Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Homolytic Cleavage of Diboron(4) Compounds by Diazabutadienes

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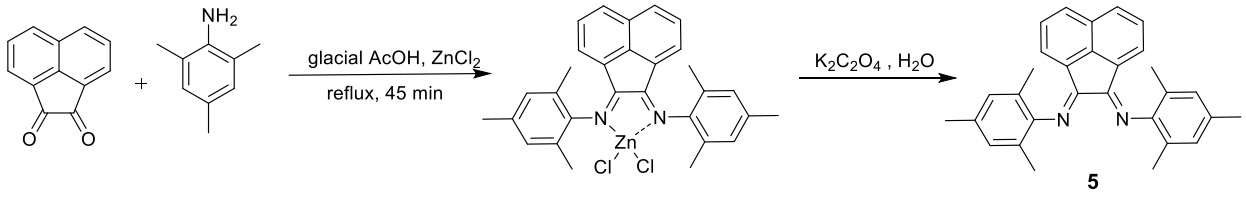
1 General Information

Unless otherwise noted all the reactions were performed in an argon filled MBraun glove box or using standard Schlenk technique. All chemicals were purchased either from Sigma Aldrich or Avra-chemicals and used without further purification unless otherwise mentioned. Bis(catecholato)diboron, bis(pinacolato)diboron, tetrakis(dimethylamino)diborane and bis(neopentylglycolato)diboron were obtained from AllyChem Co. Ltd., China and were used as received. bis(dithiocatecholato)diboron was prepared according to the reported literature procedure.[1] Reagent grade solvents were purchased form SD Fine Chemicals (India), distilled and deoxygenated by 3 freeze pump thaw cycles before use. $CDCl_3$ and C_6D_6 were purchased from either Cambridge Isotope Laboratories or Sigma Aldrich and deoxygenated by freeze pump thaw cycle and stored over molecular sieves before use. All NMR spectra (^1H (400 MHz), $^{13}C\{^1H\}$ (100 MHz), ^{11}B (128 MHz)) were recorded by a Bruker Avance 400 MHz NMR spectrometer at an ambient temperature. ^1H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm) whereas ^{13}C NMR spectra were reported relative to TMS using the carbon signals of the deuterated solvent ($CDCl_3$: 77.16 ppm, C_6D_6: 128.06 ppm). ^{11}B NMR signals are quoted relative to $BF_3{\cdot}Et_2O$. For Electrospray ionization (ESI) mass spectral analysis, Agilent 6538 Ultra high definition (UHD) accurate Mass-Q-TOF (LC-HRMS) and Bruker Daltonics make Esquire 300 Plus ESI model mass spectrometers were used and the HRMS has been acquired in negative ion mode. UV/Vis spectra was recordes on UV-2600, Shimadzu. Melting point of the compounds were recorded on ANALLAB SCIENTIFIC INSTRUMENTS PVT. LTD.

DippDAB ((1*E*,2*E*)-*N*^{1},*N*^{2}-bis(2,6-diisopropylphenyl)ethane-1,2-diimine) and MesDAB ((1*E*,2*E*)-*N*^{1},*N*^{2}-dimesitylethane-1,2-diimine) were prepared according to literature procedures.[2] B_2DAN_2(2,2'(3*H*, 3'*H*)-Bi-1*H*-naphtho[1,8-*de*]-1,3,2-diazaborine) andtTetra(hydroxy)diborane were also prepared according to literature procedures.[3,4]

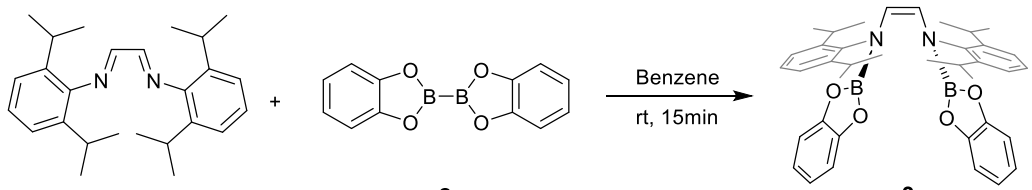
2 Synthetic Procedures

2.1 Synthesis of (1E,2E)-N^1,N^2-dimesitylacenaphthylene-1,2-diimine (compound 5).



Following the similar reported procedure,[5] 50 ml Schlenk round bottom flask with magnetic stir bar, acenaphthenequinone (500 mg, 2.74 mmol) and dry $ZnCl_2$ (1.0 g, 7.34 mmol) were suspended in glacial acetic acid (7.5 mL). The flask was warmed to 55 °C, and 2,4,6 trimethyl aniline (0.9 ml, 6.4 mmol) was added. The reaction mixture was refluxed for 45 min resulting in the formation of orange coloured precipitate of Zn-complex. The precipitate was collected by filtration through a Buckner funnel. The solid precipitate was washed with diethyl ether (4x25 ml) to remove any trace of acetic acid and dried under reduced pressure. This orange precipitate was suspended in CH_2Cl_2 (100 mL) in a separating funnel, and an excess amount of aq. solution of potassium oxalate was added. After shaking for 15 min, white precipitate of $Zn(C_2O_4)$ appears, suspended in the aqueous phase. The organic phase was separated and washed with water (2 × 20 mL) followed by drying with sodium sulphate. Removal of solvent under reduced pressure give a red powder. The crude product was purified by flash chromatography, eluting with 5-10% hexane/EtOAc mixture to afford **5** in 92% yield (1.04 gm, 2.49 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, J = 8 Hz, 2H), 7.39 (t, J = 8 Hz, 2H), 6.97 (s, 4H), 6.77 (d, J = 8 Hz, 2H), 2.37 (s, 6H), 2.09 (s, 12H).

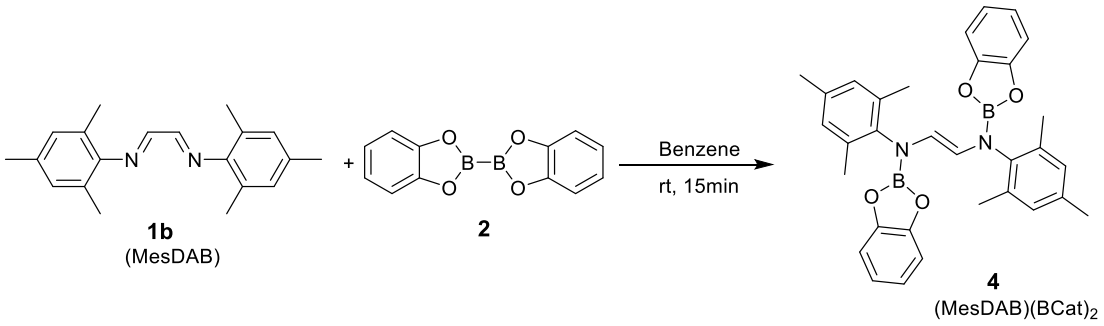
2.2 Synthesis of compound 3: (Z)-N1,N2-bis(benzo[d][1,3,2]dioxaborol-2-yl)-N1,N2-bis(2,6-diisopropylphenyl)-ethene-1,2-diamine (DippDAB(Bcat)$_2$)



1a (DippDAB) **2** (B_2cat_2) **3** (DippDAB)(Bcat)$_2$

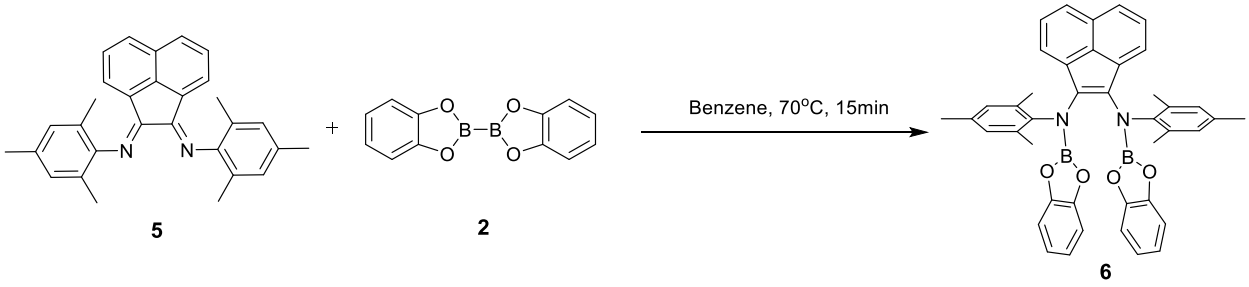
Under the nitrogen atmosphere, equivalent amount of DippDAB (188 mg, 0.5 mmol) and B_2Cat_2 (119 mg, 0.5 mmol) were mixed in 20 mL of benzene. The reaction mixture was stirred for 15 min at room temperature, resulted in a pale-yellow solution. The solvent was removed under reduced pressure to obtain compound **3** DippDAB(Bcat)$_2$ in quantitative yield (>99.9%, 307 mg, 0.5 mmol). Crystals suitable for diffraction were obtained via slow evaporation of solvent from the solution of DippDAB(Bcat)$_2$ in benzene, at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ (ppm) 7.36-7.21 (m, 6H), 6.79-6.75 (m, 4H), 6.47-6.43 (m, 4H), 4.97 (s, 2H), 4.41 (br, 2H) 3.38 (br, 2H), 1.58 (br, 6 H), 1.45 (br, 6 H), 1.17 (br, 6H), 1.07 (br, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ (ppm) 148.8, 141.0, 128.0, 124.7, 122.2, 116.2, 111.6, 28.8, 28.0, 25.4, 24.4, 23.9. ^{11}B NMR (128 MHz, C_6D_6): δ (ppm) 25.6. ESI-HRMS: m/z 631.3569 ($(M+H_2O)-H)^-$ (found), m/z 631.351(calculated). mp 171 °C.

2.3 Synthesis of compound 4: (E)-N1,N2-bis(benzo[d][1,3,2]dioxaborol-2-yl)-N^1,N^2-dimesitylethene-1,2-diamine (MesDAB(Bcat)$_2$)



Under a nitrogen atmosphere, equivalent amount of MesDAB (146 mg, 0.5 mmol) and B_2cat_2 (119 mg, 0.5 mmol) were mixed in 20 mL of benzene. The reaction mixture was stirred for 15 min at room temperature, resulted in a pale-yellow solution. The solvent was removed under reduced pressure to obtain MesDAB(Bcat)$_2$ in quantitative yield (>99.9%, 265 mg, 0.5 mmol). Crystals suitable for diffraction were obtained via slow evaporation of solvent from a solution of MesDAB(Bcat)$_2$ in benzene at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ (ppm) 6.87 (s, 4H), 6.73-6.71 (m, 4H), 6.46-6.44 (m, 4H), 4.91 (s, 2H), 2.49 (s, 12H), 2.17 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6): δ (ppm) 149.0, 141.2, 136.7, 136.6, 130.1, 122.2, 115.9, 111.7, 21.2, 18.9. ^{11}B NMR (128 MHz, C_6D_6): δ (ppm) 25.4. ESI-HRMS: m/z 547.2519 ((M+H_2O)-H)$^-$ (found), m/z 547.257(calculated). mp 110 °C.

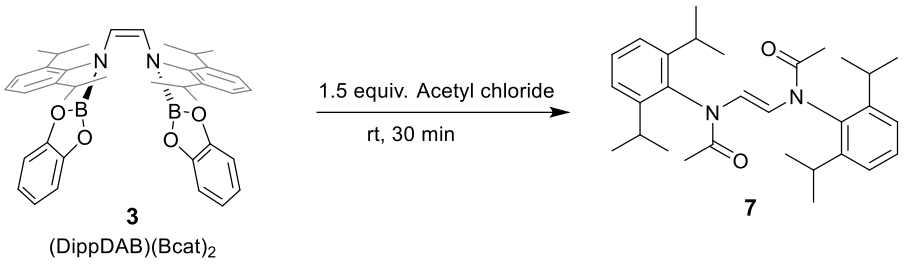
2.4 Synthesis of compound 6



In a nitrogen filled glovebox, Mes-BIAN (208 mg, 0.5 mmol) was treated with same equivalent of B_2Cat_2 (119 mg, 0.5 mmol) in 5 ml of THF stirred for 15 min at room temperature resulted in a red precipitate. The filtrate was decanted and the residue was dried under reduced pressure to obtain the compound **6** (86%, 281 mg, 0.43 mmol). ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 7.27 (d, 2H, J = 8 Hz), 6.97 (t, 2H, J = 8 Hz), 6.9-6.84 (m, 6H), 6.72-6.66 (m, 4H), 6.51-6.45 (m, 4H), 2.65 (s, 6H), 2.31 (s, 6H), 2.17 (br, 6H). ^{11}B NMR

(128 MHz, C_6D_6): δ (ppm) 23.6. ESI-HRMS: m/z 671.2982 $((M+H_2O)-H)^-$ (found), m/z 671.288(calculated). mp 190 °C.

2.5 Synthesis of compound 7



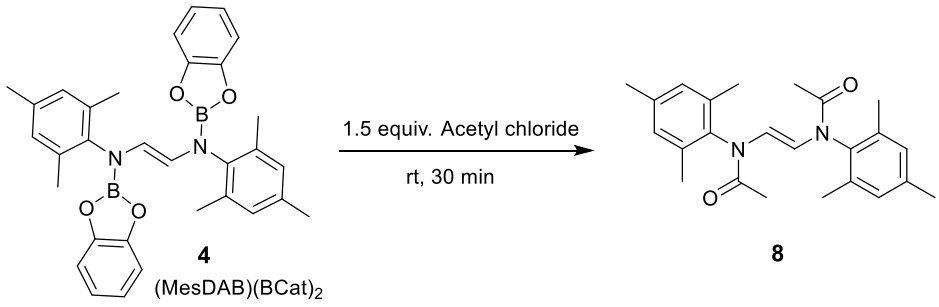
3
(DippDAB)(Bcat)$_2$

7

Under a nitrogen atmosphere, DippDAB(Bcat)$_2$ (265 mg, 0.5mmol) was dissolved in 25 ml of benzene followed by addition of 1.5 equivalents of acetyl chloride (54 µl, 0.75mmol) at room temperature. The reaction was stirred for 1 h, resulting in a colour change from pale yellow to orange. The solvent was evaporated and the crude product was purified by flash chromatography eluting with a 30 % EtOAc-hexane mixture. Evaporation of solvent gave colourless compound **7** along with catechol as an impurity (yield 90%, 208 mg, 0.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 (t, 2H, J= 7.7Hz), 7.28 (d, 4H, J= 7.7 Hz), 6.75 (s, 2H), 2.74 (sept, 4H, J=6.8Hz), 1.70 (s, 6H), 1.17(d, 12H, J= 6.9Hz), 1.21 (d, 12H, J= 6.8Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.8, 146.3, 133.6, 130.2, 125.3, 117.3, 28.2, 25.2, 23.9, 22.5

Note: A crystal obtained from the solution of crude mixture in benzene was used for single crystal XRD. The molecular structure confirms the formation of **7** along with the presence of catechol in the unit cell.

2.6 Synthesis of compound 8



4
(MesDAB)(BCat)$_2$

8

In a nitrogen filled glovebox, by following the above procedure, MesDAB(Bcat)$_2$ (**4**) (306 mg, 0.5 mmol) was treated with 1.5 equivalents of acetyl chloride (54 µL, 0.75 mmol) in 5 ml of benzene at room temperature for 30 min resulting a colour change from pale yellow to light green. The solvent was evaporated and the crude product was purified by flash chromatography eluting with a 10-20% EtOAc-hexane mixture resulted a colourless crystal (yield 90%, 170 mg, 0.45 mmol) ^{1}H NMR (400 MHz, $CDCl_3$)

δ (ppm) 6.98 (s, 4H), 6.63 (s, 2H), 2.33 (s, 6H), 2.08 (s, 12H), 1.68 (s, 6H) ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 169.0, 139.2, 135.8, 134.7, 130.6, 114.3, 22.2, 21.5, 17.7

2.7 General procedure for the reaction of Diazabutadienes and diborons in NMR scale

Equimolar amount (0.1 mmol) of diazabutadienes and diborons (B_2(thiocat)$_2$, B_2pin_2, B_2neop_2, $B_2(OH)_4$, $B_2(NMe_2)_4$ or B_2DAN_2) were taken in 4 ml vial, followed by addition of 0.5 ml of benzene-*d*6 and stirred at room temperature for 15 min (in case of B_2(thiocat)$_2$) or at 70 ^{o}C for 12h. The reaction mixture was then analyzed by ^{1}H and ^{11}B NMR.

NMR of compound 9

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 7.23-7.20 (m, 2H), 7.18-7.14 (m, 8H), 6.63 (m, 4H), 5.41 (s, 2H), 4.17 (m, 2H), 3.30 (m, 2H), 1.49-1.23 (br, 24H). ^{11}B NMR (128 MHz, C_6D_6): δ (ppm) 47.

NMR of compound 10

^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 7.22 (br, 4H), 6.78-6.74 (m, 4H), 6.61 (m, 4H), 5.70 (s, 2H), 2.06 (m, 18H). ^{11}B NMR (128 MHz, C_6D_6): δ (ppm) 48. ^{13}C NMR (100 MHz, C_6D_6) δ (ppm) 142.7, 139.5, 136.7, 135.6, 130.6, 126.7, 125.5, 124.

3 Mechanistic studies

3.1 Variable temperature NMR study

A variable temperature NMR study was conducted for compound **3** in Toluene-*d*8. The temperature was varied from room temperature to -50 ^{o}C and the spectrum was recorded at the temperature variance of 10 ^{o}C. As the temperature was lowered the broad peaks for the proton of isopropyl groups at δ = 4.36, and 1.52, ppm clearly splitted into a septate and doublets at -10 ^{o}C. Moreover, a gradual down field shift has been observed in one of the two types of isopropyl units. The septet at 4.36 ppm and doublets at 1.56 and 1.43 ppm at room temperature gradually shifts to downfield region till the temperature was reduced to -50 ^{o}C. This provides further evidence the presence of intra-molecular Hydrogen bonding between the H14 and O1. Also, the ^{13}C NMR spectrum at lower temperature shows the peaks corresponding to the isopropyl groups in compound **3**.

^{1}H NMR of Compound **3** (500 MHz, Toluene-*d*8 at -50 ^{o}C): 6.44-6.42 (m, 4H), 4.94 (s, 2H), 4.43 (septet, *J* = 7 Hz, 2H), 3.35 (septet, *J* = 7 Hz, 2H), 1.62 (d, *J* = 7 Hz, 6H), 1.48 (d, *J* = 7 Hz, 6H), 1.17 (d, *J* = 7 Hz, 6H), 1.04 (d, *J* = 7 Hz, 6H). Aromatic protons of compound 3 overlaps with the protonated Toluene present as trace impurity in Toluene-*d*8.

^{13}C NMR of Compound **3** (125 MHz, Toluene-*d*8, at -40 ^{o}C): Some peaks of aromatic carbon of compound 3 overlaps with the protonated toluene present as trace impurities in Toluene-*d*8. The values for isopropyl groups are: δ (ppm) 28.6, 27.6, 25.4, 24.4, 24.0, 23.6.

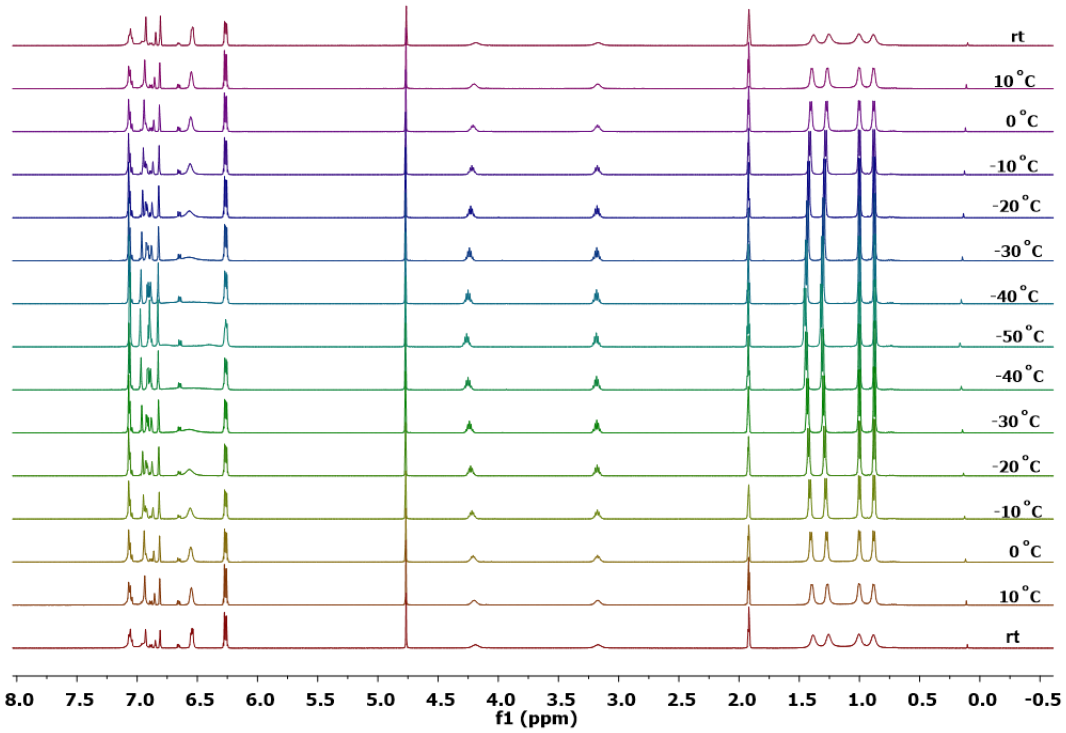


Figure S1 Variable temperature ^{1}H NMR spectra of compound **3** from room temperature to -50 °C.

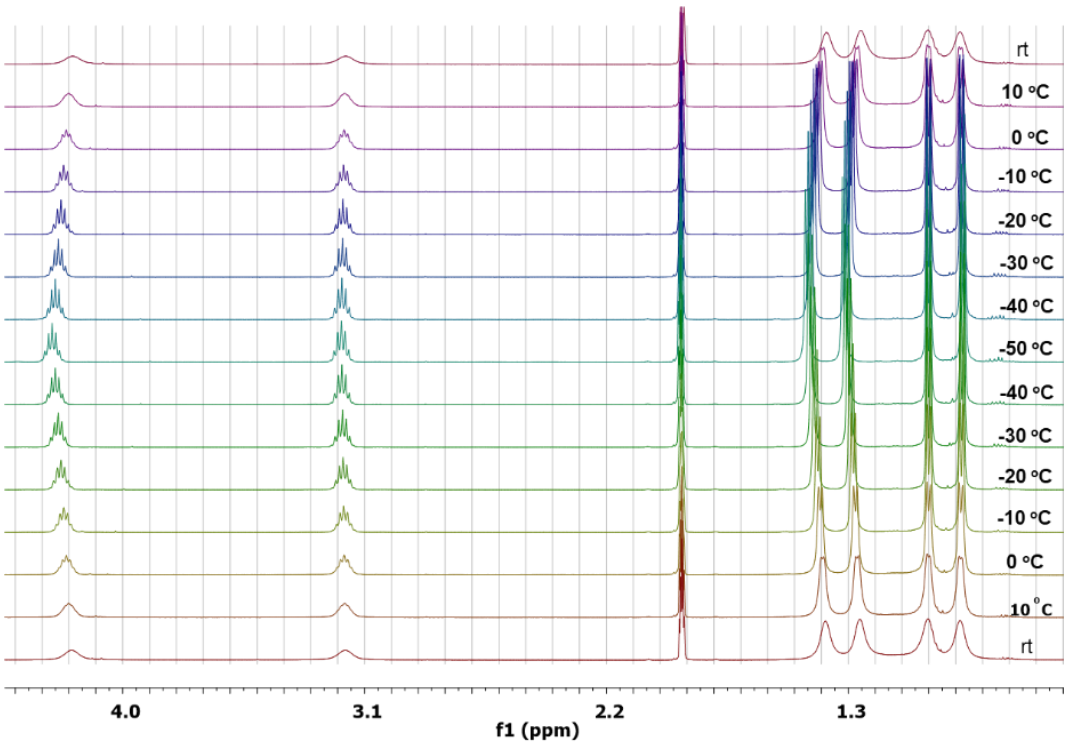


Figure S2 Expended plot of Figure S1, highlighting the downfield shift in the signals.

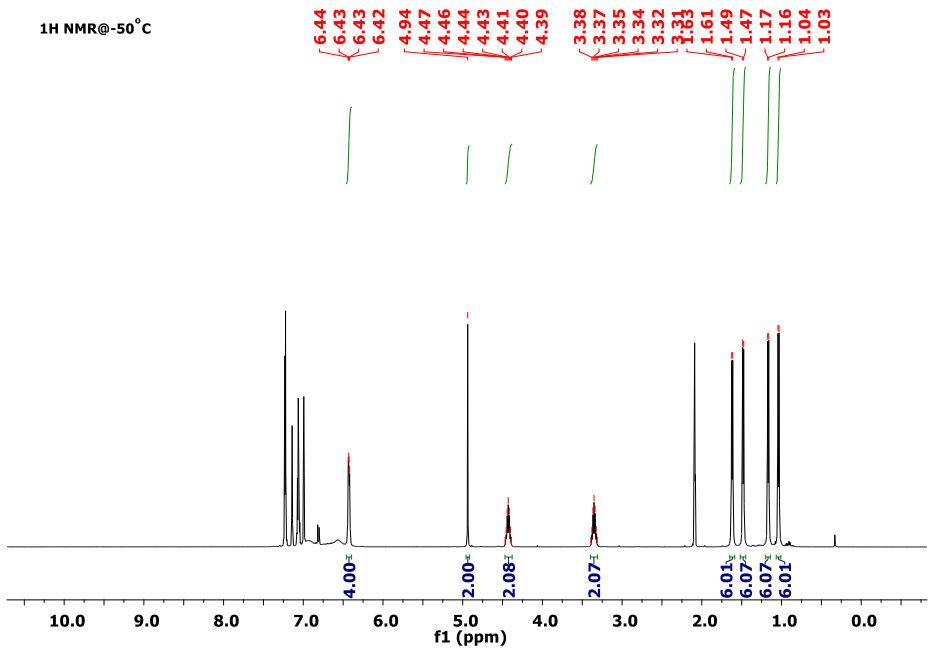


Figure S3 ^{1}H NMR of compound **3** at -50 °C in Toluene-*d*8.

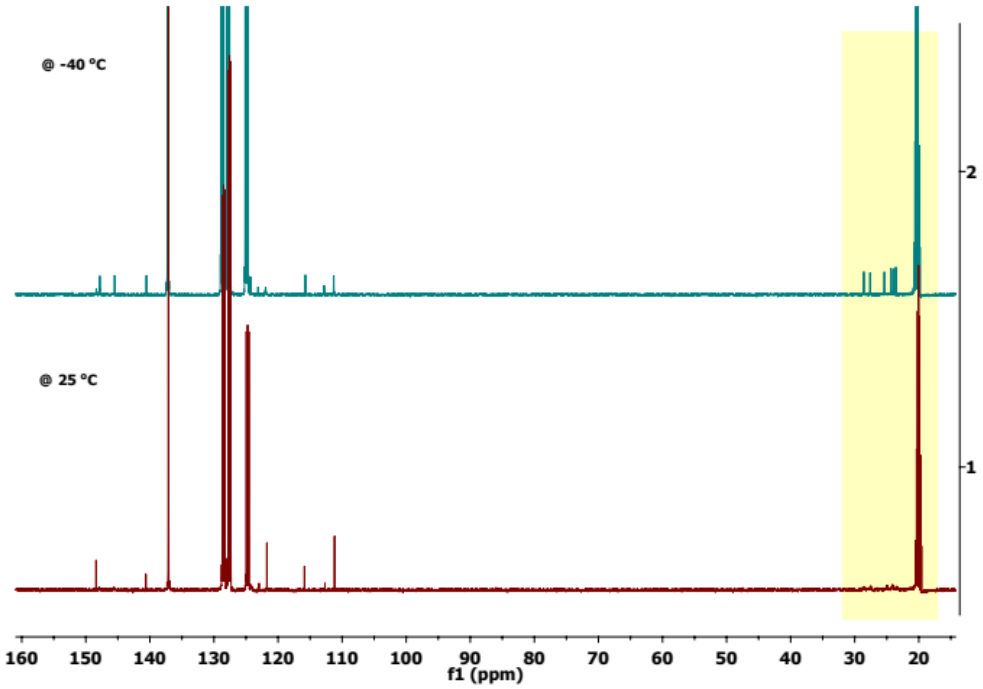
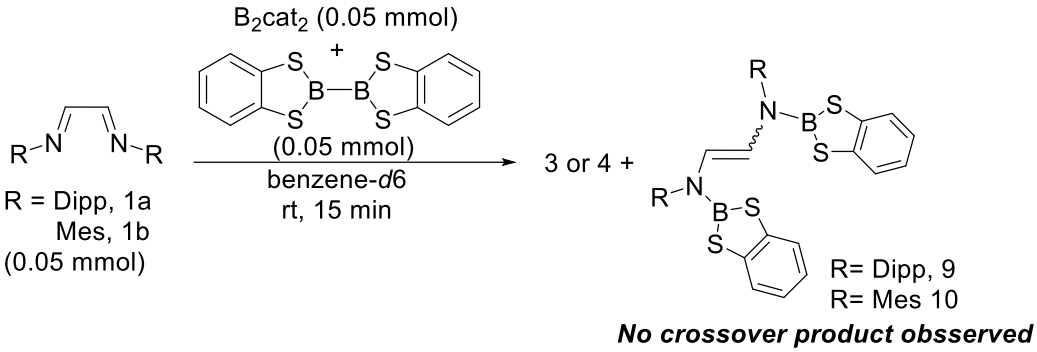
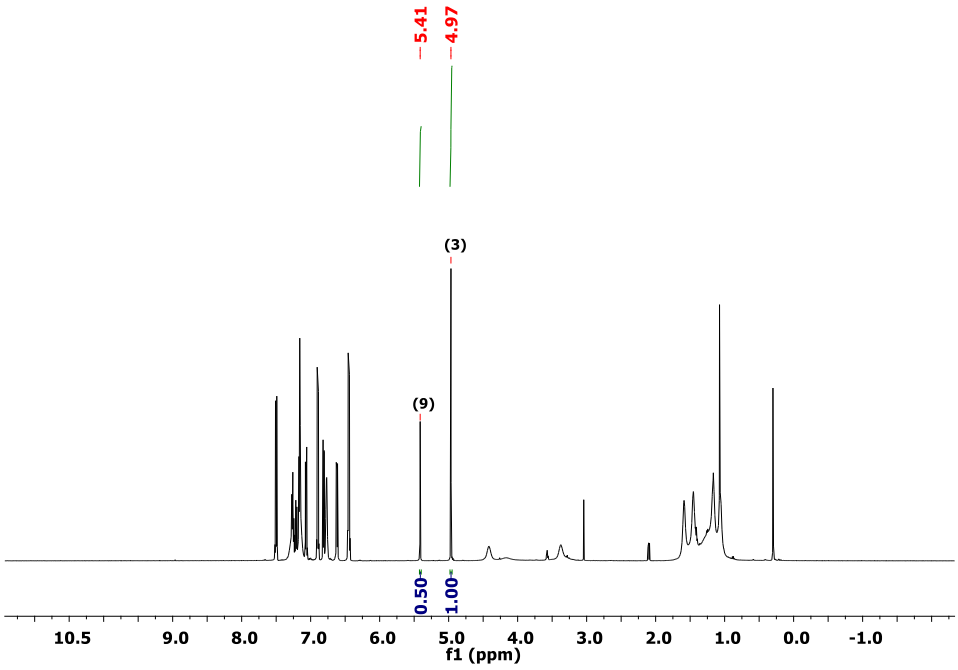


Figure S4 Stack plot of ^{13}C NMR of compound 3 at -40 °C and 25 °C in Toluene-*d*8.

3.2 Crossover experiment



Equivalent amount (0.05 mmol each) of B_2cat_2, $B_2(dithiocat)_2$, and DABs (1a or 1b) were taken in a 4 ml vial and 0.6 ml benzene-*d*6 was added. The mixture was stirred at room temperature for 15 min and NMR was recorded. The NMR analysis shows that in case of 1a, the Compound **3** and **9** formed in 68:32 ratio whereas in case of 1b, compound **4** and **10** formed in 38:62 ratio. No crossover product was observed in any of the cases. This result further supports the argument of a concerted reaction mechanism for cleavage of diboron by DABs.



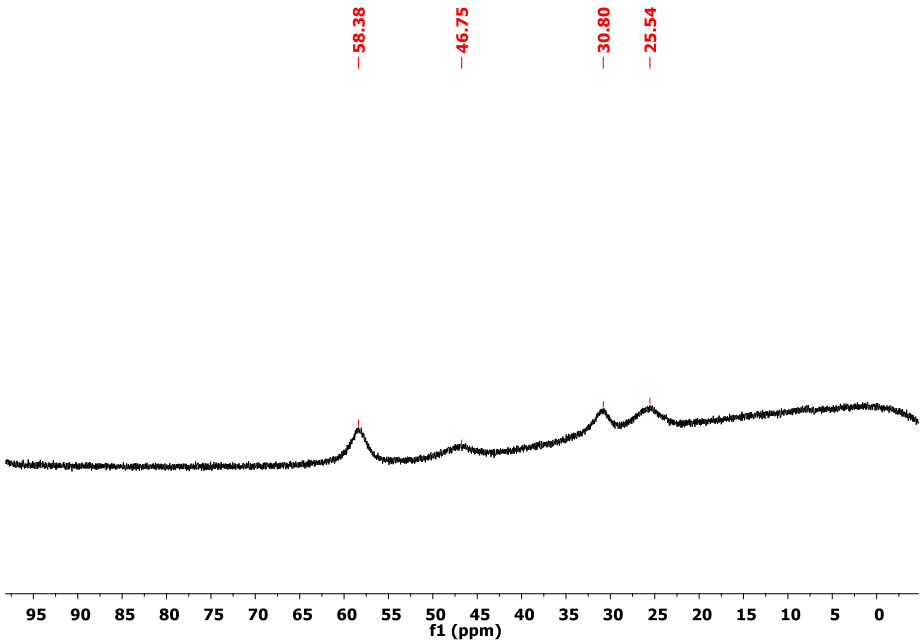
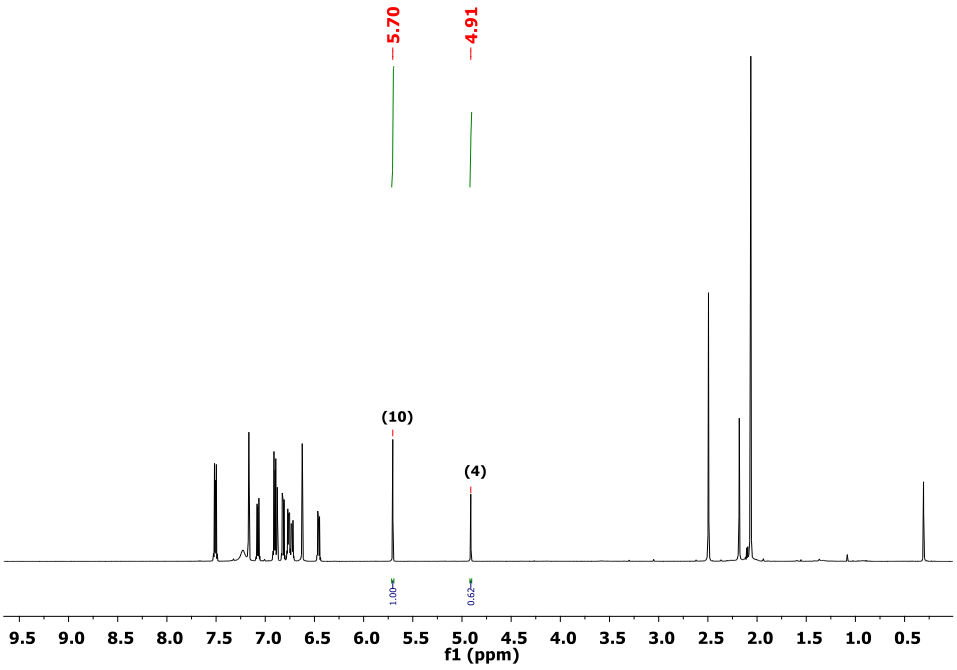


Figure S5 ^{1}H (top) and ^{11}B (bottom) NMR of crossover experiment in C_6D_6 having equivalent amount (0.05mmol each) of B_2cat_2, $B_2(dithiocat)_2$ and DippDAB



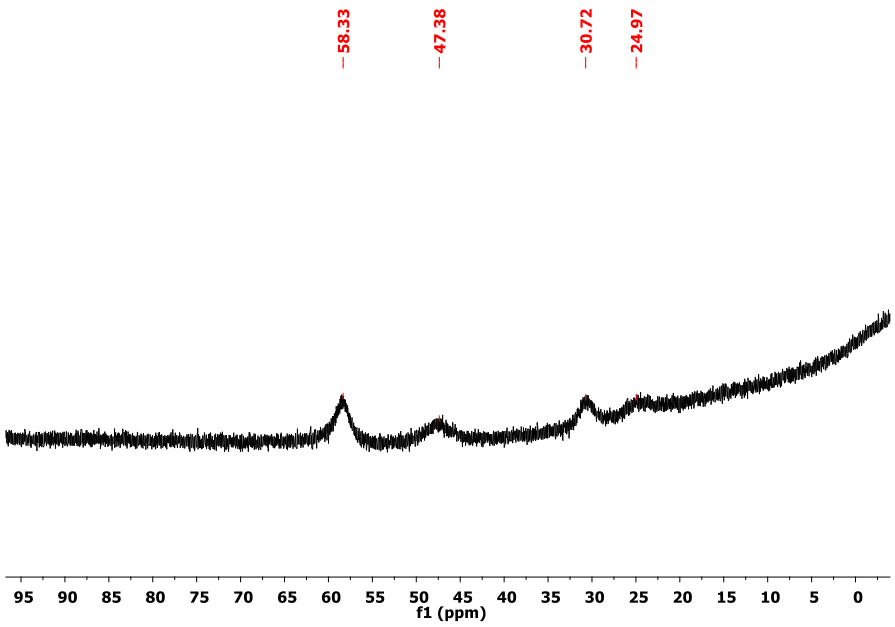


Figure S6 ^{1}H (top) and ^{11}B (bottom) NMR of crossover experiment in C_6D_6 having equivalent amount (0.05mmol each) of B_2cat_2, $B_2(dithiocat)_2$ and MesDAB

3.3 UV-Visible experiment

UV-Visible experiment was performed to study the possible existence of photochemical cis-trans isomerization in compounds **3** and **4**. Reaction of DABs with B_2cat_2 was carried out under dark condition and the UV-Vis spectrum of this sample was recorded. The same sample was then exposed to white light for 30 min and UV-Vis spectrum was recorded again. No observable changes in the spectra were observed for both the compounds (3 and 4), eliminating the possibility of photochemical cis-trans isomerization.

(a) (b)

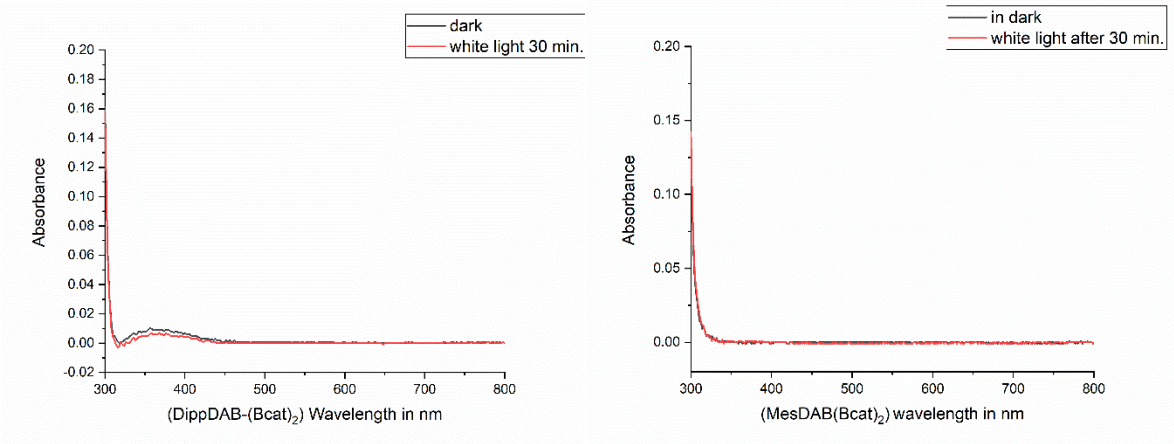


Figure S7 UV-visible spectra of compound **3** and **4**.

4 X-ray crystallographic data

4.1 Molecular structure of compound 3, (DippDAB)(Bcat)$_2$

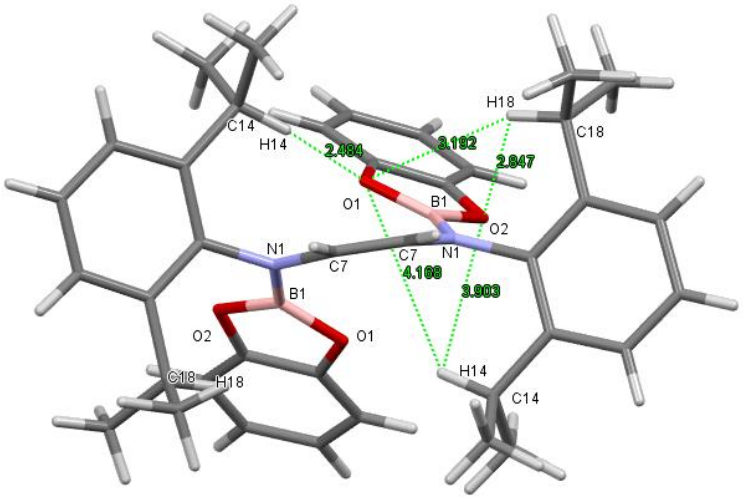


Figure S8 Crystal structure of compound 3.

4.2 Molecular structure of compound 4, (MesDAB)(Bcat)$_2$

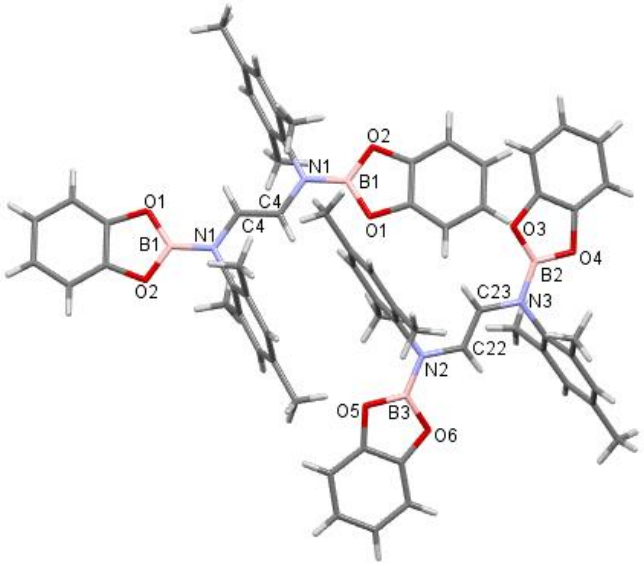


Figure S9 Crystal structure of compound 4.

4.3 Molecular structure of compound 7

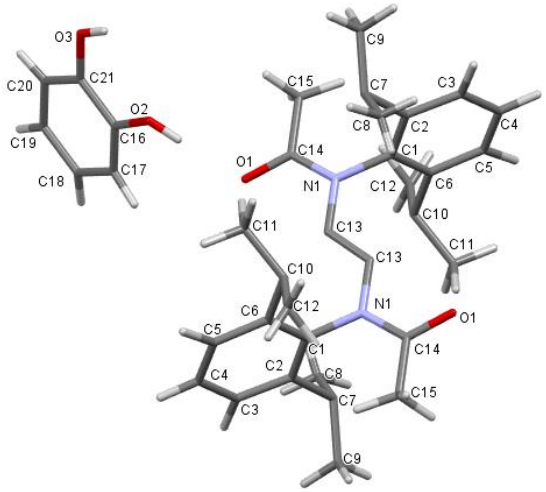


Figure S10 Crystal structure of compound 7.

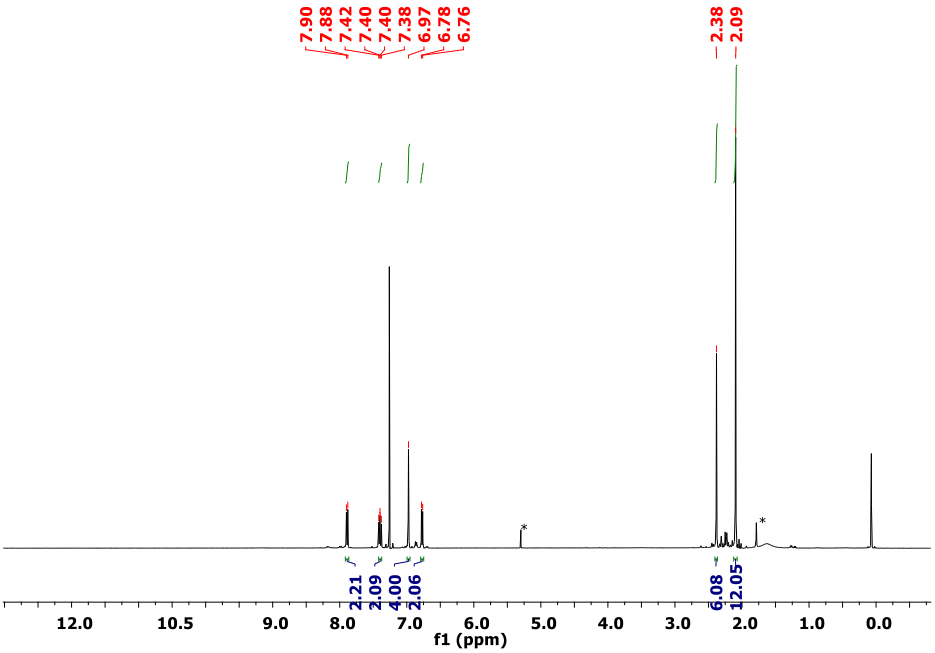
4.4 Single crystal X-ray crystallographic data

Specifications	Compound **3**	Compound **4**	Compound **7**
Empirical formula	$C_{38}H_{44}B_2N_2O_4$	$C_{32}H_{32}B_2N_2O_4$	$C_{40}H_{56}N_6O_4$
Formula weight	614.37	530.22	342.5
Temperature/K	100	100	296
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C 2/c	P 2_1/n	P-1
a/Å	22.8528(9)	12.8055(2)	8.8240(2)
b/Å	13.7386(5)	15.3364(2)	10.8160(3)
c/Å	12.6423(5)	22.2271(3)	11.5045(3)
α/°	90	90	110.590(1)
β/°	118.405(2)	103.073(1)	93.642(1)
γ/°	90	90	105.942(1)
Volume/Å^3	3491.4(2)	4252.05(10)	972.67(6)
Z	4	6	2
ρ_{calc}g/cm^3	1.169	1.242	1.170
μ/mm^{-1}	0.074	0.080	0.076
F (000)	1312.0	1680.0	370.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	5258	12995	5940
Goodness-of-fit on F^2	0.935	1.020	1.027
R(reflections)	0.0719 (3797)	0.0478 (8995)	0.0667 (3955)
wR2(reflections)=	0.2106 (5258)	0.1325 (12995)	0.2373 (5940)
Theta (max	30.417	30.532	30.589
Npar	296	550	322

5 NMR spectra

(1E,2E)-N^1,N^2-dimesitylacenaphthylene-1,2-diimine (compound 5)

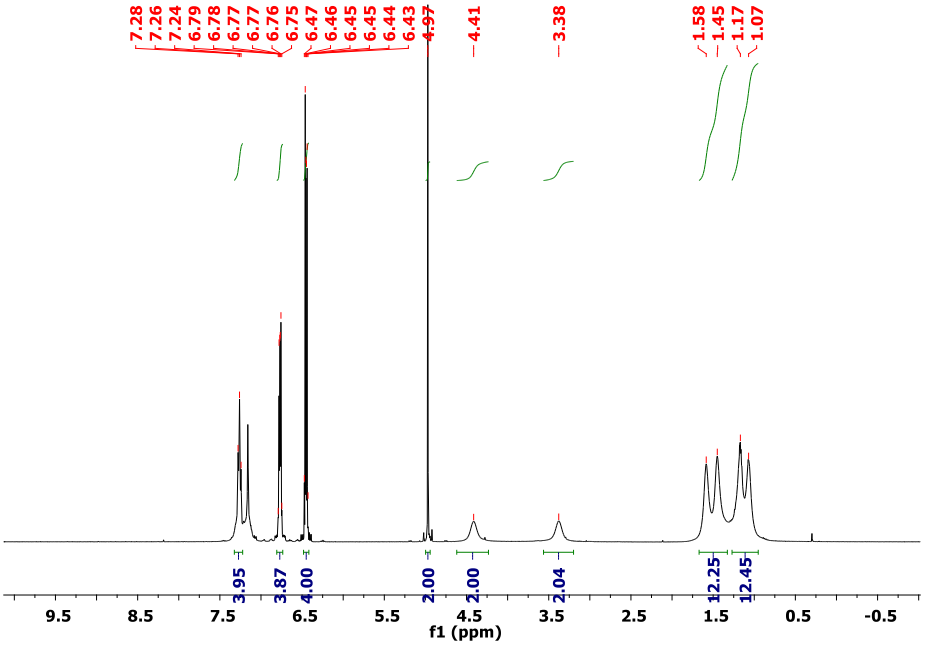
^{1}H NMR, C_6D_6, 400 MHz



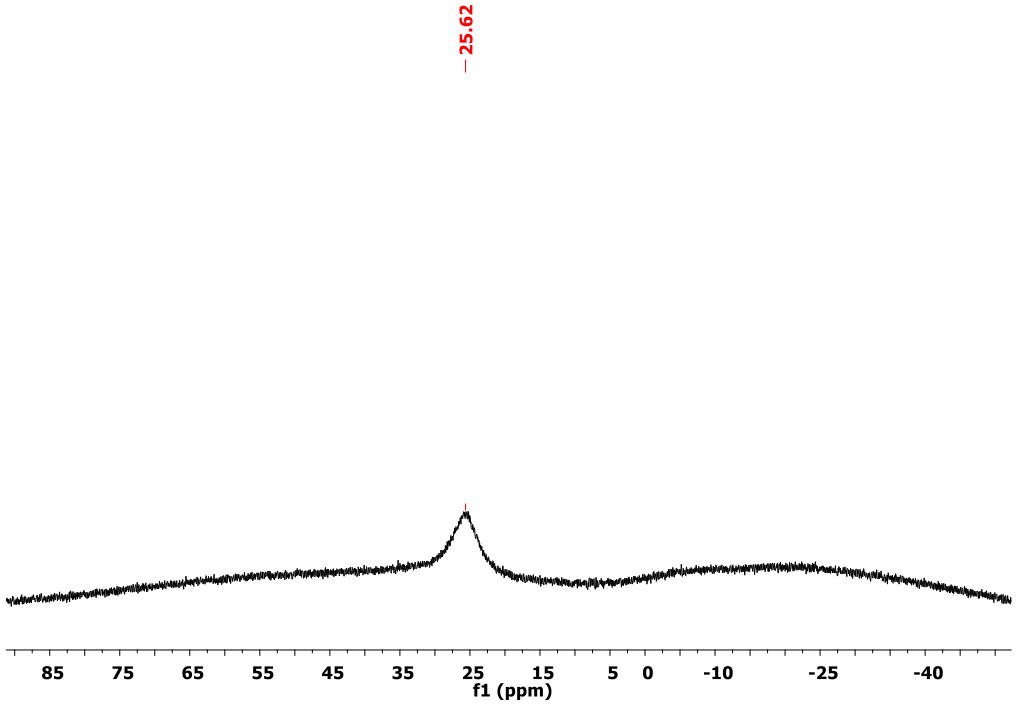
***** DCM as impurity.

DippDAB(Bcat)$_2$ (3)

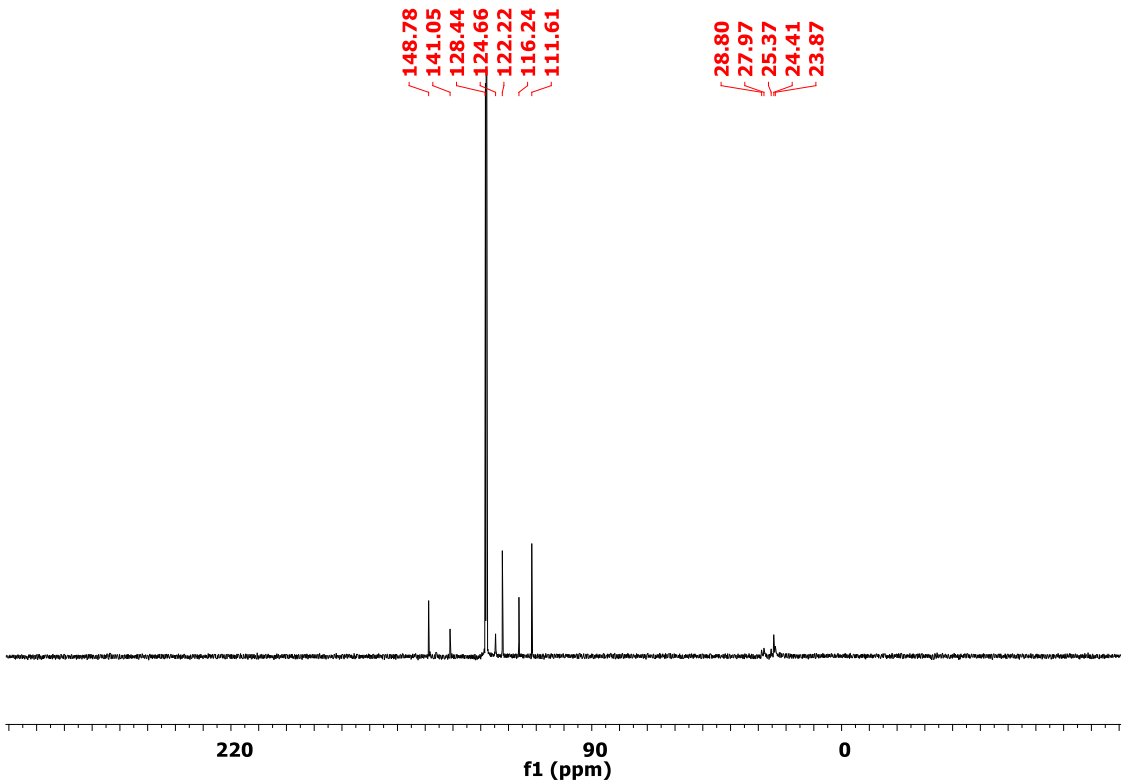
^{1}H NMR, C_6D_6, 400 MHz



^{11}B NMR, C_6D_6, 128 MHz

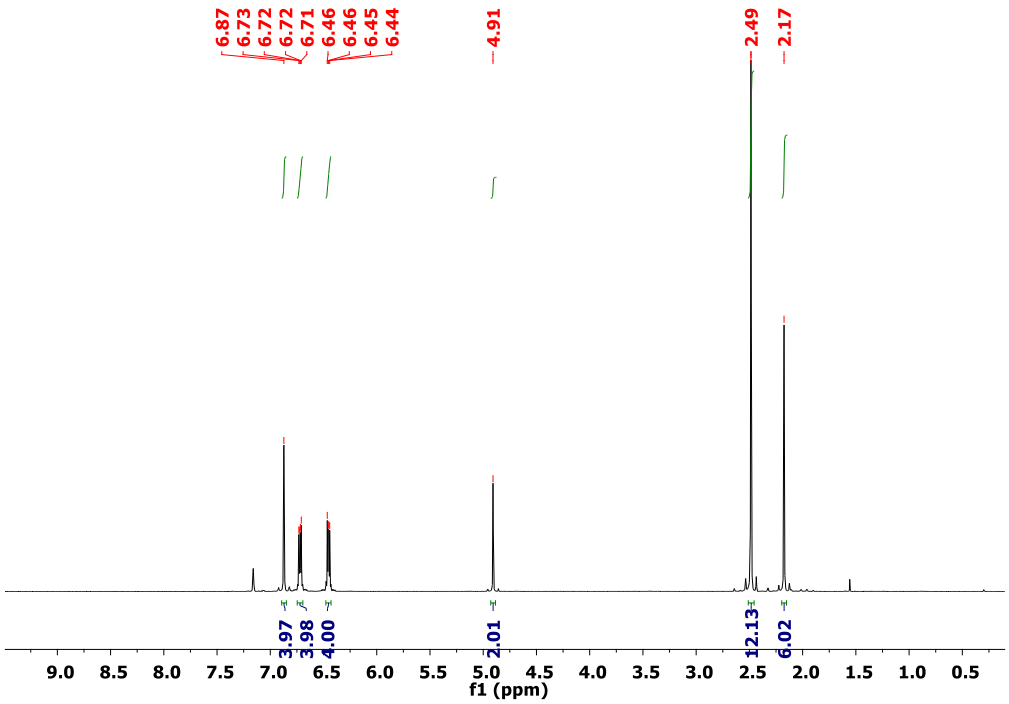


^{13}C NMR, C_6D_6, 100 MHz

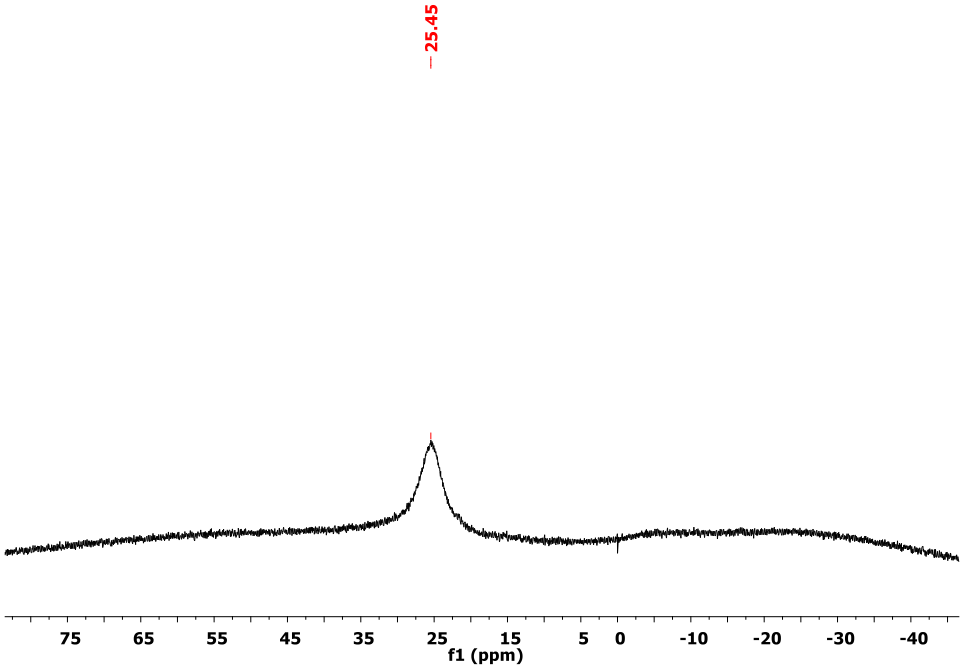


MesDAB(Bcat)$_2$ (4)

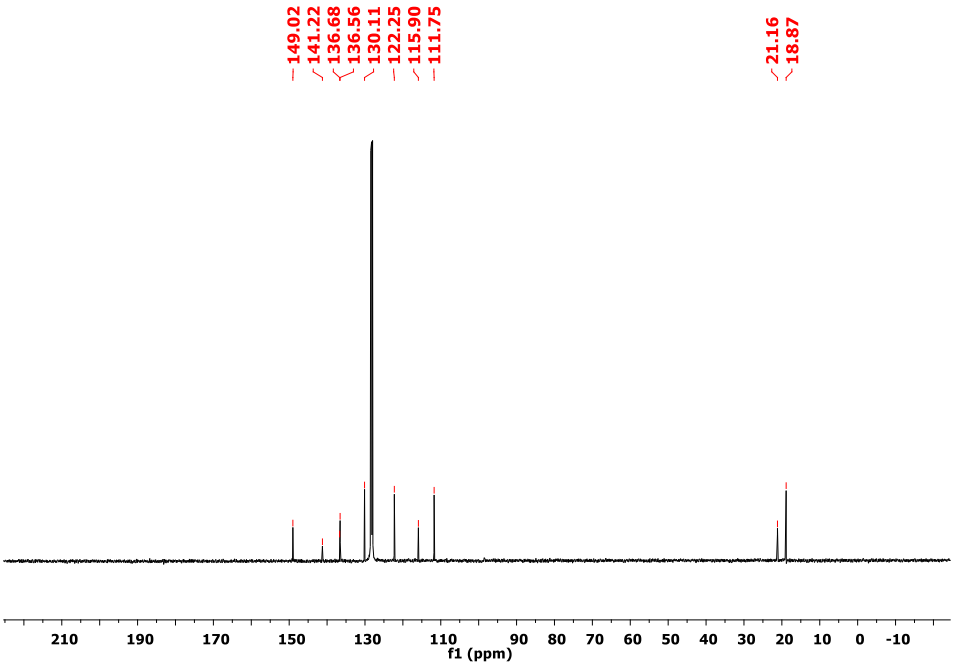
^{1}H NMR, C_6D_6, 400 MHz



^{11}B NMR, C_6D_6, 128 MHz

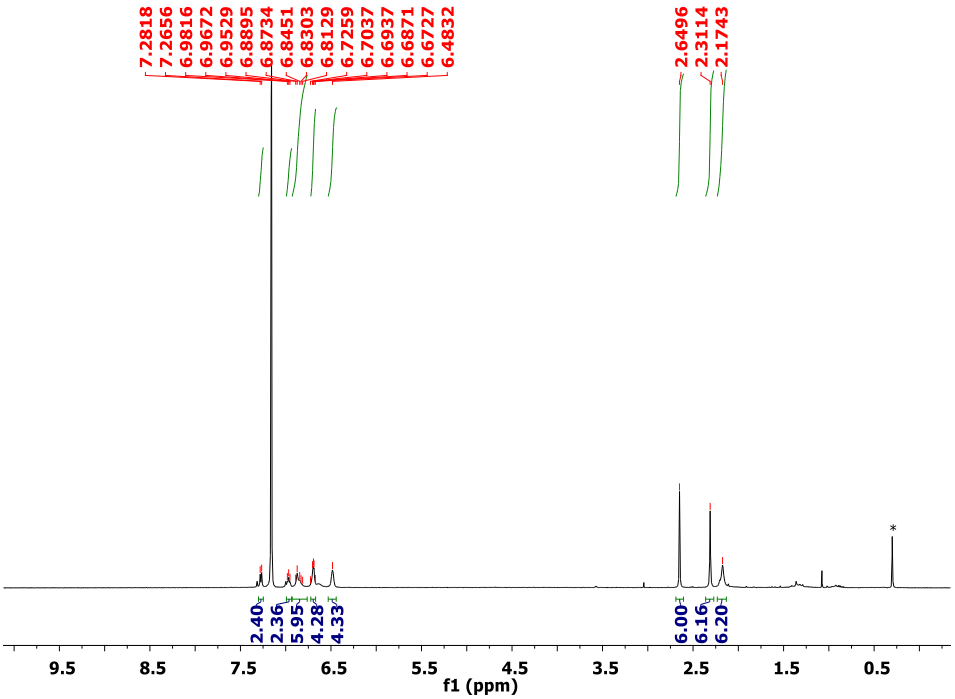


^{13}C NMR, C_6D_6, 100 MHz



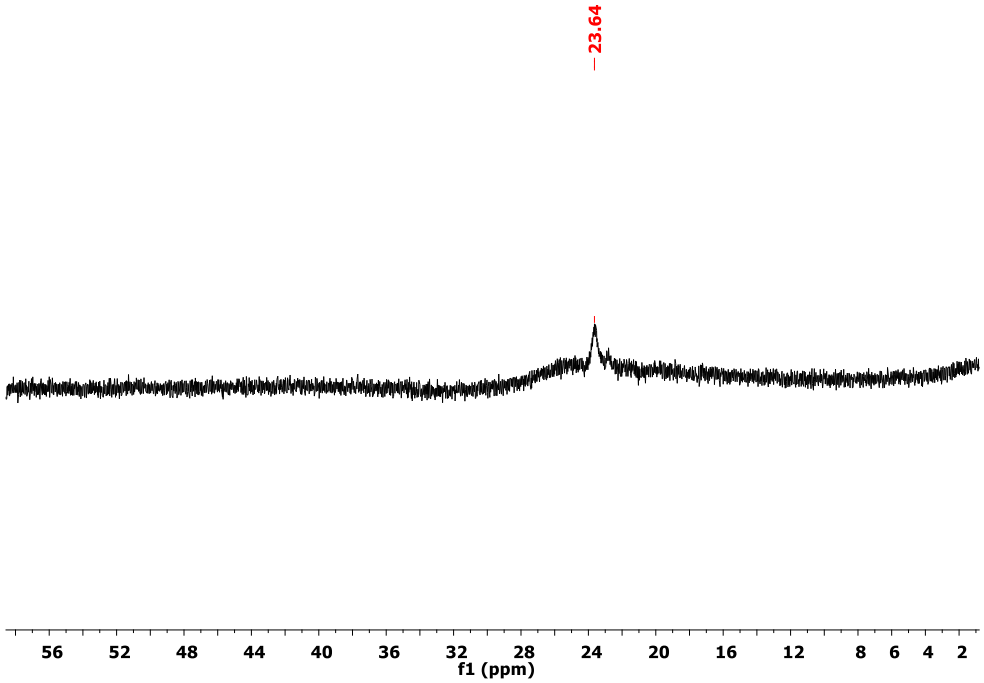
Compound 6

^{1}H NMR, C_6D_6, 400 MHz



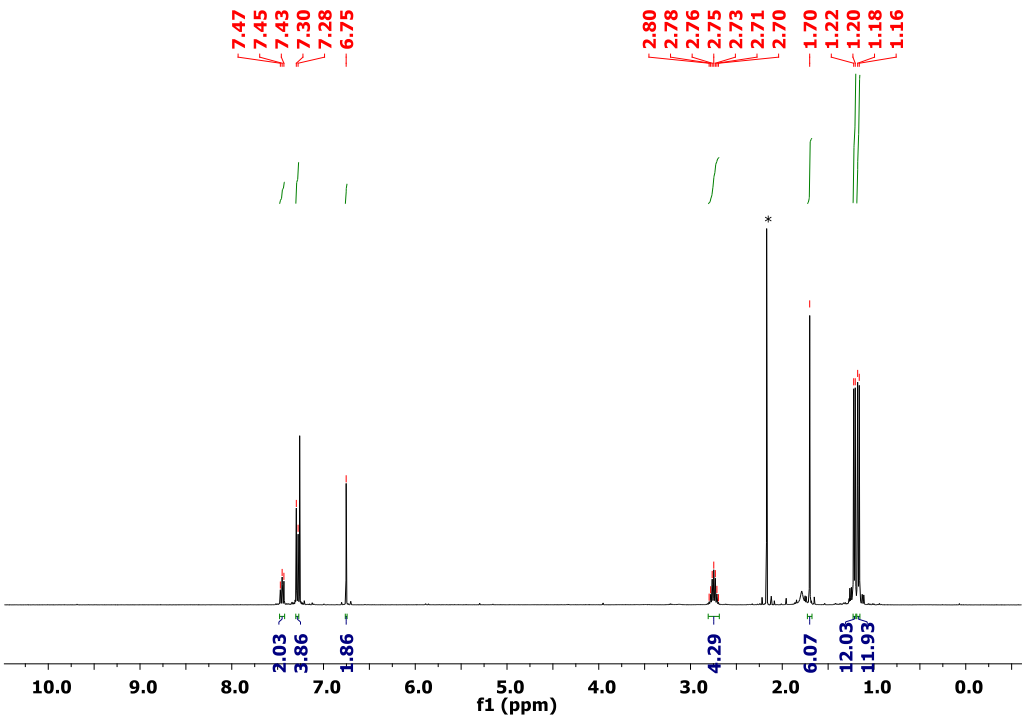
* Silicone grease

^{11}B NMR, C_6D_6, 128 MHz

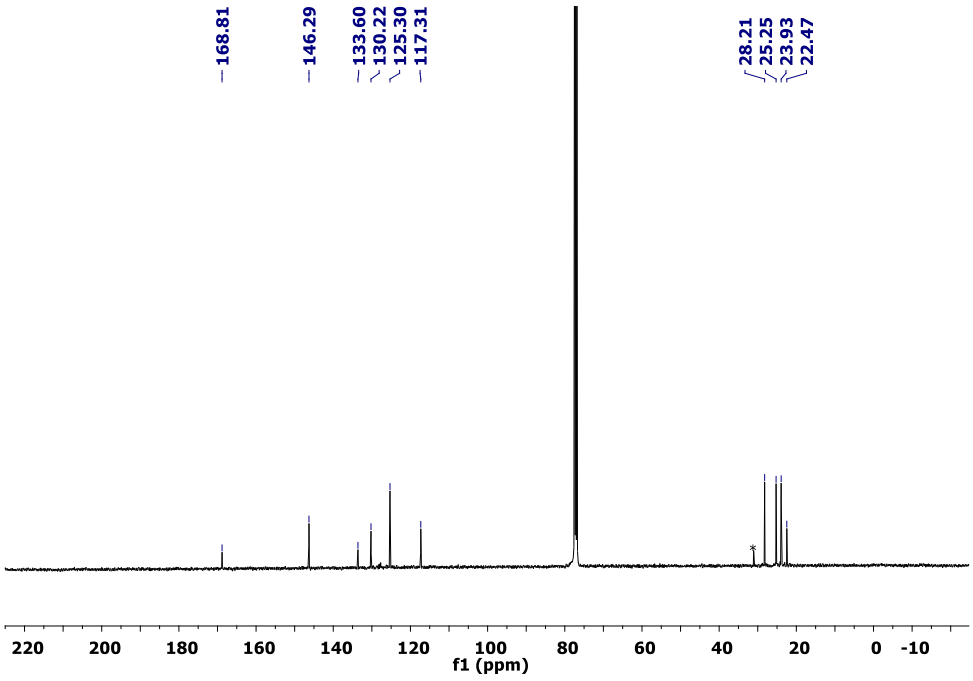


Compound 7

^{1}H NMR, C_6D_6, 400 MHz



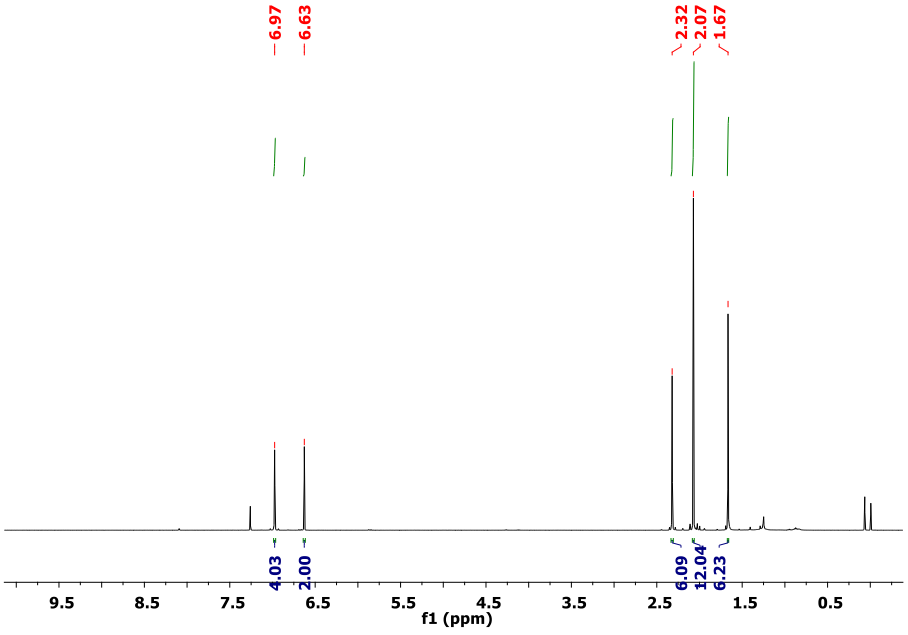
^{13}C NMR, C_6D_6, 100 MHz



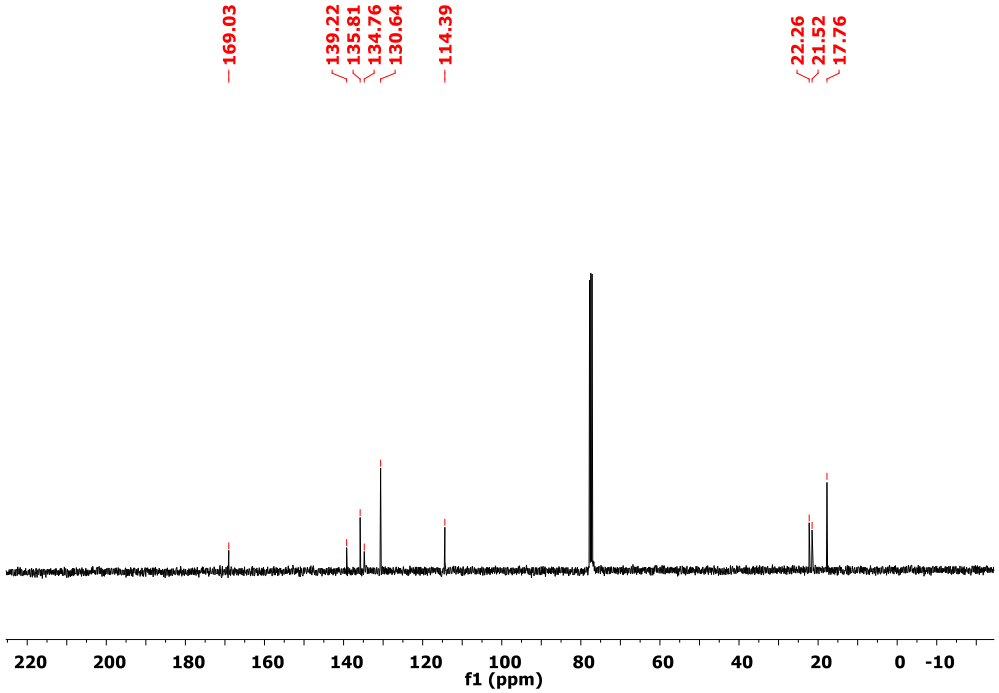
***** acetone as impurity

Compound 8

^{1}H NMR, C_6D_6, 400 MHz

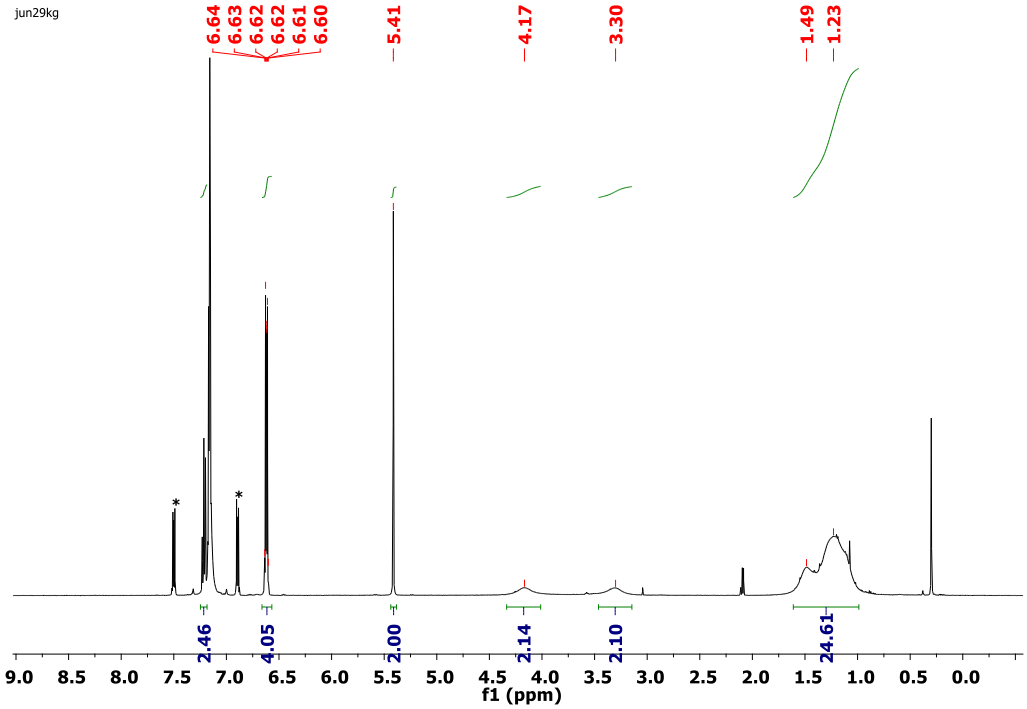


^{13}C NMR, C_6D_6, 100 MHz



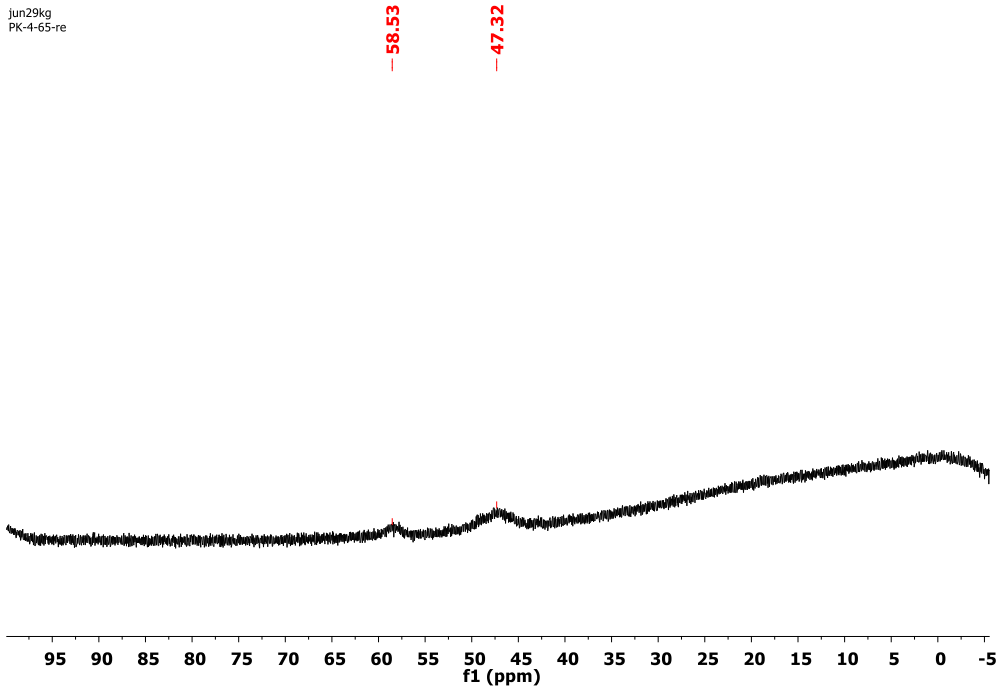
Compound 9

^{1}H NMR, C_6D_6, 400 MHz



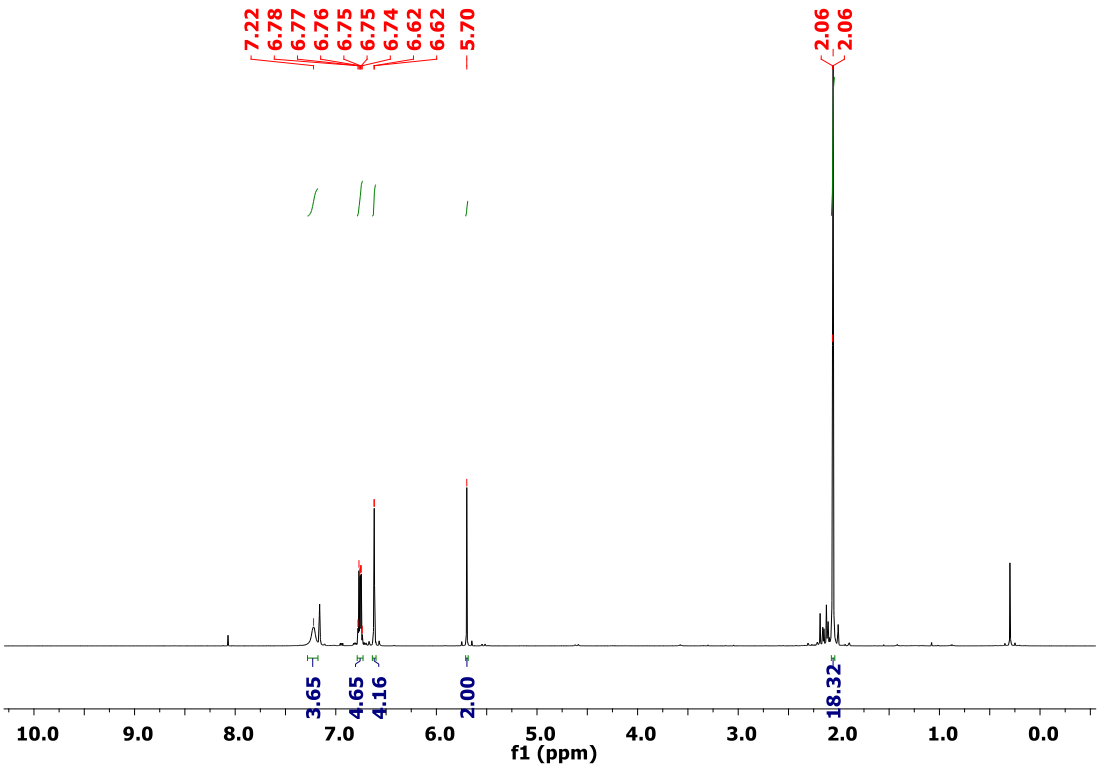
* B_2(dithiocat)$_2$

^{11}B NMR, C_6D_6, 128 MHz

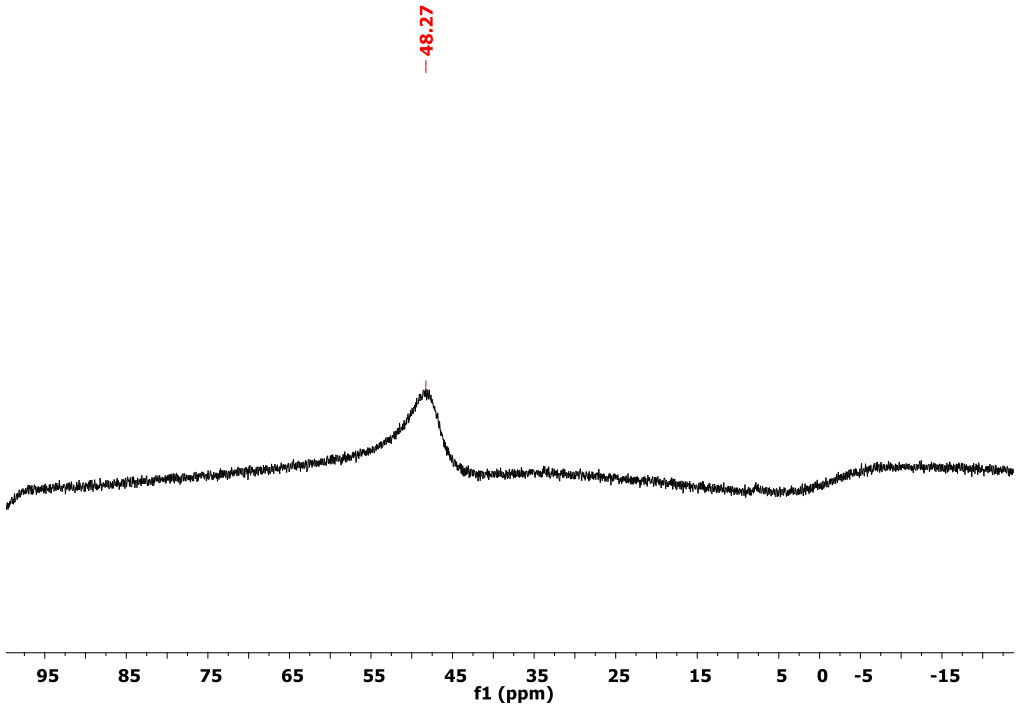


Compound 10

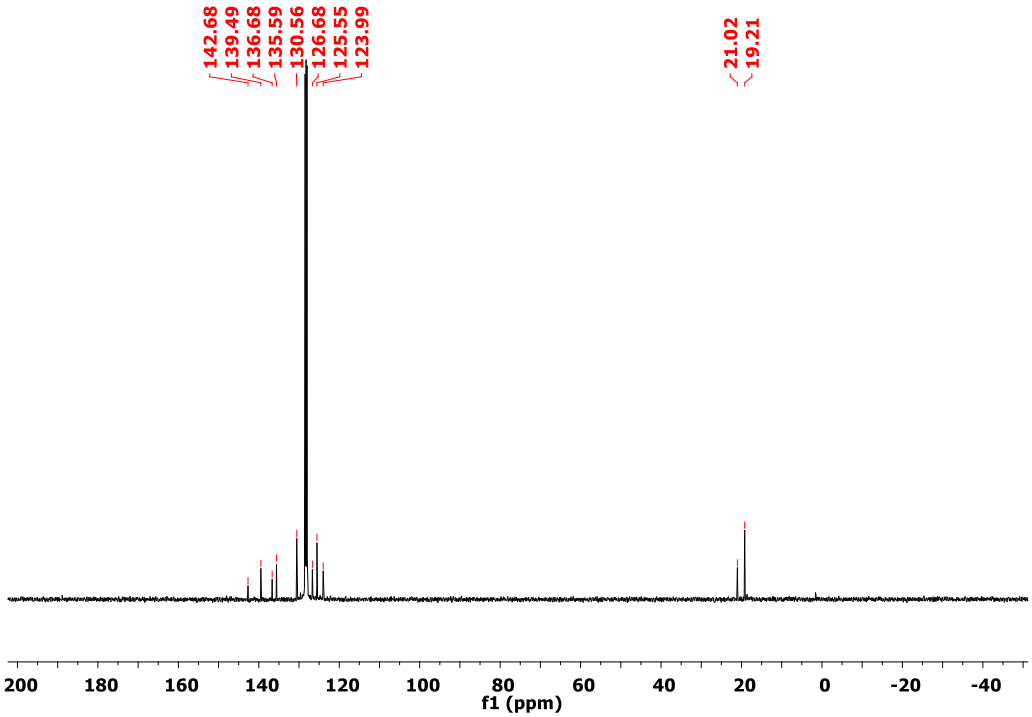
^{1}H NMR, C_6D_6, 400 MHz



^{11}B NMR, C_6D_6, 128 MHz



^{13}C NMR, C_6D_6, 100 MHz



6 ESI-HRMS spectra

Compound 3

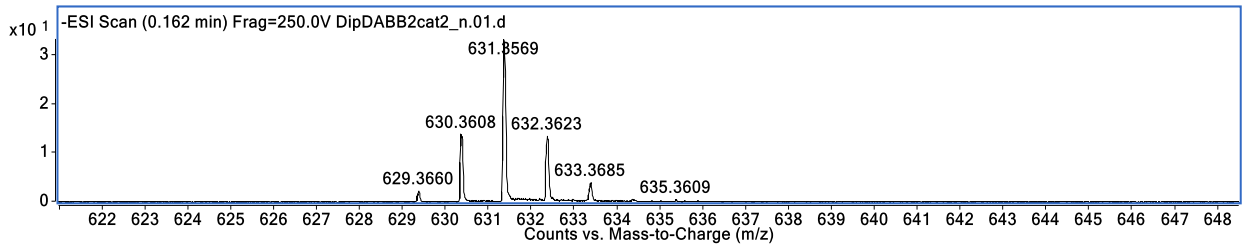


Figure S11 Mass spectrum of compound **3** in benzene, showing the ion peak at 631.3569 (m/z) which corresponds to $((M+H_2O)-H)^-$ of compound **3**. Calculated mass of compound **3** is 631.3515 u.

Compound 4

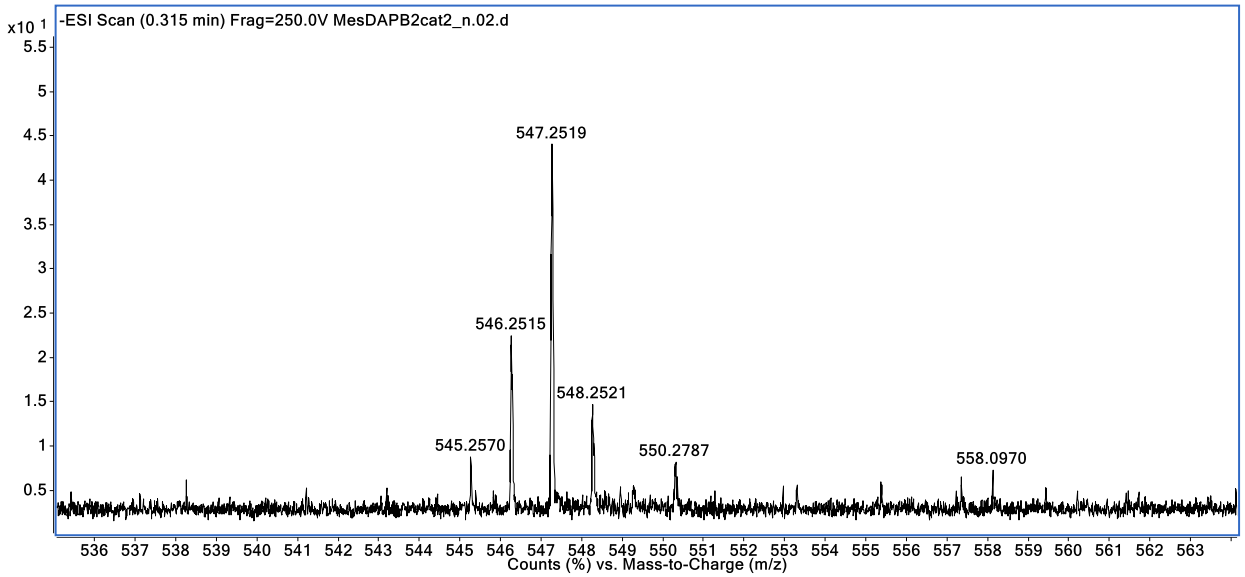


Figure S12 Mass spectrum of compound **4** in benzene, showing the ion peak at 547.2519 (m/z) which corresponds to $((M+H_2O)-H)^-$ of compound **4**. Calculated mass of compound **4** is 547.2576 u.

Compound 6

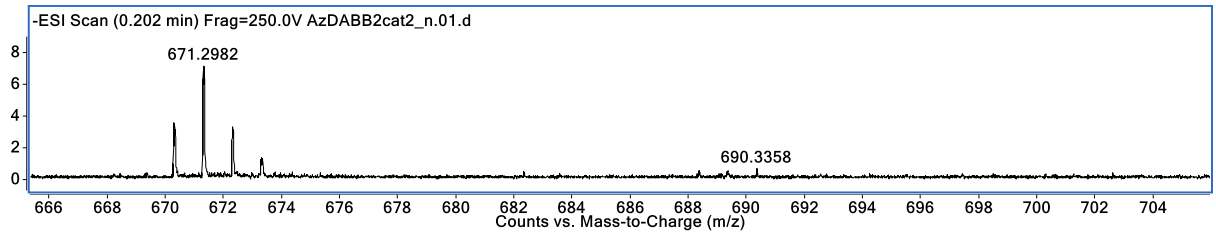


Figure S13 Mass spectrum of compound **6** in benzene, showing the ion peak at 671.2982 (m/z) which corresponds to $((M+H_2O)-H)^-$ of compound **6**. Calculated mass of compound **6** is 671.2889 u.

7 References

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