Advanced Synthesis & Catalysis

Accepted Article

Title: Rhodium-Catalyzed Cascade Annulation of Benzimidates and Nitroalkenes for the Synthesis of Difunctionalized Indenes

Authors: Ningning Lv, Zhengkai Chen, Yue Liu, Zhanxiang Liu, and Yuhong Zhang

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201900427

Link to VoR: http://dx.doi.org/10.1002/adsc.201900427

10.1002/adsc.201900427

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Rhodium-Catalyzed Cascade Annulation of Benzimidates and Nitroalkenes for the Synthesis of Difunctionalized Indenes

Ningning Lv,[a] Zhengkai Chen,[b] Yue Liu,[a] Zhanxiang Liu,[a] Yuhong Zhang,*[a,c]

[a] Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, Hangzhou 310027, People's Republic of China
Fax: (+ 86)-571-8795-3244; e-mail: yhzhang@zju.edu.cn

[b] Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China

[c] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

Received: ((will be filled in by the editorial staff))

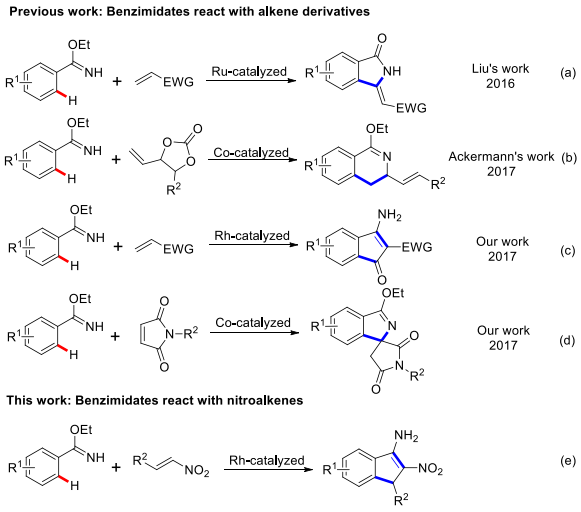
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract: A facile and expeditious protocol for the synthesis of difunctionalized indenes from readily available benzimidates and nitroalkenes through rhodium-catalyzed C-H activation and cyclization is reported here. The transformation exhibits powerful reactivity, tolerates a large number of functional groups, and proceeds in moderate to high yields under an ambient atmosphere, providing a straightforward method to access structurally diverse and valuable difunctionalized indene derivatives.

Keywords: indene synthesis; cascade annulation; rhodium-catalyzed; C-H activation; arenes

In the past few decades, transition-metal-catalyzed directed C-H functionalization reactions have been applied as an attractive and powerful strategy for the synthesis of complex and useful molecules without preactivation of starting materials.[1] In most cases, a directing group is usually necessary to ensure the reactivity and selectivity of the transformations.[2] Therefore, numerous directing groups have been successfully exploited to realize diverse C-H activation reactions.[3] Among these transformations, further removal of the directing groups is inevitable after completion of the reaction. To streamline the reaction process, the employment of traceless[4] or transient directing groups[5] has drawn great attention and been applied as a versatile tool to assemble various useful products.

Benzimidate, as a powerful traceless directing group,[6] has been frequently used for the synthesis of structurally diverse heterocycles through reacting with diverse coupling partners,[6] especially with different kinds of alkenes.[7] In 2016, Liu and co-workers demonstrated that ruthenium-catalyzed annulation of benzimidates and acrylates can construct the lactam derivatives (Scheme 1a).[7a] Later, Ackermann and co-workers reported the cascade C−H/N−H allylation of aryl imidates in the presence of low-cost cobalt(III) catalyst (Scheme 1b).[7b] Recently, our group disclosed an efficient approach for the assembly of difunctionalized indenones via Rh-catalyzed multistep cascade reactions of benzimidates and alkenes, which involves a completely different reaction pathway compared with Liu's work (Scheme 1c).[7c] Shortly after, we realized the Co-catalyzed spirocycle synthesis between benzimidates and maleimides by liberation of a molecule of hydrogen, avoiding the using of external stoichiometric oxidants (Scheme 1d).[7d] It is found that benzimidate could be applied as a powerful directing group, which can reacts with different alkene substrates through different reaction processes to obtain a series of useful heterocycles. Inspired by these instructive works, we envisaged that we could use nitroalkenes as the coupling partners to enable novel heterocycle synthesis (Scheme 1e).



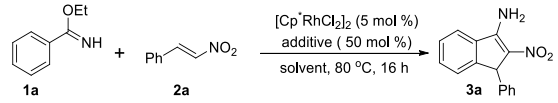
Scheme 1. Benzimidates reacting with different alkene substrates.

Nitroalkenes are valuable and commonly used synthons, which can react with a broad range of different nucleophiles and employed as dienophiles in

10.1002/adsc.201900427

Diels−Alder reactions.[8] However, applications of substituted nitroalkenes in transition-metal-catalyzed C-H activation reactions have been rarely reported.[9,10] Herein, we communicate the first example of Rh(III)-catalyzed C-H activation and cascade annulation of benzimidates and nitroalkenes for the formation of difunctionalized indenes, which constitute a kind of important synthetic intermediates and biologically active molecules.[11]

Table 1. Optimization of Reaction Conditions.[a]

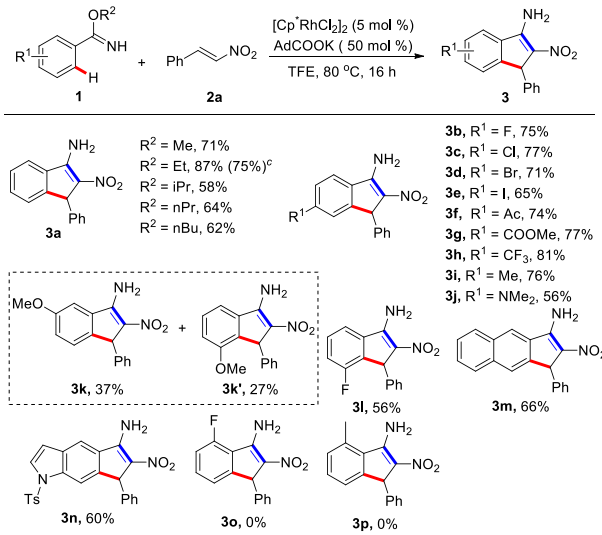


Entry	Additive	Solvent	Yield (%)[b]
1	AgOAc	CF_3CH_2OH	41
2	$Cu(OAc)_2$	CF_3CH_2OH	nr
3	NaOAc	CF_3CH_2OH	77
4	KOAc	CF_3CH_2OH	82
5	CsOAc	CF_3CH_2OH	75
6	CsOPiv	CF_3CH_2OH	72
7	PhCOOK	CF_3CH_2OH	80
8	AdCOOK	CF_3CH_2OH	87
9	HOAc	CF_3CH_2OH	49
10	-	CF_3CH_2OH	68
11	AdCOOK	THF	nr
12	AdCOOK	DCE	nr
13	AdCOOK	MeOH	nr
14[c]	AdCOOK	CF_3CH_2OH	nr
15[d]	AdCOOK	CF_3CH_2OH	nr
16[e]	AdCOOK	CF_3CH_2OH	nr
17[f]	AdCOOK	CF_3CH_2OH	nr

[a] Reactions were carried out by using **1a** (0.2 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), additive (50 mol %), solvent (2.0 mL), 80 °C, air, 16 h; AdCOOK = potassium adamantanecarboxylate.
[b] Isolated yield; nr = no reaction.
[c] $Pd(OAc)_2$ was used.
[d] $[Ru(p\text{-cymene})Cl_2]_2$ was used.
[e] $Cp^*Co(CO)I_2$ was used.
[f] Without $[Cp^*RhCl_2]_2$.

We initiated our investigation by choosing benzimidate **1a** and nitroalkene **2a** as model substrates to optimize the reaction conditions. To our delight, the reaction proceeded smoothly upon the commonly used catalytic combination of $[Cp^*RhCl_2]_2$/AgOAc in TFE and the desired 2-nitro-3-aminoindene **3a** was obtained in 41% yield (Table 1, entry 1). Then, different additives, including $Cu(OAc)_2$, NaOAc, KOAc, CsOAc, CsOPiv, PhCOOK, AdCOOK and HOAc, were tested to examine the reactivity of the transformation (Table 1, entries 2-9). The result revealed that the above additives could lead to the moderate to high efficiency except for $Cu(OAc)_2$, among which AdCOOK was proven to be the best candidate to give the desired product in 87% yield. Noteworthy was that the reaction could also occur in the absence of additive, affording the product **3a** in acceptable yield (Table 1, entry 10). The effect of solvents upon the reaction was examined and TFE (CF_3CH_2OH) was regarded as the optimal solvent to deliver the target product **3a** in the highest yield (Table 1, entries 11-13). Furthermore, lowering or raising the temperature results in a decrease in the reaction yield; the optimal temperature is 80 °C (see Supporting Information for details). Other common metal catalysts in the field of C-H functionalization, such as $Pd(OAc)_2$, $[Ru(p\text{-cymene})Cl_2]_2$, and $Cp^*Co(CO)I_2$, appear to be invalid in the reaction (Table 1, entries14-16). No reaction was observed in the absence of $[Cp^*RhCl_2]_2$ (Table 1, entry 17). Additionally, reducing the loading of the Rh catalyst resulted in lower reaction yield (see Supporting Information for details).

Table 2. Scope of Benzimidates.



[a] *Reaction conditions:***1** (0.2 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AdCOOK (50 mol %), TFE (2.0 ml), 80 °C, air, 16 h.
[b] Isolated yield.
[c] 2 mmol scale.

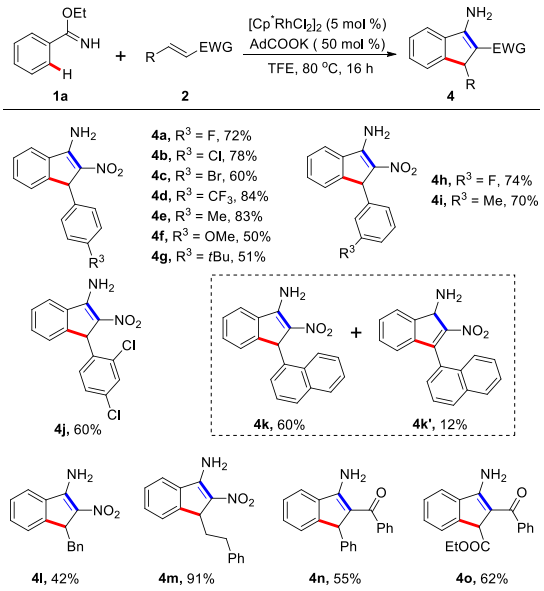
With the optimized reaction conditions in hand, we investigated the generality and limitation of the protocol with a variety of benzimidates as shown in Table 2. The effect of diverse alkoxy groups in the benzimidate was first tested, which demonstrated that different alkoxy groups could all smoothly afford the desired product **3a** in good yield, and the ethoxy group gave the superior result in 87% yield. The structure of **3a** was determined by single-crystal X-ray diffraction analysis.[12] The reaction could be performed on 2 mmol scale with no obvious efficiency decrease. The transformation showed broad substrate scope, as illustrated by the good tolerance of a wide variety of functional groups, furnishing the corresponding 2-nitro-3-aminoindene in good to excellent yields (**3b-3j**). The survival of halogen substituents provides the possibility for further derivatization through various coupling reactions. With regard to *meta*-OMe substituted

10.1002/adsc.201900427

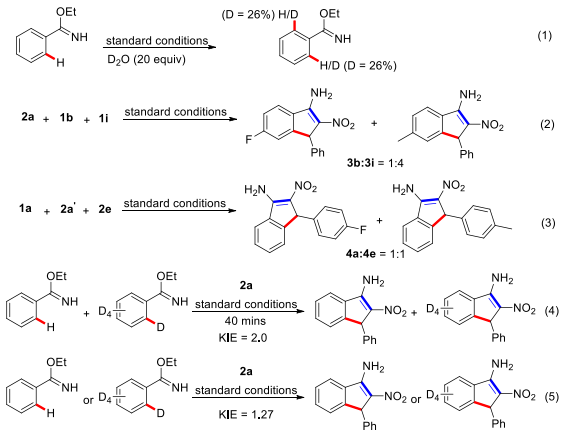
benzimidate, a mixture of regioselective products was isolated with the ratio of 1.37:1 (**3k, 3k'**). However, the single isomer was obtained in reasonable yield as for *meta*-F substituted benzimidate (**3l**). Significantly, the ethyl 2-naphthimidate could also serve as a viable substrate in the reaction to afford the corresponding product **3m** in 66% yield. Indole-substituted imidate was also compatible with the reaction system to give the fused indene product **3n** in a reasonable yield. The reaction is sensitive to steric hindrance of the benzimidate, as demonstrated by the fact that *ortho*-substituted substrates did not participate in the transformation (**3o**,**p**).

After examining the compatibility of the various benzimidates, the generality of the present transformation were further explored by the employment of various alkenes (Table 3). A variety of phenylsubstituted nitroalkenes proved to be effective coupling partners under current catalytic system. Different electron-withdrawing and electron-donating substituents on the *para* or *meta* position of the aromatic *β*-nitrostyrenes were well tolerated to lead to the corresponding products in moderate to excellent yields (**4a-4j**). *(E)*-1-(2-nitrovinyl) naphthalene can also couple with benzimidate under the standard conditions, giving the mixture of double bond migration products with the ratio of 5:1 (**4k+4k'**). With respect to aliphatic nitroalkenes, the reaction proceeded well to provide the coupling products in moderate to excellent yields (**4l-4m**). To further extend the reaction scope, chalcone and ethyl 3-benzoylacrylate were examined in the current reaction, and the corresponding products could be yielded with moderate efficiency (**4n-4o**), greatly underscoring the good compatibility and utility of the protocol.

Table 3. Scope of alkenes.

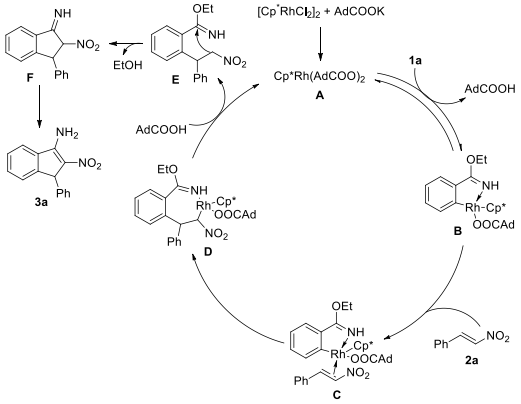


[a]*Reaction conditions:***1a** (0.2 mmol), **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), AdCOOK (50 mol %), TFE (2.0 ml), 80 °C, air, 16 h.



Scheme 2. Mechanistic investigations.

To gain further insight into the reaction mechanism, a set of control experiments were conducted as shown in Scheme 2. The benzimidate **1a** was subjected into the standard conditions in the presence of 20 equiv D_2O, and the deuterium in corporation at the dual *ortho*-carbon of substrate **1a** was obtained at a level of 26%, which suggest that the rhodium-catalyzed C-H cleavage is reversible (Scheme 2, eq 1). The intermolecular competition experiment of electronically differentiated **1b** and **1i** with **2a** was performed, and the result revealed that the more electron-donating benzimidate showed preferable reactivity (Scheme 2, eq 2), implying C-H activation probably occurs through an electrophilic aromatic substitution (S_EAr) process. It is observed that electronic effect of nitroalkenes have no apparent impact the reaction (Scheme 2, eq 3). The kinetic isotope effect (KIE) value of 2.0 was observed from the competitive reactions of **1a** and **1a-D$_5$** with **2a** at a low conversion (Scheme 2, eq 4). Moreover, a similar value of 1.27 was obtained from two parallel reactions (Scheme 2, eq 5). The above results indicated that the cleavage of the C-H bond might not be involved in the turnover-limiting step.



Scheme 3. The proposed mechanism

On the basis of the preliminary mechanistic studies and previous literature reports,[7c,9a,9b,10a,10b] a plausible

reaction mechanism is proposed as outlined in Scheme 3. Initially, the active catalyst Cp*Rh(AdCOO)$_2$ **A** is generated through ligand exchange between [Cp*RhCl$_2$]$_2$ and AdCOOK, which underwent coordination with **1a** and C-H metallation process to form rhodacycle complex **B** with the loss of AdCOOH. The H/D exchange experiment revealed that the activation process is reversible (Scheme 2, eq 1). Then, the coordination of complex **B** and nitroalkene gave a rhodium species **C**, which occurred the migratory insertion into the nitroalkene to afford intermediate **D**, followed by protonation process, leading to alkylated product **E**. Subsequently, the intramolecular ester condensation of **E** generated the intermediate **F**, which eventually isomerized to the thermodynamically more stable product **3a**.

In summary, we have developed a mild and powerful approach for the assembly of structurally diverse indenes scaffolds via rhodium(III)-catalyzed C-H activation and annulation reaction from readily available benzimidates and nitroalkenes. The transformation showed broad substrate scope and good functional group compatibility under mild conditions. The reaction could be easily scaled up to gram scale. This methodology may offer an efficient tool for the synthesis of biologically or pharmaceutically useful molecules. Further studies on the synthesis of other valuable cyclic compounds via C-H activation are underway.

Experimental Section

General procedure for the synthesis of difunctionalized indenes

To a test tube with a stir bar was added benzimidates (**1**, 0.20 mmol), nitroalkenes (**2**, 0.30 mmol), [Cp*RhCl$_2$]$_2$ (0.01 mmol, 6.0 mg), AdCOOK (0.1 mmol, 21.8 mg) in TFE (2.0 mL) was stirred at 80 °C for 16 h, cooled to room temperature, filtered through a pad of celite, and then washed with CH_2Cl_2 (10 mL × 3). Organic solvents were removed under reduced pressure and the crude reaction mixture was purified by column chromatography on silica gel column with EtOAc/petroleum ether (1:5~1:2, v/v) as an eluent to afford the desired product **3** or **4**.

Acknowledgements

Funding from Natural Science Foundation of China (Nos. 21472165, 21672186, 21602202) and Important Project of Zhejiang province (2017C03049) is highly acknowledged

References

[1] For selected reviews: a) L. Ackermann, *Acc. Chem. Res.* **2014**, *47*, 281–295; b) S. R. Neufeldt, M. S. Sanford, *Acc. Chem. Res.* **2012**, *45*, 936–946; c) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788–802; d) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem., Int. Ed.* **2012**, *51*, 10236–10254; *Angew. Chem.* **2012,** *124*, 10382–10401; e) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215–1292; f) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885–1898; g) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068–5083; h) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931; i) T. Satoh, M. Miura, *Chem. -Eur. J.* **2010,** *16*, 11212–11222.

[2] For selected reviews: a) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2012,** *45*, 814–825; b) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879–5918; c) Y. Yang, J. Lan, J. You, *Chem. Rev.* **2017**, *117*, 8787–8863; d) Y. Hu, B. Zhou, C. Wang, *Acc. Chem. Res.* **2018**, *51*, 816–827.

[3] Z. Chen, B. Wang, J. Zhang, W. Yu, Z. Liu, Y. Zhang, *Org. Chem. Front.* **2015**, *2*, 1107–1295.

[4] a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007,** *9*, 1407–1409; b) Q. Lu, S. Gressies, S. Cembellin, F. J. R. Klauck, C. G. Daniliuc, F. Glorius, *Angew. Chem., Int. Ed.* **2017**, *56*, 12778–12782; *Angew. Chem.* **2017,** *129*, 12954–12958; c) A. Mandal, H. Sahoo, S. Dana, M. Baidya, *Org. Lett.* **2017**, *19*, 4138–4141; d) C. Kuai, L. Wang, B. Li, Z. Yang, X. Cui, *Org. Lett.* **2017**, *19*, 2102–2105; e) F. Xie, S. Yu, Z. Qi, X. Li, *Angew. Chem., Int. Ed.* **2016**, *55*, 15351–15355; *Angew. Chem.* **2016,** *128*, 15577–15581; f) B. Li, H. Xu, H. Wang, B. Wang, *ACS Catal.* **2016**, *6*, 3856–3862; g) L. Li, W. W. Brennessel, W. D. Jones, *J. Am. Chem. Soc.* **2008,** *130*, 12414–12419; h) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010,** *132*, 6908–6909; i) F. W. Patureau, T. Besset, N. Kuhl, F. Glorius, *J. Am. Chem. Soc.* **2011,** *133*, 2154–2156; j) K. Muralirajan, K. Parthasarathy, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2011,** *50*, 4169–4172; *Angew. Chem.* **2011,** *123*, 4255–4258; k) B.-J. Li, H.-Y. Wang, Q.-L. Zhu, Z.-J. Shi, *Angew. Chem.,Int. Ed.* **2012,** *51*, 3948–3952; *Angew. Chem.* **2012,** *124*, 4014–4018; l) J. H. Kim, T. Gensch, D. Zhao, L. Stegemann, C. A. Strassert, F. Glorius, *Angew. Chem. Int. Ed.* **2015,** *54*, 10975–10979; *Angew. Chem.* **2015,** *127*, 11126–11130.

[5] For a recent review and representative examples, see: a) D.-S. Kim, W.-J. Park, C.-H. Jun, *Chem. Rev.* **2017,** *117*, 8977–9015; b) P. Gandeepan, L. Ackermann, *Chem.* **2018,** *4*, 199–222; c) S. S. John-Campbell, J. A. Bull, *Org. Biomol. Chem.* **2018,** *16*, 4582–4595; d) C.-H. Jun, H. Lee, J.-B. Hong, *J. Org. Chem.* **1997,** *62*, 1200–1201; e) R. B. Bedford, S. J. Coles, M. B. Hursthouse, M. E. Limmert, *Angew. Chem. Int. Ed.* **2003,** *42*, 112–114; *Angew. Chem.* **2003,** *115*, 116–118; f) F. Mo, G. Dong, *Science.* **2014,** *345*, 68–72; g) F.-L. Zhang, K. Hong, T.-J. Li, H. Park, J.-Q. Yu, *Science*. **2016,** *351*, 252–256; h) Y. Xu, T. Su, Z. Huang, G. Dong, *Angew. Chem. Int. Ed.* **2016,** *55*, 2559–2563; *Angew. Chem.* **2016,** *128*, 2605–2609; i) Y. Liu, H. Ge, *Nat. Chem.* **2017,** *9*, 26–32; j) K. Yang, Q. Li, Y. Liu, G. Li, H. Ge, *J. Am. Chem. Soc.* **2016,** *138*, 12775–12778; k) Q.–J. Yao, S. Zhang, B.–B. Zhan, B.–F. Shi, *Angew. Chem. Int. Ed.* **2017,** *56*, 6617–6621; *Angew. Chem.* **2017,** *129*, 6717–6721.

[6] a) D.-G. Yu, M. Suri, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 8802–8805; b) Q. Wang, X. Li, *Org. Lett.* **2016**, *18*, 2102–2105; c) H. Li, H. Wang, S. Yu, X. Yang, X. Li, *Org. Lett.* **2016**, *18*, 3662–3665; d) S. Yu, G. Tang, Y. Li, X. Zhou, Y. Lan, X. Li, *Angew. Chem. Int. Ed*. **2016,** *55*, 8696–8700; *Angew. Chem.* **2016,** *128*, 8838–8842; e) F. Wang, H. Wang, Q. Wang, S. Yu, X. Li, *Org. Lett.* **2016**, *18*, 1306–1309; f) J. Wang, S. Zha, K. Chen, F. Zhang, C. Song, J. Zhu, *Org. Lett.* **2016**, *18*, 2062–2065; g) X. Wang, N. Jiao, *Org. Lett.* **2016**, *18* , 2150–2153; h) H. Wang, L. Li, S. Yu, Y. Li, X. Li, *Org. Lett.* **2016**, *18*, 2914–2917.

[7] a) X.-G. Li, M. Sun, K. Liu, P.-N. Liu, *Adv. Synth. Catal.* **2015,** *357*, 395-399; b) H. Wang, M. M. Lorion, L. Ackermann, *ACS Catal*. **2017**, *7*, 3430–3433; c) N. Lv, Z. Chen, Y. Liu, Z. Liu, Y. Zhang, *Org. Lett.* **2017**, *19*, 2588–2591; d) N. Lv, Y. Liu, C. Xiong, Z. Liu, Y. Zhang, *Org. Lett.* **2017**, *19*, 4640–4643.

[8] For select reviews on nitroalkenes and their use, see: (a) A. G. M. Barrett, G. G. Graboski, *Chem. Rev.* **1986,** *86*, 751–762; b) S. E. Denmark, A. Thorarensen, *Chem. Rev*. **1996,** *96*, 137–166; c) O. M. Berner, L. Tedeschi, D. Enders, *Eur. J. Org. Chem*. **2002,** *2002*, 1877–1894; d) A. G. Doyle, E. N. Jacobsen, *Chem. Rev.* **2007,** *107*, 5713–5743; e) A. Z. Halimehjani, I. N. N. Namboothiri, S. E. Hooshmand, *RSC Adv.* **2014,** *4*, 31261–31299; f) A. Z. Halimehjani, I. N. N. Namboothiri, S. E. Hooshmand, *RSC Adv.* **2014,** *4*, 48022–48084.

[9] a) T. Potter, D. N. Kamber, B. Q. Mercado, J. A. Ellman, *ACS Catal*. **2017,** *7*, 150–153; b) D. Bai, Q. Jia, T. Xu, Q. Zhang, F. Wu, C. Ma, B. Liu, J. Chang, X. Li, *J. Org. Chem.* **2017,** *82*, 9877–9884; c) T. J. Potter, Y. Li, M. D. Ward, J. A. Ellman, *Eur. J. Org. Chem.* **2018,** *2018*, 4381–4388; d) A. Mishra, U. Mukherjee, W. Sarkar, S. L. Meduri, A. Bhowmik, I. Deb, *Org. Lett.* **2019,** 21, 2056-2059.

[10] During preparation of the manuscript, similar reactions were reported by the Cui and Sharma groups. a) B. Wu, Z. Yang, H. Zhang, L. Wang, X. Cui, *Chem. Commun.* **2019**, *55*, 4190-4193; b) B. Chaudhary, P. Auti, S. D. Shiinde, P. A. Yakkala, D. Giri, S. Sharma, *Org. Lett.* **2019,** 21, 2763-2767.

[11] a) T. George, R. Tahilramani, C. L. Kaul, R. S. Grewal, *J. Pharm. Sci.* **1969,** *58*, 47–50; b) J. Augstein, A. L. Ham, P. R. Leeming, *J. Med. Chem.* **1972,** *15*, 466–470; c) K. P. Bogeso, *J. Med. Chem.* **1983,** *26*, 935–947; d) K. P. Bogeso, A. V. Christensen, J. Hyttel, T. Liljefors, *J. Med. Chem.* **1985,** *28*, 1817–1828; e) M. Pan, T. J.Mabry, J. M. Beale, B. M. Mamiya, *Phytochemistry*, **1997,** *45*, 517–519; f) M. Froimowitz, K.-M. Wu, A. Moussa, R. M. Haidar, J. Jurayj, C. George, E. L.Gardner, *J. Med. Chem.* **2000,** *43*, 4981–4992; g) H. Minegishi, Y. Futamura, S. Fukashiro, M. Muroi, M. Kawatani, H. Osada, H. Nakamura, *J. Med. Chem.* **2015,** *58*, 4230–4241.

[12] CCDC-1873798 and -1873799 (3a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

10.1002/adsc.201900427

COMMUNICATION

Rhodium-Catalyzed Cascade Annulation of Benzimidates and Nitroalkenes for the Synthesis of Difunctionalized Indenes

Adv. Synth. Catal. **2019**, *Volume*, Page – Page

Ningning Lv, Zhengkai Chen, Yue Liu, Zhanxiang Liu, Yuhong Zhang*