Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Aqueous Biphasic Iron-Catalyzed Asymmetric Transfer Hydrogenation of Aromatic Ketones

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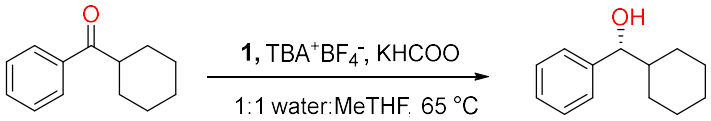
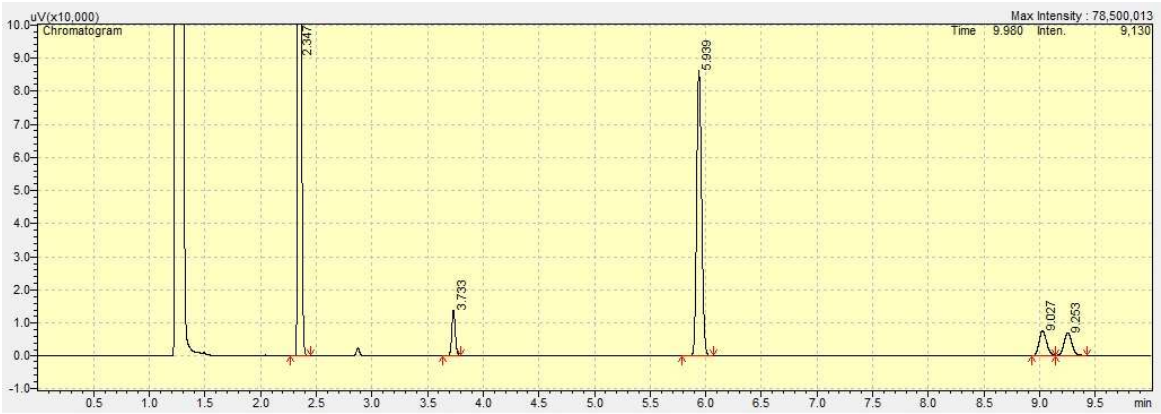
Fig. S1.1 Reaction for cyclohexylphenylketone in Fig. 2

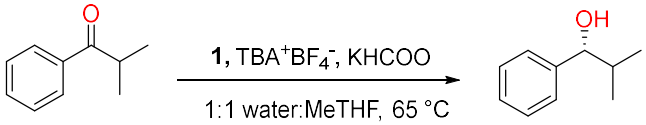


GC analysis conditions: column temperature 170 °C



Retention time: Di-*tert*-butylbenzene (DTBB): 2.347; Inhibitor found in MeTHF: 3.733; ketone: 5.939; (R)-alcohol: 9.027; (S)-alcohol: 9.253.

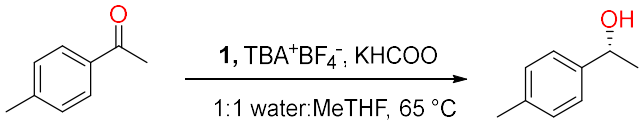
Fig. S2 Reaction for *iso*butyrophenone in Fig. 2



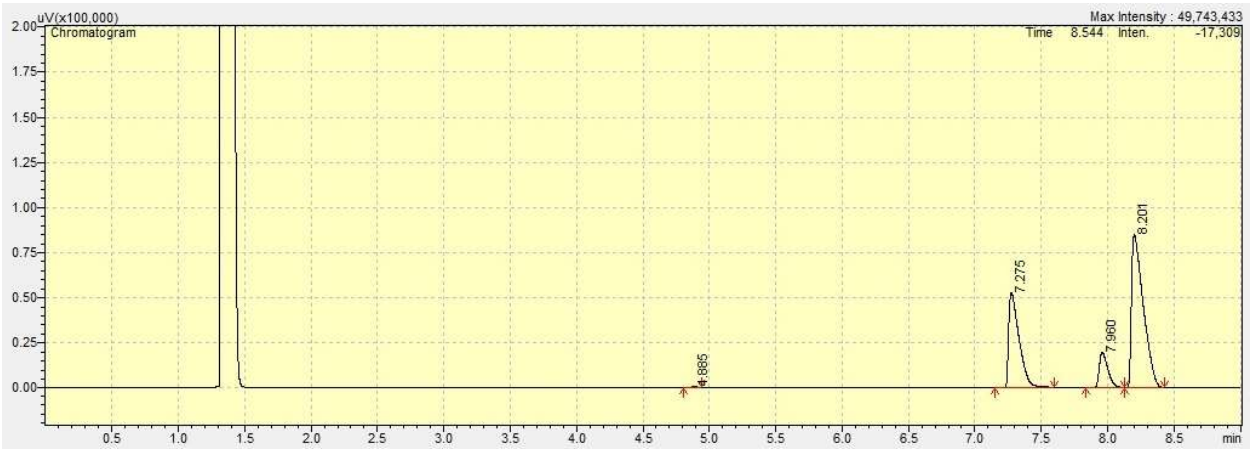
GC analysis conditions: column temperature 100 °C

Retention time: DTBB: 40.132; ketone: 14.950; (R)-alcohol: 64.570; (S)-alcohol: 67.310.

Fig. S3 Reaction for 4'-methylacetophenone in Fig. 2

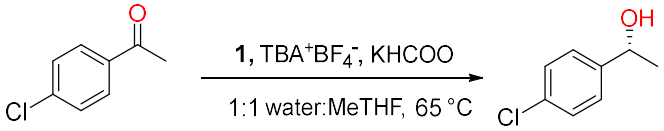


GC analysis conditions: column temperature 130 °C

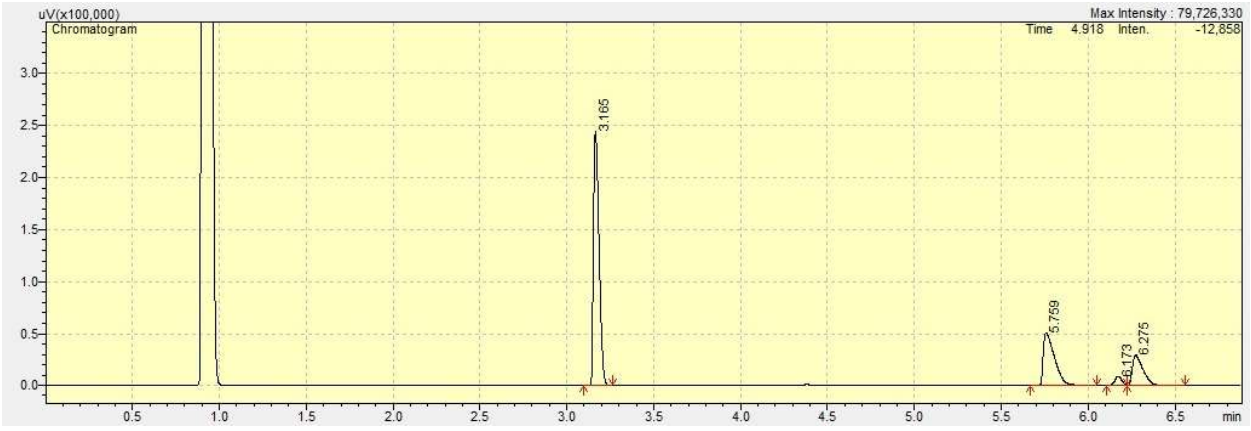


Retention time: DTBB: 8.201; ketone: 4.885; (R)-alcohol: 7.275; (S)-alcohol: 7.960.

Fig. S4 Reaction for 4'-chloroacetophenone in Fig. 2

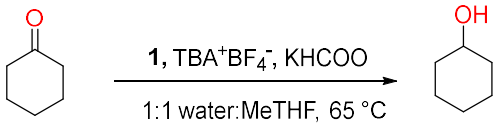


GC analysis conditions: column temperature 145 °C

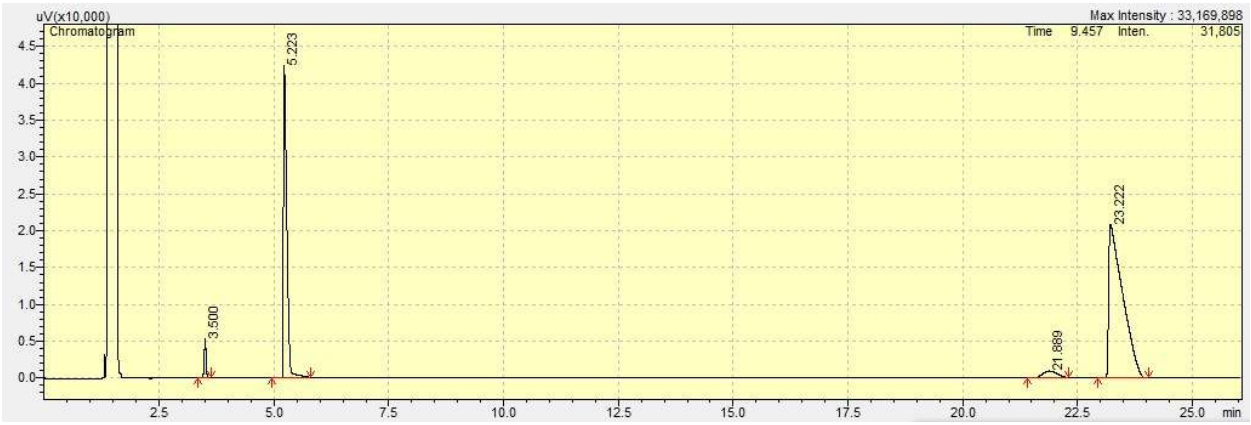


Retention time: DTBB: 3.165; ketone: 2.828; (R)-alcohol: 5.759; (S)-alcohol: 6.275; Impurity found in 4'-chloroacetophenone substrate: 6.173.

Fig. S5 Reaction for cyclohexanone in Fig. 2

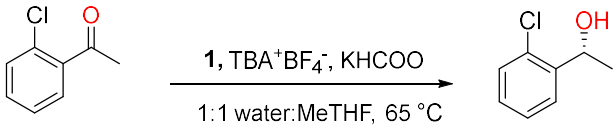


GC analysis conditions: column temperature 110 °C

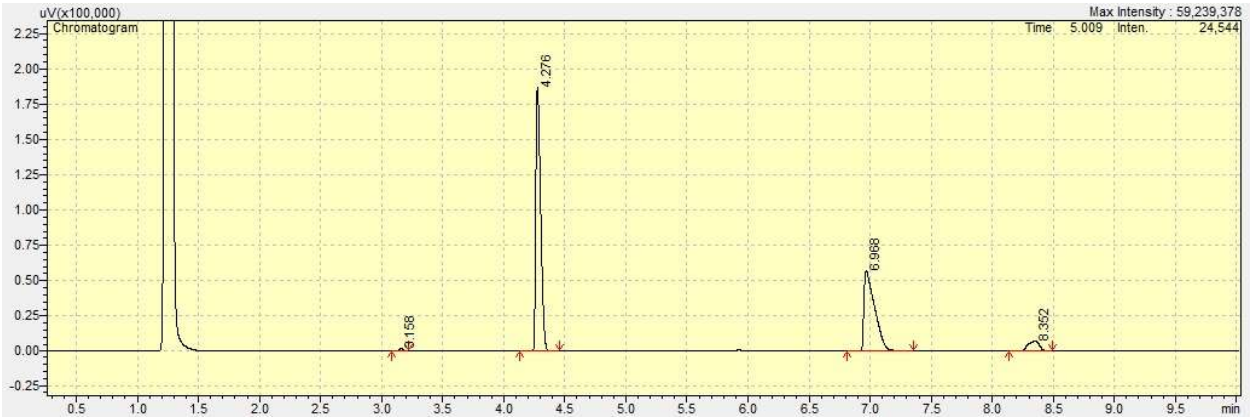


Retention time: DTBB: 23.222; Inhibitor found in MeTHF: 21.889; ketone: 3.500; alcohol: 5.223.

Fig. S6 Reaction for 2'-chloroacetophenone in Fig. 2

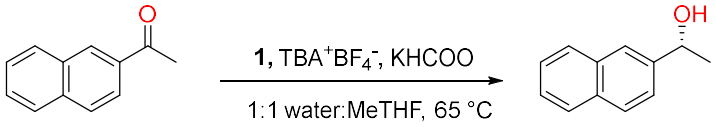


GC analysis conditions: column temperature 145 °C



Retention time: DTBB: 4.276; ketone: 3.158; (R)-alcohol: 6.968; (S)-alcohol: 8.352.

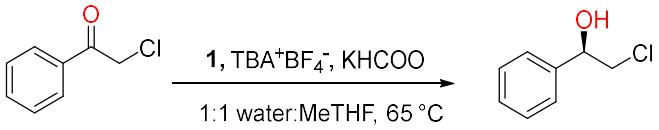
Fig. S7 Reaction for 2-acetonaphthone in Fig. 2



GC analysis conditions: column temperature 150 °C

Retention time: DTBB: 2.818; Inhibitor found in MeTHF: 5.301; ketone: 11.344; (R)-alcohol: 18.952; (S)-alcohol: 20.136.

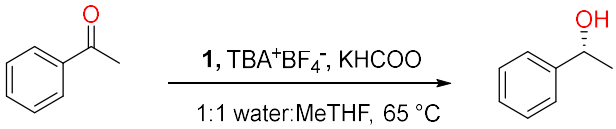
Fig. S8 Reaction for 2-chloroacetophenone in Fig. 2



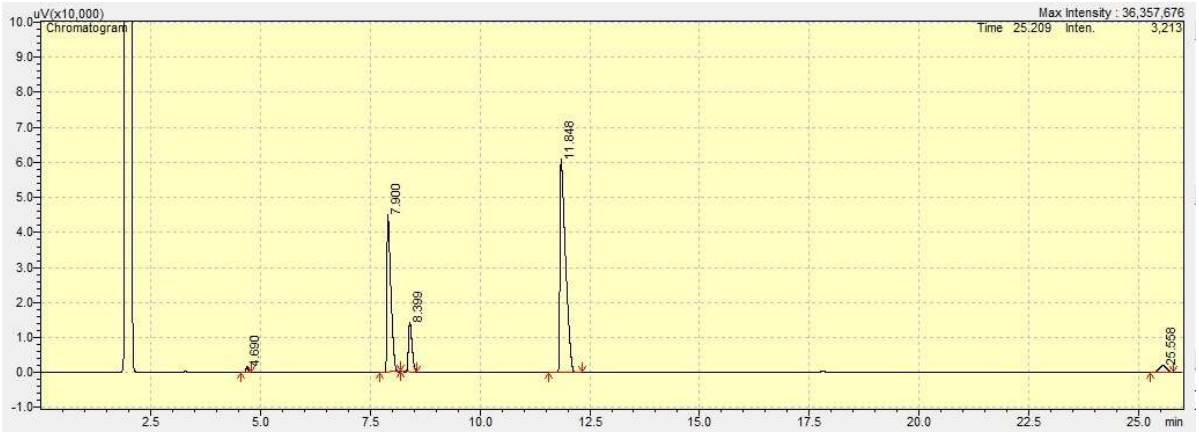
GC analysis conditions: column temperature 120 °C

Retention time: DTBB: 13.279; Inhibitor found in MeTHF: 29.966; ketone: 17.138; (R)-alcohol: 35.131; (S)-alcohol: 39.332.

Fig. S9 Reaction for acetophenone in Fig. 2

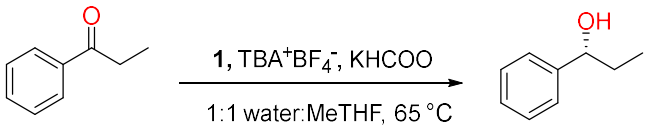


GC analysis conditions: column temperature 130 °C



Retention time: DTBB: 11.848; Inhibitor found in MeTHF: 25.558; ketone: 4.690; (R)-alcohol: 7.900; (S)-alcohol: 8.399.

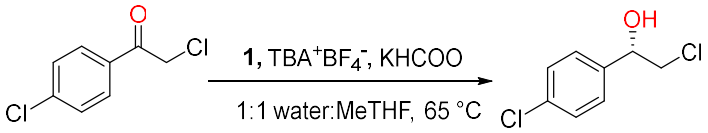
Fig. S10 Reaction for propiophenone in Fig. 2



GC analysis conditions: column temperature 120 °C

Retention time: DTBB: 13.394; Inhibitor found in MeTHF: 12.637; ketone: 5.745; (R)-alcohol: 13.859; (S)-alcohol: 14.578.

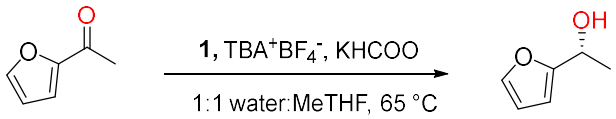
Fig. S11 Reaction for 2,4'-dichloroacetophenone in Fig. 2



GC analysis conditions: column temperature 145 °C

Retention time: DTBB: 3.169; Inhibitor found in MeTHF: 6.196; ketone: 9.348; (S)-alcohol: 20.261; (R)-alcohol: 22.887.

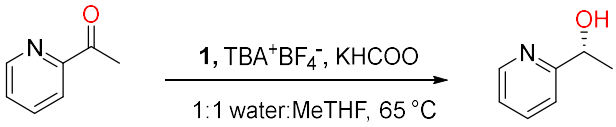
Fig. S12 Reaction for 2-acetylfuran in Fig. 2



GC analysis conditions: column temperature 90 °C for 20 min, ramp at 5 °C/min to 140 °C, hold 5 min.

Retention time: DTBB: 30.218; ketone: 5.368; (R)-alcohol: 11.487; (S)-alcohol: 12.023.

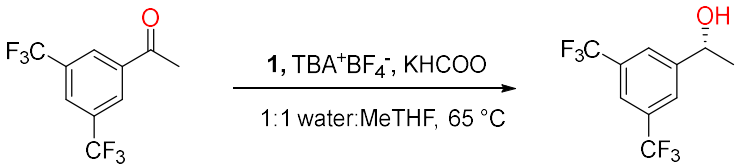
Fig. S13 Reaction for 2-acetylpyridine in Fig. 2



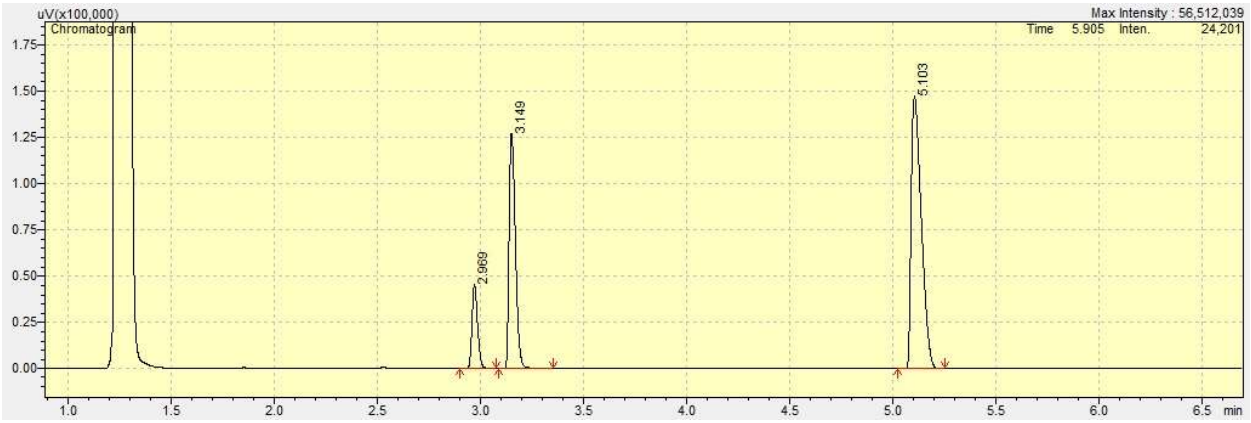
GC analysis conditions: column temperature 100 °C

Retention time: DTBB: 42.731; ketone: 5.010; racemic alcohol mixture: 17.320.

Fig. S14 Reaction for 3',5'-bis(trifluoromethyl)acetophenone in Fig. 2

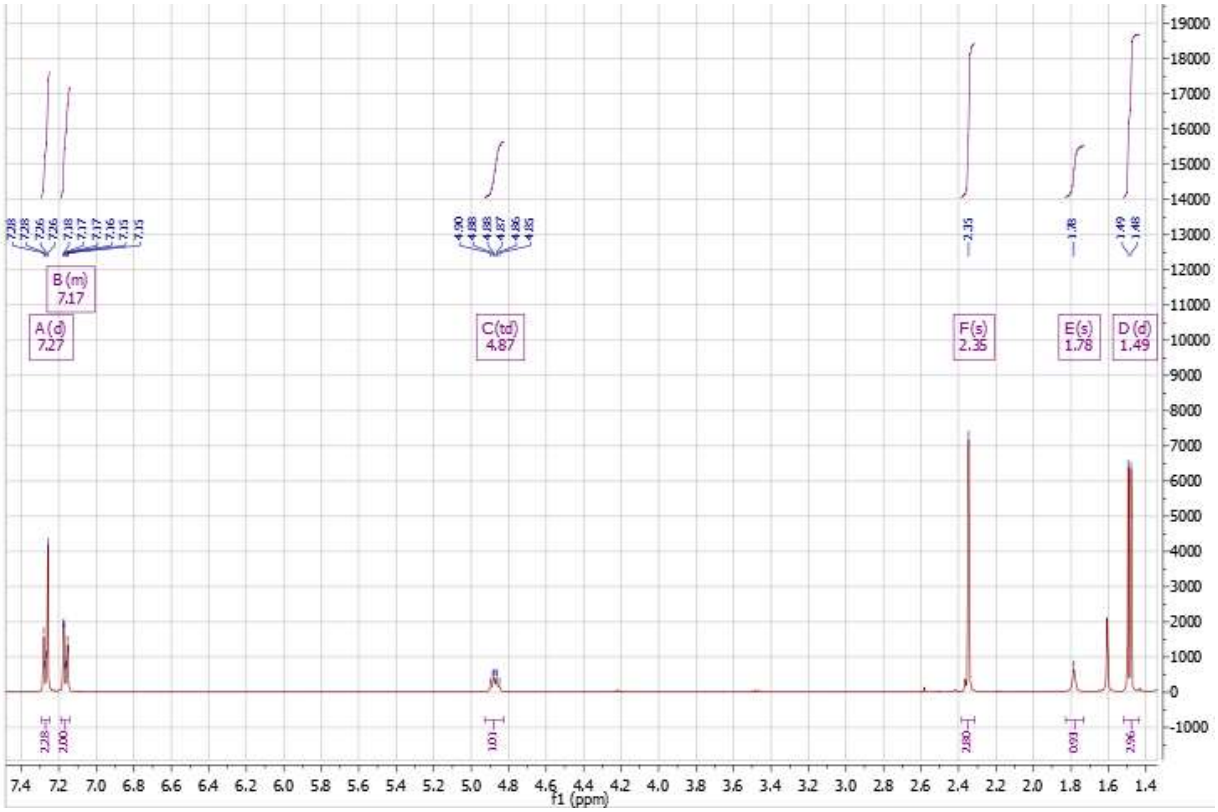


GC analysis conditions: column temperature 140 °C



Retention time: DTBB: 5.103; ketone: 1.620; (R)-alcohol: 2.969; (S)-alcohol: 3.149.
Note: The major product is the (S)-alcohol.

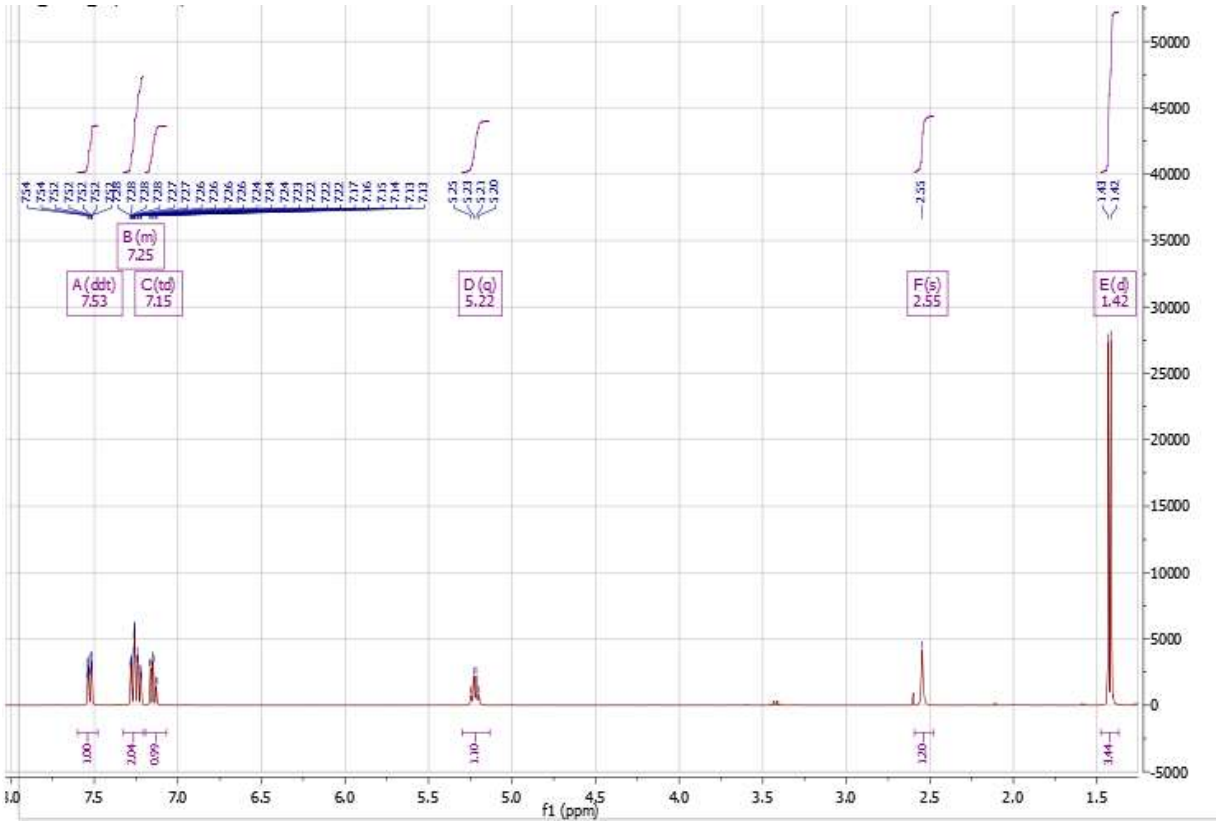
Fig. S15 ^{1}H NMR for the isolated 1-(4'-methylphenyl)ethanol (from 4'-methylacetophenone)



^{1}H NMR (400 MHz, Chloroform-*d,* δ 7.26) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.19 – 7.14 (d, *J* = 8.2 Hz, 2H), 4.87 (td, *J* = 7.3, 5.3 Hz, 1H), 2.35 (s, 3H), 1.78 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H).

Isolated 60 mg (85% yield) by removing the MeTHF *in vacuo*, then performing a silica flash column using ether:pentane (1:4), then ether:pentane (3:2) to collect the product alcohol as a colourless oil.

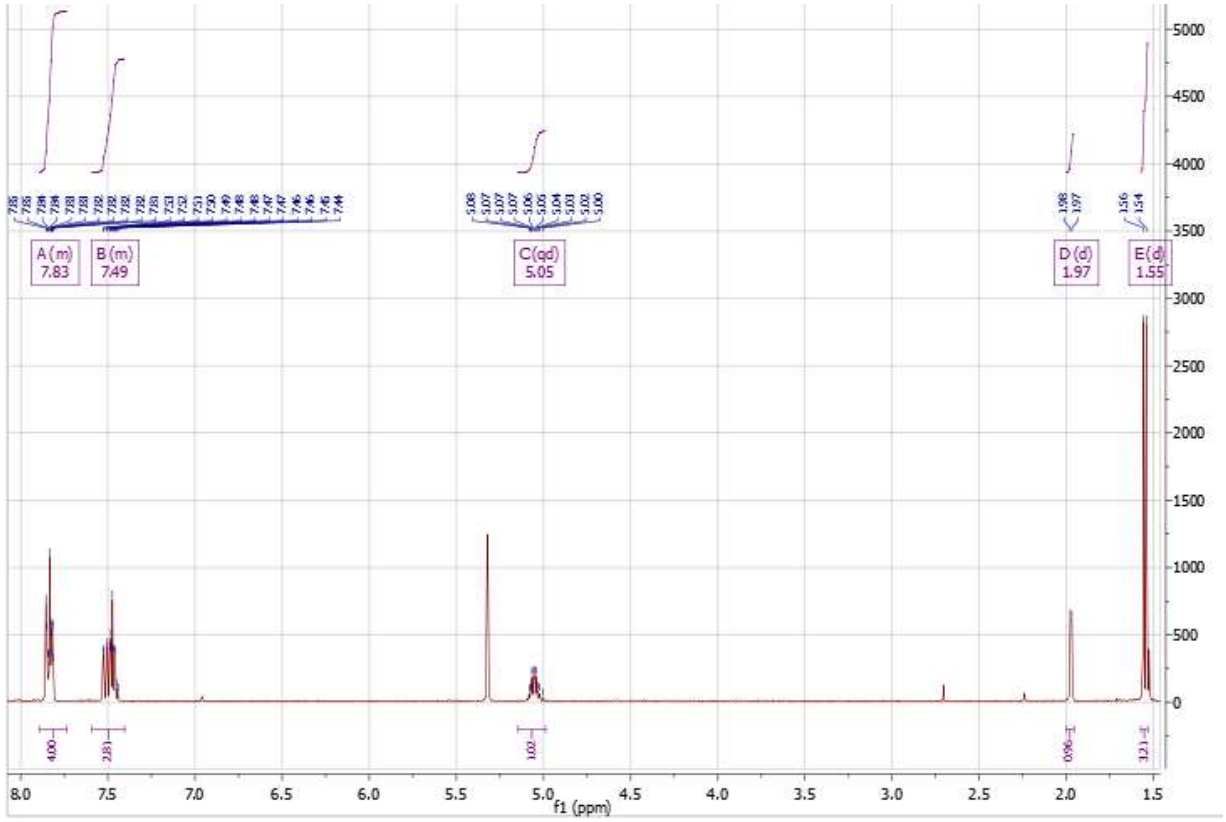
Fig. S16 [1]H NMR for the isolated 1-(2'-chlorophenyl)ethanol (from 2'-chloroacetophenone)



[1]H NMR (400 MHz, Chloroform-*d,* δ 7.26) δ 7.53 (ddt, *J* = 7.7, 1.8, 0.5 Hz, 1H), 7.33 – 7.21 (m, 2H), 7.15 (td, *J* = 7.6, 1.7 Hz, 1H), 5.22 (q, *J* = 6.4 Hz, 1H), 2.55 (s, 1H), 1.42 (d, *J* = 6.4 Hz, 3H).

Isolated 93 mg (97% yield) by removing the MeTHF *in vacuo*, then performing a silica flash column using ether:pentane (1:9), then ether:pentane (3:2) to collect the product alcohol as a colourless oil.

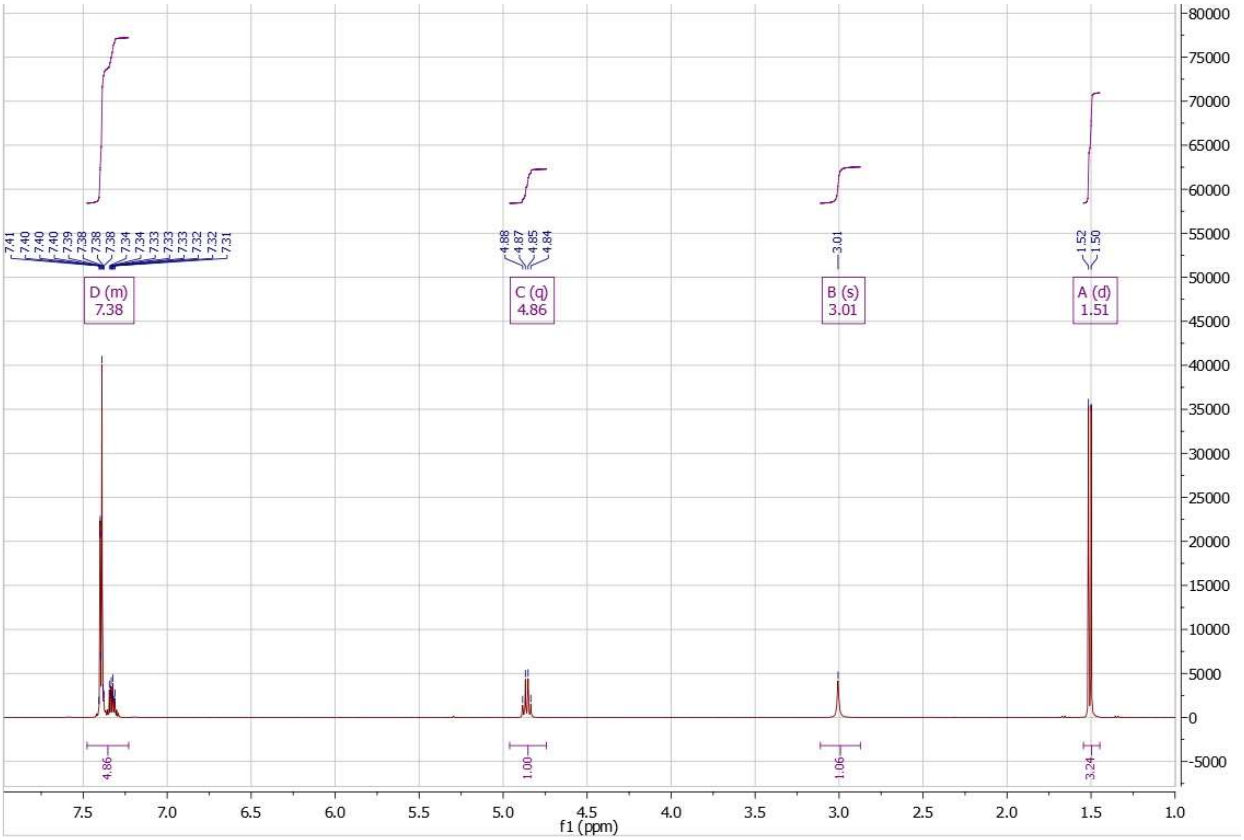
Fig. S17 ^{1}H NMR for the isolated 1-(2-naphthalenyl)ethanol (from 2-acetonaphthone)



^{1}H NMR (400 MHz, Methylene Chloride-d_2, δ 5.32) δ 7.89 – 7.74 (m, 4H), 7.59 – 7.40 (m, 3H), 5.05 (qd, *J* = 6.4, 3.9 Hz, 1H), 1.97 (d, *J* = 3.7 Hz, 1H), 1.55 (d, *J* = 6.5 Hz, 3H).

Isolated 89 mg (96% yield) by removing the MeTHF *in vacuo*, then performing a silica flash column using hexanes:ethylacetate (20:1), then hexanes:ethylacetate (2:1) to collect the product alcohol as a colourless solid.

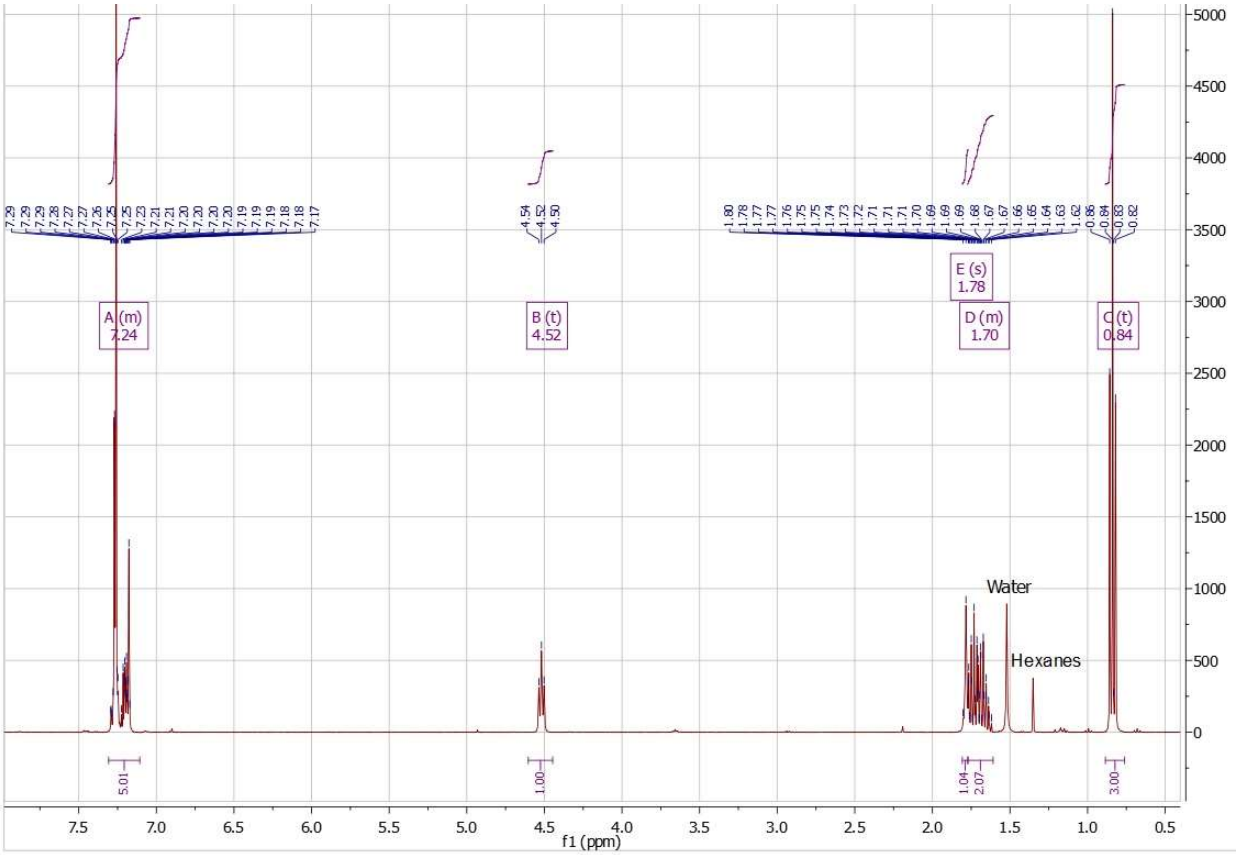
Fig. S18 [1]H NMR for the isolated 1-phenylethanol (from acetophenone)



[1]H NMR (400 MHz, Chloroform-*d,* δ 7.26) δ 7.48 – 7.23 (m, 5H), 4.86 (q, *J* = 6.5 Hz, 1H), 3.01 (s, 1H), 1.51 (d, *J* = 6.5 Hz, 3H).

Isolated 139 mg (96% yield) by removing the MeTHF *in vacuo*, then performing a column using ethylacetate:hexanes (1:5) (R_f = 0.41) to obtain the product alcohol as a colourless oil.

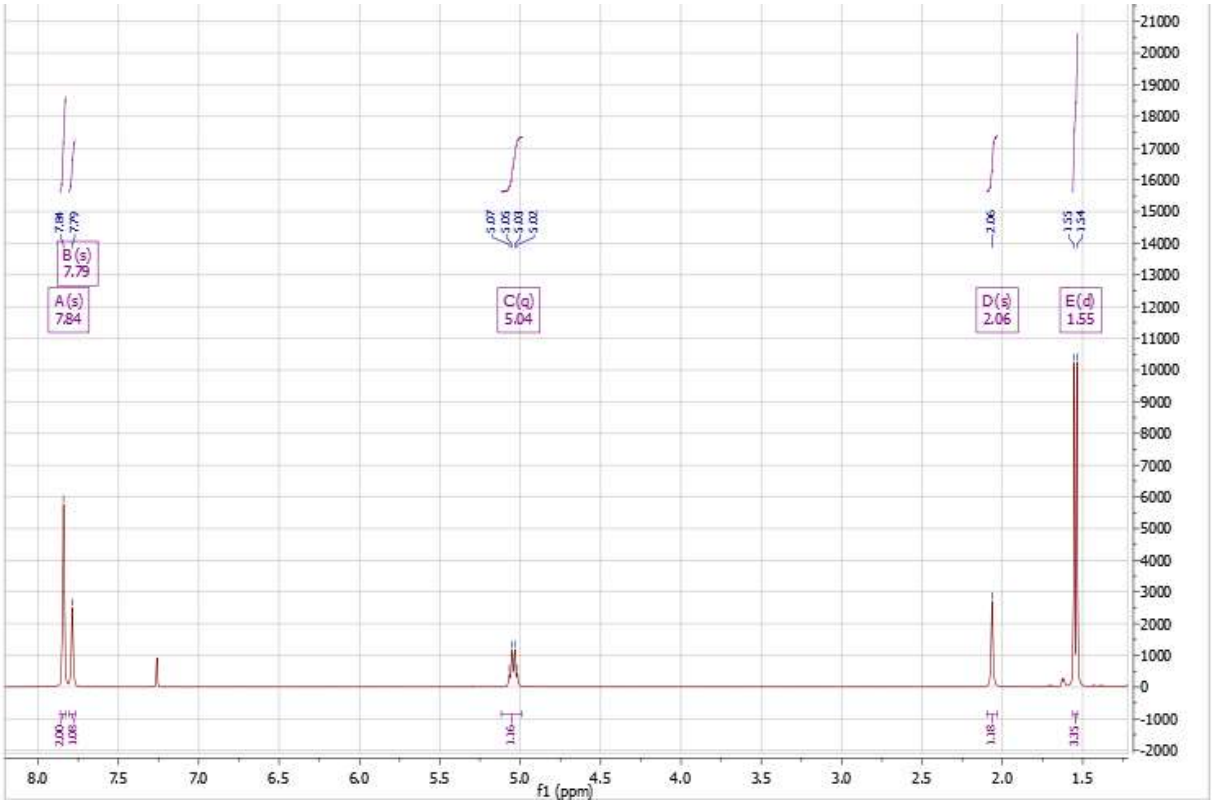
Fig. S19 [1]H NMR for the isolated 1-phenyl-1-propanol (from propiophenone)



[1]H NMR (400 MHz, Chloroform-*d,* δ 7.26) δ 7.31 – 7.11 (m, 5H), 4.52 (t, *J* = 6.6 Hz, 1H), 1.78 (s, 1H), 1.77 – 1.61 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

Isolated 132 mg (93% yield) by removing the MeTHF *in vacuo*, then performing a silica flash column using hexanes:ethylacetate (95:5) to collect the product alcohol as a slightly yellow oil.

Fig. S20 [1]H NMR for the isolated 1-[3',5'-bis(trifluoromethyl)phenyl]ethanol (from 3',5'-bis(trifluoromethyl)acetophenone)



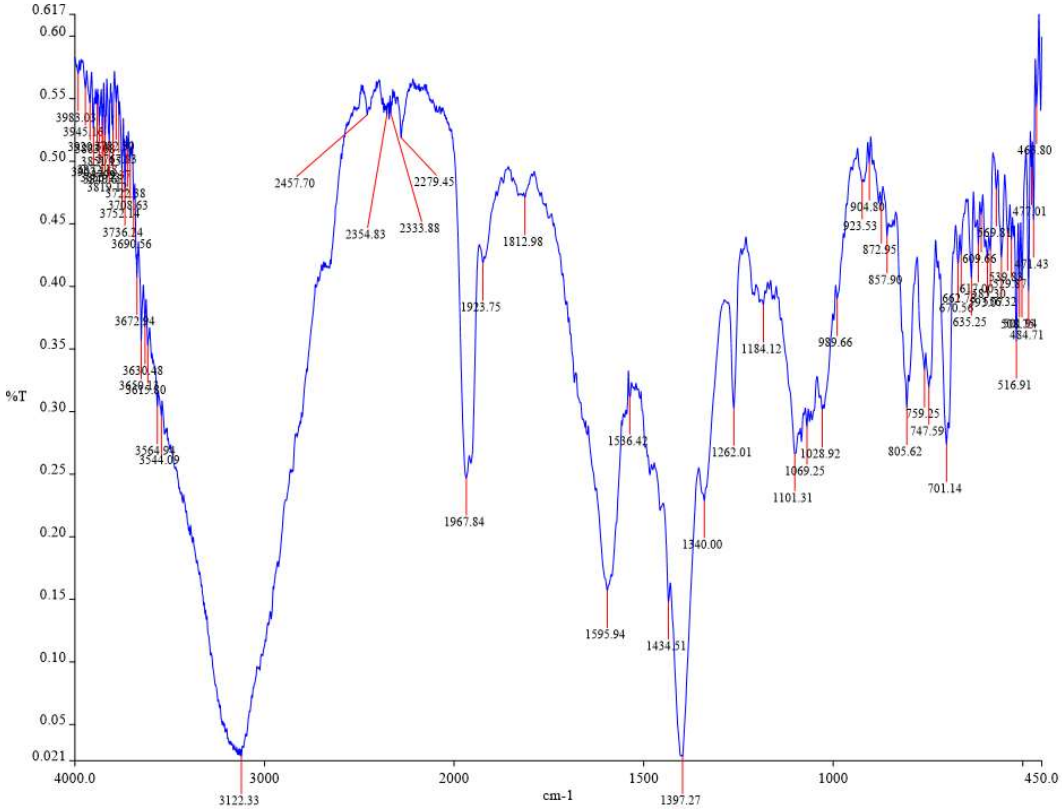
[1]H NMR (400 MHz, Chloroform-*d,* δ 7.26) δ 7.84 (s, 2H), 7.79 (s, 1H), 5.04 (q, *J* = 6.5 Hz, 1H), 2.06 (s, 1H), 1.55 (d, *J* = 6.5 Hz, 3H). [19]F NMR (377 MHz, Chloroform-*d*) δ -62.87.

Isolated 310 mg (98% yield) by removing the MeTHF *in vacuo*, then performing a silica flash column using hexanes:ethylacetate (4:1) to collect the product alcohol as a colourless solid.

Fig. S21 Procedure for the ATH of 2,4'-dichloroacetophenone in *iso*propanol

In a glovebox at 30 °C, **1** (10 mg, 0.012 mmol) and 2,4'-dichloroacetophenone (1.125 g, 5.95 mmol, 500 eq.) were placed in a vial and *iso*propanol (5 mL) was added. This mixture was stirred for 20 min to ensure that the substrate was dissolved. In a separate vial, potassium *tert*-butoxide (2.7 mg, 0.023 mmol, 2 eq.) was dissolved in *iso*propanol (1 mL). The basic *iso*propanol was then injected into the substrate and catalyst solution to begin the reaction. Samples of the reaction were injected into GC vials filled with air-containing *iso*propanol every 10 minutes. The results showed no conversion after 60 minutes.

Fig. S22 IR of iron-formato complex **3**



Activated Iron-Formato Coordination Stretch (cm^{-1})	
CO ligand of **3**	1967
Coordinated Formato CO	1595
CO ligand of **2**[S1]	1923

Fig. S23 ^{1}H NMR of activated hydride complex with THF as the cosolvent

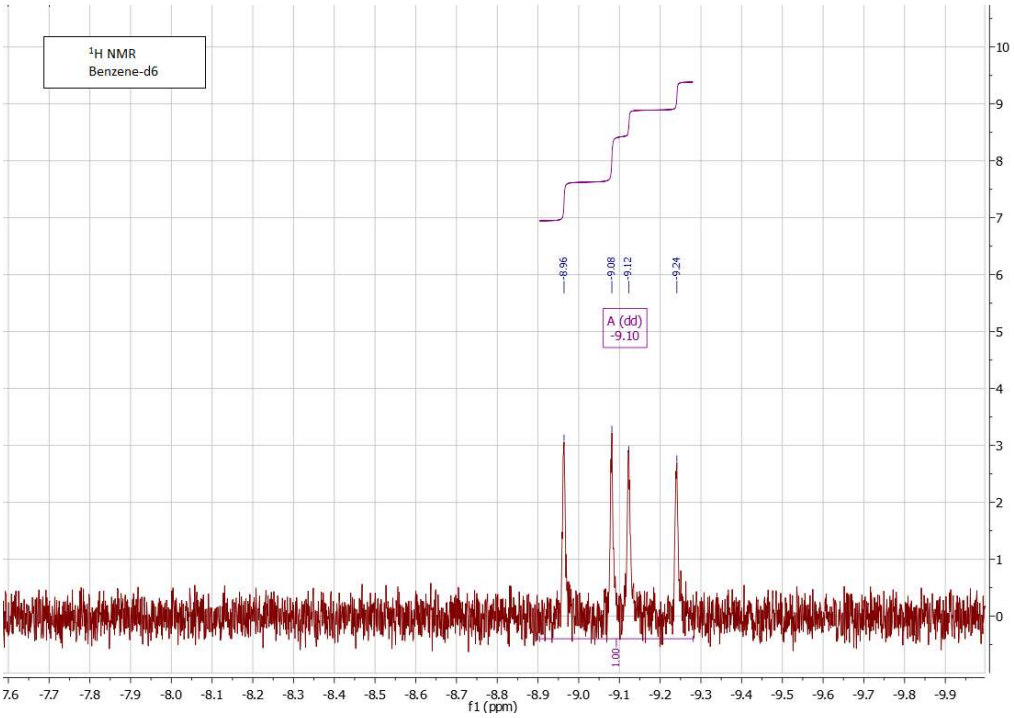
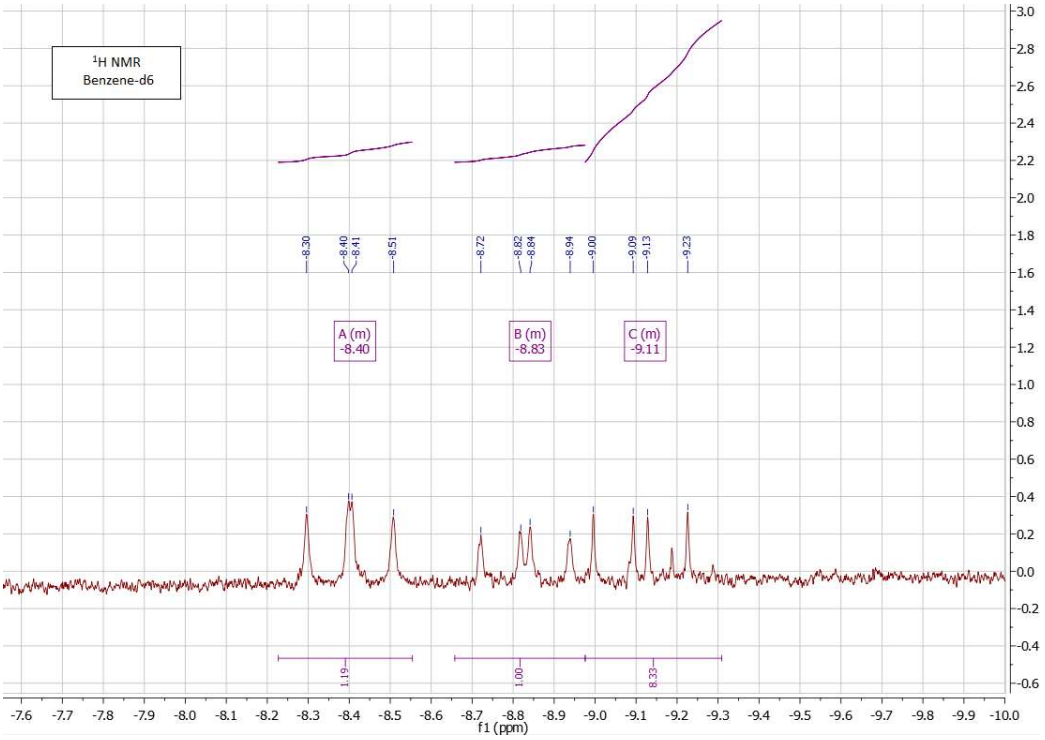


Fig. S24 ^{1}H NMR of activated hydride complex with MeTHF as the cosolvent



References

(S1) W. Zuo; A. J. Lough; Y. F. Li; R. H. Morris. *Science,* 2013, ***342***, 1080.