# Photoinduced Fragmentation Borylation of Cyclic Alcohols and Hemiacetals

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**ABSTRACT:** A visible-light photoinduced fragmentation borylation of *O*-phthalimido cycloalkanols with bis(catecholato)diboron is described. Structurally diverse keto and formyloxy alkyl boronic esters are shown to be conveniently prepared by radical-mediated ring opening of cyclic alcohols and hemiacetals, respectively. The reactions proceed under mild conditions in the absence of additives or photocatalysts, display excellent functional group tolerance, and are shown to allow cleavage of 4-, 5-, 6-, and 7-membered ring substrates. The mechanism proceeds via sequential homolytic N–O and C–C bond cleavages, the latter of which involves  $\beta$ -scission of an alkoxy radical, generating a carbonyl and an alkyl radical that is trapped by the diboron reagent. Spectroscopic studies suggest direct photoexcitation of either the phthalimide or diboron substrates with blue light can initiate a radical chain mechanism.

arbon-carbon single bond cleavage reactions provide a powerful platform for diversification of organic molecules. These methods allow nontraditional and often dramatic structural changes, which can be beneficial for accessing new chemical space in the search for compounds with novel bioactivities.<sup>1</sup> This is particularly attractive in carbocyclic and heterocyclic ring systems, where fragmentation provides structures vastly different to those of the parent substrates. However, the inertness of C-C bonds makes this challenging, especially for heterolytic cleavage pathways, which typically require multiple activating groups,<sup>2</sup> strained ring systems,<sup>3</sup> or directing groups.<sup>4</sup> By contrast, homolytic C-C bond cleavage can allow fragmentation of nonactivated and unstrained cycloalkanes, for example, via  $\beta$ -scission of high energy heteroatom-centered radicals (Figure 1a).<sup>5</sup> Recent developments in visible-light photocatalysis have provided valuable methods to achieve such deconstructive functionalizations of cyclic alcohols<sup>6</sup> and oximes<sup>7</sup> under mild conditions.<sup>1b,8</sup>

We and others recently reported a range of radical-mediated borylation reactions that allow access to alkyl boronic esters by substitution of native functional groups, including carboxylic acids,<sup>9</sup> amines,<sup>10</sup> and alcohols.<sup>11</sup> While these are useful methods for transforming feedstock chemicals into highly

versatile organoboron compounds,<sup>12</sup> the nature of substitution reactions means they do not provide products of greater functional complexity than that of the substrate. We recognized the potential to expand on these radical borylations by taking advantage of homolytic C–C bond cleavage via  $\beta$ scission of alkoxy radicals derived from readily available cycloalkanols. In comparison to deoxygenative borylations,<sup>11</sup> such a process would benefit from providing boronic ester products that retain the oxygen functionality (Figure 1b).

In our previously reported radical borylations, we demonstrated that these reactions proceed under catalyst- and additive-free conditions by taking advantage of photoinduced electron-transfer (PET) reactions of electron donor–acceptor (EDA) complexes formed between the substrate and bis-(catecholato)diboron  $[B_2(cat)_2]$ .<sup>9a,10a,13</sup> Therefore, we rea-

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b) Divergent radical borylation pathways of activated cycloalkanols



Figure 1. Radical-mediated ring-opening functionalizations of cycloalkanes.

soned that O-activated cycloalkanols could form EDA complexes with  $B_2(cat)_2$  to initiate fragmentation borylations under similar conditions. Previous reports by the groups of Guo and Zuo demonstrated the feasibility of photoinduced fragmentation borylations of oxime esters,<sup>14</sup> including under catalyst-free conditions; however, they were limited to ring opening of strained cyclobutanes. To date, reports of fragmentation borylations of cycloalkanol derivatives have relied on the use of hazardous peroxide substrates under copper catalysis.<sup>15</sup> To access alkoxy radicals under photoinduced, catalyst-free conditions, we selected O-phthalimido cycloalkanols 1 as radical precursors (Figure 1c),  $\frac{1}{10}$  as these species are easily prepared and stable and we have previously shown that the phthalimide moiety forms complexes with  $B_2(cat)_2$ <sup>9a</sup> The use of these reagents as alkoxy radical precursors under visible-light photocatalysis was pioneered by the groups of Chen and Meggers in 2016, both of which involved 1,5-hydrogen atom transfer reactions and trapping of the resulting alkyl radicals with various alkenes.<sup>17</sup> Their application was subsequently extended to  $\beta$ -scission reactions.<sup>18</sup> Interestingly, all of these reports utilized the Ophthalimido substrates in overall reductive transformations that required superstoichiometric quantities of Hantzsch ester as the reductant. To the best of our knowledge, there are no reports of their use in redox neutral photoinduced alkoxy radical-mediated reactions, nor are there examples of trapping the intermediate alkyl radicals with heteroatom-based reagents. Herein, we report that O-phthalimido cycloalkanols and hemiacetals undergo photoinduced fragmentation borylations with  $B_2(cat)_2$  to provide acyclic keto and formyloxy alkyl boronic esters, without the need for catalysts or other additives.

We began our investigation by studying the reaction of *O*-phthalimido 1-methylcyclopentanol 1a with  $B_2(cat)_2$  (Table 1). Pleasingly, irradiation of an *N*,*N*-dimethylacetamide

#### Table 1. Optimization Studies<sup>a</sup>

	-	
	B <sub>2</sub> (cat) <sub>2</sub> (1.5 equiv) DMAc (0.05 M)	
Me	blue LEDs, N <sub>2</sub> , RT, 20 h	Me B(pin)
1a	<i>then</i> pinacol, Et <sub>3</sub> N, 1 h	2
entry	deviation from standard conditions	yield (%)
1	None	90
2	1.2 equiv of $B_2(cat)_2$	92
3	1.0 equiv of $B_2(cat)_2$	83
4	$B_2(pin)_2$ instead of $B_2(cat)_2$	0
5	$B_2(NMe_2)_2$ instead of $B_2(cat)_2$	0
6	$B_2(OH)_2$ instead of $B_2(cat)_2$	50
7	DMF as solvent	70
8	MeCN as solvent	38
9	EtOAc as solvent	45
10	THF as solvent	0
11	No light	19
12	Under air	0

<sup>*a*</sup>Reactions were performed on a 0.10 mmol scale and irradiated with a 40 W Kessil lamp. Yields were determined by <sup>1</sup>H NMR using diethyl phthalate as an internal standard.

(DMAc) solution of 1a and 1.5 equiv of  $B_2(cat)_2$  with blue LEDs at rt for 20 h yielded the desired  $\delta$ -keto boronic ester 2 in 90% yield (entry 1). To facilitate isolation of the boronic ester product, the initially formed catechol boronic ester was converted to the stable pinacol boronic ester by in situ transesterification with pinacol. The amount of  $B_2(cat)_2$  could be lowered to 1.2 equiv without reduction in efficiency (entries 2 and 3). The important role of the catechol ligand on the diboron reagent was highlighted through the unsuccessful reactions with bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) and  $B_2(NMe_2)_4$  (entries 4 and 5). Interestingly, a moderate yield of 2 could also be obtained using tetrahydroxydiboron  $[B_2(OH)_4]$  (entry 6). Evaluation of various solvents indicated that higher yields were achieved with more Lewis basic solvents, such as DMAc and DMF (entries 7-10). The use of Lewis basic solvents has been reported to promote EDA complex formation with  $B_2(cat)_{2y}^{10c}$  facilitate homolytic substitution of  $B_2(cat)_2$  by alkyl radicals, and stabilize chain propagating boryl radical intermediates.<sup>19</sup> A control reaction performed in the dark showed that an inefficient thermal reaction was also operative (entry 11), which is in agreement with previously reported decarboxylative and deaminative borylations with  $B_2(cat)_2$ .<sup>9a,10</sup> Finally, the reaction was found to be sensitive to oxygen, as no product formed if the reaction was run open to air (entry 12).

With the optimum conditions in hand, we first examined the scope of the fragmentation borylation of *O*-phthalimido cycloalkanols, which are easily prepared from readily available cyclic alcohols (Scheme 1).<sup>20</sup> A broad range of functionalized 1-alkyl cyclobutanols were efficiently borylated, providing acyclic  $\delta$ -keto boronic esters 3–25. The mild conditions tolerated aryl (13–17), heteroaryl (18–20), and alkyl carboxylate esters (21–25), as well as various useful synthetic handles, including alkyl tosylates (11), bromides (12, 23), and aryl halides (15, 16). Various cyclopentanols were also

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<sup>*a*</sup>Reactions were carried out on a 0.10–0.50 mmol scale. Yields are of isolated products after chromatographic purification. The regioisomeric ratios (r.r.) and diastereomer ratios (r.r.) were determined by <sup>1</sup>H NMR analysis of the purified product. <sup>*b*</sup>Yields in parentheses were obtained on a 3.5 mmol scale.

borylated in high yield (26-31), including those with additional substituents, which provided mixtures of regioisomers (28, 29). This ring-opening strategy was also successfully applied to bridged bicycles, which regioselectively generated the secondary boronic esters 30 and 31 in good yields. Pleasingly, the 5,5-fused bicyclic product 31 was formed with complete diastereoselectivity, which highlights the potential utility of this method in the stereoselective synthesis of complex molecular architectures. Interestingly, a secondary cyclopentanol provided the corresponding aldehyde 32, albeit in low yield. This example is notable given the lower thermodynamic driving force for fragmentation due to the formation of a weaker carbonyl bond, and also the known instability of aliphatic aldehydes in the presence of  $B_2(cat)_2$ . The borylation protocol was also suitable for ring opening of O-phthalimido cyclohexanols (33-36) and cycloheptanols (37), although lower yields were obtained compared to the more strained 4- and 5-membered ring substrates. The successful borylation of these larger ring substrates contrasts the reactivity previously observed by Wang and co-workers, who reported them to be inert to their Hantzsch estermediated fragmentation alkynylation and alkenylation conditions.<sup>18b</sup> Finally, the synthetic utility of this photoinduced fragmentation borylation reaction was demonstrated by synthesizing boronic ester 6 in high yield on a preparative

scale (3.5 mmol), and through successful derivatizations of the boronic ester group, including hydrolysis, fluorination, and arylation.<sup>20</sup>

The scope of the fragmentation borylation was then extended to O-phthalimido cyclic hemiacetals (Scheme 2a).<sup>18b</sup> Both tetrahydrofuran and tetrahydropyran derivatives were successfully borylated to provide  $\gamma$ - and  $\delta$ -formyloxy boronic esters, respectively, in moderate to good yields (38-46). Substitution adjacent to the oxygen of the cyclic ether was tolerated, including alkyl (39), aryl (40, 42), and protected alcohol groups (43-45). In addition, a glucal derivative was successfully borylated in good yield to provide the densely functionalized boronic ester 46, which bears three contiguous stereocenters and may serve as a versatile building block in synthetic chemistry. We also investigated a one-pot activation/ fragmentation borylation sequence to enable direct access to formyloxy boronic esters from cyclic enol ethers (Scheme 2b). Sequential treatment of 3,4-dihydro-2H-pyran in acetonitrile with N-hydroxyphthalimide and triphenylphosphine hydrobromide, followed by  $B_2(cat)_2$  and DMAc and subsequent blue-light irradiation, provided boronic ester 41 in 44% yield, which is comparable to that obtained from the isolated Ophthalimido substrate (51%, Scheme 2a).

The success of this fragmentation borylation reaction is intriguing given the potential alternative mechanistic pathways

B<sub>2</sub>(cat)<sub>2</sub> (1.2 equiv) DMAc (0.05 M) B(nin) blue LEDs, N<sub>2</sub>, RT, 20 h then pinacol, Et<sub>3</sub>N, 1 h 38-46 n = 1\_2 `n B(pin B(pin) B(pin) 38, 32% 39.44% 40, 34% B(pin) B(pin) B(pin) . Ph OBn **43**, 57% **42** 45% 41 51% ΟΜε B(pin) B(pin) B(pin) OMe 0= 0/ MeC `Me `Ph **44**, 65% 45, 68% **46**, 63% b) PPh3•HBr (10 mol%) MeCN, RT, 10 h B(pin) then B<sub>2</sub>(cat)<sub>2</sub>, DMAc blue LEDs, N<sub>2</sub>, RT, 20 h 1.0 equiv 1.2 equiv **41**, 44% then pinacol, Et<sub>3</sub>N, 1 h

## Scheme 2. Cyclic Hemiacetal Fragmentation Borylation<sup>a</sup>

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a) Potential competing reaction pathways

<sup>*a*</sup>Reactions were carried out on a 0.10–0.50 mmol scale. Yields are of isolated products after chromatographic purification.

of the postulated phthalimide radical anion intermediate 47 (Figure 2a). For formation of the desired alkoxy radical 48, homolytic cleavage of the N-O bond of the O-phthalimido group in 47 must occur. However, in the case of substrates derived from hemiacetals (X = O), prior work by the group of Sammis has shown that radical anions 47 undergo preferential intramolecular elimination to form carbonyls 49 and phthalimide radical anion 50.22 This pathway was also investigated by Chen,<sup>17a</sup> who concluded that protonation of radical anion 47, or coordination to tin, was required for successful alkoxy radical formation. As our fragmentation borylation reactions proceed under aprotic conditions, we postulate that a key boron-oxygen interaction prevents undesired elimination of 47, thus favoring alkoxy radical formation. Another competing pathway is the direct Oborylation of alkoxy radicals 48 to form borate esters 51, a process that has been widely exploited for the generation of alkyl radicals from catechol boronic esters.<sup>23</sup> As this process is facile, O-borylation becomes competitive if  $\beta$ -scission of 48 is slow. Indirect evidence for this was provided by the lower yields obtained when the reactions were performed at higher concentration,<sup>20</sup> and the observation of cycloalkanol side products formed after hydrolysis of borates 51 during workup.

Based on these observations, and additional competition experiments, spectroscopic studies, and quantum yield measurements,<sup>20</sup> we propose the mechanism shown in Figure 2b. Surprisingly, UV/vis analysis of DMAc solutions of 1a and  $B_2(cat)_2$  did not support the formation of an EDA complex. However, the absorbance spectra of both species extended to 450 nm; therefore, a radical chain process could be initiated by photoexcitation of either 1a or DMAc·B<sub>2</sub>(cat)<sub>2</sub> complex 52.<sup>9a</sup> This initiation generates the DMAc-stabilized boryl radical 53 and *O*-borylated phthalimide radical 54, both of which are chain propagating species. Subsequent homolytic N–O bond



Figure 2. Potential competing pathways and proposed mechanism.

cleavage of **54** and rapid  $\beta$ -scission of alkoxy radical **56** form the keto-substituted alkyl radical **57** and the phthalimide-B(cat) byproduct **55**. Borylation of **57** with B<sub>2</sub>(cat)<sub>2</sub> proceeds via a two-step process involving initial formation of radical complex **58**, with subsequent B–B bond cleavage facilitated by complexation with DMAc to form **59**.<sup>19</sup> This provides the boronic ester product **60** and DMAc-stabilized boryl radical **53**. Chain propagation to generate **54** could occur via SET and boron transfer,<sup>10c</sup> or via boryl radical addition to phthalimide **1a**, analogous to tin radical-mediated reactions of *N*alkoxyphthalimides.<sup>16</sup>

In conclusion, we have developed the first photoinduced catalyst- and additive-free C–C bond cleavage/borylation of O-activated cyclic alcohols and hemiacetals. This was achieved using readily available O-phthalimido cycloalkanols, which efficiently reacted with  $B_2(cat)_2$  in a photoinitiated radical chain mechanism. This borylation reaction benefits from providing distally difunctionalized products, wherein structural reorganization of cyclic alcohols enables retention of the oxygen functionality, therefore providing keto and formyloxy alkyl boronic esters. Given the mild conditions, and the ready availability of cyclic alcohols and hemiacetals from feedstock chemicals, this new radical borylation strategy could find wide application for the preparation of synthetically and biologically important boron-containing molecules.

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#### **Supporting Information**

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Experimental procedures and characterization data for new compounds (PDF)

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## Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) (a) Roque, J. B.; Kuroda, Y.; Göttemann, L. T.; Sarpong, R. Deconstructive diversification of cyclic amines. *Nature* 2018, 564, 244. (b) Morcillo, S. P. Radical-Promoted C-C Bond Cleavage: A Deconstructive Approach for Selective Functionalization. *Angew. Chem., Int. Ed.* 2019, 58, 14044.

(2) Drahl, M. A.; Manpadi, M.; Williams, L. J. C-C Fragmentation: Origins and Recent Applications. *Angew. Chem., Int. Ed.* **2013**, *52*, 11222.

(3) Fumagalli, G.; Stanton, S.; Bower, J. F. Recent Methodologies That Exploit C-C Single-Bond Cleavage of Strained Ring Systems by Transition Metal Complexes. *Chem. Rev.* **2017**, *117*, 9404.

(4) Dermenci, A.; Coe, J. W.; Dong, G. Direct Activation of Relatively Unstrained Carbon-Carbon Bonds in Homogeneous Systems. *Org. Chem. Front.* **2014**, *1*, 567.

(5) (a) Murakami, M.; Ishida, N.  $\beta$ -Scission of Alkoxy Radicals in Synthetic Transformations. *Chem. Lett.* **2017**, *46*, 1692. (b) Wu, X.; Zhu, C. Recent Advances in Radical-Mediated C–C Bond Fragmentation of Non-Strained Molecules. *Chin. J. Chem.* **2019**, *37*, 171. (c) Sivaguru, P.; Wang, Z.; Zanoni, G.; Bi, X. Cleavage of Carbon-Carbon Bonds by Radical Reactions. *Chem. Soc. Rev.* **2019**, *48*, 2615.

(6) (a) Yayla, H. G.; Wang, H.; Tarantino, K. T.; Orbe, H. S.; Knowles, R. R. Catalytic Ring-Opening of Cyclic Alcohols Enabled by PCET Activation of Strong O-H Bonds. J. Am. Chem. Soc. 2016, 138, 10794. (b) Guo, J.-J.; Hu, A.; Chen, Y.; Sun, J.; Tang, H.; Zuo, Z. Photocatalytic C-C Bond Cleavage and Amination of Cycloalkanols by Cerium(III) Chloride Complex. Angew. Chem., Int. Ed. 2016, 55, 15319. (c) Jia, K.; Zhang, F.; Huang, H.; Chen, Y. Visible-Light-Induced Alkoxyl Radical Generation Enables Selective C(sp<sup>3</sup>)-C(sp<sup>3</sup>) Bond Cleavage and Functionalizations. J. Am. Chem. Soc. 2016, 138, 1514. (d) Wang, D.; Mao, J.; Zhu, C. Visible Light-Promoted Ring-Opening Functionalization of Unstrained Cycloalkanols via Inert C-C Bond Scission. *Chem. Sci.* 2018, 9, 5805. (e) Wang, J.; Huang, B.; Shi, C.; Yang, C.; Xia, W. Visible-Light-Mediated Ring-Opening Strategy for the Regiospecific Allylation/Formylation of Cycloalkanols. *J. Org. Chem.* 2018, 83, 9696. (f) Hu, A.; Chen, Y.; Guo, J.-J.; Yu, N.; An, Q.; Zuo, Z. Cerium-Catalyzed Formal Cycloaddition of Cycloalkanols with Alkenes through Dual Photoexcitation. *J. Am. Chem. Soc.* 2018, 140, 13580. (g) Ota, E.; Wang, H.; Frye, N. L.; Knowles, R. R. A Redox Strategy for Light-Driven, Out-of-Equilibrium Isomerizations and Application to Catalytic C-C Bond Cleavage Reactions. *J. Am. Chem. Soc.* 2019, 141, 1457. (h) Chen, Y.; Du, J.; Zuo, Z. Selective C-C Bond Scission of Ketones via Visible-Light-Mediated Cerium Catalysis. *Chem.* 2020, 6, 266.

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(7) (a) Dauncey, E. M.; Morcillo, S. P.; Douglas, J. J.; Sheikh, N. S.; Leonori, D. Photoinduced Remote Functionalisations by Iminyl Radical Promoted C-C and C-H Bond Cleavage Cascades. Angew. Chem., Int. Ed. 2018, 57, 744. (b) Yu, X.-Y.; Chen, J.-R.; Wang, P.-Z.; Yang, M.-N.; Liang, D.; Xiao, W.-J. A Visible-Light-Driven Iminyl Radical-Mediated C-C Single Bond Cleavage/Radical Addition Cascade of Oxime Esters. Angew. Chem., Int. Ed. 2018, 57, 738. (c) Zhao, B.; Tan, H.; Chen, C.; Jiao, N.; Shi, Z. Photoinduced C-C Bond Cleavage and Oxidation of Cycloketoxime Esters. Chin. J. Chem. 2018, 36, 995. (d) Zhao, B.; Chen, C.; Lv, J.; Li, Z.; Yuan, Y.; Shi, Z. Photoinduced Fragmentation-Rearrangement Sequence of Cycloketoxime Esters. Org. Chem. Front. 2018, 5, 2719. (e) Dauncey, E. M.; Dighe, S. U.; Douglas, J. J.; Leonori, D. A Dual Photoredox-Nickel Strategy for Remote Functionalization via Iminyl Radicals: Radical Ring-Opening-Arylation, -Vinylation and -Alkylation Cascades. Chem. Sci. 2019, 10, 7728.

(8) (a) Guo, J.-J.; Hu, A.; Zuo, Z. Photocatalytic Alkoxy Radical-Mediated Transformations. *Tetrahedron Lett.* **2018**, *59*, 2103. (b) Jia, K.; Chen, Y. Visible-Light-Induced Alkoxyl Radical Generation for Inert Chemical Bond Cleavage/Functionalization. *Chem. Commun.* **2018**, *54*, 6105. (c) Yu, X.-Y.; Chen, J.-R.; Xiao, W.-J. Visible Light-Driven Radical-Mediated C-C Bond Cleavage/Functionalization in Organic Synthesis. *Chem. Rev.* **2020**, DOI: 10.1021/acs.chemrev.0c00030.

(9) (a) Fawcett, A.; Pradeilles, J.; Wang, Y.; Mutsuga, T.; Myers, E. L.; Aggarwal, V. K. Photoinduced Decarboxylative Borylation of Carboxylic Acids. *Science* 2017, 357, 283. (b) Li, C.; Wang, J.; Barton, L. M.; Yu, S.; Tian, M.; Peters, D. S.; Kumar, M.; Yu, A. W.; Johnson, K. A.; Chatterjee, A. K.; Yan, M.; Baran, P. S. Decarboxylative Borylation. *Science* 2017, 356, No. eaam7355. (c) Hu, D.; Wang, L.; Li, P. Decarboxylative Borylation of Aliphatic Esters under Visible-Light Photoredox Conditions. *Org. Lett.* 2017, *19*, 2770. (d) Wang, J.; Shang, M.; Lundberg, H.; Feu, K. S.; Hecker, S. J.; Qin, T.; Blackmond, D. G.; Baran, P. S. Cu-Catalyzed Decarboxylative Borylation. *ACS Catal.* 2018, *8*, 9537.

(10) (a) Wu, J.; He, L.; Noble, A.; Aggarwal, V. K. Photoinduced Deaminative Borylation of Alkylamines. J. Am. Chem. Soc. 2018, 140, 10700. (b) Hu, J.; Wang, G.; Li, S.; Shi, Z. Selective C-N Borylation of Alkyl Amines Promoted by Lewis Base. Angew. Chem., Int. Ed. 2018, 57, 15227. (c) Sandfort, F.; Strieth-Kalthoff, F.; Klauck, F. J. R.; James, M. J.; Glorius, F. Deaminative Borylation of Aliphatic Amines Enabled by Visible Light Excitation of An Electron Donor-Acceptor Complex. Chem. - Eur. J. 2018, 24, 17210.

(11) (a) Wu, J.; Bär, R. M.; Guo, L.; Noble, A.; Aggarwal, V. K. Photoinduced Deoxygenative Borylations of Aliphatic Alcohols. *Angew. Chem., Int. Ed.* **2019**, *58*, 18830. (b) Friese, F. W.; Studer, A. Deoxygenative Borylation of Secondary and Tertiary Alcohols. *Angew. Chem., Int. Ed.* **2019**, *58*, 9561. (c) Lu, X.; Zhang, Z.-Q.; Yu, L.; Zhang, B.; Wang, B.; Gong, T.-J.; Tian, C.-L.; Xiao, B.; Fu, Y. Free Radical Pathway Cleavage of C-O Bonds for the Synthesis of Alkylboron Compounds. *Chin. J. Chem.* **2019**, *37*, 11.

(12) Sandford, C.; Aggarwal, V. K. Stereospecific Functionalizations and Transformations of Secondary and Tertiary Boronic Esters. *Chem. Commun.* **2017**, *53*, 5481.

(13) Crisenza, G. E. M.; Mazzarella, D.; Melchiorre, P. Synthetic Methods Driven by the Photoactivity of Electron Donor-Acceptor Complexes. J. Am. Chem. Soc. 2020, 142, 5461.

(14) (a) Zhang, J.-J.; Duan, X.-H.; Wu, Y.; Yang, J.-C.; Guo, L.-N. Transition-Metal Free C-C Bond Cleavage/Borylation of Cycloketone Oxime Esters. *Chem. Sci.* **2019**, *10*, 161. (b) Anand, D.; He, Y.; Li, L.; Zhou, L. A Photocatalytic sp<sup>3</sup> C-S, C-Se and C-B Bond Formation Through C-C Bond Cleavage of Cycloketone Oxime Esters. *Org. Biomol. Chem.* **2019**, *17*, 533.

(15) (a) Seihara, T.; Sakurai, S.; Kato, T.; Sakamoto, R.; Maruoka, K. Synthesis of Functionalized Organoboron/Silicon Compounds by Copper-Catalyzed Coupling of Alkylsilyl Peroxides and Diboron/Silylborane Reagents. Org. Lett. 2019, 21, 2477. (b) Yang, J.-C.; Chen, L.; Yang, F.; Li, P.; Guo, L.-N. Copper-Catalyzed Borylation of Cycloalkylsilyl Peroxides via Radical C-C Bond Cleavage. Org. Chem. Front. 2019, 6, 2792.

(16) (a) Kim, S.; Lee, T. A.; Song, Y. Facile Generation of Alkoxy Radicals from N-Alkoxyphthalimides. Synlett 1998, 1998, 471.
(b) Martín, A.; Rodríguez, M. S.; Suárez, E. Synthesis of Alditols by Reductive Radical Fragmentation of N-Phthalimido Glycosides. Preparation of Chiral Synthetic Intermediates. Tetrahedron Lett. 1999, 40, 7525. (c) Zlotorzynska, M.; Zhai, H.; Sammis, G. M. Chemoselective Oxygen-Centered Radical Cyclizations Onto Silyl Enol Ethers. Org. Lett. 2008, 10, 5083. (d) Zhu, H.; Wickenden, J. G.; Campbell, N. E.; Leung, J. C. T.; Johnson, K. M.; Sammis, G. M. Construction of Carbo- and Heterocycles Using Radical Relay Cyclizations Initiated by Alkoxy Radicals. Org. Lett. 2009, 11, 2019.
(e) Zhu, H.; Leung, J. C. T.; Sammis, G. M. Strategies to Control Alkoxy Radical-Initiated Relay Cyclizations for the Synthesis of Oxygenated Tetrahydrofuran Motifs. J. Org. Chem. 2015, 80, 965.

(17) (a) Zhang, J.; Li, Y.; Zhang, F.; Hu, C.; Chen, Y. Generation of Alkoxyl Radicals by Photoredox Catalysis Enables Selective C(sp<sup>3</sup>)-H Functionalization under Mild Reaction Conditions. *Angew. Chem., Int. Ed.* **2016**, *55*, 1872. (b) Wang, C.; Harms, K.; Meggers, E. Catalytic Asymmetric C-H Functionalization Under Photoredox Conditions by Radical Translocation and Stereocontrolled Alkene Addition. *Angew. Chem., Int. Ed.* **2016**, *55*, 13495.

(18) (a) 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. (b) Shi, J.-L.; Wang, Z.; Zhang, R.; Wang, Y.; Wang, J. Visible-Light-Promoted Ring-Opening Alkynylation, Alkenylation, and Allylation of Cyclic Hemiacetals through  $\beta$ -Scission of Alkoxy Radicals. *Chem. - Eur. J.* **2019**, 25, 8992.

(19) Cheng, Y.; Mück-Lichtenfeld, C.; Studer, A. Transition Metal-Free 1,2-Carboboration of Unactivated Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 6221.

(20) See Supporting Information for details.

(21) Li, J.; Wang, H.; Qiu, Z.; Huang, C.-Y.; Li, C.-J. Metal-Free Direct Deoxygenative Borylation of Aldehydes and Ketones. J. Am. Chem. Soc. **2020**, 142, 13011.

(22) Zlotorzynska, M.; Sammis, G. M. Photoinduced Electron-Transfer-Promoted Redox Fragmentation of *N*-Alkoxyphthalimides. *Org. Lett.* **2011**, *13*, 6264.

(23) Schaffner, A.-P.; Renaud, P. B-Alkylcatecholborane-Mediated Radical Reactions. *Eur. J. Org. Chem.* 2004, 2004, 2291.