JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Nickel-Catalyzed Alkene Carboacylation via Activation of Amide C-N Bonds

James A. Walker, Kevin L. Vickerman, Jenna N. Humke, and Levi M. Stanley

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b06191 • Publication Date (Web): 14 Jul 2017

ACS Publications

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Nickel-Catalyzed Alkene Carboacylation via Activation of Amide C-N Bonds

James A. Walker Jr.,† Kevin L. Vickerman,† Jenna N. Humke, and Levi M. Stanley*

Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

Supporting Information Placeholder

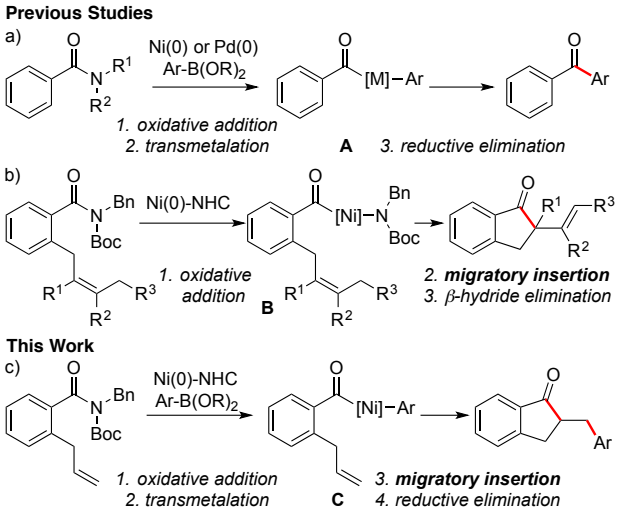
ABSTRACT: We report nickel-catalyzed formal carboacylation of *ortho*-allylbenzamides with arylboronic acid pinacol esters. These carboacylation reactions are triggered by the oxidative addition of an activated amide C-N bond to a nickel(0) catalyst and proceed via alkene insertion into a nickel(II)-acyl bond. The *exo*-selective carboacylation reactions generate 2-benzyl-2,3-dihydro-1*H*-inden-1-ones in moderate-to-high yields (46-99%) from a variety of arylboronic acid pinacol esters and substituted *ortho*-allylbenzamides. These results demonstrate that amides are practical substrates for alkene carboacylation via activation of an amide C-N bond, and this approach bypasses challenges associated with alkene carboacylation triggered by C-C bond activation.

Carboacylation of alkenes in the presence of a transition-metal catalyst is an emerging reaction that enables the difunctionalization of an alkene with formation of two C-C σ-bonds.[1-3] Among the most studied and developed approaches to alkene carboacylation are reactions initiated by activation of a C-C σ-bond of a ketone. While much progress has been made to understand the mechanistic pathways and utility of these carboacylation reactions, the development of alkene carboacylation reactions is limited by the requirement for substrates containing either a quinoline directing group[1] or a strained cyclic ketone.[2] The ability to perform alkene carboacylation reactions without a requirement for strained ketone substrates or substrates containing directing groups has the potential to expand the utility of these reactions with readily accessible substrates.[3,4]

Recently, studies by a number of groups have demonstrated Suzuki-Miyaura coupling of benzamides with arylboron compounds to generate a variety of aromatic ketones.[5] The Suzuki-Miyaura-type coupling reactions involve C-N activation of an activated benzamide via oxidative addition and transmetalation with an arylboron compound to generate acyl-metal-aryl intermediate **A** (Scheme 1a). Subsequent reductive elimination forms a diaryl ketone. The ability to intercept acyl-metal intermediates with an alkene offers the potential to develop a new class of alkene functionalization reactions. During the course of our studies, Garg and co-workers reported Mizoroki-Heck cyclizations of *ortho*-allylbenzamides that involve insertion of an alkene into an acyl-nickel(II)-amido intermediate **B** (Scheme 1b).[6] Subsequent β-hydride elimination forms 2-vinylindanones containing a quaternary carbon center.

The potential to develop a new class of alkene carboacylation reactions via activation of amide C-N bonds[5,7] led us to investigate nickel-catalyzed carboacylations of *ortho*-allylbenzamides. We envisioned a process involving activation of the C-N bond of a benzamide via oxidative addition and transmetalation with an arylboron compound to generate acyl-nickel(II)-aryl intermediate **C** (Scheme 1c). Migratory insertion of the tethered alkene and reductive elimination would generate 2-benzylindanones, the product of a formal alkene carboacylation reaction. In contrast to the recently reported Mizoroki-Heck cyclization reactions which involve the formation of a single C-C σ-bond, the proposed formal carboacylation reactions involve difunctionalization of an alkene with the formation of two C-C σ-bonds. The development of this approach to alkene carboacylation offers the potential to expand these reactions beyond strained cyclic ketones and ketones containing a quinoline directing group. We now report the first nickel-catalyzed carboacylations triggered by C-N bond activation of *ortho*-allylbenzamides to form a variety of 2-benzyl-2,3-dihydro-1*H*-inden-1-ones in up to 99% yield.

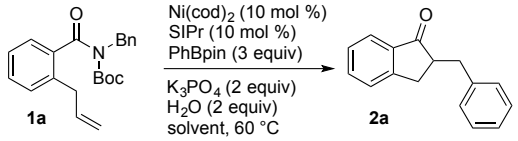
Scheme 1. Synthesis of Ketones via Transition Metal-Catalyzed Activation of Amide C-N Bonds



To identify reaction conditions for the nickel-catalyzed carboacylation of *ortho*-allylbenazamides, we evaluated the model reaction of *tert*-butyl(2-allylbenzoyl)(benzyl)carbamate (**1a**) with phenylboronic acid pinacol ester (PhBpin) in the presence of a catalyst generated from $Ni(cod)_2$ and 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidine (SIPr) (Table 1). The nickel carbene complex catalyzed the model reaction to form indanone **2a** in 20% yield when the reaction was conducted in toluene at 90 °C with 1.2 equiv of PhBpin (entry 1). The yield of indanone **2a** increased to 30% when the reaction was run with 3.0 equiv of PhBpin (entry 3). However, the major product of these reactions is generated

from isomerization of the *ortho*-allylbenzamide starting material. To further improve the yield of the model reaction and minimize alkene isomerization, we investigated the impact of the identity of the solvent (entries 3-7). When the model reaction was carried out in THF, indanone **2a** was generated in 75% yield with the formation of 24% yield of the isomerized starting material (entry 7).

Table 1. Identification of Reaction Conditions for Ni-Catalyzed Carboacylation of 1a with PhBpin[a]



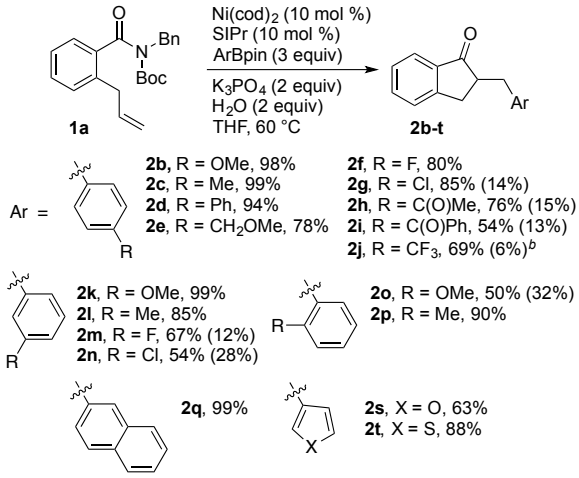
entry	temp. (°C)	solvent	conv. (%)[b]	yield (%)[b,c]
1[d]	90	toluene	67	20 (35)
2[e]	90	toluene	49	21 (27)
3	90	toluene	100	30 (43)
4	90	benzene	70	27 (45)
5	90	dioxane	84	26 (46)
6[f]	90	DME	82	46 (9)
7[f]	90	THF	99	75 (24)
8[f]	80	THF	100	78 (9)
9[f]	70	THF	100	83 (4)
10[f]	60	THF	100	97 (0)
11	40	THF	48	39 (0)
12[e]	60	THF	65	55 (0)
13[d]	60	THF	39	39 (0)
14[f,g]	60	THF	100	95 (0)
15[h]	60	THF	40	38 (0)
16[i]	60	THF	100	88 (11)

[a]Reaction conditions: **1a** (0.100 mmol), $Ni(cod)_2$ (0.010 mmol), SIPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolidin-2-ylidene (0.010 mmol), K_3PO_4 (0.200 mmol), H_2O (0.200 mmol), solvent (1.0 M), 12 h. [b]Determined by ^1H NMR spectroscopy of the crude reaction mixture using dibromomethane as an internal standard. [c]Yields of alkene isomerization product *tert*-butyl benzyl(2-(prop-1-en-1-yl)benzoyl)carbamate determined by ^1H NMR spectroscopy are shown in parentheses. [d]PhBpin (1.2 equiv). [e]PhBpin (2 equiv). [f]Isolated yields of **3a**. [g]5 mol% $Ni(cod)_2$ and 5 mol% SIPr. [h]2.5 mol% $Ni(cod)_2$ and 2.5 mol% SIPr. [i]Reaction run with SIPr•HCl (0.010 mmol) in place of SIPr.

To further increase the ratio of indanone **2a** relative to the isomerized starting material, we investigated the impact of reaction temperature (entries 7-11). Lowering the reaction temperature to 60 °C led to the formation of indanone **2a** in 97% yield without observable isomerization of the *ortho*-allylbenzamide (entry 10). Consistent with our observations of reactions run in toluene (entries 1-3), the yield of indanone **2a** decreases upon lowering the number of equivalents of PhBpin when the reaction is run in THF at 60 °C (compare entry 10 with entries 12 and 13). The model reaction catalyzed by 5 mol % of the nickel catalyst formed **2a** in 95% yield (entry 14). However, decreasing the catalyst loading to 2.5 mol % led to incomplete conversion and formation of **2a** in only 38% yield (entry 15). The model reaction occurs to form **2a** in 88% yield with 11% isomerization of **1a** when the nickel carbene catalyst is generated *in situ* from $Ni(cod)_2$ and SIPr•HCl (entry 16).

With a practical catalyst system identified for the model reaction of **1a** with PhBpin, we next evaluated carboacylation reactions of **1a** with a broad range of arylboronic acid pinacol esters (ArBpin) (Scheme 2). The carboacylation of **1a** with a range of *para*-substituted, electron-rich ArBpin reagents generated ketones **2b**-**e** in good-to-excellent yields (78-99%). The reaction of **1a** with *para*-substituted electron-deficient ArBpin reagents formed indanones **2f**-**2j** in moderate-to-high yields (54-85%). The carboacylation of **1a** with ArBpin compounds containing electron-donating groups at the *meta*-position formed ketones **2k**-**2l** in 85-99% yield, while *meta*-halogenated ArBpin compunds reacted with **1a** to form **2m**-**2n** in 54-67% yield. Reactions of ArBpin reagents containing electron-donating groups at the *ortho*-position with **1a** were also possible and generated the carboacylation products **2o** and **2p** in 50% and 90% yield. However, reactions of **1a** with *ortho*-halogenated ArBpin reagents did not occur under our reaction conditions. The scope of alkene carboacylation is not limited to substituted ArBpin compounds but also includes boronic acid pinacol esters of polycyclic arenes and heteroarenes. The carboacylation reactions of **1a** with heteroarylboronic acid pinacol esters formed ketone products **2r**-**2s** in 63-88% yields. Reactions of **1a** with arylboronic acids and alkylboronic acid pinacol esters did not occur under our standard reaction conditions.

Scheme 2. Scope of Arylboronic Acid Pinacol Esters[a]

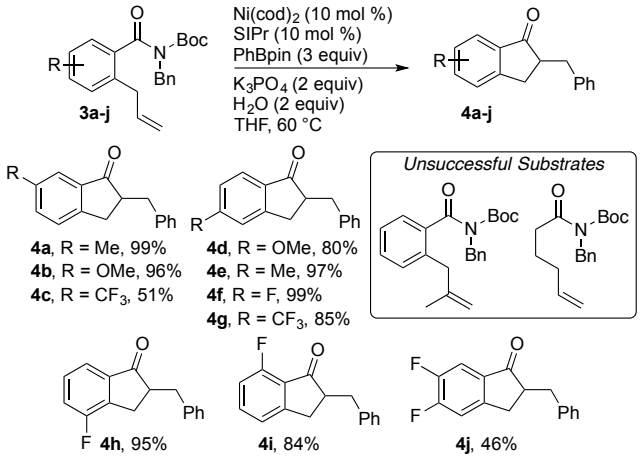


[a]Reaction conditions: **1a** (0.100 mmol), $Ni(cod)_2$ (0.010 mmol), SIPr (0.010 mmol), K_3PO_4 (0.200 mmol), H_2O (0.200 mmol), ArBPin (0.300 mmol), THF (0.100 mL), 16 h. Yields of **2b**-**t** are isolated yields after column chromatography. Yields of alkene isomerization product *tert*-butyl benzyl(2-(prop-1-en-1-yl)benzoyl)carbamate determined by ^1H NMR spectroscopy are shown in parentheses. [b]20 mol % $Ni(cod)_2$, 20 mol % SIPr, and 0.20 mL THF.

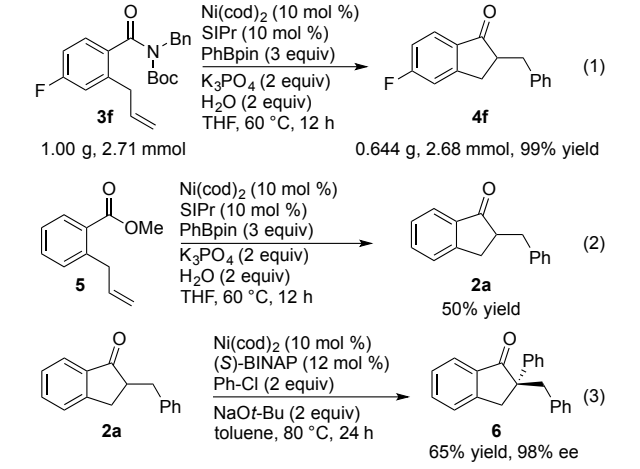
With the scope of arylboronic acid pinacol esters established, we sought to evaluate nickel-catalyzed carboacylations of a variety of substituted *ortho*-allylbenzamides **3a**-**j** (Scheme 3). Reactions of PhBpin with **3a-3c** containing electron-donating and electron-withdrawing groups at the 5-position occur to form indanones **4a**-**4c** in moderate-to-excellent yields (51-99%). Carboacylations of 4-substituted *ortho*-allylbenzamides containing either electron-donating or electron-withdrawing groups occur to generate ketones **4d**-

4g in 80-99% yield. Carboacylations of 3- and 6-fluorinated *ortho*-allylbenzamides generated indanones **4h-4i** in excellent yields (84-95%), while the reaction of a 4,5-difluorinated *ortho*-allylbenzamide formed indanone **4j** in 46% yield. *ortho*-Allylbenzamides containing substituted allyl units were unreactive under our standard reaction conditions, and reactions conducted at elevated temperatures led exclusively to isomerization of the alkene. The carboacylation of the acyclic 5-hexenamide derivative, *tert*-butyl benzyl(hex-5-enoyl)carbamate, with PhBpin did not form the corresponding cyclic ketone.

Scheme 3. Carboacylation of Benzamides 3a-j[a]



[a]Reaction conditions: **3a-j** (0.100 mmol), $Ni(cod)_2$ (0.010 mmol), SIPr (0.010 mmol), K_3PO_4 (0.200 mmol), H_2O (0.200 mmol), PhBpin (0.300 mmol), THF (0.100 mL), 12 h. Yields of **4a-j** are isolated yields after column chromatography.

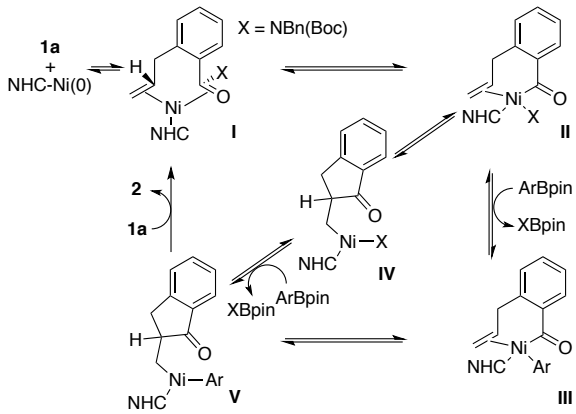


To highlight the utility of our alkene carboacylation reaction, we conducted a series of experiments to show that the carboacylation reaction 1) can be conducted on the gram scale, 2) encompasses an *ortho*-allylbenzoate ester, and 3) can be sequenced with nickel-catalyzed, enantioselective α-arylation to form an indanone derivative containing a quaternary stereogenic center. The reaction of 4-fluorinated *ortho*-allylbenzamide **3f** with PhBpin can be conducted on a gram scale to form the product **4f** in nearly quantitative yield (eq 1). In addition, the carboacylation of methyl 2-allylbenzoate **5** with PhBpin forms indanone **2a** in 50% yield (eq 2).[8] The modest yield of **2a** can be attributed to alkene isomerization of **5** to form methyl 2-(prop-1-en-1-yl)benzoate in 25% yield.

Highly enantioenriched indanone derivatives containing a quaternary stereogenic center are readily prepared by nickel-catalyzed α-arylation of the racemic 2-benzylindanones generated from our carboacylation reactions.[9] For example, the α-arylation of **2a** occurs in the presence of a catalyst generated from $Ni(cod)_2$ and (*S*)-BINAP to form indanone **6** in 65% yield and 98% ee (eq 3).

Two potential mechanistic pathways for the carboacylation of **1a** with ArBpin are presented in Scheme 4. After coordination of the NHC-Ni(0) catalyst to **1a** to form complex **I**, oxidative addition of the amide C-N bond to the Ni(0) center is likely to form the acyl-nickel(II)-amido complex **II**. At this stage, the mechanism of the formal carboacylation may diverge based on the ordering of the subsequent transmetalation and migratory insertion events. If transmetalation of ArBpin with complex **II** occurs first, acyl-nickel(II)-aryl complex **III** would be generated. Subsequent migratory insertion of the tethered alkene into the Ni-C(acyl) bond would form alkyl-nickel(II)-aryl complex **V**. Reductive elimination of the indanone product **2** from **V** and coordination of another molecule of **1a** would close the catalytic cycle. Alternatively, if migratory insertion precedes transmetallation, alkyl-nickel(II)-amido complex **IV** would be formed by insertion of the tethered alkene into the Ni-C(acyl) bond of complex **II**.[6] Subsequent transmetalation of ArBpin with complex **IV** would form complex **V** and the indanone **2** upon reductive elimination.

Scheme 4. Potential Mechanistic Pathways for Ni-Catalyzed Carboacylation via Amide C-N Activation.

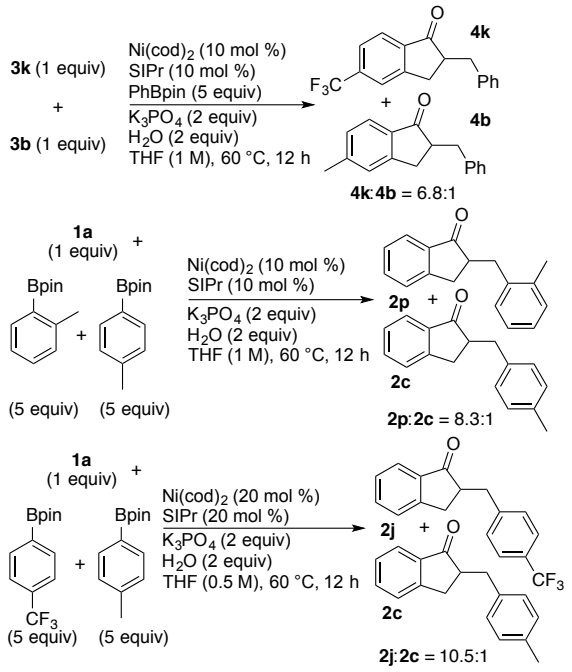


Our working hypothesis is that transmetalation of ArBpin with complex **II** precedes migratory insertion of the tethered alkene based on two observations. First, the identity of the ArBpin significantly impacts the amount of alkene isomerization observed under our reaction conditions (see Scheme 2). Second, alkene isomerization is not observed in the absence of ArBpin. Taken together, these results are consistent with transmetalation of ArBpin with complex **II** occurring first to form complex **III** followed by migratory insertion to generate complex **V**.

To gain additional insight into the mechanism of the formal carboacylation reaction, we conducted a series of competition experiments (Scheme 5). The competition experiment between 4-(trifluoromethyl)- and 4-methylbenzamides **3k** and **3b** formed ketones **4k** and **4b** in a 6.8:1 ratio favoring the trifluoromethyl-substituted ketone **4k**. Although this result is consistent with the relative reactivity of electron-deficient and electron-rich benzamides in the context of Suzuki-

Miyaura and Negishi coupling,[5b,10] it contrasts the more facile nature of oxidative addition into electron-rich benzamide **3b** versus electron-deficient benzamide **3k** due to the increased amidic resonance that would be expected for **3k** versus **3b**.[11] In addition, this result suggests that the ratio of products observed is not determined by the relative rates of oxidative addition of **3k** and **3b**. Competition experiments between the pinacol ester of 4-tolylboronic acid with the pinacol esters of 2-tolylboronic acid or 4-(trifluoromethyl)pheylboronic acid formed ketones **2p** and **2c** in an 8.3:1 ratio and ketones **2j** and **2c** in a 10.5:1 ratio. The observation that ketones derived from reactions with sterically hindered and electron-deficient arylboron nucleophiles are favored suggests that transmetalation is fast relative to reductive elimination and the ratio of products is determined by the relative rates of either reductive elimination or migratory insertion into the Ni-C(acyl) bond of complex **III**. Given that a nearly equimolar ratio of **4k** and **4b** would be expected from the competition between **3k** and **3b** if reductive elimination was turnover-limiting, we propose that migratory insertion of the alkene into the Ni-C(acyl) bond is the elementary step critical to determining product ratios.

Scheme 5. Competition Experiments between Substituted Benzamides or Arylboronic Acid Pinacol Esters



In summary, we have developed the first nickel-catalyzed alkene carboacylation reactions initiated by activation of amide C-N bonds. These processes enable coupling of a variety of *ortho*-allylbenzamides and arylboronic acid pinacol esters to form two new C-C bonds and the indanone products in up to 99% yield. Moreover, the development of this approach to alkene carboacylation bypasses challenges associated with related alkene carboacylation reactions that rely on C-C bond activation and further demonstrates the utility of amides as powerful building blocks in organic synthesis. Studies are ongoing in our laboratory to further leverage the synthetic potential of this transformation and to gain additional mechanistic understanding of the nickel-catalyzed alkene carboacylation reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization data, and copies of NMR spectra for new compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

* E-mail: lstanley@iastate.edu

Author Contributions

† J.A.W. Jr. and K.L.V. contributed equally to this work.

ACKNOWLEDGMENT

We thank the National Science Foundation (CHE-1352080) for supporting this work.

REFERENCES

(1) (a) Dreis, A. M.; Douglas, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 412. (b) Wentzel, M. T.; Reddy, V. J.; Hyster, T. K.; Douglas, C. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6121. (c) Rathbun, C. M.; Johnson, J. B. *J. Am. Chem. Soc.* **2011**, *133*, 2031. (d) Lutz, J. P.; Rathbun, C. M.; Stevenson, S. M.; Powell, B. M.; Boman, T. S.; Baxter, C. E.; Zona, J. M.; Johnson, J. B. *J. Am. Chem. Soc.* **2012**, *134*, 715. (e) Dreis, A. M.; Douglas, C. J. *Top. Curr. Chem.* **2014**, *346*, 85.

(2) (a) Liu, L.; Ishida, N.; Murakami, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2485. (b) Xu, T.; Dong, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 7567. (c) Xu, T.; Ko, H. M.; Savage, N. A.; Dong, G. *J. Am. Chem. Soc.* **2012**, *134*, 20005. (d) Souillart, L.; Parker, E.; Cramer, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 3001. (e) Xu, T.; Dong, G. *Angew. Chem., Int. Ed.* **2014**, *53*, 10733. (f) Lu, G.; Fang, C.; Xu, T.; Dong, G.; Liu, P. *J. Am. Chem. Soc.* **2015**, *137*, 8274. (g) Souillart, L.; Cramer, N. *Chimia* **2015**, *69*, 187.

(3) For recent examples of carbonylative approaches to formal alkene carboacylation, see: (a) Liu, C.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 10250. (b) Fusano, A.; Sumino, S.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2011**, *13*, 2114. (c) Seashore-Ludlow, B.; Danielsson, J.; Somfai, P. *Adv. Synth. Catal.* **2012**, *354*, 205. (d) McMahon, C. M.; Renn, M. S.; Alexanian, E. J. *Org. Lett.* **2016**, *18*, 4148.

(4) For other approaches to formal alkene carboacylation, see: (a) Oguma, K.; Miura, M.; Satoh, T.; Nomura, M. *J. Organomet. Chem.* **2002**, *648*, 297. (b) Yamane, M.; Kubota, Y.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 331. (c) Ouyang, X.-H.; Song, R.-J.; Li, J.-H. *Eur. J. Org. Chem.* **2014**, 3395. (d) Ouyang, X.-H.; Song, R.-J.; Li, Y.; Liu, B.; Li, J.-H. *J. Org. Chem.* **2014**, *79*, 4582. (e) Park, J.-W.; Kou, K. G. M.; Kim, D. K.; Dong, V. M. *Chem. Sci.* **2015**, *6*, 4479.

(5) For recent examples, see: (a) Li, X.; Zou, G. *Chem. Commun. (Cambridge, U. K.)* **2015**, *51*, 5089. (b) Meng, G. R.; Szostak, M. *Org. Lett.* **2015**, *17*, 4364. (c) Weires, N. A.; Baker, E. L.; Garg, N. K. *Nat. Chem.* **2016**, *8*, 75. (d) Liu, C. W.; Meng, G. R.; Liu, Y. M.; Liu, R. Z.; Lalancette, R.; Szostak, R.; Szostak, M. *Org. Lett.* **2016**, *18*, 4194. (e) Meng, G. R.; Shi, S. C.; Szostak, M. *ACS Catal.* **2016**, *6*, 7335. (f) Meng, G. R.; Szostak, M. *Org. Biomol. Chem.* **2016**, *14*, 5690. (g) Lei, P.; Meng, G. G.; Szostak, M. *ACS Catal.* **2017**, *7*, 1960. (h) Liu, C. W.; Liu, Y. M.; Liu, R. Z.; Lalancette, R.; Szostak, R.; Szostak, M. *Org. Lett.* **2017**, *19*, 1434. For decarbonylative coupling of benzamides with arylboronic acids, see: (i) Shi, S.; Meng. G.; Szostak, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 6959. For recent reviews, see: (j) Meng, G. R.; Shi, S. C.; Szostak, M. *Synlett* **2016**, *27*, 2530. (k) Dander, J. E.; Garg, N. K. *ACS Catal.* **2017**, *7*, 1413. (l) Liu, C.; Szostak, M. *Chem. Eur. J.* **2017**, *23*, 7157.

(6) Medina, J. M.; Moreno, J.; Racine, S.; Du, S.; Garg, N. K. *Angew. Chem., Int. Ed.* **2017**, *56*, 6567.

(7) For additional examples of amide C-N bond activation, see: (a) Hie, L.; Nathel, N. F. F.; Shah, T. K.; Baker, E. L.; Hong, X.; Yang, Y. F.; Liu, P.; Houk, K. N.; Garg, N. K. *Nature* **2015**, *524*, 79. (b) Simmons, B. J.; Weires, N. A.; Dander, J. E.; Garg, N. K. *ACS Catal.* **2016**, *6*, 3176. (c) Shi, S. C.; Szostak, M. *Org. Lett.* **2016**, *18*, 5872. (d) Szostak, R.; Shi, S. C.; Meng, G. R.; Lalancette, R.; Szostak, M. *J. Org. Chem.* **2016**, *81*, 8091. (e) Meng, G.; Lei, P.; Szostak, M. *Org. Lett.* **2017**, *19*, 2158. (f) Weires, N. A.; Caspi, D. D.; Garg, N. K. *ACS Catal.* **2017**, *7*, 4381.

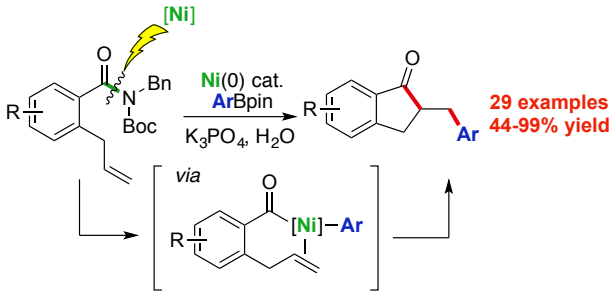
(8) For recent examples of transition metal-catalyzed activation of ester C-O bonds, see: (a) Amaike, K.; Muto, K.; Yamaguchi, Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 13573. (b) Xu, H.; Muto, K.; Yamaguchi, J.; Zhao, C.; Itami, K.; Musaev, D. G. *J. Am. Chem. Soc.* **2014**, *136*, 14834. (c) Muto, K.; Yamaguchi, J.; Musaev, D. G.; Itami, K. *Nat. Commun.* **2015**, *6*, 7508. (d) Hie, L.; Nathel, N. F. F.; Hong, X.; Yang Y.-F.; Houk, K. N.; Garg, N. K. *Angew. Chem., Int. Ed.* **2016**, *55*, 2810. (e) Wu, H.; Xu, B.; Li, Y.; Hong, F.; Zhu, D.; Jian, J.; Pu, X.; Zeng, Z. *J. Org. Chem.* **2016**, *81*, 2987. (f) Halima, T. B.; Zang, W.; Yalaoui, I.; Hong, X.; Yang, Y.; Houk, K. N.; Newman, S. G. *J. Am. Chem. Soc.* **2017**, 139, 1311. (g) Hoang, G. T.; Walsh, D. J.; McGarry, K. A.; Anderson, C. B.; Douglas, C. J. *J. Org. Chem.* **2017**, *82*, 2972.

(9) Ge, S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 16330.

(10) Shi, S.; Szostak, M. *Synthesis*, ASAP. DOI: 10.1055/s-0036-1588845.

(11) Szostak, R.; Meng, G.; Szostak, M. *J. Org. Chem.* **2017**, *82*, 6373.

TOC Graphic



Alkene Carboacylation Triggered by Amide C-N Bond Activation