

# Transfer Hydrogenation of Aldehydes, Allylic Alcohols, Ketones and Imines Using Molybdenum Cyclopentadienone Complexes

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## Supporting Information

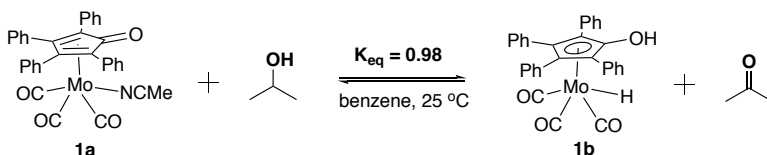
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## General Procedures

All air-sensitive compounds were prepared and handled under a nitrogen atmosphere using standard Schlenk and inert-atmosphere box techniques. All solvents used including benzene and benzene- $d_6$  were dried over molecular sieves (4Å) and degassed by standard freeze-pump-thaw process three times. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar or Strem, and used as received. Molybdenum complex **1a**<sup>1</sup>, N-benzylideneaniline<sup>2</sup> (entry 8, substrate table), and (E)-N-(1-phenylethylidene)aniline<sup>3</sup> (entry 9, substrate table) were prepared as described in the literature.  $^1\text{H}$  and  $^{13}\text{C}$  were recorded in benzene- $d_6$ ,  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$  and acetonitrile- $d_3$  solutions using Varian Mercury 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million (ppm) relative to tetramethylsilane and referenced to residual protium in the solvent (benzene- $d_6$ :  $\delta$  7.16,  $\text{CDCl}_3$ :  $\delta$  7.26,  $\text{CD}_2\text{Cl}_2$ :  $\delta$  5.32 and acetonitrile- $d_3$ :  $\delta$  1.94). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ( $\text{CD}_2\text{Cl}_2$ :  $\delta$  53.84). Spectral features are tabulated in the following order: chemical shift ( $\delta$ , ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); number of protons; coupling constants (J, Hz). Electrospray ionization mass spectrometry was performed on an LTQ-Orbitrap XL instrument (Thermo Fisher Scientific (San Jose, CA)), capable of resolutions up to 100,000 at  $m/z$  400; Data were preliminarily analyzed in Thermo Fisher's Qual Browser tool, and then exported as text files for further processing in MatLab. Infrared (IR) spectra were recorded on a Nicolet 6700 FT/IR spectrometer. Elemental Analysis was conducted with Perkin Elmer 2400 Series II combustion analyzer at University of California Berkeley Microanalytical Facility.

### Stoichiometric Reduction of Ketones by **1a** and determination of $K_{\text{eq}}$ at 25 °C



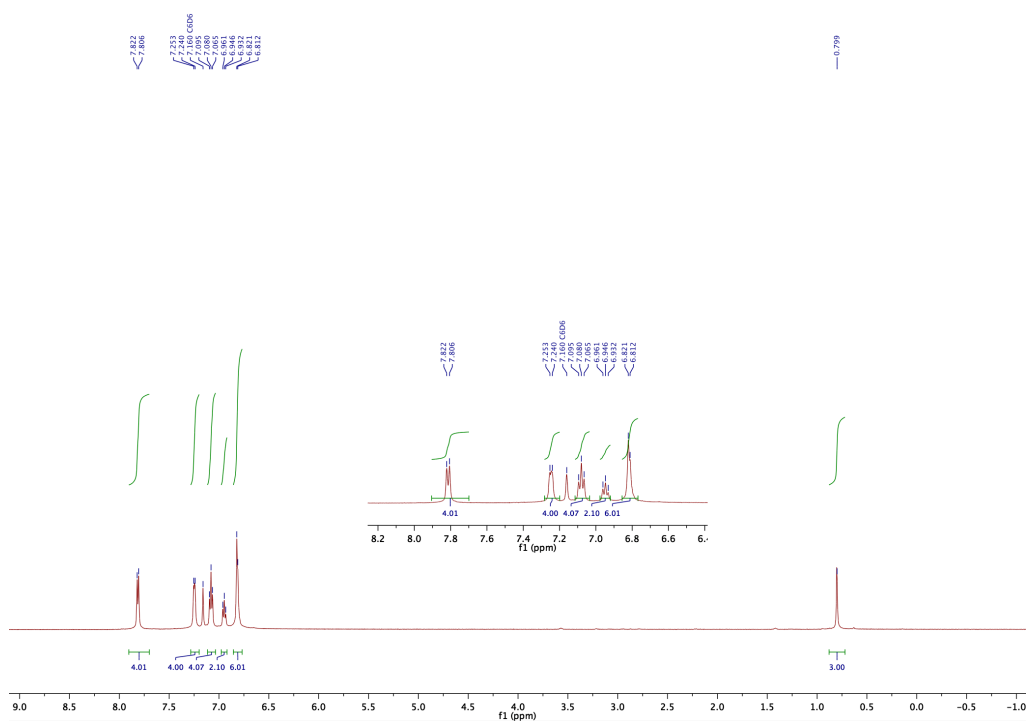
In a J. Young NMR tube was prepared a solution of **1a** (30.3 mg, 50  $\mu\text{mol}$ ) and 2-propanol

(3.8  $\mu$ L, 50  $\mu$ mol) in benzene- $d_6$  (0.4 mL), and this sample solution was monitored by  $^1\text{H}$  NMR spectroscopy over time at 25  $^\circ\text{C}$ . The peaks that correspond to acetone ( $\delta$  1.55) and molybdenum hydride complex **1b** (Mo-H,  $\delta$  -3.88) as well as acetonitrile ( $\delta$  0.63) grew in at the expense of 2-propanol ( $\text{CHCH}_3\text{CH}_3\text{OH}$ ,  $\delta$  3.66) and **1a** (Ar,  $\delta$  7.81). After 12 h, about 45 % of **1a** and 2-propanol was converted to **1b** and acetone. Extended reaction times did not result in major change in the composition of the reaction mixture. Under the same reaction condition, the initial loading of 2-propanol was increased to 2 equivalents (7.6  $\mu$ L, 60  $\mu$ mol) and 3 equivalents (11.4  $\mu$ L, 90  $\mu$ mol). The concentrations of each components in the reaction mixture were taken at 12 hours point, and the  $K_{\text{eq}} = 0.98$  was taken from the average of those three experiments.

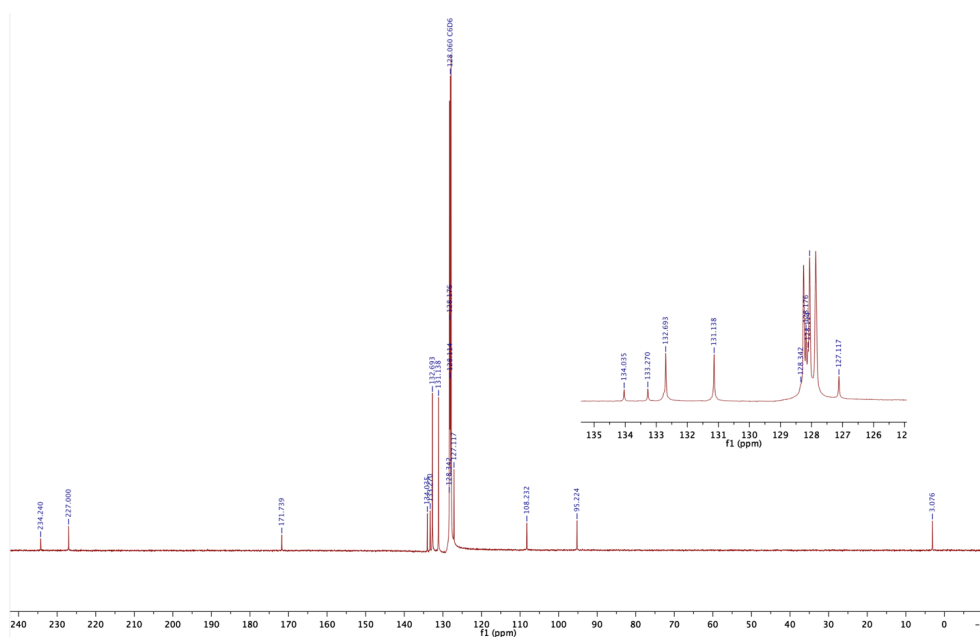
### **In situ characterization of proposed molybdenum hydride complex 1b**

As the molybdenum hydride complex **1b** exist in equilibrium with complex **1a** in the presence of 2-propanol, the reaction mixture of a stoichiometric reaction of complex **1a** with 2-propanol was used for in situ characterization of complex **1b**.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and high-resolution mass spectroscopy were recorded at the 6-hour point where both **1a** and **1b** can be well resolved by NMR with a minimum amount of decomposition. HRMS (ESI) of this reaction mixture was diluted and collected in acetonitrile (1.0 mM). Ions associated with the sodium adduct  $[(\text{C}_5\text{Ph}_4\text{OH})\text{Mo}(\text{H})(\text{CO})_3(\text{Na})]^+$  of **1b** were observed: calcd (found) for  $[\text{C}_{32}\text{H}_{22}\text{MoNaO}_4]^+$   $m/z$  591.0472 ( $m/z$  591.0492).

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of molybdenum complex **1a** in benzene- $d_6$  are shown in Figures S1 and S2. Molybdenum complex **1a**<sup>1</sup> were prepared as described in the literature.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.37-6.99 (m, 20H, Ph), 2.38 (s, 3H, Me) matches with the literature data. While the literature reported complex **1a** to be relatively air-stable, we found it to decompose readily to unidentified product under air.

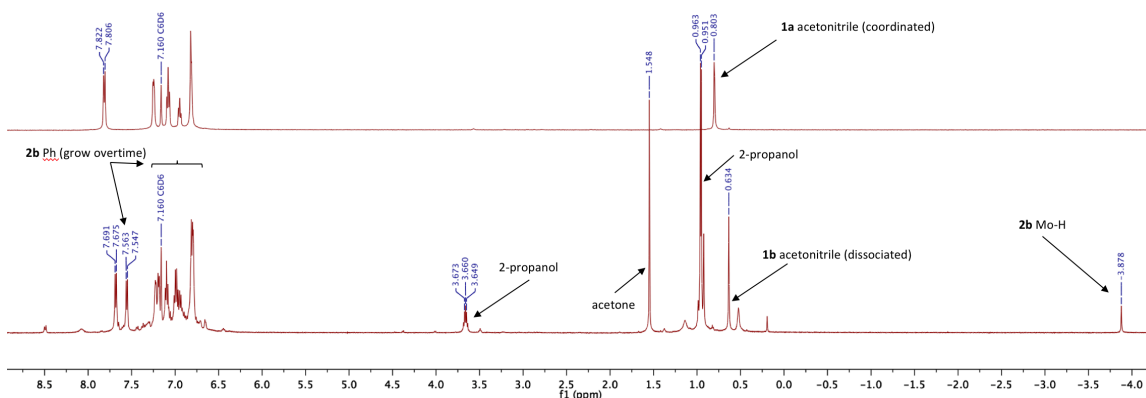


**Figure S1.** <sup>1</sup>H NMR of **1a** (benzene-d<sub>6</sub>, 500 MHz) δ 7.81 (m, 4H), 7.25 (m, 4H), 7.08 (m, 4H), 6.96 (m, 2H), 6.82 (m, 6H), 0.80 (s, 3H)



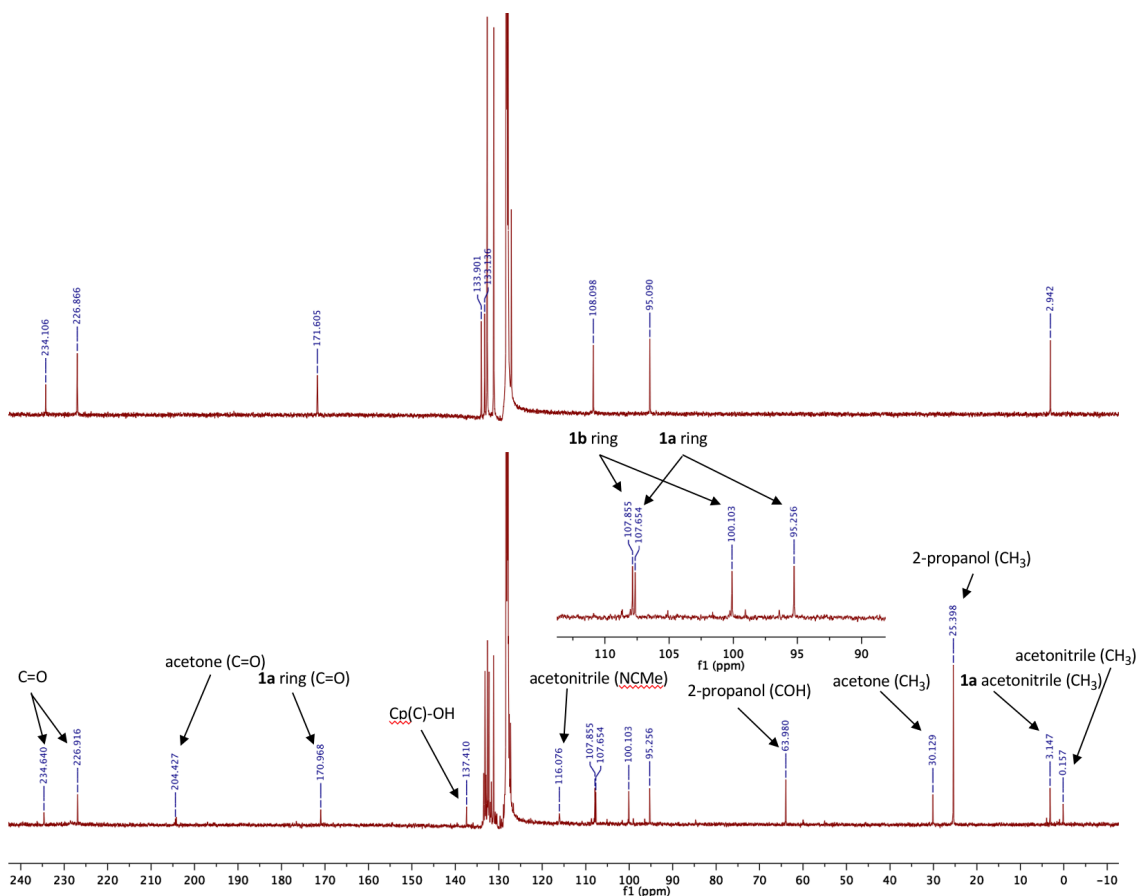
**Figure S2.** <sup>13</sup>C NMR of **1a** (benzene-d<sub>6</sub>, 500 MHz) δ 224.24 (CO), 227.00 (CO), 171.74 (CO ring), 134.04 (Ph), 133.27 (Ph), 132.69 (Ph), 131.14 (Ph), 128.34 (Ph), 128.18 (Ph), 128.11 (Ph), 127.12 (NCMe), 108.23 (Cp ring), 95.22 (Cp ring), 3.08 (acetonitrile CH<sub>3</sub>)

When the reaction of **1a** with a stoichiometric amount of isopropanol were monitored by  $^1\text{H}$  NMR, dihydrogen were partially transferred from 2-propanol to **1a** to form acetone and **1b**. Acetonitrile from **1a** was dissociated, and clear molybdenum hydride resonance at  $\delta$  -3.88 ppm as well as the phenyl proton signals associated with **1b** grow in over time (Figure S3).



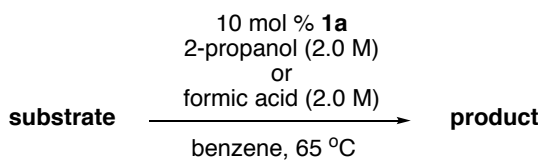
**Figure S3.**  $^1\text{H}$  NMR of reaction mixture of **1a** with 2-propanol (benzene- $\text{d}_6$ ). Top: **1a**, Bottom: Reaction mixture of **1a** with 2-propanol.

In  $^{13}\text{C}$  NMR, the presence of up field shifted cyclopentadienyl signals (**1b** ring) as well as the new phenol peak (Cp(C)-OH) at  $\delta$  137.41 ppm support the aromatization of the cyclopentadiene ring, thus the formation of proposed molybdenum hydride complex **1b** (Figure S4).



**Figure S4.**  $^{13}\text{C}$  NMR (benzene- $d_6$ ) of reaction mixture of **1a** with 2-propanol. Top: **1a**, Bottom: Reaction mixture of **1a** with 2-propanol.

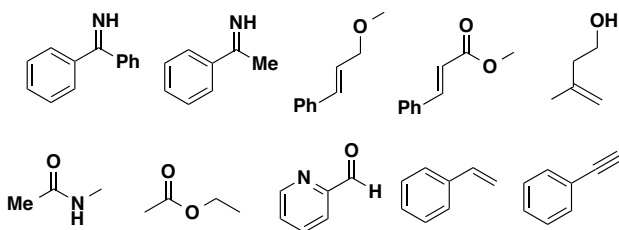
### Catalytic Transfer Hydrogenation of Aldehydes, Alkenols, Ketones and or Imines by **1a** with 2-propanol as Reducing Agent at 65 °C



In a typical experiment, to a solution of substrate (1.0 mmol) and molybdenum complex **1a** (0.1 mmol) in benzene (3.0 mL) was added 2-propanol (0.46 mL) or formic acid to glass vial (20 mL) with airtight cap under nitrogen atmosphere. This reaction mixture was heated to 65 °C and stirred with cap sealed. When the reaction was complete, solvent removed under reduced pressure and the residue was dissolved in  $\text{CDCl}_3$  and its  $^1\text{H}$ -NMR spectrum recorded. The residue hydrogenated products were purified by column chromatography

and their  $^1\text{H}$ -NMR spectra matched those reported in the literature<sup>4</sup>. For the transfer hydrogenation of 3-propenol, (entry 4, substrate table) crotonyl alcohol (entry 5, substrate table) and 4-pentenal (entry 3, substrate table), formic acid was used as reducing reagent for ease of isolation.

#### Substrates that were not hydrogenated



#### Internal Competition Experiment with Benzaldehyde and Acetophenone

In a J. Young NMR tube was prepared a solution of benzaldehyde (0.33 M), acetophenone (0.33 M), molybdenum complex **1a** (0.033 M), and 2-propanol (2.0 M) in benzene- $d_6$  (0.4 mL), and this sample solution was monitored by  $^1\text{H}$  NMR spectroscopy over time at 65 °C. After 1 hour, 44.8 % of benzaldehyde was converted to benzyl alcohol, and only 0.95 % of acetophenone was converted to 1-phenylethanol, which corresponds to 47:1 selectivity difference favoring benzaldehyde.

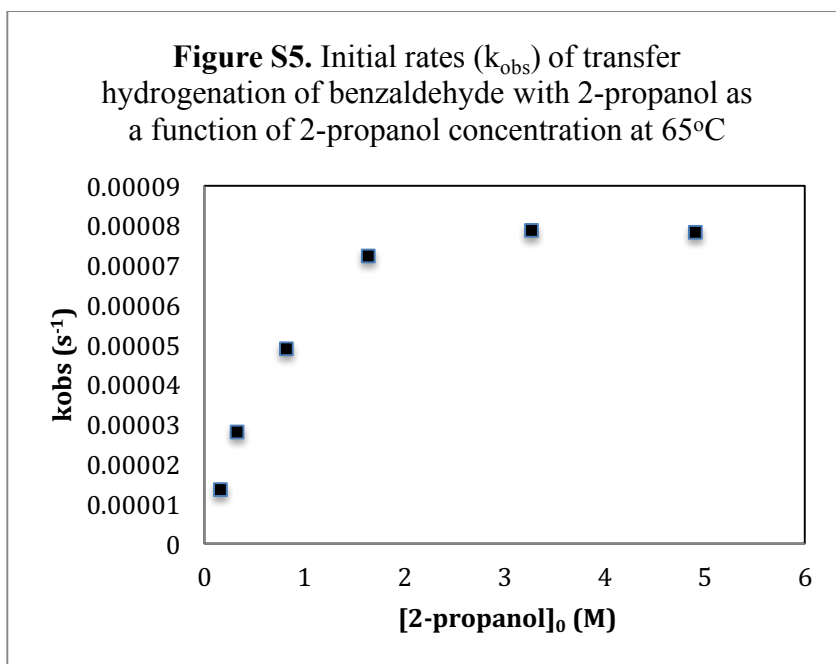
#### Effect of 2-propanol Concentration on the Rate of Transfer Hydrogenation of Benzaldehyde by **1a** with 2-propanol at 65 °C

A solution of benzaldehyde (0.33 M), molybdenum complex **1a** (0.033 M), and 2-propanol in benzene- $d_6$  (0.4 mL) was charged into a sealed NMR tube, and this sample solution was monitored by  $^1\text{H}$  NMR spectroscopy over time at 65 °C. The first  $^1\text{H}$  NMR spectrum was recorded within 5 minutes of mixing, and the decrease of benzaldehyde ( $\text{PhCHO}$ ,  $\delta$  9.47) and the increase in the benzyl alcohol ( $\text{PhCH}_2\text{OH}$ ,  $\delta$  4.43) as well as the acetone ( $\delta$  1.55) peak integrations was analyzed to quantify the initial rates of transfer hydrogenation according to  $-\text{d}[\text{PhCHO}]/\text{dt} = \text{d}[\text{PhCH}_2\text{OH}]/\text{dt} = \text{d}[\text{acetone}]/\text{dt} = k_{\text{obs}}[\text{PhCHO}]$ . The results are summarized in the Table S1 and Figure S5.

**Table S1.** Effect of added 2-propanol concentration on the rate of transfer hydrogenation of benzaldehyde catalyzed by **1** (0.33 M) in benzene-d<sub>6</sub> at 65 °C.

[ <b>1a</b> ] <sub>0</sub> (M)	[Benzaldehyde] <sub>0</sub> (M)	[2-propanol] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
0.0330	0.33	0.16	1.4(0.1)×10 <sup>-5</sup>
0.0330	0.33	0.33	2.3(0.1)×10 <sup>-5</sup>
0.0330	0.33	0.82	4.9(0.1)×10 <sup>-5</sup>
0.0330	0.33	1.63	7.2(0.2)×10 <sup>-4</sup>
0.0330	0.33	3.27	7.9(0.1)×10 <sup>-4</sup>
0.0330	0.33	4.90	7.8(0.2)×10 <sup>-4</sup>

<sup>a</sup> Data points reported are average of two sets of experiments.



#### NMR Measurement of Rate Constant for Reduction of Benzaldehyde by **1a** at 65 °C

In a J. Young NMR tube was prepared a solution of benzaldehyde (0.33 M), molybdenum complex **1a** and 2-propanol (2.0 M) in benzene-d<sub>6</sub> (0.4 mL), and this sample solution was monitored by <sup>1</sup>H NMR spectroscopy over time at 65 °C. The first <sup>1</sup>H NMR spectrum was recorded within 5 minutes of mixing, and the reaction was monitored for three to five half-lives. The decrease of benzaldehyde (PhCOH, δ 9.47) and the increase in the benzyl alcohol (PhCH<sub>2</sub>OH, δ 4.43) as well as the acetone (δ 1.55) peak integrations were used to quantify the conversion of the transfer hydrogenation according to -d[PhCHO]/dt =



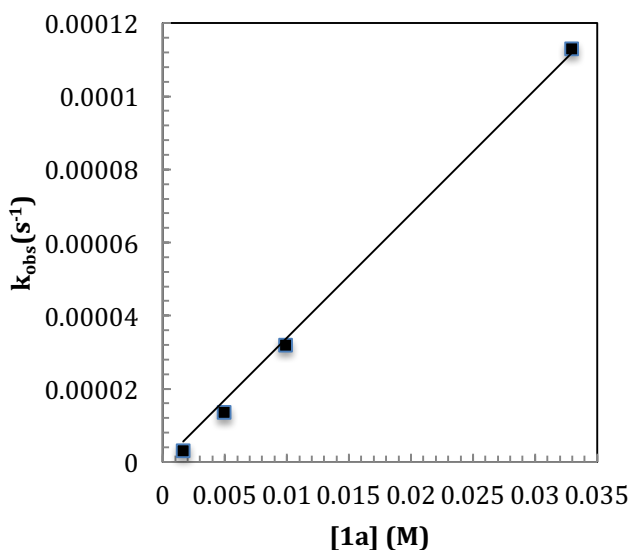
$d[\text{PhCH}_2\text{OH}]/dt = d[\text{acetone}]/dt = k_{\text{obs}}[\text{PhCHO}]$ . The results are summarized in the Table S2 and Figure S6.

**Table S2.** Effect of Mo concentration on the rate of transfer hydrogenation of benzaldehyde with 2-propanol in benzene-d<sub>6</sub> at 65 °C.

[1a] <sub>0</sub> (M)	[Benzaldehyde] <sub>0</sub> (M)	[2-propanol] <sub>0</sub> (M)	$k_{\text{obs}}$ (s <sup>-1</sup> ) <sup>a</sup>
0.0016	0.33	2.0	$3.0(0.1) \times 10^{-6}$
0.0049	0.33	2.0	$1.4(0.1) \times 10^{-5}$
0.0099	0.33	2.0	$3.2(0) \times 10^{-5}$
0.0330	0.33	2.0	$1.1(0.1) \times 10^{-4}$

<sup>a</sup> Data points reported are average of two sets of experiments.

**Figure S6.** Plot of observed rate versus concentration of [1a] for the transfer hydrogenation of benzaldehyde with 2-propanol in d-benzene at 65 °C



Slope = 0.0034,  $R^2=0.99733$ , Intercept was set to be zero.

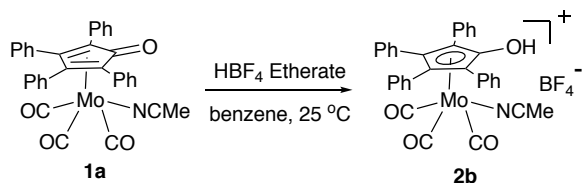
$$k_{\text{obs}} = 3.4(0.3) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

The rate of catalytic transfer hydrogenation conforms to a rate law:

$$\text{Rate} = k[1a][\text{benzaldehyde}][2\text{-propanol}]$$

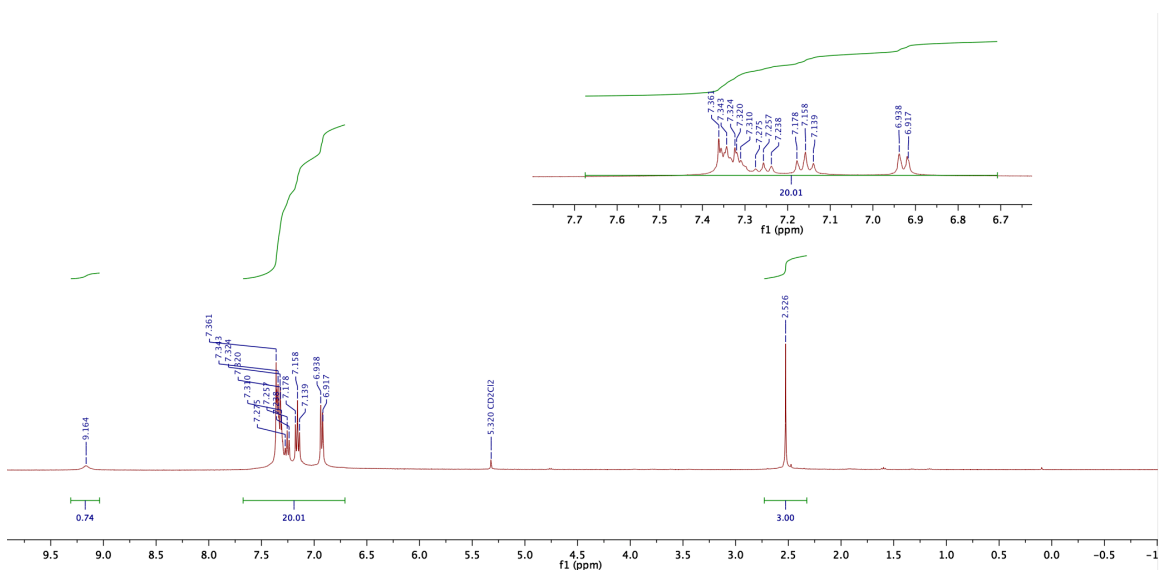
for  $[2\text{-propanol}]_0 < 1.6(0.2) \text{ M}$  and then saturates in  $[2\text{-propanol}]$ . This indicates that formation of molybdenum hydride **1b** is rate-limiting at modest  $[2\text{-propanol}]$ .

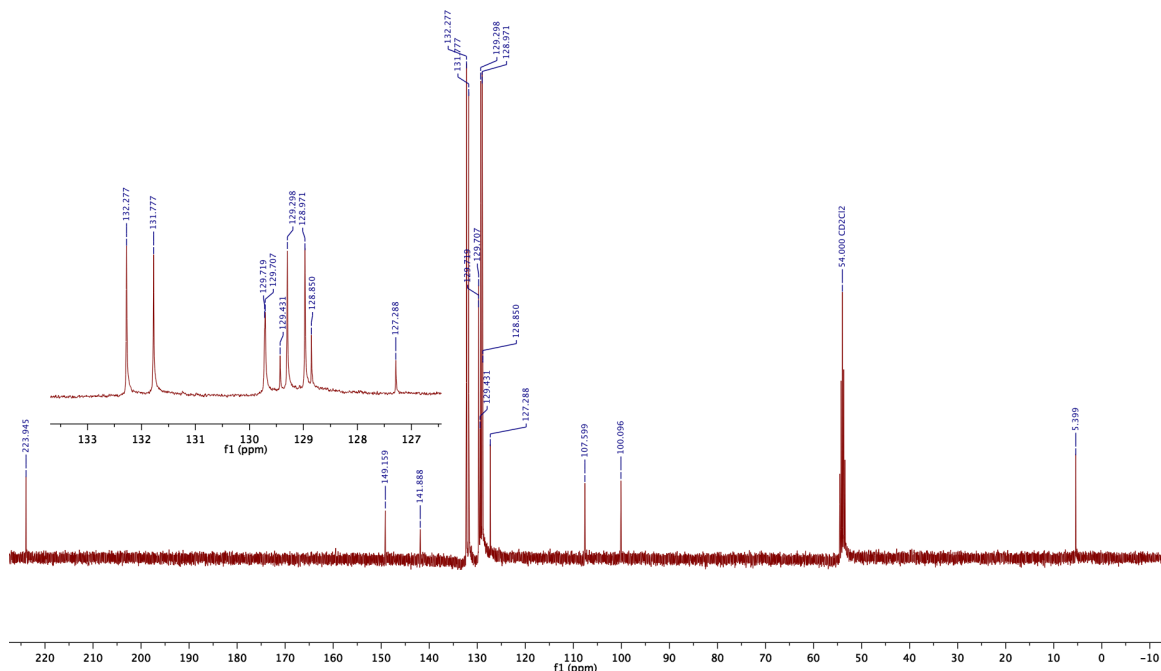
### Synthesis and Characterization of Molybdenum Complex **2b**



To a solution of molybdenum complex **1a** (30.0 mg, 1.0 equivalent) in benzene (5 mL) in a glass vial under nitrogen was added tetrafluoroboric acid (50  $\mu\text{L}$ , excess) in one portion at room temperature with stirring. After 5 minutes, the product was collected as pale yellow precipitation by vacuum filtration and washed with benzene (5.0 mL) and hexanes (5.0 mL) to give yellow powder (32 mg, 93 % yield).

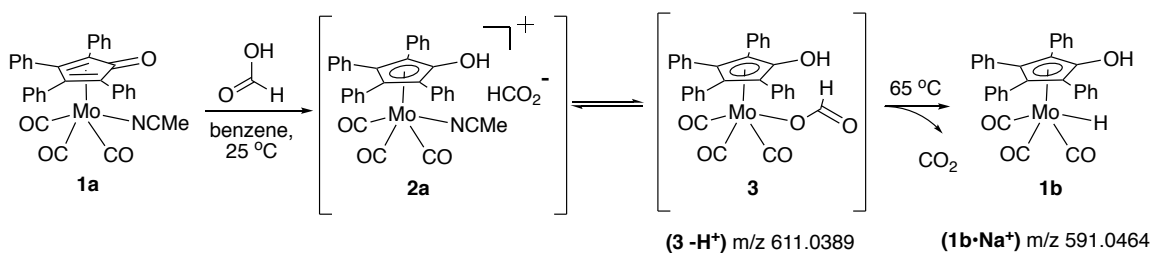
IR (KBr Disk,  $\text{cm}^{-1}$ ) 3053, 2936, 2049 (CO), 1968(CO). HRMS (ESI) calcd (found) for  $[(\text{C}_5\text{Ph}_4\text{OH})\text{Mo}(\text{CO})_3(\text{NCCH}_3)]^+ \text{2b} [\text{C}_{34}\text{H}_{24}\text{MoNO}_4]^+ m/z 608.0762 (m/z = 608.0741)$ .





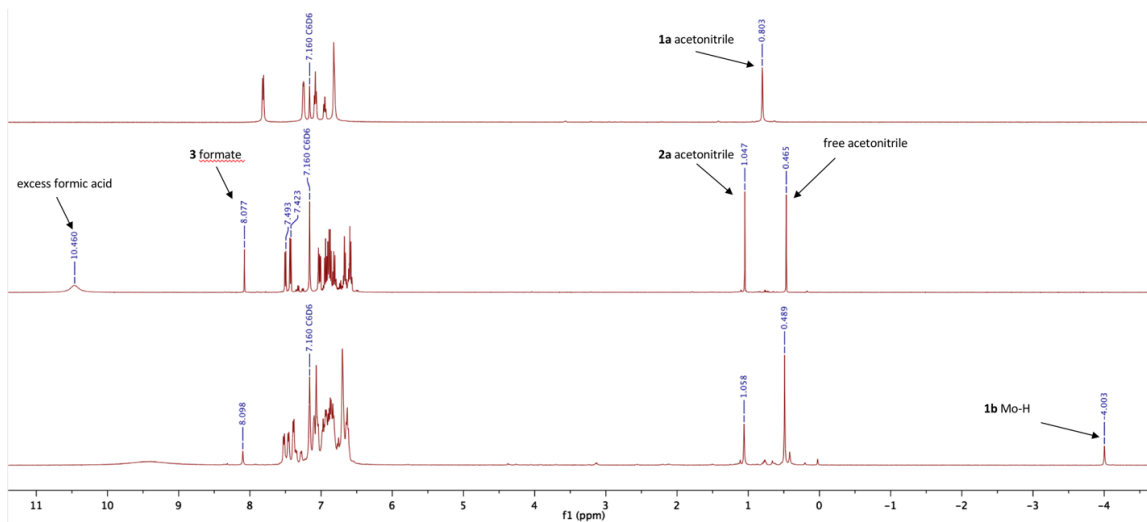
**Figure S8.**  $^{13}\text{C}$  NMR of **2b** ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  223.95 (CO), 149.16 (Ph), 141.89 (Ph), 132.24 (Ph), 131.72 (Ph), 129.70 (Ph), 129.36 (Ph), 129.29 (Ph), 128.95 (Ph), 127.22 (NCMe), 107.54 (Cp ring), 100.00 (Cp ring), 5.40 (acetonitrile  $\text{CH}_3$ ).

### In situ characterization of molybdenum formate intermediate **3**



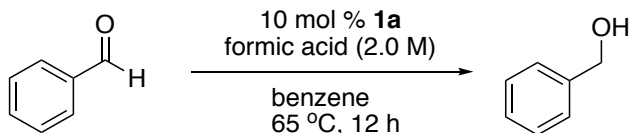
A solution of molybdenum complex **1a** (0.033 M, 1 equivalent) formic acid (0.33 M, 10 equivalent) in benzene- $d_6$  (0.4 mL) were charged to a sealed NMR tube, and the first  $^1\text{H}$  NMR spectrum was recorded within 5 minutes of mixing at 25 °C. The acetonitrile ( $\delta$  0.80) originated from molybdenum complex **1a** disappeared, and two new peaks ( $\delta$  1.05,  $\delta$  0.47) appeared in 1:1 ratio. Those two peaks are proposed to correspond to acetonitrile in the reaction intermediate **2a** (0.017 M) and dissociated acetonitrile in dynamic exchange with the molybdenum formate complex **3** ( $\delta$  8.08, 0.016 M). Composition of this reaction mixture does not change at 25 °C over 12 hours. When this reaction mixture was heated to

65 °C for 30 minutes, molybdenum hydride species **1b** formed in situ ( $\delta$  -4.00, 0.013M) as the decarboxylation product from **3** (0.012 M) in expense of the reaction intermediate **2a** (0.008 M). Extended reaction at 65 °C resulted in the decomposition to unknown product. When acetonitrile- $d_3$  was adopted as solvent, no reaction was observed at 25 °C. HRMS (ESI) of molybdenum formate complex **3** was collected in dichloromethane (1.0 mM). calcd (found) for  $[C_{33}H_{21}MoO_6]^-$  m/z 611.0395 (m/z 611.0386).



**Figure S9.**  $^1H$  NMR (benzene- $d_6$ ) of reaction of **1a** with formic acid. Top: complex **1a**, prior to addition of formic acid. Middle: Complex **1a** with excess formic acid (5 min). Bottom: Reaction mixture after heating to 65°C for 30 min.

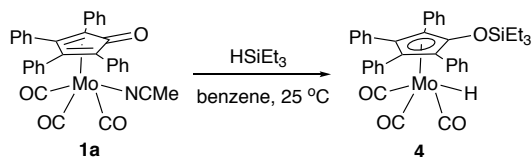
In the presence of dihydrogen acceptor such as benzaldehyde, molybdenum complex **1a** with formic acid added as reducing reagent can perform transfer hydrogenation.



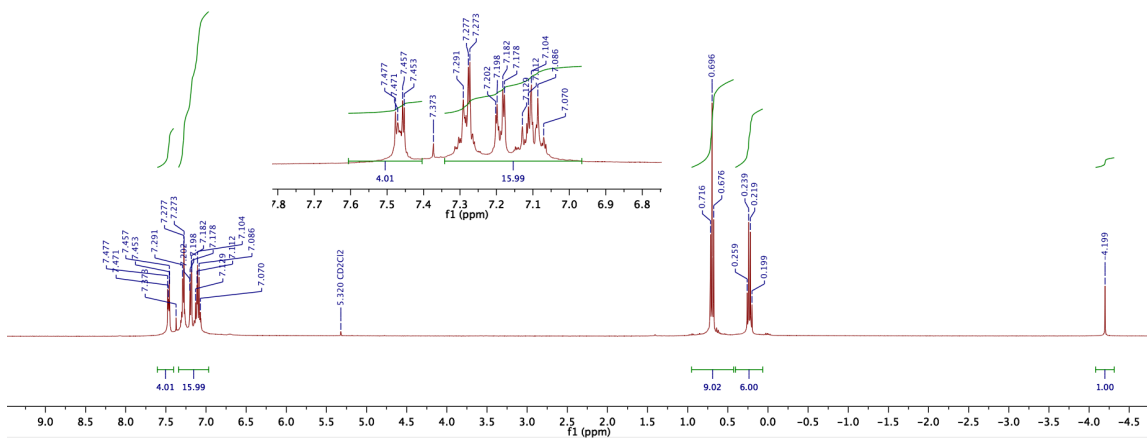
To a solution of benzaldehyde (1.0 mmol) and molybdenum complex **1a** (0.1 mmol) in benzene (3.0 mL) was added formic acid (0.46 mL) to glass vial (20 mL) with airtight cap under nitrogen atmosphere. This reaction mixture was heated to 65 °C and stirred with cap sealed. When the reaction was complete, solvent was evaporated and the residue was dissolved in  $CDCl_3$  and its  $^1H$ -NMR spectrum recorded. The residue benzyl alcohol was

isolated by column chromatography (90% yield) and their  $^1\text{H}$ -NMR spectra matched those reported in the literature<sup>4d</sup>.

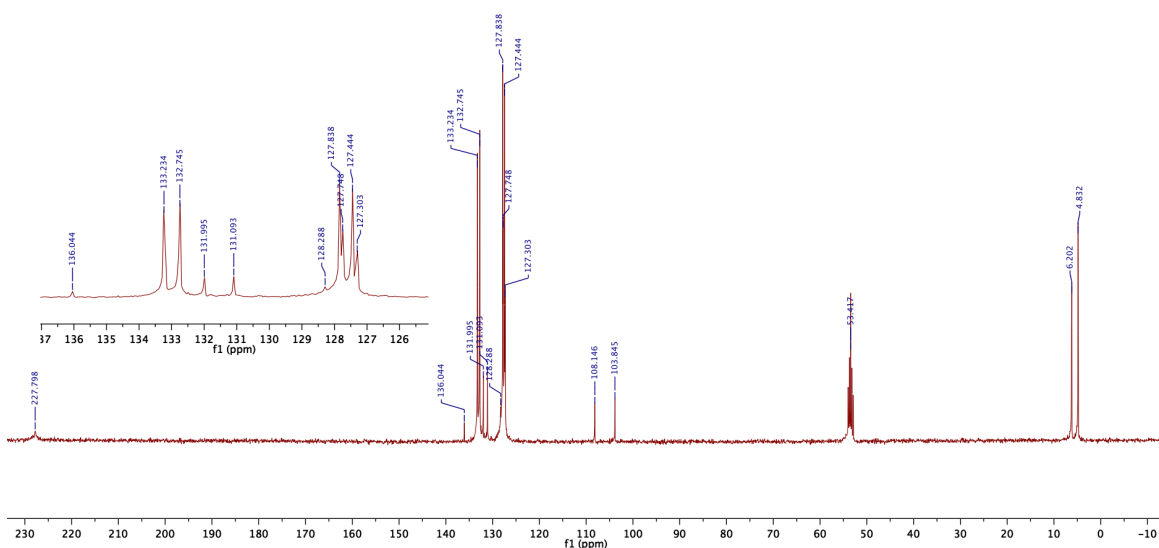
### Synthesis and Characterization of Molybdenum Complex 4



To a solution of molybdenum complex **1a** (135.0 mg, 1.0 equivalent) in benzene (5 mL) in a glass vial under nitrogen was added triethylsilane (28.5 mg, 1.1 equivalent) in one portion at room temperature. After stirring for 30 minutes, solvent and excess triethylsilane were removed under reduced pressure, and the residue was washed with hexanes (5 mL) for three times. The dried product was collected as pale brown powder (128 mg, 84 % yield). IR (KBr Disk,  $\text{cm}^{-1}$ ) 3051, 2095, 2873, 2009 (CO), 1924(CO). HRMS (ESI) calcd (found) for  $[\text{C}_{38}\text{H}_{35}\text{MoO}_4\text{Si}]^-$  681.1362 (681.1356).



**Figure S10.**  $^1\text{H}$  NMR of **4** ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  7.48-7.46 (m, 4H), 7.37 (s, residual benzene) 7.29-7.07 (m, 16H), 0.70 (t,  $J = 8.0$  Hz, 9H), 0.23 (q,  $J = 8.0$  Hz, 6H), -4.20 (s, 1H).



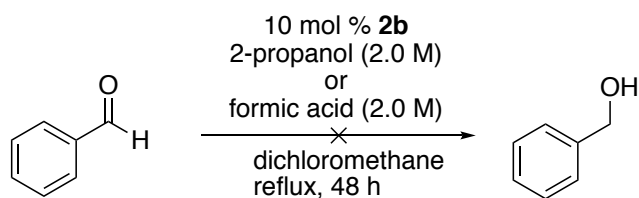
**Figure S11.**  $^{13}\text{C}$  NMR of **4** ( $\text{CD}_2\text{Cl}_2$ , 400 MHz)  $\delta$  227.80 (CO), 136.04 (COSi ring), 133.723 (Ph), 132.75 (Ph), 132.00 (Ph), 131.09 (Ph), 128.29 (Ph), 127.84 (Ph), 127.75 (Ph), 127.44 (Ph), 127.30 (Ph), 108.15 (Cp ring), 103.85 (Cp ring), 6.20 ( $\text{CH}_2$ ), 4.83 ( $\text{CH}_3$ ).

### Elemental Analysis of compound **2b** and **4**

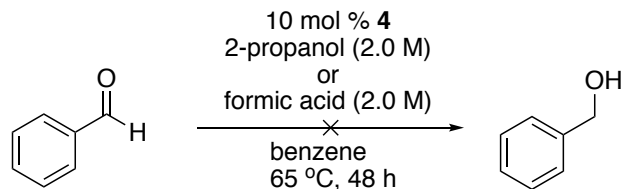
The elemental analysis of compounds **2b** and **4** reported in Table S3 reveal some impurities that could not be removed upon isolation. The deviation in compound **2b** can be attributed to the residual tetrafluoroboric acid while the error for compound **4** is likely caused by the residual solvent (benzene).

**Table S3.** Combustion analysis of compound **2b** and **4**

	Proposed formula	Elemental Composition		C [%]	H [%]	N [%]
<b>2b</b>	$\{[\text{Ph}_4\text{C}_5\text{OH}]\text{Mo}(\text{CO})_3(\text{MeCN})\}^+\text{BF}_4^-$	$\text{C}_{34}\text{H}_{24}\text{MoNO}_4\text{BF}_4$	Theoretical	58.90	3.49	2.02
			Measured	54.64	3.58	1.87
<b>4</b>	$[\text{Ph}_4\text{C}_5\text{OSiEt}_3]\text{MoH}(\text{CO})_3$	$\text{C}_{38}\text{H}_{35}\text{MoO}_4\text{Si}$	Theoretical	67.05	5.33	0
			Measured	68.23	5.65	0

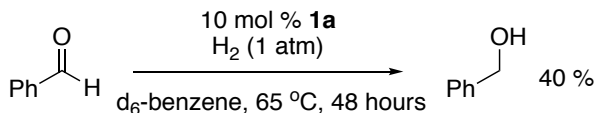


In a J. Young NMR tube was prepared a solution of benzaldehyde (0.33 M), molybdenum complex **2b** (0.033 M), and 2-propanol or formic acid in  $\text{CD}_2\text{Cl}_2$  (0.4 mL), and this sample solution was monitored by  $^1\text{H}$  NMR spectroscopy over time at 65 °C. The first  $^1\text{H}$  NMR spectrum was recorded within 5 minutes of mixing, and the reaction was monitored over two days. No change in the composition was observed in either case where 2-propanol or formic acid was added as reducing reagent.



In a J. Young NMR tube was prepared a solution of benzaldehyde (0.33 M), molybdenum complex **4** (0.033 M), and 2-propanol or formic acid in benzene- $\text{d}_6$  (0.4 mL), and this sample solution was monitored by  $^1\text{H}$  NMR spectroscopy over time at 65 °C. The first  $^1\text{H}$  NMR spectrum was recorded within 5 minutes of mixing, and the reaction was monitored over two days. No change in the composition was observed in case of 2-propanol added as reducing reagent. Molybdenum complex **4** decomposed to unknown product in case of formic acid added as reducing reagent, and no reduction was observed for benzaldehyde.

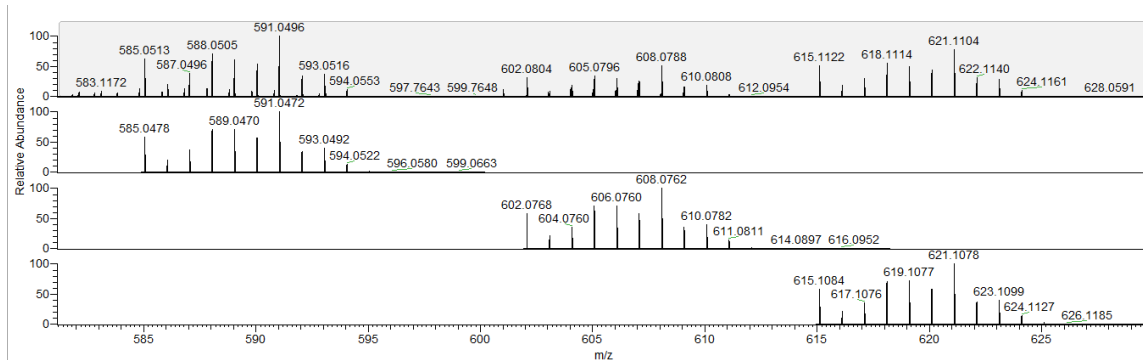
### Hydrogenation of Benzaldehyde Catalyzed by **1a**



In a J. Young NMR tube was prepared a solution of benzaldehyde (0.33 M), molybdenum complex **1** (0.033 M) in  $\text{d}_6$ -benzene (0.4 mL). This NMR tube was flushed several times with hydrogen gas and sealed tight. The sample solution was monitored by  $^1\text{H}$  NMR spectroscopy over time at ambient temperature and then 65 °C. The first  $^1\text{H}$  NMR spectrum was recorded within 5 minutes of mixing, and the reaction was monitored at ambient

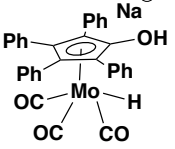
temperature over 12 hours, but only trace formation of benzyl alcohol was observed. Then the reaction mixture was heated to 65 °C, and benzaldehyde was gradually hydrogenated to benzyl alcohol up to 40% conversion over 48 hours.

**Figure S12. HRMS (ESI) Data of 1a/1b**

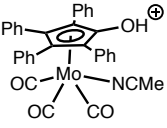
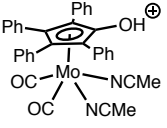


(A) Representative experimental data at 100,000 resolution, 1.0 kV spray, 5 uL/min injection rate, 275°C capillary temperature, in positive ion mode. The reaction mixture in benzene-d<sub>6</sub> was diluted in acetonitrile. (B) Simulated spectrum for C<sub>32</sub>H<sub>22</sub>MoNaO<sub>4</sub><sup>+</sup> (**1b**) with Gaussian profile at 100,000 resolution. (C) Simulated spectrum for C<sub>34</sub>H<sub>24</sub>MoNO<sub>4</sub><sup>+</sup> (**1a**-NCMe) with Gaussian profile at 100,000 resolution. (D) Simulated spectrum for C<sub>33</sub>H<sub>27</sub>MoN<sub>2</sub>O<sub>3</sub><sup>+</sup> (**1a**-(NCMe)<sub>2</sub> minus CO) with Gaussian profile at 100,000 resolution.

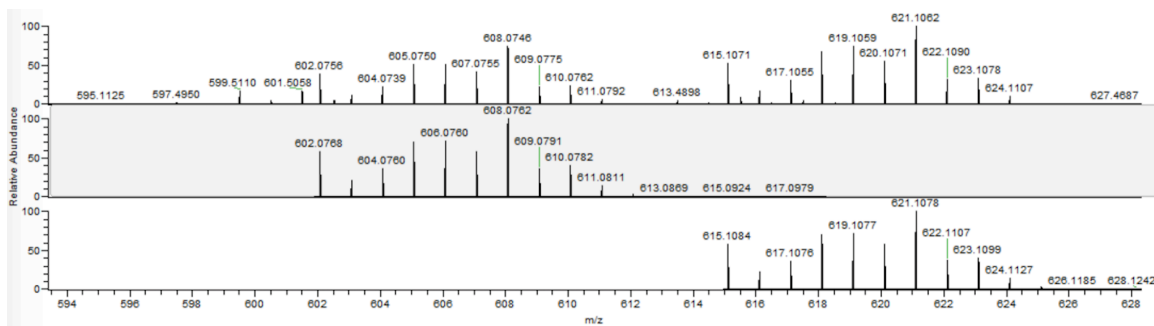
**Table S4 ESI-MS Assignments for Molybdenum Complex 1a/1b.**

Assignment	Measured m/z	Meas. Rel. Intensity	Theoretical m/z	Theo. Rel. Intensity	Δ ppm	Peak Area
$\text{C}_{32}\text{H}_{22}^-\text{MoNaO}_4^+$ 	585.0525	64.48	585.0478	58.76	7.92	218.44
	586.0558	21.66	586.0512	20.49	7.96	71.26
	587.0511	38.61	587.0461	36.66	8.43	136.52
	588.0515	72.84	588.0471	70.91	7.42	250.90
	589.0491	61.70	589.0461	71.00	5.19	195.93
	590.0520	53.93	590.0478	56.89	6.99	182.90
	591.0492	100.00	591.0466	100.00	4.46	339.03
	592.0545	33.73	592.0499	34.35	7.80	113.14



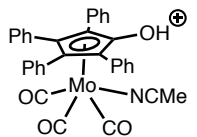
	593.0514	37.13	593.0486	39.77	4.69	122.09
	594.0563	11.65	594.0520	13.61	7.20	37.49
	595.0582	0.18	595.0550	2.49	5.43	0.60
$C_{34}H_{24}^-$ $MoNO_4^+$ 	602.0822	59.57	602.0768	58.26	8.91	97.43
	603.0849	15.89	603.0801	21.59	8.03	24.10
	604.0790	37.45	604.0751	36.42	6.47	60.03
	605.0811	73.59	605.0761	71.10	8.31	120.83
	606.0773	58.47	606.0752	71.47	3.58	89.68
	607.0816	52.45	607.0768	58.12	8.00	85.10
	608.0799	100.00	608.0756	100.00	7.08	161.10
	609.0835	29.50	609.0789	36.36	7.67	47.97
	610.0811	39.47	610.0777	39.84	5.63	66.69
	611.0840	7.52	611.0808	14.39	5.10	12.59
$C_{35}H_{27}^-$ $MoN_2O_3^+$ 	615.1116	63.49	615.1084	57.93	5.13	174.64
	616.1153	21.99	616.1117	22.10	5.86	58.35
	617.1100	36.55	617.1068	36.27	5.15	100.72
	618.1128	74.89	618.1078	71.18	8.14	209.48
	619.1093	63.37	619.1068	71.88	4.10	168.61
	620.1112	56.13	620.1084	58.73	4.56	154.34
	621.1097	100.00	621.1073	100.00	3.91	277.47
	622.1135	37.38	622.1105	37.25	4.78	101.51
	623.1139	38.23	623.1094	39.76	7.27	102.37
	624.1167	13.85	624.1126	14.73	6.55	35.80
	625.1190	0.26	625.1157	2.87	5.15	0.71

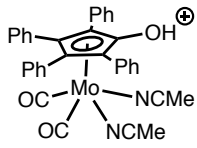
**Figure S13. HRMS (ESI) Data of 2b**



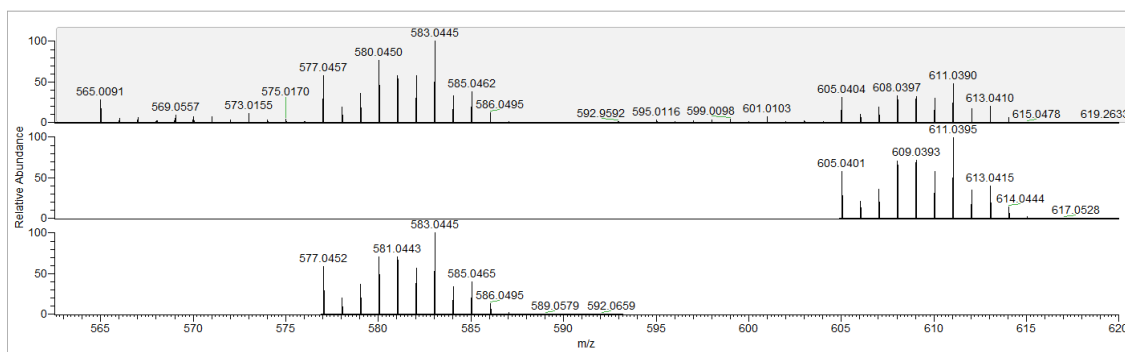
(A) Representative experimental data at 100,000 resolution, 4.0 kV spray, 10uL/min injection rate, 175°C capillary temperature, in positive ion mode. Sample was dissolved in dichloromethane which was diluted in acetonitrile. (B) Simulated spectrum for  $C_{34}H_{24}MoNO_4^+$  with Gaussian profile at 100,000 resolution. (C) Simulated spectrum for  $C_{35}H_{27}MoN_2O_3^+$  with Gaussian profile at 100,000 resolution.

**Table S5. ESI-MS Assignments for Molybdenum Complex 2b.**

Assignment	Measured m/z	Meas. Rel. Intensity	Theoretical m/z	Theo. Rel. Intensity	$\Delta$ ppm	Peak Area
$C_{34}H_{24}MoNO_4^+$ 	602.0749	52.10	602.0768	58.26	-3.07	27223.04
	603.0791	16.27	603.0801	21.59	-1.62	8185.53
	604.0732	30.72	604.0751	36.42	-3.18	16290.97
	605.0753	69.10	605.0761	71.10	-1.33	35371.98
	606.0743	69.87	606.0752	71.47	-1.41	35213.09
	607.0758	54.91	607.0768	58.12	-1.62	28027.92
	608.0741	100.00	608.0756	100.00	-2.54	52267.60
	609.0777	30.86	609.0789	36.36	-1.94	15705.72
	610.0767	32.49	610.0777	39.84	-1.64	16591.24
	611.0795	8.96	611.0808	14.39	-2.17	4583.32
	612.0820	1.10	612.0840	2.78	-3.27	603.25
	615.1071	53.59	615.1084	57.93	-2.11	28931.29

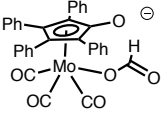
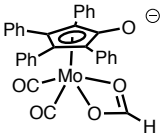
$C_{35}H_{27}MoN_2O_3^+$ 	616.1109	16.45	616.1117	22.10	-1.37	9103.88
	617.1055	31.74	617.1068	36.27	-2.07	17413.05
	618.1069	68.67	618.1078	71.18	-1.42	37848.88
	619.1063	70.77	619.1068	71.88	-0.76	39223.81
	620.1068	56.00	620.1084	58.73	-2.64	30403.27
	621.1067	100.00	621.1073	100.00	-0.92	56373.88
	622.1091	32.14	622.1105	37.25	-2.40	17512.57
	623.1080	33.54	623.1094	39.76	-2.26	18145.62
	624.1107	9.67	624.1126	14.73	-2.98	5254.95
	625.1130	1.17	625.1157	2.87	-4.36	704.44

**Figure S14. HRMS (ESI) Data of 3**

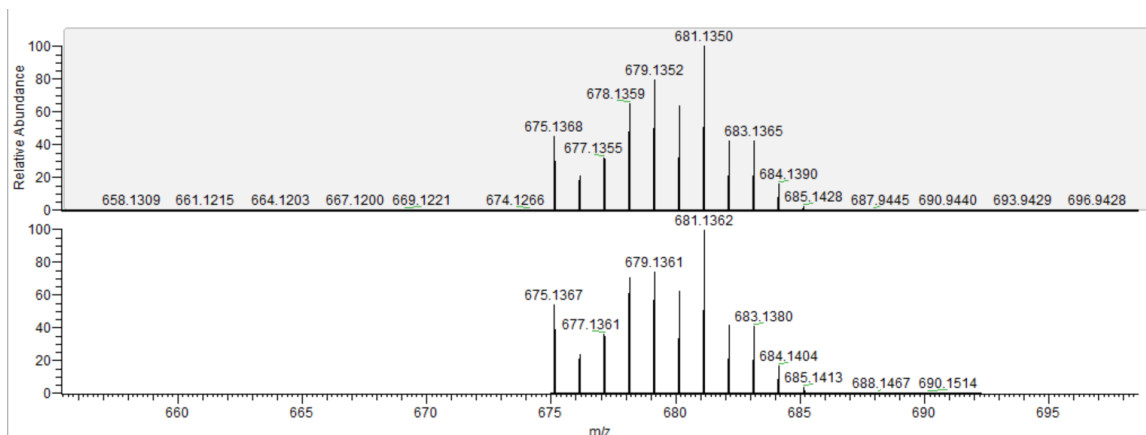


(A) Representative experimental data at 100,000 resolution, 4.0 kV spray, 10uL/min injection rate, 175°C capillary temperature, in negative ion mode. Sample was dissolved in dichloromethane which was diluted in acetonitrile. (B) Simulated spectrum for  $C_{33}H_{21}MoO_6^-$  with Gaussian profile at 100,000 resolution. (C) Simulated spectrum for  $C_{32}H_{21}MoO_5^-$  with Gaussian profile at 100,000 resolution.

**Table S6. ESI-MS Assignments for Molybdenum Complex 3.**

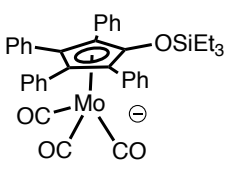
Assignment	Measured m/z	Meas. Rel. Intensity	Theoretical m/z	Theo. Rel. Intensity	$\Delta$ ppm	Peak Area
$\text{C}_{33}\text{H}_{21}\text{MoO}_6^-$ 	605.0400	64.78	605.0401	58.36	-0.09	106.06
	606.0433	21.77	606.0435	21.03	-0.34	35.86
	607.0391	41.02	607.0383	36.44	1.25	67.31
	608.0402	70.10	608.0394	70.97	1.35	116.72
	609.0382	67.37	609.0383	71.34	-0.27	110.30
	610.0400	63.94	610.0401	57.65	-0.21	108.33
	611.0386	100.00	611.0389	100.00	-0.63	163.65
	612.0425	36.73	612.0422	35.52	0.46	59.58
	613.0417	41.58	613.0409	40.03	1.20	71.68
	614.0448	13.69	614.0442	14.10	0.87	23.09
	615.0474	2.03	615.0473	2.76	0.19	3.22
$\text{C}_{32}\text{H}_{21}\text{MoO}_5^-$ 	577.0463	57.49	577.0452	58.82	1.90	187.21
	578.0489	18.94	578.0485	20.53	0.65	59.97
	579.0436	36.02	579.0435	36.70	0.24	115.94
	580.0448	76.45	580.0445	70.88	0.63	243.68
	581.0434	57.72	581.0434	70.84	-0.09	182.42
	582.0459	57.87	582.0452	56.88	1.20	191.58
	583.0443	100.00	583.0439	100.00	0.57	318.09
	584.0479	33.65	584.0472	34.47	1.23	108.46
	585.0461	38.04	585.0460	39.91	0.16	122.00
	586.0496	12.46	586.0492	13.67	0.62	39.77
	587.0529	1.92	587.0524	2.55	0.98	5.84

**Figure S15. HRMS (ESI) Data of 4**



(A) Representative experimental data at 100,000 resolution, 4.0 kV spray, 10uL/min injection rate, 175°C capillary temperature, in negative ion mode, acetonitrile. (B) Simulated spectrum for  $C_{38}H_{35}MoO_4Si^-$  with Gaussian profile at 100,000 resolution.

**Table S7. ESI-MS Assignments for Molybdenum Complex 4**

Assignment	Measured m/z	Meas. Rel. Intensity	Theoretical m/z	Theo. Rel. Intensity	$\Delta$ ppm	Peak Area
$C_{38}H_{35}MoO_4Si^-$	675.1359	45.99	675.1378	54.45	-2.77	151313.59
	676.1392	21.45	676.1410	23.79	-2.60	68744.34
	677.1347	33.16	677.1361	35.97	-2.07	108632.81
	678.1358	65.80	678.1372	70.56	-2.03	210488.32
	679.1357	79.70	679.1363	73.86	-0.82	261586.14
	680.1362	64.38	680.1377	62.09	-2.24	207205.05
	681.1356	100.00	681.1368	100.00	-1.76	331083.09
	682.1371	43.12	682.1398	41.86	-3.94	139303.10
	683.1358	43.26	683.1388	41.15	-4.45	143540.04
	684.1384	16.49	684.1417	16.72	-4.92	54167.40
	685.1431	2.33	685.1446	3.76	-2.07	7024.93

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