JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

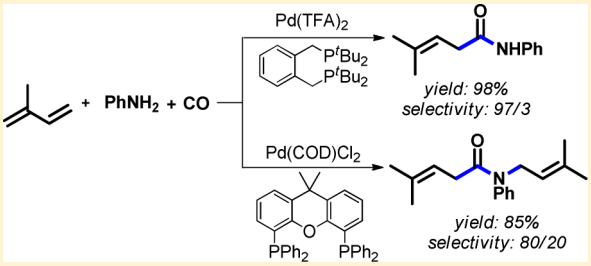
Selective Palladium-Catalyzed Aminocarbonylation of 1,3-Dienes: Atom-Efficient Synthesis of β,γ-Unsaturated Amides

Xianjie Fang,† Haoquan Li,† Ralf Jackstell, and Matthias Beller*

Leibniz-Institut für Katalyse e.V., an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Supporting Information

ABSTRACT: Carbonylation reactions constitute important methodologies for the synthesis of all kinds of carboxylic acid derivatives. The development of novel and efficient catalysts for these transformations is of interest for both academic and industrial research. Here, the first palladium-based catalyst system for the aminocarbonylation of 1,3-dienes is described. This atom-efficient transformation proceeds under additive-free conditions and provides straightforward access to a variety of β,γ-unsaturated amides in good to excellent yields, often with high selectivities.



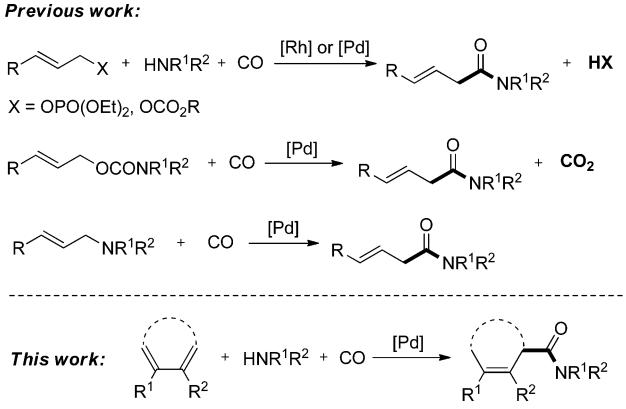
INTRODUCTION

The atom-economic synthesis of amides continues to be one of the major challenges in synthetic organic chemistry.[1] The amide bond is the key backbone of all natural peptides in biological systems and is also an important functional group in organic building blocks and industrial chemicals.[2] Traditionally, amides are synthesized by reactions of carboxylic acids and their derivatives with amines,[3] which suffers from harsh conditions. In addition, large amounts of side products are often produced. In this respect, the development of more efficient catalytic methodologies is still highly important. For example, in recent years, the palladium-catalyzed aminocarbonylation of aryl halides,[4] alkynes,[5] and alkenes[6] has become a powerful tool for the synthesis of aromatic amides, α,β-unsaturated amides, and aliphatic amides, respectively.

On the basis of our long-standing interest in transition-metal-catalyzed carbonylation reactions,[4a] we recently became interested in the carbonylation of allyl derivatives to give the corresponding homoallylic compounds, which are synthetically important but not easily accessible.[7] In the past, effective carbonylation methods for the reaction of allylic carbonates,[8] acetates,[9] chlorides,[10] amines,[11] ethers,[12] phosphates,[9b,e,13] and alcohols[14] to form β,γ-unsaturated esters have been developed. However, there are few examples known that allow the synthesis of related β,γ-unsaturated amides via carbonylation (Scheme 1).[8a,11,15]

A major problem for any aminocarbonylation methodology is the competing direct amination of the substrate. In fact, such aminations of allyl-X compounds should proceed faster than carbonylations. Moreover, a general drawback of these reactions is the stoichiometric generation of byproducts (e.g., salts). Alternatively, β,γ-unsaturated carboxylic acid derivatives might also be synthesized by carbonylation of 1,3-dienes. Despite the inherent advantage of this atom-economic green route (100% atom-efficient route), the carbonylation of 1,3-dienes has scarcely been explored in academic laboratories.[16] Compared to the well-studied alkoxycarbonylation of 1,3-dienes,[17] to the best of our knowledge comparable aminocarbonylation reactions to β,γ-unsaturated amides have not yet been reported (Scheme 1).

Scheme 1. Synthesis of β,γ-Unsaturated Amides via Carbonylation Reactions



On the basis of our previous work on the direct hydroamination of 1,3-dienes,[18] herein we describe the first general catalyst system for the direct aminocarbonylation of 1,3-dienes. Applying a variety of aromatic amines leads to β,γ-unsaturated amides in good yields and selectivities under neutral conditions.

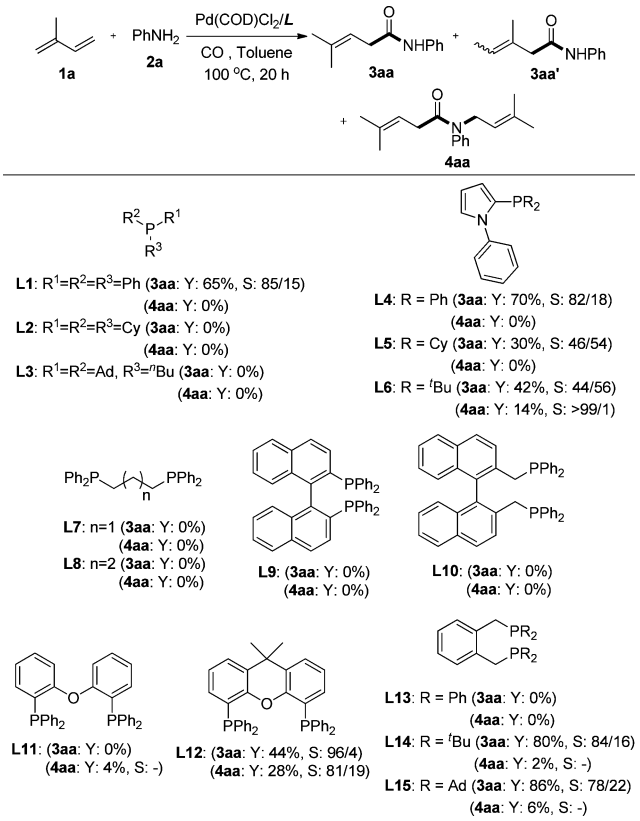
RESULTS AND DISCUSSION

Initially, we investigated the aminocarbonylation of isoprene (**1a**) with aniline (**2a**) as a model reaction in the presence of [Pd(COD)Cl$_2$] and different phosphine ligands **L1**−**L15** (Scheme 2). In general, we observed two kinds of carbonylated products: the 1:1 adduct **3aa** and the 2:1 adduct **4aa**. In both cases, different regioisomers can be formed. Notably, a preferential

Received: August 19, 2014
Published: October 17, 2014

   dx.doi.org/10.1021/ja507530f | J. Am. Chem. Soc. 2014, 136, 16039−16043

Scheme 2. Influence of the Ligand on the Palladium-Catalyzed Aminocarbonylation of Isoprene (1a) with Aniline (2a)[a]

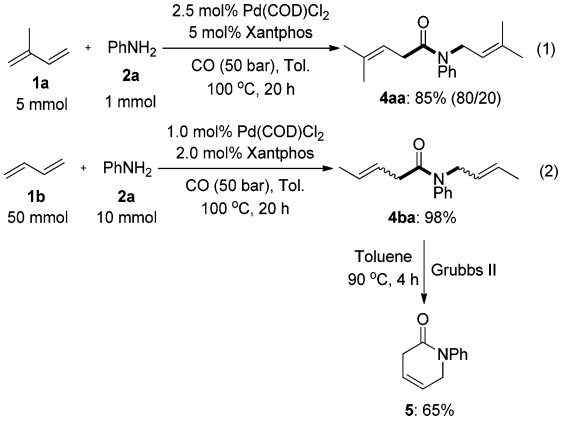


[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), [Pd(COD)Cl_2] (2.5 mol %), monodentate ligand (10.0 mol %), bidentate ligand (5.0 mol %), CO (50 bar), toluene (2 mL), 100 °C, 20 h; yield and the ratios of isomers were determined by GC analysis. Y, yield; S, **3aa**/**3aa**′ ratio.

attack at the sterically less hindered position is observed. Nevertheless, minor amounts of **3aa**′ are also formed (for details, see Supporting Information).

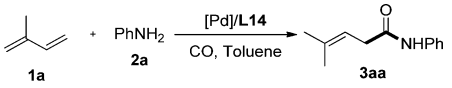
Unfortunately, the application of monodentate ligands **L2** and **L3** gave none of the desired product **3aa**. However, to our delight, **L1** and cataCXium ligands[19] **L4**–**L6** provided desired product **3aa** in moderate to good yield. Further investigations showed that selected commercially available bidentate ligands **L7**–**L11** exhibited no activity in the formation of **3aa**. However, when Xantphos (**L12**) was used, desired product **3aa** is obtained in 44% yield. In addition, significant amounts of the 2:1 adduct **4aa** are formed (yield, 28%). Next, some 1,2-bis-(phosphinomethyl)benzene ligands with different steric properties were tested, **L13**–**L15**. BuPox[20] (**L14**) was identified as the most promising ligand, and the reaction afforded desired product **3aa** in 80% yield with good selectivity.

In the presence of Xantphos (**L12**) as ligand, significant amounts of the 2:1 adduct **4aa** were obtained. Apparently, the yield of **4aa** is strongly affected by the molar ratio of **1a** to **2a**. Indeed, as the molar ratio of **1a** to **2a** increased to 5:1, the isolated yield of **4aa** increased to 85% (eq 1). From an industrial point of view, it is interesting that 1,3-butadiene (**1b**) furnished the corresponding product **4ba** in excellent yield at low catalyst loading (eq 2). Considering the 1,7-diene structural motif, product **4** provides the possibility of further transformations. Indeed, ring-closing metathesis of **4ba** occurred smoothly using Grubbs II catalyst to give 1-phenyl-1,6-dihydropyridin-2(3*H*)-one **5** in 65% yield (eq 2).



In order to improve the methodology further, we evaluated the influence of critical reaction parameters (e.g., palladium precursor, catalyst loading, temperature, CO pressure) for the model reaction using **L14** as the ligand of choice. As shown in Table 1, using typical palladium precursors such as Pd(OAc)$_2$,

Table 1. Investigation of Reaction Conditions for Palladium-Catalyzed Aminocarbonylation of Isoprene (1a) with Aniline (2a)[a]



entry	[Pd]	temp. (°C)	yield (%)[b]	sel.[c]
1	Pd(COD)Cl_2	100	80	84:16
2	Pd(OAc)$_2$	100	0	
3	Pd(acac)$_2$	100	0	
4	$PdCl_2$	100	89	84:16
5[d]	$PdCl_2$	100	19	>99:1
6	Pd(dba)$_2$	100	0	
7[e]	Pd(dba)$_2$	100	89	92:8
8[f]	Pd(dba)$_2$	100	0	
9[g]	Pd(dba)$_2$	100	0	
10[h]	Pd(dba)$_2$	100	61	94:6
11[i]	Pd(dba)$_2$	100	77	95:5
12	Pd(CH_3CN)$_2Cl_2$	100	84	87:13
13	Pd($PhCN$)$_2Cl_2$	100	70	88:12
14	[Pd(cinnamyl)Cl]$_2$	100	87	93:7
15	[Pd(allyl)Cl]$_2$	100	64	94:6
16	Pd(TFA)$_2$	100	>99	88:12
17[j]	Pd(TFA)$_2$	100	57	92:8
18[k]	Pd(TFA)$_2$	100	78	91:9
19[l]	Pd(TFA)$_2$	100	95	88:12
20[m]	Pd(TFA)$_2$	100	78	88:12
21	Pd(TFA)$_2$	80	>99	95:5
22	**Pd(TFA)$_2$**	**60**	**>99**	**97:3**
23	Pd(TFA)$_2$	40	79	>99:1

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), [Pd] (2.5 mol %), **L14** (5.0 mol %), toluene (2 mL), CO (50 bar), 20 h. [b]Yield determined by GC analysis. [c]Sel. = **3aa**/**3aa**′ ratio; the ratio of isomers was determined by GC analysis. [d]3 Å molecular sieve (200 mg). [e]TFA (10 mol %). [f]HOAc (10 mol %). [g]H_3PO_4 (10 mol %). [h]Camphorsulfonic acid (10 mol %). [i]*p*-TsOH·H_2O (10 mol %). [j][Pd] (1.5 mol %), **L14** (3.0 mol %). [k][Pd] (1.5 mol %), **L14** (3.0 mol %), TFA (10 mol %). [l]CO (40 bar). [m]CO (20 bar).

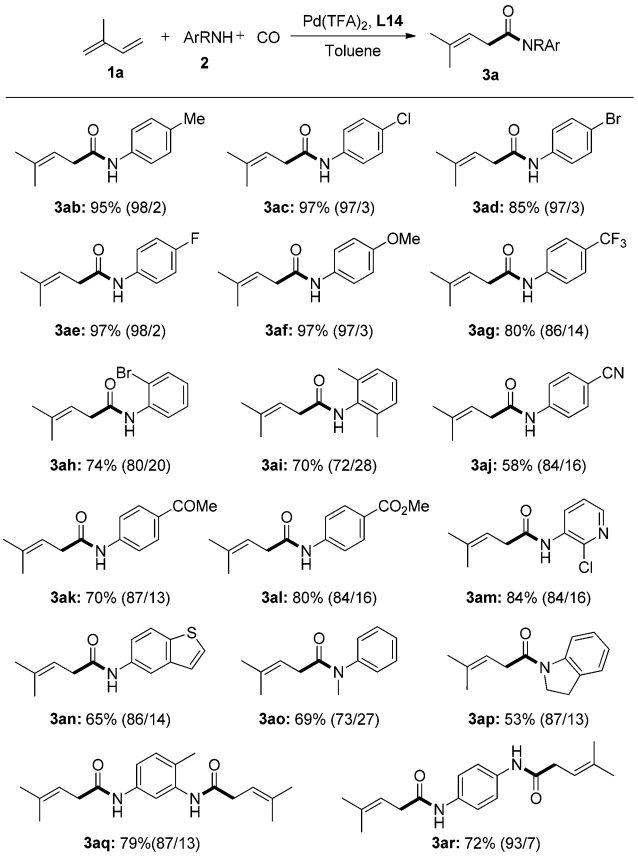
dx.doi.org/10.1021/ja507530f | J. Am. Chem. Soc. 2014, 136, 16039–16043

$Pd(acac)_2$, and $Pd(dba)_2$ under the standard reaction conditions, no conversion was observed (Table 1, entries 2, 3, and 6). However, using $Pd(dba)_2$ in the presence of 10 mol % of either trifluoroacetic acid, camphersulfonic acid, or *p*-toluenesulfonic acid gave the desired product in 61−89% yield (Table 1, entries 7, 10, and 11). Notably, the use of weaker acids such as acetic acid and phosphoric acid gave no product (Table 1, entries 8 and 9). Apparently, a strong acid is required to generate the catalytically active palladium species (see mechanistic discussion below). Interestingly, the addition of molecular sieves impedes the reaction, and the product yield is decreased from 89 to only 19% (Table 1, entries 4 and 5). Without molecular sieves, the use of other palladium chloride precursors resulted in the formation of desired product **3aa** in 64−89% yield with good selectivity (Table 1, entries 1, 4, and 12−15). To our delight, quantitative GC yield of desired amide **3aa** was obtained when $Pd(TFA)_2$ was used as the catalyst precursor (Table 1, entry 16). Lowering the catalyst loading revealed an optimal loading of 2.5 mol % of [Pd] (Table 1, entry 17). However, at low catalyst loading, the addition of trifluoroacetic acid also improved the conversion and restored the catalyst activity (Table 1, entry 18). The yield of desired amide **3aa** decreased when lowering the CO pressure (Table 1, entries 19 and 20). Interestingly, lowering the reaction temperature to 80 or 60 °C also resulted in full conversion and excellent chemo- and regioselectivity. Here, the regioselectivity for **3aa** increased to 97:3 (Table 1, entries 21 and 22).

With optimized reaction conditions established (Table 1, entry 22), we examined the scope of this novel aminocarbonylation process with respect to amines (Scheme 3). A variety of aromatic amines with electron-neutral, electron-deficient, and electron-rich substituents led to the corresponding carbonylative products in good yields and selectivities. Functional groups including reactive halide (**3ad** and **3ah**), nitrile (**3aj**), ketone (**3ak**), and ester (**3al**) groups, which provide useful handles for further synthetic transformations, are well-tolerated. **2i**, as an example of a bulky substrate, was smoothly transformed to the corresponding *β,γ*-unsaturated amide (**3ai**) in good yield. Interestingly, heteroaromatic amines (**3am** and **3an**) proved to be efficient coupling partners and gave the corresponding amides in decent yields with good selectivities. Even secondary aromatic amines (**2o** and **2p**) underwent this transformation and afforded the desired products in moderate to good yields (**3ao** and **3ap**). Considering the importance of diamides, which are widely applied for agrochemicals and used in the polymer industry, we tested the dicarbonylation of phenylenediamines. As shown in Scheme 3, the reactions of isoprene **1a** with *m*-phenylenediamine **2q** and *p*-phenylenediamine **2r** gave the desired diamides, again in good yields and selectivities (**3aq** and **3ar**). Unfortunately, no conversion at all was observed when benzylic amine or *n*-butylamine was used as coupling partner. Apparently, in the presence of these more basic amines, the catalyst activity disappeared.

Next, we evaluated the scope of 1,3-dienes using aniline **2a** as a standard coupling partner (Table 2). Phenyl-substituted 1,3-diene **1c** furnished the corresponding desired product in high yield with excellent regioselectivity, albeit in low stereoselectivity (Table 2, entry 2). Furthermore, sterically crowded 1,3-diene **1d** was smoothly transformed to the corresponding *β,γ*-unsaturated amide with excellent selectivity (Table 2, entry 3). The cyclic 1,3-diene **1e** was also efficiently transformed to the desired *β,γ*-unsaturated amide (Table 2, entry 4). From a synthetic point of view, the synthesis of functionalized *β,γ*-unsaturated amides from functionalized 1,3-dienes is important, which is reflected in products **3fa** and **3ga**, which are obtained

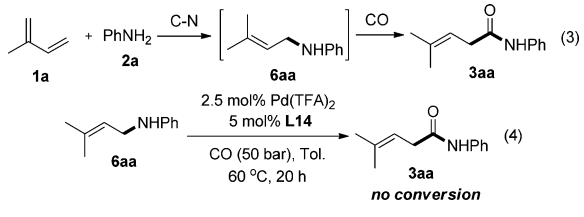
Scheme 3. Palladium-Catalyzed Aminocarbonylation of Isoprene (1a) with Aromatic Amines (2)[a]



[a]Reaction conditions: **1a** (1.0 mmol), **2** (1.0 mmol), [$Pd(TFA)_2$] (2.5 mol %), **L14** (5.0 mol %), CO (50 bar), toluene (2 mL), (**3ab**−**3ae**: 60 °C; **3af** and **3am**: 80 °C; others: 100 °C), 20 h; isolated yield; the ratio of isomers was determined by GC analysis; in the cases of **3aq** and **3ar**, a slight excess of **1a** (2.1 mmol) was used.

in a straightforward manner using our protocol (Table 2, entries 5 and 6).

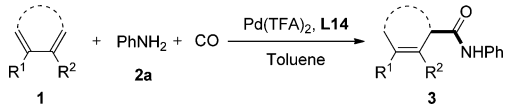
On the basis of previous work on carbonylation of allylic amines[15] and alkoxycarbonylation of allylic alcohols,[14f] we initially thought that this transformation proceeds via a sequential C−N coupling/carbonylation reactions (eq 3). However, the corresponding allylamine **6aa** was not observed in the reaction mixture. In agreement with this observation, no carbonylation of the synthesized allylamine **6aa** took place under the standard conditions (eq 4). Hence, a sequential C−N coupling/carbonylation pathway seems unlikely in the present reaction process. Although the detailed mechanism of the palladium-catalyzed aminocarbonylation of 1,3-dienes is not clear, we suggest the following catalytic cycle based on our preliminary observations[17q] and previous work on aminocarbonylation of olefins[6fg] (Scheme 4).



Initially, the catalytic cycle should start from the cationic palladium hydride species **A**. Formation of **A** proceeds in situ

dx.doi.org/10.1021/ja507530f | J. Am. Chem. Soc. 2014, 136, 16039−16043

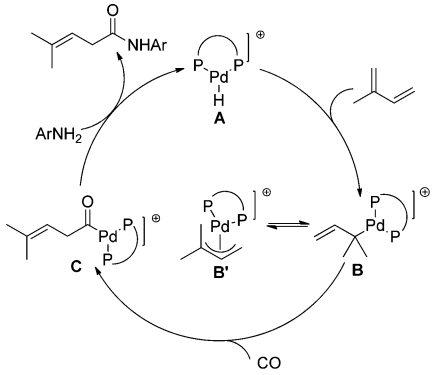
Table 2. Palladium-Catalyzed Aminocarbonylation of 1,3-Dienes (1) with Aniline (2a)[a]



Entry	1	3	Yield (selectivity)
1	1a	3aa	3aa: 98% (97/3)
2	1c	3ca	3ca: 74% (*E*/*Z*: 46/54)
3[b]	1d	3da	3da: 60%
4[c]	1e	3ea	3ea: 60%
5	1f	3fa	3fa: 83% (*E*/*Z*: 44/56)
6	1g	3ga	3ga: 72% (*E*/*Z*: 73/27)

[a]Reaction conditions: **1** (1.0 mmol), **2a** (1.0 mmol), [Pd(TFA)$_2$] (2.5 mol %), **L14** (5.0 mol %), CO (50 bar), toluene (2 mL), 60 °C, 20 h; isolated yield; the ratio of isomers was determined by GC analysis. [b]**1d** (2.0 mmol), 100 °C. [c]**1e** (5.0 mmol), [Pd(COD)Cl$_2$] (2.5 mol %), **L12** (5.0 mol %), 100 °C.

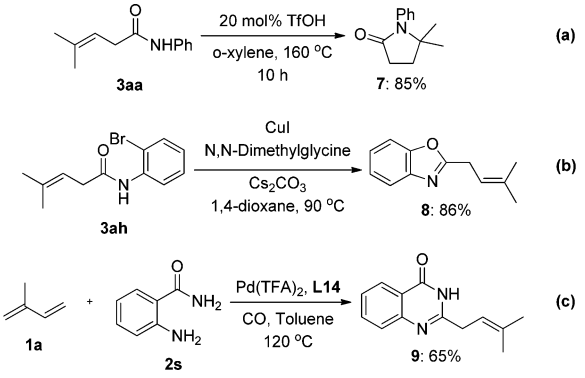
Scheme 4. Proposed Catalytic Cycle



by reaction of palladium(II) trifluoroacetate and aniline in the presence of the ligand. Notably, no formation of the corresponding hydride is observed at room temperature. However, heating this mixture at 60 °C for 6 h led to the formation of the respective hydride (for details, see the Supporting Information). In agreement with previous investigations on 1,3-diene amination, insertion of isoprene into the H-palladium bond of the active cationic palladium hydride species **A** will lead to π-allyl-Pd complex **B**′.[18a,b] Then, CO addition and insertion to give the corresponding acyl palladium complex **C** takes place. Finally, aminolysis of intermediate **C** leads to the desired product and regenerates the palladium hydride species **A**. With respect to the formation of the active catalyst, it should be noted that catalysis does not proceed at room temperature.

Finally, it should be noted that this novel procedure for the preparation of all kinds of β,γ-unsaturated amides also provides convenient access to important heterocyclic compounds. For example, intramolecular hydroamination of **3aa** occurred smoothly under acidic conditions to give γ-lactam **7** in good yield (Scheme 5a). In addition, substituted benzoxazoles are

Scheme 5. Synthetic Applications



easily available. This is exemplified by the reaction of **3ah** to **8** via a Cu-catalyzed C−O coupling reaction[21] (Scheme 5b). Interestingly, 2-allyl quinazolinone **9** was directly produced using 2-aminobenzamide **2s** as the coupling partner. This one-pot transformation proceeds by a sequential aminocarbonylation/condensation pathway (Scheme 5c).

CONCLUSIONS

In summary, we developed the first general aminocarbonylation reactions of 1,3-dienes. In the presence of different palladium phosphine complexes, carbonylation (1:1 adduct) or a selective hydroamination−carbonylation sequence (2:1 adduct) was observed. Using different aromatic amines, a variety of synthetically useful β,γ-unsaturated amides are produced in good to excellent yields. Combining this procedure with established functionalizations allows for an efficient preparation of various heterocyclic compounds. The high atom economy and additive-free reaction conditions make this protocol attractive for synthetic applications, and we believe it will complement the current methodologies for carbonylations in organic synthesis.

ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

Matthias.Beller@catalysis.de

Author Contributions

[†]X.F. and H.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the BMBF (Germany) and the State of Mecklenburg-Vorpommern. We thank Dr. Wolfgang Baumann, Dr. Christine Fischer, Susann Buchholz, and Susanne Schareina for their technical and analytical support.

REFERENCES

(1) (a) Constable, D. J. C.; Dunn, P. J.; Hayler, J. D.; Humphrey, G. R.; Leazer, J. L.; Linderman, R. J.; Lorenz, K.; Manley, J.; Pearlman, B. A.; Wells, A.; Zaks, A.; Zhang, T. Y. *Green Chem.* **2007**, *9*, 411. (b) Pattabiraman, V. R.; Bode, J. W. *Nature* **2011**, *480*, 471.

(2) (a) Humphrey, J. M.; Chamberlin, A. R. *Chem. Rev.* **1997**, *97*, 2243. (b) Bode, J. W. *Curr. Opin. Drug Discovery Dev.* **2006**, *9*, 765. (c) Cupido, T.; Tulla-Puche, J.; Spengler, J.; Albericio, F. *Curr. Opin. Drug Discovery Dev.* **2007**, *10*, 768.

(3) For reviews, see: (a) Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009**, *38*, 606. (b) Montalbetti, C. A. G. N.; Falque, V. *Tetrahedron* **2005**, *61*, 10827. (c) Han, S.-Y.; Kim, Y.-A. *Tetrahedron* **2004**, *60*, 2447.

(4) For reviews see: (a) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114. Recent examples: (b) Wu, X.-F.; Schranck, J.; Neumann, H.; Beller, M. *ChemCatChem* **2012**, *4*, 69. (c) Wu, X.-F.; Neumann, H.; Beller, M. *Chem.—Eur. J.* **2012**, *18*, 419. (d) Wu, X.-F.; Neumann, H.; Beller, M. *Chem.—Eur. J.* **2012**, *16*, 9750. (e) Reeves, D. C.; Rodriguez, S.; Lee, H.; Haddad, N.; Krishnamurthy, D.; Senanayake, C. H. *Org. Lett.* **2011**, *13*, 2495. (f) Hermange, P.; Lindhardt, A. T.; Tanning, R. H.; Bjerglund, K.; Lupp, D.; Skrydstrup, T. *J. Am. Chem. Soc.* **2011**, *133*, 6061. (g) Nielsen, D. U.; Neumann, K.; Tanning, R. H.; Lindhardt, A. T.; Modvig, A.; Skrydstrup, T. *J. Org. Chem.* **2012**, *77*, 6155.

(5) For recent reviews and compendia on carbonylation of alkynes, see: (a) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2014**, *114*, 1783. (b) Doherty, S.; Knight, J. G.; Smyth, C. H. Recent developments in alkyne carbonylation. In *Modern Carbonylation Methods*; Kollár, L., Ed.; Wiley-VCH: Weinheim, Germany, 2008. (c) Brennführer, A.; Neumann, H.; Beller, M. *ChemCatChem* **2009**, *1*, 28.

(6) For reviews, see: (a) El Ali, B.; Alper, H.; Beller, M.; Bolm, C. In *Transition Metals for Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2008; pp 49−67. (b) Kiss, G. *Chem. Rev.* **2001**, *101*, 3435. Recent examples: (c) Dong, C.; Alper, H. *Tetrahedron: Asymmetry* **2004**, *15*, 35. (d) Lee, S. I.; Son, S. U.; Chung, Y. K. *Chem. Commun.* **2002**, 1310. (e) Li, W.; Liu, C.; Zhang, H.; Ye, K.; Zhang, G.; Zhang, W.; Duan, Z.; You, S.; Lei, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 2443. (f) Fang, X.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 14089. (g) Jiménez-Rodriguez, C.; Núñez-Magro, A. A.; Seidensticker, T.; Eastham, G. R.; Furst, M. R. L.; Cole-Hamilton, D. J. *Catal. Sci. Technol.* **2014**, *4*, 2332.

(7) (a) Wenkert, E.; Buckwalter, B. L.; Sathe, S. S. *Synth. Commun.* **1973**, *3*, 261. (b) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (c) Armesto, D.; Ortiz, M. J.; Agarrabeitia, A. R. *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W., Lenci, F., Eds.; CRC Press: Boca Raton, FL, 2004; p 77. (d) Bajracharya, G. B.; Koranne, P. S.; Nadaf, R. N.; Gabr, R. K. M.; Takenaka, K.; Takizawa, S.; Sasai, H. *Chem. Commun.* **2010**, *46*, 9064. (e) Martin-Fontecha, M.; Agarrabeitia, A. R.; Ortiz, M. J.; Armesto, D. *Org. Lett.* **2010**, *12*, 4082.

(8) (a) Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* **1984**, *49*, 1341. (b) Mitsudo, T.-a.; Suzuki, N.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1994**, *59*, 7759.

(9) (a) Koyasu, Y.; Matsuzaka, H.; Hiroe, Y.; Uchida, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1987**, 575. (b) Murahashi, S.; Imada, Y.; Taniguchi, Y.; Higashiura, S. *Tetrahedron Lett.* **1988**, *29*, 4945. (c) Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *J. Org. Chem.* **1988**, *53*, 3832. (d) Iwasaki, M.; Kobayashi, Y.; Li, J. P.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *J. Org. Chem.* **1991**, *56*, 1922. (e) Murahashi, S.; Imada, Y.; Taniguchi, Y.; Higashiura, S. *J. Org. Chem.* **1993**, *58*, 1538.

(10) (a) Dent, W. T.; Long, R.; Whitfield, G. H. *J. Chem. Soc.* **1964**, 1588. (b) Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4350. (c) Okano, T.; Okabe, N.; Kiji, J. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2589. (d) Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433. (e) Kiji, J.; Okano, T.; Higashimae, Y.; Fukui, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1029. (f) Tommasi, S.; Perrone, S.; Rosato, F.; Salomone, A.; Troisi, L. *Synthesis* **2012**, 423.

(11) Murahashi, S.-I.; Imada, Y.; Nishimura, K. *Tetrahedron* **1994**, *50*, 453.

(12) (a) Neibecker, D.; Poirier, J.; Tkatchenko, I. *J. Org. Chem.* **1989**, *54*, 2459. (b) Bonnet, M. C.; Coombes, J.; Manzano, B.; Neibecker, D.; Tkatchenko, I. *J. Mol. Catal.* **1989**, *52*, 263.

(13) Takeuchi, R.; Akiyama, Y. *J. Organomet. Chem.* **2002**, *651*, 137.

(14) (a) Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4350. (b) Knifton, J. F. *J. Organomet. Chem.* **1980**, *188*, 223. (c) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1065. (d) Naigre, R.; Alper, H. *J. Mol. Catal. A: Chem.* **1996**, *111*, 11. (e) Satoh, T.; Ikeda, M.; Kushino, Y.; Miura, M.; Nomura, M. *J. Org. Chem.* **1997**, *62*, 2662. (f) Liu, Q.; Wu, L.; Jiao, H.; Fang, X.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 8064.

(15) (a) Murahashi, S.-I.; Imada, Y.; Nishimura, K. *J. Chem. Soc., Chem. Commun.* **1988**, 1578. (b) Miyazawa, M.; Wang, S.-Z.; Takeda, H.; Yamamoto, K. *Synlett* **1992**, 323. (c) Imada, Y.; Shibata, O.; Murahashi, S.-I. *J. Organomet. Chem.* **1993**, *451*, 183.

(16) For ruthenium or nickel-catalyzed reductive couplings of diene with paraformaldehyde, see: (a) Smejkal, T.; Han, H.; Breit, B.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 10366. (b) Köpfer, A.; Sam, B.; Breit, B.; Krische, M. J. *Chem. Sci.* **2013**, *4*, 1876.

(17) (a) Sielcken, O.; Agterberg, F.; Haasen, N. Patent EP 728733, 1996; *Chem. Abstr. 124*, 342675 P. (b) Bertleff, W.; Maerkl, R.; Kuehn, G.; Panitz, P.; Kummer, R. Patent EP 0267497, 1988; *Chem. Abstr. 109*, 057058 Y. (c) Maerkl, R.; Bertleff, W.; Wilfinger, H. J.; Schuch, G.; Harder, W.; Kuehn, G.; Panitz, P. US Patent 4,894,474, 1990; *Chem. Abstr. 110*, 192257 Y. (d) Gresham, W. F.; Brooks, R. E. US Patent 2,542,767, 1951. (e) Tsuji, J.; Kiji, J.; Hosaka, S. *Tetrahedron Lett.* **1964**, *12*, 605. (f) Hosaka, S.; Tsuji, J. *Tetrahedron* **1971**, *27*, 3821. (g) Tsuji, J.; Mori, Y.; Hara, M. *Tetrahedron* **1972**, *28*, 3721. (h) Matsuda, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 524. (i) Knifton, J. F. *J. Catal.* **1979**, 27. (j) Drent, E.; Jager, W. US Patent 5,350,876, 1994. (k) Drent, E. Patent EP 235864, 1986; *Chem. Abstr. 125*, 238907 D. (l) Agterberg, F.; Sielcken, O.; DAmore, M.; Bruner, H. Patent EP 728732, 1996; *Chem. Abstr. 125*, 221199 Y. (m) Jenck, J. US Patent 4,454,333, 1984; *Chem. Abstr. 99*, 070228Y. (n) Drent, E. Patent EP 577205, 1992; *Chem. Abstr. 121*, 05700 W. (o) Vasapollo, G.; Somasunderam, A.; El Ali, B.; Alper, H. *Tetrahedron Lett.* **1994**, *35*, 6203. (p) Garlaschelli, L.; Marchionna, M.; Carmela, M.; Longoni, G. *J. Organomet. Chem.* **1989**, *378*, 457. (q) Beller, M.; Krotz, A.; Baumann, W. *Adv. Synth. Catal.* **2002**, *344*, 517. (r) Fang, X.; Li, H.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 9030.

(18) For hydroamination of 1,3-dienes, see: (a) Löber, O.; Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4366. (b) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828. Our works, see: (c) Banerjee, D.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 1630. (d) Banerjee, D.; Junge, K.; Beller, M. *Org. Chem. Front* **2014**, *1*, 368.

(19) Zapf, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Fuhrmann, C.; Shaikh, N.; Dingerdissen, U.; Beller, M. *Chem. Commun.* **2004**, 38.

(20) (a) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1976**, 365. (b) Tooze, R. P.; Eastham, G. R.; Whiston, K.; Wang, X. L. Patent WO96/19434, 1996. (c) Jiménez-Rodriguez, C.; Foster, D. F.; Eastham, G. R.; Cole-Hamilton, D. J. *Chem. Commun.* **2004**, 1720. (d) Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Inorg. Chem. Commun.* **2005**, *8*, 878. (e) Jiménez-Rodriguez, C.; Eastham, G. R.; Cole-Hamilton, D. J. *Dalton Trans.* **2005**, 1826. (f) Fleischer, I.; Jennerjahn, R.; Cozzula, D.; Jackstell, R.; Franke, R.; Beller, M. *ChemSusChem* **2013**, *6*, 417.

(21) Liu, B.; Zhang, Y.; Huang, G.; Zhang, X.; Niu, P.; Wu, J.; Yu, W.; Chang, J. *Org. Biomol. Chem.* **2014**, *12*, 3902.