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## Visible-light-promoted radical amidoarylation of arylacrylamides towards amidated oxindoles\*

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# A visible-light-promoted intermolecular radical amidation/cyclization of arylacrylamides was realized by using *N*-aminopyridinium salts as the source of amidyl radicals. The reaction exhibits a broad scope and good functional group tolerance, and a variety of amide-tethered-oxindoles were prepared in this way in moderate to good yields.

C–N bond-forming reactions have drawn persistent interest from chemists because of the importance of nitrogen-containing compounds in materials science and in medicinal chemistry. Among the various strategies used for the construction of C–N bonds, those mediated by nitrogen-centered radicals have been gaining prominence, with accumulating studies showing that the high reactivity of N-radicals can be exploited to tackle a number of challenging synthetic problems.<sup>1</sup> Multiple methods have been developed for the generation of N-radicals under mild conditions, which greatly enhances their usefulness in organic synthesis.<sup>2</sup>

The radical amination of alkenes constitutes a highly valuable type of reaction for the preparation of nitrogen-containing compounds.<sup>3</sup> Significant progress has been made over the past few years, which is to a great extent attributable to the employment of visible-light photoredox catalysis.<sup>4</sup> For instance, excellent protocols have been reported for the anti-Markovnikov hydroamination<sup>2f,5,6</sup> and amination/difunctionalization (Scheme 1a).<sup>7–10</sup> It is noteworthy that primary amidyl radicals, which have been sparingly employed to react with alkenes because of a lack of an effective means of generation, have begun to be used for the construction of the C-N bond.<sup>6-9</sup> Despite this advancement, most of the investigations in this line have focused on protected amidyl radicals, and intermolecular olefin amidation with aryl and alkyl-attached primary amidyl radicals has been much less explored. In view of the great synthetic potential of amidyl radicals as well as the structural importance of amides, it would be highly desirable to broadly investigate the reactivity and efficacy of common amidyl radicals towards the addition of alkenes.

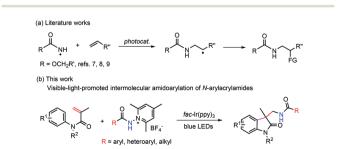
Oxindoles represent an important class of naturally occurring heterocycles that show highly effective biological and physiological activities.<sup>11</sup> Oxindoles can be efficiently prepared from N-phenylacrylamides via radical addition/intramolecular aromatic substitution.<sup>12</sup> Our previous study shows that by reacting aminium radicals with N-phenylacrylamides, aminated oxindoles can be accessed readily in good yields.<sup>13</sup> Considering the significance of the amidyl group in medicinal chemistry, it would be desirable to incorporate the amidyl group into oxindoles by this strategy. Chang et al. reported an effective photochemical protocol for the preparation of amidated oxindoles through the reaction of benzoyl azides with *N*-phenylacrylamides.<sup>14</sup> We envisioned that by reacting amidyl radicals with N-phenylacrylamides, the scope of the reaction could be expanded. N-Aminopyridinium salts have recently been demonstrated to be highly efficient precursors toward N-centered radicals (Scheme 1b);<sup>15,16</sup> they were expected to fulfill our need to deliver the primary aryl and alkyl amidyl radicals under mild conditions. Indeed, our results verified the viability of our design, and the reaction of N-phenylacrylamides with N-aminopyridinium salts was performed under blue light irradiation with fac-Ir(ppy)<sub>3</sub> as the photocatalyst (Scheme 1b). It is worth noting that the reaction

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**Scheme 1** Photochemical protocols for the intermolecular addition of primary amidyl radicals to alkenes.

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exhibited good functional tolerance, and the alkyl-substituted amido group can be introduced into the oxindole motif as well as the aryl and heteroaryl-substituted amido group.

Initially, we selected N-phenylacrylamide 1a and N-aminopyridinium salt 2a as the model substrates to investigate the feasibility of the reaction under visible-light irradiation (40 W Kessil blue LEDs, 50% intensity) in the presence of a photocatalyst (Table 1). A systematic survey of the reaction conditions with variation in the photocatalyst, solvent and base revealed the optimum conditions to be: fac-Ir(ppy)<sub>3</sub> as the photocatalyst, K<sub>3</sub>PO<sub>4</sub> as the base in 1,2-dichloroethane (DCE) at room temperature, and blue-light irradiation for 36 h. Under these conditions, the desired product 3a was isolated in good yield (with 2a as the limiting substrate). The structure of 3a was confirmed by X-ray crystallographic analysis (CCDC no. 2122102<sup>†</sup>).<sup>17</sup> Other catalysts, such as Cu(dap)<sub>2</sub>Cl and eosin Y, were ineffective under the current conditions (Table 1, entries 2 and 3). Replacing DCE with MeCN, dichloromethane (DCM), or CHCl<sub>3</sub> resulted in lower yields (entries 4-6). Additionally, the yield was diminished when K2CO3 or Et3N was used as the base or in the absence of a base (entries 7-9). Control experiments indicate that both photocatalyst and light irradiation are necessary for the reaction to take place (entries 10 and 11).

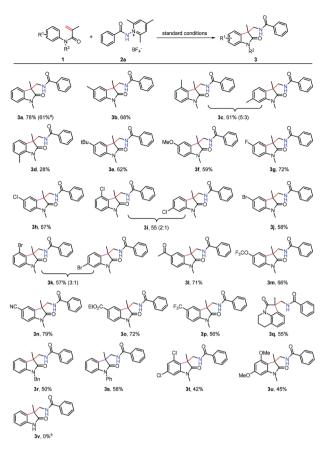
To test the generality of this reaction, the scope of arylacrylamides **1** was investigated, and the results are shown in Scheme 2. Both electron-donating and electron-withdrawing groups on the *N*-phenyl ring were well tolerated, and the corresponding products were obtained in moderate to good yields. Notably, a broad range of functional groups such as the halo (**3g**-**3k**) and cyano (**3n**) groups were well tolerated, which offers the potential for further transformations. This protocol

Table 1 Optimization of the reaction conditions<sup>a</sup>

	$ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & $	fac-Ir(ppy) <sub>3</sub> (2.0 mol%) DCE, K <sub>3</sub> PO <sub>4</sub> (1.2 equiv.) Ar, 36 h, blue LEDs	
Entry	Deviation from the	standard condition	ns Yield <sup><math>b</math></sup> (%)
	Standard conditions		81 (78 <sup>c</sup> ) Trace <sup>d</sup>

1	Standard conditions	81 (78 <u>°</u> )
2	Eosin Y instead of $Ir(ppy)_3$	Trace <sup>d</sup>
3	Cu(dap) <sub>2</sub> Cl instead of Ir(ppy) <sub>3</sub>	N.R.
4	MeCN instead of DCE	56
5	DCM instead of DCE	74
6	CHCl <sub>3</sub> instead of DCE	64
7	K <sub>2</sub> CO <sub>3</sub> instead of K <sub>3</sub> PO <sub>4</sub>	64
8	Et <sub>3</sub> N instead of K <sub>3</sub> PO <sub>4</sub>	41
9	No base	61
10	In the dark	N.R.
11	No photocatalyst	N.R.

<sup>*a*</sup> Reaction conditions: **1a** (0.15 mmol, 1.5 equiv.), **2a** (0.1 mmol, 1.0 equiv.),  $K_3PO_4$  (0.12 mmol, 1.2 equiv.), *fac*-Ir(ppy)<sub>3</sub> (2.0 mol%), DCE (1.0 mL), 40 W Kessil blue LEDs (50% intensity), room temperature, 36 h, under an argon atmosphere. <sup>*b*</sup> Isolated yields. <sup>*c*</sup> The reaction was conducted at the 0.2 mmol scale. <sup>*d*</sup> Reaction time was 24 h. Detailed information concerning the screening of the reaction conditions is presented in Tables S1–S5 in the ESI.†

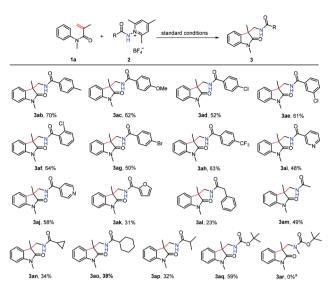


Scheme 2 Scope of arylacrylamides. The reactions were conducted at the 0.2 mmol scale. Isolated yield. <sup>a</sup> 1a (6.0 mmol, 1.5 equiv.), 2a (4.0 mmol, 1.0 equiv.), base (4.8 mmol, 1.2 equiv.), *fac*-Ir(ppy)<sub>3</sub> (2.0 mol%), DCE (30 mL), 40 W Kessil blue LEDs (100% intensity), room temperature, 42 h, under argon atmosphere. <sup>b</sup> A complex mixture was generated.

is applicable to gram-scale preparation. As such, 3a was obtained in 61% yield upon isolation when the reaction was performed at the 4.0 mmol scale. However, the expected product 3v was not obtained when the *N*-unprotected acrylamide was used as the substrate. In this case, the reaction only delivered a complex mixture.

We next turned our attention to examine the scope of *N*-aminopyridinium salts 2 under the standard conditions (Scheme 3). It can be seen that a range of substrates bearing electron-donating and electron withdrawing groups on the phenyl ring of pyridinium salts can be converted to the expected products (**3ab-3ah**), and heteroaryl aminopyridinium salts such as pyridine (**3ai** and **3aj**) and furan (**3ak**) were also suitable substrates for the present reaction. Moreover, alkyl and alkyloxyl-substituted amidyl groups can be introduced into the oxindole motif as well, although the yields of **3al-3ap** were considerably lower than those obtained using their aryl-substituted to the presence of competitive pathways (C-H abstraction from the solvent, for example) that *N*-alkyl amidyl radicals are liable to undergo. This method did not work for

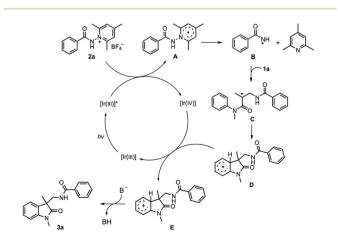
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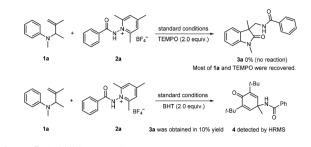
Scheme 3 Scope of aminopyridinium salts. The reactions were conducted at the 0.2 mmol scale. Isolated yields.<sup>a</sup> No reaction took place.

the *N*-disubstituted aminopyridinium salt **2r**, possibly as a result of steric hindrance caused by the *N*-methyl group.

The present reactions are believed to take place following the radical pathway shown in Scheme 4. Taking the reaction of 1a with 2a as an example, it can be seen that the reaction is initiated by the single electron transfer between the *N*-aminopyridinium salt 2a and the excited [Ir(III)]\*, which generates radical A and [Ir(n)]. Radical A then undergoes fragmentation to give the amidyl radical **B**, which is subsequently trapped by 1a to produce the radical intermediate C. The latter undergoes cyclization to afford radical D. Oxidation by [Ir(IV)] converts D to the carbocation E, from which 3a is finally generated by deprotonation. K<sub>3</sub>PO<sub>4</sub> has a beneficial effect on the reaction, probably because it can enhance the basicity of the system to make the deprotonation easier. This radical mechanism was supported by the inhibition experiment with 2,2,6,6tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-tert-butyl-4methylphenol (BHT) (Scheme 5). The reaction of 1a and 2a was



Scheme 4 Proposed mechanism.



Scheme 5 Inhibition experiment.

completely inhibited in the presence of 2.0 equiv. of TEMPO, and the yield of **3a** was significantly decreased when 2.0 equiv. of BHT was added into the reaction vessel. In the latter case, the BHT-trapped product **4** was also detected by HRMS. That the reaction could not take place without *fac*-Ir(ppy)<sub>3</sub> and light irradiation (Table 1, entries 10 and 11) reveals the necessity of photoexcitation of the catalyst during the reaction.

In summary, we have developed an effective protocol for the preparation of amidyl-attached oxindoles *via* photoinduced and *fac*-Ir(ppy)<sub>3</sub>-catalyzed amidoarylation of arylacrylamides with *N*-aminopyridinium salts as the amidyl radical precursors. This method allows a variety of substituted arylacrylamides and *N*-aminopyridinium salts to be converted to the desired products in moderate to good yields. Further attempts to expand the synthetic scope of the intermolecular radical amidation of unactivated olefins are ongoing in our laboratory.

#### Author contributions

Y.-Z. Wang and W. Yu contributed to the conceptualization of this study. Y.-Z. Wang carried out all the experimental work. Y.-Z. Wang and W. Yu wrote the manuscript. Y.-Z. Wang, W.-J. Lin, H.-C. Liu and W. Yu reviewed the final version of the manuscript.

#### Conflicts of interest

There are no conflicts to declare.

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#### Notes and references

 (a) S. Z. Zard, Recent progress in the generation and use of nitrogen-centred radicals, *Chem. Soc. Rev.*, 2008, 37, 1603– 1618; (b) B. Quiclet-Sire and S. Z. Zard, Some aspects of radical chemistry in the assembly of complex molecular architectures, *Beilstein. J. Org. Chem.*, 2013, 9, 557–576; (*c*) T. Xiong and Q. Zhang, New amination strategies based on nitrogen-centered radical chemistry, *Chem. Soc. Rev.*, 2016, **45**, 3069–3087.

- 2 (a) C.-M. Chou, J. Guin, C. Mück-Lichtenfeld, S. Grimme and A. Studer, Radical-transfer hydroamination of olefins with N-aminated dihydropyridines, Chem. - Asian I., 2011, 6, 1197-1209; (b) T. W. Greulich, C. G. Daniliuc and A. Studer, N-Aminopyridinium, salts as precursors for N-centered radicals-direct amidation of arenes and heteroarenes, Org. Lett., 2015, 17, 254-257; (c) J. Davies, S. G. Booth, S. Essafi, R. A. W. Dryfe and D. Leonori, Visible-light-mediated generation of nitrogen-centered radicals: Metal-free hydroimination and iminohydroxylation cyclization reactions, Angew. Chem., Int. Ed., 2015, 54, 14017-14021; (d) Y. Xia, L. Wang and A. Studer, Site-selective remote radical C-H functionalization of unactivated C-H bonds in amides using sulfone reagents, Angew. Chem., Int. Ed., 2018, 57, 12940-12944; (e) S. P. Morcillo, E. M. Dauncey, J. H. Kim, J. J. Douglas, N. S. Sheikh and D. Leonori, Photoinduced remote functionalization of amides and amines using electrophilic nitrogen radicals, Angew. Chem., Int. Ed., 2018, 57, 12945-12949; (f) S. W. Lardy and V. A. Schmidt, Intermolecular radical mediated anti-Markovnikov alkene hydroamination using N-hydroxyphthalimide, J. Am. Chem. Soc., 2018, 140, 12318-12322; (g)L.-H. Li, Υ. Wei and М. Shi, N-Hydroxyphthalimide imidate esters as amidyl radical precursors in the visible light photocatalyzed C-H amidation of heteroarenes, Org. Chem. Front., 2021, 8, 1935-1940; (h) M.-J. Luo, X.-H. Ouyang, Y.-P. Zhu, Y. Li and J.-H. Li, Metal-free electrochemical [3+2] heteroannulation of anilines with pyridines enabled by dual C-H radical aminations, Green Chem., 2021, 23, 9024-9029.
- 3 (a) R. S. Neale, Nitrogen radicals as synthetic intermediates. N-halide rearrangements and additions to unsaturated hydrocarbons, *Synthesis*, 1971, 1–15; (b) L. Stella, Nitrogen-centered radicals, in *Radicals in Organic Synthesis*, ed. P. Renaud and M. P. Sibi, John Wiley & Sons, Ltd., 2001, vol. 2, pp. 407–426; (c) H. Jiang and A. Studer, Intermolecular radical carboamination of alkenes, *Chem. Soc. Rev.*, 2020, 49, 1790–1811.
- 4 (a) J.-R. Chen, X.-Q. Hu, L.-Q. Lu and W.-J. Xiao, Visible light photoredox-controlled reactions of N-radicals and radical ions, *Chem. Soc. Rev.*, 2016, 45, 2044–2056;
  (b) M. D. Kärkäs, Photochemical generation of nitrogencentered amidyl, hydrazonyl, and imidyl radicals: Methodology developments and catalytic applications, *ACS Catal.*, 2017, 7, 4999–5022; (c) Y. Zhao and W. Xia, Recent advances in radical-based C–N bond formation via photo-/ electrochemistry, *Chem. Soc. Rev.*, 2018, 47, 2591–2608;
  (d) X.-Y. Yu, Q.-Q. Zhao, J. Chen, W.-J. Xiao and J.-R. Chen, When light meets nitrogen-centered radicals: From reagents to catalysts, *Acc. Chem. Res.*, 2020, 53, 1066–1083.
- 5 (*a*) J. M. Andrew, C. L. Brendan, X. Zhang, G. N. Saeed, C. S. Trevor and R. R. Knowles, Catalytic intermolecular hydroaminations of unactivated olefins with secondary

alkyl amines, *Science*, 2017, 355, 727–730; (*b*) Q. Zhu, D. E. Graff and R. R. Knowles, Intermolecular anti-Markovnikov hydroamination of unactivated alkenes with sulfonamides enabled by proton-coupled electron transfer, *J. Am. Chem. Soc.*, 2018, **140**, 741–747; (*c*) D. C. Miller, J. M. Ganley, A. J. Musacchio, T. C. Sherwood, W. R. Ewing and R. R. Knowles, Anti-Markovnikov hydroamination of unactivated alkenes with primary alkyl amines, *J. Am. Chem. Soc.*, 2019, **141**, 16590–16594.

- 6 H. Jiang and A. Studer, Anti-markovnikov radical hydroand deuteroamidation of unactivated alkenes, *Chem. – Eur. J.*, 2019, **25**, 7105–7109.
- 7 (a) Q. Qin, Y.-Y. Han, Y.-Y. Jiao, Y. He and S. Yu, Photoredox-catalyzed diamidation and oxidative amidation of alkenes: Solvent-enabled synthesis of 1,2-diamides and α-amino ketones, Org. Lett., 2017, 19, 2909–2912;
  (b) X.-D. An, Y.-Y. Jiao, H. Zhang, Y. Gao and S. Yu, Photoredox-induced radical relay toward functionalized β-amino alcohol derivatives, Org. Lett., 2018, 20, 401–404;
  (c) X.-D. An, H. Zhang, Q. Xu, L. Yu and S. Yu, Stereodivergent synthesis of α-aminomethyl cinnamyl ethers via photoredox-catalyzed radical relay reaction, Chin. J. Chem., 2018, 36, 1147–1150; (d) X.-D. An and S. Yu, Photoredox-catalyzed radical relay reaction toward functionalized vicinal siamines, Synthesis, 2018, 50, 3387–3394.
- 8 (a) H. Jiang and A. Studer, Amidyl radicals by oxidation of α-amido-oxy acids: Transition-metal-free amidofluorination of unactivated Alkenes, Angew. Chem., Int. Ed., 2018, 57, 10707–10711; (b) H. Jiang and A. Studer, Transition-metal-free three-component radical 1,2-amidoalkynylation of unactivated alkenes, Chem. Eur. J., 2019, 25, 516–520; (c) H. Jiang, G. Seidler and A. Studer, Carboamination of unactivated alkenes through three-component radical conjugate addition, Angew. Chem., Int. Ed., 2019, 58, 16528–16532; (d) C. You and A. Studer, Three-component 1,2-carboamination of vinyl boronic esters via amidyl radical induced 1,2-migration, Chem. Sci., 2021, 12, 15765–15769.
- 9 X. Yi and X. Hu, Intermolecular oxidative amination of unactivated alkenes by dual photoredox and copper catalysis, *Chem. Sci.*, 2021, **12**, 1901–1906.
- 10 J. Shen, J. Xu, L. He, Y. Ouyang, L. Huang, W. Li, Q. Zhu and P. Zhang, Photoinduced rapid multicomponent cascade reaction of aryldiazonium salts with unactivated alkenes and TMSN<sub>3</sub>, *Org. Lett.*, 2021, 23, 1204–1208.
- (a) D. A. Sandham, C. Adcock, K. Bala, L. Barker, Z. Brown, G. Dubois, D. Budd, B. Cox, R. A. Fairhurst, M. Furegati, C. Leblanc, J. Manini, R. Profit, J. Reilly, R. Stringer, A. Schmidt, K. L. Turner, S. J. Watson, J. Willis, G. Williams and C. Wilson, 7-Azaindole-3-acetic acid derivatives: Potent and selective CRTh2 receptor antagonists, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 4794–4798; (b) M. Ishikura, K. Yamada and T. Abe, Simple indole alkaloids and those with a nonrearranged monoterpenoid unit, *Nat. Prod. Rep.*, 2010, **27**, 1630–1680; (c) A. J. Kochanowska-Karamyan and M. T. Hamann, Marine indole alkaloids: Potential new drug leads for the control of depression and anxiety, *Chem.*

*Rev.*, 2010, **110**, 4489–4497; (*d*) K. Ding, Y. Lu, Z. Nikolovska-Coleska, G. Wang, S. Qiu, S. Shangary, W. Gao, D. Qin, J. Stuckey, K. Krajewski, P. P. Roller and S. Wang, Structure-based design of spiro-oxindoles as potent, specific small-molecule inhibitors of the MDM2–p53 Interaction, *J. Med. Chem.*, 2006, **49**, 3432–3435.

- 12 (a) G. R. Humphrey and J. T. Kuethe, Practical methodologies for the synthesis of indoles, *Chem. Rev.*, 2006, 106, 2875–2911; (b) J.-R. Chen, X.-Y. Yu and W.-J. Xiao, Tandem radical cyclization of N-Arylacrylamides: An emerging platform for the construction of 3,3-disubstituted oxindoles, *Synthesis*, 2015, 47, 604–629; (c) J. Singh and A. Sharma, Visible light mediated synthesis of oxindoles, *Adv. Synth. Catal.*, 2021, 363, 4284–4308.
- 13 Y.-Z. Wang, W.-J. Lin, J.-Y. Zou, W. Yu and X.-Y. Liu, Preparation of oxindoles via visible-light-induced amination/cyclization of arylacrylamides with alkyl amines, *Adv. Synth. Catal.*, 2020, **362**, 3116–3120.
- 14 D. B. Bagal, S.-W. Park, H.-J. Song and S. Chang, Visible light sensitization of benzoyl azides: cascade cyclization toward oxindoles via a non-nitrene pathway, *Chem. Commun.*, 2017, **53**, 8798–8801.
- 15 (a) T. W. Greulich, C. G. Daniliuc and A. Studer, N-Aminopyridinium salts as precursors for N-centered radicals –direct amidation of arenes and heteroarenes, *Org. Lett.*, 2015, 17, 254–257; (b) S. Jung, H. Lee, Y. Moon, H.-Y. Jung and S. Hong, Site-selective C–H acylation of pyridinium derivatives by photoredox catalysis, *ACS Catal.*,

2019, 9, 9891-9896; (c) Y. Moon, B. Park, I. Kim, G. Kang, S. Shin, D. Kang, M.-H. Baik and S. Hong, Visible light induced alkene aminopyridylation using N-aminopyridinium salts as bifunctional reagents, Nat. Commun., 2019, 10, 4117-4125; (d) D. Forster, W. Guo, O. Wang and J. Zhu, Photoredox catalytic three-component amidoazidation of 1,3-dienes, ACS Catal., 2021, 11, 10871-10877; (e) W. Guo, Q. Wang and J. Zhu, Selective 1,2-aminoisothiocyanation of 1,3-dienes under visible-light photoredox catalysis, Angew. Chem., Int. Ed., 2021, 60, 4085-4089; (f) W.-L. Yu, H.-W. Jiang, L. Yan, Z.-T. Feng, Y.-C. Luo and P.-F. Xu, Visible-light induced generation of bifunctional nitrogen-centered radicals: a concise synthetic strategy to construct bicyclo[3.2.1] octane and azepane cores, Sci. China: Chem., 2021, 64, 274-280; (g) K. Miyazawa, T. Koike and M. Akita, Aminohydroxylation of olefins with iminopyridinium ylides by dual Ir photocatalysis and Sc(OTf)<sub>3</sub> catalysis, Tetrahedron, 2016, 72, 7813-7820.

- 16 For reviews, see: (a) S. L. Rössler, B. J. Jelier, E. Magnier, G. Dagousset, E. M. Carreira and A. Togni, Pyridinium salts as redox-active functional group transfer reagents, *Angew. Chem., Int. Ed.*, 2020, 59, 9264–9280; (b) F.-S. He, S. Ye and J. Wu, Recent advances in pyridinium salts as radical reservoirs in organic synthesis, *ACS Catal.*, 2019, 9, 8943–8960.
- 17 CCDC 2122102† (*N*-((1,3-dimethyl-2-oxoindolin-3-yl) methyl)benzamide, 3a) contains the supplementary crystal-lographic data for this paper.