

Bu₄Ni-Catalyzed C–O Bond Formation by Using a Cross-Dehydrogenative Coupling (CDC) Reaction

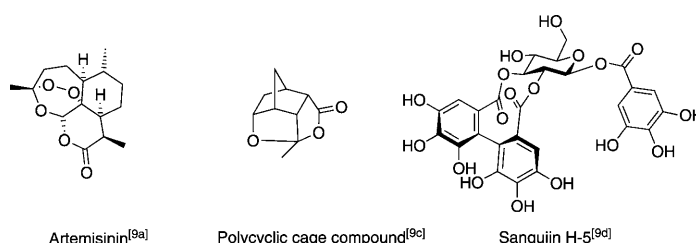
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The cleavage and functionalization of C–H bonds is of fundamental interest for both academia and industry. Generally, the transformation relies on transition metals,^[1] which are involved in four major approaches: 1) electrophilic activation of the C–H bond by a high-valent transition metal; 2) oxidative addition to the C–H bond by low-valent transition metals; 3) C–H bond activation by σ -bond metathesis, and 4) insertion of a metal carbenoid/nitrenoid into the C–H bond. After extensive studies, transition-metal-catalyzed C–H activation has arisen as an excellent synthetic method to build complex structures because it reduces prefunctionalization while improving atom economy and energy efficiency. However, the use of expensive metal catalysts and the problems involved in removing the residual metals from the final products, which is usually a difficult and tedious process, limits the practical applications of this strategy. The discovery of an efficient C–H transformation that does not require a metal catalyst would be of great value. This strategy would eliminate the requirement to remove traces of metal from the final products and solve the problem of disposal of the metal catalyst from the reaction mixtures. Recently, several groups disclosed a variety of novel C–C bond formations by using C–H activation under transition-metal-free conditions.^[2,3] The cross-dehydrogenative coupling (CDC) reaction, beyond traditional cross-couplings, has been the object of increasing interest over the last ten years. However, transition-metal catalysts, such as iron and copper salts, were usually required to promote this transformation.^[4,5]

The formation of C–O bonds is a fundamental transformation in synthetic organic chemistry.^[6] Therefore, the catalytic use of transition metals in C–O construction through C–H functionalization is of great interest.^[7] However, the

catalytic formation of C–O bonds through C–H functionalization under transition-metal-free conditions is less explored.^[8]

α -Acyloxy ethers appear frequently as a structural unit^[9] in biological and medicinal molecules of interest and are also useful synthetic intermediates^[10] in organic synthesis. (Scheme 1) Conventional routes to this ubiquitous class of



Scheme 1. Selected examples of α -acyloxy ethers.

compounds have relied on the addition of a carboxylic acid to an alkenyl ether,^[11] the nucleophilic substitution of a carboxylic acid to an α -halo ether,^[12] the esterification of a hemiacetal,^[9b,e,13] or a two-step synthesis.^[14] Herein, we report a simple and efficient method to construct α -acyloxy ethers by using Bu₄Ni as a catalyst and *tert*-butyl hydroperoxide (TBHP) as the oxidant. The transformation involves the CDC reaction of the C–H bond and the O–H group, without the aid of a transition-metal catalyst.

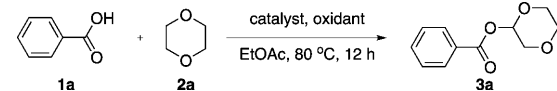
We began our investigation by examining the coupling of benzoic acid (**1a**) and 1,4-dioxane (**2a**) under metal-free conditions (Table 1, entry 1). From a wide range of candidates, the combination of Bu₄Ni (20 mol %) and TBHP (2.2 equiv, 70 % aqueous solution) was found to be particularly effective and produced the desired 1,4-dioxan-2-yl benzoate (**3a**) in 95 % yield. Table 1 shows the impact of catalyst and oxidant on the efficiency of the C–H oxidation process. The choice of oxidant has a paramount effect on this transformation; replacing TBHP with other common oxidants halted the formation of the desired product (Table 1, entries 2–8). In the absence of Bu₄Ni, no **3a** was formed (Table 1, entry 10). Other quaternary ammonium iodides, such as Me₄Ni and Me₃BnNi, were also tested resulting in the desired product **3a** in decreased yields (Table 1, entries 11 and 12). Both Bu₄NCl and Bu₄NBr showed negligible activity (Table 1, entries 13 and 14). Notably, the addi-

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Table 1. Optimization of the reaction conditions.^[a]



Entry	Catalyst	Oxidant	Yield ^[b] [%]
1	Bu ₄ NI	TBHP	95
2	Bu ₄ NI	oxone	— ^[c]
3	Bu ₄ NI	NaClO	— ^[c]
4	Bu ₄ NI	H ₂ O ₂	— ^[c]
5	Bu ₄ NI	<i>t</i> BuOCl	— ^[c]
6	Bu ₄ NI	(<i>t</i> BuO) ₂	— ^[c]
7	Bu ₄ NI	O ₂	— ^[c]
8	Bu ₄ NI	benzoquinone	— ^[c]
9	Bu ₄ NI	—	— ^[c]
10	—	TBHP	— ^[c]
11	Me ₄ NI	TBHP	52
12	Me ₃ BnNI	TBHP	88
13	Bu ₄ NCl	TBHP	<5
14	Bu ₄ NBr	TBHP	<5
15	PdCl ₂	TBHP	<5
16	Pd(OAc) ₂	TBHP	<5
17	CuCl	TBHP	<5
18	CuI	TBHP	<5
19	RuCl ₃ · <i>n</i> H ₂ O	TBHP	<5
20	Bu ₄ NI	TBHP	94 ^[d]

[a] Reaction conditions: benzoic acid (0.5 mmol), 1,4-dioxane (10 mmol), and catalyst (20 mol %) in EtOAc (2.0 mL) at 80 °C for 5 h unless otherwise noted. [b] Yield of isolated product. [c] Product not observed. [d] 100 mmol of benzoic acid was added.

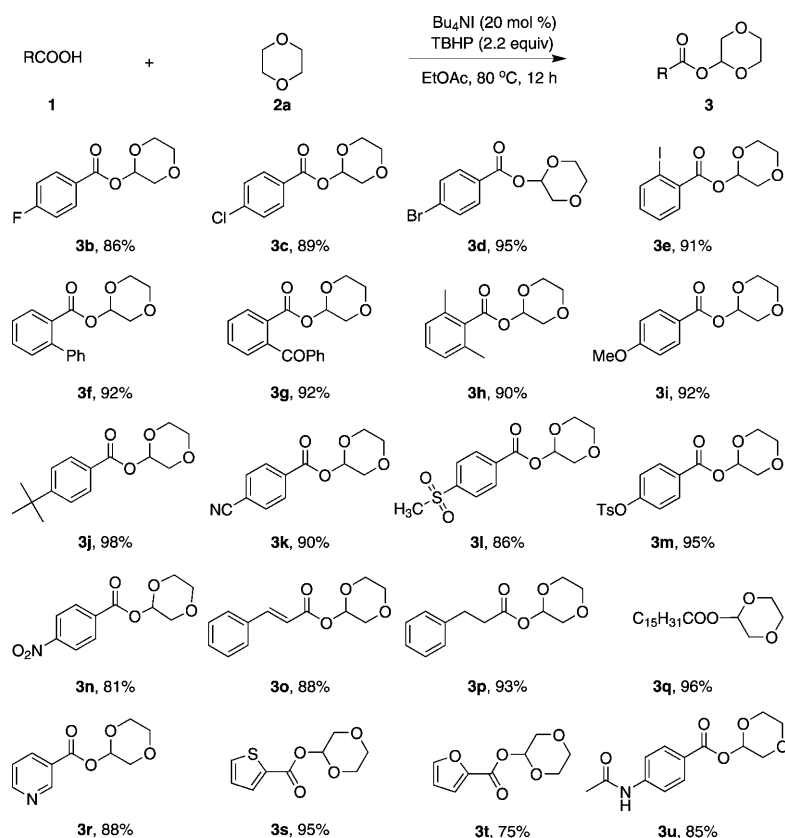
tion of various metal catalysts, such as Pd, Cu, and Ru salts, suppressed the transformation (Table 1, entries 15–19). Grati-fyingly, the presence of air and/or moisture hardly has any effect on the reaction, which is in stark contrast to most transition-metal-catalyzed reactions. The present methodology was also tested on a larger scale (100 mmol) and the product was obtained in 94 % yield (Table 1, entry 20).

Once the viability of the method was established, this approach was then applied to the coupling of 1,4-dioxane to a variety of carboxylic acids and the results of which are shown in Scheme 2. The process exhibits a broad scope and a high compatibility with functional groups, such as halide, keto, ether, cyano, sulfone, trifluoro-methane sulfonate (OTs), nitro, alkene, and amide functional groups. Different substitution patterns on the aryl ring were tolerated; *ortho*-, *meta*-, and

para-substituted aromatic acids reacted with 1,4-dioxane to give the corresponding products. Both electronic and steric effects of the aromatic acids hardly influenced the reactivity, giving the desired products in good to excellent yields. Notably, the presence of halide and even iodo substituents on the aromatic groups did not interfere with the C–H activation process, affording products **3b–3e** that could be further functionalized by transition-metal-catalyzed cross-coupling reactions. Even aliphatic acids also reacted with 1,4-dioxane to form products **3p** or **3q** in excellent yields of 93 and 96 %, respectively. Furthermore, when heteroarenes, such as pyridine, thiophene, and furan were reacted, the corresponding products **3r–3t** were also obtained in high yields.

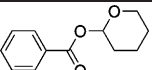
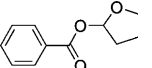
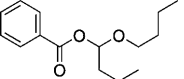
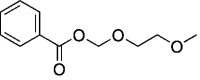
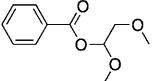
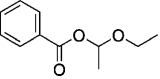
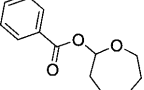
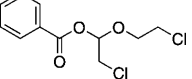
After testing the coupling reaction of 1,4-dioxane with carboxylic acids, other target ethers were investigated. As shown in Table 2, a variety of ethers, including cyclic and acyclic ethers, were found to be coupling partners and the desired products were formed in satisfactory to excellent yields. When unsymmetrical 1,2-dimethoxyethane was reacted with benzoic acid, two regioisomers, **4da** and **4db**, were obtained with an excellent combined yield (Table 2, entry 4). Notably, the methodology was also suitable for bis(2-chloroethyl) ether (Table 2, entry 7).

The results in Scheme 2 and Table 2 showed the potential of the unprecedented C–O bond-forming reaction, therefore we next investigated the reaction mechanism to help further



Scheme 2. Coupling of 1,4-dioxane to a variety of carboxylic acids; reaction conditions: carboxylic acid (0.5 mmol), 1,4-dioxane (10 mmol), Bu₄NI (20 mol %), TBHP (2.2 equiv, 70 % aqueous solution), EtOAc (2.0 mL), 80 °C, 12 h.

Table 2. Reaction of benzoic acid with ethers.^[a]

$\text{C}_6\text{H}_5\text{COOH} + \text{R}^1\text{CH}_2\text{OR}^2 \xrightarrow[\text{EtOAc, 80 } ^\circ\text{C, 5 h}]{\text{Bu}_4\text{NI (20 mol\%), TBHP (2.2 equiv)}} \text{C}_6\text{H}_5\text{COOCH(R}^1\text{)CH}_2\text{OR}^2$			
Entry	Ether	Product	Yield ^[b] [%]
1			4a 96
2			4b 86
3	Bu ₂ O		4c 82
			4da 37
4	DME		4db 54
5	Et ₂ O		4e 86
6			4f 90
7	ClCH ₂ CH ₂ OCH ₂ CH ₂ Cl		4g 66

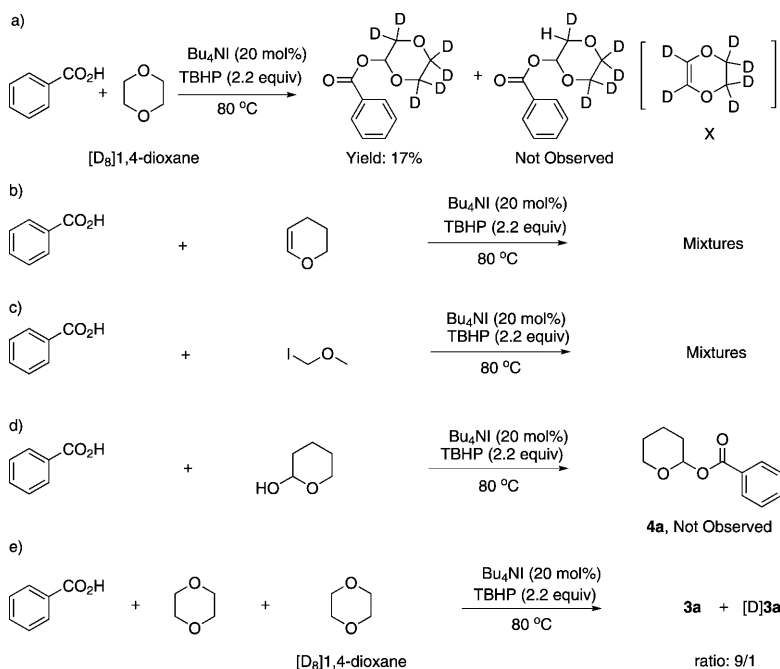
[a] Reaction conditions: carboxylic acid (0.5 mmol), 1,4-dioxane (10 mmol), Bu₄NI (20 mol %), TBHP (2.2 equiv, 70 % aqueous solution), EtOAc (2.0 mL), 80 °C, 12 h. [b] Yield of isolated product. DME = 1,2-dimethoxyethane.

expansion. We suspected that the addition of the carboxylic acid to the alkenyl ether could be involved in the catalytic cycle. In fact, when 1,4-dioxane was replaced with [D₈]1,4-dioxane, product [D]**3a** was achieved in low yield. However, no hydrogen-incorporated product was observed (Scheme 3a). Additionally, complicated mixtures were observed when dihydropyran was used as the ether (Scheme 3b). Based upon these results, alkenyl ether might not act as an intermediate in this transformation.^[11] The reaction of benzoic acid and iodomethyl methyl ether resulted in mixtures, which means that the nucleophilic substitution of car-

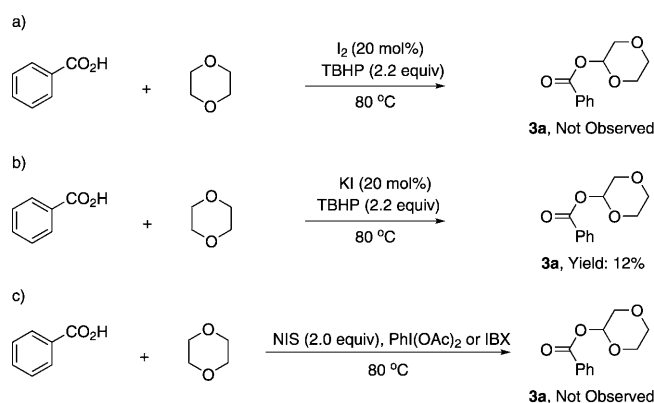
boxylic acid to the α-halo ether^[12] is an unlikely pathway for the catalytic cycle (Scheme 3c). Notably, hemiacetal was also excluded as an intermediate in this transformation based upon a control experiment (Scheme 3d).^[9b,e,13] Moreover, a kinetic isotopic effect (KIE) experiment was conducted under the optimized conditions (Scheme 3e). The reaction shows a significant *k*_H/*k*_D of 9.0, implying that C–H bond cleavage is the rate-limiting step of this transformation. (The KIE was determined by ¹H NMR spectroscopy by analyzing the ratio of **3a** and [D]**3a**).

Addition of a radical-trapping reagent, in this case 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO), to the reaction medium suppressed the transformation, which indicated that the C–O bond formation is probably a radical process. A brown color in the reaction mixture indicated the generation of iodine in this reaction system. A control experiment, in which Bu₄NI was replaced with iodine, showed no coupling, which discounted iodine as the active catalyst (Scheme 4a). Switching the catalyst to KI provided the desired product **3a** in low yield (Scheme 4b). In addition, we demonstrated that hypervalent iodine reagents do not act as oxidants in the reaction, based on a control experiment (Scheme 4c).

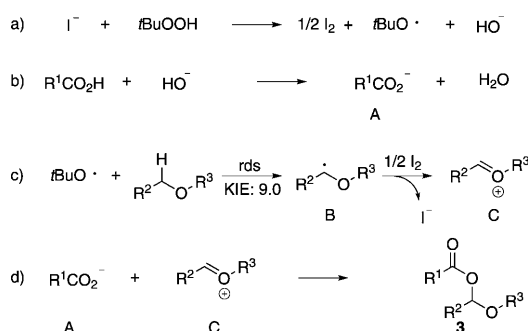
Based on these observations and literature reports,^[3a,5m,15] a plausible catalytic cycle has been proposed in Scheme 5. The mechanism involves four steps: firstly, TBHP decomposes to the *tert*-butoxyl radical and a hydroxyl anion in the presence of Bu₄NI (Scheme 5, step a); next the carboxylic acid is deprotonated by the hydroxyl anion, which gives the anionic species A (Scheme 5, step b); on the ether, hydrogen is extracted from the C–H bond adjacent to an oxygen atom, to give the intermediate B and iodine oxidation generates an oxonium ion C (Scheme 5, step c). Finally, nucle-



Scheme 3. Investigation into the reaction mechanism.



Scheme 4. Investigation into the role of iodide.



Scheme 5. A plausible reaction mechanism.

philic addition of **A** to **C** generates the desired product **3** (Scheme 5, step d). Overall, the I_2/I^- redox process plays a key role in the C–O bond formation, by promoting the reductive cleavage of the O–O bond in the peroxide (Scheme 5, step a) and in the oxidation of the carbon radical to an oxonium ion (Scheme 5, step c).

In summary, we have developed a new method for the construction of C–O bonds by using the CDC reaction. The methodology is distinguished by 1) the lack of expensive transition metals required for the transformation; 2) the direct use of commercially available materials; 3) operational simplicity; 4) the fact that an inert atmosphere or dry solvents are not required; and 5) a wide tolerance of various functional groups. We believe that this is the most simple and straightforward methodology available for the synthesis of α -acyloxy ethers to date. Investigation on an asymmetric version, a detailed mechanism, and synthetic applications of this reaction are underway in our laboratory.

Experimental Section

General procedures for preparation of **3 and **4**:** Carboxylic acid (0.5 mmol), ether (10 mmol or 15 mmol), EtOAc (2.0 mL), Bu_4NI (0.1 mmol, 20 mol %), and TBHP (2.2 equiv, 70 % aqueous solution) were added to a tube under air. The reaction mixture was heated in an oil bath at 80 °C for the designated time. Removal of the organic solvent under vacuum followed by purification with flash silica gel column chro-

matography (eluting with petroleum ether and ethyl acetate mixtures) afforded products in moderate to high yields.

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Keywords: carboxylic acids • cross-coupling • ethers • oxidation • reaction mechanisms

- [1] For reviews on this topic, see: a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655; b) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976–10011; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826; c) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074–1086; d) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196–5217; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115; e) I. A. I. Mkhaliid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931; f) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147–1169; g) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703; h) B.-J. Li, i) S.-D. Yang, Z.-J. Shi, *Synlett* **2008**, 949–957; i) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424; j) S. S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298–2311; *Angew. Chem. Int. Ed.* **1998**, *37*, 2180–2192; k) K. Godula, D. Sames, *Science* **2006**, *312*, 67–72.
- [2] M. Klussmann, D. Sureshkumar, *Synthesis* **2011**, 353–369.
- [3] For C–C formation through C–H activation under transition-metal-free conditions, see: a) S. J. Pastine, K. M. McQuaid, D. Sames, *J. Am. Chem. Soc.* **2005**, *127*, 12180–12181; b) N. Dietl, M. Engeser, H. Schwarz, *Angew. Chem.* **2009**, *121*, 4955–4957; *Angew. Chem. Int. Ed.* **2009**, *48*, 4861–4863; c) G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini, *Chem. Eur. J.* **2009**, *15*, 4248–4252; d) V. Chudasama, R. J. Fitzmaurice, S. Caddick, *Nat. Chem.* **2010**, *2*, 592–596; e) W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong, A. Lei, *J. Am. Chem. Soc.* **2010**, *132*, 16737–16740; f) C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li, Z.-J. Shi, *Nat. Chem.* **2010**, *2*, 1044–1049; g) E. Shirakawa, K. Itoh, T. Higashino, T. Hayashi, *J. Am. Chem. Soc.* **2010**, *132*, 15537–15539; h) G. Deng, W. Chen, C.-J. Li, *Adv. Synth. Catal.* **2009**, *351*, 353–356; i) A. S. K. Tsang, M. H. Todd, *Tetrahedron Lett.* **2009**, *50*, 1199–1202; j) J. C. Conrad, J. Kong, B. N. Laforgeza, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 11640–11641; k) Y. Ye, C. Zheng, R. Fan, *Org. Lett.* **2009**, *11*, 3156–3159; l) D. Chenga, W. Bao, *Adv. Synth. Catal.* **2008**, *350*, 1263–1266; m) K. C. Nicolaou, R. Reingruber, D. Sarlah, S. Bräse, *J. Am. Chem. Soc.* **2009**, *131*, 2086–2087.
- [4] For reviews on this topic, see: a) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335–344; b) C. J. Scheuermann, *Chem. Asian J.* **2010**, *5*, 436–451.
- [5] For representative examples on C–C or C–X bond formation by using a CDC reaction, see: a) Z. Shi, C. Zhang, S. Li, D. Pan, S. Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 4642–4646; *Angew. Chem. Int. Ed.* **2009**, *48*, 4572–4576; b) Y.-Z. Li, B.-J. Li, X.-Y. Lu, S. Lin, Z.-J. Shi, *Angew. Chem.* **2009**, *121*, 3875–3878; *Angew. Chem. Int. Ed.* **2009**, *48*, 3817–3820; c) O. Baslé, C. J. Li, *Chem. Commun.* **2009**, 4124–4126; d) W.-J. Yoo, C. A. Correia, Y. Zhang, C. J. Li, *Synlett* **2009**, 138–142; e) Y. Shen, M. Li, S. Wang, T. Zhan, Z. Tan, C. Guo, *Chem. Commun.* **2009**, 953–955; f) H. Richter, O. G. Mancheño, *Eur. J. Org. Chem.* **2010**, 4460–4467; g) O. Baslé, C.-J. Li, *Green Chem.* **2007**, *9*, 1047–1050; h) Y. Zhang, C.-J. Li, *Angew. Chem.* **2006**, *118*, 1983–1986; *Angew. Chem. Int. Ed.* **2006**, *45*, 1949–1952; i) Z. Li, R. Yu, H. Li, *Angew. Chem.* **2008**, *120*, 7607–7610; *Angew. Chem. Int. Ed.* **2008**, *47*, 7497–7500; j) L.

- Wang, H. Fu, Y. Jiang, Y. Zhao, *Chem. Eur. J.* **2008**, *14*, 10722–10726; k) Z. Wang, Y. Zhang, H. Fu, Y. Jiang, Y. Zhao, *Org. Lett.* **2008**, *10*, 1863–1866; l) Z. Li, L. Cao, C.-J. Li, *Angew. Chem.* **2007**, *119*, 6625–6627; *Angew. Chem. Int. Ed.* **2007**, *46*, 6505–6507; m) Y. Zhang, C.-J. Li, *J. Am. Chem. Soc.* **2006**, *128*, 4242–4243; n) Á. Pintér, A. Sud, D. Sureshkumar, M. Klusmann, *Angew. Chem.* **2010**, *122*, 5124–5128; *Angew. Chem. Int. Ed.* **2010**, *49*, 5004–5007; o) Z. Li, H. Li, X. Guo, L. Cao, R. Yu, H. Li, S. Pan, *Org. Lett.* **2008**, *10*, 803–805; p) P. P. Pradhan, J. M. Bobbitt, W. F. Bailey, *J. Org. Chem.* **2009**, *74*, 9524–9527; q) F. Benfatti, M. G. Capdevila, L. Zoli, E. Benedetto, P. G. Cozzi, *Chem. Commun.* **2009**, 5919–5921.
- [6] S. V. Ley, A. W. Thomas, *Angew. Chem.* **2003**, *115*, 5558–5607; *Angew. Chem. Int. Ed.* **2003**, *42*, 5400–5449.
- [7] a) T. Yoneyama, R. H. Crabtree, *J. Mol. Catal. A: Chem.* **1996**, *108*, 35–40; b) A. R. Dick, K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2004**, *126*, 2300–2301; c) L. V. Desai, K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2004**, *126*, 9542–9543; d) R. Giri, J. Liang, J.-G. Lei, J.-J. Li, D.-H. Wang, X. Chen, I. C. Naggar, C. Guo, B. M. Foxman, J.-Q. Yu, *Angew. Chem.* **2005**, *117*, 7586–7590; *Angew. Chem. Int. Ed.* **2005**, *44*, 7420–7424; e) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790–6791; f) Z. Ye, W. Wang, F. Luo, S. Zhang, J. Cheng, *Org. Lett.* **2009**, *11*, 3974–3977.
- [8] a) M. Uyanik, H. Okamoto, T. Yasui, K. Ishihara, *Science* **2010**, *328*, 1376–1379; b) J. Jin, Y. Li, Z.-j. Wang, W.-X. Qian, W.-L. Bao, *Eur. J. Org. Chem.* **2010**, 1235–1238; c) T. Dohi, A. Maruyama, M. Yoshimura, K. Morimoto, H. Tohma, Y. Kita, *Angew. Chem.* **2005**, *117*, 6349–6352; *Angew. Chem. Int. Ed.* **2005**, *44*, 6193–6196.
- [9] a) China cooperative research group on qinghaosu, *Kexue Tongbao* **1977**, *22*, 142; b) C. Singh, S. Chaudhary, S. K. Puri, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1436–1441; c) H.-J. Wu, S.-H. Tsai, J.-H. Chern, H.-C. Lin, *J. Org. Chem.* **1997**, *62*, 6367–6373; d) X. Su, D. S. Surry, R. J. Spandl, D. R. Spring, *Org. Lett.* **2008**, *10*, 2593–2596; e) R. K. Haynes, H.-W. Chan, M.-K. Cheung, W.-L. Lam, M.-K. Soo, H.-W. Tsang, A. Voerste, I. D. Williams, *Eur. J. Org. Chem.* **2002**, 113–132; f) M. A. A. Orabi, S. Taniguchi, M. Yoshimura, T. Yoshida, K. Kishino, H. Sakagami, T. Hatano, *J. Nat. Prod.* **2010**, *73*, 870–879; g) M. C. de La Torre, G. Domínguez, B. Rodríguez, A. Perales, M. S. J. Simmonds, W. M. Blaney, *Tetrahedron* **1994**, *50*, 13553–13566; h) L. Cirillo, E. Bedini, M. Parrilli, *Eur. J. Org. Chem.* **2008**, 5704–5714; i) H. Takamura, S. Kikuchi, Y. Nakamura, Y. Yamagami, T. Kishi, I. Kadota, Y. Yamamoto, *Org. Lett.* **2009**, *11*, 2531–2534.
- [10] a) R. Jasti, J. Vitale, S. D. Rychnovsky, *J. Am. Chem. Soc.* **2004**, *126*, 9904–9905; b) J. E. Dalgard, S. D. Rychnovsky, *J. Am. Chem. Soc.* **2004**, *126*, 15662–15663; c) I. D. Gridnev, S. Kikuchi, A. S. Touchy, I. Kadota, Y. Yamamoto, *J. Org. Chem.* **2007**, *72*, 8371–8375; d) S. Chamberland, K. A. Woerpel, *Org. Lett.* **2004**, *6*, 4739–4741; e) J. Lage Robles, C. G. Bochet, *Org. Lett.* **2005**, *7*, 3545–3547.
- [11] a) W. J. Croxall, F. J. Glavis, H. T. Neher, *J. Am. Chem. Soc.* **1948**, *70*, 2805–2807; b) G. F. Woods, D. N. Kramer, *J. Am. Chem. Soc.* **1947**, *69*, 2246; c) B. B. Corson, H. E. Tiefenthal, W. J. Heintzelman, *J. Org. Chem.* **1956**, *21*, 371–372.
- [12] a) R. K. Summerbell, H. E. Lunk, *J. Am. Chem. Soc.* **1958**, *80*, 604–605; b) C. D. Hurd, F. O. Green, *J. Am. Chem. Soc.* **1941**, *63*, 2201–2204.
- [13] M. A. Huffman, J. H. Smitrovich, J. D. Rosen, G. N. Boice, C. Qu, T. D. Nelson, J. M. McNamara, *J. Org. Chem.* **2005**, *70*, 4409–4413.
- [14] a) D. J. Kopecky, S. D. Rychnovsky, *J. Org. Chem.* **2000**, *65*, 191–198; b) C. Semeyn, R. H. Blaauw, H. Hiemstra, W. N. Speckamp, *J. Org. Chem.* **1997**, *62*, 3426–3427; c) Y. Zhang, T. Rovis, *Org. Lett.* **2004**, *6*, 1877–1879.
- [15] a) S. Pan, J. Liu, H. Li, Z. Wang, X. Guo, Z. Li, *Org. Lett.* **2010**, *12*, 1932–1935; b) A. Clerici, C. Greco, W. Panzeri, N. Pastori, C. Punta, O. Porta, *Eur. J. Org. Chem.* **2007**, 4050–4055; c) E. C. McLaughlin, H. Choi, K. Wang, G. Chiou, M. P. Doyle, *J. Org. Chem.* **2009**, *74*, 730–738; d) L.-S. Li, S. Das, S. C. Sinha, *Org. Lett.* **2004**, *6*, 127–130; e) L. J. Csányi, K. Jáký, I. Pálkó, A. Rockenbauer, L. Korecz, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3801–3805.

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