# SUPPLEMENTARY INFORMATION

## $H_2$ activation using the first 1:1:1 hetero-tri(aryl)borane

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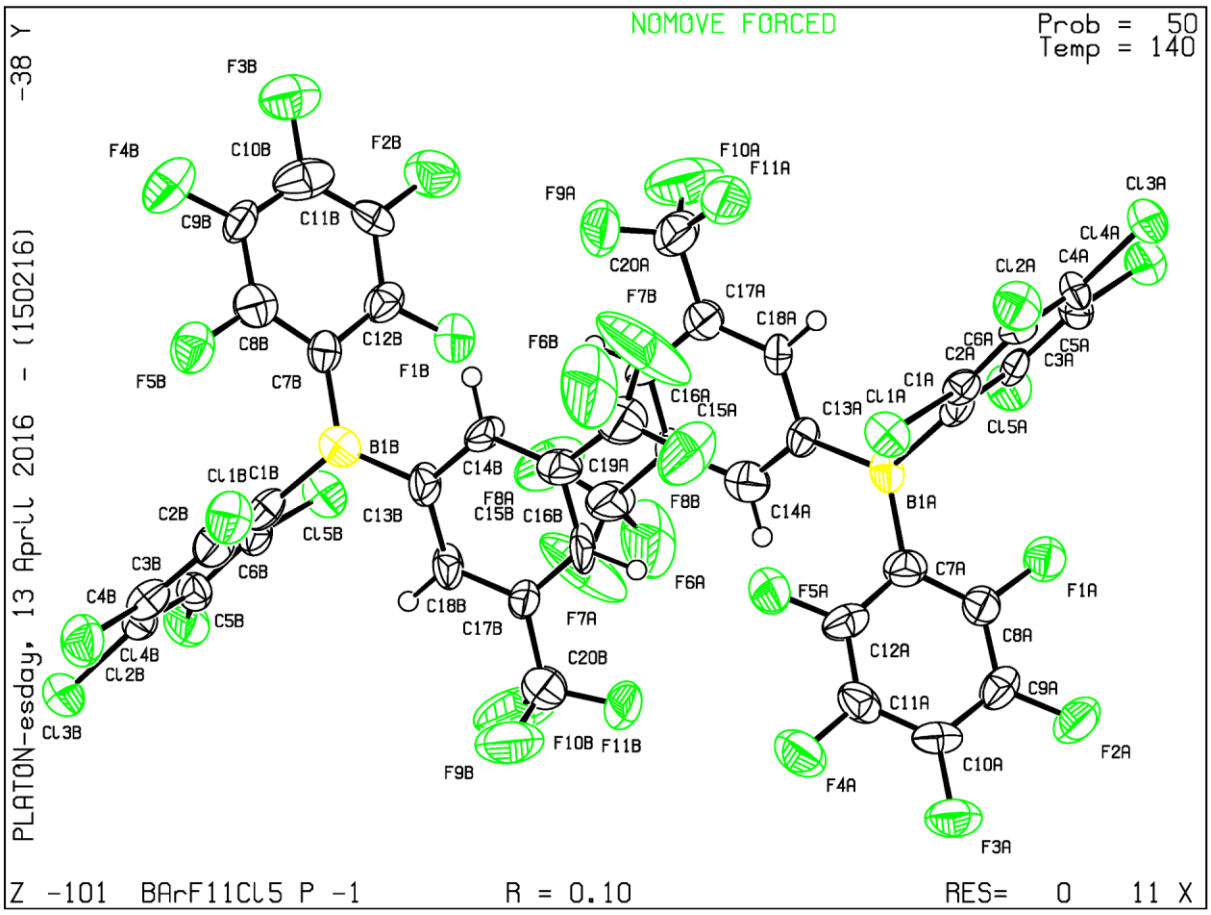


***Figure S1*** *X*-ray crystallographic structure of $B(C_6F_5)\{3,5\text{-}(CF_3)_2C_6H_3\}(C_6Cl_5)$ **3**

# SUPPLEMENTARY INFORMATION

## "Gutmann-Beckett method" for measurement of Lewis acidity

**3** (Lewis acid) is combined with a three-fold excess of $OPEt_3$ (Lewis base) in *ca.* 0.8 $cm^3$ $CD_2Cl_2$ in a NMR tube, rapidly generating the Lewis acid-base adduct $Et_3PO$–**3**, and $^{1}H$, $^{11}B$, $^{19}F$ and $^{31}P\{^{1}H\}$ NMR spectra obtained.

**$Et_3POB(C_6F_5)\{3,5\text{-}(CF_3)_2C_6H_3\}(C_6Cl_5)$ $Et_3PO$–3**

$^{1}H$ NMR (500.2 MHz, $CD_2Cl_2$, 25 °C, δ): +7.81 (s, 2H, $Ar^{F6}$ 2,6-H), +7.68 (s, 1H, $Ar^{F6}$ 4-H), +1.89 (br.m, 6H, Et $CH_2$), +1.10 (br.m, 9H, Et $CH_3$); $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C, δ): +2.51 (br.s); $^{19}F$ NMR (470.7 MHz, $CD_2Cl_2$, 25 °C, δ): −62.9 (s, 6F, $Ar^{F6}$ 3,5-$CF_3$), −131.3 (m, 2F, $Ar^{F5}$ 2,6-F), −158.8 (t, $^{3}J_{FF}$ = 19.9 Hz, 1F, $Ar^{F5}$ 4-F), −163.8 (m, 2F, $Ar^{F5}$ 3,5-F); $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CD_2Cl_2$, 25 °C, δ): +76.49 (s).

# SUPPLEMENTARY INFORMATION

## $H_2$ cleavage by FLPs

Equimolar quantities (*ca.* 30 μmol) of Lewis acid (**3**) and Lewis base {either $P(^tBu)_3$, 2,2,6,6-tetramethylpiperidine (tmp), or 2,6-lutidine} are combined in *ca.* 0.8 $cm^3$ $CD_2Cl_2$ in a NMR tube fitted with a J.Young valve. $^1H$, $^{11}B$, $^{19}F$ and $^{31}P\{^1H\}$ NMR spectra are obtained. The solution is degassed in the NMR tube by three freeze-pump-thaw cycles, before being frozen and the head-space of the NMR tube filled with 1 bar $H_2$ (dried by passing through a $P_2O_5$ column). The NMR tube is allowed to warm to room temperature, shaken, and the resulting reaction monitored by $^1H$ and $^{11}B$ NMR spectroscopy. A final set of $^1H$, $^{11}B$, $^{19}F$ and $^{31}P\{^1H\}$ NMR spectra are then obtained.

**$[(^tBu)_3PH][HB(C_6F_5)\{3,5\text{-}(CF_3)_2C_6H_3\}(C_6Cl_5)]$ $[(^tBu)_3PH][H\text{–}3]$**

Spectral data at 57% conversion (164 hours reaction time).

$^1H$ NMR (500.2 MHz, $CD_2Cl_2$, 25 °C, δ): +7.68 (s, 2H, $Ar^{F6}$ 2,6-H), +7.47 (s, 1H, $Ar^{F6}$ 4-H), +5.10 (d, $^1J_{HP}$ = 430 Hz, 1H), +4.08 (br.q, $^1J_{HB}$ = 88 Hz, 1H), +1.61 (d, $^3J_{HP}$ = 15.7 Hz, 27H); $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C, δ): −14.3 (d, $^1J_{BH}$ = 88 Hz); $^{19}F$ NMR (470.7 MHz, $CD_2Cl_2$, 25 °C, δ): −62.3 (s, 6F, $Ar^{F6}$ 3,5-$CF_3$), −130.8 (br.m, 2F, $Ar^{F5}$ 2,6-F), −160.4 (t, $^3J_{FF}$ = 20.3 Hz, 1F, $Ar^{F5}$ 4-F), −167.2 (m, 2F, $Ar^{F5}$ 3,5-F); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CD_2Cl_2$, 25 °C, δ): +59.9 (s).

**$[Me_4H_6C_5NH_2][HB(C_6F_5)\{3,5\text{-}(CF_3)_2C_6H_3\}(C_6Cl_5)]$ [tmp–H][H–3]**

Spectral data at 38% conversion (164 hours reaction time)*;* resonances for tmp correspond to a rapid equilibrium between $[tmp\text{–}H]^+$ and free tmp.

$^1H$ NMR (500.2 MHz, $CD_2Cl_2$, 25 °C, δ): +7.63 (s, 2H, $Ar^{F6}$ 2,6-H), +7.52 (s, 1H, $Ar^{F6}$ 4-H), +3.98 (br.q, $^1J_{HB}$ = 84 Hz, 1H), +2.90 (vbr.s, tmp $NH_2$), +1.67 (m, tmp 4-H), +1.42 (m, tmp 3,5-H), +1.17 (s, tmp 2,6-$CH_3$); $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C, δ): −13.9 (d, $^1J_{BH}$ = 84 Hz); $^{19}F$ NMR (470.7 MHz, $CD_2Cl_2$, 25 °C, δ): −62.5 (s, 6F, $Ar^{F6}$ 3,5-$CF_3$), −130.9 (br.m, 2F, $Ar^{F5}$ 2,6-F), −162.9 (t, $^3J_{FF}$ = 20.3 Hz, 1F, $Ar^{F5}$ 4-F), −165.9 (m, 2F, $Ar^{F5}$ 3,5-F).

**$[Me_2H_3C_5NH][HB(C_6F_5)\{3,5\text{-}(CF_3)_2C_6H_3\}(C_6Cl_5)]$ [lutidine–H][H–3]**

Spectral data at 64% conversion (164 hours reaction time)*;* resonances for lutidine correspond to a rapid equilibrium between $[lutidine\text{–}H]^+$ and free lutidine.

$^1H$ NMR (500.2 MHz, $CD_2Cl_2$, 25 °C, δ): +7.67 (s, 2H, $Ar^{F6}$ 2,6-H), +7.62 (t, $^3J_{HH}$ = 7.7 Hz, lutidine 4-H), +7.45 (s, 1H, $Ar^{F6}$ 4-H), +7.09 (d, $^3J_{HH}$ = 7.7 Hz, lutidine 3,5-H), +4.08 (br.q, $^1J_{HB}$ = 88 Hz, 1H), +2.50 (s, lutidine 2,6-$CH_3$); $^{11}B$ NMR (160.5 MHz, $CD_2Cl_2$, 25 °C, δ): −14.3 (d, $^1J_{BH}$ = 88 Hz); $^{19}F$ NMR (470.7 MHz, $CD_2Cl_2$, 25 °C, δ): −62.4 (s, 6F, $Ar^{F6}$ 3,5-$CF_3$), −131.0 (br.m, 2F, $Ar^{F5}$ 2,6-F), −160.5 (t, $^3J_{FF}$ = 21.2 Hz, 1F, $Ar^{F5}$ 4-F), −167.3 (m, 2F, $Ar^{F5}$ 3,5-F).

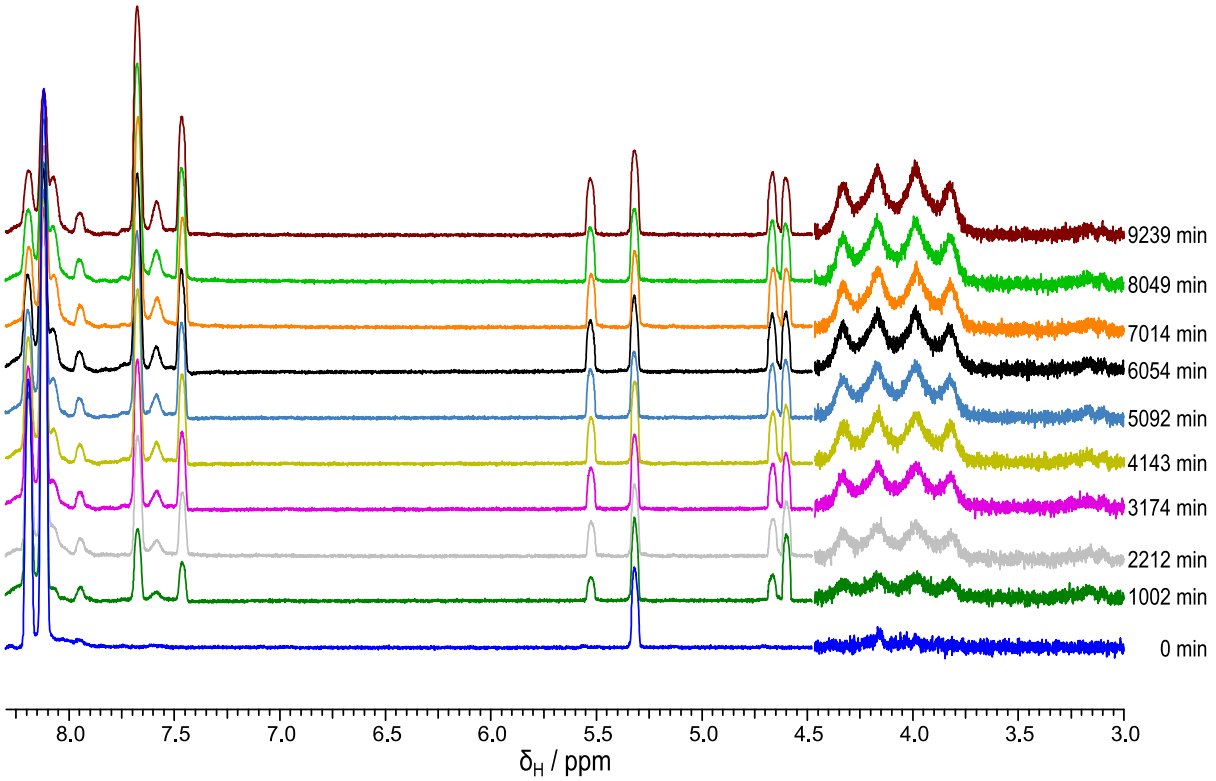


***Figure S2a*** $^{1}$H NMR spectra showing the progress of $H_2$ cleavage by the **3**/P($^{t}$Bu)$_3$ FLP

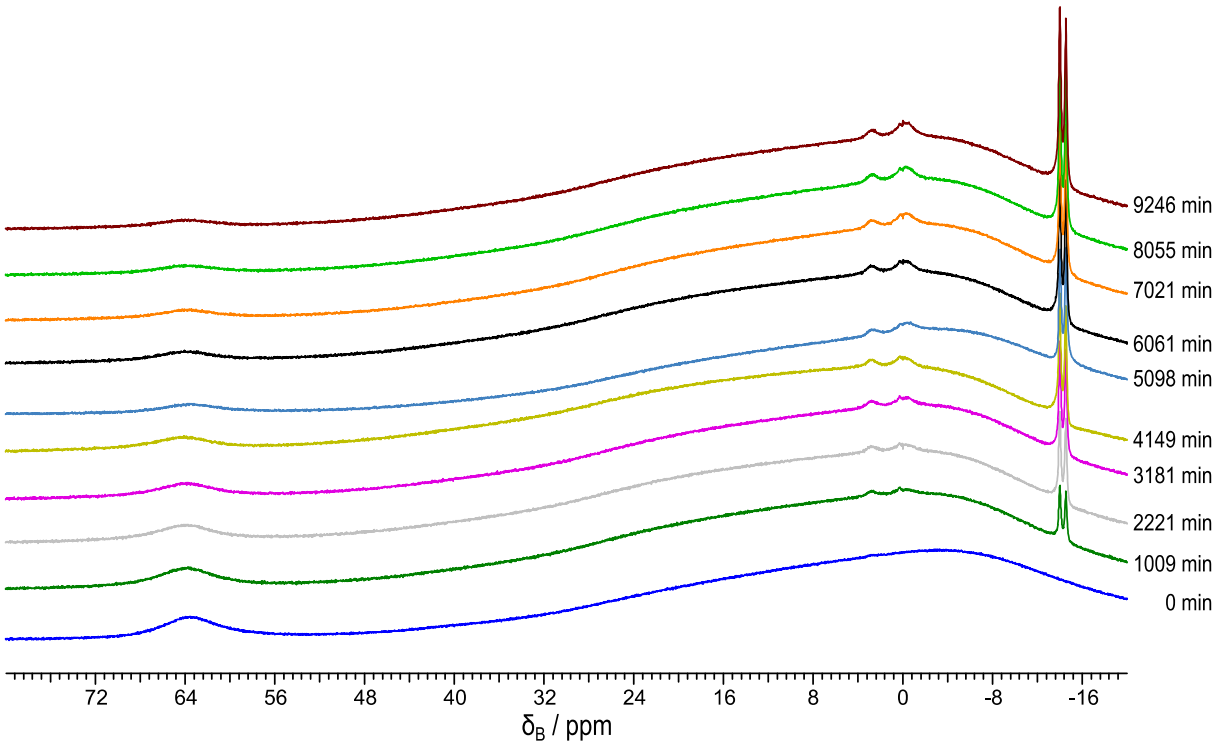


***Figure S2b*** $^{11}$B NMR spectra showing the progress of $H_2$ cleavage by the **3**/P($^{t}$Bu)$_3$ FLP

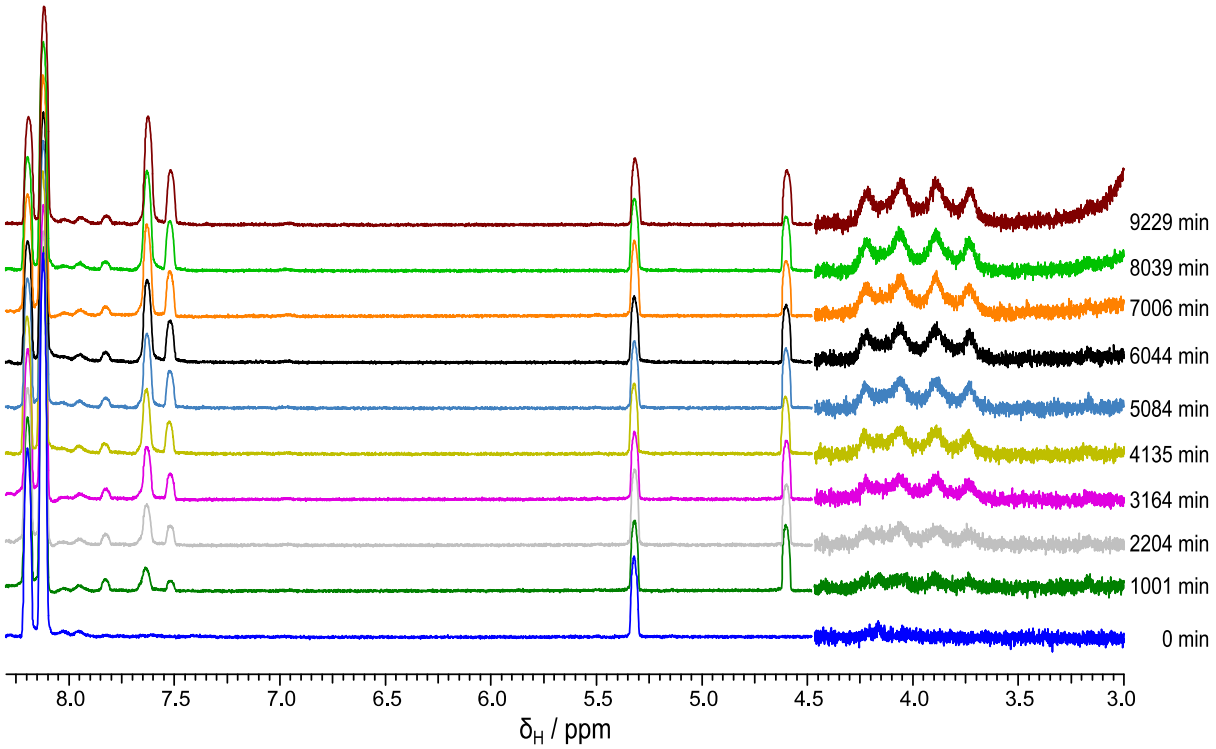


***Figure S3a*** $^{1}$H NMR spectra showing the progress of $H_2$ cleavage by the **3**/tmp FLP

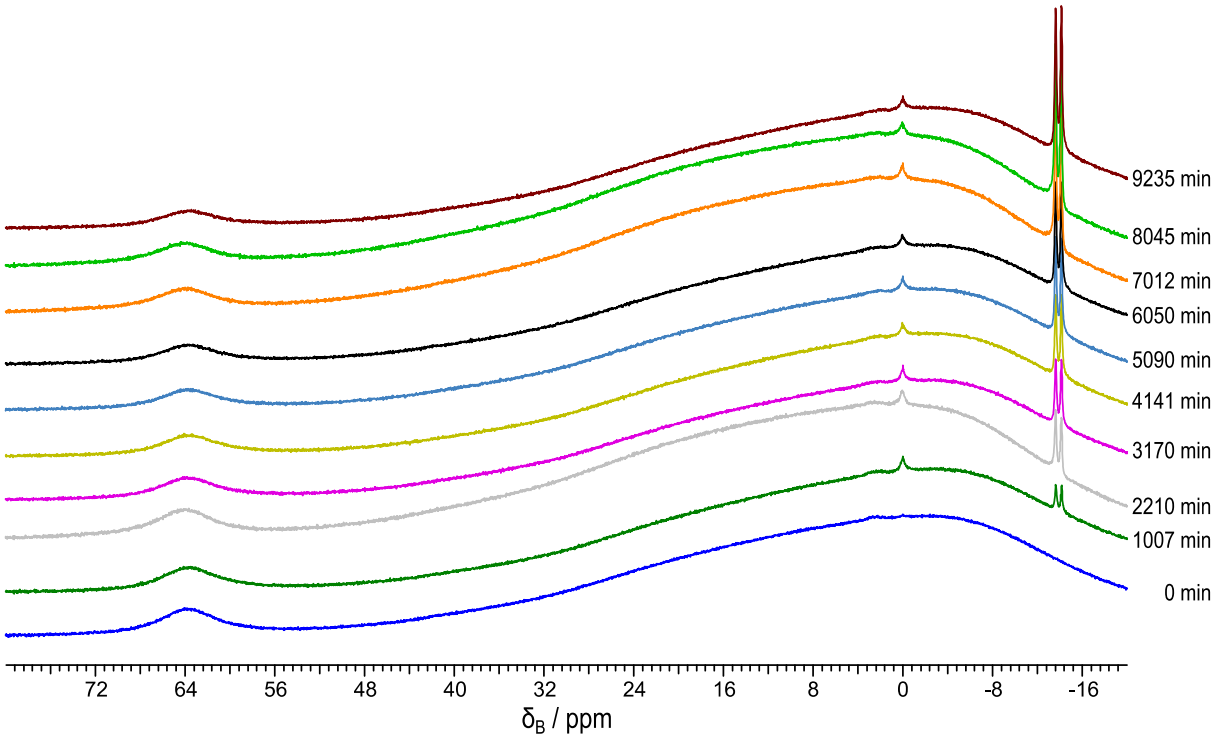


***Figure S3b*** $^{11}$B NMR spectra showing the progress of $H_2$ cleavage by the **3**/tmp FLP

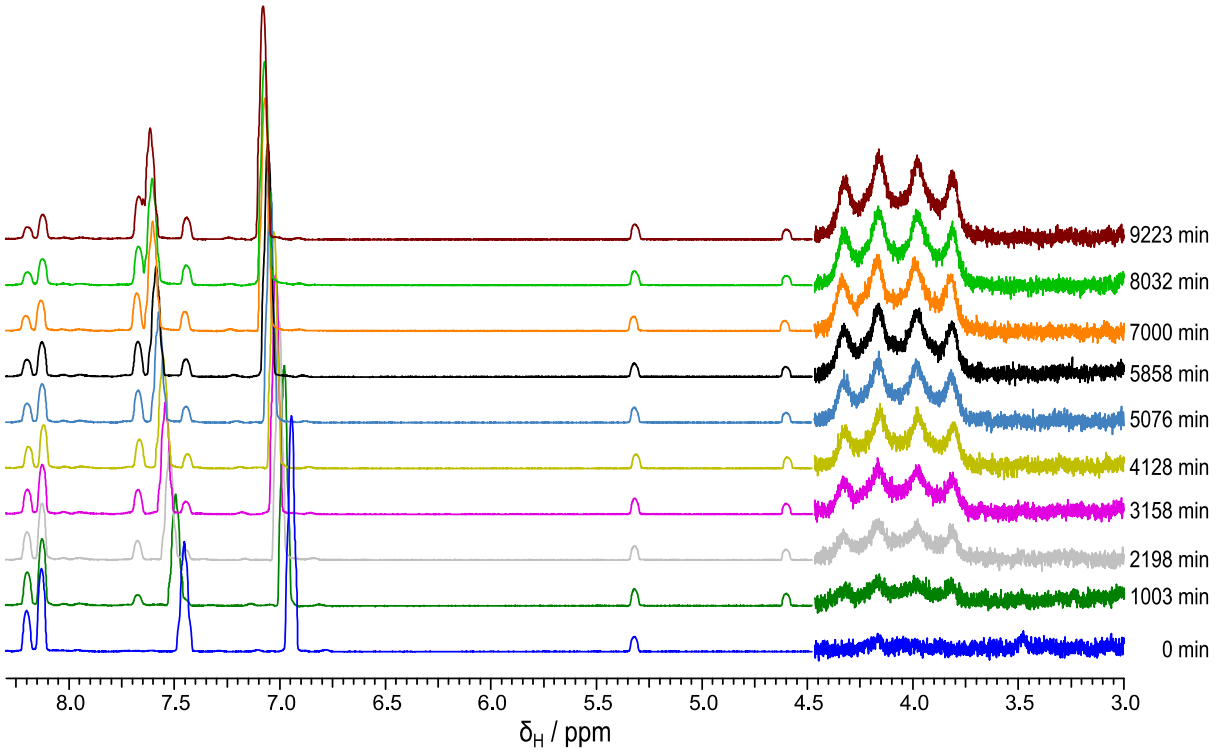


***Figure S4a*** $^{1}H$ NMR spectra showing the progress of $H_2$ cleavage by the **3**/lutidine FLP

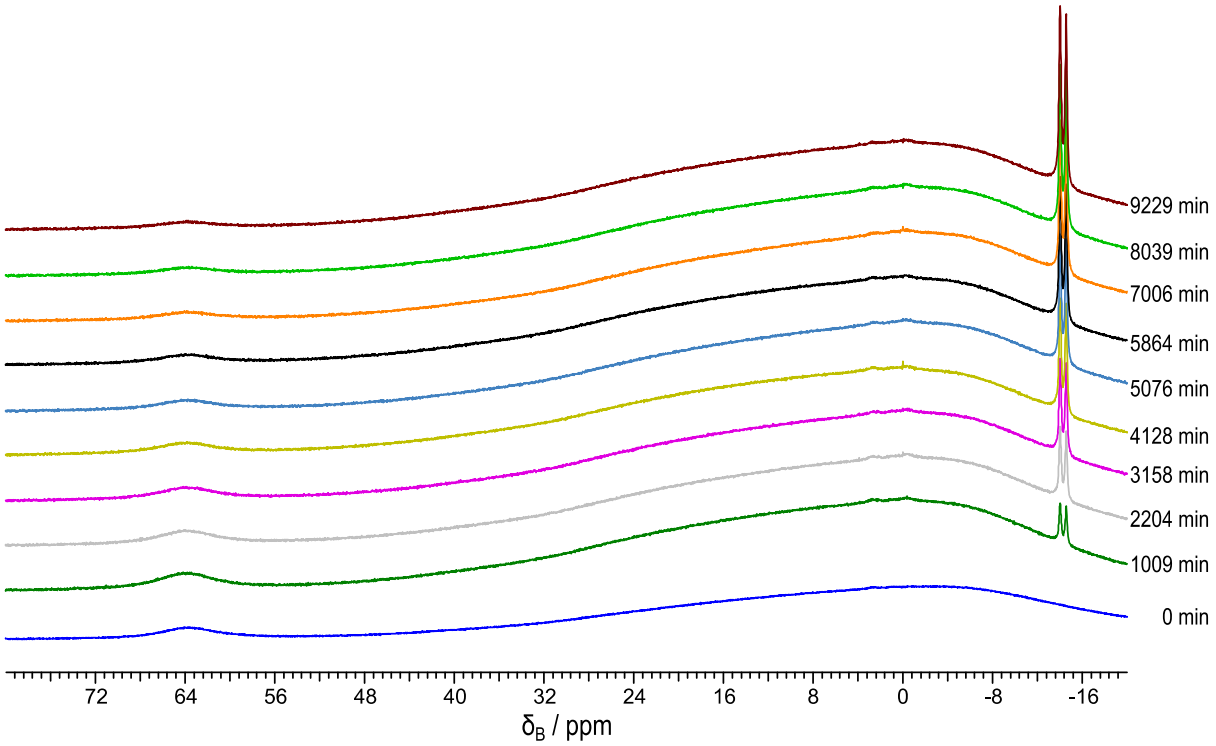


***Figure S4b*** $^{11}B$ NMR spectra showing the progress of $H_2$ cleavage by the **3**/lutidine FLP

>90% consumed **3**, is converted to the target $H_2$ cleavage product $[H–3]^-$; non-negligible by-products are however observed in reactions where the Lewis base is $P(^tBu)_3$ (Figure S2) or tmp (Figure S3). The signals in the range $\delta_B$ −4 - +4 ppm are indicative of tetrahedral boron and it is speculated that these are the water adduct **3**–$OH_2$, or the hydroxide [**3**–OH]$^-$. Similarly, this explains the by-product resonances observable in aromatic region of the $^1H$ spectra.

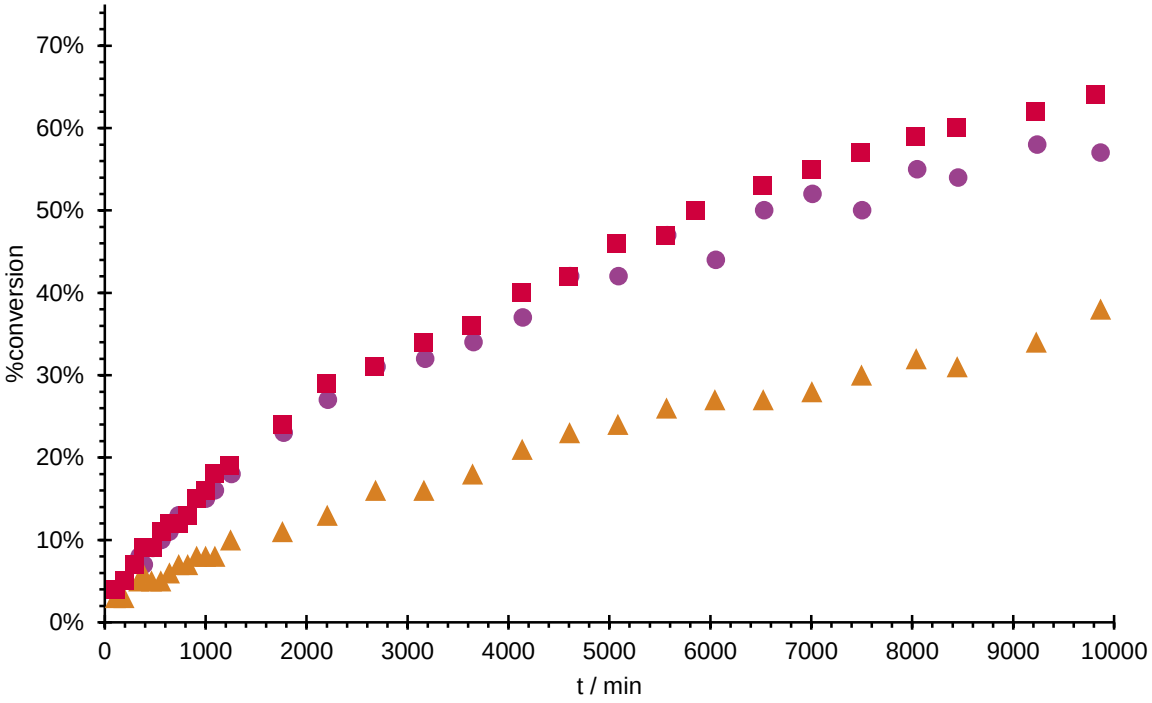


***Figure S5*** Percentage conversion of **3** to $[H–3]^-$ (monitored by $^1H$ NMR spectroscopy of $Ar^{F6}$ 2,6-/4-H resonances), by reaction of a FLP with $H_2$ in $CD_2Cl_2$ at 20 °C, with varying Lewis base:

● $P(^tBu)_3$, ▲ tmp, ■ lutidine.