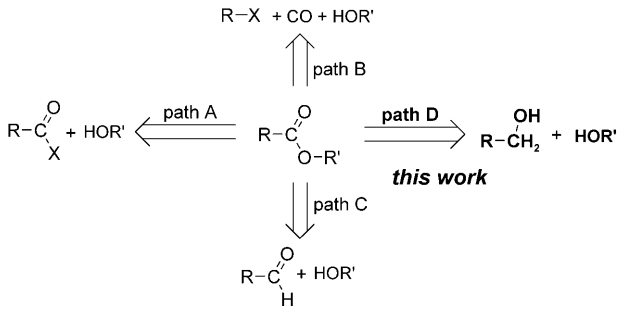
Oxidative Esterification

DOI: 10.1002/anie.201008073

Palladium-Catalyzed Aerobic Oxidative Direct Esterification of Alcohols**

*Chao Liu, Jing Wang, Lingkui Meng, Yi Deng, Yao Li, and Aiwen Lei**

Ester groups are among the highly important and abundant functional groups in chemistry and can be found in bulk chemicals, fine chemicals, natural products, and polymers.[1] Traditionally, esters are prepared by the reaction of activated acid derivatives (acyl chlorides and anhydrides) with alcohols (Scheme 1, path A),[2] a multistep process that often produces large amounts of unwanted by-products. A more direct approach, which uses developments in transition-metal-catalyzed cross-coupling reactions, involves the carbonylation of aryl halides (Scheme 1, path B);[3] however, the high temperature and high CO pressure required as well as the presence of halide anions make this reaction environmentally unfavorable.[4] Further efforts have been devoted to the direct synthesis of esters from the oxidative esterification of aldehydes with alcohols,[5] in which stoichiometric amounts of metal salts like $KHSO_5$ (oxone) or MnO_2 have to be employed as oxidants (Scheme 1, path C).[6] The required aldehydes are normally synthesized by selective oxidation of alcohols.[7] All of the above three methods require several reaction steps and produce unwanted by-products, therefore it is part of the challenges of green and sustainable chemistry to update these old processes.

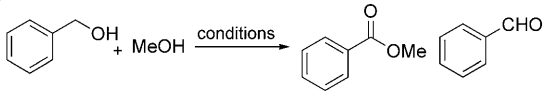


Scheme 1. Approaches for the synthesis of ester groups.

Alcohols (as some of the most fundamental compounds) are usually readily available as bulk chemicals. Traditionally, alcohols could be converted into esters by multiple steps. However, direct conversion of alcohols into esters in the presence of catalysts could represent a step forward toward green, economic, and sustainable processes (Scheme 1, path D).[8] In recent years, palladium-catalyzed oxidation reactions have been widely investigated;[7a,c,9] much more attention has been paid to highly selective oxidations using O_2 as the terminal oxidant.[7a,10] To the best of our knowledge, no results regarding the palladium-catalyzed aerobic oxidative direct esterification from two different alcohols have been reported. Herein, we communicate our recent progress in this field.

Benzylic alcohol and methanol were used in the model reaction and molecular oxygen was employed as the oxidant (Table 1). Initially, different palladium catalyst precursors were tested in methanol with Na_2CO_3 as the base (Table 1, entries 1–3). $[PdCl_2(CH_3CN)_2]$ showed the best result with 53% yield of the desired product **2a**, as determined by GC,

Table 1: Impact of reaction parameters on the oxidative esterification of benzylic alcohols with methanol.[a]



1a **2a** **3a**

Entry	Solvent	Base	Catalyst	Yield [%][b]	
				2a	**3a**
1	MeOH	Na_2CO_3	$[PdCl_2(PPh_3)_2]$	44	51
2	MeOH	Na_2CO_3	$[Pd(OAc)_2]$	48	42
3	MeOH	Na_2CO_3	$[PdCl_2(CH_3CN)_2]$	53	38
4	MeOH	–	$[PdCl_2(CH_3CN)_2]$	n.d.	n.d.
5	MeOH	Cs_2CO_3	$[PdCl_2(CH_3CN)_2]$	64	34
6	MeOH	NEt_3	$[PdCl_2(CH_3CN)_2]$	n.r.	n.r.
7	MeOH	K_3PO_4	$[PdCl_2(CH_3CN)_2]$	12	48
8	MeOH	NaO*t*Bu	$[PdCl_2(CH_3CN)_2]$	74	n.d.
9[c]	DMSO	NaO*t*Bu	$[PdCl_2(CH_3CN)_2]$	n.d.	n.d.
10[c]	THF	NaO*t*Bu	$[PdCl_2(CH_3CN)_2]$	n.d.	n.d.

[a] Reaction conditions: 0.5 mmol benzylic alcohol, 5 mol% Pd catalyst, 1.0 mmol base, 2 mL solvent, 45 °C, oxygen balloon, overnight. [b] Determined by GC–MS by using biphenyl as internal standard. [c] MeOH/**1a** = 5:1. n.d. = not determined; n.r. = no reaction.

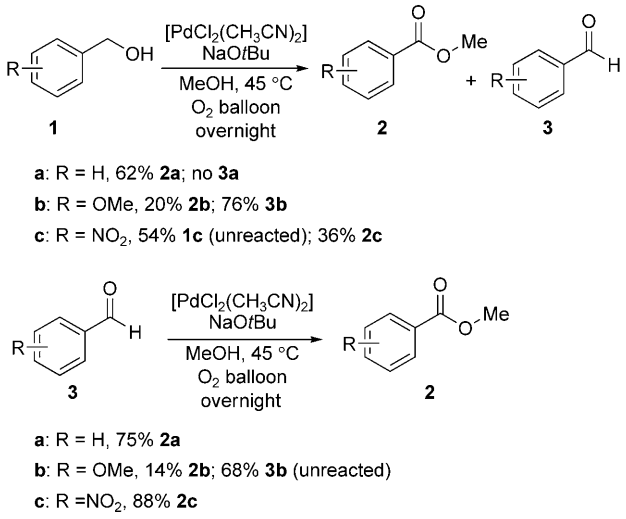
[*] C. Liu, J. Wang, L. Meng, Y. Deng, Y. Li, Prof. A. Lei
College of Chemistry and Molecular Sciences
Wuhan University (P. R. China)
Fax: (+86) 27-6875-4067
E-mail: aiwenlei@whu.edu.cn
Homepage: http://www.chem.whu.edu.cn/GCI_WebSite/main.htm
Prof. A. Lei
State Key Laboratory for Oxo Synthesis and Selective Oxidation
Lanzhou Institute of Chemical Physics
Chinese Academy of Sciences, 730000 Lanzhou (P. R. China)

[**] This work was supported by the National Natural Science Foundation of China (20772093, 20972118, and 20832003), the Fundamental Research Funds for the Central Universities, and Program for New Century Excellent Talents in University. We thank Prof. Xinquan Hu (Zhejiang University of Technology) for providing several benzylic alcohols as gifts. We thank Prof. Matthias Beller (Rostock University) for sharing information on work in this area.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201008073.

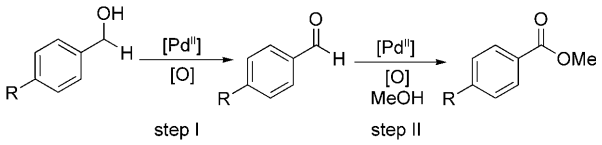
and 38% yield of the aldehyde **3a**. By-products of benzylic formate could not be detected by GC–MS; no reaction was observed without addition of a base (Table 1, entry 4). Base screening showed that the organic base NEt_3 (Table 1, entry 6) was ineffective while a stronger base (NaO*t*Bu) gave the best reactivity with a 74% yield of the ester, as determined by GC; the aldehyde could not be observed (Table 1, entry 8). Solvent effects were also tested: using MeOH as solvent afforded the best result (Table 1, entries 8–10). No benzylic formate was detected even in other solvents (DMSO, THF; Table 1, entries 9–10).

The conditions of entry 8 in Table 1 were then applied to investigate the substrate scope. Unfortunately, the reaction was very sensitive to the substituent on the phenyl ring of the benzylic alcohol. Unsubstituted benzyl alcohol gave the desired product **2a** smoothly and no aldehyde **3a** was observed (Scheme 2, (**a**)), but for strongly electron-donating



Scheme 2. Substitution effect on the oxidative esterification reaction.

groups (EDGs), such as the methoxy group, no 4-methoxybenzyl alcohol could be found while 4-methoxybenzaldehyde **3b** was observed in 76% yield by NMR spectroscopy; in addition, 20% of the desired methyl ester **2b** was detected (Scheme 2, (**b**)). However, for the strongly electron-withdrawing groups (EWGs), such as *p*-NO_2, conversion of the substrate 4-nitrobenzyl alcohol **1c** was incomplete (54% unreacted); no formation of the aldehyde was observed and 36% of the desired ester **2c** was detected (Scheme 2, (**c**)). In addition, the esterifications of three typical aldehydes with different electronic properties were carried out under the same conditions. The benzaldehyde gave the corresponding ester in high selectivity and good yield (Scheme 2 bottom, (**a**)). The benzaldehyde substituted with the strongly electron-donating group *p*-OMe gave the desired product **2b** in only 14% yield in NMR spectroscopy, with 68% of aldehyde **3b** remaining unreacted (Scheme 2 bottom, (**b**)). For the benzaldehyde substituted with the strongly electron-withdrawing group *p*-NO_2, the reaction proceeded smoothly; 88% of the desired ester **2c** was isolated, no aldehyde was left (Scheme 2 bottom, (**c**)). Consistent with these results, the following pathway was proposed (Scheme 3) and a possible mechanism was outlined (see the Supporting Information).



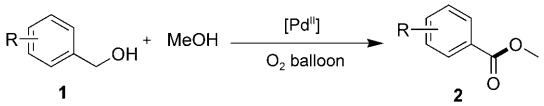
Scheme 3. Possible pathway for the oxidative esterification reaction.

Firstly, benzylic alcohol coordinates to the Pd^{II} center followed by β-hydride elimination to generate benzaldehyde (step I), which directly reacts with another alcohol to form the corresponding hemiacetal. The desired ester is a result of the palladium-catalyzed β-hydride elimination of the hemiacetal (step II). In these two reaction steps, the nature of the substituent R has a significant influence on the reactivity of the intermediates. An electron-donating group such as *p*-OMe makes the C–H bonds of CH_2 more electron-rich so that the β hydride can be easily eliminated and it thus becomes easier to form the corresponding aldehyde (Scheme 2, (**b**)). However, a strongly electron-withdrawing group such as *p*-NO_2 makes the C–H bonds more electron-deficient so that the β hydride cannot be easily eliminated; thus, it is relatively difficult to form the corresponding aldehyde (Scheme 2, (**c**)). For the aldehyde intermediate product, the carbonyl group is also strongly influenced by the electronic properties of the substitutent on the phenyl ring. The electron-donating *p*-OMe group passivates the carbonyl group and thus hinders the formation of the corresponding hemiacetal, so that the reaction will prefer the aldehyde step (Scheme 2 bottom, (**b**)). However, the electron-withdrawing group *p*-NO_2 activates the carbonyl group and makes it more electron-deficient, thus the carbonyl group easily reacts with another alcohol to form the corresponding hemiacetal followed by palladium-catalyzed β-hydride elimination to result in the desired product (Scheme 2 bottom, (**c**)).

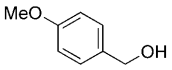
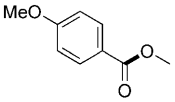
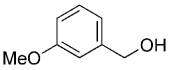
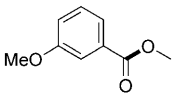
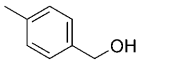
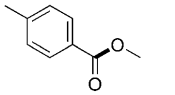
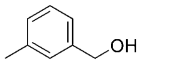
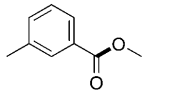
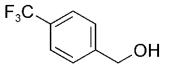
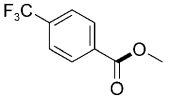
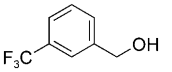
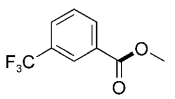
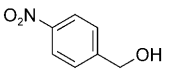
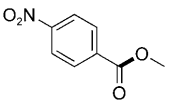
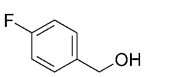
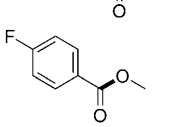
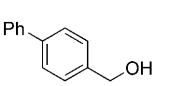
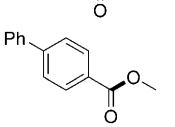
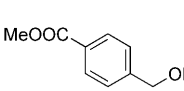
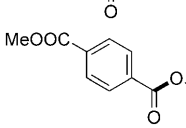
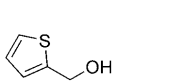
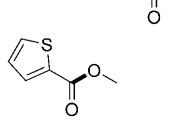
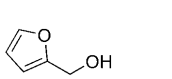
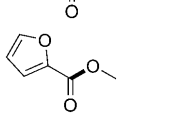
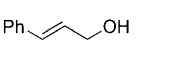
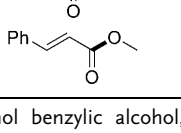
According to this hypothesis, a more electron-deficient palladium center is required, as it can promote the harder to accomplish β-hydride elimination of the electron-deficient benzylic alcohols and can coordinate to the corresponding aldehyde of the electron-rich benzylic alcohols to ease the formation of the hemiacetal. To make the catalyst more electron-deficient, a silver salt ($AgBF_4$) was added to remove the anionic ligand Cl^- from the palladium catalyst precursor. Good results were achieved with 61% and 75% yield of the desired methyl 4-methoxybenzoate and methyl 4-nitrobenzoate (Table 2, entries 1 and 7), respectively.

The optimized conditions were then used for a variety of substituted benzylic alcohols and it could be shown that the substitution sensitivity had been overcome (Table 2). Various substituted benzylic alcohols could be employed in this aerobic oxidative esterification reaction. The desired ester was isolated in 61% yield when the benzylic alcohol

Table 2: Oxidative esterification of different benzylic alcohols with methanol.[a]



1 2

Entry	Substrate	Product	2	Yield [%][b]
1[c,d]			**2b**	61
2			**2d**	86
3			**2e**	87
4			**2f**	89
5[c]			**2g**	55
6			**2h**	86
7[c]			**2c**	75
8			**2i**	88
9			**2j**	75
10			**2k**	60
11			**2l**	82
12			**2m**	63
13			**2n**	63

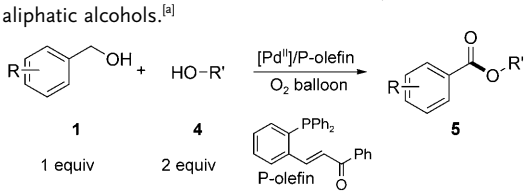
[a] Reaction conditions: 0.5 mmol benzylic alcohol, 5 mol% $[PdCl_2(CH_3CN)_2]$, 10 mol% $AgBF_4$, 1.0 mmol NaO*t*Bu, 45 °C, O_2 balloon, 2 mL MeOH, overnight. [b] Yield of isolated product. [c] 10 mol% $[PdCl_2(CH_3CN)_2]$, 20 mol% $AgBF_4$. [d] 36% of the corresponding aldehyde was isolated.

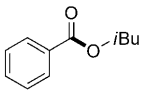
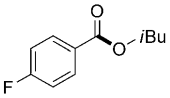
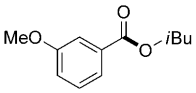
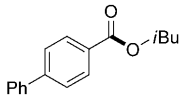
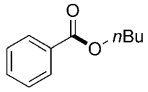
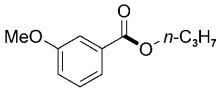
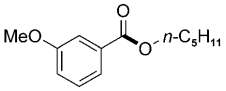
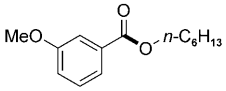
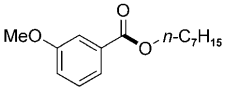
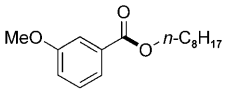
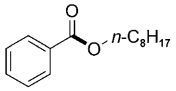
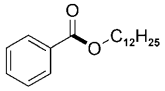
substituted with the strongly electron-donating group *p*-OMe was employed; the corresponding aldehyde was isolated in 36% yield (Table 2, entry 1). However, when the methoxy group was situated in the *meta* position, the alcohol was completely converted into the corresponding ester with a yield of 86% (Table 2, entry 2). For the methyl group, both *para* and *meta* position led to good results (87% and 89% yield, respectively; Table 2, entries 3 and 4). Strongly electron-withdrawing groups such as $-CF_3$ and $-NO_2$ could also be tolerated under the standard conditions (Table 2, entries 5, 6, and 7), but the different positions of the $-CF_3$ group on the substituted phenyl ring have a significant influence on the reactivity of the reaction, as the benzylic alcohol substituted with a CF_3 group in the *para* position only gave 55% of the desired ester. In GC–MS, no aldehyde was observed but some starting alcohol remained. In the case of *m*-CF_3-substituted benzylic alcohol, complete conversion was observed and the desired product was isolated in up to 86% yield. Other substituents on the phenyl ring (*p*-F, *p*-Ph, *p*-COOMe) gave moderate to good yields (Table 2, entries 8, 9, and 10). It is worth noting that heterocycles such as thiophene-2-methanol and furan-2-methanol could also be used in this aerobic oxidative esterification reaction and gave the corresponding esters in moderate to good yields (Table 2, entries 11 and 12). Even for cinnamyl alcohol as allylic alcohol substrate, the desired ester was isolated in 63% yield (Table 2, entry 13). For all reactions in Table 2, no benzyl formates or benzyl benzoates were observed in GC–MS.

After successful application of the oxidative esterification to benzylic alcohols with methanol, we tried to extend the newly developed protocol to long-chain aliphatic alcohols (Table 3). Isobutanol was the first aliphatic alcohol used in this oxidative esterification reaction. The desired product could be obtained by addition of an electron-deficient P-olefin ligand,[11] which was previously developed in our laboratory,[12] to the optimized catalyst system ($[PdCl_2(CH_3CN)_2]$ + Ag salt) in THF solution. Several benzylic alcohols were introduced and moderate to good yields of the desired esters were obtained by employing O_2 as the oxidant (Table 3, entries 1–4). However, when *n*-butanol was used as substrate, aldol condensation of butyraldehyde with benzaldehyde (derived for the oxidation of their corresponding alcohols) dominated the reaction. By exchanging the THF solvent for nonpolar hexane, no aldol condensation product was formed. The desired cross-esterification product was obtained in moderate yield (Table 3, entry 5). It was noteworthy that the ratio of benzylic alcohol and aliphatic alcohol is 1:2 and only trace amounts of another possible cross-esterification product (benzyl butyrate) were observed. Other long-chain aliphatic alcohols were then employed as substrates. *n*-Propyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl alcohols, and even *n*-dodecyl alcohol could be utilized to afford the desired products (Table 3, entries 6–10 and 12).

In conclusion, we have successfully developed the first palladium-catalzyed direct aerobic oxidative esterification of benzylic alcohols with methanol and various long-chain aliphatic alcohols. By considering the effects of substitution and potential mechanistic pathways, we have been able to show the applicability of this method to a range of different substrates to give their corresponding esters in moderate to high yields. The challenging esterification reactions of long-chain aliphatic alcohols were accomplished by using a P-olefin ligand to control the selectivity. The direct nature of this route

Table 3: Oxidative esterification of different benzylic alcohols with long-chain aliphatic alcohols.[a]



Entry	Product	5	Yield[%][b]
1[c]		**5a**	74
2[c]		**5b**	84
3[c]		**5c**	63
4[c]		**5d**	42
5		**5e**	46
6		**5f**	40
7		**5g**	44
8		**5h**	44
9		**5i**	41
10		**5j**	51
11[d]		**5k**	50
12[d]		**5l**	54

[a] Reaction conditions: 0.5 mmol benzylic alcohol, 1.0 mmol aliphatic alcohol **4**, 0.05 mmol $[PdCl_2(CH_3CN)_2]$, 0.10 mmol P-olefin ligand, 0.10 mmol Ag_2CO_3, 2.25 mmol K_3PO_4, O_2 balloon, 1.5 mL hexane, 60 °C, overnight. [b] Yield of isolated product. [c] 1.0 mmol scale with 5.0 equivalents of isobutanol, $AgBF_4$ instead of Ag_2CO_3 in 2 mL of THF. [d] Yield determined by NMR spectroscopy.

and the use of O_2 as the oxidant represent a step toward an environmentally benign and sustainable process. Studies into the mechanistic pathway and the improvement of the reaction efficiency are currently underway.

Experimental Section

General procedure for reactions in Table 2: In a glove box, $[PdCl_2(CH_3CN)_2]$ (6.5 mg, 0.025 mmol), NaO*t*Bu (96.1 mg, 1.0 mmol), and $AgBF_4$ (9.7 mg, 0.05 mmol) were filled into a Schlenk tube. The Schlenk tube was taken out of the box and put into an ice–water bath. An O_2 balloon was fixed and the Schlenk tube was purged 3 times. Benzylic alcohol (0.5 mmol) and MeOH (2.0 mL) were consecutively added to the tube. Then the reaction mixture was heated to 45 °C by oil bath and was stirred overnight. Then the reaction was quenched with a saturated aqueous NH_4Cl solution and extracted with diethyl ether (3 × 10 mL). The organic layers were combined and the pure product was obtained by flash column chromatography (petroleum ether and diethyl ether).

General procedure for reactions in Table 3: In a glove box, $[PdCl_2(CH_3CN)_2]$ (13.0 mg, 0.05 mmol), P-olefin ligand (39.2 mg, 0.10 mmol), K_3PO_4 (477.0 mg, 2.25 mmol), and Ag_2CO_3 (27.6 mg, 0.10 mmol) were filled into a Schlenk tube. The Schlenk tube was taken out of the box, an O_2 balloon was fixed, and the Schlenk tube was purged 3 times. Under stirring, hexane (1.5 mL) was injected into the tube. Subsequently, benzylic alcohol (0.5 mmol) and aliphatic alcohol (1.0 mmol) were consecutively added to the tube. The reaction mixture was stirred at 60 °C overnight. Then the reaction was quenched with a saturated aqueous NH_4Cl solution and extracted with diethyl ether (3 × 10 mL). The organic layers were combined and the pure product was obtained by flash column chromatography (petroleum ether and diethyl ether).

Received: December 21, 2010
Published online: April 7, 2011

Keywords: aerobic oxidation · alcohols · aldehydes · oxidative esterification · palladium

[1] J. Otera, *Esterification: Methods, Reactions, and Applications*, Wiley-VCH, Weinheim, **2003**.
[2] R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed., Wiley-VCH, New York, **1999**.
[3] a) A. Schoenberg, R. F. Heck, *J. Org. Chem.* **1974**, *39*, 3327–3331; b) A. Brennführer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176–4196; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114–4133.
[4] a) C. F. J. Barnard, *Organometallics* **2008**, *27*, 5402–5422; b) C. F. J. Barnard, *Org. Process Res. Dev.* **2008**, *12*, 566–574.
[5] a) K. Ekoue-Kovi, C. Wolf, *Chem. Eur. J.* **2008**, *14*, 6302–6315; b) W.-J. Yoo, C.-J. Li, *Tetrahedron Lett.* **2007**, *48*, 1033–1035; c) W.-J. Yoo, C.-J. Li, *J. Org. Chem.* **2006**, *71*, 6266–6268; d) B. Xu, X. Liu, J. Haubrich, C. M. Friend, *Nat. Chem.* **2010**, *2*, 61–65; e) X.-F. Wu, C. Darcel, *Eur. J. Org. Chem.* **2009**, 1144–1147.
[6] a) B. R. Travis, M. Sivakumar, G. O. Hollist, B. Borhan, *Org. Lett.* **2003**, *5*, 1031–1034; b) B. E. Maki, K. A. Scheidt, *Org. Lett.* **2008**, *10*, 4331–4334.
[7] a) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362–365; b) R. A. Sheldon, I. W. C. E. Arends, G.-J. ten Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774–781; c) M. S. Sigman, D. R. Jensen, *Acc. Chem. Res.* **2006**, *39*, 221–229; d) R. Liu, C. Dong, X. Liang, X. Wang, X. Hu, *J. Org. Chem.* **2005**, *70*, 729–731; e) R. Liu, X. Liang, C. Dong, X. Hu, *J. Am. Chem. Soc.* **2004**, *126*, 4112–4113; f) T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037–3058; g) M. J. Schultz, M. S. Sigman, *Tetrahedron* **2006**, *62*, 8227–8241.
[8] a) B. Xu, X. Liu, J. Haubrich, R. J. Madix, C. M. Friend, *Angew. Chem.* **2009**, *121*, 4270–4273; *Angew. Chem. Int. Ed.* **2009**, *48*,

4206 – 4209; b) R. L. Oliveira, P. K. Kiyohara, L. M. Rossi, *Green Chem.* **2009**, *11*, 1366 – 1370; c) H. Miyamura, T. Yasukawa, S. Kobayashi, *Green Chem.* **2010**, *12*, 776 – 778; d) N. A. Owston, A. J. Parker, J. M. J. Williams, *Chem. Commun.* **2008**, 624 – 625; e) T. Zeng, G. Song, C.-J. Li, *Chem. Commun.* **2009**, 6249 – 6251; f) J. Zhang, M. Gandelman, L. J. W. Shimon, D. Milstein, *Dalton Trans.* **2007**, 107 – 113; g) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840 – 10841; h) T. Zweifel, J. V. Naubron, H. Grützmacher, *Angew. Chem.* **2009**, *121*, 567 – 571; *Angew. Chem. Int. Ed.* **2009**, *48*, 559 – 563; i) N. A. Owston, T. D. Nixon, A. J. Parker, M. K. Whittlesey, J. M. J. Williams, *Synthesis* **2009**, 1578 – 1581; j) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Angew. Chem.* **2008**, *120*, 2481 – 2483; *Angew. Chem. Int. Ed.* **2008**, *47*, 2447 – 2449; k) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Organometallics* **2008**, *27*, 2795 – 2802; l) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Chem. Asian J.* **2008**, *3*, 1479 – 1485.

[9] a) C. Bianchini, P. K. Shen, *Chem. Rev.* **2009**, *109*, 4183 – 4206; b) S. Krishnan, J. T. Bagdanoff, D. C. Ebner, Y. K. Ramtohul, U. K. Tambar, B. M. Stoltz, *J. Am. Chem. Soc.* **2008**, *130*, 13745 – 13754; c) S. S. Stahl, *Angew. Chem.* **2004**, *116*, 3480 – 3501; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400 – 3420.

[10] a) S. F. J. Hackett, R. M. Brydson, M. H. Gass, I. Harvey, A. D. Newman, K. Wilson, A. F. Lee, *Angew. Chem.* **2007**, *119*, 8747 – 8750; *Angew. Chem. Int. Ed.* **2007**, *46*, 8593 – 8596; b) F.-Z. Su, Y.-M. Liu, L.-C. Wang, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem.* **2008**, *120*, 340 – 343; *Angew. Chem. Int. Ed.* **2008**, *47*, 334 – 337; c) H. Wang, S.-X. Deng, Z.-R. Shen, J.-G. Wang, D.-T. Ding, T.-H. Chen, *Green Chem.* **2009**, *11*, 1499 – 1502; d) H. Yang, X. Han, Z. Ma, R. Wang, J. Liu, X. Ji, *Green Chem.* **2010**, *12*, 441 – 451; e) X. Ye, M. D. Johnson, T. Diao, M. H. Yates, S. S. Stahl, *Green Chem.* **2010**, *12*, 1180 – 1186; f) S.-I. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba, F. Mizukami, *Science* **2002**, *295*, 105 – 107; g) R. A. Periana, O. Mironov, D. Taube, G. Bhalla, C. J. Jones, *Science* **2003**, *301*, 814 – 818; h) S. S. Stahl, *Science* **2005**, *309*, 1824 – 1826; i) C. Zhang, N. Jiao, *Angew. Chem. Int. Ed.* **2010**, *49*, 6174 – 6177; j) Z. Shi, B. Zhang, Y. Cui, N. Jiao, *Angew. Chem. Int. Ed.* **2010**, *49*, 4036 – 4041; k) C. Zhang, N. Jiao, *J. Am. Chem. Soc.* **2010**, *132*, 28 – 29; l) A. E. King, T. C. Brunold, S. S. Stahl, *J. Am. Chem. Soc.* **2009**, *131*, 5044 – 5045; m) 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.

[11] We have screened several other phosphine ligands and N-ligands. PPh_3 and dppf mainly gave the corresponding aldehydes of benzylic alcohols detected by GC–MS. No reaction occurred when TMEDA and DMEDA were applied as ligands. 1,10-Phenanthroline mainly converted the starting alcohols into the corresponding aldehydes, the desired esters could not be detected. 2,2′-Bipyridine provided mainly the aldehyde and only a trace amount of the desired ester.

[12] X. Luo, H. Zhang, H. Duan, Q. Liu, L. Zhu, T. Zhang, A. Lei, *Org. Lett.* **2007**, *9*, 4571 – 4574.

