Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Oxidative Addition of Elemental Selenium to 1,4,2,5-Diazadiborinine

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Contents:

1. Physical and spectroscopic data for compounds 2,3 and 4

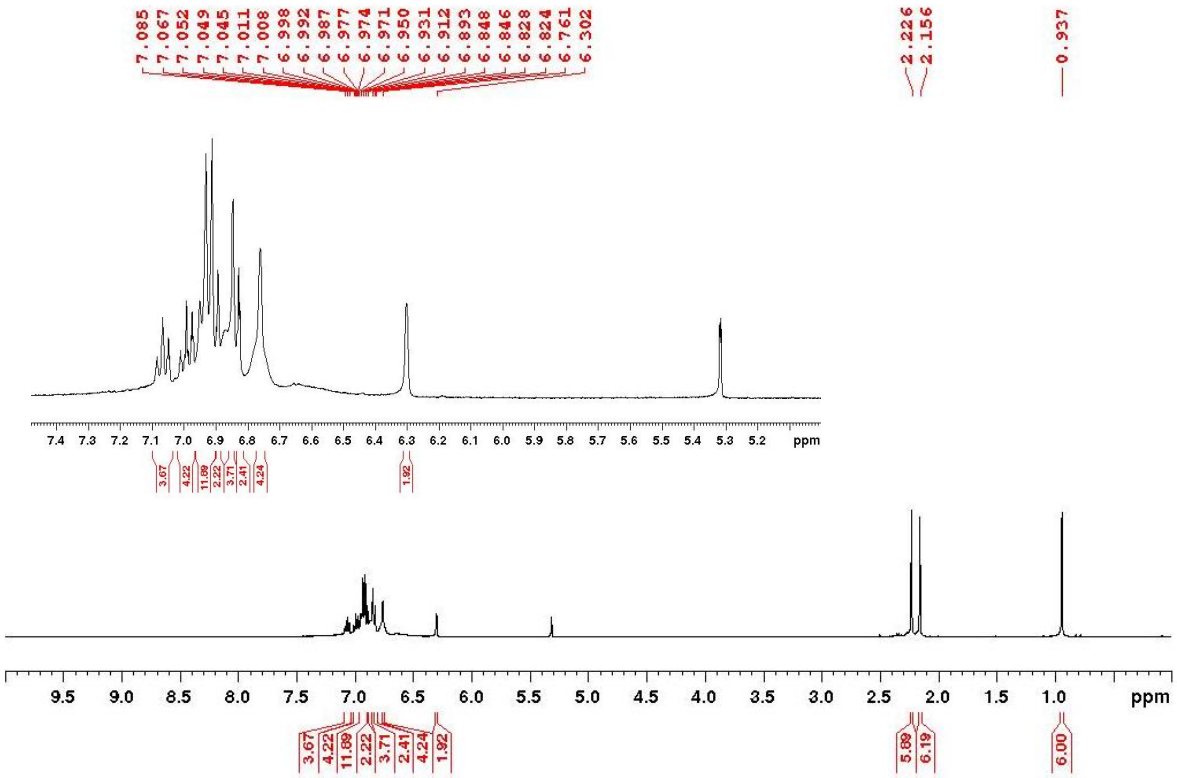


Figure S1. ^{1}H NMR spectrum of **2**

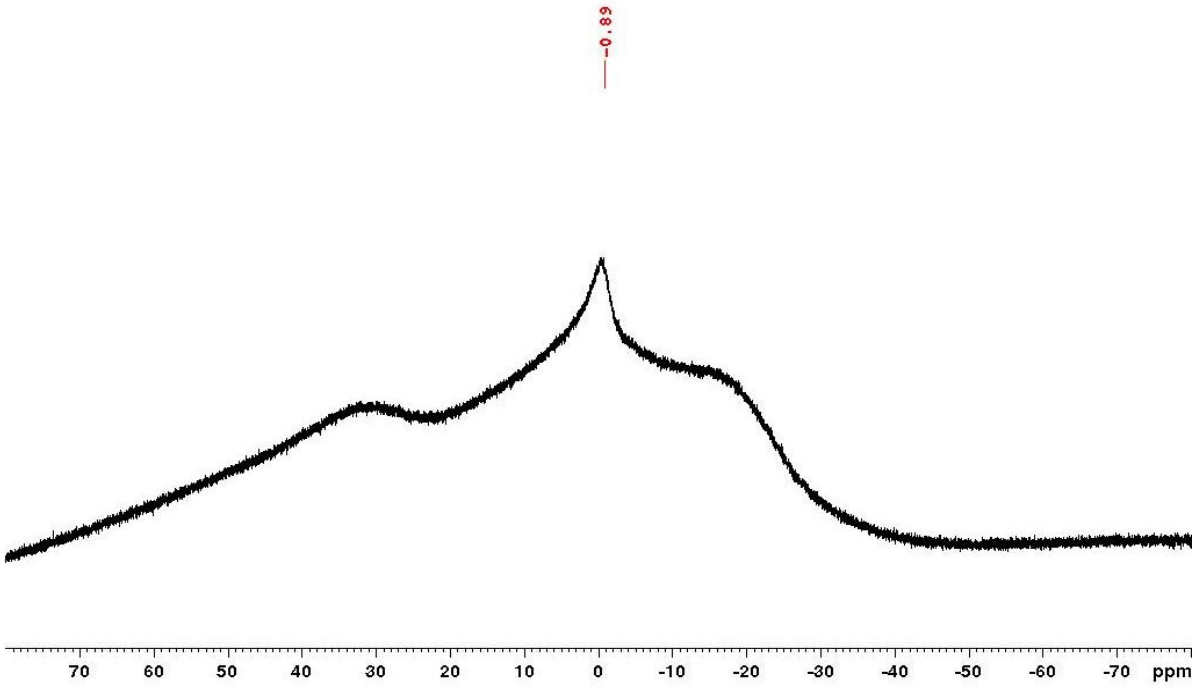


Figure S2.^{11}B NMR spectrum of **2**

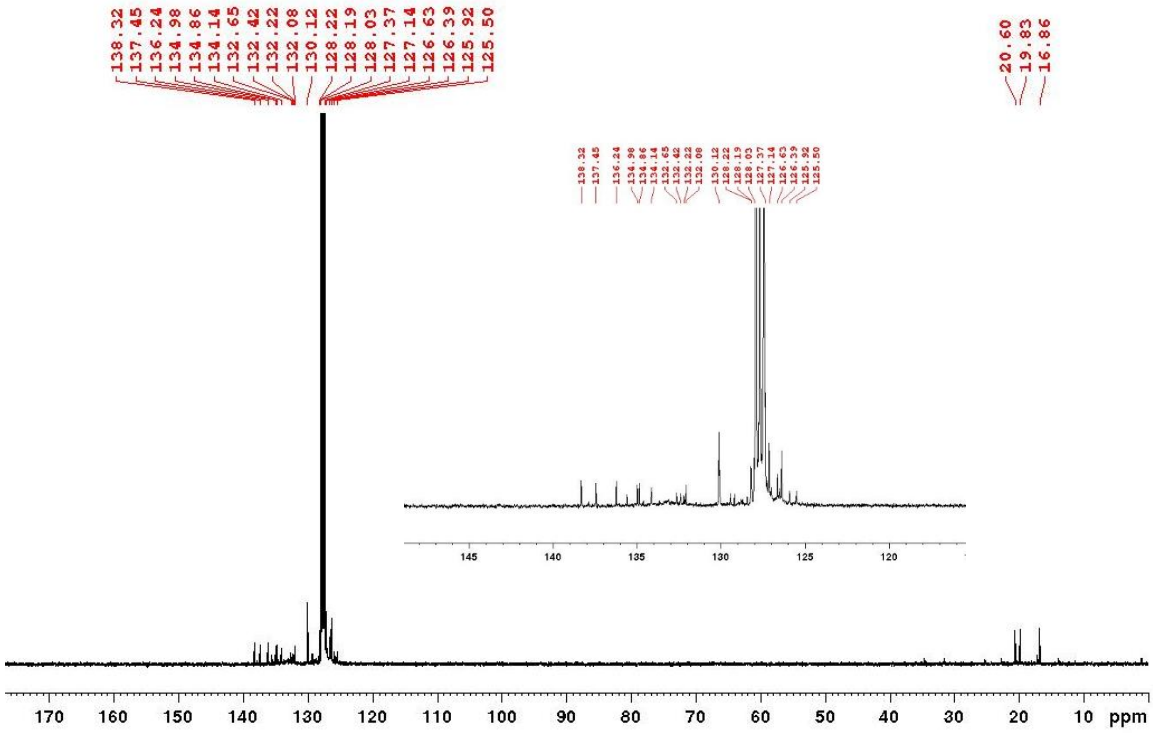


Figure S3. ^{13}C NMR spectrum of **2**

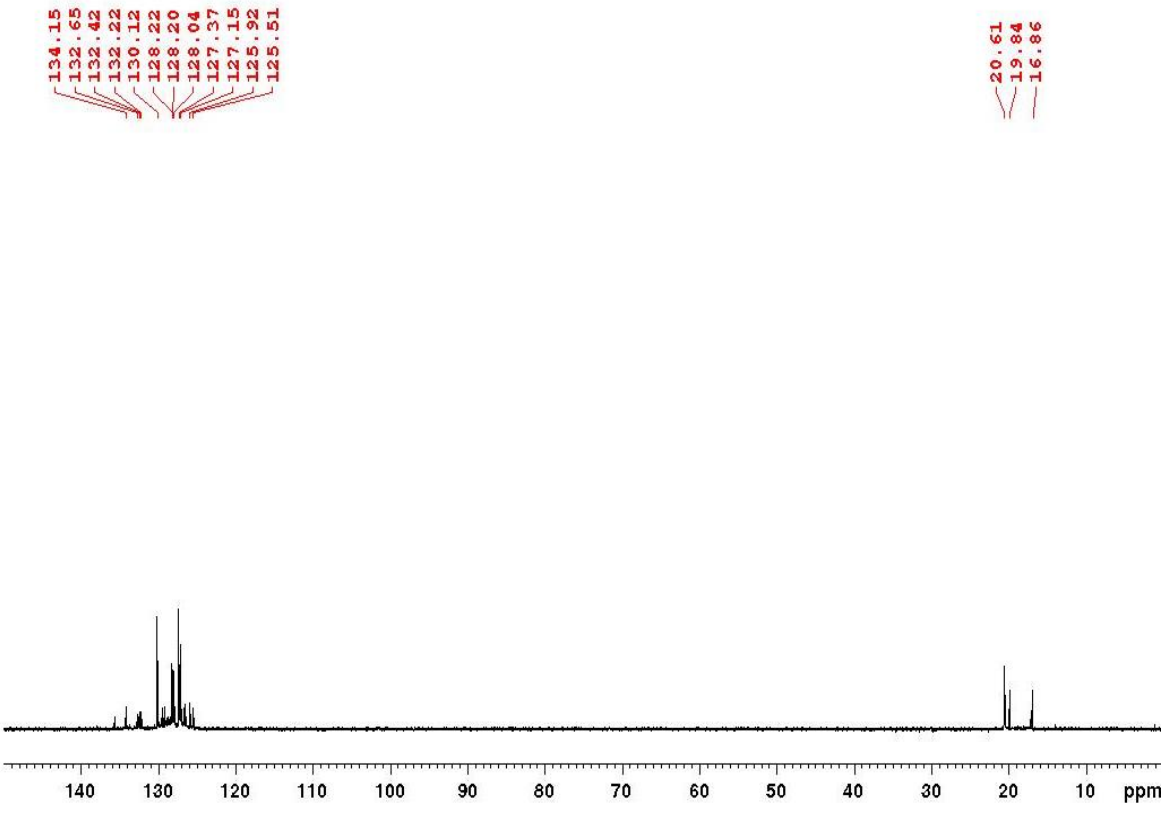


Figure S4.^{13}C NMR (DEPT 135) spectrum of **2**

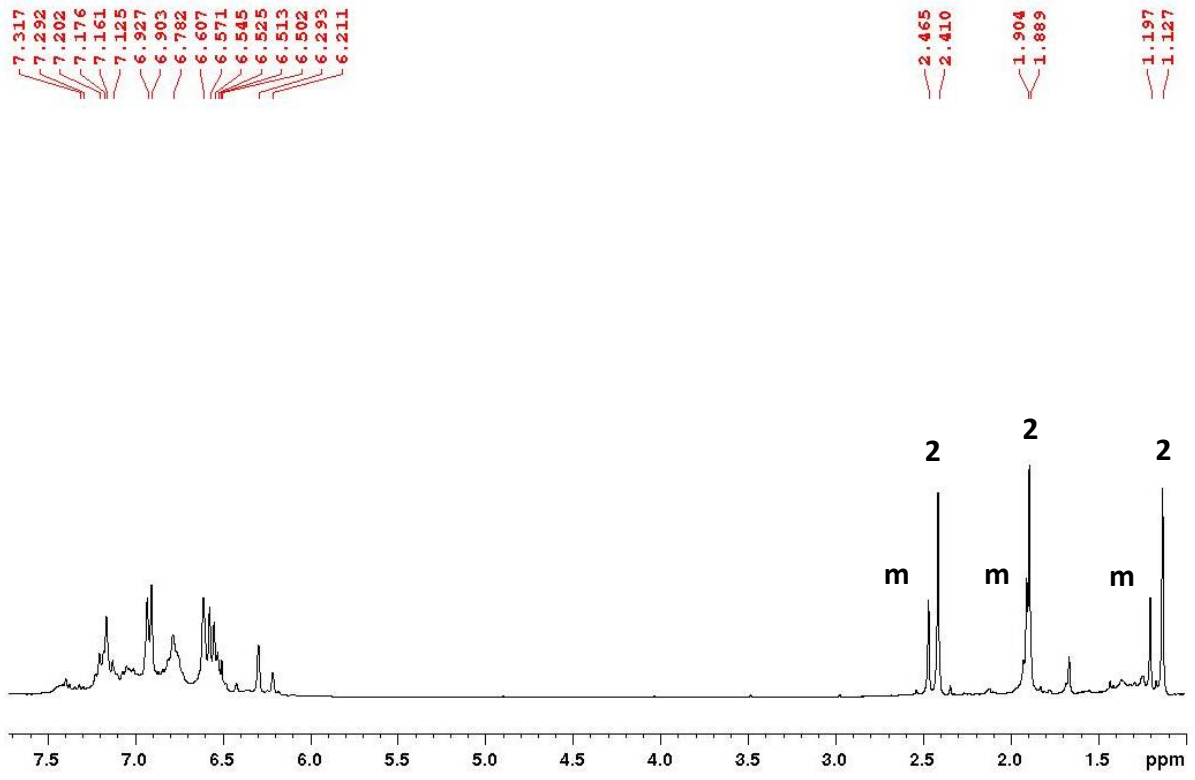


Figure S5.[1]H NMR spectrum of crude mixture containing of **2** and a minor product **m** in C_6D_6

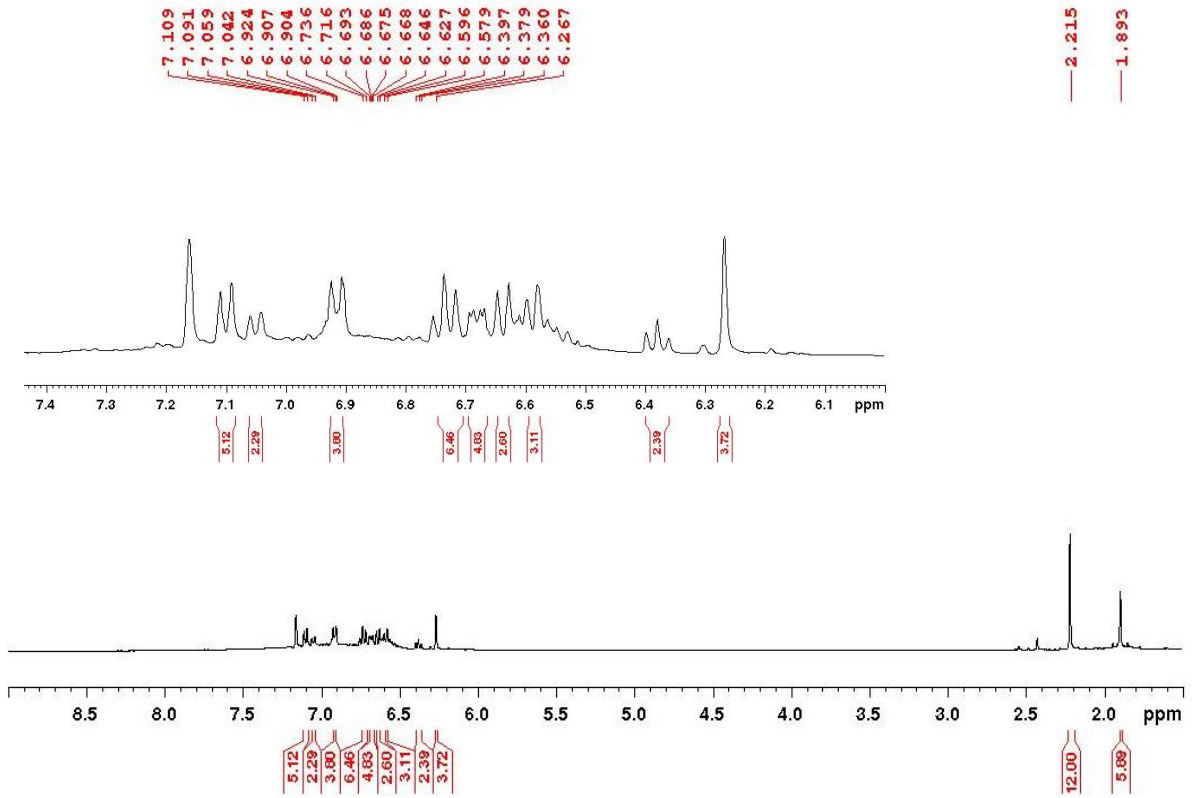


Figure S6.[1]H NMR spectrum of **3**

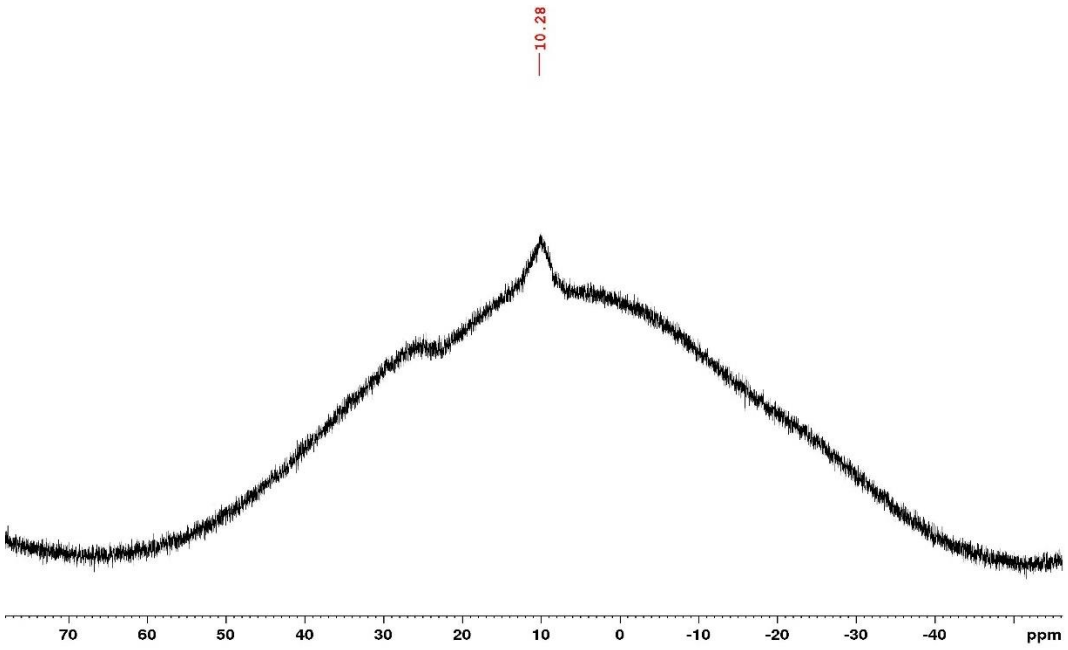


Figure S7.[11]B NMR spectrum of **3**

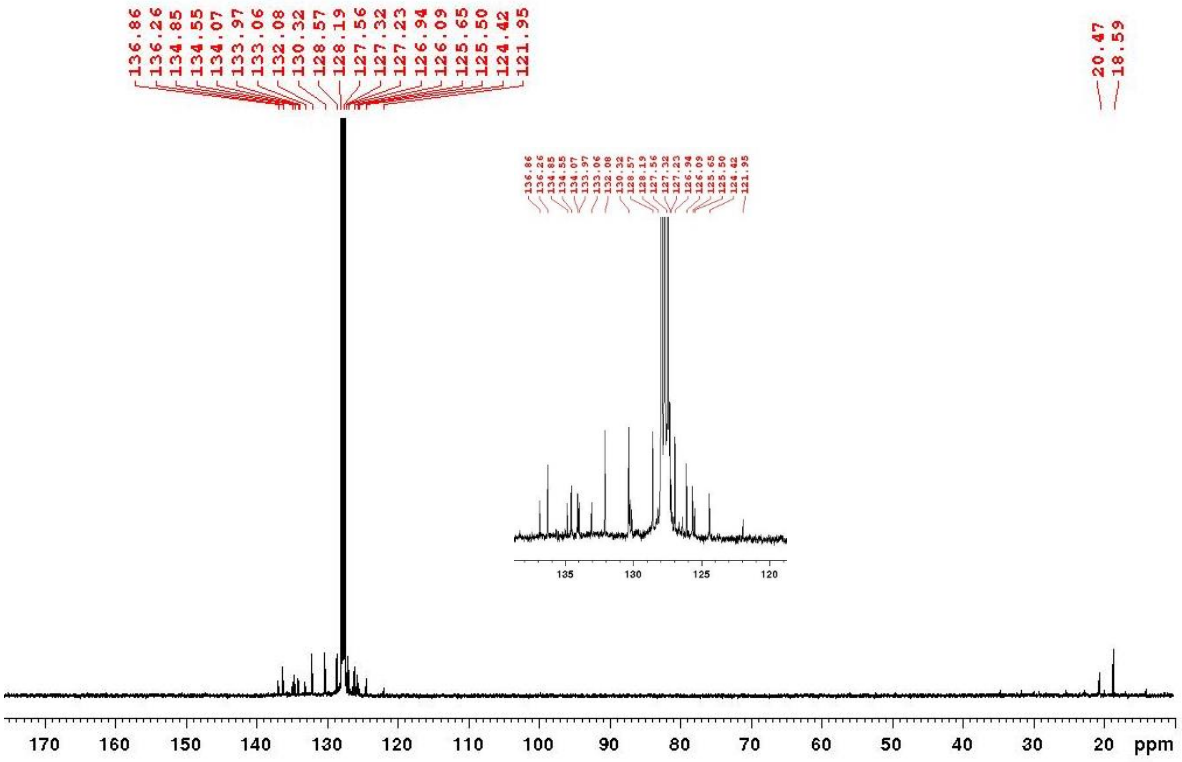


Figure S8. [13]C NMR spectrum of **3**

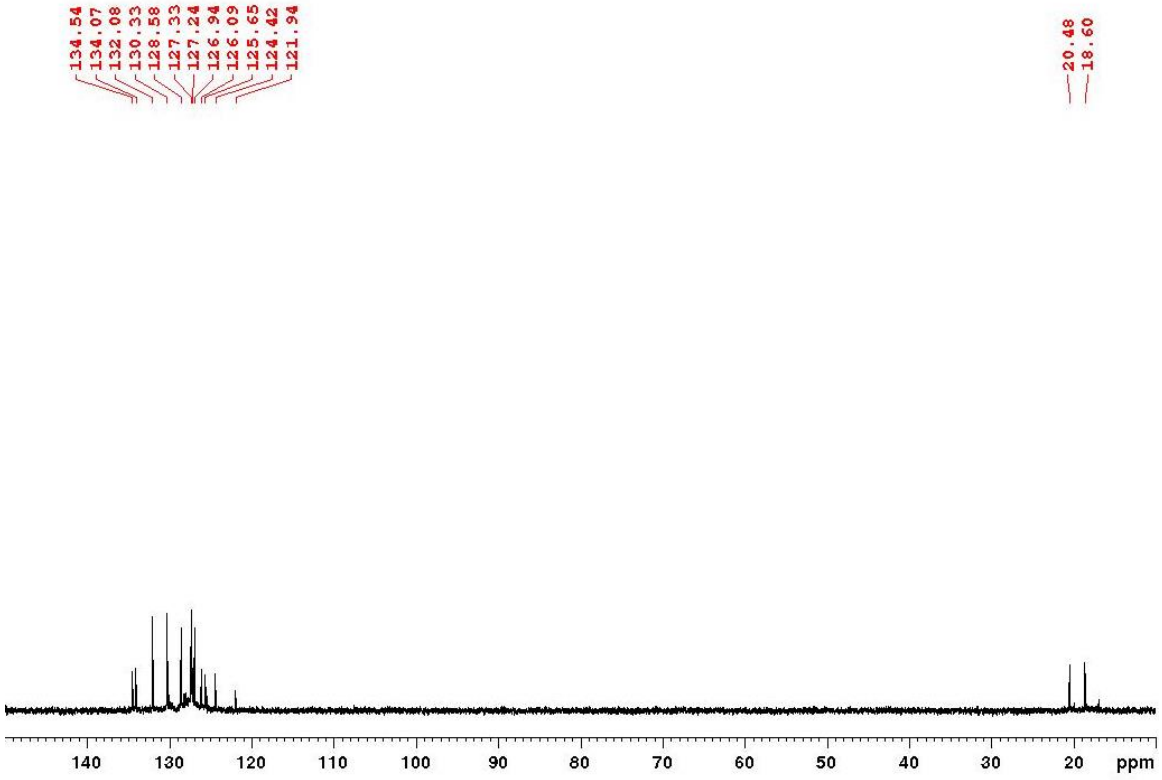


Figure S9. ^{13}C NMR (DEPT 135) spectrum of **3**

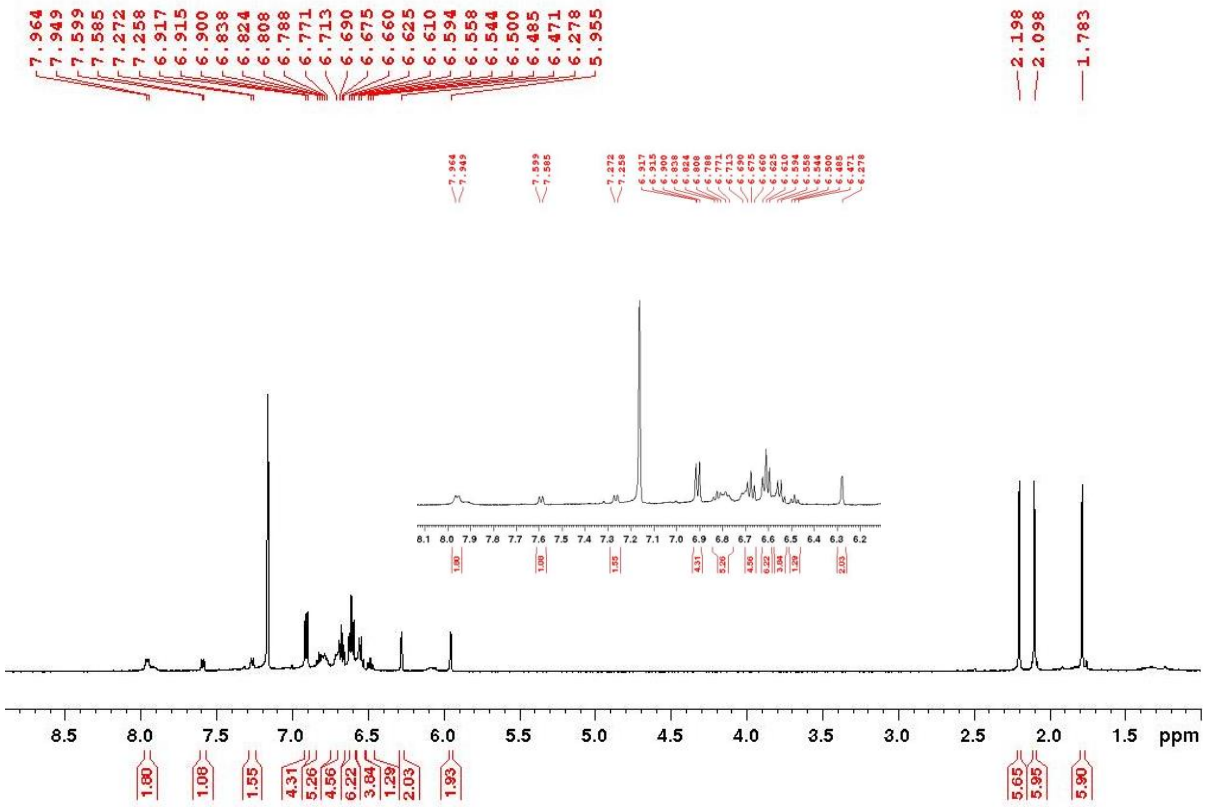


Figure S10.^{1}H NMR spectrum of **4**

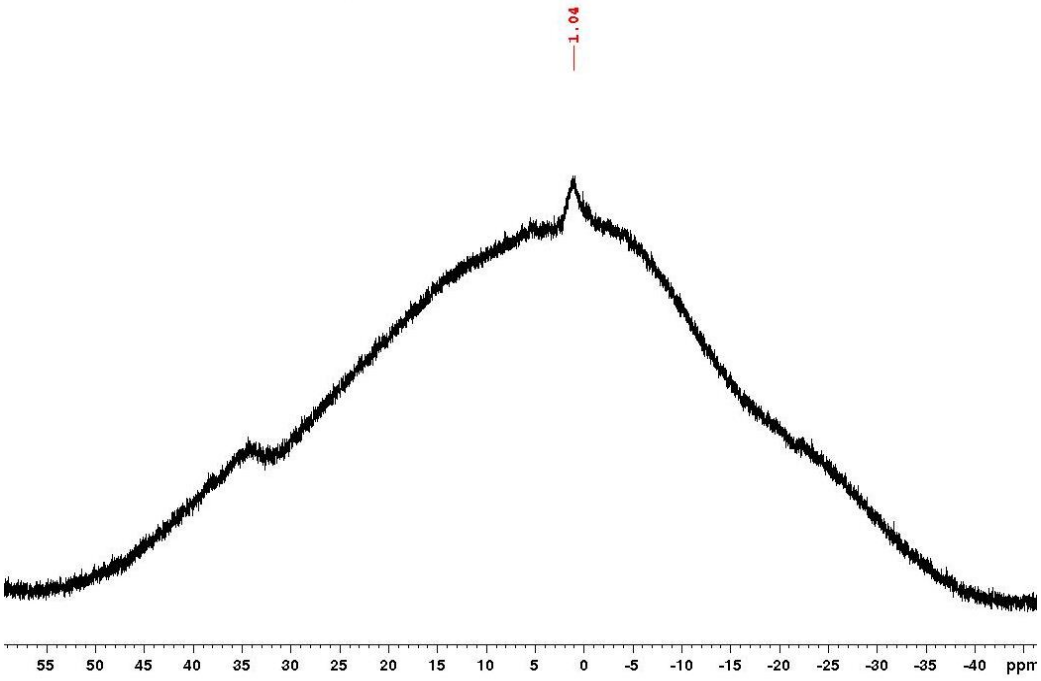


Figure S11.[11]B NMR spectrum of **4**

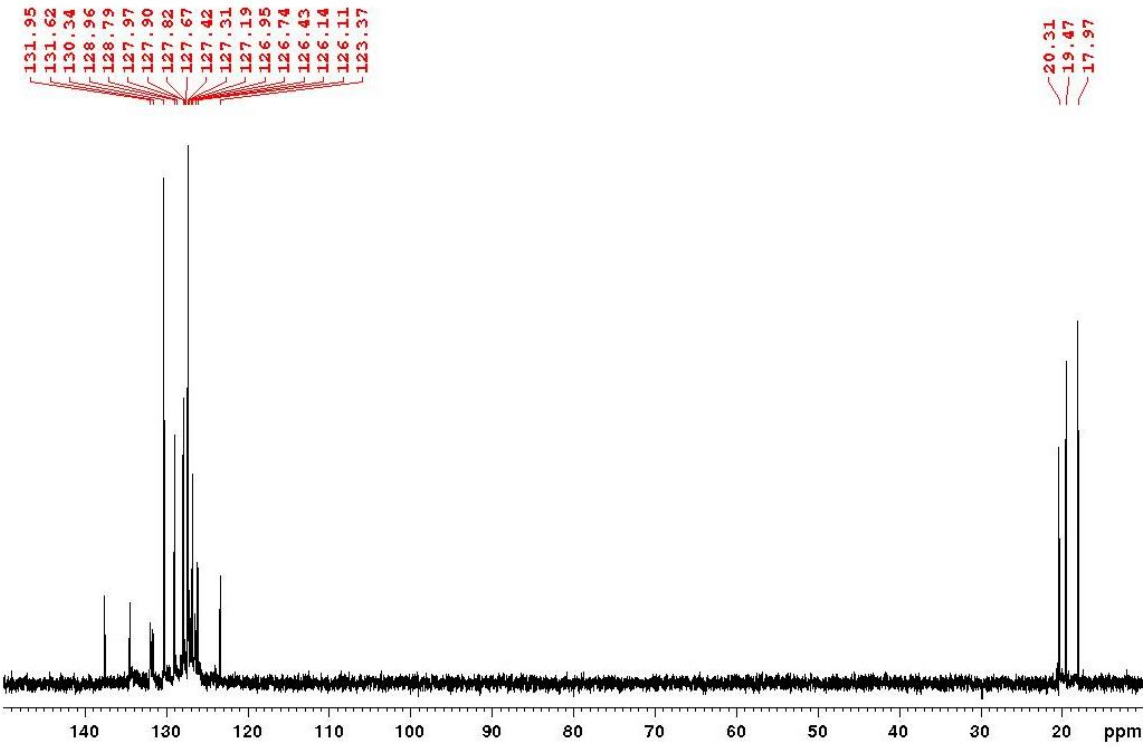


Figure S12.[13]C NMR spectrum of **4**

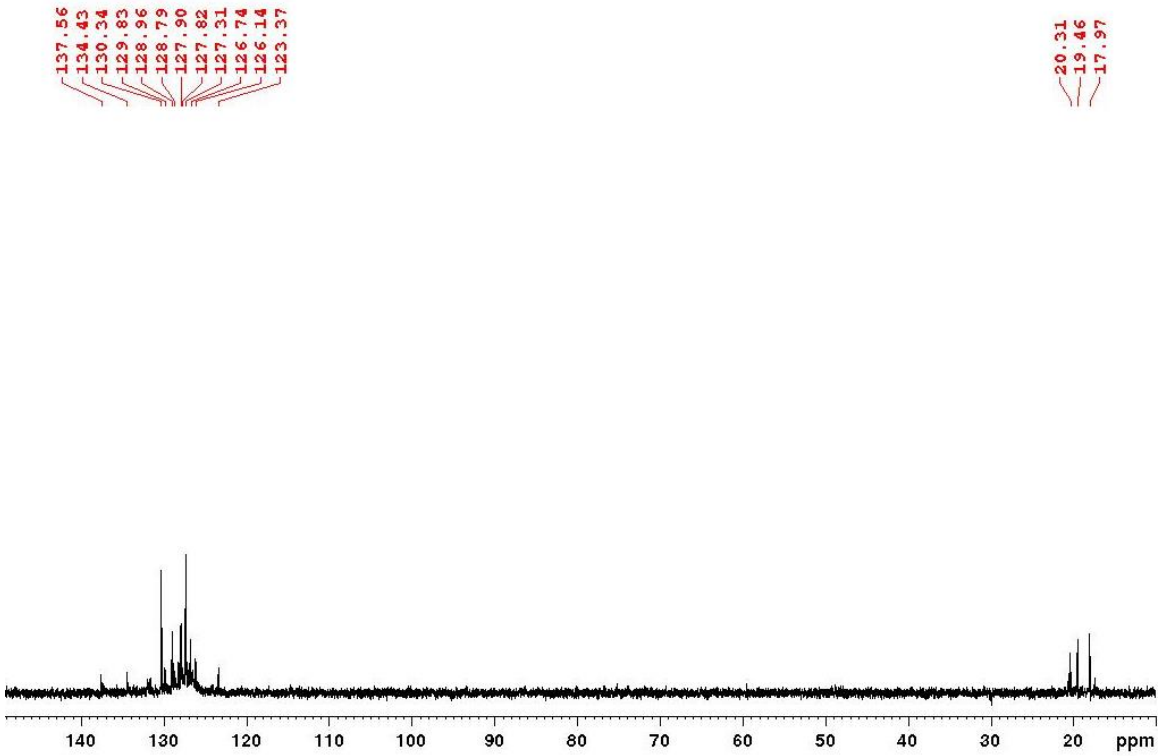


Figure S13.^{13}C NMR (DEPT 135) spectrum of **4**

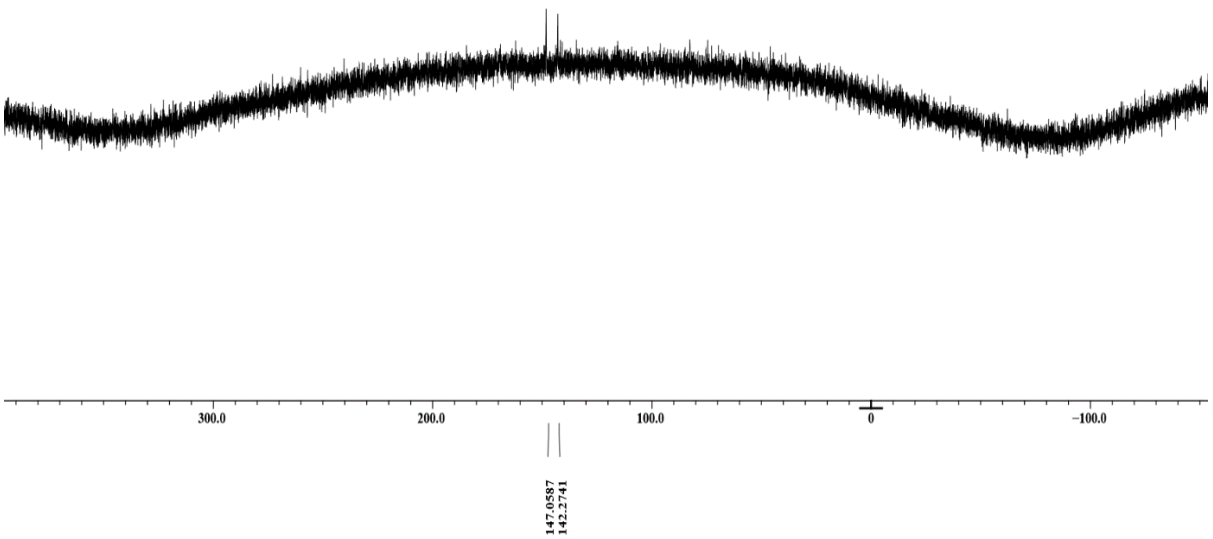


Figure S14.^{77}Se{^{1}H} NMR spectrum of **4** (*presence of two peaks is putatively due to inequivalent selenium atoms in Se NMR time scale, as predicted by X-ray diffractometry and DFT studies: see Table S3)

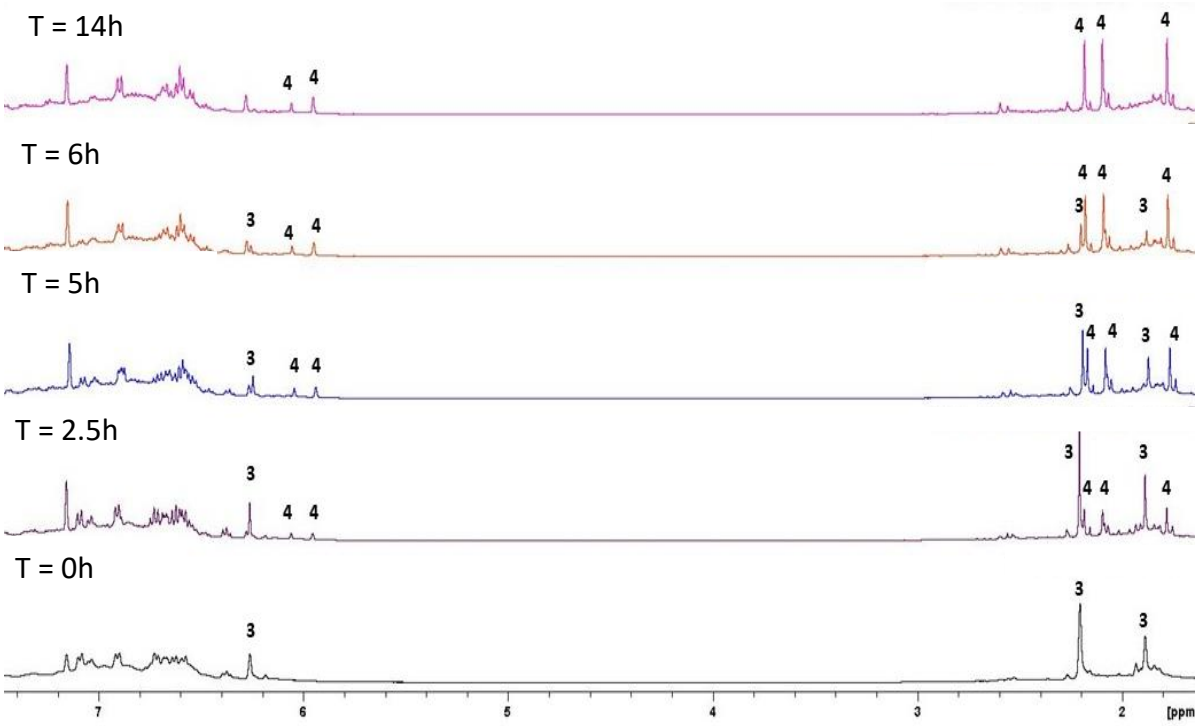


Figure S15.[1]H NMR spectrum in monitoring the formation of **4** during the reaction of **3** with Se at 80 °C.

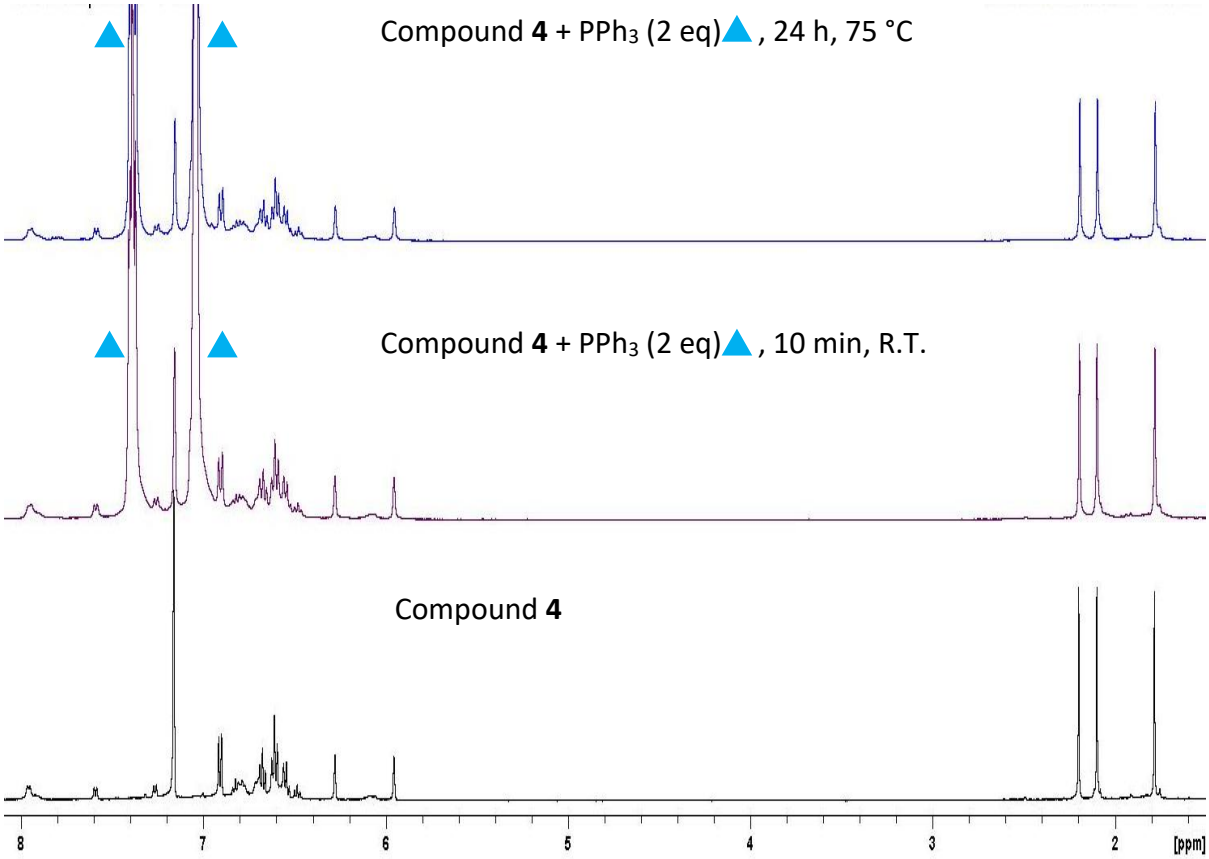


Figure S16.[1]H NMR spectrum in monitoring of reaction of **4** and PPh_3 (2 eq)

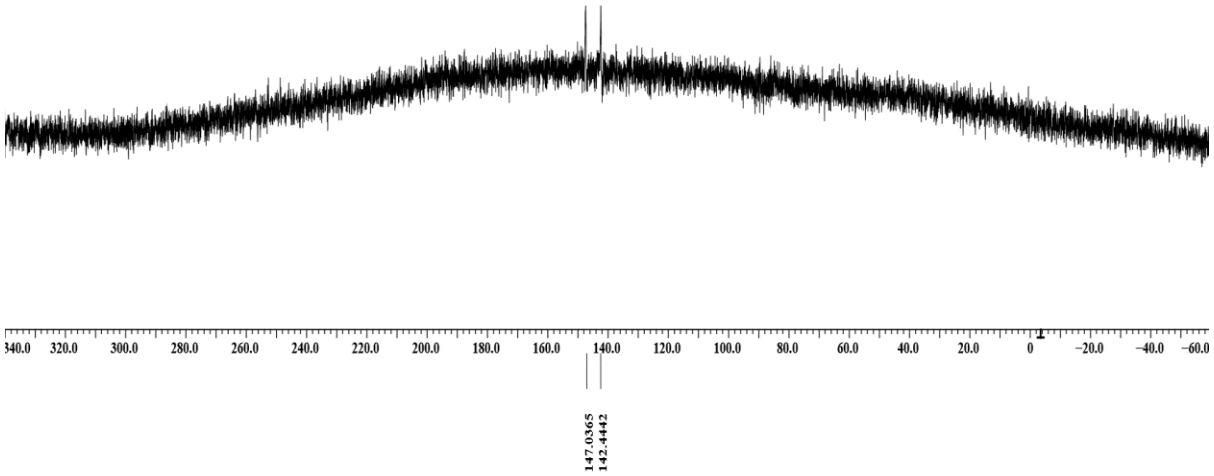


Figure S17.$^{77}Se\{^{1}H\}$ NMR spectrum of a mixture of **4** and PPh_3 after heating at 75 ^{o}C for 24 h

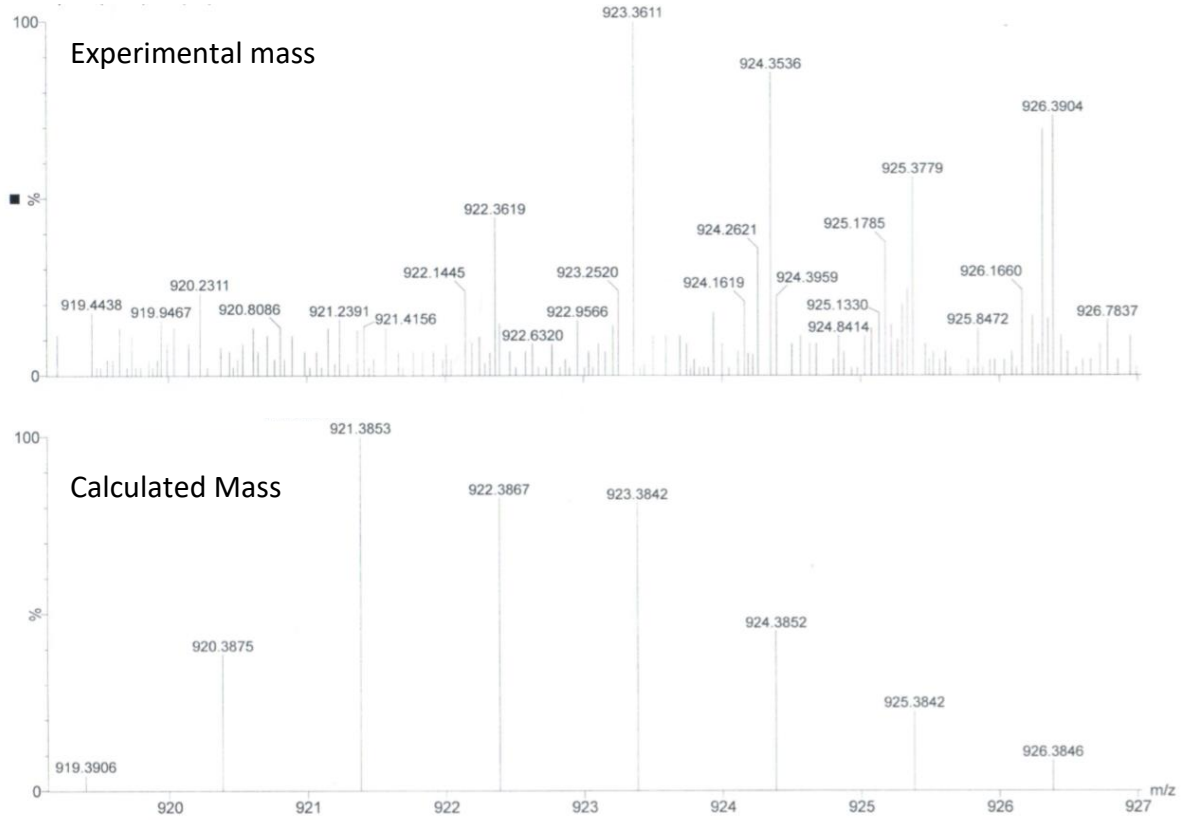


Figure S18. Electrospray ionization (ESI) mass spectra of compound **2** with isotopic distributions.

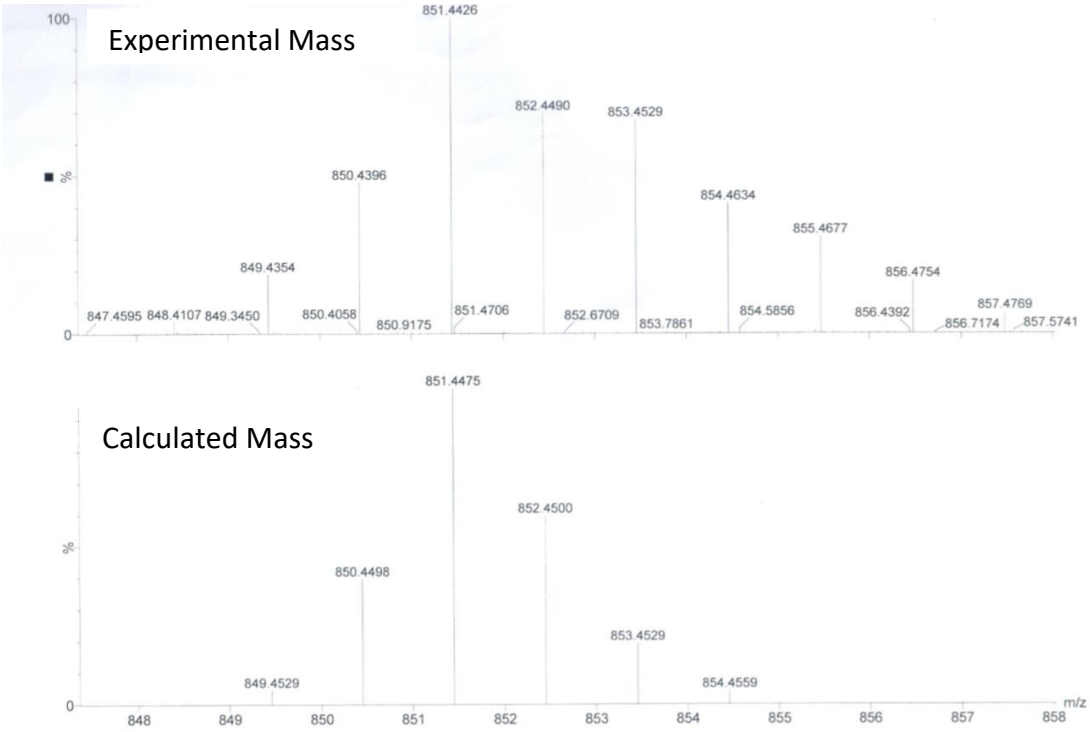


Figure S19. Electrospray ionization (ESI) mass spectra of compound **3** with isotopic distributions.

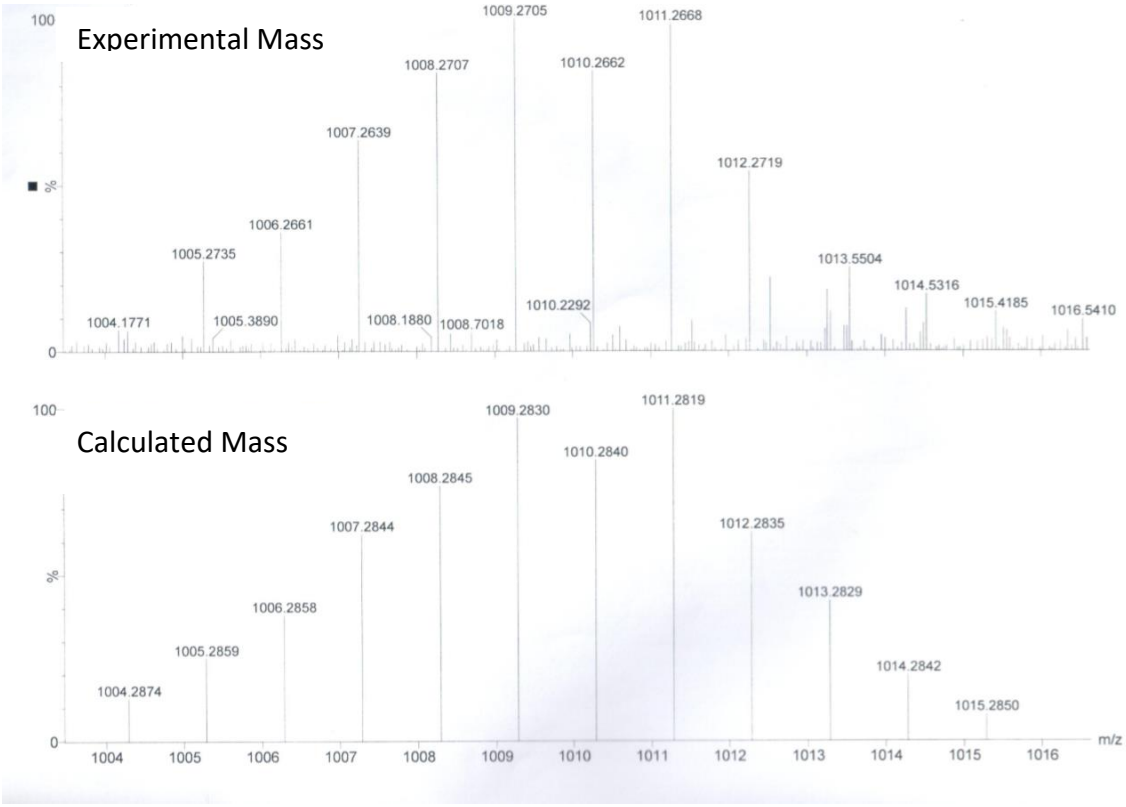


Figure S20. Electrospray ionization (ESI) mass spectra of compound **4** with isotopic distributions.

2. UV/Vis absorption spectroscopy

The UV/Vis absorption spectroscopy for compound **3** was computed with the time dependent DFT (TD-DFT) method at the B3LYP/6-311G(d,p) level.

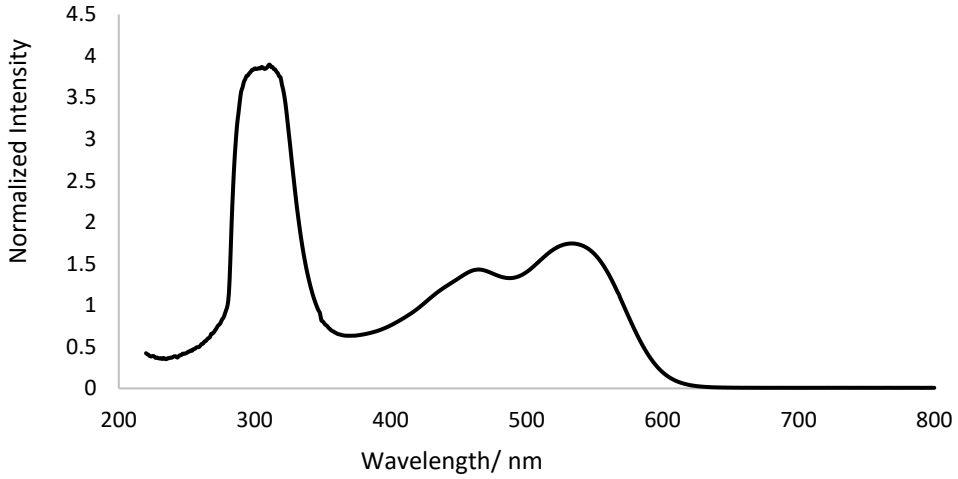


Figure S21. UV Vis absorption spectra of **3** in toluene

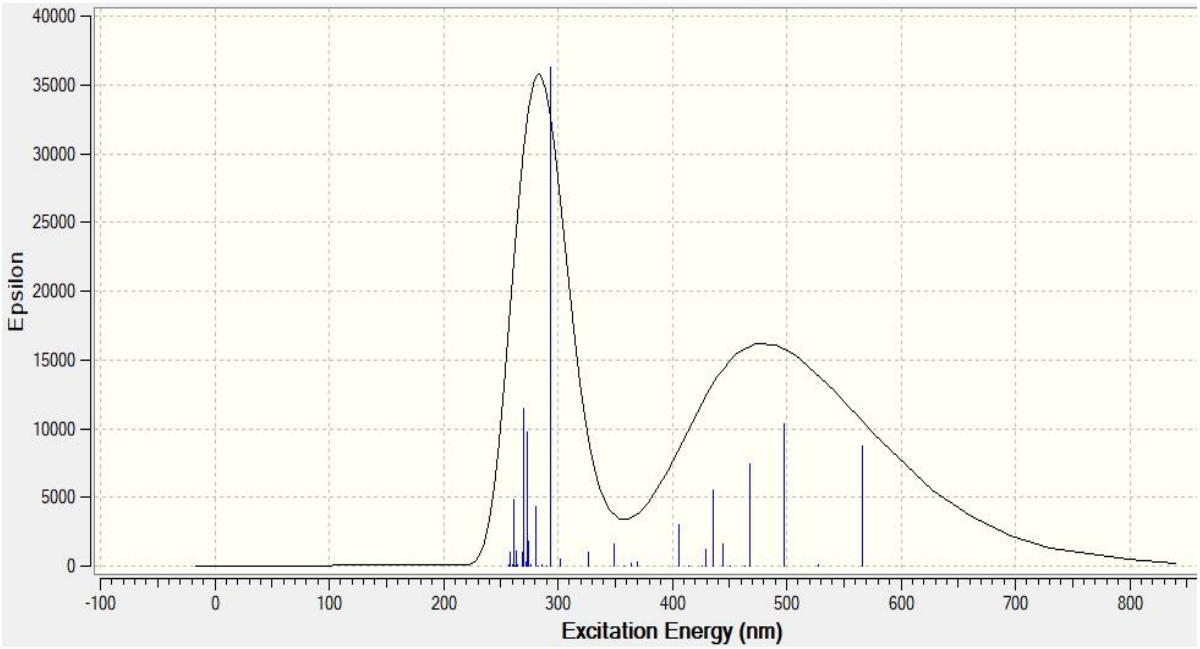


Figure S22. Calculated UV Vis absorption spectra of **3** by TD-DFT at B3LYP/6-311G(d,p) level of theory

3. Crystallographic data

X-ray data collection and structural refinement. Intensity data for compounds **2**, **3** and **4** were collected at 100 K using a Bruker D8 Quest diffractometer. The structure was solved by Intrinsic Phasing (SHELXTL XT-2014) [1] and refined for all data by full-matrix least squares methods on F^2.[2] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. The restraint RIGU for the whole molecule was used in the refinement of rei1167m cif. CCDC: 1902297-1902299 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center viawww.ccdc.cam.ac.uk/data_request/cifwww.ccdc.cam.ac.uk/data_request/cif

Table S1. Summary of Data collection and structure refinement for compounds **2**,**3** and **4**.

	2	**3**	**4**
Formula	$C_{66}H_{58}B_2Cl_2N_4$	$C_{60}H_{52}B_2N_4$	$C_{60}H_{52}B_2N_4Se_2$
Fw	999.68	850.67	1008.59
Cryst syst	triclinic	triclinic	triclinic
Space group	P -1	P -1	P -1
Size (mm^3)	0.100 x 0.140 x 0.160	0.040 x 0.220 x 0.240	0.020 x 0.100 x 0.120
T/K	100(2)	100(2)	100(2)
a, Å	8.0320(2)	12.2084(6)	13.734(6)
b, Å	12.9483(3)	14.2682(8)	14.180(5)
c, Å	13.2734(3)	15.0075(8)	15.375(6)
α, deg	93.7410(9)	114.4228(17)	65.974(7)
β, deg	92.4577(8)	98.0538(17)	75.771(9)
γ, deg	104.6101(9)	90.2251(18)	62.708(8)
V, A^3	1330.44(5)	2351.2(2)	2423.9(17)
Z	1	2	2
d calcd $g.cm^{-3}$	1.248	1.202	2423.9(17)
μ, mm^{-1}	0.169	0.069	1.571
Refl collected	55990	26578	18578
T_{max}/T_{min}	0.9830/0.9740	0.9970/0.984	0.9690/0.8340
N_{measd}	8530	10210	8527
[R int]	0.0564	0.1030	0.1418
R [I>2sigma(I)]	0.0468	0.0665	0.0959
Rw[I>2sigma(I)]	0.0702	0.1403	0.2213
GOF	1.026	1.035	1.026
Largest diff peak/hole[$e \cdot Å^{-3}$]	0.363/-0.260	0.258/-0.301	0.812/-0.873

4. Computational details

Gaussian 09E was used for the density functional theory (DFT) calculations.[3] Geometry optimization and frequency calculations of compounds **2**, **3** and **4** were performed at the B3LYP/6-311G(d,p)level of theory. NBO calculations for compounds **2**, **3** and **4** were performed at B3LYP/6-311G(d,p) level.[4] NMR shielding tensors for compounds **2**,**3** and **4** were computed with the Gauge-Independent Atomic Orbital (GIAO) method at the B3LYP/6-311G(d,p) level. The calculated boron chemical shifts were derived with reference to that of $BF_3.Et_2O$.

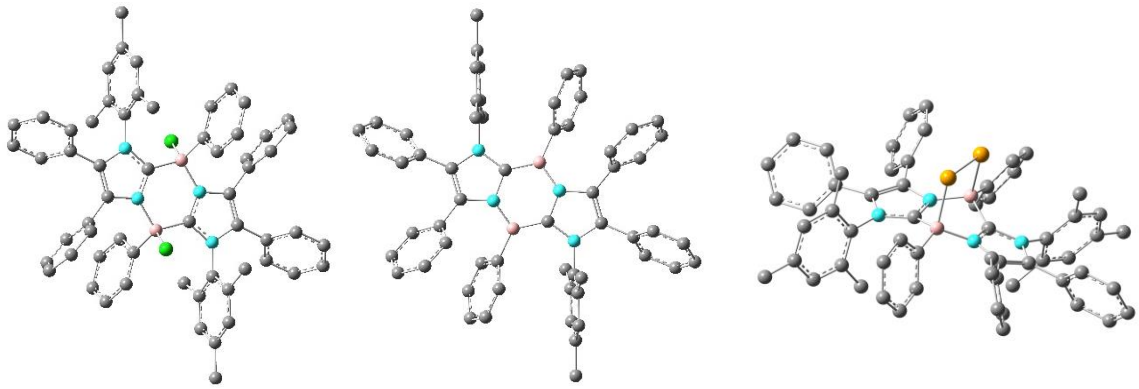


Figure S23. The optimized structures of **2** (left), **3** (center) and **4** (right).

Table S2. Selected Bond Lengths and Wiberg Bond Index (WBI) for the optimized geometries of compound **3**.

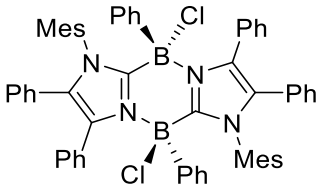
Bond (Å)	X-ray data	Optimized structure	WBI Value
B1-N1	1.457(4)	1.4574	0.9144
B1-C1	1.496(4)	1.4960	1.1868
B2-N3	1.462(4)	1.4624	0.9144
B2-C2	1.494(4)	1.4942	1.1867
N3-C1	1.407(3)	1.4073	1.1223
N1-C2	1.406(3)	1.4058	1.1223

Table S3. Selected Bond Lengths and Wilberg Bond Index (WBI) for the optimized geometries of compound **4**.

Bond (Å)	X-ray data	Optimized structure	WBI Value
B1-N3	1.577(13)	1.5775	0.6503
B1-C2	1.588(15)	1.5876	0.8489
B2-N1	1.566(13)	1.5656	0.6503
B2-C1	1.600(15)	1.6004	0.8489
N1-C2	1.334(11)	1.3342	1.2873
N3-C1	1.357(12)	1.3573	1.2873
B1-Se1	2.114(12)	2.1139	0.8674
B2-Se2	2.114(13)	2.1144	0.8674
Se1-Se2	2.3543(18)	2.3543	0.5955

Table S4: Optimized structures of a) **2** b) **3** and c) **4**. (atom, x-, y-, z- positions in Å).

a) **2**



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H	-2.27895100	6.34159600	0.98311400
C	-2.46303300	5.10678900	-2.17278600
C	-2.29998500	5.61883700	0.17545600
C	-2.34090500	3.75110600	-1.88486500
H	-2.57250300	5.42964300	-3.20195900
C	-2.17546000	4.26243100	0.46350600
C	-2.19263400	3.31391200	-0.56372700
H	-2.34943500	3.02319400	-2.68651400
H	-2.04818500	3.93893900	1.48902200
C	-2.16885400	1.85585100	-0.27363600
C	-3.27018500	1.05869600	-0.14790400
N	-1.04265500	1.02883000	-0.16347300
C	-4.69902700	1.44113300	-0.16496800
N	-2.80352400	-0.24927700	0.02528400
B	0.45315700	1.52314600	-0.21161300
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C	-5.19107400	2.33126900	0.79894300
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C	-3.68489400	-1.37413600	0.27035900
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C	0.67095800	2.65435200	0.92349400
Cl	0.73421500	2.17858500	-1.99610100
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C	-4.15258100	-1.58438200	1.58099300
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H	1.51820700	4.18006100	-0.32702200
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C	3.68490900	1.37412500	-0.27039800
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C	1.33334300	4.86920500	1.69584600
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C	-0.27320900	-2.36775100	-2.24149300
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H	-1.51822500	-4.18002900	0.32701300

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H	-5.36942100	-2.83427100	2.81307500
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H	-4.01425500	-1.13866100	3.67582900
C	2.19257800	-3.31387800	0.56383500
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C	4.11963600	2.16420900	0.79945400
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C	-0.38931500	-3.30723100	-3.26407300
C	-1.33328000	-4.86919300	-1.69584100
C	-6.34377000	-4.66673200	1.05331800
C	2.34076500	-3.75103000	1.88499700
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C	5.43432600	3.49605100	-0.76952800
H	5.36944000	2.83416900	-2.81316400
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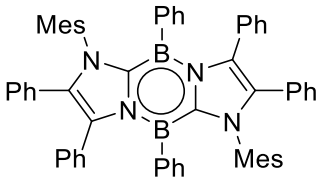
H	6.88706100	-3.41774800	-1.53998400
C	7.39083500	-2.23918000	0.18917100
H	7.57585500	-0.98066800	1.92506700
C	6.34385800	4.66663900	-1.05345500
H	2.53913600	-7.10118300	1.36669100
H	8.43045700	-2.54655900	0.19912900
H	6.79700700	5.05139700	-0.13762900
H	7.14791600	4.38837600	-1.73991400
H	5.78862400	5.48760600	-1.51944400

b) **3**



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C	-1.05816300	-2.86091100	0.48839300
C	-1.87079000	-3.67491000	-0.31590100
H	-2.16702600	-3.32608700	-1.29863200
C	-2.30600400	-4.92787500	0.10890900
H	-2.93106200	-5.53003700	-0.54218700
C	-1.93826900	-5.41043400	1.36291200
H	-2.27571500	-6.38623200	1.69566100
C	-1.12568400	-4.62978600	2.18198500
H	-0.82638400	-4.99530500	3.15903200
C	-0.69318100	-3.37957600	1.74494900
H	-0.05435900	-2.78943900	2.39607900
C	1.41046400	0.16602500	0.06857500
C	3.10528900	-1.34656800	-0.06299700
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H	0.73723000	-3.03777700	-2.37879900
C	1.17628300	-5.13253700	-2.20303900
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H	1.75505200	-7.16161300	-1.76742600
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H	2.83131300	-6.56596500	0.38886400
C	2.38919300	-4.47293400	0.21128200

H	2.85925800	-4.21747400	1.15337000
C	4.48815900	-1.86239900	-0.17041500
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H	6.43726700	-3.70431200	-2.27077100
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H	8.10085000	-3.28382700	-0.47468400
C	6.72620200	-2.14246200	0.72664800
H	7.44371600	-1.95611500	1.51785200
C	5.43524300	-1.63415200	0.83678100
H	5.16039600	-1.06502500	1.71491700
C	3.78330100	1.04103000	0.16642500
C	4.15866700	1.57093200	1.41071500
C	5.14986600	2.55151300	1.43664600
H	5.44660500	2.96694500	2.39498300
C	5.76354500	3.01395400	0.27209000
C	5.36434800	2.46619300	-0.94621900
H	5.82953200	2.81324500	-1.86391900
C	4.37769200	1.48177700	-1.02448600
C	3.97177300	0.91918400	-2.36432000
H	4.43273200	-0.05766000	-2.53952600
H	4.28884400	1.58390400	-3.17022100
H	2.88966800	0.78652400	-2.43224600
C	6.81034200	4.09986200	0.33347300
H	7.39277500	4.14658400	-0.58905100
H	7.50286400	3.93937300	1.16398800
H	6.34540700	5.08021300	0.48299100
C	3.50824300	1.12296500	2.69527300
H	3.25701700	0.06071700	2.68195100
H	2.57738300	1.67277700	2.86066100
H	4.16490000	1.31472000	3.54651400

C	1.05833900	2.86109900	0.48792300
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H	0.05435700	2.79041200	2.39554300
C	1.12606600	4.63047500	2.18098000
H	0.82674700	4.99634800	3.15788800
C	1.93887800	5.41071800	1.36174800
H	2.27649100	6.38654700	1.69423400
C	2.30662200	4.92771200	0.10791800
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C	1.87119200	3.67470600	-0.31654900
H	2.16743700	3.32553100	-1.29915500
C	-1.41041400	-0.16587800	0.06868100
C	-3.10531500	1.34660600	-0.06282200
C	-1.93143200	2.04095400	-0.17400400
C	-1.80403600	3.46133600	-0.55805300
C	-2.39036600	4.47275900	0.21145700
H	-2.86083400	4.21693800	1.15324500
C	-2.37546000	5.79577900	-0.22197300
H	-2.83350500	6.56556300	0.38913900
C	-1.77044900	6.13133000	-1.43019300
H	-1.75634200	7.16202400	-1.76648600
C	-1.17644800	5.13327000	-2.20209400
H	-0.70155800	5.38518300	-3.14400000
C	-1.19267900	3.81216700	-1.77037000
H	-0.73637600	3.03874100	-2.37797100
C	-4.48824500	1.86226400	-0.17037000
C	-5.43532700	1.63411100	0.83684300
H	-5.16041500	1.06524200	1.71512700
C	-6.72636200	2.14219600	0.72654100
H	-7.44388200	1.95592900	1.51775900
C	-7.09510200	2.88770900	-0.39068600
H	-8.10113400	3.28306300	-0.47511800

C	-6.16197700	3.12303400	-1.39787500
H	-6.43754700	3.70339200	-2.27123200
C	-4.87106800	2.61481800	-1.29000500
H	-4.14939400	2.80641500	-2.07421500
C	-3.78315400	-1.04106200	0.16642700
C	-4.15872700	-1.57095600	1.41064800
C	-5.14981700	-2.55166000	1.43640000
H	-5.44670900	-2.96708500	2.39469300
C	-5.76316200	-3.01423400	0.27172800
C	-5.36376000	-2.46647200	-0.94651900
H	-5.82870200	-2.81362500	-1.86430100
C	-4.37721900	-1.48193200	-1.02460600
C	-3.97107500	-0.91932000	-2.36436300
H	-4.43208300	0.05748100	-2.53967200
H	-4.28792700	-1.58407600	-3.17032200
H	-2.88896800	-0.78657500	-2.43206900
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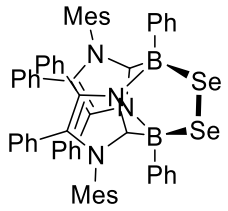
H	-7.39166600	-4.14751100	-0.58993700
H	-7.50290900	-3.93953100	1.16293700
C	-3.50862200	-1.12290500	2.69534000
H	-2.57785500	-1.67278800	2.86104200
H	-4.16552600	-1.31451900	3.54641900
H	-3.25729500	-0.06068600	2.68198500
N	0.86510800	-1.12065700	-0.03759700
N	2.79952200	-0.00510200	0.11351300
N	-0.86510100	1.12082800	-0.03757000
N	-2.79946800	0.00517500	0.11369600

c) **4**



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H	0.19111900	2.87523000	-1.88172900
C	1.22372500	4.70558900	-1.51118400
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C	1.95306700	5.46477200	-0.59940000
H	2.29330900	6.46057600	-0.86237600
C	2.23220800	4.93291900	0.65645600
H	2.79577800	5.51310400	1.37958000
C	1.78276300	3.65790400	0.99324800
H	2.01364300	3.27505300	1.98204500
C	1.41686300	0.15444100	-0.04497300
C	2.06720100	-1.99552700	-0.08279600
C	3.17266300	-1.22879500	-0.33805200
C	3.65474600	1.19976000	-0.60952600
C	3.71223700	1.70303100	-1.91786900
C	4.64395000	2.70182100	-2.19488800
H	4.69453700	3.10342300	-3.20216300
C	5.50826800	3.19578800	-1.21639800
C	5.43247400	2.65417600	0.06500600
H	6.10185900	3.01976500	0.83742700
C	4.51849500	1.65135200	0.39542400
C	4.49571800	1.07655000	1.78875100

H	4.96967500	1.76465700	2.49125500
H	5.04865300	0.13260300	1.82671900
H	3.48004800	0.87766100	2.13659200
C	6.47473800	4.31013900	-1.53399600
H	5.97913700	5.28401200	-1.45603200
H	6.86528200	4.22361900	-2.55102200
H	7.32099200	4.31500000	-0.84370800
C	2.80727900	1.18642500	-3.00860400
H	3.13861300	1.54809800	-3.98347800
H	1.77921900	1.52492200	-2.85984200
H	2.78260800	0.09374100	-3.04080700
C	4.57841700	-1.65864200	-0.50813800
C	5.32186500	-1.35285300	-1.65542900
H	4.87417400	-0.77265000	-2.45109500
C	6.63516000	-1.79458700	-1.78899900
H	7.19409600	-1.54730800	-2.68451800
C	7.22746800	-2.55293200	-0.78220200
H	8.24992800	-2.89743500	-0.88875800
C	6.49743900	-2.86623700	0.36222900
H	6.94834000	-3.45614000	1.15215600
C	5.18639200	-2.42162200	0.49957900
H	4.62273000	-2.66800000	1.39082800
C	2.08865500	-3.46573700	0.08869700
C	2.60015200	-4.27657900	-0.93199000
H	2.89482300	-3.82612400	-1.87255000
C	2.73331900	-5.64931300	-0.74908200
H	3.12862500	-6.26288800	-1.55095300
C	2.35861200	-6.23165500	0.45930100
H	2.45946300	-7.30163400	0.60350600
C	1.85180900	-5.43178100	1.48184400
H	1.55856800	-5.87748300	2.42572500
C	1.71952800	-4.05853900	1.30230400

H	1.33136500	-3.43760700	2.10113800
C	-1.04332100	-2.87094200	0.09882400
C	-0.78073400	-3.43324700	-1.16092400
H	-0.19137300	-2.87509500	-1.88177100
C	-1.22396900	-4.70548800	-1.51123100
H	-0.98998300	-5.10867500	-2.49093700
C	-1.95317800	-5.46472400	-0.59938400
H	-2.29348100	-6.46050100	-0.86238000
C	-2.23210100	-4.93296000	0.65655800
H	-2.79554400	-5.51320200	1.37973800
C	-1.78259500	-3.65797000	0.99336900
H	-2.01329800	-3.27520400	1.98224000
C	-1.41680200	-0.15448400	-0.04490400
C	-2.06712800	1.99550000	-0.08266900
C	-3.17258800	1.22876800	-0.33790100
C	-3.65476500	-1.19970900	-0.60954200
C	-4.51832900	-1.65156300	0.39555600
C	-5.43237200	-2.65423300	0.06515400
H	-6.10160100	-3.01995900	0.83765200
C	-5.50856100	-3.19550300	-1.21644200
C	-4.64458900	-2.70126900	-2.19500000
H	-4.69560100	-3.10246600	-3.20240900
C	-3.71267600	-1.70257100	-1.91795600
C	-2.80784200	-1.18612700	-3.00886700
H	-2.77824700	-0.09350700	-3.03738200
H	-3.14280700	-1.54303900	-3.98426800
H	-1.78102500	-1.52989200	-2.86339400
C	-6.47504300	-4.30993800	-1.53368400
H	-5.98223500	-5.28432000	-1.44475500
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H	-3.47943200	-0.87842100	2.13671200
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H	-5.04788100	-0.13293400	1.82719300
C	-4.57834500	1.65861300	-0.50804200
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H	-4.62325000	2.66667900	1.39158100
C	-6.49769600	2.86547600	0.36256600
H	-6.94888900	3.45481000	1.15275100
C	-7.22732900	2.55293000	-0.78232100
H	-8.24977800	2.89744300	-0.88896100
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H	-7.19328600	1.54871800	-2.68537300
C	-5.32137200	1.35361500	-1.65581500
H	-4.87331800	0.77405200	-2.45175100
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H	-2.89519100	3.82620600	-1.87211200
C	-2.73370600	5.64928800	-0.74848300
H	-3.12920600	6.26289700	-1.55023200
C	-2.35886300	6.23155200	0.45989600
H	-2.45980700	7.30150500	0.60422500
C	-1.85181200	5.43162500	1.48227300
H	-1.55846300	5.87726000	2.42615300
C	-1.71941600	4.05841500	1.30257800
H	-1.33106900	3.43745500	2.10129900
N	0.97791000	-1.12348400	0.05203600
N	2.75164400	0.10548500	-0.32920200
N	-0.97784400	1.12343900	0.05214400
N	-2.75159900	-0.10551400	-0.32907100
Se	0.52031400	1.07565100	2.60622500
Se	-0.52000700	-1.07573900	2.60624500

Table S5. Experimental and calculated ^{11}B NMR chemical shifts of compounds **2**, **3** and **4**.

	Isotropic Values	Calculated δ (^{11}B)[ppm]	Experimental δ (^{11}B)[ppm]
2	104.0800	−0.6621	−0.89
	104.0803	−0.6624	
3	83.4751	19.9	10.28
	83.4775	19.9	
4	104.8418	−1.4239	1.04
	104.8409	−1.4230	
$BF_3.Et_2O$ (Reference)	103.4179	-	-

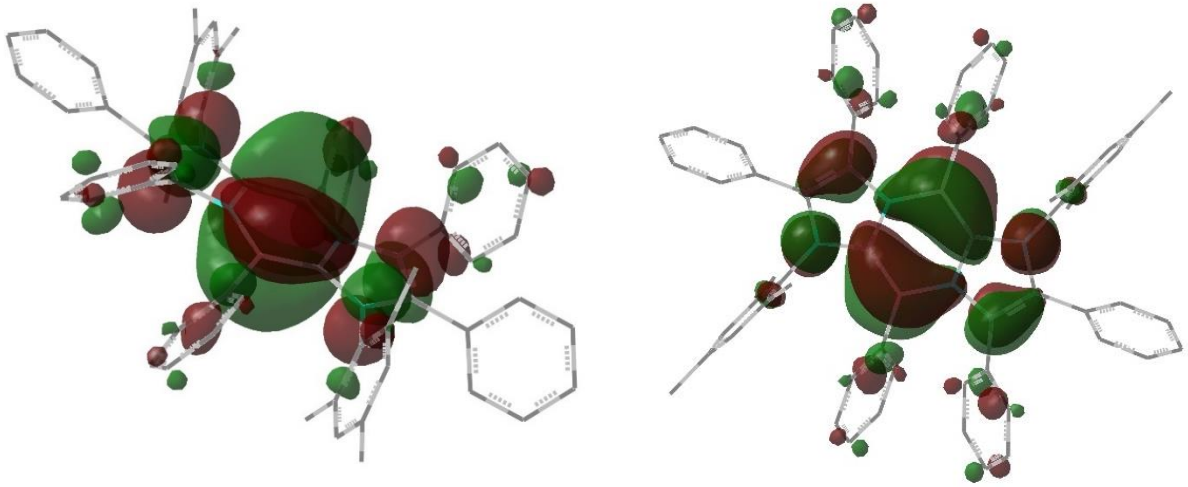

Figure S24. Side view (left) and front view (right) of the HOMO of **3**.

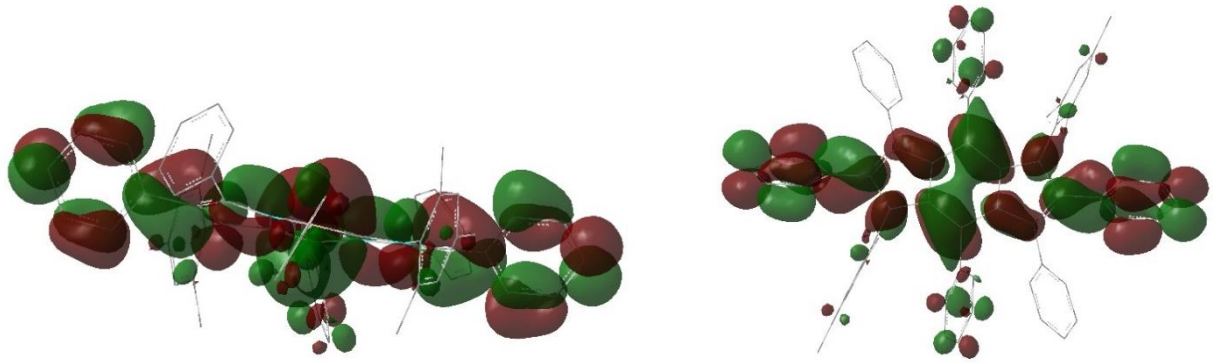

Figure S25. Side view (left) and front view (right) of the LUMO of **3**.

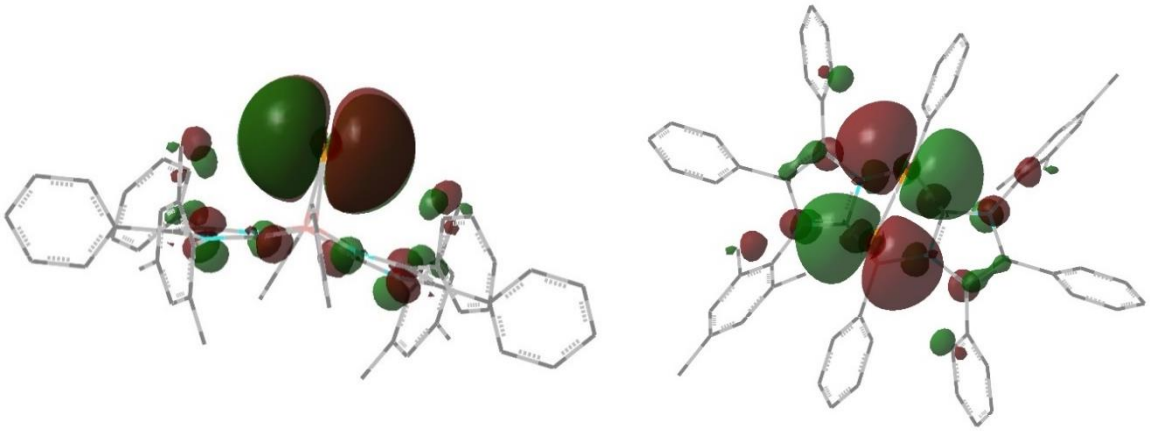

Figure S26. Side view (left) and top view (right) of the HOMO of **4**.

5. References

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3. Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.
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