CHEMISTRY
A EUROPEAN JOURNAL

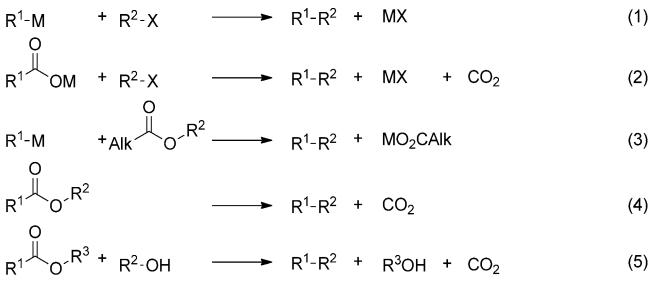
COMMUNICATION

DOI: 10.1002/chem.201301033

Synthesis of Arylacetates from Benzylic Alcohols and Oxalate Esters through Decarboxylative Coupling

Matthias F. Grünberg and Lukas J. Gooßen*[a]

The development of sustainable methodologies for carbon–carbon bond formation is among the key objectives in modern organic synthesis. Catalytic cross-coupling reactions have proven to be efficient and versatile tools for assembling even complex molecular structures.[1] In classical redox-neutral cross-coupling reactions, carbon electrophiles, for example, aryl halides [Eq. (1); X = halide], are regiospecifically coupled with carbon nucleophiles, for example, organometallic compounds (M = main-group metal). Along with the C–C coupling products, byproducts are formed resulting from the leaving groups, usually metal salts. Within the last decade, several strategies have been developed to overcome the major limitations of this concept, that is, the necessity to generate sensitive organometallic reagents in an extra reaction step, the use of environmentally questionable organohalides, and the formation of salt waste.



One of these strategies consists in replacing traditional with decarboxylative coupling reactions, which draw on carboxylate salts rather than organometallic reagents as the carbon nucleophiles [Eq. (2)].[2] This reaction type has found application, for example, in syntheses of biaryls[3] and arylketones[4] and for the introduction of either allyl or benzyl groups.[5] Another strategy involves using carboxylates in the place of organohalides in cross-coupling reactions with organometallic reagents [Eq. (3)].[6] A prominent example is the Tsuji–Trost allylation (R^2 = allyl).[7] The two above approaches are combined in catalytic decarboxylation reactions of allyl carboxylates [Eq. (4); R^2 = allyl].[8] The allyl carboxylate substrates provide both the electrophilic allyl group and the carbon nucleophile that is masked initially, but liberated at the Pd catalyst by extrusion of CO_2, which is the only byproduct generated in the overall process. This attractive reaction type was discovered by Saegusa and Tsuji et al.[9] and has been led to synthetic maturity by the research groups of Tunge,[10] Stoltz[11] and others.[8] Unfortunately, an extra step is required to preform the starting material, which often generates a lot of waste. Moreover, the reaction is known only for allylic and benzylic esters. However, recent reports by the research groups of both Garg and Shi, that aryl carboxylates (R^2 = aryl) can undergo oxidative additions to catalyst metals that are capable of mediating decarboxylative processes indicate that this attractive concept may soon become more generally applicable, maybe even to biaryl synthesis.[6,12]

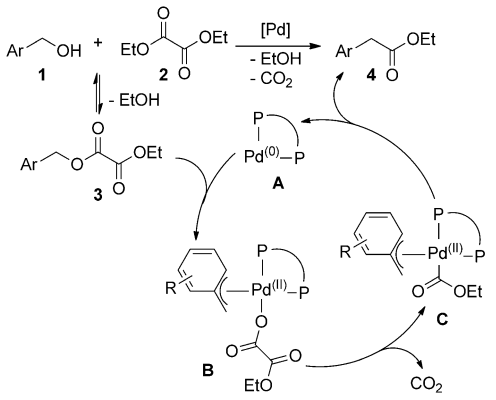
To the best of our knowledge, there is still no example of a regiospecific intermolecular decarboxylative cross-coupling reaction between an alcohol and either a carboxylic acid or ester [Eq. (5); R^3 = H or alkyl].[13] We envisioned that this kind of C–C coupling should be achievable by combining a reversible transesterification between an alcohol and an appropriate alkyl carboxylate with a catalytic decarboxylation of the resulting ester. In the overall process, CO_2 and an alcohol would be the only byproducts. As a first example of such a process, we herein disclose a synthesis of α-arylacetic acid esters from benzylic alcohols and diethyl oxalate (Scheme 1).

α-Arylacetic acids are an important product class because many of its members possess unique biological and pharmaceutical activities (Figure 1).[14] Well-known representatives include the nonsteroidal anti-inflammatory drugs, diclofenac and indomethacin, and the antihistamine, olopatadine. Arylacetic acids are also versatile intermediates used, for example, in the synthesis of agrochemicals like spiromesifen and pinoxaden.

The overall reaction (Scheme 1, top), in which CO_2 and ethanol are the only byproducts, compares favorably with classical arylacetic acid syntheses such as the hydrolysis of benzyl cyanides and the transition metal catalyzed carbonylation of benzylic halides or alcohols.[15] It is also a valuable alternative to modern arylacetic acid syntheses, involving, for example, the oxidative carbonylation of toluene,[16] the

[a] M. F. Grünberg, Prof. Dr. L. J. Gooßen
Department of Chemistry, University of Kaiserslautern
Erwin-Schrödinger-Strasse 54, 67663 Kaiserslautern (Germany)
Fax: (+49) 631-205-3921
E-mail: goossen@chemie.uni-kl.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201301033.



Scheme 1. Synthesis of α-arylacetates from benzylic alcohols.

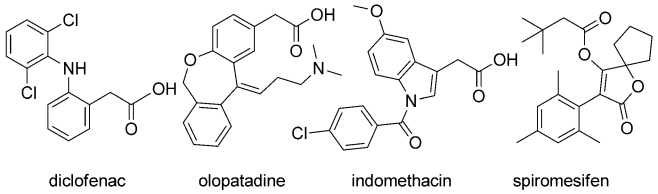


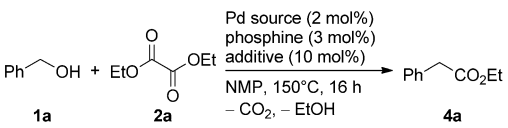
Figure 1. Biologically active arylacetic acid derivatives.

oxidation of terminal alkynes,[17] the electrocatalytic carboxylation of benzyl halides,[18] transition metal catalyzed cross-coupling reactions between aryl halides and enolates,[19] malonates,[20] cyanoacetates,[21] or acetoacetates,[22] carbene-transfer reactions from ethyl diazoacetate,[23] and coupling reactions of α-haloacetate esters,[24] each of which have their individual drawbacks.

The mechanistic concept for the development of the new cross-coupling process is outlined in Scheme 1, bottom. The benzylic alcohol substrate **1** undergoes reversible transesterification with diethyl oxalate (**2**) leading to the benzyl ethyl oxalate **3**, which oxidatively adds to the Pd(0) catalyst, **A**. The resulting benzyl complex, **B**, extrudes CO_2 to give acylpalladium(II) species **C**. Arylacetic ester **4** is then liberated by reductive elimination, regenerating Pd species **A**.

As starting point for catalyst development, we chose reaction conditions similar to those used by Fu, Liu et al. for the decarboxylative coupling of potassium oxalate monoesters with aryl halides.[4c] When heating benzyl ethyl oxalate (**3a**) with 2 mol% $Pd(OAc)_2$ and 3 mol% 1,3-bis(diphenylphosphino)propane (dppp) to 150°C, ethyl phenylacetate (**4a**) was indeed obtained, albeit in low yield (38%). Because we had observed that the presence of nucleophilic additives had a profound effect on the related coupling of α-oxocarboxylates,[25] we screened various Lewis bases and found that the addition of 4-(dimethylamino)pyridine (DMAP) increased the yield to 64%. To confirm that under these reaction conditions, transesterification takes place at a reasonable rate, diethyl oxalate was heated with benzyl alcohol to 150°C. To our delight, the benzyl ester was detected within only a few minutes.

Table 1. Optimization of the reaction conditions.



1a 2a 4a

Entry	Pd source	Phosphine	Additive	Yield [%]
1	$Pd(OAc)_2$	dppp	–	11
2	$Pd(OAc)_2$	dppp	DMAP	70
3	$Pd(OAc)_2$	dppp	*t*-butylamine	11
4	$Pd(OAc)_2$	dppp	diethylamine	14
5	$Pd(OAc)_2$	dppp	2,6-lutidine	18
6	$Pd(OAc)_2$	dppp	TMP	39
7	$Pd(OAc)_2$	dppp	DABCO	89
8	$Pd(OAc)_2$	dppp	$P(p\text{Tol})_3$	20
9[a]	$Pd(OAc)_2$	dppp	DABCO	75
10	$[Pd(dba)_2]$	dppp	DABCO	74
11	$[Pd(acac)_2]$	dppp	DABCO	71
12	$Pd(OAc)_2$	–	DABCO	0
13	$Pd(OAc)_2$	PPh_3	DABCO	0
14	$Pd(OAc)_2$	PCy_3	DABCO	0
15	$Pd(OAc)_2$	dppb	DABCO	36
16	$Pd(OAc)_2$	dppe	DABCO	75
17[b]	$Pd(OAc)_2$	dppp	DABCO	82
18[c]	$Pd(OAc)_2$	dppp	DABCO	69

Reaction conditions: 0.50 mmol **1a**, 0.60 mmol **2a**, 2 mol% Pd source, either 6 mol% monodentate or 3 mol% bidentate ligand, 10% additive, 1 mL NMP, 150°C, 16 h, GC yields with *n*-tetradecane as internal standard. [a] 0.55 mmol **2a**; [b] 140°C; [c] 2 mol% dppp. acac = Acetylacetonate, Cy = cyclohexyl, dba = dibenzylidene acetone, dppb = 1,2-bis(diphenylphosphino)butane, dppe = 1,2-bis(diphenylphosphino)ethane, NMP = *N*-methylpyrrolidine, TMP = 2,2,6,6-tetramethylpiperidine.

After these successful trial experiments, we systematically investigated the combined transesterification/decarboxylation process for the model reaction of benzyl alcohol (**1a**) with diethyl oxalate (**2a**) in the presence of various catalyst systems (Table 1). Using 2 mol% $Pd(OAc)_2$ and 3 mol% dppp as the catalysts, the desired product (**4a**) was obtained in only 11% yield (Table 1, entry 1). Whereas primary and secondary amines, sterically hindered pyridines, and phosphines had little effect on the reaction outcome, the addition of strongly nucleophilic tertiary amines led to a marked increase in conversion (Table 1, entries 2–8). The best results were obtained with the nontoxic inexpensive base, 1,4-diazabicyclo[2.2.2]octane (DABCO). The highest yields, based on benzyl alcohol, were obtained when diethyl oxalate was used in slight excess (1.2:1; Table 1, entries 7, 9).

Variation of the Pd source revealed that $Pd(OAc)_2$ is most effective (Table 1, entries 10–11). The properties of the phosphine ligands have a profound influence on the reaction outcome (Table 1, entries 12–16). In the absence of phosphine or when using monodentate ligands, the product is formed in trace amounts at best. Similar to other coupling reactions of oxalates,[4c] the reaction is effectively promoted only by using bidentate phosphines. The reason for this condition is unclear at this stage. Interestingly, the yields strongly depend on the bite angle, the yield being highest when using dppp. Phosphines bridged by either longer or shorter carbon chains are less effective. Lowering the temperature to 140°C still furnished the product in reasonable yield

(Table 1, entry 17); below this temperature, the rate-determining decarboxylation of the palladium carboxylate no longer occurred and the reaction became sluggish.

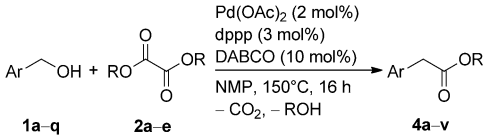
Further control experiments were conducted to elucidate the role of the individual components in the catalytic process.[26] The influence of $Pd(OAc)_2$ and the basic amine on the esterification step was found to be minimal. However, even the presence of small quantities of dppp accelerate the equilibration.[27] This observation explains why better results are obtained when the phosphine is added in an amount that is slightly in excess of that of Pd (Table 1, entries 7, 18). The amine additive strongly affected the decarboxylation of the oxalate. Both diethyl and benzyl ethyl oxalate decomposed with formation of CO_2 when stirred at 150 °C in the presence of DABCO, presumably through a reversible nucleophilic addition process. This result is in agreement with the observation that whereas the decarboxylative coupling is slow in the absence of the amine, in the presence of too much DABCO, the oxalate undergoes decarboxylation faster than it undergoes cross-coupling, thus causing unreacted benzyl alcohol to be left behind.

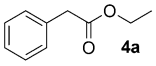
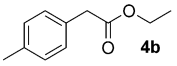
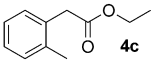
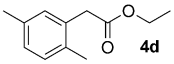
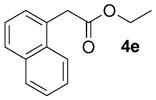
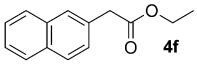
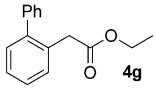
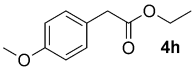
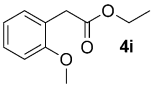
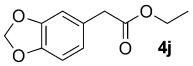
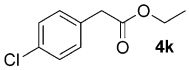
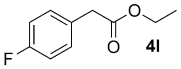
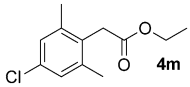
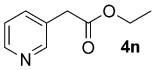
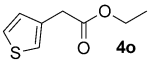
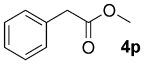
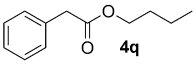
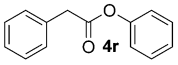
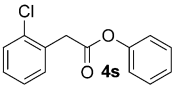
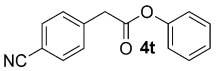
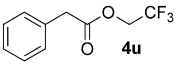
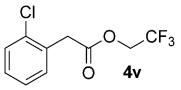
The scope of the new transformation was investigated using the optimized catalyst system, that is, $Pd(OAc)_2$ (2 mol %), dppp (3 mol %), and DABCO (10 mol %). As can be seen from the examples in Table 2, various benzylic alcohols with common functional groups, such as halides and methoxy groups, were converted in good yields into the corresponding arylacetic esters. Even alcohol **1m**, which contains two shielding methyl groups in *ortho* positions and an exposed chloro substituent in the *para* position, gave the desired ester **4m** in 56 % yield. Heterocyclic derivatives were also successfully transformed.

Some benzylic alcohols with an electron-withdrawing group in the *para* position did not give satisfactory yields in the reaction with dialkyl oxalates; for example, the transformation of 4-cyanobenzylic alcohol (**1q**) led to less than 5 % yield of the expected product. We attributed this result to the relatively low reactivity of such substrates in the transesterification step. Consequently, we replaced ethyl oxalate with the more activated derivatives, either diphenyl- or bis(2,2,2-trifluoroethyl) oxalate. This change did indeed lead to an increase in the efficiency of the process, so that 4-cyanobenzyl alcohol (**1q**) could also be converted into the corresponding arylacetate (**4t**). The reaction works reliably also on gram scale. Phenylacetic ester **4a** was synthesized in 95 % yield on 50 mmol scale in concentrated solution (7.8 g product/50 g solvent) with only 1 mol % of the Pd catalyst. As expected, analogous reactions with either simple alkanols or phenol did not give C–C coupling products, although the mixed oxalate esters were formed. In the reaction with allyl alcohols, only decomposition products were detected. However, first results indicate that the transformation may be extendable to α-ketoacids.

In conclusion, a catalyst system consisting of $Pd(OAc)_2$/dppp and DABCO efficiently promotes the decarboxylation of benzyl oxalates to give arylacetates under reaction conditions allowing the continuous generation of these materials from benzylic alcohols and dialkyl oxalates. The overall process represents an intermolecular regiospecific C–C bond-forming reaction in which volatile alcohols and carbon dioxide are released as the only byproducts. This process may lead to the development of a new generation of salt-free cross-coupling reactions, for example, the dream reaction between alkyl benzoates and phenols to give the corresponding biaryl compound.

Table 2. Scope of the reaction.



Product	Yield [%]	Product	Yield [%]
 **4a**	95	 **4b**	93
 **4c**	88	 **4d**	81
 **4e**	59	 **4f**	58
 **4g**	85	 **4h**	82
 **4i**	75	 **4j**	66
 **4k**	74	 **4l**	90
 **4m**	56	 **4n**	41
 **4o**	55	 **4p**	84
 **4q**	88	 **4r**	42
 **4s**	70	 **4t**	54
 **4u**	75	 **4v**	81

Reaction conditions: 1.00 mmol benzylic alcohol, 1.20 mmol oxalate, 2 mol % $Pd(OAc)_2$, 3 mol % dppp, 10 mol % DABCO, 2 mL NMP, 150 °C, 16 h.

Experimental Section

Standard procedure for the synthesis of arylacetic esters: A crimp-cap reaction vessel was charged with palladium(II) acetate (4.58 mg, 0.02 mmol), 1,3-bis(diphenylphosphino)propane (12.4 mg, 0.03 mmol), and 1,4-diazabicyclo[2.2.2]octane (11.2 mg, 0.10 mmol). Under an inert

atmosphere, a degassed solution of the benzylic alcohol (1.00 mmol) and the oxalate (1.20 mmol) in NMP (2 mL) was added using a syringe. The reaction mixture was stirred at 150 °C for 16 h and then cooled to room temperature. The slight pressure buildup caused by the partially dissolved CO_2 was carefully released by piercing the septum with a syringe needle before uncapping. Ethyl acetate (20 mL) was added and the mixture was washed with water (20 mL) and a saturated aqueous bicarbonate solution (20 mL). The organic layer was separated, dried over $MgSO_4$, and filtered, followed by removal of solvents in vacuo (40 °C, 200 mbar). The remaining residue was further purified by flash chromatography (SiO_2; ethyl acetate/hexane, 1:10), yielding the corresponding esters **4** (41–95 %).

Acknowledgements

We thank the DFG and the Landesgraduiertenförderung Rheinland Pfalz (scholarship to M.F.G.) for financial support and S. Schlicher for technical assistance.

Keywords: arylacetic esters · decarboxylation · homogeneous catalysis · palladium · transesterification

[1] a) A. de Meijere, Francois Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, **2004**; b) E. Negishi, A. de Meijere, *Handbook of Organopalladium Chemistry for Organic Synthesis, Vol. 1 & 2*, Wiley, Hoboken, **2002**.

[2] a) M. Nilsson, *Acta Chem. Scand.* **1966**, *20*, 423–426; b) M. Nilsson, C. Ullenius, *Acta Chem. Scand.* **1968**, *22*, 1998–2002; c) L. J. Gooßen, G. Deng, L. M. Levy, *Science* **2006**, *313*, 662–664; d) N. Rodríguez, L. J. Gooßen, *Chem. Soc. Rev.* **2011**, *40*, 5030–5048; e) L. J. Gooßen, F. Collet, K. Gooßen, *Isr. J. Chem.* **2010**, *50*, 617–629; f) J. Cornella, I. Larrosa, *Synthesis* **2012**, 653–676; g) R. Shang, L. Liu, *Sci. China Chem.* **2011**, *54*, 1670–1687.

[3] a) P. Forgione, M. C. Brochu, M. St-Onge, K. H. Thesen, M. D. Bailey, F. Bilodeau, *J. Am. Chem. Soc.* **2006**, *128*, 11350–11351; b) J.-M. Becht, C. Catala, C. Le Drian, A. Wagner, *Org. Lett.* **2007**, *9*, 1781–1783; c) L. J. Gooßen, B. Zimmermann, T. Knauber, *Angew. Chem.* **2008**, *120*, 7211–7214; *Angew. Chem. Int. Ed.* **2008**, *47*, 7103–7106; d) R. Shang, Y. Fu, Y. Wang, Q. Xu, H. Z. Yu, L. Liu, *Angew. Chem.* **2009**, *121*, 9514–9518; *Angew. Chem. Int. Ed.* **2009**, *48*, 9350–9354; e) L. J. Gooßen, P. P. Lange, N. Rodríguez, C. Linder, *Chem. Eur. J.* **2010**, *16*, 3906–3909; f) L. J. Goossen, B. Zimmermann, C. Linder, N. Rodríguez, P. P. Lange, J. Hartung, *Adv. Synth. Catal.* **2009**, *351*, 2667–2674; g) F. Zhang, M. F. Greaney, *Org. Lett.* **2010**, *12*, 4745–4747.

[4] a) L. J. Gooßen, F. Rudolphi, C. Oppel, N. Rodríguez, *Angew. Chem.* **2008**, *120*, 3085–3088; *Angew. Chem. Int. Ed.* **2008**, *47*, 3043–3045; b) F. Rudolphi, B. Song, L. J. Goossen, *Adv. Synth. Catal.* **2011**, *353*, 337–342; c) R. Shang, Y. Fu, J. B. Li, S. L. Zhang, Q. X. Guo, L. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 5738–5739.

[5] a) J. Wang, Z. Cui, Y. Zhang, H. Li, L.-M. Wu, Z. Liu, *Org. Biomol. Chem.* **2011**, *9*, 663–666; b) R. Shang, Z. Huang, X. Xiao, X. Lu, Y. Fu, L. Liu, *Adv. Synth. Catal.* **2012**, *354*, 2465–2472.

[6] For example of aryl carboxylate activation, see: a) K. W. Quasdorf, X. Tian, N. K. Garg, *J. Am. Chem. Soc.* **2008**, *130*, 14422–14423; b) B. T. Guan, Y. Wang, B. J. Li, D. G. Yu, Z. J. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 14468–14470.

[7] a) J. Tsuji, H. Takahashi, M. Morikawa, *Tetrahedron Lett.* **1965**, *6*, 4387–4388; b) B. M. Trost, M. L. Crawley, *Chem. Rev.* **2003**, *103*, 2921–2943.

[8] For a review, see: J. D. Weaver, A. Recio, A. J. Grenning, J. A. Tunge, *Chem. Rev.* **2011**, *111*, 1846–1913.

[9] a) T. Tsuda, Y. Chujo, S.-I. Nishi, K. Tawara, T. Saegusa, *J. Am. Chem. Soc.* **1980**, *102*, 6381–6384; b) I. Shimizu, T. Yamada, J. Tsuji, *Tetrahedron Lett.* **1980**, *21*, 3199–3202.

[10] a) D. K. Rayabarapu, J. A. Tunge, *J. Am. Chem. Soc.* **2005**, *127*, 13510–13511; b) R. R. P. Torregrosa, Y. Ariyarathna, K. Chattopadhyay, J. A. Tunge, *J. Am. Chem. Soc.* **2010**, *132*, 9280–9282; c) A. Recio, III, J. D. Heinzman, J. A. Tunge, *Chem. Commun.* **2012**, *48*, 142–144.

[11] a) J. T. Mohr, D. C. Behenna, A. W. Harned, B. M. Stoltz, *Angew. Chem.* **2005**, *117*, 7084–7087; *Angew. Chem. Int. Ed.* **2005**, *44*, 6924–6927; b) J. A. Enquist Jr., B. M. Stoltz, *Nature* **2008**, *453*, 1228–1231.

[12] J. Choe, J. Yang, K. Park, T. Palani, S. Lee, *Tetrahedron Lett.* **2012**, *53*, 6908–6912.

[13] For the intermolecular coupling of allyl acetates, see: T. Tsuda, M. Okada, S. Nishi, T. Saegusa, *J. Org. Chem.* **1986**, *51*, 421–426.

[14] F. Bellina, R. Rossi, *Chem. Rev.* **2010**, *110*, 1082–1146.

[15] a) For a review, see: B. Liégault, J. L. Renaud, C. Bruneau, *Chem. Soc. Rev.* **2008**, *37*, 290–299; b) M. B. Smith, J. March, *March's Advanced Organic Chemistry, Vol. 5*, Wiley, Hoboken, **2001**.

[16] P. Xie, Y. Xie, B. Qian, H. Zhou, C. Xia, H. Huang, *J. Am. Chem. Soc.* **2012**, *134*, 9902–9905.

[17] a) Z. Zhu, J. H. Espenson, *J. Org. Chem.* **1995**, *60*, 7728–7732; b) K.-P. Zeller, M. Kowallik, P. Haiss, *Org. Biomol. Chem.* **2005**, *3*, 2310–2318.

[18] a) O. Sock, M. Troupel, J. Périchon, *Tetrahedron Lett.* **1985**, *26*, 1509–1512; b) T. León, A. Correa, R. Martin, *J. Am. Chem. Soc.* **2013**, *135*, 1221–1224.

[19] For selected examples, see: a) W. W. Leake, R. Levine, *J. Am. Chem. Soc.* **1959**, *81*, 1627–1630; b) M. van Leeuwen, A. McKillop, *J. Chem. Soc. Perkin Trans. 1* **1993**, 2433–2434; c) M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 1473–1478; d) M. Jørgensen, S. Lee, X. Liu, J. P. Wolkowski, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 12557–12565; e) D. A. Culkin, J. F. Hartwig, *Acc. Chem. Res.* **2003**, *36*, 234–245; f) W. A. Moradi, S. L. Buchwald, *J. Am. Chem. Soc.* **2001**, *123*, 7996–8002; g) S. Lee, N. A. Beare, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 8410–8411; h) B. Song, T. Himmler, L. J. Gooßen, *Adv. Synth. Catal.* **2011**, *353*, 1688–1694.

[20] a) Y. Kondo, K. Inamoto, M. Uchiyama, T. Sakamoto, *Chem. Commun.* **2001**, 2704–2705; b) I. Özdemir, M. Yiğit, E. Çetinkaya, B. Çetinkaya, *Tetrahedron Lett.* **2004**, *45*, 5823–5825; c) B. Song, F. Rudolphi, T. Himmler, L. J. Gooßen, *Adv. Synth. Catal.* **2011**, *353*, 1565–1574; d) Y.-S. Feng, W. Wu, Z.-Q. Xu, Y. Li, M. Li, H.-J. Xu, *Tetrahedron* **2012**, *68*, 2113–2120.

[21] R. Shang, D.-S Ji, L. Chu, Y. Fu, L. Liu, *Angew. Chem.* **2011**, *123*, 4562–4566; *Angew. Chem. Int. Ed.* **2011**, *50*, 4470–4474.

[22] a) J. G. Zeevaart, C. J. Parkinsona, C. B. de Koning, *Tetrahedron Lett.* **2004**, *45*, 4261–4264; b) J. G. Zeevaarta, C. J. Parkinsona, C. B. de Koning, *Tetrahedron Lett.* **2007**, *48*, 3289–3293.

[23] a) I. Rivilla, B. P. Gómez-Emeterio, M. R. Fructos, M. M. Díaz-Requejo, P. J. Pérez, *Organometallics* **2011**, *30*, 2855–2860; b) C. Peng, W. Zhang, G. Yan, J. Wang, *Org. Lett.* **2009**, *11*, 1667–1670.

[24] a) M. Sato, N. Miyaura, A. Suzuki, *Chem. Lett.* **1989**, *18*, 1405–1408; b) L. J. Gooßen, *Chem. Commun.* **2001**, 669–670; c) X.-X. Liu, M.-Z. Deng, *Chem. Commun.* **2002**, 622–623; d) C. Liu, C. He, W. Shi, M. Chen, A. Lei, *Org. Lett.* **2007**, *9*, 5601–5604; e) Z.-Y. Peng, J.-P. Wang, J. Cheng, X.-M. Xie, Z. Zhang, *Tetrahedron* **2010**, *66*, 8238–8241; f) J. C. Folest, J. Périchon, J. F. Fauvarque, A. Jutand, *J. Organomet. Chem.* **1988**, *342*, 259–261.

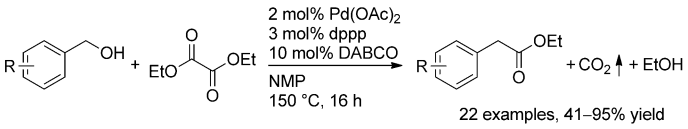
[25] a) N. Rodríguez, F. Manjolinho, M. F. Grünberg, L. J. Gooßen, *Chem. Eur. J.* **2011**, *17*, 13688–13691; b) F. Manjolinho, M. F. Grünberg, N. Rodríguez, L. J. Gooßen, *Eur. J. Org. Chem.* **2012**, 4680–4683.

[26] See also the Supporting Information.

[27] a) M. Myers, E. F. Connor, T. Glauser, A. Möck, G. Nyce, J. L. Hedrick, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 844–851; b) S. Gabillet, D. Lecercle, O. Loreau, S. Dézard, J.-M. Gomis, F. Taran, *Synthesis* **2007**, 515–522.

Received: March 18, 2013
Published online: ■■ ■■, 0000

COMMUNICATION



dppp = 1,3-bis(diphenylphosphino)propane
DABCO = 1,4-diazobicyclo[2.2.2]octane
NMP = *N*-methylpyrrolidine

Follow that dream: By combining a reversible transesterification between benzylic alcohols and dialkyl oxalates with catalytic decarboxylation of the resulting esters, a regiospecific C–C-bond-forming reaction to give α-arylacetates was achieved. In the overall process, CO_2 and a volatile alcohol are the only byproducts. Various α-arylacetates were thus synthesized in high yields from easily accessible starting materials in the presence of catalytic amounts of $Pd(OAc)_2$, dppp, and DABCO (see scheme).

Coupling Reactions

M. F. Grünberg,
*L. J. Gooßen** ..... ▮▮▮▮–▮▮▮▮

Synthesis of Arylacetates from Benzylic Alcohols and Oxalate Esters through Decarboxylative Coupling