Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Dehydrogenation of Ammonia Borane through the Third Equivalent of Hydrogen

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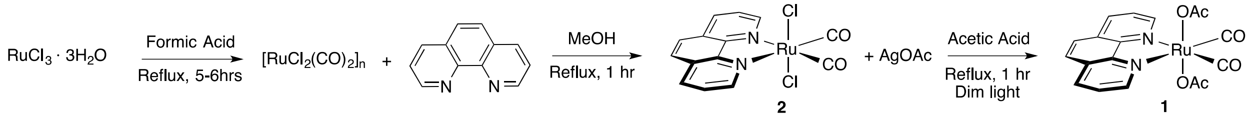
I. Synthesis of 1 and Related Compounds



$[RuCl_2(CO)_2]_n$

Following a modified Krishnamurthy and Shashikala's synthetic procedure,[1] rutheniumdichlorodicarbonyl polymer was synthesized by adding $RuCl_3$•$3H_2O$ (500 mg, 1.91 mmol, 1 equiv.) to a round bottom flask with a stir bar. Formic acid 97% (4 mL, 103 mmol, 53 equiv.) was added to the flask and a reflux condenser was added to the apparatus with a nitrogen line fitted to the top of the condenser. Ice water was recycled through the condenser from a bucket with a water pump. The initially black/red reaction mixture was refluxed in an oil bath for 5-6 hours when the reaction turns a light yellow. The reaction mixture was allowed to cool to room temperature then sealed and refrigerated overnight to allow the polymerization to approach completion. The formic acid was removed via a vacuum line and oil bath set at 70°C. The resulting light yellow residue was dried on the schlenk line overnight to remove residual solvent. The residue was then washed with hexanes (5 mL) and filtered to obtain a light yellow powder in 85% yield (371mg). FTIR (ν, cm^{-1}): 2098.03, 2033.35 (M − CO's). 2140 is an often seen side product of $[Ru(CO)_3Cl_2]_2$. The polymer is used without further purification through the subsequent reactions.

[(phen)RuCl$_2$(CO)$_2$] (**2**)

Following a modified Thomas et. al.'s synthetic procedure,[2] phenanthrolinerutheniumdichlorodicarbonyl was synthesized by adding [RuCl$_2$(CO)$_2$]$_n$ (250 mg, 1.1 mmol, 1 equiv.) to a round bottom flask with a stirbar. 1,10-phenanthroline (212 mg, 1.1 mmol, 1 equiv.) was added to the flask. MeOH (25 mL) was added to the flask and a reflux condenser was added to the apparatus with a nitrogen line fitted to the top of the condenser. Ice water was recycled through the condenser from a bucket with a water pump. The initially light yellow reaction mixture was refluxed in an oil bath for 1 hour until the reaction turns into a lemon yellow. The reaction was allowed to cool to room temperature then the mixture was filtered. The yellow powder was dried on a vacuum line overnight to remove residual solvent and yielded 66% yield (295 mg). Note: This compound is light sensitive in solution.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.53 (dd, *J* = 5.1, 1.4 Hz, 2H), 8.60 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.07 (s, 2H), 7.99 (dd, *J* = 8.2, 5.1 Hz, 2H).

FTIR (ν, cm^{-1}): 2062.03, 2011.93 (M − CO's).

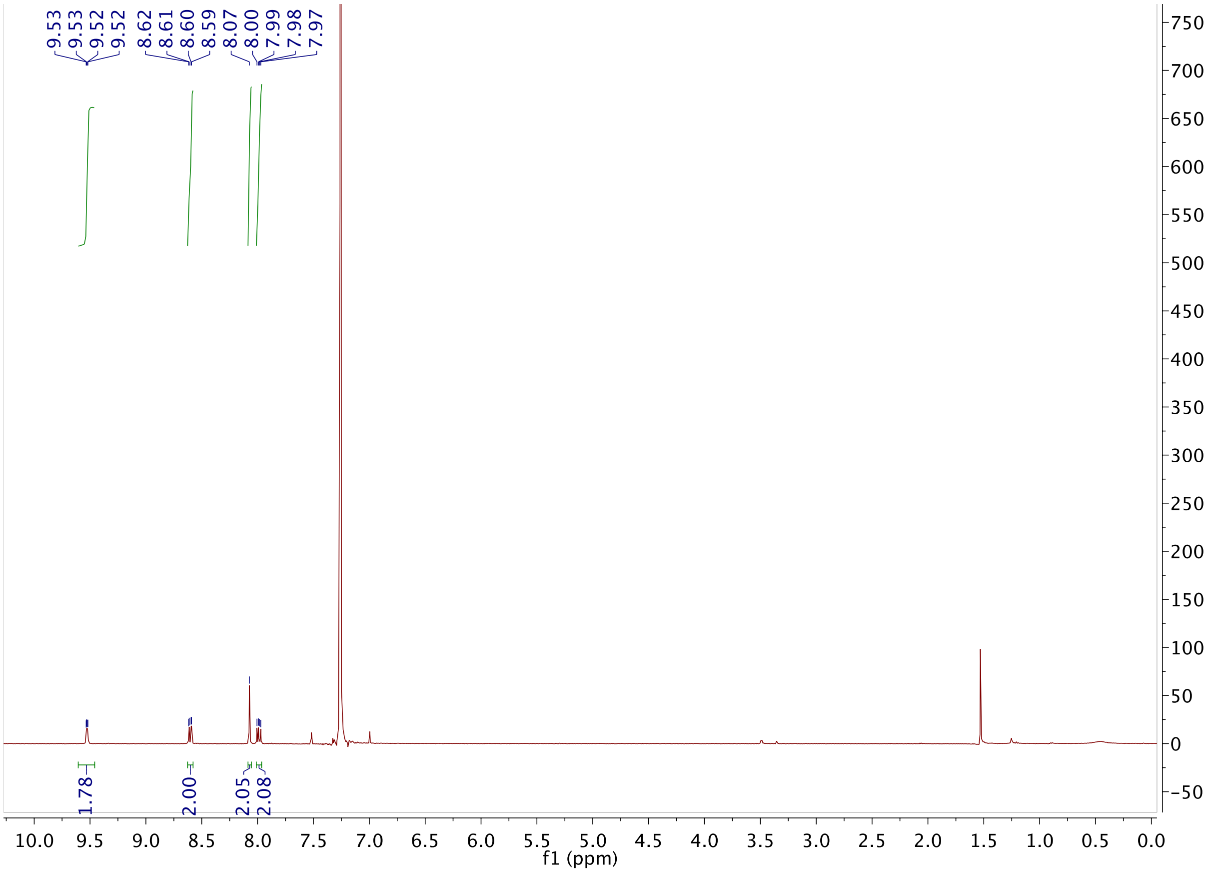


Figure S1: ^{1}H spectra of [(phen)RuCl$_2$(CO)$_2$], (**2**).

[(phen)Ru(OAc)$_2$(CO)$_2$] (1)

Following a modified Thomas et. al.'s synthetic procedure, phenrutheniumdiacetatedicarbonyl was synthesized by adding [(phen)RuCl$_2$(CO)$_2$] (295 mg, 0.72 mmol, 1 equiv.) to a round bottom flask with a stir bar. Silver acetate (242 mg, 1.45 mmol, 2 equiv.) was added to the flask. Acetic acid (8 mL) was added to the flask and the round bottom flask was wrapped in aluminum foil. A reflux condenser was added to the apparatus with a nitrogen line fitted to the top of the condenser. Ice water was recycled through the condenser from a bucket with a water pump. The initially grey/yellow reaction mixture was refluxed in an oil bath for 1 hour. The reaction was allowed to cool to room temperature then the mixture was filtered. The filtrate was collected and all solvent was removed in vacuo. The yellow residue was dried on a vacuum line overnight to remove residual solvent. A minimum volume of hot MeOH was added to the residue and the product was recrystallized in MeOH overnight yielding yellow crystals in 62% yield (203 mg). Note: This compound is light sensitive in solution.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (dd, *J* = 5.1, 1.4 Hz, 2H), 8.57 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.05 (s, 2H), 7.94 (dd, *J* = 8.3, 5.1 Hz, 2H), 1.58 (s, 6H).

FTIR (ν, cm^{-1}): 2057.48, 1990.73 (M − CO's).

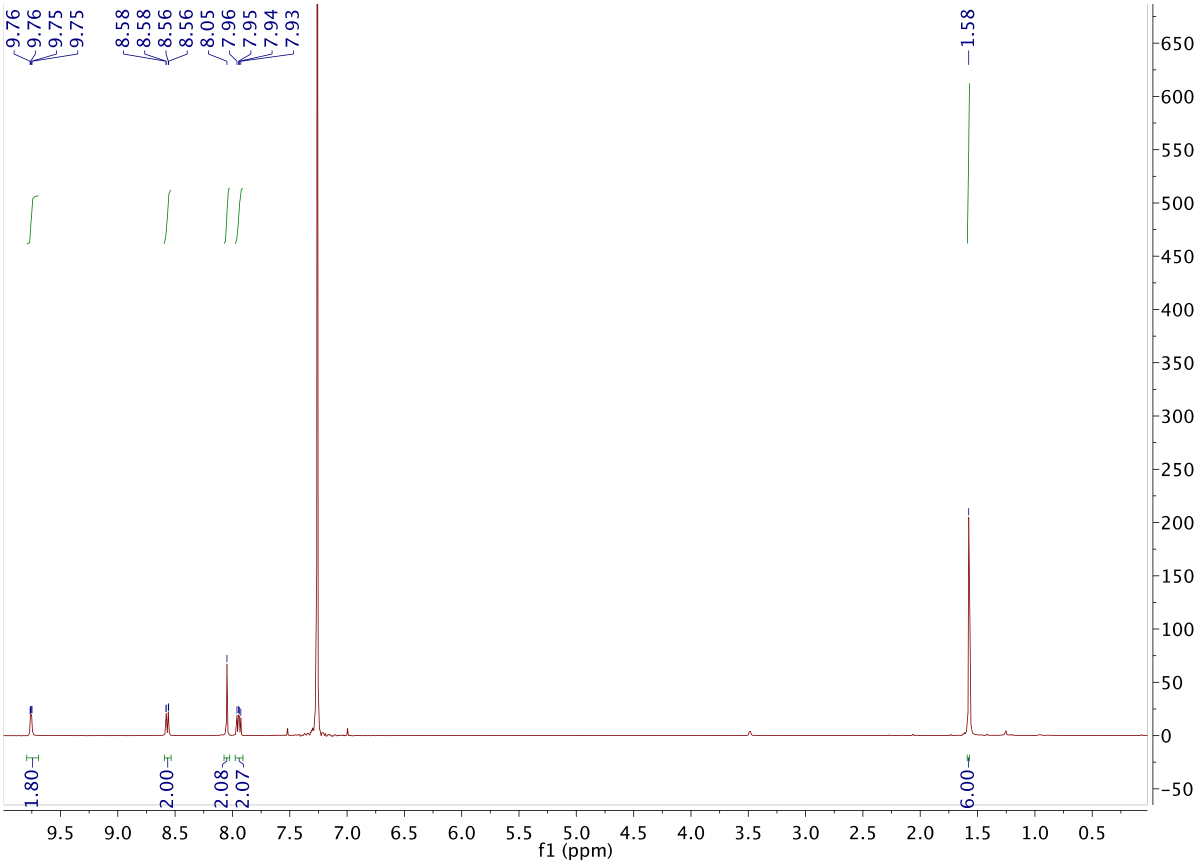
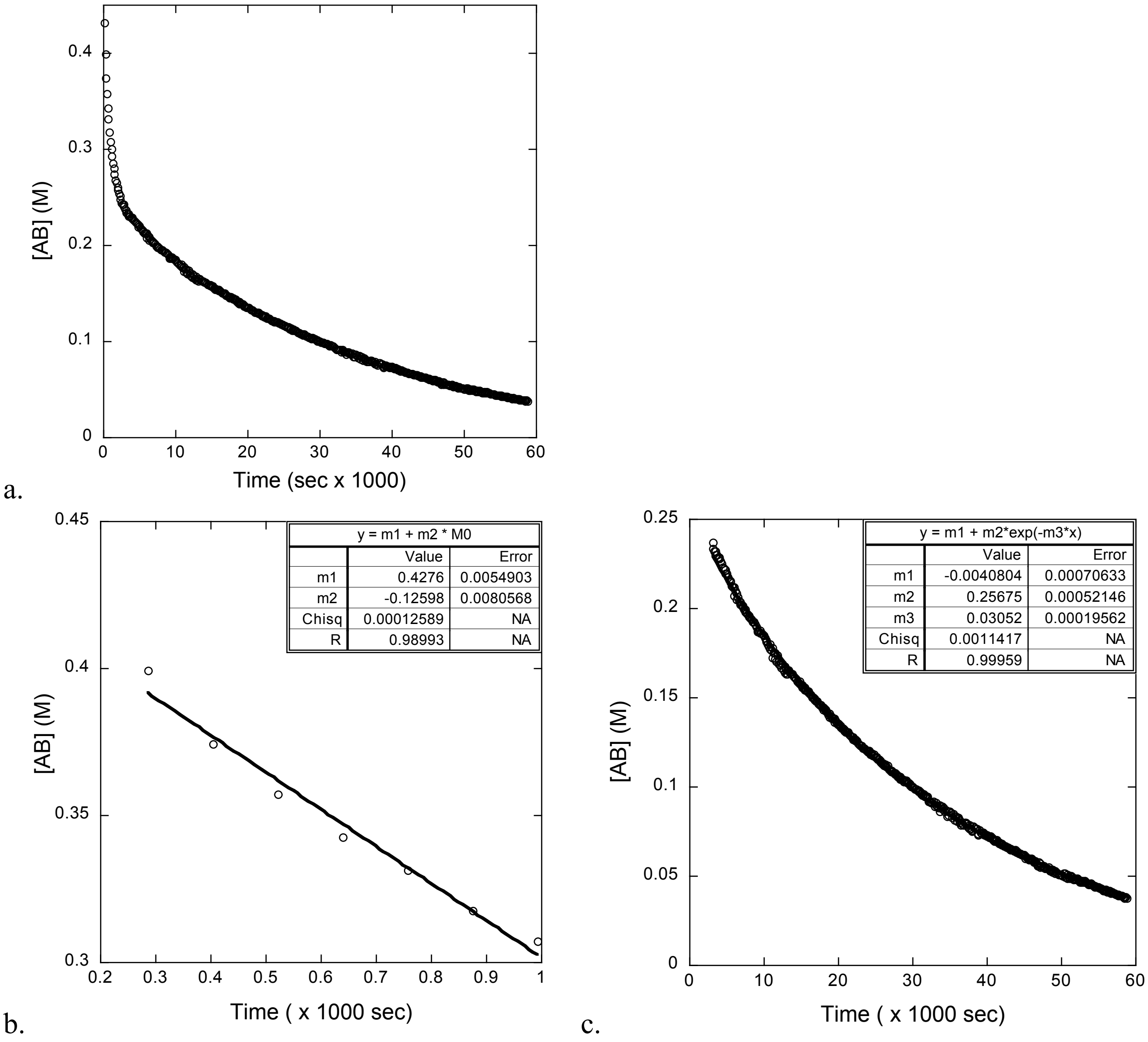


Figure S2: ^{1}H spectra of [(phen)Ru(OAc)$_2$(CO)$_2$], **1**.

II. Kinetic Profiles of 1 Catalyzed AB Dehydrogenation via^{11}B NMR

A. Kinetics for AB dehydrogenation by **1** at 1 mol% catalyst loading

1-catalyzed AB dehydrogenation run at 70 °C was determined using ^{11}B NMR with 7.7 mg AB (0.25 mmol) and **1** (1.2 mg, 2.5 μmol, 1 mol%) in diglyme (0.4 mL) and benzene-d_6 (0.2 mL).



y = m1 + m2 * M0

	Value	Error
m1	0.4276	0.0054903
m2	-0.12598	0.0080568
Chisq	0.00012589	NA
R	0.98993	NA

y = m1 + m2*exp(-m3*x)

	Value	Error
m1	-0.0040804	0.00070633
m2	0.25675	0.00052146
m3	0.03052	0.00019562
Chisq	0.0011417	NA
R	0.99959	NA

Figure S3: Kinetics for AB dehydrogenation catalyzed by **1**. (a). Entirety of graph. (b) Fast portion of dehydrogenation fitted linearly. (c) Slow portion of reaction fitted to exponential decay equation. The entirely of the kinetic profile does not fit exponential decay, thus it is split into a linear and an exponential portion for easier rate comparisons with air and water exposure experiments.

B. Kinetics for Hg drop test in AB dehydrogenation catalyzed by **1** at 10 mol% catalyst loading

1-catalyzed AB dehydrogenation run at 70 °C was determined using ^{11}B NMR with 7.7 mg AB (0.25 mmol) and **1** (12.0 mg, 25 μmol, 10 mol%) in diglyme (0.4 mL) and benzene-d_6 (0.2 mL). In the run with Hg, ca. 100 μL of Hg were added.

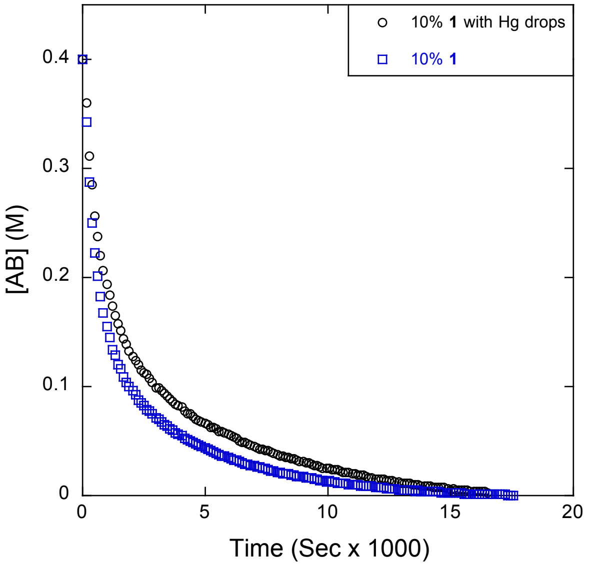
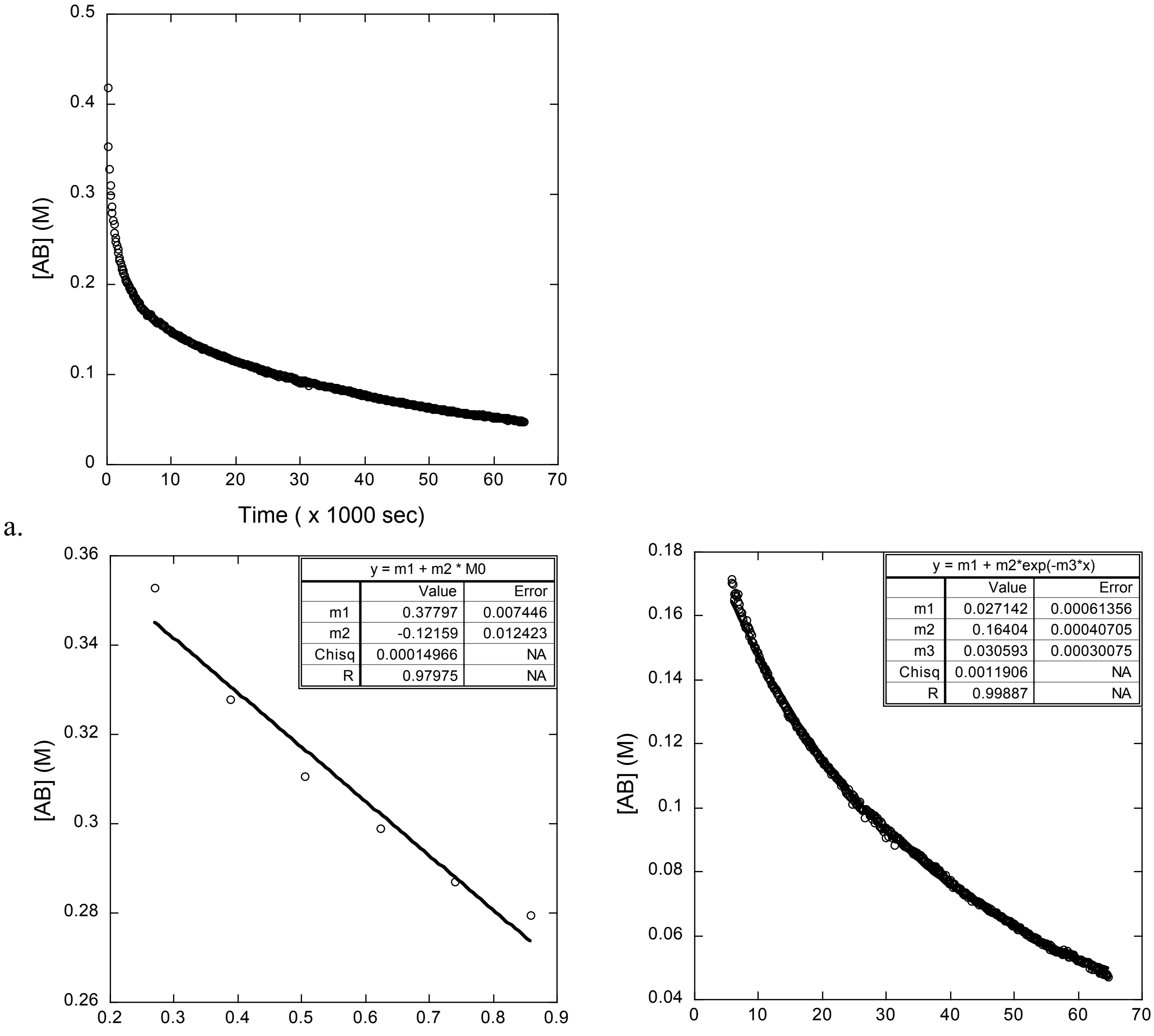


Figure S4: Kinetics for AB dehydrogenation catalyzed by **1** with Hg (black circles) and without (blue squares).

C. Kinetics for AB dehydrogenation catalyzed by **1** after **1**'s exposure to air and water

1-catalyzed AB dehydrogenation run at 70 °C was determined using ^{11}B NMR after **1** (1.2 mg, 2.5 µmol, 1 mol%) in diglyme (0.4 mL) and benzene-d_6 (0.2 mL) was submerged in an ultrasonic cleaning bath for 20 minutes open to air, and then the addition of 7.7 mg of AB (0.25mmol).



a.

b.

y = m1 + m2 * M0

	Value	Error
m1	0.37797	0.007446
m2	-0.12159	0.012423
Chisq	0.00014966	NA
R	0.97975	NA

c.

y = m1 + m2*exp(-m3*x)

	Value	Error
m1	0.027142	0.00061356
m2	0.16404	0.00040705
m3	0.030593	0.00030075
Chisq	0.0011906	NA
R	0.99887	NA

Figure S5: Kinetics for AB dehydrogenation catalyzed by **1** after catalyst/solvent system was exposed to air. Note similarity to reaction with no air exposure in Figure S3. (a). Entirety of graph. (b). Fast portion of dehydrogenation fitted linearly. (c) Slow portion of reaction fitted to exponential decay equation.

III. Control Reactions of 1 with Borazine

See main text (experimental section) for procedures and the spectra of the reaction of **1** with borazine.

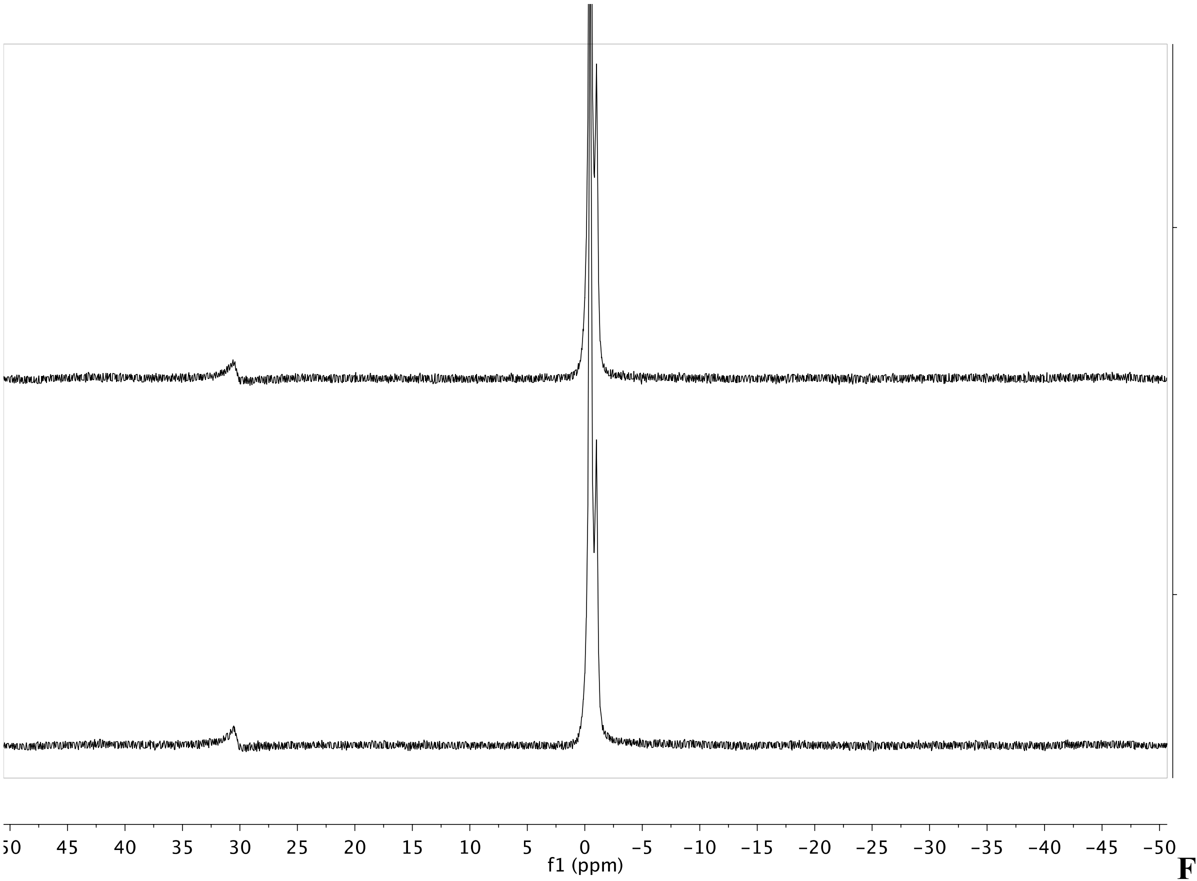


Figure S6: Control reaction of no catalyst **1**. ^{11}B spectra borazine in diglyme/benzene-d_6. Bottom: initial. Top: 24 hr in a 70 °C oil bath. 15% decrease based on peak height (31 ppm) relative to ^{11}B standard. Boron external standard BF_3-OEt_2 is at 0 ppm.

IV. Representative ^{11}B Spectra of AB Dehydrogenations

A. End of Reaction ^{11}B and ^{1}H Spectra for AB Dehydrogenation Catalyzed by **1**

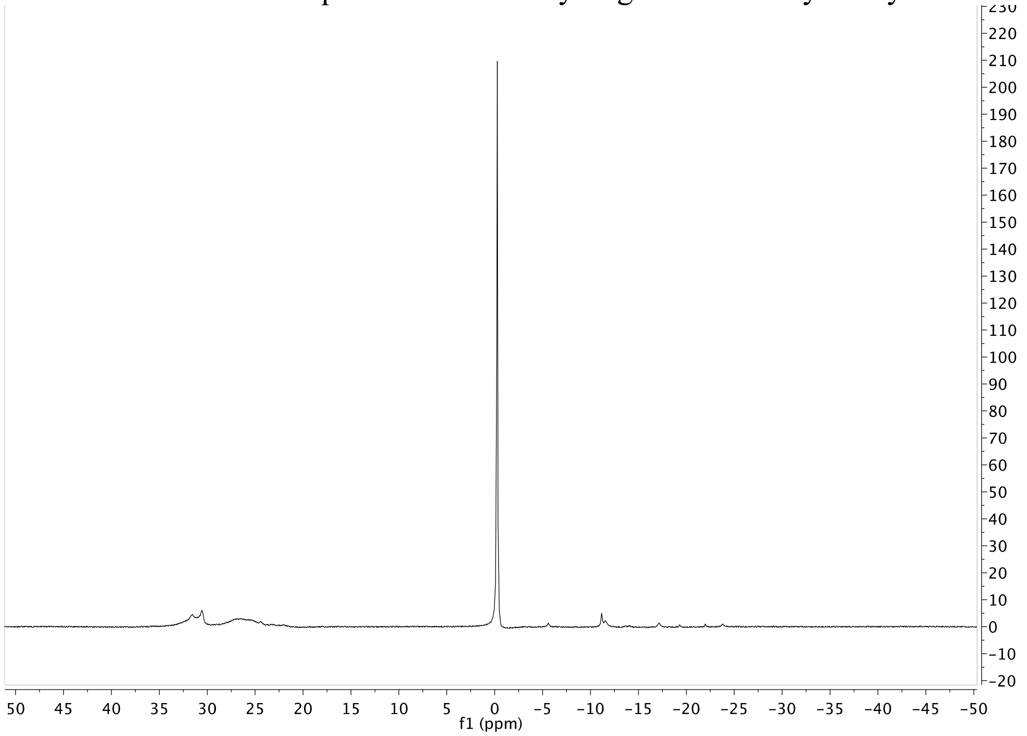


Figure S7: ^{11}B spectra of end of AB dehydrogenation reaction catalyzed by **1** (10 mol% Ru, 1:2 benzene-d_6 : diglyme). Note presence of broad polyunsaturated peaks at 23-33 ppm. Other intermediates include borazine (31 ppm), BF_3-OEt_2 external standard (0 ppm), amine borane cyclic tetramer (-5, -11, -23 ppm), cyclotriborazane (-11 ppm), residual AB (-22 ppm), and aminodiborane (-27 ppm).

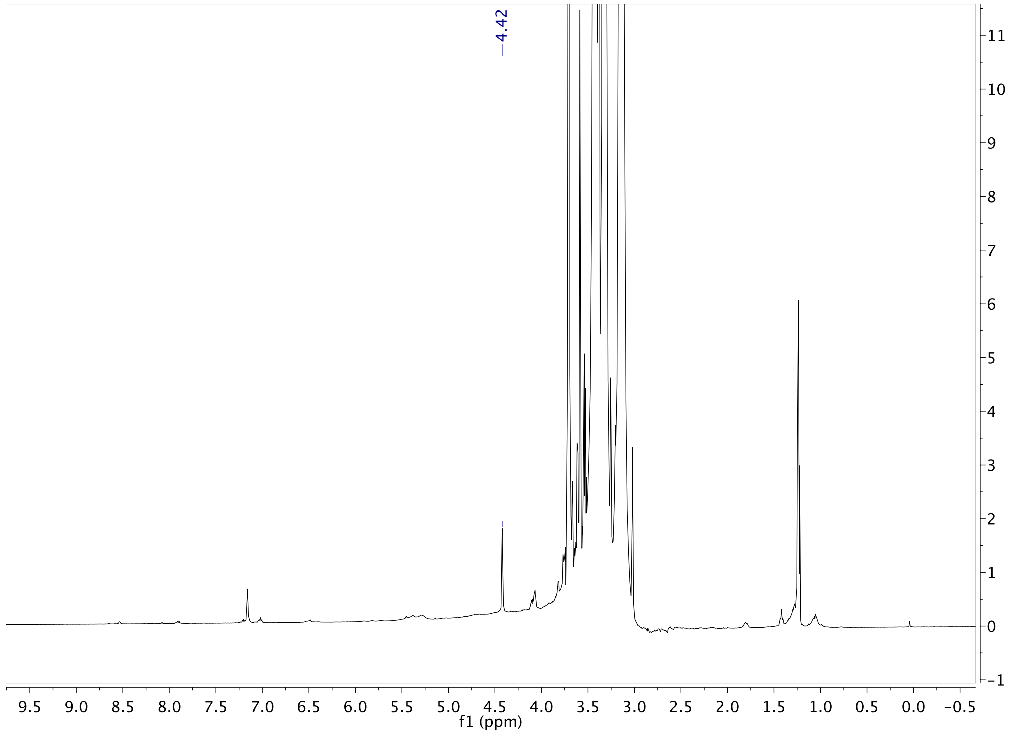
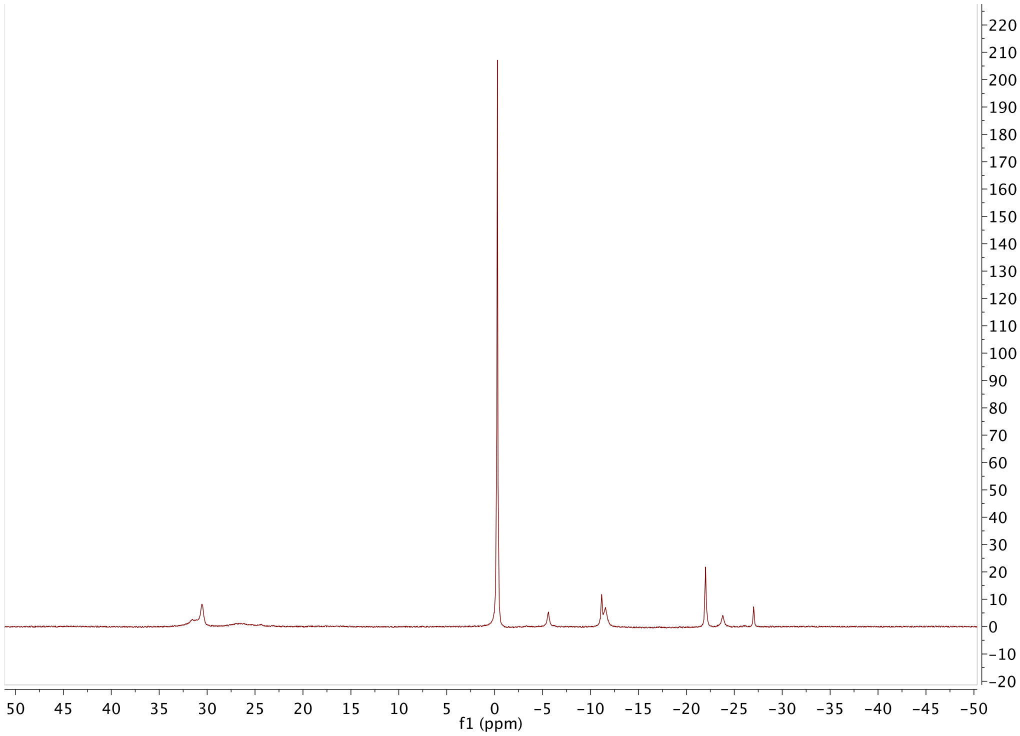


Figure S8: ^{1}H spectra of end of AB dehydrogenation reaction catalyzed by **1**. Note H_2 gas formation at 4.42 ppm.

B. End of Reaction ^{11}B and ^{1}H Spectra for AB Dehydrogenation Catalyzed by **1** After Catalyst Exposure to Air/Water



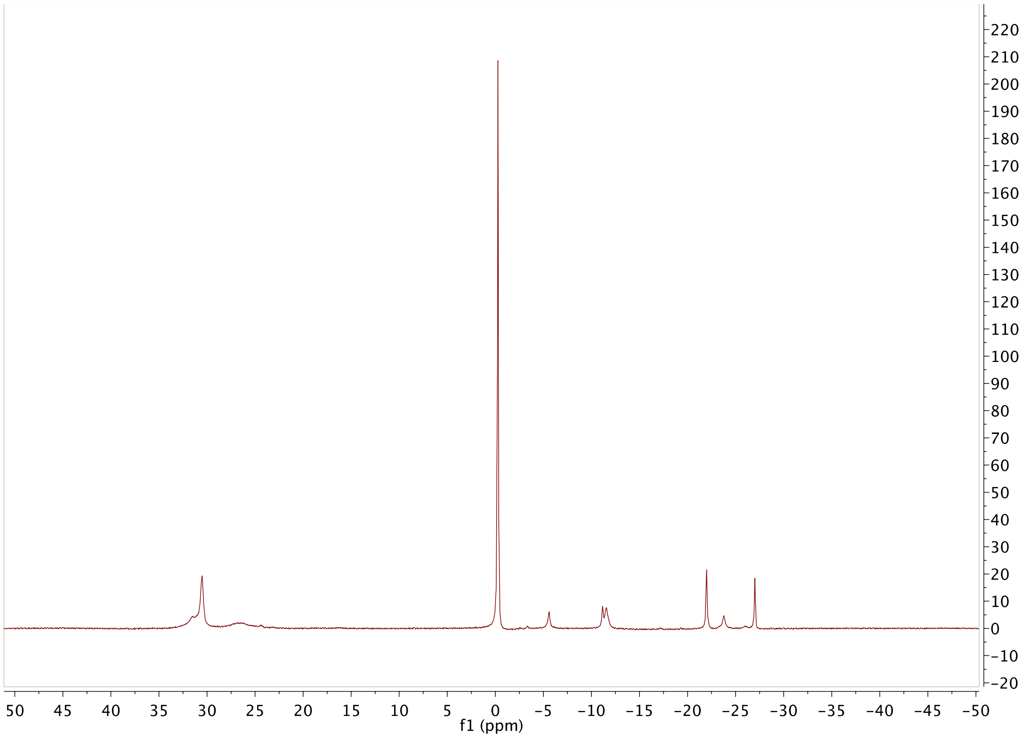


Figure S9: Top: ^{11}B spectra of end of AB dehydrogenation reaction catalyzed by **1** (1 mol% Ru, 1:2 benzene-d_6 : diglyme) after **1** and solvents were exposed to air and sonicated for 20 min. Note presence of broad polyunsaturated peaks at 23-33 ppm. Other intermediates include borazine (31 ppm), BF_3-OEt_2 external standard (0 ppm), amine borane cyclic tetramer (-5, -11, -23 ppm), cyclotriborazane (-11 ppm), residual AB (-22 ppm), and aminodiborane (-27 ppm). Bottom: ^{11}B spectra of end of AB dehydrogenation reaction catalyzed by **1** (1 mol% Ru, 1:2 C_6D_6: diglyme) The boron intermediates of the two spectra are comparable, no evidence of $B(OH)_3$, the hydrolysis of boron byproducts at 20 ppm.

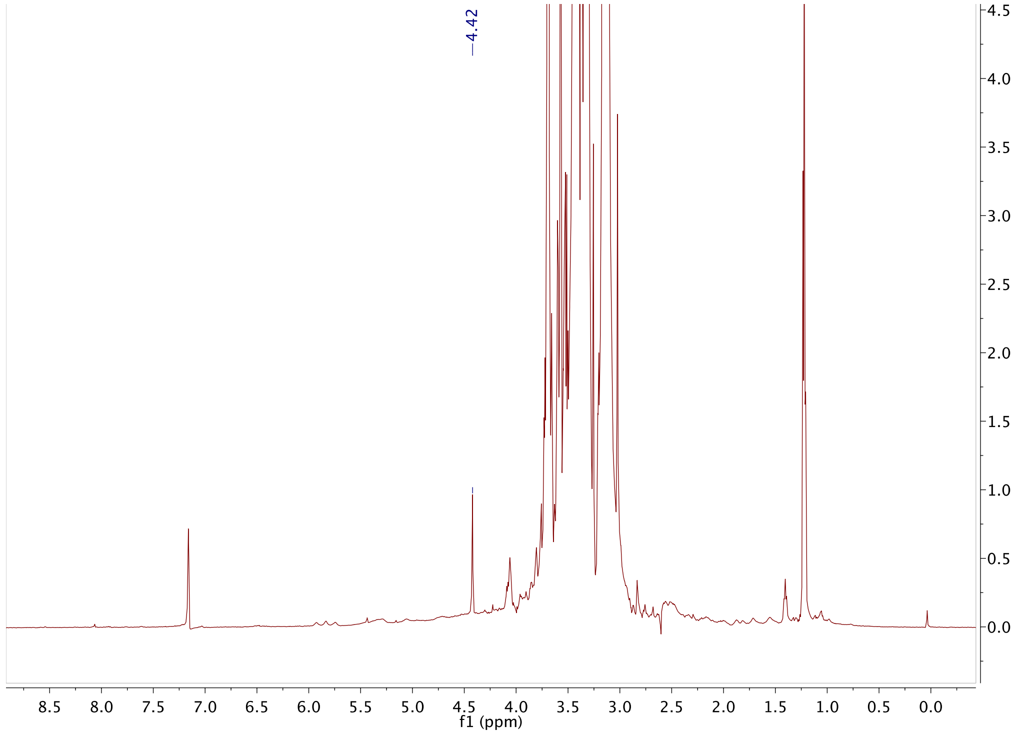
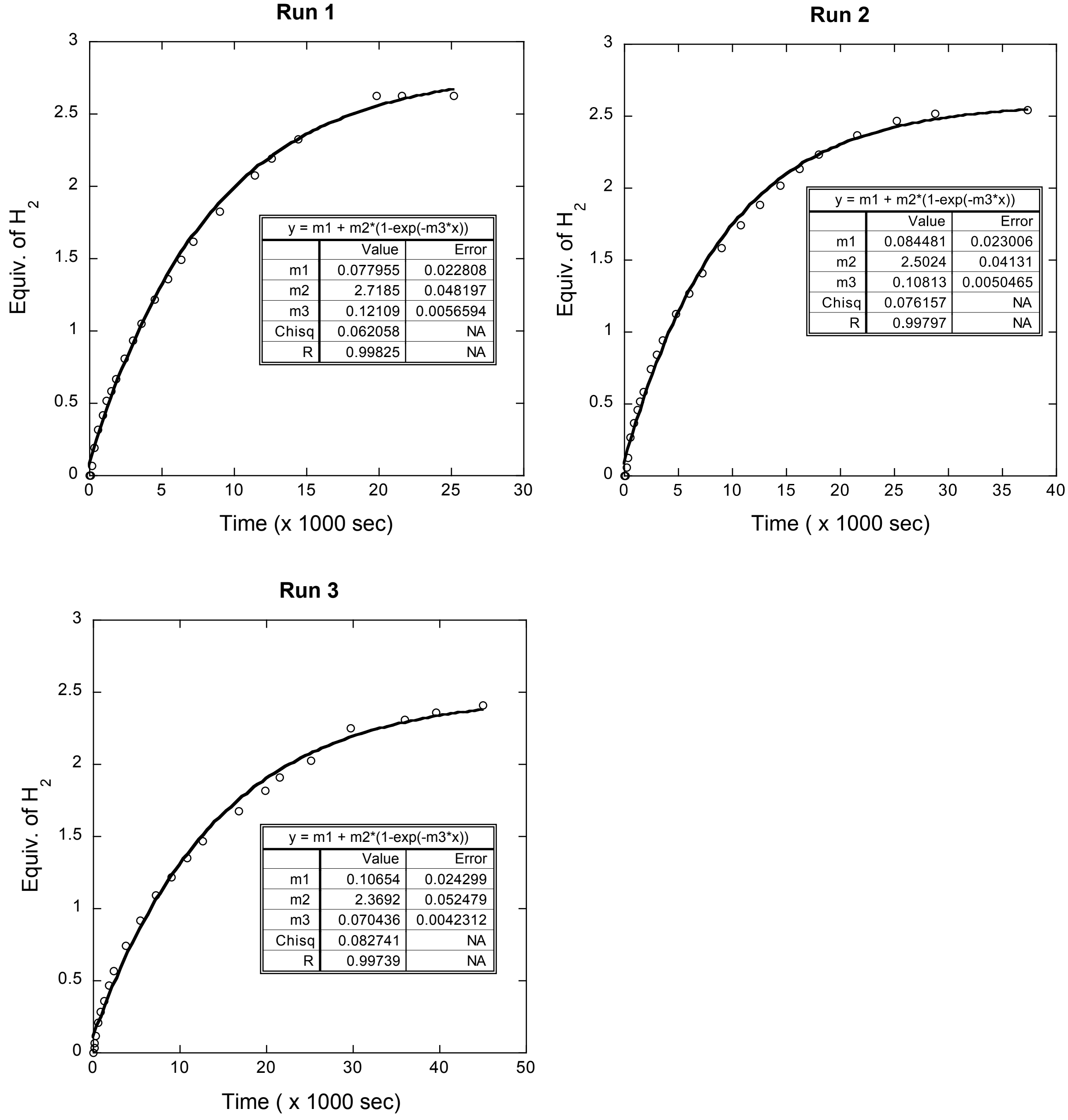


Figure S10: ^{1}H spectra of end of AB dehydrogenation reaction catalyzed by **1** after **1** and solvents (diglyme/benzene-*d*$_6$) were exposed to air and submerged in an ultrasonic cleaning bath for 20 min. Note H_2 gas formation at 4.42 ppm.

V. Eudiometry

A. Catalyst **1** Reuse Reactions. See main text for in detail procedures.



Run 1

y = m1 + m2*(1-exp(-m3*x))	Value	Error
m1	0.077955	0.022808
m2	2.7185	0.048197
m3	0.12109	0.0056594
Chisq	0.062058	NA
R	0.99825	NA

Run 2

y = m1 + m2*(1-exp(-m3*x))	Value	Error
m1	0.084481	0.023006
m2	2.5024	0.04131
m3	0.10813	0.0050465
Chisq	0.076157	NA
R	0.99797	NA

Run 3

y = m1 + m2*(1-exp(-m3*x))	Value	Error
m1	0.10654	0.024299
m2	2.3692	0.052479
m3	0.070436	0.0042312
Chisq	0.082741	NA
R	0.99739	NA

Figure S11: Eudiometry data for successive runs with 1.0 mol% catalyst **1** at 70 °C.

B. Representative H_2 quantification of [(phen)RuCl$_2$(CO)$_2$] (**2**) and 2 equivalents of TlOTf

AB dehydrogenation eudiometry run at 70 °C with 7.7 mg AB (0.25 mmol), **2** (10.2 mg, 25 µmol, 10 mol%), and TlOTf (17.7 mg, 50 µmol, 20 mol%) in diglyme (0.6 mL).

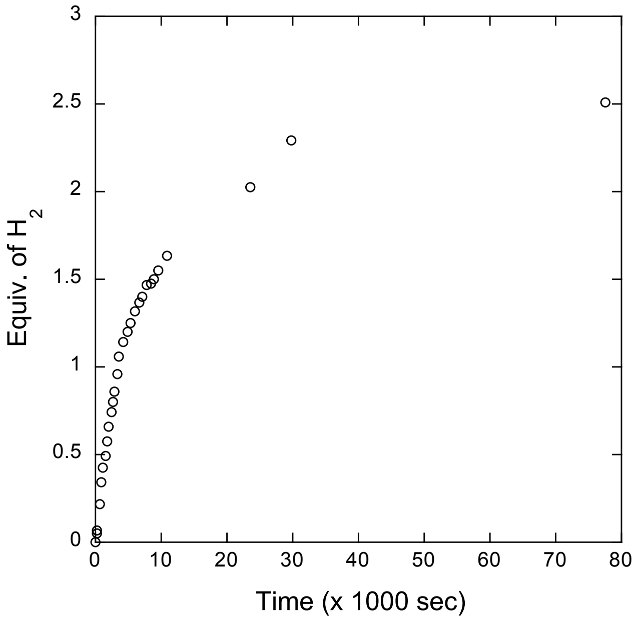


Figure S12: Eudiometry data for 10 mol% catalyst **2** and 2 equiv. TlOTf at 70 °C.

VI. References

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[1] G. N. Krishnamurthy, N. Shashikala, *J. Serb. Chem. Soc.* 2009, **74**, 1085–1096.
[2] D. Black, G. Deacon, N. Thomas, *Aust. J. Chem.* 1982, **35**, 2445-2453.