Supporting Information


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**General Information:** Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions, and all reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) employed in the reaction was distilled from sodium-benzophenone. Acetonitrile employed in the reaction was distilled from CaH$_2$. Petroleum ether refers to the fraction with a boiling point in the range of 60-90 °C. Reactions were monitored by thin layer chromatography (TLC), and chromatograms were visualized by fluorescence quenching under UV light at 254 nm. Column chromatography was performed using Qingdao Haiyang flash silica gel (300-400 mesh). $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million (ppm, tetramethyl silane as the internal standard) and are referenced to residual protium in the NMR solvent (CDCl$_3$: δ 7.26; DMSO-$d_6$: δ 2.50). Chemical shifts for carbon are reported in parts per million (ppm, tetramethyl silane as the internal standard) and are referenced to the carbon resonances of the solvent (CDCl$_3$: δ 77.00; DMSO-$d_6$: δ 39.52).

$^1$H NMR data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). Data for $^{13}$C NMR spectra are reported in terms of chemical shift. Melting point was measured with Shanghai Shen Guang WRS-1B digital melting point instrument. IR spectra were recorded on Nicolet Magna-I 550 spectrometer.

1. Preparation of Substrates 1 and 2:

1.1 Preparation of C,N-Cyclic Azomethine Imines 1a-k:

   a) The C,N-cyclic azomethineimines 1a-j were prepared by the reported procedure.$^1$

   b) N-benzylisoquinolinium imide 1k were prepared using the reported procedure.$^2$

   ![Chemical Reaction](image)

   Isoquinoline (10 mmol) and O-(2,4-dinitrophenyl)hydroxylamine (12 mmol) were added to H$_2$O/THF (1:1 mixture, 10 mL). The reaction flask was sealed with a septum, and the resulting suspension was stirred at 40 °C for 16 h. During this period, the reaction mixture turned dark red. The reaction was poured into aqueous NaOH (2.5 N, 60 mL) at room temperature and stirred for 5 min, and then benzyoyl chloride (15 mmol) was added in one portion. After 5 h, the reaction was diluted with H$_2$O (50 mL) and extracted with CHCl$_3$. The combined organic phase was washed with 2.5 N NaOH. The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to afford the N-benzylisoquinolinium imide 1k as beige solid (93%).

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1.2 Preparation of Benzyne Precursor 2:
2-(Trimethylsilyl)aryl triflates 2 were prepared according to literature methods.\(^3\)

2. General procedure for the [3+2] Annulation Reactions

\[
\begin{align*}
\text{N,N-cyclic azomethineimines} & \overset{(0.2 \text{ mmol})}{\longrightarrow} \text{benzyne precursor} 2 \overset{(0.6 \text{ mmol})}{\longrightarrow} \\
\text{Cyclization Reaction} & \overset{\text{R, THF, r.t.}}{\longrightarrow} \text{Product} 3
\end{align*}
\]

C,N-cyclic azomethineimines\(^1\) (0.2 mmol) and benzyne precursor 2 (0.6 mmol) were added to a 10 mL of Schlenk tube. Then anhydrous THF (1.2 mL) and 1 M TBAF in THF (0.8 mmol) was added while stirring. The reaction was carried out under nitrogen atmosphere at room temperature. After the reaction completed, the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to afford the corresponding products 3a-p.

3. Preparation of Compounds 4

\[
\begin{align*}
\text{N-Benzoyl indazolo[3,2-\alpha]-5,6-dihydroisoquinolines} & \overset{(0.2 \text{ mmol})}{\longrightarrow} \text{anhydrous THF (1.2 mL)} \\
\text{LiBHEt}_3 \text{in THF (1M, 0.4 mmol)} & \overset{\text{THF, r.t.}}{\longrightarrow} \text{Product} 4
\end{align*}
\]

N-Benzoyl indazolo[3,2-\alpha]-5,6-dihydroisoquinolines (0.2 mmol) and anhydrous THF (1.2 mL) was added to a 10 mL of Schlenk tube, LiBHEt\(_3\) in THF (1M, 0.4 mmol) was added while stirring under nitrogen atmosphere at room temperature. After the reaction completed the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the corresponding products 4a-c, 4e.

Compound 4e (0.2 mmol, 54.0 mg) was added to a 10 mL of Schlenk tube equipped with a stirrer bar. Then anhydrous CH\(_2\Cl_2\) (2.0 mL) was added while stirring under nitrogen atmosphere. Then methyl trifluoromethansulfonate (0.2 mmol, 23 \(\mu\text{L}\)) was added dropwise while stirring. The reaction mixture was concentrated after completed, and the residue was purified by silica gel column chromatography (dichloromethane/methanol = 200/1) to afford the product 4f (96%) as white solid.
4. Heck Coupling of 4c

\[
\begin{array}{c}
\text{Br} \quad \text{N} \\
\text{4c} \\
\text{Pd(OAc)}_2, \text{PPH}_3, \\
\text{Et}_3\text{N}, \text{DMA}, 100^\circ \text{C} \\
\text{4d} \\
\text{MeO}_{2}\text{C} \\
\end{array}
\]

Pd(OAc)\textsubscript{2} (10 mol%, 2.2 mg) and PPh\textsubscript{3} (20 mol%, 5.2 mg) was added to a 10 mL Schlenk tube. 4c (0.2 mmol, 50.9 mg) and anhydrous DMA (1.0 mL) was added while stirring under nitrogen atmosphere following Et\textsubscript{3}N (0.16 mmol, 22 μL). Then methyl acrylate (1.0 mmol, 90 μL) was added at atmosphere. Then the temperature of reaction mixture was increased to 100 °C and stirred further for 2.5 h. After completed, the reaction was diluted with H\textsubscript{2}O (2 mL) and the mixture was extracted with ethyl acetate. Then the combined organic phases were washed with saturated NaCl solution. The organic phase was dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the product 4d in 72% yield.

5. References

6. Characterization Data of Products 3 and 4

1-Benzoyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3a):
Yield: 91% (59.4 mg), white solid, m.p. 167-168 °C; \(^1\text{H NMR (400 MHz, CDCl}_3\):} \(\delta 8.14-8.03 \text{(m, 3H), 7.49-7.43 \text{(m, 2H), 7.36-7.32 \text{(m, 2H), 7.29 (d,} J = 7.6 \text{ Hz, 1H), 7.24-7.22 \text{(m, 1H), 7.15-7.10 \text{(m, 2H), 5.65 \text{(s, 1H), 2.94-2.86 \text{(m, 3H), 2.56-2.53 \text{(m, 1H);} \(^{13}\text{C NMR (100 MHz, CDCl}_3\):} \(\delta 166.8, 139.3, 134.7, 133.4, 133.2, 132.0, 130.8, 129.2, 128.6, 128.3, 127.7, 127.6, 127.3, 126.4, 125.0, 122.8, 117.9, 64.3, 48.5, 28.2}{;} \text{IR (KBr, cm}^{-1}{):} v 3072, 2869, 1645, 1466, 1393, 756, 693; \text{ HRMS (EI) calculated for C}\textsubscript{22}H\textsubscript{18}N\textsubscript{2}O [M\textsuperscript{+} 326.1419, found 326.1418.}

1-Benzoyl-7-methyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3b):
Yield: 87% (59.2 mg), white solid, m.p. 201-202 °C; \(^1\text{H NMR (400 MHz, CDCl}_3\):} \(\delta 8.11-8.03 \text{(m, 3H), 7.49-7.43 \text{(m, 2H), 7.36-7.32 \text{(m, 2H), 7.29 (d,} J = 7.6 \text{ Hz, 1H), 7.24-7.22 \text{(m, 1H), 7.15-7.10 \text{(m, 2H), 5.65 \text{(s, 1H), 2.94-2.86 \text{(m, 3H), 2.56-2.53 \text{(m, 1H);} \(^{13}\text{C NMR (100 MHz, CDCl}_3\):} \(\delta 166.7, 139.3, 135.9, 134.7, 133.1, 132.0, 131.7, 130.7, 130.2, 129.1, 128.4,} \]
128.2, 128.1, 128.0, 127.6, 124.9, 122.8, 117.8, 64.2, 48.6, 27.7, 21.1; IR (KBr, cm$^{-1}$): ν 3027, 2910, 1640, 1467, 1403, 1276, 764, 697; HRMS (EI) calcd for C$_2$H$_{23}$N$_2$O [M$^+$] 340.1576, found 340.1567.

1-Benzoyl-5-methyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3c)

Yield: 82% (55.8 mg), white solid, m.p. 209-210 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.12-8.03 (m, 3H), 7.49-7.46 (m, 1H), 7.43-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.29-7.25 (m, 2H), 7.13 (t, $J$ = 7.6 Hz, 2H), 5.64 (s, 1H), 2.98-2.84 (m, 2H), 2.75-2.66 (m, 1H), 2.58-2.53 (m, 1H), 2.19 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.9, 139.2, 136.3, 134.8, 133.5, 132.0, 131.8, 130.8, 129.2, 128.6, 128.3, 127.6, 126.3, 125.6, 125.0, 123.0, 117.9, 64.6, 48.3, 25.8, 19.2; IR (KBr, cm$^{-1}$): ν 3066, 2919, 2841, 1644, 1466, 1386, 764, 689; HRMS (EI) calcd for C$_2$H$_{23}$N$_2$O [M$^+$] 340.1576, found 340.1577.

1-Benzoyl-5-methyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3d)

Yield: 64% (43.6 mg), white solid, m.p. 143-144 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.07-8.03 (m, 3H), 7.48-7.46 (m, 1H), 7.43-7.41 (m, 2H), 7.36-7.28 (m, 4H), 7.19-7.18 (m, 1H), 6.94 (s, 1H), 5.64 (s, 1H), 2.91-2.87 (m, 3H), 2.55-2.51 (m, 1H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.9, 139.3, 137.0, 134.8, 133.2, 130.9, 130.3, 129.2, 129.0, 128.8, 128.3, 127.7, 127.3, 125.0, 122.9, 120.4, 117.9, 64.2, 48.5, 28.2, 21.0; IR (KBr, cm$^{-1}$): ν 3041, 2930, 2862, 1643, 1462, 1371, 1205, 756, 693, 605; HRMS (EI) calcd for C$_2$H$_{23}$N$_2$O [M$^+$] 340.1576, found 340.1583.

1-Benzoyl-5-methyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3e)

Yield: 9% (6.1 mg), yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.10-8.06 (m, 3H), 7.67-7.63 (m, 1H), 7.49-7.47 (m, 1H), 7.44-7.42 (m, 3H), 7.19-7.18 (m, 1H), 7.12-7.11 (m, 1H), 6.96-6.93 (m, 2H), 5.71 (s, 1H), 2.94-2.90 (m, 3H), 2.63-2.61 (m, 1H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.4, 138.1, 135.6, 134.8, 133.4, 130.9, 130.3, 129.3, 128.8, 127.7, 127.3, 126.2, 125.6, 124.2, 122.8, 120.4, 118.0, 63.5, 42.0, 29.7, 19.3; IR (KBr, cm$^{-1}$): ν 3022, 2923, 2862, 1645, 1462, 1370, 1203, 756, 697, 604; HRMS (EI) calcd for C$_2$H$_{23}$N$_2$O [M$^+$] 340.1576, found 340.1567.

1-Benzoyl-7-chloro-5,6-dihydroindazolo[3,2-a]isoquinoline (3f)

Yield: 86% (62.1 mg), white solid, m.p. 219-220 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.09-8.00 (m, 3H), 7.51-7.47 (m, 1H), 7.44-7.40 (m, 3H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.29 (d, $J$ = 7.6 Hz, 1H), 7.23 (dd, $J$ = 8.4 Hz, $J$ = 2.0 Hz, 1H), 7.17 (t, $J$ = 7.6 Hz, 1H), 7.06 (d, $J$ = 8.0 Hz, 1H), 5.62 (s, 1H), 2.96-2.86 (m, 3H), 2.57-2.53 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.9, 139.3, 134.7, 133.9, 132.5, 132.2, 132.0, 129.1, 128.6, 127.8, 127.6, 125.1, 122.7, 118.0, 64.1, 48.1, 27.8; IR (KBr, cm$^{-1}$): ν 3028, 2891, 1640, 1468, 1401, 1272, 931, 763, 703; HRMS (EI) calcd for C$_2$H$_{23}$ClN$_2$O [M$^+$] 360.1029, found 360.1033.

1-Benzoyl-7-bromo-5,6-dihydroindazolo[3,2-a]isoquinoline (3g)

Yield: 81% (65.7 mg), white solid, m.p. 199-200 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 8.08-8.00 (m, 3H), 7.59 (d, $J$ = 1.6 Hz, 1H), 7.51-7.47 (m, 1H), 7.44-7.40 (m, 2H), 7.39-7.33 (m, 2H), 7.29-7.27 (m, 1H), 7.17 (t, $J$ = 7.6 Hz, 1H), 7.01 (d, $J$ = 8.0 Hz, 1H), 5.62 (s, 1H), 2.95-2.85 (m, 3H), 2.57-2.52 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.9, 139.3, 134.7, 134.3, 132.5, 132.4, 130.9, 130.5, 130.3, 129.1, 128.6,
127.8, 125.1, 122.7, 120.0, 118.0, 63.9, 48.3, 27.8; IR (KBr, cm⁻¹): ν 3076, 2916, 2845, 1642, 1468, 1399, 1274, 764, 700; HRMS (EI) calcd for C₂₂H₁₇Br(79)N₂O [M⁺] 404.0524, found 404.0522.

1-Benzoyl-6-bromo-5,6-dihydroindazolo[3,2-a]isoquinoline (3h)
Yield: 75% (60.8 mg), white solid, m.p. 202-203 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.00 (m, 3H), 7.50-7.47 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.29 (m, 3H), 7.24-7.22 (m, 1H), 7.14 (t, J = 7.6 Hz, 1H), 5.61 (s, 1H), 2.96-2.86 (m, 3H), 2.58-2.53 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 139.3, 135.7, 134.7, 132.7, 131.5, 131.1, 130.9, 129.6, 129.3, 129.1, 128.6, 127.8, 125.1, 122.7, 121.1, 118.0, 64.1, 48.1, 28.0; IR (KBr, cm⁻¹): ν 3144, 2905, 1633, 1459, 1378, 1271, 1065, 759, 697, 612; HRMS (EI) calcd for C₂₂H₁₇Br(79)N₂O [M⁺] 404.0524, found 404.0517.

1-Benzoyl-5-bromo-5,6-dihydroindazolo[3,2-a]isoquinoline (3i)
Yield: 69% (55.9 mg), white solid, m.p. 196-197 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.10-8.01 (m, 3H), 7.53 (d, J = 7.6 Hz, 1H), 7.49-7.47 (m, 1H), 7.45-7.41 (m, 3H), 7.35 (t, J = 7.6 Hz, 1H), 7.28-7.23 (m, 2H), 7.17-7.14 (m, 1H), 5.65 (s, 1H), 3.01-2.99 (m, 1H), 2.90-2.75 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.0, 139.2, 134.7, 134.1, 133.5, 132.7, 131.4, 131.0, 129.1, 128.6, 127.8, 127.7, 127.0, 125.1, 125.0, 122.8, 118.1, 64.3, 48.2, 29.3; IR (KBr, cm⁻¹): ν 3023, 2831, 1644, 1465, 1386, 1271, 1065, 759, 697, 611; HRMS (EI) calcd for C₂₂H₁₇Br(79)N₂O [M⁺] 404.0524, found 404.0519.

1-Benzoyl-5,6-dihydrobenzo[f]indazolo[3,2-a]isoquinoline (3j)
Yield: 71% (53.5 mg), white solid, m.p. 78-79 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.13-8.06 (m, 3H), 7.87-7.83 (m, 3H), 7.54 (d, J = 8.4 Hz, 1H), 7.51-7.46 (m, 3H), 7.44-7.41 (m, 2H), 7.39-7.38 (m, 1H), 7.36-7.32 (m, 1H), 7.14 (t, J = 7.6 Hz, 1H), 5.76 (s, 1H), 3.14-3.08 (m, 3H), 3.02-2.99 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 139.4, 134.8, 133.3, 132.5, 131.5, 130.9, 129.2, 129.1, 129.0, 128.6, 128.4, 127.7, 127.1, 126.6, 125.9, 125.5, 125.1, 123.0, 122.9, 118.1, 64.9, 48.1, 24.9; IR (KBr, cm⁻¹): ν 3105, 2831, 1644, 1465, 1386, 1271, 1019, 764, 689, 611; HRMS (EI) calcd for C₂₆H₂₀N₂O [M⁺] 376.1576, found 376.1580.

1-Benzoyl-10,11-dimethyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3k)
Yield: 82% (58.1 mg), white solid, m.p. 191-192 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.04-7.94 (m, 3H), 7.46-7.44 (m, 2H), 7.42-7.38 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.26-7.22 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.02 (s, 1H), 5.62 (s, 1H), 2.93-2.87 (m, 3H), 2.59-2.53 (m, 1H), 2.29 (s, 3H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 137.3, 136.6, 134.9, 133.4, 133.3, 132.3, 130.8, 130.7, 129.2, 128.6, 127.7, 127.6, 127.2, 126.4, 123.8, 119.1, 64.3, 48.5, 28.3, 20.0, 19.8; IR (KBr, cm⁻¹): ν 3015, 2933, 1642, 1463, 1392, 1271, 754, 697; HRMS (EI) calcd for C₂₆H₂₃N₂O [M⁺] 376.1576, found 376.1580.

1-Benzoyl-9-methyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3l)
Yield: 38% (25.9 mg), white solid, m.p. 221-222 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.98-9.91 (m, 3H), 7.55-7.52 (m, 1H), 7.45-7.37 (m, 3H), 7.28-7.24 (m, 2H), 7.17 (t, J = 8.0 Hz, 1H), 7.09-7.07 (m, 1H), 6.82 (d, J = 7.6 Hz, 1H), 5.81 (s, 1H), 3.17-3.11 (m, 1H), 2.91-2.85 (m, 1H), 2.71-2.65 (m, 2H), 2.00 (s,
$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.0, 140.9, 136.3, 135.3, 134.3, 131.9, 131.2, 131.0, 130.6, 129.1, 128.1, 128.0, 127.9, 127.8, 127.7, 125.5, 115.1, 66.8, 51.7, 28.3, 19.7; IR (KBr, cm$^{-1}$): $\nu$ 3010, 2926, 2878, 1637, 1432, 1387, 1265, 1073, 766, 691; HRMS (EI) calcd for C$_{23}$H$_{20}$N$_2$O [M]$^+$ 340.1576, found 340.1566.

1-Benzoyl-12-methyl-5,6-dihydroindazolo[3,2-a]isoquinoline (3l')
Yield: 45% (30.6 mg), white solid, m.p. 209-210 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86-7.84 (m, 2H), 7.51-7.48 (m, 1H), 7.45-7.41 (m, 2H), 7.33 (d, $J$ = 7.2 Hz, 1H), 7.30-7.26 (m, 1H), 7.22-7.16 (m, 2H), 7.14-7.06 (m, 3H), 5.43 (s, 1H), 3.46-3.41 (m, 1H), 3.14-3.06 (m, 1H), 2.97-2.91 (m, 1H), 2.72-2.67 (m, 1H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.5, 140.2, 136.2, 135.5, 133.3, 132.5, 131.1, 130.9, 129.9, 128.5, 127.8, 127.7, 127.1, 126.4, 126.3, 120.4, 66.5, 48.2, 28.7, 19.3; IR (KBr, cm$^{-1}$): $\nu$ 3005, 2932, 2867, 1655, 1454, 1333, 1268, 1186, 1070, 758, 696, 603; HRMS (EI) calcd for C$_{23}$H$_{20}$N$_2$O [M]$^+$ 340.1576, found 340.1569.

1-Benzoyl-9-methoxy-5,6-dihydroindazolo[3,2-a]isoquinoline (3m)
Yield: 56% (39.9 mg), white solid, m.p. 222-223 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J$ = 7.2 Hz, 2H), 7.66 (d, $J$ = 7.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.32-7.28 (m, 2H), 7.19-7.12 (m, 3H), 6.99-6.96 (m, 1H), 6.58 (d, $J$ = 8.4 Hz, 1H), 6.36-6.34 (m, 1H), 5.76 (s, 1H), 3.59 (s, 3H), 3.09-3.02 (m, 1H), 2.84-2.74 (m, 2H), 2.57-2.53 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.0, 157.0, 141.6, 134.9, 134.1, 131.8, 130.8, 129.8, 129.2, 127.7, 127.6, 127.1, 124.8, 119.7, 110.5, 108.7, 101.4, 65.3, 55.2, 49.4, 28.2; IR (KBr, cm$^{-1}$): $\nu$ 2987, 2868, 1643, 1450, 1393, 1256, 1081, 934, 778, 691; HRMS (EI) calcd for C$_{23}$H$_{20}$N$_2$O$_2$ [M]$^+$ 356.1525, found 356.1531.

1-Benzoyl-9-bromo-5,6-dihydroindazolo[3,2-a]isoquinoline (3n)
Yield: 43% (34.9 mg), white solid, m.p. 176-177 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05-7.97 (m, 3H), 7.77-7.75 (m, 1H), 7.49-7.45 (m, 1H), 7.42-7.39 (m, 2H), 7.31-7.25 (m, 2H), 7.23-7.21 (m, 1H), 7.14 (t, $J$ = 8.0 Hz, 1H), 7.09-7.07 (m, 1H), 5.83 (s, 1H), 3.18-3.13 (m, 1H), 2.92-2.88 (m, 1H), 2.76-2.66 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.2, 142.9, 136.1, 136.1, 131.8, 130.8, 129.8, 129.2, 127.7, 127.6, 127.1, 124.8, 119.7, 110.5, 108.7, 101.4, 65.3, 55.2, 49.4, 28.2; IR (KBr, cm$^{-1}$): $\nu$ 3073, 2921, 2851, 1650, 1590, 1442, 1372, 1249, 1209, 1131, 1084, 778; HRMS (EI) calcd for C$_{22}$H$_{17}$Br(79)N$_2$O [M]$^+$ 404.0524, found 404.0531.

1-Benzoyl-9,10-dihydrobenzo[4,5]indazolo[3,2-a]isoquinoline (3o)
Yield: 32% (24.1 mg), white solid, m.p. 155-156 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (d, $J$ = 7.2 Hz, 2H), 7.85-7.80 (m, 4H), 7.49-7.45 (m, 1H), 7.42-7.39 (m, 2H), 7.31-7.25 (m, 2H), 7.23-7.21 (m, 1H), 7.14 (t, $J$ = 8.0 Hz, 1H), 7.09-7.07 (m, 1H), 5.83 (s, 1H), 3.18-3.13 (m, 1H), 2.92-2.88 (m, 1H), 2.76-2.66 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 173.0, 139.5, 137.1, 135.3, 132.9, 132.2, 130.8, 130.6, 129.6, 129.2, 128.9, 128.7, 128.6, 128.2, 127.8, 126.5, 126.1, 125.8, 124.4, 122.5, 116.9, 67.5, 52.1, 28.3; IR (KBr, cm$^{-1}$): $\nu$ 3045, 2923, 2834, 1632, 1454, 1401, 1271, 813, 754, 702; HRMS (EI) calcd for C$_{26}$H$_{20}$N$_2$O [M]$^+$ 376.1576, found 376.1577.
1-Benzoyl-indazolo[3,2-α]isoquinoline (3p)

Yield: 92% (59.7 mg), white solid, m.p. 167-168 °C; 1H NMR (400 MHz, CDCl3): δ 7.98 (d, J = 7.6 Hz, 1H), 7.92-7.90 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 1H), 7.30-7.28 (m, 1H), 7.27-7.24 (m, 2H), 7.15 (td, J = 7.6 Hz, J = 0.8 Hz, 1H), 7.02-7.00 (m, 1H), 6.96-6.94 (m, 1H), 5.93 (d, J = 7.6 Hz, 1H), 5.73 (s, 1H), 5.52 (d, J = 8.0 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 167.1, 139.2, 137.5, 134.2, 134.1, 131.1, 129.1, 129.0, 128.8, 128.5, 128.0, 126.9, 125.5, 122.1, 117.4, 108.0, 64.0; IR (KBr, cm⁻¹): ν 3060, 2944, 2826, 1646, 1455, 1352, 1262, 851, 748, 701, 670; HRMS (EI) calcd for C22H16N2O [M]+ 324.1263, found 324.1265.

5,6-Dihydroindazolo[3,2-α]isoquinoline (4a)

Yield: 90% (39.6 mg), colorless liquid; 1H NMR (400 MHz, CDCl3): δ 8.03 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.42 (td, J = 1.6 Hz, J = 7.6 Hz, 1H), 7.36-7.32 (m, 2H), 7.31-7.27 (m, 1H), 4.66 (t, J = 7.2 Hz, 2H), 3.28 (t, J = 7.2 Hz, 2H).

12-Methoxy-5,6-dihydroindazolo[3,2-α]isoquinoline (4b)

Yield: 90% (39.6 mg), colorless liquid; 1H NMR (400 MHz, CDCl3): δ 8.51 (d, J = 8.0 Hz, 1H), 7.40-7.36 (m, 1H), 7.32-7.21 (m, 4H), 6.44 (d, J = 7.2 Hz, 1H), 4.58 (t, J = 6.8 Hz, 2H), 4.00 (s, 3H), 3.22 (t, J = 6.8 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 153.7, 150.4, 132.8, 131.9, 128.1, 127.9, 127.8, 126.0, 123.8, 122.3, 120.3, 118.2, 117.8, 47.8, 29.1.

12-Bromo-5,6-dihydroindazolo[3,2-α]isoquinoline (4c)

Yield: 95% (56.8 mg), colorless liquid; 1H NMR (400 MHz, CDCl3): δ 8.38 (d, J = 7.6 Hz, 1H), 7.65 (dd, J = 0.8 Hz, J = 8.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.35-7.30 (m, 2H), 7.25-7.21 (m, 1H), 7.19-7.17 (m, 1H), 4.59 (t, J = 6.8 Hz, 2H), 3.22 (t, J = 6.4 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 149.7, 133.4, 131.6, 129.3, 128.1, 127.7, 127.4, 126.7, 111.2, 110.3, 99.6, 55.2, 48.2, 29.8; IR (KBr, cm⁻¹): ν 3073, 2923, 2855, 1620, 1262, 1108, 756, 728; HRMS (EI) calcd for C16H11BrN2 [M]+ 298.0106, found 298.0104.

5,6-dihydroindazolo[3,2-α]isoquinolin-12-yl-3-methyl acrylate (4d)

Yield: 72% (43.8 mg), light yellow solid, m.p. 155-156 °C; 1H NMR (400 MHz, CDCl3): δ 8.32 (d, J = 16.0 Hz, 1H), 7.78-7.74 (m, 2H), 7.37-7.32 (m, 5H), 6.38 (d, J = 16.0 Hz, 1H), 4.60 (t, J = 6.4 Hz, 2H), 3.81 (s, 3H), 3.24 (t, J = 6.4 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 167.2, 148.9, 144.5, 133.3, 131.9, 128.9, 128.2, 128.0, 127.6, 127.3, 127.2, 125.8, 122.2, 119.6, 118.9, 116.7, 51.7, 48.4, 29.7; IR (KBr, cm⁻¹): ν 3035, 2922, 2851, 1625, 1443, 1371, 1260, 1037, 912, 823, 727, 681; HRMS (EI) calcd for C19H16NO2 [M]+ 304.1212, found 304.1210.

9,10-Dihydrobenzo[4,5]indazolo[3,2-α]isoquinoline (4e)
Yield: 97% (52.4 mg), colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.71 (d, $J = 7.6$ Hz, 1H), 8.31 (d, $J = 8.0$ Hz, 1H), 7.87-7.84 (m, 1H), 7.67 (d, $J = 8.8$ Hz, 1H), 7.61 (d, $J = 9.6$ Hz, 1H), 7.51-7.45 (m, 3H), 7.42-7.40 (m, 1H), 7.38-7.34 (m, 1H), 4.56 (t, $J = 6.4$ Hz, 2H), 3.25 (t, $J = 6.4$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.6, 134.0, 133.2, 131.2, 129.2, 128.6, 128.5, 128.4, 128.2, 128.1, 127.4, 126.1, 125.5, 125.0, 123.4, 117.8, 113.6, 47.9, 30.2; IR (KBr, cm$^{-1}$): v 2924, 1619, 1458, 1355, 1280, 1019, 805, 740; HRMS (EI) calcd for C$_{19}$H$_{14}$N$_2$ [M]$^+$ 270.1157, found 270.1160.

7-Methyl-9,10-dihydrobenzo[4,5]indazolo[3,2-a]isoquinolin-7-ium trifluoromethanesulfonate (4f) Yield: 96% (83.4 mg), white solid, m.p. $>300 \, ^{\circ}$C; $^1$H NMR (400 MHz, dms-o-d$_6$): $\delta$ 8.72 (d, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 9.2$ Hz, 2H), 8.22 (d, $J = 7.6$ Hz, 1H), 8.12 (d, $J = 9.6$ Hz, 1H), 7.83 (t, $J = 7.6$ Hz, 1H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.68-7.65 (m, 3H),, 4.76 (t, $J = 6.4$ Hz, 2H), 4.42 (s, 3H), 3.44 (t, $J = 6.4$ Hz, 2H). $^{13}$C NMR (100 MHz, dms-o-d$_6$): $\delta$ 139.8, 137.7, 135.5, 135.0, 132.0, 130.6, 130.3, 129.1, 129.0, 127.9, 127.4, 126.9, 125.5, 124.4, 123.2, 111.9, 110.4, 44.1, 33.6, 27.6. IR (KBr, cm$^{-1}$): v 2962, 1625, 1444, 1320, 1261, 1023, 827, 756, 677; HRMS (EI) calcd for C$_{21}$H$_{15}$F$_3$N$_2$O$_3$S$^+$ [M]$^+$ 434.0906, found 434.0909.
7. Copies of NMR Spectra of the Products 3 and 4
$3n$
30
8. 2D $^1$H-$^1$H NOESY Spectra of Product 3l, 4b, 4d, 4f