View Article Online View Journal



# Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Cai, Z. Zhou, W. Wu, B. Yao, S. Zhang and X. Li, *Org. Biomol. Chem.*, 2016, DOI: 10.1039/C6OB01765G.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/obc

### Journal Name

### ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



## Pd-Catalyzed C(sp<sup>3</sup>)-C(sp<sup>2</sup>) Cross-Coupling of Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> with Vinyl Bromides and Triflates

Guilong Cai, Zhibing Zhou, Wenchao Wu, Bo Yao,\* Shaowen Zhang, and Xiaofang Li\*

Pd-catalyzed C(sp<sup>3</sup>)-C(sp<sup>2</sup>) cross-coupling of Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> with vinyl bromides and triflates had been developed for efficient synthesis of various allyltrimethylsilanes. The cross-coupling reaction was conducted under room temperature with low catalyst loading of either Pd(PPh<sub>3</sub>)<sub>4</sub> or Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and exhibited high efficiency and broad substrate scope. In combination of the cross-coupling with Lewis-acid catalyzed Hosomi-Sakurai reaction, a novel three-component one-pot cascade reaction was then accomplished to deliver homoallylic alcohols and ethers with high regioselectivity and diastereoselectivity. The three-component reaction defined the yttrium complex as a novel one-carbon synthon, which could either trigger bifunctionalization of alkenes or link two electrophiles and would find applications in organic synthesis.

### Introduction

Published on 18 August 2016. Downloaded by Cornell University Library on 18/08/2016 14:35:45.

Organometallic chemistry of rare-earth metals has been extensively studied in the past several decades.<sup>1</sup> Rare-earth metal alkyl/aryl complexes were often applied as reactants or catalysts in organic transformations and polymerizations.<sup>2,3,4</sup> Although these compounds were proposed to be key intermediates in many reactions, examples on organic reactions using discrete organorare-earth metal complexes as reactants were rare. In 1984, Fujiwara reported the first cross-coupling reaction of rare-earth metal aryl complexes (PhYbI) with organic halides by transition-metal catalysis.<sup>5</sup> In 2010, Knochel reported a novel method for the preparation of triaryl lanthanum (Ar<sub>3</sub>La) and demonstrated efficient cross-coupling of these reagents with aryl iodides in the presence of  $Pd(PPh_3)_4$ .<sup>6</sup> Besides these reports, Molander and his coworkers discovered that lanthanide salts exhibited positive effects in Pd-catalyzed C(sp<sup>3</sup>)-C(sp<sup>2</sup>) cross-coupling of triethylaluminium with aryl bromides. They proposed that ethyl lanthanide complexes might be formed in-situ and act as the actual coupling partner.7

Homoleptic rare-earth metal trialkyl/triaryl complexes are a type of important compounds with unique structural properties and reactivity.<sup>8</sup> The stability and reactivity of these complexes is highly dependent on the relative sizes of the ligands to the central metals. Due to the steric bulk of the trimethylsilylmethyl ligands, Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> exhibited proper stability and good reactivity at ambient temperature and therefore were widely used as starting materials in organorare-earth metal chemistry.<sup>8,9</sup> With Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> as the coupling partner,

we recently reported the first Pd-catalyzed C(sp<sup>3</sup>)-C(sp<sup>2</sup>) crosscoupling of discrete rare-earth metal alkyl complexes with aryl bromides.<sup>10</sup> The reaction delivered a variety of benzyltrimethylsilanes with diverse functional groups efficiently under mild conditions (Scheme 1). Furthermore, αfound to be coupled with bromostyrene was also  $Ln(CH_2SiMe_3)_3(THF)_2$ to furnish the corresponding allyltrimethylsilane, albeit in moderate yield.

Allylsilanes are a type of bench-stable nucleophilic allylation reagents in organic synthesis. They have broad applications in the synthesis of homoallylic alcohols<sup>11</sup> and amines,<sup>12</sup> ethers,<sup>13</sup>



Scheme 1. Application of Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>n</sub> as a one-carbon synthon

<sup>&</sup>lt;sup>a.</sup> Key Laboratory of Cluster Science of Ministry of Education, School of Chemistry, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, China. E-mail: yaobo@bit.edu.cn, xfli@bit.edu.cn.

<sup>&</sup>lt;code>+Electronic Supplementary Information (ESI)</code> available: Experimental details, compound characterization, copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. See DOI: 10.1039/x0xx00000x

### ARTICLE

unsaturated ketones<sup>14</sup> and so on by Lewis acid-catalyzed Hosomi-Sakurai reactions with eletrophiles.<sup>15</sup> Although many synthetic methods for the preparation of allylsilanes existed,<sup>16</sup> development of new methods by transition metal catalysis<sup>17</sup> remains significant. In connection with our ongoing project in application of organorare-earth metal complexes to organic synthesis, we developed Pd-catalyzed cross-coupling of Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> with vinyl bromides and triflates for the construction of allyltrimethylsilanes. Since the obtained allyltrimethylsilanes could undergo the Hosomi-Sakurai reaction with carbon electrophiles, we further developed a three-component reaction<sup>18</sup> by a one-pot cascade method to give homoallylic alcohols and ethers efficiently (Scheme 1). This three-component reaction applied Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> as a novel nucleophilic one-carbon synthon<sup>19</sup> to trigger bifunctionalization of alkenes (Type A) or to link two electrophilic moieties (Type B).

### **Results and discussion**

Published on 18 August 2016. Downloaded by Cornell University Library on 18/08/2016 14:35:45.

#### Cross-Coupling of Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> with Vinyl Bromides

We commenced our study with the investigation of the crosscoupling of  $Y(CH_2SiMe_3)_3(THF)_2$  **1** with vinyl bromides. When abromostyrene **2a** was chosen as the test substrate, several Pd catalyst/ligand systems were screened. Under the Pd<sub>2</sub>(dba)<sub>3</sub>/XPhos conditions, which were optimal for the crosscoupling of  $Y(CH_2SiMe_3)_3(THF)_2$  **1** with aryl bromides,<sup>10</sup> abromostyrene **2a** was coupled with **1** smoothly to deliver allyltrimethylsilane **3a** in moderate yield (76%). Further screening other palladium catalysts showed that both of the less bulky ligand coordinated Pd(0) complex Pd(PPh<sub>3</sub>)<sub>4</sub> and the air-stable Pd(II) complex Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> exhibited better catalytic

Table 1. Cross-coupling of 1 with vinyl bromides 2<sup>a</sup>



 $^{o}Conditions:$  Vinyl bromide 2 (1.0 equiv., 0.3 mmol), Pd(PPh\_3)\_2Cl\_2 (1 mol%), Y(CH\_2SiMe\_3)\_3(THF)\_2 (0.33 equiv., 0.1 mmol), dry toluene (4 mL) at room temperature, N\_2, 1 h.

equiv., 0.1 mmol), vinyl bromide (1 equiv., 0.3 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (1 mol%), toluene (4 mL), room temperature, 1 h. Several a-bromostyrene derivatives bearing methyl, ethyl and methoxy groups were found to be coupled with the yttrium the 1 nicely afford complex to corresponding allyltrimethylsilanes (**3b-3d**) in very excellent yield. And  $\beta$ bromostyrenes prepared from cinnamic acid and its derivatives were also coupled with 1 to deliver the coupling products (3e-3h) in almost quantitative yield. It is worthwhile to mention that functional groups such as chlorine and bromine on the phenyl rings were well tolerated. The functional groups in the products provided a handle for further transformations (Scheme 3).

### Cross-Coupling of Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> with Vinyl Triflates

To further enlarge the substrate scope of the cross-coupling reaction for the synthesis of allyltrimethylsilanes, we continued to test vinyl triflates **4** as the coupling partners because they could be easily accessible from a large number of commercial ketones and aldehydes. Initial study on the model reaction of 1-phenylvinyl triflate **4a** with  $Y(CH_2SiMe_3)_3(THF)_2$  **1** in the presence of various palladium catalysts revealed that Pd(PPh\_3)<sub>4</sub>





<sup>a</sup>Conditions: Vinyl triflate **4** (1.0 equiv., 0.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1 mol%), Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (0.33 equiv., 0.1 mmol), dry toluene (4 mL) at room temperature. N<sub>2</sub>. 45 min.

Journal Name

### Journal Name

was the best catalyst and the cross-coupling product 5a was isolated in 96% yield under the new optimum conditions. Then a series of acyclic 1-aryl-vinyl triflates were synthesized from various methyl ketones and the cross-coupling of them furnished the allyltrimethylsilanes (5b-5e) in the yield as high as the reactions of vinyl bromides. And a lot of cyclic vinyl triflates prepared from cyclic ketones were also found to be coupled with the yttrium complex 1 very well, delivering the desired products (5f-5k) in very excellent yield. Both electron-donating methyl (5b and 5d), tert-butyl (5c), and methoxy (5h) groups, and electron-withdrawing chlorine (5i) and bromine (5j) in these substrates were well tolerated. Particularly, the aromatic C-Cl and C-Br bonds in the products could be further transformed into various C-C and C-heteroatom bonds by many synthetic methods. The cross-coupling of 2,2-diphenylvinyl triflate 4I gave the corresponding product (5I) in much lower yield than other reactions.

### Three-Component Reactions of $Y(CH_2SiMe_3)_3(THF)_2$ , Alkenes with Aldehydes (or Acetals)

In the cross-coupling reactions above, only 0.33 equiv. of  $Y(CH_2SiMe_3)_3(THF)_2$  was needed for the full conversion of the vinyl bromides or triflates. Therefore, all the three alkyl groups of the yttrium complex were transferred into the products, leading to the formation of 0.33 equiv of YBr<sub>3</sub> or  $Y(OTf)_3$  as the byproduct. As Ln(III) salts had been widely used as Lewis-acid



Scheme 2. The three-component reaction

This journal is © The Royal Society of Chemistry 20xx

### ARTICLE

catalysts in many organic transformations,4c,20 we wondered if the Y(III) salts could trigger the subsequence 408676128476761 reaction of the in-situ generated allyltrimethylsilanes with carbon electrophiles. To test the feasibility of this idea, we conducted the experiment by a one-pot cascade way. The crosscoupling of Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> **1** with a-bromostyrene **2a** under the cross-coupling conditions for 2 h followed by the reaction with 1.1 equiv. of benzaldehyde 6a at 100 °C for 3 h afforded the trimethylsilyl-protected homoallylic alcohol 7 in74% yield. However, another parallel reaction with acidic workup delivered the homoallylic alcohol 8a instead in similar yield (Scheme 2A). Encouraged by this result, we then investigated various carbon electrophiles for the three-component one-pot cascade reaction and found that only aromatic aldehydes and acetals were well tolerant to the reaction conditions above. A variety of aromatic aldehydes bearing either electronwithdrawing (Cl, Br, NO<sub>2</sub>) or electron-donating (Me) groups were applied as the electrophiles for the three-component reaction with Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> 1 and a-bromostyrene 2a. All these reactions went smoothly to deliver the terminal products in good yields (8b-8e) without any other catalysts or reagents needed. Besides, the reaction of 1 and 2a with benzaldehyde dimethyl acetal 6f gave the methyl homoallyl ether 8f in 80% vield.

Although the three component reaction with abromostyrene 2a had been successfully developed, the reaction for vinyl triflate  $\boldsymbol{4}$  or  $\boldsymbol{\beta}\text{-bromostyrene}~\boldsymbol{2e}$  only gave poor yield probably due to the lower Lewis acidity of Y(OTf)<sub>3</sub> from vinyl triflates or the lower reactivity of the allyltrimethylsilane 3e from  $\beta$ -bromostyrene. To improve the reaction efficiency, the conditions were modified for the second step by using TiCl<sub>4</sub> as the catalyst and CH<sub>2</sub>Cl<sub>2</sub> as the solvent. Under the new conditions, the reaction of some representative alkenes was carefully investigated and the regioselectivity and diastereoselectivity in the reaction was also discussed. First, the reaction of βbromostyrene 2e with 1 and 6f furnished the γ-substituted product 9a in very excellent yield and high diastereoselectivity (92% yield and 3:1 dr) without  $\alpha$ -substituted product **9b** observed by NMR (Scheme 2B). Second, the cyclic vinyl triflate with a six-membered ring 4g reacted with 1 and 6f to give the  $\alpha$ -substituted product **10b** in 93% yield without the ysubstituted product 10a detected by NMR (Scheme 2C). The regioselectivity might be controlled by the steric hindrance of  $\alpha$ - and y-positions of the allylsilane intermediate. Therefore, the reaction of the cyclic vinyl triflate with a seven-membered ring **4k** delivered both of the  $\alpha$ - and  $\gamma$ -substituted products with the α-product 11b as the major (Scheme 2D). The yttrium complex 1 had been utilized as a nucleophilic one-carbon synthon, which reacted with two types of electrophiles. The first reaction formally applied this reagent to trigger the bifunctionalization of alkenes, while the other two reactions utilized it as a CH<sub>2</sub> linker.

### Application in the Multi-Functionalization of Styrene

To demonstrate the applications of the new methodologies above in organic synthesis, we further performed a three-step reaction of vinyl bromide **2g** with **1** and **6f**. After the first cross-

### ARTICLE



coupling with **1** in the presence of  $Pd(PPh_3)_2Cl_2$ , the Hosomi-Sakurai reaction with **6f** in the presence of  $TiCl_4$ , and the second cross-coupling with **1** in the presence of  $Pd_2(dba)_3/XPhos$ , the vinyl bromide **2g** was finally transformed into the product **12** in 72% yield and 2.8:1 dr (Scheme 3). This experiment showed the high efficiency, excellent chemoselectivity and good condition compatibility of each step, thus providing a nice strategy for the construction of multi-functionalized styrenes.

### Conclusions

Published on 18 August 2016. Downloaded by Cornell University Library on 18/08/2016 14:35:45

In summary, we had developed the Pd-catalyzed cross-coupling of Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> 1 with various vinyl bromides 2 and triflates 4 for the construction of allytrimethylsilanes. The easy access to various vinyl bromides and triflates from commercial alkynes, ketones and aldehydes, the mild conditions for the cross-coupling, high efficiency and good functionality tolerance made this new method a powerful tool for the synthesis of allyltrimethylsilanes. In combination of the cross-coupling with Lewis-acid catalyzed Hosomi-Sakurai reaction, a novel three-component one-pot cascade reaction were realized for the efficient synthesis of homoallylic alcohols and ethers with high regioselectivity and good diastereoselectivity. This threecomponent reaction applied Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> 1 as a novel one-carbon synthon, which either triggered the bifunctionalization of alkenes or was connected with two electrophiles. And the application of these methods in the synthesis of complex molecules such as natural products or unnatural organic functional materials is under way.

### Acknowledgements

All authors have given approval for the final version of the manuscript. The authors declare no competing financial interest. We thank the National Natural Science Foundation of China (21274012, 21322401 and 21490570) and Beijing Institute of Technology (the 111 Project B07012) for financial support.

### Notes and references

- 1 S. Kobayashi, Lanthanides: Chemistry and uses in Organic Synthesis, Springer, Berlin, 1999.
- 2 P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, Chem. Rev., 2006, **106**, 2404.
- (a) F. Lauterwasser, P. G. Hayes, S. Bräse, W. E. Piers and L. L. Schafer, Organometallics, 2004, 23, 2234. (b) B.-T. Guan and Z. Hou, J. Am. Chem. Soc., 2011, 133, 18086. (c) B.-T. Guan, B.-

L. Wang, M. Nishiura and Z. Hou, Angew. Chem., Int. Ed. 2013 52, 4418. (d) G. Song, B. Wang, M. Nishiuraland S. Hous Chem. -Eur. J., 2015, 21, 8394.

- 4 (a) H. B. Kagan and J. L. Namy, Tetrahedron, 1986, 42, 6573.
  (b) T. Imamoto, J. Syn. Org. Chem. Jpn., 1988, 46, 540. (c) G. A. Molander, Chem. Rev., 1992, 92, 29. (d) M. N. Bochkarev, Chem. Rev., 2002, 102, 2089. (e) Y. Sumino and A. Ogawa, J. Syn. Org. Chem. Jpn., 2003, 61, 201. (f) M. N. Bochkarev, Coord. Chem. Rev., 2004, 248, 825.
- 5 K. Yokoo, T. Fukagawa, Y. Yamanaka, H. Taniguchi and Y. Fujiwara, J. Org. Chem., 1984, **49**, 3237.
- S. H. Wunderlich and P. Knochel, Chem. -Eur. J., 2010, 16, 3304.
  M. Shenglof, D. Gelman, G. A. Molander and J. Blum,
- Tetrahedron Lett., 2003, **44**, 8593. 8 M. Zimmermann and R. Anwander, Chem. Rev., 2010, **110**, 6194.
- 9 (a) M. F. Lappert and R. Pearce, J. Chem. Soc., Chem. Commun., 1973, 126. (b) J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McMeeking, R. Pearce and M. F. Lappert, J. Chem. Soc., Chem. Commun., 1978, 140. (c) H. Schumann and J. Müller, J. Organomet. Chem., 1978, 146, C5. (d) H. Schumann, D. M. M. Freckmann and S. Z. Dechert, Anorg. Allg. Chem., 2002, 628, 2422.
- 10 G. Cai, Y. Huang, T. Du, S. Zhang, B. Yao and X. Li, Chem. Commun., 2016, 52, 5425.
- (a) T. Hayashi, K. Kabeta, I. Hamachi and M. Kumada, Tetrahedron Lett., 1983, 24, 2865. (b) D. R. Gauthier and E. M. Carreira, Angew. Chem., Int. Ed., 1996, 35, 2363. (c) M. Suginome, T. Iwanami and Y. Ito, J. Am. Chem. Soc., 2001, 123, 4356. (d) S. E. Denmark and J.-P. Fu, Chem. Rev., 2003, 103, 2763.
- (a) S. Yamasaki, K. Fujii, R. Wada, M. Kanai and M. Shibasaki, J. Am. Chem. Soc., 2002, **124**, 6536. (b) H. Kiyohara, Y. Nakamura, R. Matsubara and S. Kobayashi, Angew. Chem., Int. Ed., 2006, **45**, 1615; (c) Q.-Y. Song, B.-L. Yang and S.-K. Tian, J. Org. Chem., 2007, **72**, 5407.
- (a) M. E. Jung and A. Maderna, J. Org. Chem., 2004, 69, 7755;
  (b) H. M. Zerth, N. M. Leonard and R. S. Mohan, Org. Lett., 2003, 5, 55;
  (c) D. Kampen and B. List, Synlett, 2006, 2589.
- 14 J. S. Yadav, B. V. S. Reddy, M. S. Reddy and G. Parimala, Synthesis, 2003, 2390.
- Early reports on Hosomi-Sakurai reaction: (a) A. Hosomi and H.Sakurai, J. Am. Chem. Soc., 1977, 99, 1673. (b) A. Hosomi, M. Endo and H.Sakurai, Chem. Lett., 1976, 941. (c) A. Hosomi and H.Sakurai, Tetrahedron Lett., 1976, 17, 1295-1298. For a review, see: (d) A. Hosomi, Acc. Chem. Res., 1988, 21, 200-206.
- 16 Reviews on allylsilane synthesis: (a) T. K. Sarkar, Synthesis, 1990, 969–983. (b) T. K. Sarkar, Synthesis, 1990, 1101.
- Selected references on the synthesis of allylsilanes by transition-metal catalysis: (a) L. Guo, M. Leiendecker, C.-C. Hsiao, C. Baumann and M. Rueping, Chem. Commun., 2015, **51**, 1937. (b) R. Shimizu, H. Egami, Y. Hamashima and M. Sodeoka, Angew. Chem., Int. Ed., 2012, **51**, 4577. (c) H. Teare, E. G. Robins, E. Arstad, S. K. Luthra and V. Gouverneur, Chem. Commun., 2007, 2330. (d) W. Affo, H. Ohmiya, T. Fujioka, Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, Y. Imamura, T. Mizuta and K. Miyoshi, J. Am. Chem. Soc., 2006, **128**, 8068. (e) J. Mo, L. Xu and J. Xiao, J. Am. Chem. Soc., 2005, **127**, 751. (f) T. Hayashi, Y. Katsuro and M. Kumada, Tetrahedron Lett., 1980, **21**, 3915.
- 18 (a) S. Kobayashi, Chem. Soc. Rev., 1999, 28, 1. (b) I. Ugi, Pure Appl. Chem., 2001, 73, 187. (c) D. M. D'Souza and T. J. J. Mueller, Chem. Soc. Rev., 2007, 36, 1095. (d) S. Perreault and T. Rovis, Chem. Soc. Rev., 2009, 38, 3149. (e) M. S. Singh and S. Chowdhury, Rsc Adv., 2012, 2, 4547. (f) C. M. R. Volla, L. Atodiresei and M. Rueping, Chem. Rev., 2014, 114, 2390.
- 19 (a) A. R. Katritzky, S. Zhang, A. H. M. Hussein, Y. Fang and P. J. Steel, J. Org. Chem., 2001, 66, 5606. (b) K. S. Gayen and D. K.

### ARTICLE

**Organic & Biomolecular Chemistry Accepted Manuscript** 

View Article Online DOI: 10.1039/C6OB01765G

### Journal Name

Maiti, RSC Adv., 2014, **4**, 10204. (c) P. S. Mahajan, S. D. Tanpure, N. A. More, J. M. Gajbhiye and S. B. Mhaske, RSC Adv., 2015, **5**, 101641. (d) K. Sun, X. Wang, Y. Jiang, Y. Lv, L. Zhang, B. Xiao, D. Li, Z. Zhu and L. Liu, Chem. –Asian J., 2015, **10**, 536. (e) S. Tong, Q. Wang, M.-X. Wang and J. Zhu, Chem. – Eur. J., 2016, **22**, 8332. (f) M.-N. Zhao, Z.-H. Ren, L. Yu, Y.-Y. Wang and Z.-H. Guan, Org. Lett., 2016, **18**, 1194.

20 (a) M. Boomhoff, A. K. Yadav, J. Appun and C. Schneider, *Org. Lett.*, 2014, 16, 6236. (b) C. Liu, J. Lv, S. Luo and J.-P. Cheng, *Org. Lett.*, 2014, 16, 5458. (c) X. Xiao, H. Mei, Q. Chen, X. Zhao, L. Lin, X. Liu and X. Feng, *Chem. Commun.*, 2015, 51, 580.