Electronic Supplementary Material (ESI) for Dalton Transactions
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Supporting Information for:

Hydroboration of an Alkene by Amine-Borane Catalysed by a $[Rh(PR_3)_2]^+$ fragment. Mechanistic Insight and Tandem Hydroboration/Dehydrogenation.

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Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk and glove-box techniques. Glassware was oven dried at 130 ºC overnight and flamed under vacuum prior to use. Pentane was dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.[1] *t*-butylethene (TBE) was dried over sodium, vacuum distilled and stored over 3 Å molecular sieves. 1,2-$C_6H_4F_2$ and CD_2Cl_2 were dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. $H_3B{\cdot}NMe_3$ was purchased from Aldrich and sublimed before use (5 × 10^{-2} Torr, 298 K). $H_3B{\cdot}NMe_2H$ was purchased from Acros and sublimed twice before use (5 × 10^{-2} Torr, 298 K). $Na[BAr^{Cl}{}_4]$[2], and $[Rh(P^iBu_2{}^tBu)_2][BAr^F{}_4]$[3] **(B)** were prepared by literature methods. All other chemicals are commercial products and were used as received. NMR spectra were recorded on a Varian Mercury VX 300 MHz or a Varian Unity Plus 500 MHz spectrometer at room temperature. In 1,2-$C_6H_4F_2$, ^{1}H NMR spectra were referenced to the centre of the downfield solvent multiplet (δ = 7.07). ^{31}P NMR spectra and ^{11}B NMR spectra were referenced externally against 85% H_3PO_4 and $BF_3.OEt_2$ respectively. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF-Q instrument interfaced with a glovebox.[4] Microanalyses were performed by Elemental Microanalysis Ltd.

Synthesis of new complexes

$[Rh(P^iBu_2{}^tBu)_2][BAr^{Cl}{}_4]$

Preparation same as the literature procedure for **B** substituting $[BAr^F{}_4]^-$ for $[BAr^{Cl}{}_4]^-$ (Ar^{Cl}= 3,5-$C_6H_5Cl_2$). Yield: 65 %.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.04 – 6.99 (m, 12H, $BAr^{Cl}{}_4$), 1.90 – 1.74 (m, 8H, ^{i}Bu{CH/CH_2}), 1.72 – 1.63 (m, 4H, ^{i}Bu{CH_2}), 1.14 (dd, 18H, J = 7.5, J = 7.3, ^{t}Bu{Me}), 1.00 – (–0.80) (br, 24H, ^{i}Bu{Me}).

^{31}P {^{1}H} NMR (CD_2Cl_2, 202 MHz): δ 64.2 (br).

$[Rh(P^iBu_2{}^tBu)_2(\eta^2\text{-}Me_3N{\cdot}H_2BCH_2CH_2CMe_3))][BAr^F{}_4]$ (2)

1,2-$C_6H_4F_2$ (1 mL) was added to a Young's crystallisation tube containing **B** (0.050 g, 0.037 mmol) and $H_3B{\cdot}NMe_3$ (0.0027 g, 0.037 mmol). TBE (24 μL, 0.183 mmol) was then added and the tube sealed. After 5 days the purple solution was layered with pentane and held at 5 ºC yielding the product as deep

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purple crystals. Yield: 0.042 g (72 %). Crystals suitable for single crystal X-ray diffraction were grown by using $Rh(P^iBu_2{}^tBu)_2][BAr^{Cl}{}_4]$.

^{1}H NMR (1,2-$C_6H_4F_2$, 500 MHz): δ 8.34 (s, 8H, $BAr^F{}_4$), 7.69 (s, 4H, $BAr^F{}_4$), 2.94 (s, 9H, NMe_3), 2.18 (br, 4H, ^{i}Bu{CH}), 1.97 – 1.79 (m, 8H, ^{i}Bu{CH_2}), 1.73 - 1.70 (m, 2H, CH_2), 1.34 – 1.20 (m, 44H, ^{i}Bu{Me}, ^{t}Bu{Me}, CH_2), 1.02 (s, 9H, C{Me}), -7.07 (br, 2H, BH_2).

^{1}H {^{11}B} NMR (1,2-$C_6H_4F_2$, 500 MHz): δ 8.34 (s, 8H, $BAr^F{}_4$), 7.69 (s, 4H, $BAr^F{}_4$), 2.93 (s, 9H, NMe_3), 2.18 (br, 4H, ^{i}Bu{CH}), 1.97 – 1.79 (m, 8H, ^{i}Bu{CH_2}), 1.72 - 1.70 (m, 2H, CH_2), 1.34 – 1.20 (m, 44H, ^{i}Bu{Me}, ^{t}Bu{Me}, CH_2), 1.02 (s, 9H, C{Me}), -7.07 (apparent triplet, 2H, $^2J_{HP}$ = 32 and $^1J_{RhH}$ = 32, BH_2).

^{31}P {^{1}H} NMR (1,2-$C_6H_4F_2$, 202 MHz): δ 53.8 (d, $^1J_{RhP}$ = 182).

^{11}B NMR (1,2-$C_6H_4F_2$, 160 MHz): δ 37.9 (br, BH_2), -6.1 (s, $BAr^F{}_4$).

Anal. Calcd for $C_{65}H_{90}B_2F_{24}NP_2Rh$ (1527.85 gmol^{-1}): C, 51.10; H, 5.94; N, 0.92. Found: C, 51.51; H, 5.86; N, 0.97.

ESI-MS (1,2-$C_6H_4F_2$, 60ºC) positive ion: *m/z* 664.4840 [M$^+$] (calc. 664.4758).

Catalytic Formation of 3

1,2-$C_6H_4F_2$ (435 μL) and TBE (15 μL, 0.117 mmol) were added to a high pressure NMR tube containing **B** (0.0080 g, 0.006 mmol) and $H_3B{\cdot}NMe_3$ (0.0085 g, 0.117 mmol).The tube was sealed and in situ analysis by ^{1}H and ^{11}B NMR spectroscopy indicated the formation of **3**. Only ~70% conversion is achieved with ~ 30% $H_3B{\cdot}NMe_3$ unreacted.

^{1}H NMR (1,2-$C_6H_4F_2$, 500 MHz): δ 2.51 (s, 9H, NMe_3), 2.40 – 1.93 (m, 2H, BH_2), 1.43 – 1.40 (m, 2H, $CH_2C\underline{H}_2CMe_3$), 1.02 (s, 9H, CMe_3), 0.55 (br, 2H, $C\underline{H}_2CH_2CMe_3$).

^{11}B NMR (1,2-$C_6H_4F_2$, 160 MHz): δ -0.83 (t, $^1J_{HB}$ = 96).

Oxidation of 3

1,2-$C_6H_4F_2$ (0.4 mL) and TBE (350 μL, 1.4 mmol) were added to a Young's NMR tube containing **B** (0.038 g, 0.028 mmol) and $H_3B{\cdot}NMe_3$ (0.100 g, 1.371 mmol). After 6 days the solution was transferred to a round bottomed flask and THF (2 mL) followed by EtOH (2 mL), NaOH (2M, 2 mL) and H_2O_2 (35 %

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aq. solution, 3 mL) were added. The solution was stirred at 40 ºC for 16 hours to ensure complete oxidation. The reaction mixture was extracted with Et_2O (3 x 20 mL), and the organic phase washed with a 2M aq. NaOH solution (20 mL), H_2O (20 mL) and finally brine (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated to yield the expected $HOCH_2CH_2{}^tBu$ as the only product (^1H NMR spectroscopy).

Kinetics

5 mol% of B

1,2-$C_6H_4F_2$ (435 μL) and TBE (15 μL, 0.117 mmol) were added to a high pressure NMR tube containing **B** (0.0080 g, 0.006 mmol) and $H_3B{\cdot}NMe_3$ (0.0085 g, 0.117 mmol). The sample was shaken twice and then immediately followed by ^{11}B NMR spectroscopy. Catalysis had slowed dramatically at ~70% completion at which point the solution was transferred to another NMR tube containing a further 20 equivalents of TBE (15 μL, 0.117 mmol) and $H_3B{\cdot}NMe_3$ (0.0085 g, 0.117 mmol). Catalysis was seen to restart at a slightly lower initial rate (1 x 10^{-6} Ms^{-1} *versus* 4 x 10^{-6} Ms^{-1}).

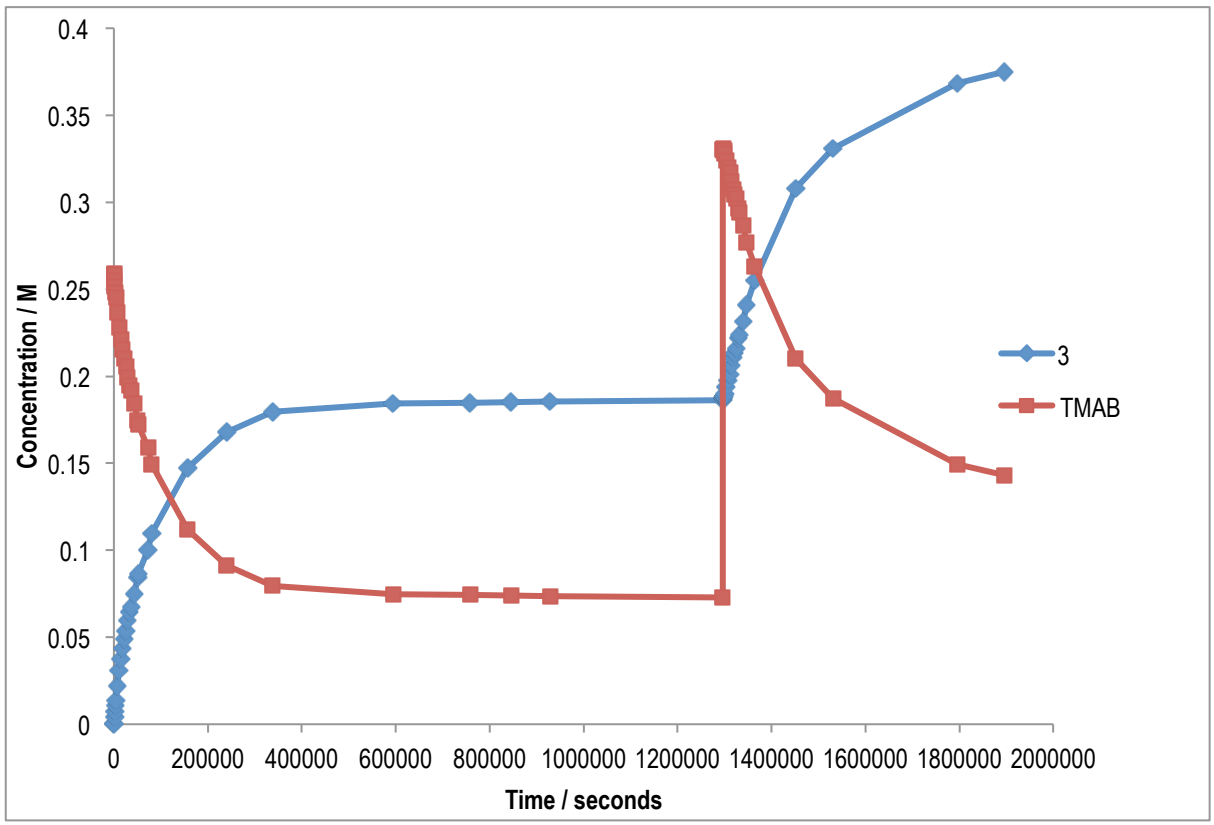

Figure S-1: Plot of concentration *versus* time for the hydroboration of TBE by $H_3B{\cdot}NMe_3$ catalysed by B (5 mol%)

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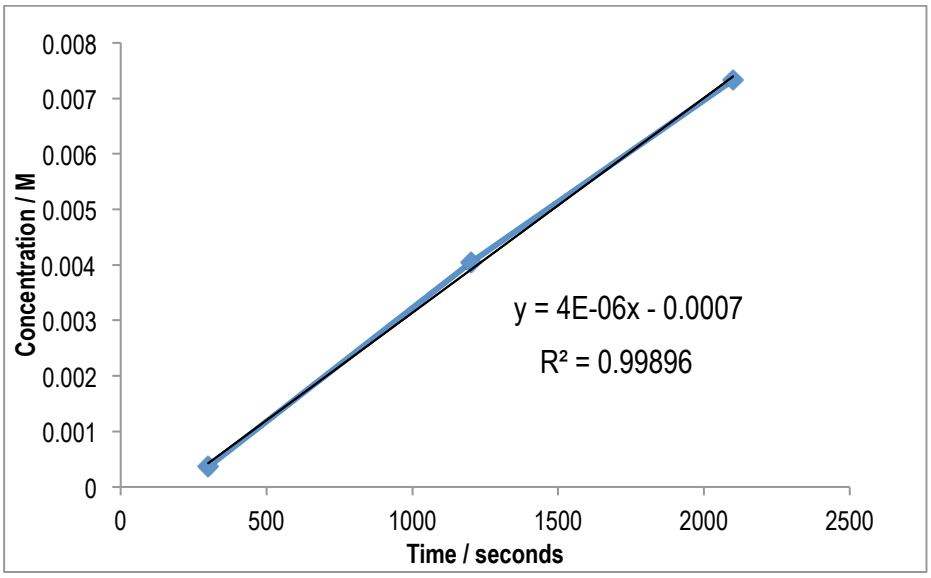

Figure S-2: Initial rate over 2100 seconds (5 mol% B)

10 mol% of B

1,2-$C_6H_4F_2$ (435 μL) and TBE (15 μL, 0.117 mmol) were added to a high pressure NMR tube containing **B** (0.0160 g, 0.0117 mmol) and $H_3B{\cdot}NMe_3$ (0.0085 g, 0.117 mmol). The sample was shaken twice and then immediately followed by ^{11}B NMR spectroscopy. An initial rate of 7 x 10^{-6} Ms^{-1} was seen over the first 2100 seconds.

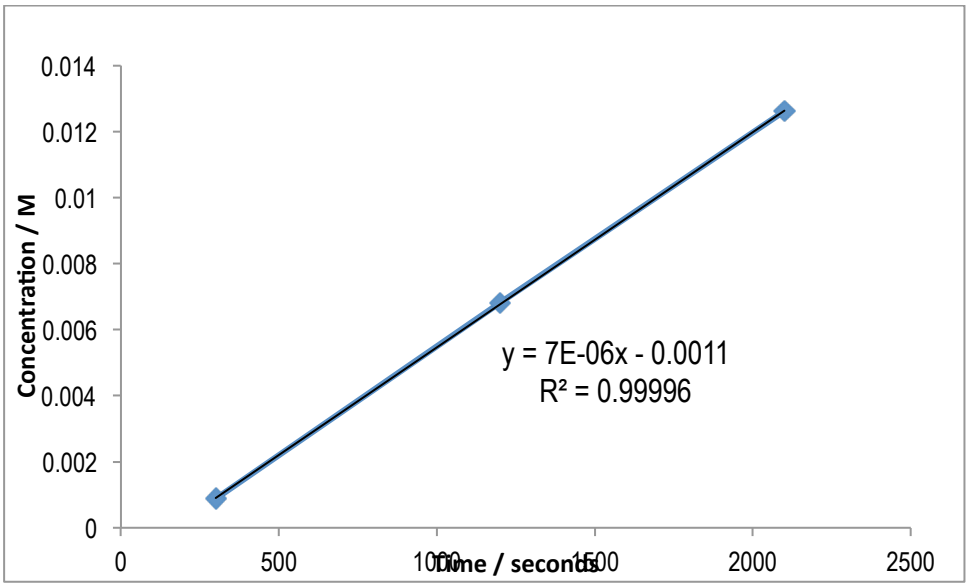

Figure S-3: Initial rate over 2100 seconds (10 mol% B)

2 fold excess of TBE at 5 mol% of B

1,2-$C_6H_4F_2$ (420 μL) and TBE (30 μL, 0.234 mmol) were added to a high pressure NMR tube containing **B** (0.0080 g, 0.006 mmol) and $H_3B{\cdot}NMe_3$ (0.0085 g, 0.117 mmol). The sample was shaken twice and then immediately followed by ^{11}B NMR spectroscopy. An initial rate of 8 x 10^{-6} Ms^{-1} was seen over the first 2100 seconds.

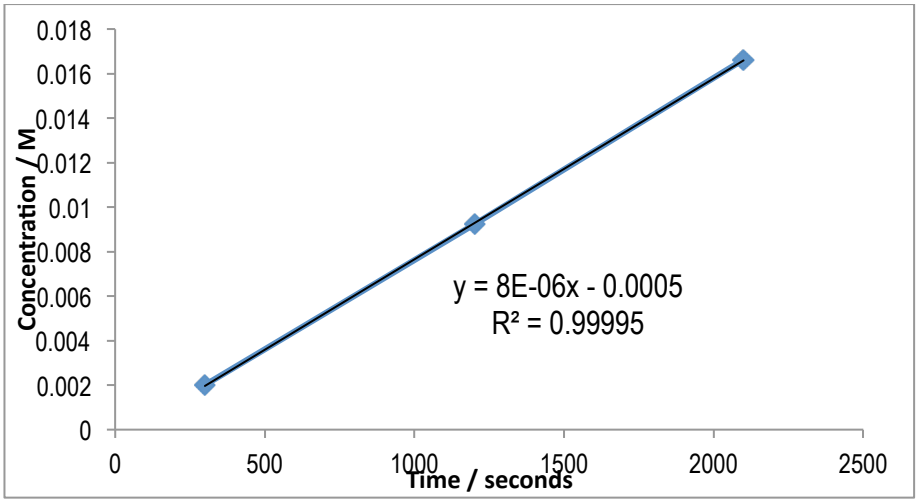

Figure S-4: Initial rate over 2100 seconds with a 2 fold excess of TBE (5 mol% B)

10 fold excess of TMAB at 5 mol% of B

1,2-$C_6H_4F_2$ (435 μL) and TBE (15 μL, 0.117 mmol) were added to a high pressure NMR tube containing **B** (0.0080 g, 0.006 mmol) and $H_3B{\cdot}NMe_3$ (0.085 g, 1.17 mmol). The sample was shaken twice and then immediately followed by ^{11}B NMR spectroscopy. An initial rate of 4 x 10^{-6} Ms^{-1} was seen over the first 2100 seconds.

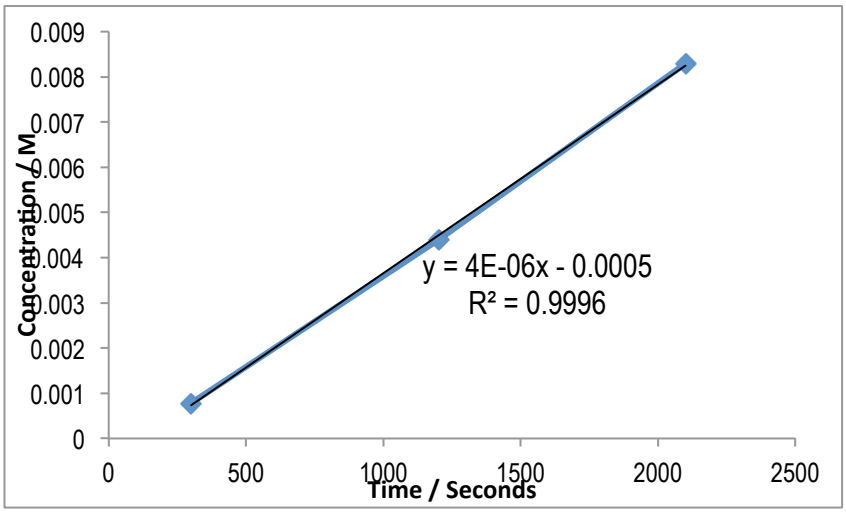

Figure S-5: Initial rate over 2100 seconds with a 10 fold excess of TMAB (5 mol% B)

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Equilibrium constant

350 μL of a 0.0187 M solution of $H_3B{\cdot}NMe_3$ in 1,2-$C_6H_4F_2$ was added to a high pressure NMR tube containing **2** (0.010 g, 0.0065 mmol). After 3 hours, analysis by ^1H NMR spectroscopy gave an equilibrium constant, K of 1.62.

$$K = \frac{[\mathbf{2}][TMAB]}{[\mathbf{1}][\mathbf{3}]}$$

DMAB + TBE

10 fold excess of TBE at 5 mol%

A solution of DMAB (0.0086 g, 0.146 mmol) in 1,2-$C_6H_4F_2$ (2 mL) was added dropwise with stirring over a period of 30 minutes to a Young's flask containing **B** (0.010 g, $7.3x10^{-3}$ mmol), TBE (0.188 mL, 1.46 mmol) and 1,2-$C_6H_4F_2$ (3 mL). After 2 hours, analysis by ^{11}B NMR spectroscopy showed 3 major products; **4**, **5** and $[H_2BNMe_2]_2$.

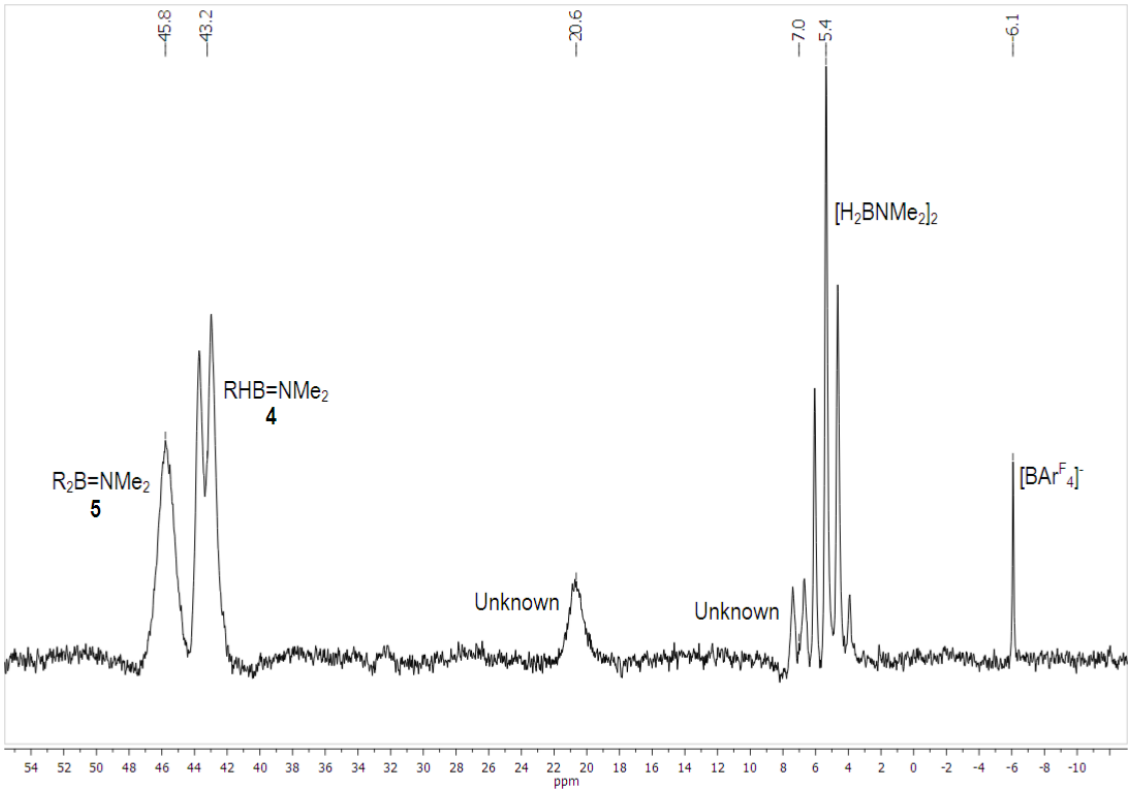

Figure S-6: ^{11}B NMR spectrum from the reaction of $H_3B{\cdot}NMe_2H$ and TBE catalysed by B (5 mol%) showing tandem hydroboration/dehydrogenation. (R = $CH_2CH_2{}^tBu$)

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References

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