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## Palladium-catalyzed oxidative cyclization of aniline-tethered alkylidenecyclopropanes with O<sub>2</sub>: a facile protocol to selectively synthesize 2- and 3-vinylindoles<sup>†</sup>

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A novel palladium-catalyzed oxidative cyclization of aniline-tethered alkylidenecyclopropanes using molecular oxygen as the terminal oxidant through  $\beta$ -carbon elimination of aminopalladation intermediates is disclosed. The reaction opens up an effective way to obtain a series of 2- and 3-vinylindoles which are important synthetic intermediates in many natural indole derivatives.

Indole derivatives are important structural motifs in many natural products and pharmaceuticals which exhibit a wide range of promising biological activities.<sup>1</sup> Moreover, 2- and 3-vinylindoles are key intermediates for the synthesis of biologically interesting polycyclic products.<sup>2</sup> During the past few decades, great efforts have been devoted to the development of efficient and practical strategies for the synthesis of these synthetic intermediates.<sup>3-7</sup> Although vinylindoles could be accessed through a variety of reactions such as Wittig,<sup>3</sup> cross-coupling,<sup>4</sup> S<sub>N</sub>2'-type,<sup>5</sup> elimination<sup>6</sup> or others,<sup>7</sup> current synthetic methodologies lack substrate diversity as functional indoles such as formylindole or haloindole or related species, possessing a leaving group, require an advanced preparation. Therefore, the development of novel strategies leading to a broad range of 2- and 3-substituted vinyl-indoles is still an on-going challenge that one needs to address.

Palladium-catalyzed aza-Wacker-type cyclization has been proved to be an effective approach for the preparation of indoles.<sup>8</sup> In this context, two distinct strategies have been explored to establish



Scheme 1 Pd-catalyzed aza-Wacker-type cycloaddition for the synthesis of indole.

the indole structures: (a) using terminal alkenes followed by a  $\beta$ -hydride elimination (Scheme 1, eqn (a))<sup>8,9</sup> and (b) using aryl substituted alkenes followed by an 1,2-aryl migratory reaction of the aminopalladated intermediate (Scheme 1, eqn (b)).<sup>10</sup> Inspired by these methodologies, and with the hope to construct at the same time the indole framework and the vinyl group, we hypothesized that the aminopalladated intermediate may undergo a β-carbon and a β-hydride eliminations continuously to form the required vinylindole in a single-pot operation bypassing the abovementioned two-step pathway. Based on this hypothesis and our ongoing efforts to explore novel synthetic routes to indole-fused scaffolds,<sup>11</sup> we decided to prepare ortho-aminoaryl-tethered alkylidenecyclopropanes from the important building blocks alkylidenecyclopropanes (ACPs),<sup>12</sup> with aniline.<sup>13</sup> Fortunately, we were delighted to observe that these substrates could undergo the above proposed cyclization to selectively give the desired 2- or 3-vinylindoles as described below (Scheme 1, eqn (c)).

We initially investigated the reaction of **1a**, as a model substrate, by employing  $Pd(OAc)_2$  as a palladium source and  $K_2CO_3$  as an additive in toluene at 100 °C under an atmosphere of  $O_2$  (balloon). Although in low yield (28%), we were pleased to observe that the reaction proceeded as expected to give 2-vinylindole **2a** 

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 $\label{eq:table_$ 

	Ph NHTs -	catalyst, additive oxidant, solvent, 100 °C, 12 h	Ph N 2a Ts		
Entry <sup>a</sup>	Catalyst	Additive (equiv.)	Solvent	Oxidant	Yield <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub>	$K_2CO_3$ (2.0)	Toluene	O <sub>2</sub>	$28(24)^c$
2	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub>	$K_2 CO_3 (2.0)$	Toluene	$O_2$	8
3	PdCl <sub>2</sub>	$K_2CO_3(2.0)$	Toluene	02	0
4	$Pd(dppb)Cl_2$	$K_2CO_3(2.0)$	Toluene	02	12
5	$Pd(PPh_3)_2Cl_2$	$K_2CO_3(2.0)$	Toluene	02	39 <sup>c</sup>
$6^d$	$Pd(PPh_3)_2Cl_2$	$KaCO_{3}(2.0)$	Toluene	BQ	19
$7^e$	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	$K_2CO_3(2.0)$	Toluene	CuCl <sub>2</sub>	13
8 <sup>f</sup>	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	$K_2CO_3(2.0)$	Toluene	AgOAc	13
9	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	$\tilde{KHCO}_3(1.0)$	Toluene	$O_2$	55
10	PdIPrCl <sub>2</sub>	$KHCO_3(1.0)$	Toluene	02	38
11	$Pd[P(4-MeOC_6H_4)_3]_2Cl_2$	$KHCO_3(1.0)$	Toluene	02	52
12	$Pd[P(4-FC_{6}H_{4})_{3}]_{2}Cl_{2}$	$KHCO_3(1.0)$	Toluene	02	64
13	$Pd[P(4-CF_{3}C_{6}H_{4})_{3}]_{2}Cl_{2}$	$KHCO_3(1.0)$	Toluene	02	$74(63)^{c}$
14	$Pd[P(C_6F_5)_3]_2Cl_2$	KHCO <sub>3</sub> (1.0)	Toluene	$\overline{O_2}$	8 )
$15^g$	$Pd[P(4-CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	Toluene	Air	50

<sup>*a*</sup> Reactions were performed with **1a** (0.2 mmol), additive and 10 mol% of catalyst in solvent (2.0 mL) under O<sub>2</sub> (1 atm; balloon) at 100 °C in 12 h. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Yield of the isolated products. <sup>*d*</sup> Using 2.0 equiv. BQ under Ar. <sup>*e*</sup> Using 2.0 equiv. CuCl<sub>2</sub> under Ar. <sup>*f*</sup> Using 2.0 equiv. AgOAc under Ar. <sup>*g*</sup> The reaction was performed in air.

(Table 1, entry 1). We then further screened different Pd-catalysts, such as Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, PdCl<sub>2</sub>, Pd(dppb)Cl<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Table 1, entries 2-5), and various typical aza-Wacker oxidants including BQ, CuCl<sub>2</sub> and AgOAc (Table 1, entries 6-8), but none of these conditions could offer a yield better than 39% (Table 1, entry 5). Additional screening of the nature of solvents and additives (for further details, see the ESI<sup>+</sup>) revealed that the presence of 1.0 equiv. of KHCO<sub>3</sub> in toluene provided the best result (55%, Table 1, entry 9). Next, the nature of ligands on palladium was tested, such as N-heterocyclic carbene and phosphine ligands with either electron-donating or electronwithdrawing substituents, and we were pleased to observe the formation of 2a in 74% yield when the complex  $Pd[P(4-CF_3C_6H_4)_3]_2Cl_2$ was used in the presence of  $KHCO_3$  (1.0 equiv.) in toluene under molecular oxygen at 100 °C within 12 h (Table 1, entry 13, for further details, see the ESI<sup>†</sup>).

Under the optimized conditions, we next surveyed the substrate scope of this reaction and the results are shown in Scheme 2. We first examined the effect of the position of substituents on the benzene ring. As for substrates **1b–1e**, the reactions proceeded smoothly to furnish the corresponding 2-vinylindoles **2b–2e** in yields ranging from 56% to 65% regardless of the positions of the substituents (*ortho-, meta-*, or *para*-position on the benzene ring). Then, the electronic effect at the *para*-position of the benzene ring was examined. Substrates with both electron-donating and electron-withdrawing groups could afford the desired products **2f–2k** in yields ranging from 33% to 70%. The structure of **2f** has been confirmed by X-ray diffraction analysis.<sup>14</sup> When substrates **11** (R<sup>1</sup> = Ph and R<sup>2</sup> = 5-Cl) and **1m** (R<sup>1</sup> = 2-ClC<sub>6</sub>H<sub>4</sub> and R<sup>2</sup> = 5-Cl) were tested, the corresponding products **2l** and **2m** were obtained in 59% and 60% yields, respectively. To further investigate the scope



Scheme 2 Substrate scope for the synthesis of 2-vinylindoles 2.<sup>a</sup>

of this reaction, we prepared functionalized substrates with a heteroaromatic group (furan 1n and thiophene 1o) or with an alkyl chain (methyl group 1p and *n*-butyl group 1q). The experimental results showed that 10 and 1q were suitable substrates for this reaction under the current reaction conditions, giving the corresponding products 20 and 2q in 40% and 45% yields, respectively. However, the yields of 2n and 2p were low, probably due to the formation of byproducts (for detailed information, see the ESI<sup>+</sup>). Other N-sulfonyl protecting groups such as 4-bromobenzene sulfonyl (Bs) 1r, 4-nitrobenzene sulfonyl (Ns) 1s and the N-carbonyl protecting group (Ac) 1t were compatible under these reaction conditions. To our delight, when using the substrate 1u without the protecting group on the nitrogen atom, the reaction still proceeded smoothly giving 2u in 31% yield. We also got the product 2u through detosylation of 2a in 81% yield.

However, when using the substrate **3a**, which has no substituent on the alkylidene moiety, the reaction proceeded to furnish the 3-vinylindole **4a** in 48% yield (Table 2, entry 5) rather than the 2-vinylindole. Taking into account the lessons from the previous transformation (**1** into **2**), we reinvestigated this reaction in detail. After screening the ligands of the catalysts and the additives, we found that when 10 mol% of Pd[P(4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub> and 1.0 equiv. of KHCO<sub>3</sub> were used in toluene under O<sub>2</sub> at 100 °C, the yield of **4a** could reach 60% (Table 2, entry 2).

With these optimized reaction conditions in hand, the substrate scope for 3 was explored and the results are shown in Scheme 3. Substrates 3 having both electron-donating and electron-withdrawing substituents ( $R^1$ ) at different positions of the aromatic ring were tolerated, providing the 3-vinylindole derivatives (4b–4g) in moderate yields ranging from 39% to 58%. In addition, when methyl sulfonyl and 2,4-dimethoxybenzene sulfonyl were used as the *N*-protecting

Table 2 Optimization of conditions for the Pd-catalyzed oxidative cyclization of  ${\bf 3a}$ 

	H Ja NHTs	catalyst, additive oxidant, solvent, 100 °C, 12 h	4a Ts		
Entry <sup>a</sup>	Catalyst	Additive (1.0 equiv.)	Solvent	Oxidant	Yield <sup>b</sup> (%)
1	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	KHCO3	Toluene	O <sub>2</sub>	41
2	$Pd[P(4-MeOC_6H_4)_3]_2Cl_2$	KHCO <sub>3</sub>	Toluene	$O_2$	$60(58)^{c}$
3	PdIPrCl <sub>2</sub>	KHCO <sub>3</sub>	Toluene	$O_2$	24
4	$Pd[P(4-FC_{6}H_{4})_{3}]_{2}Cl_{2}$	KHCO <sub>3</sub>	Toluene	$O_2$	56
5	$Pd[P(4-CF_{3}C_{6}H_{4})_{3}]_{2}Cl_{2}$	KHCO <sub>3</sub>	Toluene	$O_2$	48
6	$Pd[P(C_6F_5)_3]_2Cl_2$	KHCO <sub>3</sub>	Toluene	0 <sub>2</sub>	17
7	$Pd[P(4-MeOC_6H_4)_3]_2Cl_2$	NaHCO <sub>3</sub>	Toluene	0 <sub>2</sub>	39
8	$Pd[P(4-MeOC_6H_4)_3]_2Cl_2$	Na <sub>3</sub> PO <sub>4</sub>	Toluene	02	50
9	$Pd[P(4-MeOC_6H_4)_3]_2Cl_2$	NaOAc	Toluene	02	8
$10^d$	$Pd[P(4-MeOC_6H_4)3]_2Cl_2$	KHCO <sub>3</sub>	Toluene	$O_2$	45

<sup>*a*</sup> Reactions were performed with **1a** (0.2 mmol), additive and 10 mol% of catalyst in solvent (2.0 mL) under O<sub>2</sub> (1 atm; balloon) at 100 °C in 12 h. <sup>*b*</sup> Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>*c*</sup> Yield of the isolated products. <sup>*d*</sup> Using 2.0 equiv. KHCO<sub>3</sub>.



groups, the reactions took place efficiently to afford the corresponding 3-vinylindoles **4h** and **4i** in 55% and 48% yields, respectively.

To further investigate the reaction mechanism, two control experiments were performed and the results are shown in Scheme 4. 2-Vinylindole 5 could not be transformed into 3-vinylindole 6 under our standard reaction conditions, suggesting that 5 was not an intermediate in this reaction. Subsequently, a deuterium-labeling experiment was conducted to obtain more information on the mechanism. The treatment of [D]-7 with  $Pd[P(4-MeOC_6H_4)_3]_2Cl_2$  produced [D]-8 in 60% yield with 66% D content. The deuterium atom at the double bond of the ACP



Scheme 4 Control experiments to investigate the mechanism.



moiety was therefore transferred to the 2-position of the 3-vinylindole, shedding some light on the reaction mechanism.

On the basis of previous reports<sup>8,9</sup> and our control experiments, a plausible mechanism<sup>15</sup> for this reaction is outlined in Scheme 5. First, the electrophilic Pd(II) species coordinated with the substrate 1 or 3 activates the double bond of the ACPs to form complexes **A** or **D**. If  $R \neq H$ , **A** could undergo a 5-endo-aminopalladation to form **B**. Then following a  $\beta$ -carbon elimination, the Pd-alkyl intermediate C is obtained. Finally, the intermediate C undergoes a  $\beta$ -hydride elimination to form the product 2. The reduced Pd catalyst was then oxidized directly by molecular oxygen to regenerate the Pd(II) catalyst. However, if R = H, complex D would undergo a 4-exoaminopalladation to yield E. Following a  $\beta$ -aryl elimination, the Pd-aryl intermediate F would be formed and this process transfers the alkylidene cyclopropane to the aniline nitrogen and places Pd on the ortho-position of the aniline. Next, F undergoes a 5-endo-carbonpalladation to generate G. Subsequently, G could undergo a  $\beta$ -carbon elimination and a  $\beta$ -hydride elimination to form the product 4a. Another possible mechanism for the generation of 4a is outlined in the ESI.<sup>†</sup>

In conclusion, a facile and versatile palladium-catalyzed oxidative cyclization of aniline-tethered alkylidenecyclopropanes with molecular oxygen could selectively provide either 2- or 3-vinylindoles in moderate to good yields. Different reaction mechanisms have also been proposed on the basis of control experiments. Further investigations on expanding the scope of this reaction toward a variety of novel and potentially useful polycyclic indole derivatives as well as the application of this protocol to natural product synthesis are in progress.

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## Notes and references

- (a) R. J. Sundberg, The Chemistry of Indoles, Academic Press, New York, 1970; (b) Alkaloids Chemical and Biological Perspectives, ed. S. W. Pelletier, Wiley-Interscience, New York, 1983, vol. 4, p. 211;
   (c) R. J. Sundberg, Indoles, Academic Press, San Diego, 1996;
   (d) J. P. Michael, Nat. Prod. Rep., 1998, 15, 571; (e) D. J. Faulkner, Nat. Prod. Rep., 1999, 16, 155; (f) M. Lounasmaa and A. Tolvanen, Nat. Prod. Rep., 2000, 17, 175; (g) S. Cacchi and G. Fabrizi, Chem. Rev., 2005, 105, 2873; (h) G. R. Humphrey and J. T. Kuethe, Chem. Rev., 2006, 106, 2875.
- 2 (a) W. E. Noland, G.-M. Xia, K. R. Gee, M. J. Konkel, M. J. Wahlstrom, J. J. Condoluci and D. L. Rieger, Tetrahedron, 1996, 52, 4555; (b) C.-G. Yang, J. Wang, X.-X. Tang and B. Jiang, Tetrahedron: Asymmetry, 2002, 13, 383; (c) R. S. Kusurkar and S. K. Goswami, Tetrahedron, 2004, 60, 5315; (d) C. Gioia, A. Hauville, L. Bernardi, F. Fini and A. Ricci, Angew. Chem., Int. Ed., 2008, 47, 9236; (e) S. B. Jones, B. Simmons and D. W. C. MacMillan, J. Am. Chem. Soc., 2009, 131, 13606; (f) M. L. Bennasar, E. Zulaica, D. Sole, T. Roca, D. Garcia-Diaz and S. Alonso, J. Org. Chem., 2009, 74, 8359; (g) M. Amat, B. Checa, N. Llor, E. Molins and J. Bosch, Chem. Commun., 2009, 2935; (h) B. Cheng, J. D. Sunderhaus and S. F. Martin, Org. Lett., 2010, 12, 3622; (i) M. Amat, N. Llor, B. Checa, E. Molins and J. Bosch, J. Org. Chem., 2010, 75, 178; (i) C. Gioia, L. Bernardi and A. Ricci, Synthesis, 2010, 161; (k) C.-W. Zheng, Y.-P. Lu, J.-K. Zhang, X.-K. Chen, Z. Chai, W.-Y. Ma and G. Zhao, Chem. - Eur. J., 2010, 16, 5853; (l) B. Tan, G. Hernndez-Torres and C. F. Barbas III, J. Am. Chem. Soc., 2011, 133, 12354; (m) M. Mizutani, F. Inagaki, T. Nakanishi, C. Yanagihara, I. Tamai and C. Mukai, Org. Lett., 2011, 13, 1796; (n) B. D. Horning and D. W. C. MacMillan, J. Am. Chem. Soc., 2013, 135, 6442; (o) J. Jin and F.-G. Qiu, Adv. Synth. Catal., 2014, 356, 340; (p) M. L. Bennasar, D. Sole, T. Roca and M. Valldosera, Tetrahedron, 2015, 71, 2246; (q) B. Cheng, J. D. Sunderhaus and S. F. Martin, Tetrahedron, 2015, 71, 7323; (r) H. Zheng, X. Liu, C. Xu, Y. Xia, L. Lin and X. Feng, Angew. Chem., Int. Ed., 2015, 54, 10958.
- 3 (a) U. Pindur and M. Eitel, Helv. Chim. Acta, 1988, 71, 1060; (b) M. Eitel and U. Pindur, Synthesis, 1989, 364; (c) U. Pindur and L. Pfeuffer, Monatsh. Chem., 1989, 120, 157; (d) C. A. Faler and M. M. Joullie, Org. Lett., 2007, 9, 1987; (e) P. N. Naik, A. Khan and R. S. Kusurkar, Tetrahedron, 2013, 69, 10733; (f) S. Zhong, M. Nieger, A. Bihlmeier, M. Shi and S. Braese, Org. Biomol. Chem., 2014, 12, 3265.
- 4 (a) H. Hagiwara, T. Choshi, H. Fujimoto, E. Sugino and S. Hibino, *Chem. Pharm. Bull.*, 1998, 46, 1948; (b) A. Padwa, S. M. Lynch, J. M. Mejia-Oneto and H. Zhang, *J. Org. Chem.*, 2005, 70, 2206; (c) Z. Cui, Y.-J. Chen, W.-Y. Gao, C.-G. Feng and G.-Q. Lin, *Org. Lett.*, 2014, 16, 1016.
- 5 (a) Y. A. M. Mohamed, F. Inagaki, R. Takahashi and C. Mukai, *Tetrahedron*, 2011, **67**, 5133; (b) I. Ambrogio, A. Arcadi, S. Cacchi, G. Fabrizi, A. Goggiamani and F. Marinelli, *Tetrahedron*, 2013, **69**, 9494.
- 6 (a) U. Pindur, M. H. Kim and M. Eitel, *Tetrahedron Lett.*, 1990, 31, 1551; (b) J. Sapi, Y. Grebille, J. Y. Laronze and J. Levy, *Synthesis*, 1992, 383.
- 7 (a) B. Saroja and P. C. Srinivasan, Synthesis, 1986, 748;
  (b) T. Balasubramanian and K. K. Balasubramanian, J. Chem. Soc., Chem. Commun., 1994, 1237; (c) J.-Y. Merour, A.-S. Bourlot and E. Desarbre, Tetrahedron Lett., 1995, 36, 3527; (d) H. Lebel, M. Davi, S. Diez-Gonzalez and S. P. Nolan, J. Org. Chem., 2007, 72, 144; (e) W. E. Noland, C. L. Etienne and N. P. Lanzatella, J. Heterocycl. Chem., 2011, 48, 381; (f) K. Suzuki, H. Iwasaki, F. Ichiyoshi, M. Tominaga, N. Kojima,

M. Ozeki and M. Yamashita, *Heterocycles*, 2015, **91**, 1244; (g) Manisha, S. Dhiman, J. Mathew and S. S. V. Ramasastry, *Org. Biomol. Chem.*, 2016, **14**, 5563; (*h*) J.-b. Wang, R. Lonsdale and M. T. Reetz, *Chem. Commun.*, 2016, **52**, 8131.

- 8 (a) L. S. Hegedus, G. F. Allen and E. L. Waterman, J. Am. Chem. Soc., 1976, 98, 2674; (b) L. S. Hegedus, G. F. Allen, J. J. Bozell and E. L. Waterman, J. Am. Chem. Soc., 1978, 100, 5800; (c) P. J. Harrington and L. S. Hegedus, J. Org. Chem., 1984, 49, 2657; (d) L. S. Hegedus, Angew. Chem., Int. Ed., 1988, 27, 1113; (e) T. E. Müller and M. Beller, Chem. Rev., 1998, 98, 675; (f) P. J. Harrington, L. S. Hegedus and K. F. McDaniel, J. Am. Chem. Soc., 1987, 109, 4335; (g) T. Kondo, T. Okada and T.-a. Mitsudo, J. Am. Chem. Soc., 2002, 124, 186; (h) A. Minatti and K. Muñiz, Chem. Soc. Rev., 2007, 36, 1142; (i) R. I. McDonald, G. Liu and S. S. Stahl, Chem. Rev., 2011, 111, 2981.
- 9 (a) M. E. Krolski, A. F. Renaldo, D. E. Rudisill and J. K. Stille, J. Org. Chem., 1988, 53, 1170; (b) A. Kasahara, T. Izumi, S. Murakami, K. Miyamoto and T. Hino, J. Heterocycl. Chem., 1989, 26, 1405; (c) R. C. Larock, T. R. Hightower, L. A. Hasvold and K. P. Peterson, J. Org. Chem., 1996, 61, 3584; (d) M. Yamaguchi, M. Arisawa and M. Hirama, Chem. Commun., 1998, 1399; (e) D. R. Adams, M. A. J. Duncton, J. R. A. Roffey and J. Spencer, Tetrahedron Lett., 2002, 43, 7581; (f) D. Tsvelikhovsky and S. L. Buchwald, J. Am. Chem. Soc., 2010, 132, 14048; (g) S. W. Youn, J. H. Bihn and B. S. Kim, Org. Lett., 2011, 13, 3738.
- 10 S. W. Youn and S. R. Lee, Org. Biomol. Chem., 2015, 13, 4652.
- (a) L. Huang, H.-B. Yang, D.-H. Zhang, Z. Zhang, X.-Y. Tang, Q. Xu and M. Shi, *Angew. Chem., Int. Ed.*, 2013, 52, 6767; (b) Z. Zhang, X.-Y. Tang, Q. Xu and M. Shi, *Chem. Eur. J.*, 2013, 19, 10625; (c) L.-Y. Mei, Y. Wei, X.-Y. Tang and M. Shi, *J. Am. Chem. Soc.*, 2015, 137, 8131; (d) Y.-S. Zhang, X.-Y. Tang and M. Shi, *Org. Chem. Front.*, 2015, 2, 1516.
- 12 For selected reviews, see: (a) I. Nakamura and Y. Yamamoto, Adv. Synth. Catal., 2002, 344, 111; (b) E. Nakamura and S. Yamago, Acc. Chem. Res., 2002, 35, 867; (c) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, Chem. Rev., 2003, 103, 1213; (d) M. Rubin, M. Rubina and V. Gevorgyan, Chem. Rev., 2007, 107, 3117; (e) L.-X. Shao and M. Shi, Curr. Org. Chem., 2007, 11, 1135; (f) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, Chem. Soc. Rev., 2008, 37, 320; (g) M. Shi, L.-X. Shao, J.-M. Lu, Y. Wei, K. Mizuno and H. Maeda, Chem. Rev., 2010, 110, 5883; (h) H. Pellissier, Tetrahedron, 2010, 66, 8341; (i) G. Audran and H. Pellissier, Adv. Synth. Catal., 2010, 152, 575; (j) A. Masarwa and I. Marek, Chem. Eur. J., 2010, 16, 9712; (k) M. Shi, J.-M. Lu, Y. Wei and L.-X. Shao, Acc. Chem. Res., 2012, 45, 641; (l) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, Chem. Rev., 2014, 114, 7317; (m) H. Pellissier, Tetrahedron, 2014, 70, 4991.
- 13 (a) A. I. Siriwardana, M. Kamada, I. Nakamura and Y. Yamamoto, J. Org. Chem., 2005, 70, 5932; (b) K. Chen, Z. Zhang, Y. Wei and M. Shi, Chem. Commun., 2012, 48, 7696; (c) K. Chen, R. Sun, Q. Xu, Y. Wei and M. Shi, Org. Biomol. Chem., 2013, 11, 3949; (d) L.-Z. Yu, Q. Xu, X.-Y. Tang and M. Shi, ACS Catal., 2016, 6, 526; (e) L.-Z. Yu, X.-B. Hu, Q. Xu and M. Shi, Chem. Commun., 2016, 52, 2701; (f) L.-Z. Yu, Z.-Z. Zhu, X.-B. Hu, X.-Y. Tang and M. Shi, Chem. Commun., 2016, 52, 6581.
- 14 The crystal data of **2f** have been deposited in CCDC with number 1491285.
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