Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Organocatalytic hydroborylation promoted by *N*-heterocyclic olefins

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Contents

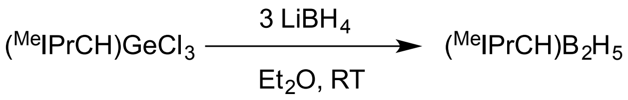
Experimental Procedures:

General. All reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or in an inert atmosphere glovebox (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[1] manufactured by Innovative Technology, Inc., degassed (freeze−pump−thaw method), and stored under an atmosphere of nitrogen prior to use. MeOTf, $Li[BH_4]$, $THF•BH_3$, Ph_2CO, $(4\text{-Cl-Ph})_2CO$, MeCO(Ph), ^tBuCOMe, $4\text{-}CH_3CO\text{-}C_6H_4\text{-}CHO$ and MesCHO were purchased from Aldrich and used as received. $IPrCH_2$,[2] $^{Me}IPrCH_2$,[2] $IPrCHGeCl_3$,[3] $^{Me}IPrCHGeCl_3$,[3] and $(^{Me}IPrCH)SiMe_3$[3] were prepared according to literature procedures. ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra were recorded on a Varian VNMRS-500 spectrometer and referenced externally to $SiMe_4$ (^1H, $^{13}C\{^1H\}$), $F_3B•OEt_2$ (^{11}B), or $CFCl_3$ ($^{19}F\{^1H\}$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp apparatus and are uncorrected.

X-ray Crystallography. Crystals of appropriate quality for X-ray diffraction studies were removed from either a Schlenk tube under a stream of nitrogen, or from a vial (glove box) and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a low-temperature stream of nitrogen. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Cu Kα radiation, with the crystal cooled to −100 °C. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods programs SHELXT-2014,[4] and refinements were completed using the program SHELXL-2014.[4] Hydrogen atoms were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms, and were given thermal parameters 20 % greater than those of their parent atoms.

Synthetic Procedures.

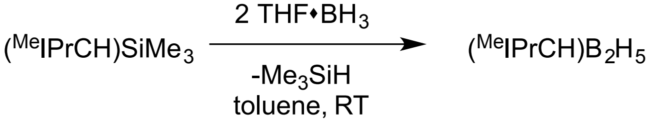
Synthesis of (^{Me}IPrCH)B_2H_5 (3a) from (^{Me}IPrCH)$GeCl_3$.



$$(^{Me}\mathrm{IPrCH})\mathrm{GeCl_3} \xrightarrow[\mathrm{Et_2O,\ RT}]{3\ \mathrm{LiBH_4}} (^{Me}\mathrm{IPrCH})\mathrm{B_2H_5}$$

To a mixture of (^{Me}IPrCH)$GeCl_3$ (0.148 g, 0.24 mmol) and $LiBH_4$ (0.017 g, 0.75 mmol) was added 10 mL of Et_2O at room temperature, which was accompanied by vigorous bubbling. Stirring was continued for 4 hrs. The resulting yellow precipitate was allowed to settle and the supernatant filtered through a plug of Celite. The volatiles were evaporated from the filtrate to give (^{Me}IPrCH)B_2H_5 (**3a**) as an off-white solid (0.093 g, 85 %). X-ray quality crystals of **3a** were obtained by placing a saturated toluene solution layered with hexanes at −30 °C for 24 hrs.

Alternate Synthesis of (^{Me}IPrCH)B_2H_5 (3a) from (^{Me}IPrCH)$SiMe_3$.



$$(^{Me}\mathrm{IPrCH})\mathrm{SiMe_3} \xrightarrow[\substack{\mathrm{-Me_3SiH} \\ \mathrm{toluene,\ RT}}]{2\ \mathrm{THF{\bullet}BH_3}} (^{Me}\mathrm{IPrCH})\mathrm{B_2H_5}$$

To (^{Me}IPrCH)$SiMe_3$ (0.084 g, 0.17 mmol) in 5 mL of toluene was added dropwise THF•BH_3 (1.0 M solution in THF, 0.340 mL, 0.34 mmol) at ambient temperature. After 12 hrs of stirring at room temperature, the resulting mixture was evaporated to dryness, and the remaining residue was washed with hexanes (2 x 3 mL) and the remaining solid dried *in vacuo* to yield (^{Me}IPrCH)B_2H_5 (**3b**) in the form of a colorless solid (0.065 g, 84 %).

^{1}H NMR (498 MHz, C_6D_6): δ = 7.21 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, Ar*H*), 7.07 (d, $^{3}J_{HH}$ = 7.3 Hz, 4H, Ar*H*), 6.06 (s, 2H, N-C*H*), 2.78 (sept, 4H, $^{3}J_{HH}$ = 6.6 Hz, C*H*(CH_3)$_2$), 1.62 (br, 1H, C*H*(B_2H_5)), 1.43 (d, $^{3}J_{HH}$ = 7.3 Hz, 12H, CH(CH_3)$_2$), 1.09 (br, 4H, BH_2), 1.01 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CH(CH_3)$_2$), -0.88 (br, 1H, (BH_2)$_2$-μ-*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 9.3 (H_3*C*-CN), 11.9 (br, C*C*H(B_2H_5)), 24.2 (CH(*C*H_3)$_2$), 24.4 (CH(*C*H_3)$_2$), 29.0 (*C*H(CH_3)$_2$), 55.7 (C*C*HGeCl_3), 122.7 (N*C*-CH_3), 124.7 (Ar*C*), 130.6 (Ar*C*), 131.6 (Ar*C*), 146.7 (ArC), 165.2 (N*C*N). ^{11}B{^{1}H} (159.8 MHz, C_6D_6): δ = -29.0. Anal. calcd. for $C_{30}H_{46}N_2B_2$: C, 78.96; H, 10.16; N, 6.14. Found: C, 77.93; H, 10.30; N, 6.11 %. Mp (°C): 176.

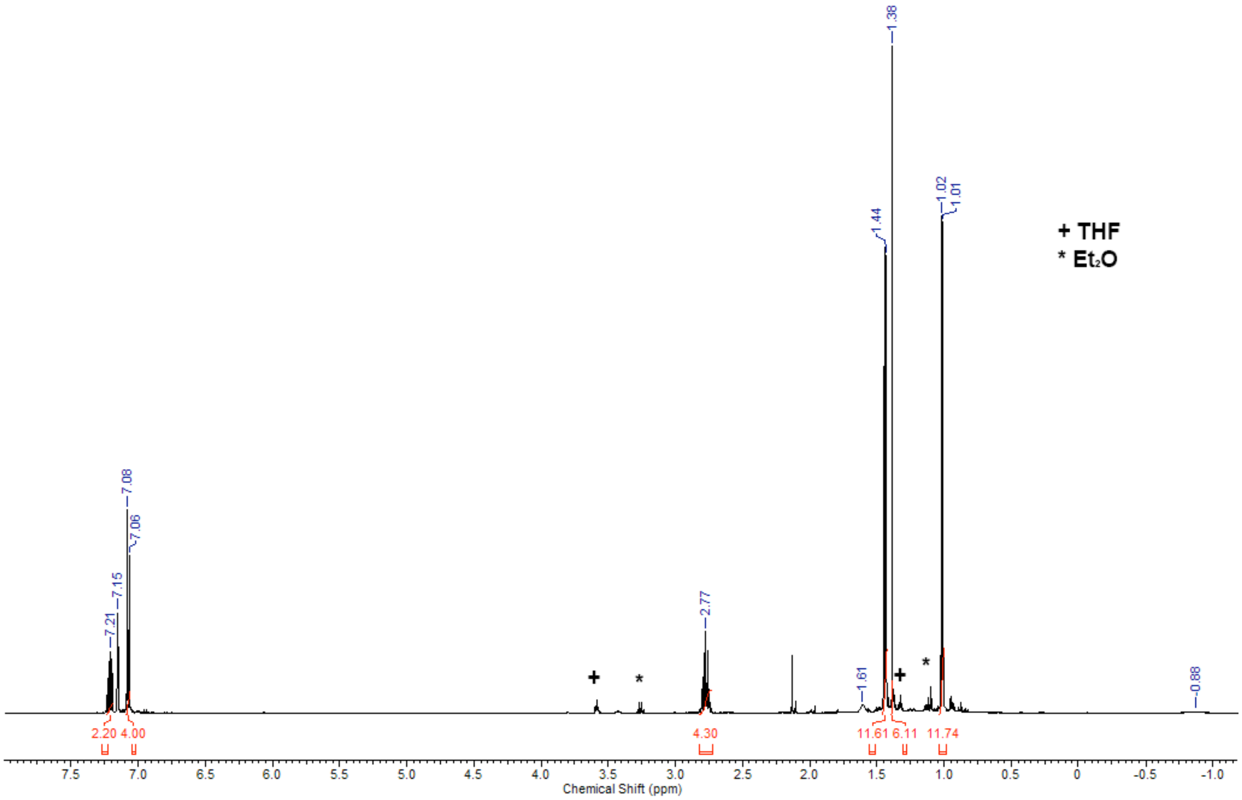


Fig. S1. ^{1}H NMR spectrum of **3a** in C_6D_6.

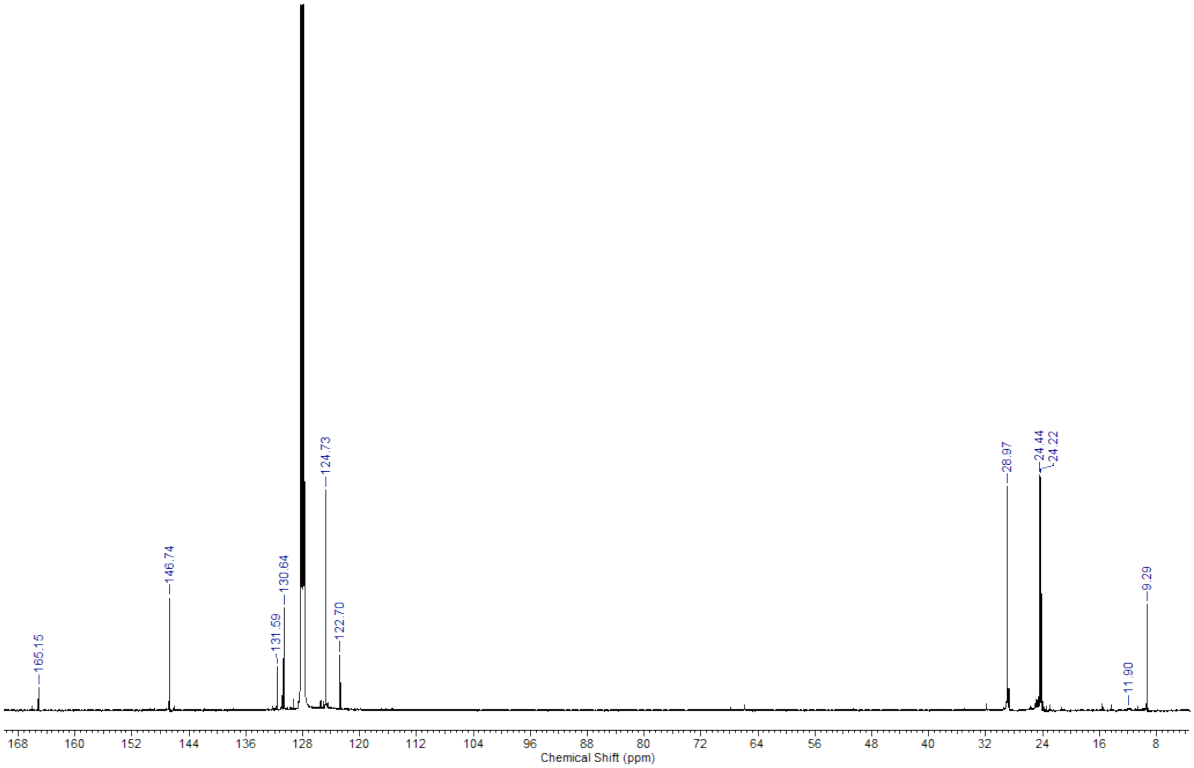
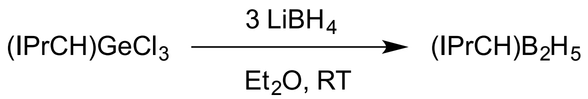


Fig. S2. $^{13}C\{^1H\}$ NMR spectrum of **3a** in C_6D_6.

Synthesis of (IPrCH)B_2H_5 (3b):



$$(IPrCH)GeCl_3 \xrightarrow[Et_2O,\ RT]{3\ LiBH_4} (IPrCH)B_2H_5$$

To a mixture of solid (IPrCH)$GeCl_3$ (0.298 g, 0.51 mmol) and $LiBH_4$ (0.032 g, 1.51 mmol) was added 10 mL of Et_2O at room temperature, leading to the immediate bubbling of the reaction mixture. Stirring was continued for 12 hrs. The resulting precipitate was allowed to settle and the supernatant was filtered through a plug of Celite. The volatiles were removed under vacuum from the filtrate to give (IPrCH)B_2H_5 (**3b**) as an off-white solid (0.201 g, 92 %). X-ray quality crystals of **3b** were obtained from a saturated toluene solution layered with hexanes placed at −30 °C for 24 hrs.

^{1}H NMR (498 MHz, C_6D_6): δ = 7.18 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Ar*H*), 7.04 (d, $^3J_{HH}$ = 7.3 Hz, 4H, Ar*H*), 6.05 (s, 2H, N-C*H*), 2.87 (sept, 4H, $^3J_{HH}$ = 6.6 Hz, C*H*(CH_3)$_2$), 1.67 (br, 1H, C*H*(B_2H_5)), 1.40 (d, $^3J_{HH}$ = 7.3 Hz, 12H, CH(CH_3)$_2$), 1.10 (br, 4H, BH_2), 1.03 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CH(CH_3)$_2$), -0.89 (br, 1H, (BH_2)$_2$-μ-*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 12.5 (br, *C*H(B_2H_5)), 21.4 (C*C*H(B_2H_5)), 24.0 (CH(*C*H_3)$_2$), 25.1 (CH(*C*H_3)$_2$), 29.2 (*C*H(CH_3)$_2$), 119.8 (N*C*H), 124.3 (Ar*C*), 130.8 (Ar*C*), 133.1 (Ar*C*), 146.5 (ArC), 165.9 (N*C*N). ^{11}B{^{1}H} NMR (159.8 MHz, C_6D_6): δ = -28.9. Anal. calcd. for $C_{28}H_{42}N_2B_2$: C, 78.53; H, 9.89; N, 6.54. Found: C, 77.34; H, 9.83; N, 6.66 %. Mp (°C): 136 (decomposition). Despite repeated attempts, analyses for carbon content were repeatedly low. See Figs. S3 and S4 for copies of the NMR spectra for **3b**.

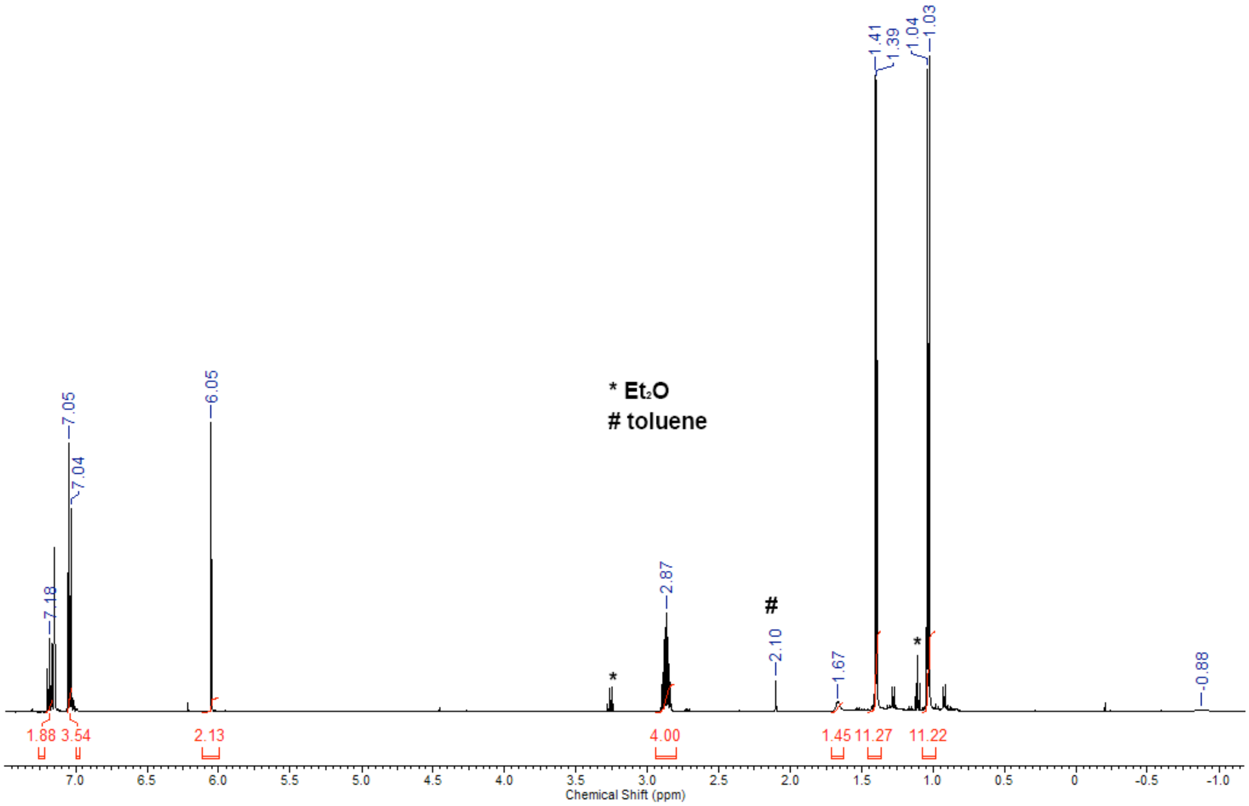


Fig. S3. ^{1}H NMR spectrum of **3b** in C_6D_6.

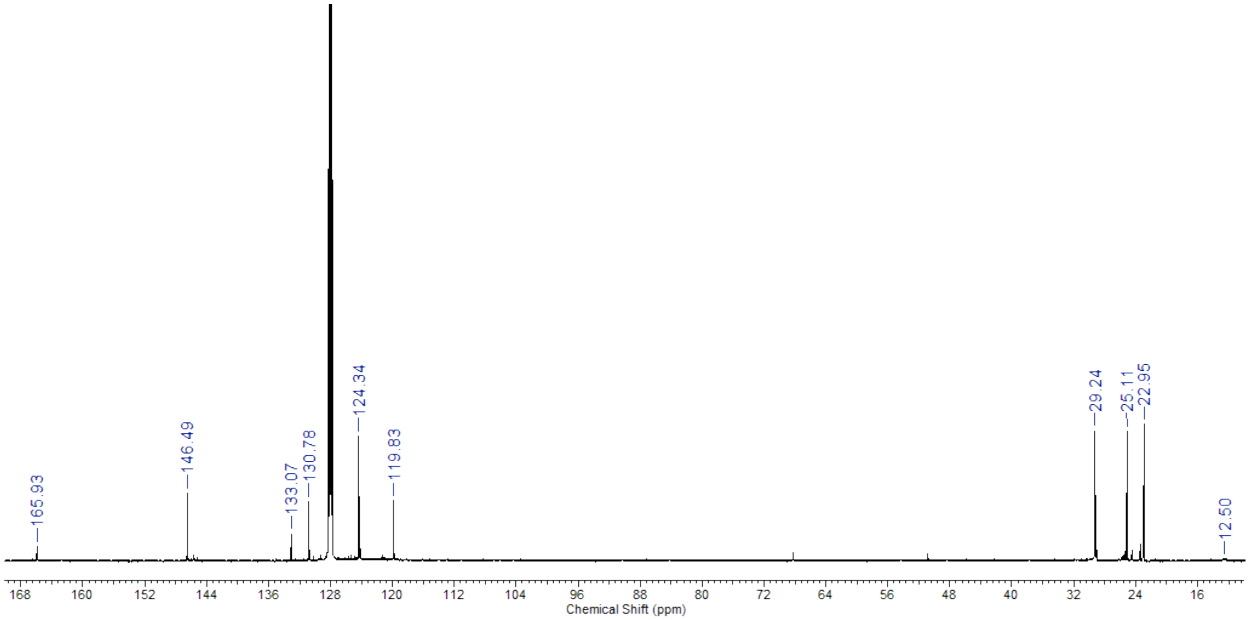


Fig. S4. $^{13}C\{^1H\}$ NMR spectrum of **3b** in C_6D_6.

Synthesis of (IPrCH)B_2H_4OTf (4):

$$\text{(IPrCH)}B_2H_5 \xrightarrow[\text{-}CH_4]{\text{3 MeOTf}} \text{(IPrCH)}B_2H_4\text{OTf}$$

To (IPrCH)B_2H_5 (103 mg, 0.24 mmol) in 10 mL of fluorobenzene was added MeOTf (123 mg, 0.75 mmol) and stirring was continued for 16 hrs. The resulting cloudy mixture was filtered through a pad of Celite and the solvent was evaporated from the filtrate *in vacuo*. The remaining off-white solid was washed with hexanes (3 x 2 mL) and (IPrCH)B_2H_4OTf (**4**) was recovered as a white solid (0.115 g, 83 %). X-ray quality crystals of **4** were obtained from a saturated CH_2Cl_2 solution layered with hexanes, placed at −30 °C for 24 hrs.

^{1}H NMR (699.76 MHz, $CDCl_3$): δ = 7.12 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 7.00 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 6.97 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 6.04 (d, $^3J_{HH}$ = 1.5 Hz, 2H, *H*CN), 2.63 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.60 (d, 2H, -C*H*B_2H_4(OTf)), 1.39 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.32 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.95 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$). The hydrides attached to the ^{11}B atoms could not be detected reliably in variable temperature experiments due to severe broadening and possible overlap with Dipp ^{i}Pr-group signals. ^{13}C{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ = 12.8 (br, *C*H(B_2H_5)), 22.5 (CH(CH_3)$_2$), 22.6 (CH(CH_3)$_2$), 25.1 (CH(CH_3)$_2$), 25.2 (CH(CH_3)$_2$), 29.3 (*C*H(CH_3)$_2$), 29.4 (*C*H(CH_3)$_2$), 120.9 (H*C*N), 124.53 (Ar*C*), 124.55 (Ar*C*), 131.6 (Ar*C*), 131.7 (Ar*C*), 145.9 (Ar*C*), 146.3 (Ar*C*), 161.5 (N*C*N). ^{11}B{^{1}H} (159.8 MHz, C_6D_6): δ = -11.1 (-*B*H(OTf)) -26.7 (-*B*H_2-). ^{19}F NMR (376.3 MHz, C_6D_6): δ = -76.5. Anal. calcd. for $C_{29}H_{41}B_2F_3N_2O_3S$: C, 60.44; H, 7.17; N, 4.86. Found C, 59.56; H, 7.16; N, 4.63; %. Mp: 161 °C.

Reaction of IPrCH_2 with HBPin:

IPrCH_2 (0.100 g, 0.248 mmol) was dissolved in 2 mL of THF and stirred for 5 minutes. To this solution, HBPin (0.032 g, 0.25 mmol) was added dropwise. NMR analysis after 30 hours, showed a 42% conversion of IPrCH_2 to a product tentatively formulated as IPrCH_2B(H)Pin and 7% conversion to a new unknown product was observed. Attempts to isolate pure IPrCH_2B(H)Pin by fractional crystallization have been unsuccessful so far.

NMR Data for $IPrCH_2B(H)Pin$: ^1H NMR (500 MHz, C_6D_6): 7.21-7.18 (m, 2H, Ar*H*), 7.15 (m, 1H, Ar*H*), 7.13 (d, 2H, Ar*H*), 7.11 (t, 1H, Ar*H*) 5.66 (s, 2H, *H*CN), 4.01 (sept, 2H, $CH(CH_3)_2$), 3.86 (m, 2H, $CH(CH_3)_2$, 1.54 (s, 2H, CH_2B), 1.30 (d, 6H, $CH(CH_3)_2$), 1.28 (d, 6H, $CH(CH_3)_2$, 1.23 (d, 6H, $CH(CH_3)$, 1.16 (d, 6H, $CH(CH_3)$ 1.01 (s, 12H, $BOC(CH_3)_2$); the borate B-H resonance could not be found. ^{11}B NMR (128.169 MHz, C_6D_6): 21.9.

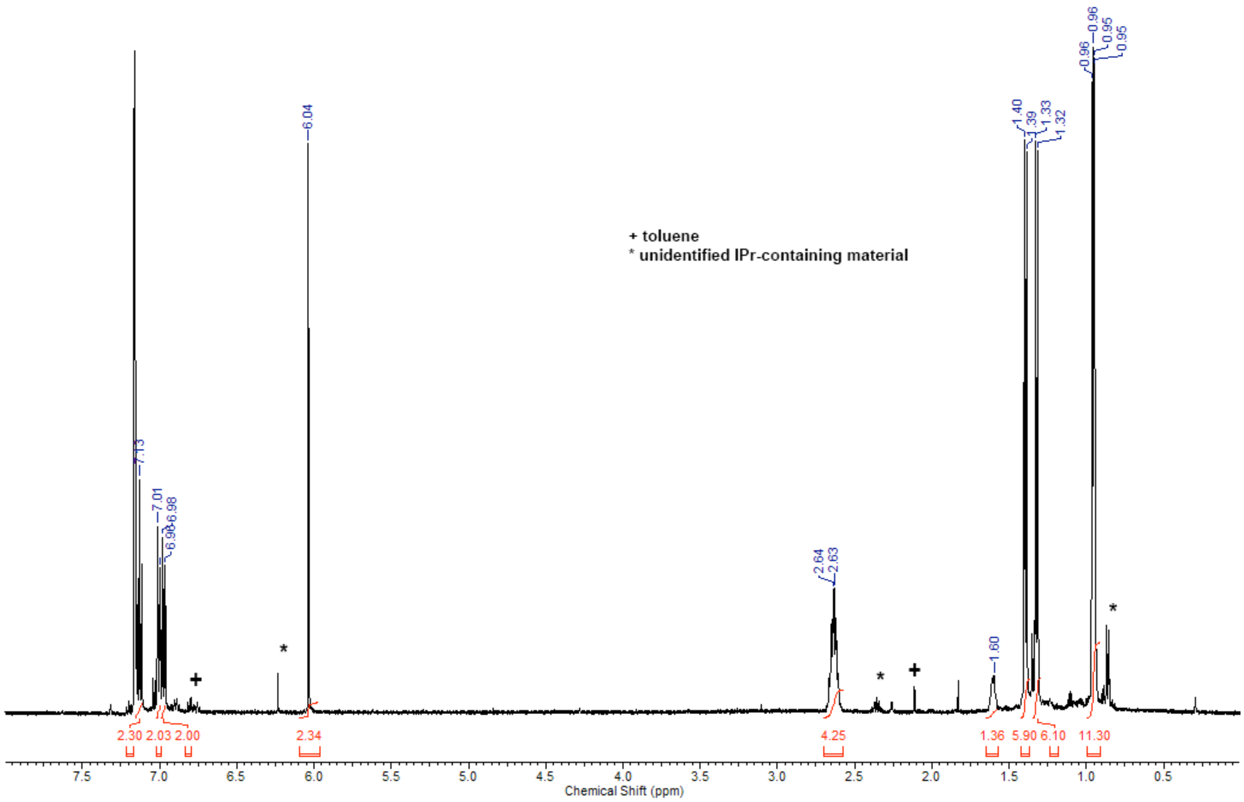


Fig. S5. ^{1}H NMR spectrum of **4** in C_6D_6.

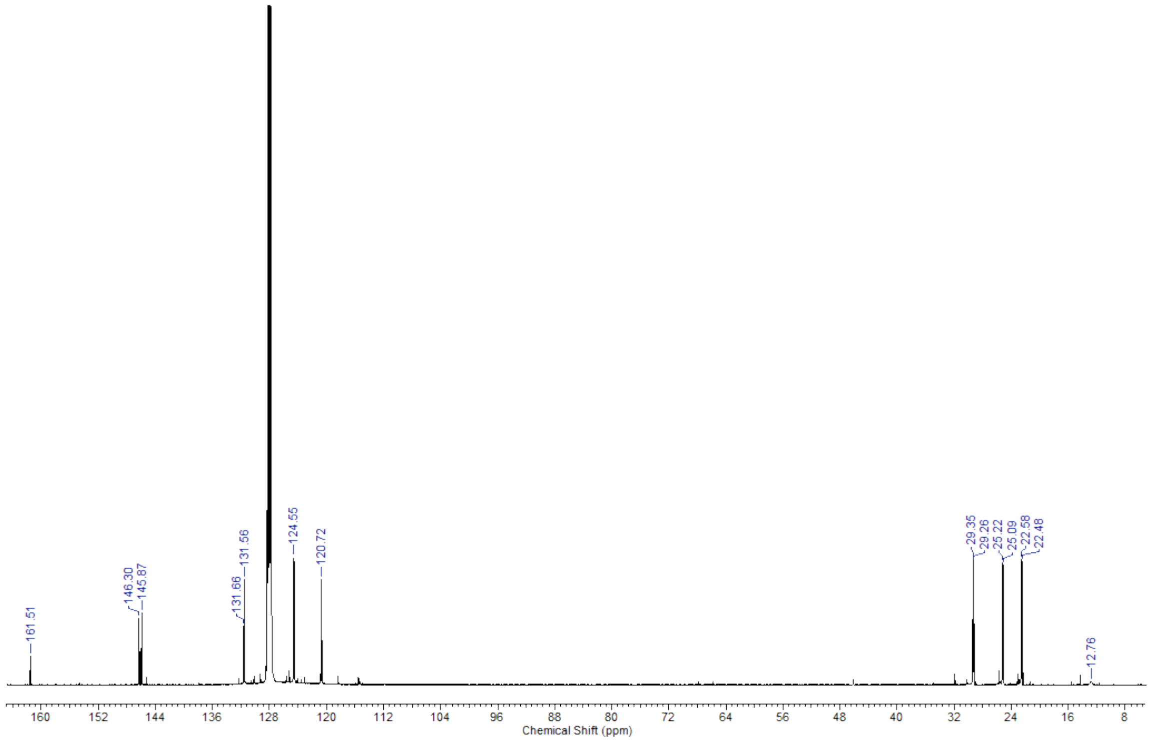


Fig. S6. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

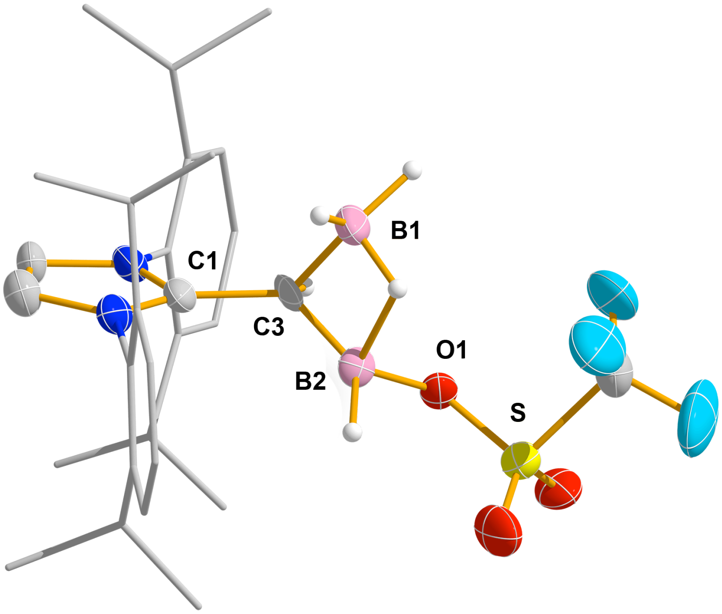


Fig. S7. POV-ray depiction of the molecular structure of **4**. Ellipsoids are drawn at a 30% probability with all carbon-bound hydrogen except the one attached to C4A omitted; the flanking Dipp-groups rendered as wireframe for clarity. Selected bond lengths (Å) and angles (°) [minor orientation]: C1−C3 1.505(5), C3−B1 1.569(6), C3−B2 1.546(6), B1–B2 1.926(7), O1–B2 1.533(6); B2−C3−B1 76.4(3), C1−C3−B1−B2 117.3(4).

General procedure for the hydroborylation of various aldehydes and ketones:

$$1.1\ \text{HBPin} + \text{R-CO-R'} \xrightarrow[\text{THF, RT}]{\text{5 mol\% IPrCH}_2} \text{R-CHR'-O(BPin)}$$

A solution containing the ketone/aldehyde (0.50 mmol) dissolved in 1.6 mL of THF was combined with a 0.4 mL THF solution of the NHO catalyst (1-5 mol%, 0.005-0.025 mmol; $IPrCH_2$ 0.010 g; 0.011 g $^{Me}IPrCH_2$) in a 20 mL scintillation vial and stirred for 5 minutes at room temperature. Afterwards, HBPin (0.070 g, 0.55 mmol) was added and the reaction progress was monitored by ^1H NMR spectroscopy, with sampling of 0.2 mL aliquots after various times.

Cat.	Cat. [mol%]	R/R′ (in RC(O)R′)	t	Yield [%][a]	TOF [h^{-1}]
$IPrCH_2$	5	Ph/Ph	18 hrs	99	1.1
$IPrCH_2$	5	Ph/Ph	5 h at 60 °C	>99	4.0
$IPrCH_2$	5	Mes/H	12 min	>99	99
$IPrCH_2$	5	4-MeCO(C_6H_4)/H	6 min	>99	116
$IPrCH_2$	5	Ph/Me	18 hrs	73	0.8
$IPrCH_2$	1	4-Cl(C_6H_4)/4-Cl(C_6H_4)	15 min	>99	396
$IPrCH_2$	5	4-Cl(C_6H_4)/4-Cl(C_6H_4)	5 min	>99	238
$IPrCH_2$	2	Mes/H	1 hrs	>99	50
$IPrCH_2$	5	cyclohexanone	18 hrs	58	0.6
$IPrCH_2$	5	Cy/H	3 hrs	> 99	6.7
$^{Me}IPrCH_2$	5	4-Cl(C_6H_4)/4-Cl(C_6H_4)	5 min	>99	2380
IPr	5	Mes/H	24 hrs	79	0.7
IPr	5	4-Cl(C_6H_4)/4-Cl(C_6H_4)	24 hrs	9	0.08

[a] Yield determined by ^1H NMR integration in C_6D_6.

Catalytic hydroboration of MesCHO using $^{Me}IPrCH_2$ as a catalyst:

$$1.1\ \mathrm{HBPin} + \mathrm{MesCHO} \xrightarrow[\mathrm{THF,\ RT}]{5\ \mathrm{mol\%}\ ^{Me}\mathrm{IPrCH_2}} \mathrm{MesCH_2O(BPin)}$$

MesCHO (0.50 mmol, 0.074 g) was dissolved in THF (1.6 mL) in a 20 mL scintillation vial and a solution containing $IPrCH_2$ (5 mol%, 0.025 mmol, 0.009 g) in 0.4 mL of THF was added and the mixture stirred for 5 min at room temperature. Afterwards HBPin (0.070 g, 0.55 mmol) was added and the reaction progress was monitored by ^1H NMR spectroscopy which indicated that full conversion to the borylated product $MesCH_2O(BPin)$ was achieved after 5 minutes.

Catalytic hydroboration of MesCHO testing IPr as a catalyst:

$$1.1\ \mathrm{HBPin} + \mathrm{MesCHO} \xrightarrow[\mathrm{THF,\ RT}]{5\ \mathrm{mol\%\ IPr}} \mathrm{MesCH_2O(BPin)}$$

MesCHO (0.50 mmol, 0.074 g) was dissolved in THF (1.6 mL) in a 20 mL scintillation vial and a solution containing $IPrCH_2$ (5 mol%, 0.025 mmol, 0.009 g) in 0.4 mL of THF was added and the mixture stirred for 5 min at room temperature. Afterwards HBPin (0.070 g, 0.55 mmol) was added and the extent of reaction was monitored by ^1H NMR spectroscopy with a 79 % conversion into $MesCH_2O(BPin)$ detected after 24 hrs.

Catalytic hydroboration of $(4\text{-}Cl\text{-}C_6H_4)_2CO$ testing IPr as a catalyst:

$$1.1\ \mathrm{HBPin} + (4\text{-}\mathrm{Cl}\text{-}\mathrm{C_6H_4})_2\mathrm{CO} \xrightarrow[\mathrm{THF,\ RT}]{5\ \mathrm{mol\%\ IPr}} (4\text{-}\mathrm{Cl}\text{-}\mathrm{C_6H_4})_2\mathrm{CHO(BPin)}$$

$(4\text{-}Cl\text{-}C_6H_4)_2CO$ (0.50 mmol, 0.126 g) was dissolved in 1.6 mL of THF in a 20 mL scintillation vial and a solution containing IPr (5 mol%, 0.025 mmol, 0.009 g) in 0.4 mL of THF was added, and the mixture stirred for 5 min at room temperature. Afterwards HBPin (0.070 g, 0.55 mmol) was added and the reaction progress was monitored by ^{1}H NMR spectroscopy, revealing the formation of a small amount (9 % conversion) of (4-Cl-C_6H_4)$_2$CHO(BPin) after 24 hrs.

Catalytic hydrosilylation of MesCHO using IPrCH$_2$ as a catalyst:

$$1.1\ \mathrm{Ph(Me)SiH_2} + \mathrm{MesCHO} \xrightarrow[\text{THF, RT}]{\text{5 mol\% IPrCH}_2} \mathrm{MesCH_2OSiH(Me)Ph}$$

MesCHO (0.50 mmol, 0.074 g) was dissolved in THF (1.6 mL) in a 20 mL scintillation vial and a solution containing IPrCH$_2$ (5 mol%, 0.025 mmol, 0.009 g) in 0.4 mL of THF was added and the mixture stirred for 5 min at room temperature. Afterwards Ph(Me)SiH$_2$ (0.066 g, 0.54 mmol) was added and the reaction progress was monitored by ^{1}H NMR spectroscopy, indicating a 28 % conversion into the previously unknown silylated product MesCH$_2$OSiH(Me)Ph after 2 hrs at 60 °C. [6]

^{1}H NMR (498 MHz, C_6D_6): δ = 7.60-7.53 (m, 2H, Ph*H*), 7.23-7.12 (m, 3H, Ph*H*), 6.72 (s, 2H, Mes*H*), 5.08 (q, $^3J_{HH}$ = 2.9 Hz, 1H, SiH), 4.70 (s, 2H, CH$_2$), 2.26 (s, 6H, 2,6-Me), 2.11 (s, 3H, 4-Me), 0.32 (d, $^3J_{HH}$ =2.8 Hz, 3H, SiMe).

^{1}H NMR Data for R-CHR′-O(BPin):

Ph$_2$CH(OBpin):[5]

^{1}H NMR (498 MHz, C_6D_6): δ = 7.44 (m, 2H, Ar*H*), 7.07 (m, 2H, Ar*H*), 6.99 (m, 1H, Ar*H*), 6.42 (s, 1H, Ph$_2$C*H*(OBPin)), 0.97 (s, 12H, BPin).

(4-Cl-C_6H_4)$_2$CH(OBpin):[6]

^{1}H NMR (498 MHz, C_6D_6): δ = 7.04 (br, 8H, Ar*H*), 6.11 (s, 1H, (4-Cl-C_6H_4)$_2$C*H*(OBPin)), 0.96 (s, 12H, BPin).

PhCH(OBpin)Me:[5]

^{1}H NMR (498 MHz, C_6D_6): δ = 7.38-7.34 (m, $^3J_{HH}$ = 7.3 Hz, 2H, Ar*H*), 7.16-7.02 (m, 3H, Ar*H*), 5.41 (q, $^3J_{HH}$ = 6.4 Hz, 1H, PhC*H*(OBPin)Me), 1.45 (d, $^3J_{HH}$ = 6.4 Hz, 3H, -C(OBPin)H(CH_3)), 1.02 (s, 6H, BPin), 0.99 (s, 6H, BPin).

4-MeC(O)-C_6H_4-CH_2(OBPin):[6]

^{1}H NMR (498 MHz, C_6D_6): δ = 7.73 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar*H*), 7.20 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar*H*), 4.87 (s, 1H, 4-MeC(O)-C_6H_4-CH_2(OBPin)), 2.07 (s, 3H, 4-H_3CCO-), 1.03 (s, 12H, BPin).

MesCH_2(OBPin):[6]

^{1}H NMR (498 MHz, C_6D_6): δ = 6.72 (s, 2H, Ar*H*), 4.87 (s, 2H, MesCH_2(OBPin)), 2.37 (s, 6H, 2,6-Me), 2.10 (s, 3H, 4-Me), 1.03 (s, 12H, BPin).

Table S1. Crystallographic Experimental Details for (IPrCH)B_2H_5 (**3b**).

A. Crystal Data

formula	95.5%($C_{28}H_{42}B_2N_2$), 4.5%($C_{28}H_{41}BGeN_2$)•C_7H_8 [a]
formula weight	520.39
crystal dimensions (mm)	0.255 × 0.166 × 0.046
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters	
a (Å)	10.5280(2)
b (Å)	21.2551(4)
c (Å)	15.0977(3)
β (°)	96.2800(10)
V (Å^3)	3358.19(11)
Z	4
ρcalcd (g cm^{-3})	1.035
μ (mm^{-1})	0.473

B. Data Collection and Refinement Conditions

diffractometer	Bruker APEX II CCD
radiation (λ[Å])	Cu Kα (1.54178)
temperature (°C)	–100
scan type	ω and φ scans (1°) (10 s exposures)
data collection 2θ limit (deg)	135
total data collected	22040 ($-12 \leq h \leq 12$, $-25 \leq k \leq 25$, $-16 \leq l \leq 18$)
independent reflections	6165 ($R_{\text{int}} = 0.0334$)2
number of observed reflections (*NO*)	4508 [$Fo^2 \geq 2\sigma(Fo^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*)
refinement method	full-matrix least-squares on F^2 (*SHELXL-2014/7*)[d]
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8497 – 1.0000
data/restraints/parameters	6165 / 2 / 391
goodness-of-fit (*S*) [all data]	1.039
final *R* indices	
R_1 [$Fo^2 \geq 2\sigma(Fo^2)$]	0.0598
wR_2 [all data]	0.1784
largest difference peak and hole	0.467 and –0.242 e Å^{-3}

[a] The elongation of the ADP for B2 and the largest peak in the difference map being ca. 2 angstroms from C4 suggest partial Ge occupation of this site and refinement with a 4.5% Ge-H occupancy significantly improved the model. The occupancy of the minor component was allowed to refine freely. As our initial idea was to make a IPrCHGeH hydride species via the synthetic route applied a germanium contamination cannot be excluded in his crystal.

Table S2. Crystallographic Experimental Details for (IPrCH)B_2H_4OTf (**4**).

A. Crystal Data

formula	$C_{29}H_{41}B_2F_3N_2O_3S$
formula weight	576.32
crystal dimensions (mm)	0.528 × 0.208 × 0.126
crystal system	orthorhombic
space group	*Pnma* (No. 62)
unit cell parameters	
a (Å)	18.1783(3)
b (Å)	9.80200(10)
c (Å)	17.8683(3)
V (Å^3)	3358.19(11)
Z	4
ρcalcd (g cm^{-3})	1.202
μ (mm^{-1})	1.311

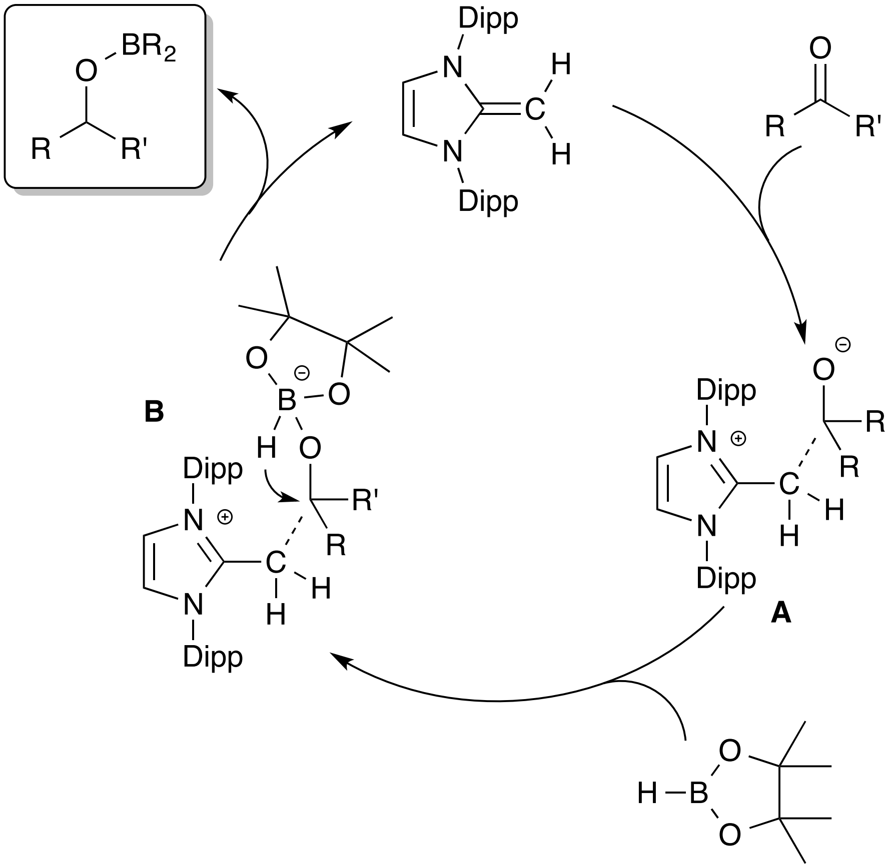
B. Data Collection and Refinement Conditions

diffractometer	Bruker APEX II CCD
radiation (λ[Å])	Cu Ka (1.54178)
temperature (°C)	–100
scan type	ω and φ scans (1°) (10 s exposures)
data collection 2θ limit (deg)	142
total data collected	21558 ($-22 \le h \le 22$, $-22 \le k \le 20$, $-12 \le l \le 12$)
independent reflections	3336 (Rint = 0.0416)
number of observed reflections (*NO*)	2950 [$Fo^2 \ge 2\sigma(Fo^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*)
refinement method	full-matrix least-squares on F^2 (*SHELXL-2014/7*)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.5411 – 1.0000
data/restraints/parameters	3336 / 1 / 219
goodness-of-fit (S) [all data]	1.057
final R indices	
R_1 [$Fo^2 \ge 2\sigma(Fo^2)$]	0.0759
wR_2 [all data]	0.2293
largest difference peak and hole	0.283 and –0.367 e Å^{-3}

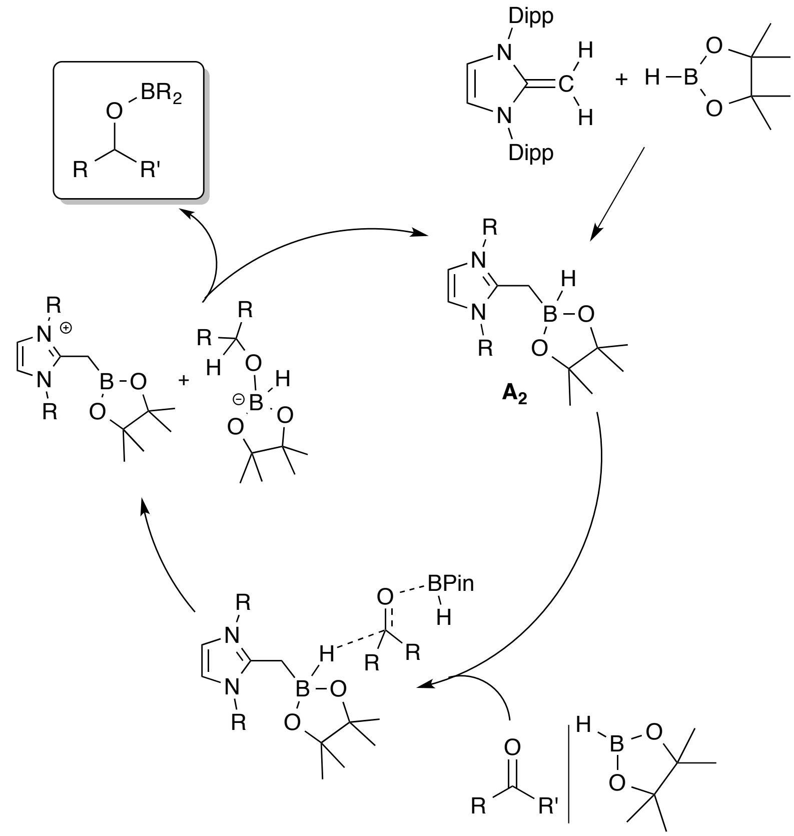
2. Computational Studies

Density Functional theory (DFT) calculations (full geometry optimisation) were carried out on **3a** starting from the geometry of its crystal structure and on the intermediates **A** and **B** proposed in Scheme S1 with the Gaussian09 program package[7] (BP86 functional with def2-SVP basis set for B, C, H, N, O, F, S). The optimized structures were in reasonable agreement with the observed molecular structures. All stationary points were characterized by frequency analyses. For all calculated molecules and intermediates there are no imaginary frequencies. The optimized structures were subjected to natural bond orbital (NBO) analysis.[8]

It should be emphasized that the computation was carried out for a single, isolated (gas phase) species. There may well be significant differences among gas-phase, solution, and solid-state data.



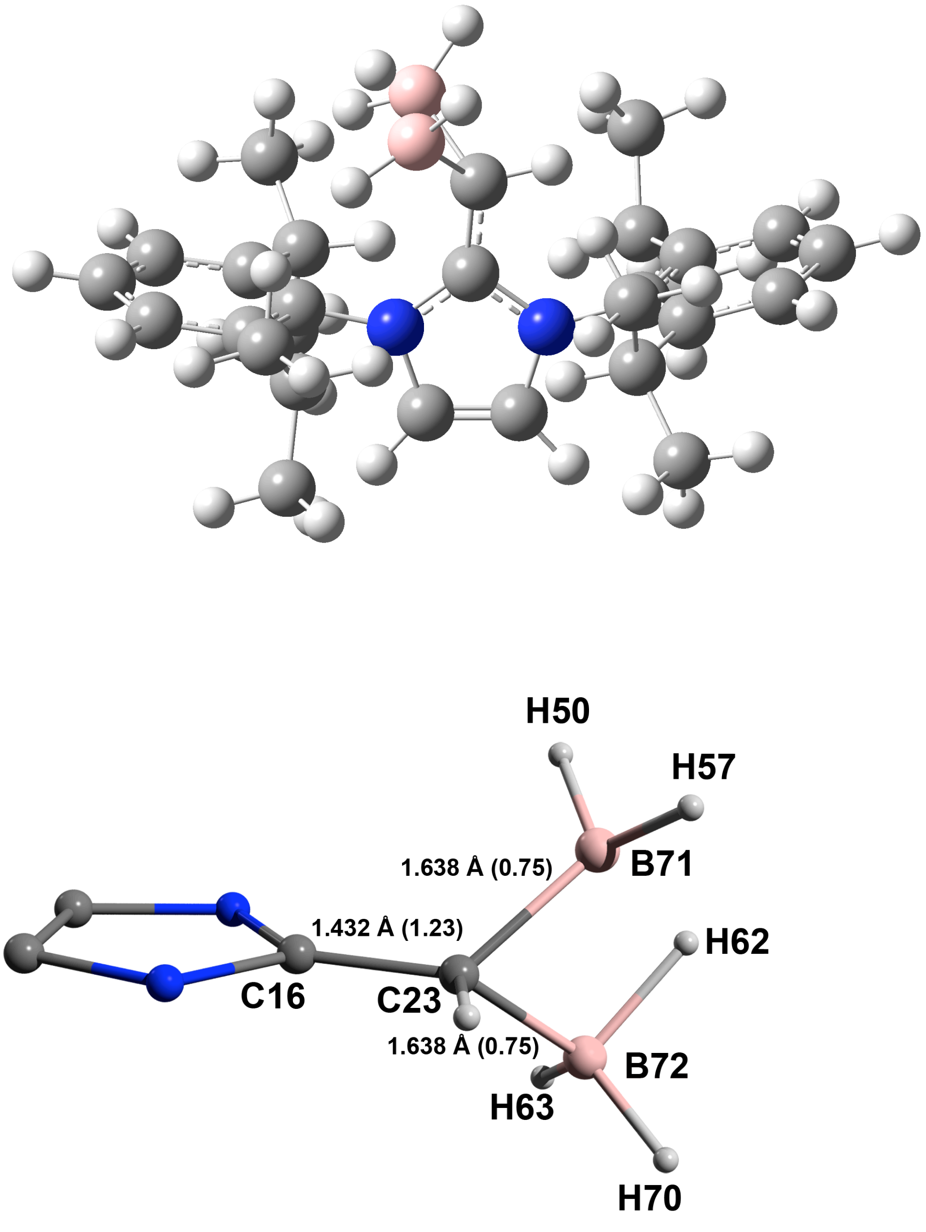
Scheme S1. Proposed mechanism for the hydroborylation of R(CO)R′ using IPrCH$_2$ as catalyst.



Scheme S2. Alternative mechanism for the hydroborylation of R(CO)R′ with [IPrCH$_2$-B(H)Pin] (**A$_2$**) as a catalyst.

Optimization results for (IPrCH)B_2H_5 (3a)

Fig. S8. POV-ray depiction of the optimized structure of **3a** (top) with a second view (bottom) in which the Dipp-groups have been omitted for clarity. Atom numbers as they appear in the output-file. Selected computed bond lengths and Wiberg bond indices (in parentheses) are shown in the bottom view. xyz-coordinates for the optimized structure of **(IPrCH)B_2H_5**, checked to be a minimum on the energy hyper-surface by a frequency analysis.



Optimized xyz-coordinates for **(IPrCH)B$_2$H$_5$ (3a)**:

C	3.12670500	-3.43990900	-1.34733200
C	-2.64173600	-3.07141100	-1.73163000
C	-2.83346400	-3.67618900	0.72368900
C	2.49488700	-2.58700500	-0.22626400
C	-2.41693000	-2.58447100	-0.28066200
C	2.43800800	-3.35858200	1.11039400
C	0.70142000	0.00007100	-1.92189500
C	-0.66144600	0.00008400	-1.87299900
C	3.21179100	-1.24629900	-0.06522400
C	4.58060200	-1.21500400	0.27244300
C	-3.12278700	-1.24660900	-0.04652500
C	-4.50515500	-1.21447000	0.22957900
C	2.54876700	-0.00000600	-0.22846200
C	5.25945000	-0.00007000	0.44035300
C	-2.44991800	0.00002800	-0.15937300
C	0.08286000	-0.00001300	0.28219000
C	-2.64185100	3.07165500	-1.73133400
C	-5.18915300	-0.00001200	0.37347400
C	3.21186200	1.24625700	-0.06527500
C	4.58067200	1.21489600	0.27239100
C	-3.12280300	1.24664800	-0.04642100
C	-4.50517000	1.21446500	0.22968700
C	0.25692300	-0.00009600	1.70407600
C	3.12689000	3.43975300	-1.34757800
C	-2.41697000	2.58454400	-0.28043500
C	2.49504900	2.58700100	-0.22640600
C	2.43828300	3.35871000	1.11018100
C	-2.83347200	3.67613800	0.72406300
H	2.55671900	-4.38259200	-1.48498700
H	-2.10695500	-4.02828100	-1.91066000
H	4.17499000	-3.71900000	-1.10884900
H	3.13608900	-2.90155800	-2.31785600
H	-3.72120100	-3.24495300	-1.92850200
H	-2.27892600	-2.33795800	-2.48017700
H	-2.21149100	-4.58392700	0.57816100
H	-3.89191100	-3.98429200	0.58825300
H	1.88122700	-4.31065500	0.98297600
H	1.39715000	0.00009100	-2.76556000
H	-1.41082000	0.00011500	-2.66878600
H	3.45530600	-3.61279400	1.47712600
H	1.44729100	-2.37471700	-0.52544300
H	-1.32873500	-2.41138900	-0.14465300
H	5.12280300	-2.16374100	0.41078900
H	-2.69843200	-3.33165900	1.76790800
H	-5.05525000	-2.16199600	0.33380300
H	1.92509400	-2.76815200	1.89621700
H	-2.27906500	2.33829800	-2.47998700
H	6.32814400	-0.00009500	0.70789100
H	3.13619400	2.90131100	-2.31805300
H	-1.57750000	-1.51170900	2.27352000
H	-3.72132700	3.24520500	-1.92813500
H	-6.26841900	-0.00002900	0.59485400
H	-2.10709200	4.02855500	-1.91027300

H	1.44742600	2.37476600	-0.52552500
H	5.12292900	2.16360800	0.41069200
H	-1.32876600	2.41146100	-0.14449600
H	0.08335500	-1.55329700	3.53409500
H	1.33722800	-0.00014600	1.92541200
H	-5.05527600	2.16197500	0.33399700
H	4.17520600	3.71878400	-1.10916200
H	2.55697200	4.38246800	-1.48529600
H	-1.19160200	-0.00010500	3.51260100
H	-1.57737400	1.51162600	2.27362900
H	1.92533700	2.76840400	1.89607400
H	-3.89193100	3.98423800	0.58871600
H	-2.21152200	4.58390400	0.57861000
H	3.45561600	3.61286500	1.47685600
H	1.88158600	4.31082100	0.98268800
H	-2.69838200	3.33148900	1.76823500
H	0.08347800	1.55298500	3.53421600
B	-0.60614200	-0.93941200	2.73187500
B	-0.60606700	0.93921400	2.73195000
N	1.15318300	0.00001900	-0.60069200
N	-1.04418300	0.00004500	-0.52477500

NBO results for (IPrCH)B_2H_5 (3a).

```
46. (1.97202) BD ( 1) C  16 - C  23 (1.432 Å, WBI = 1.23)
          ( 51.47%)   0.7174* C  16 s( 45.05%)p 1.22( 54.94%)d 0.00(  0.01%)
          ( 48.53%)   0.6967* C  23 s( 29.86%)p 2.35( 70.10%)d 0.00(  0.04%)
62. (1.95249) BD ( 1) C  23 - H  58  (WBI = 0.86)
          ( 63.84%)   0.7990* C  23 s( 23.22%)p 3.30( 76.75%)d 0.00(  0.02%)
          ( 36.16%)   0.6013* H  58 s( 99.94%)p 0.00(  0.06%)
 63. (1.80478) BD ( 1) C  23 - B  71  (1.638 Å, WBI = 0.75)
          ( 69.63%)   0.8344* C  23 s( 23.40%)p 3.27( 76.59%)d 0.00(  0.01%)
          ( 30.37%)   0.5511* B  71 s( 19.61%)p 4.09( 80.26%)d 0.01(  0.14%)
 64. (1.80477) BD ( 1) C  23 - B  72  (1.638 Å, WBI = 0.75)
          ( 69.63%)   0.8344* C  23 s( 23.40%)p 3.27( 76.60%)d 0.00(  0.01%)
          ( 30.37%)   0.5511* B  72 s( 19.61%)p 4.09( 80.26%)d 0.01(  0.14%)
79. (1.97672) BD ( 1) H  50 - B  71  (WBI = 0.97)
          ( 52.08%)   0.7217* H  50 s( 99.97%)p 0.00(  0.03%)
          ( 47.92%)   0.6922* B  71 s( 29.81%)p 2.35( 70.17%)d 0.00(  0.02%)
80. (1.97257) BD ( 1) H  57 - B  71  (WBI = 0.96)
          ( 50.69%)   0.7119* H  57 s( 99.96%)p 0.00(  0.04%)
          ( 49.31%)   0.7022* B  71 s( 29.22%)p 2.42( 70.76%)d 0.00(  0.02%)
81. (1.97672) BD ( 1) H  63 - B  72  (WBI = 0.97)
          ( 52.08%)   0.7217* H  63 s( 99.97%)p 0.00(  0.03%)
          ( 47.92%)   0.6922* B  72 s( 29.81%)p 2.35( 70.17%)d 0.00(  0.02%)
82. (1.97257) BD ( 1) H  70 - B  72  (WBI = 0.96)
          ( 50.69%)   0.7119* H  70 s( 99.96%)p 0.00(  0.04%)
          ( 49.31%)   0.7022* B  72 s( 29.22%)p 2.42( 70.76%)d 0.00(  0.02%)
116. (0.87542) LP*( 1) H  62           s( 99.92%)p 0.00(  0.08%)
```

```
 117. (0.59294) LP*( 1) B  71          s( 21.32%)p 3.69( 78.58%)d 0.00(  0.09%)
 118. (0.59294) LP*( 1) B  72          s( 21.32%)p 3.69( 78.58%)d 0.00(  0.09%)
```

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis (hyperconjugation energy [E(2)] = kcal/mol):

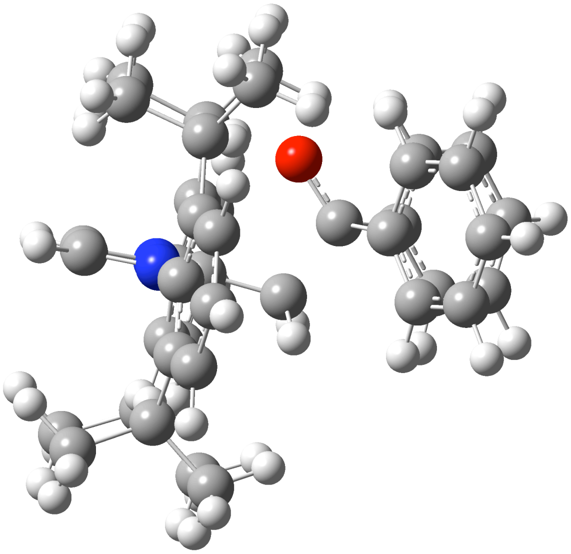
```
79. BD (   1) H  50 - B  71       /116. LP*(   1) H  62                5.84
80. BD (   1) H  57 - B  71       /116. LP*(   1) H  62                5.85
81. BD (   1) H  63 - B  72       /116. LP*(   1) H  62                5.84
82. BD (   1) H  70 - B  72       /116. LP*(   1) H  62                5.85
```

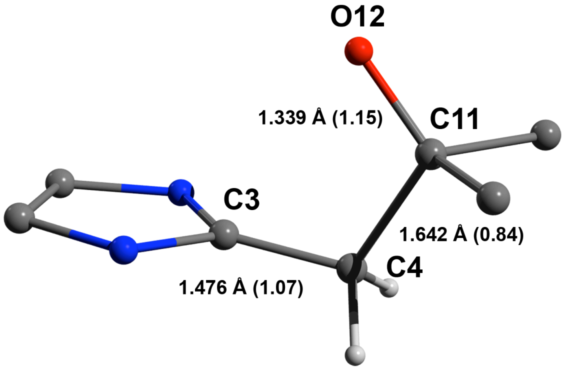
Natural Population Analysis (NPA Charges)

```
C   16    0.53773
C   23   -0.76759
H   50   -0.03568
H   51    0.22335
H   57   -0.00569
H   58    0.27574
H   62    0.12355
H   63   -0.03568
H   70   -0.00569
B   71   -0.09914
B   72   -0.09913
N   73   -0.41815
N   74   -0.41442
```

Optimization results for Intermediate A

Fig. S9. Ball-and-stick representation of the optimised structure of proposed Intermediate **A** (top). Ball-and-stick depiction of the optimized structure of Intermediate **A** (bottom) with Dipp-groups and protons on IPr and Ph_2CO omitted for clarity; atom numbers as they appear in the output-file. Selected computed bond lengths and Wiberg bond indices (in parentheses) are shown in the bottom view. xyz-coordinates for the optimized structure of Intermediate **A**, checked to be a minimum on the energy hyper-surface by a frequency analysis.





Optimized xyz-coordinates for Intermediate **A**:

C	0.86499400	-2.40963600	-1.71889900
C	-0.50182800	-2.47764500	-1.71725900
C	0.10374300	-0.87675700	-0.25216700
C	0.06840600	0.11758800	0.83840600
H	1.61598100	-2.98233800	-2.26931100
H	-1.19324400	-3.12412400	-2.26368700
H	1.02267500	0.03468600	1.39377800
N	1.22690600	-1.40945100	-0.81990700
N	-0.96123800	-1.51585400	-0.82069700
H	-0.76146000	-0.15122600	1.52092100
C	-0.10592400	1.63832900	0.24317900
O	-0.05143000	1.62957900	-1.09440800
C	1.01053900	2.53320200	0.90335000
C	1.60045200	3.51660700	0.08585300
C	1.41205900	2.46005300	2.25489200
C	2.56478800	4.40219800	0.59744200
H	1.26766000	3.54576900	-0.96379900
C	2.38564700	3.33511200	2.77012200
H	0.95556100	1.72028700	2.93431400
C	2.96661700	4.31247300	1.94253400
H	3.00886400	5.16956800	-0.05879500
H	2.68869200	3.25592000	3.82745100
H	3.72574300	5.00208600	2.34615000
C	-1.44357200	2.25578400	0.80181300
C	-2.08475100	3.20161100	-0.02432600
C	-1.99993200	2.00477500	2.07472700
C	-3.24129200	3.87542100	0.40182200
H	-1.63582500	3.37532700	-1.01497600
C	-3.16855200	2.66301800	2.50156100
H	-1.51915200	1.29367000	2.76761300
C	-3.79454100	3.60449900	1.66698100
H	-3.71815200	4.61877500	-0.25899000
H	-3.58863400	2.44117100	3.49666800
H	-4.70550600	4.12637500	2.00228900
C	2.61414200	-1.12743400	-0.48039000
C	3.20823900	-1.90323800	0.55117800
C	3.32998800	-0.15433300	-1.23581100
C	4.57411200	-1.68289600	0.82536500
C	4.69306600	0.01346700	-0.90942100
C	5.30962000	-0.73733900	0.10082100
H	5.06597900	-2.26434200	1.62088500
H	5.28332500	0.75945300	-1.46014700
H	6.37563500	-0.57822600	0.32904000
C	-2.37198400	-1.36306400	-0.49488000
C	-3.18067200	-0.50818800	-1.29835300
C	-2.88829100	-2.14949700	0.56987600
C	-4.55554500	-0.46843000	-0.98080700
C	-4.27018400	-2.05621400	0.83559100
C	-5.09513400	-1.22698400	0.06701800
H	-5.21819100	0.18465900	-1.56588100
H	-4.70408400	-2.64742900	1.65713600
H	-6.17259700	-1.16624900	0.28872400
C	2.67303200	0.67635900	-2.33794400

C	2.44454800	-2.96580100	1.34547400
C	-2.60991300	0.33783400	-2.43848900
C	-2.02596700	-3.10301400	1.40050200
H	1.64719500	0.95047000	-1.96782200
H	-1.63043900	0.74716300	-2.06906300
H	-0.96228000	-2.92212700	1.13703100
H	1.37113900	-2.89641200	1.06864700
C	2.54496600	-0.11485900	-3.66058000
C	3.41002200	1.99934600	-2.61281400
C	2.53345400	-2.72771200	2.86758100
C	2.92089900	-4.38765400	0.97383400
C	-2.16488000	-2.84737800	2.91554100
C	-2.33727100	-4.57602400	1.05334600
C	-2.37015300	-0.49130700	-3.72253600
C	-3.49652900	1.54600600	-2.79004100
H	-1.63370300	-1.30665000	-3.58545600
H	-3.31562500	-0.94404800	-4.09465200
H	-1.97387200	0.16605500	-4.52446000
H	-2.94791100	2.21193600	-3.48741600
H	-4.43981800	1.24844900	-3.29973600
H	-3.75471000	2.14304700	-1.89333800
H	3.57434600	2.57994100	-1.68327100
H	4.39259800	1.84729900	-3.11249600
H	2.79555300	2.62592400	-3.29146500
H	3.54289000	-0.41260500	-4.05186200
H	1.93247100	-1.03246200	-3.56006300
H	2.05483000	0.51649800	-4.43083200
H	2.18258600	-1.71202400	3.14216900
H	1.90972200	-3.46647100	3.41321900
H	3.57363700	-2.83611300	3.23990400
H	2.81050300	-4.58555000	-0.11226700
H	3.99126100	-4.53300600	1.23138700
H	2.33512400	-5.15521400	1.52224900
H	-3.39053200	-4.83147700	1.29568100
H	-2.18481900	-4.78329200	-0.02592600
H	-1.68227700	-5.26357000	1.62905900
H	-1.94579900	-1.79099600	3.17292200
H	-3.18885500	-3.07506000	3.27901800
H	-1.46322100	-3.49268000	3.48438600

NBO results for Intermediate A.

```
7. (1.97339) BD ( 1) C   3 - C   4  (1.476 Å, WBI = 1.07)
           ( 51.94%)   0.7207* C   3 s( 42.42%)p 1.36( 57.57%)d 0.00(  0.02%)
           ( 48.06%)   0.6932* C   4 s( 26.81%)p 2.73( 73.15%)d 0.00(  0.05%)
13. (1.92568) BD ( 1) C   4 - C  11  (1.642 Å, WBI = 0.84)
           ( 54.69%)   0.7395* C   4 s( 26.85%)p 2.72( 73.14%)d 0.00(  0.01%)
           ( 45.31%)   0.6731* C  11 s( 22.33%)p 3.48( 77.63%)d 0.00(  0.05%)
16. (1.98830) BD ( 1) C  11 - O  12  (1.339 Å, WBI = 1.15)
           ( 35.59%)   0.5966* C  11 s( 25.12%)p 2.97( 74.68%)d 0.01(  0.20%)
           ( 64.41%)   0.8025* O  12 s( 36.74%)p 1.72( 63.19%)d 0.00(  0.07%)
```

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis (hyperconjugation energy [E(2)] = kcal/mol):

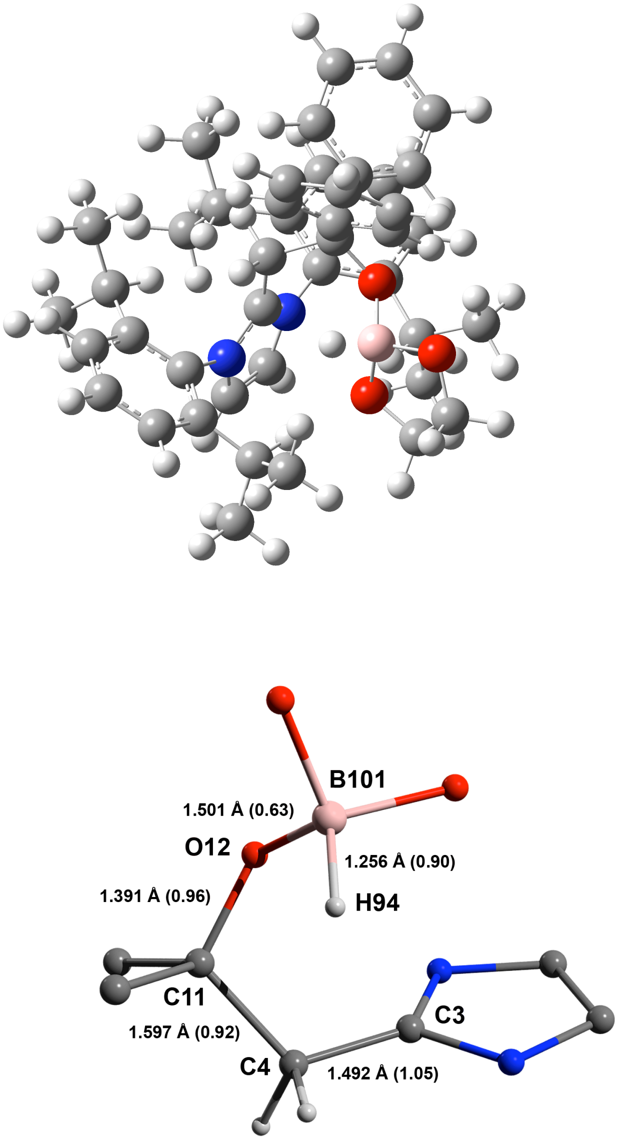
157. LP (2) O 12 /759. BD*(1) C 4 - C 11 **10.71**

Natural Population Analysis (NPA Charges)

C	3	0.56799
C	4	-0.55345
H	7	0.26480
N	8	-0.38124
N	9	-0.38066
H	10	0.25728
C	11	0.33006
O	12	-0.87581

Optimization results for Intermediate B

Fig. S10. Ball-and-stick representation of the optimised structure of proposed Intermediate **B** (top). Ball-and-stick depiction of the optimized structure of Intermediate **B** (bottom) with Dipp-groups and protons on IPr and Ph_2CO omitted for clarity; atom numbers as they appear in the output-file. Selected computed bond lengths and Wiberg bond indices (in parentheses) are shown in the bottom view. xyz-coordinates for the optimized structure of Intermediate **B**, checked to be a minimum on the energy hyper-surface by a frequency analysis.



Optimized xyz-coordinates for Intermediate **B**:

C	-1.46610200	1.64675600	-2.18322000
C	-0.12957300	1.62535400	-2.47520300
C	-0.37942200	0.80866900	-0.39645800
C	-0.16895200	0.29883300	0.98971100
H	-2.32805200	1.97115000	-2.77127200
H	0.41624500	1.92278700	-3.37412900
H	-1.18626600	0.16815000	1.40335700
N	-1.61159300	1.15285400	-0.89371000
N	0.53621200	1.12402600	-1.36194700
H	0.32667000	1.09207400	1.58937400
C	0.62924200	-1.07585100	1.14047200
O	0.68636100	-1.74249600	-0.07891800
C	-0.01813600	-1.93546100	2.27015800
C	0.16029300	-3.33593500	2.22764400
C	-0.68826700	-1.38038800	3.38153400
C	-0.32242100	-4.15058300	3.26321200
H	0.64724900	-3.78411100	1.34922700
C	-1.17368600	-2.19735300	4.41939000
H	-0.85041300	-0.29316000	3.45835700
C	-0.99079000	-3.58823000	4.36601600
H	-0.18248700	-5.24203200	3.20142800
H	-1.70025400	-1.73893200	5.27236700
H	-1.37138500	-4.23105900	5.17601000
C	2.07760600	-0.81259800	1.64430100
C	3.16410600	-1.45656800	1.02318700
C	2.33449900	-0.02607800	2.78979600
C	4.47049200	-1.31196400	1.52407000
H	2.95815800	-2.07856500	0.14226100
C	3.63855300	0.12495400	3.28991000
H	1.50247400	0.45060000	3.33335400
C	4.71674700	-0.51879200	2.65659200
H	5.30402400	-1.82996900	1.02233600
H	3.81018400	0.73799500	4.18966400
H	5.73960800	-0.40989900	3.05160600
C	-2.87986100	1.17711300	-0.17289500
C	-3.07874000	2.19686900	0.80251700
C	-3.89659800	0.24186600	-0.51408300
C	-4.31083700	2.21639100	1.48684400
C	-5.10988600	0.32375600	0.20386900
C	-5.31536200	1.28398000	1.20061400
H	-4.48792900	2.98867100	2.25144700
H	-5.91025900	-0.39431800	-0.02938000
H	-6.26948100	1.31448600	1.75037000
C	1.99440700	1.11481900	-1.28703500
C	2.72426400	0.17159800	-2.06078400
C	2.62905500	2.15065000	-0.54425600
C	4.13175200	0.25893300	-2.01088200
C	4.03753000	2.16767500	-0.52214400
C	4.78492800	1.22716800	-1.24096100
H	4.72710100	-0.46104300	-2.59288500
H	4.55678500	2.94671000	0.05605600
H	5.88552600	1.25972300	-1.21112400
C	-3.76435600	-0.77635000	-1.64398500

C	-2.06871000	3.31131300	1.08178200
C	2.07248200	-0.84998700	-2.99144200
C	1.86362300	3.29702600	0.11997200
H	-2.68413400	-0.90696800	-1.88015500
H	0.99301600	-0.91901200	-2.73515500
H	0.80458100	2.98572300	0.23243200
H	-1.11648600	3.05402800	0.57436900
C	-4.49709800	-0.26667200	-2.90812800
C	-4.29335900	-2.16859000	-1.24659300
C	-1.75444200	3.47076400	2.58311600
C	-2.55620100	4.64488400	0.47008900
C	2.38593000	3.64563700	1.52706300
C	1.86979300	4.54207900	-0.79749100
C	2.21795600	-0.38863000	-4.46152900
C	2.64498800	-2.27101300	-2.81311700
H	1.79937500	0.62597900	-4.63360800
H	3.28338800	-0.35741800	-4.77773200
H	1.68512200	-1.08834300	-5.13894700
H	2.18975500	-2.95357300	-3.55979000
H	3.74519500	-2.31416500	-2.96297300
H	2.39407300	-2.66981300	-1.81096300
H	-3.78695200	-2.53800300	-0.33331200
H	-5.39249200	-2.17689100	-1.08005300
H	-4.08349300	-2.89337900	-2.05976400
H	-5.58826000	-0.15282800	-2.72786200
H	-4.11992500	0.71864700	-3.25470300
H	-4.36564200	-0.98530600	-3.74392000
H	-1.40861400	2.51829200	3.03395200
H	-0.95963900	4.23032800	2.73494800
H	-2.64282700	3.80899200	3.15648200
H	-2.73766800	4.55166400	-0.62035900
H	-3.50594400	4.97675200	0.94012700
H	-1.80372200	5.44664500	0.62497000
H	2.90576600	4.90888300	-0.95699500
H	1.43618500	4.32085900	-1.79450000
H	1.28204800	5.36883200	-0.34501600
H	2.43539900	2.74899100	2.17739200
H	3.40314500	4.08900100	1.49088100
H	1.72481600	4.39592900	2.00883400
O	-0.80920000	-1.79996700	-2.06408700
H	-1.53296700	-2.05041700	0.06294800
C	-0.93316500	-2.88948600	-2.96016500
C	-0.99995200	-4.14855100	-2.05561300
H	-1.84153600	-2.78191400	-3.60296900
H	-0.05429500	-2.93824600	-3.65277100
H	-2.07065500	-4.42696500	-1.86199600
H	-0.51257800	-5.03484900	-2.52515600
B	-0.55577900	-2.34198900	-0.67039000
O	-0.33577800	-3.77840900	-0.87708900

NBO results for Intermediate B.

7. (1.97412) BD (1) C 3 - C 4 (1.492 Å, WBI = 1.05)
(51.39%) 0.7169* C 3 s(41.84%)p 1.39(58.15%)d 0.00(0.02%)
(48.61%) 0.6972* C 4 s(26.86%)p 2.72(73.10%)d 0.00(0.04%)
13. (1.94933) BD (1) C 4 - C 11 (1.597 Å, WBI = 0.92)

```
           ( 52.61%)   0.7253* C   4 s( 28.37%)p 2.52( 71.61%)d 0.00(  0.02%)
           ( 47.39%)   0.6884* C  11 s( 24.72%)p 3.04( 75.24%)d 0.00(  0.04%)
  16. (1.98470) BD ( 1) C  11 - O  12  (1.391 Å, WBI = 0.96)
           ( 33.67%)   0.5803* C  11 s( 21.44%)p 3.65( 78.35%)d 0.01(  0.21%)
           ( 66.33%)   0.8144* O  12 s( 37.52%)p 1.66( 62.42%)d 0.00(  0.05%)
 112. (1.97035) BD ( 1) H  94 - B 101  (1.256 Å, WBI = 0.90)
           ( 57.81%)   0.7603* H  94 s( 99.96%)p 0.00(  0.04%)
           ( 42.19%)   0.6496* B 101 s( 36.89%)p 1.71( 63.07%)d 0.00(  0.04%)
 169. (1.92437) LP ( 1) O  12          s( 27.34%)p 2.66( 72.63%)d 0.00(  0.03%)
 170. (1.87002) LP ( 2) O  12          s(  0.01%)p 1.00( 99.96%)d 0.00(  0.04%)
 171. (1.65849) LP ( 3) O  12          s( 35.11%)p 1.85( 64.87%)d 0.00(  0.03%)
 175. (0.43146) LP*( 1) B 101          s( 62.67%)p 0.59( 37.28%)d 0.00(  0.05%)
 176. (0.39231) LP*( 2) B 101          s(  0.44%)p99.99( 99.20%)d 0.83(  0.36%)
 177. (0.37899) LP*( 3) B 101          s(  0.03%)p99.99( 99.56%)d12.57(  0.41%)
```

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis (hyperconjugation energy [E(2)] = kcal/mol):

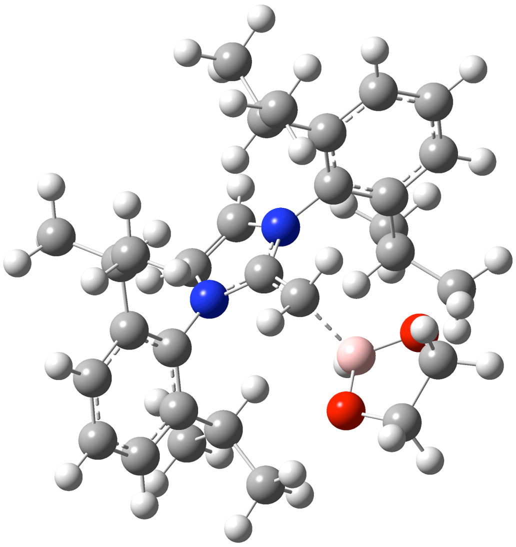
16. BD (1) C 11 - O 12	/177. LP*(3) B 101	**21.04**
170. LP (2) O 12	/176. LP*(2) B 101	**20.05**
171. LP (3) O 12	/175. LP*(1) B 101	**126.92**
171. LP (3) O 12	/177. LP*(3) B 101	**162.51**

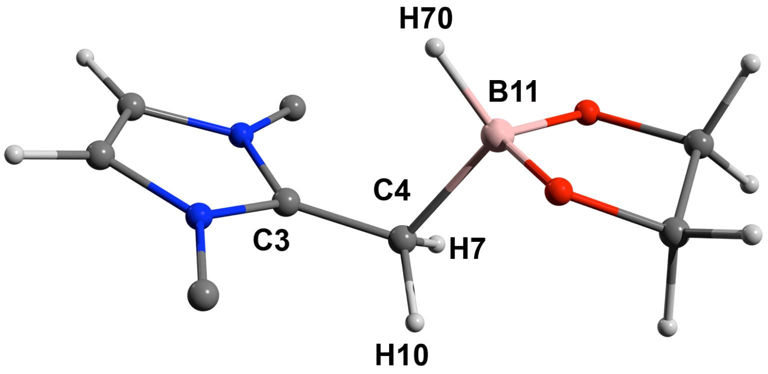
Natural Population Analysis (NPA Charges)

C	3	0.54720
C	4	-0.53830
H	7	0.28516
N	8	-0.37124
N	9	-0.36584
H	10	0.26309
C	11	0.31861
O	12	-0.78474
H	94	-0.16388
B	101	0.90685

Optimization results for Intermediate A_2

Fig. S11. Ball-and-stick representation of the optimised structure of proposed Intermediate $\mathbf{A_2}$ (top). Ball-and-stick depiction of the optimized structure of Intermediate $\mathbf{A_2}$ (bottom) with Dipp-groups and protons on IPr omitted for clarity; atom numbers as they appear in the output-file. Selected computed bond lengths and Wiberg bond indices (in parentheses) are shown in the bottom view. xyz-coordinates for the optimized structure of Intermediate $\mathbf{A_2}$, checked to be a minimum on the energy hyper-surface by a frequency analysis.





Optimized xyz-coordinates for Intermediate **A$_2$**:

C	-0.73086400	0.77087600	-2.19166600
C	0.63537700	0.79798700	-2.19845300
C	-0.02631700	0.26308300	-0.09067700
C	-0.01584900	-0.21896400	1.26196000
H	-1.46045300	0.96220200	-2.98328500
H	1.34836600	1.01866900	-2.99744600
H	-0.95020900	0.02994800	1.79541500
N	-1.13369700	0.43522400	-0.89479200
N	1.06513200	0.47670200	-0.90630800
H	0.88286400	0.10909100	1.81471700
B	0.07098600	-2.02658000	1.32413800
C	-2.51290000	0.38435900	-0.45790600
C	-3.07880800	1.54918700	0.13047000
C	-3.25982800	-0.80649400	-0.66588600
C	-4.43234300	1.49152100	0.51965500
C	-4.61100900	-0.80094900	-0.25973000
C	-5.19258900	0.32965100	0.32772300
H	-4.90032700	2.37671100	0.97881300
H	-5.21505400	-1.71007800	-0.40365400
H	-6.24879600	0.30593600	0.64020900
C	2.45137400	0.46874800	-0.48843300
C	3.24318400	-0.68257500	-0.74784800
C	2.97723600	1.63526600	0.13275000
C	4.59833300	-0.63492900	-0.35889600
C	4.33744500	1.62039600	0.50217800
C	5.14142400	0.49791400	0.26033700
H	5.23694900	-1.51282000	-0.54149300
H	4.77570800	2.50800200	0.98522600
H	6.20194300	0.50688100	0.55871800
C	-2.67193200	-2.04861700	-1.33361300
C	-2.29221300	2.84752000	0.31968400
C	2.69738000	-1.92055000	-1.45834900
C	2.14202500	2.89526800	0.36763500
H	-1.57199200	-1.91269400	-1.38390900
H	1.59059600	-1.84172500	-1.46061200
H	1.08436100	2.64696500	0.14043000
H	-1.23596100	2.64745300	0.04326100
C	-3.20212500	-2.19291700	-2.77810500
C	-2.91720800	-3.32772800	-0.50790400
C	-2.29350500	3.31890000	1.78853800
C	-2.81068800	3.95260800	-0.62687300
C	2.18994900	3.36570300	1.83566600
C	2.56569900	4.02386100	-0.59853500
C	3.17902200	-1.96042600	-2.92666200
C	3.04228600	-3.22696700	-0.71592200
H	2.89041300	-1.04759800	-3.48916500
H	4.28529500	-2.04931500	-2.98438600
H	2.74335100	-2.83497900	-3.45421000
H	2.55087600	-4.08452300	-1.22150200
H	4.13512100	-3.42955500	-0.71795300
H	2.67849600	-3.18868300	0.33136800
H	-2.51183100	-3.21805000	0.51930800
H	-3.99742100	-3.58252300	-0.44931400

H	-2.40363700	-4.18671500	-0.98838100
H	-4.30326500	-2.34196300	-2.79126000
H	-2.98134400	-1.29698400	-3.39593500
H	-2.73811500	-3.07067600	-3.27514400
H	-1.89861000	2.53382000	2.46468700
H	-1.66058000	4.22341700	1.90642100
H	-3.31458700	3.58350800	2.13556800
H	-2.76496600	3.63393400	-1.68869400
H	-3.86627200	4.21472000	-0.40173500
H	-2.20497200	4.87729800	-0.52078000
H	3.61974100	4.32790900	-0.42440000
H	2.48066800	3.70625000	-1.65823900
H	1.92819200	4.92241800	-0.45876800
H	1.87236700	2.56104600	2.52941300
H	3.21024400	3.68722700	2.13345400
H	1.51501100	4.23412700	1.98643800
H	0.02291700	-2.42662400	0.14652100
O	1.31194400	-2.42271700	1.99015900
O	-1.03598300	-2.46127700	2.18491400
C	0.98530300	-2.68508700	3.34293300
C	-0.48421600	-3.15258000	3.29203500
H	-1.04399800	-2.91613100	4.22704500
H	-0.53970200	-4.26158200	3.13981400
H	1.07788000	-1.76030300	3.97378500
H	1.67619500	-3.44702700	3.76945900

NBO results for Intermediate A_2.

```
7. (1.97629) BD ( 1) C   3 - C   4  (1.436 Å, WBI = 1.23)
            ( 52.30%)   0.7232* C   3 s( 44.29%)p 1.26( 55.70%)d 0.00(  0.01%)
            ( 47.70%)   0.6906* C   4 s( 26.90%)p 2.72( 73.06%)d 0.00(  0.05%)
8. (1.65807) BD ( 2) C   3 - C   4
            ( 28.57%)   0.5345* C   3 s(  0.06%)p99.99( 99.89%)d 0.90(  0.05%)
            ( 71.43%)   0.8452* C   4 s( 14.58%)p 5.86( 85.40%)d 0.00(  0.02%)
C4 – B11 (1.811 Å, WBI = 0.57)
15. (1.97493) BD ( 1) B  11 - H  70  (1.244 Å, WBI = 0.92)
            ( 43.22%)   0.6574* B  11 s( 34.08%)p 1.93( 65.89%)d 0.00(  0.03%)
            ( 56.78%)   0.7535* H  70 s( 99.96%)p 0.00(  0.04%)
  124. (0.52565) LP*( 1) B  11          s( 28.61%)p 2.49( 71.38%)d 0.00(  0.02%)
   125. (0.41111) LP*( 2) B  11          s( 37.11%)p 1.69( 62.59%)d 0.01(  0.30%)
   126. (0.37415) LP*( 3) B  11          s(  0.10%)p99.99( 99.33%)d 5.61(  0.57%)
```

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis (hyperconjugation energy [E(2)] = kcal/mol):

8. BD (2) C   3 - C   4   /124. LP*(1) B 11   **159.17**

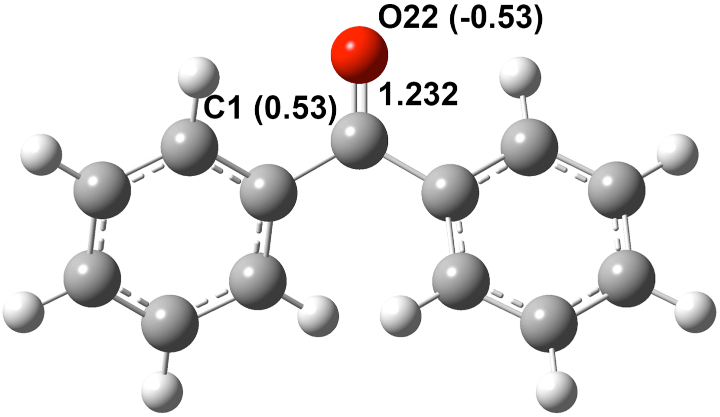
Natural Population Analysis (NPA Charges)

C   3   0.52216
C   4 -0.79774

H	7	0.27430
N	8	-0.41439
N	9	-0.41399
H	10	0.27039
B	11	0.78526
H	70	-0.14033

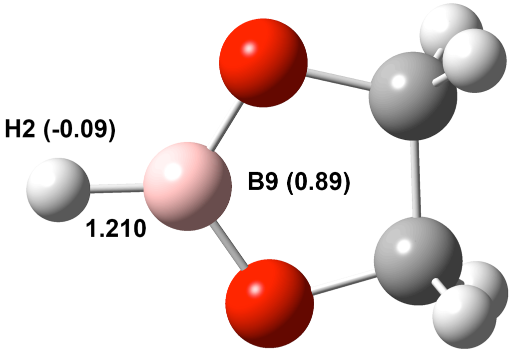
Optimization results for Ph_2CO

Fig. S12. Ball-and-stick representation of the optimized structure of Ph_2CO. with the C-O distance and the NPA charges for C1 and O22 in parentheses, checked to be a minimum on the energy hyper-surface by a frequency analysis.



Optimization results for HBPin

Figure S13. Ball-and-stick representation of the optimised structure of HBPin (Me-Groups replaced with H), with the H-B distance and the NPA charges for H2 and B9 in parentheses, checked to be a minimum on the energy hyper-surface by a frequency analysis.



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