Supplementary Information for:

Cycloaddition Reactions Between Dicyclohexylboron Azides and Alkynes

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1. Experimental

1.1 General Experimental

Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. A nitrogen-filled glove box (MBRAUN) was used to manipulate solids including storage starting materials, room temperature reactions, product recovery and sample preparation for analysis. Molecular sieves (4 Å) were dried at 120 ºC for 24 h prior to use. All solvents (toluene, DCM, THF, pentane, hexane) were dried by employing a Grubbs-type column system (Innovative Technology), degassed and stored over molecular sieves under a nitrogen atmosphere. Deuterated solvents were dried over molecular sieves before use. Cy_2BCl (1M in hexanes) (Aldrich), $TMSN_3$ (TCI), PhC≡CH (Aldrich), *p*-Tol-C≡CH (Aldrich), 4-^{t}BuPh-C≡CH (Aldrich), TMS-C≡CH (TCI) and Ph_2PCl (Aldrich) were used as received. $Ph_2P(=O)C≡CH$ was prepared according to literature methods.[1] ^1H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded on a Bruker Avance III or a Bruker Avance 500 spectrometer. Solid state ^{11}B and ^{13}C NMR spectra were run on an Agilent DD2-600 spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to d_8-toluene, d_6-benzene, d_5-bromobenzene and CD_2Cl_2 as internal standards. NMR spectra were referenced to 85% H_3PO_4 (^{31}P) and $BF_3 \cdot Et_2O/CDCl_3$ (^{11}B). The description of signals include: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br. = broad. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). All spectra were analysed assuming a first order approximation. A Perkin-Elmer Analyser was used for carbon, hydrogen and nitrogen elemental analyses. High resolution mass spectrometry was performed in house employing DART or electrospray ionisation techniques in positive ion mode. Mass spectral data were recorded on an AB/Sciex QStarXL mass spectrometer (ESI) or a JEOL AccuTOF model JMS-T1000LC mass spectrometer (DART).

Caution: Covalent azides are potentially explosive and reactions were performed on small scale behind blast shields.

1.2 Experimental Details:

1.2.1 Synthesis of Cy_2BN_3 (1)

Dicyclohexyl borane (1 ml of a 1M solution in hexane, 1 mmol) was added dropwise to a solution of trimethylsilylazide (115 mg, 1 mmol) in toluene (2 ml). The resultant solution was stirred for 4h at room temperature affording a colourless, cloudy solution. The solvent and TMSCl by-product were removed *in vacuo* to afford Cy_2BN_3 as an off-white oil (197 mg, 0.91 mmol, 91%)[2] which was used directly in subsequent reactions.

^{1}H NMR (400 MHz, d_6-benzene, 298 K): 1.44 (s, br., 3H, Cy), 1.30 (s, br., 2H, Cy), 0.96-0.98 (m, br., 6H, Cy); ^{13}C NMR (500 MHz, C_6D_5Br, 298 K): 31.7 (br., Cy), 27.8 (m, Cy), 27.3 (s, Cy), 26.8 (s, Cy); ^{11}B NMR (128 MHz, d_6-benzene, 298 K): 61.3 (br. s). Elemental analysis calcd (%) for C 65.77, H 10.12, N 19.18%; Obs. C 65.63, H 9.99, N 17.84%.

Figure 1 ^{1}H NMR spectrum of **1** (400 MHz, d_6-benzene, 298 K).

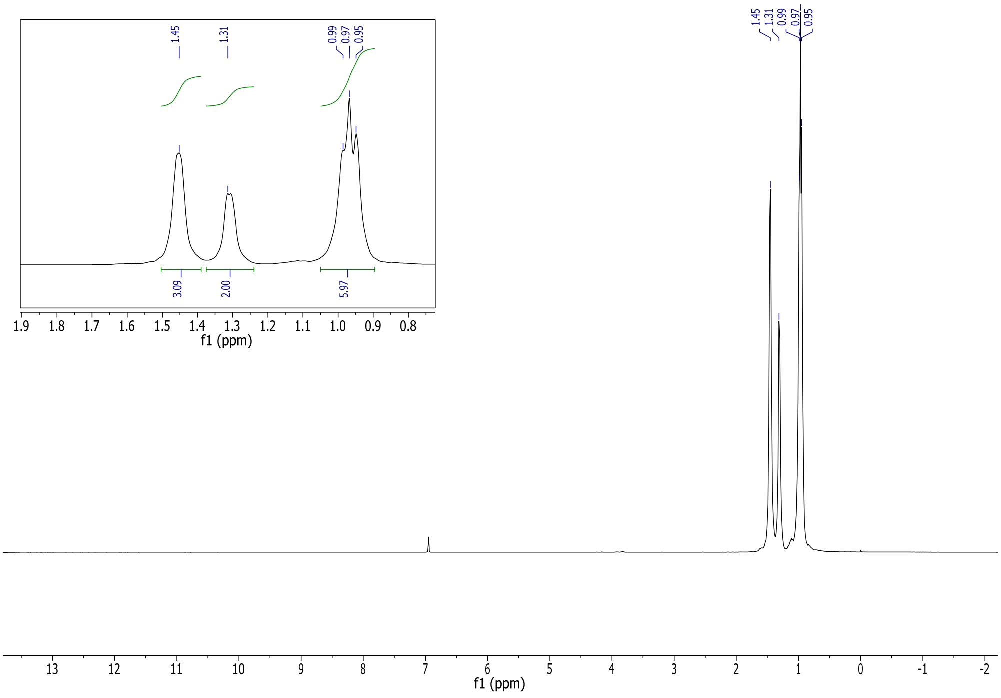


Figure 2 ^{11}B NMR spectrum of **1** (128 MHz, d_6-benzene, 298 K).

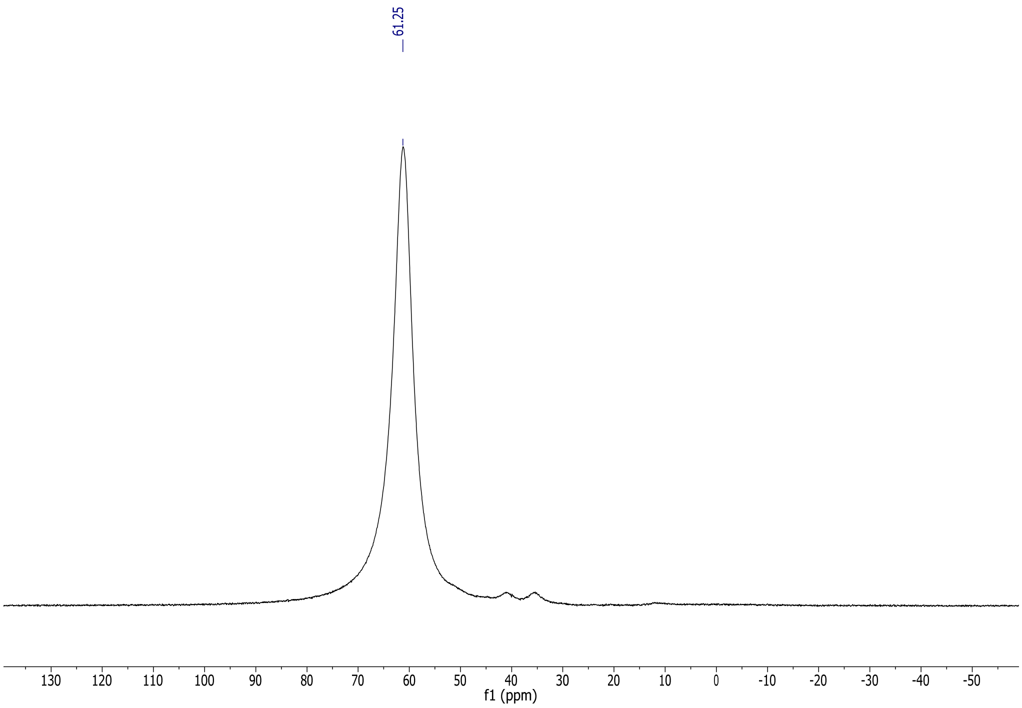
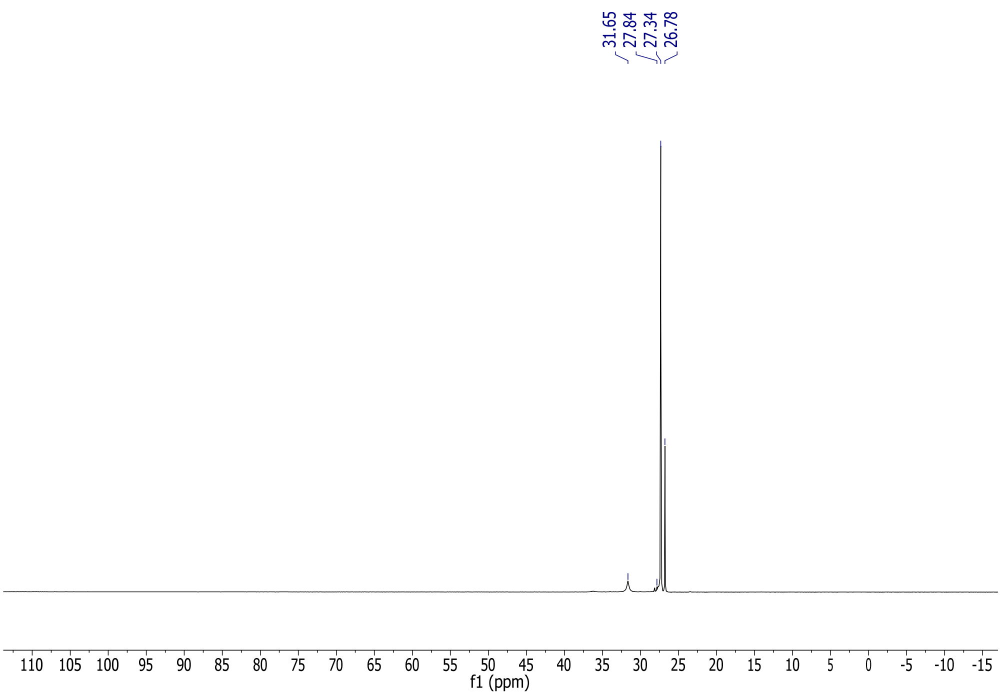


Figure 3 ^{13}C NMR spectrum of **1** (100 MHz, C_6D_5Br, 298 K).



The thermal stability of **1** was investigated by NMR spectroscopy: Cy_2BCl (0.5 ml of a 1M solution in hexane, 0.5 mmol) was added to a solution of $TMSN_3$ (58 mg, 0.5 mmol) in toluene (2 ml). The resultant solution was left to stand for 2h at room temperature affording a colourless, cloudy solution. The solvent and TMSCl by-product were removed *in vacuo* to afford Cy_2BN_3 as an off white oil. The Cy_2BN_3 was redissolved in d_8-toluene and the NMR spectrum was measured after 4 h at the respective temperature.

Figure 4 Decomposition of the boron azide **1** at various temperatures as seen in the ^{1}H NMR spectrum (400 MHz, d_8-toluene, 298 K).

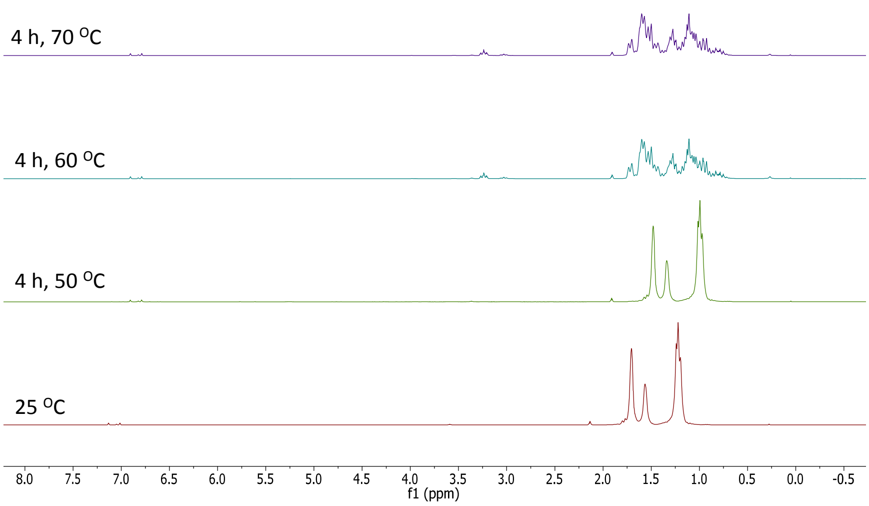
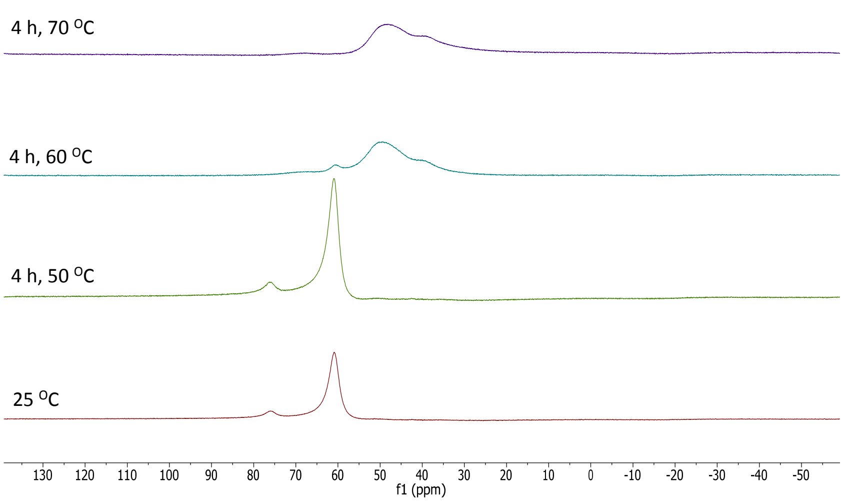
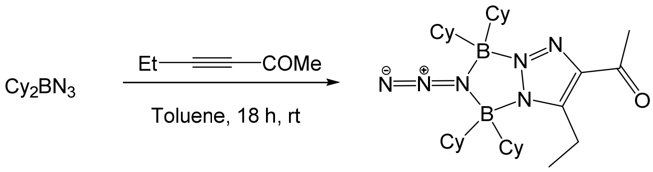


Figure 5 Decomposition of the boron azide **1** at various temperatures as seen in the ^{11}B NMR spectrum (128 MHz, d_8-toluene, 298 K).



1.2.2 Synthesis of 2



2

EtC≡CCOMe (96 mg, 1 mmol) in toluene (5 ml) was added to neat Cy_2BN_3 (1 mmol) prepared *in situ* as described above. The resulting solution was stirred for 18 h affording a purple solution. Slow evaporation of the toluene solution afforded colourless crystals of **2** suitable for X-ray diffraction. The residual solvent was removed and the crystalline solid washed with hexane (3 × 2 ml) to afford pure **2** (137 mg, 0.25 mmol, 51% relative to Cy_2BN_3).

^{1}H NMR (500 MHz, d_6-benzene, 298 K): 2.78 (q, 7.5 Hz, 2H, -C<u>H</u>$_2$CH$_3$), 2.28 (s, 3H, -C<u>H</u>$_3$), 2.12 (d, br., 12.3 Hz, 2H, <u>Cy</u>), 2.02 (d, br., 9.3 Hz, 2H, <u>Cy</u>), 1.89-1.76 (m, 16H, <u>Cy</u>), 1.81-1.76 (m, 2H, <u>Cy</u>), 1.50-1.17 (m, 22H, <u>Cy</u>), 1.12 (t, 7.5 Hz, 3H, -CH$_2$C<u>H</u>$_3$); ^{13}C NMR (500 MHz d_6-benzene, 298 K): 191.6 (s, <u>C</u>=O), 145.8 (s, <u>C</u>-triazole), 145.0 (s, <u>C</u>-triazole), 30.3, 29.8, 29.6, 28.9, 28.6, 27.5, 27.2, 18.3, 12.4; ^{11}B NMR (128 MHz, d_6-benzene, 298 K): 8.2 (br. s). Elemental analysis calcd (%) for $C_{30}H_{52}N_6B_2O$: C 67.43, H 9.81, N 15.73%; Obs. C 67.87, H 9.58, N 15.38%; *m/z* (+ESI-MS): 315.3 [M-Cy_2BN_3]$^+$; *m/z* (DART-MS): 630.5 [(M-Cy_2BN_3)$_2$+H]$^+$, 316.3 [(M+H)-Cy_2BN_3]$^+$.

Figure 6 ^{1}H NMR spectrum of **2** (400 MHz, d_6-benzene, 298 K).

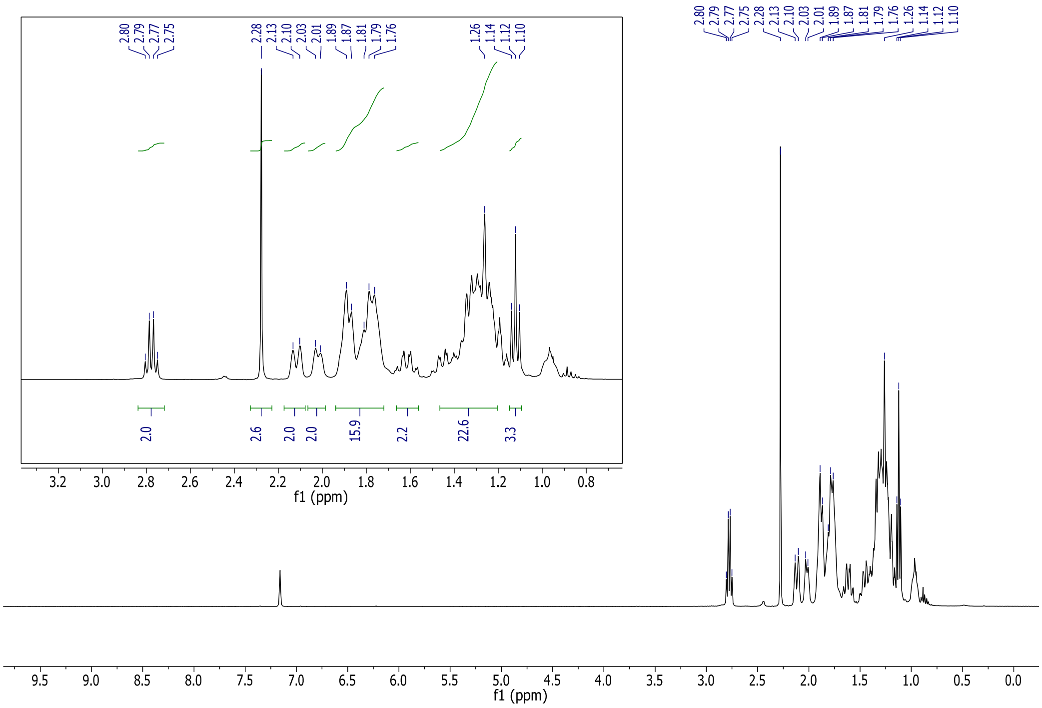


Figure 7 ^{11}B NMR spectrum of **2** (128 MHz, d_6-benzene, 298 K).

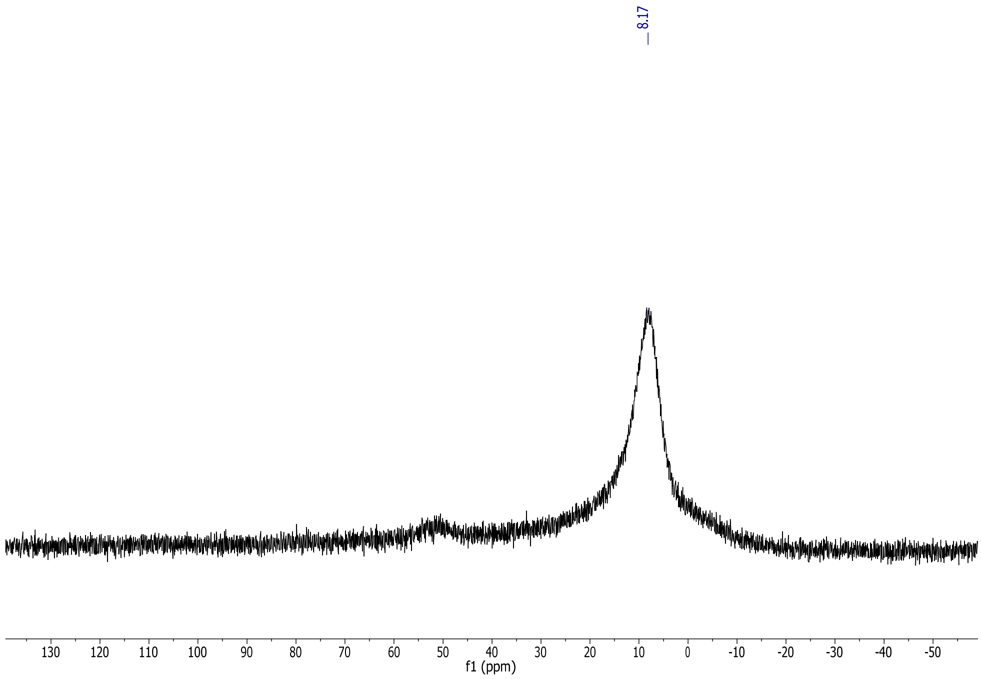


Figure 8 ^{13}C NMR spectrum of **2** (100 MHz d_6-benzene, 298 K).

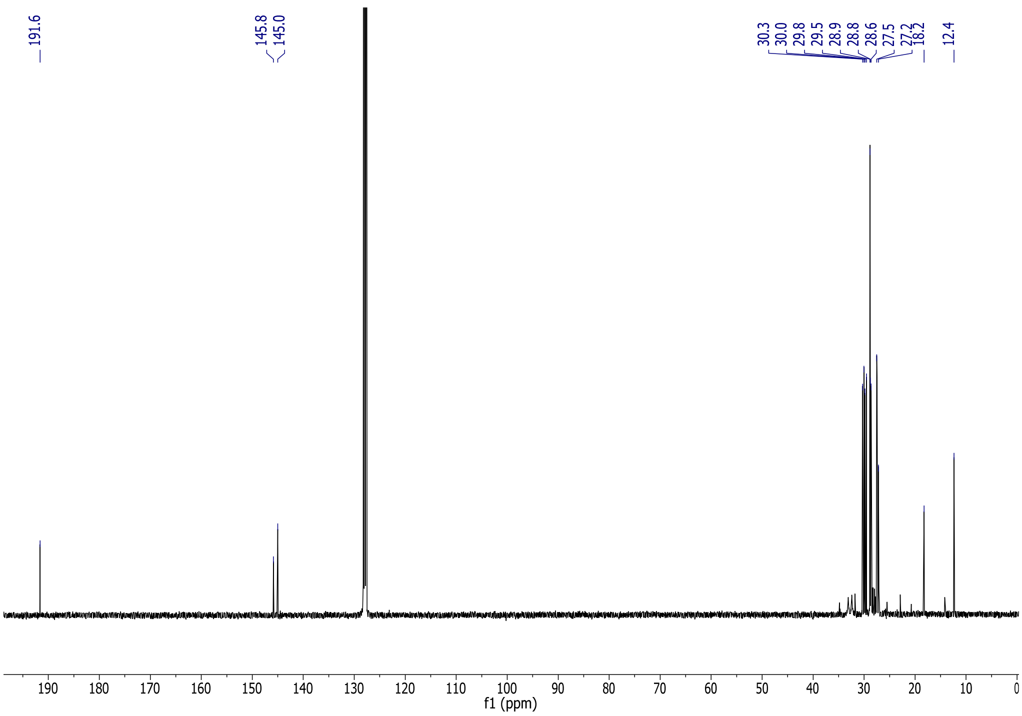
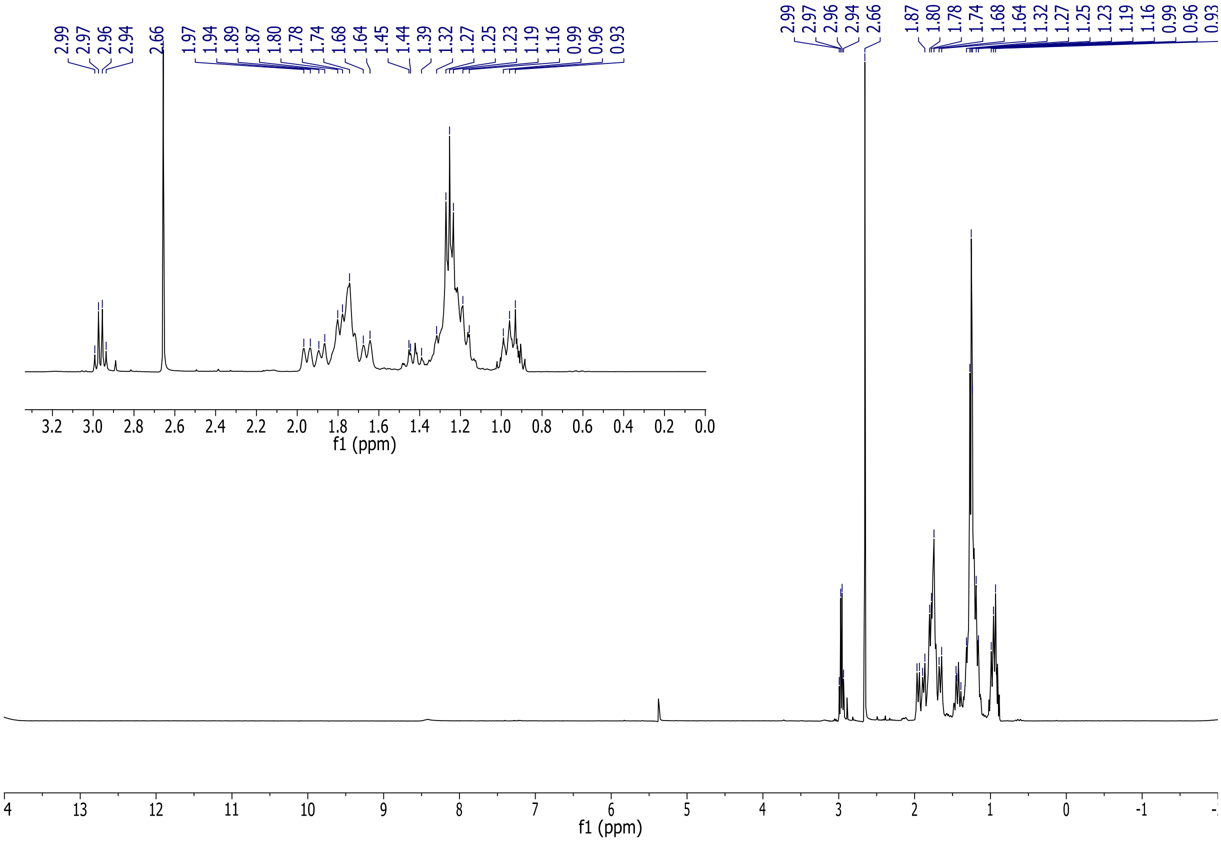
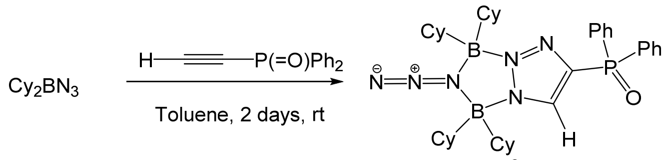


Figure 9 *in situ* ^{1}H NMR spectrum of **2** (400 MHz, CD_2Cl_2, 298 K).



1.2.3 Synthesis of 3



3

$Ph_2P(=O)C{\equiv}CH$ (226 mg, 1 mmol) in toluene (3 ml) was added to Cy_2BN_3 (1 mmol) prepared *in situ* as described above in toluene (2 ml) and the resulting solution was stirred for 2 days at room temperature. The solvent was removed *in vacuo* and the resulting solid was redissolved in DCM (*ca.* 1 ml) to afford a saturated solution. Storage of the solution at -35 ºC afforded colourless crystals suitable for X-ray diffraction. The supernatant was decanted off and the crystalline solid washed with hexane (3 × 2 ml) to give pure **3** (157 mg, 0.23 mmol, 47%).

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): 8.29 (s, 1H), 8.00 (m, 4H, *o*-C<u>H</u>), 7.68 (m, 2H, *p*-C<u>H</u>), 7.61 (m, 4H, *m*-C<u>H</u>), 1.98 (d, 11.4 Hz, 2H, <u>Cy</u>), 1.83-1.93 (m, br., 14H, <u>Cy</u>), 1.48 (t, 13.6 Hz, 4H, <u>Cy</u>), 1.55-1.24 (m, br., 20H, <u>Cy</u>), 1.14 (t, br., 12.2 Hz, 2H, <u>Cy</u>), 1.04 (t, br., 11.1 Hz, 2H, <u>Cy</u>);^{13}C{1H} NMR (100 MHz, CD_2Cl_2, 298K): 132.8 (d, 2.9 Hz), 131.8, 131.7, 130.3, 130.1, 129.1 (d, $^3J_{PH}$ = 12 Hz), 129.0, 30.1, 30.0, 28.9, 28.9, 28.9 28.1, 27.8, 27.6; ^{11}B NMR (128 MHz, d_6-benzene, 298K): 9.31 (br. s); ^{31}P NMR (162 MHz, CD_2Cl_2, 298K): 14.4 (q, $^3J_{PH}$ = 12 Hz); Elemental analysis calcd (%) for $C_{38}H_{55}N_6B_2PO$: C 68.69; H 8.34; N 12.65%; Obs. C 68.37, H 8.17; N 12.40%.

Figure 10 ^{1}H NMR spectrum of **3** (400 MHz, CD_2Cl_2, 298 K).

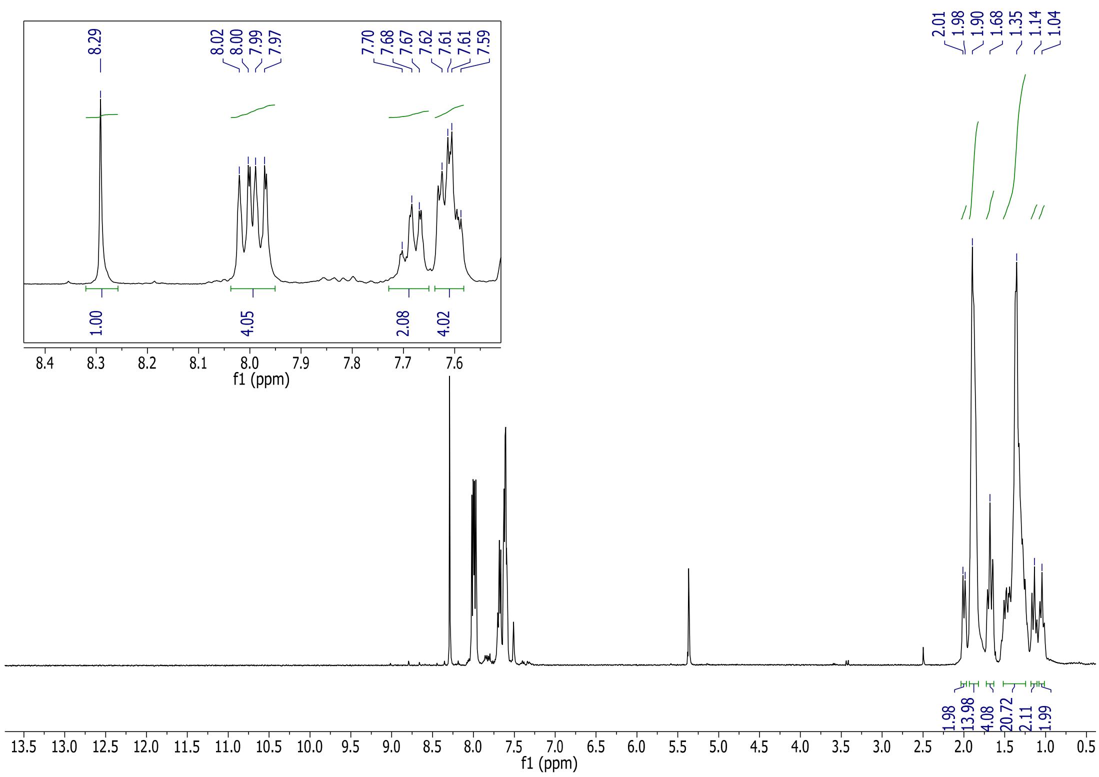


Figure 11 ^{11}B NMR spectrum of **3** (128 MHz, CD_2Cl_2, 298 K).

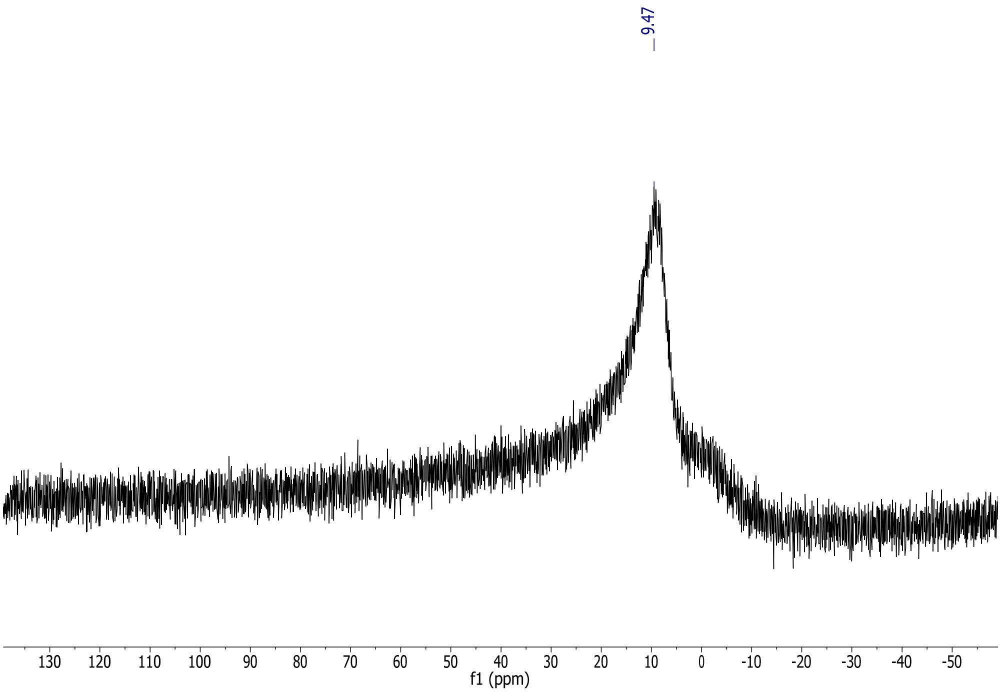


Figure 12 ^{31}P NMR spectrum of **3** (160 MHz, CD_2Cl_2, 298 K).

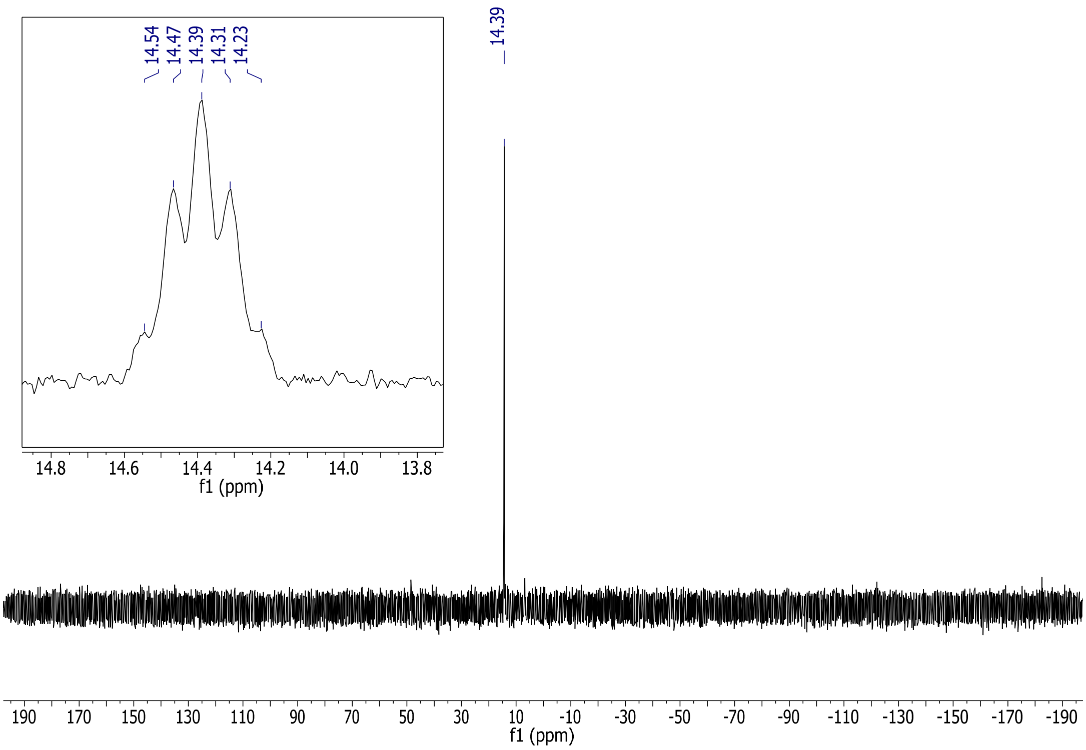


Figure 13 ^{13}C NMR spectrum of **3** (100 MHz d_6-benzene, 298 K).

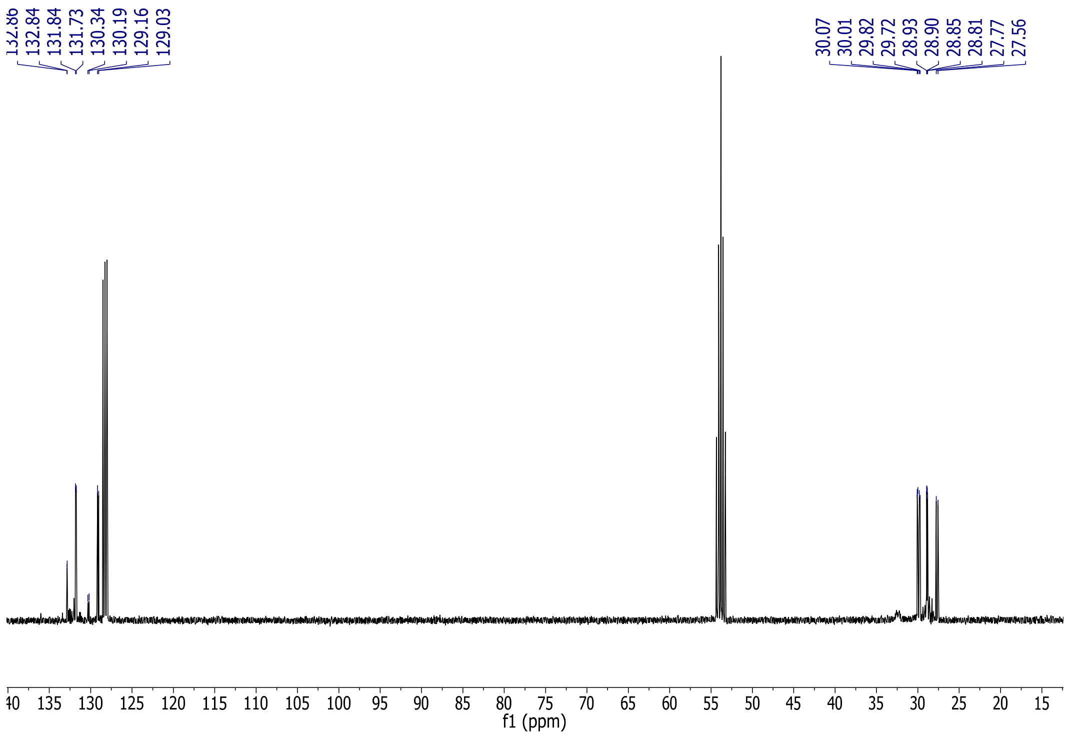
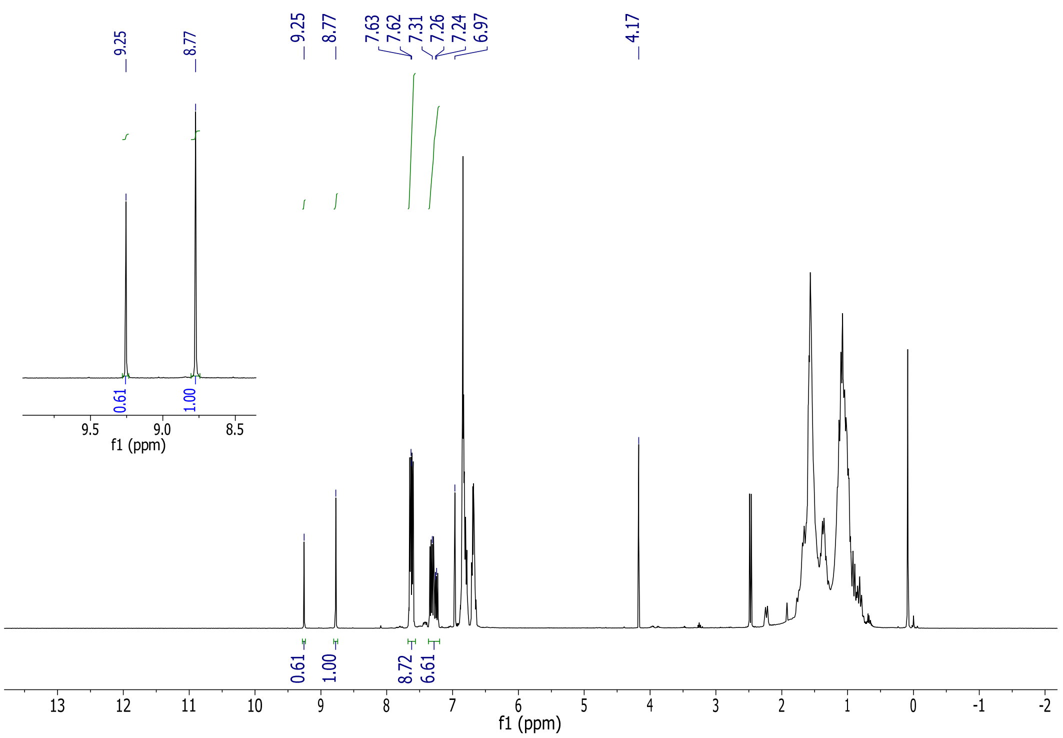
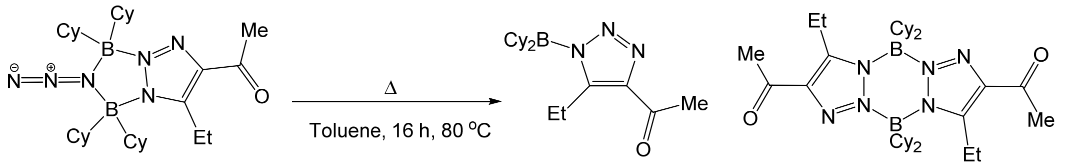


Figure 14 *in situ* ^{1}H NMR spectrum of the 1:1 reaction between Cy_2BN_3 and $Ph_2P(=O)C{\equiv}CH$ (400 MHz, C_6D_6, 298 K).



1.2.4 Synthesis of 4



A solution of **2** (27 mg, 0.05 mmol) and a large excess of EtC≡CCOMe (100 mg, 0.96 mmol) were heated to 90 °C in toluene (5 ml) for 16h. The toluene solvent and excess EtC≡CCOMe were removed *in vacuo* to give a residue which was redissolved in CD_2Cl_2 (0.7 ml) and characterised by ^{1}H and ^{11}B NMR spectroscopy. Although the alkyl region of the ^{1}H NMR spectrum is complicated by the presence of the cyclohexyl groups, the appearance of two new peaks due to the CH_2-protons in the Et group (δ = 2.41 and 2.96 ppm) and the terminal CH_3 group adjacent to the carbonyl (δ = 2.32 and 2.66 ppm) were particularly diagnostic of the formation of two new products. In addition, this was observed by the presence of a new species (**4**) (δ = 7.7 ppm) and also a peak at δ = 51.6 ppm [a result of the decomposition of the Cy_2BN_3 (Fig. 4) released from the intermediate **2**] in the ^{11}B NMR spectrum.

^{1}H NMR (400 MHz, CD_2Cl_2, 298K): 2.96 (q, 2H, 7.5 Hz, -C$\underline{H}_2$CH$_3$), 2.65 (s, 3H, C$\underline{H}_3$), 2.41 (q, 7.5 Hz, 9H, -CH$_2$CH$_3$), 2.32 (s, 13H, -CH$_3$), 1.97-1.64 (m, br., Cy), 1.47-1.39 (m, br., Cy), 1.30-1.16 (m, br., Cy), 1.25 (t, 7.5 Hz, -CH$_2$C$\underline{H}_3$), 0.95 (t, br., 11.9 Hz, Cy); ^{11}B NMR (128 MHz, CD_2Cl_2, 298K): 51.6 (br., s, decomposed Cy_2BN_3), 7.6 (br. s, compound **4**). *m/z* (+ESI-MS): 315.3 [M$^+$-Cy$_2$BN$_3$]$^+$; *m/z* (DART-MS): 630.5 [(M$^+$-Cy$_2$BN$_3$)$_2$+H]$^+$, 316.3 [(M+H)-Cy$_2$BN$_3$]$^+$.

Figure 15 ^{1}H NMR spectrum of **4** (400 MHz, CD_2Cl_2, 298 K).

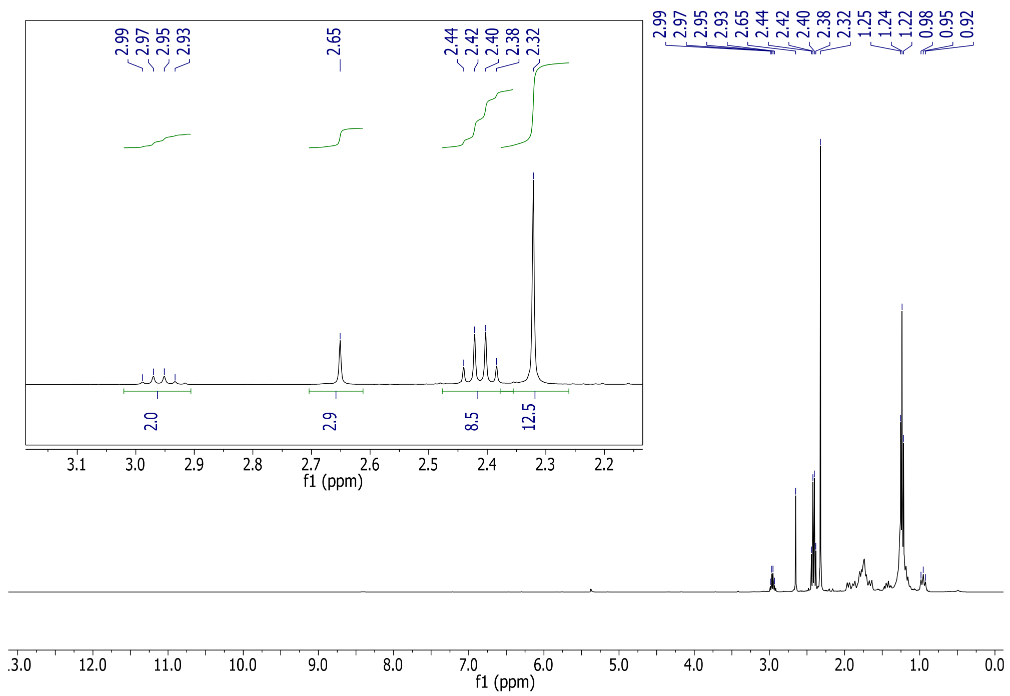
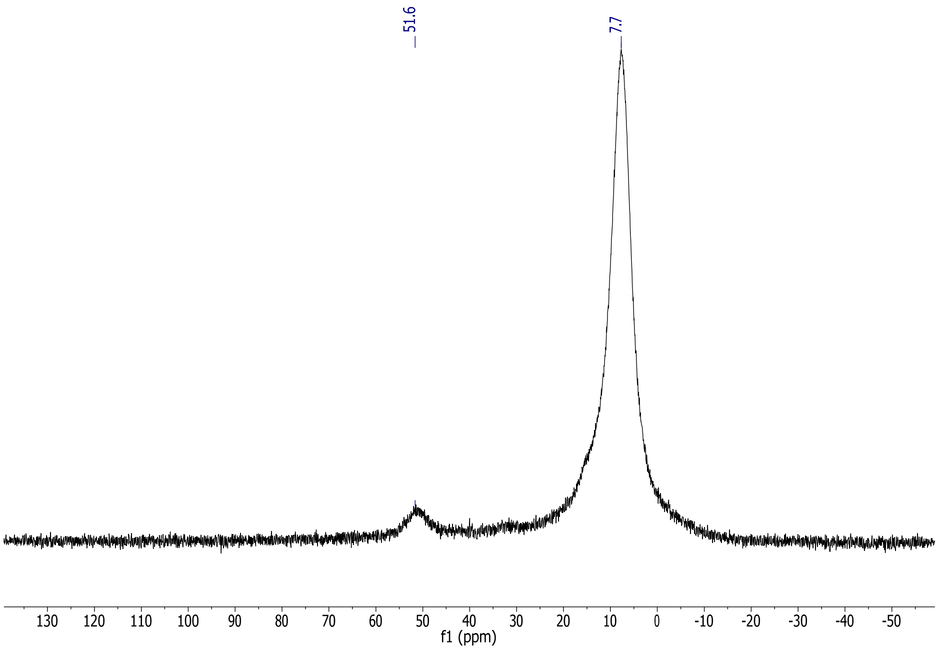
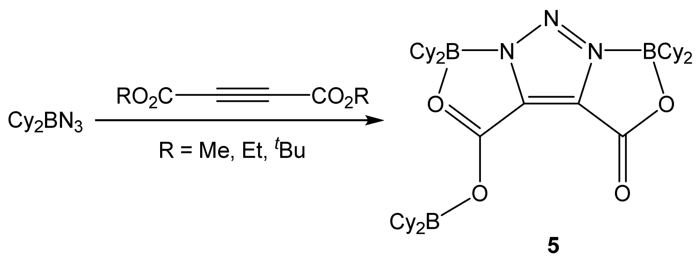


Figure 16 ^{11}B NMR spectrum of **4** (128 MHz, CD_2Cl_2, 298 K).



1.2.5 Syntheses of 5



5

Depending upon the acetylene used the rate of reaction with Cy_2BN_3 varied significantly and as a consequence the preperation of **5** was varied accordingly:

a) Reaction of Cy_2BN_3 with $MeO_2CC{\equiv}CCO_2Me$

$MeO_2CC{\equiv}CCO_2Me$ (142 mg, 1 mmol) in toluene (2 ml) was added to neat Cy_2BN_3 (1 mmol). The solution was allowed to stir for 48 h at room temperature affording a pale yellow solution. The resulting solution was left to stand for 7 days during which pure crystals of **5** formed suitable for X-ray analysis. The supernatant was decanted off and the resultant crystals washed with hexane (3 × 2 ml) and dried *in vacuo* to afford **5** (89 mg, 0.13 mmol, 39% relative to Cy_2BN_3).

b) Reaction of Cy_2BN_3 with $EtO_2CC{\equiv}CCO_2Et$

$EtO_2CC{\equiv}CCO_2Et$ (170 mg, 1 mmol) in toluene (2 ml) was added to Cy_2BN_3 (1 mmol) (prepared *in situ*) in toluene (2 ml). The solution left for 18 h resulting in a yellow solution. The resulting solution was cooled to -35 ºC for 2 days during which pure crystals of **5** formed suitable for X-ray analysis. The supernatant was decanted off and the resulting crystals washed with hexane (3 × 2 ml) and dried *in vacuo* to afford **5** (137 mg, 0.20 mmol, 61% relative to Cy_2BN_3).

c) Reaction of Cy_2BN_3 with $^tBuO_2CC{\equiv}CCO_2{}^tBu$

$^tBuO_2CC{\equiv}CCO_2{}^tBu$ (226 mg, 1 mmol) in toluene (5 ml) was layered onto of Cy_2BN_3 (1 mmol) prepared *in situ* in toluene (5 ml). The solution was left to stand for 4 h affording colourless crystals of **5** (148 mg, 0.22 mmol, 65% relative to Cy_2BN_3).

^{13}C CP-MAS NMR (151 MHz, 298 K); 161.8 (triazole C), 103.3 (triazole C), 28.4 (br., cyclohexyl C atoms); ^{11}B Onepul-MAS NMR (192 MHz, 298K): 12.9, 9.9, 8.8, 6.4. Elemental analysis calcd (%) for $C_{40}H_{66}N_3O_4B_3$: C 70.09, H 9.71, N 6.13%; Obs. C 70.38, H 9.72, N 6.09%.

Figure 17 ^{13}C CP-MAS NMR spectrum of **5**.

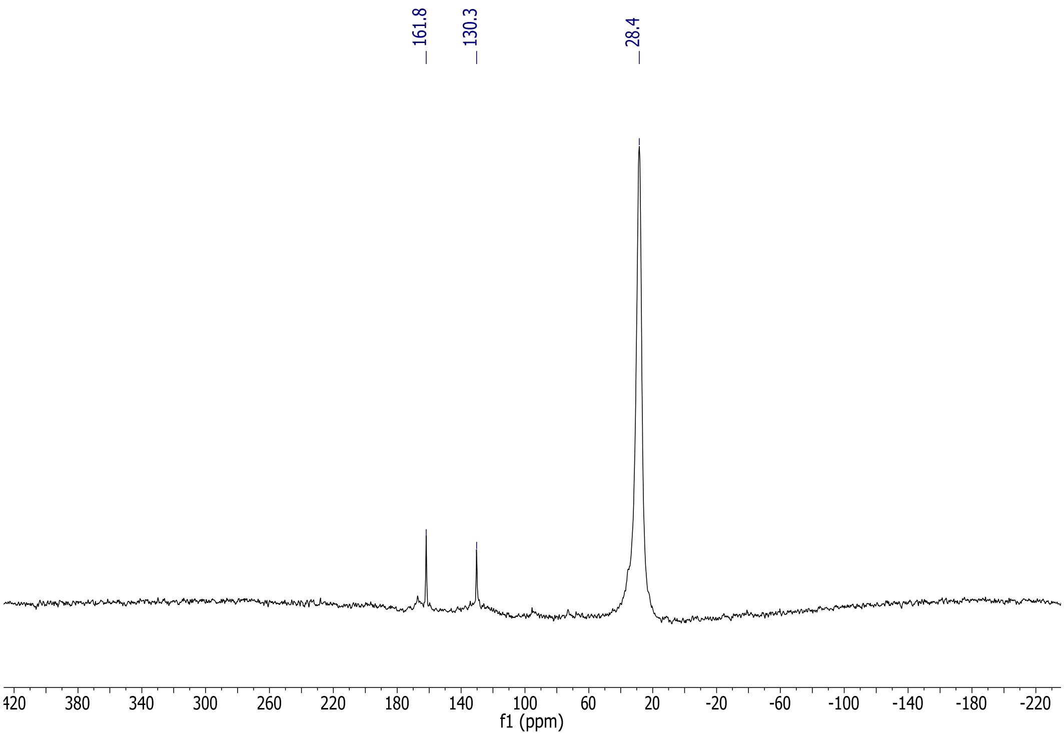
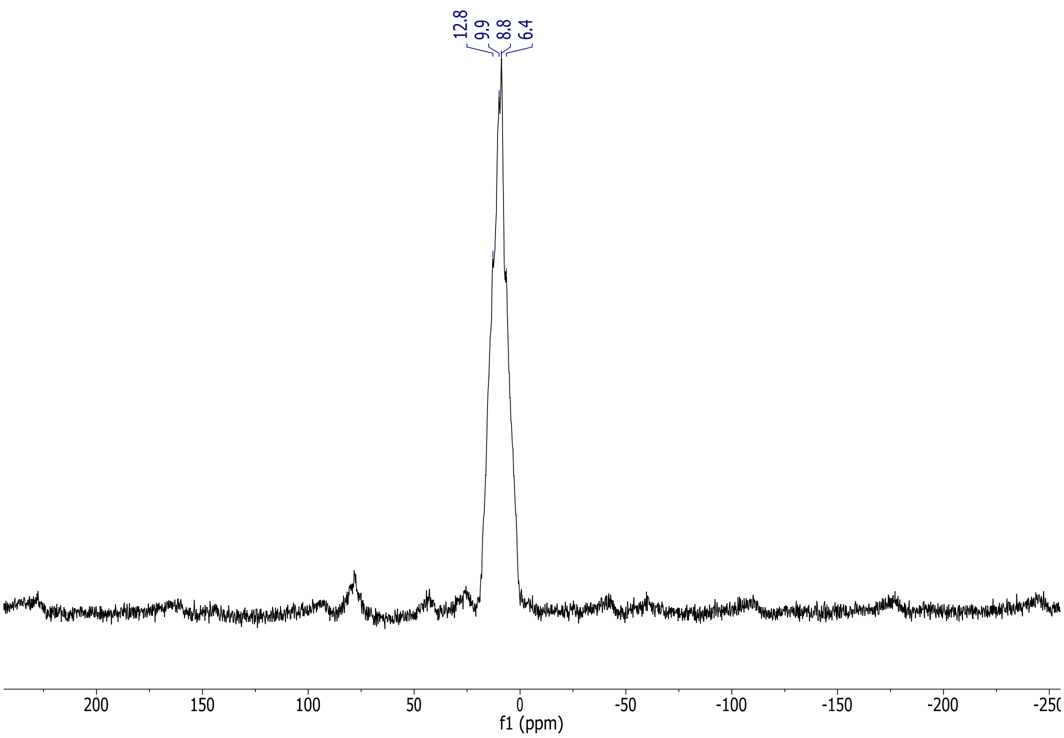


Figure 18 ^{11}B Onepul-MAS NMR spectrum of **5**.



1.2.6 in situ NMR studies of the reaction on Cy_2BN_3 with $RCO_2C{\equiv}CCO_2R$ (R = Me, Et, ^{t}Bu)

In the glove box, the appropriate amount of $RCO_2C{\equiv}CCO_2R$ (R = Me or Et) was added to a solution of Cy_2BN_3 (1 mmol) in d_6-benzene (0.5 ml). The solution was then transferred to an NMR tube, sealed with a cap and parafilm and NMR taken of the reaction mixture. The equivalent NMR study with ^{t}BuCO$_2$C≡CCO$_2$^{t}Bu was not possible due to the rapidity of the reaction.

Figure 19 Reaction of Cy_2BN_3 with $MeO_2CC{\equiv}CCO_2Me$ in a 1:1 stoichiometric ratio [^{1}H NMR (400 MHz, d_6-benzene, 298 K)].

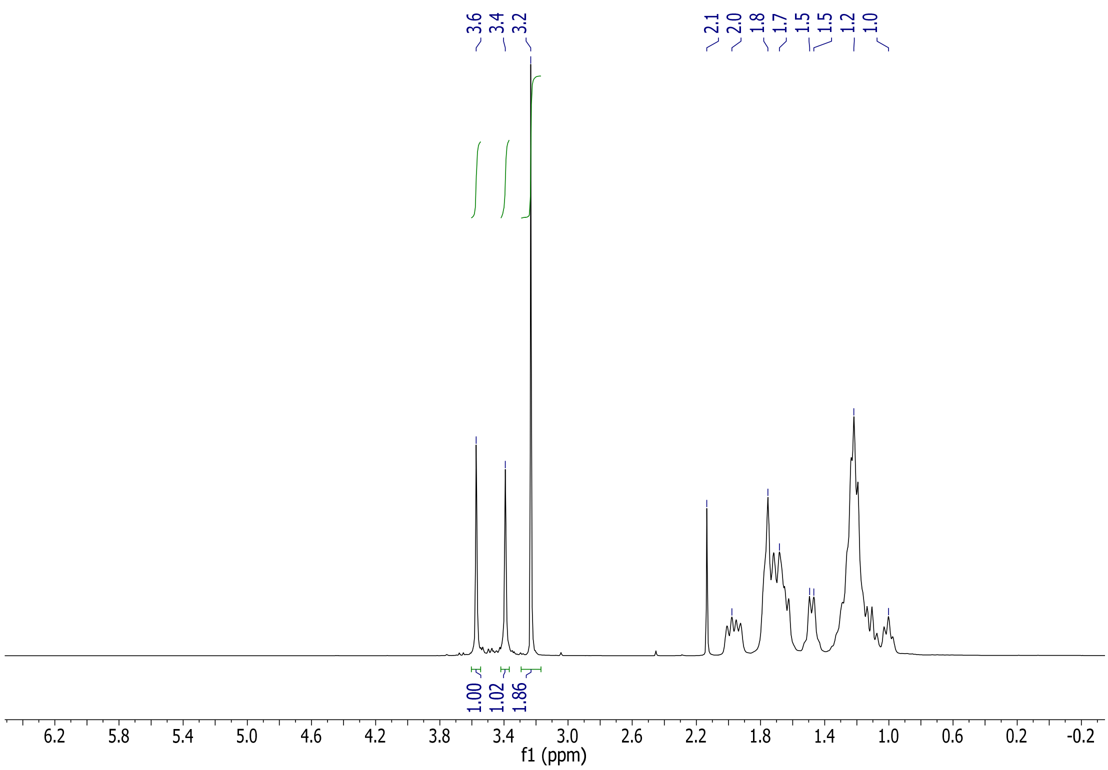


Figure 20 Reaction of Cy_2BN_3 with $MeO_2CC{\equiv}CCO_2Me$ in a 1:1 stoichiometric ratio [^{11}B NMR (128 MHz, d_6-benzene, 298 K)].

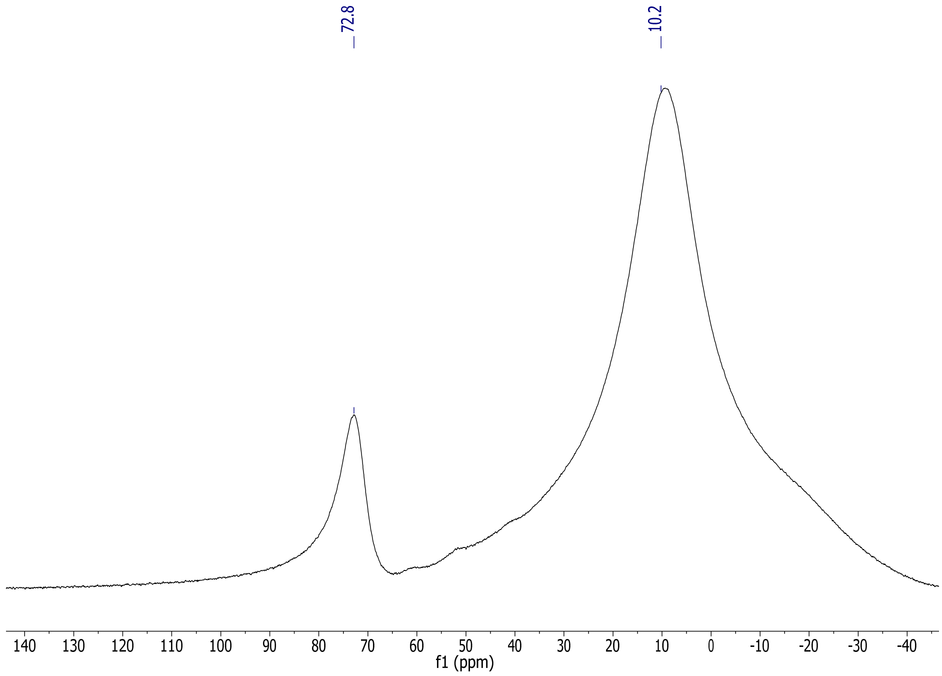


Figure 21 Reaction of Cy_2BN_3 with $MeO_2CC{\equiv}CCO_2Me$ in a 1:1 stoichiometric ratio [^{13}C NMR (100 MHz, d_6-benzene, 298 K)].

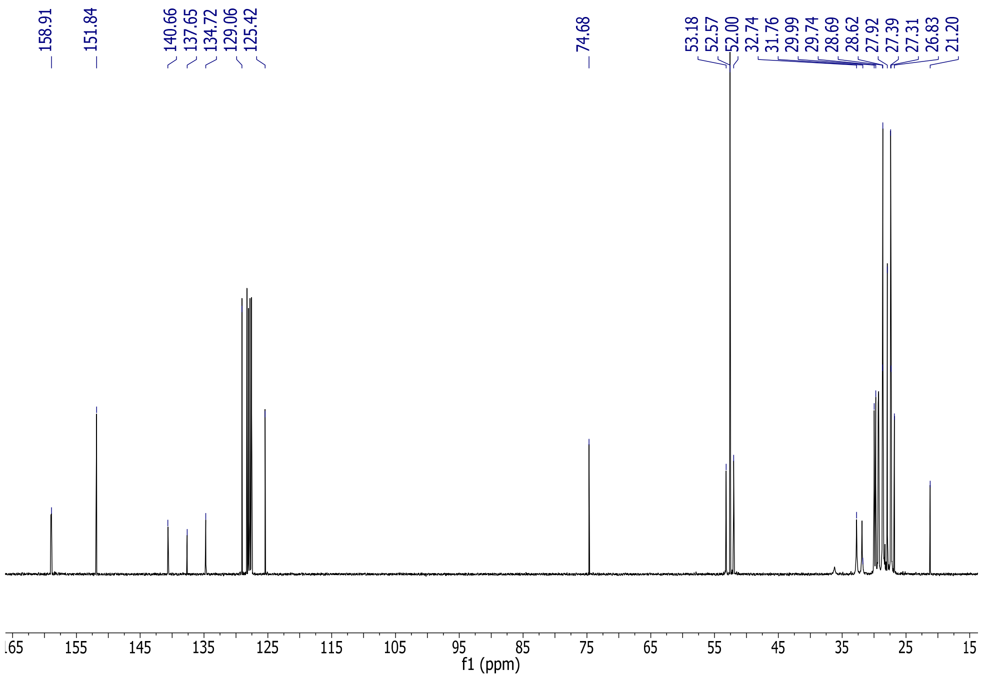


Figure 22 Reaction of Cy_2BN_3 with $EtO_2CC{\equiv}CCO_2Et$ in a 1:1 stoichiometric ratio ^{1}H NMR (400 MHz, d_6-benzene, 298 K)].

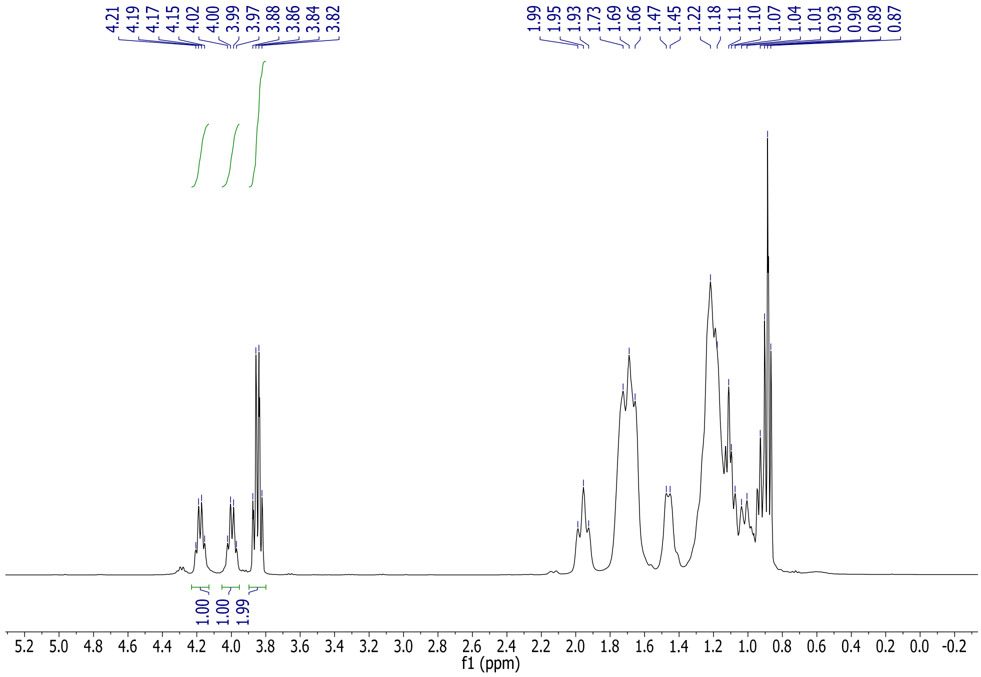


Figure 23 Reaction of Cy_2BN_3 with $EtO_2CC{\equiv}CCO_2Et$ in a 1:1 stoichiometric ratio [^{13}C NMR (100 MHz, d_6-benzene, 298 K)].

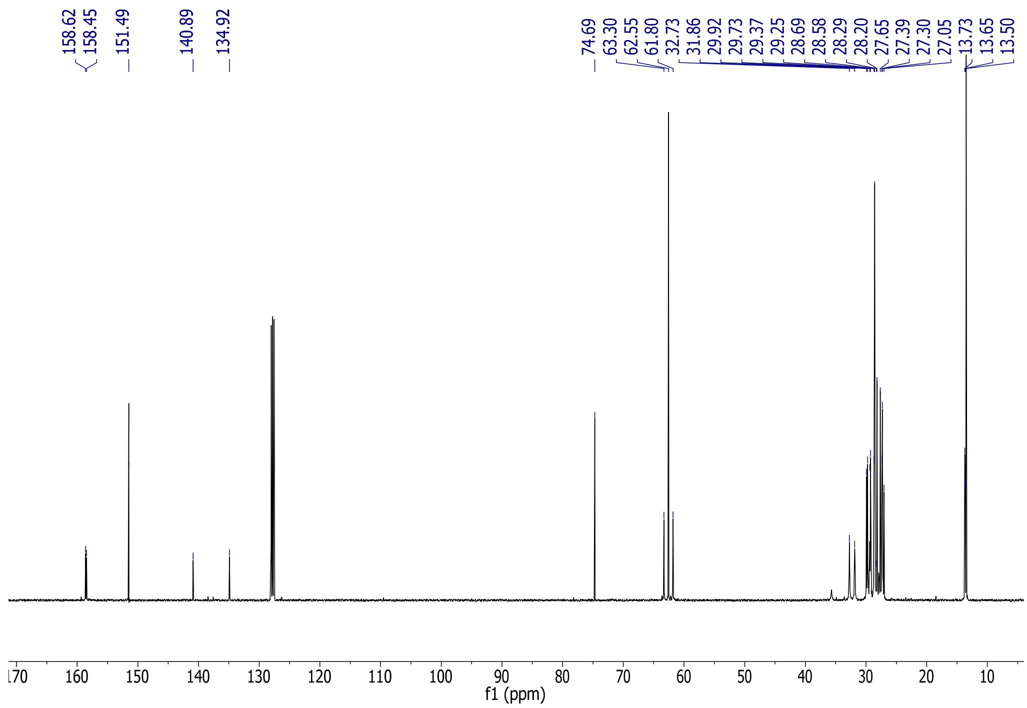


Figure 24 Reaction of Cy_2BN_3 with $EtO_2CC{\equiv}CCO_2Et$ in a 3:1 stoichiometric ratio [^{1}H NMR (400 MHz, d_6-benzene, 298 K)].

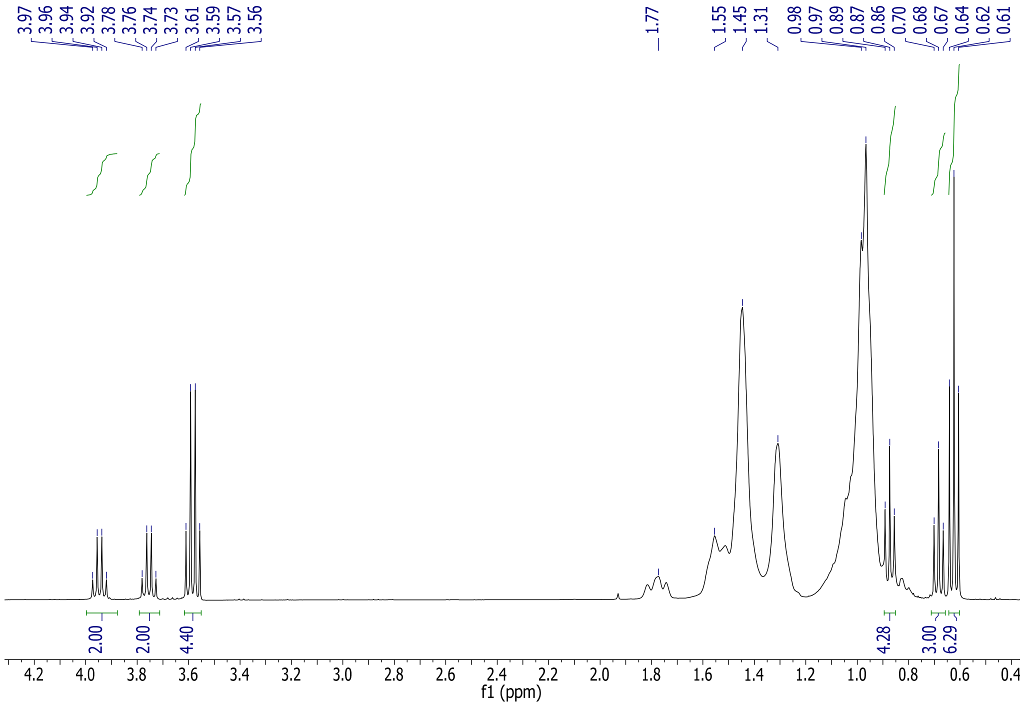


Figure 25 Reaction of Cy_2BN_3 with $EtO_2CC{\equiv}CCO_2Et$ in a 3:1 stoichiometric ratio [^{1}H NMR (400 MHz, d_6-benzene, 298 K)]. Red = immediately after $EtO_2CC{\equiv}CCO_2Et$ addition; blue = 12h after $EtO_2CC{\equiv}CCO_2Et$ addition.

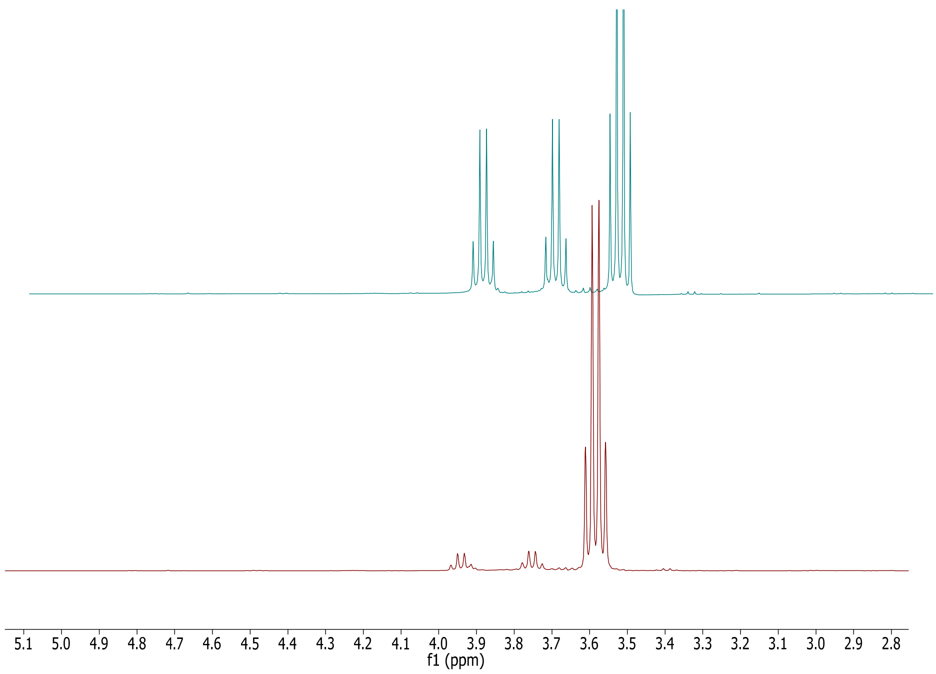


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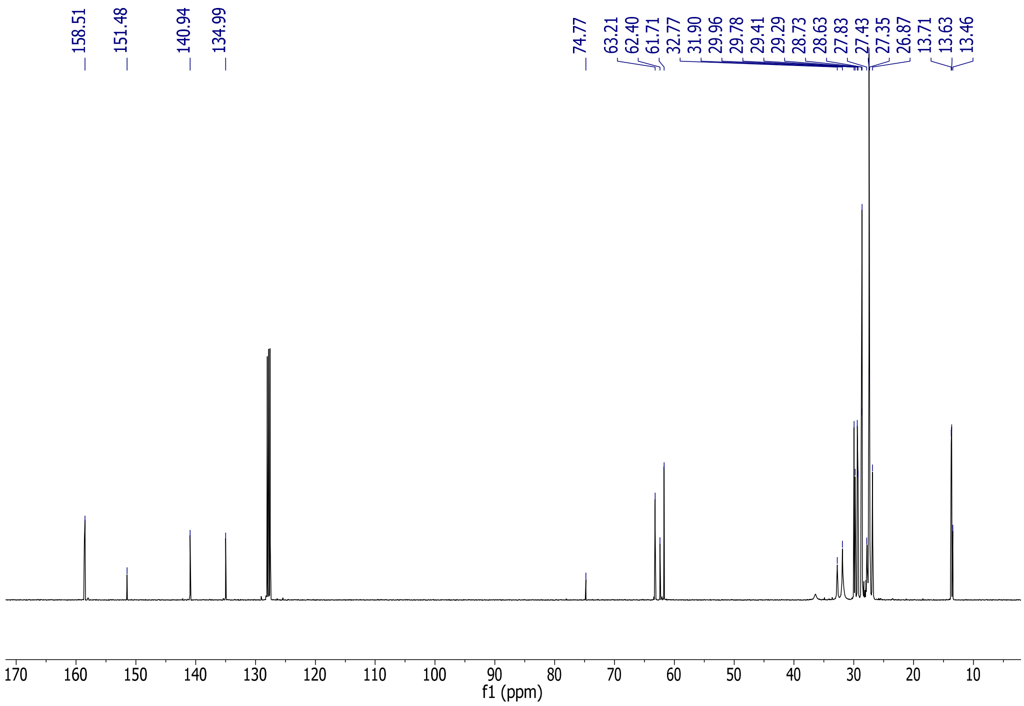
Figure 26 Reaction of Cy_2BN_3 with $EtO_2CC{\equiv}CCO_2Et$ in a 3:1 stoichiometric ratio [^{13}C NMR (100 MHz, d_6-benzene, 298 K)].



2. DFT Studies:

Gas phase geometry-optimised structures for both $(Cy_2BN_3)_2$ (**1**) and **2** were determined using the B3LYP functional and 6-311G*+ basis set within Jaguar.[3] Additional NBO analyses[4] were undertaken to probe the dominant Lewis structure for **2**. The frontier orbitals, NBO partial charges and bond orders of **1** are shown in Fig. 25. Those for **2** are shown in Fig. 26.

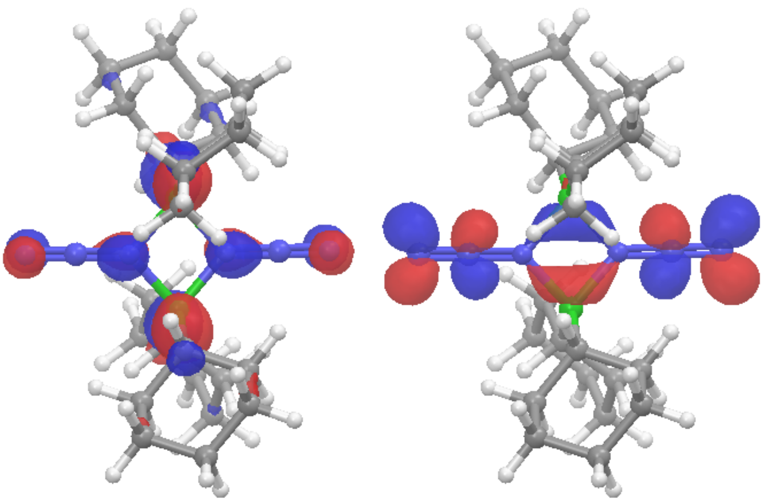
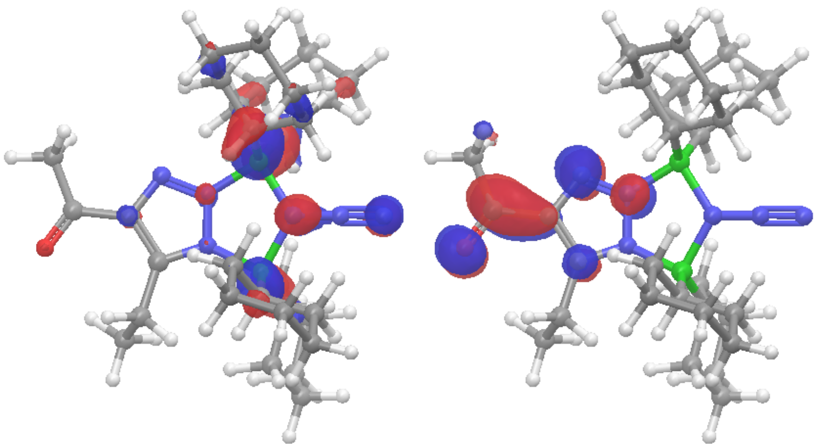


Figure 27 HOMO (left) and LUMO (centre) plus NBO partial charges and bond orders (right) for **1**.



-0.2490 eV -0.0719 eV

Figure 28 HOMO (left) and LUMO (centre) plus NBO partial charges and bond orders (right) for **2**.

3. Crystallographic Details:

X-ray diffraction studies to determine the solid-state structure of crystalline materials were undertaken on single crystals grown under an inert atmosphere and protected from atmospheric air and moisture using an inert per-fluorinated polyether oil. Crystals were examined on a Bruker APEX-II diffractometer using monochromatic Mo-Kα radiation and a CCD area detector. Data were collected at 150(2) K with temperatures maintained using an Oxford Cryostream cooler. Data were collected and processed using APEX-II software and an absorption correction applied using SAINT. Structure solution and refinement used the SHELXTL suite of programs. Crystallographic data are presented in Table 1, with full structural data available in cif format as ESI. We thank Dr M. Pilkington (Brock University) for diffractometer time for these studies

Table 1: Selected Crystallographic Data for **2**, **3** and **5**

Compound	**2**	**3**	**5**
Empirical Formula	$C_{30}H_{52}B_2N_6O$	$C_{38}H_{55}B_2N_6OP$	$C_{80}H_{132}B_6N_6O_8$
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	*P-1*	*P-1*	*P-1*
a/Å	9.1297(4)	9.5954(13)	10.3184(10)
b/Å	9.2734(4)	11.785(15)	14.6317(15)
c/Å	19.1974(8)	17.351(2)	15.0290(16)
α/º	79.937(2)	97.004(4)	69.271(5)
β/º	80.421(2)	97.151(4)	88.761(5)
γ/º	73.642(2)	101.004(5)	75.300(5)
V/Å^3	1523.67(11)	1808.3(4)	2046.8(4)
Z	2	2	1*
T /K	150(2)	150(2)	150(2)
D_c/g.cm^{-3}	1.165	1.220	1.112
Crystal size/mm	0.40 × 0.40 × 0.20	0.41 × 0.06 × 0.04	0.32 × 0.22 × 0.13
Total data	20407	17751	26138
Unique data	5345	6296	7186
R_{int}	0.026	0.033	0.040
$R_1[F^2>2\sigma(F^2)]$	0.055	0.058	0.070
wR_2 (all data)	0.136	0.123	0.161
GoF	1.105	1.121	1.210
ρ_{min}/ρ_{max}/eÅ^{-3}	−0.27/+0.23	−0.33/+0.42	−0.21/+0.29

* molecule lies about a crystallographic inversion centre.

4. References:

1. X. Yang, D. Matsuo, Y. Suzuma, J.-K. Fang, F. Xu, A. Orita, J. Otera, S. Kajiyama, N. Koumura and K. Hara, *Synlett*, 2011, **16**, 2402.

2. Cy_2BN_3·Py has been synthesised previously from the reaction on (Cy)(Ph)BCl and NaN_3 in pyridine. See: Gmelin Handbook: B: B-Verb.4, **8**, 260.

3. Jaguar, version 7.7, Schrodinger, LLC, New York, NY, 2010

4. NBO 5.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001); http://www.chem.wisc.edu/~nbo5