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Nitryl Radical-Triggered Semipinacol-Type Rearrangement, Lactonization, and Cycloetherification of Olefins

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We report the development of a practical photocatalytic strategy to access various nitro-containing cyclic compounds from olefins *via* semipinacol-type rearrangement, cycloetherification, and lactonization reactions, employing *N*-nitrosuccinimide as a bench-stable, non-metal-based nitrating reagent. Mechanistic insights suggest that this light-driven process occurs *via* NO_2 radical pathway mediated by a photoredox catalyst, which triggers an N–N bond fragmentation. Subsequent Giese-type addition of nitryl radicals to activated olefins takes place, leading to the formation of nitro-containing β-functionalized ketones, lactones and cycloethers. The reaction proceeds under mild reaction conditions and tolerates a wide range of functional groups and structural variations.

Introduction

Nitro-containing compounds are privileged building blocks and intermediates in the preparation of various pharmaceuticals,[1] drugs,[2] and materials.[3,4] On the other hand, nitro group is a valuable functionality in organic synthesis and serves as a precursor to amines, aldehydes, carboxylic acids, and many other vital functionalities.[5,6] Hence, the development of methodologies to access different classes of nitro-derived molecules is an alluring research target.[7,8] To this day, the plurality of nitration methods are still restricted and the majority of them utilize a so called 'mixed acid' approach that requires the use of hazardous nitric and sulfuric acids to generate reactive nitronium (NO_2^+) species.[9–11] It is generally observed that these harsh nitration protocols lead to limited regioselectivity and low functional group tolerance as well as the formation of various by-products resulting from undesired oxidation and hydrolysis processes.[12] In this context, there is a high demand for mild and practical protocols to expand the chemical space of molecules containing nitro groups. Therefore, extensive research has been carried out to make nitration safer and sustainable,[13,14] and the use of reagents like alkyl nitrites,[15] nitroalkanes,[16] metal nitrites,[17] etc.[18] has played a decisive role. Our research group has recently introduced a series of bench-stable, organic NO_2-transfer reagents based on pyrrolidinone (**I**),[19] succinimide (**II**), phthalimide (**III**),[20] and saccharin (**IV**) scaffolds.

These reagents are easily accessible from the corresponding inexpensive amides in a single chemical step and can be activated using various manifolds, delivering in reaction media nitryl radicals or nitronium species under mild and non-acidic reaction conditions. Using these reagents, we have achieved the synthesis of a broad array of nitro-derived molecules *via* direct nitration of aromatic and heteroaromatic systems, *ipso*-nitration reactions, and diverse functionalization of olefins and alkynes, while delicately balancing the level of chemo-, regio- and diastereoselectivity (Scheme 1B).[21,22] For example, our previous works established that reagent **II** provides a nitryl radical formation *via* a mesolytic N–N bond fragmentation under visible-light photoredox-catalyzed conditions.[23] Taking advantage of this process, we considered whether radical nitration mediated by visible-light photoredox catalysis[24] could open a new route to valuable nitro-containing compounds *via* nitro-induced cyclization reactions.

Rearrangement and intramolecular cyclization reactions have received wide attention in synthetic chemistry and are powerful tools to construct all-carbon quaternary centers.[25] Recent developments in semipinacol-type rearrangements of allylic alcohols allow the formation of β-functionalized ketones, along with the construction of new C_{sp^3}–FG bond in a single chemical operation.[26,27] For example, cyclic and acyclic alkenyl alcohols can be transformed into functionalized ketones simply by reacting with electrophilic or radical species, including but not limited to trifluoromethyl,[28,29] alkyl,[30,31] aryl,[32,33] acyl,[34] azido,[35] selenium,[36] nitrosonium,[37] halide,[38] *N*-centered radicals,[39] etc.,[40] expanding the repertoire of this chemistry and its application in natural product synthesis.[41] Herein, we

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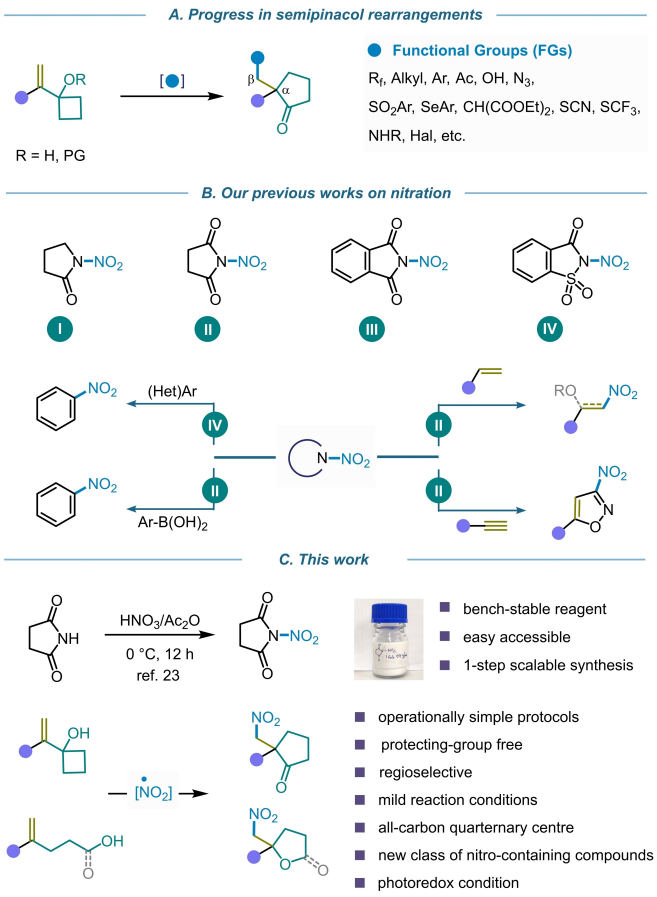


Scheme 1. A. Previously reported semipinacol rearrangements. B. Our previous works on nitration. C. This work on nitration-induced semipinacol rearrangement, lactonization, and cycloetherification of olefins.

report a nitryl radical-triggered semipinacol-type rearrangement to forge a novel route to densely-functionalized NO_2-containing compounds under mild and visible light-mediated photoredox reaction conditions, using *N*-nitrosuccinimide as a redox active nitrating reagent. Furthermore, the process has been successfully applied to nitrative lactonization and cycloetherification of olefins, delivering the corresponding nitro-adducts with excellent level of chemo- and diastereoselectivity.

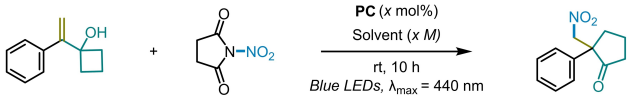
Results and Discussion

Our initial investigations focused on the development of reaction conditions for the semipinacol-type rearrangement by utilizing cycloalkanol-substituted styrene derivative **A** as a model substrate[42] and *N*-nitrosuccinimide **II** as nitrating reagent. We assumed that after addition of a nitryl radical to olefin and subsequent single-electron reduction (SET), the benzylic cation intermediate would undergo 1,2 alkyl migration of the cycloalkanol moiety. Indeed, carrying out the reaction under photoredox conditions in acetonitrile and in the presence of *fac*-Ir(ppy)$_3$ (2 mol%) as photocatalyst under blue LED's irradiation resulted in the formation of 2-aryl-2-nitrocyclopentanone derivative **1** in 57% yield (Table 1, entry 1). The initial reaction conditions, including photocatalysts, solvents, concentrations and stoichiometries were carefully evaluated and the main observations are summarized in Table 1 (see supplementary information, page S4–S7). The screening of Ir- and Ru-based photocatalysts resulted in reduced product yields (entries 2–4), while using lower catalyst loading of *fac*-Ir(ppy)$_3$ furnished the desired product in 63% (entry 5). Further modulation of substrate concentration increased the amount of **1** up to 72% (entry 9), whereas poor yields were obtained using **III** or **IV** as nitrating reagents (entry 10–11). The highest yield of 78% was achieved using 1.5 equivalents of reagent **II** (entry 12).

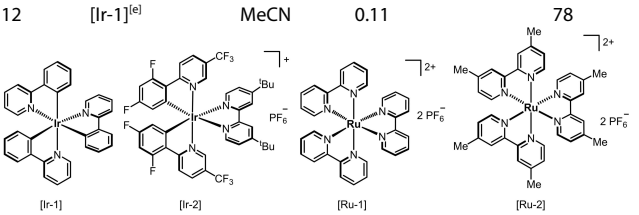
With the optimized reaction conditions in hand, the generality of this protocol was explored with respect to allylic alcohol derivatives (Scheme 2). Several electron-withdrawing and electron-donating substituents on the benzene ring of 1-(1-arylvinyl)cyclobutanol at *ortho*-, *meta*-, and *para*-positions were well tolerated (**1**–**7**). Likewise, polycyclic aromatic adducts containing naphthalene (**4**), and biphenyl (**8**) substituents produced the corresponding migration products in good to excellent yields.

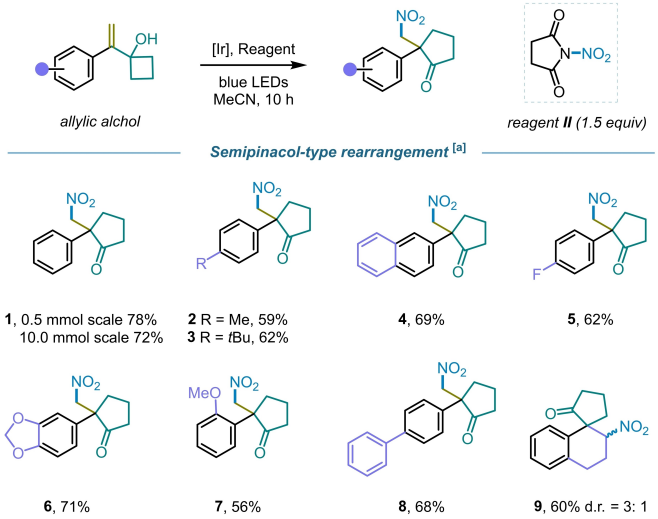
Interestingly, 1-(3,4-dihydronaphthalen-1-yl)cyclobutan-1-ol also smoothly underwent nitrative rearrangement reaction, yielding the β-nitrospiroketone **9** in 60%, however as a mixture of diastereoisomers (d.r. 3:1). Unfortunately, the transformation was limited to aryl substituted allylic alcohols, most likely due to the inefficiency of *fac*-Ir(ppy)$_3$ to oxidize a non-benzylic position. For example, carrying out the reaction with 1-(1-tertbutylvinyl)-cyclobutanol resulted in complex mixture formation.

Table 1. [a] General conditions: **A** (0.5 mmol, 1 equiv), photocatalyst (1.0 mol%), *N*-nitrosuccinimide **II** (2.0 equiv), and solvent (*x* M), 350 W blue LEDs, rt, 10 h. [b] Catalyst (2.0 mol%) was added. [c] Reagent **III** (1.5 equiv) was added. [d] Reagent **IV** (1.5 equiv) was added. [e] Reagent **II** was used in an amount of 1.5 equivalent.



Entry	PC [1 mol%]	Solvent	Concentration [M]	1 [%][a]
1	[Ir-1][b]	MeCN	0.68	57
2	[Ir-2] [b]	MeCN	0.68	15
3	[Ru-1] [b]	MeCN	0.68	49
4	[Ru-2] [b]	MeCN	0.68	53
5	[Ir-1]	MeCN	0.68	63
6	[Ir-1]	CH_2Cl_2	0.68	50
7	[Ir-1]	HFIP	0.68	0
8	[Ir-1]	Dioxane	0.68	32
9	[Ir-1]	MeCN	0.11	72
10	[Ir-1][c]	MeCN	0.11	48
11	[Ir-1][d]	MeCN	0.11	17
12	[Ir-1][e]	MeCN	0.11	78



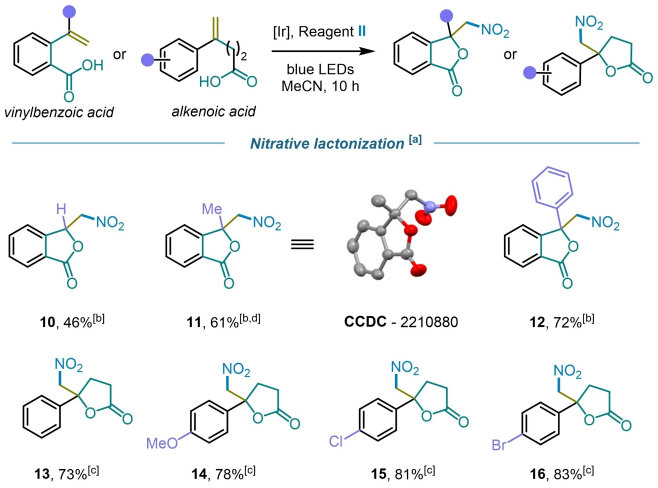


Scheme 2. [a] General conditions: allylic alcohol (0.5 mmol, 1 equiv), *fac*-Ir(ppy)$_3$ (1.0 mol%), *N*-nitrosuccinimide (1.5 equiv), and solvent (0.11 M), 350 W blue LEDs, rt, 10 h.

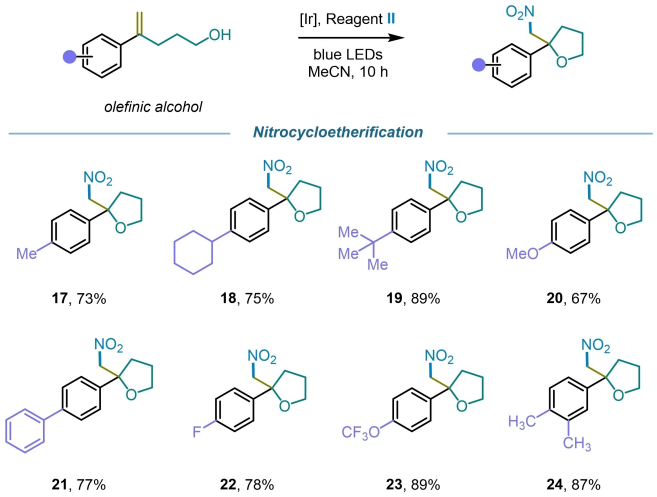
The development of synthetic methods to introduce NO_2-containing lactones has attracted our attention owing to the limited literature reports available to date. As of now, only nitro lactonization by ferric nitrate is known at high reaction temperatures,[43] thus a milder protocol can serve as a beneficial entry to synthesize nitro-containing lactones. Using our simple and room temperature protocol, we speculated that readily available olefinic acids can undergo the nitro lactonization reaction to access cyclic systems with oxa-carbon quaternary center motif. Indeed, applying our optimized conditions for semipinacol rearrangement to benzoic acid derivatives, the corresponding nitro-derived adducts can be obtained (Scheme 3). For example, 2-vinylbenzoic acid derivative yielded nitro-substituted lactone **10** in a moderate 46% yield, while an increased yield of up to 72% was observed for lactones **11** and **12** bearing benzylic oxa-carbon quaternary centers.[44] Alkenoic acids carrying various substituents at arene moiety were examined next. Notably, regardeless of the electronic diversity of the substituents, the reactions proceeded efficiently with the formation of the desired lactones in up to 83% isolated yield (**13**–**16**).

Encouraged by the great reactivity of carboxylic and alkenoic acids, we decided to apply our strategy to the synthesis of tetrahydrofuran derivatives *via* previously unexplored nitrocycloetherification reaction of olefinic alcohols, since the tetrahydrofuran (THF) motif is one of the privilege structural components of many synthetic and natural products. Without any further adjustment of the initial reaction conditions, and despite the fact that olefinic alcohols are less reactive than the corresponding acid derivatives, our photoredox catalyzed protocol similarly demonstrated a high level of chemoselectivity (Scheme 4). Olefinic alcohols with different aryl substituents smoothly underwent the cyclization reaction besides the presence in their structures of either the electron-donating methyl (**17**, **24**), cyclohexyl (**18**), *tert*-butyl (**19**), methoxy (**20**), and phenyl (**21**) or the electron-poor (**22**, **23**) substituents. In addition, disubstituted styrene derivative also provided cycloetherification adduct **24** in good yield.

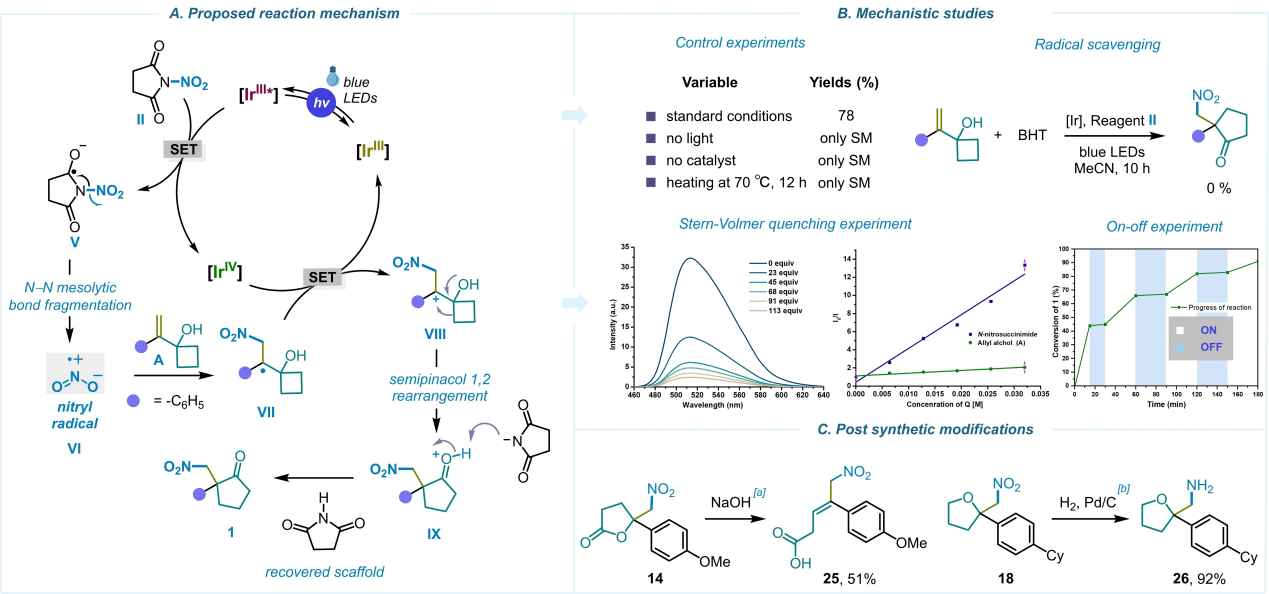
Following the successful exploration of the scope over a wide variety of nitro-containing scaffolds, we next aimed to elucidate the mechanism of this transformation using experimental and spectroscopic methods.[45] Preliminary examination revealed that the desired product **1** could not be generated if radical scavenger butylated hydroxytoluene (BHT) was present in the reaction media (Scheme 5B, see supplementary information, page S10). No product formation or only trace amounts were detected when the reaction was carried out at elevated temperatures (70 °C) or in the absence of a photocatalyst or visible light. In addition, an on/off light experiment was



Scheme 3. [a] General conditions: olefinic carboxylic acids or alkenoic acids (0.5 mmol, 1 equiv), *fac*-Ir(ppy)$_3$ (1.0 mol%), *N*-nitrosuccinimide (1.5 equiv), and MeCN (0.11 M), 350 W blue LEDs, rt, 10 h. [b] Vinylbenzoic acids were used as starting materials. [c] Alkenoic acids were used. [d] Hydrogen atoms have been removed for clarity in the X-ray image.



Scheme 4. [a] General conditions: olefinic alcohols (0.5 mmol, 1 equiv), *fac*-Ir(ppy)$_3$ (1.0 mol%), *N*-nitrosuccinimide **II** (1.5 equiv), and MeCN (0.11 M), 350 W blue LEDs, rt, 10 h.



Scheme 5. A. Proposed mechanism. B. Mechanistic studies. C. Post-functionalization of **14** and **18**. [a] **14** (0.5 mmol), NaOH (1.5 mmol), EtOH (3 mL), rt, 12 h. [b] **18** (0.5 mmol), H_2 1 atm, Pd on Carbon (10 mol%), (1.5 mmol), MeOH (6 mL), rt, 50 °C, 5 h.

conducted, confirming that the reaction proceeds only under irradiation (Scheme 5B, see supplementary information, page S10). Based on the above information and literature reports,[23] the mechanistic details of our proposed transformation are further outlined in Scheme 5. *N*-nitrosuccinimide (**II**) (−1.39 V vs SCE) triggers an intermolecular deactivation process of photo-excited state of Ir^{III*} ($E_{1/2}^{IV/III*}$ = −1.73 V vs SCE in MeCN) (K = 2 × 10^8 $M^{-1}s^{-1}$, see supplementary information, page S8), generating species **I**. Sequentially, a mesolytic N–N bond fragmentation takes place to liberate nitryl radical **VI**. This species undergoes a selective Giese-type addition[46] to the β-position of olefin **A** to form the preferred and stabilized benzyl radical intermediate **VII**. The catalytic cycle is completed with a single electron transfer step from **VII** to Ir^{IV}, thereby regenerating the ground-state of the photocatalyst and delivering α-hydroxy carbocation **VIII**. The latter species undergoes an intramolecular ring expansion *via* 1,2-alkyl shift to afford five-membered oxonium intermediate **IX**, which in the presence of the base leads to the formation of **1**. Interestingly, the core scaffold of the succinimide reagent can also be completely recovered.

Owing to the fundamental importance of nitro compounds, we next explored the synthetic utility of nitro-derived cyclic building blocks prepared with our protocols. While treatment of the nitrolactone **14** under basic reaction conditions afforded valuable nitropentenoic acid **25** in 51% isolated yield, which is an exceptionally challenging scaffold to prepare using existing synthetic methodologies. On the other hand, the nitro group can easily be reduced to the amino derivative without opening the cycle, as shown in the example of the synthesis of amino cycloether **26** from **18** (Scheme 5C).

Conclusion

In conclusion, we have successfully developed a visible-light-induced photoredox-catalyzed semipinacol-type rearrangement, which is triggered by the nitryl radicals and occurs via 1,2 alkyl migration. Using *N*-nitrosuccinimide as a bench stable and non- metal-based nitrating reagent, this strategy enables the direct generation of the C_{sp}^3–NO_2 bond as well as the construction of all-carbon quaternary center motif, expanding the chemical space of nitro-containing compounds. The protocol is mild, operationally simple, and tolerates a wide array of functionalities. In addition, the same reaction conditions have been successfully applied to nitrative cycloetherification and lactonization reactions of olefins, which also operate with a high level of chemoselectivity. Subsequent studies are aimed at extending synthetic utility of this organic nitrating reagents in a complimentary electrochemical fashion.

Experimental Section

General Procedures for the Preparation of Substrates 1–24.

A flame dried 20 mL crimp cap vial, equipped with a magnetic stir bar, was charged with *fac*-Ir(ppy)$_3$ (3.3 mg, 5 µmol, 1.0 mol%) and *N*-nitrosuccinimide (reagent **II**) (108 mg, 0.75 mmol, 1.5 equiv). The contents of the vial were then subjected to three vacuum/argon cycles. The corresponding alkene (0.5 mmol, 1.0 equiv) and anhydrous MeCN (5 mL) were added under an argon atmosphere, and the solution was sparged with argon for 5 min. The reaction mixture was stirred at room temperature under blue LEDs irradiation for 10 h. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column chromatography (automated system) or manually on a silica

column using an eluent of EtOAc:Hexane (v/v) to afford the desired nitro compound.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: cycloetherification · lactonization · *N*-nitrosuccinimide · radical nitration · semipinacol rearrangement

[1] C. Kannigadu, D. N'Da, *Curr. Pharm. Des.* **2020**, *26*, 4658–4674.
[2] K. Nepali, H. Y. Lee, J. P. Liou, *J. Med. Chem.* **2019**, *62*, 2851–2893.
[3] F. R. F. Fan, Y. Yao, L. Cai, L. Cheng, J. M. Tour, A. J. Bard, *J. Am. Chem. Soc.* **2004**, *126*, 4035–4042.
[4] A. A. Kulkarni, *Beilstein J. Org. Chem.* **2014**, *10*, 405–424.
[5] N. Ono, *The Nitro Group in Organic Synthesis*; Wiley-VCH, Weinheim, **2003**.
[6] A. G. Barrett, G. G. Graboski, *Chem. Rev.* **1986**, *86*, 751-726.
[7] G. Yan, M. Yang, *Org. Biomol. Chem.* **2013**, *11*, 2554–2566.
[8] N. Kornblum, *Org. React.* **2011**, *12*, 101–156.
[9] a) M. Carmack, G. R. Baizer, L. W. Handrick, H. Kissinger, E. H. Sprecht, *J. Am. Chem. Soc.* **1947**, *69*, 785–790; b) A. Topchiev, *Nitration of Hydrocarbons and Other Organic Compounds*, Pergamon, Oxford, **1959**, 283–314.
[10] G. A. Olah, V. P. Reddy, G. K. S. Prakash, *Synthesis* **1992**,1087–1089.
[11] E. S. Halberstadt, E. D. Hughes, C. K. Ingold, *Nature* **1946**, *158*, 514.
[12] a) J. G. Hoggett, *Nitration and aromatic reactivity*, Cambridge University Press, Cambridge, **2009**; b) G. A. Olah, R. Malhotra, S. C. Narang, *Nitration: Methods and Mechanisms*, VCH Publishers, Inc, New York, **1989**.
[13] G. Yan, M. Yang, *Org. Biomol. Chem.* **2013**, *11*, 2554–2566.
[14] S. S. Patel, D. B. Patel, H. D. Patel, *ChemistrySelect* **2021**, *6*, 1337–1356.
[15] S. Z. Song, Y. Dong, G. P. Ge, Q. Li, W. T. Wei, *Synthesis* **2020**, *52*, 796–806.
[16] R. Ballini, *Studies in Natural Products Chemistry*, Elsevier, Amsterdam, **1997**, *19*, 117–184.
[17] S. Maity, S. Manna, S. Rana, T. Naveen, A. Mallick, D. Maiti, *J. Am. Chem. Soc.* **2013**, *135*, 3355–3358.
[18] S. Patra, I. Mosiagin, R. Giri, D. Katayev, *Synthesis* **2022**, *54*, 3432–3472.
[19] P. Romea, M. Aragones, J. Garcia, J. Vilarrasa, *J. Org. Chem.* **1991**, *56*, 7038–7042.
[20] H. F. Kauffman, A. Burger, *J. Org. Chem.* **1954**, *19*, 1662–1670.
[21] R. Calvo, K. Zhang, A. Passera, D. Katayev, *Nat. Commun.* **2019**, *10*, 3410.
[22] K. Zhang, A. Budinská, A. Passera, D. Katayev, *Org. Lett.* **2020**, *22*, 2714–2719.
[23] K. Zhang, B. Jelier, A Passera, G. Jeschke, D. Katayev, *Chem. Eur. J.* **2019**, *25*, 12929–1293.
[24] For selected reviews on photoredox catalysis; a) M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926; b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; c) X. Yang, D. Wang, *ACS Appl. Energ. Mater.* **2018**, *1*, 6657–6693; d) L. Candish, K. D. Collins, G. C. Cook, J. J. Douglas, A. Gómez-Suárez, A. Jolit, S. Keess, *Chem. Rev.* **2022**, *122*, 2907–2980; e) L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034–10072; *Angew. Chem.* **2018**, *130*, 10188–10228; f) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075–10166.
[25] a) G. Pandey, A. Mishra, J. Khamrai, *Tetrahedron* **2018**, *74*, 4903–4915; b) P. Hu, H. M. Chi, K. C. DeBacker, X. Gong, J. H. Keim, I. T. Hsu, S. A. Snyder, *Nature* **2019**, *569*, 703–707; c) G. Wu, J. R. Wu, Y. Huang, Y. W. Yang *Chem. Asian J.* **2021**, *16*, 1864–187.
[26] a) S. Kim, S. Lee, *Tetrahedron Lett.* **1991**, *32*, 6575–6578; b) X. M. Zhang, B. S. Li, S. H. Wang, K. Zhang, F. M. Zhang, Y. Q. Tu, *Chem. Sci.* **2021**, *12*, 9262–9274.
[27] a) A. X. Gao, S. B. Thomas, S. A. Snyder, *Molecular Rearrangements in Organic Synthesis*; Wiley: Hoboken, **2016**, 1–34; b) Y. Xing, C. Li, J. Meng, Z. Zhang, X. Wang, Z. Wang, Y. Ye, K. Sun, *Adv. Synth. Catal.* **2021**, *363*, 3913–3936.
[28] B. Sahoo, J. L. Li, F. Glorius, *Angew. Chem. Int. Ed.* **2015**, *54*, 11577–11580; *Angew. Chem.* **2015**, *127*, 11740–11744.
[29] a) Y. J. Kim, D. Y. Kim, *J. Fluorine Chem.* **2018**, *211*, 119–123; b) W. Sha, W. Zhang, S. Ni, H. Mei, J. Han, Y. Pan, *J. Org. Chem.* **2017**, *82*, 9824–9831.
[30] S. Yao, K. Zhang, Q. Q. Zhou, Y. Zhao, D. Q. Shi, W. J. Xiao, *Chem. Commun.* **2018**, *54*, 8096–8099.
[31] M. H. Xu, K. L. Dai, Y. Q. Tu, X. M. Zhang, F. M. Zhang, S. H. Wang, *Chem. Commun.* **2018**, *54*, 7685–7688.
[32] a) X. Z. Shu, M. Zhang, Y. He, H. Frei, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136*, 5844–5847; b) D. H. Lukamto, M. J. Gaunt, *J. Am. Chem. Soc.* **2017**, *139*, 9160–9163.
[33] a) Y. J. Kim, D. Y. Kim *Org. Lett.* **2019**, *21*, 1021–1025; b) S. J. Kwon, D. Y. Kim, *Org. Lett.* **2016**, *18*, 4562–4565.
[34] J. J. Zhang, Y. B. Cheng, X. H. Duan, *Chin. J. Chem.* **2017**, *35*, 311–315.
[35] S. Alazet, J. Preindl, R. Simonet-Davin, S. Nicolai, A. Nanchen, T. Meyer, J. Waser, *J. Org. Chem.* **2018**, *83*, 12334–12356.
[36] a) Y. J. Kim, D. Y. Kim, *Tetrahedron Lett.* **2019**, *60*, 1538–1542; b) D. Y. Kim, *Synth. Commun.* **2019**, *49*, 2203–2209; c) H. I. Jung, D. Y. Kim, *Synlett* **2019**, *30*, 1361–1365.
[37] J. W. Dong, T. Ding, S. Y. Zhang, Z. M. Chen, Y. Q. Tu, *Angew. Chem. Int. Ed.* **2018**, *57*, 13192–13196; *Angew. Chem.* **2018**, *130*, 13376–13380.
[38] a) C. Chen, J. C. Kang, C. Mao, J. W. Dong, Y. Y. Xie, T. M. Ding, Y. Q. Tu, Z. M. Chen, S. Y. Zhang, *Green Chem.* **2019**, *21*, 4014–4019; b) F. Romanov-Michailidis, L. Guénée, A. Alexakis, *Angew. Chem. Int. Ed.* **2013**, *52*, 9266–9270; *Angew. Chem.* **2013**, *125*, 9436–9440; c) F. Romanov-Michailidis, M. Romanov-Michailidis, M. Pupier, A. Alexakis, *Chem. Eur. J.* **2015**, *21*, 5561–558; d) Y. Kim, D. Y. Kim, *Asian J. Org. Chem.* **2019**, *8*, 679–682.
[39] a) W. H. Urry, K. Nicolaides, *J. Am. Chem. Soc.* **1952**, *74*, 5163–5168; b) W. Z. Weng, J. G. Sun, P. Li, B. Zhang, *Chem. Eur. J.* **2017**, *23*, 9752–9755; c) T. C. Ma, S. Yao, M. M. Qiao, F. Yuan, D. Q. Shi, W. J. Xiao *Org. Chem. Front.* **2021**, *8*, 4224–4229; d) S. Liu, Y. Huang, J. Wang, F. L. Quing, X. H. Xu, *J. Am. Chem. Soc.* **2022**, *144*, 1962–1970; e) J. Jang, D. Y. Kim *Asian J. Org. Chem.* **2022**, *11*, e202200531.
[40] a) X. F. Song, A. H. Ye, Y. Y. Xie, J. W. Dong, C. Chen, Y. Zhang, Z. M. Chen, *Org. Lett.* **2019**, *21*, 9550–9554; b) S. Sarkar, A. Banerjee, W. Yao, E. V. Patterson, M. Y. Ngai, *ACS Catal.* **2019**, *9*, 10358–10364; c) B. Zhu, T. Shen, X. Q. Huang, Y. C. Zhu, S. Song, N. Jiao, *Angew. Chem. Int. Ed.* **2019**, *58*, 11028–11032; *Angew. Chem.* **2019**, *131*, 11144–11148; d) Y. Yin, W. Z. Weng, J. G. Sun, B. Zhang, *Org. Biomol. Chem.* **2018**, *16*, 2356–2361; e) Y. J. Kim, D. Y. Kim, *Org. Lett.* **2019**, *21*, 1021–1025.
[41] a) Z. L. Song, C. A. Fan, Y. Q. Tu, *Chem. Rev.* **2011**, *111*, 7523–7556; b) Z. Xin, H. Wang, H. He, S. Gao, *Tetrahedron Lett.* **2021**, *71*, 153029–153037.
[42] The following references are used to access all starting materials; a) J. Zhang, A. Jalil, J. He, Z. Yu, Y. Cheng, G. Li, Y. Du, K. Zhao, *Chem. Commun.* **2021**, *57*, 7426–7429; b) F. Romanov-Michailidis, M. Romanova Michaelides, M. Pupier, A. Alexakis, *Chem. Eur. J.* **2015**, *21*, 5561–5583; c) A. Bunescu, Q. Wang, J. Zhu, *Eur. J. Chem.* **2014**, *20*, 14633–14636; d) T. M. F. Alves, M. O. Costa, B. A. D. Bispo, F. L. Pedrosa, M. A. B. Ferreira, *Tetrahedron Lett.* **2016**, *57*, 3334–3338; e) L. Zhou, C. K. Tan, X. Jiang, F. Chen, Y. Y. Yeung, *J. Am. Chem. Soc.* **2010**, *132*, 15474–15476; f) N. Tsuji, J. L. Kennemur, T. Buyck, S. Lee, S. Prévost, P. S. J. Kaib, D.

Bykov, C. Farès, B. List, *Science* **2018**, *359*, 1501–1505; g) R. Giri, I. Mosiagin, I. Franzoni, N. Y. Nötel, S. Patra, D. Katayev *Angew. Chem. Int. Ed.* **2022**, *61*, e202209143; *Angew. Chem.* **2022**, *134*, e2022091.
[43] T. Yoshimura, Y. Umeda, R. Takahashi, J. I. Matsuo, *J. Chem. Pharm. Bull.* **2020**, *68*, 1220–1220.
[44] Deposition number 2210880 (**11**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallo-graphic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.
[45] L. Buzzetti, G. E. M. Crisenza, P. Melchiorre, *Angew. Chem. Int. Ed.* **2019**, *58*, 3730–3786; *Angew. Chem.* **2019**, *131*, 3768–3786.
[46] a) B. Giese, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 753–764; *Angew. Chem.* **1983**, *95*, 771–782; *Angew. Chem. Int. Ed.* **1983**, *22*, 753–764; b) B. Giese, *Angew. Chem. Int. Ed.* **1985**, *24*, 553–565; *Angew. Chem.* **1985**, *97*, 555–567; c) A. L. Gant Kanegusuku, J. L. Roizen, *Angew. Chem. Int. Ed.* **2021**, *60*, 21116–21149; *Angew. Chem.* **2021**, *133*, 21286–21319.

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