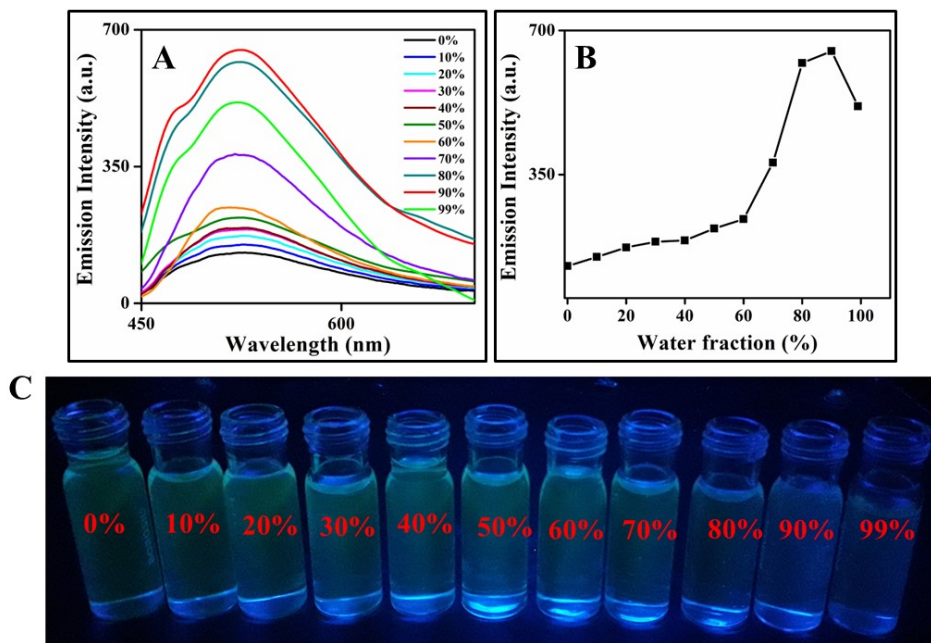
Fig. S30. (A) Emission spectra of **6** in different water fractions in THF and water mixture binary solvent; λ_{ex} = 420 nm. (B) Plots of emission intensity *vs* water fraction. (C) Fluorescent images in different water fractions (under UV light).
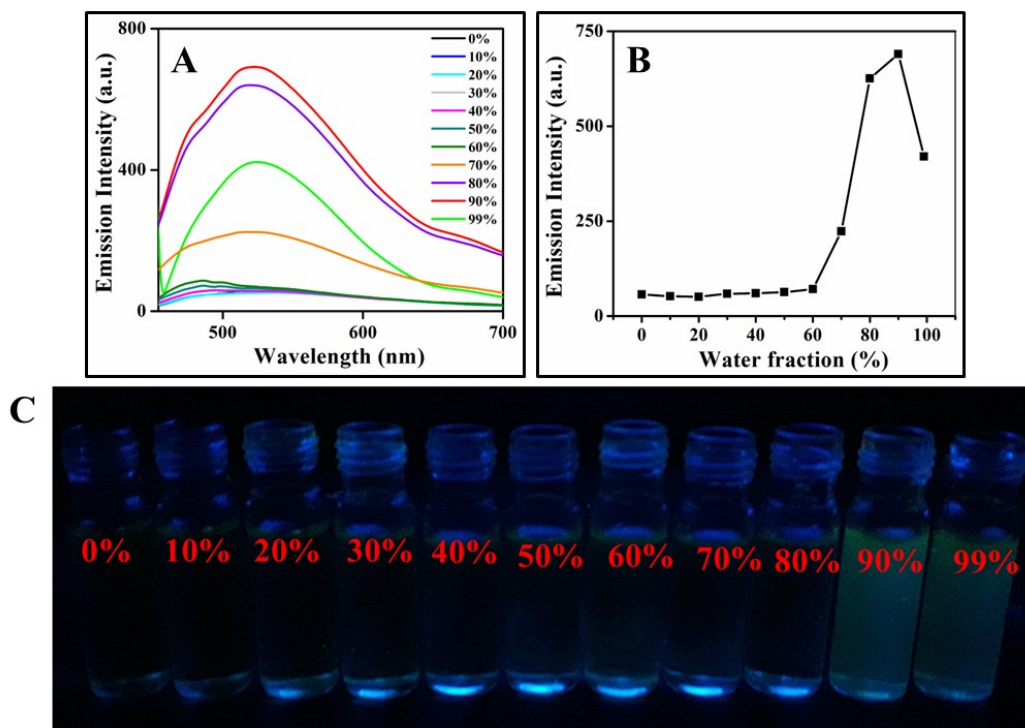
Fig. S31. (A) Emission spectra of **7** in different water fractions in THF and water mixture binary solvent; λ_{ex} = 420 nm. (B) Plots of emission intensity *vs* water fraction. (C) Fluorescent images of in different water fractions (under UV light).
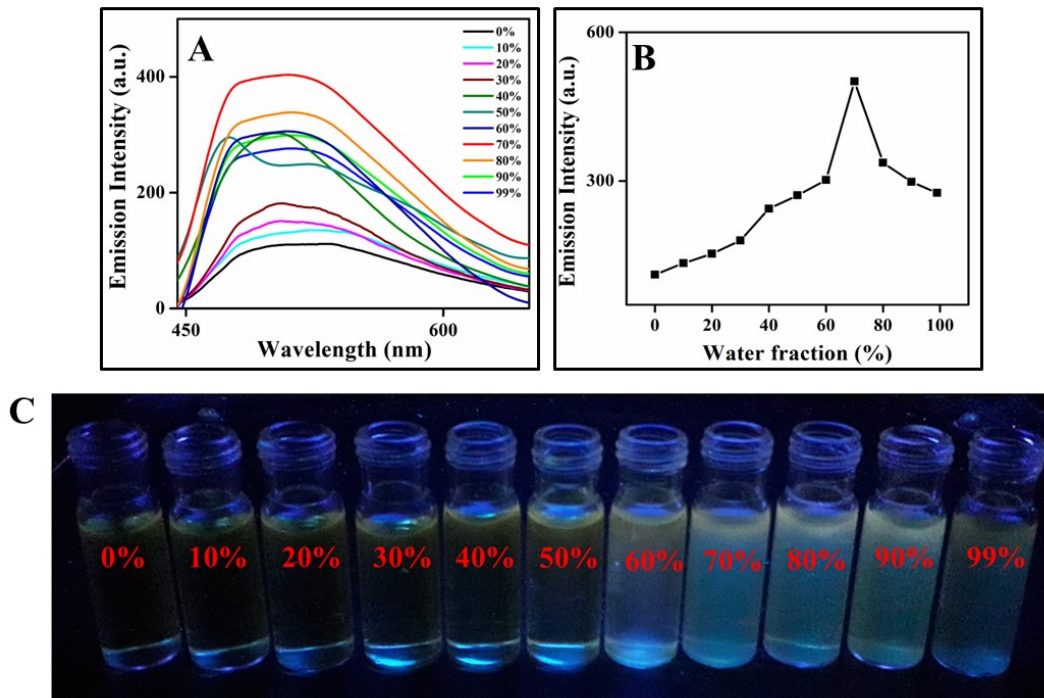
Fig. S32. (A) Emission spectra of **8** in different water fractions in THF and water mixture binary solvent; λ_{ex} = 420 nm. (B) Plots of emission intensity *vs* water fraction. (C) Fluorescent images of in different water fractions (under UV light).
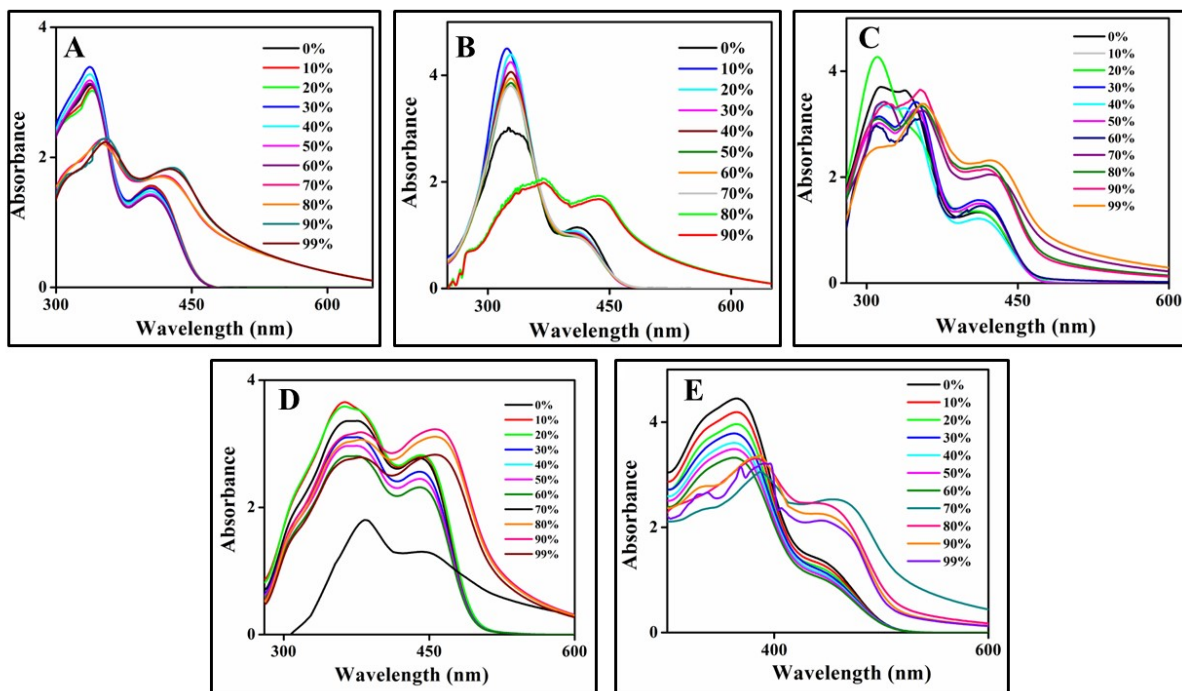
Fig. S33. UV-visible absorption spectra of compounds **6-10 (A-E)** in THF-H$_2$O (0-90 %) mixture with different water fractions.
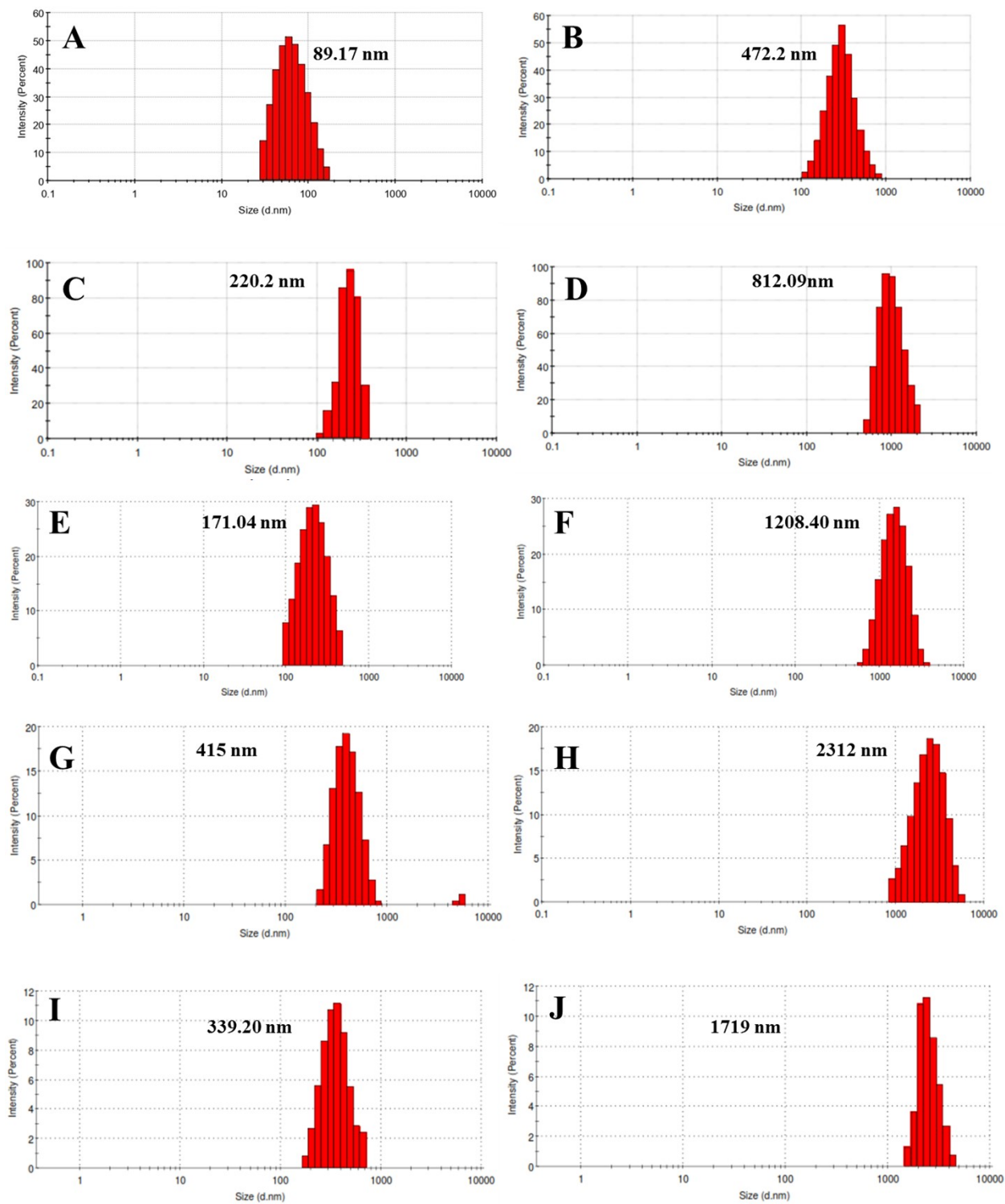
Fig. S34. DLS images of compounds (6-10) with particle size distribution in THF-H_2O mixture (A, B) **6** (60 & 90%), (C, D) **7** (70 & 90%), (E, F) **8** (50 & 70%), (G, H) **9** (70 & 90%) and (I, J) **10** (70 & 90%)

Table S5. Results from DLS for the complex **6-10.**

Complex	Percentage of water (%)	Particle size (nm)
6	60 & 90	89.17 & 472.2
7	70 & 90	220.2 & 812.09
8	50 & 70	171.04 & 1208. 04
9	70 & 90	415 & 2312
10	70 & 90	339.20 & 1719
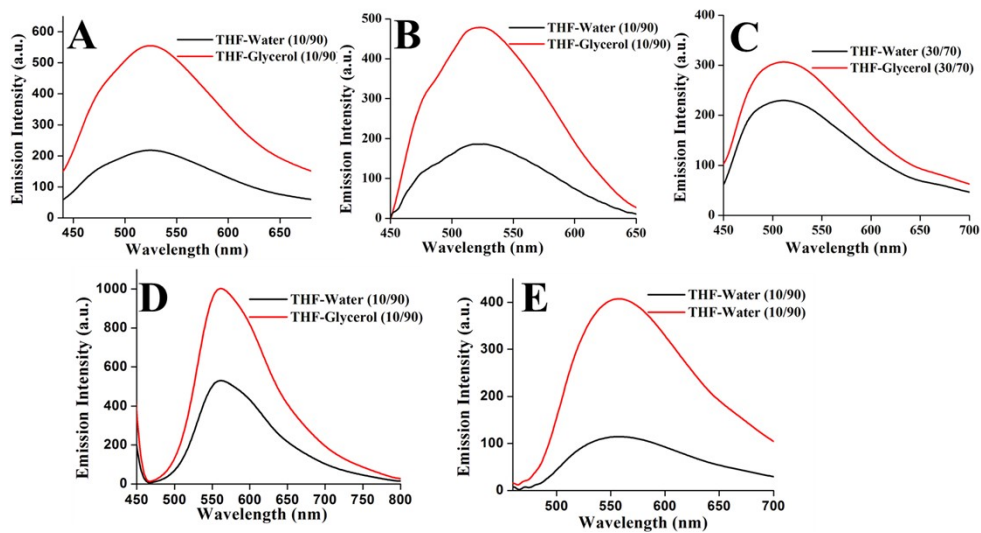
Fig. S35. Emission spectra of **6 -10** in THF-H_2O and THF-glycerol.
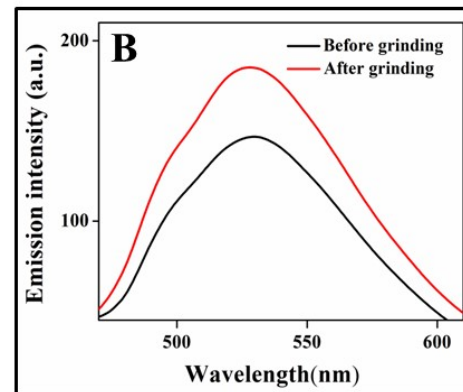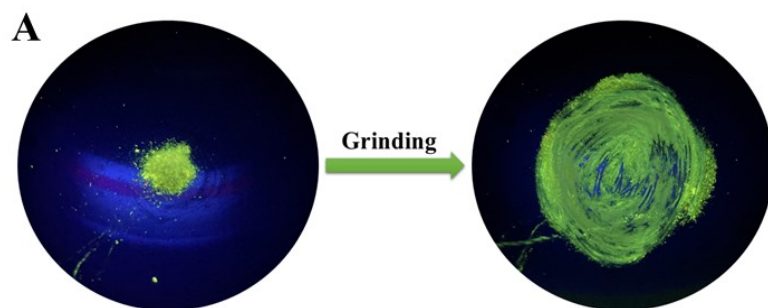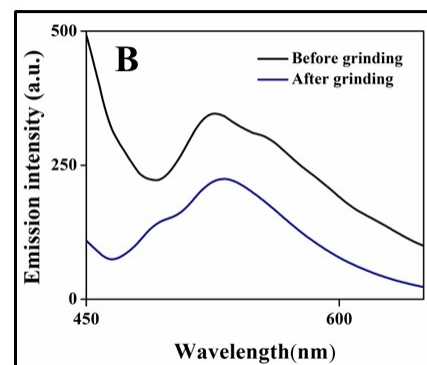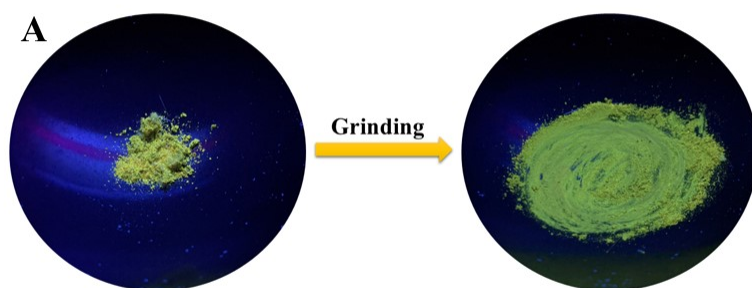
Fig. S36. (A). Images of the boron compounds (**7 & 8**) under UV-lamp. (B) Solid state emission spectra of compounds (**7 & 8**) crystals and ground samples.
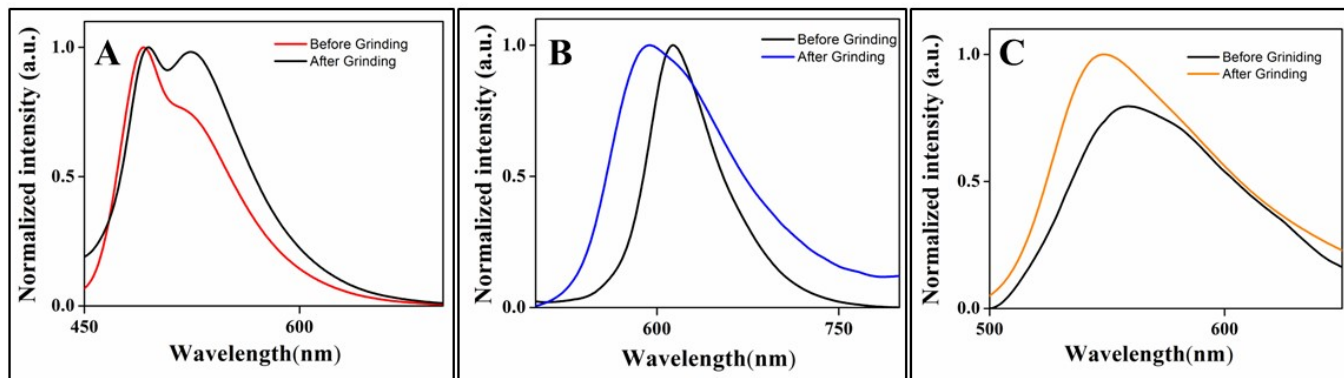
Fig. S37. (A) Normalized spectrum of the compound **6** before and after grinding. (B) Normalized spectrum of the compound **9** before and after grinding. (C) Normalized spectrum of the compound **10** before and after grinding.
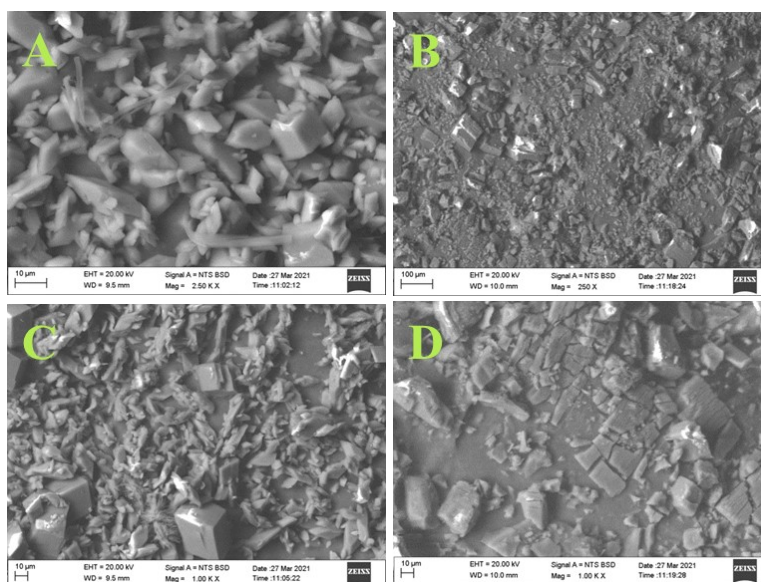
Fig. S38. SEM images of compounds **9 &10** (**A&B**) before and (**C&D**) after grinding respectively.

Table S6. Crystal parameters and structure refinement data for compound **6-10**.

| Parameters	6	7	8
Empirical formula	$C_{28}H_{25}BN_6O_4$	$C_{31}H_{29}BN_6O_6,2(C_2H_3N),H_2O$	$C_{55}H_{75}B\,N_{7\cdot50}O_3$
Formula weight	520.35	692.53	900.53
Temperature	100(2) K	295(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2$_1$/c	P-1
Unit cell dimensions	a = 9.9278(5) Å b = 14.8243(8) Å c = 17.6465(10) Å α = 104.209(3)° β = 91.481(3)° γ = 94.206(3)°	a= 12.1862(5) Å b = 28.1636(12) Å c = 10.6937(5) Å α = 90° β = 107.529(4)° γ = 90°	a= 14.3032(13) Å b = 14.3886(14) Å c = 14.4404(14) Å α = 93.878° β = 113.614(4)° γ = 90.966(5)°
Volume	2508.3(2) Å^3	3499.7(3) Å^3	2713.6(5) Å^3
Z	4	4	2
Density (calculated)	1.378 Mg/m^3	1.314 Mg/m^3	1.102 Mg/m^3
Absorption coefficient	0.094 mm^{-1}	0.093 mm^{-1}	0.069 mm^{-1}
F(000)	1088	1456	974
Crystal size (mm^3)	0.45 x 0.30 x 0.080	0.32 x 0.12 x 0.09	0.45 x 0.20 x 0.17
Theta range for data collection	1.613 to 28.359°	3.75 to 28.75°	1.420 to 26.455°
Index ranges	-13<=h<=13, -19<=k<=19, -23<=l<=23	-16<=h<=12, -28<=k<=38, -10<=l<=14	-17<=h<=16, -17<=k<=17, -14<=l<=18
Reflections collected	21795	19478	15200
Independent reflections	21795[R(int) = 0.0572]	8402[R(int) = 0.0596]	10400 [R(int) = 0.0513]
Completeness to theta = 25.000°	99.3 %	96.7 %	94.3 %
Data / restraints / parameters	21795/7/727	8402/1/485	10400 / 105 / 672
Goodness-of-fit on F^2	1.024	1.026	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0650, wR2 = 0.1467	R1 = 0.0596, wR2 = 0.10896	R1 = 0.0704, wR2 = 0.1644
R indices (all data)	R1 = 0.1012, wR2 = 0.1665	R1 = 0.1089, wR2 = 0.1445	R1 = 0.1448, wR2 = 0.2010
Largest diff. peak and hole (e.Å^{-3})	1.550, -0.462	0.194, -0.216	0.448, -0.283

Parameters	**9**	10
Empirical formula	$C_{46}H_{53}B_2 N_9O_3$	$C_{43}H_{36}BN_7O_4$
Formula weight	801.59	725.60
Temperature	100(2) K	100(2)K
Wavelength	0.71073 Å	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 13.9824(9) Å b = 19.1267(12) Å c = 20.5066(13) Å α = 90.406(4)° β = 108.715(3)° γ = 90.449(3)°	a = 11.3918(7) Å b = 11.9970 (8) Å c = 13.9478 (8) Å α = 75.157(3)° β = 89.324(3)° γ = 79.110(4)°
Volume	5193.8(6) Å^3	1808.1(2) Å^3
Z	4	2
Density (calculated)	1.025Mg/m^3	1.333 Mg/m^3
Absorption coefficient	0.065 mm^{-1}	0.087 mm^{-1}
F(000)	1704	760
Crystal size (mm^3)	0.29 x 0.15 x 0.10	0.30 x 0.12 x 0.07
Theta range for data collection	1.487 to 25.027°	1.511 to 28.399°
Index ranges	-16<=h<=16, -22<=k<=22, -24<=1<=24	-15<=h<=15, -16<=k<=15, -18<=1<=18
Reflections collected	36644	17847
Independent reflections	18339[R(int) = 0.0348]	8985 [R(int) = 0.0361]
Completeness to theta = 25.000°	99.8 %	100.0 %
Data / restraints / parameters	18339 /115/ 1096	8985 / 0 / 505
Goodness-of-fit on F^2	1.047	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0682, wR2 = 0.1870	R1 = 0.0424, wR2 = 0.0989
R indices (all data)	R1 = 0.1011, wR2 = 0.2119	R1 = 0.0675, wR2 = 0.1133
Largest diff. peak and hole (e$^.$Å^{-3})	0.688, -0.404	0.314, -0.251

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