JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01662 • Publication Date (Web): 26 Sep 2018

Just Accepted

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Additive- and Photocatalyst-free Borylation of Arylazo Sulfones under Visible Light

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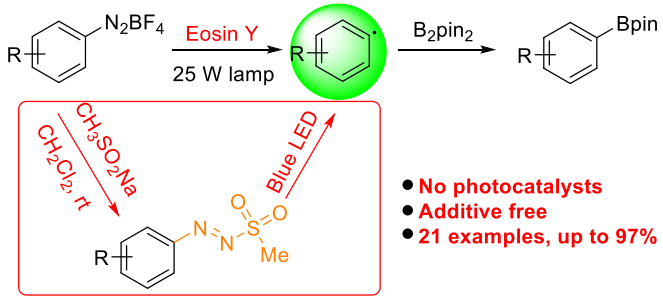


Abstract: We developed a photocatalyst-free and additive-free, visible light induced borylation reaction using arylazo sulfones as starting material. This protocol shows some advantage such as mild conditions, simple equipment, and wide substrate scope, which gives a complementary protocol for the preparation of arylboronates.

Aryl boronic acids and arylboronates are important building blocks in chemical, medicinal and material science areas.[1] Their preparation fall among one of the most active areas in the realm of organic synthesis. The classical method involves reactions of aryl Grignard or aryl lithium with trialkoxyboranes, followed by transesterification or hydrolysis. This methodology suffers from limited functional group tolerance and the requirement of anhydrous conditions.[2] Later on, a variety of transition metals such as palladium,[3] copper,[4] nickel,[5] and zinc[6] have been applied in transition metal-catalyzed borylation reactions. In order to reduce the costs and metal residue in the final medicinal products, more attention has been focused on the transition metal-free methods. Although Sandmeyer-type borylation of aryl amine and base-mediated borylation of aryl halides have been reported,[7] harsh conditions and longer reaction time are usually required.

Recently, several groups reported metal-free UV photoinduced borylation,[8] in which specialized equipment was required. Evidently, it is more convenient and practical to use visible-light and

regular glassware. Very recently, photocatalysis has opened up new avenues for the generation of radical species under visible-light-induced conditions.[9] This new paradigm has found numerous applications in synthetic chemistry including borylation reactions. For example, Yan reported visible light induced borylation of aryldiazonium salts (Figure 1, Path A).[10] Fu reported visible light photoredox borylation of aryl halides;[11] These reactions are convenient and efficient, however, they inevitably required expensive photocatalysts, ligands, additives or bases. Recently, Glorius disclosed the first example of transition metal-free, visible light induced decarboxylative borylation of aryl N-hydroxyphthalimide esters.[12] The starting material of the reaction is aryl carboxylic acids. Unlike carboxyl group, the NH_2 group is ortho-para directing group. We herein report a complementary visible-light-induced borylation method for arylamine derivatives and this method does not require expensive photocatalyst or ligand under mild condition. Our preliminary mechanistic studies support the free radical mechanism for the photoinduced borylation process. Based on Yan's research, we conjectured that the colored arylazo compounds prepared from colorless aryldiazonium salts could produce the aryl radicals under visible light. Arylazo sulfones are stable and easy to obtain from aryldiazonium salts. Inspired by Protti and Fagnoni's recent work of transition metal-free arylation of arylazo sulfones,[13] we present a catalyst and additive-free, visible-light-induced borylation reaction involving arylazo sulfones as aryl radical precursors (Figure 1).

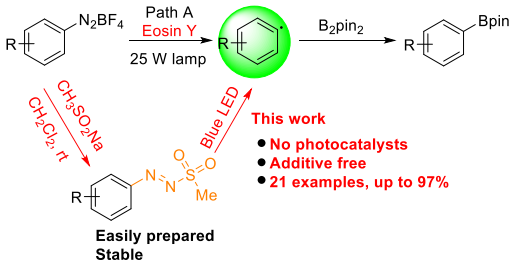
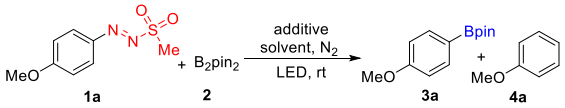


Figure 1. Outline of This Work

We started our investigation by using 4-methoxyphenylazo mesylate (**1a**) with bis(pinacolato)diboron (B_2pin_2) under visible-light induced condition (Table 1). A solution of **1a** and 1.5 equiv of B_2pin_2 in acetonitrile was placed in a Schlenk tube under N_2 atmosphere, and irradiated with a 30 W blue LED light without photocatalyst. To our delight, the desired arylboronate **3a** was observed in 81% yield as detected by ^1H NMR analysis of the crude reaction mixture (entry 1). Next, other solvents (methanol, DMF, THF, ethyl acetate and toluene) were screened, but no

improvement was observed (entry 2 to entry 6) compared with acetonitrile as solvent. Efforts to improve the yield then shifted to examine the additive effect. The use of $NaBF_4$ (entry 7), pyridine (entry 9) and *N,N,N',N'*-tetramethyldiaminomethane (TMDAM, entry 8) as additive provides much lower yield. Surprisingly, 10% water as cosolvent (entry 11) increased the yields to 86%, and the byproduct **4a** was not detected. When 2.0 equiv of B_2pin_2 was used, 97% yield was observed (entry 12). The yield of **3a** decreased when reaction was irradiated with CFL lamp (entry 13) or white LED light (entry 14). Control experiment was performed in the absence of light, the yield was much lower (17%, entry 15).

Table 1. Reaction Optimization[a]



1a 2 3a 4a

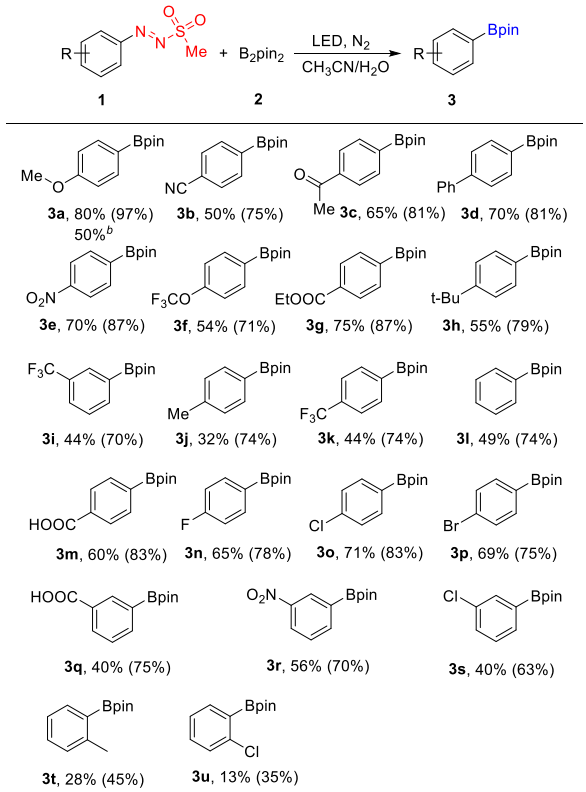
entry	2 (eq.)	solvent	addtive (eq.)	convn (%)	yield (%)[b] 3a	4a
1	1.5	CH_3CN	none	100	81	8
2	1.5	CH_3OH	none	100	79	10
3	1.5	DMF	none	100	19	19
4	1.5	THF	none	84	25	24
5	1.5	EtOAc	none	100	72	10
6	1.5	toluene	none	100	35	22
7	1.5	CH_3CN	$NaBF_4$ (1)	100	68	6
8	1.5	CH_3CN	TMDAM (1)	100	55	16
9	1.5	CH_3CN	Pyridine (1)	100	72	10
10	1.5	CH_3CN/H_2O (19/1)	none	100	82	n.d.
11	1.5	CH_3CN/H_2O (9/1)	none	100	86	n.d.
12	**2**	**CH_3CN/H_2O (9/1)**	**none**	**100**	**97**	**n.d.**
13[c]	2	CH_3CN/H_2O (9/1)	none	80	35	10
14[d]	2	CH_3CN/H_2O (9/1)	none	87	45	5
15[e]	2	CH_3CN/H_2O (9/1)	none	30	17	n.d.

[a]Reaction conditions: N_2 atmosphere and 30 W blue LED light irradiation, **1a** (0.1 mmol), B_2pin_2 (0.15-0.2 mmol), additive (0.5 mmol), solvent (1 mL), rt., 17 h in a Schlenk tube. [b]Determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard. [c]The reaction was carried out under 30 W CFL lamps. [d]The reaction was carried out under 30 W white LED light. [e]No light.

With the optimized condition in hand, we next examined substrate scope of this transformation (Scheme 1). A variety of arylazo sulfones can be used regardless of their electronic nature. Notably,

both electron-rich and electron-deficient arylazo sulfones could be tolerated. *para*-Substituted arylazo sulfones gave moderate to excellent yields. These new borylation conditions possessed excellent functional group compatibility, such as ether (**3a**), cyano (**3b**), ketone (**3c**), nitro (**3e**), carboxyl (**3m**), alkyl (**3h** and **3j**) and aryl (**3d**) groups. Chloro- (**3o**), bromo-(**3p**) and fluoro-(**3n**) groups were tolerated in the reaction, where those products were difficult to be prepared by the conventional transition metal-catalyzed borylation of arylhalides. *meta*-Substituted substrates produced borylation products in moderate yields (**3q**, **3r** and **3s**). However, *ortho*-substituted arylazo sulfones afforded lower yield (**3t** and **3u**) due to steric hindrance. Noteworthy, the arylazo sulfones can generate reactive intermediates under solar light,[14] we also investigated the borylation of arylazo sulfones under solar light. Sun light was convenient to induce the borylation of **1a** to obtain the **3a**, but the isolated yield was only 50%.

Scheme 1. Substrate Scope for Visible-Light Photoinduced Borylation of 1 with 2[a]

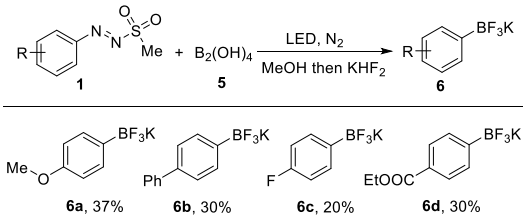


[a]Reaction conditions: N_2 atmosphere and 30 W blue LED light irradiation, **1** (0.5 mmol), **2** (1 mmol), solvent (5 mL), rt., 17 h in a Schlenk tube. Isolated yields and NMR yields are shown in parentheses. [b]The reaction was carried out under natural sunlight (17 h).

We further attempted reaction of arylazo sulfones with a more atom economical borylating

reagent bisboronic acid. By condition optimization, the change from the previous conditions was using MeOH as the solvent. Because of the inconvenience to isolate the arylboronic acid, aqueous KHF_2 was added to obtain the aryltrifluoroborate (Scheme 2). In this study, the yields were about 30% and the reaction was inferior to the borylation using B_2pin_2 as the borylating reagent. When bisboronic acid was as the borylating reagent, the conversion rate of arylazo sulfones was high, the unsatisfied yields may be due to the low reactivity between the bisboronic acid and aryl radical. Since ArBpin is the most widely used reagents for cross-coupling reactions, we did not further optimize the reaction for other borylating reagents such as bis(neopentanediolato)diboron and bis(catecholato)diboron.

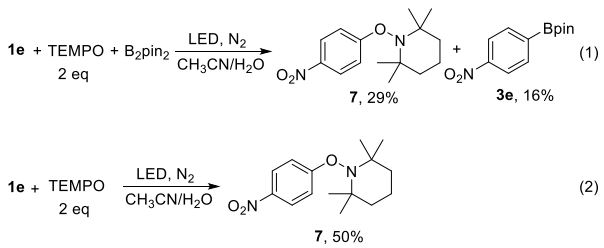
Scheme 2. Visible-Light Photoinduced Borylation with Bisboronic Acid[a].



[a]Reaction conditions: N_2 atmosphere and 30 W blue LED light irradiation, Arylazo Sulfone (1 mmol), bisboronic acid (2 mmol), MeOH (10 mL), rt, 17 h in a Schlenk tube, then KHF_2. Isolated yields.

We hypothesize that borylation of arylazo sulfones proceed though a radical mechanism. To gain insight into the reaction mechanism, radical trapping experiments were undertaken (Scheme 3). The addition of 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) to the reaction was observed to suppress the reaction (equation 1). The borylation product was obtained in only 16% yield together with the TEMPO adduct in 29% yield. On the other hand, TEMPO was added to the reaction mixture without B_2pin_2 and the aryl-TEMPO adduct was isolated in 50% yield (equation 2), which suggests the reaction involves a radical mechanism. Although the mechanism is not entirely clear, aryl radicals can be obtained via homolysis of N-S bond occurring from the $1n\pi^*$ state and loss of a N_2 molecule,[13] it is possible that the radical reacts with sp^2-sp^3 Lewis base-diboron adduct to produce the arylboronates.

Scheme 3. Preliminary Mechanistic Studies.



In conclusion, we developed a catalyst-free, visible-light photoinduced borylation reaction using arylazo sulfones at room temperature. As a substrate, arylazo sulfones with various functional groups can be prepared easily. Significantly, the reaction system is operationally simple without any photocatalyst or additive. This protocol shows advantages for the synthesis of arylboronates and represents an important approach to the reported C-B bond formation methods. We believe that this work will find wide applications in some fields. Further studies on the mechanism are under way in our laboratory.

EXPERIMENTAL SECTION

General experimental information:

Only if otherwise mentioned, all solvents and reagents were commercially available and utilized without any purification. Reactions were monitored by thin layer chromatography (TLC), and organic solutions were concentrated under reduced pressure on Eyela rotary evaporator. The products were obtained by column chromatography on silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). High-resolution mass spectra were recorded by TOF using the electrospray ionization (ESI) or electron impact ionization (EI) method.

General procedure for the synthesis of arylazo sulfones (1a~1u)[13]

Arylamine (10 mmol) as dissolved in a mixture of 5 mL of distilled water and 4 mL of 50% hydrofluoroboric acid. After cooling the reaction mixture to 0 °C using ice bath and the sodium nitrite (760 mg in 4 mL distilled water) was added dropwise in 5 min interval of time. The resulting mixture was stirred for 1h and the precipitate was collected by filtration and redissolved in minimum amount of acetone. Diethyl ether was added until precipitation of aryl diazonium tetrafluoroborate, which is filtered, washed several times with diethyl ether. To a cooled (0 °C) suspension of the

appropriate diazonium salt in CH_2Cl_2 was added sodium methanesulfinate (1.2 equiv) in one portion. The temperature was allowed to rise to room temperature and the solution stirred overnight. The resulting mixture was then filtered and the obtained solution evaporated. The crude product was was purified by dissolution in cold CH_2Cl_2 and precipitation by adding n-hexane.

1-(4-methoxyphenyl)-2-(methylsulfonyl)diazene (1a).[13] Yield: 53% (1.1 g). Yellow solid. Mp: 81-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 3.94 (s, 3H), 3.19 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.7, 143.2, 127.4, 115.0, 56.0, 34.9.

4-((methylsulfonyl)diazenyl)benzonitrile (1b).[13] Yield: 85% (1.8 g). Yellow solid. Mp: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H), 3.28 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.8, 133.8, 124.8, 118.1, 117.4, 35.0.

1-(4-((methylsulfonyl)diazenyl)phenyl)ethan-1-one (1c).[13] Yield: 44% (1.0 g). Yellow solid. Mp: 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.7 Hz, 2H), 8.03 (d, J = 8.7 Hz, 2H), 3.26 (s, 3H), 2.69 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.8, 151.2, 141.5, 129.7, 124.6, 34.9, 27.0.

1-([1,1'-biphenyl]-4-yl)-2-(methylsulfonyl)diazene (1d). Yield: 54% (1.0 g). Brown solid. Mp: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 7.1 Hz, 2H), 7.48 (m, 3H), 3.24 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.2, 148.1, 139.1, 129.2, 129.0, 128.3, 127.4, 125.3, 34.9. HRMS (EI) m/z: Calcd for $C_{13}H_{12}N_2O_2S$ [M^+]: 260.0619, Found: 260.0612.

1-(methylsulfonyl)-2-(4-nitrophenyl)diazene (1e).[15] Yield: 48% (1.2 g). Orange solid. Mp: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 9.0 Hz, 2H), 8.12 (d, J = 9.0 Hz, 2H), 3.29 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.9, 151.1, 125.2, 35.0.

1-(methylsulfonyl)-2-(4-(trifluoromethoxy)phenyl)diazene (1f). Yield: 18.6% (500 mg). Yellow solid. Mp: 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 3.24 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.0, 146.8, 126.5, 121.3, 120.2 (q, J = 260.0 Hz), 34.9. HRMS (EI) m/z: Calcd for $C_8H_7F_3N_2O_3S$ [M^+]: 268.0129, Found: 268.0132.

Ethyl 4-((methylsulfonyl)diazenyl)benzoate (1g). Yield: 55% (1.4 g). Yellow solid. Mp: 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 3.25 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.2, 151.2, 135.9, 131.0, 124.3, 61.9, 34.9, 14.3. HRMS (ESI) m/z: Calcd for $C_{10}H_{13}N_2O_4S$ [M+H]$^+$: 257.0591,

Found: 257.0595.

1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)diazene (1h).[13] Yield: 56% (1.3 g). Yellow solid. Mp: 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H), 3.21 (s, 3H), 1.38 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.9, 147.0, 126.7, 124.6, 35.6, 34.8, 31.0.

1-(methylsulfonyl)-2-(3-(trifluoromethyl)phenyl)diazene (1i). Yield: 56% (1.4 g). Yellow solid. Mp: 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.76 (t, J = 7.9 Hz, 1H), 3.27 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.0, 132.6 (q, J = 33.7 Hz), 131.3 (q, J = 3.5 Hz), 130.6, 127.2, 123.2 (q, J = 272.7 Hz), 121.7 (q, J = 3.8 Hz), 35.0. HRMS (EI) m/z: Calcd for $C_8H_7F_3N_2O_2S$ [M^+]: 252.0180, Found: 252.0175.

1-(methylsulfonyl)-2-(p-tolyl)diazene (1j).[15] Yield: 36% (715 mg). Orange solid. Mp: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 3.21 (s, 3H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.2, 147.0, 130.4, 124.8, 34.8, 22.0.

1-(methylsulfonyl)-2-(4-(trifluoromethyl)phenyl)diazene (1k). Yield: 44% (1.2 g). Yellow solid. Mp: 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 3.27 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.7, 136.0 (q, J = 33.1 Hz), 127.0 (q, J = 3.7 Hz), 124.7, 123.2 (q, J = 273.0 Hz), 34.9. HRMS (EI) m/z: Calcd for $C_8H_7F_3N_2O_2S$ [M^+]: 252.0180, Found: 252.0178.

1-(methylsulfonyl)-2-phenyldiazene (1l).[13] Yield: 65% (1.2 g). Orange solid. Mp: 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 3.23 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.0, 135.3, 129.8, 124.6, 34.8.

4-((methylsulfonyl)diazenyl)benzoic acid (1m). Yield: 66% (1.5 g). Yellow solid. Mp: 133-134 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.58 (s, 1H), 8.21 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H), 3.49 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ 166.7, 151.3, 131.5, 124.6, 35.3. HRMS (ESI) m/z: Calcd for $C_8H_7N_2O_4S$ [M-H]$^-$: 227.0132, Found: 227.0131.

4-((methylsulfonyl)diazenyl)benzoic acid (1n). Yield: 69% (1.4 g). Yellow solid. Mp: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.28 (dd, J = 11.7, 5.2 Hz, 2H), 3.23 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9 (d, J = 259.4 Hz), 145.6 (d, J = 2.9 Hz), 127.3 (d, J = 9.9 Hz), 117.1 (d, J = 23.3 Hz), 34.9. HRMS (EI) m/z: Calcd for $C_6H_4N_2F$ [M-CH_3SO_2]$^+$: 123.0359, Found: 123.0361.

1-(4-chlorophenyl)-2-(methylsulfonyl)diazene (1o).[13] Yield: 50% (1.3 g). Yellow solid. Mp: 61-

63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 3.23 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.4, 141.8, 130.2, 125.8, 34.9.

1-(4-bromophenyl)-2-(methylsulfonyl)diazene (1p).[15] Yield: 56% (1.7 g). Yellow solid. Mp: 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 3.23 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.7, 133.2, 130.6, 125.9, 34.9.

3-((methylsulfonyl)diazenyl)benzoic acid (1q). Yield: 22% (500 mg). Yellow solid. Mp: 121-123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.41 (d, J = 7.7 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 7.9 Hz, 1H), 3.27 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.5, 149.1, 135.9, 133.2, 131.3, 128.4, 124.8, 35.3. HRMS (ESI) m/z: Calcd for $C_8H_7N_2O_4S$ $[M-H]^-$: 227.0132, Found: 227.0133.

1-(methylsulfonyl)-2-(3-nitrophenyl)diazene (1r). [15] Yield: 57% (1.3 g). Yellow solid. Mp: 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (t, J = 1.9 Hz, 1H), 8.54 (dd, J = 8.2, 1.2 Hz, 1H), 8.32 (t, J = 12.5 Hz, 1H), 7.84 (t, J = 8.1 Hz, 1H), 3.30 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.3, 149.1, 130.9, 129.5, 128.8, 119.5, 35.1.

1-(3-chlorophenyl)-2-(methylsulfonyl)diazene (1s). Yield: 64% (1.4 g). Yellow solid. Mp: 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.64 (dd, J = 8.0, 0.7 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 3.24 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.7, 135.9, 134.9, 130.8, 123.7, 123.6, 34.9. HRMS (EI) m/z: Calcd for $C_6H_4N_2Cl$ $[M-CH_3SO_2]^+$: 139.0063, Found: 139.0068.

1-(methylsulfonyl)-2-(o-tolyl)diazene (1t). Yield: 71% (1.4 g). Yellow solid. Mp: 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 3.20 (s, 3H), 2.67 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.1, 141.7, 135.5, 132.1, 127.0, 116.5, 34.8, 17.6. HRMS (EI) m/z: Calcd for $C_8H_{10}N_2O_2S$ $[M^+]$: 198.0463, Found: 198.0461.

1-(2-chlorophenyl)-2-(methylsulfonyl)diazene (1u).[16] Yield: 64% (1.4 g). Yellow solid. Mp: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 8.2, 1.2 Hz, 1H), 7.62 (m, 2H), 7.45 – 7.38 (m, 1H), 3.24 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.0, 138.5, 136.1, 131.5, 127.8, 118.1, 34.7.

General procedure for the preparation of arylboronic esters (3a~3u)

B_2pin_2 (1 mmol), Arylazo Sulfones (0.5 mmol) were added to a Schlenk tube which was purged

thoroughly with N_2. MeCN (4.5 mL) and water (0.5 ml) ware added via syringe and and the reaction mixture was stirred at room temperature with the irradiation of a 30 W blue LED or natural sunlight for about 17 h. The solution was then concentrated under reduced pressure, diluted with EtOAc and washed with water. The aqueous layer was washed with EtOAc, the combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography.

General Procedure for the Preparation of trifluoroborates (6a~6d)

$B_2(OH)_4$ (2 mmol), Arylazo Sulfones (1 mmol) were added to a Schlenk tube which was purged thoroughly with N_2. MeOH (10 mL) was added via syringe and the reaction mixture was stirred at room temperature with the irradiation of a 30 W blue LED for about 17 h. The solution was then concentrated under reduced pressure. The concentrated crude reaction was taken up in MeOH (15 mL) and cooled to 0 ºC, to this cooled mixture was added 3.5 equivalents of a 4.5 M aqueous KHF_2 solution, and the reaction was stirred for 10 min at 0 ºC before removing the bath and allowing the mixture to stir at rt for 20 min. he mixture was concentrated under reduced pressure. Acetone (50 mL) was added into the flask and the solution was passed through Celite pad. The collected solvent was concentrated and then dissolved in a minimal volume of acetone (3 mL). The addition of Et_2O (25 mL) led to the precipitation of the desired product. The collected solid was washed with Et_2O.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a).[8b] R_f=0.5 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 80% (94 mg). A 50% (58 mg) yield was obtained under natural sunlight. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.2, 136.5, 113.3, 83.6, 55.1, 24.9.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (3b).[8b] R_f=0.5 (petroleum ether/ethyl acetate=5/1). Eluent: petroleum ether/ethyl acetate=100/1. Yield: 58% (66 mg). Pale yellow solid. Mp: 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 1.35 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 135.1, 131.2, 118.9, 114.5, 84.5, 24.9.

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (3c).[8b] R_f=0.3 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=100/1. Yield: 65% (80 mg). White solid. Mp: 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.9 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 2.62 (s, 3H), 1.36 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.5, 139.0, 134.9, 127.3,

84.2, 26.8, 24.9.

2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d).[8b] R_f=0.5 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 70% (100 mg). Mahogany solid. Mp: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.4 Hz, 2H), 7.65 – 7.58 (m, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 1.36 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.9, 141.0, 135.3, 128.8, 127.6 127.3, 126.5, 83.9, 24.9.

4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (3e).[7a] R_f=0.4 (petroleum ether/ethyl acetate=5/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 70% (87 mg). Mahogany solid. Mp: 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 1.37 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.8, 135.7, 122.4, 84.6, 24.9.

4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (3f).[7h] R_f=0.6 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 54% (78 mg). Yellow solid. Mp: 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 1.34 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.7, 136.5, 120.4 (q, J = 257.4 Hz), 119.9, 84.1, 24.9.

Ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3g).[8b] R_f=0.4 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 75% (103 mg). Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.36 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 134.6, 132.7, 128.6, 84.2, 61.1, 24.9, 14.3.

2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h).[7h] R_f=0.6 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 55% (72 mg). Pale yellow solid. Mp: 58-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 1.33 (d, 21H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.5, 134.7, 124.7, 83.6, 34.9, 31.2, 24.9.

4,4,5,5-tetramethyl-2-(3-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3i).[7a] R_f=0.7 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 44% (60 mg). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 1.36 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.0 , 131.4 (q, J = 3.7 Hz), 130.0 (q, J = 32.0 Hz), 128.0, 127.8 (q, J = 3.7 Hz), 124.3 (q, J = 272.4 Hz), 84.3, 24.9.

4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (3j).[8b] R_f=0.6 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether /ethyl acetate=200/1. Yield: 32% (35 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.4, 134.8, 128.5, 83.6, 24.9, 21.8.

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3k).[8b] R_f=0.7 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 44% (60 mg). Yellow solid. Mp: 69-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 7.9 Hz, 2H), 1.36 (s, 12H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 134.0, 131.8 (q, J = 32.0 Hz), 123.3 (q, J = 3.8 Hz), 123.1 (q, J = 272.5 Hz), 83.2, 23.8.

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3l).[8b] R_f=0.5 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 49% (50 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.3 Hz, 2H), 1.35 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 134.8, 131.3, 127.7, 83.8, 24.9.

4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3m).[7c] R_f=0.7 (ethyl acetat). Eluent: petroleum ether/ethyl acetate=20/1). Yield: 60% (75 mg). White solid. Mp: 230-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 1.37 (s, 12H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.9, 134.8, 131.4, 129.2, 84.3, 24.9.

2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n).[8b] R_f=0.6 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 65% (72 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.4, 6.3 Hz, 2H), 7.05 (t, J = 8.9 Hz, 2H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.1 (d, J = 250.4 Hz), 136.0 (d, J = 8.2 Hz), 113.8 (d, J = 20.2 Hz), 82.9, 23.8.

2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o).[8b] R_f=0.6 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 71% (85 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz,2H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.5, 136.1, 128.0, 84.0, 24.9.

2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p).[7a] R_f=0.6 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 69% (98 mg). White solid. Mp: 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 1.34 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 136.3, 131.0, 126.2, 84.1, 24.9.

2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q).[8b] R_f=0.5 (petroleum ether/ethyl acetate=2/1). Eluent: petroleum ether/ethyl acetate=30/1. Yield: 40% (49 mg). White solid. Mp: 209-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.05 (d, J = 7.3 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 1.37 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.1, 140.0, 136.6, 132.9, 128.8, 127.9, 84.2, 24.9.

2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r).[7a] R_f=0.7 (petroleum ether/ethyl acetate=5/1). Eluent: petroleum ether/ethyl acetate=120/1. Yield: 56% (70 mg). Yellow solid. Mp: 40-41 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 1.3 Hz, 1H), 8.30 (dd, J = 8.2, 1.2 Hz, 1H), 8.10 (d, J = 7.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 1.37 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.9, 140.7, 129.4, 128.8, 125.9, 84.6, 24.9.

2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s).[7a] R_f=0.8 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 40% (48 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 1.3 Hz, 1H), 8.30 (dd, J = 8.2, 1.2 Hz, 1H), 8.10 (d, J = 7.3 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 1.37 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.6, 134.1, 132.7, 131.3, 129.2, 84.2, 24.9.

4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (3t).[8b] R_f=0.7 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 27% (3o mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.0 Hz, 1H), 7.40 – 7.29 (m, 1H), 7.20 – 7.14 (m, 2H), 2.55 (s, 3H), 1.36 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.9, 135.9, 130.8, 129.8, 124.7, 83.4, 24.9, 22.3.

4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (3u).[11] R_f=0.7 (petroleum ether/ethyl acetate=20/1). Eluent: petroleum ether/ethyl acetate=200/1. Yield: 27% (30 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.1 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.25 – 7.20 (m, 1H), 1.37 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.6, 136.4, 131.9, 129.4, 125.8, 84.2, 24.8.

Potassium (4-methoxyphenyl)trifluoroborate (6a).[8b] Yield: 37% (80 mg). White solid. Mp: 240-242 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.21 (d, J = 8.1 Hz, 2H), 6.65 (d, J = 8.0 Hz, 2H), 3.66 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 157.6, 132.7, 112.3, 55.0.

Potassium (4-biphenyl)trifluoroborate (6b).[17] Yield: 31% (80 mg). White solid. Mp: > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (d, J = 7.4 Hz, 2H), 7.48 – 7.35 (m, 6H), 7.29 (t, J = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 141.9, 137.3, 132.4, 129.2, 127.0, 126.8, 125.1.

Potassium (4-fluorophenyl)trifluoroborate (6c).[8b] Yield: 20% (40 mg). White solid. Mp: > 250 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31 (t, J = 7.4 Hz, 2H), 6.87 (t, J = 9.0 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 161.4 (d, J = 238.4 Hz), 133.3 (d, J = 6.6 Hz), 113.1 (d, J = 18.4 Hz).

Potassium (4-fluorophenyl)trifluoroborate (6d).[8b] Yield: 31% (80 mg). White solid. Mp: 184-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, J = 7.7 Hz, 2H), 7.45 (d, J = 7.9 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 167.1, 131.9, 127.6, 127.1, 60.5, 14.7.

Radical capturing experiments

(1) B_2pin_2 (1 mmol), 4-nitrophenylazo mesylate (0.5 mmol) and 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) (1 mmol) were added to a Schlenk tube which was purged thoroughly with N_2. MeCN (4.5 mL) and water (0.5 ml) ware added via syringe and and the reaction mixture was stirred at room temperature with the irradiation of a 30 W blue LED for about 17 h. The solution was then concentrated under reduced pressure, diluted with EtOAc and washed with water. The aqueous layer was washed with EtOAc, the combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography, yielding compound **7** (40 mg, 29%), compound **3e** (20 mg 16%).

(2) 4-nitrophenylazo mesylate (0.5 mmol) and 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) (1 mmol) were added to a Schlenk tube which was purged thoroughly with N_2. MeCN (4.5 mL) and water (0.5 ml) ware added via syringe and and the reaction mixture was stirred at room temperature with the irradiation of a 30 W blue LED for about 17 h. The solution was then concentrated under reduced pressure, diluted with EtOAc and washed with water. The aqueous layer was washed with EtOAc, the combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography, yielding compound **7** (70 mg, 50%).

2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine (7).[18] White solid. Mp: 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 9.4 Hz, 2H), 7.26 (br, 2H), 1.66 – 1.58 (m, 5H), 1.49 – 1.40 (m, 1H), 1.25 (s, 6H), 0.99 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 168.7, 141.1, 125.6, 114.2, 60.9, 39.7, 32.3, 20.5, 16.9.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Photograph of the reaction setup, study of key reaction parameters and NMR spectra (PDF)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We are very grateful to Professor Xiaoxun Li at School of Pharmacy, Shandong University, for providing valuable suggestions. This work was supported by National Natural Science Foundation of China (Grant No. 21672127), Key Research and Development Project of Shandong Province (Grant No. 2017CXGC1401) and the Fundamental Research Funds of Shandong University (Grant No. 2016JC018).

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