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Supplementary Information

Crystalline potassium boryl dithiolate and diselenolate

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Contents

1. Experimental Procedures

General Procedures: All reactions were performed under an atmosphere of nitrogen by using standard Schlenk or dry box techniques. The solvents were dried over Na metal, K metal or CaH_2. ^{1}H, ^{11}B, $^{13}C\{^{1}H\}$ and ^{77}Se spectra were obtained with a BRUKER AVANCE III HD 500MHz spectrometer. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, br = broad signal. Coupling constants *J* are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Waters Q-Tof Premier Mass Spectrometer. Element analyses (C, H, and N) were determined with an elemental Vairo EL III analyzer (Bruker, Germany). Melting points were measured on a X4 Melting Point apparatus (Beijing Tech, CN) in sealed capillaries and are uncorrected. $[DmpBH(\mu\text{-}H)]_2$ (Dmp = 2, 6-bis(2,4,6-trimethylphenyl)phenyl) was synthesized according to literature procedures.[S1]

Synthesis of **1**:

S_8 (0.171g, 0.670 mmol) was added to a 5 mL toluene solution of $[DmpBH(\mu\text{-}H)]_2$ (0.554 g, 0.850 mmol) and the resulting mixture was heated at 130 °C for 2 days. After filtration, the filtrate was stored at –20 ºC overnight to give colourless crystals of **1** in 59% yield (0.371 g).

Mp: 258.3 °C (dec.); ^{1}H NMR (500 MHz, C_6D_6): δ = 7.17 (t, *J* =7.5, 2H, Ar-*H*), 6.93 (d, *J* = 7.5 Hz, 4H, Ar-*H*), 6.78 (s, 8H, Ar-*H*), 2.20 (s, 12H, C*H*$_3$), 1.99 (s, 24H, C*H*$_3$); $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ = 146.0 (*C*^{q}), 140.0 (*C*^{q}), 136.7 (*C*^{q}), 136.3(*C*^{q}), 130.4 (*C*H), 128.4 (*C*H), 128.4 (*C*H), 21.4 (*C*H$_3$), 21.0 (*C*H$_3$), B–C was not observed; ^{11}B NMR (160 MHz, C_6D_6): δ = 65.6 (br). HRMS (ESI): m/z calcd for $C_{48}H_{51}B_2S_3$: 745.3349 $[(M+H)]^+$; found: 745.3364.

Synthesis of **2**:

[DmpBH(μ-H)]$_2$ (0.783 g, 1.201 mmol) was dissolved in toluene (5 mL) and Se (1.896 g, 24.00 mmol) was added. The resulting mixture was heated at 130 °C for 4 days. After filtration, the filtrate was stored at –20 ºC overnight to give a yellow solid of **2** in 50% yield (0.533 g).

Mp: 287.5 ºC; ^{1}H NMR (500 MHz, C_6D_6, 298K): δ = 7.16 (t, J = 7.5 Hz, 2H, Ar-*H*), 6.92 (d, J = 7.5 Hz, 4H, Ar-*H*), 6.77 (s, 8H, Ar-*H*), 2.18 (s, 12H, C*H*$_3$), 2.03 (s, 24H, C*H*$_3$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298K): δ = 144.9 (*C*^{q}), 140.4 (*C*^{q}), 136.9 (*C*^{q}), 136.4 (*C*^{q}), 130.2 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 21.4 (*C*H$_3$), 21.3 (*C*H$_3$), B–*C* was not observed; ^{11}B NMR (160 MHz, C_6D_6, 298K): δ = 71.6 (s); ^{77}Se NMR (95 MHz, C_6D_6, 298K): δ = 617.8, 527.6; HRMS (ESI): m/z calcd for $C_{48}H_{51}B_2Se_3$: 886.1725 [(M+H)]$^+$; found: 886.1709.

Synthesis of **3**:

KC_8 (2.902 g, 21.80 mmol) was added slowly into a 15 mL THF solution of **1** (2.091 g, 2.701 mmol) at room temperature for 2 days. After filtration, the filtrate was stored at –20 ºC overnight to give a white solid of **3** in 56% yield. (0.762 g).

Mp: 225 °C (dec.); ^{1}H NMR (500 MHz, THF-D_8): δ = 6.96 (t, J = 7.5 Hz, 1H, Ar-*H*), 6.72 (s, 4H, Ar-*H*), 6.57 (d, J = 7.0 Hz, 2H, Ar-*H*), 3.62 – 3.59 (m, 2H, THF-C*H*$_2$), 2.31 (s, 12H, C*H*$_3$), 2.21 (s, 6H, C*H*$_3$), 1.80 – 1.73 (m, 2H, THF-C*H*$_2$); ^{13}C{^{1}H} NMR (126 MHz, THF-D_8): δ = 144.3(*C*^{q}), 139.1 (*C*^{q}),138.9 (*C*^{q}), 135.2 (*C*^{q}), 127.40 (*C*H), 126.4 (*C*H), 123.9 (*C*H), 68.0 (THF-*C*$_1$*C*$_4$), 26.2 (THF-*C*$_2$*C*$_3$), 22.7 (*C*H$_3$), 20.92 (*C*H$_3$), B–C was not observed; ^{11}B NMR (160 MHz, THF-D_8): δ = 72.7 (br). Anal. Calcd for $C_{88}H_{107}B_3K_6O_4S_6$: C, 62.61; H, 6.39; N, 0. Found: C, 63.04; H, 6.67; N, 0.

Synthesis of **4**:

KC_8 (1.512 g, 11.20 mmol) was added slowly into a 15 mL THF solution of **2** (1.239 g, 1.401 mmol) at room temperature for 2 days. After filtration, the filtrate was stored at –20 ºC overnight to give yellow crystals of **4** in 55% yield. (0.604 g).

Mp: 172.3 ºC (dec); ^{1}H NMR (500 MHz, THF-d_8, 298K): δ = 6.98 (t, J = 7.5 Hz, 1H, Ar-*H*), 6.73 (s, 4H, Ar-*H*), 6.58 (d, J = 7.5 Hz, 2H, Ar-*H*), 3.63–3.59 (m, 4H, thf-C*H*$_2$), 2.34 (s, 12H, C*H*$_3$), 2.22 (s, 6H, C*H*$_3$), 1.78–1.74 (m, 4H, thf-C*H*$_2$); ^{13}C{^{1}H} NMR (126 MHz, THF-d_8, 298K): δ = 143.6 (*C*^{q}), 138.8 (*C*^{q}), 137.8 (*C*^{q}), 135.4 (*C*^{q}), 127.6 (*C*H), 126.9 (*C*H), 124.1 (*C*H), 68.0 (thf-*C*$_1$*C*$_4$), 26.2 (thf-*C*$_2$*C*$_3$), 23.3 (*C*H$_3$), 21.0 (*C*H$_3$), B–*C* was not observed; ^{11}B NMR (160 MHz, THF-d_8, 298K): δ = 74.7 (br); ^{77}Se NMR (95 MHz, THF-d_8, 298K): δ = 210.3, the two B–*Se* were not observed. Anal. Calcd for $C_{32}H_{41}BK_2O_2Se_3$: C, 49.05; H, 5.27; N, 0. Found: C, 49.49; H, 5.58; N, 0.

Synthesis of **5**:

$B(OH)_3$ (1.366 g, 22.10 mmol) was added slowly to a 15 mL toluene solution of **3** (1.239 g, 2.202 mmol) at room temperature and the resluting mixture was stirred for 3 hours. All volatiles were removed under vacuum and the residue was extracted with toluene. After filtration, the filtrate was concentrated under reduced pressure and stored at –20 ºC. White crystals of **5** were obtained in 31% yield (0.121 g).

Mp: 161.6 °C (dec); ^{1}H NMR (500 MHz, C_6D_6): δ = 7.20 (t, J = 7.5 Hz, 1H, Ar-*H*), 6.94 (d, J = 7.5 Hz, 2H, Ar-*H*), 6.86 (s, 4H, Ar-*H*), 2.18 (s, 12H, C*H*$_3$), 2.17 (s, 6H, C*H*$_3$), S-H was not observed; ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 143.8 (*C*^{q}), 139.4 (*C*^{q}), 137.0 (*C*^{q}), 136.2 (*C*^{q}), 129.8 (*C*H), 128.5 (*C*H), 128.2 (*C*H), 21.5 (*C*H$_3$), 21.2 (*C*H$_3$), B–C was not observed; ^{11}B NMR (160 MHz, C_6D_6): δ = 65.0 (br); HRMS (ESI): m/z calcd for $C_{24}H_{27}BS_2$: 391.1725 $[(M+H)]^+$; found: 391.1705.

Synthesis of **6**:

$B(OH)_3$ (0.395 g, 6.400 mmol) was added slowly into a 15 mL toluene solution of **4** (0.500g g, 0.638 mmol) at room temperature and the resluting mixture was stirred for for 5 hours. All volatiles were removed under vacuum and the residue was extracted with toluene. After filtration, the filtrate was concentrated under reduced pressure and stored at –20 ºC. White crystals of **6**[S2] were obtained in 91% yield (0.208 g).

^{1}H NMR (500 MHz, C_6D_6): δ = 7.24 (t, J = 7.5 Hz, 1H, Ar-*H*), 6.94 (d, J = 7.5 Hz, 2H, Ar-*H*), 6.84 (s, 4H, Ar-*H*), 3.83 (s, 2H, O–*H*), 2.16 (s, 6H, C*H*$_3$), 2.08 (s, 12H, C*H*$_3$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 146.6 (*C*^{q}), 140.1 (*C*^{q}), 137.1 (*C*^{q}), 135.9 (*C*^{q}), 130.3 (*C*H), 129.0 (*C*H), 128.4 (*C*H), 21.1 (*C*H$_3$), 20.8 (*C*H$_3$), B–C was not observed; ^{11}B NMR (160 MHz, C_6D_6): δ = 29.9 (br).

2. Crystallographic Details

All crystallographic intensity data was collected using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector, and PhotonJet-S microfocus sealed tube X-ray sources for generating Cu Kα radiation (λ = 1.54184 Å). A suitable single crystal identified by microscopy was mounted on a Nylon loop with paratone oil, and then quickly placed onto the instrument. The crystal temperature was held at 173 K using an Oxford Cryosystems CryostreamPlus 800 open-flow N_2 cryostat. Reflections were recorded, indexed and corrected for absorption with the *CrysAlis*^{pro} software suit.[S3] All structures were solved by intrinsic phasing (ShelXT-2015),[S4,S5] and refined to convergence by full-matrix least squares methods based on F^2 (SHELX-2018)[S6] embedded in the Olex2.[S7] All non-hydrogen atoms were refined with anisotropic displacement parameters (ADPs). Hydrogen atoms attached to carbon (CH) were placed in calculated positions and refined within a riding model, with U_{iso}(H) = 1.2 U_{eq} (C) of the carrier atom (U_{iso}(H) = 1.5 U_{eq} (C) for methyl groups). Due to non-ideal solvent masking, beam stop clipping and the minor presence of diffuse scattering, OMIT instruction was applied during structure refinement. The threshold (*Iobs-Icalc*)/σ(W)>10 was chosen for omitting these reflections.

In the crystal structure of **3**, one terphenyl ring was found to be disordered. Based on the residual electron density located in this region, the disorder was successfully divided into two components using PART command, and a free variable was introduced for the occupancy refinements. The occupancies of both components were constrained to sum to 1.0. To get reasonable geometry and ADPs for the disorder atoms, some structural and thermal parameter restraints (SADI, SIMU and ISOR) were adopted in the refinements.

The large adps for O2A, O2B, O3A and O3B atoms are attributable to the disordered THF.

PROBLEM: Unit Cell Contains Solvent Accessible VOIDS of . 106 Ang**3.

Response: It was masking ~4e and removal of solvent mask would only result in a slight change of R1 factor from 7.28 to 7.68. Therefore, we did not mask this data as the reviewer suggested.

Table S1. X-ray Data for 1-4.

Compounds	**1**	**2**	**3**	**4**
Formula	$C_{48}H_{50}B_2S_3$	$C_{48}H_{50}B_2Se_3$	$C_{88}H_{107}B_3K_6O_4S_6$	$C_{32}H_{41}BK_2O_2Se_3$
Formula weight	744.68	885.38	1688.12	783.54
Temperature (K)	173.00(10)	172.99(10)	173.00(10)	172.99(10)
Wavelength (Å)	1.54184	1.54184	1.54184	1.54184
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	$P2_1/n$
a (Å)	12.6674(2)	12.83960(10)	14.8368(5)	12.7889(3)
b (Å)	20.0273(4)	19.9939(2)	17.0181(6)	12.3813(4)
c (Å)	16.7069(3)	16.8684(2)	20.5205(7)	22.4926(6)
α (°)	90	90	88.753(3)	90
β (°)	95.1670(10)	95.4230(10)	70.986(3)	95.480(2)
γ (°)	90	90	68.924(3)	90
V (°)	4221.21(13)	4310.97(8)	4544.1(3)	3545.27(17)
Z	4	4	2	4
Density (calcd. g/cm^{-3})	1.172	1.364	1.234	1.468
Absorption coeff. (mm^{-1})	1.833	3.334	4.205	6.076
Reflections collected	29111	25645	44043	20480
Independent reflections	7446 [R_{int} =0.0680]	7597 [R_{int} = 0.0430]	15953 [R_{int} = 0.0710]	6220 [R_{int} = 0.0747]
Data/restraints/parameters	7446/0/490	7597/0/490	15953/1832/1303	6220/216/414
R_1 [I>2sigma(I)]	0.0679	0.0360	0.0768	0.0528
wR_2 [all data]	0.2323	0.0925	0.1763	0.1269
GOF	1.118	1.171	1.105	1.043
CCDC No	2366072	2388453	2366073	2388454

3. Computational Details

All calculations were performed with the Gaussian 16 package.[S8] Geometry optimizations of **3** and **4** were carried out with the M06-2X functional[S9]. The def2-SVP basis set[S10] was used for all the atoms of **3** and **4**. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy. Natural population analysis (NPA), natural bond orbital (NBO), Wiberg bond indices (WBI) were calculated with the natural bond orbital (NBO) 7.0 program package[S11] at the same level as used for the geometry optimization. Optimized structures were visualized by the Gaussview 6.0[S12] program. Multiwfn program (version 3.8)[S13] was used for the topological analysis for the quantum theory of atoms in molecules (QTAIM). The wavefunction files (.wfn) for the topological analysis was obtained from Gaussian 16 at the M06-2X/def2-SVP level of theory using the optimized geometry. Pictures of NBOs were generated by means of the ChemCraft 1.8 program.[S14]

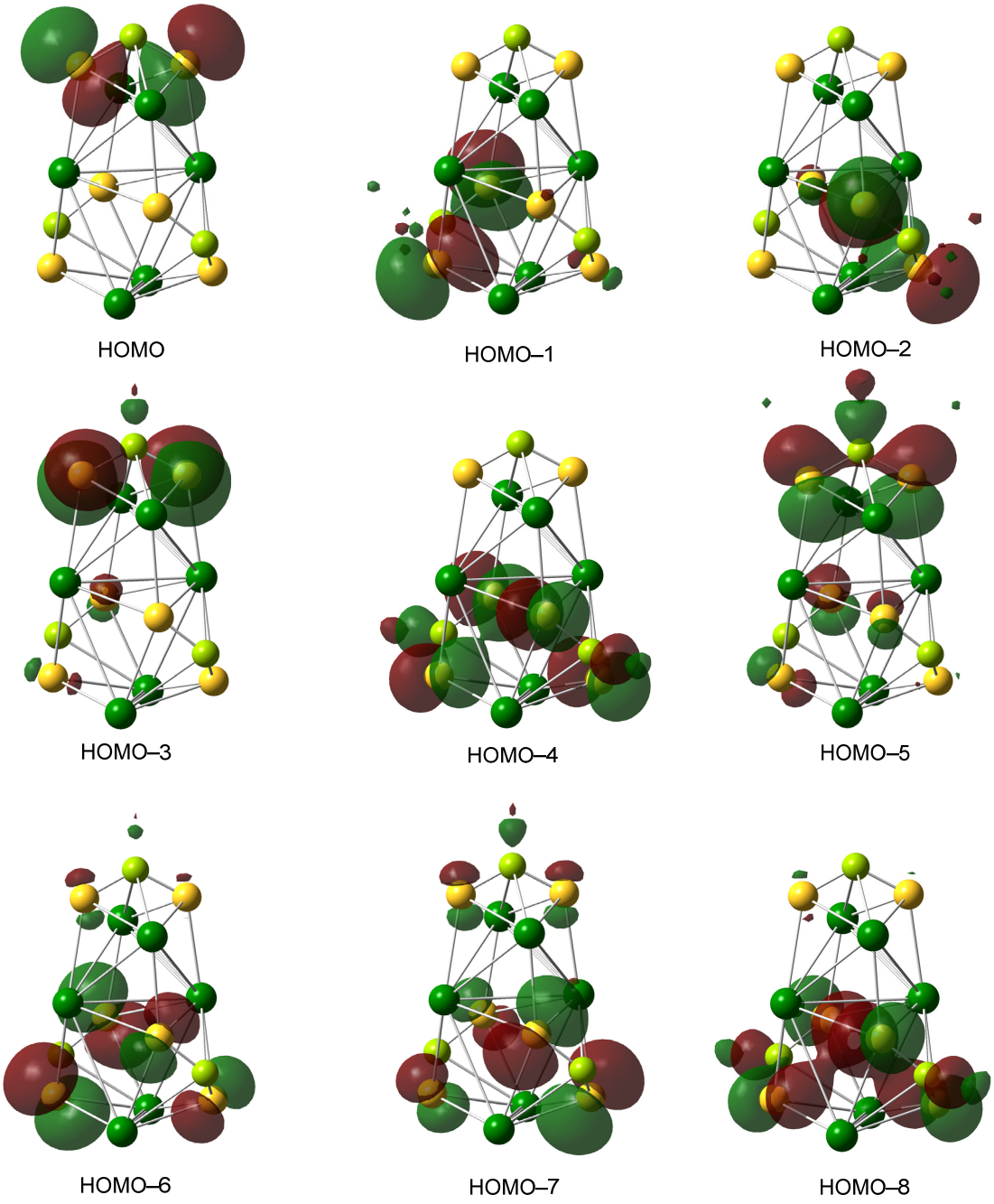


Fig. S1 Selected frontier molecular orbitals of **3** (isovalue = 0.03; the Dmp group and coordinated solvents are omitted for clarity.).

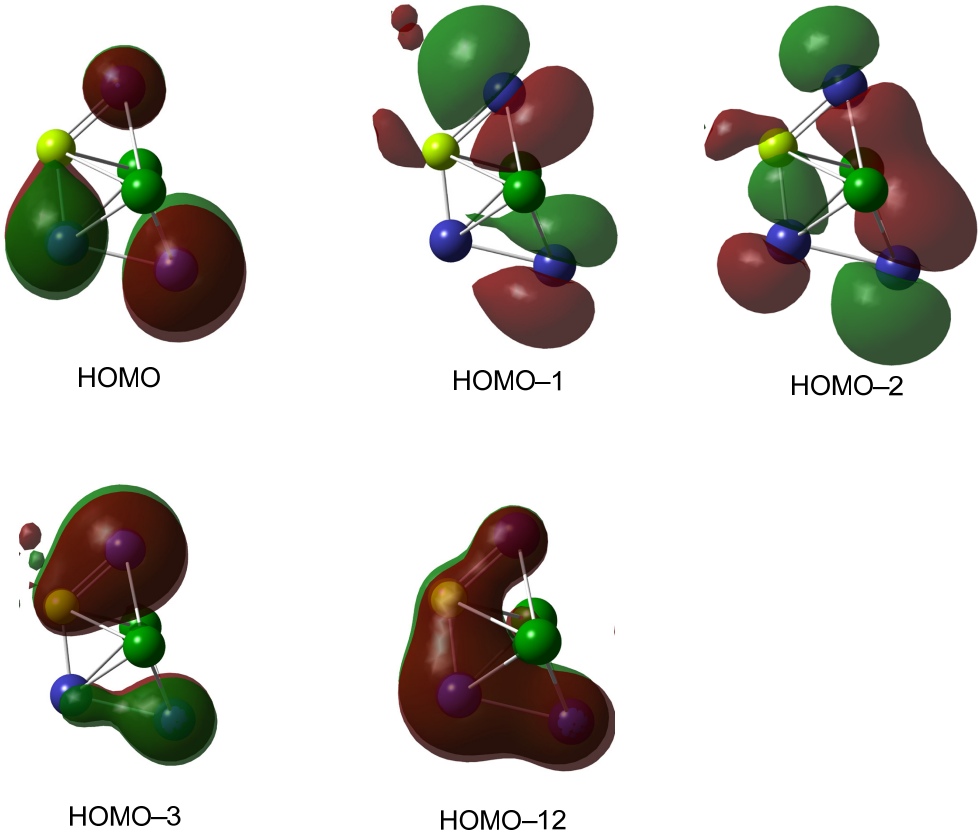


Fig. S2 Selected frontier molecular orbitals of **4** (isovalue = 0.03; the Dmp group and coordinated solvents are omitted for clarity.).

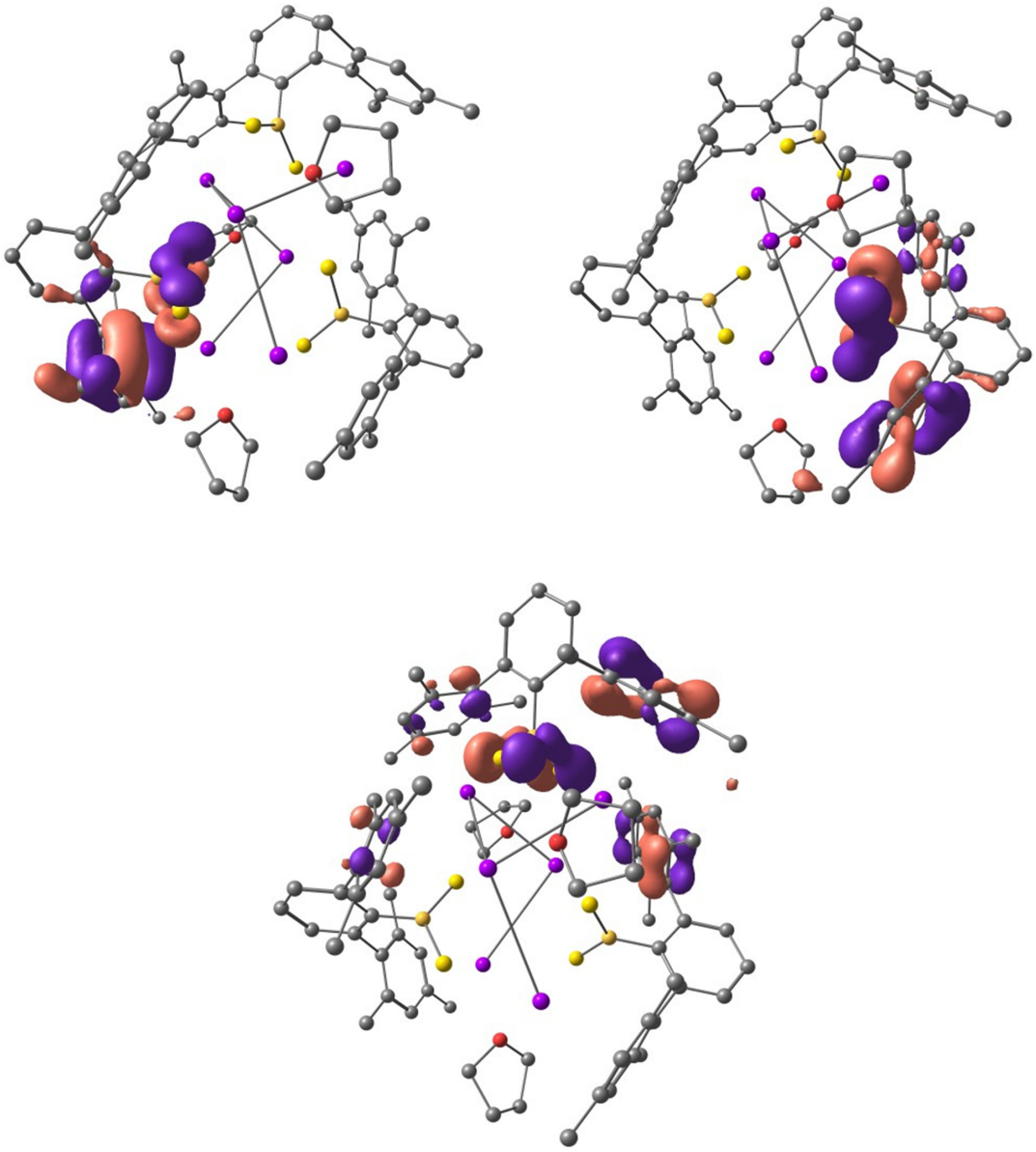


Fig. S3 Selected NBO orbitals of **3** invovling B–S double bond.

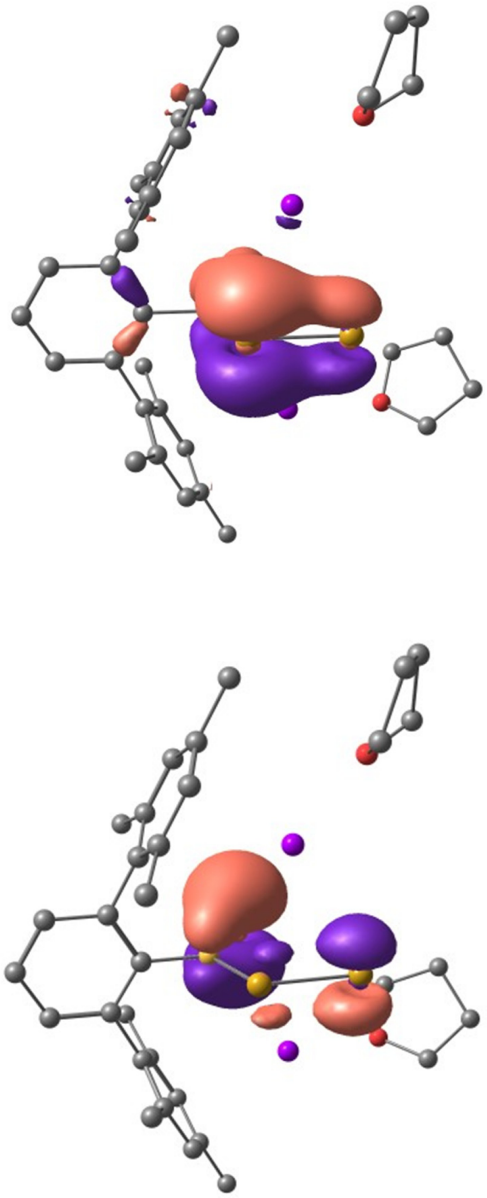


Fig. S4 Selected NBO orbitals of **4** invovling B–Se double bond.

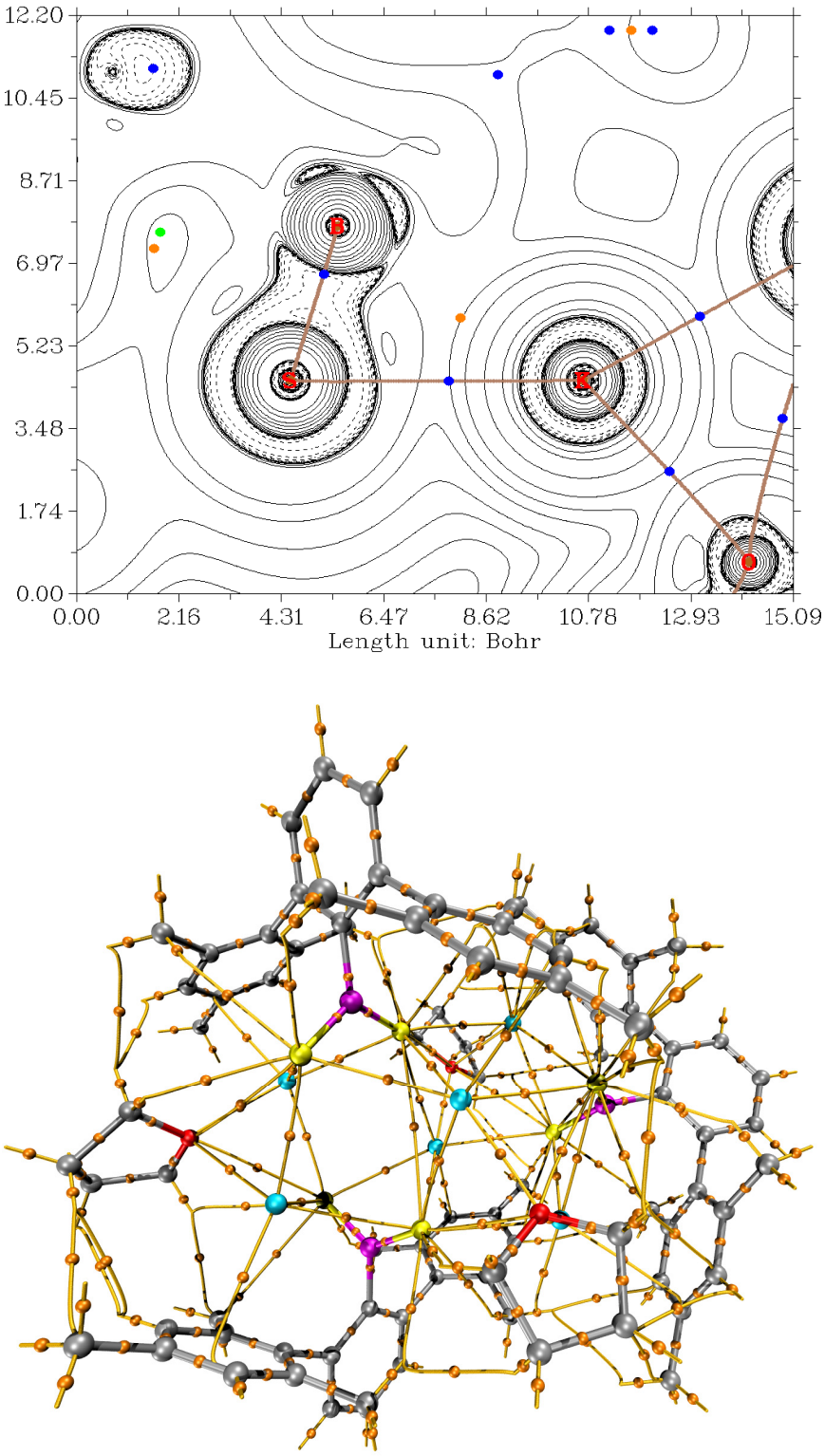


Fig. S5 Topological analyses for **3**. Plot of the Laplacian of the electron density on the BSK plane (top) and AIM (bottom) with bond paths and BCPs.

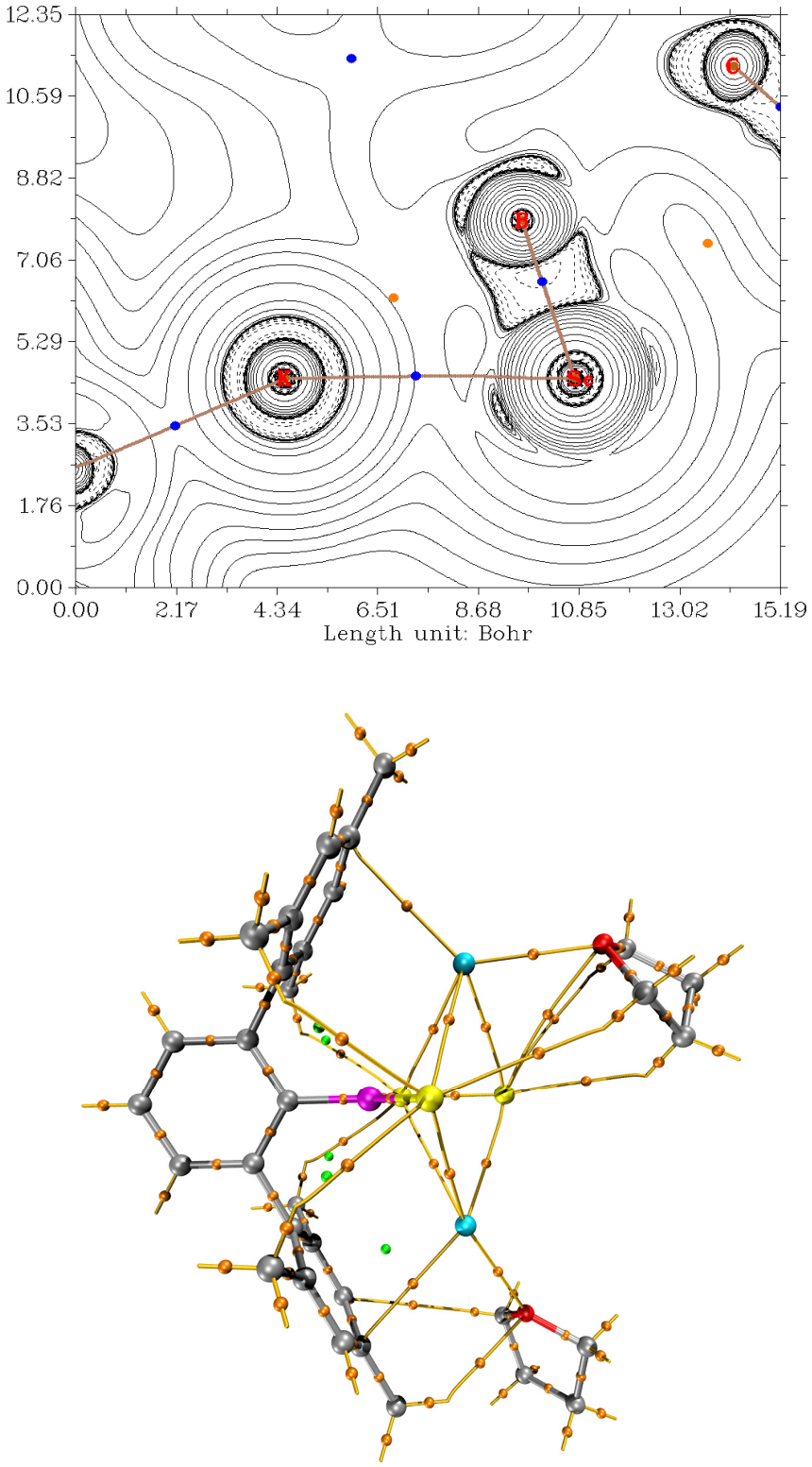


Fig. S6 Topological analyses for **4**. Plot of the Laplacian of the electron density on the BSeK plane (top) and AIM (bottom) with bond paths and BCPs.

Table S2. Selected topological parameters of **3** (in a.u.).

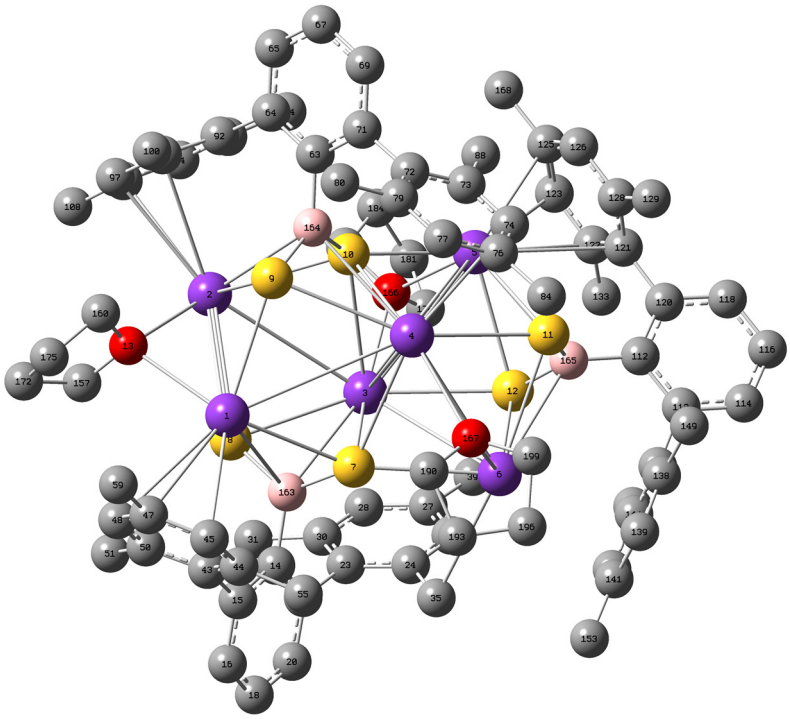
		ρBCP	∇^2ρBCP
BCP326	S7···K1	0.0122	0.0415
BCP344	S8···K1	0.0142	0.0478
BCP361	S12···K6	0.0140	0.0471
BCP363	S7···K4	0.0102	0.0338
BCP365	S7···K3	0.0138	0.0470
BCP369	S11···K6	0.0135	0.0450
BCP388	S9···K1	0.0152	0.0522
BCP391	S8···K3	0.0127	0.0424
BCP413	S12···K3	0.0138	0.0450
BCP414	S8···K2	0.0134	0.0451
BCP415	S11···K4	0.0121	0.0390
BCP421	S9···K4	0.0115	0.0385
BCP436	S10···K3	0.0085	0.0278
BCP439	S9···K2	0.0123	0.0414
BCP460	S12···K5	0.0146	0.0495
BCP462	S11···K5	0.0121	0.0409
BCP466	S10···K2	0.0152	0.0522
BCP496	S10···K5	0.0166	0.0604

Table S3. Selected topological parameters of **4** (in a.u.).

		ρBCP	∇^2ρBCP
BCP162	Se3···K5	0.0118	0.0388
BCP167	Se3···K4	0.0119	0.0395
BCP168	Se1···K5	0.0106	0.0400
BCP171	Se1···K4	0.0100	0.0380
BCP176	Se2···K5	0.0118	0.0401
BCP179	Se2···K4	0.0122	0.0414

4. Cartesian Coordinates

3



K	-3.85619300	-1.25695600	1.06743900
K	-3.49910400	1.47603700	-1.45166200
K	0.12594300	-0.55978000	-1.99192100
K	-0.04491200	0.44685100	2.13208500
K	2.24762500	2.41532900	-0.87383600
K	2.26339600	-2.42913800	0.91085300
S	-0.86039700	-2.28740900	0.45828600
S	-2.90810700	-1.60741100	-1.91612000
S	-3.04896400	1.65810100	1.74129800
S	-0.72251400	2.30830800	-0.34868600
S	3.15508900	0.53903700	1.61257300
S	3.24245800	-0.51285100	-1.39609700
O	-5.64868500	0.28638500	-0.33903300
C	-2.09686900	-4.32893000	-1.26305000
C	-3.11955900	-5.11071300	-0.68194300
C	-3.25908200	-6.46556000	-1.00776800
H	-4.05944800	-7.04574000	-0.54046700
C	-2.39454800	-7.07208300	-1.91606400
H	-2.51035700	-8.12733500	-2.16870900
C	-1.37826200	-6.31519800	-2.49451200
H	-0.68622500	-6.77641500	-3.20432100
C	-1.22251000	-4.96120600	-2.17378600
C	-0.08508000	-4.21044700	-2.79580900

C	1.17781000	-4.22796100	-2.16711900
C	2.24798200	-3.55291100	-2.75731700
H	3.22502400	-3.55625700	-2.26514200
C	2.10527600	-2.87223100	-3.97430700
C	0.84903000	-2.87526900	-4.58464400
H	0.72131800	-2.36792800	-5.54555400
C	-0.24918700	-3.54398000	-4.02187600
C	-1.57267900	-3.58202200	-4.73976000
H	-1.85788800	-4.61876300	-4.97405300
H	-1.52722400	-3.01387200	-5.67880900
H	-2.36228700	-3.15680800	-4.10172500
C	1.36975100	-5.00006600	-0.88642000
H	0.67138100	-4.64175300	-0.11168600
H	2.40638200	-4.91381000	-0.52921300
H	1.15611500	-6.06906200	-1.03484800
C	3.28880000	-2.18677600	-4.60414300
H	3.64274100	-1.37209800	-3.95280100
H	3.03515700	-1.77722700	-5.59168100
H	4.12469600	-2.89141200	-4.72964500
C	-4.08757700	-4.52254100	0.30035300
C	-3.78552600	-4.52539200	1.67779800
C	-4.71061100	-3.98969000	2.58204800
H	-4.47188800	-3.99671100	3.64932100
C	-5.94017900	-3.47072500	2.15958100
C	-6.23348600	-3.50810100	0.79210300
H	-7.20308000	-3.14140800	0.44248800
C	-5.33120300	-4.03300900	-0.14398200
C	-5.69276400	-4.09545500	-1.60415000
H	-6.70034600	-3.69412700	-1.77938200
H	-5.66310900	-5.13272300	-1.96857900
H	-4.96325700	-3.51728900	-2.19314200
C	-2.49548100	-5.12264800	2.17102500
H	-2.42305800	-5.05502000	3.26516700
H	-1.64148500	-4.59256300	1.72049100
H	-2.42134700	-6.18096000	1.87913500
C	-6.90991000	-2.88794600	3.15610600
H	-6.92979400	-3.48094400	4.08060000
H	-7.92795400	-2.84963500	2.74651000
H	-6.62155500	-1.86140600	3.43464000
C	-1.96079400	4.34763800	1.34683600
C	-2.72157700	5.27242800	0.59802600
C	-2.75062300	6.62682300	0.95277000
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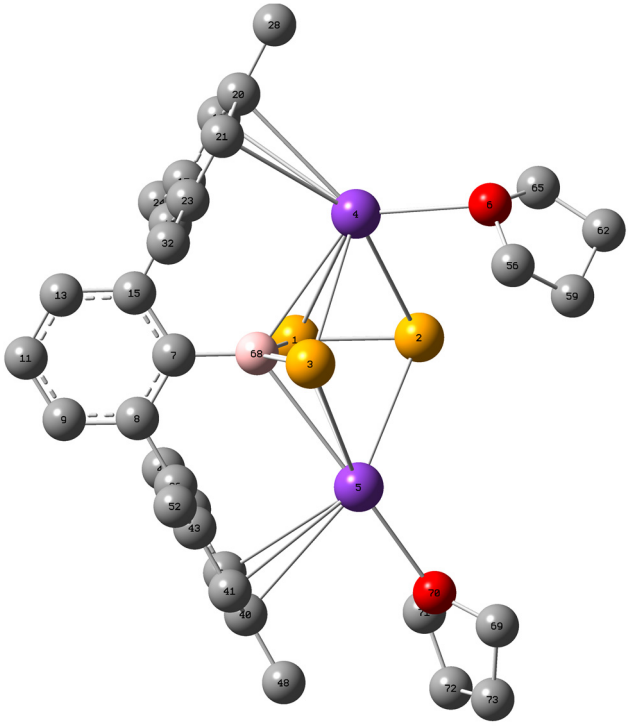
4



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5. NMR, IR and HRMS spectra

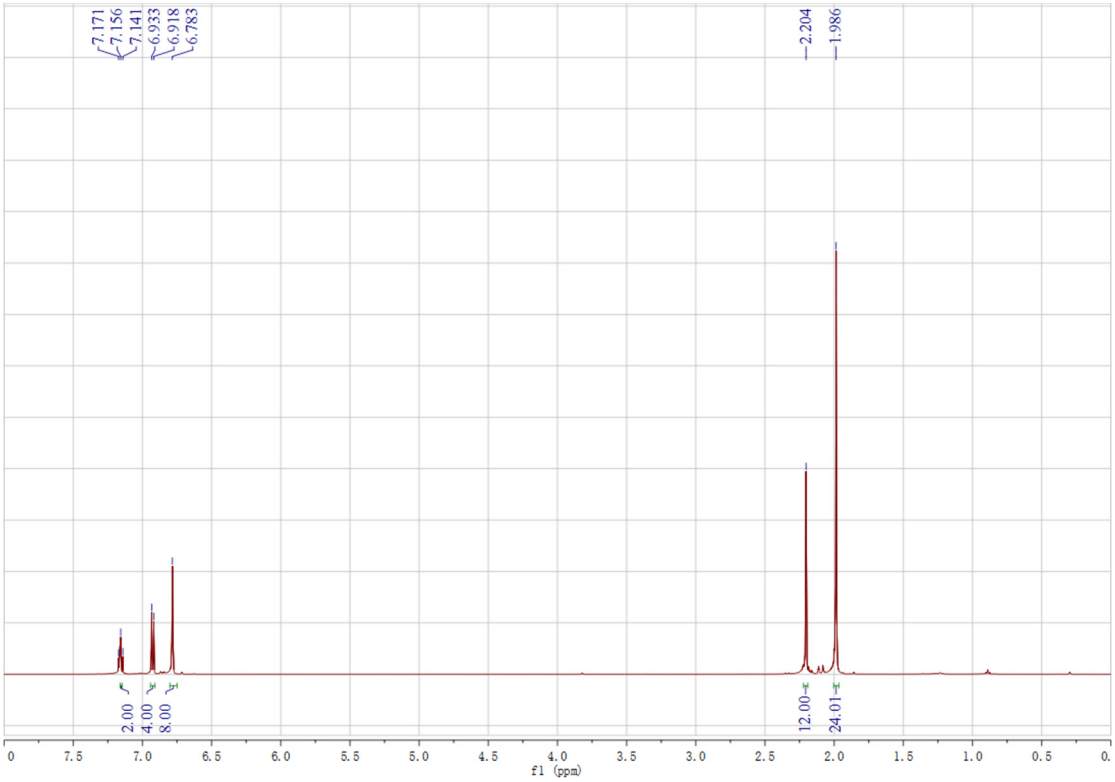

Fig. S7 ^{1}H NMR spectrum of **1** in C_6D_6.

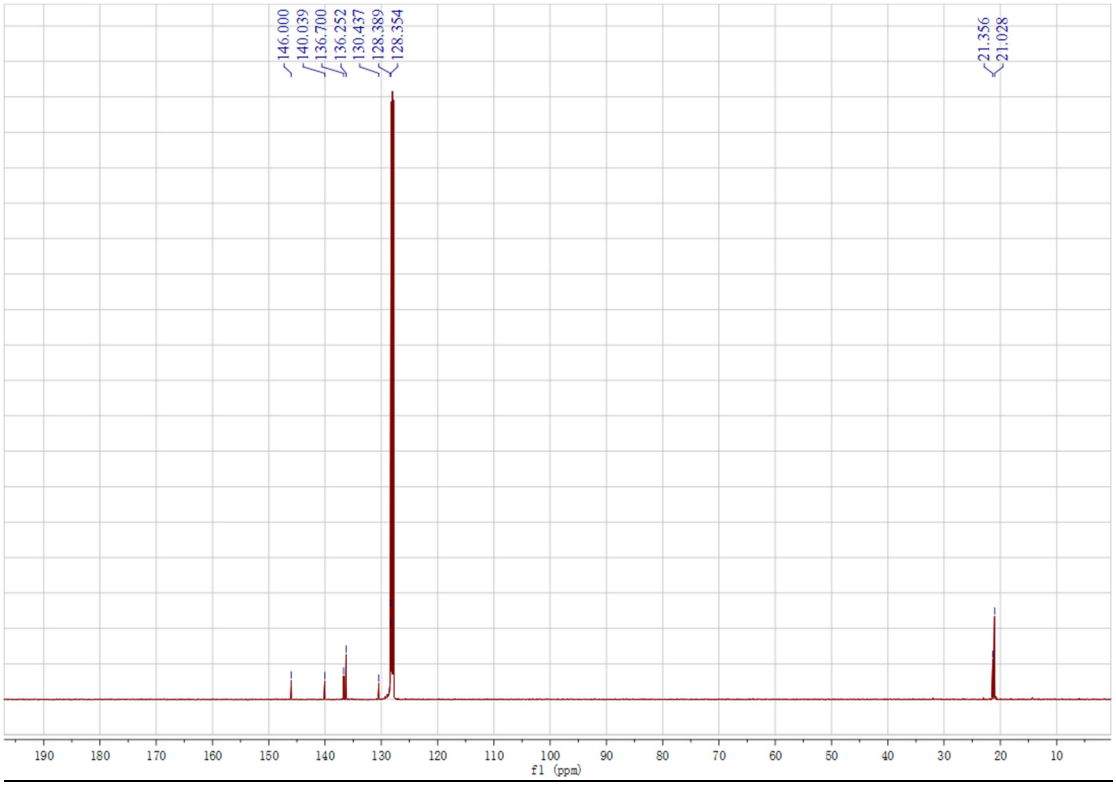

Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6.

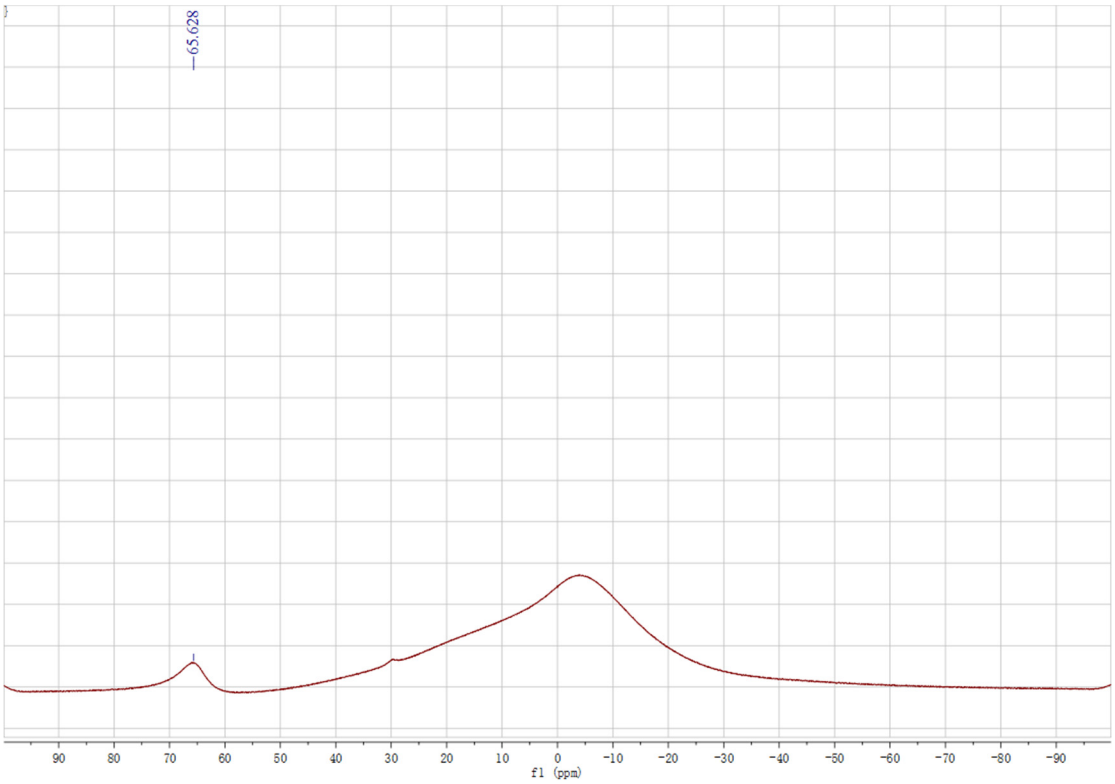

Fig. S9 ^{11}B NMR spectrum of **1** in C_6D_6.

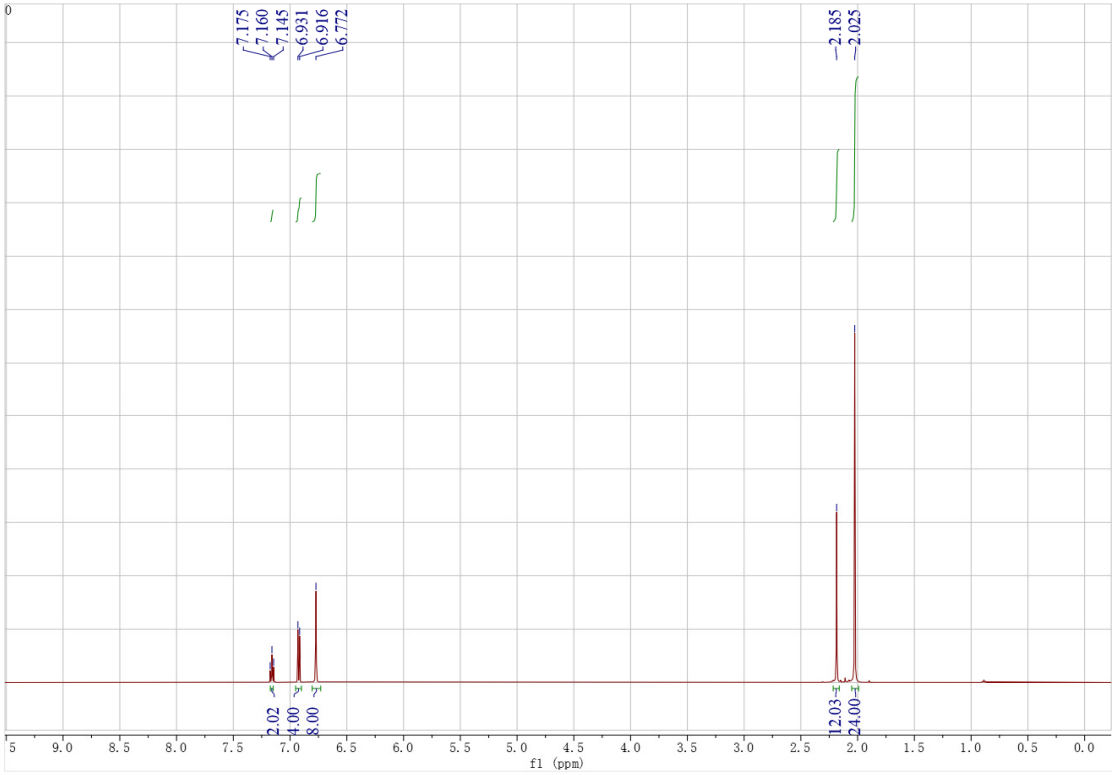

Fig. S10 ^{1}H NMR spectrum of **2** in C_6D_6.

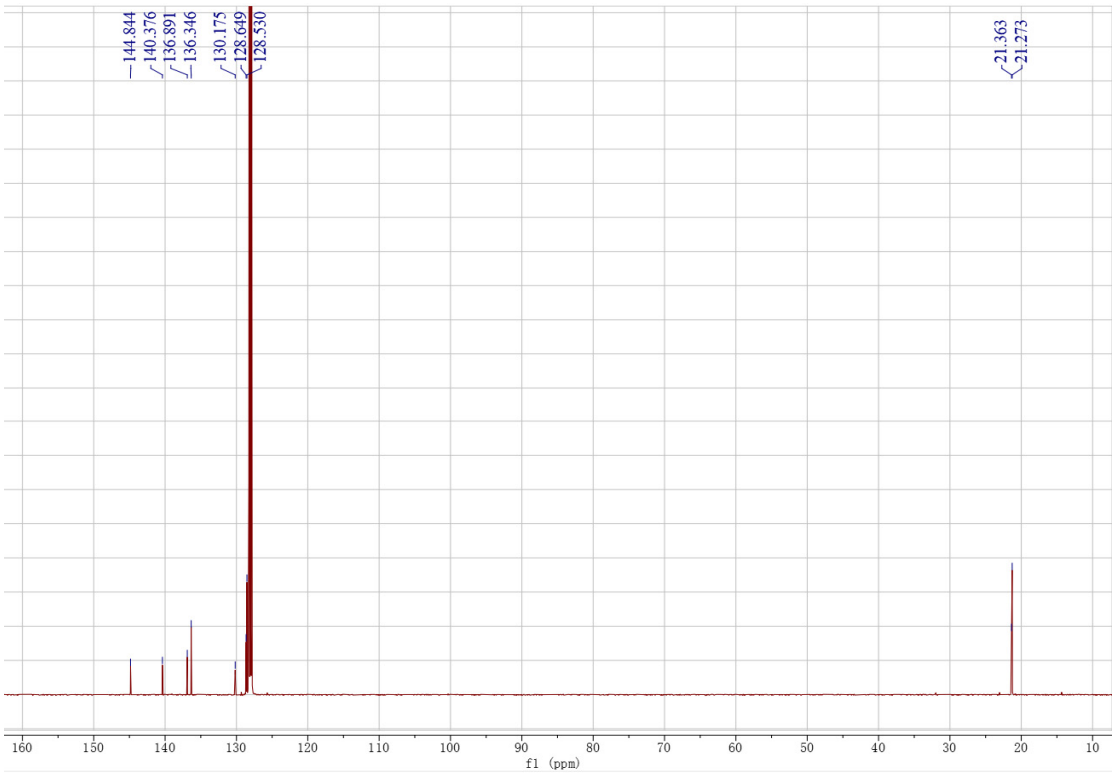

Fig. S11 $^{13}C\{^{1}H\}$NMR spectrum of **2** in C_6D_6.

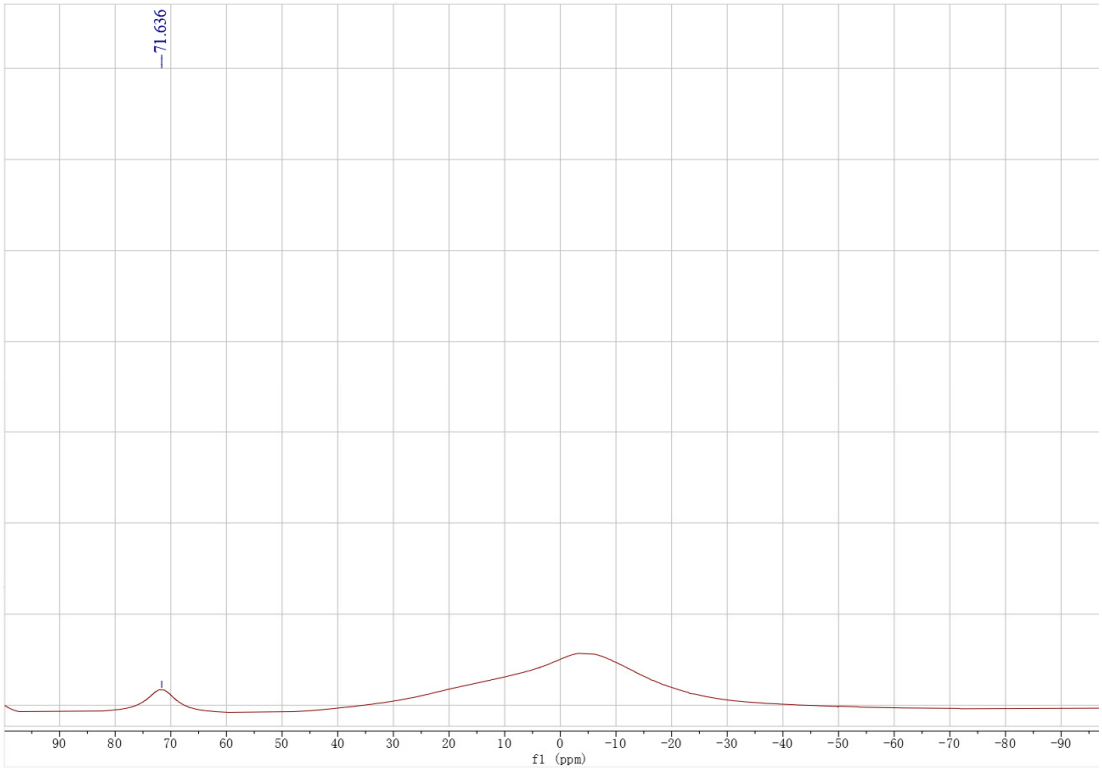

Fig. S12 ^{11}B NMR spectrum of **2** in C_6D_6.

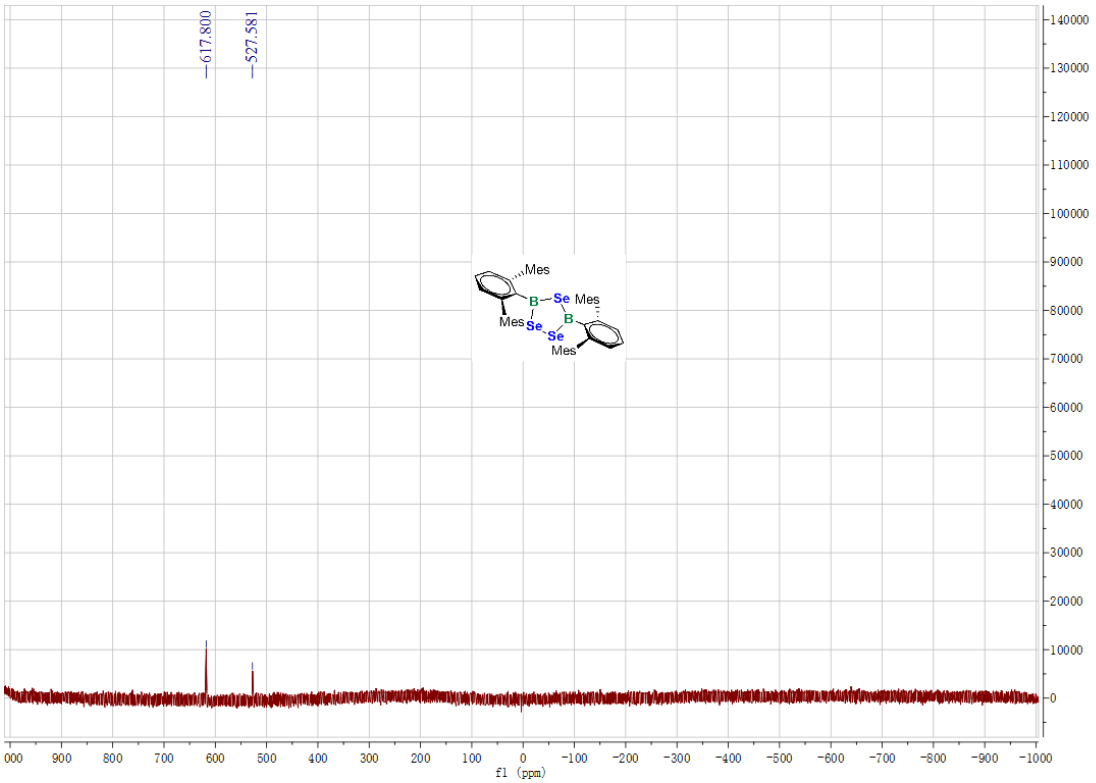

Fig. S13 ^{77}Se NMR spectrum of **2** in C_6D_6.

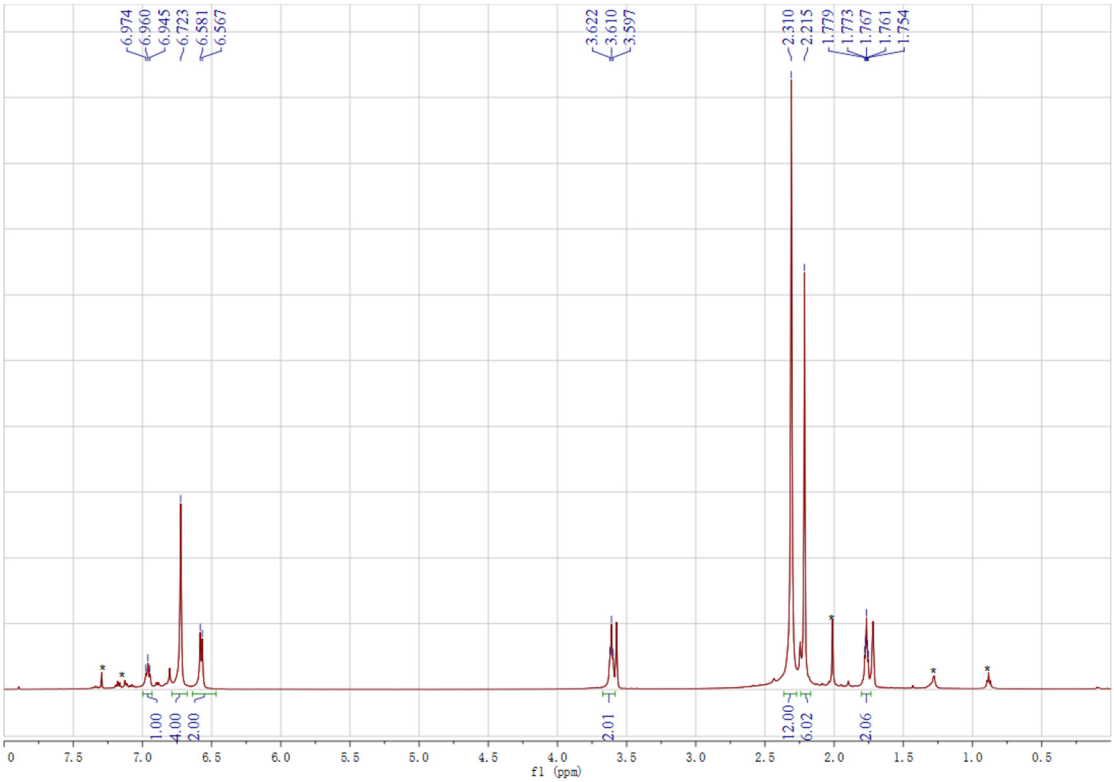

Fig. S14 ^{1}H NMR spectrum of **3** in THF-D_8. (**n*-hexane, toluene)

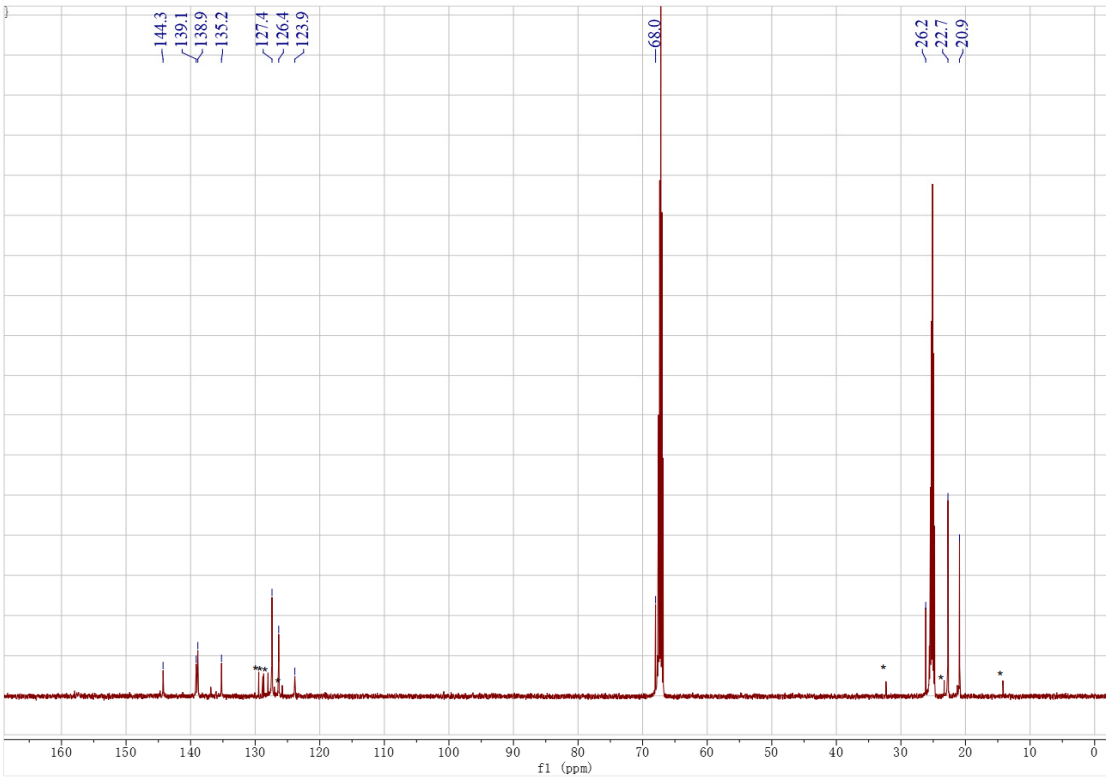

Fig. S15 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in THF-D_8. (**n*-hexane, toluene)

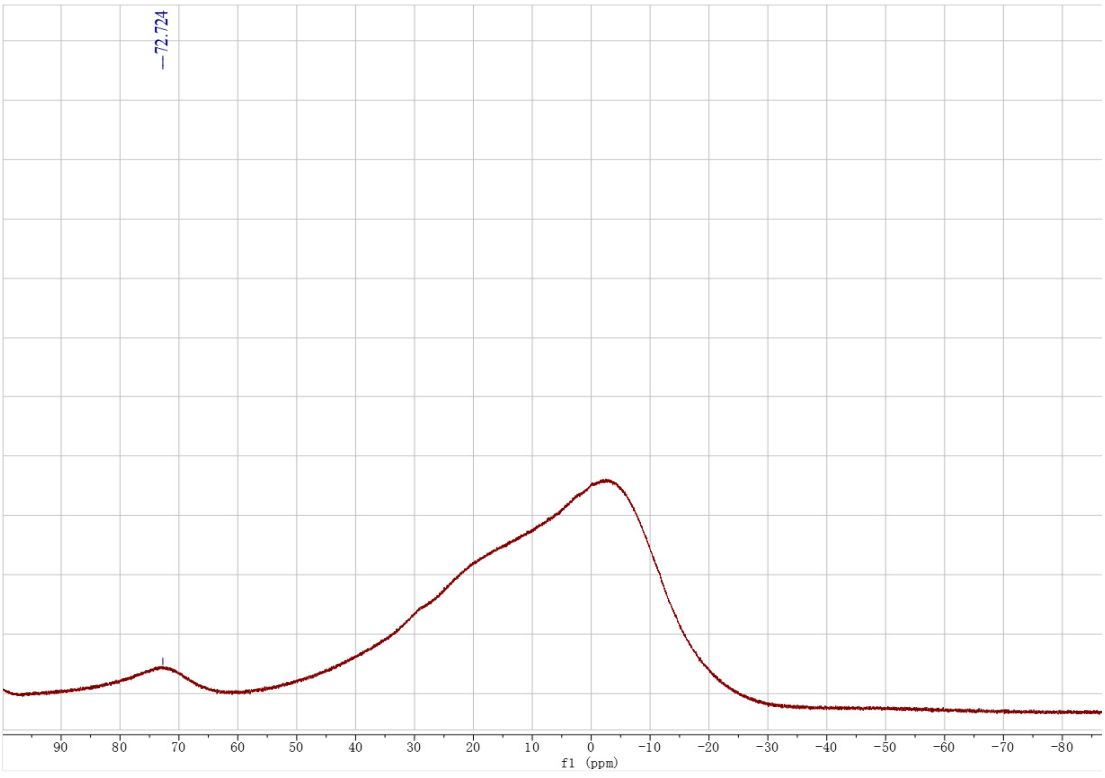

Fig. S16 ^{11}B NMR spectrum of **3** in THF-D_8.

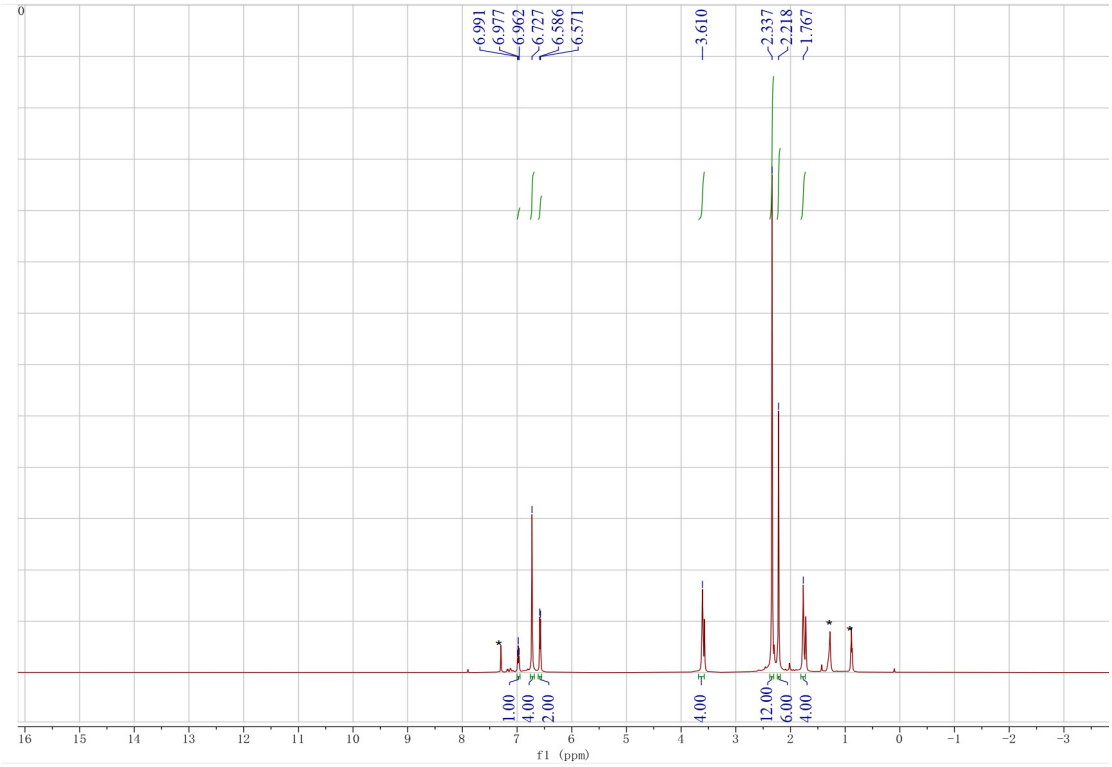

Fig. S17 ^{1}H NMR spectrum of **4** in THF-D$_8$.

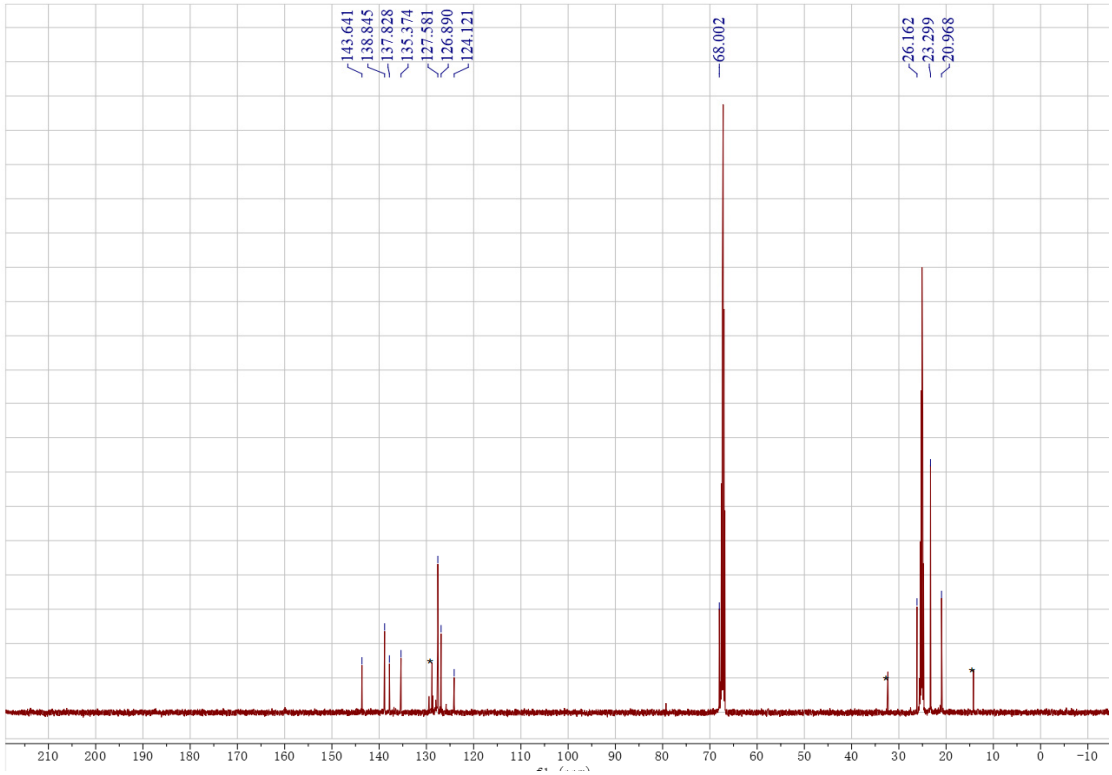

Fig. S18 ^{13}C{^{1}H} NMR spectrum of **4** THF-D$_8$.

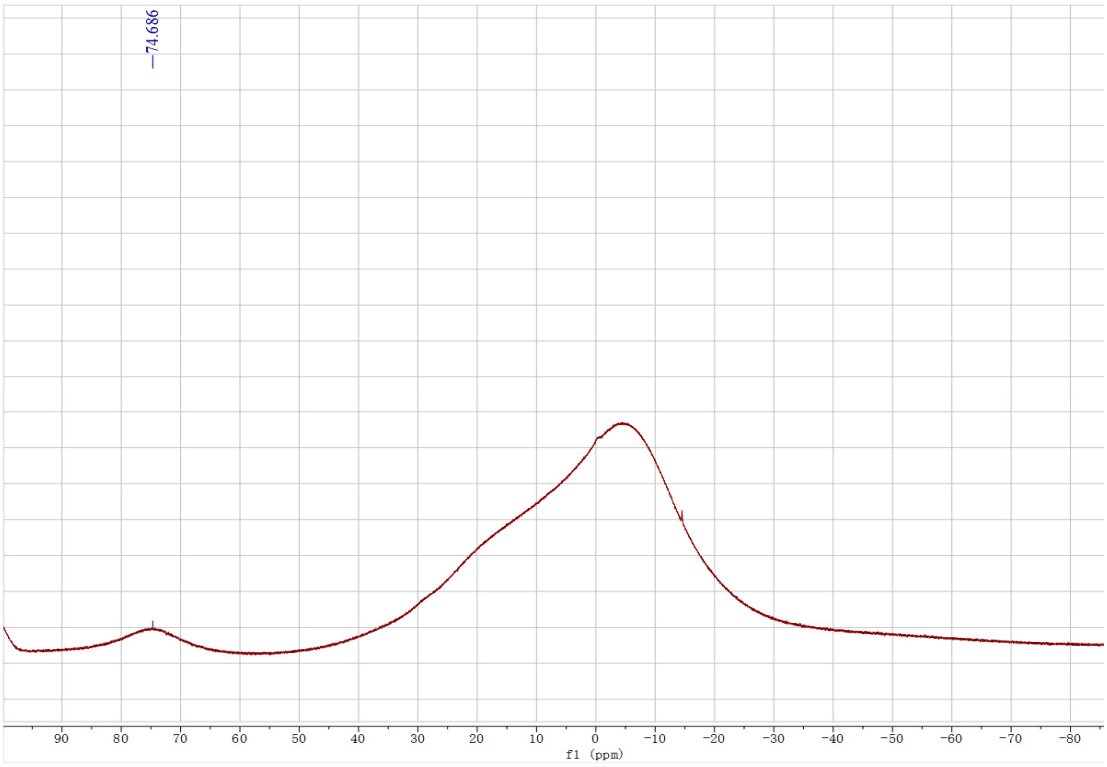

Fig. S19 ^{11}B NMR spectrum of **4** in THF-D$_8$.

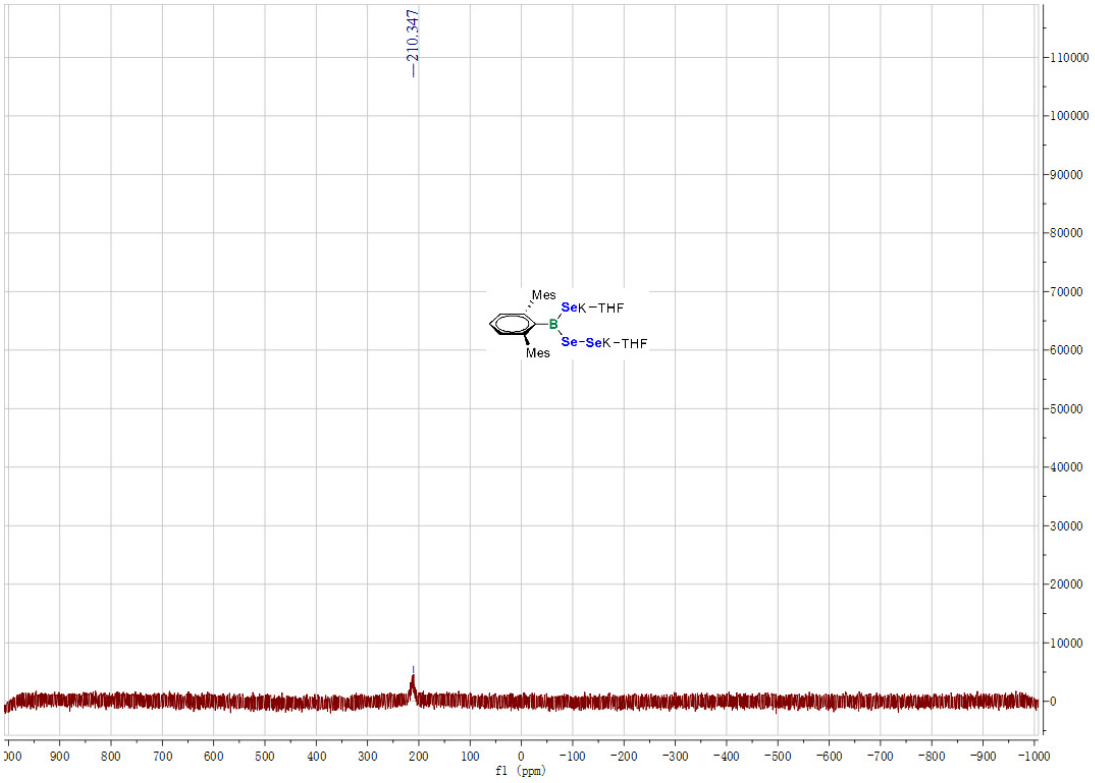

Fig. S20 ^{77}Se NMR spectrum of **4** in THF-D$_8$.

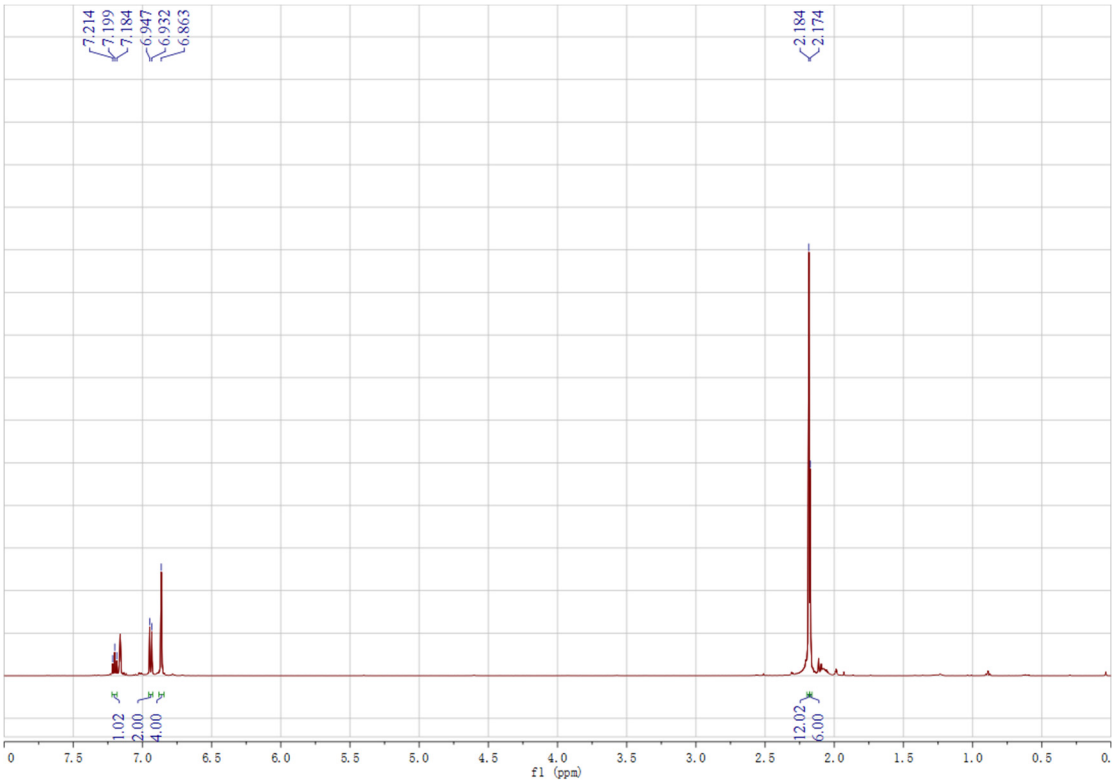

Fig. S21 ^{1}H NMR spectrum of **5** in C_6D_6.

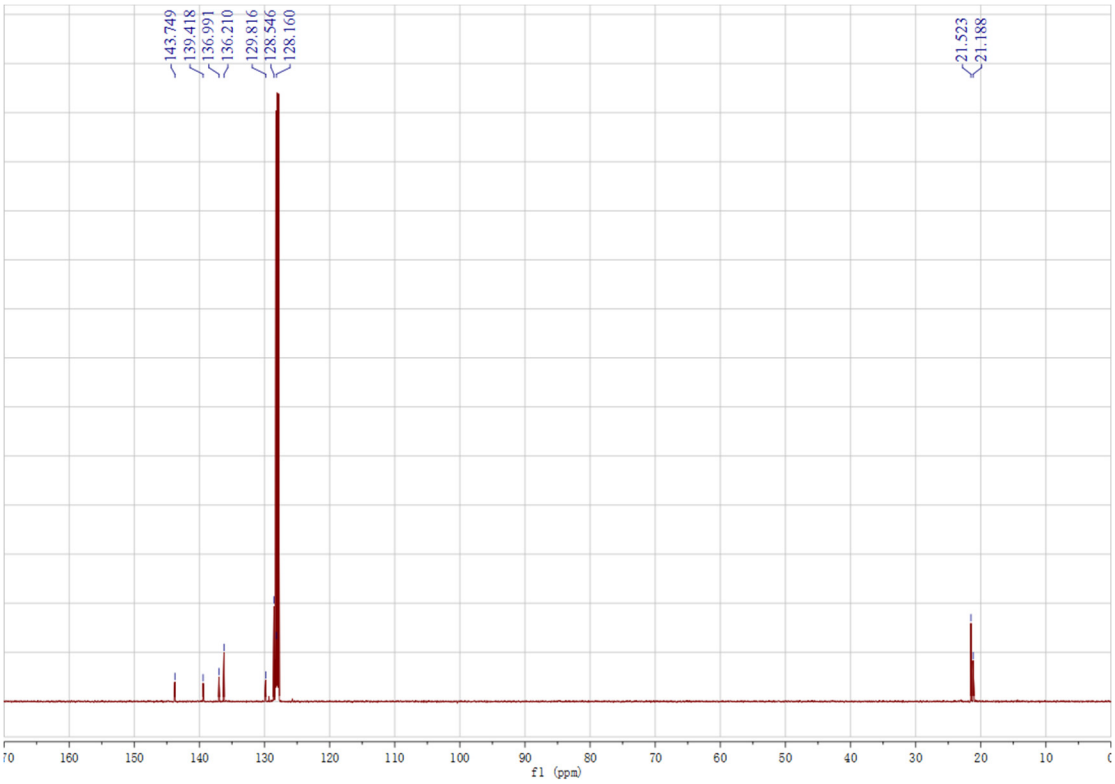

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

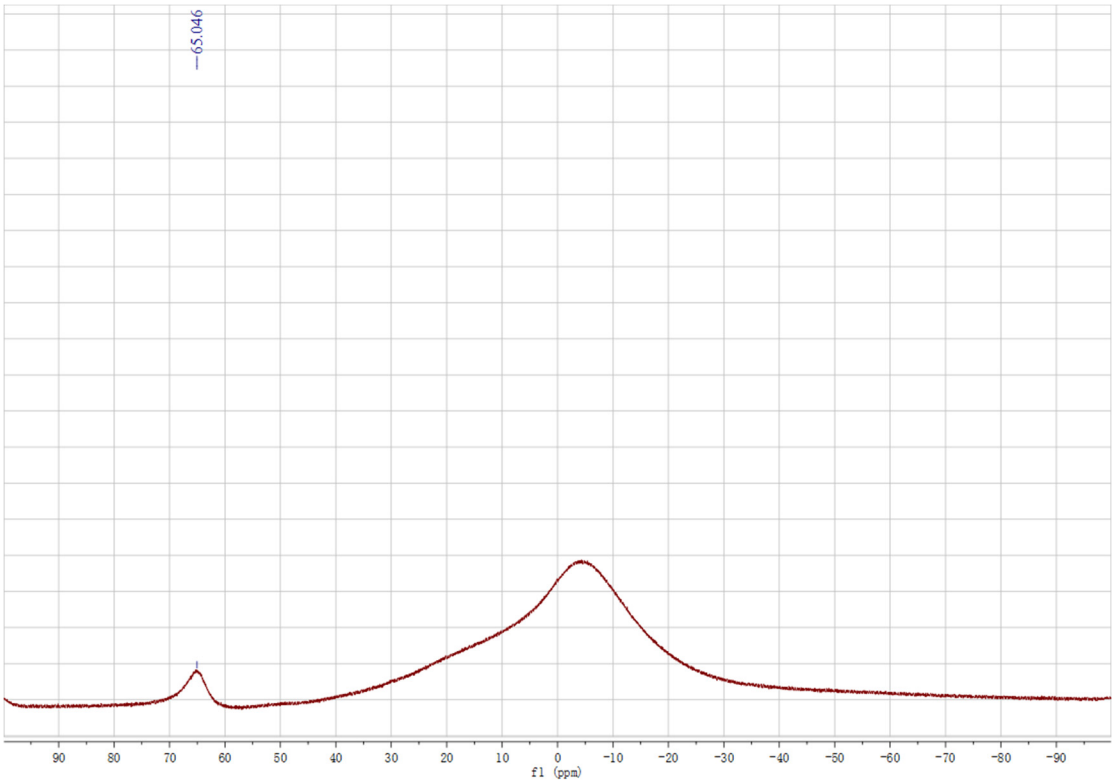

Figure S23. ^{11}B NMR spectrum of **5** in C_6D_6.

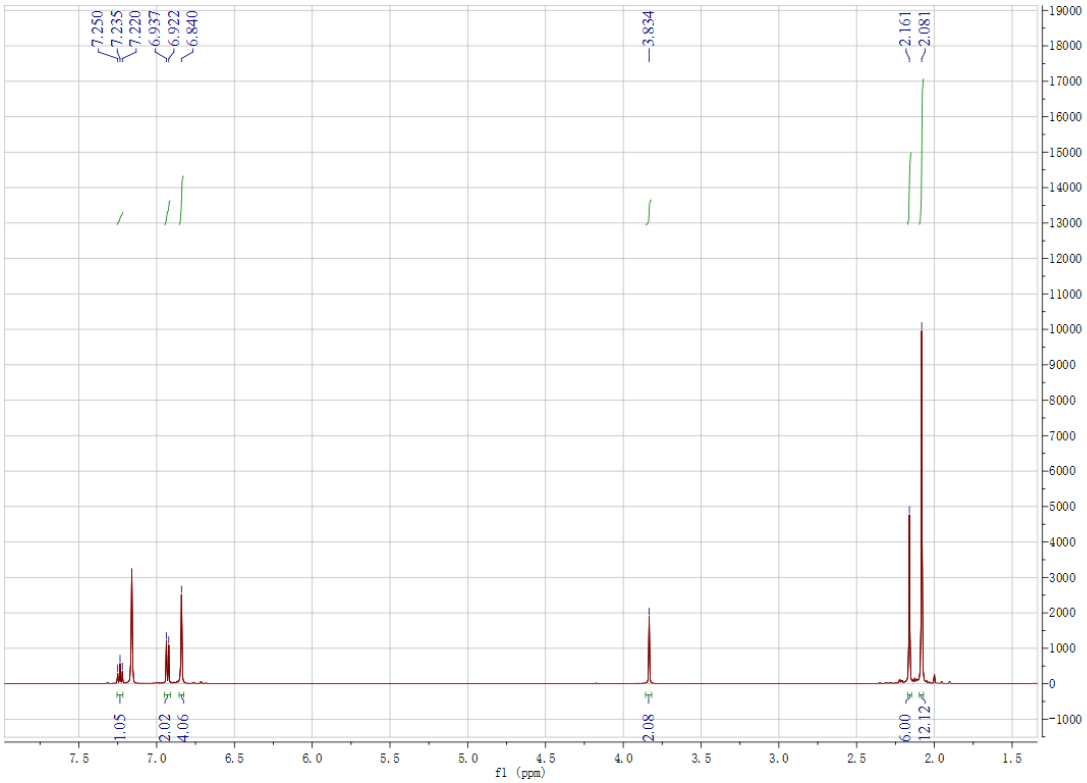

Fig. S24. ^{1}H NMR spectrum of **6** in C_6D_6.

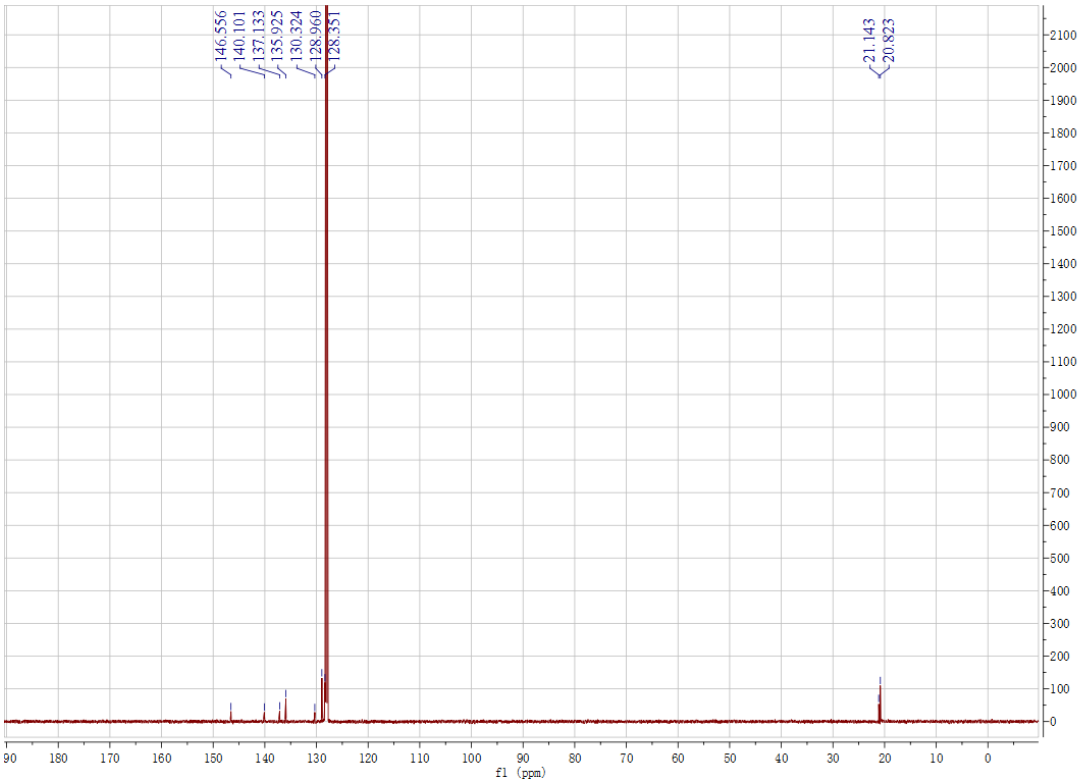

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

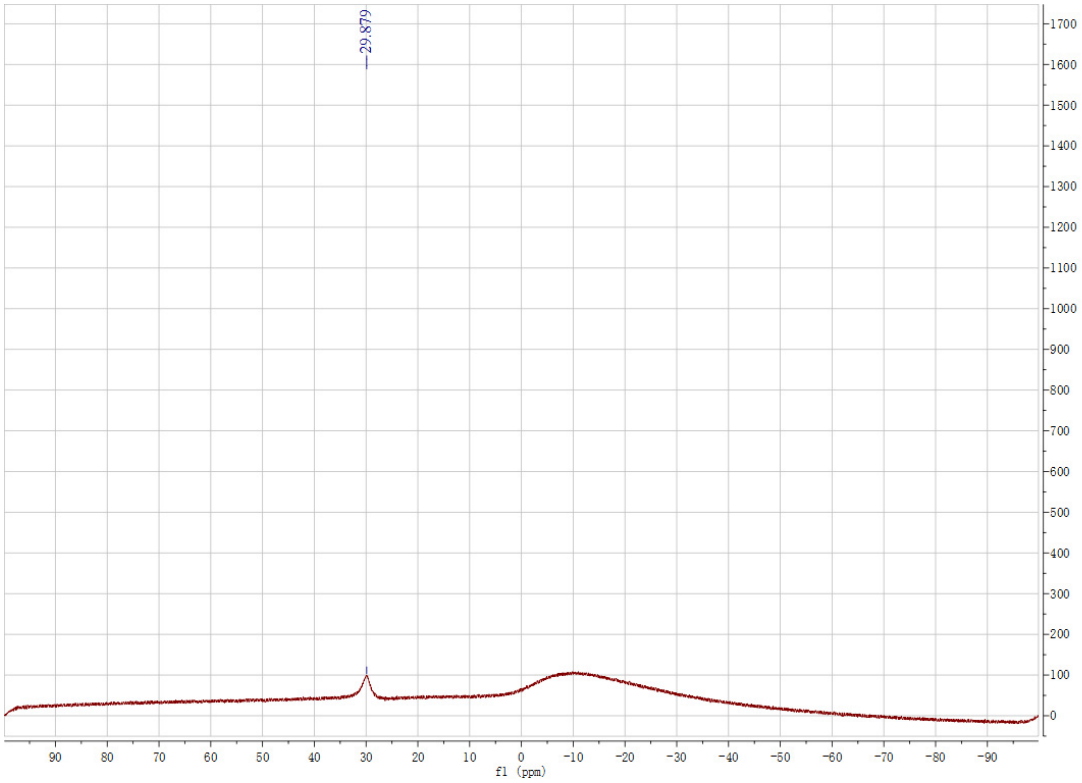

Figure S26. ^{11}B NMR spectrum of **6** in C_6D_6.

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