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Cycloaddition

[HCo(CO)$_4$]-Catalyzed Three-component Cycloaddition of Epoxides, Imines, and Carbon Monoxide: Facile Construction of 1,3-Oxazinan-4-ones**

*Lixia Liu and Huailin Sun**

Abstract: *The three-component [3+2+1] cycloaddition of epoxides, imines, and carbon monoxide to produce 1,3-oxazinan-4-ones has been developed by using [HCo(CO)$_4$] as the catalyst. The reaction occurs for a wide variety of imines and epoxides, under 60 bar of CO pressure at 50 °C, to produce 1,3-oxazinan-4-ones with different substitution patterns in high yields, and provides an efficient and atom-economic route to heterocycles from simple and readily available starting materials. A plausible mechanism involves [HCo(CO)$_4$]-induced ring-opening of the epoxide, followed by sequential addition of carbon monoxide and the imine, and then ring closure to form the product accompanied by regeneration of [HCo(CO)$_4$].*

Transition-metal-catalyzed multicomponent cycloadditions (MCCs) are among the most efficient methodologies for the synthesis of heterocycles as it has the advantages of both cycloadditions and multicomponent reactions, namely atom economy and multibond formation in one step.[1–3] This strategy is especially desired for the synthesis of heterocycles, having increased ring sizes, using relatively simple and readily available starting materials. The key to such syntheses is the incorporation of the heteroatom-containing substrates into the cyclic adducts, together with those commonly used to construct carbocycles through MCCs. To date, many types of heterocyclic structures containing a single heteroatom, such as oxygen- or nitrogen-containing five- and six-membered rings,[4–9] have been synthesized by MCCs. However, syntheses of heterocycles with more than one heteroatom within the cyclic skeleton require the incorporation of more heteroatom-containing substrates, and such methods have rarely been reported.

Recently, Arndsten and co-workers reported syntheses of Münchnones,[10] imidazoles,[11] imidazolines,[12] and imidazolones[13] by palladium-catalyzed multicomponent cyclization methods. Alper and co-workers have described formation of benzo[*e*]-1,3-oxazin-4-one and 4(3H)-quinazolinone derivatives through similar palladium-catalyzed reactions.[14] Petricci and co-workers have also demonstrated the construction of benzo[*d*]-1,3-oxazin-6-ones by similar multicomponent reactions.[15] While these reactions are quite efficient, they all involve elimination of small molecules as by-products. A transition-metal-catalyzed MCC involving incorporation of two isocyanates to form pyrimidine-2,4-diones has been developed by Louie et al.,[16] Kondo et al.,[9b] and Murakami et al.[17] However, the only transition-metal-catalyzed MCC which incorporates two different heteroatom-containing substrates, without losing any atoms, is reported by the group of Coates, and it employs epoxides, isocyanates, and carbon monoxide (CO) as starting materials to give 1,3-oxazinane-2,4-diones.[18] To date, synthesis of other heterocycles by sequential addition of different heteroatom-containing substrates still remains a challenge for MCC methods.

Herein we report a new transition-metal-catalyzed MCC which uses epoxides, imines, and CO as building blocks to construct 1,3-oxazinan-4-ones (**1**). This heterocycle is useful as a key intermediate in the total synthesis of natural products,[19] or as a precursor for the synthesis of β-hydroxy acids,[20] β-hydroxy esters,[21] β-hydroxy amides,[22] α,β-epoxy-carboxylic acids,[23] and 1,3-amino alcohol derivatives,[24] all of which are valuable synthetic intermediates for the synthesis of pharmaceutically important compounds. To date there are only two major synthetic routes to such heterocycles, including acid-catalyzed dehydration-condensation of various aldehydes or ketones with appropriate hydroxy amides,[25] and hetero-Diels–Alder cycloadditions between aldehydes and 2-aza-3-silyloxy-1,3-butadienes.[26] While these approaches are widely used, they often require multiple steps owning to the fact that the reactants are not easily obtained by classical routes, thus, making substrate variation difficult to achieve. In contrast, the present MCC method turns out to be a much more convenient and versatile methodology for the synthesis of a wide variety of substituted derivatives of **1** from the readily available starting materials.

In the course of our study on alternating copolymerization of imines and CO to synthesize polypeptides,[27] we used the silylcobalt complex [Ph$_3$SiCo(CO)$_4$] (**2**) as a precatalyst, which upon reacting with oxirane and CO may generate an acylcobalt species to act as the catalyst for the copolymerization reaction. To our surprise, when oxirane (**3a**) and the pivaladehyde imine **4a** were treated with catalytic amounts of **2** under 60 bar of CO pressure, a large amount of a crystalline solid, which was characterized to be 2-*tert*-butyl-3-methyl-1,3-oxazinan-4-one (**1a**) rather than the desired polypeptide, was obtained (Scheme 1). The structure of **1a** was unambiguously confirmed by single-crystal X-ray diffraction analysis in addition to ^{1}H and ^{13}C NMR spectroscopy, as well as IR and

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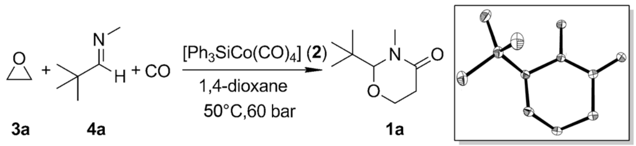


Scheme 1. The three-component [3+2+1] cycloaddition of epoxides, imines, and CO with [Ph$_3$SiCo(CO)$_4$] (**2**) as the catalyst.

HRMS analyses (see the Supporting Information). Thus, a three-component [3+2+1] cycloaddition of epoxides, imines, and CO to form 1,3-oxazinan-4-one has taken place.

This result lead us to pay attention to a report from Jia,[28] in which it was revealed that the reaction of acetylcobalt tetracarbonyl with phenylaldehyde imines, followed by addition of propylene oxide and CO could give rise to 2-phenyl-3-alkyl-1,3-oxazinan-4-one, although no information about the yield and experimental details were provided. We examined the reaction by using phenoxyacetylcobalt tetracarbonyl to react with **3a** and **4a** in the presence of CO.[29] Only a small amount of **1a** could be obtained, and the polypeptide turned out to be the major product. This reaction demonstrated that the acylcobalt complex could not effectively catalyze the three-component cycloaddition of oxirane, imines and CO.

To gain insight into the details of the **2**-catalyzed cycloaddition, in situ IR spectroscopy was used to monitor the reaction. An initiation period of about 50 minutes was observed before consumption of **4a**, and then the reaction proceeded smoothly to give **1a** as the product. This induction period is quite similar to the phenomena observed by Coates and co-workers, involving ring-opening of tetrahydropyran by **2** to form an alkylcobalt, which underwent β-hydrogen elimination to produce [HCo(CO)$_4$], the catalyst for subsequent reactions.[30] Thus, it should be reasonable to hypothesize that **2** might also react with oxirane to generate [HCo(CO)$_4$] as the catalyst for the cycloaddition reaction. This hypothesis was verified by direct application of [HCo(CO)$_4$], which was generated in situ from alcoholysis of **2** with methanol, according to Coates and co-workers, and showed that the cycloaddition proceeded at a markedly higher reaction rate without an induction period to afford **1a** in good yield (Table 1, entry 1). Methods for generation of [HCo(CO)$_4$] and the reaction conditions have been optimized, and the best results were obtained by using **2**/MeOH as the catalyst and toluene as solvent under 60 bar CO at 50 °C, as shown in Table 1.

Table 1: [HCo(CO)$_4$]-catalyzed cycloaddition of **3a**, **4a**, and CO for synthesis of **1a**. A 5 mol% catalyst loading was used and based on the amount of imine used.[a]

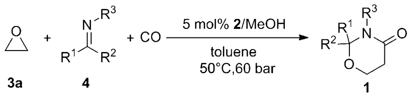
Entry	Catalyst	Solvent	T [°C]	P [bar]	t [h][b]	Yield [%][c]
1	**2**/MeOH	1,4-dioxane	50	60	21.5	68
2	[Co$_2$(CO)$_8$]/H$_2$[d]	1,4-dioxane	50	60	26	60
3	[NaCo(CO)$_4$]/p-TsOH	1,4-dioxane	50	60	24	65
4	**2**/MeOH	1,4-dioxane	50	60	21	78
5	**2**/MeOH	1,4-dioxane	80	60	9	58
6	**2**/MeOH	1,4-dioxane	50	30	24	73
7	**2**/MeOH	THF	50	60	28	80
8	**2**/MeOH	CH$_2$Cl$_2$	50	60	25	83
9	**2**/MeOH	PhCl	50	60	21	83
10	**2**/MeOH	toluene	50	60	19	90
11	**2**/MeOH	benzene	50	60	22	80

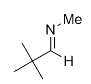
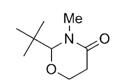
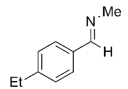
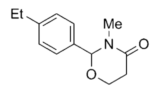
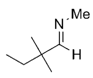
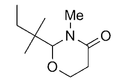
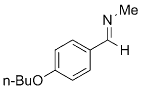
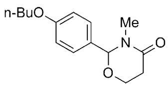
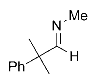
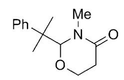
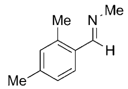
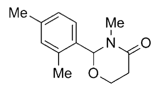
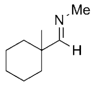
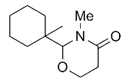
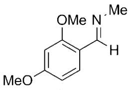
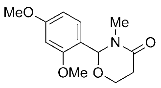
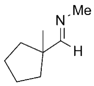
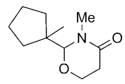
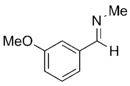
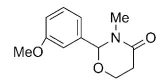
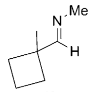
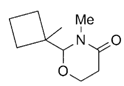
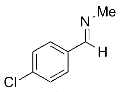
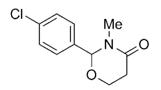
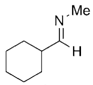
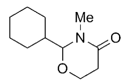
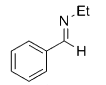
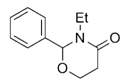
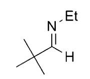
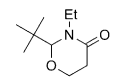
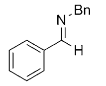
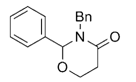
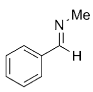
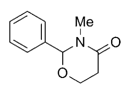
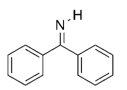
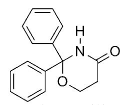
[a] Oxirane was used in equal amounts (entries 1–3) or in a ratio of 1.3:1 (entries 4–11) to the imine. [b] Times needed for completion of the reaction as determined by in situ IR. [c] Yield of isolated product. [d] P(H$_2$)/P(CO) = 1:3. p-TsOH = *para*-toluenesulfonic acid.

To explore the scope of the reaction, various imines were used under the optimized reaction conditions. A wide variety of stable imines were used and gave the desired products in good to excellent yields as shown in Table 2. For example, the imines **4a–c** from *tert*-alkyl aldehydes reacted nicely to give **1a**–**c** in 75-90% yields (entries 1–3). The cyclic *tert*-alkyl-substituted imines **4d**–**f** also afforded the desired products **1d**–**f** in similarly yields (entries 4–6). Although imines formed from primary and secondary alkyl aldehydes are usually unstable, because of the ease of rearrangement to alkenyl amines which might inhibit the cycloaddition, the cyclohexyl aldehyde imine **4g** could still react under the above-mentioned reaction conditions, thus unexpectedly giving **1g** in moderate yield (entry 7). It was noted that steric hindrance of N-alkyl groups have a strong influence on the reaction rates, probably because of the attack of imines on the acylcobalt intermediates is the rate-determining step of the reaction (see below). Although both N-ethyl- and N-benzyl-substituted imines could react successfully with **3a**, they both required higher reaction temperatures and longer reaction times, and gave the products in lower yields (entries 8, 16 and 17). Interestingly, imines derived from aryl aldehydes generally lead to high yields of the desired products (entries 9–15). Of particular note is that the ketimine **3r** also underwent the cycloaddition to give the product **1r** in good yield (entry 18).

Next, this cycloaddition reaction was easily extended to the use of other epoxides as substrates in place of oxirane (Table 3). For example, propylene oxide (**3b**) reacted with both the alkyl imine **4a** and aryl imine **4i**, to give the products **1s** and **1t**, respectively (entries 1 and 2). High regioselectivity was observed, thus leading to formation of the 6-methyl-substituted isomer as products, although in the reaction of **3b** and **4i** a small amount of the 5-methyl isomer was also obtained. This outcome is consistent with previous knowledge on regioselective ring-opening of propylene oxide at the less substituted carbon atom by a cobaltate anion.[31] Styrene oxide (**3c**) was also successfully used to react with both **4a** and **4i**, and the 5-phenyl products with opposite regioselectivity, relative to the case of propylene oxide, were always obtained, due to the higher stability of the benzylic carbocation.[32] Moreover, the reactions of styrene oxide have high diastereoselectivity, thus giving only the *trans*-2,5-disubstituted products (entries 3 and 4). This result can be rationalized by predominant formation of the chairlike conformation of the six-membered cyclic transition state with both substituents located at equatorial positions. Surprisingly, even when cyclohexane oxide (**3d**) was used, the reaction occured to give the desired products **1w** and **1x**, albeit in lower yields (entries 5 and 6). Details for structure determination of all the products are provided in the Supporting Information.

Table 2: The scope with respect to the imine used for the synthesis of 1,3-oxazinan-4-ones.

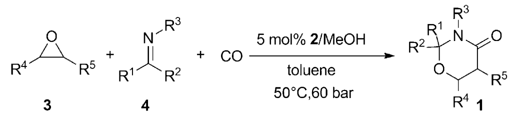


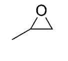
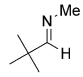
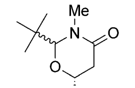
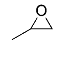
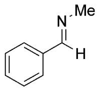
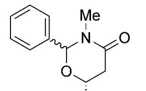
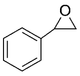
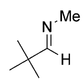
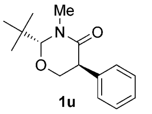
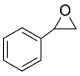
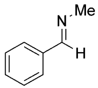
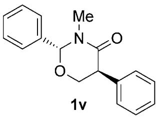
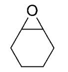
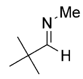
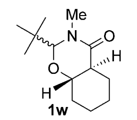
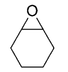
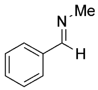
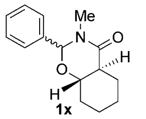
Entry	4	1 [a]	Entry	4	1 [a]
1	 **4a**	 **1a** (36h, 90%)	10	 **4j**	 **1j** (36h, 90%)
2	 **4b**	 **1b** (48h, 75%)	11	 **4k**	 **1k** (48h, 90%)
3	 **4c**	 **1c** (48h, 77%)	12	 **4l**	 **1l** (36h, 94%)
4	 **4d**	 **1d** (48h,70%)	13[b]	 **4m**	 **1m** (72h, 81%)
5	 **4e**	 **1e** (48h, 85%)	14	 **4n**	 **1n** (36h, 92%)
6	 **4f**	 **1f** (48h, 91%)	15	 **4o**	 **1o** (36h, 86%)
7	 **4g**	 **1g** (48h, 65%)	16	 **4p**	 **1p** (72h, 84%)
8[b]	 **4h**	 **1h** (96h, 46%)	17[b]	 **4q**	 **1q** (72h, 55%)
9	 **4i**	 **1i** (24h, 90%)	18	 **4r**	 **1r** (48h, 71%)

[a] Yield of isolated product. [b] Reactions run at 60 °C.

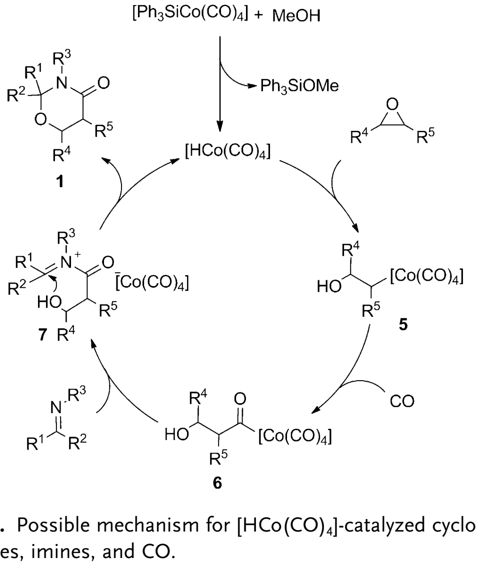
From the above results and on the basis of existing knowledge about cobalt-catalyzed reactions, a plausible mechanism for the cycloaddition is proposed as shown in Scheme 2. The first step involves ring-opening of the epoxide by [$HCo(CO)_4$], which is generated in situ from **2** and methanol, to form the alkylcobalt tetracarbonyl **5**.[33] Insertion of CO leads to the acylcobalt species **6**, to which a imine adds to produce the adduct **7**. Intramolecular attack of the hydroxy group on the cationic acyliminium carbon atom results in the ring closure to give the final product as mentioned in the literature,[34] accompanied by regeneration of [$HCo(CO)_4$].

Table 3: The scope with respect to the epoxides used for the synthesis of 1,3-oxazinan-4-ones.



Entry	3	4	1	t [h]	Yield [%][a]
1	 **3b**	 **4a**	 **1s**	36	90 (56:44)[b]
2[c]	 **3b**	 **4i**	 **1t**	36	83 (80:20)[b]
3	 **3c**	 **4a**	 **1u**	48	71
4	 **3c**	 **4i**	 **1v**	48	89
5[d]	 **3d**	 **4a**	 **1w**	60	30 (67:33)[e]
6	 **3d**	 **4i**	 **1x**	60	66 (61:39)[e]

[a] Yield of the isolated product. [b] Ratios of *cis* to *trans* isomers. [c] The 5-methyl isomer of **1t** was also obtained as a minor product.
[d] Reactions run at 60 °C. [e] Ratios of two diastereomers. See the Supporting Information.



Scheme 2. Possible mechanism for [$HCo(CO)_4$]-catalyzed cycloaddition of epoxides, imines, and CO.

In situ IR study revealed that the reaction under the standard reaction conditions followed first-order kinetic in the imine, but was not affected by epoxide concentration (Figure 1). This result indicates that imine addition to the acylcobalt species is indeed the rate-determining step of the reaction.

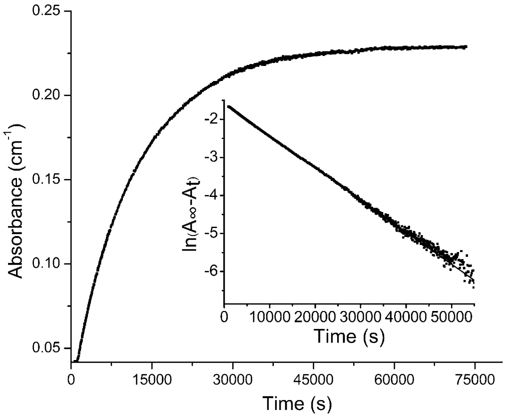


Figure 1. Reaction profile observed by in situ IR for the reaction of **3a**, **4a**, and CO under the optimized reaction conditions, thus showing the increase of product absorbance with time. The inset exhibits the first-order kinetic features of the reaction, that is, first order in imine.

In conclusion, we have successfully developed a highly efficient three-component [3+2+1] cycloaddition of epoxides, imines, and CO using [$HCo(CO)_4$] as the catalyst. The reaction takes place for a wide variety of imines and epoxides to produce 1,3-oxazinan-4-ones with different substitution patterns in high yields, and provides a convenient and atom-economic route to prepare the heterocycles from simple and readily available starting materials. All evidence supports the mechanism involving the ring-opening of epoxides by [$HCo(CO)_4$] as the initial step, with subsequent insertion of CO. Attack of the imine on the acylcobalt species constitutes the rate-determining step of the reaction. Further study of this reaction will be focused on the details of the mechanism and control of the stereochemistry of the products by asymmetric catalysis. Related works are underway in our laboratory.[35]

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Keywords: cobalt · cycloaddition · epoxides · heterocycles · multicomponent reactions

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[1] For general reviews on transition-metal-catalyzed heterocycles synthesis, see: a) X. Wu, H. Neumann, M. Beller, *Chem. Rev.* **2013**, *113*, 1; b) A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Chem. Rev.* **2013**, *113*, 3084; c) I. Nakamura, Y. Yamamoto, *Chem. Rev.* **2004**, *104*, 2127; d) N. T. Patil, Y. Yamamoto, *Chem. Rev.* **2008**, *108*, 3395.

[2] For synthesis of heterocycles by multicomponent reactions, see: a) J. S. Quesnel, B. A. Arndtsen, *Pure Appl. Chem.* **2013**, *85*, 377; b) B. A. Arndtsen, *Chem. Eur. J.* **2009**, *15*, 302; c) I. Marek, *Tetrahedron* **2005**, *61*, 11299.

[3] For synthesis of heterocycles by cycloaddition reactions, see: a) S. Perreault, T. Rovis, *Chem. Soc. Rev.* **2009**, *38*, 3149; b) N. Weding, M. Hapke, *Chem. Soc. Rev.* **2011**, *40*, 4525.

[4] a) P. R. Chopade, J. Louie, *Adv. Synth. Catal.* **2006**, *348*, 2307; b) N. Chatani, *Chem. Rec.* **2008**, *8*, 201; c) B. Heller, M. Hapke, *Chem. Soc. Rev.* **2007**, *36*, 1085; d) J. A. Varela, C. Saá, *Chem. Rev.* **2003**, *103*, 3787.

[5] a) N. Chatani, M. Tobisu, T. Asaumi, S. Murai, *J. Am. Chem. Soc.* **1999**, *121*, 7160; b) M. Tobisu, N. Chatani, T. Asaumi, S. Murai, *J. Am. Chem. Soc.* **2000**, *122*, 12663; c) N. Chatani, K. Amako, M. Tobisu, S. Murai, *J. Org. Chem.* **2003**, *68*, 1591.

[6] a) N. Chatani, M. Tobisu, T. Asaumi, S. Murai, *Synthesis* **2000**, 925; b) T. Kondo, M. Nomura, Y. Ura, *J. Am. Chem. Soc.* **2006**, *128*, 14816; c) P. Mathur, R. K. Joshi, D. K. Rai, *Dalton Trans.* **2012**, *41*, 5045; d) T. Ozawa, H. Horie, T. Kurahashi, S. Matsubara, *Chem. Commun.* **2010**, *46*, 8055.

[7] a) T. Fukuyama, Y. Higashibeppu, R. Yamaura, I. Ryu, *Org. Lett.* **2007**, *9*, 587; b) B. Wu, R. Hua, *Tetrahedron Lett.* **2010**, *51*, 6433.

[8] a) H. Hoberg, G. Burkhart, *Synthesis* **1979**, 525; b) H. Bönnemann, *Angew. Chem.* **1985**, *97*, 264; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248; c) T. Takahashi, F. Y. Tsai, K. Nakajima, *J. Am. Chem. Soc.* **2002**, *124*, 5059; d) M. M. McCormick, H. A. Duong, J. Louie, *J. Am. Chem. Soc.* **2005**, *127*, 5030.

[9] a) H. A. Duong, J. Louie, *J. Organomet. Chem.* **2005**, *690*, 5098; b) T. Kondo, M. Nomura, Y. Ura, *Tetrahedron Lett.* **2006**, *47*, 7107; c) K. M. Oberg, E. E. Lee, T. Rovis, *Tetrahedron* **2009**, *65*, 5056.

[10] a) R. Dhawan, R. D. Dghaym, B. A. Arndtsen, *J. Am. Chem. Soc.* **2003**, *125*, 1474; b) R. Dhawan, B. A. Arndtsen, *J. Am. Chem. Soc.* **2004**, *126*, 468; c) R. Dhawan, R. D. Dghaym, B. A. Arndtsen, *Org. Lett.* **2006**, *8*, 3927.

[11] A. R. Siamaki, B. A. Arndtsen, *J. Am. Chem. Soc.* **2006**, *128*, 6050.

[12] a) R. D. Dghaym, R. Dhawan, B. A. Arndtsen, *Angew. Chem.* **2001**, *113*, 3328; *Angew. Chem. Int. Ed.* **2001**, *40*, 3228; b) S. Bontemps, J. S. Quesnel, K. Worrall, B. A. Arndtsen, *Angew. Chem.* **2011**, *123*, 9110; *Angew. Chem. Int. Ed.* **2011**, *50*, 8948; c) K. Worrall, B. Xu, S. Bontemps, B. A. Arndtsen, *J. Org. Chem.* **2011**, *76*, 170; d) B. Xu, K. Worrall, B. A. Arndtsen, *Molecules* **2012**, *17*, 13759.

[13] A. R. Siamaki, D. A. Black, B. A. Arndtsen, *J. Org. Chem.* **2008**, *73*, 1135.

[14] a) C. Larksarp, H. Alper, *J. Org. Chem.* **1999**, *64*, 9194; b) C. Larksarp, H. Alper, *J. Org. Chem.* **2000**, *65*, 2773.

[15] J. Salvadori, E. Balducci, S. Zaza, E. Petricci, *J. Org. Chem.* **2010**, *75*, 1841.

[16] H. A. Duong, J. Louie, *Tetrahedron* **2006**, *62*, 7552.

[17] T. Miura, M. Morimoto, M. Murakami, *J. Am. Chem. Soc.* **2010**, *132*, 15836.

[18] T. L. Church, C. M. Byrne, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2007**, *129*, 8156.

[19] a) F. Berhal, S. Takechi, N. Kumagai, M. Shibasaki, *Chem. Eur. J.* **2011**, *17*, 1915; b) T. Ginman, Y. Gravenfors, *J. Med. Chem.* **2013**, *56*, 4181.

[20] a) G. Cardillo, M. A. Hashem, C. Tomasini, *J. Chem. Soc. Perkin. Trans. 1* **1990**, 1487; b) E. Bandini, G. Martelli, G. Spunta, A. Bongini, M. Panunzio, *Synlett* **1999**, 1735.

[21] M. Panunzio, E. Bandini, E. Campana, P. Vicennati, *Tetrahedron: Asymmetry* **2002**, *13*, 2113.

[22] a) D. Ntirampebura, L. Ghosez, *Tetrahedron Lett.* **1999**, *40*, 7079; b) D. Ntirampebura, L. Ghosez, *Synthesis* **2002**, 2043.

[23] M. Panunzio, A. Bongini, M. Monari, E. Tamanini, E. Bandini, *Tetrahedron* **2004**, *60*, 8347.

[24] a) M. Panunzio, E. Tamanini, P. Vicennati, *Tetrahedron* **2006**, *62*, 12270; b) M. Panunzio, E. Bandini, *Synthesis* **2008**, 1753.

[25] a) T. Kametani, K. Kigasawa, M. Hiiragi, *Heterocycles* **1977**, *7*, 919; b) T. Kametani, K. Kigasawa, M. Hiiragi, *Heterocycles* **1978**, *9*, 819; c) F. Fülöp, G. Bernáth, K. Pihlaja, *Adv. Heterocycl. Chem.* **1997**, *69*, 349; d) A. N. Cayley, K. A. Gallagher, R. J. K. Taylor, *Synthesis* **2008**, 3846.

[26] a) M. Panunzio, E. Bandini, A. Millemaggi, *Synthesis* **2007**, 2060; b) Y. Watanabe, T. Washio, J. Krishnamurthi, M. Anada, S. Hashimoto, *Chem. Commun.* **2012**, *48*, 6969.

[27] H. Sun, J. Zhang, Q. Liu, L. Yu, J. Zhao, *Angew. Chem.* **2007**, *119*, 6180–6184; *Angew. Chem. Int. Ed.* **2007**, *46*, 6068–6072.

[28] L. Jia, *Polym. Prepr.* **2010**, *51*, 406.

[29] Y. Zhang, H. Sun, *Chem. J. Chin. Univ.* **2014**, *35*, 54.

[30] C. M. Byrne, T. L. Church, J. W. Kramer, G. W. Coates, *Angew. Chem.* **2008**, *120*, 4043–4047; *Angew. Chem. Int. Ed.* **2008**, *47*, 3979–3983.

[31] a) R. F. Heck, *J. Am. Chem. Soc.* **1963**, *85*, 1460; b) J. Kreisz, F. Ungváry, A. Sisak, L. Markó, *J. Organomet. Chem.* **1991**, *417*, 89.

[32] a) H. Alper, H. Arzoumanian, J. F. Petrignani, M. S. Maldonado, *J. Chem. Soc. Chem. Commun.* **1985**, 340; b) T. Murai, E. Yasui, S. Murai, *J. Am. Chem. Soc.* **1989**, *111*, 7938.

[33] J. Kreisz, A. Sisak, L. Markó, F. Ungváry, *J. Organomet. Chem.* **1993**, *451*, 53.

[34] a) H. Böhme, K. Hartke, *Chem. Ber.* **1963**, *96*, 600; b) V. V. Vintonyak, M. Calà, F. Lay, B. Kunze, F. Sasse, M. E. Maier, *Chem. Eur. J.* **2008**, *14*, 3709.

[35] After preparation of the manuscript, a report appeared on an identical reaction using [$Co_2(CO)_8$]/LiCl as the catalyst. We thank the referee for reminding us of the important information. For details, see: Y. Zhang, J. Ji, X. Zhang, S. Lin, Q. Pan, L. Jia, *Org. Lett.* **2014**, *16*, 2130.