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Benzylic C(sp^3)−H Functionalization for C−N and C−O Bond Formation via Visible Light Photoredox Catalysis

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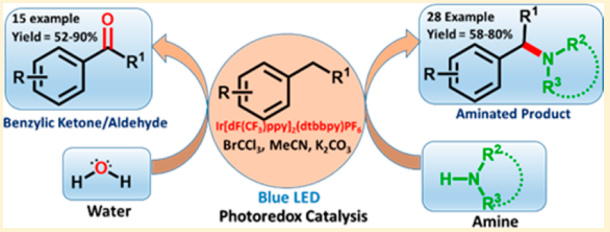
Supporting Information

ABSTRACT: A visible light mediated highly selective benzylic C−H bond functionalization for intermolecular C−N and C−O bond formation is reported. This cross-dehydrogenative coupling reaction demonstrates a straightforward protocol for incorporating the heteroaromatics to the benzylic position. Benzylic oxidation of various alkyl aryls to corresponding carbonyl compounds has also been reported.



INTRODUCTION

Catalytic functionalization of unactivated C(sp^3)−H in a selective and efficient manner remains a most exciting and challenging topic in modern organic chemistry.[1] The assortment of C−H bonds with different electronic and steric environments in a molecule with high bond dissociation energy (BDE) makes this protocol more delicate and difficult.[2] Extensive research in this area has led to discoveries of a few precious methods for saturated C−H bond functionalization for halogenation,[3] oxidation,[4] and amination[5] reactions using metal catalysis. Functionalization of hydrocarbons for C−C bond formation using a carbon centered radical, generated through *tert*-butyl hydroperoxide (TBHP), di-*tert*-butyl peroxide (DTBP), $K_2S_2O_8$, and hypervalent iodine are also known in literature.[6] Directed aliphatic C−H functionalization for C−X (X = O, N, or I) bond formation is achieved with remarkable success.[7,8]

Functionalization of comparatively reactive benzylic C(sp^3)−H over aromatic C(sp^2)−H bond is relatively less well studied; hence, there is a fundamental research interest in this area. Although significant advances have been made in this area by directing group strategies using transition metal catalysis,[9] a major limitation remains the choice of appropriate directing group and its removal.[10] Another popular approach in this area has been the oxidative nondirected C(sp^3)−H bond functionalization using transition metal[11,12] $PhI(OAc)_2$,[13] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[14] and iodoarene[15] as an oxidant; however, this protocol requires an adjacent heteroatom. Recently, oxidative cross-dehydrogenative couplings (CDC) under metal free conditions using oxidants such as DDQ, hypervalent iodine, and *n*-Bu_4NI/TBHP have also been reported for C−C and C−N bond forming reactions (Scheme 1).[16,17] However, owing to the requirement for a strong oxidizing agent, selectivity and applicability have to be compromised. The redox-neutral approach for C−H functionalization via internal hydride transfer has also attracted much attention recently.[18]

An interesting and emerging strategy for the functionalization of the C(sp^3)−H bond via visible light photoredox catalysis is gaining importance in organic synthesis.[19] This atom and step economic strategy with resource efficiency has shifted the routine functional group transformation chemistry toward ideal reactions. During the past decade, considerable success has been made in this area to functionalize the *α*-C(sp^3)−H bond in *t*-amines, alcohols, and ethers and used as main streamline reactions in synthetic chemistry.[20] Although reports on simple C(sp^3)−H functionalization are infrequent in literature,[21] we had reported earlier a protocol for C−O bond formation using 1,4-dicyanonaphthalene (DCN) as a light harvesting photocatalyst (Scheme 1).[22] However, when the same protocol was extended for C−N bond formation, this reaction did not succeed possibly because of competetive electron transfer. To overcome this problem, another concept for benzylic C−N bond formation was developed to produce benzyl cation and trap it by an amine by employing a captodative amine radical, generated by 9,10-dicyanoanthracene (DCA, 410 nm) photocatalysis of *N*-methoxyacetamide[23] followed by another electron transfer (Scheme 1). Very recently, a visible light induced protocol for benzylic oxidation using riboflavin tetraacetate (RFT)/Fe catalyst and molecular oxygen has also appeared (Scheme 1).[24] Therefore, it was felt necessary to develop a highly selective benzylic C(sp^3)−H functionalization for C−N as well as C−O bond formation via visible light photoredox catalysis. We report herein a simple and common strategy for the benzylic C−H functionalization for the C−O as well as C−N bond formations using

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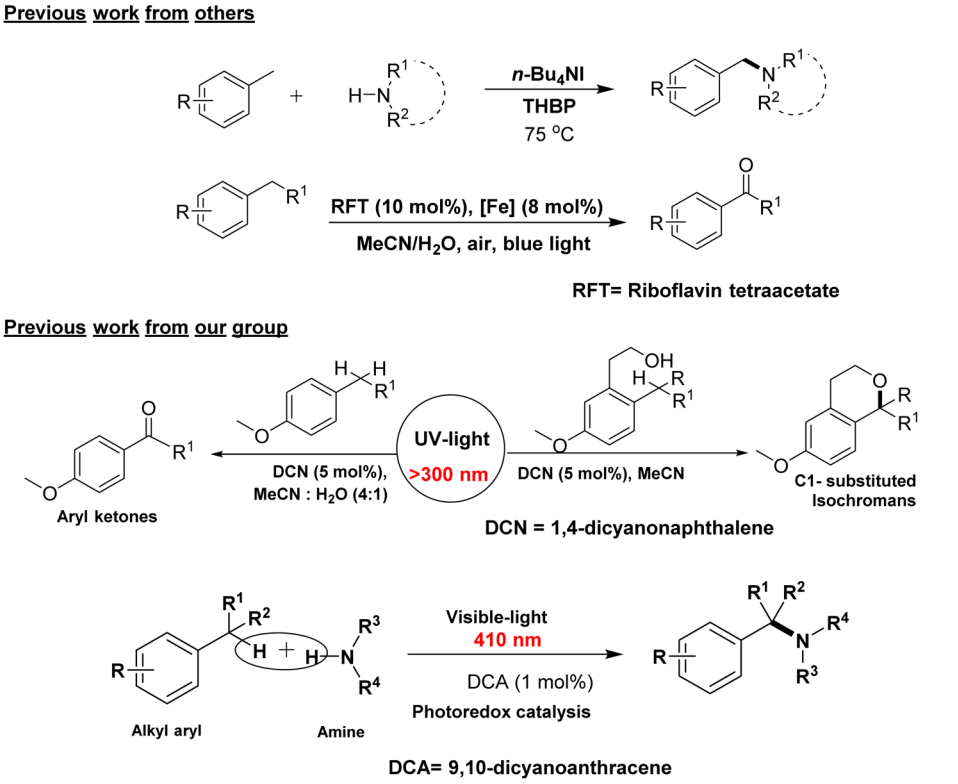
Scheme 1. Benzylic C(sp^3)−H Functionalization Reaction



$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**1**) as a visible light absorbing photoredox catalyst.

Concept. The excited state of the $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ [(Ir(III)*] (**1**) catalyst, achieved by visible light excitation, was designed to transfer an electron to $BrCCl_3$ (**2**) to produce a strong oxidant [Ir(IV)], as well as trichloromethyl radical ($^{\bullet}CCl_3$).[25] A single electron transfer (SET) reaction between highly electron deficient Ir(IV) and electron rich aromatics **3** was expected to generate the corresponding arene radical cation **4**. H-Abstraction from the benzylic C−H of **4** by trichloromethyl radical ($^{\bullet}CCl_3$) was envisioned to produce reactive intermediate **5**, which was expected to react with an amine nucleophile **9** to give **6**. Furthermore, it was also envisioned that the reaction of **5** with moisture could also produce **8** via the corresponding alcohol **7** following the second catalytic cycle as shown in Figure 1.

RESULTS AND DISCUSSIONS

In order to evaluate this proposed concept, initially a reaction between 4-methoxy ethylbenzene **3a** (1 mmol) and different amines (such as pyrrolidine, tosylamine, and $(Boc)_2NH$) was carried out by irradiation with blue LED in the presence of [Ir(III)] (**1**, 1 mol %) as a photocatalyst, $BrCCl_3$ (**2**, 1.5 mmol), and lutidine (1.5 mmol) as a base in CH_3CN. Lutidine was used to neutralize HBr if formed during the course of the reaction. However, no product formation **11** was observed, albeit some degradation of amines was noted (Scheme 2). Therefore, we attempted this reaction using more nucleophilic *N*-heterocyclic amine **9a** (1.5 mmol). After 14 h of irradiation, when ∼80% **3a** disappeared, the reaction was stopped and concentrated. Column chromatography of the crude reaction mixture delightfully gave **6a** in 80% yield (based on recovery of starting material) along with a minor amount of **8a** (15%) (Table 1, entry 1).

A comparative study with Ru(II) $[Ru(bpy)_3Cl_2]$ suggested that the [Ir(III)] catalyst was more efficient (Table 1, entry 2) than Ru(II). Optimization experiments using different bases (Table 1, entries 1, 5, and 6), oxidative quenchers (Table 1, entries 5, 7, and 8), and solvents established that K_2CO_3 is a better base, and CBr_4 and $BrCCl_3$ are comparable oxidants, whereas sodium persulfate salt diminished the overall yield (Table 1, entry 8), and acetonitrile is the most effective solvent for this reaction (Table 1, entries 1, 3, and 4).

A control experiment confirmed that there was no product formation in the absence of light, photocatalyst, or oxidative quencher (Table 1, entries 9, 10, and 11). Our effort toward

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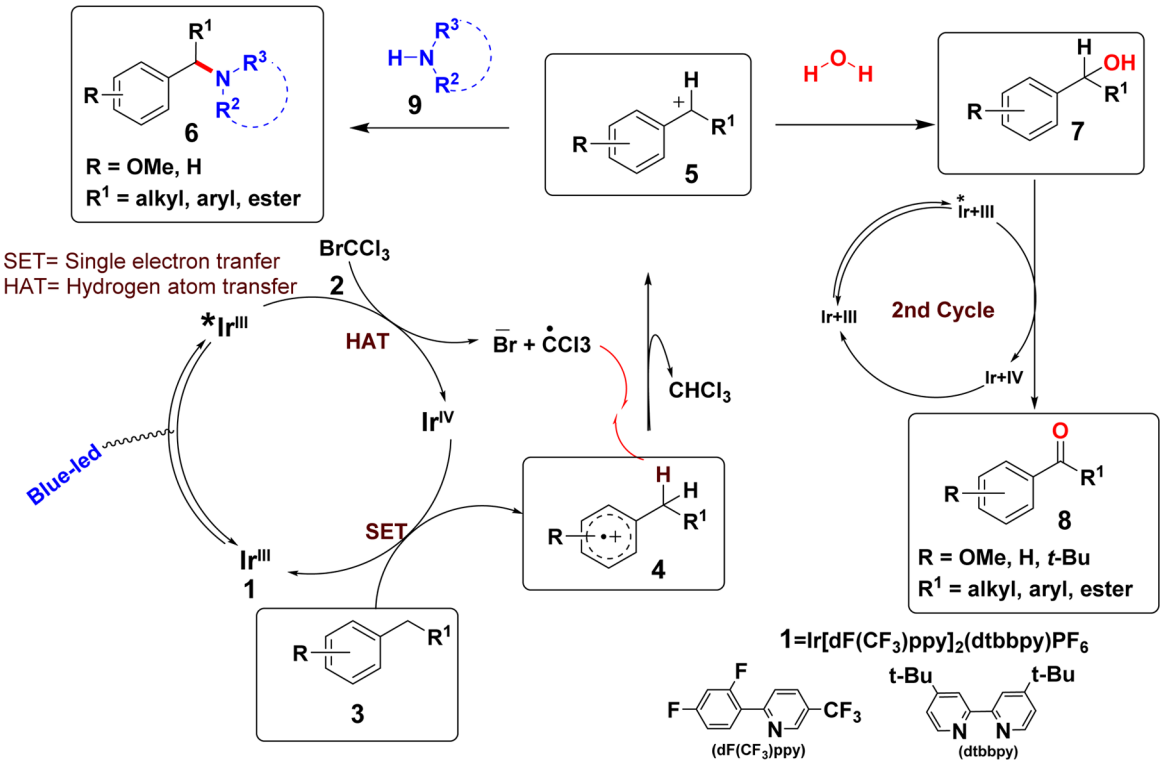


Figure 1. Concept of benzylic C(sp^3)−H functionalization for C−N and C−O bond formation via visible light photoredox catalysis.

Scheme 2. Study of Different Amines

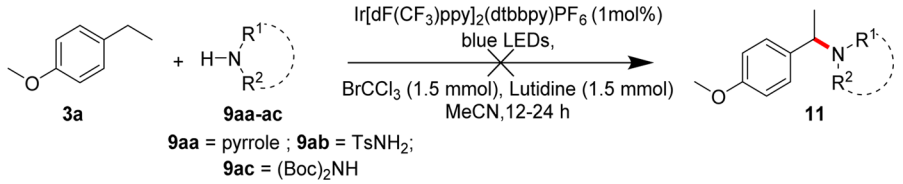
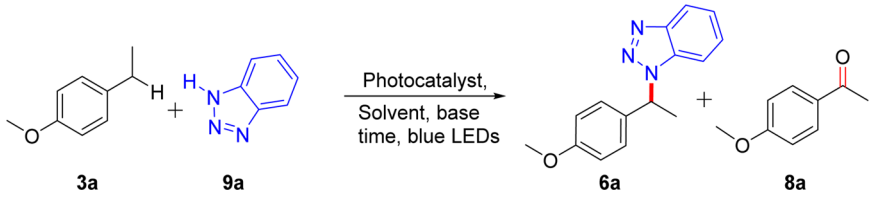


Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	base	time (h)	oxidative quencher	**6a** yield[b] (%)	**8a** yield (%)
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	lutidine	12	$BrCCl_3$	65	15
2	$Ru(bpy)_3Cl_2$	MeCN	lutidine	20	$BrCCl_3$	40	10
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMF	lutidine	20	$BrCCl_3$	35	12
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMSO	lutidine	18	$BrCCl_3$	50	15
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	16	$BrCCl_3$	75	5
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	Cs_2CO_3	16	$BrCCl_3$	70	5
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	16	$CCBr_4$	65	15
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	16	$Na_2S_2O_8$	35	20
9		MeCN	K_2CO_3	12	$BrCCl_3$	0	0
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	12		0	0
11[c]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	16	$BrCCl_3$	0	0

[a]Reaction conditions: 4-methoxyethylbenzene (**3a**, 1.0 mmol), benzotrizole (**9a**, 1.5 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol %), oxidative quencher (1.5 mmol), and base (1.5 mmol) in CH_3CN (5 mL) were irradiated under degassed conditions at rt using blue LED for 12−20 h. Optimum conditions highlighted in bold. [b]Isolated yield of the product **6a**. [c]Reaction was carried out in the dark.

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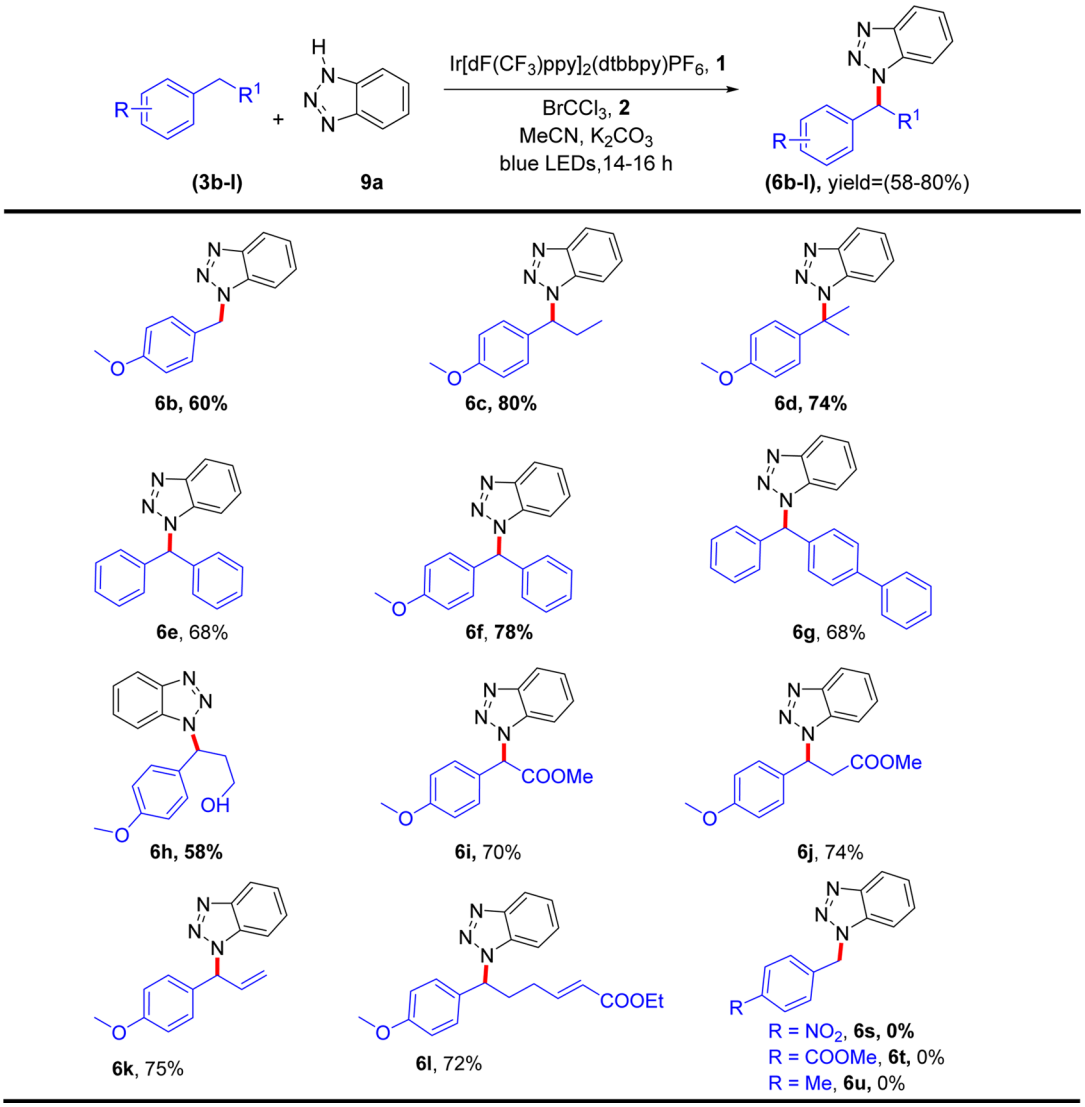
Table 2. Scope of Alkyl Aryl Partner[a]



[a]Reaction conditions: alkyl aryl (**3**, 1.0 mmol), benzotrizole (**9a**, 1.5 mmol), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1 mol %), $BrCCl_3$ (1.5 mmol), and K_2CO_3 (1.5 mmol) in CH_3CN (5 mL) were irradiated under degassed conditions at rt using blue LED for 10−16 h. Reported yields refer to isolated yield of the product **6**.

complete elimination **8a** did not succeed. A control experiment, in identical manner (Table 1,entry 5) but without **9a**, also led to the formation of **8a** (∼10−15%). Therefore, in the presence of **9a**, **6a** is formed along with **8a** due to the presence of moisture.

The generality of this reaction (Table 1 entry 8) was established using various benzylic hydrocarbons, and results are shown in Table 2. To our delight, diphenylmethane, a relatively less electron rich substrate, reacted as well (Table 2, entry **6e**), and electron rich diphenylmethane and biphenyl gave corresponding products in excellent yields (Table 2, entries **6f** and **6g**). Furthermore, functional group tolerance of this methodology was also demonstrated through the preparation of **6h**−**6l**.

This interesting result encouraged us to establish the regioselectivity of this reaction by studying substrates having two different benzylic positions. For example, reaction with 6-methoxytetralene gave **6m** (Table 3) exclusively in excellent yield. Similar selectivity was also observed with the substrates having anelectronically different benzylic position (Table 3, entry **6n**−**6r**). This regioselectivity could be explained by the relative resonance stabilization of the preferred benzylic carbocation by the −OMe group. Substrates bearing electron withdrawing groups such as $-NO_2$ and $-CO_2Me$ were unable to react (entry **6s** and **6t**). A simple dialkylated substrate such as *p*-xylene was also found to be unreactive under these reaction conditions (entry **6u**).

Furthermore, the scope of this reaction was explored with a range of nitrogen heterocycles. For example, reaction with 5-methoxyindane with different heterocyclic amine nucleophiles is summarized in Table 4. The electron withdrawing and electron donating substituents at the 5-position of the benzotriazole ring gave corresponding products in comparable yields (Table 4, entry **10a**, **10c**).[26] Thus, this protocol can be used directly to incorporate potential biologically active groups such as imidazole, benzimidazole, and tetrazole moieties to the benzylic C−H bond (Table 4, entries **10h**−**10j**) of aromatic hydroarbons.

After successfully demonstrating benzylic C−N bond formation through this protocol, we anticipated that this

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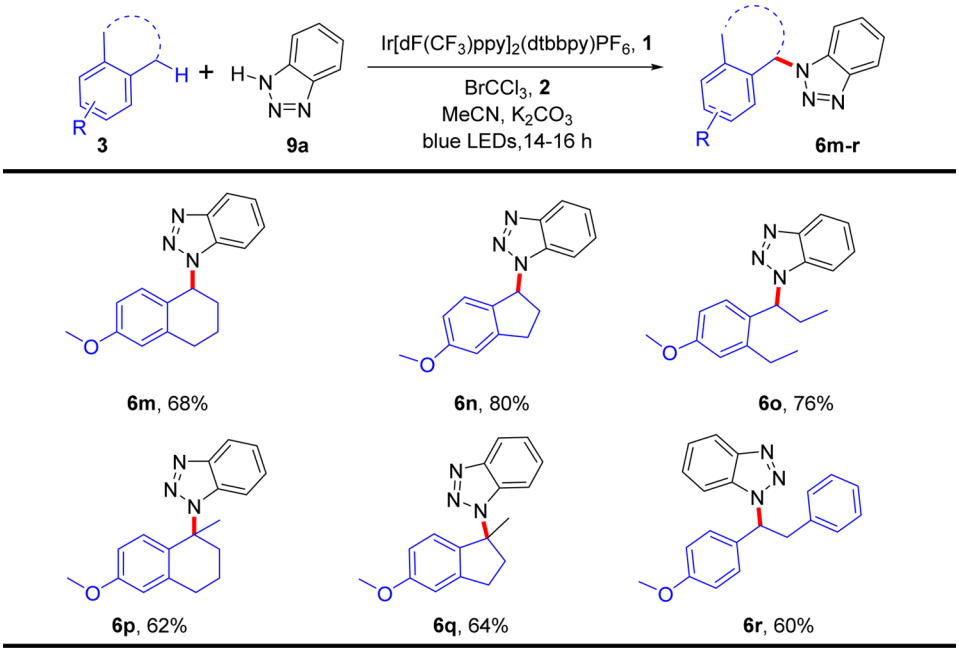
Table 3. Regioselectivity in Benzylic Amination[a]



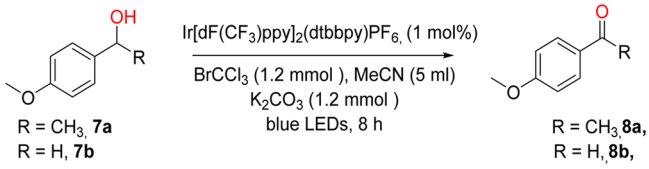
[a]Reaction conditions: alkyl aryl (**3**, 1.0 mmol), benzotrizole (**9a**, 1.5 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (1 mol %), BrCCl$_3$ (1.5 equiv, 1.5 mmol), and K$_2$CO$_3$ (1.5 equiv, 1.5 mmol) in CH$_3$CN (5 mL) were irradiated under degassed conditions at rt using blue LED for 16 h. Reported yields refer to isolated yield of the product **6**.

reaction could also be used for the oxidation of the benzylic position because a small quantity of **8a** was formed during the reaction of **3a** with benzotriazole. Direct oxidation of the benzylic (sp^3)C−H into ketone or aldehyde has been a hot topic of research where many methodologies ranging from stoichiometric use of traditional oxidants[27] to metal catalysis in the presence of either THBP[28] or molecular oxygen[29,30] are reported. Several other oxidants[31] have also been evaluated for this oxidation reaction.

Photoredox catalyzed benzylic oxidation is also reported using 10-methyl-9-phenylacridinium derivatives[32] as light absorbing species in the presence of fluorous-tagged decatungstate,[33] metal porphyrin,[34] and riboflavin tetraacetate (RFT, a vitamin B$_2$ derivative)[24,35] and oxygen. Recently, we have also reported a photoredox protocol for the regio- and chemoselective benzylic oxidation using 1,4-dicyanonaphthalene (DCN) as a photocatalyst and H$_2$O as an oxygen source.[29] However, the use of high intensity UV light (>300 nm) somewhat dwarfs this strategy. Therefore, we contemplated using the present protocol for the benzylic oxidation reaction. Irradiation (22−24 h) of a mixture containing **3a** (1 mmol), [Ir(III)] **1** (1 mol %), BrCCl$_3$ (2.2 mmol), and K$_2$CO$_3$ (2.2 mmol) in moist CH$_3$CN, under identical reaction conditions as described above, provided the corresponding 4-methoxy acetophenone (**8a**) in 62% yield. The strategy was found to be general as exemplified with the number of substrates as shown in Table 5, entries **8a**−**8r**. There was no reaction observed with arenes having electron deficient substituents (entries **8p** and **8q**), as well as with *p*-xylene as mentioned above (entry **8r**). Regio- and chemoselectivity was also established by isolating selectively **8i**, **8j**, and **8l** in good yields. It may be worth mentioning that oxidation of 4-methylanisole produced *para*-anisaldehyde (Table 5, entry **8b**), used as a fragrance and flavoring agent in the food industry,[36] in good yields. Potential use of this reaction could be found in the preparation of **8a** by this simple reaction, which is of high commercial value as a fragrance, food flavoring agent,[36] and antimycobacterial agent.[37]

To implicate the corresponding alcohol as an intermediate (Figure 1) in these oxidations, authentic samples of 1-(4-methoxyphenyl)ethan-1-ol (**7a**) and 4-methoxybenzylalcohol (**7b**) were exposed to the identical reaction conditions as described above which gave **8a** and **8b**, respectively, in 82% and 85% yields (Scheme 3). To provide compelling evidence

Scheme 3. Oxidation of Benzylic Alcohol



of **7a** as an intermediate, **3a** was irradiated for a very short period of time (1−2 h) and analysis of the photolysate by GC showed the formation of **7a**.

CONCLUSION

A visible light photoredox catalyzed reaction using **1** [Ir(III)] is developed for the highly selective benzylic C(sp^3)−H amination, as well as oxidation. This method incorporates potent bioactive azole moieties such as imidazole, benzotriazole, benzimidazole, and tetrazole directly at the benzylic position. Furthermore, the same protocol is extended for the selective benzylic oxidation to prepare industrially and academically important molecules. This straightforward, atom-economic procedure is a new addition to benzylic C−H functionalization for C−N and C−O bond forming reactions.

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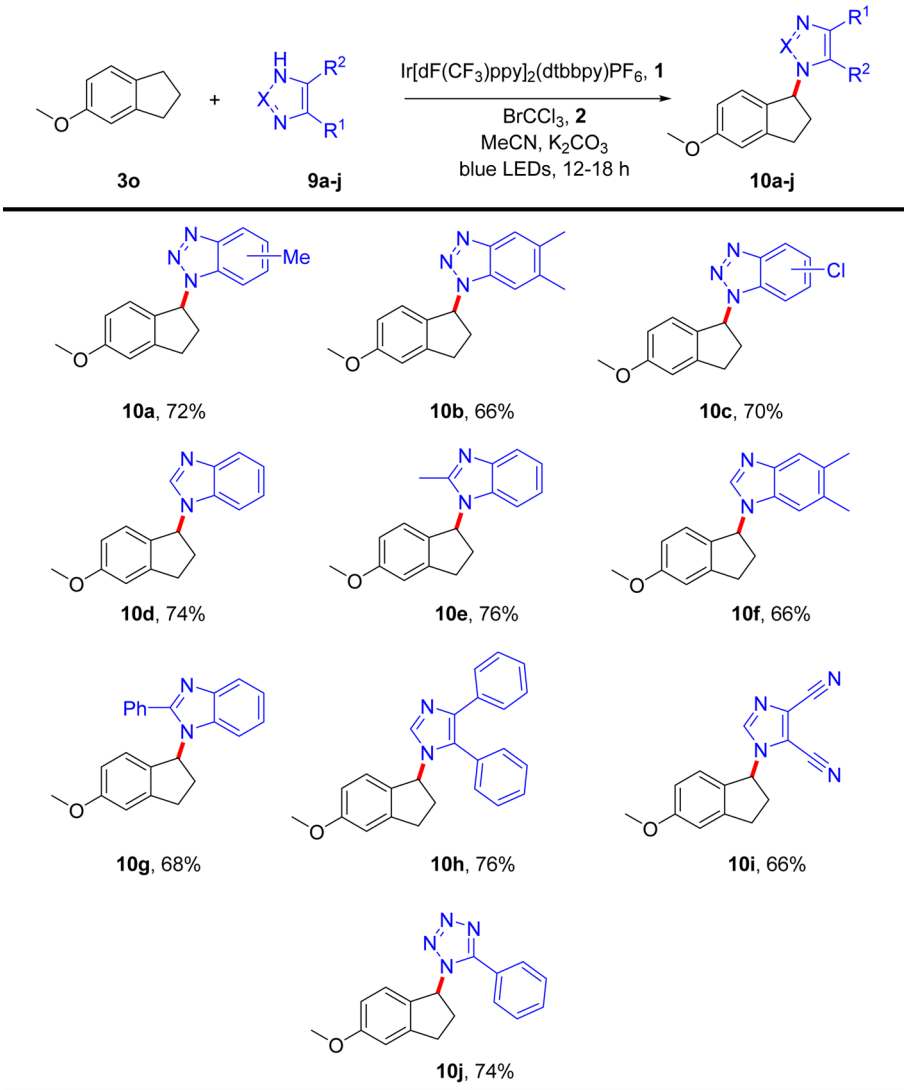
Table 4. Scope of Nucleophiles[a]



[a]Reaction conditions: 5-methoxyindane **3o** (1.0 mmol), nitrogen nucleophile (**9**, 1.5 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ **1** (1 mol %), BrCCl$_3$ **2** (1.5 mmol), and K_2CO_3 (1.5 mmol) in CH_3CN (5 mL) were irradiated under degassed conditions at rt using blue LED for 12−18 h. Reported yields refer to isolated yield of the product **10**.

EXREIMENTAL SECTION

General Information. All glass wares were washed with detergent, rinsed with acetone, and dried in an oven at 125 °C prior to use. Moisture sensitive reactions were carried out in argon atmosphere, and sensitive reagents were added via syringe and cannula techniques. Commercial reagents and solvents were purified and stored according to procedures prescribed in literature. TLC (thin layer chromatography) was performed on silica gel coated aluminum plates, which were visualized by UV fluorescence or by staining with iodine and alcoholic solution of phosphomolybodic acid. CC (column chromatography) was performed on silica gel 60−120, 100−200, or 230−400 mesh. NMR (nuclear magnetic resonance) spectra were recorded on a spectrophotometer at 400 MHz for ^{1}H and 101 MHz for ^{13}C or 800 MHz for ^{1}H and 202 MHz for ^{13}C using deuteriated solvent. Chemical shifts are reported in ppm. Proton coupling constants (J) are reported as absolute values in Hz with multiplicity (s, singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet). Data for NMR spectra are described in terms of chemical shift (δ in ppm) relative to TMS δ (0.00) for proton NMR and the central line of $CDCl_3$ (δ 77.0) for ^{13}C NMR. HRMS (high resolution mass spectra) were performed on Q-TOF using the electron spray ionization (ESI) technique. GCMS (Gas chromatography) was performed with a split-mode capillary injection system and mass detectors using an Agilent HP-1 column (30 m, 0.32 mm ID). Melting points of the products were uncorrected.

General Procedure for Visible Light Photoredox Reactions. *Benzylic C−N Bond Forming Reaction.* An oven dry 25 mL round-bottom flask, equipped with a rubber septum and magnetic stir bar, was charged with alkyl aryl **3** (1.0 mmol), BrCCl$_3$ **2** (1.5 mmol), MeCN (10 mL), K_2CO_3 (1.5 mmol), Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$, (**1**, 1 mol %), and nucleophlic *N*-heterocyclic amine **9** (1.5 mmol) under argon atmosphere. The flask was degassed 3 times using freeze−pump−thaw method. The round-bottom flask was stirred at room temperature at a distance of approximately 2.0 cm from a blue light-emitting diode (LED, λ_{max} = 445 ± 10 nm, 700 mA, 3.0 W) for 16 h. After the reaction was completed (progress of the reaction monitored by TLC), the mixture was poured into a separatory funnel containing 20 mL of EtOAc and 10 mL of H_2O; layers were separated, and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic phases were washed with water and brine (10 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude reaction mixture was purified by

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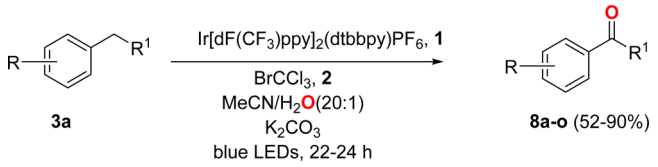
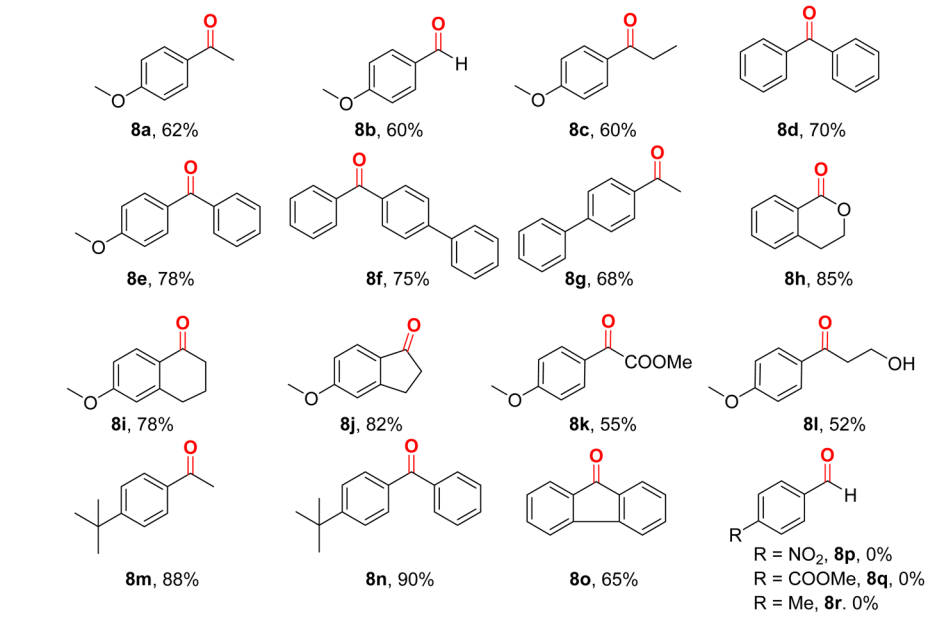
Table 5. Benzylic Oxidation





[a]Reaction conditions: alkyl-aryl (**3**, 1.0 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol %), $BrCCl_3$ (2.2 mmol), and K_2CO_3 (2.2 mmol) in CH_3CN/H_2O (20:1, 10 mL) were irradiated under degassed conditions at rt using blue LED for 22−24 h. Reported yields refer to isolated yields of the product **8**.

silica gel chromatography using pet-ether/ethyl acetate to afford pure product **6**.

1-(1-(4-Methoxyphenyl)ethyl)-1H-benzo[d][1,2,3]triazole (***6a***). Yield 189.8 mg, 75%; thick liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.96−7.90 (m, 1H), 7.26−7.20 (m, 2H), 7.19−7.11 (m, 3H), 6.75 (m, 2H), 5.93 (q, J = 7.1 Hz, 1H), 3.67 (s, 3H), 2.05 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.3, 146.3, 132.2, 132.0, 127.6, 126.9, 123.7, 119.8, 114.1, 110.2, 58.5, 55.2, 21.0. HRMS (ESI, QTOF) calculated for $C_{15}H_{15}N_3O$, $[M + Na]^+$ 276.1107; found 276.1098.

1-(4-Methoxybenzyl)-1H-benzo[d][1,2,3]triazole (***6b***). Yield 138.6 mg, 58%; thick liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.97 (d, J = 8.2 Hz, 1H), 7.35−7.22 (m, 3H), 7.16 (d, J = 8.3 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 5.70 (s, 2H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.6, 146.3, 129.1, 127.3, 126.7, 123.8, 120.0, 114.3, 109.8, 55.2, 51.9. HRMS (ESI, QTOF) calculated for $C_{14}H_{13}N_3O$, $[M + Na]^+$ 262.0951; found 262.0944.

1-(1-(4-Methoxyphenyl)propyl)-1H-benzo[d][1,2,3]triazole (***6c***). Yield 213.6 mg, 80%; thick liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.95 (d, J = 8.2 Hz, 1H), 7.34−7.12 (m, 5H), 6.82−6.66 (m, 2H), 5.58 (t, J = 7.7 Hz, 1H), 3.66 (s, 3H), 2.65 (m, 1H), 2.41 (m, 1H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.3, 146.2, 132.6, 131.1, 128.1, 126.9, 123.7, 119.8, 114.0, 109.9, 64.8, 55.2, 27.9, 11.2. HRMS (ESI, QTOF) calculated for $C_{16}H_{17}N_3O$, $[M + Na]^+$ 290.1264; found 290.1258.

1-(2-(4-Methoxyphenyl)propan-2-yl)-1H-benzo[d][1,2,3]triazole (***6d***). Yield 197.7 mg, 74%; thick liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.96 (m, 1H), 7.21−7.14 (m, 1H), 7.07 (m, 3H), 6.77 (m, 2H), 6.64 (m, 1H), 3.71 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 158.9, 146.9, 136.1, 132.0, 126.6, 126.3, 123.4, 119.8, 114.0, 112.2, 64.3, 55.2, 29.7. HRMS (ESI, QTOF) calculated for $C_{16}H_{17}N_3O$, $[M + Na]^+$ 290.1264; found 290.1259.

1-Benzhydryl-1H-benzo[d][1,2,3]triazole (***6e***). Yield 197.7 mg, 68%; white solid, mp 155−157 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.13−8.05 (m, 1H), 7.39 (s, 1H), 7.38−7.31 (m, 8H), 7.25−7.19 (m, 4H), 7.12−7.05 (m, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.3, 137.7, 133.0, 128.8, 128.4, 128.3, 127.3, 123.9, 120.2, 110.6, 67.2. HRMS (ESI, QTOF) calculated for $C_{19}H_{15}N_3$, $[M + Na]^+$ 308.1158; found 308.1153.

1-((4-Methoxyphenyl)(phenyl)methyl)-1H-benzo[d][1,2,3]triazole (***6f***). Yield 245.8 mg, 78%; white solid, mp 163−164 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.04−7.98 (m, 1H), 7.29−7.24 (m, 6H), 7.19 (s, 1H), 7.14−7.06 (m, 4H), 7.02 (dd, J = 6.9, 2.6 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.6, 146.3, 138.1, 133.0, 129.8, 129.7, 128.8, 128.3, 128.0, 127.3, 123.8, 120.2, 114.1, 110.6, 66.7, 55.3. HRMS (ESI, QTOF) calculated for $C_{20}H_{17}N_3O$, $[M + H]^+$ 316.1444; found 316.1464.

1-([1,1′-Biphenyl]-4-yl(phenyl)methyl)-1H-benzo[d][1,2,3]triazole (***6g***). Yield 245.6 mg, 68%; white solid, mp 179−180 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.08−8.01 (m, 1H), 7.51 (m, 2.7 Hz, 4H), 7.41−7.34 (m, 3H), 7.30 (m, 6H), 7.25 (s, 1H), 7.23−7.17 (m, 3H), 7.13−7.08 (m, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.3, 141.3, 140.2, 137.6, 136.6, 133.0, 128.8, 128.8, 128.8, 128.5, 128.3, 127.6, 127.5, 127.4, 127.1, 123.9, 120.2, 110.5, 66.9. HRMS (ESI, QTOF) calculated for $C_{25}H_{19}N_3$, $[M + H]^+$ 362.1652; found 362.1666.

3-(1H-Benzo[d][1,2,3]triazol-1-yl)-3-(4-methoxyphenyl)propan-1-ol (***6h***). Yield 164.2 mg, 58%; thick liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.02 (d, J = 8.2 Hz, 1H), 7.42−7.36 (m, 2H), 7.32 (d, J = 8.2 Hz, 3H), 6.84 (d, J = 8.3 Hz, 2H), 6.11 (dd, J = 9.0, 6.3 Hz, 1H), 3.76 (s, 3H), 3.69 (m, 1H), 3.63−3.52 (m, 1H), 2.97 (m, 1H), 2.75−2.61 (m, 1H), 2.01 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.4, 145.9, 132.8, 130.8, 128.2, 127.1, 124.0,

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119.7, 114.2, 110.0, 59.2, 58.6, 55.2, 37.4. HRMS (ESI, QTOF) calculated for $C_{16}H_{17}N_3O_2$, $[M + Na]^+$ 306.1213; found 306.1206.

*Methyl 2-(1H-Benzo[d][1,2,3]triazol-1-yl)-2-(4-methoxyphenyl)-acetate (**6i**).* Yield 208.0 mg, 70%; thick liquid. ^1H NMR (400 MHz, chloroform-*d*) δ 8.10−8.00 (m, 1H), 7.37−7.29 (m, 4H), 7.21−7.16 (m, 1H), 6.92 (d, J = 8.4 Hz, 2H), 6.87 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 168.4, 160.3, 146.4, 132.5, 129.7, 127.5, 124.2, 123.9, 120.0, 114.4, 111.1, 65.2, 55.3, 53.1. HRMS (ESI, QTOF) calculated for $C_{16}H_{15}N_3O_3$, $[M + Na]^+$ 320.1006; found 320.1001.

*Methyl 3-(1H-Benzo[d][1,2,3]triazol-1-yl)-3-(4-methoxyphenyl)-propanoate (**6j**).* Yield 230.2 mg, 74%; thick liquid. ^1H NMR (400 MHz, chloroform-*d*) δ 7.96 (d, J = 8.3 Hz, 1H), 7.36−7.28 (m, 2H), 7.23−7.18 (m, 2H), 6.81−6.70 (m, 2H), 6.17 (dd, J = 9.0, 5.9 Hz, 1H), 3.89 (dd, J = 16.7, 9.0 Hz, 1H), 3.68 (s, 3H), 3.56 (s, 3H), 3.30 (dd, J = 16.8, 5.9 Hz, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 170.6, 159.7, 146.2, 132.75, 130.11, 128.00, 127.29, 124.01, 119.89, 114.36, 109.86, 58.92, 55.25, 52.10, 40.18. HRMS (ESI, QTOF) calculated for $C_{17}H_{17}N_3O_3$, $[M + Na]^+$ 334.1162; found 334.1159.

*1-(1-(4-Methoxyphenyl)allyl)-1H-benzo[d][1,2,3]triazole (**6k**).* Yield 198.8 mg, 75%; thick liquid. ^1H NMR (400 MHz, chloroform-*d*) δ 8.00 (d, J = 7.8 Hz, 1H), 7.27 (t, J = 7.0 Hz, 2H), 7.22−7.13 (m, 3H), 6.88−6.73 (m, 2H), 6.62−6.44 (m, 2H), 5.40 (d, J = 9.3 Hz, 1H), 5.10 (d, J = 15.9 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.6, 146.4, 134.5, 132.3, 129.2, 128.8, 127.1, 123.8, 120.1, 119.3, 114.2, 110.5, 65.3, 55.3. HRMS (ESI, QTOF) calculated for $C_{16}H_{15}N_3O$, $[M + Na]^+$ 288.1107; found 288.1111.

*Ethyl (2E,4E)-6-(1H-Benzo[d][1,2,3]triazol-1-yl)-6-(4-methoxyphenyl)hexa-2,4-dienoate (**6l**).* Yield 262.9 mg, 72%; thick liquid. ^1H NMR (800 MHz, chloroform-*d*) δ 8.05 (dd, J = 8.3, 1.0 Hz, 1H), 7.38 (dd, J = 6.8, 1.2 Hz, 1H), 7.35−7.31 (m, 2H), 7.30−7.27 (m, 2H), 6.94 (d, J = 15.7 Hz, 1H), 6.87−6.82 (m, 2H), 5.85−5.68 (m, 2H), 4.18 (m, 2H), 3.76 (s, 3H), 3.04−2.89 (m, 1H), 2.61 (m, 1H), 2.23 (m, 2H), 1.28 (t, J = 7.04 Hz, 3H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 166.3, 159.6, 146.7, 146.2, 132.6, 130.6, 128.0, 127.2, 124.0, 122.6, 120.0, 114.3, 109.7, 62.2, 60.3, 55.3, 33.1, 29.0, 14.2. HRMS (ESI, QTOF) calculated for $C_{21}H_{23}N_3O_3$, $[M + Na]^+$ 388.1632; found 388.1615.

*1-(6-Methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-1H-benzo[d][1,2,3]triazole (**6m**).* Yield 189.8 mg, 68%; white solid, mp 136−138 °C.; ^1H NMR (400 MHz, chloroform-*d*) 8.05 (dd, J = 8.3, 1.1 Hz, 1H), 7.32−7.23 (m, 2H), 6.86 (m, 1H), 6.78 (d, J = 2.6 Hz, 1H), 6.70 (d, J = 8.6 Hz, 1H), 6.61 (dd, J = 8.6, 2.7 Hz, 1H), 6.30 (dd, J = 8.3, 6.0 Hz, 1H), 3.79 (s, 3H), 3.03 (dd, J = 8.9, 5.4 Hz, 1H), 2.95−2.90 (m, 1H), 2.42−2.31 (m, 2H), 2.02 (m, 1H), 1.97−1.90 (m, 1H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 159.2, 146.5, 139.3, 132.1, 129.7, 126.8, 124.9, 123.6, 120.0, 113.8, 112.9, 110.9, 58.7, 55.2, 31.0, 29.6, 20.9. HRMS (ESI, QTOF) calculated for $C_{17}H_{17}N_3O$, $[M + Na]^+$ 302.1264; found 302.1262.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-1H-benzo[d][1,2,3]-triazole (**6n**).* Yield 212.1 mg, 80%; thick liquid. ^1H NMR (400 MHz, chloroform-*d*): δ 8.10−7.98 (m, 1H), 7.35−7.22 (m, 2H), 6.97−6.87 (m, 3H), 6.72 (dd, J = 8.5, 2.4 Hz, 1H), 6.59 (dd, J = 8.4, 6.1 Hz, 1H), 3.82 (s, 3H), 3.29 (m, 1H), 3.16−3.05 (m, 1H), 2.94−2.80 (m, 1H), 2.51 (dd, J = 8.0, 5.8 Hz, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.7, 146.7, 145.5, 131.6, 131.3, 126.9, 125.6, 123.7, 120.1, 113.5, 110.5, 110.0, 64.4, 55.4, 33.0, 31.0; HRMS (ESI, QTOF) calculated for $C_{16}H_{15}N_3O$, $[M + Na]^+$ 288.1107; found 288.1109.

*1-(1-(2-Ethyl-4-methoxyphenyl)propyl)-1H-benzo[d][1,2,3]-triazole (**6o**).* Yield 224.3 mg, 76%; thick liquid. ^1H NMR (800 MHz, chloroform-*d*) ^1H NMR (800 MHz, chloroform-*d*) δ 8.08−7.97 (m, 1H), 7.45−7.41 (m, 1H), 7.35−7.32 (m, 1H), 7.31−7.28 (m, 2H), 6.75 (d, J = 7.6 Hz, 2H), 5.99 (dd, J = 9.2, 5.8 Hz, 1H), 3.77 (s, 3H), 2.84−2.71 (m, 2H), 2.66 (dd, J = 14.8, 7.5 Hz, 1H), 2.42−2.35 (m, 1H), 1.15 (t, J = 7.6 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 159.3, 146.2, 143.6, 132.6, 128.2, 128.0, 126.9, 123.6, 119.9, 114.6, 111.2, 110.0, 61.1, 55.1, 28.3, 25.3, 15.1, 11.5. HRMS (ESI, QTOF) calculated for $C_{18}H_{21}N_3O$, $[M + Na]^+$ 318.1577; found 318.1570.

*1-(6-Methoxy-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1H-benzo[d][1,2,3]triazole (**6p**).* Yield 181.6 mg, 62%; thick liquid. ^1H NMR (800 MHz, chloroform-*d*) δ 8.02 (d, J = 8.3 Hz, 1H), 7.24−7.20 (m, 1H), 7.11 (m, 1H), 6.85 (d, J = 8.7 Hz, 1H), 6.77 (d, J = 2.7 Hz, 1H), 6.64 (dd, J = 8.7, 2.7 Hz, 1H), 6.36 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H), 3.02−2.91 (m, 2H), 2.42 (m, 1H), 2.33 (s, 3H), 2.18 (m, 1H), 2.02−1.95 (m, 1H), 1.89−1.82 (m, 1H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 158.9, 138.4, 130.5, 129.0, 126.4, 123.2, 119.8, 113.5, 113.2, 112.2, 64.0, 55.2, 38.6, 30.3, 30.1, 20.3. HRMS (ESI, QTOF) calculated for $C_{18}H_{19}N_3O$, $[M + Na]^+$ 316.1420; found 316.1416.

*1-(5-Methoxy-1-methyl-2,3-dihydro-1H-inden-1-yl)-1H-benzo[d]-[1,2,3]triazole (**6q**).* Yield 178.6 mg, 64%; thick liquid. ^1H NMR (800 MHz, chloroform-*d*) δ 8.03 (m, 1H), 7.26−7.23 (m, 1H), 7.15 (m, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 2.4 Hz, 1H), 6.78 (dd, J = 8.4, 2.5 Hz, 1H), 6.46 (d, J = 8.5 Hz, 1H), 3.85 (s, 3H), 3.09 (t, J = 7.2 Hz, 2H), 2.71 (d, J = 13.5 Hz, 1H), 2.60−2.45 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 159.2, 146.5, 139.3, 132.1, 129.7, 126.8, 124.9, 123.6, 120.0, 113.8, 112.9, 110.9, 58.7, 55.2, 31.0, 29.6, 21.0. HRMS (ESI, QTOF) calculated for $C_{17}H_{17}N_3O$, $[M + Na]^+$ 302.1264; found 302.1267.

*1-(1-(4-Methoxyphenyl)-2-phenylethyl)-1H-benzo[d][1,2,3]-triazole (**6r**).* Yield 197.5 mg, 60%; white solid, mp 139−141 °C. ^1H NMR (800 MHz, chloroform-*d*) δ 8.05−7.96 (m, 1H), 7.34−7.26 (m, 5H), 7.17−7.10 (m, 3H), 7.07−7.03 (m, 2H), 6.87−6.77 (m, 2H), 5.91 (t, J = 7.8 Hz, 1H), 4.09 (dd, J = 14.0, 8.7 Hz, 1H), 3.75 (s, 3H), 3.72 (dd, J = 14.0, 6.8 Hz, 1H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 159.4, 146.0, 137.2, 132.8, 130.8, 129.1, 128.4, 128.2, 127.0, 126.7, 123.7, 119.9, 114.1, 109.6, 64.8, 55.2, 41.4. HRMS (ESI, QTOF) calculated for $C_{21}H_{19}N_3O$, $[M + Na]^+$ 352.1420; found 352.1414.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-5-methyl-1H-benzo[d]-[1,2,3]triazole (**10a-1**; **10a-2**).* Yield 201.0 mg, 72%; thick liquid. ^1H NMR (400 MHz, chloroform-*d*) ^1H NMR (400 MHz, chloroform-*d*) δ 7.88−7.66 (m, 2H), 7.04 (dd, J = 13.8, 8.5 Hz, 2H), 6.93−6.78 (m, 4H), 6.75−6.60 (m, 4H), 6.55−6.38 (m, 2H), 3.76 (s, 6H), 3.20 (dd, J = 10.5, 5.0 Hz, 2H), 3.03 (m, 2H), 2.78 (m, 2H), 2.48−2.41 (m, 2H), 2.39 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.7, 160.6, 147.3, 145.5, 145.3, 137.4, 133.7, 132.1, 131.5, 131.4, 130.1, 129.0, 126.0, 125.6, 125.5, 119.5, 118.9, 113.48, 113.45, 110.0, 109.9, 109.5, 64.4, 64.1, 55.4, 33.0, 32.8, 30.99, 30.96, 22.0, 21.4. HRMS (ESI, QTOF) calculated for $C_{17}H_{17}N_3O$, $[M + Na]^+$ 302.1264; found 302.1253.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-5,6-dimethyl-1H-benzo[d][1,2,3]triazole (**10b**).* Yield 293.5 mg, 66%; thick liquid. ^1H NMR (400 MHz, chloroform-*d*): δ 7.76 (s, 1H), 6.97−6.84 (m, 2H), 6.77−6.63 (m, 2H), 6.50 (t, J = 7.4 Hz, 1H), 3.80 (s, 3H), 3.28 (m, 1H), 3.07 (m, 1H), 2.82 (m, 1H), 2.50 (m, 1H), 2.33 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 160.4, 145.7, 145.1, 136.9, 133.3, 131.5, 130.5, 125.3, 118.8, 113.3, 109.8, 109.6, 63.9, 55.2, 32.6, 30.8, 20.8, 20.2. HRMS (ESI, QTOF) calculated for $C_{18}H_{19}N_3O$, $[M + H]^+$ 294.1601; found 294.1604.

*5-Chloro-1-(5-methoxy-2,3-dihydro-1H-inden-1-yl)-1H-benzo[d]-[1,2,3]triazole (**10c-1**; **10c-2**).* Yield 215.3 mg, 72%; thick liquid. ^1H NMR (400 MHz, chloroform-*d*) δ 7.92−7.86 (m, 2H), 7.15 (m, 2H), 6.86−6.80 (m, 4H), 6.75−6.59 (m, 4H), 6.47 (m, 2H), 3.74 (s, 6H), 3.19 (m, 2H), 3.01 (m, 2H), 2.86−2.71 (m, 2H), 2.46−2.28 (m, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.8, 147.2, 145.5, 145.3, 145.1, 133.1, 132.1, 130.70, 130.67, 130.2, 129.5, 127.7, 125.5, 125.4, 124.8, 120.9, 119.2, 113.6, 113.6, 111.3, 110.04, 110.01, 110.0, 64.6, 64.4, 55.3, 55.3, 33.0, 32.9, 30.89, 30.85. HRMS (ESI, QTOF) calculated for $C_{16}H_{14}ClN_3O$, $[M + Na]^+$ 322.0718; found 322.0714.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-1H-benzo[d]imidazole (**10d**).* Yield 195.5 mg, 74% thick liquid. ^1H NMR (400 MHz, chloroform-*d*): δ 7.79−7.70 (m, 1H), 7.65 (d, J = 1.3 Hz, 1H), 7.26−7.10 (m, 3H), 6.98 (d, J = 8.3 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.71 (dd, J = 8.5, 2.5 Hz, 1H), 5.84 (t, J = 6.6 Hz, 1H), 3.76 (s, 3H), 3.05 (dd, J = 9.1, 5.8 Hz, 1H), 2.95 (m, 1H), 2.76−2.57 (m,

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1H), 2.36−2.16 (m, 1H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 160.7, 145.6, 144.3, 141.9, 133.2, 131.5, 125.7, 122.6, 122.1, 120.4, 113.6, 110.4, 110.1, 60.2, 55.4, 33.7, 30.6. HRMS (ESI, QTOF) calculated for $C_{17}H_{16}N_2O$, $[M + H]^+$ 265.1335; found 265.1337.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-2-methyl-1H-benzo[d]-imidazole (**10e**).* Yield 211.4 mg, 76%; white solid, mp 125−127 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.23−7.01 (m, 2H), 6.87 (d, m,, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.64 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.91 (t, *J* = 8.3 Hz, 1H), 3.76 (s, 3H), 3.19−3.07 (m, 1H), 2.99 (m, 1H), 2.62 (d, *J* = 15.6 Hz, 4H), 2.33 (m, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.4, 151.6, 144.5, 131.7, 125.2, 121.74, 121.71, 118.9, 113.3, 110.1, 60.1, 55.4, 32.0, 30.6, 14.6. HRMS (ESI, QTOF) calculated for $C_{18}H_{18}N_2O$, $[M + H]^+$ 279.1492; found 279.1488.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-5,6-dimethyl-1H-benzo[d]imidazole (**10f**).* Yield 192.8 mg, 66%; thick liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.32 (d, *J* = 9.4 Hz, 2H), 5.79 (d, *J* = 8.4 Hz, 1H), 5.74 (s, 1H), 5.65 (s, 1H), 5.52 (dd, *J* = 8.5, 2.3 Hz, 1H), 4.59 (t, *J* = 6.7 Hz, 1H), 2.58 (s, 3H), 1.93−1.81 (m, 1H), 1.74 (m, 1H), 1.52−1.39 (m, 1H), 1.11 (s, 3H), 1.09 (s, 3H), 1.04 (m, 1H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 160.6, 145.5, 142.9, 141.1, 131.84, 131.78, 131.69, 131.0, 125.7, 120.3, 113.5, 110.5, 110.1, 60.1, 55.4, 33.7, 30.6, 20.6, 20.2. HRMS (ESI, QTOF) calculated for $C_{19}H_{20}N_2O$, $[M + H]^+$ 293.1653; found 293.1648.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-2-phenyl-1H-benzo[d]-imidazole (**10g**).* Yield 231.3 mg, 68%; white solid, mp 293−294 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.87−7.71 (m, 3H), 7.52 (dd, *J* = 5.4, 1.9 Hz, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.67 (dd, *J* = 18.4, 8.2 Hz, 2H), 6.14 (t, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.18 (m, 1H), 2.99 (m, 1H), 2.70−2.53 (m, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.2, 154.4, 144.2, 143.7, 133.33, 132.28, 130.8, 129.7, 129.5, 128.7, 124.8, 122.2, 122.0, 120.0, 113.2, 112.5, 110.1, 61.0, 55.4, 32.0, 30.4. HRMS (ESI, QTOF) calculated for $C_{23}H_{20}N_2O$, $[M + H]^+$ 341.1648; found 341.1644.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-4,5-diphenyl-4,5-dihydro-1H-imidazole (**10h**).* Yield 278.0 mg, 76%; thick liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.40 (d, *J* = 6.6 Hz, 5H), 7.36−7.31 (m, 2H), 7.19 (s, 1H), 7.12 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.04 (dd, *J* = 19.0, 7.8 Hz, 2H), 6.77−6.70 (m, 2H), 5.30 (t, *J* = 7.0 Hz, 1H), 3.75 (s, 3H), 2.97 (m, 1H), 2.76 (m, *J* = 16.0, 7.7 Hz, 1H), 2.44 (m, 1H), 2.15−2.03 (m, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.5, 145.4, 137.9, 134.9, 134.6, 133.0, 131.12, 131.10, 129.1, 128.8, 128.7, 128.1, 126.5, 126.2, 125.4, 113.6, 109.9, 59.5, 55.5, 35.8, 30.4. HRMS (ESI, QTOF) calculated for $C_{25}H_{22}N_2O$, $[M + H]^+$ 367.1805; found 367.1808.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-1H-imidazole-4,5-dicarbonitrile (**10i**).* Yield 117.0 mg, 66%; white solid, mp 138−140 °C. ^{1}H NMR (800 MHz, chloroform-*d*) δ 7.37 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.94−6.82 (m, 2H), 5.83 (dd, *J* = 7.8, 4.0 Hz, 1H), 3.84 (s, 3H), 3.16 (m, 1H), 3.05 (m, 1H), 2.94−2.77 (m, 1H), 2.27 (m, 1H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 161.6, 146.3, 139.83, 139.81, 139.79, 128.8, 125.7, 123.5, 114.4, 111.6, 111.4, 110.2, 107.8, 63.4, 55.5, 34.7, 30.4. HRMS (ESI, QTOF) calculated for $C_{15}H_{12}N_4O$, $[M + Na]^+$ 287.0903; found 287.0895.

*1-(5-Methoxy-2,3-dihydro-1H-inden-1-yl)-5-phenyl-1H-tetrazole (**10j**).* Yield 146.0 mg, 74%; white solid, mp 75−77 °C. ^{1}H NMR (800 MHz, chloroform-*d*) δ 8.22−8.01 (m, 2H), 7.43 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.35 (t, *J* = 6.2 Hz, 1H), 3.77 (s, 3H), 3.43−3.35 (m, 1H), 3.07−2.99 (m, 1H), 2.78 (q, *J* = 7.3 Hz, 2H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 165.0, 160.8, 145.9, 131.3, 130.0, 128.7, 127.5, 126.7, 125.6, 113.3, 109.8, 67.8, 55.3, 32.4, 30.9. HRMS (ESI, QTOF) calculated for $C_{17}H_{16}N_4O$, $[M + Na]^+$ 315.1216; found 315.1208.

General Procedure for Benzylic Oxidation. An oven dry 25 mL round-bottom flask, equipped with a rubber septum and magnetic stir bar was charged with 4-methoxyethylbenzene **3** (1.0 mmol), $BrCCl_3$ **2** (2.2 mmol), K_2CO_3 (2.2 mmol), $MeCN/H_2O$ (20:1; 10 mL), and $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ **1** (1 mol %) under argon atmosphere. The flask was degassed 3 times using freeze−pump−thaw method. The round-bottom flask was stirred at room temperature at a distance of approximately 2 cm from blue light-emitting diodes (LED, λ_{max} = 445 ± 10 nm, 700 mA, 3.0 W) for 22−24 h. After reaction was completed (progress of the reaction was monitored by TLC), the mixture was poured into a separatory funnel containing 20 mL of EtOAc and 10 mL of H_2O, layers were separated, and the aqueous layer was extracted with ethyl acetate (2 × 10 mL).The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude reaction mixture was purified by silica gel chromatography using pet-ether/ethyl acetate to afford pure product **8**. The identity of reported compounds was confirmed by matching ^{1}H and ^{13}C and GCMS data of compound **8b**,[28a] **8c**,[38] **8d**,[28a] **8e**,[22] **8g**,[38] **8i**,[38] **8j**,[38] **8k**,[31h] **8l**,[22] **8m**,[22] **8n**,[22] and **8o**[28a] authentic samples. The ^{1}H and ^{13}C data of representative compounds **8a**, **8f**, and **8h** are given below.

*1-(4-Methoxyphenyl)ethan-1-one (**8a**).* Yield 93.6 mg, 62%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 196.4, 163.2, 130.3, 130.0, 113.4, 55.1, 26.0.

*[1,1′-Biphenyl]-4-yl(phenyl)methanone (**8f**).* Yield 165.7 mg, 75%; white solid, mp 100−102 °C. ^{1}H NMR (800 MHz, chloroform-*d*) δ 7.93−7.79 (m, 4H), 7.73−7.68 (m, 2H), 7.67−7.62 (m, 2H), 7.62−7.57 (m, 1H), 7.49 (dt, *J* = 15.7, 7.7 Hz, 4H), 7.40 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (201 MHz, chloroform-*d*) δ 196.3, 145.2, 139.9, 137.7, 136.2, 132.3, 130.7, 130.0, 128.9, 128.3, 128.1, 127.3, 126.9.

*Isochroman-1-one (**8h**).* Yield 125.8 mg, 85%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 4.42 (t, *J* = 6.0 Hz, 2H), 2.96 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 164.9, 139.4, 133.5, 130.03, 130.00, 129.98, 127.4, 127.1, 125.0, 76.7, 67.1, 27.5.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00970.

^{1}H NMR and ^{13}C NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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