OL Organic Letters

pubs.acs.org/OrgLett Letter

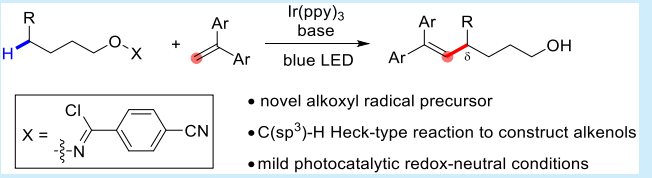
Radical C(sp^3)−H Heck-type Reaction of *N*-Alkoxybenzimidoyl Chlorides with Styrenes to Construct Alkenols

Di Fang, Yidan Zhang, and Yiyun Chen*

Cite This: *Org. Lett.* 2022, 24, 2050−2054 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We report the first radical C(sp^3)−H Heck-type reaction of aliphatic alcohols for selective δ- and ε-alkenol synthesis by photoredox catalysis. *N*-Alkoxybenzimidoyl chlorides are developed as novel alkoxyl radical precursors with tunable redox potentials. Various alkenols can be constructed by the inert C(sp^3)−H Heck-type reaction of 4-cyano-*N*-alkoxybenzimidoyl chlorides with styrene derivatives under redox-neutral conditions, which can be performed on the gram scale and can be easily derivatized.

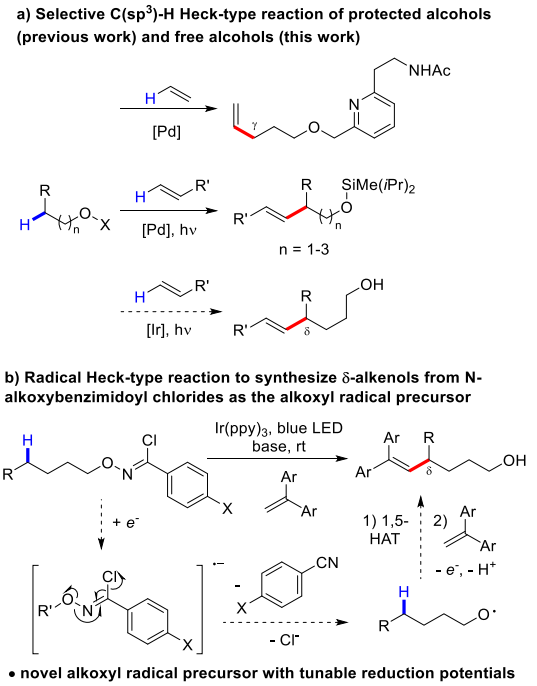


Downloaded via Yiyun Chen on March 25, 2022 at 07:17:14 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

The Heck reaction is a powerful method for introducing the olefin moiety to the molecule of interest, with wide-ranging industrial and pharmaceutical applications.[1] The transition-metal-catalyzed Heck reaction is the method of choice for building C(sp^2)−C(sp^2) bonds with aryl and alkenyl halides.[2] The radical Heck-type reaction with alkyl halides is attractive for constructing C(sp^3)−C(sp^2) bonds, as the undesirable β-hydride elimination from the alkyl-metal intermediate is minimized.[3] Because the accessibility of aliphatic halide groups at the given site of molecules is limited, recent years have witnessed the selective C(sp^3)−H Heck-type reaction by the intramolecular directing-group strategy at aliphatic carboxylates and amides.[4] However, the C(sp^3)−H Heck-type reaction for constructing alkenols is elusive, and only isolated examples have been reported on protected alkenol synthesis (Scheme 1a).[5] Yu pioneered the benzyl ether linker strategy to construct benzyl ethers of γ-alkenol via five-membered cyclopalladation,[5a] and Gevorgyan developed an iodinated alkylsilyl ether auxiliary to synthesize silyl ethers of β-, γ-, or δ-alkenols by the hydrogen atom transfer (HAT) relay.[5b]

While effective, extra deprotection steps are required to reveal free alcohol groups from the protected ethers of alkenols. To date, a selective C(sp^3)−H Heck-type reaction to construct δ-alkenols has not been achieved, where δ-alkenol products present in many bioactive natural products and may easily derivatize to bifunctional building blocks. The alkoxyl radical is a reactive intermediate in organic synthesis, and its 1,5-HAT reactivity provides an attractive entry to the inert δ-C(sp^3)−H functionalization of alcohols.[6,7] The recently emerged photoredox catalysis has enabled alkoxyl radical generation under mild conditions,[8] and we as well as other groups have achieved δ-C(sp^3)−H vinylation with vinyl sulfones and vinyl boronic acids as the radical acceptors.[9] In contrast with these derivatized alkene building blocks, terminal alkenes are more readily available and synthetically appealing.

Scheme 1. Selective C(sp^3)−H Radical Heck-type Reaction to Synthesize Alkenols



Received: February 21, 2022
Published: March 7, 2022



© 2022 American Chemical Society

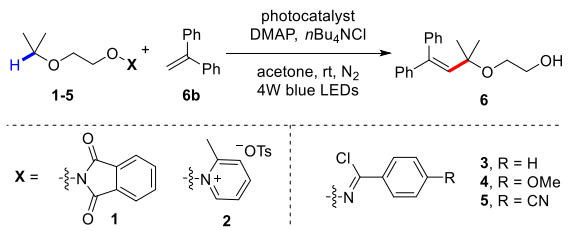
https://doi.org/10.1021/acs.orglett.2c00593
Org. Lett. 2022, 24, 2050−2054

However, δ-C(sp^3)−H Heck-type reactions with terminal alkenes have not been reported.

We envision that the lack of success in this transformation is due to the incompatibility of the alkoxyl radical generation with the radical Heck-type reaction. In fact, our previous efforts on this transformation with known photocatalytic alkoxyl radical precursors gave unfruitful results *vide infra*. *N*-Alkoxybenzimidoyl chlorides were previously reported to generate alkoxyl radicals under heating conditions with azodiisobutyronitrile (AIBN) and tributyltin, but the generated alkoxyl radicals were quenched under the reaction conditions and resulted in no synthetic application to date.[10] We hypothesize that the photocatalysis might empower this underdeveloped radical precursor with new reactivity, and the single-electron reduction will induce the redox fragmentation with arylnitrile and chloride elimination as the driving force to yield the alkoxyl radical (Scheme 1b). Herein we report the discovery of *N*-alkoxybenzimidoyl chlorides as novel alkoxyl radical precursors with tunable redox potentials by aryl substituents, where the 4-cyano-*N*-alkoxybenzimidoyl chloride derivative enables a radical Heck-type reaction under redox-neutral photocatalytic conditions to synthesize various alkenols.

We started the investigation with the known alkoxyl radical precursors *N*-alkoxyphthalimide **1** and *N*-alkoxypyridinium salt **2**, which generated alkoxyl radicals via single-electron reduction and demonstrated the δ-C(sp^3)−H vinylation reactivity with vinyl sulfones or vinyl boronic acids.[9a,d] However, with the use of diphenylethylene **6b** as the Heck-type acceptor and $Ir(ppy)_3$ as the photocatalyst, no product **6** formation was observed from either **1** or **2** (Table 1, entry 1; see Table S1 for details). We then synthesized *N*-alkoxybenzimidoyl chlorides **3**−**5** with different electronic substituents.[11] The unsubstituted *N*-alkoxybenzimidoyl chloride **3** was reactive under AIBN and tributyltin conditions;[10] however, it gave no conversion in the photocatalytic conditions (entry 1). The installation of the electron-rich 4-methoxy substitution did not help convert **4** either (entry 1). Pleasingly, the electron-deficient *N*-alkoxybenzimidoyl chloride **5** with 4-cyano-substitution increased the reduction potentials and afforded the δ-C(sp^3)−H radical Heck-type product **6** in 80% yield, and Heck-type isomers at other C(sp^3)−H sites were not observed (76% isolated yield, entry 2). The change from $Ir(ppy)_3$ to other photocatalysts $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$, Ph-Acr-Mes$BF_4$, or $Ru(bpy)_3(PF_6)_2$ gave decreased or no conversion of **5** (entries 3−5). The addition of bases was essential to neutralize the released HCl: The switch of 4-dimethylaminopyridine (DMAP) to Et_3N afforded a similar 75% yield of **6**, and the removal of the base resulted in no **6** formation (entries 6 and 7). The use of tetrabutylammonium chloride as the additive was the most effective (entry 8 and Table S3). The photocatalyst and light irradiation were required for the transformation (entries 9 and 10).

Table 1. Optimization of the δ-C(sp^3)−H Radical Heck-type Reaction[a,b,c]



entry	reaction conditions[a]	conv (%)[b]	yield (%)[b]
1	**1**−**4**, $Ir(ppy)_3$	<5[c]	<5
2	**5**, $Ir(ppy)_3$	>145	80 (76)
3	**5**, $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	40	17
4	**5**, Ph-Acr-MesBF_4	17	0
5	**5**, $Ru(bpy)_3(PF_6)_2$	<5	0
6	entry 2, Et_3N instead of DMAP	>145	75
7	entry 2, no DMAP	>145	<5
8	entry 2, no nBu_4NCl	>145	55
9	entry 2, no $Ir(ppy)_3$	<5	0
10	entry 2, no $h\nu$	<5	0

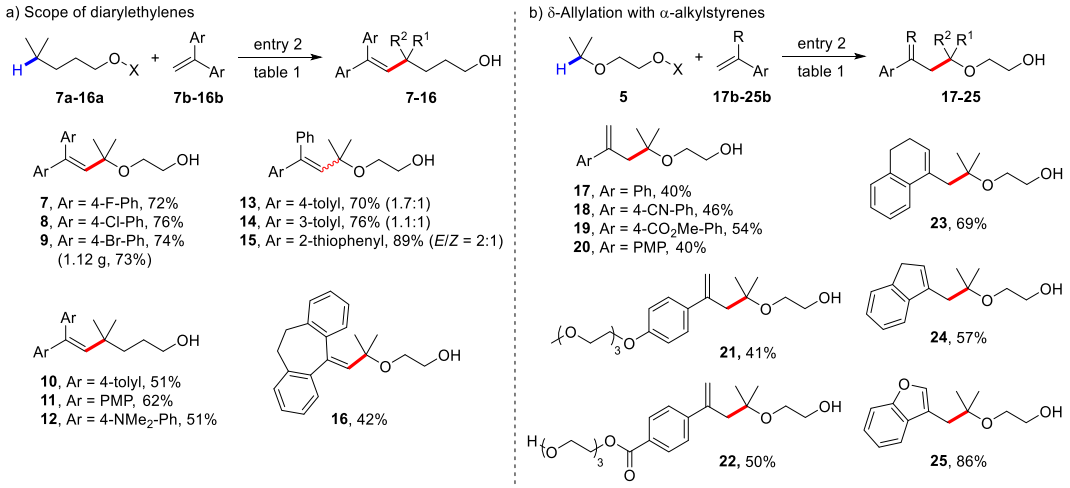
[a]Reaction conditions: alkoxyl radical precursor (0.15 mmol, 1.5 equiv), **6b** (0.1 mmol, 1.0 equiv), photocatalyst (0.002 mmol, 0.02 equiv), DMAP (0.2 mmol, 2.0 equiv), and nBu_4NCl (0.2 mmol, 2.0 equiv) in 1.0 mL of acetone under N_2 with 4 W blue LED irradiation at rt for 12 h, unless otherwise noted. [b]Conversions and yields were determined by ^1H NMR analysis, and isolated yields are in parentheses. [c]Conversion of **2** was >95%.

With 4-cyano-*N*-alkoxybenzimidoyl chloride as the alkoxyl radical precursor, we next tested the scope of the δ-C(sp^3)−H radical Heck-type reaction with different terminal alkenes (Scheme 2a). Diarylethylenes **7**−**9b** substituted with electron-deficient fluorides, chlorides, or bromides gave δ-alkenols **7**−**9** in 72−76% yields, whereas electron-rich diarylethylenes **10**−**12b** afforded **10**−**12** in slightly decreased 51−62% yields.[12] Unsymmetrical diarylethylenes **13**−**15b** gave δ-alkenols **13**−**15** in 70−89% yields as E/Z isomers, and heterocyclic thiophene was tolerated. Dibenzosuberane derivative **16b** afforded exocyclic alkene **16** in 42% yield. The reaction was easily scaled up to 3.5 mmol to obtain 1.12 g of **9** in an uncompromised 73% yield.

With terminal alkene α-alkyl styrenes **17**−**22b**, the δ-alkenylation switched to δ-allylation with exclusive ε-alkenol **17**−**22** formation in 40−56% yield (Scheme 2b), in which the ethylene glycols and free alcohol groups were well tolerated. The ε-alkenols **23**−**25** were readily obtained from exocyclic alkenes **23**−**25b** in 57−86% yields, where dihydronaphthalene, indene, and benzofuran adducts could not be easily synthesized by other methods. We next explored the *N*-alkoxybenzimidoyl chloride scopes for the δ-C(sp^3)−H radical Heck-type reaction (Scheme 3). The structurally diversified **26**−**30a** afforded δ-alkenols **26**−**30** with tertiary cyclohexyl, cyclopentyl, indanyl, or piperidyl substituents in 44−77% yields. Various aryl substituents on diarylethylenes were tolerated to provide secondary δ-alkenols **31**−**37** in 59−72% yields. When chemically equivalent δ- and ε-C(sp^3)−H bonds were both presented, the δ-alkenylation adducts **38**−**41** selectively resulted in 41−57% yields without ε-alkenylation.[13] The bystander terminal alkene and alkyne moiety were unaffected under the reaction conditions to afford **42** and **43** in 54−66% yield, which unsaturated functional groups were not tolerated in the transition-metal-catalyzed Heck reactions.[1b] Even when ε-C(sp^3)−H was activated by the adjacent heteroatoms or in the activated benzylic positions, δ-alkenylation adducts **44**−**46** were preferentially obtained in 48−58% yields with a greater than 20:1 δ/ε ratio. The primary δ-C(sp^3)−H in **47a** also reacted to give δ-alkenol **47** in a slightly decreased 46% yield. The secondary and tertiary δ-alkenols **48** and **49** could be synthesized in 56−60% yields without the alkoxyl radical β-fragmentation side products.

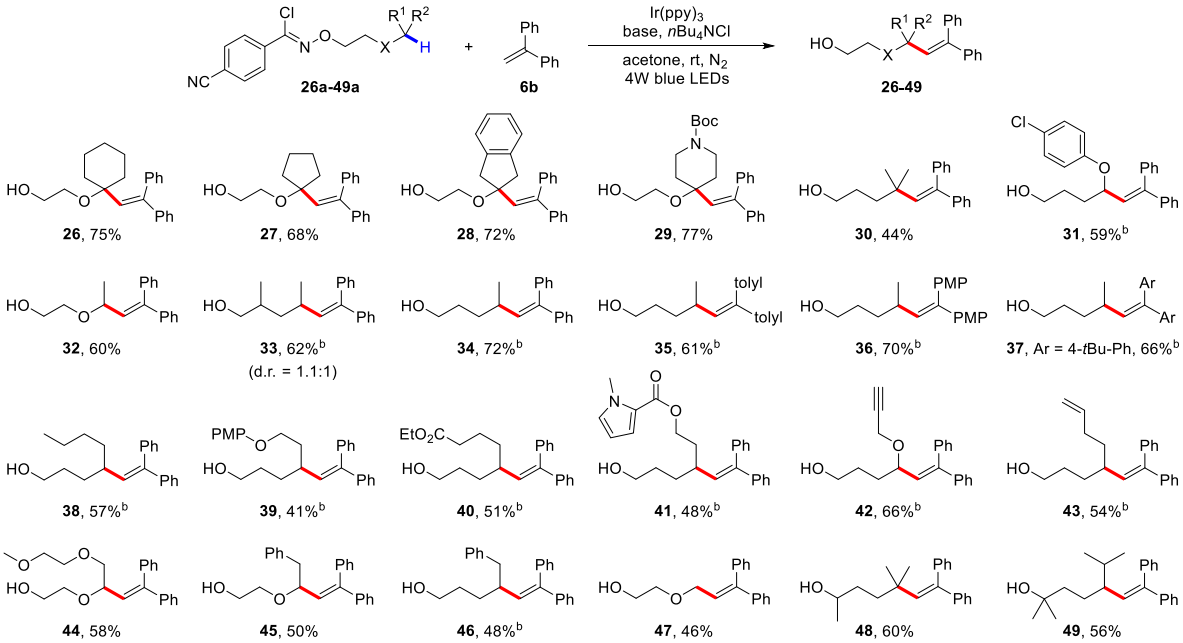
https://doi.org/10.1021/acs.orglett.2c00593
Org. Lett. 2022, 24, 2050−2054

Scheme 2. Substrate Scope of Terminal Alkenes[a]



[a]Reaction conditions: entry 2 in Table 1. Yields are those of isolated products. X = 4-cyano-*N*-alkoxybenzimidoyl chlorides.

Scheme 3. Substrate Scope of *N*-Alkoxybenzimidoyl Chlorides[a,b]



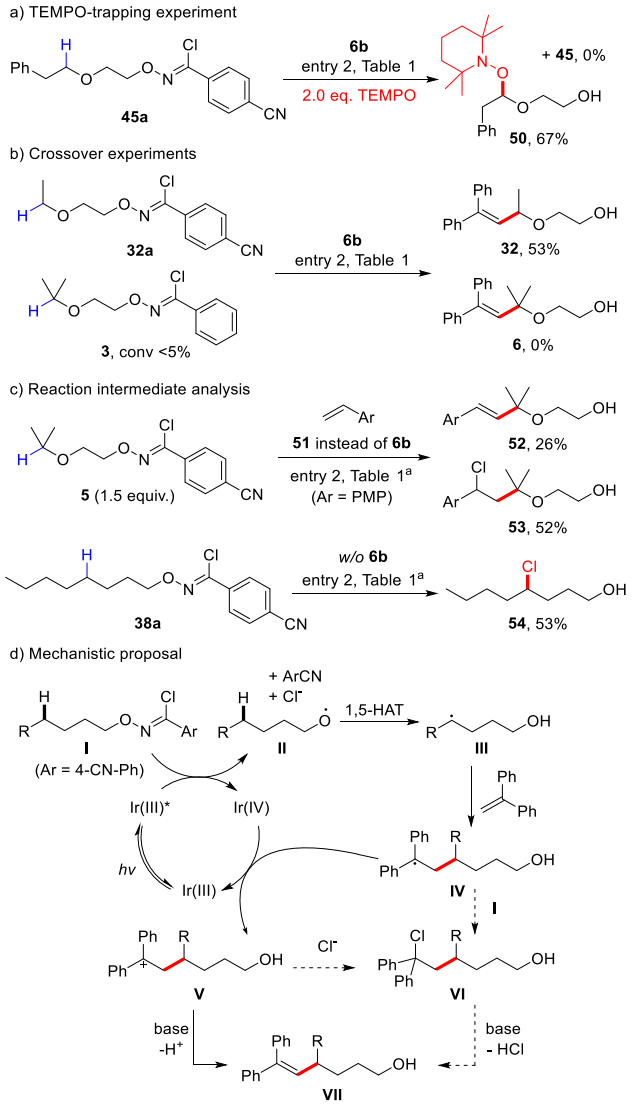
[a]Reaction conditions: entry 2 in Table 1. Yields are those of isolated products. [b]$NaHCO_3$ instead of DMAP.

We next carried out mechanistic investigations (Scheme 4). When (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was added to the reaction of **45a**, the δ-C(sp^3)-TEMPO addition adduct **50** was observed in 67% yield together with the inhibition of product **45** (Scheme 4a). The crossover experiment of **32a** with the unsubstituted *N*-alkoxybenzimidoyl chloride **3** provided **32** from **32a**, whereas *N*-alkoxybenzimidoyl chloride **3** was not converted to afford its δ-C(sp^3)−H Heck-type adduct (Scheme 4b). In addition, the crossover experiment of **32a** with the free alcohol of **3** also only provided **32** from **32a**, and free alcohol conversion was not observed. (See Scheme S2.) Together, these results suggested intramolecular 1,5-HAT rather than intermolecular HAT reactivity from the alkoxyl radical, which also explained the excellent δ/ε selectivity for alcohols. We further measured the fluorescence quenching of $Ir(ppy)_3$ (E^*_{Ox} = −1.73 V vs SCE) by *N*-alkoxybenzimidoyl chlorides (Figures S5 and S6). 4-Cyano-*N*-alkoxybenzimidoyl chloride **5** (E_p = −1.52 V vs SCE in MeCN) effectively quenched the excited $Ir(ppy)_3$, whereas unsubstituted **3** (E_p = −1.98 V vs SCE in MeCN) or 4-methoxy-*N*-alkoxybenzimidoyl chloride **4** (E_p = −2.33 V vs SCE in MeCN) gave no quenching. These results suggested the single-electron reduction of *N*-alkoxybenzimidoyl chlorides by the excited photocatalyst, where redox potentials could be tuned by aryl substituents.[11]

We then analyzed the side products to investigate the radical Heck-type reaction mechanism (Schemes S5 and S6). When styrene **51** was used as the alkene acceptor, δ-C(sp^3)−H Heck-type adduct **52** was observed in only 26% yield, whereas styrene carbochlorination adduct **53** was obtained in 52% yield (Scheme 4c). When the reaction time was extended, the conversion of **52** to **53** did not occur. These observations

https://doi.org/10.1021/acs.orglett.2c00593
Org. Lett. 2022, 24, 2050−2054

Scheme 4. Mechanistic Investigations and Proposal[a]



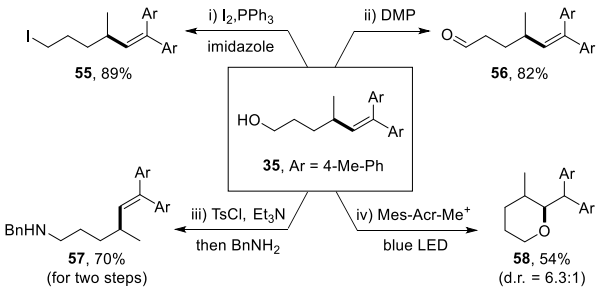
[a]$NaHCO_3$ was used as the base.

suggested that 1,2-diaryl alkenes and α-alkyl styrenes benefited the Heck-type product formation, which did not result from the hydrochloride elimination of the carbochlorination adduct. We next examined the reaction products from **38a** in the absence of diarylethylenes. The δ-C(sp^3)-chlorination adduct 4-chlorooctan-1-ol **54** was obtained in 53% yield, resulting from the chlorine abstraction of **38a** by the δ-alkyl radical. These results suggested the chain reaction of *N*-alkoxybenzimidoyl chlorides by the alkyl radical's chlorine abstraction; however, it was not the main reaction pathway in the presence of terminal alkenes due to the facile radical alkene additions.[14]

We propose the tentative reaction mechanism from the mechanistic investigations (Scheme 4d). The excited Ir(III)* from the light irradiation reduced 4-cyano-*N*-alkoxybenzimidoyl chloride **I** by single-electron transfer to generate the radical anion. The radical anion then intramolecularly fragmented to yield alkoxyl radical **II**, with 1,4-dicyanobenzene and chloride anion elimination as the driving force.[15] Alkoxyl radical **II** underwent 1,5-HAT to yield δ-alkyl (nonbenzylic) radical **III** followed by radical diarylethylene addition to afford benzyl radical **IV**. Benzyl radical **IV** was readily oxidized to carbocation **V** by Ir(IV) to terminate the reaction and turn over $Ir(ppy)_3$, yielding the δ-C(sp^3)−H Heck-type adduct **VII** facilitated by the base.

Various alkenols from the δ-C(sp^3)−H radical Heck-type reaction are readily derivatized to valuable bifunctional building blocks (Scheme 5). The alcohol moiety in δ-alkenol

Scheme 5. Product Derivatizations of δ-Alkenols



35 easily transformed to iodide **55** in 89% yield by the Appel reaction, and Dess−Martin oxidation afforded the unconjugated alkenal **56** in 82% yield. δ-Alkenol **35** transformed to δ-amino-alkene **57** in 70% yield in two synthetic steps. Under photoredox conditions, δ-alkenol **35** underwent 6-exo cyclization smoothly to produce tetrahydropyran **58** in 54% yield with a 6.3:1 d.r. ratio, widely presenting in many bioactive natural products.[16]

In conclusion, we have reported the first regioselective and chemoselective radical Heck-type reaction to synthesize various δ-alkenols and ϵ-alkenols from alkoxybenzimidoyl chlorides and styrenes. 4-Cyano-*N*-alkoxybenzimidoyl chlorides are developed for the first time to generate alkoxyl radicals under mild photoredox catalysis conditions, and the reaction mechanisms are investigated in detail. The tunable reactivity of this novel alkoxyl radical precursor may bring new opportunities for inert C−H and C−C bond functionalization, and further investigations are under way in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c00593.

Experimental procedures, reaction optimizations, detailed mechanistic investigations, new compound characterizations, and NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yiyun Chen − *State Key Laboratory of Bioorganic and Natural Products Chemistry, Centre of Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China; School of Chemistry and Material Sciences, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China; School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China;* orcid.org/0000-0003-0916-0994; Email: yiyunchen@sioc.ac.cn

https://doi.org/10.1021/acs.orglett.2c00593
Org. Lett. 2022, 24, 2050−2054

Authors

Di Fang − *State Key Laboratory of Bioorganic and Natural Products Chemistry, Centre of Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China*

Yidan Zhang − *State Key Laboratory of Bioorganic and Natural Products Chemistry, Centre of Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Shanghai 200032, China; School of Chemistry and Material Sciences, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.2c00593

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support was provided by the National Natural Science Foundation of China 91753126, 21622207, CAS Interdisciplinary Innovation Team JCTD-2020-16, Program of Shanghai Academic/Technology Research Leader 21XD1424700, and Strategic Priority Research Program of the Chinese Academy of Sciences XDB20020200.

■ REFERENCES

(1) (a) de Meijere, A.; Meyer, F. E. Fine Feathers Make Fine Birds: The Heck Reaction in Modern Garb. *Angew. Chem., Int. Ed. Engl.* **1995**, *33*, 2379−2411. (b) Beletskaya, I. P.; Cheprakov, A. V. The Heck reaction as a sharpening stone of palladium catalysis. *Chem. Rev.* **2000**, *100*, 3009−3066.

(2) Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. Advances in the Heck chemistry of aryl bromides and chlorides. *Tetrahedron* **2001**, *57*, 7449−7476.

(3) (a) Tang, S.; Liu, K.; Liu, C.; Lei, A. Olefinic C-H functionalization through radical alkenylation. *Chem. Soc. Rev.* **2015**, *44*, 1070−1082. (b) Kurandina, D.; Chuentragool, P.; Gevorgyan, V. Transition-Metal-Catalyzed Alkyl Heck-Type Reactions. *Synthesis* **2019**, *51*, 985−1005.

(4) (a) He, J.; Wasa, M.; Chan, K. S. L.; Shao, Q.; Yu, J. Q. Palladium-Catalyzed Transformations of Alkyl C-H Bonds. *Chem. Rev.* **2017**, *117*, 8754−8786. (b) Zhang, Q.; Shi, B. F. Site-selective functionalization of remote aliphatic C-H bonds via C-H metallation. *Chem. Sci.* **2021**, *12*, 841−852.

(5) (a) Tanaka, K.; Ewing, W. R.; Yu, J. Q. Hemilabile Benzyl Ether Enables γ-C(sp^3)-H Carbonylation and Olefination of Alcohols. *J. Am. Chem. Soc.* **2019**, *141*, 15494−15497. (b) Chuentragool, P.; Yadagiri, D.; Morita, T.; Sarkar, S.; Parasram, M.; Wang, Y.; Gevorgyan, V. Aliphatic Radical Relay Heck Reaction at Unactivated C(sp^3)-H Sites of Alcohols. *Angew. Chem., Int. Ed.* **2019**, *58*, 1794−1798.

(6) (a) Čeković, Ž. Reactions of carbon radicals generated by 1,5-transposition of reactive centers. *J. Serb. Chem. Soc.* **2005**, *70*, 287−318. (b) Chiba, S.; Chen, H. sp^3 C-H oxidation by remote H-radical shift with oxygen- and nitrogen-radicals: a recent update. *Org. Biomol. Chem.* **2014**, *12*, 4051−4060. (c) Salamone, M.; Bietti, M. Tuning reactivity and selectivity in hydrogen atom transfer from aliphatic C-H bonds to alkoxyl radicals: role of structural and medium effects. *Acc. Chem. Res.* **2015**, *48*, 2895−2903.

(7) (a) Francisco, C. G.; Freire, R.; Herrera, A. J.; Perez-Martin, I.; Suarez, E. Intramolecular 1,5- versus 1,6-hydrogen abstraction reaction promoted by alkoxy radicals in carbohydrate models. *Org. Lett.* **2002**, *4*, 1959−1961. (b) Zhu, H.; Wickenden, J. G.; Campbell, N. E.; Leung, J. C.; Johnson, K. M.; Sammis, G. M. Construction of carbo- and heterocycles using radical relay cyclizations initiated by alkoxy radicals. *Org. Lett.* **2009**, *11*, 2019−2022. (c) Guan, H.; Sun, S.; Mao, Y.; Chen, L.; Lu, R.; Huang, J.; Liu, L. Iron(II)-Catalyzed Site-Selective Functionalization of Unactivated C(sp^3)-H Bonds Guided by Alkoxyl Radicals. *Angew. Chem., Int. Ed.* **2018**, *57*, 11413−11417. (d) Zhu, Y.; Huang, K.; Pan, J.; Qiu, X.; Luo, X.; Qin, Q.; Wei, J.; Wen, X.; Zhang, L.; Jiao, N. Silver-catalyzed remote Csp^3-H functionalization of aliphatic alcohols. *Nat. Commun.* **2018**, *9*, 2625−2632.

(8) (a) Jia, K.; Chen, Y. Visible-light-induced alkoxyl radical generation for inert chemical bond cleavage/functionalization. *Chem. Commun.* **2018**, *54*, 6105−6112. (b) Wu, X.; Zhu, C. Recent advances in alkoxy radical-promoted C-C and C-H bond functionalization starting from free alcohols. *Chem. Commun.* **2019**, *55*, 9747−9756. (c) Tsui, E.; Wang, H.; Knowles, R. R. Catalytic generation of alkoxy radicals from unfunctionalized alcohols. *Chem. Sci.* **2020**, *11*, 11124−11141. (d) Guo, W.; Wang, Q.; Zhu, J. Visible light photoredox-catalysed remote C-H functionalisation enabled by 1,5-hydrogen atom transfer (1,5-HAT). *Chem. Soc. Rev.* **2021**, *50*, 7359−7377. (e) Chang, L.; An, Q.; Duan, L.; Feng, K.; Zuo, Z. Alkoxy Radicals See the Light: New Paradigms of Photochemical Synthesis. *Chem. Rev.* **2022**, *122*, 2429−2486. (f) Li, G. X.; Hu, X.; He, G.; Chen, G. Photoredox-mediated remote C(sp^3)-H heteroarylation of free alcohols. *Chem. Sci.* **2019**, *10*, 688−693.

(9) (a) Zhang, J.; Li, Y.; Zhang, F.; Hu, C.; Chen, Y. Generation of Alkoxyl Radicals by Photoredox Catalysis Enables Selective C(sp^3)-H Functionalization under Mild Reaction Conditions. *Angew. Chem., Int. Ed.* **2016**, *55*, 1872−1875. (b) Wang, C.; Harms, K.; Meggers, E. Catalytic Asymmetric Csp^3-H Functionalization under Photoredox Conditions by Radical Translocation and Stereocontrolled Alkene Addition. *Angew. Chem., Int. Ed.* **2016**, *55*, 13495−13498. (c) Kim, I.; Park, B.; Kang, G.; Kim, J.; Jung, H.; Lee, H.; Baik, M. H.; Hong, S. Visible-Light-Induced Pyridylation of Remote C(sp^3)-H Bonds by Radical Translocation of N-Alkoxypyridinium Salts. *Angew. Chem., Int. Ed.* **2018**, *57*, 15517−15522. (d) Bao, X.; Wang, Q.; Zhu, J. Remote C(sp^3)-H Arylation and Vinylation of N-Alkoxypyridinium Salts to δ-Aryl and δ-Vinyl Alcohols. *Chem. - Eur. J.* **2019**, *25*, 11630−11634.

(10) de Lijser, H. J.; Burke, C. R.; Rosenberg, J.; Hunter, J. Highly efficient formation of nitriles and alkoxy radicals from N-alkoxybenziminoyl chlorides in solution. *J. Org. Chem.* **2009**, *74*, 1679−1684.

(11) Zhang, J.; Li, Y.; Xu, R.; Chen, Y. Donor-Acceptor Complex Enables Alkoxyl Radical Generation for Metal-Free C(sp^3)-C(sp^3) Cleavage and Allylation/Alkenylation. *Angew. Chem., Int. Ed.* **2017**, *56*, 12619−12623.

(12) The products from electron-rich diarylethenes and **5** were unstable and prone to ethylene glycol elimination. (See the Supporting Information for details.)

(13) Dorigo, A. E.; Houk, K. N. Transition structures for intramolecular hydrogen-atom transfers: the energetic advantage of seven-membered over six-membered transition structures. *J. Am. Chem. Soc.* **1987**, *109*, 2195−2197.

(14) The quantum yield of the reaction was measured as 2.06, which suggested that the chain reaction may also exist (Figures S7 and S8).

(15) Zhang, W.; Zou, Z.; Wang, Y.; Wang, Y.; Liang, Y.; Wu, Z.; Zheng, Y.; Pan, Y. Leaving Group Assisted Strategy for Photoinduced Fluoroalkylations Using N-Hydroxybenzimidoyl Chloride Esters. *Angew. Chem., Int. Ed.* **2019**, *58*, 624−627.

(16) Hamilton, D. S.; Nicewicz, D. A. Direct catalytic anti-markovnikov hydroetherification of alkenols. *J. Am. Chem. Soc.* **2012**, *134*, 18577−18580.