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Letter

Visible-Light-Driven Aryl Migration and Cyclization of α-Azido Amides

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Cite This: *Org. Lett.* 2021, 23, 4527–4531

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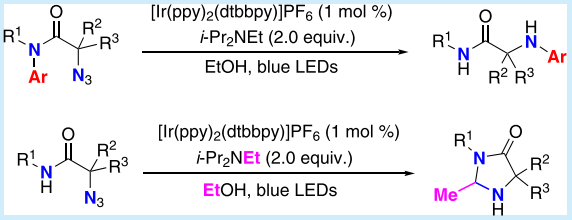
ABSTRACT: This paper reports two new visible-light-promoted radical reactions of α-azido amides. By catalysis of $[Ir(ppy)_2(dtbbpy)]PF_6$ with *i*-Pr_2NEt as the reducing agent, *N*-aryl α-azido tertiary amides were first converted to the corresponding aminyl radicals through reduction of the azido group; the aminyl radicals then underwent N-to-N aryl migration to give α-anilinyl-functionalized amides. α-Azido secondary amides, on the other hand, reacted with the solvent ethanol and *i*-Pr_2NEt to afford the imidazolinone products.

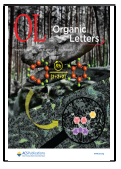


Molecular rearrangements are a fundamental class of organic transformations that are indispensable tools in organic synthesis.[1] The Smiles rearrangement, which involves intramolecular migration of an aryl group between two nucleophilic centers, has long been of great interest to chemists because of its synthetic usefulness in the functionalization of aromatic rings.[2] Although Smiles rearrangements are traditionally categorized as intramolecular nucleophilic aromatic substitution (S_NAr) reactions, the aryl migration can be more conveniently implemented under mild conditions through radical pathways. Many studies have been devoted recently to the radical Smiles-type rearrangement, and as a result, a variety of new methods have been developed for aryl migration between a carbon atom and a heteroatom atom as well as between two carbon atoms.[3] Despite these advances, however, there are certain issues concerning this radical rearrangement that still remain to be addressed. For example, aryl migrations between two electronegative atoms such as oxygen or nitrogen atoms have only scarcely been reported,[4,5] and there are no literature examples involving aminyl-radical-mediated migration between two nitrogen atoms.[6]

Organic azides are versatile compounds that have manifold applications in the preparation of nitrogen-containing compounds.[7] Although the chemistry of organic azides is mostly exploited with regard to their ionic properties, they are also useful precursors to nitrogen-centered radicals.[8] For instance, the azido group can react with tributyltin radical or indium hydride to form the corresponding *N*-(tributylstannyl)aminyl radicals[9] and indium–aminyl radicals.[10] In 2011, Liu reported an elegant visible-light photocatalytic method for reducing alkyl or aryl azides to amines via the intermediacy of aminyl radicals.[11] That study paved a new pathway for the generation of aminyl radicals from simple azides, which has recently been employed to effect azide-involved C–N coupling[12−14] and P–N coupling[15] under visible-light photoredox catalysis.[16] Despite these achievements, however, the synthetic usefulness of this methodology has not been sufficiently investigated, and new reaction patterns need to be explored to expand the scope of radical amination reactions of azides.

Recently, in the course of our investigation of the iron-catalyzed amination reactions of α-azido carbonyl compounds,[17,18] we found that iron(II) salts or complexes can enable the transformation of α-azido amides into imidazolinones via intramolecular $C(sp^3)$–H insertion mediated by iron–imido species.[18,19] We envisioned that by conversion of the azido group into an aminyl radical, a different reaction pathway would be opened for these precursors. The method of visible-light photoredox catalysis[20] would provide a convenient means to generate aminyl radicals from α-azido amides. Indeed, after some exploration of the reaction conditions, we found that *N*-phenyl α-azido amides can be converted readily into the corresponding aminyl radicals via single electron transfer (SET) under blue-light irradiation with $[Ir(ppy)_2(dtbbpy)]PF_6$ as the photocatalyst and *i*-Pr_2NEt as the reductant. The thus-formed aminyl radical attacks the *N*-phenyl group to engender 1,4-phenyl transfer from the amido nitrogen to the azido nitrogen with high efficacy in ethanol. Apart from this rearrangement, α-azido amides can also react with the solvent ethanol and *i*-Pr_2NEt to afford imidazolinone products if there is a hydrogen atom on the amido nitrogen. The present reactions reveal some new aspects concerning the reactions of aminyl radicals that will have implications in organic synthesis.

Received: April 2, 2021
Published: May 27, 2021

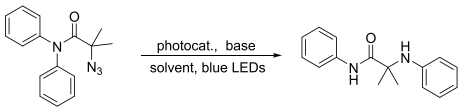


Initially, to explore the radical reaction of *N*-phenyl-α-azido amides, compound **1a** was chosen as the model compound for screening of the reaction conditions for photoredox catalysis. [Cu(DPEphos)(bcp)]PF_6 was first employed as the photocatalyst. Under blue-light irradiation, this complex can be reduced by Et_3N or *i*-Pr_2NEt to the [Cu^0] form, which is a powerful SET reductant.[21] It was hoped that the azido group of **1a** could be reduced by this [Cu^0] species to the corresponding aminyl radical. We found that when **1a** was irradiated with blue LEDs in acetonitrile in the presence of 2 mol % [Cu(DPEphos)(bcp)]PF_6 and 2.0 equiv of Et_3N under an argon atmosphere, the phenyl migration product **2a** was obtained in 32% yield. The structure of **2a** was confirmed by X-ray crystallographic analysis (CCDC 2016463). Encouraged by the initial success, more photocatalytic conditions were explored, and the results are summarized in Table 1. [Ir(ppy)$_2$(dtbbpy)]PF_6 proved to be a more powerful photoctalyst than [Cu(DPEphos)(bcp)]PF_6 (entry 2), and in subsequent experiments, [Ir(ppy)$_2$(dtbbpy)]PF_6 was fixed as the photocatalyst to optimize the solvent. Ethanol and methanol were found to be suitable solvents for the reaction, in which **2a** can be generated in high yield. When Et_3N was replaced with *i*-Pr_2NEt, the yield of **2a** was raised to 90% in ethanol. A 1 mol% loading of [Ir(ppy)$_2$(dtbbpy)]PF_6 was enough to guarantee a high yield (entry 9). Notably, the reaction proceeded equally well under an aerobic atmosphere (entry 10), and the yield did not decrease on a preparative scale (5 mmol; entry 11). Control experiments indicated that light, photocatalyst, and trialkylamine are all necessary for the reaction to take place (entries 15−17). Additional information about screening of the reaction conditions is provided in Table S1.

The optimized conditions (Table 1, entry 10) were then applied to differently substituted 2-azido-2-methyl-*N*,*N*-diphenylpropanamides (**1**) to reveal the influence of the electronic nature of the *N*-phenyl ring on its migration aptitude. As shown in Table 2, for substrates bearing two identical aryl rings (**1b−f**), the substituent has a large impact on the yield of the rearrangement products. The introduction of methoxy or Br at the *para* position reduced the yield substantially. In cases where only one phenyl ring bears a substituent at the *para* or *meta* position (**1g−k**), the reaction delivered two products in a ratio varying between 0.8 and 1.2, indicating that the electronic nature of the substituent does not influence the migration selectivity very much. This result is consistent with a mechanism of radical-involved phenyl migration. *o*-Methyl-substituted **1l** also reacted to give the phenyl migration product as a pair of isomers (**2l** and **2l′**) in a combined yield of 48%.

This protocol works equally well when one *N*-phenyl ring in **1** was replaced with an alkyl group. Compounds **3a−n** underwent rearrangement smoothly to give products **4a−n** in good yields (Scheme 1). Compounds incorporating a ring (**4o** and **4p**) or having only one alkyl group at the α-position (**4q−aa**) can be converted in the same way. Notably, pyridyl can also migrate (**4ac**), and its migration aptitude is stronger than that of the phenyl group (**4ad** and **4ad′**). However, the yield was considerably lower in the case of *N*-phenyl-2-(phenylamino)hex-5-enamide (**4u**), and the reaction was also less efficient for 2-azido-*N*,*N*-diphenylacetamide (**3ab**).

Table 1. Screening of the Reaction Conditions[a]

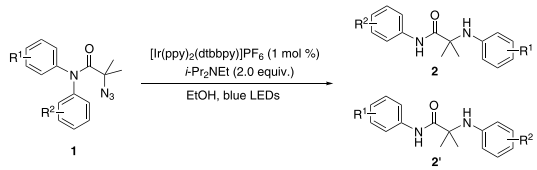


1a 2a

entry	photocat.[b] (mol %)	reductant (equiv)	solvent	time (h)	yield of **2a** (%)[c]
1	[Cu^I] (2)	Et_3N (2.0)	MeCN	24	32
2	[Ir^{III}] (2)	Et_3N (2.0)	MeCN	24	49
3	[Ir^{III}] (2)	Et_3N (2.0)	DCE	24	43
4	[Ir^{III}] (2)	Et_3N (2.0)	THF	24	35
5	[Ir^{III}] (2)	Et_3N (2.0)	DMF	24	trace[d]
6	[Ir^{III}] (2)	Et_3N (2.0)	MeOH	24	80
7	[Ir^{III}] (2)	Et_3N (2.0)	EtOH	24	78
8	[Ir^{III}] (2)	*i*-Pr_2NEt (2.0)	EtOH	24	90
9	[Ir^{III}] (1)	*i*-Pr_2NEt (2.0)	EtOH	5	90
10	***[Ir^{III}] (1)***	***i*-Pr_2NEt (2.0)***	***EtOH***	***5***	***90***[e]
11	***[Ir^{III}] (2)***	***i*-Pr_2NEt (2.0)***	***EtOH***	***24***	***93***[f]
12	[Ir^{III}] (1)	*i*-Pr_2NEt (1.5)	EtOH	5	80
13	[Ir^{III}] (1)	*i*-Pr_2NEt (1.0)	EtOH	5	51
14	[Ir^{III}] (1)	*i*-Pr_2NEt (0.5)	EtOH	5	25
15	–	*i*-Pr_2NEt (2.0)	EtOH	5	N.R.
16	[Ir^{III}] (1)	–	EtOH	5	N.R.
17	[Ir^{III}] (1)	*i*-Pr_2NEt (2.0)	EtOH	5	N.R.[g]

[a]The reaction was conducted on a 0.2 mmol scale in 2 mL of solvent under an argon atmosphere at ambient temperature (30−35 °C), unless otherwise indicated. A 10 W blue LED strip was used as the light source. [b][Cu^I] = [Cu(DPEphos)(bcp)]PF_6; [Ir^{III}] = [Ir(ppy)$_2$(dtbbpy)]PF_6. [c]Isolated yields. [d]Most of **1a** was recovered. [e]The reaction was conducted under an aerobic atmosphere. [f]The reaction was conducted on a 5 mmol scale. [g]Control experiment in the dark.

Table 2. Influence of Electronic Effects on the Migration Aptitude



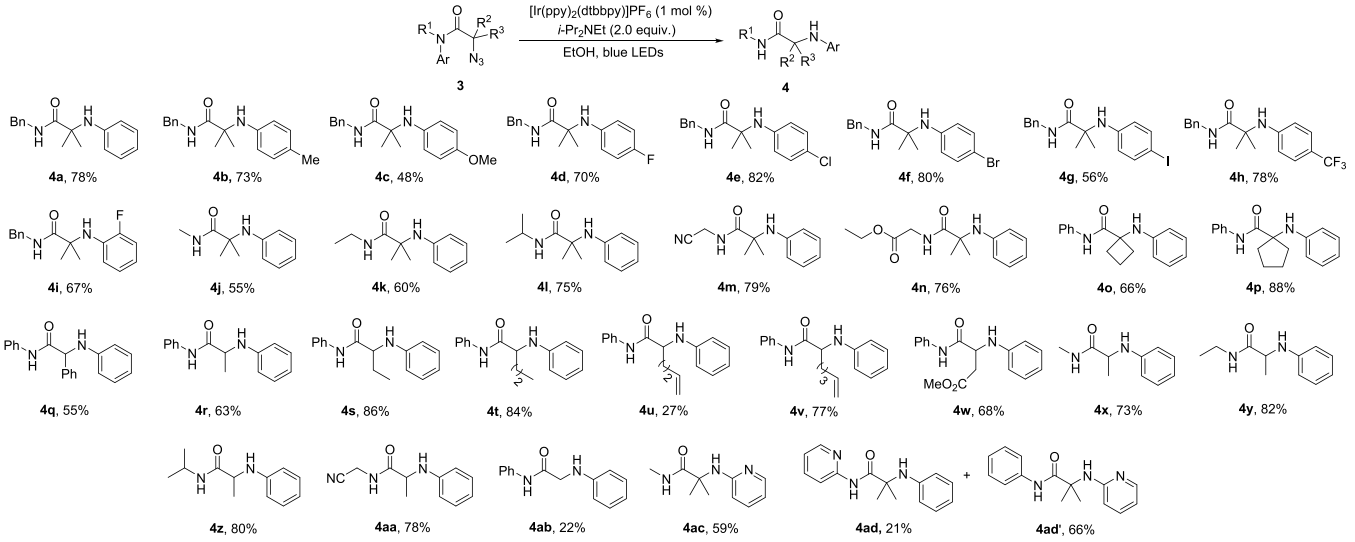
1 2 2′

substrate	R^1	R^2	product(s), yield (%)
1b	*p*-Me	*p*-Me	**2b**, 84
1c	*p*-OMe	*p*-OMe	**2c**, 38[a]
1d	*p*-Br	*p*-Br	**2d**, 51
1e	*p*-Ph	*p*-Ph	**2e**, 93
1f	*m*-Me	*m*-Me	**2f**, 71
1g	H	*p*-Me	**2g** + **2g′** (1:1.2),[b] 87
1h	H	*p*-F	**2h** + **2h′** (1:1),[b] 72
1i	H	*p*-Br	**2i** + **2i′** (1:1),[b] 88
1j	H	*p*-CF_3	**2j** + **2j′** (1:0.8), 91
1k	H	*m*-Me	**2k** + **2k′** (1:0.8),[b] 92
1l	H	*o*-Me	**2l** + **2l′** (1:0.8),[b] 48

[a]50% of **1c** was recovered. [b]The ratio was determined on the basis of ^{1}H NMR spectra.

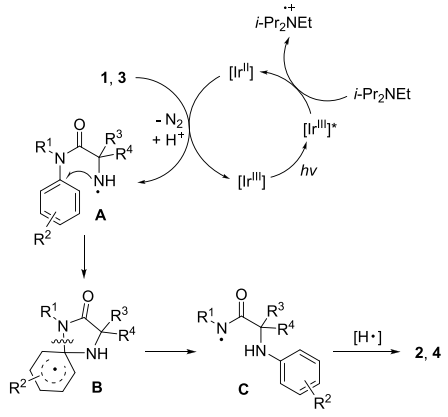
https://doi.org/10.1021/acs.orglett.1c01120
Org. Lett. 2021, 23, 4527−4531

Scheme 1. Reaction Scope



These 1,4-aryl migration reactions can be rationalized with the mechanism illustrated in Scheme 2. The reaction is initiated by SET between visible-light-excited $[Ir^{III}]^*$ and *i*-Pr_2NEt, which gives rise to the reduced $[Ir^{II}]$ and *i*-Pr_2NEt radical cation. Compound **1** or **3** is then reduced by $[Ir^{II}]$ to the corresponding aminyl radical **A** after extrusion of dinitrogen and protonation, with $[Ir^{III}]$ being regenerated at the same time. Ethanol facilitates the generation of **A** by providing a proton. The involvement of this reduction process is confirmed by the reaction of 2-azido-*N*,*N*-dibenzyl-2-methylpropanamide (**5**) under the same conditions, which gave the reduction product 2-amino-*N*,*N*-dibenzyl-2-methylpropanamide (**6**) in 85% yield (Scheme S1). **A** subsequently undergoes aryl migration via intermediacy of azaspirocyclohexadienyl radical **B** to afford amidyl radical **C**, from which **2** or **4** is generated by accepting a hydrogen atom.

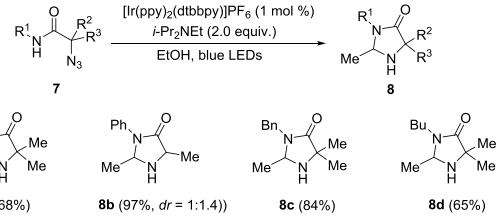
Scheme 2. Proposed Mechanism for 1,4-Aryl Migration



Theoretical (DFT) analysis indicates that phenyl migration from the amidyl nitrogen to the azido nitrogen is thermodynamically favorable (Figure S3). Interestingly, under the current circumstance, no fused heterocyclic products were obtained, in contrast with analogous reactions involving attack of iminyl radicals.[22] Moreover, from Scheme 1 it can be seen that the aminyl radical preferably attacks the phenyl ring rather than abstracting a hydrogen atom from the amido-nitrogen-attached $C(sp^3)$–H bond (**4a**–**n**).

When the standard conditions were applied to 2-azido-2-methyl-*N*-phenylpropanamide (**7a**), however, no phenyl migration product was obtained; instead, the reaction afforded imidazolidin-4-one **8a** in 68% yield (Scheme 3). The same transformation also took place for other α-azido amides bearing only one substituent on the amido nitrogen (**8b**–**d**).

Scheme 3. Reaction of Substrates Monosubstituted at the Amido Nitrogen



Compounds **8** apparently derived from the reaction of **7** with EtOH or *i*-Pr_2NEt, both of which have an ethyl moiety incorporated into their structures. To elucidate where the $CHCH_3$ group in **8** came from, control experiments were conducted in which the solvent and reductant were changed, and the results are presented in Scheme 4. It can be seen that both the tertiary amine and the solvent can participate the reaction. When butan-1-ol was used as the solvent, the reaction of **7a** delivered **9a** as well as **8a**. By contrast, only **8a** was generated when the reaction was conducted in propan-2-ol. On the other hand, replacing *i*-Pr_2NEt with tripropylamine resulted in the formation of **10a** as well as **8a**, and the reaction afforded only **8a** when 1-methylpiperidine was used in place of *i*-Pr_2NEt.

A plausible mechanism is proposed to account for the formation of imidazolidinones **8** (Scheme 5). In the reaction of **7a** as an example, the excited catalyst $[Ir^{III}]^*$ is first reduced by *i*-Pr_2NEt to $[Ir^{II}]$; the latter then reduces **7a** to aminyl radical **A**. Because of the unfavorable conformational effect driving the phenyl group away from the nitrogen radical center, **A** does not undergo phenyl migration; instead, it abstracts a hydrogen atom from the solvent (or from *i*-Pr_2NEt) to form amine **D**

https://doi.org/10.1021/acs.orglett.1c01120
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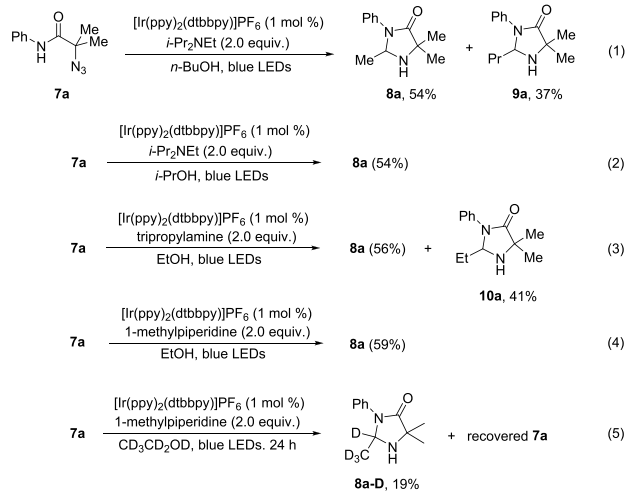
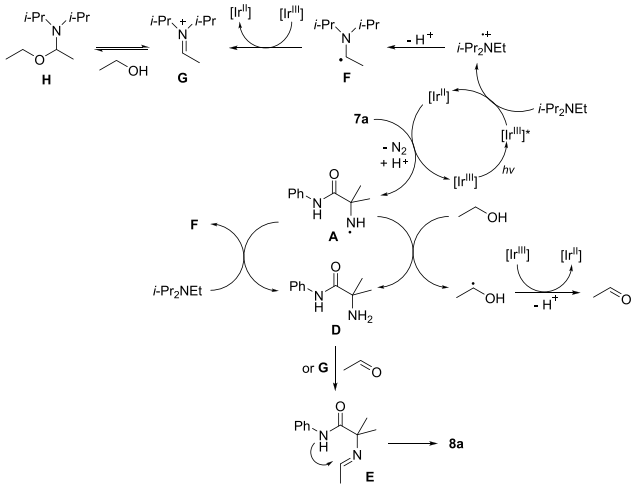
Scheme 4. Control Experiments with Variation of the Tertiary Amine and Solvent



Scheme 5. Plausible Mechanism for the Formation of Imidazolidin-4-ones



and α-hydroxy ethyl radical (or **F**). α-Hydroxy ethyl radical is electron-rich and thus can be oxidized by $[Ir^{III}]$ to give acetaldehyde. The latter then reacts with **D** to afford imidazolidin-4-one **8a**.[23] Apart from this pathway, **8a** can also be formed through the reaction of **D** with iminium **G**, which in turn comes from *i*-Pr_2NEt radical cation following deprotonation and a second SET oxidation.

The involvement of hydrogen atom transfer (HAT) from the solvent to the aminyl radical was further confirmed by the reaction of **7a** in deuterated ethanol. Under the conditions of CD_3CD_2OD and 1-methylpiperidine, **8a-D** was obtained in a moderate yield of 19% (Scheme 4, eq 5), which is much lower than that in ethanol under otherwise identical conditions.

In summary, we have realized 1,4-aryl migration from the amido nitrogen in *N*-substituted-*N*-aryl α-azido amides to the azido group under visible-light irradiation by employing $[Ir(ppy)_2(dtbbpy)]PF_6$ as the photocatalyst and *i*-Pr_2NEt as the reductant. The reaction proceeds via the intermediacy of an aminyl radical derived from SET reduction of the azido group. This migration allows a wide variety of *N*-aryl-α-azido amides to be converted to α-anilinyl-functionalized amides in good yields. α-Azido secondary amides, on the other hand, reacted with *i*-Pr_2NEt and the solvent ethanol to generate imidazolidin-4-one products. The present reactions not only broaden the scope of the radical Smiles rearrangement but also reveal new aspects to exploit the synthetic utility of aminyl radicals in organic synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01120.

General experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR spectra, computational details, and crystallographic data for compound **2a** (PDF)

Accession Codes

CCDC 2016463 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the National Natural Science Foundation of China (21772077) and the State Key Laboratory of Applied Organic Chemistry for financial support.

REFERENCES

(1) (a) Smith, M. B. *March's Advanced Organic Chemistry*, 8th ed.; John Wiley & Sons, 2020. (b) Rojas, C. M. *Molecular Rearrangements in Organic Synthesis*; John Wiley & Sons, 2015.

(2) (a) Snape, T. J. A truce on the Smiles rearrangement: revisiting an old reaction—the Truce−Smiles rearrangement. *Chem. Soc. Rev.* **2008**, *37*, 2452−2458. (b) Holden, C. M.; Greaney, M. F. Modern aspects of the Smiles rearrangement. *Chem. - Eur. J.* **2017**, *23*, 8992−9008.

(3) For reviews of radical aryl migration reactions, see: (a) Studer, A.; Bossart, M. Radical aryl migration reactions. *Tetrahedron* **2001**, *57*, 9649−9667. (b) Chen, Z.-M.; Zhang, X.-M.; Tu, Y.-Q. Radical aryl migration reactions and synthetic applications. *Chem. Soc. Rev.* **2015**, *44*, 5220−5245. (c) Li, W.; Xu, W.; Xie, J.; Yu, S.; Zhu, C. Distal radical migration strategy: an emerging synthetic means. *Chem. Soc. Rev.* **2018**, *47*, 654−667. (d) Zhang, G.; Liu, Y.; Zhao, J.; Li, Y.; Zhang, Q. Radical cascade reactions of unsaturated C−C bonds involving migration. *Sci. China: Chem.* **2019**, *62*, 1476−1491.

(4) For an example of O-to-O aryl migration, see: Wang, S.-F.; Cao, X.-P.; Li, Y. Efficient aryl migration from an aryl ether to a carboxylic acid group to form an ester by visible-light photoredox catalysis. *Angew. Chem., Int. Ed.* **2017**, *56*, 13809−13813.

(5) For examples of O-to-N aryl migration, see: (a) Chang, X.; Zhang, Q.; Guo, C. Electrochemical reductive Smiles rearrangement for C−N Bond formation. *Org. Lett.* **2019**, *21*, 10−13. (b) Lawson, C. A.; Dominey, A. P.; Williams, G. D.; Murphy, J. A. Visible light-mediated Smiles rearrangements and annulations of non-activated aromatics. *Chem. Commun.* **2020**, *56*, 11445−11448.

(6) For a recent ionic Smiles rearrangement involving aryl migration from amide nitrogen to aniline nitrogen, see: Costil, R.; Dale, H. J. A.; Fey, N.; Whitcombe, G.; Matlock, J. V.; Clayden, J. Heavily substituted atropisomeric diarylamines by unactivated Smiles rearrangement of *N*-aryl anthranilamides. *Angew. Chem., Int. Ed.* **2017**, *56*, 12533−12537.

(7) (a) Scriven, E. F. V.; Turnbull, K. Azides: Their preparation and synthetic uses. *Chem. Rev.* **1988**, *88*, 297−368. (b) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. Organic azides: An exploding diversity of a unique class of compounds. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188−5240. (c) *Organic Azides: Syntheses and Applications*; Bräse, S., Banert, K., Eds.; John Wiley & Sons, 2010.

(8) (a) Minozzi, M.; Nanni, D.; Spagnolo, P. From azides to nitrogen-centered radicals: Applications of azide radical chemistry to organic synthesis. *Chem. - Eur. J.* **2009**, *15*, 7830−7840. (b) Jimeno, C.; Renaud, P. Radical Chemistry with Azides. In *Organic Azides: Syntheses and Applications*; Bräse, S., Banert, K., Eds.; John Wiley & Sons, 2010; pp 239−267.

(9) (a) Kim, S.; Joe, G. H.; Do, J. Y. Highly efficient intramolecular addition of aminyl radicals to carbonyl groups: a new ring expansion reaction leading to lactams. *J. Am. Chem. Soc.* **1993**, *115*, 3328−3329. (b) Kim, S.; Do, J. Y. 1,2-Radical rearrangements of aryl, furanyl and thiophenyl groups from carbon to nitrogen. *J. Chem. Soc., Chem. Commun.* **1995**, 1607−1608. (c) Benati, L.; Nanni, D.; Sangiorgi, C.; Spagnolo, P. Radical chain reactions of α-azido-β-keto esters with tributyltin hydride. A novel entry to amides and lactams through regiospecific nitrogen insertion. *J. Org. Chem.* **1999**, *64*, 7836−7841. (d) Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G.; Rizzoli, C. Cyclizations of *N*-stannylaminyl radicals onto nitriles. *Org. Lett.* **2004**, *6*, 417−420.

(10) Benati, L.; Bencivenni, G.; Leardini, R.; Nanni, D.; Minozzi, M.; Spagnolo, P.; Scialpi, R.; Zanardi, G. Reaction of azides with dichloroindium hydride: Very mild production of amines and pyrrolidin-2-imines through possible indium−aminyl radicals. *Org. Lett.* **2006**, *8*, 2499−2502.

(11) Chen, Y.; Kamlet, A. S.; Steinman, J. B.; Liu, D. R. A biomolecule-compatible visible-light-induced azide reduction from a DNA-encoded reaction-discovery system. *Nat. Chem.* **2011**, *3*, 146−153.

(12) Huang, X.; Webster, R. D.; Harms, K.; Meggers, E. Asymmetric catalysis with organic azides and diazo compounds Initiated by photoinduced electron transfer. *J. Am. Chem. Soc.* **2016**, *138*, 12636−12642.

(13) Konev, M. O.; McTeague, T. A.; Johannes, J. W. Nickel-catalyzed photoredox-mediated cross-coupling of aryl electrophiles and aryl azides. *ACS Catal.* **2018**, *8*, 9120−9124.

(14) Wu, Y.; Zhang, Y.; Jiang, M.; Dong, X.; Jalani, H. B.; Li, G.; Lu, H. Synergistic combination of visible-light photo-catalytic electron and energy transfer facilitating multicomponent synthesis of β-functionalized α,α-diarylethylamines. *Chem. Commun.* **2019**, *55*, 6405−6408.

(15) Wu, Y.; Chen, K.; Ge, X.; Ma, P.; Xu, Z.; Lu, H.; Li, G. Redox-Neutral P(O)−N Coupling between P(O)−H Compounds and Azides via Dual Copper and Photoredox Catalysis. *Org. Lett.* **2020**, *22*, 6143−6149.

(16) Azides can also be converted to nitrenes by the action of a transition metal photocatalyst under visible-light irradiation. See: (a) Farney, E. P.; Yoon, T. P. Visible-light sensitization of vinyl azides by transition-metal photocatalysis. *Angew. Chem., Int. Ed.* **2014**, *53*, 793−797. (b) Scholz, S. O.; Farney, E. P.; Kim, S.; Bates, D. M.; Yoon, T. P. Spin-selective generation of triplet nitrenes: olefin aziridination through visible-light photosensitization of azidoformates. *Angew. Chem., Int. Ed.* **2016**, *55*, 2239−2242. (c) Brachet, E.; Ghosh, T.; Ghosh, I.; Kōnig, B. Visible light C−H amidation of heteroarenes with benzoyl azides. *Chem. Sci.* **2015**, *6*, 987−992. (d) Zhang, Y.; Dong, X.; Wu, Y.; Li, G.; Lu, H. Visible-light-induced intramolecular C(sp^2)−H amination and aziridination of azidoformates via a triplet nitrene pathway. *Org. Lett.* **2018**, *20*, 4838−4842.

(17) (a) Yang, T.; Fan, X.; Zhao, X.; Yu, W. Iron-catalyzed acyl migration of tertiary α-azidyl ketones: Synthetic approach toward enamides and isoquinolones. *Org. Lett.* **2018**, *20*, 1875−1879. (b) Yang, T.; Lin, Y.; Yang, C.; Yu, W. Iron-catalysed 1,2-acyl migration of tertiary α-azido ketones and 2-azido-1,3-dicarbonyl compounds. *Green Chem.* **2019**, *21*, 6097−6102.

(18) (a) Zhao, X.; Liang, S.; Fan, X.; Yang, T.; Yu, W. Iron-catalyzed intramolecular C−H amination of α-azidyl amides. *Org. Lett.* **2019**, *21*, 1559−1563. (b) Liang, S.; Zhao, X.; Yang, T.; Yu, W. Iron−phosphine complex-catalyzed intramolecular C(sp^3)−H amination of azides. *Org. Lett.* **2020**, *22*, 1961−1965.

(19) For a similar ruthenium-catalyzed intramolecular C(sp^3)−H amination of 2-azidoacetamides, see: Zhou, Z.; Chen, S.; Qin, J.; Nie, X.; Zheng, X.; Harms, K.; Riedel, R.; Houk, K. N.; Meggers, E. Catalytic enantioselective intramolecular C(sp^3)−H amination of 2-azidoacetamides. *Angew. Chem., Int. Ed.* **2019**, *58*, 1088−1093.

(20) For reviews of generation of nitrogen-centered radicals by visible-light photoredox catalysis, see: (a) Yu, X.-Y.; Zhao, Q.-Q.; Chen, J.; Xiao, W.-J.; Chen, J.-R. When light meets nitrogen-centered radicals: From reagents to catalysts. *Acc. Chem. Res.* **2020**, *53*, 1066−1083. (b) Kärkäs, M. D. Photochemical generation of nitrogen-centered amidyl, hydrazonyl, and imidyl radicals: Methodology developments and catalytic applications. *ACS Catal.* **2017**, *7*, 4999−5022.

(21) Michelet, B.; Deldaele, C.; Kajouj, S.; Moucheron, C.; Evano, G. A general copper catalyst for photoredox transformations of organic halides. *Org. Lett.* **2017**, *19*, 3576−3579.

(22) Li, D.; Li, Y.; Yu, W. *tert*-Butyl hypochlorite-induced cyclization of ethyl 2-(*N*-arylcarbamoyl)-2-iminoacetates. *Synthesis* **2017**, *49*, 4283−4291.

(23) Samulis, L.; Tomkinson, N. C. O. Preparation of the MacMillan imidazolidinones. *Tetrahedron* **2011**, *67*, 4263−4267.

https://doi.org/10.1021/acs.orglett.1c01120
Org. Lett. 2021, 23, 4527−4531