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Phosphine-Free NNN-Manganese Complex Catalyzed α-Alkylation of Ketones with Primary Alcohols and Friedländer Quinoline Synthesis

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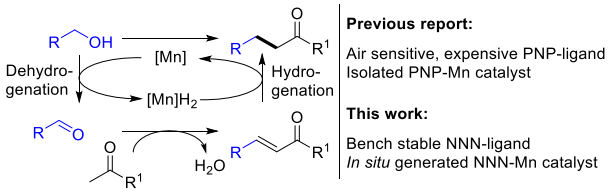
Abstract. Herein, we report a very simple and inexpensive catalytic system based on Earth's abundant transition metal manganese and on a bench-stable phosphine-free NNN-pincer ligand for an atom-efficient α-alkylations of ketones with primary alcohols via hydrogen-autotransfer C-C bond formation protocol. The precatalyst could be generated *in situ* and could be activated by using catalytic amount of base under milder conditions. A range of ketones were efficiently diversified with a broad range of primary alcohols in good to excellent isolated yields. Remarkably, this catalyst could also be employed for the synthesis of quinoline derivatives using 2-aminobenzyl alcohol as an alkylating agent. The later reaction is highly benign producing only hydrogen and water as byproducts.

Keywords: Alkylation; Manganese catalysts; Hydrogen-autotransfer; Friedländer reaction; NNN-pincer.

The use of *borrowing-hydrogenation* or *hydrogen-autotransfer* strategy for the alkylations of ketones or amines have emerged as an eco-friendly repertoire for the construction of C-C or C-N bonds in compared to the traditional methods.[1] Typically, this concept involves the transition-metal-catalyzed dehydrogenation of alcohols followed by the condensation of the *in situ* generated aldehydes with the ketones or the amines. Subsequently, the borrowed hydrogen reduces the intermediates (e.g. enones or imines) to yield the desired alkylated products and water as a sole by-product (Scheme 1).[1b, 1c, 1g, 2]

Using this strategy, the α-alkylation of ketones have emerged as a very eco-friendly and attractive protocol as it avoids the use of stoichiometric strong bases, cryogenic temperature, and alkyl halides as alkylating agents.[2a, 3] Several homogeneous catalysts with transition metals such as Ru,[4] Ir,[5] Pd,[6] Re[7] etc. have already been developed for such reactions. Recently, non-precious iron[8]- and cobalt[9]-catalyzed α-alkylation of ketones using alcohols as alkylating agents have been reported. In contrast, only recently the manganese catalyzed[10] such reaction has been disclosed by the Beller group using a manganese complex of a tridendate aliphatic $[(iPr)_2PCH_2CH_2]_2NH$ ligand.[11]

Mainly, the current state-of-the-art manganese catalysts established by the studies of Milstein,[12] Beller,[7,11,13] Kempe,[14] Kirchner,[10f,15] Sortais,[16] Boncella[17] and others[18] utilizes diethylamine-core PNP ligands, pyridinyl-core PNP and PN^3P ligands and triazinyl-core PN^5P ligands. However, the major concerns of these phosphine based pincer ligands in base-metal catalysis are not only their cost, which are usually more expensive than the nonprecious metals by many folds, but also the difficulties lie in their preparations and handling under standard laboratory conditions.

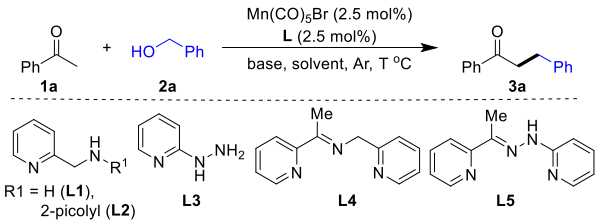


Scheme 1. Mn-catalyzed *hydrogen-autotransfer* strategy for the α-alkylation of ketones with alcohols.

In search for simple, overall inexpensive and sustainable catalytic process, our recent research focuses on the development of an alternative, cheap, and bench stable ligands for promoting bifunctional catalysis. Recently, we have disclosed olefinations of methylheteroarenes with alcohols catalyzed by a manganese complex derived from non-innocent hydrazone-type NNN-pincer ligand.[19] Herein, we report on the α-alkylation of ketones under *hydrogen-autotransfer* conditions using primary alcohols as

alkylating agents. The Mn-complex stabilized by the NNN-ligand mediate the reaction under low catalyst loading and tolerate reducible functional groups such as fluoro, chloro, bromo, and iodo despite of the involvement of the hydrogen under the reaction condition. The same catalyst also promote the Friedländer annulation reactions for the green synthesis of quinoline derivatives using 2-aminobenzyl alcohol *via* acceptorless dehydrogenative coupling where water and dihydrogen were produced as by-products.

Table 1. Optimization of the reaction conditions for the manganese catalyzed α-alkylation of acetophenone **1a** with benzyl alcohol **2a**.[a)]



Entry	Ligand	Solvent	Base [mol%]	T [°C]	Yield [%][b)]
1	**L1**	*t*-AmOH	*t*-BuOK (20)	120	31
2	**L2**	*t*-AmOH	*t*-BuOK (20)	120	42
3	**L3**	*t*-AmOH	*t*-BuOK (20)	120	10
4	**L4**	*t*-AmOH	*t*-BuOK (20)	120	29
5	**L5**	*t*-AmOH	*t*-BuOK (20)	120	89
6	**L5**	*t*-AmOH	*t*-BuOK (20)	140	99 (91)[c)]
7	**L5**	*t*-AmOH	*t*-BuOLi (20)	140	72
8	**L5**	*t*-AmOH	*t*-BuONa (20)	140	73
9	**L5**	*t*-AmOH	Cs_2CO_3 (20)	140	32
10	**L5**	*t*-AmOH	*t*-BuOK (10)	140	99
11[d)]	**L5**	*t*-AmOH	*t*-BuOK (10)	140	99
12	**L5**	toluene	*t*-BuOK (10)	140	67
13	**L5**	1,4–dioxane	*t*-BuOK (10)	140	73
14	**L5**	*t*-BuOH	*t*-BuOK (10)	120	68
15[e)]	-	*t*-AmOH	*t*-BuOK (10)	140	10
16[f)]	**L5**	*t*-AmOH	–	140	–
17[g)]	**L5**	*t*-AmOH	*t*-BuOK (10)	140	12
18[h)]	PNP-Mn	*t*-AmOH	Cs_2CO_3 (5)	140	88

[a)] General reaction conditions: $Mn(CO)_5Br$ (2.5 μmol) and a ligand (2.5 μmol) were stirred at 80 °C in *t*-AmOH (0.5 mL) for 2 h, after which a base, acetophenone **1a** (0.1 mmol), and benzyl alcohol **2a** (0.12 mmol) were added and the reaction was heated to 120 or 140 °C for 24 h. [b)] Determined by GC–MS analysis of the crude mixture using bromobenzene as standard. [c)] Isolated yield was given in the parenthesis. [d)] 2 mol% catalyst was used. [e)] **L5** was not used. [f)] Base was not used. [g)] $Mn(CO)_5Br$ was not used. [h)] From Ref 11.

To optimize the reaction conditions, preliminary experiments were done with acetophenone **1a** (1 equiv.) and benzyl alcohol **2a** (1.2 equiv.) as substrates using 2.5 mol% of an *in situ* generated manganese complex and a base (20 mol%) at 120 °C under argon atmosphere (Table 1). The Mn-complexes, derived from 2-picolylamine **L1** and di(2-picolyl)amine **L2**, independently utilized for the transfer hydrogenations of aldehydes and ketones by Sortais[16b] and Beller,[13c] were found to be inefficient for the α-benzylation of **1a** (31% and 42% yields of **3a**, respectively; entries 1,2). Similarly, unsatisfactory results were obtained when 2-hydrazinyl pyridine **L3** and imine-type pincer ligand **L4** were used (entries 3,4). However, very high catalytic activity was observed when the hydrazone-type pincer ligand **L5** derived from 2-hydrazinyl pyridine was used (89% yield, entry 5).[20] The yield could significantly be improved to 99% by increasing the temperature to 140 °C and the desired product **3a** was isolated in 91% yield under these conditions (entry 6). The use of other bases were found to be detrimental for this reaction (entries 7-9). The base and the manganese loading could be lowered to 10 and 2 mol%, respectively without any loss of catalytic activities (entries 10,11). Other solvents like toluene, 1,4-dioxane and *t*-BuOH were found to be less suitable (entries 12-14). A series of control experiments demonstrate the necessity of the metal precursor $Mn(CO)_5Br$, **L5** and *t*-BuOK, as traces of **3a** were obtained in their absence (entries 15-17). It should be noted that the PNP-Mn catalyst developed by the Beller group delivered 88% of **3a** under their conditions.[11]

Utilizing this optimized conditions (Table 1, entry 11), we have demonstrated the scope of this Mn-catalyzed α-alkylation reactions (see Table 2). Initially, the reactions of different substituted ketones with benzyl alcohol derivatives were tested. As shown in Table 2, a series of acetophenone derivatives with electron rich such as 4-Me (**1b**), and 3-OMe (**1c**) and electron deficient such as 4-F (**1d**), and 4-Cl (**1e**) functional groups were α-benzylated in 68-90% yields. However, 4-cyano- and 4-carboethoxy acetophenones (**1f,g**) were found to be unsuitable coupling partner. When methylnapthyl ketone **1h**, α-tetralone **1i** and methyl thiophenyl ketone **1j** were used, the desired products were obtained in 65-82% yields. With the success with arylmethyl ketone we have turn our attention to more challenging alkylmethyl ketone. While mixture of compounds were obtained when *iso*-propylmethyl ketone **1k** was used, *tert*-butylmethyl ketones **1l** was found to be suitable coupling partner delivering the product in 64% yield.

The compatibility of different primary alcohols for this Mn-catalyzed C-C bond formation reaction were then evaluated. Consequently, structurally diverse primary

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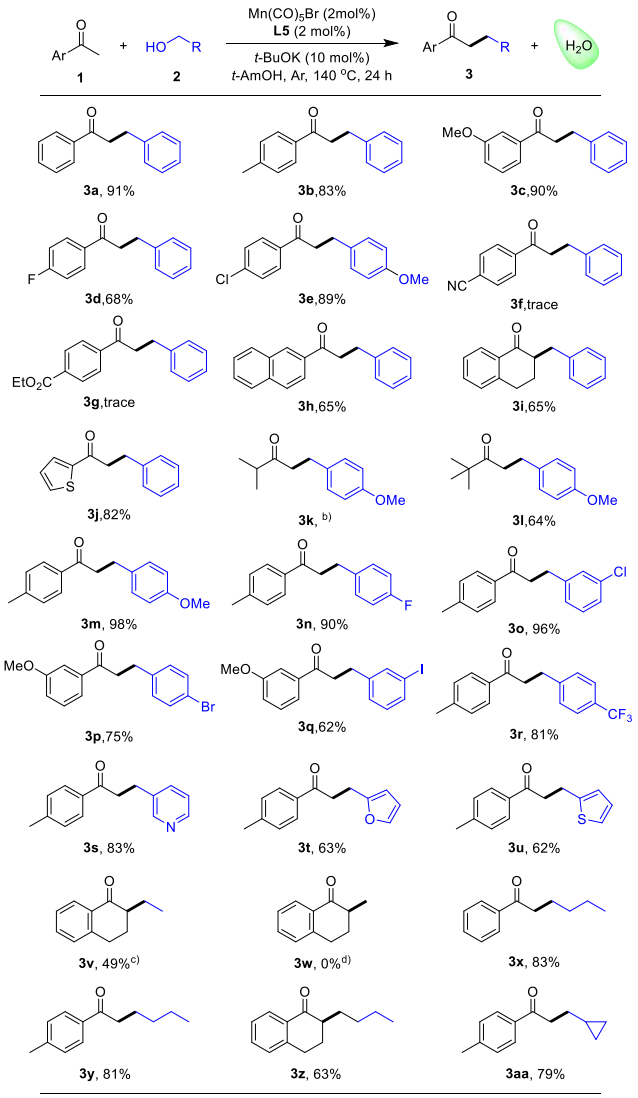
Table 2. Scope of the Mn–catalyzed α-alkylations of ketones with alcohols.[a)]

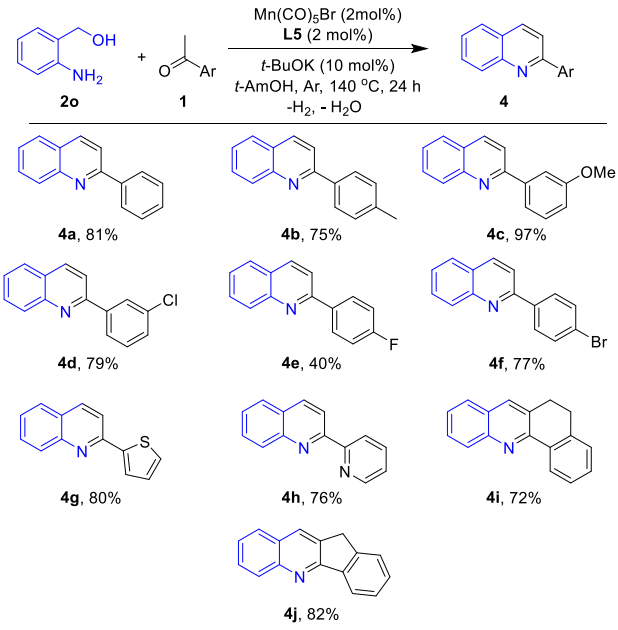


a) Reaction conditions: $Mn(CO)_5Br$ (5 μmol) and the ligand **L5** (5 μmol) were stirred at 80 °C in *t*-AmOH (1.0 mL) for 2 h, after which *t*-BuOK (0.02 mmol), ketones **1a-l** (0.2 mmol), and primary alcohols **2a-n** (0.24 mmol) were added and the reaction was heated to 140 oC for 24 h. Yields of the isolated products were given. b) Mixture of compounds. c) 1:1 mixture of *t*-AmOH:EtOH (1.0 mL) was used. d) 1:1 mixture of *t*-AmOH:MeOH (1.0 mL) was used.

alcohols were used as alkylating agents and the results are summarized in Table 2. Remarkable, reducible halogen functional groups such as fluoro, chloro, bromo and iodo at 3- or 4-position of the benzyl alcohol were tolerated delivering the alkylated products **3n-q** in 62-96% yields. Similarly, 4-CF_3-benzyl alcohols **2g** also underwent smooth α-alkylation reaction and the product **3r** was isolated in 81% yield. Pyridine, furan, and thiophen containing heteroaromatic alcohols **2h-j** were also found to be viable coupling partners delivering the products **3s-u** in 62-83% yields. Furthermore, synthetically more challenging aliphatic alcohols could also be used for this strategy. For example, α-ethylation of α-tetralone **1i** took place when ethanol **2k** was used as an electrophile and the product **3v** was isolated in moderate 49% yield. However, no product was observed when methanol **3w** was used. Whereas, when higher alcohol *n*-butanol **2m** was used as an alkylating agent the corresponding α-butylated ketones **3x-z** were isolated in 63-83% yields. Strained cyclopropyl methanol **2n** was also found to be viable coupling partner and the product **3aa** was isolated in 79% yield.

The NNN-Mn complex developed in this work also revealed an efficient activity for the syntheses of quinoline derivatives when 2-aminobenzyl alcohol was used as coupling partner (Table 3). Traditionally, the Friedländer annulation reactions[21] utilizes the condensation reactions of 2–aminobenzaldehydes with ketones under acidic or basic conditions and often suffers from the issues like the limited stability of 2–aminobenzaldehydes, self-condensations etc.[13c] Using comparatively more stable 2–aminobenzyl alcohols and catalytic amount of base, the acceptorless dehydrogenative coupling allows greener synthesis of quinolines.[10a, 10e, 10f, 14c, 21] Recently, Fe-, Co-, Ni-, and Cu-based catalysts have been employed for such reactions.[10d, 10e, 13c, 16b, 22]

Table 3. Scope of Mn–catalyzed Friedländer quinoline syntheses.[a)]



a) Reaction conditions: $Mn(CO)_5Br$ (5 μmol) and the ligand **L5** (5 μmol) were stirred at 80 °C in *t*-AmOH (1.0 mL) for 2 h, after which *t*-BuOK (0.02 mmol), the ketones **1a-p** (0.2 mmol), and the amino alcohol **2o** (0.24 mmol) were added and the reaction was heated to 140 °C for 24 h. Yields of the isolated products were given.

The manganese catalyst described in Table 1 for the α-alkylation of ketones also displayed efficient activities for Friedländer annulation reaction using 2–aminobenzyl alcohol **2o**. As shown in Table 3, 2-phenylquinoline **4a** was isolated in 81% yield from the

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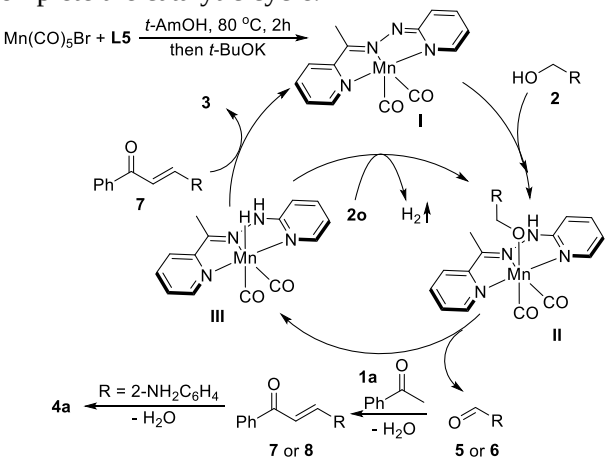
reaction of **2o** and **1a** (Table 3) in a comparatively shorter reaction time than the reported examples.[9a, 9d] A wide range of aryl ketones with different electronic substituents also underwent smooth annulation reactions delivering the quinolines in 40-97% yields (Table 3). More interestingly, heteroaromatic methylketones, such as 2-acetylthiophene **1j** and 2-acetylpyridine **1o** performed well for this reaction to yield the corresponding quinolies **4g** and **4h** in 76% and 80% yields, respectively. The use of α-tetralone **1i** as coupling partner resulted in formation of 5,6-dihydrobenzo[c]acridine **4i** in 72% yield. Similarly, fused 11H-indeno[1,2-b]quinoline **4j** was obtained in 82% yield when 1-indanone **1p** was used.

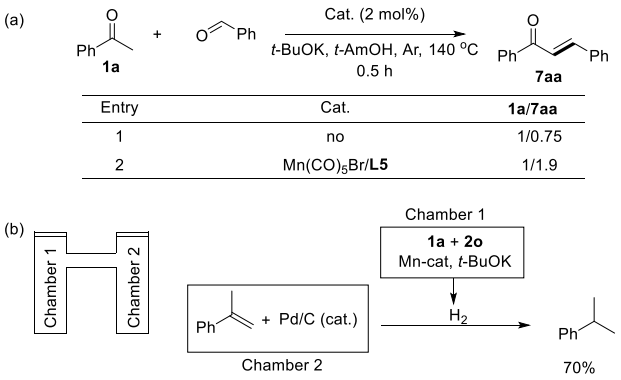
A probable mechanistic cycle is proposed in Scheme 2 based on literature reports and our observations.[11,19,23] The manganese complex **I** generated in presence of base dehydrogenate the alcohol via an alkoxy complex **II**. The liberated aldehyde **5** or the aminoaldehyde **6** then undergo aldol condensation with the ketone to generate the α,β-unsaturated compounds **7** and **8** with the release of one molecule of water. The hydrogenation of **7** then yields the desired product **3** and regenerate the catalyst. In case of **8**, it undergoes fast dehydative cyclization to yield the quinoline product **4a**. We believe that the manganese complex **III** then react with one molecule of **2o** to liberate one molecule of dihydrogen and complete the catalytic cycle.[22f]



Scheme 2. Proposed mechanism.

Previously, we and others have shown the involvement of the dehydrogenation catalyst in the CC-bond forming aldol condensation process.[19, 23] To probe whether the NNN-Mn complex is also involved in the aldol reaction we have perform the reaction of benzaldehyde with **1a** in presence and absence of the catalyst (Scheme 3a). The observed 2.3 fold rate acceleration is an indicative of the involvement of the catalyst in the key CC-bond formation process.

Then the acceptorless liberation of molecular hydrogen was probed by performing the Pd/C catalyzed hydrogenation of α-methyl styrene in an H-shaped bridged tube (Scheme 3b) using the liberated dihydrogen in the annulation reaction. In such experiment, the manganese catalyzed annulation reaction of **2o** with **1a** was carried out in one chamber and the other chamber contains α-methyl styrene and Pd/C. The observed 70% yield of cumene conclusively support the acceptorless liberation of dihydrogen.



Entry	Cat.	1a/7aa
1	no	1/0.75
2	$Mn(CO)_5Br$/**L5**	1/1.9

Scheme 3. Control experiments.

In conclusion, we have demonstrated that a Mn-complex of a bench stable NNN-pincer ligand is an efficient catalyst for the α-alkylation of ketones with primary alcohols in presence of catalytic amount of base. This catalyst also showed efficient catalytic activity for Friedländer quinoline synthesis. This is the first example when an inexpensive phosphine-free NNN-pincer ligand is being used for the manganese catalyzed ketone alkylation reactions and acceptorless dehydrogenative synthesis of quinolines.

Experimental Section

General procedure for Mn–catalyzed α-alkylation of ketones with alcohols: In a 15 mL Schlenk tube, $Mn(CO)_5Br$ (1.10 mg, 0.0040 mmol, 2.0 mol%) and **L5** (0.9 mg, 0.004 mmol) were stirred at 80 °C in *t*-AmOH (2.0 mL) for 2 h under argon. Then *t*-BuOK (1.1 mg, 0.01 mmol), ketone (0.2 mmol), and corresponding primary alcohol (0.24 mmol) were added and the tube was closed before the mixture was placed in a preheated oil bath at 140 °C for 24 h under Ar atmosphere. The progress of the reaction was monitored by TLC. Upon completion, the solvent was evaporated and the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.

General procedure for Mn–catalyzed Friedländer quinoline synthesis: In a 15 mL Schlenk tube, $Mn(CO)_5Br$ (1.1 mg, 0.0040 mmol, 2.0 mol%) and **L5** (0.9 mg, 0.004 mmol) were stirred at 80 °C in *t*-AmOH (2.0 mL) for 2 h under argon. Base *t*-BuOK (1.1 mg, 0.01 mmol), ketone (0.2 mmol) and 2-aminobenzyl alcohol (0.24 mmol) were mixed. The mixture was then stirred at 140 °C for 24 h under Ar atmosphere. The progress of the reaction was monitored by TLC. Upon completion, the solvent was evaporated and the residue was purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.

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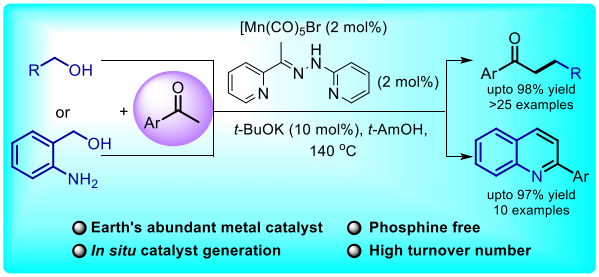
Phosphine-Free NNN-Manganese Complex Catalyzed α-Alkylation of Ketones with Primary Alcohols and Friedländer Quinoline Synthesis



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