

Supporting Information

Electrochemically promoted C-3 amination of 2H-indazoles

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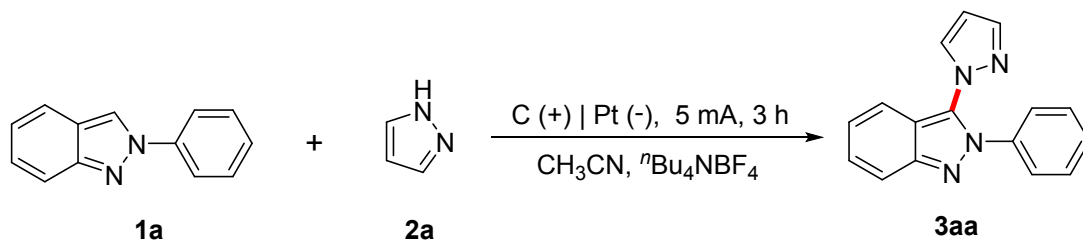
Table of Contents

1. General considerations.....	2
2. Representative procedure for the model reaction.....	2
3. Cyclic voltammetry (CV) measurements.....	3
4. Control experiments	4
5. Characterization data for all products.....	5
6. ¹ H and ¹³ C NMR spectra of the products.....	20

1. General considerations

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to the general methods. All ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz or a 600 MHz Bruker FT-NMR spectrometer (400/100 MHz, or 600/150 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2 .

2. Representative procedure for the model reaction



A 50 mL vial was charged with 2-phenyl-2H-indazole (**1a**, 0.20 mmol), 1H-pyrazole (**2a**, 0.40 mmol, 2.0 equiv.), $^t\text{Bu}_4\text{NBF}_4$ (100 mg), CH_3CN (10 mL) and a magnetic stir bar. The vial was equipped with platinum electrode (1.5 cm \times 1.5 cm \times 0.3 mm) as cathode, graphite rod (Φ 6 mm) as the anode. The whole cell was undivided cell. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at room temperature for 3 hours. After completing reaction, it was monitored with TLC. The solvent was removed with a rotary evaporator. The pure product 2-phenyl-3-(1H-pyrazol-1-yl)-2H-indazole (**3aa**) was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

3. Cyclic voltammetry (CV) measurements

According to the reported procedure (see: J. B. McManus, N. P. R. Onuska and D. A. Nicewicz, *J. Am. Chem. Soc.* 2018, **140**, 9056–9060), cyclic voltammetry measurements were performed in a three-electrode cell under air at room temperature. The working electrode was the glassy carbon electrode, the counter electrode a platinum wire. The reference was saturated calomel electrode. The cyclic voltammetry (CV) measurements were determined by using $n\text{Bu}_4\text{NBF}_4$ in dry and degassed CH_3CN as electrolyte. The results were summarized in the following Figure S1. The applied potential range is 4.0 to 0.0 V at a sweep rate of 100 mV/s using a CHI 760E electrochemical workstation under ambient conditions. From Figure S1, it was found that the oxidation peak potential of 2-phenyl-2*H*-indazole (**1a**) (1.89 V vs Ag/AgCl) is lower than 1*H*-pyrazole (**2a**) (2.21 V vs Ag/AgCl). Therefore, 2-phenyl-2*H*-indazole (**1a**) is more easily oxidized at the surface of the anode.

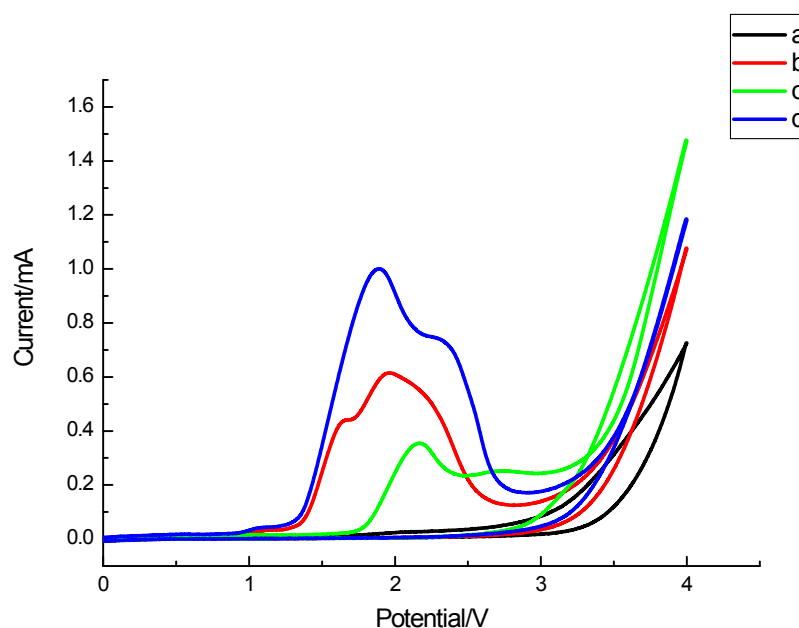
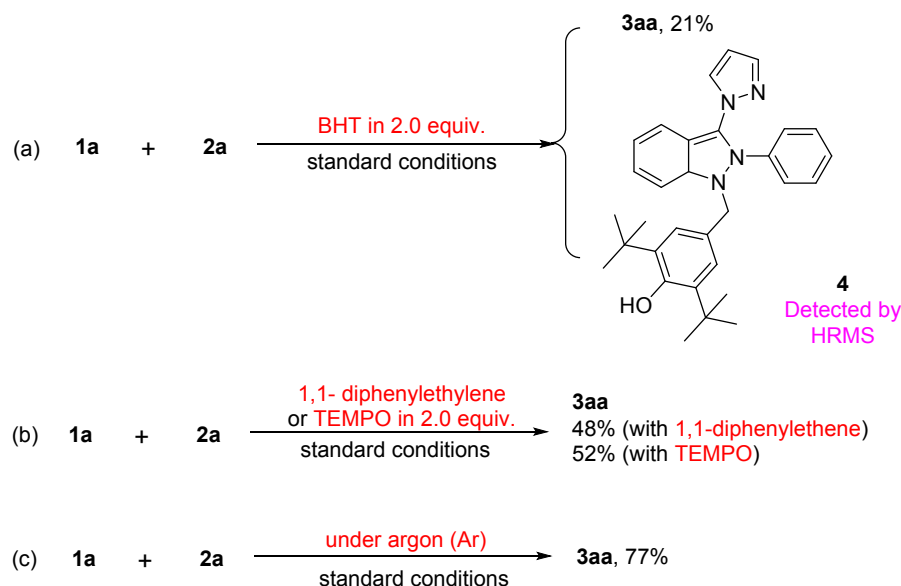


Figure S1 The cyclic voltammetry of related compounds in $n\text{Bu}_4\text{NBF}_6$ (50 mg) of CH_3CN (5.0 mL) using glassy carbon as the working electrode, and a Pt wire and Ag/AgCl as the counter and reference electrodes at 100 mVs^{-1} scan rates. (a) blank; (b) **1a** (0.20 mmol); (c) **2a** (0.40 mmol); (d) **1a** (0.20 mmol) + **2a** (0.40 mmol).

4. Control experiments

To obtain a deeper understanding of this protocol, control experiments were conducted. When a radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT), 1,1-diphenylethylene or (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) in 2.0 equiv. was added to the model reaction, the amination of 2-phenyl-2*H*-indazole was not completely inhibited, demonstrating a possible radical pathway in this system (Scheme S1). In addition, a free-radical intermediate **B** could be trapped by BHT, and the corresponding adduct was detected by HRMS analysis (Figure S2). Keeping the other conditions fixed, the template reaction could still proceed in an argon atmosphere, providing a 77% yield of **3aa**.



Scheme S1 Control experiments.

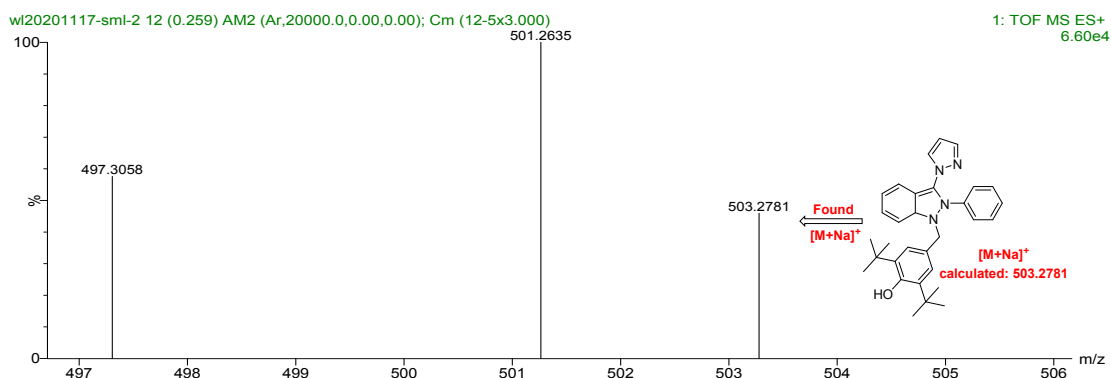
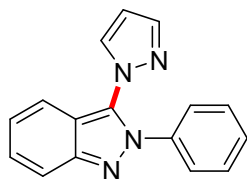
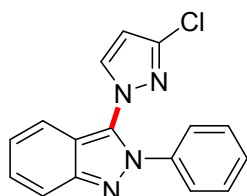


Figure S2 HRMS analysis of the reaction mixture.

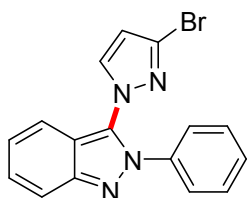
5. Characterization data for all products



2-Phenyl-3-(1H-pyrazol-1-yl)-2H-indazole (3aa): White solid; m.p. = 101.8–103.6 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.81 (d, *J* = 1.6 Hz, 1H), 7.79–7.77 (m, 1H), 7.58–7.55 (m, 1H), 7.51–7.50 (m, 1H), 7.39–7.35 (m, 6H), 7.19–7.15 (m, 1H), 6.46–6.45 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.9, 142.3, 138.4, 132.3, 129.9, 129.1, 128.7, 127.4, 124.1, 123.6, 118.7, 118.0, 117.5, 107.8. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₆H₁₃N₄]⁺: 261.1135, Found: 261.1139.

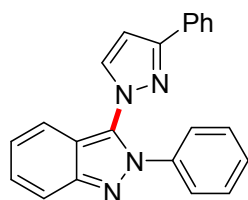


3-(3-Chloro-1H-pyrazol-1-yl)-2-phenyl-2H-indazole (3ab): Light yellow solid; m.p. = 86.5–87.9 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.83 (d, *J* = 9.0 Hz, 1H), 7.773–7.771 (m, 1H), 7.49–7.47 (m, 1H), 7.40–7.37 (m, 6H), 7.22–7.20 (m, 1H), 6.38–6.37 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ: 147.9, 143.0, 138.4, 131.2, 129.2, 128.7, 127.3, 126.4, 124.1, 123.9, 119.1, 118.39, 118.37, 106.3. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₆H₁₂ClN₄]⁺: 295.0745, Found: 295.0742.

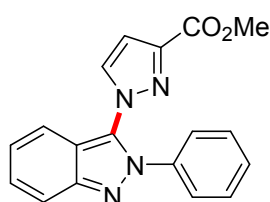


3-(3-Bromo-1H-pyrazol-1-yl)-2-phenyl-2H-indazole (3ac): Light yellow solid; m.p. = 84.7–86.3 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.84–7.81 (m, 1H), 7.75–7.74 (m, 1H), 7.46–7.44 (m, 1H), 7.41–7.33 (m, 6H), 7.20–7.16 (m, 1H), 6.45–6.44 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.8, 143.6, 138.4, 129.1, 128.6, 127.2, 124.0, 123.8,

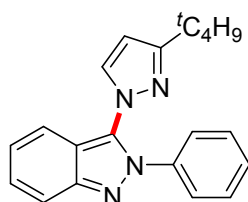
119.0, 118.4, 118.3, 117.3, 110.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{16}H_{12}N_4]^+$: 339.0240, Found: 339.0244.



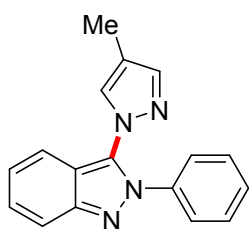
2-Phenyl-3-(3-phenyl-1H-pyrazol-1-yl)-2H-indazole (3ad): Light yellow solid; m.p. = 136.9–137.6 °C. 1H NMR (600 MHz, $CDCl_3$) δ : 7.85 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.46–7.45 (m, 3H), 7.43–7.34 (m, 7H), 7.20–7.17 (m, 1H), 6.75 (d, J = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ : 154.1, 148.0, 138.4, 133.6, 132.2, 130.2, 129.2, 128.8, 128.7, 128.5, 127.5, 125.9, 124.3, 123.6, 119.0, 118.0, 117.4, 105.3. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{22}H_{17}N_4]^+$: 337.1448, Found: 337.1443.



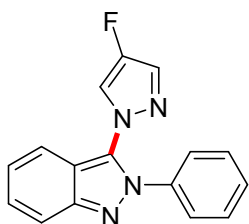
Methyl 1-(2-phenyl-2H-indazol-3-yl)-1H-pyrazole-3-carboxylate (3ae): Light yellow solid; m.p. = 100.3–101.8 °C. 1H NMR (600 MHz, $CDCl_3$) δ : 7.89 (d, J = 2.4 Hz, 1H), 7.83–7.82 (m, 1H), 7.43–7.41 (m, 1H), 7.40–7.37 (m, 1H), 7.36–7.33 (m, 5H), 7.20–7.17 (m, 1H), 7.03–7.02 (m, 1H), 3.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ : 158.1, 147.8, 142.0, 138.3, 135.8, 129.1, 128.69, 128.66, 127.2, 124.0, 123.9, 118.6, 118.3, 118.2, 112.9, 52.2. HRMS (ESI) ($[M+Na]^+$) Calcd. for $[C_{18}H_{14}N_4O_2Na]^+$: 341.1009, Found: 341.1014.



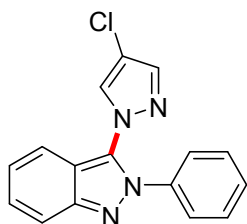
3-(3-(*tert*-Butyl)-1*H*-pyrazol-1-yl)-2-phenyl-2*H*-indazole (3af): Light yellow solid; m.p. = 126.9–127.8 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.76–7.75 (m, 1H), 7.63–7.62 (m, 1H), 7.41–7.40 (m, 1H), 7.37–7.33 (m, 6H), 7.17–7.14 (m, 1H), 6.32 (d, *J* = 2.4 Hz, 1H), 1.31 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ: 164.7, 147.9, 138.6, 132.4, 130.4, 128.9, 128.4, 127.3, 124.1, 123.3, 119.0, 117.9, 117.1, 104.6, 32.2, 30.2. HRMS (ESI) ([*M*+*H*]⁺) Calcd. for [C₂₀H₂₁N₄]⁺: 317.1761, Found: 317.1766.



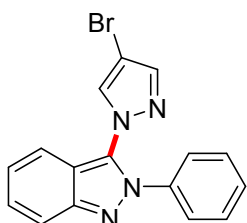
3-(4-Methyl-1*H*-pyrazol-1-yl)-2-phenyl-2*H*-indazole (3ag): Light yellow solid; m.p. = 94.9–96.4 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.75 (d, *J* = 8.8 Hz, 1H), 7.60 (s, 1H), 7.57–7.55 (m, 1H), 7.38–7.32 (m, 6H), 7.27 (s, 1H), 7.15–7.12 (m, 1H), 2.09 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.8, 143.2, 138.5, 130.4, 130.2, 129.0, 128.5, 127.2, 124.0, 123.3, 118.8, 118.3, 117.9, 117.3, 8.7. HRMS (ESI) ([*M*+*H*]⁺) Calcd. for [C₁₇H₁₅N₄]⁺: 275.1291, Found: 275.1294.



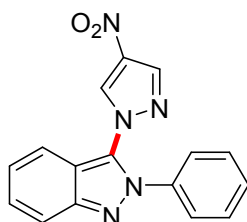
3-(4-Fluoro-1*H*-pyrazol-1-yl)-2-phenyl-2*H*-indazole (3ah): Light yellow solid; m.p. = 126.7–127.5 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.78–7.75 (m, 1H), 7.67–7.66 (m, 1H), 7.55–7.53 (m, 1H), 7.40–7.34 (m, 7H), 7.19–7.15 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 150.5 (d, *J* = 249.0 Hz), 147.8, 138.2, 130.4 (d, *J* = 13.6 Hz), 129.6, 129.2, 128.9, 127.4, 124.1, 123.9, 118.3, 118.13, 118.07 (d, *J* = 26.7 Hz), 117.5. HRMS (ESI) ([*M*+*H*]⁺) Calcd. for [C₁₆H₁₂FN₄]⁺: 279.1041, Found: 249.1044.



3-(4-Chloro-1H-pyrazol-1-yl)-2-phenyl-2H-indazole (3ai): Light yellow solid; m.p. = 136.2–137.9 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.78–7.77 (m, 1H), 7.73 (s, 1H), 7.54–7.52 (m, 2H), 7.41–7.35 (m, 6H), 7.19–7.17 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ: 147.8, 141.0, 138.1, 129.9, 129.3, 129.1, 128.9, 127.5, 124.1, 124.0, 118.3, 118.2, 117.5, 112.7. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₆H₁₂ClN₄]⁺: 295.0745, Found: 295.0747.

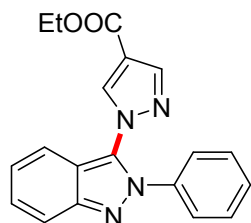


3-(4-Bromo-1H-pyrazol-1-yl)-2-phenyl-2H-indazole (3aj): Light yellow solid; m.p. = 125.4–127.3 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.79–7.77 (m, 2H), 7.56–7.53 (m, 2H), 7.43–7.37 (m, 6H), 7.21–7.18 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ: 147.8, 143.1, 138.2, 132.1, 129.3, 129.0, 129.0, 127.5, 124.2, 124.1, 118.3, 118.2, 117.5, 96.0. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₆H₁₂BrN₄]⁺: 339.0240, Found: 339.0246.

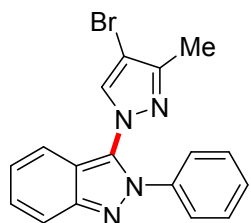


3-(4-Nitro-1H-pyrazol-1-yl)-2-phenyl-2H-indazole (3ak): Light yellow solid; m.p. = 172.8–174.3 °C. ¹H NMR (600 MHz, CDCl₃) δ: 8.33 (s, 1H), 8.25 (s, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.55–7.54 (m, 1H), 7.46–7.45 (m, 3H), 7.43–7.39 (m, 3H), 7.26–7.25 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ: 147.9, 137.70, 137.66, 137.3, 131.4, 129.62,

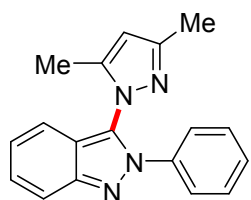
129.58, 127.8, 127.7, 124.9, 124.4, 118.5, 117.7, 117.6. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{16}H_{12}N_5O_2]^+$: 306.0986, Found: 306.0990.



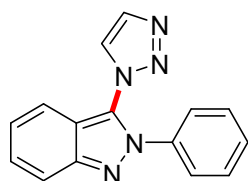
Ethyl 1-(2-phenyl-2H-indazol-3-yl)-1H-pyrazole-4-carboxylate (3al): Light yellow solid; m.p. = 99.8–101.6 °C. 1H NMR (600 MHz, $CDCl_3$) δ : 8.18 (s, 1H), 8.06 (s, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.54–7.52 (m, 1H), 7.40–7.37 (m, 6H), 7.21–7.19 (m, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ : 162.1, 147.8, 143.1, 138.0, 135.7, 129.3, 129.0, 128.7, 127.5, 124.2, 118.2, 118.1, 117.6, 117.3, 60.6, 14.2. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{19}H_{17}N_4O_2]^+$: 333.1346, Found: 333.1342



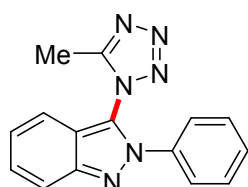
3-(4-Bromo-3-methyl-1H-pyrazol-1-yl)-2-phenyl-2H-indazole (3am): Light yellow solid; m.p. = 86.4–88.1 °C. 1H NMR (600 MHz, $CDCl_3$) δ : 7.76 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 9.6 Hz, 1H), 7.43–7.35 (m, 7H), 7.18–7.16 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 150.8, 147.9, 138.3, 132.4, 129.4, 129.3, 128.9, 127.4, 124.2, 123.8, 118.6, 118.1, 117.6, 97.1, 12.0. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{17}H_{14}N_4]^+$: 353.0396, Found: 353.0399.



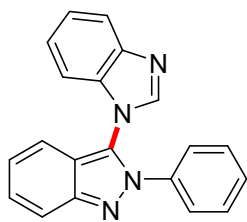
3-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-phenyl-2*H*-indazole (3an): Light yellow oil. ¹H NMR (600 MHz, CDCl₃) δ: 7.79 (d, *J* = 9.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.39–7.33 (m, 6H), 7.17–7.14 (m, 1H), 5.98 (s, 1H), 2.31 (s, 3H), 1.80 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 151.3, 147.9, 142.9, 138.6, 129.1, 128.6, 128.3, 127.2, 123.5, 123.4, 118.9, 118.7, 118.1, 106.8, 13.6, 10.8. HRMS (ESI) ([*M*+*H*]⁺) Calcd. for [C₁₈H₁₇N₄]⁺: 289.1448, Found: 289.1452.



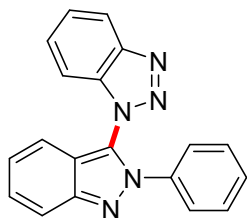
2-Phenyl-3-(1*H*-1,2,3-triazol-1-yl)-2*H*-indazole (3ao): Light yellow solid; m.p. = 117.5–118.7 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.80–7.78 (m, 2H), 7.69–7.68 (m, 1H), 7.50–7.48 (m, 1H), 7.41–7.32 (m, 6H), 7.23–7.19 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.8, 137.6, 133.9, 129.3, 129.2, 127.6, 126.5, 125.9, 124.5, 124.3, 118.1, 118.0, 117.8. HRMS (ESI) ([*M*+*Na*]⁺) Calcd. for [C₁₅H₁₁N₅Na]⁺: 284.0907, Found: 284.0911.



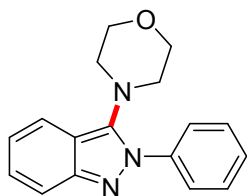
3-(5-Methyl-1*H*-tetrazol-1-yl)-2-phenyl-2*H*-indazole (3ap): Light yellow solid; m.p. = 97.9–99.8 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.89–7.87 (m, 1H), 7.49–7.43 (m, 4H), 7.40–7.35 (m, 3H), 7.32–7.28 (m, 1H), 2.20 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 154.3, 148.1, 137.2, 129.8, 129.7, 127.8, 125.4, 124.1, 121.5, 118.7, 117.2, 8.6. HRMS (ESI) ([*M*+*Na*]⁺) Calcd. for [C₁₅H₁₂N₆Na]⁺: 299.1016, Found: 299.1020.



3-(1H-Benzo[d]imidazol-1-yl)-2-phenyl-2H-indazole (3aq): Light yellow solid; m.p. = 151.6–153.5 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.90–7.89 (m, 1H), 7.87–7.84 (m, 1H), 7.43–7.41 (m, 1H), 7.40–7.36 (m, 2H), 7.33–7.28 (m, 6H), 7.19–7.16 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ: 148.3, 143.0, 142.6, 137.9, 134.3, 129.5, 129.1, 127.6, 125.1, 124.6, 123.9, 123.8, 123.6, 120.8, 118.6, 118.3, 118.0, 110.4. HRMS (ESI) ([M+H]⁺) Calcd. for [C₂₀H₁₅N₄]⁺: 311.1291, Found: 311.1296.

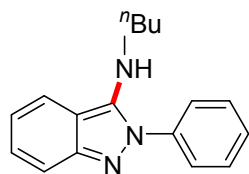


1-(2-Phenyl-2H-indazol-3-yl)-1H-benzo[d][1,2,3]triazole (3ar): Light yellow solid; m.p. = 138.2–139.7 °C. ¹H NMR (600 MHz, CDCl₃) δ: 8.16–8.15 (m, 1H), 7.90–7.89 (m, 1H), 7.47–7.41 (m, 3H), 7.39–7.36 (m, 3H), 7.30–7.28 (m, 3H), 7.22–7.19 (m, 2H). ¹³C NMR (150 MHz, CDCl₃) δ: 148.2, 145.3, 138.1, 134.3, 129.3, 129.13, 129.08, 127.6, 125.0, 124.8, 124.5, 124.2, 120.5, 118.60, 118.57, 118.2, 109.4. HRMS (ESI) ([M+Na]⁺) Calcd. for [C₁₉H₁₃N₅Na]⁺: 334.1063, Found: 334.1066.

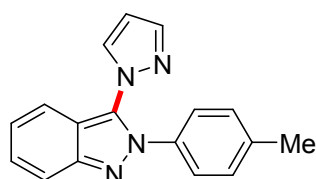


4-(2-Phenyl-2H-indazol-3-yl)morpholine (3as): Light yellow solid; m.p. = 150.3–152.3 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.81–7.78 (m, 3H), 7.65–7.63 (m, 1H), 7.51–7.47 (m, 2H), 7.41–7.38 (m, 1H), 7.25–7.22 (m, 1H), 6.99–6.96 (m, 1H), 3.73–3.71 (m, 4H), 3.27–3.25 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.2, 141.8,

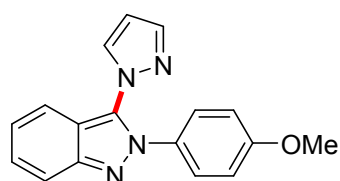
139.8, 128.9, 128.0, 126.5, 124.8, 120.7, 120.4, 118.1, 114.5, 66.9, 51.4. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₇H₁₈N₃O]⁺: 280.1444, Found: 280.1443.



N-Butyl-2-phenyl-2H-indazol-3-amine (3at): Light yellow solid; m.p. = 146.3–147.3 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.67–7.66 (m, 1H), 7.63–7.61 (m, 2H), 7.55–7.52 (m, 2H), 7.50–7.49 (m, 1H), 7.46–7.43 (m, 1H), 7.22–7.19 (m, 1H), 6.85–6.82 (m, 1H), 4.11 (s, 1H), 3.51 (q, *J* = 6.6 Hz, 2H), 1.63–1.58 (m, 2H), 1.41–1.35 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 148.9, 140.7, 138.7, 129.6, 128.5, 127.0, 125.4, 121.0, 118.2, 117.0, 109.3, 45.9, 32.5, 19.9, 13.7. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₇H₂₀N₃]⁺: 266.1652, Found: 266.1658.

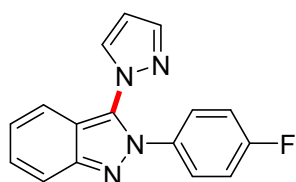


3-(1H-Pyrazol-1-yl)-2-(p-tolyl)-2H-indazole (3ba): Light yellow solid; m.p. = 118.2–119.6 °C. ¹H NMR (600 MHz, CDCl₃) δ: 7.814–7.811 (m, 1H), 7.78–7.76 (m, 1H), 7.56–7.55 (m, 1H), 7.503–7.499 (m, 1H), 7.37–7.34 (m, 1H), 7.25–7.24 (m, 2H), 7.18–7.15 (m, 3H), 6.46–6.45 (m, 1H), 2.36 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ: 147.8, 142.3, 138.8, 136.0, 132.3, 129.8, 129.7, 127.2, 123.9, 123.5, 118.7, 118.0, 117.5, 107.7, 21.1. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₇H₁₅N₄]⁺: 275.1291, Found: 275.1294.

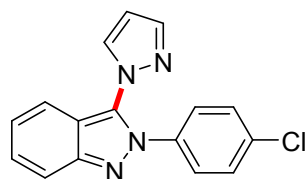


2-(4-Methoxyphenyl)-3-(1H-pyrazol-1-yl)-2H-indazole (3ca): Light yellow solid;

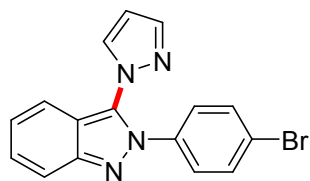
m.p. = 120.3–121.9 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.81–7.80 (m, 1H), 7.78–7.75 (m, 1H), 7.56–7.54 (m, 1H), 7.501–7.496 (m, 1H), 7.37–7.33 (m, 1H), 7.31–7.27 (m, 2H), 7.17–7.13 (m, 1H), 6.89–6.87 (m, 2H), 6.45–6.44 (m, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 159.6, 147.7, 142.2, 132.3, 131.5, 129.8, 127.2, 125.4, 123.4, 118.6, 117.9, 117.4, 114.3, 107.7, 55.4. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $[\text{C}_{17}\text{H}_{15}\text{N}_4\text{O}]^+$: 291.1240, Found: 291.1243.



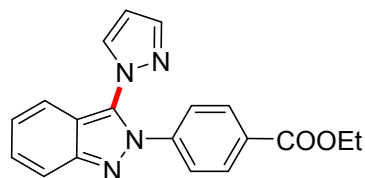
2-(4-Fluorophenyl)-3-(1H-pyrazol-1-yl)-2H-indazole (3da): Light yellow solid; m.p. = 82.1–83.2 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.795–7.791 (m, 1H), 7.76–7.74 (m, 1H), 7.54–7.51 (m, 2H), 7.37–7.32 (m, 3H), 7.17–7.13 (m, 1H), 7.07–7.03 (m, 2H), 6.46–6.45 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 162.2 (d, $J = 247.9$ Hz), 147.8, 142.4, 134.5 (d, $J = 3.0$ Hz), 132.3, 127.4, 125.9 (d, $J = 9.0$ Hz), 123.7, 118.5, 117.9, 117.5, 116.0 (d, $J = 22.0$ Hz), 107.9. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $[\text{C}_{16}\text{H}_{12}\text{FN}_4]^+$: 279.1041, Found: 279.1043.



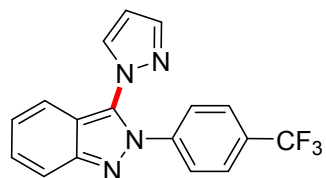
2-(4-Chlorophenyl)-3-(1H-pyrazol-1-yl)-2H-indazole (3ea): Light yellow solid; m.p. = 123.8–124.9 °C. ^1H NMR (400 MHz, CDCl_3) δ : 7.81–7.80 (m, 1H), 7.76–7.74 (m, 1H), 7.55–7.50 (m, 2H), 7.37–7.27 (m, 5H), 7.17–7.13 (m, 1H), 6.48–6.47 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ : 147.9, 142.5, 136.9, 134.5, 132.4, 129.8, 129.2, 127.6, 125.1, 123.8, 118.5, 118.0, 117.6, 108.0. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $[\text{C}_{16}\text{H}_{12}\text{ClN}_4]^+$: 295.0745, Found: 295.0742.



2-(4-Bromophenyl)-3-(1H-pyrazol-1-yl)-2H-indazole (3fa): Light yellow solid; m.p. = 140.3–142.6 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.81–7.80 (m, 1H), 7.75–7.73 (m, 1H), 7.553–7.547 (m, 1H), 7.52–7.47 (m, 3H), 7.37–7.33 (m, 1H), 7.23–7.20 (m, 2H), 7.17–7.13 (m, 1H), 6.48–6.47 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 147.9, 142.5, 137.4, 132.4, 132.2, 129.8, 127.6, 125.3, 123.8, 122.5, 118.5, 118.0, 117.7, 108.0. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₆H₁₂BrN₄]⁺: 339.0240, Found: 339.0242.

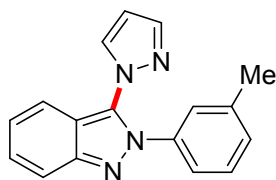


Ethyl 4-(3-(1H-pyrazol-1-yl)-2H-indazol-2-yl)benzoate (3ga): Light yellow solid; m.p. = 125.6–126.2 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.07–8.04 (m, 2H), 7.83–7.82 (m, 1H), 7.77–7.75 (m, 1H), 7.60–7.58 (m, 1H), 7.53–7.51 (m, 1H), 7.42–7.35 (m, 3H), 7.18–7.14 (m, 1H), 6.51–6.50 (m, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 165.4, 148.2, 142.6, 141.8, 132.4, 130.4, 130.2, 129.9, 127.7, 124.0, 123.5, 118.5, 118.1, 117.8, 108.1, 61.2, 14.1. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₉H₁₇N₄O₂]⁺: 333.1346, Found: 333.1349.

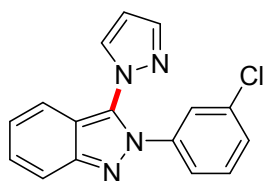


3-(1H-Pyrazol-1-yl)-2-(4-(trifluoromethyl)phenyl)-2H-indazole (3ha): Light yellow solid; m.p. = 128.6–129.5 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.842–7.838 (m, 1H), 7.78–7.76 (m, 1H), 7.66–7.63 (m, 2H), 7.62–7.61 (m, 1H), 7.53–7.51 (m, 1H), 7.48–7.46 (m, 2H), 7.41–7.37 (m, 1H), 7.12–7.17 (m, 1H), 6.54–6.53 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.3, 142.8, 141.3, 132.5, 130.4 (q, *J* = 33.0 Hz), 130.0,

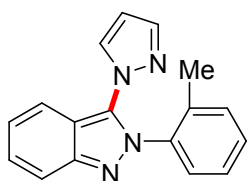
127.9, 126.3 (q, $J = 3.7$ Hz), 124.2, 124.0, 123.6 (q, $J = 270.7$ Hz), 118.6, 118.2, 117.9, 108.3. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_7H_{12}F_3N_4]^+$: 329.1009, Found: 329.1013.



3-(1*H*-Pyrazol-1-yl)-2-(*m*-tolyl)-2*H*-indazole (3ia): Light yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ : 7.79–7.75 (m, 2H), 7.56–7.54 (m, 1H), 7.49–7.48 (m, 1H), 7.35–7.31 (m, 1H), 7.260–7.257 (m, 1H), 7.22–7.18 (m, 1H), 7.15–7.11 (m, 2H), 7.05–7.03 (m, 1H), 6.42–6.41 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 147.7, 142.1, 139.2, 138.2, 132.2, 129.8, 129.3, 128.7, 127.2, 124.7, 123.4, 120.8, 118.6, 117.9, 117.4, 107.6, 21.1. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{17}H_{15}N_4]^+$: 275.1291, Found: 275.1295.

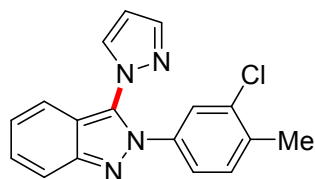


2-(3-Chlorophenyl)-3-(1*H*-pyrazol-1-yl)-2*H*-indazole (3ja): Light yellow solid; m.p. = 81.7–83.8 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.83–7.82 (m, 1H), 7.76–7.74 (m, 1H), 7.58–7.57 (m, 1H), 7.53–7.51 (m, 1H), 7.45–7.44 (m, 1H), 7.38–7.31 (m, 2H), 7.28–7.24 (m, 1H), 7.18–7.14 (m, 2H), 6.51–6.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 148.0, 142.6, 139.4, 134.8, 132.4, 130.0, 129.9, 128.7, 127.7, 124.3, 123.9, 121.8, 118.5, 118.1, 117.7, 108.1. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{16}H_{12}ClN_4]^+$: 295.0745, Found: 295.0745.

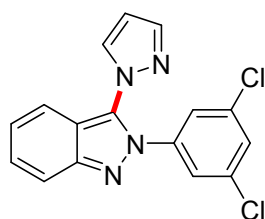


3-(1*H*-Pyrazol-1-yl)-2-(*o*-tolyl)-2*H*-indazole (3ka): Light yellow oil. 1H NMR (400

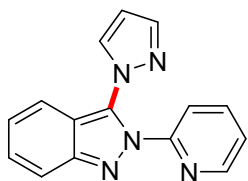
MHz, CDCl₃) δ : 7.77–7.74 (m, 2H), 7.709–7.705 (m, 1H), 7.40–7.32 (m, 4H), 7.28–7.26 (m, 2H), 7.21–7.17 (m, 1H), 6.34–6.33 (m, 1H), 1.99 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 148.1, 142.0, 137.6, 135.4, 131.7, 131.0, 130.9, 129.9, 127.28, 127.25, 126.6, 123.3, 119.4, 117.9, 115.4, 107.5, 17.1. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₇H₁₅N₄]⁺: 275.1291, Found: 275.1296.



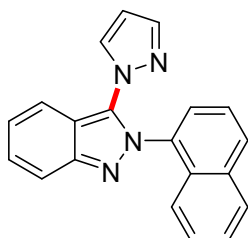
2-(3-Chloro-4-methylphenyl)-3-(1H-pyrazol-1-yl)-2H-indazole (3la): Light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ : 7.83–7.82 (m, 1H), 7.76–7.74 (m, 1H), 7.57–7.56 (m, 1H), 7.53–7.51 (m, 1H), 7.443–7.438 (m, 1H), 7.38–7.33 (m, 1H), 7.20–7.13 (m, 2H), 7.07–7.05 (m, 1H), 6.50–6.49 (m, 1H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 147.9, 142.5, 137.1, 136.7, 134.7, 132.4, 131.1, 129.8, 127.5, 124.6, 123.8, 121.7, 118.5, 118.0, 117.6, 108.0, 19.7. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₇H₁₅ClN₄]⁺: 309.0902, Found: 309.0905.



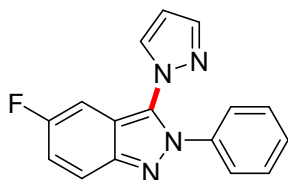
2-(3,5-Dichlorophenyl)-3-(1H-pyrazol-1-yl)-2H-indazole (3ma): Light yellow solid; m.p. = 135.1–136.2 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.87–7.86 (m, 1H), 7.75–7.73 (m, 1H), 7.65–7.64 (m, 1H), 7.51–7.48 (m, 1H), 7.39–7.33 (m, 2H), 7.245–7.240 (m, 2H), 7.19–7.15 (m, 1H), 6.57–6.56 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 148.2, 142.9, 139.9, 135.4, 132.5, 129.9, 128.5, 128.1, 124.3, 122.3, 118.5, 118.2, 117.8, 108.5. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₆H₁₂Cl₂N₄]⁺: 329.0355, Found: 329.0358.



3-(1H-Pyrazol-1-yl)-2-(pyridin-2-yl)-2H-indazole (3na): Light yellow solid; m.p. = 111.1–112.9 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.37–8.35 (m, 1H), 7.80–7.74 (m, 4H), 7.65–7.63 (m, 1H), 7.55–7.53 (m, 1H), 7.37–7.33 (m, 1H), 7.26–7.23 (m, 1H), 7.16–7.12 (m, 1H), 6.48–6.47 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 151.3, 148.4, 148.0, 141.9, 138.4, 132.7, 130.3, 127.7, 123.8, 123.4, 118.8, 118.5, 118.2, 117.6, 107.2. HRMS (ESI) ([M+Na]⁺) Calcd. for [C₁₅H₁₁N₅Na]⁺: 284.0907, Found: 284.0910.

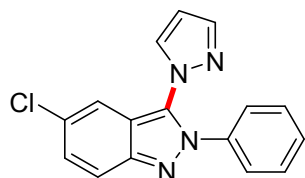


2-(Naphthalen-1-yl)-3-(1H-pyrazol-1-yl)-2H-indazole (3oa): Light yellow solid; m.p. = 113.9–115.3 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.96–7.94 (m, 1H), 7.90–7.88 (m, 1H), 7.82–7.77 (m, 2H), 7.61 (s, 1H), 7.52–7.46 (m, 3H), 7.43–7.40 (m, 3H), 7.25–7.21 (m, 2H), 6.162–6.157 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.3, 142.0, 134.6, 133.9, 132.6, 131.2, 130.3, 129.7, 128.1, 127.8, 127.5, 126.8, 125.1, 124.8, 123.5, 122.4, 119.4, 118.0, 115.8, 107.4. HRMS (ESI) ([M+H]⁺) Calcd. for [C₂₀H₁₆N₄]⁺: 311.1291, Found: 311.1294.

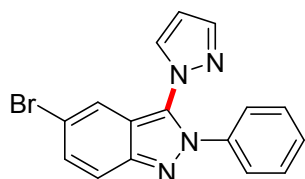


5-Fluoro-2-phenyl-3-(1H-pyrazol-1-yl)-2H-indazole (3pa): Light yellow solid; m.p. = 102.2–103.7 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.79–7.72 (m, 2H), 7.462–7.456 (m, 1H), 7.35–7.34 (m, 5H), 7.17–7.12 (m, 2H), 6.43–6.42 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 159.2 (d, *J* = 242.0 Hz), 145.2, 142.4, 138.2, 132.3, 130.2 (d, *J* = 8.9 Hz),

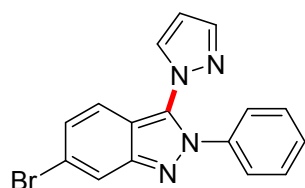
129.1, 128.7, 123.9, 120.3 (d, $J = 9.8$ Hz), 119.1 (d, $J = 29.1$ Hz), 117.0 (d, $J = 11.8$ Hz), 107.9, 101.2 (d, $J = 25.3$ Hz). HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{16}H_{12}FN_4]^+$: 279.1041, Found: 279.1043.



5-Chloro-2-phenyl-3-(1H-pyrazol-1-yl)-2H-indazole (3qa): Light yellow solid; m.p. = 133.7–134.9 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.804–7.800 (m, 1H), 7.71–7.68 (m, 1H), 7.565–7.560 (m, 1H), 7.46–7.45 (m, 1H), 7.38–7.32 (m, 5H), 7.29–7.27 (m, 1H), 6.44–6.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 146.2, 142.5, 138.1, 132.2, 129.6, 129.3, 129.2, 128.9, 128.8, 124.0, 119.6, 117.8, 117.5, 108.0. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{16}H_{12}ClN_4]^+$: 295.0745, Found: 295.0747.

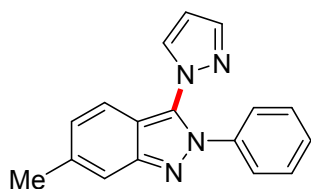


5-Bromo-2-phenyl-3-(1H-pyrazol-1-yl)-2H-indazole (3ra): Light yellow solid; m.p. = 139.8–141.6 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.81–7.76 (m, 2H), 7.65–7.63 (m, 1H), 7.464–7.458 (m, 1H), 7.42–7.32 (m, 6H), 6.45–6.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 146.2, 142.6, 138.1, 132.2, 131.1, 129.4, 129.2, 128.9, 124.0, 121.0, 119.8, 118.5, 117.2, 108.1. HRMS (ESI) ($[M+H]^+$) Calcd. for $[C_{16}H_{12}BrN_4]^+$: 339.0240, Found: 339.0242.

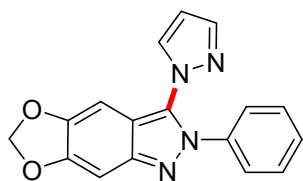


6-Bromo-2-phenyl-3-(1H-pyrazol-1-yl)-2H-indazole (3sa): Light yellow solid; m.p. = 148.6–149.9 °C. 1H NMR (400 MHz, $CDCl_3$) δ : 7.96–7.95 (m, 1H), 7.820–7.816 (m,

1H), 7.48–7.46 (m, 2H), 7.40–7.38 (m, 3H), 7.36–7.33 (m, 2H), 7.25–7.23 (m, 1H), 6.47–6.45 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.4, 142.6, 138.1, 132.2, 130.6, 129.3, 129.0, 127.4, 124.2, 121.5, 120.4, 116.1, 108.1. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₆H₁₂BrN₄]⁺: 339.0240, Found: 339.0242.



6-Methyl-2-phenyl-3-(1H-pyrazol-1-yl)-2H-indazole (3ta): Light yellow solid; m.p. = 139.8–141.2 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.80–7.79 (m, 1H), 7.51 (s, 1H), 7.49–7.48 (m, 1H), 7.46–7.44 (m, 1H), 7.36–7.34 (m, 5H), 7.02–6.99 (m, 1H), 6.44–6.43 (m, 1H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.5, 142.2, 138.5, 137.4, 132.3, 129.8, 129.1, 128.5, 126.6, 124.1, 118.2, 116.2, 116.0, 107.7, 22.2. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₇H₁₅N₄]⁺: 275.1291, Found: 275.1292.



2-Phenyl-3-(1H-pyrazol-1-yl)-2H-[1,3]dioxolo[4,5-f]indazole (3ua): Light yellow solid; m.p. = 183.6–184.9 °C. ¹H NMR (400 MHz, CDCl₃) δ: 7.81–7.80 (m, 1H), 7.46–7.45 (m, 1H), 7.35–7.32 (m, 3H), 7.29–7.27 (m, 2H), 7.01 (s, 1H), 6.73 (s, 1H), 6.45–6.44 (m, 1H), 5.97 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 150.2, 147.0, 145.6, 142.2, 138.5, 132.3, 129.6, 129.1, 128.1, 123.5, 113.9, 107.7, 101.2, 94.2, 93.3. HRMS (ESI) ([M+H]⁺) Calcd. for [C₁₇H₁₃N₄O₂]⁺: 305.1033, Found: 305.1035.

6. ¹H and ¹³C NMR spectra of the products

