

A Single Electron Transfer (SET) Approach to C–H Amidation of Hydrazones via Visible-Light Photoredox Catalysis

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S Supporting Information



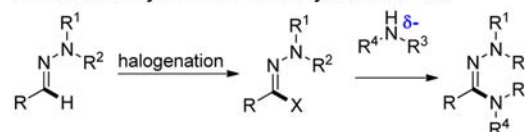
ABSTRACT: The reductive single electron transfer (SET) umpolung amination of aldehyde-derived hydrazones has been developed through visible-light-promoted photoredox catalysis. The ideal transformation of hydrazones into the corresponding hydrazonamide through selective carbon–hydrogen (C–H) bond functionalization represents one of the most step- and atom-economical methods. This SET umpolung strategy features mild conditions and a remarkably broad substrate scope, offering an entirely new substrate class to direct C–H amination.

The formation of carbon–nitrogen (C–N) bonds is a straightforward approach for the synthesis of nitrogen-containing compounds, which widely exist in natural products, biologically active molecules, and medicines.¹ Therefore, the development of efficient and step-economical methods for incorporation of an amino group into organic molecules has attracted considerable attention in the synthetic chemistry community for a long time.² Transition-metal-catalyzed C(sp²)–N bond formations, particularly the copper-mediated Ullmann-type³ and palladium-catalyzed Buchwald–Hartwig amination/amidation,⁴ have significantly advanced the installation of the amine moiety on aromatic substrates. A variety of synthetically valuable arene C–H amination methods are associated with ligand directed,⁵ radical aromatic substitution⁶ or intramolecular⁷ C–N bond formation. In addition, aminations of alkenes and alkynes have been extensively developed with Pd, Rh, Au, or Cu as well as other catalysts.⁸ Despite these significant advances, these developed methods of elegantly constructing C(sp²)–N bonds are still restricted to carbon–carbon π bond substrates (alkenes, alkynes, or arenes).

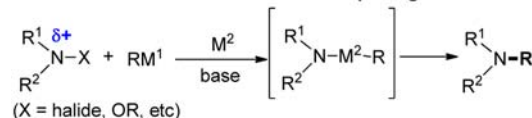
Hydrazones belong to a critical class of compounds because of their many applications in synthetic organic chemistry.⁹ The current C(sp²)–N bond formation strategies of hydrazones employ preactivated starting materials such as hydrazonoyl halides to react with amines which attack as nucleophiles (Scheme 1A).¹⁰ To explore the ideal transformation of hydrazones into the corresponding hydrazonamides through C–H bond functionalization would represent one of the most step- and atom-economical methods. However, it is also a great challenge. It is known that polarity inversions are alternative pathways for the preparation of otherwise difficult to access target compounds.¹¹ In particular, umpolung amination

Scheme 1. Amination/Amidation Strategy

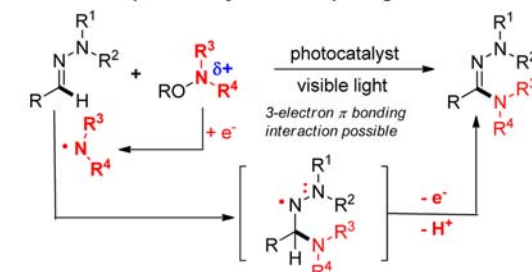
A. Traditional synthesis of benzohydrazonamides



B. Previous works: well-established umpolung amination strategy



C. This work: photocatalytic SET umpolung amidation strategy



reactions catalyzed by transition metals are very appealing and garner great interest from chemists in recent years (Scheme 1B).¹² Meanwhile, visible-light mediated photoredox catalysis, which uses its unique ability to induce single electron transfer

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(SET) processes, has emerged as a powerful tool in synthetic organic chemistry¹³ and attracts increasing attention.

Inspired by the effectiveness of these two types of catalytic modes, we recognized that a SET umpolung strategy for productive C–N bond formation could be developed through an alternative mechanistic approach. The combination of both SET and umpolung steps in a single mechanism is an attractive concept and will be used to create more important chemical transformations. We envisioned that electrophilic nitrogen-centered radicals could be produced through an SET pathway via photoredox catalysis, thus inducing facile C–N bond formation by direct addition to a C=N bond, analogous to the role of traditional metal catalyzed cross-couplings, finally it could undergo a stepwise single-electron oxidation and deprotonation process for C(sp²)–N bond construction (Scheme 1C). Herein, we report the development of a SET umpolung amination through visible light photoredox catalysis. This report describes the first, to the best of our knowledge, examples of visible-light-induced direct C(sp²)–H amination of aldehyde hydrazones.

To validate the feasibility of this SET umpolung amination concept, the readily accessible aldehyde hydrazone **1a** was chosen as a model substrate, and *N*-methyl-*N*-((phenylsulfonyl)oxy) sulfonamide **2a** was used as an aminating reagent. At the outset of this research, hydrazone **1a** was reacted with 2 equiv of sulfonamide **2a** in the presence of 2 equiv of sodium carbonate and a photocatalyst *fac*-Ir(ppy)₃ in degassed CH₃CN (0.1 M) under visible light irradiation with blue LEDs (5 W, λ_{max} = 455 nm). The desired product **3a** was isolated in 42% yield (Table 1, entry 1), which showed this novel amination

The solubility is likely to be very important when 1,2-dichloroethane is used as a solvent. However, the performance of the reaction using K₂HPO₄ did not show a significant difference (75% yield, entry 10), which indicated the specific working details regarding the base remain unclear in the reaction system. Several other photocatalysts, such as Ir(ppy)₂(dtbbpy) PF₆ and Ru(bpy)₃(PF₆)₂, were not superior to *fac*-Ir(ppy)₃ toward the conversion of **1a** (entries 12–13). In addition, the use of electron-rich (**2b**) or -poor (**2c**) benzenesulfonyl groups on the amine moiety did not offer better results. Other types of radical precursors, such as *N*-chloride (**2d**) and a *N*-Boc hydroxylamine derivative (**2e**), did not work at all (Supporting Information). Finally, control experiments demonstrated that the photocatalyst *fac*-Ir(ppy)₃ and visible light were necessary for this transformation (entries 14–15).

With the optimized reaction conditions in hand, we examined the scope of this SET umpolung C–N bond formation protocol. The representative examples are shown in Scheme 2. This method showed excellent chemoselectivity with good functional group compatibility. Despite the multiple reacting sites in hydrazones **1**, monofunctionalization proceeded selectively to form the hydrazonamides, and the corresponding amidated arenes were not observed. Aryl aldehyde derived hydrazones bearing either electron-donating (for example, methyl or alkoxy) or electron-withdrawing (for example, trifluoromethyl, halide, or carbomethoxy) substituents could react smoothly to furnish the desired products in moderate to good yields (**3aa–ag**). In addition, the position of the substituents on the aryl ring has no effect on this reaction. With the same protocol, *meta*- or *ortho*-substituted (methyl, Cl) hydrazones were also converted into the expected products with good efficiency (**3ba–cb**). When the substrates with multiple substituents on the phenyl ring were used, they all underwent amidation (**3da–ea**). Remarkably, heteroaromatic (thiophene **1fa** and quinoline **1ga**) hydrazones were found to be tolerated in this transformation (**3fa–ga**).

We then turned our attention and investigated the effect of different *N*-substituents of hydrazones in this transformation as outlined in Scheme 3. When the nitrogen atom was connected with two alkyl groups, the reaction could take place with optimal levels of efficiency (**3ha–ia**). Next, one alkyl group was replaced by a phenyl group, and the desired products were also obtained. Whether the electron-poor or -rich substituents on were utilized on the aldehyde-derived moieties (**1ka–ma**), or one on the aryl group was linked to the nitrogen atom (**1pa–qa**), the reactions all proceeded very smoothly, resulting in the exclusive formation of the C(sp²)–H amidated products. The hydrazone connected with two phenyl groups (**1ra**) was still accommodated well by this protocol in 76% yield. Unfortunately, *N*-Boc and *N*-Bs hydrazones (**1sa–ta**) failed to give the desired products. We speculated that this activity difference may be explained by the three-electron π -bond interaction between the amino radical with the adjacent nitrogen atom.^{14a} This interaction could affect stabilization of the intermediate. Overall, this SET umpolung amination reaction proved to be effective on a broad range of hydrazone substrates that encompass diverse substitutions.

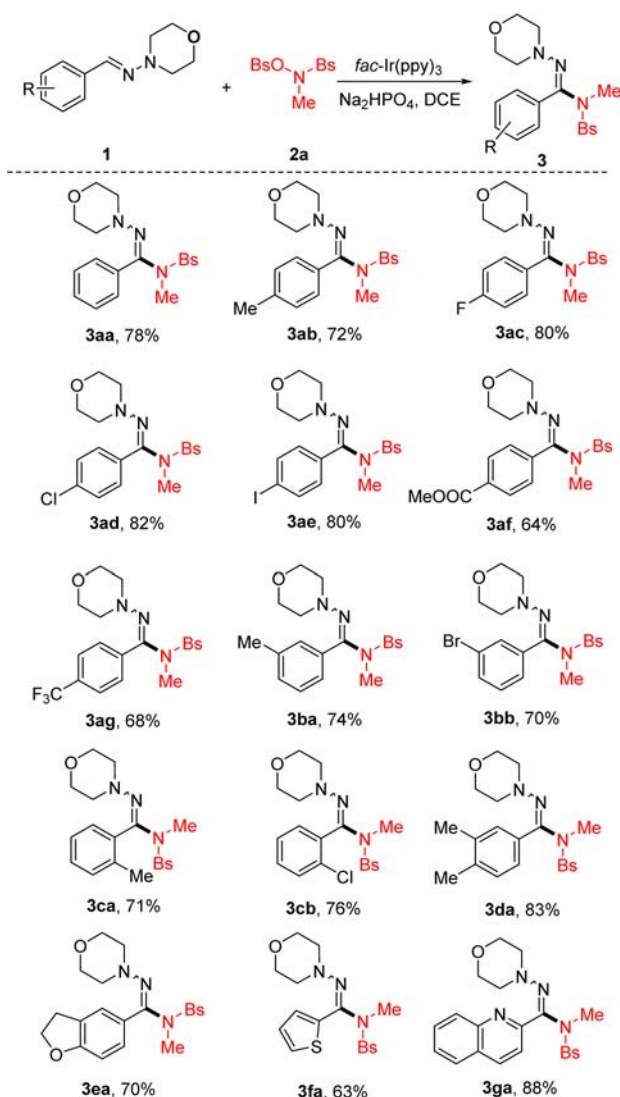
To gain mechanistic insight into the SET umpolung amination reaction, some preliminary mechanistic experiments were performed. The radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was introduced into the photochemical system, and the amination reaction could be

Table 1. Optimization of the reaction conditions^a

entry	photocatalyst	base	solvent	yields (%) ^b
1	<i>fac</i> -Ir(ppy) ₃	Na ₂ CO ₃	CH ₃ CN	42
2	<i>fac</i> -Ir(ppy) ₃	Na ₂ CO ₃	DMF	47
3	<i>fac</i> -Ir(ppy) ₃	Na ₂ CO ₃	DMSO	36
4	<i>fac</i> -Ir(ppy) ₃	Na ₂ CO ₃	DCM	48
5	<i>fac</i> -Ir(ppy) ₃	Na ₂ CO ₃	DCE	56
6	<i>fac</i> -Ir(ppy) ₃	K ₂ CO ₃	DCE	48
7	<i>fac</i> -Ir(ppy) ₃	NaOAc	DCE	62
8	<i>fac</i> -Ir(ppy) ₃	NaHCO ₃	DCE	60
9	<i>fac</i> -Ir(ppy) ₃	Na ₂ HPO ₄	DCE	78
10	<i>fac</i> -Ir(ppy) ₃	K ₂ HPO ₄	DCE	75
11	<i>fac</i> -Ir(ppy) ₃	none	DCE	23
12	Ru(bpy) ₃ (PF ₆) ₂	Na ₂ HPO ₄	DCE	30
13	Ir(ppy) ₂ (dtbbpy)PF ₆	Na ₂ HPO ₄	DCE	41
14	none	Na ₂ HPO ₄	DCE	0
15 ^c	<i>fac</i> -Ir(ppy) ₃	Na ₂ HPO ₄	DCE	0

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), base (0.2 mmol, 2.0 equiv), photocatalyst (0.002 mmol, 2.0 mol %), and solvent (1 mL), argon atmosphere, irradiation with a 5 W blue light LEDs at 25 °C, 76 h. ^bIsolated yields. ^cIn dark. DMF = *N,N*-dimethylformamide, DMSO = dimethyl sulfoxide, DCM = dichloromethane, DCE = 1,2-dichloroethane, Bs = Benzenesulfonyl.

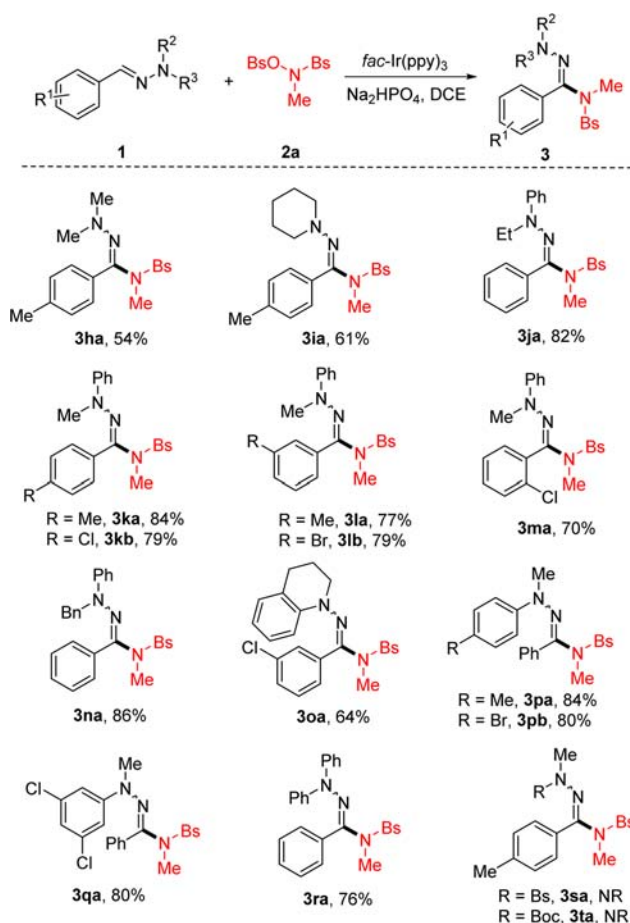
strategy is feasible. Other solvents, such as DMF, DMSO, and DCM, could not give improved results (entries 2–4). A 56% yield was achieved when DCE was used as the solvent (entry 5). We then screened inorganic bases, such as K₂CO₃, NaOAc, and NaHCO₃ (entries 6–8). It was found that the base also played an important role in neutralizing the byproduct PhSO₃H. Na₂HPO₄ proved to be the best choice (entry 9).

Scheme 2. Scope of Aromatic Aldehyde Hydrazones in the SET Amidation Reaction^{a,b}

^aReaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), Na_2HPO_4 (0.2 mmol, 2.0 equiv), $fac-Ir(ppy)_3$ (0.002 mmol, 2.0 mol %), DCE (1 mL), irradiation with a 5 W blue light LEDs at 25 °C, argon atmosphere, 76–90 h. ^bIsolated yields.

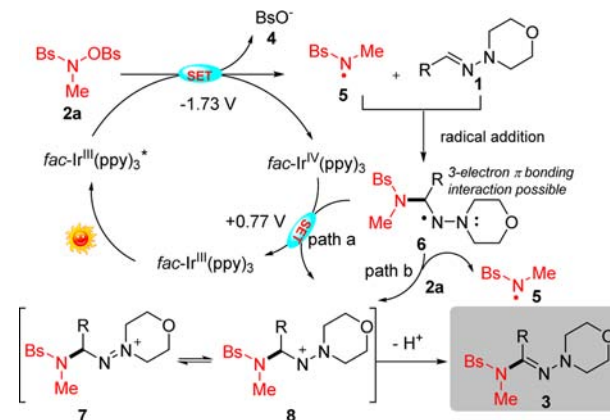
terminated completely, indicating that a single-electron-transfer radical process is operating.

Based on the current results and literature precedents,¹⁴ the plausible reaction pathway of this visible-light photoredox catalyzed umpolung amination reaction is outlined in Scheme 4. Under visible-light irradiation, the photocatalyst $fac-Ir^{III}(ppy)_3$ undergoes a metal-to-ligand charge transfer (MLCT) process to produce the strongly reducing excited state Ir^{III*} (−1.73 V vs SCE in CH_3CN). Then a single electron transfer process from this species to **2a** would generate electrophilic nitrogen-centered radical intermediate **5** and Ir^{IV} (+0.77 V vs SCE in CH_3CN). Subsequent *N*-centered radical direct addition to the C=N bond induces facile C–N bond formation, leading to the aminyl radical intermediate **6**. Nitrogen-centered radical **6** can be stabilized by the adjacent nitrogen through possible three-electron π bonding interaction. At this stage, a key aminyl radical-polar crossover step between **6** and Ir^{IV} can take place, and the radical intermediate **6** may

Scheme 3. Scope of *N*-Substituent Hydrazones in the SET Amidation Reaction^{a,b}

^aReaction conditions: **1** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), Na_2HPO_4 (0.2 mmol, 2.0 equiv), $fac-Ir(ppy)_3$ (0.002 mmol, 2.0 mol %), DCE (1 mL), irradiation with a 5 W blue light LEDs at 25 °C, argon atmosphere, 80–90 h. ^bIsolated yields.

Scheme 4. Plausible Reaction Pathways



undergo a stepwise single-electron oxidation to produce the diazenium cation **7** or **8** with the regeneration of the photocatalyst (path a).^{14a} On the other hand, the possibility of having radical chain processes where **6** is oxidized by another equivalent of **2a** to generate **8** and **5** is not ruled out (path b). Further tautomerization and deprotonation of diazenium cation gives the final product **3** in the presence of base.

In conclusion, we have successfully developed the visible-light photoredox-catalyzed C(sp²)-H amidation of aldehyde hydrazones for the first time. This transformation proceeds via a reductive SET umpolung mechanism, in which sequential SET processes involving the photocatalyst enable both SET and umpolung steps in the same mechanism. Mild reaction conditions, a broad substrate scope, and excellent functional group compatibility (fluorides chlorides, bromides, and iodides as well as esters included) are attractive features of this method. This strategy also complements precedented work, and further exploration of this reductive SET umpolung strategy will continue to be a focus of research in our laboratory.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs-orglett.6b02711.

Experimental procedures, characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Butcher, N. J.; Boukouvala, S.; Sim, E.; Minchin, R. F. *Pharmacogenomics J.* **2002**, 2, 30. (b) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, 106, 2651. (c) Robinson, G. E.; Cunningham, O. R.; Dekhane, M.; McManus, J. C.; O'Kearney-McMullan, A.; Mirajkar, A. M.; Mishra, V.; Norton, A. K.; Venugopalan, B.; Williams, E. G. *Org. Process Res. Dev.* **2004**, 8, 925. (d) Saibabu Kotti, S. R. S.; Timmons, C.; Li, G. *Chem. Biol. Drug Des.* **2006**, 67, 101.
- (2) (a) Bariwal, J.; Van der Eycken, E. *Chem. Soc. Rev.* **2013**, 42, 9283. (b) Xiong, T.; Zhang, Q. *Chem. Soc. Rev.* **2016**, 45, 3069. (c) Ouyang, K.; Hao, W.; Zhang, W.-X.; Xi, Z. *Chem. Rev.* **2015**, 115, 12045. (d) Shin, K.; Kim, H.; Chang, S. *Acc. Chem. Res.* **2015**, 48, 1040.
- (3) (a) Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed.* **2009**, 48, 6954. (b) Ma, D.; Cai, Q. *Acc. Chem. Res.* **2008**, 41, 1450. (c) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, 108, 3054. (d) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2010**, 1, 13. (e) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, 42, 5400. (f) Deldaele, C.; Evano, G. *ChemCatChem* **2016**, 8, 1319.
- (4) (a) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, 47, 6338. (b) Hartwig, J. F. *Acc. Chem. Res.* **2008**, 41, 1534. (c) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, 40, 5068.
- (5) (a) Zhou, Y.; Yuan, J.; Yang, Q.; Xiao, Q.; Peng, Y. *ChemCatChem* **2016**, 8, 2178. (b) Ryu, J.; Kwak, J.; Shin, K.; Lee, D.; Chang, S. *J. Am. Chem. Soc.* **2013**, 135, 12861. (c) Zhu, D.; Yang, G.; He, J.; Chu, L.; Chen, G.; Gong, W.; Chen, K.; Eastgate, M. D.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2015**, 54, 2497. (d) Hermann, G. N.; Becker, P.; Bolm, C. *Angew. Chem., Int. Ed.* **2016**, 55, 3781. (e) Hwang, H.; Kim, J.; Jeong, J.; Chang, S. *J. Am. Chem. Soc.* **2014**, 136, 10770. (f) (a) Allen, L. J.; Cabrera, P. J.; Lee, M.; Sanford, M. S. *J. Am. Chem. Soc.* **2014**, 136, 5607. (b) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. *Science* **2015**, 349, 1326. (c) Brachet, E.; Ghosh, T.; Ghosh, I.; König, B. *Chem. Sci.* **2015**, 6, 987. (d) Song, L.; Zhang, L.; Luo, S.; Cheng, J.-P. *Chem. - Eur. J.* **2014**, 20, 14231. (e) Qin, Q.; Yu, S. *Org. Lett.* **2014**, 16, 3504. (f) Grohmann, C.; Wang, H.; Glorius, F. *Org. Lett.* **2012**, 14, 656. (g) Lerchen, A.; Vázquez-Céspedes, S.; Glorius, F. *Angew. Chem., Int. Ed.* **2016**, 55, 3208.
- (7) (a) McIntosh, J. A.; Coelho, P. S.; Farwell, C. C.; Wang, Z. J.; Lewis, J. C.; Brown, T. R.; Arnold, F. H. *Angew. Chem.* **2013**, 125, 9479. (b) He, G.; Lu, C.; Zhao, Y.; Nack, W. A.; Chen, G. *Org. Lett.* **2012**, 14, 2944. (c) Chng, L. L.; Yang, J.; Wei, Y.; Ying, J. Y. *Chem. Commun.* **2014**, 50, 9049. (d) Choi, S.; Chatterjee, T.; Choi, W. J.; You, Y.; Cho, E. J. *ACS Catal.* **2015**, 5, 4796.
- (8) (a) Hu, X.-Q.; Qi, X.; Chen, J.-R.; Zhao, Q.-Q.; Wei, Q.; Lan, Y.; Xiao, W.-J. *Nat. Commun.* **2016**, 7, 11188. (b) Fu, S.; Yang, H.; Li, G.; Deng, Y.; Jiang, H.; Zeng, W. *Org. Lett.* **2015**, 17, 1018. (c) Hemric, B. N.; Shen, K.; Wang, Q. *J. Am. Chem. Soc.* **2016**, 138, 5813. (d) Shen, K.; Wang, Q. *Chem. Sci.* **2015**, 6, 4279. (e) Liwosz, T. W.; Chemler, S. R. *J. Am. Chem. Soc.* **2012**, 134, 2020. (f) Xiong, P.; Xu, F.; Qian, X. Y.; Yohannes, Y.; Song, J.; Lu, X.; Xu, H. C. *Chem. - Eur. J.* **2016**, 22, 4379. (g) Trenner, J.; Depken, C.; Weber, T.; Breder, A. *Angew. Chem., Int. Ed.* **2013**, 52, 8952. (h) Miasiewicz, S.; Gaillard, B.; Kern, N.; Weibel, J. M.; Pale, P.; Blanc, A. *Angew. Chem., Int. Ed.* **2016**, 55, 9088. (i) Huang, L.; Arndt, M.; Goßen, K. t.; Heydt, H.; Goossen, L. J. *Chem. Rev.* **2015**, 115, 2596. (j) Wolfe, S.; Pilgrim, W.; Garrard, T.; Chamberlain, P. *Can. J. Chem.* **1971**, 49, 1099. (k) Deng, Z.; Wei, J.; Liao, L.; Huang, H.; Zhao, X. *Org. Lett.* **2015**, 17, 1834. (l) Zheng, G.; Li, Y.; Han, J.; Xiong, T.; Zhang, Q. *Nat. Commun.* **2015**, 6, 7011. (m) Chen, Q.-A.; Chen, Z.; Dong, V. M. *J. Am. Chem. Soc.* **2015**, 137, 8392. (n) Wu, L.; Qiu, S.; Liu, G. *Org. Lett.* **2009**, 11, 2707.
- (9) Lazny, R.; Nodzevska, A. *Chem. Rev.* **2010**, 110, 1386.
- (10) (a) Hegarty, A.; Rigopoulos, P.; Rowe, J. *Aust. J. Chem.* **1987**, 40, 1777. (b) Wolkoff, P. *Can. J. Chem.* **1975**, 53, 1333.
- (11) (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 239. (b) Bugaut, X.; Glorius, F. *Chem. Soc. Rev.* **2012**, 41, 3511. (c) Smith, A. B., III; Adams, C. M. *Acc. Chem. Res.* **2004**, 37, 365.
- (12) (a) He, C.; Chen, C.; Cheng, J.; Liu, C.; Liu, W.; Li, Q.; Lei, A. *Angew. Chem., Int. Ed.* **2008**, 47, 6414. (b) Matsuda, N.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem.* **2012**, 124, 3702. (c) Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2011**, 13, 2395. (d) Zhou, S.; Yang, Z.; Chen, X.; Li, Y.; Zhang, L.; Fang, H.; Wang, W.; Zhu, X.; Wang, S. *J. Org. Chem.* **2015**, 80, 6323. (e) Matsuda, N.; Hirano, K.; Satoh, T.; Miura, M. *J. Am. Chem. Soc.* **2013**, 135, 4934. (f) Rucker, R. P.; Whittaker, A. M.; Dang, H.; Lalic, G. *Angew. Chem., Int. Ed.* **2012**, 51, 3953. (g) Barker, T. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2009**, 131, 15598. (h) Faulkner, A.; Scott, J. S.; Bower, J. F. *J. Am. Chem. Soc.* **2015**, 137, 7224. (i) Ye, Z.; Dai, M. *Org. Lett.* **2015**, 17, 2190. (j) Corpet, M.; Gosmini, C. *Synthesis* **2014**, 46, 2258. (k) Dong, X.; Liu, Q.; Dong, Y.; Liu, H. *Chem. - Eur. J.* **2016**, DOI: 10.1002/chem.201601607.
- (13) (a) Zhang, M.; Li, W.; Duan, Y.; Xu, P.; Zhang, S.; Zhu, C. *Org. Lett.* **2016**, 18, 3266. (b) Li, W.; Duan, Y.; Zhang, M.; Cheng, J.; Zhu, C. *Chem. Commun.* **2016**, 52, 7596. (c) Lei, T.; Liu, W.-Q.; Li, J.; Huang, M.-Y.; Yang, B.; Meng, Q.-Y.; Chen, B.; Tung, C.-H.; Wu, L.-Z. *Org. Lett.* **2016**, 18, 2479. (d) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev.* **2013**, 113, 5322. (e) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Soc. Rev.* **2016**, 45, 2044. (f) Zhang, M.; Duan, Y.; Li, W.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2016**, 52, 4761. (g) Douglas, J. J.; Albright, H.; Sevrin, M. J.; Cole, K. P.; Stephenson, C. R. *Angew. Chem., Int. Ed.* **2015**, 54, 14898. (h) Cheng, Y.; Yu, S. *Org. Lett.* **2016**, 18, 2962. (i) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, 116, 10035.
- (14) (a) Xu, P.; Wang, G.; Zhu, Y.; Li, W.; Cheng, Y.; Li, S.; Zhu, C. *Angew. Chem., Int. Ed.* **2016**, 55, 2939. (b) Xie, J.; Zhang, T.; Chen, F.; Mehrkens, N.; Rominger, F.; Rudolph, M.; Hashmi, A. K. *Angew. Chem., Int. Ed.* **2016**, 55, 2934. (c) Prieto, A.; Melot, R.; Bouyssi, D.; Melot, R.; Bouyssi, D.; Monteiro, N. *ACS Catal.* **2016**, 6, 1093. (d) Xie, J.; Zhang, T.; Chen, F.; Mehrkens, N. *Angew. Chem., Int. Ed.* **2016**, 55, 2934. (e) Cecere, G.; König, C. M.; Allea, J. L.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2013**, 135, 11521.