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COMMUNICATION

Efficient Synthesis of Phthalimides via Cobalt-Catalyzed C(sp^2)–H Carbonylation of Benzoyl Hydrazides with Carbon Monoxide

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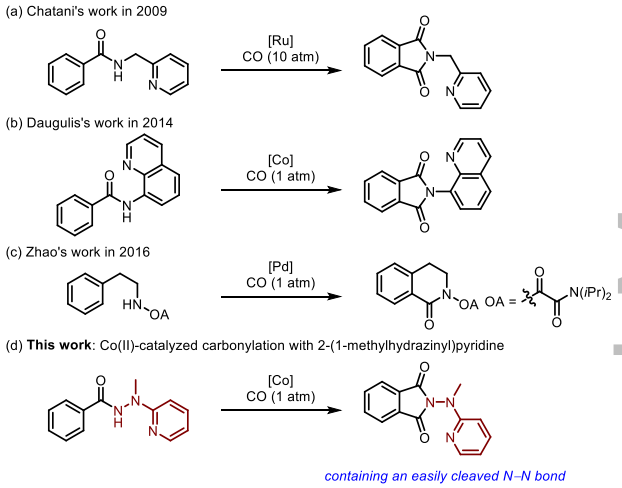
Abstract: A cobalt-catalyzed C–H carbonylation of benzoyl hydrazides has been developed by using 2-(1-methylhydrazinyl)pyridine as the bidentate directing group. This transformation is mild, efficient, operationally simple, and highly functional-group-tolerant. The protocol has generated a broad range of phthalimide derivatives in good to excellent yields. The ligand moiety can be readily removed through hydrogenolysis.

Keywords: Phthalimides; Cobalt catalyst; C−H carbonylation; Benzoyl hydrazides; Hydrogenolysis

Introduction

Over the past few decades, transition-metal-catalyzed direct C–H functionalization has become a powerful methodology for efficient construction of organic building blocks, providing an attractive alternative to the traditional cross-coupling reactions without prefunctionalization of the starting materials.[1] Meanwhile, significant progress has been made in the carbonylation of C–H bonds using CO as the C1 feedstock.[2] The first carbonylation via directed, transition-metal-catalyzed functionalization of a C–H bond was disclosed by Murahashi in 1955, in which $Co_2(CO)_8$ was employed as the catalyst.[3] Since this pioneering work, numerous metals have been found to be effective in carbonylation of C(sp^2)–H or C(sp^3)–H bonds, such as palladium,[4] ruthenium,[5] and rhodium,[6] and various methodologies have been developed for direct carbonylation of C–H bonds by employing monodentate[4-6] directing groups. As for the bidentate[7] directing-based C(sp^2)–H carbonylation, Chatani and co-workers developed a Ru-catalyzed carbonylation of aromatic amides with CO by utilizing the bidendate pyridine-2-ylmethyamine moiety in 2009 (Scheme 1a).[7a] Subsequently, Daugulis's group reported a Co-catalyzed C–H carbonylation directed by 8-aminoquinoline[8] in the presence of an atmospheric pressure of CO (Scheme 1b),[7d] and a Pd-catalyzed C–H carbonylation assisted by oxalyl amide for 3,4-dihydroisoquinolinone was described by Zhao *et al.* (Scheme 1c).[7f]



Scheme 1. Bidentate Directing-based C(sp^2)–H Carbonylation with CO.

The phthalimide unit is a key synthetic constituent of many bioactive molecules and pharmaceuticals[9] such as thalidomide,[10] amphotalide,[11] taltrimide,[12] and talmetoprim[13] (Figure 1), and they display outstanding biological and pharmacological activities, such as sedative, antifungal, antiepileptic or antibacterial activity. Consequently, development of a direct and efficient method to rapidly construct phthalimide derivatives is still highly desirable. Recently, our group developed a novel bidentate directing group 2-(1-methylhydrazinyl)pyridine applied in cobalt-catalyzed C−H functionalization.[14] Compared with other bidentate directing groups, the ligand can be reductively cleaved under mild conditions. Herein we

describe a cobalt-catalyzed C(sp^2)–H carbonylation[15] assisted by this bidentate directing group, a useful method for facile synthesis of phthalimide derivatives (Scheme 1d).

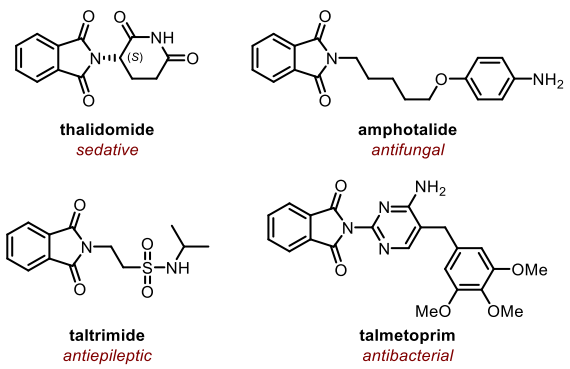
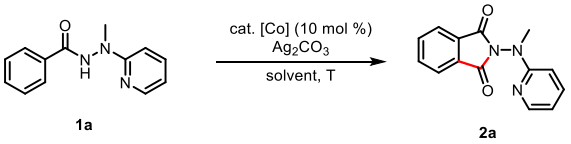


Figure 1. Phthalimide motifs in pharmaceuticals.

Results and Discussion

Initially, N'-methyl-N'-(2-pyridinyl)benzohydrazide (**1a**)[16] was chosen as a substrate. To our delight, treatment of **1a** with an atmospheric pressure of CO in the presence of $Co(OAc)_2·4H_2O$ (10 mol %), Ag_2CO_3 (2.0 equiv.) and NaOAc (1.0 equiv.) in PhCl at 150 °C for 12 h afforded the desired phthalimide product **2a** in 65% yield (Table 1, entry 1). Lowering the reaction temperature to 120 or 100 °C improved the yield to 75% or 90%, respectively (entries 2 and 3). Encouraged by this result, we then investigated other cobalt salts and found that trace product was obtained from the $CoBr_2$-catalytic system, while product **2a** was isolated in 55% yield with $Co(acac)_2$ (entries 4 and 5). Solvent screening showed that the use of toluene resulted in 91% for the product (entries 6 and 7). We then chose more environmentally friendly toluene as the solvent to carry out the further investigation. Surprisingly, the reaction still proceeded smoothly in 99% yield without NaOAc (entry 8). The yield decreased to 90% when the amount of Ag_2CO_3 was reduced from 2.0 equiv. to 1.0 equiv. in the absence of NaOAc (entry 9). Nevertheless, the product could be obtained in 99% yield with 1.2 equiv. of Ag_2CO_3 added as the oxidant (entry 10). When 5.0 mol % or 2.5 mol % of $Co(OAc)_2·4H_2O$ was used, the yield was slightly decreased (entries 11 and 12). When $Mn(OAc)_3·2H_2O$ was used as oxidant instead of Ag_2CO_3, only a trace amount of product was obtained (entry 13). The yield dropped when the temperature was lowered to 80-90 °C (entries 14 and 15). Control experiments showed that both the catalyst and the oxidant were essential for the carbonylation reaction (entries 16 and 17). Note that when the reaction of substrate **1a** was carried out under Daugulis's conditions,[7d] phthalimide **2a** was obtained in only 17% yield.

Table 1. Optimization of the Reaction Conditions.[a]



entry	[Co]	Ag_2CO_3 (equiv.)	solvent	T (°C)	yield (%)[b]
1[c]	$Co(OAc)_2·4H_2O$	2.0	PhCl	150	65
2[c]	$Co(OAc)_2·4H_2O$	2.0	PhCl	120	75
3[c]	$Co(OAc)_2·4H_2O$	2.0	PhCl	100	90
4[c]	$CoBr_2$	2.0	PhCl	100	trace
5[c]	$Co(acac)_2$	2.0	PhCl	100	55
6[c]	$Co(OAc)_2·4H_2O$	2.0	toluene	100	91
7[c]	$Co(OAc)_2·4H_2O$	2.0	TFE	100	30
8	$Co(OAc)_2·4H_2O$	2.0	toluene	100	99
9	$Co(OAc)_2·4H_2O$	1.0	toluene	100	90
10	$Co(OAc)_2·4H_2O$	**1.2**	**toluene**	**100**	**99**
11[d]	$Co(OAc)_2·4H_2O$	1.2	toluene	100	94
12[e]	$Co(OAc)_2·4H_2O$	1.2	toluene	100	91
13[f]	$Co(OAc)_2·4H_2O$	1.2	toluene	100	trace
14	$Co(OAc)_2·4H_2O$	1.2	toluene	90	94
15	$Co(OAc)_2·4H_2O$	1.2	toluene	80	89
16	/	1.2	toluene	100	ND
17	$Co(OAc)_2·4H_2O$	/	toluene	100	ND

[a] Reaction conditions: **1a** (0.2 mmol), $Co(OAc)_2·4H_2O$ (10 mol %), Ag_2CO_3, CO (1 atm), solvent (2 mL), 12 h, sealed tube. [b] Isolated yield. [c] NaOAc (1.0 equiv.) was added. [d] $Co(OAc)_2·4H_2O$ (5 mol %). [e] $Co(OAc)_2·4H_2O$ (2.5 mol %). [f] $Mn(OAc)_3·2H_2O$ was used instead of Ag_2CO_3.

With the optimized conditions established, we then explored the scope of the current C–H carbonylation reaction (Scheme 2). In general, the reaction showed good functional group tolerance and provided the desired phthalimide products in good to excellent yields. First, substrates with a variety of either electron-donating (**2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h** and **2i**) or electron-withdrawing (**2j**, **2k**, **2l**, **2m**, **2n**, **2o** and **2p**) *para*-substituents on the aromatic ring were compatible with the catalytic system. However, the benzoyl hydrazides bearing a strong electron-withdrawing group on the benzene ring led to slightly reduced yields (**2q**, **2r**). Although *meta*-substituted benzoyl hydrazides afforded the corresponding products in excellent yields with high regioselectivity (**2s-2u**), the piperamide gave two regioisomers with a ratio of 1:1 (**2ab**/**2ab'**). A possible reason for such a difference in the selectivity is the free rotation of the methoxy group in **1t**, causing a shielding effect that prevents the metal from approaching the C−H bond. Thus, C−H activation would take place selectively at the other side. In contrast, the 1,3-dioxo group in

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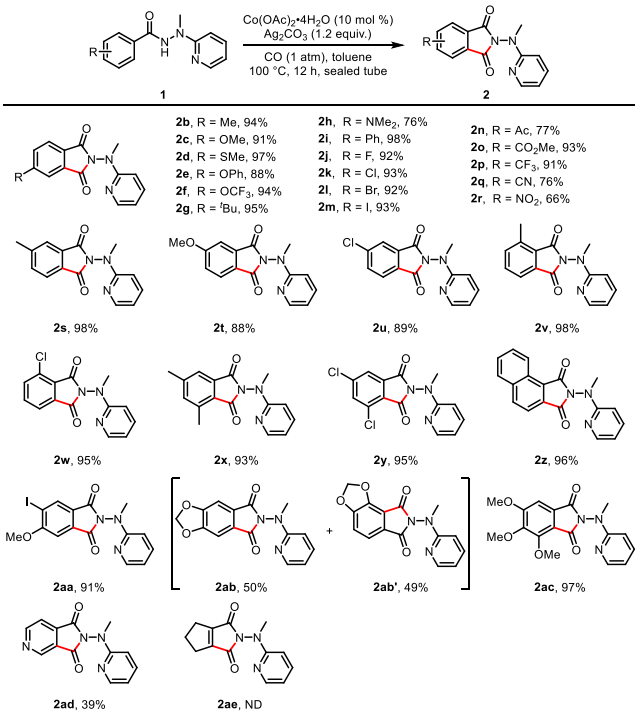
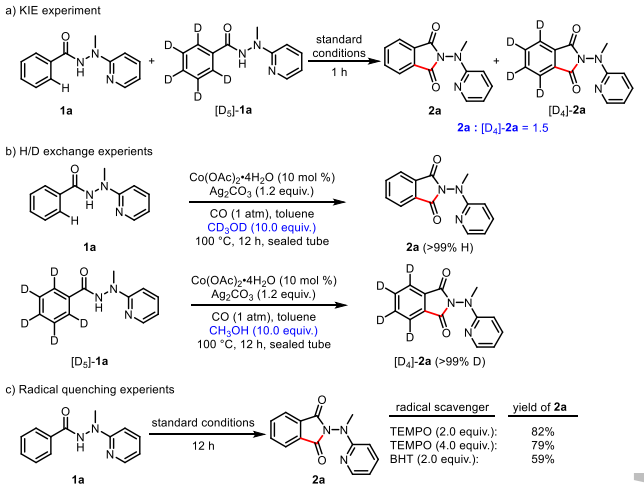


Scheme 2. Substrate Scope of the Benzoyl Hydrazides.

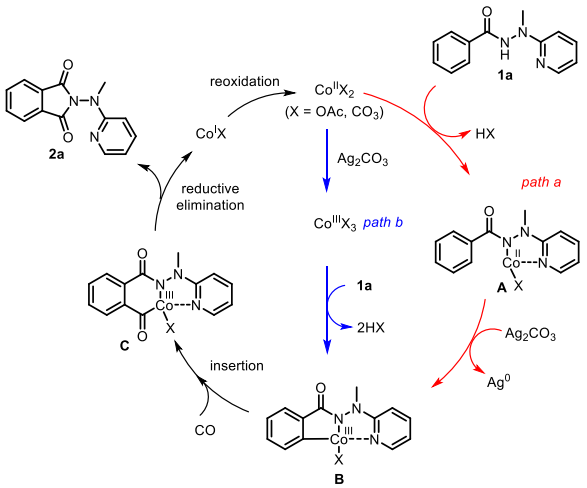
hydrazide **1ab** is locked so that the metal can approach the C−H bond without any unfavorable interactions and C–H activation could take place at both *ortho* positions of the carbonyl group. *ortho*-Substituted aromatic hydrazides provided the corresponding phthalimides in 95-98% yields (**2v**, **2w**). Multisubstituted benzoyl hydrazides behaved similarly (**2x**, **2y**, **2aa** and **2ac**). 1-Naphthamide derivative gave an excellent yield of 96% (**2z**). As a heteroaromatic substrate, isonicotinamide seemed to be less efficient under the standard reaction conditions, generating **2ad** in only 39% yield. The hydrazide with a cyclopentene moiety failed to give the desired product (**2ae**).

Relevant experiments were carried out to probe the mechanism of the carbonylation reaction (Scheme 3). The intermolecular competition experiment between **1a** and [D_5]-**1a** gave the carbonylation products **2a** and [D_4]-**2a** with a ratio of 1.5:1 (Scheme 3a), suggesting that the C–H bond activation step is not the rate determining step. When **1a** and [D_5]-**1a** were subjected to the standard conditions with the addition of 10 equiv. of CD_3OD and CH_3OH, respectively (Scheme 3b), no H/D exchange was observed, which indicated that the C–H bond cleavage should be an irreversible process. Furthermore, addition of radical scavengers such as TEMPO (2.0 equiv.) or BHT (2.0 equiv.) led only to slight decrease in the yield of **2a** (82% and 59%, respectively), and increasing the amount of TEMPO to 4.0 equiv. still gave a yield of 79% for **2a** (Scheme 3c), which implied that a single electron transfer (SET) process might not be involved in the reaction.



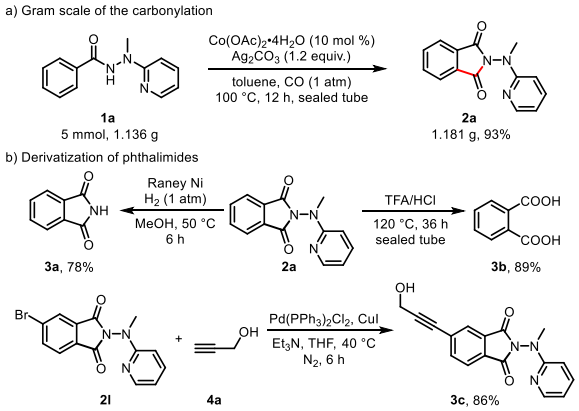
Scheme 3. Mechanistic Studies of the C−H Activation.

A plausible mechanism for the carbonylation reaction is proposed in Scheme 4. Hydrazide **1a** first coordinates with the Co^{II} complex to give intermediate **A**, which leads to the 5-membered cobaltacycle **B** upon oxidation of Co^{II} with Ag_2CO_3 and the subsequent carboxylate or carbonate-mediated *ortho*-proton abstraction (path a).[15l,15m,15u,17] Alternatively, the reaction may proceed with oxidation of Co^{II} to Co^{III} by Ag_2CO_3 prior to the chelation with **1a** and the subsequent C–H activation, generating intermediate **B** (path b).[15h,15j,15n,15p,15r] Insertion of carbon monoxide into the C–Co bond in **B** affords the 6-membered cobaltacycle **C**, which undergoes reductive elimination to give phthalimide **2a** with simultaneous release of the Co^{I} species. The Co^{I} species is reoxidized to the Co^{II} species by Ag_2CO_3 to complete the catalytic cycle.



Scheme 4. Proposed Mechanism.

To demonstrate the synthetic utility of this method, several notable transformations were conducted (Scheme 5). First, carbonylation of hydrazide **1a** was scaled up to gram scale with comparable yield and efficiency under the standard reaction conditions (Scheme 5a). Treatment of compound **2a** with Raney Ni successfully cleaved the N−N bond to give phthalimide **3a** in 78% yield.[18] In addition, treatment of **2a** under acidic conditions afforded the ring opening product **3b** in 89% isolated yield. Sonogashira coupling of bromide **2l** with propargyl alcohol **4a** afforded internal alkyne **3c** in good yields.



Scheme 5. Gram Scale Reactions and Product Derivatizations.

Conclusion

In summary, we have developed a cobalt-catalyzed carbonylation of C–H bonds of benzoyl hydrazides directed by the 2-(1-methylhydrazinyl)pyridine unit under an atmospheric pressure of CO. The present protocol has several distinct advantages. First, the reaction exhibited high regioselectivity and broad substrate scope with good functional group tolerance, providing a variety of phthalimides in good to excellent yields. Second, the 2-methylaminopyridine moiety within the product structure can be easily removed through hydrogenolysis under mild conditions. Third, the reaction may be facilely scaled up.

Experimental Section

General Procedure for Cobalt-Catalyzed Carbonylation

A 25-mL oven-dried sealed tube was charged with hydrazide **1** (0.20 mmol), $Co(OAc)_2{\cdot}4H_2O$ (5.0 mg, 0.02 mmol), Ag_2CO_3 (66.2 mg, 0.24 mmol). The tube was evacuated and filled with CO (1 atm), then toluene (2 mL) was added. The tube was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (5.0 mL), filtered through a plug of *Celite*, and concentrated in vacuo. The residue was purified by column chromatography [silica gel; *n*-hexanes/EtOAc (5:1 ~ 3:1, v/v)] to afford corresponding product **2**.

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References

[1] For selected reviews on transition-metal-catalyzed C–H functionalization, see: a) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074. b) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242. c) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068. d) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788. e) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. f) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281. g) S. A. Girard, T. Knauber, C.-J. Li, *Angew. Chem., Int. Ed.* **2014**, *53*, 74. h) N. Kuhl, N. Schröder, F. Glorius, *Adv. Synth. Catal.* **2014**, *356*, 1443. i) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007. j) B. Su, Z.-C. Cao, Z.-J. Shi, *Acc. Chem. Res.* **2015**, *48*, 886. k) J. Li, S. De Sarkar, L. Ackermann, *Top. Organomet. Chem.* **2015**, *55*, 217. l) W. Liu, L. Ackermann, *ACS Catal.* **2016**, *6*, 3743.

[2] a) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731. b) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624. c) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147. d) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740. e) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879. f) B.-J. Li, Z.-J. Shi, *Chem. Soc. Rev.* **2012**, *41*, 5588. g) G. Rouquet, N. Chatani, *Angew. Chem., Int. Ed.* **2013**, *52*, 11726. h) M. Gulías, J. L. Mascareñas, *Angew. Chem., Int. Ed.* **2016**, *55*, 11000. i) R.-Y. Zhu, M. E. Farmer, Y.-Q. Chen, J.-Q. Yu, *Angew. Chem., Int. Ed.* **2016**, *55*, 10578. j) N. Rajesh, N. Barsu, B. Sundararaju, *Tetrahedron Lett.* **2018**, *59*, 862. (k) J.-B. Peng, F.-P. Wu, X.-F. Wu, *Chem. Rev.* **2018**. DOI: 10.1021/acs.chemrev.8b00068.

[3] S. Murahashi, *J. Am. Chem. Soc.* **1955**, *77*, 6403.

[4] For Pd-catalyzed carbonylation of C(sp^2)–H bond, see: a) K. Orito, M. Miyazawa, T. Nakamura, A. Horibata H. Ushito, H. Nagasaki, M. Yuguchi, S. Yamashita, T. Yamazaki, M. Tokuda, *J. Org. Chem.* **2006**, *71*, 5951. b) R. Giri, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 14082. c) C. E. Houlden, M. Hutchby, C. D. Bailey, J. G. Ford, S. N. G. Tyler, M. R. Gagné, G. C. Lloyd-Jones, K. I. Booker-Milburn, *Angew. Chem., Int. Ed.* **2009**, *48*, 1830. d) R. Giri, J. K. Lam, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 686. e) B. Haffemayer, M. Gulias, M. J. Gaunt, *Chem. Sci.* **2011**, *2*, 312. f) Y. Lu, D. Leow, X. Wang, K. M. Engle, J.-Q. Yu, *Chem. Sci.* **2011**, *2*, 967. g) Z.-H. Guan, M. Chen, Z.-H. Ren, *J. Am. Chem. Soc.* **2012**, *134*, 17490. h) S. Luo, F.-X. Luo,

X.-S. Zhang, Z.-J. Shi, *Angew. Chem., Int. Ed.* **2013**, *52*, 10598. i) W. Li, Z. Duan, X. Zhang, H. Zhang, M. Wang, R. Jiang, H. Zeng, C. Liu, A. Lei, *Angew. Chem., Int. Ed.* **2015**, *54*, 1893. j) H. Taneda, K. Inamoto, Y. Kondo, *Org. Lett.* **2016**, *18*, 2712. k) A. Chandrasekhar, S. Sankararaman, *J. Org. Chem.* **2017**, *82*, 11487. l) C. Zhang, Y. Ding, Y. Gao, S. Li, G. Li, *Org. Lett.* **2018**, *20*, 2595. For Pd-catalyzed carbonylation of C(sp^3)–H bond, see: l) E. J. Yoo, M. Wasa, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 17378. m) A. McNally, B. Haffemayer, B. S. L. Collins, M. J. Gaunt, *Nature* **2014**, *510*, 129.

[5] a) E. J. Moore, W. R. Pretzer, T. J. O'Connell, J. Harris, L. LaBounty, L. Chou, S. S. Grimmer, *J. Am. Chem. Soc.* **1992**, *114*, 5888. b) Y. Ie, N. Chatani, T. Ogo, D. R. Marshall, T. Fukuyama, F. Kakiuchi, S. Murai, *J. Org. Chem.* **2000**, *65*, 1475. c) K. Inamoto, J. Kadokawa, Y. Kondo, *Org. Lett.* **2013**, *15*, 3962.

[6] a) Z.-H. Guan, Z.-H. Ren, S. M. Spinella, S. Yu, Y.-M. Liang, X. Zhang, *J. Am. Chem. Soc.* **2009**, *131*, 729. b) Y. Du, T. K. Hyster, T. Rovis, *Chem. Commun.* **2011**, *47*, 12074. c) B. Gao, S. Liu, Y. Lan, H. Huang, *Organometallics* **2016**, *35*, 1480.

[7] a) S. Inoue, H. Shiota, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2009**, *131*, 6898. b) N. Hasegawa, V. Charra, S. Inoue, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 8070. c) N. Hasegawa, K. Shibata, V. Charra, S. Inoue, Y. Fukumoto, N. Chatani, *Tetrahedron* **2013**, *69*, 4466. d) L. Grigorjeva, O. Daugulis, *Org. Lett.* **2014**, *16*, 4688. e) C. Wang, L. Zhang, C. Chen, J. Han, Y. Yao, Y. Zhao, *Chem. Sci.* **2015**, *6*, 4610. f) L. Zhang, C. Wang, J. Han, Z.-B. Huang, Y. Zhao, *J. Org. Chem.* **2016**, *81*, 5256.

[8] V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2005**, *127*, 13154.

[9] H. Miyachi, A. Azuma, A. Ogasawara, E. Uchimura, N. Watanabe, Y. Kobayashi, F. Kato, M. Kato, *J. Med. Chem.* **1997**, *40*, 2858.

[10] a) S. K. Teo, W. A. Colburn, W. G. Tracewell, K. A. Kook, D. I. Stirling, M. S. Jaworsky, M. A. Scheffler, S. D. Thomas, O. L. Laskin, *Clin Pharmacokinet* **2004**, *43*, 311. b) J. Y. Hui, M. Hoffmann, G. Kumar, *Reproductive Toxicology* **2014**, *48*, 115. c) B. G. Pereira, L. F. Batista, P. A. F. de Souza, G. R. da Silva, S. P. Andrade, R. Serakides, W. da Nova Mussel, A. Silva-Cunha, S. L. Fialho, *Biomedicine & Pharmacotherapy* **2015**, *71*, 21.

[11] D. Bout, H. Dupas, M. Capron, P. T. Van Ky, A. Capron, *Journal of Immunological Methods* **1977**, *15*, 1.

[12] a) K. Koivisto, J. Sivenius, T. Keränen, J. Partanen, P. Riekkinen, G. Gothoni, O. Tokola, P. J. Neuvonen, *Epilepsia* **1986**, *27*, 87. b) E. M. Airaksinen, K. Koivisto, T. Keränen, A. Pitkänen, P. J. Riekkinen, S. S. Oja, K. M. Marnela, J. V. Partanen, O. Tokola, G. Goth':oni, P. J. Neuvonen, M. M. Airaksinen, *Epilepsy. Res.* **1987**, *1*, 308. c) M. Iivanainen, O. Waltimo, O. Tokola, J. Parantainen, M. Tamminen, H. Allonen, P. J. Neuvonen, *Acta Neurol Scand.* **1990**, *82*, 121.

[13] E. Molina, H. G. Díaz, M. P. González, E. Rodríguez, E. Uriarte, *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 515.

[14] a) S. Zhai, S. Qiu, X. Chen, J. Wu, H. Zhao, C. Tao, Y. Li, B. Cheng, H. Wang, H. Zhai, *Chem. Commun.* **2018**, *54*, 98. b) H. Zhao, X. Shao, T. Wang, S. Zhai, S. Qiu, C. Tao, H. Wang, H. Zhai, *Chem. Commun.* **2018**, *54*, 4927.

[15] For selected recent reviews on the Co-catalyzed C–H bond functionalization, see: a) N. Yoshikai, *Synlett* **2011**, *2011*, 1047. b) K. Gao, N. Yoshikai, *Acc. Chem. Res.* **2014**, *47*, 1208. c) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2015**, *6*, 498. d) Y. Kommagalla, N. Chatani, *Coord. Chem. Rev.* **2017**, *350*, 117. e) D. R. Chambers, R. E. Sullivan, D. B. C. Martin, *Organometallics* **2017**, *36*, 1630. For selected examples on Co(II)-catalyzed functionalization, see: f) L. Grigorjeva, O. Daugulis, *Angew. Chem., Int. Ed.* **2014**, *53*, 10209. g) X.-G. Liu, S.-S. Zhang, C.-Y. Jiang, J.-Q. Wu, Q. Li, H. Wang, *Org. Lett.* **2015**, *17*, 5404. h) J. Zhang, H. Chen, C. Lin, Z. Liu, C. Wang, Y. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 12990. i) O. Planas, C. J. Whiteoak, V. Martin-Diaconescu, I. Gamba, J. M. Luis, T. Parella, A. Company, X. Ribas, *J. Am. Chem. Soc.* **2016**, *138*, 14388. j) N. Barsu, S. K. Bolli, B. Sundararaju, *Chem. Sci.* **2017**, *8*, 2431. k) P. Williamson, A. Galván, M. J. Gaunt, *Chem. Sci.* **2017**, *8*, 2588. l) L. Zeng, S. Tang, D. Wang, Y. Deng, J.-L. Chen, J.-F. Lee, A. Lei, *Org. Lett.* **2017**, *19*, 2170. m) L. Zeng, H. Li, S. Tang, X. Gao, Y. Deng, G. Zhang, C.-W. Pao, J.-L. Chen, J.-F. Lee, A. Lei, *ACS Catal.* **2018**, 5448. n) D. Kalsi, N. Barsu, B. Sundararaju, *Chem. Eur. J.* **2018**, *24*, 2360. For selected examples on other carbonyl source, see: o) X. Wu, Y. Zhao, H. Ge, *J. Am. Chem. Soc.* **2015**, *137*, 4924. p) J. Ni, J. Li, Z. Fan, A. Zhang, *Org. Lett.* **2016**, *18*, 5960. q) X. Wu, J. Miao, Y. Li, G. Li, H. Ge, *Chem. Sci.* **2016**, *7*, 5260. r) F. Ling, C. Ai, Y. Lv, W. Zhong, *Adv. Synth. Catal.* **2017**, *359*, 3707. s) T. T. Nguyen, L. Grigorjeva, O. Daugulis, *Chem. Commun.* **2017**, *53*, 5136. t) J. Han, N. Wang, Z.-B. Huang, Y. Zhao, D.-Q. Shi, *J. Org. Chem.* **2017**, *82*, 6831. u) F. Ling, C. Zhang, C. Ai, Y. Lv, W. Zhong, *J. Org. Chem.* **2018**. *83*, 5698.

[16] Compound **1a** decomposed under the reaction conditions if the methyl group on the hydrazide N' was replaced with a hydrogen.

[17] a) W. Ma, L. Ackermann, *ACS Catal.* **2015**, *5*, 2822. b) T. Yamaguchi, Y. Kommagalla, Y. Aihara, N. Chatani, *Chem. Commun.* **2016**, *52*, 10129. c) F. Zou, X. Chen, W. Hao, *Tetrahedron* **2017**, *73*, 758.

[18] L.-W. Qi, J.-H. Mao, J. Zhang, B. Tan, *Nat. Chem.* **2017**, *10*, 58.

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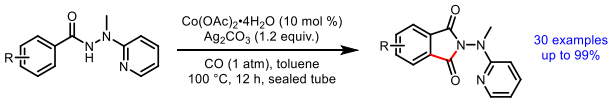

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