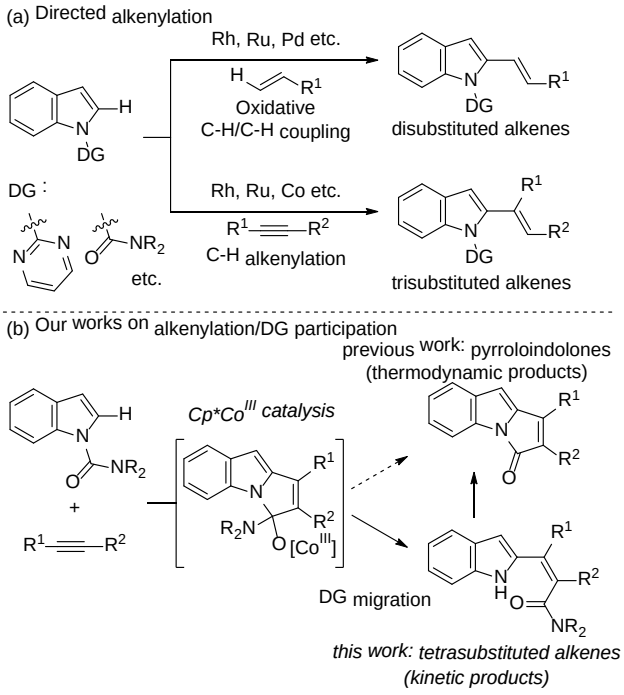
Stereoselective Synthesis of Tetrasubstituted Alkenes via Cp*Co^{III}-Catalyzed C-H Alkenylation/Directing Group Migration Sequence

Hideya Ikemoto,[a] Ryo Tanaka,[b] Ken Sakata,[c,d] Motomu Kanai,[a] Tatsuhiko Yoshino,*[b,d] and Shigeki Matsunaga*[b,d]

Abstract: A highly atom-economical and stereoselective synthesis of tetrasubstituted α,β-unsaturated amides was achieved via a Cp*Co^{III}-catalyzed C-H alkenylation/directing-group migration sequence. A carbamoyl-directing group, which is typically removed after C-H functionalization, worked as an internal acylating agent and migrated onto the alkene moiety of the product. The directing-group migration was realized with the Cp*Co^{III} catalyst, while a related Cp*Rh^{III} catalyst did not promote the migration process. The product was further converted into two types of tricyclic compounds, one of which had fluorescent properties.

Tetrasubstituted alkenes are found in many biologically active molecules[1] and natural products.[2] They are also important synthetic intermediates for the synthesis of highly congested vicinal stereogenic carbon centers via various difunctionalization reactions of tetrasubstituted alkenes.[3-5] Stereoselective synthesis of all-carbon tetrasubstituted alkenes, however, remains a great challenge due to their congested nature and difficulties in controlling stereoselectivity. The most general strategies for their construction involve carbometalation of internal alkynes and successive cross-coupling reactions or addition to electrophiles.[6] Although remarkable advances have been made in these strategies, the use of stoichiometric organometallic reagents is still inevitable.[7] On the other hand, transition-metal-catalyzed C-H bond functionalizations[8] have emerged as atom-[9] and step-economical[10] methods for synthesizing di- and tri-substituted alkenes.[11] These reactions generally proceed via either a transition metal-catalyzed C-H/C-H oxidative coupling reaction with alkenes or a redox-neutral alkyne insertion at C-H bonds without stoichiometric amounts of organometallic reagents (Scheme 1a). In the latter reactions, proto-demetalation or reductive elimination to form an alkenyl-H bond occurs after alkyne insertion, making the formation of the fourth C-C bond difficult.

We previously reported the Cp*Co^{III}-catalyzed[12-15] synthesis of pyrroloindolones, in which C-H alkenylation and successive intramolecular nucleophilic addition to a carbamoyl directing group of indole proceeded without proto-demetalation (Scheme 1b, previous work).[15] During the course of our further studies of this reaction, we found that the tetrasubstituted alkene was formed as a kinetically controlled product (Scheme 1b, this work). The obtained tetrasubstituted alkene, which is difficult to stereoselectively access by other methods, is considered to be formed via directing-group migration.[16] Here we report the optimized conditions for this atom-economical directing-group migration process in which the carbamoyl group works not only as a directing group, but also as an internal acylating agent.



Scheme 1. (a) Previous work: di- and trisubstituted alkene synthesis via C-H functionalization (b) This work: synthesis of tetrasubstituted olefins via C-H alkenylation/DG migration sequence.

Optimization studies using *N*-morpholinocarbamoyl indole **2a** and alkyne **3a** under Cp*Co^{III}/KOAc catalysis are summarized in Table 1. The best reaction conditions for the synthesis of pyrroloindolone **5** using Cp*Co^{III}-arene catalyst **1a** are shown in entry 1, in which C-H alkenylation, successive intramolecular nucleophilic addition to the carbamoyl directing-group, and elimination of an amine proceed with high selectivity. When the reaction temperature was decreased to 100 °C, the yield of **5** dropped to 23% along with the alkenylation product **6** (22%). After careful analysis of the reaction mixture, we

[a] H. Ikemoto, Prof. Dr. M. Kanai
Graduate School of Pharmaceutical Sciences
The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

[b] R. Tanaka, Dr. T. Yoshino, Prof. Dr. S. Matsunaga
Faculty of Pharmaceutical Sciences
Hokkaido University
Kita-ku, Sapporo 060-0812, Japan
E-mail: smatsuna@pharm.hokudai.ac.jp

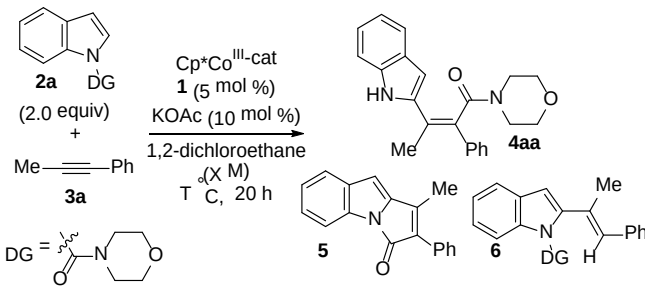
[c] Dr. K. Sakata
Faculty of Pharmaceutical Sciences, Hoshi University
Ebara, Shinagawa-ku, Tokyo 142-8501, Japan

[d] Dr. K. Sakata, Dr. T. Yoshino, Prof. Dr. S. Matsunaga
ACT-C, Japan Science and Technology Agency

Supporting information for this article is given via a link at the end of the document.

identified **4aa** as a major product (37% yield, entry 2). To decelerate the undesired proto-demetalation leading to **6**, the concentration was decreased to 0.05 M and the desired alkene **4aa** was obtained in 40% yield with moderate selectivity. Although further minor modification of the reaction conditions was unfruitful, screening of Cp*Co^{III} catalysts led to improvement (entries 4-6). For our desired reaction, the [Cp*Co^{III}(CH$_3$CN)$_3$]X$_2$ catalysts[17] **1b-X** had higher reactivity and selectivity than the Cp*Co^{III}-arene catalyst **1a**, and the best catalyst **1b-SbF$_6$** afforded 69% yield (entry 6). We screened the reaction conditions again using **1b-SbF$_6$** and determined that 5 mol % KOAc was optimal (entry 7) to give **4aa** in 80% yield (74% isolated yield). The reactivity dramatically decreased without the catalytic amount of KOAc (entry 8), indicating that KOAc had an important role in efficient C-H bond cleavage via a concerted metalation-deprotonation mechanism.[18] We also confirmed that Cp*Rh^{III} catalyst **1c**[19,20] did not promote the desired directing-group migration, and only a small amount of the alkenylated product **6** was obtained, even after screening of the carboxylate additives (entries 9-11). These results indicate that high nucleophilicity of the C-Co bond is essential.[12a,15]

Table 1. Optimization studies and control experiments[a]

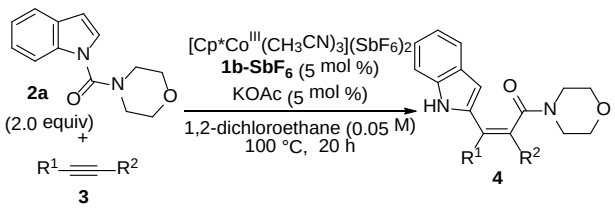


Entry	Cat.[b]	X [M]	T [°C]	% Yield[c]		
				4aa	**5**	**6**
1	**1a**	0.1	130	0	82	10
2	**1a**	0.1	100	37	23	22
3	**1a**	0.05	100	40	<1	10
4	**1b-BF$_4$**	0.05	100	50	5	6
5	**1b-PF$_6$**	0.05	100	50	4	6
6	**1b-SbF$_6$**	0.05	100	69	7	5
7[d]	**1b-SbF$_6$**	0.05	100	80 (74)[e]	5	6
8[f]	**1b-SbF$_6$**	0.05	100	10	0	0
9[d]	**1c** (Rh)	0.05	100	0	0	0
10[g]	**1c** (Rh)	0.05	100	0	0	3
11[h]	**1c** (Rh)	0.05	100	0	0	8

[a] The reaction was performed in **2a** (0.40 mmol) and **3a** (0.20 mmol). [b] **1a** = [Cp*Co(C$_6$H$_6$)](PF$_6$)$_2$, **1b-X** = [Cp*Co(CH$_3$CN)$_3$]X$_2$, **1c** = [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$. [c] Determined by ^{1}H NMR analysis with an internal standard. [d] KOAc (5 mol %) was used. [e] Isolated yield of **4aa** after purification by silica gel column chromatography. [f] Reaction was run without KOAc. [g] CsOAc (5 mol %) was used instead of KOAc. [h] CsOPiv (5 mol %) was used instead of KOAc.

The optimal reaction conditions were then applied to various alkynes, as summarized in Table 2. The C-H alkenylation/DG migration sequence of indole **2a** proceeded well with various aryl/alkyl alkynes that have electron-donating and electron-withdrawing substituents on the aromatic rings, and products were obtained in 55%–77% yield (entries 1-7). The indicated products were obtained as single regioisomers in all cases. Good reactivities and high selectivities were also observed with other alkyl substituents, such as Et or Pr on alkynes (entries 8, 9). Diaryl-substituted alkynes were also compatible to give the desired products in 71%–99% yield (entries 10-13). A functionalized alkyne **3n** bearing a silyl ether unit also gave **4an** in 76% yield without deprotection (entry 14). An alkyne **3o** with a thiophene ring gave tetrasubstituted alkene **4ao**, containing two different heteroaromatic rings, in 70% yield (entry 15). While a TMS-protected alkyne **3p** resulted in moderate yield (entry 16), dialkylalkyne **3q** exclusively afforded the alkenylation product **6aq** (entry 17). No reaction proceeded with a terminal alkyne **4r** (entry 18).

Table 2. Substrate scope of C-H alkenylation/DG migration with alkynes[a]



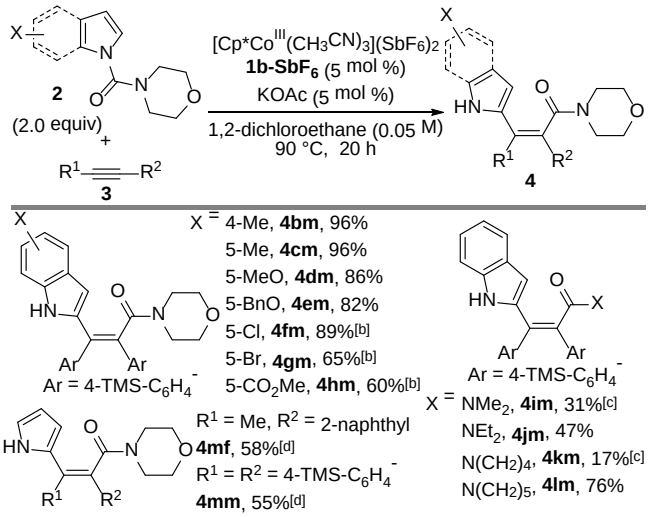
Entry	R^1	R^2	**3**	**4**	% Yield[b]
1	Me	Ph	**3a**	**4aa**	74
2	Me	4-Me-C$_6$H$_4$	**3b**	**4ab**	55
3[c]	Me	4-Cl-C$_6$H$_4$	**3c**	**4ac**	77
4[c]	Me	4-Br-C$_6$H$_4$	**3d**	**4ad**	58
5[c]	Me	4-CO$_2$Et-C$_6$H$_4$	**3e**	**4ae**	74
6	Me	2-naphthyl	**3f**	**4af**	71
7	Me	6-MeO-naphth-2-yl	**3g**	**4ag**	69
8	Et	Ph	**3h**	**4ah**	76
9	Pr	Ph	**3i**	**4ai**	69
10[d]	Ph	Ph	**3j**	**4aj**	87
11[d]	4-Me-C$_6$H$_4$	4-Me-C$_6$H$_4$	**3k**	**4ak**	85
12[d]	4-Br-C$_6$H$_4$	4-Br-C$_6$H$_4$	**3l**	**4al**	71
13[d]	4-TMS-C$_6$H$_4$	4-TMS-C$_6$H$_4$	**3m**	**4am**	99
14	TBDPSO(CH$_2$)$_3$-	Ph	**3n**	**4an**	76
15	Bu	2-thienyl	**3o**	**4ao**	70
16	TMS	Ph	**3p**	**4ap**	54
17	Pr	Pr	**3q**	**4aq**	0
18	H	Ph	**3r**	**4ar**	0

[a] Reaction was run using **1b-SbF$_6$** (5 mol %), KOAc (5 mol %), **2a** (0.40 mmol), **3** (0.20 mmol) in 1,2-dichloroethane (4.0 mL) under Ar atmosphere at 100 °C unless otherwise noted. [b] Isolated yield of pure **4** (single regioisomer) after purification by silica gel column chromatography. [c] Reaction was run at 0.033 M. [d] Reaction was run at 90 °C.

The scope of indole is summarized in Table 3. Both electron-donating and electron-withdrawing substituents were compatible, and various 4- or 5-substituted indoles resulted in 60%–96% yield (**4bm**-**4hm**). Indoles with other carbamoyl directing groups also gave the corresponding tetrasubstituted alkenes **4im**-**4lm** although the reactivity was significantly affected by the structure of the directing group. Moreover, *N*-carbamoyl pyrrole **4m** also

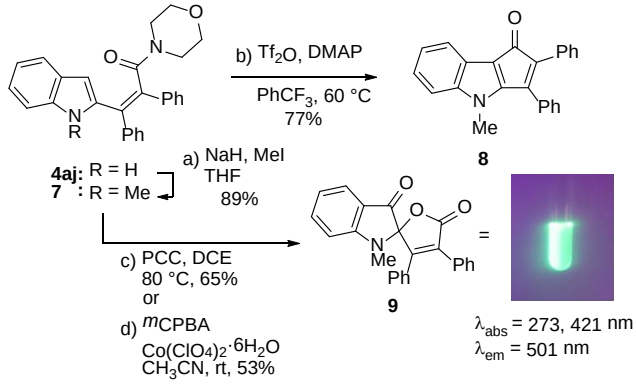
underwent the desired alkenylation/DG migration reaction to give pyrrole-substituted tetrasubstituted alkenes **4mf** and **4mm**. The DG migration during the first C-H functionalization inhibits the second functionalization of another C-H bond of the pyrrole ring.

Table 3. Substrate scope of C-H alkenylation/DG migration with indoles and pyrroles[a]



[a] Reaction was run using **1b-SbF$_6$** (5 mol %), KOAc (5 mol %), **2** (0.40 mmol), **3** (0.20 mmol) in 1,2-dichloroethane (4.0 mL) under Ar atmosphere at 90 °C unless otherwise noted. Isolated yields of **4** (single regioisomer) after purification by silica gel column chromatography are listed. [b] Reaction was run at 80 °C for 12 h. [c] 100 °C [d] Reaction was run using KOAc (10 mol %) in 1,2-dichloroethane (2.0 mL) at 100 °C.

The product **4aj** was further converted to two different tricyclic compounds, **8** and **9** (Scheme 2). After *N*-methylation (**7**), treatment with Tf_2O and DMAP[21] promoted electrophilic cyclization at the C3 position to afford **8**. On the other hand, the spirocyclic compound **9** was obtained by oxidation using PCC[22] or *m*CPBA/$Co(ClO_4)_2$.[23] Spirocycle **9** exhibited green fluorescence with a maximum emission wavelength of 501 nm. Our synthetic method is expected to provide easy access to various substituted analogs of this fluorescent molecule.



Scheme 2. Transformation of **4aj** to tricyclic compounds.

A plausible catalytic cycle with the Cp*Co^{III} complex in the presence of KOAc is shown in Figure 1. As the initial step, three acetonitrile ligands dissociate from $[Cp^*Co^{III}(CH_3CN)_3](SbF_6)_2$, and ligand exchange with acetate would generate a catalytically active monocationic species **I**. After coordination of the carbamoyl group of indole **2** (**II**), regioselective C-H metalation at the C2-position would occur via a concerted metalation-deprotonation (CMD) mechanism[18] to afford indolyl-Co species **III**. The result without KOAc (Table 1: entry 8) indicates that an electrophilic aromatic substitution (S_EAr) pathway and/or a CMD pathway with external bases other than an acetate would compete, but an acetate-assisted CMD pathway would be dominant under the optimal conditions. Insertion of alkyne **3** to the C-Co bond generates the key alkenyl-Co intermediate (**IV**). Nucleophilic addition of the C-Co bond to the carbamoyl-directing group proceeds to afford the intermediate **V**. A low concentration was essential to avoid undesired proto-demetalation of **IV** leading to **6**. Elimination of the indole would result in DG migration, giving tetrasubstituted alkene **4**. Our previous report revealed that pyrroloindolone **5** is a major product at 130 °C,[15] and we confirmed the formation of **5** from **4** at 130 °C in the presence of **1a**/KOAc or KOAc (see Supporting Information). These data suggested that **4** is a kinetically favored primary product that undergoes cyclization, leading to a thermodynamically favored product **5**, although direct formation of **5** from **V** at 130 °C is also possible to some extent.

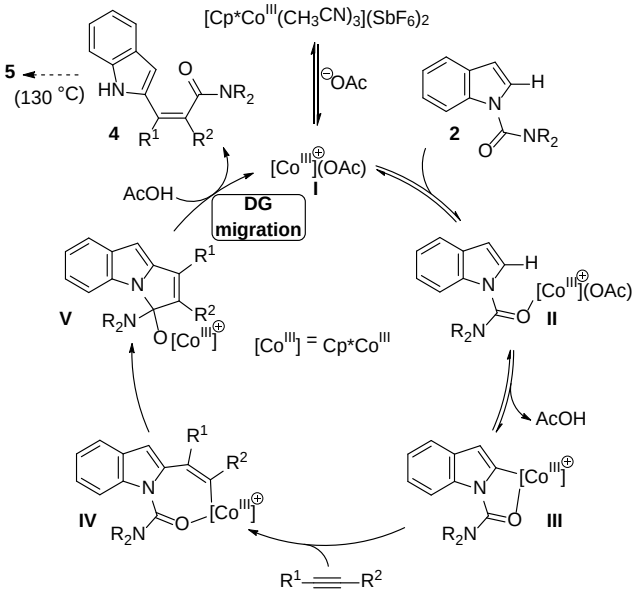


Figure 1. Plausible catalytic cycle of C-H alkenylation/DG migration sequence with indole and alkyne.

In conclusion, the Cp*Co^{III}-catalyzed directing-group migration reaction of carbamoyl-protected indoles/pyrrole and alkynes afforded tetrasubstituted alkenes **4** in 17%–99% yield with complete stereoselectivity and high atom-economy under carefully optimized reaction conditions. The product was easily converted to tricyclic compound **8** and a fluorescent spirocycle **9**.

Acknowledgements

This work was supported in part by JST ACT-C Grant Number JPMJCR12Z6, Japan, JSPS KAKENHI Grant Number JP15H05802 in Precisely Designed Catalysts with Customized Scaffolding, JSPS KAKENHI Grant Number JP15H05993, Toray Science Foundation, and the Naito Foundation (S.M.). H.I. thanks JSPS for fellowships. We acknowlege Professors Masako Kato and Masaki Yoshida in Hokkaido University for fluorescence spectroscopy.

Keywords: catalysis • C-H activation • cobalt • first-row transition metal• indole

[1] a) A. S. Levenson, V. C. Jordan, *Eur. J. Cancer.* **1999**, *35*, 1628; b) P. Prasit, Z. Wang, C. Brideau, C.-C. Chan, S. Charleson, W. Cromlish, D. Ethier, J. F. Evans, A. W. Ford-Hutchinson, J. Y. Gauthier, R. Gordon, J. Guay, M. Gresser, S. Kargman, B. Kennedy, Y. Leblanc, S. Léger, J. Mancini, G. P. O'Neill, M. Ouellet, M. D. Percival, H. Perrier, D. Riendeau, I. Rodger, P. Tagari, M. Thérien, P. Vickers, E. Wong, L.-J. Xu, R. N. Young, R. Zamboni, S. Boyce, N. Rupniak, M. Forrest, D. Visco, D. Patrick, *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1773.

[2] a) M. R. Elliot, A.-L. Dhimane, M. Malacria, *J. Am. Chem. Soc.* **1997**, *119*, 3427; b) A. Arnone, U. Brambilla, G. Nasini, O. V. de Pava, *Tetrahedron* **1995**, *51*, 13357.

[3] Recent reports on hydrogenation of tetrasubstituted alkenes: a) D. H. Woodmansee, A. Pfaltz, *Chem. Commun.* **2011**, *47*, 7912; b) Y. Zou, J. G. Millar, *Tetrahedron Lett.* **2011**, *52*, 4224; c) S. Cardinal, N. Voyer, *Tetrahedron Lett.* **2013**, *54*, 5178; a report on asymmetric hydrogenation: d) W. Tang, S. Wu, X. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 9570.

[4] Reports on epoxidation of tetrasubstituted alkenes: a) B. D. Brandes, E. N. Jacobsen, *Tetrahedron Lett.* **1995**, *36*, 5123; b) T. Poon, B. P. Mundy, F. G. Favaloro, C. A. Goudreau, A. Greenberg, R. Sullivan, *Synthesis* **1998**, 832; a review on asymmetric epoxidation: c) Q.-H. Xia, H.-Q. Ge, C.-P. Ye, Z.-M. Liu, K.-X. Su, *Chem. Rev.* **2005**, *105*, 1603.

[5] For reports on asymmetric dihydroxylation of tetrasubstituted alkenes, see: a) K. Morikawa, J. Park, P. G. Andersson, T. Hashiyama, K. B. Sharpless, *J. Am. Chem. Soc.* **1993**, *115*, 8463; b) C. Döbler, G. M. Mehltretter, U. Sundermeier, M. Beller, *J. Am. Chem. Soc.* **2000**, *122*, 10289; for a review on asymmetric dihydroxylation, see: c) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483.

[6] Reviews on the synthesis of tetrasubstituted alkenes, see: a) A. B. Flynn, W. W. Ogilvie, *Chem. Rev.* **2007**, *107*, 4698; b) E. Negishi, Z. Hunag, G. Wang, S. Mohan, C. Wang, H. Hattori, *Acc. Chem. Res.* **2008**, *41*, 1474.

[7] Recent reports on the synthesis of all-carbon tetrasubstituted alkenes: a) F. Xue, J. Zhao, T. S. A. Hor, T. Hayashi, *J. Am. Chem. Soc.* **2015**, *137*, 3189; b) W. You, Y. Li, M. K. Brown, *Org. Lett.* **2013**, *15*, 1610; c) V. Kotek, H. Dvořáková, T. Tobrman, *Org. Lett.* **2015**, *17*, 608.

[8] General reviews on C-H bond functionalization: a) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885; b) W. R. Gutekunst, P. S. Baran, *Chem. Soc. Rev.* **2011**, *40*, 1976; c) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788; d) S. R. Neufeldt, M. S. Sanford, *Acc. Chem. Res.* **2012**, *45*, 936; e) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem.* **2012**, *124*, 9092; *Angew. Chem. Int. Ed.* **2012**, *51*, 8960; f) Z. Chen, B. Wang, J. Zhang, W. Yu, Z. Liu, Y. Zhang, *Org. Chem. Front.* **2015**, *2*. 1107; g) L. Ackermann, *Org. Process Res. Dev.* **2015**, *19*, 260; h) T. Gensch, M. N. Hopkinson, F. Glorius, J. Wencel-Delord, *Chem. Soc. Rev.* **2016**, *45*, 2900; i) Y. Park, Y. Kim, S. Chang, *Chem. Rev.* **2017**, DOI: 10.1021/acs.chemrev.6b00644; j) J. R. Hummel, J. A. Boerth, J. A. Ellman, *Chem. Rev.* **2017**, DOI: 10.1021/acs.chemrev.6b00661.

[9] B. M. Trost, *Science* **1991**, *254*, 1471.

[10] P. A. Wender, B. L. Miller, *Nature* **2009**, *460*, 197.

[11] Selected reviews on C-H alkenylation: (a) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633; (b) V. Ritleng, C. Sirlin, M. Preffer, *Chem. Rev.* **2002**, *102*, 1731; (c) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.* **2007**, *107*, 5318; (d) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; (e) B. Karimi, H. Behzadnia, D. Elhamifar, P. F. Akhavan, F. K. Esfahani, A. Zamani, *Synthesis* **2010**, 1399; (f) K. M. Engle, J.-Q. Yu, *J. Org. Chem.* **2013**, *78*, 8927; (g) V. P. Boyarskiy, D. S. Ryabukhin, N. A. Bokach, A. V. Vasilyev, *Chem. Rev.* **2016**, *116*, 5894.

[12] Reviews on cobalt-catalyzed C-H functionalization including Cp^*Co^{III} catalysis: a) T. Yoshino, S. Matsunaga, *Adv. Synth. Catal.* **2017**, *359*, 1245; b) S. Wang, S.-Y. Chen, X.-Q. Yu, *Chem. Commun.* **2017**, *53*, 3165; c) M. Usman, Z.-H. Ren, Y.-Y. Wang, Z.-H. Guan, *Synthesis* **2017**, *49*,1419; d) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498.

[13] Reviews on low-valent cobalt-catalyzed C-H functionalization: a) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208; b) L. Ackermann, *J. Org. Chem.* **2014**, *79*, 8948.

[14] Selected examples of Cp^*Co^{III}-catalyzed C-H functionalization reactions: a) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem.* **2013**, *125*, 2263; *Angew. Chem. Int. Ed.* **2013**, *52*, 2207; b) D.-G. Yu, T. Gensch, F. de Azambuja, S. Vásquez-Céspedes, F. Glorius, *J. Am. Chem. Soc.* **2014**, *136*, 17722; c) J. Li, L. Ackermann, *Angew. Chem.* **2015**, *127*, 3706; *Angew. Chem. Int. Ed.* **2015**, *54*, 3635; d) J. R. Hummel, J. A. Ellman, *J. Am. Chem. Soc.* **2015**, *137*, 490; e) J. Park, S. Chang, *Angew. Chem.* **2015**, *127*, 14309; *Angew. Chem. Int. Ed.* **2015**, *54*, 14103; related hydroarylation reactions of alkynes: f) M. Sen, B. Emayavaramban, N. Barsu, J. R. Premkumar, B. Sundararaju, *ACS Catal.* **2016**, *6*, 279; g) S. Wang, J.-T. Hou, M.-L. Feng, X.-Z. Zhang, S.-Y. Chen, X.-Q. Yu, *Chem. Commun.* **2016**, *52*, 2709; h) R. Tanaka, H. Ikemoto, M. Kanai, T. Yoshino, S. Matsunaga, *Org. Lett.* **2016**, *18*, 5732; i) S. S. Bera, S. Debbarma, A. K. Ghosh, S. Chand, M. S. Maji, *J. Org. Chem.* **2017**, *82*, 420. For other examples, see references [12].

[15] H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.* **2014**, *136*, 5424.

[16] Cp^*Co^{III}-catalyzed directing group migration: A. Lerchen, T. Knecht, C. G. Daniliuc, F. Glorius, *Angew. Chem.* **2016**, *128*, 15391; *Angew. Chem. Int. Ed.* **2016**, *55*, 15166.

[17] G. Fairhurst, C. White, *J. Chem. Soc., Dalton Trans.* **1979**, 1524. This type of catalyst precursor was first used as a catalyst for C-H functionalization by Glorius and co-worker in reference 14b.

[18] Reviews on carboxylate-assisted concerted metalation-deprotonation mechanism in C-H activation: D. Lapointe, K. Fagnou, *Chem. Lett.* **2010**, *39*, 1118; b) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315 and references therein

[19] Cp^*Rh^{III}-catalyzed alkenylation of carbamoyl-protected indoles: D. J. Schipper, M. Hutchinson, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6910. For more detailed discussion of this difference between Cp^*Co^{III} and Cp^*Rh^{III} catalysis, see reference [15].

[20] Reviews on Cp^*Rh^{III} catalyzed C-H functionalization, see: a) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212; b) F. W. Patureau, J. Wencel-Delord, F. Glorius, *Aldrichimica Acta* **2012**, *45*, 31; c) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; d) S. Chiba, *Chem. Lett.* **2012**, 41, 1554; e) N. Kuhl, N. Schröder, F. Glorius, *Adv. Synth. Catal.* **2014**, *356*, 1443; f) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007; g) B. Ye, N. Cramer, *Acc. Chem. Res.* **2015**, *48*, 1308.

[21] G. Bélanger, R. Larouche-Gauthier, F. Ménard, M. Nantel. F. Barabé *J. Org. Chem.* **2006**, *71*, 704.

[22] C. N. S. S. P. Kumar, C. L. Devi, V. J. Rao, S. Palaniappan, *Synlett* **2008**, 2023.

[23] M. Y. Hyun, S. H. Kim, Y. J. Song, H. G. Lee, Y. D. Jo, J. H. Kim, I. H. Hwang, J. Y. Noh, J. Kang, C. Kim, *J. Org. Chem.* **2012**, *77*, 7307.