Regioselective hydroarylation and arylation of maleimides with indazoles via a Rh(III)-catalyzed C−H activation

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General Information. All reagents were purchased from commercial sources and used without further purification. $^1$H NMR spectra were determined on 400 MHz spectrometer as solutions in CDCl$_3$. Chemical shifts are expressed in parts per million ($\delta$) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplate) and coupling constants ($J$) were given in Hz. $^{13}$C{$^1$H} NMR spectra were recorded at 100 MHz in CDCl$_3$. Chemical shifts as internal standard are referenced to CDCl$_3$ ($\delta = 7.26$ for $^1$H and $\delta = 77.16$ for $^{13}$C{$^1$H} 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. Melting points (M.p.) were determined after recrystallization of solid compounds from a solution of dichloromethane/petroleum ether (1:3).

Starting Materials. All 2H-indazoles was prepared by the reported method.$^1$

![General procedure for the preparation of N-aryl & N-alkyl maleimides derivatives](image)

General procedure for the preparation of $N$-aryl & $N$-alkyl maleimides derivatives:$^2$ Maleic anhydride (2.0 equiv) were stirred in acetic acid (1.5 mL per mmol of amine) until maleic anhydride was dissolved completely. Then primary amine was added (1.0 equiv) to the reaction mixture and refluxed for 6 h at 125 °C. After completion of the reaction, the reaction mixture was allowed to cool down at room temperature and transfer to a 250 mL beaker. Saturated NaHCO$_3$ aqueous solution was added to the beaker containing reaction mixture until effervescence of CO$_2$ stop. Then, the aqueous mixture was extracted with ethyl acetate (3 x 10 mL). The organic phase was dried over anhydrous Na$_2$SO$_4$. The crude residue was obtained after evaporating the solvent in vacuum. Then crude residue was further washed with 1(N) HCl (2 x
20 mL) and brine solution (5 mL) respectively. The aqueous mixture was again extracted with ethyl acetate (3 x 10 mL). Finally, excess solvent was removed under reduced pressure and the residue was purified by column chromatography using ethyl acetate/hexane to get extra pure maleimide with high yields.

2. Characterization data for the synthesized products:

![Image of 1-Benzyl-1H-pyrrole-2,5-dione (2h)](image)

1-Benzyl-1H-pyrrole-2,5-dione (2h): Yellow solid (90%, 33 mg); $R_f = 0.50$ (PE : EA = 80 : 20); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30-7.20 (m, 5H), 6.64 (s, 2H), 4.62 (s, 2H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta$ 170.5, 136.3, 134.2, 128.8, 128.4, 127.9, 41.5.

![Reaction scheme](image)

Typical experimental procedure for the synthesized compounds (3aa-3ga): A mixture of 2-($p$-tolyl)-2$H$-indazole (0.2 mmol, 41.6 mg) (1a), [Cp*RhCl$_2$]$_2$ (2 mol%, 2.4 mg), AgSbF$_6$ (10 mol%, 6.8 mg), and AgOAc (10 mol%, 3.3 mg) were taken in an oven dried screw-capped reaction tube. Then 1,2-DCE (2 mL) and AcOH (0.5 equiv, 6.0 mg) were added to the mixture and stirred for 5 min at room temperature under open atmosphere. After that, 1-phenyl-1$H$-pyrrole-2,5-dione (2a) (0.24 mmol, 41.5 mg) was added, and the resultant mixture was stirred at 110 °C for 3 h. After completion of the reaction (TLC), the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na$_2$SO$_4$. 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 (72:28) as an eluting solvent to afford the pure product 3aa (67 mg, 89%) as a light yellow solid.

![Chemical structure of 3aa](image)

**3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-phenylpyrrolidine-2,5-dione (3aa):** Light yellow solid (89%, 67 mg); R_f = 0.50 (PE : EA = 72 : 28); M.p. 143-144 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.24 (s, 1H), 7.71-7.65 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.35-7.28 (m, 5H), 7.23 (s, 1H), 7.15-7.11 (m, 1H), 6.92-6.90 (m, 2H), 4.21 (t, J = 8.4 Hz, 1H), 3.26 (d, J = 8.4 Hz, 2H), 2.46 (s, 3H); ^13C{^1H} NMR (100 MHz, CDCl_3): δ 176.1, 175.1, 149.7, 140.1, 137.7, 132.7, 131.8, 131.2, 129.7, 128.9, 128.4, 127.09, 127.07, 126.3, 125.3, 122.6, 122.4, 120.6, 117.9, 43.9, 38.0, 21.3; Anal. Calcd for C_{24}H_{19}N_{3}O_{2}: C, 75.57; H, 5.02; N, 11.02%; Found: C, 75.38; H, 4.98; N, 11.11%.

![Chemical structure of 3ba](image)

**3-(2-(2H-Indazol-2-yl)-5-methoxyphenyl)-1-phenylpyrrolidine-2,5-dione (3ba):** Brown solid (73%, 58 mg); R_f = 0.45 (PE : EA = 65 : 35); M.p. 148-149 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.21 (s, 1H), 7.71-7.65 (m, 2H), 7.42 (d, J = 8.8 Hz, 1H), 7.35-7.28 (m, 4H), 7.13 (t, J = 7.6 Hz, 1H), 7.00-6.98 (m, 1H), 6.94 (d, J = 2.8 Hz, 1H), 6.89-6.87 (m, 2H), 4.20-4.16 (m, 1H), 3.89 (s,
3-(5-Fluoro-2-(2H-indazol-2-yl)phenyl)-1-phenylpyrrolidine-2,5-dione (3ca): White solid (81%, 62 mg); $R_f = 0.50$ (PE : EA = 67 : 33); M.p. 177-178 °C; $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 8.23 (s, 1H), 7.71-7.65 (m, 2H), 7.50-7.47 (m, 1H), 7.35-7.29 (m, 4H), 7.23-7.13 (m, 3H), 6.89-6.87 (m, 2H), 4.22 (t, $J = 8.4$ Hz, 1H), 3.27-3.25 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$): $\delta$ 175.3, 174.6, 162.7 (d, $J_{C-F} = 249.0$ Hz), 149.9, 136.4, 136.3, 135.5 (d, $J_{C-F} = 8.0$ Hz), 131.6, 129.2 (d, $J_{C-F} = 8.0$ Hz), 129.0, 128.6, 127.3, 126.3, 125.5, 122.7 (d, $J_{C-F} = 8.0$ Hz), 120.6, 117.9 (d, $J_{C-F} = 10.0$ Hz), 117.6, 116.0 (d, $J_{C-F} = 22.0$ Hz), 43.9, 37.7; Anal. Calcd for C$_{23}$H$_{16}$FN$_3$O$_2$: C, 71.68; H, 4.18; N, 10.90%; Found: C, 71.85; H, 4.23; N, 10.79%.

3-(5-Chloro-2-(2H-indazol-2-yl)phenyl)-1-phenylpyrrolidine-2,5-dione (3da): White solid (91%, 73 mg); $R_f = 0.50$ (PE : EA = 71 : 29); M.p. 158-159 °C; $^1H$ NMR (400 MHz, CDCl$_3$): $\delta$ 8.23 (s, 1H), 7.71-7.62 (m, 2H), 7.49-7.42 (m, 3H), 7.34-7.27 (m, 4H), 7.16-7.13 (m, 1H), 6.87-
6.83 (m, 2H), 4.25-4.21 (m, 1H), 3.28-3.24 (m, 2H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 175.3, 174.6, 149.9, 138.5, 135.5, 134.5, 131.6, 131.2, 129.2, 128.9, 128.5, 128.3, 127.4, 126.2, 125.2, 122.9, 122.5, 120.6, 117.9, 44.1, 37.7; HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ Calcd for C$_{23}$H$_{16}$ClN$_3$O$_2$Na: 424.0823; found: 424.0816.

**Ethyl-3-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-4-(2H-indazol-2-yl)benzoate (3ea):** Light yellow solid (79%, 69 mg); $R_f$ = 0.45 (PE : EA = 69 : 31); M.p. 169-170 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.32 (s, 1H), 8.19-8.16 (m, 2H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.63-7.59 (m, 2H), 7.34-7.27 (m, 4H), 7.17-7.13 (m, 1H), 6.88-6.86 (m, 2H), 4.47-4.38 (m, 3H), 3.37-3.34 (m, 2H), 1.46-1.42 (m, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 175.5, 174.9, 165.2, 150.2, 143.3, 133.0, 132.8, 131.7, 131.5, 130.3, 129.0, 128.5, 127.6, 126.9, 126.3, 125.1, 123.1, 122.7, 120.7, 118.0, 61.8, 44.6, 37.9, 14.4; HRMS (ESI-TOF) $m/z$: [M + H]$^+$ Calcd for C$_{26}$H$_{22}$N$_3$O$_4$: 440.1605; found: 440.1602.

**3-(2-(2H-Indazol-2-yl)-4-methylphenyl)-1-phenylpyrrolidine-2,5-dione (3fa):** Yellow solid (93%, 71 mg); $R_f$ = 0.45 (PE : EA = 74 : 26); M.p. 138-139 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.27 (s, 1H), 7.71-7.66 (m, 2H), 7.34-7.28 (m, 7H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.91-6.89 (m, 2H),
4.21-4.17 (m, 1H), 3.22-3.20 (m, 2H), 2.43 (s, 3H); $^{13}$C{$_{1}$H} NMR (100 MHz, CDCl$_3$): $\delta$ 176.1, 175.1, 149.7, 139.7, 139.3, 131.8, 130.4, 129.8, 128.8, 128.3, 127.7, 127.0, 126.3, 125.2, 122.5, 122.3, 120.5, 117.9, 43.6, 37.8, 20.9; Anal. Calcd for C$_{24}$H$_{19}$N$_3$O$_2$: C, 75.57; H, 5.02; N, 11.02%; Found: C, 75.76; H, 5.05; N, 11.10%.

3-(2-(2H-Indazol-2-yl)-4-methoxyphenyl)-1-phenylpyrrolidine-2,5-dione (3ga): Light yellow solid (88%, 69 mg); $R_f$ = 0.45 (PE : EA = 59 : 41); M.p. 147-148 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25 (s, 1H), 7.68-7.63 (m, 2H), 7.30-7.25 (m, 5H), 7.11 (t, $J$ = 7.6 Hz, 1H), 7.03-7.01 (m, 2H), 6.87 (d, $J$ = 8.0 Hz, 2H), 4.13 (t, $J$ = 8.0 Hz, 1H), 3.81 (s, 3H), 3.16 (d, $J$ = 8.0 Hz, 2H); $^{13}$C{$_{1}$H} NMR (100 MHz, CDCl$_3$): $\delta$ 176.3, 175.1, 159.7, 149.7, 140.7, 131.8, 131.7, 128.8, 128.3, 127.1, 126.3, 125.2, 124.6, 122.6, 122.3, 120.6, 117.9, 115.4, 112.7, 55.7, 43.4, 37.8; Anal. Calcd for C$_{24}$H$_{19}$N$_3$O$_3$: C, 72.53; H, 4.82; N, 10.57%; Found: C, 72.75; H, 4.88; N, 10.48%.

3-(4-Chloro-2-(2H-indazol-2-yl)phenyl)-1-phenylpyrrolidine-2,5-dione (3ha): Brown solid (85%, 68 mg); $R_f$ = 0.45 (PE : EA = 70 : 30); M.p. 153-154 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$
8.25 (s, 1H), 7.70-7.62 (m, 2H), 7.51-7.45 (m, 2H), 7.36-7.27 (m, 5H), 7.14 (t, J = 8.0 Hz, 1H), 6.87-6.84 (m, 2H), 4.23 (t, J = 8.0 Hz, 1H), 3.21 (d, J = 7.6 Hz, 2H); $^{13}$C{\textsuperscript{1}H} NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 175.5, 174.7, 149.9, 140.7, 134.4, 132.3, 131.6, 131.2, 129.7, 128.9, 128.4, 127.4, 127.1, 126.2, 125.1, 122.9, 122.4, 120.6, 117.9, 43.8, 37.6; Anal. Calcd for C\textsubscript{23}H\textsubscript{16}ClN\textsubscript{3}O\textsubscript{2}: C, 68.75; H, 4.01; N, 10.46%; Found: C, 68.90; H, 3.97; N, 10.35%.

3-(5-Chloro-4-fluoro-2-(2H-indazol-2-yl)phenyl)-1-phenylpyrrolidine-2,5-dione (3ia): White solid (87%, 72 mg); R\text{f} = 0.50 (PE : EA = 65 : 35); M.p. 173-174 °C; $^1$H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 8.23 (s, 1H), 7.71-7.58 (m, 3H), 7.33-7.25 (m, 5H), 7.15 (t, J = 8.4 Hz, 1H), 6.86-6.83 (m, 2H), 4.22 (t, J = 8.0 Hz, 1H), 3.25 (d, J = 8.0 Hz, 2H); $^{13}$C{\textsuperscript{1}H} NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 175.0, 174.4, 158.2 (d, $J_{C,F}$ = 252.0 Hz), 150.0, 136.6 (d, $J_{C,F}$ = 4.0 Hz), 133.5 (d, $J_{C,F}$ = 6.0 Hz), 131.5, 129.5, 129.0, 128.6, 127.6, 126.2, 125.4, 123.2, 122.6, 121.5 (d, $J_{C,F}$ = 19.0 Hz), 120.6, 118.9 (d, $J_{C,F}$ = 23.0 Hz), 117.9, 43.8, 37.6; Anal. Calcd for C\textsubscript{23}H\textsubscript{15}ClFN\textsubscript{3}O\textsubscript{2}: C, 65.80; H, 3.60; N, 10.01%; Found: C, 65.64; H, 3.62; N, 9.92%.

3-(2-(5-Methoxy-2H-indazol-2-yl)-5-methylphenyl)-1-phenylpyrrolidine-2,5-dione (3ja): Brown gummy mass (86%, 70 mg); R\text{f} = 0.55 (PE : EA = 64 : 36); $^1$H NMR (400 MHz, CDCl\textsubscript{3}):
δ 8.07 (s, 1H), 7.54 (d, J = 9.6 Hz, 1H), 7.36-7.25 (m, 5H), 7.21 (s, 1H), 7.01-6.98 (m, 1H), 6.95-6.93 (m, 2H), 6.88 (d, J = 2.4 Hz, 1H), 4.20 (t, J = 8.0 Hz, 1H), 3.82 (s, 3H), 3.20 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 176.1, 175.1, 155.6, 146.5, 139.7, 137.5, 132.4, 131.8, 131.4, 129.5, 128.8, 128.3, 126.8, 126.3, 124.1, 122.3, 122.1, 119.2, 96.4, 55.4, 44.0, 37.8, 21.1; Anal. Calcd for C₂₅H₂₁N₃O₃: C, 72.98; H, 5.14; N, 10.21%; Found: C, 72.76; H, 5.19; N, 10.31%.

3-(2-(5-Fluoro-2H-indazol-2-yl)-5-methylphenyl)-1-phenylpyrrolidine-2,5-dione (3ka): Yellow solid (76%, 60 mg); Rₜ = 0.40 (PE : EA = 71 : 29); M.p. 175-176 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.20 (s, 1H), 7.63-7.60 (m, 1H), 7.39-7.24 (m, 7H), 7.12-7.07 (m, 1H), 6.94-6.92 (m, 2H), 4.24-4.20 (m, 1H), 3.27-3.24 (m, 2H), 2.46 (s, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 176.1, 175.1, 160.0, 147.2, 140.3, 137.5, 132.5, 131.6 (d, J₈₋₋₈ = 36.0 Hz), 129.8, 129.0, 128.5, 127.0, 126.2, 125.4 (d, J₈₋₋₈ = 8.0 Hz), 121.7 (d, J₈₋₋₈ = 12.0 Hz), 120.1 (d, J₈₋₋₈ = 10.0 Hz), 118.9, 118.6, 102.9 (d, J₈₋₋₈ = 24.0 Hz), 44.0, 37.9, 21.3; Anal. Calcd for C₂₅H₂₁F₂N₃O₂: C, 72.17; H, 4.54; N, 10.52%; Found: C, 72.31; H, 4.61; N, 10.43%.
3-(2-(5-Chloro-2H-indazol-2-yl)-5-methylphenyl)-1-phenylpyrrolidine-2,5-dione (3la): White solid (81%, 67 mg); R_f = 0.50 (PE : EA = 68 : 32); M.p. 179-180 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.19 (s, 1H), 7.67 (s, 1H), 7.58 (d, J = 9.2 Hz, 1H), 7.38-7.29 (m, 5H), 7.24-7.21 (m, 2H), 6.92-6.90 (m, 2H), 4.20 (t, J = 7.2 Hz, 1H), 3.25-3.23 (m, 2H), 2.46 (s, 3H); ^13C{^1H} NMR (100 MHz, CDCl_3): δ 176.0, 175.0, 148.0, 140.4, 137.3, 132.6, 131.8, 131.4, 129.8, 129.0, 128.55, 128.50, 128.3, 127.0, 126.2, 125.0, 122.7, 119.5, 119.3, 44.0, 37.9, 21.3; Anal. Calcd for C_{24}H_{18}ClN_3O_2: C, 69.31; H, 4.36; N, 10.10%; Found: C, 69.18; H, 4.32; N, 10.04%.

3-(4-Chloro-2-(5-fluoro-2H-indazol-2-yl)phenyl)-1-phenylpyrrolidine-2,5-dione (3ma): Yellow solid (92%, 77 mg); R_f = 0.50 (PE : EA = 70 : 30); M.p. 160-161 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.24 (s, 1H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 2H), 7.40-7.27 (m, 5H), 7.14-7.09 (m, 1H), 6.91 (d, J = 8.4 Hz, 2H), 4.29-4.25 (m, 1H), 3.25-3.22 (m, 2H); ^13C{^1H} NMR (100 MHz, CDCl_3): δ 175.5, 174.7, 158.9 (d, J_{C-F} = 240.0 Hz), 147.3, 140.5, 134.6, 132.4, 131.6, 131.1, 129.8, 128.9, 128.5, 127.1, 126.1, 125.2 (d, J_{C-F} = 9.0 Hz), 121.8 (d, J_{C-F} = 12.0 Hz), 120.1 (d, J_{C-F} = 9.0 Hz), 119.2 (d, J_{C-F} = 29.0 Hz), 102.9 (d, J_{C-F} = 25.0 Hz), 43.8, 37.6; Anal. Calcd for C_{23}H_{15}ClFN_3O_2: C, 65.80; H, 3.60; N, 10.01%; Found: C, 65.96; H, 3.53; N, 10.10%.
3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-methylpyrrolidine-2,5-dione (3ab): Light yellow solid (80%, 51 mg); R\textsubscript{f} = 0.40 (PE : EA = 69 : 29); M.p. 134-135 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.19 (s, 1H), 7.71-7.64 (m, 2H), 7.36 (d, \(J = 8.0\) Hz, 1H), 7.32-7.25 (m, 2H), 7.11 (t, \(J = 8.8\) Hz, 2H), 4.03-3.99 (m, 1H), 3.07 (t, \(J = 9.6\) Hz, 2H), 2.68 (s, 3H), 2.43 (s, 3H); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 177.4, 176.3, 149.5, 140.1, 137.5, 133.1, 130.8, 129.5, 126.95, 126.91, 125.3, 124.4, 122.8, 120.5, 117.7, 43.5, 38.1, 25.0, 21.2; Anal. Calcd for C\textsubscript{19}H\textsubscript{17}N\textsubscript{3}O\textsubscript{2}: C, 71.46; H, 5.37; N, 13.16%; Found: C, 71.26; H, 5.34; N, 13.04%.

![Chemical Structure of 3ab](image)

3-(5-Bromo-2-(2H-indazol-2-yl)phenyl)-1-methylpyrrolidine-2,5-dione (3nb): Yellow gummy mass (88%, 67 mg); R\textsubscript{f} = 0.45 (PE : EA = 69 : 29); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.19 (s, 1H), 7.69 (d, \(J = 8.4\) Hz, 1H), 7.65-7.59 (m, 2H), 7.50 (d, \(J = 2.4\) Hz, 1H), 7.36-7.30 (m, 2H), 7.12 (t, \(J = 8.0\) Hz, 1H), 4.07-4.03 (m, 1H), 3.10-3.07 (m, 2H), 2.66 (s, 3H); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 176.5, 175.7, 149.7, 139.0, 135.3, 133.7, 132.1, 128.4, 127.3, 125.2, 123.5, 122.9, 122.5, 120.5, 117.8, 43.5, 37.9, 25.1; Anal. Calcd for C\textsubscript{18}H\textsubscript{14}BrN\textsubscript{3}O\textsubscript{2}: C, 56.27; H, 3.67; N, 10.94%; Found: C, 56.15; H, 3.71; N, 11.01%.

![Chemical Structure of 3nb](image)

3-(2-(5-Methoxy-2H-indazol-2-yl)-5-methylphenyl)-1-methylpyrrolidine-2,5-dione (3jb): White solid (84%, 58 mg); R\textsubscript{f} = 0.45 (PE : EA = 68 : 32); M.p. 165-167 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.06 (s, 1H), 7.56 (d, \(J = 9.2\) Hz, 1H), 7.36 (d, \(J = 8.4\) Hz, 1H), 7.27 (s, 1H), 7.13 (s,
1H), 7.04-7.01 (m, 1H), 6.91 (d, J =2.4 Hz, 1H), 4.06-4.02 (m, 1H), 3.85 (s, 3H), 3.10-3.05 (m, 2H), 2.72 (s, 3H), 2.44 (s, 3H); 13C{1H} NMR (100 MHz, CDCl3): δ 177.5, 176.3, 155.6, 146.4, 139.8, 137.6, 133.0, 131.0, 129.5, 126.8, 124.2, 122.3, 122.1, 119.1, 96.4, 55.4, 43.6, 38.1, 25.0, 21.2; Anal. Calcd for C20H19N3O3: C, 68.75; H, 5.48; N, 12.03%; Found: C, 68.96; H, 5.43; N, 11.92%.

3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-cyclohexylpyrrolidine-2,5-dione (3ac): Yellow gummy mass (75%, 58 mg); Rf = 0.50 (PE : EA = 75 : 25); 1H NMR (400 MHz, CDCl3): δ 8.26 (s, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.35-7.29 (m, 2H), 7.24 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.02 (s, 1H), 3.94-3.85 (m, 2H), 3.07-3.00 (m, 1H), 2.92-2.86 (m, 1H), 2.42 (s, 3H), 2.14 (s, 1H), 2.06-1.97 (m, 2H), 1.75 (d, J = 10.8 Hz, 2H), 1.60 (d, J = 11.2 Hz, 1H), 1.40 (d, J = 9.2 Hz, 1H), 1.25-1.19 (m, 3H); 13C{1H} NMR (100 MHz, CDCl3): δ 177.6, 176.2, 149.6, 140.2, 138.0, 133.7, 129.3, 129.0, 127.1, 126.8, 125.5, 122.4, 122.2, 120.5, 117.8, 52.0, 42.0, 38.0, 28.7, 25.8, 25.0, 21.3; Anal. Calcd for C24H25N3O2: C, 74.39; H, 6.50; N, 10.84%; Found: C, 74.62; H, 6.53; N, 10.96%.
3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-(p-tolyl)pyrrolidine-2,5-dione (3ad): White solid (83%, 65 mg); R_f = 0.50 (PE : EA = 71 : 29); M.p. 155-156 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.24 (s, 1H), 7.71-7.66 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.32-7.27 (m, 2H), 7.22 (s, 1H), 7.16-7.12 (m, 3H), 6.79 (d, J = 8.4 Hz, 2H), 4.19 (t, J = 8.0 Hz, 1H), 3.25-3.23 (m, 2H), 2.46 (s, 3H), 2.33 (s, 3H); ^13C{^1H} NMR (100 MHz, CDCl_3): δ 176.3, 175.2, 149.7, 140.1, 138.4, 137.7, 132.8, 131.1, 129.6, 129.2, 127.08, 127.02, 126.1, 125.3, 122.5, 122.4, 120.6, 117.9, 43.9, 38.0, 21.29, 21.24; Anal. Calcd for C_{25}H_{21}N_{3}O_{2}: C, 75.93; H, 5.35; N, 10.63%; Found: C, 76.05; H, 5.32; N, 10.55%.

![Image of 3ad](image_url)

3-(5-Chloro-2-(2H-indazol-2-yl)phenyl)-1-(p-tolyl)pyrrolidine-2,5-dione (3dd): White solid (69%, 57 mg); R_f = 0.55 (PE : EA = 70 : 30); M.p. 192-194 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.24 (s, 1H), 7.72-7.64 (m, 2H), 7.50-7.43 (m, 3H), 7.33-7.29 (m, 1H ), 7.17-7.11 (m, 3H), 6.74 (d, J = 8.4 Hz, 2H), 4.26-4.22 (m, 1H), 3.29-3.26 (m, 2H ), 2.32 (s, 3H); ^13C{^1H} NMR (100 MHz, CDCl_3): δ 175.4, 174.7, 150.0, 138.6, 135.6, 134.7, 131.0, 129.7, 129.2, 129.0, 128.4, 127.4, 126.1, 125.3, 123.0, 122.6, 120.6, 118.0, 44.0, 37.8, 21.2; Anal. Calcd for C_{24}H_{18}ClN_{3}O_{2}: C, 69.31; H, 4.36; N, 10.10%; Found: C, 69.45; H, 4.41; N, 9.98%.

![Image of 3dd](image_url)
3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-(4-methoxyphenyl)pyrrolidine-2,5-dione (3ae):

Yellow solid (82%, 67 mg); R_f = 0.45 (PE : EA = 68 : 32); M.p. 188-189 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.23 (s, 1H), 7.71-7.65 (m, 2H), 7.38 (d, \(J = 8.0\) Hz, 1H), 7.30 (t, \(J = 8.4\) Hz, 2H), 7.22 (s, 1H), 7.13 (t, \(J = 7.6\) Hz, 1H), 6.84-6.78 (m, 4H), 4.19 (t, \(J = 8.4\) Hz, 1H), 3.77 (s, 3H), 3.26-3.24 (m, 2H), 2.46 (s, 3H); \(^{13}\)C\(\{^1\)H\} NMR (100 MHz, CDCl\(_3\)): δ 176.4, 175.4, 159.4, 149.7, 140.1, 137.7, 132.8, 131.2, 129.6, 127.6, 127.1, 127.0, 125.4, 124.5, 122.6, 122.4, 120.6, 117.9, 114.3, 55.5, 43.9, 38.0, 21.3; Anal. Calcd for C\(_{25}\)H\(_{21}\)N\(_3\)O\(_3\): C, 72.98; H, 5.14; N, 10.21%; Found: C, 73.21; H, 5.07; N, 10.11%.

\[\text{structure image}\]

3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-(4-chlorophenyl)pyrrolidine-2,5-dione (3af):

White solid (90%, 74 mg); R_f = 0.50 (PE : EA = 70 : 30); M.p. 190-191 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 8.20 (s, 1H), 7.69 (d, \(J = 8.4\) Hz, 1H), 7.60 (d, \(J = 8.4\) Hz, 1H), 7.38 (d, \(J = 8.0\) Hz, 1H), 7.31-7.22 (m, 5H), 7.13 (t, \(J = 8.4\) Hz, 1H), 6.76 (d, \(J = 8.8\) Hz, 2H), 4.22-4.18 (m, 1H), 3.37-3.19 (m, 2H), 2.46 (s, 3H); \(^{13}\)C\(\{^1\)H\} NMR (100 MHz, CDCl\(_3\)): δ 175.7, 174.8, 149.7, 140.0, 137.4, 134.0, 132.3, 132.0, 130.3, 129.8, 129.0, 127.5, 127.1, 127.0, 125.2, 122.7, 122.4, 120.6, 117.9, 44.5, 37.9, 21.2; Anal. Calcd for C\(_{24}\)H\(_{18}\)ClN\(_3\)O\(_2\): C, 69.31; H, 4.36; N, 10.10%; Found: C, 69.43; H, 4.38; N, 10.04%.
3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-(m-tolyl)pyrrolidine-2,5-dione (3ag): Yellow gummy mass (87%, 68 mg); R_f = 0.45 (PE : EA = 75 : 25); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.24 (s, 1H), 7.72-7.66 (m, 2H), 7.38 (d, \(J = 8.0\) Hz, 1H), 7.30 (t, \(J = 8.4\) Hz, 2H), 7.23-7.19 (m, 2H), 7.16-7.09 (m, 2H), 6.72 (d, \(J = 8.0\) Hz, 1H), 6.55 (s, 1H), 4.22-4.18 (m, 1H) 3.38-3.21 (m, 2H), 2.46 (s, 3H), 2.26 (s, 3H); \(^{13}\)C\({_1\})H NMR (100 MHz, CDCl\(_3\)): \(\delta\) 176.1, 175.2, 149.7, 140.0, 139.0, 137.6, 132.7, 131.6, 131.5, 129.6, 129.3, 128.7, 127.1, 127.0, 125.3, 123.4, 122.6, 122.4, 120.6, 118.0, 44.1, 38.1, 21.3, 21.2; Anal. Calcd for C\(_{25}\)H\(_{21}\)N\(_3\)O\(_2\): C, 75.93; H, 5.35; N, 10.63%; Found: C, 76.13; H, 5.31; N, 10.55%.

**Typical experimental procedure for the synthesized compounds (4aa–4ga):** A mixture of 2-(p-tolyl)-2H-indazole (0.2 mmol, 41.6 mg) (1a), [Cp*RhCl\(_2\)]\(_2\) (2 mol%, 2.4 mg), AgSbF\(_6\) (10 mol%, 6.8 mg), AgOAc (10 mol%, 3.3 mg), and NaOAc (0.5 equiv, 8.2 mg) were taken in an oven dried screw-capped reaction tube. Then 1,2-DCE (2 mL) was added to the mixture and stirred for 5 min at room temperature under open atmosphere. After that, 1-phenyl-1H-pyrrole-2,5-dione (2a) (0.24 mmol, 41.5 mg) was added, and the resultant mixture was stirred at 110 °C for 5 h. After completion of the reaction (TLC), the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na\(_2\)SO\(_4\). 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 (79:21) as an eluting solvent to afford the pure product 4aa (50 mg, 67%) as a yellow solid.

3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-phenyl-1H-pyrrole-2,5-dione (4aa): Yellow solid (67%, 50 mg); R_f = 0.50 (PE : EA = 79 : 21); M.p. 125-126 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.29 (s, 1H), 7.74-7.68 (m, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.34-7.29 (m, 3H), 7.26-7.25 (m, 1H), 7.14 (t, J = 8.0 Hz, 1H), 7.00-6.98 (m, 2H), 6.48 (s, 1H), 2.51 (s, 3H); ^13C{^1H} NMR (100 MHz, CDCl_3): δ 169.2, 167.8, 149.7, 145.4, 139.4, 137.3, 132.1, 131.9, 131.4, 129.0, 127.7, 127.1, 126.7, 126.0, 125.4, 124.7, 124.5, 122.9, 122.8, 120.7, 117.6, 21.2; Anal. Calcd for C_{24}H_{17}N_{3}O_2: C, 75.98; H, 4.52; N, 11.08%; Found: C, 75.86; H, 4.56; N, 11.03%.

3-(5-Fluoro-2-(2H-indazol-2-yl)phenyl)-1-phenyl-1H-pyrrole-2,5-dione (4ca): Light yellow solid (52%, 39 mg); R_f = 0.50 (PE : EA = 78 : 22); M.p. 129-130 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.27 (s, 1H), 7.74-7.69 (m, 2H), 7.66-7.62 (m, 1H), 7.57-7.55 (m, 1H), 7.38-7.27 (m, 5H), 7.18-7.14 (m, 1H), 7.01-6.99 (m, 2H), 6.42 (s, 1H); ^13C{^1H} NMR (100 MHz, CDCl_3): δ
167.5, 163.4, 149.9, 143.3, 131.2, 129.3, 129.1, 127.9, 127.8, 127.7, 127.5, 127.1, 126.0, 124.8, 123.0 (d, $J_{C-F} = 19.0$ Hz), 120.7, 118.6, 118.4, 118.3 (d, $J_{C-F} = 14.0$ Hz), 117.7; Anal. Calcd for C$_{23}$H$_{14}$FN$_3$O$_2$: C, 72.06; H, 3.68; N, 10.96%; Found: C, 72.24; H, 3.66; N, 11.03%.

3-(2-(5-Methoxy-2H-indazol-2-yl)-5-methylphenyl)-1-phenyl-1H-pyrrole-2,5-dione (4ja):
Brown solid (71%, 58 mg); $R_f=0.45$ (PE : EA = 72 : 28); M.p. 162-163 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (s, 1H), 7.60-7.52 (m, 3H), 7.45-7.43 (m, 1H), 7.34-7.30 (m, 2H), 7.27-7.24 (m, 1H), 7.04-7.00 (m, 3H), 6.91 (d, $J = 2.0$ Hz, 1H), 6.49 (s, 1H), 3.85 (s, 3H), 2.50 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 169.3, 167.9, 155.7, 146.7, 145.7, 139.1, 137.4, 132.1, 131.9, 131.5, 129.0, 127.7, 126.5, 126.1, 125.2, 124.5, 123.4, 123.0, 122.3, 119.0, 96.5, 55.4, 21.2; Anal. Calcd for C$_{25}$H$_{19}$N$_3$O$_3$: C, 73.34; H, 4.68; N, 10.26%; Found: C, 73.17; H, 4.71; N, 10.14%.

3-(2-(5-Chloro-2H-indazol-2-yl)-5-methylphenyl)-1-phenyl-1H-pyrrole-2,5-dione (4la):
Yellow solid (69%, 56 mg); $R_f=0.45$ (PE : EA = 72 : 28); M.p. 141-142 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25 (s, 1H), 7.70 (s, 1H), 7.64 (d, $J = 9.2$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.47-7.45 (m, 1H), 7.35-7.31 (m, 2H), 7.28-7.24 (m, 2H), 6.99 (d, $J = 7.6$ Hz, 2H), 6.52 (s, 1H),
2.51 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 169.1, 167.8, 148.0, 145.5, 139.7, 137.0, 132.2, 132.0, 131.4, 129.1, 128.6, 128.4, 127.8, 126.8, 126.0, 125.3, 124.7, 124.1, 123.2, 119.4, 119.2, 21.2; Anal. Calcd for C$_{24}$H$_{16}$ClN$_3$O$_2$: C, 69.65; H, 3.90; N, 10.15%; Found: C, 69.80; H, 3.92; N, 10.09%.

3-(2-(2H-Indazol-2-yl)-4-methylphenyl)-1-(m-tolyl)-1H-pyrrole-2,5-dione (4ag): Light yellow liquid (64%, 50 mg); $R_f$ = 0.45 (PE : EA = 79 : 21); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.30 (s, 1H), 7.74-7.70 (m, 2H), 7.55 (t, $J = 4.8$ Hz, 2H), 7.45 (d, $J = 7.2$ Hz, 1H), 7.35-7.31 (m, 1H), 7.21-7.13 (m, 2H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.82 (d, $J = 7.6$ Hz, 1H), 6.66 (s, 1H), 6.51 (s, 1H), 2.51 (s, 3H), 2.22 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 169.3, 167.9, 149.7, 145.5, 139.4, 139.0, 137.4, 132.1, 131.9, 131.3, 128.8, 128.6, 127.1, 126.8, 126.6, 125.4, 124.9, 124.7, 123.2, 122.9, 122.8, 120.8, 117.7, 21.3, 21.2; Anal. Calcd for C$_{25}$H$_{19}$N$_3$O$_2$: C, 76.32; H, 4.87; N, 10.68%; Found: C, 76.44; H, 4.84; N, 10.71%.

3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-(p-tolyl)-1H-pyrrole-2,5-dione (4ad): Yellow solid (76%, 59 mg); $R_f$ = 0.50 (PE : EA = 77 : 23); M.p. 135-136 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.28 (s, 1H), 7.71 (t, $J = 8.4$ Hz, 2H), 7.57-7.53 (m, 2H), 7.45-7.43 (m, 1H), 7.34-7.30 (m, 1H),
7.15-7.10 (m, 3H), 6.87 (d, J = 8.4 Hz, 2H), 6.45 (s, 1H), 2.50 (s, 3H), 2.30 (s, 3H); $^{13}$C{$^{1}$H}\ NMR (100 MHz, CDCl$_3$): $\delta$ 169.4, 168.0, 149.7, 145.2, 139.4, 137.8, 137.4, 132.1, 131.9, 129.7, 128.8, 127.1, 126.7, 126.0, 125.5, 124.9, 124.5, 122.9, 122.8, 120.7, 117.7, 21.26, 21.20; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for C$_{25}$H$_{20}$N$_3$O$_2$: 394.1550; found: 394.1548.

3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-(4-chlorophenyl)-1H-pyrrole-2,5-dione (4af): Yellow solid (77%, 63 mg); R$_f$ = 0.55 (PE : EA = 70 : 30); M.p. 149-150 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.31 (s, 1H), 7.74-7.65 (m, 2H), 7.55 (t, J = 8.0 Hz, 2H), 7.46 (d, J = 9.6 Hz, 1H), 7.34-7.32 (m, 1H), 7.30-7.24 (m, 2H), 7.16-7.14 (m, 1H), 6.93-6.90 (m, 2H), 6.52 (s, 1H), 2.50 (s, 3H); $^{13}$C{$^{1}$H}\ NMR (100 MHz, CDCl$_3$): $\delta$ 168.9, 167.4, 149.7, 145.9, 139.4, 137.3, 133.3, 132.3, 131.9, 130.0, 129.2, 127.2, 127.1, 126.8, 126.5, 125.2, 124.6, 122.9, 122.8, 120.7, 117.5, 21.2; Anal. Calcd for C$_{24}$H$_{16}$ClN$_3$O$_2$: C, 69.65; H, 3.90; N, 10.15%; Found: C, 69.47; H, 3.92; N, 10.12%.

3-(2-(2H-Indazol-2-yl)-5-methylphenyl)-1-benzyl-1H-pyrrole-2,5-dione (4ah): Yellow gummy mass (81%, 63 mg); R$_f$ = 0.45 (PE : EA = 79 : 21); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.22 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.56-7.48 (m, 3H), 7.42-7.40 (m, 1H), 7.30-7.26 (m, 1H), 7.21-7.20 (m,
3-(2-(2H-Indazol-2-yl)-4-methylphenyl)-1-phenyl-1H-pyrrole-2,5-dione (4fa): Yellow solid (79%, 59 mg); R<sub>f</sub> = 0.50 (PE : EA = 79 : 21); M.p. 116-117 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.20 (s, 1H), 7.64-7.59 (m, 3H), 7.38 (s, 1H), 7.30 (d, <i>J</i> = 7.6 Hz, 1H), 7.24-7.19 (m, 3H), 7.16 (t, <i>J</i> = 4.4 Hz, 1H), 7.07-7.03 (m, 1H), 6.92-6.90 (m, 2H), 6.28 (s, 1H) 2.42 (s, 3H); <sup>13</sup>C<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>): δ 169.3, 168.0, 149.8, 144.9, 142.5, 139.6, 131.5, 131.4, 129.9, 129.0, 127.7, 127.2, 126.5, 126.2, 126.1, 124.5, 122.9, 122.2, 120.7, 117.7, 21.5; HRMS (ESI-TOF) <i>m/z</i>: [M + Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>Na: 402.1213; found: 402.1215.

3-(2-(2H-Indazol-2-yl)-4-methoxyphenyl)-1-phenyl-1H-pyrrole-2,5-dione (4ga): Light yellow solid (55%, 43 mg); R<sub>f</sub> = 0.50 (PE : EA = 70 : 30); M.p. 136-137 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.28 (s, 1H), 7.81 (d, <i>J</i> = 8.4 Hz, 1H), 7.74-7.71 (m, 2H), 7.36-7.27 (m, 4H), 7.18-7.10 (m, 3H), 7.03 (d, <i>J</i> = 7.2 Hz, 2H), 6.18 (s, 1H), 3.93 (s, 3H); <sup>13</sup>C<sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>):
δ 169.4, 168.3, 162.0, 149.8, 141.2, 132.9, 129.0, 127.7, 124.5, 123.0, 122.9, 120.7, 117.8, 114.7, 112.3, 56.0; Anal. Calcd for C$_{24}$H$_{17}$N$_3$O$_3$: C, 72.90; H, 4.33; N, 10.63%; Found: C, 72.68; H, 4.29; N, 10.71%.

Methyl (E)-3-(2-(2H-indazol-2-yl)-5-methylphenyl)acrylate (4ai): Yellow liquid (81%, 47 mg); R$_f$ = 0.50 (PE : EA = 78 : 22); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.09 (s, 1H), 7.80 (d, $J$ = 9.2 Hz, 1H), 7.72 (d, $J$ = 8.4 Hz, 1H), 7.56-7.44 (m, 3H), 7.37-7.32 (m, 2H), 7.16-7.13 (m, 1H), 6.41 (d, $J$ = 16.0 Hz, 1H), 3.71 (s, 3H), 2.46(s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): δ 166.8, 149.8, 139.9, 139.4, 138.0, 131.4, 130.0, 128.0, 127.0, 126.8, 125.3, 122.5, 122.4, 120.8, 120.4, 118.1, 51.8, 21.3; Anal. Calcd for C$_{18}$H$_{16}$N$_2$O$_2$: C, 73.95; H, 5.52; N, 9.58%; Found: C, 74.16; H, 5.55; N, 9.49%.

Methyl (E)-3-(2-(5-fluoro-2H-indazol-2-yl)-5-methylphenyl)acrylate (4ki): Yellow liquid (53%, 32 mg); R$_f$ = 0.45 (PE : EA = 71 : 29); $^1$H NMR (400 MHz, CDCl$_3$): δ 8.05 (s, 1H), 7.78-7.75 (m, 1H), 7.56 (s, 1H), 7.50-7.42 (m, 2H), 7.34-7.27 (m, 2H), 7.18-7.12 (m, 1H), 6.40 (d, $J$ = 16.0 Hz, 1H), 3.72 (s, 3H), 2.47 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): δ 166.8, 158.8 (d, $J_{C-F}$ = 240.0 Hz), 147.3, 139.7 (d, $J_{C-F}$ = 7.0 Hz), 137.8, 131.5, 130.1, 128.1, 126.9, 125.4 (d, $J_{C-F}$ = 9.0 Hz), 121.7, 121.6, 120.5 (d, $J_{C-F}$ = 70.0 Hz), 120.2, 118.6 (d, $J_{C-F}$ = 29.0 Hz), 102.7 (d, $J_{C-F}$
= 23.0 Hz), 51.9, 21.3; Anal. Calcd for C_{18}H_{15}FN_{2}O_{2}: C, 69.67; H, 4.87; N, 9.03%; Found: C, 69.43; H, 4.91; N, 8.91%.

3. Mechanistic investigations:

![Mechanistic diagram]

Preparation of 2-(4-methylphenyl-2,6-\textit{d}_{2})-2\textit{H}-indazole (1\textit{a}-\textit{d}_{2}).\textsuperscript{3} A mixture of 2-(\textit{p}-tolyl)-2\textit{H}-indazole (0.2 mmol, 41.6 mg) (1\textit{a}), [Cp*RhCl\textsubscript{2}]\textsubscript{2} (2 mol%, 2.4 mg), AgSbF\textsubscript{6} (10 mol%, 6.8 mg), and AgOAc (10 mol%, 3.3 mg) were taken in an oven dried screw-capped reaction tube. Then 1,2-DCE (2 mL) and AcOH (0.5 equiv, 6.0 mg) was added to the mixture and stirred for 5 min at room temperature under open atmosphere. After that, D\textsubscript{2}O (1 mL) was added, and the resultant mixture was stirred at 110 °C for 3 h. Then, the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na\textsubscript{2}SO\textsubscript{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 (85:15) as an eluting solvent to afford the pure product 1\textit{a}-\textit{d}_{2} as a white solid. The deuterium incorporation was determined using 400 MHz \textit{1}H NMR as 100%.
**Intermolecular experiment.**\(^4\) 1-Phenyl-1\(H\)-pyrrole-2,5-dione (2a) (0.24 mmol, 41.5 mg) was reacted with 2-(\(p\)-tolyl)-2\(H\)-indazole (1a) (0.1 mmol, 20.8 mg) and 2-(4-methylphenyl-2,6-\(d_2\))-2\(H\)-indazole (1a-\(d_2\)) (0.1 mmol, 21.0 mg) for 15 min under standard reaction condition. The resulting solution was then diluted with dichloromethane (3 x 10 mL) and washed with brine (2 x 5 mL) and water (5 mL). The organic phase was dried over anhydrous Na\(_2\)SO\(_4\). 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 (72:28) as an eluting solvent to afford 3aa and a mixture of unreacted 1a and 1a-\(d_2\) as a light yellow solid. The KIE was found to be 6.1 after 15 min at \(\sim\)20% conversion, based on 400 MHz \(^1\)H NMR of the product 3aa and 3aa-\(d_1\).

**Parallel Experiment study.**\(^4\) In a set of two experiments: in first set, 1-phenyl-1\(H\)-pyrrole-2,5-dione (2a) (0.12 mmol, 20.7 mg) was reacted with 2-(\(p\)-tolyl)-2\(H\)-indazole (1a) (0.1 mmol, 20.8 mg) under standard reaction conditions. Whereas in another set, 2-(4-methylphenyl-2,6-\(d_2\))-2\(H\)-indazole (1a-\(d_2\)) (0.1 mmol, 21.0 mg) was used instead of 1a in the reaction with 1-phenyl-1\(H\)-pyrrole-2,5-dione (2a) under the standard reaction conditions. The two reactions were allowed to stir at 110 \(^\circ\)C with stirring for 15, 25, 35 and 45 minutes. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography, affording the product 3aa or 3aa-\(d_1\). The KIE value was determined to be 4.68.
<table>
<thead>
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<th>Yield</th>
<th>t/min.</th>
<th>15</th>
<th>25</th>
<th>35</th>
<th>45</th>
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<tr>
<td>3aa</td>
<td></td>
<td>16.4%</td>
<td>23.5%</td>
<td>31%</td>
<td>38.4%</td>
</tr>
<tr>
<td>3aa-d₁</td>
<td></td>
<td>3.5%</td>
<td>5.0%</td>
<td>6.6%</td>
<td>8.2%</td>
</tr>
</tbody>
</table>

$k_{H}/k_{D}=0.735/0.157=4.68$

![Graph showing yield vs. time for reactions 1a and 1a-d2]

**Experimental procedure of 3aa on 5 mmol scale:** A mixture of 2-(p-tolyl)-2H-indazole (5.0 mmol, 1.04 g) (1a), [Cp*RhCl₂]₂ (2 mol%, 61.8 mg), AgSbF₆ (10 mol%, 171.8 mg), AgOAc (10 mol%, 83.5 mg), and AcOH (0.5 equiv, 150.0 mg) were taken in an oven dried round-bottom pressure flask (100 mL). Then 1,2-DCE (50 mL) was added to the mixture and stirred for 5 min at room temperature under open atmosphere. After that, 1-phenyl-1H-pyrrole-2,5-dione (2a) (6.0 mmol, 1.03 g) was added, and the resultant mixture was stirred at 110 °C for 3 h. After completion of the reaction (TLC), the reaction was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over anhydrous Na₂SO₄. 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 (72:28) as an eluting solvent to afford the pure product 3aa (1.58 g, 83%) as a light yellow solid.

4. References:
5. NMR spectra for the synthesized products
3al
Current Data Parameters

**NMR** Dr. A MAJRA-2019-13C  
**SPINO** 419  
**PROCRO** 1

**F2 - Acquisition Parameters**

- **Date:** 20180317  
- **Time:** 20:45  
- **INTERINT:** 0  
- **PMODIF:** 5 mm  
- **POLANG:**  
- **POL2:**  
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- **SOAVENT:**  
- **MS:** 420  
- **DS:** 2  
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- **AQ:** 0.4815744 sec  
- **NG:** 186  
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- **DI:** 2.00000000 sec  
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- **TD0:** 1  

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- **SR1:** 13C  
- **DF:** 8.900 usec  
- **PI1:** 54.60000000 W  

**--------- CHANNEL 2 ---------**

- **SF2:** 400.151405 MHz  
- **SR2:** 1H  
- **CDPDG12:** wait.0 usec  
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**F2 - Processing parameters**

- **SI:** 16KHz  
- **SF:** 100.617967 MHz  
- **WR:**  
- **SUB:** 0  
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- **BC:** 0  
- **FC:** 1.00