- Supplementary Information -

Alkali-Metal Mediated Reactivity of a Diaminobromoborane: Mono- and Bis-Borylation of Naphthalene Versus Boryl Lithium or Hydroborane Formation

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Experimental

General

All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen or argon. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors except for ethers which were stored over activated 4 Å sieves. Deuterated solvent was distilled from potassium, degassed by three freeze-pump-thaw cycles and stored under nitrogen. Lithium and high-sodium lithium (0.5% Na) were purchased from Aldrich. ^{1}H, ^{13}C, ^{11}B, and ^{7}Li NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, 128.3, and 155.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS (^{1}H and ^{13}C), external 1.0 M Et_2OBF_3 (^{11}B), and external 1.0 M LiCl (^{7}Li). FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental microanalyses were carried out by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

Preparation of C_6H_4-1,2-(NH-2,4,6-$Pr^i_3C_6H_2)_2$ ($PDAH_2$)

$Pd(OAc)_2$ (0.45 g, 2.0 mmol) and P^tBu_3 (1.21 g, 6.0 mmol) were dissolved in toluene (200 ml) and stirred until dissolved. 1,2-dibromobenzene (9.91 g, 42.0 mmol), $TrippNH_2$ (18.42 g, 84.0 mmol) and $NaOBu^t$ (14.51 g, 151.0 mmol; suspension in 100 ml toluene) were added to the reaction mixture while stirring. The mixture was refluxed for 48 hours at 120 °C, after which it was quenched with aqueous NH_4Cl (110 g in 200 ml deionised H_2O). The toluene layer was separated, washed with deionised H_2O (3 × 100 ml), and dried over $MgSO_4$. Volatiles were removed *in vacuo*, yielding a dark brown solid. MeOH (60 ml) was added and, following sonication, **$PDAH_2$** was yielded as a cream free-flowing powder, which was isolated by filtration, washed with ice cold MeOH and dried *in vacuo* for 4 hours. Yield: 13.42 g, 62%. Recrystallisation of **$PDAH_2$** from Et_2O (5 ml) at 5 °C yielded colourless crystals suitable for X-ray diffraction. Anal. calc'd for $C_{36}H_{52}N_2$: C, 84.32, H, 10.22, N, 5.46. Found: C, 84.27, H, 10.26, N, 5.56. ^{1}H NMR (C_6D_6, 298 K): δ 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.41 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CH(CH_3)$_2$), 3.01 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 3.46 (sept, = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 5.26 (s, 2H, NH), 6.57 (m, 2H, Ar-H), 6.69 (m, 2H, Ar-H), 7.36 (s, 4H, tripp-Ar-H). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 23.44, 24.24, 24.66 (CH(*C*H$_3$)$_2$), 28.48, 34.49 (*C*H(CH$_3$)$_2$), 114.91, 120.33, 121.85 (Ar-*C*H), 134.91, 137.16, 145.50, 146.65 (Ar-*C*). FTIR v/cm^{-1} (Nujol): 591 (w), 618 (w), 647 (w), 674 (w), 747 (s), 944 (w), 1049 (w), 1071 (w), 1153 (w), 1170 (w), 1195 (w), 1215 (w), 1253 (m), 1278 (w), 1318 (w), 1402 (m), 1499 (m), 1594 (m), 1607 (w), 3144 (m, br), 3348 (s).

Preparation of C_6H_4-1,2-(N-2,4,6-$Pr^i_3C_6H_2)_2BBr$ (1)

To a cooled (0 °C) suspension of CaH_2 (1.07 g, 25.3 mmol) in toluene (20 ml), solutions of **$PDAH_2$** (7.69 g, 15.0 mmol) in toluene (30 ml) and BBr_3 (15.8 ml, 15.8 mmol, 1.0 M solution in heptane) in toluene (20 ml) were simultaneously added dropwise, while stirring. The resultant pale brown

suspension was allowed to warm to room temperature and stirred for 24 hours. Filtration, followed by removal of volatiles *in vacuo*, afforded a cream, free-flowing powder. Recrystallisation of the powder from toluene (20 ml) at –30 °C overnight yielded colourless crystals of **1** suitable for X-ray diffraction. Yield: 3.99 g, 44%. Anal. calc'd for $C_{36}H_{50}BBrN_2$: C, 71.84, H, 8.38, N, 4.66. Found: C, 71.79, H, 8.39, N, 4.60. ^{1}H NMR (C_6D_6, 298 K): δ 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 2.97 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 3.16 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 6.72 (m, 2H, Ar-*H*), 6.93 (m, 2H, Ar-*H*), 7.40 (s, 4H, tripp-Ar-*H*). ^{13}C{^{1}H} NMR (d_8-THF, 298 K): δ 24.03, 24.11, 24.28 (CH(*C*H$_3$)$_2$), 28.99, 34.48 (*C*H(CH$_3$)$_2$), 110.74, 120.80, 121.95 (Ar-*C*H), 131.61, 138.15, 146.67, 148.81 (Ar-*C*). ^{11}B{^{1}H} NMR (d_8-THF, 298 K): δ 24.6 (s, br). FTIR v/cm^{-1} (Nujol): 593 (w), 651 (w), 740 (w), 793 (m), 877 (m), 922 (w), 945 (w), 1015 (w), 1071 (w), 1113 (w), 1172 (m), 1200 (w), 1270 (s), 1314 (m), 1545 (m), 1581 (m), 1607 (m).

Preparation of {C$_6$H$_4$-1,2-(N-2,4,6-Pr$^i_3$C$_6$H$_2$)$_2$B}-2-C$_{10}$H$_7$ (2) and {C$_6$H$_4$-1,2-(N-2,4,6-Pr$^i_3$C$_6$H$_2$)$_2$B}$_2$-2,6-C$_{10}$H$_6$ (3)

A solution of **1** (0.30 g, 0.5 mmol) and naphthalene (0.06 g, 0.5 mmol) in THF (15 ml) was added dropwise to a cooled (–10 °C) mixture of lithium powder (0.03 g, 5.0 mmol), while stirring. The resulting suspension was sonicated† at low temperature (–10 °C) for 0.5 hours to afford a dark green suspension. Further stirring of the resultant suspension at low temperature (–10 °C) for 5.5 hours, followed by removal of volatiles *in vacuo*, yielded a yellow-brown solid. This solid was extracted into hexane, and the resulting yellow-red solution was filtered away from precipitated solids. Removal of volatiles *in vacuo* yielded a pale orange oil. Fractional crystallisation of the oil from pentane (2 ml) at 5 °C afforded colourless crystals of the 2-borylated and 2,7-borylated naphthalenes **2** and **3** suitable for X-ray diffraction. Yields (average of five reactions): **2** 0.15 g, 46%; **3** 0.10 g, 34%. Yields for five individual reactions (**2**/**3**): 44/35, 45/34, 46/34, 46/34, 48/31%.

Repeating the reaction in a 2:1 ratio of **1** (0.30 g, 0.5 mmol) to naphthalene (0.03 g, 0.25 mmol) under identical experimental and work up conditions afforded **3** with substantially decreased quantities of **2**. Yield of **3** (average of five reactions): 0.24 g, 82%. Yields for **3** from five individual reactions 80, 82, 83, 84, 84. Any **2** present from these reactions could not be crystallised due to the low quantities formed under these conditions which was determined by NMR spectroscopy to be ~4-6% of the reaction mixture. † Reactions conducted without brief sonication exhibited sluggish initiations and produced only trace amounts of **2** and **3**.

2: Anal. calc'd for $C_{46}H_{57}BN_2$: C, 85.16, H, 8.86, N, 4.32. Found: C, 85.04, H, 8.77, N, 4.35. ^{1}H NMR (C_6D_6, 298 K): δ 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 3.10 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$, 3.35 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$, 6.90 (m, 2H, Ar-*H*), 7.01 (m, 2H, naphthalene Ar-*H*), 7.05 (m, 2H, Ar-*H*), 7.21 (m, 3H, naphthalene Ar-*H*), 7.50 (s, 4H, tripp-Ar-*H*), 7.57 (m, 1H, naphthalene Ar-*H*), 7.96 (s, 1H, naphthalene Ar-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 23.87, 24.29, 24.42 (CH(*C*H$_3$)$_2$), 25.17, 28.85, 34.62 (*C*H(CH$_3$)$_2$), 110.61, 113.70, 120.36, 121.40, 121.69, 122.33, 125.65 (Ar-*C*H), 126.5, 127.0, 128.47, 130.55, 134.01, 134.59, 136.24, 139.02, 146.67, 148.81 (Ar-*C*). ^{11}B NMR (C_6D_6, 298 K): δ 27.3 (s, br). FTIR v/cm^{-1} (Nujol): 737 (m), 747 (m), 878 (m), 1054 (w), 1098 (s), 1307 (w), 1340 (w), 1579 (m), 1603 (m), 2342 (m), 2725 (w).

3: Anal. calc'd for $C_{82}H_{106}B_2N_4$: C, 84.22, H, 9.14, N, 4.79. Found: C, 84.08, H, 9.08, N, 4.69. ^{1}H NMR (C_6D_6, 298 K): δ 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 1.49 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 3.01 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$, 3.26 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$, 6.63 (m, 4H, Ar-*H*), 6.89 (m, 2H, naphthalene Ar-*H*), 6.93 (m, 4H, Ar-*H*), 7.04 (m, 2H, naphthalene Ar-*H*), 7.20 (m, 2H, naphthalene Ar-*H*), 7.50 (s, 8H, tripp-Ar-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 23.38, 23.67, 24.16, 24.65, 25.18 (CH(*C*H$_3$)$_2$), 28.78, 28.85, 34.60 (*C*H(CH$_3$)$_2$), 109.16, 110.44, 119.64, 120.27, 121.69, 121.93 (Ar-*C*H), 131.65, 133.65,

137.43, 138.39, 146.47, 147.38, 148.25 (Ar-*C*). ^{11}B NMR (C_6D_6, 298 K): δ 25.8 (s, br). FTIR v/cm^{-1} (Nujol): 738 (m), 838 (w), 878 (m), 944 (w), 977 (w), 1054 (s), 1171 (w), 1292 (w), 1312 (w), 1364 (m), 1382 (s), 1398 (m), 1548 (m), 1578 (m), 1607 (m), 2342 (w), 2586 (m), 3147 (w, br).

Preparation of [{C$_6$H$_4$-1,2-(N-2,4,6-Pr$^i_3$C$_6$H$_2$)$_2$B}Li(THF)$_2$] (4)

A solution of **1** (0.60 g, 1.0 mmol) and naphthalene (0.13 g, 1.0 mmol) in THF (15 ml) was added dropwise to a cooled (–10 °C) mixture of high-sodium lithium powder (0.07 g, 10.0 mmol), while stirring. The resulting suspension was stirred for 6 hours at –10 °C to afford a red/brown suspension. Volatiles were removed *in vacuo* at –10 °C, and the resulting dark brown solid was extracted into hexane. Filtration of the solution away from the precipitated solids, followed by removal of volatiles *in vacuo* yielded complex **4** as an off-white powder. Yield (average): 0.45 g, 85%. Yields for five individual reactions: 82, 83, 85, 85, and 90%. Recrystallisation of the powder from hexane (10 ml) at 5 °C yielded colourless crystals of **2** suitable for X-ray diffraction. Anal. calc'd for $C_{44}H_{66}BLiN_2O_2$: C, 78.55, H, 9.89, N, 4.16. Found: C, 78.62, H, 10.00, N, 4.13.^{1}H NMR (C_6D_6, 298 K): δ 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.42 (m, 8H, THF-C*H*$_2$), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.53 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 3.06 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.18 (m, 8H, THF-C*H*$_2$O), 3.68 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 6.83 (m, 2H, Ar-*H*), 7.02 (m, 2H, Ar-*H*), 7.38 (s, 4H, tripp-Ar-*H*). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 24.10, 24.59, 24.99 (CH(*C*H$_3$)$_2$), 28.45, 34.64 (*C*H(CH$_3$)$_2$), 107.78, 116.73, 120.72 (Ar-*C*H), 140.90, 141.44, 145.55, 147.31 (Ar-*C*). ^{11}B NMR (C_6D_6, 298 K): δ 51.0 (s, br). ^{7}Li NMR (C_6D_6, 298 K): δ 0.6 (s). FTIR v/cm^{-1} (Nujol): 588 (w), 735 (m), 944 (w), 1044 (m), 1166 (w), 1224 (w), 1344 (m), 1583 (w), 1606 (w), 2029 (w).

Preparation of C_6H_4-1,2-(N-2,4,6-$Pr^i_3C_6H_2)_2BH$ (5)

A solution of **1** (0.60 g, 1.0 mmol) and naphthalene (0.13 g, 1.0 mmol) in DME (15 ml) was added dropwise to potassium metal (0.08 g, 2.0 mmol; oxide free) at ambient temperature, while stirring. The resulting suspension was stirred for 6 hours at ambient temperature to afford a red-brown suspension. Volatiles were removed *in vacuo*, and the resulting dark brown solid was extracted into hexane. Filtration of the solution away from the precipitated solids, followed by removal of volatiles *in vacuo*, yielded **5** as a pale pink powder. Recrystallisation of the powder from hexane (10 ml) at 5 °C yielded colourless crystals of **5** suitable for X-ray diffraction. Carrying the reaction out at –10 or –78 °C made no difference to the outcome of the reaction. Yield (average): 0.45 g, 82%. Yields for five individual reactions: 79, 80, 81, 83, 86%. Anal. calc'd for $C_{36}H_{51}BN_2$: C, 82.74, H, 9.84, N, 5.36. Found: C, 82.85, H, 10.00, N, 5.28. ^{1}H NMR (C_6D_6, 298 K): δ 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 1.43 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$, 3.02 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, CH(CH$_3$)$_2$, 3.19 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, CH(CH$_3$)$_2$, 6.81 (m, 2H, Ar-H), 7.00 (m, 2H, Ar-H), 7.41 (s, 4H, tripp-Ar-H). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 23.38, 24.19, 25.18 (CH(*C*H$_3$)$_2$), 28.78, 34.60 (*C*H(CH$_3$)$_2$), 110.44, 120.26, 121.69 (Ar-*C*H), 133.65, 138.38, 146.47, 148.25 (Ar-*C*). ^{11}B NMR (C_6D_6, 298 K): δ 26.2 (s, br). FTIR v/cm^{-1} (Nujol): 596 (w), 649 (w), 738 (m), 838 (w), 877 (m), 944 (w) 1017 (m), 1099 (m), 1151 (w), 1273 (m), 1309 (w), 1579 (w), 1607 (m), 1635 (m, br), 2585 (w), 3441 (s, br).

X-ray Crystallography

Figure S1. Structure of $PDAH_2$

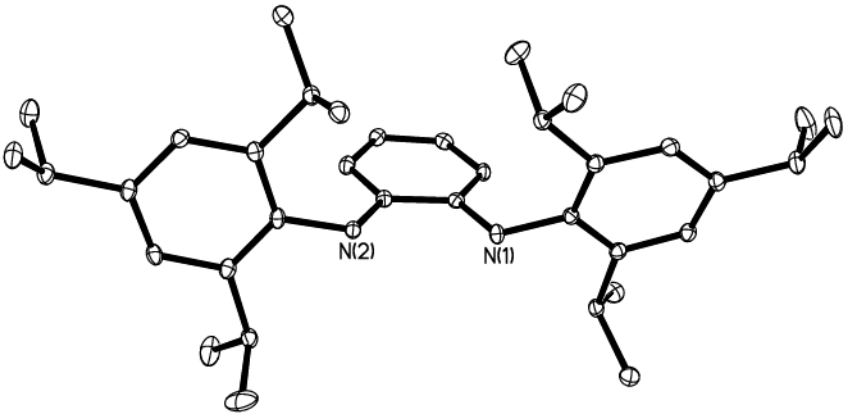


Figure S2. Structure of 1

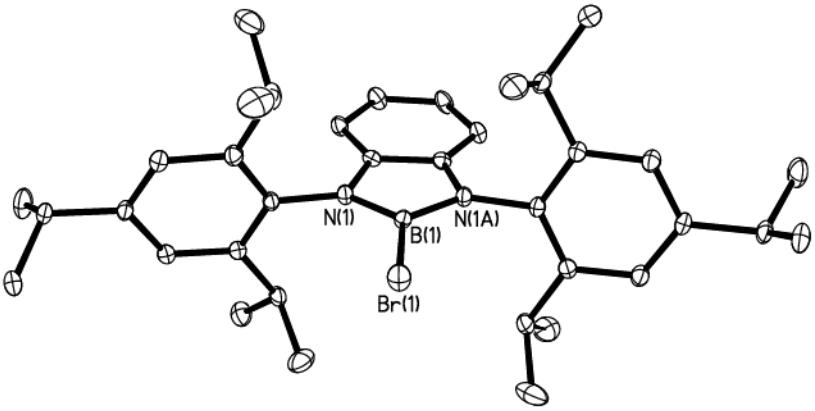


Figure S3. Structure of 2

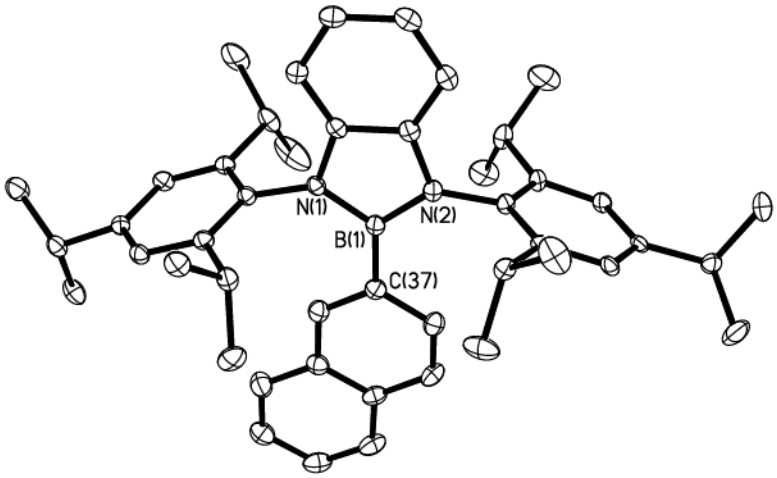


Figure S4. Structure of 3

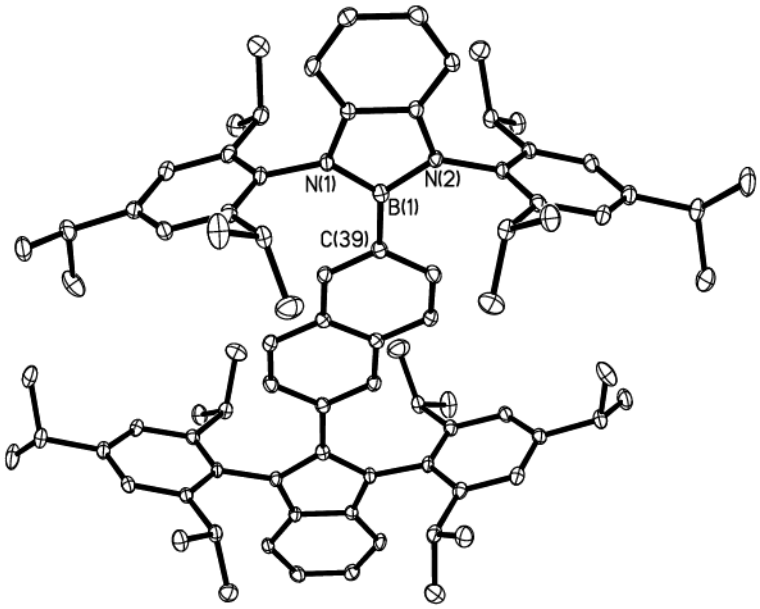


Figure S5. Structure of 4

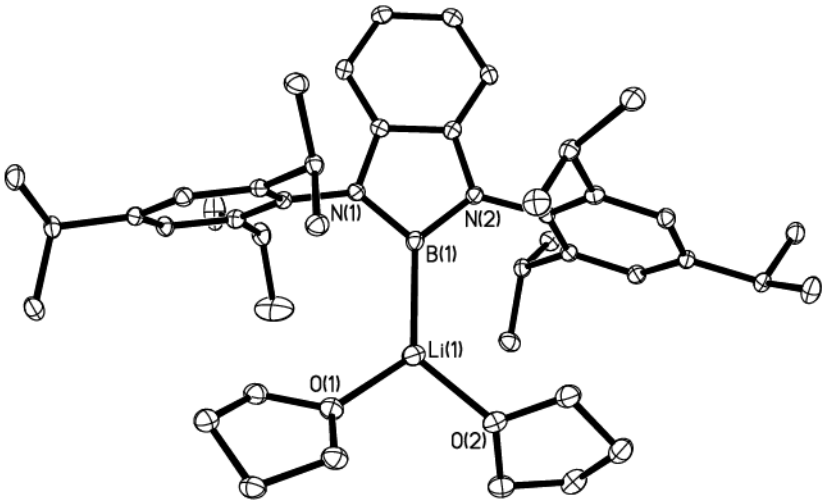
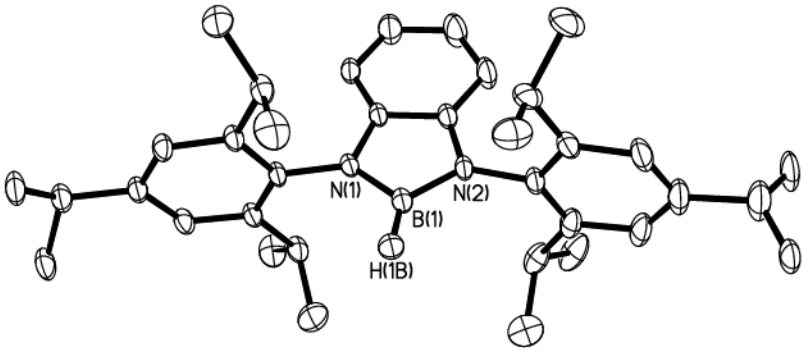


Figure S6. Structure of 5



Crystallographic Data (CCDC 862666-862671)

Table 1. Crystal data and structure refinement for **$PDAH_2$**.

Identification code	**$PDAH_2$**	
Chemical formula	$C_{36}H_{52}N_2$	
Formula weight	512.80	
Temperature	90(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	orthorhombic, Pbca	
Unit cell parameters	a = 10.9044(19) Å	α = 90°
	b = 10.2756(18) Å	β = 90°
	c = 56.353(10) Å	γ = 90°
Cell volume	6314.3(19) $Å^3$	
Z	8	
Calculated density	1.079 g/cm^3	
Absorption coefficient μ	0.062 mm^{-1}	
F(000)	2256	
Crystal colour and size	colourless, 0.21 × 0.14 × 0.03 mm^3	
Reflections for cell refinement	5467 (θ range 2.36 to 27.46°)	
Data collection method	Bruker SMART APEX CCD diffractometer	
	ω rotation with narrow frames	
θ range for data collection	2.00 to 24.99°	
Index ranges	h −12 to 12, k −10 to 12, l −67 to 58	
Completeness to θ = 24.99°	99.1 %	
Intensity decay	0%	
Reflections collected	29753	
Independent reflections	5510 (R_{int} = 0.071)	
Reflections with $F^2>2\sigma$	3961	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.619 and 0.746	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.027, 7.667	
Data / restraints / parameters	5510 / 2 / 361	
Final R indices [$F^2>2\sigma$]	R1 = 0.0591, wR2 = 0.117	
R indices (all data)	R1 = 0.0889, wR2 = 0.131	
Goodness-of-fit on F^2	1.08	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.35 and −0.21 e $Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **$PDAH_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	0.62698(18)	0.0225(2)	0.14581(3)	0.0176(4)
N(2)	0.51819(18)	−0.0520(2)	0.10401(3)	0.0171(4)
C(1)	0.6159(2)	0.1166(2)	0.12773(4)	0.0162(5)
C(2)	0.6579(2)	0.2435(2)	0.13008(4)	0.0192(6)
C(3)	0.6421(2)	0.3336(3)	0.11196(4)	0.0207(5)
C(4)	0.5836(2)	0.2972(3)	0.09115(4)	0.0202(6)
C(5)	0.5442(2)	0.1698(3)	0.08842(4)	0.0203(5)
C(6)	0.5610(2)	0.0784(2)	0.10604(4)	0.0167(5)
C(7)	0.6385(2)	0.0634(2)	0.17032(4)	0.0167(5)
C(8)	0.5344(2)	0.0723(2)	0.18484(4)	0.0182(5)

C(9)	0.5495(2)	0.1119(2)	0.20833(4)	0.0198(6)
C(10)	0.6635(2)	0.1440(2)	0.21763(4)	0.0197(5)
C(11)	0.7646(2)	0.1317(2)	0.20278(4)	0.0195(6)
C(12)	0.7553(2)	0.0896(2)	0.17944(4)	0.0180(5)
C(13)	0.4055(2)	0.0445(3)	0.17543(4)	0.0208(6)
C(14)	0.3483(2)	0.1688(3)	0.16608(5)	0.0316(7)
C(15)	0.3215(2)	–0.0201(3)	0.19351(5)	0.0319(7)
C(16)	0.6825(2)	0.1938(3)	0.24287(4)	0.0255(6)
C(17)	0.5788(3)	0.1614(3)	0.25975(4)	0.0364(7)
C(18)	0.7111(3)	0.3382(3)	0.24249(5)	0.0469(9)
C(19)	0.8727(2)	0.0691(3)	0.16524(4)	0.0204(6)
C(20)	0.9480(2)	–0.0413(3)	0.17635(4)	0.0263(6)
C(21)	0.9500(2)	0.1923(3)	0.16351(5)	0.0296(7)
C(22)	0.4447(2)	–0.0856(2)	0.08362(4)	0.0177(5)
C(23)	0.4949(2)	–0.1489(2)	0.06394(4)	0.0197(5)
C(24)	0.4173(2)	–0.1802(3)	0.04495(4)	0.0208(6)
C(25)	0.2943(2)	–0.1474(2)	0.04480(4)	0.0198(6)
C(26)	0.2475(2)	–0.0828(2)	0.06460(4)	0.0192(5)
C(27)	0.3196(2)	–0.0518(2)	0.08404(4)	0.0177(5)
C(28)	0.6290(2)	–0.1896(3)	0.06280(4)	0.0225(6)
C(29)	0.6421(3)	–0.3347(3)	0.06730(6)	0.0459(8)
C(30)	0.6898(3)	–0.1506(4)	0.03932(5)	0.0426(9)
C(31)	0.2138(2)	–0.1770(3)	0.02341(4)	0.0229(6)
C(32)	0.1712(3)	–0.0512(3)	0.01151(5)	0.0336(7)
C(33)	0.1045(2)	–0.2628(3)	0.02985(4)	0.0278(6)
C(34)	0.2632(2)	0.0106(2)	0.10605(4)	0.0197(5)
C(35)	0.2305(2)	–0.0949(3)	0.12411(4)	0.0241(6)
C(36)	0.1507(2)	0.0931(3)	0.10062(4)	0.0254(6)

Table 3. Bond lengths [Å] and angles [°] for **PDAH$_2$**.

N(1)–C(1)	1.409(3)	N(1)–C(7)	1.449(3)
N(1)–H(1N)	0.880(10)	N(2)–C(6)	1.423(3)
N(2)–C(22)	1.443(3)	N(2)–H(2N)	0.885(10)
C(1)–C(2)	1.389(3)	C(1)–C(6)	1.417(3)
C(2)–C(3)	1.389(3)	C(2)–H(2)	0.9500
C(3)–C(4)	1.386(3)	C(3)–H(3)	0.9500
C(4)–C(5)	1.387(4)	C(4)–H(4)	0.9500
C(5)–C(6)	1.379(3)	C(5)–H(5)	0.9500
C(7)–C(12)	1.400(3)	C(7)–C(8)	1.403(3)
C(8)–C(9)	1.395(3)	C(8)–C(13)	1.529(3)
C(9)–C(10)	1.390(3)	C(9)–H(9)	0.9500
C(10)–C(11)	1.390(3)	C(10)–C(16)	1.526(3)
C(11)–C(12)	1.388(3)	C(11)–H(11)	0.9500
C(12)–C(19)	1.524(3)	C(13)–C(14)	1.516(4)
C(13)–C(15)	1.522(3)	C(13)–H(13)	1.0000
C(14)–H(14A)	0.9800	C(14)–H(14B)	0.9800
C(14)–H(14C)	0.9800	C(15)–H(15C)	0.9800
C(15)–H(15B)	0.9800	C(15)–H(15A)	0.9800
C(16)–C(17)	1.515(3)	C(16)–C(18)	1.516(4)
C(16)–H(16)	1.0000	C(17)–H(17A)	0.9800
C(17)–H(17C)	0.9800	C(17)–H(17B)	0.9800
C(18)–H(18B)	0.9800	C(18)–H(18C)	0.9800
C(18)–H(18A)	0.9800	C(19)–C(21)	1.524(4)
C(19)–C(20)	1.534(4)	C(19)–H(19)	1.0000
C(20)–H(20C)	0.9800	C(20)–H(20B)	0.9800

C(20)–H(20A)	0.9800	C(21)–H(21A)	0.9800
C(21)–H(21B)	0.9800	C(21)–H(21C)	0.9800
C(22)–C(23)	1.397(3)	C(22)–C(27)	1.408(3)
C(23)–C(24)	1.402(3)	C(23)–C(28)	1.523(3)
C(24)–C(25)	1.383(3)	C(24)–H(24)	0.9500
C(25)–C(26)	1.395(3)	C(25)–C(31)	1.522(3)
C(26)–C(27)	1.386(3)	C(26)–H(26)	0.9500
C(27)–C(34)	1.525(3)	C(28)–C(29)	1.519(4)
C(28)–C(30)	1.533(3)	C(28)–H(28)	1.0000
C(29)–H(29B)	0.9800	C(29)–H(29C)	0.9800
C(29)–H(29A)	0.9800	C(30)–H(30A)	0.9800
C(30)–H(30C)	0.9800	C(30)–H(30B)	0.9800
C(31)–C(33)	1.526(4)	C(31)–C(32)	1.529(4)
C(31)–H(31)	1.0000	C(32)–H(32A)	0.9800
C(32)–H(32C)	0.9800	C(32)–H(32B)	0.9800
C(33)–H(33B)	0.9800	C(33)–H(33C)	0.9800
C(33)–H(33A)	0.9800	C(34)–C(36)	1.522(4)
C(34)–C(35)	1.530(3)	C(34)–H(34)	1.0000
C(35)–H(35A)	0.9800	C(35)–H(35B)	0.9800
C(35)–H(35C)	0.9800	C(36)–H(36B)	0.9800
C(36)–H(36C)	0.9800	C(36)–H(36A)	0.9800

C(1)–N(1)–C(7)	119.8(2)	C(1)–N(1)–H(1N)	110.3(16)
C(7)–N(1)–H(1N)	113.7(16)	C(6)–N(2)–C(22)	118.09(19)
C(6)–N(2)–H(2N)	111.5(17)	C(22)–N(2)–H(2N)	111.9(17)
C(2)–C(1)–N(1)	123.2(2)	C(2)–C(1)–C(6)	118.8(2)
N(1)–C(1)–C(6)	118.0(2)	C(1)–C(2)–C(3)	121.0(2)
C(1)–C(2)–H(2)	119.5	C(3)–C(2)–H(2)	119.5
C(4)–C(3)–C(2)	119.9(2)	C(4)–C(3)–H(3)	120.0
C(2)–C(3)–H(3)	120.0	C(3)–C(4)–C(5)	119.4(2)
C(3)–C(4)–H(4)	120.3	C(5)–C(4)–H(4)	120.3
C(6)–C(5)–C(4)	121.5(2)	C(6)–C(5)–H(5)	119.3
C(4)–C(5)–H(5)	119.3	C(5)–C(6)–C(1)	119.2(2)
C(5)–C(6)–N(2)	122.7(2)	C(1)–C(6)–N(2)	118.0(2)
C(12)–C(7)–C(8)	120.7(2)	C(12)–C(7)–N(1)	119.0(2)
C(8)–C(7)–N(1)	120.3(2)	C(9)–C(8)–C(7)	118.5(2)
C(9)–C(8)–C(13)	119.5(2)	C(7)–C(8)–C(13)	122.0(2)
C(10)–C(9)–C(8)	122.2(2)	C(10)–C(9)–H(9)	118.9
C(8)–C(9)–H(9)	118.9	C(9)–C(10)–C(11)	117.5(2)
C(9)–C(10)–C(16)	123.5(2)	C(11)–C(10)–C(16)	119.0(2)
C(12)–C(11)–C(10)	122.8(2)	C(12)–C(11)–H(11)	118.6
C(10)–C(11)–H(11)	118.6	C(11)–C(12)–C(7)	118.3(2)
C(11)–C(12)–C(19)	118.6(2)	C(7)–C(12)–C(19)	123.0(2)
C(14)–C(13)–C(15)	110.7(2)	C(14)–C(13)–C(8)	110.0(2)
C(15)–C(13)–C(8)	113.7(2)	C(14)–C(13)–H(13)	107.4
C(15)–C(13)–H(13)	107.4	C(8)–C(13)–H(13)	107.4
C(13)–C(14)–H(14A)	109.5	C(13)–C(14)–H(14B)	109.5
H(14A)–C(14)–H(14B)	109.5	C(13)–C(14)–H(14C)	109.5
H(14A)–C(14)–H(14C)	109.5	H(14B)–C(14)–H(14C)	109.5
C(13)–C(15)–H(15C)	109.5	C(13)–C(15)–H(15B)	109.5
H(15C)–C(15)–H(15B)	109.5	C(13)–C(15)–H(15A)	109.5
H(15C)–C(15)–H(15A)	109.5	H(15B)–C(15)–H(15A)	109.5
C(17)–C(16)–C(18)	112.2(2)	C(17)–C(16)–C(10)	114.2(2)
C(18)–C(16)–C(10)	110.0(2)	C(17)–C(16)–H(16)	106.6
C(18)–C(16)–H(16)	106.6	C(10)–C(16)–H(16)	106.6
C(16)–C(17)–H(17A)	109.5	C(16)–C(17)–H(17C)	109.5
H(17A)–C(17)–H(17C)	109.5	C(16)–C(17)–H(17B)	109.5

H(17A)–C(17)–H(17B)	109.5	H(17C)–C(17)–H(17B)	109.5
C(16)–C(18)–H(18B)	109.5	C(16)–C(18)–H(18C)	109.5
H(18B)–C(18)–H(18C)	109.5	C(16)–C(18)–H(18A)	109.5
H(18B)–C(18)–H(18A)	109.5	H(18C)–C(18)–H(18A)	109.5
C(12)–C(19)–C(21)	112.5(2)	C(12)–C(19)–C(20)	109.7(2)
C(21)–C(19)–C(20)	110.2(2)	C(12)–C(19)–H(19)	108.1
C(21)–C(19)–H(19)	108.1	C(20)–C(19)–H(19)	108.1
C(19)–C(20)–H(20C)	109.5	C(19)–C(20)–H(20B)	109.5
H(20C)–C(20)–H(20B)	109.5	C(19)–C(20)–H(20A)	109.5
H(20C)–C(20)–H(20A)	109.5	H(20B)–C(20)–H(20A)	109.5
C(19)–C(21)–H(21A)	109.5	C(19)–C(21)–H(21B)	109.5
H(21A)–C(21)–H(21B)	109.5	C(19)–C(21)–H(21C)	109.5
H(21A)–C(21)–H(21C)	109.5	H(21B)–C(21)–H(21C)	109.5
C(23)–C(22)–C(27)	120.5(2)	C(23)–C(22)–N(2)	121.7(2)
C(27)–C(22)–N(2)	117.7(2)	C(22)–C(23)–C(24)	118.5(2)
C(22)–C(23)–C(28)	122.5(2)	C(24)–C(23)–C(28)	119.0(2)
C(25)–C(24)–C(23)	122.3(2)	C(25)–C(24)–H(24)	118.9
C(23)–C(24)–H(24)	118.9	C(24)–C(25)–C(26)	117.8(2)
C(24)–C(25)–C(31)	121.1(2)	C(26)–C(25)–C(31)	121.2(2)
C(27)–C(26)–C(25)	122.3(2)	C(27)–C(26)–H(26)	118.8
C(25)–C(26)–H(26)	118.8	C(26)–C(27)–C(22)	118.6(2)
C(26)–C(27)–C(34)	120.7(2)	C(22)–C(27)–C(34)	120.5(2)
C(29)–C(28)–C(23)	110.6(2)	C(29)–C(28)–C(30)	111.1(2)
C(23)–C(28)–C(30)	112.3(2)	C(29)–C(28)–H(28)	107.5
C(23)–C(28)–H(28)	107.5	C(30)–C(28)–H(28)	107.5
C(28)–C(29)–H(29B)	109.5	C(28)–C(29)–H(29C)	109.5
H(29B)–C(29)–H(29C)	109.5	C(28)–C(29)–H(29A)	109.5
H(29B)–C(29)–H(29A)	109.5	H(29C)–C(29)–H(29A)	109.5
C(28)–C(30)–H(30A)	109.5	C(28)–C(30)–H(30C)	109.5
H(30A)–C(30)–H(30C)	109.5	C(28)–C(30)–H(30B)	109.5
H(30A)–C(30)–H(30B)	109.5	H(30C)–C(30)–H(30B)	109.5
C(25)–C(31)–C(33)	112.2(2)	C(25)–C(31)–C(32)	110.7(2)
C(33)–C(31)–C(32)	110.9(2)	C(25)–C(31)–H(31)	107.6
C(33)–C(31)–H(31)	107.6	C(32)–C(31)–H(31)	107.6
C(31)–C(32)–H(32A)	109.5	C(31)–C(32)–H(32C)	109.5
H(32A)–C(32)–H(32C)	109.5	C(31)–C(32)–H(32B)	109.5
H(32A)–C(32)–H(32B)	109.5	H(32C)–C(32)–H(32B)	109.5
C(31)–C(33)–H(33B)	109.5	C(31)–C(33)–H(33C)	109.5
H(33B)–C(33)–H(33C)	109.5	C(31)–C(33)–H(33A)	109.5
H(33B)–C(33)–H(33A)	109.5	H(33C)–C(33)–H(33A)	109.5
C(36)–C(34)–C(27)	113.3(2)	C(36)–C(34)–C(35)	109.9(2)
C(27)–C(34)–C(35)	109.7(2)	C(36)–C(34)–H(34)	107.9
C(27)–C(34)–H(34)	107.9	C(35)–C(34)–H(34)	107.9
C(34)–C(35)–H(35A)	109.5	C(34)–C(35)–H(35B)	109.5
H(35A)–C(35)–H(35B)	109.5	C(34)–C(35)–H(35C)	109.5
H(35A)–C(35)–H(35C)	109.5	H(35B)–C(35)–H(35C)	109.5
C(34)–C(36)–H(36B)	109.5	C(34)–C(36)–H(36C)	109.5
H(36B)–C(36)–H(36C)	109.5	C(34)–C(36)–H(36A)	109.5
H(36B)–C(36)–H(36A)	109.5	H(36C)–C(36)–H(36A)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$) for **$PDAH_2$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	0.0192(11)	0.0189(12)	0.0148(10)	–0.0018(8)	–0.0018(8)	–0.0045(9)
N(2)	0.0181(10)	0.0179(12)	0.0153(10)	–0.0008(9)	–0.0019(8)	–0.0002(9)
C(1)	0.0133(11)	0.0192(14)	0.0160(11)	0.0008(10)	0.0027(9)	0.0000(10)
C(2)	0.0150(12)	0.0273(15)	0.0152(12)	–0.0045(10)	–0.0014(9)	–0.0014(11)
C(3)	0.0191(12)	0.0192(14)	0.0237(13)	–0.0014(11)	0.0039(10)	–0.0019(11)
C(4)	0.0176(12)	0.0254(15)	0.0176(12)	0.0033(10)	0.0011(10)	–0.0002(11)
C(5)	0.0169(12)	0.0281(15)	0.0159(11)	0.0006(11)	–0.0002(10)	–0.0017(11)
C(6)	0.0143(12)	0.0200(14)	0.0158(11)	–0.0003(10)	0.0019(9)	–0.0023(11)
C(7)	0.0210(13)	0.0153(13)	0.0139(11)	0.0016(10)	0.0006(9)	0.0013(11)
C(8)	0.0203(12)	0.0166(13)	0.0178(12)	0.0017(10)	–0.0011(10)	0.0002(11)
C(9)	0.0184(12)	0.0228(15)	0.0180(12)	0.0027(10)	0.0040(10)	0.0017(11)
C(10)	0.0234(13)	0.0200(14)	0.0158(12)	0.0001(10)	0.0006(10)	–0.0004(11)
C(11)	0.0181(13)	0.0215(14)	0.0188(12)	–0.0005(10)	–0.0026(10)	–0.0011(11)
C(12)	0.0188(12)	0.0176(13)	0.0177(11)	0.0025(10)	0.0000(10)	0.0005(11)
C(13)	0.0171(12)	0.0284(15)	0.0169(12)	–0.0019(11)	0.0002(10)	–0.0003(11)
C(14)	0.0214(14)	0.0331(17)	0.0404(16)	0.0081(13)	–0.0080(12)	–0.0033(13)
C(15)	0.0241(15)	0.0386(18)	0.0329(15)	0.0064(13)	–0.0046(12)	–0.0092(13)
C(16)	0.0279(14)	0.0329(16)	0.0157(12)	–0.0020(11)	–0.0001(10)	–0.0020(13)
C(17)	0.0354(16)	0.059(2)	0.0147(13)	–0.0069(13)	0.0045(11)	–0.0088(16)
C(18)	0.078(3)	0.0371(19)	0.0259(15)	–0.0104(14)	0.0043(15)	–0.0110(18)
C(19)	0.0207(13)	0.0253(15)	0.0151(11)	–0.0027(10)	0.0000(10)	0.0008(12)
C(20)	0.0232(13)	0.0300(16)	0.0256(13)	–0.0021(12)	0.0014(11)	0.0026(12)
C(21)	0.0238(14)	0.0350(17)	0.0300(14)	0.0030(12)	0.0073(11)	–0.0016(13)
C(22)	0.0220(13)	0.0190(13)	0.0120(11)	0.0023(10)	–0.0010(10)	–0.0047(11)
C(23)	0.0195(12)	0.0246(14)	0.0150(12)	0.0024(10)	0.0002(10)	–0.0026(11)
C(24)	0.0237(13)	0.0259(15)	0.0127(11)	–0.0029(10)	0.0028(10)	–0.0023(12)
C(25)	0.0209(13)	0.0249(15)	0.0137(11)	0.0025(10)	–0.0009(10)	–0.0041(11)
C(26)	0.0160(11)	0.0226(14)	0.0190(12)	0.0009(11)	–0.0005(10)	0.0004(11)
C(27)	0.0209(13)	0.0180(13)	0.0142(11)	0.0021(10)	0.0012(10)	–0.0028(11)
C(28)	0.0185(13)	0.0307(16)	0.0184(12)	–0.0063(11)	0.0007(10)	–0.0004(12)
C(29)	0.0181(14)	0.0366(19)	0.083(2)	–0.0006(17)	–0.0047(15)	0.0034(14)
C(30)	0.0218(14)	0.083(3)	0.0234(14)	–0.0068(15)	0.0049(12)	–0.0074(16)
C(31)	0.0210(13)	0.0314(16)	0.0163(12)	–0.0024(11)	0.0006(10)	–0.0023(12)
C(32)	0.0391(17)	0.0389(18)	0.0228(14)	0.0026(13)	–0.0082(12)	–0.0052(14)
C(33)	0.0241(13)	0.0401(18)	0.0193(13)	–0.0027(12)	–0.0024(11)	–0.0069(13)
C(34)	0.0196(13)	0.0222(14)	0.0173(12)	–0.0023(10)	–0.0008(10)	–0.0018(11)
C(35)	0.0241(14)	0.0281(16)	0.0201(12)	–0.0021(11)	0.0039(11)	–0.0004(12)
C(36)	0.0268(14)	0.0281(16)	0.0215(13)	–0.0027(11)	0.0019(11)	0.0013(12)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **$PDAH_2$**.

	x	y	z	U(eq)
H(1N)	0.5732(18)	–0.0402(18)	0.1437(4)	0.021
H(2N)	0.5779(17)	–0.109(2)	0.1064(4)	0.021
H(2)	0.6981	0.2691	0.1443	0.023
H(3)	0.6714	0.4201	0.1138	0.025
H(4)	0.5707	0.3591	0.0789	0.024
H(5)	0.5048	0.1449	0.0741	0.024

H(9)	0.4794	0.1172	0.2183	0.024
H(11)	0.8434	0.1530	0.2089	0.023
H(13)	0.4140	–0.0166	0.1617	0.025
H(14A)	0.2676	0.1494	0.1593	0.047
H(14B)	0.4013	0.2063	0.1538	0.047
H(14C)	0.3389	0.2312	0.1791	0.047
H(15C)	0.3041	0.0410	0.2064	0.048
H(15B)	0.3618	–0.0977	0.2000	0.048
H(15A)	0.2446	–0.0454	0.1858	0.048
H(16)	0.7573	0.1492	0.2491	0.031
H(17A)	0.5044	0.2077	0.2548	0.055
H(17C)	0.6013	0.1880	0.2759	0.055
H(17B)	0.5635	0.0674	0.2595	0.055
H(18B)	0.7775	0.3549	0.2312	0.070
H(18C)	0.7365	0.3663	0.2584	0.070
H(18A)	0.6378	0.3866	0.2377	0.070
H(19)	0.8493	0.0423	0.1488	0.024
H(20C)	0.9787	–0.0137	0.1919	0.039
H(20B)	1.0173	–0.0624	0.1660	0.039
H(20A)	0.8960	–0.1184	0.1783	0.039
H(21A)	0.9017	0.2616	0.1561	0.044
H(21B)	1.0231	0.1749	0.1539	0.044
H(21C)	0.9750	0.2197	0.1795	0.044
H(24)	0.4503	–0.2256	0.0317	0.025
H(26)	0.1633	–0.0593	0.0648	0.023
H(28)	0.6732	–0.1431	0.0758	0.027
H(29B)	0.6152	–0.3547	0.0835	0.069
H(29C)	0.7281	–0.3602	0.0654	0.069
H(29A)	0.5914	–0.3828	0.0559	0.069
H(30A)	0.6509	–0.1978	0.0262	0.064
H(30C)	0.7773	–0.1724	0.0399	0.064
H(30B)	0.6802	–0.0568	0.0369	0.064
H(31)	0.2649	–0.2258	0.0117	0.027
H(32A)	0.1248	–0.0722	–0.0029	0.050
H(32C)	0.2427	0.0018	0.0073	0.050
H(32B)	0.1187	–0.0024	0.0225	0.050
H(33B)	0.0496	–0.2151	0.0405	0.042
H(33C)	0.1337	–0.3418	0.0378	0.042
H(33A)	0.0600	–0.2868	0.0154	0.042
H(34)	0.3265	0.0685	0.1134	0.024
H(35A)	0.1694	–0.1538	0.1172	0.036
H(35B)	0.1968	–0.0543	0.1384	0.036
H(35C)	0.3044	–0.1443	0.1282	0.036
H(36B)	0.1701	0.1549	0.0879	0.038
H(36C)	0.1263	0.1410	0.1149	0.038
H(36A)	0.0832	0.0366	0.0956	0.038

Table 6. Crystal data and structure refinement for **1**.

Identification code	**1**
Chemical formula	$C_{43}H_{58}BBrN_2$
Formula weight	693.63
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	Monoclinic, C2/c

Unit cell parameters	a = 17.3321(7) Å	α = 90°
	b = 10.0841(4) Å	β = 91.785(2)°
	c = 22.7728(10) Å	γ = 90°
Cell volume	3978.3(3) Å^3	
Z	4	
Calculated density	1.158 g/cm^3	
Absorption coefficient μ	1.063 mm^{-1}	
F(000)	1480	
Crystal colour and size	colourless, 0.38 × 0.33 × 0.31 mm^3	
Reflections for cell refinement	6889 (θ range 2.34 to 26.60°)	
Data collection method	Bruker SMART 1000 CCD diffractometer ω rotation with narrow frames	
θ range for data collection	2.52 to 27.41°	
Index ranges	h –22 to 21, k –11 to 12, l –29 to 28	
Completeness to θ = 26.00°	99.5 %	
Intensity decay	0%	
Reflections collected	23033	
Independent reflections	4440 (R_{int} = 0.0409)	
Reflections with $F^2>2\sigma$	3541	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.69 and 0.73	
Structure solution	Patterson synthesis	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0614, 2.0030	
Data / restraints / parameters	4440 / 0 / 188	
Final R indices [$F^2>2\sigma$]	R1 = 0.0419, wR2 = 0.1059	
R indices (all data)	R1 = 0.0567, wR2 = 0.1106	
Goodness-of-fit on F^2	1.053	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.759 and –0.466 e Å^{-3}	

Table 7. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	0.0000	0.04079(3)	0.7500	0.03428(13)
B(1)	0.0000	0.2314(3)	0.7500	0.0196(6)
N(1)	–0.05595(9)	0.31379(16)	0.77618(7)	0.0212(4)
C(1)	–0.03358(11)	0.44631(18)	0.76644(9)	0.0208(4)
C(2)	–0.06726(12)	0.56387(19)	0.78420(10)	0.0257(5)
C(3)	–0.03307(12)	0.6825(2)	0.76725(10)	0.0303(5)
C(4)	–0.12405(11)	0.28393(19)	0.80882(9)	0.0206(4)
C(5)	–0.19676(11)	0.2908(2)	0.77944(9)	0.0227(4)
C(6)	–0.26239(12)	0.2683(2)	0.81200(9)	0.0262(4)
C(7)	–0.25672(12)	0.23904(19)	0.87241(9)	0.0240(4)
C(8)	–0.18387(12)	0.2314(2)	0.89945(9)	0.0265(5)
C(9)	–0.11623(12)	0.2535(2)	0.86852(9)	0.0252(4)
C(10)	–0.20354(12)	0.3207(2)	0.71378(9)	0.0285(5)
C(11)	–0.27762(14)	0.3950(3)	0.69544(11)	0.0374(6)
C(12)	–0.19621(16)	0.1930(3)	0.67742(11)	0.0454(6)
C(13)	–0.32937(12)	0.2197(2)	0.90772(9)	0.0273(5)
C(14)	–0.38263(15)	0.3403(3)	0.90257(12)	0.0444(7)
C(15)	–0.37268(13)	0.0930(3)	0.88969(11)	0.0361(5)
C(16)	–0.03753(13)	0.2487(3)	0.90080(10)	0.0365(6)

C(17)	–0.03100(16)	0.3585(3)	0.94731(13)	0.0489(7)
C(18)	–0.02262(18)	0.1115(3)	0.92814(13)	0.0545(8)

Table 8. Bond lengths [Å] and angles [°] for **1**.

Br(1)–B(1)	1.922(3)	B(1)–N(1)#1	1.422(2)
B(1)–N(1)	1.422(2)	N(1)–C(1)	1.411(2)
N(1)–C(4)	1.446(2)	C(1)–C(2)	1.387(3)
C(1)–C(1)#1	1.403(4)	C(2)–C(3)	1.395(3)
C(3)–C(3)#1	1.410(4)	C(4)–C(9)	1.396(3)
C(4)–C(5)	1.410(3)	C(5)–C(6)	1.396(3)
C(5)–C(10)	1.526(3)	C(6)–C(7)	1.407(3)
C(7)–C(8)	1.390(3)	C(7)–C(13)	1.527(3)
C(8)–C(9)	1.404(3)	C(9)–C(16)	1.530(3)
C(10)–C(11)	1.533(3)	C(10)–C(12)	1.539(4)
C(13)–C(14)	1.530(3)	C(13)–C(15)	1.531(3)
C(16)–C(17)	1.534(4)	C(16)–C(18)	1.536(4)

N(1)#1–B(1)–N(1)	108.5(2)	N(1)#1–B(1)–Br(1)	125.75(11)
N(1)–B(1)–Br(1)	125.75(11)	C(1)–N(1)–B(1)	107.04(16)
C(1)–N(1)–C(4)	120.72(15)	B(1)–N(1)–C(4)	132.22(17)
C(2)–C(1)–C(1)#1	121.27(11)	C(2)–C(1)–N(1)	130.03(18)
C(1)#1–C(1)–N(1)	108.69(10)	C(1)–C(2)–C(3)	117.77(18)
C(2)–C(3)–C(3)#1	120.94(12)	C(9)–C(4)–C(5)	122.08(17)
C(9)–C(4)–N(1)	119.36(18)	C(5)–C(4)–N(1)	118.53(17)
C(6)–C(5)–C(4)	118.11(18)	C(6)–C(5)–C(10)	120.90(18)
C(4)–C(5)–C(10)	120.99(17)	C(5)–C(6)–C(7)	121.34(19)
C(8)–C(7)–C(6)	118.66(18)	C(8)–C(7)–C(13)	120.81(18)
C(6)–C(7)–C(13)	120.52(19)	C(7)–C(8)–C(9)	122.02(19)
C(4)–C(9)–C(8)	117.78(19)	C(4)–C(9)–C(16)	122.20(18)
C(8)–C(9)–C(16)	119.98(19)	C(5)–C(10)–C(11)	113.68(17)
C(5)–C(10)–C(12)	110.89(19)	C(11)–C(10)–C(12)	110.2(2)
C(7)–C(13)–C(14)	111.31(18)	C(7)–C(13)–C(15)	111.77(17)
C(14)–C(13)–C(15)	110.7(2)	C(9)–C(16)–C(17)	110.8(2)
C(9)–C(16)–C(18)	111.1(2)	C(17)–C(16)–C(18)	111.3(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+3/2

Table 9. Anisotropic displacement parameters ($Å^2$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	0.0375(2)	0.01831(15)	0.0477(2)	0.000	0.01121(15)	0.000
B(1)	0.0211(16)	0.0176(14)	0.0202(16)	0.000	0.0036(12)	0.000
N(1)	0.0192(8)	0.0197(8)	0.0251(9)	0.0008(7)	0.0055(7)	–0.0004(6)
C(1)	0.0194(10)	0.0206(9)	0.0223(10)	–0.0006(8)	–0.0022(8)	–0.0020(7)
C(2)	0.0188(10)	0.0247(10)	0.0339(12)	–0.0027(9)	0.0037(8)	0.0003(7)
C(3)	0.0222(11)	0.0201(10)	0.0489(14)	–0.0034(9)	0.0044(10)	0.0028(8)
C(4)	0.0194(10)	0.0200(9)	0.0227(10)	–0.0004(8)	0.0046(8)	–0.0025(7)
C(5)	0.0219(10)	0.0241(9)	0.0223(10)	–0.0005(8)	0.0028(8)	–0.0026(8)
C(6)	0.0235(11)	0.0312(10)	0.0240(11)	–0.0012(9)	0.0030(8)	–0.0051(8)
C(7)	0.0245(11)	0.0257(10)	0.0222(10)	–0.0013(8)	0.0081(8)	–0.0030(8)
C(8)	0.0255(11)	0.0307(10)	0.0235(11)	0.0001(9)	0.0049(8)	–0.0012(8)
C(9)	0.0210(11)	0.0301(10)	0.0244(11)	0.0003(9)	0.0018(8)	0.0015(8)

C(10)	0.0231(10)	0.0416(12)	0.0207(11)	0.0039(9)	0.0020(8)	–0.0085(9)
C(11)	0.0332(13)	0.0472(14)	0.0319(13)	0.0100(11)	0.0010(10)	–0.0003(11)
C(12)	0.0476(15)	0.0619(17)	0.0263(13)	–0.0075(12)	–0.0036(11)	0.0070(13)
C(13)	0.0241(11)	0.0373(11)	0.0211(10)	–0.0006(9)	0.0079(8)	–0.0036(9)
C(14)	0.0398(14)	0.0426(13)	0.0521(16)	0.0006(12)	0.0235(12)	0.0054(11)
C(15)	0.0284(12)	0.0438(12)	0.0369(13)	–0.0023(11)	0.0121(10)	–0.0102(10)
C(16)	0.0204(11)	0.0618(16)	0.0273(12)	0.0086(11)	0.0013(9)	0.0045(10)
C(17)	0.0395(15)	0.0576(17)	0.0486(16)	0.0058(14)	–0.0118(12)	–0.0139(12)
C(18)	0.0524(17)	0.0615(18)	0.0487(17)	–0.0016(14)	–0.0162(13)	0.0253(14)

Table 10. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **1**.

	x	y	z	U(eq)
H(2)	–0.1121	0.5636	0.8071	0.031
H(3)	–0.0547	0.7645	0.7791	0.036
H(10)	–0.1591	0.3791	0.7041	0.034
H(11A)	–0.3222	0.3366	0.7001	0.056
H(11B)	–0.2749	0.4222	0.6542	0.056
H(11C)	–0.2831	0.4737	0.7202	0.056
H(12A)	–0.1487	0.1463	0.6895	0.068
H(12B)	–0.1944	0.2156	0.6356	0.068
H(12C)	–0.2408	0.1357	0.6839	0.068
H(13)	–0.3129	0.2103	0.9500	0.033
H(14A)	–0.4032	0.3477	0.8621	0.067
H(14B)	–0.3534	0.4207	0.9129	0.067
H(14C)	–0.4254	0.3299	0.9294	0.067
H(15A)	–0.3890	0.0988	0.8482	0.054
H(15B)	–0.4182	0.0828	0.9138	0.054
H(15C)	–0.3386	0.0163	0.8955	0.054
H(16)	0.0030	0.2649	0.8713	0.044
H(17A)	–0.0390	0.4450	0.9285	0.073
H(17B)	0.0204	0.3558	0.9664	0.073
H(17C)	–0.0703	0.3448	0.9768	0.073
H(18A)	–0.0616	0.0933	0.9574	0.082
H(18B)	0.0289	0.1099	0.9472	0.082
H(18C)	–0.0256	0.0437	0.8973	0.082

Table 11. Crystal data and structure refinement for **2**.

Identification code	**2**	
Chemical formula	$C_{46}H_{57}BN_2$	
Formula weight	648.75	
Temperature	90(2) K	
Radiation, wavelength	CuKα, 1.54184 Å	
Crystal system, space group	monoclinic, $P21_1/c$	
Unit cell parameters	a = 10.8044(3) Å	α = 90°
	b = 14.1728(4) Å	β = 98.594(3)°
	c = 25.7680(7) Å	γ = 90°
Cell volume	3901.51(19) $Å^3$	
Z	4	
Calculated density	1.104 g/cm^3	
Absorption coefficient μ	0.468 mm^{-1}	
F(000)	1408	

Crystal colour and size	colourless, 0.3385 × 0.1399 × 0.1016 mm^3
Reflections for cell refinement	10396 (θ range 3.47 to 74.51°)
Data collection method	SuperNova, Single source at offset), Atlas ω scans
θ range for data collection	3.47 to 74.68°
Index ranges	h –13 to 13, k –17 to 16, l –32 to 30
Completeness to θ = 67.50°	99.9 %
Intensity decay	0%
Reflections collected	26148
Independent reflections	7772 (R_{int} = 0.0450)
Reflections with $F^2>2\sigma$	6166
Absorption correction	gaussian
Min. and max. transmission	0.954 and 1.355
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0667, 4.0434
Data / restraints / parameters	7772 / 284 / 596
Final R indices [$F^2>2\sigma$]	R1 = 0.0716, wR2 = 0.1737
R indices (all data)	R1 = 0.0895, wR2 = 0.1861
Goodness-of-fit on F^2	1.082
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	0.485 and –0.479 e $Å^{-3}$

Table 12. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	0.15173(16)	0.60491(12)	0.23458(7)	0.0234(4)
N(2)	0.28564(17)	0.58074(12)	0.31085(7)	0.0258(4)
C(1)	0.0832(2)	0.61064(13)	0.27631(8)	0.0234(4)
C(2)	–0.0425(2)	0.62733(14)	0.27645(9)	0.0265(5)
C(3)	–0.0863(2)	0.62830(15)	0.32481(9)	0.0316(5)
C(4)	–0.0047(2)	0.61325(16)	0.37116(9)	0.0323(5)
C(5)	0.1221(2)	0.59709(15)	0.37090(9)	0.0297(5)
C(6)	0.1649(2)	0.59534(14)	0.32298(8)	0.0255(4)
C(7)	0.09332(19)	0.61885(14)	0.18154(8)	0.0231(4)
C(8)	0.0818(2)	0.71112(15)	0.16160(8)	0.0247(4)
C(9)	0.0382(2)	0.72258(15)	0.10862(8)	0.0272(5)
C(10)	0.0040(2)	0.64634(15)	0.07540(8)	0.0257(4)
C(11)	0.0109(2)	0.55645(15)	0.09715(8)	0.0260(4)
C(12)	0.0547(2)	0.54071(15)	0.15003(8)	0.0253(4)
C(13)	0.1219(2)	0.79590(16)	0.19626(9)	0.0347(5)
C(14)	0.2443(4)	0.8359(3)	0.18367(15)	0.0837(13)
C(15)	0.0199(4)	0.87018(19)	0.19237(12)	0.0607(9)
C(16)	–0.0325(2)	0.65964(16)	0.01652(8)	0.0304(5)
C(17)	0.0838(3)	0.6787(2)	–0.00856(10)	0.0427(6)
C(18)	–0.1288(3)	0.73744(19)	0.00268(10)	0.0441(6)
C(19)	0.0680(2)	0.43983(15)	0.17099(9)	0.0311(5)
C(20)	0.1627(2)	0.38535(17)	0.14437(11)	0.0417(6)
C(21)	–0.0577(2)	0.38766(16)	0.16500(10)	0.0350(5)
C(22)	0.3925(12)	0.5719(5)	0.3520(5)	0.0229(15)
C(23)	0.4234(5)	0.4802(4)	0.3710(2)	0.0233(11)
C(24)	0.5355(6)	0.4683(4)	0.4055(2)	0.0254(11)
C(25)	0.6113(5)	0.5453(4)	0.4226(2)	0.0254(12)
C(26)	0.5739(4)	0.6350(3)	0.40465(17)	0.0258(10)

C(27)	0.4621(5)	0.6502(4)	0.3707(2)	0.0242(10)
C(28)	0.3408(5)	0.3962(3)	0.3529(2)	0.0266(10)
C(29)	0.3951(6)	0.3366(4)	0.3128(3)	0.0494(16)
C(30)	0.3146(7)	0.3364(4)	0.3992(2)	0.0524(16)
C(31)	0.7327(5)	0.5361(3)	0.46130(18)	0.0311(11)
C(32)	0.8004(7)	0.4441(5)	0.4579(3)	0.061(2)
C(33)	0.7045(5)	0.5549(4)	0.51674(18)	0.0393(12)
C(34)	0.4246(5)	0.7500(3)	0.3531(2)	0.0322(11)
C(35)	0.5034(6)	0.7892(4)	0.3147(3)	0.0524(15)
C(36)	0.4249(8)	0.8167(4)	0.3998(2)	0.064(2)
C(22A)	0.3839(12)	0.5424(5)	0.3494(6)	0.0298(17)
C(23A)	0.4042(5)	0.4442(5)	0.3527(2)	0.0317(12)
C(24A)	0.5047(5)	0.4121(5)	0.3881(2)	0.0442(14)
C(25A)	0.5802(7)	0.4740(6)	0.4209(3)	0.061(2)
C(26A)	0.5574(7)	0.5694(6)	0.4172(3)	0.061(2)
C(27A)	0.4577(6)	0.6054(5)	0.3819(2)	0.0420(14)
C(28A)	0.3214(5)	0.3735(4)	0.3198(2)	0.0321(11)
C(29A)	0.2706(5)	0.3006(3)	0.3553(2)	0.0398(12)
C(30A)	0.3869(6)	0.3243(4)	0.2787(3)	0.0480(14)
C(31A)	0.6875(6)	0.4274(7)	0.4586(3)	0.105(4)
C(32A)	0.6476(6)	0.3689(4)	0.4969(2)	0.0593(18)
C(33A)	0.7998(6)	0.4871(6)	0.4712(3)	0.0489(16)
C(34A)	0.4344(6)	0.7111(5)	0.3786(2)	0.0481(15)
C(35A)	0.4184(10)	0.7530(6)	0.4319(3)	0.087(3)
C(36A)	0.5400(8)	0.7622(5)	0.3567(3)	0.079(2)
C(37)	0.3927(2)	0.57850(16)	0.22182(9)	0.0299(5)
C(38)	0.3730(2)	0.59187(18)	0.16811(9)	0.0356(5)
C(39)	0.4706(2)	0.58585(17)	0.13656(10)	0.0335(5)
C(40)	0.4468(3)	0.5981(2)	0.08174(10)	0.0459(7)
C(41)	0.5419(3)	0.5909(2)	0.05201(11)	0.0454(6)
C(42)	0.6635(3)	0.57266(19)	0.07616(12)	0.0452(6)
C(43)	0.6897(3)	0.56185(19)	0.12944(11)	0.0441(6)
C(44)	0.5932(2)	0.56680(16)	0.16097(10)	0.0341(5)
C(45)	0.6146(2)	0.55370(18)	0.21623(10)	0.0371(6)
C(46)	0.5184(2)	0.55894(17)	0.24520(10)	0.0341(5)
B(1)	0.2813(2)	0.58720(16)	0.25491(10)	0.0248(5)

Table 13. Bond lengths [Å] and angles [°] for **2**.

N(1)–C(1)	1.396(3)	N(1)–C(7)	1.431(3)
N(1)–B(1)	1.441(3)	N(2)–C(6)	1.402(3)
N(2)–B(1)	1.438(3)	N(2)–C(22A)	1.447(10)
N(2)–C(22)	1.452(9)	C(1)–C(2)	1.380(3)
C(1)–C(6)	1.398(3)	C(2)–C(3)	1.397(3)
C(2)–H(2)	0.9500	C(3)–C(4)	1.391(3)
C(3)–H(3)	0.9500	C(4)–C(5)	1.390(3)
C(4)–H(4)	0.9500	C(5)–C(6)	1.382(3)
C(5)–H(5)	0.9500	C(7)–C(12)	1.400(3)
C(7)–C(8)	1.404(3)	C(8)–C(9)	1.386(3)
C(8)–C(13)	1.521(3)	C(9)–C(10)	1.394(3)
C(9)–H(9)	0.9500	C(10)–C(11)	1.389(3)
C(10)–C(16)	1.521(3)	C(11)–C(12)	1.392(3)
C(11)–H(11)	0.9500	C(12)–C(19)	1.528(3)
C(13)–C(15)	1.517(4)	C(13)–C(14)	1.518(4)
C(13)–H(13)	1.0000	C(14)–H(14A)	0.9800
C(14)–H(14C)	0.9800	C(14)–H(14B)	0.9800
C(15)–H(15B)	0.9800	C(15)–H(15C)	0.9800

C(15)–H(15A)	0.9800	C(16)–C(17)	1.521(3)
C(16)–C(18)	1.521(3)	C(16)–H(16)	1.0000
C(17)–H(17C)	0.9800	C(17)–H(17B)	0.9800
C(17)–H(17A)	0.9800	C(18)–H(18A)	0.9800
C(18)–H(18B)	0.9800	C(18)–H(18C)	0.9800
C(19)–C(20)	1.524(3)	C(19)–C(21)	1.534(3)
C(19)–H(19)	1.0000	C(20)–H(20B)	0.9800
C(20)–H(20C)	0.9800	C(20)–H(20A)	0.9800
C(21)–H(21B)	0.9800	C(21)–H(21C)	0.9800
C(21)–H(21A)	0.9800	C(22)–C(27)	1.386(8)
C(22)–C(23)	1.411(8)	C(23)–C(24)	1.401(7)
C(23)–C(28)	1.519(6)	C(24)–C(25)	1.396(7)
C(24)–H(24)	0.9500	C(25)–C(26)	1.392(6)
C(25)–C(31)	1.530(7)	C(26)–C(27)	1.398(6)
C(26)–H(26)	0.9500	C(27)–C(34)	1.521(6)
C(28)–C(29)	1.519(7)	C(28)–C(30)	1.524(7)
C(28)–H(28)	1.0000	C(29)–H(29C)	0.9800
C(29)–H(29B)	0.9800	C(29)–H(29A)	0.9800
C(30)–H(30A)	0.9800	C(30)–H(30C)	0.9800
C(30)–H(30B)	0.9800	C(31)–C(32)	1.504(7)
C(31)–C(33)	1.528(6)	C(31)–H(31)	1.0000
C(32)–H(32B)	0.9800	C(32)–H(32C)	0.9800
C(32)–H(32A)	0.9800	C(33)–H(33B)	0.9800
C(33)–H(33C)	0.9800	C(33)–H(33A)	0.9800
C(34)–C(35)	1.506(8)	C(34)–C(36)	1.529(7)
C(34)–H(34)	1.0000	C(35)–H(35C)	0.9800
C(35)–H(35B)	0.9800	C(35)–H(35A)	0.9800
C(36)–H(36A)	0.9800	C(36)–H(36B)	0.9800
C(36)–H(36C)	0.9800	C(22A)–C(27A)	1.392(8)
C(22A)–C(23A)	1.410(9)	C(23A)–C(24A)	1.386(7)
C(23A)–C(28A)	1.515(7)	C(24A)–C(25A)	1.395(8)
C(24A)–H(24A)	0.9500	C(25A)–C(26A)	1.375(10)
C(25A)–C(31A)	1.546(8)	C(26A)–C(27A)	1.399(8)
C(26A)–H(26A)	0.9500	C(27A)–C(34A)	1.518(8)
C(28A)–C(30A)	1.527(7)	C(28A)–C(29A)	1.535(6)
C(28A)–H(28A)	1.0000	C(29A)–H(29D)	0.9800
C(29A)–H(29F)	0.9800	C(29A)–H(29E)	0.9800
C(30A)–H(30F)	0.9800	C(30A)–H(30E)	0.9800
C(30A)–H(30D)	0.9800	C(31A)–C(32A)	1.404(8)
C(31A)–C(33A)	1.475(8)	C(31A)–H(31A)	1.0000
C(32A)–H(32F)	0.9800	C(32A)–H(32E)	0.9800
C(32A)–H(32D)	0.9800	C(33A)–H(33D)	0.9800
C(33A)–H(33E)	0.9800	C(33A)–H(33F)	0.9800
C(34A)–C(35A)	1.529(8)	C(34A)–C(36A)	1.530(8)
C(34A)–H(34A)	1.0000	C(35A)–H(35D)	0.9800
C(35A)–H(35F)	0.9800	C(35A)–H(35E)	0.9800
C(36A)–H(36E)	0.9800	C(36A)–H(36F)	0.9800
C(36A)–H(36D)	0.9800	C(37)–C(38)	1.382(3)
C(37)–C(46)	1.428(3)	C(37)–B(1)	1.581(3)
C(38)–C(39)	1.427(3)	C(38)–H(38)	0.9500
C(39)–C(44)	1.405(3)	C(39)–C(40)	1.408(4)
C(40)–C(41)	1.374(4)	C(40)–H(40)	0.9500
C(41)–C(42)	1.392(4)	C(41)–H(41)	0.9500
C(42)–C(43)	1.368(4)	C(42)–H(42)	0.9500
C(43)–C(44)	1.416(4)	C(43)–H(43)	0.9500
C(44)–C(45)	1.420(4)	C(45)–C(46)	1.370(3)
C(45)–H(45)	0.9500	C(46)–H(46)	0.9500

C(1)–N(1)–C(7)	121.25(17)	C(1)–N(1)–B(1)	109.15(17)
C(7)–N(1)–B(1)	129.57(18)	C(6)–N(2)–B(1)	108.77(17)
C(6)–N(2)–C(22A)	121.0(7)	B(1)–N(2)–C(22A)	128.5(7)
C(6)–N(2)–C(22)	121.0(7)	B(1)–N(2)–C(22)	129.9(7)
C(22A)–N(2)–C(22)	17.1(3)	C(2)–C(1)–N(1)	130.37(19)
C(2)–C(1)–C(6)	121.3(2)	N(1)–C(1)–C(6)	108.33(19)
C(1)–C(2)–C(3)	117.9(2)	C(1)–C(2)–H(2)	121.0
C(3)–C(2)–H(2)	121.0	C(4)–C(3)–C(2)	120.6(2)
C(4)–C(3)–H(3)	119.7	C(2)–C(3)–H(3)	119.7
C(5)–C(4)–C(3)	121.3(2)	C(5)–C(4)–H(4)	119.3
C(3)–C(4)–H(4)	119.3	C(6)–C(5)–C(4)	117.9(2)
C(6)–C(5)–H(5)	121.0	C(4)–C(5)–H(5)	121.0
C(5)–C(6)–C(1)	120.9(2)	C(5)–C(6)–N(2)	130.4(2)
C(1)–C(6)–N(2)	108.66(18)	C(12)–C(7)–C(8)	121.49(19)
C(12)–C(7)–N(1)	119.71(18)	C(8)–C(7)–N(1)	118.73(18)
C(9)–C(8)–C(7)	117.93(19)	C(9)–C(8)–C(13)	120.74(19)
C(7)–C(8)–C(13)	121.26(19)	C(8)–C(9)–C(10)	122.28(19)
C(8)–C(9)–H(9)	118.9	C(10)–C(9)–H(9)	118.9
C(11)–C(10)–C(9)	118.02(19)	C(11)–C(10)–C(16)	120.42(19)
C(9)–C(10)–C(16)	121.46(19)	C(10)–C(11)–C(12)	122.13(19)
C(10)–C(11)–H(11)	118.9	C(12)–C(11)–H(11)	118.9
C(11)–C(12)–C(7)	118.00(19)	C(11)–C(12)–C(19)	119.75(18)
C(7)–C(12)–C(19)	122.10(19)	C(15)–C(13)–C(14)	112.0(3)
C(15)–C(13)–C(8)	111.6(2)	C(14)–C(13)–C(8)	110.5(2)
C(15)–C(13)–H(13)	107.5	C(14)–C(13)–H(13)	107.5
C(8)–C(13)–H(13)	107.5	C(13)–C(14)–H(14A)	109.5
C(13)–C(14)–H(14C)	109.5	H(14A)–C(14)–H(14C)	109.5
C(13)–C(14)–H(14B)	109.5	H(14A)–C(14)–H(14B)	109.5
H(14C)–C(14)–H(14B)	109.5	C(13)–C(15)–H(15B)	109.5
C(13)–C(15)–H(15C)	109.5	H(15B)–C(15)–H(15C)	109.5
C(13)–C(15)–H(15A)	109.5	H(15B)–C(15)–H(15A)	109.5
H(15C)–C(15)–H(15A)	109.5	C(17)–C(16)–C(10)	109.78(19)
C(17)–C(16)–C(18)	110.5(2)	C(10)–C(16)–C(18)	112.95(19)
C(17)–C(16)–H(16)	107.8	C(10)–C(16)–H(16)	107.8
C(18)–C(16)–H(16)	107.8	C(16)–C(17)–H(17C)	109.5
C(16)–C(17)–H(17B)	109.5	H(17C)–C(17)–H(17B)	109.5
C(16)–C(17)–H(17A)	109.5	H(17C)–C(17)–H(17A)	109.5
H(17B)–C(17)–H(17A)	109.5	C(16)–C(18)–H(18A)	109.5
C(16)–C(18)–H(18B)	109.5	H(18A)–C(18)–H(18B)	109.5
C(16)–C(18)–H(18C)	109.5	H(18A)–C(18)–H(18C)	109.5
H(18B)–C(18)–H(18C)	109.5	C(20)–C(19)–C(12)	110.43(19)
C(20)–C(19)–C(21)	110.75(19)	C(12)–C(19)–C(21)	112.38(19)
C(20)–C(19)–H(19)	107.7	C(12)–C(19)–H(19)	107.7
C(21)–C(19)–H(19)	107.7	C(19)–C(20)–H(20B)	109.5
C(19)–C(20)–H(20C)	109.5	H(20B)–C(20)–H(20C)	109.5
C(19)–C(20)–H(20A)	109.5	H(20B)–C(20)–H(20A)	109.5
H(20C)–C(20)–H(20A)	109.5	C(19)–C(21)–H(21B)	109.5
C(19)–C(21)–H(21C)	109.5	H(21B)–C(21)–H(21C)	109.5
C(19)–C(21)–H(21A)	109.5	H(21B)–C(21)–H(21A)	109.5
H(21C)–C(21)–H(21A)	109.5	C(27)–C(22)–C(23)	121.9(7)
C(27)–C(22)–N(2)	121.0(6)	C(23)–C(22)–N(2)	117.0(5)
C(24)–C(23)–C(22)	117.9(6)	C(24)–C(23)–C(28)	120.9(5)
C(22)–C(23)–C(28)	121.2(5)	C(25)–C(24)–C(23)	121.1(5)
C(25)–C(24)–H(24)	119.4	C(23)–C(24)–H(24)	119.4
C(26)–C(25)–C(24)	118.8(5)	C(26)–C(25)–C(31)	118.3(5)
C(24)–C(25)–C(31)	123.0(5)	C(25)–C(26)–C(27)	122.0(5)

C(25)–C(26)–H(26)	119.0	C(27)–C(26)–H(26)	119.0
C(22)–C(27)–C(26)	117.8(6)	C(22)–C(27)–C(34)	122.3(5)
C(26)–C(27)–C(34)	119.7(5)	C(29)–C(28)–C(23)	112.1(4)
C(29)–C(28)–C(30)	111.1(5)	C(23)–C(28)–C(30)	111.4(4)
C(29)–C(28)–H(28)	107.4	C(23)–C(28)–H(28)	107.4
C(30)–C(28)–H(28)	107.4	C(32)–C(31)–C(33)	111.8(5)
C(32)–C(31)–C(25)	114.5(4)	C(33)–C(31)–C(25)	108.8(4)
C(32)–C(31)–H(31)	107.1	C(33)–C(31)–H(31)	107.1
C(25)–C(31)–H(31)	107.1	C(35)–C(34)–C(27)	112.8(4)
C(35)–C(34)–C(36)	110.8(5)	C(27)–C(34)–C(36)	111.8(4)
C(35)–C(34)–H(34)	107.0	C(27)–C(34)–H(34)	107.0
C(36)–C(34)–H(34)	107.0	C(27A)–C(22A)–C(23A)	121.9(8)
C(27A)–C(22A)–N(2)	117.8(6)	C(23A)–C(22A)–N(2)	120.3(6)
C(24A)–C(23A)–C(22A)	117.6(7)	C(24A)–C(23A)–C(28A)	119.3(5)
C(22A)–C(23A)–C(28A)	123.1(5)	C(23A)–C(24A)–C(25A)	121.5(6)
C(23A)–C(24A)–H(24A)	119.3	C(25A)–C(24A)–H(24A)	119.3
C(26A)–C(25A)–C(24A)	119.6(6)	C(26A)–C(25A)–C(31A)	125.0(7)
C(24A)–C(25A)–C(31A)	115.3(7)	C(25A)–C(26A)–C(27A)	121.1(6)
C(25A)–C(26A)–H(26A)	119.5	C(27A)–C(26A)–H(26A)	119.5
C(22A)–C(27A)–C(26A)	118.3(7)	C(22A)–C(27A)–C(34A)	121.7(6)
C(26A)–C(27A)–C(34A)	120.1(6)	C(23A)–C(28A)–C(30A)	113.2(5)
C(23A)–C(28A)–C(29A)	110.2(4)	C(30A)–C(28A)–C(29A)	110.5(5)
C(23A)–C(28A)–H(28A)	107.6	C(30A)–C(28A)–H(28A)	107.6
C(29A)–C(28A)–H(28A)	107.6	C(28A)–C(29A)–H(29D)	109.5
C(28A)–C(29A)–H(29F)	109.5	H(29D)–C(29A)–H(29F)	109.5
C(28A)–C(29A)–H(29E)	109.5	H(29D)–C(29A)–H(29E)	109.5
H(29F)–C(29A)–H(29E)	109.5	C(28A)–C(30A)–H(30F)	109.5
C(28A)–C(30A)–H(30E)	109.5	H(30F)–C(30A)–H(30E)	109.5
C(28A)–C(30A)–H(30D)	109.5	H(30F)–C(30A)–H(30D)	109.5
H(30E)–C(30A)–H(30D)	109.5	C(32A)–C(31A)–C(33A)	120.8(6)
C(32A)–C(31A)–C(25A)	114.4(6)	C(33A)–C(31A)–C(25A)	114.1(6)
C(32A)–C(31A)–H(31A)	101.0	C(33A)–C(31A)–H(31A)	101.0
C(25A)–C(31A)–H(31A)	101.0	C(31A)–C(32A)–H(32F)	109.5
C(31A)–C(32A)–H(32E)	109.5	H(32F)–C(32A)–H(32E)	109.5
C(31A)–C(32A)–H(32D)	109.5	H(32F)–C(32A)–H(32D)	109.5
H(32E)–C(32A)–H(32D)	109.5	C(31A)–C(33A)–H(33D)	109.5
C(31A)–C(33A)–H(33E)	109.5	H(33D)–C(33A)–H(33E)	109.5
C(31A)–C(33A)–H(33F)	109.5	H(33D)–C(33A)–H(33F)	109.5
H(33E)–C(33A)–H(33F)	109.5	C(27A)–C(34A)–C(35A)	111.9(6)
C(27A)–C(34A)–C(36A)	111.2(6)	C(35A)–C(34A)–C(36A)	109.8(6)
C(27A)–C(34A)–H(34A)	108.0	C(35A)–C(34A)–H(34A)	108.0
C(36A)–C(34A)–H(34A)	108.0	C(34A)–C(35A)–H(35D)	109.5
C(34A)–C(35A)–H(35F)	109.5	H(35D)–C(35A)–H(35F)	109.5
C(34A)–C(35A)–H(35E)	109.5	H(35D)–C(35A)–H(35E)	109.5
H(35F)–C(35A)–H(35E)	109.5	C(34A)–C(36A)–H(36E)	109.5
C(34A)–C(36A)–H(36F)	109.5	H(36E)–C(36A)–H(36F)	109.5
C(34A)–C(36A)–H(36D)	109.5	H(36E)–C(36A)–H(36D)	109.5
H(36F)–C(36A)–H(36D)	109.5	C(38)–C(37)–C(46)	116.4(2)
C(38)–C(37)–B(1)	120.9(2)	C(46)–C(37)–B(1)	122.7(2)
C(37)–C(38)–C(39)	123.1(2)	C(37)–C(38)–H(38)	118.5
C(39)–C(38)–H(38)	118.5	C(44)–C(39)–C(40)	119.4(2)
C(44)–C(39)–C(38)	118.9(2)	C(40)–C(39)–C(38)	121.6(2)
C(41)–C(40)–C(39)	120.7(3)	C(41)–C(40)–H(40)	119.7
C(39)–C(40)–H(40)	119.7	C(40)–C(41)–C(42)	120.0(3)
C(40)–C(41)–H(41)	120.0	C(42)–C(41)–H(41)	120.0
C(43)–C(42)–C(41)	120.6(3)	C(43)–C(42)–H(42)	119.7
C(41)–C(42)–H(42)	119.7	C(42)–C(43)–C(44)	120.7(3)

C(42)–C(43)–H(43)	119.6	C(44)–C(43)–H(43)	119.6
C(39)–C(44)–C(43)	118.6(2)	C(39)–C(44)–C(45)	118.4(2)
C(43)–C(44)–C(45)	123.0(2)	C(46)–C(45)–C(44)	121.1(2)
C(46)–C(45)–H(45)	119.5	C(44)–C(45)–H(45)	119.5
C(45)–C(46)–C(37)	122.1(2)	C(45)–C(46)–H(46)	118.9
C(37)–C(46)–H(46)	118.9	N(2)–B(1)–N(1)	105.08(19)
N(2)–B(1)–C(37)	128.5(2)	N(1)–B(1)–C(37)	126.4(2)

Symmetry transformations used to generate equivalent atoms:

Table 14. Anisotropic displacement parameters ($Å^2$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	0.0280(9)	0.0204(8)	0.0215(8)	–0.0014(7)	0.0028(7)	–0.0014(7)
N(2)	0.0278(9)	0.0225(9)	0.0260(9)	0.0013(7)	0.0002(7)	–0.0016(7)
C(1)	0.0327(11)	0.0131(9)	0.0244(10)	–0.0014(7)	0.0041(8)	–0.0036(8)
C(2)	0.0308(11)	0.0171(10)	0.0309(11)	0.0010(8)	0.0023(9)	–0.0018(8)
C(3)	0.0383(13)	0.0187(10)	0.0396(13)	–0.0014(9)	0.0116(10)	–0.0003(9)
C(4)	0.0458(13)	0.0230(11)	0.0306(11)	–0.0012(9)	0.0139(10)	–0.0052(10)
C(5)	0.0395(12)	0.0240(11)	0.0251(11)	0.0020(8)	0.0034(9)	–0.0057(9)
C(6)	0.0339(11)	0.0146(9)	0.0274(11)	–0.0001(8)	0.0028(9)	–0.0027(8)
C(7)	0.0247(10)	0.0220(10)	0.0225(10)	–0.0001(8)	0.0033(8)	–0.0002(8)
C(8)	0.0260(10)	0.0208(10)	0.0277(11)	–0.0008(8)	0.0052(8)	–0.0010(8)
C(9)	0.0353(12)	0.0186(10)	0.0280(11)	0.0021(8)	0.0061(9)	0.0002(9)
C(10)	0.0258(11)	0.0257(11)	0.0252(10)	–0.0009(8)	0.0018(8)	0.0008(8)
C(11)	0.0298(11)	0.0209(10)	0.0267(10)	–0.0044(8)	0.0019(8)	–0.0023(9)
C(12)	0.0259(10)	0.0212(10)	0.0288(11)	–0.0010(8)	0.0043(8)	–0.0005(8)
C(13)	0.0560(15)	0.0210(11)	0.0266(11)	–0.0023(9)	0.0040(10)	–0.0084(10)
C(14)	0.098(3)	0.083(3)	0.077(2)	–0.044(2)	0.034(2)	–0.064(2)
C(15)	0.109(3)	0.0218(12)	0.0467(16)	–0.0093(11)	–0.0035(17)	0.0157(15)
C(16)	0.0413(13)	0.0242(11)	0.0250(11)	–0.0017(8)	0.0022(9)	–0.0007(10)
C(17)	0.0536(16)	0.0482(15)	0.0267(12)	–0.0031(11)	0.0079(11)	–0.0100(13)
C(18)	0.0635(18)	0.0356(14)	0.0307(13)	0.0004(10)	–0.0008(12)	0.0121(13)
C(19)	0.0416(13)	0.0208(10)	0.0285(11)	0.0006(9)	–0.0025(9)	0.0005(9)
C(20)	0.0423(14)	0.0213(11)	0.0605(17)	0.0026(11)	0.0045(12)	0.0040(10)
C(21)	0.0467(14)	0.0230(11)	0.0351(12)	0.0017(9)	0.0051(10)	–0.0004(10)
C(22)	0.030(3)	0.016(3)	0.022(3)	0.003(4)	0.001(2)	0.000(3)
C(23)	0.031(3)	0.014(2)	0.025(3)	–0.001(2)	0.006(2)	–0.002(2)
C(24)	0.038(3)	0.018(2)	0.020(3)	–0.0049(19)	0.001(2)	0.000(2)
C(25)	0.039(3)	0.021(3)	0.016(2)	–0.0045(18)	0.002(2)	0.006(2)
C(26)	0.032(2)	0.019(2)	0.025(2)	–0.0023(17)	0.0002(17)	–0.0025(18)
C(27)	0.031(2)	0.017(3)	0.023(2)	0.004(2)	–0.0017(18)	–0.003(2)
C(28)	0.027(2)	0.017(2)	0.034(3)	–0.0007(19)	0.000(2)	–0.0023(19)
C(29)	0.051(4)	0.035(3)	0.066(5)	–0.026(3)	0.023(3)	–0.016(3)
C(30)	0.071(4)	0.040(3)	0.046(3)	0.002(2)	0.010(3)	–0.027(3)
C(31)	0.033(2)	0.025(2)	0.033(2)	–0.0037(19)	–0.0006(19)	0.004(2)
C(32)	0.050(4)	0.042(4)	0.080(5)	–0.020(4)	–0.025(4)	0.024(3)
C(33)	0.044(3)	0.045(3)	0.026(2)	0.008(2)	–0.002(2)	–0.004(2)
C(34)	0.039(3)	0.015(2)	0.038(3)	0.005(2)	–0.008(2)	–0.0025(19)
C(35)	0.078(4)	0.025(3)	0.057(4)	0.009(2)	0.019(3)	0.001(3)
C(36)	0.117(6)	0.025(3)	0.053(4)	0.006(2)	0.024(4)	0.022(3)
C(22A)	0.029(3)	0.036(4)	0.024(3)	0.005(5)	0.000(2)	–0.009(4)
C(23A)	0.029(3)	0.037(3)	0.028(3)	0.007(2)	0.001(2)	–0.001(3)

C(24A)	0.032(3)	0.056(4)	0.040(3)	0.022(3)	–0.008(2)	–0.013(3)
C(25A)	0.055(4)	0.072(5)	0.047(4)	0.036(4)	–0.025(3)	–0.037(3)
C(26A)	0.066(5)	0.070(5)	0.037(3)	0.029(4)	–0.021(4)	–0.040(4)
C(27A)	0.050(3)	0.044(4)	0.029(3)	0.009(3)	–0.003(2)	–0.021(3)
C(28A)	0.035(3)	0.030(3)	0.028(3)	0.004(2)	–0.003(2)	0.002(2)
C(29A)	0.044(3)	0.031(3)	0.044(3)	0.004(2)	0.002(2)	–0.002(2)
C(30A)	0.062(4)	0.038(3)	0.045(3)	0.000(3)	0.015(3)	0.008(3)
C(31A)	0.053(4)	0.139(8)	0.106(6)	0.090(6)	–0.043(4)	–0.048(4)
C(32A)	0.056(4)	0.051(3)	0.062(4)	0.027(3)	–0.024(3)	–0.008(3)
C(33A)	0.038(3)	0.054(5)	0.052(4)	0.006(4)	0.000(3)	–0.007(4)
C(34A)	0.064(4)	0.041(4)	0.035(3)	0.001(3)	–0.005(3)	–0.029(3)
C(35A)	0.130(8)	0.083(6)	0.051(4)	–0.017(4)	0.024(4)	–0.023(5)
C(36A)	0.097(6)	0.058(4)	0.088(6)	0.015(4)	0.034(5)	–0.022(4)
C(37)	0.0316(11)	0.0240(11)	0.0336(12)	–0.0018(9)	0.0034(9)	–0.0014(9)
C(38)	0.0304(12)	0.0418(14)	0.0339(12)	–0.0037(10)	0.0027(9)	–0.0006(10)
C(39)	0.0350(12)	0.0287(12)	0.0371(12)	–0.0048(10)	0.0065(10)	–0.0044(10)
C(40)	0.0404(14)	0.0613(18)	0.0357(13)	–0.0036(12)	0.0051(11)	–0.0044(13)
C(41)	0.0522(16)	0.0488(16)	0.0375(14)	–0.0029(12)	0.0140(12)	–0.0026(13)
C(42)	0.0507(16)	0.0353(14)	0.0549(16)	0.0057(12)	0.0256(13)	0.0062(12)
C(43)	0.0411(14)	0.0378(14)	0.0563(16)	0.0141(12)	0.0173(12)	0.0111(11)
C(44)	0.0376(13)	0.0201(11)	0.0458(14)	0.0043(9)	0.0103(10)	0.0030(9)
C(45)	0.0301(12)	0.0340(13)	0.0471(14)	0.0118(11)	0.0052(10)	0.0062(10)
C(46)	0.0351(12)	0.0312(12)	0.0351(12)	0.0061(10)	0.0021(10)	0.0000(10)
B(1)	0.0293(12)	0.0164(11)	0.0271(12)	–0.0018(9)	–0.0011(9)	–0.0018(9)

Table 15. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **2**.

	x	y	z	U(eq)
H(2)	–0.0977	0.6378	0.2447	0.032
H(3)	–0.1725	0.6393	0.3260	0.038
H(4)	–0.0363	0.6140	0.4036	0.039
H(5)	0.1777	0.5876	0.4027	0.036
H(9)	0.0313	0.7846	0.0945	0.033
H(11)	–0.0150	0.5040	0.0752	0.031
H(13)	0.1372	0.7732	0.2334	0.042
H(14A)	0.3074	0.7858	0.1863	0.126
H(14C)	0.2731	0.8863	0.2086	0.126
H(14B)	0.2314	0.8616	0.1480	0.126
H(15B)	0.0020	0.8933	0.1562	0.091
H(15C)	0.0478	0.9228	0.2159	0.091
H(15A)	–0.0561	0.8424	0.2025	0.091
H(16)	–0.0703	0.5992	0.0017	0.037
H(17C)	0.1252	0.7360	0.0067	0.064
H(17B)	0.0598	0.6874	–0.0465	0.064
H(17A)	0.1413	0.6251	–0.0021	0.064
H(18A)	–0.2027	0.7243	0.0193	0.066
H(18B)	–0.1531	0.7400	–0.0355	0.066
H(18C)	–0.0925	0.7981	0.0153	0.066
H(19)	0.1011	0.4433	0.2093	0.037
H(20B)	0.1722	0.3215	0.1590	0.063
H(20C)	0.2436	0.4179	0.1504	0.063
H(20A)	0.1331	0.3816	0.1066	0.063
H(21B)	–0.0952	0.3870	0.1279	0.053

H(21C)	–0.1141	0.4200	0.1856	0.053
H(21A)	–0.0441	0.3227	0.1776	0.053
H(24)	0.5604	0.4068	0.4174	0.031
H(26)	0.6259	0.6875	0.4158	0.031
H(28)	0.2587	0.4216	0.3354	0.032
H(29C)	0.4753	0.3098	0.3290	0.074
H(29B)	0.4082	0.3761	0.2829	0.074
H(29A)	0.3368	0.2855	0.3007	0.074
H(30A)	0.2526	0.2879	0.3868	0.079
H(30C)	0.2821	0.3768	0.4250	0.079
H(30B)	0.3923	0.3062	0.4156	0.079
H(31)	0.7901	0.5873	0.4528	0.037
H(32B)	0.7498	0.3925	0.4690	0.092
H(32C)	0.8812	0.4463	0.4810	0.092
H(32A)	0.8142	0.4334	0.4217	0.092
H(33B)	0.6654	0.6171	0.5179	0.059
H(33C)	0.7826	0.5534	0.5415	0.059
H(33A)	0.6474	0.5064	0.5263	0.059
H(34)	0.3365	0.7469	0.3346	0.039
H(35C)	0.5902	0.7958	0.3319	0.079
H(35B)	0.4709	0.8511	0.3024	0.079
H(35A)	0.5003	0.7463	0.2847	0.079
H(36A)	0.3645	0.7943	0.4219	0.096
H(36B)	0.4016	0.8803	0.3870	0.096
H(36C)	0.5088	0.8182	0.4205	0.096
H(24A)	0.5225	0.3464	0.3900	0.053
H(26A)	0.6102	0.6116	0.4390	0.073
H(28A)	0.2482	0.4087	0.3007	0.039
H(29D)	0.2129	0.2578	0.3338	0.060
H(29F)	0.2261	0.3331	0.3806	0.060
H(29E)	0.3404	0.2643	0.3742	0.060
H(30F)	0.4571	0.2868	0.2963	0.072
H(30E)	0.4182	0.3717	0.2562	0.072
H(30D)	0.3274	0.2828	0.2572	0.072
H(31A)	0.7178	0.3794	0.4349	0.126
H(32F)	0.6105	0.4077	0.5220	0.089
H(32E)	0.7194	0.3341	0.5153	0.089
H(32D)	0.5850	0.3242	0.4800	0.089
H(33D)	0.8257	0.5101	0.4387	0.073
H(33E)	0.8677	0.4499	0.4908	0.073
H(33F)	0.7806	0.5408	0.4926	0.073
H(34A)	0.3550	0.7221	0.3540	0.058
H(35D)	0.3513	0.7195	0.4460	0.131
H(35F)	0.3967	0.8200	0.4277	0.131
H(35E)	0.4968	0.7463	0.4562	0.131
H(36E)	0.6191	0.7522	0.3802	0.118
H(36F)	0.5216	0.8299	0.3541	0.118
H(36D)	0.5472	0.7373	0.3218	0.118
H(38)	0.2906	0.6057	0.1514	0.043
H(40)	0.3642	0.6115	0.0651	0.055
H(41)	0.5246	0.5982	0.0150	0.055
H(42)	0.7290	0.5677	0.0555	0.054
H(43)	0.7735	0.5509	0.1455	0.053
H(45)	0.6970	0.5411	0.2334	0.045
H(46)	0.5358	0.5492	0.2820	0.041

Table 16. Crystal data and structure refinement for **3**.

Identification code	**3**	
Chemical formula	$C_{82}H_{106}B_2N_4$	
Formula weight	1169.33	
Temperature	90(2) K	
Radiation, wavelength	Cu Kα, 1.5418 Å	
Crystal system, space group	triclinic, P $\bar{1}$	
Unit cell parameters	a = 8.9943(4) Å	α = 116.671(5)°
	b = 15.0193(8) Å	β = 90.773(4)°
	c = 15.0285(7) Å	γ = 96.829(4)°
Cell volume	1796.16(17) Å^3	
Z	1	
Calculated density	1.081 g/cm^3	
Absorption coefficient μ	0.457 mm^{-1}	
F(000)	636	
Crystal colour and size	colourless, 0.255 × 0.058 × 0.045 mm^3	
Reflections for cell refinement	5714 (θ range 3.3 to 74.29°)	
Data collection method	SuperNova, Single source at offset), Atlas ω scans	
θ range for data collection	3.30 to 67.49°	
Index ranges	h –10 to 10, k –17 to 17, l –18 to 17	
Completeness to θ = 67.49°	99.8 %	
Intensity decay	0%	
Reflections collected	12346	
Independent reflections	6450 (R_{int} = 0.036)	
Reflections with $F^2>2\sigma$	4448	
Absorption correction	analytical	
Min. and max. transmission	0.935 and 0.980	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.183,	
Data / restraints / parameters	6450 / 1 / 409	
Final R indices [$F^2>2\sigma$]	R1 = 0.0797, wR2 = 0.231	
R indices (all data)	R1 = 0.104, wR2 = 0.248	
Goodness-of-fit on F^2	1.00	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.62 and –0.30 e Å^{-3}	

Table 17. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	0.1843(3)	0.7464(2)	0.3677(2)	0.0216(6)
N(1)	0.1653(3)	0.69348(17)	0.26011(16)	0.0200(5)
N(2)	0.0833(3)	0.68764(17)	0.40121(16)	0.0192(5)
C(1)	0.0564(3)	0.6091(2)	0.2315(2)	0.0210(6)
C(2)	–0.0022(3)	0.5378(2)	0.1372(2)	0.0259(6)
C(3)	–0.1154(4)	0.4629(2)	0.1298(2)	0.0278(6)
C(4)	–0.1673(3)	0.4597(2)	0.2153(2)	0.0266(6)
C(5)	–0.1072(3)	0.5310(2)	0.3102(2)	0.0230(6)
C(6)	0.0050(3)	0.6061(2)	0.3176(2)	0.0198(6)
C(7)	0.2332(3)	0.7165(2)	0.18524(19)	0.0208(6)
C(8)	0.3756(3)	0.6895(2)	0.1568(2)	0.0232(6)
C(9)	0.4408(3)	0.7184(2)	0.0878(2)	0.0245(6)

C(10)	0.3713(3)	0.7736(2)	0.0501(2)	0.0251(6)
C(11)	0.2291(3)	0.7959(2)	0.0776(2)	0.0245(6)
C(12)	0.1564(3)	0.7672(2)	0.1446(2)	0.0227(6)
C(13)	0.4568(4)	0.6328(2)	0.1997(2)	0.0281(6)
C(14)	0.4092(4)	0.5187(3)	0.1396(3)	0.0380(8)
C(15)	0.6265(4)	0.6571(3)	0.2059(2)	0.0340(7)
C(16)	0.4557(4)	0.8093(3)	–0.0178(3)	0.0332(7)
C(17)	0.3548(4)	0.8262(3)	–0.0891(3)	0.0400(8)
C(18)	0.5630(4)	0.9050(3)	0.0455(3)	0.0445(9)
C(19)	–0.0009(3)	0.7912(2)	0.1707(2)	0.0278(6)
C(20)	–0.1015(4)	0.7712(4)	0.0800(3)	0.0469(10)
C(21)	0.0038(5)	0.8994(3)	0.2525(3)	0.0490(10)
C(22)	0.0424(3)	0.7060(2)	0.49999(19)	0.0195(6)
C(23)	0.1347(3)	0.6813(2)	0.5594(2)	0.0204(6)
C(24)	0.0927(3)	0.7021(2)	0.6550(2)	0.0227(6)
C(25)	–0.0362(3)	0.7455(2)	0.6914(2)	0.0255(6)
C(26)	–0.1245(3)	0.7680(2)	0.6302(2)	0.0243(6)
C(27)	–0.0885(3)	0.7487(2)	0.5335(2)	0.0213(6)
C(28)	0.2773(3)	0.6360(2)	0.5213(2)	0.0247(6)
C(29)	0.2425(4)	0.5235(2)	0.4472(2)	0.0327(7)
C(30)	0.3920(3)	0.6512(3)	0.6050(2)	0.0300(7)
C(31)	–0.0742(3)	0.7698(2)	0.7979(2)	0.0288(7)
C(32)	–0.0634(5)	0.8826(3)	0.8625(2)	0.0471(9)
C(33)	–0.2274(4)	0.7162(3)	0.8005(3)	0.0465(9)
C(34)	–0.1837(3)	0.7791(2)	0.4703(2)	0.0249(6)
C(35)	–0.1476(4)	0.8922(3)	0.5046(3)	0.0377(8)
C(36)	–0.3519(3)	0.7496(3)	0.4713(2)	0.0324(7)
C(37)	0.4059(3)	0.9748(2)	0.5970(2)	0.0240(6)
C(38)	0.3039(3)	0.8914(2)	0.5401(2)	0.0249(6)
C(39)	0.2935(3)	0.8460(2)	0.4334(2)	0.0218(6)
C(40)	0.3895(3)	0.8928(2)	0.3899(2)	0.0223(6)
C(41)	0.4945(3)	0.9791(2)	0.4471(2)	0.0212(6)

Table 18. Bond lengths [Å] and angles [°] for **3**.

B(1)–N(1)	1.443(4)	B(1)–N(2)	1.441(4)
B(1)–C(39)	1.573(4)	N(1)–C(1)	1.397(4)
N(1)–C(7)	1.441(3)	N(2)–C(6)	1.402(4)
N(2)–C(22)	1.445(3)	C(1)–C(2)	1.385(4)
C(1)–C(6)	1.399(4)	C(2)–C(3)	1.387(4)
C(2)–H(2)	0.9500	C(3)–C(4)	1.392(4)
C(3)–H(3)	0.9500	C(4)–C(5)	1.393(4)
C(4)–H(4)	0.9500	C(5)–C(6)	1.385(4)
C(5)–H(5)	0.9500	C(7)–C(12)	1.400(4)
C(7)–C(8)	1.404(4)	C(8)–C(9)	1.403(4)
C(8)–C(13)	1.517(4)	C(9)–C(10)	1.391(4)
C(9)–H(9)	0.9500	C(10)–C(11)	1.383(4)
C(10)–C(16)	1.523(4)	C(11)–C(12)	1.402(4)
C(11)–H(11)	0.9500	C(12)–C(19)	1.515(4)
C(13)–C(15)	1.518(4)	C(13)–C(14)	1.537(5)
C(13)–H(13)	1.0000	C(14)–H(14A)	0.9800
C(14)–H(14B)	0.9800	C(14)–H(14C)	0.9800
C(15)–H(15A)	0.9800	C(15)–H(15C)	0.9800
C(15)–H(15B)	0.9800	C(16)–C(17)	1.520(5)
C(16)–C(18)	1.523(5)	C(16)–H(16)	1.0000
C(17)–H(17A)	0.9800	C(17)–H(17C)	0.9800

C(17)–H(17B)	0.9800	C(18)–H(18B)	0.9800
C(18)–H(18C)	0.9800	C(18)–H(18A)	0.9800
C(19)–C(20)	1.517(5)	C(19)–C(21)	1.530(5)
C(19)–H(19)	1.0000	C(20)–H(20C)	0.9800
C(20)–H(20B)	0.9800	C(20)–H(20A)	0.9800
C(21)–H(21A)	0.9800	C(21)–H(21B)	0.9800
C(21)–H(21C)	0.9800	C(22)–C(27)	1.400(4)
C(22)–C(23)	1.405(4)	C(23)–C(24)	1.393(4)
C(23)–C(28)	1.522(4)	C(24)–C(25)	1.394(4)
C(24)–H(24)	0.9500	C(25)–C(26)	1.384(4)
C(25)–C(31)	1.527(4)	C(26)–C(27)	1.400(4)
C(26)–H(26)	0.9500	C(27)–C(34)	1.518(4)
C(28)–C(30)	1.533(4)	C(28)–C(29)	1.538(4)
C(28)–H(28)	1.0000	C(29)–H(29C)	0.9800
C(29)–H(29B)	0.9800	C(29)–H(29A)	0.9800
C(30)–H(30B)	0.9800	C(30)–H(30C)	0.9800
C(30)–H(30A)	0.9800	C(31)–C(32)	1.519(5)
C(31)–C(33)	1.521(5)	C(31)–H(31)	1.0000
C(32)–H(32A)	0.9800	C(32)–H(32C)	0.9800
C(32)–H(32B)	0.9800	C(33)–H(33B)	0.9800
C(33)–H(33C)	0.9800	C(33)–H(33A)	0.9800
C(34)–C(36)	1.527(4)	C(34)–C(35)	1.529(4)
C(34)–H(34)	1.0000	C(35)–H(35C)	0.9800
C(35)–H(35B)	0.9800	C(35)–H(35A)	0.9800
C(36)–H(36A)	0.9800	C(36)–H(36B)	0.9800
C(36)–H(36C)	0.9800	C(37)–C(38)	1.373(4)
C(37)–C(41)#1	1.414(4)	C(37)–H(37)	0.9500
C(38)–C(39)	1.429(4)	C(38)–H(38)	0.9500
C(39)–C(40)	1.396(4)	C(40)–C(41)	1.413(4)
C(40)–H(40)	0.9500	C(41)–C(37)#1	1.414(4)
C(41)–C(41)#1	1.421(6)		

N(2)–B(1)–N(1)	105.1(2)	N(2)–B(1)–C(39)	127.9(3)
N(1)–B(1)–C(39)	127.0(3)	C(1)–N(1)–C(7)	119.9(2)
C(1)–N(1)–B(1)	109.0(2)	C(7)–N(1)–B(1)	131.1(2)
C(6)–N(2)–B(1)	108.8(2)	C(6)–N(2)–C(22)	119.4(2)
B(1)–N(2)–C(22)	131.4(2)	C(2)–C(1)–N(1)	130.1(3)
C(2)–C(1)–C(6)	121.4(3)	N(1)–C(1)–C(6)	108.5(2)
C(1)–C(2)–C(3)	118.3(3)	C(1)–C(2)–H(2)	120.9
C(3)–C(2)–H(2)	120.9	C(2)–C(3)–C(4)	120.6(3)
C(2)–C(3)–H(3)	119.7	C(4)–C(3)–H(3)	119.7
C(3)–C(4)–C(5)	121.2(3)	C(3)–C(4)–H(4)	119.4
C(5)–C(4)–H(4)	119.4	C(6)–C(5)–C(4)	118.3(3)
C(6)–C(5)–H(5)	120.8	C(4)–C(5)–H(5)	120.8
C(5)–C(6)–C(1)	120.3(3)	C(5)–C(6)–N(2)	131.1(2)
C(1)–C(6)–N(2)	108.6(2)	C(12)–C(7)–C(8)	122.0(2)
C(12)–C(7)–N(1)	119.0(2)	C(8)–C(7)–N(1)	119.1(2)
C(9)–C(8)–C(7)	117.1(3)	C(9)–C(8)–C(13)	121.3(3)
C(7)–C(8)–C(13)	121.7(2)	C(10)–C(9)–C(8)	122.4(3)
C(10)–C(9)–H(9)	118.8	C(8)–C(9)–H(9)	118.8
C(11)–C(10)–C(9)	118.6(3)	C(11)–C(10)–C(16)	122.5(3)
C(9)–C(10)–C(16)	119.0(3)	C(10)–C(11)–C(12)	121.7(3)
C(10)–C(11)–H(11)	119.1	C(12)–C(11)–H(11)	119.1
C(7)–C(12)–C(11)	118.1(3)	C(7)–C(12)–C(19)	122.1(2)
C(11)–C(12)–C(19)	119.8(3)	C(8)–C(13)–C(15)	113.1(2)
C(8)–C(13)–C(14)	110.9(3)	C(15)–C(13)–C(14)	109.9(3)
C(8)–C(13)–H(13)	107.6	C(15)–C(13)–H(13)	107.6

C(14)–C(13)–H(13)	107.6	C(13)–C(14)–H(14A)	109.5
C(13)–C(14)–H(14B)	109.5	H(14A)–C(14)–H(14B)	109.5
C(13)–C(14)–H(14C)	109.5	H(14A)–C(14)–H(14C)	109.5
H(14B)–C(14)–H(14C)	109.5	C(13)–C(15)–H(15A)	109.5
C(13)–C(15)–H(15C)	109.5	H(15A)–C(15)–H(15C)	109.5
C(13)–C(15)–H(15B)	109.5	H(15A)–C(15)–H(15B)	109.5
H(15C)–C(15)–H(15B)	109.5	C(17)–C(16)–C(10)	114.2(3)
C(17)–C(16)–C(18)	110.0(3)	C(10)–C(16)–C(18)	109.6(3)
C(17)–C(16)–H(16)	107.6	C(10)–C(16)–H(16)	107.6
C(18)–C(16)–H(16)	107.6	C(16)–C(17)–H(17A)	109.5
C(16)–C(17)–H(17C)	109.5	H(17A)–C(17)–H(17C)	109.5
C(16)–C(17)–H(17B)	109.5	H(17A)–C(17)–H(17B)	109.5
H(17C)–C(17)–H(17B)	109.5	C(16)–C(18)–H(18B)	109.5
C(16)–C(18)–H(18C)	109.5	H(18B)–C(18)–H(18C)	109.5
C(16)–C(18)–H(18A)	109.5	H(18B)–C(18)–H(18A)	109.5
H(18C)–C(18)–H(18A)	109.5	C(12)–C(19)–C(20)	112.4(3)
C(12)–C(19)–C(21)	110.7(3)	C(20)–C(19)–C(21)	111.5(3)
C(12)–C(19)–H(19)	107.3	C(20)–C(19)–H(19)	107.3
C(21)–C(19)–H(19)	107.3	C(19)–C(20)–H(20C)	109.5
C(19)–C(20)–H(20B)	109.5	H(20C)–C(20)–H(20B)	109.5
C(19)–C(20)–H(20A)	109.5	H(20C)–C(20)–H(20A)	109.5
H(20B)–C(20)–H(20A)	109.5	C(19)–C(21)–H(21A)	109.5
C(19)–C(21)–H(21B)	109.5	H(21A)–C(21)–H(21B)	109.5
C(19)–C(21)–H(21C)	109.5	H(21A)–C(21)–H(21C)	109.5
H(21B)–C(21)–H(21C)	109.5	C(27)–C(22)–C(23)	122.1(2)
C(27)–C(22)–N(2)	118.4(2)	C(23)–C(22)–N(2)	119.5(2)
C(24)–C(23)–C(22)	117.6(2)	C(24)–C(23)–C(28)	121.5(2)
C(22)–C(23)–C(28)	120.8(2)	C(23)–C(24)–C(25)	122.0(3)
C(23)–C(24)–H(24)	119.0	C(25)–C(24)–H(24)	119.0
C(26)–C(25)–C(24)	118.6(2)	C(26)–C(25)–C(31)	121.6(3)
C(24)–C(25)–C(31)	119.8(3)	C(25)–C(26)–C(27)	122.1(3)
C(25)–C(26)–H(26)	118.9	C(27)–C(26)–H(26)	118.9
C(22)–C(27)–C(26)	117.5(3)	C(22)–C(27)–C(34)	121.6(2)
C(26)–C(27)–C(34)	120.8(3)	C(23)–C(28)–C(30)	113.4(2)
C(23)–C(28)–C(29)	111.6(2)	C(30)–C(28)–C(29)	109.9(2)
C(23)–C(28)–H(28)	107.2	C(30)–C(28)–H(28)	107.2
C(29)–C(28)–H(28)	107.2	C(28)–C(29)–H(29C)	109.5
C(28)–C(29)–H(29B)	109.5	H(29C)–C(29)–H(29B)	109.5
C(28)–C(29)–H(29A)	109.5	H(29C)–C(29)–H(29A)	109.5
H(29B)–C(29)–H(29A)	109.5	C(28)–C(30)–H(30B)	109.5
C(28)–C(30)–H(30C)	109.5	H(30B)–C(30)–H(30C)	109.5
C(28)–C(30)–H(30A)	109.5	H(30B)–C(30)–H(30A)	109.5
H(30C)–C(30)–H(30A)	109.5	C(32)–C(31)–C(33)	111.1(3)
C(32)–C(31)–C(25)	110.9(3)	C(33)–C(31)–C(25)	112.0(3)
C(32)–C(31)–H(31)	107.5	C(33)–C(31)–H(31)	107.5
C(25)–C(31)–H(31)	107.5	C(31)–C(32)–H(32A)	109.5
C(31)–C(32)–H(32C)	109.5	H(32A)–C(32)–H(32C)	109.5
C(31)–C(32)–H(32B)	109.5	H(32A)–C(32)–H(32B)	109.5
H(32C)–C(32)–H(32B)	109.5	C(31)–C(33)–H(33B)	109.5
C(31)–C(33)–H(33C)	109.5	H(33B)–C(33)–H(33C)	109.5
C(31)–C(33)–H(33A)	109.5	H(33B)–C(33)–H(33A)	109.5
H(33C)–C(33)–H(33A)	109.5	C(27)–C(34)–C(36)	112.9(2)
C(27)–C(34)–C(35)	110.0(2)	C(36)–C(34)–C(35)	110.4(3)
C(27)–C(34)–H(34)	107.8	C(36)–C(34)–H(34)	107.8
C(35)–C(34)–H(34)	107.8	C(34)–C(35)–H(35C)	109.5
C(34)–C(35)–H(35B)	109.5	H(35C)–C(35)–H(35B)	109.5
C(34)–C(35)–H(35A)	109.5	H(35C)–C(35)–H(35A)	109.5

H(35B)–C(35)–H(35A)	109.5	C(34)–C(36)–H(36A)	109.5
C(34)–C(36)–H(36B)	109.5	H(36A)–C(36)–H(36B)	109.5
C(34)–C(36)–H(36C)	109.5	H(36A)–C(36)–H(36C)	109.5
H(36B)–C(36)–H(36C)	109.5	C(38)–C(37)–C(41)#1	121.6(3)
C(38)–C(37)–H(37)	119.2	C(41)#1–C(37)–H(37)	119.2
C(37)–C(38)–C(39)	122.0(3)	C(37)–C(38)–H(38)	119.0
C(39)–C(38)–H(38)	119.0	C(40)–C(39)–C(38)	116.4(3)
C(40)–C(39)–B(1)	121.4(2)	C(38)–C(39)–B(1)	122.2(2)
C(39)–C(40)–C(41)	122.5(3)	C(39)–C(40)–H(40)	118.7
C(41)–C(40)–H(40)	118.7	C(40)–C(41)–C(37)#1	122.6(3)
C(40)–C(41)–C(41)#1	119.8(3)	C(37)#1–C(41)–C(41)#1	117.6(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1

Table 19. Anisotropic displacement parameters ($Å^2$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	0.0190(15)	0.0264(16)	0.0227(15)	0.0138(13)	0.0024(12)	0.0040(12)
N(1)	0.0204(11)	0.0230(11)	0.0159(11)	0.0095(9)	0.0019(9)	–0.0015(9)
N(2)	0.0212(11)	0.0209(11)	0.0140(11)	0.0075(9)	0.0000(8)	–0.0002(9)
C(1)	0.0247(14)	0.0211(13)	0.0176(13)	0.0095(11)	0.0023(10)	0.0018(11)
C(2)	0.0318(16)	0.0280(15)	0.0132(12)	0.0065(11)	0.0013(11)	–0.0013(12)
C(3)	0.0338(16)	0.0239(14)	0.0180(13)	0.0045(11)	–0.0023(11)	–0.0020(12)
C(4)	0.0276(15)	0.0242(14)	0.0265(15)	0.0121(12)	–0.0019(12)	–0.0045(11)
C(5)	0.0285(15)	0.0235(14)	0.0188(13)	0.0119(11)	0.0031(11)	0.0008(11)
C(6)	0.0210(13)	0.0224(13)	0.0161(12)	0.0092(11)	0.0012(10)	0.0016(10)
C(7)	0.0224(14)	0.0243(13)	0.0139(12)	0.0081(11)	0.0029(10)	–0.0015(11)
C(8)	0.0229(14)	0.0243(14)	0.0166(12)	0.0055(11)	0.0004(10)	–0.0018(11)
C(9)	0.0217(14)	0.0291(14)	0.0190(13)	0.0085(11)	0.0024(11)	0.0000(11)
C(10)	0.0304(15)	0.0217(13)	0.0198(13)	0.0080(11)	0.0025(11)	–0.0032(11)
C(11)	0.0291(15)	0.0247(14)	0.0216(14)	0.0129(12)	0.0023(11)	0.0006(11)
C(12)	0.0223(14)	0.0243(13)	0.0195(13)	0.0097(11)	0.0005(11)	–0.0032(11)
C(13)	0.0319(16)	0.0314(15)	0.0209(14)	0.0113(12)	0.0062(12)	0.0063(12)
C(14)	0.0389(18)	0.0363(18)	0.0428(19)	0.0215(15)	0.0034(15)	0.0048(14)
C(15)	0.0313(17)	0.0436(18)	0.0316(16)	0.0202(15)	0.0027(13)	0.0090(14)
C(16)	0.0377(18)	0.0357(16)	0.0345(17)	0.0224(14)	0.0152(14)	0.0065(13)
C(17)	0.054(2)	0.0421(19)	0.0266(16)	0.0206(15)	0.0061(15)	–0.0034(16)
C(18)	0.0342(18)	0.053(2)	0.061(2)	0.042(2)	0.0015(16)	–0.0065(16)
C(19)	0.0288(16)	0.0346(16)	0.0265(15)	0.0196(13)	0.0054(12)	0.0042(12)
C(20)	0.0290(18)	0.081(3)	0.042(2)	0.038(2)	0.0026(15)	0.0054(17)
C(21)	0.043(2)	0.0380(19)	0.059(2)	0.0144(18)	0.0163(18)	0.0110(16)
C(22)	0.0229(13)	0.0214(13)	0.0140(12)	0.0090(10)	0.0026(10)	–0.0008(10)
C(23)	0.0232(14)	0.0208(13)	0.0175(13)	0.0097(11)	0.0016(10)	0.0001(10)
C(24)	0.0250(14)	0.0261(14)	0.0201(13)	0.0138(11)	0.0008(11)	0.0010(11)
C(25)	0.0284(15)	0.0288(14)	0.0188(13)	0.0112(11)	0.0035(11)	0.0002(12)
C(26)	0.0235(14)	0.0288(14)	0.0194(13)	0.0098(11)	0.0056(11)	0.0035(11)
C(27)	0.0216(14)	0.0211(13)	0.0199(13)	0.0096(11)	0.0006(10)	–0.0029(10)
C(28)	0.0265(14)	0.0306(15)	0.0215(14)	0.0152(12)	0.0040(11)	0.0063(12)
C(29)	0.0346(17)	0.0338(16)	0.0318(16)	0.0152(14)	0.0033(13)	0.0114(13)
C(30)	0.0260(15)	0.0420(17)	0.0290(15)	0.0220(14)	0.0031(12)	0.0061(13)
C(31)	0.0312(16)	0.0388(17)	0.0177(14)	0.0137(12)	0.0048(11)	0.0056(13)
C(32)	0.074(3)	0.043(2)	0.0187(15)	0.0101(15)	0.0098(16)	0.0039(18)
C(33)	0.051(2)	0.060(2)	0.0235(16)	0.0180(16)	0.0102(15)	–0.0068(18)

C(34)	0.0234(14)	0.0306(15)	0.0213(13)	0.0119(12)	0.0027(11)	0.0051(11)
C(35)	0.0346(18)	0.0341(17)	0.049(2)	0.0233(15)	–0.0025(15)	0.0039(14)
C(36)	0.0264(16)	0.0457(18)	0.0303(16)	0.0221(14)	0.0006(12)	0.0040(13)
C(37)	0.0291(15)	0.0248(14)	0.0166(13)	0.0084(11)	0.0019(11)	0.0028(11)
C(38)	0.0241(14)	0.0258(14)	0.0259(14)	0.0137(12)	0.0029(11)	–0.0018(11)
C(39)	0.0208(13)	0.0240(13)	0.0224(14)	0.0121(11)	0.0014(11)	0.0033(11)
C(40)	0.0249(14)	0.0243(13)	0.0174(13)	0.0091(11)	0.0019(11)	0.0031(11)
C(41)	0.0226(14)	0.0210(13)	0.0214(14)	0.0106(11)	0.0015(10)	0.0036(11)

Table 20. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **3**.

	x	y	z	U(eq)
H(2)	0.0341	0.5399	0.0790	0.031
H(3)	–0.1579	0.4135	0.0659	0.033
H(4)	–0.2450	0.4081	0.2089	0.032
H(5)	–0.1424	0.5281	0.3683	0.028
H(9)	0.5360	0.6995	0.0660	0.029
H(11)	0.1793	0.8316	0.0505	0.029
H(13)	0.4262	0.6533	0.2692	0.034
H(14A)	0.3005	0.5030	0.1407	0.057
H(14B)	0.4616	0.4838	0.1693	0.057
H(14C)	0.4350	0.4966	0.0704	0.057
H(15A)	0.6726	0.6224	0.2387	0.051
H(15C)	0.6561	0.7299	0.2447	0.051
H(15B)	0.6604	0.6346	0.1385	0.051
H(16)	0.5176	0.7562	–0.0589	0.040
H(17A)	0.2806	0.7662	–0.1254	0.060
H(17C)	0.4159	0.8390	–0.1368	0.060
H(17B)	0.3030	0.8843	–0.0512	0.060
H(18B)	0.5052	0.9594	0.0845	0.067
H(18C)	0.6246	0.9240	0.0018	0.067
H(18A)	0.6281	0.8932	0.0908	0.067
H(19)	–0.0457	0.7456	0.1984	0.033
H(20C)	–0.0629	0.8167	0.0524	0.070
H(20B)	–0.2037	0.7827	0.0995	0.070
H(20A)	–0.1028	0.7014	0.0294	0.070
H(21A)	0.0642	0.9086	0.3115	0.073
H(21B)	–0.0985	0.9126	0.2703	0.073
H(21C)	0.0486	0.9462	0.2280	0.073
H(24)	0.1537	0.6863	0.6965	0.027
H(26)	–0.2125	0.7975	0.6547	0.029
H(28)	0.3255	0.6712	0.4840	0.030
H(29C)	0.1907	0.4870	0.4805	0.049
H(29B)	0.3365	0.4968	0.4239	0.049
H(29A)	0.1782	0.5151	0.3901	0.049
H(30B)	0.3535	0.6106	0.6378	0.045
H(30C)	0.4091	0.7224	0.6539	0.045
H(30A)	0.4868	0.6303	0.5766	0.045
H(31)	0.0025	0.7449	0.8267	0.035
H(32A)	0.0371	0.9151	0.8611	0.071
H(32C)	–0.0820	0.8966	0.9313	0.071
H(32B)	–0.1386	0.9091	0.8367	0.071
H(33B)	–0.3054	0.7401	0.7740	0.070
H(33C)	–0.2450	0.7305	0.8695	0.070

H(33A)	–0.2305	0.6435	0.7596	0.070
H(34)	–0.1561	0.7436	0.3998	0.030
H(35C)	–0.1789	0.9290	0.5723	0.057
H(35B)	–0.2013	0.9101	0.4590	0.057
H(35A)	–0.0392	0.9102	0.5043	0.057
H(36A)	–0.3740	0.6765	0.4462	0.049
H(36B)	–0.4076	0.7699	0.4285	0.049
H(36C)	–0.3819	0.7834	0.5397	0.049
H(37)	0.4096	1.0022	0.6677	0.029
H(38)	0.2383	0.8631	0.5726	0.030
H(40)	0.3840	0.8655	0.3192	0.027

Table 21. Crystal data and structure refinement for **4**.

Identification code	**4**	
Chemical formula	$C_{44}H_{66}BLiN_2O_2$	
Formula weight	672.74	
Temperature	90(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/n$	
Unit cell parameters	a = 10.3828(7) Å	α = 90°
	b = 23.8027(17) Å	β = 91.7790(10)°
	c = 17.1319(12) Å	γ = 90°
Cell volume	4231.9(5) $Å^3$	
Z	4	
Calculated density	1.056 g/cm^3	
Absorption coefficient μ	0.062 mm^{-1}	
F(000)	1472	
Crystal colour and size	COLOURLESS, 0.25 × 0.12 × 0.06 mm^3	
Reflections for cell refinement	9424 (θ range 2.37 to 27.56°)	
Data collection method	Bruker SMART APEX CCD area detector ω	
θ range for data collection	2.26 to 27.65°	
Index ranges	h –13 to 13, k –31 to 29, l –17 to 22	
Completeness to θ = 25.00°	99.3 %	
Intensity decay	0%	
Reflections collected	25786	
Independent reflections	9597 (R_{int} = 0.0350)	
Reflections with $F^2>2\sigma$	7293	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.561 and 0.746	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0523, 2.6250	
Data / restraints / parameters	9597 / 0 / 463	
Final R indices [$F^2>2\sigma$]	R1 = 0.0639, wR2 = 0.1445	
R indices (all data)	R1 = 0.0874, wR2 = 0.1555	
Goodness-of-fit on F^2	1.139	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.513 and –0.237 e $Å^{-3}$	

Table 22. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Li(1)	–0.1449(3)	0.19347(15)	0.3426(2)	0.0323(8)
B(1)	0.0434(2)	0.18993(9)	0.27719(12)	0.0217(4)
N(1)	0.13205(15)	0.23595(6)	0.25594(9)	0.0202(3)
N(2)	0.11780(15)	0.14097(6)	0.24980(8)	0.0196(3)
C(1)	0.24299(18)	0.21576(8)	0.22183(10)	0.0198(4)
C(2)	0.35062(19)	0.24369(8)	0.19466(11)	0.0227(4)
C(3)	0.44794(19)	0.21185(9)	0.16168(11)	0.0261(4)
C(4)	0.43796(19)	0.15370(8)	0.15648(11)	0.0254(4)
C(5)	0.33071(18)	0.12532(8)	0.18417(11)	0.0223(4)
C(6)	0.23387(18)	0.15694(7)	0.21696(10)	0.0197(4)
C(7)	0.12660(17)	0.29324(7)	0.28063(10)	0.0198(4)
C(8)	0.08266(18)	0.33546(8)	0.22862(10)	0.0223(4)
C(9)	0.07940(18)	0.39067(8)	0.25506(11)	0.0221(4)
C(10)	0.11730(17)	0.40562(8)	0.33125(10)	0.0206(4)
C(11)	0.15970(17)	0.36290(8)	0.38147(11)	0.0209(4)
C(12)	0.16600(17)	0.30700(8)	0.35762(10)	0.0203(4)
C(13)	0.0321(2)	0.32049(8)	0.14674(11)	0.0283(4)
C(14)	0.0654(3)	0.36411(10)	0.08539(13)	0.0520(7)
C(15)	–0.1137(3)	0.31200(16)	0.14952(16)	0.0654(9)
C(16)	0.10821(19)	0.46684(7)	0.35615(11)	0.0223(4)
C(17)	–0.0270(2)	0.48017(9)	0.38388(15)	0.0362(5)
C(18)	0.2097(2)	0.48381(8)	0.41794(12)	0.0299(4)
C(19)	0.21421(18)	0.26187(8)	0.41454(11)	0.0215(4)
C(20)	0.35574(19)	0.27146(9)	0.43907(12)	0.0294(4)
C(21)	0.12878(19)	0.25839(8)	0.48570(11)	0.0258(4)
C(22)	0.07853(17)	0.08342(7)	0.25188(10)	0.0190(4)
C(23)	0.12517(18)	0.04808(8)	0.31244(10)	0.0215(4)
C(24)	0.07979(18)	–0.00715(8)	0.31495(11)	0.0222(4)
C(25)	–0.01097(18)	–0.02786(7)	0.26046(11)	0.0211(4)
C(26)	–0.05349(18)	0.00797(8)	0.20059(11)	0.0224(4)
C(27)	–0.00962(18)	0.06321(8)	0.19443(10)	0.0203(4)
C(28)	0.21842(19)	0.07026(8)	0.37542(11)	0.0239(4)
C(29)	0.1448(2)	0.09852(10)	0.44117(12)	0.0337(5)
C(30)	0.3083(2)	0.02473(9)	0.41001(12)	0.0316(5)
C(31)	–0.05776(19)	–0.08855(8)	0.26110(11)	0.0238(4)
C(32)	0.0165(2)	–0.12331(8)	0.20238(12)	0.0286(4)
C(33)	–0.0499(2)	–0.11622(9)	0.34164(12)	0.0336(5)
C(34)	–0.05540(18)	0.09984(8)	0.12615(10)	0.0218(4)
C(35)	–0.0242(2)	0.07246(8)	0.04797(11)	0.0265(4)
C(36)	–0.1999(2)	0.11254(9)	0.13020(12)	0.0297(4)
O(1)	–0.21665(14)	0.25683(6)	0.39513(8)	0.0318(3)
C(37)	–0.2702(2)	0.25285(9)	0.47190(12)	0.0327(5)
C(38)	–0.3059(2)	0.31213(9)	0.49481(12)	0.0318(5)
C(39)	–0.2072(2)	0.34731(9)	0.45198(13)	0.0341(5)
C(40)	–0.1930(2)	0.31518(9)	0.37635(12)	0.0303(4)
O(2)	–0.25938(14)	0.13217(6)	0.37075(9)	0.0342(3)
C(41)	–0.2105(2)	0.07617(10)	0.38691(15)	0.0390(5)
C(42)	–0.3201(2)	0.03546(10)	0.36669(16)	0.0429(6)
C(43)	–0.4015(2)	0.06911(10)	0.30792(13)	0.0371(5)
C(44)	–0.3906(2)	0.12799(10)	0.34019(13)	0.0343(5)

Table 23. Bond lengths [Å] and angles [°] for **4**.

Li(1)–O(1)	1.919(4)	Li(1)–O(2)	1.952(4)
Li(1)–B(1)	2.285(4)	B(1)–N(2)	1.482(3)
B(1)–N(1)	1.483(3)	N(1)–C(1)	1.393(2)
N(1)–C(7)	1.429(2)	N(2)–C(6)	1.398(2)
N(2)–C(22)	1.430(2)	C(1)–C(2)	1.393(3)
C(1)–C(6)	1.405(2)	C(2)–C(3)	1.396(3)
C(2)–H(2)	0.9500	C(3)–C(4)	1.391(3)
C(3)–H(3)	0.9500	C(4)–C(5)	1.398(3)
C(4)–H(4)	0.9500	C(5)–C(6)	1.389(3)
C(5)–H(5)	0.9500	C(7)–C(12)	1.407(2)
C(7)–C(8)	1.410(3)	C(8)–C(9)	1.391(3)
C(8)–C(13)	1.525(3)	C(9)–C(10)	1.398(2)
C(9)–H(9)	0.9500	C(10)–C(11)	1.395(3)
C(10)–C(16)	1.522(2)	C(11)–C(12)	1.394(3)
C(11)–H(11)	0.9500	C(12)–C(19)	1.525(2)
C(13)–C(14)	1.525(3)	C(13)–C(15)	1.529(3)
C(13)–H(13)	1.0000	C(14)–H(14A)	0.9800
C(14)–H(14B)	0.9800	C(14)–H(14C)	0.9800
C(15)–H(15C)	0.9800	C(15)–H(15B)	0.9800
C(15)–H(15A)	0.9800	C(16)–C(18)	1.525(3)
C(16)–C(17)	1.529(3)	C(16)–H(16)	1.0000
C(17)–H(17A)	0.9800	C(17)–H(17C)	0.9800
C(17)–H(17B)	0.9800	C(18)–H(18B)	0.9800
C(18)–H(18C)	0.9800	C(18)–H(18A)	0.9800
C(19)–C(21)	1.532(3)	C(19)–C(20)	1.533(3)
C(19)–H(19)	1.0000	C(20)–H(20A)	0.9800
C(20)–H(20B)	0.9800	C(20)–H(20C)	0.9800
C(21)–H(21C)	0.9800	C(21)–H(21B)	0.9800
C(21)–H(21A)	0.9800	C(22)–C(27)	1.408(3)
C(22)–C(23)	1.410(3)	C(23)–C(24)	1.398(3)
C(23)–C(28)	1.522(3)	C(24)–C(25)	1.396(3)
C(24)–H(24)	0.9500	C(25)–C(26)	1.395(3)
C(25)–C(31)	1.524(2)	C(26)–C(27)	1.397(3)
C(26)–H(26)	0.9500	C(27)–C(34)	1.523(2)
C(28)–C(29)	1.536(3)	C(28)–C(30)	1.537(3)
C(28)–H(28)	1.0000	C(29)–H(29A)	0.9800
C(29)–H(29C)	0.9800	C(29)–H(29B)	0.9800
C(30)–H(30B)	0.9800	C(30)–H(30C)	0.9800
C(30)–H(30A)	0.9800	C(31)–C(33)	1.529(3)
C(31)–C(32)	1.530(3)	C(31)–H(31)	1.0000
C(32)–H(32A)	0.9800	C(32)–H(32C)	0.9800
C(32)–H(32B)	0.9800	C(33)–H(33A)	0.9800
C(33)–H(33B)	0.9800	C(33)–H(33C)	0.9800
C(34)–C(35)	1.533(3)	C(34)–C(36)	1.534(3)
C(34)–H(34)	1.0000	C(35)–H(35B)	0.9800
C(35)–H(35C)	0.9800	C(35)–H(35A)	0.9800
C(36)–H(36B)	0.9800	C(36)–H(36C)	0.9800
C(36)–H(36A)	0.9800	O(1)–C(37)	1.447(2)
O(1)–C(40)	1.448(2)	C(37)–C(38)	1.514(3)
C(37)–H(37B)	0.9900	C(37)–H(37A)	0.9900
C(38)–C(39)	1.528(3)	C(38)–H(38B)	0.9900
C(38)–H(38A)	0.9900	C(39)–C(40)	1.516(3)
C(39)–H(39B)	0.9900	C(39)–H(39A)	0.9900
C(40)–H(40B)	0.9900	C(40)–H(40A)	0.9900
O(2)–C(44)	1.448(3)	O(2)–C(41)	1.450(3)

C(41)–C(42)	1.526(3)	C(41)–H(41B)	0.9900
C(41)–H(41A)	0.9900	C(42)–C(43)	1.522(3)
C(42)–H(42A)	0.9900	C(42)–H(42B)	0.9900
C(43)–C(44)	1.510(3)	C(43)–H(43A)	0.9900
C(43)–H(43B)	0.9900	C(44)–H(44A)	0.9900
C(44)–H(44B)	0.9900		

O(1)–Li(1)–O(2)	102.92(17)	O(1)–Li(1)–B(1)	127.55(19)
O(2)–Li(1)–B(1)	129.08(19)	N(2)–B(1)–N(1)	99.77(15)
N(2)–B(1)–Li(1)	130.27(16)	N(1)–B(1)–Li(1)	129.79(16)
C(1)–N(1)–C(7)	119.61(15)	C(1)–N(1)–B(1)	112.06(15)
C(7)–N(1)–B(1)	126.97(15)	C(6)–N(2)–C(22)	121.35(15)
C(6)–N(2)–B(1)	112.19(15)	C(22)–N(2)–B(1)	126.41(15)
C(2)–C(1)–N(1)	131.14(17)	C(2)–C(1)–C(6)	120.60(17)
N(1)–C(1)–C(6)	108.27(16)	C(1)–C(2)–C(3)	118.31(17)
C(1)–C(2)–H(2)	120.8	C(3)–C(2)–H(2)	120.8
C(4)–C(3)–C(2)	120.84(18)	C(4)–C(3)–H(3)	119.6
C(2)–C(3)–H(3)	119.6	C(3)–C(4)–C(5)	121.19(18)
C(3)–C(4)–H(4)	119.4	C(5)–C(4)–H(4)	119.4
C(6)–C(5)–C(4)	118.02(17)	C(6)–C(5)–H(5)	121.0
C(4)–C(5)–H(5)	121.0	C(5)–C(6)–N(2)	131.25(17)
C(5)–C(6)–C(1)	121.04(17)	N(2)–C(6)–C(1)	107.71(15)
C(12)–C(7)–C(8)	120.37(16)	C(12)–C(7)–N(1)	119.09(16)
C(8)–C(7)–N(1)	120.54(16)	C(9)–C(8)–C(7)	118.58(17)
C(9)–C(8)–C(13)	120.62(17)	C(7)–C(8)–C(13)	120.69(17)
C(8)–C(9)–C(10)	122.40(17)	C(8)–C(9)–H(9)	118.8
C(10)–C(9)–H(9)	118.8	C(11)–C(10)–C(9)	117.70(17)
C(11)–C(10)–C(16)	123.12(16)	C(9)–C(10)–C(16)	119.17(16)
C(12)–C(11)–C(10)	122.14(17)	C(12)–C(11)–H(11)	118.9
C(10)–C(11)–H(11)	118.9	C(11)–C(12)–C(7)	118.80(16)
C(11)–C(12)–C(19)	120.16(16)	C(7)–C(12)–C(19)	121.03(16)
C(8)–C(13)–C(14)	113.31(17)	C(8)–C(13)–C(15)	108.38(17)
C(14)–C(13)–C(15)	111.0(2)	C(8)–C(13)–H(13)	108.0
C(14)–C(13)–H(13)	108.0	C(15)–C(13)–H(13)	108.0
C(13)–C(14)–H(14A)	109.5	C(13)–C(14)–H(14B)	109.5
H(14A)–C(14)–H(14B)	109.5	C(13)–C(14)–H(14C)	109.5
H(14A)–C(14)–H(14C)	109.5	H(14B)–C(14)–H(14C)	109.5
C(13)–C(15)–H(15C)	109.5	C(13)–C(15)–H(15B)	109.5
H(15C)–C(15)–H(15B)	109.5	C(13)–C(15)–H(15A)	109.5
H(15C)–C(15)–H(15A)	109.5	H(15B)–C(15)–H(15A)	109.5
C(10)–C(16)–C(18)	113.61(16)	C(10)–C(16)–C(17)	110.57(16)
C(18)–C(16)–C(17)	110.53(16)	C(10)–C(16)–H(16)	107.3
C(18)–C(16)–H(16)	107.3	C(17)–C(16)–H(16)	107.3
C(16)–C(17)–H(17A)	109.5	C(16)–C(17)–H(17C)	109.5
H(17A)–C(17)–H(17C)	109.5	C(16)–C(17)–H(17B)	109.5
H(17A)–C(17)–H(17B)	109.5	H(17C)–C(17)–H(17B)	109.5
C(16)–C(18)–H(18B)	109.5	C(16)–C(18)–H(18C)	109.5
H(18B)–C(18)–H(18C)	109.5	C(16)–C(18)–H(18A)	109.5
H(18B)–C(18)–H(18A)	109.5	H(18C)–C(18)–H(18A)	109.5
C(12)–C(19)–C(21)	111.12(15)	C(12)–C(19)–C(20)	111.30(15)
C(21)–C(19)–C(20)	111.32(16)	C(12)–C(19)–H(19)	107.6
C(21)–C(19)–H(19)	107.6	C(20)–C(19)–H(19)	107.6
C(19)–C(20)–H(20A)	109.5	C(19)–C(20)–H(20B)	109.5
H(20A)–C(20)–H(20B)	109.5	C(19)–C(20)–H(20C)	109.5
H(20A)–C(20)–H(20C)	109.5	H(20B)–C(20)–H(20C)	109.5
C(19)–C(21)–H(21C)	109.5	C(19)–C(21)–H(21B)	109.5
H(21C)–C(21)–H(21B)	109.5	C(19)–C(21)–H(21A)	109.5

H(21C)–C(21)–H(21A)	109.5	H(21B)–C(21)–H(21A)	109.5
C(27)–C(22)–C(23)	120.78(16)	C(27)–C(22)–N(2)	119.30(16)
C(23)–C(22)–N(2)	119.88(16)	C(24)–C(23)–C(22)	118.39(17)
C(24)–C(23)–C(28)	120.80(16)	C(22)–C(23)–C(28)	120.76(16)
C(25)–C(24)–C(23)	122.20(17)	C(25)–C(24)–H(24)	118.9
C(23)–C(24)–H(24)	118.9	C(26)–C(25)–C(24)	117.87(17)
C(26)–C(25)–C(31)	119.41(17)	C(24)–C(25)–C(31)	122.60(17)
C(25)–C(26)–C(27)	122.32(17)	C(25)–C(26)–H(26)	118.8
C(27)–C(26)–H(26)	118.8	C(26)–C(27)–C(22)	118.38(16)
C(26)–C(27)–C(34)	120.15(16)	C(22)–C(27)–C(34)	121.47(16)
C(23)–C(28)–C(29)	110.59(16)	C(23)–C(28)–C(30)	113.21(16)
C(29)–C(28)–C(30)	109.65(16)	C(23)–C(28)–H(28)	107.7
C(29)–C(28)–H(28)	107.7	C(30)–C(28)–H(28)	107.7
C(28)–C(29)–H(29A)	109.5	C(28)–C(29)–H(29C)	109.5
H(29A)–C(29)–H(29C)	109.5	C(28)–C(29)–H(29B)	109.5
H(29A)–C(29)–H(29B)	109.5	H(29C)–C(29)–H(29B)	109.5
C(28)–C(30)–H(30B)	109.5	C(28)–C(30)–H(30C)	109.5
H(30B)–C(30)–H(30C)	109.5	C(28)–C(30)–H(30A)	109.5
H(30B)–C(30)–H(30A)	109.5	H(30C)–C(30)–H(30A)	109.5
C(25)–C(31)–C(33)	114.00(16)	C(25)–C(31)–C(32)	109.91(15)
C(33)–C(31)–C(32)	110.28(16)	C(25)–C(31)–H(31)	107.5
C(33)–C(31)–H(31)	107.5	C(32)–C(31)–H(31)	107.5
C(31)–C(32)–H(32A)	109.5	C(31)–C(32)–H(32C)	109.5
H(32A)–C(32)–H(32C)	109.5	C(31)–C(32)–H(32B)	109.5
H(32A)–C(32)–H(32B)	109.5	H(32C)–C(32)–H(32B)	109.5
C(31)–C(33)–H(33A)	109.5	C(31)–C(33)–H(33B)	109.5
H(33A)–C(33)–H(33B)	109.5	C(31)–C(33)–H(33C)	109.5
H(33A)–C(33)–H(33C)	109.5	H(33B)–C(33)–H(33C)	109.5
C(27)–C(34)–C(35)	111.00(15)	C(27)–C(34)–C(36)	111.13(15)
C(35)–C(34)–C(36)	110.89(16)	C(27)–C(34)–H(34)	107.9
C(35)–C(34)–H(34)	107.9	C(36)–C(34)–H(34)	107.9
C(34)–C(35)–H(35B)	109.5	C(34)–C(35)–H(35C)	109.5
H(35B)–C(35)–H(35C)	109.5	C(34)–C(35)–H(35A)	109.5
H(35B)–C(35)–H(35A)	109.5	H(35C)–C(35)–H(35A)	109.5
C(34)–C(36)–H(36B)	109.5	C(34)–C(36)–H(36C)	109.5
H(36B)–C(36)–H(36C)	109.5	C(34)–C(36)–H(36A)	109.5
H(36B)–C(36)–H(36A)	109.5	H(36C)–C(36)–H(36A)	109.5
C(37)–O(1)–C(40)	109.71(15)	C(37)–O(1)–Li(1)	122.73(17)
C(40)–O(1)–Li(1)	125.36(16)	O(1)–C(37)–C(38)	106.18(17)
O(1)–C(37)–H(37B)	110.5	C(38)–C(37)–H(37B)	110.5
O(1)–C(37)–H(37A)	110.5	C(38)–C(37)–H(37A)	110.5
H(37B)–C(37)–H(37A)	108.7	C(37)–C(38)–C(39)	102.32(17)
C(37)–C(38)–H(38B)	111.3	C(39)–C(38)–H(38B)	111.3
C(37)–C(38)–H(38A)	111.3	C(39)–C(38)–H(38A)	111.3
H(38B)–C(38)–H(38A)	109.2	C(40)–C(39)–C(38)	102.61(17)
C(40)–C(39)–H(39B)	111.2	C(38)–C(39)–H(39B)	111.2
C(40)–C(39)–H(39A)	111.2	C(38)–C(39)–H(39A)	111.2
H(39B)–C(39)–H(39A)	109.2	O(1)–C(40)–C(39)	105.81(16)
O(1)–C(40)–H(40B)	110.6	C(39)–C(40)–H(40B)	110.6
O(1)–C(40)–H(40A)	110.6	C(39)–C(40)–H(40A)	110.6
H(40B)–C(40)–H(40A)	108.7	C(44)–O(2)–C(41)	109.00(16)
C(44)–O(2)–Li(1)	122.36(17)	C(41)–O(2)–Li(1)	121.51(17)
O(2)–C(41)–C(42)	106.65(18)	O(2)–C(41)–H(41B)	110.4
C(42)–C(41)–H(41B)	110.4	O(2)–C(41)–H(41A)	110.4
C(42)–C(41)–H(41A)	110.4	H(41B)–C(41)–H(41A)	108.6
C(43)–C(42)–C(41)	102.16(18)	C(43)–C(42)–H(42A)	111.3
C(41)–C(42)–H(42A)	111.3	C(43)–C(42)–H(42B)	111.3

C(41)–C(42)–H(42B)	111.3	H(42A)–C(42)–H(42B)	109.2
C(44)–C(43)–C(42)	102.28(19)	C(44)–C(43)–H(43A)	111.3
C(42)–C(43)–H(43A)	111.3	C(44)–C(43)–H(43B)	111.3
C(42)–C(43)–H(43B)	111.3	H(43A)–C(43)–H(43B)	109.2
O(2)–C(44)–C(43)	104.77(18)	O(2)–C(44)–H(44A)	110.8
C(43)–C(44)–H(44A)	110.8	O(2)–C(44)–H(44B)	110.8
C(43)–C(44)–H(44B)	110.8	H(44A)–C(44)–H(44B)	108.9

Symmetry transformations used to generate equivalent atoms:

Table 24. Anisotropic displacement parameters ($Å^2$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li(1)	0.0259(18)	0.0318(19)	0.0394(19)	–0.0046(15)	0.0052(15)	–0.0034(15)
B(1)	0.0232(11)	0.0192(10)	0.0226(10)	–0.0019(8)	–0.0011(8)	–0.0019(8)
N(1)	0.0195(8)	0.0200(8)	0.0212(7)	–0.0025(6)	0.0023(6)	–0.0001(6)
N(2)	0.0195(8)	0.0192(7)	0.0202(7)	–0.0008(6)	0.0008(6)	–0.0016(6)
C(1)	0.0203(9)	0.0224(9)	0.0166(8)	–0.0015(7)	–0.0005(7)	0.0011(7)
C(2)	0.0258(10)	0.0193(9)	0.0230(9)	–0.0005(7)	0.0009(7)	–0.0022(7)
C(3)	0.0216(10)	0.0306(10)	0.0262(9)	–0.0001(8)	0.0041(7)	–0.0027(8)
C(4)	0.0234(10)	0.0276(10)	0.0254(9)	–0.0015(8)	0.0027(7)	0.0044(8)
C(5)	0.0245(10)	0.0190(9)	0.0232(9)	–0.0013(7)	–0.0008(7)	0.0023(7)
C(6)	0.0214(9)	0.0207(9)	0.0169(8)	0.0005(7)	–0.0021(7)	–0.0021(7)
C(7)	0.0184(9)	0.0187(9)	0.0224(9)	–0.0022(7)	0.0020(7)	–0.0015(7)
C(8)	0.0216(9)	0.0253(9)	0.0198(9)	–0.0017(7)	–0.0008(7)	–0.0002(7)
C(9)	0.0237(10)	0.0202(9)	0.0225(9)	0.0012(7)	–0.0008(7)	0.0019(7)
C(10)	0.0190(9)	0.0201(9)	0.0225(9)	–0.0030(7)	0.0002(7)	–0.0001(7)
C(11)	0.0191(9)	0.0223(9)	0.0212(9)	–0.0012(7)	–0.0015(7)	–0.0001(7)
C(12)	0.0167(9)	0.0216(9)	0.0226(9)	0.0004(7)	0.0010(7)	0.0002(7)
C(13)	0.0364(12)	0.0257(10)	0.0224(9)	–0.0065(8)	–0.0057(8)	0.0034(8)
C(14)	0.101(2)	0.0327(13)	0.0215(11)	0.0007(9)	–0.0072(12)	0.0002(13)
C(15)	0.0365(15)	0.115(3)	0.0433(15)	–0.0333(16)	–0.0134(12)	–0.0048(16)
C(16)	0.0272(10)	0.0161(8)	0.0234(9)	–0.0009(7)	–0.0029(7)	0.0015(7)
C(17)	0.0290(11)	0.0258(11)	0.0535(14)	–0.0113(10)	–0.0033(10)	0.0062(9)
C(18)	0.0328(11)	0.0219(10)	0.0345(11)	–0.0066(8)	–0.0076(9)	0.0002(8)
C(19)	0.0235(9)	0.0185(9)	0.0223(9)	0.0005(7)	–0.0018(7)	0.0013(7)
C(20)	0.0233(10)	0.0305(11)	0.0343(11)	0.0076(8)	–0.0005(8)	0.0024(8)
C(21)	0.0236(10)	0.0272(10)	0.0265(10)	0.0031(8)	–0.0003(8)	–0.0002(8)
C(22)	0.0183(9)	0.0172(8)	0.0215(8)	–0.0021(7)	0.0023(7)	0.0001(7)
C(23)	0.0198(9)	0.0241(9)	0.0205(9)	–0.0010(7)	–0.0010(7)	–0.0011(7)
C(24)	0.0234(10)	0.0202(9)	0.0229(9)	0.0022(7)	–0.0005(7)	0.0006(7)
C(25)	0.0216(9)	0.0174(8)	0.0243(9)	–0.0004(7)	0.0035(7)	–0.0011(7)
C(26)	0.0220(10)	0.0226(9)	0.0225(9)	–0.0016(7)	–0.0018(7)	–0.0011(7)
C(27)	0.0201(9)	0.0200(9)	0.0209(8)	–0.0002(7)	0.0003(7)	0.0007(7)
C(28)	0.0242(10)	0.0245(9)	0.0228(9)	0.0015(7)	–0.0047(7)	–0.0041(8)
C(29)	0.0356(12)	0.0394(12)	0.0259(10)	–0.0065(9)	–0.0044(9)	–0.0029(10)
C(30)	0.0283(11)	0.0345(11)	0.0315(10)	0.0054(9)	–0.0078(8)	–0.0030(9)
C(31)	0.0227(10)	0.0183(9)	0.0302(10)	0.0010(7)	0.0002(8)	–0.0035(7)
C(32)	0.0322(11)	0.0217(9)	0.0320(10)	–0.0003(8)	0.0031(8)	–0.0017(8)
C(33)	0.0439(13)	0.0247(10)	0.0325(11)	0.0032(8)	0.0059(9)	–0.0061(9)
C(34)	0.0233(10)	0.0193(9)	0.0226(9)	0.0008(7)	–0.0025(7)	–0.0005(7)
C(35)	0.0283(10)	0.0285(10)	0.0227(9)	0.0015(8)	–0.0007(8)	0.0018(8)
C(36)	0.0282(11)	0.0326(11)	0.0285(10)	0.0060(8)	0.0011(8)	0.0061(9)

O(1)	0.0315(8)	0.0321(8)	0.0324(8)	–0.0029(6)	0.0084(6)	0.0007(6)
C(37)	0.0305(11)	0.0371(12)	0.0308(11)	0.0002(9)	0.0069(9)	0.0020(9)
C(38)	0.0252(10)	0.0395(12)	0.0308(10)	–0.0082(9)	0.0029(8)	0.0005(9)
C(39)	0.0271(11)	0.0345(12)	0.0408(12)	–0.0051(9)	0.0007(9)	–0.0012(9)
C(40)	0.0238(10)	0.0330(11)	0.0340(11)	0.0035(9)	0.0008(8)	0.0025(8)
O(2)	0.0244(8)	0.0340(8)	0.0442(9)	–0.0010(7)	0.0024(6)	–0.0046(6)
C(41)	0.0270(11)	0.0391(13)	0.0509(14)	0.0095(10)	0.0010(10)	–0.0023(10)
C(42)	0.0344(13)	0.0367(13)	0.0577(15)	0.0099(11)	0.0016(11)	–0.0065(10)
C(43)	0.0380(13)	0.0413(13)	0.0322(11)	0.0012(9)	0.0015(9)	–0.0107(10)
C(44)	0.0269(11)	0.0426(13)	0.0333(11)	0.0004(9)	–0.0021(9)	–0.0008(9)

Table 25. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **4**.

	x	y	z	U(eq)
H(2)	0.3576	0.2834	0.1985	0.027
H(3)	0.5219	0.2302	0.1425	0.031
H(4)	0.5052	0.1329	0.1337	0.031
H(5)	0.3243	0.0856	0.1807	0.027
H(9)	0.0504	0.4193	0.2201	0.027
H(11)	0.1851	0.3722	0.4336	0.025
H(13)	0.0717	0.2839	0.1316	0.034
H(14A)	0.0369	0.3507	0.0336	0.078
H(14B)	0.1588	0.3701	0.0864	0.078
H(14C)	0.0219	0.3996	0.0968	0.078
H(15C)	–0.1542	0.3467	0.1672	0.098
H(15B)	–0.1323	0.2815	0.1859	0.098
H(15A)	–0.1479	0.3024	0.0973	0.098
H(16)	0.1226	0.4904	0.3088	0.027
H(17A)	–0.0907	0.4703	0.3428	0.054
H(17C)	–0.0332	0.5204	0.3956	0.054
H(17B)	–0.0436	0.4584	0.4310	0.054
H(18B)	0.1960	0.4627	0.4661	0.045
H(18C)	0.2027	0.5241	0.4285	0.045
H(18A)	0.2957	0.4755	0.3990	0.045
H(19)	0.2085	0.2249	0.3869	0.026
H(20A)	0.4084	0.2720	0.3926	0.044
H(20B)	0.3850	0.2411	0.4739	0.044
H(20C)	0.3643	0.3075	0.4664	0.044
H(21C)	0.1322	0.2942	0.5140	0.039
H(21B)	0.1598	0.2282	0.5203	0.039
H(21A)	0.0397	0.2506	0.4684	0.039
H(24)	0.1118	–0.0314	0.3551	0.027
H(26)	–0.1144	–0.0057	0.1627	0.027
H(28)	0.2734	0.0995	0.3511	0.029
H(29A)	0.0892	0.1282	0.4191	0.051
H(29C)	0.2063	0.1149	0.4792	0.051
H(29B)	0.0918	0.0705	0.4671	0.051
H(30B)	0.2584	–0.0014	0.4413	0.047
H(30C)	0.3754	0.0424	0.4432	0.047
H(30A)	0.3485	0.0042	0.3676	0.047
H(31)	–0.1504	–0.0885	0.2433	0.029
H(32A)	0.0045	–0.1070	0.1501	0.043
H(32C)	–0.0157	–0.1620	0.2020	0.043
H(32B)	0.1084	–0.1232	0.2173	0.043

H(33A)	0.0406	–0.1197	0.3589	0.050
H(33B)	–0.0893	–0.1536	0.3386	0.050
H(33C)	–0.0960	–0.0931	0.3790	0.050
H(34)	–0.0079	0.1363	0.1298	0.026
H(35B)	0.0691	0.0670	0.0453	0.040
H(35C)	–0.0541	0.0969	0.0050	0.040
H(35A)	–0.0678	0.0360	0.0436	0.040
H(36B)	–0.2262	0.1370	0.0866	0.045
H(36C)	–0.2170	0.1314	0.1797	0.045
H(36A)	–0.2487	0.0773	0.1269	0.045
H(37B)	–0.2060	0.2370	0.5097	0.039
H(37A)	–0.3474	0.2284	0.4705	0.039
H(38B)	–0.2973	0.3176	0.5520	0.038
H(38A)	–0.3950	0.3215	0.4771	0.038
H(39B)	–0.2395	0.3859	0.4420	0.041
H(39A)	–0.1243	0.3493	0.4820	0.041
H(40B)	–0.2563	0.3286	0.3362	0.036
H(40A)	–0.1052	0.3200	0.3564	0.036
H(41B)	–0.1839	0.0726	0.4427	0.047
H(41A)	–0.1351	0.0682	0.3547	0.047
H(42A)	–0.2874	0.0005	0.3432	0.052
H(42B)	–0.3696	0.0259	0.4134	0.052
H(43A)	–0.3664	0.0667	0.2550	0.045
H(43B)	–0.4921	0.0561	0.3060	0.045
H(44A)	–0.4072	0.1561	0.2985	0.041
H(44B)	–0.4527	0.1339	0.3821	0.041

Table 26. Crystal data and structure refinement for **5**.

Identification code	**5**	
Chemical formula	$C_{36}H_{51}BN_2$	
Formula weight	522.60	
Temperature	90(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	orthorhombic, Pnma	
Unit cell parameters	a = 12.866(2) Å	α = 90°
	b = 14.546(3) Å	β = 90°
	c = 17.544(3) Å	γ = 90°
Cell volume	3283.2(11) Å^3	
Z	4	
Calculated density	1.057 g/cm^3	
Absorption coefficient μ	0.060 mm^{-1}	
F(000)	1144	
Crystal colour and size	COLOURLESS, 0.17 × 0.07 × 0.05 mm^3	
Reflections for cell refinement	1167 (θ range 2.32 to 25.87°)	
Data collection method	Bruker SMART APEX CCD diffractometer	
	ω rotation with narrow frames	
θ range for data collection	1.96 to 25.00°	
Index ranges	h –15 to 9, k –17 to 16, l –10 to 20	
Completeness to θ = 25.00°	99.8 %	
Intensity decay	0%	
Reflections collected	11131	
Independent reflections	3005 (R_{int} = 0.062)	
Reflections with $F^2>2\sigma$	1715	
Absorption correction	semi-empirical from equivalents	

Min. and max. transmission	0.651 and 0.746
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.118, 2.590
Data / restraints / parameters	3005 / 243 / 214
Final R indices [$F^2>2\sigma$]	R1 = 0.0842, wR2 = 0.214
R indices (all data)	R1 = 0.145, wR2 = 0.257
Goodness-of-fit on F^2	1.03
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	0.56 and –0.60 e $Å^{-3}$

Table 27. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	0.3670(5)	0.2500	0.3692(3)	0.0408(13)
N(1)	0.4581(3)	0.2500	0.32364(19)	0.0365(9)
N(2)	0.4006(3)	0.2500	0.4465(2)	0.0396(10)
C(1)	0.5448(4)	0.2500	0.3713(2)	0.0390(11)
C(2)	0.6490(4)	0.2500	0.3551(3)	0.0481(13)
C(3)	0.7181(5)	0.2500	0.4147(3)	0.0715(17)
C(4)	0.6829(5)	0.2500	0.4886(3)	0.086(2)
C(5)	0.5779(5)	0.2500	0.5070(3)	0.0706(17)
C(6)	0.5089(4)	0.2500	0.4471(3)	0.0451(12)
C(7)	0.4739(4)	0.2500	0.2422(2)	0.0403(12)
C(8)	0.4832(3)	0.1661(2)	0.20418(18)	0.0434(9)
C(9)	0.5002(3)	0.1689(3)	0.12545(19)	0.0484(10)
C(10)	0.5085(4)	0.2500	0.0848(3)	0.0467(13)
C(11)	0.4736(3)	0.0762(2)	0.2460(2)	0.0531(10)
C(12)	0.5467(4)	0.0020(3)	0.2167(3)	0.0748(14)
C(13)	0.3614(4)	0.0440(3)	0.2449(3)	0.0831(15)
C(14)	0.5275(5)	0.2500	–0.0011(3)	0.0554(14)
C(15)	0.4848(4)	0.1651(3)	–0.0399(2)	0.0667(13)
C(16)	0.3442(4)	0.2500	0.5175(3)	0.0473(13)
C(17)	0.3207(3)	0.1660(3)	0.5523(2)	0.0552(10)
C(18)	0.2744(3)	0.1697(4)	0.6242(2)	0.0729(14)
C(19)	0.2515(5)	0.2500	0.6614(3)	0.082(2)
C(20)	0.3437(3)	0.0759(3)	0.5145(2)	0.0625(11)
C(21)	0.3944(4)	0.0064(4)	0.5692(3)	0.0903(17)
C(22)	0.2457(4)	0.0355(4)	0.4796(3)	0.0835(15)
C(23)	0.2096(6)	0.2500	0.7425(4)	0.103(2)
C(24)	0.1009(5)	0.2500	0.7478(3)	0.0721(18)
C(25)	0.2780(6)	0.2150(8)	0.7981(4)	0.092(4)

Table 28. Bond lengths [Å] and angles [°] for **5**.

B(1)–N(1)	1.418(7)	B(1)–N(2)	1.424(6)
B(1)–H(1B)	1.12(5)	N(1)–C(1)	1.394(6)
N(1)–C(7)	1.443(5)	N(2)–C(6)	1.393(6)
N(2)–C(16)	1.442(6)	C(1)–C(2)	1.370(7)
C(1)–C(6)	1.407(6)	C(2)–C(3)	1.374(8)
C(2)–H(2A)	0.9500	C(3)–C(4)	1.373(8)
C(3)–H(3A)	0.9500	C(4)–C(5)	1.388(9)
C(4)–H(4A)	0.9500	C(5)–C(6)	1.376(7)
C(5)–H(5A)	0.9500	C(7)–C(8)	1.396(4)
C(8)–C(9)	1.399(5)	C(8)–C(11)	1.505(5)

C(9)–C(10)	1.383(4)	C(9)–H(9A)	0.9500
C(10)–C(14)	1.526(7)	C(11)–C(13)	1.517(6)
C(11)–C(12)	1.522(6)	C(11)–H(11A)	1.0000
C(12)–H(12A)	0.9800	C(12)–H(12B)	0.9800
C(12)–H(12C)	0.9800	C(13)–H(13A)	0.9800
C(13)–H(13B)	0.9800	C(13)–H(13C)	0.9800
C(14)–C(15)	1.513(5)	C(14)–H(14A)	1.0000
C(15)–H(15A)	0.9800	C(15)–H(15B)	0.9800
C(15)–H(15C)	0.9800	C(16)–C(17)	1.399(5)
C(17)–C(18)	1.396(5)	C(17)–C(20)	1.498(6)
C(18)–C(19)	1.370(6)	C(18)–H(18A)	0.9500
C(19)–C(23)	1.520(8)	C(20)–C(22)	1.520(6)
C(20)–C(21)	1.540(6)	C(20)–H(20A)	1.0000
C(21)–H(21A)	0.9800	C(21)–H(21B)	0.9800
C(21)–H(21C)	0.9800	C(22)–H(22A)	0.9800
C(22)–H(22B)	0.9800	C(22)–H(22C)	0.9800
C(23)–C(24)	1.402(9)	C(23)–C(25)	1.409(9)
C(23)–H(25F)	0.9175	C(24)–H(24A)	0.9800
C(24)–H(24B)	0.9800	C(24)–H(24C)	0.9800
C(25)–H(25A)	0.9800	C(25)–H(25B)	0.9800
C(25)–H(25C)	0.9800		

N(1)–B(1)–N(2)	106.6(5)	N(1)–B(1)–H(1B)	122(2)
N(2)–B(1)–H(1B)	132(2)	C(1)–N(1)–B(1)	108.9(4)
C(1)–N(1)–C(7)	118.8(4)	B(1)–N(1)–C(7)	132.4(4)
C(6)–N(2)–B(1)	108.1(4)	C(6)–N(2)–C(16)	119.8(4)
B(1)–N(2)–C(16)	132.1(5)	C(2)–C(1)–N(1)	131.1(4)
C(2)–C(1)–C(6)	121.2(5)	N(1)–C(1)–C(6)	107.7(4)
C(1)–C(2)–C(3)	118.4(5)	C(1)–C(2)–H(2A)	120.8
C(3)–C(2)–H(2A)	120.8	C(4)–C(3)–C(2)	120.4(6)
C(4)–C(3)–H(3A)	119.8	C(2)–C(3)–H(3A)	119.8
C(3)–C(4)–C(5)	122.7(6)	C(3)–C(4)–H(4A)	118.6
C(5)–C(4)–H(4A)	118.6	C(6)–C(5)–C(4)	116.8(5)
C(6)–C(5)–H(5A)	121.6	C(4)–C(5)–H(5A)	121.6
C(5)–C(6)–N(2)	130.7(5)	C(5)–C(6)–C(1)	120.6(5)
N(2)–C(6)–C(1)	108.7(4)	C(8)#1–C(7)–C(8)	121.9(4)
C(8)#1–C(7)–N(1)	119.0(2)	C(8)–C(7)–N(1)	119.0(2)
C(7)–C(8)–C(9)	117.4(3)	C(7)–C(8)–C(11)	121.3(3)
C(9)–C(8)–C(11)	121.3(3)	C(10)–C(9)–C(8)	123.1(3)
C(10)–C(9)–H(9A)	118.5	C(8)–C(9)–H(9A)	118.5
C(9)#1–C(10)–C(9)	117.1(4)	C(9)#1–C(10)–C(14)	121.4(2)
C(9)–C(10)–C(14)	121.4(2)	C(8)–C(11)–C(13)	109.9(3)
C(8)–C(11)–C(12)	113.6(3)	C(13)–C(11)–C(12)	111.3(4)
C(8)–C(11)–H(11A)	107.2	C(13)–C(11)–H(11A)	107.2
C(12)–C(11)–H(11A)	107.2	C(11)–C(12)–H(12A)	109.5
C(11)–C(12)–H(12B)	109.5	H(12A)–C(12)–H(12B)	109.5
C(11)–C(12)–H(12C)	109.5	H(12A)–C(12)–H(12C)	109.5
H(12B)–C(12)–H(12C)	109.5	C(11)–C(13)–H(13A)	109.5
C(11)–C(13)–H(13B)	109.5	H(13A)–C(13)–H(13B)	109.5
C(11)–C(13)–H(13C)	109.5	H(13A)–C(13)–H(13C)	109.5
H(13B)–C(13)–H(13C)	109.5	C(15)#1–C(14)–C(15)	109.3(5)
C(15)#1–C(14)–C(10)	112.7(3)	C(15)–C(14)–C(10)	112.7(3)
C(15)#1–C(14)–H(14A)	107.3	C(15)–C(14)–H(14A)	107.3
C(10)–C(14)–H(14A)	107.3	C(14)–C(15)–H(15A)	109.5
C(14)–C(15)–H(15B)	109.5	H(15A)–C(15)–H(15B)	109.5
C(14)–C(15)–H(15C)	109.5	H(15A)–C(15)–H(15C)	109.5
H(15B)–C(15)–H(15C)	109.5	C(17)#1–C(16)–C(17)	121.8(5)

C(17)#1–C(16)–N(2)	119.0(2)	C(17)–C(16)–N(2)	119.0(2)
C(18)–C(17)–C(16)	116.9(4)	C(18)–C(17)–C(20)	121.2(4)
C(16)–C(17)–C(20)	121.9(3)	C(19)–C(18)–C(17)	123.7(5)
C(19)–C(18)–H(18A)	118.1	C(17)–C(18)–H(18A)	118.1
C(18)#1–C(19)–C(18)	116.9(6)	C(18)#1–C(19)–C(23)	121.5(3)
C(18)–C(19)–C(23)	121.5(3)	C(17)–C(20)–C(22)	110.7(4)
C(17)–C(20)–C(21)	112.4(4)	C(22)–C(20)–C(21)	110.4(4)
C(17)–C(20)–H(20A)	107.7	C(22)–C(20)–H(20A)	107.7
C(21)–C(20)–H(20A)	107.7	C(20)–C(21)–H(21A)	109.5
C(20)–C(21)–H(21B)	109.5	H(21A)–C(21)–H(21B)	109.5
C(20)–C(21)–H(21C)	109.5	H(21A)–C(21)–H(21C)	109.5
H(21B)–C(21)–H(21C)	109.5	C(20)–C(22)–H(22A)	109.5
C(20)–C(22)–H(22B)	109.5	H(22A)–C(22)–H(22B)	109.5
C(20)–C(22)–H(22C)	109.5	H(22A)–C(22)–H(22C)	109.5
H(22B)–C(22)–H(22C)	109.5	C(24)–C(23)–C(25)#1	125.2(6)
C(24)–C(23)–C(25)	125.2(6)	C(24)–C(23)–C(19)	114.6(6)
C(25)#1–C(23)–C(19)	115.3(6)	C(25)–C(23)–C(19)	115.3(6)
C(24)–C(23)–H(25F)	108.7	C(19)–C(23)–H(25F)	98.1
C(23)–C(24)–H(24A)	109.5	C(23)–C(24)–H(24B)	109.5
H(24A)–C(24)–H(24B)	109.5	C(23)–C(24)–H(24C)	109.5
H(24A)–C(24)–H(24C)	109.5	H(24B)–C(24)–H(24C)	109.5
C(23)–C(25)–H(25A)	109.5	C(23)–C(25)–H(25B)	109.5
H(25A)–C(25)–H(25B)	109.5	C(23)–C(25)–H(25C)	109.5
H(25A)–C(25)–H(25C)	109.5	H(25B)–C(25)–H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z

Table 29. Anisotropic displacement parameters ($Å^2$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	0.061(3)	0.031(3)	0.031(2)	0.000	0.001(2)	0.000
N(1)	0.055(2)	0.030(2)	0.0249(17)	0.000	–0.0027(16)	0.000
N(2)	0.053(2)	0.041(2)	0.0250(18)	0.000	0.0036(17)	0.000
C(1)	0.059(3)	0.032(2)	0.026(2)	0.000	0.000(2)	0.000
C(2)	0.056(3)	0.056(3)	0.032(2)	0.000	0.006(2)	0.000
C(3)	0.058(3)	0.109(5)	0.048(3)	0.000	0.002(3)	0.000
C(4)	0.061(3)	0.154(6)	0.043(3)	0.000	–0.010(3)	0.000
C(5)	0.062(3)	0.121(5)	0.029(2)	0.000	–0.003(2)	0.000
C(6)	0.054(3)	0.053(3)	0.028(2)	0.000	–0.001(2)	0.000
C(7)	0.062(3)	0.036(2)	0.0226(19)	0.000	–0.001(2)	0.000
C(8)	0.065(2)	0.0361(19)	0.0289(15)	–0.0019(14)	–0.0037(15)	–0.0014(17)
C(9)	0.072(3)	0.041(2)	0.0320(16)	–0.0072(15)	–0.0016(16)	–0.0007(19)
C(10)	0.059(3)	0.052(3)	0.030(2)	0.000	–0.001(2)	0.000
C(11)	0.091(3)	0.0314(18)	0.0371(17)	–0.0029(15)	–0.0011(18)	–0.0048(19)
C(12)	0.124(4)	0.033(2)	0.068(3)	–0.002(2)	0.005(3)	0.009(2)
C(13)	0.108(4)	0.058(3)	0.083(3)	0.013(3)	0.005(3)	–0.025(3)
C(14)	0.068(4)	0.066(3)	0.033(2)	0.000	0.001(2)	0.000
C(15)	0.101(3)	0.070(3)	0.0289(18)	–0.0062(18)	0.001(2)	0.001(3)
C(16)	0.054(3)	0.062(3)	0.027(2)	0.000	0.001(2)	0.000
C(17)	0.054(2)	0.074(3)	0.0381(18)	0.0167(18)	0.0016(16)	0.005(2)
C(18)	0.064(3)	0.118(4)	0.037(2)	0.025(2)	0.0046(19)	–0.001(3)
C(19)	0.063(4)	0.151(6)	0.032(3)	0.000	0.006(3)	0.000
C(20)	0.062(2)	0.062(2)	0.064(2)	0.031(2)	0.010(2)	0.010(2)

C(21)	0.081(3)	0.096(4)	0.093(3)	0.060(3)	0.017(3)	0.018(3)
C(22)	0.077(3)	0.066(3)	0.107(4)	0.006(3)	0.000(3)	0.008(3)
C(23)	0.075(4)	0.193(6)	0.041(3)	0.000	0.009(3)	0.000
C(24)	0.067(4)	0.122(5)	0.027(3)	0.000	0.002(3)	0.000
C(25)	0.074(5)	0.178(10)	0.024(3)	–0.001(4)	0.002(3)	0.015(5)

Table 30. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **5**.

	x	y	z	U(eq)
H(1B)	0.287(4)	0.2500	0.343(3)	0.049
H(2A)	0.6728	0.2500	0.3038	0.058
H(3A)	0.7907	0.2500	0.4048	0.086
H(4A)	0.7324	0.2500	0.5288	0.103
H(5A)	0.5549	0.2500	0.5584	0.085
H(9A)	0.5063	0.1124	0.0987	0.058
H(11A)	0.4924	0.0881	0.3004	0.064
H(12A)	0.6176	0.0264	0.2140	0.112
H(12B)	0.5245	–0.0175	0.1657	0.112
H(12C)	0.5451	–0.0508	0.2513	0.112
H(13A)	0.3165	0.0924	0.2654	0.125
H(13B)	0.3545	–0.0115	0.2762	0.125
H(13C)	0.3408	0.0301	0.1924	0.125
H(14A)	0.6045	0.2500	–0.0091	0.067
H(15A)	0.4944	0.1706	–0.0951	0.100
H(15B)	0.4105	0.1593	–0.0284	0.100
H(15C)	0.5217	0.1107	–0.0212	0.100
H(18A)	0.2578	0.1133	0.6487	0.088
H(20A)	0.3939	0.0879	0.4721	0.075
H(21A)	0.4589	0.0325	0.5897	0.136
H(21B)	0.4101	–0.0505	0.5416	0.136
H(21C)	0.3466	–0.0069	0.6113	0.136
H(22A)	0.2203	0.0762	0.4392	0.125
H(22B)	0.1922	0.0293	0.5191	0.125
H(22C)	0.2613	–0.0252	0.4581	0.125
H(24A)	0.0740	0.3099	0.7315	0.108
H(24B)	0.0803	0.2385	0.8007	0.108
H(24C)	0.0725	0.2017	0.7149	0.108
H(25A)	0.2431	0.2143	0.8478	0.138
H(25B)	0.3399	0.2540	0.8010	0.138
H(25C)	0.2985	0.1523	0.7843	0.138
H(25F)	0.2339	0.3066	0.7571	0.138

DFT Calculations

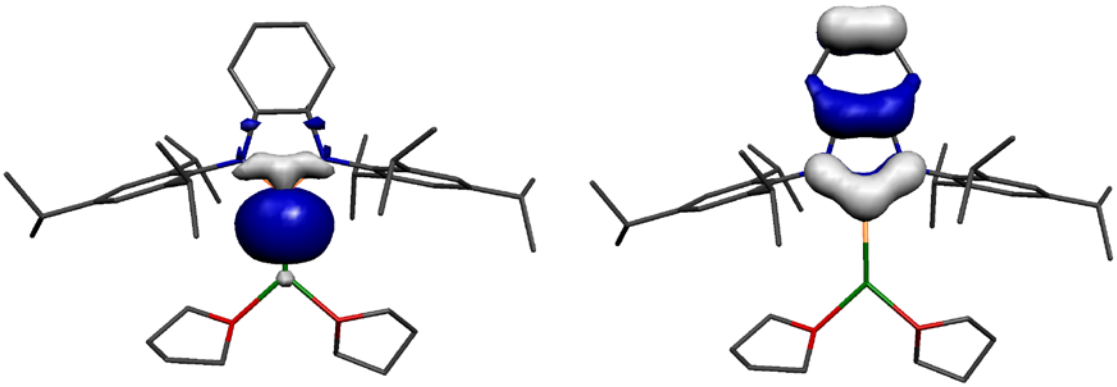
General

Restricted geometry optimisations were performed for the full model of **4** using coordinates derived from the experimental X-ray crystal structure. No constraints were imposed on the structure during the geometry optimisation. Calculations were performed using the Amsterdam Density Functional (ADF) suite version 2009.01.[1,2] Slater type orbital (STO) triple-ζ-plus polarisation all-electron basis sets (from the ZORA/TZP database of the ADF suite) were employed. Scalar relativistic approaches were used within the ZORA Hamiltonian for the inclusion of relativistic effects and the local density approximation (LDA) with the correlation potential due to Vosko et al.[3] was used in all of the calculations. Gradient corrections were performed using the functionals of Becke[4] and Perdew.[5] MOLEKEL[6] was used to prepare the three-dimensional plot of the electron density. The Atoms in Molecules analysis[7,8] for **4** was carried out with Xaim-1.0.[9]

The Mulliken charges on boron and lithium were calculated to be –0.26 and +0.59. The Nalewajski-Mrozek bond indices for the Li-B and Li-O bonds were computed to be 0.41 and 0.09 (av.), which reflects the highly polarised-covalent and dative bonding, respectively; the corresponding B-N indices were calculated to be 1.32 (av.), which suggests some π-donation from the amine lone pairs into the formally vacant boron 2p-orbital and these bonding features are confirmed by visual inspection of the HOMO and HOMO–1 Kohn Sham molecular orbitals, Figure S7. The HOMO orbital is a sp hybrid boron lone pair (70.5%) with a smaller contribution from lithium (19.7%) and this represents the principal bonding interaction between boron and lithium. We employed Bader's Atoms in Molecules to analyse the topological electron density [$\rho(\mathbf{r})$] in the B-Li bond in **4**. For closed–shell interactions the Laplacian of the electron density [$\nabla^2\rho(\mathbf{r})$] is typically positive. The electronic energy density $H(\mathbf{r})$ of the charge distribution is defined as $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$ where $G(\mathbf{r})$ is the kinetic energy density and $V(\mathbf{r})$ is the potential energy. For **4**, the B-Li bond critical point (BCP) values for $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, $G(\mathbf{r})$, $V(\mathbf{r})$, and $H(\mathbf{r})$ are 0.02723, 0.0748, 0.01992, –0.02114, and –

0.00122, respectively. These BCP values are typical of a predominantly closed shell, ionic B-Li interaction.

Figure S7. Kohn Sham Orbitals for 4



(a) (b)

(a) HOMO (184a, –3.190 eV) and (b) HOMO–1 (183a, –4.089 eV).

Final Calculated Coordinates and Energy for 4

1.H	-1.376944	2.499796	-5.195381
2.H	-2.922446	1.637043	-5.155250
3.C	-2.199716	2.189206	-4.534885
4.H	-0.219105	0.290987	-4.668046
5.H	-2.695679	3.095918	-4.160957
6.H	-1.744962	-0.597242	-4.421140
7.C	-0.996842	0.044608	-3.928454
8.H	-4.294957	0.757974	-3.748732
9.H	-5.833312	-1.661039	-3.432189
10.C	-1.651354	1.329634	-3.384038
11.H	-7.576446	-1.589435	-3.067735
12.H	-6.590436	0.696286	-3.130327
13.H	3.302091	-0.323951	-3.383179
14.H	-0.528448	-0.523636	-3.111596
15.H	4.162147	2.050917	-3.133593
16.H	-0.862900	1.908139	-2.883869
17.C	-6.571222	-1.396192	-2.662122
18.C	-4.017055	0.707989	-2.693161
19.H	-2.301422	-3.328544	-2.579129
20.C	-6.425306	0.077575	-2.232495
21.C	-2.696689	0.995806	-2.323448
22.C	3.434509	-0.493239	-2.303621
23.H	4.421794	-0.959237	-2.155896
24.C	4.335407	1.862913	-2.063248
25.H	-6.416661	-2.064599	-1.801183
26.H	-8.510372	0.323598	-1.653433
27.H	5.371353	1.506310	-1.951259
28.H	2.660519	-1.199216	-1.970056

29.H	-4.474220	-4.031459	-1.740405
30.C	-5.006841	0.379361	-1.757288
31.H	4.246462	2.819894	-1.531271
32.H	2.313311	1.228247	-1.707874
33.H	1.805992	-3.976342	-1.661970
34.C	-7.511121	0.449117	-1.211828
35.C	3.321416	0.832383	-1.531600
36.C	-2.540137	-3.020559	-1.547822
37.H	-2.804870	-5.778307	-1.252323
38.H	-2.679061	-1.932148	-1.515050
39.H	-7.410676	1.490988	-0.877913
40.C	-3.713209	-3.814329	-0.979940
41.H	3.979806	-3.195713	-0.884096
42.H	-2.318829	3.794460	-0.874013
43.C	-2.351756	0.944362	-0.951593
44.H	4.190498	-4.959473	-0.701063
45.H	-7.465775	-0.196806	-0.322108
46.C	2.110739	-4.261171	-0.645467
47.O	-1.391099	-3.353970	-0.698118
48.C	-3.021446	-5.074210	-0.434530
49.H	1.783421	-5.299597	-0.455239
50.C	-1.303326	3.780962	-0.475600
51.N	-1.016806	1.245127	-0.533508
52.C	3.602190	-4.092083	-0.372271
53.C	-4.636322	0.336293	-0.410638
54.H	-1.159175	5.925537	-0.271769
55.H	-4.190491	-3.251308	-0.164509
56.C	-0.628619	2.570964	-0.290712
57.C	-0.646108	4.973191	-0.134098
58.H	5.519558	0.016022	-0.162224
59.Li	0.036692	-2.025664	-0.235883
60.B	0.043543	0.278542	-0.155295
61.H	-0.877726	-5.201363	0.109200
62.C	-3.328921	0.619943	0.015945
63.C	3.457984	0.630205	-0.026525
64.H	-3.613009	-5.601814	0.325601
65.C	-1.724561	-4.502998	0.137422
66.H	-5.387048	0.098404	0.345714
67.C	0.686555	2.551130	0.233356
68.O	1.441005	-3.371193	0.289172
69.C	0.658329	4.953340	0.382077
70.N	1.093894	1.213301	0.323852
71.C	4.684176	0.217479	0.514419
72.H	1.151529	5.890341	0.643577
73.C	1.338925	3.740547	0.570275
74.C	2.377160	0.866621	0.852159
75.H	2.351037	3.722005	0.977949
76.C	3.622209	-3.886898	1.151572
77.H	-1.862649	-4.156158	1.175287
78.H	7.292782	1.347171	1.458414
79.H	4.519407	-3.359172	1.499448
80.C	2.356664	-3.060718	1.397177

81.H	3.567830	-4.856172	1.670211
82.H	2.553681	-1.979462	1.373502
83.C	-3.007902	0.591050	1.506417
84.H	6.674532	-1.058577	1.688757
85.H	-2.642887	-1.559796	1.590164
86.H	-1.938111	0.812066	1.606988
87.C	4.884821	0.067362	1.891306
88.H	-3.582472	2.670878	1.883073
89.H	-4.303565	-1.098594	2.048714
90.C	-3.244790	-0.802672	2.113314
91.C	7.215954	0.873763	2.446651
92.H	-4.874721	1.495761	2.231801
93.C	6.260932	-0.337384	2.414605
94.H	8.225612	0.568725	2.762874
95.C	-3.788155	1.668547	2.282953
96.H	1.847640	-3.316136	2.337351
97.C	2.556454	0.754636	2.250864
98.H	0.201018	-0.659217	2.535992
99.H	6.849552	1.633159	3.154369
100.C	3.808759	0.353550	2.739380
101.H	0.737936	1.747345	2.719863
102.H	-2.958745	-0.813288	3.176097
103.H	-3.496556	1.659360	3.344425
104.C	1.405582	1.029408	3.216613
105.C	0.585146	-0.247372	3.481769
106.C	6.230698	-1.028641	3.785435
107.H	5.538807	-1.882640	3.797641
108.H	7.232912	-1.395664	4.049645
109.H	3.940510	0.261632	3.817555
110.H	1.202111	-1.013375	3.978394
111.H	-0.271615	-0.023832	4.136118
112.H	5.920578	-0.333030	4.579266
113.H	2.481196	2.551101	4.380303
114.C	1.855818	1.662104	4.543911
115.H	2.424974	0.953887	5.166180
116.H	0.975481	1.968374	5.127500

Final Energy: –668.78537685 eV

References

1. C. Fonseca-Guerra, J. G. Snijders, G. te Velde E. J. Baerends, *Theor. Chem. Acc.* **1998,** *99*, 391.
2. G. Te Velde, F. M. Bickelhaupt, S. J. A. Van Gisbergen, C. Fonseca-Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.
3. S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.
4. A. D. Becke, *Phys. Rev. A.* **1988**, *38*, 3098.
5. J. P. Perdew, *Phys. Rev. B.* **1986**, *33*, 8822.
6. S. Portmann H. P. Luthi, *Chimia* **2000**, *54*, 766.
7. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, New York, 1990.
8. R. F. W. Bader, *J. Phys. Chem. A.*, **1998**, *102*, 7314.
9. http://www.quimica.urv.es/XAIM.