ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Xia, Q. Bao, Y. Li, L. Wang, B. Zhang, H. Liu and Y. Liang, *Chem. Commun.*, 2019, DOI: 10.1039/C9CC00611G.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C9CC00611G

Journal Name

COMMUNICATION

Ligand-Controlled Regiodivergent π-Allyl Palladium Catalysis Enables a Switch between [3+2] and [3+3] Cycloadditions

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

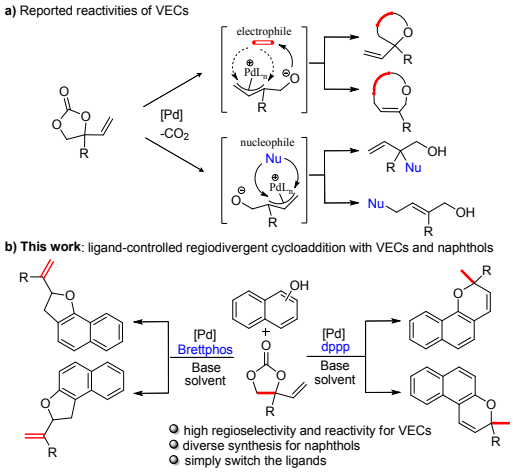
DOI: 10.1039/x0xx00000x

www.rsc.org/

Yu Xia,[a] Qiao-Fei Bao,[a] Yuke Li,[b] Li-Jing Wang,[c] Bo-Sheng Zhang,[a] Hong-Chao Liu,[a] and Yong-Min Liang*[a]

Reported herein is the use of ligands to tune the regioselectivity and reactivity of palladium-catalyzed [3+2] and [3+3] cycloadditions. Diverse synthesis with vinylethylene carbonates (VECs) as well as free naphthols has been explored to construct four different valuable polycyclic frameworks in a broad substrate scope.

Transition-metal-catalyzed cycloadditions constitute one of the most significant classes of organic reactions for building the challenging but synthetically valuable cyclic framworks that exist in natural products, bioactive reagents and pharmaceutical molecules.[1] Within this class of reactions, catalytic [3+2][1d,2] and [3+3][3] cycloadditions have enabled the highly efficient construction of midsize carbocycles and heterocycles. Meanwhile free naphthols, frequently-used as starting materials in cycloaddition, also have been a focal point of attention for chemists. The [3+2] and [3+3] transformations with free naphthols are expedient strategies to access naphthofuran and benzochromene structural motifs that are widely distributed compounds in biologically active products.[4] Because of the different reactivities of 1-naphthol and 2-naphthol, it is difficult for them to be used in cycloadditions at the same time. Therefore, the development of novel and efficient synthetic methods to improve the reactivity of 1-naphthol and 2-naphthol is highly desired. Transition-metal catalytic strategies that allow the divergent synthesis of skeletally diverse cycloadditions in particular, are desirable methodologies.



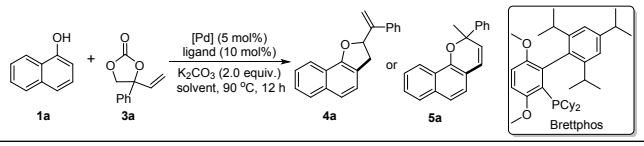
Scheme 1 Regioselectivity and reactivity of VECs

Vinylehtylene carbonates (VECs), regarded as π-allyl surrogates upon decarboxylation, have found various applications in organic chemistry.[5] Because of the diverse reactivities of π-allyl species, nucleophilic additions[6] and electrophilic cycloadditions[7] are feasible to deliver functionalized building blocks to their desired locations (Scheme 1a). Recently, Zhang et al. have developed diversified [3+2] cycloadditions with various electrophilic partners.[8] Zhao and co-workers reported some cycloaddition methods to synthesize highly functionalized rings of different sizes.[9] Although eminent approaches have been made regarding the regioselectivity of the π-allyl, the regiodivergent nature of π-allyl is seldom reflected in cycloaddition reactions. And with respect to the cycloaddition with VECs and nucleophiles, we urgently need to fill the gap in this field. Alternatively, under specific conditions, nucleophilic internal or terminal attack has enabled the construction of versatile alcohol compounds with high stereo- and regioselectivity. In this regard, the Kleij's group employed a series of nucleophiles, such as phenol, thiophenol and aniline, to realize π-allyl asymmetric synthesis.[10] Notably, most nucleophiles attack the Pd-π-allyl intermediate at one of the two terminal carbons, so the π-allyl central carbon atom is

[a]*Y. Xia, Q.-F. Bao, B.-S. Zhang, H.-C. Liu, Prof. Y.-M. Liang, State Key Laboratory of Applied Organic Chemistry, School of Chemistry and Chemical Engineering,Lanzhou University, Lanzhou 730000 (P. R. China) E-mail: liangym@lzu.edu.cn liangym@lzu.edu.cn*
[b]*Department of Chemistry and Centre for Scientific Modeling and Computation, Chinese University of Hong Kong, Shatin, Hong Kong, China*
[c]*Key Laboratory of Medicinal Chemistry, and Molecular Diagnosis of the Ministry of Education, College of Chemistry & Environmental Science, HeBei University, 180 Wusi Donglu, Baoding 071002, P. R. China.*
†Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data and copies of NMR spectra. CCDC 1890681, 1890679 and 1890680. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

View Article Online DOI: 10.1039/C9CC00611C

Table 1. Optimization of the reaction conditions.[a]



1a 3a 4a 5a

Entry	[Pd]	Ligand	Solvent	Yield (%)[b]	[**4a**:**5a**][c]
1	$[Pd(C_3H_5)Cl]_2$	XPhos	MeCN	61	12:1
2	$[Pd(C_3H_5)Cl]_2$	XPhos	toluene	66	16:1
3	$[Pd(C_3H_5)Cl]_2$	XPhos	1,4-dioxane	trace	-
4	$[Pd(C_3H_5)Cl]_2$	PPh_3	toluene	42	1:1
5	$[Pd(C_3H_5)Cl]_2$	P-(2-furyl)$_3$	toluene	37	3:1
6	$[Pd(C_3H_5)Cl]_2$	Brettphos	toluene	70	16:1
7	$[Pd(C_3H_5)Cl]_2$	Davephos	toluene	51	15:1
8	$[Pd(C_3H_5)Cl]_2$	DPEphos	toluene	40	1:>20
9	$[Pd(C_3H_5)Cl]_2$	dppp	toluene	55	1:>20
10	$Pd(OAc)_2$	Brettphos	toluene	59	14:1
11	$Pd_2(dba)_3{\cdot}CHCl_3$	Brettphos	toluene	55	10:1
12[d]	**$[Pd(C_3H_5)Cl]_2$**	**Brettphos**	**toluene**	**73**	**25:1**
13[e]	$[Pd(C_3H_5)Cl]_2$	Brettphos	toluene	60	20:1
14[d,f]	$[Pd(C_3H_5)Cl]_2$	Brettphos	toluene	77	>20:1

[a]Reactions were carried out using **1a** (0.2 mmol), **3a** (0.4 mmol), [Pd] (5.0 mol%), ligand (10.0 mol%), K_2CO_3 (2.0 equiv), solvent (2 ml), 90 °C, 12 h. [b]Isolated yields. [c]Regioselectivity determined by 1H-NMR analysis of crude reaction mixture. [d] [Pd] (2.5 mol%), ligand (5.0 mol%). [e][Pd] (1.0 mol%), ligand (2.0 mol%), 24h. [f]**1a** was replaced by 2-naphthol (**2a**).

rarely involved in any reaction.[11] Therefore, taking advantage of central carbon enables π-allyl to extend applications in organic synthesis.

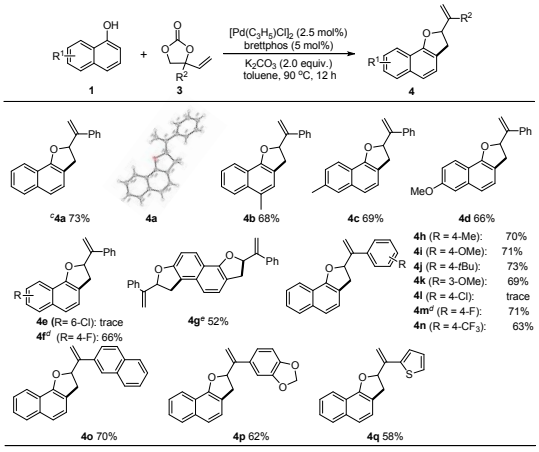
Based on the studies of regioselectivity and regio diversity,[12] ligand−controlled strategy is a challenging but straightforward way to our destination. We envisaged controlling the coordination of the catalyst to the π-allyl and the selectivity of nucleophilic addition through adjusting the steric and electronic effect of ligand. One remarkable feature of our design is that naphthol as a C,O-bis(nucleophile)s is difficult to react with umpolung VECs.[9c,13] Therefore catalyst-π-allyl system can be tuned by ligand without other influences in general. Meanwhile taking care of both 1-naphthol and 2-naphthol can greatly improve applicability of the reactions.

On the basis of this catalytic cycloaddition design plan, therefore we began by employing classical palladium/ligand system and 1-naphthol (**1a**)/phenyl VEC (**2a**) as partners to explore the reactions (Table 1). Encouragingly, our anticipated annulation products **4a** and slight **5a** were obtained in common yield 61% with 12:1 regioselectivity (entry 1). Subsequently, various solvents were executed; the yield and selectivity were slightly improved by using toluene (entries 2–3). Further experiments on the effect of the ligands were carried out (entries 4–9). By using small steric ligands, such as PPh_3 and P-(2-furyl)$_3$, the regioselectivity dramatically declined. Then, the bulky ligands were examined, producing the desired product in 70% yield and 16:1 selectivity. Fortunately, the use of bidentate ligands DPEphos or dppp switched the main product to **5a** in moderate yield and excellent regioselectivity (>20:1) (entries 8–9). No better results were obtained after screening on the palladium catalysts (entries 10–11). The subsequent adjustment of the Pd catalyst/ligand loading ratio produced better yield and superior selectivity (entry 12). Additionally, it should be noted that the loading of 1.0 mol% Pd catalyst and 2.0 mol% ligand was also tolerated to give **4a** in 60% yield with high regioselectivity (entry 13). Meanwhile 2-naphthol (**2a**) was entirely compatible with these reaction conditions (entry 14), which replaced the **1a** as the starting material. The optimized reaction conditions (denoted reaction condition **A**): **1** (0.2 mmol), **3** (0.4 mmol), $[Pd(C_3H_5)Cl]_2$ (2.5 mol%), Brettphos (5.0 mol%), K_2CO_3 (2.0 equiv), toluene (2 ml), 90 °C, 12 h.

With the optimized reaction conditions in hand, we first explored the scope of 1-naphthol's [3+2] cycloaddition (Table 2). A range of 1-naphthols containing electron-donating groups performed well in obtaining the corresponding products (**4a–4d**) in good yield with excellent regioselectivity (>20:1). Unfortunately, because of the influence of palladium(0) oxidative addition by chloro group, substrate **1e** failed to give the corresponding product **4e**. The group of F on the naphthol performed in this reaction (66% yield and reselectivity 2:1 for **4f**). Notably, 1,6-dihydroxynaphthalene was tolerated to give a novel tetracyclic compound at a yield of 52% (**4g**). Afterwards, a series of VECs, including electron-donating groups at the phenyl ring, worked smoothly in this transformation in 63–73% yield (**4h–4k**). Alternatively, VECs of containing electron-withdrawing group, with the exception of the chloro group (**3l**), also gave the corresponding products in 63–71% yield (**4m–4n**). Substitutions of polyaromatics as well as dioxolane fused phenyl ring, performed well, and were in good yield (**4o–4p**). Heteroaryl substituted VEC was also compatible to afford the product **4q** (yield for 58%).

To further ascertain the scope of the chosen reaction conditions, we investigated the 2-naphthol's [3+2]

Table 2 Substrate scope with respect to the 1-naphthol's [3+2] cycloaddition.[a,b]

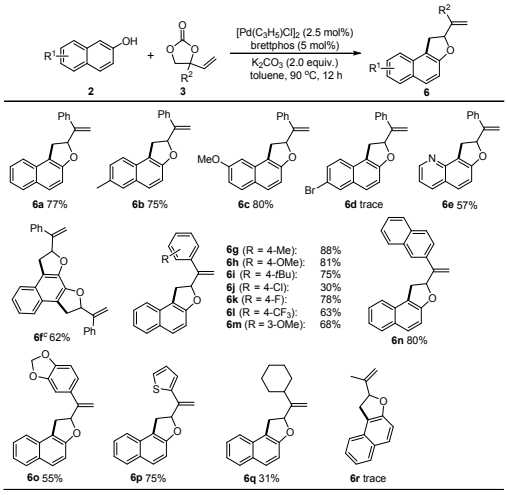


[a]Reaction condition **A**. Isolated yields are shown. [b]Unless otherwise noted, the regioselectivity ratio = >20:1.[c]The gram scale reaction of **4a** sees ESI. [d]The regioselectivity ratio of **4f** = 2:1 and **4k** = 14:1. [e]**3a** (0.6 mmol), K_2CO_3 (3.0 equiv).

cycloadditions (Table 3). The fundamental structure of the 2-naphthol was explored, thus affording a corresponding product in 77% yield with excellent regioselectivity (>20:1) (**6a**). The presence of electron-donating groups on 2-naphthol, such as methyl and methoxy, performed well (75–77% yield for **6b–6c**). The bromo group on the 2-naphthol failed to give a naphthofuran compound (**6d**). Gratifyingly, 7-hydroxyquinoline participated in this reaction to deliver **6e** in moderate yield. Meanwhile, the 2,3-dihydroxynaphthalene also underwent smoothly, affording a unique product with a double cycloaddition (62% yield for **6f**). For the variation on the VEC **3**, both electron-donating and electron-withdrawing groups at the *para*- or *meta*- position on the phenyl group were achieved in moderate to excellent yield (**6g–6m**). Remarkably, substitutions of heteroaryl, polyaromatic even dioxolane fused phenyl ring were applied with good yield results (**6n–6p**). Screening on the alkyl VECs, cyclohexyl was tolerated to give **6q** in 31% yield. But the methyl VEC failed to obtain the corresponding product **6r**. The structure of **6n** was confirmed by X-ray crystal structure analysis (see ESI).

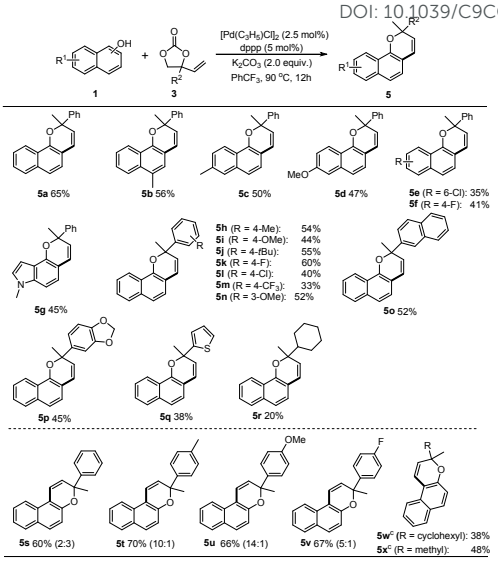
Subsequently, the scope of [3+3] cycloaddition with naphthols was investigated (Table 4) under the optimal conditions **B** (Screening the conditions **B** sees ESI). Toward this end, we studied the effect of electrons on the 1-naphthol. Whether investigating electron-donating or electron-withdrawing groups on the naphthol, they all afforded the products in 35–65% yield (**5a–5f**). It is noteworthy that 4-hydroxyindole could provide the cycloaddition product in a moderate yield (**5g**). Next, various electron-donating and electron-withdrawing substituents at *para*- or *meta*- positions on the phenyl group of VECs were all tolerated and gave 33–60% yield (**5h–5n**). Ultimately, VECs, containing thienyl, naphthyl, dioxolane and cyclohexyl ring, also produced the desired products (**5o–5r**). In spite of unsatisfied regioselectivity of 2-naphthol's [3+3] cycloaddition, we also explored the effect of substituents in order to improve the reaction.

Table 3 Substrate scope with respect to 2-naphthol's [3+2] cycloaddition[a,b]



[a]Reaction conditions **A** and isolated yields are shown. [b]Unless otherwise noted, the regioselectivity ratio = >20:1. [c]**3a** (0.6 mmol) and K_2CO_3 (3.0 equiv).

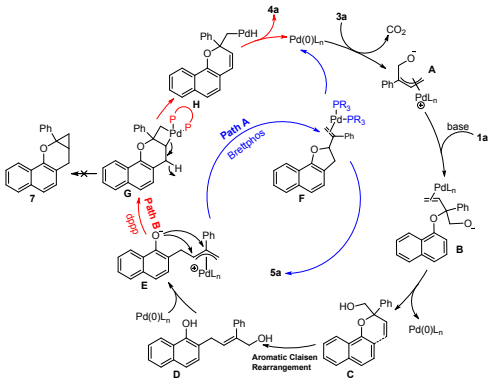
Table 4 Substrate Scope with Respect to [3+3] cycloaddition.[a,b]



[a]Reaction conditions **B** (screening the conditions **B** sees ESI). Isolated yields are shown. [b]Unless otherwise noted, the regioselectivity ratio = >20:1. [c]The regioselectivity ratio **5w** = 12:1 and **5x** = 3:1.

Compared with the unsubstituted substrate **3a**, monosubstituted substrates bearing electron-withdrawing and electron-donating groups enhanced the selectivity of cycloaddition (**5s–5v**). Especially, the electron-donating groups dramatically improved the reaction regioselectivity. And the alkyl VECs such as cyclohexyl and methyl group reacted under the reaction conditions but showed different selectivity (**5w and 5r**). The structure of **5j** was confirmed by X-ray crystal structure analysis (see ESI).

A plausible mechanism for the [3+2] and [3+3] cycloaddition is depicted in Scheme 2, which features ligand-controlled π-allyl regioselectivity.[10d,14] The catalytic cycle is initiated by Pd-π-allyl intermediate **A,** formed from Pd(0) and **3a**. Under the action of the base, the nucleophile **1a** attacks the internal carbon atom of Pd-allyl **A** to afford vinylpalladium **B**. The intermediate **B** undergoes reductive elimination of Pd(II)L_n to deliver the tertiary allylic aryl ether **C**. An aromatic Claisen rearrangement occurs smoothly under this reaction condition, producing the intermediate **D**. The previously freed Pd(0) reacts with **D** via



Scheme 2 Proposed Mechanism

allylation once again and then obtains the alternative intermediate **E**. On one hand, by using Brettphos as ligand, oxygen ion selectively attacks the internal carbon atom to afford [3+2] cycloaddition product **4a** (**Path A**). On the other hand, under the control of ligand dppp, oxygen ion selectively attacks π-allylpalladium intermediate at its central carbon atom rather than external carbon atom to form the cyclicpalladium **G**. Regrettably, we did not detect the product **7** of direct reductive elimination. Following by β-H elimination and reductive elimination, the desired product **5a** is produced and Pd(0) is regenerated to the next reaction cycle (**Path B**).

In summary, we here present an efficient and diverse cycloaddition between naphthols and VECs under palladium/ligand catalysis. By simply switching the ligands, an unprecedented π-allyl regiodivergent is realized to enable [3+2] and [3+3] cycloadditions. Meanwhile, both 1-naphthols and 2-naphthols are also tolerated in this method, thus greatly improving the economics of the reactions. The compatibility with gram scale reaction further enhanced the synthetic practicality of this method. These discoveries shed light on the development of new catalytic domino reactions for challenging π-allyl regiodivergent and regioselectivity via ligand-controlled methodologies.

We thank the National Natural Science Foundation of China (21532001 and 21772075).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For reviews see: (a) M. Lautens, W. Klute, W. Tam, *Chem. Rev.,* 1996, **96**, 49; (b) K. E. O. Ylijoki, J. M. Stryker, *Chem. Rev.,* 2013, **113**, 2244. For related examples see: (c) R. T. Yu, E. E. Lee, G. Malik, T. Rovis, *Angew. Chem. Int. Ed.,* 2009, **48**, 2379; (d) B. M. Trost, Z. Huang, G. M. Murhade, *Science,* 2018, **362**, 564.

2 For reviews see: (a) J. He, J. Ling, P. Chiu, *Chem. Rev.,* 2014, **114**, 8037. For related examples see: (b) M. Pineschi, F. Bertolini, V. Di Bussolo, P. Crotti, *Cur. Org. Synth.,* 2009, **6**, 290; (c) X.-R. Song, X.-F. Xia, B. Song, X. Tian, H.-T. Zhu, A.-X. Zhou, X.-Y. Liu, Y.-M. Liang, *Asian J. Org. Chem.,* 2013, **2**, 755; (d) R. Long, J. Huang, W. Shao, S. Liu, Y. Lan, J. Gong, Z. Yang, *Nat. Commun.,* 2014, **5**, 5707; (e) D.-C. Wang, M.-S. Xie, H.-M. Guo, G.-R. Qu, M.-C. Zhang, S.-L. You, *Angew. Chem. Int. Ed.,* 2016, **55**, 14111; (f) Q. Cheng, H.-J. Zhang, W.-J. Yue, S.-L. You, *Chem,* 2017, **3**, 428.

3 For reviews see: (a) Richard P. Hsung, Aleksey V. Kurdyumov, N. Sydorenko, *Eur. J. Org. Chem.,* 2005, **2005**, 23; (b) X. Xu, M. P. Doyle, *Acc. Chem. Res.,* 2014, **47**, 1396. For related examples see: (c) R. Shintani, T. Hayashi, *J. Am. Chem. Soc.,* 2006, **128**, 6330; (d) A. H. Stoll, S. B. Blakey, *Chem. Sci.,* 2011, **2**, 112; (e) Y.-P. Han, X.-S. Li, M. Li, X.-Y. Zhu, Y.-M. Liang, *Adv. Synth. Catal.,* 2018, **360**, 2796.

4 (a) P. K. Frederiksen, M. Jørgensen, P. R. Ogilby, *J. Am. Chem. Soc.,* 2001, **123**, 1215; (b) Y. Nishibayashi, Y. Inada, M. Hidai, S. Uemura, *J. Am. Chem. Soc.,* 2002, **124**, 7900; (c) K. K. Park, S.-H. Kim, J. W. Park, *J. Photochem. Photobio. A,* 2004, **163**, 241; (d) S. Claessens, B. Kesteleyn, T. Nguyen Van, N. De Kimpe, *Tetrahedron,* 2006, **62**, 8419; e) A. V. Karnik, A. M. Kulkarni, N. J. Malviya, B. R. Mourya, B. L. Jadhav, *Eur. J. Med. Chem.,* 2008, **43**, 2615; (f) X.-F. Hou, S. Yao, A. Mándi, T. Kurtán, C.-P. Tang, C.-Q. Ke, X.-Q. Li, Y. Ye, *Org. Lett.,* 2012, **14**, 460; (g) L. Shao, Y.-H. Wang, D.-Y. Zhang, J. Xu, X.-P. Hu, *Angew. Chem. Int. Ed.,* 2016, **55**, 5014; (h) D. Wang, X. Tong, *Org. Lett.,* 2017, **19**, 6392.

5 For reviews see: (a) J. D. Weaver, A. Recio, A. J. Grenning, J. A. Tunge, *Chem. Rev.,* 2011, **111**, 1846; (b) W. Guo, J. E. Gómez, À. Cristòfol, J. Xie, A. W. Kleij, *Angew. Chem. Int. Ed.,* 2018, **57**, 13735. For related examples see: (c) S.-S. Zhang, J.-Q. Wu, Y.-X. Lao, X.-G. Liu, Y. Liu, W.-X. Lv, D.-H. Tan, Y.-F. Zeng, H. Wang, *Org. Lett.,* 2014, **16**, 6412; (d) S.-S. Zhang, J.-Q. Wu, X. Liu, H. Wang, *ACS Catal.,* 2015, **5**, 210.

6 A. Khan, S. Khan, I. Khan, C. Zhao, Y. Mao, Y. Chen, Y. J. Zhang, *J. Am. Chem. Soc.,* 2017, **139**, 10733.

7 (a) K. Liu, M. T. Hovey, K. A. Scheidt, *Chem. Sci.,* 2014, **5**, 4026; (b) U. Orcel, J. Waser, *Chem. Sci.,* 2017, **8**, 32; (c) S. Singha, T. Patra, C. G. Daniliuc, F. Glorius, *J. Am. Chem. Soc.,* 2018, **140**, 3551; (d) Y. Wei, S. Liu, M.-M. Li, Y. Li, Y. Lan, L.-Q. Lu, W.-J. Xiao, *J. Am. Chem. Soc.,* 2019, **141**, 133.

8 (a) A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing, Y. J. Zhang, *Angew. Chem. Int. Ed.,* 2014, **53**, 6439; (b) A. Khan, L. Yang, J. Xu, L. Y. Jin, Y. J. Zhang, *Angew. Chem. Int. Ed.,* 2014, **53**, 11257; (c) A. Khan, J. Xing, J. Zhao, Y. Kan, W. Zhang, Y. J. Zhang, *Chem. Eur. J.,* 2015, **21**, 120; (d) L. Yang, A. Khan, R. Zheng, L. Y. Jin, Y. J. Zhang, *Org. Lett.,* 2015, **17**, 6230; (e) K. Liu, I. Khan, J. Cheng, Y. J. Hsueh, Y. J. Zhang, *ACS Catal.,* 2018, **8**, 11600.

9 (a) L.-C. Yang, Z.-Q. Rong, Y.-N. Wang, Z. Y. Tan, M. Wang, Y. Zhao, *Angew. Chem. Int. Ed.,* 2017, **56**, 2927; (b) Z.-Q. Rong, L.-C. Yang, S. Liu, Z. Yu, Y.-N. Wang, Z. Y. Tan, R.-Z. Huang, Y. Lan, Y. Zhao, *J. Am. Chem. Soc.,* 2017, **139**, 15304; (c) L.-C. Yang, Z. Y. Tan, Z.-Q. Rong, R. Liu, Y.-N. Wang, Y. Zhao, *Angew. Chem. Int. Ed.,* 2018, **57**, 7860.

10 (a) W. Guo, L. Martínez-Rodríguez, R. Kuniyil, E. Martin, E. C. Escudero-Adán, F. Maseras, A. W. Kleij, *J. Am. Chem. Soc.,* 2016, **138**, 11970; (b) J. E. Gómez, W. Guo, A. W. Kleij, *Org. Lett.,* 2016, **18**, 6042; (c) A. Cai, W. Guo, L. Martínez-Rodríguez, A. W. Kleij, *J. Am. Chem. Soc.,* 2016, **138**, 14194; (d) J. Xie, W. Guo, A. Cai, E. C. Escudero-Adán, A. W. Kleij, *Org. Lett.,* 2017, **19**, 6388.

11 For examples of attacking central carbon see: (a) H. M. R. Hoffmann, A. R. Otte, A. Wilde, S. Menzer, D. J. Williams, *Angew. Chem. Int. Ed. Engl.,* 1995, **34**, 100; (b) R. Shintani, S. Park, T. Hayashi, *J. Am. Chem. Soc.,* 2007, **129**, 14866; (c) S. Duan, B. Cheng, X. Duan, B. Bao, Y. Li, H. Zhai, *Org. Lett.,* 2018, **20**, 1417; (d) J.-Q. Huang, W. Liu, B.-H. Zheng, X. Y. Liu, Z. Yang, C.-H. Ding, H. Li, Q. Peng, X.-L. Hou, *ACS Catal.,* 2018, **8**, 1964.

12 (a) A. M. Castaño, A. Aranyos, K. J. Szabó, J.-E. Bäckvall, *Angew. Chem. Int. Ed. Engl.,* 1995, **34**, 2551; (b) B. M. Trost, J. Xu, T. Schmidt, *J. Am. Chem. Soc.,* 2008, **130**, 11852; (c) J. Liu, Q. Liu, R. Franke, R. Jackstell, M. Beller, *J. Am. Chem. Soc.,* 2015, **137**, 8556; (d) D. Ding, T. Mou, M. Feng, X. Jiang, *J. Am. Chem. Soc.,* 2016, **138**, 5218; (e) S.-y. Baek, J. Y. Lee, D. Ko, M.-H. Baik, E. J. Yoo, *ACS Catal.,* 2018, **8**, 6353; (f) C. Yuan, Y. Wu, D. Wang, Z. Zhang, C. Wang, L. Zhou, C. Zhang, B. Song, H. Guo, *Adv. Synth. Catal.,* 2018, **360**, 652; (g) D. Ding, G. Zhu, X. Jiang, *Angew. Chem. Int. Ed.,* 2018, **57**, 9028.

13 For examples of umpolung VECs see: (a) W. Guo, R. Kuniyil, J. E. Gómez, F. Maseras, A. W. Kleij, *J. Am. Chem. Soc.,* 2018, **140**, 3981; (b) H. Wang, S. Qiu, S. Wang, H. Zhai, *ACS Catal.,* 2018, **8**, 11960.

14 For ligand effect in π-allyl reactions see: R. Shintani, S. Park, F. Shirozu, M. Murakami, T. Hayashi, *J. Am. Chem. Soc.,* 2008, **130**, 16174.For oxygen attacks the central carbon atom of allyl see: 1) M. G. Organ, M. Miller and Z. Konstantinou, *J. Am. Chem. Soc.*, 1998, **120**, 9283; 2) R. Shintani, T. Ito and T. Hayashi, *Org. Lett.*, 2012, **14**, 2410.