SUPPLEMENTARY INFORMATION

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

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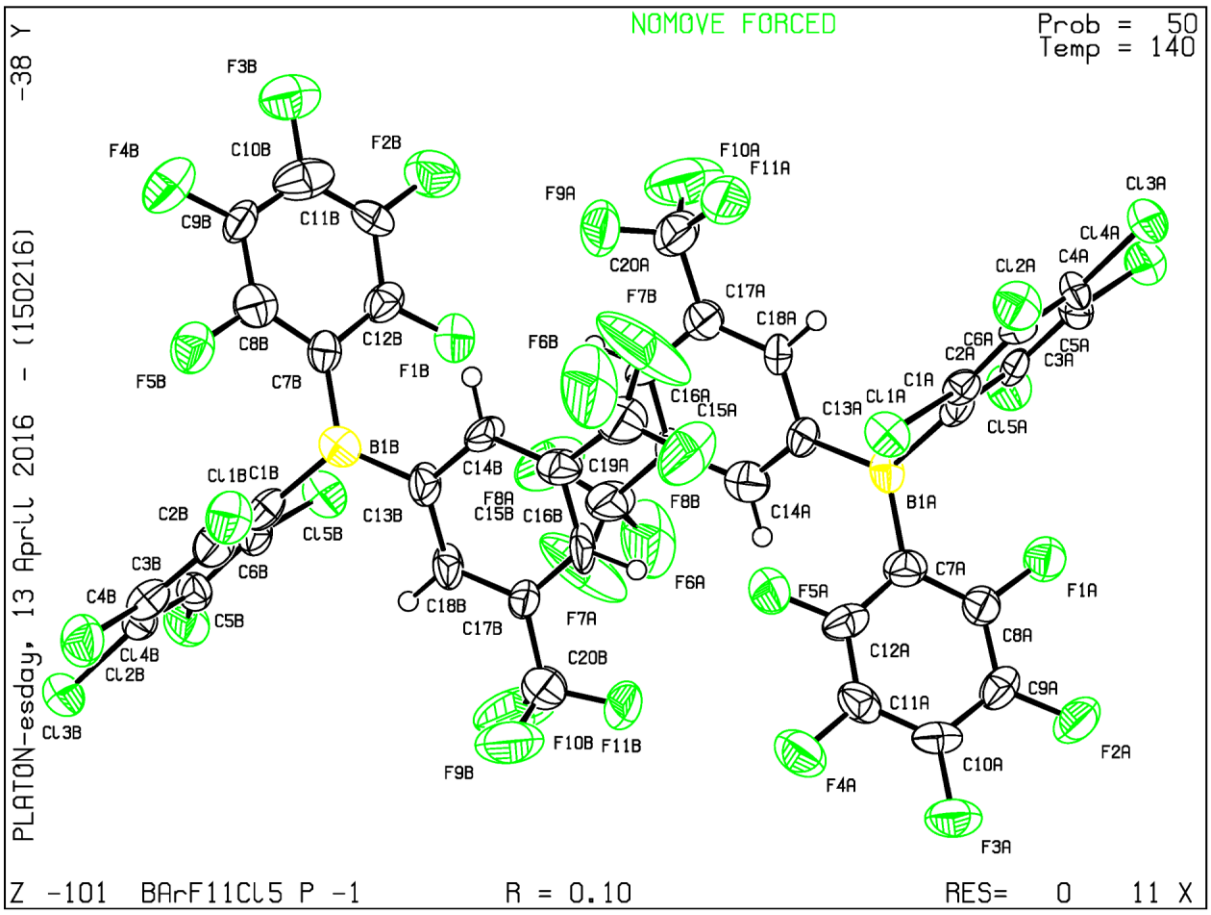

Figure S1 *X*-ray crystallographic structure of $B(C_6F_5)\{3,5\text{-}(CF_3)_2C_6H_3\}(C_6Cl_5)$ **3**

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).

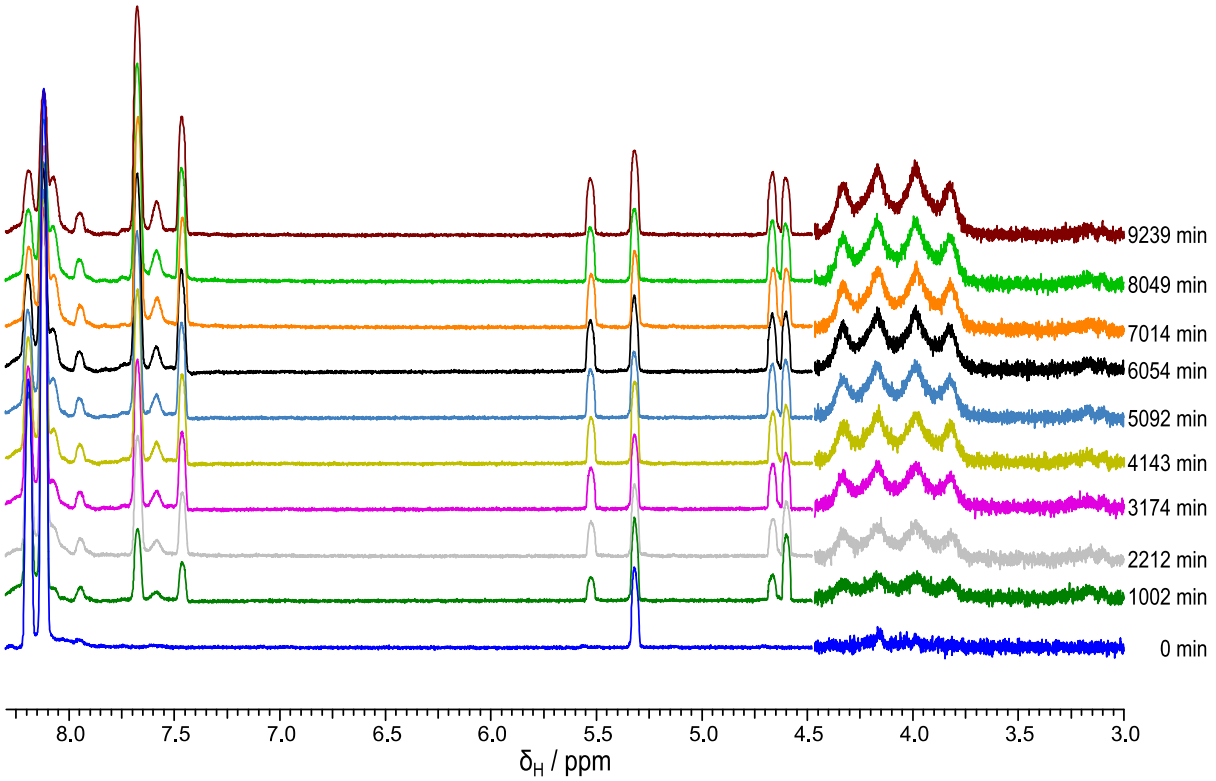

Figure S2a ^{1}H NMR spectra showing the progress of H_2 cleavage by the **3**/P(^{t}Bu)$_3$ FLP

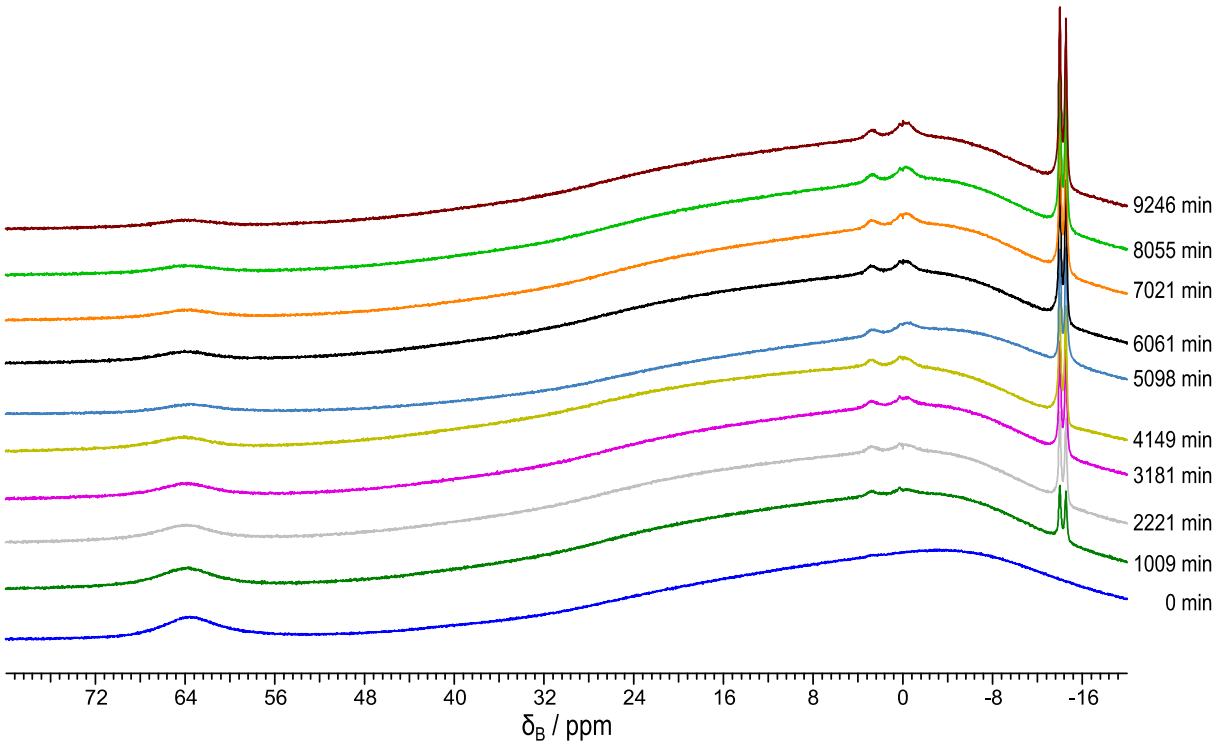

Figure S2b ^{11}B NMR spectra showing the progress of H_2 cleavage by the **3**/P(^{t}Bu)$_3$ FLP

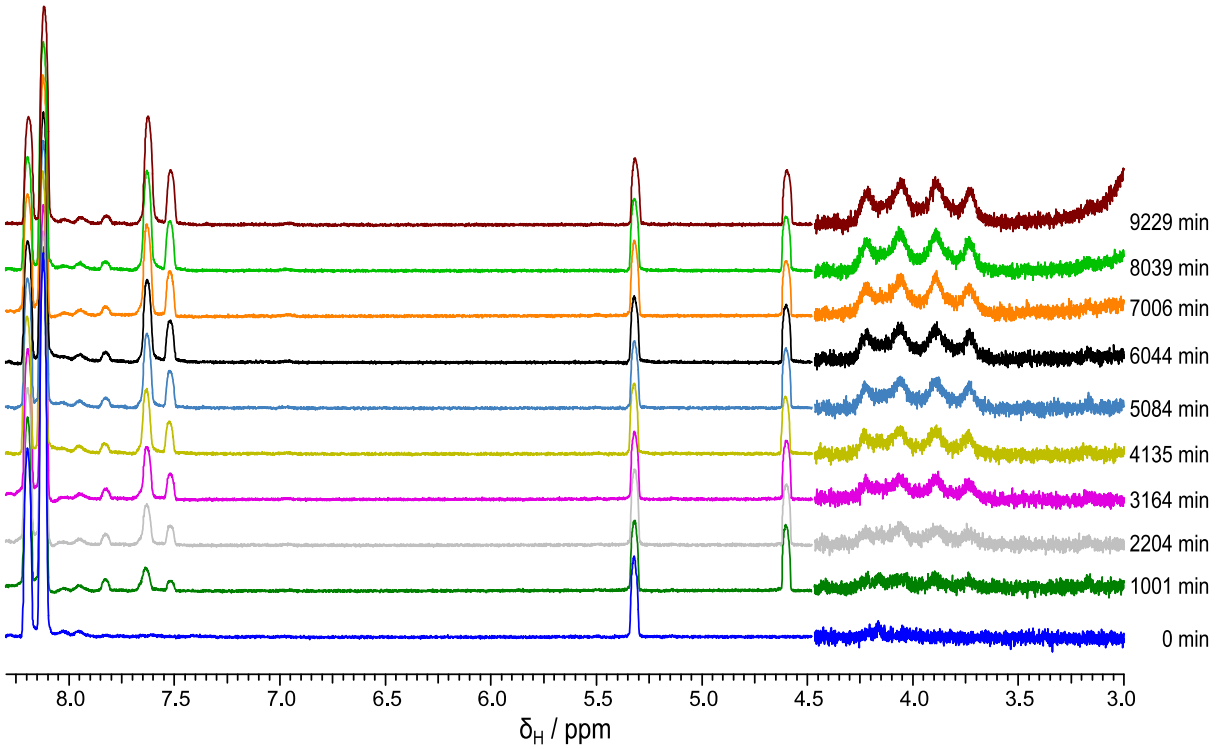

Figure S3a ^{1}H NMR spectra showing the progress of H_2 cleavage by the **3**/tmp FLP

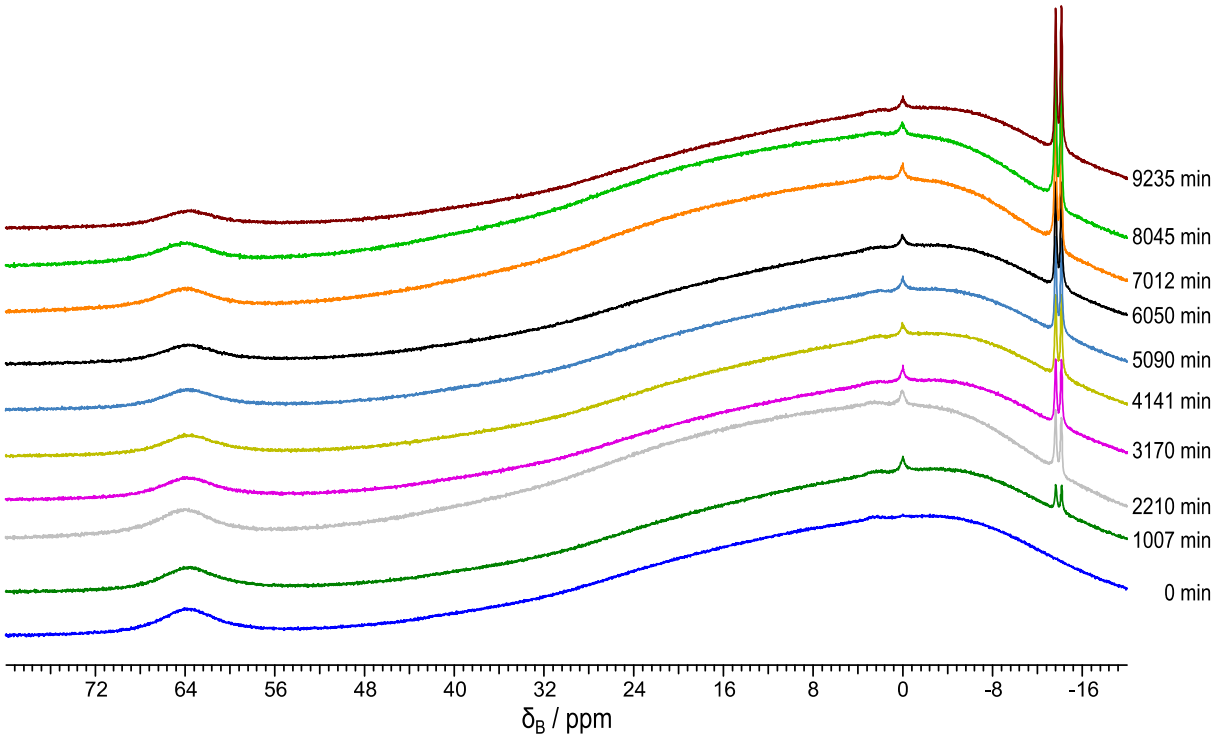

Figure S3b ^{11}B NMR spectra showing the progress of H_2 cleavage by the **3**/tmp FLP

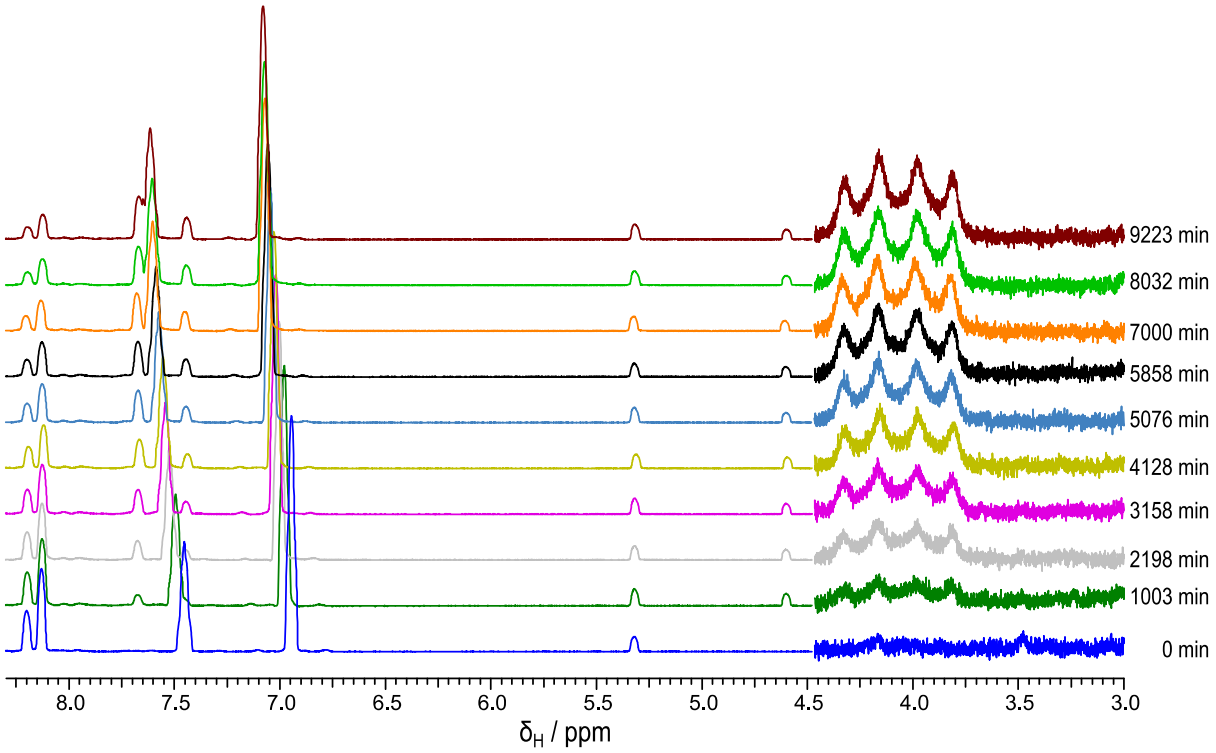

Figure S4a ^{1}H NMR spectra showing the progress of H_2 cleavage by the **3**/lutidine FLP

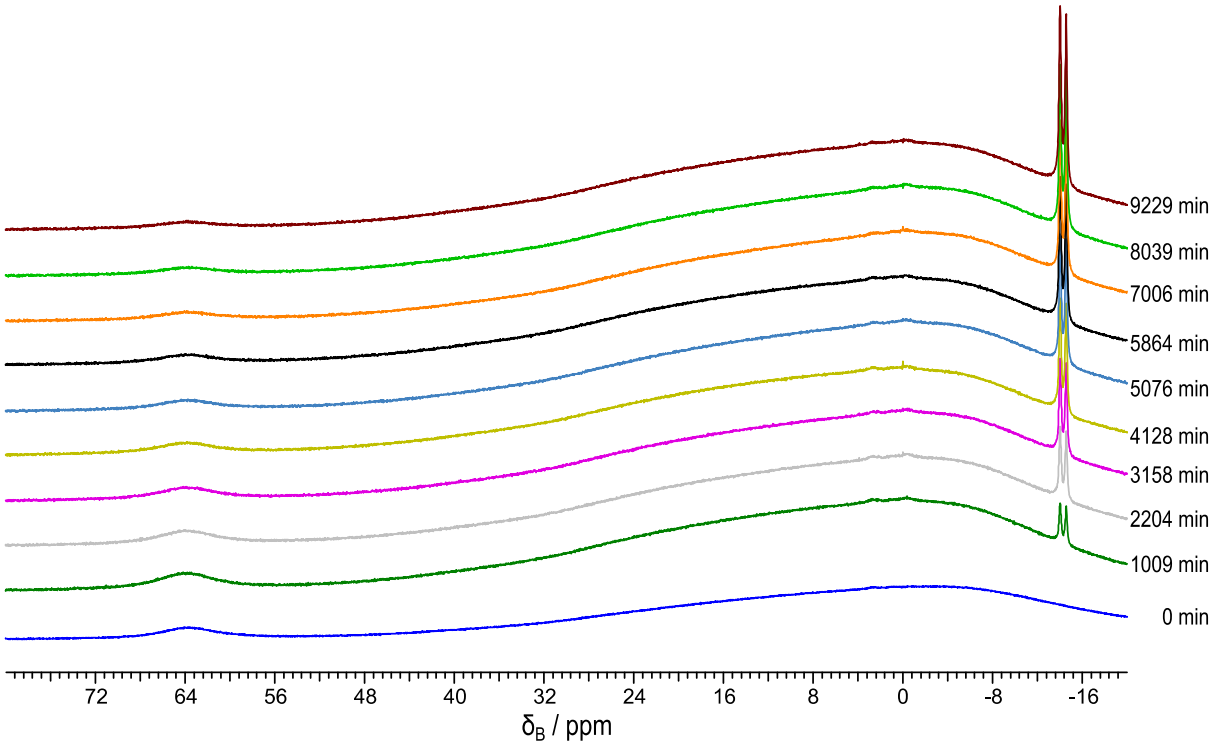

Figure S4b ^{11}B NMR spectra showing the progress of H_2 cleavage by the **3**/lutidine FLP

>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 δ_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.

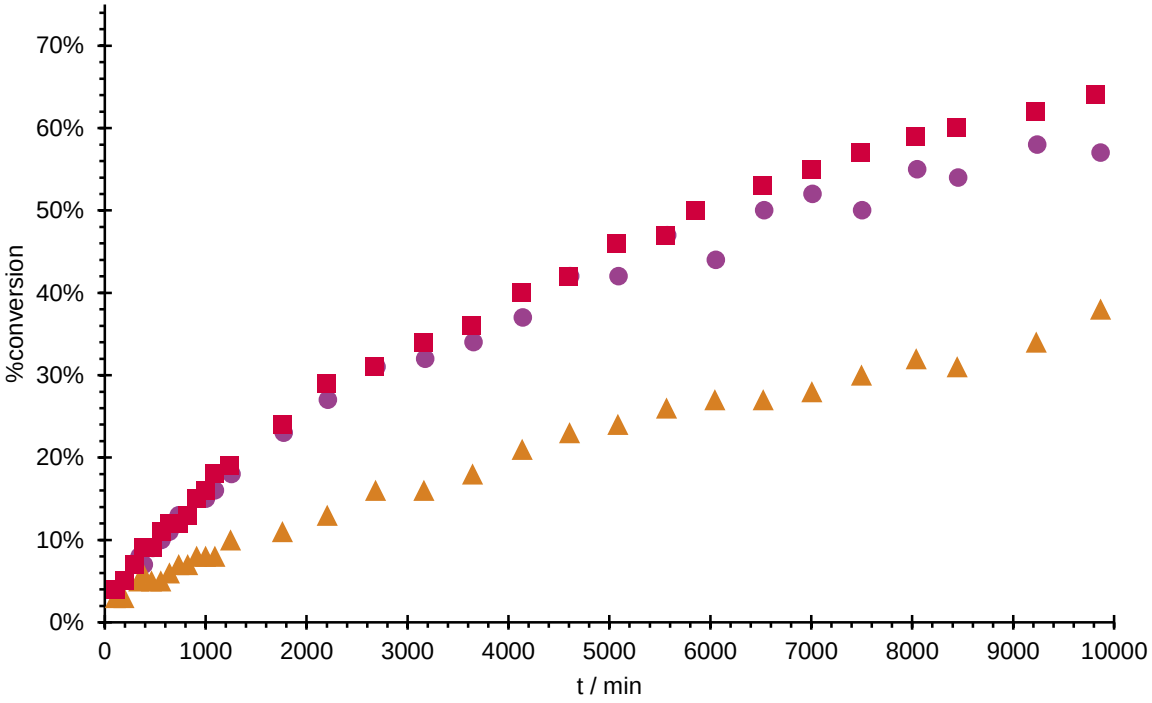

Figure S5 Percentage conversion of **3** to $[H–3]^-$ (monitored by ^1H NMR spectroscopy of Ar^{F6} 2,6-/4-H resonances), by reaction of a FLP with H_2 in CD_2Cl_2 at 20 °C, with varying Lewis base:

● $P(^tBu)_3$, ▲ tmp, ■ lutidine.