C–H Activation

International Edition: DOI: 10.1002/anie.201505769
German Edition: DOI: 10.1002/ange.201505769

Iridium-Catalyzed *ortho*-Arylation of Benzoic Acids with Arenediazonium Salts

*Liangbin Huang, Dagmar Hackenberger, and Lukas J. Gooßen**

Abstract: *In the presence of catalytic [{IrCp*Cl$_2$}$_2$] and Ag_2CO_3, Li_2CO_3 as the base, and acetone as the solvent, benzoic acids react with arenediazonium salts to give the corresponding diaryl-2-carboxylates under mild conditions. This C–H arylation process is generally applicable to diversely substituted substrates, ranging from extremely electron-rich to electron-poor derivatives. The carboxylate directing group is widely available and can be removed tracelessly or employed for further derivatization. Orthogonality to halide-based cross-couplings is achieved by the use of diazonium salts, which can be coupled even in the presence of iodo substituents.*

The design of efficient synthetic routes to construct biaryls is of great importance due the prevalence of this structural unit in pharmaceuticals, agrochemicals, and functional materials.[1] Established methods to access this substructure include the Ullmann reaction, catalytic cross-couplings of preformed organometallic reagents, and decarboxylative couplings.[2,3]

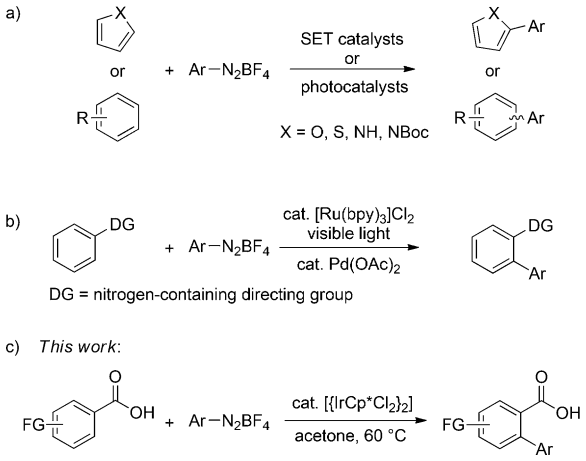
C–H Arylating reactions have been studied extensively as an alternative to these intrinsically regioselective couplings since in principle, they do not require prefunctionalization steps. The regioselectivity of the C–H arylation can be controlled by various directing groups.[4] However, these often need to be introduced and later removed in additional reaction steps, increasing the complexity of the overall synthetic sequence.

The use of carboxylates as directing groups represents a tremendous advance in this area.[5] Benzoic acids are widely available in great structural diversity, and after *ortho*-arylation, the carboxylate group can be removed tracelessly,[6] or converted into other functionalities via decarboxylative cross-couplings.[7] However, the low coordinating ability of this group poses substantial challenges with regard to the reactivity and selectivity of the C–H activating step. Substantial progress in this field has been made by the groups of Yu,[8] Daugulis,[9] Larrosa,[6d,f,10] Su,[6g] and others,[6h,11] who developed transformations based on aryl halides, arylboronic acids, and (hetero)arenes as the aryl sources. The limitations of these approaches are the high reaction temperatures, the cost of the substrates, the restriction to specific substrates and substitution patterns, and the use of stoichiometric silver salts as halide scavengers and/or oxidants.

[*] Dr. L. Huang, D. Hackenberger, Prof. Dr. L. J. Gooßen
FB Chemie-Organische Chemie
Technische Universität Kaiserslautern
Erwin-Schrödinger-Strasse Geb. 54, 67663 Kaiserslautern (Germany)
E-mail: goossen@chemie.uni-kl.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201505769.

We believe that this field could benefit significantly from the use of arenediazonium salts as aryl electrophiles, because these are readily available from low-cost anilines in great structural diversity, and their intrinsic reactivity is high even at low temperatures.[12] The use of diazonium salts in C–H arylating reactions was pioneered by Pschorr[13] and Gomberg and Bachmann.[14] Modern versions of such nondirected (hetero)arylations were reported by the groups of Heinrich, König, Felpin, and Martín, respectively (Scheme 1a).[15] The

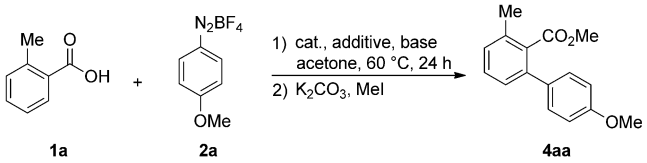


Scheme 1. Direct C–H arylation of (hetero)arenes with arenediazonium salts.

only *ortho*-directed arylations were disclosed by Sanford, who used pyridine and other nitrogen-based directing groups in a photoredox/palladium-catalyzed reaction (Scheme 1b),[16] and Chang and co-workers, who employed *tert*-butyl amides to arylate electron-poor arenediazonium salts.[17]

In order to probe whether a C–H arylation of benzoic acids with arenediazonium salts could be directed into the *ortho* position of the weakly coordinating carboxylate group, we treated 2-methylbenzoic acid (**1a**) with 4-methoxybenzenediazonium tetrafluoroborate (**2a**) (Table 1).[18] At the desired low reaction temperature of 60 °C, many state-of-the-art catalysts widely employed in *ortho*-arylations, including [{RhCp*Cl$_2$}$_2$],[19] Pd(OAc)$_2$,[8,9] and [{Ru(*p*-cym)Cl$_2$}$_2$],[20] were inactive in this challenging transformation (entries 1–3).[4] [{IrCp*Cl$_2$}$_2$]/Ag_2CO_3, a system similar to that employed in C–H aminations, alkenylation, and alkynylations,[21] was the only catalyst to give the desired 2-arylbenzoic acid **3**. After some optimization, we managed to achieve high yields even with the ecofriendly solvent acetone (entry 4), which sets this apart from many other C–H activating reactions that

Table 1: Optimization of the *ortho*-arylation conditions.[a]



1a **2a** **4aa**

Entry	Catalyst	Additive (equiv)	Base (equiv)	Yield [%][b]
1	$[\{RhCp^*Cl_2\}_2]$	Ag_2CO_3 (1.0)	–	n.d.
2	$Pd(OAc)_2$	Ag_2CO_3 (1.0)	–	n.d.
3	$[\{Ru(p\text{-cym})Cl_2\}_2]$	Ag_2CO_3 (1.0)	–	n.d.
4	$[\{IrCp^*Cl_2\}_2]$	Ag_2CO_3 (1.0)	–	80
5	$[\{IrCp^*Cl_2\}_2]$	Ag_2CO_3 (0.15)	–	21
6	$[\{IrCp^*Cl_2\}_2]$	Ag_2CO_3 (0.15)	Li_2CO_3 (1.0)	74
7	$[\{IrCp^*Cl_2\}_2]$	Ag_2CO_3 (0.15)	Li_2CO_3 (0.5)	82 (83)
8	$[\{IrCp^*Cl_2\}_2]$	Ag_2CO_3 (0.15)	Li_2CO_3 (0.3)	76
9	$[\{IrCp^*Cl_2\}_2]$	–	Li_2CO_3 (0.5)	n.d.
10	$[\{IrCp^*Cl_2\}_2]$	Tl_2CO_3 (0.15)	Li_2CO_3 (0.5)	10
11	–	Ag_2CO_3 (0.15)	Li_2CO_3 (0.5)	n.d.
12	[Ir(cod)(acac)]	Ag_2CO_3 (0.15)	Li_2CO_3 (0.5)	n.d.
13[c]	$[\{IrCp^*Cl_2\}_2]$	Ag_2CO_3 (0.15)	Li_2CO_3 (0.5)	73
14[d]	$[\{IrCp^*Cl_2\}_2]$	Ag_2CO_3 (0.15)	Li_2CO_3 (0.5)	78 (83)

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), catalyst (3 mol%), Ag_2CO_3, base, and 1 mL acetone, 60°C, 24 h. [b] GC yields after esterification with K_2CO_3 (2 equiv) and MeI (5 equiv) in MeCN with tetradecane as the internal standard; yields of isolated products are given in parentheses. [c] 0.6 mmol **1a**. [d] **2a** 0.6 mmol.

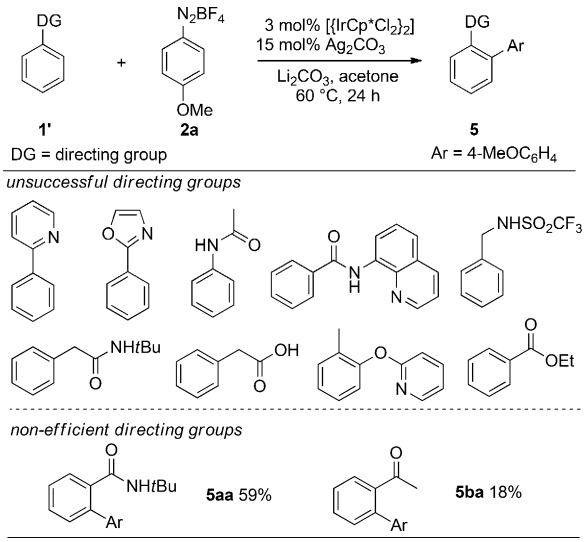
are restricted to ecologically questionable halogenated solvents such as DCE and HFIP.[17,21c–f,h,i]

The amount of silver carbonate can be reduced to catalytic quantities if another carbonate base is added (entries 5–8). In this context, Li_2CO_3 is particularly effective. Some silver is required to open up coordination sites at the iridium by removing coordinated chloride, and in its absence, no product is formed. Interestingly, the reaction did not proceed well when thallium carbonate was used as a halide abstractor, indicating that the role of the silver might be more complex (entries 9 and 10). No reaction occurred with iridium(I) complexes (entry 12).[22]

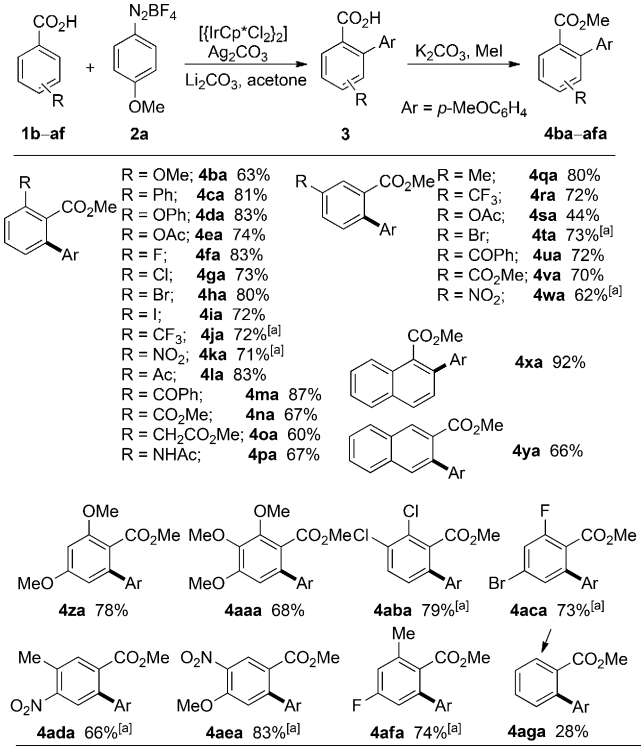
Substrates **1a** and **2a** are best employed in a 1:1 ratio. Excess diazonium salt does not improve the yields, and excess benzoic acid slightly lowers the yield (entries 13 and 14).

Under these optimal conditions, the free carboxylate is not only the simplest and thus most desirable, but also the most effective directing group. Other widely employed, but more complex directing groups were found to be inactive in this context. These include methylene carboxylates and amides and even the strongly coordinating pyridine, NHAc, and Daugulis amide groups (Scheme 2). Weakly coordinating groups such as carboxamides and ketones gave low to moderate yields. This is in agreement with a report by Chang et al.,[17] which appeared recently. Their arylation of benzoic acid *tert*-butyl amides remained limited to certain electron-deficient diazonium salts, even though fluorinated solvents and higher iridium catalyst loadings were used.

Regioselective monoarylation occurs for *meta*-substituted benzoic acids selectively at the less hindered *ortho*-position (**4qa–wa**, Scheme 3). Various functional groups are tolerated

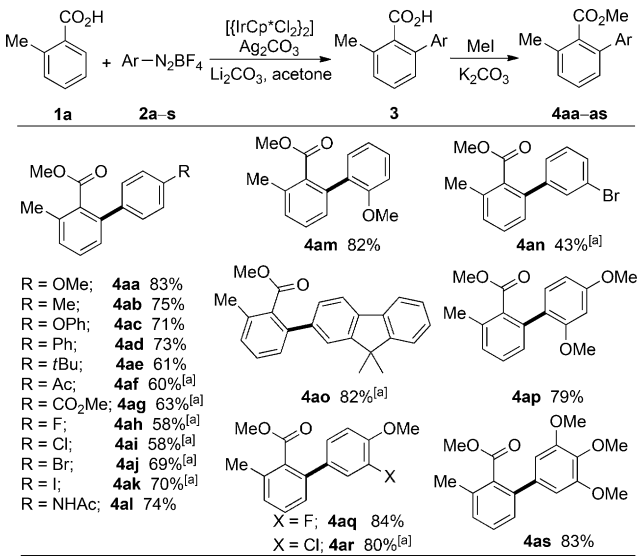


Scheme 2. Screening of other directing groups for the selective *ortho*-arylation with diazonium salts. Reaction conditions: **1′** (0.5 mmol), **2a** (0.5 mmol), $[\{IrCp^*Cl_2\}_2]$ (3 mol%), Ag_2CO_3 (0.15 equiv), Li_2CO_3 (0.5 equiv), acetone (1 mL), 60°C, 24 h. Yields of isolated products are given.



Scheme 3. Substrate scope of benzoic acids. Reaction conditions: **1b–af** (1 mmol), **2a** (1 mmol), $[\{IrCp^*Cl_2\}_2]$ (3 mol%), Ag_2CO_3 (0.15 equiv), Li_2CO_3 (0.5 equiv), acetone (2 mL), 60°C, 24 h. Yields of isolated products are given. [a] AgOTf (0.2 equiv), AgOAc (0.3 equiv), Li_2CO_3 (0.3 equiv).

including methoxy, halo, ester, acyl, carboxylate, and even acetamino groups. The tolerance of the latter functionality is particularly remarkable and opens up opportunities for



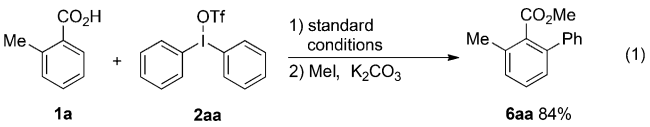
Scheme 4. Direct C–H arylation of benzoic acid with various arenediazonium salts. Reaction conditions: **1a** (1 mmol), **2a–s** (1 mmol), $[\{IrCp^*Cl_2\}_2]$ (3 mol%), Ag_2CO_3 (0.15 equiv), Li_2CO_3 (0.5 equiv), acetone (2 mL), 60°C, 24 h. Yields of isolated products are given. [a] AgOTf (0.2 equiv), AgOAc (0.3 equiv), Li_2CO_3 (0.3 equiv).

orthogonal difunctionalizations, since acetamido groups are powerful directing groups in combination with other catalysts.[16] The tolerance of bromo and iodo groups demonstrates the orthogonality of the present transformation to traditional cross-coupling processes. Unsubstituted benzoic acid gives a nearly 1:1 ratio of mono- to di-arylation product (**4aga**). Interestingly, doubly *meta*-substituted benzoic acids show no conversion, illustrating how strongly steric factors influence this reaction. Cinnamic acid did not show any conversion to the C–H arylation product.[17]

The reaction is also widely applicable with regard to the diazonium salt coupling partner (Scheme 4). *ortho*-Toluic acid was successfully coupled both with electron-rich and electron-deficient aromatic diazonium salts. A wealth of functional groups is tolerated in the *para*, *ortho*, or *meta* positions. Even reactive iodo substituents do not give rise to unwanted side products. Protodediazotization is the only significant side reaction occasionally observed. Unfortunately, heteroarene diazonium salts could not yet be converted.

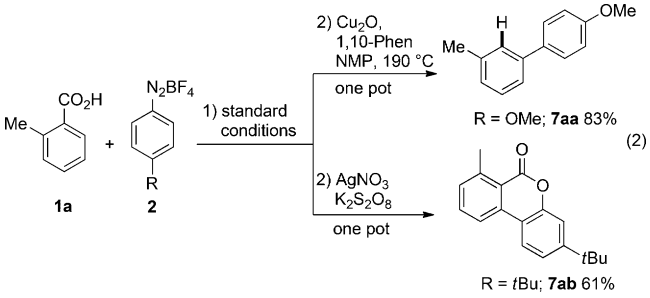
Control experiments confirmed that aryl triflates, tosylates, and halides are inactive as carbon electrophiles under the reaction conditions. However, C–H arylation can alternatively be achieved with diaryliodonium salt electrophiles [Eq. (1)].

The products in Schemes 3 and 4 were converted into the corresponding esters to simplify chromatographic purification, but the carboxylic acid can also be isolated in unmodified form. Optional in situ protodecarboxylation directly



(1)

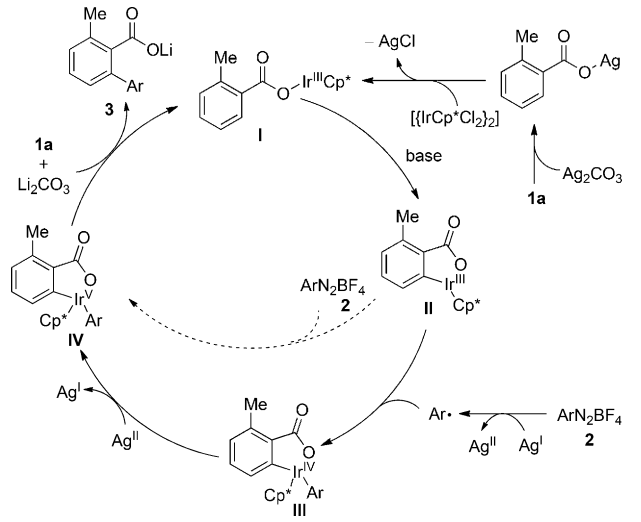
leads to the parent biaryl, whereas oxidative cyclization furnishes structurally interesting lactones [Eq. (2)].[23] Both these reactions can be combined with the arylation in convenient one-pot protocols.



(2)

The addition of stoichiometric amounts of TEMPO as a radical scavenger shuts down the reaction, which suggests single-electron-transfer processes may be involved (see the Supporting Information).

A plausible catalytic cycle for this process is outlined in Scheme 5.[17] The catalytically active species **I** is generated by replacing a chloride with a benzoate ligand at the Ir^{III} precursor. In the presence of the carbonate base, the cyclometalated Ir^{III} complex **II** is likely to form and may be converted directly to the Ir^{V} species **IV** by oxidative addition of the diazonium salt. However, the oxidation of Cp^*Ir^{III} complexes is known to be difficult via two-electron processes,[24] so this may also be a stepwise process involving one-electron-transfer steps. This would explain the influence of the radical scavenger and the difference between silver and thallium cocatalysts.[25] The biaryl product **3** is released via reductive elimination and salt metathesis with a benzoate substrate, regenerating the Ir^{III} species **I**. In-depth mechanistic studies are underway to fully clarify the reaction pathway.



Scheme 5. Proposed mechanism for Ir^{III}-catalyzed *ortho*-arylation of benzoic acids with arenediazonium salts.

In conclusion, the carboxylate-directed *ortho*-arylation of benzoic acids with arenediazonium salts allows the convenient synthesis of a wide variety of diaryl carboxylates under remarkably mild conditions. In the presence of a Cp^*Ir^{III} catalyst, simple carboxylates are the most efficient directing groups, so that even substrates with functionalities that act as powerful directing groups with other catalysts selectively yield *ortho*-aryl benzoates. The carboxylate may then be utilized as a leaving group in various decarboxylative couplings. The use of diazonium salts as electrophiles, rare in C–H activations, makes this process orthogonal to aryl halide couplings.

Experimental Section

An oven-dried 20 mL vessel was charged with $[\{IrCp^*Cl_2\}_2]$ (23.9 mg, 0.03 mmol, 3 mol%), Ag_2CO_3 (41.2 mg, 0.15 mmol, 15 mol%), Li_2CO_3 (40 mg, 0.50 mmol, 50 mol%), the benzoic acid **1** (1 mmol), and the arenediazonium salt **2** (1 mmol). After the vessel had been flushed with three alternating vacuum and nitrogen purge cycles, degassed acetone (2 mL) was added via syringe. The resulting mixture was stirred at 60 °C for 24 h. After the reaction was complete, the mixture was allowed to cool to room temperature. MeCN (3 mL), K_2CO_3 (414 mg, 3 mmol), and MeI (310 μL, 5 mmol) were added and the mixture was stirred at 50 °C for another 2 h. The mixture was allowed to cool to room temperature. Brine (20 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/hexane gradient) yielding the diarylbenzoic acid in the form of its methyl ester.

Acknowledgements

We thank Umicore for donating chemicals, the DFG (SFB/TRR-88, "3MET"), the Alexander von Humboldt Foundation (fellowship to L.H.), and the Stipendienstiftung Rheinland-Pfalz (fellowship to D.H.) for financial support.

Keywords: benzoic acid · biaryl synthesis · C–H arylation · diazonium salts · iridium

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12607–12611
Angew. Chem. **2015**, *127*, 12798–12802

[1] D. A. Horton, G. T. Bourne, M. L. Smythe, *Chem. Rev.* **2003**, *103*, 893–930.

[2] a) *Synthesis of Biaryls* (Ed.: I. Cepanec), Elsevier Science, Oxford, **2004**, pp. 1–349; b) P. E. Fanta, *Chem. Rev.* **1946**, *38*, 139–196; c) G. Bringmann, R. Walter, R. Weirich, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 977–991; *Angew. Chem.* **1990**, *102*, 1006–1019; d) C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085; *Angew. Chem.* **2012**, *124*, 5150–5174; e) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; f) V. B. Phapale, D. J. Cárdenas, *Chem. Soc. Rev.* **2009**, *38*, 1598–1607; g) E. Negishi, *Acc. Chem. Res.* **1982**, *15*, 340–348; h) W. I. Dzik, P. P. Lange, L. J. Gooßen, *Chem. Sci.* **2012**, *3*, 2671–2678.

[3] Selected references for biaryl formation: a) C.-L. Sun, Z.-J. Shi, *Chem. Rev.* **2014**, *114*, 9219–9280; b) L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Science* **2012**, *337*, 1644–1648.

[4] a) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792–9826; *Angew. Chem.* **2009**, *121*, 9976–10011; b) H. Bonin, M. Sauthier, F.-X. Felpin, *Adv. Synth. Catal.* **2014**, *356*, 645–671; c) I. Hussain, T. Singh, *Adv. Synth. Catal.* **2014**, *356*, 1661–1696; d) G. P. Chiusoli, M. Catellani, M. Costa, E. Motti, N. Della Ca', G. Maestri, *Coord. Chem. Rev.* **2010**, *254*, 456–469.

[5] a) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788–802; b) Y.-H. Zhang, B.-F. Shi, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 6097–6100; *Angew. Chem.* **2009**, *121*, 6213–6216; c) R. Giri, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 14082–14083; d) T.-S. Mei, R. Giri, N. Maugel, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2008**, *47*, 5215–5219; *Angew. Chem.* **2008**, *120*, 5293–5297.

[6] a) P. Mamone, G. Danoun, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2013**, *52*, 6704–6708; *Angew. Chem.* **2013**, *125*, 6836–6840; b) S. Bhadra, W. I. Dzik, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2013**, *52*, 2959–2962; *Angew. Chem.* **2013**, *125*, 3031–3035; c) S. Mochida, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 5776–5779; d) J. Cornella, M. Righi, I. Larrosa, *Angew. Chem. Int. Ed.* **2011**, *50*, 9429–9432; *Angew. Chem.* **2011**, *123*, 9601–9604; e) J. Luo, S. Preciado, I. Larrosa, *J. Am. Chem. Soc.* **2014**, *136*, 4109–4112; f) J. Luo, S. Preciado, I. Larrosa, *Chem. Commun.* **2015**, *51*, 3127–3130; g) Y. Zhang, H. Zhao, M. Zhang, W. Su, *Angew. Chem. Int. Ed.* **2015**, *54*, 3817–3821; *Angew. Chem.* **2015**, *127*, 3888–3892; h) X. Qin, D. Sun, Q. You, Y. Cheng, J. Lan, J. You, *Org. Lett.* **2015**, *17*, 1762–1765.

[7] a) L. J. Gooßen, G. Deng, L. M. Levy, *Science* **2006**, *313*, 662–664; b) A. Fromm, C. van Wüllen, D. Hackenberger, L. J. Gooßen, *J. Am. Chem. Soc.* **2014**, *136*, 10007–10023; c) P. P. Lange, L. J. Gooßen, P. Podmore, T. Underwood, N. Sciammetta, *Chem. Commun.* **2011**, *47*, 3628–3630; d) L. J. Goossen, T. Knauber, *J. Org. Chem.* **2008**, *73*, 8631–8634.

[8] a) R. Giri, N. Maugel, J.-J. Li, D.-H. Wang, S. P. Breazzano, L. B. Saunders, J.-Q. Yu, *J. Am. Chem. Soc.* **2007**, *129*, 3510–3511; b) D.-H. Wang, T.-S. Mei, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 17676–17677; c) K. M. Engle, P. S. Thuy-Boun, M. Dang, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 18183–18193.

[9] H. A. Chiong, Q.-N. Pham, O. Daugulis, *J. Am. Chem. Soc.* **2007**, *129*, 9879–9884.

[10] C. Arroniz, A. Ironmonger, G. Rassias, I. Larrosa, *Org. Lett.* **2013**, *15*, 910–913.

[11] a) H. Gong, H. Zeng, F. Zhou, C.-J. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 5718–5721; *Angew. Chem.* **2015**, *127*, 5810–5813; b) X. Qin, X. Li, Q. Huang, H. Liu, D. Wu, Q. Guo, J. Lan, R. Wang, J. You, *Angew. Chem. Int. Ed.* **2015**, *54*, 7167–7170; *Angew. Chem.* **2015**, *127*, 7273–7276; c) Z. Wu, S. Chen, C. Hu, Z. Li, H. Xiang, X. Zhou, *ChemCatChem* **2013**, *5*, 2839–2842.

[12] a) C. Galli, *Chem. Rev.* **1988**, *88*, 765–792; b) A. Roglans, A. Pla-Quintana, M. Moreno-Mañas, *Chem. Rev.* **2006**, *106*, 4622–4643; c) F. Mo, G. Dong, Y. Zhang, J. Wang, *Org. Biomol. Chem.* **2013**, *11*, 1582–1593; d) L. He, G. Qiu, Y. Gao, J. Wu, *Org. Biomol. Chem.* **2014**, *12*, 6965–6971; e) D. P. Hari, B. König, *Angew. Chem. Int. Ed.* **2013**, *52*, 4734–4743; *Angew. Chem.* **2013**, *125*, 4832–4842.

[13] R. Pschorr, *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 496–501.

[14] M. Gomberg, W. E. Bachmann, *J. Am. Chem. Soc.* **1924**, *46*, 2339–2343.

[15] a) D. P. Hari, P. Schroll, B. König, *J. Am. Chem. Soc.* **2012**, *134*, 2958–2961; b) A. Wetzel, V. Ehrhardt, M. R. Heinrich, *Angew. Chem. Int. Ed.* **2008**, *47*, 9130–9133; *Angew. Chem.* **2008**, *120*, 9270–9273; c) F. P. Crisóstomo, T. Martín, R. Carrillo, *Angew. Chem. Int. Ed.* **2014**, *53*, 2181–2185; *Angew. Chem.* **2014**, *126*, 2213–2217; d) A. Honraedt, M.-A. Raux, E. L. Grognec, D. Jacquemin, F.-X. Felpin, *Chem. Commun.* **2014**, *50*, 5236–5238.

[16] D. Kalyani, K. B. McMurtrey, S. R. Neufeldt, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18566–18569.

[17] K. Shin, S.-W. Park, S. Chang, *J. Am. Chem. Soc.* **2015**, 137, 8584 – 8592.
[18] See also Table S2 in the Supporting Information.
[19] This catalyst was also used for double C–H activating dehydrogenative couplings: a) J. Wencel-Delord, C. Nimphius, H. Wang, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 13001 – 13005; *Angew. Chem.* **2012**, *124*, 13175 – 13180; b) J. Wencel-Delord, C. Nimphius, F. W. Patureau, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 2247 – 2251; *Angew. Chem.* **2012**, *124*, 2290 – 2294; c) N. Kuhl, M. N. Hopkinson, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 8230 – 8234; *Angew. Chem.* **2012**, *124*, 8354 – 8358; d) Y. Shang, X. Jie, H. Zhao, P. Hu, W. Su, *Org. Lett.* **2014**, *16*, 416 – 419; e) X. Qin, H. Liu, D. Qin, Q. Wu, J. You, D. Zhao, Q. Guo, X. Huang, J. Lan, *Chem. Sci.* **2013**, *4*, 1964 – 1969; f) J. Dong, Z. Long, F. Song, N. Wu, Q. Guo, J. Lan, J. You, *Angew. Chem. Int. Ed.* **2013**, *52*, 580 – 584; *Angew. Chem.* **2013**, *125*, 608 – 612; g) M. Itoh, K. Hirano, T. Satoh, Y. Shibata, K. Tanaka, M. Miura, *J. Org. Chem.* **2013**, *78*, 1365 – 1370; h) K. Morimoto, M. Itoh, K. Hirano, T. Satoh, Y. Shibata, K. Tanaka, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 5359 – 5362; *Angew. Chem.* **2012**, *124*, 5455 – 5458.
[20] L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315 – 1345.
[21] a) K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, *72*, 5362 – 5367; b) K. L. Engelman, Y. Feng, E. A. Ison, *Organometallics* **2011**, *30*, 4572 – 4577; c) J. Ryu, J. Kwak, K. Shin, D. Lee, S. Chang, *J. Am. Chem. Soc.* **2013**, *135*, 12861 – 12868; d) H. Kim, K. Shin, S. Chang, *J. Am. Chem. Soc.* **2014**, *136*, 5904 – 5907; e) J. Kim, S. Chang, *Angew. Chem. Int. Ed.* **2014**, *53*, 2203 – 2207; *Angew. Chem.* **2014**, *126*, 2235 – 2239; f) T. Kang, Y. Kim, D. Lee, Z. Wang, S. Chang, *J. Am. Chem. Soc.* **2014**, *136*, 4141 – 4144; g) Y. Quan, Z. Xie, *J. Am. Chem. Soc.* **2014**, *136*, 15513 – 15516; h) F. Xie, Z. Qi, S. Yu, X. Li, *J. Am. Chem. Soc.* **2014**, *136*, 4780 – 4787; i) D. Lee, S. Chang, *Chem. Eur. J.* **2015**, *21*, 5364 – 5368; j) C. Suzuki, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2015**, *17*, 1597 – 1600; k) D. A. Frasco, C. P. Lilly, P. D. Boyle, E. A. Ison, *ACS Catal.* **2013**, *3*, 2421 – 2429; l) Y. Xia, Z. Liu, S. Feng, Y. Zhang, J. Wang, *J. Org. Chem.* **2015**, *80*, 223 – 236.
[22] a) K.-I. Fujita, M. Nonogawa, R. Yamaguchi, *Chem. Commun.* **2004**, 1926 – 1927; b) B. Join, T. Yamamoto, K. Itami, *Angew. Chem. Int. Ed.* **2009**, *48*, 3644 – 3647; *Angew. Chem.* **2009**, *121*, 3698 – 3701.
[23] For selected examples for the functionalization of 2-phenylbenzoic acid, see a) Y. Wang, A. V. Gulevich, V. Gevorgyan, *Chem. Eur. J.* **2013**, *19*, 15836 – 15840; b) C. Wang, S. Rakshit, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 14006 – 14008; c) J. Gallardo-Donaire, R. Martin, *J. Am. Chem. Soc.* **2013**, *135*, 9350 – 9353; d) D.-B. Zhou, G.-W. Wang, *Org. Lett.* **2015**, *17*, 1260 – 1263; e) T. Fukuyama, S. Maetani, K. Miyagawa, I. Ryu, *Org. Lett.* **2014**, *16*, 3216 – 3219.
[24] L. S. Park-Gehrke, J. Freudenthal, W. Kaminsky, A. G. DiPasquale, J. M. Mayer, *Dalton Trans.* **2009**, 1972 – 1983.
[25] a) M. C. Lehman, D. R. Pahls, J. M. Meredith, R. D. Sommer, D. M. Heinekey, T. R. Cundari, E. A. Ison, *J. Am. Chem. Soc.* **2015**, *137*, 3574 – 3584; b) J. Kan, S. Huang, J. Lin, M. Zhang, W. Su, *Angew. Chem. Int. Ed.* **2015**, *54*, 2199 – 2203; *Angew. Chem.* **2015**, *127*, 2227 – 2231.

Received: June 23, 2015
Published online: September 3, 2015

