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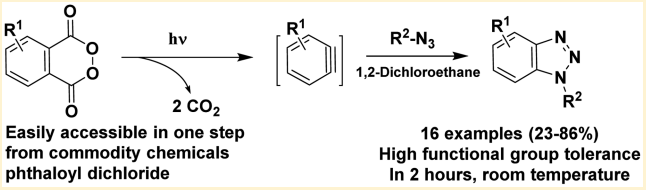
[3 + 2] Cycloadditions of Azides with Arynes via Photolysis of Phthaloyl Peroxide Derivatives

Denghu Chang, Dan Zhu, and Lei Shi*

Institute of Organic Chemistry, The Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150080, China

Supporting Information

ABSTRACT: Photolysis of phthaloyl peroxides yields arynes, which undergo [3 + 2] cycloadditions with azides. This reaction tolerates a variety of organic azides and phthaloyl peroxides and affords the corresponding benzotriazoles in moderate to good yields at room temperature.



1,3-Dipolar cycloadditions (Huisgen reactions) of arynes **2** with azides have long been known to provide an efficient access to benzotriazoles.[1] Notably, organic azides are an easily handled class of 1,3-dipoles as they neither dimerize nor easily hydrolyze as many other 1,3-dipoles. In fact, they are easily introduced into molecules and generally considered stable under acidic, basic, and even most oxidative and many reductive conditions. Kobayashi's discovery that arynes can easily be prepared by fluoride-induced 1,2-elimination of *o*-(trimethylsilyl)aryl triflates **1**[2] has triggered a renaissance of aryne chemistry,[3] and Larock and others have demonstrated that this method can also be used for the formation of benzotriazoles via 1,3-dipolar cycloaddition with azides (top, Scheme 1).[4] Novák and co-workers have disclosed the first use of more stable imidazolylsulfonates as a triflate alternative in the 1,3-dipolar cycloaddition of arynes **2** with azides (middle, Scheme 1).[5] More recently, Schnarr and co-workers have reported that the photochemical generation of arynes provides some advantages over the fluoride-induced generation and synthesized 10 different substituted benzotriazoles by irradiation of triazene **5** in the presence of azides (bottom, Scheme 1).[6] However, the starting material **5** had to be synthesized in a four-step synthesis from commercially available *ortho*-aminobenzyl alcohol.

We now report that even better results can be achieved when phthaloyl peroxide **6**, easily accessible in one step from the commodity chemicals phthaloyl dichloride **7** and sodium percarbonate, is irradiated in the presence of azides. While thermolysis of phthaloyl peroxide **6** in the presence of arenes and alkenes has been reported to give hydroxylation[7] and dihydroxylation products,[8] respectively, via the dicarbonyl radical **8**, photolysis of **6** was found to lead to bisdecarboxylation with formation of benzyne, which underwent [2 + 2] and [2 + 4] cycloadditions with alkenes and 1,3-dienes, respectively[9] (Scheme 2). In the following, we report that one can also obtain [3 + 2] cycloadducts of benzyne in moderate to good yields when **6** is photolyzed in the presence of organic azides.

The photochemical reaction of benzyl azide (0.3 mmol) with phthaloyl peroxide (PPO, 1.2 equiv) was employed to optimize the procedure. Several common solvents[10] were initially screened, and 1,2-dichloroethane (DCE) was found to be the optimal solvent, providing 20% of the desired product at a concentration of 0.03 M at room temperature (Table 1, entry 1). Decreasing the concentration of benzyl azide to 0.0067 M could improve its conversion, leading to the isolation of benzotriazole in 30% yield (Table 1, entry 2). A slight decrease in yield from 30 to 26% was observed when the reaction time was further prolonged from 2 to 8 h (Table 1, entry 3). Notably, the key to achieve higher yields was the use of excess phthaloyl peroxide. When the quantity of phthaloyl peroxide was increased from 1.2 to 5 equiv, the yield was improved from 30 to 81% (after purification by column chromatography, Table 1, entries 2 and 4−7). More than 5 equiv of phthaloyl peroxide seemed to be unnecessary (Table 1, entry 8), and the reaction time of 2 h and the addition of phthaloyl peroxide in one portion are appropriate (Table 1, entries 9 and 10). The presence of additives such as benzophenone and benzil exhibited a deleterious effect (Table 1, entries 11 and 12). As expected, irradiation of the phthalic anhydride instead of phthaloyl peroxide did not provide the corresponding [3 + 2] cycloaddition (Table 1, entry 13). As a consequence, the reaction conditions described in entry 7 were chosen for all subsequent work as the standard.

The scope of this method is illustrated in Scheme 3. Moderate to good yields were obtained with a variety of alkyl or aryl azides; benzyl (**10a**), carbonyl (**10b**, **10c**, **10d**, **10h**, and **10i**), aryl (**10e**, **10f**), allyl (**10g**), and hydroxyl (**10j**) groups were perfectly accommodated. In general, the aliphatic azides gave higher isolated yields than aryl azides, potentially due to formation of nitrenes upon photolysis of the aryl azides.[10] In accordance with Larock's investigation,[4a] the reaction of trimethylsilyl azide with phthaloyl peroxide did not stop at

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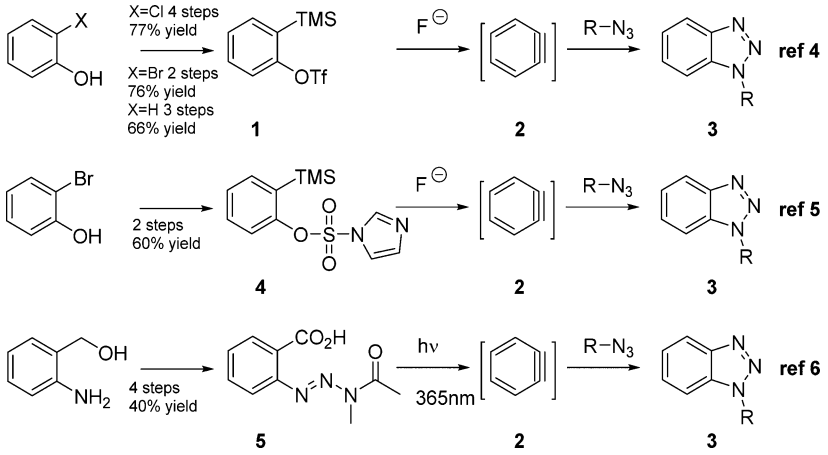
Scheme 1. Synthesis of Benzotriazoles via [3 + 2] Cycloaddition of Arynes with Azides



Scheme 2. Thermolytic and Photolytic Cleavage of Phthaloyl Peroxide

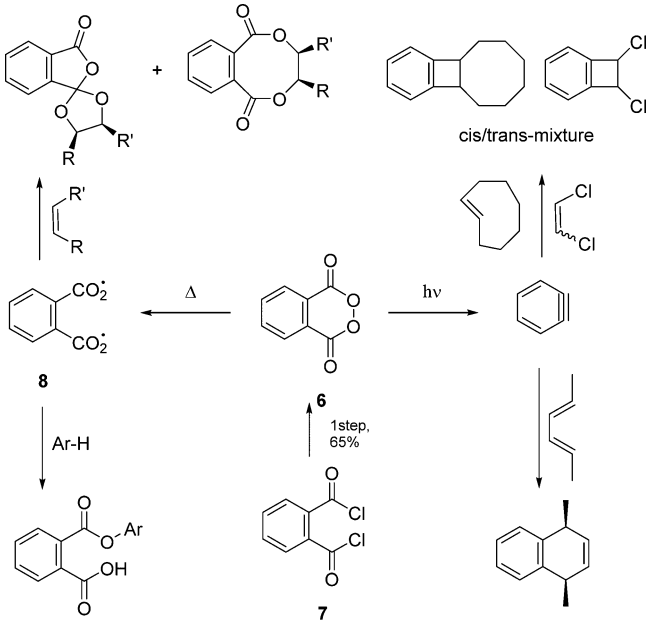
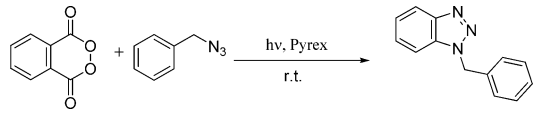


Table 1. Optimization of the Reaction Conditions[a]



entry	PPO (equiv)[b]	time (h)	yield (%)[c]
1[d]	1.2	2	20
2	1.2	2	30
3	1.2	8	26
4	2	2	51
5	3	2	68
6	4	2	76
7	**5**	**2**	**81**
8	10	2	82
9	5	0.5	45
10[e]	5	2	71
11[f]	3	2	55
12[g]	3	2	59
13[h]	5	2	0
14[i]	5	2	16
15[j]	5	2	30
16[k]	5	2	80

[a]In all but entry 1, 0.3 mmol of benzyl azide was dissolved in 45 mL of DCE to give 0.0067 M solutions. The corresponding solvent was degassed for 2−3 min under N_2 and then irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter under constant stirring at room temperature. [b]PPO = phthaloyl peroxide. [c]Isolated yield. [d]Concentration of benzyl azide is 0.03 M. [e]Add 3 equiv of PPO at first; 1 h later, add another 2 equiv of PPO. [f]Additive (30 mol %): benzophenone. [g]Additive (30 mol %): benzil. [h]Phthalic anhydride used instead of PPO. [i]Degassed by O_2. [j]Degassed by air. [k]With 1.5 mmol H_2O.

the [3 + 2] cycloaddition stage but underwent desilylation, followed by phenylation with another equivalent of benzyne to afford **10e**, the same product obtained with phenyl azide. It was noteworthy that azides bearing a free NH group or electron-withdrawing groups such as sulfonyl and phosphoryl groups did not work in this photoinduced benzyne [3 + 2] cycloaddition.

Having confirmed that the photoinduced benzyne [3 + 2] cycloaddition proceeded smoothly with a number of azides, our attention was next given to an examination of the second reaction partner, the aryne. Although highly reactive, phthaloyl peroxide derivatives have been shown to have thermal stability greater than that of benzoyl peroxides.[11] With successful access to a series of substituted phthaloyl peroxides, aryne precursors **11a** and **11b** were found to produce the expected benzotriazoles in 17 and 74% yield (Table 2, entries 1 and 2). On the other hand, the unsymmetrically substituted aryne precursors generated an inseparable mixture of isomeric products (Table 2, entries 3−5). In line with thermally equilibrated benzyne intermediates, the same ratio of isomeric benzotriazoles **12c** (1:1) and **12d** (3:7) was obtained by photolysis of 4-methyl or 4-fluoro phthaloyl peroxides as by treatment of *o*-(trimethylsilyl)aryl imidazolylsulfonates with fluoride (Table 2, entries 3 and 4).[5] Moreover, the benzyne bearing a NO_2 group, which is hard to obtain through the ordinary methodologies, could be smoothly produced using the corresponding phthaloyl peroxide as the benzyne precursor. Interestingly, *ortho*-F phthaloyl peroxide was found to react with benzyl azide in a completely regioselective manner, furnishing a single isomer (Table 2, entry 6), in agreement with Garg's related research.[4h]

In conclusion, we have reported a photoinduced aryne [3 + 2] cycloaddition for the rapid and efficient synthesis of

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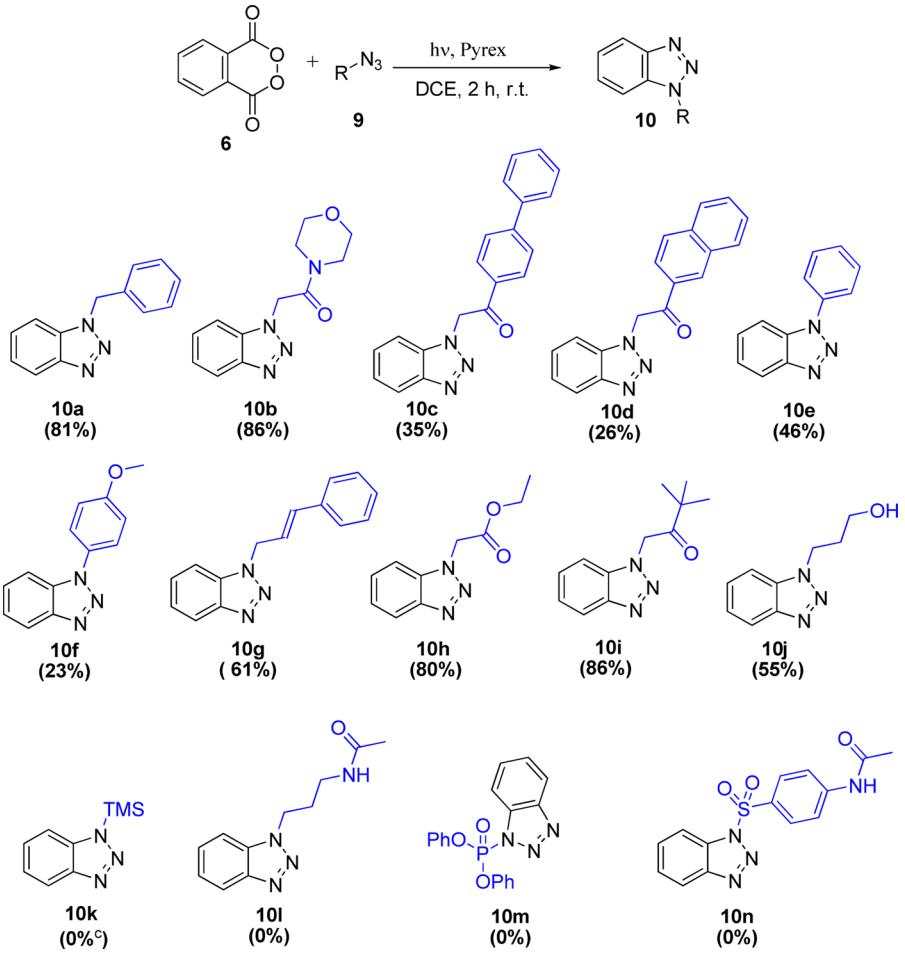
Scheme 3. Scope of Photoinduced Benzyne [3 + 2] Cycloaddition[a,b]



[a]**9** (0.3 mmol), PPO (5.0 equiv), DCE (45 mL). The reaction mixture in the quartz tube was degassed for 2−3 min under N_2 and then irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter under constant stirring at room temperature for 2 h. [b]Isolated yield. [c]**10e** was isolated in 15% yield after purification by column chromatography.

benzotriazole and analogues from cheap and readily accessible phthaloyl peroxides. It is particularly noteworthy that, compared to poor yields and a limited substrate scope of photochemically induced [2 + 2] and [2 + 4] cycloadditions,[9] the Huisgen cycloaddition of organic azides with benzynes, photolytically generated from substituted phthaloyl peroxides, tolerates a wide range of functional groups and furnishes various benzotriazole derivatives in good yields under very mild conditions (ambient temperature and neutral medium). With the utilization of phthaloyl peroxides instead of widely used *ortho*-silyl phenyl triflates, the formation of potentially genotoxic trifluoromethanesulfonate side product is eliminated. Further applications of phthaloyl peroxide derivatives as benzyne precursors are currently ongoing in our laboratory.

EXPERIMENTAL SECTION

Commercially available reagents were used without further purification, for example, benzyl azide (94%). The reaction solvent (DCE) was dried by refluxing over CaH_2 and freshly distilled prior to use. All reactions were monitored by thin-layer chromatography and visualized by a UV lamp (254 nm) or by staining with a solution of 10 g of phosphomolybdic acid and 100 mL of EtOH, followed by heating. Flash column chromatography was performed using 230−400 mesh silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were obtained on 400M or 600M instruments. HRMS spectra were recorded on a Q-TOF LC/MS system. Coupling constants are reported in hertz (Hz). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to protium; s = singlet, br s = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet, coupling constant (Hz), and integration). Data for ^{1}H NMR are reported in parts per million relative to residual solvent peak ($CDCl_3$: 7.26 ppm). Data for ^{13}C NMR are reported in parts per million relative to residual solvent peak ($CDCl_3$: 77.16 ppm). Melting point ranges were determined on an apparatus and were uncorrected. The light source used for the photochemical reactions was a 500 W medium-pressure mercury lamp.

Except for **11a**, **11c**, **12a**, **12b**, and **12e**, other compounds are known.

Representative Procedure for Phthaloyl Peroxide 6 Synthesis.[8d] According to Siegel's method,[8d] to a solution of phthaloyl chloride (0.40 g, 1.5 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL) was added solid sodium percarbonate (Aldrich available H_2O_2: 20−30%) (0.34 g, 2.2 mmol, 1.5 equiv) in one portion. The heterogeneous reaction mixture was stirred vigorously for 3 h (rapid stirring is required). The reaction mixture was filtered through Celite and concentrated to provide the phthaloyl peroxide **6** as a white solid matching existing characterization data:[8d] mp 118−119 °C, decomposition; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, J = 5.8, 3.3 Hz, 2H), 8.03 (dd, J = 5.8, 3.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 136.6, 130.3, 123.7.

Following the general procedure, naphtho[2,3-*d*][1,2]dioxine-1,4-dione **11a** was synthesized as a white solid: mp 118 °C,

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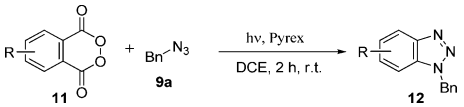
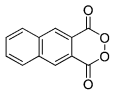
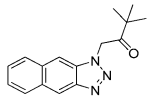
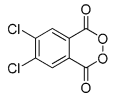
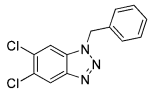
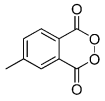
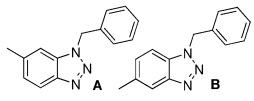
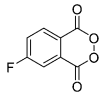
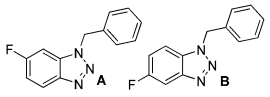
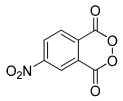
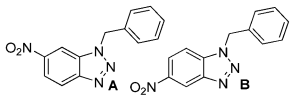
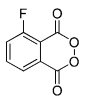
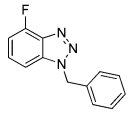
Table 2. Scope of Phthaloyl Peroxide Derivatives, Benzyne Precursor[a]



entry	PPO derivatives	benzotriazoles	yield[b]
1[c]	 **11a**	 **12a**	17%
2	 **11b**	 **12b**	74%
3[d]	 **11c**	 **12c**	87% **A**:**B** 1:1
4[d]	 **11d**	 **12d**	82% **A**:**B** 3:7
5[d]	 **11e**	 **12e**	72% **A**:**B** 3:5
6	 **11f**	 **12f**	46%

[a]**9a** (0.3 mmol), **11** (5.0 equiv), DCE (45 mL). The reaction mixture in the quartz tube was degassed for 2−3 min under N_2 and then irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter under constant stirring at room temperature for 2 h. [b]Isolated yield. [c]1-Azido-3,3-dimethylbutan-2-one (0.3 mmol), naphtho[2,3-*d*][1,2]dioxine-1,4-dione (2.8 equiv). [d]The regioisomeric ratio was determined by ^{1}H NMR spectroscopic analysis of the mixture of isomeric products.

decomposition; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 2H), 8.18 (dd, J = 6.0, 3.3 Hz, 2H), 7.88 (dd, J = 6.0, 3.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 135.7, 133.4, 131.4, 130.2, 118.4; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{12}H_7O_4$) requires m/z 215.0344, found m/z 215.0353.

Following the general procedure, peroxide **11b** was synthesized as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.6, 142.6, 132.0, 122.8.

Following the general procedure, 6-methylbenzo[*d*][1,2]dioxine-1,4-dione **11c** was synthesized as a white solid: mp 120 °C, decomposition; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 1H), 8.07 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4, 162.3, 148.7, 137.5, 130.4, 130.3,123.6, 121.1, 22.2; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_9H_7O_4$) requires m/z 179.0344, found m/z 179.0350.

Following the representative procedure, peroxide **11d** was synthesized as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, J = 8.6, 4.9 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.70 (t, J = 8.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.4 (d, J = 264.1 Hz), 161.2, 133.8 (d, J = 9.6 Hz), 126.6 (d, J = 9.6 Hz), 124.6 (d, J = 21.5 Hz), 120.2 (d, J = 3.2 Hz), 117.1 (d, J = 21.5 Hz).

Following the representative procedure, peroxide **11e** was prepared as pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.4, 152.4, 132.5, 130.7, 127.9, 125.5.

Following the representative procedure, peroxide **11f** was prepared as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 1H), 8.07−7.98 (m, 1H), 7.71 (t, J = 9.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1 (d, J = 273.1 Hz), 161.3 (d, J = 3.4 Hz), 157.7 (d, J = 4.9 Hz), 138.8 (d, J = 9.6 Hz), 126.7 (d, J = 4.7 Hz), 125.3, 125.0 (d, J = 21.0 Hz), 111.7 (d, J = 7.8 Hz).

Synthesize Azido Compounds According to Schnarr's Method.[6] **Compound 9b**: light brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 2H), 3.61−3.67 (m, 6H), 3.37 (d, J = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 66.7, 50.6, 45.6, 42.4.

Compound 9c: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.63 (dd, J = 5.3, 3.3 Hz, 2H), 7.55−7.37 (m, 3H), 4.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.9, 147.0, 139.6, 133.2, 129.2, 128.7, 127.7, 127.4, 55.0.

Compound 9d: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.07−7.80 (m, 4H), 7.66−7.57 (m, 2H), 4.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 136.1, 132.5, 131.9, 129.9, 129.8, 129.2, 129.1, 128.1, 127.3, 123.4, 55.1.

Compound 9e: orange oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (t, J = 7.4 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 129.9, 125.0, 119.2.

Compound 9f: dark brown solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, J = 7.7 Hz, 2H), 6.89 (d, J = 7.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 132.5, 120.2, 115.3, 55.7.

Compound 9g: brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.19 (m, 5H), 6.63 (d, J = 15.8 Hz, 1H), 6.22 (dt, J = 15.7, 6.6 Hz, 1H), 3.91 (d, J = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 134.6, 128.7, 128.3, 126.7, 122.5, 53.1.

Compound 9h: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, J = 7.1 Hz, 2H), 3.84 (s, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 61.9, 50.4, 14.1.

Compound 9i: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (s, 2H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 53.0, 43.5, 26.3.

Compound 9j: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74−3.71 (m, 2H), 3.43 (t, J = 6.6 Hz, 2H), 2.06 (br s, 1H), 1.84−1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 59.9, 48.5, 31.5.

Compound 9l: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (br s, 1H), 3.65−3.10 (m, 4H), 1.93 (d, J = 2.4 Hz, 3H), 1.79−1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 49.2, 37.1, 28.7, 23.1.

Synthesis of Benzotriazoles from Photolysis. In a 50 mL quartz tube, phthaloyl peroxide **6** (246.2 mg, 1.5 mmol, 5.0 equiv) and a corresponding azido compound (0.3 mmol, 1.0 equiv) were added, followed by DCE (45 mL). The reaction mixture was degassed via a nitrogen bubbler for 2−3 min and then irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter under constant stirring at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and purified over silica using flash column chromatography with triethylamine to give the corresponding benzotriazole. Spectral data matched those obtained from the Schnarr and Larock methods.[4a,6]

Following the general procedure, **10a** was synthesized as a white solid: 50.9 mg, 81% isolated yield; mp 117−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1H), 7.47−7.23 (m, 8H), 5.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 134.9, 133.0, 129.1,

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J. Org. Chem. 2015, 80, 5928−5933

128.60, 127.7, 127.5, 124.0, 120.2, 109.9, 52.4; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{13}H_{12}N_3$) requires m/z 210.1031, found m/z 210.1029.

Following the general procedure, **10b** was synthesized as a white solid: 63.5 mg, 86% isolated yield; mp 218−219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 5.50 (s, 2H), 3.64 (s, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 146.2, 133.7, 128.2, 124.4, 120.2, 110.1, 66.8, 66.5, 50.0, 46.2, 42.7; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{12}H_{15}N_4O_2$) requires m/z 247.1195, found m/z 247.1196.

Following the general procedure, **10c** was synthesized as a yellow solid: 32.6 mg, 35% isolated yield; mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, J = 9.6 Hz, 3H), 7.75 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H), 7.52−7.34 (m, 6H), 6.12 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.1, 147.3, 146.2, 139.4, 133.9, 132.7, 129.2, 129.0, 128.7, 127.9, 127.8, 127.4, 124.1, 120.2, 109.7, 54.0; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{20}H_{16}N_3O$) requires m/z 314.1293, found m/z 314.1300.

Following the general procedure, **10d** was synthesized as a white solid: 22.9 mg, 26% isolated yield; mp 137−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.16−7.86 (m, 5H), 7.72−7.57 (m, 2H), 7.55−7.36 (m, 3H), 6.24 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.4, 146.3, 136.3, 134.0, 132.5, 131.5, 130.6, 129.9, 129.5, 129.4, 128.1, 128.0, 127.5, 124.2, 123.6, 120.4, 109.7, 54.1; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{18}H_{14}N_3O$) requires m/z 288.1137, found m/z 288.1136.

Following the general procedure, **10e** was synthesized as a brown solid: 27.0 mg, 46% isolated yield; mp 84−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.3 Hz, 1H), 7.78 (dd, J = 15.6, 8.2 Hz, 3H), 7.70−7.36 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.7, 137.2, 132.5, 130.0, 128.8, 128.4, 124.5, 123.0, 120.5, 110.5; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{12}H_{10}N_3$) requires m/z 196.0875, found m/z 196.0875.

Following the general procedure, **10f** was synthesized as a pale yellow solid: 15.5 mg, 23% isolated yield; mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 1H), 7.66 (d, J = 8.3 Hz, 3H), 7.52 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.7 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 146.4, 132.7, 130.0, 128.1, 124.7, 124.4, 120.3, 115.1, 110.4, 55.8; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{13}H_{12}N_3O$) requires m/z 226.0980, found m/z 226.0986.

Following the general procedure, **10g** was synthesized as a white solid: 42.8 mg, 61% isolated yield; mp 62−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.62−7.20 (m, 8H), 6.67 (d, J = 15.9 Hz, 1H), 6.39 (dt, J = 15.6, 6.3 Hz, 1H), 5.44 (d, J = 6.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 135.6, 134.5, 133.0, 128.8, 128.5, 127.5, 126.7, 124.0, 122.3, 120.2, 109.8, 50.7; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{15}H_{14}N_3$) requires m/z 236.1188, found m/z 236.1186.

Following the general procedure, **10h** was synthesized as a pale yellow solid: 49.4 mg, 80% isolated yield; mp 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.52−7.42 (m, 2H), 7.38−7.34(m, 1H), 5.39 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 145.9, 133.4, 128.0, 124.2, 120.1, 109.4, 62.4, 49.1, 14.1; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{10}H_{12}N_3O_2$) requires m/z 206.0930, found m/z 206.0926.

Following the general procedure, **10i** was synthesized as a white solid: 56.0 mg, 86% isolated yield; mp 96−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 5.61 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.3, 145.8, 133.6, 127.7, 124.1, 119.9, 109.4, 52.0, 43.6, 26.2; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{12}H_{16}N_3O$) requires m/z 218.1293, found m/z 218.1290.

Following the general procedure, **10j** was synthesized as a colorless oil: 29.5 mg, 55% isolated yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 4.81 (t, J = 6.6 Hz, 2H), 3.65 (t, J = 5.7 Hz, 2H), 2.31−2.15 (m, 2H), 2.11 (br s, 1H),; ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.0, 133.3, 127.5, 124.1, 120.1, 109.5, 59.0, 44.6, 32.2; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_9H_{12}N_3O$) requires m/z 178.0980, found m/z 178.0982.

Synthesis of 3,3-dimethyl-1-(1*H*-naphtho[2,3-*d*][1,2,3]-triazol-1-yl)butan-2-one 12a Using Photolysis of Compound 11a. In a 50 mL quartz tube, 1-azido-3,3-dimethylbutan-2-one (42.4 mg, 0.3 mmol, 1.0 equiv) and naphtho[2,3-*d*][1,2]dioxine-1,4-dione **11a** (177.2 mg, 0.83 mmol, 2.8 equiv) were added, followed by DCE (45 mL). The reaction mixture was degassed via a nitrogen bubbler for 2−3 min and then irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter under constant stirring at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and purified over silica using flash column chromatography with triethylamine to give the corresponding benzotriazole **12a**: yellow solid; 13.9 mg, 17% isolated yield; mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.72 (s, 1H), 7.53−7.40 (m, 2H), 5.73 (s, 2H), 1.39 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.4, 145.4, 133.2, 132.4, 130.7, 129.6, 128.0, 126.8, 124.8, 118.4, 104.9, 52.1, 43.8, 26.4; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{16}H_{18}N_3O$) requires m/z 268.1450, found m/z 268.1459.

Synthesis of Benzotriazoles Using Photolysis of Phthaloyl Peroxide Derivatives. In a 50 mL quartz tube, (azidomethyl)-benzene (40 μL, 0.3 mmol, 1.0 equiv) and a corresponding phthaloyl peroxide (1.5 mmol, 5.0 equiv) were added, followed by DCE (45 mL). The reaction mixture was degassed via a nitrogen bubbler for 2−3 min and then irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter under constant stirring at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and purified over silica using flash column chromatography with triethylamine to give the corresponding benzotriazole.

Following the general procedure, 1-benzyl-5,6-dichloro-1*H*-benzo-[*d*][1,2,3]triazole **12b** was synthesized as a white solid: 61.4 mg, 74% isolated yield; mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.49 (s, 1H), 7.38 (s, 3H), 7.29 (s, 2H), 5.83 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.4, 134.0, 132.7, 131.9, 129.4, 129.0, 127.7, 121.1, 111.1, 52.8; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{13}H_{10}Cl_2N_3$) requires m/z 278.0252, found m/z 278.0255.

Following the general procedure, **12c** was synthesized as a white solid: mixture of regioisomers; 58.4 mg, 87% isolated yield; mp 96−98 °C; ^{1}H NMR of the 5-methyl isomer (400 MHz, $CDCl_3$) δ 7.83 (s), 7.41−7.32 (m), 7.31−7.27 (m), 5.82 (s), 2.49 (s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.0, 135.0, 134.0, 131.4, 129.6, 129.0, 128.4, 127.6, 119.0, 109.3, 52.3, 21.5; ^{1}H NMR of the 6-methyl isomer (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz), 7.41−7.32 (m), 7.31−7.27 (m), 7.18 (d, J = 8.5 Hz), 7.15 (s), 5.81 (s), 2.47 (s); ^{13}C NMR (150 MHz, $CDCl_3$) 145.0, 138.1, 135.0, 133.3, 129.0, 128.4, 127.6, 126.3, 119.5, 108.9, 52.0, 22.0; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{14}H_{14}N_3$) requires m/z 224.1188, found m/z 224.1189. Spectral data matched those obtained from Novák's method.[5]

Following the general procedure, **12d** was synthesized as a white solid: mixture of regioisomers; 55.6 mg, 82% isolated yield; mp 100−101 °C; ^{1}H NMR of the 5-fluoro isomer (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz), 7.38−7.35 (m), 7.32−7.28 (m), 7.20 (t, J = 8.8 Hz), 5.86 (s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7 (d, J = 243 Hz), 146.5 (d, J = 12.5 Hz), 134.4, 129.8, 129.1, 128.7, 127.6, 117.5 (d, J = 28 Hz), 110.7 (d, J = 10.5 Hz), 104.6 (d, J = 24.4 Hz), 52.6; ^{1}H NMR of the 6-fluoro isomer (400 MHz, $CDCl_3$) δ 8.04 (dd, J_1 = 9.1 Hz, J_2 = 4.6 Hz), 7.38−7.35 (m), 7.32−7.28 (m), 7.13 (t, J = 9.0 Hz), 6.99 (d, J = 7.8 Hz), 5.82 (s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1 (d, J = 248 Hz), 143.2, 134.3, 133.2 (d, J = 12.5 Hz), 129.1, 128.7, 127.6, 121.5 (d, J = 10.8 Hz), 114.0 (d, J = 27.0 Hz), 95.5 (d, J = 27.5 Hz), 52.4; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{13}H_{11}FN_3$) requires m/z 228.0937, found m/z 228.0943. Spectral data matched those obtained from Novák's method.[5]

Following the general procedure, 1-benzyl-5/6-nitro-1*H*-benzo[*d*]-[1,2,3]triazole **12e** was synthesized as a white solid: mixture of regioisomers; 45.0 mg, 72% isolated yield; mp 96−97 °C; ^{1}H NMR of the 5-nitro isomer (400 MHz, $CDCl_3$) δ 9.02 (s), 8.35−8.30 (m),

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8.28−8.18 (m), 7.48−7.28 (m), 5.93 (s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.6, 144.8, 135.5, 133.8, 129.4, 129.1, 127.8, 122.6, 117.5, 110.5, 53.0; ^{1}H NMR of the 6-nitro isomer (400 MHz, $CDCl_3$) δ 9.02 (s), 8.35−8.30 (m), 8.28−8.18 (m), 7.48−7.28 (m), 5.96 (s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.6, 147.0, 133.7, 132.1, 129.5, 129.2, 127.8, 121.2, 119.1, 107.1, 53.1; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{13}H_{11}N_4O_2$) requires m/z 255.0882, found m/z 255.0890.

Following the general procedure, **12f** was synthesized as a yellow solid: 31.2 mg, 46% isolated yield; mp 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.26 (m, 6H), 7.16 (d, J = 8.3 Hz, 1H), 7.01 (t, J = 8.9 Hz, 1H), 5.87 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5 (d, J = 259.3 Hz), 136.7 (d, J = 18.2 Hz), 135.7 (d, J = 6.6 Hz), 134.4, 129.2, 128.7, 128.4 (d, J = 6.9 Hz), 127.7, 108.7 (d, J = 16.9 Hz), 105.9 (d, J = 4.9 Hz), 52.6; HRMS (ES+) exact mass calcd for $[M + H]^+$ ($C_{13}H_{11}FN_3$) requires m/z 228.0937, found m/z 228.0935.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all synthetic compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00517.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lshi@hit.edu.cn. Homepage: http://homepage.hit.edu.cn/pages/shilei.

Notes

The authors declare no competing financial interest.

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