Electronic Supplementary Material (ESI) for Dalton Transactions.

Contents page

NMR data

1,5-Diazabicyclo(4.3.0)non-5-ene (DBN) Adducts

2 - B_2Cat_2(DBN)

DBN (50 μL, 0.4 mmol) was added to B_2Cat_2 (200 mg 0.4 mmol) in DCM. The product could be recrystallised from DCM/DCB (90/10). The mixture was then layered with pentane to obtain the title compound as a white solid. Yield: 206 mg 68%

^{1}H NMR (500 MHz, d_2-DCM, major isomer) δ/ppm: 7.5-6.5 (8H overlapping br m), 3.42 (4H, m), 3.22 (2H, t, J = 5.0 Hz), 3.11 (2H, t, J = 7.3 Hz), 2.02 (2H, pent, 7.5 Hz) 1.90 (2H, t, 5.5 Hz).

^{11}B{^{1}H} NMR (160 MHz, d_2-DCM, major isomer) δ/ppm: 36.0 (br), 7.0 (br).

^{13}C{^{1}H} NMR (126 MHz, d_2-DCM, major isomer) δ/ppm:164.2, 149.2 (br), 131.0, 128.5, 122.2 (br), 119.3 (br), 111.8 (br), 110.4 (br), 52.8, 43.5, 40.5, 31.5, 20.0, 19.7.

Elemental analysis: Calculated for $C_{19}H_{20}B_2N_2O_4$: C, 63.04%; H, 5.57%; N, 7.74%, Found C, 62.92%; H, 5.70%; N, 7.81%

3 - $B_2Cat_2(DBN)_2$ (mixture of isomers)

DBN (100 μL, 0.8 mmol) was added to B_2Cat_2 (100 mg, 0.4 mmol) in DCB (1ml). The mixture was stirred for 2hrs and the desired product precipitated as a microcrystalline solid. Yield: the yield was consistently above 100% due to the presence of tightly bound DCB solvent also observed in the X-ray structure. Elemental analysis is consistent for DCB being retained in the lattice.

^{1}H NMR (500 MHz, d_2-DCM – sample recrystallised from DCB taken from batch sent for combustion analysis) δ/ppm: 7.47 (DCB), 7.24 (DCB), 6.64 (2H, m), 6.60(2H, m), 6.52 (4H, m), 3.28 (8H, br m), 3.00-3.09 (8H, br m), 1.88 (4H, pent) 1.72 (4H, br m).

^{11}B{^{1}H} NMR (160 MHz, DCM – sample recrystallised from DCB taken from batch sent for combustion analysis) δ/ppm: 12.7 (br s), 4.6 (br s).

^{13}C{^{1}H} NMR (126 MHz, d_2-DCM – sample recrystallised from DCB taken from batch sent for combustion analysis) δ/ppm: 163.1 (br), 153.8, 148.8, 132.8, 131.0 (DCB), 128.5 (DCB), 118.8, 118.4, 118.2, 109.2, 51.4, 43.5 (br), 42.0 (br), 41.3 (br), 32.0 (br), 31.42 (br), 20.4 (br).

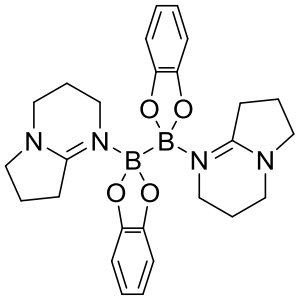
Elemental analysis: Calculated for $C_{38}H_{40}B_2Cl_4N_4O_4$ ($B_2Cat_2(DBN)_2$•DCB_2): C, 58.50%; H, 5.17%; N, 7.18%, Found C, 58.32%; H, 5.26%; N, 7.39%

It is noteworthy that the ^{11}B NMR spectra of this compound in the absence of DCB (i.e. made in DCM from combining 1 equivalent of B_2Cat_2 with 2 equivalents of DBN) is different, suggesting that even a stoichiometric quantity of DCB can alter the equilibrium position of DBN binding and 1,1 / 1,2-isomerisation. The data above are from the recrystallised sample which contains DCB in the unit cell.

Without DCB:

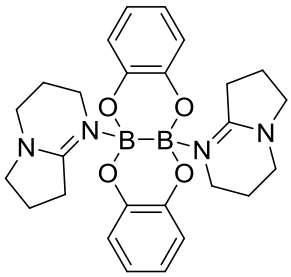
^{11}B{^{1}H} NMR (128 MHz, d_2-DCM) δ 12.3 (br s), 4.0 (br s).

3a - 1,1-$B_2Cat_2(DBN)_2$



DBN (100 μL, 0.8 mmol) was added to B_2Cat_2 (100 mg, 0.4 mmol) in DCM/DCB (50/50). The title compound was obtained by layering this mixture with pentane and filtering off the resulting white crystals, 134 mg (yield 65%).

3b - 1,2-$B_2Cat_2(DBN)_2$



DBN (100 μL, 0.8 mmol) was added to B_2Cat_2 (100 mg, 0.4 mmol) in DCM. The mixture was heated in a 60°C oil bath for 5 min, and then layered with pentene to obtain, following filtration, the title compound as white crystals, 133 mg (yield 65%)

Ligand redistribution between **3** - $B_2Cat_2(DBN)_2$ - and 1 equivalent of **1** - B_2Cat_2

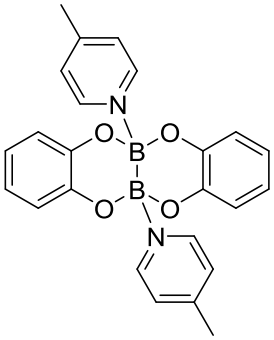
3b (20 mg, 0.041 mmol) was dissolved in d_2-DCM (0.5ml) to which **1** (10mg, 0.041 mmol) was added. The mixture was stirred for a few minutes before recording NMR spectra of the crude reaction mixture.

^{1}H NMR (400 MHz, d_2-DCM) δ/ppm: 7.48 (DCB) 7.40 (1H, br), 7.25 (DCB), 7.22 (1H, overlapping DCB peak), 6.86 (6H, v br), 3.41 (4H, m), 3.23 (2H, t), 3.12 (2H, t), 2.03 (2H, pent), 1.91 (2H, pent).

$^{11}B\{^1H\}$ NMR (128 MHz, d_2-DCM) δ/ppm: 34.8, 30.8, 14.16 (Cat_2B^-), 7.3, 0.5.

Picoline adducts

4b - $B_2Cat_2(pic)_2$ – dissolved in $CDCl_3$



Picoline (163 μL, 1.6 mmol) was added to B_2Cat_2 (200 mg, 0.8 mmol) in DCM (10 ml). The reaction mixture was stirred at room temperature for 90 mins then reduced to dryness under vacuum. The title compound was obtained by redissolving this in DCB (7 ml), filtering the supernatant, layering with pentane (approx. 7 ml) and filtering off the resulting large yellow crystalline blocks.

NMR spectra, mixture of 1,1-and 1,2-isomers:

^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.40 (d, 4H), 7.45 (m, 1.7H), 7.17 (m, 6H), 7.01 (m, 4H), 6.75 (m 2H), 6.74 (m, 2.3H), 2.40 (s, 6H).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ/ppm: 20.2 (br s), 5.4 (br s).

^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$) δ/ppm: 151.8, 149.8, 147.5, 143.9, 132.4, 130.5, 127.7, 125.7, 120.5, 119.3, 119.1, 111.2, 21.3.

Elemental analysis: Calculated for $C_{24}H_{22}B_2N_2O_4$: C, 67.98%; H, 5.23%; N, 6.61%, Found C, 67.83%; H, 5.13%; N, 6.52%

4b - $B_2Cat_2(pic)_2$ – dissolved in THF

40 mg of 1,2-isomer obtained by recrystallization from DCB was redissolved in THF (approx. 3 ml), filtered and reduced in volume (to approximately 1 ml) under vacuum, the resulting solution was cooled to -20 ^{O}C overnight to yield yellow crystals of a distinctly different morphology (rough plates).

NMR spectra, mixture of 1,1-and 1,2-isomers:

^{1}H NMR (400 MHz, d_8-THF) δ/ppm: 8.14 (m, 3.86H), 7.26 (m, 1.8H), 7.03 (m, 5.3H), 6.60 (m, 2.1H), 6.45 (m 3.8H), 6.27 (s 1.7H), 2.11 (s, 6H).

^{11}B{^{1}H} NMR (128 MHz, d_8-THF) δ/ppm: 20.7 (br s), 6.0 (br s).

^{13}C{^{1}H} NMR (100 MHz, d_8-THF) δ/ppm: 152.7, 151.5, 149.5, 145.5, 133.2, 131.7, 129.3, 126.6, 121.0, 119.7, 119.3, 111.6, 21.2.

The NMR spectra are consistent with those previously reported by Marder *et al*.,

Crystallography

Data for compounds **2a** (**$B_2Cat_2(DBN)$**), **3a** (the 1,1-isomer of **$B_2Cat_2(DBN)_2$**), **3b** (the 1,2-isomer of **$B_2Cat_2(DBN)_2$**), **$4b_{(DCB)}$** and **$4b_{(THF)}$** (the 1,2-isomers of **$B_2Cat_2(pic)_2$** as its DCB and THF solvates respectively) were recorded on an Agilent Supernova diffractometer, with Mo Kα radiation (mirror monochromator, λ=0.7107 Å). The CrysAlisPro[3] software package was used for data collection, cell refinement and data reduction.

For all data sets the CrysAlisPro software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

All structures were solved using direct[4] or charge flipping[4a] methods and refined against F^2 using the Crystals[5] software package. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all located in a difference map and repositioned geometrically.

	2a $B_2Cat_2(DBN)$	**3a 1,1-isomer of $B_2Cat_2(DBN)_2$**	**3b 1,2-isomer of $B_2Cat_2(DBN)_2$**	**$4b_{(DCB)}$ 1,2-isomer $B_2Cat_2(pic)_2$•(DCB)**	**$4b_{(THF)}$ 1,2-isomer $B_2Cat_2(pic)_2$•(THF)**
CCDC reference	**1047163**	**1047162**	**1047161**	**1047164**	**1047165**
Empirical Formula	$C_{26}H_{32}B_2N_4O_4$, $2(C_{19}H_{20}B_2N_2O_4)$	$C_{26}H_{32}B_2N_4O_4$• $2(C_6H_4Cl_2)$	$C_{26}H_{32}B_2N_4O_4$• $2(CH_2Cl_2)$	$C_{24}H_{22}B_2N_2O_4$• $C_6H_4Cl_2$	2 x $C_{24}H_{22}B_2N_2O_4$• C_4H_4O
Colour	Colourless	Colourless	Colourless	Yellow	Yellow
Fw / g mol^{-1}	1210.16	780.16	656.03	571.07	920.22
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, *I*2/a	Monoclinic,*P* 2_1/c	Monoclinic,*P* 2_1/n
***T* / K**	150	150	150	150	150
a / Å	9.0422(9)	8.5427(3)	20.784 (2)	11.2480(4)	14.8432(14)
b / Å	10.6101(10)	10.6291(4)	8.1816 (8)	17.8619(5)	17.7593(16)
c / Å	16.1806(14)	10.8732(4)	18.346 (2)	14.4481(5)	18.992(3)
α / deg	82.739(8)	76.955(3)	90	90	90
β / deg	86.594(7)	85.336(3)	101.392 (12)	107.602	109.020(14)
γ / deg	76.681(8)	72.748(3)	90	90	90
Vol / Å^3	1497.7(2)	918.44(6)	3058.2 (6)	2766.87(18)	4733.1(10)
Z	2	1	4	4	4
calc. density (Mg m^{-3})	1.342	1.411	1.425	1.337	1.291
radiation	Mo *K*α, λ = 0.71073 Å	Mo *K*α, λ = 0.71073 Å	Mo *K*α, λ = 0.71073 Å	Mo *K*\αλ = 0.71073 Å	Mo *K*\αλ = 0.71073 Å
abs. coeff. (mm^{-1})	0.09	0.34	0.429	0.275	0.087
F(000)	634	406	1368	1184	1936
θ range (deg)	2.8 – 23.3	2.7 – 25.7	3.3 - 29.3	3.564 – 29.367	3.584 – 23.625
no. of reflns collected / unique	9056/4230	6309/3468	6346/3819	13127 / 6370	17634 / 9399
R_{int}	0.050	0.017	-	0.034	0.065
no. of data / restraints / parameters	4215/6/415	3458/0/235	3819/0/191	6359 / 0 / 362	6465 / 0 / 622
R (data with [I^2 > 2σ(I^2)])	0.088 (2864)	0.044 (2899)	0.0856 (3819)	0.060 (4675)	0.086 (3331)
wR (all data)	0.204	0.110	0.1993	0.1200	0.2075
S	1.01	0.95	1.096	0.9821	0.9875
Δρmax, min / e·Å^{-3}	0.61, −0.64	0.77, −0.41	0.430, −0.401	0.90, -1.23	0.98, -0.91

Key bond metrics

Bond metric	**2a** – 1,1-B_2Cat_2(DBN)		
B-B	1.712 (10)		
B-C or N	1.610 (9)		
BB̂C or N	110.2 (5)		
Σ angles at B	114.7(5)	109.8(5)	105.0(5)
	329.5 (9 - sqrt of sum of squares)		
CC¨ĈB	-		
NĈN	-		

Bond metric	**3a** – 1,1-isomer of $B_2Cat_2(DBN)_2$			**3b** – 1,2-isomer of $B_2Cat_2(DBN)_2$		
B-B	1.715 (5)			1.756 (15)		
B-C or N	1.631 (3)			1.617 (8)		
BB̂C or N	108.3 (2)			113.7 (3)		
Σ angles at B	115.5(2)	115.3(2)	103.40(16)	111.9(6)	113.8(7)	106.3(5)
	334.2 (3 - sqrt of sum of squares)			332.0 (10 - sqrt of sum of squares)		
CC¨ĈB	-			-		
NĈN	-			-		

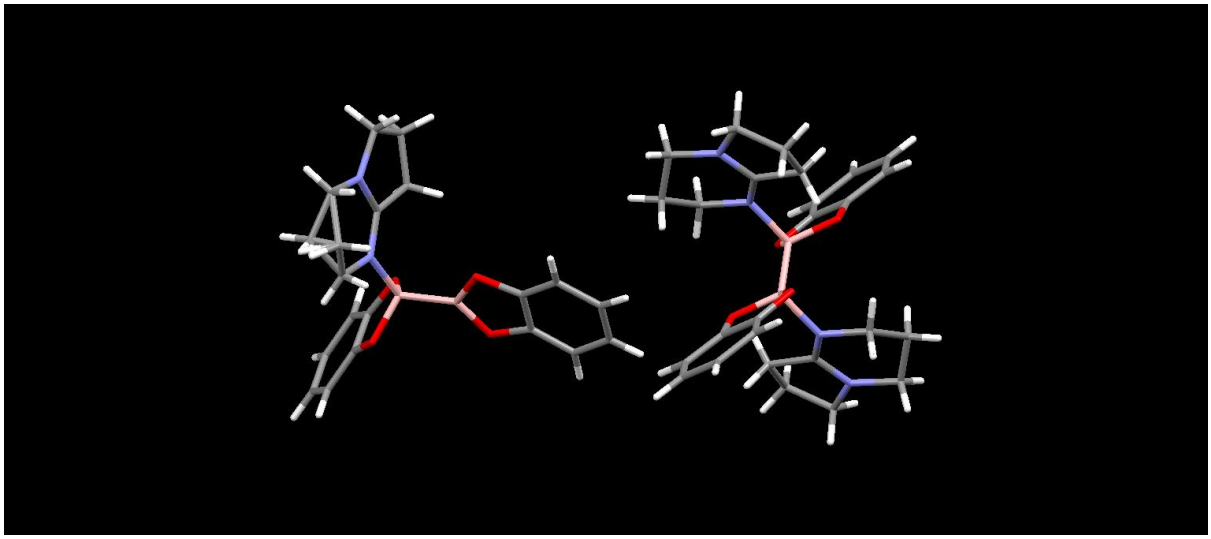
Bond metric	**$4b_{(DCB)}$** 1,2-$B_2Cat_2(pic)_2$•DCB						**1,1-$B_2(pic)_2Cat_2$•THF** Marder et al.[4]
B-B	1.714 (3)						1.713 (4)
B-C or N	1.624 (3)			1.619 (3)			1.659 (2)
BB̂N	116.53 (18)			116.87 (18)			108.6 (2)
Σ angles at B	113.26 (19)	109.17 (18)	110.08 (18)	113.07 (19)	109.35 (18)	108.58 (18)	-
	332.51 (32 - sqrt of sum of squares)			331.0 (32 - sqrt of sum of squares)			-
CC¨ĈB	178.56			178.34			-

Bond metric	**$4b_{(THF)}$** – molecule 1 1,2- $B_2Cat_2(pic)_2$•THF					
B-B	1.692 (11)					
B-N	1.625 (10)			1.627 (9)		
BB̂N	117.3 (6)			115.4 (6)		
Σ angles at B	113.7 (6)	108.7 (6)	109.2 (6)	113.1 (6)	109.7 (6)	109.6 (6)
	331.6 (10 - sqrt of sum of squares)			331.0 (10 - sqrt of sum of squares)		
CC¨ĈB	176.9			176.1		

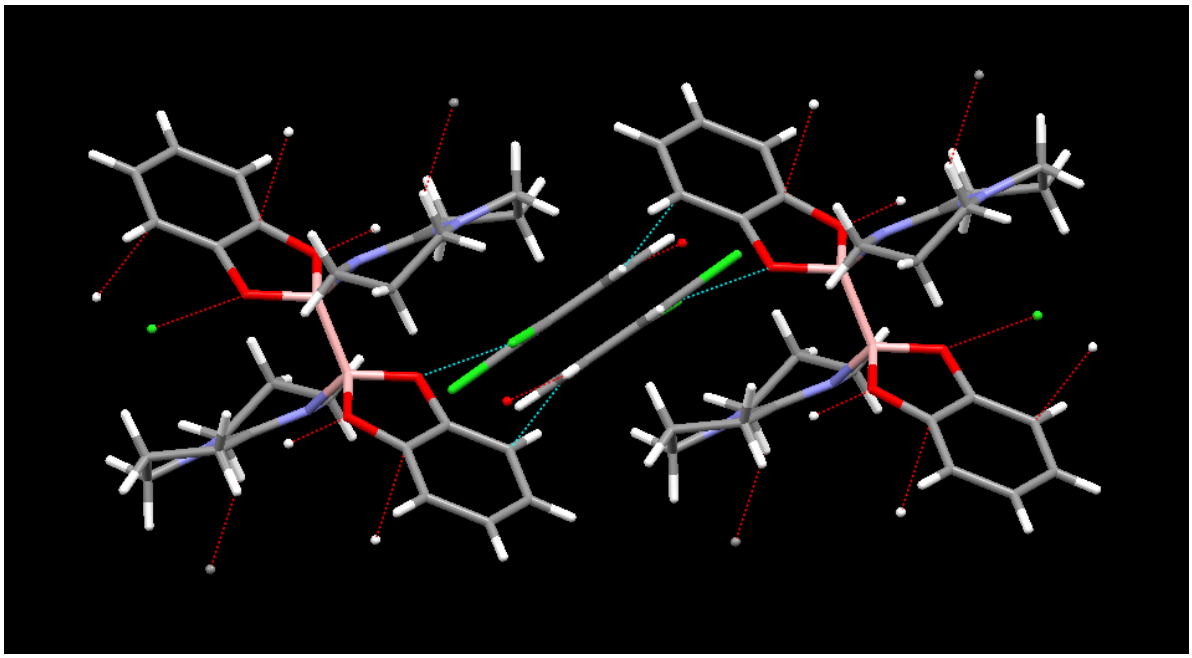
Bond metric	**$4b_{(THF)}$** – molecule 2 1,2- $B_2Cat_2(pic)_2$•THF					
B-B	1.700 (11)					
B-N	1.639 (9)			1.598 (10)		
BB̂N	116.2 (6)			117.8 (6)		
Σ angles at B	113.5 (6)	108.5 (6)	111.4 (6)	112.1 (6)	107.9 (6)	108.3 (6)
	333.4 (10 - sqrt of sum of squares)			328.3 (10 - sqrt of sum of squares)		
CC¨ĈB	175.8			177.5		

Packing structures

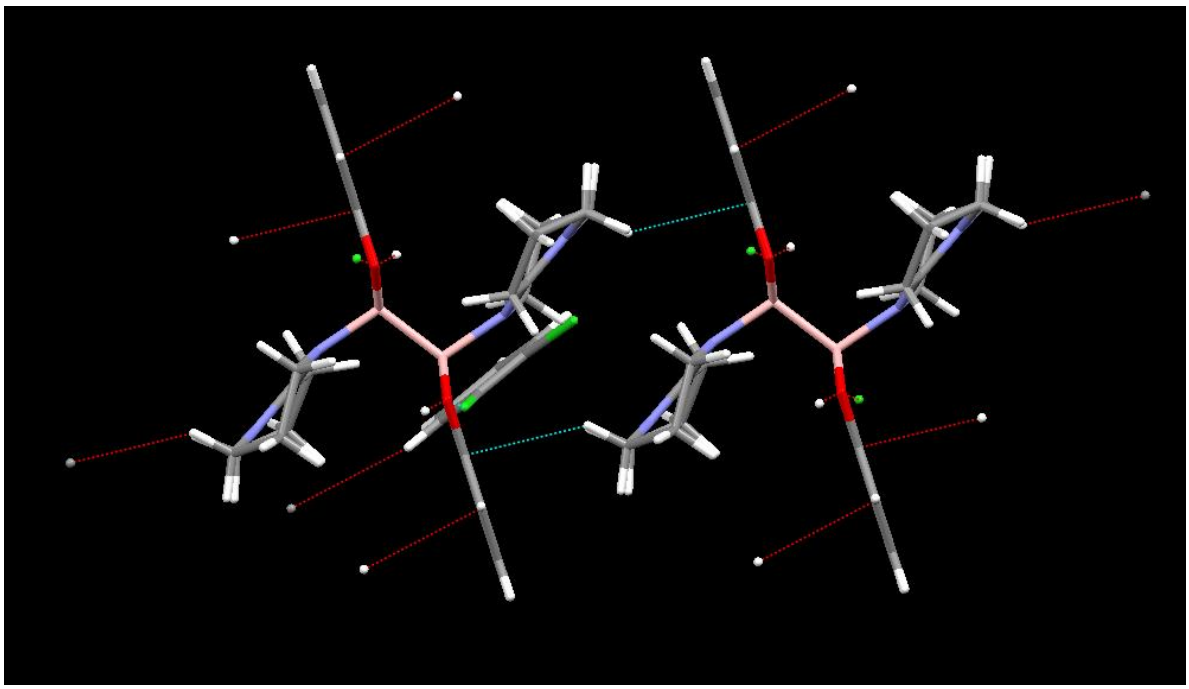
2a and **3a** – $B_2Cat_2(DBN)_{1\ and\ 2}$
Co-crystal of $B_2Cat_2(DBN)$ and $B_2Cat_2(DBN)_2$



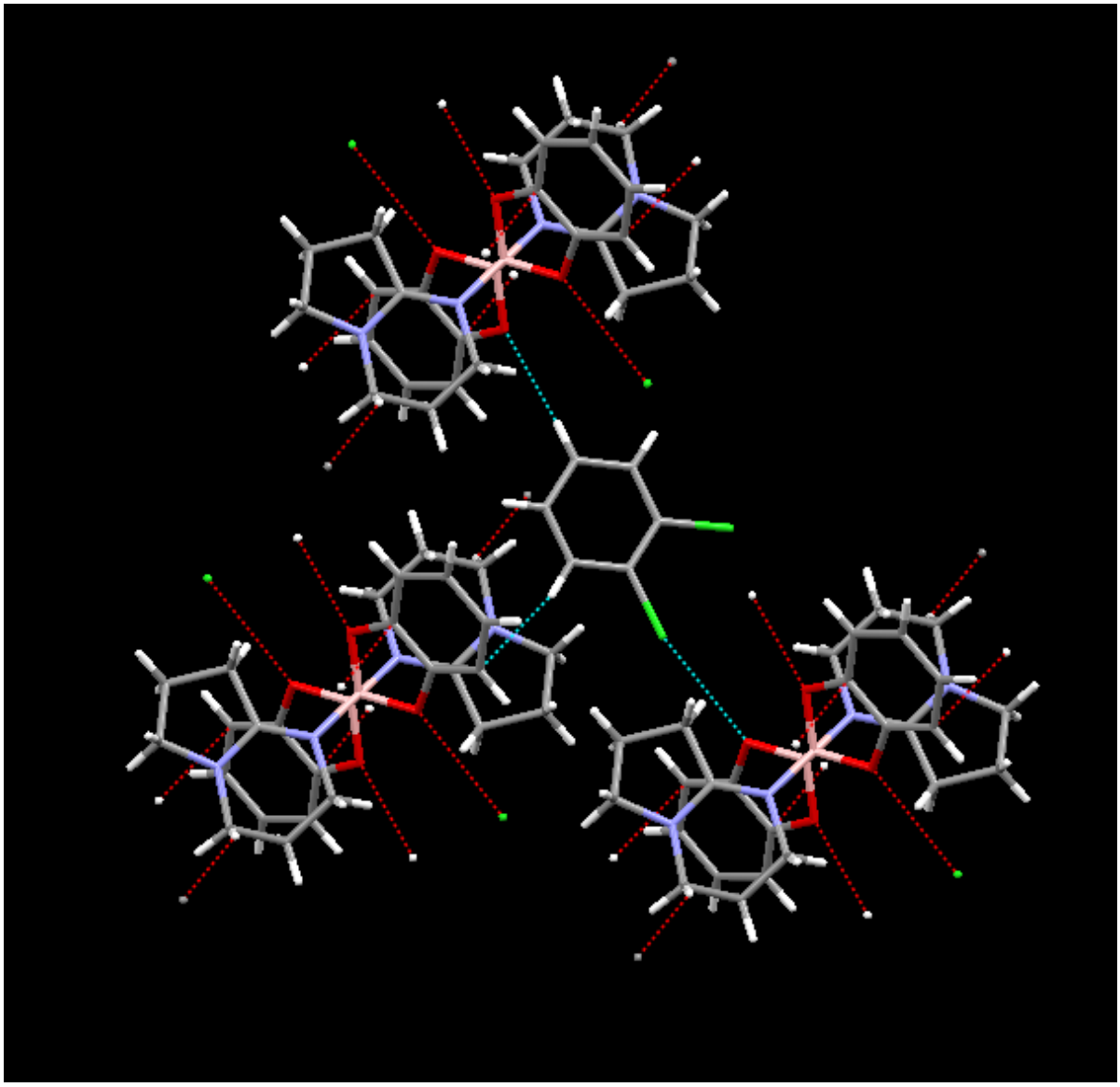
3a – 1,1-isomer of $B_2Cat_2(DBN)_2$
DCB-Cl…OCat and DCB-H…Cat



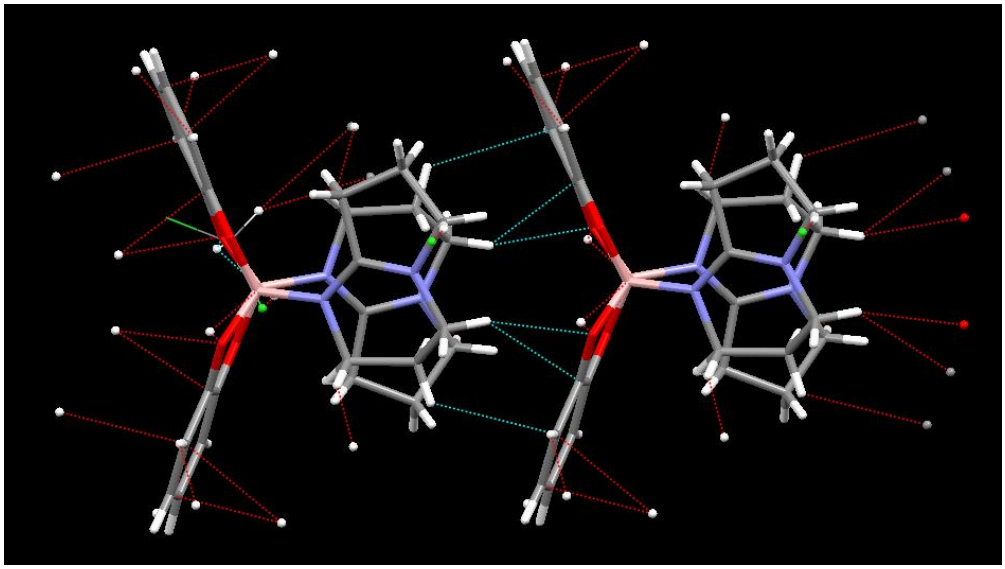
DBN…Cat



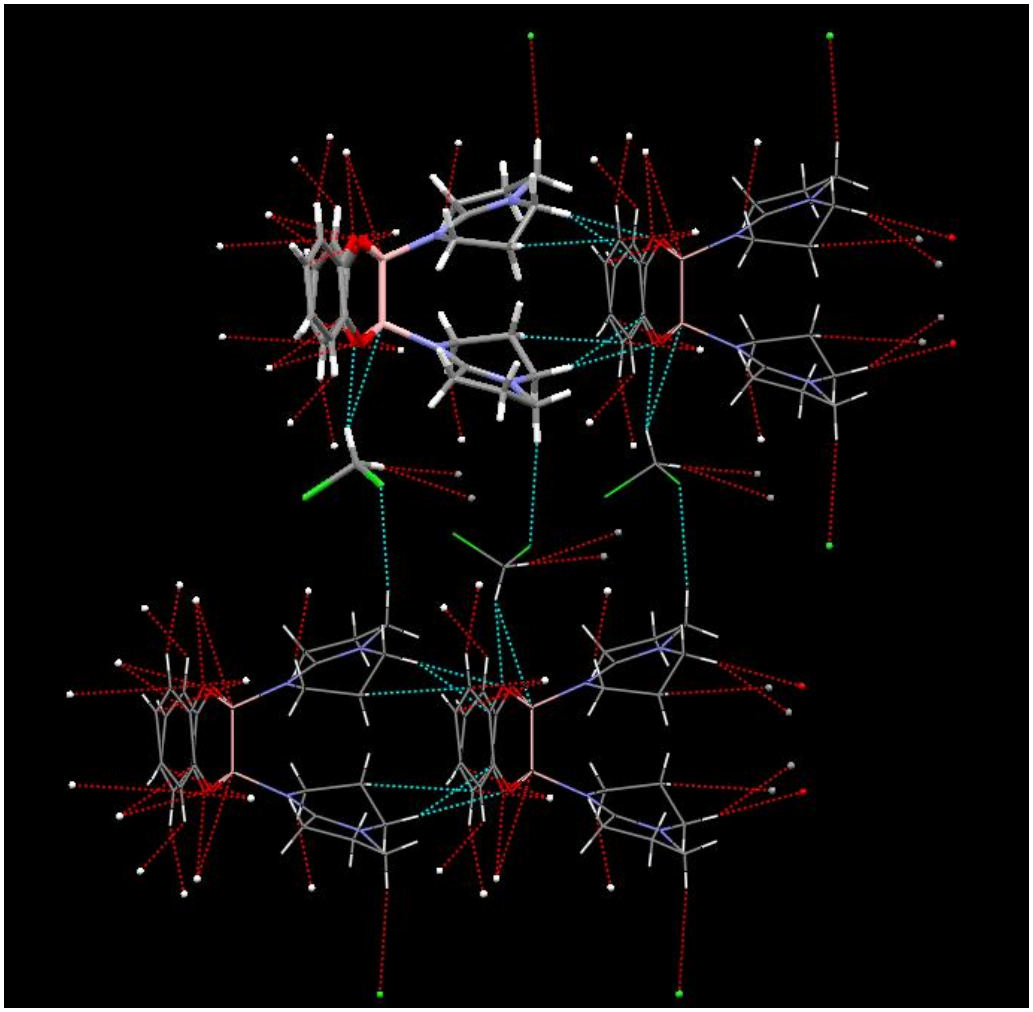
DCB-H…OCat, DCB-H…Cat and DCB-Cl…OCat



3b – 1,2-isomer of $B_2Cat_2(DBN)_2$
DBN…Cat

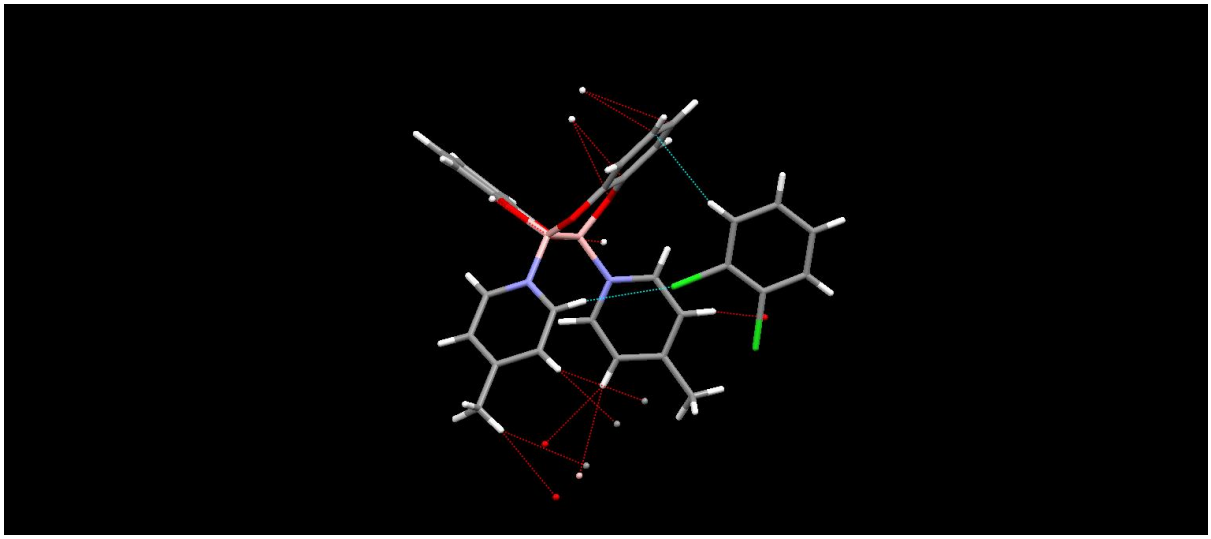


Cat-O…H-DCM-Cl…DBN

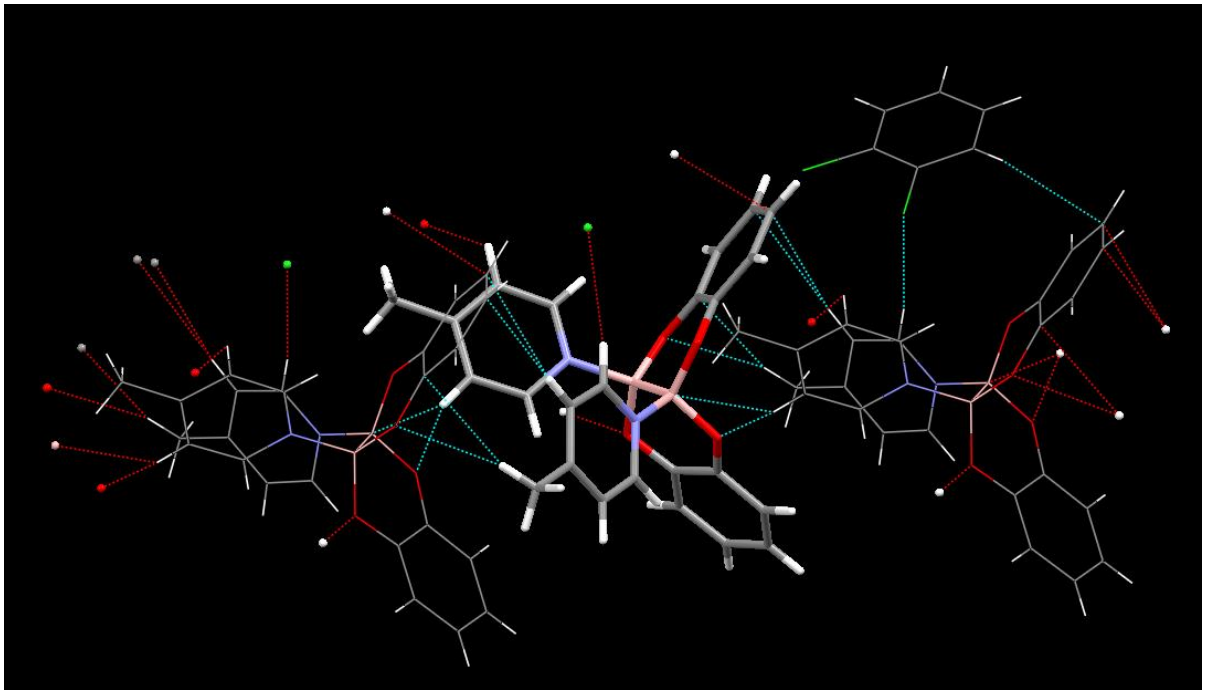


4b$_{(DCB)}$ – 1,2-isomer $B_2Cat_2(pic)_2$•DCB

Bridging DCB: Cat…H-DCB-Cl…pic



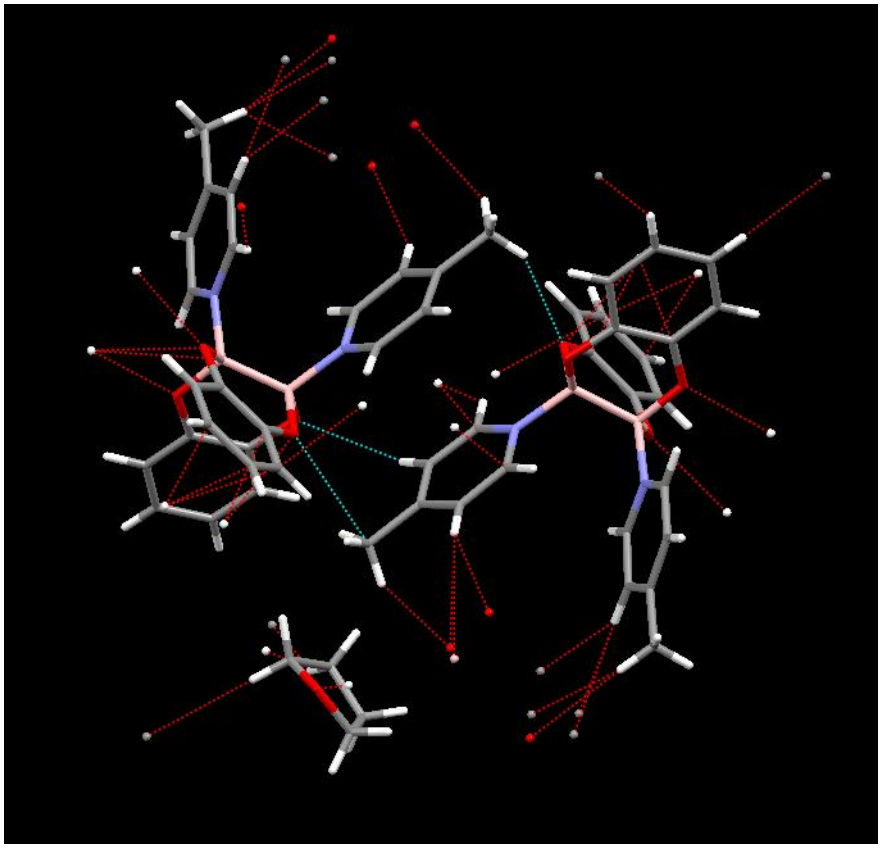
Head to tail chains: Cat…pic-BB-Cat…pic



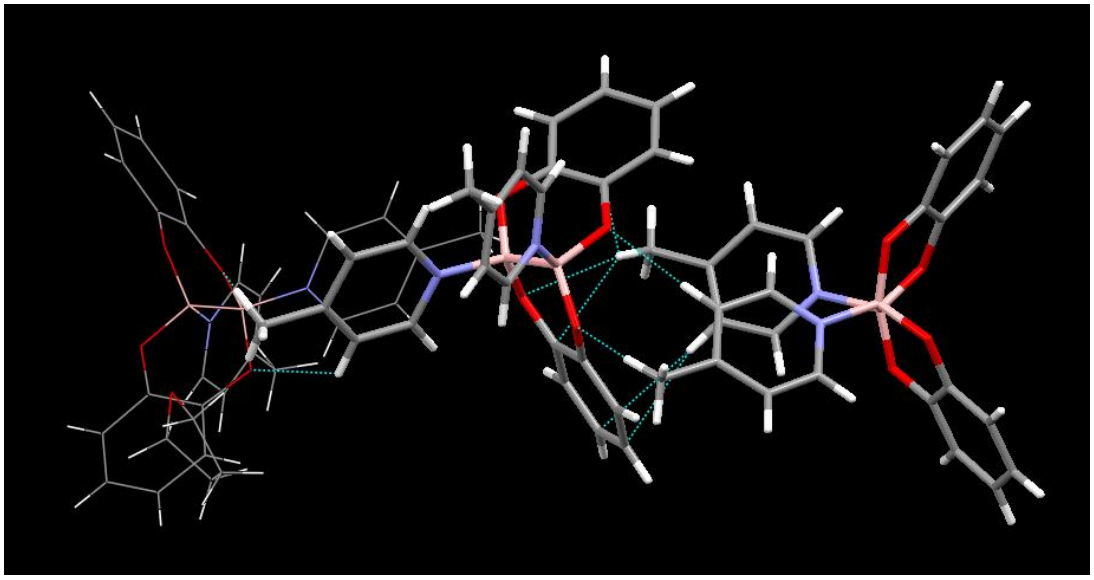
4b$_{(THF)}$ – 1,2-isomer $B_2Cat_2(pic)_2$• THF

This compound crystallised with two independent molecules in the asymmetric unit and displays a complex packing structure, with two distinct sets of close contacts.

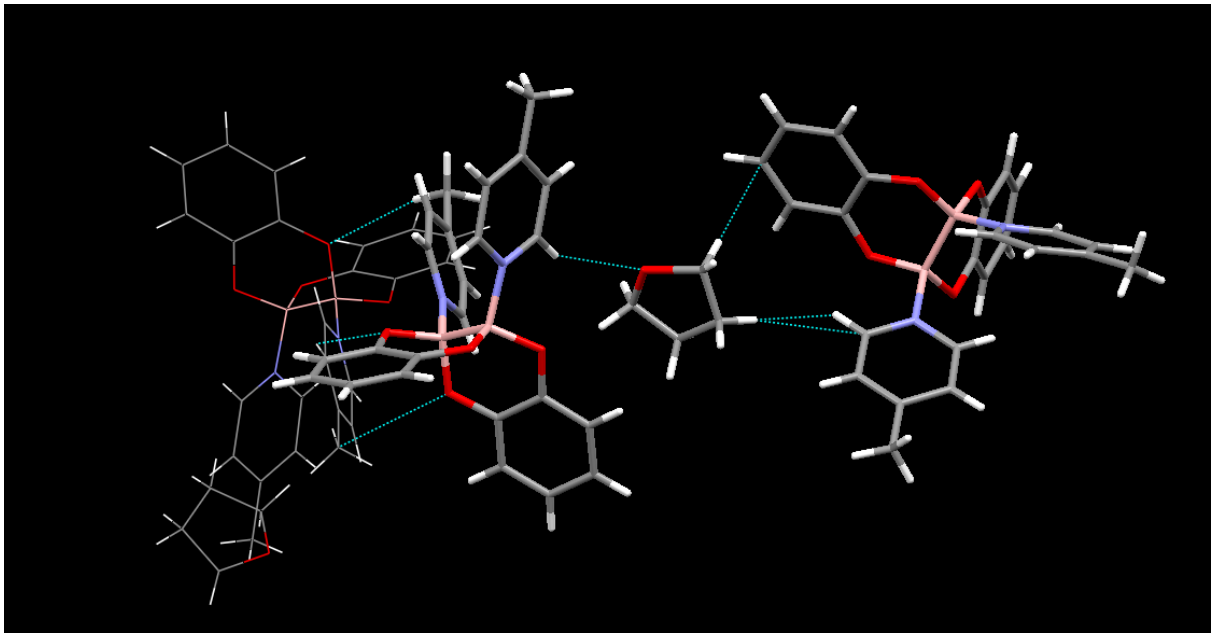
Dimer of independent molecules in asymmetric unit: Cat-O…pic



Head to tail interaction: Cat…pic



Intramolecular bridging THF: Cat…H-THF-H…pic and intermolecular bridging pic…O-THF-H…Cat/pic



3 CrysAlisPro, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171 .NET)
(compiled Oct 27 2011,15:02:11)

3a Bruker Analytical X-ray Systems, Inc., **2006**. Apex2, Version 2 User Manual, M86-E01078, Madison, WI.

4 SIR92, Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M.C.,
Polidori, G. & Camalli, M. *J. Appl. Cryst.* **1994** 27, 435.

4a Palatinus, L. & Chapuis, G. *J. Appl. Cryst.* **2007** 40, 786-790.

5 Crystals, Version 14.40b, January 2012, Betteridge, P.W., Carruthers, J.R., Cooper, R.I., Prout, K. & Watkin, D.J. *J. Appl. Cryst.* **2003** 36, 1487.

6 For a comparison with $B_2Cat_2pic_2$ see: P. Nguyen, C. Dai, N.J. Taylor, W.P. Power, T.B. Marder, N.L. Pickett, N.C. Norman, *Inorg. Chem.* **1995** 34 4290-4291

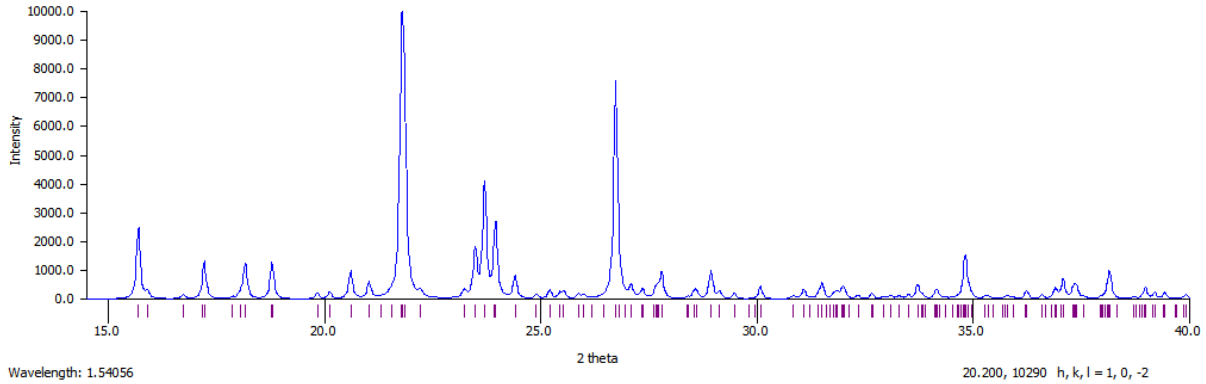
PXRD

Powder samples were mounted on a custom made powder stage sealed under argon with silicone grease and a Kapton® cover (1,1-$Cat_2B_2DBN_2$) and under a drop of crystallography oil (1,2-Cat_2B_2picoline$_2$.DCB_2).Diffraction data for 1,1-$Cat_2B_2DBN_2$ were recorded on a Philips X'Pert power diffractometer using Cu *K*\α radiation, data for 1,1-$Cat_2B_2DBN_2$ was instead recorded using a Bruker AXS, D8 Discover powder diffractometer using Cu *K*\α radiation.

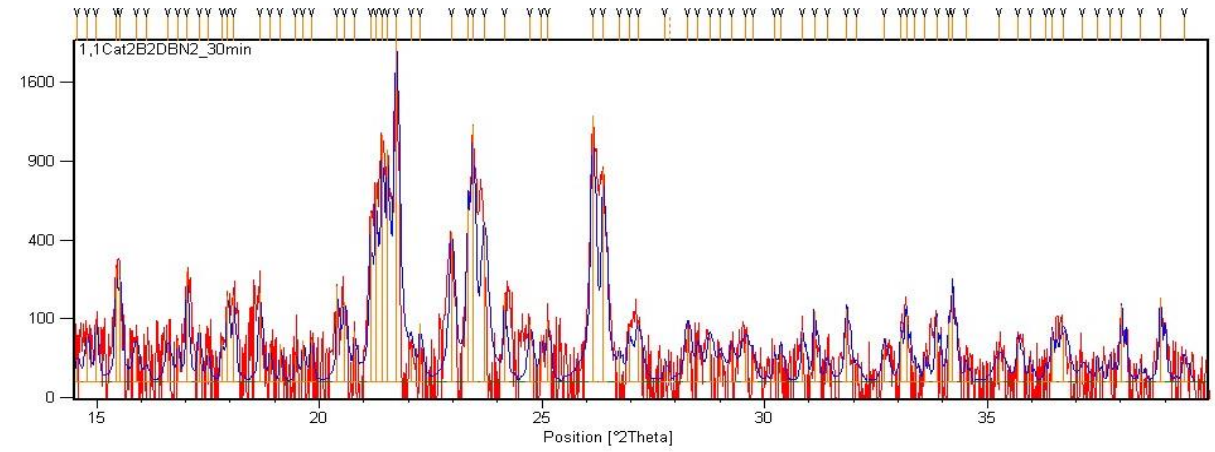
The resulting data were processed using X'Pert HighScore Plus sotftware (version 2.0a (2.0.1) 2004), PANalytical B.V., Almelo, The Netherlands. Powder patterns for molecular structures obtained by single crystal diffraction were simulated using Mercury 2.4.6 (Build RC5) 2011.

3a – 1,1-$B_2Cat_2(DBN)_2$•DCB

Simulated PXRD from single crystal measurement (150 K)

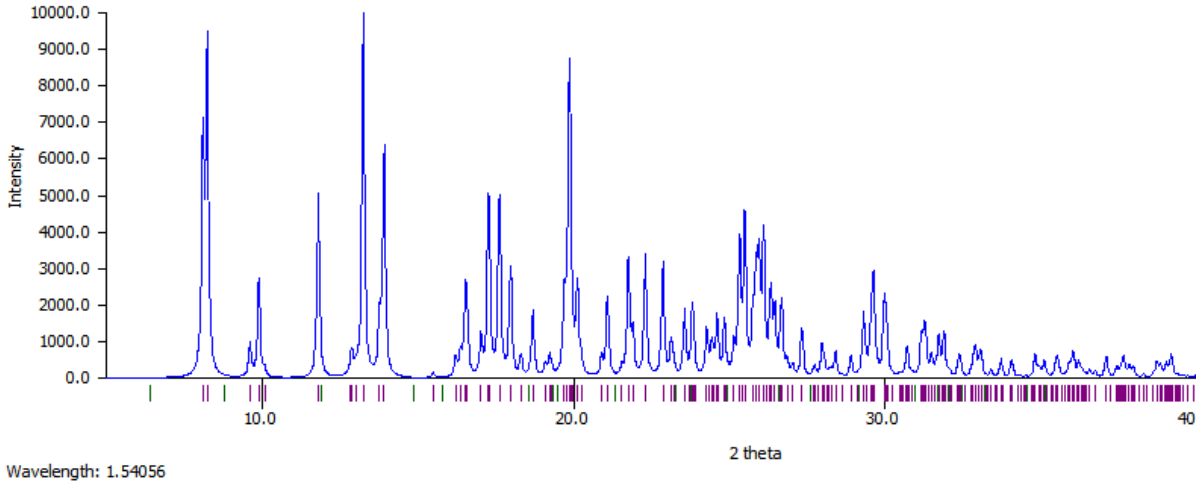


Observed PXRD from microcrystalline powder measurement (r.t.)

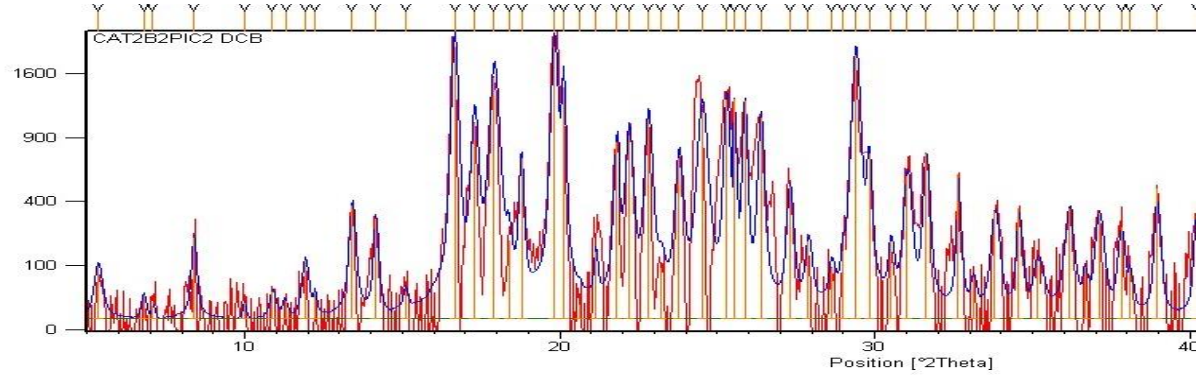


3b$_{(DCB)}$ – 1,2-$B_2Cat_2(pic)_2$•DCB

Simulated PXRD from single crystal measurement (150 K)



Observed PXRD from microcrystalline powder measurement (r.t.)



Computational Work

Calculations were performed using the Gaussian09 suite of programmes[7] Structures were pre-optimised at the HF/3-21G level followed by optimisation at the M06-2X/6-311G(d,p) level with inclusion of a PCM model for solvent correction (DCM)[8]. In all cases, structures were confirmed as minima by frequency analysis and the appropriate absence of imaginary frequencies. Full Cartesian coordinates for the M06-2X/6-311G(d,p) structures, and their relative energies, are provided below.

Computational details

1,5-Diazabicyclo(4.3.0)non-5-ene (DBN) Adducts

Structures

1,5-Diazabicyclo(4.3.0)non-5-ene (DBN) Adducts

- 1,1-B_2Cat_2(DBN) **2a**
- 1,2-B_2Cat_2(DBN) **2b**
- 1,1-$B_2Cat_2(DBN)_2$ **3a**
- 1,2-$B_2Cat_2(DBN)_2$ **3b**

Comparison of key bond metrics of calculated and experimentally determined (X-ray) structures

1,1-B_2Cat_2(DBN) **2a**

1,1-$B_2Cat_2(DBN)_2$ **3a**

1,2-$B_2Cat_2(DBN)_2$ **3b**

7 Gaussian 09, Revision C1, 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, Jr., J. A.; 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, 2009.

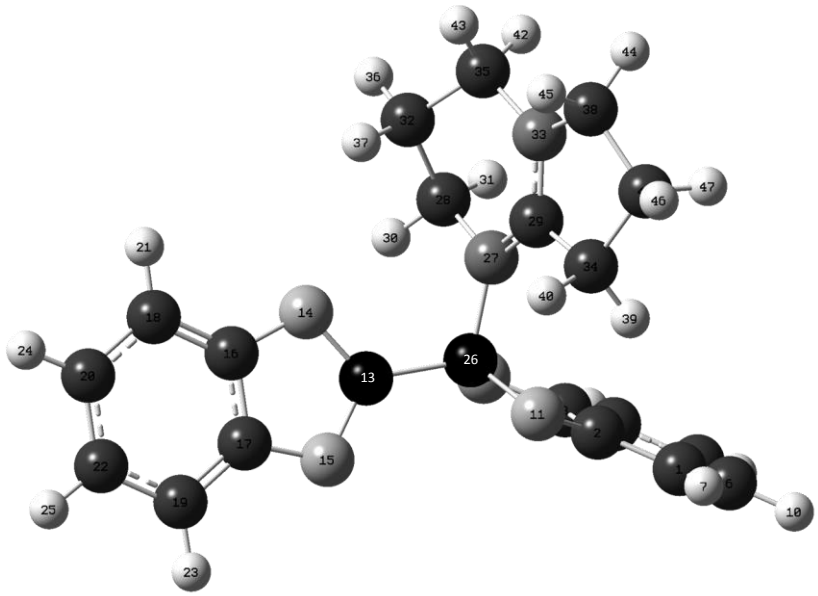
8 http://comp.chem.umn.edu/info/DFT.htm]]

Computational details

Mono Adducts	Bis Adducts

		2a 1,1-B_2Cat_2(DBN)	**2b** 1,2-B_2Cat_2(DBN)	**3a** 1,1-$B_2Cat_2(DBN)_2$	**3b** 1,2-$B_2Cat_2(DBN)_2$	**units**
DBN Adducts	Calculation Method	RM062X	RM062X	RM062X	RM062X	
	Basis Set	6-311G(d,p)	6-311G(d,p)	6-311G(d,p)	6-311G(d,p)	
	Charge	0	0	0	0	
	Spin	Singlet	Singlet	Singlet	Singlet	
	E(RM062X)	-1196.224037	-1196.228322	-1579.664401	-1579.668056	**au**
	Energy (relative)	0	-2.68909	0	-2.29153	**kcalmol^{-1}**
	RMS Gradient Norm	0.00000338	0.00000563	0.00001094	0.00000266	**au**
	Imaginary Freq	0	0	0	0	
	Dipole Moment	11.4762	13.1505	2.5767	21.2058	**Debye**
	Point Group	C1	C1	C1	C1	

2a – 1,1-B_2Cat_2(DBN)



Tag	Symbol	X	Y	Z
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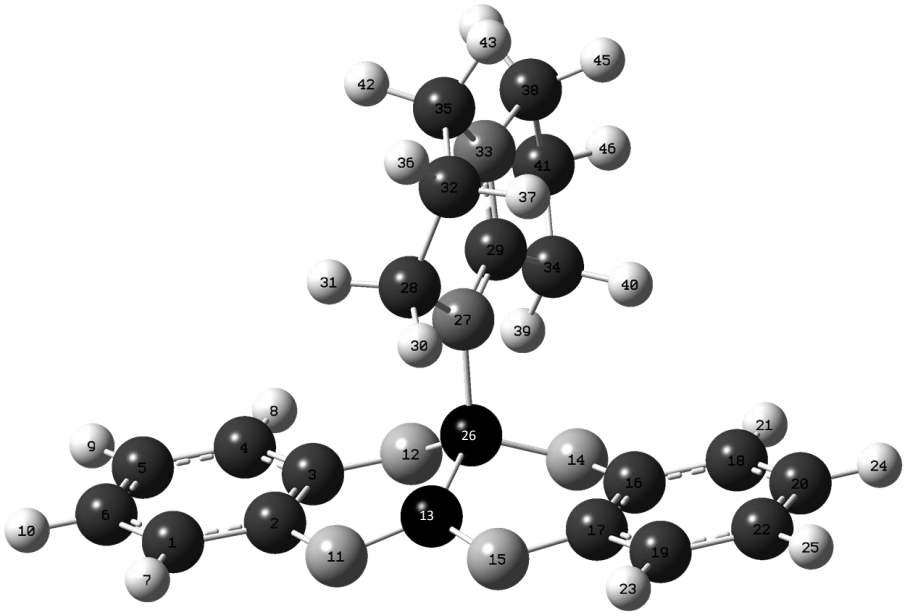
2	C	1.9290220	-2.0797850	0.8086400
3	C	2.0653340	-1.9499890	-0.5828060
4	C	3.1514800	-2.4875790	-1.2430220
5	C	4.1150510	-3.1647000	-0.4772760
6	C	3.9794830	-3.2898200	0.8980480
7	H	2.7473820	-2.8420540	2.6385470
8	H	3.2479510	-2.3879690	-2.3174370
9	H	4.9770940	-3.5953100	-0.9725740
10	H	4.7356900	-3.8169960	1.4671490
11	O	0.7799270	-1.4942330	1.2275360
12	O	1.0134020	-1.2768640	-1.1020710
13	B	-1.4157170	-0.6615040	-0.0775650
14	O	-2.1606360	0.5001590	-0.3269020
15	O	-2.2905240	-1.7424100	0.0460370
16	C	-3.4767210	0.1215330	-0.3590900
17	C	-3.5553260	-1.2475080	-0.1298690
18	C	-4.5994760	0.8942970	-0.5724470
19	C	-4.7634990	-1.9135250	-0.1003970
20	C	-5.8296770	0.2308330	-0.5461030
21	H	-4.5244300	1.9591660	-0.7512960
22	C	-5.9095100	-1.1419790	-0.3149050
23	H	-4.8126680	-2.9795270	0.0795580
24	H	-6.7387880	0.7959810	-0.7096410
25	H	-6.8794270	-1.6233400	-0.3010060
26	B	0.2934840	-0.7080920	0.0768590
27	N	0.8101760	0.8152840	0.1907090
28	C	0.7051670	1.5782060	-1.0627870
29	C	1.1471610	1.4729730	1.2650850
30	H	0.0525260	1.0212470	-1.7336770
31	H	1.6948090	1.6250960	-1.5284510
32	C	0.1615410	2.9757580	-0.8061890
33	N	1.3729390	2.7917330	1.2895830
34	C	1.3279660	0.9121670	2.6551530

35	C	1.0671130	3.6929910	0.1837870
36	H	0.1093720	3.5397850	-1.7374400
37	H	-0.8477350	2.8872850	-0.3975410
38	C	1.6706630	3.3056480	2.6261260
39	H	1.8746240	-0.0252270	2.6432820
40	H	0.3362290	0.7118800	3.0712090
41	C	2.0579010	2.0421620	3.3960640
42	H	2.0000430	4.0126670	-0.2895990
43	H	0.5785040	4.5774470	0.5989990
44	H	2.4734740	4.0423780	2.5720030
45	H	0.7781870	3.7901340	3.0366660
46	H	1.7853080	2.0998800	4.4478000
47	H	3.1352390	1.8868020	3.3267330

2b – 1,2-B_2Cat_2(DBN)



Tag	Symbol	X	Y	Z
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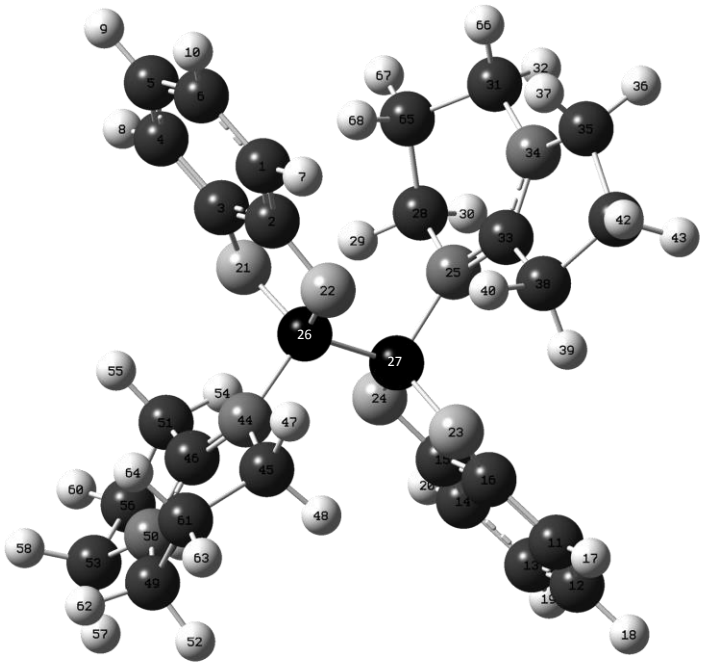
4	C	-3.4958230	-0.7341130	-1.3505420
5	C	-4.6850410	-1.1033410	-0.7330130
6	C	-4.6560160	-1.8357570	0.4484040
7	H	-3.3689950	-2.7860840	1.9038170
8	H	-3.4967450	-0.1596760	-2.2696390
9	H	-5.6305220	-0.8107470	-1.1736410
10	H	-5.5746310	-2.1260640	0.9425070
11	O	-1.0690340	-2.2986400	0.9474990
12	O	-1.1372270	-0.7196300	-1.4834940
13	B	0.0874380	-1.6868320	0.5314540
14	O	1.2589880	-0.7010570	-1.5012040
15	O	1.2703090	-2.2477430	0.9472360
16	C	2.3962600	-1.0226180	-0.8470830
17	C	2.4188790	-1.7582540	0.3604830
18	C	3.6184840	-0.6308310	-1.3950830
19	C	3.6267710	-2.0644410	0.9711790
20	C	4.8258780	-0.9477370	-0.7833920
21	H	3.5906380	-0.0752240	-2.3253120
22	C	4.8336270	-1.6612100	0.4099420
23	H	3.5951130	-2.6360800	1.8913650
24	H	5.7564690	-0.6299710	-1.2381230
25	H	5.7666450	-1.9111530	0.8990440
26	B	0.0669730	-0.4983130	-0.6561850
27	N	0.0609660	1.0044580	-0.1315120
28	C	-0.1321570	1.3004830	1.2941600
29	C	0.1054420	2.0141080	-0.9606310
30	H	0.3203360	0.4905970	1.8678380
31	H	-1.2047400	1.3104090	1.5187250
32	C	0.5081800	2.6307620	1.6702930
33	N	-0.0028890	3.2922330	-0.6035940

34	C	0.3061130	1.9208430	-2.4499290
35	C	-0.0364180	3.7421060	0.7826930
36	H	0.3094080	2.8593640	2.7171450
37	H	1.5902070	2.5545620	1.5363730
38	C	0.1167940	4.2170090	-1.7330150
39	H	-0.2466280	1.0857730	-2.8744750
40	H	1.3700050	1.7426410	-2.6272390
41	C	-0.1414000	3.3060520	-2.9376240
42	H	-1.0634160	4.0031680	1.0537390
43	H	0.5753110	4.6433020	0.8599200
44	H	-0.6144820	5.0199020	-1.6323450
45	H	1.1206270	4.6543660	-1.7441360
46	H	0.3950620	3.6336760	-3.8255270
47	H	-1.2089680	3.2915590	-3.1616090

3a – 1,1-$B_2Cat_2(DBN)_2$



Tag	Symbol	X	Y	Z
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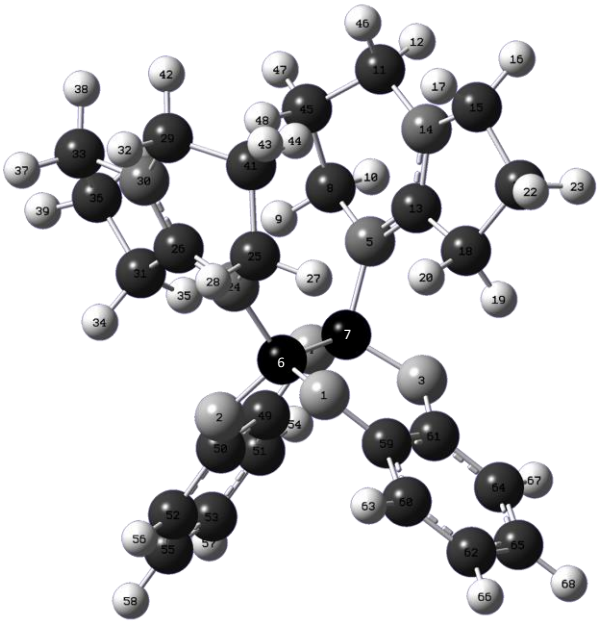
4	C	-1.09185	0.621368	-3.43912
5	C	-1.0389	1.290094	-4.67463
6	C	-0.0287	2.199876	-4.95043
7	H	1.764328	3.186502	-4.20629
8	H	-1.87277	-0.09678	-3.21798
9	H	-1.80003	1.089208	-5.41944
10	H	-0.00535	2.705173	-5.90868
11	C	4.770724	0.295718	2.899394
12	C	4.847198	-0.58113	3.995708
13	C	3.89315	-1.57026	4.186229
14	C	2.822947	-1.7232	3.28824
15	C	2.751909	-0.86153	2.212334
16	C	3.718494	0.141762	2.018656
17	H	5.508682	1.074608	2.746143
18	H	5.664889	-0.47956	4.699441
19	H	3.970538	-2.23648	5.037331
20	H	2.070785	-2.4907	3.428449
21	O	0.060781	0.352345	-1.28785
22	O	1.771577	1.91229	-1.75228
23	O	3.426747	0.873837	0.922601
24	O	1.810826	-0.80566	1.247858

25	N	3.018357	-0.81743	-0.92548
26	B	1.17818	1.112507	-0.62012
27	B	2.33799	0.140847	0.202372
28	C	2.222174	-1.99325	-1.30945
29	H	1.25886	-1.90512	-0.81284
30	H	2.718399	-2.89489	-0.93442
31	C	3.413179	-2.10141	-3.48725
32	H	3.889313	-3.07871	-3.36263
33	C	3.952339	-0.43662	-1.74857
34	N	4.255418	-1.06885	-2.8938
35	C	5.268786	-0.37029	-3.6824
36	H	5.959023	-1.0876	-4.12942
37	H	4.780676	0.192544	-4.48646
38	C	4.830628	0.779605	-1.60428
39	H	5.19804	0.892391	-0.58932
40	H	4.202974	1.646629	-1.83165
41	C	5.93051	0.545546	-2.6504
42	H	6.295189	1.469961	-3.09417
43	H	6.773471	0.028334	-2.18952
44	N	0.498404	2.191681	0.3705
45	C	1.144257	3.498331	0.550039
46	C	-0.43734	1.874725	1.217654
47	H	1.598045	3.769686	-0.40008
48	H	1.945318	3.394508	1.29035
49	C	-0.53302	4.094196	2.29559
50	N	-0.89349	2.687625	2.179801
51	C	-1.17017	0.560009	1.284812
52	H	0.138132	4.226805	3.14965
53	C	-1.96118	2.087726	2.978084
54	H	-0.48968	-0.27168	1.116574
55	H	-1.92514	0.549878	0.495084
56	C	-1.79162	0.593422	2.688467
57	H	-1.82624	2.340924	4.030951
58	H	-2.93286	2.471838	2.647687
59	H	-1.09283	0.161774	3.407326
60	H	-2.73249	0.050032	2.749156
61	C	0.130304	4.542496	0.999505
62	H	-1.44469	4.664421	2.491463
63	H	0.619387	5.50541	1.148217
64	H	-0.62693	4.663285	0.220572
65	C	2.046813	-2.06524	-2.81985
66	H	3.336262	-1.89716	-4.5578

3b – 1,2-$B_2Cat_2(DBN)_2$



Tag	Symbol	X	Y	Z
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4	O	-0.82873	-0.27121	1.403262
5	N	0.186003	-0.22068	-0.80038
6	B	1.814361	-0.6693	1.450432
7	B	0.296435	-0.89586	0.664043
8	C	-0.50459	1.067005	-0.97546
9	H	-0.66604	1.495138	0.009638
10	H	-1.49193	0.87512	-1.40875
11	C	0.545016	1.352809	-3.21833
12	H	-0.35042	1.362198	-3.84639
13	C	0.83616	-0.67688	-1.83353
14	N	0.966112	-0.02464	-2.99885
15	C	1.830152	-0.71157	-3.95784
16	H	1.400595	-0.64994	-4.95896
17	H	2.813674	-0.2272	-3.97301
18	C	1.560513	-1.99773	-1.91769
19	H	0.933218	-2.79988	-1.54073
20	H	2.4488	-1.95806	-1.28152
21	C	1.888539	-2.14029	-3.41238
22	H	2.856404	-2.60587	-3.58647
23	H	1.124476	-2.7483	-3.8973
24	N	2.730964	0.522862	0.869477
25	C	3.929758	0.244202	0.063377
26	C	2.40557	1.774735	1.014902

27	H	3.874197	-0.78567	-0.27287
28	H	4.80962	0.321713	0.711113
29	C	4.089383	2.642735	-0.57069
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31	C	1.320679	2.31733	1.91077
32	H	5.054688	2.860516	-0.10288
33	C	2.514543	4.106202	0.822099
34	H	1.691888	2.269588	2.937993
35	H	0.414584	1.717507	1.869456
36	C	1.147401	3.760175	1.419959
37	H	3.190712	4.551222	1.559
38	H	2.453581	4.77052	-0.04171
39	H	0.856729	4.442486	2.215874
40	H	0.38604	3.799887	0.637341
41	C	4.052049	1.215979	-1.10213
42	H	3.928319	3.371051	-1.36935
43	H	4.957869	1.008316	-1.67208
44	H	3.194666	1.089448	-1.77197
45	C	0.28218	2.014034	-1.87318
46	H	1.342683	1.866417	-3.76202
47	H	-0.27416	2.940853	-2.01769
48	H	1.231324	2.264452	-1.3921
49	C	-0.78702	-0.34456	2.752791
50	C	0.428881	-0.39198	3.478983
51	C	-1.99178	-0.33107	3.454259
52	C	0.372056	-0.41733	4.873495
53	C	-2.03007	-0.35148	4.845561
54	H	-2.90406	-0.29774	2.868877
55	C	-0.83861	-0.3975	5.559324
56	H	1.31665	-0.45146	5.404963
57	H	-2.98319	-0.33803	5.360601
58	H	-0.84438	-0.41808	6.642665
59	C	2.122502	-3.06982	1.372292
60	C	2.889105	-4.14931	1.810627
61	C	0.78496	-3.30018	0.969021
62	C	2.379082	-5.44408	1.847586
63	H	3.9084	-3.93943	2.11576
64	C	0.287441	-4.6034	1.016075
65	C	1.067442	-5.67149	1.449691
66	H	3.002918	-6.26113	2.189996
67	H	-0.7385	-4.75203	0.698028
68	H	0.648218	-6.67036	1.473972
67	H	1.473198	-2.95099	-3.09464
68	H	1.494096	-1.18064	-3.15068

Comparison of key bond metrics of calculated and experimentally determined (X-ray) structures

	2a 1,1-B_2Cat_2(DBN)				
	metric	Calculated value	Experimental value	3 x esd	Exp - Calc
Bond lengths	BB	1.7168	1.712	0.03	-0.0048
	B-C/N	1.61264	1.61	0.027	-0.00264
	B-O sp3 a	1.47604	1.492	0.024	0.01596
	B-O sp3 b	1.49387	1.5	0.024	0.00613
	B-O sp2 a	1.39604	1.391	0.024	-0.00504
	B-O sp2 b	1.40233	1.416	0.024	0.01367
Bond angles	O-B-O sp3	104.69172	105	1.5	0.30828
	O-B-O sp2	108.92075	109	1.5	0.07925

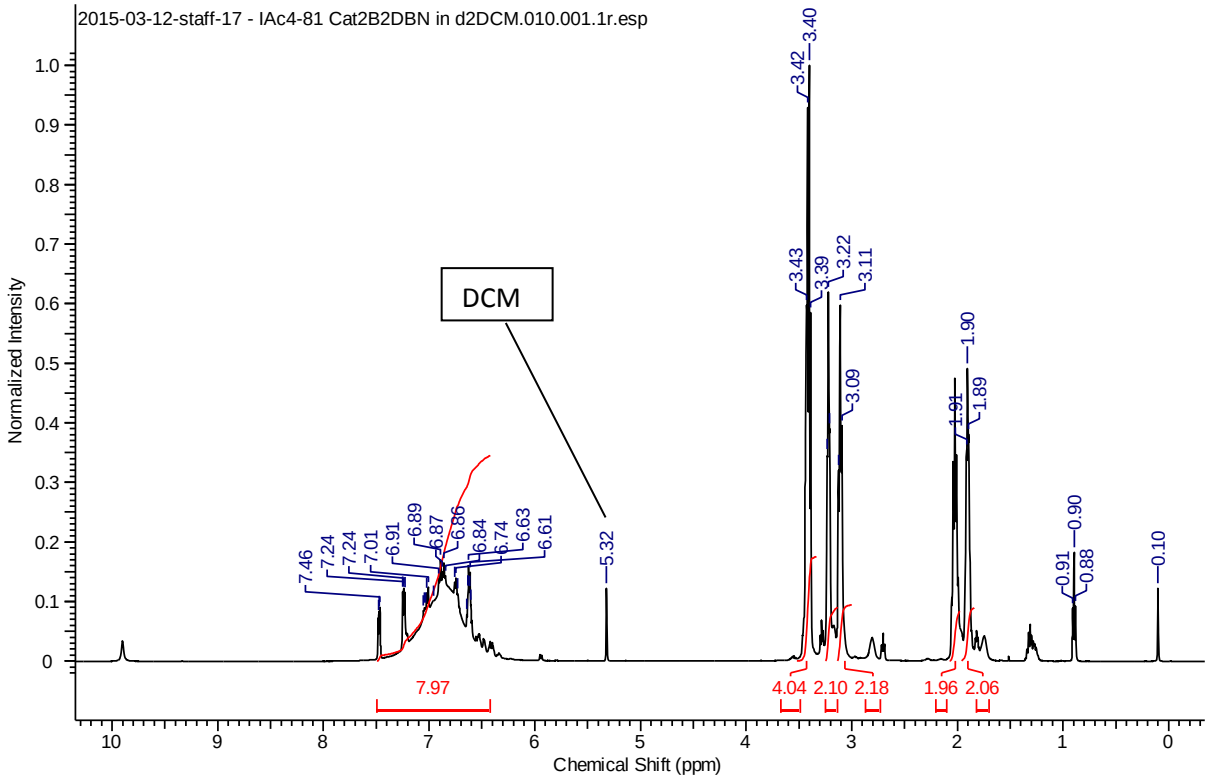
	3a 1,1-$B_2Cat_2(DBN)_2$				
	metric	Calculated value	Experimental value	3 x esd	Exp - Calc
Bond lengths	BB	1.72214	1.715	0.015	-0.00714
	B-C/N	1.62888	1.631	0.009	0.00212
	B-C/N	1.61494	1.631	0.009	0.01606
	B-O sp3 a	1.49713	1.508	0.009	0.01087
	B-O sp3 b	1.5056	1.506	0.009	0.0004
	B-O sp3 c	1.50783	1.508	0.009	0.00017
	B-O sp3 d	1.50741	1.506	0.009	-0.00141
Bond angles	O-B-O sp3	103.20071	103.4	0.48	0.19929
	O-B-O sp3	103.0973	103.4	0.48	0.3027

	3b 1,2-$B_2Cat_2(DBN)_2$				
	metric	Calculated value	Experimental value	3 x esd	Exp - Calc
Bond lengths	BB	1.72448	1.756	0.045	0.03152
	B-C/N	1.61636	1.617	0.024	0.00064
	B-C/N	1.61211	1.617	0.024	0.00489
	B-O sp3 a	1.48447	1.479	0.027	-0.00547
	B-O sp3 b	1.48412	1.461	0.027	-0.02312
	B-O sp3 c	1.48317	1.461	0.027	-0.02217
	B-O sp3 d	1.48763	1.479	0.027	-0.00863
Bond angles	O-B-O sp3	107.6648	106.3	1.5	-1.3648
	O-B-O sp3	108.49136	106.3	1.5	-2.19136

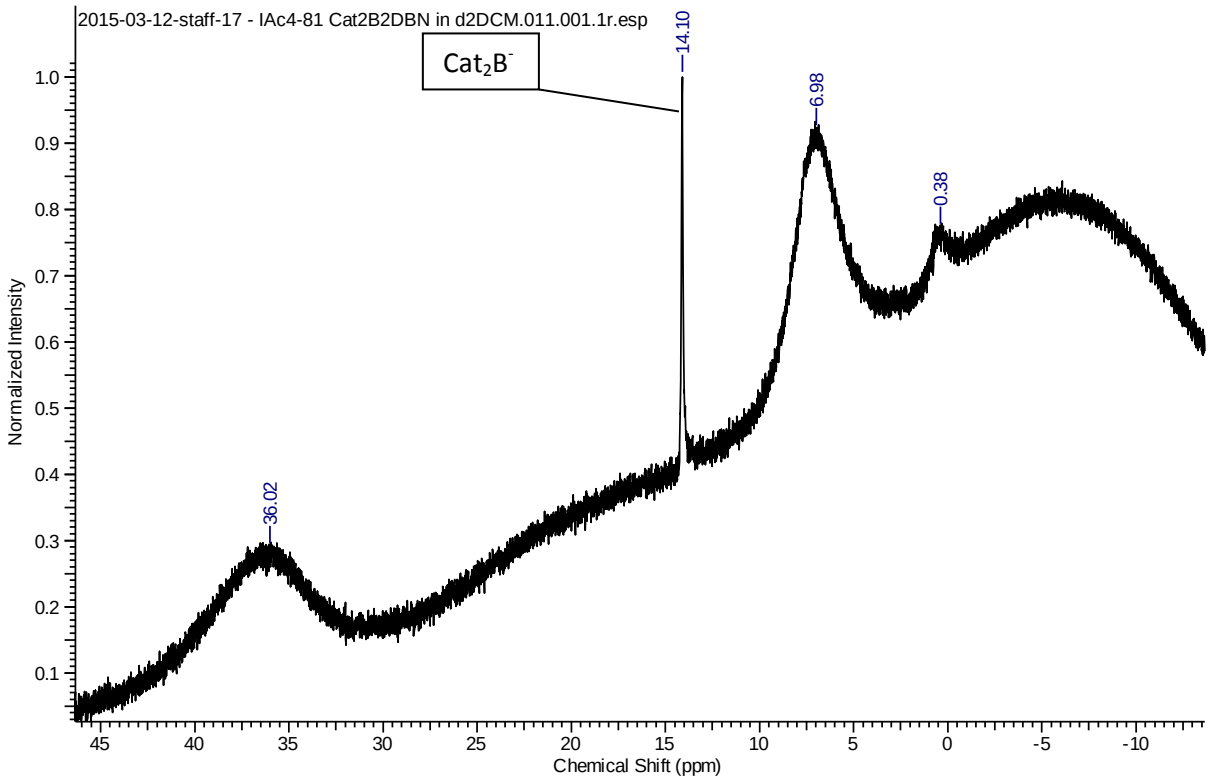
NMR Spectra

2 – $B_2Cat_2(DBN)$

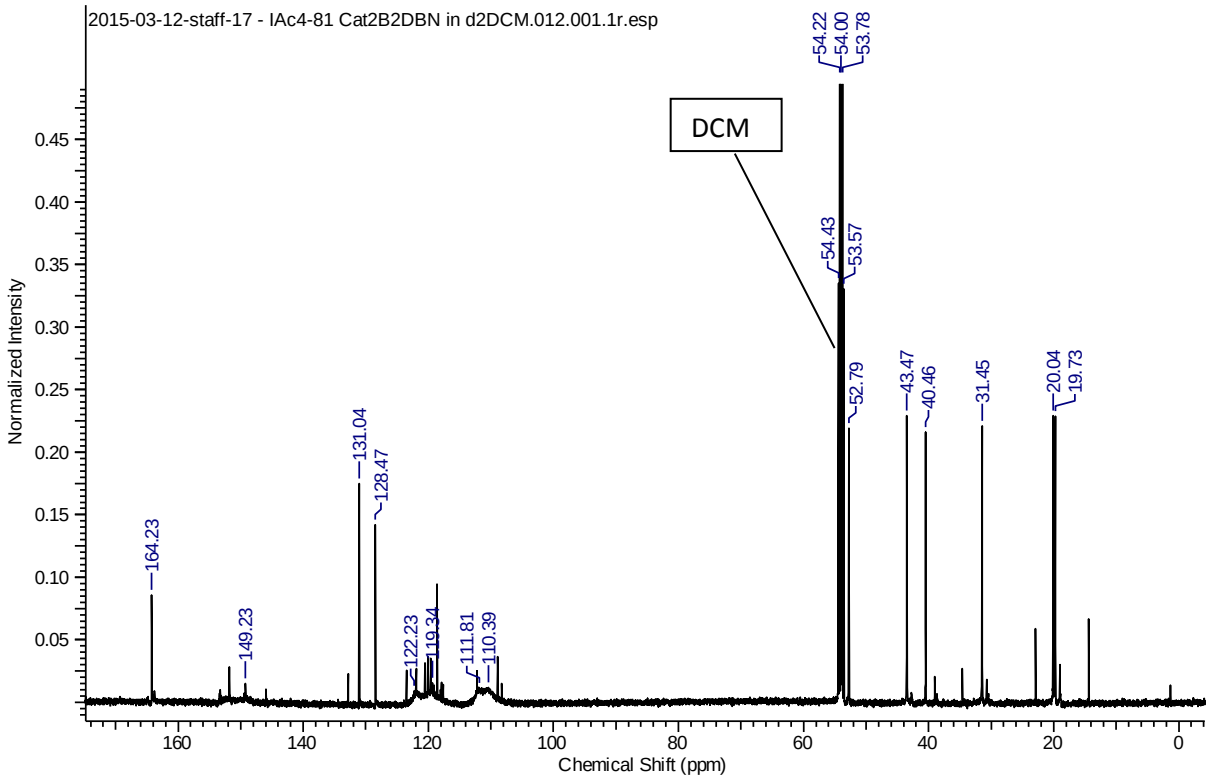
^1H NMR (d_2-DCM, 500 MHz)



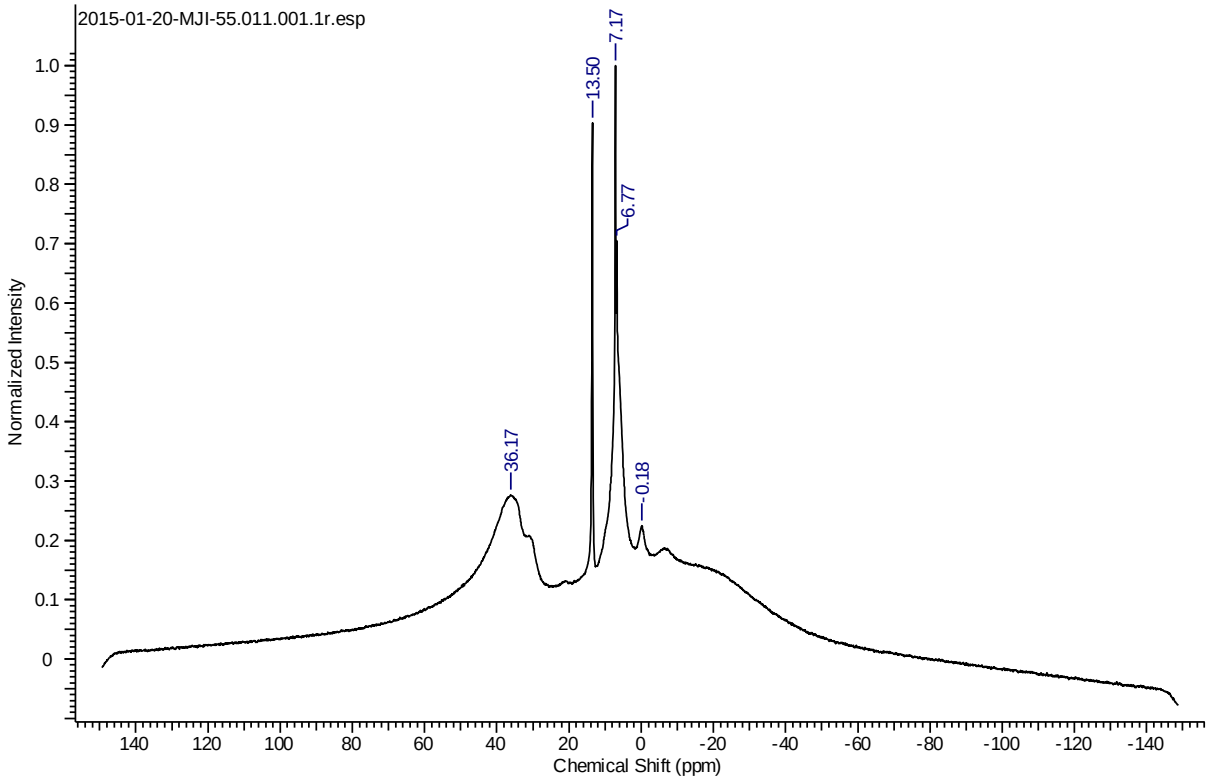
^{11}B NMR (d_2-DCM, 160 MHz)



^{13}C NMR (d_2-DCM, 126 MHz)

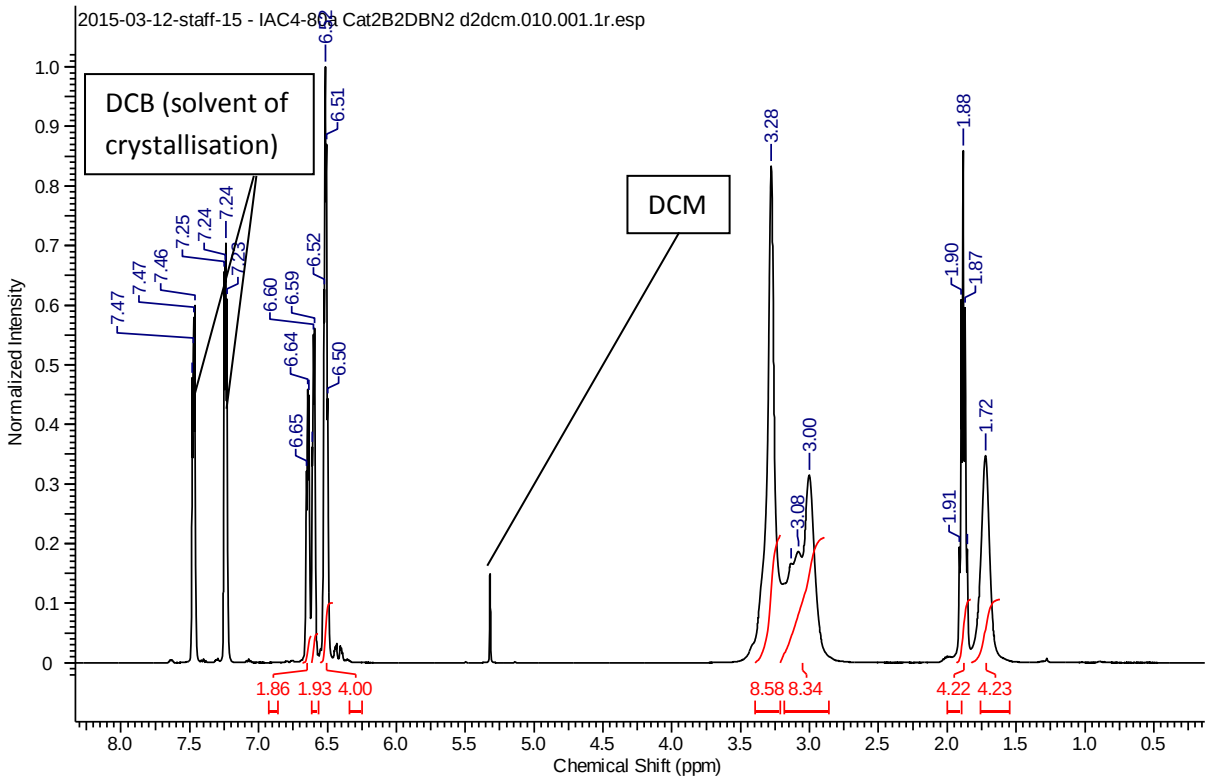


2 – B_2Cat_2(DBN) run in protio DCM with a d6-DMSO capillary insert. The pair of upfield (sp^2/sp^3) resonances are more clearly visible in this spectra (sharp resonance at 13.5 ppm attributable to the $BCat_2$ anion).

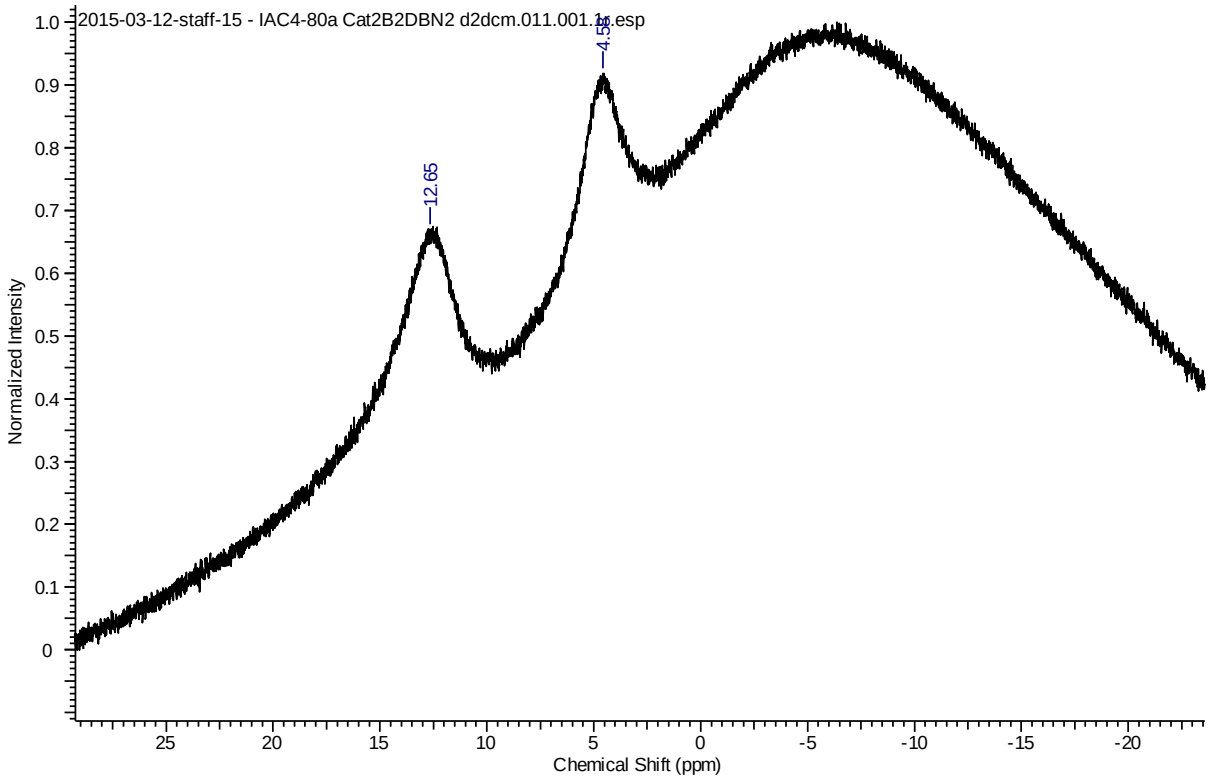


3 – $B_2Cat_2(DBN)_2$

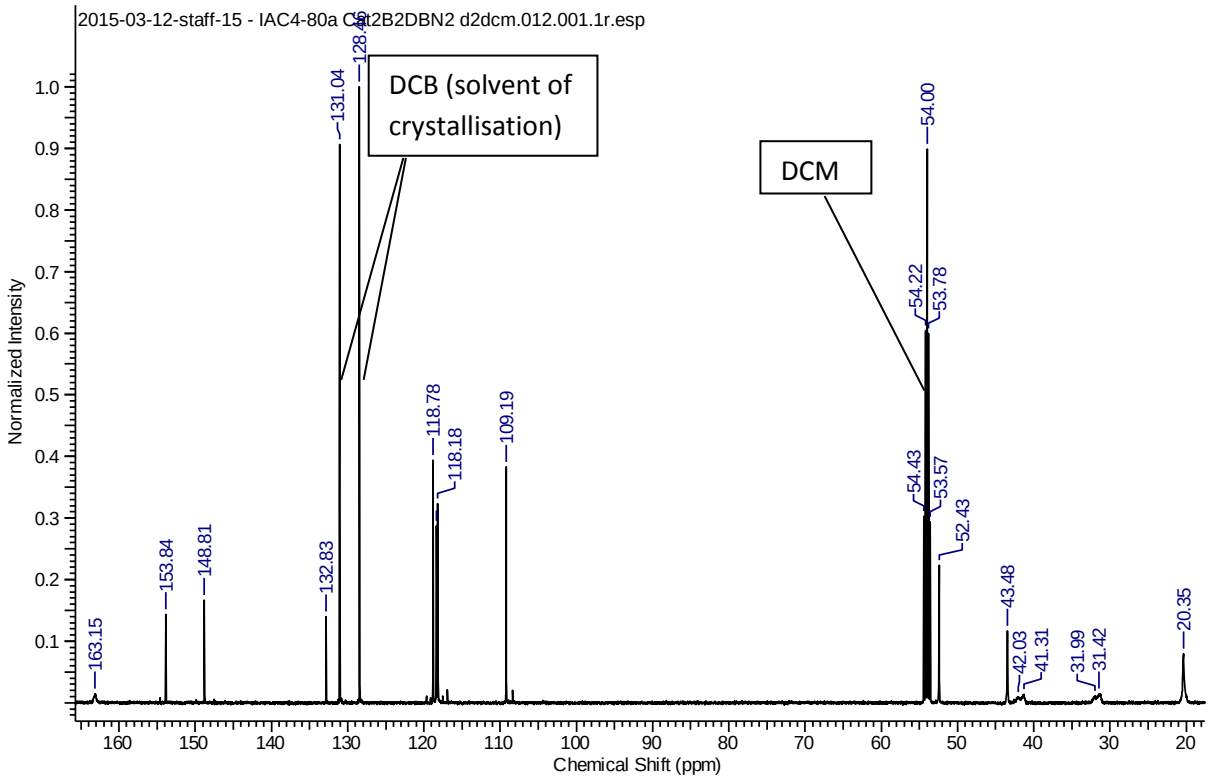
^{1}H NMR (d_2-DCM, 500 MHz)



^{11}B NMR (d_2-DCM, 160 MHz)

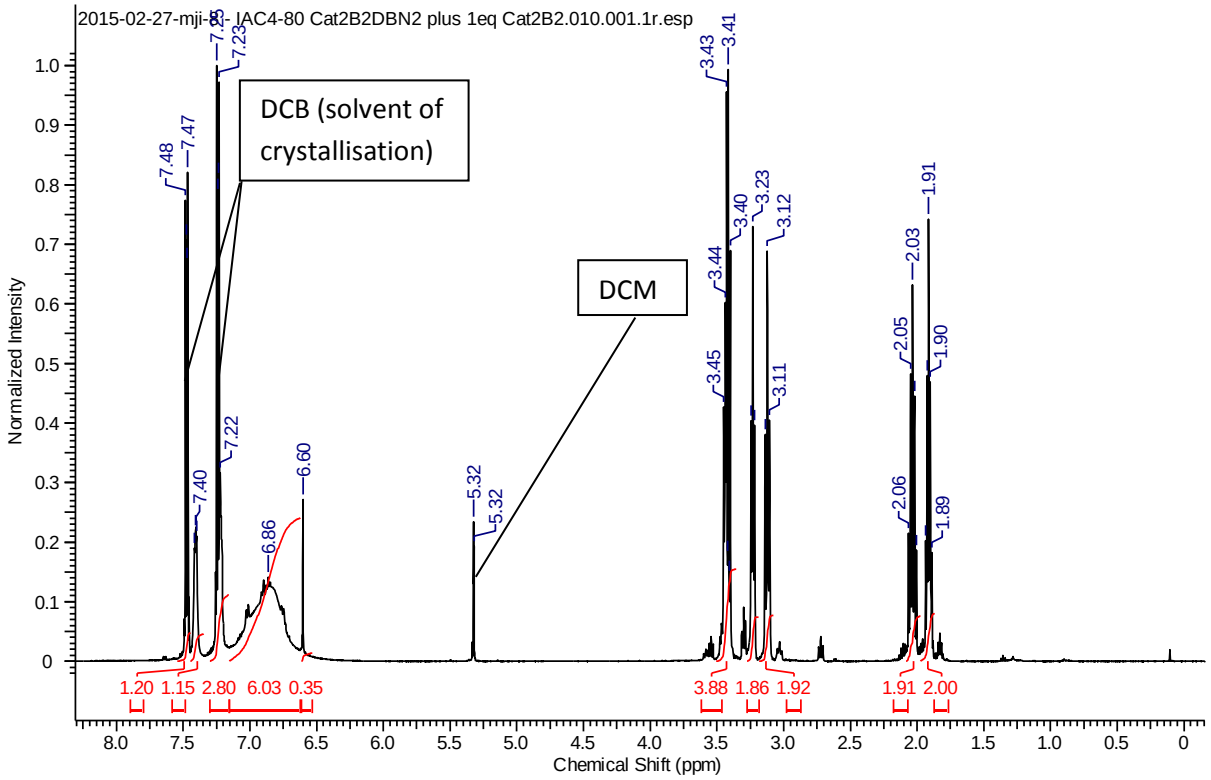


^{13}C NMR (d_2-DCM, 126 MHz)

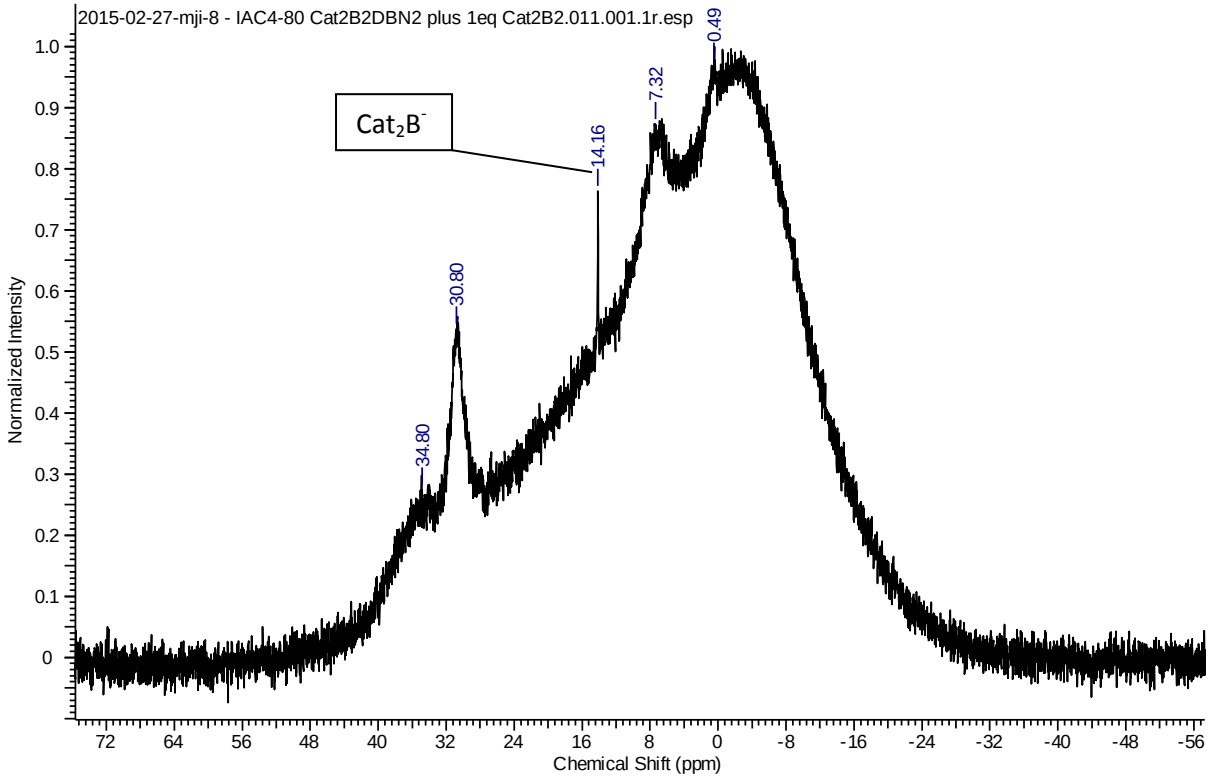


Ligand redistribution between **3** – $B_2Cat_2(DBN)_2$ and 1 equivalent of **1** – B_2Cat_2

^{1}H NMR (d_2-DCM, 500 MHz)

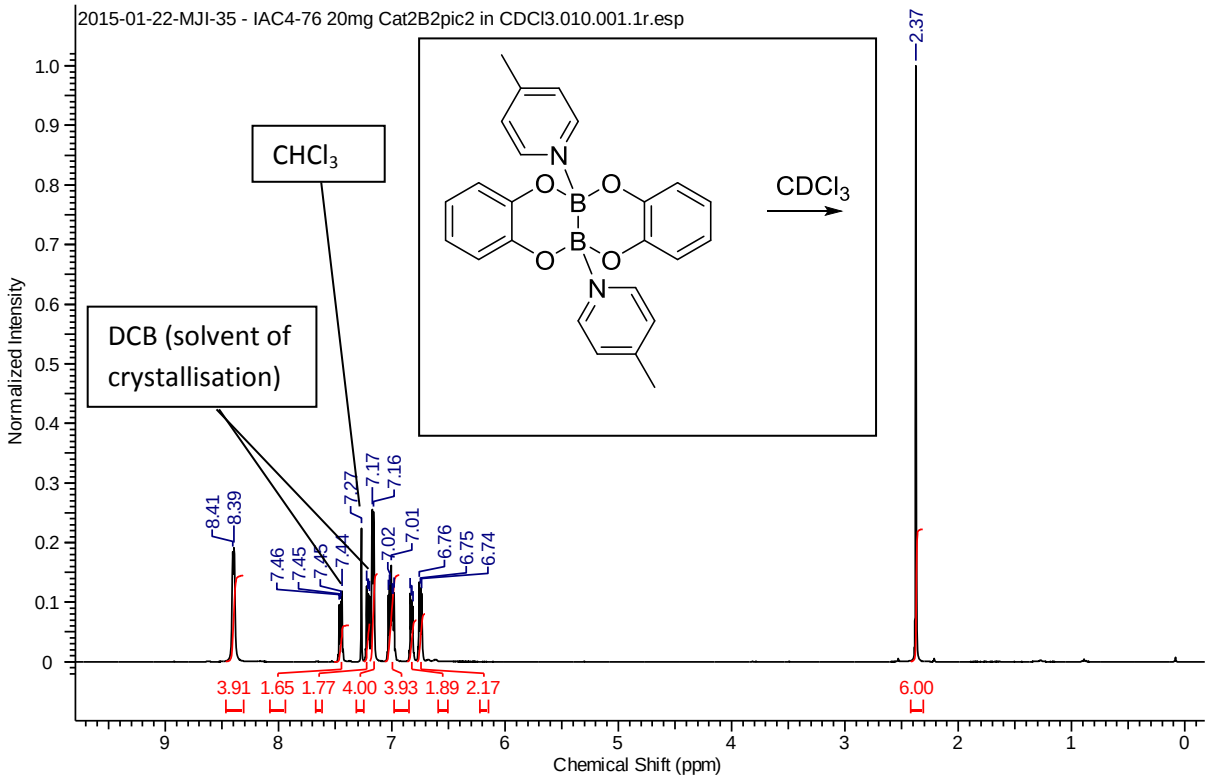


^{11}B NMR (d_2-DCM, 160 MHz)

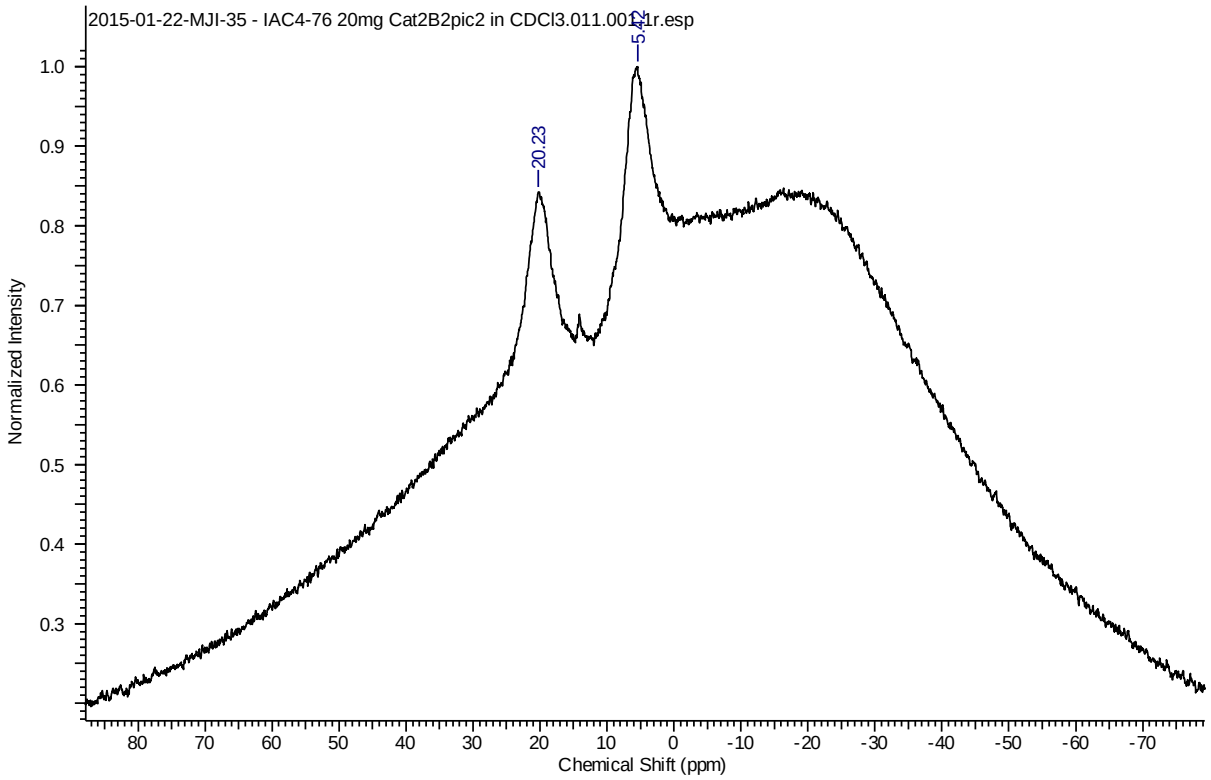


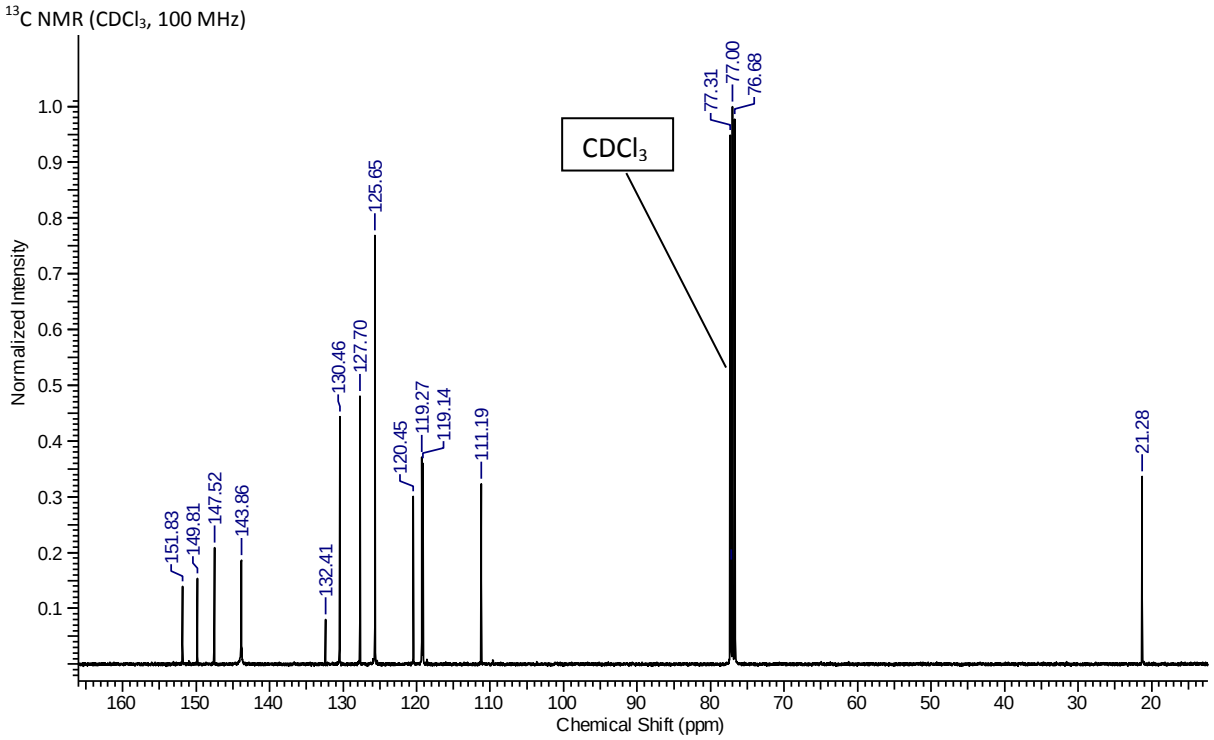
4b – Crystals of 1,2-$B_2Cat_2pic_2$•(DCB) redissolved in $CDCl_3$

^{1}H NMR ($CDCl_3$, 400 MHz)



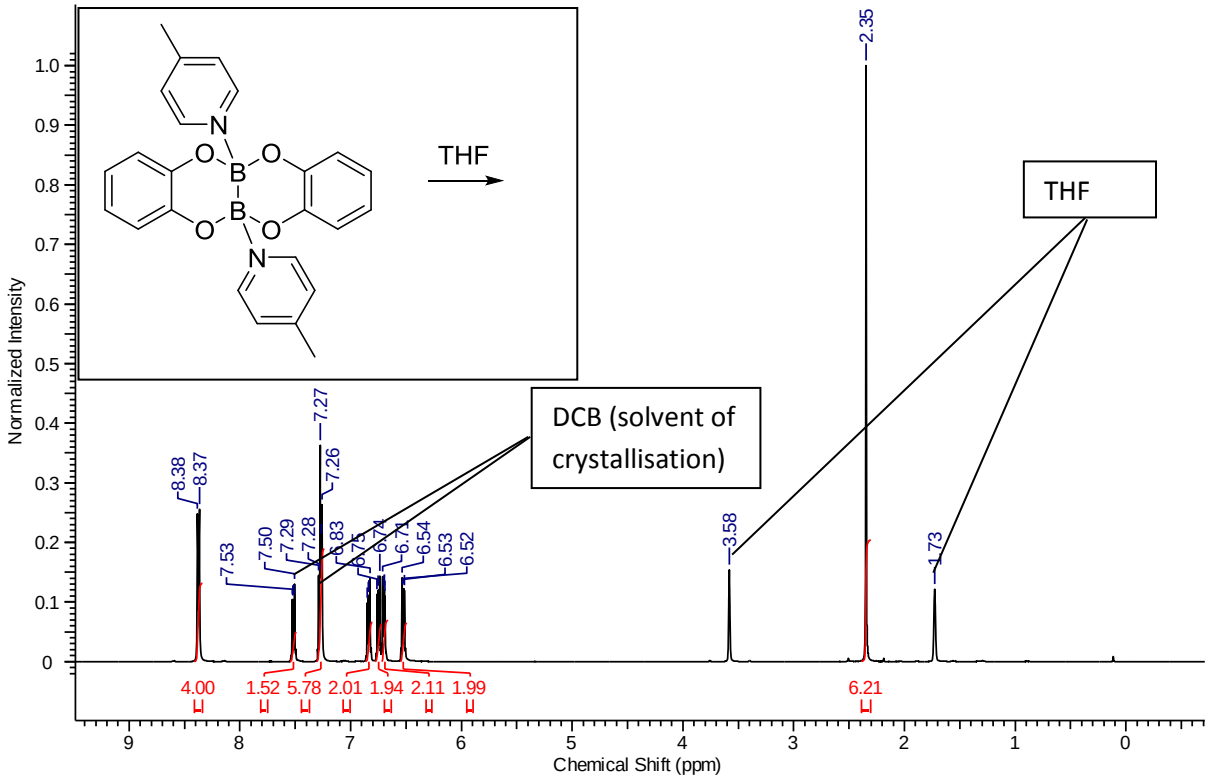
^{11}B NMR ($CDCl_3$, 128 MHz)



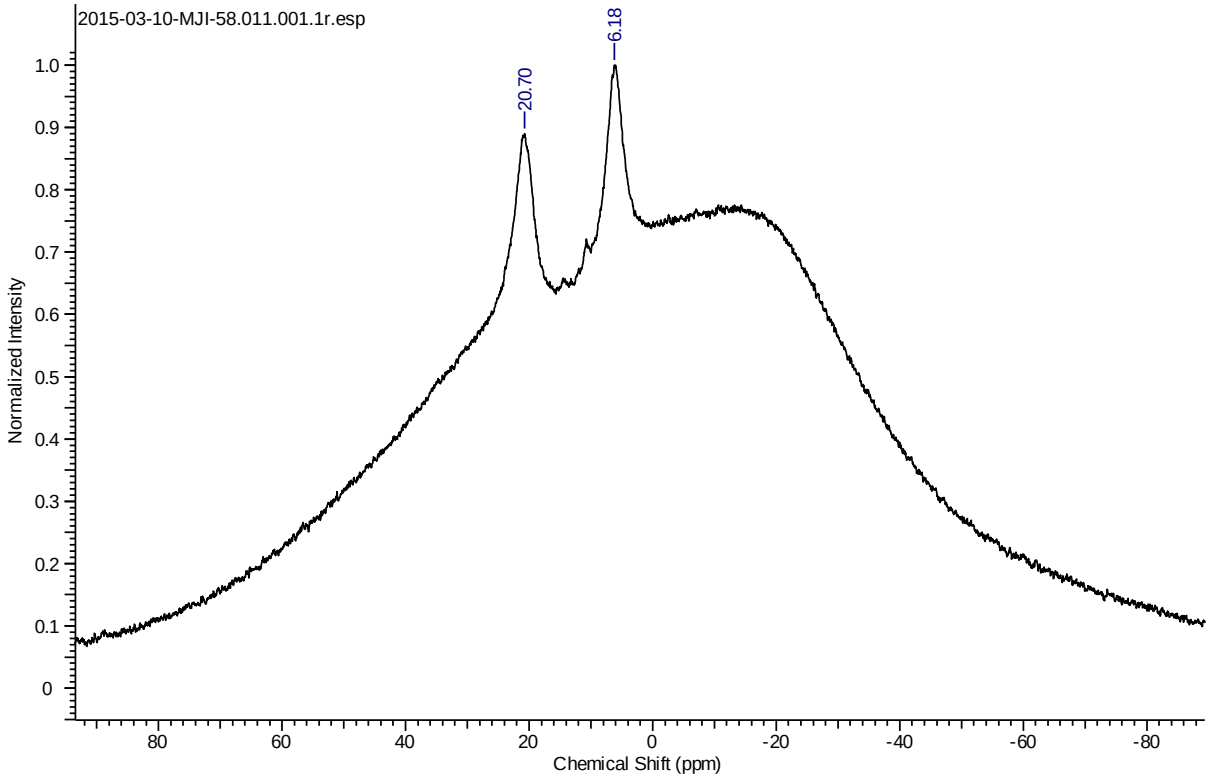

13C NMR (CDCl3, 100 MHz)
Normalized Intensity
Chemical Shift (ppm)
CDCl3
151.83
149.81
147.52
143.86
132.41
130.46
127.70
125.65
120.45
119.27
119.14
111.19
77.31
77.00
76.68
21.28

4b – Crystals of 1,2-$B_2Cat_2pic_2$•(DCB) redissolved in THF

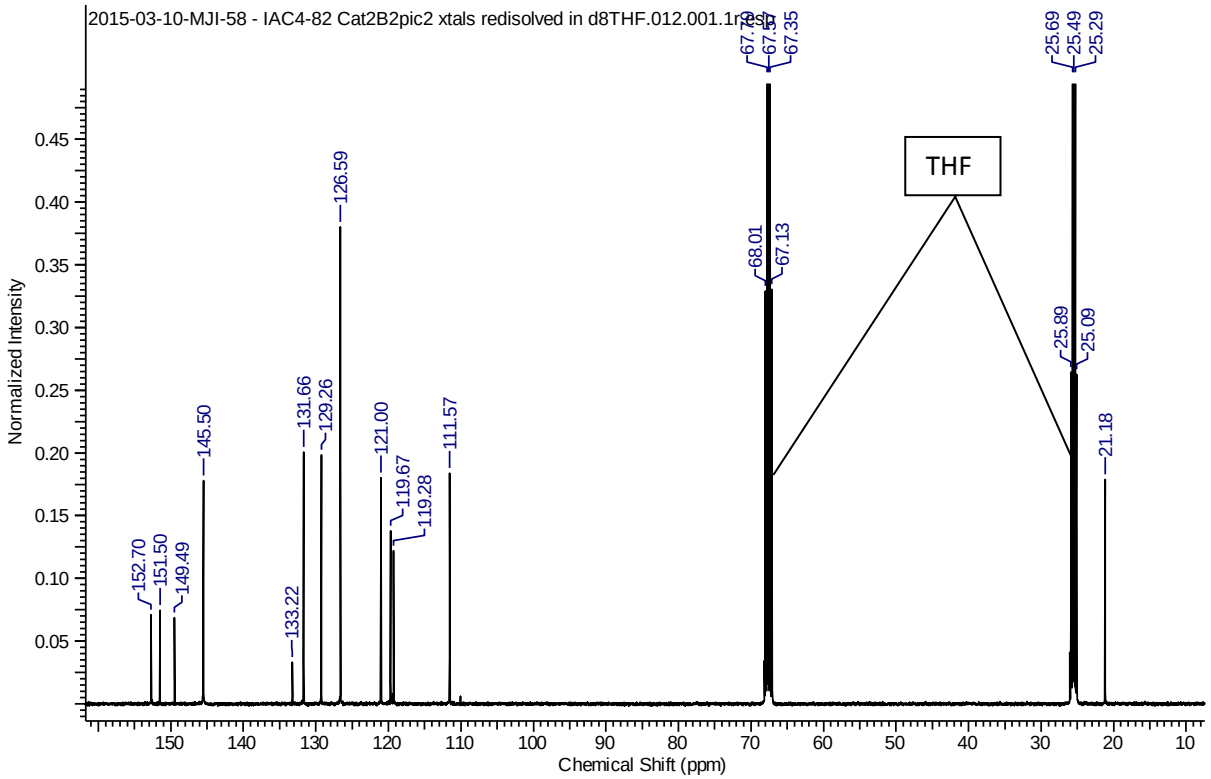
^{1}H NMR (d_8-THF, 400 MHz)



^{11}B NMR (d_8-THF, 128 MHz)



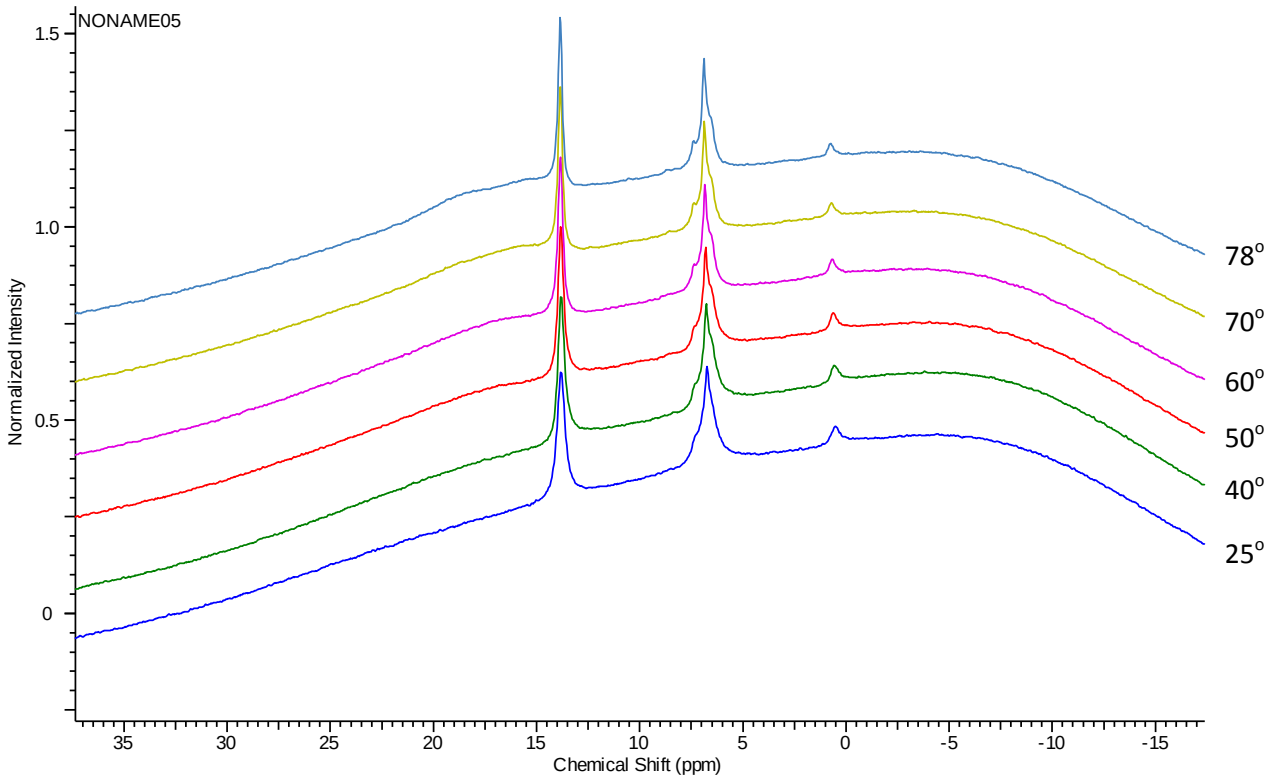
^{13}C NMR (d_8-THF, 100 MHz)



VT NMR

3 – $B_2Cat_2(DBN)_2$ in DCB 25° – 78°

^{11}B NMR spectra (recorded with d6-DMSO capillary insert)

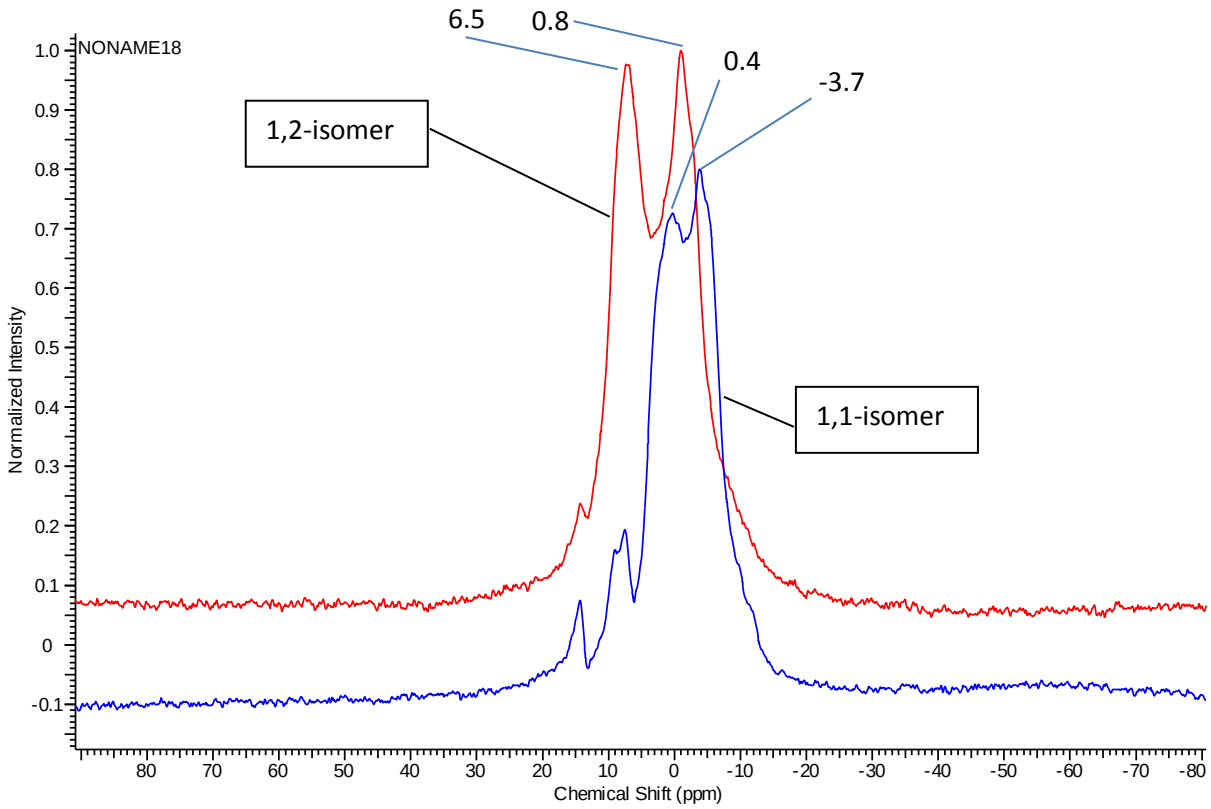


Solid state NMR spectra

Spectra were recorded using a Bruker Advance III 400MHz CPMAS spectrometer fitted with a wide bore probe. Samples were placed in a zirconia rotor and spun at 5000Hz for all spectra.

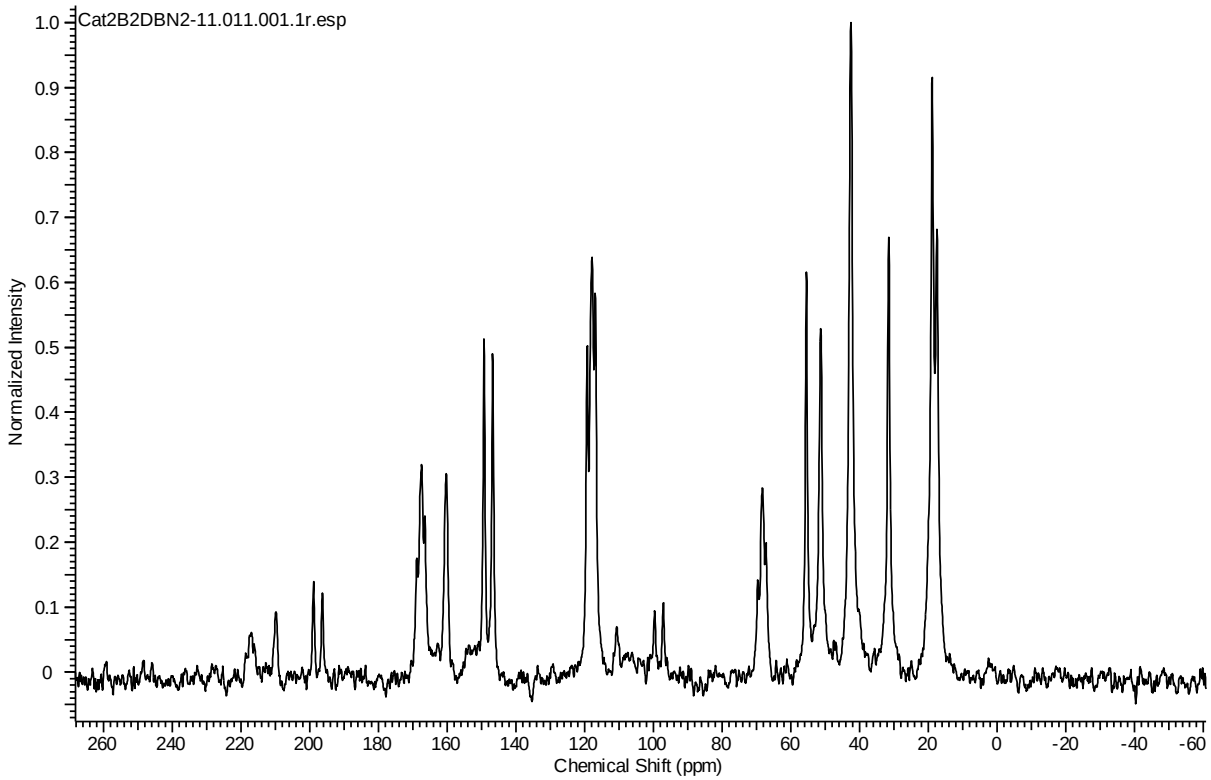
^{11}B MAS NMR

3a and **3b** – $B_2Cat_2(DBN)_2$ (overlay of both isomers)



^{13}C MAS NMR

3a – 1,1-$B_2Cat_2(DBN)_2$



$B_2Cat_2(DBN)_2$ (both isomers? **3a**/**3b**)