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Bismuth(III) Triflate Catalyzed Three-Component Reactions of Indoles, Ketones, and α-Bromoacetaldehyde Acetals Enable Indole-to-Carbazole Transformation

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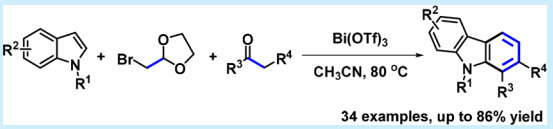
Supporting Information

ABSTRACT: A three-component reaction of indoles, α-bromoacetaldehyde acetals, and ketones was developed by using bismuth(III) triflate as the catalyst to realize a straightforward approach for synthesizing carbazole derivatives. The reaction was established mechanistically through the autotandem catalysis of $Bi(OTf)_3$ in the following two steps: (i) Friedel−Crafts-type alkylation of indole with α-bromoacetaldehyde acetal, which produced a tryptaldehyde-type intermediate and (ii) [4 + 2] annulation of this intermediate with the ketone component.



Carbazole and its derivatives are important nitrogen-containing heterocycles because their structural core is omnipresent in natural products and biologically active compounds.[1] Given their structural rigidity and extensive π-conjugation, carbazole derivatives are widely applied in preparing organic photoelectronic materials and chromophores.[2] In view of their widespread significance, cost-effective methods must be developed for synthesizing carbazoles. At the early stage of the process, carbazole synthesis relies heavily on the Fischer−Borsche method via a multistep procedure.[3] In the past two decades, transition-metal-catalyzed cyclization strategies have been widely applied in carbazole[4] and 1-(hetero)aryl carbazoles synthesis.[5] The Cadogan cyclization of 2-nitrobiaryls with the use of suitable reducing reagents, such as phosphines, phosphites, and carbon monoxide, has provided an alternative approach for accessing substituted carbazoles.[6] This type of reaction can also be performed in the presence of PhMgBr under mild and transition-metal-free conditions.[7] Carbazoles can also be synthesized from indole derivatives via different strategies, such as Diels−Alder reaction,[8] electrocyclic reaction,[9] and ketosulfoxide cyclization.[10] Although these strategies can synthesize carbazoles, new reaction systems are being continuously explored to improve efficiency and reduce cost.

The direct conversion of 2,3-unsubstituted indoles into carbazoles has an intrinsically high synthetic potential because simple indoles are readily available. At present, this transformation can generally be realized through the following three approaches (Figure 1): (i) [2 + 4] annulation, in which indoles are reacted with a carbon-based 1,4-biselectrophile, such as a 1,4-dicarbonyl compound, or their alkyne-, allene-, dihydrofuran-, and donor-and-acceptor-cyclopropane-type variations, with the aid of an acid or transition-metal catalyst to create carbazole scaffolds (see Figure S1 in Supporting Information (SI));[11] (ii) [2 + 2′ + 2′] annulation, in which indoles are reacted with two molecules of alkene or alkyne in the presence of a transition-metal catalyst to form carbazoles;[12] and (iii) [2 + 2′ + 2″] annulation, in which indoles are reacted with two different molecules, and each of them contribute two carbons to construct a carbazole ring.[13] Among these three approaches, the third is considered the most attractive route for carbazole

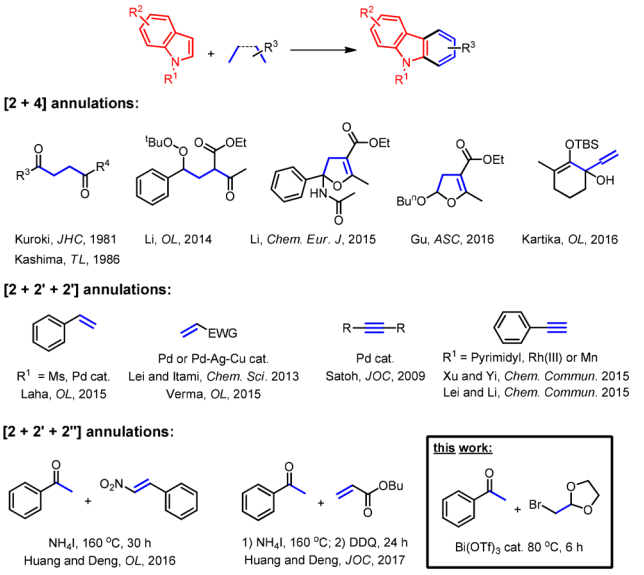


Figure 1. Representative works on indole-to-carbazole transformations starting from 2,3-unsubstituted indoles.

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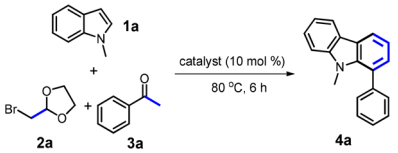
synthesis not only because it uses easily available substrate and transition-metal-free reaction conditions but also because it synthesizes carbazoles with a high potential of molecular diversity and complexity. However, to date, only a few [2 + 2′ + 2″] annulation reactions have been reported,[13] and the productivity for creating molecular diversity and complexity has yet to be fully displayed. In this work, we used α-bromoacetaldehyde acetal and a simple ketone as a reagent couple to react with 2,3-unsubstituted indole. The established [2 + 2′ + 2″] annulation reaction provided a straightforward approach for accessing various carbazoles that are otherwise difficult to synthesize through other methods.

Our studies started with a three-component reaction of *N*-methylindole **1a**, α-bromoacetaldehyde ethylene acetal **2a**, and acetophenone **3a**. The reaction was performed in acetonitrile at 80 °C. As shown in Table 1, no reaction occurred in the absence of catalyst (Table 1, entry 1). Triflic acid can promote this reaction, and the yield of **4a** reached 30% after 6 h (entry 2). Several readily available Lewis acids were examined. $Fe(OTf)_3$ was proven to be an ineffective catalyst (entry 3). $Cu(OTf)_2$, $Al(OTf)_3$, and $Sc(OTf)_3$ can promote the reaction, but the maximum yield reached only 65% (entries 4–6). The best result was obtained when $Bi(OTf)_3$ was used as the acid catalyst (entry 7).[14] The results indicate that better results were obtained with dipolar and aprotic solvents, such as acetonitrile or 1,4-dioxane (entries 7–11). Further inspection revealed that the amount of **1a** also markedly affected the reaction. The optimal yield was achieved in the presence of 2.0 equiv of **1a** in the reaction mixture (entries 7 and 12). The yield of **4a** decreased when the reaction temperature or catalyst amount was reduced or when the reaction time was shortened (entries 13–15). Thus, the optimal conditions were confirmed as follows: $Bi(OTf)_3$ catalyst (10 mol %), acetonitrile solvent, **1a**/**2a**/**3a** at 2/1/1, 80 °C, and 6 h. It should be noted that, with this catalyst, reactions scaled up to multigram quantities provided uniform results (entry 7).

Table 1. Condition Optimization of the Reaction between 1a, 2a, and 3a[a]

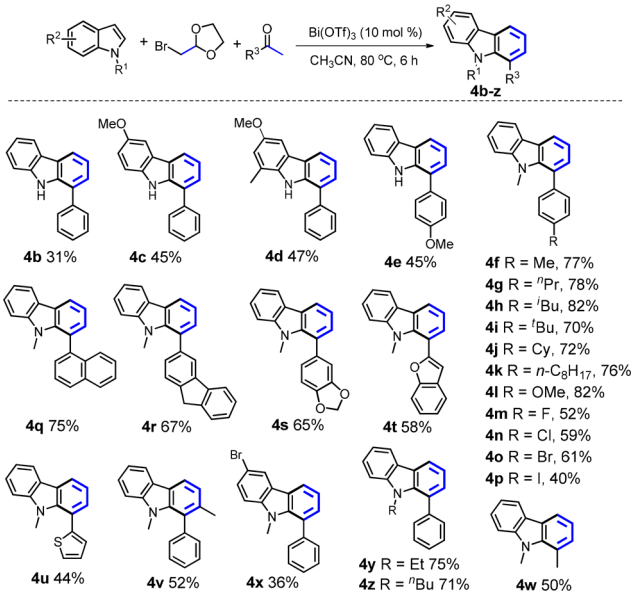


entry	catalyst	solvent	yield (%)[b]
1	–	MeCN	0
2	TfOH	MeCN	30 (trace)[c]
3	$Fe(OTf)_3$	MeCN	<5
4	$Cu(OTf)_2$	MeCN	55
5	$Al(OTf)_3$	MeCN	39
6	$Sc(OTf)_3$	MeCN	65
7	$Bi(OTf)_3$	MeCN	81 (80)[h]
8	$Bi(OTf)_3$	1,4-dioxane	74
9	$Bi(OTf)_3$	DCE	52
10	$Bi(OTf)_3$	PhMe	15
11	$Bi(OTf)_3$	EtOH	trace
12[d]	$Bi(OTf)_3$	MeCN	45
13[e]	$Bi(OTf)_3$	MeCN	53
14[f]	$Bi(OTf)_3$	MeCN	49
15[g]	$Bi(OTf)_3$	MeCN	47

[a]**1a** (0.6 mmol), **2a** (0.3 mmol), **3a** (0.3 mmol), catalyst (0.03 mmol), 80 °C, 6 h. [b]Isolated yield, calculated with respect to **2a**. [c]TfOH, 0.003 mmol (1 mol %). [d]**1a**/**2a**/**3a** is 1/1/1. [e]$Bi(OTf)_3$, 0.015 mmol. [f]50 °C. [g]3 h. [h]10 mmol scale reaction.

Once a set of optimized conditions was obtained, we probed the scope of the reaction with respect to both the indole and ketone components. In particular, we intended to assess the usefulness of $Bi(OTf)_3$-catalyzed [2 + 2′ + 2″] annulation in synthesizing N–H carbazoles from the N–H indole, which has been proven to be difficult for indole-to-carbazole transformation.[15] As shown in Scheme 1, when the N–H indole was used as the substrate, the reaction proceeded sluggishly, and the expected carbazole **4b** was isolated only in 31% yield. The nitrogen in the indole might coordinate with the bismuth(III) species, thus deactivating the catalyst. This imposed thus a negative effect on the reaction. When electron-donating N–H indoles or acetophenones were used as substrates, the selectivity to the target carbazole was slightly increased (**4c–e**). Nonetheless, the reactions exhibited no yield above 50%.

Scheme 1. Substrate Scope of the $Bi(OTf)_3$-Catalyzed [2 + 2′ + 2″] Annulation Reaction of 2,3-Unsubstitued Indoles, 2a, and Ketones



The reactions with *N*-alkylindoles proceeded generally well. Upon repeating the reaction with **1a** and **2a**, acetophenones with different functional groups on the arene ring worked well under the standard conditions, efficiently offering the corresponding functionalized carbazoles **4f–p** with yields ranging from 40% to 82%. Various functional groups, such as fluoro (**4m**), chloro (**4n**), bromo (**4o**), iodo (**4p**), *tert*-butyl (**4i**), cyclohexyl (**4j**), and methoxy (**4l**), can well tolerate the $Bi(OTf)_3$-promoted conditions. 1-Acetonaphthone and 1-(9*H*-fluoren-3-yl)ethanone, which are sterically demanding ketones, were successfully engaged in this reaction, delivering the corresponding carbazoles, namely, **4q** and **4r**, with 75% and 67% yields, respectively. Aryl methyl ketones with heterocyclic functionalities, such as 3,4-methylenedioxyacetophenone, 2-acetylthiophene, and 2-acetylbenzofuran, could also be used uneventfully, and the heterocyclic fragments were delivered into the product without structural damage (**4s–u**). Carbazole synthesis with propiophenone was also successful, albeit with a

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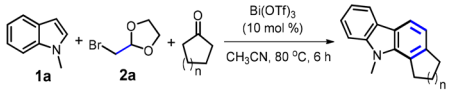
slightly lower efficiency (**4v**). The results for the use of other *N*-alkylindoles, such as *N*-ethylindole and *N*-butylindole, were mostly similar to those for *N*-methylindole. Nonetheless, the presence of an electron-withdrawing group in the indole ring was detrimental for the carbazole synthesis. For example, when 5-bromo-1-methylindole was used, only 36% of yield was obtained under identical conditions (**4x**).

Then, we attempted to use an aliphatic ketone in the three-component reaction. Although the result obtained for the linear aliphatic ketone was not as good as that for the aryl methyl ketone, the attained synthetic efficiency was acceptable. For example, when acetone was reacted with **1a** and **2a**, the expected product, **4w**, was obtained in 50% yield (Scheme 1). A number of cyclic aliphatic ketones, such as cyclopentanone, cyclohexanone, and cycloheptanone, participated readily in this reaction, providing the expected carbazoles with generally good yields (Scheme 2). Given that **4ab**-type carbazoles can be

Scheme 2. Reactions of 1a, 2a, and Cyclic Ketones

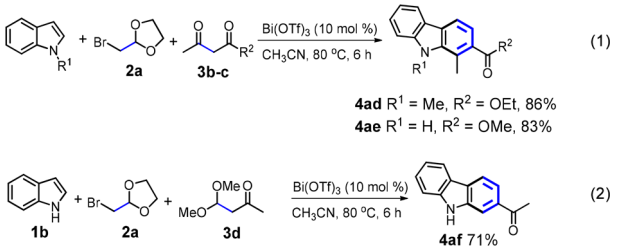


4aa n = 1, 75%; **4ab** n = 2, 86%; **4ac** n = 3, 85%

converted easily into benzo[α]carbazoles through dehydrogenative aromatization reaction,[16] and that many cyclohexanone derivatives are commercially available, this result provides another significant feature for extending our protocol to the synthesis of benzo[α]carbazoles. 2-Bromopriopionaldehyde diethyl acetal was also used instead of **2a** in the model reaction. However, the expected product was not obtained.

In addition, we performed experiments in which 1,3-dicarbonyl compounds served as the ketone components in the three-component reaction. As shown in Scheme 3, ethyl

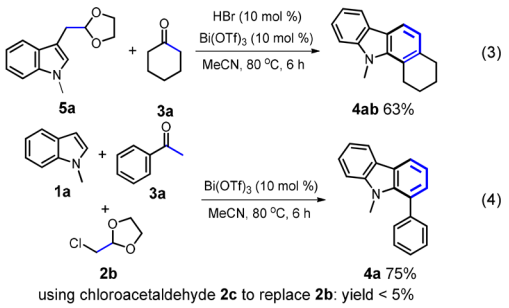
Scheme 3. Reactions of Indoles, 2a, and 1,3-Dicarbonyls



acetoacetate reacted smoothly with **1a** and **2a** in the presence of the Bi(OTf)$_3$ catalyst, affording the corresponding carbazole derivative **4ad** in 86% yield (eq 1). The use of N−H indole achieved nearly the same results as that with **1a** for carbazole synthesis, indicating that the high electrophilicity of the ketocarbonyl in the β-ketoester remedied the poor reactivity of the N−H indole. 4,4-Dimethoxy-2-butanone **3d** can also react with **1b** and **2a** with the aid of a catalytic amount of Bi(OTf)$_3$ to afford 3-acetylcarbazole **4af** in 71% yield (Scheme 3, eq 2). These results suggest that the current three-component reaction is compatible with structurally distinct substrates with different electronic properties. It is therefore an efficient and practical protocol for accessing substituted carbazoles with high atom and step economy.

To elucidate the mechanism, additional experiments were conducted. From a theoretical perspective, under strong acidic conditions, both sides of α-bromoacetaldehyde ethylene acetal **2a**, namely, bromomethyl and aldo-carbonyl groups, can react with a nucleophile. Given that the nucleophilicity of **1a** was considerably higher than that of **3a**, **1a** should exhibit the priority to react with an electrophile. If the carbazole formation was triggered by a reaction of the bromomethyl side of **2a**, then (i) a tryptaldehyde should be generated as an intermediate and (ii) replacing **2a** with α-chloroacetaldehyde ethylene acetal **2b** should notably influence the synthetic efficiency. Therefore, control experiments were performed. As shown in Scheme 4, in

Scheme 4. Control Experiments

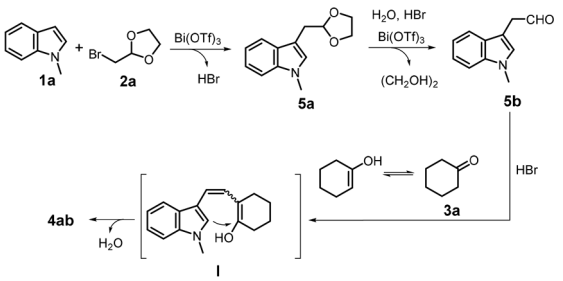


using chloroacetaldehyde **2c** to replace **2b**: yield < 5%

the presence of Bi(OTf)$_3$ and HBr, a tryptaldehyde derivative **5a** can react with cyclohexanone to form a carbazole derivative **4ab** in 63% yield (eq 3). Here, HBr was added, on purpose, to mimic a real reaction system, in which HBr is generated as a concomitant of the Friedel−Crafts-type alkylation of **1a** and **2a**. The three-component reaction of **1a**, **2b**, and **3a** also proceeded under the optimal conditions, producing **4a** in 75% yield. However, by contrast, the use of α-chloroacetaldehyde **2c** instead of **2b** drastically reduced the reaction yield, as inseparable gum-like products were formed (eq 4). These results imply that the acetal structure of **2b** weakened the reactivity of the aldehyde side, thereby ensuring the chloromethyl group exhibited the priority to react with indole to form tryptaldehyde. This phenomenon can also be verified by the results in Figure S2 in the SI. When α-bromoacetaldehyde diethyl acetal **2d** and α-bromoacetaldehyde dimethyl acetal **2e** were used to synthesize **4a**, the obtained maximum yields were substantially lower than that by the reaction with **2a**, although the maximum yields were reached earlier under identical conditions. Compared with the cyclic acetal **2a**, **2d** and **2e** were less stable under acidic conditions and tended to give α-bromoacetaldehyde via a deacetalization reaction in the presence of water (exist in the solvent and air), thereby destroying the selectivity to **4a**.

Thus, a plausible mechanism for the reaction of **1a**, **2a**, and **3a** was proposed, and it is depicted in Scheme 5. The initial

Scheme 5. Plausible Mechanism



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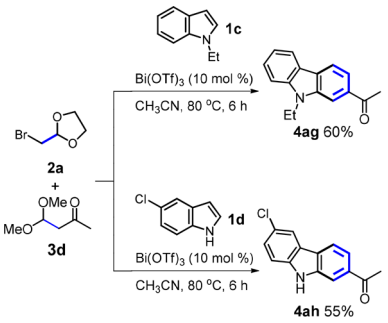
event should be an acid-catalyzed Friedel−Crafts alkylation of **1a** with **2a**, which would generate a tryptaldehyde-type acetal **5a**. Given that the solvent and reagents were not absolutely dry, trace amounts of water were in the reaction system. As such, **5a** underwent deacetalization to give a tryptaldehyde derivative **5b**. Then, the enol form of **3a** trapped **5b** to give a C3-vinylndole derivative **I**. Finally, **4ab** was formed through an intramolecular condensation reaction. These experimental results implied that (i) the tryptaldehyde derivative **5b** may be unstable, as it can react with itself or **1a**,[17] and the acetal **5a** acted like a reservoir of **5b** that gradually released it in the course of the reaction, thereby maximizing the reaction selectivity; and (ii) the last step of the reaction involved the formation of a π-expanded carbazole ring, which conceivably shifted the reaction equilibrium to the product side. Its efficiency depended not only on the electrophilicity of the carbonyl group in the ketone component but also on the nucleophilicity of the C2 position of indole system. Therefore, N−H indoles and electron-poor indoles were reluctant to participate in the reaction.

The utility of this approach in constructing carbazole scaffolds was also demonstrated in the synthesis of two compounds. A carbazole derivative **4ag** was used as the intermediate to synthesize a europium complex, which is a promising candidate for use as a visible-light excitable red phosphor for luminescence applications.[18] The previous method for synthesizing this compound was established based on the three-step synthesis with isolation and purification of intermediates at each step. It also involved the use of expensive reagents and catalysts, such as 4-acetylphenylboronic acid and $Pd(PPh_3)_4$. By using three easily available chemicals, such as *N*-ethylindole **1c**, **2a**, and **3d**, as starting materials, **4ag** can be synthesized in 60% yield through a one-step reaction (Scheme 6). Similarly, a carbazole

Scheme 6. Synthesis of 4ag and 4ah



derivative **4ah**, which is an intermediate for synthesizing the nonsteroidal anti-inflammatory animal drug Carprofen,[19] can be obtained in 55% yield in a one-step reaction of 5-chloroindole **1d**, **2a**, and **3d** (Scheme 6). The existing two-step method used to access this compound involves the acetylation of carbazole, followed by chlorination with trichloroisocyanuric acid.[20] Thus, the proposed three-component reaction offers a straightforward method for synthesizing **4ah**.

In summary, we developed a new three-component indole-to-carbazole reaction involving indoles, α-bromoacetaldehyde acetals, and ketones, by which structurally diverse carbazoles were synthesized in a straightforward manner with generally good yields. From a mechanistic perspective, this approach involves a tandem reaction driven by an acid catalyst. In view of the large number of commercially available ketones and the easy access to 2,3-unsubstituted indoles, the proposed method is a promising strategy for the synthesis of carbazole libraries with high diversity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01707.

Experimental procedures, spectroscopic data of the obtained products, and copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Knölker, H. J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303. (b) Schmidt, A. W.; Reddy, K. R.; Knölker, H. J. *Chem. Rev.* **2012**, *112*, 3193. (c) Ito, C.; Itoigawa, M.; Sato, A.; Hasan, C. M.; Rashid, M. A.; Tokuda, H.; Mukainaka, T.; Nishino, H.; Furukawa, H. J. *J. Nat. Prod.* **2004**, *67*, 1488. (d) Zhang, F. F.; Gan, L. L.; Zhou, C.-H. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 1881. (e) Liu, C.; Pan, B.; Gu, Y. *Chin. J. Catal.* **2016**, *37*, 979.

(2) (a) Dumur, F. *Org. Electron.* **2015**, *25*, 345. (b) Lellouche, J.-P.; Koner, R. R.; Ghosh, S. *Rev. Chem. Eng.* **2013**, *29*, 413. (c) Li, J.; Grimsdale, A. C. *Chem. Soc. Rev.* **2010**, *39*, 2399. (d) Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28*, 1297.

(3) (a) Robinson, B. *Chem. Rev.* **1969**, *69*, 227. (b) Muller, S.; Webber, M. J.; List, B. *J. Am. Chem. Soc.* **2011**, *133*, 18534.

(4) For recent carbazole formation by transition-metal-catalyzed cyclization, see: (a) Kumar, V. P.; Gruner, K. K.; Kataeva, O.; Knölker, H. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 11073. (b) Antonchick, A. P.; Samanta, R.; Kulikov, K.; Lategahn, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 8605. (c) Cho, S. H.; Yoon, J.; Chang, S. *J. Am. Chem. Soc.* **2011**, *133*, 5996. (d) Hernandez-Perez, A. C.; Collins, S. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 12696. (e) Gensch, T.; Rönnefahrt, M.; Czerwonka, R.; Jäger, A.; Kataeva, O.; Bauer, I.; Knölker, H.-J. *Chem. - Eur. J.* **2012**, *18*, 770. (f) Hesse, R.; Jäger, A.; Schmidt, A. W.; Knölker, H.-J. *Org. Biomol. Chem.* **2014**, *12*, 3866 and references cited therein.

(5) (a) Suárez, A.; Suárez-Pantiga, S.; Nieto-Faza, O.; Sanz, R. *Org. Lett.* **2017**, *19*, 5074. (b) Uwa, K.; Tseng, Y.-Y.; Kamikawa, K. *Eur. J. Org. Chem.* **2017**, *2017*, 892. (c) Parisien-Collette, S.; Hernandez-Perez, A. C.; Collins, S. K. *Org. Lett.* **2016**, *18*, 4994.

(6) (a) Cadogan, J. I. G.; Cameron-Wood, M. *Proc. Chem. Soc.* **1962**, 361. (b) Sanz, R.; Escribano, J.; Pedrosa, M. R.; Aguado, R.; Arnaiz, F.

DOI: 10.1021/acs.orglett.8b01707
Org. Lett. XXXX, XXX, XXX−XXX

J. *Adv. Synth. Catal.* **2007**, *349*, 713. (c) Kuethe, J. T.; Childers, K. G. *Adv. Synth. Catal.* **2008**, *350*, 1577.
(7) Gao, H.; Xu, Q. L.; Yousufuddin, M.; Ess, D. H.; Kürti, L. *Angew. Chem., Int. Ed.* **2014**, *53*, 2701.
(8) Van Broeck, P. I.; Van Doren, P. E.; Toppet, S. M.; Hoornaert, G. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 415.
(9) (a) Rawat, M.; Wulff, W. D. *Org. Lett.* **2004**, *6*, 329. (b) Liu, Y.; Nappi, M.; Arceo, E.; Vera, S.; Melchiorre, P. *J. Am. Chem. Soc.* **2011**, *133*, 15212.
(10) (a) Oikawa, Y.; Yonemitsu, O. *J. Org. Chem.* **1976**, *41*, 1118. (b) Tsang, W. C. P.; Zheng, N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 14560.
(11) (a) Kashima, C.; Hibi, S.; Maruyama, T.; Omote, Y. *Tetrahedron Lett.* **1986**, *27*, 2131. (b) Kuroki, M.; Tsunashima, Y. *J. Heterocycl. Chem.* **1981**, *18*, 709. (c) Liu, C.; Gu, Y. *Adv. Synth. Catal.* **2016**, *358*, 2260. (d) Matsuda, Y.; Naoe, S.; Oishi, S.; Fujii, N.; Ohno, H. *Chem. - Eur. J.* **2015**, *21*, 1463. (e) Zheng, X.; Lv, L.; Lu, S.; Wang, W.; Li, Z. *Org. Lett.* **2014**, *16*, 5156. (f) Zhao, J.; Li, P.; Xia, C.; Li, F. *Chem. - Eur. J.* **2015**, *21*, 16383. (g) Matsuda, Y.; Naoe, S.; Oishi, S.; Fujii, N.; Ohno, H. *Chem. - Eur. J.* **2015**, *21*, 1463. (h) Guo, B.; Huang, X.; Fu, C.; Ma, S. *Chem. - Eur. J.* **2016**, *22*, 18343. (i) Thies, N.; Hrib, C. G.; Haak, E. *Chem. - Eur. J.* **2012**, *18*, 6302. (j) Kulkarni, A.; Quang, P.; Torok, B. *Synthesis* **2009**, *2009*, 4010. (k) Stepherson, J. R.; Ayala, C. E.; Tugwell, T. H.; Henry, J. L.; Fronczek, F. R.; Kartika, R. *Org. Lett.* **2016**, *18*, 3002. (l) Wu, J.; Yang, Z.; Zhang, S.; Jiang, C.; Li, Q.; Huang, Z.; Wang, H. *ACS Catal.* **2015**, *5*, 6453. (m) Suárez, A.; García-García, P.; Fernández-Rodríguez, M. A.; Sanz, R. *Adv. Synth. Catal.* **2014**, *356*, 374.
(12) (a) Laha, J. K.; Dayal, N. *Org. Lett.* **2015**, *17*, 4742. (b) Ozaki, K.; Zhang, H.; Ito, H.; Lei, A.; Itami, K. *Chem. Sci.* **2013**, *4*, 3416. (c) Yamashita, M.; Horiguchi, H.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 7481. (d) Shi, L.; Zhong, X.; She, H.; Lei, Z.; Li, F. *Chem. Commun.* **2015**, *51*, 7136. (e) Verma, A. V.; Danodia, A. K.; Saunthwal, R. K.; Patel, M.; Choudhary, D. *Org. Lett.* **2015**, *17*, 3658. (f) Saunthwal, R. K.; Saini, K. M.; Patel, M.; Verma, A. K. *Tetrahedron* **2017**, *73*, 2415. (g) Guo, T.; Jiang, Q.; Huang, F.; Chen, J.; Yu, Z. *Org. Chem. Front.* **2014**, *1*, 707.
(13) (a) Chen, S.; Li, Y.; Ni, P.; Huang, H.; Deng, G. *Org. Lett.* **2016**, *18*, 5384. (b) Chen, S.; Wang, L.; Zhang, J.; Hao, Z.; Huang, H.; Deng, G. *J. Org. Chem.* **2017**, *82*, 11182. (c) Chen, S.; Li, Y.; Ni, P.; Yang, B.; Huang, H.; Deng, G.-J. *J. Org. Chem.* **2017**, *82*, 2935. (d) Pindur, U.; Rogge, M.; Rehn, C.; Massa, W.; Peschel, B. *J. Heterocycl. Chem.* **1994**, *31*, 981.
(14) $Bi(OTf)_3$ has been widely used as a Lewis acid catalyst in organic reactions. See some reviews: (a) Gaspard-Iloughmane, H.; Le Roux, C. *Eur. J. Org. Chem.* **2004**, *2004*, 2517. (b) Ollevier, T. *Org. Biomol. Chem.* **2013**, *11*, 2740. (c) Ondet, P.; Lemière, G.; Duñach, E. *Eur. J. Org. Chem.* **2017**, *2017*, 761.
(15) Guo, B.; Huang, X.; Fu, C.; Ma, S. *Chem. - Eur. J.* **2016**, *22*, 18343.
(16) (a) Gribble, G. W.; Silva, R. A.; Saulnier, M. G. *Synth. Commun.* **1999**, *29*, 729. (b) Olsen, R. J.; Cummings, O. W. *J. Heterocycl. Chem.* **1981**, *18*, 439.
(17) (a) Yang, Q.; Wang, L.; Guo, T.; Yu, Z. *J. Org. Chem.* **2012**, *77*, 8355. (b) Ravichandiran, P.; Lai, B.; Gu, Y. *Chem. Rec.* **2017**, *17*, 142.
(18) He, P.; Wang, H. H.; Liu, S. G.; Shi, J. X.; Wang, G.; Gong, M. L. *Inorg. Chem.* **2009**, *48*, 11382−11387.
(19) Fox, S. M.; Johnston, S. A. *J. Am. Vet. Med. A* **1997**, *210*, 1493.
(20) Manchand, P. S.; Coffen, D. L.; Belica, P. S. F.; Wong, H. S.; Berger, L. *Heterocycles* **1994**, *39*, 833.

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