**Alkylation**

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# N−H Imine as a Powerful Directing Group for Cobalt-Catalyzed Olefin Hydroarylation

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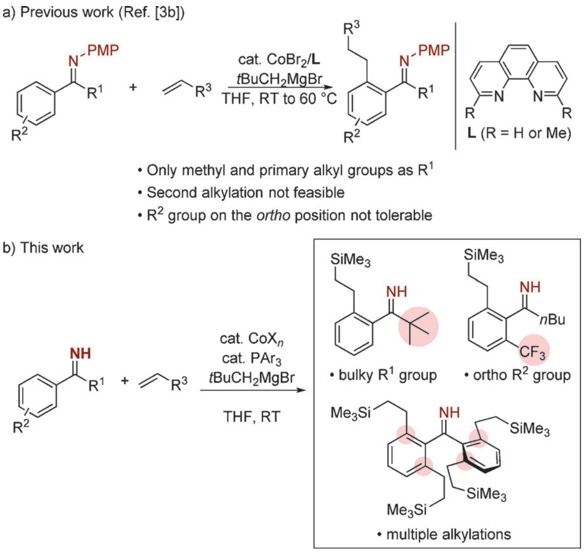
**Abstract:** *N-alkyl and N-aryl imines have been frequently used as directing groups in rhodium- and cobalt-catalyzed hydroarylation reactions of olefins and alkynes. However, the scope of such hydroarylation reactions has been limited by the difficulty of preparation of sterically hindered imines by condensation, and also by the steric bulkiness of the imine group itself. Reported herein is that an N−H imine serves as an alternative and highly effective directing group for cobalt-catalyzed hydroarylation of olefins, and unlocks many of the limitations associated with the previously employed N-aryl imine directing group. The power of this minimal nitrogen directing group is manifested in a fourfold ortho alkylation of benzophenone imine, and it occurs rapidly at ambient temperature.*

The addition of arenes to olefins and alkynes (hydroarylation) by directed C−H activation has evolved as an atom- and step-economical approach to the regioselective alkylation and alkenylation of aromatic compounds. Much of the advance in this type of transformation has been made using catalysts based on precious transition metals such as ruthenium, rhodium, and iridium.[1,2] In contrast, cost-effective alternative catalysts based on 3d transition metals such as cobalt, iron, and manganese have recently been explored.[3–5] In particular, we and Petit et al. have demonstrated that low-valent cobalt complexes serve as competent catalysts for hydroarylation reactions directed by electron-rich *para*-methoxyphenyl (PMP) imine.[3b–i,6] For example, cobalt-phenanthroline-type catalysts allow *ortho* alkylation of aryl N-PMP imines at mild temperatures (Scheme 1 a).[3b] The use of a PMP imine, however, poses a few major limitations in such hydroarylation reactions and other cobalt-catalyzed C−H functionalization reactions.[7] First, the imines are typically limited to those prepared from less hindered aryl ketones (e.g., acetophenone, propiophenone, tetralone), because the imine preparation becomes less feasible with bulkier ketones. The same limitation often applies to other N-aryl and N-alkyl-imine-directed C−H functionalizations using different transition metals.[8–12] Second, the reaction typically stops at the monoalkylation stage, because the steric repulsion between the imine and the newly introduced alkyl group interfere with the second C−H activation. For the same reason, *ortho*-monosubstituted imines are reluctant to participate in the reaction.



***Scheme 1.*** Cobalt-catalyzed, imine-directed olefin hydroarylation. THF = tetrahydrofuran.

An N−H imine has recently been used as a unique directing group for aromatic C−H functionalization reactions, such as rhodium- and ruthenium-catalyzed annulations with either alkynes or allenes to form indene derivatives,[13] and rhodium- and manganese-catalyzed dehydrogenative annulations with alkynes to form isoquinolines.[14,15] Herein, we report that the N−H imine serves as a powerful directing group in cobalt-catalyzed hydroarylations of vinylsilanes and alkyl olefins, and unlocks many of the limitations associated with the PMP imine (Scheme 1 b). Unlike N-substituted imines, bulky N−H imines are readily accessible, and have proved to exhibit excellent reactivity in the *ortho* C−H functionalization. The strong directing ability of an N−H imine,[16] combined with its minimum steric size, enables highly efficient fourfold *ortho* alkylation of benzophenone imines at room temperature.[17]

The present study commenced with screening of reaction conditions for the addition of phenyl butyl imine (**1a**) to vinyltrimethylsilane (1.5 equiv; Table 1). With a brief screening of catalytic systems comprising $CoBr_2$ (10 mol %), tertiary phosphine (20 mol %), and $tBuCH_2MgBr$ (50 mol %),[18] we were able to quickly identify $P(3\text{-}MeOC_6H_4)_3$ as an excellent ligand to promote the C−H activation for exclusively afford-

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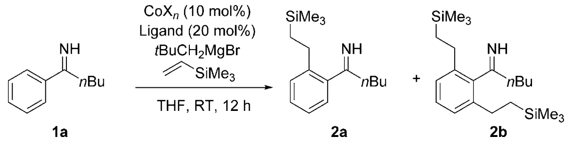
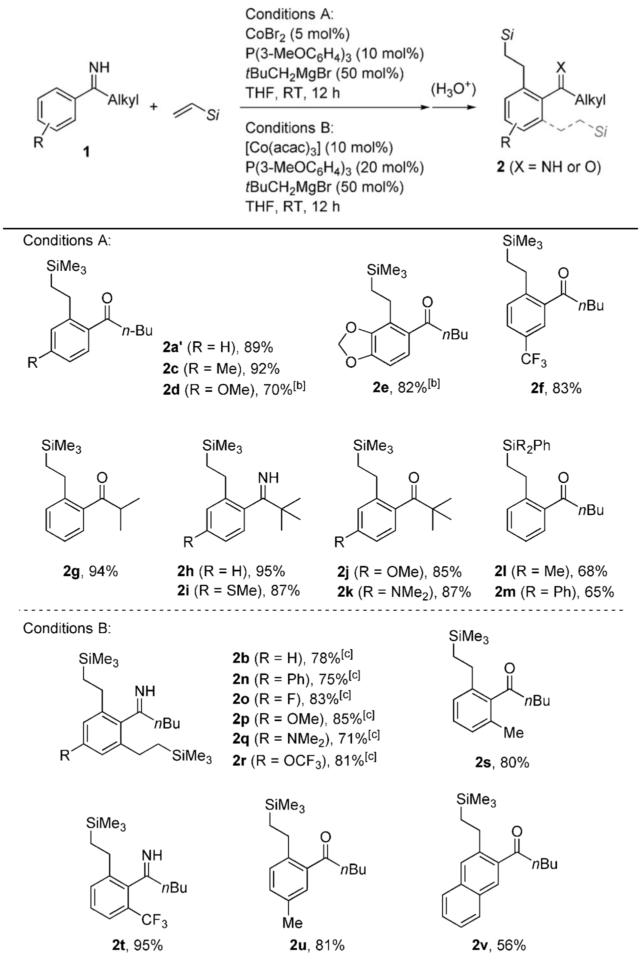
***Table 1:*** Effect of reaction conditions on addition of N-H imine **1a** vinyltrimethylsilane.[a]



| Entry | CoX$_n$ | Ligand | Yield [%][b] (**2a**/**2b**) |
|---|---|---|---|
| 1 | CoBr$_2$ | P(4-ClC$_6$H$_4$)$_3$ | 79/0 |
| 2 | CoBr$_2$ | P(3-FC$_6$H$_4$)$_3$ | 82/0 |
| 3 | CoBr$_2$ | P(3-MeOC$_6$H$_4$)$_3$ | 96/0 |
| 4[c] | CoBr$_2$ | 1,10-phenanthroline | 9/0 |
| 5[d] | CoBr$_2$ | P(3-MeOC$_6$H$_4$)$_3$ | 92/0 |
| 6 | CoCl$_2$ | P(3-MeOC$_6$H$_4$)$_3$ | 71/0 |
| 7 | CoI$_2$ | P(3-MeOC$_6$H$_4$)$_3$ | 66/13 |
| 8 | [Co(acac)$_2$] | P(3-MeOC$_6$H$_4$)$_3$ | 26/53 |
| 9 | [Co(acac)$_3$] | P(3-MeOC$_6$H$_4$)$_3$ | 31/46 |
| 10[e] | [Co(acac)$_3$] | P(3-MeOC$_6$H$_4$)$_3$ | 4/83 |

[a] Reaction conditions: **1a** (0.2 mmol), vinyltrimethylsilane (0.3 mmol, 1.5 equiv), Co salt (10 mol%), ligand (20 mol%), tBuCH$_2$MgBr (50 mol%), THF at room temperature for 12 h. [b] Determined by GC using *n*-tridecane as an internal standard. [c] The loading of 1,10-phenanthroline was 10 mol%. [d] The loadings of CoBr$_2$ and P(3-MeOC$_6$H$_4$)$_3$ were 5 mol% and 10 mol%, respectively. [e] The amount of vinyltrimethylsilane was 0.5 mmol (2.5 equiv). acac = acetylacetonate.

***Table 2:*** Addition of aryl alkyl N–H imines to vinylsilane.[a]



[a] Unless otherwise noted, the reaction was performed using 0.3 mmol of imine and 0.45 mmol (1.5 equiv) of vinylsilane, followed by acidic hydrolysis (for the ketone products) or direct purification (for the imine products). [b] CoBr$_2$ (10 mol%) and P(4-ClC$_6$H$_4$)$_3$ were used as the precatalysts. [c] 0.75 mmol (2.5 equiv) of vinylsilane was used.

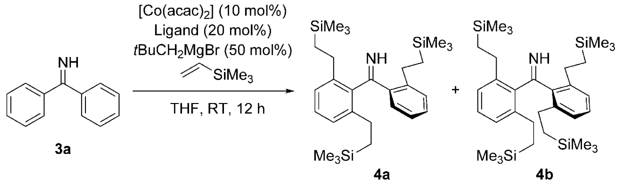
ing the monoalkylation product **2a** in high yield (entries 1–3). Note that 1,10-phenanthroline, which was the optimum ligand for the analogous reaction using the PMP imine (Scheme 1a),[3b] exhibited a substantially lower catalytic activity (Table 1, entry 4). The loading of CoBr$_2$ and P(3-MeOC$_6$H$_4$)$_3$ could be reduced by half without significant decrease in the yield of **2a** (entry 5). Interestingly, the cobalt source was found to have profound influence on the catalytic activity. While CoCl$_2$ was simply inferior to CoBr$_2$ (entry 6), other cobalt salts such as CoI$_2$, [Co(acac)$_2$], and [Co(acac)$_3$] caused the second C–H activation of **2a** to give the dialkylation product **2b** (entries 7–9). In particular, the acetylacetonate salts afforded **2b** as the major product (ca. 50% yield), even with the limited amount of vinylsilane (1.5 equiv). When using 2.5 equivalents of vinylsilane and the [Co(acac)$_3$]/P(3-MeOC$_6$H$_4$)$_3$ catalytic system, the yield of **2b** was improved to 83%, and it was accompanied by only a small amount of **2a** (4%; entry 10).

Having established the efficient catalytic systems, we explored the scope of aryl alkyl imines in the *ortho*-alkylation reaction using vinylsilanes (Table 2). The catalytic system employing CoBr$_2$ as the precatalyst (conditions A) was applicable to selective monoalkylation of either *para-* or *meta*-substituted aryl butyl imines to afford the products **2c–f** in good yields. As was the case with a series of cobalt-catalyzed C–H functionalization reactions using PMP imines,[3b–i] the 3,4-methylenedioxy group served as a secondary directing group to assist exclusive alkylation of the proximal *ortho* C–H bond (**2e**). The more hindered aryl isopropyl imine and aryl *t*-butyl imines were also amenable to monoalkylation under reaction conditions A, thus affording the products **2g–k** in high yields. Vinylsilanes other than vinyltrimethylsilane could be employed as the alkylating agents (see **2l** and **2m**).

The catalytic system employing [Co(acac)$_3$] (conditions B; Table 2) efficiently promoted dialkylation of aryl butyl imines bearing a variety of *para* substituents by using excess vinylsilane, thus affording the products **2n–r** in good yields. Note, however, that aryl isopropyl and aryl *t*-butyl imines only underwent monoalkylation but did not afford any dialkylation products under the same reaction conditions, presumably because the second C–H activation is hampered by severe steric repulsion between the initially installed alkyl group and either the secondary or tertiary alkyl group. Reaction conditions B further proved effective for the alkylation of *ortho*-monosubstituted imines, which were inert under reaction conditions A (**2s** and **2t**). In addition, monoalkylation of some *meta*-substituted imines, which reacted rather sluggishly under reaction conditions A, were alkylated in moderate to good yields under reaction conditions B (**2u** and **2v**).

The capability of the N–H imine directing group was further manifested in the *ortho* alkylation of the benzophe-

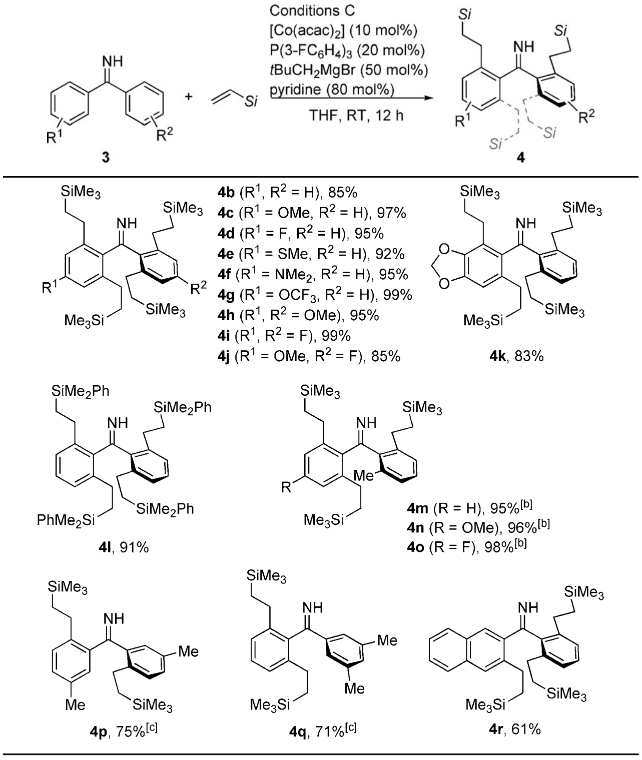
***Table 3:*** Addition of benzophenone N–H imine to vinyltrimethylsilane.[a]



| Entry | Ligand | Additive | Yield [%][b] (**4a**/**4b**) |
|---|---|---|---|
| 1 | P(3-MeOC$_6$H$_4$)$_3$ | – | 60/9 |
| 2 | P(3-FC$_6$H$_4$)$_3$ | – | 71/10 |
| 3 | P(3-FC$_6$H$_4$)$_3$ | Pyridine (80 mol%) | 50/38[c] |
| 4 | P(3-FC$_6$H$_4$)$_3$ | Pyridine (80 mol%) | <1/91[d] |

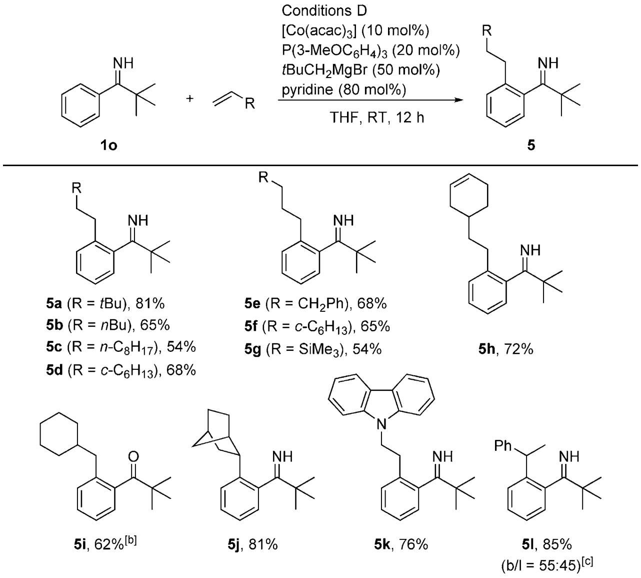
[a] Reaction conditions: **3a** (0.2 mmol), vinyltrimethylsilane (1.2 mmol, 6 equiv), [Co(acac)$_2$] (10 mol%), ligand (20 mol%), $t$BuCH$_2$MgBr (50 mol%), THF at room temperature for 12 h. [b] Estimated by GC analysis. [c] Reaction time = 10 min. [d] Reaction time = 20 min.

***Table 4:*** Addition of diarylketone N–H imines to vinylsilane.[a]



[a] Unless otherwise noted, the reaction was performed using 0.3 mmol of imine and 1.8 mmol (6 equiv) of vinylsilane. [b] 1.05 mmol (3.5 equiv) of vinylsilane was used. [c] 0.90 mmol (3 equiv) of vinylsilane was used.

***Table 5:*** Addition of N–H imine to alkyl olefins.[a]

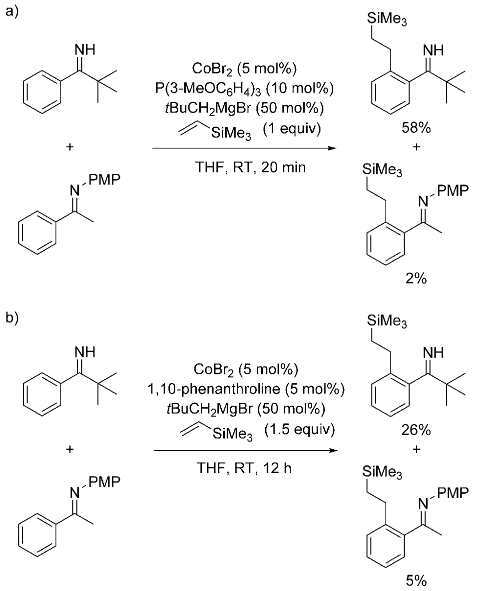


[a] The reaction was performed using 0.3 mmol of imine and 0.45 mmol (1.5 equiv) of olefin. [b] The reaction mixture was hydrolyzed with 3 N HCl. [c] The ratio of branched and linear isomers determined by $^1$H NMR spectroscopy.

none imine **3a** (Table 3). Catalytic systems comprising [Co(acac)$_2$], P(3-MeOC$_6$H$_4$)$_3$ or P(3-FC$_6$H$_4$)$_3$, and $t$BuCH$_2$MgBr promoted the addition of **3a** to excess vinyltrimethylsilane (6 equiv) to afford the trialkylation product **4a** as the major product along with a small amount of tetraalkylation product **4b** at the reaction time of 12 hours (entries 1 and 2). Strikingly, the addition of pyridine (80 mol%) to the [Co(acac)$_2$]/P(3-FC$_6$H$_4$)$_3$ system gave rise to a dramatic acceleration of the reaction. The starting material **3a** was completely consumed within 5 minutes, and the reaction contained a mixture of **4a**, **4b**, and a trace amount of the dialkylation product at the reaction time of 10 minutes (entry 3). At 20 minutes, the mixture almost completely converged to **4b** in high yield (entry 4).[19] This tetraalkylation is remarkable in comparison with previously reported directed hydroarylation reactions of parent benzophenone, which gave either mono- or dialkylation products.[2b,20,21]

Under the pyridine-modified conditions (conditions C), a variety of benzophenone imines smoothly participated in multiple alkylations (Table 4). Various *para*-substituted imines were tetraalkylated with vinyltrimethylsilane to afford the highly hindered benzophenone imines **4b–j** in excellent yields. Imines bearing the secondary directing 3,4-methylenedioxy group was also amenable to tetraalkylation (**4k**). Vinyldimethylphenylsilane could be used in place of vinyltrimethylsilane without a problem (**4l**). Not unexpectedly, diaryl imines bearing an *ortho*-methyl group afforded the trialkylation products **4m–o** in excellent yields. In contrast, substrates bearing *meta*-methyl groups were alkylated only at the *ortho* positions distal from the methyl group (**4p** and **4q**). Likewise, naphth-2-yl phenyl imine underwent a threefold alkylation to afford the product **4r** in a moderate yield.

The [Co(acac)$_3$]/P(3-MeOC$_6$H$_4$)$_3$ system, when modified with pyridine (conditions D),[22] also allowed N–H imine-directed hydroarylation of alkyl olefins, as demonstrated using phenyl $t$-butyl imine (**1o**) as the model substrate (Table 5). With respect to 1-alkenes, not only isomerization-free $t$-butylethylene but also alkenes bearing various primary or secondary alkyl groups participated in the reaction to afford the corresponding *ortho*-alkylation products **5a–h** in moderate to good yields, while competitive isomerization of the unreacted 1-alkenes to the internal isomers was observed. Methylenecyclohexane, norbornene, and vinyl carbazole could also be used as alkylating agents (**5i–k**). The reaction with styrene led to a mixture of branched and linear alkylation products (**5l**), which was in contrast to the branched selectivity typically observed for the cobalt-catalyzed, PMP imine-directed styrene hydroarylation.[3d,e] Unstrained internal alkenes such as cyclohexene failed to participate in the reaction.



***Scheme 2.*** Competition experiments using N–H and N-PMP imines. Yields were determined by GC using *n*-tridecane as an internal standard.

To gain insight into the directing ability of the N–H imine in comparison to that of the N-PMP imine, we performed two competition experiments using phenyl *tert*-butyl N–H imine and acetophenone N-PMP imine (Scheme 2). First, the competition under the reaction conditions optimized for the N–H imine (i.e., conditions A) resulted in fast and predominant alkylation of the N–H imine within a short reaction time of 20 minutes (Scheme 2a). This observation clearly demonstrates that the presence of the N-PMP imine causes little interference of the C–H alkylation of the N–H imine. Notably, the competition under the cobalt/phenanthroline catalytic system, optimized for the N-PMP imine, also resulted in preferential alkylation of the N–H imine albeit with low yields of both the alkylation products after 12 hours (Scheme 2b). Note that the cobalt/phenanthroline system proved highly effective for the reaction of the N-PMP imine alone (i.e., full conversion within 6 h).[3b] Thus, the result of this competition may be rationalized by interference of the reaction of the N-PMP imine by stronger coordination of the N–H imine to the cobalt catalyst. Taken together, these competition experiments would point to superior coordination ability of the N–H imine to a low-valent cobalt center regardless of the supporting ligand (i.e., phosphine or phenanthroline). Besides the competition experiments, we also performed alkylation reactions of imines bearing deuterated aryl groups to probe the distribution of the *ortho*-deuterium atoms in the alkylation products (see Scheme S2 in the Supporting Information). Assuming a catalytic cycle involving C–H oxidative addition, alkene insertion into Co–H, and reductive elimination, the results of the deuterium-labeling experiments may be explained by reversibility of the first two steps, generation of linear and branched alkyl cobalt species by the alkene insertion, and exclusive reductive elimination of the linear alkylcobalt species.[23,24]

In summary, we have demonstrated that N–H imine serves as a robust and powerful directing group for cobalt-catalyzed olefin hydroarylation. Benefiting from the ease of preparation, the superior coordination ability, and the minimum steric size, this directing group has enabled a series of hydroarylations which are not possible with N-aryl and N-alkyl imines, including the fourfold *ortho* alkylation of benzophenone imines. Further studies on the use of N–H imines in cobalt-catalyzed and other transition-metal-catalyzed C–H functionalization are currently in progress.

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[18] The primary role of $t$BuCH$_2$MgBr is to reduce the Co$^{II}$ precatalyst to a low-valent Co species (presumably with the oxidation state of Co$^0$; see Ref. [3c]). While the reason for the necessity of a greater amount (50 mol %) of $t$BuCH$_2$MgBr than required for the reduction (e.g., 20 mol % for 10 mol % of Co$^{II}$) is not clear, we consider it less likely that the excess Grignard reagent acts as a base to deprotonate the N−H or C−H protons.

[19] See Table S1 for the result of monitoring of the reaction progress. We identified that the dialkylation product bears one alkyl group on each aryl ring (rather than two alkyl groups on one aryl ring; Scheme S1).

[20] a) F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, S. Murai, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62 – 83; b) C. P. Lenges, M. Brookhart, *J. Am. Chem. Soc.* **1999**, *121*, 6616 – 6623; c) K. Tsuchikama, M. Kasagawa, Y. K. Hashimoto, K. Endo, T. Shibata, *J. Organomet. Chem.* **2008**, *693*, 3939 – 3942.

[21] For a related tetraalkylation of anthraquinone derivatives, see: D. Matsumura, K. Kitazawa, S. Terai, T. Kochi, Y. Le, M. Nitani, Y. Aso, F. Kakiuchi, *Org. Lett.* **2012**, *14*, 3882 – 3885.

[22] Without pyridine, the reactions of 1-alkenes became sluggish. In contrast, the reactions in Table 2 were slowed by the addition of pyridine. While we consider that pyridine acts as a ligand to cobalt, we do not understand its exact role (e.g., to accelerate the alkylation reaction, to prevent deactivation of the catalyst, or both).

[23] The C−H activation and the alkene insertion may take place in a single step by a ligand-to-ligand hydrogen transfer (LLHT) mechanism (see Refs [3g–i] and [24]). Even if that is the case, the present deuterium labeling experiments would also suggest the reversibility of the LLHT process.

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