Note

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Visible-Light-Induced Regioselective Cross-Dehydrogenative Coupling of 2*H*-Indazoles with Ethers

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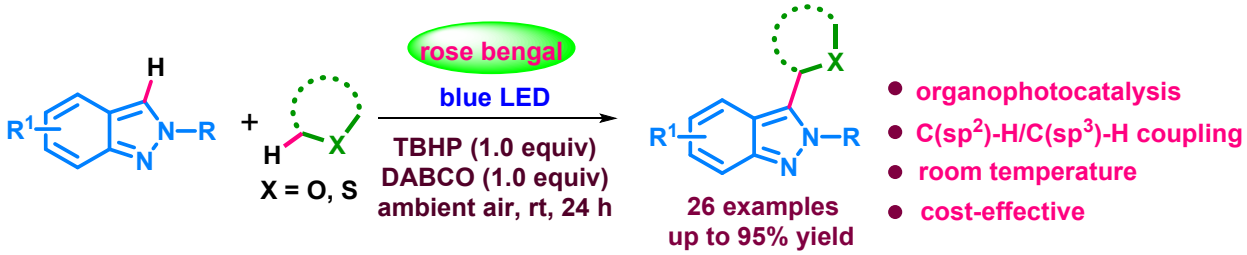


ABSTRACT

A visible-light-promoted regioselective C(sp^2)-H/C(sp^3)-H cross-dehydrogenative coupling between 2*H*-indazoles and ethers has been achieved using a catalytic amount of rose bengal as an organophotoredox-catalyst and *tert*-butyl hydroperoxide (TBHP) as an oxidant at ambient temperature under aerobic conditions. A variety of C-3 oxyalkylated 2*H*-indazoles have been synthesized in moderate to good yields. Mechanistic studies suggest a radical pathway of the present reaction.

Indazole, a nitrogen-based fused heterocycle possesses a large number of biological activities such as anti-tumour,[1a] anti-HIV,[1b] anti-microbial,[1c] anti-inflammatory,[1d] anti-depressant,[1e] anti-cancer,[1f] anti-platelet,[1g] anti-contraceptive,[1f] and anti-malarial.[1g] In pharmaceutical chemistry, indazoles are also known to be an efficient bioisostere of indoles and benzimidazoles.[1] There are several marketed drugs with indazole moeity such as MK-4827 (anticancer agent),[2a] pazopanib (votrient, tyrosine kinase inhibitor),[2b] bendazac (votrient, tyrosine kinase inhibitor),[2c] and gamendazole (Fig 1.).[1h] Moreover it is used as bacterial gyrase β-inhibitors[3a] and estrogen receptors.[3b] Considering the broad applications of indazole in

pharmaceutical chemistry, several methodologies have been developed for the synthesis and functionalization of this moiety.[4] Recently phosphonylation,[5a] trifluoromethylation,[5b] and thiocyanation[5c] on indazole moiety have been reported by our group also. Regardless the significance of such functionalizations, there is still great demand to develop straightforward, mild, and environmentally friendly method for synthesis of functionalized indazoles.

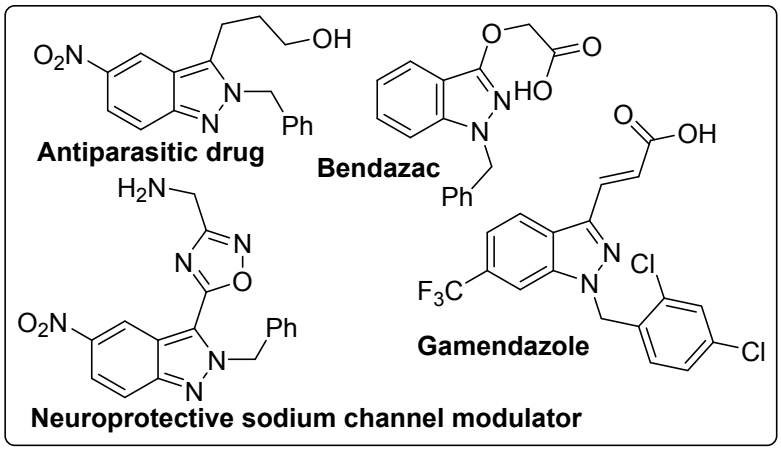


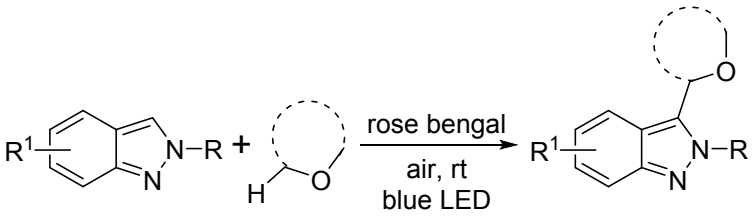
Fig 1. 2*H*-Indazole-containing some biologically active molecules.

On the other hand, cyclic ethers are important in the field of pharmaceutical chemistry and natural product.[6] The synthesis of cyclic ether functionalized complex organic molecules becomes a challenging task in synthetic organic chemistry due to the inertness of simple ethers. Although a numerous methodologies have been developed for α-C-H functionalization of ethers, most of these approaches require transition-metal catalysts, ligands, and harsh reaction conditions.[7]

Recently, visible-light-mediated photoredox-catalyzed direct functionalization of C-H bond has drawn a significant attention from the synthetic chemistry community.[8] Inexpensive organic dyes like rose bengal (RB), eosin Y, methylene blue, etc., have utilized as an alternatives of transition-metal-containing photoredox catalysts due to their synthetic versatility, inexpensiveness, nontoxicity, and better environmental perspective.[9] In 2015, Wang and co-

workers described a visible-light-mediated eosin Y-catalyzed vinylation of THF using alkyne as vinylating agent.[8g] With our ongoing studies on organophotoredox catalysis,[10] herein we described an environmentally benign visible-light-promoted method for oxyalkylation of 2*H*-indazole via cross-dehydrogenative coupling between 2*H*-indazoles and ethers using rose bengal as photo-redox-catalyst under aerobic conditions at room temperature (Scheme 1).

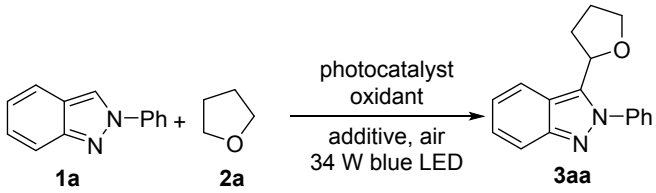
Scheme 1. Visible-Light-Mediated Oxyalkylation of Indazoles



Initially, the reaction was carried out using 2-phenyl-2*H*-indazole (**1a**) (0.25 mmol) as model substrate and rose bengal (2 mol %) as a photocatalyst under irradiation with 34 W blue LED lamp. Delightfully, 2-phenyl-3-(tetrahydrofuran-2-yl)-2*H*-indazole (**3aa**) was formed in 30% yield after 24 h using tetrahydrofuran (THF) as an oxyalkylating reagent and DABCO as an additive under ambient air (Table 1, entry 1). Even, no improvement of the yield was observed after 36 h. No desired product was obtained in the absence of photocatalyst (Table 1, entry 2). After that, we screened the effect of different oxidants such as H_2O_2, TBHP, DTBP, $K_2S_2O_8$, and $PhI(OAc)_2$ (Table 1, entries 3-7). Interestingly, 90% yield of the oxyalkylated product was obtained in presence of TBHP (Table 1, entry 4). Other photo-redox-catalysts, such as eosin Y, eosin B, and Rhodamine 6G were not effective like rose bengal (Table 1, entries 8-10). The coupling product was formed in 37% yield in presence of eosin Y and molecular sieves 4 Å/ HCOOH (Table 1, entry 8). We also checked the effect of different bases like DBU, Et_3N, K_2CO_3, Na_2CO_3, and Cs_2CO_3 but these were not suitable for this protocol (Table 1, entries 11-15). No formation of the product was found in absence of base (Table 1, entry 16). The yields of

the product decreased with decreasing the loading of both rose bengal and DABCO but no significant improvement of the reaction yield was found with increasing the amounts of both catalyst and base (Table 1, entry 17 and 18). The yield of the reaction decreased with decreasing as well as increasing the amount of TBHP (Table 1, entry 19). The desired product was formed in 42% yield in presence of 1.0 mL THF (Table 1, entry 20). Other classical photoredox catalysts like $Ru(bpy)_3Cl_2 \cdot 6H_2O$ and $Ir(ppy)_3$ were not suitable for this reaction (Table 1, entries 21 and 22). Furthermore, the desired coupling product was not observed under the irradiation with 5 W blue LED and 10 W white LED (Table 1, entry 23). Thus the optimized yield (90%) was achieved using 2 mol % rose bengal, 1.0 equiv DABCO, and 1.0 equiv TBHP (5.0-6.0 M in dacane) under irradiation with 34 W blue LED for 24 h at room temperature under aerobic condition (Table 1, entry 4).

Table 1. Representative Results for Optimization of the Reaction[a]



1a 2a 3aa

entry	photocatalyst (mol %)	oxidant (equiv)	additive (equiv)	yield (%)
1	rose bengal	O_2	DABCO	30
2	-	O_2	DABCO	NR
3	rose bengal	H_2O_2	DABCO	trace
4	**rose bengal**	**TBHP**	**DABCO**	**90**
5	rose bengal	DTBP	DABCO	trace
6	rose bengal	$K_2S_2O_8$	DABCO	35
7	rose bengal	$PhI(OAc)_2$	DABCO	30
8	eosin Y	TBHP	DABCO	trace, 37%[b]
9	eosin B	TBHP	DABCO	NR
10	Rhodamine 6G	TBHP	DABCO	NR

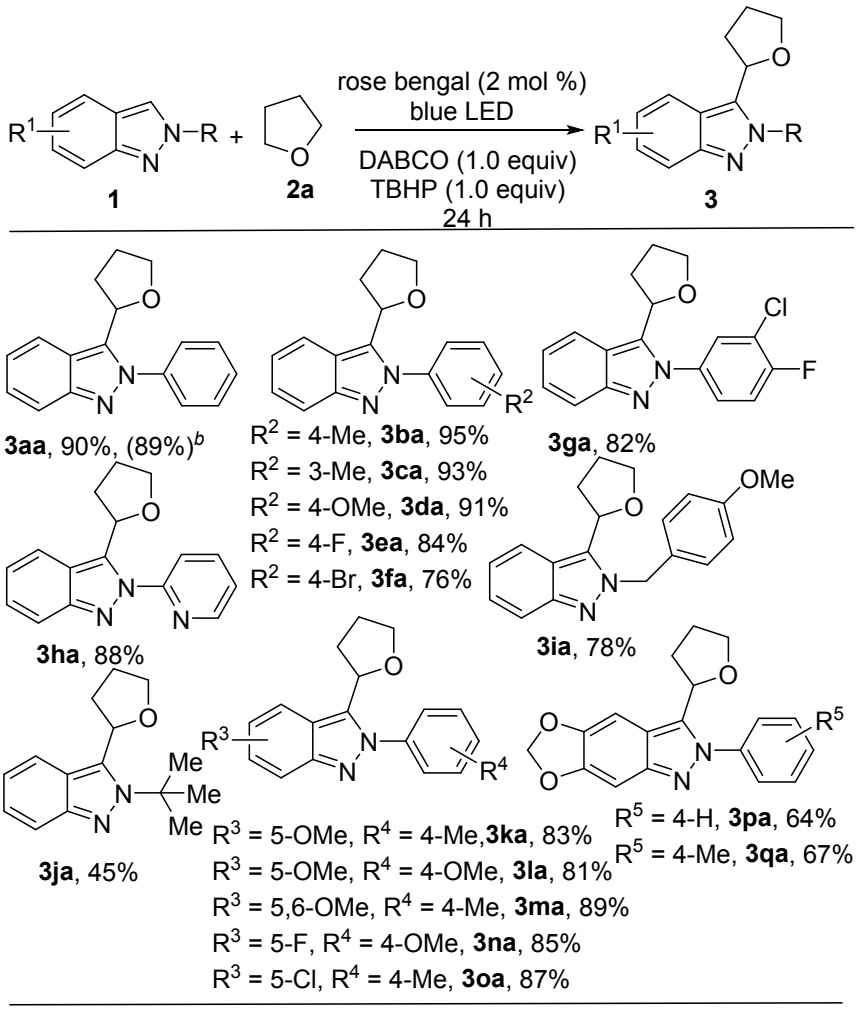
11	rose bengal	TBHP	DBU	20
12	rose bengal	TBHP	Et_3N	NR
13	rose bengal	TBHP	K_2CO_3	20
14	rose bengal	TBHP	Na_2CO_3	35
15	rose bengal	TBHP	Cs_2CO_3	58
16	rose bengal	TBHP	-	NR
17	rose bengal	TBHP	DABCO	67[c], 91[d]
18	rose bengal	TBHP	DABCO	52[e], 88[f]
19	rose bengal	TBHP	DABCO	45[g], 35[h]
20	rose bengal	TBHP	DABCO	42[i]
21	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	TBHP	DABCO	28
22	$Ir(ppy)_3$	TBHP	DABCO	trace
23	rose bengal	TBHP	DABCO	NR[j]

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (2.0 mL), photocatalyst (2 mol %), base (1.0 equiv), oxidant (1.0 equiv), 34 W blue LED, 24 h, air, room temperature. NR = no reaction. [b]4 Å MS/ HCOOH instead of DABCO. [c]1 mol % rose bengal, and [d]3 mol % rose bengal. [e]0.5 equiv DABCO and [f]2.0 equiv DABCO. [g]0.5 equiv TBHP (5.0-6.0 M in dacane), and [h]2.0 equiv TBHP (5.0-6.0 M in dacane), [i]1.0 mL THF, [j]Irradiation with 5 W blue LED and 10 W white LED.

After getting the optimized reaction conditions, we examined the substrate scope of this cross-coupling reaction with various substituted 2*H*-indazoles. As shown in Scheme 2, we first varied the substituent at N-2 position of 2*H*-indazoles. Electron-donating groups like –Me and –OMe containing 2-phenyl-2*H*-indazole afforded the corresponding C-3 oxyalkylated products in excellent yields (**3ba-3da**). Halogen (F, Cl, and Br)-containing 2*H*-indazoles also worked well under the optimized reaction conditions (**3ea-3ga**). Pyridinyl substituted 2*H*-indazole also underwent the reaction very smoothly (**3ha**). In addition, 4-methoxybenzyl and *tert*-butyl substituted 2*H*-indazoles gave the oxyalkylated products in moderate yields (**3ia** and **3ja**). Next we investigated various substituents in the arene part of 2*H*-indazoles. Both electron-releasing (Me and OMe) and halogen (F and Cl) containing 2*H*-indazole provided the desired products (**3ka-3oa**) in good yields. 2-Phenyl-2*H*-[1,3]dioxolo[4,5-*f*]indazole derivatives (**1p** and **1q**) were also well tolerable in the present reaction (**3pa** and **3qa**). Electron-withdrawing group containing

2*H*-indazole in phenyl ring did not undergo the oxyalkylation. Ortho-substituted 2-phenyl-2*H*-indazoles could not form the desired products. Next to validate the applicability of the present protocol, a gram-scale reaction was carried out by taking **1a** in 5 mmol scale under the optimized conditions. To our delight 2-phenyl-3-(tetrahydrofuran-2-yl)-2*H*-indazole (**3aa**) was formed in 89% yield. However, 2*H*-indazole and 1*H*-indazole remained unreactive under the optimized reaction conditions. An inseparable mixture of products was obtained in case of *cbz*-protected 2*H*-indazole.

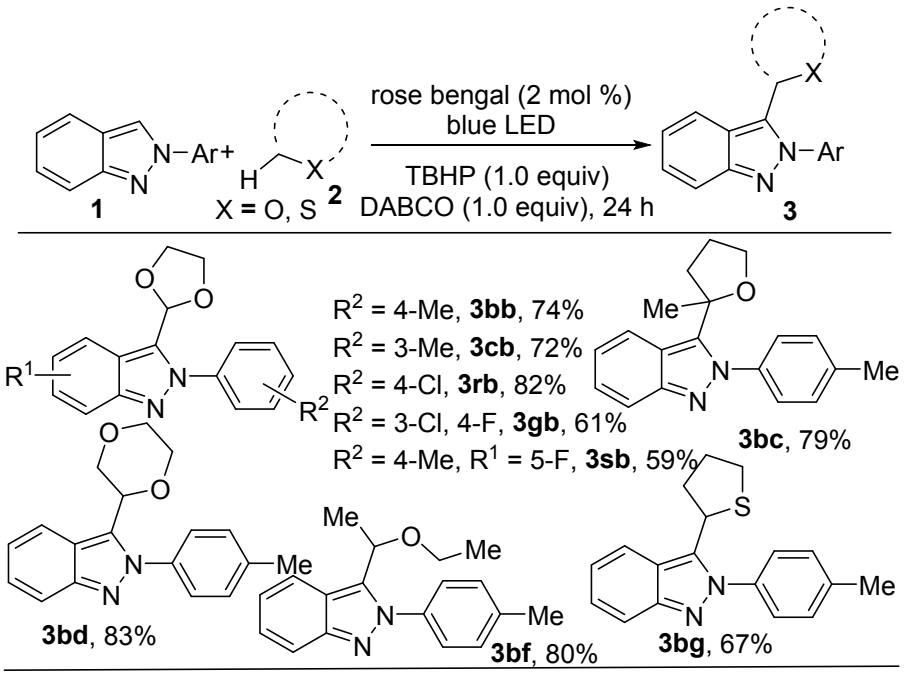
Scheme 2. Substrate Scope of 2*H*-Indazoles[a]



[a]Reaction conditions: **1** (0.25 mmol), **2a** (2.0 mL), rose bengal (2 mol %), DABCO (1.0 equiv), and TBHP (5.0-6.0 M in dacane, 1.0 equiv), 34 W blue LED, 24 h, ambient air, room temperature. [b]5 mmol scale.

Next, to show the general applicability of the present methodology, we investigated our reaction taking different ethers (Scheme 3). 2-Phenyl-2*H*-indazole substituted with 4-Me and 3-Me in the *N*-phenyl ring smoothly reacted with 1,3-dioxolane (**2b**) to provide the desired products (**3bb** and **3cb**) in good yields. Halogen substituted 2*H*-indazoles also worked well (**3rb** and **3gb)**. 5-Fluoro-2-(*p*-tolyl)-2*H*-indazole also reacted with 1,3-dioxolane (**3sb**, 59%). Moreover, 2-methyltetrahydrofuran, 1,4-dioxane furnished the coupling products (**3bc** and **3bd**) without any difficulties. Aliphatic ether like diethyl ether also participated in this coupling reaction to afford the desired product with good yield (**3bf**, 80%). It is also notable that tetrahydrothiophene reacted well under the present reaction condition to give the corresponding product **3bg** in 67% yield. 2-Phenyl-2*H*-indazole did not form the coupling products with cycloalkanes like cyclopentane and cyclohexane. Other heterocycles such as indole and 1-methyl indole did not couple with ethers under the present reaction conditions.

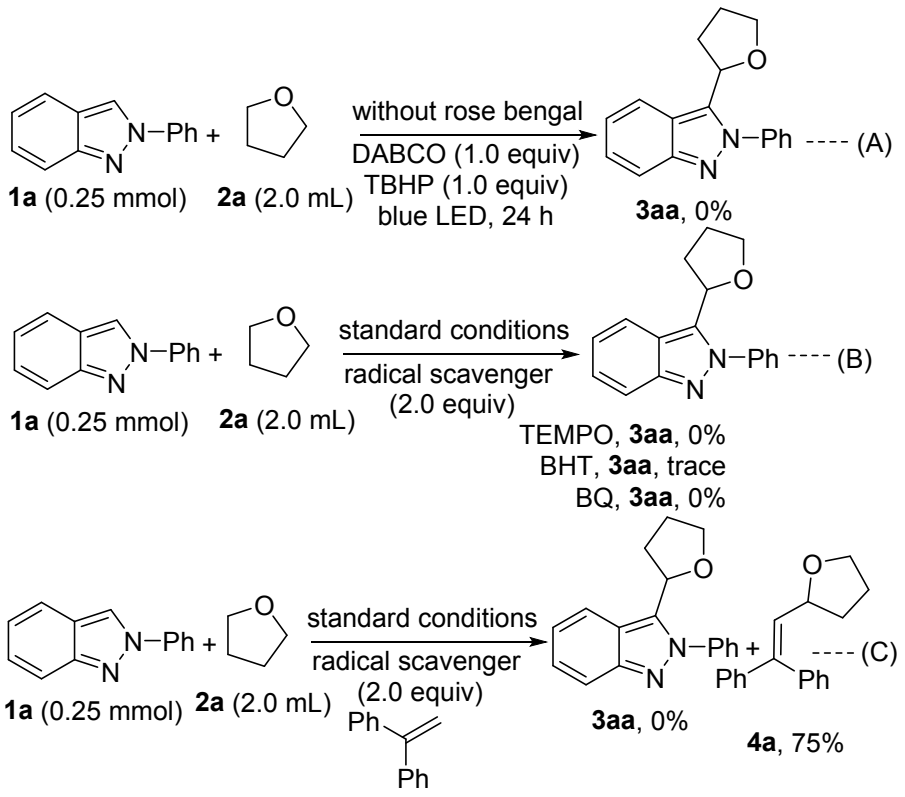
Scheme 3. Substrate Scope of Ethers[a]



[a]Reaction conditions: **1** (0.25 mmol), **2** (2.0 mL), rose bengal (2 mol %), DABCO (1.0 equiv), and TBHP (5.0-6.0 M in dacane, 1.0 equiv), 34 W blue LED, 24 h, air, room temperature.

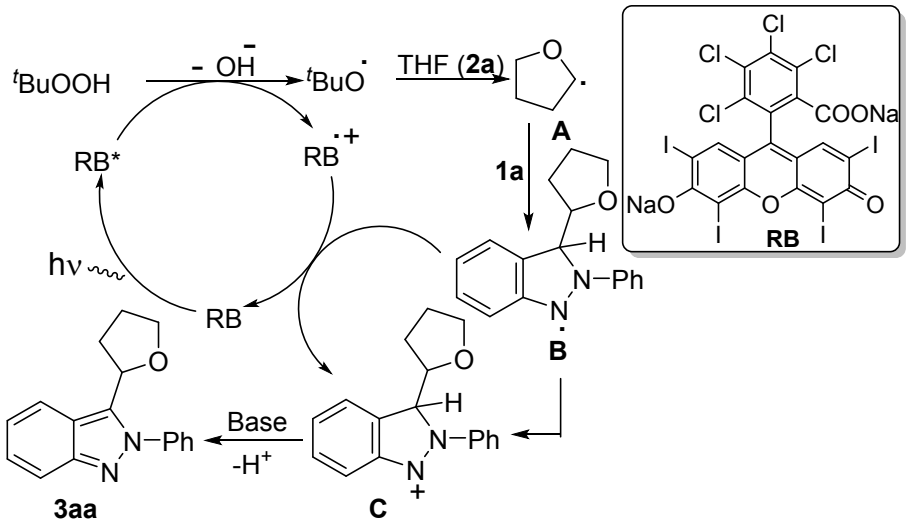
A few control experiments were carried out to get the mechanistic insights of the current protocol (Scheme 4). The product was not obtained in absence of photocatalyst (Scheme 4, eq A). 2-Phenyl-2*H*-indazole (**1a**) did not produce the corresponding *α*-oxyalkylated product (**3aa**) in the presence of radical scavengers like 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2,6-di-*tert*-butyl-4-methyl phenol (BHT), and *p*-benzoquinone (BQ) (Scheme 4, eq B). Moreover, with the addition of stoichiometric amount 1,1-diphenylethylene, the present reaction completely suppressed along with the formation of 2-(2,2-diphenylvinyl)tetrahydrofuran (**4a**) in 75% yield (Scheme 4, eq C). These observations clearly reveal the radical mechanistic pathway of the present reaction.

Scheme 4. Mechanistic Studies



Based on mechanistic studies and previous literature reports,[4e,7a] a radical mechanism for the formation of 2-phenyl-3-(tetrahydrofuran-2-yl)-2*H*-indazole (**3aa**) is presented in Scheme 5. Initially, RB is transformed to its excited-state RB* under blue LED irradiation. Next, a hydroxide anion and *tert*-butyloxy radical are formed via a single electron-transfer process (SET) between RB* and TBHP. Then, *tert*-butyloxy radical takes up a proton from α-C(sp^3)-H of THF (**2a**) to form an alkoxyalkyl radical intermediate **A**. After that the alkoxyalkyl radical undergoes reaction at C-3 position of 2-phenyl-2*H*-indazole (**1a**) to produce the radical intermediate (**B**). Subsequently intermediate **B** is oxidized by $RB^{\bullet+}$ to generate cationic intermediate **C**. Finally, 3-oxyalkylated 2*H*-indazole (**3aa**) is obtained via deprotonation of intermediate **C**.

Scheme 5. Proposed Mechanistic Pathway



In summary, we have disclosed a convenient route for the oxyalkylation of 2*H*-indazoles via C−H/C−H cross-dehydrogenative coupling (CDC) between 2*H*-indazole and ethers under irradiation of blue LED at room temperature. A wide range of functional groups on 2*H*-indazole were well tolerant under the optimized reaction conditions. Metal-free and mild reaction conditions, broad substrates scope, ambient air, and gram-scale synthesis are the attractive features of this methodology. To the best of our knowledge we are not aware of any previous literature reports for such visible-light-promoted oxyalkylation of 2*H*-indazoles. We believe that the present methodology opens a new door in organic synthesis to synthesize oxyalkylated 2*H*-indazoles.

EXPERIMENTAL SECTION

General Information: All reagents were bought from commercial sources and used as recieved without further purification. All reactions involving moisture sensitive reactants were executed using oven dried glassware. All commercially available solvents were used after distillation. ^{1}H NMR spectra were determined on 400 MHz spectrometer as solutions in $CDCl_3$ and $^{13}C\{^{1}H\}$

spectra were recorded at 100 MHz spectrometer in $CDCl_3$ solution. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants (J) are given in Hz. Chemical shifts are referenced to $CDCl_3$ (δ = 7.26 for ^1H and δ = 77.16 for $^{13}C\{^1H\}$ NMR) as internal standard. NMR spectra uses the following abbreviations to describe the multiplicity: s (singlet), d (doublet), t (triplet), and m (multiplet). The progress of reaction was checked by TLC plates (silica gel coated glass slide) and the spots were visualized under UV light.

General Procedure for the Preparation of 2*H*-indazoles (1)

A mixture of aryl aldehydes (3.0 mmol), the appropriate anilines (3.0 mmol), molecular sieves 4 Å MS (3 gm), and dichloromethane (15 mL) was taken in a dried round-bottom flask. Then the mixture was stirred at room temperature under ambient air. After 24 h, the mixture was filtered through Celite and the filtrate was concentrated under reduced pressure to provide the pure imines without additional purification. The desired imine (3.0 mmol) was then dissolved in dry DMSO (15 mL) and copper iodide (20 mol %, 114 mg), TMEDA (20 mol %, 69.7 mg), and sodium azide (2.0 equiv, 390 mg) were added to it. After that the reaction mixture was stirred at 120 °C for 24 h. Next, the brown mixture was allowed to reach room temperature, diluted with ethyl acetate (20 mL) and water (20 mL). The precipitate was filtered through a short pad of Celite and the filtrates were extracted with ethyl acetate. The combined organic layers were concentrated under reduced pressure and the crude mixtures were purified by column chromatography using ethyl acetate in hexanes (3-5%) as an eluent to give pure indazoles. Compounds **1a**,[4b] **1b**,[4b] **1d**,[4d] **1f**,[4d] **1h**,[4b] **1j**,[4d] **1o**,[4d] **1p**,[4d] **1r**,[4b] and **1s**[4b] are known, and the spectroscopic and physical data are completely matched with those from the literature.

2-(m-Tolyl)-2H-indazole (1c): Yellow Solid (525 mg, 84%); mp 63−65 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.25 (s, 1H), 7.70-7.68 (m, 1H), 7.64 (s, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.53 (d, J =

8.0 Hz, 1H), 7.28-7.19 (m, 2H), 7.08 (d, J = 8.4 Hz, 1H), 7.01-6.97 (m, 1H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 149.7, 140.4, 139.8, 129.5, 129.3, 128.7, 126.8, 122.7, 122.4, 121.7, 120.5, 120.4, 117.9, 21.5; Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45%; Found C, 80.91; H, 5.78; N, 13.40%.

2-(4-Fluorophenyl)-2H-indazole (1e): Yellow Solid (484 mg, 76%); mp 96−98 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.31 (s, 1H), 7.86-7.83 (m, 2H), 7.78 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.35-7.31 (m, 1H), 7.20 (t, J = 8.8 Hz, 2H), 7.14-7.10 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 162.1 ($J_{C\text{-}F}$ = 247.0 Hz), 149.9, 136.9, 127.0, 122.9, 122.8 ($J_{C\text{-}F}$ = 9.0 Hz), 122.6, 120.5, 120.4, 117.9, 116.5 ($J_{C\text{-}F}$ = 22.0 Hz); Anal. Calcd for $C_{13}H_9FN_2$: C, 73.57; H, 4.27; N, 13.20%; Found C, 73.78; H, 4.21; N, 13.30%.

2-(3-Chloro-4-fluorophenyl)-2H-indazole(1g): Yellow Solid (584.6 mg, 79%); mp 83−85 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.34 (s, 1H), 8.03-8.01 (m, 1H), 7.78-7.75 (m, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.35-7.27 (m, 2H), 7.14-7.11 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.5 ($J_{C\text{-}F}$ = 249.0 Hz), 150.1, 137.2 ($J_{C\text{-}F}$ = 4.0 Hz), 127.5 ($J_{C\text{-}F}$ = 21.0 Hz), 123.4, 123.0, 122.4, 122.3, 120.56, 120.50, 120.4, 118.0, 117.6, 117.3; Anal. Calcd for $C_{13}H_8ClFN_2$: C, 63.30; H, 3.27; N, 11.36%; Found C, 63.11; H, 3.24; N, 11.29%.

2-(4-Methoxybenzyl)-2H-indazole (1i): Yellowish Brown Solid (586 mg, 82%); mp 86−88 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.76 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.21-7.16 (m, 3H), 7.00-6.96 (m, 1H), 6.82-6.79 (m, 2H), 5.44 (s, 2H), 3.71 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 159.8, 149.0, 129.7, 127.8, 126.0, 122.6, 122.1, 121.7, 120.2, 117.6, 114.4, 57.1, 55.4; Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76%; Found C, 75.79; H, 5.97; N, 11.67%.

5-Methoxy-2-(p-tolyl)-2H-indazole (1k): Brown Solid (622 mg, 87%); mp 95−97 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (s, 1H), 7.62-7.56 (m, 3H), 7.16 (d, J = 8.4 Hz, 2H), 6.93-6.90 (m, 1H), 6.75 (d, J = 2.4 Hz, 1H), 3.71 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.4, 146.6, 138.3, 137.4, 130.0, 122.7, 121.8, 120.4, 119.28, 119.26, 96.3, 55.3, 21.0; Anal. Calcd for $C_{15}H_{14}N_2O$: C 75.61; H, 5.92; N, 11.76%; Found: C, 75.43; H, 5.98; N, 11.83%.

5-Methoxy-2-(4-methoxyphenyl)-2H-indazole (***1l***): Brown Solid (587.5 mg, 77%); mp 133−135 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (s, 1H), 7.64 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 9.2 Hz, 1H), 6.94-6.88 (m, 3H), 6.76 (d, J = 2.0 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.0, 155.4, 146.5, 134.2, 122.7, 122.0, 121.6, 119.3, 119.1, 114.6, 96.3, 55.6, 55.4; Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02%; Found C, 71.00; H, 5.51; N, 11.13%.

5,6-Dimethoxy-2-(p-tolyl)-2H-indazole (1m): Yellowish Brown Solid (716.5 mg, 89%); mp 102−104 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.01 (s, 1H), 6.78 (s, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.8, 148.2, 146.3, 138.2, 136.8, 129.9, 119.8, 119.0, 117.2, 96.9, 95.7, 55.8, 20.9; Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44%; Found C, 71.81; H, 6.06; N, 10.52%.

5-Fluoro-2-(4-methoxyphenyl)-2H-indazole (1n): Yellowish Solid (523 mg, 72%); mp 128−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (s, 1H), 7.78-7.73 (m, 3H), 7.27-7.24 (m, 1H), 7.13-7.08 (m, 1H), 7.04-7.00 (m, 2H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.5, 158.7 ($J_{C\text{-}F}$ = 238.0 Hz), 147.0, 134.0, 122.4, 120.5 ($J_{C\text{-}F}$ = 8.0 Hz), 119.9, 119.8, 118.3, 118.0, 114.7, 102.7 ($J_{C\text{-}F}$ = 24.0 Hz), 55.7; Anal. Calcd for $C_{14}H_{11}FN_2O$: C, 69.41; H, 4.58; N, 11.56%; Found C, 69.21; H, 4.53; N, 11.64%.

2-(p-Tolyl)-2H-[1,3]dioxolo[4,5-f]indazole (1q): Yellowish solid (514.5 mg, 68%); mp 148−150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.05 (s, 1H), 6.87 (s, 1H), 5.96 (s, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 149.6, 147.2, 145.9, 138.2, 137.0, 130.0, 119.9, 119.6, 118.4, 101.0, 94.9, 94.2, 21.0; Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10%; Found: C, 71.26; H, 4.83; N, 11.01%.

General Experimental Procedure for the Synthesis of 3:

Indazoles (0.25 mmol), ether (2.0 mL), rose bengal (2 mol %, 5 mg), DABCO (1.0 equiv, 28 mg) and TBHP (1.0 equiv, 5.0-6.0 M in dacane, 0.035 mL) were taken in an oven-dried reaction vessel equipped with a magnetic stir bar. Then reaction mixture was irradiated using a Kessil 34 W blue LED at room temperature under open atmosphere for 24 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was quenched with 10 mL water/ethyl acetate (1:3). Then the reaction mixture was extracted with ethyl acetate and the organic phase was dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure the crude residue was obtained. Finally it was purified by column chromatography on silica gel (60-120 mesh) using petroleum ether/ethylacetate as an eluent to afford the pure products.

2-Phenyl-3-(tetrahydrofuran-2-yl)-2H-indazole (3aa): Colourless gummy (59 mg, 90%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.80 (m, 1H), 7.75-7.72 (m, 1H), 7.60-7.56 (m, 2H), 7.55-7.49 (m, 3H), 7.34-7.30 (m, 1H), 7.12-7.08 (m, 1H), 5.20 (t, J = 7.6 Hz, 1H), 4.19-4.14 (m, 1H), 3.94-3.89 (m, 1H), 2.31-2.22 (m, 2H), 2.21-2.13 (m, 1H), 2.10-2.01 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 149.0, 140.1, 136.2, 129.27, 129.21, 126.6, 126.5, 121.8, 120.8, 120.2, 118.0, 73.9, 68.9, 32.5, 26.8; Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60%; Found C, 77.41; H, 6.13; N, 10.69%.

3-(Tetrahydrofuran-2-yl)-2-(p-tolyl)-2H-indazole (3ba): Colourless gummy (66 mg, 95%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.46-7.44 (m, 2H), 7.32-7.29 (m, 3H), 7.10-7.07 (m, 1H), 5.18 (t, J = 7.6 Hz, 1H), 4.18-4.13 (m, 1H), 3.93-3.87 (m, 1H), 2.44 (s, 3H), 2.28-2.21 (m, 2H), 2.20-2.12 (m, 1H), 2.08-1.99 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.8, 139.2, 137.5, 136.1, 129.7, 126.4, 126.1, 121.7, 120.8, 120.0, 117.9, 74.0, 68.9, 32.4, 26.7, 21.3; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{18}H_{18}N_2O$: 279.1491; Found 279.1479.

3-(Tetrahydrofuran-2-yl)-2-(m-tolyl)-2H-indazole (3ca): Light yellow gummy (65 mg, 93%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.79 (m, 1H), 7.74-7.72 (m, 1H), 7.42-7.38 (m, 2H), 7.35-7.29 (m, 3H), 7.11-7.07 (m, 1H), 5.20 (t, J = 7.6 Hz, 1H), 4.20-4.14 (m, 1H), 3.94-3.89 (m, 1H), 2.44 (s, 3H), 2.29-2.23 (m, 2H), 2.20-2.16 (m, 1H), 2.08-2.03 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.9, 139.9, 139.5, 136.2, 129.9, 128.9, 127.1, 126.6, 123.4, 121.7, 120.8, 120.1, 117.9, 74.0, 68.9, 32.5, 26.8, 21.4; Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06%; Found C, 77.49; H, 6.55; N, 9.99%.

2-(4-Methoxyphenyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3da): Light yellow gummy (67 mg, 91%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.50-7.47 (m, 2H), 7.32-7.28 (m, 1H), 7.11-7.07 (m, 1H), 7.03-7.01 (m, 2H), 5.16 (t, J = 7.6 Hz, 1H), 4.18-4.12 (m, 1H), 3.93-3.89 (m, 1H), 3.87 (s, 3H), 2.28-2.22 (m, 2H), 2.20-2.12 (m, 1H), 2.09-2.00 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.1, 148.8, 136.2, 133.0, 127.6, 126.5, 121.7, 120.7, 120.0, 117.8, 114.3, 74.0, 68.9, 55.7, 32.4, 26.8; Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52%; Found C, 73.65; H, 6.10; N, 9.60%.

2-(4-Fluorophenyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3ea): Light yellow gummy (59 mg, 84%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.78 (m, 1H), 7.73-7.71 (m, 1H), 7.59-7.56 (m, 2H),

7.34-7.30 (m, 1H), 7.24-7.19 (m, 2H), 7.12-7.08 (m, 1H), 5.15 (t, J = 7.6 Hz, 1H), 4.17-4.11 (m, 1H), 3.94-3.88 (m, 1H), 2.30-2.22 (m, 2H), 2.21-2.13 (m, 1H), 2.11-2.02 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 162.8 ($J_{C\text{-}F}$ = 252 Hz), 149.0, 136.2, 128.3 ($J_{C\text{-}F}$ = 8 Hz), 126.8, 122.0, 121.5, 120.7, 120.2, 117.9, 117.5, 116.2 ($J_{C\text{-}F}$ = 23 Hz), 73.7, 68.9, 32.3, 26.8; Anal. Calcd for $C_{17}H_{15}FN_2O$: C, 72.33; H, 5.36; N, 9.92%; Found C, 72.51; H, 5.31; N, 9.82%.

2-(4-Bromophenyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3fa): Colourless gummy (65 mg, 76%); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.68-7.66 (m, 1H), 7.51-7.48 (m, 2H), 7.37-7.30 (m, 2H), 7.12-7.09 (m, 1H), 5.17 (t, J = 7.6 Hz, 1H), 4.18-4.12 (m, 1H), 3.95-3.89 (m, 1H), 2.32-2.25 (m, 2H), 2.21-2.16 (m, 1H), 2.12-2.03 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 143.4, 138.4, 132.4, 128.0, 127.6, 126.9, 122.2, 120.8, 120.4, 118.0, 103.0, 73.7, 68.9, 32.3, 26.8; Anal. Calcd for $C_{17}H_{15}BrN_2O$: C, 59.49; H, 4.41; N, 8.16%; Found C, 59.34; H, 4.35; N, 8.05%.

2-(3-Chloro-4-fluorophenyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3ga): Light yellow gummy (65 mg, 82%); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.70 (m, 3H), 7.54-7.50 (m, 1H), 7.35-7.28 (m, 2H), 7.13-7.09 (m, 1H), 5.17 (t, J = 7.6 Hz, 1H), 4.17-4.11 (m, 1H), 3.96-3.90 (m, 1H), 2.32-2.24 (m, 2H), 2.23-2.16 (m, 1H), 2.14-2.05 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.4 ($J_{C\text{-}F}$ = 251 Hz), 149.1, 136.6, 136.1, 128.9, 127.1, 126.3 ($J_{C\text{-}F}$ = 8 Hz), 122.3, 122.0, 120.7, 120.3, 118.0, 117.0 ($J_{C\text{-}F}$ = 22 Hz), 73.5, 68.9, 32.1, 26.8; Anal. Calcd for $C_{17}H_{14}ClFN_2O$: C, 64.46; H, 4.46; N, 8.84%; Found C, 64.63; H, 4.50; N, 8.75%.

2-(Pyridin-2-yl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3ha): yellow gummy (58 mg, 88%); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.52-8.51 (m, 1H), 8.11-8.09 (m, 1H), 7.93-7.87 (m, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.33-7.27 (m, 2H), 7.05-7.01 (m, 1H), 6.08-6.04 (m, 1H), 4.29-4.23 (m, 1H), 4.02-3.97 (m, 1H), 2.69-2.59 (m, 1H), 2.13-2.05 (m, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ

153.5, 149.3, 147.7, 138.78, 138.72, 127.4, 122.8, 122.6, 121.7, 121.0, 118.6, 117.7, 76.5, 69.3, 34.1, 26.5; Anal. Calcd for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.84%; Found C, 72.21; H, 5.67; N, 15.90%.

2-(4-Methoxybenzyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3ia):Yellow gummy (60 mg, 78%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61-8.58 (m, 3H), 8.31 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.85-7.80 (m, 1H), 7.56-7.52 (m, 1H), 7.05-7.02 (m, 3H), 5.75-5.72 (m, 1H), 4.22-4.16 (m, 1H), 4.11-4.06 (m, 1H), 3.89 (s, 3H), 2.75-2.70 (m, 1H), 2.44-2.39 (m, 1H), 2.25-2.20 (m, 1H), 2.17-2.12 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 168.8, 161.8, 159.7, 151.6, 133.5, 131.1, 130.3, 129.2, 126.5, 125.2, 121.6, 114.0, 78.8, 69.4, 55.5, 30.1, 26.1; Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08%; Found C, 74.19; H, 6.50; N, 8.97%.

2-(Tert-butyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3ja): Colourless gummy (27 mg, 45%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (t, J = 8.4 Hz, 2H), 7.23-7.19 (m, 1H), 7.01-6.98 (m, 1H), 5.66 (t, J = 7.2 Hz, 1H), 4.33-4.28 (m, 1H), 4.00-3.95 (m, 1H), 2.42-2.37 (m, 1H), 2.31-2.22 (m, 2H), 2.20-2.14 (m, 1H), 1.81 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.5, 135.0, 125.4, 121.4, 121.0, 120.9, 117.8, 75.1, 69.0, 61.9, 33.4, 31.3, 26.9; Anal. Calcd for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.47%; Found C, 73.95; H, 8.31; N, 11.39%.

5-Methoxy-3-(tetrahydrofuran-2-yl)-2-(p-tolyl)-2H-indazole (3ka): Colourless gummy (64 mg, 83%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.61 (m, 1H), 7.44-7.41 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.03-7.01 (m, 1H), 6.98 (d, J = 2.0 Hz, 1H), 5.15 (t, J = 7.6 Hz, 1H), 4.18-4.12 (m, 1H), 3.93-3.87 (m, 1H), 3.86 (s, 3H), 2.43 (s, 3H), 2.24-2.17 (m, 2H), 2.16-2.11 (m, 1H), 2.06-2.00 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 154.9, 154.7, 139.0, 137.7, 134.6, 129.7, 126.1, 121.3, 120.0, 119.3, 97.1, 74.1, 68.8, 55.5, 32.1, 26.7, 21.3; Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08%; Found: C, 73.84; H, 6.59; N, 9.01%.

5-Methoxy-2-(4-methoxyphenyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (***3la)***: Yellow gummy (65.5 mg, 81%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 (d, J = 8.8 Hz, 1H), 7.47-7.45 (m, 2H), 7.03-6.97 (m, 4H), 5.13 (t, J = 7.6 Hz, 1H), 4.15-4.13 (m, 1H), 3.92-3.88 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.23-2.17 (m, 2H), 2.15-2.08 (m, 1H), 2.06-1.99 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.9, 154.9, 145.6, 134.7, 133.2, 127.5, 121.3, 119.9, 119.2, 114.3, 97.1, 74.1, 68.8, 55.7, 55.5, 32.0, 26.7; Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.21; N, 8.64%; Found C, 70.50; H, 6.18; N, 8.58%.

5,6-Dimethoxy-3-(tetrahydrofuran-2-yl)-2-(p-tolyl)-2H-indazole (3ma): Light yellow gummy (75 mg, 89%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.39 (m, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 2.0 Hz, 2H), 5.13 (t, J = 7.6 Hz, 1H), 4.16-4.11 (m, 1H), 3.936 (s, 6H), 3.933-3.86 (m, 1H), 2.42 (s, 3H), 2.21-2.08 (m, 3H), 2.05-1.98 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 151.7, 147.6, 145.6, 138.7, 137.7, 134.8, 129.7, 126.0, 114.5, 97.8, 95.8, 74.2, 68.8, 56.0, 55.9, 32.3, 26.7, 21.3; Anal. Calcd for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55; N, 8.28%; Found C, 70.79; H, 6.51; N, 8.38%.

5-Fluoro-2-(4-methoxyphenyl)-3-(tetrahydrofuran-2-yl)-2H-indazole (3na): Yellow gummy (66 mg, 85%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-7.67 (m, 1H), 7.48-7.44 (m, 2H), 7.38-7.35 (m, 1H), 7.14-7.08 (m, 1H), 7.04-7.00 (m, 2H), 5.12 (t, J = 7.6 Hz, 1H), 4.17-4.12 (m, 1H), 3.92-3.89 (m, 1H), 3.88 (s, 3H), 2.24-2.12 (m, 3H), 2.07-2.01 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.2, 158.1 ($J_{C\text{-}F}$ = 238 Hz), 146.2, 136.4 ($J_{C\text{-}F}$ = 8 Hz), 132.8, 127.5, 119.9, 119.8, 119.2, 119.1, 118.2, 117.9, 114.4, 103.3 ($J_{C\text{-}F}$ = 24 Hz), 73.9, 68.9, 55.7, 32.4, 26.7; Anal. Calcd for $C_{18}H_{17}FN_2O_2$: C, 69.22; H, 5.49; N, 8.97%; Found C, 69.05; H, 5.53; N, 9.06%.

5-Chloro-3-(tetrahydrofuran-2-yl)-2-(p-tolyl)-2H-indazole (3oa): Light yellow gummy (68 mg, 87%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 1.2 Hz, 1H), 7.65 (d, J = 9.2 Hz, 1H), 7.43-

7.41 (m, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.25-7.22 (m, 1H), 5.12 (t, J = 7.6 Hz, 1H), 4.20-4.15 (m, 1H), 3.93-3.87 (m, 1H), 2.45 (s, 3H), 2.25-2.14 (m, 3H), 2.09-2.01 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 147.2, 139.6, 137.2, 136.1, 129.9, 127.9, 127.2, 126.0, 120.4, 119.7, 119.4, 74.0, 69.0, 32.7, 26.7, 21.3; Anal. Calcd for $C_{18}H_{17}ClN_2O$: C, 69.12; H, 5.48; N, 8.96%; Found: C, 68.93; H, 5.45; N, 8.88%.

2-Phenyl-3-(tetrahydrofuran-2-yl)-2H-[1,3]dioxolo[4,5-f]indazole (3pa): Light yellow gummy (49 mg, 64%); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.45 (m, 5H), 6.99 (d, J = 10.4 Hz, 2H), 5.96 (d, J = 1.6 Hz, 2H), 5.11 (t, J = 7.6 Hz, 1H), 4.16-4.11 (m, 1H), 3.91-3.85 (m, 1H), 2.23-2.12 (m, 3H), 2.08-2.02 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 149.4, 146.5, 145.4, 140.0, 129.2, 128.8, 126.2, 115.7, 101.0, 95.6, 94.2, 73.9, 68.8, 32.4, 29.8, 26.7; HRMS (ESI-TOF) m/z: [M + Na]+ Calcd for $C_{18}H_{16}N_2O_3$: 331.1053; Found 331.1049.

3-(Tetrahydrofuran-2-yl)-2-(p-tolyl)-2H-[1,3]dioxolo[4,5-f]indazole (3qa): Light yellow gummy (54 mg, 67%); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.38 (m, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 11.2 Hz, 2H), 5.95 (d, J = 1.2 Hz, 2H), 5.09 (t, J = 7.6 Hz, 1H), 4.16-4.10 (m, 1H), 3.90-3.85 (m, 1H), 2.43 (s, 3H), 2.22-2.09 (m, 3H), 2.05-1.98 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 149.3, 146.4, 145.3, 138.8, 137.6, 135.5, 129.7, 126.0, 120.0, 101.0, 95.7, 94.2, 74.0, 68.8, 32.4, 26.7, 21.3; Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69%; Found: C, 70.64; H, 5.66; N, 8.62%.

3-(1,3-Dioxolan-2-yl)-2-(p-tolyl)-2H-indazole (3bb): Colourless gummy (52 mg, 74%); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.57-7.55 (m, 2H), 7.34-7.30 (m, 3H), 7.15-7.12 (m, 1H), 6.13 (s, 1H), 4.23-4.21 (m, 2H), 4.07-4.05 (m, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 148.7, 139.3, 137.4, 131.2, 129.8, 126.6,

126.0, 122.7, 121.0, 120.8, 117.9, 98.5, 65.8, 21.3; Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99%; Found: C, 73.00; H, 5.70; N, 10.07%.

3-(1,3-Dioxolan-2-yl)-2-(m-tolyl)-2H-indazole (3cb): Red gummy (50 mg, 72%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.51-7.47 (m, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.35-7.29 (m, 2H), 7.16-7.12 (m, 1H), 6.15 (s, 1H), 4.27-4.19 (m, 2H), 4.10-4.02 (m, 2H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.7, 139.7, 139.5, 131.3, 130.0, 128.9, 126.8, 126.7, 123.2, 122.7, 121.0, 120.8, 117.9, 98.4, 65.8, 21.4; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{17}H_{16}N_2O_2$: 281.1284; Found 281.1279.

2-(4-Chlorophenyl)-3-(1,3-dioxolan-2-yl)-2H-indazole (3rb): Brown gummy (61.5 mg, 82%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86-7.84 (m, 1H), 7.75-7.73 (m, 1H), 7.67-7.65 (m, 2H), 7.52-7.49 (m, 2H), 7.36-7.32 (m, 1H), 7.17-7.13 (m, 1H), 6.13 (s, 1H), 4.24-4.18 (m, 2H), 4.11-4.05 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 148.9, 138.4, 135.2, 131.3, 129.4, 127.4, 127.0, 123.0, 121.3, 120.8, 117.9, 98.2, 65.8; Anal. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.31%; Found: C, 64.08; H, 4.42; N, 9.22%.

2-(3-Chloro-4-fluorophenyl)-3-(1,3-dioxolan-2-yl)-2H-indazole (3gb): Light yellow gummy (48.5 mg, 61%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.83 (m, 2H), 7.73 (d, J = 8.8 Hz, 1H), 7.64-7.61 (m, 1H), 7.36-7.28 (m, 2H), 7.17-7.14 (m, 1H), 6.15 (s, 1H), 4.23-4.17 (m, 2H), 4.12-4.06 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.4 ($J_{C\text{-}F}$ = 251 Hz), 155.8, 150.8, 148.9, 128.6, 127.2, 126.0 ($J_{C\text{-}F}$ = 9 Hz), 123.2, 121.8, 121.4, 120.7, 117.9, 117.7, 116.9 ($J_{C\text{-}F}$ = 23 Hz), 98.1, 65.8; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{16}H_{12}ClFN_2O_2$: 319.0644; Found 319.0644.

3-(1,3-Dioxolan-2-yl)-5-fluoro-2-(p-tolyl)-2H-indazole (3sb): Light yellow gummy (44 mg, 59%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.71 (m, 1H), 7.56-7.53 (m, 2H), 7.43-7.40 (m, 1H),

7.32 (d, J = 8.0 Hz, 2H), 7.15-7.10 (m, 1H), 6.07 (s, 1H), 4.25-4.21 (m, 2H), 4.12-4.03 (m, 2H); 2.45 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 146.1, 138.3 (J_{C-F} = 230 Hz), 129.9 (J_{C-F} = 5 Hz), 125.8, 125.5, 120.5, 120.0 (J_{C-F} = 10 Hz), 118.4, 118.2, 103.5 (J_{C-F} = 24 Hz), 98.3, 65.8, 21.3; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{17}H_{15}FN_2O_2$: 299.1190; Found 299.1190.

3-(2-Methyltetrahydrofuran-2-yl)-2-(p-tolyl)-2H-indazole (3bc): Light yellow liquid (58 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96-7.93 (m, 1H), 7.68-7.65 (m, 1H), 7.33-7.26 (m, 5H), 7.08-7.04 (m, 1H), 3.89-3.85 (m, 1H), 3.66-3.61 (m, 1H), 2.45 (s, 3H), 2.35-2.29 (m, 1H), 1.94-1.83 (m, 2H), 1.81-1.73 (m, 1H), 1.64 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 148.5, 141.7, 139.5, 139.3, 129.2, 127.0, 126.4, 122.4, 121.3, 119.7, 117.5, 82.7, 67.5, 39.5, 29.2, 25.9, 21.4; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{19}H_{20}N_2O$: 293.1648; Found 293.1648.

3-(1,4-Dioxan-2-yl)-2-(p-tolyl)-2H-indazole (3bd): Yellow gummy (61 mg, 83%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.44-7.42 (m, 2H), 7.35-7.30 (m, 3H), 7.15-7.11 (m, 1H), 4.98-4.95 (m, 1H), 4.10-4.05 (m, 1H), 3.97-3.94 (m, 1H), 3.86-3.79 (m, 4H), 2.46 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 148.8, 139.6, 137.2, 131.8, 129.9, 126.6, 126.0, 122.3, 121.2, 120.9, 118.0, 71.6, 69.5, 67.1, 66.5, 21.3; HRMS (ESI-TOF) m/z: [M + H]+ Calcd for $C_{18}H_{18}N_2O_2$: 295.1441; Found 295.1441.

3-(1-Ethoxyethyl)-2-(p-tolyl)-2H-indazole (3bf): Yellow gummy (56 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.39-7.37 (m, 2H), 7.34-7.30 (m, 3H), 7.12-7.08 (m, 1H), 4.83 (q, J = 6.8 Hz, 1H), 3.30 (q, J = 7.2 Hz, 2H), 2.45 (s, 3H), 1.62 (d, J = 6.8 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H) ; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 148.8, 139.4, 137.6, 137.5, 129.8, 126.7, 126.2, 121.6, 121.0, 120.0, 117.7, 70.4, 64.2, 22.0, 21.3, 15.3; Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99%; Found C, 76.94; H, 7.13; N, 10.07%.

3-(Tetrahydrothiophen-2-yl)-2-(p-tolyl)-2H-indazole (3bg): Colourless gummy (49 mg, 67%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.42-7.40 (m, 2H), 7.34-7.29 (m, 3H), 7.10-7.06 (m, 1H), 4.84-4.80 (m, 1H), 3.34-3.27 (m, 1H), 3.10-3.05 (m, 1H), 2.45 (s, 3H), 2.43-2.35 (m, 3H), 2.00-1.92 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 149.0, 139.4, 137.2, 135.8, 129.9, 126.5, 126.2, 121.2, 121.1, 119.6, 118.3, 44.0, 38.2, 34.0, 31.9, 21.4; Anal. Calcd for $C_{18}H_{18}N_2S$: C, 73.43; H, 6.16; N, 9.52%; Found C, 73.58; H, 6.13; N, 9.42%.

2-(2,2-Diphenylvinyl)tetrahydrofuran (4a):[7c] Colourless liquid (94 mg, 75%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.27 (m, 5H), 7.24-7.19 (m, 5H), 3.79-3.73 (m, 1H), 3.69-3.65 (m, 1H), 3.55-3.49 (m, 1H), 2.93-2.89 (m, 1H), 2.67-2.61 (m, 1H), 1.82-1.77 (m, 1H), 1.71-1.65 (m, 1H), 1.37-1.32 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 127.9, 127.7, 127.4, 127.1, 127.0, 126.8, 85.6, 79.3, 76.5, 66.8, 42.4, 32.1, 26.6, 26.2.

ASSOCIATED CONTENT

Supporting information

Scanned copies of ^{1}H, and ^{13}C{^{1}H} NMR spectra of the synthesized compounds are available as supporting information. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest

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