Electronic Supplementary Information

Four-component, three-step cascade reaction: An effective synthesis of indazole fused triazolo[5,1-c]quinoxalines

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Table of content

1. Optimization Data.................................................................................................................................................. S-1
2. Table S1: Optimization of reaction conditions for the formation of intermediate 6a................................................................. S-2
3. Table S2: One-pot sequential cascade synthesis of indazole fused triazolo [5,1-c] Quinoxalines(7) ........................................................................................................ S-3
4. Chemistry: General methods....................................................................................................................................... S-8
5. Procedure for the synthesis of compound 7.................................................................................................................. S-8
6. Analytical data of 7....................................................................................................................................................... S-9
7. Procedure for the synthesis of compound 3 and 6a.......................................................... S-18
8. Single crystal X-ray data for compound 7q ................................................................................................................. S-20
9. References ............................................................................................................................................................... S-20
10. Copies of 1H and 13C NMR spectra of compounds ............................................................................................... S-21
1. Optimization Data:
Initially, CuI and K$_2$CO$_3$ in DMF at 120 °C. The reaction was completed within 2 h affording the desired 2-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)-2H-indazole$^{6a}$ in 88% yield (entry 1, Table 1). The use of other Cu catalysts, e.g. Cu(OAc)$_2$, Cu(OAc)$_2$:H$_2$O and CuCl was found to be less effective (entries 2-4, Table 1). The use of other bases e.g. Cs$_2$CO$_3$, Na$_2$CO$_3$ and DBU was found to be less effective (entries 5-7, Table 1). Further, the solvents, such as DMSO, CH$_3$CN, toluene and ethanol (entries 8-11, Table 1) were also studied but found to be less effective than DMF. By lowering the reaction temperature to 90 °C led to poor substrate conversion (entry 12, Table 1). By lowering or increased the reaction time led to poor yield (entry 13 and 14, Table 1). Overall, the combination of CuI and K$_2$CO$_3$ in DMF at 120 °C under air for 2 h (entry 1, Table 1) is the optimised condition for the synthesis of $^{6a}$.

2. Table S1: Optimization of reaction conditions for the formation of intermediate $^{6a}$

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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Solvent</th>
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3. Table S2: One-pot sequential cascade synthesis of indazole fused triazolo[5,1-c]quinoxalines (7):

**Entry** | **o-Iodoaniline (2)** | **Acetylene (4)** | **Indazole fused triazolo[5,1-c]quinoxalines (7)** | **Yield** \(^b\) (%)
--- | --- | --- | --- | ---
1 | 2a | 4a | 7a | 71
2 | 2a | 4b | 7b | 68
3 | 2a | 4c | 7c | 68

aReaction conditions: 1a (0.67 mmol) and 2a (0.67 mmol) was heated at 110 °C, 40 min, and then 4a (0.67 mmol), 5 (0.67 mmol), catalyst (10 mol%), base (0.81 mmol), solvent (3 mL), air. bIsolated yields.
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$^a$Reaction conditions: 1a (0.67 mmol) and 2a (0.67 mmol) was heated at 110 °C, 40 min, and then 4a (0.67 mmol), 5 (0.67 mmol), CuI (10 mol%), K2CO3 (0.81 mmol), DMF (3 mL), air, 2 h followed by Pd catalyst (10 mol %), Cu(OAc)$_2$ (1.01 mmol), AcOH (2.03 mmol), O2 additive at 120 °C for 16 h. $^b$Isolated yields.
Chemistry

General methods: Unless stated otherwise, solvents and chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (100-200 mesh) using hexane and ethyl acetate. \(^1\)Hand \(^1\)C NMR spectra were determined in CDCl\(_3\), DMSO-
\(_d_6\) and TFA solutions by using 400 or 100 MHz spectrometers, respectively. Proton chemical shifts (\(\delta\)) are relative to tetramethylsilane (TMS, \(\delta = 0.00\)) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as b (broad). Coupling constants (\(J\)) are given in hertz. Melting points were determined using a melting point apparatus and are uncorrected. MS spectra were obtained on a mass spectrometer. HRMS data were recorded by electrospray ionization with a Q-TOF mass analyzer. 2-Azidobenzaldehyde\(^1\) were prepared according to the known procedure.

General Procedure for the One-pot sequential cascade synthesis of indazole fused triazolo[5,1-c]quinoxalines (7):

2-Azidobenzaldehyde (1a) (0.67 mmol), 2-Iodoaniline (2a) (0.67 mmol) were taken in an oven dried Schlenck tube and it was closed with nitrogen balloon and stirred for 40 min at 110 °C. The completion of first step was monitored by TLC. Upon cooling to room temperature, Alkyne (4) (0.67 mmol), NaN\(_3\) (5) (0.67 mmol), CuI (10 mol%), \(\text{K}_2\text{CO}_3\) (0.81 mmol) and DMF (3 ml) solvent were added in same pot and the resulting reaction mixture was heated at 120 °C for 2 h under open air. After completion of the reaction was monitored by TLC, to the same pot Pd(OAc)\(_2\) (10 mol%), Cu(OAc)\(_2\) (1.01 mmol), AcOH (2.03 mmol) was added. Subsequently, the vessel was placed under vacuum and backfilled with O\(_2\). The resulting reaction mixture was stirred at 120 °C for 16h. Then, it was quenched with saturated NH\(_4\)Cl (10 mL) and extracted with EtOAc (10 mL \(\times\) 3). The combined EtOAc layer was collected, dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated. The residue was purified using column chromatography over silica gel with EtOAc / hexane to give desired product of (7).
1-Phenylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7a):

Yellow solid; Yield: 71%; mp: 198-201 °C; Rf = 0.4 (20% EtOAc/ n-hexane); 1H NMR (400 MHz, CDCl3): δ 8.81 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 8.8 Hz, 1H), 7.80-7.75 (m, 4H), 7.62 (d, J = 6.4 Hz, 3H), 7.42 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 159.7, 149.2, 131.0, 130.8, 130.6 (2C), 129.6, 129.4, 129.2 (2C), 127.7, 126.0, 124.4, 123.6, 121.5, 121.4, 118.3, 117.6, 117.4, 117.1, 113.5; HR-MS (ESI+) m/z calculated for [C21H14N3]+ = [M + H]+ 336.1250, found 336.1249.

1-(p-Tolyl)indazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7b):

Yellow solid; Yield: 68%; mp: 221-223 °C; Rf = 0.5 (20% EtOAc/ n-hexane); 1H NMR (400 MHz, CDCl3): δ 8.82-8.79 (m, 2H), 7.88 (d, J = 8.8 Hz, 1H), 7.79-7.72 (m, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.8 Hz, 3H), 7.03-6.95 (m, 2H), 2.55 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 149.5, 141.8, 139.5, 130.4 (2C), 129.3 (2C), 128.9, 128.4, 128.0, 127.7, 125.8, 125.7, 124.3, 123.0, 122.7, 121.9, 118.3, 117.5, 117.3, 117.0, 21.6; HR-MS (ESI+) m/z calculated for [C22H16N3]+ = [M + H]+ 350.1400, found 350.1406.

1-(4-Methoxyphenyl)indazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7c):

White color solid; Yield: 68%; mp: 235-240 °C; Rf = 0.4 (20% EtOAc/ n-hexane); 1H NMR (400 MHz, CDCl3): δ 8.80-8.79 (m, 2H), 7.88 (d, J = 8.4 Hz, 1H), 7.75 (t, J = 5.6 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.04-6.97 (m, 2H), 3.97 (s, 3H); 13C NMR (100 MHz, CDCl3): δ 160.7, 149.6, 141.6 (2C), 131.9 (2C), 128.9,
128.4, 128.1, 125.8, 124.3, 123.1, 123.0, 122.7, 121.9, 118.3, 117.6, 117.3, 117.1, 114.1 (2C), 55.5; HR-MS (ESI+) m/z calculated for [C_{22}H_{16}N_{5}O]^+ = [M + H]^+ 366.1363, found 366.1355.

1-(Pyridin-2-yl)indazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7d):

Yellow solid; Yield: 65%; mp: 158-160 °C; R_f= 0.5 (50% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.95-8.90 (m, 3H), 8.18 (d, \(J = 7.6\) Hz, 1H), 7.99 (t, \(J = 7.0\) Hz, 1H), 7.92 (d, \(J = 8.8\) Hz, 1H), 7.81-7.73 (m, 2H), 7.51-7.45 (m, 3H), 7.12 (t, \(J = 7.6\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.7, 149.7, 149.4, 141.3, 137.0, 129.1, 128.4, 128.0, 125.8, 124.8, 124.0, 123.8, 123.2, 122.9, 122.7, 121.4, 118.3, 118.1, 117.6, 117.1; HR-MS (ESI+) m/z calculated for [C\(_{20}\)H\(_{18}\)N\(_{6}\)]^+ = [M + H]^+ 337.1198, found 337.1202.

1-Butylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7e):

Pale yellow solid; Yield:62%; mp: 166-168 °C; R_f= 0.6 (10% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.76 (dd, \(J_1 = 9.2\) Hz, \(J_2 = 9.2\) Hz, 2H), 8.18 (d, \(J = 8.8\) Hz, 1H), 7.94 (d, \(J = 8.8\) Hz, 1H), 7.76-7.68 (m, 2H), 7.53 (t, \(J = 7.8\) Hz, 1H), 7.54 (t, \(J = 7.6\) Hz, 1H), 3.47 (t, \(J = 7.8\) Hz,2H), 2.00-1.96 (m, 2H), 1.62-1.52 (m, 2H), 1.02 (t, \(J = 7.4\) Hz, 3H ); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.3, 141.7, 128.6, 128.2, 128.0, 125.4, 124.2, 123.4, 122.8, 122.1, 120.0, 118.2, 117.9, 117.0, 116.8, 32.1, 26.9, 22.4, 13.9; HR-MS (ESI+) m/z calculated for [C\(_{19}\)H\(_{18}\)N\(_{5}\)]^+ = [M + H]^+ 316.1555, found 316.1562.

1-Pentylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7f):

White solid: Yield: 68%; mp: 158-160 °C; R_f= 0.4 (20% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.74 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 8.8\) Hz, 2H), 8.15 (d, \(J = 8.4\) Hz, 1H), 7.92 (d, \(J =
8.8 Hz, 1H), 7.74-7.68 (m, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 3.45 (t, J = 7.8 Hz, 2H), 2.01-1.94 (m, 2H), 1.57-1.52 (m, 2H), 1.48-1.38 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.5, 141.9, 128.7, 128.3, 128.1, 125.6, 124.3, 123.5, 122.9, 122.2, 120.1, 118.2, 118.0, 117.1, 116.9, 31.5, 29.8, 27.2, 22.5, 14.0; HR-MS (ESI+) m/z calculated for [C₂₀H₂₀N₅]⁺ = [M + H]⁺ 330.1716, found 330.1719.

1-Hexylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7g):

![Image of 1-Hexylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7g)]

Pale yellow solid; Yield: 67%; mp: 132-135 °C; Rᶠ = 0.4 (10% EtOAc/ n-hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.71 (dd, J₁ = 9.6 Hz, J₂ = 9.6 Hz, 2H), 8.12 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.73-7.66 (m, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 3.42 (t, J = 7.8 Hz, 2H), 1.99-1.92 (m, 2H), 1.60-1.53 (m, 2H), 1.42-1.30 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.4, 141.8, 128.6, 128.2, 128.0, 125.5, 124.2, 123.4, 122.8, 122.1, 120.0, 118.2, 117.9, 117.0, 116.8, 31.6, 30.0, 29.0, 27.2, 22.6, 14.1; HR-MS (ESI+) m/z calculated for [C₂₁H₂₂N₅]⁺ = [M + H]⁺ 344.1882, found 344.1875.

6-Methyl-1-phenylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7h):

![Image of 6-Methyl-1-phenylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7h)]

Light yellow solid; Yield: 70%; mp: 213-215 °C; Rᶠ = 0.5 (20% EtOAc/ n-hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.67 (d, J = 8.8 Hz, 1H), 8.61 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 6.0 Hz, 2H), 7.59 (t, J = 12.0 Hz, 4H), 7.41 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 2.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆): δ 153.8, 146.0, 144.0, 135.4, 135.3 (2C), 134.8, 134.3, 133.3 (2C), 132.5, 128.5, 128.2, 127.6, 127.5, 126.3, 125.7, 122.6, 122.1, 121.7, 121.3, 26.3; HR-MS (ESI+) m/z calculated for [C₂₂H₁₆N₅]⁺ = [M + H]⁺ 350.1402, found 350.1406.

6-Methyl-1-(p-tolyl)indazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7i):
White solid; Yield: 66%; mp: 215-217 °C; Rf = 0.6 (20% EtOAc/ n-hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.68 (d, $J = 8.4$ Hz, 1H), 8.61 (s, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 3H), 7.03-6.95 (m, 2H), 2.65 (s, 3H), 2.54 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.3, 141.6, 139.4, 139.2, 130.4 (2C), 129.9, 129.2 (2C), 127.8, 127.7, 123.9, 123.5, 122.7 (2C), 121.9, 121.4, 117.9, 117.4, 117.1, 116.7, 21.6 (2C); HR-MS (ESI+) m/z calculated for [C$_{23}$H$_{18}$N$_3$]$^+$ = [M + H]$^+$ 364.1561, found 364.1562.

6-Methyl-1-(pyridin-2-yl)indazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7j):

Yellow solid; Yield: 65%; mp: 197-200 °C; Rf = 0.6 (50% EtOAc/ n-hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.85 (d, $J = 4.4$ Hz, 1H), 8.69 (d, $J = 8.4$ Hz, 1H), 8.61 (s, 1H), 8.17 (d, $J = 8.0$ Hz, 1H), 7.98 (t, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.8$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.51-7.43 (m, 3H), 7.10 (t, $J = 7.6$ Hz, 1H), 2.65 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.7, 149.5, 149.4, 141.1, 139.2, 137.0, 130.2, 127.7, 124.8, 123.7 (2C), 123.2, 122.7 (2C), 121.4, 118.0 (2C), 117.4, 116.8 (2C), 21.6; HR-MS (ESI+) m/z calculated for [C$_{21}$H$_{18}$N$_6$]$^+$ = [M + H]$^+$ 351.1357, found 351.1358.

1-Butyl-6-methylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7k):

Whitesolid; Yield:65%; mp: 177-179 °C; Rf = 0.5 (20% EtOAc/ n-hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.63 (d, $J = 8.4$ Hz, 1H), 8.52 (s, 1H), 8.16 (d, $J = 8.8$ Hz, 1H), 7.92 (d, $J = 8.8$ Hz, 1H), 7.51 (t, $J = 9.6$ Hz, 2H), 7.32 (t, $J = 7.8$ Hz, 1H), 3.45 (t, $J = 7.8$ Hz, 2H), 2.62 (s, 3H), 2.0-1.92 (m, 2H), 1.62-1.57 (m, 2H), 1.02 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz,
CDCl₃): δ 149.2, 141.6, 139.0, 129.7, 127.8, 124.0, 123.3, 123.2, 122.9, 121.7, 120.0, 117.9, 117.8, 116.9, 116.6, 32.1, 26.9, 22.4, 21.5, 13.9; HR-MS (ESI+) m/z calculated for [C₂₀H₂₀N₅]⁺ = [M + H]⁺ 330.1714, found 330.1719.

6-Methyl-1-pentylindazolo[2,3-α][1,2,3]triazolo[5,1-c]quinoxaline (7l):

White solid; Yield: 68%; mp: 126-128 °C; Rᵢₒ = 0.4 (20% EtOAc/ n-hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H), 8.13 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.51 (t, J = 4.6 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 3.43 (t, J = 7.8 Hz, 2H), 2.61 (s, 3H), 1.99-1.94 (m, 2H), 1.59-1.53 (m, 2H ), 1.45-1.39 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H);
¹³C NMR (100 MHz, CDCl₃): δ 149.2, 141.6, 139.0, 129.7, 127.8, 124.0, 123.3, 123.2, 122.9, 121.7, 120.0, 117.9, 117.8, 116.9, 116.6, 31.5, 29.7, 27.2, 22.5, 21.5, 14.1; HR-MS (ESI+) m/z calculated for [C₂₁H₂₂N₅]⁺ = [M + H]⁺ 344.1880, found 344.1875.

1-Hexyl-6-methylindazolo[2,3-α][1,2,3]triazolo[5,1-c]quinoxaline (7m):

White solid; Yield: 68%; mp: 125-127 °C; Rᵢₒ = 0.4 (20% EtOAc/ n-hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, J = 8.0 Hz, 1H), 8.50 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.30 (t, J = 9.2 Hz, 1H), 3.43 (t, J = 7.6 Hz, 2H), 2.61 (s, 3H), 1.99-1.92 (m, 2H), 1.59-1.53 (m, 2H ), 1.42-1.32 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H);
¹³C NMR (100 MHz, CDCl₃): δ 149.2, 141.6, 139.0, 129.7, 127.7, 124.0, 123.3, 123.2, 122.9, 121.7, 120.0, 117.9, 117.7, 116.9, 116.6, 31.6, 30.0, 29.0, 27.2, 22.6, 21.5,14.1; HR-MS (ESI+) m/z calculated for [C₂₂H₂₄N₅]⁺ = [M + H]⁺ 358.2032, found 358.2032.

6,8-Dimethyl-1-phenylindazolo[2,3-α][1,2,3]triazolo[5,1-c]quinoxaline (7n):
Off white solid; Yield: 65%; mp: 205-210 °C; Rf= 0.6 (20% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.54 (s, 1H), 7.83 (d, \(J = 8.8\) Hz, 1H), 7.75-7.73 (m, 2H), 7.60-7.57 (m, 3H), 7.34 (d, \(J = 10.0\) Hz, 2H), 6.95 (t, \(J = 7.6\) Hz, 1H), 6.84 (d, \(J = 8.8\) Hz, 1H), 3.23 (s, 3H), 2.58 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.5, 140.9, 138.2, 133.6, 131.2, 131.0, 130.6 (2C), 129.4, 128.5 (2C), 127.2, 125.1, 122.8, 122.6, 122.5, 121.7, 121.4, 117.7, 116.0, 114.9, 24.6, 21.2; HR-MS (ESI+) m/z calculated for \([C_{23}H_{18}N_3]^+ = [M + H]^+\) 364.1554, found 364.1562.

**6,8-Dimethyl-1-(p-toly)indazolo[2,3-\(a\)]1,2,3triazolo[5,1-c]quinoxaline (7o):**

![Structure Image]

Yellow solid; Yield: 60%; mp: 203-205 °C; Rf= 0.6 (10% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.47 (s, 1H), 7.82 (d, \(J = 8.8\) Hz, 1H), 7.64 (d, \(J = 8.0\) Hz, 2H), 7.41 (d, \(J = 7.6\) Hz, 2H), 7.36 (t, \(J = 7.6\) Hz, 1H), 7.30 (s, 1H), 6.97 (t, \(J = 7.4\) Hz, 1H), 6.92 (d, \(J = 8.4\) Hz, 1H), 3.17 (s, 3H), 2.56 (s, 3H), 2.55 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.6, 141.1, 139.3, 138.2, 133.7, 131.3, 130.4 (2C), 129.2 (2C), 128.1, 127.2, 125.2, 122.7 (2C), 122.4, 122.0, 121.7, 117.7, 116.1, 114.9, 24.6, 21.6, 21.2; HR-MS (ESI+) m/z calculated for \([C_{24}H_{20}N_3]^+ = [M + H]^+\) 378.1730, found 378.1719.

**1-(4-Methoxyphenyl)-6,8-dimethylindazolo[2,3-\(a\)]1,2,3triazolo[5,1-c]quinoxaline (7p):**

![Structure Image]

Pale yellow solid; Yield: 65%; mp: 215-217 °C; Rf= 0.4 (20% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.42 (s, 1H), 7.79 (d, \(J = 6.8\) Hz, 1H), 7.66 (d, \(J = 6.4\) Hz, 2H), 7.34 (t, \(J = 5.8\) Hz, 1H), 7.26 (s, 1H), 7.12 (d, \(J = 6.4\) Hz, 2H), 6.97-6.90 (m, 2H), 3.97 (s, 3H), 3.13 (s, 3H), 2.52 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.5, 148.6, 140.8, 138.2, 133.6, 131.8 (2C), 131.2, 127.2, 125.2, 123.3, 122.8, 122.6, 122.3, 122.0, 121.5, 117.7, 116.0, 114.9, 114.0
(2C), 55.5, 24.6, 21.2; HR-MS (ESI+) m/z calculated for [C_{23}H_{20}N_5O]^{+} = [M + H]^+ 394.1677, found 394.1668.

1-Butyl-6,8-dimethylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7q):

Off white solid; Yield: 65%; mp: 136-138 °C; Rf = 0.6 (20% EtOAc/ n-hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.46 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.32-7.28 (m, 2H), 3.44 (t, J = 7.8 Hz, 2H), 3.20 (s, 3H), 2.55 (s, 3H), 1.99-1.91 (m, 2H), 1.62-1.54 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆): δ 149.2, 141.8, 138.9, 134.4, 132.1, 128.2, 126.2, 124.3, 123.6, 123.4, 123.3, 120.8, 119.2, 116.9, 115.8, 34.3, 29.3, 27.0, 24.7, 23.5, 16.3; HR-MS (ESI+) m/z calculated for [C_{21}H_{22}N_{5}]^{+} = [M + H]^+ 344.1870, found 344.1875.

6,8-Dimethyl-1-pentylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7r):

Chemical Formula: C_{22}H_{23}N_{5}
Exact Mass: 357.1953

Whitesolid; Yield: 62%; mp: 138-141 °C; Rf = 0.5 (20% EtOAc/ n-hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.49 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.34-7.30 (m, 3H), 3.45 (t, J = 7.8 Hz, 2H), 3.23 (s, 3H), 2.56 (s, 3H), 2.01-1.93 (m, 2H), 1.57-1.52 (m, 2H), 1.46-1.40 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃ + DMSO-d₆): δ 149.1, 141.7, 138.9, 134.4, 132.1, 128.2, 126.1, 124.3, 123.6, 123.4, 123.3, 120.8, 119.1, 116.9, 115.8, 33.6, 31.9, 29.5, 26.9, 24.7, 23.5, 16.4; HR-MS (ESI+) m/z calculated for [C_{22}H_{23}N_{5}]^{+} = [M + H]^+ 358.2036, found 358.2032.

1-Hexyl-6,8-dimethylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7s):
Yellow solid; Yield: 60%; mp: 148-150 °C; Rf = 0.6 (20% EtOAc/ n-hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.44 (s, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.46 (t, $J = 7.8$ Hz, 1H), 7.30-7.26 (m, 2H), 3.42 (t, $J = 7.8$ Hz, 2H), 3.18 (s, 3H), 2.53 (s, 3H), 1.99-1.91 (m, 2H), 1.59-1.52 (m, 2H), 1.40-1.33 (m, 4H), 0.89 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.3, 140.9, 137.9, 133.3, 131.0, 127.1, 125.1, 123.1, 122.4, 122.2, 119.7, 119.6, 118.0, 115.7, 114.7, 31.6, 30.0, 29.0, 27.4, 24.7, 22.6, 21.1, 14.1; HR-MS (ESI+) m/z calculated for [C$_{23}$H$_{26}$N$_3$]$^+$ = [M + H]$^+$ 372.2184, found 372.2188.

6-Fluoro-1-phenylindazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7t):

White solid; Yield: 61%; mp: 231-233 °C; Rf = 0.5 (10% EtOAc/ n-hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.71 (d, $J = 4.0$ Hz, 1H), 8.42 (d, $J = 6.0$ Hz, 1H), 7.80-7.62 (m, 6H), 7.45-7.37 (m, 2H), 6.93 (d, $J = 6.0$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$-TFA-d): $\delta$ 163.0 (d, $J = 249.8$ Hz), 149.4, 141.6, 130.6 (2C), 129.9 (2C), 128.7 (2C), 128.2, 124.9 (d, $J = 11.5$ Hz), 123.4, 123.3, 122.4, 121.6, 121.1, 120.6 (d, $J = 9.3$ Hz), 117.5, 117.3 (d, $J = 7.6$ Hz), 117.0, 104.4 (d, $J = 28.3$ Hz); HR-MS (ESI+) m/z calculated for [C$_{21}$H$_{12}$FN$_3$]$^+$ = [M + H]$^+$ 354.1150, found 354.1155.

6-Fluoro-1-(p-tolyl)indazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7u):
Light yellow solid; Yield: 62%; mp: 234-236 °C; Rf = 0.6 (10% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.80-8.77 (m, 1H), 8.47 (dd, \(J_1 = 2.4\) Hz, \(J_2 = 2.4\) Hz, 1H), 7.86 (d, \(J = 8.8\) Hz, 1H), 7.63 (d, \(J = 8.0\) Hz, 2H), 7.50-7.45 (m, 1H), 7.42 (t, \(J = 8.0\) Hz, 3H), 7.01 (t, \(J = 7.4\) Hz, 1H), 6.95 (d, \(J = 8.8\) Hz, 1H), 2.55 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 162.9 (d, \(J = 249.2\) Hz), 149.5, 141.9, 139.7, 130.4 (2C), 129.3 (2C), 128.1, 127.5, 125.2 (d, \(J = 11.4\) Hz), 123.2, 123.0, 122.4, 121.9, 121.4, 120.5 (d, \(J = 9.3\) Hz), 117.5, 117.3, 116.9 (d, \(J = 23.8\) Hz), 104.4 (d, \(J = 28.3\) Hz), 21.6; HR-MS (ESI+) m/z calculated for [C\(_{22}\)H\(_{14}\)FN\(_5\)]\(^+\) = [M + H]\(^+\) 368.1306, found 368.1311.

1-Butyl-6-fluoroindolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7v):

White solid; Yield: 62%; mp: 187-189 °C; Rf = 0.4 (10% EtOAc/ n-hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.77-8.73 (m, 1H), 8.39 (dd, \(J_1 = 2.8\) Hz, \(J_2 = 2.8\) Hz, 1H), 8.13 (d, \(J = 8.4\) Hz, 1H), 7.90 (d, \(J = 8.8\) Hz, 1H), 7.52 (t, \(J = 7.6\) Hz, 1H), 7.46-7.41 (m, 1H), 7.33 (t, \(J = 7.6\) Hz, 1H), 3.44 (t, \(J = 7.8\) Hz, 2H), 1.99-1.91 (m, 2H), 1.63-1.54 (m, 2H ), 1.02 (t, \(J = 7.4\) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 162.9 (d, \(J = 251.2\) Hz), 149.3, 141.9, 128.1, 125.1 (d, \(J = 11.4\) Hz), 123.6, 123.1, 122.0, 121.7, 120.4 (d, \(J = 9.1\) Hz), 120.0, 117.9, 117.0, 116.6 (d, \(J = 23.9\) Hz), 104.1 (d, \(J = 28.3\) Hz), 32.0, 26.9, 22.4, 13.9; HR-MS (ESI+) m/z calculated for [C\(_{19}\)H\(_{17}\)FN\(_3\)]\(^+\) = [M + H]\(^+\) 334.1468, found 334.1468.

6-Fluoro-1-pentyldiazolo[2,3-a][1,2,3]triazolo[5,1-c]quinoxaline (7w):
Yellow solid; Yield: 65%; mp: 157-159 °C; R_f = 0.3 (10% EtOAc/ n-hexane); ^1H NMR (400 MHz, CDCl_3): δ 8.74-8.70 (m, 1H), 8.37 (dd, J_1 = 2.8 Hz, J_2 = 2.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.45-7.40 (m, 1H), 7.32 (t, J = 7.6 Hz, 1H), 3.41 (t, J = 7.8 Hz, 2H), 1.99-1.92 (m, 2H), 1.58-1.51 (m, 2H), 1.47-1.38 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^13C NMR (100 MHz, CDCl_3): δ 162.9 (d, J = 249.2 Hz), 149.3, 141.9, 128.1, 125.1 (d, J = 11.6 Hz), 123.7, 123.1, 122.0, 121.7, 120.4 (d, J = 9.2 Hz), 120.0, 117.9, 117.0, 116.6 (d, J = 23.8 Hz), 104.1 (d, J = 28.2 Hz), 31.4, 29.7, 27.1, 22.5, 14.0; HR-MS (ESI+) m/z calculated for [C_20H_19FN_5]^+ = [M + H]^+ 348.1623, found 348.1624.

Procedure for the synthesis of compound 3a:
2-Azidobenzaldehyde (1) (0.67 mmol) and 2-iodoaniline (2) (0.67 mmol) were taken in a 10mL oven dried Schlenck tube and it was closed with nitrogen balloon and stirred for 40 min at 110 °C. After completion of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and was purified by column chromatography on silica gel with EtOAc / Hexane to give desired product of 3a.

2-(2-Iodophenyl)-2H-indazole (3a):

Yellow solid; Yield: 70%; mp: 99-101 °C; R_f = 0.5 (20% EtOAc/ n-hexane); ^1H NMR (400 MHz, DMSO- d_6): δ 8.62 (s, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.61-7.56 (m, 2H), 7.35-7.29 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H); ^13C NMR (100 MHz, CDCl_3): δ 149.4, 143.8, 140.0, 130.8, 129.0, 128.3, 126.8, 124.9, 122.4, 122.0, 120.5, 118.0, 94.2; HR-MS (ESI+) m/z calculated for [C_13H_10IN_2]^+ = [M + H]^+ 320.9885, found 320.9889.

Procedure for the synthesis of compound 6a:
To a round bottom flask containing 2-(2-iodophenyl)-2H-indazole (3a) (0.67 mmol), phenyl acetylene (4a) (0.67 mmol) and sodium azide (5) (0.67 mmol) in DMF (3 mL). Then after CuI (10 mol%), K_2CO_3 (0.81 mmol) were added reaction mixture. The reaction mixture was stirred at 120 °C for 2h under open air. After completion of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and diluted with water extracted extracted with EtOAc (20 mL × 3). The combined EtOAc layer was collected, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified using column chromatographyover silica gel with EtOAc / hexane to give desired product of (6)
2-(2-(4-Phenyl-1H-1,2,3-triazol-1-yl)phenyl)-2H-indazole (6):

Brown colour solid; Yield: 60%; mp: 126-128 °C; Rf = 0.3 (20% EtOAc/ n-hexane); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88-7.85 (m, 2H), 7.78 (s, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.72-7.70 (m,2H), 7.55-7.53 (m, 3H), 7.35-7.27 (m,5H), 7.07 ( t, $J = 7.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.8, 148.2, 134.9, 132.1, 130.5, 130.2, 129.7, 128.8 (2C), 128.4, 128.1,127.4, 126.9, 125.8 (2C), 125.0, 122.8, 122.6, 120.7, 120.6, 117.7; HR-MS (ESI+) m/z calculated for [C$_{21}$H$_{16}$N$_5$]$^+$ = [M + H]$^+$ 338.1412, found 338.1406.

Single crystal X-ray data for compound (7q):

X-ray intensity data measurements of all sulphonamides were carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer equipped with Incoatech multilayer mirrors optics. The intensity measurements were carried out with Mo micro-focus sealed tube diffraction source (Mo-K$_\alpha$ = 0.72 Å) at 100(2) K temperature. The X-ray generator was operated at 50 kV and 1.4 mA. A preliminary set of cell constants and an orientation matrix were calculated from two sets of 20 frames. Data were collected with $\omega$ scan width of 0.5° at different settings of $\varphi$ and $2\theta$ with a frame time of 40 seconds keeping the sample–to-detector distance fixed at 4.00 cm. The X-ray data collection was monitored by APEX3 program (Bruker, 2016).All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). SHELX-97 was used for structure solution and full matrix least-squares refinement on F$^2$. Molecular diagrams were generated using ORTEP-33 and Mercury programs. Geometrical calculations were performed using SHELXTL and PLATON. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An ORTEP III view of both compounds were drawn with 50% probability displacement ellipsoids and H–atoms are shown as small spheres of arbitrary radii.
**Fig. S-1** X-ray crystal structure of 7q (ORTEP diagram). Thermal ellipsoids are drawn at the 50% probability level.

Crystallographic data for 7q (C_{21}H_{21}N_{5}): M = 343.43, Crystal dimensions 0.490 x 0.270 x 0.130 mm³, Monoclinic, space group C 2/c, a = 12.2671(5) Å, b = 18.1570(8) Å, c = 15.9123(7) Å, α = 90°, β = 96.146(2)°, γ = 90°, V = 3523.8(3) Å³, Z = 8, ρcalc = 1.295 Mg/m³, μ (Cu-Kα) = 0.080 mm⁻¹, F(000) = 1456, θmax = 28.725°, T = 100(2) K, 54074 reflections collected, 4570 unique reflections (R(int) = 0.0669), 4570 observed (I > 2σ(I)) reflections, multi-scan absorption correction, Tmin = 0.962, Tmax = 0.990, 238 refined parameters, No. of restraints 0, S = 1.069, R1 = = 0.0633, wR2 = 0.1532 (all data R1 = 0.0842, wR2 = 0.1666), maximum and minimum residual electron densities; Δρmax = 0.282, Δρmin = -0.216 (eÅ⁻³). Crystallographic data for compound intermediate deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 1863988

**References:**
Copies of $^1$H and $^{13}$C NMR spectra of product Compound- 7a
Compound- **7b**
Compound-7c
Compound- 7d
Compound- 7e
Compound: 7f
Compound- 7h
Compound- 7i
Compound - 7j
Compound - 7m
Compound-7n
Compound- 70
Compound- 7r
Compound- 7s
Compound- 7t
Compound- 7u
Compound- 3a