ORGANIC CHEMISTRY FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2018, **5**, 1466

Catalyst-controlled synthesis of 4-amino-isoquinolin-1(2*H*)-one and oxazole derivatives†

Ben Niu,[a] Ruixing Liu,[b] Yin Wei *[b] and Min Shi*[a,c,b]

Received 3rd February 2018,
Accepted 5th March 2018

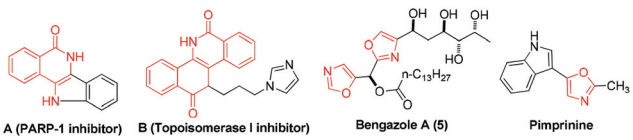
DOI: 10.1039/c8qo00125a

rsc.li/frontiers-organic

A facile synthetic method to access 4-amino-isoquinolin-1(2*H*)-one and oxazole derivatives was disclosed in this paper. The reaction of *N*-(pivaloyloxy)-amides with ynamides produced 4-amino-isoquinolin-1(2*H*)-ones in good yields in the presence of Cp*Rh(III) catalyst through a C–H bond functionalization. Using $Sc(OTf)_3$ as the catalyst, oxazole derivatives were obtained in good yields from the same reaction. This protocol features good functional group tolerance and excellent regioselectivity.

Isoquinolin-1(2*H*)-ones are probably the most ubiquitous heterocycles that widely exist in natural products, medicinal agents and functional materials.[1] Notably, 4-amino-isoquinolin-1(2*H*)-ones are also prevalent core structural units. Many compounds containing 4-amino-isoquinolin-1(2*H*)-one motifs exhibit potent biological activities.[1a–e] For example, molecule **A** is a new scaffold that can be used as a kind of PARP-1 inhibitor (Scheme 1). Compound **B** is designed as a topoisomerase I (Top1) inhibitor as shown in Scheme 1. Owing to their indispensable biomedical value, the exploration of their synthetic method has been carried out during the past few years. However, the methods that have been explored for the synthesis of 4-amino-isoquinolin-1(2*H*)-one frameworks are very limited and have some obvious drawbacks,[1a–e,2] such as harsh reaction conditions, multiple-step sequences and a longer reaction time. Therefore, it is quite urgent to develop simpler, general, and convenient processes for the synthesis of 4-amino-isoquinolin-1(2*H*)-one derivatives using easily available starting materials.

On the other hand, oxazoles are of great importance due to their presence in a number of biologically active compounds and pharmaceuticals,[3] such as bengazole A (5) and pimprinine (Scheme 1). They are also versatile synthetic blocks in organic synthesis.[4] During the past few decades, numerous outstanding studies to access oxazole molecules have been accomplished.[5,6] Among these synthetic methods, transition metal catalyses with Au,[5a–d] Pd,[5e] Ag,[5f] Cu,[5g–i] and Co[7] play a predominant role. For example, in 2011, Davies and co-workers employed conjugated *N*-ylides and ynamides to directly produce highly substituted and functionalized 1,3-oxazoles (Scheme 2, eqn (1)).[5c] In 2012, Jiang and co-workers developed a highly efficient copper-catalyzed aerobic transformation of internal alkynes and nitriles to functionalized 1,3-oxazoles (Scheme 2, eqn (2)).[5i] More recently, Wang's group explored a new method for the synthesis of 5-aminooxazoles by using Cp*Co(III) as a catalyst (Scheme 2, eqn (3)).[7] However, these procedures are often accompanied by complex metal catalysts, vigorous reaction conditions, and expensive or toxic reagents. Therefore, the development of straightforward and convenient methods for the synthesis of oxazoles is also of great significance and highly pursued in synthetic chemistry.



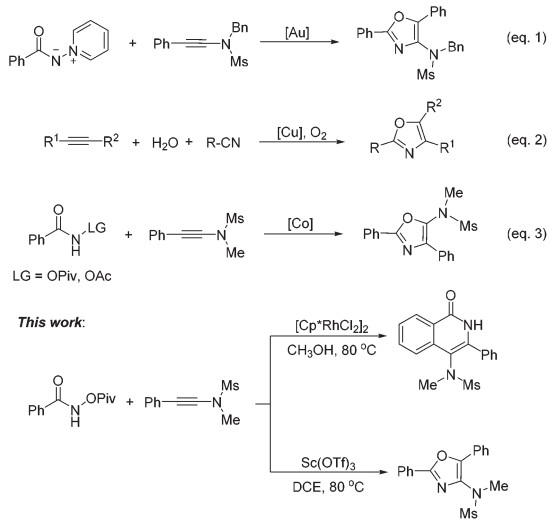
Scheme 1 Biologically active natural products containing 4-amino-isoquinolin-1(2*H*)-ones and oxazoles.

In this paper, we wish to report our new findings in the synthesis of 4-amino-isoquinolin-1(2*H*)-one and oxazole derivatives from the reaction of easily available *N*-(pivaloyloxy)-amides and ynamides using different metal catalysts (Scheme 2, this work).

In the past few decades, transition-metal-catalyzed direct C–H bond functionalization has emerged as a powerful tool for the formation of carbon–carbon and carbon–heteroatom bonds.[8] It is a classical reaction pattern that alkenes, alkynes,

[a]*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Meilong Road No. 130, Shanghai, 200237, China*
[b]*State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, University of Chinese Academy of Sciences, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, China. E-mail: weiyin@sioc.ac.cn, mshi@mail.sioc.ac.cn*
[c]*State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, P. R. China*

†Electronic supplementary information (ESI) available: Experimental procedures and characterization data of new compounds. CCDC 1545423 and 1545434. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8qo00125a



Scheme 2 Approaches for the synthesis of oxazoles.

allenes or arenes serve as active counterparts to cross-coupling with metallacyclic complexes derived from C–H bond activation to give various functionalized molecules (Fig. 1). We envisioned whether ynamides could be taken as compatible counterparts to directly form 4-amino-isoquinolin-1(2*H*)-one frameworks.

To test our hypothesis, we commenced our study with *N*-(pivaloyloxy)benzamide **1a** and *N*-methyl-*N*-(phenylethynyl) methanesulfonamide **2a** in the presence of Cp*Rh(III) (2 mol%) and CsOAc (1.0 eq.) in CH_3OH at 80 °C. To our delight, the desired product **3aa** was obtained in 85% yield (Table 1, entry 1). Various bases, such as LiOAc or NaOAc, were tested in the reaction, but they did not further improve the yield (Table 1, entries 2 and 3). Afterwards, we carried out this reaction in different solvents, such as acetonitrile, 1,2-dichloroethane and toluene (Table 1, entries 4–6), but none of the desired product was observed. Other metal catalysts such as $[Cp^*IrCl_2]_2$, $[Cp^*RuCl_2]_2$ and $[(p\text{-cymene})RuCl_2]_2$ did not catalyze the reaction (Table 1, entries 7–9). When CsF (1.0 eq.) was used as an additive, the reaction also performed very well, giving the desired product **3aa** in 85% yield (Table 1, entry 10). Next, we found that this reaction proceeded more smoothly when PivOH (1.0 eq.) was used as an additive under otherwise identical conditions, affording **3aa** in 87% yield (Table 1, entry 11). Based on the above results, we then performed this reaction at different temperatures, but no better results were obtained (entries 12–15). Therefore, we identified that the reaction should be carried out in MeOH and $[Cp^*RhCl_2]_2$ should

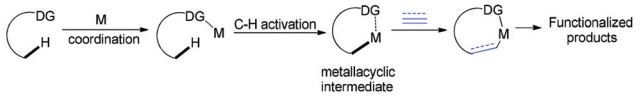
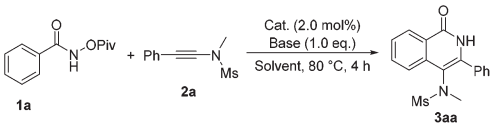


Fig. 1 The general reaction pattern of C–H bond activation with the unsaturated bond.

Table 1 Optimization of the reaction conditions for the synthesis of **3aa**



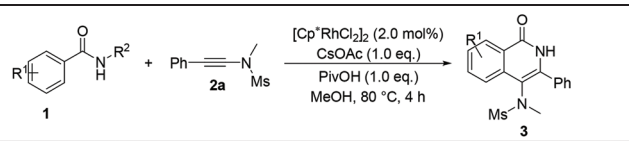
Entry[a]	Cat.	Additive	Base	Solvent	Yield[b], %
1	$[Cp^*RhCl_2]_2$	—	CsOAc	MeOH	85
2	$[Cp^*RhCl_2]_2$	—	LiOAc	MeOH	82
3	$[Cp^*RhCl_2]_2$	—	NaOAc	MeOH	69
4	$[Cp^*RhCl_2]_2$	—	CsOAc	DCE	nr
5	$[Cp^*RhCl_2]_2$	—	CsOAc	MeCN	nr
6	$[Cp^*RhCl_2]_2$	—	CsOAc	Toluene	nr
7	$[Cp^*IrCl_2]_2$	—	CsOAc	MeOH	nr
8	$[Cp^*RhCl_2]_2$	—	CsOAc	MeOH	nr
9	$[(p\text{-Cymene})RuCl_2]_2$	—	CsOAc	MeOH	nr
10	$[Cp^*RhCl_2]_2$	CsF	CsOAc	MeOH	85
11	**$[Cp^*RhCl_2]_2$**	**PivOH**	**CsOAc**	**MeOH**	**87**
12[c]	$[Cp^*RhCl_2]_2$	PivOH	CsOAc	MeOH	59
13[d]	$[Cp^*RhCl_2]_2$	PivOH	CsOAc	MeOH	67
14[e]	$[Cp^*RhCl_2]_2$	PivOH	CsOAc	MeOH	79
15[f]	$[Cp^*RhCl_2]_2$	PivOH	CsOAc	MeOH	73

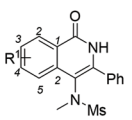
[a] The reactions were carried out using **1a** (0.2 mmol), **2a** (0.2 mmol), cat. (2.0 mol%), base (1.0 eq.) and solvent (2.0 mL) in a Schlenk tube. [b] Isolated yields. [c] T = RT. [d] T = 40 °C. [e] T = 60 °C. [f] T = 100 °C.

be used as the catalyst with CsOAc as a base in the presence of PivOH (Table 1, entry 11).

Having the optimized reaction conditions in hand, we examined the scope of benzamides bearing diverse substituents on the aromatic ring and the results are shown in Table 2. When the leaving group R^2 is the OPiv anion, we first examined the electronic effect at the *para*-position of the benzene ring. As for substrates **1b–1h**, regardless of whether they have electron-rich or electron-poor aromatic rings, the reactions could proceed smoothly to furnish the desired products **3ba–3ha** in 61–88% yields. The corresponding disubstituted sub-

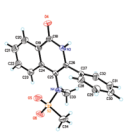
Table 2 Substrate scope of benzamides[a]





R^1 = H, R^2 = OPiv, **3aa**, 87%
R^1 = 4-OMe, R^2 = OPiv, **3ba**, 71%
R^1 = 4-Me, R^2 = OPiv, **3ca**, 85%
R^1 = 4-CF_3, R^2 = OPiv, **3da**, 61%
R^1 = 4-I, R^2 = OPiv, **3ea**, 81%
R^1 = 4-Cl, R^2 = OPiv, **3fa**, 80%
R^1 = 4-CN, R^2 = OPiv, **3ga**, 78%
R^1 = 4-NO_2, R^2 = OPiv, **3ha**, 88%
R^1 = 3,5-Me, R^2 = OPiv, **3ia**, 71%
R^1 = 2-Me, R^2 = OPiv, nr

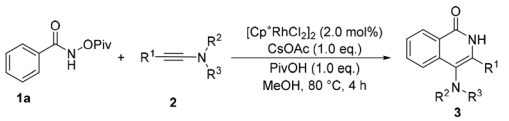
R^1 = H, R^2 = OMe, **3aa**, 60%
R^1 = H, R^2 = OFmoc, nr
R^1 = H, R^2 = OPh, **3aa**, 33%
R^1 = H, R^2 = OBz, **3aa**, 71%
R^1 = H, R^2 = OBoc, **3aa**, 62%

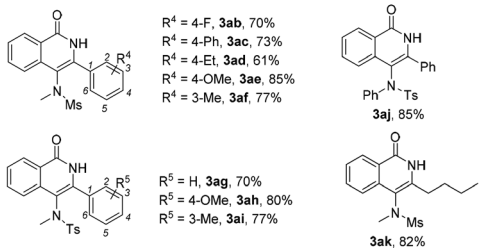


x-ray crystal structure of **3aa**

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (2.0 mol%), CsOAc (1.0 eq.) and PivOH (1.0 eq.) in MeOH at 80 °C for 4 h.

Table 3 Substrate scope of ynamides[a]





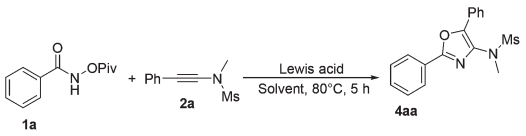
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.0 mol%), CsOAc (1.0 eq.) and PivOH (1.0 eq.) in MeOH at 80 °C for 4 h.

strate (3,5-dimethyl) was also tolerated under the identical conditions, providing the desired product **3ia** in 71% yield. However, the *ortho*-substituted substrate could not be transformed into the desired product. When R^2 was replaced by other leaving groups, including OMe, OPh, OBz, and OBoc, the yield of **3aa** was inferior to that of the OPiv leaving group. The use of OFmoc as the leaving group did not give the desired product. The structure of **3aa** has been unequivocally determined by X-ray diffraction and its ORTEP drawing is shown in Table 2.[9]

Subsequently, the substrate scope of ynamides was also investigated and the results are summarized in Table 3. First, ynamides containing aryls were investigated. When R^2 and R^3 were mesly and methyl groups, the effect of R^4 group at the benzene ring was first examined. We found that a variety of substituents were well tolerated, regardless of their electronic nature and the substituted position at the benzene ring, affording the corresponding products **3ab–3af** in good yields. Moreover, the R^2 and R^3 groups at the nitrogen atom were also explored and the reaction of *N*-tosyl ynamide and *N*-phenyl ynamide with **1a** proceeded efficiently, providing the desired products **3ag–3aj** in 70%–85% yields. Furthermore, alkyl-substituted ynamide also exhibited high reactivity in this reaction, and the corresponding product was obtained in 82% yield (**3ak**).

Based on previous studies,[10] ynamides could be activated by acids to form the corresponding keteniminium species. Therefore, we envisaged whether a Lewis acid could catalyze this reaction in a totally different reaction mode. Therefore, we turned our attention to investigate the reaction of *N*-(pivaloyloxy)benzamide **1a** with *N*-methyl-*N*-(phenylethynyl)methanesulfonamide **2a** in the presence of a catalytic amount of the Lewis acid. Initially, we performed the reaction in DCE using $AgSbF_6$ as the catalyst, and found that the desired cycloadduct **4aa** was obtained in 55% yield (Table 4, entry 1). This result encouraged us to further optimize the reaction conditions for the synthesis of product **4aa**. Next, we examined a set of Lewis

Table 4 Optimization of the reaction conditions[a]



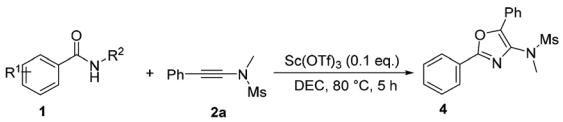
Entry[a]	Lewis acid	Solvent	Yield (%)
1	$AgSbF_6$	DCE	55
2	$Sc(OTf)_3$	DCE	78
3	$In(OTf)_3$	DCE	70
4	$Eu(OTf)_3$	DCE	21
5	$Yb(OTf)_3$	DCE	17
6	CF_3COOH	DCE	nr
7	$Sc(OTf)_3$	CH_3OH	nr
8	$Sc(OTf)_3$	CH_3CN	Trace
9[b]	**$Sc(OTf)_3$**	**DCE**	**80**
10[c]	$Sc(OTf)_3$	DCE	35

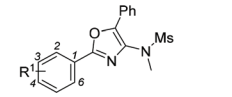
[a] The reactions were carried out using **1a** (0.2 mmol), **2a** (1.3 eq.), Lewis acid (0.2 eq.) and solvent (2.0 mL) in a Schlenk tube. [b] Lewis acid (0.1 eq.). [c] At room temperature.

acids and found that $Sc(OTf)_3$ afforded **4aa** in higher yield (78%) and inferior results were obtained when $In(OTf)_3$, $Yb(OTf)_3$ or $Eu(OTf)_3$ was used as the catalyst under identical conditions (Table 4, entries 2–5). However, a Brønsted acid such as CF_3COOH failed to transform the corresponding substrates into the desired product (Table 4, entry 6). We also screened several different solvents, such as CH_3OH and CH_3CN, but the desired product was not acquired (Table 4, entries 7 and 8). Reducing the catalyst loading to 0.1 eq. improved the yield of **5aa** to 80% (Table 4, entry 9). Finally, we identified that carrying out the reaction at room temperature afforded the desired product **5aa** in 35% yield, which is different from the previous work reported by Wang and Li (Table 4, entry 10).[7]

Under the optimized conditions, we next surveyed the substrate scope of benzamides and the results are shown in Table 5. When the leaving group R^2 is the OPiv anion, we first

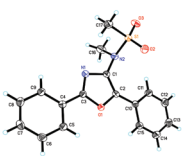
Table 5 Substrate scope of benzamides[a]





5

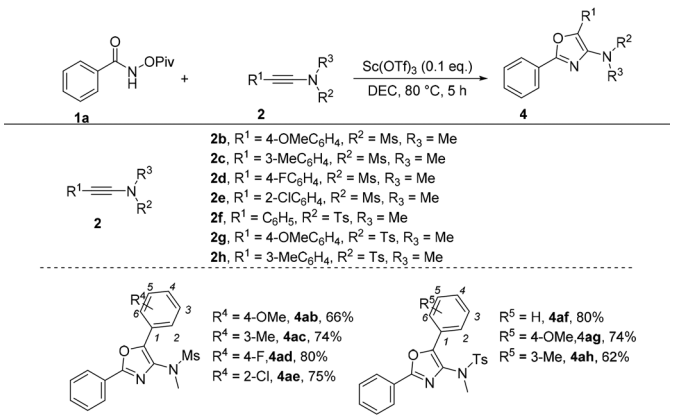
R1 = H, R2 = OPiv, **4aa**, 80%
R1 = 3,5-Me, R2 = OPiv, **4ba**, 65%
R1 = 2-Me, R2 = OPiv, **4ca**, 75%
R1 = 4-CF3, R2 = OPiv, **4da**, 55%
R1 = 4-Me, R2 = OPiv, **4ea**, 71%
R1 = 4-Br, R2 = OPiv, **4fa**, 70%
R1 = H, R2 = OBz, **4aa**, 34%
R1 = H, R2 = OMe, **4aa**,42%
R1 = H, R2 = OBoc, **4aa**, 31%



x-ray crystal structure of **4aa**

[a] The reactions were carried out using **1a** (0.2 mmol), **2a** (1.3 eq.), $Sc(OTf)_3$ (0.1 eq.) and DCE (2.0 mL) in a Schlenk tube.

Table 6 Substrate scope of ynamides[a]



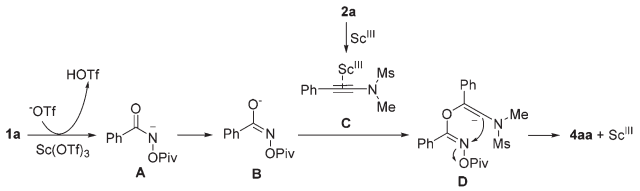
[a] The reactions were carried out using **1a** (0.2 mmol), **2** (1.3 eq.), $Sc(OTf)_3$ (0.1 eq.) and DCE (2.0 mL) in a Schlenk tube.

examined the disubstituted and *ortho*-substituted substrates and found that they were well tolerated under the optimal reaction conditions, providing the desired products **4ba** and **4ca** in 65% and 75% yields, respectively. The electronic effect at the *para*-position of the benzene ring was then examined. Regardless of whether they have electron-rich or electron-poor substitution groups, all of the reactions proceeded smoothly to furnish the desired products **4da–4fa** in 55–71% yields. The structure of **4aa** has been unambiguously determined by X-ray diffraction and its ORTEP drawing is shown in Table 5.[11] However, benzamides bearing other leaving groups, including OMe, OBz, and OBoc, afforded the corresponding products in poor yields.

Subsequently, the optimized reaction conditions were then challenged with the diversity of ynamides by taking **1a** as the reaction partner (Table 6). First, when R^2 and R^3 were Me and Ms groups, a diversified range of substituents on the benzene ring including both electron-donating and electron-withdrawing groups at the *para*-position were tolerated, giving the corresponding products **4ab** and **4ad** in 66 and 80% yields, respectively. In the case of the *meta*-substituted substrate (3-methyl) or *ortho*-substituted substrate (2-chloro), the reactions also performed very well, providing the corresponding products **4ac** and **4ae** in 74% and 75% yields, respectively. When R^2 and R^3 were tosyl and methyl groups, the desired products **4af–4ah** were achieved in 62%–80% yields.

A plausible reaction mechanism for the formation of **4aa** is proposed in Scheme 3. Intermediate **A** is formed upon the treatment of **1a** with $Sc(OTf)_3$, which undergoes an isomerization to give intermediate **B**. The reaction of intermediate **B** with intermediate **C**, generated upon the activation of **2a** with $Sc(OTf)_3$, provides intermediate **D**. Next, the desired product **4aa** is formed through an intramolecular nucleophilic attack along with the release of the OPiv anion.

In summary, we have developed an efficient and convenient synthetic protocol to produce oxazole or 4-amino-isoquinolin-1(2*H*)-one derivatives from the reaction of *N*-(pivaloyloxy)-



Scheme 3 A plausible reaction mechanism.

amides with ynamides by employing different metal catalysts. In the presence of Cp*Rh(III) catalyst, 4-amino-isoquinolin-1(2*H*)-one derivatives could be produced in good yields under mild reaction conditions. The use of $Sc(OTf)_3$ as the catalyst gave oxazole derivatives in good yields. The reaction can be performed with easily available starting materials and exhibits a broad substrate scope along with moderate to good yields and good functional group tolerance.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We are grateful for the financial support from the National Basic Research Program of China (973)-2015CB856603, the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDB20000000 and sioczz201808, the National Natural Science Foundation of China (20472096, 21372241, 21572052, 20672127, 21421091, 21372250, 21121062, 21302203, 20732008, 21772037 and 21772226), and the Fundamental Research Funds for the Central Universities 222201717003.

Notes and references

1 (*a*) L. h. Li and W. K. S. Chua, *Tetrahedron Lett.*, 2011, **52**, 1574; (*b*) V. Tyagi, S. Khan, A. Giri, H. M. Gauniyal, B. Sridhar and P. M. S. Chauhan, *Org. Lett.*, 2012, **14**, 3126; (*c*) J. Chen, H. Peng, J. He, X. Huan, Z. Miao and C. Yang, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 2669; (*d*) E. Kiselev, N. Empey, K. Agama, Y. Pommier and M. Cushman, *J. Org. Chem.*, 2012, **77**, 5167; (*e*) P. G. Jagtap, E. Baloglu, G. Southan, W. Williams, A. Roy, A. Nivorozhkin, N. Landrau, K. Desisto, A. L. Salzman and C. Szabó, *Org. Lett.*, 2005, **7**, 1753; (*f*) A. Saeed and Z. Ashraf, *Pharm. Chem. J.*, 2008, **42**, 277; (*g*) J. H. Rigby, U. S. M. Maharoof and M. E. Mateo, *J. Am. Chem. Soc.*, 2000, **122**, 6624; (*h*) V. A. Glushkov and Y. V. Shklyaev, *Chem. Heterocycl. Compd.*, 2001, **37**, 663.

2 G. Tan, X. Huang, Q. Wu, L.-Q. Zhang and J. You, *RSC Adv.*, 2014, **4**, 49186. You's work revealed that more reaction

time (16 h) was required when the methoxyl group was used as the leaving group.

3 (*a*) D. Davyt and G. Serra, *Mar. Drugs*, 2010, **8**, 2755; (*b*) Z. Jin, *Nat. Prod. Rep.*, 2006, **23**, 464; (*c*) S. Heng, K. R. Gryncel and E. R. Kantrowitz, *Bioorg. Med. Chem.*, 2009, **17**, 3916; (*d*) J. A. Bull, E. P. Balskus, R. A. J. Horan, M. Langner and S. V. Ley, *Angew. Chem., Int. Ed.*, 2006, **45**, 6714; (*e*) I. E. Kibriz, M. Sacmaci, E. Sahin and I. P. Yildirim, *Tetrahedron*, 2017, **73**, 1795; (*f*) X. Wu, X. Geng, P. Zhao, J. Zhang, Y. Wu and A. Wu, *Chem. Commun.*, 2017, **53**, 3438; (*g*) C. Wan, L. Gao, Q. Wang, J. Zhang and Z. Wang, *Org. Lett.*, 2010, **12**, 3902; (*h*) G. Jégou and S. A. Jenekhe, *Macromolecules*, 2001, **34**, 7926; (*i*) H. Tong, L. Wang, X. Jing and F. Wang, *Macromolecules*, 2003, **36**, 2584; (*j*) V. S. C. Yeh, *Tetrahedron*, 2004, **60**, 11995.

4 (*a*) J. M. Atkins and E. Vedejs, *Org. Lett.*, 2005, **7**, 3351; (*b*) E. Vedejs and D. A. Barda, *Org. Lett.*, 2000, **2**, 1033; (*c*) A. V. Gulevich, A. S. Dudnik, N. Chernyak and V. Gevorgyan, *Chem. Rev.*, 2013, **113**, 3084.

5 (*a*) Y. Luo, K. Ji, Y. Li and L. Zhang, *J. Am. Chem. Soc.*, 2012, **134**, 17412; (*b*) I. Cano, E. Alvarez, M. C. Nicasio and P. J. Perez, *J. Am. Chem. Soc.*, 2011, **133**, 191; (*c*) P. W. Davies, A. Cremonesi and L. Dumitrescu, *Angew. Chem., Int. Ed.*, 2011, **50**, 8931; (*d*) A. D. Gillie, R. J. Reddy and P. W. Davies, *Adv. Synth. Catal.*, 2016, **358**, 226; (*e*) J. Zheng, M. Zhang, L. Huang, X. Hu, W. Wu, H. Huang and H. Jiang, *Chem. Commun.*, 2014, **50**, 3609; (*f*) Y. Hu, R. Yi, F. Wu and B. Wan, *J. Org. Chem.*, 2013, **78**, 7714; (*g*) W. He, C. Li and L. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 8482; (*h*) C. Wan, J. Zhang, S. Wang, J. Fan and Z. Wang, *Org. Lett.*, 2010, **12**, 2338; (*i*) X. Li, L. Huang, H. Chen, W. Wu, H. Huang and H. Jiang, *Chem. Sci.*, 2012, **3**, 3463; (*j*) D. R. Williams and L. Fu, *Org. Lett.*, 2010, **12**, 808; (*k*) D. Bonne, M. Dekhane and J. P. Zhu, *Angew. Chem., Int. Ed.*, 2007, **46**, 2485.

6 For some selected reviews, see: (*a*) A. V. Gulevich, A. S. Dudnik, N. Chernyak and V. Gevorgyan, *Chem. Rev.*, 2013, **113**, 3084; (*b*) A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180.

7 X.-L. Han, C.-J. Zhou, X.-G. Liu, S.-S. Zhang, H. Wang and Q. Li, *Org. Lett.*, 2017, **19**, 6108. According to Li and co-workers, they did not find that $Sc(OTf)_3$ could catalyze this transformation at room temperature.

8 (*a*) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174; (*b*) X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2009, **48**, 5094; (*c*) G. Song, F. Wang and X. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651; (*d*) B. Liu, F. Hu and B.-F. Shi, *ACS Catal.*, 2015, **5**, 1863; (*e*) J.-W. Xu, Z.-Z. Zhang, W.-H. Rao and B.-F. Shi, *J. Am. Chem. Soc.*, 2016, **138**, 10750; (*f*) X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2009, **121**, 5196; (*g*) B. Ye and N. Cramer, *Acc. Chem. Res.*, 2015, **48**, 1308; (*h*) J. Wencel-Delord, T. Droge, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, **40**, 4740; (*i*) G. Rouquet and N. Chatani, *Angew. Chem., Int. Ed.*, 2013, **125**, 11942; (*j*) Y. Zhao, S. Li, X. Zheng, J. Tang, Z. She, G. Gao and J. You, *Angew. Chem., Int. Ed.*, 2017, **56**, 4286; (*k*) Z. Long, Y. Yang and J. You, *Org. Lett.*, 2017, **19**, 2781.

9 The crystal data of **3aa** have been deposited in CCDC with number 1545434.†

10 G. Evano, M. Lecomte, P. Thilmany and C. Theunissen, *Synthesis*, 2017, 3183.

11 The crystal data of **4aa** have been deposited in CCDC with number 1545423.†

