ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2018, **5**, 1664

Palladium-catalyzed intermolecular dearomatic allenylation of hydrocycloalk[*b*]indoles with 2,3-allenyl carbonates†

Run-Duo Gao,‡[a,b] Yizhan Zhai,‡[a,b] Shu-Li You *[a,b] and Shengming Ma *[a,c]

Received 10th February 2018,
Accepted 14th March 2018

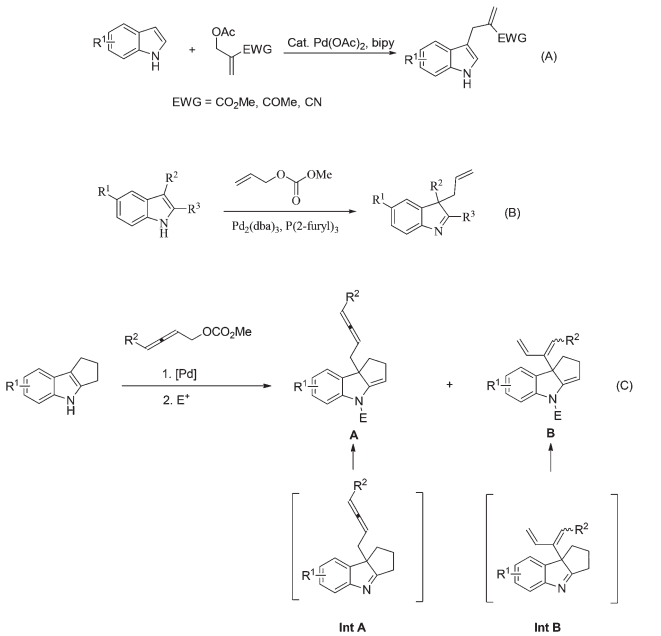
DOI: 10.1039/c8qo00163d

rsc.li/frontiers-organic

A palladium-catalyzed intermolecular dearomatic allenylation of hydrocycloalk[*b*]indoles with 2,3-allenyl carbonates has been developed, providing access to functionalized allenes containing an indoline unit under optimized conditions. Both terminal and non-terminal allenes could react smoothly with an exclusive chemoselectivity and good yields by applying different reaction parameters.

Indoles are attractive and fundamental structural motifs in numerous natural products and pharmaceuticals.[1] In addition, the nucleophilicity of C-3 of indoles leads to numerous transformations.[2] In 2004, Ma's group developed a palladium-catalyzed functionalization of 2-electron-deficient group-substituted acetates with indoles (Scheme 1A).[2e] Starting from 2008, Rawal (Scheme 1B),[3a] Du,[3b] and You[3c,d] reported that 2,3-disubstituted indoles could react with allylic carbonates in the presence of a palladium catalyst. On the other hand, allenes are playing an increasingly important role in organic chemistry and medicinal chemistry.[4,5] Much attention has been paid to the reaction of 2,3-allenol derivatives with different nucleophiles.[6–8] Herein, we wish to provide an efficient method for synthesizing functionalized allenes *via* the dearomatization of hydrocycloalk[*b*]indoles (Scheme 1C).

In principle, there are two types of reactivities for such a coupling reaction of 2,3-allenyl carbonates, generating two different products, allenes **A** and 1,3-dienes **B**, upon the treatment with an electrophile. We initiated our study with 1,2,3,4-tetrahydrocyclopenta[*b*]indole **1a**[9] and buta-2,3-dienyl methyl carbonate **2a**[10a–c] followed by an immediate trapping of the possible imine product **Int A** or **Int B** with methyl chloroformate. The formation of enamine **4aaa** was observed, albeit in <10% yield using P, N ligand **L1** or monophosphine ligand **L2**.



Scheme 1 (A) Palladium-catalyzed functionalization of electron-deficient alkenes with indoles. (B) Dearomatization of indoles derivatives with allylic carbonate. (C) Dearomatization of hydrocycloalk[*b*]indoles with 2,3-allenyl carbonates.

Bisphosphines with the difference of a length of carbon chain had a very limited influence on the reaction. Interestingly, decent levels of the reaction were observed by using commercially available dpbp **L8** and DPEphos **L9** (Table 1).

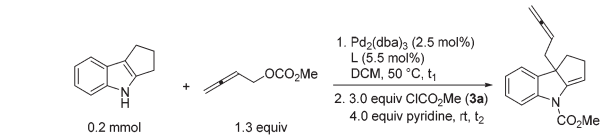
Further optimization of the reaction conditions indicated that increasing the amount of substrate **2a** to 2.0 equiv. had no influence on the reaction. Elevating the reaction temperature even led to a worse result (entry 3, Table 2). Adding molecular sieves had a slight influence on the reaction (entries 4 and 5, Table 2).

[a]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China. E-mail: masm@sioc.ac.cn, slyou@sioc.ac.cn*
[b]*University of Chinese Academy of Sciences, Beijing 100049, P. R. China*
[c]*Department of Chemistry, Fudan University, 220 Handan Lu, Shanghai 200433, P.R. China*

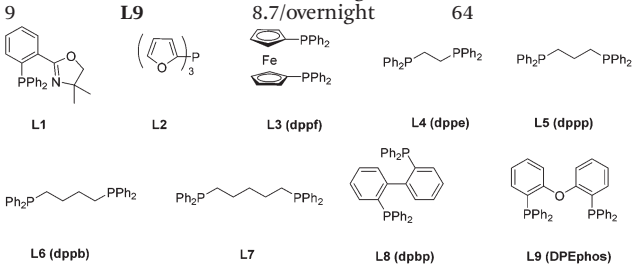
†Electronic supplementary information (ESI) available: Preparation and characterisation data as well as ^{1}H and ^{13}C NMR spectra of all compounds. See DOI: 10.1039/c8qo00163d

‡These authors contributed equally.

Table 1 Identifying the ligand[a]



Entry	Ligand	t_1/t_2 (h)	NMR yield of **4aaa**[b] (%)
1[c]	**L1**	6.5/10	6
2[c]	**L2**	9.7/11.3	5
3	**L3**	6.5/10	10
4	**L4**	6.5/10	NR
5	**L5**	9.7/11.3	8
6	**L6**	9.7/11.3	26
7	**L7**	9/13	8
8	**L8**	32.7/overnight	53
9	**L9**	8.7/overnight	64



[a] Reaction conditions: The reactions were carried out using 0.2 mmol of **1a**, 0.26 mmol of **2a**, 2.5 mol% of $Pd_2(dba)_3$, 5.5 mol% of **L** and 2 mL of DCM at 50 °C. After the reactions were complete, 0.8 mmol of pyridine and 0.6 mmol of $ClCO_2Me$ were added at room temperature. [b] Determined by using CH_2Br_2 as the internal standard. [c] 11 mol% of **L** was added.

Interestingly, there is a profound base effect: with *N*,*O*-bis-(trimethylsilyl)-acetamide (BSA) as the base, the reaction afforded the best result (entries 6–9, Table 2). By reducing the concentration, the yield could be further improved (entry 10, Table 2).

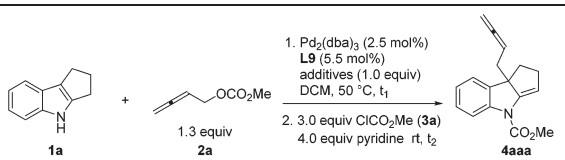
The scope for the electrophilic trapping reagent was also studied. In addition to chloroformate, different acyl chlorides such as acetyl chloride, propionyl chloride, isobutyryl chloride, chloroacetyl chloride, benzoyl chloride, cinnamoyl chloride, and benzenesulfonyl chloride may be applied (Table 3).

However, when non-terminal hepta-2,3-dienyl methyl carbonate **2b**[10c,d] was applied under conditions **A**, only 38% yield of **4abb** was obtained (entry 1, Table 4). Thus, we commenced to optimize the reaction conditions for the substituted allenylic carbonates. With $ZnCl_2$, no product was generated (entry 2, Table 4). There was a slight increase in the yield when 1 equiv. Et_3B was added since Et_3B may further activate indoles by forming a N–B bond[11] (entry 3, Table 4).

When we reduced the amount of Et_3B, the yield decreased (entries 4–6, Table 4). To our delight, when we carried out the reaction at room temperature, 91% yield could be obtained (entry 9, Table 4). Unfortunately, the product could not be purified due to the contamination of the dba from the catalyst. Therefore other Pd catalysts were tested (entries 10–12, Table 4). Finally, $Pd(acac)_2$, DPEphos, BSA and Et_3B in DCM at room temperature were defined as the optimized reaction conditions for further study (conditions **B**).

With conditions **A** and **B** in hand, we began to investigate the scope of this reaction. Satisfactory yields could be observed

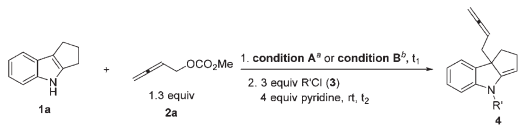
Table 2 Optimization of reaction conditions: reaction of 1,2,3,4-tetrahydrocyclopenta[*b*]indole **1a** and 2,3-butadienyl carbonate **2a**[a]



Entry	Additives	t_1/t_2 (h)	Yield of **4aaa**[b] (%)
1	—	8.7/overnight	64
2[c]	—	11.5/15	64
3[d]	—	3.5/13.5	56
4[e,f]	3 Å MS	8/overnight	66
5[e,f]	4 Å MS	8/overnight	58
6[f]	KO^{t}Bu	8.5/13.5	13
7[f]	K_3PO_4	7.5/15.5	61
8[f]	$MgSO_4$	9.6/12.5	59
9	BSA	6.5/15.5	83
10[g]	BSA	10/3	87 (80[h])
11[i]	BSA	6.7/16.8	83

[a] Reaction conditions: Unless otherwise specified, the reactions were carried out using 0.2 mmol of **1a**, 1.3 equiv. of **2a**, 1.0 equiv. of additive, 2.5 mol% of $Pd_2(dba)_3$, and 5.5 mol% of **L9** in 2.0 mL of DCM at 50 °C. After the reactions were complete, 0.8 mmol of pyridine and 0.6 mmol of $ClCO_2Me$ were added at room temperature. [b] The yield was determined by NMR analysis of the crude product. [c] The reaction was carried out with 2.0 equiv. of **2a**. [d] The reaction was carried out at 80 °C. [e] 100 mg of additive was added. [f] The reactions were carried out using 0.2 mmol of **1a**, 1.3 equiv. of **2a**, 1.0 equiv. of additive, 2.5 mol% of $Pd_2(dba)_3$, and 5.5 mol% of **L9** in 2.0 mL of DCM at 50 °C. After the reactions were complete, the additive was filtered from the solution. 2 mL of DCM, 0.8 mmol of pyridine and 0.6 mmol of $ClCO_2Me$ were added at room temperature. [g] The reaction was carried out in 4 mL of DCM. [h] Isolated yield. [i] The reaction was carried out in 1 mL of DCM.

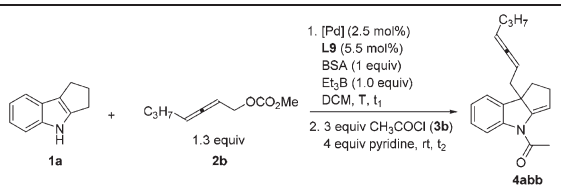
Table 3 The scope of the electrophilic trapping reagents for the reaction of **1a** and **2a**



Entry	R′	Conditions (**A**/**B**)	t_1/t_2 (h)	Yield of **4**[c] (%)
1	 (**3b**)	**A**	6.5/21	79 (**4aab**)
2	 (**3c**)	**A**	6.3/16.8	86 (**4aac**)
3	 (**3d**)	**B**	8/3	91 (**4aad**)
4	 (**3e**)	**B**	8/3	88 (**4aae**)
5	 (**3f**)	**A**	6.4/21.3	63 (**4aaf**)
6	 (**3g**)	**A**	6.3/29.8	58 (**4aag**)
7	 (**3h**)	**B**	8/3	58 (**4aah**)

[a] Conditions **A**: The reaction was carried out using 0.2 mmol of **1a**, 1.3 equiv. of **2a**, 1.0 equiv. of BSA, 2.5 mol% of $Pd_2(dba)_3$, and 5.5 mol% of **L9** in 4.0 mL of DCM at 50 °C and monitored by TLC or LC-MS. After the reaction was complete, 4.0 equiv. of pyridine and 3.0 equiv. of corresponding **3** were added at room temperature. [b] Conditions **B**: The reaction was carried out using 0.2 mmol of **1a**, 1.3 equiv. of **2a**, 1 equiv. of BSA, 1 equiv. of Et_3B, 4 mol% of $Pd(acac)_2$, and 6 mol% of **L9** in 4.0 mL of DCM at room temperature and monitored by TLC or LC-MS. After the reaction was complete, 4.0 equiv. of pyridine and 3.0 equiv. of corresponding **3** were added at room temperature. [c] Isolated yield.

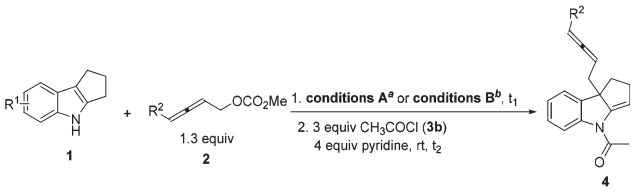
Table 4 Further optimization with hepta-2,3-dienyl methyl carbonate **2b**[a]



Entry	[Pd]	T (°C)	t_1/t_2 (h)	Yield of **4abb**[b] (%)
1[c]	$Pd_2(dba)_3$	50	9/12	38
2[d]	$Pd_2(dba)_3$	50	7.8/—	—
3	$Pd_2(dba)_3$	50	8/8.3	41
4	$Pd_2(dba)_3$	45	9/11.2	45
5[e]	$Pd_2(dba)_3$	45	9/11.2	37
6[f]	$Pd_2(dba)_3$	45	9/11.2	26
7	$Pd_2(dba)_3$	40	8/8	60
8	$Pd_2(dba)_3$	35	8/11.3	81
9	$Pd_2(dba)_3$	rt	9/11.3	91
10[g]	$Pd(OAc)_2$	rt	9/10.8	77
11[g]	$Pd(cod)Cl_2$	rt	9/11.3	68
12[g]	$Pd(acac)_2$	rt	8/12.3	92

[a] Reaction conditions: The reaction was carried out using 0.2 mmol of **1a**, 1.3 equiv. of **2b**, 1 equiv. of BSA, 1 equiv. of Et_3B, 2.5 mol% of [Pd] and 5.5 mol% of **L9** in 4.0 mL of DCM at room temperature and monitored by TLC or LC-MS. After the reaction was complete, 4 equiv. of pyridine and 3 equiv. of CH_3COCl (**3b**) were added at room temperature. [b] The yield was determined by NMR analysis. [c] No Et_3B was added. [d] The reaction was carried out with 2 equiv. of $ZnCl_2$ instead of Et_3B. [e] 0.5 equiv. of Et_3B was added. [f] 0.1 equiv. of Et_3B was added. [g] 4 mol% [Pd] and 6 mol% of **L9** were added.

Table 5 The scope for the reaction of 1,2,3,4-tetrahydrocyclopenta[*b*]indole and 2,3-allenylic carbonate derivative

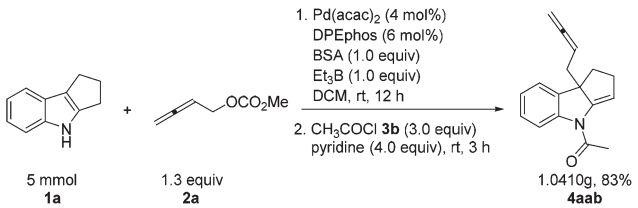


Entry	R^1	R^2	Conditions (**A**/**B**)	t_1/t_2 (h)	Yield of **4**[c] (%)	dr[d]
1	7-Me (**1b**)	H (**2a**)	**A**	5.6/21.8	83 (**4bab**)	—
2	6-Me, 8-Me (**1c**)	H (**2a**)	**B**	8/12.3	81 (**4cab**)	—
3	7-MeO (**1d**)	H (**2a**)	**A**	4.5/20	88 (**4dab**)	—
4	7-Ph (**1e**)	H (**2a**)	**A**	4.5/19	89 (**4eab**)	—
5	7-F (**1f**)	H (**2a**)	**A**	4.5/17.4	85 (**4fab**)	—
6	7-Cl (**1g**)	H (**2a**)	**A**	4.5/16.5	85 (**4gab**)	—
7	7-Br (**1h**)	H (**2a**)	**A**	5.3/22	78 (**4hab**)	—
8	6-Br (**1i**)	H (**2a**)	**B**	10/11.5	80 (**4iab**)	—
9	H (**1a**)	n-C_3H_7 (**2b**)	**B**	8/13	68 (**4abb**)	1.2/1
10	H (**1a**)	n-C_7H_{15} (**2c**)	**B**	10/8	60 (**4acb**)	1.4/1
11	H (**1a**)	 (**2d**)	**B**	10/13	48 (**4adb**)	1.1/1
12	H (**1a**)	 (**2e**)	**B**	8/11	68 (**4aeb**)	1.2/1
13	H (**1a**)	 (**2f**)	**B**	8/9	78 (**4afb**)	1.4/1

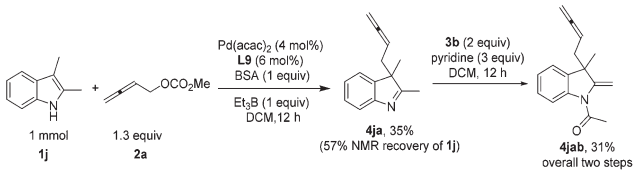
[a] Conditions **A**: The reaction was carried out using 0.2 mmol of **1**, 1.3 equiv. of **2**, 1 equiv. of BSA, 2.5 mol% of $Pd_2(dba)_3$, and 5.5 mol% of **L9** in 4.0 mL of DCM at 50 °C and monitored by TLC or LC-MS. After the reaction was complete, 4.0 equiv. of pyridine and 3.0 equiv. of CH_3COCl (**3b**) were added at room temperature. [b] Conditions **B**: The reaction was carried out using 1.0 mmol of **1**, 1.3 equiv. of **2**, 1 equiv. of BSA, 1 equiv. of Et_3B, 4 mol% of $Pd(acac)_2$, and 6 mol% of **L9** in 20 mL of DCM at room temperature and monitored by TLC or LC-MS. After the reaction was complete, 4.0 equiv. of pyridine and 3.0 equiv. of CH_3COCl (**3b**) were added at room temperature. [c] Isolated yield. [d] Determined by quantitative ^{13}C NMR experiment.

regardless of the electronic properties on the indole moiety (entries 1–8, Table 5). It is worth noting that the MeO, F, Cl, and Br groups could also be tolerated. For allenylic carbonates, R^2 may be C_3H_7 and C_7H_{15}, alkenyl, alkynyl and phenethyl groups (entries 9–13, Table 5).

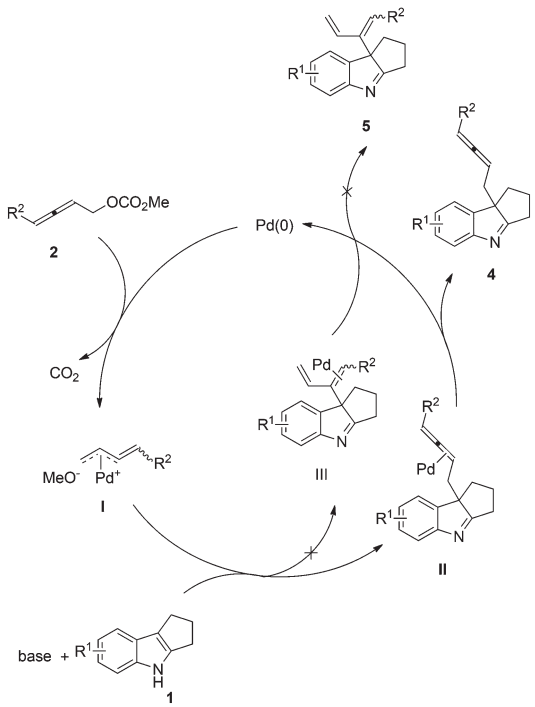
The reaction may be easily conducted on 5 mmol scale of **1a**, affording **4aab** in 83% yield.



For acyclic indoles, the dearomatization reaction could also be conducted smoothly to afford indoline with an exocyclic C–C double bond **4jab** (Scheme 2).



Scheme 2 Dearomatic reaction of acyclic indole **1j**.



Scheme 3 A proposed mechanism.

A possible mechanism is proposed. The oxidative addition of Pd(0) with 2,3-allenyl carbonates would yield, after releasing CO_2, methyleneallylic palladium intermediate **I**, which could react with the indole to yield the product **4** *via* intermediate **II** by releasing the catalytically active Pd(0) to finish the catalytic cycle. Since 1,3-diene product **5** was not detected in this reaction, the C3-carbon atom of the indole is acting as a soft nucleophile attacking the C1-atom in allenyl carbonates **2** (Scheme 3).[12]

In summary, a palladium-catalyzed intermolecular dearomatization of hydrocycloalk[*b*]indoles with 2,3-allenyl carbonates was first developed with a high chemoselectivity affording functionalized allene-substituted hydrocycloalk[*b*]indolines. Both mono-substituted and 1,3-disubstituted allenes could be generated smoothly with nucleophilic indoles. Further exploration of synthesizing optically active allenes with various nucleophiles is ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the National Basic Research Program of China (2015CB856600 for S. Ma and S.-L. You), the National Natural Science Foundation of China (21572252 for S.-L. You), and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB20000000 and QYZDY-SSW-SLH012 for S.-L. You) is greatly appreciated. We thank Penglin Wu for reproducing the results for **4fab** and **4adb** presented in Table 5 and **4aag** presented in Table 3.

Notes and references

1 (*a*) S. Takano and K. Ogasawara, *Alkaloids*, 1989, **36**, 225; (*b*) J. A. Joule and K. Mills, *Heterocyclic Chemistry*, Blackwell Science, Oxford, 4th edn, 2000; (*c*) P. M. Dewick, *Medicinal Natural Products: A Biosynthetic Approach*, Wiley, New York, 2nd edn, 2002.

2 For selected examples, see: (*a*) O. Ottoni, A. de V. F. Neder, A. K. B. Dias, R. P. A. Cruz and L. B. Aquino, *Org. Lett.*, 2001, **3**, 1005; (*b*) J. Zhou and Y. Tang, *J. Am. Chem. Soc.*, 2002, **124**, 9030; (*c*) D. A. Evans, K. A. Scheidt, K. R. Fandrick, H. W. Lam and J. Wu, *J. Am. Chem. Soc.*, 2003, **125**, 10780; (*d*) M. Bandini, A. Melloni and A. Umani-Ronchi, *Org. Lett.*, 2004, **6**, 3199; (*e*) S. Ma and S. Yu, *Tetrahedron Lett.*, 2004, **45**, 8419; (*f*) H. Y. Cheung, W.-Y. Yu, F. L. Lam, T.-L. Terry, Z. Zhou, T. Chan and A. S. C. Chan, *Org. Lett.*, 2007, **9**, 4295; (*g*) A. B. Zaitsev, S. Gruber and P. S. Pregosin, *Chem. Commun.*, 2007, 4692; (*h*) I. Usui, S. Schmidt, M. Keller and B. Breit, *Org. Lett.*, 2008, **10**, 1207; (*i*) W. Liu, H. He, L.-X. Dai and S.-L. You, *Org. Lett.*, 2008, **10**, 1815; (*j*) B. Sundararaju, M. Achard, B. Demerseman, L. Toupet, G. V. M. Sharma and C. Bruneau, *Angew. Chem., Int. Ed.*, 2010, **49**, 2782; (*k*) Y. Tao, B. Wang, J. Zhao, Y. Song, L. Qu and J. Qu, *J. Org. Chem.*, 2012, **77**, 2942; (*l*) W. Chen, Y. Gao, S. Mao, Y. Zhang, Y. Wang and Y. Wang, *Org. Lett.*, 2012, **14**, 5920; (*m*) D. Das and S. Roy, *Adv. Synth. Catal.*, 2013, **355**, 1308.

3 (*a*) N. Kagawa, J. P. Malerich and V. H. Rawal, *Org. Lett.*, 2008, **10**, 2381; (*b*) Y. Liu and H. Du, *Org. Lett.*, 2013, **15**, 740; (*c*) Q.-L. Xu, L.-X. Dai and S.-L. You, *Chem. Sci.*, 2013, **4**, 97; (*d*) R.-D. Gao, Q.-L. Xu, B. Zhang, L.-X. Dai and S.-L. You, *Chem. – Eur. J.*, 2016, **22**, 11601.

4 For reviews, see: (*a*) *Modern Allene Chemistry*, ed. N. Krause and A. S. K. Hashmi, Wiley-VCH, Weinhein, 2005, vol. 1, 2; (*b*) A. Hoffmann-Röder and N. Krause, *Angew. Chem., Int. Ed.*, 2002, **41**, 2933; (*c*) S. Ma, *Acc. Chem. Res.*, 2003, **36**, 701; (*d*) S. Ma, *Chem. Rev.*, 2005, **105**, 2829; (*e*) M. Brasholz, H.-U. Reissig and R. Zimmer, *Acc. Chem. Res.*, 2009, **42**, 45; (*f*) S. Ma, *Acc. Chem. Res.*, 2009, **42**, 1679; (*g*) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria and A. Simonneau, *Chem. Rev.*, 2011, **111**, 1954; (*h*) F. Inagaki, S. Kitagaki and C. Mukai, *Synlett*, 2011, 594; (*i*) F. López and J. L. Mascareñas, *Chem. – Eur. J.*, 2011, **17**, 418; (*j*) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria and A. Simonneau, *Chem. Rev.*, 2011, **111**, 1954; (*k*) S. Yu and S. Ma, *Angew. Chem., Int. Ed.*, 2012, **51**, 3074; (*l*) J. Ye and S. Ma, *Acc. Chem. Res.*, 2014, **47**, 989.

5 For some of the most recent typical examples, see: (*a*) T. Jiang, T. Bartholomeyzik, J. Mazuela, J. Willersinn and J.-E. Bäckvall, *Angew. Chem., Int. Ed.*, 2015, **54**, 6024; (*b*) J. Liu, Z. Han, X. Wang, Z. Wang and K. Ding, *J. Am. Chem. Soc.*, 2015, **137**, 15346; (*c*) J. Dai, M. Wang, G. Chai, C. Fu and S. Ma, *J. Am. Chem. Soc.*, 2016, **138**, 2532; (*d*) S. Ganss and B. Breit, *Angew. Chem., Int. Ed.*, 2016, **55**, 9738; (*e*) W. Yuan, L. Song and S. Ma, *Angew. Chem., Int. Ed.*, 2016, **55**, 3140; (*f*) W. Zhao and J. Montgomery, *J. Am. Chem. Soc.*, 2016, **138**, 9763; (*g*) H. Zhou, Y. Wang, L. Zhang, M. Cai and S. Luo, *J. Am. Chem. Soc.*, 2017, **139**, 3631; (*h*) S. Chen, X. Han, J. Wu, Q. Li, Y. Chen and H. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 9939; (*i*) Z. Yang, D. Peng, X. Du, Z. Huang and S. Ma, *Org. Chem. Front.*, 2017, **4**, 1829; (*j*) E. Y. Tsai, R. Y. Liu, Y. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2018, **140**, 2007.

6 For Pd-catalyzed such reactions generating optically active allenes with an axial chirality, see: (*a*) Y. Imada, K. Ueno, K. Kutsuwa and S.-I. Murahashi, *Chem. Lett.*, 2002, **31**, 140; (*b*) B. M. Trost, D. R. Fandrick and D. C. Dinh, *J. Am. Chem. Soc.*, 2005, **127**, 14186; (*c*) Y. Imada, M. Nishida, K. Kutsuwa, S. Murahashi and T. Naota, *Org. Lett.*, 2005, **7**, 5837; (*d*) Y. Imada, M. Nishida and T. Naota, *Tetrahedron Lett.*, 2008, **49**, 4915; (*e*) T. Nemoto, M. Kanematsu, S. Tamura and Y. Hamada, *Adv. Synth. Catal.*, 2009, **351**, 1773; (*f*) B. Wan, G. Jia and S. Ma, *Org. Lett.*, 2012, **14**, 46.

7 For Pd-catalyzed such reactions generating optically active allenes with a central chirality, see: (*a*) B. Wan and S. Ma,

Angew. Chem., Int. Ed., 2013, **52**, 441; (*b*) Q. Li, C. Fu and S. Ma, *Angew. Chem., Int. Ed.*, 2014, **53**, 6511.

8 For Pd-catalyzed such a reaction generating optically active allenes with both an axial chirality and a central chirality, see: J. Dai, X. Duan, J. Zhou, C. Fu and S. Ma, *Chin. J. Chem.*, 2018, **36**, 387.

9 (*a*) C. M. So, C. P. Lau and F. Y. Kwong, *Org. Lett.*, 2007, **9**, 2795; (*b*) S. Gore, S. Baskaran and B. König, *Org. Lett.*, 2012, **14**, 4568.

10 (*a*) H. Luo and S. Ma, *Eur. J. Org. Chem.*, 2013, 3041; (*b*) H. Luo, D. Ma and S. Ma, *Org. Synth.*, 2017, **94**, 153; (*c*) H. Wang, B. Beiring, D. Yu, K. D. Collins and F. Glorius, *Angew. Chem., Int. Ed.*, 2013, **52**, 12430; (*d*) X. Huang, T. Cao, Y. Han, X. Jiang, W. Lin, J. Zhang and S. Ma, *Chem. Commun.*, 2015, **51**, 6956.

11 A. Lin, J. Yang and M. Hashim, *Org. Lett.*, 2013, **15**, 1950.

12 J. Tsuji and T. Mandai, *J. Organomet. Chem.*, 1993, **451**, 15.