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Selective C-alkylation between Alcohols Catalyzed by N-Heterocyclic Carbene Molybdenum

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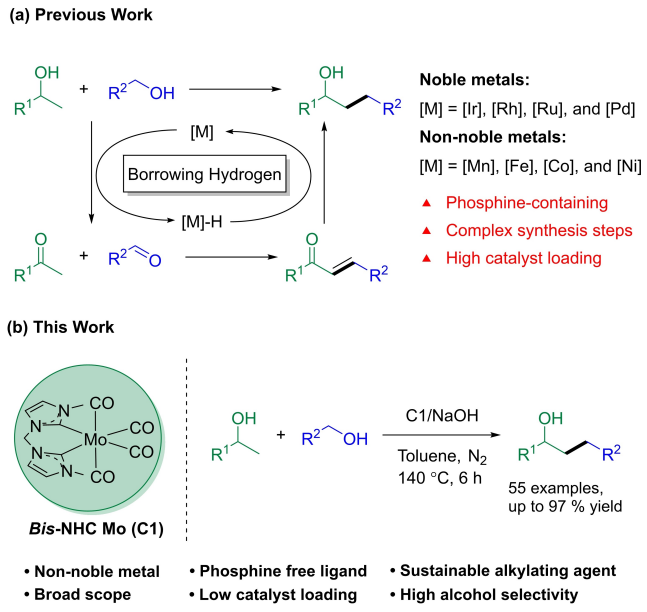
Abstract: The first implementation of a molybdenum complex with an easily accessible *bis*-N-heterocyclic carbene ligand to catalyze β-alkylation of secondary alcohols via borrowing-hydrogen (BH) strategy using alcohols as alkylating agents is reported. Remarkably high activity, excellent selectivity, and broad substrate scope compatibility with advantages of catalyst usage low to 0.5 mol%, a catalytic amount of NaOH as the base, and H_2O as the by-product are demonstrated in this green and step-economical protocol. Mechanistic studies indicate a plausible outer-sphere mechanism in which the alcohol dehydrogenation is the rate-determining step.

The depletion of petroleum resources makes it imperative to find possible sustainable routes to produce renewable fuels and chemicals instead of the traditional petrochemical industry.[1] As derivatives of abundant and indigestible biomass, alcohols are considered as potential ideal starting materials for chemical reactions. However, due to their relatively poor reactivity, pre-activation of alcohol substrates to turn into a better leaving group like sulfonate or halide for subsequent conversion is often required in traditional methods.[2] Therefore, a more sustainable and more efficient strategy for alcohol transformation in line with the concept of sustainable and green chemistry is sought after in both academia and industry.[3] With merits in avoiding external reagents usage and generation of waste, recently, modern processes based on borrowing hydrogen strategy have attracted much attention.[3c,4] Since the pioneering work of Grigg[5] and Watanabe,[6] numerous endeavors have been made towards homogeneous catalyzed alkylation of amine, amide, alcohols, ketones, and related compounds with alcohols as alkylating agents through a borrowing-hydrogen (BH) strategy.[7]

As one of the most important C–C bond formation reactions, β-alkylation of alcohols plays a vital role in the structural complexity and diversity of alcohols.[8] Comparing to the traditional protocols including oxidation of secondary alcohols to the corresponding ketones, alkylation with alkylating agents like alkyl halides, and reduction of the β-alkylated ketones, the direct the *C*-alkylation between alcohols utilizing a BH strategy (Scheme 1a) has advantages of its ease of operation, availability of raw materials, and H_2O as the by-product, so it has attracted great intention recently.[3c,9]

Until now, noble-metal catalysis (e.g., Ir,[10] Rh,[11] Ru,[12] and Pd[13]) are generally required in these approaches (Scheme 1a). With the desire for sustainability and environmental benignness as well as for different reactivity, the replacements by non-noble metal catalysis have been a topic of current interest. Despite the recent efforts using earth-abundant metal catalysts like Mn,[14] Fe,[15] Co,[16] and Ni[17], sophisticated or toxic phosphine-containing ligands with multiple synthesis steps and higher catalyst loadings are still needed (Scheme 1a). In addition, how to achieve high selectivity avoiding the formation of the undesired by-product ketones presents another crucial issue. Therefore, the development of new non-noble metal catalysts with easily accessible, practical, and phosphine-free ligands for the efficient and highly selective *C*-alkylation between alcohols would be highly desirable.

With the issue of "Cheap Metals for Noble Tasks",[18] molybdenum, which is commonly found in active sites of formate dehydrogenase enzymes, is considered as an appropriate alternative transition metal to blaze a cheaper, greener, and atom-economic trail for BH reactions. On one hand,



Scheme 1. β-alkylation of secondary alcohols via borrowing hydrogen strategy.

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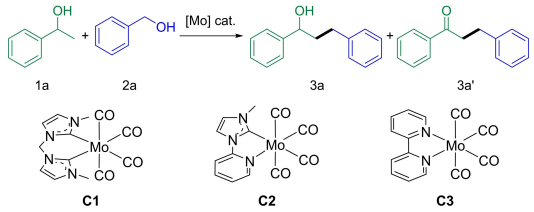
Bullock,[19] Beller,[20] Berke,[21] Topf[22] and Waymouth[23] reported molybdenum complexes in catalyzed hydrogenation reactions and transfer hydrogenation reactions. On the other hand, recently *N*-alkylation of amine by alcohol catalyzed by Cr(III) and W(0) complexes have been disclosed by Kempe's group[24] and our group[25], respectively. These results indicate the potential of VIB group metal catalysts, especially molybdenum, in BH/HA reactions.

Based on our experience in BH reactions with Mn(I) complexes, d^6 transition metal complexes with phosphine-free and strong electron-donating *N*-heterocyclic carbene (NHC) ligands showed capacity in achieving potent BH transformations.[26] Although the d^6 Mo(0) complexes can be regarded as a potential candidate to develop and enrich the application of d^6 transition metal catalysts,[27] the desired *C*-alkylation between alcohols via BH by Mo(0) catalysis has not been disclosed yet to the best of our knowledge. Herein, we demonstrate the first implementation of the NHC-Mo(0) complex as a remarkably active and selective catalyst for the β-alkylation of secondary alcohols using alcohols as alkylating agents via BH strategy (Scheme 1b).

The β-alkylation of 1-phenylethanol (**1a**) with benzyl alcohol (**2a**) was chosen as a benchmark reaction (Table 1). Initially, three Mo complexes with different bidentate ligands, including *bis*-NHC (**C1**), pyridyl-NHC (**C2**), and 2,2′-bipyridine (**C3**)[28] were synthesized from the cheap precursor $Mo(CO)_6$. and screened at 150 °C using 1.0 eq. KO^{t}Bu as a base. It is shown that the *bis*-NHC Mo(0) complex **C1** significantly outperforms the other two Mo(0) complexes. This result manifests the crucial role of the strong σ-donating *bis*-NHC ligand (Table 1, entries 1–3), which leads to a higher Mo–H orbital energy (Scheme S6) to drive the hydride donation. Having established the most active precatalyst, further optimization of the reaction condition using **C1** has been done with different bases and temperatures (Table 1; for more details see Table S1 in SI). NaOH, which is cheap and readily available, is selected as the optimized base for its satisfactory result (Table 1, entry 6). The reaction temperature can be reduced to 140 °C without an obvious drop in yield (Table 1, entries 7–8). Notably, the catalytic effect is still outstanding even with only 0.5 mol% of catalyst loading and 0.5 eq. NaOH, indicating the superior catalytic properties of **C1** (Table 1, entries 10 and 12). In control experiments, the absence of **C1** or NaOH will greatly deteriorate the reaction results, which proves the vital roles of catalyst and base for the reaction (Table 1, entries 11 and 13).

With the advent of the optimal condition, a variety of primary alcohols were tested to probe the versatility of our catalytic system (Table 2). It was found that benzyl alcohols bearing electron-donating substituents, including methyl, isopropyl, and methoxy group, can provide the desired secondary alcohol products **3b**–**3f** in good yields (83-88%). The yields for the electron-deficient substrates with trifluoromethyl groups decreased slightly to 76% and 64% (**3g** and **3h**). As for halo-substituents, it turned out that the *meta*-substituted benzyl alcohols required a relatively harsh reaction condition

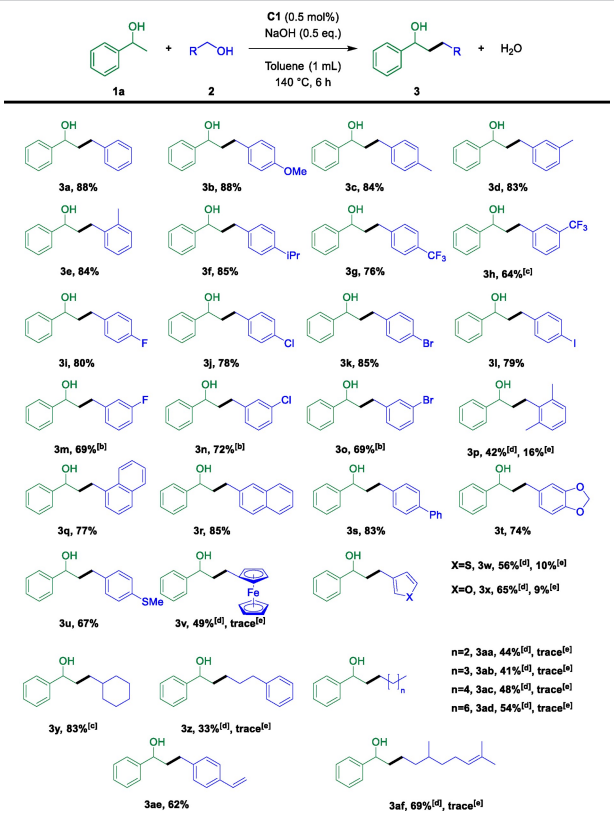
Table 1. Screening of Reaction Conditions.



Entry[a]	Cat. [mol %]	T [°C]	Base [eq.]	(3a + 3a′) Yield[b] [%]	3a/3a′ [c]
1	C1 (5.0)	150	KO^{t}Bu (1.0)	87	91/9
2	C2 (5.0)	150	KO^{t}Bu (1.0)	4	–
3	C3 (5.0)	150	KO^{t}Bu (1.0)	0	–
4	C1 (5.0)	150	NaO^{t}Bu (1.0)	94	94/6
5	C1 (5.0)	150	KOH (1.0)	84	93/7
6	C1 (5.0)	150	NaOH (1.0)	96	95/5
7	C1 (5.0)	140	NaOH (1.0)	98	93/7
8	C1 (5.0)	130	NaOH (1.0)	14	–
9	C1 (2.0)	140	NaOH (1.0)	99	93/7
10	C1 (0.5)	140	NaOH (1.0)	95	98/2
11	-	140	NaOH (1.0)	26	–
12	C1 (0.5)	140	NaOH (0.5)	99	99/1 (88)[d]
13	C1 (0.5)	140	–	0	–

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), Toluene (1.0 mL), 6 h. [b] Determined by GC with 1,4-di-*tert*-butylbenzene as an internal standard. [c] Determined by ^{1}H NMR. [d] Isolated yield of **3a** given in parentheses.

Table 2. Scope of Primary Alcohol.[a]



[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), **C1** (0.5 mol%), NaOH (0.5 eq.), toluene (1 mL), at 140 °C for 6 h, isolated yield. [b] **C1** (2 mol%), NaOH (1.0 eq.), at 140 °C for 24 h. [c] **C1** (2 mol%), NaOH (1.0 eq.), at 150 °C for 12 h. [d] **C1** (5 mol%), NaOH (1.0 eq), at 150 °C for 24 h. [e] NaOH (1.0 eq), at 150 °C for 24 h, GC yield.

(**3m**–**3o**), while smooth transformations were obtained for the *para*-halo-substituted substrates in 78–85% yields (**3i**–**3l**) under optimized condition. 2,6-Dimethylbenzyl alcohol showed steric impact on the reactivity (**3p**, 42%), whereas 2-methyl alcohol and 1-naphthalenemethanol furnished the products **3e** (84%) and **3q** (77%) effectively. 2-Naphthalenemethanol and 4-biphenylmethanol with extended aromatic systems can also convert to the corresponding products in attractive yields of 85% for **3r** and 83% for **3s**. Heteroatom-containing substrates also operated with slightly lower yields (**3t**, 74%; **3u**, 67%) or under more severe reaction conditions to generate products **3v**–**3x** in 49–65% yields.

The applicability of aliphatic primary alcohols has also been investigated. Under the conditions of higher catalyst (2–5 mol%) and base (1.0 eq.) loadings, temperature (150 °C), and reaction time (12–24 h), the reactions of **2y**–**2ad** with **1a** were conducted to form the target products **3y**–**3ad** in 33–83% yields, exhibiting decreased activity than benzyl alcohols. Remarkably, in the case of vinyl-containing substrates, selective transformations of 4-vinyl benzyl alcohol (**2ae**) and citronellol (**2af**) to the desired products with preservation of the C=C bond were achieved, highlighting the chemoselectivity of this protocol.

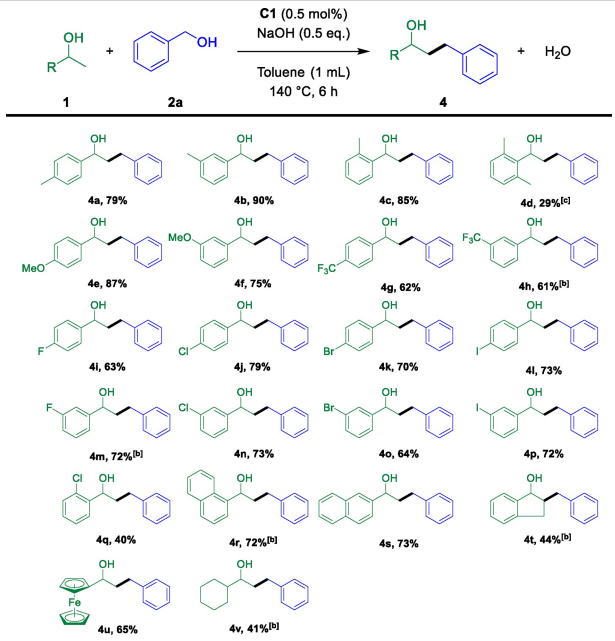
After successfully varying primary alcohols, structurally diverse secondary alcohols were also studied (Table 3). The position of methyl on the phenyl ring has no obvious impact on the formation of **4a**–**4c** (79%-90%), whereas significant suppression existed in the formation of **4d** (29%) with 2,6-dimethyl groups. For the naphthyl group, a harsher reaction condition was needed for 1-(1-naphthyl)ethanol to afford **4r** (72%) than 1-(2-naphthyl)ethanol to afford **4s** (73%), showing the impact of the steric effect. Comparing to electron-withdrawing halo and trifluoromethyl groups, electron-donating groups, such as methyl and methoxy, facilitate the processes of β-alkylation (**4a**–**4q**). It is noteworthy that substrate containing 2-chloro substitution led to a lower yield of **4q** (40%) than 3-chloro (**4n**, 73%) or 4-chloro (**4j**, 79%) substitution. 1-Indanol, 1-ferrocenylethanol, and 1-cyclohexylethanol were alkylated by **2a** to give **4t**, **4u**, and **4v** in 44%, 65%, and 41% yields, respectively.

Encouraged by these promising results, a gram-scale reaction and synthetic application of Vitamin E derivation were carried out to further demonstrated the synthetic potentials of this protocol. Firstly, 1.25 g of **3a** with 78% yield was delivered by coupling of **1a** with **2a** (Scheme 2a). Furthermore, the Vitamin E derivatives **6** could be synthesized in 70% yield by this β-alkylation process catalyzed by *bis*-NHC Mo complex **C1**.

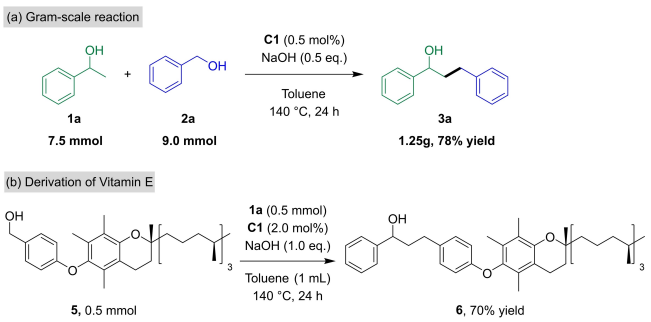
To better understand the reaction mechanism, control experiments have been conducted (Scheme 3; for more details see SI). The smooth transformation upon adding 3 drops Hg to the reaction mixture [Eq. (1)] implies a homogenous nature of this Mo catalysis. A radical process could be ruled out by the observed high yield in the presence of 1.0 eq. of a radical scavenger, TEMPO [Eq.(2)]. Under the standard condition, the β-alkylation reaction was performed with 1.0 mmol **1a** and 0.5 mmol **2a** to generate **3a** and **3a*** in 71% and 10% yields [Eq. (3)], respectively. Similar results can also be obtained by the reaction between acetophenone **1a*** and benzyl alcohol **2a** in a molar ratio of 1:2 (Scheme S2). Additionally, the results of control experiments revealed the vital role of NaOH for the condensation of acetophenone with benzaldehyde to afford chalcone **3a****, while the absence of **C1** has no obvious effect on it [Eq. (4)]. With **1a** or **2a** as the hydrogen source, transfer hydrogenation of chalcone **3a**** to **3a** could be achieved in 71% and 41% yields, respectively [Eq. (5)]. Although our attempts for direct observation of the Mo–H species by ^{1}H NMR failed, a considerable concentration of H_2 (ca. 18700 ppm) was detected from the headspace of the vessel during the reaction by GC analysis [Eq. (6)] (Figure S1–S5, Table S3). These results imply a BH process involving dehydrogenation, condensation, and hydrogenation for this reaction.[29]

To gain further mechanistic insight, we performed deuterium-labeling and kinetic isotope effect (KIE) experiments [Eqs. (7–8)]. Similar to previous work,[26c] no incorporation of

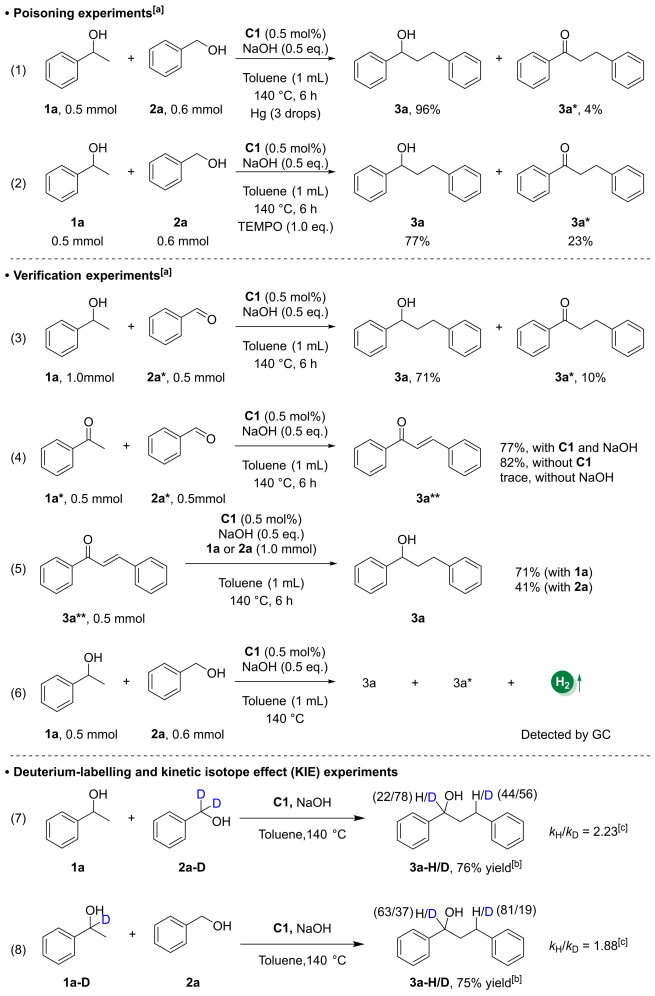
Table 3. Scope of Secondary Alcohol.[a]



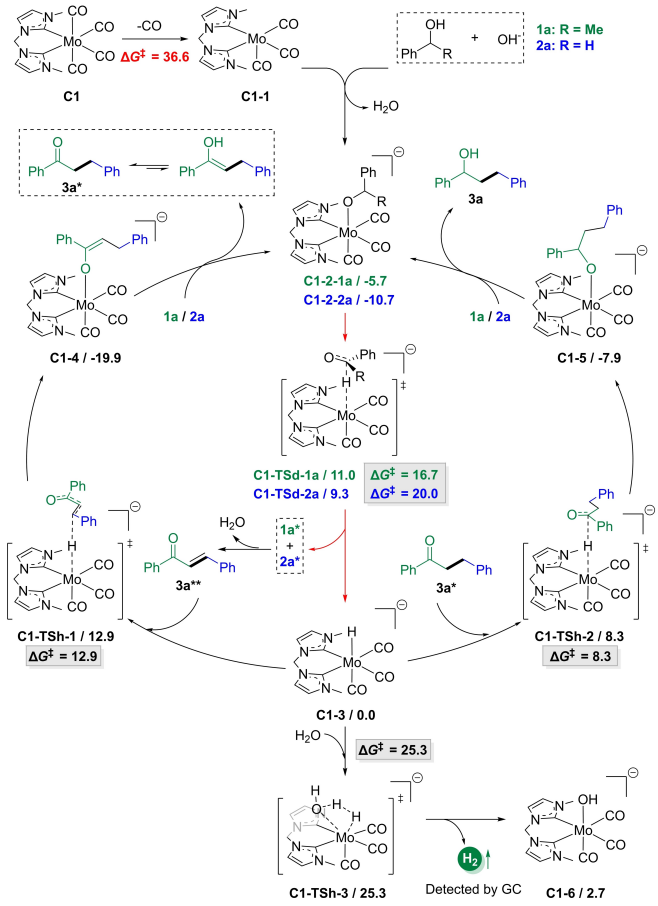
[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), **C1** (0.5 mol%), NaOH (0.5 eq.), toluene (1 mL), at 140 °C for 6 h, isolated yield. [b] **C1** (2 mol%), NaOH (1.0 eq.), at 140 °C for 24 h. [c] **C1** (5 mol%), NaOH (1.0 eq.), at 150 °C for 24 h.



Scheme 2. Gram-scale reaction and synthetic application.



Scheme 3. Preliminary mechanism studies. [a] GC yield. [b] Reaction condition: **1a-H/D** (0.5 mmol), **2a-H/D** (0.6 mmol), **C1** (2.0 mol%), NaOH (0.5 eq.), toluene (1 mL), at 140 °C for 24 h, isolated yield. [c] Reaction condition: **1a-H/D** (0.5 mmol), **2a-H/D** (0.6 mmol), **C1** (0.5 mol%), NaOH (0.5 eq.), toluene (1 mL), at 140 °C.



Scheme 4. Plausible reaction pathways. Free energies are given in kcal/mol.

deuterium atom at the β-position was observed, indicating the absence of H/D exchange during the reaction. The kinetic isotope effect was investigated by the coupling of **1a** with **2a-D** or **1a-D** with **2a**, and the k_H/k_D values were found to be 2.23 and 1.88, respectively, suggesting that the dehydrogenation of alcohols is most likely the rate-determining step (RDS).

Based on the experimental observations and precedents in the literature,[26] a plausible mechanism and its results of density functional theory calculations were depicted in Scheme 4. Firstly, a CO molecule dissociates from **C1** under heating to form **C1-1** for the coming substrate. The activation free energy of CO dissociation is calculated as 36.6 kcal/mol (Scheme S3),[30] in accordance with the relatively high reaction temperature (140 °C). Next, alkoxo-Mo intermediates **C1-2-1a** and **C1-2-2a** were generated by deprotonation of alcohol substates to start the catalytic cycle. An outer-sphere hydride transfer process is proposed via transition state **C1-TSd-1a** or **C1-TSd-2a** with calculated free energy barriers of 16.7 kcal/mol or 20.0 kcal/mol, respectively, resulting in the reactive Mo hydride intermediate **C1-3**. Next, the cross-aldol condensation between **1a*** and **2a*** without metal-catalysis leads to chalcone **3a****. Based on the experimental results and reaction potential energy profile, it is suggested that 1,4-hydrogenation to generate enol (tautomerization to ketone **3a***) via **C1-TSh-1** ($\Delta G^{\neq} = 12.8$ kcal/mol) is more preferred than 1,2-hydrogenation via **C1-TSh-1b** ($\Delta G^{\neq} =$ 14.3 kcal/mol, see Scheme S4). Finally, the reduction of the ketone **3a*** by another Mo hydride species **C1-3** takes place via **C1-TSh-2** ($\Delta G^{\neq} = 8.3$ kcal/mol) to the desired alcohol product **3a**. A facile 1,4-hydrogenation (**C1-TSh-1**, 12.9 kcal/mol) followed by a faster carbonyl hydrogenation step (**C1-TSh-2**, 8.3 kcal/mol) guarantees the selective formation of alcohol rather than ketone as the final product. The higher free energy barrier of the dehydrogenation than that of the hydrogenation suggests the alcohol dehydrogenation to be the RDS, which is in line with the results of the observed KIE values. And the Gibbs free energy of **C1-TSh-3** for H_2 formation is calculated as high as 25.3 kcal/mol, which is much higher than **C1-TSh-1** and **C1-TSh-2** (Scheme S5). Therefore, the hydride of **C1-3** prefers to transfer to the unsaturated intermediates **3a**** or **3a*** to yield the desired product **3a**, which is consistent with the experimental result that only a small amount of H_2 was detected during the reaction (Table S3).

In conclusion, we reported the first implementation of a non-noble molybdenum catalyst with an easily accessible

phosphine-free *bis*-NHC ligand to achieve efficient β-alkylation of secondary alcohols via BH strategy, using readily available and biomass-derived alcohols as alkylating agents. This green and step-economical approach features remarkably high activity, excellent selectivity, and broad substrate scope compatibility with the advantage of catalyst usage low to 0.5%, a catalytic amount of NaOH as the base, and H_2O as the by-product. Based on the mechanistic studies, a direct outer-sphere mechanism for this non-bifunctional *bis*-NHC Mo(0) is suggested and the dehydrogenation of the alcohols substrates plays an important role in the rate-determining step.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Alcohols · Alkylation · Molybdenum catalysis · *N*-heterocyclic carbene · Borrowing hydrogen

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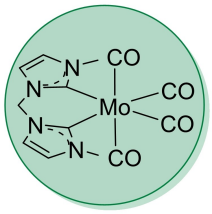
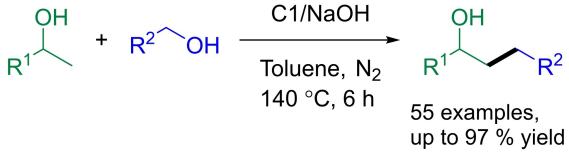


***Bis*-NHC Mo (C1)**



55 examples,
up to 97 % yield

- **Non-noble metal**
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- **Phosphine free ligand**
- **Low catalyst loading**
- **Sustainable alkylating agent**
- **High alcohol selectivity**

*J. Liu, W. Li, Dr. Y. Li, Prof. Dr. Y. Liu, Prof. Dr. Z. Ke**

1 – 6

Selective C-alkylation between Alcohols Catalyzed by N-Heterocyclic Carbene Molybdenum

The first molybdenum-catalyzed C-alkylation between alcohols via borrowing hydrogen is reported.