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Methylation of C(sp^3)−H/C(sp^2)−H Bonds with Methanol Catalyzed by Cobalt System

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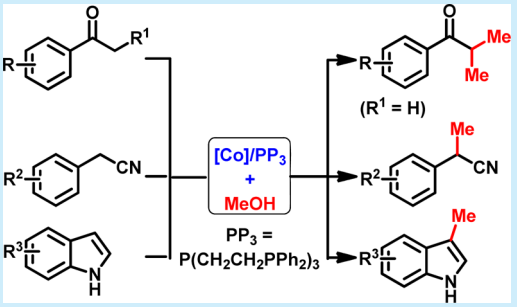
Supporting Information

ABSTRACT: A highly efficient Co-based catalytic system, composed of a commercially available Co salt, a tetradentate phosphine ligand P(CH$_2$CH$_2$PPh$_2$)$_3$(PP$_3$), and a base (denoted as [Co]/PP$_3$/base), is developed for the methylation of C(sp^3)−H and C(sp^2)-H bonds using methanol as a methylating reagent. The Co(BF$_4$)$_2$·6H$_2$O/PP$_3$/K$_2$CO$_3$ catalytic system showed high catalytic activity for the methylation of C−H bonds in aryl alkyl ketones, aryl acetonitriles, and indoles, with wide substrate scope and good functional group tolerance, and methyl-substituted products were obtained in good to excellent yields at 100 °C. This cheap, readily available, and highly efficient Co-based catalytic system may have promising applications in methylation reaction using methanol.



Direct functionalization of C−H bonds of organic compounds is an attractive method for efficient synthesis of biologically active compounds in terms of atom-, step-, and redox-economy.[1] Most of the developed C−H functionalization reactions employ second- and third-row transition metals, such as Pd, Rh, Ru, and Ir complexes, as catalyst. Earth-abundant and inexpensive first-row transition-metal catalysts recently attracted much attention in the area of C−H activation/functionalization reactions.[2] Co is analogous to Rh and is a promising catalyst in this aspect.[3]

The methylation reaction is one of the most essential chemical transformations in organic synthesis for the discovery of new molecules and pharmaceutical ingredients,[4] and development of methyl functionalization is therefore a topic of current interest. However, the methylation of relatively inert C(sp^3)-H bonds in ketones is challenging.[5] In this regard, methanol as an abundant simple aliphatic alcohol and biodegradable liquid has been used as C1 source.[4a,5c,6] In addition, the use of the hydrogen-transfer approach using methanol offers a convenient protocol that has been applied to regioselective methylation of C−H bonds in ketones.[5a−d,7] Importantly, the methylated products are ubiquitous in many drug- and biomolecules, and this motif plays a vital role in their activities (Scheme S1).[8] Generally, homogeneous catalysts based on expensive and rare second/third-row transition-metal catalysts such as Rh, Ir, and Ru have been developed.[5a−d,7] In 2014, Donohoe et al. reported the [Cp*RhCl$_2$]$_2$-catalyzed methylation of ketones using methanol under mild conditions (65 °C) with relatively high catalyst loading (5−7.5 mol %) and an excess amount of Cs$_2$CO$_3$ (Scheme S2a).[5c] Later, [Cp*IrCl$_2$]$_2$ was utilized for the methylation of ketones with methanol in the presence of base (e.g., KOH) (Scheme S2b)[5b] or in combination with a monodentate phosphine ligand (Scheme S2c).[5a] Another Ir-based catalytic system, N-heterocyclic carbene (NHC)/phosphine Ir complex, was also found to be efficient for the methylation of ketones using methanol (Scheme S2d).[5d] Seayad et al. showed that [Cp*RuCl$_2$]$_2$/dpephos along with LiO^{t}Bu showed good catalytic efficiency for the α-methylation of ketones (Scheme S2e).[5e] Although these systems provided good activity, the procedures were all based on noble metal complexes. The replacement of the scarce and expensive noble metals by cheaper, more abundant, and less toxic first-row transition metals, such as Co, would enhance the sustainability of the methylation reaction with methanol, which was rarely reported up to now.

Herein, we developed a highly efficient, Co-based catalytic system, composed of a commercially available Co salt and a tetradentate phosphine ligand P(CH$_2$CH$_2$PPh$_2$)$_3$(PP$_3$) together with a base, denoted as [Co]/PP$_3$/base, for the methylation of C(sp^3)−H bonds in aryl alkyl ketones and aryl acetonitriles, as well as C(sp^2)−H bonds in indoles using methanol as a methylating reagent (Schemes 1). In particular, the Co(BF$_4$)$_2$·6H$_2$O/PP$_3$/K$_2$CO$_3$ catalytic system showed high catalytic activity with wide substrate scope and good functional group tolerance, and various kinds of methyl-substituted products were obtained in good to excellent yields at 100 °C. The

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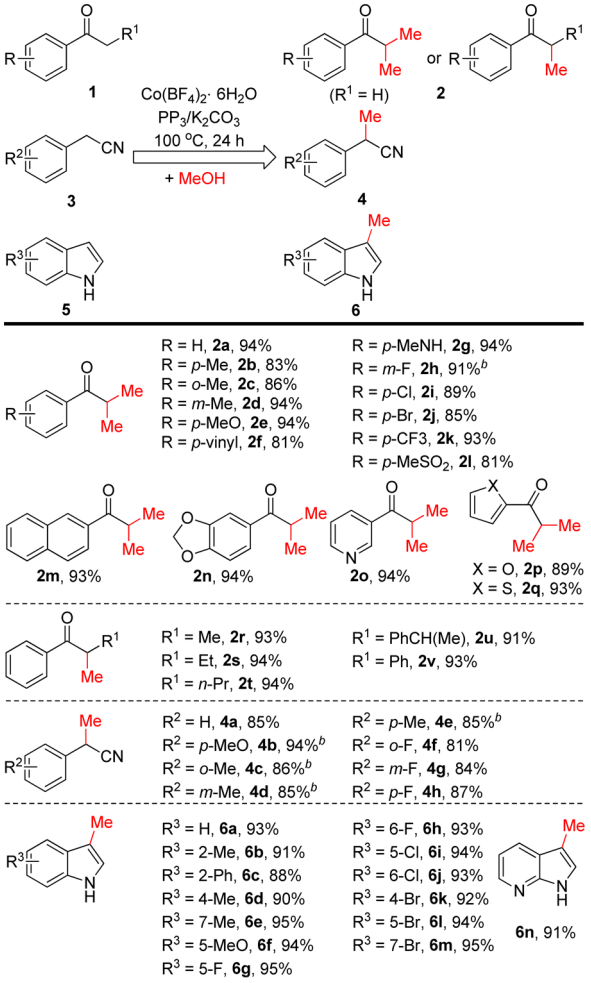
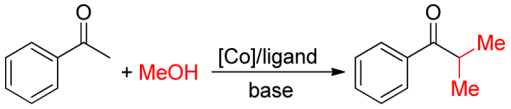
Scheme 1. Methylation of C(sp^3)−H Bonds in Ketones and Nitriles and C(sp^2)−H Bonds in Indoles with MeOH[a]



[a]Reaction conditions: ketone **1**, nitrile **3**, or indole **5** (1 mmol), $Co(BF_4)_2{\cdot}6H_2O$ (1 mol %), PP_3 (1 mol %), K_2CO_3 (1 mmol), MeOH (3 mL), 100 °C, 24 h, unless otherwise stated. [b]$Co(BF_4)_2{\cdot}6H_2O$ (2.5 mol %), PP_3 (2.5 mol %), 48 h. All yields given were isolated yields. For details of yields determination and products characterization, see the SI.

Table 1. Cobalt-Catalyzed *N*-Methylation of Acetophenone (1a) with MeOH[a]



entry	[Co]	base	1a conversion[b] (%)	2a yield[b] (%)
1[c]			<1	<1
2	$Co(acac)_2$	Cs_2CO_3	91	82
3		Cs_2CO_3	7	0
4[c]	$Co(acac)_2$	Cs_2CO_3	2	0
5	$Co(acac)_2$		2	0
6	$Co(BF_4)_2{\cdot}6H_2O$	Cs_2CO_3	90	85
7	$Co(ClO_4)_2\ 6H_2O$	Cs_2CO_3	89	85
8	$CoCl_2{\cdot}6H_2O$	Cs_2CO_3	90	83
9	$CoBr_2$	Cs_2CO_3	91	83
10	CoF_2	Cs_2CO_3	82	78
11	$Co(NO_3)_2{\cdot}6H_2O$	Cs_2CO_3	88	80
12	$Co(OAc)_2{\cdot}4H_2O$	Cs_2CO_3	83	78
13	$Co_2(CO)_8$	Cs_2CO_3	3	0
14	$Fe(BF_4)_2\ 6H_2O$	Cs_2CO_3	5	0
15	$Co(BF_4)_2{\cdot}6H_2O$	CsOH	92	86
16	$Co(BF_4)_2{\cdot}6H_2O$	CsOAc	4	0
17	$Co(BF_4)_2{\cdot}6H_2O$	K_2CO_3	100	98
18	$Co(BF_4)_2{\cdot}6H_2O$	Na_2CO_3	7	0
19	$Co(BF_4)_2{\cdot}6H_2O$	Li_2CO_3	2	0
20	$Co(BF_4)_2{\cdot}6H_2O$	KOH	84	79
21	$Co(BF_4)_2{\cdot}6H_2O$	KO^{t}Bu	93	87
22	$Co(BF_4)_2{\cdot}6H_2O$	K_3PO_4	97	91
23[d]	$Co(BF_4)_2{\cdot}6H_2O$	K_2CO_3	100	>99
24[e]	$Co(BF_4)_2{\cdot}6H_2O$	K_2CO_3	92	88
25[d,f]	$Co(BF_4)_2{\cdot}6H_2O$	K_2CO_3	95	88
26[d,g]	$Co(BF_4)_2{\cdot}6H_2O$	K_2CO_3	100	>99
27[d,g,h]	$Co(BF_4)_2{\cdot}6H_2O$	K_2CO_3	93	89

[a]Reaction conditions: **1a** (1 mmol), Co species (5 mol %), PP_3 (5 mol %), base (1 mmol), MeOH (3 mL), oil bath 140 °C, 24 h. [b]Determined by GC using dodecane as an internal standard. [c]No PP_3. [d]100 °C. [e]80 °C. [f]K_2CO_3 (0.5 mmol). [g]$Co(BF_4)_2{\cdot}6H_2O$ (1 mol %), PP_3 (1 mol %). [h]Reaction time 12 h.

reaction mechanism exploration indicated that the methylation of ketone went through a hydrogen-borrowing process with an enone as an intermediate.

Initially, the methylation of acetophenone (**1a**) with methanol was selected as a model reaction to optimize the reaction conditions. As shown in Table 1, almost no isobutyrophenone (**2a**) was formed when a blank experiment was performed in the absence of any catalyst and base at 140 °C within 24 h (<1%) (Table 1, entry 1). Interestingly, $Co(acac)_2$ in combination with the PP_3 ligand and Cs_2CO_3 base afforded a **2a** yield of 82% (Table 1, entry 2), indicating the high efficiency of this cobalt-based catalytic system. The methylation reaction of **1a** hardly occurred in the absence of $Co(acac)_2$, or PP_3, or Cs_2CO_3 (Table 1, entries 2 vs 3−5), suggesting that all the three components were indispensable for obtaining high **2a** yield. To get the optimal catalytic system, the Co catalysts, ligands, and bases were explored at 140 °C, respectively. $Co(BF_4)_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $CoBr_2$, CoF_2, $Co(NO_3)_2{\cdot}6H_2O$ and $Co(OAc)_2{\cdot}4H_2O$ were all efficient for the reaction in the presence of PP_3 and Cs_2CO_3, affording **2a** in yields of 78−85% (Table 1, entries 6−12), while $Co_2(CO)_8$ was inactive (Table 1, entry 13). For comparison, $Fe(BF_4)_2{\cdot}6H_2O$ was examined as well, but showed no catalytic activity (Table 1, entry 14). Hence, $Co(BF_4)_2{\cdot}6H_2O$ was selected as the Co catalyst for further investigation owing to its higher catalytic activity compared to other Co catalysts.

The base had significant influence on the reaction (Table 1, entries 6, 15−22). CsOH exhibited comparable activity to Cs_2CO_3, affording a **2a** yield of 86%, while CsOAc hardly showed activity (entries 6, 15, 16). Examination of other alkali metal carbonates, including K_2CO_3, Na_2CO_3, and Li_2CO_3, demonstrated that K_2CO_3 afforded a **2a** yield of 98% (Table 1, entry 17), showing better performance than Cs_2CO_3, while Na_2CO_3 and Li_2CO_3 were inactive (Table 1, entries 18, 19). These results suggested that potassium salts might be more favorable to the reaction. Subsequently, K_3PO_4, KO^{t}Bu, and KOH, were detected, which all promoted the methylation of **1a** (**2a** yields 79−91%, entries 20−22), showing activities slightly lower than that of K_2CO_3. Notably, though KOH has higher basicity than K_2CO_3, it displayed lower catalytic activity (Table 1, entries 17 vs 20), while K_3PO_4 showed comparable activity to

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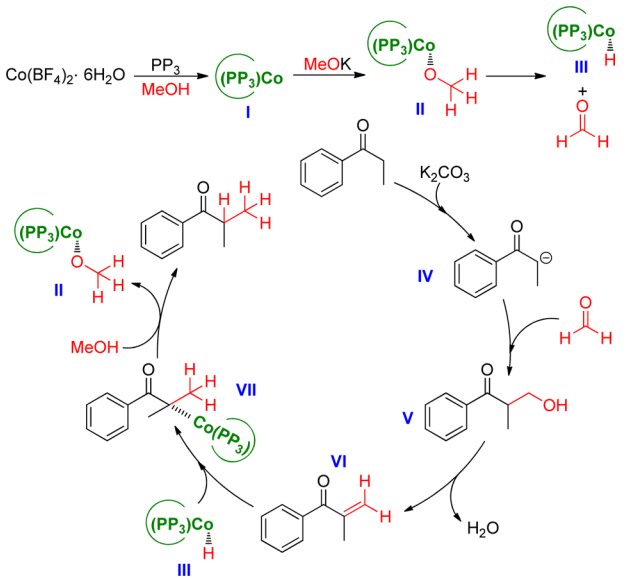
K_2CO_3 (Table 1, entries 17 vs 20, 22). The above results indicated that K_2CO_3 was the most suitable base. Other ligands, including commercially available tri-, bi-, and monodentate phosphine ligands (e.g., triphos, dppe, and PPh_3) and nitrogen-containing ligands, (e.g., biPy or *o*-phenanthroline), were explored for the methylation of **1a**, among which none afforded appreciable amounts of **2a** (Table S1, entries 1−5), indicating that PP_3 was an exclusively effective ligand for this reaction.

On the basis of the above results, a catalytic system, composed of $Co(BF_4)_2{\cdot}6H_2O$, PP_3 and K_2CO_3, was used to explore the optimal reaction conditions. The appropriate reaction temperature was critical to achieve high catalytic efficiency (Table 1, entries 17, 23, 24). The yield of **2a** reached >99% when the temperature decreased to 100 °C, while further decreasing the temperature to 80 °C led to slightly low yield of **2a** (88%). At 100 °C, decreasing the K_2CO_3 amount to 0.5 equiv resulted in a **2a** yield of 88% (Table 1, entry 25), while the yield of **2a** remained constant as the loading of $Co(BF_4)_2{\cdot}6H_2O$ and PP_3 decreased to 1 mol % (Table 1, entry 26). Though the yield of **2a** reached 89% within 12 h (Table 1, entry 27), a reaction time of 24 h was used to ensure the complete conversion of **1a**. For further detailed screening of various reaction parameters, see Table S1. Therefore, the optimized reaction conditions for the methylation of C−H bonds are obtained as shown in Scheme 2.

Scheme 2. Proposed Reaction Mechanism for the Methylation of C(sp^3)−H Bond in Acetophenone Using Methanol



Taking the optimal reaction conditions in hand, the methylation of C(sp^3)−H bonds in a broad range of acetophenone derivatives was investigated (Scheme 1). Besides acetophenone (**1a**), methylation of the derivatives with both electron-donating and electron-withdrawing groups on the benzene ring was also performed well, selectively producing dimethylated products in good to excellent yields (81−94% for **2a**−**l**). No obvious difference in reactivity was observed between acetophenone substrates with electron-donating groups (CH_3−, CH_3O−, CH_2=CH−, MeNH−) and those with electron-withdrawing groups (F−, Cl−, Br−, CF_3−, CH_3SO_2−). The reactivity of the acetophenones with a methyl group at different positions on the benzene ring increased in the order of *para*- (**1b**) < *ortho*- (**1c**) < *meta*- (**1d**). The vinyl group is easily reduced by many reductants (e.g., H_2, hydrosilanes, or boranes). However, herein, the vinyl group on the benzene ring of **1f** was well preserved, and **2f** was obtained in 81% yield. For substrate **1g**, with a methylamino group, the product **2g** was obtained in a yield of 94%. Dehalogenation was generally observed for substrates with halogen substituents, especially in reactions involving strong base/transition-metal species or those conducted under high temperature. In this work, no dehalogenation occurred in the methylation of the substrates with halogen substituents (e.g., F−, Cl−, and Br−) on the benzene ring, and the corresponding dimethylated products **2h**−**j** were obtained in high yields (85−91%) as well. This indicated that the present catalytic system was tolerant to dehalogenation under the experimental conditions. The acetophenone derivatives, with other bulky electron-withdrawing groups on the benzene ring (e.g., CF_3^- and $CH_3SO_2^-$), also showed high reactivity, achieving a 93% yield of **2k** and 81% yield of **2l**, respectively. Moreover, 2-acetonaphthone (**1m**) also exhibited high reactivity, with a 93% yield of **2m** being achieved. 3,4-Methylenedioxyacetophenone (**1n**), with an oxygen-containing cyclic ring, led to the corresponding dimethylated product **2n** in 94% yield. Ketones with nitrogen-, oxygen-, or sulfur-containing heterocyclic rings (**1o**−**q**) were also well methylated by the catalytic system, producing **2o**−**q** in yields of 89−94%.

Subsequently, the methylation of *α*-substituted acetophenone derivatives with a high degree of steric hindrance was performed (Scheme 1). Propiophenone (**1r**), butyrophenone (**1s**), or valerophenone (**1t**), with a methyl, ethyl, or propyl group at the *α*-position, respectively, all exhibited excellent reactivity, affording monomethylated products (**2r**−**t**) in excellent yields of 93−94%. Notably, the sterically hindered substrates 1,3-diphenyl-1-butanone (**1u**) and 2-phenylacetophenone (**1v**) also showed excellent reactivity, with yields of the corresponding monomethylated products achieving 91% (**2u**) and 93% (**2v**), respectively, probably due to stabilization of the intermediates by the aromatic ring, as shown in the proposed mechanism (Scheme 2).

To explore the versatility of this catalytic system, it was applied in the methylation of C(sp^3)-H bond of phenylacetonitriles (Scheme 1). For methylation of benzeneacetonitrile (**3a**), *α*-methylphenylacetonitrile (**4a**) was obtained in a yield of 85%. Benzene acetonitrile derivatives with an electron-withdrawing group (F−) (**3f**−**h**) on the benzene ring also performed well, with the monomethylated products (**4f**−**h**) being obtained in 81−87% yields. Comparatively, the reactivity of benzeneacetonitrile derivatives with electron-donating groups (Me−, MeO−, **3b**−**e**) was inferior, giving 85−94% yields of **4b**−**e** under harsher reaction conditions, probably owing to the weaker acidity of the *α*-methylene group.

This catalytic system was also very effective for the methylation of C(sp^2)−H bonds in indoles (Scheme 1). Using indole (**5a**) as the substrate, 3-methyl-1*H*-indole (**6a**) was obtained in a yield of 93%, higher than that obtained over the Ru complex in the presence of CO_2/H_2.[9] For the substrates with a methyl or phenyl group at the 2-position, the 3-methyl-substituted products **6b** and **6c** were obtained in isolated yields of 91% and 88%, respectively. The indoles with electron-donating groups on the benzene ring at different positions gave rise to excellent product yields (90−95% for **6d**−**f**). Moreover,

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the indoles with halogen substituents (including F−, Cl−, Br−) all showed high reactivity, achieving 92−95% yields for **6g−m** without dehalogenated byproducts being detected. 7-Azoindole (**5n**) also displayed high reactivity, giving **6n** in a yield of 91%.

To explore the possible reaction mechanism, some control experiments and deuterium-labeling experiments were performed. For the methylation of acetophenone, 2-methyl-1-phenylprop-2-en-1-one (**VI** in Scheme 2) was reported to be a possible intermediate.[5c] In this work, using **VI** as the substrate, nearly quantitative yield of isobutyrophenone (**2a**) was obtained in the presence of $Co(BF_4)_2{\cdot}6H_2O/PP_3$ with or without K_2CO_3 (Scheme S3a). Hence, it suggested that the base was only needed for the formation of **VI** from acetophenone and played no role in the subsequent hydrogenation step. As shown in Scheme S3b−e, the methylation of **1a** occurred in the presence of $Co(BF_4)_2{\cdot}6H_2O/PP_3/K_2CO_3$ in CD_3OD (Scheme S3b), giving hexa- and heptadeuterium-substituted products **2a**, which indicated that the C−H bond at the α-position of the substrate broke during the reaction process and the methyl group was surely supplied by methanol. In addition, the formation of the new C−H/D bond at the α-position (**1a**) was through hydrogen transfer from cobalt-hydride intermediate, which went through H/D exchange with byproduct H_2O during the reaction process. This was further verified by the methylation reaction of **1a** with CH_3OD under otherwise identical reaction conditions, in which unsubstituted and mono-, di-, and trideuterium-substituted products **2a** were obtained (Scheme S3c). When propiophenone was utilized as the substrate, monomethylated product was formed. Hence, tri- and tetradeuterium substituted products **2a** were formed with CD_3OD as the solvent (Scheme S3d), while unsubstituted and mono- and dideuterium-substituted products **2a** were detected in the presence of CH_3OD (Scheme S3e). This was consistent with the proposed reaction process involving 2-methyl-1-phenylprop-2-en-1-one (**VI** in Scheme 2) formation, monohydride transfer, and H/D exchange between methanol and the byproduct H_2O.

Taking the methylation of propiophenone using methanol as an example, a possible reaction pathway was proposed on the basis of the above results, as illustrated in Scheme 2. First, in the presence of the base, the Co salt coordinated with PP_3 to yield complex (**I**), and a Co−methoxy complex (**II**) was further formed in methanol, which then transformed into the Co−hydride (**III**) intermediate through β-hydride abstraction, releasing formaldehyde. For the substrate propiophenone, a nucleophilic carbon anion (**IV**) was formed in the presence of the base (K_2CO_3), which then attacked formaldehyde to generate alcohol intermediate (**V**). Intermediate **VI** was then formed through a dehydration reaction, which further coordinated with Co−hydride (**III**) to produce intermediate **VII**. Finally, methylated product **2a** was produced through hydrogen transfer from methanol and recoordination of Co complex with methoxide.

In summary, a readily available and highly efficient cobalt-based catalytic system was developed for the methylation of the $C(sp^3)$−H bond in aryl alkyl ketones/aryl acetonitriles, as well as $C(sp^2)$−H bond in indoles using methanol, and various kinds of methylated products were obtained in good to excellent yields. This type of Co-based catalytic system may find promising applications in methylation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b02462.

Experimental details, Schemes S1−S3, Table S1, as well as isolation and characterization of the products (PDF)

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Notes

The authors declare no competing financial interest.

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