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Authors: Asim Kumar Ghosh, Krishna Kanta Das, and Alakananda Hajra

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ortho-Allylation of 2-Arylindazoles with Vinyl Cyclic Carbonate and Diallyl Carbonate *via* Manganese-Catalyzed C–H Bond Activation

Asim Kumar Ghosh,[a] Krishna Kanta Das,[a] and Alakananda Hajra*[a]

[a]Department of Chemistry, Visva-Bharati (A Central University), Santiniketan 731235, India

Email: alakananda.hajra@visva-bharati.ac.in

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Abstract. A manganese-catalyzed directed C–H allylation of 2-arylindazole has been developed. Both vinyl cyclic carbonate and diallyl carbonate are effectively used for *ortho*-allylation *via* decarboxylation. The mechanism was investigated and possibly Mn(I)-catalyzed C–H bond activation is not involved in the rate-determining step.

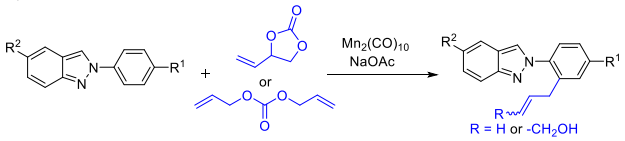
Keywords: C–H activation; manganese; allylation; decarboxylation; diastereoselective.

Introduction

In the past decades, transition metal-catalyzed C–H bond activation has emerged as an endurable method to improve step- and atom-economy in organic synthesis.[1] Precious 4d and 5d transition metals such as Pd,[2a] Rh,[2b] Ru,[2c] and Ir[2d] are extensively used in the traditional C–H functionalizations. Nowadays, earth-abundant 3d transition metals with lower toxicity have drawn much attention.[3] In this context, manganese has proved to be an efficient catalyst because of its low-cost and non-toxic nature.[4] Many research groups, such as those of Wang,[5] Ackermann,[6] Kuninobu, Takai,[7] and Glorius,[8] have made pioneering contributions in the use of Mn catalytic technology.

The incorporation of allyl groups in a molecule has drawn great interest due to the extensive utilization of allylated compounds in organic synthesis, biochemistry, and medicinal chemistry.[9] Traditionally, allylation is performed by metal-catalyzed cross-coupling[10a] and Friedel-Crafts reactions in presence of a Lewis acid.[10b] However, limited substrate scope, low regioselectivity, multistep reactions, and over allylation have restricted their application. Allylation through *ortho*-C–H activation will be a more advantageous method.[11]

Indazole, an important biologically active N-containing heterocycle, has a variety of applications in medicinal chemistry and material sciences. The substituted 2*H*-indazole moieties exhibit valuable pharmacological activities, such as HIV-protease inhibition and antimicrobial, antitumor, anti-inflammatory, and anticancer properties.[12] There are several marketed drugs, such as bendazac (tyrosine kinase inhibitor, votrient),[13a] gamendazole,[13b] and pazopanib,[13c] etc., containing indazole moiety. Moreover, indazole derivatives have shown photo-physical properties and are applied as fluorescent probes.[14] Hence, the synthesis and functionalization of indazoles have attracted considerable attention.[15-17] Considering the importance of allyl group and indazole moiety, it is highly desirable to develop a useful method to synthesis hybrid compounds containing the two pharmacophores. In this article, we have reported a manganese-catalyzed *ortho* selective C–H allylation of 2-arylindazoles with vinyl cyclic carbonate as well as diallyl carbonate (Scheme 1).



Scheme 1. Indazole-directed C–H allylation

Results and Discussion

Initially, we started our investigation with coupling between 2-(*p*-tolyl)-2*H*-indazole (**1b**) and 4-vinyl-1,3-dioxolan-2-one (**2**) in presence of 5 mol% $Mn_2(CO)_{10}$ as a catalyst and 20 mol% NaOAc as an additive in 1,4-dioxane at 100 °C under N_2 atmosphere. To our delight, allylated product **3b** was obtained in 90% yield with high diastereoselectivity after 10 h (Table 1, entry 1). Manganese (II) salts were examined but the desired product was not observed (Table 1, entries 2 and 3). Moreover, $MnBr(CO)_5$ was tested as a catalyst and afforded the product in 85% yield (Table 1, entry 4). The reaction was carried out without additive but unsatisfactory

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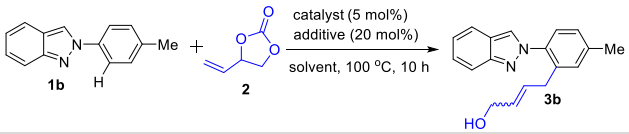
result was obtained (Table 1, entry 5). Furthermore, the use of additives other than NaOAc was screened but no improvement of the yield was observed (Table 1, entries 6-9). A variety of solvents were also examined (Table 1, entries 10-14) such as chlorobenzene, CH_3CN, THF, 1,2-DCE and TFE. Among them, 1,4-dioxane was found to be the appropriate solvent (Table 1, entry 1). Besides, no desired product was formed in absence of $Mn_2(CO)_{10}$ catalyst (Table 1, entry 15). The reaction was observed to be air sensitive (Table 1, entry 16) and an inert atmosphere was needed. Lower yield of the product was observed with both increasing and decreasing the reaction temperature (Table 1, entry 17). In addition, no further improvement of the yield and no difunctionalization product were obtained upon increasing the quantity of substrate **2** (Table 1 entry 18). Finally, the optimized reaction conditions was accomplished by using **1b** (0.2 mmol), **2** (0.3 mmol), 5 mol% of $Mn_2(CO)_{10}$, and 20 mol% of NaOAc in 1,4-dioxane (1.5 mL) for 10 h at 100 °C (Table 1, entry 1).

Table 1. Optimization of the reaction conditions.[a]



Entry	Catalyst 5 mol%	Additives (20 mol%)	Solvent (1.5 mL)	Yield (%)	*E*/*Z* Ratio
1	$Mn_2(CO)_{10}$	NaOAc	1,4-dioxane	90	6.9
2	$Mn(OAc)_2$	NaOAc	1,4-dioxane	nr	-
3	$MnCl_2$	NaOAc	1,4-dioxane	nr	-
4	$MnBr(CO)_5$	NaOAc	1,4-dioxane	85	6.1
5	$Mn_2(CO)_{10}$	-	1,4-dioxane	35	-
6	$Mn_2(CO)_{10}$	K_2CO_3	1,4-dioxane	32	-
7	$Mn_2(CO)_{10}$	Na_2CO_3	1,4-dioxane	41	-
8	$Mn_2(CO)_{10}$	Et_3N	1,4-dioxane	26	-
9	$Mn_2(CO)_{10}$	KOAc	1,4-dioxane	74	5.8
10	$Mn_2(CO)_{10}$	NaOAc	chlorobenzene	nr	-
11	$Mn_2(CO)_{10}$	NaOAc	CH_3CN	nr	-
12	$Mn_2(CO)_{10}$	NaOAc	THF	Trace	-
13	$Mn_2(CO)_{10}$	NaOAc	1,2-DCE	79	5.1
14	$Mn_2(CO)_{10}$	NaOAc	TFE	89	6.9
15	-	NaOAc	1,4-dioxane	nr	-
16	$Mn_2(CO)_{10}$	NaOAc	1,4-dioxane	Trace[b]	-
17	$Mn_2(CO)_{10}$	NaOAc	1,4-dioxane	85[c], 78[d]	6.9
18	$Mn_2(CO)_{10}$	NaOAc	1,4-dioxane	87[e]	6.7

[a] Reaction conditions: All reactions were carried out with **1b (**0.2 mmol**)**, **2 (**0.3 mmol**)**, $Mn_2(CO)_{10}$ (5 mol%), NaOAc (20 mol%), solvent (1.5 mL) for 10 h at 100 °C under N_2.
[b] Under air.
[c] Stirred at 120 °C,
[d] Stirred at 80 °C,
[e] 3.0 Equiv of **2** was used. nr = no reaction.

With the optimized reaction conditions in hand, we have evaluated their utility and limitations in the present manganese-catalyzed C–H allylation of 2-arylindazoles (Scheme 2). In the presence of electron-donating groups like -Me and -OMe at phenyl ring of 2-arylindazole, the corresponding products were obtained in excellent yield (**3b** and **3c**). Halogen like -F, -Cl and -Br substituted substrates gave moderate to good yields of the desired product (**3d-3f**, **3h** and **3k**). An electron-withdrawing group like -COOEt (**1g**) also produced the desired product (**3g**) with 67% yield. Disubstituted indazoles (**1i-1n**) were examined and effectively gave the *ortho*-allylation product without any difficulties (**3i-3n**). Moreover, 1-phenyl-1*H*-pyrazole (**1o**) was also reacted under the optimized reaction conditions and gave the desired product (**3o**) in 61% yield. On the other hand, *ortho*- and *meta*-substituted substrates did not give the expected product possibly due to the difficulty of the formation of five membered manganacyclic intermediate.

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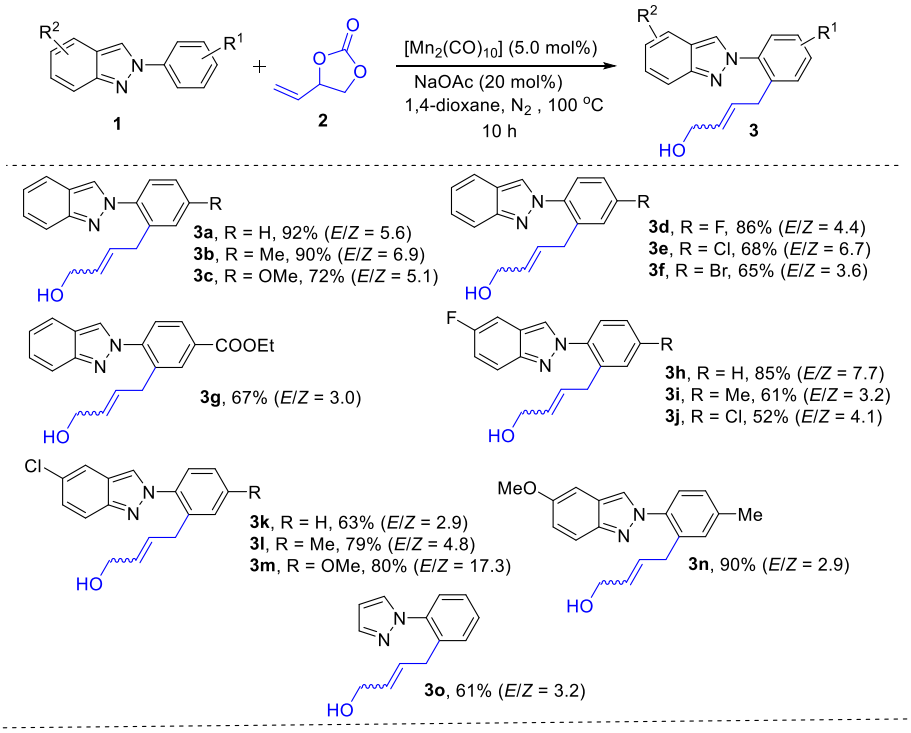
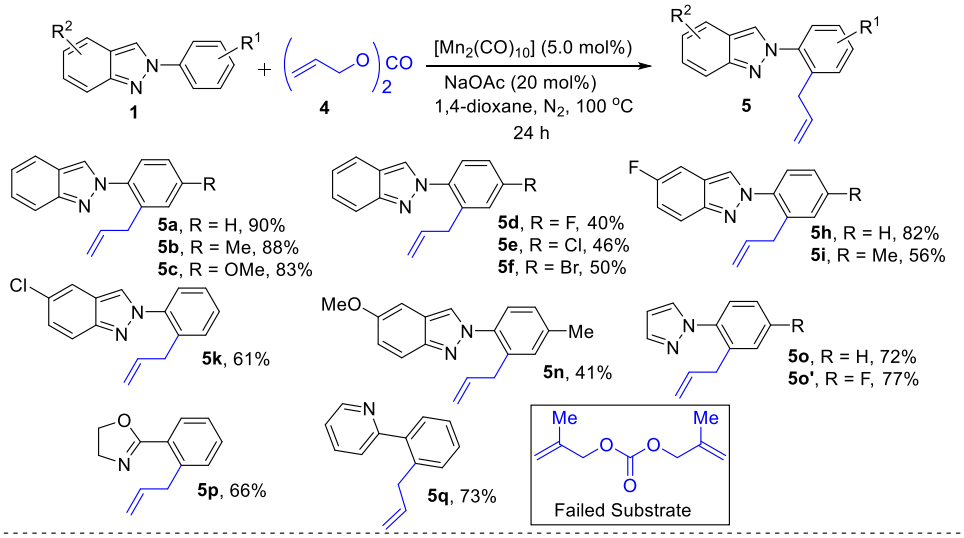


Scheme 2. Substrate scope of indazoles. *Reaction conditions*: **1** (0.2 mmol), **2** (0.3 mmol) in presence of $Mn_2[CO]_{10}$ (5 mol%), NaOAc (20 mol%), 1,4-dioxane (1.5 mL) at 100 °C for 10 h under N_2.

We have extended the present methodology using diallyl carbonate (**4**) for allylation as depicted in Scheme 3. The 2-arylindazole containing both electron-rich (-Me, -OMe) and electron-deficient (-F, -Cl, and -Br) groups on the phenyl ring of indazole reacted with diallyl carbonate gave the corresponding products **5b**-**5f** in 40-88% yields. The introduction of -F and -Cl groups at the C-5 position of the indazole ring did not affect the reaction efficiency (**5h**, **5k**). Moreover, disubstituted 2-arylindazole was reacted smoothly to give the expected products **5i** and **5n** in moderate yields. Interestingly, 1-phenyl-1*H*-pyrazole, 2-phenyl-4,5-dihydrooxazole, and 2-phenylpyridine were suitable substrates for this *ortho*-allylation reaction and gave the desired products (**5o**-**5q**) in 66-77% yields. However, dimethallyl carbonate was unable to provide the desired product under the present reaction conditions.



Scheme 3. Substrate scope of indazoles. *Reaction conditions*: **1** (0.2 mmol), **4** (0.3 mmol) in presence of $Mn_2(CO)_{10}$ (5 mol%), NaOAc (20 mol%), 1,4-dioxane (1.5 mL) at 100 °C for 24 h under N_2.

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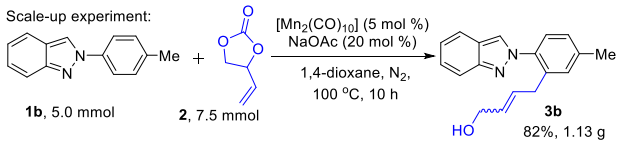
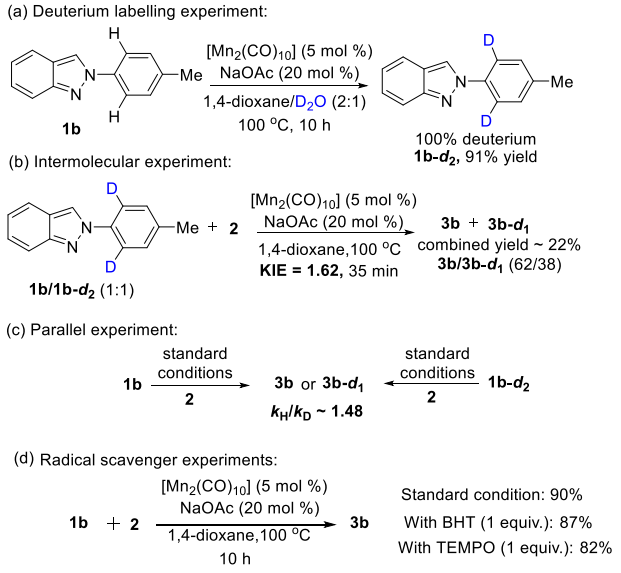
In order to show the synthetic applicability of this process, a gram scale reaction was carried out between 2-(*p*-tolyl)-2*H*-indazole (**1b**, 5 mmol) and 4-vinyl-1,3-dioxolan-2-one (**2**, 7.5 mmol) under the optimized reaction conditions as well as in the normal laboratory setup. Gratifyingly, the desired product was obtained in 82% yield (Scheme 4).



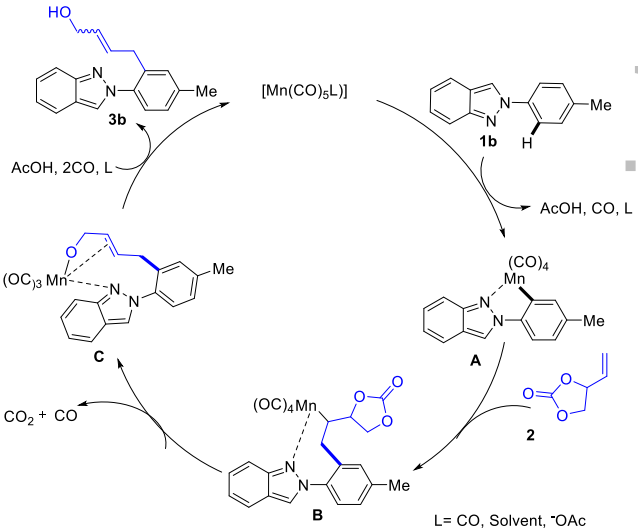
Scheme 4. Scale-up synthesis of 3b.

To explore the mechanistic route of the reaction, a series of controlled experiments were performed (Scheme 5). Firstly, H/D exchange experiment was carried out by using **1b** with D_2O as a co-solvent under our standard reaction condition. The ^1H NMR analysis showed that 100% deuterium was impregnated at the *ortho*-position of the phenyl ring in **1b-d₂** which indicating that a reversible deprotonative C–H bond activation step might be involved in the reaction (Scheme 5a). The intermolecular competition experiment (KIE = 1.62, Scheme 5b) and the parallel experiment (k_H/k_D = 1.48, Scheme 5c) indicate that Mn-catalyzed C–H bond activation step may not be involved in the rate-determining step. Finally, the reaction was carried out in the presence of radical scavengers like 2,6-di-tertbutyl-4-methylphenol (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), but the reaction efficiency did not alter which indicates that the reaction may not be involved in radical path (Scheme 5d).



Scheme 5. Control Experiments.

On the basis of control experiments and previous literature reports,[6b,8a] a plausible reaction pathway is proposed in Scheme 6. Initially, base-assisted cyclomanganation of 2-(*p*-tolyl)-2*H*-indazole (**1b**) forms a five membered manganacycle **A**. Next, coordination of 4-vinyl-1,3-dioxolan-2-one (**2**) with **A** leads to seven-membered manganacyclic intermediate **B**. It undergoes *β*-oxygen elimination to afford intermediate **C** through CO_2 gas evolution which accelerates the ring-opening of cyclic carbonate. Finally, the protonation of the **C** provides the desired product **3b** and regenerate the active Mn(I) complex.



Scheme 6. Plausible mechanistic pathway.

Conclusion

In conclusion, we have reported a $[Mn_2(CO)_{10}]$ catalyzed directed C–H allylation of 2-arylindazoles with both vinyl cyclic carbonate and diallyl carbonate under mild reaction conditions. The present reaction could be carried on a gram scale. Moreover, this method is associated with high functional groups tolerance. The kinetics studies have been conducted and it was observed that the C–H bond activation step may not be involved in the rate-determining step. To the best of our knowledge, this is the first report on the directed *ortho*-allylation of 2-arylindazole. We believe that this protocol of Mn-catalyzed directed C(sp^2)–H allylation of 2-arylindazoles will achieve significant applications in academic and industrial research.

Experimental section

General Information: All reagents were purchased from commercial sources and used without further purification. ^1H NMR spectra were determined on 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants (J) were given in Hz. $^{13}C\{^1H\}$ NMR spectra were recorded at 100 MHz in $CDCl_3$. Chemical shifts are referenced to $CDCl_3$ (δ = 7.26 for ^1H

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and δ = 77.16 for $^{13}C\{^1H\}$ NMR) as internal standard. TLC was done on silica gel coated glass slide. All solvents were dried and distilled before use. All reactions involving moisture sensitive reactants were executed using oven dried glassware. All the reactions were heated in oil bath. All 2-arylindazoles were prepared by the reported methods. [17]

Typical Experimental Procedure for the Synthesized Compounds (3a-3o): A mixture of 2-(*p*-tolyl)-2*H*-indazole (0.2 mmol, 41.6 mg) (**1b**), $Mn_2(CO)_{10}$ (5 mol%, 3.8 mg), and NaOAc (20 mol%, 3.2 mg) was taken in an oven dried screw-capped reaction tube. Then the reaction vessel was evacuated and filled with nitrogen for three times. After that, 4-vinyl-1,3-dioxolan-2-one (**2**) (0.3 mmol) and 1,4-dioxane (1.5 mL) were added, and the resultant mixture was stirred at 100 °C in oil bath for 10 h. After completion of the reaction (TLC), the reaction was cooled to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (70:30) as an eluting solvent to afford the pure product **3b** (50 mg, 90%) as a yellow gummy mass.

4-(2-(2*H*-Indazol-2-yl)phenyl)but-2-en-1-ol (3a): Colorless gummy mass (92%, 48.5 mg); R_f = 0.50 (PE / EA = 75 : 25); ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.78-7.34 (m, 2H), 7.40-7.37 (m, 5H), 7.14 (s, 1H), 5.63-5.36 (m, 2H), 3.90 (s, 2H), 3.34-3.30 (m, 2H), 1.84 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 149.31, 140.03, 136.16, 131.02, 130.79, 130.09, 129.78, 129.57, 127.25, 127.05, 126.69, 124.80, 122.38, 120.39, 117.90, 63.22, 34.35; *Minor isomer* : δ 139.85, 136.67, 130.50, 129.90, 129.70, 129.62, 127.17, 126.86, 124.97, 122.50, 122.01, 117.83, 58.04, 29.45; *Three peaks are missing due to overlap;* Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60%; Found: C, 77.43; H, 6.14; N, 10.50%.

4-(2-(2*H*-Indazol-2-yl)-5-methylphenyl)but-2-en-1-ol (3b): Yellow gummy mass (90%, 50 mg); R_f = 0.50 (PE / EA = 70 : 30); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05-8.04 (m, 1H), 7.79-7.75 (m, 1H), 7.72-7.69 (m, 1H), 7.35-7.30 (m, 2H), 7.28-7.24 (m, 1H), 7.17-7.10 (m, 3H), 5.62-5.25 (m, 1H), 3.93-3.89 (m, 2H), 3.29-3.23 (m, 2H), 2.39 (s, 3H), 2.24 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 149.16, 139.62, 137.54, 135.74, 131.24, 130.89, 129.69, 127.79, 126.77, 126.56, 124.86, 122.23, 121.90, 120.33, 117.78, 63.10, 34.25, 21.28; *Minor isomer* : δ 149.26, 139.78, 137.36, 136.25, 132.17, 130.97, 129.98, 129.56, 127.70, 126.72, 125.02, 122.34, 121.38, 117.72, 57.91, 29.30; *Two peaks are missing due to overlap*; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O$: 279.1492; found: 279.1495.

4-(2-(2*H*-Indazol-2-yl)-5-methoxyphenyl)but-2-en-1-ol (3c): Colorless gummy mass (72%, 42 mg); R_f = 0.50 (PE / EA = 65 : 35); ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.63-7.55 (m, 2H), 7.19 (t, *J* = 8.8 Hz, 2H), 6.99 (t, *J* = 8.4 Hz, 1H), 6.72-6.69 (m, 2H), 5.48-5.20 (m, 2H), 3.79-3.76 (m, 2H), 3.70 (s, 3H), 3.14-3.07 (m, 2H), 2.32 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 160.21, 149.00, 137.73, 133.10, 131.18, 129.31, 128.58, 128.18, 126.66, 125.19, 122.28, 120.34, 117.67, 115.54, 111.99, 63.05, 55.64, 34.46; *Minor isomer* : δ 160.31, 149.16, 138.16, 132.18, 130.32, 129.21, 127.88, 126.77, 126.26, 125.29, 122.36, 121.87, 121.38, 115.86, 111.99, 57.91, 29.47; *One peak is missing due to overlap*; Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52%; Found: C, 73.26; H, 6.19; N, 9.44%.

4-(5-Fluoro-2-(2*H*-indazol-2-yl)phenyl)but-2-en-1-ol (3d): Colorless gummy mass (86%, 48.5 mg); R_f = 0.55 (PE / EA = 70 : 30); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.77-7.71 (m, 2H), 7.40-7.35 (m, 2H), 7.15-7.05 (m, 3H), 5.64-5.42 (m, 2H), 3.95 (s, 2H), 3.32-3.26 (m, 2H), 1.72 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 162.88 (C-F, $^1J_{C\text{-}F}$ = 248.0 Hz), 149.41, 139.07, 136.16, 131.77, 128.87, 128.74 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 126.85, 124.97, 122.60 (C-F, $^3J_{C\text{-}F}$ = 11.0 Hz), 120.37, 117.90, 117.29 (C-F, $^2J_{C\text{-}F}$ = 23.0 Hz), 114.13 (C-F, $^2J_{C\text{-}F}$ = 23.0 Hz), 63.16, 34.28; *Minor isomer* : δ 164.23, 138.99, 136.01, 130.81, 127.02, 125.14, 122.05, 117.82, 116.96, 114.17, 113.94, 58.05, 29.41; *Four peaks are missing due to C-F coupling and overlap*; Anal. Calcd for $C_{17}H_{15}FN_2O$: C, 72.33; H, 5.36; N, 9.92%; Found: C, 72.12; H, 5.33; N, 10.01%.

4-(5-Chloro-2-(2*H*-indazol-2-yl)phenyl)but-2-en-1-ol (3e): Yellow gummy mass (68%, 40.5 mg); R_f = 0.50 (PE / EA = 70 : 30); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.79-7.70 (m, 2H), 7.39-7.33 (m, 4H), 7.17-7.13 (m, 1H), 5.64-5.51 (m, 1H), 5.49-5.41 (m, 1H), 3.96 (d, *J* = 5.2 Hz, 2H), 3.36-3.29 (m, 2H), 1.69 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 149.54, 138.09, 135.38, 131.78, 130.70, 130.49, 128.74, 128.31, 127.43, 126.93, 124.79, 122.64, 122.13, 120.38, 117.95, 63.21, 34.24; *Minor isomer* : δ 138.59, 135.56, 132.26, 130.78, 128.66, 127.34, 127.11, 124.98, 122.75, 121.45, 117.87, 58.12, 29.40; *Four peak are missing due to overlap*; Anal. Calcd for $C_{17}H_{15}ClN_2O$: C, 68.34; H, 5.06; N, 9.38%; Found: C, 68.54; H, 5.11; N, 9.49%.

4-(5-Bromo-2-(2*H*-indazol-2-yl)phenyl)but-2-en-1-ol (3f): Yellow gummy mass (65%, 44 mg); R_f = 0.50 (PE / EA = 70 : 30); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.79-7.70 (m, 2H), 7.54-7.48 (m, 2H), 7.36-7.26 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.63-5.39 (m, 2H), 3.95 (d, *J* = 4.4 Hz, 2H), 3.35-3.28 (m, 2H), 2.28 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 149.45, 138.99, 138.30, 133.64, 131.73, 130.76, 130.41, 128.64, 128.53, 126.98, 124.80, 123.50, 122.64, 120.38, 117.86, 63.12, 34.16; *Minor isomer* : δ 149.55, 138.83, 138.78, 138.24, 133.43, 130.32, 128.49, 127.15, 124.98, 123.66, 122.75, 122.07, 117.78, 58.03, 29.28; *Two peaks are missing due to overlap*; Anal. Calcd for $C_{17}H_{15}BrN_2O$: C, 59.49; H, 4.41, N, 8.16%; Found: C, 59.66; H, 4.43; N, 8.09%.

Ethyl 3-(4-hydroxybut-2-en-1-yl)-4-(2*H*-indazol-2-yl)benzoate (3g): Colorless gummy mass (67%, 45 mg); R_f = 0.50 (PE / EA = 55 : 45); ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 8.10-8.02 (m, 2H), 7.79 (t, *J* = 8.4 Hz, 1H), 7.74-7.71 (m, 1H), 7.52-7.47 (m, 1H), 7.38-7.33 (m, 1H), 7.18-7.13 (m, 1H), 5.68-5.40 (m, 2H), 4.44-4.39 (m, 2H), 3.99-3.93 (m, 2H), 3.49-3.43 (m, 2H), 1.72 (br, 1H), 1.42 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 165.85, 149.67, 143.49, 136.24, 132.36, 132.05, 131.51, 130.55, 129.17, 128.57, 127.23, 127.10, 124.66, 122.74, 120.43, 118.01, 63.21, 61.61, 34.53, 14.45; *Minor isomer* : δ 165.80, 149.74, 143.28, 136.87, 131.35, 129.08, 128.48, 127.05, 124.87, 122.84, 122.20, 117.91, 58.22, 29.72; *Six peaks are missing due to overlap*; Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33%; Found: C, 71.23; H, 5.95; N, 8.41%.

4-(2-(5-Fluoro-2*H*-indazol-2-yl)phenyl)but-2-en-1-ol (3h): Colorless gummy mass (85%, 47.9 mg); R_f = 0.45 (PE / EA = 75 : 25); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.77-7.73 (m, 1H), 7.46-7.34 (m, 4H), 7.30-7.28 (m, 1H), 7.17-7.12 (m, 1H), 5.66-5.36 (m, 2H), 3.97-3.93 (m, 2H), 3.36-3.29 (m, 2H), 1.76 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 158.73 (C-F, $^1J_{C\text{-}F}$ = 239.0 Hz), 146.76, 139.88, 136.05, 131.01, 130.87, 129.93, 129.77, 127.34, 126.97, 124.89 (C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 119.94 (C-F, $^3J_{C\text{-}F}$ = 5.0 Hz), 118.34 (C-F, $^2J_{C\text{-}F}$ = 28.0 Hz), 102.76 (C-F, $^2J_{C\text{-}F}$ = 25.0 Hz), 63.27, 34.31; *Minor isomer* : δ 158.68 (C-F, $^1J_{C\text{-}F}$ = 240.0 Hz), 146.85, 139.69, 136.56, 130.58, 130.03, 129.71, 127.26, 120.04 (C-F, $^3J_{C\text{-}F}$ = 5.0 Hz), 118.50 (C-F, $^2J_{C\text{-}F}$ = 29.0 Hz), 58.08, 29.42; *Five peaks are missing due to C-F coupling and overlap*; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}FN_2O$: 283.1241; found: 283.1244.

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4-(2-(5-Fluoro-2*H*-indazol-2-yl)-5-methylphenyl)but-2-en-1-ol (3i): Yellow gummy mass (61%, 36 mg); R_f = 0.50 (PE / EA = 72 : 28); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 1H), 7.77-7.21 (m, 1H), 7.30-7.24 (m, 2H), 7.19-7.11 (m, 3H), 5.65-5.36 (m, 2H), 3.96-3.93 (m, 2H), 3.31-3.24 (m, 2H), 2.41 (s, 3H), 1.77 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 158.63 (C-F, $^1J_{C\text{-}F}$ = 238.0 Hz), 146.68, 139.83, 137.49, 135.67, 131.34, 130.87, 129.91, 127.87 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 126.73, 124.95 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 121.15, 120.01, 118.34 (C-F, $^2J_{C\text{-}F}$ = 19.0 Hz), 102.76 (C-F, $^2J_{C\text{-}F}$ = 22.0 Hz), 63.29, 34.28, 21.35; *Minor isomer* : δ 146.77, 140.00, 137.29, 136.17, 132.23, 131.08, 125.13 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 121.48, 121.26, 119.94 (C-F, $^3J_{C\text{-}F}$ = 5.0 Hz), 118.17 (C-F, $^2J_{C\text{-}F}$ = 29.0 Hz), 102.76 (C-F, $^2J_{C\text{-}F}$ = 24.0 Hz), 58.06, 29.34; *Four peaks are missing due to C-F coupling and overlap*; Anal. Calcd for $C_{18}H_{17}FN_2O$: C, 72.95; H, 5.78; N, 9.45%; Found: C, 72.81; H, 5.73; N, 9.56%.

4-(5-Chloro-2-(5-fluoro-2*H*-indazol-2-yl)phenyl)but-2-en-1-ol (3j): Colorless gummy mass (52%, 32.8 mg); R_f = 0.55 (PE / EA = 65 : 35); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.77-7.24 (m, 1H), 7.39-7.33 (m, 3H), 7.29-7.27 (m, 1H), 7.17-7.12 (m, 1H), 5.64-5.43 (m, 2H), 3.98 (d, J = 5.6 Hz, 2H), 3.35-3.28 (m, 2H), 1.78 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 158.76 (C-F, $^1J_{C\text{-}F}$ = 239.0 Hz), 146.94, 138.38, 138.21, 135.52, 131.81, 130.75, 128.66, 128.19, 127.47, 124.90 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 121.31, 120.02 (C-F, $^3J_{C\text{-}F}$ = 6.0 Hz), 118.63 (C-F, $^2J_{C\text{-}F}$ = 29.0 Hz), 102.75 (C-F, $^2J_{C\text{-}F}$ = 29.0 Hz), 63.16, 34.15; *Minor isomer* : δ 138.43, 137.99, 135.68, 132.25, 130.52, 128.96, 128.74, 127.39, 125.07 (C-F, $^3J_{C\text{-}F}$ = 7.0 Hz), 121.50, 121.43, 121.36, 120.02 (C-F, $^3J_{C\text{-}F}$ = 14.0 Hz), 118.79 (C-F, $^2J_{C\text{-}F}$ = 28.0 Hz), 102.86, 58.11, 29.31; *One peak is missing due to C-F coupling and overlap;* Anal. Calcd for $C_{17}H_{14}ClFN_2O$: C, 64.46; H, 4.46; N, 8.84%; Found: C, 64.65; H, 4.43; N, 8.78%.

4-(2-(5-Chloro-2*H*-indazol-2-yl)phenyl)but-2-en-1-ol (3k): Colorless gummy mass (63%, 37.5 mg); R_f = 0.50 (PE / EA = 70 : 30); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03, 7.74-7.70 (m, 2H), 7.46-7.34 (m, 4H), 7.28-7.27 (m, 1H), 5.66-5.37 (m, 2H), 3.97-3.93 (m, 2H), 3.35-3.28 (m, 2H), 2.05 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 147.66, 139.74, 136.05, 131.05, 130.90, 130.60, 129.85, 129.68, 128.13, 127.36, 126.95, 124.46, 122.37, 119.48, 119.09, 63.24, 34.28; *Minor isomer* : δ 147.76, 139.55, 136.54, 132.23, 130.08, 130.00, 129.61, 128.29, 128.03, 127.27, 124.62, 119.43, 58.11, 29.43; *Three peaks are missing due to overlap*; Anal. Calcd for $C_{17}H_{15}ClN_2O$: C, 68.34; H, 5.06; N, 9.38%; Found: C, 68.17; H, 5.04; N, 9.50%.

4-(2-(5-Chloro-2*H*-indazol-2-yl)-5-methylphenyl)but-2-en-1-ol (3l): Colorless gummy mass (79%, 49 mg); R_f = 0.45 (PE / EA = 75 : 25); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.78 (m, 1H), 7.51-7.46 (m, 2H), 7.05-7.02 (m, 2H), 6.94 (t, J = 10.4 Hz, 2H), 5.42-5.12 (m, 2H), 3.73-3.70 (m, 2H), 3.07-3.00 (m, 2H), 2.18 (s, 3H), 1.59 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 147.55, 139.93, 137.32, 135.64, 131.37, 130.90, 129.79, 127.97, 127.93, 127.88, 126.70, 124.51, 122.31, 119.43, 119.05, 63.23, 34.25, 21.34; *Minor isomer* : δ 147.66, 140.09, 136.14, 131.09, 129.94, 129.74, 128.13, 127.84, 124.67, 119.37, 58.04, 29.33; *Six peaks are missing due to overlap*; Anal. Calcd for $C_{18}H_{17}ClN_2O$: C, 69.12; H, 5.48; N, 8.96%; Found: C, 69.25; H, 5.51; N, 9.03%.

4-(2-(5-Chloro-2*H*-indazol-2-yl)-5-methoxyphenyl)but-2-en-1-ol (3m): Yellow gummy mass (80%, 52.5 mg); R_f = 0.50 (PE / EA = 60 : 40); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.73-7.68 (m, 2H), 7.33-7.25 (m, 2H), 6.90-6.84 (m, 2H), 5.65-5.37 (m, 2H), 3.95 (d, J = 5.2 Hz, 2H), 3.86 (s, 3H), 3.29-3.23 (m, 2H), 1.81 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 160.42, 147.45, 137.65, 132.93, 131.19, 129.50, 128.20, 128.14, 128.07, 124.76, 122.30, 119.40, 119.05, 116.03, 112.11, 63.27, 55.73, 34.49; *Minor isomer* : δ 130.25, 127.97, 124.90, 122.35, 115.71, 112.07, 58.11, 29.56; *Ten peaks are missing due to overlap*; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}ClN_2O_2$: 329.1051; found: 329.1042.

4-(2-(5-Methoxy-2*H*-indazol-2-yl)-5-methylphenyl)but-2-en-1-ol (3n): Colorless gummy mass (90%, 55.4 mg); R_f = 0.50 (PE / EA = 60 : 40); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.74 (s, 1H), 7.34-7.12 (m, 4H), 6.99 (s, 1H), 5.67-5.49 (m, 2H), 4.01 (s, 2H), 3.92 (s, 3H), 3.38-3.33 (m, 2H), 2.48 (s, 3H), 2.21 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 155.38, 146.10, 139.42, 137.67, 135.73, 131.22, 130.83, 129.94, 127.78, 126.77, 123.85, 121.72, 121.55, 119.19, 96.37, 63.23, 55.45, 34.27, 21.28; *Minor isomer* : δ 155.46, 139.60, 137.49, 136.24, 130.96, 129.79, 127.69, 124.03, 121.88, 119.16, 58.00, 29.34; *Seven peaks are missing due to overlap*; Anal. Calcd for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08%; Found: C, 73.85; H, 6.59; N, 8.99%.

4-(2-(5-Methoxy-2*H*-indazol-2-yl)-5-methylphenyl)but-2-en-1-ol (3o): Colorless gummy mass (61%, 26 mg); R_f = 0.50 (PE / EA = 75 : 25); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 11.2 Hz, 1H), 7.58 (s, 1H), 7.36-7.31 (m, 4H), 6.44 (t, J = 4.0 Hz, 1H), 5.67-5.46 (m, 2H), 4.06-4.00 (m, 2H), 3.39-3.32 (m, 2H), 1.71 (br, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *Major isomer* : δ 139.77, 136.04, 130.82, 130.74, 130.53, 130.25, 129.74, 128.89, 127.28, 126.75, 106.40, 63.49, 34.48; *Minor isomer* : δ 139.54, 136.64, 130.41, 129.10, 127.18, 126.81, 106.54, 58.17, 29.56; *Four peaks are missing due to overlap*; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O$: 215.1179; found: 215.1177.

Typical Experimental Procedure for the Synthesized Compounds (5a-5q): A mixture of 2-(*p*-tolyl)-2*H*-indazole (0.2 mmol, 41.6 mg) (**1b**), $Mn_2(CO)_{10}$ (5 mol%, 3.8 mg), and NaOAc (20 mol%, 3.2 mg) was taken in an oven dried screw-capped reaction tube. Then the reaction vessel was evacuated and filled with nitrogen for three times. After that, diallyl carbonate (**4)** (0.3 mmol) and 1,4-dioxane (1.5 mL) were added, and the resultant mixture was stirred at 100 °C in oil bath for 24 h. After completion of the reaction (TLC), the reaction was cooled to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (95:5) as an eluting solvent to afford the pure product **5b** (43.6 mg, 88%) as a yellow gummy mass.

2-(2-Allylphenyl)-2*H*-indazole (5a): Yellow gummy mass (90%, 42 mg); R_f = 0.50 (PE / EA = 95 : 5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.48-7.44 (m, 2H), 7.41-7.33 (m, 3H), 7.17-7.13 (m, 1H), 5.90-5.76 (m, 1H), 5.02-5.00 (m, 1H), 4.93-4.88 (m, 1H), 3.32 (d, J = 6.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.3, 140.0, 136.4, 135.8, 130.7, 129.4, 127.1, 127.0, 126.5, 124.7, 122.2, 121.9, 120.4, 117.9, 116.6, 35.4; Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96%; Found: C, 82.14; H, 5.98; N, 11.88%.

2-(2-Allyl-4-methylphenyl)-2*H*-indazole (5b): Yellow gummy mass (88%, 43.6 mg); R_f = 0.50 (PE / EA = 95 : 5), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.80-7.78 (m, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.35-7.31 (m, 2H), 7.19-7.15 (m, 1H), 7.13-7.11 (m, 2H), 5.88-5.80 (m, 1H), 5.01-4.98 (m, 1H), 4.93-4.88 (m, 1H), 3.27 (d, J = 6.4 Hz, 2H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.3, 139.5, 137.7, 136.6, 135.5, 131.2, 127.7, 126.8, 126.4, 124.8, 122.1, 121.9, 120.4, 117.9, 116.4, 35.4, 21.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2$: 249.1386; found: 249.1381.

2-(2-Allyl-4-methoxyphenyl)-2*H*-indazole (5c): Yellow gummy mass (83%, 43.8 mg); R_f = 0.50 (PE / EA = 90 : 10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.37-7.31 (m, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.89-6.85 (m, 2H), 5.87-5.77 (m,

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1H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.92 (d, *J* = 17.2 Hz, 1H), 3.86 (s, 3H), 3.24 (d, *J* = 6.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 160.1, 149.2, 137.5, 136.2, 133.3, 128.1, 126.4, 125.0, 122.1, 121.9, 120.3, 117.9, 116.8, 115.5, 112.1, 55.6, 35.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O$: 265.1335; found: 265.1332.

2-(2-Allyl-4-fluorophenyl)-2*H*-indazole (5d): Colorless gummy mass (40%, 20 mg); R_f = 0.50 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.07 (s, 1H), 7.79-7.7.76 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.43-7.40 (m, 1H), 7.37-7.33 (m, 1H), 7.17-7.14 (m, 1H), 7.13-7.11 (m, 1H), 7.09-7.07 (m, 1H), 7.06-7.03 (m, 1H), 5.86-5.76 (m, 1H), 5.07-5.04 (m, 1H), 4.96-4.92 (m, 1H), 3.26 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 162.9 (C-F, $^1J_{C\text{-}F}$ = 248.0 Hz), 135.5, 128.8 (C-F, $^3J_{C\text{-}F}$ = 10.0 Hz), 127.1, 126.7, 125.0, 124.9, 122.4, 120.4, 118.0, 117.5, 117.4, 117.2 (C-F, $^2J_{C\text{-}F}$ = 22.0 Hz), 114.0 (C-F, $^2J_{C\text{-}F}$ = 22.0 Hz), 35.4; Anal. Calcd for $C_{16}H_{13}FN_2$: C, 76.17; H, 5.19; N, 11.10%; Found: C, 76.33; H, 5.21; N, 11.19%.

2-(2-Allyl-4-chlorophenyl)-2*H*-indazole (5e): Colorless gummy mass (46%, 24.6 mg); R_f = 0.50 (PE / EA = 92 : 8); ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.08 (s, 1H), 7.78-7.76 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.40-7.38 (m, 2H), 7.36-7.33 (m, 2H), 7.16-7.12 (m, 1H), 5.86-5.76 (m, 1H), 5.06-5.04 (m, 1H), 4.96-4.91 (m, 1H), 3.29 (d, *J* = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 149.5, 135.5, 130.6, 129.8, 128.2, 127.2, 126.8, 124.8, 122.9, 122.8, 122.5, 120.5, 120.4, 117.9, 117.5, 35.3; Anal. Calcd for $C_{16}H_{13}ClN_2$: C, 71.51; H, 4.88; N, 10.42%; Found: C, 71.66; H, 4.84; N, 10.31%.

2-(2-Allyl-4-bromophenyl)-2*H*-indazole (5f): Colorless gummy mass (50%, 31 mg); R_f = 0.45 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.08 (s, 1H), 7.79-7.76 (m, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.51-7.49 (m, 1H), 7.36-7.31 (m, 2H), 7.16-7.12 (m, 1H), 5.86-5.76 (m, 1H), 5.06-5.04 (m, 1H), 4.96-4.91 (m, 1H), 3.28 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 149.6, 139.1, 138.1, 135.5, 133.6, 130.3, 128.5, 126.8, 124.7, 123.4, 122.5, 122.1, 120.4, 118.0, 117.4, 35.3; Anal. Calcd for $C_{16}H_{13}BrN_2$: C, 61.36; H, 4.18; N, 8.94%; Found: C, 61.58; H, 4.21; N, 9.01%.

2-(2-Allylphenyl)-5-fluoro-2*H*-indazole (5h): Yellow gummy mass (82%, 41 mg); R_f = 0.50 (PE / EA = 93 : 7); ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.06 (s, 1H), 7.78-7.74 (m, 1H), 7.48-7.35 (m, 4H), 7.31-7.28 (m, 1H), 7.17-7.12 (m, 1H), 5.88-5.78 (m, 1H), 5.01-4.98 (m, 1H), 4.91-4.86 (m, 1H), 3.30 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 158.6 (C-F, $^1J_{C\text{-}F}$ = 241.0 Hz), 146.8, 139.9, 136.3, 135.8, 130.8, 129.6, 127.2, 126.9, 124.9 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 121.3, 121.1, 120.0 (C-F, $^3J_{C\text{-}F}$ = 10.0 Hz), 118.2 (C-F, $^2J_{C\text{-}F}$ = 29.0 Hz), 116.6, 102.7 (C-F, $^2J_{C\text{-}F}$ = 25.0 Hz), 35.5; Anal. Calcd for $C_{16}H_{13}FN_2$: C, 76.17; H, 5.19; N, 11.10%; Found: C, 76.04; H, 5.15; N, 11.02%.

2-(2-Allyl-4-methylphenyl)-5-fluoro-2*H*-indazole (5i): Yellow gummy mass (56%, 29.8 mg); R_f = 0.50 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.03 (s, 1H), 7.71-7.73 (m, 1H), 7.31-7.27 (m, 2H), 7.18-7.10 (m, 3H), 5.86-5.76 (m, 1H), 5.00-4.97 (m, 1H), 4.91-4.86 (m, 1H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 158.6 (C-F, $^1J_{C\text{-}F}$ = 238.0 Hz), 146.7, 139.6, 137.5, 136.5, 135.4, 131.3, 126.6, 124.9 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 120.0 (C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 118.0 (C-F, $^2J_{C\text{-}F}$ = 28.0 Hz), 116.5, 102.7 (C-F, $^2J_{C\text{-}F}$ = 24.0 Hz), 35.4, 21.3; Anal. Calcd for $C_{17}H_{15}FN_2$: C, 76.67; H, 5.68; N, 10.52%; Found: C, 76.88; H, 5.71; N, 10.59%.

2-(2-Allylphenyl)-5-chloro-2*H*-indazole (5k): Yellow gummy mass (61%, 32.7 mg); R_f = 0.50 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.05 (s, 1H), 7.74-7.70 (m, 2H), 7.48-7.35 (m, 5H), 7.28-7.25 (m, 1H), 5.87-5.77 (m, 1H), 5.00-4.98 (m, 1H), 4.89-4.85 (m, 1H), 3.28 (d, *J* = 6.4 Hz, 2H);$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 147.7, 139.8, 136.2, 135.8, 130.8, 129.7, 128.0, 127.9, 127.2, 126.9, 124.4, 122.3, 119.5, 119.1, 116.7, 35.5; Anal. Calcd for $C_{16}H_{13}ClN_2$: C, 71.51; H, 4.88; N, 10.42%; Found: C, 71.36; H, 4.86; N, 10.53%.

2-(2-Allyl-4-methylphenyl)-5-methoxy-2*H*-indazole (5n): Colorless gummy mass (41%, 22.7 mg); R_f = 0.50 (PE / EA = 90 : 10); ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.93 (s, 1H), 7.67 (d, *J* = 9.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.05-7.02 (m, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 5.88-5.78 (m, 1H), 5.01-4.98 (m, 1H), 4.93-4.88 (m, 1H), 3.86 (s, 3H), 3.27 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 155.4, 146.2, 139.3, 137.8, 136.7, 135.5, 131.2, 127.7, 126.7, 123.8, 121.9, 121.4, 119.4, 116.4, 96.4, 55.5, 35.5, 21.3; Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06%; Found: C, 77.85; H, 6.56; N, 10.11%.

1-(2-Allylphenyl)-1*H*-pyrazole (5o):[11c] Yellow gummy mass (72%, 26.5 mg); R_f = 0.50 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.72 (d, *J* = 1.6 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.38-7.30 (m, 4H), 6.42 (d, *J* = 2.0 Hz, 1H), 5.89-5.79 (m, 1H), 5.03-4.95 (m, 1H), 4.94-4.90 (m, 1H), 3.33 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 140.4, 139.8, 136.6, 135.8, 130.9, 130.7, 128.7, 127.1, 126.6, 116.3, 106.3, 35.6; Anal. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21%; Found: C, 78.39; H, 6.53; N, 15.09%.

1-(2-Allyl-4-fluorophenyl)-1*H*-pyrazole (5o'):[11c] Yellow gummy mass (77%, 31 mg); R_f = 0.50 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.71 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.32-7.28 (m, 1H), 7.05-6.97 (m, 2H), 6.42 (t, *J* = 2.4 Hz, 1H), 5.58-5.75 (m, 1H), 5.07-5.04 (m, 1H), 4.98-4.93 (m, 1H), 3.26 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 162.4 (C-F, $^1J_{C\text{-}F}$ = 247.0 Hz), 140.6, 138.7 (C-F, $^3J_{C\text{-}F}$ = 8.0 Hz), 135.8 (C-F, $^2J_{C\text{-}F}$ = 25.0 Hz), 131.1, 128.4 (C-F, $^3J_{C\text{-}F}$ = 9.0 Hz), 117.2, 117.1, 117.0, 113.9 (C-F, $^2J_{C\text{-}F}$ = 23.0 Hz), 106.4, 35.5; Anal. Calcd for $C_{12}H_{11}FN_2$: C, 71.27; H, 5.48; N, 13.85%; Found: C, 71.07; H, 5.46; N, 13.93%.

2-(2-Allylphenyl)-4,5-dihydrooxazole (5p): Colorless gummy mass (66%, 24.6 mg); R_f = 0.50 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.78-7.76 (m, 1H), 7.40-7.35 (m, 1H), 7.27-7.24 (m, 2H), 6.04-5.94 (m, 1H), 5.05-5.04 (m, 1H), 5.02-4.97 (m, 1H), 4.38 (t, *J* = 9.6 Hz, 2H), 4.07 (t, *J* = 9.6 Hz, 2H), 3.78 (d, *J* = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 165.0, 140.4, 137.6, 130.8, 130.4, 130.1, 127.2, 126.1, 115.6, 67.0, 55.4, 38.4; Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%; Found: C, 77.21; H, 7.03; N, 7.54%.

2-(2-Allylphenyl)pyridine (5q):[11b] Yellow gummy mass (73%, 28.5 mg); R_f = 0.50 (PE / EA = 95 : 5); ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.58 (d, *J* = 4.8 Hz, 1H), 7.63-7.59 (m, 1H), 7.30-7.13 (m, 6H), 5.83-5.64 (m, 1H), 4.87-4.76 (m, 2H), 3.40 (d, *J* = 6.4 Hz, 2H);$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 159.7, 149.1, 140.3, 137.5, 136.1, 130.0, 129.8, 128.4, 126.3, 125.1, 124.1, 121.7, 115.6, 37.4; Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17%; Found: C, 85.98; H, 6.75; N, 7.27%.

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References

[1] a) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev*. **2009**, *38*, 3242-3272; b) P. Gandeepan, T. Müller, D. Zell, G. Cera, S. Warratz, L. Ackermann, *Chem. Rev*. **2019**, *119*, 2192- 2452.

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[2] a) T. W. Lyons, M. S. Sanford, *Chem. Rev*. **2010**, *110*, 1147-1169; b) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev*. **2010**, *110*, 624-655; c) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev*. **2012**, *112*, 5879-5918; d) Q. Cheng, H.-F. Tu, C. Zheng, J. -P. Qu, G. Helmchen, S. -L. You, *Chem. Rev*. **2019**, *119*, 1855-1969.

[3] a) K. Gao, N. Yoshikai, *Acc. Chem. Res*. **2014**, *47*, 1208–1219; b) R. Shang, L. Ilies, E. Nakamura, *Chem. Rev*. **2017**, *117*, 9086-9139; c) S. Rana, J. P. Biswas, S. Paul, A. Paik, D. Maiti, *Chem. Soc. Rev*. **2020**, *50*, 243-472.

[4] a) W. Liu, L. Ackermann, *ACS Catal*. **2016**, *6*, 6, 3743–3752; b) Y. Hu, B. Zhou, C. Wang, *Acc. Chem. Res*. **2018**, *51*, 3, 816–827.

[5] a) B. Zhou, H. Chen, C. Wang, *J. Am. Chem. Soc*. **2013**, *135*, 1264-1267; b) S. Ali, J. Huo, C. Wang, *Org. Lett*. **2019**, *21* (17), 6961-6965.

[6] a) Y.-F. Liang, L. Massignan, W. Liu, L. Ackermann, *Chem.–Eur. J*. **2016**, *22*, 14856-14859; b) H. Wang, M. M. Lorion, L. Ackermann, *Angew. Chem. Int. Ed*. **2017**, *56*, 6339-6342.

[7] a) Y. Kuninobu, Y. Nishina, T. Takeuchi, K. Takai, *Angew. Chem. Int. Ed*. **2007**, *46*, 6518-6520; b) S. Sueki, Z. Wang, Y. Kuninobu, *Org. Lett*. **2016**, *18*, 304-307.

[8] a) Q. Lu, F. J. R. Klauck, F. Glorius, *Chem. Sci*. **2017**, *8*, 3379-3383; b) S. Cembellín, T. Dalton, T. Pinkert, F. Schafers, F. Glorius, *ACS Catal*. **2020**, *10*, 197-202.

[9] a) B. M. Trost, O. R. Thiel, H.-C. Tsui, *J. Am. Chem. Soc*. **2002**, *124*, 11616-11617; b) J. L. Farmer, H. N. Hunter, M. G. Organ, *J. Am. Chem. Soc*. **2012**, *134*, 17470-17473.

[10] a) H. Ohmiya, Y. Makida, T. Tanaka, M. Sawamura *J. Am. Chem. Soc*. **2008**, *130*, 17276−17277; b) M. Niggemann, M. J. Meel, *Angew. Chem. Int. Ed*. **2010**, *49*, 3684−3687.

[11] a) M. Nakamura, A. Hajra, K. Endo, E. Nakamura, *Angew. Chem. Int. Ed*. **2005**, *44*, 7248−7251; b) H. Wang, N. Schroder, F. Glorius, *Angew. Chem. Int. Ed*. **2013**, *52*, 5386–5389; c) S. Asako, J. Norinder, L. Ilies, N. Yoshikai, E. Nakamura, *Adv. Synth. Catal*. **2014**, *356*, 1481–1485; d) S. Debbarma, S. S. Bera, M. S. Maji, *J. Org. Chem*. **2016**, *81*, 11716−11725; e) N. K. Mishra, S. Sharma, J. Park, S. Han, I. S. Kim, *ACS Catal*. **2017**, *7*, 2821−2847; f) M. S. Raja, S. S. Bera, M. S. Maji, *Org. Lett*. **2018**, *20*, 134-137; g) A. Kumar, N. Muniraj, K. R. Prabhu, *Adv. Synth. Catal*. **2019**, *361*, 4933−4940; h) S. Dutta, T. Bhattacharya, D. B. Werz, D. Maiti, *Chem*. **2021**, *7*(3), 555-605.

[12] a) W. Han, J. C. Pelletier, C. N. Hodge, *Bioorg. Med. Chem. Lett*. **1998**, *8*, 3615-3620; b) M. De Lena, V. Lorusso, A. Latorre, G. Fanizza, G. Gargano, L. Caporusso, M. Guida, A. Catino, E. Crucitta, D. Sambiasi, A. Mazzei, *Eur. J. Cancer*. **2001**, *37*, 364−368.

[13] a) H. Shen, S. Gou, J. Shen, Y. Zhu, Y. Zhang, X. Chen, *Bioorg. Med. Chem. Lett*. **2010**, *20*, 2115−2118; b) A. Veerareddy, G. Surendrareddy, P. K. Dubey, *Synth. Commun*. **2013**, *43*, 2236−2241; c) Y. Jia, J. Zhang, J. Feng, F. Xu, H. Pan, W. Xu, *Chem. Biol. Drug Des*. **2014**, *83*, 306−316.

[14] Y. Cheng, G. Li, Y. Liu, Y. Shi, G. Gao, D. Wu, J. Lan, J. You, *J. Am. Chem. Soc*. **2016**, *138*, 4730-4738.

[15] a) S. V. Kumar, S. Ellairaja, V. Satheesh, V. S. Vasantha, T. Punniyamurthy, *Org. Chem. Front*. **2018**, *5*, 2630-2635; b) C. Guo, B. Li, H. Liu, X. Zhang, X. Zhang, X. Fan, *Org. Lett*. **2019**, *21*, 7189-7193.

[16] a) A. K. Ghosh, S. Samanta, P. Ghosh, S. Neogi, A. Hajra, *Org. Biomol. Chem*. **2020**, *18*, 3093-3097; b) P. Ghosh, S. Samanta, A. Hajra, *Org. Biomol. Chem*. **2020**, *18*, 1728-1732; c) J. Li, L. Shi, S. –P. Zhang, X. –Y. Wang, X. Zhu, X. -Q. Hao, M. -P. Song, *J. Org. Chem*. **2020**, *85*, 16, 10835-10845; d) A. K. Ghosh, P. Ghosh, A. Hajra, *J. Org. Chem*. **2020**, *85*, 23, 15752–15759.

[17] a) K. Basu, M. Poirier, R. T. Ruck, *Org. Lett*. **2016**, *18*, 3218-3221; b) P. Ghosh, S. Mondal, A. Hajra, *J. Org. Chem*. **2018**, *83*, 13618−13623; c) G. Bogonda, H. Y. Kim, K. Oh, *Org. Lett*. **2018**, *20*, 2711-2715; d) S. Neogi, A. K. Ghosh, K. Majhi, S. Samanta, G. Kibriya, A. Hajra, *Org. Lett*. **2020**, *22*, 5605-5609; e) S. Ghosh, S. Mondal, A. Hajra, *Adv. Synth. Catal*. **2020**, *362*, 3768-3794.

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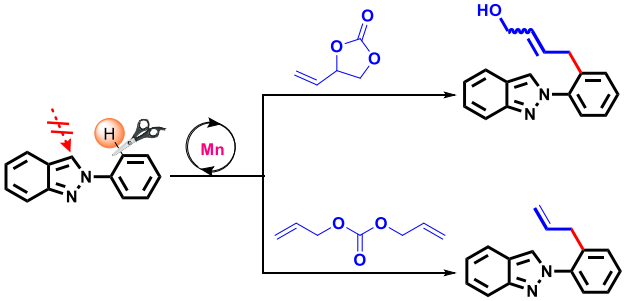
Asim Kumar Ghosh, Krishna Kanta Das, and Alakananda Hajra*



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