

SUPPLEMENTARY INFORMATION

H₂ activation using the first 1:1:1 hetero-tri(aryl)borane

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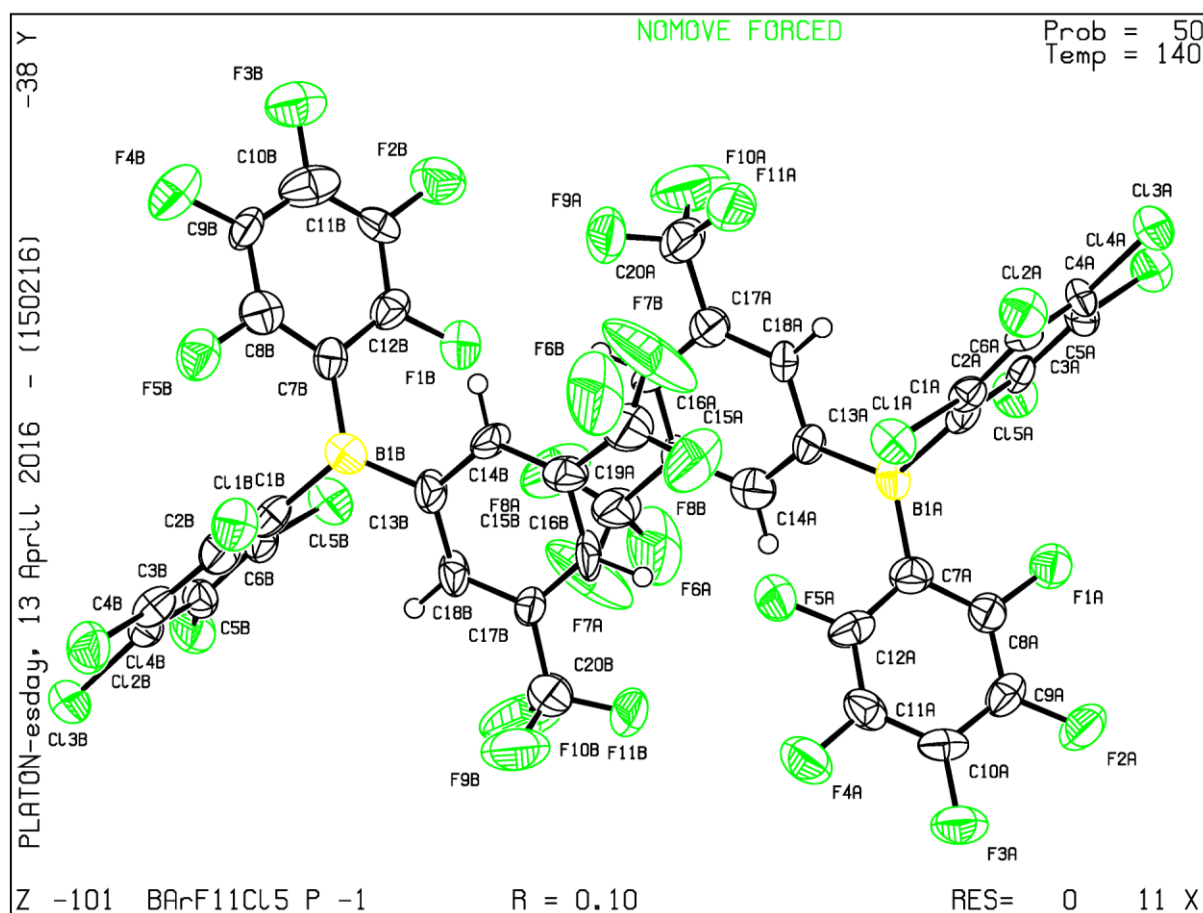


Figure S1 X-ray crystallographic structure of $B(C_6F_5)\{3,5-(CF_3)_2C_6H_3\}(C_6Cl_5)_3$

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“Gutmann-Beckett method” for measurement of Lewis acidity

3 (Lewis acid) is combined with a three-fold excess of OPEt₃ (Lewis base) in *ca.* 0.8 cm³ CD₂Cl₂ in a NMR tube, rapidly generating the Lewis acid-base adduct Et₃PO–**3**, and ¹H, ¹¹B, ¹⁹F and ³¹P{¹H} NMR spectra obtained.

Et₃POB(C₆F₅){3,5-(CF₃)₂C₆H₃}(C₆Cl₅) Et₃PO–**3**

¹H NMR (500.2 MHz, CD₂Cl₂, 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 CH₂), +1.10 (br.m, 9H, Et CH₃); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): +2.51 (br.s); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): -62.9 (s, 6F, Ar^{F6} 3,5-CF₃), -131.3 (m, 2F, Ar^{F5} 2,6-F), -158.8 (t, ³J_{FF} = 19.9 Hz, 1F, Ar^{F5} 4-F), -163.8 (m, 2F, Ar^{F5} 3,5-F); ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 25 °C, δ): +76.49 (s).

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H₂ 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 cm³ CD₂Cl₂ in a NMR tube fitted with a J.Young valve. ¹H, ¹¹B, ¹⁹F and ³¹P{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 H₂ (dried by passing through a P₂O₅ column). The NMR tube is allowed to warm to room temperature, shaken, and the resulting reaction monitored by ¹H and ¹¹B NMR spectroscopy. A final set of ¹H, ¹¹B, ¹⁹F and ³¹P{¹H} NMR spectra are then obtained.

[(^tBu)₃PH][HB(C₆F₅)₃,5-(CF₃)₂C₆H₃](C₆Cl₅) [^tBu₃PH][H-3]

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

¹H NMR (500.2 MHz, CD₂Cl₂, 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); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): -14.3 (d, ¹J_{BH} = 88 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): -62.3 (s, 6F, Ar^{F6} 3,5-CF₃), -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); ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 25 °C, δ): +59.9 (s).

[Me₄H₆C₅NH₂][HB(C₆F₅)₃,5-(CF₃)₂C₆H₃](C₆Cl₅) [tmp-H][H-3]

Spectral data at 38% conversion (164 hours reaction time); resonances for tmp correspond to a rapid equilibrium between [tmp-H]⁺ and free tmp.

¹H NMR (500.2 MHz, CD₂Cl₂, 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 NH₂), +1.67 (m, tmp 4-H), +1.42 (m, tmp 3,5-H), +1.17 (s, tmp 2,6-CH₃); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): -13.9 (d, ¹J_{BH} = 84 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): -62.5 (s, 6F, Ar^{F6} 3,5-CF₃), -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).

[Me₂H₃C₅NH][HB(C₆F₅)₃,5-(CF₃)₂C₆H₃](C₆Cl₅) [lutidine-H][H-3]

Spectral data at 64% conversion (164 hours reaction time); resonances for lutidine correspond to a rapid equilibrium between [lutidine-H]⁺ and free lutidine.

¹H NMR (500.2 MHz, CD₂Cl₂, 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-CH₃); ¹¹B NMR (160.5 MHz, CD₂Cl₂, 25 °C, δ): -14.3 (d, ¹J_{BH} = 88 Hz); ¹⁹F NMR (470.7 MHz, CD₂Cl₂, 25 °C, δ): -62.4 (s, 6F, Ar^{F6} 3,5-CF₃), -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).

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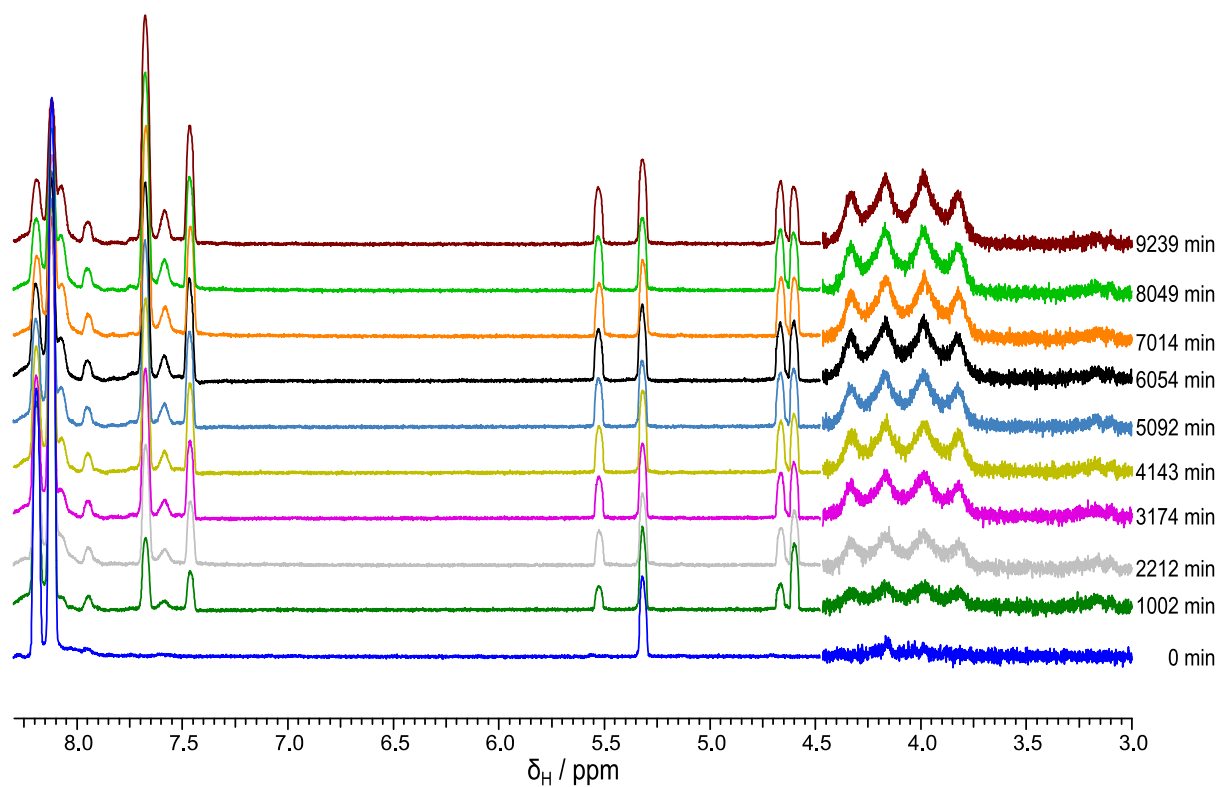


Figure S2a ^1H NMR spectra showing the progress of H_2 cleavage by the $3/\text{P}(\text{tBu})_3$ FLP

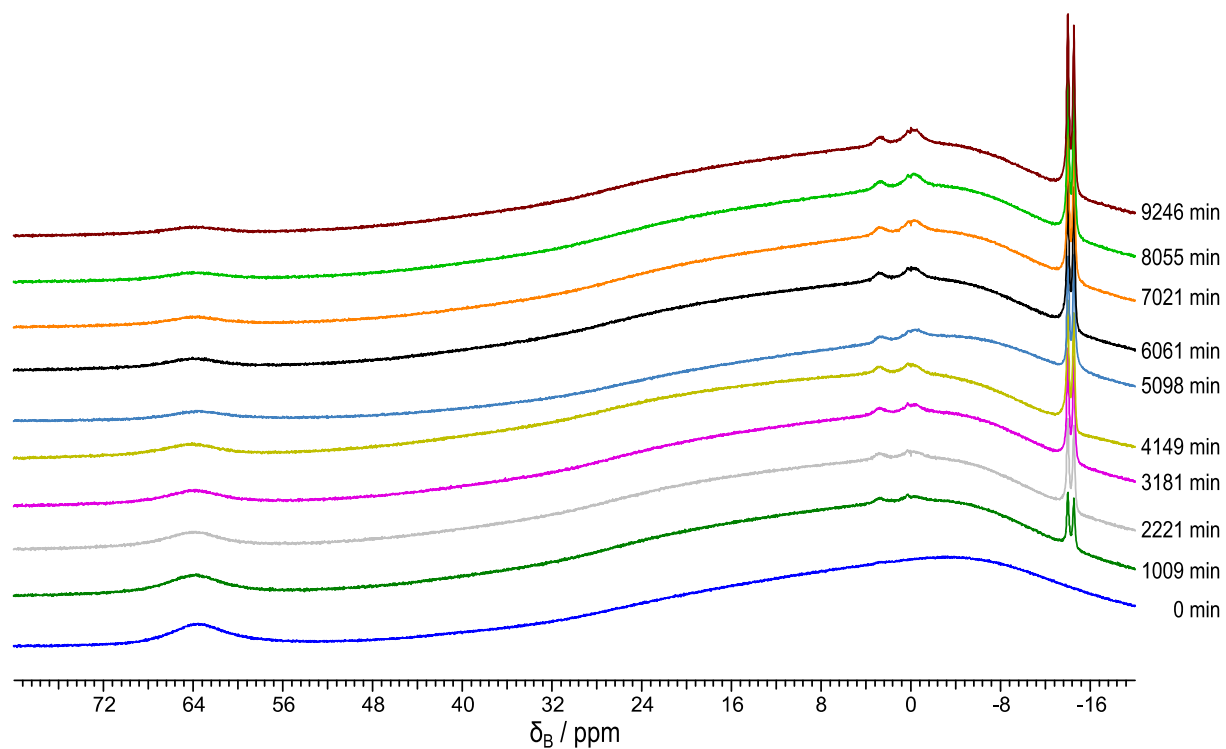


Figure S2b ^{11}B NMR spectra showing the progress of H_2 cleavage by the $3/\text{P}(\text{tBu})_3$ FLP

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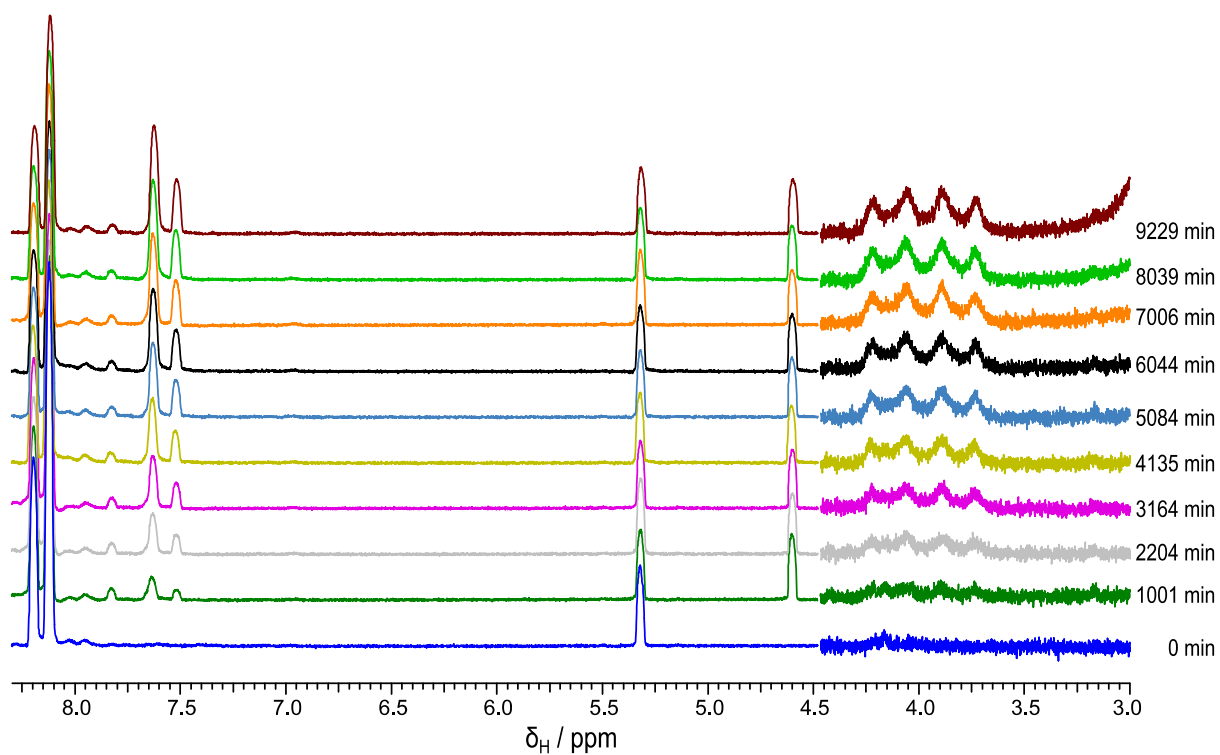


Figure S3a ^1H NMR spectra showing the progress of H_2 cleavage by the 3/tmp FLP

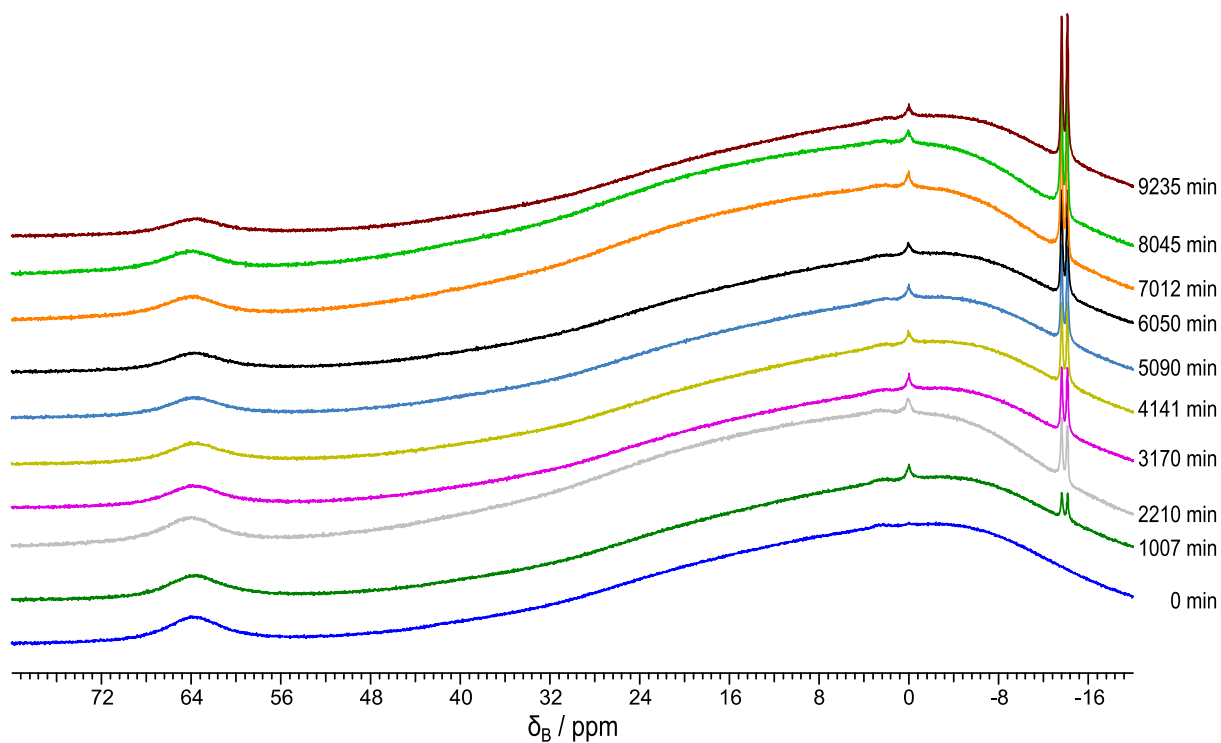


Figure S3b ^{11}B NMR spectra showing the progress of H_2 cleavage by the 3/tmp FLP

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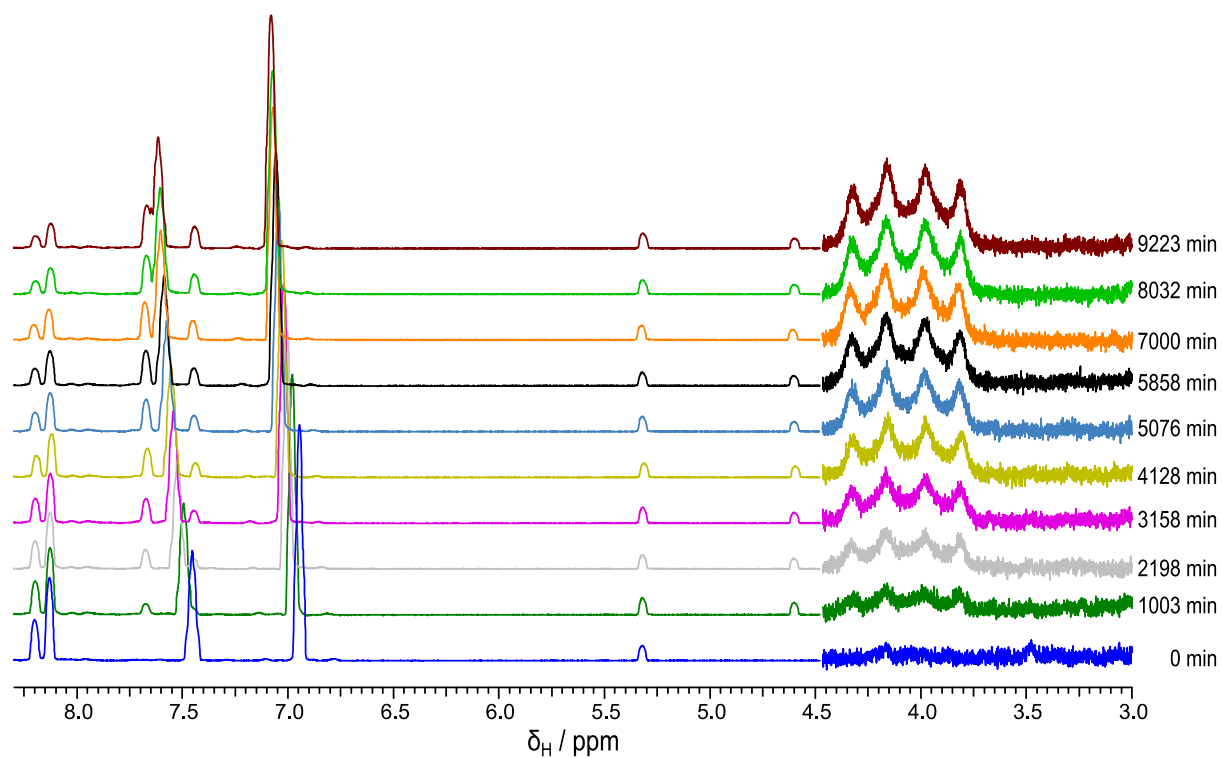


Figure S4a ^1H NMR spectra showing the progress of H_2 cleavage by the 3/lutidine FLP

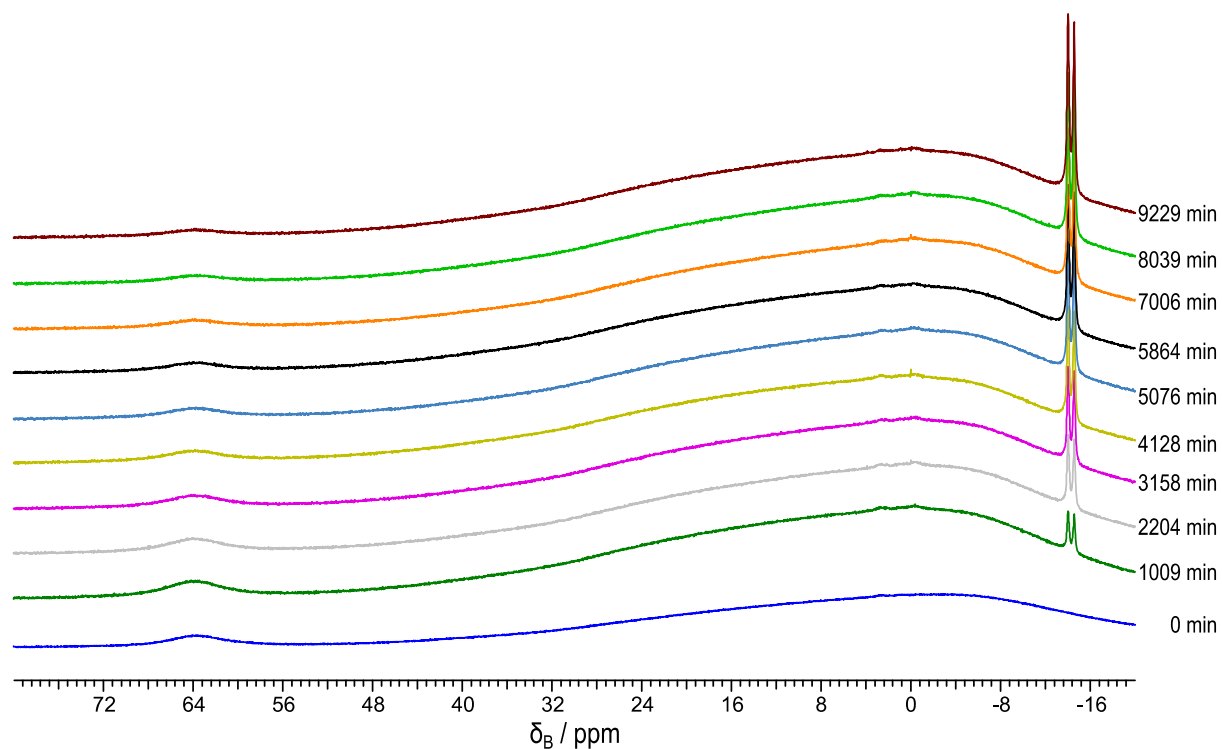


Figure S4b ^{11}B NMR spectra showing the progress of H_2 cleavage by the 3/lutidine FLP

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>90% consumed **3**, is converted to the target H₂ 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**-OH₂, or the hydroxide [**3**-OH]⁻. Similarly, this explains the by-product resonances observable in aromatic region of the ¹H spectra.

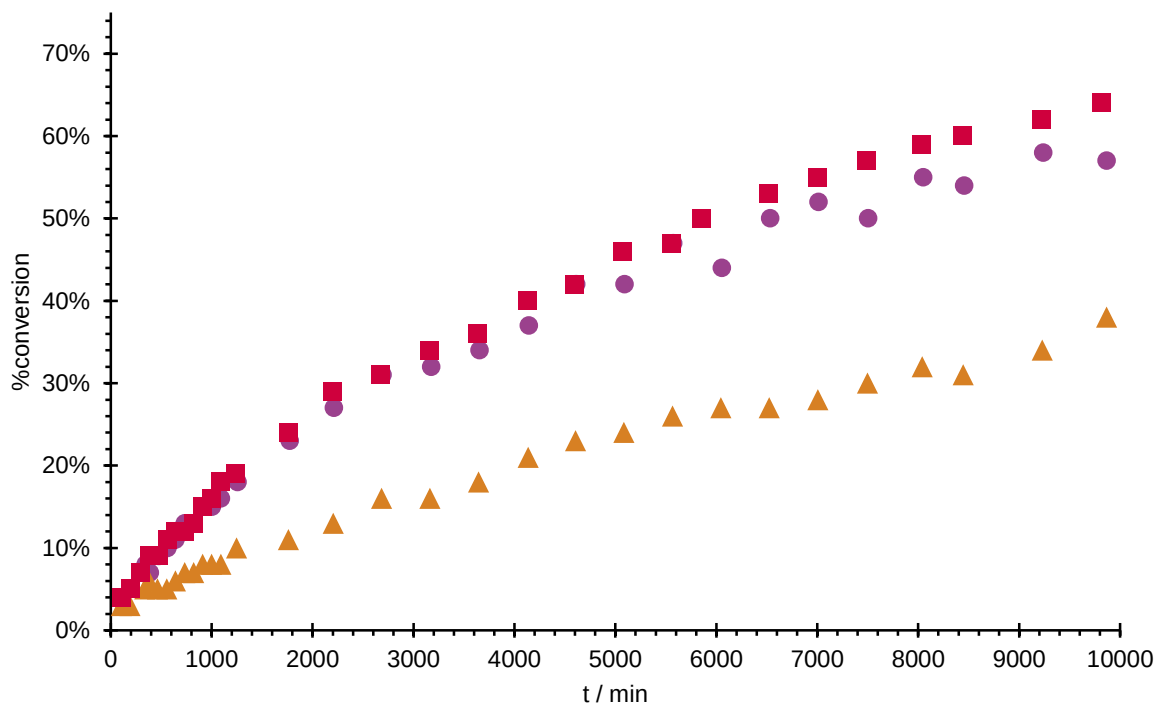


Figure S5 Percentage conversion of **3** to [H-**3**]⁻ (monitored by ¹H NMR spectroscopy of Ar^{F6} 2,6-/4-H resonances), by reaction of a FLP with H₂ in CD₂Cl₂ at 20 °C, with varying Lewis base:

● P(^tBu)₃, ▲ tmp, ■ lutidine.