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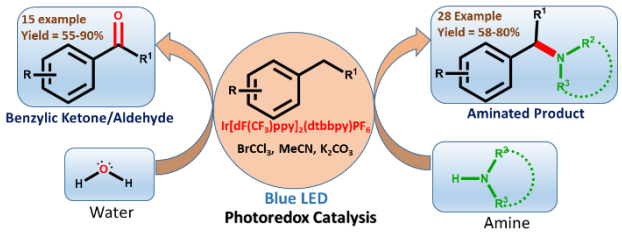


Abstract: A visible light mediated highly selective benzylic C–H bond functionalization for inter molecular C–N and C–O bond formation is reported. This cross-dehydrogenative coupling reaction demonstrates a straightforward protocol for incorporating the heteroaromatics to benzylic position. Benzylic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

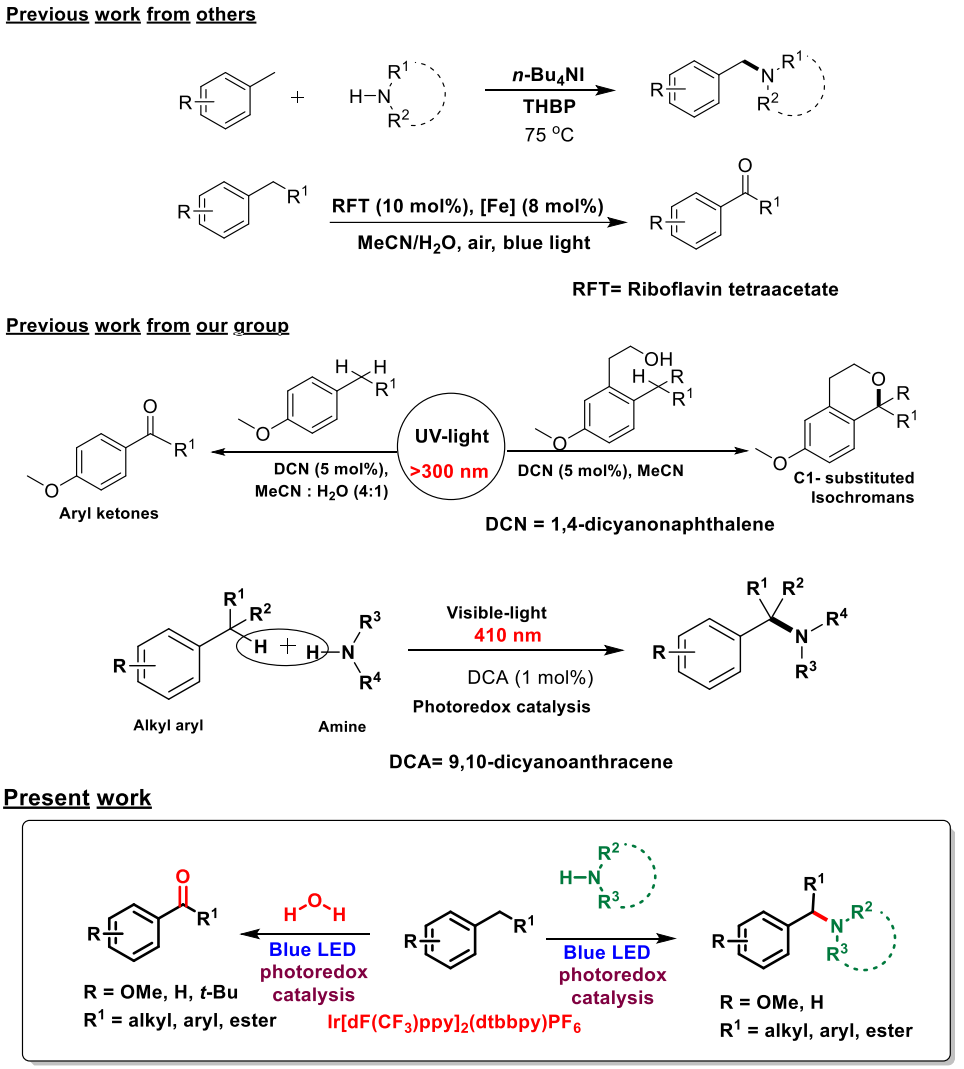
Introduction:

Catalytic functionalization of un-activated C(sp^3)–H in a selective and efficient manner remains most exciting and challenging topic in modern organic chemistry.[1] Assortment of C–H bonds with different electronic and steric environment in a molecule with high bond dissociation energy (BDE) makes this protocol more delicate and difficult.[2] Extensive research in this area have led to discoveries of few precious methods for saturated C–H bond functionalization for halogenation,[3] oxidation[4] and amination[5] reactions using metal catalysis. Functionalization of hydrocarbon for C–C bond formation using carbon centered radical, generated through TBHP, 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, 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 not so well studied, hence, there is a fundamental research interest in this area. Although significant advances have been made in this area by directing group strategy using transition metal catalysis,[9] major limitation remains the choice of appropriate directing group and its removal.[10] Another popular approach in this area has been the oxidative non-directed C(sp^3)–H bond functionalization using transition metal[11,12] $PhI(OAc)_2$,[13] 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, *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 of 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 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 towards ideal reactions. During last decade, considerable success has been made in this area to functionalize the α-C(sp^3)–H bond in *t*-amines, alcohols, ethers and used as main streamline reactions in synthetic chemistry.[20] Although, reports on simple C(sp^3)–H functionalization is infrequent in literature,[21] we had reported earlier a protocol for C–O bond formation using DCN (1,4-dicyanonaphthalene) as a light harvesting photocatalyst (Scheme 1).[22] However, when same protocol was extended for C–N bond formatiom, 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 its trapping by an amine by employing a captodative amine radical, generated by DCA (9-10 dicyanoanthracene, 410 *nm*) photocatalysis of *N*-methoxyacetamide[23] followed by another electron transfer (Scheme 1). Very recently, visible light induced protocol for benzylic oxidation using RFT (Rivoflavin tetraacetate)/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 $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**1**) as a visible light absorbing photoredox catalyst.

Scheme 1: Benzylic C(sp^3)–H Functionalization Reaction:



Concept: Excited state of 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 an strong oxidant [Ir(IV)] as well as trichloromethyl radical ($^{\cdot}CCl_3$).[25] SET (single electron transfer) reaction between highly electron deficient Ir(IV) and electron rich aromatics **3** was expected to generate corresponding arene radical cation **4**. H-abstraction from benzylic C–H of **4** by trichloromethyl radical ($^{\cdot}CCl_3$) 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* corresponding alcohol **7** following the 2nd catalytic cycle as shown in Fig. 1.

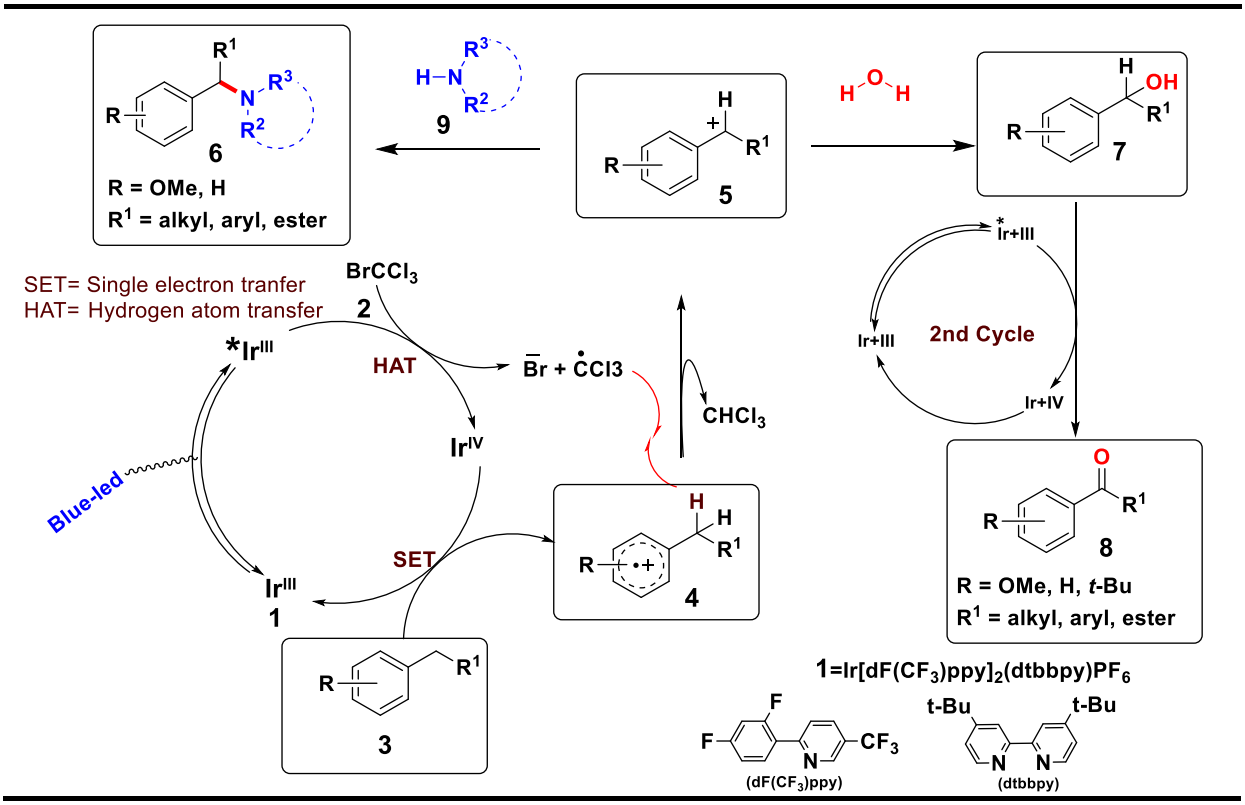
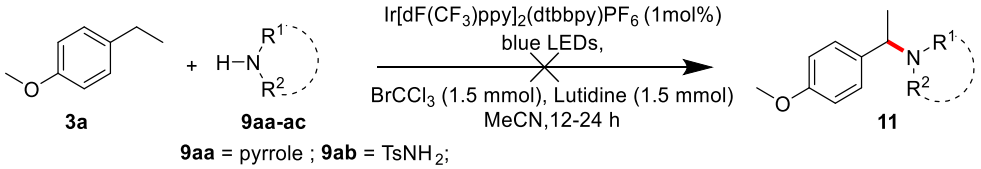


Figure 1: Concept of Benzylic C(sp^3)–H Functionalization for C–N and C–O Bond Formation Via Visible-Light-Photoredox Catalysis.

Results and Discussions:

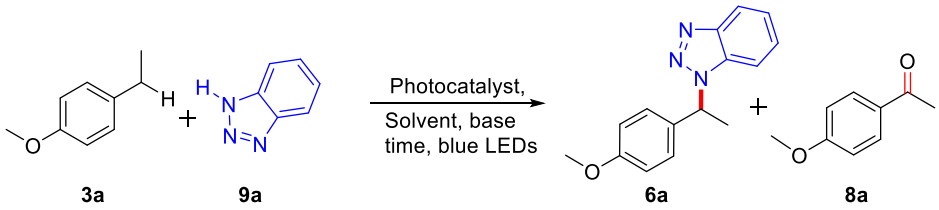
In order to evaluate this proposed concept, initially a reaction between 4-methoxy ethyl benzene **3a** (1 mmol) and diffrent amines (such as pyrrolidine, tosylamine and $(Boc)_2NH$) were carried out by irridiating with blue LED in the presence of [Ir(III)] (**1,** 1 mol%) as a photocatalyst, $BrCCl_3$ (**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 were noted (Scheme 2). Therefore, we attempted this reaction using more nucleophlic *N*-heterocyclic amine **9a** (1.5 mmol). After 14 h of irradiation, when ~80 % **3a** was disappeared, reaction was stopped and cocentrated. Column chromatography of the crude reaction mixture delightfully gave **6a** in 80 % yield (based on recovery of starting material) along with minor amount of **8a** (15%) (Table 1, entry 1).

Scheme 2: Study of Diffrent Amine



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

Table 1: Optimization of Reaction Conditions.[a]



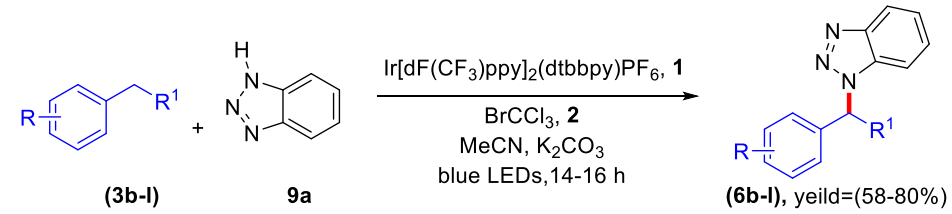
3a 9a 6a 8a

Entry	Catalyst	Solvent	Base	Time(h)	Oxidative Quencher	Product 6a Yield[b] (%)	Ketone 8a Yield(%)
1	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	Lutidine	12 h	$BrCCl_3$	65	15
2	$Ru(bpy)_3Cl_2$	MeCN	Lutidine	20 h	$BrCCl_3$	40	10
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMF	Lutidine	20 h	$BrCCl_3$	35	12
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMSO	Lutidine	18 h	$BrCCl_3$	50	15
5	**$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$**	**MeCN**	**K_2CO_3**	**16 h**	**$BrCCl_3$**	**75**	**5**
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	Cs_2CO_3	16 h	$BrCCl_3$	70	5
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	16 h	$CCBr_4$	65	15
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	16 h	$Na_2S_2O_8$	35	20
9	----------	MeCN	K_2CO_3	12 h	$BrCCl_3$	0	0
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	12 h	---------	0	0
11[c]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	K_2CO_3	16 h	$BrCCl_3$	0	0

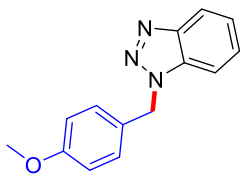
[a]Reaction conditions: 4-methoxyethylbenzene (**3a**, 1.0 mmol), benzotrizole (**9a**, 1.5 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol%), oxidative quencher (1.5 mmol) base (1.5 mmol) in CH_3CN (5 mL) were irradiated under degassed condition at rt using blue LED for 12–20 h; [b]Isolated yield of the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

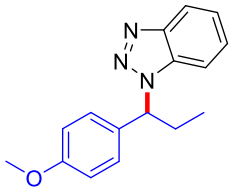
A control experiment confirmed that there was no product formation in the absence of light, photocatalyst or oxidative quencher (Table 1, entry 9, 10, 11). Our effort towards complete elimination **8a** did not succeded. A control experiment, in identical manner (Table 1,entry 5), but without **9a** also led the formation of **8a** (~10-15%). Therefore, in the presence of **9a, 6a** is formed along with **8a** due to the presence of moisture.

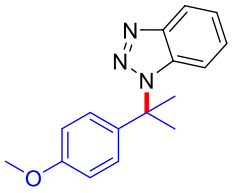
Table 2: Scope of Alkyl Aryls Partner[a,b]

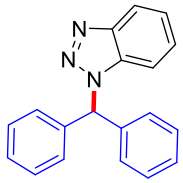


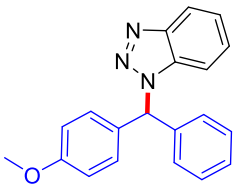
(3b-l) 9a (6b-l), yeild=(58-80%)

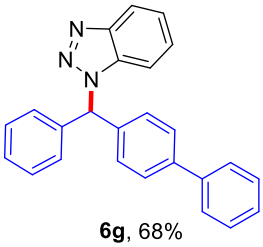

6b, 60%

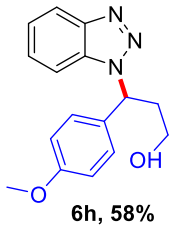

6c, 80%

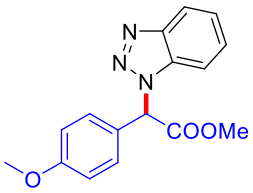

6d, 74%


6e, 68%

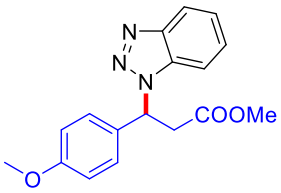

6f, 78%


6g, 68%

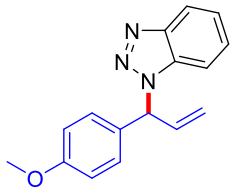

6h, 58%

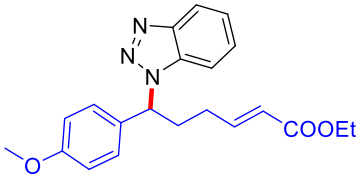


6i, 70%

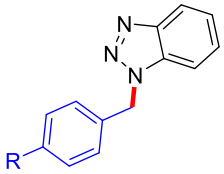


6j, 74%


6k, 75%



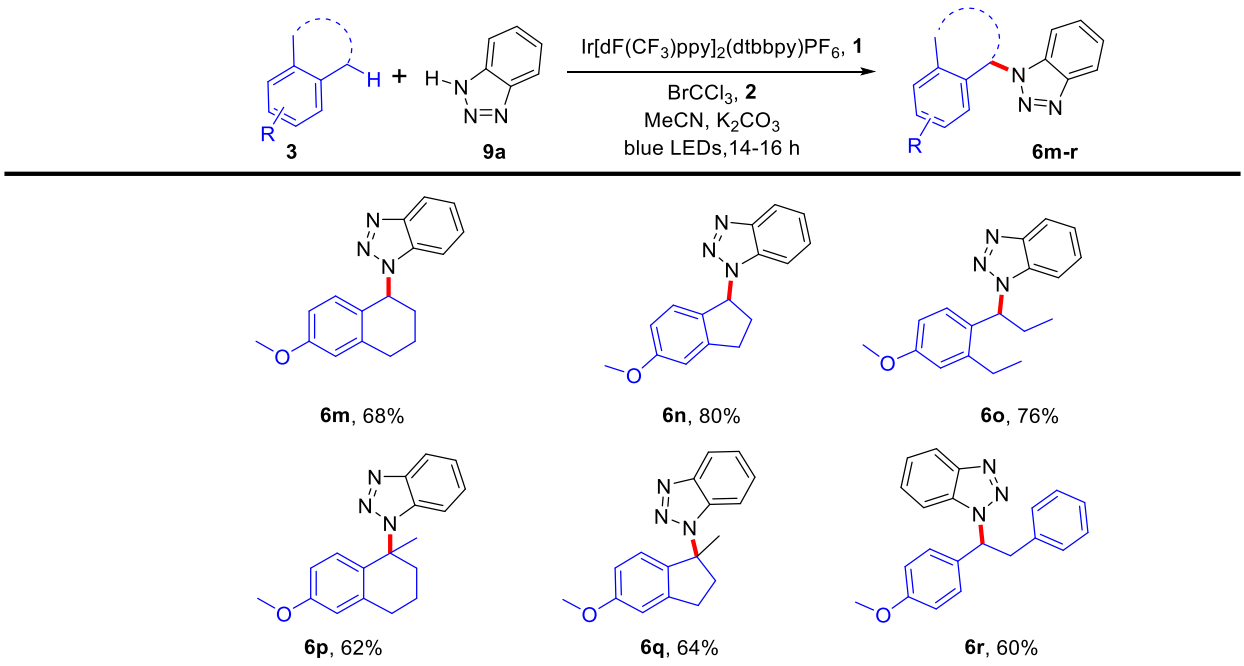
6l, 72%


R = NO_2, **6s, 0%**
R = COOMe, **6t,** 0%
R = Me, **6u,** 0%

[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 condition at rt using blue LED for 10-16 h. [b]Isolated yield of the product **6**.

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 also reacted as well (Table 2, entry **6e**) and electron rich diphenylmethane and biphenyl gave corresponding products in excellent yields (Table 2, entry **6f** and **6g**). Furthermore, functional group tolerance of this methodology was also demonstrated through the preparation of **6h-6l**.

Table 3: Regioselectivity in Benzylic Amination[a,b]

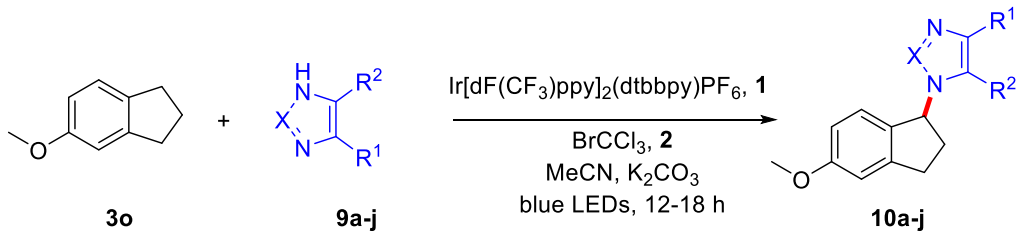


[a]Reaction conditions: alkyl aryl (**3**, 1.0 mmol), benzotrizole (**9a**, 1.5 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol%) , $BrCCl_3$ (1.5 eq, 1.5 mmol) and K_2CO_3 (1.5 eq, 1.5 mmol) in CH_3CN (5 mL) were irradiated under degassed condition at rt using blue LED for 16 h. [b]Isolated yield of the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

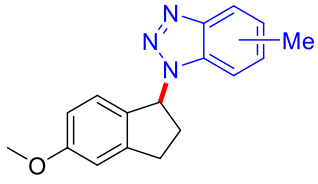
This interesting result encouraged us to establish the regioselectivity of this reaction by studying substrates having two different benzylic positions. For example, reaction with 6-methoxytetralene gave **6m** (Table 3) exclusively in excellent yield. Similar selectivity was also observed with the substrates having electronically different benzylic position (Table 3, entry **6n-6r**). This regioselectivity could be explained by the relative resonance stabilization of preferred benzylic carbocation by –OMe group. Substrates bearing electron withdrawing groups such as $–NO_2$ and $–CO_2Me$ were unable to react (entry **6s** and **6t)**. Simple di-alkylated substrate such as *p*-xylene was also found to un-react under this 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 substituent at 5-position of benzotriazole ring gave corresponding products in comparative 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 moiety to the benzylic C–H bond (Table 4, entry **10h-10j**) of aromatic hydroarbons.

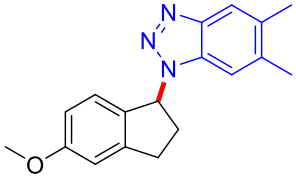
Table 4: Scope of Nucleophiles[a,b]



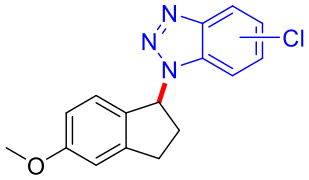
3o + **9a-j** → **10a-j**



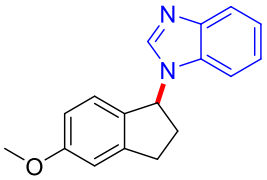
10a, 72%



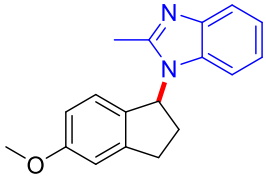
10b, 66%



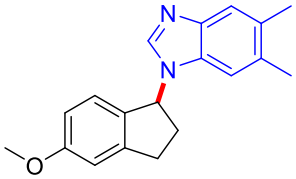
10c, 70%



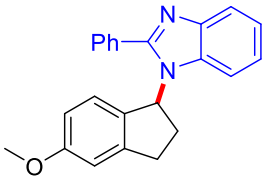
10d, 74%



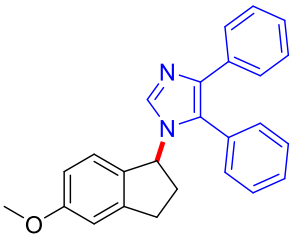
10e, 76%



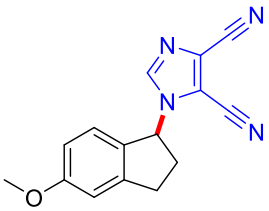
10f, 66%



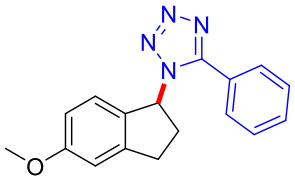
10g, 68%



10h, 76%



10i, 66%



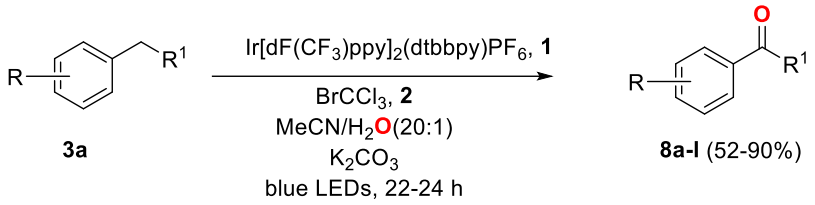
10j, 74%

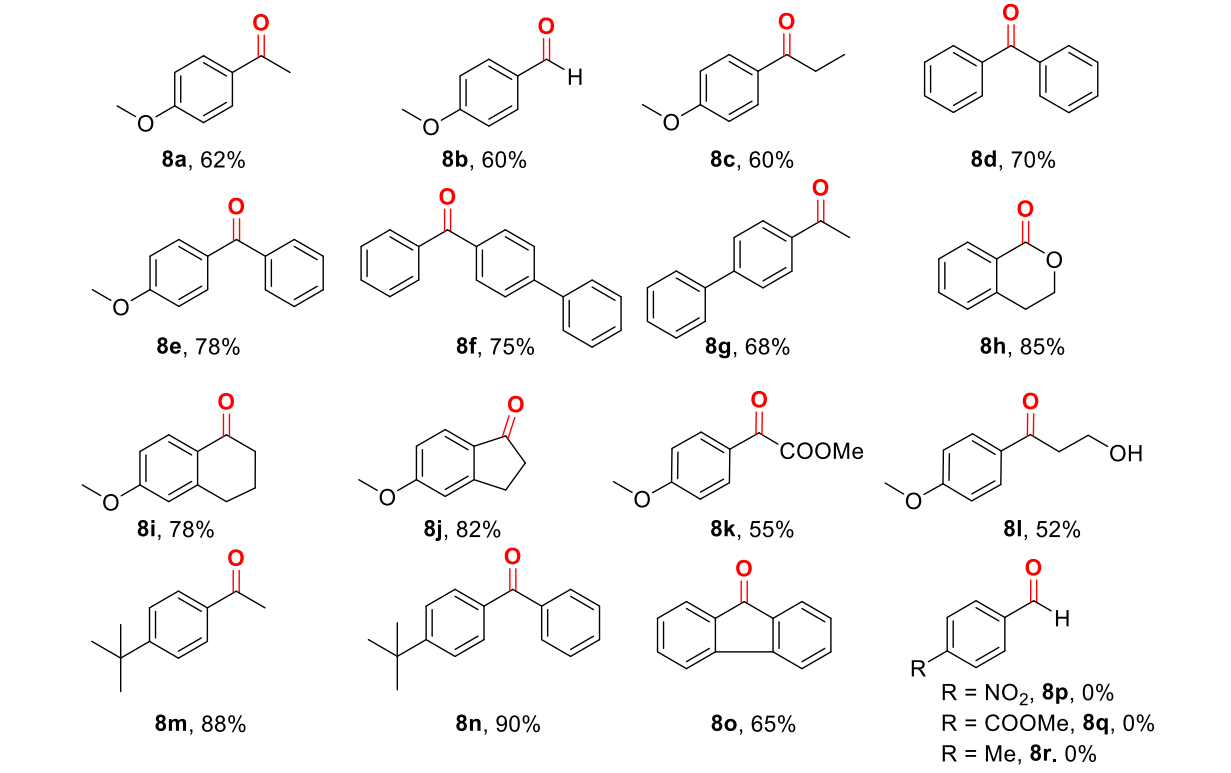
[a]Reaction conditions: 5-methoxyindane **3o** (1.0 mmol), nitrogen nucleophile (**9**, 1.5 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ **1** (1 mol%) , BrCCl$_3$ **2** (1.5 mmol) and K$_2$CO$_3$ (1.5 mmol) in CH$_3$CN (5 mL) were irradiated under degassed condition at rt using blue LED for 12-18 h. [b]Isolated yield of the product **10**.

After demonstrating successfully benzylic C–N bond formation through this protocol, we anticipated that this reaction could as well be used for the oxidation of benzylic position because

small quantity of **8a** was formed during the reaction of **3a** with benzotriazole. Direct oxidation of 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 either in the presence of THBP[28] or molecular oxygen[29,30] are reported. Several other oxidants[31] have also been evaluated for this oxidation reaction.

Table 5: Benzylic Oxidation



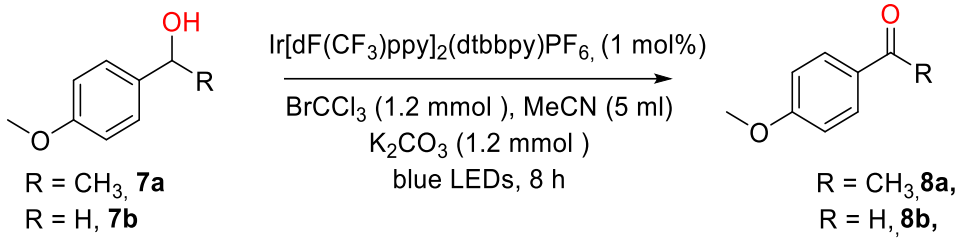


[a]Reaction conditions: alkyl-aryl (**3**, 1.0 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1 mol%) , $BrCCl_3$ (2.2 mmol) and K_2CO_3 (2.2 mmol) in CH_3CN:H_2O (20:1, 10 mL) were irradiated under degassed condition at rt using blue LED for 22-24 h. [b]Isolated yields of the product **8**.

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 DCN (1,4-dicyanonaphthalene) as a photocataloyst and H_2O as an oxygen source.[29] However, the use of high intensity UV light (>300 nm) somewhat dwarfs this strategy. Therefore, we contemplated to use this 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_2CO_3 (2.2 mmol) in moist CH_3CN, under identical reaction condition as described above, provided corresponding 4-methoxy acetophenone (**8a)** in 62 % yield. The strategy was found to be general as exmplefied with the number of substrates as shown in Table-5, entry **8a-8r**. There was no reaction observed with arenes having electron deficient substituents (entry **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 worthy to mention that oxidation of 4-methylanisole produced *para*-anisaldehye (Table 5, entry **8b**), used as a fragnance and favouring agent in 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 values as a fragnance, food favouring agent[36] and as a antimycobacterial agent.[37]

Scheme 3: Oxidation of Benzylic Alcohol



To implicate corresponding alcohol as an intermediate (Fig. 1) in these oxidations, authentic samples of 1-(4-methoxyphenyl)ethan-1-ol (**7a)** and 4-methoxybenzylalcohol **(7b)** were exposed to the identical reaction conditon as described above which gave **8a** and **8b**, respectively, in 82%, 85% yields (Scheme 3). To provide compelling evidence of **7a** as an intermediate, **3a** was irradiated for a very short period of time (1-2 h) and analysis 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 moiety such as imidazole, benzotriazole, benzimidazole and tetrazole directly at benzylic position. Furthermore, same protocol is extended for the selective benzylic oxidation to prepare industrially and academically important molecules. This straight forward, atom-economy procedure is a new addition to benzylic C–H functionalization for C–N as well as C–O bond forming reactions.

EXRERIMENTAL 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 aluminium plates which were visualized by UV fluorescence and/or by staining with iodine, alcoholic solution of phosphomolybodic acid. CC (Column Chromatography) was performed on silica gel 60–120/, 100–200/, 230–400 mesh. NMR (Nuclear Magnetic Resonance) spectra were recorded on a 400 MHz for ^{1}H and 101 MHz for ^{13}C, respectively and/or 800 MHz and 202 MHz for ^{1}H and ^{13}C, respectively instruments using deuteriated solvent. Chemical shifts are reported in ppm. Proton coupling constants (J) are reported as absolute values in Hz and 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 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 point of the products were uncorrected.

General procedure for visible light photoredox reactions:

Benzylic C–N bod forming reaction: An oven dry 25 mL round bottom flask, equipped with a rubber septum and magnetic stir bar was charged with alkyl aryls **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 diodes (LED, λ_{max} = 445 ±10 nm, 700 mA, 3.0 W) for 16 h. After 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 extracted with ethyl acetate (2×10 mL). The combined organic phases were washed with water, brine (10 mL) and 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 **6**.

1-(1-(4-methoxyphenyl)ethyl)-1H-benzo[d][1,2,3]triazole ***(6a).*** (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).*** (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).*** (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).*** (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).*** (197.7 mg, 68%); White solid, Mp. 155-157 ^{0}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).*** (245.8 mg, 78%); White solid, Mp. 163-164 ^{0}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).*** (245.6 mg, 68%); White solid, Mp. 179-180 ^{0}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).*** (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, 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).*** (208.0 mg, 70%); Thick liquid; ^{1}H 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).*** (230.2 mg, 74%); Thick liquid; ^{1}H 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).*** (198.8 mg, 75%); Thick liquid; ^{1}H 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).*** (262.9 mg, 72%); Thick liquid; ^{1}H 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).*** (189.8 mg, 68%); White solid, Mp. 136-138 ^{0}C;; ^{1}H 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).*** (212.1mg, 80%); Thick liquid; ^{1}H 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).*** (224.3 mg, 76%); Thick liquid; ^{1}H NMR (800 MHz, Chloroform-*d*) ^{1}H 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).*** (181.6 mg, 62%); Thick liquid; ^{1}H 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).*** (178.6 mg, 64%); Thick liquid; ^{1}H 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).*** (197.5 mg, 60%); White solid, Mp. 139-141 ^{0}C; ^{1}H 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).*** (201.0 mg, 72%); Thick liquid; ^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H 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).*** (293.5 mg, 66%); Thick liquid; ^{1}H 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).*** (215.3 mg, 72%); Thick liquid; ^{1}H 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).*** (195.5 mg, 74%) Thick liquid; ^{1}H 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, 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).*** (211.4 mg, 76%); White solid, Mp. 125-127 ^{0}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).*** (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).*** (231.3 mg, 68%); White solid, Mp. 293-294 ^{0}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).*** (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).*** (117.0 mg, 66%); White solid, 138-140 ^{0}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).*** (146.0 mg, 74%); White solid, 75-77 ^{0}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 a 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 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 were 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] **8o**[28a] authentic samples. The ^{1}H, ^{13}C data of representative compounds **8a**, **8f** and **8h** are given below.

1-(4-methoxyphenyl)ethan-1-one ***(8a).*** (93.6 mg, 62 %); Color less 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).*** (165.7 mg, 75%); White solid, Mp. 100-102 ^{0}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).*** (125.8 mg, 85%); Color less 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.

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Supporting Information:

Copies of ^{1}H NMR and ^{13}C NMR spectra of products. The Supporting Information is available free of charge on the ACS Publications website at DOI:

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