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Palladium-catalyzed olefination of aryl/alkyl halides with trimethylsilyldiazomethane *via* carbene migratory insertion†

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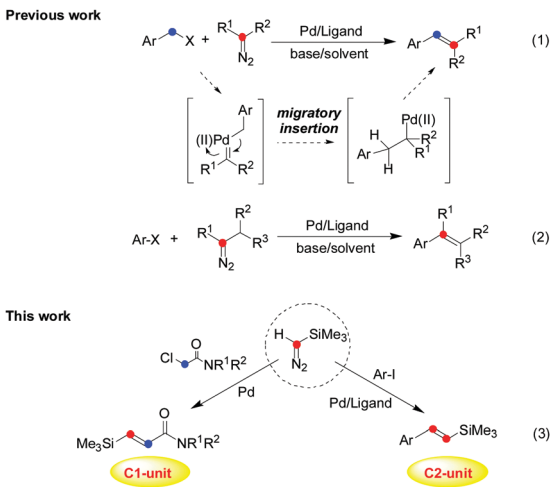
The direct olefination of aryl/alkyl halides with trimethylsilyldiazomethane (TMSD) as a C1- or C2-unit was achieved successfully *via* a metal carbene migratory insertion process, which offered a new access to afford (*E*)-vinyl silanes and (*E*)-silyl-substituted α,β-unsaturated amides in good yields and high chemoselectivity.

Transition-metal-catalyzed cross-coupling reactions *via* carbene migratory insertion (CMI) have received much attention and have been extensively established as reliable and versatile methods for carbon–carbon bond-forming reactions in the past decades.[1] Accordingly, the key step of carbene coupling reactions is the migratory insertions of an aryl or alkyl group into the metal–carbene intermediate, which makes metal carbene migratory insertion as a powerful strategy for carbon–carbon bond-forming transformations.[2] In particular, since Van Vranken and co-workers[3] reported the first example of palladium carbene migratory insertion in 2001, palladium-catalyzed carbene migratory insertion of aryl halides has been well demonstrated for the synthesis of versatile molecules through a cross-coupling process, and the corresponding intermediate or mechanistic process has been revealed by several groups (Scheme 1, eqn (1) and (2)).[1,2] Thus, in principle these diazo compounds or other carbene precursors can be used in the construction of alkenes by carbon–carbon bond-forming carbene migratory insertion and subsequent β-hydrogen elimination. Among various alkenes, vinyl silanes occupy an important position in organic synthesis,[4] which have wide applications due to the characteristic properties of silicon and privileged functions as versatile precursors and potent nucleophiles. Vinyl silanes



Scheme 1 Palladium-catalyzed cross-coupling reaction through metal carbene migratory insertion (CMI): from the classic method (previous work) to controllable carbene migratory insertion (this work).

would be used to construct many characteristic molecules by organic transformation involving the Hiyama cross-coupling reactions[5] and crotylation reactions,[6] even the Hosomi–Sakurai-type allylation[7] and so on. For these reasons, numerous efforts have been directed to the preparation of vinyl silanes, which utilize carbonyl compounds,[8] alkynes,[9] vinyl halides,[10] terminal olefins,[11] and aryl iodies[12] as starting materials. However, limitations still exist with many of the current methods, which often make the preparation of vinyl silanes challenging, especially in the control of chemoselectivity. Therefore, the development of novel and efficient olefination reactions with new catalytic systems is highly desirable in synthetic chemistry. As reported, little attention has been paid to a simple olefination process to provide alkenes containing a silyl group by carbene migratory insertion.[13] Meanwhile, chemical transformations involving two molecules of diazo compounds in the carbene migratory insertion have not been well realized in the past.[14] Inspired by previous works on the metal carbene migratory

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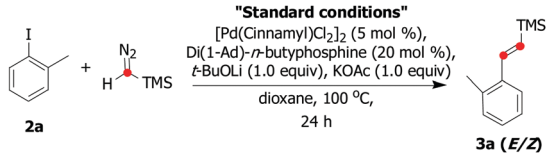
Table 1 Optimization of the reaction conditions[a]



Entry	Deviation from the standard conditions	Yield[b] (%) 2a/(E)-3a/(Z)-3a
1	None	0/99/<1
2	10 mol% $PdCl_2$	64/30/6
3	10 mol% $Pd(MeCN)_2Cl_2$	45/50/5
4	10 mol% $Pd(PhCN)_2Cl_2$	38/57/5
5	10 mol% $Pd(PPh_3)_4$	65/23/12
6	K_2CO_3 as the base	70/30/0
7[c]	DIEA as the base	70/30/0
8	Ag_2CO_3 as the base	0/38/62
9	Li_2CO_3 as the base	81/19/0
10	THF instead of dioxane	24/50/26
11	Toluene instead of dioxane	64/36/0
12	DCE instead of dioxane	75/25/0
13	DMSO instead of dioxane	0/73/27
14	PPh_3 as the ligand	53/14/33
15	DavePhos as the ligand	62/15/23
16	PCy_3 as the ligand	60/20/20
17	Xphos as the ligand	67/15/18
18	XantPhos as the ligand	80/14/6
19	Using 10 mol% [Pd(π-cinnamyl)Cl_2]$_2$	0/97/3
20	Without KOAc	40/20/40

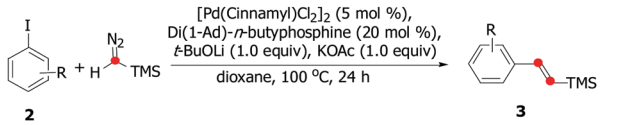
[a] **2a** (0.1 mmol), TMSD (3.0 equiv.), [Pd(π-cinnamyl)Cl_2]$_2$ (5 mol%), di(1-ad)-*n*-butylphosphine (20 mol%), *t*-BuOLi (1.0 equiv.), KOAc (1.0 equiv.), dry dioxane (1 mL), 100 °C, 24 hours. [b] The yield was determined by GC-MS. [c] DIEA = *N*,*N*-diisopropylethylamine.

insertion process,[1–3] attempts to obtain vinyl silanes with TMSD as a C1- or C2-unit have been made in this work (Scheme 1).

Our effort began by selecting aryl iodide **2a** as a model substrate to examine the carbene insertion reaction of TMSD. By optimizing various reaction parameters, we found that the combination of [Pd(π-cinnamyl)Cl_2]$_2$, di(1-ad)-*n*-butylphosphine, *t*-BuOLi, KOAc in dry 1,4-dioxane at 100 °C gave the best result after 24 hours (Table 1). As described in Table 1, replacing [Pd(π-cinnamyl)Cl_2]$_2$ with $PdCl_2$, $Pd(MeCN)_2Cl_2$ or others diminished the reaction yield and stereoselectivity (entries 2–5). Several bases were investigated (entries 6–9), and *t*-BuOLi was found to be the best choice (entry 1). Additionally, the effect of the solvent on the selectivity and catalytic efficiency was evaluated, and 1,4-dioxane proved to be effective (entry 1 and entries 10–13). When various phosphine ligands (PPh_3, DavePhos, PCy_3, Xphos, and XantPhos) were tested, **3a** could also be detected but in relatively lower yields and stereoselectivities (entries 14–18). Increasing the catalyst loading did not influence the conversation significantly (entry 19). When KOAc was removed, only 20% yield of (*E*)-**3a** was detected (entry 20).

With the optimized reaction conditions in hand, we explored the substrate scope of aryl iodides to yield the corresponding (*E*)-vinyl silanes. As shown in Table 2, good yields and stereoselectivity were obtained for the *ortho*-substituted aryl iodide with electron-rich substituents (**2a**, **2c**, and **2d**), whereas lower *E*/*Z* selectivity was obtained for the *ortho*-substituted aryl iodides with electron-deficient substituents (**2b** and **2e–2h**),

Table 2 The substrate scope for the palladium-catalyzed olefination of aryl iodides with trimethylsilyldiazomethane *via* carbene migratory insertion[a]



Entry	Ar-I	Product	Yield[b] (%)	Ratio[c] (*E*/*Z*)
1	2-MeC_6H_4 (**2a**)	**3a**	65	99 : 1
2	2-FC_6H_4 (**2b**)	**3b**	30	82 : 18
3	2-ClC_6H_4 (**2c**)	**3c**	69	99 : 1
4	2-$MeOC_6H_4$ (**2d**)	**3d**	45	99 : 1
5	2-$(CF_3)C_6H_4$ (**2e**)	**3e**	38	88 : 12
6	2-$NO_2C_6H_4$ (**2f**)	**3f**	32	88 : 12
7	2-$(CF_3O)C_6H_4$ (**2g**)	**3g**	36	74 : 26
8	2-CNC_6H_4 (**2h**)	**3h**	56	88 : 12
9	3-MeC_6H_4 (**2i**)	**3i**	53	91 : 9
10	3-ClC_6H_4 (**2j**)	**3j**	42	83 : 17
11	3-$MeOC_6H_4$ (**2k**)	**3k**	49	99 : 1
12	3-$(CF_3)C_6H_4$ (**2l**)	**3l**	44	87 : 13
13	3-$NO_2C_6H_4$ (**2m**)	**3m**	36	88 : 12
14	3-CNC_6H_4 (**2n**)	**3n**	60	99 : 1
15	4-MeC_6H_4 (**2o**)	**3o**	59	95 : 5
16	4-FC_6H_4 (**2p**)	**3p**	31	81 : 19
17	4-ClC_6H_4 (**2q**)	**3q**	54	85 : 15
18	4-$MeOC_6H_4$ (**2r**)	**3r**	51	99 : 1
19	4-$(CF_3)C_6H_4$ (**2s**)	**3s**	49	92 : 8
20	4-$(CF_3O)C_6H_4$ (**2t**)	**3t**	41	85 : 15
21	4-$NO_2C_6H_4$ (**2u**)	**3u**	31	86 : 14
22	4-CNC_6H_4 (**2v**)	**3v**	57	99 : 1
23	4-*t*BuC_6H_4 (**2w**)	**3w**	36	99 : 1
24	C_6H_5 (**2x**)	**3x**	50	85 : 15
25	3,5-$(Me)_2C_6H_3$ (**2y**)	**3y**	41	99 : 1
26	2-$CO_2MeC_6H_4$ (**2z**)	**3z**	45	99 : 1

[a] **2** (0.75 mmol), TMSD (3.0 equiv.), [Pd(π-cinnamyl)Cl_2]$_2$ (5 mol%), di(1-ad)-*n*-butylphosphine (20 mol%), *t*-BuOLi (1.0 equiv.), KOAc (1.0 equiv.), dry dioxane (1 mL), 100 °C, 24 hours. [b] Isolated yields. [c] Determined by NMR.

suggesting that the electronic effect would be crucial for *E*/*Z* stereocontrol. Substrates (**2i–2v**) having *m*- or *p*-substituents were also suitable for the olefination reaction, giving moderate to good yields. In particular, the reactions of **2k**, **2n**, **2r**, and **2v** proceeded smoothly to afford the corresponding (*E*)-vinyl silanes with excellent *E*/*Z* selectivity (99 : 1). The alkene **3w** containing a sterically hindered *t*-Bu group was isolated in 36% yield. Notably, the carboxylic ester moiety was also tolerated in this reaction (**2z**), even though a strong base was required. Surprisingly, some aryl bromides could also be used for the olefination reaction (Scheme 2). Both **3a** and **3x** afforded moderate yields and excellent *E*/*Z* selectivity.

Encouraged by these initial findings, we then further explored the efficiency and practicality of this method. Considering the importance of the β-silyl-α,β-unsaturated amide scaffolds in the organic syntheses which can be employed into diverse types of chemical transformation such as Michael addition,[15] total syntheses of (+)-lactacystin,[16] tandem Stille reaction[17] and so on,[18] we thus examined the carbene insertion reaction of chloride-substituted acetamide **4** with TMSD. Unfortunately, β-silyl-α,β-unsaturated amide was not detected under the aforementioned optimized reaction conditions using **4a** as a model substrate. To our delight, when KOAc was removed,

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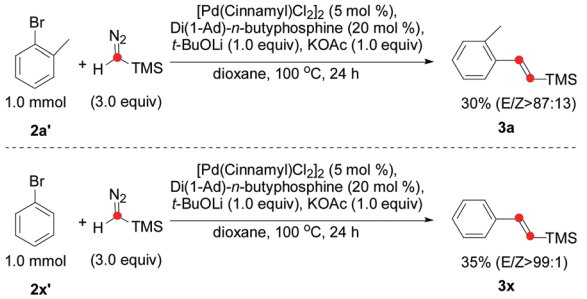
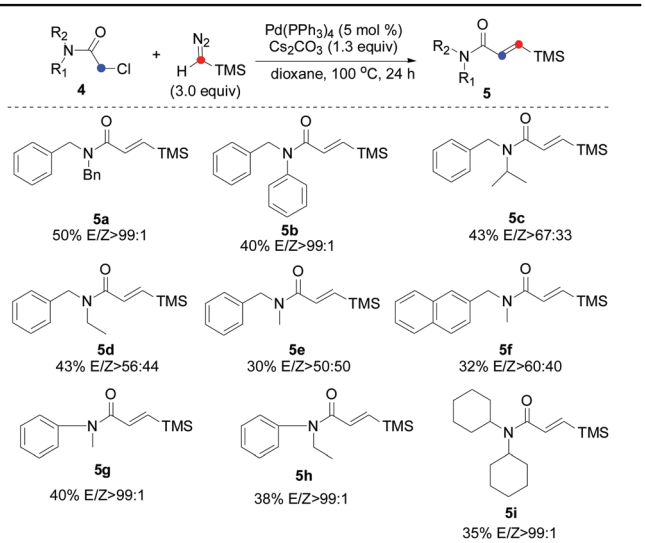


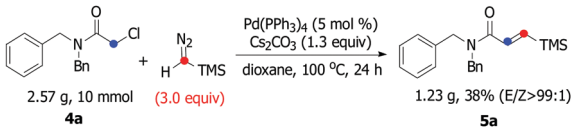
Scheme 2 The palladium-catalyzed olefination of aryl bromides with trimethylsilyldiazomethane.

a small amount of **5a** was detected. After screening several parameters such as different Pd sources, bases and solvents (for details, see the ESI†), we found that a protocol based on $Pd(PPh_3)_4$ and Cs_2CO_3 in dry dioxane at 100 °C for 24 hours provided the desired product in 50% yield and excellent *E*/*Z* selectivity (99 : 1).

We next evaluated the scope and limitations on the α-chloroacetamide partners using the optimized conditions. As described in Table 3, compounds **4a** and **4b** smoothly participated in the reaction to afford **5a** and **5b** in 50% and 40% yields with excellent *E*/*Z* selectivity (99 : 1), whereas the reaction of **4c**, **4d**, **4e**, and **4f** resulted in a lower stereoselectivity (**5c**, **5d**, **5e**, and **5f**), suggesting that the steric-hindrance effect would be crucial for the *E*/*Z* stereocontrol. The results show that variation of the amide by replacing the benzyl moiety with a phenyl group had significant influence on the course of the reaction (**5g** and **5h**). Interesting, bulkier dicyclohexyl-substituted acetamide **4i** was also a suitable substrate, giving the corresponding product **5i** in satisfactory yield and excellent *E*/*Z* selectivity. To show the synthetic potential of our developed catalytic system, a palladium-catalyzed carbene coupling reaction

Table 3 The substrate scope for the palladium-catalyzed olefination of α-chloroacetamides with trimethylsilyldiazomethane *via* carbene migratory insertion



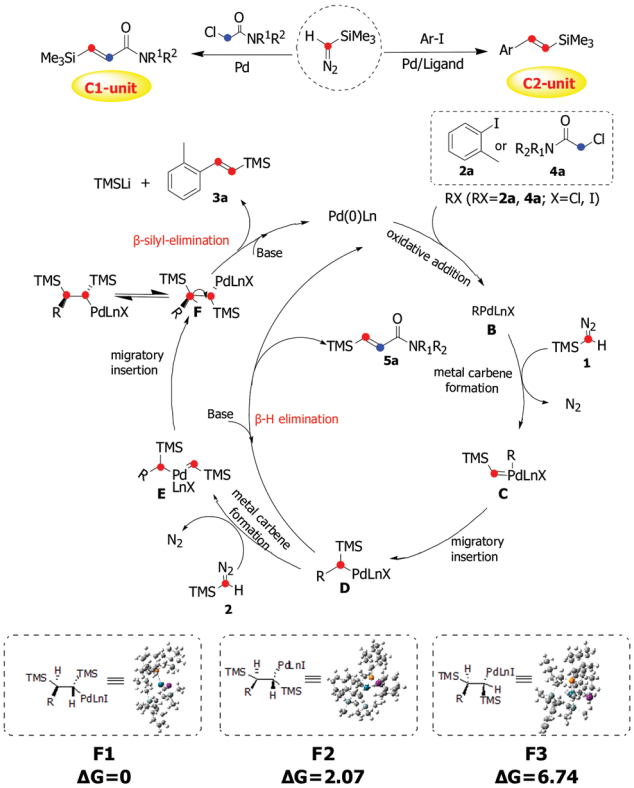


Scheme 3 Gram-scale synthesis of **5a**.

between **4a** (α-chloroacetamides) and **TMSD** was carried out on a gram scale, furnishing the corresponding product **5a** (1.23 g, 38%) (Scheme 3).

On the basis of our experimental observations and previous works on related reactions and the DFT calculations on the conformer energetics of **F**,[13,14] the mechanism was proposed as shown in Scheme 4. Initially, oxidative addition of **2a**/**4a** generates the arylpalladium/alkylpalladium species **B**, which reacts with one molecule of TMSD to form the palladium carbene complex **C**. Then intermediate **D** was formed by the migratory insertion of **C**. **5a** would be obtained *via* β-H elimination of intermediate **D**. From intermediate **D**, the carbene complex **E** was afforded through insertion of a second molecule of TMSD, followed by migratory insertion to give intermediate **F**. Due to the steric reasons, the anti-relationship between two TMS groups will be more favorable in this insertion process. Finally, the product **3a** was obtained through β-silyl-elimination of **F** with high stereoselectivity.

In conclusion, we have developed novel and stereospecific protocols for obtaining (*E*)-vinyl silanes and (*E*)-silyl-substituted



Scheme 4 Plausible mechanistic pathway *via* carbene migratory insertion for palladium-catalyzed olefination of aryl/alkyl halides with trimethylsilyl-diazomethane.

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α,β-unsaturated amides in good yields with a good level of *E*/*Z* stereoselectivities, which would be a worthwhile valuable complement to the existing methods. These methods turned out to be convenient, with easily available and inexpensive aryl/alkyl halides as starting materials. Notably, it is the first example which shows that two molecules of diazo compounds could be used as a C2-unit in the palladium-catalyzed olefination of aryl halides, in which the trimethylsilyldiazomethane (TMSD)-initiated double carbene migratory insertion was for the first time realized in this work. In addition, it is possible that the corresponding vinyl silanes were produced with a possible pathway involving palladium carbene formation, migratory insertion and finally β-*syn*-elimination or reductive elimination. Further investigation into the application of this protocol is currently underway in our lab.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For reviews, see: (*a*) Y. Xia, D. Qiu and J. Wang, *Chem. Rev.*, 2017, **117**, 13810; (*b*) Y. Xia and J. Wang, *Chem. Soc. Rev.*, 2017, **46**, 2306; (*c*) Y. Xia, Y. Zhang and J. Wang, *ACS Catal.*, 2013, **3**, 2586; (*d*) Q. Xiao, Y. Zhang and J. Wang, *Acc. Chem. Res.*, 2013, **46**, 236; (*e*) Z. Liu and J. Wang, *J. Org. Chem.*, 2013, **78**, 1002; (*f*) Z. Shao and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 560; (*g*) J. Barluenga and C. Valdés, *Angew. Chem., Int. Ed.*, 2011, **50**, 7486; (*h*) Y. Zhang and J. Wang, *Eur. J. Org. Chem.*, 2011, 1015.

2 For recent examples, see: (*a*) X. Hu, X. Chen, Y. Shao, H. Xie, Y. Deng, Z. Ke, H. Jiang and W. Zeng, *ACS Catal.*, 2018, **8**, 1308; (*b*) Y. Gao, G. Wu, Q. Zhou and J. Wang, *Angew. Chem., Int. Ed.*, 2018, **57**, 2716; (*c*) K. Wang, Y. Pang, T. Chang and J. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 13140; (*d*) Q. Zhou, S. Li, Y. Zhang and J. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 16013; (*e*) Z. Zhang, Z. Sheng, W. Yu, G. Wu, R. Zhang, W. D. Chu, Y. Zhang and J. Wang, *Nat. Chem.*, 2017, **9**, 970; (*f*) H. Zhang, G. Wu, H. Yi, T. Sun, B. Wang, Y. Zhang, G. Dong and J. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 3945, and references cited therein.

3 K. L. Greenman, D. S. Carter and D. L. Van Vranken, *Tetrahedron*, 2001, **57**, 5219.

4 (*a*) T. A. Blumenkopf and L. E. Overman, *Chem. Rev.*, 1986, **86**, 857; (*b*) I. Fleming, I. A. Barbero and D. Walter, *Chem. Rev.*, 1997, **97**, 2063; (*c*) T. Hiyama and E. Shirakawa, *Top. Curr. Chem.*, 2002, **219**, 61.

5 (*a*) S. E. Denmark and J. H.-C. Liu, *Angew. Chem., Int. Ed.*, 2010, **49**, 2978; (*b*) Y. Nakao and T. Hiyama, *Chem. Soc. Rev.*, 2011, **40**, 4893; (*c*) C. Thiot, C. Mioskowski and A. Wagner, *Eur. J. Org. Chem.*, 2009, 3219.

6 (*a*) C. E. Masse and J. S. Panek, *Chem. Rev.*, 1995, **95**, 1293; (*b*) S. E. Denmark and J. Fu, *Chem. Rev.*, 2003, **103**, 2763.

7 A. Hosomi, M. Endo and H. Sakurai, *Chem. Lett.*, 1976, 941.

8 (*a*) D. R. Williams, A. I. Morales-Ramos and C. M. Williams, *Org. Lett.*, 2006, **8**, 4393; (*b*) J. McNulty and P. Das, *Chem. Commun.*, 2008, 1244.

9 (*a*) O. Buisine, G. Berthon-Gelloz, J.-F. Briere, S. Sterin, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq and I. E. Marko, *Chem. Commun.*, 2005, 3856; (*b*) T. Konno, K. Taku, S. Yamada, K. Moriyasu and T. Ishihara, *Org. Biomol. Chem.*, 2009, **7**, 1167; (*c*) C. Belger and B. Plietker, *Chem. Commun.*, 2012, **48**, 5419.

10 (*a*) K. Fugami, K. Oshima, K. Utimoto and H. Nozaki, *Tetrahedron Lett.*, 1986, **27**, 2161; (*b*) M. Murata, S. Watanabe and Y. Masuda, *Tetrahedron Lett.*, 1999, **40**, 9255; (*c*) A. Krasovskiy and B. H. Lipshutz, *Org. Lett.*, 2011, **13**, 3818.

11 (*a*) B. Marciniec, E. Walczuk-Gusciora and C. Pietraszuk, *Organometallics*, 2001, **20**, 3423; (*b*) Y. Jiang, O. Blacque and H. Berke, *Dalton Trans.*, 2011, **40**, 2578; (*c*) J. R. McAtee, S. E. S. Martin, D. T. Ahneman, K. A. Johnson and D. A. Watson, *Angew. Chem., Int. Ed.*, 2012, **51**, 3663; (*d*) J. R. McAtee, S. E. S. Martin, A. P. Cinderella, W. B. Reid, K. A. Johnson and D. A. Watson, *Tetrahedron*, 2014, **70**, 4250; (*e*) J. R. McAtee, S. B. Krause and D. A. Watson, *Adv. Synth. Catal.*, 2015, **357**, 2317; (*f*) H. Yamashita, T. Hayashi, T. Kobayashi, M. Tanaka and M. Goto, *J. Am. Chem. Soc.*, 1988, **110**, 4417; (*g*) H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1997, **16**, 4696; (*h*) F. Stchr, D. Sturmayr, G. Kickelbick and U. Schubert, *Eur. J. Inorg. Chem.*, 2002, 2305; (*i*) S. Gatard, C. H. Chen, B. Foxman and O. Ozerov, *Organometallics*, 2008, **27**, 6257; (*j*) J. Gu and C. Cai, *Chem. Commun.*, 2016, **52**, 10779; (*k*) P. Pawluc, J. Szudkowska, G. Hreczycho and B. Marciniec, *J. Org. Chem.*, 2011, **76**, 6438.

12 (*a*) K. Karabelas and A. Hallberg, *Tetrahedron Lett.*, 1985, **26**, 3131; (*b*) K. Karabelas and A. Hallberg, *J. Org. Chem.*, 1986, **51**, 5286; (*c*) T. Jeffery, *Tetrahedron Lett.*, 1999, **40**, 1673.

13 (*a*) T. Aoyama, S. Toyama, N. Tamaki and T. Shioiri, *Chem. Pharm. Bull.*, 1983, **31**, 2957; (*b*) N. Hashimoto, T. Aoyama and T. Shioiri, *Chem. Pharm. Bull.*, 1982, **30**, 119; (*c*) T. Aoyama and T. Shioiri, *Chem. Pharm. Bull.*, 1981, **29**, 3249; (*d*) N. Hashimoto, T. Aoyama and T. Shioiri, *Heterocycles*, 1981, **15**, 975; (*e*) N. Hashimoto, T. Aoyama and T. Shioiri, *Chem. Pharm. Bull.*, 1981, **29**, 1475; (*f*) T. Aoyama and T. Shioiri, *Tetrahedron Lett.*, 1980, **21**, 4461; (*g*) S. Xu, Y. Gao, R. Chen, K. Wang, Y. Zhang and J. Wang, *Chem. Commun.*, 2016, **52**, 4478; (*h*) S. Xu, R. Chen, Z. Fu, Q. Zhou, Y. Zhang and J. Wang, *ACS Catal.*, 2017, **7**, 1993.

14 (*a*) D. Sole, L. Vallverdu, X. Solans, M. Font-Bardia and J. Bonjoch, *Organometallics*, 2004, **23**, 1438; (*b*) R. Kudirka, L. David and V. Vranken, *J. Org. Chem.*, 2008, **73**, 3585.

15 (*a*) H. Tomoko, T. Nana, K. Satoko, K. Tiyako, T. Nahoko, C. Nao, S. Chikako, N. Aya and A. Morio, *Chem. Lett.*, 2007, **36**, 54; (*b*) G. W. Klumpp, A. J. C. Mierop, J. J. Vrielink, A. Brugman and M. Schakel, *J. Am. Chem. Soc.*, 1985, **107**, 6742; (*c*) K. Mikiko, N. Satomi, C. Nao, T. Nahoko and A. Morio, *Chem. Lett.*, 2007, **36**, 736; (*d*) M. Ihara, Y. Ishida, Y. Tokunaga, C. Kabuto and K. Fukumoto, *J. Chem. Soc., Chem. Commun.*, 1995, 2085; (*e*) I. Fleming and N. D. Kindon, *J. Chem. Soc., Chem. Commun.*, 1987, 1177.

16 (*a*) E. P. Balskus and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2006, **128**, 6810; (*b*) J. Clayden, D. W. Watson, M. Helliwell and M. Chambers, *Chem. Commun.*, 2003, 2582.

17 (*a*) K. Cherry, A. Duchene, J. Thibonnet, J. L. Parrain and M. Abarbri, *Synthesis*, 2005, 2349; (*b*) K. Cherry, M. Abarbri, J. L. Parrain and A. Duchene, *Tetrahedron Lett.*, 2003, **44**, 5791.

18 (*a*) B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2004, **126**, 13942; (*b*) S. R. Wilson and M. J. Di Grandi, *J. Org. Chem.*, 1991, **56**, 4766; (*c*) Y. Karibe, H. Kusama and N. Iwasawa, *Angew. Chem., Int. Ed.*, 2012, **51**, 6214; (*d*) X. Wang, N. Masaki, S. Eloisa and M. Ruben, *J. Am. Chem. Soc.*, 2016, **138**, 15531; (*e*) J. L. Pan, C. Chen, Z. G. Ma, J. Zhou, L. R. Wang and S. Y. Zhang, *Org. Lett.*, 2017, **19**, 5216; (*f*) P. K. Kundu and S. K. Ghosh, *Org. Biomol. Chem.*, 2009, **7**, 4611; (*g*) M. J. C. Buckle, I. Fleming, S. Gil and K. L. C. Pang, *Org. Biomol. Chem.*, 2004, **2**, 749; (*h*) W. Oppolzer, R. J. Mills, W. Pachinger and T. Stevenson, *Helv. Chim. Acta*, 1986, **69**, 1542.