SUPPORTING INFORMATION

B-H Functionalization of Hydrogen-Rich $[(Cp^*V)_2(B_2H_6)_2]$: Synthesis and Structures of $[(Cp^*V)_2(B_2X_2)_2H_8]$ (X = Cl, SePh; $Cp^* = \eta^5\text{-}C_5Me_5$)

Anagha Haridas,[†] Sourav Kar,[†] Beesam Raghavendra,[†] Thierry Roisnel,[‡] Vincent Dorcet,[‡] and Sundargopal Ghosh*,[†]

[†]Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India. Tel: +91 44- 22574230; Fax: +91 44-22574202; E-mail: sghosh@iitm.ac.in

[‡]Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes, UMR 6226, F-35000 Rennes, France

I EXPERIMENTAL

I.1 Supplementary Data

I.2 Spectroscopic details

I Experimental

I.1 Supplementary Data

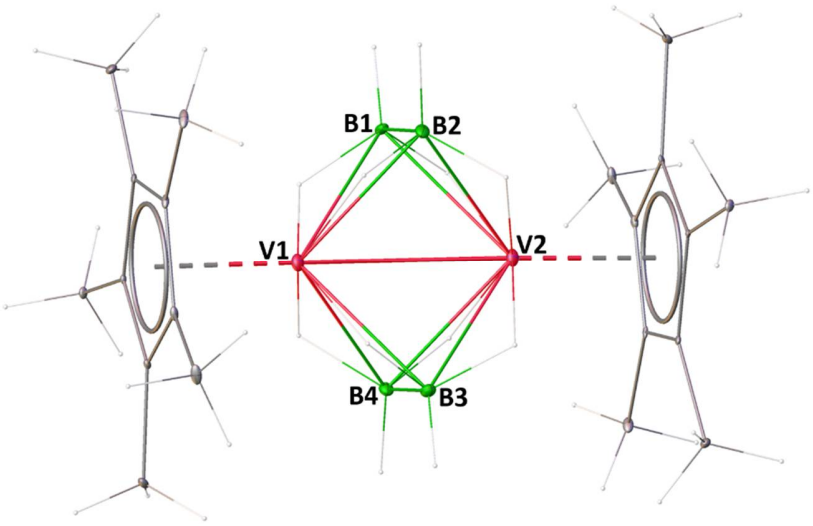

Figure S1. Molecular structure and labeling diagram for compound **1**. Selected bond lengths (Å) and bond angles (°): V1-V2 2.7820(9), V1-B1 2.300(4), V1-B2 2.295(4), V1-B3 2.301(4), V1-B4 2.307(4), B1-B2 1.752(7); B2-V1-V2 53.20(11), B2-V1-B1 44.81(16), B2-B1-V1 67.4(2), B2-V1-B1 44.81(16), B1-V1-B4 88.98(16).

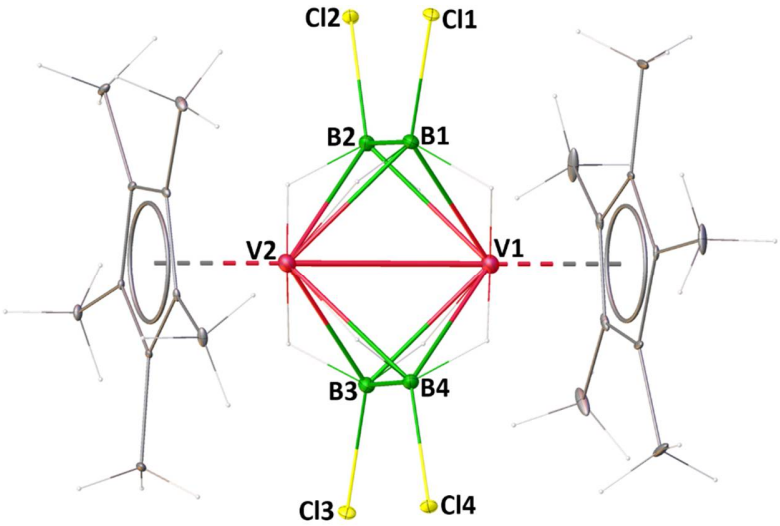

Figure S2. Molecular structure and labeling diagram for compound **2**. Selected bond lengths (Å) and bond angles (°): V1-V2 2.8389(6), V1-B1 2.302(3), V1-B2 2.302(3), V1-B3 2.306(3), B1-Cl1 1.844(3),B2-Cl2 1.844(3) B1-B2 1.755(5); B2-V1-V2 52.06(8), B1-V2-B2 44.64(12), B2-B1-V1 67.61(16), B2-V1-B1 44.80(12), B1-V1-B4 86.86(12), V1-B2-Cl2 140.52(18),V2-B2-Cl2 143.26(19), B2-B1-Cl1 115.7(2).

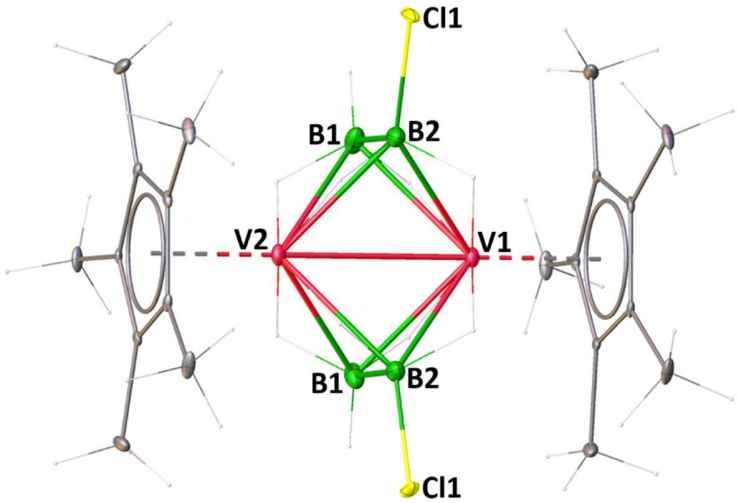

Figure S3. Molecular structure and labeling diagram for compound **3**. Selected bond lengths (Å) and bond angles (°): V1-V2 2.7946(7), V1-B1 2.304(3), V1-B2 2.293(3), B2-Cl1 1.791(3), B1-B2 1.746(4); B2-V1-V2 52.40(7),V1-B2-V2 75.14(9), B2-V2-B1 105.14(10), B2-B1-V1 67.61(16), B2-V1-B1 44.64(10), B2-V1-B1 105.02(10), B2-V1-B2 88.38(14), V1-B2-Cl1 143.38(15),V2-B2-Cl1 141.02(15), B1-B2-Cl1 113.63(19).

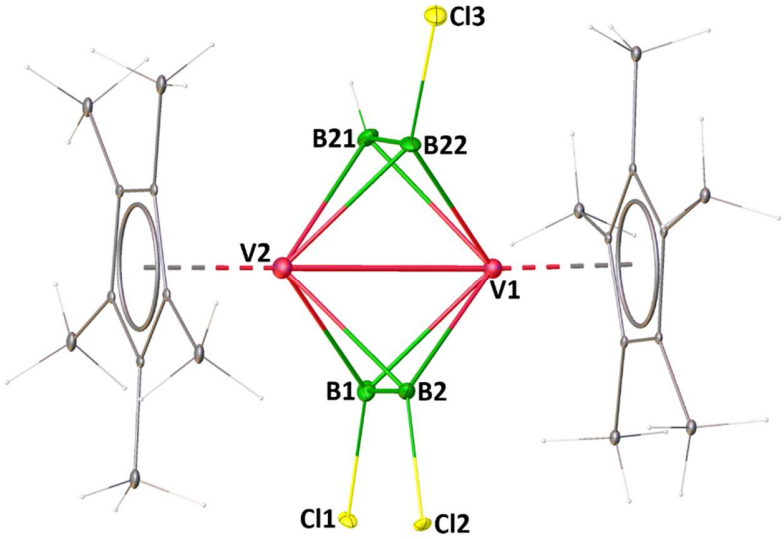

Figure S4. Molecular structure and labeling diagram for compound **4**. Selected bond lengths (Å) and bond angles (°): V1-V2 2.8105(15), V1-B2 2.268(9), V1-B22 2.295(7), B1-Cl1 1.825(9), V1-B21 2.328(9), B1-B2 1.732(13), B21-B22 1.749(15) ; V1-V2-B1 52.0(2),B1-V2-B21 88.6(4), B1-V2-B22 104.2(3), B21-V2-B22 44.3(5), B1-V2-B2 44.6(4), V2-B22-Cl3 143.8(5), V1-B22-Cl3 140.9(5), V2-B22-V1 75.3(2), V2-B21-V1 74.3(3),V2-B1-B2 66.8(4).

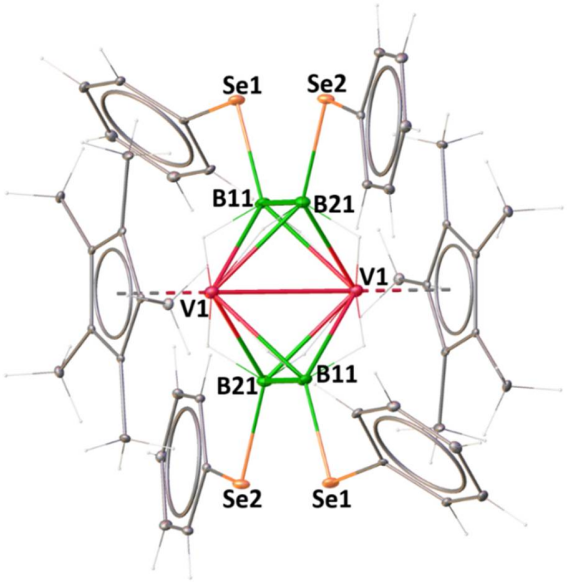

Figure S5. Molecular structure and labeling diagram for compound **5**. Selected bond lengths (Å) and bond angles (°): V1-V1 2.8595(10), V1-B11 2.331(3), V1-B21 2.333(3), B11-Se1 2.029(3), B11-B21 1.741(5) ; V1-V1-B11 52.28(8),B21-V1-B21 104.22(10), B21-V1-B11 87.56(12), B21-V1-B11 44.00(11), V1-B21-V1 75.78(10), V1-B21-Se2 145.44(16), V1-B21-B11 67.38(15).

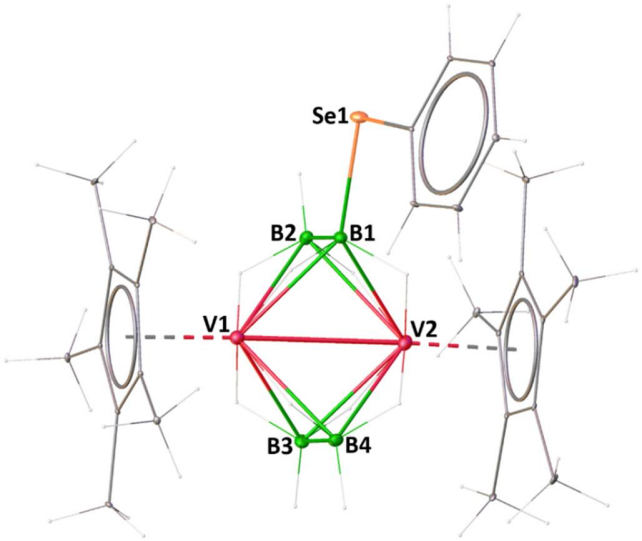

Figure S6. Molecular structure and labeling diagram for compound **6**. Selected bond lengths (Å) and bond angles (°): V1-V2 2.7996(5), V1-B2 2.320(2), V1-B1 2.310(2), B1-B2 1.745(3), B3-B4 1.759(3), B1-Se1 2.024(2) ; V2-V1-B1 52.78(5),V2-V1-B2 52.95(5), B3-V1-B2 88.58(8), B4-V1-B1 88.50(8), B2-V1-B1 44.29(8), B3-V1-B4 44.99(8), V1-B1-V2 74.55(6), B1-B2-V2 67.60(10), V1-B1-Se1 143.06(11).

I.2 Spectroscopic details

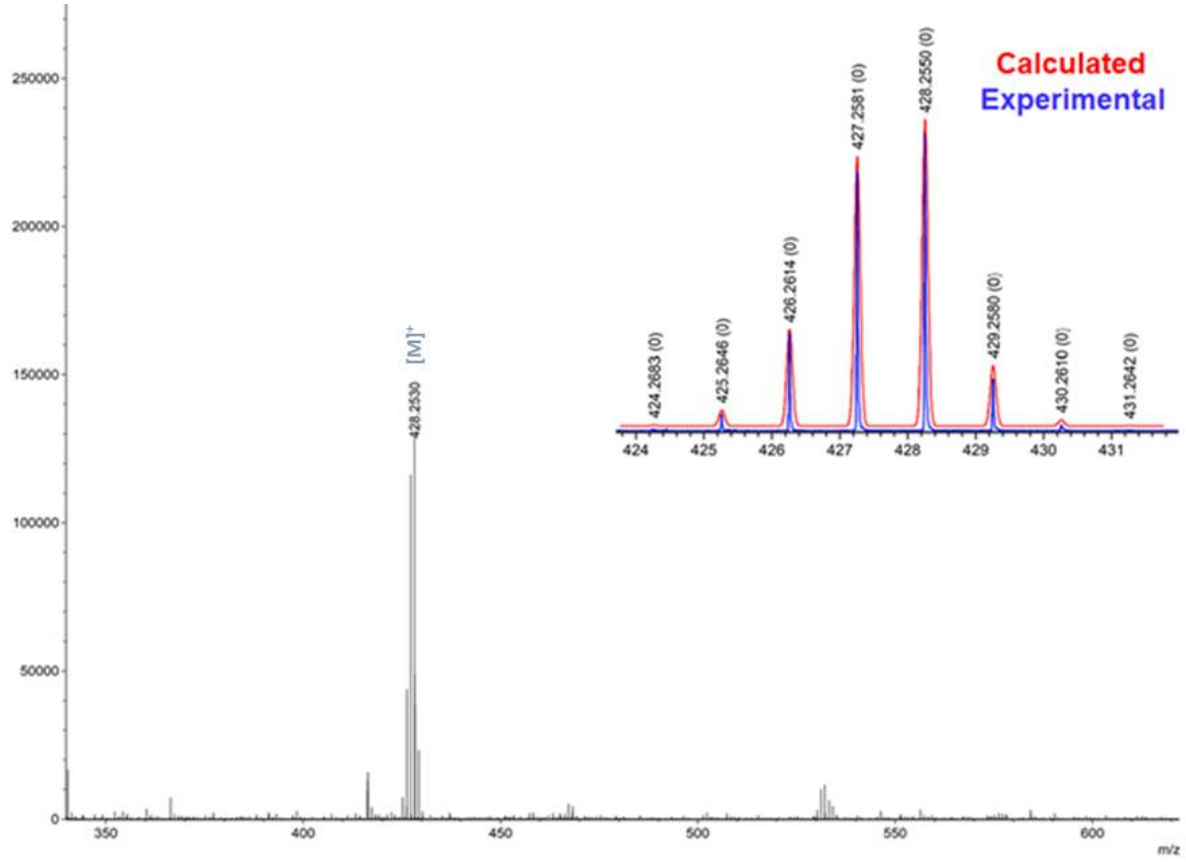

Figure S7. ESI-MS spectrum of compound **1**

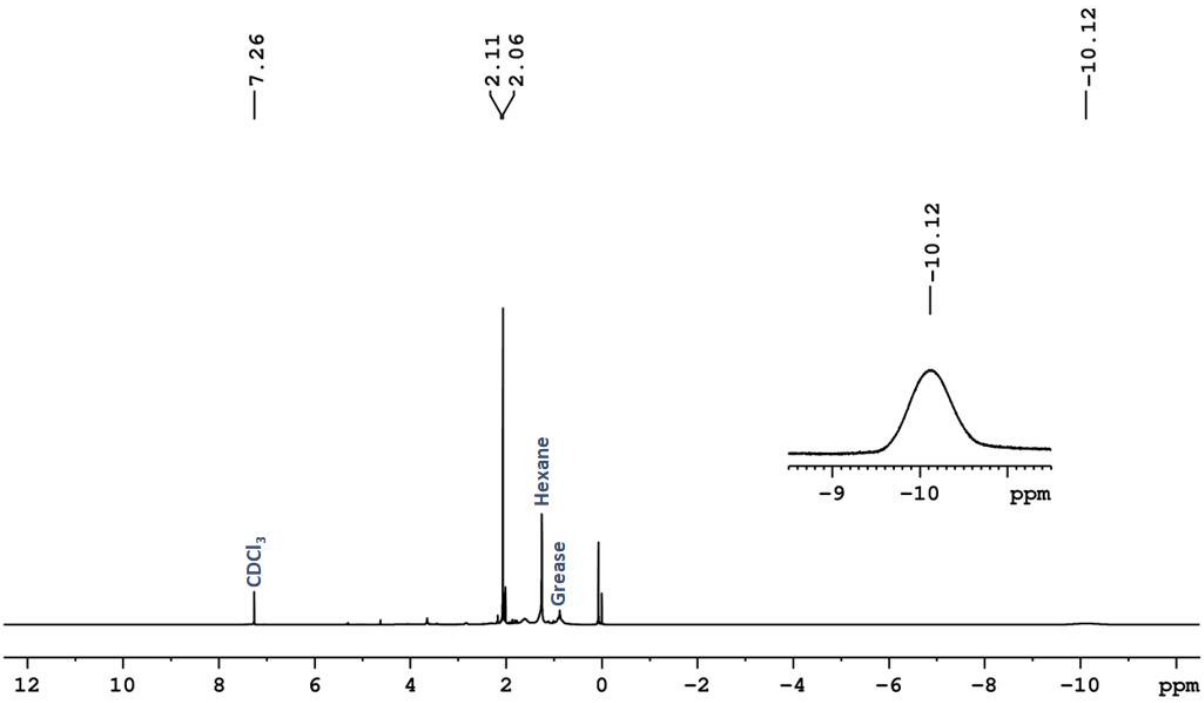

Figure S8. ^{1}H NMR spectrum of compound **1** in $CDCl_3$

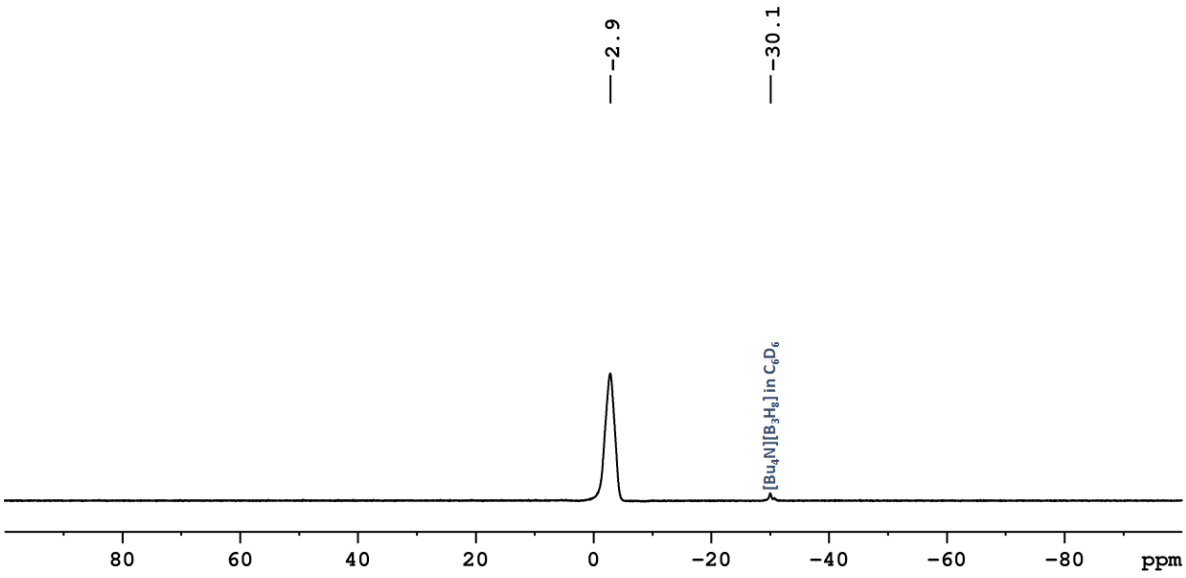

Figure S9. $^{11}B\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$

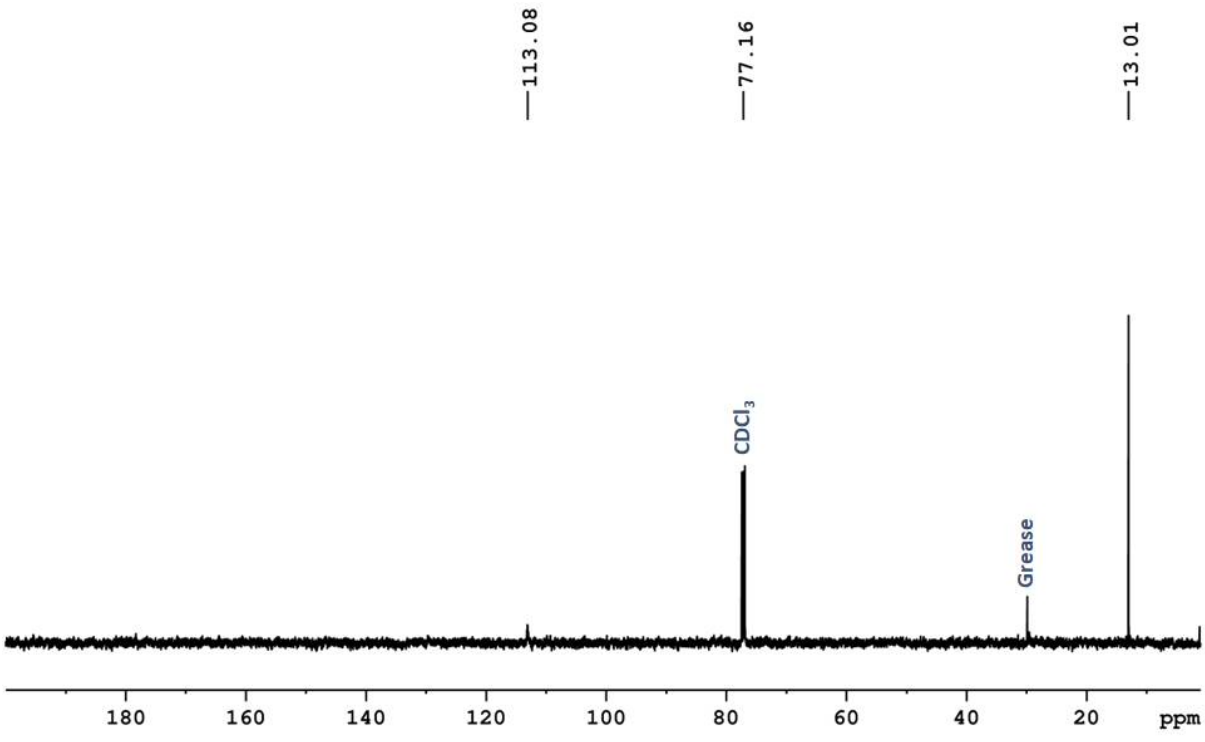

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$

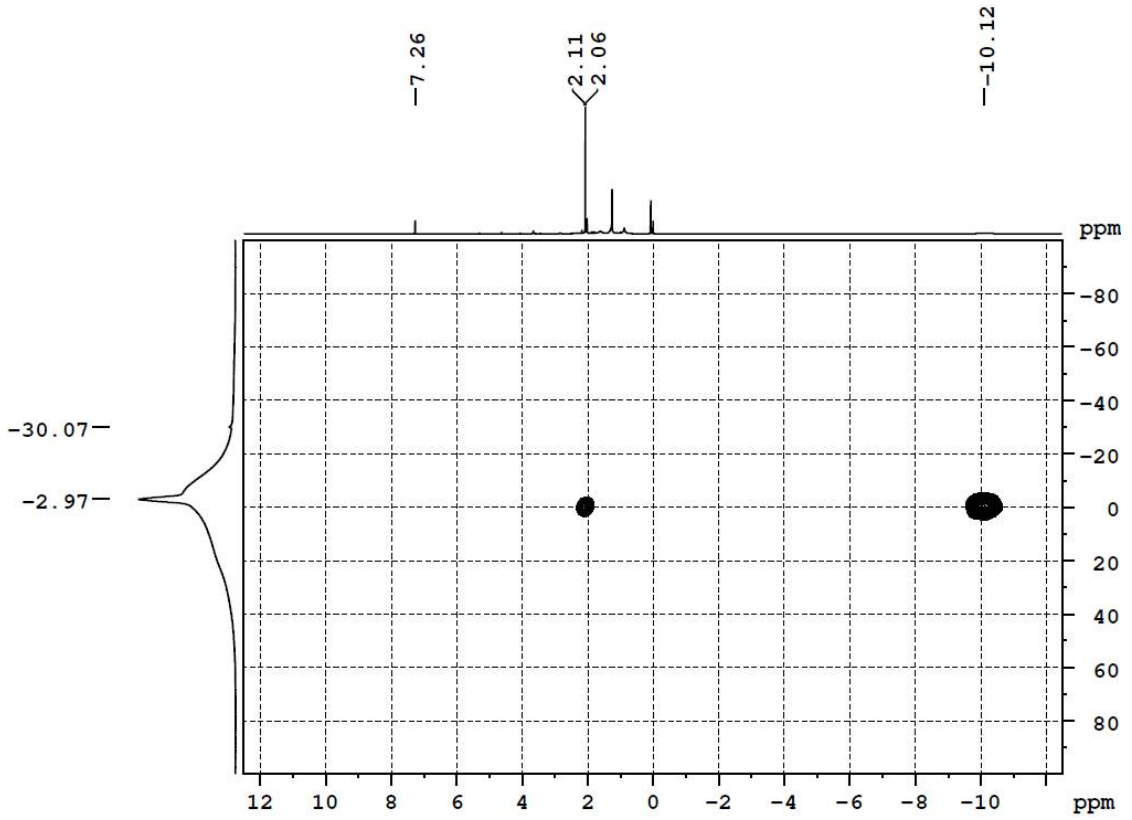

Figure S11. ^{1}H-^{11}B HSQC NMR spectrum of compound **1** in $CDCl_3$

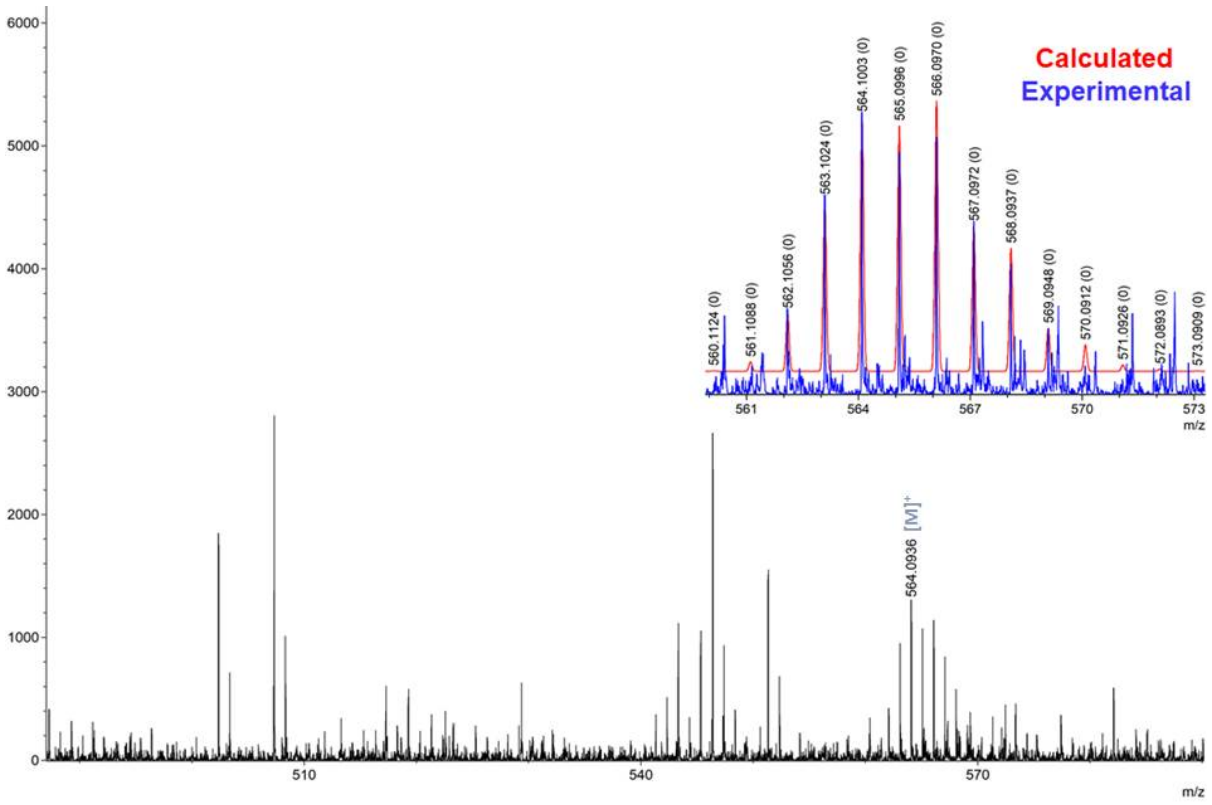

Figure S12. ESI-MS spectrum of compound **2**

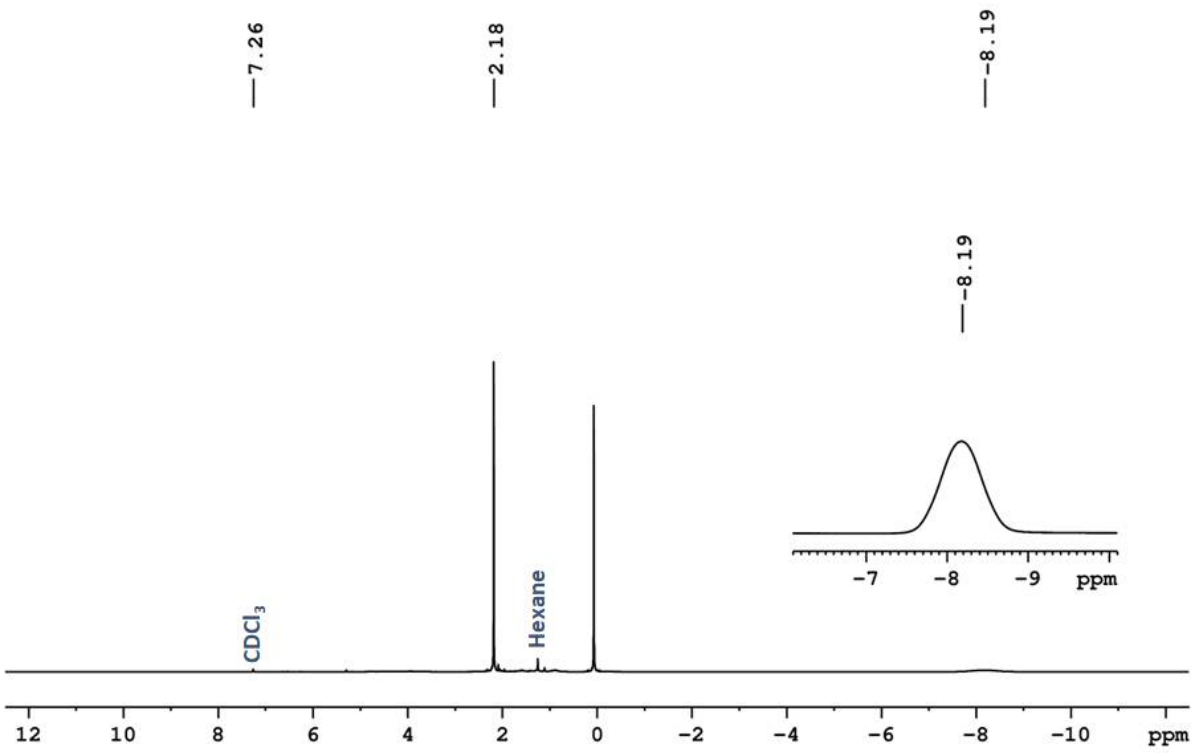

Figure S13. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

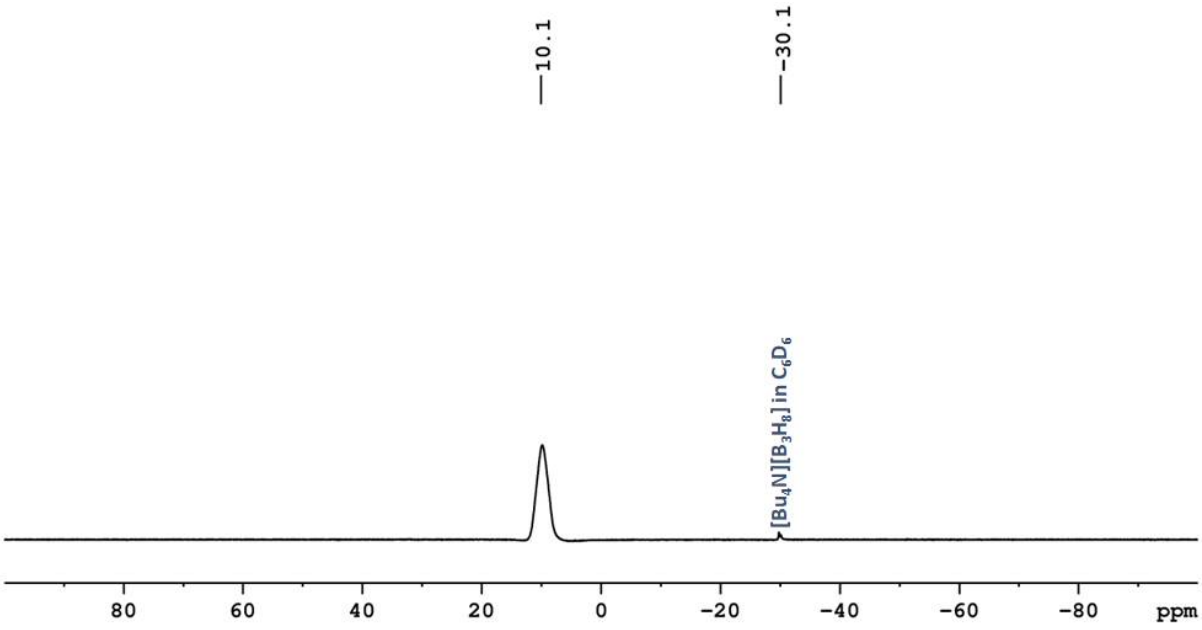

Figure S14. $^{11}B\{^{1}H\}$ NMR spectrum of compound **2** in $CDCl_3$

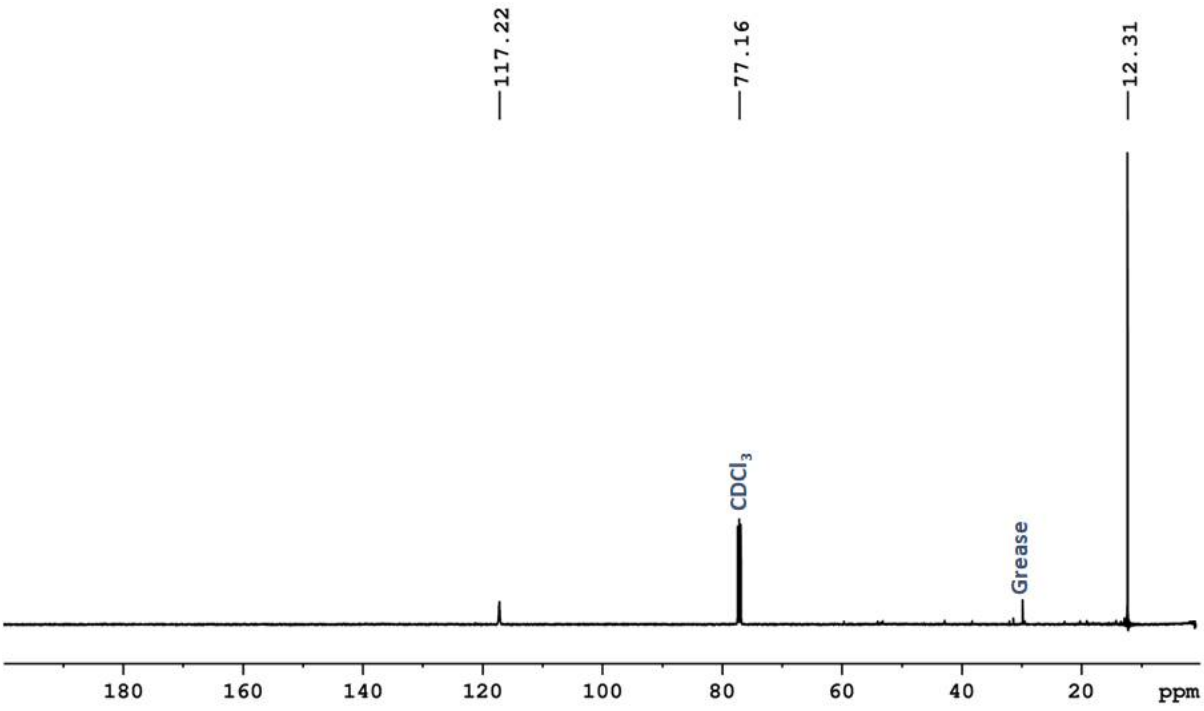

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** in $CDCl_3$

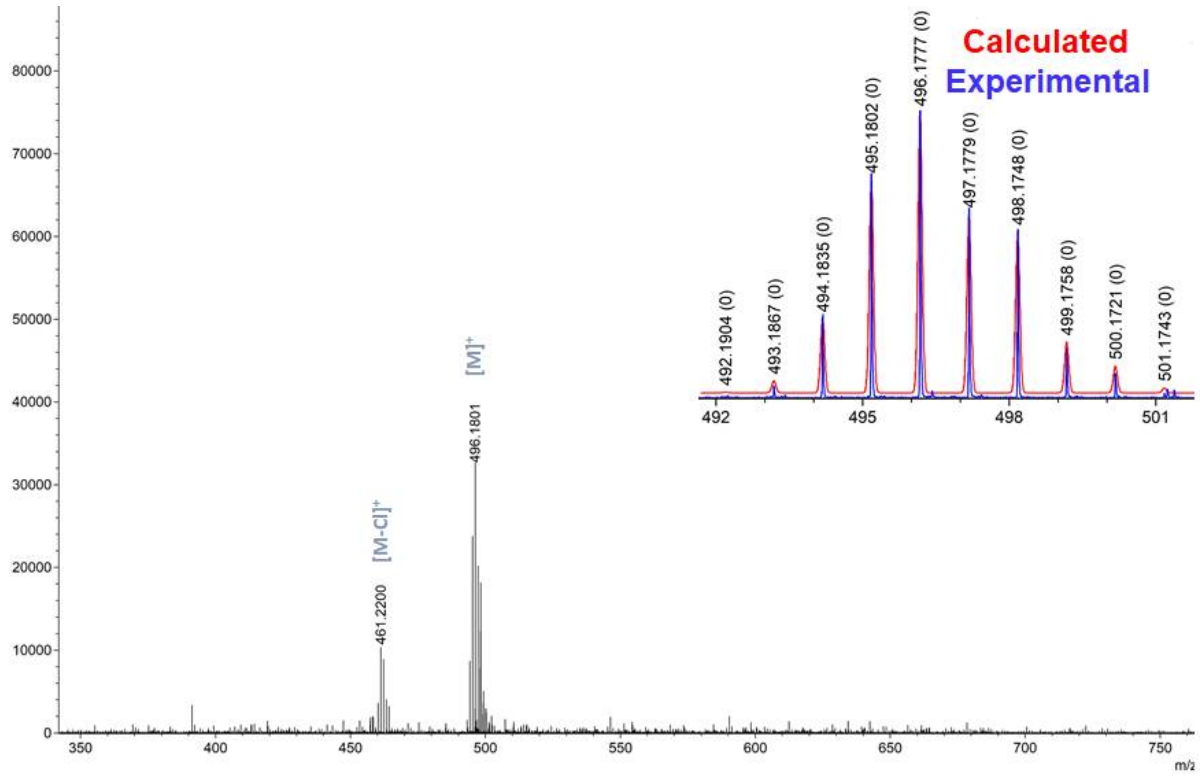

Figure S16. ESI-MS spectrum of compound **3**

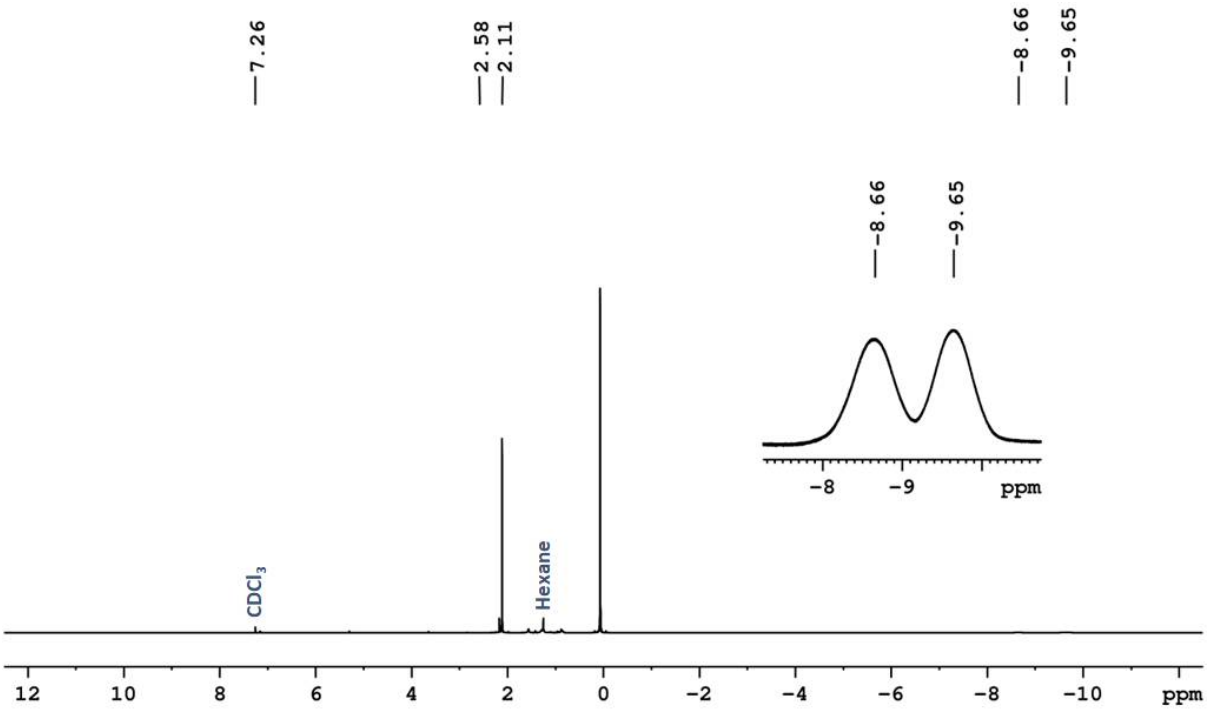

Figure S17. ^{1}H NMR spectrum of compound **3** in $CDCl_3$

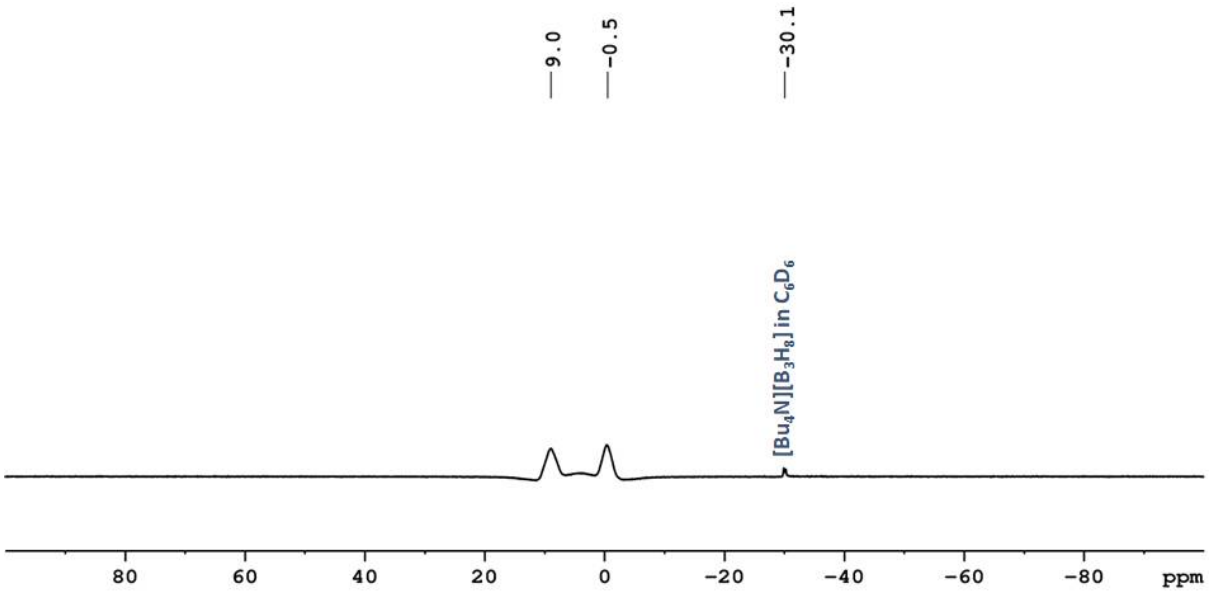

Figure S18. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$

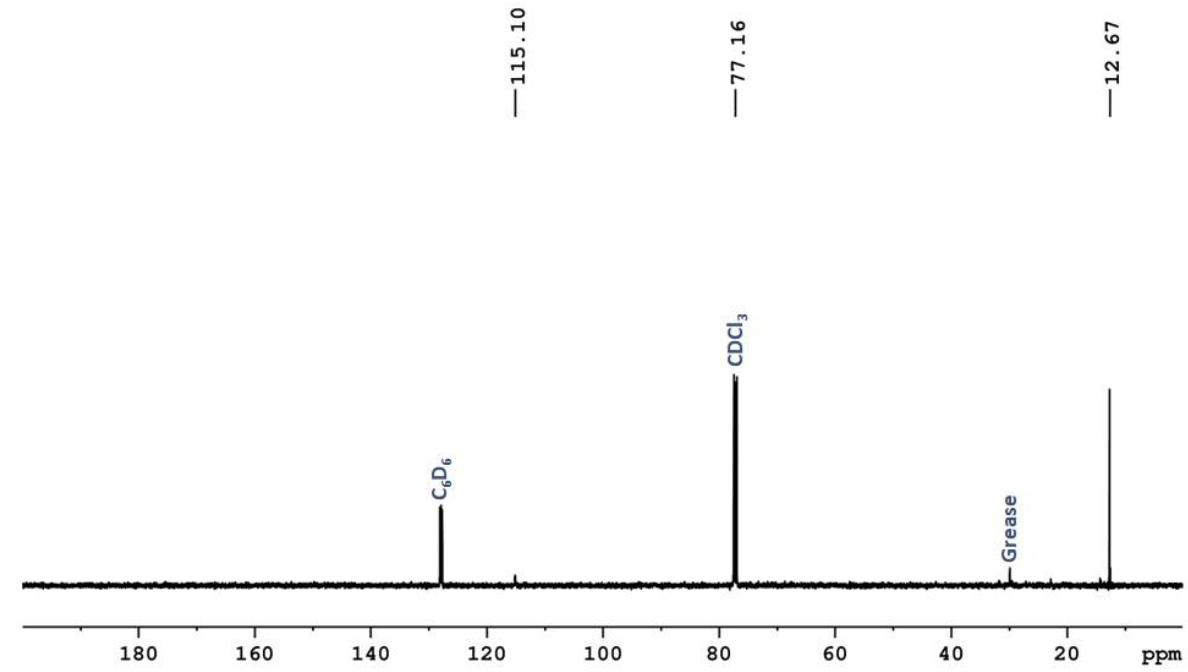

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$

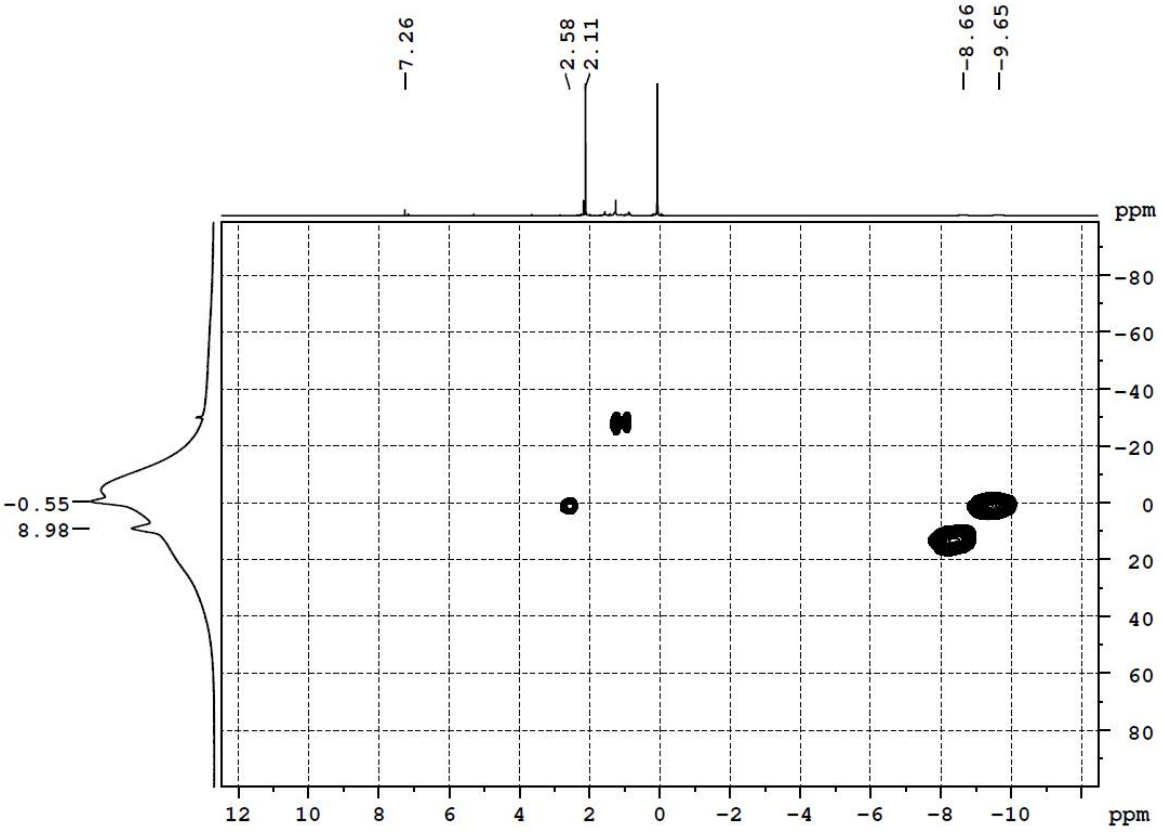

Figure S20. ^{1}H-^{11}B HSQC NMR spectrum of compound **3** in $CDCl_3$

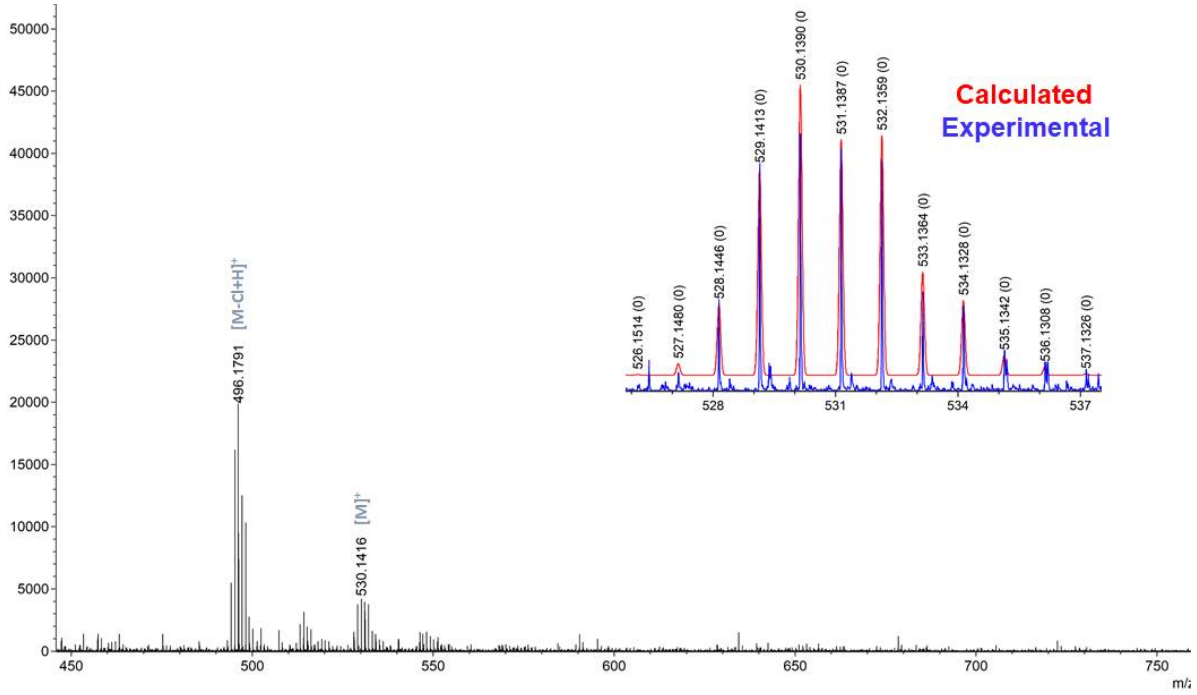

Figure S21. ESI-MS spectrum of compound **4**

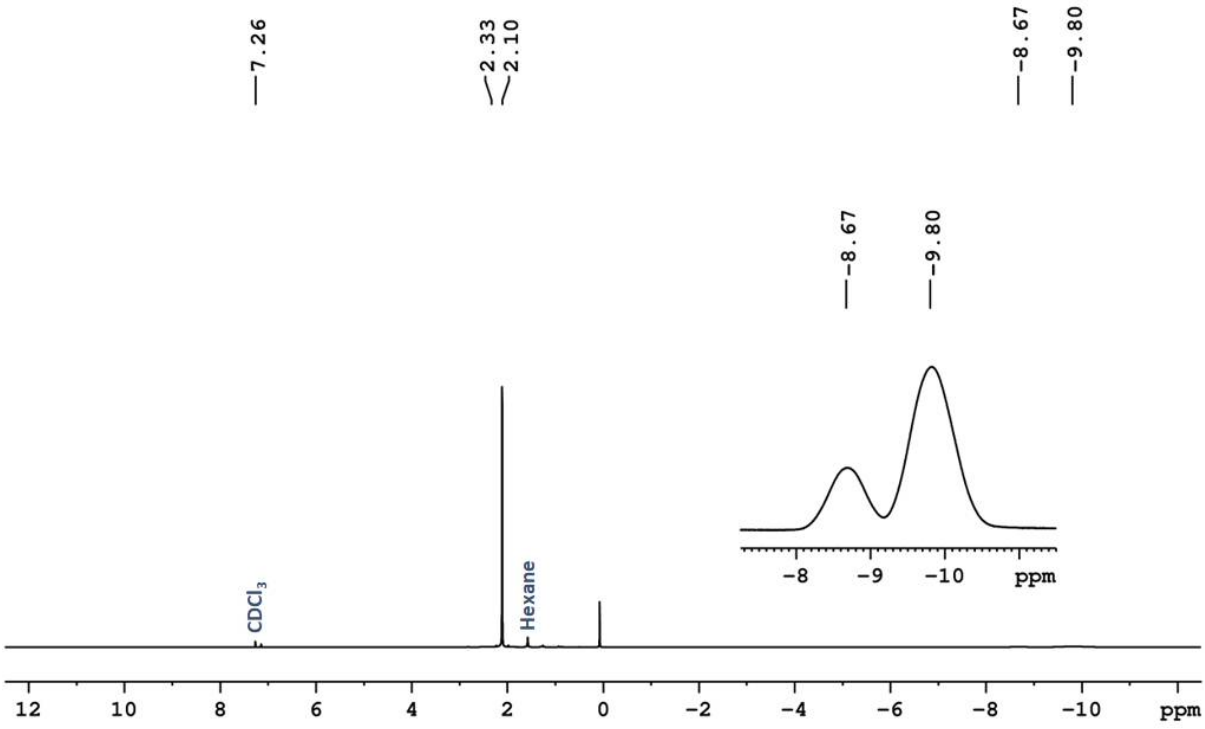

Figure S22. ^{1}H NMR spectrum of compound **4** in $CDCl_3$

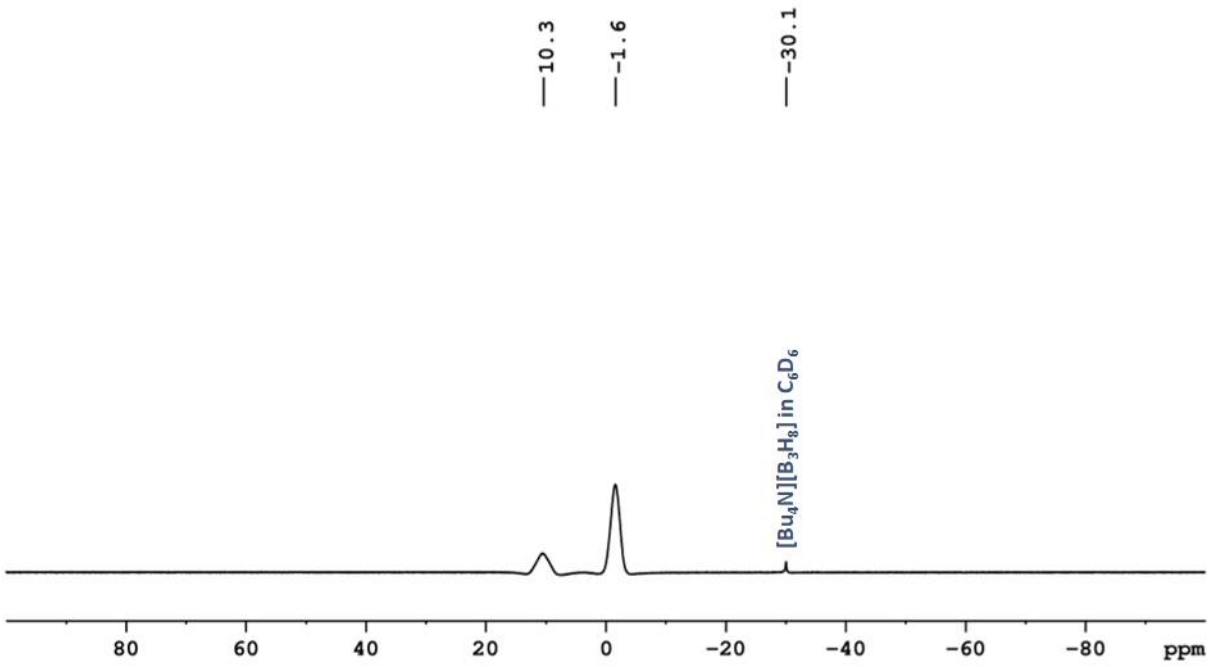

Figure S23. $^{11}B\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$

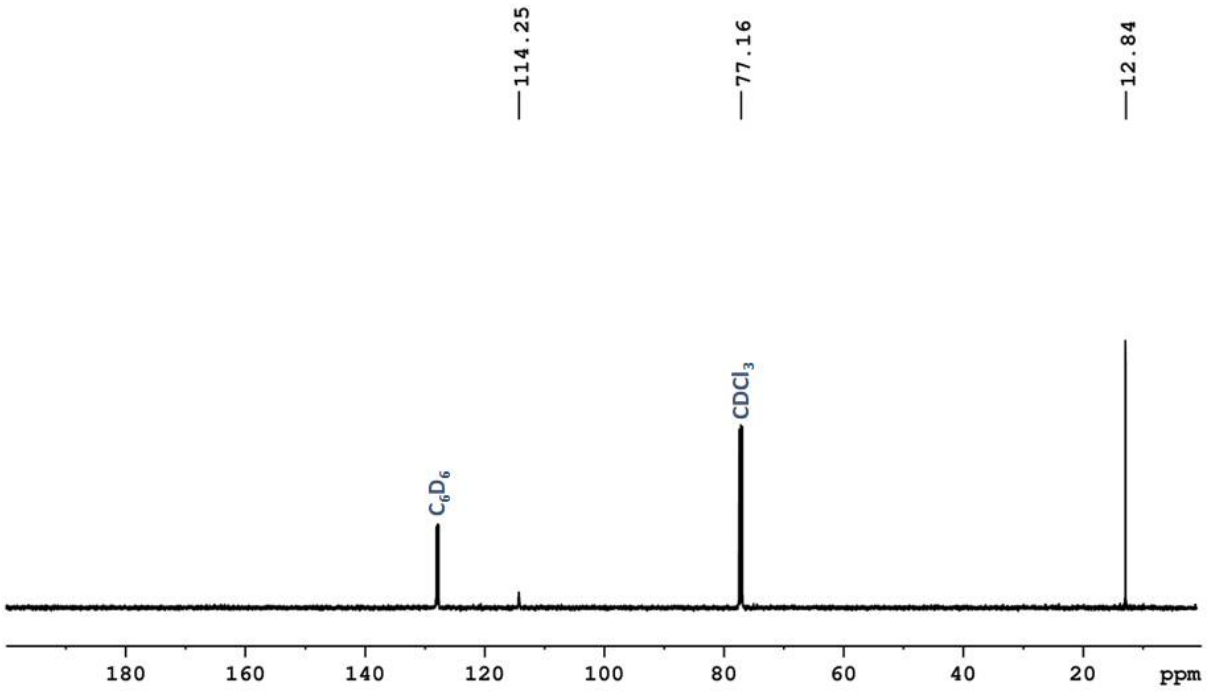

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$

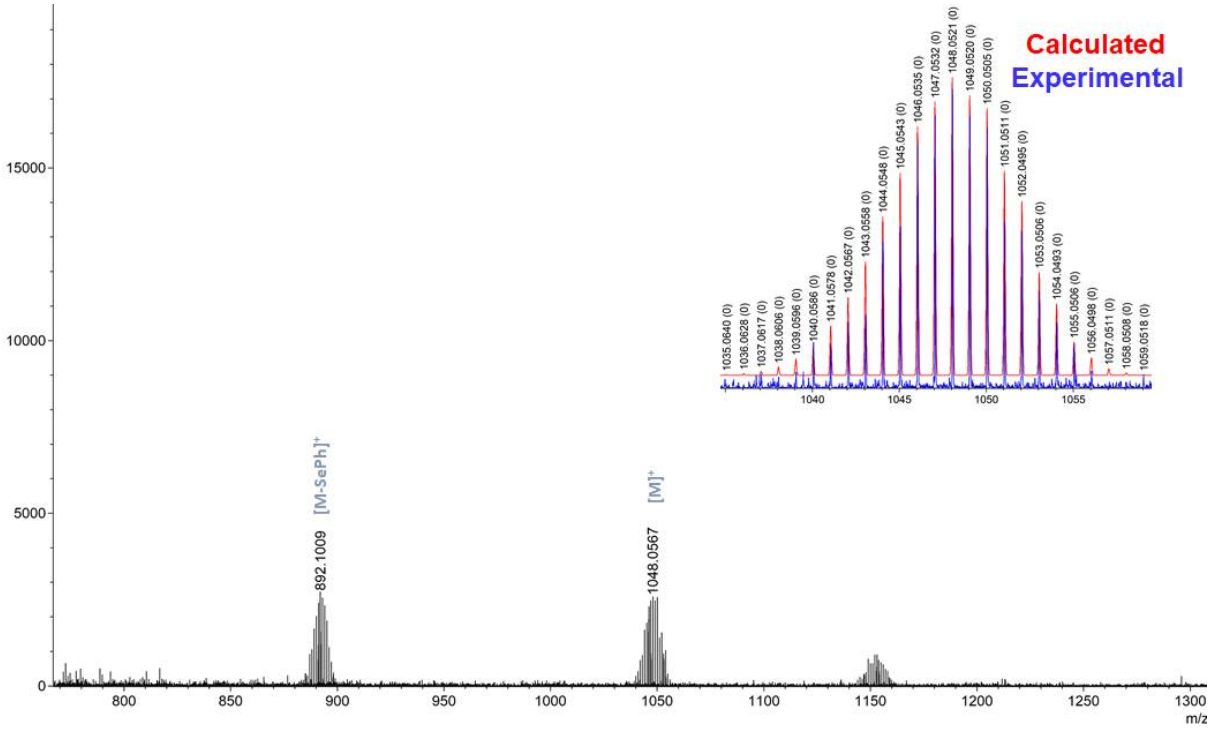

Figure S25. ESI-MS spectrum of compound **5**

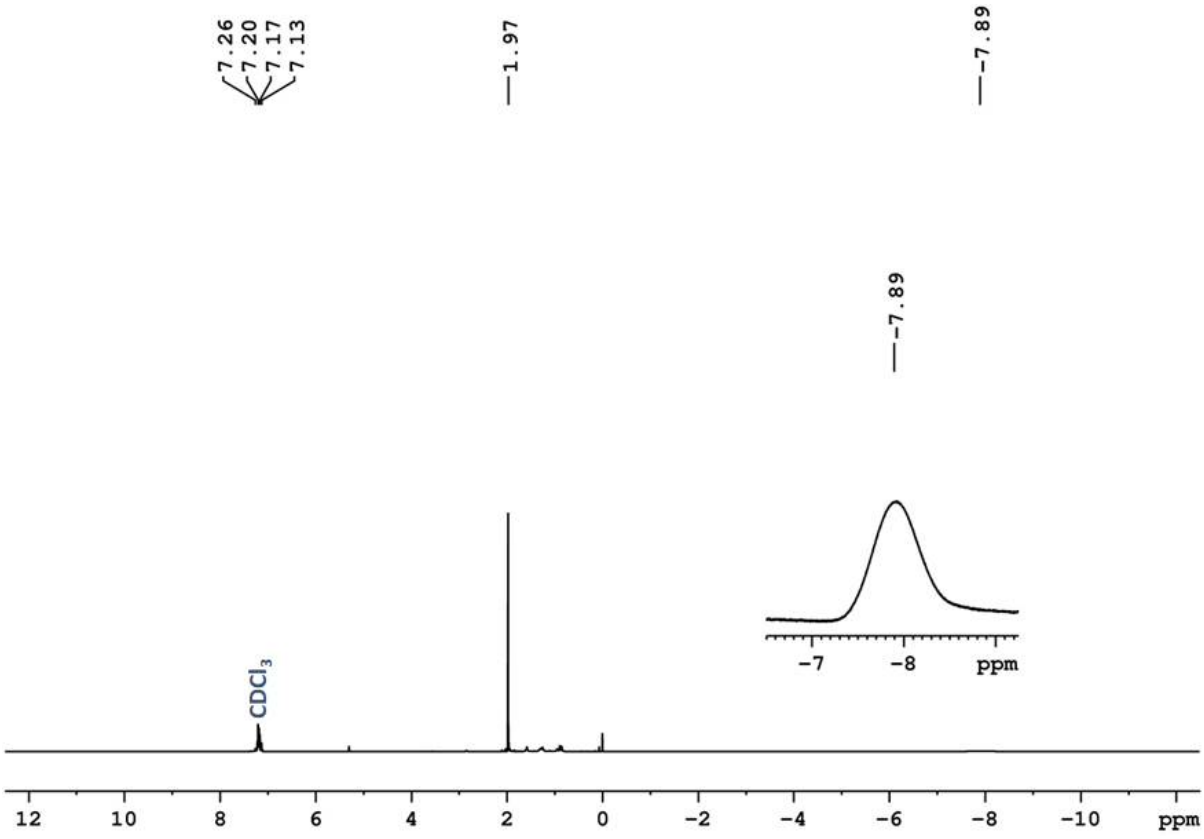

Figure S26. ^{1}H NMR spectrum of compound **5** in $CDCl_3$

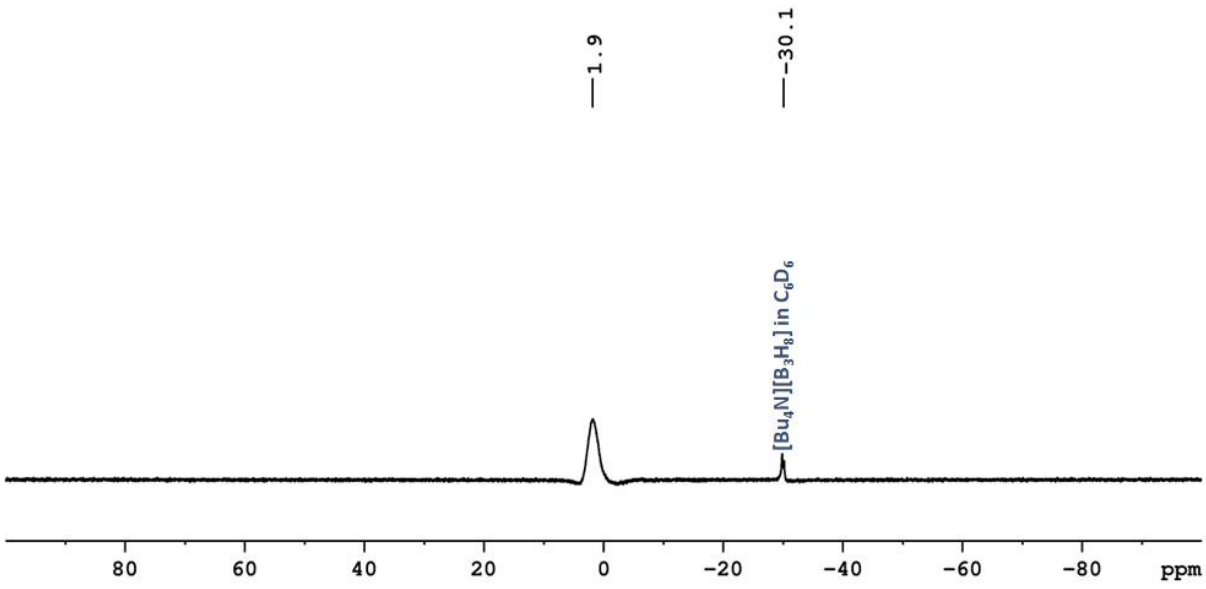

Figure S27. $^{11}B\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$

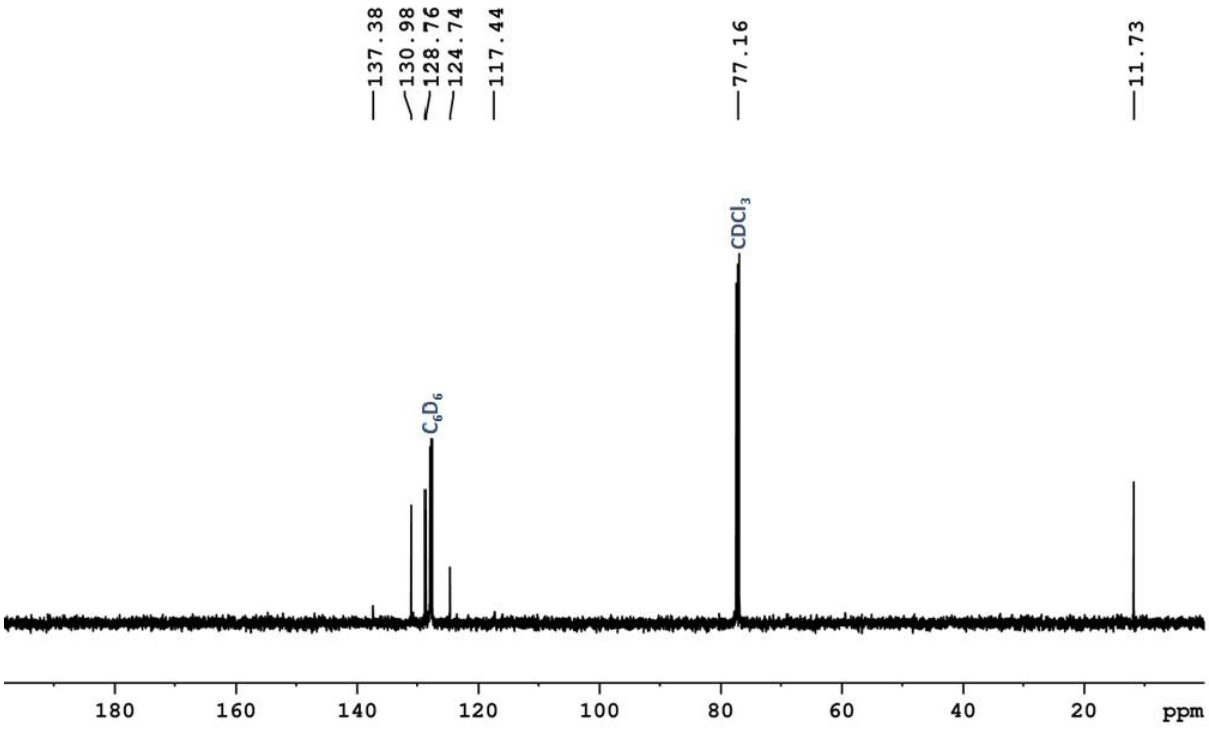

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$

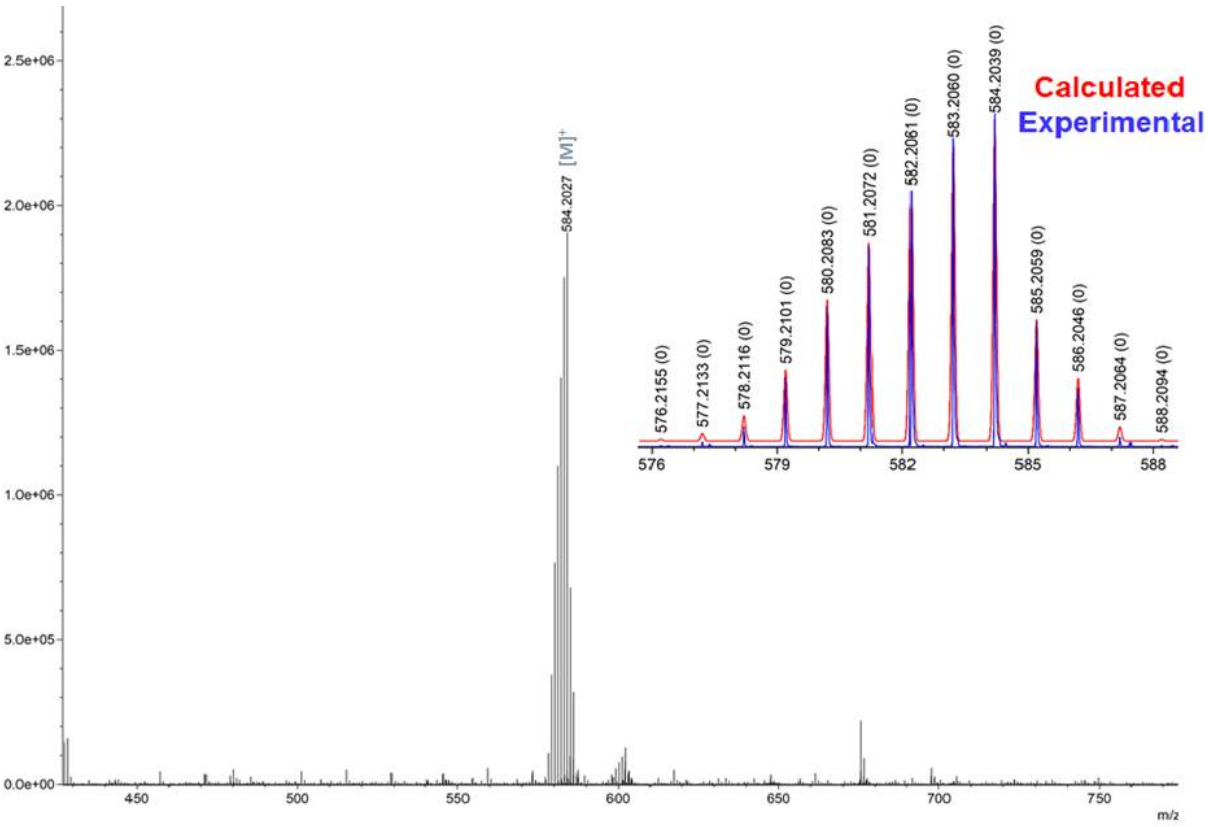

Figure S29. ESI-MS spectrum of compound **6** in $CDCl_3$

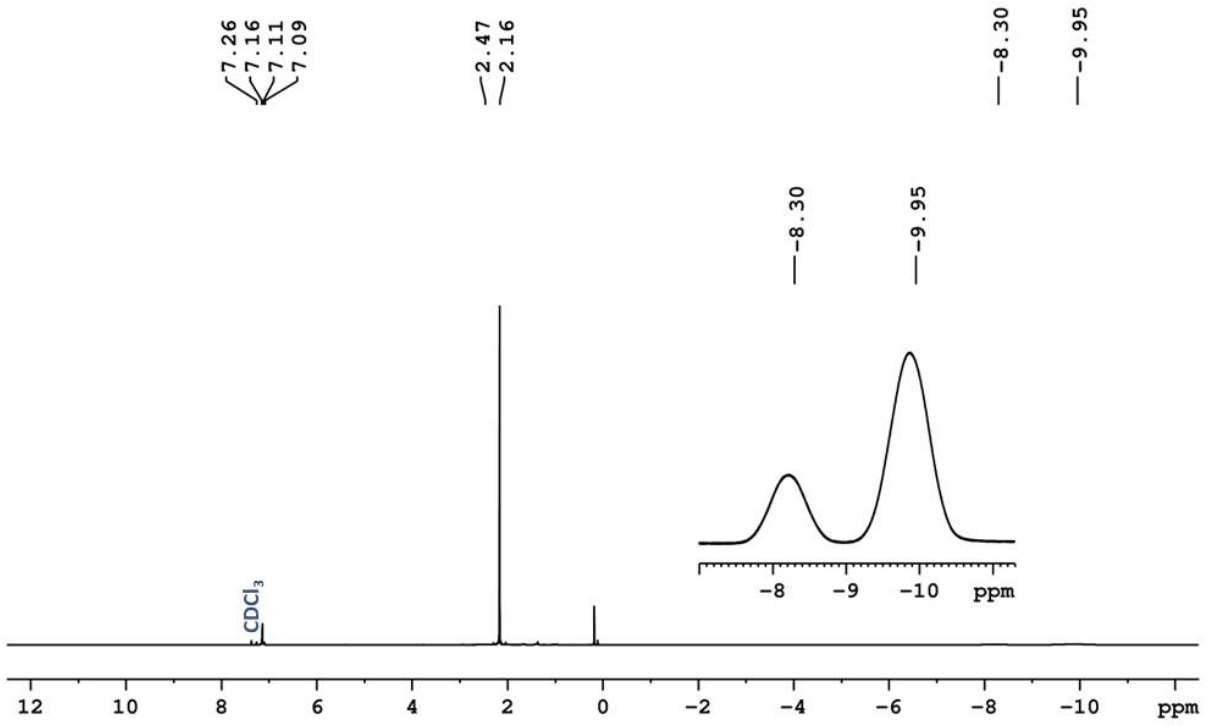

Figure S30. ^1H NMR spectrum of compound **6** in $CDCl_3$

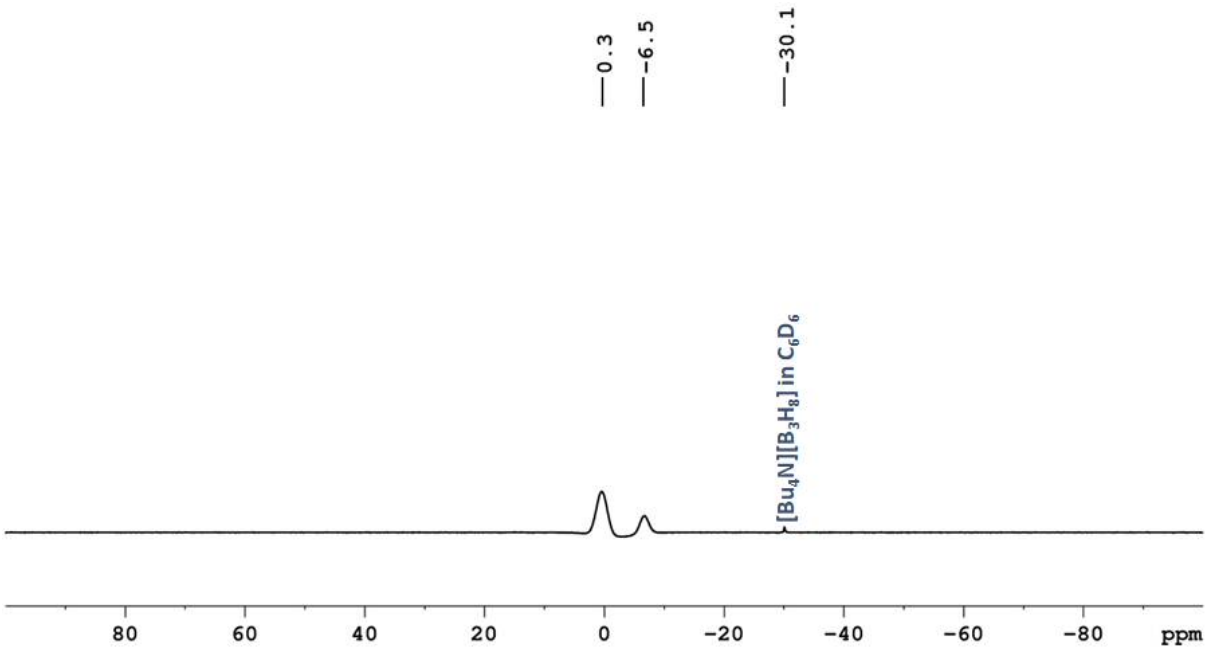

Figure S31. $^{11}B\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$

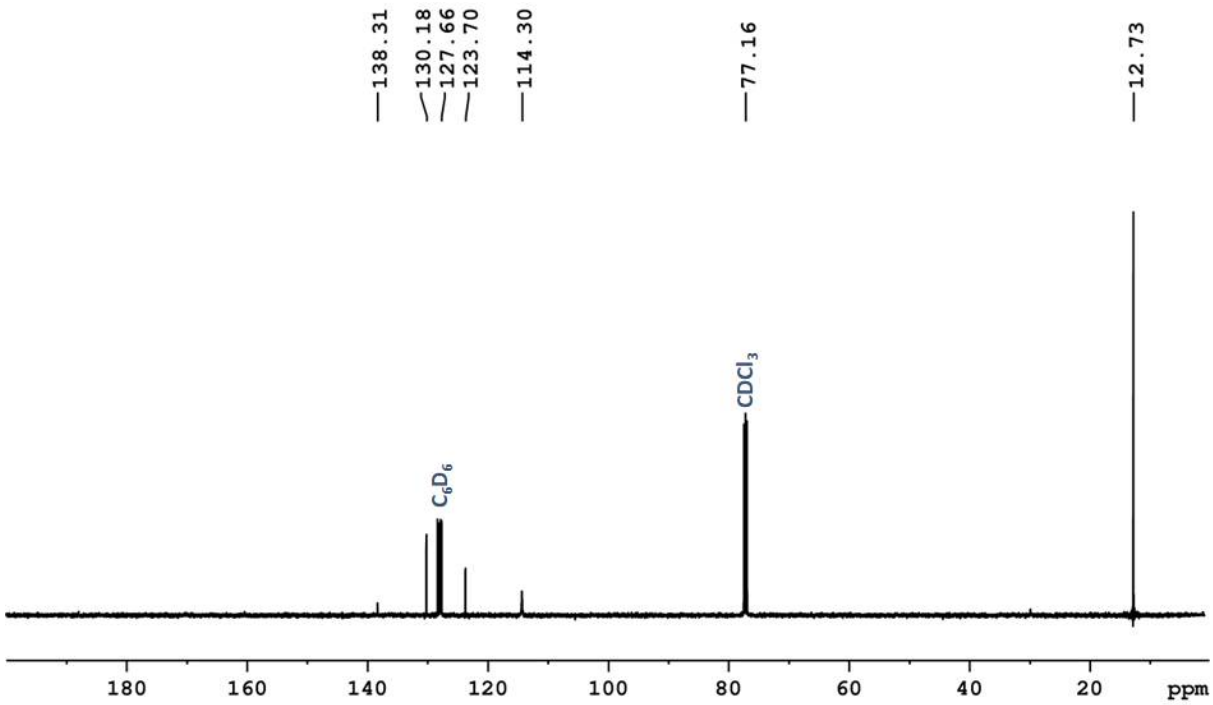

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$

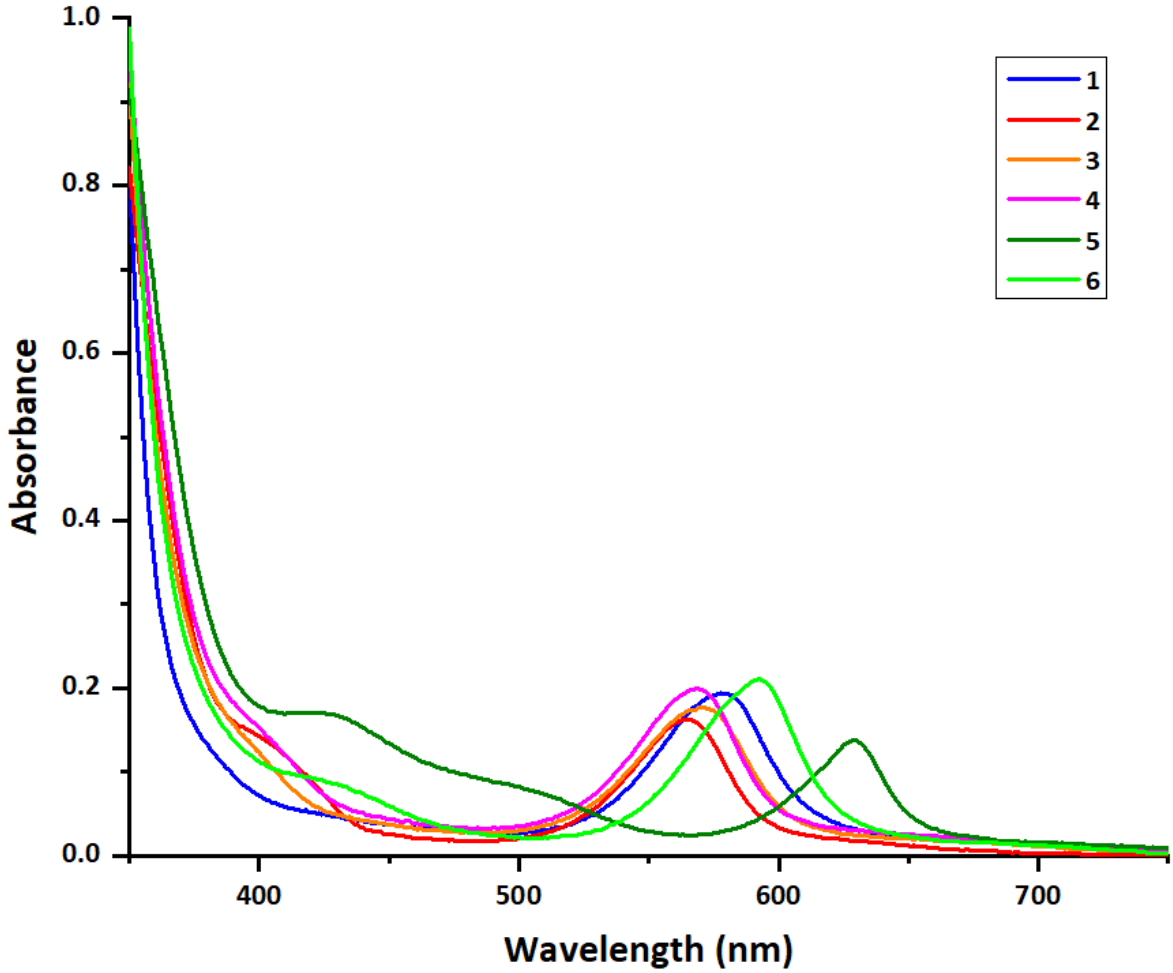

Figure S33. UV-Vis spectra of compounds **1-6** in CH_2Cl_2

II. Supplementary Data

Table S1. Experimental and calculated bond distances of **1**-**6** (**E** = Cl or Se).

	$d_{V\text{-}V}$		$d_{V\text{-}B}$		$d_{B\text{-}B}$		$d_{B\text{-}E}$	
	Expt.	Cal.	Expt.	Cal.	Expt.	Cal.	Expt.	Cal.
1	2.78	2.73	2.30	2.27	1.75	1.75	-	-
2	2.83	2.79	2.30	2.28	1.75	1.76	1.84	1.85
3	2.79	2.76	2.29	2.27	1.74	1.75	1.79	1.86
4	2.81	2.77	2.29	2.27	1.74	1.75	1.84	1.85
5	2.85	2.79	2.32	2.26	1.74	1.74	2.03	2.01
6	2.79	2.75	2.30	2.26	1.75	1.74	2.02	2.00

Table S2. Calculated natural charges (q_V, q_B, and q_E), natural valance population (**Pop**) and HOMO–LUMO gaps of **1**-**6** (**E** = Cl or Se).

	q_V	q_B	q_E	Pop(V_{val})	Pop(B_{val})	Pop(E_{val})	$\Delta E_{H\text{-}L}$ (ev)
1	0.527	-0.428	-	4.480	3.408	-	2.72
	0.527	-0.428	-	4.480	3.407	-	
		-0.428	-		3.408	-	
		-0.428	-		3.407	-	
2	0.487	-0.241	-0.191	4.519	3.208	7.180	2.76
	0.487	-0.242	-0.189	4.519	3.209	7.179	
		-0.231	-0.190		3.198	7.179	
		-0.231	-0.191		3.199	7.180	
3	0.510	-0.452	-	4.497	3.432	-	2.74
	0.510	-0.212	-0.212	4.497	3.179	7.201	
		-0.452	-		3.432	-	
		-0.212	-0.212		3.179	7.201	
4	0.496	-0.463	-	4.510	3.443	-	2.76
	0.496	-0.217	-0.207	4.510	3.184	7.197	
		-0.226	-0.193		3.194	7.182	
		-0.229	-0.194		3.197	7.183	
5	0.547	-0.456	0.247	4.457	3.435	5.734	2.32
	0.548	-0.467	0.259	4.456	3.446	5.722	
		-0.457	0.249		3.435	5.732	
		-0.467	0.259		3.445	5.722	
6	0.474	-0.515	0.269	4.534	3.494	5.712	1.39
	0.474	-0.468	-	4.533	3.449	-	
		-0.462	-		3.449	-	
		-0.464	-		3.443	-	

Table S3. Electron density, $\rho(r)$, Laplacian of electron density, $\nabla^2\rho(r)$, total energy density, H(r), potential energy density, V(r) and kinetic energy density, G(r) in a.u. of selected bond critical points (BCPs) of **1**, **2** and **5**.

Compound	BCP	$\rho(r)$	$\nabla^2\rho(r)$	H(r)	G(r)	V(r)
1	V1-V2	0.0487	-0.0039	-0.0173	0.0164	-0.0337
2	V1-V2	0.0464	-0.0066	-0.0157	0.0141	-0.0299
5	V1-V1	0.0461	-0.0005	-0.0152	0.0151	-0.0304

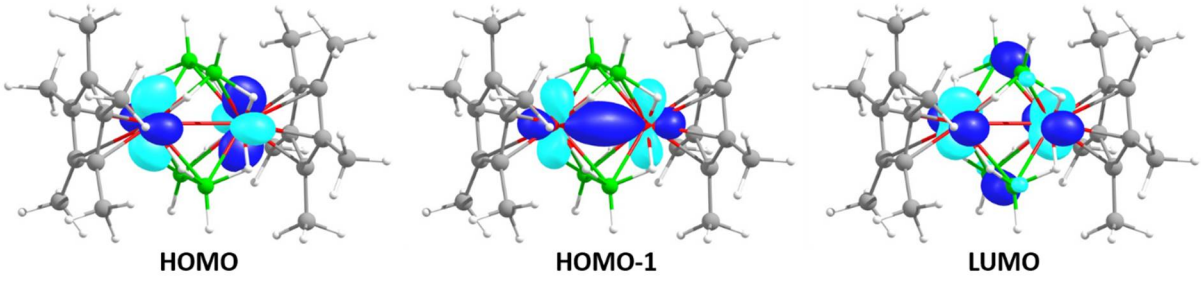

Figure S34. Selected frontier molecular orbitals of compound **1**.

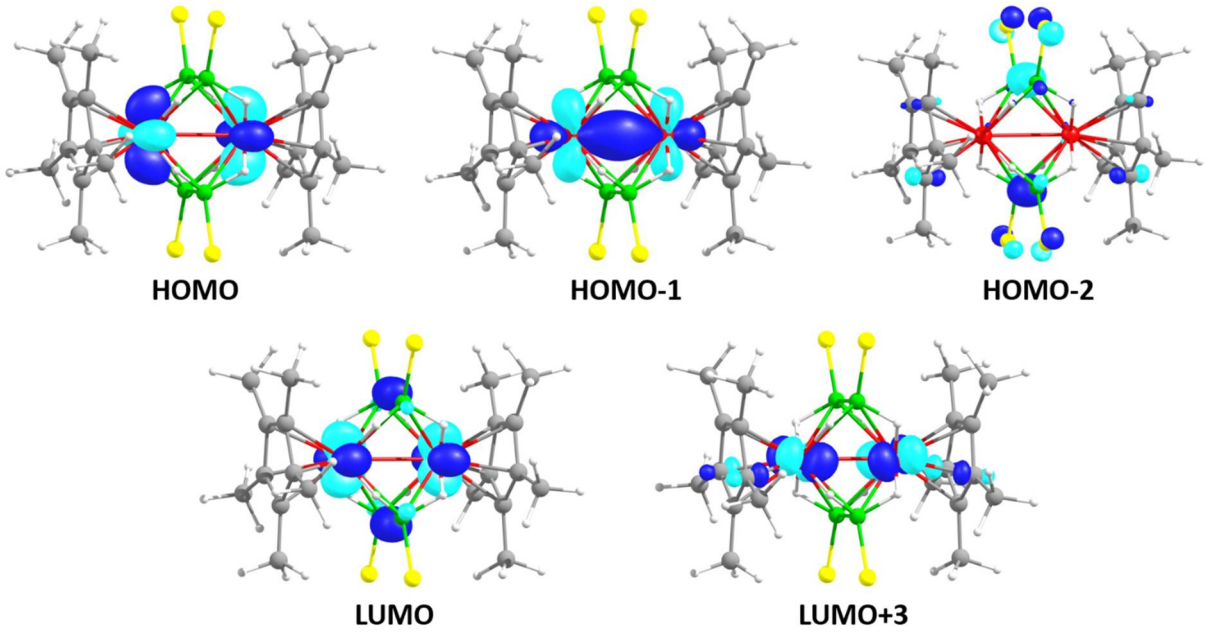

Figure S35. Selected frontier molecular orbitals of compound **2**.

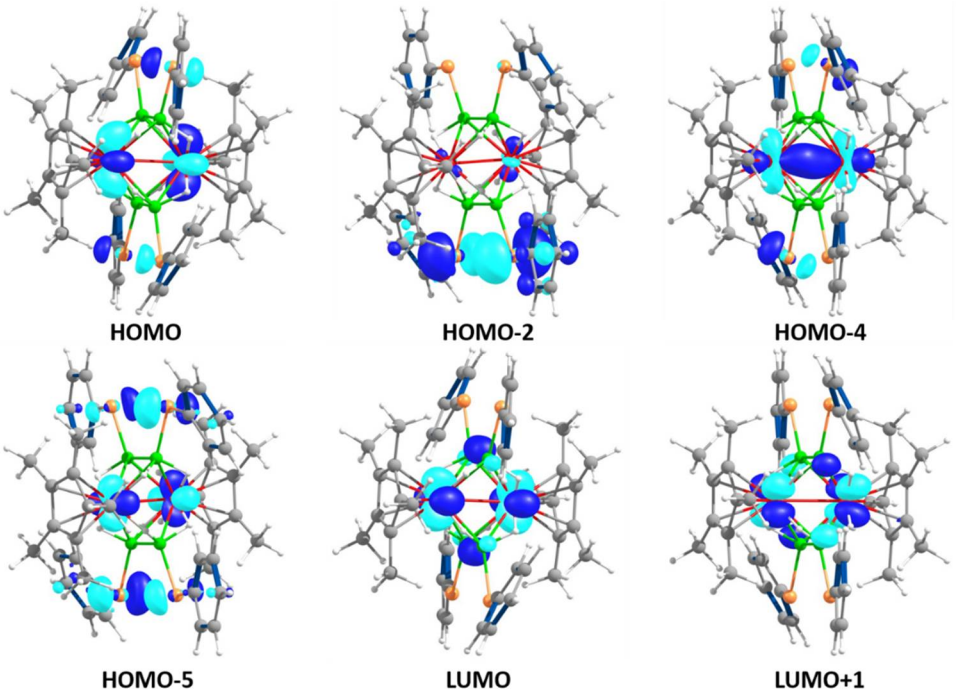

Figure S36. Selected frontier molecular orbitals of compound **5**.

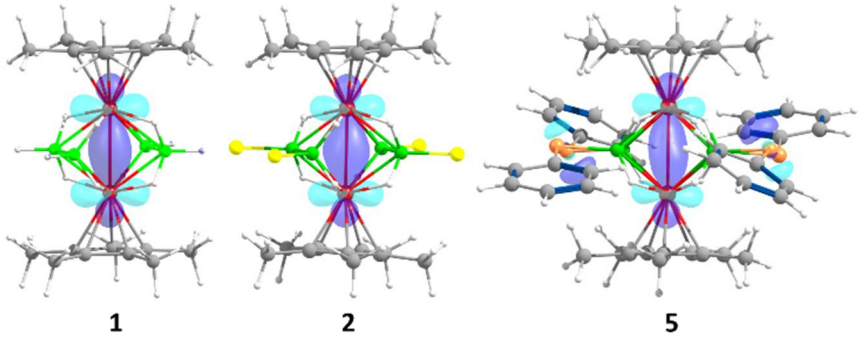

Figure S37. HOMO-1 of 1 and 2, HOMO-4 of 5 showing V-V interactions.

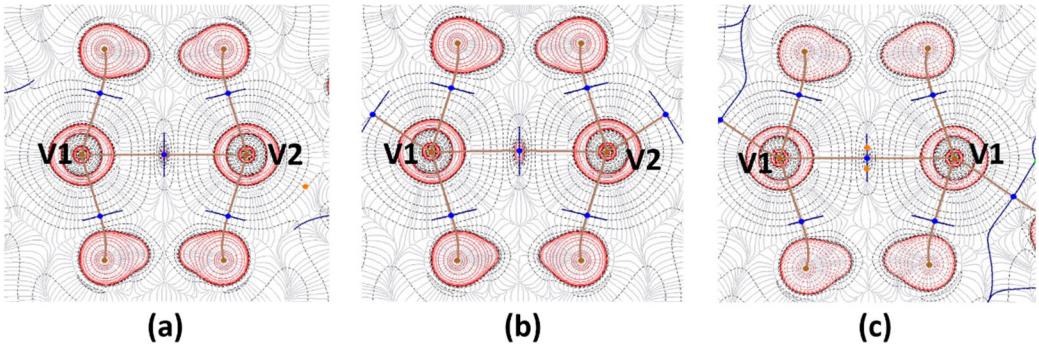

Figure S38. Contour line diagrams of the Laplacian of the electron density, $\nabla^2\rho(r)$ of V1-V2-H, V1-V2-H and V1-V1-H planes in **1** (a), **2** (b) and **5** (c) respectively. Solid red lines indicate areas of charge concentration ($\nabla^2\rho(r)<0$) while dashed black lines show areas of charge depletion ($\nabla^2\rho(r)>0$). Blue dots indicate BCPs.

Table S4. TD-DFT calculated electronic transition configuration for **1** along with their corresponding excitation energies, wavelength and oscillator strengths

HOMO is 114

No	Transition configurations (%)[a]	Excitation Energy (ev)	Wavelength (nm)		Osc, Strength
			Cal.	Expt.	
1	HOMO-1→LUMO(98)	1.7797	696.6578		0.0
2	HOMO-1→LUMO+3(12) HOMO→LUMO(89)	2.2491	551.2613	579	0.0598
3	HOMO→LUMO+2(100)	2.4513	505.7895		0.0008
4	HOMO→LUMO+1(97)	2.5359	488.9159		0.0
5	HOMO-1→LUMO+1(94)	2.6002	476.8256		0.0001
6	HOMO-1→LUMO+2(99)	2.6908	460.7707		0.0
7	HOMO-1→LUMO+4(95)	2.9858	415.2461		0.0
8	HOMO-2→LUMO(79) HOMO→LUMO+4(18)	2.9896	414.7183		0.0
9	HOMO→LUMO+3(93)	3.0186	410.7340		0.0
10	HOMO-3→LUMO(45) HOMO-1→LUMO+5(53)	3.0706	403.7783		0.0

[a]components with greater than 10% contribution shown

Table S5. TD-DFT calculated electronic transition configuration for **2** along with their corresponding excitation energies, wavelength and oscillator strengths

HOMO is 146

No	Transition configurations (%)[a]	Excitation Energy (ev)	Wavelength (nm)		Osc, Strength
			Cal.	Expt.	
1	HOMO-1→LUMO(95)	2.0406	607.5869		0.0001
2	HOMO→LUMO+1(100)	2.1822	568.1614		0.0
3	HOMO-1→LUMO+3(11) HOMO→LUMO(89)	2.2947	540.3067	565	0.0591
4	HOMO→LUMO+2(97)	2.5959	477.6154		0.0
5	HOMO-1→LUMO+1(99)	2.6093	475.1626		0.0001
6	HOMO-2→LUMO(89)	2.7357	453.2082	410(S)[b]	0.0168
7	HOMO-1→LUMO+2(93)	2.8448	435.8274		0.0002
8	HOMO-3→LUMO(27) HOMO→LUMO+4(72)	2.8908	428.8923		0.0
9	HOMO→LUMO+3(92)	2.9502	420.2569		0.0
10	HOMO-4→LUMO(95)	2.9873	415.0376		0.0

[a]components with greater than 10% contribution shown, [b]shoulder peak

Table S6. TD-DFT calculated electronic transition configuration for **5** along with their corresponding excitation energies, wavelength and oscillator strengths

HOMO is 262

No	Transition configurations (%)[a]	Excitation Energy (ev)	Wavelength (nm)		Osc, Strength
			Cal.	Expt.	
1	HOMO-5→LUMO(14) HOMO-2→LUMO(18) HOMO→LUMO(66)	1.6763	739.6300		0.0278
2	HOMO-1→LUMO(89)	1.6856	735.5493		0.0001
3	HOMO-2→LUMO(80) HOMO→LUMO(13)	1.7349	714.6474	630	0.0304
4	HOMO-3→LUMO(88)	1.7578	705.3373		0.0001
5	HOMO-4→LUMO(91)	1.8168	682.4317		0.0001
6	HOMO→LUMO+1(100)	2.0281	611.3317		0.0021
7	HOMO-5→LUMO(62) HOMO-2→LUMO+1(26)	2.2907	541.2502	508(s)[b]	0.0326
8	HOMO-3→LUMO+1(17) HOMO-1→LUMO+1(78)	2.4002	516.5577		0.0001
9	HOMO→LUMO+2(94)	2.4178	512.7975		0.0
10	HOMO-4→LUMO+1(13) HOMO-3→LUMO+1(72)	2.4982	496.2941		0.0

[a]components with greater than 10% contribution shown, [b]shoulder peak