## Photocatalysis

## Visible-Light/Photoredox-Mediated sp<sup>3</sup> C—H Functionalization and Coupling of Secondary Amines with Vinyl Azides in Flow Microreactors

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**Abstract:** Structurally diverse imidazole derivatives were synthesized by a visible-light/ $[Ru(bpy)_3][(PF_6)_2]$ -mediated coupling of vinyl azides and secondary amines in flow microreactors. This operationally simple and atom-economical protocol allows the formation of three new C–N bonds through the functionalization of sp<sup>3</sup> C–H bonds adjacent to the secondary nitrogen atom. In order to get mechanistic insight of the coupling reaction, several control experiments were carried out and discussed.

Visible-light-mediated organic transformations have received considerable attention in scientific community due to its sustainable and green perspectives.<sup>[1]</sup> Photochemical methods provide remarkable reaction pathways, which are otherwise difficult to achieve through conventional strategies.<sup>[1,2]</sup> Compared to UV-light-mediated transformations,<sup>[3]</sup> visible-lightmediated strategies are particularly attractive as visible light is safer to handle and organic compounds are more stable in visible light towards photodecomposition. With the advent of the commercially available and relatively stable transition-metal photoredox catalysts, researchers enjoyed developing newer carbon-carbon and carbon-heteroatom bond-forming reactions using visible light.<sup>[1,2,4]</sup> A large number of such reactions involve visible-light-mediated photoredox generation of a radical cation on a tertiary nitrogen atom as the key step in the overall transformation.<sup>[5]</sup> Examples of the visible-light-mediated generation of a radical cation on a secondary nitrogen atom

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504292. and the functionalization of sp<sup>3</sup> C–H bonds adjacent to the secondary nitrogen atom are rare.<sup>[6]</sup> Presented in this communication are the results of a visible-light-mediated photoredox functionalization of sp<sup>3</sup> C–H bonds adjacent to the secondary nitrogen atom, yielding structurally diverse imidazole derivatives.

Vinyl azides are very reactive species and have been employed as a pivotal three-atom synthon for the formation of diverse N-heterocycles.<sup>[7]</sup> We initially selected vinyl azide 1 for our investigations as it can undergo nucleophilic attack<sup>[7f]</sup> along with the liberation of N<sub>2</sub>, thus providing an intermediate suitable for the key step. We envisioned that vinyl azides 1 might be attacked by secondary amines 2 to generate tertiary amines 3, which should form nitrogen-centered radical cation 5 under a visible-light-mediated photoredox catalysis, eventually yielding imidazole derivatives 8 through a series of cascade reactions (Scheme 1). Thus, the overall process might be considered as the functionalization of sp<sup>3</sup> C–H bonds adjacent to a secondary nitrogen atom.

In order to test the hypothesis, the reaction of vinyl azide **1 a** and 1,2,3,4-tetrahydroisoquinoline (**2 a**) was taken as a model reaction, and the effect of light, catalyst, oxidant, and solvent was studied in a batch reactor (Table 1). The reaction did not proceed in the absence of light or photocatalyst in CH<sub>3</sub>CN (entries 1–3). However, using  $[Ru(bpy)_3][PF_6]_2$  (1 mol%) and *tert*-butyl hydroperoxide (TBHP; 5 equiv) as an oxidant in anhydrous acetonitrile led to the generation of a spot, which was found to be **9a** instead of **8a** (entry 4). The structure of the unexpected imidazole derivative **9a** was confirmed by single-crystal X-ray crystallography (Figure 1).

Increasing the stoichiometry of TBHP did not increase the product yield, but decreasing it led to a low yield of the imidazole 9a (Table 1, entries 5 and 6). It is worth mentioning that the reaction was found to be moisture sensitive as it gave poor yield of 9a (10%) along with several uncharacterized products using [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6 H<sub>2</sub>O as the photocatalyst (entry 7). The reaction did not proceed with organic dyes, such as rose Bengal and eosin Y (entries 8 and 9). Exploring other sources of oxidation, the reaction gave a poor yield of the imidazole **9a** (25%, entry 10). Moreover, employing H<sub>2</sub>O<sub>2</sub> as an oxidant was found unsuccessful and produced a very complex mixture (entry 11). Next, we screened several solvents and among them acetonitrile was found to be the best (entries 12 and 13). Furthermore, increasing the amount of  $[Ru(bpy)_3][PF_6]_2$ did not increase the product yield significantly whereas decreasing it lowered the product yield (entries 14 and 15).

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Scheme 1. Proposed coupling of vinyl azides 1 with secondary amines 2 to yield imidazole derivatives 8 under a visible-light photoredox catalysis.

Table 1. Evaluation of reaction conditions. <sup>[a]</sup>					
	O N <sub>3</sub>	$\rightarrow$ + $\stackrel{HN}{\longrightarrow}$ 2a	o o o N ya		N N Sa (Not formed)
Entry	Light <sup>[b]</sup>	Photocatalyst	Oxidant	Solvent	Yield [%] <sup>[c]</sup>
1	no	-	TBHP	CH₃CN	ND <sup>[h]</sup>
2	yes	-	TBHP	CH₃CN	ND
3	no	[Ru(bpy) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	TBHP	CH₃CN	ND
4	yes	$[Ru(bpy)_3][PF_6]_2$	TBHP	CH₃CN	55
5 <sup>[d]</sup>	yes	[Ru(bpy) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	TBHP	CH₃CN	54
6 <sup>[e]</sup>	yes	[Ru(bpy)₃][PF <sub>6</sub> ] <sub>2</sub>	TBHP	CH₃CN	35
7	yes	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> ·6H <sub>2</sub> O	TBHP	CH₃CN	10
8	yes	rose Bengal	TBHP	CH₃CN	ND
9	yes	eosin Y	TBHP	CH₃CN	ND
10	yes	[Ru(bpy) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	$O_2$ balloon	CH₃CN	25
11	yes	$[Ru(bpy)_3][PF_6]_2$	$H_2O_2$	CH₃CN	ND
12	yes	[Ru(bpy)₃][PF6]2	TBHP	toluene	41
13	yes	[Ru(bpy) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	TBHP	CHCl₃	32
14 <sup>[f]</sup>	yes	$[Ru(bpy)_3][PF_6]_2$	TBHP	CH₃CN	56
15 <sup>[g]</sup>	yes	[Ru(bpy) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub>	TBHP	CH₃CN	45

[a] Reaction condition: vinyl azide **1a** (0.2 mmol), 1,2,3,4-tetrahydroisoquinoline (**2a**; 0.2 mmol), photocatalyst (1 mol%), oxidant (5 equiv), anhydrous solvent (10 mL), rt, stir, 12 h. [b] White LED (11 W) kept at a distance of approximately 10 cm from the reaction flask. [c] Isolated yield. [d] 10 equivalents of TBHP used. [e] 3 equivalents of TBHP used. [f] 2 equivalents of [Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> used. [h] ND = not detected on TLC.



**Figure 1.** ORTEP diagram of **9a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.<sup>[14]</sup>

Despite optimizing various reaction conditions, the yield of imidazole 9a was not very high in the batch reactor. Therefore, we decided to apply a flow microreactor technology for our photochemical synthetic transformations. Due to a very large surface to volume ratio, high illumination homogeneity, enhanced heat- and mass-transfer capability, and reduced safety hazards, microreactors are considered very suitable for photochemical reactions.<sup>[8,9]</sup> A flow microreactor for the synthesis of imidazole 9a by visible-light/[Ru(bpy)3][PF6]2-mediated coupling of vinyl azide 1a and amine 2a was easily assembled by wrapping a visible-light-transparent perfluoroalkoxy (PFA) capillary microreactor (ID = 0.76 mm, Length = 10 m, and volume = 4.53 mL) over a white LED light source (Figure 2).<sup>[9c]</sup> Solutions of vinyl azide 1a and amine **2a** in acetonitrile,  $[Ru(bpy)_3][PF_6]_2$  in acetonitrile, and TBHP in toluene were kept in three separate syringes and connections were made through an X-junction. The effect of residence time over the coupling of vinyl azide 1 a and 1,2,3,4-tetrahydroisoguinoline (2 a) was studied in the flow microreactor. The relative flow rates were managed in such a way that the catalyst loading and oxidant were 1 mol% and five equivalents, respectively, in the final reaction mixture after X-junction. Full conversion of 9a (65% yield) was obtained in a residence time of 44 min (see Table S1 in the Supporting Information for details). Improved yields of 9a (55% in batch versus 65% in flow) and reduced reaction times (12 h in batch versus 44 min in flow) can be explained by considering a high photon flux, and increased illumination homogeneity in the flow microreactor.

Having optimized flow microreactor conditions for the visible-light-mediated coupling of vinyl azide **1a** and amine **2a** in hand, we attempted to explore the scope of this synthetic transformation. Vinyl azides used in our study were prepared either from the Knoevenagel condensation of aldehydes with phenacyl azides or bromination followed by an azide substitution/elimination of styrenes (see the Supporting Information for details). Thus, a number of structurally diverse vinyl azides were subjected to the visible-light/[Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>-mediated microfluidic conditions to synthesize imidazole derivatives (Figure 3). The reaction worked well with vinyl azides derivation for heteroaromatic aldehydes and aromatic aldehydes containing halogen, and electron-donating and -withdrawing



Figure 2. Coupling of vinyl azides 1 with amines 2 to yield imidazole derivatives 9 mediated by visible light and a photocatalyst in a flow microreactor.

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Figure 3. Coupling of vinyl azides 1 with amines 2 to yield imidazole derivatives 9 mediated by visible light and  $[Ru(bpy)_3][PF_6]_2$  in the flow microreactor depicted in Figure 1; residence time = 44 min.

substituents (9a-m and 9o-v). The yields of imidazoles were relatively low when vinyl azides derived from aromatic aldehydes containing an electron-donating group were used (9 a, d, f, i, j, q, r, t and v). It also worked well with vinyl azides derived from aliphatic aldehydes (9n). The reaction was equally successful with vinyl azides derived from phenacyl azides bearing halogen, and electron-donating and -withdrawing substituents (9a-v). Good yields of imidazoles were also obtained using styrene-derived vinyl azides (9z, a'and b'). The reaction was compatible with cyclic secondary amines, such as 1,2,3,4tetrahydroisoquinoline (2 a) and 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (2b). It is worth noting that the reaction also worked with acyclic secondary amines, such as N-benzyl aniline (2c, 9w), N-benzyl-p-anisidine (2d, 9x), and dibenzyl amine (2e, 9y), though the product yields were comparatively lower (35–58%). Simple secondary amines, such as pyrrolidine, piperidine, and morpholine, gave complex reaction mixtures, from which desired imidazole products could not be separated.

The evolution of the nitrogen under visible-light irradiation in the presence of the photoredox catalyst indicated that the decomposition of the vinyl azide occurred possibly in a photosensitized manner.<sup>[10]</sup> In order to gain some mechanistic insight into the reaction, vinyl azide 1b, which was carefully chosen in order to minimize the side reactions of 2Hazirine and had both the ortho positions blocked by two chlorine atoms, was treated with [Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (1 mol%) in acetonitrile and irradiated with a white LED light in the absence of amines (Scheme 2). After workup, 2H-azirine 10a (88%) was isolated under visible-light irradiation. However, no conversion was observed in absence of the photocatalyst in light or with the photocatalyst in dark. Furthermore, vinyl azide 1b was converted into 2H-azirine 10a under the thermal decomposition in 69% yield. These experiments confirmed the visible-light/transition-metal-sensitized decomposition of vinyl azides under our imidazole-forming procedures.





Scheme 2. Visible-light/transition-metal-mediated decomposition of vinyl azide 1 b to 2*H*-azirine 10 a.

Facile conversions of vinyl azide **1b** to 2*H*-azirine **10a** explains why the expected imidazole **8a** was not obtained under our reaction conditions. After 2*H*-azirine formation, the sp<sup>2</sup> carbon directly attached to the azide ( $N_3$ ) group of the vinyl azide **1** becomes highly electrophilic and is attacked by the amine **2**, leading to the formation of the imidazole **9**.

Next, we performed a few experiments to check whether  $[Ru(bpy)_3][PF_6]_2$  oxidizes<sup>[11]</sup> secondary amines to imines under visible-light irradiation (Scheme 3). The oxidation of 1,2,3,4-tet-rahydroisoquinoline (**2a**) to 3,4-dihydroisoquinoline (**11a**) has



Scheme 3. Oxidation of 1,2,3,4-tetrahydroisoquinoline (2 a) to 3,4-dihydroisoquinoline (11 a) under visible-light/transition-metal and conventional conditions.

been successfully carried out using various catalysts under photoirradiation.<sup>[12]</sup> In a control experiment, **2a** was treated with  $[Ru(bpy)_3][PF_6]_2$  (1 mol%) and TBHP (2 equiv) in acetonitrile and irradiated with a white LED light (Scheme 3). Under these conditions, **2a** was rapidly oxidized to **11a**. Although, **2a** was slowly oxidized to **11a** in dark, no conversion was observed in the absence of  $[Ru(bpy)_3][PF_6]_2$  either in light or in dark. These experiments suggested that the secondary amines used for the imidazole synthesis might have been oxidized to imines through the generation of a radical cation on the nitrogen atom of the secondary amine.

Next, we reacted 2*H*-azirine **10a** with 1,2,3,4-tetrahydroisoquinoline (**2a**) and 3,4-dihydroisoquinoline (**11a**) separately to study the imidazole synthesis (Scheme 4). The reaction of 2*H*azirine **10a** with imine **11a** gave a high yield of imidazole **90** (88%) without photoirradiation, whereas the reaction of **10a** with amine **2a** gave 65% yield of **90** under the visible-light ir-



Scheme 4. Control experiments: Coupling of 2*H*-azirine 10 a with amine 2 a and imine 11 a under various conditions.

radiation. The reaction of **10a** with **2a** in dark gave a complex mixture, in which the desired imidazole **9o** was not detected on TLC.

Based on these observations, the formation of imidazoles 9 can be explained by a plausible mechanism depicted in Scheme 5. The 2*H*-azirine **10** is generated from vinyl azide  $1^{[10,13]}$  by visible-light photosensitization, and imine **11** is generated from amine **2** by photoredox catalysis. Next, **10** and **11** react to yield an intermediate **12**, which undergoes ring opening and cyclization in a concerted manner to yield zwitterion **13**. The zwitterion **13** rearranges to another intermediate **14**, which further oxidizes to imidazole **9**. However, there may be an alternative mechanism, in which the highly reactive 2*H*-azirine **10** is attacked by the amine **2** to yield an intermediate **15**, which rearranges to compound **18** through intermediates **16** 



**Scheme 5.** Mechanistic rationalization for the visible-light/[Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub><sup>-</sup> mediated coupling of vinyl azides 1 and amines 2 to yield imidazoles 9.

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and **17**. Compound **18** has a tertiary nitrogen atom, which can undergo photoredox catalysis under our reaction conditions and oxidizes to imidazole **9**.

In conclusion, we have developed a synthetic strategy for structurally diverse imidazoles that relies on visible-light/  $[Ru(bpy)_3][PF_6]_2$ -mediated coupling of vinyl azides and secondary amines. A series of 28 imidazoles were synthesized using  $[Ru(bpy)_3][PF_6]_2$  (1 mol%) as a photocatalyst and TBHP as an oxidant in flow microreactors. The synthetic protocol developed utilizes visible light to functionalize sp<sup>3</sup> C–H bonds adjacent to a secondary amine. This atom-economical protocol allows the formation of three new C–N bonds in the overall process.

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- For recent reviews on visible-light photocatalysis, see: a) R. Brimioulle, D. Lenhart, M. M. Maturi, T. Bach, Angew. Chem. Int. Ed. 2015, 54, 3872; Angew. Chem. 2015, 127, 3944; b) D. P. Hari, B. Konig, Chem. Commun. 2014, 50, 6688; c) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, Chem. Rev. 2013, 113, 5322; d) D. Ravelli, M. Fagnoni, A. Albini, Chem. Soc. Rev. 2013, 42, 97; e) H. Jiang, C. Huang, J. Guo, C. Zeng, Y. Zhang, S. Yu, Chem. Eur. J. 2012, 18, 15158; f) L. Shi, W. Xia, Chem. Soc. Rev. 2012, 41, 7687; g) J. Xuan, W.-J. Xiao, Angew. Chem. Int. Ed. 2012, 51, 6828; Angew. Chem. 2012, 124, 6934; h) J. M. R. Narayanam, C. R. J. Stephenson, Chem. Soc. Rev. 2011, 40, 102; i) R. A. Angnes, Z. Li, C. R. D. Correia, G. B. Hammond, Org. Biomol. Chem. 2015, 13, 9152; j) D. M. Schultz, T. P. Yoon, Science 2014, 343, 1239176; k) M. Reckenthäler, A. G. Griesbeck, Adv. Synth. Catal. 2013, 355, 2727.
- [2] a) J. D. Cuthbertson, D. W. C. MacMillan, *Nature* 2015, *519*, *74*; b) G.
   Palmisano, V. Augugliaro, M. Pagliaro, L. Palmisano, *Chem. Commun.* 2007, 3425; c) G. Pandey, D. Jadhav, S. K. Tiwari, B. Singh, *Adv. Synth. Catal.* 2014, *356*, 2813.
- [3] For selected recent publications on UV-light-mediated organic transformations, see: a) G. Pandey, S. Pal, R. Laha, *Angew. Chem. Int. Ed.* 2013, *52*, 5146; *Angew. Chem.* 2013, *125*, 5250; b) D. Cantillo, C. Mateos, J. A. Rincon, O. de Frutos, C. O. Kappe, *Chem. Eur. J.* 2015, *21*, 12894; c) K. Yamada, M. Okada, T. Fukuyama, D. Ravelli, M. Fagnoni, I. Ryu, *Org.Lett.* 2015, *17*, 1292.
- [4] For selected recent publications on visible-light photocatalysis, see:
  a) Q. Wei, J.-R. Chen, X.-Q. Hu, X.-C. Yang, B. Lu, W.-J. Xiao, Org.Lett. **2015**, *17*, 4464; b) C. C. Nawrat, C. R. Jamison, Y. Slutskyy, D. W. C. Mac-Millan, L. E. Overman, J. Am. Chem. Soc. **2015**, *137*, 11270; c) H. Huo, C. Wang, K. Harms, E. Meggers, J. Am. Chem. Soc. **2015**, *137*, 9551; d) J. Jin, D. W. C. MacMillan, Angew. Chem. Int. Ed. **2015**, *54*, 1565; Angew. Chem. **2015**, *127*, 1585; e) M. D. Karkas, B. S. Matsuura, C. R. J. Stephenson, Science **2015**, *349*, 1285; f) G. Pandey, R. Laha, Angew. Chem. Int. Ed. **2015**, DOI: 10.1002/anie.201506990.
- [5] a) S. Mühmel, D. Alpers, F. Hoffmann, M. Brasholz, Chem. Eur. J. 2015, 21, 12308; b) M. Nakajima, E. Fava, S. Loescher, Z. Jiang, M. Rueping,

Angew. Chem. Int. Ed. 2015, 54, 8828; Angew. Chem. 2015, 127, 8952; c) J. Xie, S. Shi, T. Zhang, N. Mehrkens, M. Rudolph, A. S. K. Hashmi, Angew. Chem. Int. Ed. 2015, 54, 6046; Angew. Chem. 2015, 127, 6144; d) L. Ruiz Espelt, I. S. McPherson, E. M. Wiensch, T. P. Yoon, J. Am. Chem. Soc. 2015, 137, 2452; e) J. W. Beatty, C. R. J. Stephenson, Acc. Chem. Res. 2015, 48, 1474; f) J. Hu, J. Wang, T. H. Nguyen, N. Zheng, Beilstein J. Org. Chem. 2013, 9, 1977; g) P. Kohls, D. Jadhav, G. Pandey, O. Reiser, Org. Lett. 2012, 14, 672; h) A. G. Condie, J. C. Gonzalez-Gomez, C. R. J. Stephenson, J. Am. Chem. Soc. 2010, 132, 1464; i) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny, D. C. Fabry, Chem. Commun. 2011, 47, 2360.

- [6] a) T. H. Nguyen, S. A. Morris, N. Zheng, Adv. Synth. Catal. 2014, 356, 2831; b) S. Maity, M. Zhu, R. S. Shinabery, N. Zheng, Angew. Chem. Int. Ed. 2012, 51, 222; Angew. Chem. 2012, 124, 226; c) J. Wang, N. Zheng, Angew. Chem. Int. Ed. 2015, 54, 536; Angew. Chem. 2015, 127, 546.
- [7] For selected recent articles and reviews on vinyl azides, see: a) B. Hu,
  S. G. DiMagno, Org. Biomol. Chem. 2015, 13, 3844; b) P. R. Adiyala, G. S.
  Mani, J. B. Nanubolu, K. C. Shekar, R. A. Maurya, Org. Lett. 2015, 17,
  4308; c) F.-L. Zhang, Y.-F. Wang, G. H. Lonca, X. Zhu, S. Chiba, Angew.
  Chem. Int. Ed. 2014, 53, 4390; Angew. Chem. 2014, 126, 4479; d) N.
  Jung, S. Brase, Angew. Chem. Int. Ed. 2012, 51, 12169; Angew. Chem.
  2012, 124, 12335; e) L. Xiang, Y. Niu, X. Pang, X. Yang, R. Yan, Chem.
  Commun. 2015, 51, 6598; f) W. Chen, M. Hu, J. Wu, H. Zou, Y. Yu, Org.
  Lett. 2010, 12, 3863.
- [8] For selected recent articles and reviews on photochemical reactions in flow microreactors, see: a) Y. Su, N. J. W. Straathof, V. Hessel, T. Noel, *Chem. Eur. J.* **2014**, *20*, 10562; b) X. Wang, G. D. Cuny, T. Noel, *Angew. Chem. Int. Ed.* **2013**, *52*, 7860; *Angew. Chem.* **2013**, *125*, 8014; c) K. Asano, Y. Uesugi, J.-i. Yoshida, *Org. Lett.* **2013**, *15*, 2398; d) M. Neumann, K. Zeitler, *Org. Lett.* **2012**, *14*, 2658; e) J. W. Tucker, Y. Zhang, T. F. Jamison, C. R. J. Stephenson, *Angew. Chem. Int. Ed.* **2012**, *51*, 4144; *Angew. Chem.* **2012**, *124*, 4220; f) E. K. Lumley, C. E. Dyer, N. Pamme, R. W. Boyle, *Org. Lett.* **2012**, *14*, 5724; g) D. Cantillo, O. de Frutos, J. A. Rincón, C. Mateos, C. O. Kappe, *J. Org. Chem.* **2014**, *79*, 8486; h) J. W. Beatty, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2014**, *136*, 10270; j) D. Cantillo, O. de Frutos, J. A. Rincón, C. Mateos, C. O. Kappe, *Org. Lett.* **2014**, *16*, 896.
- [9] a) R. A. Maurya, C. P. Park, D. P. Kim, *Beilstein J. Org. Chem.* 2011, *7*, 1158;
  b) C. P. Park, R. A. Maurya, J. H. Lee, D.-P. Kim, *Lab Chip* 2011, *11*, 1941;
  c) D. Chandrasekhar, S. Borra, J. S. Kapure, G. S. Shivaji, G. Srinivasulu,
  R. A. Maurya, *Org.Chem. Front.* 2015, *2*, 1308; d) A. Talla, B. Driessen,
  N. J. W. Straathof, L.-G. Milroy, L. Brunsveld, V. Hessel, T. Noel, *Adv. Synth. Catal.* 2015, *357*, 2180; e) N. J. W. Straathof, B. J. P. Tegelbeckers, V.
  Hessel, X. Wang, T. Noel, *Chem. Sci.* 2014, *5*, 4768.
- [10] a) E. P. Farney, T. P. Yoon, Angew. Chem. Int. Ed. 2014, 53, 793; Angew. Chem. 2014, 126, 812; b) J. Xuan, X.-D. Xia, T.-T. Zeng, Z.-J. Feng, J.-R. Chen, L.-Q. Lu, W.-J. Xiao, Angew. Chem. Int. Ed. 2014, 53, 5653; Angew. Chem. 2014, 126, 5759.
- [11] S.-I. Murahashi, T. Naota, H. Taki, J. Chem. Soc. Chem. Commun. 1985, 613.
- [12] a) S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, ACS Catal.
  2011, 1, 1150; b) L. Huang, J. Zhao, S. Guo, C. Zhang, J. Ma, J. Org. Chem. 2013, 78, 5627; c) G. Jiang, J. Chen, J.-S. Huang, C.-M. Che, Org. Lett. 2009, 11, 4568; d) X. Lang, W. Ma, Y. Zhao, C. Chen, H. Ji, J. Zhao, Chem. Eur. J. 2012, 18, 2624; e) F. Su, S. C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, Angew. Chem. Int. Ed. 2011, 50, 657; Angew. Chem. 2011, 123, 683.
- [13] a) C. J. Moody, J. Chem. Soc. Perkin Trans. 1 1987, 913; b) G. L'abbé, Angew. Chem. Int. Ed. Engl. 1975, 14, 775; Angew. Chem. 1975, 87, 831; c) K. Banert, B. Meier, E. Penk, B. Saha, E.-U. Wurthwein, S. Grimme, T. Ruffer, D. Schaarschmidt, H. Lang, Chem. Eur. J. 2011, 17, 1128; d) K. Banert, B. Meier, Angew. Chem. Int. Ed. 2006, 45, 4015; Angew. Chem. 2006, 118, 4120; e) X. Zhang, S. K. Sarkar, G. K. Weragoda, S. Rajam, B. S. Ault, A. D. Gudmundsdottir, J. Org. Chem. 2014, 79, 653.
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