Electronic Supplementary Material (ESI) for Chemical Communications


**Supplementary Information for**

# Magnesium-catalysed hydroboration of aldehydes and ketones

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## General Experimental Procedures

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. NMR spectra were collected at 298 K on a Bruker AV300 spectrometer operating at 75.5 MHz ($^{13}$C), 96.3 MHz ($^{11}$B). The spectra were referenced relative to residual solvent resonances or an external $BF_3.OEt_2$ standard ($^{11}$B). Solvents (Toluene, hexane) were dried by passage through a commercially available (Innovative Technologies) solvent purification system, under nitrogen and stored in ampoules over molecular sieves. $C_6D_6$ and $d_8$-toluene were purchased from Fluorochem Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. Di-n-butylmagnesium (1.0 M solution in n-heptane), pinacolborane (HBpin), aldehydes and ketones were purchased from Sigma-Aldrich Ltd. and used without further purification. [LMg$^n$Bu] (L = HC{(Me)CN(2,6-$^i$Pr$_2$C$_6$H$_3$)}$_2$) was synthesised by a literature procedures.[1]

### Stoichiometric reactions

*Reaction of **1** with 1 equivalent of HBpin.*

In a Youngs tap NMR tube HBpin (14.54 μL, 0.1 mmol) was added to a solution of **1** (50 mg, 0.1 mmol) in $C_6D_6$. The resulting $^{11}$B NMR spectrum showed complete consumption of HBpin after 10 minutes at room temperature and the appearance of a sharp singlet at 37.5 ppm attributable to the formation of $^n$BuBpin. $^1$H NMR data confirmed the formation of [LMgH]$_2$ as the major product (~75%) along with other ill-defined species deemed to contain the loosely bound borate anions [H$_2$Bpin]$^-$ and [H$^n$BuBpin]$^-$. $^1$H NMR data for [LMgH]$_2$ ($C_6D_6$, 300 MHz): 7.01-7.18 (m, 6H, Ar-*H*), 4.84 (s, 1H, NCMeC*H*), 4.03 (s, 1H, Mg-*H*), 3.06 (sept, 4H, $^i$Pr-C*H*, $^3J$ = 6.8 Hz), 1.50 (s, 6H, NCC*H*$_3$), 1.12, 0.97 (two d, 12H each, $^i$Pr-C*H*$_3$, $^3J$ = 6.8 Hz). Lit: $^1$H NMR ($C_6D_6$, 400 MHz): 6.96-7.15 (m, 6H, Ar-*H*), 4.84 (s, 1H, NCMeC*H*), 4.03 (s, 1H, Mg-*H*), 3.05 (sept, 4H, $^i$Pr-C*H*, $^3J$ = 6.9 Hz), 1.49 (s, 6H, NCC*H*$_3$), 1.12, 0.97 (two d, 12H each, $^i$Pr-C*H*$_3$, $^3J$ = 6.9 Hz). NMR data for the [$^n$BuBpin] by-product: $^1$H NMR ($C_6D_6$, 300 MHz): 0.90-1.62 (m, 9H, $^n$Bu-*H*), 1.04 (s, 12H, pin-*H*). $^{13}$C NMR ($C_6D_6$, 75 MHz): 82.7 (O*C*), 26.8, 25.8, 24.7, 14.2 ($^n$Bu-*C*), 24.6 (OC*C*H$_3$). $^{11}$B NMR ($C_6D_6$, 96 MHz): 37.5 (s).

*Reaction of **1** with 1 equivalent of HBpin and benzophenone.*

Addition of one equivalent of benzophenone (18.3 mg, 0.1 mmol) to a solution of **1** (50 mg, 0.1 mmol) and HBpin (14.54 μL, 0.1 mmol) in $C_6D_6$ resulted in disappearance of the Mg-hydride singlet at 4.03 ppm accompanied by full conversion to [LMgOCHPh$_2$]$_2$, **3**, after 8 hours at room temperature, as identified by $^1$H NMR. **3** was also synthesised independently by reduction of benzophenone with [LMg(pyrH)(pyr)][2] (obtained by reaction of [LMgH] with two equivalents of pyridine; pyrH = 4-dihydropyridide). $^1$H NMR ($C_6D_6$, 300 MHz): 7.80 (dm, 4H, *o*-Ph-*H*, $^3J$ = 8.2 Hz), 7.46-7.48 (m, 4H, Ar-*H*), 6.91-7.33 (m, 8H, Ph/Ar-*H*), 6.06 (s, 1H, Ph$_2$C*H*OMg), 5.06 (s, 1H, *H*C(CMeNAr)$_2$), 3.44, 3.33, 2.76, 2.68 (four sept., 1H each,

$^{i}$Pr-C*H*, $^{3}J$ = 6.8 Hz), 1.72 (s, 6H, NCC*H*$_3$), 1.08, 1.05, 0.92, 0.89 (four d, 6H each, $^{i}$Pr-C*H*$_3$, $^{3}J$ = 6.8 Hz). $^{13}$C NMR ($C_6D_6$, 75 MHz): 169.0 (N*C*Me), 145.6 (*i*-Ar-*C*), 142.4 (*i*-Ph-*C*, *o*-Ar-*C*), 127.6 (*o*/*m*-Ph-*C*), 125.3, 125.2, (*p*-Ar/Ph-*C*), 124.8 (*m*-Ar-*C*), 93.8 (NCMe*C*H), 78.2 (O*C*HPh$_2$), 28.6 ($^{i}$Pr-*C*H), 24.4, 24.1 ($^{i}$Pr-*C*H$_3$). Elemental analysis calc. for $C_{42}H_{52}MgN_2O$: C, 80.69; H, 8.38; N, 4.48%. Found: C, 80.86; H, 8.40; N, 4.53%.

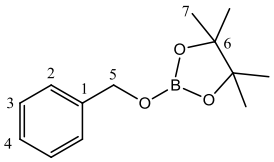
*Reaction of **3** with one equivalent of benzophenone and HBpin.*

Addition of a further equivalent of HBpin (14.54 μL, 0.1 mmol) and benzaldehyde (18.3 mg, 0.1 mmol) to a solution of **3** (0.1 mmol) in $C_6D_6$ yielded colourless crystals of **4** suitable for X-ray crystallography after one day at room temperature. $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.50 (dm, 4H, *o*-Ph-*H*, $^{3}J$ = 8.2 Hz), 7.32-7.34 (m, 4H, Ar-*H*), 7.02-7.21 (m, 18H, Ph/Ar-*H*), 6.50 (s, 1H, C*H*OBpin), 6.03 (s, 1H, C*H*OMg), 5.01 (s, 1H, *H*C(CMeNAr)$_2$), 3.19-3.52 (m, 4H, $^{i}$Pr-C*H*), 1.11 (s, 6H, NCC*H*$_3$), 1.10 (d, 12H, $^{i}$Pr-C*H*$_3$, $^{3}J$ = 7.2 Hz), 1.03 (s, 12H, pin-C*H*$_3$), 0.97, 0.95 (two d, 6H each, $^{i}$Pr-C*H*$_3$, $^{3}J$ = 7.2 Hz). $^{13}$C NMR ($C_6D_6$, 75 MHz): 170.3 (ArN*C*Me), 144.3 (*i*-Ar-*C*), 140.4 (*o*-Ar-*C*), 147.4, 130.0, 129.4, 128.1 (broad, *Ph*$_2$CHOB), 143.9, 128.5, 127.5, 127.0 (sharp, *Ph*$_2$CHOMg), 126.8 (*m*-Ar-*C*), 125.9 (*p*-Ar-*C*), 97.2 (H*C*(CMeNAr)$_2$), 82.8 (pin-O*C*), 76.5 (*C*HOB), 76.2 (*C*HOMg), 29.7, 28.5 (broad, $^{i}$Pr-*C*H), 25.3-26.4 (broad, $^{i}$Pr-*C*H$_3$), 25.1 (NC*C*H$_3$), 25.0 (pin-*C*H$_3$). $^{11}$B NMR ($C_6D_6$, 96 MHz): 15.9 (s, Ph$_2$CHO*B*pin).

**Catalytic hydroboration of aldehydes and ketones**.

5 to 100 μL (0.05-1.00 mol%) of an 0.04 M stock solution of the magnesium precatalyst were added to 0.5 mL of a $C_6D_6$ solution containing 400 μmol of the aldehyde or ketone and 58 μL (400 μmol) of pinacolborane. The mixture was transferred to a sealed Youngs tap NMR tube and the reaction was regularly monitored by $^1H$ and $^{11}B$ NMR at room temperature until complete conversion of the reactants. Scale-up reactions were carried out in dry toluene under argon with 2 mmol of the aldehyde/ketone, 2.05 mmol of pinacolborane and 0.05 - 1.00 mol% catalyst loading. Pinacolborane was added dropwise due to the highly exothermic nature of the reactions. After 8 hours stirring at room temperature the products were hydrolysed with methanol and 1M aqueous HCl. The mixture was refluxed for one hour prior to extraction with diethyl ether or dichloromethane. After drying over $MgSO_4$ and removal of organic solvents the resulting alcohols were either purified by Kugelrohr distillation or recrystallisation from methanol.

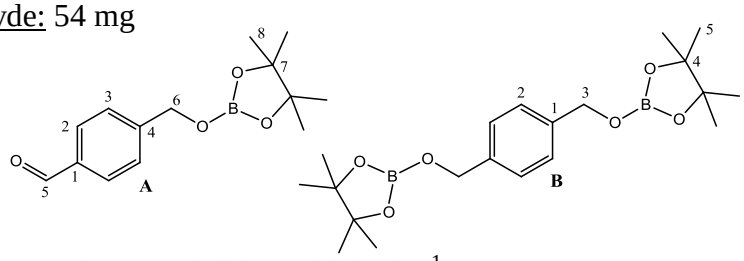
Benzaldehyde: 40.8 μL



*2-benzyloxypinacolborane*. $^1H$ NMR ($C_6D_6$, 300 MHz): 7.31-7.34 (dm, 2H, *H*-2, $^3J$ = 7.3 Hz), 7.04-7.21 (m, 3H, *H-3/4*), 4.96 (s, 2H, *H-5*), 1.05 (s, 12H, *H-7*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): 140.0 (C-1), 128.5 (C-3), 127.5 (C-4), 127.0 (C-2), 82.7 (C-6), 66.9 (C-5), 24.7 (C-7). $^{11}B$ NMR ($C_6D_6$, 96 MHz): 26.0 (s, *B*-O).

Scale-up: 203 μL (2 mmol).
*Benzyl alcohol*: distillation in vacuo (75 $^oC$, 0.3 mbar) yielded a colourless oil (126 mg, 1.17 mmol, 58%). $^1H$ NMR ($CDCl_3$, 300 MHz): 7.16-7.38 (m, 5H), 4.60 (s, 2H), 2.40 (br. s, 1H, O*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): 140.9, 128.4, 127.4, 127.0, 64.7. ESI-MS $[M+Na]^+$ Calcd: 131.13; Found: 131.12.

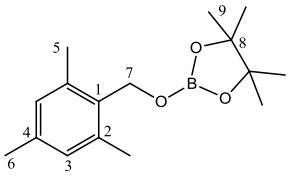
Terephthaldialdehyde: 54 mg



**A.** *4-((pinacolboran-2-yl)oxymethyl)benzaldehyde*. $^1H$ NMR ($C_6D_6$, 300 MHz): 9.65 (s, 1H, *H-5*), 7.51 (d, 2H, *H-2*, $^3J$ = 8.1 Hz), 7.16 (d, 2H, *H-3*, $^3J$ = 8.1 Hz), 4.80 (s, 2H, *H-6*), 1.04 (s, 12H, *H-8*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): 190.8 (C-5), 140.1 (C-1), 139.1 (C-4), 127.1 (C-2), 82.7 (C-7), 66.7 (C-6), 24.7 (C-8). $^{11}B$ NMR ($C_6D_6$, 96 MHz): 25.9 (s, *B*-O).
**B.** *phenyl-1,4-bis(2-methoxypinacolborane)*. $^1H$ NMR ($C_6D_6$, 300 MHz): 7.24 (s, 4H, *H-2*), 4.88 (s, 4H, *H-3*), 1.03 (s, 12H, *H-5*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): 136.2 (C-1), 129.8 (C-2), 126.8 (C-3), 83.0 (C-4), 66.2 (C-3), 24.6 (C-5). $^{11}B$ NMR ($C_6D_6$, 96

MHz): 25.9 (s, *B*-O). Elemental analysis for $C_{20}H_{32}B_2O_6$ ($M_W$ = 390.1). Calcd: C, 61.58; H, 8.27%. Found: C, 61.58; H, 8.19%.
Scale-up: 268 mg (2 mmol).
*(para-hydroxymethyl)benzyl alcohol*: recrystallisation from methanol yielded colourless crystals (260 mg, 1.94 mmol, 97%). $^1$H NMR ($CDCl_3/C_5D_5N$ 95:5, 300 MHz): 7.22 (s, 4H), 5.39 (br, 2H, O*H*), 4.57 (s, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3/C_5D_5N$ 95:5, 75 MHz): 140.6, 126.4, 63.8.

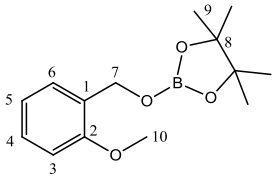
2,4,6-mesitylaldehyde: 59.0 µL




*2-(mesitylmethoxy)pinacolborane*. $^1$H NMR ($C_6D_6$, 300 MHz): 6.70 (s, 2H, *H-3*), 5.00 (s, 2H, *H-7*), 2.34 (s, 6H, *H-5*), 2.10 (s, 3H, *H-6*), 1.03 (s, 12H, *H-9*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): 137.7 (C-2), 137.4 (C-4), 132.9 (C-1), 129.3 (C-3), 82.5 (C-8), 61.5 (C-7), 24.7 (C-9), 21.0 (C-6), 19.6 (C-5). $^{11}$B NMR ($C_6D_6$, 96 MHz): 25.9 (s, *B*-O).

Scale-up: 295 µL (2 mmol).
*Mesitylmethanol*: distillation *in vacuo* (100 °C, 0.06 mbar) yielded a colourless oil (226 mg, 1.50 mmol, 75%). $^1$H NMR ($CDCl_3$, 300 MHz): 6.89 (s, 1H), 6.85 (s, 2H), 4.50 (s, 2H), 2.59 (br. s, O*H*), 2.36 (s, 6H), 2.25 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 137.7, 137.4, 131.4, 128.9, 66.6, 20.9, 19.5. ESI-MS $[M+Na]^+$ Calcd: 173.21; Found: 173.08.

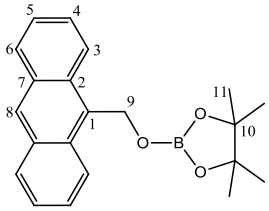
2-methoxybenzaldehyde: 54 mg




*2-(2-methoxybenzyl)oxypinacolborane*. $^1$H NMR ($C_6D_6$, 300 MHz): 7.62 (ddd, 1H, *H-6*, $^3J$ = 7.4 Hz, $^4J$ = 1.9 Hz, $^4J$ = 0.8 Hz), 7.06 (td, 1H, *H-4*, $^3J$ = 8.2 Hz, $^4J$ = 1.9 Hz), 6.87 (td, 1H, *H-5*, $^3J$ = 7.4 Hz, $^4J$ = 0.8 Hz), 6.47 (dd, 1H, *H-3*, $^3J$ = 8.2 Hz, $^4J$ = 0.8 Hz), 5.25 (s, 2H, *H-7*), 3.25 (s, 3H, *H-10*), 1.04 (s, 12H, *H-9*). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz): 156.8 (C-2), 135.5, 128.3, 127.4, 120.7, 110.1, 82.6, 62.6, 54.7, 24.7. $^{11}$B NMR ($C_6D_6$, 96 MHz): 26.0 (s, *B*-O).

Scale-up: 272 mg (2 mmol).
*2-methoxybenzyl alcohol:* distillation *in vacuo* (125 °C, 0.05 mbar) yielded a colourless oil (242 mg, 1.75 mmol, 88%). $^1$H NMR ($CDCl_3$, 300 MHz): 7.26 (ddd, 1H), 7.22 (td, 1H), 6.90 (td, 1H), 6.8 (dd, 1H), 4.62 (s, 2H), 3.74 (s, 3H), 2.96 (br. s, 1H, O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 157.0, 129.3, 128.5, 128.4, 120.6, 110.1, 61.1, 55.1. ESI-MS $[M+Na]^+$ Calcd: 161.15; Found: 161.06.

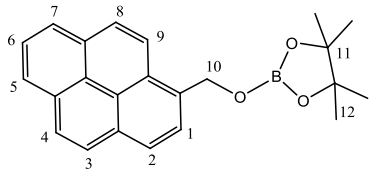
9-Anthralaldehyde: 83 mg



*2-(anthracen-9-ylmethoxy)pinacolborane.* $^{1}$H NMR ($C_6D_6$, 300 MHz): 8.56 (dd, 2H, *H-3*, $^{3}J$ = 9.0 Hz, $^{4}J$ = 0.9 Hz), 8.09 (s, 1H, *H-8*), 7.73 (dm, 2H, *H-6*, $^{3}J$ = 8.5 Hz), 7.31 (ddd, 2H, *H-4*, $^{3}J$ = 9.0 Hz, $^{3}J$ = 6.6 Hz, $^{4}J$ = 1.5 Hz), 7.21 (ddd, 2H, *H-5*, $^{3}J$ = 8.5 Hz, $^{3}J$ = 6.6 Hz, $^{4}J$ = 0.9 Hz), 5.88 (s, 2H, *H-9*), 1.00 (s, 12H, *H-11*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 131.9 (C-1), 131.2 (C-2), 130.4 (C-7), 129.2 (C-6), 128.8 (C-8), 126.2 (C-4), 125.1 (C-3/5), 82.8 (C-10), 59.6 (C-9), 24.7 (C-11). $^{11}$B NMR ($C_6D_6$, 96 MHz): 26.03 (s, *B*-O). Elemental analysis for $C_{21}H_{23}BO_3$ ($M_W$ = 334.2). Calcd: C, 75.47; H, 6.94%. Found: C, 75.56; H, 6.96%.

Scale-up: 413 mg (2 mmol).
*9-anthracenemethanol*: recrystallisation from $Et_2O$ yielded pale yellow crystals (350 mg, 1.68 mmol, 84%). $^{1}$H NMR ($CDCl_3$, 300 MHz): 8.48 (s, 1H), 8.44 (d, 2H, $^{3}J$ = 8.9 Hz), 8.03 (d, 2H, $^{3}J$ = 8.6 Hz), 7.58 (ddd, 2H, $^{3}J$ = 8.9, 6.5 Hz, $^{4}J$ = 1.3 Hz), 7.49 (ddd, 2H, $^{3}J$ = 8.6, 6.5 Hz, $^{4}J$ = 0.9 Hz), 5.69 (s, 2H), 1.66 (br, 1H, O*H*). $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 75 MHz): 131.5, 131.0, 130.2, 129.1, 128.4, 126.5, 125.1, 123.8, 57.4.

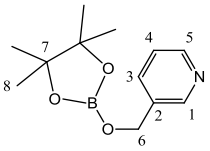
1-pyrenecarboxaldehyde: 92 mg



*2-(pyren-1-ylmethoxy)pinacolborane.* $^{1}$H NMR ($C_6D_6$, 300 MHz): 8.06 (d, 1H, *H-1*, $^{3}J$ = 7.7 Hz), 8.01 (d, 1H, *H-9*, $^{3}J$ = 9.4 Hz), 7.78 (d, 1H, $^{3}J$ = 8.1 Hz), 7.77 (d, 1H, *H-2*, $^{3}J$ = 7.7 Hz), 7.75 (d, 1H, $^{3}J$ = 7.7 Hz), 7.59-7.65 (m, 5H), 5.58 (s, 2H, *H-10*), 1.04 (s, 12H, *H-12*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 132.9, 131.5, 131.2, 131.0, 127.7, 127.6, 127.3, 125.8, 125.7, 125.2, 125.0, 124.8, 123.1, 82.9 (C-11), 65.5 (C-10), 24.7 (C-12). $^{11}$B NMR ($C_6D_6$, 96 MHz): 26.2 (s, *B*-O). Elemental analysis for $C_{23}H_{23}BO_3$ ($M_W$ = 358.2). Calcd: C, 77.11; H, 6.47%. Found: C, 77.05; H, 6.56%.

Scale-up: 461 mg (2 mmol).
*1-pyrenemethanol*: recrystallisation from $CH_2Cl_2$ yielded pale orange crystals (265 mg, 1.14 mmol, 57%). $^{1}$H NMR ($CDCl_3$/$C_5D_5N$ 95:5, 300 MHz): 8.30 (d, 1H, $^{3}J$ = 9.2 Hz), 8.02-8.05 (m, 4H), 7.97 (d, 1H, $^{3}J$ = 9.2 Hz), 7.88-7.91 (m, 2H), 7.85 (t, 1H, $^{3}J$ = 7.6 Hz), 5.35 (s, 2H), 4.49 (br, 1H, O*H*). $^{13}$C{$^{1}$H} NMR ($CDCl_3$/ $C_5D_5N$ 95:5, 75 MHz): 135.1, 130.9, 130.5, 130.4, 128.2, 127.2, 127.1, 126.7, 125.5, 125.3, 124.7, 124.6, 125.5, 124.3, 123.0, 62.5. ESI-MS $[M+Na]^+$ Calcd: 255.27; Found: 255.08.

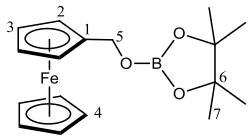
3-pyridinecarboxaldehyde: 37.5 µL




*2-(pyrid-3-ylmethoxy)pinacolborane.* $^{1}$H NMR (300 MHz, $C_6D_6$): 8.78 (d, 1H, *H-1*, 1.09, $^{4}J$ = 1.8 Hz), 8.57 (dd, 1H, *H-5*, $^{3}J$ = 5.0, $^{4}J$ = 1.2 Hz), 7.45 (dt, 1H, *H-3*, $^{3}J$ = 7.8, $^{4}J$ = 1.2 Hz), 6.85 (dd, 1H, *H-4*, $^{3}J$ = 7.8, 5.0 Hz), 4.85 (s, 2H, *H-6*), 1.14 (s, 12H, *H-8*). $^{13}$C{$^{1}$H} NMR (75 MHz, $C_6D_6$): 149.3 (C-1), 149.2 (C-5), 134.9 (C-2), 134.3 (C-3), 123.2 (C-4), 82.9 (C-7), 24.6 (C-8). $^{11}$B NMR (96 MHz, $C_6D_6$): 25.9 (s, *B*-O).

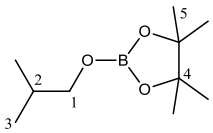
Scale-up: 188 µL (2 mmol).
*Pyridine-3-methanol:* neutralisation with $NaOH_{aq}$ prior to extraction. Distillation *in vacuo* (100 $^{o}$C, 0.1 mbar) yielded a colourless oil (120 mg, 1.10 mmol, 55%). $^{1}$H NMR ($CDCl_3$, 300 MHz): 8.89 (br. s, 1H), 8.44 (d, 1H, $^{3}J$ = 4.8 Hz), 7.72 (dt, 1H, $^{3}J$ = 7.8, $^{4}J$ = 1.7 Hz), 7.27 (dd, 1H, $^{3}J$ = 7.8, 4.8 Hz), 4.70 (s, 2H), 3.82 (br. s, 1H, O*H*). $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 75 MHz): 148.5, 148.2, 136.5, 135.0, 123.5, 62.4. ESI-MS $[M+H]^+$ Calcd: 110.06; Found: 110.06.

Ferrocenaldehyde: 86 mg




*2-(ferrocenylmethoxy)pinacolborane.* $^{1}$H NMR (300 MHz, $C_6D_6$): 4.74 (s, 2H, *H-5*), 4.20 (br. s, 2H, *H-3*), 3.96 (s, 5H, *H-4*), 3.94 (br. s, 2H, *H-2*), 1.06 (s, 12H, *H-7*). $^{13}$C{$^{1}$H} NMR (75 MHz, $C_6D_6$): 86.0 (C-1), 82.6 (C-6), 69.0 (C-3), 68.8 (C-4), 68.5 (C-2), 63.4 (C-5), 24.8 (C-7). $^{11}$B NMR (96 MHz, $C_6D_6$): 25.9 (s, *B*-O).
*Not enough ferrocenaldehyde available for scale-up.*

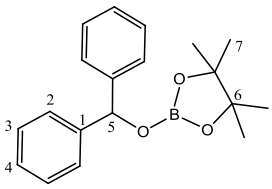
Isobutyraldehyde: 36.5 µL




*2-(isobutyroxy)pinacolborane.* $^{1}$H NMR (300 MHz, $C_6D_6$): 3.69 (d, 2H, *H-1*, $^{3}J$ = 6.5 Hz), 1.77 (nonet, 1H, *H-2*, $^{3}J$ = 6.5 Hz), 1.05 (s, 12H, *H-5*), 0.83 (d, 6H, *H-3*, $^{3}J$ = 6.5 Hz). $^{13}$C{$^{1}$H} NMR (75 MHz, $C_6D_6$): 82.3 (C-4), 71.7 (C-1), 30.3 (C-2), 24.7 (C-5), 18.9 (C-3). $^{11}$B NMR (96 MHz, $C_6D_6$): 25.7 (s, *B*-O).

Scale-up: 183 µL (2 mmol).
*Isobutanol:* the borate ester was hydrolysed with aqueous HCl. After extraction with diethyl ether, drying over $MgSO_4$ and filtering, sodium isobutanolate was precipitated by addition of sodium metal. ESI-MS $[M-H]^-$ Calcd: 73.11; Found: 73.08.

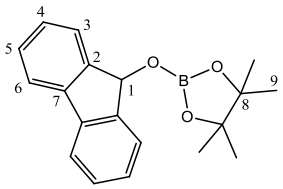
Benzophenone: 73 mg




*2-(diphenylmethoxy)pinacolborane*. $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.49 (dm, 4H, *H-2*, $^{3}J$ = 7.1 Hz), 7.12-7.18 (m, 4H, *H*-3), 7.06 (tt, 2H, *H-4*, $^{3}J$ = 7.3 Hz, $^{4}J$ = 1.4 Hz), 6.48 (s, 1H, *H-5*), 1.04 (s, 12H, *H-7*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 143.8 (C-1), 128.5 (C-3), 127.5 (C-4), 126.9 (C-2), 82.8 (C-6), 78.5 (C-5), 24.6 (C-7). $^{11}$B NMR ($C_6D_6$, 96 MHz): 26.0 (s, *B*-O).

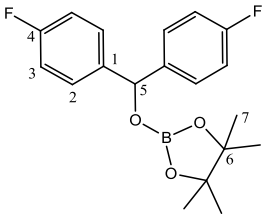
Scale-up: 364 mg (2 mmol).
*Diphenylcarbinol:* recrystallised from toluene as a colourless solid (336 mg, 1.83 mmol, 92%). $^{1}$H NMR ($CDCl_3$, 300 MHz): 7.24-7.37 (m, 10H), 5.25 (s, 1H), 3.39 (br. s, 1H, O*H*). $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 75 MHz): 142.0, 128.4, 127.4, 126.9, 85.4. ESI-MS $[M+Na]^+$ Calcd: 207.22; Found: 207.08.

9-fluorenone: 72 mg



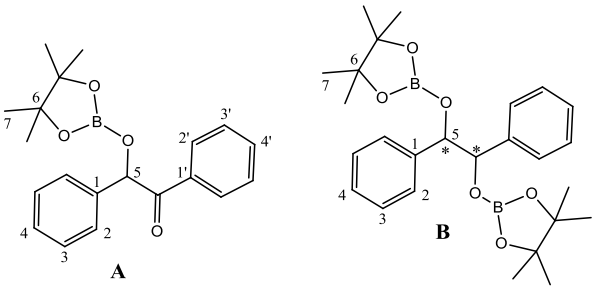

*2-(fluoren-9-yloxy)pinacolborane*. $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.64-7.67 (m, 2H, *H-3*), 7.37-7.39 (m, 2H, *H-6*), 7.14 (dt, 2H, *H-5*, $^{3}J$ = 7.4 Hz, $^{4}J$ = 1.4 Hz), 7.09 (dt, 2H, *H-4*, $^{3}J$ = 7.4 Hz, $^{4}J$ = 1.4 Hz), 6.20 (s, 1H, *H-1*), 1.09 (s, 12H, *H-9*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 145.1 (C-2), 140.8 (C-7), 129.2 (C-5), 127.8 (C-4), 125.6 (C-3), 120.2 (C-6), 83.2 (C-8), 76.9 (C-1), 24.7 (C-9). $^{11}$B NMR ($C_6D_6$, 96 MHz): 26.7 (s, *B*-O).

Scale-up: 360 mg (2 mmol).
*9-fluorenol:* recrystallisation from a methanol/toluene solution yielded a colourless solid (300 mg, 1.65 mmol, 82%). $^{1}$H NMR ($CDCl_3$, 300 MHz): 7.61-7.66 (m, 2H), 7.38 (dd, 2H, $^{3}J$ = 7.3 Hz, $^{4}J$ = 1.3 Hz), 7.35 (dt, 2H, $^{3}J$ = 7.3 Hz, $^{4}J$ = 1.3 Hz), 7.32 (dt, 2H, $^{3}J$ = 7.3 Hz, $^{4}J$ = 1.2 Hz), 5.58 (br. s, 1H), 3.04 (s, 1H, O*H*). $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 75 MHz): 145.6, 139.9, 129.0, 127.7, 125.1, 119.9, 75.1. ESI-MS $[M+Na]^+$: Calcd: 205.21; Found: 205.06.

4,4'-difluorobenzophenone: 87 mg 

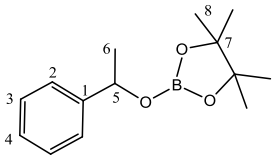
*2-(bis(parafluorophenyl)methoxy)pinacolborane*. $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.27 (dddd, 2H, *H-2*, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $^{4}J_{H\text{-}F}$ = 5.4 Hz, $^{4}J$ = 2.7 Hz, $^{5}J$ = 2.1 Hz), 6.87 (tdd, 2H, *H-3*, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $^{3}J_{H\text{-}F}$ = 8.8 Hz, $^{4}J$ = 3.0 Hz, $^{5}J$ = 2.1 Hz), 6.31 (s, 1H, *H-5*), 1.10 (s, 12H, *H-7*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 162.5 (d, *C-4*, $^{1}J_{C\text{-}F}$ = 247 Hz), 139.4 (d, *C-1*, $^{4}J_{C\text{-}F}$ = 3 Hz), 128.5 (d, *C-2*, $^{3}J_{C\text{-}F}$ = 8 Hz), 115.4 (d, *C-3*, $^{2}J_{C\text{-}F}$ = 22 Hz), 83.0 (C-6), 77.0 (C-5), 24.5 (C-7). $^{11}$B NMR ($C_6D_6$, 96 MHz): 26.0 (s, *B*-O).

Scale-up: 170 mg (0.77 mmol).
*Bis(parafluorophenyl)methanol:* isolated as a low-melting colourless solid (133 mg, 0.60 mmol, 78%). $^{1}$H NMR ($CDCl_3$, 300 MHz): 7.26-7.36 (m, 4H), 6.98-7.07 (m, 4H), 5.21 (s, 1H), 1.72 (br., 1H, O*H*). $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 75 MHz): 162.0 (d, $^{1}J_{C\text{-}F}$ = 245 Hz), 137.6 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 128.4 (d, $^{1}J_{C\text{-}F}$ = 8 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 84.0. ESI-MS $[M+H]^+$ Calcd: 221.22; Found: 221.18.

Benzil: 84 mg 

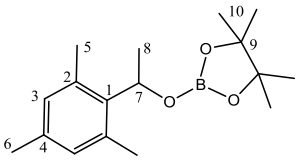

**A**. *2-(1,2-diphenylethoxy)pinacolborane*. $^{1}$H NMR from mixture of mono- and dihydroborated benzil ($C_6D_6$, 300 MHz): 7.98-8.07 (m, 2H, *H-2'*), 7.56-7.61 (m, 2H, *H-4'*), 7.00-7.32 (m, Ph-*H*), 6.55 (s, 1H, *H-5*), 1.14 (s, 12H, *H-7*).
**B**. *2,2'-(1,2-diphenylethyl-1,2-dioxy)dipinacolborane*. $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.00-7.32 (m, 10H, Ph-*H*), 5.67 (s, 1.2H, major diastereomer, 60%), 5.52 (s, 0.8H, minor diastereomer, 40%), 1.17 + 1.04 (two s, 7.2H each, *H-7*, major diastereomer), 1.22 + 1.05 (two s, 4.8H each, *H-7*, minor diastereomer); Elemental analysis for $C_{26}H_{36}B_2O_6$ ($M_w$ = 466.18). Calcd: C, 66.99; H, 7.78%. Found: C, 67.03; H, 7.69.

Scale-up: 380 mg (1.80 mmol).
*1,2-diphenylethane-1,2-diol:* recrystallisation from a methanol/toluene solution yielded a colourless solid (276 mg, 1.29 mmol, 72%). $^{1}$H NMR ($CDCl_3$, 300 MHz): 7.22-7.36 (m, 10H), 4.83 (s, 2H), 2.10 (br., 2H, O*H*). $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 75 MHz): 139.7, 128.2, 128.1, 127.0, 78.0. ESI-MS $[M+Na]^+$ Calcd: 237.25; Found: 237.09.

Acetophenone: 46.8 µL 

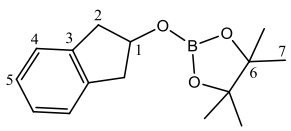
*2-(phenylethoxy)pinacolborane.* $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.47 (dm, 2H, *H-2*, $^{3}J$ = 7.2 Hz), 7.22-7.28 (m, 2H, *H-3*, $^{3}J$ = 7.2 Hz), 7.16 (tt, 1H, *H-4*, $^{3}J$ = 7.4 Hz, $^{4}J$ = 1.4 Hz), 5.50 (q, 1H, *H-5*, $^{3}J$ = 6.6 Hz), 1.56 (d, 3H, *H-6*, $^{3}J$ = 6.6 Hz), 1.14 + 1.11 (two s, 6H each, *H-8*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 145.3 (C-1), 128.5, 127.3, 125.7, 82.5 (C-7), 72.9 (C-5), 25.7 (C-6), 24.7 + 24.6 (C-8). $^{11}$B NMR ($C_6D_6$, 96 MHz): 25.7 (s, *B*-O).

Scale-up: 233 µL (2 mmol).
*1-phenylethanol:* distilled by Kugelrohr as a colourless liquid at 70 $^{o}$C, 1 mbar (164 mg, 13.4 mmol, 67%). $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.19-7.38 (m, 5H), 4.79 (q, 1H, $^{3}J$ = 6.6 Hz), 2.80 (br. s, 1H, O*H*), 1.42 (d, 3H, $^{3}J$ = 6.6 Hz). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 146.0, 128.5, 127.1, 125.4, 70.2, 25.2. ESI-MS $[M+Na]^{+}$ Calcd: 145.15; Found: 145.13.

2,4,6-trimethylacetophenone: 66.6 µL 

*2-(1-mesitylethoxy)pinacolborane.* $^{1}$H NMR ($C_6D_6$, 300 MHz): 6.70 (s, 2H, *H-3*), 5.83 (q, 1H, *H-7*, $^{3}J$ = 6.7 Hz), 2.45 (s, 6H, *H-5*), 2.08 (s, 3H, *H-6*), 1.50 (d, 3H, *H-8*), 0.98 + 0.95 (two s, 6H each, *H-10*).
$^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 137.4 (C-2), 136.1 (C-4), 135.7 (C-1), 130.3 (C-3), 82.3 (C-9), 70.2 (C-7), 24.7 + 24.5 (C-10), 22.0 (C-6), 20.8 (C-5). $^{11}$B NMR ($C_6D_6$, 96 MHz): 25.7 (s, *B*-O).

Scale-up: 333 µL (2 mmol).
*1-mesitylethanol:* isolated as a low-melting colourless solid (253 mg, 1.54 mmol, 77%). $^{1}$H NMR ($C_6D_6$, 300 MHz): 6.82 (s, 2H), 4.75 (q, 1H, $^{3}J$ = 6.6 Hz), 2.47 (br., 1H, O*H*), 2.40 (s, 6H), 2.22 (s, 3H), 1.52 (d, 3H, $^{3}J$ = 6.6 Hz). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 136.2, 136.1, 135.5, 130.4, 76.5, 20.8, 20.7, 20.4. ESI-MS $[M-H]^{+}$: 165.0429; $[M+Na]^{+}$ Calcd: 187.23; Found: 187.20.

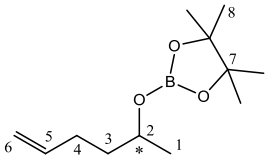
2-indanone: 53 mg 

*2-(indan-2-yloxy)pinacolborane.* $^{1}$H NMR ($C_6D_6$, 300 MHz): 7.00-7.04 (m, 4H, *H-4/5*), 5.01 (tt, 1H, *H-1*, $^{3}J$ = 4.6 Hz, $^{3}J$ = 5.9 Hz), 3.01 (d, 2H, *H-2a*, $^{3}J$ = 5.9 Hz), 2.99 (d, 2H, *H-2b*, $^{3}J$ = 4.6 Hz), 1.05 (s, 12H, *H-7*). $^{13}$C{$^{1}$H} NMR ($C_6D_6$, 75 MHz): 141.1

(C-3), 126.8 (C-5), 124.9 (C-4), 82.5 (C-6), 75.6 (C-1), 42.0 (C-2), 24.7 (C-7). $^{11}$B NMR ($C_6D_6$, 96 MHz): 25.7 (s, *B*-O).

Scale-up: 183 mg (1.37 mmol)
*2-indanol:* isolated as a cream-coloured solid (171 mg, 1.27 mmol, 93%). $^1$H NMR ($CDCl_3$, 300 MHz): 7.18-7.32 (m, 4H), 4.73 (tt, $^3J$ = 3.3 Hz, $^3J$ = 5.8 Hz), 3.60 (br., 1H, O*H*), 3.25 (dd, 2H, $^2J$ = 16.3 Hz, $^3J$ = 5.8 Hz), 2.94 (dd, 2H, $^2J$ = 16.3 Hz, $^3J$ = 3.3 Hz). $^{13}$C{$^1$H} NMR ($CDCl_3$, 75 MHz): 140.7, 126.6, 125.0, 73.2, 42.6. ESI-MS $[M+Na]^+$ Calcd: 157.16; Found: 157.11.

5-hexen-2-one: 46.7 µL




*2-(hex-5-en-2-yloxy)pinacolborane*. $^1$H NMR ($C_6D_6$, 300 MHz): 5.73 (ddt, 1H, *H-5*, $^3J_{cis}$ = 10.2 Hz, $^3J_{trans}$ = 17.0 Hz, $^3J$ = 6.7 Hz), 4.98 (ddt, 1H, *H-6*$_{trans}$, $^2J$ = 2.1 Hz, $^3J_{trans}$ = 17.0 Hz, $^4J$ = 1.7 Hz), 4.92 (ddt, 1H, *H-6*$_{cis}$, $^2J$ = 2.1 Hz, $^3J_{cis}$ = 10.2 Hz, $^4J$ = 1.3 Hz), 4.28 (ddq, 1H, *H-2*, $^3J$ = 7.9 Hz, $^3J$ = 4.8 Hz, $^3J$ = 6.2 Hz), 2.03-2.19 (m, 2H, *H-4a/b*), 1.60 (dddd, 1H, *H-3a*, $^3J$ = 6.7 Hz, $^3J$ = 8.1 Hz, $^3J$ = 8.7 Hz, $^2J$ = 13.6 Hz), 1.38 (dddd, 1H, *H-3b*, $^3J$ = 4.7 Hz, $^3J$ = 6.7 Hz, $^3J$ = 9.0 Hz, $^2J$ = 13.6 Hz), 1.14 (d, 3H, *H-1*, $^3J$ = 6.2 Hz), 1.05 (s, 12H, *H-8*).
$^{13}$C{$^1$H} NMR ($C_6D_6$, 75 MHz): 138.6 (C-5), 114.7 (C-6), 82.2 (C-7), 70.3 (C-2), 37.8 (C-4), 30.3 (C-3), 24.7 (C-8), 22.8 (C-1). $^{11}$B NMR ($C_6D_6$, 96 MHz): 25.6 (s, *B*-O).

Scale-up: 234 µL (2 mmol).
*5-hexen-2-ol:* purified by vacuum transfer as a colourless oil (133 mg, 1.33 mmol, 66%).$^1$H NMR ($C_6D_6$, 300 MHz): 5.92 (ddt, 1H, *H-5*, $^3J_{cis}$ = 10.1 Hz, $^3J_{trans}$ = 17.0 Hz, $^3J$ = 6.7 Hz), 5.13 (ddt, 1H, *H-6*$_{trans}$, $^2J$ = 3.7 Hz, $^3J_{trans}$ = 17.0 Hz, $^4J$ = 1.3 Hz), 5.03 (ddt, 1H, *H-6*$_{cis}$, $^2J$ = 2.3 Hz, $^3J_{cis}$ = 10.1 Hz, $^4J$ = 1.3 Hz), 3.83-3.96 (m, 1H, *H-2*), 2.16-2.43 (m, 2H, *H-4a/b*), 1.52-1.76 (m, 1H, *H-3a/b*), 1.28 (d, 3H, *H-1*, $^3J$ = 6.2 Hz), 1.16 (s, 1H, O*H*). $^{13}$C{$^1$H} NMR ($C_6D_6$, 75 MHz): 139.2, 114.4, 66.7, 39.1, 30.7, 24.9. ESI-MS $[M+H]^+$ Calcd: 101.17; Found: 101.10.

## Crystallographic experiments

Data were collected at 150 K on a Nonius KappaCCD diffractometer equipped with a low temperature device, using graphite monochromated Mo$K_\alpha$ radiation ($\lambda$= 0.71073 Å). Data were processed using the Nonius Software.[2] Structure solution, followed by full-matrix least squares refinement was performed using the WinGX-1.70 suite of programs throughout.[3]

## X-ray structure of 4

Table S1. Crystal data and structure refinement for **4**.

| | | |
|---|---|---|
| Empirical formula | $C_{61}H_{75}BMgN_2O_4$ | |
| Formula weight | 935.35 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | Orthorhombic, P b c a | |
| Unit cell dimensions | $a$ = 19.2649(2) Å | $\alpha$ = 90°. |
| | $b$ = 20.4622(3) Å | $\beta$ = 90°. |
| | $c$ = 26.9490(4) Å | $\gamma$ = 90°. |
| Volume | 10623.4(2) A3 | |
| Z, | 8 | |
| Calculated density | 1.170 mg.m$^{-3}$ | |
| Absorption coefficient | 0.082 mm$^{-1}$ | |
| $F$(000) | 4032 | |
| Crystal size | 0.55 x 0.50 x 0.40 mm | |
| $\theta$ range for data collection | 3.69 to 25.39°. | |
| Limiting indices | -23<=h<=23, -24<=k<=24, -32<=l<=32 | |
| Reflections collected / unique | 115166 / 9691 [$R$(int) = 0.0914] | |
| Completeness to $\theta$ = 25.39 | 99.2 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9679 and 0.9563 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9691 / 0 / 636 | |
| Goodness-of-fit on $F^2$ | 1.080 | |
| Final $R$ indices [I>2$\sigma$(I)] | $R_1$ = 0.0543, w$R_2$ = 0.1281 | |
| $R$ indices (all data) | $R_1$ = 0.0893, w$R_2$ = 0.1465 | |
| Largest diff. peak and hole | 0.276 and -0.310 e.A$^{-3}$ | |

Table S2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($A^2$ x $10^3$) for **4**. $U_{(eq)}$ is defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

| | x | y | z | $U_{(eq)}$ |
|---|---|---|---|---|
| Mg | 5679(1) | 2388(1) | 3861(1) | 24(1) |
| B | 6617(1) | 3340(1) | 3753(1) | 12(1) |
| N(1) | 5399(1) | 1576(1) | 4264(1) | 26(1) |
| N(2) | 4873(1) | 2327(1) | 3371(1) | 30(1) |
| O(1) | 6564(1) | 2640(1) | 3542(1) | 27(1) |
| O(2) | 7315(1) | 3389(1) | 3937(1) | 31(1) |
| O(3) | 6035(1) | 3222(1) | 4171(1) | 23(1) |
| O(4) | 6367(1) | 3849(1) | 3440(1) | 37(1) |
| C(1) | 4721(1) | 1421(1) | 4272(1) | 31(1) |
| C(2) | 4438(1) | 933(1) | 4646(1) | 41(1) |
| C(3) | 4221(1) | 1677(1) | 3952(1) | 35(1) |
| C(4) | 4289(1) | 2033(1) | 3510(1) | 35(1) |
| C(5) | 3645(2) | 2045(2) | 3186(1) | 55(1) |
| C(6) | 5864(1) | 1149(1) | 4532(1) | 28(1) |
| C(7) | 6150(1) | 1348(1) | 4990(1) | 28(1) |
| C(8) | 5976(1) | 2008(1) | 5221(1) | 31(1) |
| C(9) | 5260(1) | 2004(1) | 5468(1) | 42(1) |
| C(10) | 6516(2) | 2243(1) | 5597(1) | 42(1) |
| C(11) | 6587(1) | 916(1) | 5238(1) | 35(1) |
| C(12) | 6744(1) | 311(1) | 5048(1) | 39(1) |
| C(13) | 6465(1) | 121(1) | 4601(1) | 39(1) |
| C(14) | 6021(1) | 529(1) | 4330(1) | 33(1) |
| C(15) | 5729(2) | 285(1) | 3838(1) | 42(1) |
| C(16) | 6304(2) | 86(1) | 3483(1) | 55(1) |
| C(17) | 5245(2) | -305(2) | 3911(1) | 61(1) |
| C(18) | 4916(1) | 2573(1) | 2869(1) | 34(1) |
| C(19) | 5270(1) | 2188(1) | 2517(1) | 41(1) |
| C(20) | 5567(2) | 1523(1) | 2655(1) | 50(1) |
| C(21) | 6161(2) | 1299(2) | 2321(1) | 72(1) |
| C(22) | 4992(2) | 999(2) | 2663(1) | 70(1) |
| C(23) | 5307(2) | 2410(2) | 2032(1) | 51(1) |
| C(24) | 5006(2) | 2991(2) | 1895(1) | 55(1) |
| C(25) | 4680(2) | 3371(2) | 2244(1) | 47(1) |
| C(26) | 4629(1) | 3184(1) | 2737(1) | 37(1) |
| C(27) | 4273(1) | 3639(1) | 3102(1) | 38(1) |
| C(28) | 3522(2) | 3790(2) | 2953(1) | 58(1) |
| C(29) | 4683(2) | 4281(1) | 3138(1) | 49(1) |
| C(30) | 7278(1) | 2416(1) | 3476(1) | 32(1) |
| C(31) | 7288(1) | 1678(1) | 3495(1) | 41(1) |
| C(32) | 7520(2) | 2660(1) | 2968(1) | 45(1) |
| C(33) | 7657(1) | 2765(1) | 3912(1) | 32(1) |
| C(34) | 7559(1) | 2407(1) | 4406(1) | 35(1) |
| C(35) | 8423(1) | 2885(2) | 3821(1) | 50(1) |
| C(36) | 5751(1) | 3769(1) | 4441(1) | 25(1) |
| C(37) | 4966(1) | 3730(1) | 4453(1) | 27(1) |
| C(38) | 4624(1) | 3144(1) | 4538(1) | 31(1) |
| C(39) | 3903(1) | 3116(1) | 4545(1) | 41(1) |
| C(40) | 3522(1) | 3677(2) | 4472(1) | 49(1) |
| C(41) | 3856(1) | 4265(2) | 4399(1) | 50(1) |
| C(42) | 4574(1) | 4290(1) | 4390(1) | 38(1) |
| C(43) | 6077(1) | 3825(1) | 4959(1) | 26(1) |

| | | | | |
|---|---|---|---|---|
| C(44) | 5677(1) | 3933(1) | 5380(1) | 34(1) |
| C(45) | 5985(2) | 4021(1) | 5840(1) | 42(1) |
| C(46) | 6700(1) | 3999(1) | 5888(1) | 41(1) |
| C(47) | 7100(1) | 3896(1) | 5473(1) | 35(1) |
| C(48) | 6795(1) | 3814(1) | 5011(1) | 30(1) |
| C(49) | 6798(1) | 4374(1) | 3291(1) | 39(1) |
| C(50) | 6588(1) | 4978(1) | 3585(1) | 37(1) |
| C(51) | 6072(1) | 5397(1) | 3424(1) | 45(1) |
| C(52) | 5854(2) | 5913(1) | 3720(1) | 50(1) |
| C(53) | 6151(2) | 6014(1) | 4178(1) | 48(1) |
| C(54) | 6667(2) | 5601(1) | 4341(1) | 47(1) |
| C(55) | 6882(1) | 5091(1) | 4044(1) | 41(1) |
| C(56) | 6767(1) | 4481(1) | 2736(1) | 42(1) |
| C(57) | 7114(2) | 5008(2) | 2532(1) | 53(1) |
| C(58) | 7106(2) | 5128(2) | 2029(1) | 61(1) |
| C(59) | 6746(2) | 4713(2) | 1715(1) | 64(1) |
| C(60) | 6409(2) | 4181(2) | 1913(1) | 62(1) |
| C(61) | 6416(2) | 4065(2) | 2420(1) | 50(1) |

Table S3. Bond lengths [Å] **4**.

| | |
|---|---|
| Mg-O(1) | 1.9789(16) |
| Mg-O(3) | 2.0194(16) |
| Mg-N(2) | 2.044(2) |
| Mg-N(1) | 2.0561(19) |
| Mg-B | 2.673(2) |
| B-O(4) | 1.424(3) |
| B-O(2) | 1.438(3) |
| B-O(1) | 1.544(3) |
| B-O(3) | 1.606(3) |
| N(1)-C(1) | 1.344(3) |
| N(1)-C(6) | 1.446(3) |
| N(2)-C(4) | 1.331(3) |
| N(2)-C(18) | 1.446(3) |
| O(1)-C(30) | 1.460(3) |
| O(2)-C(33) | 1.439(3) |
| O(3)-C(36) | 1.443(3) |
| O(4)-C(49) | 1.416(3) |
| C(1)-C(3) | 1.395(3) |
| C(1)-C(2) | 1.520(3) |
| C(2)-H(2A) | 0.9800 |
| C(2)-H(2B) | 0.9800 |
| C(2)-H(2C) | 0.9800 |
| C(3)-C(4) | 1.403(3) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.516(4) |
| C(5)-H(5A) | 0.9800 |
| C(5)-H(5B) | 0.9800 |
| C(5)-H(5C) | 0.9800 |
| C(6)-C(7) | 1.411(3) |
| C(6)-C(14) | 1.413(3) |
| C(7)-C(11) | 1.392(3) |
| C(7)-C(8) | 1.524(3) |
| C(8)-C(9) | 1.531(3) |
| C(8)-C(10) | 1.531(3) |
| C(8)-H(8) | 1.0000 |
| C(9)-H(9A) | 0.9800 |

| | |
|---|---|
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| C(10)-H(10A) | 0.9800 |
| C(10)-H(10B) | 0.9800 |
| C(10)-H(10C) | 0.9800 |
| C(11)-C(12) | 1.375(4) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(13) | 1.376(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.400(4) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.525(4) |
| C(15)-C(16) | 1.519(4) |
| C(15)-C(17) | 1.538(4) |
| C(15)-H(15) | 1.0000 |
| C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 |
| C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-C(19) | 1.409(4) |
| C(18)-C(26) | 1.412(4) |
| C(19)-C(23) | 1.386(4) |
| C(19)-C(20) | 1.522(4) |
| C(20)-C(21) | 1.527(4) |
| C(20)-C(22) | 1.543(4) |
| C(20)-H(20) | 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) | 1.372(4) |
| C(23)-H(23) | 0.9500 |
| C(24)-C(25) | 1.374(4) |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.385(4) |
| C(25)-H(25) | 0.9500 |
| C(26)-C(27) | 1.518(4) |
| C(27)-C(28) | 1.533(4) |
| C(27)-C(29) | 1.537(4) |
| C(27)-H(27) | 1.0000 |
| C(28)-H(28A) | 0.9800 |
| C(28)-H(28B) | 0.9800 |
| C(28)-H(28C) | 0.9800 |
| C(29)-H(29A) | 0.9800 |
| C(29)-H(29B) | 0.9800 |
| C(29)-H(29C) | 0.9800 |
| C(30)-C(31) | 1.510(3) |
| C(30)-C(32) | 1.530(3) |
| C(30)-C(33) | 1.557(3) |
| C(31)-H(31A) | 0.9800 |
| C(31)-H(31B) | 0.9800 |
| C(31)-H(31C) | 0.9800 |
| C(32)-H(32A) | 0.9800 |
| C(32)-H(32B) | 0.9800 |
| C(32)-H(32C) | 0.9800 |
| C(33)-C(35) | 1.517(3) |

| | |
|---|---|
| C(33)-C(34) | 1.531(3) |
| C(34)-H(34A) | 0.9800 |
| C(34)-H(34B) | 0.9800 |
| C(34)-H(34C) | 0.9800 |
| C(35)-H(35A) | 0.9800 |
| C(35)-H(35B) | 0.9800 |
| C(35)-H(35C) | 0.9800 |
| C(36)-C(37) | 1.514(3) |
| C(36)-C(43) | 1.535(3) |
| C(36)-H(36) | 1.0000 |
| C(37)-C(42) | 1.383(3) |
| C(37)-C(38) | 1.387(3) |
| C(38)-C(39) | 1.391(3) |
| C(38)-H(38) | 0.9500 |
| C(39)-C(40) | 1.379(4) |
| C(39)-H(39) | 0.9500 |
| C(40)-C(41) | 1.377(4) |
| C(40)-H(40) | 0.9500 |
| C(41)-C(42) | 1.385(4) |
| C(41)-H(41) | 0.9500 |
| C(42)-H(42) | 0.9500 |
| C(43)-C(44) | 1.388(3) |
| C(43)-C(48) | 1.390(3) |
| C(44)-C(45) | 1.387(4) |
| C(44)-H(44) | 0.9500 |
| C(45)-C(46) | 1.384(4) |
| C(45)-H(45) | 0.9500 |
| C(46)-C(47) | 1.374(4) |
| C(46)-H(46) | 0.9500 |
| C(47)-C(48) | 1.389(3) |
| C(47)-H(47) | 0.9500 |
| C(48)-H(48) | 0.9500 |
| C(49)-C(56) | 1.513(4) |
| C(49)-C(50) | 1.523(4) |
| C(49)-H(49) | 1.0000 |
| C(50)-C(55) | 1.379(4) |
| C(50)-C(51) | 1.384(4) |
| C(51)-C(52) | 1.386(4) |
| C(51)-H(51) | 0.9500 |
| C(52)-C(53) | 1.378(4) |
| C(52)-H(52) | 0.9500 |
| C(53)-C(54) | 1.376(4) |
| C(53)-H(53) | 0.9500 |
| C(54)-C(55) | 1.379(4) |
| C(54)-H(54) | 0.9500 |
| C(55)-H(55) | 0.9500 |
| C(56)-C(61) | 1.381(4) |
| C(56)-C(57) | 1.383(4) |
| C(57)-C(58) | 1.377(4) |
| C(57)-H(57) | 0.9500 |
| C(58)-C(59) | 1.385(5) |
| C(58)-H(58) | 0.9500 |
| C(59)-C(60) | 1.375(5) |
| C(59)-H(59) | 0.9500 |
| C(60)-C(61) | 1.385(4) |
| C(60)-H(60) | 0.9500 |
| C(61)-H(61) | 0.9500 |

Table S4. Angles [°] for **4**

| | |
|---|---|
| O(1)-Mg-O(3) | 70.51(6) |
| O(1)-Mg-N(2) | 112.90(8) |
| O(3)-Mg-N(2) | 125.24(8) |
| O(1)-Mg-N(1) | 131.82(8) |
| O(3)-Mg-N(1) | 123.65(8) |
| N(2)-Mg-N(1) | 95.31(8) |
| O(1)-Mg-B | 34.91(6) |
| O(3)-Mg-B | 36.82(6) |
| N(2)-Mg-B | 119.16(8) |
| N(1)-Mg-B | 145.50(8) |
| O(4)-B-O(2) | 118.02(17) |
| O(4)-B-O(1) | 115.95(16) |
| O(2)-B-O(1) | 104.64(15) |
| O(4)-B-O(3) | 106.83(16) |
| O(2)-B-O(3) | 114.94(16) |
| O(1)-B-O(3) | 94.20(13) |
| O(4)-B-Mg | 111.66(13) |
| O(2)-B-Mg | 130.23(13) |
| O(1)-B-Mg | 47.17(8) |
| O(3)-B-Mg | 48.89(8) |
| C(1)-N(1)-C(6) | 116.80(18) |
| C(1)-N(1)-Mg | 117.04(15) |
| C(6)-N(1)-Mg | 126.15(14) |
| C(4)-N(2)-C(18) | 118.1(2) |
| C(4)-N(2)-Mg | 119.17(16) |
| C(18)-N(2)-Mg | 122.72(15) |
| C(30)-O(1)-B | 105.98(15) |
| C(30)-O(1)-Mg | 141.43(14) |
| B-O(1)-Mg | 97.92(11) |
| B-O(2)-C(33) | 110.50(16) |
| C(36)-O(3)-B | 120.06(15) |
| C(36)-O(3)-Mg | 137.26(13) |
| B-O(3)-Mg | 94.29(10) |
| C(49)-O(4)-B | 121.60(18) |
| N(1)-C(1)-C(3) | 125.0(2) |
| N(1)-C(1)-C(2) | 121.0(2) |
| C(3)-C(1)-C(2) | 114.1(2) |
| C(1)-C(2)-H(2A) | 109.5 |
| C(1)-C(2)-H(2B) | 109.5 |
| H(2A)-C(2)-H(2B) | 109.5 |
| C(1)-C(2)-H(2C) | 109.5 |
| H(2A)-C(2)-H(2C) | 109.5 |
| H(2B)-C(2)-H(2C) | 109.5 |
| C(1)-C(3)-C(4) | 130.9(2) |
| C(1)-C(3)-H(3) | 114.6 |
| C(4)-C(3)-H(3) | 114.6 |
| N(2)-C(4)-C(3) | 123.7(2) |
| N(2)-C(4)-C(5) | 121.4(2) |
| C(3)-C(4)-C(5) | 114.9(2) |
| C(4)-C(5)-H(5A) | 109.5 |
| C(4)-C(5)-H(5B) | 109.5 |
| H(5A)-C(5)-H(5B) | 109.5 |
| C(4)-C(5)-H(5C) | 109.5 |
| H(5A)-C(5)-H(5C) | 109.5 |
| H(5B)-C(5)-H(5C) | 109.5 |
| C(7)-C(6)-C(14) | 120.8(2) |
| C(7)-C(6)-N(1) | 120.4(2) |

| | |
|---|---|
| C(14)-C(6)-N(1) | 118.9(2) |
| C(11)-C(7)-C(6) | 118.3(2) |
| C(11)-C(7)-C(8) | 120.0(2) |
| C(6)-C(7)-C(8) | 121.7(2) |
| C(7)-C(8)-C(9) | 111.8(2) |
| C(7)-C(8)-C(10) | 113.5(2) |
| C(9)-C(8)-C(10) | 109.0(2) |
| C(7)-C(8)-H(8) | 107.4 |
| C(9)-C(8)-H(8) | 107.4 |
| C(10)-C(8)-H(8) | 107.4 |
| C(8)-C(9)-H(9A) | 109.5 |
| C(8)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| C(8)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(8)-C(10)-H(10A) | 109.5 |
| C(8)-C(10)-H(10B) | 109.5 |
| H(10A)-C(10)-H(10B) | 109.5 |
| C(8)-C(10)-H(10C) | 109.5 |
| H(10A)-C(10)-H(10C) | 109.5 |
| H(10B)-C(10)-H(10C) | 109.5 |
| C(12)-C(11)-C(7) | 121.7(2) |
| C(12)-C(11)-H(11) | 119.2 |
| C(7)-C(11)-H(11) | 119.2 |
| C(11)-C(12)-C(13) | 119.7(2) |
| C(11)-C(12)-H(12) | 120.1 |
| C(13)-C(12)-H(12) | 120.1 |
| C(12)-C(13)-C(14) | 121.7(2) |
| C(12)-C(13)-H(13) | 119.1 |
| C(14)-C(13)-H(13) | 119.1 |
| C(13)-C(14)-C(6) | 117.8(2) |
| C(13)-C(14)-C(15) | 118.8(2) |
| C(6)-C(14)-C(15) | 123.4(2) |
| C(16)-C(15)-C(14) | 111.5(2) |
| C(16)-C(15)-C(17) | 108.2(2) |
| C(14)-C(15)-C(17) | 111.7(2) |
| C(16)-C(15)-H(15) | 108.4 |
| C(14)-C(15)-H(15) | 108.4 |
| C(17)-C(15)-H(15) | 108.4 |
| C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 |
| C(15)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 |
| C(15)-C(17)-H(17A) | 109.5 |
| C(15)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |
| C(15)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| C(19)-C(18)-C(26) | 121.1(2) |
| C(19)-C(18)-N(2) | 117.6(2) |
| C(26)-C(18)-N(2) | 121.3(2) |
| C(23)-C(19)-C(18) | 118.4(3) |
| C(23)-C(19)-C(20) | 120.4(3) |
| C(18)-C(19)-C(20) | 121.1(2) |
| C(19)-C(20)-C(21) | 114.0(3) |
| C(19)-C(20)-C(22) | 110.7(3) |

| | |
|---|---|
| C(21)-C(20)-C(22) | 109.7(3) |
| C(19)-C(20)-H(20) | 107.4 |
| C(21)-C(20)-H(20) | 107.4 |
| C(22)-C(20)-H(20) | 107.4 |
| 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(19) | 121.1(3) |
| C(24)-C(23)-H(23) | 119.4 |
| C(19)-C(23)-H(23) | 119.4 |
| C(23)-C(24)-C(25) | 119.9(3) |
| C(23)-C(24)-H(24) | 120.1 |
| C(25)-C(24)-H(24) | 120.1 |
| C(24)-C(25)-C(26) | 122.3(3) |
| C(24)-C(25)-H(25) | 118.9 |
| C(26)-C(25)-H(25) | 118.9 |
| C(25)-C(26)-C(18) | 117.2(3) |
| C(25)-C(26)-C(27) | 119.0(2) |
| C(18)-C(26)-C(27) | 123.9(2) |
| C(26)-C(27)-C(28) | 112.4(2) |
| C(26)-C(27)-C(29) | 109.4(2) |
| C(28)-C(27)-C(29) | 109.2(2) |
| C(26)-C(27)-H(27) | 108.6 |
| C(28)-C(27)-H(27) | 108.6 |
| C(29)-C(27)-H(27) | 108.6 |
| C(27)-C(28)-H(28A) | 109.5 |
| C(27)-C(28)-H(28B) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 |
| C(27)-C(28)-H(28C) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 |
| C(27)-C(29)-H(29A) | 109.5 |
| C(27)-C(29)-H(29B) | 109.5 |
| H(29A)-C(29)-H(29B) | 109.5 |
| C(27)-C(29)-H(29C) | 109.5 |
| H(29A)-C(29)-H(29C) | 109.5 |
| H(29B)-C(29)-H(29C) | 109.5 |
| O(1)-C(30)-C(31) | 108.85(19) |
| O(1)-C(30)-C(32) | 107.04(19) |
| C(31)-C(30)-C(32) | 110.6(2) |
| O(1)-C(30)-C(33) | 101.88(17) |
| C(31)-C(30)-C(33) | 115.3(2) |
| C(32)-C(30)-C(33) | 112.5(2) |
| C(30)-C(31)-H(31A) | 109.5 |
| C(30)-C(31)-H(31B) | 109.5 |
| H(31A)-C(31)-H(31B) | 109.5 |
| C(30)-C(31)-H(31C) | 109.5 |
| H(31A)-C(31)-H(31C) | 109.5 |
| H(31B)-C(31)-H(31C) | 109.5 |
| C(30)-C(32)-H(32A) | 109.5 |
| C(30)-C(32)-H(32B) | 109.5 |

| | |
|---|---|
| H(32A)-C(32)-H(32B) | 109.5 |
| C(30)-C(32)-H(32C) | 109.5 |
| H(32A)-C(32)-H(32C) | 109.5 |
| H(32B)-C(32)-H(32C) | 109.5 |
| O(2)-C(33)-C(35) | 108.0(2) |
| O(2)-C(33)-C(34) | 109.11(19) |
| C(35)-C(33)-C(34) | 109.8(2) |
| O(2)-C(33)-C(30) | 103.16(18) |
| C(35)-C(33)-C(30) | 114.2(2) |
| C(34)-C(33)-C(30) | 112.3(2) |
| C(33)-C(34)-H(34A) | 109.5 |
| C(33)-C(34)-H(34B) | 109.5 |
| H(34A)-C(34)-H(34B) | 109.5 |
| C(33)-C(34)-H(34C) | 109.5 |
| H(34A)-C(34)-H(34C) | 109.5 |
| H(34B)-C(34)-H(34C) | 109.5 |
| C(33)-C(35)-H(35A) | 109.5 |
| C(33)-C(35)-H(35B) | 109.5 |
| H(35A)-C(35)-H(35B) | 109.5 |
| C(33)-C(35)-H(35C) | 109.5 |
| H(35A)-C(35)-H(35C) | 109.5 |
| H(35B)-C(35)-H(35C) | 109.5 |
| O(3)-C(36)-C(37) | 110.44(17) |
| O(3)-C(36)-C(43) | 111.14(17) |
| C(37)-C(36)-C(43) | 113.11(18) |
| O(3)-C(36)-H(36) | 107.3 |
| C(37)-C(36)-H(36) | 107.3 |
| C(43)-C(36)-H(36) | 107.3 |
| C(42)-C(37)-C(38) | 118.5(2) |
| C(42)-C(37)-C(36) | 120.0(2) |
| C(38)-C(37)-C(36) | 121.5(2) |
| C(37)-C(38)-C(39) | 120.9(2) |
| C(37)-C(38)-H(38) | 119.6 |
| C(39)-C(38)-H(38) | 119.6 |
| C(40)-C(39)-C(38) | 119.7(3) |
| C(40)-C(39)-H(39) | 120.2 |
| C(38)-C(39)-H(39) | 120.2 |
| C(41)-C(40)-C(39) | 120.0(2) |
| C(41)-C(40)-H(40) | 120.0 |
| C(39)-C(40)-H(40) | 120.0 |
| C(40)-C(41)-C(42) | 120.1(3) |
| C(40)-C(41)-H(41) | 119.9 |
| C(42)-C(41)-H(41) | 119.9 |
| C(37)-C(42)-C(41) | 120.8(2) |
| C(37)-C(42)-H(42) | 119.6 |
| C(41)-C(42)-H(42) | 119.6 |
| C(44)-C(43)-C(48) | 118.2(2) |
| C(44)-C(43)-C(36) | 121.9(2) |
| C(48)-C(43)-C(36) | 119.8(2) |
| C(45)-C(44)-C(43) | 120.9(2) |
| C(45)-C(44)-H(44) | 119.5 |
| C(43)-C(44)-H(44) | 119.5 |
| C(46)-C(45)-C(44) | 120.4(2) |
| C(46)-C(45)-H(45) | 119.8 |
| C(44)-C(45)-H(45) | 119.8 |
| C(47)-C(46)-C(45) | 119.1(2) |
| C(47)-C(46)-H(46) | 120.5 |
| C(45)-C(46)-H(46) | 120.5 |
| C(46)-C(47)-C(48) | 120.8(2) |
| C(46)-C(47)-H(47) | 119.6 |

| | |
|---|---|
| C(48)-C(47)-H(47) | 119.6 |
| C(47)-C(48)-C(43) | 120.6(2) |
| C(47)-C(48)-H(48) | 119.7 |
| C(43)-C(48)-H(48) | 119.7 |
| O(4)-C(49)-C(56) | 111.5(2) |
| O(4)-C(49)-C(50) | 108.2(2) |
| C(56)-C(49)-C(50) | 112.7(2) |
| O(4)-C(49)-H(49) | 108.1 |
| C(56)-C(49)-H(49) | 108.1 |
| C(50)-C(49)-H(49) | 108.1 |
| C(55)-C(50)-C(51) | 118.2(3) |
| C(55)-C(50)-C(49) | 119.5(2) |
| C(51)-C(50)-C(49) | 122.1(2) |
| C(50)-C(51)-C(52) | 120.6(3) |
| C(50)-C(51)-H(51) | 119.7 |
| C(52)-C(51)-H(51) | 119.7 |
| C(53)-C(52)-C(51) | 120.3(3) |
| C(53)-C(52)-H(52) | 119.8 |
| C(51)-C(52)-H(52) | 119.8 |
| C(54)-C(53)-C(52) | 119.5(3) |
| C(54)-C(53)-H(53) | 120.3 |
| C(52)-C(53)-H(53) | 120.3 |
| C(53)-C(54)-C(55) | 119.8(3) |
| C(53)-C(54)-H(54) | 120.1 |
| C(55)-C(54)-H(54) | 120.1 |
| C(54)-C(55)-C(50) | 121.6(3) |
| C(54)-C(55)-H(55) | 119.2 |
| C(50)-C(55)-H(55) | 119.2 |
| C(61)-C(56)-C(57) | 118.1(3) |
| C(61)-C(56)-C(49) | 122.7(3) |
| C(57)-C(56)-C(49) | 119.2(3) |
| C(58)-C(57)-C(56) | 121.7(3) |
| C(58)-C(57)-H(57) | 119.1 |
| C(56)-C(57)-H(57) | 119.1 |
| C(57)-C(58)-C(59) | 119.8(3) |
| C(57)-C(58)-H(58) | 120.1 |
| C(59)-C(58)-H(58) | 120.1 |
| C(60)-C(59)-C(58) | 119.0(3) |
| C(60)-C(59)-H(59) | 120.5 |
| C(58)-C(59)-H(59) | 120.5 |
| C(59)-C(60)-C(61) | 120.9(3) |
| C(59)-C(60)-H(60) | 119.5 |
| C(61)-C(60)-H(60) | 119.5 |
| C(56)-C(61)-C(60) | 120.5(3) |
| C(56)-C(61)-H(61) | 119.8 |
| C(60)-C(61)-H(61) | 119.8 |

Table S5. Anisotropic displacement parameters ($A^2$ x $10^3$) for publication. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Mg | 26(1) | 26(1) | 21(1) | 1(1) | -1(1) | -3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| B | 13(1) | 11(1) | 11(1) | 0(1) | -2(1) | 1(1) |
| N(1) | 28(1) | 26(1) | 25(1) | 2(1) | 0(1) | -3(1) |
| N(2) | 35(1) | 32(1) | 23(1) | 1(1) | -5(1) | -4(1) |
| O(1) | 26(1) | 32(1) | 24(1) | -2(1) | 4(1) | -1(1) |
| O(2) | 35(1) | 27(1) | 30(1) | 2(1) | -1(1) | -4(1) |
| O(3) | 24(1) | 24(1) | 22(1) | -2(1) | 4(1) | -1(1) |
| O(4) | 33(1) | 38(1) | 41(1) | 0(1) | -4(1) | -2(1) |
| C(1) | 33(1) | 29(1) | 30(1) | -1(1) | 2(1) | -7(1) |
| C(2) | 38(2) | 43(2) | 42(2) | 10(1) | 3(1) | -11(1) |
| C(3) | 27(1) | 41(1) | 38(2) | 3(1) | -2(1) | -9(1) |
| C(4) | 33(1) | 38(1) | 34(1) | 0(1) | -9(1) | -7(1) |
| C(5) | 47(2) | 63(2) | 55(2) | 14(2) | -21(2) | -18(2) |
| C(6) | 28(1) | 27(1) | 28(1) | 7(1) | 4(1) | -5(1) |
| C(7) | 28(1) | 27(1) | 29(1) | 5(1) | 2(1) | -5(1) |
| C(8) | 36(1) | 33(1) | 24(1) | 4(1) | -1(1) | -5(1) |
| C(9) | 49(2) | 45(2) | 33(2) | -1(1) | 12(1) | -4(1) |
| C(10) | 57(2) | 36(1) | 34(2) | 3(1) | -11(1) | -5(1) |
| C(11) | 35(1) | 37(1) | 34(1) | 9(1) | -4(1) | -8(1) |
| C(12) | 38(2) | 33(1) | 46(2) | 16(1) | -3(1) | 0(1) |
| C(13) | 46(2) | 25(1) | 47(2) | 5(1) | 4(1) | 0(1) |
| C(14) | 37(1) | 27(1) | 34(1) | 5(1) | 3(1) | -5(1) |
| C(15) | 56(2) | 31(1) | 39(2) | -4(1) | -4(1) | 3(1) |
| C(16) | 73(2) | 41(2) | 50(2) | -9(1) | 10(2) | -11(2) |
| C(17) | 58(2) | 60(2) | 66(2) | -20(2) | -3(2) | -17(2) |
| C(18) | 37(1) | 44(2) | 22(1) | 2(1) | -8(1) | -8(1) |
| C(19) | 51(2) | 47(2) | 25(1) | -5(1) | -8(1) | -4(1) |
| C(20) | 67(2) | 53(2) | 30(2) | -13(1) | -9(1) | 7(2) |
| C(21) | 94(3) | 81(2) | 39(2) | -19(2) | -1(2) | 28(2) |
| C(22) | 99(3) | 47(2) | 62(2) | -13(2) | -27(2) | -7(2) |
| C(23) | 61(2) | 66(2) | 27(2) | -6(1) | -4(1) | -3(2) |
| C(24) | 69(2) | 72(2) | 24(2) | 11(1) | -7(1) | -8(2) |
| C(25) | 54(2) | 54(2) | 33(2) | 12(1) | -10(1) | -2(1) |
| C(26) | 36(1) | 44(2) | 30(1) | 5(1) | -9(1) | -5(1) |
| C(27) | 37(2) | 41(1) | 36(2) | 7(1) | -8(1) | -2(1) |
| C(28) | 42(2) | 68(2) | 64(2) | 2(2) | -13(2) | 5(2) |
| C(29) | 53(2) | 45(2) | 48(2) | 6(1) | -7(1) | -4(1) |
| C(30) | 29(1) | 35(1) | 31(1) | 1(1) | 9(1) | 3(1) |
| C(31) | 43(2) | 37(2) | 44(2) | -4(1) | 4(1) | 5(1) |
| C(32) | 46(2) | 54(2) | 33(2) | 1(1) | 17(1) | 3(1) |
| C(33) | 28(1) | 33(1) | 35(1) | 2(1) | 2(1) | 1(1) |
| C(34) | 37(1) | 33(1) | 36(1) | 6(1) | -3(1) | 3(1) |
| C(35) | 30(2) | 57(2) | 62(2) | 6(2) | 5(1) | -2(1) |
| C(36) | 27(1) | 23(1) | 24(1) | -2(1) | 3(1) | 0(1) |
| C(37) | 28(1) | 33(1) | 21(1) | -2(1) | 1(1) | 1(1) |
| C(38) | 26(1) | 38(1) | 28(1) | -2(1) | 4(1) | 1(1) |
| C(39) | 31(1) | 49(2) | 44(2) | -9(1) | 6(1) | -7(1) |
| C(40) | 25(1) | 64(2) | 57(2) | -7(2) | 1(1) | 7(1) |
| C(41) | 37(2) | 55(2) | 58(2) | 1(2) | 2(1) | 16(1) |
| C(42) | 35(2) | 35(1) | 43(2) | -1(1) | 3(1) | 4(1) |
| C(43) | 32(1) | 22(1) | 25(1) | -1(1) | 0(1) | -1(1) |
| C(44) | 34(1) | 38(1) | 30(1) | -6(1) | 2(1) | 0(1) |
| C(45) | 49(2) | 47(2) | 29(1) | -10(1) | 3(1) | 0(1) |
| C(46) | 51(2) | 39(2) | 32(2) | -5(1) | -11(1) | -7(1) |
| C(47) | 32(1) | 33(1) | 39(2) | 2(1) | -8(1) | -6(1) |
| C(48) | 30(1) | 30(1) | 30(1) | 2(1) | 1(1) | -3(1) |
| C(49) | 34(1) | 40(2) | 43(2) | 0(1) | -3(1) | 2(1) |
| C(50) | 33(1) | 40(2) | 38(2) | -2(1) | 0(1) | -3(1) |
| C(51) | 43(2) | 45(2) | 48(2) | -7(1) | -6(1) | 3(1) |
| C(52) | 40(2) | 49(2) | 61(2) | -8(2) | 2(1) | 4(1) |
| C(53) | 43(2) | 48(2) | 54(2) | -15(1) | 13(1) | -8(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(54) | 51(2) | 52(2) | 38(2) | -6(1) | 2(1) | -10(1) |
| C(55) | 42(2) | 41(2) | 41(2) | 0(1) | -1(1) | -5(1) |
| C(56) | 38(2) | 48(2) | 41(2) | -6(1) | 3(1) | 1(1) |
| C(57) | 55(2) | 59(2) | 44(2) | -5(2) | 2(1) | 0(2) |
| C(58) | 69(2) | 66(2) | 49(2) | 5(2) | 7(2) | -1(2) |
| C(59) | 67(2) | 85(3) | 38(2) | 2(2) | 1(2) | 14(2) |
| C(60) | 65(2) | 78(2) | 44(2) | -4(2) | -4(2) | -4(2) |
| C(61) | 53(2) | 56(2) | 40(2) | -5(1) | -3(1) | 0(1) |

## X-ray structure of $[PhC(OBpin)]_2$

Table S6. Crystal data and structure refinement for $[PhC(OBpin)]_2$.

| | | |
|---|---|---|
| Empirical formula | $C_{26}H_{36}B_2O_6$ | |
| Formula weight | 466.17 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | Monoclinic, P 1 $2_1$/n 1 | |
| Unit cell dimensions | $a$ = 8.2719(2) Å | $\alpha$ = 90° |
| | $b$ = 9.9302(2) Å | $\beta$ = 102.8300(10)° |
| | $c$ = 15.8441(3) Å | $\gamma$ = 90° |
| Volume | 1268.97(5) Å$^3$ | |
| Z | 2 | |
| Calculated density | 1.220 mg.m$^{-3}$ | |
| Absorption coefficient | 0.083 mm$^{-1}$ | |
| F(000) | 500 | |
| Crystal size | 0.60 x 0.60 x 0.60 mm | |
| $\theta$ range for data collection | 4.53 to 27.48° | |
| Limiting indices | -10<=h<=10, -12<=k<=12, -20<=l<=20 | |
| Reflections collected / unique | 21410 / 2878 [$R$(int) = 0.0307] | |
| Completeness to $\theta$ = 27.48 | 99.2 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9516 and 0.9516 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2878 / 0 / 158 | |
| Goodness-of-fit on $F^2$ | 1.070 | |
| Final $R$ indices [I>2$\sigma$(I)] | $R_1$ = 0.0469, w$R_2$ = 0.1190 | |
| $R$ indices (all data) | $R_1$ = 0.0520, w$R_2$ = 0.1233 | |
| Largest diff. peak and hole | 0.421 and -0.263 e.Å$^3$ | |

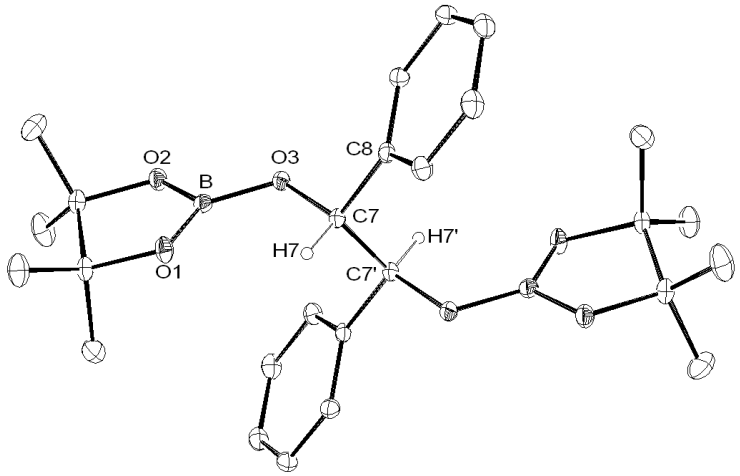



**Fig S1.** ORTEP representation of $[PhC(OBpin)]_2$. Thermal ellipsoids at 20% probability. Hydrogen atoms omitted except that attached to C(7). Selected bond lengths (Å) and angles (o): B-O(3) 1.3709(17), O(3)-C(7) 1.4272(15), C(7)-C(8) 1.5160(17), C(7)-C(7') 1.546(2); O(3)-C(7)-C(8) 109.67(10), O(3)-C(7)-C(7') 106.86(12), C(8)-C(7)-C(7') 112.12(12).

Table S7. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for [PhC(OBpin)]$_2$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalised $U_{ij}$ tensor.

| | x | y | z | $U_{(eq)}$ |
|---|---|---|---|---|
| B | 733(2) | 3221(2) | 3743(1) | 25(1) |
| O(1) | -385(1) | 3674(1) | 3034(1) | 33(1) |
| O(2) | 1330(1) | 1961(1) | 3673(1) | 32(1) |
| O(3) | 1290(1) | 3957(1) | 4482(1) | 27(1) |
| C(1) | -810(2) | 2514(1) | 2452(1) | 29(1) |
| C(2) | -2430(2) | 1949(2) | 2604(1) | 44(1) |
| C(3) | -1040(3) | 3001(2) | 1526(1) | 45(1) |
| C(4) | 704(2) | 1551(2) | 2776(1) | 32(1) |
| C(5) | 233(3) | 72(2) | 2785(1) | 54(1) |
| C(6) | 2103(3) | 1741(3) | 2316(1) | 60(1) |
| C(7) | 458(2) | 5161(1) | 4637(1) | 23(1) |
| C(8) | 1708(2) | 6288(1) | 4887(1) | 24(1) |
| C(9) | 3342(2) | 6009(1) | 5299(1) | 28(1) |
| C(10) | 4481(2) | 7049(2) | 5533(1) | 33(1) |
| C(11) | 4001(2) | 8372(2) | 5363(1) | 35(1) |
| C(12) | 2377(2) | 8666(2) | 4952(1) | 36(1) |
| C(13) | 1232(2) | 7623(1) | 4714(1) | 30(1) |

Table S8. Bond lengths [Å] for $[PhC(OBpin)]_2$.

| | |
|---|---|
| B-O(2) | 1.3584(18) |
| B-O(1) | 1.3634(18) |
| B-O(3) | 1.3709(17) |
| O(1)-C(1) | 1.4684(15) |
| O(2)-C(4) | 1.4595(16) |
| O(3)-C(7) | 1.4272(15) |
| C(1)-C(3) | 1.5172(19) |
| C(1)-C(2) | 1.520(2) |
| C(1)-C(4) | 1.568(2) |
| C(2)-H(2A) | 0.9800 |
| C(2)-H(2B) | 0.9800 |
| C(2)-H(2C) | 0.9800 |
| C(3)-H(3A) | 0.9800 |
| C(3)-H(3B) | 0.9800 |
| C(3)-H(3C) | 0.9800 |
| C(4)-C(6) | 1.510(2) |
| C(4)-C(5) | 1.521(2) |
| C(5)-H(5A) | 0.9800 |
| C(5)-H(5B) | 0.9800 |
| C(5)-H(5C) | 0.9800 |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-C(8) | 1.5160(17) |
| C(7)-C(7)#1 | 1.546(2) |
| C(7)-H(7) | 1.0000 |
| C(8)-C(9) | 1.3922(19) |
| C(8)-C(13) | 1.3926(19) |
| C(9)-C(10) | 1.3917(19) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.382(2) |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.388(2) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(13) | 1.397(2) |
| C(12)-H(12) | 0.9500 |
| C(13)-H(13) | 0.9500 |

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

Table S9. Bond angles [°] for $[PhC(OBpin)]_2$.

| | |
|---|---|
| O(2)-B-O(1) | 115.45(12) |
| O(2)-B-O(3) | 120.08(12) |
| O(1)-B-O(3) | 124.45(12) |
| B-O(1)-C(1) | 106.37(10) |
| B-O(2)-C(4) | 106.19(11) |
| B-O(3)-C(7) | 120.67(10) |
| O(1)-C(1)-C(3) | 108.51(11) |
| O(1)-C(1)-C(2) | 106.69(11) |
| C(3)-C(1)-C(2) | 110.22(13) |
| O(1)-C(1)-C(4) | 102.16(10) |

| | |
|---|---|
| C(3)-C(1)-C(4) | 115.45(12) |
| C(2)-C(1)-C(4) | 113.05(12) |
| C(1)-C(2)-H(2A) | 109.5 |
| C(1)-C(2)-H(2B) | 109.5 |
| H(2A)-C(2)-H(2B) | 109.5 |
| C(1)-C(2)-H(2C) | 109.5 |
| H(2A)-C(2)-H(2C) | 109.5 |
| H(2B)-C(2)-H(2C) | 109.5 |
| C(1)-C(3)-H(3A) | 109.5 |
| C(1)-C(3)-H(3B) | 109.5 |
| H(3A)-C(3)-H(3B) | 109.5 |
| C(1)-C(3)-H(3C) | 109.5 |
| H(3A)-C(3)-H(3C) | 109.5 |
| H(3B)-C(3)-H(3C) | 109.5 |
| O(2)-C(4)-C(6) | 106.95(13) |
| O(2)-C(4)-C(5) | 107.20(12) |
| C(6)-C(4)-C(5) | 110.53(15) |
| O(2)-C(4)-C(1) | 103.48(10) |
| C(6)-C(4)-C(1) | 114.11(14) |
| C(5)-C(4)-C(1) | 113.85(13) |
| C(4)-C(5)-H(5A) | 109.5 |
| C(4)-C(5)-H(5B) | 109.5 |
| H(5A)-C(5)-H(5B) | 109.5 |
| C(4)-C(5)-H(5C) | 109.5 |
| H(5A)-C(5)-H(5C) | 109.5 |
| H(5B)-C(5)-H(5C) | 109.5 |
| C(4)-C(6)-H(6A) | 109.5 |
| C(4)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(4)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| O(3)-C(7)-C(8) | 109.67(10) |
| O(3)-C(7)-C(7)#1 | 106.86(12) |
| C(8)-C(7)-C(7)#1 | 112.12(12) |
| O(3)-C(7)-H(7) | 109.4 |
| C(8)-C(7)-H(7) | 109.4 |
| C(7)#1-C(7)-H(7) | 109.4 |
| C(9)-C(8)-C(13) | 118.98(12) |
| C(9)-C(8)-C(7) | 120.68(12) |
| C(13)-C(8)-C(7) | 120.35(12) |
| C(10)-C(9)-C(8) | 120.42(13) |
| C(10)-C(9)-H(9) | 119.8 |
| C(8)-C(9)-H(9) | 119.8 |
| C(11)-C(10)-C(9) | 120.36(14) |
| C(11)-C(10)-H(10) | 119.8 |
| C(9)-C(10)-H(10) | 119.8 |
| C(10)-C(11)-C(12) | 119.88(13) |
| C(10)-C(11)-H(11) | 120.1 |
| C(12)-C(11)-H(11) | 120.1 |
| C(11)-C(12)-C(13) | 119.85(14) |
| C(11)-C(12)-H(12) | 120.1 |
| C(13)-C(12)-H(12) | 120.1 |
| C(8)-C(13)-C(12) | 120.51(13) |
| C(8)-C(13)-H(13) | 119.7 |
| C(12)-C(13)-H(13) | 119.7 |

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

Table S10. Anisotropic displacement parameters ($A^2$ x $10^3$) for $[PhC(OBpin)]_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| B | 25(1) | 26(1) | 26(1) | -1(1) | 9(1) | -2(1) |
| O(1) | 45(1) | 23(1) | 27(1) | -6(1) | 4(1) | 3(1) |
| O(2) | 35(1) | 29(1) | 30(1) | -8(1) | 3(1) | 4(1) |
| O(3) | 25(1) | 26(1) | 29(1) | -7(1) | 4(1) | 2(1) |
| C(1) | 41(1) | 24(1) | 23(1) | -6(1) | 8(1) | -2(1) |
| C(2) | 40(1) | 51(1) | 40(1) | -7(1) | 7(1) | -9(1) |
| C(3) | 71(1) | 38(1) | 26(1) | 1(1) | 9(1) | 2(1) |
| C(4) | 41(1) | 31(1) | 26(1) | -7(1) | 9(1) | 0(1) |
| C(5) | 81(1) | 28(1) | 45(1) | -5(1) | -4(1) | 4(1) |
| C(6) | 52(1) | 84(2) | 51(1) | -12(1) | 28(1) | 7(1) |
| C(7) | 24(1) | 22(1) | 22(1) | -5(1) | 5(1) | 0(1) |
| C(8) | 29(1) | 24(1) | 20(1) | -3(1) | 8(1) | -4(1) |
| C(9) | 28(1) | 28(1) | 29(1) | -2(1) | 9(1) | -2(1) |
| C(10) | 28(1) | 39(1) | 34(1) | -5(1) | 9(1) | -8(1) |
| C(11) | 42(1) | 34(1) | 33(1) | -5(1) | 15(1) | -17(1) |
| C(12) | 51(1) | 24(1) | 34(1) | 0(1) | 12(1) | -6(1) |
| C(13) | 36(1) | 27(1) | 28(1) | 0(1) | 5(1) | -1(1) |

## References

1. Dove, A. P.; Gibson, V. C.; Hormnirun, P.; Marshall, E. L.; Segal, J. A.; White, A. J. P.; Williams, D. J. *Dalton. Trans.* **2003**, 3088.
2. Hill, M. S.; MacDougall, D. J.; Mahon, M. F. *Dalton Trans.*, **2010**, *39*, 11129
3. DENZO-SCALEPACK Otwinowski, Z.; Minor, W. "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p.307-326, **1997**, C.W. Carter, Jr. & R. M. Sweet, Eds., Academic Press.
4. Farrugia, L.J. *J. Appl. Cryst.* **1999**, *32*, 837.
5. Green, S. P.; Jones, C.; Stasch, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 9079.