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Brief Communication

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Metal-Free Catalytic Approach for Allylic C−H Amination Using *N*-Heterocycles via sp^3 C−H Bond Activation

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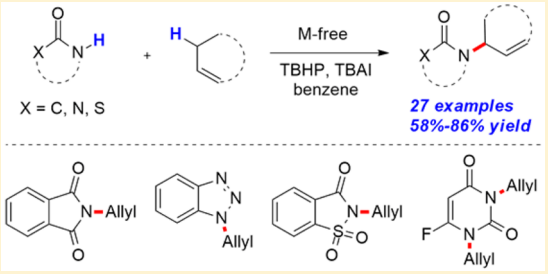
Supporting Information

ABSTRACT: A versatile metal-free synthesis of allylic *N*-heterocycles has been developed using a TBAI/TBHP oxidation system. This general protocol could be applied for the C−N bond formation of electron-deficient phthalimides, imidazoles, triazoles, and sulfonamides with cyclic and acylic olefins. The practical use of the method is demonstrated by the amidation of functionalized biologically active substrates.



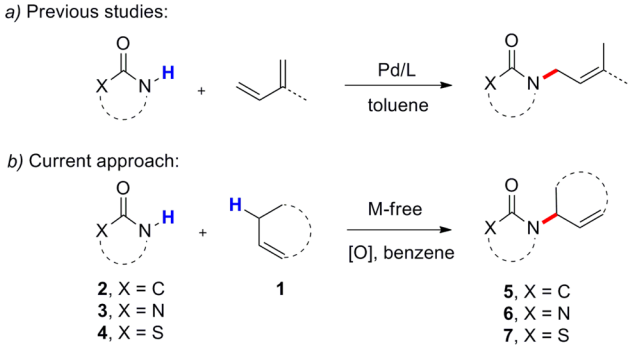
C(sp^3)−H bond activation of allylic hydrogen has demonstrated promise for the construction of highly functionalized olefins. Much attention has been drawn in recent years to selective allylic C−H transformations including oxygenation,[1−5] alkylation,[6−9] and esterification.[10−12]

The allylic amines are presented in a wide variety of pharmaceuticals and bioactive products.[13] Efficient approaches employing prefunctionalized allylic coupling partners have been developed for the introduction of C−N bond into organic molecules and biological systems.[14] In contrast, direct oxidative coupling of the C−H and N−H bond has shown advantages over the condensation of amines and carboxylic acid derivatives in terms of atom economy. Recent developments on direct amination of allylic sp^3 C−H using transition-metal catalysts have provided great tools for homolytic allylic C−H bond abstraction.[15−23] Metal-free oxidation methods were also been established for the amination of ethers, ketones, and arenes through radical pathways.[24−29]

Although significant advances have been achieved in this field, more efficient and versatile strategies for allylic C(sp^3)−H bond functionalization are still in demand. Until now, only a few examples of metal-free direct allyic amination have been reported.[30,31] The selective addition of electron-deficient *N*-heterocycles to olefins has scarcely been studied.

Along with our interest in selective sp^3 C−H bond functionalization[32] and inspired by Beller's palladium-catalyzed hydroamidation of 1,3-dienes[33,34] (Scheme 1a), we hypothesized that a radical-initiated allylic amination process would benefit from the simple conditions and high regioselectivity of the stabilized allyl radicals (Scheme 1b). After investigating a range of *N*-heterocyclic amides and azoles for cross-dehydrogenative coupling (CDC) reactions[35−42] with linear and cyclic olefins using a well-established TBAI/TBHP oxidation system,[43−48] we herein report a general metal-free amination protocol for the atom-efficient construction of a broad range of *N*-allylic heterocycles.

Scheme 1. Regioselective Synthesis of Allylic Amides Using Different Catalytic Systems



In initial reaction development, we tested several peroxides and catalysts with cyclohexene **1a** and nitrophthalimide **2a**. We first used DTBP as oxidant and a catalytic amount of $Cu(OAc)_2$ in benzene at 80 °C for 12 h, and a trace amount of coupling product was obtained (Table 1, entry 1). CuI and $Fe(acac)_3$ (0.1 equiv) were ineffective (entries 2 and 3). When $Pd(OAc)_2$ was used, the desired product was furnished in moderate yield (entry 4, 65%).

Switching the oxidant to TBHP, no product was detected in the absence of catalyst (entry 5). Low conversions were observed with copper, iron, and potassium catalysts (entries 6−10). Palladium acetate provided similar moderate yield (62%, entry 11). To our delight, tetrabutylammonium iodide (TBAI) could promote the reaction to form the target coupling product with high regioselectivity and good yield (entry 12). Altering the loading of catalyst and oxidant provided similar results (entries 13−15). The reaction did occur when carried out in

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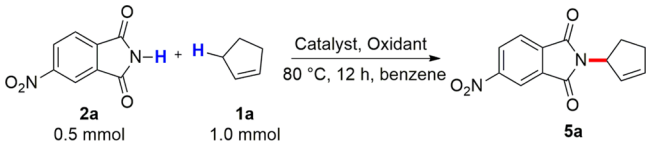
Table 1. Optimization of the Reaction Conditions



entry	oxidant (equiv)	catalyst (equiv)	solvent	yield (%)
1	DTBP (2)	$Cu(OAc)_2$ (0.1)	benzene	trace
2	DTBP (2)	CuI (0.1)	benzene	0
3	DTBP (2)	$Fe(acac)_3$ (0.1)	benzene	0
4	DTBP (2)	$Pd(OAc)_2$ (0.1)	benzene	65
5	TBHP (2)		benzene	0
6	TBHP (2)	CuBr (0.1)	benzene	trace
7	TBHP (2)	CuI (0.1)	benzene	12
8	TBHP (2)	$Cu(acac)_2$ (0.1)	benzene	15
9	TBHP (2)	$Fe(acac)_3$ (0.1)	benzene	0
10	TBHP (2)	KI (0.1)	benzene	trace
11	TBHP (2)	$Pd(OAc)_2$ (0.1)	benzene	62
12	TBHP (2)	TBAI (0.1)	benzene	78
13	TBHP (2)	TBAI (0.2)	benzene	83
14	TBHP (2)	TBAI (0.2)	benzene	81
15	TBHP (2)	TBAI (0.2)	benzene	82
16	TBHP (2)	TBAI (0.2)	DMSO	13
17	TBHP (2)	TBAI (0.2)	DMF	28
18	TBHP (2)	TBAI (0.2)	toluene	56
19	TBHP (2)	TBAI (0.2)	EtOAc	68
20	TBHP (2)	TBAI (0.2)	MeCN	32

other solvents, but much lower conversions were observed (entries 16−20).

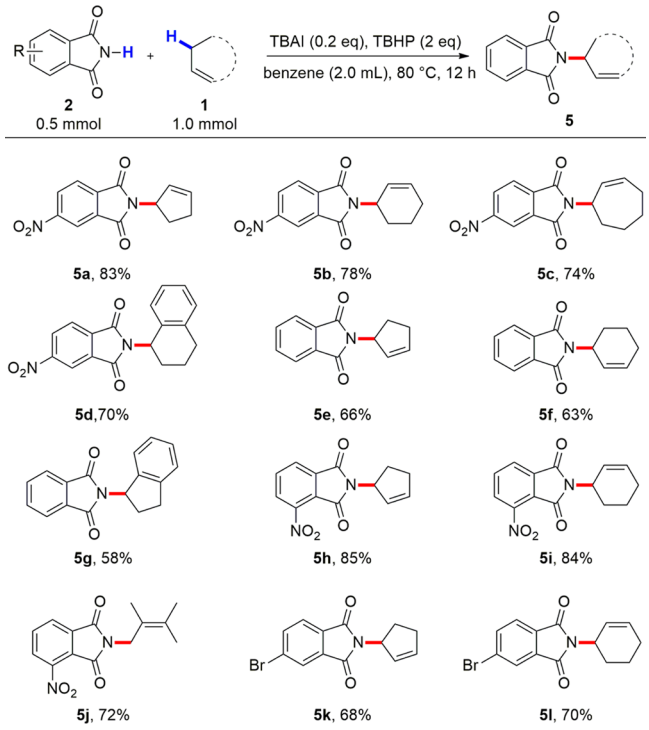
With the optimized conditions in hand (Table 1, entry 13), we investigated other phthalimides for this oxidative amination of olefins. Substrates with electron-withdrawing groups went through a cross-dehydrogenative coupling process with linear and cyclic olefins (Scheme 2). The yields decreased slightly with larger cyclic rings (**5a−d**). Bromo-substituted phthalimides provided higher yields than the unsubstituted substrates (**5k** and **5l**).

Next, we tried to extend the scope of this methodology to similar amides and azoles. As we expected, this direct allylic amination protocol could be applied to *N*-heteroarene systems such as benzotriazoles and benzimidazoles (Scheme 3).

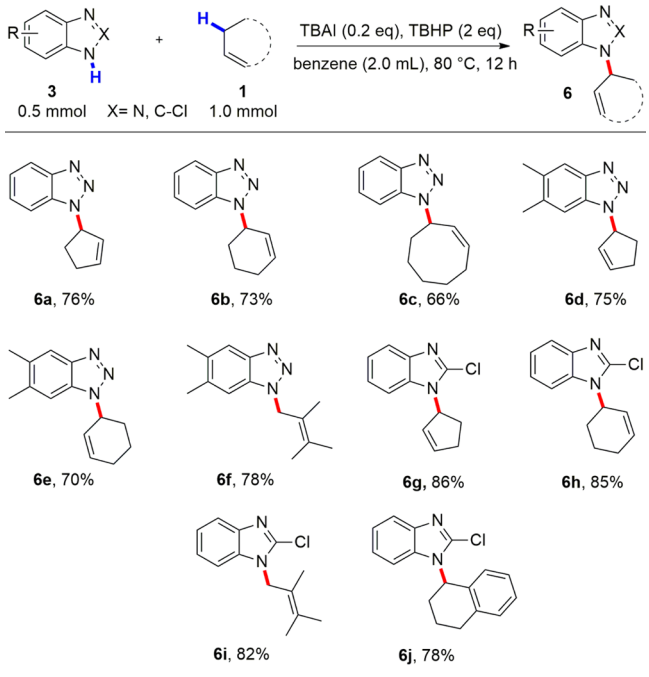
Cyclopentene, cyclohexene, cyclooctene, and tetramethylethylene could all react with benzimidazoles to afford the allylic amination compounds **6a−f** in high yields. 2-chlorobenzotriazole also reacted smoothly to furnish the amination products **6g−i** in 82%−86% yields. Notably, benzylic hydrogen in tetrahydronaphthalene could also tolerate these conditions to furnish **6j** in 78% yield.

To further explore the generality of this protocol, we also tested the pharmacologically useful sulfonamide derivatives.[49,50] A variety of olefins with allylic sp^3 hydrogens were activated by the TBAI−TBHP oxidation system (Scheme 4). The reactions of indene and tetramethylethylene with saccharin resulted in the formation of **7a** and **7b** in 72% and 68% yield, respectively. In addition, the reactions with methyl and ethyl crotonate furnished the corresponding products in similar yields (**7c**, 66% and **7d**, 64%). Interestingly, naturally insufficient *β*-pinene could tolerate the peroxide to form its saccharin derivative without commonly occurred oxidative polymerization (**7e**, 62%).

Scheme 2. Amidation of Allylic Alkanes with Phthalimides



Scheme 3. Amidation of Various Allylic Olefins with Imidazoles and Triazoles



Finally, we chose one of the nucleobases, uracil, as an example of functionalized biologically important amide substrate to demonstrate the utility of our procedure. Undeniably, the reaction of tetramethylethylene with fluorinated uracil **8a** provided disubstituted product **8b** in 40% yield. In a similar manner, partially protected chlorouracil derivative **8c** was converted into the mono-*N*-allylic product **8d** in 35% yield (Scheme 5).

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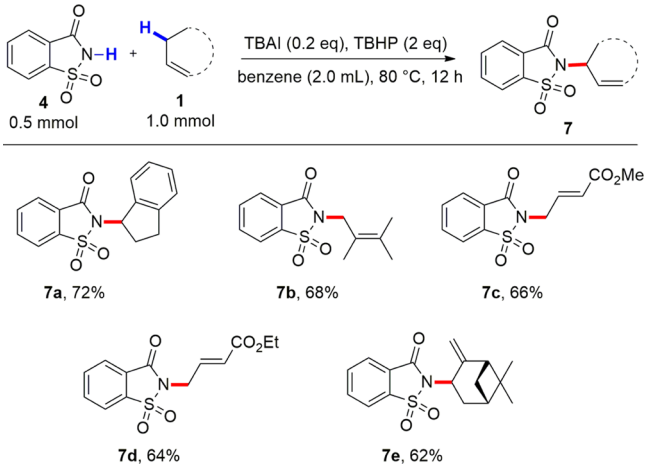
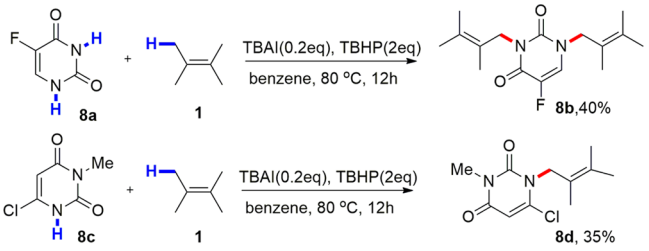
Scheme 4. Amidation of Various Allylic Alkanes and Esters with Saccharin

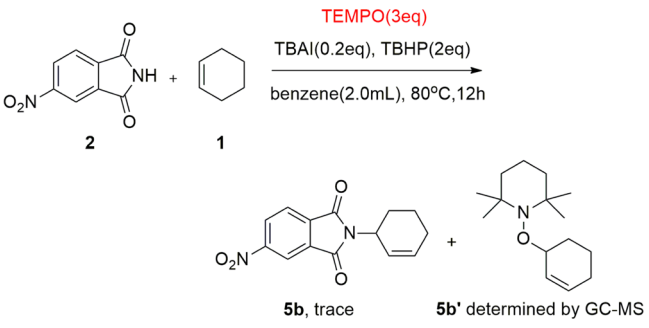


Scheme 5. Amidation of Tetramethylethylene with Uracil Derivatives



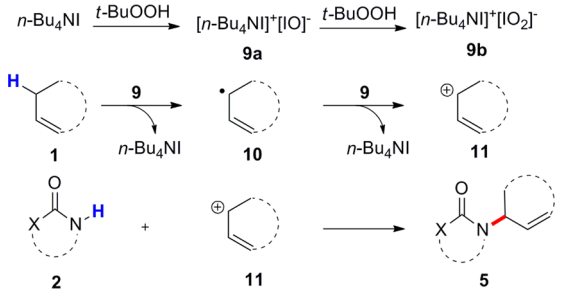
According to previous reports,[46−48] it is believed that the active hypoiodite $[n\text{-Bu4N}]^+[IO]$ or iodite $[n\text{-Bu}_4\text{N}]^+[IO_2]$ species is the crucial intermediate in sp^3 C−H amination reactions. To investigate the mechanism of this reaction, a control experiment was carried out by using nitrophthalimide and cyclohexene with the radical-trapping reagent 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (Scheme 6). As

Scheme 6. Radical-Trapping Control Experiment



expected, the formation of the desired product **5b** was suppressed. Only the TEMPO−cyclohexane adduct **5b′** was obtained (determined by LC−MS analysis). This control experiment suggests that the coupling reaction might go through a radical pathway. Therefore, a plausible mechanism is proposed on the basis of the results (Scheme 7). First, *n*-Bu_4NI was oxidized by TBHP to form the active hypoiodite **9a** or iodite **9b** species. Then the homolysis of allylic C−H bond with **9** gives the allylic radical **10**, which is oxidized by active iodine species to give the allylic cation **11**. At last, the nucleophilic

Scheme 7. Possible Mechanism for Metal-Free Synthesis of *N*-Allyl Heterocycles



attack of amine **2** to the allylic cation **11** furnishes the desired product **5**. The regiochemistry obtained with tetraethylethylene (**5j**, **6f**, **6i**, **7b**, **8b**, and **8d**), which is not consistent with the proposed cationic mechanism, may be due to the fact that the rearranged carbon cation is sterically hindered and therefore not favored for the amination.

CONCLUSIONS

In summary, we have demonstrated a general protocol for the CDC coupling of functionalized electron-poor *N*-heterocycles with cyclic and acyclic olefins via sp^3 C−H bond activation. This metal-free amination pathway presents a direct access to a variety of allyl-substituted heterocycles as useful synthetic intermediates and important bioactive agents.

EXPERIMENTAL SECTION

General Considerations. Commercially available reagents were used as received without purification. TBHP (5.5 M in decane) was purchased from Sigma-Aldrich. Column chromatography was carried out on silica gel (300−400 mesh). Analytical thin−layer chromatography was performed on glass plates of silica gel GF-254 with detection by UV. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a 400 M spectrometer. The chemical shift references were as follows. ^1H NMR ($CDCl_3$): 7.26 ppm. ^{13}C NMR ($CDCl_3$): 77.16 ppm. HRMS spectra were carried out on TOF MS EI^+ and ESI. Melting point determination was taken on a Melt-Temp apparatus (X-4) and was uncorrected.

General Procedure. To a Schlenk tube equipped with a magnetic stir bar were added TBAI (37 mg, 0.1 mmol) and heterocyclic sbustrate (**2**, **3**, or **4**, 0.5 mmol) with olefin **1** (1 mmol) in 2 mL of benzene. Then TBHP (5.5 M in decane, 1 mmol, 0.2 mL) was added before the vial was sealed, and the reaction mixture was stirred at 80 °C for 12 h. After required reaction time, the mixture was cooled to room temperature, diluted in ethyl acetate, and washed with brine. The aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the product.

*2-(Cyclopent-2-enyl)-5-nitroisoindoline-1,3-dione (**5a**).* Light yellow solid. Mp: 77−78 °C. Yield: 107 mg (83%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.1 Hz, 1H), 8.57 (dd, J = 8.1, 2.0 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 6.13 (dq, J = 4.5, 2.3 Hz, 1H), 5.62 (dq, J = 4.5, 2.2 Hz, 1H), 5.41 (dtd, J = 7.2, 4.9, 2.7 Hz, 1H), 2.82 (dddd, J = 14.0, 9.4, 4.7, 2.7 Hz, 1H), 2.51−2.42 (m, 1H), 2.37 (dtd, J = 13.9, 9.2, 4.5 Hz, 1H), 2.10 (ddt, J = 14.0, 9.5, 4.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 165.8, 151.8, 136.7, 136.6, 133.6, 129.2, 127.3, 124.4, 118.6, 57.0, 32.4, 28.2. HRMS (TOF MS EI^+): m/z calcd for $[C_{13}H_{10}N_2O_4]$ 258.0641, found 258.0635.

*2-(Cyclohex-2-enyl)-5-nitroisoindoline-1,3-dione (**5b**).* Pale yellow solid. Mp: 86−87 °C. Yield: 105 mg (78%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 1.9 Hz, 1H), 8.58 (dd, J = 8.1, 2.0 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 6.02−5.92 (m, 1H), 5.54 (d, J = 10.1 Hz, 1H), 4.98−4.88 (m, 1H), 2.24−2.06 (m, 3H), 1.99−1.88 (m, 2H),

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1.79−1.66 (m, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 166.1, 165.8, 151.9, 136.6, 133.6, 131.0, 129.3, 125.7, 124.4, 118.7, 48.5, 27.2, 24.4, 21.8. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{14}H_{12}N_2O_4$] 272.0797, found 272.0804.

2-(Cyclohept-2-enyl)-5-nitroisoindoline-1,3-dione (**5c**). White solid. Mp: 108−109 °C. Yield: 105 mg (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 1.9 Hz, 1H), 8.59 (dd, J = 8.1, 2.0 Hz, 1H), 8.03 (d, J = 8.1 Hz, 1H), 6.01−5.83 (m, 1H), 5.71 (dt, J = 11.4, 2.5 Hz, 1H), 5.02 (d, J = 11.7 Hz, 1H), 2.41−2.25 (m, 2H), 2.23−2.11 (m, 1H), 2.10−2.02 (m, 1H), 1.86−1.76 (m, 1H), 1.69 (dddd, J = 14.1, 12.6, 8.4, 3.1 Hz, 2H), 1.51−1.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 165.6, 151.9, 136.6, 133.6, 132.4, 132., 129.3, 124.5, 118.8, 52.6, 33.0, 29.1, 28.7, 26.3. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{15}H_{14}N_2O_4$] 286.0954, found 286.0957.

5-Nitro-2-(1,2,3,4-tetrahydronaphthalen-1-yl)isoindoline-1,3-dione (**5d**). Pale yellow solid. Mp: 130−131 °C. Yield: 113 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66−8.57 (m, 2H), 8.03 (d, J = 8.1 Hz, 1H), 7.16 (d, J = 4.1 Hz, 2H), 7.06 (dt, J = 8.4, 4.2 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 5.59 (dd, J = 10.4, 5.8 Hz, 1H), 3.03 (ddd, J = 16.3, 11.5, 4.5 Hz, 1H), 2.85 (d, J = 16.6 Hz, 1H), 2.39 (ddd, J = 10.6, 9.8, 8.3 Hz, 1H), 2.17−2.10 (m, 2H), 1.93−1.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 165.8, 151.9, 138.1, 136.5, 133.9, 133.5, 129.5, 129.4, 127.4, 126.3, 125.8, 124.6, 118.8, 50.2, 29.4, 28.1, 22.3. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{18}H_{14}N_2O_4$] 322.0954, found 322.0958.

2-(Cyclopent-2-enyl)isoindoline-1,3-dione (**5e**). White solid. Mp: 73−74 °C. Yield: 69 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, J = 5.4, 3.1 Hz, 2H), 7.68 (dd, J = 5.5, 3.0 Hz, 2H), 6.08 (dq, J = 4.5, 2.3 Hz, 1H), 5.62 (dq, J = 4.5, 2.2 Hz, 1H), 5.41−5.35 (m, 1H), 2.80 (dddd, J = 16.4, 9.4, 4.7, 2.6 Hz, 1H), 2.44 (dddd, J = 16.2, 9.0, 4.7, 2.2 Hz, 1H), 2.33 (dtd, J = 13.7, 9.2, 4.5 Hz, 1H), 2.10 (ddd, J = 18.5, 9.5, 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 135.7, 133.9, 132.3, 128.1, 123.2, 56.2, 32.4, 28.3. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{13}H_{11}NO_2$] 213.0790, found 213.0794.

2-(Cyclohex-2-enyl)isoindoline-1,3-dione (**5f**). White solid. Mp: 101−102 °C. Yield: 72 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, J = 5.5, 3.0 Hz, 2H), 7.70 (dd, J = 5.4, 3.1 Hz, 2H), 6.03−5.75 (m, 1H), 5.55 (d, J = 10.1 Hz, 1H), 5.03−4.62 (m, 1H), 2.24−2.02 (m, 3H), 1.99−1.82 (m, 2H), 1.80−1.66 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 134.0, 132.2, 130.2, 126.7, 123.2, 47.6, 27.3, 24.4, 21.9. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{14}H_{13}NO_2$] 227.0946, found 227.0940.

2-(2,3-Dihydro-1H-inden-1-yl)isoindoline-1,3-dione (**5g**). White solid. Mp: 126−127 °C. Yield: 77 mg (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, J = 5.4, 3.0 Hz, 2H), 7.71 (dd, J = 5.4, 3.1 Hz, 2H), 7.30 (d, J = 7.3 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 7.18−7.04 (m, 2H), 5.89 (dd, J = 8.7, 6.8 Hz, 1H), 3.51−3.21 (m, 1H), 3.07−2.93 (m, 1H), 2.52 (qdd, J = 9.0, 7.7, 3.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 144.0, 140.6, 134.1, 132.2, 128.2, 126.7, 125.0, 123.5, 123.3, 54.9, 31.3, 29.9. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{17}H_{13}NO_2$] 263.0946, found 263.0940.

2-(Cyclopent-2-enyl)-4-nitroisoindoline-1,3-dione (**5h**). Light yellow solid. Mp: 127−128 °C. Yield: 109 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62−8.59 (m, 1H), 8.57 (dd, J = 8.1, 2.0 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 6.13 (dq, J = 4.5, 2.3 Hz, 1H), 5.62 (dq, J = 4.5, 2.2 Hz, 1H), 5.41 (dtd, J = 7.2, 4.9, 2.7 Hz, 1H), 2.82 (dddd, J = 14.0, 9.4, 4.7, 2.7 Hz, 1H), 2.51−2.42 (m, 1H), 2.37 (dtd, J = 13.9, 9.2, 4.5 Hz, 1H), 2.10 (ddt, J = 14.0, 9.5, 4.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 162.8, 145.2, 136.6, 135.3, 134.3, 128.4, 127.1, 126.9, 123.8, 57.0, 32.4, 28.0. HRMS (ESI): calcd for $C_{13}H_{10}N_2NaO_4$ (M + Na)$^+$ 281.0538, found 281.0531.

2-(Cyclohex-2-enyl)-4-nitroisoindoline-1,3-dione (**5i**). Pale white solid. Mp: 105−107 °C. Yield: 114 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, J = 7.7, 5.1 Hz, 2H), 7.89 (t, J = 7.8 Hz, 1H), 6.01−5.88 (m, 1H), 5.52 (d, J = 10.1 Hz, 1H), 5.00−4.84 (m, 1H), 2.25−2.01 (m, 3H), 1.99−1.85 (m, 2H), 1.78−1.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 162.8, 145.2, 135.3, 134.2, 130.9, 128.5, 126.9, 125.7, 123.7, 48.45, 27.1, 24.3, 21.8. HRMS (ESI): calcd for $C_{14}H_{12}N_2NaO_4$ (M + Na)$^+$ 295.0695, found 295.0687.

2-(2,3-Dimethylbut-2-enyl)-4-nitroisoindoline-1,3-dione (**5j**). Light yellow solid. Mp: 110−111 °C. Yield: 98 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13−8.03 (m, 2H), 7.90 (dd, J = 8.0, 7.5 Hz, 1H), 4.34 (s, 2H), 1.90 (s, 3H), 1.67 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 163.2, 145.2, 135.3, 134.3, 131.2, 128.5, 127.0, 123.9, 121.5, 41.6, 21.2, 20.6, 16.5. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{14}H_{14}N_2O_4$] 274.0954, found 274.0958.

5-Bromo-2-(cyclopent-2-enyl)isoindoline-1,3-dione (**5k**). White solid. Mp: 123−125 °C. Yield: 98 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 1.4 Hz, 1H), 7.81 (dd, J = 7.9, 1.6 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 6.08 (dq, J = 4.5, 2.3 Hz, 1H), 5.60 (dq, J = 4.4, 2.2 Hz, 1H), 5.39−5.28 (m, 1H), 2.84−2.73 (m, 1H), 2.48−2.38 (m, 1H), 2.32 (dtd, J = 13.8, 9.2, 4.5 Hz, 1H), 2.07 (ddd, J = 18.6, 9.5, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 166.8, 136.9, 135.9, 133.9, 130.8, 128.8, 127.7, 126.5, 124.5, 56.4, 32.3, 28.2. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{13}H_{10}BrNO_2$] 290.9895, found 290.9888.

5-Bromo-2-(cyclohex-2-enyl)isoindoline-1,3-dione (**5l**). White solid. Mp: 123−125 °C. Yield: 107 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 1.6 Hz, 1H), 7.83 (dd, J = 7.9, 1.6 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 5.97−5.90 (m, 1H), 5.53 (d, J = 10.1 Hz, 1H), 4.92−4.83 (m, 1H), 2.23−2.03 (m, 3H), 1.98−1.85 (m, 2H), 1.78−1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.5, 166.9, 137.0, 133.9, 130.8, 130.5, 128.9, 126.6, 126.3, 124.6, 47.9, 27.2, 24.4, 21.9. HRMS (TOF MS EI$^+$): m/z calcd for [$C_{14}H_{12}BrNO_2$] 305.0051, found 305.0057.

1-(Cyclopent-2-enyl)-1H-benzo[d][1,2,3]triazole (**6a**). Yellow oil. Yield: 69 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 6.27 (td, J = 4.4, 2.2 Hz, 1H), 6.12 (ddd, J = 8.6, 5.1, 2.4 Hz, 1H), 5.95 (td, J = 4.3, 2.1 Hz, 1H), 2.86−2.74 (m, 1H), 2.73−2.55 (m, 2H), 2.19 (tt, J = 6.8, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 137.1, 132.0, 128.5, 126.9, 123.8, 120.1, 110.3, 65.9, 32.1, 30.2. HRMS (ESI): calcd for $C_{11}H_{11}N_3Na$ (M + Na)$^+$ 208.0851, found 208.0838.

1-(Cyclohex-2-enyl)-1H-benzo[d][1,2,3]triazole (**6b**). Yellow oil. Yield: 72 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 8.3, 0.9 Hz, 1H), 7.61−7.58 (m, 1H), 7.41 (ddd, J = 8.3, 6.9, 1.0 Hz, 1H), 7.33 (ddd, J = 8.0, 6.9, 1.0 Hz, 1H), 6.21−6.11 (m, 1H), 5.87 (ddd, J = 7.4, 2.2, 1.3 Hz, 1H), 5.64−5.56 (m, 1H), 2.34−2.20 (m, 3H), 2.17−2.07 (m, 1H), 1.99−1.88 (m, 1H), 1.87−1.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 132.9, 132.2, 126.9, 125.1, 123.8, 120.1, 110.6, 56.3, 29.8, 24.7, 20.6. HRMS (ESI): calcd for $C_{12}H_{13}N_3Na$ (M + Na)$^+$ 222.1007, found 222.0990.

(Z)-1-(Cyclooct-2-enyl)-1H-benzo[d][1,2,3]triazole (**6c**). Yellow oil. Yield: 75 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.3 Hz, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.48−7.43 (m, 1H), 7.39−7.32 (m, 1H), 5.98−5.85 (m, 2H), 5.78 (ddd, J = 11.7, 7.1, 4.3 Hz, 1H), 2.44 (ddd, J = 17.1, 11.5, 4.6 Hz, 2H), 2.36−2.16 (m, 2H), 1.89−1.73 (m, 4H), 1.62 (dt, J = 11.9, 8.6 Hz, 1H), 1.57−1.45 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 132.5, 131.8, 128.9, 127.0, 124.0, 120.2, 110.1, 57.9, 35.7, 29.1, 26.6, 26.2, 24.6. HRMS (ESI): calcd for $C_{14}H_{17}N_3Na$ (M + Na)$^+$ 250.1320, found 250.1308.

1-(Cyclopent-2-enyl)-5,6-dimethyl-1H-benzo[d][1,2,3] triazole (**6d**). Light yellow solid. Mp: 56−57 °C. Yield: 78 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.23 (s, 1H), 6.25 (dd, J = 5.6, 2.2 Hz, 1H), 6.05 (ddd, J = 8.4, 5.0, 2.4 Hz, 1H), 5.96−5.90 (m, 1H), 2.83−2.74 (m, 1H), 2.69−2.55 (m, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 2.22−2.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 137.1, 136.8, 133.5, 131.1, 128.7, 119.1, 109.7, 65.7, 32., 30.2, 21.0, 20.5. HRMS (ESI): calcd for $C_{13}H_{15}N_3Na$ (M + Na)$^+$ 236.1164, found 236.1162.

1-(Cyclohex-2-enyl)-5,6-dimethyl-1H-benzo[d][1,2,3] triazole (**6e**). Light yellow solid. Mp: 69−70 °C. Yield: 80 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.31 (s, 1H), 6.30−6.04 (m, 1H), 5.84 (d, J = 10.1 Hz, 1H), 5.51 (td, J = 5.7, 2.8 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 2.23 (ddd, J = 19.7, 11.5, 3.0 Hz, 3H), 2.14−2.03 (m, 1H), 1.92 (dd, J = 9.9, 3.7 Hz, 1H), 1.84−1.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 137.1, 133.5, 132.5, 131.2, 125.3, 119.1,

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109.9, 56.0, 29.6, 24.7, 21.0, 20.6, 20.4. HRMS (ESI): calcd for $C_{14}H_{17}N_3Na$ $(M + Na)^+$ 250.1320, found 250.1317.

*1-(2,3-Dimethylbut-2-enyl)-5,6-dimethyl-1H-benzo[d][1,2,3]-triazole (**6f**).* Light yellow solid. Mp: 108−109 °C. Yield: 89 mg (78%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.12 (s, 1H), 5.17 (s, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.98 (s, 3H), 1.72 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 137.3, 133.4, 132.0, 130.8, 122.0, 118.9, 109.1, 50.9, 21.0, 20.6, 20.4, 16.0. HRMS (ESI): calcd for $C_{14}H_{19}N_3Na$ $(M + Na)^+$ 252.1477, found 252.1472.

*2-Chloro-1-(cyclopent-2-enyl)-1H-benzo[d]imidazole (**6g**).* Colorless oil. Yield: 93 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.25−7.11 (m, 2H), 6.19 (dt, J = 7.7, 2.1 Hz, 1H), 5.83 (ddd, J = 5.7, 4.0, 1.9 Hz, 1H), 5.78 (ddd, J = 10.5, 5.4, 2.9 Hz, 1H), 2.76 (ddt, J = 13.8, 11.3, 4.6 Hz, 1H), 2.63−2.49 (m, 2H), 2.13−1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 140.4, 136.0, 133.9, 128.9, 122.6, 122.4, 119.5, 111.2, 62.8, 32.0, 29.0. HRMS (ESI): calcd for $C_{12}H_{12}ClN_2$ $(M + H)^+$ 219.0689, found 219.0681.

*2-Chloro-1-(cyclohex-2-enyl)-1H-benzo[d]imidazole (**6h**).* Colorless oil. Yield: 99 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.62 (m, 1H), 7.50 (dd, J = 7.1, 1.5 Hz, 1H), 7.26−7.16 (m, 2H), 6.17−6.02 (m, 1H), 5.77 (dd, J = 10.1, 2.1 Hz, 1H), 5.31−5.19 (m, 1H), 2.30−2.18 (m, 2H), 2.08 (td, J = 9.1, 3.5 Hz, 2H), 2.03−1.92 (m, 1H), 1.89−1.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 140.4, 134.1, 132.2, 126.3, 122.7, 122.4, 119.5, 111.8, 53.9, 28.6, 24.5, 21.5. HRMS (ESI): calcd for $C_{13}H_{14}ClN_2$ $(M + H)^+$ 233.0846, found 233.0841.

*2-Chloro-1-(2,3-dimethylbut-2-enyl)-1H-benzo[d]imidazole (**6i**).* Colorless oil. Yield: 95 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.64 (m, 1H), 7.26−7.20 (m, 3H), 4.83 (s, 2H), 1.97 (s, 3H), 1.74 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 141.2, 135.4, 130.0, 123.1, 122.7, 121.8, 119.5, 110.0, 47.2, 21.2, 20.6, 15.2. HRMS (ESI): calcd for $C_{13}H_{16}ClN_2$ $(M + H)^+$ 235.1002, found 235.0997.

*2-Chloro-1-(1,2,3,4-tetrahydronaphthalen-1-yl)-1H-benzo[d]-imidazole (**6j**).* Yellow oil. Yield: 108 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.1 Hz, 1H), 7.20 (dt, J = 20.9, 7.4 Hz, 3H), 7.07−6.95 (m, 2H), 6.76 (d, J = 7.8 Hz, 1H), 6.63 (d, J = 7.2 Hz, 1H), 5.96−5.85 (m, 1H), 3.12−2.89 (m, 2H), 2.35−2.22 (m, 2H), 2.19−2.08 (m, 1H), 2.03−1.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 141.0, 137.6, 133.6, 133.1, 129.4, 127.9, 127.4, 126.7, 122.8, 122.4, 119.5, 111.8, 56.0, 29.6, 29.4, 22.0. HRMS (ESI): calcd for $C_{17}H_{16}ClN_2$ $(M + H)^+$ 283.1002, found 283.0998.

*(R)-2-(2,3-Dihydro-1H-inden-1-yl)benzo[d]isothiazol-3(2H)-one 1,1-Dioxide (**7a**).* White solid. Mp: 112−113 °C. Yield: 107 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, J = 7.0, 1.0 Hz, 1H), 7.86 (dd, J = 6.9, 0.8 Hz, 1H), 7.79 (td, J = 7.5, 1.3 Hz, 1H), 7.74 (td, J = 7.4, 1.3 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.30−7.14 (m, 3H), 5.72 (t, J = 7.3 Hz, 1H), 3.42−3.30 (m, 1H), 3.05−2.93 (m, 1H), 2.62 (ddd, J = 13.4, 6.9, 0.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 144.2, 138.3, 137.7, 134.7, 134.3, 128.7, 127.3, 126.7, 125.0, 124.9, 124.7, 120.8, 57.3, 31.1, 29.8. HRMS (ESI): calcd for $C_{16}H_{13}NNaO_3S$ $(M + Na)^+$ 322.0514, found 322.0509.

*2-(2,3-Dimethylbut-2-en-1-yl)benzo[d]isothiazol-3(2H)-one 1,1-Dioxide (**7b**).* White solid. Mp: 110−111 °C. Yield: 89 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.00 (m, 1H), 7.92−7.77 (m, 3H), 4.43 (s, 2H), 1.90 (s, 3H), 1.72 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 138.0, 134.7, 134.3, 132.1, 127.5, 125.2, 120.9, 120.8, 42.2, 21.3, 20.5, 16.4. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{13}H_{15}NO_3S]$ 265.0773, found 265.0779.

*(E)-Methyl 4-(1,1-Dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)but-2-enoate (**7c**).* Colorless oil. Yield: 91 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13−8.02 (m, 1H), 7.98−7.80 (m, 3H), 6.97 (dt, J = 15.7, 5.5 Hz, 1H), 6.12 (dt, J = 15.7, 1.7 Hz, 1H), 4.50 (dd, J = 5.5, 1.7 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 158.7, 139.8, 137.8, 135.2, 134.7, 127.2, 125.5, 124.4, 121.3, 51.9, 39.2. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{12}H_{11}NO_5S]$ 281.0358, found 281.0363.

*(E)-Ethyl 4-(1,1-Dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)but-2-enoate (**7d**).* Colorless oil. Yield: 95 mg (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.04 (m, 1H), 7.97−7.82 (m, 3H), 6.96 (dt, J = 15.6, 5.4 Hz, 1H), 6.10 (dt, J = 15.6, 1.7 Hz, 1H), 4.50 (dd, J = 5.4, 1.7 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 158.7, 139.4, 137.8, 135.2, 134.7, 127.2, 125.5, 124.7, 121.3, 60.8, 39.2, 14.3. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{13}H_{13}NO_5S]$ 295.0514, found 295.0506.

*2-((1R,3R,5S)-6,6-Dimethyl-2-methylenebicyclo[3.1.1] heptan-3-yl)benzo[d]isothiazol-3(2H)-one 1,1-Dioxide (**7e**).* White solid. Mp: 130−131 °C. Yield: 97 mg (62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, J = 6.7, 1.4 Hz, 1H), 7.93−7.78 (m,3H), 5.72−5.63 (m, 1H), 4.36 (ddd, J = 15.7, 3.7, 1.9 Hz, 1H), 4.17 (dd, J = 15.7, 1.3 Hz, 1H), 2.38 (dt, J = 8.7, 5.6 Hz, 2H), 2.31 (s, 1H), 2.28−2.17 (m, 2H), 2.08 (ddd, J = 5.6, 2.9, 1.8 Hz, 1H), 1.27 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 141.1, 138.0, 134.8, 134.3, 127.5, 125.3, 122.5, 121.0, 43.9, 43.8, 40.7, 38.3, 31.6, 31.4, 26.2, 21.0. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{17}H_{19}NO_3S]$ 317.1086, found 317.1090.

*1,3-Bis(2,3-dimethylbut-2-enyl)-5-fluoropyrimidine-2,4(1H,3H)-dione (**8b**).* White solid. Mp: 73−74 °C. Yield: 58 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, J = 5.5 Hz, 1H), 4.66 (s, 2H), 4.39 (s, 2H), 1.85 (s, 3H), 1.79 (s, 3H), 1.76 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (d, J = 25 Hz), 150.8, 140.2 (d, J = 234 Hz), 131.8 (d, J = 469 Hz), 124.9, 124.5, 121.6, 121.3, 50.1, 44.4, 21.3, 21.1, 20.5, 20.4, 16.4, 15.1. {^{1}H}^{19}F NMR (376 MHz, $CDCl_3$): δ_F −164.5 (CF). HRMS (TOF MS EI$^+$): m/z calcd for $[C_{16}H_{23}FN_2O_2]$ 294.1744, found 294.1750.

*6-Chloro-1-(2,3-dimethylbut-2-enyl)-3-methylpyrimidine-2,4-(1H,3H)-dione (**8d**).* Colorless oil. Yield: 41 mg (35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (s, 1H), 4.77 (s, 2H), 3.34 (s, 3H), 1.78 (s, 3H), 1.71 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 151.7, 146.3, 129.6, 121.5, 102.1, 49.3, 28.6, 21.4, 20.3, 14.5. HRMS (TOF MS EI$^+$): m/z calcd for $[C_{11}H_{15}ClN_2O_2]$ 242.0822, found 242.0825.

Radical-Trapping Procedure. To a Schlenk tube equipped with a magnetic stir bar were added TBAI (37 mg, 0.1 mmol) and nitrophthalimide (0.5 mmol) with olefin 1 (1 mmol) in 2 mL of benzene. Then TBHP (5.5 M in decane, 1 mmol, 0.2 mL) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (2 mol) were added before the vial was sealed, and the reaction mixture was stirred at 80 °C for 12 h. After the required reaction time, the mixture was cooled to room temperature. As expected, the formation of desired product **5b** was suppressed, and only the TEMPO−cyclohexane adduct **5b′** was observed (determined by LC−MS analysis, calcd for $[M + H]^+$ $[C_{15}H_{28}NO]^+$ 238.22, obsd 238.15). The result indicates that the transformation may proceed through a radical pathway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01383.

^{1}H, ^{13}C, and ^{19}F NMR spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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