Electronic supplementary information (ESI) for

Lithium amide catalyzed hydroboration of nitriles

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General

All experiments for air-sensitive compounds were performed under an atmosphere of dry argon, by using standard Schlenk and glovebox techniques.

Chemicals and Solvents: Commercially available liquid nitriles were distilled under reduced pressure prior use. Solvents (n-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å). Crystalline LiN(SiMe$_3$)$_2$ (Sigma-Aldrich, 97%), was used as received. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (HBpin) was purchased from Sigma-Aldrich (97%) and stored at -30 °C in argon filled Glovebox. Solvents used for GC were distilled under reduced pressure prior use (ethyl acetate).

$^1$H-NMR, $^{13}$C-NMR, $^{11}$B-NMR and $^{19}$F-NMR Spectroscopy: Nuclear magnetic resonance spectra were recorded on a Bruker Avance 400 (400 MHz), Bruker Avance 400 (400 MHz) and Bruker Avance 600 (600 MHz). $^1$H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartet. Chemical shift $\delta$ is given in ppm to residual solvent peak.

Gas chromatography with FID (GC-FID): HP6890 GC-System with injector 7683B and Agilent 7820A System. Column: HP-5, 19091J-413 (30 m × 0.32 mm × 0.25 μm), carrier gas: N$_2$. GC-FID was used for kinetic studies. Calibration with internal standard n-pentadecane and analytically pure samples.

Gas chromatography with mass-selective detector (GC-MS): Agilent 6890N Network GC-System, mass detector 5975 MS. Column: HP-5MS (30 m × 0.25 mm × 0.25 μm, 5% phenylmethylsiloxane, carrier gas: H$_2$. Standard heating procedure: 50 °C (2 min), 25 °C/min -> 300 °C (5 min).

General method for catalytic hydroboration reactions: In an argon-filled glovebox, a flame-dried 4 mL reaction vial was charged with Li(hmds) (0.02 mmol), the substrate (0.2 mmol), C$_6$D$_6$ (0.6 ml) and hexamethylbenzene (0.02 mmol) as internal standard for NMR quantification. HBpin (0.43 mmol) was added to the reaction mixture and stirred at RT for 20h. The reaction mixture was transferred in J.Young NMR tube and the yield was calculated by $^1$H-NMR spectroscopy. The same reaction mixture was heated at 50 °C or 70 °C for 20 h to get higher yield for selected substrates.

Kinetic experiments

In a glovebox 4-methoxybenzonitrile (0.5 mmol) and desired amount of Li(hmds) (0.0286 mmol, 0.04 mmol, 0.05 mmol, 0.0747 mmol, 0.099 mmol) were mixed in a reaction vial (4 ml). 2.5 ml toluene, 50 μl pentadecane and 152 μl (1.047 mmol) HBpin were added to the reaction vial. Certain amount of aliquot was quenched by p-toluenesulfonic acid at a regular time intervals. The aliquot was work up with aq. NaHCO$_3$/EtOAc. The ethyl acetate part was dried over anhydrous Na$_2$SO$_4$ followed by conversion of 4-methoxybenzonitrile was monitored by GC-FID. The data point is taken up to ca. 20 % conversion of 4-methoxybenzonitrile. To determine the order of reaction with respect to 4-methoxybenzonitrile and HBpin we have varied the concentration of respective reagent keeping the concentrations of other reagents constant.
X-ray crystallography

Experimental of N-(2-fluorobenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine

Single clear colourless block-shaped crystals of N-(2-fluorobenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine were obtained by crystallisation from hexane at -30 °C. A suitable crystal 0.32×0.28×0.12 mm$^3$ was selected and mounted on a suitable support on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at a steady $T = 100.2(5)$ K during data collection. The structure was solved with the ShelX (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2016/6 of ShelXL (Sheldrick, 2015) using Least Squares minimisation.

Experimental of N-(cyclopropylmethyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine

Single clear colourless needle-shaped crystals of N-(cyclopropylmethyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine were obtained by recrystallisation from hexane at -30 °C. A suitable crystal 0.18×0.10×0.02 mm$^3$ was selected and mounted on a suitable support on an SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady $T = 100.4(8)$ K during data collection. The structure was solved with the ShelX (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2016/6 of ShelXL (Sheldrick, 2015) using Least Squares minimisation.

Experimental of [C$_6$H$_5$C(NSiMe$_3$)$_2$•NCC$_6$H$_5$]$_2$

Single clear colourless block-shaped crystals of [C$_6$H$_5$C(NSiMe$_3$)$_2$•NCC$_6$H$_5$]$_2$ were obtained by recrystallisation from hexane at -30 °C. A suitable crystal 0.25×0.12×0.11 mm$^3$ was selected and mounted on a suitable support on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady $T = 99.97(17)$ K during data collection. The structure was solved with the ShelX (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2016/6 of ShelXL (Sheldrick, 2015) using Least Squares minimisation.
Fig. S1a: $^{11}$B-NMR spectrum of the reaction mixture of LiN(TMS)$_2$+HBpin (1:1) in C$_6$D$_6$.

Fig. S1b: $^1$H-NMR spectra of Li(hmds) (top), (Me$_3$Si)$_2$N-Bpin (middle) and the reaction mixture of Li(hmds)+HBpin (1:1) in C$_6$D$_6$. 
Fig. S2a: Final $^{11}$B-NMR spectra of the catalytic reactions. The description of each reaction is mentioned in the respective spectrum.
Fig. S2b: Final $^1$H-NMR spectrum of the catalytic reaction mixture between Li(hmds), HBpin and PhCN.

Fig. S3: $^{11}$B-NMR spectrum of the equimolar mixture of Li(hmds), HBpin and PhCN in C$_6$D$_6$.

Fig. S4. Molecular view of $[C_6H_5C(NSiMe_3)_2 \bullet NCC_6H_5]_2$
Fig. S5. $^1$H-NMR spectra of the mixture of Li(hmds)+PhCN (1:2), after 1 h (top), after 24 h (middle) and isolated $[\text{PhC}^2\text{Li}^\cdot\text{NCC}_6\text{H}_5]^2_2$ (bottom) in $\text{C}_6\text{D}_6$.

Fig. S6: $^{11}$B-NMR spectrum of the reaction mixture of $[\text{C}_6\text{H}_5\text{C}^2\text{Li}^\cdot\text{NCC}_6\text{H}_5]^2_2$+HBpin (1:1) in $\text{C}_6\text{D}_6$. 
Kinetic data for Li(hmds) catalysed hydroboration of 4-Metoxybenzonitrile

Determination of reaction order with respect to Li(hmds). The reaction conditions are mentioned in the respective figure.

<table>
<thead>
<tr>
<th>Catalyst (mmol)</th>
<th>4-Methoxybenzonitrile (mmol)</th>
<th>HBpin (mmol)</th>
<th>ln([Li(hmds)])</th>
<th>ln([HBpin])</th>
<th>ln(kobs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0286</td>
<td>0.00833</td>
<td>-3.55435</td>
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<tr>
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<td>0.0507</td>
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<td>0.099</td>
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<td></td>
</tr>
</tbody>
</table>

Slope = 1.12
Fig. S8: Determination of reaction order with respect to HBpin. The reaction conditions are mentioned in the respective figure.
The reaction order with respect to 4-methoxybenzonitrile. The reaction conditions are mentioned in the respective figure.

<table>
<thead>
<tr>
<th>4-Methoxybenzonitrile (mmol)</th>
<th>$k_{obs}/min$</th>
<th>$\ln([4\text{-}\text{Methoxybenzonitrile}])$</th>
<th>$\ln(k_{obs})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.467</td>
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<td>0.6</td>
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<td>0.755</td>
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<td>-0.28104</td>
<td>-3.68489</td>
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<td>0.9</td>
<td>0.02691</td>
<td>-0.10536</td>
<td>-3.61526</td>
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</tbody>
</table>

Slope = 0.87
Kinetic data for \([C_6H_5C(\text{NSiMe}_3)_2\text{Li}\cdot\text{NCC}_6H_5]_2\) catalysed hydromoration of 4-Methoxybenzonitrile

### Fig. S10: Determination of reaction order with respect to \([C_6H_5C(\text{NSiMe}_3)_2\text{Li}\cdot\text{NCC}_6H_5]_2\)

#### (a) and (b)

- Catalyst: 0.01338 mmol
- 4-Methoxybenzonitrile: 0.5 mmol
- HBpin = 1.047 mmol

#### (c) and (d)

- Catalyst: 0.02489 mmol
- 4-Methoxybenzonitrile: 0.5 mmol
- HBpin = 1.047 mmol

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**Plot of \(k_{\text{obs}}/\text{min} vs [C_6H_5C(\text{NSiMe}_3)_2\text{Li}\cdot\text{NCC}_6H_5]_2]/\text{mM}**

<table>
<thead>
<tr>
<th>Li-amidate (mmol)</th>
<th>(k_{\text{obs}}/\text{min})</th>
<th>(\ln([\text{Li-amidate}]))</th>
<th>(\ln(k_{\text{obs}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01338</td>
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<td>0.02489</td>
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<td>-4.69329</td>
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<td>0.04965</td>
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<td>-3.75331</td>
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**Slope = 1.03**

**Plot of \(\ln(k_{\text{obs}})\) vs \(\ln([C_6H_5C(\text{NSiMe}_3)_2\text{Li}\cdot\text{NCC}_6H_5]_2])\)**

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Fig. S10: Determination of reaction order with respect to \([C_6H_5C(\text{NSiMe}_3)_2\text{Li}\cdot\text{NCC}_6H_5]_2\). The reaction conditions are mentioned in the respective figure.
Reduction of ethylbenzoate in absence or presence of acetonitrile

**Reaction condition:** In an argon-filled glovebox, a flame-dried 4 mL reaction vial was charged with ethylbenzoate (0.2 mmol), toluene (1 ml) and pentadecane as internal standard for GC. HBpin (0.4 mmol) was added to the reaction mixture. A stock solution of CH$_3$CN (varying quantity) and Li(hmds) (0.02 mmol) were added to the reaction mixture. Blank experiment was performed without catalyst and CH$_3$CN. In a separate reaction vial [C$_6$H$_5$C(NSiMe$_3$)$_2$Li•NCC$_6$H$_5$]$_2$ (5 mol% i.e. 10 mol% w.r.t Li) was added as catalyst. The reaction mixtures were stirred for 15 minutes and quenched with H$_2$O and extracted with ethyl acetate. The ethyl acetate part was dried over anhydrous Na$_2$SO$_4$ followed by conversion of ethylbenzoate was quantified by GC-FID.

![Fig. S11: Conversion of ethylbenzoate in absence of presence of CH$_3$CN.](image)

Fig. S11: Conversion of ethylbenzoate in absence of presence of CH$_3$CN.
Crystallographic data and refinement parameters of 2o, 2w and $[C_6H_5C(NSiMe_3)_2\cdot[NC_6H_5]_2]_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2o</th>
<th>2w</th>
<th>$[C_6H_5C(NSiMe_3)_2\cdot[NC_6H_5]_2]_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_{19}H_{30}B_2FNO_4$</td>
<td>$C_{64}H_{124}B_8N_4O_{16}$</td>
<td>$C_{40}H_{56}Li_2N_6Si_4$</td>
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<tr>
<td>CCDC number</td>
<td>1954455</td>
<td>1954454</td>
<td>1954456</td>
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<tr>
<td>$D_{calc}$/ g cm$^{-3}$</td>
<td>1.184</td>
<td>1.135</td>
<td>1.095</td>
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<td>$\mu$/mm$^{-1}$</td>
<td>0.699</td>
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<tr>
<td>Formula Weight</td>
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<td>Colour</td>
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<td>clear colourless</td>
<td>clear colourless</td>
</tr>
<tr>
<td>Shape</td>
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<td>block</td>
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<tr>
<td>Size/mm$^3$</td>
<td>0.32×0.28×0.12</td>
<td>0.18×0.10×0.02</td>
<td>0.25×0.12×0.11</td>
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<tr>
<td>$T$/K</td>
<td>100.2(5)</td>
<td>100.4(8)</td>
<td>99.97(17)</td>
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<tr>
<td>Crystal System</td>
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<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P2_1/n$</td>
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<tr>
<td>$a$/Å</td>
<td>10.01437(11)</td>
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<td>9.92510(10)</td>
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<td>$b$/Å</td>
<td>11.94446(13)</td>
<td>11.85320(10)</td>
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<td>$c$/Å</td>
<td>17.7398(2)</td>
<td>12.99940(10)</td>
<td>19.6197(2)</td>
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<tr>
<td>$\alpha'$</td>
<td>90</td>
<td>90</td>
<td>98.2060(10)</td>
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<tr>
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<td>94.7737(10)</td>
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<td>90</td>
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<td>CuK$\alpha$</td>
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<td>$\Theta$max/f</td>
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<td>76.171</td>
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<tr>
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<td>Independent Refl.</td>
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<td>Largest Peak</td>
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<td>GooF</td>
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<td>$wrR_2$ (all data)</td>
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<tr>
<td>$wrR_2$</td>
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<td>0.0841</td>
<td>0.0882</td>
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<tr>
<td>$R_1$ (all data)</td>
<td>0.0342</td>
<td>0.0356</td>
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<tr>
<td>$R_1$</td>
<td>0.0330</td>
<td>0.0332</td>
<td>0.0350</td>
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</table>
Fig. S12: ORTEP of 2o.

Fig. S13: ORTEP of 2w.
Characterization Data

\[
\begin{align*}
\text{H NMR (400.13 MHz, C}_6\text{D}_6\text{) } & \delta 7.58 (2H, m), 7.25 (2H, m), 7.11 (1H, m), 4.60 (2H, s), 1.03 (24H, s) \\
\text{C NMR (100.62 MHz, C}_6\text{D}_6\text{) } & \delta 143.8, 128.4, 126.6, 82.6, 47.9, 24.7. \\
\text{B NMR (128.38 MHz, C}_6\text{D}_6\text{) } & \delta 26.1
\end{align*}
\]


\[
\begin{align*}
\text{H NMR (400.13 MHz, C}_6\text{D}_6\text{) } & \delta 7.63 (1H, d, J = 7.7 Hz), 7.24 (1H, t, J = 7.2 Hz), 7.07 (1H, t, J = 7.2 Hz) (this peak merged with unreacted starting material), 6.99 (1H, d, J = 7.4 Hz), 4.60 (2H, s), 2.13 (3H, s), 1.04 (24H, s). \\
\text{C NMR (150.92 MHz, C}_6\text{D}_6\text{) } & \delta 141.2, 135.3, 130.1, 126.2, 126.0, 125.8, 82.6, 45.4, 24.7, 19.1. \\
\text{B NMR (128.38 MHz, C}_6\text{D}_6\text{) } & \delta 26.2
\end{align*}
\]


\[
\begin{align*}
\text{H NMR (400.13 MHz, C}_6\text{D}_6\text{) } & \delta 7.51 (2H, d, J = 7.7 Hz), 7.07 (2H, d, J = 7.8 Hz), 4.59 (2H, s), 2.15 (3H, s), 1.04 (24H, s). \\
\text{C NMR (100.62 MHz, C}_6\text{D}_6\text{) } & \delta 140.9, 135.7, 129.1, 128.1, 82.5, 47.6, 24.8, 21.2 \\
\text{B NMR (128.38 MHz, C}_6\text{D}_6\text{) } & \delta 25.7
\end{align*}
\]


\[
\begin{align*}
\text{H NMR (400.13 MHz, C}_6\text{D}_6\text{) } & \delta 7.56 (2H, d, J = 8.5 Hz), 6.87 (2H, d, J = 8.7 Hz), 4.57 (2H, s), 3.36 (3H, s), 1.06 (24H, s). \\
\text{C NMR (100.62 MHz, C}_6\text{D}_6\text{) } & \delta 159.0, 136.1, 129.5, 113.9, 82.5, 54.8, 47.3, 24.7 \\
\text{B NMR (128.38 MHz, C}_6\text{D}_6\text{) } & \delta 26.5
\end{align*}
\]
1H NMR (400.13 MHz, C6D6) δ 7.43 (1H, d, J = 7 Hz), 7.39 (1H, s) 7.20 (1H, t, J = 7.4 Hz), 6.96 (1H, d, J = 8 Hz), 4.60 (2H, s), 2.20 (3H, s), 1.05 (24H, s).

13C NMR (150.92 MHz, C6D6) 143.7, 137.5, 129.0, 127.4, 125.1, 82.6, 47.8, 24.

11B NMR (128.38 MHz, C6D6) δ 26.5


\[ \text{N(Bpin)_2} \]

1H NMR (400.13 MHz, C6D6) δ 7.35 (1H, d, J = 10.2 Hz), 7.23 (1H, d, J = 7.6 Hz), 7.03-6.98 (1H, m), 6.78-6.75 (1H, m) 4.48 (2H, s), 1.01 (24H, s).

13C NMR (100.62 MHz, C6D6) δ 164.73-162.30 (JCF = 244 Hz), 146.62-146.55 (JCF = 7 Hz), 129.81-129.73 (JCF = 8 Hz), 123.64, 115.08-114.83 (JCF = 20 Hz), 82.73, 47.49, 24.72 ppm

11B NMR (128.38 MHz, C6D6) δ 26.4


\[ \text{N(Bpin)_2} \]

1H NMR (400.13 MHz, C6D6) δ 7.35 (1H, d, J = 10.2 Hz), 7.23 (1H, d, J = 7.6 Hz), 7.03-6.98 (1H, m), 6.78-6.75 (1H, m) 4.48 (2H, s), 1.01 (24H, s).

13C NMR (100.62 MHz, C6D6) δ 164.73-162.30 (JCF = 244 Hz), 146.62-146.55 (JCF = 7 Hz), 129.81-129.73 (JCF = 8 Hz), 123.64, 115.08-114.83 (JCF = 20 Hz), 82.73, 47.49, 24.72 ppm

19F NMR (564.68 MHz, C6D6) δ –113.9

\[
\begin{align*}
1^1\text{H NMR} & \ (400.13 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 7.56 \ (1\text{H}, t, J = 7.6 \text{ Hz}), \ 6.96 \ (1\text{H}, t, J = 7.5 \text{ Hz}), \ 6.91-6.79 \ (m, \text{2H}), \ 4.78 \ (2\text{H}, \text{s}), \ 1.02 \ (24\text{H}, \text{s}) \\
\end{align*}
\]

\[
\begin{align*}
13^1\text{C NMR} & \ (100.62 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 162.4-159.96 \ (J_{\text{CF}} = 245 \text{ Hz}), \ 130.62-130.47 \ (J_{\text{CF}} = 15 \text{ Hz}), \ 128.71-128.67 \ (J_{\text{CF}} = 4 \text{ Hz}), \ 123.84-123.81 \ (J_{\text{CF}} = 3 \text{ Hz}), \ 115.28-115.07 \ (J_{\text{CF}} = 21 \text{ Hz}), \ 82.7, \ 41.7, \ 24.6. \\
\end{align*}
\]

\[
\begin{align*}
11^1\text{B NMR} & \ (128.38 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 26.1 \text{ ppm} \\
19^1\text{F NMR} & \ (564.68 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ -118.2 \text{ ppm} \\
\end{align*}
\]

**Scale up:** 16.7 mg Li(hmds) (10 mol% with respect to substrate) was dissolved in 3 ml toluene. To this solution 305 µl HBpin (2.1 equivalent with respect to substrate) and 108.5 µl (1 mmol) 2-fluorobenzonitrile were added respectively. The solution was stirred for 20 h. The solution was evaporated to dryness. The solid compound was dissolved in hexane (2 ml), filtered and evaporated to dryness. The isolated crude yield is 93% (352 mg). The crude product was dissolved in 1 ml hexane and kept at -30 °C for overnight. Colourless crystal were formed and the yield of the crystal is 73% (275 mg).

\[
\begin{align*}
1^1\text{H NMR} & \ (400.13 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 7.41 \ (s, \text{4H}), \ 4.47 \ (2\text{H}, \text{s}), \ 1.01 \ (24\text{H}, \text{s}) \\
\end{align*}
\]

\[
\begin{align*}
13^1\text{C NMR} & \ (100.62 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 147.7, \ 129.0, \ 128.8, \ 128.2, \ 126.3, \ 125.3 \ (m), \ 124.2, \ 82.8, \ 47.5, \ 24.7 \text{ ppm} \\
11^1\text{B NMR} & \ (128.38 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 25.8 \\
19^1\text{F NMR} & \ (564.68 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ -61.9 \\
\end{align*}
\]


\[
\begin{align*}
1^1\text{H NMR} & \ (400.13 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 7.42-7.39 \ (m, \text{2H}), \ 6.96 \ (2\text{H}, t, J = 8.6 \text{ Hz}), \ 4.45 \ (2\text{H}, \text{s}), \ 1.02 \ (24\text{H}, \text{s}) \\
\end{align*}
\]

\[
\begin{align*}
13^1\text{C NMR} & \ (100.62 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 162.3-161 \ (J_{\text{CF}} = 243 \text{ Hz}), \ 139.5 \ (J_{\text{CF}} = 3 \text{ Hz}), \ 129.8 \ (m), \ 115.1 \ (m), \ 82.6, \ 47.1, \ 24.7 \text{ ppm} \\
11^1\text{B NMR} & \ (128.38 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ 26.6 \\
19^1\text{F NMR} & \ (564.68 \text{ MHz}, \text{C}_6\text{D}_6) \ \delta \ -116.9 \\
\end{align*}
\]

$^1$H NMR (400.13 MHz, C$_6$D$_6$) δ 7.34 (2H, d, $J = 8.3$ Hz), 7.19 (2H, d, $J = 8.3$ Hz), 4.43 (2H, s), 1.02 (24H, s).

$^{13}$C NMR (100.62 MHz, C$_6$D$_6$) δ 142.3, 132.5, 129.6, 128.5, 82.7, 47.2, 24.7 ppm

$^{11}$B NMR (128.38 MHz, C$_6$D$_6$) δ 25.9 ppm

Data are in accordance with the reported values: C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot, M. F. Mahon, Chem. Sci., 2016, 7, 628–641.

![Chemical structure](image1)

$^1$H NMR (400.13 MHz, C$_6$D$_6$) δ 7.33 (2H, d, $J = 8$ Hz), 7.27 (2H, d, $J = 8$ Hz), 4.41 (2H, s), 1.02 (24H, s).

$^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 142.7, 131.5, 129.9, 120.6, 82.7, 47.2, 24.7 ppm

$^{11}$B NMR (128.38 MHz, C$_6$D$_6$) δ 26.2 ppm

Data are in accordance with the reported values: S. Saha, M. S. Eisen, ACS Catal., 2019, 9, 5947-5956

![Chemical structure](image2)

$^1$H NMR (400.13 MHz, C$_6$D$_6$) δ 7.52 (2H, d, $J = 8.5$ Hz), 7.14 (2H, d, $J = 8.5$ Hz), 4.40 (2H, s), 1.01 (24H, s).

$^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 143.4, 137.5, 130.2, 92.0, 82.7, 47.3, 24.7 ppm

$^{11}$B NMR (128.38 MHz, C$_6$D$_6$) δ 25.8 ppm

Data are in accordance with the reported values: S. Das, J. Bhattacharjee, T. K. Panda, New J. Chem. 2019, 43, 16812-16818

![Chemical structure](image3)

$^1$H NMR (400.13 MHz, C$_6$D$_6$) δ 7.47 (2H, d, $J = 8$ Hz), 7.20 (2H, d, $J = 8$ Hz), 4.53 (2H, s), 2.03 (3H, s), 1.04 (24H, s).

$^{13}$C NMR (100.62 MHz, C$_6$D$_6$) δ 140.8, 136.8, 128.8, 127.1, 82.6, 47.4, 24.7, 15.8 ppm

$^{11}$B NMR (128.38 MHz, C$_6$D$_6$) δ 25.9 ppm

Data are in accordance with the reported values: S. Das, J. Bhattacharjee, T. K. Panda, New J. Chem., 2019, 43, 16812-16818

![Chemical structure](image4)

$^1$H NMR (400.13 MHz, C$_6$D$_6$) δ 7.59 (2H, d, $J = 8.6$ Hz), 6.69 (2H, d, $J = 8.6$ Hz), 4.60 (2H, s), 2.57 (6H, s), 1.07 (24H, s).

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\[ ^{13}\text{C NMR (100.62 MHz, } C_6D_6\text{)} \delta 149.9, 132.3, 129.3, 113.0, 82.5, 47.4, 40.6, 24.8 \text{ ppm} \]
\[ ^{11}\text{B NMR (128.38 MHz, } C_6D_6\text{)} \delta 25.9 \]


\[ ^{1}\text{H NMR (400.13 MHz, } C_6D_6\text{)} \delta 8.63 (1H, d, J = 6 \text{ Hz}), 7.19 (1H, d, J = 6 \text{ Hz}), 4.42 (2H, s), 1.01 (24H, s). \]
\[ ^{13}\text{C NMR (151 MHz, } C_6D_6\text{)} \delta 151.7, 150.2, 122.4, 82.8, 47.0, 4.7 \]
\[ ^{11}\text{B NMR (128.38 MHz, } C_6D_6\text{)} \delta 25.8 \text{ ppm} \]

Data are in accordance with the reported values: S. Saha, M. S. Eisen, *ACS Catal.*, 2019, **9**, 5947-5956

\[ ^{1}\text{H NMR (400.13 MHz, } C_6D_6\text{)} \delta 7.11-7.10 (m, 1H), 6.92-6.90 (m, 1H), 6.81-6.79 (m, 1H), 4.69 (2H, s), 1.05 (24H, s). \]
\[ ^{13}\text{C NMR (100.62 MHz, } C_6D_6\text{)} \delta 147.3, 126.6, 125.2, 124.2, 82.8, 42.7, 42.8 \]
\[ ^{11}\text{B NMR (128.38 MHz, } C_6D_6\text{)} \delta 26.1 \]


\[ ^{1}\text{H NMR (400.13 MHz, } C_6D_6\text{)} \delta 7.15-7.14 (1H, m), 6.27 (1H, m), 6.17-6.15 (1H, m), 4.58 (2H, s), 1.05 (24H, s). \]
\[ ^{13}\text{C NMR (100.62 MHz, } C_6D_6\text{)} \delta 156.9, 140.9, 110.0, 105.4, 82.3, 40.9, 24.4 \text{ ppm} \]
\[ ^{11}\text{B NMR (128.38 MHz, } C_6D_6\text{)} \delta 26.03 \]


\[ ^{1}\text{H NMR (400.13 MHz, } C_6D_6\text{)} \delta 3.44 (1H, q, J = 6.8 \text{ Hz}), 1.30 (1H, t, J = 6.7 \text{ Hz}), 1.07 (24H, s). \]
\[ ^{13}\text{C NMR (100.62 MHz, } C_6D_6\text{)} \delta 83.1, 39.1, 24.9, 19.2 \]
\[ ^{11}\text{B NMR (128.38 MHz, } C_6D_6\text{)} \delta 26.1 \]

\[ \text{N(Bpin)}_2 \]

\(^1\)H NMR (400.13 MHz, C\(_6\)D\(_6\)) \(\delta \) 3.26 (2H, d, \(J = 7.1 \text{ Hz}\)), 2.09-1.99 (1H, m), 1.08 (24H, s), 1.02 (6H, m)
\(^{13}\)C NMR (100.62 MHz, C\(_6\)D\(_6\)) \(\delta \) 82.2, 51.8, 31.2, 24.8, 20.3.
\(^{11}\)B NMR (128.38 MHz, C\(_6\)D\(_6\)) \(\delta \) 26.2

Data are in accordance with the reported values: C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. Liptrota, M. F. Mahon, Chem. Sci., 2016, 7, 628–641.

\[ \text{N(Bpin)}_2 \]

\(^1\)H NMR (400.13 MHz, C\(_6\)D\(_6\)) \(\delta \) 3.30 (2H, d, \(J = 7 \text{ Hz}\)), 1.91-1.87 (2H, m), 1.74-1.61 (4H, m), 1.31-1.10 (5H, m), 1.08 (24H, s), 0.45-0.43 (4H, m).
\(^{13}\)C NMR (101 MHz, C\(_6\)D\(_6\)) \(\delta \) 82.3, 48.8, 24.8, 14.9, 3.8 ppm.
\(^{11}\)B NMR (128.38 MHz, C\(_6\)D\(_6\)) \(\delta \) 25.9

Data are in accordance with the reported values: C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. Liptrota, M. F. Mahon, Chem. Sci., 2016, 7, 628–641.

\[ \text{N(Bpin)}_2 \]

\(^1\)H NMR (400.13 MHz, C\(_6\)D\(_6\)) \(\delta \) 3.64-3.62 (2H, m), 3.59-3.58 (2H, m), 3.23 (3H, s), 1.07 (24H, s).
\(^{13}\)C NMR (100.62 MHz, C\(_6\)D\(_6\)) \(\delta \) 82.4, 74.6, 58.4, 43.4, 24.7.
\(^{11}\)B NMR (128.38 MHz, C\(_6\)D\(_6\)) \(\delta \) 26.05


Scale up: 16.7 mg Li(hmds) (10 mol% with respect to substrate) was dissolved in 3 ml toluene. To this solution 305 µl HBpin (2.1 equivalent with respect to substrate) and 73.6 µl (1 mmol) 2-cyclopropanecarbonitrile were added. The solution was heated at 50 °C for 20 h. The solvent was removed and dissolved in 2 ml hexane. The hexane solution was filtered and evaporated to dryness. The isolated crude yield 87% (280 mg). The crude product was dissolved in 1 ml hexane and kept at -30 °C for overnight. Colourless crystal were formed and the yield of the isolated compound is 65% (210 mg).
Scale up: 16.7 mg Li(hmds) (10 mol% with respect to substrate) was dissolved in 3 ml toluene. To this solution 305 µl HBpin (2.1 equivalent with respect to substrate) and 105 µl (1 mmol) (S)-(+)-2-methylbutyronitrile were added. The solution was heated at 70 °C for 20 h. The solvent was removed and dissolved in 2 ml hexane. The hexane solution was filtered and evaporated to dryness. The isolated crude yield 70% (semisolid: 240 mg). The characterization data is given below.

\[ \text{H NMR (400.13 MHz, C}_6\text{D}_6\text{)} \delta 3.43-3.25 (2H, m), 1.91-1.82 (1H, m), 1.62-1.55 (1H, m), 1.26-1.19 (1H, m), 1.08 (24H, s), 1.04 (3H, d, } J = 6.8 \text{ Hz), 0.98 (3H, t, } J = 7.4 \text{ Hz).} \]

\[ \text{C NMR (150 MHz, C}_6\text{D}_6\text{)} \delta 82.3, 50.3, 37.9, 27.3, 24.8, 17.3, 11.9 \text{ ppm.} \]

\[ \text{B NMR (128.38 MHz, C}_6\text{D}_6\text{)} \delta 26.3 \]

The crude hydroborylated product (240 mg, 0.7 mmol) is transferred to a Schleck tube in hexane solvent (5 ml). 1 ml hydrochloric acid solution in diethyl ether (1M) was added and the mixture is stirred for approximately 1h at room temperature. A white suspension is formed after addition of hydrochloric acid solution. The volatile are removed under reduced pressure and the solid is filtered and washed with ethyl acetate (10 ml) to wash off impurities. The remaining solid is then flushed with methanol into a separate container and the filtrate is dried under reduced pressure to give a solid (68 mg, 78%).

\[ \text{H NMR (400.13 MHz, D}_2\text{O): } \delta 3.01-2.97 (1H, m), \delta 2.85-2.81 (1H, m) 1.80-1.71 (1H, m), 1.46-1.40 (1H, m), 1.31-1.22 (1H, m), 0.99 (3H, d, } J = 6.8 \text{ Hz), 0.92 (3H, t, } J = 7.2 \text{ Hz).} \]

\[ \text{C NMR (151 MHz, D}_2\text{O)} \delta 44.9, 32.7, 26.2, 16.0, 10.3 \]

\[ \text{H and } ^{13}\text{C Data are in accordance with the reported values: L. Claes, M. Janssen, D. E. De Vos, ChemCatChem, 2019, 11, 4297–4306.} \]

Optical rotation: \( \alpha^{20.7}_{\text{SSS}} +6.3^\circ \) (in methanol).

This value is in well agreement with literature reported value of (S)-(+)2-methylbutylamine: H. Brunner, J. Wachter, J. Schmidbauer, G. M. Sheldrick and P. G. Jones, Organometallics, 1986, 5, 2212-2219.
NMR spectra (in C₆D₆) of hydroborated amine products in the reaction mixture

\[ \text{N} \left( \text{Bpin} \right) \text{N(} \text{Bpin}) \text{2} \]

\(^1\text{H-NMR spectrum, 2a}\)

\[ \text{N} \left( \text{Bpin} \right) \text{N(} \text{Bpin}) \text{2} \]

\(^{13}\text{C-NMR spectrum, 2a}\)
\(^1\)H-NMR spectrum, 2b

\[\text{N(Bpin)}_2\]

\(^{13}\)C-NMR spectrum, 2b
$^{1}H$-NMR spectrum, 2c

$^{13}C$-NMR spectrum, 2c
$\text{MeS} \quad \text{N}(\text{Bpin})_2$

**$^1$H-NMR spectrum, 2d**

$\text{MeS} \quad \text{N}(\text{Bpin})_2$

**$^{13}$C-NMR spectrum, 2d**
$\text{Me}_2\text{N} - \text{N}(\text{Bpin})_2$

$^1\text{H-NMR spectrum, 2e}$

$\text{Me}_2\text{N} - \text{N}(\text{Bpin})_2$

$^{13}\text{C-NMR spectrum, 2e}$
\[ \text{**F**}_{3}\text{C} \quad \begin{array}{c} \text{N(Bpin)}_2 \\ \end{array} \]

**\[^1\text{H-}\text{NMR spectrum, 2f}\]**

\[ \text{\begin{array}{c} \text{F}_{3}\text{C} \\ \text{N(Bpin)}_2 \end{array}} \]

\[ \text{\begin{array}{c} \text{\begin{array}{c} \text{F}_{3}\text{C} \\ \text{N(Bpin)}_2 \end{array}} \end{array}} \]

**\[^{13}\text{C-}\text{NMR spectrum, 2f}\]**
$^{19}$F-NMR spectrum, 2f

$^1$H-NMR spectrum, 2g
$^{13}$C-NMR spectrum, 2g

$^{19}$F-NMR spectrum, 2g
$^{13}$C-NMR spectrum, 2h

$^1$H-NMR spectrum, 2h
$\text{Br} - \text{N}(\text{Bpin})_2$

$^1\text{H-NMR spectrum, 2i}$

$^\text{13}\text{C-NMR spectrum, 2i}$
\( \text{IN (Bpin)}_2 \)

\( ^1\text{H-NMR spectrum, 2j} \)

\( \text{IN (Bpin)}_2 \)

\( ^{13}\text{C-NMR spectrum, 2j} \)
$^1$H-NMR spectrum, 2k

$^1$C-NMR spectrum, 2k
$^1$H-NMR spectrum, 2l

$^{13}$C-NMR spectrum, 2l
$^1$H-NMR spectrum, 2m

$^{13}$C-NMR spectrum, 2m
\[ \text{N}(\text{Bpin})_2 \]

$^{19}\text{F}-\text{NMR}$ spectrum, $2m$

$^1\text{H}-\text{NMR}$ spectrum, $2n$
$\text{\textsuperscript{13}C-NMR spectrum, 2n}$

$\text{\textsuperscript{1}H-NMR spectrum, 2o}$
$^{1}H$-NMR spectrum, $2s$

$^{13}C$-NMR spectrum, $2s$
$N(B\text{pin})_2$

$^1H$-NMR spectrum, 2u

$^13C$-NMR spectrum, 2u
$\text{H-NMR spectrum, 2v}$

$\text{C-NMR spectrum, 2v}$
$^{1}H$-NMR spectrum, 2w

$^{13}C$-NMR spectrum, 2w
$^{1}H$-NMR spectrum, 2r

$^{13}C$-NMR spectrum, 2r
$^3$H-NMR spectrum, 2q

$^{13}$C-NMR spectrum, 2q
$^1$H-NMR spectrum, 2p

$^{13}$C-NMR spectrum, 2p
1H-NMR spectrum, 2t

13C-NMR spectrum, 2t
$^1$H-NMR spectrum, 2x

$^{13}$C-NMR spectrum, 2x

N$(\text{Bpin})_2$
\[ \text{Methanol} \]

$^1$H-NMR of 2x' in D$_2$O

\[ \text{\textbf{H}_{3}\text{Cl}^+} \]

$^1$H-NMR of 2x' in D$_2$O

\[ \text{\textbf{C}_{13}\text{NMR of 2x'} in D}_2\text{O} \]