

Catalysis

Palladium-Catalyzed Carbonylation of sec- and tert-Alcohols

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Dedicated to Professor Jan-Erling Bäckvall on the occasion of his 70th birthday

Abstract: A general palladium-catalyzed synthesis of linear esters directly from sec- and tert-alcohols is described. Compared to the classic Koch–Haaf reaction, which leads to branched products, this new transformation gives the corresponding linear esters in high yields and selectivity. Key for this protocol is the use of an advanced palladium catalyst system with **L2** (py^lbpx) as the ligand. A variety of aliphatic and benzylic alcohols can be directly used and the catalyst efficiency for the benchmark reaction is outstanding (turnover number up to 89000).

Various catalytic carbonylation reactions of olefins, including hydroformylations and alkoxycarbonylations, are powerful tools in both industrial production and organic synthesis to create all kinds of carbonyl compounds including acids, esters, amides, alcohols, and aldehydes.^[1] So far, most scientific efforts in this area have been devoted to the development of advanced catalyst systems to improve the activity and selectivity as well as the extension of the range of nucleophiles such as water,^[2] alcohols,^[3] amines,^[4] and amides.^[5] On the other hand, the carbonylation of substrates other than unsaturated carbon-carbon bonds^[3a,6] and organic (pseudo)halides^[7] has been much less explored. Despite significant improvements on the oxidative carbonylation of C-H/Ar-H bonds in the past decades, obvious drawbacks (for example, harsh reaction conditions, narrow substrate scope, and/or poor selectivity) still exist due to the presence of stoichiometric amount of oxidants.^[8] Advantageously, using alcohols in such transformations avoids the necessity of an external oxidant.^[9] However, the poor leaving ability of the hydroxy group and the possible side reactions caused by the released water have hindered wider applications of these substrates. As a result, only functionalized and/or special alcohols have

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 buppering information and the offerb identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201701950.

Angew. Chem. Int. Ed. 2017, 56, 1-6

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been carbonylated in the past. For example, the palladiumcatalyzed carbonylation of allylic alcohols to give β , γ -unsaturated carbonyl compounds was explored by the groups of Miura and Alper as well as us.^[10] Obviously, in this case the hydroxy group is activated and the stabilized (π -allyl)palladium intermediate facilitates the cleavage of the C–O bond. In the context of the carbonylation of benzyl alcohol and its analogs, a significant amount of halides is added to generate the corresponding benzyl halide, which initiates the catalytic cycle.^[11] It is the same case for the industrial carbonylation of methanol, which produces acetic acid with rhodium- or iridium-based catalyst systems in the presence of iodide (Monsanto^[12] and Cativa^[13] process).

Interestingly, when using *tert*-alcohols as substrates, the cobalt-catalyzed carbonylation (Koch–Haaf reaction) is applied for the synthesis of branched esters/acids (Scheme 1).^[14] In this case, the cationic intermediates are generated from the dehydration of *tert*-alcohols, followed by carbon monoxide (CO) insertion to give the branched compounds. In fact, this transformation is carried out using over-stoichiometric amounts of strong mineral acids (H₂SO₄ or a mix of HF/BF₃) under harsh reaction conditions.



Scheme 1. Catalytic carbonylation reactions of alcohols: branched versus linear selectivity.

Compared to Koch–Haaf reaction, the carbonylation of *sec-* and *tert-*alcohols to give linear compounds is not developed. Early studies revealed that ruthenium/cobalt binary catalysts were not effective for the conversion of butanols into C5 homologous alcohols regarding activity and selectivity.^[15] Although palladium–phosphine complexes constitute state-of-the-art catalysts for the alkoxycarbonylation of olefins, their application in the carbonylation of alcohols is still in its infancy. *tert*-Butanol has been carbonylated with low

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activity, poor chemo- and regioselectivity, and/or high catalyst loading.^[16] A general problem of such reactions is the formation of the corresponding ether from the alcohol. Hence, the methoxycarbonylation in methanol gave methyl *tert*-butyl ether instead of the desired esters.^[17] Moreover, the application of *sec*-alcohols to give linear esters has not been studied yet.^[18]

Based on our continuous interest in transition-metalcatalyzed reactions with CO, recently we became attracted to investigate the carbonylation of alcohols in more detail. Herein we report the first general and efficient protocol for the carbonylation of various *sec-* and *tert*-alcohols to give linear esters using a specific palladium–phosphine catalyst system (Scheme 1).

At the beginning of our study, *tert*-butanol **1a** was used as the model substrate due to its availability and industrial relevance. As shown in Table 1, the carbonylation was carried out with the industrially applied palladium catalyst (Pd/L1/ H⁺, 0.05/0.2/1.5 mol%)^[19] under 40 bar pressure of CO at 120 °C in MeOH for 20 h. However, only 14% yield of the desired ester **2a** was obtained (Table 1, entry 1). Notably, substantial formation of palladium black was observed after the reaction which shows the detrimental effect of in situ generated water by the dehydration of the alcohol.

Table 1: Pd-catalyzed carbonylation of *tert*-butanol **1a**: Investigation of ligands, Pd precursors, and acids.



Entry	Ligand	Pd source	Acid (x)	Yield [%] ^[b]
1	LI	Pd(acac) ₂	PTSA (1.5)	14
2	L2	Pd(acac) ₂	PTSA (1.5)	76
3	L3	Pd(acac) ₂	PTSA (1.5)	61
4	L4	Pd(acac) ₂	PTSA (1.5)	14
5	L5	Pd(acac) ₂	PTSA (1.5)	0
6	L6	Pd(acac) ₂	PTSA (1.5)	trace
7	L7	Pd(acac) ₂	PTSA (1.5)	0
8	L2	Pd(OAc) ₂	PTSA (1.5)	90
9	L2	PdCl ₂	PTSA (1.5)	86
10	L2	$Pd_2(dba)_3$	PTSA (1.5)	94
11	L2	Pd₂(dba)₃	PTSA (0.75)	68
12	L2	$Pd_2(dba)_3$	PTSA (3)	92
13	L2	$Pd_2(dba)_3$	CF ₃ SO ₃ H (1.5)	50
14	L2	$Pd_2(dba)_3$	CH ₃ CO ₂ H (1.5)	0
15	L2	$Pd_2(dba)_3$	H ₂ SO ₄ (0.75)	62
16 ^[c]	L2	$Pd_2(dba)_3$	PTSA (0.625)	75

[a] Reaction conditions: **1a** (20 mmol), [Pd] (0.05 mol% Pd), **L1–L3** (0.2 mol%) or **L4–L7** (0.4 mol%), CO (40 bar), MeOH (3 mL), 120 °C, 20 h. [b] The yield of **2a** was determined by GC analysis using *iso*-octane as internal standard. [c] TON = 89000, **1a** (120 mmol), [Pd₂(dba)₃] (0.0005 mmol), **L2** (0.1 mmol), PTSA (0.75 mmol), CO (40 bar), MeOH (16 mL), 100 °C, 100 h. PTSA, *p*-toluenesulfonic acid (monohydrate). "BuPAd₂, di(1-adamantyl)-*n*-butylphosphine.

Very recently, we introduced the new ligands L2 and L3 for the alkoxycarbonylation of various alkenes.^[20] Here, the additional basic pyridine substituent increases the rate of the nucleophilic attack on the intermediate palladium acyl complex. Notably, this last step in the alkoxycarbonylation cycle is often rate-determining. When the benchmark reaction was performed in the presence of these two ligands (both contain a racemic mixture and meso compound), to our delight the linear ester was obtained in 76% and 61% yields, respectively (Table 1, entries 2 and 3). Interestingly, this transformation which requires a strong acid to proceed at all is significantly improved by the ligand with built-in basic sites. Other well-known carbonylation ligands L4-7 were also investigated and very low yield of 2a or no product was observed under identical reaction conditions (Table 1, entries 4-7).

To improve the catalyst system further on, several palladium sources such as $PdCl_2$, $Pd(OAc)_2$, and $Pd_2(dba)_3$ were tested in the presence of **L2** (Table 1, entries 8–10). Using Pd^0 as the catalyst precursor, the yield of **2a** was increased to 94% suggesting the facile generation of the crucial palladium hydride species in the catalytic cycle (Table 1, entry 10). In addition, amounts of PTSA as well as other types of acids were investigated in the reaction, and **2a** was afforded in moderated to high yields (Table 1, entries 11–15). Notably, the reaction worked well with only 11.2 ppm palladium loading and gave the desired ester in high yield with a turnover number (TON) of 89000 (Table 1, entry 16)! The high productivity and selectivity indicated that the in situ formed water was tolerated well with our catalyst systems of **L2**.

Encouraged by these results, we investigated the Pdcatalyzed carbonylation of *sec*-alcohols. With cyclohexanol **3a** as a model substrate, the reaction was carried out under similar conditions to that for *tert*-alcohols. Unfortunately, less than 10% yield of the desired product **4a** was detected. To improve the yield, the reaction conditions including acids, catalyst loading as well as reaction temperature and time were optimized again and **4a** was attained in 82% yield finally (see Table S1 in the Supporting Information for details).

Next, the carbonylation of both model systems was compared under similar reaction conditions (Scheme 2). As shown in Figure 1, almost all of *tert*-alcohol **1b** was converted within 30 minutes into the corresponding ether **1ba** by



Scheme 2. Reaction pathways of the carbonylation of *tert*- and *sec*-alcohols.

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Figure 1. Compounds distribution in the carbonylation of a) *tert*-alcohol **1 b** and b) *sec*-alcohol **3 a**.

nucleophilic attack and the internal alkene **1bb** by dehydration (the ether was also converted into the alkene). Subsequent isomerization of the internal alkene to the desired but thermodynamically unfavored terminal olefin **1bc**, which was observed in a very small amount, is the key and limiting reaction step. Final alkoxycarbonylation of **1bc** gives the desired product **2b**, which drives the equilibrium to the expected direction. In the context of *sec*-alcohol **3a**, the corresponding ether **3aa** and alkene **3ab** were formed with relatively lower activity owing to the thermodynamic instability of the *sec*-cationic intermediate. In this case, the slow step is the conversion of the ether into the desired alkene.

With optimized reaction conditions in hand, the carbonylation of various *tert*-alcohols was explored. Using $[Pd_2-(dba)_3]/L2/PTSA$ (0.1/0.8/6 mol%) as the catalyst, 12 different alcohols were converted smoothly into the linear esters under comparably mild conditions (Table 2, 20 bar pressure of CO, 100°C, 20 h).

Specifically, other aliphatic alcohols (**1b**,**c**) were transformed into the desired products (**2b**,**c**) in almost quantitative yields with high selectivity. α,α -Dimethylbenzyl alcohol and its analogs **1d**-**i** with substituents on the aromatic ring including fluoride, chloride, bromide, and methoxy groups gave products **2d**-**i** in very high yields and selectivity. The same was true for α,α -diphenylethanol **1j**. Interestingly, dicarbonylated compounds **2k** and **2l**, which could be applied in polymerizations as monomers, were afforded directly in 96% and 57% isolated yields by the carbonylation of di-*tert*alcohols **1k** and **1l**, respectively. Table 2: The carbonylation of tert-alcohols 1 b-l

tert-Alcohol	Linear ester	Yield/%	nliso
1b OH	2b O OMe	94	97/3
1c	2c O OMe	98 ^[b]	>99/1
$\begin{matrix} R \\ \textbf{1d} \ C_{6}H_{5} \\ \textbf{1e} \ 4\text{-}FC_{6}H_{4} \\ \textbf{1f} \ 4\text{-}CIC_{6}H_{4} \\ \textbf{1g} \ 4\text{-}SC_{6}C_{6}H_{4} \\ \textbf{1h} \ 4\text{-}OMeC_{6}H_{4} \\ \textbf{1i} \ 2\text{-}naphthyl \end{matrix} \end{matrix} \\ \begin{matrix} OH \\ \textbf{1i} \end{matrix}$	$\begin{matrix} R \\ \mathbf{2d} & C_{G}H_5 \\ \mathbf{2e} & 4\text{-}FO_{G}H_4 \\ \mathbf{2f} & 4\text{-}CO_{G}H_4 \\ \mathbf{2g} & 4\text{-}BC_{G}H_4 \\ \mathbf{2h} & 4\text{-}OMC_{G}H_4 \\ \mathbf{2h} & 4\text{-}OMC_{G}H_4 \\ \mathbf{2i} & 2\text{-}naphthyl \end{matrix}$	99 97 98 99 97 98	>99/1 >99/1 >99/1 >99/1 >99/1 >99/1
1j OH	2j OMe	99	>99/1
1k OH OH	2k MeO ₂ C CO ₂ Me	96	>99/1
11 OH 	21 MeO ₂ C CO ₂ Me	57	99/1
1a OH	R 2m Et 2n [/] Pr 2o cyclohexyl 2p (tetrahydrofuran-2-yl)methyl	97 ^[b,c] 94 ^[b,c] 92 ^[c] 97 ^[c]	>99/1 >99/1 >99/1 >99/1

[a] Reaction conditions: 1 (2 mmol), $Pd_2(dba)_3$ (0.1 mol%), L2 (0.8 mol%), PTSA (6 mol%), CO (20 bar), MeOH (2 mL), 100°C, 20 h. The yields were determined by isolated products. [b] GC yields using *iso*octane as internal standard. [c] 120°C.

Due to the difference in reactivity various primary and secondary alcohols can be used as nucleophiles in the carbonylation of tertiary alcohols. Hence, carbonylation of **1a** with EtOH, 'PrOH, cyclohexanol, and tetrahydrofurfuryl alcohol afforded the corresponding esters **2m**-**p** again in high yields and selectivity.

Finally, the carbonylation of several sec-alcohols was studied with $[Pd_2(dba)_3]/L2/CF_3SO_3H (0.5/3/30 \text{ mol }\%)$ as the catalyst under 40 bar pressure of CO at 140 °C. As shown in Table 3, cyclic alcohols **3a-d** with five- to eight-membered rings were converted into the corresponding esters 4a-d in high yields. With 4-methylcyclohexanol 3e as the substrate, the desired product 4e was attained in 80% yield with high selectivity. Furthermore, the catalyst system allowed for the carbonylation of α -arylethanols **3 f**-i containing electrondonating (methoxy) or withdrawing (fluoride and chloride) group on the phenyl ring and the corresponding products 4 fi were obtained in high yields. Interestingly, both 1-indanol 3j and 1-tetralol 3k worked well and the desired products 4j and 4k were afforded in high isolated yields and selectivity. When employing 2- and 3-hexanol as the substrates, moderate yields and selectivity were observed for the esters 41 and 4m. Other aliphatic sec-alcohols including α, α -di-iso-propylethanol **3n** and α -tert-butylethanol **30** proved to be suitable substrates, too. Notably, nature provides a variety of secondary terpenols,

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sec-Alcohol	Linear ester	Yield/%	nliso
3a n = 0 3b n = 1 3c n = 2 3d n = 3	4a n = 0 4b n = 1 4c n = 2 4d n = 3 4d n = 3	82 ^[b] 84 ^[b] 81 84	
3e OH	4e 0 4 1 0 4 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	80 ^[b]	2/(1+3+4)= 84/16
$\begin{matrix} {\sf R} \\ {\tt 3f} \; {\sf C}_6{\sf H}_5 & {\sf OH} \\ {\tt 3g} \; {\tt 4}\text{-}{\sf FC}_6{\sf H}_4 & {\sf R} \\ {\tt 3h} \; {\tt 4}\text{-}{\sf CIC}_6{\sf H}_4 & {\sf R} \\ {\tt 3i} \; {\tt 4}\text{-}{\sf MeOC}_6{\sf H}_4 \end{matrix}$	R 4f C ₆ H5 4g 4-FC6H4 3h 4-CIC ₆ H4 3i 4-MeOC ₆ H4	90 84 83 85	78/22 79/21 80/20 64/36
3j n = 1 3k n = 2	4j n = 1 0 4k n = 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	89 98	1/2 = 88/12 1/2 = 9/91
31 OH	41 0 3 1 OMe	51 ^[b]	1/2/3 = 67/26/7
3m OH	4m O ² ³ ² OMe	65 ^[b]	1/2/3 = 67/26/7
3n OH	4n O OMe	86 ^[b]	99/1
30 OH	40 O OMe	82 ^[b]	99/1
3рОН	4p	44	1/2 = 56/44

[a] Reaction conditions: **3** (1 mmol), $Pd_2(dba)_3$ (0.5 mol%), **L2** (3 mol%), CF_3SO_3H (30 mol%), CO (40 bar), MeOH (2 mL), 140 °C, 48 h, the yield was determined by isolated products. [b] **3** (3 mmol), MeOH (6 mL), GC yield using *iso*-octane as internal standard.

which might be used directly in this novel reaction. Hence, as an example for renewable alcohols, the carbonylation of borneol 3p was investigated and the corresponding ester 4pwas indeed obtained without further optimization, albeit in moderate yield.

In conclusion, a novel type of carbonylation reaction of secondary and tertiary alcohols has been developed. Contrary to classic Koch–Haaf reactions, this transformation delivers the linear esters as the main products. Key to success is the use of a specific palladium catalyst system with ligand **L2**, which allows the carbonylation of various *tert*- and *sec*-alcohols to give the corresponding esters in moderate to high yields and selectivity. Complementary to the industrially applied carbonylation reactions of olefins, our protocol broadens the substrate scope for such processes and is of interest for the valorization of renewables.

Acknowledgements

This work is supported by Evonik Performance Materials GmbH and the State of Mecklenburg-Vorpommern. We thank the analytical team of LIKAT for their kind support.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alcohols \cdot carbonylation \cdot catalysis \cdot esters \cdot palladium

- a) M. Beller, Catalytic Carbonylation Reactions, Springer, Berlin, 2006; b) L. Kollär, Modern Carbonylation Methods, Wiley-VCH, Weinheim, 2008.
- [2] a) J. J. R. Frew, K. Damian, H. Van Rensburg, A. M. Z. Slawin, R. P. Tooze, M. L. Clarke, *Chem. Eur. J.* 2009, *15*, 10504–10513;
 b) J. J. R. Frew, M. L. Clarke, U. Mayer, H. Van Rensburg, R. P. Tooze, *Dalton Trans.* 2008, 1976–1978.
- [3] a) G. Kiss, *Chem. Rev.* 2001, 101, 3435–3456; b) A. A. Núñez Magro, L.-M. Robb, P. J. Pogorzelec, A. M. Z. Slawin, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Sci.* 2010, 1, 723–730.
- [4] T. Xu, F. Sha, H. Alper, J. Am. Chem. Soc. 2016, 138, 6629-6635.
- [5] H. Q. Li, K. W. Dong, H. Neumann, M. Beller, Angew. Chem. Int. Ed. 2015, 54, 10239–10243; Angew. Chem. 2015, 127, 10377– 10381.
- [6] a) M. Li, F. Yu, X. Qi, P. Chen, G. Liu, Angew. Chem. Int. Ed. 2016, 55, 13843-13848; Angew. Chem. 2016, 128, 14047-14052;
 b) C. Zhu, B. Yang, Y. Qiu, J.-E. Bäckvall, Angew. Chem. Int. Ed. 2016, 55, 14405-14408; Angew. Chem. 2016, 128, 14617-14620;
 c) J. Cheng, X. Qi, M. Li, P. Chen, G. Liu, J. Am. Chem. Soc. 2015, 137, 2480-2483; d) J. Liu, Q. Liu, R. Franke, R. Jackstell, M. Beller, J. Am. Chem. Soc. 2015, 137, 8556-8563; e) J. Liu, Z. Han, X. Wang, Z. Wang, K. Ding, J. Am. Chem. Soc. 2015, 137, 15346-15349; f) P. Roesle, L. Caporaso, M. Schnitte, V. Goldbach, L. Cavallo, S. Mecking, J. Am. Chem. Soc. 2014, 136, 16871-16881; g) T. M. Konrad, J. A. Fuentes, A. M. Z. Slawin, M. L. Clarke, Angew. Chem. Int. Ed. 2010, 49, 9197-9200; Angew. Chem. 2010, 122, 9383-9386; h) E. Drent, P. Arnoldy, P. H. M. Budzelaar, J. Organomet. Chem. 1993, 455, 247-253.
- [7] I. Ryu, Chem. Soc. Rev. 2001, 30, 16-25.
- [8] a) P. Xie, Y. Xie, B. Qian, H. Zhou, C. Xia, H. Huang, J. Am. Chem. Soc. 2012, 134, 9902–9905; b) Q. Liu, H. Zhang, A. Lei, Angew. Chem. Int. Ed. 2011, 50, 10788–10799; Angew. Chem. 2011, 123, 10978–10989; c) S. Tsunoi, I. Ryu, T. Okuda, M. Tanaka, M. Komatsu, N. Sonoda, J. Am. Chem. Soc. 1998, 120, 8692–8701; d) T. Sakakura, M. Tanaka, J. Chem. Soc. Chem. Commun. 1987, 758–759.
- [9] For the production of Ibuprofen based on the alcohol carbonylation, see: V. Elango, M. A. Murphy, B. L. Smith, K. G. Davenport, G. N. Mott, G. L. Moss, EP284310A1, 1988.
- [10] a) Q. Liu, L. Wu, H. Jiao, X. Fang, R. Jackstell, M. Beller, Angew. Chem. Int. Ed. 2013, 52, 8064-8068; Angew. Chem.
 2013, 125, 8222-8226; b) W.-J. Xiao, H. Alper, J. Org. Chem.
 1998, 63, 7939-7944; c) T. Satoh, M. Ikeda, Y. Kushino, M. Miura, M. Nomura, J. Org. Chem. 1997, 62, 2662-2664.
- [11] a) Y.-S. Lin, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 723 734; b) H. Zhou, J. Cheng, S. Lu, H. Fu, H. Wang, *J. Organomet. Chem.* **1998**, *556*, 239–242; c) T. Imamoto, T. Kusumoto, M. Yokoyama, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 643–644.

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- [12] C. M. Thomas, G. Süss-Fink, Coord. Chem. Rev. 2003, 243, 125– 142.
- [13] A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. P. Elliott, T. Ghaffar, H. Green, T. R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers, R. J. Watt, *J. Am. Chem. Soc.* 2004, 126, 2847–2861.
- [14] H. Koch, W. Haaf, Justus Liebigs Ann. Chem. 1958, 618, 251– 266.
- [15] P. Andrianary, G. Jenner, J. Organomet. Chem. 1987, 322, 89-98.
- [16] a) K. Qiao, Y. Deng, New J. Chem. 2002, 26, 667-670; b) S. Jayasree, A. Seayad, R. V. Chaudhari, Org. Lett. 2000, 2, 203-206.
- [17] H. Zhou, S. Lu, H. Li, J. Chen, H. Fu, H. Wang, J. Mol. Catal. A 1997, 116, 329–333.
- [18] a) T. G. Ostapowicz, M. Schmitz, M. Krystof, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed. 2013, 52, 12119–12123;

Angew. Chem. 2013, 125, 12341-12345; J.-P. Simonato, T. Walter, P. Métivier, J. Mol. Catal. A: Chem. 2001, 171, 91-94.

- [19] a) C. Jimenez Rodriguez, D. F. Foster, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* 2004, 1720–1721; b) W. Clegg, M. R. J. Elsegood, G. R. Eastham, R. P. Tooze, X. Lan Wang, K. Whiston, *Chem. Commun.* 1999, 1877–1878.
- [20] a) K. Dong, X. Fang, S. Gülak, R. Franke, A. Spannenberg, H. Neumann, R. Jackstell, M. Beller, *Nat. Commun.* 2017, *8*, 14117–14123; b) K. Dong, R. Sang, R. Franke, A. Spannenberg, H. Neumann, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* 2017, https://doi.org/10.1002/anie.201700317; *Angew. Chem.* 2017, https://doi.org/10.1002/ange.201700317.

Manuscript received: February 22, 2017 Final Article published:

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be directly used.

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tert- and sec-alcohols to give the linear

esters. The reactions complement the

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