Electronic Supplementary Information (ESI)

A facile synthesis of 2H-indazoles under neat conditions and further transformation into aza-γ-carboline alkaloid analogues in a tandem one-pot fashion

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Table of Contents

Experimental section .................................................................................................................................................. (S2)
Methods for 2-azidoaldehyde preparation and its spectral data ......................................................................... (S3-S4)
General procedure for 2H-indazole synthesis and stepwise/one-pot methods for indazolo[2,3-a]quinoxalines synthesis ........................................................................................................................................ (S5-S6)
X-ray crystal structure data for 2-(4-Methoxybenzyl)-2H-indazole (3k)……… (S7)
Spectral data of all compounds (3a-x), 5 and (6a-i)......................................................................................... (S8-S22)
Copies of 1H, 13C NMR spectra of all compounds S3, S4, (4a-z), (5) and (6a-i)... .............................................. (S23-S59)
References .............................................................................................................................................................. (S60)
Experimental Section

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. \(^1\)H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl\(_3\); chemical shifts (\(\delta\) in ppm) and coupling constants (\(J\) in Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (\(\delta\)\(_H\) = 0.00 ppm) or CHCl\(_3\) (\(\delta\)\(_H\) = 7.25 ppm). \(^{13}\)C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl\(_3\); chemical shifts (\(\delta\) in ppm) are reported relative to CHCl\(_3\) (\(\delta\)\(_C\) = 77.00 ppm). In the \(^1\)H-NMR, the following abbreviations are used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br s = broad singlet, sept = septet. The assignment of signals were confirmed by \(^1\)H and \(^{13}\)C spectral data. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF using multimode source. Microwave experiments were carried out with CEM Discover Labmate\textsuperscript{TM} instrument in 10 ml vial, closed vessel, Power: 250W, Temperature: 60 °C-100 °C for 50-100 minutes. Melting points were determined using melting point apparatus manufactured by GUNA enterprises, India and are uncorrected. All small scale reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled prior to use. We gave all spectral data for known and unknown compounds.
(A) General procedure for 2-azidoaldehyde preparation:¹

(B) General procedure for the synthesis of 1-azido-2-naphthaldehyde (S4):¹b

All 2-azidobenzaldehydes were prepared by using literature known methods except S₄.

1-Chloro-2-naphthaldehyde S₂: The general procedure was followed using 1.33 mL of α-tetralone (10.0 mmol), 1.9 mL of POCl₃ (20.0 mmol), and 4.0 ml of DMF. Purification by column chromatography with hexane:EtOAc/20:1 afforded S₂ as a slightly yellow oil (70-75%). (Caution: Reaction should be carried at room temperature as the product is volatile). For spectral data see reference 1.

1-Chloro-2-naphthaldehyde S₃: The general procedure was followed using 1.465 g of chloroalkenal (7.57 mmol), DDQ (15.15 mmol), and 60 ml of chlorobenzene. The reaction mixture was refluxed at 130 °C for 72 h. It was then poured into saturated aqueous NaHCO₃ solution and extracted with ethyl acetate (3 × 20 mL). The ethyl acetate extract was dried over Na₂SO₄. Evaporation of the solvent and purification of the residue over a silicagel column using hexane:ethyl acetate/99:1 as eluent furnished the saturated chloroaldehyde S₃ (1.0 g, 95%) as a pale yellow solid. IR (MIR-ATR, 4000–600 cm⁻¹): vₘₐₓ = 3059, 2867, 2746, 1683, 1650, 1618, 1594, 1557, 1455, 1318, 1218, 993, 894, 812, 754. ¹H NMR (CDCl₃, 400 MHz): δH = 10.74 (s, 1H), 8.48-8.44 (m, 1H), 7.92 (d, 1H, J = 8.8 Hz), 7.88-7.85 (m, 1H), 7.79 (d, 1H, J = 8.8 Hz),
7.70-7.65 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta_C = 190.4, 138.8, 137.0, 130.8, 129.7, 129.6, 128.4, 127.0, 125.4, 123.3$. HR-MS (ESI+) m/z calculated for [C$_{11}$H$_8$ClO]$: [M+H]: 191.0258; found: 191.0262.

1-Azido-2-naphthaldehyde S4: To a solution of 1-chloro-2-napthaldehyde (2.0 mmol, 1.0 equiv) in 3.0 mL of DMSO was added NaN$_3$ (2.4 mmol, 1.2 equiv). The mixture was stirred at ambient temperature and monitored by TLC. Once the starting material disappeared, the reaction mixture was poured in ice cold water (30.0 mL) and extracted with dichloromethane (10 mL×2). The DCM layer was washed with water (10 mL×2), brine (20 mL×1). The organic layer was dried over Na$_2$SO$_4$, filtered and concentrated to afford the crude product. Purification by column chromatography with hexane/EtOAc afforded the final analytically pure product. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{\text{max}} = 3041, 2865, 2110, 2027, 1984, 1926, 1684, 1618, 1592, 1455, 1377, 1330, 1258, 1217, 812, 752$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 10.25$ (s, 1H), 8.48-8.46 (m, 1H), 7.94 (d, 1H, $J = 8.3$ Hz), 7.90-7.87 (m, 1H), 7.81 (d, 1H, $J = 8.3$ Hz), 7.71-7.66 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta_C = 193.6, 129.7, 129.5, 128.7, 125.6, 121.8, 116.2$. HR-MS (ESI+) m/z calculated for [C$_{13}$H$_{11}$N$_2$]$^+$: [M+H]$^+$: 198.0662; found: 198.0661.
(C) General procedure for the synthesis of 2H-indazole (3a-x):

2-Azidobenzaldehyde 1 (1 mmol), amine 2 (1 mmol) were taken in a 10 mL microwave vessel and sealed with microwave septum. It was then placed in to CEM Discover system under the irradiation conditions: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 60-100 °C for 50-100 min (hold time) depending on the components. After completion, the mixture was cooled to room temperature. The reaction mixture was diluted with EtOH and slight amount of charcoal was added, filtered, dried in vacuo and recrystallized using ethanol and few of them are purified on a silica gel column chromatography (hexane/ethylacetate 90:10 to 85:15). All the compounds were confirmed by FTIR, 1H NMR, 13C NMR and HR-MS Spectral analyses and 3k was further confirmed by XRD. Among 24 compounds, 10 (3b, 3c, 3n, 3p, 3s-3x) are unknown and 14 (3a, 3d-3m, 3o, 3q and 3r) are known.

(D) General procedure for the synthesis of indazolo[2,3-a]quinoxalines (6a-i) in stepwise:

2H-indazole 3 (1 mmol) and aldehyde 4 (1 mmol) were taken in 10 mL microwave vessel and added 1% TFA in toluene, sealed with microwave septum. It was then placed in to CEM Discover system under the irradiation conditions: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 110 °C for 30 min (hold time). After completion, the mixture was cooled to room temperature. Then 0.5 equivalent of DDQ was added and treated under the same conditions as above for 15 min. On cooling to room temperature, the reaction mixture was quenched with NaHCO3, extracted with ethylacetate, dried over Na2SO4 and was purified on a silica gel column chromatography (hexane/ethylacetate 90:10) which furnished the respective solids (6a-i). All the compounds were confirmed by FTIR, 1H NMR, 13C NMR and HR-MS spectral analyses.
Table 1: Screening of % TFA and its solvent for Pictet-Spengler strategy:

<table>
<thead>
<tr>
<th>S.no</th>
<th>% TFA in solvent</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>50% TFA in DCE</td>
<td>85</td>
<td>97</td>
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<tr>
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<td>10% TFA in DCE</td>
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<td>85</td>
</tr>
<tr>
<td>6</td>
<td>5% TFA in toluene</td>
<td>110</td>
<td>97</td>
</tr>
<tr>
<td>7</td>
<td>1% TFA in toluene</td>
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<td>96</td>
</tr>
<tr>
<td>8</td>
<td>Toluene</td>
<td>110</td>
<td>15</td>
</tr>
</tbody>
</table>

(E) General procedure for sequential one-pot synthesis of indazolo[2,3-a]quinoxaline (6a-i):

2-Azidobenzaldehyde 1 (1 mmol), diamine 2 (1 mmol) were taken in a 10 mL microwave vessel and sealed with microwave septum. It was then placed in to CEM Discover system under the irradiation conditions: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 85 °C for 60 min (hold time). Once indazole formation was confirmed by TLC, aldehyde 4 and 1% TFA in toluene were added and treated under the microwave condition: 3-5 min run time with high stirring. Maximum power and maximum pressure were set at 250 W and 300 psi respectively, with a set temperature of 110 °C for 30 min (hold time). After completion, the mixture was cooled to room temperature. Then 0.5 equivalent of DDQ was added and treated under the same conditions as above for 15 min. On cooling to room temperature, the reaction mixture was quenched with NaHCO₃, extracted with ethylacetate, dried over Na₂SO₄ and was purified on a silica gel column chromatography (hexane/ethylacetate 90:10) furnished the respective solids (6a-i). All the compounds were confirmed by FTIR, ¹H NMR, ¹³C NMR and HR-MS spectral analyses.
(G) X-ray crystal structure data for 2-(4-Methoxybenzyl)-2H-indazole (3k) CCDC 994876:

<table>
<thead>
<tr>
<th>Operator</th>
<th>K. Ravikumar</th>
</tr>
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<tbody>
<tr>
<td>Diffractometer</td>
<td>Oxford Super Nova</td>
</tr>
<tr>
<td>Empirical formula</td>
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<tr>
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<td>Wavelength/Å</td>
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<td>Space group</td>
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</tr>
<tr>
<td>a/Å</td>
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<td>b/Å</td>
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<tr>
<td>c/Å</td>
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<tr>
<td>α/°</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
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</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
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<tr>
<td>Z</td>
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<tr>
<td>ρ_{cal}mg/mm³</td>
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<tr>
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<td>Crystal size/mm³</td>
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</tr>
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<tr>
<td>Independent reflections</td>
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<td>Goodness-of-fit on F²</td>
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<tr>
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</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R1 = 0.0463, wR2 = 0.1079</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.146 and -0.128</td>
</tr>
</tbody>
</table>
Spectral data of all compounds (3a-x), 5 and (6a-i):

2-Phenyl-2H-indazole (3a):[12] Reaction time = 50 min; Cream solid (94%), Mp 74–76 °C. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): ʋ\(_{\text{max}}\) = 3128, 3055, 2923, 2852, 1628, 1595, 1519, 1496, 1379, 1314, 1204, 1046, 780, 751. \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ\(_{H}\) = 8.42 (s, 1H), 7.92 (d, 2H, J = 7.3 Hz), 7.82 (d, 1H, J = 8.8 Hz), 7.72 (d, 1H, J = 8.3 Hz), 7.54 (t, 2H, J = 7.8 Hz), 7.43-7.40 (m, 1H), 7.36-7.32 (m, 1H), 7.13 (dd, 1H, J\(_a\) = 7.8 and J\(_b\) = 6.8 Hz). \(^13\)C NMR (CDCl\(_3\), 100 MHz): δ\(_C\) = 149.8, 140.6, 129.6, 127.9, 126.9, 122.8, 122.5, 121.0, 120.5, 120.4, 118.0. HR-MS (ESI+) m/z calculated for [C\(_{13}\)H\(_{11}\)N\(_2\)]\(^+\) = [M+H]\(^+\): 195.0917; found: 195.0908.

2-(2,3-dimethylphenyl)-2H-indazole (3b): Reaction time = 50 min; Brown solid (97%), Mp 68–70 °C. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): ʋ\(_{\text{max}}\) = 3052, 2945, 2921, 1625, 1583, 1515, 1482, 1387, 1346, 1265, 1192, 1110, 1081, 1029, 957, 780, 755, 713, 662. \(^1\)H NMR (CDCl\(_3\), 400 MHz): δ\(_{H}\) = 8.05 (s, 1H), 7.79 (d, 1H, J = 8.8 Hz), 7.72 (d, 1H, J = 8.3 Hz), 7.34-7.27 (m, 2H), 7.21 (m, 2H), 7.14-7.11 (m, 1H), 2.35 (s, 3H), 2.03 (s, 3H). \(^13\)C NMR (CDCl\(_3\), 100 MHz): δ\(_C\) = 149.2, 140.5, 138.5, 133.0, 130.7, 126.3, 125.9, 124.7, 124.5, 122.1, 121.9, 120.3, 117.9, 20.3, 14.3. HR-MS (ESI+) m/z calculated for [C\(_{15}\)H\(_{15}\)N\(_2\)]\(^+\) = [M+H]\(^+\): 223.1230; found: 223.1221.
2-(2-Bromo-4-methylphenyl)-2H-indazole (3c): Reaction time = 50 min; Brown solid (90%), Mp 66–68 ºC. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3057, 2921, 1521, 1500, 1386, 1200, 1070, 1030, 954, 820, 784, 755, 646. \) \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta_H = 8.25 \) (s, 1H), 7.8 (d, 1H, \( J = 8.8 \) Hz), 7.74 (d, 1H, \( J = 8.3 \) Hz), 7.57 (s, 1H), 7.49 (d, 1H, \( J = 7.8 \) Hz), 7.37-7.33 (m, 1H), 7.26 (d, 1H, \( J = 7.3 \) Hz), 7.16-7.12 (m, 1H), 2.43 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta_C = 149.3, 141.0, 137.8, 134.0, 129.0, 128.4, 126.8, 125.2, 122.3, 121.9, 120.5, 118.5, 118.0, 20.9. \) HR-MS (ESI+) m/z calculated for \([C_{14}H_{12}BrN_2]^+ = [M+H]^+\): 287.0178; found: 287.0168.

2-(4-Methoxy-2-methylphenyl)-2H-indazole (3d).\(^{[3]}\) Reaction time = 50 min; Brown solid (92%), Mp 82–84 ºC. IR (MIR-ATR, 4000–600 cm⁻¹) \( \nu_{\text{max}} = 2923, 2854, 1612, 1568, 1545, 1452, 1409, 1264, 1153, 1094, 1004, 806, 748, 696. \) \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta_H = 8.06 \) (s, 1H), 7.80 (d, 1H, \( J = 8.8 \) Hz), 7.74 (d, 1H, \( J = 8.3 \) Hz), 7.36-7.33 (m, 2H), 7.17-7.13 (m, 1H), 6.88-6.83 (m, 2H), 3.87 (s, 3H), 2.2 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta_C = 159.9, 149.1, 135.5, 133.7, 127.7, 126.3, 124.6, 122.0, 122.0, 120.2, 117.9, 116.1, 111.6, 55.5, 18.0. \) HR-MS (ESI+) m/z calculated for \([C_{15}H_{15}N_2O]^+ = [M+H]^+\): 239.1179; found: 239.1188.

2-(3,4,5-trimethoxyphenyl)-2H-indazole (3e).\(^{[4]}\) Reaction time = 50 min; Brown solid (90%), Mp 82–84 ºC. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3124, 2937, 2830, 1599, 1518, 1504, 1467, 1423, 1319, 1225, 1122, 1072, 998, 830, 753, 729. \) \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta_H = 8.36 \) (s,
1H), 7.78 (d, 1H, J = 8.8 Hz), 7.69 (d, 1H, J = 8.3 Hz), 7.32 (dd, 1H, J_\text{a} = 8.3 and J_\text{b} = 7.3 Hz), 7.13-7.09 (m, 3H), 3.96-3.95 (m, 6H), 3.90 (s, 3H). 

^{13}\text{C NMR (CDCl}_3\text{, 100 MHz): }\delta_\text{C} = 153.8, 137.9, 136.6, 126.9, 122.7, 122.5, 120.7, 120.3, 117.8, 98.9, 61.0, 56.4. 

HR-MS (ESI+)
m/z calculated for [C_{16}H_{17}N_{2}O_{3}]^+ = [M+H]^+: 285.1234; found: 285.1224.

2-(2-Bromophenyl)-2H-indazole (3f):^{[5]} Reaction time = 50 min; Brown solid (86%), Mp 82–84 °C. IR (MIR-ATR, 4000–600 cm^{-1}): \nu_{\text{max}} = 3429, 3063, 3031, 2927, 2852, 1660, 1578, 1562, 1475, 1346, 1147, 938, 765, 695. 

^{1}H NMR (CDCl_3, 400 MHz): \delta_H = 8.13 (br s, 1H), 7.83 (d, 1H, J = 8.8 Hz), 7.76 (d, 2H, J = 7.8 Hz), 7.63-7.56 (m, 1H), 7.50-7.48 (m, 1H), 7.36-7.35 (m, 2H), 7.16 (t, 1H, J = 7.6 Hz). 

^{13}\text{C NMR (CDCl}_3\text{, 100 MHz): }\delta_\text{C} = 149.4, 140.3, 133.8, 130.5, 128.9, 128.3, 126.9, 125.2, 122.5, 121.9, 120.6, 118.9, 118.0. 

HR-MS (ESI+) m/z calculated for [C_{13}H_{10}BrN_{2}]^+ = [M+H]^+: 285.1234; found: 285.1224

2-(2H-Indazol-2-yl)aniline (3g):^{[6]} Reaction time = 60 min; Off white (86%), Mp 76–78 °C. IR (MIR-ATR, 4000–600 cm^{-1}): \nu_{\text{max}} = 3438, 3330, 3056, 1615, 1516, 1502, 1464, 1385, 1349, 1314, 1248, 1193, 1144, 1048, 954, 787, 744. 

^{1}H NMR (CDCl_3, 400 MHz): \delta_H = 8.16 (s, 1H), 7.72 (dd, 2H, J = 19.1 and J = 8.8 Hz), 7.33-7.27 (m, 2H), 7.21-7.15 (m, 1H), 7.12-7.08 (m, 1H), 6.79 (m, 2H). 

^{13}\text{C NMR (CDCl}_3\text{, 100 MHz): }\delta_\text{C} = 149.5, 141.5, 129.5, 126.8, 126.5, 125.0, 123.7, 122.2, 121.9, 120.4, 118.0, 117.5, 117.5. 

HR-MS (ESI+) m/z calculated for [C_{13}H_{12}N_{3}]^+ = [M+H]^+: 210.1026; found: 210.1018.
2-(Pyridin-2-yl)-2H-indazole (3h):[2] Reaction time = 50 min; Cream solid (88%), Mp 104–106 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3396, 3149, 3057, 3010, 2926, 1627, 1591, 1573, 1516, 1376, 1201, 1144, 954, 778, 756, 734 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 9.1 \) (s, 1H), 8.49 (d, 1H, \( J = 3.4 \) Hz), 8.27 (d, 1H, \( J = 8.3 \) Hz), 7.89–7.85 (m, 1H), 7.76–7.71 (m, 2H), 7.34–7.26 (m, 2H), 7.11–7.07 (m, 1H). \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta_C = 151.8, 150.3, 148.3, 138.9, 127.6, 122.8, 122.7, 122.4, 121.2, 120.6, 118.0, 114.1 \). HR-MS (ESI⁺) m/z calculated for [C\(_{12}\)H\(_{10}\)N\(_3\)]⁺ = [M+H]⁺: 196.0869; found: 196.0862.

2-(6-methylpyridin-2-yl)-2H-indazole (3i):[1b&2] Reaction time = 50 min; Pale yellow solid (89%), Mp 106–108 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3156, 3051, 2925, 1627, 1603, 1570, 1518, 1474, 1428, 1374, 1329, 1207, 1072, 910, 787, 756 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 9.14 \) (s, 1H), 8.07 (d, 1H, \( J = 8.3 \) Hz), 7.78–7.72 (m, 3H), 7.33 (dd, 1H, \( J_a = 7.8 \) and \( J_b = 6.8 \) Hz), 7.15–7.10 (m, 2H), 2.62 (s, 3H). \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta_C = 157.8, 151.2, 150.2, 139.0, 127.4, 122.5, 122.3, 122.2, 122.0, 120.6, 118.0, 110.9, 24.2 \). HR-MS (ESI⁺) m/z calculated for [C\(_{13}\)H\(_{12}\)N\(_3\)]⁺ = [M+H]⁺: 210.1026; found: 210.1021.

2-Benzyl-2H-indazole (3j):[1b&2] Reaction time = 50 min; Brown solid (94%), Mp 44–46 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3060, 3031, 2936, 1627, 1514, 1495, 1469, 1422, 1309, 1153, 1135, 1009, 981, 907, 838, 782, 754, 703, 643 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 7.86 \) (s, 1H), 7.73 (d, 1H), 7.61 (d, 1H), 7.35–7.24 (m, 6H), 7.08–7.04 (m, 1H), 5.57 (s, 2H). \(^{13}\)C NMR
(CDCl₃, 100 MHz): δC = 149.0, 135.8, 129.0, 128.4, 128.0, 126.0, 122.9, 122.1, 121.8, 120.2, 117.6, 57.5.

HR-MS (ESI+) m/z calculated for [C₁₄H₁₃N₂]+ = [M+H]+: 209.1073; found: 209.1073.

2-(4-Methoxybenzyl)-2H-indazole (3k):[⁷] Reaction time = 50 min; Off white solid (96%), Mp 114–118 °C. IR (MIR-ATR, 4000–600 cm⁻¹): νmax = 3121, 2930, 2835, 1993, 1611, 1513, 1390, 1247, 1178, 1028, 792, 759. ¹H NMR (CDCl₃, 400 MHz): δH = 7.83 (s, 1H), 7.72 (d, 1H, J = 8.8 Hz), 7.6 (d, 1H, J = 8.3 Hz), 7.29-7.24 (m, 3H), 7.07-7.04 (m, 1H), 6.88 (m, 2H, J = 8.8 Hz), 5.52 (s, 2H), 3.78 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δC = 159.7, 148.9, 129.6, 127.7, 125.9, 122.5, 122.0, 121.7, 120.1, 117.5, 114.3, 57.0, 55.3. HR-MS (ESI+) m/z calculated for [C₁₅H₁₅N₂O]⁺ = [M+H]⁺: 239.1179; found: 239.1188.

2-Cyclohexyl-2H-indazole (3l):[²] Reaction time = 50 min; Peach solid (92 %), Mp 80–82 °C. IR (MIR-ATR, 4000–600 cm⁻¹): νmax = 3395, 3150, 3047, 2935, 2849, 1621, 1509, 1449, 1373, 1306, 1227, 1148, 976, 895, 751, 727, 647. ¹H NMR (CDCl₃, 400 MHz): δH = 7.94 (s, 1H), 7.72 (d, 1H, J = 8.8 Hz), 7.67 (d, 1H, J = 8.8 Hz), 7.31-7.27 (m, 1H), 7.10-7.07 (m, 1H), 4.42 (tt, 1H, Jₐ = 11.7 Hz and Jₖ = 3.5 Hz), 2.29 (d, 2H, J = 10.8 Hz), 1.99-1.95 (m, 3H), 1.92-1.86 (m, 1H), 1.82-1.74 (m, 1H), 1.57-1.45 (m, 2H), 1.40-1.30 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δC = 148.2, 125.6, 121.4, 121.4, 120.1, 117.4, 62.9, 34.0, 25.5, 25.8. HR-MS (ESI+) m/z calculated for [C₁₃H₁₇N₂]⁺ = [M+H]⁺: 201.1386; found: 201.1385.
2-(Tert-butyl)-2\textit{H}-indazole (3m):\textsuperscript{[2&8]} Reaction time = 50 min; Dark brown solid (91%), Mp 115–118 °C. IR (MIR-ATR, 4000–600 cm\textsuperscript{-1}): \textit{v}_{\text{max}} = 3395, 3150, 3037, 2935, 2846, 1621, 1519, 1446, 1373, 1250, 1227, 1148, 972, 891, 751, 713, 643. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta_H = 8.0\) (s, 1H), 7.73 (d, 1H, \(J = 8.8\) Hz), 7.62 (d, 1H, \(J = 8.3\) Hz), 7.26–7.22 (m, 1H), 7.04–7.01 (m, 1H), 1.71 (s, 9H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta_C = 148.3, 125.6, 121.4, 121.3, 120.2, 119.3, 117.5, 60.0, 30.2\). HR-MS (ESI+) m/z calculated for [C\textsubscript{11}H\textsubscript{15}N\textsubscript{2}]\textsuperscript{t} = [M+H]\textsuperscript{t}: 175.1230; found: 175.1230.

\[ \text{N,N-diethyl-4-(2\textit{H}-indazol-2-yl)pentan-1-amine (3n):} \] Reaction time = 50 min; Brown liquid (95%). IR (MIR-ATR, 4000–600 cm\textsuperscript{-1}): \textit{v}_{\text{max}} = 3058, 2968, 2933, 287, 2800, 1627, 1513, 1454, 1382, 1291, 1200, 1138, 1069, 972, 754, 665. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta_H = 7.92\) (s, 1H), 7.71 (d, 1H, \(J = 8.3\) Hz), 7.64 (d, 1H, \(J = 8.3\) Hz), 7.27–7.23 (m, 1H), 7.07–7.03 (m, 1H), 4.63–4.54 (m, 1H), 2.59–2.31 (m, 6H), 2.07 (ddt, 1H, \(J_a = 19, J_b = 8.7\) and \(J_c = 5.3\) Hz), 1.93–1.84 (m, 1H), 1.64 (d, 3H, \(J = 6.8\) Hz), 1.46–1.36 (m, 1H), 1.29–1.21 (m, 1H), 1.01–0.93 (m, 6H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta_C = 148.4, 125.6, 121.5, 121.4, 120.8, 120.1, 117.5, 60.1, 52.4, 46.7, 35.4, 23.8, 21.9, 11.5\). HR-MS (ESI+) m/z calculated for [C\textsubscript{16}H\textsubscript{26}N\textsubscript{3}]\textsuperscript{t} = [M+H]\textsuperscript{t}: 260.2121; found: 260.2125.

5-Bromo-2-phenyl-2\textit{H}-indazole (3o):\textsuperscript{[2]} Reaction time = 50 min; Cream solid (90%), Mp 126–128 °C. IR (MIR-ATR, 4000–600 cm\textsuperscript{-1}): \textit{v}_{\text{max}} = 3745, 3127, 2920, 2849, 1597, 1509, 1463, 1371,
1199, 1039, 872, 807, 753, 727. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 8.36-8.34$ (m, 1H), 7.88 (d, 3H, $J = 8.3$ Hz), 7.68 (d, 1H, $J = 9.3$ Hz), 7.53 (t, 2H, $J = 7.6$ Hz), 7.44-7.37 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta_C = 148.3$, 140.2, 130.5, 129.7, 128.3, 123.9, 122.5, 121.0, 119.9, 119.7, 116.0. HR-MS (ESI+) m/z calculated for [C$_{13}$H$_{10}$BrN$_2$]$^+$ = [M+H]$^+$: 273.0022; found: 273.0016.

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2-(5-Bromo-2H-indazole-2-yl)aniline (3p): Reaction time = 60 min; Pale brown solid (87%), Mp 88–90 °C. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{\text{max}} = 3746, 3457, 3336, 2923, 2853, 2312, 1993, 1618, 1510, 1454, 1367, 1188, 1037, 802, 749$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 8.17$ (s, 1H), 7.9 (d, 1H, $J = 8.8$ Hz), 7.4 (dd, 1H, $J_a = 9$ and $J_b = 1.7$ Hz), 7.33-7.31 (m, 1H), 7.27-7.22 (m, 1H), 6.90-6.82 (m, 2H), 4.87 (br s, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta_C = 147.8$, 141.3, 130.3, 129.7, 126.1, 124.9, 123.1, 123.0, 122.5, 119.2, 118.2, 117.6. HR-MS (ESI+) m/z calculated for [C$_{13}$H$_{10}$BrN$_3$]$^+$ = [M+H]$^+$: 288.0131; found: 288.0131.

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5-Bromo-2-(pyridine-2-yl)-2H-indazole (3q):$^{[9]}$ Reaction time = 60 min; Yellow solid (89%), Mp 176–178 °C. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{\text{max}} = 3143, 2921, 2851, 1621, 1592, 1502, 1431, 1368, 1194, 1056, 1035, 802, 776$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta_H = 9.05$ (s, 1H), 8.52-8.51 (m, 1H), 8.26 (d, 1H, $J = 8.3$ Hz), 7.93-7.88 (m, 2H), 7.64 (d, 1H, $J = 8.8$ Hz), 7.39-7.27 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta_C = 151.5$, 148.9, 148.4, 139.0, 131.2, 123.5, 123.2, 123.1, 120.0, 119.8, 116.8, 114.1. HR-MS (ESI+) m/z calculated for [C$_{13}$H$_9$BrN$_3$]$^+$ = [M+H]$^+$: 273.9974; found: 273.9964.
2-Benzyl-5-bromo-2H-indazole (3r): Reaction time = 50 min; Brown solid (93%), Mp 52–54 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3063, 3031, 2934, 1730, 1500, 1454, 1342, 1141, 1039, 803, 706 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 7.82 \) (s, 1H), 7.77 (d, 1H, \( J = 1 \) Hz), 7.6 (d, 1H, \( J = 8.8 \) Hz), 7.38-7.31 (m, 4H), 7.27-7.25 (m, 2H), 5.56 (s, 2H). \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta_C = 147.3, 135.4, 129.6, 129.0, 128.6, 128.0, 123.3, 122.4, 122.3, 119.3, 115.3, 57.7 \). HR-MS (ESI⁺) m/z calculated for [C₁₄H₁₁BrN₂]⁺ = [M+H]⁺: 287.0178; found: 287.0170.

6-Bromo-2-phenyl-2H-indazole (3s): Reaction time = 50 min; Peach solid (86%), Mp 102–104 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3126, 3080, 3056, 1620, 1594, 1536, 1506, 1462, 1375, 1203, 1034, 920, 808, 758, 685 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 8.39 \) (s, 1H), 7.99 (s, 1H), 7.89 (d, 2H, \( J = 7.8 \) Hz), 7.61-7.52 (m, 3H), 7.45-7.41 (m, 1H), 7.22 (dd, 1H, \( J_a = 9.3 \) and \( J_b = 1.5 \) Hz). \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta_C = 150.4, 140.2, 129.7, 128.2, 126.3, 121.8, 121.3, 121.0, 120.9, 120.8, 120.3 \). HR-MS (ESI⁺) m/z calculated for [C₁₃H₁₀BrN₂]⁺ = [M+H]⁺: 273.0022; found: 273.0011.

2-(6-Bromo-2H-indazol-2-yl)aniline (3t): Reaction time = 60 min; Pale yellow solid (84%), Mp 176–178 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3457, 3336, 2923, 2853, 2312, 1993, 1618, 1510, 1454, 1367, 1188, 1037, 802, 749 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 8.2 \) (s, 1H), 7.95 (s, 1H), 7.62 (d, 1H, \( J = 8.8 \) Hz), 7.33-7.22 (m, 4H), 6.96-6.80 (m, 2H), 4.86 (br s, 2H). \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta_C = 150.1, 148.5, 141.3, 129.7, 127.7, 126.2, 124.9, 121.8, \)
120.8, 120.4, 119.9, 119.6, 118.2, 117.9, 110.7. HR-MS (ESI+) m/z calculated for [C_{13}H_{10}BrN_{3}]^+ = [M+H]^+: 288.0131; found: 288.0131.

6-Bromo-2-(4-methoxybenzyl)-2H-indazole (3u): Reaction time = 50 min; Pale yellow solid (90%), Mp 88–90 °C. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \(\nu_{\text{max}}\) = 3124, 2933, 2835, 1612, 1513, 1248, 1176, 1035, 911, 807, 735, 593. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_H\) = 7.9 (s, 1H), 7.82 (s, 1H), 7.48 (d, \(J = 8.8\) Hz), 7.26 (d, 2H, \(J = 8.8\) Hz), 7.14 (dd, 1H, \(J_a = 8.8\) and \(J_b = 1.5\) Hz), 6.9 (d, 2H, \(J = 8.3\) Hz), 5.5 (s, 2H), 3.8 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta_C\) = 159.8, 149.6, 129.7, 127.3, 125.4, 123.0, 121.6, 120.6, 120.0, 114.4, 57.1, 55.3. HR-MS (ESI+) m/z calculated for [C_{15}H_{14}BrN_{2}O]^+ = [M+H]^+: 317.0284; found: 317.0275.

6-Bromo-2-(6-methylpyridin-2-yl)-2H-indazole (3v): Reaction time = 70 min; Cream solid (87%), Mp 110–112 °C. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \(\nu_{\text{max}}\) = 3164, 3040, 2918, 1621, 1630, 1577, 1497, 1477, 1455, 1371, 1266, 1209, 1077, 1034, 989, 922, 844, 790, \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta_H\) = 9.12 (s, 1H), 8.04 (d, 1H, \(J = 8.3\) Hz), 7.94 (s, 1H), 7.78 (t, 1H, \(J = 7.8\) Hz), 7.6 (d, 1H, \(J = 8.8\) Hz), \(J = 7.17\) (d, 2H, \(J = 7.3\) Hz), 2.62 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta_C\) = 157.9, 150.9, 150.7, 139.0, 126.4, 122.6, 122.5, 121.5, 121.1, 120.8, 120.4, 110.9, 24.24. HR-MS (ESI+) m/z calculated for [C_{13}H_{11}BrN_{3}]^+ = [M+H]^+: 288.0131; found: 288.0130.
2-(4-methoxybenzyl)-2H-benzo[g]indazole (3w): Reaction time = 90 min; Brown solid (75%), Mp 110–112 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3050, 2930, 2835, 1612, 1512, 1460, 1247, 1177, 1032, 955, 813, 746, 697 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 8.59 \) (d, 1H, \( J = 7.8 \) Hz), 7.79-7.75 (m, 2H), 7.58-7.49 (m, 2H), 7.46 (d, 1H, \( J = 9.3 \) Hz), 7.33 (d, 1H, \( J = 8.8 \) Hz), 7.25 (d, 2H, \( J = 8.8 \) Hz), 6.87 (d, 2H, \( J = 8.8 \) Hz), 5.55 (s, 2H), 3.77 (s, 3H). \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta_C = 159.6, 146.3, 132.4, 129.6, 128.3, 128.1, 126.5, 125.5, 123.6, 123.5, 122.3, 119.1, 118.4, 114.3, 56.7, 55.3 \). HR-MS (ESI+) m/z calculated for \([\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}]^+ = [\text{M+H}]^+\): 289.1335; found: 289.1329.

2-Benzyl-2H-benzo[g]indazole (3x): Reaction time = 100 min; Olive green solid (68 %), Mp 50–52 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3481, 3308, 3052, 3030, 2929, 1651, 1613, 1546, 1456, 1426, 1326, 1143, 1101, 812, 739, 696.562 \). \(^1\)H NMR (CDCl₃, 400 MHz): \( \delta_H = 8.61 \) (d, 1H, \( J = 7.8 \) Hz), 7.81-7.79 (m, 2H), 7.60-7.52 (m, 2H), 7.51-7.45 (m, 1H), 7.37-7.31 (m, 4H), 7.29-7.24 (m, 2H), 5.63 (s, 2H). \(^{13}\)C NMR (CDCl₃, 100 MHz): \( \delta_C = 146.4, 136.2, 132.2, 129.6, 128.9, 128.6, 128.3, 128.2, 127.9, 126.5, 125.6, 123.9, 123.7, 122.4, 121.8, 119.1, 118.4, 116.1, 57.2 \). HR-MS (ESI+) m/z calculated for \([\text{C}_{18}\text{H}_{15}\text{N}_2]^+ = [\text{M+H}]^+\): 259.1230; found: 259.12403.
Isolated intermediate (5) and its spectral data:

6-(2-methoxyphenyl)-5,6-dihydroindazolo[2,3-a]quinoxaline (5): lemon yellow solid (99%), Mp 48–50 °C. IR (MIR-ATR, 4000–600 cm⁻¹): ʋmax = 3271, 3064, 2935, 2835, 1602, 1583, 1494, 1464, 1359, 1250, 1102, 744, 677. ¹H NMR (CDCl₃, 400 MHz): δH = 8.16 (d, 1H, J = 7.8 Hz), 7.77 (d, 1H, J = 8.8 Hz), 7.29-7.25 (m, 2H), 7.1 (d, 1H, J = 8.8 Hz), 7.06 (td, 1H, Ja = 7.7 and Jb = 1.2 Hz), 6.96-6.86 (m, 3H), 6.80-6.74 (m, 2H), 6.68 (d, J = 7.3 Hz), 6.61 (s, 1H), 4.78 (br.s, 1H), 3.92 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz): δC = 156.3, 149.4, 136.5, 129.6, 128.9, 128.4, 128.1, 127.8, 126.8, 124.7, 121.6, 120.9, 119.5, 119.1, 119.0, 117.5, 117.4, 114.8, 110.6, 55.5, 49.2. HR-MS (ESI+) m/z calculated for [C₂₁H₁₈N₃O]⁺ = [M+H]⁺: 328.1444; found: 328.1432.

6-(2-Methoxyphenyl)indazolo[2,3-a]quinoxaline (6a): Yellow color solid (96%), Mp 140-144 °C. IR (MIR-ATR, 4000–600 cm⁻¹): ʋmax = 3064, 2929, 2836, 1602, 1581, 1465, 1359, 1250, 1161, 1024, 952, 745, 677. ¹H NMR (CDCl₃, 400 MHz): δH = 8.9 (dd, 1H, Ja = 8.3 and Jb = 1Hz), 8.3 (dd, 1H, Ja = 7.8 and Jb = 1Hz), 8.07 (s, 1H), 7.82-7.81 (m, 2H), 7.61-7.56 (m, 3H), 7.27-7.15 (m, 4H), 3.36 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δC = 157.4, 152.2, 149.2, 138.2, 131.5, 130.4, 129.1, 128.1, 128.0, 126.8, 123.0, 121.3, 120.8, 117.6, 117.2, 116.4, 111.2, 55.5. HR-MS (ESI+) m/z calculated for [C₂₁H₁₆N₃O]⁺ = [M+H]⁺: 326.1288; found: 326.1292.
6-(3,4-Dimethoxyphenyl)indazolo[2,3-\textit{a}]quinoxaline (6\textit{b}): Off white solid (96\%), Mp 168-170 °C. IR (MIR-ATR, 4000–600 cm\textsuperscript{-1}): \(\nu_{\text{max}} = 3064, 2993, 2835, 1603, 1578, 1502, 1432, 1260, 1138, 1025, 950, 760, 674\). \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta_{\text{H}} = 8.80\ (d, 1\text{H}, J = 7.8\ \text{Hz}),\ 8.19\ (d, 1\text{H}, J = 8.3\ \text{Hz}),\ 7.72\text{-7.65\ (m, 3\text{H})},\ 7.52\text{-7.47\ (m, 3\text{H})},\ 7.20\text{-7.17\ (m, 1\text{H})},\ 7.09\ (d, 1\text{H}, J = 8.3\ \text{Hz}),\ 4.01\ (s, 3\text{H}),\ 3.96\ (s, 3\text{H})\). \(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta_{\text{C}} = 153.7,\ 150.8,\ 149.2,\ 138.0,\ 130.4,\ 129.7,\ 128.8,\ 128.1,\ 128.0,\ 127.7,\ 125.7,\ 122.9,\ 121.9,\ 121.4,\ 117.4,\ 117.2,\ 116.4,\ 111.9,\ 111.1,\ 56.1,\ 56.0\). HR-MS (ESI+) m/z calculated for \([\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2]^+ = [\text{M+H}]^+\): 356.1394; found: 356.1396.

6-(Benzod[\textit{d}][1,3]dioxol-5-\textit{yl})indazolo[2,3-\textit{a}]quinoxaline (6\textit{c}): Pale yellow solid (97\%), Mp 216-218 °C. IR (MIR-ATR, 4000–600 cm\textsuperscript{-1}): \(\nu_{\text{max}} = 3065, 2955, 2923, 2853, 1607, 1577, 1499, 1445, 1358, 1247, 1038, 933, 739, 673\). \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta_{\text{H}} = 8.86\ (dd, 1\text{H}, J_a = 8.3\ \text{and}\ J_b = 1.5\ \text{Hz}),\ 8.23\ (dd, 1\text{H}, J_a = 7.6\ \text{and}\ J_b = 1.2\ \text{Hz}),\ 8.07\ (d, 1\text{H}, J = 8.8\ \text{Hz}),\ 7.80\text{-7.73\ (m, 3\text{H})},\ 7.58\ (t, 1\text{H}, J = 7.6\ \text{Hz}),\ 7.48\text{-7.43\ (m, 2\text{H})},\ 7.29\text{-7.25\ (m, 1\text{H})},\ 7.07\ (d, 1\text{H}, J = 7.8\ \text{Hz}),\ 6.13\ (s, 2\text{H})\). \(^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta_{\text{C}} = 153.8,\ 149.9,\ 149.6,\ 148.5,\ 138.3,\ 132.0,\ 130.1,\ 129.2,\ 128.5,\ 128.4,\ 128.0,\ 126.0,\ 123.6,\ 123.4,\ 121.6,\ 109.7,\ 108.9,\ 101.9\). HR-MS (ESI+) m/z calculated for \([\text{C}_{21}\text{H}_{14}\text{N}_3\text{O}_2]^+ = [\text{M+H}]^+\): 340.1081; found: 340.1081.
6-(4-Isopropylphenyl)indazolo[2,3-a]quinoxaline (6d): Pale yellow solid (95%), Mp 172-174 °C. IR (MIR-ATR, 4000–600 cm⁻¹): ʋ_max = 3063, 2958, 2868, 1609, 1577, 1478, 1358, 1227, 1105, 954, 831, 759, 744. ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.84 (d, 1H, J = 7.3 Hz), 8.23 (d, 1H, J = 7.8 Hz), 8.03 (d, 1H, J = 8.3 Hz), 2.07 (d, 2H, J = 8.3 Hz), 7.75-7.69 (m, 3H), 7.54-7.49 (m, 3H), 7.21 (t, 1H, J = 7.1 Hz), 3.09 (dt, 1H, J_a = 13.7 and J_b = 6.8 Hz), 1.39 (d, 6H, J = 6.8 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ_C = 154.2, 151.3, 149.3, 138.1, 135.8, 129.9, 128.9, 128.1, 128.0, 127.7, 127.0, 125.8, 123.0, 121.4, 117.4, 117.2, 116.4, 34.3, 24.0. HR-MS (ESI+) m/z calculated for [C_{23}H_{20}N_{3}]⁺ = [M+H]⁺: 338.1652; found: 338.1643.

6-(4-Chlorophenyl)indazolo[2,3-a]quinoxaline (6e): Off white solid (92%), Mp 168-170 °C. IR (MIR-ATR, 4000–600 cm⁻¹): ʋ_max = 3396, 2954, 2922, 2852, 1659, 1550, 1478, 1360, 1227, 1160, 1091, 950, 830, 758, 739. ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.86 (dd, 1H, J_a = 8.3 and J_b = 1.5 Hz), 8.82 (dd, 1H, J_a = 8.1 and J_b = 1.2 Hz), 8.05 (d, 1H, J = 8.8 Hz), 7.88 (d, 2H, J = 8.3 Hz), 7.80-7.71 (m, 2H), 7.63-7.60 (m, 3H), 7.58-7.54 (m, 1H), 7.27-7.23 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ_C = 152.8, 149.3, 138.0, 136.4, 130.3, 129.3, 129.2, 128.3, 128.2, 127.8, 126.5, 123.4, 121.0, 117.6, 117.0, 116.5. HR-MS (ESI+) m/z calculated for [C_{20}H_{17}ClN_{3}]⁺ = [M+H]⁺: 330.0793; found: 330.0793.
6-(2-Nitophenyl)indazolo[2,3-a]quinoxaline (6f): Light brown solid (89%), Mp 178-180 °C. IR (MIR-ATR, 4000–600 cm⁻¹): ʋₘₐₓ = 3065, 2923, 2853, 1608, 1526, 1345, 1228, 1160, 1088, 950, 757, 742, 704. ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.89 (d, 1H, J = 8.3 Hz), 8.38 (d, 1H, J = 8.3 Hz), 8.20 (d, 1H, J = 8.3 Hz), 8.06 (d, 1H, J = 8.3 Hz), 7.91-7.88 (m, 1H), 7.84-7.72 (m, 4H), 7.54 (t, 1H, J = 7.6 Hz), 7.17 (t, 1H, J = 7.6 Hz), 7.02 (d, 1H, J = 8.3 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ_C = 150.7, 149.2, 148.0, 137.8, 132.9, 131.4, 130.9, 130.0, 129.7, 128.3, 128.1, 125.6, 125.3, 123.7, 119.5, 117.7, 116.9, 116.5. HR-MS (ESI+) m/z calculated for [C₂₀H₁₃N₄O₂]⁺ = [M+H]⁺: 341.103; found: 341.1038.

6-(5-Bromo-2-fluorophenyl)indazolo[2,3-a]quinoxaline (6g): Lemon yellow solid (86%), Mp 214-217 °C. IR (MIR-ATR, 4000–600 cm⁻¹): ʋₘₐₓ = 3066, 2920, 2851, 1607, 1575, 1477, 1358, 1210, 1102, 961, 812, 757, 742, 685. ¹H NMR (CDCl₃, 400 MHz): δ_H = 8.86 (d, 1H, J = 8.3 Hz), 8.24 (dd, 1H, J = 8.3 Hz), 8.05 (d, 1H, J = 8.3 Hz), 7.90 (dd, 1H, J_a = 5.9 and J_b = 2.4 Hz), 7.83-7.79 (m, 1H), 7.76-7.71 (m, 2H), 7.57 (t, 1H, J = 7.6 Hz), 7.39 (d, 1H, J = 8.3 Hz), 7.27-7.24 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ_C = 160.6, 158.1, 149.2, 147.3, 137.8, 134.9, 133.9, 133.8, 130.1, 129.8, 128.4, 128.3, 127.7, 127.6, 125.9, 123.7, 120.2, 120.1, 118.3, 118.1, 117.6, 117.5, 117.0, 116.5. HR-MS (ESI+) m/z calculated for [C₂₀H₁₂BrF₃N]⁺ = [M+H]⁺: 392.0193; found: 392.0197.
1-Methyl-6-(4-nitrophenyl)indazolo[2,3-a]quinoxaline (6h): Golden yellow (89%), Mp 236-
238 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3020, 2921, 1624, 1415, 1345, 1297, 1128, 
935, 746, 687 \). \( ^1 \)H NMR (CDCl₃, 400 MHz): \( \delta_H = 8.83 \) (d, 1H, \( J = 7.3 \) Hz), \( 8.48 \) (d, 1H, \( J = 8.3 \) Hz), \( 7.98-7.89 \) (m, 3H), \( 7.80-7.70 \) (m, 3H), \( 6.97 \) (t, 1H, \( J = 7.8 \) Hz), \( 6.08 \) (d, 1H, \( J = 8.3 \) Hz), \( 2.82 \) (s, 3H). \( ^{13} \)C NMR (CDCl₃, 100 MHz): \( \delta_C = 147.1, 146.8, 145.3, 143.8, 
142.1, 135.0, 131.8, 131.7, 131.2, 130.6, 129.9, 128.5, 128.4, 128.1, 126.0, 125.4, 124.5, 122.9, 
118.9, 109.5, 17.1. HR-MS (ESI+) m/z calculated for \([C_{21}H_{15}N_4O_2]^+\): 355.1190 [M+H]^+; found: 
355.1183.

9-Bromo-6-(2-methoxyphenyl)indazolo[2,3-a]quinoxaline (6i): Yellow solid (90%), Mp 180-
182 °C. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}} = 3067, 2998, 2955, 1600, 1580, 1462, 1279, 1247, 
1103, 1024, 931, 751, 682 \). \( ^1 \)H NMR (CDCl₃, 400 MHz): \( \delta_H = 8.85 \) (dd, 1H, \( J_a= 8.3 \) and \( J_b = 
1Hz), 8.29 (dd, 1H, \( J_a = 7.8 \) and \( J_b = 1Hz), 7.92 (d, 1H, \( J = 9.3 \) Hz), 7.84-7.74 (m, 2H), 7.66-
7.59 (m, 3H), 7.35 (d, 1H, \( J = 1.5 \) Hz), 7.26-7.22 (m, 1H), 7.18 (d, 1H, \( J = 8.3 \) Hz), 3.32 (s, 3H). 
\( ^{13} \)C NMR (CDCl₃, 100 MHz): \( \delta_C = 157.2, 152.0, 147.5, 138.3, 131.9, 131.5, 130.5, 130.2, 129.3, 
128.4, 127.9, 126.4, 126.1, 123.3, 121.5, 118.8, 118.7, 116.4, 116.3, 111.2, 55.5. HR-MS (ESI+) 
m/z calculated for \([C_{21}H_{15}BrN_3O]^+\) = [M+H]^+: 404.0393; found: 404.0398.
Copies of $^1\text{H}$, $^{13}\text{C}$ NMR Spectra of all Compounds (S3, S4, 3a-w, 5 and 6a-i):
$^1$H NMR (400 MHz) spectrum of compound S3 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound S3 in CDCl$_3$
$^{1}$H NMR (400 MHz) spectrum of compound S4 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound S4 in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3a in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3a in CDCl$_3$
$^{1}$H NMR (400 MHz) spectrum of compound 3b in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3b in CDCl$_3$
\textbf{1}^\text{H} \text{NMR} (400 \text{ MHz}) \text{ spectrum of compound } 3c \text{ in CDCl}_3

\begin{figure}
\centering
\includegraphics[width=\textwidth]{1HNMR_spectrum.png}
\end{figure}

\textbf{13}^\text{C} \text{NMR} (100 \text{ MHz}) \text{ spectrum of compound } 3c \text{ in CDCl}_3

\begin{figure}
\centering
\includegraphics[width=\textwidth]{13CNMR_spectrum.png}
\end{figure}
\(^1H\) NMR (400 MHz) spectrum of compound 3d in CDCl\(_3\)

\(^13C\) NMR (100 MHz) spectrum of compound 3d in CDCl\(_3\)
$^1$H NMR (400 MHz) spectrum of compound 3e in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3e in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3f in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3g in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3g in CDCl$_3$
$^1$H NMR (400MHz) spectrum of compound 3h in CDCl$_3$ 

$^{13}$C NMR (100MHz) spectrum of compound 3h in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3i in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3i in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3j in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3j in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3k in CDCl$_3$  

$^{13}$C NMR (100 MHz) spectrum of compound 3k in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3l in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3l in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3m in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3m in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3n in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3n in CDCl$_3$
\( ^1H \) NMR (400 MHz) spectrum of compound \( 3o \) in CDCl\(_3\)

\( ^{13}C \) NMR (100 MHz) spectrum of compound \( 3o \) in CDCl\(_3\)
\[ ^1H \text{ NMR (400 MHz) spectrum of compound 3p in CDCl}_3 \]

\[ ^{13}C \text{ NMR (100 MHz) spectrum of compound 3p in CDCl}_3 \]
$^1$H NMR (400 MHz) spectrum of compound 3q in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3q in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3r in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3r in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3s in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3s in CDCl$_3$
\textsuperscript{1}H NMR (400 MHz) spectrum of compound 3t in CDCl\textsubscript{3}

\textsuperscript{13}C NMR (100 MHz) spectrum of compound 3t in CDCl\textsubscript{3}
$^1$H NMR (400 MHz) spectrum of compound 3u in CDCl$_3$  

$^{13}$C NMR (100 MHz) spectrum of compound 3u in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3v in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3v in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3w in CDCl$_3$

$^{13}$C NMR (100MHz) spectrum of compound 3w in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 3x in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 3x in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 5 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 5 in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6a in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6a in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6b in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6b in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6c in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6c in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6d in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6d in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6e in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6e in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6f in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6f in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6g in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6g in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6h in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6h in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of compound 6i in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of compound 6i in CDCl$_3$
References: