Supporting Information

Photocatalytic Transition-Metal-Free Direct 3-Alkylation of 2-Aryl-2H-Indazoles in Dimethyl Carbonate†

Chunhua Ma, a Zhi-Wen Feng, a Jing Li, a Dandan Zhang, a Wei Li, a Yu-Qin Jiang, a* and Bing Yu b*

a Collaborative Innovation Centre of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Engineering Research Centre of Chiral Hydroxyl Pharmaceutical, Henan Engineering Laboratory of Chemical Pharmaceutical and Biomedical Materials, School of Chemistry and Chemical Engineering, Henan Normal University, Jianshedong Road No. 46, Xinxiang 453007, P. R. China. E-mail: jiangyuqin@htu.cn

b Green Catalysis Center, College of Chemistry, Zhengzhou University, Kexue Road No. 100, Zhengzhou 450001, P. R. China. E-mail: bingyu@zzu.edu.cn

† Dedicated to the 100th anniversary of Chemistry at Nankai University

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1. General information

N, N-Dimethylethanolamine (DABCO) was purchased from Tansoole, Shanghai, China. Other reagents were purchased from Bidepharm.com. Unless otherwise stated, all commercially available reagents were directly used without further purification. All solvents were purified by standard methods prior to use. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was carried out on 100-200 mesh of silica gel purchased from Tansoole, Shanghai, China. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 MHz in CDCl$_3$ at room temperature (20 ± 3 °C), using tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Bruker compact Qq TOF MS/MS system with the ESI technique.

Photochemical reaction was carried out under visible light irradiation by a blue LED at 35 °C. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system (See Figure A). Eight 10W blue LEDs were equipped in this Photo reactor. The blue LED's energy peak wavelength is 455 nm, peak width at half-height is 22.9 nm, lirradiance@10 W is 172.29 mW/cm$^2$. The reaction vessel is borosilicate glass test tube and no filters were applied.

![Figure A. The reaction apparatus and spectrum of blue LED](image)

The UV-Vis spectra of 2-phenyl-2$H$-indazole 1a and alkyl NHPI ester 2a were
showed in Figure B. It is obvious that the reactants 1a and 2a do not absorb light around 455 nm, suggesting that photocatalyst play a crucial role in this reaction.

![UV-Vis spectra](image)

**Figure B.** The UV-Vis spectra of the substrates 1a and 2a

## 2. Experimental procedures

### 2.1 General experimental procedures for 3-alkylated 2H-indazoles

In a 10 mL reaction vial with a stirring bar, 2-phenyl-2H-indazole 1 (0.2 mmol), alkyl NHPI esters 2 (2.0 equiv.), and 4CzIPN (5 mol%) were added. The vial was then evacuated and backfilled three times with N₂, followed by adding dimethyl carbonate (2 mL) and DABCO (1.0 equiv.). The mixture was stirred at 35 °C with 10 W blue LED irradiation for 12 h under nitrogen atmosphere. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na₂SO₄. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1) to afford the desired product 3.
Control experiments with TEMPO: In a 10 mL reaction vial with a stirring bar, 2-phenyl-2$H$-indazole 1 (0.2 mmol), alkyl NHPI esters 2 (2.0 equiv.), 4CzIPN (5 mol%) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv.) were added. The vial was then evacuated and backfilled three times with N$_2$, followed by adding dimethyl carbonate (2 mL) and DABCO (1.0 equiv.). The mixture was stirred at 35 °C with 10 W blue LED irradiation for 12 h under nitrogen atmosphere. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. No target product 3a was generated, while the formation of TEMPO trapped cyclohexyl adduct 5a was found by HRMS. It indicated that a radical pathway should be involved in this photocatalytic reaction and an alkyl radical was formed.

Control experiments with BHT: In a 10 mL reaction vial with a stirring bar, 2-phenyl-2$H$-indazole 1 (0.2 mmol), alkyl NHPI esters 2 (2.0 equiv.), 4CzIPN (5 mol%) and 2,6-di-tert-butyl-4-methyl phenol (BHT, 3.0 equiv) were added. The vial was then evacuated and backfilled three times with N$_2$, followed by adding dimethyl carbonate (2 mL) and DABCO (1.0 equiv.). The mixture was stirred at 35 °C with 10 W blue LED irradiation for 12 h under nitrogen atmosphere. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5
mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na$_2$SO$_4$. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20/1) to afford the desired product 3a in 28% yield.

2.3 Procedure for emission quenching experiment

Stern-Volmer fluorescence quenching experiments were conducted via adding the appropriate amount of DABCO to a freshly prepared solution of 4CzIPN ($1 \times 10^{-4}$ M) in dry MeCN in a screw-top quartz cuvette at room temperature. After degassing with a stream of N$_2$ for 10 minutes, the sample was irradiated at 380 nm and the fluorescence was measured from 400 nm to 800 nm.

![Emission spectra](image1)

![Linear relationship](image2)

Figure S1. (A) The emission spectra of $1 \times 10^{-4}$ M solution of 4CzIPN with various concentrations of 1a. (B) The linear relationship between $I_0/I$ ($I_0$ and I are the...
fluorescence intensities before and after adding the various concentration of DABCO, respectively) and the concentration of DABCO.

2.4 Procedure for cyclic voltammetry experiment

Cyclic voltammetry analysis of 2H-indazole 1a, NHPI ester 2a and DABCO were conducted by a potentiostat (CH instrument, 660E) with a three-electrode system (Reference electrode: SCE, working electrode: Glassy carbon, counter electrode: Pt wire). 0.1 M Bu$_4$NPF$_6$ in CH$_3$CN was used as a supporting electrolyte. The Pt disk was polished by using an alumina suspension ($d = 50$ nm) before each CV experiment.

![Figure S2. CV of DABCO (5 mM in CH$_3$CN), 1a (5 mM in CH$_3$CN) and blank (only 0.1 M Bu$_4$NPF$_6$) under nitrogen atmosphere at room temperature. The scan rate was 0.10 V/s.](image)

![Figure S3. CV of 2a (5 mM in CH$_3$CN) and blank (only 0.1 M Bu$_4$NPF$_6$) under nitrogen atmosphere at room temperature. The scan rate was 0.10 V/s.](image)
atmosphere at room temperature. The scan rate was 0.10 V/s.

3. Procedure and Results of Sensitivity Assessment

General Procedure:

The influence of parameter variations as shown in Table S1 on the reaction was investigated. Only one parameter, such as concentration, water level, oxygen level, light intensity, base dosage and catalyst dosage, was deliberately changed per experiment while maintaining the others at the standard level. Each experiment was carried out twice at the same time in order to reduce the error.

Table S1. Preparation of sensitivity assessment.

<table>
<thead>
<tr>
<th>#</th>
<th>Experiment</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High c</td>
<td>1.6 mL DMC</td>
</tr>
<tr>
<td>2</td>
<td>Low c</td>
<td>2.4 mL DMC</td>
</tr>
<tr>
<td>3</td>
<td>High H₂O</td>
<td>2.0 mL DMC + 20 μL H₂O</td>
</tr>
<tr>
<td>4</td>
<td>High O₂</td>
<td>Under air</td>
</tr>
<tr>
<td>5</td>
<td>Low I</td>
<td>9W Blue LED</td>
</tr>
<tr>
<td>6</td>
<td>High base</td>
<td>2 eq DABCO</td>
</tr>
<tr>
<td>7</td>
<td>Low base</td>
<td>0.5 eq DABCO</td>
</tr>
<tr>
<td>8</td>
<td>High catalyst</td>
<td>10% 4CzIPN</td>
</tr>
<tr>
<td>9</td>
<td>Low catalyst</td>
<td>1% 4CzIPN</td>
</tr>
<tr>
<td>10</td>
<td>Control</td>
<td>Standard procedure</td>
</tr>
</tbody>
</table>

Results:

Deviation% = \frac{\text{Average Y.} - \text{Standard Y.}}{\text{Standard Y.}}

Table S2. Results of sensitivity assessment.

<table>
<thead>
<tr>
<th>#</th>
<th>Experiment</th>
<th>Yield 1 / %</th>
<th>Yield 2 / %</th>
<th>Average Y. / %</th>
<th>Deviation / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High c</td>
<td>50</td>
<td>59</td>
<td>55</td>
<td>-37.5%</td>
</tr>
<tr>
<td>2</td>
<td>Low c</td>
<td>87</td>
<td>85</td>
<td>86</td>
<td>-2.3%</td>
</tr>
<tr>
<td>3</td>
<td>High H₂O</td>
<td>26</td>
<td>28</td>
<td>27</td>
<td>69.3%</td>
</tr>
<tr>
<td>4</td>
<td>High O₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-100%</td>
</tr>
<tr>
<td>5</td>
<td>Low I</td>
<td>82</td>
<td>88</td>
<td>85</td>
<td>-3.4%</td>
</tr>
<tr>
<td>6</td>
<td>High base</td>
<td>83</td>
<td>86</td>
<td>85</td>
<td>-3.4%</td>
</tr>
<tr>
<td>7</td>
<td>Low base</td>
<td>63</td>
<td>71</td>
<td>67</td>
<td>-23.9%</td>
</tr>
<tr>
<td>8</td>
<td>High catalyst</td>
<td>83</td>
<td>82</td>
<td>83</td>
<td>-5.7%</td>
</tr>
<tr>
<td>9</td>
<td>Low catalyst</td>
<td>89</td>
<td>92</td>
<td>91</td>
<td>3.4%</td>
</tr>
<tr>
<td>10</td>
<td>Control</td>
<td>87</td>
<td>89</td>
<td>88</td>
<td>-</td>
</tr>
</tbody>
</table>
4. Characterization of compounds

3-cyclohexyl-2-phenyl-2H-indazole (3a)\(^1\)

\[
\text{\begin{tikzpicture}
\node[draw] at (0,0) {\text{\includegraphics[width=0.9cm]{figure}}};
\end{tikzpicture}}
\]

48.6 mg, 88%; White solid, m.p. 110-111 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 8.4\) Hz, 1H), 7.71 (d, \(J = 9.0\) Hz, 1H), 7.56-7.47 (m, 5H), 7.31-7.28 (m, 1H), 7.06-7.03 (m, 1H), 3.00-2.95 (m, 1H), 2.03-1.75 (m, 7H), 1.37-1.25 (m, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 149.0, 141.3, 140.3, 129.3, 129.1, 126.6, 126.4, 121.4, 120.6, 119.6, 118.0, 37.4, 32.7, 26.7, 26.0. HRMS Calcd for C\(_{19}\)H\(_{21}\)N\(_2\) [M + H]\(^+\): m/z 277.1699, Found: 277.1710.

3-cyclohexyl-2-(p-tolyl)-2H-indazole (3b)

\[
\text{\begin{tikzpicture}
\node[draw] at (0,0) {\text{\includegraphics[width=0.9cm]{figure}}};
\end{tikzpicture}}
\]

38.9 mg, 67%; White solid, m.p. 121-122 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 8.4\) Hz, 1H), 7.70 (d, \(J = 8.8\) Hz, 1H), 7.37-7.26 (m, 5H), 7.06-7.01 (m, 1H), 3.01-2.92 (m, 1H), 2.47 (s, 3H), 2.03-1.74 (m, 7H), 1.38-1.20 (m, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 148.9, 141.2, 139.1, 137.8, 129.8, 126.3, 121.3, 120.5, 119.6, 117.9, 37.4, 32.7, 26.7, 26.0, 21.4. HRMS Calcd for C\(_{20}\)H\(_{23}\)N\(_2\) [M + H]\(^+\): m/z 291.1856, Found: 291.1851.

3-cyclohexyl-2-(4-methoxyphenyl)-2H-indazole (3c)

\[
\text{\begin{tikzpicture}
\node[draw] at (0,0) {\text{\includegraphics[width=0.9cm]{figure}}};
\end{tikzpicture}}
\]
52.0 mg, 85%; White solid, m.p. 115-116 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, $J$ = 5.6 Hz, 1H), 7.70 (d, $J$ = 6.0 Hz, 1H), 7.39 (d, $J$ = 5.6 Hz, 2H), 7.29 (t, $J$ = 4.4 Hz, 1H), 7.05-7.02 (m, 3H), 3.90 (s, 3H), 2.97-2.91 (m, 1H), 2.01-1.75 (m, 7H), 1.39-1.23 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 160.0, 148.8, 141.4, 133.3, 127.7, 126.3, 121.3, 120.5, 119.5, 117.9, 114.4, 55.7, 37.4, 32.7, 26.7, 26.0. HRMS Calcd for C$_{20}$H$_{23}$N$_2$O $[M + H]^+$: m/z 307.1805, Found: 307.1811.

3-cyclohexyl-2-(m-tolyl)-2H-indazole (3d)

30.8 mg, 53%; White solid, m.p. 125-126 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, $J$ = 8.8 Hz, 1H), 7.71 (d, $J$ = 8.8 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 1H), 7.33-7.26 (m, 3H), 7.25-7.22 (m, 1H), 7.06-7.02 (m, 1H), 3.03-2.94 (m, 1H), 2.46 (s, 3H), 2.04-1.75 (m, 7H), 1.38-1.21 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 148.9, 141.2, 140.2, 139.5, 129.9, 128.9, 127.3, 126.4, 123.4, 121.4, 120.6, 119.6, 118.0, 37.4, 32.7, 26.7, 26.0, 21.5. HRMS Calcd for C$_{20}$H$_{23}$N$_2$ [M + H]$^+$: m/z 291.1856, Found: 291.1886.

3-cyclohexyl-2-(4-fluorophenyl)-2H-indazole (3e)

48.2 mg, 82%; White solid, m.p. 71-72 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.85 (d, $J$ = 8.4 Hz, 1H), 7.69 (d, $J$ = 9.0 Hz, 1H), 7.47-7.44 (m, 2H), 7.30 (t, $J$ = 7.2 Hz, 1H), 7.23 (t, $J$ = 3.6 Hz, 2H), 7.05 (t, $J$ = 7.2 Hz, 1H), 2.94-2.88 (m, 1H), 2.01-1.76 (m, 7H), 1.37-1.25 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 162.8 (d, $J$ = 247.5 Hz), 149.0, 141.5, 136.4 (d, $J$ = 3.0 Hz), 128.4 (d, $J$ = 9.0 Hz), 126.6, 121.3, 120.8, 119.6, 117.9, 116.3 (d, $J$ = 22.5 Hz), 37.5, 32.7, 26.7, 26.0. $^{19}$F NMR (564 MHz, CDCl$_3$) δ -111.8. HRMS Calcd for C$_{19}$H$_{20}$F$_2$ [M + H]$^+$: m/z 295.1605, Found: 295.1612.
2-(4-chlorophenyl)-3-cyclohexyl-2H-indazole (3f)

55.2 mg, 89%; White solid, m.p. 146-147 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.4\) Hz, 1H), 7.70 (d, \(J = 8.8\) Hz, 1H), 7.54-7.50 (m, 2H), 7.44-7.40 (m, 2H), 7.32-7.27 (m, 1H), 7.07-7.02 (m, 1H), 2.97-2.89 (m, 1H), 2.05-1.76 (m, 7H), 1.38-1.21 (m, 3H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 147.3, 141.2, 140.0, 129.39, 129.37, 127.8, 126.5, 126.2, 120.03, 119.98, 119.5, 37.3, 32.7, 26.6, 25.9. HRMS Calcd for C\(_{19}\)H\(_{20}\)ClN\(_2\) [M + H]\(^+\): m/z 311.1310, Found: 311.1342.

2-(4-bromophenyl)-3-cyclohexyl-2H-indazole (3g)

48.3 mg, 68%; White solid, m.p. 92-93 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.8\) Hz, 1H), 7.70-7.65 (m, 3H), 7.38-7.34 (m, 2H), 7.32-7.27 (m, 1H), 7.07-7.02 (m, 1H), 2.98-2.89 (m, 1H), 2.04-1.76 (m, 7H), 1.38-1.20 (m, 3H) \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 149.2, 141.3, 139.3, 132.5, 128.1, 126.7, 123.1, 121.4, 120.9, 119.7, 117.9, 37.5, 32.7, 26.7, 26.0. HRMS Calcd for C\(_{19}\)H\(_{20}\)BrN\(_2\) [M + H]\(^+\): m/z 355.0804, Found: 355.0808.

2-(3-chlorophenyl)-3-cyclohexyl-2H-indazole (3h)

56.4 mg, 91%; White solid, m.p. 69-70 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.4\) Hz, 1H), 7.69 (d, \(J = 8.8\) Hz, 1H), 7.54-7.45 (m, 3H), 7.38-7.35 (m, 1H), 7.32-7.28 (m, 1H), 7.07-7.03 (m, 1H), 3.00-2.92 (m, 1H), 2.05-1.76 (m, 7H), 1.43-1.23 (m, 3H).
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 149.2, 141.4, 141.3, 135.1, 130.2, 129.4, 127.0, 126.8, 124.7, 121.4, 121.0, 119.7, 118.0, 37.5, 32.7, 26.9, 26.0. HRMS Calcd for C$_{19}$H$_{20}$ClN$_2$ [M + H]$^+$: m/z 311.1310, Found: 311.1317.

**2-(3-bromophenyl)-3-cyclohexyl-2H-indazole (3i)**

![Image of 2-(3-bromophenyl)-3-cyclohexyl-2H-indazole](image)

51.0 mg, 72%; White solid, m.p. 131-132 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J$ = 8.4 Hz, 1H), 7.70-7.62 (m, 3H), 7.44-7.39 (m, 2H), 7.32-7.28 (m, 1H), 7.07-7.03 (m, 1H), 3.00-2.91 (m, 1H), 2.04-1.76 (m, 7H), 1.42-1.24 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 149.2, 141.4, 141.3, 135.1, 130.2, 129.4, 127.0, 126.8, 124.7, 121.4, 121.0, 119.7, 118.0, 37.5, 32.7, 26.7, 26.0. HRMS Calcd for C$_{19}$H$_{20}$BrN$_2$ [M + H]$^+$: m/z 355.0804, Found: 355.0819.

**3-cyclohexyl-2-(4-(trifluoromethyl)phenyl)-2H-indazole (3j)**

![Image of 3-cyclohexyl-2-(4-(trifluoromethyl)phenyl)-2H-indazole](image)

60.5 mg, 88%; White solid, m.p. 98-99 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88-7.81 (m, 3H), 7.70 (d, $J$ = 8.8 Hz, 1H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.33-7.29 (m, 1H), 7.08-7.04 (m, 1H), 3.01-2.92 (m, 1H), 2.07-1.77 (m, 7H), 1.43-1.23 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 149.4, 143.2, 141.4, 131.1 (q, $J$ = 33.0 Hz), 127.0, 126.9, 126.6 (q, $J$ = 3.0 Hz), 123.9 (q, $J$ = 270 Hz), 121.4, 121.1, 119.9, 118.0, 37.5, 32.8, 26.7, 25.9. $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -62.5. HRMS Calcd for C$_{20}$H$_{20}$F$_3$N$_2$ [M + H]$^+$: m/z 345.1573, Found: 345.1564.

**3-cyclohexyl-6-methoxy-2-phenyl-2H-indazole (3m)**
3-cyclohexyl-6-fluoro-2-phenyl-2H-indazole (3n)

35.3 mg, 60%; Oily liquid; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.67 (q, $J = 4.8$ Hz, 1H), 7.56-7.52 (m, 3H), 7.46 (d, $J = 7.2$ Hz, 2H), 7.42 (dd, $J = 1.8$, 9.6 Hz, 1H), 7.12-7.08 (m, 1H), 2.96-2.91 (m, 1H), 1.92-1.74 (m, 7H), 1.35-1.24 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 157.4 (d, $J = 237.0$ Hz), 146.4, 141.4 (d, $J = 9.0$ Hz), 140.2, 129.4, 129.3, 126.5, 119.9 (d, $J = 10.5$ Hz), 118.6 (d, $J = 10.5$ Hz), 118.0 (d, $J = 28.5$ Hz), 103.8 (d, $J = 24.0$ Hz), 37.2, 32.5, 26.7, 25.9. $^{19}$F NMR (564 MHz, CDCl$_3$) δ -121.0. HRMS Calcd for C$_{19}$H$_{20}$FN$_2$ [M + H]$^+$: m/z 295.1605, Found: 295.1615.

6-chloro-3-cyclohexyl-2-phenyl-2H-indazole (3o)

32.2 mg, 52%; White solid, m.p. 134-135°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83-7.82 (m, 1H), 7.65-7.62 (m, 1H), 7.58-7.52 (m, 3H), 7.47-7.44 (m, 2H), 7.22 (dd, $J = 2.0$,
9.2 Hz, 1H), 2.98-2.89 (m, 1H), 1.94-1.83 (m, 7H), 1.41-1.25 (m, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 149.1, 141.4, 138.8, 135.1, 129.5, 127.8, 126.7, 121.3, 120.9, 119.7, 117.9, 37.5, 32.7, 26.7, 25.9. HRMS Calcd for C$_{19}$H$_{20}$ClN$_2$ [M + H]$^+$: m/z 311.1310, Found: 311.1324.

3-cyclobutyl-2-phenyl-2H-indazole (3p)

![Image of 3-cyclobutyl-2-phenyl-2H-indazole (3p)]

28.3 mg, 57%; White solid, m.p. 62-63 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.72 (d, $J = 9.0$ Hz, 1H), 7.54-7.47 (m, 5H), 7.32-7.29 (m, 1H), 7.09-7.06 (m, 1H), 3.98-3.91 (m, 1H), 2.63-2.55 (m, 2H), 2.36-2.30 (m, 2H), 2.08-1.95 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 149.0, 140.4, 139.4, 129.2, 128.9, 126.5, 126.3, 121.0, 120.6, 118.0, 33.1, 29.3, 19.1. HRMS Calcd for C$_{17}$H$_{17}$N$_2$ [M + H]$^+$: m/z 249.1386, Found: 249.1234.

3-cyclopropyl-2-phenyl-2H-indazole (3q)

![Image of 3-cyclopropyl-2-phenyl-2H-indazole (3q)]

35.1 mg, 75%; White solid, m.p. 72-73 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.72-7.68 (m, 4H), 7.55-7.52 (m, 2H), 7.48-7.45 (m, 1H), 7.30-7.27 (m, 1H), 7.06-7.03 (m, 1H), 2.18-2.13 (m, 1H), 1.04-1.01 (m, 2H), 0.94-0.91 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 148.7, 140.6, 136.8, 129.1, 128.6, 126.6, 125.9, 121.2, 121.0, 120.4, 118.0, 7.71, 7.22. HRMS Calcd for C$_{16}$H$_{15}$N$_2$ [M + H]$^+$: m/z 235.1230, Found: 235.1242.

2-phenyl-3-(tetrahydro-2H-pyran-4-yl)-2H-indazole (3r)$^2$
36.1 mg, 65%; White solid, m.p. 134-135 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.89 (d, $J$ = 8.4 Hz, 1H), 7.73 (d, $J$ = 8.4 Hz, 1H), 7.58-7.52 (m, 3H), 7.48-7.46 (m, 2H), 7.32 (t, $J$ = 6.6 Hz, 1H), 7.10-7.07 (m, 1H), 4.08 (dd, $J$ = 4.2, 12.0 Hz, 2H), 3.43-3.38 (m, 2H), 3.26-3.21 (m, 1H), 2.42-2.34 (m, 2H), 1.78 (dd, $J$ = 1.8, 13.2 Hz, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 149.0, 140.1, 139.0, 129.44, 129.38, 126.6, 126.5, 121.2, 120.9, 119.7, 118.1, 68.2, 34.7, 32.2. HRMS Calcd for C$_{18}$H$_{19}$N$_2$O $[M + H]^+$: m/z 279.1492, Found: 279.1496.

tert-butyl 4-(2-phenyl-2H-indazol-3-yl)piperidine-1-carboxylate (3s)

49.0 mg, 65%; White solid, m.p. 150-151 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, $J$ = 8.4 Hz, 1H), 7.72 (d, $J$ = 8.4 Hz, 1H), 7.56-7.55 (m, 3H), 7.48-7.46 (m, 2H), 7.31 (t, $J$ = 7.2 Hz, 1H), 7.06 (t, $J$ = 8.0 Hz, 1H), 4.32-4.13 (m, 2H), 3.11 (t, $J$ = 12.4 Hz, 1H), 2.67 (t, $J$ = 10.8 Hz, 2H), 2.21-2.13 (m, 2H), 1.86 (d, $J$ = 12.4 Hz, 2H), 1.50 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 154.9, 149.0, 140.1, 139.0, 129.5, 129.4, 126.6, 126.5, 121.2, 120.8, 119.7, 118.1, 79.9, 35.7, 31.5, 28.6. HRMS Calcd for C$_{23}$H$_{28}$N$_3$O$_2$ $[M + H]^+$: m/z 378.2176, Found:378.2174.

3-(tert-butyl)-2-phenyl-2H-indazole (3t)$^2$

28.0 mg, 56%; White solid, m.p. 143-144 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.95 (d, $J$
= 9.0 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.51-7.46 (m, 3H), 7.44-7.42 (m, 2H), 7.30-7.27 (m, 1H), 7.06-7.03 (m, 1H), 1.43 (s, 9H). 13C NMR (150 MHz, CDCl3)  δ 148.6, 144.6, 143.1, 129.5, 128.6, 128.2, 126.1, 122.8, 120.9, 119.8, 118.0, 34.9, 32.0. HRMS Calcd for C17H19N2 [M + H]+: m/z 251.1543, Found: 251.1553.

3-((1-methylcyclohexyl)-2-phenyl-2H-indazole (3u)

34.2 mg, 59%; White solid, m.p. 115-116 °C; 1H NMR (600 MHz, CDCl3)  δ 7.90 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.52-7.44 (m, 5H), 7.29-7.26 (m, 1H), 7.06-7.03 (m, 1H), 2.23-2.22 (m, 2H), 1.50-1.33 (m, 11H). 13C NMR (150 MHz, CDCl3)  δ 148.9, 143.5, 143.2, 129.5, 128.7, 127.6, 126.0, 122.9, 121.1, 120.0, 118.1, 39.4, 38.6, 29.8, 26.0, 23.0. HRMS Calcd for C20H23N2 [M + H]+: m/z 291.1856, Found: 291.1868.

3-((3r,5r,7r)-adamantan-1-yl)-2-phenyl-2H-indazole (3v)

48.5 mg, 74%; White solid, m.p. 188-189°C; 1H NMR (600 MHz, CDCl3)  δ 8.03 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.51-7.45 (m, 3H), 7.43-7.41 (m, 2H), 7.28-7.27 (m, 1H), 7.04-7.02 (m, 1H), 2.14-2.13 (m, 6H), 1.99 (s, 3H), 1.69 (q, J = 12 Hz, 6H). 13C NMR (150 MHz, CDCl3)  δ 148.7, 144.8, 143.5, 129.5, 128.5, 128.3, 126.0, 123.1, 120.6, 119.6, 118.0, 42.7, 37.9, 36.6, 28.7. HRMS Calcd for C23H25N2 [M + H]+: m/z 329.2012, Found: 329.2008.

2-phenyl-3-(1-phenylcyclopropyl)-2H-indazole (3w)
46.0 mg, 74%; White solid, m.p. 110-111 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84-7.81 (m, 2H), 7.49-7.47 (m, 2H), 7.42-7.37 (m, 4H), 7.30-7.28 (m, 2H), 7.23-7.19 (m, 1H), 7.18-7.14 (m, 1H), 7.02-6.99 (m, 2H), 1.46-1.43 (m, 2H), 1.31-1.28 (m, 2H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 148.7, 144.3, 140.6, 137.5, 128.9, 128.8, 128.5, 126.9, 126.0, 125.7, 125.2, 123.1, 122.0, 120.6, 118.2, 20.1, 19.1. HRMS Calcd for C\(_{22}\)H\(_{19}\)N\(_2\) [M + H]\(^+\): m/z 311.1543, Found: 311.1571.

3-pentyl-2-phenyl-2H-indazole (3x)\(^3\)

44.9 mg, 85%; White solid, m.p. 152-153 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73-7.66 (m, 2H), 7.56-7.47 (m, 5H), 7.34-7.29 (m, 1H), 7.10-7.05 (m, 1H), 3.03 (t, \(J = 7.6\) Hz, 2H), 1.67-1.61 (m, 2H), 1.27-1.23 (m, 4H), 0.84-0.80 (m, 3H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 148.8, 140.3, 137.1, 129.3, 129.0, 126.8, 126.3, 121.2, 121.0, 120.4, 117.7, 31.6, 29.2, 25.4, 22.3, 14.0. HRMS Calcd for C\(_{18}\)H\(_{21}\)N\(_2\) [M + H]\(^+\): m/z 265.1699, Found: 265.1714.

2-phenyl-3-(3-phenylpropyl)-2H-indazole (3y)

35.6 mg, 57%; White solid, m.p. 166-167 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 9.0\) Hz, 1H), 7.62 (d, \(J = 8.4\) Hz, 1H), 7.52-7.47 (m, 5H), 7.34-7.31 (m, 1H), 7.25 (t, \(J = 5.4\) Hz, 2H), 7.18 (t, \(J = 7.2\) Hz, 1H), 7.09-7.06 (m, 3H), 3.07 (t, \(J = 7.8\) Hz, 2H),
2.60 (t, J = 7.8 Hz, 2H), 2.02-1.96 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 148.8, 141.2, 140.1, 136.4, 129.3, 129.0, 128.5, 128.4, 126.8, 126.2, 126.1, 121.3, 121.2, 120.2, 117.8, 35.5, 30.8, 24.9. HRMS Calcd for C$_{22}$H$_{21}$N$_2$ [M + H]$^+$: m/z 313.1699, Found: 313.1702.

3-(9-bromononyl)-2-phenyl-2H-indazole (3z)

![3z](image)

48.5 mg, 61%; Oily liquid; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.72 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.56-7.49 (m, 5H), 7.33-7.31 (m, 1H), 7.09-7.07 (m, 1H), 3.39 (t, J = 6.6 Hz, 2H), 3.04 (t, J = 7.8 Hz, 2H), 1.84-1.79 (m, 2H), 1.66-1.61 (m, 2H), 1.39-1.35 (m, 2H), 1.26-1.21 (m, 8H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 148.8, 140.3, 137.0, 129.3, 129.0, 126.8, 126.3, 121.2, 121.0, 120.3, 117.8, 34.1, 32.9, 29.5, 29.32, 29.27, 29.1, 28.8, 28.2, 25.4. HRMS Calcd for C$_{22}$H$_{28}$BrN$_2$ [M + H]$^+$: m/z 399.1430, Found: 399.1434.

(E)-3-(heptadec-8-en-1-yl)-2-phenyl-2H-indazole (4a)

![4a](image)

50.7 mg, 59%; oily liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, J = 8.8 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.56-7.48 (m, 5H), 7.32 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 5.39-5.28 (m, 2H), 3.03 (t, J = 8.0 Hz, 2H), 2.03-1.96 (m, 4H), 1.69-1.61 (m, 2H), 1.27-1.23 (m, 20H), 0.88 (t, J = 6.4 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 148.7, 140.2, 137.0, 130.1, 129.8, 129.3, 129.0, 126.7, 126.3, 121.2, 121.0, 120.3, 117.7, 32.0, 29.9, 29.8, 29.6, 29.5, 29.43, 29.36, 29.13, 29.11, 27.3, 27.2, 25.4, 22.8, 14.2. HRMS Calcd for C$_{36}$H$_{43}$N$_2$ [M + H]$^+$: m/z 431.3421, Found:431.3419.
4-(2-phenyl-2H-indazol-3-yl)butan-2-one (4b)

23.7 mg, 45%; White solid, m.p. 109-110 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J$ = 8.8 Hz, 1H), 7.66 (d, $J$ = 8.4 Hz, 1H), 7.57-7.49 (m, 5H), 7.34-7.30 (m, 1H), 7.11-7.07 (m, 1H), 3.36-3.32 (m, 2H), 2.74 (t, $J$ = 8.0 Hz, 2H), 2.07 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 206.5, 148.8, 140.0, 135.0, 129.5, 129.3, 126.9, 126.2, 121.5, 121.0, 120.0, 117.9, 42.6, 30.0, 19.4. HRMS Calcd for C$_{17}$H$_{17}$N$_2$O $[M + H]^+$: m/z 265.1335, Found: 265.1329.

(5S,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-5-(2-phenyl-2H-indazol-3-yl)pentan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (4c)

47.4 mg, 43%; White solid, m.p. 240-241 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 9.0 Hz, 1H), 7.64 (d, $J$ = 8.4 Hz, 1H), 7.56-7.49 (m, 5H), 7.30 (t, $J$ = 6.6 Hz, 1H), 7.09-7.06 (m, 1H), 3.15-3.10 (m, 1H), 2.99-2.94 (m, 1H), 2.92-2.87 (m, 1H), 2.86-2.79 (m, 2H), 2.34-2.19 (m, 6H), 2.13-2.08 (m, 2H), 2.03-1.93 (m, 3H), 1.83-1.77 (m, 3H), 1.62-1.57 (m, 1H), 1.50-1.44 (m, 1H), 1.38 (s, 3H), 1.24-1.16 (m, 2H), 1.12-1.06 (m, 1H), 0.99 (s, 3H), 0.83 (d, $J$ = 6.60 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 212.0, 209.1, 208.8, 148.8, 140.1, 137.1, 129.3, 129.1, 126.8, 126.3, 121.09, 121.05, 120.2, 117.8, 56.9, 51.8, 49.1, 46.9, 45.7, 45.3, 45.1, 42.9, 38.7, 36.6, 36.1, 35.9, 35.4, 35.3, 27.7, 25.2, 22.4, 22.0, 18.8, 11.9. HRMS Calcd for C$_{36}$H$_{41}$N$_3$O$_3$ $[M + H]^+$: m/z
551.3268, Found: 551.3263.

3-(5-(2,5-dimethylphenoxy)-2-methylpentan-2-yl)-2-phenyl-2H-indazole (4d)

32.6 mg, 41%; White solid, m.p. 240-241 °C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.94 (d, $J$ = 8.8 Hz, 1H), 7.69 (d, $J$ = 8.8 Hz, 1H), 7.52-7.43 (m, 5H), 7.32-7.27 (m, 1H), 7.08-7.04 (m, 1H), 6.99 (d, $J$ = 7.6 Hz, 1H), 6.65 (d, $J$ = 7.6 Hz, 1H), 6.53 (s, 1H), 3.82 (t, $J$ = 6.0 Hz, 2H), 2.28 (s, 3H), 2.14 (s, 3H), 1.98-1.94 (m, 2H), 1.67-1.60 (m, 2H), 1.43 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 157.0, 148.7, 143.1, 142.9, 136.6, 130.5, 129.6, 128.7, 128.0, 126.2, 123.6, 122.5, 121.2, 120.9, 120.5, 118.1, 112.0, 40.8, 38.2, 30.3, 25.5, 21.5, 16.0. HRMS Calcd for C$_{27}$H$_{31}$N$_2$O $[M + H]^+$: m/z 399.2431, Found: 399.2464.

(S)-2-((tert-butoxycarbonyl)amino)-4-(2-phenyl-2H-indazol-3-yl)butanoate (4e)

36.8 mg, 45%; White solid, m.p. 238-239°C; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.71 (d, $J$ = 9.0 Hz, 1H), 7.63 (d, $J$ = 9.0 Hz, 1H), 7.56-7.51 (m, 5H), 7.32 (t, $J$ = 7.2 Hz, 1H), 7.09 (t, $J$ = 7.2 Hz, 1H), 5.00-4.99 (m, 1H), 4.31-4.30 (m, 1H), 3.58 (s, 3H), 3.18-3.03 (m, 2H), 2.26-2.22 (m, 1H), 2.01-1.95 (m, 1H), 1.42 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 172.4, 155.3, 148.8, 139.9, 134.8, 129.4, 129.2, 126.9, 126.3, 121.5, 121.2, 119.9, 117.9, 80.2, 53.1, 52.5, 32.2, 28.4, 21.4. HRMS Calcd for C$_{23}$H$_{28}$N$_3$O$_4$ $[M + H]^+$: m/z 410.2074, Found: 410.2069.
5. NMR copies of products

\[ \text{NMR copies of products} \]

\[ \text{\( ^1H \) NMR} \]  
\((600 \text{ MHz, CDCl}_3)\)

\[ \text{\( ^{13}C \) NMR} \]  
\((150 \text{ MHz, CDCl}_3)\)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(150 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(150 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^{13}$C NMR
(150 MHz, CDCl$_3$)
$^1$H NMR
(600 MHz, CDCl$_3$)

N
N
F
$^{13}$C NMR
(150 MHz, CDCl$_3$)
$^{19}$F NMR
(564 MHz, CDCl$_3$)

$^1$H NMR
(400 MHz, CDCl$_3$)
$^{13}$C NMR (150 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR
(150 MHz, CDCl$_3$)

$^1$H NMR
(400 MHz, CDCl$_3$)
$^{13}$C NMR
(150 MHz, CDCl$_3$)

$^1$H NMR
(400 MHz, CDCl$_3$)
$^{13}$C NMR
(150 MHz, CDCl$_3$)

$^{19}$F NMR
(564 MHz, CDCl$_3$)
NMeO

1H NMR
(400 MHz, CDCl₃)

13C NMR
(150 MHz, CDCl₃)
$^{1}H$ NMR
(600 MHz, CDCl$_3$)

$^{13}C$ NMR
(150 MHz, CDCl$_3$)
$^{19}$F NMR
(564 MHz, CDCl$_3$)

$^1$H NMR
(400 MHz, CDCl$_3$)
$13^\text{C} \text{NMR}$

$(150 \text{ MHz}, \text{CDCl}_3)$

$1^\text{H} \text{NMR}$

$(600 \text{ MHz}, \text{CDCl}_3)$
\[ \text{\^{13}C NMR} \]

(150 MHz, CDCl₃)

\[ \text{\^{1}H NMR} \]

(600 MHz, CDCl₃)
\[ 3q \]
\[ ^{13}C \text{ NMR} \]
(150 MHz, CDCl₃)

\[ 3r \]
\[ ^{1}H \text{ NMR} \]
(600 MHz, CDCl₃)
$^{13}$C NMR
(150 MHz, CDCl$_3$)

$^1$H NMR
(400 MHz, CDCl$_3$)
$^{13}$C NMR
(150 MHz, CDCl$_3$)

$^1$H NMR
(600 MHz, CDCl$_3$)
**$^{13}$C NMR**
(150 MHz, CDCl$_3$)

**$^1$H NMR**
(600 MHz, CDCl$_3$)
$^1$H NMR

(600 MHz, CDCl$_3$)

$^1$C NMR

(150 MHz, CDCl$_3$)

$\text{3u}$

$\text{3v}$
$^{13}$C NMR

(150 MHz, CDCl$_3$)

$^1$H NMR

(400 MHz, CDCl$_3$)
$^{13}$C NMR (150 MHz, CDCl$_3$)

N$\equiv$N

Ph

3y

H$_2$N

$^{1}$H NMR (600 MHz, CDCl$_3$)

(CH$_2$)$_9$Br

3z

N$\equiv$N

(CH$_2$)$_9$Br

3z

H$_2$N

$^{1}$H NMR (600 MHz, CDCl$_3$)
$\text{H NMR}$

(400 MHz, CDCl$_3$)
\[1^{13}C\] NMR
(150 MHz, CDCl\textsubscript{3})

\[^1H\] NMR
(400 MHz, CDCl\textsubscript{3})
$^{13}$C NMR
(150 MHz, CDCl$_3$)

$^1$H NMR
(600 MHz, CDCl$_3$)
$^1$H NMR
(400 MHz, CDCl$_3$)

$^1$C NMR
(150 MHz, CDCl$_3$)
$^{13}$C NMR
(150 MHz, CDCl$_3$)

$^1$H NMR
(600 MHz, CDCl$_3$)
6. References

