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Synthetic Methods |*Hot Paper*|

Cobalt-Catalyzed Cyclization of *N*-Methoxy Benzamides with Alkynes using an Internal Oxidant through C–H/N–O Bond Activation

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Abstract: The cyclization of substituted *N*-methoxy benzamides with alkynes in the presence of an easily affordable cobalt complex and NaOAc provides isoquinolone derivatives in good to excellent yields. The cyclization reaction is compatible with a range of functional group-substituted benzamides, as well as ester- and alcohol-substituted alkynes. The cobalt complex $[Co^{III}Cp^*(OR)_2]$ (R = Me or Ac) serves as an efficient catalyst for the cyclization reaction. Later, isoquinolone derivatives were converted into 1-chloro and 1-bromo substituted isoquinoline derivatives in excellent yields in the presence of $POCl_3$ or PBr_3.

Transition metal-catalyzed chelation-assisted cyclization of heteroatom-substituted aromatics with carbon–carbon π-bonded components through C–H bond activation is a powerful method to synthesize carbocyclic and heterocyclic molecules in a highly atom- and step-economical manner.[1] Generally, this type of cyclization is carried out in the presence of an external oxidant, which is used for the regeneration of the active catalyst. However, this method leads to a stoichiometric amount of reduced external oxidant as waste. Alternatively, this type of reaction can also be carried out by using an internal oxidant, such as an oxidizing directing group.[2] This type of group plays a dual role in the reaction, in that it acts as a directing group, as well as an oxidant to regenerate the active catalyst. For this type of cyclization, mainly second and third row transition metals such as iridium, palladium, rhodium and ruthenium complexes have been widely used as catalysts. The use of cheaper, more abundant and environmentally benign catalysts is still desirable in C–H bond functionalization reactions. In this context, complexes of cobalt have recently gained much attention for C–H bond functionalization reactions, owing to their low toxicity in comparison with other early transition metals, high abundance, and low cost.[3,4] It is also believed that the catalytic activity of some cobalt complexes would be similar to rhodium and ruthenium complexes. Very recently, isoquinoline derivatives were synthesized efficiently through a cobalt-catalyzed cyclization of aromatic ketoximes with alkynes, using an internal oxidant.[5]

Isoquinolone is a key structural unit that is present in various natural products, biologically active molecules, and pharmaceuticals.[6] Moreover, isoquinolone derivatives are widely used as key intermediates in various organic transformations.[6] Several methods have been reported for the synthesis of isoquinolone derivatives,[7] among which, metal-catalyzed cyclization of aromatic amides or nitriles with alkynes through chelation-assisted C–H bond activation is an efficient method to synthesize isoquinolone derivatives from easily available starting materials with minimal waste.[8] Rhodium, palladium, and ruthenium complexes are widely used as catalysts for this type of transformation. *N*-Alkyl or aryl benzamides reacted with alkynes in the presence of a metal catalyst and stoichiometric amount of external oxidant to provide *N*-alkyl- or aryl-substituted isoquinolone derivatives.[8] Subsequently, a similar transformation was achieved in the reaction of *N*-alkoxy benzamides with alkynes in the presence of rhodium or ruthenium catalysts, with the *N*-OR group as an internal oxidant.[2]

Our continuous interest in the development of versatile C–H bond transformations prompted us to explore the possibility of cyclization of *N*-alkoxy benzamides with alkynes in the presence of an inexpensive cobalt(III) catalyst with an internal oxidant.[9] Herein, we report a cobalt-catalyzed cyclization of substituted *N*-alkoxy benzamides with alkynes in the presence of a catalytic amount of NaOAc, giving isoquinolone derivatives in excellent yields. The catalytic reaction was compatible with substrates incorporating various sensitive functional groups, including I-, Br-, NO_2-, and CN-substituted benzamides, as well as ester- and alcohol-functionalized alkynes.

Treatment of *N*-methoxy 4-methoxybenzamide (**1a**) with diphenylacetylene (**2a**) in the presence of $[CoCp^*(CO)I_2]$ (10 mol%) and NaOAc (30 mol%) in 2,2,2-trifluoroethanol (TFE) at 120 °C for 24 h gave isoquinolone derivative **3aa** in 92% yield (isolated product; Scheme 1). In the reaction, the *N*-OMe group of amide **1a** acts as an internal oxidant. Next, the reaction was examined with various *N*-substituted amides **1b–d** (Scheme 1) under similar reaction conditions. In the reactions of **1b** and **1c** with **2a**, the expected cyclization product **3aa** was formed in trace and 41% yield, respectively, whereas substrate **1d** underwent no reaction. This result clearly reveals

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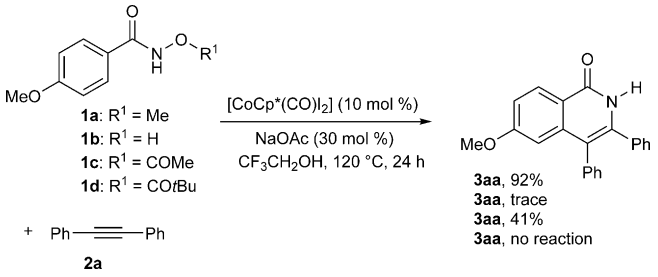


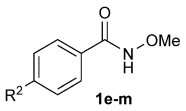
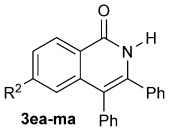
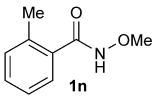
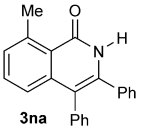
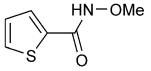
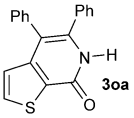
Scheme 1. Cyclization of *N*-substituted benzamides **1a–d** with alkyne **2a**.

that the *N*-OMe acts as an efficient internal oxidant in comparison to other *N*-OR sources.

The choice of solvent is crucial for the success of the reaction. Various solvents, including TFE, dichloroethane (DCE), methanol, *tert*-amyl alcohol, and 1,4-dioxane were examined. In comparison to TFE (92% yield of **3aa**; see above), DCE was less effective for the reaction, giving a 15% yield of isolated product **3aa**. Other solvents were totally ineffective (see the Supporting Information, Table 1). Although the amide's *N*-OMe group acts as an internal oxidant, a catalytic amount of acetate base is necessary to start the catalytic reaction. Thus, the reaction was examined with various bases, including NaOAc, KOAc, CsOAc, AgOAc, and $Cu(OAc)_2{\cdot}H_2O$. NaOAc and KOAc were equally effective for the reaction, giving isolated **3aa** in 92% and 90% yield, respectively. CsOAc, AgOAc, and $Cu(OAc)_2$, were partially effective, providing **3aa** in 45%, 50% and 15% yields, respectively. The reaction temperature of 120 °C was also crucial to optimizing the yield of **3aa**. When reactions were carried out at 60 and 80 °C, **3aa** was obtained in only 40% and 65% yields, respectively.

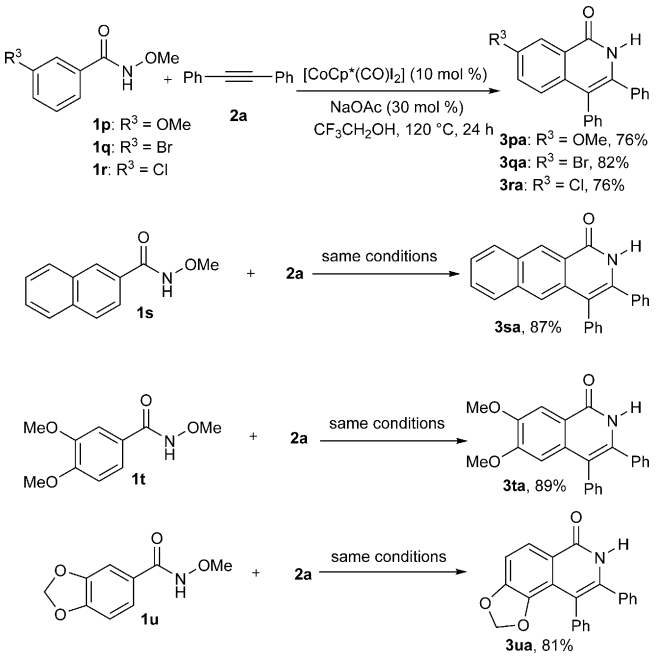
The cyclization reaction was examined with various substituted *N*-methoxy benzamides under the optimized reaction conditions (Table 1). The catalytic reaction was compatible with benzamide substrates incorporating sensitive functional groups such as I, Br, Cl, F, CN, and NO_2. Treatment of *N*-methoxy 4-methyl benzamide (**1e**) and *N*-methoxy benzamide (**1f**) with diphenylacetylene (**2a**) gave the expected isoquinolone derivatives **3ea** and **3fa** in excellent yields (Table 1, entries 1 and 2). *N*-methoxy benzamides **1g-j** with highly sensitive halide substituents such as I, Br, Cl and F also efficiently participated in the reaction, providing isoquinolone derivatives **3ga–ja** in 87–90% yield (Table 1, entries 3–6). Interestingly, *N*-methoxy benzamides **1k–m**, incorporating electron-withdrawing substituents CF_3, CN, and NO_2, reacted with **2a**, yielding isoquinolone derivatives **3ka–ma** in 82–85% yield (Table 1, entries 7–9). *N*-Methoxy *ortho*-methyl benzamide (**1n**) reacted with **2a** to afford isoquinolone derivative **3na** in 86% yield (Table 1, entry 10). The heteroaromatic amide *N*-methoxythiophene-2-carboxamide (**1o**) was also a suitable substrate for the reaction, affording the expected cyclization product **3oa** in 82% yield (Table 1, entry 11). In all of these reactions, the cyclization products were obtained in excellent yields (82–90%) and electronic effect on the aromatic system did not influence the reactivity of the reaction or the yield of product.

Table 1. The reaction of benzamides **1** with diphenylacetylene (**2a**).[a]

Entry	Amide	Product	Yield [%][b]
	 **1e-m**	 **3ea-ma**	
1	**1e**: R^2 = Me	**3ea**: R^2 = Me	90
2	**1f**: R^2 = H	**3fa**: R^2 = H	87
3	**1g**: R^2 = I	**3ga**: R^2 = I	90
4	**1h**: R^2 = Br	**3ha**: R^2 = Br	89
5	**1i**: R^2 = Cl	**3ia**: R^2 = Cl	88
6	**1j**: R^2 = F	**3ja**: R^2 = F	87
7	**1k**: R^2 = CF_3	**3ka**: R^2 = CF_3	84
8	**1l**: R^2 = CN	**3la**: R^2 = CN	85
9	**1m**: R^2 = NO_2	**3ma**: R^2 = NO_2	82
10	 **1n**	 **3na**	86
11	 **1o**	 **3oa**	82

[a] Reaction conditions: **1e–o** (50 mg), diphenylacetylene (**2a**; 1.2 equiv), $[CoCp^*(CO)I_2]$ (10 mol%), and NaOAc (30 mol%) in TFE (3.0 mL) at 120 °C for 24 h; [b] isolated product.

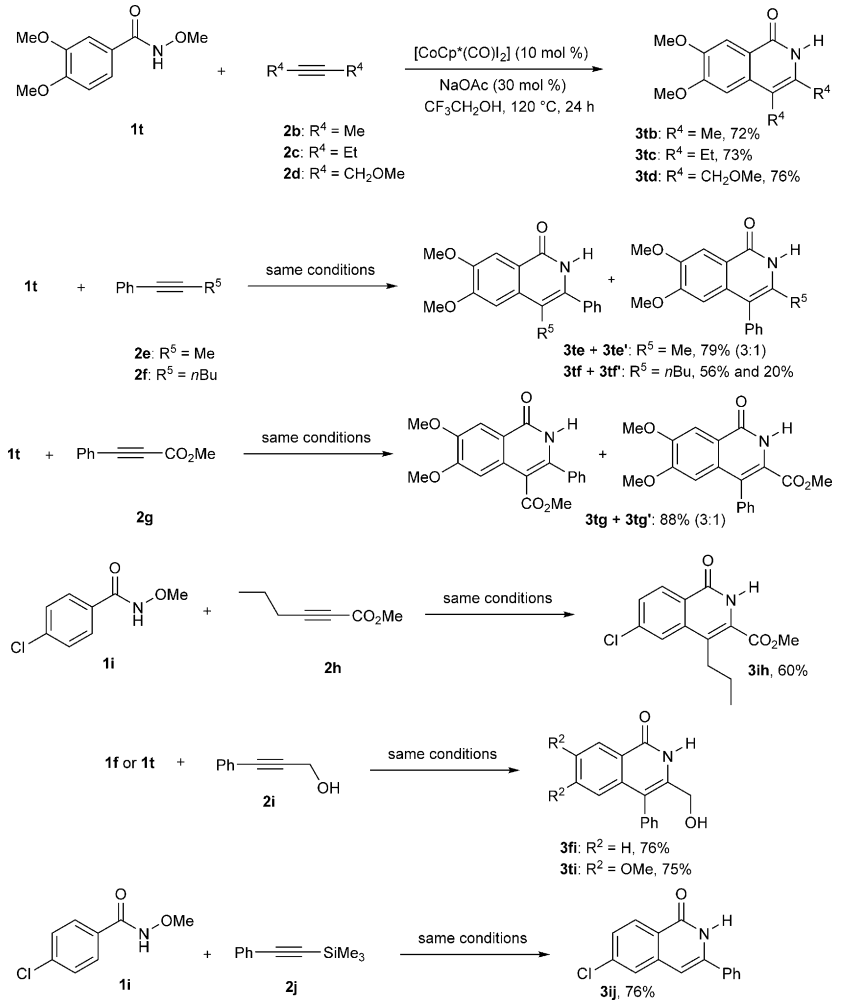
Next, the cyclization reaction was examined with various unsymmetrical benzamides **1p–u** (Scheme 2). In all of these benzamides, there are two C–H bonds for activation. Interestingly, the present cyclization is highly regioselective and only



Scheme 2. Regioselectivity studies.

a single regioselective cyclization product was observed. Thus, *meta*-methoxy-, bromo-, and chloro-substituted *N*-methoxy benzamides (**1p**–**r**) reacted with diphenylacetylene (**2a**) affording the expected isoquinolone derivatives **3pa**–**ra** in 76–82% yield, in which the C–H bond activation selectively takes place at a less hindered C6 position. In a similar fashion, *N*-methoxy-2-naphthamide (**1s**) and *N*-methoxy 3,4-dimethoxy benzamide (**1t**) provided the expected isoquinolone derivatives **3sa** and **3ta** in excellent 87 and 89% yields, respectively, in which the C–H bond activation also takes place selectively at a less hindered side. In contrast, benzamide **1u** reacted with **2a** under similar reaction conditions affording the expected cyclization product **3ua** in 81% yield, in which the C–H bond activation selectively takes place at the hindered C2 position. It is possible that, owing to the dual coordination of an ether O atom and the nitrogen atom of amide **1u**, the cyclization takes place at C2 (see the Supporting Information, page 4), whereas in the substrate **1t**, the C–H bond activation takes place at the less hindered side (C6). This is probably due to the steric hindrance of the methyl group of OMe.[9e]

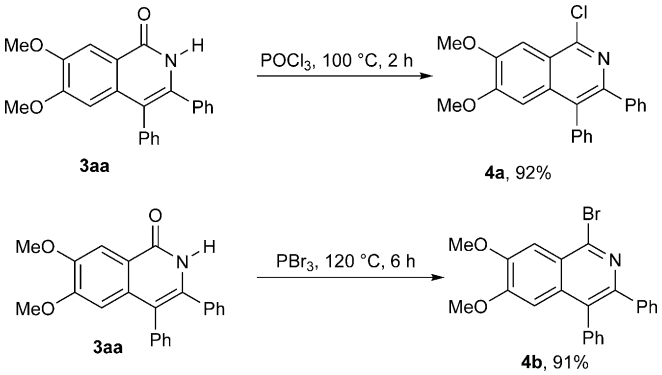
The scope of the cyclization reaction was further examined with various symmetrical and unsymmetrical alkynes (Scheme 3). Less reactive symmetrical alkynes, such as 2-butyne (**2b**), 3-hexyne (**2c**) and 1,4-dimethoxybut-2-yne (**2d**), reacted efficiently with **1t**, providing cyclization products **3tb**–**td** in 72–76% yield (Scheme 3). Unsymmetrical alkynes, such as 1-phenyl-1-propyne (**2e**) and 1-phenyl-1-hexyne (**2f**) reacted with **1t**, giving mixtures of cyclization products **3te** and **3te′** in 79% total yield in a 3:1 ratio and **3tf** and **3tf′** in a separable 56% and 20% yields, respectively. Methyl 3-phenylpropiolate (**2g**) reacted with **1t**, providing mixtures of cyclization products **3tg** and **3tg′** in 88% yield in a 3:1 ratio. Interestingly, in the cyclization of methyl hex-2-ynoate (**2h**) with **1i**, only a single regioisomeric cyclization product **3ih** was obtained in 60% yield. In the reaction, the C–H bond of **1i** was connected at the alkyl-substituted carbon of alkyne **2h** (see the Supporting Information for NOE studies). Furthermore, in the cyclization of 3-phenylprop-2-yn-1-ol (**2i**) with **1f** or **1t**, the expected cyclization products **3fi** and **3ti** were obtained in 76% and 75% yields, respectively, in a highly regioselective manner. In the reaction, the C–H bond of **1t** was connected at the Ph-substituted carbon of alkyne **2i** (see the Supporting Information for NOE studies). It is important to note that in the previously reported rhodium- and ruthenium-catalyzed reactions,



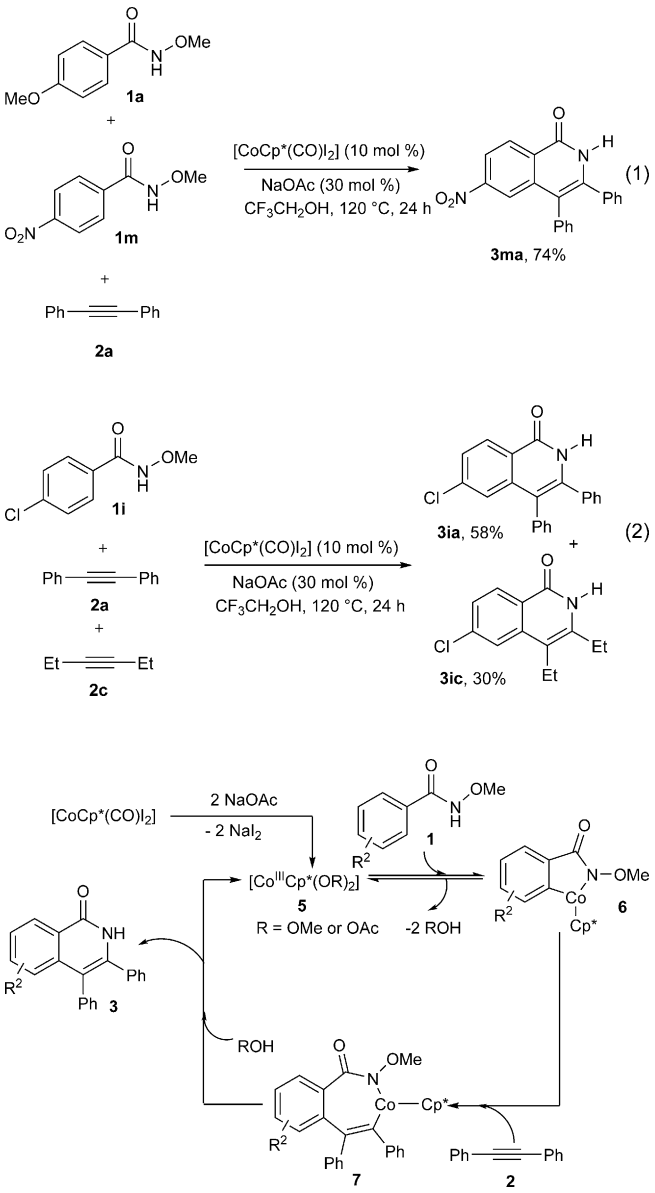
Scheme 3. Scope of alkynes.

the *ortho* C–H bond of aromatic moiety was connected at the CH_2OH substituted carbon of alkyne **2i**.[2b,c] In a similar fashion, 1-phenyl-1-trimethylsilane (**2j**) reacted with **1i** under similar reaction conditions, affording the expected cyclization product **3ij** in 76% yield in a highly regioselective manner. However, a silyl group was cleaved in the product under the reaction conditions. To avoid the $SiMe_3$ cleavage, the cyclization reaction was examined at a lower temperature (80 °C) under similar reaction conditions. However, in this reaction, product **3ij** was obtained in only 45% yield with $SiMe_3$ cleavage. In the reaction, the phenyl group of the alkyne was connected at the nitrogen atom of the amide group of **1i**. Furthermore, the cyclization reaction of **1a** as well as **1c** with terminal alkyne, phenylacetylene, was examined under the optimized reaction conditions at 120 °C, as well as at 80 °C. However, no cyclization product was obtained.

Isoquinolone derivatives can be used as a key synthetic precursor for various organic transformations.[6] In particular, highly useful 1-chloro and 1-bromo isoquinoline derivatives can be prepared easily from isoquinolone derivatives. Treatment of **3aa** with $POCl_3$ at 100 °C for 2 h gave 1-chloroisoquinoline derivative **4a** in 92% yield (Scheme 4). Similarly, **3aa** reacted with PBr_3 at 120 °C for 6 h to give 1-bromoisoquinoline derivative **4b** in 91% yield (Scheme 4).



Scheme 4. Synthesis of 1-halo isoquinoline derivatives.



Scheme 5. Proposed mechanism. R = Me or Ac.

To investigate the mode of reactivity of benzamides and alkynes, intermolecular competitive experiments were performed. Treatment of **1a** (1.0 equiv) and **1m** (1.0 equiv) with **2a** (1.0 equiv) under the optimized reaction conditions gave only product **3ma** in 74% yield [Eq. (1)]. Product **3aa** was not formed. This result clearly reveals that the reactivity of electron-withdrawing NO_2-substituted benzamide **1m** is more reactive than **1a**. Furthermore, treatment of compound **1i** (1.0 equiv) with **2a** (1.0 equiv) and **2c** (1.0 equiv) under similar reaction conditions gave product **3ia** in 58% yield along with compound **3ic** in 30% yield [Eq. (2)]. This result clearly reveals that the reactivity of **2a** is greater than that of **2c**.

A possible reaction mechanism is proposed in Scheme 5 to account for the present cyclization reaction. NaOAc likely removes the iodide ligand from $[CoCp^*(CO)I_2]$ complex, followed by ligand exchange, giving the active Co^{III} species **5**. Coordination of the nitrogen atom of **1** into a cobalt species **5** followed by *ortho*-metalation provides a five-membered cobaltacycle intermediate **6** and ROH. Coordinative insertion of alkyne **2** into the Co–C bond of intermediate **6** provides intermediate **7**. Reductive elimination followed by cleavage of the N–OMe bond of intermediate **7** in the presence of ROH gives cyclization product **3** and regenerates the active cobalt species **5** for the next catalytic cycle. In the reaction, only 30 mol% of NaOAc was used as an external acetate source to start the catalytic reaction. For the remaining conversion, the *N*-OMe group of the amide, as well as ROH, acts as a base to deprotonate the amide N–H bond and the *ortho* C–H bond of the benzamide.

In conclusion, we have described an inexpensive cobalt-catalyzed route to the cyclization of *N*-methoxy-substituted benzamides with alkynes providing isoquinolone derivatives in good to excellent yields. Thereafter, isoquinolone derivatives were

converted into highly useful 1-chloro- and 1-bromo-substituted isoquinoline derivatives in excellent yields.

Experimental Section

General procedure for the cyclization of *N*-substituted benzamides: In a 15 mL pressure tube, *N*-substituted benzamide (50 mg), [Cp*Co(CO)I_2] (10 mol%), NaOAc (30 mol%) and, if solid, alkyne [for example, diphenylacetylene **2a** (1.2 equiv)] were added. The tube was sealed with a septum and then evacuated and purged with nitrogen gas three times. To the tube were then added trifluoroethanol (TFE; 3.0 mL) and, if liquid, alkyne (**2b–j**; 1.2 equiv) via syringe and the tube was evacuated and purged with nitrogen gas three times. After that, the septum was removed and immediately replaced with a screw cap. Then, the reaction mixture was allowed to stir at 120 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite and silica gel, and the filtrate was concentrated under reduced pressure. The crude residue was purified by columbn chromatography on silica gel with ethyl acetate in dichloromethane (for ratios, see the Supporting Information) as eluent to give pure product **3**.

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Keywords: annulation · C–H activation · cobalt · heterocycles · homogeneous catalysis

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