Electrochemical Dehydrogenative C-N Coupling of Hydrazones for the Synthesis of 1H-Indazoles

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Supporting Information

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1. General Information

All reagents were obtained from commercial suppliers and used without further purification. Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether 40-60 (PE)/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass plate coated with silica gel with fluorescent indicator (GF254) using UV light. The $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADVANCE III 500 MHz using CDCl$_3$ as solvent with TMS as internal standard. Chemical shifts are given in ppm ($\delta$) referenced to CDCl$_3$ with 7.28 for $^1$H and 77.16 for $^{13}$C, and to DMSO-d$_6$ with 2.50 for $^1$H and 39.52 for $^{13}$C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. Melting points were measured on a SGW® X-4B apparatus and uncorrected. HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer.

2. General Procedure of Synthesizing the Products

$$\text{General procedure: A 10 mL three-necked round-bottomed flask was equipped with a graphite carbon anode (}\phi \ 6 \text{ mm, about 0.8 cm immersion depth in solution), a platinum plate (1 cm x 1 cm) cathode and a stirring bar. The flask was charged with hydrazone (0.2 mmol, 1 equiv.), ~Bu$_4$NBF$_4$ (0.24 mmol) and HFIP (4.0 mL). The reaction mixture was stirred and electrolyzed at a constant current of 5 mA (current density = 2.7 mA/cm$^2$) under 40 °C for 2.2-3.3 h (2.1-3.1 F). When the reaction was finished, the reaction mixture was transferred to a single-necked flask and concentrated under reduced pressure. The given residue was purified by column chromatography through silica gel to provide the desired product.}

**Procedure for gram scale synthesis of 1a:** The 5 mmol scale electrolysis of hydrazone 1a was conducted in a 50 mL three-necked round-bottomed flask with a graphite carbon anode ($\phi$ 6 mm, about 3.0 cm immersion depth in solution), a Pt plate cathode (1 cm x 1 cm). The flask was charged with hydrazone 1a (1.59 g, 5 mmol), ~Bu$_4$NBF$_4$ (1 g, 3 mmol) and HFIP (40 mL). The reaction was electrolyzed at a constant current of 17 mA (current density = 2.7 mA/cm$^2$, 2.4 F) under 40 °C for 19 h. The reaction mixture was then transferred to a single-necked flask and HFIP was recovered by rotary evaporation for repeated use. The given residue was washed with water and extracted with EtOAc (50 mL). The organic layer was washed with water (50 mL) three times, the water layer were combined, rotary evaporator to spin off most of the water and recrystallize to recover electrolyte. The organic layers dried over Na$_2$SO$_4$, and concentrated. Product 2a was isolated by column chromatography (PE/EtOAc 15:1) to afford 1.35 g (86%) as a yellow solid.

**Procedure for gram scale synthesis of 3o:** The 6 mmol scale electrolysis of hydrazone 3q was
conducted in a 50mL three-necked round-bottomed flask with a graphite carbon anode (ϕ 6 mm, about 3.7 cm immersion depth in solution), a Pt plate cathode (1 cm x 1 cm). The flask was charged with 3q (1.88 g, 6 mmol), nBu4NBF4 (1 g, 3 mmol) and HFIP (50 mL). The reaction was electrolyzed at a constant current of 20 mA (current density = 2.7 mA/cm², 2.7 F) under 40 °C for 22 h. The reaction mixture was then transferred to a single-necked flask and the HFIP was recovered by rotary evaporation for repeated use. The given residue was washed with water and extracted with EtOAc (100 mL x 3). The organic layers were combined, dried over Na2SO4, concentrated and isolated by column chromatography (PE/EtOAc 15:1) to afford a crude product. Then the crude product was recrystallized with PE/EtOAc 20:1 to afford 3o (65%, 1.2 g) as a yellow solid.

Notes:
1. HFIP can be recovered by rotary evaporation for repeated use according to the reference (recovery rate 92%).
2. nBu4NBF4 could be purified by recrystallization from water for repeated use, recovery rate 70%, NMR spectrum as the evidence for purity and identification.
3. The recovered solvent and electrolyte were reused in the reaction of substrate 1a, and the yield was 69%, which was slightly lower.

Figure S1. Electrolysis setup

3. Application

![Chemical structure images](image)

**Procedure for synthesis of 5:** To a 15 mL pressure vessel equipped with a magnetic stir bar were introduced 2a (0.2 mmol, 1.0 equiv.), NaOEt (40.8 mg, 0.6 mmol, 3.0 equiv.) and DMSO (3.0 mL). The reaction mixture was stirred at 120 °C for 3 h. After cooling to ambient temperature, the reaction mixture was diluted with DCM, the aqueous layer was extracted with DCM thrice, the organic layer was washed with brine and dried with Na2SO4. After filtration and evaporation, the crude product
was purified by column chromatography with PE/EtOAc (6:1) to afford 27 mg (70%) as a yellow solid.

**Procedure for synthesis of 6:** To a 15 mL pressure vessel equipped with a magnetic stir bar were introduced 4q (0.3 mmol, 1.0 equiv.), NaOEt (102 mg, 1.5 mmol, 5.0 equiv.) and DMSO (3.0 mL). The reaction mixture was stirred at 110 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with 2 mol/L hydrochloric acid until PH 3, then washed with water and extracted with EtOAc (20 mL x 3). The organic layer was washed with brine and dried with Na₂SO₄. After filtration and evaporation, the crude product was purified by column chromatography with DCM/MeOH (100:1) to afford 34 mg (71%) as a beige solid.

### 4. Radical Scavenger Experiments

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<tr>
<td>TEMPO (1.5 eq)</td>
<td>2.4 F</td>
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<td>10%</td>
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<tr>
<td>TEMPO (3.0 eq)</td>
<td>4.8 F</td>
<td>80%</td>
<td>12%</td>
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<tr>
<td>BHT (3.0 eq)</td>
<td>2.4 F</td>
<td>95%</td>
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<tr>
<td>BHT (5.0 eq)</td>
<td>7.2 F</td>
<td>78%</td>
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Following the general procedure (1a as the starting material), the reaction was inhibited significantly by the addition of radical scavenger TEMPO into the system. When BHT was used, there is almost no cyclized product was detected. Those results indicate this reaction might involve a radical process.

### 5. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte of "Bu₄NBF₄ (0.1 M) in HFIP (5 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate is 50 mV/s.
Figure S1 Cyclic voltammograms. a: HFIP + BuNBF₄ (0.1 M); b: TEMPO (3 mM) + HFIP + BuNBF₄ (0.1 M); c: BHT (5 mM) + HFIP + BuNBF₄ (0.1 M); d: 1a (5 mM) + HFIP + BuNBF₄ (0.1 M); e: 2a (5 mM) + HFIP + BuNBF₄ (0.1 M).
6. Synthesis and Characterization of the Products:

1-(4-nitrophenyl)-3-phenyl-1H-indazole (2a):
Following the general procedure for 2.5 h (2.4 F), 2a was purified by PE/EtOAc (50:1) and obtained as a yellow solid (53.5 mg, 85% yield); Mp = 163-165 °C; Rf = 0.40 (PE/EtOAc = 20:1); 1H NMR (500 MHz, CDCl₃) δ 8.47 - 8.41 (m, 2H), 8.13 (d, J = 8.2 Hz, 1H), 8.10 - 8.02 (m, 4H), 7.92 (d, J = 8.5 Hz, 1H), 7.61 - 7.55 (m, 3H), 7.54 - 7.49 (m, 1H), 7.43 - 7.37 (m, 1H); 13C NMR (126 MHz, CDCl₃) δ 148.3, 145.4, 145.0, 140.1, 132.3, 129.0, 129.0, 128.2, 127.9, 125.3, 124.4, 123.1, 122.2, 121.5, 110.9. The spectra data matched with values reported in the literature.¹

4-(3-phenyl-1H-indazol-1-yl)benzenesulfonamide (2b):
Following the general procedure for 2.7 h (2.5 F), 2b was purified by DCM/MeOH (100:1) and obtained as a white solid (47 mg, 68% yield); Mp = 238-239 °C; Rf = 0.50 (DCM/MeOH = 50:1); 1H NMR (500 MHz, DMSO-d₆) δ 8.20 (d, J = 8.2 Hz, 1H), 8.12 (d, J = 8.8 Hz, 2H), 8.07 (dt, J = 9.3, 4.2 Hz, 5H), 7.61 (dt, J = 11.6, 7.8 Hz, 3H), 7.52 (d, J = 3.5 Hz, 3H), 7.42 (t, J = 7.6 Hz, 1H); 13C NMR (126 MHz, DMSO-d₆) δ 146.6, 142.4, 142.0, 140.1, 132.6, 129.6, 129.3, 128.7, 128.0, 127.9, 123.5, 123.3, 122.4, 122.1, 111.7. Calculated for C₁₉H₁₅N₃O₂S [M+H]⁺: 350.0958; Found: 350.0953.

4-(3-phenyl-1H-indazol-1-yl)benzonitrile (2c):
Following the general procedure for 2.2 h (2.1 F), 2c was purified by PE/EtOAc (20:1) and obtained as a white solid (51 mg, 86% yield); Mp = 161-163 °C; Rf = 0.50 (PE/EtOAc = 15:1); 1H NMR (500 MHz, DMSO-d₆) δ 8.19 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.8 Hz, 2H), 8.09 - 8.03 (m, 5H), 7.65 - 7.56 (m, 3H), 7.55 - 7.49 (m, 1H), 7.43 (t, J = 7.5 Hz, 1H); 13C NMR (126 MHz, DMSO-d₆) δ 147.1, 143.5, 140.0, 134.5, 132.4, 129.6, 129.4, 128.9, 128.0, 123.7, 123.6, 122.5, 122.2, 119.1, 111.8, 108.8. The spectra data matched with values reported in the literature.³
ethyl 4-(3-phenyl-1H-indazol-1-yl)benzoate (2d):
Following the general procedure for 2.5 h (2.4 F), 2d was purified by PE/EtOAc (30:1) and obtained as a white solid (54 mg, 80% yield); Mp = 98-100 °C; Rf = 0.30 (PE/EtOAc = 20:1); 1H NMR (500 MHz, CDCl₃) δ 8.28 - 8.24 (m, 2H), 8.12 (dt, J = 8.1, 1.0 Hz, 1H), 8.08 - 8.04 (m, 2H), 7.97 - 7.93 (m, 2H), 7.89 (dt, J = 8.6, 0.9 Hz, 1H), 7.60 - 7.55 (m, 2H), 7.53 (ddd, J = 8.3, 6.9, 1.1 Hz, 1H), 7.51 - 7.46 (m, 1H), 7.35 (ddd, J = 8.0, 6.9, 0.9 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H); 13C NMR (126 MHz, CDCl₃) δ 166.0, 147.2, 143.8, 140.2, 132.8, 131.0, 128.9, 128.6, 128.0, 127.9, 127.6, 123.8, 122.5, 121.9, 121.6, 110.9, 61.1, 14.4. The spectra data matched with values reported in the literature.¹

3-phenyl-1-(4-(trifluoromethoxy)phenyl)-1H-indazole (2e):
Following the general procedure for 2.2 h (2.1 F), 2e was purified by PE/EtOAc (100:1) and obtained as a white solid (70 mg, 94% yield); Mp = 110-112 °C; Rf = 0.50 (PE/EtOAc = 30:1); 1H NMR (500 MHz, CDCl₃) δ 8.12 (dt, J = 8.3, 1.0 Hz, 1H), 8.07 - 8.03 (m, 2H), 7.89 - 7.84 (m, 2H), 7.79 (dt, J = 8.5, 0.9 Hz, 1H), 7.59 - 7.54 (m, 2H), 7.54 - 7.46 (m, 2H), 7.46 - 7.42 (m, 2H), 7.34 (ddd, J = 8.0, 6.9, 0.9 Hz, 1H); 13C NMR (126 MHz, CDCl₃) δ 147.3, 146.7, 140.3, 138.7, 132.9, 128.9, 128.5, 127.8, 127.5, 124.0, 123.3, 122.2, 122.2, 121.8, 120.5 (q, J_C-F = 256.81 Hz), 110.4. Calculated for C₂₀H₁₄N₂O₃ [M+H]+: 355.1053; Found: 355.1055.

1-(4-methoxyphenyl)-3-phenyl-1H-indazole (2f):
Following the general procedure for 2.2 h (2.1 F), 2f was purified by PE/EtOAc (50:1) and obtained as a white solid (47 mg, 78% yield); Mp = 130-131 °C; Rf = 0.50 (PE/EtOAc = 50:1); 1H NMR (500 MHz, CDCl₃) δ 8.07 - 8.04 (m, 2H), 7.96 (d, J = 8.9 Hz, 1H), 7.83 - 7.80 (m, 2H), 7.60 - 7.53 (m, 4H), 7.48 - 7.43 (m, 1H), 7.43 - 7.38 (m, 1H), 7.15 (d, J = 2.1 Hz, 1H), 6.97 (dd, J = 8.9, 2.1 Hz, 1H), 3.90 (s, 3H); 13C NMR (126 MHz, CDCl₃) δ 158.5, 145.5, 140.6, 133.3, 133.2, 128.8, 128.2, 127.8, 127.0, 124.9, 122.7, 121.7, 121.5, 114.7, 110.5, 55.6. The spectra data matched with values reported in the literature.³
1,3-diphenyl-1H-indazole (2g):
Following the general procedure for 3.0 h (2.8 F), 2g was purified by PE/EtOAc (100:1) and obtained as an white solid (35 mg, 70% yield); Mp = 97-98 °C; Rf = 0.30 (PE/EtOAc = 100:1); 1H NMR (500 MHz, CDCl3) δ 8.12 (dt, J = 8.1, 1.0 Hz, 1H), 8.10 - 8.05 (m, 2H), 7.83 (ddt, J = 8.8, 6.8, 1.1 Hz, 3H), 7.62 - 7.53 (m, 4H), 7.47 - 7.42 (m, 2H), 7.42 - 7.38 (m, 1H), 7.32 (dd, J = 7.9, 6.8, 0.9 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 146.1, 140.4, 140.2, 133.3, 129.5, 128.9, 128.3, 127.8, 127.1, 126.7, 123.2, 123.0, 121.9, 121.6, 110.7. The spectra data matched with values reported in the literature.

3-phenyl-1-(p-tolyl)-1H-indazole (2h):
Following the general procedure for 2.5 h (2.4 F), 2h was purified by PE/EtOAc (100:1) and obtained as a white solid (42.5 mg, 75% yield); Mp = 93-94 °C; Rf = 0.50 (PE/EtOAc = 50:1); 1H NMR (500 MHz, CDCl3) δ 8.17 - 8.05 (m, 3H), 7.78 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.7 Hz, 2H), 7.51 - 7.44 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 2.48 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 145.8, 140.4, 137.7, 136.6, 133.4, 130.0, 128.8, 128.2, 127.8, 127.0, 123.1, 123.0, 121.8, 121.5, 110.7, 21.1. The spectra data matched with values reported in the literature.

1-(4-chlorophenyl)-3-phenyl-1H-indazole (2i):
Following the general procedure for 2.3 h (2.2 F), 2i was purified by PE/EtOAc (200:1) and obtained as a white solid (48.5 mg, 80% yield); Mp = 121-123 °C; Rf = 0.30 (PE/EtOAc = 100:1); 1H NMR (500 MHz, CDCl3) δ 8.11 (dt, J = 8.2, 1.0 Hz, 1H), 8.08 - 8.03 (m, 2H), 7.81 - 7.74 (m, 3H), 7.59 - 7.52 (m, 4H), 7.52 - 7.46 (m, 2H), 7.33 (ddd, J = 8.0, 6.9, 0.9 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 146.5, 140.2, 138.7, 133.0, 132.0, 129.6, 128.9, 128.5, 127.8, 127.4, 124.0, 123.3, 122.2, 121.8, 110.5. The spectra data matched with values reported in the literature.
1-(4-bromophenyl)-3-phenyl-1H-indazole (2j):
Following the general procedure for 2.3 h (2.2 F), 2j was purified by PE/EtOAc (50:1) and obtained as a colorless oil (44 mg, 72% yield); R_f = 0.30 (PE/EtOAc = 100:1); ^1H NMR (500 MHz, CDCl_3) δ 8.13 (dd, J = 8.2, 1.1 Hz, 1H), 8.11 - 8.05 (m, 2H), 7.68 - 7.60 (m, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.51 - 7.43 (m, 4H), 7.35 - 7.28 (m, 2H); ^13C NMR (126 MHz, CDCl_3) δ 146.5, 141.9, 137.1, 133.2, 131.7, 130.8, 129.9, 129.8, 128.9, 128.4, 127.8, 127.0, 122.2, 121.8, 121.5, 110.9. The spectra data matched with values reported in the literature.²

3-phenyl-1-(2,4,6-trichlorophenyl)-1H-indazole (2k):
Following the general procedure for 2.2 h (2.1 F), 2k was purified by PE/EtOAc (100:1) and obtained as a colorless oil (59 mg, 79% yield); R_f = 0.50 (PE/EtOAc = 50:1); ^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, J = 8.2 Hz, 1H), 8.07 - 8.03 (m, 2H), 7.58 - 7.51 (m, 4H), 7.49 - 7.42 (m, 2H), 7.33 (dd, J = 8.2, 6.9 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H); ^13C NMR (126 MHz, CDCl_3) δ 147.2, 141.9, 136.5, 136.1, 133.6, 132.9, 128.9, 128.5, 127.8, 127.5, 122.1, 122.0, 121.6, 109.8. The spectra data matched with values reported in the literature.²

1-(4-bromophenyl)-3-phenyl-1H-indazole (2l):
Following the general procedure for 2.2 h (2.1 F), 2l was purified by PE/EtOAc (100:1) and obtained as a light yellow solid (58 mg, 83% yield); Mp = 122-124 °C; R_f = 0.50 (PE/EtOAc = 50:1); ^1H NMR (500 MHz, DMSO-d_6) δ 8.17 (d, J = 8.2 Hz, 1H), 8.07 - 8.02 (m, 2H), 7.90 (d, J = 8.5 Hz, 1H), 7.85 - 7.75 (m, 4H), 7.57 (dt, J = 8.5, 7.1 Hz, 3H), 7.52 - 7.46 (m, 1H), 7.37 (t, J = 7.5 Hz, 1H); ^13C NMR (126 MHz, DMSO-d_6) δ 146.0, 140.1, 139.2, 133.0, 132.8, 129.5, 129.1, 128.4, 127.9, 124.7, 123.2, 123.0, 122.0, 119.5, 111.4. The spectra data matched with values reported in the literature.²
6-fluoro-3-(4-fluorophenyl)-1-phenyl-1H-indazole (4a):
Following the general procedure for 2.7 h (2.5 F), 4a was purified by PE/EtOAc (300:1) and obtained as a light yellow solid (36 mg, 59% yield); Mp = 137-139 °C; R_f = 0.30 (PE/EtOAc = 100:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.01 - 7.97 (m, 2H), 7.98 - 7.94 (m, 1H), 7.79 - 7.74 (m, 2H), 7.58 (dd, \(J = 8.5, 7.4\) Hz, 2H), 7.46 - 7.39 (m, 2H), 7.24 (t, \(J = 8.7\) Hz, 2H), 7.08 (td, \(J = 8.9, 2.2\) Hz, 1H); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 163.0 (d, \(J_{C-F} = 248.36\) Hz), 162.7 (d, \(J_{C-F} = 245.43\) Hz), 145.4, 140.7 (d, \(J_{C-F} = 12.12\) Hz), 139.7, 129.6, 129.4 (d, \(J_{C-F} = 8.18\) Hz), 128.9 (d, \(J_{C-F} = 3.18\) Hz), 127.1, 122.9, 122.8 (d, \(J_{C-F} = 11.74\) Hz), 119.8, 115.9 (d, \(J_{C-F} = 21.84\) Hz), 111.7 (d, \(J_{C-F} = 26.06\) Hz), 96.7 (d, \(J_{C-F} = 27.08\) Hz). The spectra data matched with values reported in the literature.\(^3\)

6-chloro-3-(4-chlorophenyl)-1-phenyl-1H-indazole (4b):
Following the general procedure for 3.3 h (3.1 F), 4b was purified by PE/EtOAc (300:1) and obtained as a white solid (33 mg, 49% yield); Mp = 153-156 °C; R_f = 0.50 (PE/EtOAc = 100:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.97 - 7.93 (m, 2H), 7.92 (d, \(J = 8.7, 0.7\) Hz, 1H), 7.76 (dt, \(J = 6.1, 1.7\) Hz, 2H), 7.74 (dd, \(J = 2.0, 1.0\) Hz, 1H), 7.61 - 7.56 (m, 2H), 7.52 - 7.49 (m, 2H), 7.45 - 7.41 (m, 1H), 7.26 (dd, \(J = 8.7, 1.7\) Hz, 1H); \(^1\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 145.0, 140.8, 139.5, 134.5, 133.8, 131.2, 129.7, 129.1, 128.8, 127.3, 123.1, 123.3, 122.2, 121.4, 110.6. The spectra data matched with values reported in the literature.\(^3\)

6-methyl-1-phenyl-3-(p-tolyl)-1H-indazole (4c):
Following the general procedure for 2.3 h (2.2 F), 4c was purified by PE/EtOAc (20:1) and obtained as a white solid (52.5 mg, 88% yield); Mp = 93-95 °C; R_f = 0.70 (PE/EtOAc = 10:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.99 (d, \(J = 8.1\) Hz, 3H), 7.86 - 7.81 (m, 2H), 7.62 - 7.61 (m, 2H), 7.43 - 7.42 (m, 3H), 7.15 (dd, \(J = 8.3, 1.3\) Hz, 1H), 2.57 - 2.55 (m, 3H), 2.48 (s, 3H); \(^1\)C NMR (126 MHz, CDCl\(_3\))
δ 146.0, 141.0, 140.4, 138.1, 137.5, 130.6, 129.6, 129.5, 127.6, 126.5, 124.0, 123.1, 121.4, 121.3, 110.2, 22.1, 21.4. The spectra data matched with values reported in the literature.3

6-methoxy-3-(4-methoxyphenyl)-1-phenyl-1H-indazole(4d):
Following the general procedure for 2.3 h (2.2 F), 4d was purified by PE/EtOAc(10:1) and obtained as a white solid (53.5 mg, 81% yield); Mp = 138-139 °C; Rf = 0.50 (PE/EtOAc = 10:1); 1H NMR (500 MHz, DMSO-d6) δ 8.01 - 7.93 (m, 3H), 7.87 - 7.82 (m, 2H), 7.62 (d, J = 8.5, 7.4 Hz, 2H), 7.42 (td, J = 7.4, 1.1 Hz, 1H), 7.21 (d, J = 2.2 Hz, 1H), 7.13 - 7.09 (m, 2H), 6.96 (dd, J = 8.9, 2.1 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H); 13C NMR (126 MHz, DMSO-d6) δ 160.1, 159.9, 145.3, 141.4, 140.2, 130.1, 128.9, 126.9, 125.6, 122.8, 122.7, 117.3, 114.9, 114.2, 92.5, 55.9, 55.7. The spectra data matched with values reported in the literature.3

1-(4-fluorophenyl)-6-methyl-3-(p-tolyl)-1H-indazole(4e):
Following the general procedure for 2.2 h (2.1 F), 4e was purified by PE/EtOAc(50:1) and obtained as a white solid (55.6 mg, 88% yield); Mp = 108-111 °C; Rf = 0.50 (PE/EtOAc = 50:1); 1H NMR (500 MHz, DMSO-d6) δ 7.97 (d, J = 8.4 Hz, 1H), 7.92 - 7.87 (m, 2H), 7.85 - 7.79 (m, 2H), 7.58 (q, J = 1.0 Hz, 1H), 7.45 - 7.38 (m, 2H), 7.35 - 7.30 (m, 2H), 7.13 (dd, J = 8.4, 1.3 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H); 13C NMR (126 MHz, DMSO-d6) δ 160.8 (d, J_{C-F} = 245.0 Hz), 145.3, 140.8, 138.2 (d, J_{C-F} = 21.68 Hz), 136.5 (d, J_{C-F} = 2.69 Hz), 130.3, 130.0, 127.5, 125.0 (d, J_{C-F} = 8.75 Hz), 124.8, 121.4, 120.9, 116.9, 116.7, 110.4, 21.9, 21.4. Calculated for C_{21}H_{18}N_{2}F [M+H]^+: 317.1448; Found: 317.1452.

6-(4-nitrophenyl)-10,11-dihydro-6H-benzo[6,7]cyclohepta[1,2,3-cd]indazole(4f):
Following the general procedure for 2.5 h (2.4 F), 4f was purified by PE/EtOAc(50:1) and obtained as a yellow solid (52 mg, 76% yield); Mp = 149-152 °C; Rf = 0.30 (PE/EtOAc = 50:1); 1H NMR
6-phenyl-6H-benzo[6,7]cyclohepta[1,2,3-cd]indazole(4g):
Following the general procedure for 2.5 h (2.4 F), 4g was purified by PE/EtOAc (40:1) and obtained as a yellow solid (55 mg, 68% yield); Mp = 124-126 °C; Rf = 0.50 (PE/EtOAc = 30:1); 1H NMR (500 MHz, CDCl3) δ 8.46 (dd, J = 7.9, 1.5 Hz, 1H), 7.80 - 7.75 (m, 2H), 7.58 - 7.52 (m, 2H), 7.41 - 7.34 (m, 2H), 7.32 - 7.28 (m, 1H), 7.24 (td, J = 7.4, 1.5 Hz, 1H), 7.20 (dd, J = 8.5, 7.0 Hz, 1H), 7.15 (dd, J = 7.7, 1.5 Hz, 1H), 6.75 (d, J = 7.0 Hz, 1H), 6.43 (d, J = 12.3 Hz, 1H), 6.35 (d, J = 12.3 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 146.5, 141.7, 140.2, 134.7, 134.5, 133.9, 133.5, 132.6, 130.4, 129.4, 129.3, 129.1, 128.2, 126.5, 126.4, 122.3, 120.0, 109.0. Calculated for C21H16N3O2 [M+H]+: 342.1237; Found: 342.1236.

6-methoxy-1,3-diphenyl-1H-indazole(4h):
Following the general procedure for 2.3 h (2.2 F), 4h was purified by PE/EtOAc (20:1) and obtained as a white solid (40 mg, 67% yield); Mp = 140-142 °C; Rf = 0.50 (PE/EtOAc = 10:1); 1H NMR (500 MHz, CDCl3) δ 8.11 (dt, J = 8.2, 1.0 Hz, 1H), 8.08 - 8.04 (m, 2H), 7.72 - 7.67 (m, 3H), 7.57 - 7.52 (m, 2H), 7.49 - 7.42 (m, 2H), 7.30 (dd, J = 7.9, 6.8, 0.9 Hz, 1H), 7.12 - 7.07 (m, 2H), 3.91 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 160.0, 146.1, 141.7, 140.2, 133.2, 129.5, 128.5, 128.3, 127.7, 126.7, 123.1, 122.4, 117.8, 113.6, 92.0, 55.6. The spectra data matched with values reported in the literature.3

3-(4-chlorophenyl)-6-methoxy-1-phenyl-1H-indazole(4i):
Following the general procedure for 2.2 h (2.1 F), 4i was purified by PE/EtOAc (50:1) and obtained as a white solid (46 mg, 69% yield); Mp = 134-136 °C; Rf = 0.50 (PE/EtOAc = 30:1); ¹H NMR (500 MHz, CDCl₃) δ 8.00 - 7.94 (m, 2H), 7.89 (d, J = 8.9 Hz, 1H), 7.81 - 7.74 (m, 2H), 7.62 - 7.55 (m, 2H), 7.54 - 7.48 (m, 2H), 7.44 - 7.38 (m, 1H), 7.12 (dd, J = 2.2 Hz, 1H), 6.96 (dd, J = 8.9, 2.2 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 160.0, 144.9, 141.7, 140.1, 134.1, 131.8, 129.6, 129.0, 128.8, 126.9, 123.1, 122.0, 117.5, 113.8, 92.0, 55.6. The spectra data matched with values reported in the literature.

**isopropyl 2-((3-(4-chlorophenyl)-1-phenyl-1H-indazol-6-yl)oxy)-2-methylpropanoate(4j):**

Following the general procedure for 2.5 h (2.4 F), 4j was purified by PE/EtOAc (20:1) and obtained as a colorless oil (60 mg, 67% yield); Rf = 0.50 (PE/EtOAc = 15:1); ¹H NMR (500 MHz, CDCl₃) δ 8.00 - 7.95 (m, 2H), 7.89 (d, J = 8.9 Hz, 1H), 7.75 - 7.71 (m, 2H), 7.59 - 7.53 (m, 2H), 7.52 - 7.47 (m, 2H), 7.41 - 7.36 (m, 1H), 7.18 (d, J = 2.1 Hz, 1H), 6.94 (dd, J = 8.9, 2.1 Hz, 1H), 5.09 (p, J = 6.2 Hz, 1H), 1.67 (s, 6H), 1.20 (d, J = 6.3 Hz, 6H); ¹³C NMR (126 MHz, DMSO-d₆) δ 172.9, 155.8, 144.2, 141.1, 139.6, 133.5, 131.8, 130.2, 129.5, 129.2, 127.6, 123.2, 117.9, 117.2, 98.4, 79.9, 69.3, 25.4, 21.6. Calculated for C₂₆H₂₆N₂O₃Cl [M+H]+: 449.1626; Found: 449.1629.

**1,3-diphenyl-1H-[1,3]dioxolo[4,5-f]indazole(4k):**

Following the general procedure for 2.4 h (2.3 F), 4k was purified by PE/EtOAc (20:1) and obtained as a white solid (45 mg, 73% yield); Mp = 156-157 °C; Rf = 0.50 (PE/EtOAc = 15:1); ¹H NMR (500 MHz, CDCl₃) δ 7.98 - 7.94 (m, 2H), 7.77 - 7.73 (m, 1H), 7.74 - 7.44 (m, 1H), 7.41 - 7.36 (m, 1H), 7.36 - 7.14 (m, 1H), 6.06 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 149.3, 145.9, 145.2, 140.1, 137.1, 133.3, 129.5, 128.8, 128.1, 127.5, 126.8, 123.0, 117.5, 101.8, 98.3, 90.4. Calculated for C₂₀H₁₅N₂O₂ [M+H]+: 315.1128; Found: 315.1135.

**1,3-diphenyl-5,6-dihydro-1H-furo[3,2-f]indazole(4l):**

Following the general procedure for 2.3 h (2.2 F), 4l was purified by PE/EtOAc (40:1) and obtained as a white solid (31 mg, 50% yield); Mp = 175-179 °C; Rf = 0.70 (PE/EtOAc = 20:1); ¹H NMR (500 MHz, CDCl₃) δ 7.98 - 7.94 (m, 2H), 7.77 - 7.73 (m, 1H), 7.46 - 7.41 (m, 1H), 7.41 - 7.36 (m, 1H), 7.36 - 7.14 (m, 1H), 6.06 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 149.3, 145.9, 145.2, 140.1, 137.1, 133.3, 129.5, 128.8, 128.1, 127.5, 126.8, 123.0, 117.5, 101.8, 98.3, 90.4. Calculated for C₂₀H₁₅N₂O₂ [M+H]+: 315.1128; Found: 315.1135.
MHz, CDCl$_3$ $\delta$ 8.02 - 7.98 (m, 2H), 7.80 - 7.75 (m, 2H), 7.57 - 7.50 (m, 4H), 7.46 - 7.41 (m, 1H), 7.39 - 7.34 (m, 1H), 7.09 (s, 1H), 4.71 (t, $J = 8.3$ Hz, 2H), 3.35 (td, $J = 8.4$, 1.3 Hz, 2H);

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 161.0, 145.9, 141.4, 140.3, 133.4, 129.4, 128.8, 128.1, 127.7, 126.5, 124.8, 122.9, 118.4, 116.7, 89.8, 72.5, 29.1. Calculated for C$_{21}$H$_{17}$N$_2$O $[M+H]^+$: 313.1335; Found: 313.1347.

1-phenyl-3-(p-tolyl)-1$H$-indazole(4m) and 6-methyl-1,3-diphenyl-1$H$-indazole(4m'):
Following the general procedure for 2.2 h (2.1 F), 4m and 4m' was purified by PE/EtOAc (100:1) and obtained as a white solid (44 mg, 78% yield, 4m/4m' = 20:80 by $^1$H NMR); $\text{R}_f = 0.50$ (PE/EtOAc = 50:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 - 8.06 (m, 1.78H), 8.00 - 7.96 (m, 1.15H), 7.85 - 7.80 (m, 2.15H), 7.61 - 7.54 (m, 4.48H), 7.49 - 7.44 (m, 1.02H), 7.43 - 7.36 (m, 1.34H), 7.33 - 7.29 (m, 0.2H), 2.55 (s, 2.36H), 2.47 (s, 0.55H); $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 144.8, 140.3, 139.6, 137.6, 132.7, 129.6, 129.0, 128.3, 127.2, 126.6, 124.5, 122.5, 120.9, 120.5, 110.2, 21.5. The spectra data matched with values reported in the literature.$^3$

isopropyl 2-(3-(1-phenyl-1$H$-indazol-3-yl)phenyl)propanoate(4n) and isopropyl 2-(1,3-diphenyl-1$H$-indazol-5-yl)propanoate(4n'):
Following the general procedure for 2.5 h (2.4 F), 4n and 4n' was purified by PE/EtOAc(30:1) and obtained a colorless oil (50 mg, 65% yield, 4n/4n' = 31:69 by $^1$H NMR); $\text{R}_f = 0.50$ (PE/EtOAc = 20:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (dt, $J = 8.3$, 1.8 Hz, 0.69H), 8.07 - 8.02 (m, 1.43H), 7.97 (dt, $J = 7.8$, 2.5 Hz, 0.7H), 7.84 - 7.80 (m, 2.57H), 7.61 - 7.55 (dd, $J = 8.8$, 1.0 Hz, 0.31H), 7.60 - 7.56 (m, 2.59H), 7.54 - 7.47 (m, 2.10H), 7.44 - 7.39 (m, 1.70H), 7.33 (m, 0.86H), 5.07 (dq, $J = 12.3$, 6.2 Hz, 1H), 3.86 (dq, $J = 14.3$, 7.2 Hz, 1H), 1.61 (d, $J = 7.2$ Hz, 3H), 1.28 (d, $J = 6.3$, 2.14H), 1.28 (d, $J = 6.3$, 0.96H), 1.19 (d, $J = 6.3$ Hz, 2.02H), 1.18 (dd, $J = 6.3$ Hz, 0.94H); $^{13}$C NMR (126 MHz, DMSO-$d_6$) $\delta$ 173.9, 173.7, 145.4, 145.3, 142.1, 140.2, 139.9, 139.4, 135.8, 133.2, 133.0, 130.1, 129.7, 129.5, 128.9, 128.1, 127.8, 127.3, 127.2, 126.7, 126.4, 123.0, 122.9, 122.8, 122.7, 121.7, 120.0, 111.6, 111.4, 68.1, 68.0, 45.2, 45.0, 22.0, 21.8, 21.8, 19.6, 19.2. Calculated for C$_{25}$H$_{25}$N$_2$O$_2$ $[M+H]^+$: 385.1910; Found: 385.1903.
1,3-diphenyl-8-tosyl-1,8-dihydropyrazolo[3,4-b]indole (4o):
Following the general procedure for 2.5 h (2.4 F), 4o was purified by PE/EtOAc (20:1) and obtained as a white solid (51 mg, 69% yield); Mp = 206-210 °C; R_f = 0.70 (PE/EtOAc = 15:1); ^1H NMR (500 MHz, CDCl_3) δ 8.21 - 8.17 (m, 1H), 8.00 - 7.94 (m, 2H), 7.85 - 7.80 (m, 2H), 7.75 - 7.71 (m, 1H), 7.58 (t, J = 7.8 Hz, 2H), 7.54 - 7.50 (m, 2H), 7.50 - 7.46 (m, 1H), 7.45 - 7.40 (m, 1H), 7.35 (pd, J = 7.4, 1.5 Hz, 2H), 7.27 (d, J = 6.7 Hz, 2H), 7.01 (d, J = 8.1 Hz, 2H), 2.26 (s, 3H); ^13C NMR (126 MHz, CDCl_3) δ 145.2, 144.9, 144.7, 143.1, 140.5, 132.7, 132.0, 129.3, 128.8, 128.6, 128.2, 127.2, 127.1, 125.7, 124.8, 124.5, 124.5, 119.9, 118.3, 114.8, 21.6. Calculated for C_{28}H_{22}N_{3}O_{2}S [M+H]^+: 464.1427; Found: 464.1432.

1,3-diphenyl-1H-thieno[3,2-c]pyrazole (4p):
Following the general procedure for 2.5 h (2.4 F), 4p was purified by PE/EtOAc (20:1) and obtained as a white solid (41 mg, 75% yield); Mp = 138-139 °C; R_f = 0.50 (PE/EtOAc = 15:1); ^1H NMR (500 MHz, CDCl_3) δ 8.07 - 8.02 (m, 2H), 7.90 - 7.85 (m, 2H), 7.58 - 7.50 (m, 5H), 7.44 - 7.39 (m, 1H), 7.35 - 7.30 (m, 2H); ^13C NMR (126 MHz, CDCl_3) δ 147.8, 144.9, 144.7, 143.1, 140.5, 132.7, 132.0, 129.3, 128.8, 128.6, 128.2, 127.3, 127.1, 125.7, 124.8, 124.5, 124.5, 119.9, 118.3, 114.8, 21.6. Calculated for C_{28}H_{22}N_{3}O_{2}S [M+H]^+: 464.1427; Found: 464.1432.

ethyl 1-(4-nitrophenyl)-1H-indazole-3-carboxylate (4q):
Following the general procedure for 3.0 h (2.8 F), 4q was purified by PE/EtOAc (20:1) and obtained as a yellow solid (50 mg, 80% yield); Mp = 179-182 °C; R_f = 0.30 (PE/EtOAc = 15:1); ^1H NMR (500 MHz, CDCl_3) δ 8.49 - 8.43 (m, 2H), 8.37 (dt, J = 8.1, 1.0 Hz, 1H), 8.07 - 8.02 (m, 2H), 7.84 (dt, J = 8.6, 0.9 Hz, 1H), 7.59 (dd, J = 8.4, 7.0, 1.2 Hz, 1H), 7.47 (dd, J = 7.9, 7.0, 0.8 Hz, 1H), 4.59 (q, J = 7.1 Hz, 2H), 1.53 (t, J = 7.1 Hz, 3H); ^13C NMR (126 MHz, CDCl_3) δ 162.2, 146.2, 144.4, 140.0, 139.0, 128.7, 125.3, 125.0, 124.5, 123.2, 123.1, 110.7, 61.6, 14.4. Calculated for NaC_{16}H_{13}N_{3}O_{4} [M+Na]^+: 334.0798; Found: 334.0807.
3-((tert-butyl)-1-(4-nitrophenyl)-1H-indazole(4r):
Following the general procedure for 2.5 h (2.4 F), 4r was purified by PE/EtOAc(30:1) and obtained as a yellow solid (32 mg, 54% yield); Mp = 130-133 °C; Rf = 0.70 (PE/EtOAc = 15:1); 1H NMR (500 MHz, CDCl3) δ 8.44 - 8.38 (m, 2H), 8.02 - 7.99 (m, 2H), 7.98 (d, J = 2.1 Hz, 1H), 7.86 (dt, J = 8.6, 0.9 Hz, 1H), 7.50 (ddd, J = 8.4, 7.0, 1.1 Hz, 1H), 7.31 - 7.28 (m, 1H), 1.61 (s, 9H); 13C NMR (126 MHz, CDCl3) δ 157.3, 145.8, 144.4, 140.1, 127.5, 125.2, 124.1, 123.0, 121.7, 120.9, 110.8, 34.1, 29.8. The spectra data matched with values reported in the literature.3

3-phenyl-1H-indazole (5):
Following the general procedure for synthesis of 5, purified by PE/EtOAc (6:1) and obtained as a yellow solid (27 mg, 70% yield); Mp = 110-111 °C; Rf = 0.30 (PE/EtOAc = 6:1); 1H NMR (500 MHz, CDCl3) δ 12.52 (s, 1H), 8.13 - 8.09 (m, 2H), 8.09 - 8.05 (m, 1H), 7.61 (dd, J = 8.3, 6.9 Hz, 2H), 7.55- 7.50 (m, 1H), 7.35 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.24 (ddd, J = 8.0, 6.9, 0.9 Hz, 1H), 7.11 (dt, J = 8.4, 0.9 Hz, 1H). The spectra data matched with values reported in the literature.1

1H-indazole-3-carboxylic acid (6):
Following the general procedure for synthesis of 6, purified by DCM/MeOH (100:1) and obtained as a beige solid (34 mg, 71% yield); Rf = 0.40 (DCM/MeOH = 15:1); 1H NMR (500 MHz, DMSO-d6) δ 13.82 (s, 1H), 13.02 (s, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.5 Hz, 1H); 13C NMR (126 MHz, DMSO-d6) δ 164.2, 141.5, 136.4, 126.9, 123.0, 122.8, 121.7, 111.5. The spectra data matched with values reported in the literature.5

7. References:
8. NMR Spectra.

1-(4-nitrophenyl)-3-phenyl-1H-indazole(2a)
4-(3-phenyl-1H-indazol-1-yl)benzenesulfonamide (2b)

$^1H$ NMR (500 MHz, DMSO-d$_6$)

$^{13}C$ NMR (125 MHz, DMSO-d$_6$)
4-(3-phenyl-1H-indazol-1-yl)benzonitrile(2c)
ethyl 4-(3-phenyl-1H-indazol-1-yl)benzoate(2d)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
3-phenyl-1-(4-(trifluoromethoxy)phenyl)-1H-indazole(2e)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
1-(4-methoxyphenyl)-3-phenyl-1H-indazole(2f)

$^1$H NMR (500 MHz, CDCl$_3$)

$^1$C NMR (125 MHz, CDCl$_3$)
1,3-diphenyl-1H-indazole (2g)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
3-phenyl-1-(p-tolyl)-1H-indazole(2h)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
1-(4-chlorophenyl)-3-phenyl-1H-indazole (2i)
1-(4-bromophenyl)-3-phenyl-1H-indazole(2j)
3-phenyl-1-(2,4,6-trichlorophenyl)-1H-indazole(2k)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
1-(4-bromophenyl)-3-phenyl-1H-indazole(2l)

$^1$H NMR (500 MHz, DMSO)

$^{13}$C NMR (125 MHz, DMSO-d$_6$)

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6-fluoro-3-(4-fluorophenyl)-1-phenyl-1H-indazole(4a)
6-chloro-3-(4-chlorophenyl)-1-phenyl-1H-indazole(4b)
6-methyl-1-phenyl-3-(p-tolyl)-1\textit{H}-indazole(4c)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
6-methoxy-3-(4-methoxyphenyl)-1-phenyl-1H-indazole(4d)
1-(4-fluorophenyl)-6-methyl-3-(p-tolyl)-1H-indazole(4e)

$^1$H NMR (500 MHz, DMSO-d$_6$)

$^{13}$C NMR (125 MHz, DMSO-d$_6$)
6-(4-nitrophenyl)-10,11-dihydro-6H-benzo[6,7]cyclohepta[1,2,3-cd]indazole(4f)
6-phenyl-6H-benzo[6,7]cyclohepta[1,2,3-cd]indazole(4g)

\[^1^H\text{NMR}\ (500 \text{ MHz, } \text{CDCl}_3)\]

\[^1^C\text{NMR}\ (125 \text{ MHz, } \text{CDCl}_3)\]
6-methoxy-1,3-diphenyl-1H-indazole(4h)
3-(4-chlorophenyl)-6-methoxy-1-phenyl-1H-indazole(4i)
isopropyl 2-((3-(4-chlorophenyl)-1-phenyl-1\textit{H}-indazol-6-yl)oxy)-2-methylpropanoate(4j)
1,3-diphenyl-1H-[1,3]dioxolo[4,5-f]indazole(4k)
1,3-diphenyl-5,6-dihydro-1H-furo[3,2-f]indazole(4l)

$^1$H NMR (500 MHz, CDCl$_3$)

$^13$C NMR (125 MHz, CDCl$_3$)
1-phenyl-3-(p-tolyl)-1H-indazole(4m) and 6-methyl-1,3-diphenyl-1H-indazole(4m')
isopropyl 2-(3-(1-phenyl-1H-indazol-3-yl)phenyl)propanoate (4n) and isopropyl 2-(1,3-diphenyl-1H-indazol-5-yl)propanoate (4n')
1,3-diphenyl-8-tosyl-1,8-dihydropyrazolo[3,4-b]indole(4o)
1,3-diphenyl-1H-thieno[3,2-c]pyrazole(4p)

$^1H$ NMR (500 MHz, CDCl$_3$)

$^{13}C$ NMR (125 MHz, CDCl$_3$)
ethyl 1-(4-nitrophenyl)-1H-indazole-3-carboxylate(4q)
3-(tert-butyl)-1-(4-nitrophenyl)-1H-indazole(4r)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
3-phenyl-1\(H\)-indazole (5)

\[ \text{\textsuperscript{\textit{\text{\textsuperscript{1}H}}}NMR (500 MHz, CDCl\textsubscript{3})} \]

\[ \text{\includegraphics[width=\textwidth]{image}} \]

1\(H\)-indazole-3-carboxylic acid (6)