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Visible-light photocatalytic bicyclization of β-alkynyl propenones for accessing diastereoenriched *syn*-fluoren-9-ones†

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A novel visible-light photocatalytic bicyclization of β-alkynyl propenones with α-bromocarbonyls for highly diastereoselective synthesis of richly decorated *syn*-fluoren-9-ones is described. The reaction proceeds *via* a radical-triggered 5-*exo*-dig cyclization/1,6-*H*-abstraction/6-*endo*-trig cyclization cascade and offers a new and practical method for the assembly of 6/5/6 carbocyclic skeletons *via* C(sp³)–H alkenylation.

Visible light photoredox catalysis (VLPC) has been identified as a highly attractive and applicable synthetic tool for the collection of functionalized organic molecules *via* radical addition or cross-coupling reaction and thus has drawn considerable attention in the organic community due to its intrinsic characteristics of safety, being green and sustainability as well as availability.[1–3] In particular, visible light induced cycloaddition (VLIC) reactions, such as [2+2],[4] [3+2],[5] [4+2][6] and [2+2+2][7] cycloaddition, have been proven to be an efficient and straightforward protocol for constructing four-, five- or six-membered cycles and polycyclic structures. For example, the group of Yoon pioneered visible light induced intramolecular [2+2] cycloaddition of bis-enones for cyclobutene synthesis.[8] Later, the group of Xiao reported a visible light photocatalytic [3+2] cycloaddition of dihydroisoquinoline esters with activated alkenes toward pyrrolo[2,1-*a*]isoquinolines.[9] Subsequently, the group of Yoon described an unusual radical cation Diels–Alder cycloaddition between electron-rich dienophiles with 1,3-butadienes by means of visible light photocatalysis.[10] The same group then developed photoredox [2+2+2] cycloadditions of bis-styrenes with molecular oxygen, affording endoperoxides with high stereoselectivity.[11] Moreover, Li's group achieved visible-light photocatalytic [2+2+2] cycloadditions of 1,6-enynes with arylsulfonyl chloride to access benzo[*b*]fluorenes.[12] Recently, Xia and co-workers established a

visible light photocatalytic bicyclization of 1,7-enynes with α-bromo diethyl malonates for the synthesis of cyclopenta[*c*]-quinolines.[13] Despite these significant achievements in this field, the development of new and facile visible light induced cyclizations toward installing functionalized cyclic structures is still highly desirable.

Over the years, α-allyl-α-bromocarbonyls have been found to be highly reactive reactants that are endowed with both a radical donor and a radical acceptor, thus serving as versatile building blocks for many important targets of chemical and biomedical potential.[14] A great amount of cascade reactions triggered by α-allyl-α-bromocarbonyls under redox conditions have been developed, enabling radical addition-cyclizations for the synthesis of important polycyclic structures.[15] Recently, Zhu's group presented an efficient visible-light photoredox-catalyzed bicyclization cascade of α-allyl-α-bromocarbonyls with 2-ethynylaldehyde hydrazones for the synthesis of various tetrahydro-2*H*-cyclopenta[*a*]naphthalenes (Scheme 1a).[16] However, visible light induced bicyclization of α-allyl-α-bromocarbonyls together with their C(sp³)–H bond functionalization *via* 1,6-*H* abstraction, to the best of our knowledge, has been virtually unexplored. On the basis of the above literature survey and in continuation of our interest in radical cyclization,[17] we reasoned that the preformed β-alkynyl propenones **1** were a good radical acceptor and employed them to react with α-allyl-α-bromocarbonyls to afford polyfunctionalized fluoren-9-ones *via* photocatalytic bicyclization.

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Scheme 1 Profiles of photoinduced transformations of α-bromocarbonyls.

Interestingly, the reactions could work well, providing a wide range of richly decorated *syn*-fluoren-9-ones **3** containing two quaternary stereocenters with generally good yields and high diastereoselectivity (Scheme 1b). This reaction protocol enables successive C–C formation through C(sp^3)–H bond cleavage under the neutral–redox conditions by using α-bromocarbonyls as twice radial donors, with the advantage of atom economy and extreme convergence. Here, we report these attractive transformations.

At the outset of our studies, β-alkynyl propenone **1a** as a model substrate was subjected to the reaction of diethyl α-isopentenyl-α-bromomalonate (**2a**) in a 1 : 2 mole ratio. As depicted in Table 1, the reaction proceeded smoothly in CH$_3$CN in the presence of 2.0 equivalents of K$_2$CO$_3$ at room temperature by using 1.0 mol% of *fac*-Ir(ppy)$_3$ as a photocatalyst under argon conditions and visible light irradiation (blue LEDs), enabling radical addition–cyclization to give the expected *syn*-fluoren-9-one **3a** as a sole diastereoisomer in 51% yield (Table 1, entry 1). The stereo-structure of product **3a** was assigned by ^{1}H NMR and X-ray diffraction analysis (see the ESI†), and those of other products were assigned by analogy. The optimization of the reaction conditions was then conducted by examining visible-light photocatalysts often used in the photocatalysis, such as Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$, [Ru(bpy)$_3$](PF$_6$)$_2$, Ru(bpy)$_3$Cl$_2$·6H$_2$O, and eosin Y, indicating that all these photocatalysts completely suppressed the reaction process (entries 2–5). Fine-tuning the amount of K$_2$CO$_3$ to 1.0 equivalent facilitated this photocatalysis process, delivering *syn*-product **3a** in a higher yield of 61% (entry 6). Next, the investigation of the solvent effect revealed that other solvents, such as CH$_3$OH, toluene, tetrahydrofuran (THF), and 1,2-dichloroethane (DCE), proved to be less effective as compared with CH$_3$CN (entries 7–10). After systematic screening of various inorganic bases, such as Cs$_2$CO$_3$, K$_3$PO$_4$, and KOH, it was found that these tested bases were all inferior

in terms of reaction yields (entries 11–13). Without visible light or *fac*-Ir(ppy)$_3$ photocatalyst, the above reaction did not work (entries 14 and 15). Moreover, a lower conversion of **1a** into **3a** was observed when the identical reaction was carried out under air conditions (entry 16).

Having established the optimal reaction conditions, we next systematically investigated the scope of the photoinduced bicyclization reaction with an assortment of β-alkynyl propenone components (Scheme 2). The survey showed that the iridium-catalyzed protocol is feasible with a wide variety of β-alkynyl propenone derivatives under visible-light irradiation furnishing the corresponding cycloaddition products with good yields and excellent diastereoselectivity. At first, β-alkynyl propanones with diverse functionalities in the arylalkynyl (R^2) moiety were examined in combination with diethyl α-isopentenyl-α-bromomalonate **2a**. Substituents with either electronically rich, neutral, or poor properties in the arene ring completely oriented the diastereoselectivity to the formation of *syn*-fluoren-9-ones **3b**–**3g** with 58–68% yields. Functional groups such as ethyl (**1b**), methoxy (**1c**, PMP = *p*-methoxyphenyl), fluoride (**1e**) chloride (**1f**), and bromide (**1g**) were well tolerated under the standard conditions Alternatively, a heterocyclic 2-thienyl analogue was proven to be effective, enabling a similar radical-induced bicyclization process to give 2-thienyl substituted *syn*-fluoren-9-one **3h** in 59% yield and complete diastereoselectivity. The representative methyl group located at the 4-position of the internal arene ring was compatible with these photocatalytic conditions and the corresponding *syn*-products **3i**–**3n** were obtained in satisfactory yields. Similarly, dimethyl α-allyl-α-bromomalonate **2b** was found to show high reactivity, leading to the formation of diastereoenriched fluoren-9-ones **3o**–**3y** with yields ranging from 56% to 66%.

Table 1 Optimization of the reaction conditions^a

Entry	Cat.	Base (equiv.)	Solvent	Yield^b (%)
1	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (2.0)	CH$_3$CN	51
2	Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$	K$_2$CO$_3$ (2.0)	CH$_3$CN	N.R.
3	[Ru(bpy)$_3$](PF$_6$)$_2$	K$_2$CO$_3$ (2.0)	CH$_3$CN	N.R.
4	Ru(bpy)$_3$Cl$_2$·6H$_2$O	K$_2$CO$_3$ (2.0)	CH$_3$CN	N.R.
5	Eosin Y	K$_2$CO$_3$ (2.0)	CH$_3$CN	N.R.
6	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (1.0)	CH$_3$CN	61
7	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (1.0)	CH$_3$OH	Trace
8	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (1.0)	Toluene	35
9	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (1.0)	THF	30
10	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (1.0)	DCE	33
11	*fac*-Ir(ppy)$_3$	Cs$_2$CO$_3$ (1.0)	CH$_3$CN	20
12	*fac*-Ir(ppy)$_3$	K$_3$PO$_4$ (1.0)	CH$_3$CN	24
13	*fac*-Ir(ppy)$_3$	KOH (1.0)	CH$_3$CN	N.D.
14^c	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (1.0)	CH$_3$CN	N.R.
15	—	K$_2$CO$_3$ (1.0)	CH$_3$CN	N.R.
16^d	*fac*-Ir(ppy)$_3$	K$_2$CO$_3$ (1.0)	CH$_3$CN	33

^{a} Reaction conditions: **1a** (0.4 mmol), **2a** (0.8 mmol), cat. (1.0 mol%), base (*x* equiv.), solvent (6.0 mL), 12 W blue LED light, under Ar conditions. ^{b} Isolated yield based on **1a**. ^{c} In the dark. ^{d} In the air.

Scheme 2 Synthesis of *syn*-fluoren-9-ones **3a**–**3y**. (i) Reaction conditions: **1** (0.4 mmol), **2a**–**b** (0.8 mmol), *fac*-Ir(ppy)$_3$ (1.0 mol%), K$_2$CO$_3$ (1.0 equiv.) and CH$_3$CN (6.0 mL) in the sealed reaction tube under Ar conditions at room temperature for 24.0 hours. (ii) Isolated yields in brackets based on **1**.
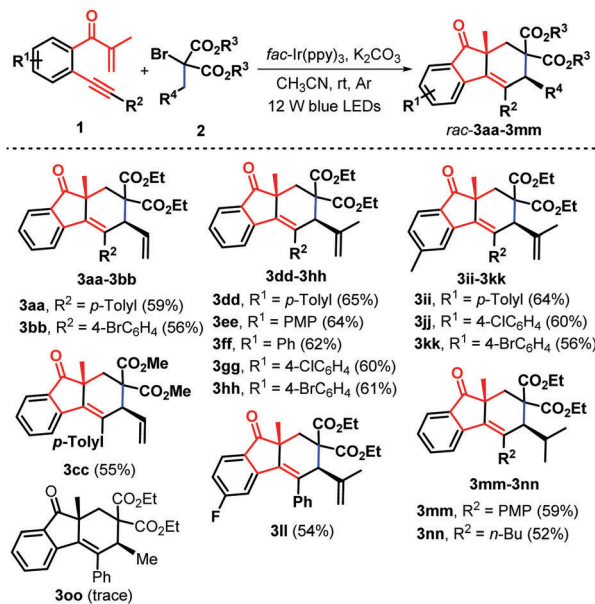
Scheme 3 Synthesis of *syn*-fluoren-9-ones **3aa–3oo**. (i) Reaction conditions: **1** (0.4 mmol), **2c–g** (0.8 mmol), *fac*-Ir(ppy)$_3$ (1.0 mol%), K$_2$CO$_3$ (1.0 equiv.) and CH$_3$CN (6.0 mL) in the sealed reaction tube under Ar conditions at room temperature for 24.0 hours. (ii) Isolated yields in brackets based on **1**.

To expand the utility of this methodology, we turned our attention to exploring the feasibility of other substituted α-bromomalonates including allyl (**2c** and **2d**), isobutenyl (**2e**), isobutyl (**2f**), and ethyl (**2g**). As anticipated, the reaction of *b*-alkynyl propenones **1** with α-bromomalonates **2c–2f** under the standard conditions offered structurally diverse *syn*-fluoren-9-ones **3aa–3nn** as sole diastereoisomers in generally good yields (Scheme 3). β-Alkynyl propenones **1** possessing electron-donating, electron-neutral, and electron-withdrawing groups linked to both the internal arene ring (*R*^{1}) and the arylalkynyl (*R*^{2}) moiety did not hamper the reaction process. Notably, regarding the scope of α-bromomalonates, besides the isopentenyl substrate, the allyl (**2c** and **2d**), isobutenyl (**2e**) and isobutyl (**2f**) analogue could be successfully engaged in the current photocatalysis. Unluckily, on replacing the allyl group with an ethyl group on the malonate unit, α-bromomalonate **2g** was an ineffective reaction partner for this photocatalysis (Scheme 3, **3oo**), which may be ascribed to the relative instability of the methylene radical intermediate **D**, generated *in situ* from C-centered radical triggered 1,6-*H*- abstraction, due to its weak captodative effect[18] (Scheme 5). It is noteworthy that the current photocatalytic protocol represents a new and practical pathway for the creation of highly diastereoenriched *syn*-fluoren-9-ones **3** through an Ir-catalyzed bicyclization cascade involving radical-triggered C(sp^3)–H bond alkenylation.

To gain further mechanistic insight into this mechanism, a preliminary controlled experiment was conducted. When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the radical scavenger was added into the reaction system under the standard conditions, the reaction was substantially inhibited and the starting material **1a** was almost completely recovered,


Scheme 4 Synthetic utility of the methodology.

indicating that this transformation may include a single electron transfer (SET) process (Scheme 4a). Then, 1,1-diphenylethylene was subjected to the reaction of **1a** with **2e** under the standard conditions, and the product **3dd** and diethyl 2-(2,2-diphenyl-vinyl)-2-(2-methylallyl)malonate **4** were isolated in 32% and 35% yields, respectively, suggesting that the transformation could involve the *in situ*-generation of a C-centered radical under visible-light photocatalytic conditions (Scheme 4b).

Based on the above results and literature survey,[14–16] a reasonable mechanism for the bicyclization reaction was proposed in Scheme 5. Initially, visible light induces [*fac*-^{III}Ir(ppy)$_3$] to the excited state [*fac*-^{III}Ir(ppy)$_3$]*, which reduces α-allyl-α-bromomalonates **2** to generate a C-centered radical **A** along with [*fac*-^{IV}Ir(ppy)$_3$] via single electron transfer (SET).[19] Subsequently, radical addition of intermediate **A** into the C–C double bond of β-alkynyl propenones **1** yields quaternary carbon radical **B**, followed by 5-*exo-dig* cyclization and 1,6-*H* atom transfer (HAT)[20] to afford the radical intermediate **D**, which undergoes 6-*endo-trig* cyclization to give *trans*-intermediate **E** due to the steric effect. At this stage, a key oxidization (SET) step between **E** and [*fac*-^{IV}Ir(ppy)$_3$] occurs, thus regenerating the photocatalyst and the cation *trans*-intermediate **F**. Further deprotonation of intermediate **F** would give the final *syn*-products **3**.

In summary, starting from readily available β-alkynyl propenones and α-bromomalonates, a new and visible-light photocatalytic
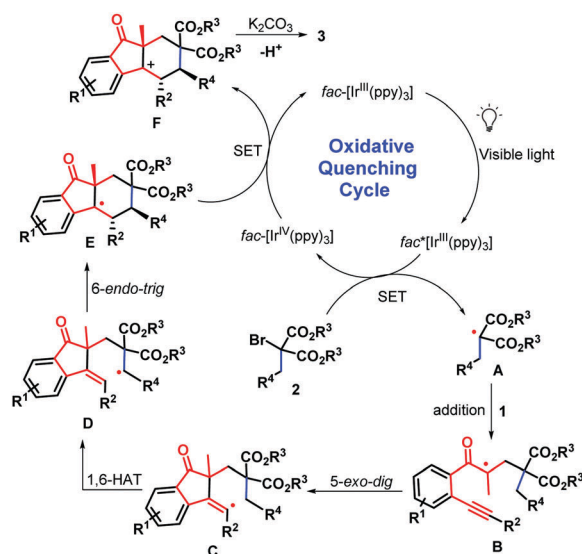
Scheme 5 Plausible reaction pathways.

bicyclization cascade was established, by which this photocatalysis completely oriented the high diastereoselectivity to assemble a wide range of structurally diverse *syn*-fluoren-9-ones with generally good yields. The present photocatalytic strategy accommodates a broad substrate scope and is distinguished by its mild conditions and high functional group compatibility. The reaction pathway including a 5-*exo-dig* cyclization/1,6-HAT/6-*endo-trig* cyclization sequence was proposed, resulting in the formation of up to three new C–C bonds and two new rings through radical-induced C(sp^3)–H bond cleavage. Further application of the photocatalysis to bioactive polycycles is currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For reviews on visible-light photoredox catalysis, see: (*a*) K. Zeitler, *Angew. Chem., Int. Ed.*, 2009, **48**, 9785; (*b*) T. P. Yoon, M. A. Ischay and J. Du, *Nat. Chem.*, 2010, **2**, 527; (*c*) J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102; (*d*) F. Teply and C. Czech, *Chem. Commun.*, 2011, **76**, 859; (*e*) J. W. Tucker and C. R. J. Stephenson, *J. Org. Chem.*, 2012, **77**, 1617.
2 For recent reviews on visible light photoredox catalysis, see: (*a*) A. E. Allen and D. W. C. MacMillan, *Chem. Sci.*, 2012, **3**, 633; (*b*) L. Shi and W. Xia, *Chem. Soc. Rev.*, 2012, **41**, 7687; (*c*) J. Xuan and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 6828; (*d*) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322.
3 For other selected papers, see: (*a*) P. V. Pham, D. A. Nagib and D. W. C. MacMillan, *Angew. Chem., Int. Ed.*, 2011, **50**, 6119; (*b*) A. McNally, C. K. Prier and D. W. C. MacMillan, *Science*, 2011, **334**, 1114; (*c*) D. A. Nagib and D. W. C. MacMillan, *Nature*, 2011, **480**, 224; (*d*) Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R. L. Davis, K. A. Joergensen and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 784; (*e*) G.-Q. Xu, J.-T. Xu, Z.-T. Feng, H. Liang, Z.-Y. Wang, Y. Qin and P.-F. Xu, *Angew. Chem., Int. Ed.*, 2018, **57**, 5110; (*f*) X. Huang, J. Lin, T. Shen, K. Harms, M. Marchini, P. Ceroni and E. Meggers, *Angew. Chem., Int. Ed.*, 2018, **57**, 5454; (*g*) M.-M. Li, Y. Wei, J. Liu, H.-W. Chen, L.-Q. Lu and W.-J. Xiao, *J. Am. Chem. Soc.*, 2017, **139**, 14707.
4 For selected recent works about photocatalytic [2+2] cycloaddition reactions, see: (*a*) J. Du and T. P. Yoon, *J. Am. Chem. Soc.*, 2009, **131**, 14604; (*b*) M. A. Ischay, Z. Lu and T. P. Yoon, *J. Am. Chem. Soc.*, 2010, **132**, 8572; (*c*) J. Du, K. L. Skubi, D. M. Schultz and T. P. Yoon, *Science*, 2014, **344**, 392; (*d*) Z. Lu and T. P. Yoon, *Angew. Chem., Int. Ed.*, 2012, **51**, 1; (*e*) M. A. Ischay, M. S. Ament and T. P. Yoon, *Chem. Sci.*, 2012, **3**, 2807; (*f*) A. E. Hurtley, Z. Lu and T. P. Yoon, *Angew. Chem., Int. Ed.*, 2014, **53**, 8991.
5 For selected recent works about photocatalytic [2+3] cycloaddition reactions, see: (*a*) Z. Lu, M. Shen and T. P. Yoon, *J. Am. Chem. Soc.*, 2011, **133**, 1162; (*b*) J. Xuan, X.-D. Xia, T. Zeng, Z.-J. Feng, J.-R. Chen, L.-Q. Lu and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2014, **126**, 5759; (*c*) S. Maity, M.-Z. Zhu, R. S. Shinabery and N. Zheng, *Angew. Chem., Int. Ed.*, 2012, **51**, 222; (*d*) T. R. Blum, Y. Zhu, S. A. Nordeen and T. P. Yoon, *Angew. Chem., Int. Ed.*, 2014, **53**, 11056; (*e*) M. Rueping, D. Leonori and T. Poisson, *Chem. Commun.*, 2011, **47**, 9615.
6 For selected recent works about photocatalytic [2+4] cycloaddition reactions, see: (*a*) M. A. Cismesia and T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426; (*b*) Z.-G. Yuan, Q. Wang, A. Zheng, K. Zhang, L.-Q. Lu, Z. Tang and W.-J. Xiao, *Chem. Commun.*, 2016, **52**, 5128; (*c*) T.-B. Xiao, X.-C. Dong, Y.-C. Tang and L. Zhou, *Adv. Synth. Catal.*, 2012, **354**, 3195; (*d*) C. Wiegand, E. Herdtweck and T. Bach, *Chem. Commun.*, 2012, **48**, 10195.
7 For selected recent reviews about photocatalytic [2+2+2] cycloaddition reactions, see: (*a*) V. Gandon, C. Aubert and M. Malacria, *Chem. Commun.*, 2006, 2209; (*b*) G. Dominguez and J. Perez-Castells, *Chem. Soc. Rev.*, 2011, **40**, 3430; (*c*) N. Weding and M. Hapke, *Chem. Soc. Rev.*, 2011, **40**, 4525.
8 M. A. Ischay, M. E. Anzoino, J. Dum and T. P. Yoon, *J. Am. Chem. Soc.*, 2008, **130**, 12886.
9 Y.-Q. Zou, L.-Q. Lu, L. Fu, N.-J. Chang, J. Rong, J.-R. Chen and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2011, **50**, 7171.
10 S. Lin, M. A. Ischay, C. G. Fry and T. P. Yoon, *J. Am. Chem. Soc.*, 2011, **133**, 19350.
11 J. D. Parrish, M. A. Ischay, Z. Lu, S. Guo, N. R. Peters and T. P. Yoon, *Org. Lett.*, 2012, **14**, 1640.
12 G.-B. Deng, Z.-Q. Wang, J.-D. Xia, P.-C. Qian, R.-J. Song, M. Hu, L.-B. Gong and J.-H. Li, *Angew. Chem., Int. Ed.*, 2013, **52**, 1535.
13 F. Gao, C. Yang, N. Ma, G.-L. Gao, D. Li and W.-J. Xia, *Org. Lett.*, 2016, **18**, 600.
14 (*a*) C. Che, Q. Huang, H. Zheng and G. Zhu, *Chem. Sci.*, 2016, **7**, 4134; (*b*) N. Zhou, Y.-X. Cheng, J. Xie and C.-J. Zhu, *Chem. Commun.*, 2017, **53**, 10707; (*c*) M.-H. Huang, W.-J. Hao and B. Jiang, *Chem. – Asian J.*, 2018, DOI: 10.1002/asia.201801119.
15 (*a*) D. Lu, Y. Wan, L. Kong and G. Zhu, *Chem. Commun.*, 2016, **52**, 13971; (*b*) H. Zhu, X. Nie, Q. Huang and G. Zhu, *Tetrahedron Lett.*, 2016, **57**, 2331; (*c*) D. Lu, Y. Wan, L. Kong and G. Zhu, *Org. Lett.*, 2017, **19**, 2929; (*d*) W. Jin, Y. Zhou, Y. Zhao, Q. Ma, L. Kong and G. Zhu, *Org. Lett.*, 2018, **20**, 1435; (*e*) Y. Yu and U. K. Tambar, *Chem. Sci.*, 2015, **6**, 2777; (*f*) A. A. S. Gietter, P. G. Gildner, A. P. Cinderella and D. A. Watson, *Org. Lett.*, 2014, **16**, 3166; (*g*) R. Ding, Z.-D. Huang, Z.-L. Liu, T.-X. Wang, Y.-H. Xu and T.-P. Loh, *Chem. Commun.*, 2016, **52**, 5617; (*h*) Y. Noda and T. Nishikata, *Chem. Commun.*, 2017, **53**, 5017; (*i*) B. Liu, J.-X. Yu, Y. Li, J.-H. Li, D.-L. He, B. Liu, J.-X. Yu, Y. Li, J.-H. Li and J.-H. Li, *Org. Lett.*, 2018, **20**, 2129.
16 N. Zhou, J. Liu, Z.-F. Yan, Z.-K. Wu, H.-L. Zhang, W.-P. Li and C.-J. Zhu, *Chem. Commun.*, 2017, **53**, 2036.
17 (*a*) J.-K. Qiu, B. Jiang, Y.-L. Zhu, W.-J. Hao, D.-C. Wang, J. Sun, P. Wei, S.-J. Tu and G. Li, *J. Am. Chem. Soc.*, 2015, **137**, 8928; (*b*) J. Sun, J.-K. Qiu, Y.-N. Wu, W.-J. Hao, C. Guo, G. Li, S.-J. Tu and B. Jiang, *Org. Lett.*, 2017, **19**, 754; (*c*) J. Li, W.-W. Zhang, X.-J. Wei, W.-J. Hao, G. Li, S.-J. Tu and B. Jiang, *Org. Lett.*, 2017, **19**, 4512; (*d*) F. Liu, J.-Y. Wang, P. Zhou, G.-G. Li, W.-J. Hao, S.-J. Tu and B. Jiang, *Angew. Chem., Int. Ed.*, 2017, **56**, 15570; (*e*) Z.-J. Shen, Y.-N. Wu, C.-L. He, L. He, W.-J. Hao, A.-F. Wang, S.-J. Tu and B. Jiang, *Chem. Commun.*, 2018, **54**, 445; (*f*) M.-H. Huang, Y.-L. Zhu, W.-J. Hao, A.-F. Wang, D.-C. Wang, F. Liu, P. Wei, S.-J. Tu and B. Jiang, *Adv. Synth. Catal.*, 2017, **359**, 2229.
18 (*a*) H. Viehe, Z. Janousek and R. Merenyi, *Acc. Chem. Res.*, 1985, **18**, 148; (*b*) Y.-L. Zhu, C.-F. Zhu, P. Zhou, W.-J. Hao, D.-C. Wang, S.-J. Tu and B. Jiang, *J. Org. Chem.*, 2018, DOI: 10.1021/acs.joc.8b00994.
19 M.-H. Huang, W.-J. Hao, G. Li, S.-J. Tu and B. Jiang, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC04618B.
20 H. Zhu, J. C. T. Leung and G. M. Sammis, *J. Org. Chem.*, 2015, **80**, 965.