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Supporting Information

Metal Coordinated Tri- and Tetraborane Analogues

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I Experimental Details

I.1 Supplementary Data

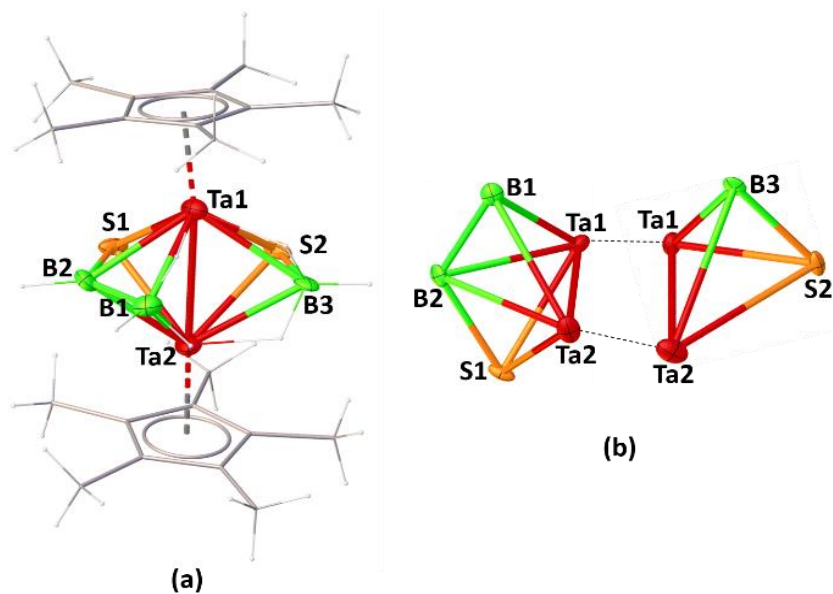


Figure S1. (a) Molecular structure of **1**. Selected bond lengths (Å) and angles (°) of **1**: Ta1-Ta2 2.763(6), S2-Ta1 2.436(9), S2-Ta2 2.542(7), B1-Ta1 2.39(2), B2-Ta2 2.46(2), B3-Ta1 2.47(2), B3-Ta2 2.561(18); B1-B2-S1 123.8(17), B1-B2-Ta1 69.6(11), S2-B3-Ta1 67.6(6); (b) cluster fusion representation of **1**.

I.2 Spectroscopic details

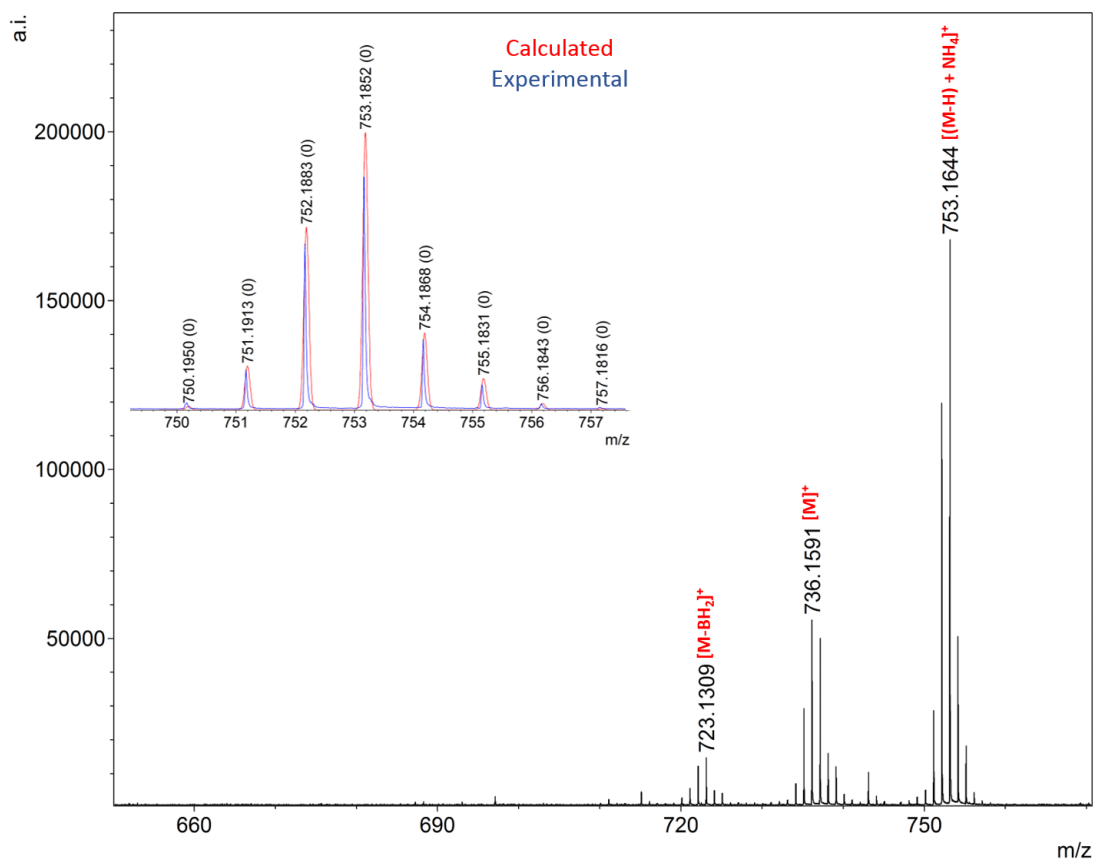
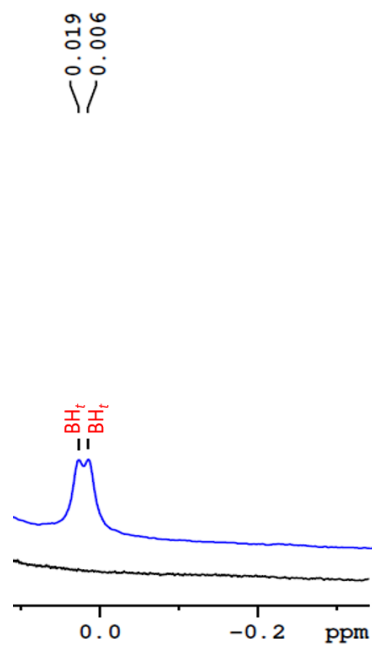
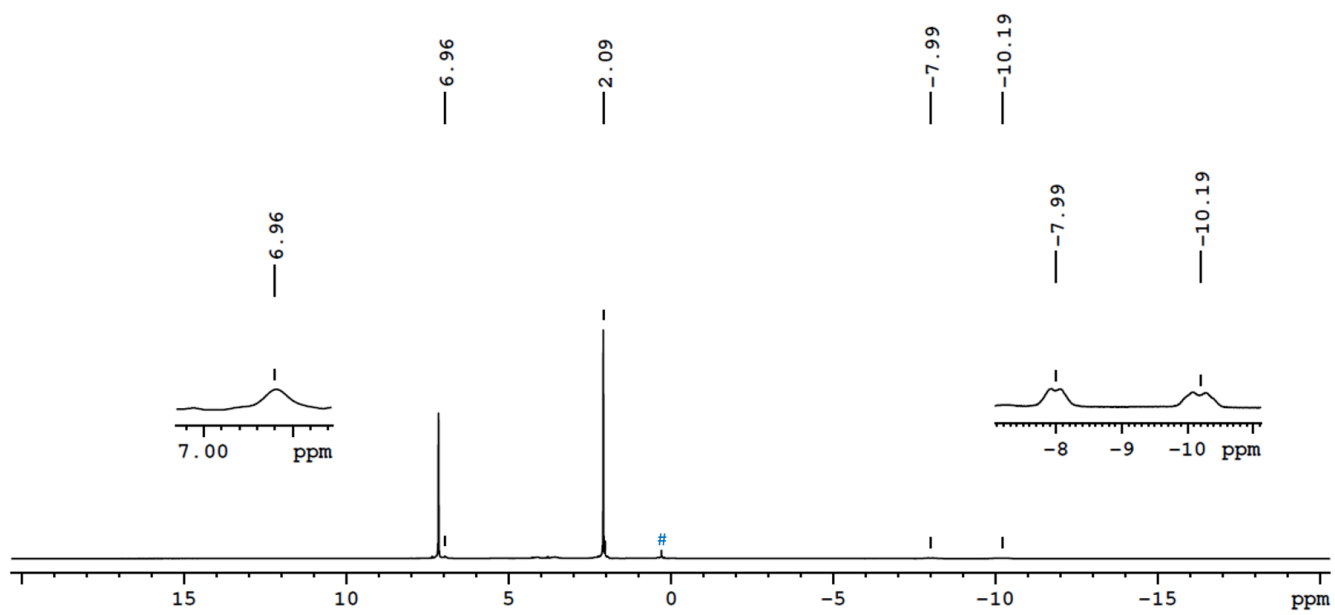


Figure S2. ESI-MS of compound **1**.



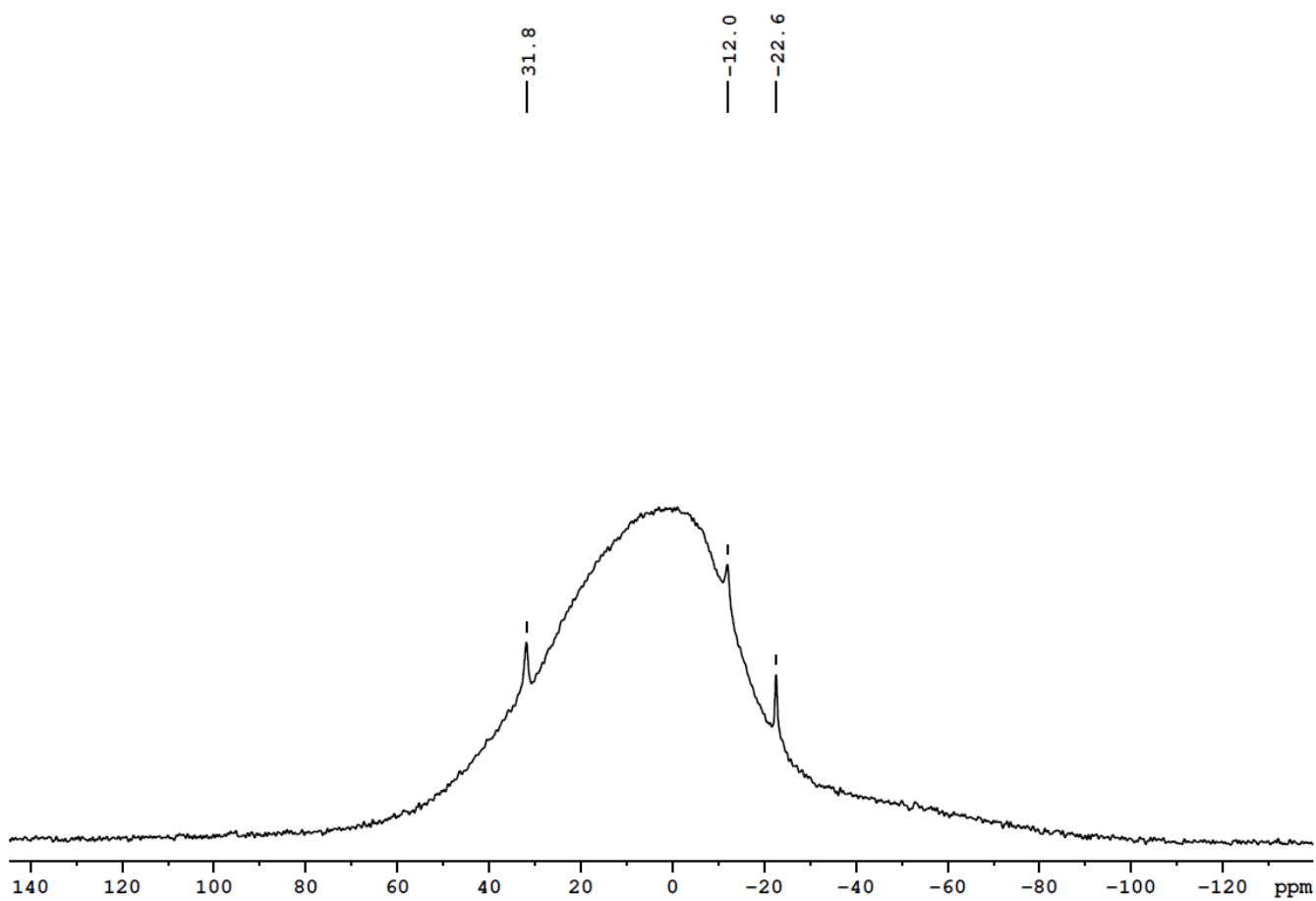


Figure S5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound 1 in *ds*-toluene.

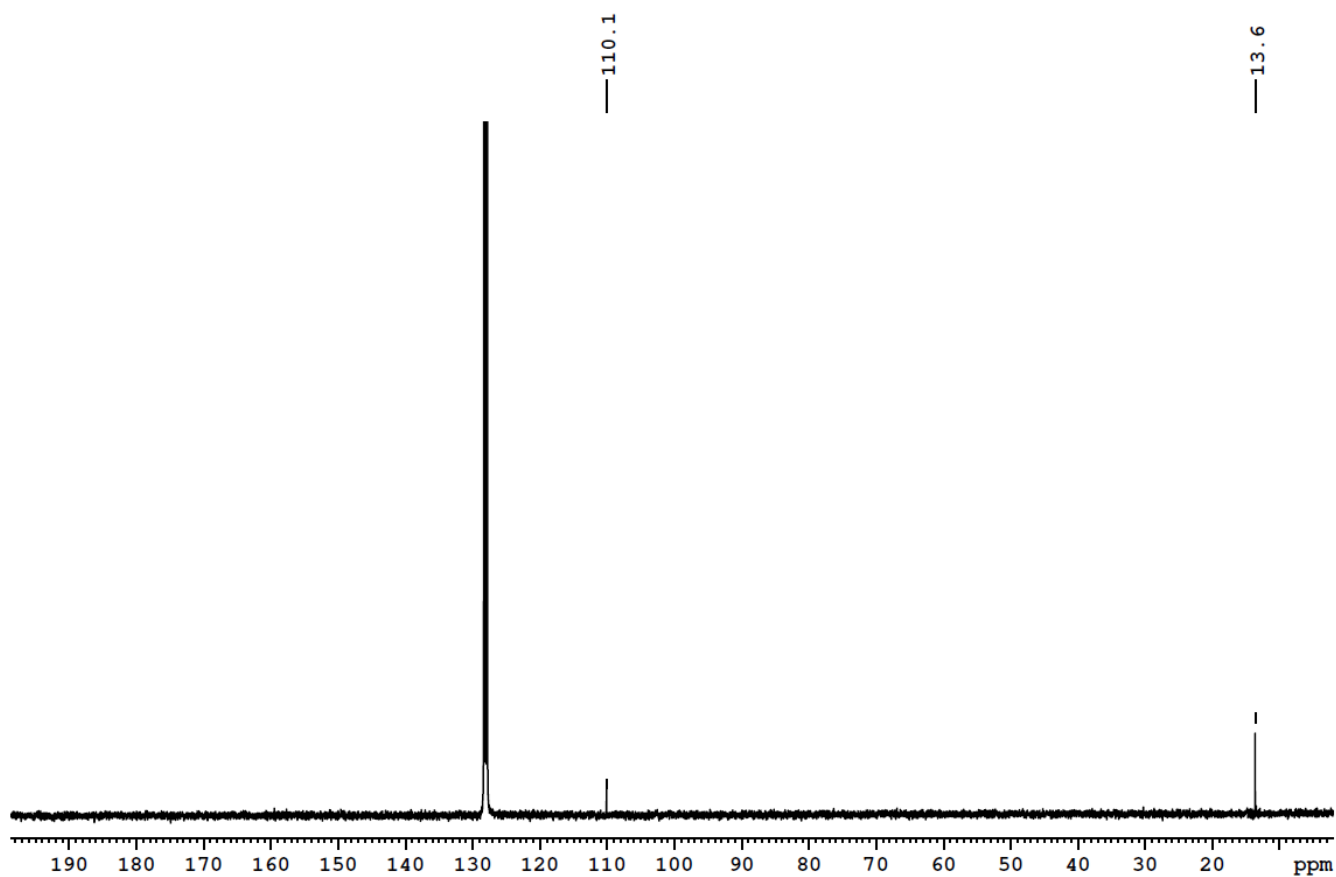


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 1 in C_6D_6 .

HRMS DST-FIST Funded, Department of Chemistry, IIT Madras

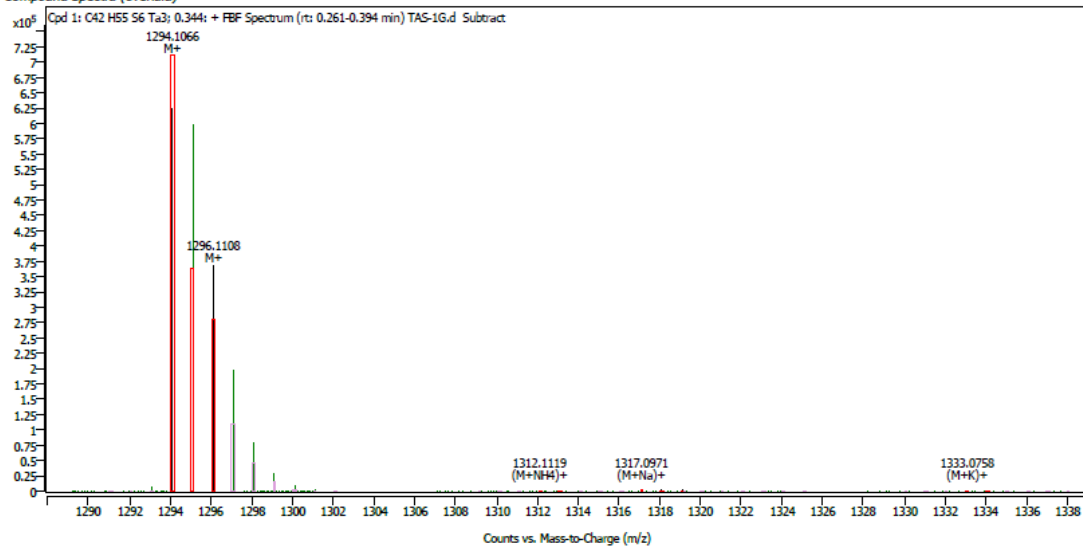
ESI Mass Report

Name	21042021-13-SGG	Data File Path	D:\MassHunter\Data\2021\APRIL-2021\SGG\TAS-1G.d
Sample ID		Acq. Time (Local)	21-04-2021 13:27:50 (UTC+05:30)
Instrument	Instrument 1	Method Path (Acq)	D:\MassHunter\Methods\TRIALS\FIA_POS_organic_01.m
MS Type	QTOF	Version (Acq SW)	6200 series TOF/6500 series Q-TOF 10.1 (48.0)
Inj. Vol. (ul)	1	IRM Status	Success
Position	P1-C9	Method Path (DA)	D:\MassHunter\Methods\10.0\PROCESSING_01.m
Plate Pos.		Target Source Path	
Operator		Result Summary	1 qualified (1 targets)

Compound Details

Cpd. 1: C42 H55 S6 Ta3

Compound Spectra (overlaid)



Compound ID Table

Cpd	Formula	Mass (Tgt)	Calc. Mass	Mass	Species	Diff(Tgt.ppm)	mDa
1	C42 H55 S6 Ta3	1291.1052	1291.1074	1294.1066 1312.1119 1317.0971 1333.0758	M+ (M+NH4)+ (M+Na)+ (M+K)+	1.72	2.21

Figure S7. HR-MS of compound 2.

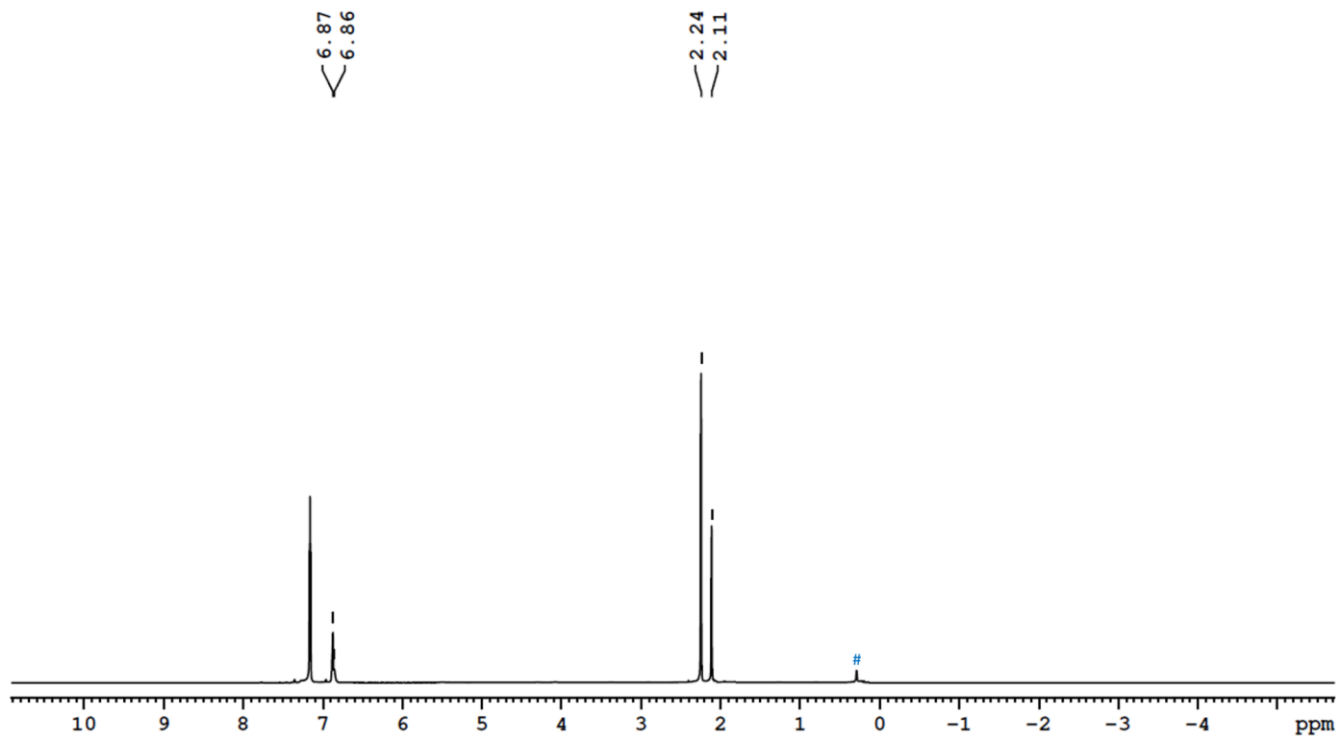


Figure S8. ¹H NMR spectrum of compound 2 in C₆D₆. (# Silicon grease)

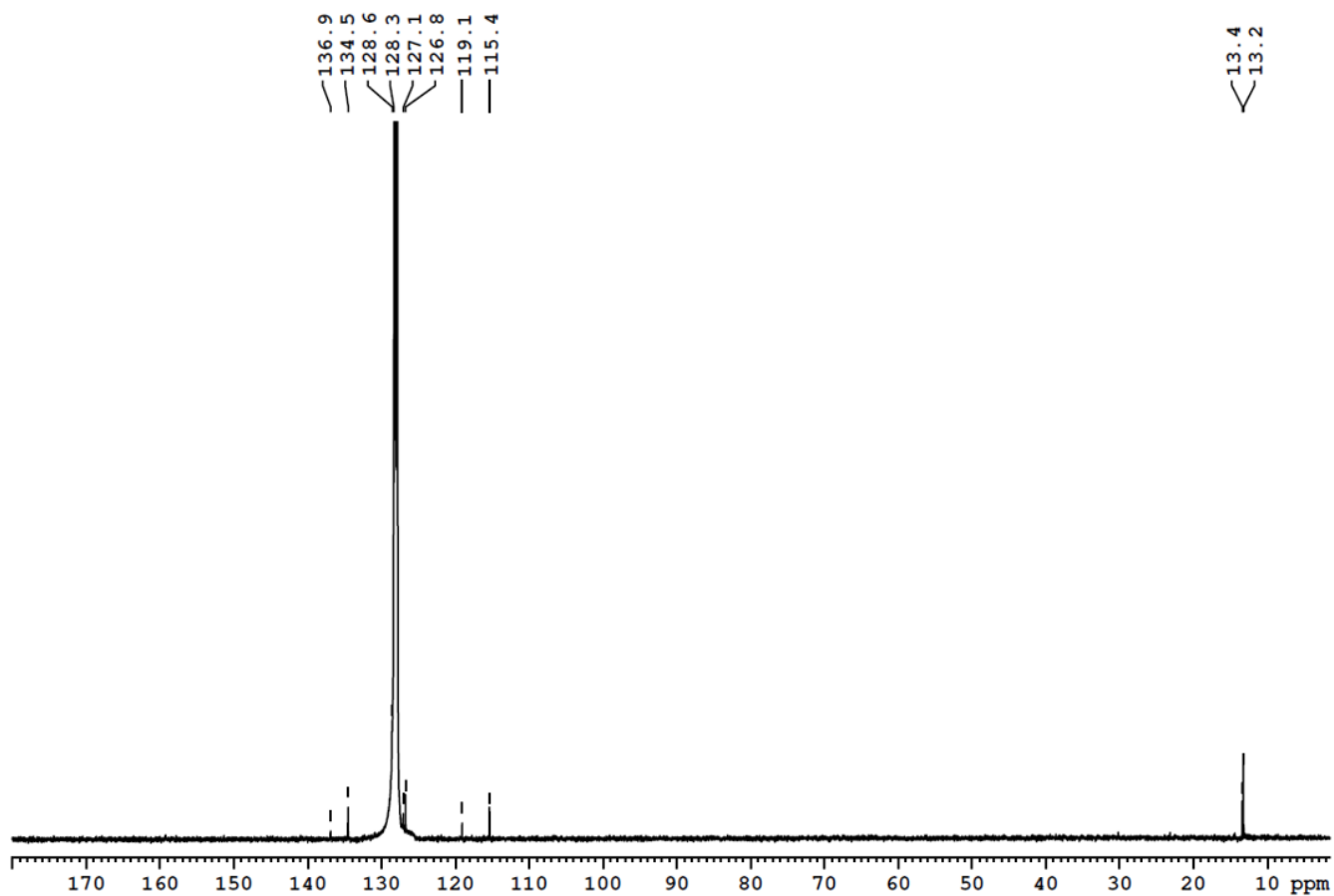


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 2 in C_6D_6 .

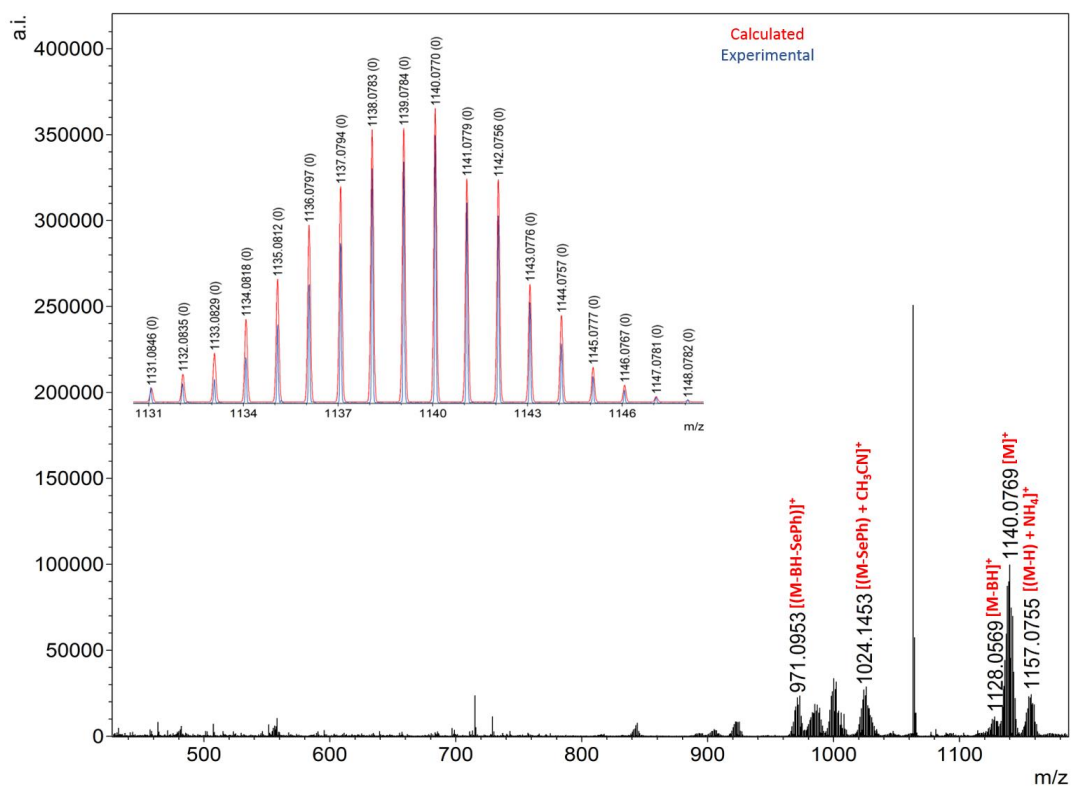


Figure S10. ESI-MS of compound 3.

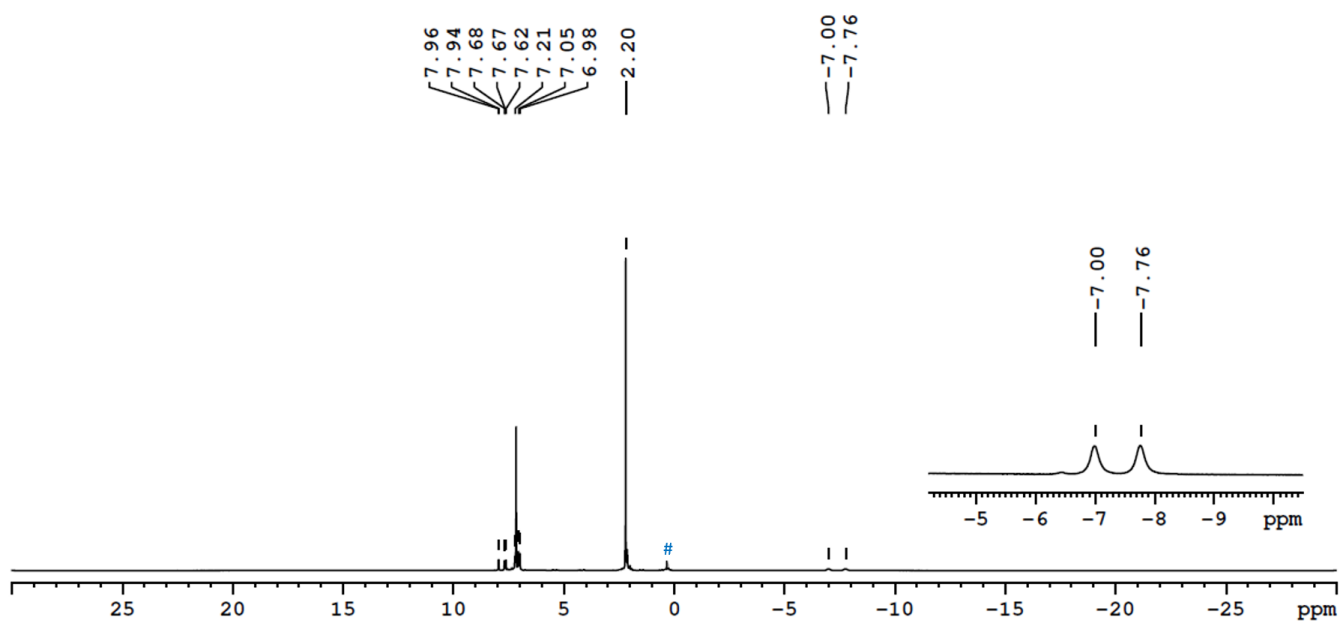


Figure S11. ^1H NMR spectrum of compound **3** in C_6D_6 . (# Silicon grease)

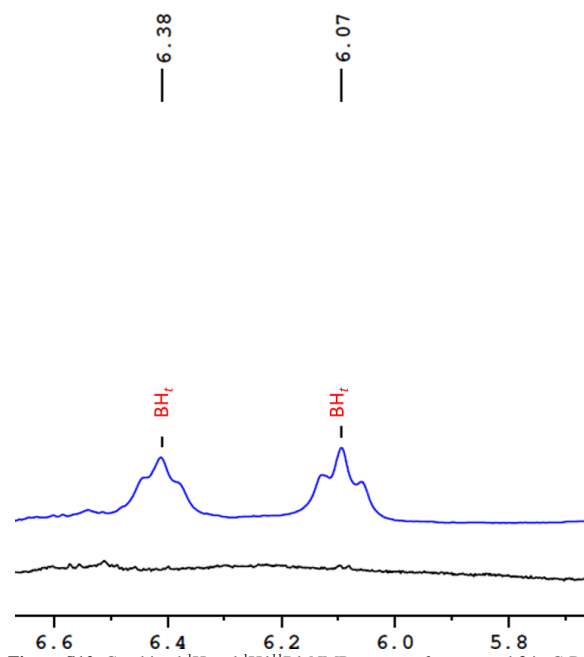


Figure S12. Combined ^1H and $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of compound **3** in C_6D_6 .

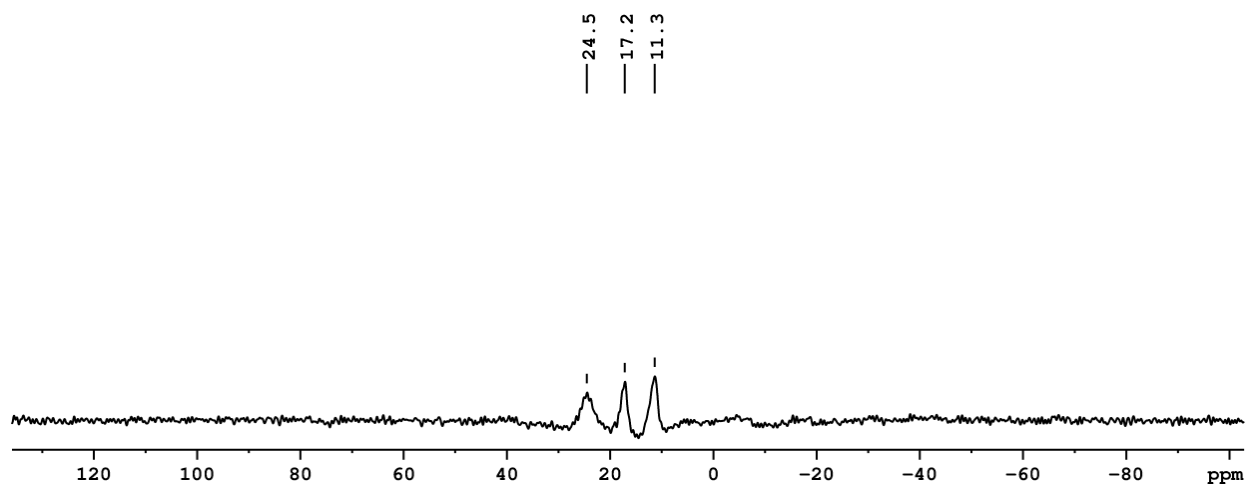


Figure S13. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **3** in CDCl_3 .¹

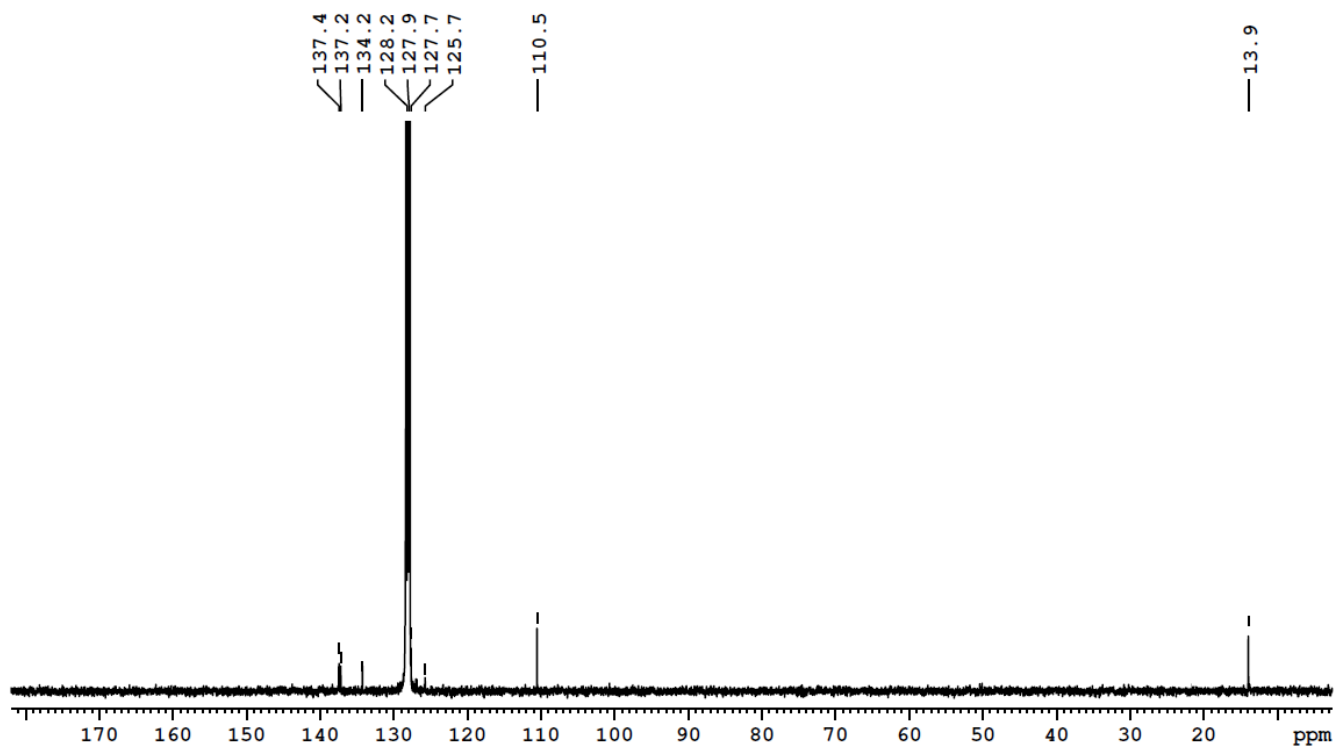


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3** in C_6D_6 .

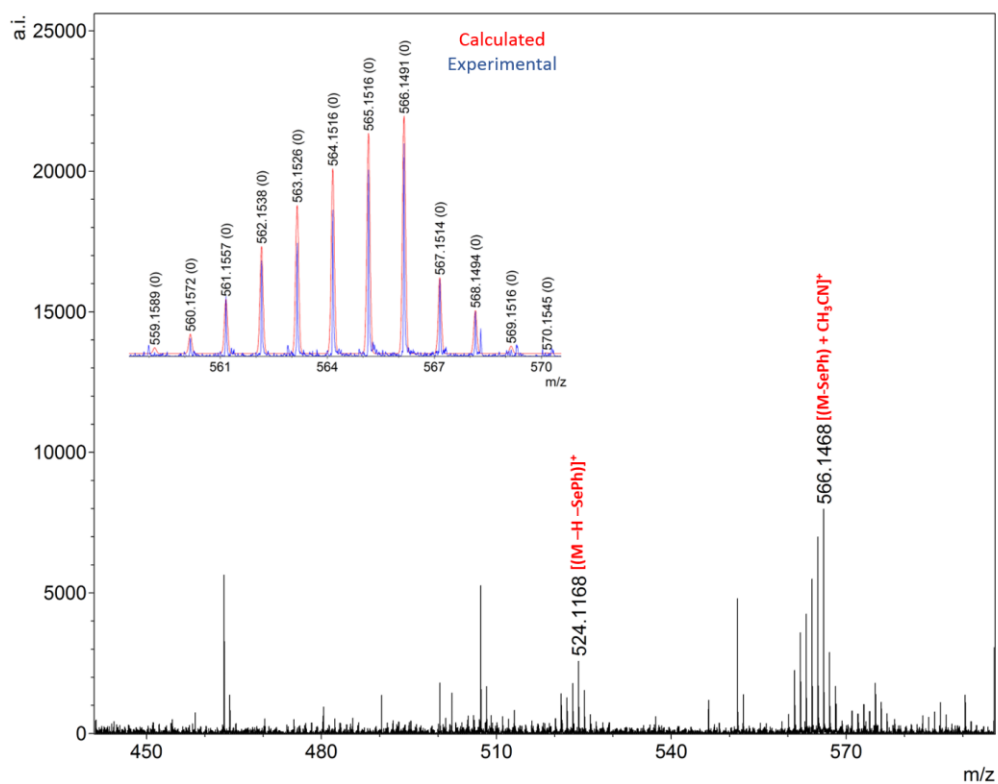


Figure S15. ESI-MS of compound 4.

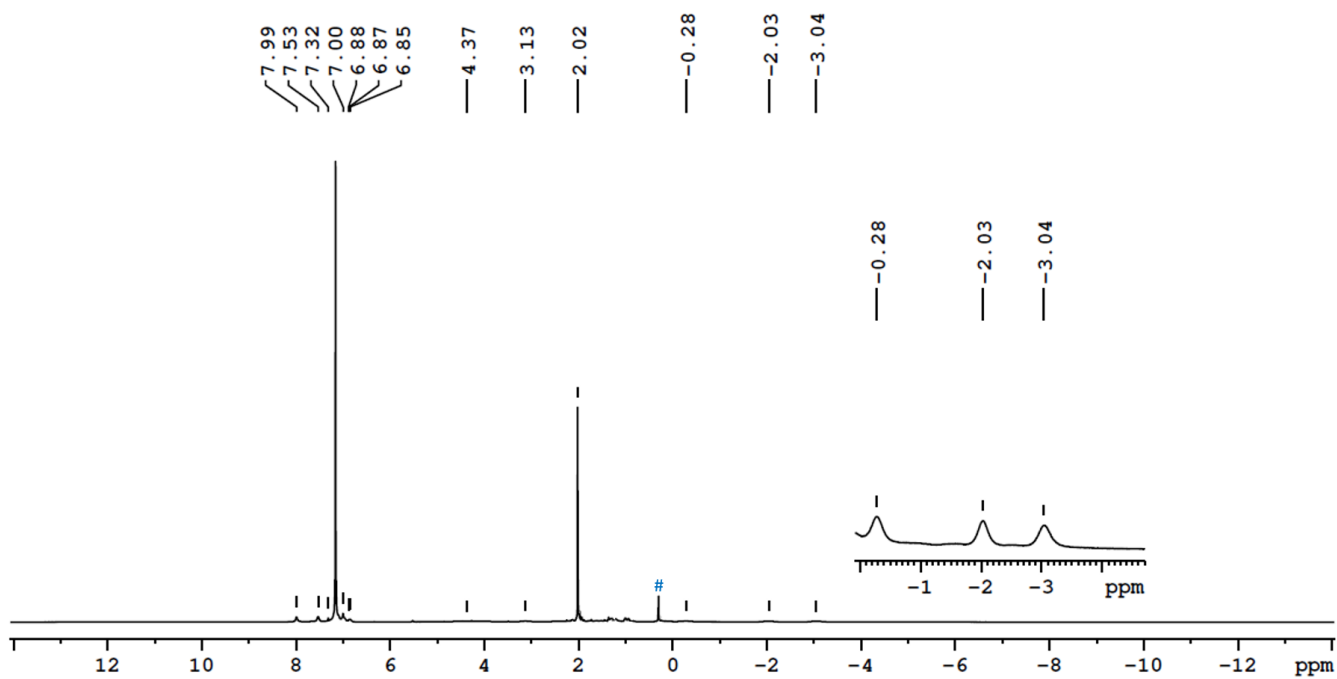


Figure S16. ¹H NMR spectrum of compound 4 in C₆D₆. (# Silicon grease)

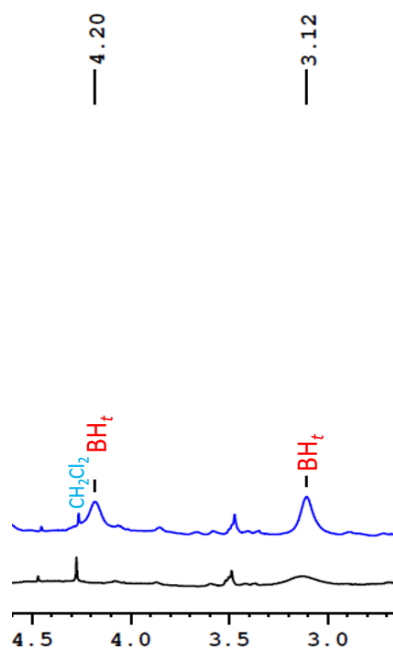


Figure S17. Combined ^1H and $^1\text{H}(^{11}\text{B})$ NMR spectra of compound **4** in C_6D_6 .

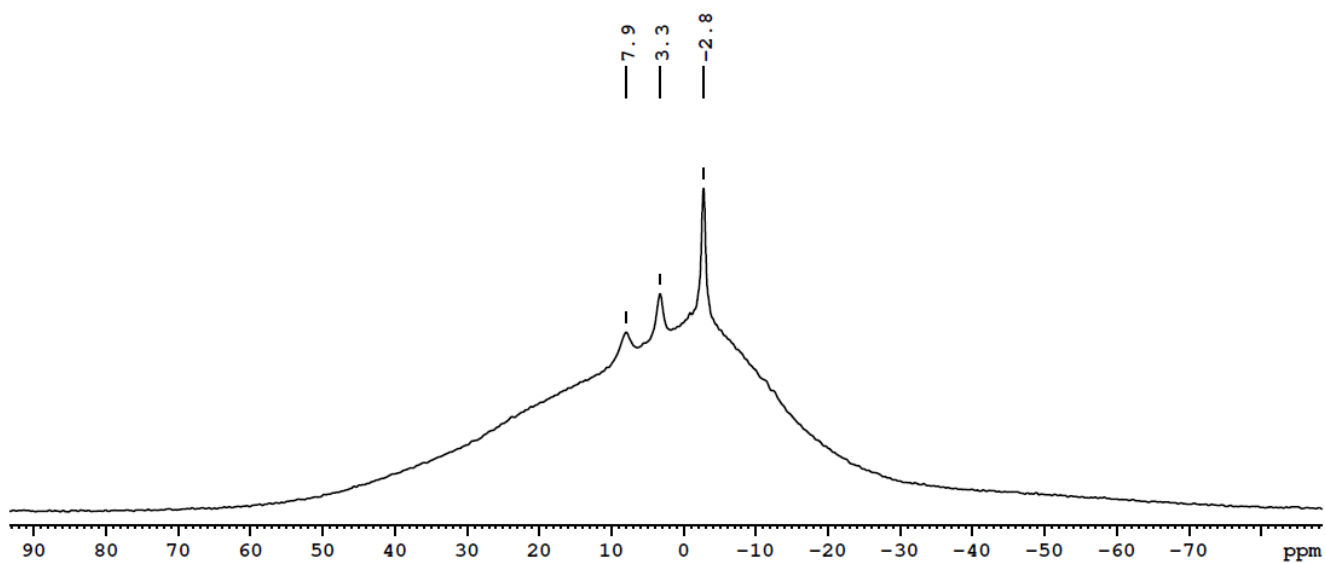


Figure S18. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **4** in C_6D_6 .

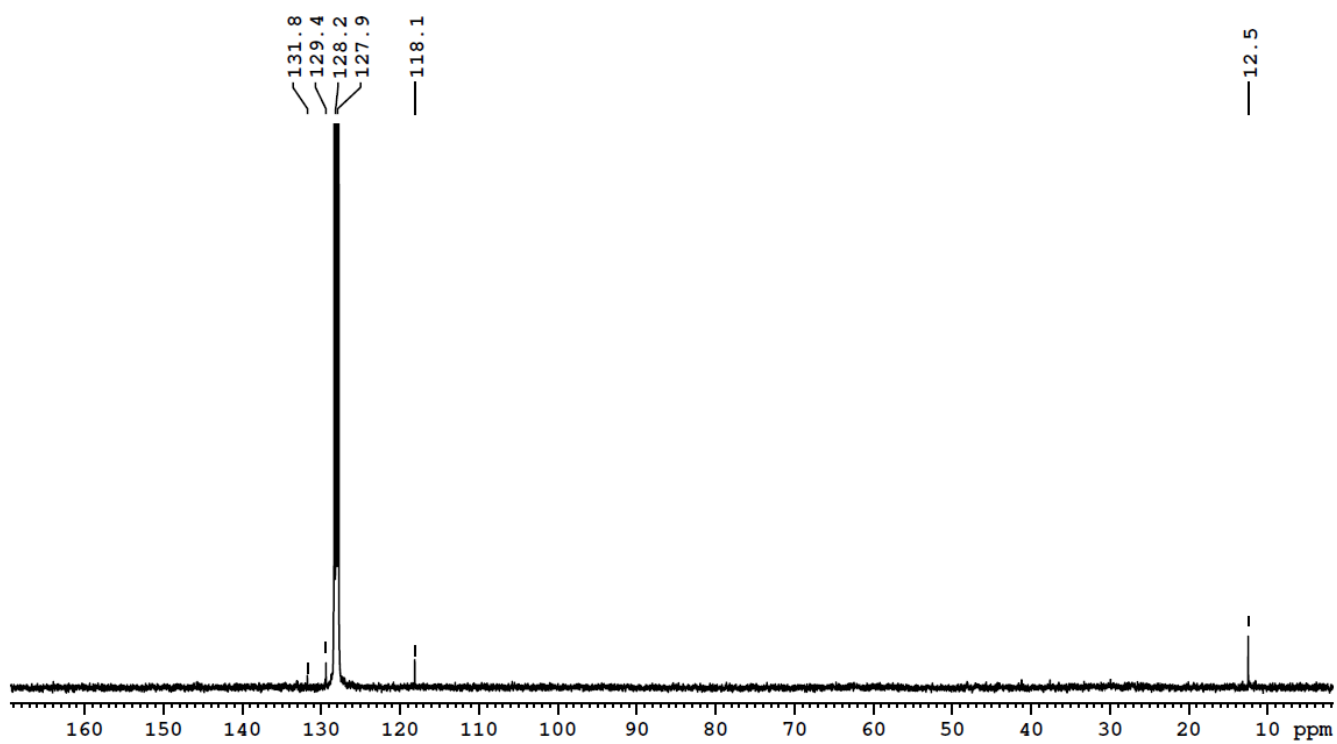


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound 4 in C_6D_6 .

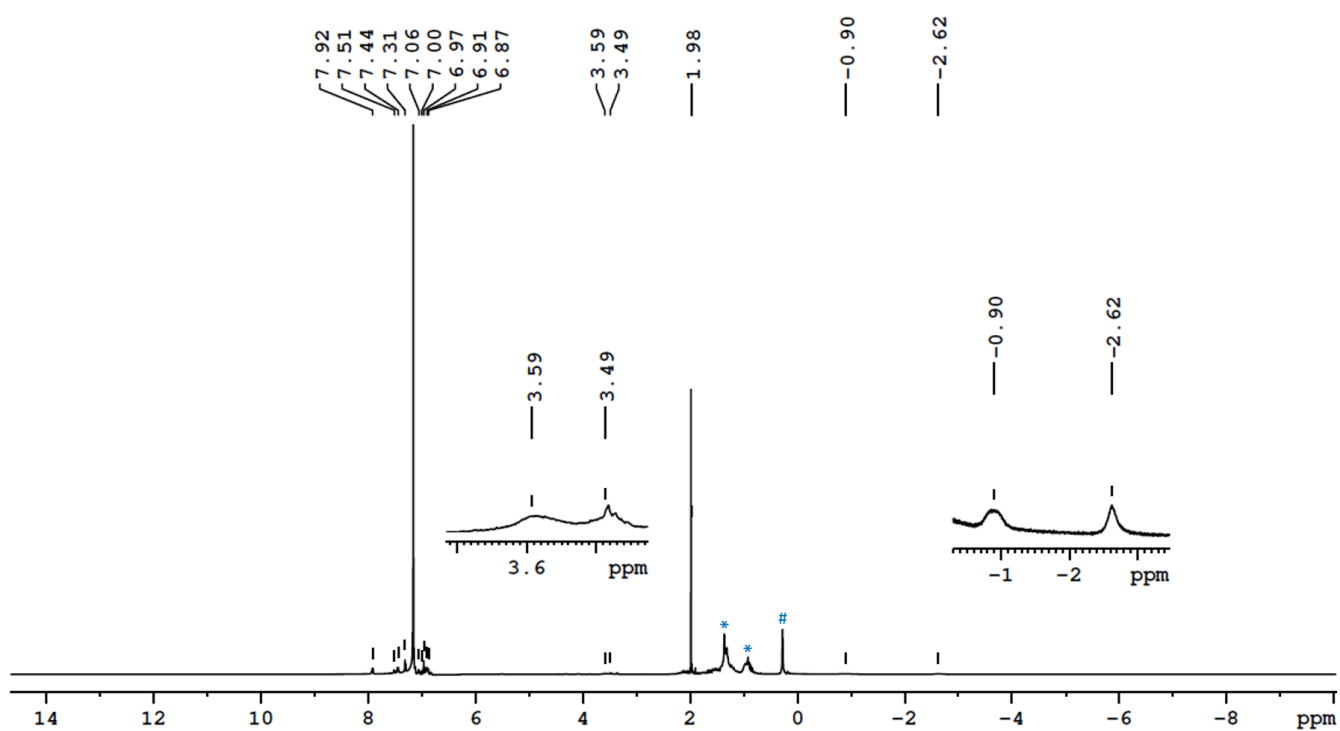


Figure S20. ^1H NMR spectrum of compound 5 in C_6D_6 . (# Silicon grease, * Grease)

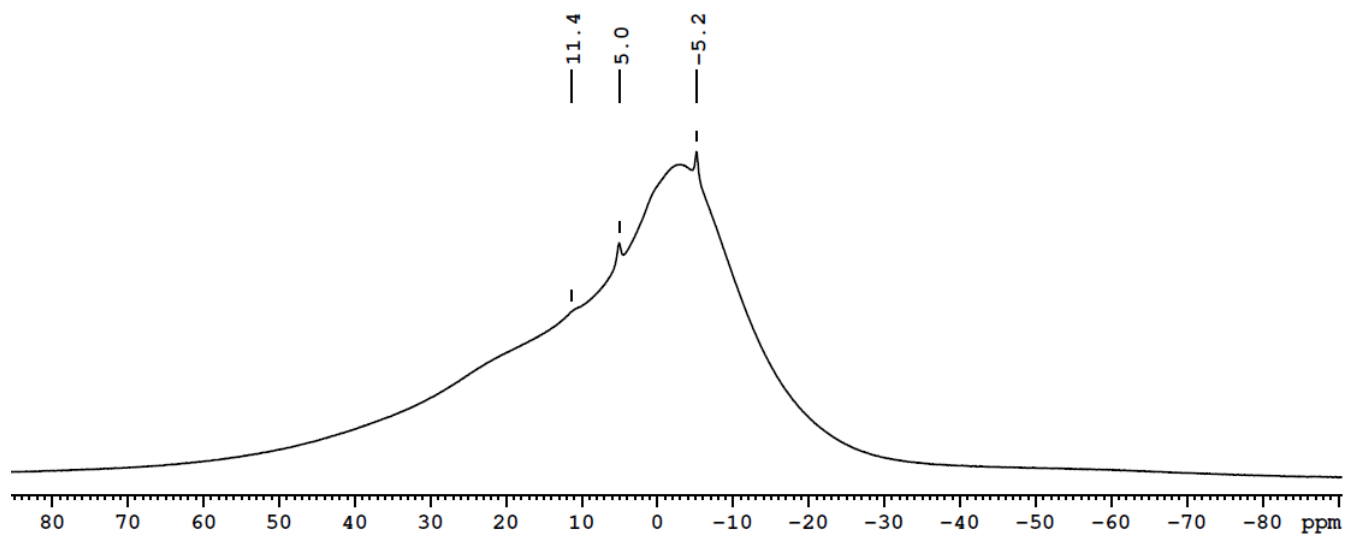


Figure S21. ^1H NMR spectrum of compound 5 in CDCl_3 .

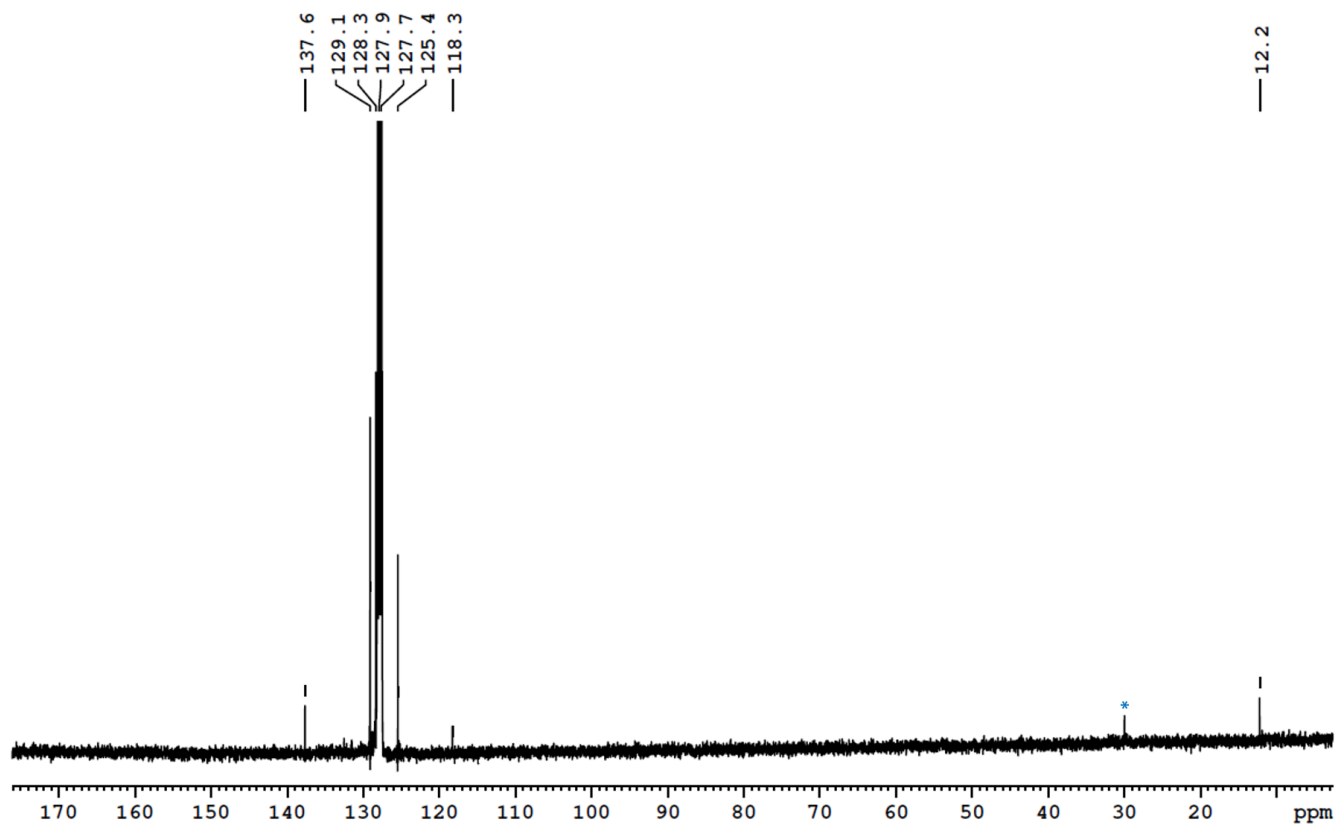


Figure S22. ^{13}C NMR spectrum of compound 5 in C_6D_6 (* Grease).

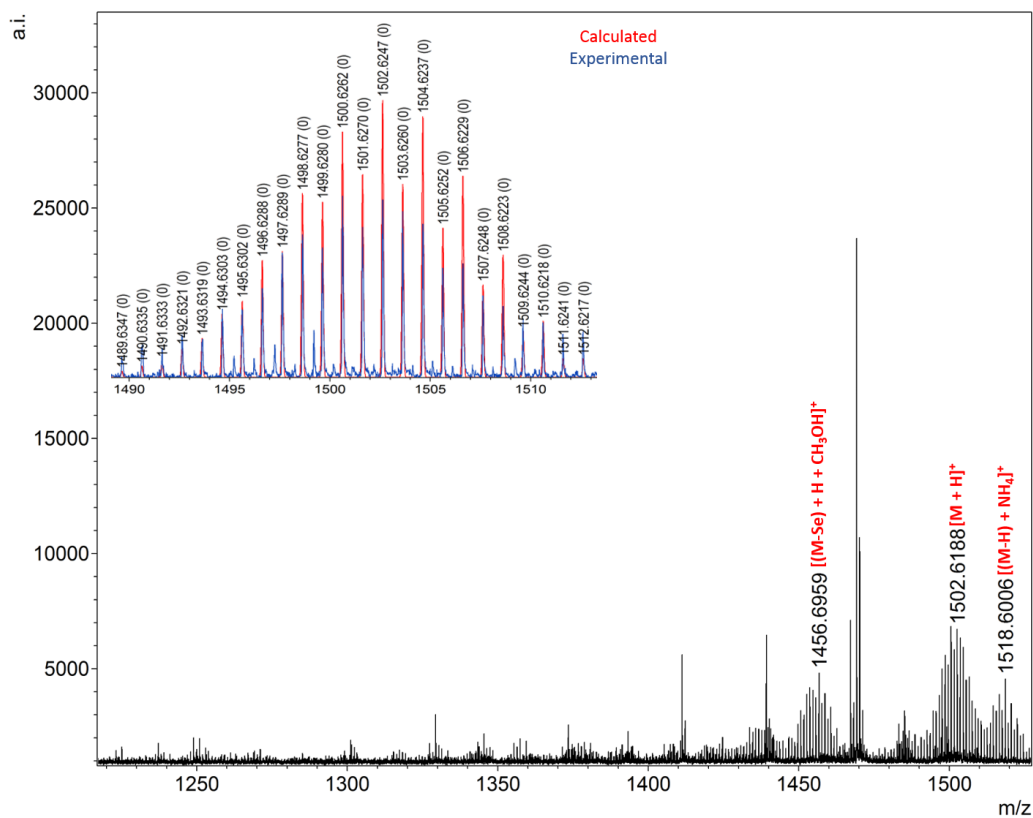


Figure S23. ESI-MS of compound 6.

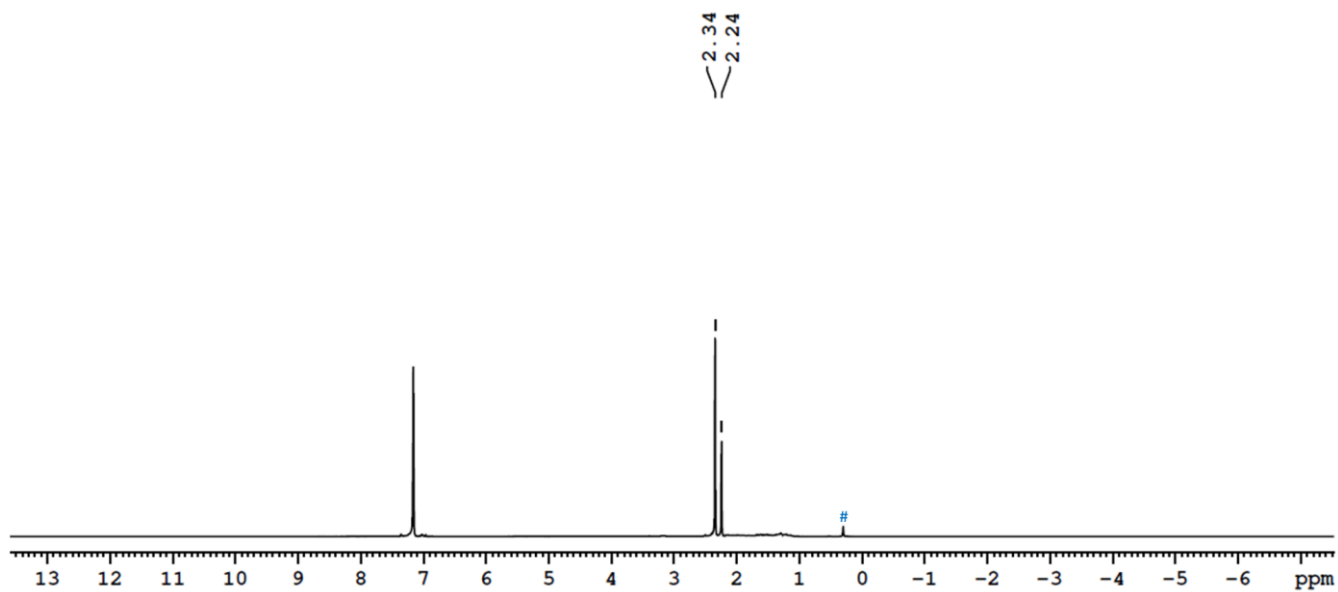


Figure S24. ¹H NMR spectrum of compound 6 in C₆D₆. (# Silicon grease)

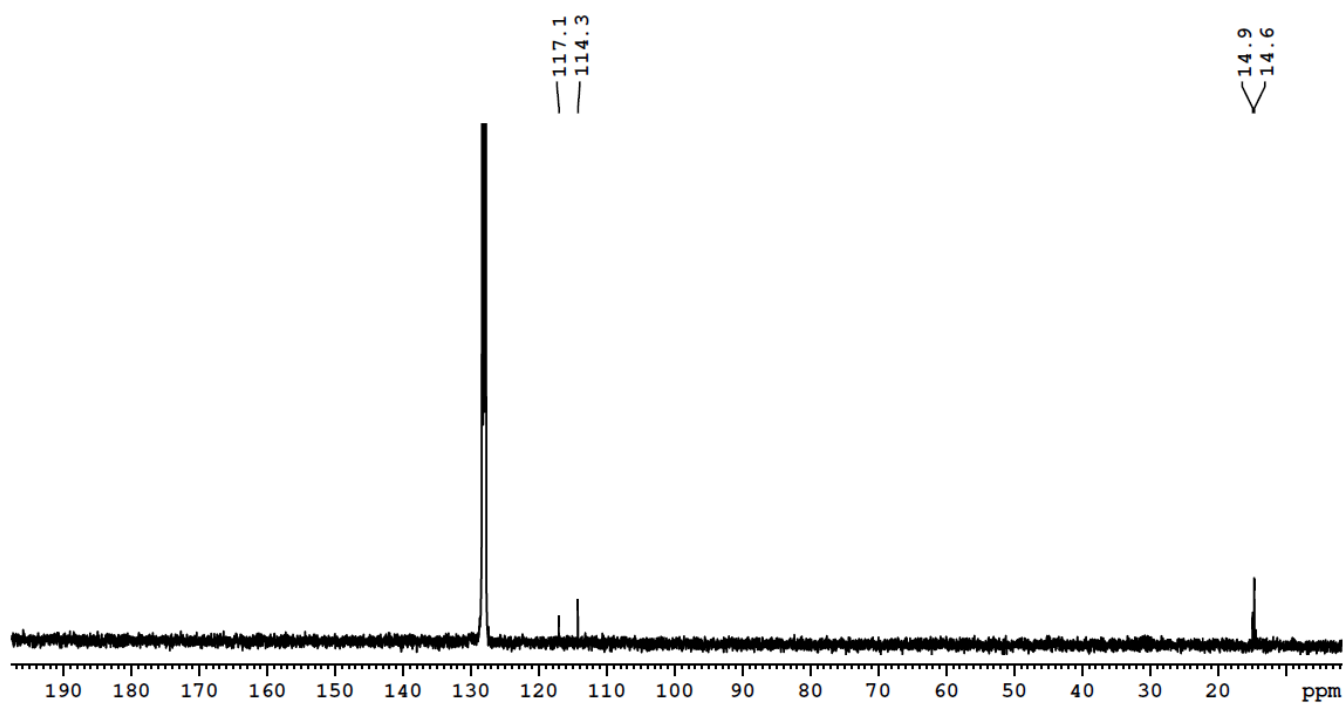


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **6** in C_6D_6 .

II. Electronic Structure Analysis

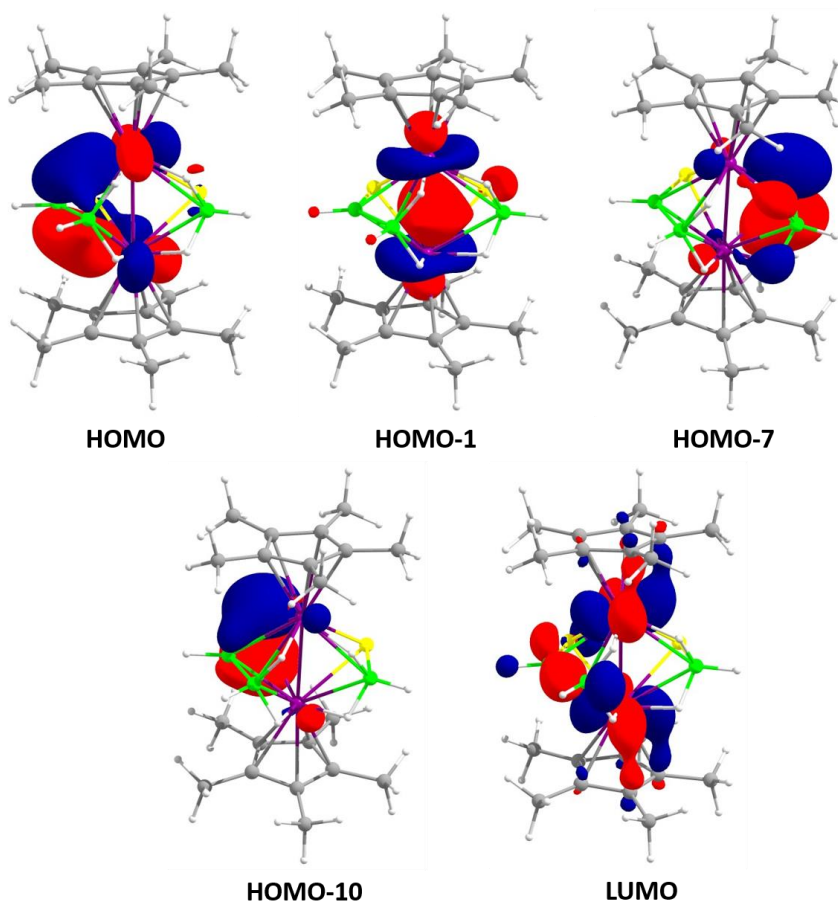


Figure S26. Selected frontier molecular orbitals of **1**.

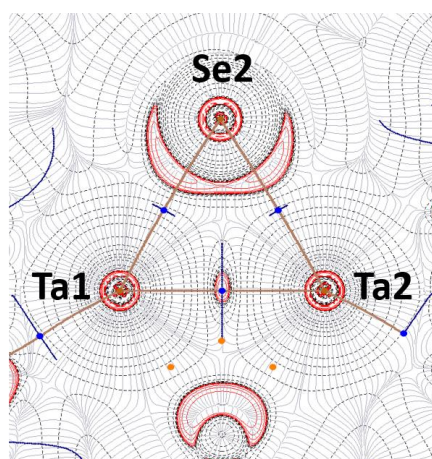


Figure S27. Contour line diagram of the Laplacian of electron density of **3** along the Ta1–Ta2–Se2 plane of **3**. [Solid red lines indicate the areas of charge concentration ($\nabla^2\rho(r) < 0$), while dashed black lines show the areas of charge depletion ($\nabla^2\rho(r) > 0$). Blue dots indicate bond critical points (BCPs), and the bold brown line depicts the bond path].

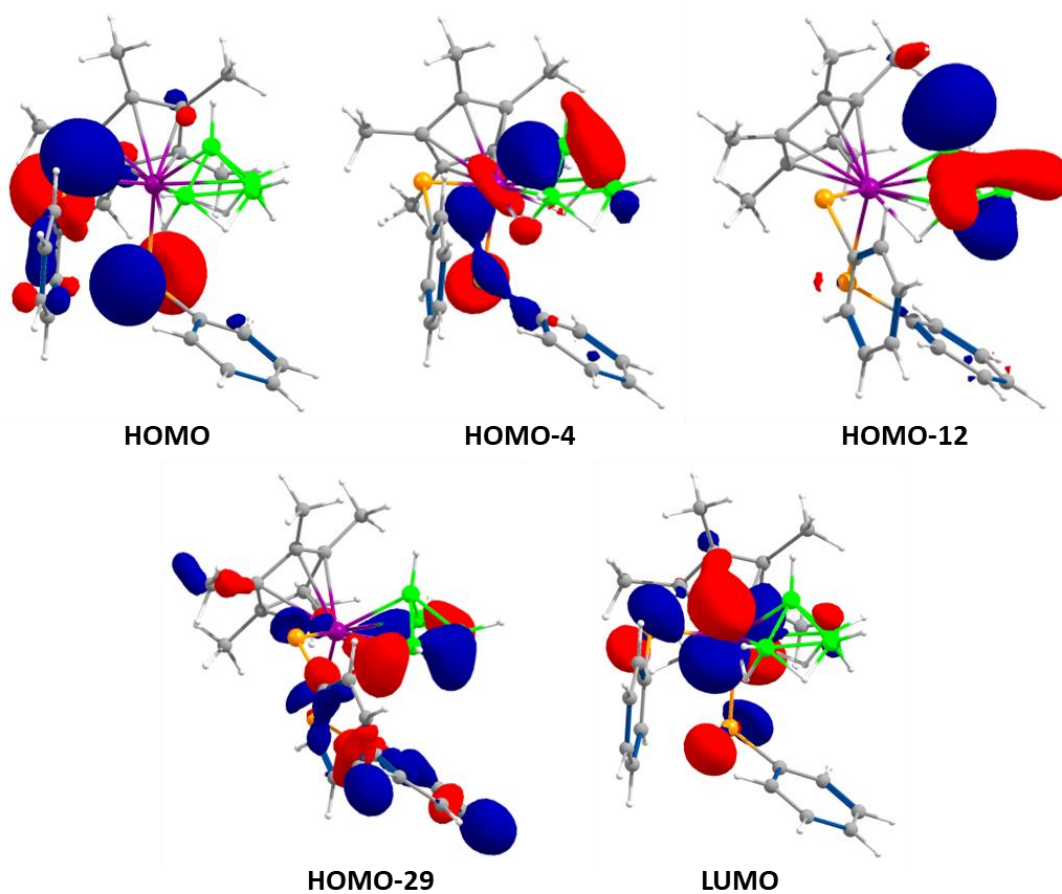


Figure S28. Selected frontier molecular orbitals of **4**.

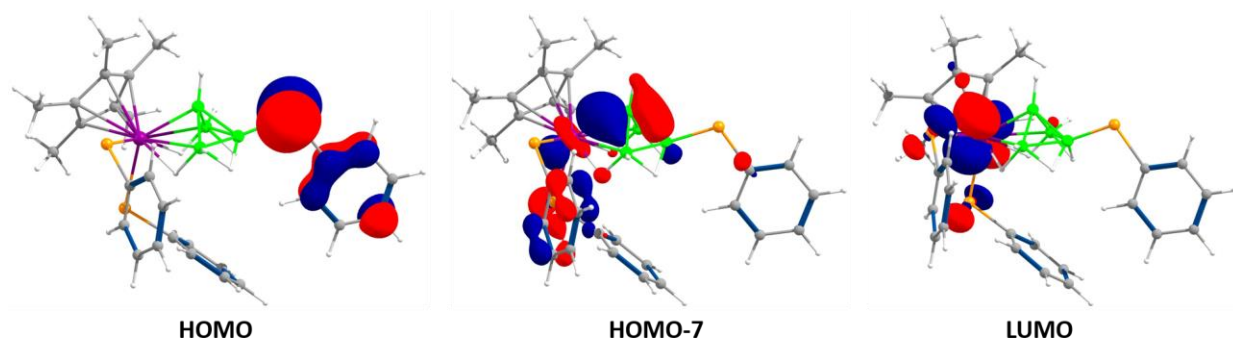


Figure S29. Selected frontier molecular orbitals of **5**.

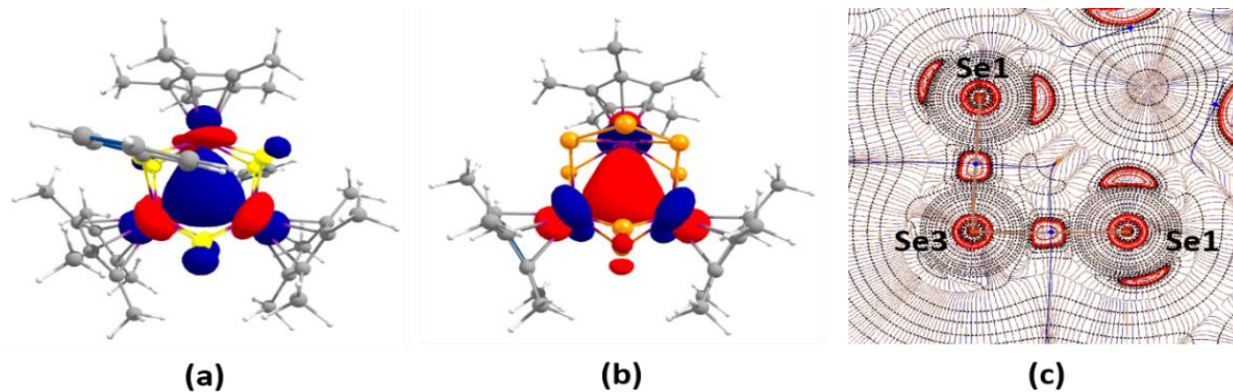


Figure S30. (a) HOMO of **2**; (b) HOMO of **6**; (c) Contour line diagram of Laplacian of electron density along the Se1–Se3–Se1 plane of **6**.

Table S1. Calculated natural charges (q_{Ta} , q_B and q_E), natural valence population (Pop) and HOMO–LUMO gaps of **1-6** and $[Cp^*TaCl_2(B_4H_8)]$ (E = S or Se).

Compounds	q_{Ta}	q_B	q_E	Pop (T_{val})	Pop (B_{val})	Pop (E_{val})	ΔE_{H-L} (eV)
1	-0.110	-0.287	0.252	5.053	3.261	5.724	3.509
	-0.109	-0.179	0.124	5.052	3.151	5.855	
		-0.219			3.189		
2	-0.126	-	-0.054	5.023		6.036	2.482
	-0.056		-0.024	4.948		6.008	
	-0.129		0.250	5.025		5.715	
			-0.058			6.040	
			-0.027			6.010	
3			0.254			5.710	3.037
	-0.153	-0.302	0.209	5.094	3.279	5.770	
	-0.168	-0.243	0.457	5.109	3.216	5.525	
		-0.319	0.455		3.294	5.527	
		-0.205	0.238	5.044	3.180	5.746	
4		-0.380	0.262		3.354	5.722	3.493
		-0.243			3.221		
		-0.173			3.151		
5	-0.102	-0.224	0.269	5.049	3.199	5.715	2.987
		-0.383	0.246		3.357	5.738	
		-0.184	0.277		3.158	5.704	
		-0.265			3.235		
6	-0.462	-	0.252	5.361	-	5.720	2.500
	-0.435		0.148	5.326		5.833	
	-0.462		0.162	5.361		5.817	
			0.181			5.799	
			-0.047			6.027 5.718	
			0.161			5.818	
$[Cp^*TaCl_2(B_4H_8)]$	0.328	-0.239	-	4.597	3.219	-	4.119
		-0.400			3.374		
		-0.218			3.194		
		-0.178			3.156		

Table S2. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV–vis electronic excitations for **1**. Experimental absorption wavelengths (λ_{exp} , nm) of **1** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) ^[a]
		Calc. (f)	Expt.	
1	2.590	479 (0.001)		HOMO-1→LUMO (98)
2	2.730	454 (0.068)	451	HOMO→LUMO (92)
3	3.108	399 (0.002)		HOMO→LUMO+1 (98)
4	3.306	375 (0.001)		HOMO-1→LUMO+1 (97)
5	3.479	356 (0.005)	343	HOMO→LUMO+2 (94)
6	3.607	344 (0.001)		HOMO-1→LUMO+2 (98)
7	3.771	329 (0.000)		HOMO→LUMO+3 (77) HOMO→LUMO+5 (20)
8	3.893	318 (0.004)		HOMO-1→LUMO+3 (62) HOMO-1→LUMO+5 (19)
9	3.936	315 (0.000)		HOMO→LUMO+4 (23) HOMO→LUMO+6 (59)
10	1.114	301 (0.0)		HOMO-2→LUMO+1 (88)

^[a]Components with greater than 10% contribution shown.

Table S3. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV–vis electronic excitations for **2**. Experimental absorption wavelengths (λ_{exp} , nm) of **2** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) ^[a]
		Calc. (f)	Expt.	
1	1.475	841 (0.002)		HOMO→LUMO (99)
2	1.806	687 (0.001)		HOMO→LUMO+1 (99)
3	2.172	571 (0.008)	603	HOMO-1→LUMO (98)
4	2.351	527 (0.001)		HOMO-1→LUMO+1 (98)
5	2.460	504 (0.008)	494	HOMO→LUMO+2 (93)
6	2.538	488 (0.002)		HOMO-2→LUMO (98)
7	2.841	436 (0.004)		HOMO-3→LUMO (61) HOMO→LUMO+3 (33)
8	2.950	420 (0.008)		HOMO-4→LUMO (80) HOMO-3→LUMO+1 (12)
9	2.970	417 (0.031)	420	HOMO-3→LUMO (23) HOMO-2→LUMO+1 (42) HOMO→LUMO+3 (24)
10	3.001	413 (0.000)		HOMO-6→LUMO (14) HOMO-1→LUMO+2 (77)
11	3.056	406 (0.035)		HOMO-5→LUMO (55) HOMO→LUMO+3 (21)
12	3.082	402 (0.033)		HOMO-5→LUMO (30) HOMO-2→LUMO+1 (36) HOMO→LUMO+3 (11)
13	3.100	400 (0.014)		HOMO-7→LUMO (35) HOMO-6→LUMO (23) HOMO-3→LUMO+1 (11)
14	3.151	393 (0.001)		HOMO-7→LUMO (45) HOMO-6→LUMO (17) HOMO-3→LUMO+1 (15)
15	3.162	392 (0.001)		HOMO-6→LUMO (14) HOMO-3→LUMO+1 (21) HOMO→LUMO+4 (53)
16	3.240	383 (0.016)		HOMO-6→LUMO (13) HOMO-3→LUMO+1 (27) HOMO→LUMO+4 (26) HOMO→LUMO+6 (14)
17	3.269	379 (0.001)		HOMO-8→LUMO (92)

18	3.311	374 (0.002)		HOMO-9→LUMO (57) HOMO→LUMO+6 (16)
19	3.321	373 (0.002)		HOMO→LUMO+5 (84)
20	3.368	368 (0.013)		HOMO-4→LUMO+1 (87)
21	3.401	365 (0.022)		HOMO-9→LUMO (17) HOMO-2→LUMO+2 (11) HOMO→LUMO+6 (46)
22	3.434	361 (0.003)		HOMO-10→LUMO (69) HOMO-1→LUMO+3 (21)
23	3.463	358 (0.011)		HOMO-6→LUMO+1 (50) HOMO-5→LUMO+1 (26)
24	3.468	358 (0.022)		HOMO-10→LUMO (14) HOMO-6→LUMO+1 (24) HOMO-5→LUMO+1 (11) HOMO-1→LUMO+3 (33) HOMO-3→LUMO+1 (15)
25	3.479	356 (0.029)		HOMO-5→LUMO+1 (47) HOMO-1→LUMO+3 (19)
26	3.575	347 (0.075)	353	HOMO-2→LUMO+2 (65)
27	3.609	344 (0.005)		HOMO-11→LUMO (52) HOMO-7→LUMO+1(30)
28	3.643	340 (0.002)		HOMO-11→LUMO (29) HOMO-7→LUMO+1 (44) HOMO-3→LUMO+2 (13)
29	3.663	339 (0.000)		HOMO-8→LUMO+1 (82)
30	3.722	333 (0.001)		HOMO-12→LUMO (32) HOMO-3→LUMO+2 (37)
31	3.753	330 (0.008)		HOMO-12→LUMO (15) HOMO-3→LUMO+2 (37) HOMO-1→LUMO+4(22)
32	3.754	330 (0.001)		HOMO-12→LUMO (16) HOMO-1→LUMO+4 (50)
33	3.761	329 (0.003)		HOMO-14→LUMO (60)
34	3.822	324 (0.000)		HOMO-9→LUMO+1 (44) HOMO→LUMO+14 (31)
35	3.835	323 (0.001)		HOMO-14→LUMO (11) HOMO-11→LUMO+1 (15) HOMO-4→LUMO+2 (44) HOMO-2→LUMO+3 (11)

36	3.851	322 (0.001)		HOMO-3→LUMO+1 (14) HOMO→LUMO+7 (25) HOMO→LUMO+14 (40)
37	3.874	320 (0.025)		HOMO-1→LUMO+5 (17) HOMO-1→LUMO+6 (16) HOMO→LUMO+7 (22)
38	3.886	319 (0.020)		HOMO-1→LUMO+5 (73)
39	3.903	318 (0.046)		HOMO→LUMO+8 (17) HOMO→LUMO+12 (30)
40	3.940	315 (0.002)		HOMO-13→LUMO (67) HOMO-2→LUMO+3 (11)
41	3.957	314 (0.058)	311	HOMO-1→LUMO+6 (53)
42	3.961	313 (0.003)		HOMO-10→LUMO+1 (28) HOMO-5→LUMO+2 (26)
43	3.969	312 (0.019)		HOMO-13→LUMO (12) HOMO-11→LUMO+1 (12) HOMO-2→LUMO+3 (25)
44	4.008	310 (0.035)		HOMO→LUMO+15 (15) HOMO→LUMO+16 (39)
45	4.010	309 (0.017)		HOMO-10→LUMO+1 (37) HOMO-5→LUMO+2 (23)
46	4.028	307 (0.062)		HOMO-11→LUMO+1 (16) HOMO-6→LUMO+2 (13) HOMO-4→LUMO+2 (11) HOMO-2→LUMO+3 (22)
47	4.054	306 (0.018)		HOMO-15→LUMO (56) HOMO-5→LUMO+2 (19)
48	4.056	305 (0.018)		HOMO-11→LUMO+1 (13) HOMO-6→LUMO+2 (50)
49	4.124	301 (0.028)		HOMO-16→LUMO (14) HOMO-7→LUMO+2 (43)
50	4.129	300 (0.001)		HOMO→LUMO+7 (22) HOMO→LUMO+10(42) HOMO→LUMO+11 (20)

^[a]Components with greater than 10% contribution shown.

Table S4. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV–vis electronic excitations for **3**. Experimental absorption wavelengths (λ_{exp} , nm) of **3** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) ^[a]
		Calc. (f)	Expt.	
1	2.327	533 (0.012)		HOMO-1→LUMO (98)
2	2.399	517 (0.038)	495	HOMO→LUMO (94)
3	2.784	445 (0.002)		HOMO→LUMO+1 (72)
4	2.816	440 (0.001)		HOMO→LUMO+2 (79)
5	2.971	417 (0.006)		HOMO-1→LUMO+1 (70) HOMO→LUMO+1 (17)
6	2.985	415 (0.005)		HOMO-1→LUMO+1 (11) HOMO-1→LUMO+2 (70) HOMO→LUMO+2 (13)
7	3.272	379 (0.005)		HOMO→LUMO+3 (86)
8	3.407	364 (0.003)		HOMO-1→LUMO+3 (84)
9	3.559	348 (0.008)		HOMO→LUMO+4 (62)
10	3.611	343 (0.005)		HOMO-1→LUMO+4 (41) HOMO→LUMO+5 (15)
11	3.681	337 (0.027)		HOMO-2→LUMO (90)
12	3.751	331 (0.014)		HOMO-3→LUMO (52)
13	3.761	330 (0.091)	335	HOMO-3→LUMO (14) HOMO-1→LUMO+4 (23) HOMO→LUMO+5 (25)
14	3.884	319 (0.008)		HOMO-3→LUMO (21) HOMO-1→LUMO+5 (22)
15	3.897	318 (0.011)		HOMO→LUMO+5 (11) HOMO→LUMO+6 (29) HOMO→LUMO+8 (24)
16	3.956	313 (0.009)		HOMO-4→LUMO (91)
17	3.972	312 (0.006)		HOMO→LUMO+5 (23) HOMO→LUMO+6 (23) HOMO→LUMO+8 (36)
18	4.031	308 (0.002)		HOMO→LUMO+7 (80)
19	4.066	305 (0.006)		HOMO→LUMO+9 (32) HOMO→LUMO+10 (25) HOMO→LUMO+11 (36)
20	4.081	304 (0.010)		HOMO-1→LUMO+5 (24) HOMO-1→LUMO+6 (52)

^[a]Components with greater than 10% contribution shown.

Table S5. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV–vis electronic excitations for **4**. Experimental absorption wavelengths (λ_{exp} , nm) of **4** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) ^[a]
		Calc. (f)	Expt.	
1	2.909	426 (0.123)	445	HOMO→LUMO (95)
2	3.278	378 (0.028)		HOMO-2→LUMO (34) HOMO-1→LUMO (63)
3	3.408	364 (0.057)	372	HOMO-2→LUMO (61) HOMO-1→LUMO (30)
4	3.452	359 (0.007)		HOMO-5→LUMO (12) HOMO-4→LUMO (63) HOMO-3→LUMO (17)
5	3.713	334 (0.002)		HOMO→LUMO+1 (92)
6	3.728	333 (0.015)		HOMO-7→LUMO (11) HOMO-5→LUMO (17) HOMO-3→LUMO (59)
7	3.769	329 (0.026)		HOMO-6→LUMO (20) HOMO-5→LUMO (40) HOMO-4→LUMO (12) HOMO-3→LUMO (13)
8	3.865	321 (0.010)		HOMO-8→LUMO (79)
9	4.057	306 (0.013)		HOMO→LUMO+2 (94)
10	4.071	305 (0.001)		HOMO-6→LUMO (63) HOMO-5→LUMO (19) HOMO-4→LUMO (13)

^[a]Components with greater than 10% contribution shown.

Table S6. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV–vis electronic excitations for **5**. Experimental absorption wavelengths (λ_{exp} , nm) of **5** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) ^[a]
		Calc. (f)	Expt.	
1	2.811	441 (0.025)		HOMO→LUMO (99)
2	2.881	430 (0.115)	445	HOMO-1→LUMO (95)
3	3.220	385 (0.016)		HOMO-3→LUMO (34) HOMO-2→LUMO (63)
4	3.375	367 (0.053)	381	HOMO-3→LUMO (60) HOMO-2→LUMO (31)
5	3.490	355 (0.015)		HOMO-8→LUMO (42) HOMO-7→LUMO (12) HOMO-6→LUMO (11)
6	3.549	349 (0.002)		HOMO-1→LUMO+1 (53) HOMO→LUMO+1 (41)
7	3.617	343 (0.005)		HOMO-1→LUMO+1 (38) HOMO→LUMO+1 (52)
8	3.689	336 (0.013)		HOMO-9→LUMO (22) HOMO-7→LUMO (35) HOMO-4→LUMO (33)
9	3.703	335 (0.018)		HOMO-7→LUMO (16) HOMO-6→LUMO (31) HOMO-4→LUMO (29)
10	3.817	325 (0.011)		HOMO-10→LUMO (74)
11	3.896	318 (0.017)		HOMO-1→LUMO+2 (76) HOMO→LUMO+2 (14)
12	3.997	310 (0.005)		HOMO-8→LUMO (22) HOMO-6→LUMO (31) HOMO→LUMO+2 (28)
13	4.001	309 (0.008)		HOMO-6→LUMO (19) HOMO→LUMO+2 (48)
14	4.073	304 (0.002)		HOMO-9→LUMO (48) HOMO-7→LUMO (17) HOMO-5→LUMO (23)
15	4.138	300 (0.005)		HOMO-2→LUMO+1 (72) HOMO-1→LUMO+3 (16)

^[a]Components with greater than 10% contribution shown.

Table S7. TD-DFT calculated energies (excitation energy (eV), λ_{calc} (nm)), oscillator strength (f), and main composition of the first UV–vis electronic excitations for **6**. Experimental absorption wavelengths (λ_{exp} , nm) of **6** are given for comparison.

No	Excitation Energy (eV)	Wavelength λ (nm)		Main electronic transition (% weight) ^[a]
		Calc. (f)	Expt.	
1	1.475	803 (0.003)		HOMO→LUMO (98)
2	1.806	753 (0.000)		HOMO→LUMO+1 (93)
3	2.172	639 (0.001)		HOMO→LUMO+2 (98)
4	2.351	613 (0.000)		HOMO-1→LUMO+1 (95)
5	2.460	594 (0.004)	627	HOMO-1→LUMO (96)
6	2.538	586 (0.000)		HOMO→LUMO+3 (93)
7	2.841	528 (0.003)		HOMO-1→LUMO+2 (96)
8	2.950	512 (0.000)		HOMO-1→LUMO+3 (95)
9	2.970	483 (0.003)		HOMO-2→LUMO (91)
10	3.001	477 (0.008)		HOMO→LUMO+4 (87)
11	3.056	468 (0.002)		HOMO-3→LUMO (92)
12	3.082	449 (0.033)		HOMO-3→LUMO+1 (64) HOMO-3→LUMO+3 (26)
13	3.100	437 (0.014)		HOMO-4→LUMO (65) HOMO→LUMO+5 (16)
14	3.151	434 (0.001)		HOMO-5→LUMO+1 (11) HOMO-4→LUMO (11) HOMO-2→LUMO+1 (51)
15	3.162	433 (0.001)		HOMO-5→LUMO (55) HOMO-4→LUMO+1 (27)
16	3.240	429 (0.016)		HOMO-3→LUMO+2 (82)
17	3.269	422 (0.001)		HOMO-1→LUMO+4 (73) HOMO→LUMO+5 (13)
18	3.311	419 (0.002)		HOMO-3→LUMO+1 (24) HOMO-3→LUMO+3 (44)
19	3.321	412 (0.002)		HOMO-4→LUMO+1 (11) HOMO-3→LUMO+3 (15) HOMO-2→LUMO+2 (53)
20	3.368	404 (0.013)		HOMO-5→LUMO (15) HOMO-4→LUMO+1 (33) HOMO-2→LUMO+2 (23)
21	3.401	403 (0.022)		HOMO-5→LUMO+1 (16) HOMO-4→LUMO (12) HOMO-1→LUMO+4 (12)

22	3.434	393 (0.051)	400	HOMO→LUMO+5 (39) HOMO-5→LUMO+1 (55) HOMO-2→LUMO+1 (15)
23	3.463	391 (0.008)		HOMO-4→LUMO+2 (29) HOMO-2→LUMO+3 (57)
24	3.468	390 (0.003)		HOMO-4→LUMO+2 (49) HOMO-2→LUMO+3 (20) HOMO-1→LUMO+5 (13)
25	3.479	384 (0.002)		HOMO-6→LUMO (78)
26	3.575	380 (0.000)		HOMO-5→LUMO+2 (73)
27	3.609	377 (0.000)		HOMO-7→LUMO (31) HOMO-4→LUMO+3(59)
28	3.643	376 (0.001)		HOMO-8→LUMO (28) HOMO-7→LUMO (18) HOMO-5→LUMO+2 (11)
29	3.663	372 (0.006)		HOMO-8→LUMO (22) HOMO-7→LUMO (35) HOMO-6→LUMO+1 (12) HOMO-4→LUMO+3 (14)
30	3.722	371 (0.015)	374	HOMO-1→LUMO+5 (33) HOMO→LUMO+7 (39)
31	3.753	367 (0.000)		HOMO-10→LUMO (12) HOMO-8→LUMO (21) HOMO-6→LUMO+1(48)
32	3.754	366 (0.020)		HOMO-1→LUMO+5 (16) HOMO→LUMO+6 (17) HOMO→LUMO+7 (25)
33	3.761	365 (0.025)		HOMO→LUMO+6 (28) HOMO→LUMO+7 (17) HOMO→LUMO+8 (12)
34	3.822	361 (0.010)		HOMO-7→LUMO+1 (40) HOMO-5→LUMO+3 (31)
35	3.835	359 (0.020)		HOMO-9→LUMO (34) HOMO-5→LUMO+3 (20) HOMO-1→LUMO+5 (13)
36	3.851	354 (0.018)		HOMO→LUMO+6 (11) HOMO→LUMO+8 (24) HOMO→LUMO+9 (36) HOMO→LUMO+12 (11)

37	3.874	353 (0.010)		HOMO-9→LUMO (28) HOMO-7→LUMO+1 (20) HOMO-5→LUMO+3 (23)
38	3.886	351 (0.001)		HOMO-10→LUMO (45) HOMO-2→LUMO+4 (19)
39	3.903	346 (0.011)		HOMO-11→LUMO (12) HOMO-8→LUMO+1 (15) HOMO-6→LUMO+2 (26) HOMO-3→LUMO+4 (17)
40	3.940	344 (0.007)		HOMO-9→LUMO+1 (26) HOMO-2→LUMO+4 (29) HOMO-1→LUMO+6 (21)
41	3.957	343 (0.004)		HOMO-9→LUMO+1 (15) HOMO-1→LUMO+6 (70)
42	3.961	340 (0.008)		HOMO-11→LUMO (19) HOMO-3→LUMO+4 (17) HOMO→LUMO+9 (12)
43	3.969	339 (0.009)		HOMO-11→LUMO (12) HOMO-3→LUMO+4 (20) HOMO→LUMO+8 (14) HOMO→LUMO+9 (18)
44	4.008	337 (0.006)		HOMO-7→LUMO+2 (39) HOMO→LUMO+8 (11) HOMO→LUMO+9 (14)
45	4.010	336 (0.015)		HOMO-13→LUMO (16) HOMO-11→LUMO (16) HOMO-6→LUMO+2 (22)
46	4.028	335 (0.005)		HOMO-10→LUMO+1 (27) HOMO-8→LUMO+1 (33) HOMO-6→LUMO+2 (25)
47	4.054	334 (0.044)	325	HOMO-6→LUMO+3 (18) HOMO-2→LUMO+4 (21)
48	4.056	331 (0.005)		HOMO-4→LUMO+4 (76)
49	4.124	330 (0.007)		HOMO-6→LUMO+3 (55)
50	4.129	327 (0.003)		HOMO-10→LUMO+1 (22) HOMO-8→LUMO+1(19) HOMO-1→LUMO+7 (20)

^[a]Components with greater than 10% contribution shown.

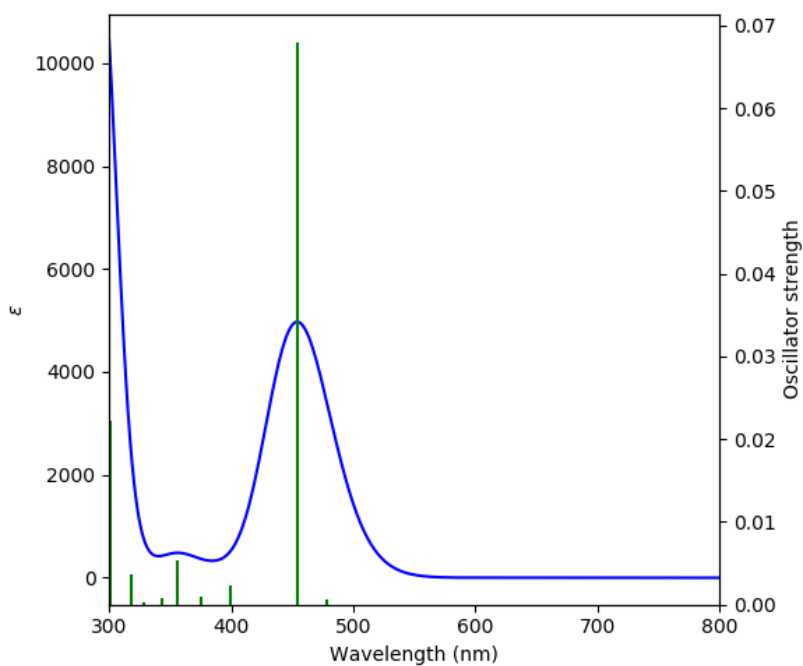


Figure S31. Absorption spectrum of **1** computed at the TD-DFT-B3LYP/6-31g(d)-sdd level of theory (ϵ in $\text{LM}^{-1}\text{cm}^{-1}$).

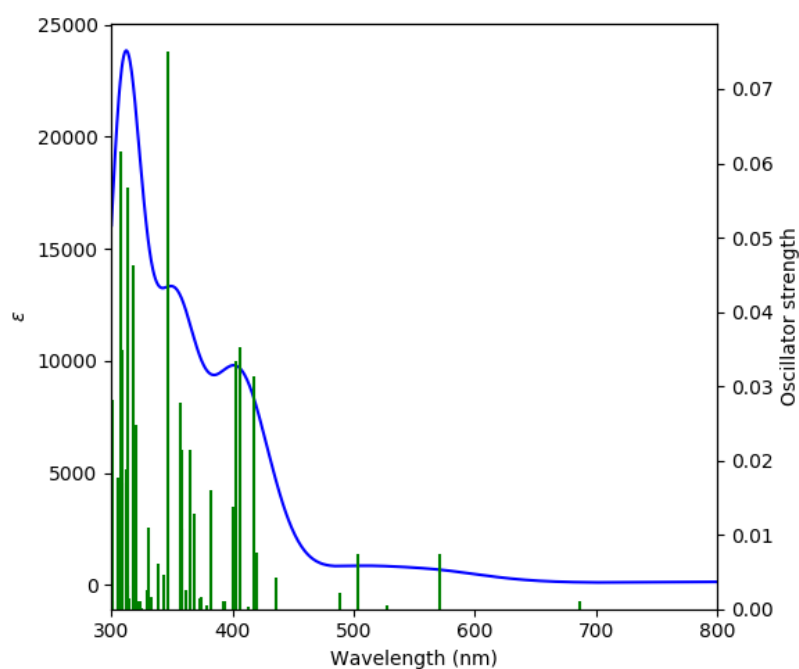


Figure S32. Absorption spectrum of **2** computed at the TD-DFT-B3LYP/6-31g(d)-sdd level of theory (ϵ in $\text{LM}^{-1}\text{cm}^{-1}$).

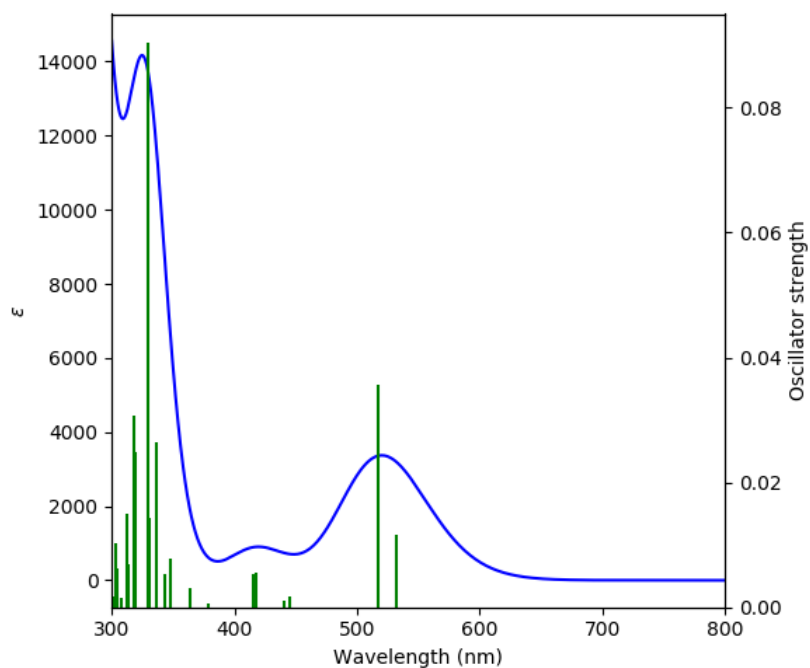


Figure S33. Absorption spectrum of **3** computed at the TD-DFT-B3LYP/6-31g(d)-sdd level of theory (ϵ in $\text{LM}^{-1}\text{cm}^{-1}$).

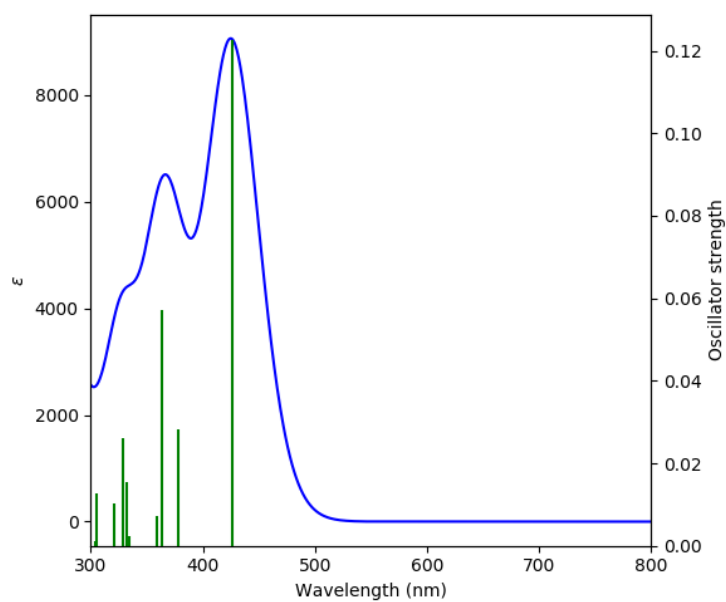


Figure S34. Absorption spectrum of **4** computed at the TD-DFT-B3LYP/6-31g(d)-sdd level of theory (ϵ in $\text{LM}^{-1}\text{cm}^{-1}$).

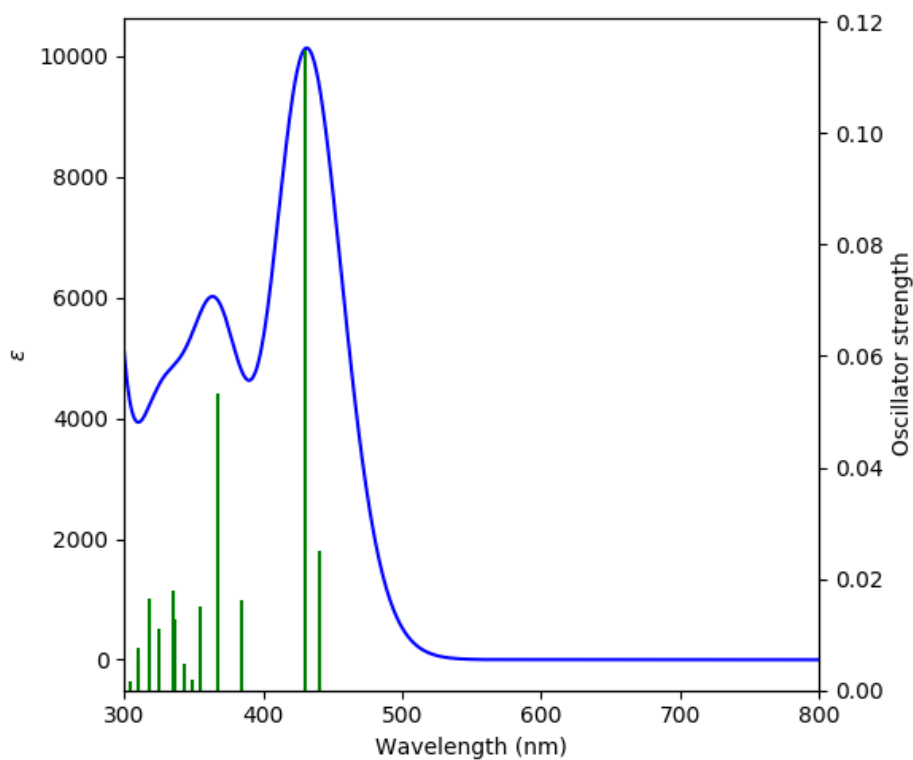


Figure S35. Absorption spectrum of **5** computed at the TD-DFT-B3LYP/6-31g(d)-sdd level of theory (ϵ in $\text{LM}^{-1}\text{cm}^{-1}$).

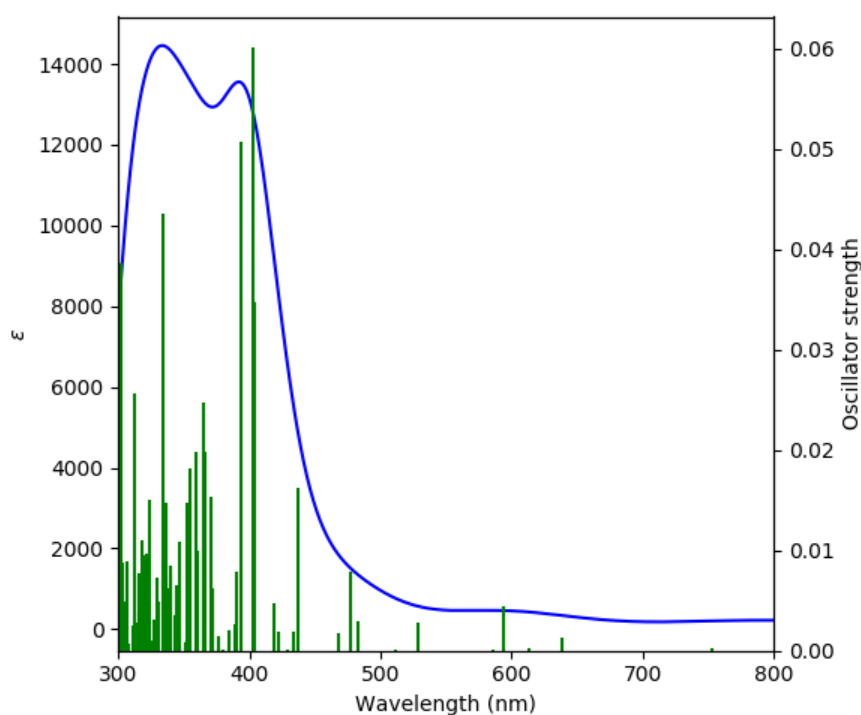


Figure S36. Absorption spectrum of **6** computed at the TD-DFT-B3LYP/6-31g(d)-sdd level of theory (ϵ in $\text{LM}^{-1}\text{cm}^{-1}$).

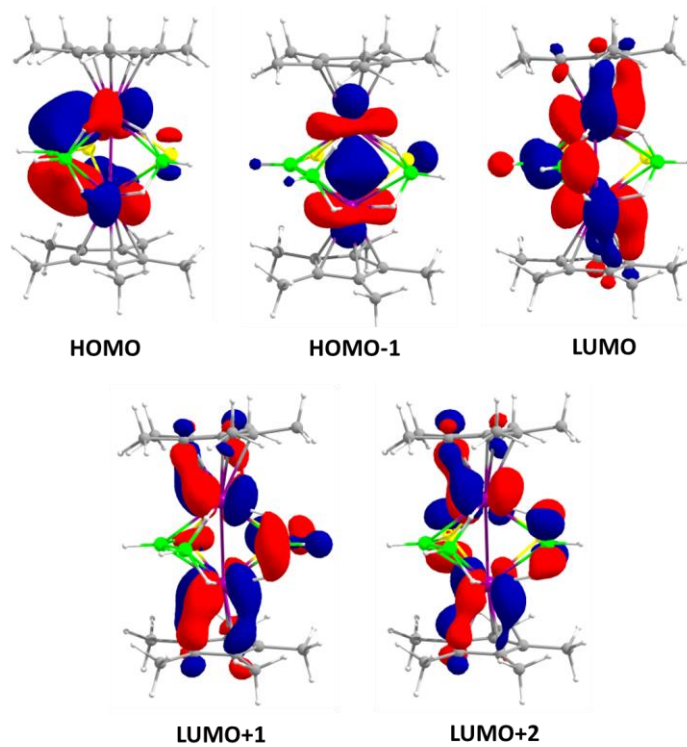


Figure S37. Selected molecular orbitals of **1** related to most intense electronic transitions.

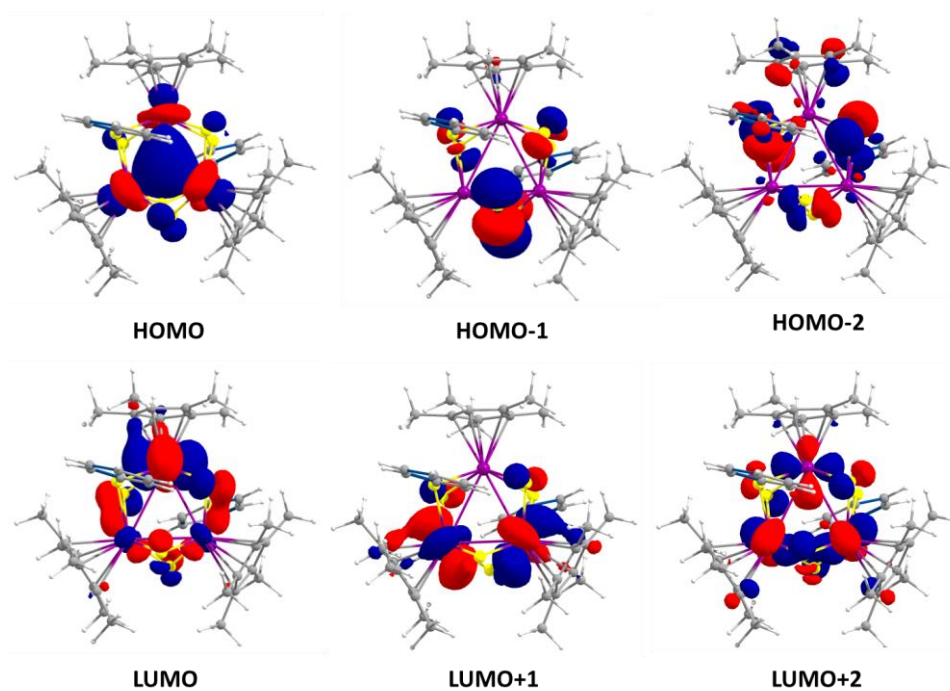


Figure S38. Selected molecular orbitals of **2** related to most intense electronic transitions.

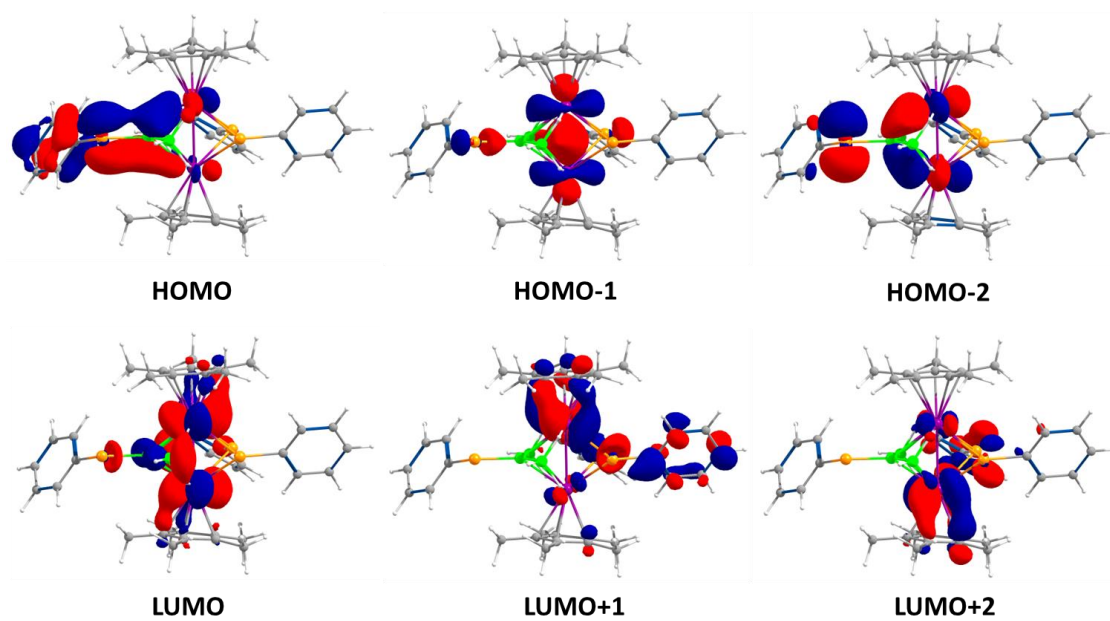


Figure S39. Selected molecular orbitals of **3** related to most intense electronic transitions.

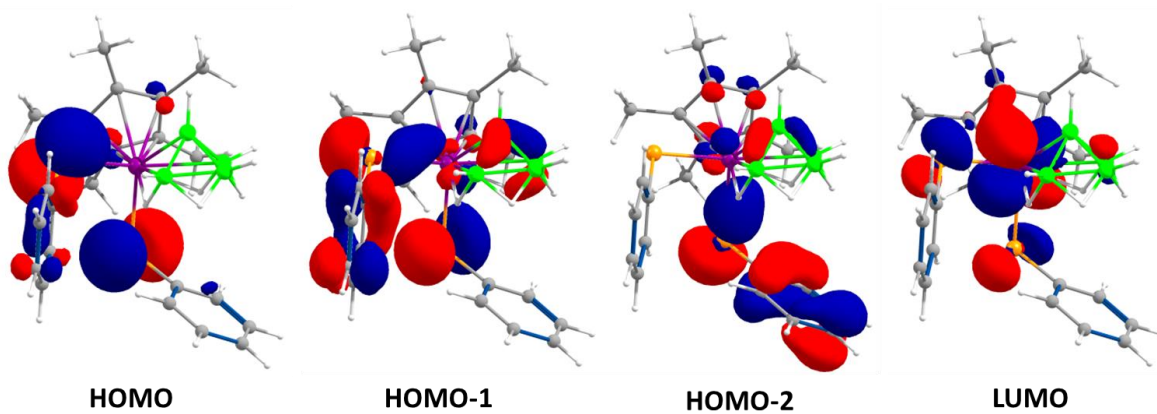


Figure S40. Selected molecular orbitals of **4** related to most intense electronic transitions.

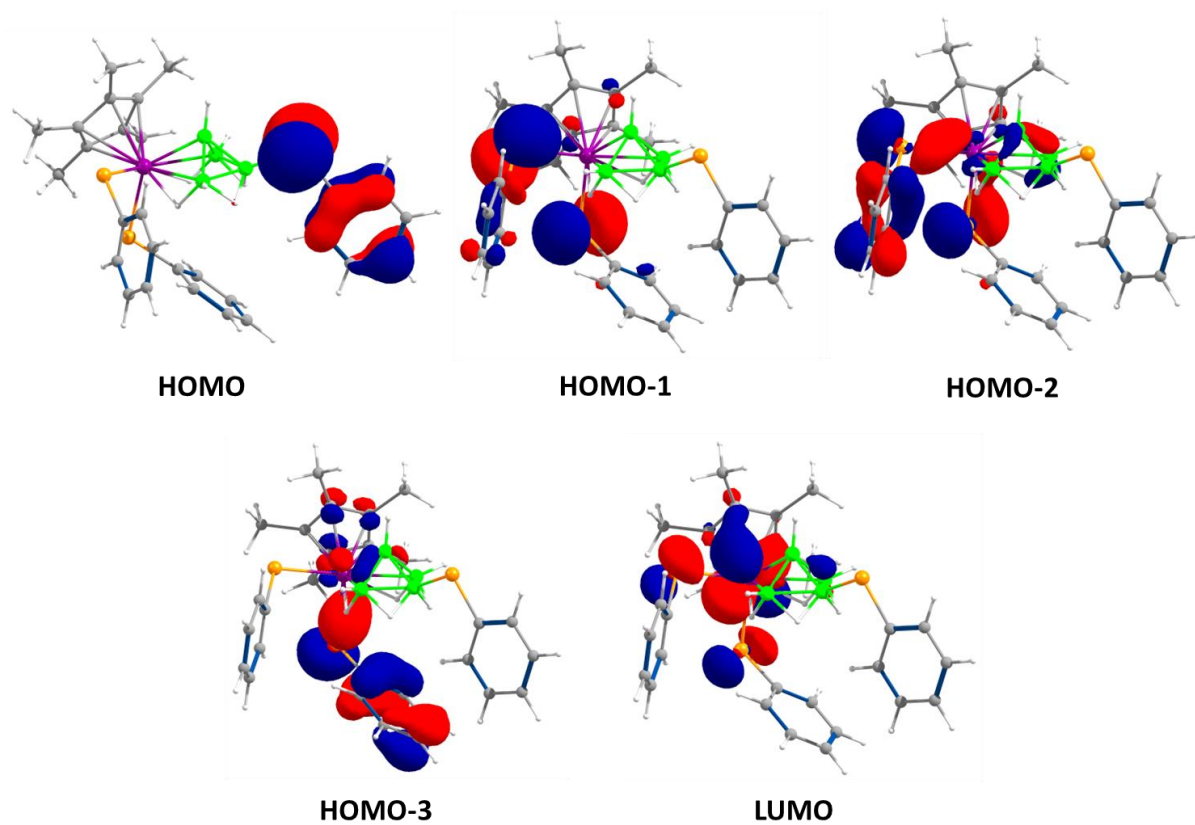


Figure S41. Selected molecular orbitals of **5** related to most intense electronic transitions.

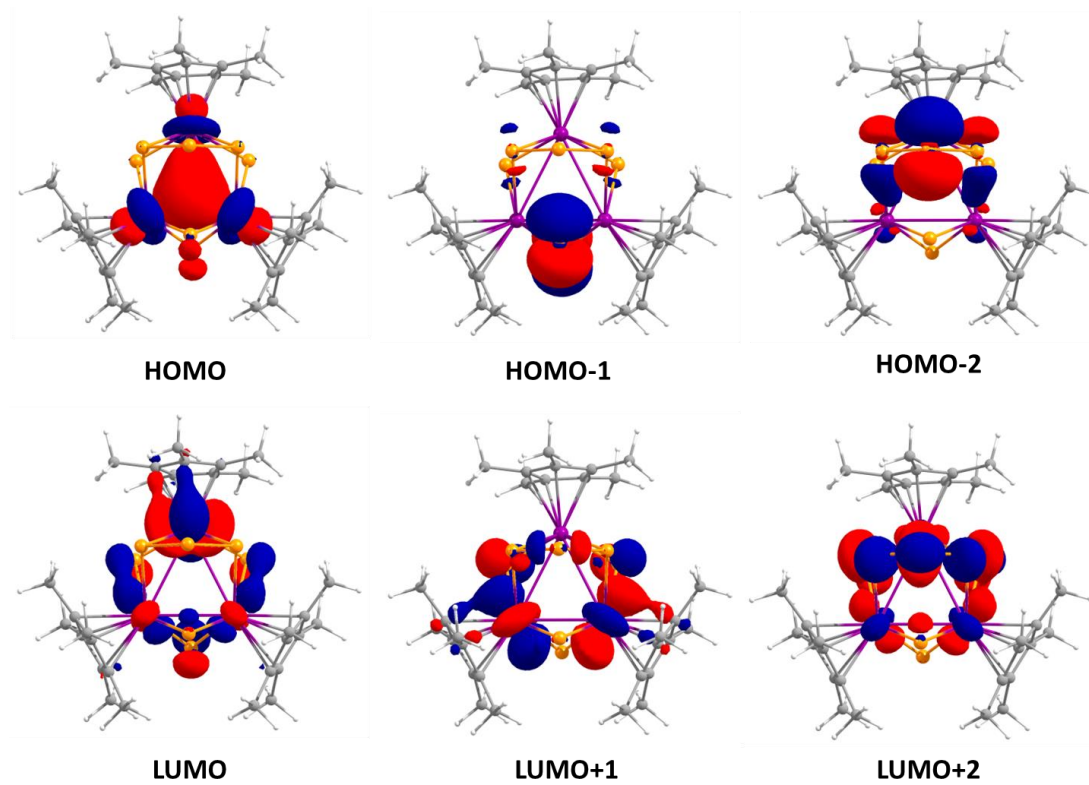


Figure S42. Selected molecular orbitals of **6** related to most intense electronic transitions.

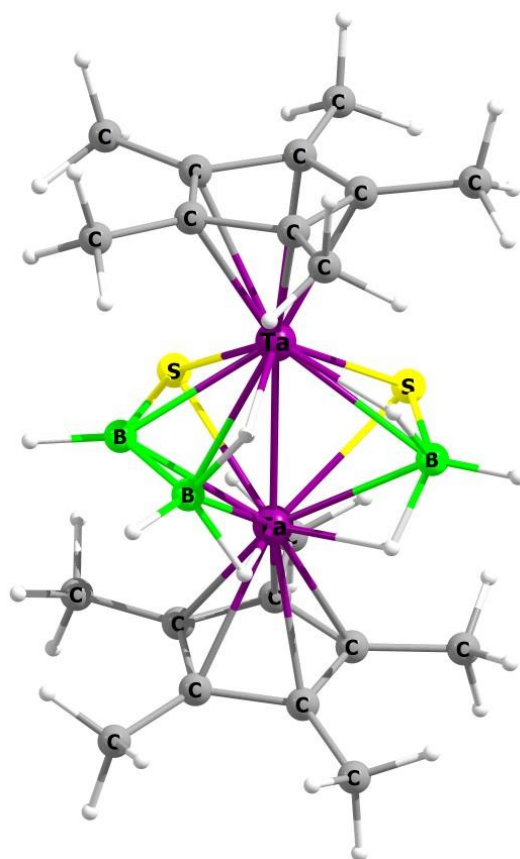


Figure S43. Optimized geometry of **1**

Total energy = -1769.67502417 a.u.

Cartesian coordinates for the calculated structure **1** (in Å)

C	3.65627200	0.15325000	-1.11706800	H	-4.82235500	-2.47234900	-1.69626300
C	3.58519800	1.13980000	-0.07034700	C	-3.40944100	-2.38536000	1.50804100
C	3.43908100	0.44924100	1.17619900	H	-2.79449600	-2.29448400	2.40797000
C	3.41531100	-0.95768300	0.90354000	H	-3.01080800	-3.21743800	0.92144100
C	3.55124900	-1.14382700	-0.50993800	H	-4.42653900	-2.65504200	1.82571300
C	3.97415100	0.42537400	-2.56462700	C	-3.36231600	0.56909400	2.72247900
H	3.56565200	1.38378200	-2.89877000	H	-4.37813300	0.59632000	3.14241000
H	3.57038900	-0.35171400	-3.22021800	H	-2.90833300	1.54963800	2.89058600
H	5.06173900	0.45849600	-2.72189300	H	-2.78646300	-0.16321400	3.29587000
C	3.78851400	2.62289200	-0.23671600	C	-3.72841300	2.63646600	0.30757400
H	4.84977300	2.88505600	-0.12041100	H	-4.78201800	2.89084900	0.49121000
H	3.22408200	3.19480400	0.50594400	H	-3.41703000	3.16241800	-0.59978500
H	3.47219400	2.96727300	-1.22570000	H	-3.14028000	3.03966200	1.13725800
C	3.42827800	1.08412800	2.54074700	C	-3.99725700	0.94489700	-2.40145600
H	2.84549100	0.49564100	3.25545200	H	-5.08524400	1.01887900	-2.54031700
H	2.99750600	2.08889800	2.51521400	H	-3.60587800	0.31148900	-3.20299200
H	4.45068500	1.16837700	2.93603400	H	-3.58019100	1.94681700	-2.53974400
C	3.38679400	-2.05602300	1.93030500	S	-0.00052300	-1.13725500	1.50224500
H	2.86823100	-1.74528100	2.84140100	S	0.00587300	1.90412400	0.88872600
H	4.40927100	-2.34571200	2.21062700	B	-0.00408800	-1.23405500	-1.65510100
H	2.87979100	-2.94871000	1.55261400	B	-0.00024600	2.04812900	-0.98379800
C	3.70773100	-2.46460400	-1.21465700	Ta	1.41766800	0.03386400	-0.18537700
H	4.76692600	-2.75684300	-1.25832200	Ta	-1.41986400	0.03734900	-0.18074000
H	3.33471000	-2.42291000	-2.24199800	H	1.06309300	-0.50504500	-1.95297200
H	3.16157700	-3.26088000	-0.70167500	H	-1.07229500	-0.50370300	-1.94993000
C	-3.59488000	-1.00639700	-0.70265900	H	-1.04841900	1.47993200	-1.46401400
C	-3.42747400	-1.10828100	0.71436100	H	0.00016900	3.13152600	-1.50043800
C	-3.40229500	0.21919200	1.25936300	H	-0.00722000	-2.04305200	-2.54366300
C	-3.55660900	1.14628400	0.17560600	H	1.04272200	1.47616000	-1.47008100
C	-3.67537500	0.38598400	-1.04004900	B	-0.00274400	-1.99140100	-0.12106400
C	-3.76939000	-2.15969900	-1.65364700	H	-0.00543800	-3.18886000	-0.15356200
H	-3.17485700	-3.02564400	-1.34863700				
H	-3.46267800	-1.89528600	-2.66979100				

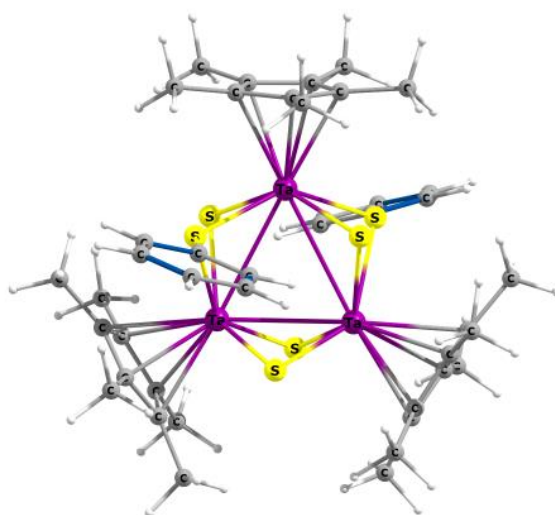


Figure S44. Optimized geometry of **2**

Total energy = -4194.36011920 a.u.

Cartesian coordinates for the calculated structure **2** (in Å)

Ta	-1.084832000	-1.061170000	-1.102378000	H	-4.694542000	0.178302000	-2.014673000
Ta	0.051216000	1.834755000	0.015452000	H	-3.519717000	0.866648000	-3.136378000
S	-0.345298000	1.019173000	-2.215902000	H	-5.213205000	-2.893938000	-0.987115000
S	-1.243834000	-1.927301000	1.193392000	H	-4.060598000	-2.750989000	0.351840000
S	-2.424772000	1.059260000	-0.039546000	H	-4.799311000	-1.304695000	-0.325631000
C	-1.607555000	-0.860530000	-4.689960000	H	-2.646263000	-5.263945000	-1.589206000
C	-4.819515000	1.205091000	1.241477000	H	-1.062364000	-4.775815000	-0.962515000
C	-2.006785000	-1.545858000	-3.413925000	H	-2.520674000	-4.412841000	-0.037920000
C	-3.457821000	0.913463000	1.434043000	H	-0.900371000	-4.294002000	-4.310025000
C	-3.921498000	0.475111000	3.771136000	H	0.143653000	-4.207804000	-2.878334000
C	-5.274220000	0.759121000	3.574961000	H	0.294766000	-2.995374000	-4.146908000
C	-4.061057000	-0.047611000	-2.875002000	H	1.314802000	3.744113000	3.076867000
C	-3.013279000	0.547333000	2.710863000	H	0.509526000	5.318530000	2.936414000
C	-5.721328000	1.125506000	2.303552000	H	-0.433275000	3.854362000	3.265715000
C	-3.270735000	-2.185816000	-1.577485000	H	0.880262000	3.689261000	-3.175935000
C	-3.122253000	-1.186519000	-2.591504000	H	2.409392000	3.550899000	-2.312658000
C	-4.392238000	-2.286054000	-0.580642000	H	1.691423000	5.147196000	-2.579743000
C	-2.109432000	-4.471202000	-1.048019000	H	-1.332331000	3.881303000	-2.944899000
C	-1.466745000	-2.769275000	-2.915923000	H	-2.622904000	3.604709000	-1.775105000
C	-2.243596000	-3.163623000	-1.777276000	H	-2.034848000	5.253042000	-2.067873000
C	-0.422997000	-3.608545000	-3.595053000	H	-2.445252000	3.795651000	2.105480000
C	0.712123000	4.002811000	-1.045851000	H	-3.147700000	3.905276000	0.491230000
C	0.247502000	4.054056000	1.225546000	H	-2.521139000	5.360359000	1.281458000
C	0.418810000	4.247548000	2.704383000	H	2.029816000	-1.527264000	5.528591000
C	1.462838000	4.097528000	-2.346259000	H	0.416965000	-1.184790000	4.882638000
C	-0.994842000	4.063714000	0.518330000	H	1.711215000	-0.004869000	4.677987000
C	-0.707792000	4.049359000	-0.886198000	H	4.637725000	-0.591821000	3.780100000
C	-1.728230000	4.201019000	-1.978481000	H	4.652168000	-0.058235000	2.091526000
C	-2.348594000	4.284708000	1.132299000	H	3.484709000	0.632809000	3.218832000
Ta	1.021996000	-1.139470000	1.091909000	H	5.078406000	-3.126956000	0.968941000
S	0.419976000	0.976930000	2.233460000	H	3.954058000	-2.880527000	-0.378632000
S	1.130695000	-1.988846000	-1.208400000	H	4.744538000	-1.496074000	0.367279000
S	2.475435000	0.908691000	0.055811000	H	2.469450000	-5.404504000	1.459184000
C	1.487241000	-1.074662000	4.686017000	H	0.888284000	-4.880483000	0.857493000
C	4.863930000	1.059937000	-1.233370000	H	2.344985000	-4.506918000	-0.065645000
C	1.887217000	-1.733685000	3.396373000	H	0.671441000	-4.473534000	4.179865000
C	3.502530000	0.762398000	-1.422344000	H	-0.349879000	-4.295552000	2.740278000
C	3.964179000	0.311828000	-3.757597000	H	-0.471697000	-3.125087000	4.050045000
C	5.316323000	0.602233000	-3.565033000	H	6.013969000	0.540366000	-4.396044000
C	4.000418000	-0.290182000	2.936456000	H	3.605467000	0.021323000	-4.742044000
C	3.057221000	0.387904000	-2.696895000	H	2.010918000	0.166460000	-2.855072000
C	5.764316000	0.978148000	-2.296847000	H	5.212211000	1.360402000	-0.248540000
C	3.159265000	-2.359031000	1.561045000	H	6.813073000	1.212502000	-2.132709000
C	3.029656000	-1.388636000	2.605196000	H	-5.167427000	1.503360000	0.255805000
C	4.290875000	-2.467846000	0.576393000	H	-1.966437000	0.329721000	2.872734000
C	1.939125000	-4.589622000	0.944979000	H	-6.770388000	1.356417000	2.136466000
C	1.313633000	-2.921374000	2.850109000	H	-5.972945000	0.700315000	4.405277000
C	2.096144000	-3.306723000	1.712572000	H	-3.562806000	0.191848000	4.757712000
C	0.229992000	-3.744696000	3.484969000	C	1.301287000	4.013889000	0.262799000
H	-2.173538000	-1.274934000	-5.536769000	C	2.761497000	4.175719000	0.575528000
H	-0.543225000	-0.990766000	-4.905819000	H	3.048626000	3.619006000	1.471728000
H	-1.804263000	0.213818000	-4.648367000	H	3.394952000	3.830394000	-0.244893000
H	-4.718349000	-0.302855000	-3.718602000	H	2.987899000	5.237729000	0.749616000

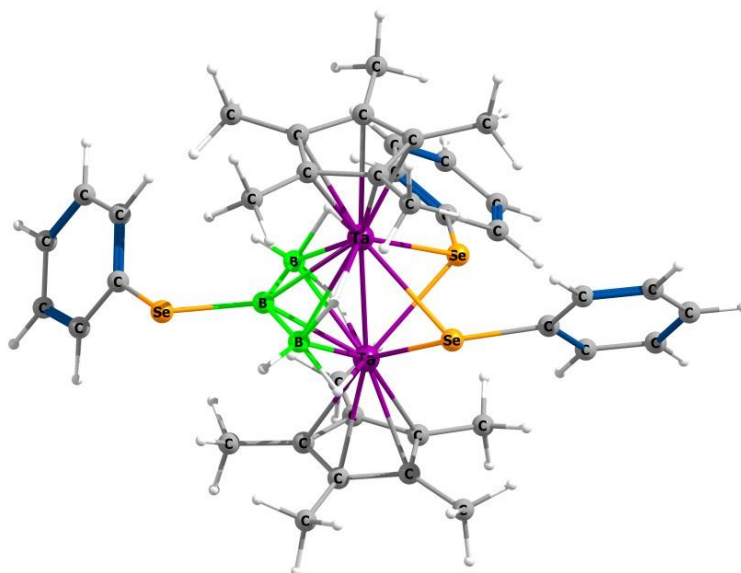


Figure S45. Optimized geometry of **3**

Total energy = -8864.36742257 a.u.

Cartesian coordinates for the calculated structure **3** (in Å)

Ta	-0.01510200	-1.25241300	-0.67279100	H	2.52660200	4.83156500	1.14561100
C	0.78498000	-3.46234500	-0.00812600	H	2.94166700	3.39561800	0.18935400
C	1.48065300	-3.09774800	-1.21373500	H	2.50228400	3.22915100	1.89243400
C	0.51226400	-3.04075400	-2.26969600	Se	-2.23888300	0.18178100	-1.58714200
C	-0.77326800	-3.37541200	-1.72278900	C	-4.02184500	-0.06670500	-0.83917100
C	-0.60421100	-3.64152300	-0.32855700	C	-4.45305800	-1.25388900	-0.23804900
C	1.42675200	-3.80176500	1.31167300	H	-3.75030200	-2.06083900	-0.07216300
H	1.67770800	-4.87136100	1.35064300	C	-5.78229600	-1.39683400	0.16554100
H	0.76438900	-3.58404600	2.15434900	H	-6.10232700	-2.32400900	0.63457500
H	2.35151400	-3.23954000	1.46664500	C	-6.69602700	-0.35949000	-0.02855900
C	2.97162600	-3.01309100	-1.38575800	H	-7.72934600	-0.47341900	0.28728700
H	3.47081600	-2.74518800	-0.45149700	C	-6.27336600	0.82232200	-0.63991400
H	3.25197700	-2.25625100	-2.12272900	H	-6.97723500	1.63341800	-0.80813800
H	3.37355200	-3.98246100	-1.71585100	C	-4.94623700	0.96522300	-1.04908300
C	0.82847700	-2.84142100	-3.72801900	H	-4.63197200	1.87800600	-1.54691200
H	-0.01897000	-2.42004900	-4.27654300	Se	-1.60135000	-0.33388500	1.42733500
H	1.08216800	-3.80271600	-4.19698000	C	-0.88410600	-0.88497300	3.16318900
H	1.68103000	-2.17060700	-3.86599600	C	0.22750500	-0.34219100	3.81632100
C	-2.03301000	-3.56934000	-2.52340600	H	0.81634000	0.43386400	3.34596700
H	-2.08448000	-2.87834100	-3.36964700	C	0.59702800	-0.80867900	5.08151000
H	-2.93102200	-3.41282200	-1.92048700	H	1.46639200	-0.37917800	5.57299400
H	-2.07656700	-4.59132700	-2.92630000	C	-0.13947900	-1.81149700	5.71336200
C	-1.64205300	-4.20762200	0.60205600	H	0.15104300	-2.16800500	6.69775400
H	-1.58010000	-5.30541300	0.61713700	C	-1.25896500	-2.34577200	5.07203800
H	-2.65637200	-3.94534600	0.28971400	H	-1.84958400	-3.11994400	5.55536100
H	-1.50704000	-3.85770000	1.62900600	C	-1.63156800	-1.88260100	3.80899400
Ta	-0.24792800	1.51770200	-0.10497700	H	-2.51449500	-2.29000900	3.32407400
C	0.31007200	3.84856600	-0.72952400	Se	3.65012600	0.76473400	-1.60993200
C	-1.12110400	3.75061700	-0.65880500	C	4.94784100	0.27537100	-0.25410600
C	-1.48461000	3.47345600	0.70080800	C	5.06750300	0.95932400	0.96287300
C	-0.27406800	3.39775800	1.46803600	H	4.38013500	1.76505200	1.19334600
C	0.83419500	3.63019900	0.57913800	C	6.06551200	0.61551900	1.87654800
C	1.11645900	4.22825300	-1.94159700	H	6.14198700	1.15633600	2.81698600
H	0.59650300	3.97199300	-2.86908700	C	6.97013800	-0.40734200	1.58221800
H	2.08564900	3.72110100	-1.95551200	H	7.74989000	-0.67032100	2.29227000
H	1.30165400	5.31167700	-1.95355200	C	6.86910100	-1.08281400	0.36492800
C	-2.07374300	4.06374700	-1.78096500	H	7.57124100	-1.87628700	0.12039900
H	-2.24145600	5.14817400	-1.84711200	C	5.86385500	-0.74511000	-0.54503900
H	-3.04520100	3.58767500	-1.62733800	H	5.79044700	-1.27290600	-1.49140700
H	-1.69253300	3.72844400	-2.74985100	B	0.72723800	0.57456000	-2.17041700
C	-2.88228400	3.44357600	1.25813000	H	1.17822800	0.82859000	-3.25646300
H	-2.93112600	2.86787800	2.18647600	H	0.05212200	-0.50029800	-2.44104700
H	-3.59211200	2.99054300	0.56098200	B	1.78024300	0.40184600	-0.88746400
H	-3.23291300	4.46221100	1.47888900	B	1.56287000	0.04382700	0.71841500
C	-0.19792900	3.31051200	2.96912600	H	2.52034300	-0.02644700	1.43513300
H	-0.34141500	4.30448400	3.41634700	H	0.83292100	0.92433400	1.34847500
H	0.77458100	2.94036800	3.30510500	H	-0.12362100	1.53661400	-2.02929000
H	-0.96495400	2.64919200	3.38169700	H	0.98263400	-1.09072700	0.95292200
C	2.27800100	3.77490600	0.97131600				

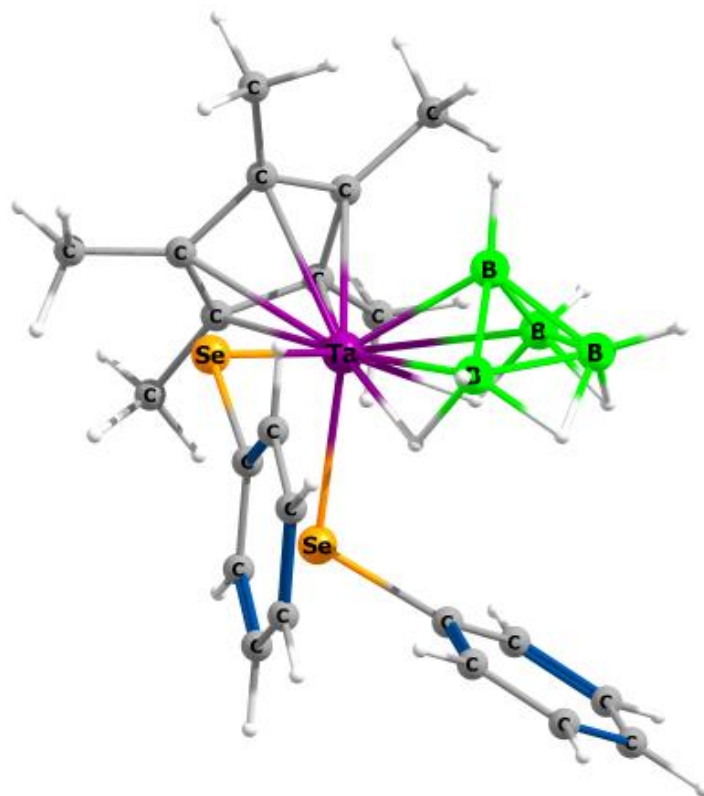


Figure S46. Optimized geometry of **4**

Total energy = -5818.84130526 a.u.

Cartesian coordinates for the calculated structure **4** (in Å)

C	-3.173821000	0.536486000	0.791028000	H	4.873919000	4.414701000	1.092802000
C	-3.098692000	-0.830618000	0.393868000	C	2.924286000	4.460381000	0.169156000
C	-2.745549000	-0.869922000	-1.000177000	H	2.803801000	5.534769000	0.281986000
C	-2.550165000	0.469726000	-1.446595000	C	1.912004000	3.712894000	-0.436938000
C	-2.790595000	1.342510000	-0.337747000	H	1.012705000	4.204581000	-0.796081000
C	-3.806470000	1.027807000	2.061834000	C	1.770903000	-2.707647000	-0.139405000
H	-4.894579000	0.888188000	1.996916000	C	2.228109000	-3.652799000	0.785296000
H	-3.615924000	2.089025000	2.228431000	H	1.525042000	-4.132301000	1.459431000
H	-3.447082000	0.482492000	2.937029000	C	3.586352000	-3.971870000	0.843246000
C	-3.519277000	-2.003669000	1.235700000	H	3.934580000	-4.703573000	1.567677000
H	-4.602544000	-2.166408000	1.145517000	C	4.492035000	-3.356149000	-0.023078000
H	-3.291759000	-1.835838000	2.291460000	H	5.548263000	-3.607557000	0.022231000
H	-3.014302000	-2.923518000	0.930135000	C	4.032202000	-2.420582000	-0.953097000
C	-2.857123000	-2.065721000	-1.903688000	H	4.728547000	-1.944214000	-1.638862000
H	-2.099160000	-2.060597000	-2.690624000	C	2.674534000	-2.097380000	-1.016819000
H	-3.846236000	-2.054572000	-2.382802000	H	2.317355000	-1.369045000	-1.738560000
H	-2.763846000	-3.007604000	-1.359951000	Se	0.669615000	1.327047000	-1.506295000
C	-2.346214000	0.889981000	-2.874334000	Se	-0.130001000	-2.395306000	-0.313948000
H	-3.319717000	1.003729000	-3.371062000	Ta	-0.756081000	0.058397000	0.281131000
H	-1.771793000	0.149618000	-3.438944000	B	0.906374000	-0.389459000	2.137637000
H	-1.819469000	1.844460000	-2.946960000	B	-0.673589000	0.097962000	2.580113000
C	-2.850735000	2.843826000	-0.418398000	H	-1.442179000	-0.445282000	3.313045000
H	-2.110880000	3.232151000	-1.123617000	B	-0.622392000	1.774121000	2.169709000
H	-2.666376000	3.311634000	0.551416000	B	0.634843000	1.027317000	3.185948000
H	-3.844180000	3.163069000	-0.762131000	H	1.114282000	-0.080897000	0.914765000
C	2.051756000	2.327498000	-0.584851000	H	0.597630000	2.197209000	2.565905000
C	3.220734000	1.700003000	-0.137803000	H	1.714970000	0.633704000	2.555775000
H	3.339203000	0.627442000	-0.255377000	H	0.884104000	1.201397000	4.335225000
C	4.230931000	2.452165000	0.466219000	H	-1.363135000	2.634753000	2.534822000
H	5.133714000	1.955209000	0.812058000	H	1.512650000	-1.365156000	2.441359000
C	4.086001000	3.832439000	0.622858000	H	-0.333973000	1.920398000	0.948003000

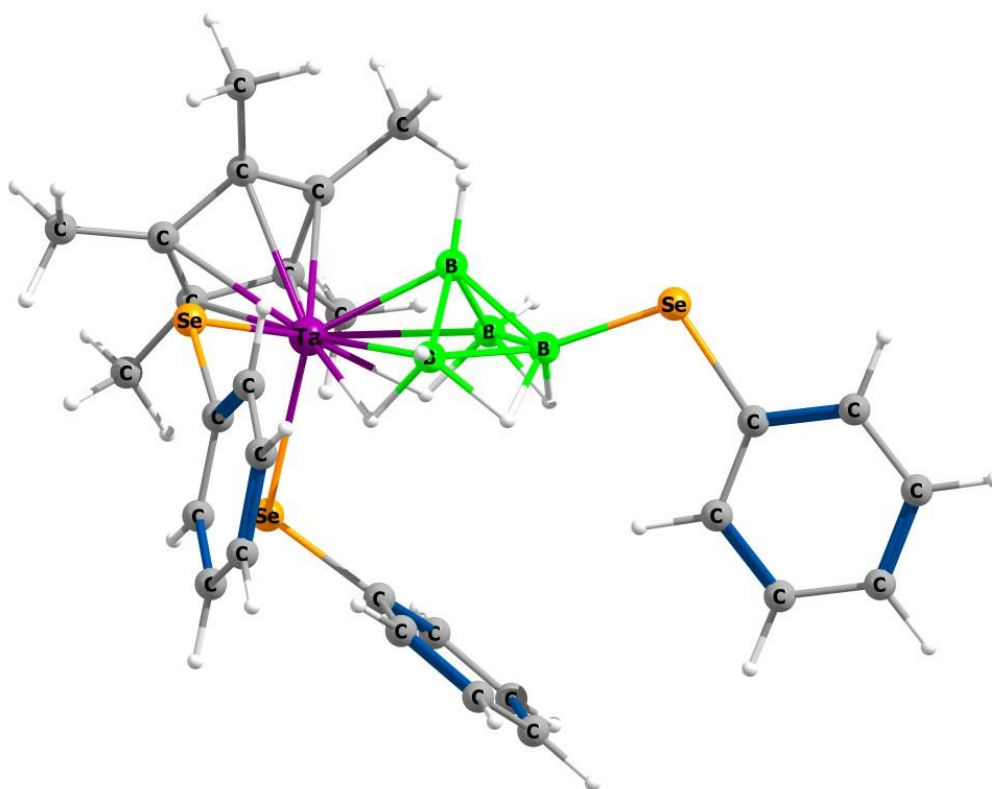


Figure S47. Optimized geometry of **5**

Total energy = -8442.61752666 a.u.

Cartesian coordinates for the calculated structure **5** (in Å)

Ta	-1.32070700	-0.55457800	0.00844500	C	-0.36211100	4.51457700	-2.94128100
C	-2.26793600	-2.56268100	1.12571400	H	0.01534100	4.82854900	-3.91091300
C	-2.11310700	-2.92369800	-0.25815500	C	-0.20130100	5.33827400	-1.82519100
C	-2.99419100	-2.10272000	-1.02236400	H	0.29986700	6.29749400	-1.92259000
C	-3.75026000	-1.28946500	-0.10690500	C	-0.69355300	4.92622500	-0.58446500
C	-3.29768700	-1.57159800	1.21465900	H	-0.58193800	5.56587100	0.28749600
C	-3.94245300	-1.07970600	2.47905600	C	-1.34107800	3.69482900	-0.45615400
H	-3.22989500	-1.02166200	3.30526800	H	-1.72301800	3.37411300	0.50833800
H	-4.38369600	-0.08696300	2.35119000	C	0.67159000	1.17757600	2.64476400
H	-4.74829500	-1.76522200	2.77580700	C	1.32963300	0.49545900	3.67607400
C	-4.99182400	-0.50936400	-0.43786600	H	0.81990300	-0.30536600	4.20351500
H	-5.08847500	0.39154700	0.17303100	C	2.63374800	0.84685500	4.03079000
H	-5.02476400	-0.20513600	-1.48546800	H	3.13512100	0.30980800	4.83166400
H	-5.86816700	-1.14495900	-0.24800500	C	3.28690300	1.88671400	3.36579800
C	-3.23155600	-2.22329900	-2.50265400	H	4.29756700	2.16697700	3.65021700
H	-3.59355200	-1.28591200	-2.93227800	C	2.63052000	2.57053200	2.33934100
H	-2.31456100	-2.49580500	-3.03123100	H	3.12902000	3.38395000	1.81854000
H	-3.98103600	-3.00136700	-2.70436400	C	1.32629700	2.22158700	1.97986700
C	-1.38953100	-4.13050500	-0.78257700	H	0.82044600	2.76311800	1.18682200
H	-0.58135200	-4.44661900	-0.12171300	C	4.98254500	-0.90751900	-0.94887200
H	-2.10207500	-4.96339400	-0.86448100	C	6.24751100	-1.34536100	-1.36770600
H	-0.96211400	-3.95520200	-1.77164100	H	6.33154500	-2.01449800	-2.21994200
C	-1.64222700	-3.26445400	2.30037000	C	7.39735300	-0.93118100	-0.69682700
H	-0.66346200	-3.68112400	2.05257300	H	8.36918100	-1.28088100	-1.03615400
H	-1.51402800	-2.58594900	3.14824500	C	7.30328700	-0.07791700	0.40530200
H	-2.28600000	-4.09246200	2.62746500	H	8.19922400	0.24249800	0.92989100
C	-1.49039700	2.86657900	-1.57443200	C	6.04588300	0.35741000	0.82434800
C	-1.00800200	3.28245800	-2.82011500	H	5.95297100	1.02105900	1.68024100
H	-1.13177800	2.64276400	-3.68840200	C	4.89088900	-0.04978800	0.15276100
H	3.92788100	0.31269000	0.49738800	H	1.87977800	0.35430400	-0.70270800
B	0.83784400	-1.89808400	0.16854900	H	1.08344200	-3.00867100	0.52262900
B	0.31733600	-1.38178600	-1.39246200	H	0.12997900	-2.05946200	-2.35562700
B	0.65055900	0.29284900	-1.31886000	H	2.00247900	-1.23095900	0.36957800
B	1.89640600	-0.93565100	-0.91386900	H	0.74840100	1.08854700	-2.19412500
Se	-2.52163500	1.23451200	-1.44989700	H	0.09139900	0.79901900	-0.28387700
Se	-1.18052900	0.74864800	2.26654700	H	0.25108100	-1.24475900	1.07932900
Se	3.46748100	-1.53690400	-1.96778800				

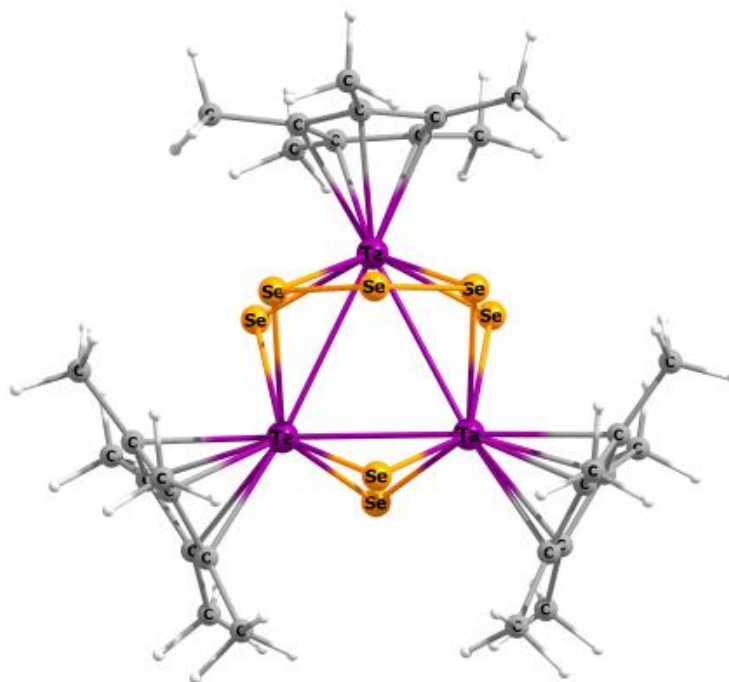


Figure S48. Optimized geometry of **6**

Total energy = -18134.5195807a.u.

Cartesian coordinates for the calculated structure **6** (in Å)

Ta	1.117318000	-1.554508000	-0.164929000	H	1.060880000	-3.649074000	2.993388000
Ta	-1.974027000	0.002166000	-0.342522000	H	2.645264000	-4.437718000	2.960414000
Se	-1.117759000	-1.667052000	1.588988000	H	2.525003000	-2.673690000	3.101445000
Se	2.000900000	-0.001663000	1.657342000	H	-5.499800000	2.715393000	0.542098000
Se	-1.039915000	-1.971895000	-1.583170000	H	-3.855289000	3.215673000	0.110531000
Se	2.040681000	0.001307000	-1.962781000	H	-4.159363000	2.443553000	1.667936000
Se	-0.956943000	-0.001349000	3.332808000	H	4.817832000	-1.445037000	0.287835000
C	2.125585000	-3.444638000	1.124186000	H	5.244756000	-3.058578000	0.885998000
C	0.034486000	-4.917752000	0.575111000	H	4.351254000	-1.925938000	1.917972000
C	1.689326000	-3.827026000	-1.121774000	H	1.307816000	-3.800037000	-3.248124000
C	2.085674000	-3.553560000	2.623624000	H	0.056455000	-4.607995000	-2.305240000
C	-4.257766000	-0.172152000	0.663859000	H	1.614309000	-5.408168000	-2.570554000
C	-4.438391000	2.437038000	0.611586000	H	-5.630690000	-0.311303000	2.304494000
C	-4.100560000	0.835489000	-1.415526000	H	-4.206039000	-1.350107000	2.473199000
C	4.463607000	-2.284274000	0.893068000	H	-4.058864000	0.381083000	2.747523000
C	1.133517000	-4.438432000	-2.377197000	H	4.478244000	-1.950632000	-1.985095000
C	2.906569000	-3.087492000	-1.032561000	H	3.339904000	-2.683134000	-3.112320000
C	-4.547813000	-0.372344000	2.125056000	H	4.533679000	-3.697923000	-2.284649000
C	3.862286000	-2.835309000	-2.164049000	H	-5.288561000	1.961448000	-2.794080000
C	3.178752000	-2.850432000	0.355479000	H	-3.669115000	1.578629000	-3.401176000
C	-4.215403000	1.089241000	-0.013616000	H	-3.875208000	2.841062000	-2.187280000
C	-4.232279000	1.859029000	-2.506583000	H	-5.393402000	-2.946621000	-0.042669000
C	1.205119000	-4.047412000	0.209490000	H	-3.847299000	-3.273384000	-0.847832000
Se	-1.111744000	1.666464000	1.590505000	H	-3.886359000	-2.970896000	0.889276000
C	-4.327762000	-2.677739000	-0.067624000	H	-5.149339000	-1.350028000	-3.290184000
C	-4.062025000	-0.581503000	-1.607803000	H	-3.539254000	-0.734376000	-3.699319000
C	-4.169668000	-1.205344000	-0.323317000	H	-3.702771000	-2.288623000	-2.883589000
C	-4.109997000	-1.276507000	-2.939746000	H	-0.766883000	4.829862000	-0.167335000
Ta	1.120076000	1.554976000	-0.164527000	H	0.352063000	5.977536000	0.589384000
Se	-1.046424000	1.987707000	-1.569183000	H	-0.367183000	4.671939000	1.544239000
C	2.127054000	3.445753000	1.125284000	H	1.054233000	3.659124000	2.988946000
C	0.042764000	4.922963000	0.562373000	H	2.642437000	4.440272000	2.961965000
C	1.702963000	3.823078000	-1.123773000	H	2.513451000	2.677136000	3.105934000
C	2.080323000	3.558049000	2.624285000	H	4.820287000	1.439351000	0.307834000
C	4.464042000	2.280567000	0.909066000	H	5.246160000	3.053910000	0.903934000
C	1.154950000	4.431094000	-2.384365000	H	4.346218000	1.925088000	1.934361000
C	2.918256000	3.081305000	-1.026358000	H	1.326573000	3.786152000	-3.251025000
C	3.879234000	2.824644000	-2.152363000	H	0.079084000	4.609356000	-2.316225000
C	3.182755000	2.847061000	0.363477000	H	1.643539000	5.395963000	-2.582477000
C	1.212976000	4.048874000	0.204573000	H	4.492473000	1.939112000	-1.968434000
H	-0.781029000	-4.820672000	-0.147554000	H	3.361428000	2.671580000	-3.102988000
H	0.340090000	-5.973497000	0.597801000	H	4.552975000	3.685674000	-2.271298000
H	-0.366251000	-4.666972000	1.560762000				

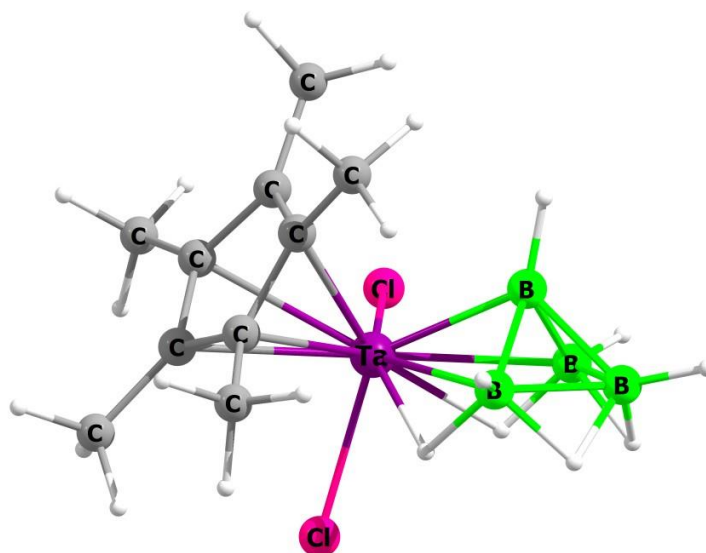


Figure S49. Optimized geometry of $[\text{Cp}^*\text{TaCl}_2\{\text{B}_4\text{H}_8\}]$

Total energy = -1471.90945645 a.u.

Cartesian coordinates for the calculated structure $[\text{Cp}^*\text{TaCl}_2\{\text{B}_4\text{H}_8\}]$ (in Å)

Ta	-0.42040900	-0.28346200	-0.09862600	C	1.07048400	2.50225700	-1.79544300
Cl	-0.32033500	-2.25253200	1.25504200	H	0.92830100	1.99695200	-2.75515000
Cl	-0.28141200	-1.32819700	-2.28362800	H	1.98562500	3.10506200	-1.87011900
C	2.00093600	-0.25011500	0.58562300	H	0.23194400	3.18501800	-1.64858900
C	1.26573000	0.62216100	1.46641900	C	2.72350700	-0.19122900	-1.91349300
C	0.80973800	1.73912800	0.70565200	H	2.22120300	0.06446700	-2.84884900
C	1.20023700	1.51933700	-0.66361600	H	2.84581000	-1.27674200	-1.89196300
C	1.96829800	0.31100600	-0.71867800	H	3.72462800	0.26151900	-1.93070500
C	2.80416300	-1.44849100	0.99960000	B	-2.04202700	1.61012600	-0.64240100
H	2.39850900	-1.91830000	1.89721200	H	-1.37242800	0.92506300	-1.45439700
H	3.83671700	-1.14102900	1.21465000	H	-3.21672500	1.31234600	-1.24435600
H	2.83708900	-2.20746500	0.21318300	H	-1.89527300	2.77506100	-0.84443600
C	1.14496400	0.47014200	2.95712300	B	-2.13029000	0.83772600	0.90671100
H	1.14093200	-0.58110600	3.25462900	H	-2.07954600	1.37506700	1.97007600
H	0.22501400	0.92579900	3.33243500	B	-2.86402500	-0.65896800	0.47227500
H	1.99197300	0.96027200	3.45644100	H	-2.18883400	-1.21315500	-0.43524900
C	0.28252200	3.02175100	1.28041200	H	-3.84030700	-0.31119500	-0.42608300
H	-0.31995300	2.85005700	2.17437300	H	-3.38395800	-1.46231200	1.17895200
H	-0.33096400	3.57348400	0.56705100	B	-3.56575900	0.90546800	-0.03604400
H	1.13164900	3.66003800	1.56224200	H	-4.56480300	1.45879200	0.29003000

Notes and references:

- [1] $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were processed with a backward linear prediction algorithm to eliminate the broad ^{11}B background signal of the NMR tube by referring to (a) Led, J. J.; Gesmar, H. Application of the linear prediction method to NMR spectroscopy. *Chem. Rev.* **1991**, *91*, 1413–1426; (b) Yang, L.; Simionescu, R.; Lough, A.; Yan, H. Some observations relating to the stability of the BODIPY fluorophore under acidic and basic conditions. *Dyes Pigm.* **2011**, *91*, 264–267; (c) Weiss, R.; Grimes, R. N. Sources of Line Width in Boron-11 Nuclear Magnetic Resonance Spectra. Scalar Relaxation and Boron-Boron Coupling in B_4H_{10} and B_5H_9 . *J. Am. Chem. Soc.* **1978**, *100*, 1401–1405.