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$Pd(O_2CCF_3)_2$/Benzoquinone: A Versatile Catalyst System for the Decarboxylative Olefination of Arene Carboxylic Acids

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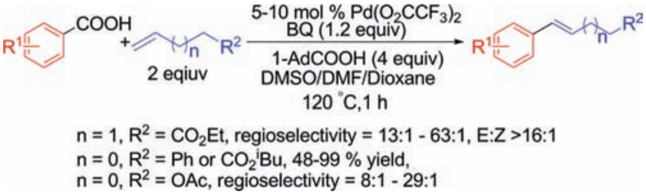
ABSTRACT



A versatile palladium catalyst system was developed to effect the decarboxylative Heck coupling of a variety of arenecarboxylic acids with a wide range of olefins. The key to obtaining the efficient catalyst system is the use of 1-adamatanecarboxylic acid as additive. Alkyl-substituted olefins with coordinating groups were observed to provide significantly improved regioselectivity compared with other alkyl-substituted olefins lacking coordinating groups, and the acetate group of allylic ester was also tolerated in this reaction.

Palladium-catalyzed arylation or olefination of olefins by aryl or vinyl halides, namely, the Heck reaction, is an important C−C bond-forming approach that has found wide applications in natural product synthesis, material science, and bioorganic chemistry.[1,2] The more than 30 year development of effective catalyst systems for the Heck reaction enables the use of a broad scope of arylating reagents ranging from deactivated aryl chlorides[3] and tosylates[4] to alkyl chlorides[5] and to arene.[6] With respect to olefin, the other coupling partner, most of the reported Heck reactions deal with styrene and electron-deficient α,*β*-unsaturated carbonyls. Recently, a few strategies have been developed to accomplish highly regioselective Heck reactions of election-rich olefins such as vinyl ethers and enamides.[7] However, to date, only a few examples of the intermolecular Heck reaction with alkyl-substituted olefin have been reported,[2a,b,3a,8] due in part to low reactivity and poor regioselectivity associated with this

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(1) (a) Bräse, S.; de MeijereA. In *Metal-Catalyzed Cross-coupling Reactions*; Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; pp 217−316. (b) Nicolauo, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442.

(2) For reviews of the Heck reaction, see: (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. (c) Daves, G. D., Jr; Hallberg, A. *Chem. Rev.* **1989**, *89*, 1433. (d) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed.* **1994**, *34*, 2379. (e) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (f) Dounay, A. B.; Overman, L. E. *Chem. Rev.* **2003**, *103*, 2945.

(3) (a) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989. (b) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 481. (c) Selvakumar, K.; Zapf, A.; Beller, M. *Org. Lett.* **2002**, *4*, 3031. (d) Yang, D.; Chen, Y.-C.; Zhu, N.-Y. *Org. Lett.* **2004**, *6*, 1577. (e) Schnyder, A.; Aemmer, J.; Indolese, A. F.; Pittelkow, U.; Studer, M. *Adv. Synth. Catal.* **2002**, *344*, 495. (f) Pröckl, S. S.; Kleist, W.; Gruber, M. A.; Kohler, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1881.

(4) (a) Fu, X.; Zhang, S.; Yin, J.; McAllister, T. L.; Jiang, S. A.; Tann, C.-H.; Thiruvengadam, T. K; Zhang, F. *Tetrahedron Lett.* **2002**, *43*, 573. (b) Hansen, A. L.; Ebran, J.-P.; Ahlquist, M.; Norrby, P.-O.; Skrydstrup, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3349.

(5) (a) Bräse, S.; Waegell, B.; de Meijere, A. *Synthesis* **1998**, 148. (b) Firmansjah, L.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 11340.

(6) (a) Fujiwara, Y.; Noritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166. (b) Karig, G.; Moon, M.-T.; Thasana, N.; Gallagher, T. *Org. Lett.* **2002**, *4*, 3115. (c) Damas, M.; de Vos, D. E.; Celen, S.; Jacobs, P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3512. (d) Yokota, T.; Tani, M.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2003**, *125*, 1476. (e) Zhang, H.; Ferreira, E. M.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 6144. (f) Beck, E. M.; Grimster, N. P.; Hatley, R.; Gaunt, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 2528. (g) Cai, G.; Fu, Y.; Li, Y.; Wan, X.; Shi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 7666.

(7) (a) Mo, J.; Xu, L; Xiao, J. *J. Am. Chem. Soc.* **2005**, *127*, 751. (b) Mo, J.; Xiao, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4152. (c) Nilsson, P.; Larhed, M.; Hallberg, A. *J. Am. Chem. Soc.* **2001**, *123*, 8217. (d) Von Schenck, H.; Äkermark, B.; Svensson, M. *J. Am. Chem. Soc.* **2003**, *125*, 3503. (e) Datta, G. K.; von Schenck, H.; Hallberg, A.; Larhed, M. *J. Org. Chem.* **2006**, *71*, 3896, and references therein.

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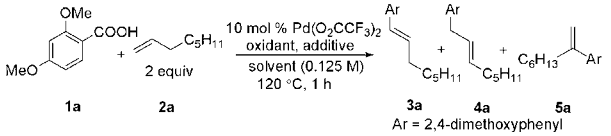
type of olefins in the Heck reaction. In this regard, very recently, White and co-workers[9a] have reported the regioselective Heck-type reaction of alkyl-substituted olefins bearing auxiliary coordinating groups with aryl boronic acids as arylating reagents, and Jiao and co-workers[9b] have described highly selective Heck coupling reaction of allylic esters with aryl iodides. Despite these advances in the Heck reaction of alkyl-substituted olefins, in view of its applications in organic synthesis, efficient Heck reactions of a wide scope of alkyl-substituted olefins with various arylating reagents, particularly those that are easily available and inexpensive, remains highly demanded.

Transition-metal-catalyzed decarboxylative cross-coupling reactions of arenecarboxylic acids or arenecarboxylates have emerged over the past few years.[10−13] This approach is particularly attractive due to the high availability and the low price of arenecarboxylic acids. Myers,[11] in his pioneering work, disclosed an efficient method for palladium-catalyzed decarboxylative Heck-type reaction of arenecarboxylic acids with styrene and α,β-unsaturated carbonyls. This work represents a milestone in the development of palladium-catalyzed decarboxylative cross-coupling reactions.[14] Nevertheless, significant room remains for improvement in view of high loadings of silver and palladium that were required in this process as well as the limiting olefin scope of this process. Herein, we report an efficient palladium-catalyzed decarboxylative Heck-type cross-coupling reaction of an array of arenecarboxylic acids with a broad spectrum of olefins including unactivated alkyl-substituted terminal olefins, wherein an inexpensive 1,4-benzoquinone (BQ) was used as an oxidant.

Table 1. Selected Screening Results for the Palladium-Catalyzed Decarboxylative Heck Coupling of 2,4-Dimethoxybenzoic Acid with 1-Octene[a]



entry	oxidant (equiv)	additive (eqiuv)	solvent (v:v)	isolated yield[b] (%)
1	BQ (1.2)		DMSO/DMF (1:20)	10
2	BQ (1.2)	$EtCO_2H$ (4)	DMSO/DMF (1:20)	26
3	BQ (1.2)	$^tBuCO_2H$ (4)	DMSO/DMF (1:20)	38
4	BQ (1.2)	1-$AdCO_2H$[c] (4)	DMSO/DMF (1:20)	50
5[d]	purified BQ (1.2)	1-$AdCO_2H$ (4)	DMSO/DMF (1:20)	70
6	**purified BQ (1.2)**	**1-$AdCO_2H$ (4)**	**DMSO/DMF/dioxane (1:15:5)**	**79**
7	purified BQ (1.2)	1-$AdCO_2H$ (4) 3-nitropyridine (0.2)	DMF	41
8	purified BQ (1.2)	1-$AdCO_2H$ (4) THTO[e] (4.4)	DMF	39
9	BQ (1.2)	$MeCO_2H$ (4)	DMSO/DMF (1:20)	trace
10	BQ (1.2)	CF_3CO_2H (4)	DMSO/DMF (1:20)	trace
11	BQ (1.2)	p-Me-$C_6H_4SO_3H$ (4)	DMSO/DMF (1:20)	trace
12[f]	purified DDQ[g]	1-$AdCO_2H$ (4)	DMSO/DMF (1:20)	0
13[h]	O_2			31

[a] Reaction conditions: **1a** (0.25 mmol), 1-octene (0.50 mmol), $Pd(O_2CCF_3)_2$ (0.025 mmol), 1,4-benzoquinone = BQ (0.30 mmol), carboxylic acid (1.0 mmol), solvent (2.1 mL). [b] Average of two runs. [c] 1-Adamatanecarboxylic acid = 1-$AdCO_2H$. [d] BQ was purified by sublimation. [e] Tetrahydrothiophene 1-oxide = THTO. [f] Rection was run in the absence of $Pd(O_2CCF_3)_2$. [g] 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone = DDQ. [h] Reaction was run for 13 h.

The model reaction of 2,4-dimethoxybenzoic acid with 2.0 equiv of 1-octene was examined with a variety of palladium sources, solvents, additives, and oxidants (Table 1). Initially, using 1.2 equiv of BQ as the oxidant and 10 mol % of $Pd(O_2CCF_3)_2$ as the catalyst provided the desired products in about 10% yield (entry 1). Because the acidic condition can enhance the ability of BQ to oxidize Pd(0) to Pd(II)[15] and prevent the possible catalyst poisoning caused by the coordinating species,[11b] the introduction of carboxylic acid to the reaction system brought about a beneficial effect (entries 2−4). Screening acids and their loadings established that 4 equivalents of bulky 1-adamantanecarboxylic acid maximized the beneficial effect from acids (entry 4). However, strong acids such as trifluoroacetic acid and p-toluenesulfonic acid and even acetic acid abolished this reaction (entries 9−11). The use of BQ purified by sublimation significantly improved the reaction with 70% yield obtained (entry 5). Further optimization showed that the reaction in DMSO/DMF/dioxane (1:15:5) furnished the best yield (entry 6). Interestingly, substituting DMSO for 0.2 equiv of 3-nitropyridine and 0.1 mL of tetrahydrothiophene-1-oxide provided products in 41% and 39% yields (entries

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(8) (a) Bräse, S.; Schroen, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1071. (b) Brunner, H.; de Courey, N. L. C.; Genêt, J.-P. *Tetrahedron Lett.* **1999**, *40*, 4815. (c) Mabic, S.; Vaysse, L.; Benezra, C.; Lepoittevin, J.-P. *Synthesis* **1999**, *7*, 1127. For the Heck reaction of allylic alcohols: (d) Larock, R. C.; Yum, E. K.; Yang, H. *Tetrahedron* **1994**, *50*, 305. (e) Chalk, A. J.; Magennis, S. A. *J. Org. Chem.* **1976**, *41*, 1206. For intramolecular olefination of C−H bond with alkyl-substituted olefins, see: (f) ref 6e. (g) Liu, C.; Han, X.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 3700. For the decarboxylative Heck reaction of an aromatic carboxlic anhydride with an alkyl-substituted olefin, see: (h) Stephan, M. S.; Teunissen, A. J. J. M.; Verzijl, G. K. M.; de Vires, J. G. *Angew. Chem., Int. Ed.* **1998**, *37*, 662.

(9) (a) Delcamp, J. H.; Brucks, A. P.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 11270. (b) Pan, D.; Chen, A; Su, Y.; Zhou, W.; Li, S.; Jia, W.; Xiao, J.; Liu, Q.; Zhang, L.; Jiao, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4729.

(10) (a) Goossen, L. J.; deng, G.; Levy, L. M. *Science* **2006**, *313*, 662. (b) Goossen, L. J.; Rodríguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L. M. *J. Am. Chem. Soc.* **2007**, *129*, 4824. (c) Goossen, L. J.; Melzer, B. *J. Org. Chem.* **2007**, *72*, 7473. (d) Goossen, L. J.; Zimmermann, B.; Knauber, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7103. (e) Duan, Z.; Ranjit, S.; Zhang, P.; Liu, X. *Chem.−Eur. J.* **2009**, *15*, 3666.

(11) (a) Myers, A. G.; Tanaka, D.; Mannion, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 11250. (b) Tanaka, D.; Romeril, S. P.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 10323. (c) Tanaka, D.; Myers, A. G. *Org. Lett.* **2004**, *6*, 433.

(12) (a) Forgione, P.; Brochu, M.-C.; St-Onge, M.; Thesen, K. H.; Bailey, M. D.; Bilodeau, F. *J. Am. Chem. Soc.* **2006**, *128*, 11350. (b) Maehara, A.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1159. (c) Becht, J.-M.; Catala, C.; Drian, C. L.; Wagner, A. *Org. Lett.* **2007**, *9*, 1781.

(13) For examples of the intramolecular rearrangement reactions via decarboxylation of esters, see: (a) Waetzig, S. R.; Tunge, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 14860. (b) Rayabarapu, D. K.; Tunge, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 13510. (c) Goossen, L. J.; Paezold, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1095.

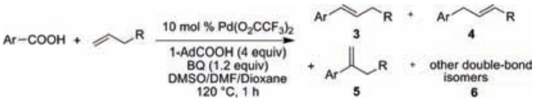
(14) Baudoin, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 1373.

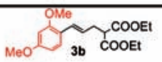
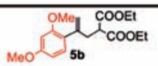
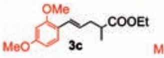
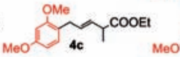
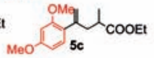
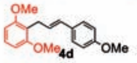
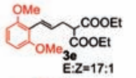
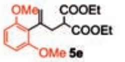
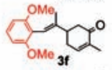
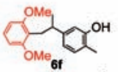
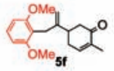
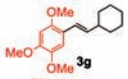
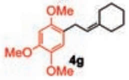
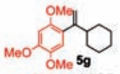
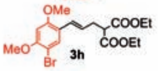
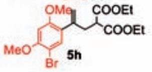
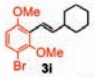
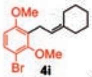
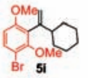
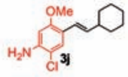
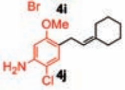
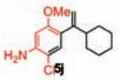
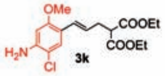
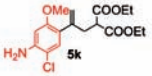
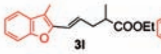
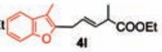
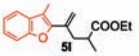
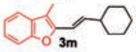
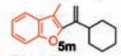
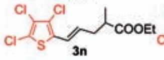
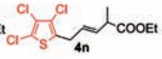
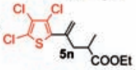
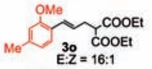
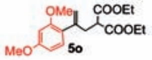
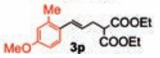
(15) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

7 and 8), respectively. Other palladium sources such as $Pd(OAc)_2$, $PdCl_2$, $Pd(CH_3CN)_2Cl_2$, and $Pd_2(dba)_3$ were ineffective. The reaction conducted with purified DDQ as an oxidant in the absence of $Pd(O_2CCF_3)_2$ did not generate the desired products in appreciable amounts, which ruled out the possibility that this reaction proceeds through a radical pathway initiated by oxidation of arene carboxylate(entry 12). In the presence of oxygen as the sole oxidant, the reaction run for 13 h provided 31% yield (entry 13).[16]

The model reaction produced three isomers (a styrenyl internal olefin **3a**, an allylic internal olefin **4a**, and a terminal olefin **5a**) as major products along with minor double-bond migrating isomers, and the selectivity of this reaction seems to be insensitive to these reaction conditions examined, which presumably stems from the intrinsic attributes of this reaction, for example, nonselective olefin insertion and nonselective β-hydride elimination.[9a] However, we achieved good regioselectivity in the decarboxylative Heck reaction of alkyl-substituted olefins by employing olefin substrates bearing auxiliary coordinating groups (see Table 2).

Table 2. Palladium-Catalyzed Decarboxylative Coupling of Arenecarboxylic Acids with Alkyl-Substituted Olefins[a]



entry	product 3	product 4	product 5	yield[b] (%) regioselectivity[c] (3:4:5:6)
1	 **3b**		 **5b**	72(67)[e] 13:0:1:0
2	 **3c**	 **4c**	 **5c**	71 29:1.2:1:1.4
3		 **4d**		70 0:70:0:0
4	 **3e** E:Z=17:1		 **5e**	85 (80)[e] 63:0:1:0
5	 **3f**	 **6f**	 **5f**	87 1.2:1:0:1
6	 **3g**	 **4g**	 **5g**	77(77)[e] 20:1:4:1.3
7	 **3h**		 **5h**	30 15:0:1:0
8	 **3i**	 **4i**	 **5i**	43 5.7:1.4:1:1.6
9	 **3j**	 **4j**	 **5j**	72 15:1:4:2
10[d]	**3j**	**4j**	**5j**	64 20:1:2.4:2.4
11	 **3k**		 **5k**	61 13:0:1:0
12	 **3l**	 **4l**	 **5l**	53 7.6:1:1.7:0
13	 **3m**		 **5m**	57 4.3:0:1:0
14	 **3n**	 **4n**	 **5n**	23 6.5:4.3:1:0
15	 **3o** E:Z = 16:1		 **5o**	24(24)[e] 26:0:1:0
16	 **3p**			0

[a] Reactions were run under the conditions of entry 6 in Table 1. [b] Isolated yields (average of two runs). [c] The ratio of $E/Z > 20:1$, as determined by ^1H NMR, unless otherwise indicated. [d] Reaction was run for 3 h with 5 mol % of $Pd(O_2CCF_3)_2$ in the absence of $1\text{-}AdCO_2H$. [e] Value in parentheses refers to the yield from reaction on a 1 mmol scale.

The decarboxylative Heck-type coupling reaction of arenecarboxylic acids with various alkyl-substituted olefins was examined under the condition of entry 6 in Table 1. As shown in Table 2, these reactions occurred in moderate-to-excellent isolated yields. The reaction condition was compatible with ester, amino, chloro, bromo, and keto substituents. Some heterocyclic carboxylic acids were effective substrates (entries 12−14). The use of olefin substrates with coordinating acetate groups led to good regioselectivities (entries 1, 2, 4, 7, and 11), as observed by White.[9a] Vinylcyclohexane provided the improved selectivity with styrenyl olefin as a major product (entries 6, 8, 9, 10, and 13), compared with linear olefins, suggesting that steric factors of substrates, to some extent, influenced the regiochemistry[17] in these reactions. The reaction of allylanisole predominately generated allylic olefin (entry 3), whose structure was also confirmed by X-ray diffraction analysis. For carvone, reactions took place exclusively at terminal double bonds (entry 5), yielding styrenyl and allylic olefins as well as arylated carvacrol generated from double-bond migration followed by structural rearrangement. The reaction of 4-amino-5-chloro-2-methoxybenzoic acid conducted with 5 mol % of $Pd(O_2CCF_3)_2$ in absence of adamantine-1-carboxylic acid led to enhancement of selectivity and a little decrease in the yield compared with the reaction under standard conditions (entry 10 vs entry 9). 2-Methoxy-4-methylbenzoic acid that is less electron rich than 2,4-dimethoxybenzoic acid also participated in this reaction, although the diminished yield was obtained (entry 15). In this case, oxidative dehydrogenation of alkyl-substituted olefin occurred presumbly due to slow decarboxylation of 2-methoxy-4-methylbenzoic acid. In contrast, 4-methoxy-2-methylbenzoic acid, a positional isomer of 2-methoxy-4-methylbenzoic acid, was completely inert under the current reaction conditions (entry 16), suggesting that at least one methoxy group *ortho* to carboxyl on aromatic ring of benzoic acid is necessary for this reaction to occur. The observation that benzoic acid bearing both an *o*-methoxy group and another electron-withdrawing group such as 3-fluoro-2-methoxybenzoic acid did not react under the current conditions indicated that this method requires sufficiently electron-rich benzoic acids.

The reaction scope was further investigated with respect to olefins under the conditions established for alkyl-substituted olefins (Table 3). Styrene proved to be a highly

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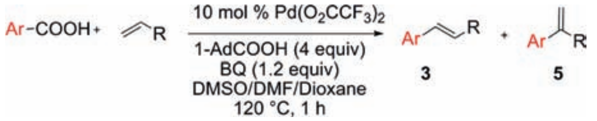
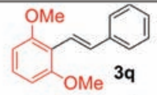
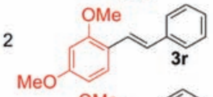
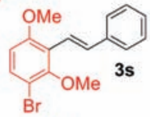
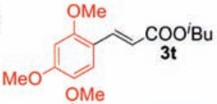
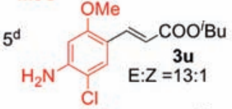
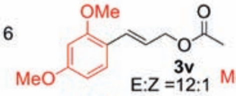
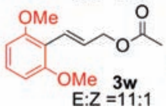
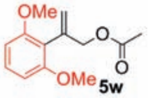
(16) In the presence of oxygen as the oxidant, Pd-catalyzed decarboxylative Heck coupling of benzoic acids with acrylates have been established, see: Fu, z.; Huang, S.; Su, W.; Hong, M. Manuscript in preparation.

(17) For the theoretical studies on the electronic and steric control of the regiochemistry in the Heck reaction, see ref 7d.

Table 3. Palladium-Catalyzed Decarboxylative Coupling of Arenecarboxylic Acids with a Variety of Olefins[a]



entry	product		yield (%)[b]	regioselectivity (3:5)[c]
1	 **3q**		99	
2	 **3r**		81	
3	 **3s**		48	
4	 **3t**		74	
5[d]	 **3u** E:Z =13:1		61	
6	 **3v** E:Z =12:1	 **5v**	53	8:1
7	 **3w** E:Z =11:1	 **5w**	80 (80)[e]	29:1

[a] Reactions were run under the conditions of entry 6 in Table 1. [b] Isolated yields (average of two runs). [c] The ratio of $E/Z > 20:1$, as determined by ^{1}H NMR, unless otherwise indicated. [d] Reaction was performed for 3 h with 5 mol % of $Pd(O_2CCF_3)_2$ in the absence of 1-$AdCO_2H$. [e] Value in parentheses refers to the yield from reaction on a 1 mmol scale.

reactive coupling partner and smoothly coupled carboxylic acids with good to excellent yields (entries 1−3). It is noteworthy that allylic ester also underwent decarboxylative Heck coupling to generate arylated allylic esters with good to excellent regioselectivity and with retention of acetate group (entries 6 and 7). Reactions of arenecarboxylic acids with electron-deficient methyl acrylate also provided good yields (entries 4 and 5).

This method is not limited to the small-scale reaction as described above (e.g., 0.2 mmol); the reactions performed on a 1 mmol scale gave yields comparable to those on a small scale (entries 1, 4, 6, and 15 in Table 2, and entry 7 in Table 3). The reaction of 2,4-dimethoxybenzoic acid with 1-octene on a gram scale provided 81% yield.

As shown in Tables 2 and 3, the reactivity of benzoic acids was observed to strongly rely on the electron density on their aromatic rings, as illustrated by the difference in reactivity between 2,4-dimethoxybenzoic acid and 2-methoxy-4-methylbenzoic acid. Generally, electron-rich benzoic acids are more reactive than less electron-rich benzoic acids, which is likely associated with decarboxylation step. Myers, on the basis of the mechanistic investigation,[5b] proposed that the decarboxylation step involves the coordination of the electron-deficient palladium(II) center to the ipso-carbon of the aromatic ring. In light of this proposal, the sufficient affinity of electron-rich benzoic acid for electron-deficient palladium center would be required for the decarboxylation process. In our reaction system, it is possible that because coordination of BQ to the palladium(II) center reduces the eletrophilicity of palladium(II) center, more electron-rich benzoic acid is required to form an efficient coordinating bond between palladium(II) center and ipso-carbon of the aromatic ring for decarboxylation process. This possibility could serve to explain why our protocol is restricted to electron-rich benzoic acid. The observation that an excessive amount of BQ slowed the desired reaction is consistent with the idea that coordination of BQ to the palladium(II) center influences the activity of palladium catalyst in this reaction, although we cannot rule out the possibility that competition between BQ and the olefin substrate for coordination to the palladium center retards this reaction. The difference in reactivity between 4-methoxy-2-methylbenzoic acid and 2-methoxy-4-methylbenzoic acid highlights the essential role of the *o*-methoxy group in the decarboxylative Heck coupling reaction. The fact that decarboxylation of 4-methoxy-2-methylbenzoic acid occurred at higher temperature with no Heck-type product formed suggests that the *o*-methoxy group possibly exerts an positive effect on the late stage of decarboxylative Heck coupling. Presumably, by weakly coordinating to palladium center, the *o*-methoxy group facilitates formation of π-olefinpalladium complex.

In summary, we have developed a versatile catalyst system for the decarboxylative Heck reaction of arenecarboxylic acids with an array of olefins, including unactivated alkyl-substituted olefins, electron-deficient olefin, and styrene. Introducing carboxylic acids to the reaction system was crucial to obtaining the efficient catalyst. Employing substrates with coordinating groups provided good selectivity for reactions of the alkyl-substituted olefins. This positive effect of coordinating groups contained in olefin on the regioselectivity was further illustrated by the reaction of allylic ester that dominantly generated linearly arylated allylic ester without elimination of an acetate group. Studies are underway to determine the origin of the beneficial effect of bulky carboxylic acid in this reaction and develop a ligand-assisted palladium-catalyzed, highly regioselective decarboxylative Heck reaction with wide substrate scope.

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Supporting Information Available: Detailed experimental procedures, characterization data for new compounds, and X-ray crystallography data for **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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