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Photoinduced intramolecular carbosulfonylation of alkynes: access to sulfone-containing dibenzazepines from sulfur dioxide†

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A photoinduced three-component reaction of *N*-benzyl-*N*-(2-ethynyl-aryl)amides, sulfur dioxide and aryldiazonium tetrafluoroborates is developed, providing an efficient and straightforward approach for the synthesis of diverse vinylsulfonylated dibenzazepine derivatives in moderate to good yields under mild conditions. This transformation proceeds smoothly at room temperature in the presence of visible light, which shows a wide range of substrate scope with good functional group compatibility. The synthetic utility of this methodology is further demonstrated through Suzuki coupling. Mechanistic studies show that this reaction is triggered by the addition of an arylsulfonyl radical to an alkyne from sulfur dioxide, followed by vinyl radical cyclization to afford the desired sulfonated dibenzazepines.

Owing to their widespread application in the synthesis of natural products and bioactive compounds, seven-membered heterocycles and derivatives have attracted much attention from both the synthetic and medicinal community.[1] Among them, the scaffold of dibenzazepine often serves as a privileged structural motif in biologically active molecules and drugs, such as Mianserin, Mirtazapine and Epinastine.[2] However, traditional methods for the synthesis of the dibenzazepine skeleton often require harsh conditions or tedious steps.[3] Therefore, the development of efficient protocols to access functionalized dibenzazepines is highly desirable.

The importance of sulfonyl compounds has been widely witnessed in organic chemistry and pharmaceutical chemistry.[4] In particular, vinyl sulfones often serve as versatile synthons in organic synthesis,[5] while they can also be used as neuroprotective agents for Parkinson's disease therapy.[6] Accordingly, great efforts have been devoted to developing efficient approaches toward the synthesis of vinyl sulfones. Among them, vicinal difunctionalization of alkynes has been demonstrated as an efficient and convenient strategy for the generation of multi-substituted alkenes in recent years, in which two functional groups can be incorporated into alkyne moieties simultaneously.[7] For example, by employing sulfonyl chlorides and arylboronic acids as reaction components, Nevado and co-workers reported an elegant nickel-catalyzed three-component intermolecular carbosulfonylation of alkynes for the construction of β,β-disubstituted vinyl sulfones (Scheme 1a).[8] Additionally, sulfonyl radical-mediated synthesis of five- or six-membered ring compounds through sulfonylation of alkynes with the simultaneous formation of C–C bonds has been widely explored.[9] Despite these achievements, to the best of our knowledge, there is no example of alkyne carbosulfonylation involving intramolecular C–H functionalization to construct sulfone-containing seven-membered ring compounds.

It is known that DABCO (SO₂)₂ and potassium/sodium metabisulfite are efficient sulfur dioxide surrogates, which have

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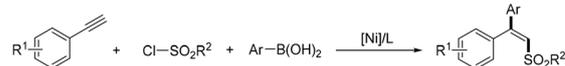
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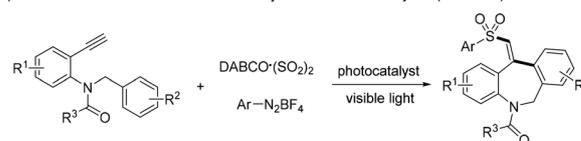
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Scheme 1 Intermolecular and intramolecular carbosulfonylation of alkynes through sulfonyl radical addition.

been successfully applied to the synthesis of sulfonyl compounds.[10] Consequently, the chemistry of sulfur dioxide insertion has become an attractive strategy for the generation of highly functionalized sulfonyl-containing molecules in organic synthesis.[11–13] For instance, our group recently described a four-component fluoroalkylsulfonylation of terminal alkynes with fluoroalkyl radicals, DABCO $(SO_2)_2$ and hydrazines, giving rise to (E)-ethyl 2,2-difluoro-4-aryl-4-sulfamoylbut-3-enoates.[14] Prompted by the advances in the construction of seven-membered ring compounds via radical processes[15] and our continuous interest in sulfonylation from sulfur dioxide, herein, we report a photoinduced three-component reaction of N-benzyl-N-(2-ethynylaryl)amides, DABCO $(SO_2)_2$ and aryldiazonium tetrafluoroborates. This protocol provides a range of sulfonated dibenzazepines in moderate to good yields under mild conditions (Scheme 1b). Additionally, this sulfonyl radical-mediated multicomponent reaction represents a rare example of carbosulfonylation of alkynes involving the insertion of sulfur dioxide and intramolecular C–H bond functionalization to furnish sulfone-containing dibenzazepines. Driven by the importance of dibenzazepines and sulfones, we envisioned that such a transformation might be beneficial for organic synthesis and drug discovery.

We began our studies by choosing N-benzyl-N-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1a**, DABCO $(SO_2)_2$ and 4-methylphenyldiazonium tetrafluoroborate **2a** as the model substrates for the optimization of the reaction conditions. Initially, the reaction was performed in DMSO at room temperature without the addition of any catalysts. To our delight, the desired sulfonated dibenzazepine **3a** was obtained in 21% yield (Table 1, entry 1). The structure of compound (Z)-**3a** was confirmed by X-ray diffraction analysis.[16] However, the yield could not be improved when the solvent or temperature was changed (data not shown in Table 1). We envisioned that an oxidative single electron transfer might be involved during the reaction process. Thus, we considered to introduce a photocatalyst, and this reaction was performed under visible light irradiation of 30 W blue LEDs. Gratifyingly, the corresponding product **3a** was afforded in 60% yield by employing Eosin-Y as the photocatalyst (Table 1, entry 2). Encouraged by this result, other photocatalysts were evaluated, and the results showed that $Ru(bpy)_3Cl_2·6H_2O$ was the best choice, providing the corresponding product **3a** in 78% yield (Table 1, entries 3 and 4). Subsequently, we investigated the solvent effect in this transformation. As a result, no better yields were obtained when the reaction was performed in DMF or DMA (Table 1, entries 5 and 6). Additionally, the yield of product **3a** was decreased when the amount of 4-methyl-phenyldiazonium tetrafluoroborate **1a**, DABCO $(SO_2)_2$ or the concentration of the reaction was changed (Table 1, entries 7–10). We also explored the reaction by using a white LED (35 W) instead of a blue LED (30 W) as the light source, and the corresponding product **3a** was generated in 57% yield (Table 1, entry 11).

With the above optimized conditions in hand, we further evaluated the reaction scope of this three-component reaction of N-benzyl-N-(2-ethynylaryl)amides **1**, DABCO $(SO_2)_2$ and aryldiazonium tetrafluoroborates **2**. As shown in Table 2, the reaction could tolerate various substituents on the aromatic

Table 1 Initial studies for the sulfonylation of N-benzyl-N-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1a** with the insertion of sulfur dioxide[a]
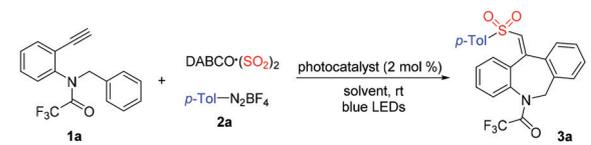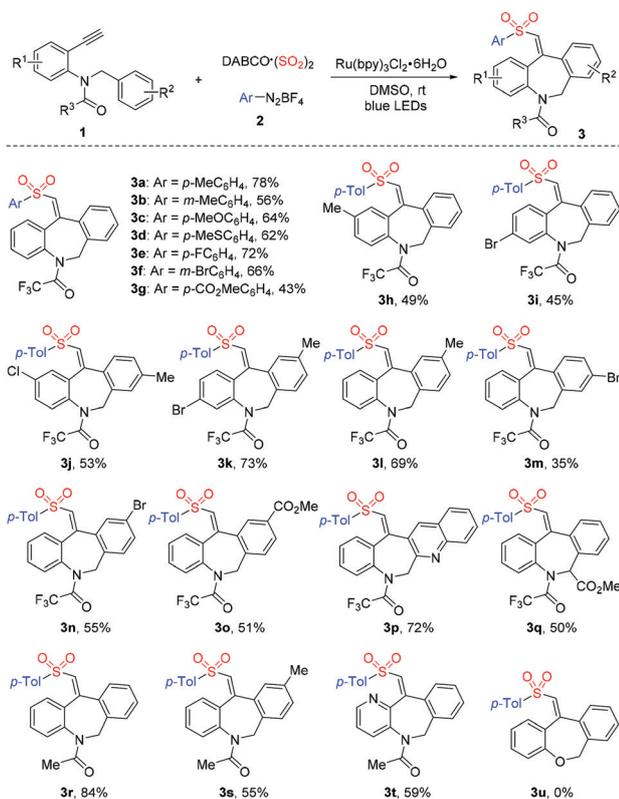

Entry	Photocatalyst	Solvent	Yield[b] (%)
1	—	DMSO	21
2	Eosin Y	DMSO	60
3	fac-Ir(ppy)$_3$	DMSO	69
4	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMSO	78
5	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMF	63
6	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMA	68
7[c]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMSO	52
8[d]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMSO	60
9[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMSO	57
10[f]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMSO	60
11[g]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMSO	57

[a] Reactions conditions: N-benzyl-N-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1a** (0.2 mmol), 4-methylphenyldiazonium tetrafluoroborate **2a** (0.3 mmol), DABCO $(SO_2)_2$ (0.2 mmol), photocatalyst (2 mol%), solvent (2.0 mL), stirred at room temperature for 24 h under blue LED (30 W) irradiation. [b] Isolated yield based on N-benzyl-N-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1a**. [c] Compound **2a** (0.4 mmol). [d] Compound **2a** (0.2 mmol). [e] DABCO $(SO_2)_2$ (0.3 mmol). [f] DMSO (4.0 mL). [g] White LED (35 W) instead of blue LED.

ring of aryldiazonium tetrafluoroborates **2**, leading to the corresponding products **3a-3g** in moderate to good yields. Different functional groups including methyl, methoxy, methylthio, fluoro, bromo and ester units were found to be compatible under the standard conditions. Subsequently, we investigated the substitution effect on the aromatic ring of the N-(2-ethynylaryl) moiety of substrate **1**. As expected, the desired sulfone-containing dibenzazepines **3h-3k** were obtained efficiently with respect to electron-donating and electron-withdrawing substituents. Additionally, diverse substrates **1** with substituents on the aryl ring of the N-benzyl moiety were evaluated, affording the desired products in moderate to good yields. For instance, sulfonated products **3l** and **3n** bearing a methyl or a bromo group on the para-position of the N-benzyl ring were generated in 69% and 55% yield, respectively. The bromo-substituent in **3n** was further applied in the Suzuki coupling reaction for further transformation (see the ESI†). The reaction of the 2-(bromomethyl)quinolone-derived substrate also proceeded smoothly to deliver the product **3p** in 72% yield. Moreover, N-benzyl-N-(2-ethynylphenyl)amide bearing an ester group at the benzylic position could be employed as the substrate, and the corresponding product **3q** was produced in 50% yield. Notably, the replacement of a trifluoroacetyl group by an acetyl group on the nitrogen resulted in the formation of products **3r-3t** in 55–84% yields. Unfortunately, the ether substrate 1-(benzyloxy)-2-ethynylbenzene was not suitable for this reaction to provide the dibenzoxepine **3u**. However, from the ^{1}H NMR spectra, it seemed that a small amount of amide rotamers would be present.

Since the combination of DABCO $(SO_2)_2$ and aryldiazonium tetrafluoroborate would provide an arylsulfonyl radical,[10] to
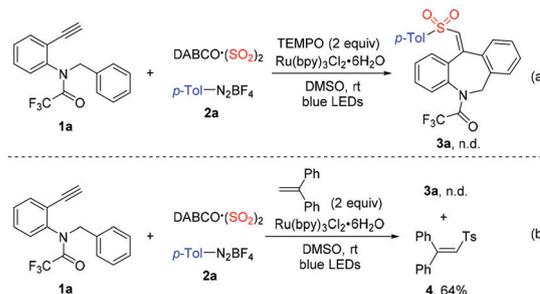
Table 2 Substrate scope for the sulfonylation of *N*-benzyl-*N*-(2-ethynylaryl)amides **1** with the insertion of sulfur dioxide[a]

3a: Ar = *p*-MeC$_6$H$_4$, 78%
3b: Ar = *m*-MeC$_6$H$_4$, 56%
3c: Ar = *p*-MeOC$_6$H$_4$, 64%
3d: Ar = *p*-MeSC$_6$H$_4$, 62%
3e: Ar = *p*-FC$_6$H$_4$, 72%
3f: Ar = *m*-BrC$_6$H$_4$, 66%
3g: Ar = *p*-CO$_2$MeC$_6$H$_4$, 43%

3h, 49%   **3i**, 45%
3j, 53%   **3k**, 73%   **3l**, 69%   **3m**, 35%
3n, 55%   **3o**, 51%   **3p**, 72%   **3q**, 50%
3r, 84%   **3s**, 55%   **3t**, 59%   **3u**, 0%

[a] Isolated yield based on *N*-benzyl-*N*-(2-ethynylaryl)amide **1**.

Scheme 2 Control experiments.

gain further insights into the mechanism of this three-component reaction, several control experiments were carried out under the standard conditions. As expected, the model reaction of *N*-benzyl-*N*-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1a**, DABCO (SO$_2$)$_2$ and 4-methylphenyldiazonium tetrafluoroborate **2a** was completely hampered in the presence of 2 equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), which suggested that a radical process was involved in this reaction (Scheme 2, eqn (a)). Additionally, to confirm the radical intermediates generated in this transformation, 2 equivalents of 1,1-diphenylethylene were added to the model reaction (Scheme 2, eqn (b)). As a result, no desired product **3a** was observed, and (2-tosylethene-1,1-diyl)dibenzene **4** was obtained in 64% yield, revealing that the 4-methylphenylsulfonyl radical was trapped by 1,1-diphenylethylene.

With the above experimental results in hand and inspired by previous reports,[10] a plausible reaction mechanism was proposed for this photoinduced alkyne carbosulfonylation process. As shown in Scheme 3, 4-methylphenyl diazonium tetrafluoroborate **2a** would react with DABCO (SO$_2$)$_2$ to generate 4-methylphenyl sulfonyl radical **A** and a tertiary amine radical cation with the release of molecular nitrogen. In the meantime, photoexcitation of Ru(II) would give rise to the excited-state Ru(II)*, which could be oxidized to Ru(III) by the tertiary amine radical cation. Alternatively, 4-methylphenyl diazonium tetrafluoroborate **2a** would undergo a single-electron transfer by the photoexcited Ru(II)* to give a 4-methylphenyl radical, which would capture sulfur dioxide

to form 4-methylphenyl sulfonyl radical **A**. Then, intermediate **A** would attack the triple bond of *N*-benzyl-*N*-(2-ethynylphenyl)-2,2,2-trifluoroacetamide **1a** to provide vinyl radical **B**, which would undergo 7-*ortho* cyclization to form a radical intermediate **C**. Subsequently, radical intermediate **C** would proceed through a single-electron oxidation by Ru(III) to produce cation intermediate **D** and regenerate the photocatalyst. Finally, the resulting cation **D** would undergo deprotonation by DABCO leading to the desired product **3a**.

In summary, we have developed an efficient and straightforward approach for the construction of sulfonylated dibenzazepines through a visible-light induced three-component reaction of *N*-benzyl-*N*-(2-ethynylaryl)amides, sulfur dioxide and aryldiazonium tetrafluoroborates. This protocol features mild reaction conditions, broad substrate scope and good functional group compatibility, giving rise to the corresponding products in moderate to good yields. Notably, by employing this method, both the vinyl sulfone moiety and the dibenzazepine scaffold can be introduced in the one-pot process, which represents a valuable strategy to access sulfonated seven-membered rings. Preliminary mechanistic studies show that this transformation proceeds through a radical addition/cyclization cascade with the insertion of sulfur dioxide.
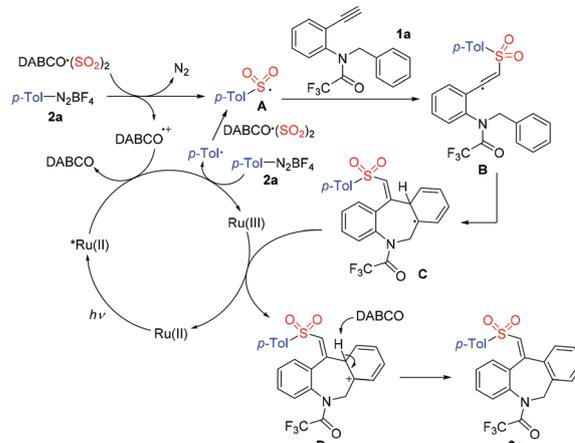
Scheme 3 Proposed mechanism.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (a) A. S. Kende, J. I. M. Hernando and J. B. J. Milbank, *Org. Lett.*, 2001, **3**, 2505; (b) A. Fürstner and O. R. Thiel, *J. Org. Chem.*, 2000, **65**, 1738; (c) F. E. Dutton, B. H. Lee, S. S. Johnson, E. M. Coscarell and P. H. Lee, *J. Med. Chem.*, 2003, **46**, 2057; (d) E. Vitaku, D. T. Smith and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 10257.

2 (a) A. Aoyama, K. Endo-Umeda, K. Kishida, K. Ohgane, T. Noguchi-Yachide, H. Aoyama, M. Ishikawa, H. Miyachi, M. Makishima and Y. Hashimoto, *J. Med. Chem.*, 2012, **55**, 7360; (b) P. Roszkowski, J. K. Maurin and Z. Czarnocki, *Beilstein J. Org. Chem.*, 2015, **11**, 1509; (c) D. V. N. S. Rao, R. Dandala, V. K. Handa, M. Sivakumaran, A. V. R. Reddy and A. Naidu, *Org. Prep. Proced. Int.*, 2007, **39**, 399; (d) R. A. Al-Qawasmeh, Y. Lee, M.-Y. Cao, X. Gu, S. Viau, J. Lightfoot, J. A. Wright and A. H. Young, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 104.

3 (a) T. Zou, X.-G. Zhang, J.-H. Li, C.-L. Deng and R.-Y. Tang, *Adv. Synth. Catal.*, 2012, **354**, 889; (b) D. Solé and F. Mariani, *J. Org. Chem.*, 2013, **78**, 8136.

4 For selected examples, see: (a) N. S. Simpkins, *Sulfones in Organic Synthesis*, Pergamon Press, Oxford, UK, 1993; (b) *The Chemistry of Sulfones and Sulfoxides*, ed. S. Patai, Z. Rappoport and C. Stirling, Wiley, Chichester, UK, 1988; (c) A.-N. R. Alba, X. Companyó and R. Rios, *Chem. Soc. Rev.*, 2010, **39**, 2018; (d) A. El-Awa, M. N. Noshi, X. Mollat du Jourdin and P. L. Fuchs, *Chem. Rev.*, 2009, **109**, 2315; (e) K. A. Scott and J. T. Njardarson, *Top. Curr. Chem.*, 2018, **376**, 5.

5 (a) J. T. Palmer, D. Rasnick, J. L. Klaus and D. Brömme, *J. Med. Chem.*, 1995, **38**, 3193; (b) D. C. Meadows, T. B. Mathews, T. W. North, M. J. Hadd, C. L. Kuo, N. Neamati and J. Gervay-Hague, *J. Med. Chem.*, 2005, **48**, 4526; (c) D. C. Meadows and J. Gervay-Hague, *Med. Res. Rev.*, 2006, **26**, 793; (d) R. Ettari, E. Nizi, M. E. Di Francesco, M. A. Dude, G. Pradel, R. Vicik, T. Schirmeister, N. Micale, S. Grasso and M. Zappala, *J. Med. Chem.*, 2008, **51**, 988; (e) R. van der Westhuyzen and E. Strauss, *J. Am. Chem. Soc.*, 2010, **132**, 12853.

6 S. Y. Woo, J. H. Kim, M. K. Moon, S. H. Han, S. K. Yeon, J. W. Choi, B. K. Jang, H. J. Song, Y. G. Kang, J. W. Kim, J. Lee, D. J. Kim, O. Hwang and K. D. Park, *J. Med. Chem.*, 2014, **57**, 1473.

7 (a) P. Gao, X.-R. Song, X.-Y. Liu and Y.-M. Liang, *Chem. – Eur. J.*, 2015, **21**, 7648; (b) H.-L. Hua, Y.-T. He, Y.-F. Qiu, Y.-X. Li, B. Song, P. Gao, X.-R. Song, D.-H. Guo, X.-Y. Liu and Y.-M. Liang, *Chem. – Eur. J.*, 2015, **21**, 1468; (c) P. Gao, Y.-W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Yang, X.-B. Yan, Q. Wang, X.-J. Gong, X.-Y. Liu and Y.-M. Liang, *Angew. Chem., Int. Ed.*, 2014, **53**, 7629; (d) Y.-P. Xiong, M.-Y. Wu, X.-Y. Zhang, C.-L. Ma, L. Huang, L.-J. Zhao, B. Tan and X.-Y. Liu, *Org. Lett.*, 2014, **16**, 1000; (e) Z. Li, A. García-Domínguez and C. Nevado, *J. Am. Chem. Soc.*, 2015, **137**, 11610; (f) M. Israr, H. Xiong, Y. Li and H. Bao, *Org. Lett.*, 2019, **21**, 7078.

8 A. García-Domínguez, S. Müller and C. Nevado, *Angew. Chem., Int. Ed.*, 2017, **56**, 9949.

9 (a) D. Zheng, J. Yu and J. Wu, *Angew. Chem., Int. Ed.*, 2016, **55**, 11925; (b) D. Sun, K. Yin and R. Zhang, *Chem. Commun.*, 2018, **54**, 1335; (c) X.-Y. Qin, L. He, J. Li, W.-J. Hao, S.-J. Tu and B. Jiang, *Chem. Commun.*, 2019, **55**, 3227; (d) Y. Liu, Q.-L. Wang, Z. Chen, H. Li, B.-Q. Xiong, P.-L. Zhang and K.-W. Tang, *Chem. Commun.*, 2020, **56**, 3011; (e) N. Zhou, M. Wu, K. Kuang, S. Wu and M. Zhang, *Adv. Synth. Catal.*, 2020, **362**, 5391.

10 For selected reviews, see: (a) G. Qiu, K. Zhou, L. Gao and J. Wu, *Org. Chem. Front.*, 2018, **5**, 691; (b) K. Hofman, N. Liu and G. Manolikakes, *Chem. – Eur. J.*, 2018, **24**, 11852; (c) G. Liu, C. Fan and J. Wu, *Org. Biomol. Chem.*, 2015, **13**, 1592; (d) G. Qiu, L. Lai, J. Cheng and J. Wu, *Chem. Commun.*, 2018, **54**, 10405; (e) G. Qiu, K. Zhou and J. Wu, *Chem. Commun.*, 2018, **54**, 12561; (f) D. Zheng and J. Wu, *Sulfur Dioxide Insertion Reactions for Organic Synthesis Nature*, Springer, Berlin, 2017; (g) S. Ye, G. Qiu and J. Wu, *Chem. Commun.*, 2019, **55**, 1013; (h) S. Ye, M. Yang and J. Wu, *Chem. Commun.*, 2020, **56**, 4145; (i) D. Zeng, M. Wang, W.-P. Deng and X. Jiang, *Org. Chem. Front.*, 2020, **7**, 3956.

11 For selected examples, see: (a) D. Zheng, Y. An, Z. Li and J. Wu, *Angew. Chem., Int. Ed.*, 2014, **53**, 2451; (b) X. Gong, M. Wang, S. Ye and J. Wu, *Org. Lett.*, 2019, **21**, 1156; (c) S. Ye, D. Zheng, J. Wu and G. Qiu, *Chem. Commun.*, 2019, **55**, 2214; (d) S. Ye, Y. Li, J. Wu and Z. Li, *Chem. Commun.*, 2019, **55**, 2489; (e) X. Gong, X. Li, W. Xie, J. Wu and S. Ye, *Org. Chem. Front.*, 1863, **2019**, 6; (f) F.-S. He, X. Gong, P. Rojsitthisak and J. Wu, *J. Org. Chem.*, 2019, **84**, 13159; (g) S. Ye, X. Li, W. Xie and J. Wu, *Asian J. Org. Chem.*, 2019, **8**, 893; (h) S. Ye, K. Zhou, P. Rojsitthisak and J. Wu, *Org. Chem. Front.*, 2020, **7**, 14; (i) J. Zhang, M. Yang, J.-B. Liu, F.-S. He and J. Wu, *Chem. Commun.*, 2020, **56**, 3225; (j) F.-S. He, Y. Yao, W. Xie and J. Wu, *Chem. Commun.*, 2020, **56**, 9649; (k) F.-S. He, Y. Yao, W. Xie and J. Wu, *Adv. Synth. Catal.*, 2020, **362**, 4744.

12 For recent selected examples, see: (a) F.-S. He, Y. Wu, X. Li, H. Xia and J. Wu, *Org. Chem. Front.*, 1873, **2019**, 6; (b) X. Wang, Y. Kuang, S. Ye and J. Wu, *Chem. Commun.*, 2019, **55**, 14962; (c) X. Gong, M. Yang, J.-B. Liu, F.-S. He, X. Fan and J. Wu, *Green Chem.*, 2020, **22**, 1906; (d) X. Gong, M. Yang, J.-B. Liu, F.-S. He and J. Wu, *Org. Chem. Front.*, 2020, **7**, 938; (e) X. Wang, Y. Lin, J.-B. Liu, F.-S. He, Y. Kuang and J. Wu, *Chin. J. Chem.*, 2020, **38**, 1098; (f) Y. Liu, Q.-L. Wang, Z. Chen, P. Chen, K.-W. Tang, Q. Zhou and J. Xie, *Org. Biomol. Chem.*, 2019, **17**, 10020; (g) Y. Liu, Q.-L. Wang, Z. Chen, Q. Zhou, P.-L. Zhang and K.-W. Tang, *Chem. Commun.*, 2019, **55**, 12212; (h) K. Zhou, J.-B. Liu, W. Xie, S. Ye and J. Wu, *Chem. Commun.*, 2020, **56**, 2554; (i) B. Ni, B. Zhang, J. Han, B. Peng, Y. Shan and T. Niu, *Org. Lett.*, 2020, **22**, 670; (j) Y. He, J. Yang, Q. Liu, X. Zhang and X. Fan, *J. Org. Chem.*, 2020, **85**, 15600.

13 For selected examples, see: (a) F. Liu, J.-Y. Wang, P. Zhou, G. Li, W.-J. Hao, S.-J. Tu and B. Jiang, *Angew. Chem., Int. Ed.*, 2017, **56**, 15570; (b) H. Wang, S. Sun and J. Cheng, *Org. Lett.*, 2017, **19**, 5844; (c) G. Li, Z. Gan, K. Kong, X. Dou and D. Yang, *Adv. Synth. Catal.*, 2019, **361**, 1808; (d) T.-H. Zhu, X.-C. Zhang, X.-L. Cui, Z.-Y. Zhang, H. Jiang, S.-S. Sun, L.-L. Zhao, K. Zhao and T.-P. Loh, *Adv. Synth. Catal.*, 2019, **361**, 3593; (e) Y. Meng, Y. Wang and X. Jiang, *Angew. Chem., Int. Ed.*, 2020, **59**, 1346; (f) S. Chen, Y. Li, M. Wang and X. Jiang, *Green Chem.*, 2020, **22**, 322; (g) X. Marset, J. Torregrosa-Crespo, R. M. Martinez-Espinosa, G. Guillena and D. J. Ramón, *Green Chem.*, 2019, **21**, 4127; (h) K. Chen, W. Chen, B. Han, W. Chen, M. Liu and H. Wu, *Org. Lett.*, 2020, **22**, 1841; (i) Y. Liu, D. Yu, Y. Guo, J.-C. Xiao, Q.-Y. Chen and C. Liu, *Org. Lett.*, 2020, **22**, 2281; (j) T. Zhang, M.-K. Pang, Z.-D. Chen, B. Zhang, J. Weng and G. Lu, *Org. Lett.*, 2020, **22**, 3072; (k) Q. Lin, Z. Ma, C. Zheng, X.-J. Hu, Y. Guo, Q.-Y. Chen and C. Liu, *Chin. J. Chem.*, 2020, **38**, 1107; (l) K. Zhou, J. Chen and J. Wu, *Chin. Chem. Lett.*, 2020, **31**, 2996; (m) Y. Yao, Z. Yi, W. Chen, W. Xie, F.-S. He and J. Wu, *Adv. Synth. Catal.*, 2021, **363**, 570.

14 (a) Y. Xiang, Y. Li, Y. Kuang and J. Wu, *Chem. – Eur. J.*, 2017, **23**, 1032; (b) Y. Li, Y. Xiang, Y. Kuang and J. Wu, *Org. Chem. Front.*, 2016, **3**, 1493.

15 (a) P. Xiong, H.-H. Xu, J. Song and H.-C. Xu, *J. Am. Chem. Soc.*, 2018, **140**, 2460; (b) Y. Zhao, J.-R. Chen and W.-J. Xiao, *Org. Lett.*, 2018, **20**, 224; (c) H. Wang, B. Wang, S. Sun and J. Cheng, *Org. Chem. Front.*, 2018, **5**, 2547; (d) D. Liu, M.-J. Jiao, X.-Z. Wang and P.-F. Xu, *Org. Lett.*, 2019, **21**, 4745; (e) T.-T. Zhang, M.-J. Luo, F. Teng, Y. Li, M. Hu and J.-H. Li, *Adv. Synth. Catal.*, 2020, **362**, 4645.

16 CCDC 2046979 contains the supplementary crystallographic data for this paper.