Supporting Information

Rhodium-catalyzed Intramolecular Cascade Sequence for the Formation of Fused Carbazole-annulated Medium-sized Rings by Cleavage of C(sp²)–H/C(sp³)–H Bonds

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1. General Information

All the reactions were carried out under argon atmosphere using standard sealed Schlenk technique. \( ^1\)H NMR (400 MHz), \( ^{13}\)C NMR (101 MHz), and \( ^{19}\)F (376 M Hz) were recorded on a NMR spectrometer with DMSO-\( d_6 \) and CDCl\(_3 \) as solvent. Chemical shifts of \( ^1\)H, \( ^{13}\)C and \( ^{19}\)F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl\(_3 \): \( \delta_H = 7.26 \) ppm, \( \delta_C = 77.16 \) ppm; DMSO-\( d_6 \): \( \delta_H = 2.50 \) ppm, \( \delta_C = 39.43 \) ppm). All coupling constants (\( J \) values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm and 365nm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer. 0.3 mm thickness. Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate (EA)/petroleum ether (PE)/dichloromethane(DCM).

2. General Procedures for the Substrates

a) General procedure for the preparation of compounds 11.[1]

\[
\text{R}^2 = \begin{align*}
\begin{array}{c}
\text{Br} \\
\end{array} \\
\begin{array}{c}
\text{n} \\
\end{array} \\
\begin{array}{c}
\text{Br} \\
\end{array}
\end{align*}
\]

\( n = 3, 4, 5 \)

\( \text{THF} \)

\( \text{n-ButLi} \)

2.5 M n-butyllithium in hexane (0.10 mol) was added to a solution of terminal alkyne (0.12 mol) in THF (40 mL) at an ice bath. The solution was heated to reflux until gas evolution ceased. The appropriate dihalide (0.14 mol) was added and the reaction mixture was heated to reflux overnight. After cooling, 2 ml of water was added carefully and extracted with EA, the organic layer was dried (\( \text{Na}_2\text{SO}_4 \)) and concentrated. Vacuum distillation of the residual oil gave the desired product.

b) General procedure for the preparation of substrates 1.[2]
To a suspension of NaOH (2 eq) in 10 mL of DMSO was added indole (1 eq), 11 (1.05 eq). The reaction mixture was then warmed to 40 °C and stirred overnight. The resulting suspension was poured into water and extracted with EA. The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, and filtered, the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, eluent: petroleum) to obtain product 12 as a yellowish oil. 12 (1eq) was added to a solution prepared by dissolution of cyanoacetic acid (1.05 eq) in Ac₂O (10 ml) at rt. The solution was heated at 85 °C for 1-4 h. Remove the solvent, dissolved in EA, washed with water, dried over Na₂SO₄, and filtered, the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, eluent: petroleum /DCM /EA = 3:1:1) to obtain product 1. Total yield 43-78%.

3. General Procedure for the Synthesis of 2

A mixture of 1 (0.2 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (5.0 mol %), CsOAc (0.4 mmol, 2.0 eq), and TEMPO (0.4 mmol, 2.0 equiv) was weighed in a sealed Schlenk tube equipped with a stir bar. Dry DMF (1.0 mL) was added and the mixture was stirred at 100 °C for 12 h under an Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using PE /EA /CH₂Cl₂ (10/1/1) as eluent to give pure product 2.

4. Gram-scale Synthesis of 2a

A mixture of 1a (1.02 g, 3.0 mmol), [Cp*RhCl₂]₂ (0.07 g, 4 mol %), CsOAc (1.15 g, 6.0 mmol), and TEMPO (0.94 g, 6.0 mmol) was weighed in a sealed Schlenk tube. Dry DMF (10 mL) was added and the mixture was heat at 100 °C for 12 h under an Ar atmosphere. After the mixture was cooled to room temperature, the solvent was evaporated under reduced
pressure and the residue was purified by a silica gel column using PE/EA/CH₂Cl₂ (10/1/1) as eluent to give pure product 2a in 89\% yield (0.88 g).

5. Transformations of 2a\(^{[3]}\)

(1) Transformation of 2a to 8

\[
\text{HO} \quad \text{CN} \quad \text{Ph} \quad + \quad \text{CO} \quad \text{Et} \quad \text{[Cp*RhCl₂]₂} \quad \text{Cu(OAc)}₂ \cdot \text{H₂O} \quad \text{DMF, 100 °C} \\
\text{2a} \quad \text{7} \quad \text{8 38%}
\]

A mixture of 2a (0.2 mmol, 1.0 equiv), ethyl acrylate (7) (0.3 mmol, 1.5 equiv), [Cp*RhCl₂]₂ (0.01 mmol, 5.0 mol \%), and Cu(OAc)₂·H₂O (0.4 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMF (1.0 mL) was added and the mixture was stirred at 100 °C for 18 h under Ar atmosphere. Afterwards, it was diluted with CH₂Cl₂ and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with EtOAc/PE, get pure product 8 in 38\% yield.

(2) Transformations of 2a to 10

\[
\text{HO} \quad \text{CN} \quad \text{Ph} \quad + \quad \text{Ph} \quad \text{[Cp*RhCl₂]₂} \quad \text{Cu(OAc)}₂ \cdot \text{H₂O} \quad \text{DMF, 100 °C} \\
\text{2a} \quad \text{9} \quad \text{10 87%}
\]

A mixture of 2a (0.2 mmol, 1 equiv), alkyne (9) (0.22 mmol, 1.1 equiv), [Cp*RhCl₂]₂ (0.01 mmol, 5.0 mol \%), and Cu(OAc)₂·H₂O (0.4 mmol, 2.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMF (1.0 mL) was added and the mixture was stirred at 100 °C for 18 h under Ar atmosphere. Afterwards, it was diluted with CH₂Cl₂ and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with EtOAc/petroleum ether.
6. Experimental Data

3-Oxo-3-(1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)propanenitrile (1a): White solid. M.p. 79 – 80 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.32 – 8.29 (m, 1H), 7.84 (s, 1H), 7.42 – 7.39 (m, 1H), 7.36 – 7.24 (m, 7H), 4.26 (t, $J = 7.2$ Hz, 2H), 3.83 (s, 2H), 2.47 (t, $J = 6.8$ Hz, 2H), 2.15 – 2.07 (m, 2H), 1.68 – 1.61 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 136.8, 135.1, 131.5, 128.4, 127.9, 126.3, 124.2, 123.5, 122.5, 115.0, 114.4, 110.3, 88.9, 81.7, 47.0, 29.7, 28.9, 25.6, 19.0. HRMS (ESI) calcd for C$_{23}$H$_{21}$N$_2$O $^+ [M+H]^+$ 341.1654, found 341.1652.

3-(4-Methyl-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1b): light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (s, 1H), 7.38 – 7.36 (m, 2H), 7.30 – 7.22 (m, 5H), 7.09 – 7.07 (m, 1H), 4.25 (t, $J = 7.2$ Hz, 2H), 3.87 (s, 2H), 2.84 (s, 3H), 2.49 (t, $J = 6.8$ Hz, 2H), 2.07 – 2.14 (m, 2H), 1.70 – 1.62 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.0, 137.8, 136.4, 133.8, 131.6, 128.4, 127.9, 125.3, 125.1, 124.3, 123.6, 115.7, 115.4, 107.8, 89.1, 81.6, 77.5, 77.2, 76.9, 46.9, 30.5, 28.7, 25.6, 23.1, 18.9. HRMS (ESI) calcd for C$_{24}$H$_{23}$N$_2$O $^+ [M+H]^+$ 355.1810, found 355.1809.

3-(4-Chloro-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1c): White solid. M.p. 66 – 68 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (s, 1H), 7.32 – 7.20 (m, 7H), 7.15 (t, $J = 7.9$ Hz, 1H), 4.19 (t, $J = 7.2$ Hz, 2H), 3.92 (d, $J = 4.4$ Hz, 2H), 2.43 (t, $J = 6.8$ Hz, 2H),
2.08 – 1.99 (m, 2H), 1.63 – 1.56 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 138.7, 136.9, 131.5, 128.4, 127.9, 127.0, 124.6, 124.5, 123.6, 123.4, 115.2, 114.7, 109.3, 89.1, 81.6, 77.6, 77.2, 76.9, 47.1, 31.6, 28.6, 25.6, 18.9. HRMS (ESI) calcd for C$_{23}$H$_{20}$ClN$_2$O $^+ [M+H]^+$ 375.1264, found 375.1253.

3-(5-Methyl-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1d): White solid. M.p. 89 – 90 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.07 (s, 1H), 7.75 (s, 1H), 7.32 – 7.20 (m, 6H), 7.09 (d, $J = 8.4$ Hz, 1H), 4.18 (t, $J = 7.1$ Hz, 2H), 3.77 (s, 2H), 2.42 (d, $J = 9.5$ Hz, 5H), 2.09 – 2.02 (m, 2H), 1.63 – 1.57 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 135.2, 134.9, 133.2, 131.5, 128.3, 127.9, 126.6, 125.6, 123.5, 122.2, 115.0, 114.0, 109.9, 88.8, 81.6, 47.0, 29.6, 28.8, 25.6, 21.5, 18.9. HRMS (ESI) calcd for C$_{24}$H$_{23}$N$_2$O $^+ [M+H]^+$ 355.1810, found 355.1806.

3-(5-Methoxy-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1e): White solid. M.p. 76 – 78 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J = 2.5$ Hz, 1H), 7.71 (s, 1H), 7.32 – 7.29 (m, 2H), 7.25 – 7.20 (m, 4H), 6.89 (dd, $J = 8.9$, 2.5 Hz, 1H), 4.16 (t, $J = 7.2$ Hz, 2H), 3.83 (s, 3H), 3.76 (s, 2H), 2.42 (t, $J = 6.8$ Hz, 2H), 2.08 – 2.01 (m, 2H), 1.62 – 1.55 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.4, 157.1, 134.7, 131.6, 131.5, 128.4, 127.9, 127.3, 123.5, 114.9, 114.7, 114.0, 111.1, 103.7, 88.8, 81.7, 55.8, 47.2, 29.5, 28.9, 25.6, 18.9. HRMS (ESI) calcd for C$_{24}$H$_{23}$N$_2$O$_2$ $^+ [M+H]^+$ 371.1760, found 371.1757.
3-(5-Fluoro-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1f): White solid. M.p. 115 – 117 °C. \( ^1H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.02 – 7.99 (m, 1H), 7.99 – 7.87 (m, 1H), 7.36 – 7.25 (m, 6H), 7.08 – 7.04 (m, 1H), 4.26 (t, \( J = 6.1 \text{ Hz}, 2H), 3.82 – 3.81 (m, 2H), 2.52 – 2.49 (m, 2H), 2.14 – 2.11 (m, 2H), 1.68 – 1.65 (m, 2H). \( ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 180.4, 160.1 (d, \( J = 239.6 \text{ Hz}), 135.9, 133.2, 131.5, 128.4, 128.0, 127.1 (d, \( J = 11.1 \text{ Hz}), 123.4, 114.8, 114.2 (d, \( J = 4.3 \text{ Hz}), 112.6 (d, \( J = 26.5 \text{ Hz}), 111.2 (d, \( J = 9.7 \text{ Hz}), 108.0 (d, \( J = 25.1 \text{ Hz}), 88.8, 81.7, 47.3, 29.5, 28.8, 25.5, 18.9. \( ^{19}F \text{NMR} (376 \text{ MHz, CDCl}_3) \delta -119.27. \text{HRMS (ESI)} \text{ calcd for C}_{23}\text{H}_{20}\text{FN}_2\text{O}^{+}[\text{M+H}]^{+} 359.1560, \text{found} 359.1557.

3-(5-Chloro-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1g): White solid. M.p. 119 – 120 °C. \( ^1H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.32 (d, \( J = 2.0 \text{ Hz}, 1H), 7.87 (s, 1H), 7.39 – 7.36 (m, 2H), 7.33 – 7.30 (m, 3H), 7.29 – 7.26 (m, 2H), 4.27 (s, 2H), 3.83 (s, 2H), 2.52 (t, \( J = 6.7 \text{ Hz}, 2H), 2.15 – 2.11 (m, 2H), 1.69 – 1.65 (m, 2H). \( ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 180.6, 135.9, 135.2, 131.5, 129.3, 128.4, 127.9, 127.3, 124.4, 123.5, 121.9, 114.9, 113.8, 111.4, 88.9, 81.7, 47.2, 29.6, 28.8, 25.6, 18.9. \text{HRMS (ESI)} \text{ calcd for C}_{23}\text{H}_{20}\text{ClN}_2\text{O}^{+}[\text{M+H}]^{+} 375.1264, \text{found} 375.1254.

3-(5-Bromo-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1h): White solid. M.p. 99 – 100 °C. \( ^1H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 8.41 (d, \( J = 1.5 \text{ Hz}, 1H), 7.79 (s, 1H), 7.37 – 7.23 (m, 7H), 4.22 (t, \( J = 7.1 \text{ Hz}, 2H), 3.80 (s, 2H), 2.48 (t, \( J = 6.7 \text{ Hz}, 2H), 2.12 – 2.05 (m, 2H), 1.67 – 1.60 (m, 2H). \( ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta 180.5, 135.7, 135.5, 131.5, 128.4, 127.9, 127.8, 127.1, 125.1, 123.5, 117.1, 114.8, 113.7, 111.7, 88.8, 81.7, 47.2, 29.6, 28.8, 25.6, 18.9. \text{HRMS (ESI)} \text{ calcd for C}_{23}\text{H}_{20}\text{BrN}_2\text{O}^{+}[\text{M+H}]^{+} 419.0759, \text{found} 419.0751.
Methyl 3-(2-cyanoacetyl)-1-(6-phenylhex-5-yn-1-yl)-1H-indole-5-carboxylate (1i): White solid. M.p. 76 – 78 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.01 (d, $J = 1.1$ Hz, 1H), 8.04 (dd, $J = 8.7$, 1.5 Hz, 1H), 7.95 (s, 1H), 7.46 (d, $J = 8.7$ Hz, 1H), 7.39 – 7.29 (m, 5H), 4.31 (t, $J = 7.2$ Hz, 2H), 3.97 (s, 3H), 3.85 (s, 2H), 2.52 (t, $J = 6.7$ Hz, 2H), 2.18 – 2.11 (m, 2H), 1.72 – 1.65 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.6, 167.5, 139.2, 136.3, 131.5, 128.4, 127.9, 125.8, 125.5, 125.4, 124.9, 123.4, 115.2, 114.7, 110.1, 88.8, 81.8, 52.2, 47.2, 29.8, 28.9, 25.6, 18.9. HRMS (ESI) calcd for C$_{25}$H$_{23}$N$_2$O$_3$ $^+[M+H]^+$ 399.1709, found 399.1704.

3-(5-Nitro-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1j): White solid. M.p. 88 – 89 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.21 (d, $J = 2.2$ Hz, 1H), 8.20 (dd, $J = 9.1$, 2.3 Hz, 1H), 8.06 (s, 1H), 7.51 (d, $J = 9.1$ Hz, 1H), 7.39 – 7.28 (m, 5H), 4.37 (t, $J = 7.2$ Hz, 2H), 3.88 (s, 2H), 2.55 (t, $J = 6.7$ Hz, 2H), 2.26 – 2.13 (m, 2H), 1.75 – 1.68 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.6, 144.3, 139.5, 137.5, 131.5, 128.4, 128.1, 125.7, 123.3, 119.6, 119.3, 115.7, 114.5, 110.5, 88.6, 81.9, 47.5, 29.8, 28.8, 25.4, 18.9. HRMS (ESI) calcd for C$_{23}$H$_{20}$N$_3$O$_3$ $^+[M+H]^+$ 386.1505, found 386.1499.

3-(6-Methyl-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1k): White solid. M.p. 100 – 102 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 8.1$ Hz, 1H), 7.77 (s, 1H), 7.36 – 7.32 (m, 2H), 7.29 – 7.24 (m, 3H), 7.18 – 7.14 (m, 2H), 4.22 (t, $J = 7.2$ Hz, 2H), 3.82 (s, 2H), 2.48 (t, $J = 6.8$ Hz, 2H), 2.44 (s, 3H), 2.14 – 2.06 (m, 2H), 1.68 – 1.61 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.4, 137.2, 134.6, 134.8, 131.5, 128.3, 127.9, 125.2, 124.1, 123.5, 122.1, 114.9, 114.4, 110.1, 88.8, 81.7, 46.9, 29.6, 28.8, 25.6, 21.8, 18.9. HRMS (ESI) calcd for C$_{24}$H$_{22}$N$_2$O$^+$ $[M+H]^+$ 355.1810, found 355.1810.
3-(6-Bromo-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (II): Yellow solid. M.p. 135 – 136 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.22 – 8.20 (m, 1H), 7.84 (d, $J$ = 4.4 Hz, 1H), 7.59 (s, 1H), 7.46 – 7.29 (m, 6H), 4.26 – 4.23 (m, 2H), 3.86 (d, $J$ = 4.5 Hz, 2H), 2.53 (t, $J$ = 6.4 Hz, 2H), 2.14 (d, $J$ = 6.8 Hz, 2H), 1.69 (d, $J$ = 6.3 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 137.6, 135.3, 131.6, 128.4, 128.0, 126.8, 125.2, 123.9, 123.4, 117.9, 114.7, 114.4, 113.3, 88.7, 81.8, 47.2, 29.7, 28.8, 25.6, 19.0. HRMS (ESI) calcd for C$_{23}$H$_{20}$BrN$_2$O $^+$ [M+H]$^+$ 419.0759, found 419.0754.

3-(7-Methyl-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1m): White solid. M.p. 124 – 125 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J$ = 8.0 Hz, 1H), 7.72 (s, 1H), 7.31 – 7.29 (m, 2H), 7.24 – 7.13 (m, 4H), 7.01 (d, $J$ = 7.2 Hz, 1H), 4.39 (t, $J$ = 7.4 Hz, 2H), 3.75 (s, 2H), 2.68 (s, 3H), 2.44 (t, $J$ = 6.8 Hz, 2H), 2.06 – 1.98 (m, 2H), 1.68 – 1.61 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.4, 136.6, 135.5, 131.5, 128.3, 127.9, 127.5, 127.4, 123.5, 121.4, 120.5, 114.9, 114.1, 88.9, 81.7, 49.5, 31.3, 29.6, 25.5, 19.7, 19.0. HRMS (ESI) calcd for C$_{24}$H$_{23}$N$_2$O $^+$ [M+H]$^+$ 355.1810, found 355.1809.

3-(7-Chloro-1-(6-phenylhex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1n): White solid. M.p. 137 – 138 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 (dd, $J$ = 7.9, 0.9 Hz, 1H), 7.79 (s, 1H), 7.37 – 7.34 (m, 2H), 7.30 – 7.25 (m, 4H), 7.21 (t, $J$ = 7.8 Hz, 1H), 4.60 (t, $J$ = 7.4 Hz, 2H), 3.84 (s, 2H), 2.48 (t, $J$ = 6.8 Hz, 2H), 2.15 – 2.08 (m, 2H), 1.71 – 1.63 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 137.5, 131.5, 129.4, 128.4, 127.9, 126.1, 124.2, 123.6,
121.3, 117.2, 114.7, 114.0, 89.1, 81.5, 49.8, 31.3, 29.8, 25.5, 19.1. **HRMS (ESI)** calcd for C_{23}H_{20}ClN_{2}O^{+} [M+H]^{+} 375.1264, found 375.1258.

3-(1-(6-(4-Fluorophenyl)hex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1o): White solid. M.p. 90 – 91 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.32 – 8.30 (m, 1H), 7.85 (s, 1H), 7.43 – 7.31 (m, 5H), 7.06 – 6.89 (m, 2H), 4.26 (t, \(J = 6.6\) Hz, 2H), 3.86 (d, \(J = 1.2\) Hz, 2H), 2.47 (t, \(J = 6.2\) Hz, 2H), 2.14 – 2.07 (m, 2H), 1.69 – 1.62 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 180.5, 162.2 (d, \(J = 248.8\) Hz), 136.8, 135.0, 133.3 (d, \(J = 8.2\) Hz), 126.3, 124.2, 123.5, 122.5, 119.5, 115.5 (d, \(J = 22.2\) Hz), 114.9, 114.4, 110.2, 88.4, 80.6, 47.0, 29.7, 28.9, 25.7, 18.9. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -111.53, HRMS (ESI) calcd for C_{23}H_{20}FN_{2}O^{+} [M+H]^{+} 359.1560, found 359.1557.

3-(1-(6-(4-Chlorophenyl)hex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1p): White solid. M.p. 130 – 131 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.32 – 8.30 (m, 1H), 7.84 (s, 1H), 7.42 – 7.39 (m, 1H), 7.36 – 7.31 (m, 2H), 7.28 – 7.23 (m, 4H), 4.25 (t, \(J = 7.1\) Hz, 2H), 3.86 (s, 2H), 2.47 (t, \(J = 6.8\) Hz, 2H), 2.13 – 2.06 (m, 2H), 1.69 – 1.61 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 180.6, 136.8, 135.2, 133.8, 132.8, 128.6, 126.3, 124.1, 123.4, 122.5, 115.0, 114.3, 110.3, 90.0, 80.6, 47.0, 29.7, 28.9, 25.7, 19.0. HRMS (ESI) calcd for C_{23}H_{20}ClN_{2}O^{+} [M+H]^{+} 375.1264, found 375.1266.
3-(1-(6-(4-Methylphenyl)hex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1q): White solid. M.p. 91 – 93 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.36 – 8.34 (m, 1H), 7.87 (s, 1H), 7.47 – 7.44 (m, 1H), 7.39 – 7.36 (m, 2H), 7.30 – 7.28 (m, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 4.30 (t, $J = 7.2$ Hz, 2H), 3.86 (s, 2H), 2.51 (t, $J = 6.7$ Hz, 2H), 2.37 (s, 3H), 2.19 – 2.12 (m, 2H), 1.72 – 1.65 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.5, 159.3, 136.9, 134.9, 132.9, 126.4, 124.2, 123.5, 122.6, 115.6, 114.9, 114.4, 114.0, 110.2, 87.2, 81.5, 55.3, 47.0, 29.7, 28.9, 25.7, 18.9. HRMS (ESI) calcd for C$_{24}$H$_{23}$N$_2$O $^+$ [M+H]$^+$ 355.1810, found 355.1807.

3-(1-(6-(4-Methoxyphenyl)hex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1r): White solid. M.p. 91 – 93 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.23 (d, $J = 8.5$ Hz, 1H), 7.82 (s, 1H), 7.39 (d, $J = 1.6$ Hz, 1H), 7.27 – 7.30 (m, 3H), 6.81 – 6.79 (m, 2H), 4.21 (t, $J = 7.2$ Hz, 2H), 3.80 – 3.78 (m, 5H), 2.46 (t, $J = 6.7$ Hz, 2H), 2.13 – 2.05 (m, 2H), 1.66 – 1.59 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.5, 159.3, 136.9, 134.9, 132.9, 126.4, 124.2, 123.5, 122.6, 115.6, 114.9, 114.4, 113.9, 110.2, 87.2, 81.5, 55.3, 46.9, 29.6, 28.8, 25.6, 18.9. HRMS (ESI) calcd for C$_{24}$H$_{23}$N$_2$O$_2$ $^+$ [M+H]$^+$ 371.1760, found 371.1760.

3-(1-(6-(Naphthalen-2-yl)hex-5-yn-1-yl)-1H-indol-3-yl)-3-oxopropanenitrile (1s): Yellow solid. M.p. 67 – 68 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 – 8.32 (m, 1H), 7.88 – 7.75 (m, 5H), 7.49 – 7.31 (m, 6H), 4.31 – 4.27 (m, 2H), 3.84 (d, $J = 2.0$ Hz, 2H), 2.55 (t, $J = 6.7$ Hz, 2H), 2.18 – 2.15 (m, 2H), 1.67 – 1.74 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 180.5, 136.8, 134.9, 133.0, 132.6, 131.2, 128.5, 128.0, 127.8, 127.6, 126.6, 126.5, 126.4, 124.2, 123.5, 122.6, 120.8, 114.9, 114.4, 110.3, 89.2, 82.1, 47.1, 29.7, 28.9, 25.7, 19.1. HRMS (ESI) calcd for C$_{27}$H$_{23}$N$_2$O $^+$ [M+H]$^+$ 391.1810, found 391.1803.
3-Oxo-3-(1-(2-((3-phenylprop-2-yn-1-yl)oxy)ethyl)-1H-indol-3-yl)propanenitrile (10): Yellow solid. M.p. 67 – 68 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 – 8.25 (m, 1H), 7.78 (s, 1H), 7.37 – 7.34 (m, 1H), 7.32 – 7.24 (m, 7H), 4.32 – 4.30 (m, 4H), 3.92 (t, $J = 5.0$ Hz, 2H), 3.73 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.9, 136.9, 136.4, 131.7, 128.8, 128.5, 128.1, 128.1, 124.1, 123.3, 122.3, 122.1, 115.1, 114.3, 110.3, 86.9, 84.5, 67.7, 59.3, 47.0, 29.6. HRMS (ESI) calcd for C$_{22}$H$_{19}$N$_2$O$_2$ $^[M+H]^+$: 343.1447, found 343.1441.

3-Oxo-3-(1-(5-phenylpent-4-yn-1-yl)-1H-indol-3-yl)propanenitrile (1u): White solid. M.p. 126 – 128 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 – 8.31 (m, 1H), 7.89 (s, 1H), 7.48 – 7.26 (m, 8H), 4.42 (t, $J = 6.8$ Hz, 2H), 3.85 (s, 2H), 2.46 (t, $J = 6.6$ Hz, 2H), 2.22 – 2.15 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 136.8, 135.0, 131.5, 128.5, 128.2, 126.4, 124.2, 123.5, 123.2, 122.6, 114.9, 114.4, 110.2, 87.5, 82.6, 46.0, 29.7, 28.3, 16.8. HRMS (ESI) calcd for C$_{22}$H$_{19}$N$_2$O $^[M+H]^+$ 327.1497, found 327.1498.

3-Oxo-3-(1-(7-phenylhept-6-yn-1-yl)-1H-indol-3-yl)propanenitrile (1v): Yellow solid. M.p. 67 – 68 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28 – 8.26 (m, 1H), 7.76 – 7.74 (m, 1H), 7.36 – 7.21 (m, 8H), 4.16 (t, $J = 6.2$ Hz, 2H), 3.74 (s, 2H), 2.38 (t, $J = 6.7$ Hz, 2H), 1.94 – 1.90 (m, 2H), 1.64 – 1.47 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 180.5, 136.8, 135.0, 131.5, 128.3, 127.8, 126.3, 124.1, 123.7, 123.4, 122.6, 114.9, 114.3, 110.2, 89.4, 81.2, 47.3, 29.6, 29.3, 28.0, 26.0. HRMS (ESI) calcd for C$_{24}$H$_{23}$N$_2$O $^[M+H]^+$ 355.1810, found 355.1803.
1-Hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2a): white solid (62.2 mg, 92%). M.p. 287 – 289 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.86 (s, 1H), 8.29 (d, $J = 7.7$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.48-7.53 (m, $J = 14.3$, 4H), 7.35 (d, $J = 6.9$ Hz, 2H), 7.27 (t, $J = 7.5$ Hz, 1H), 4.51 – 4.53 (m, 2H), 2.80 – 2.83 (m, 2H), 2.12 (s, 2H), 1.91 – 1.94 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 154.8, 144.5, 140.8, 140.5, 138.6, 129.7, 128.2, 127.8, 125.5, 122.4, 121.0, 120.0, 117.8, 117.7, 111.7, 109.6, 91.9, 43.1, 27.2, 26.4, 25.9. HRMS (ESI) calcd for C$_{23}$H$_{19}$N$_2$O$^+$ [M+H]$^+$ 339.1497, found 339.1493.

1-Hydroxy-12-methyl-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2b): white solid (60.5 mg, 86%). M.p. 255 – 257 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.50 (s, 1H), 7.53 – 7.46 (m, 4H), 7.34 (t, $J = 6.9$ Hz, 3H), 7.03 (d, $J = 7.2$ Hz, 1H), 4.53 (d, $J = 5.2$ Hz, 2H), 2.95 (s, 3H), 2.82 (d, $J = 5.2$ Hz, 2H), 2.10 (s, 2H), 1.92 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 153.9, 144.9, 141.7, 140.8, 138.4, 132.8, 129.7, 128.2, 127.8, 125.8, 122.9, 120.3, 118.1, 117.7, 112.9, 107.3, 93.1, 42.8, 26.8, 25.9, 25.6, 24.0. HRMS (ESI) calcd for C$_{24}$H$_{21}$N$_2$O$^+$ [M+H]$^+$ 353.1654, found 353.1645.

12-Chloro-1-hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2c): white solid (60.3 mg, 81%). M.p. 276 – 278 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) 11.08 (s, 1H), 8.38 (d, $J = 1.8$ Hz, 1H), 7.67 – 7.61 (m, 2H), 7.59 – 7.45 (m, 3H), 7.34 (d, $J = 6.7$ Hz, 2H), 4.53 – 4.50 (m, 2H), 2.82 – 2.79 (m, 2H), 2.11 (s, 2H), 1.93 – 1.90 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 155.5, 145.2, 141.7, 140.1, 138.8, 130.1, 128.8, 128.4, 124.7, 123.2, 118.5, 118.1, 112.4, 111.2, 92.6, 43.8, 27.5, 26.8, 26.2. HRMS (ESI) calcd for C$_{23}$H$_{18}$ClN$_2$O$^+$ [M+H]$^+$ 373.1108, found 373.1099.
1-Hydroxy-11-methyl-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2d): white solid (61.9 mg, 88%). M.p. 252 – 252 °C. 1H NMR (400 MHz, DMSO-δ) δ 10.76 (s, 1H), 8.08 (s, 1H), 7.55 – 7.45 (m, 4H), 7.35 – 7.28 (m, 3H), 4.48 (s, 2H), 2.80 (s, 2H), 2.11 (s, 2H), 1.92 (s, 2H). 13C NMR (101 MHz, DMSO-δ) δ 154.9, 144.6, 140.2, 139.2, 138.6, 129.6, 128.8, 128.2, 127.8, 126.8, 122.2, 121.1, 117.8, 111.4, 109.4, 91.5, 43.1, 27.2 26.4, 25.8, 21.1. HRMS (ESI) calcd for C24H21N2O+ [M+H]+ 353.1654, found 353.1648.

1-Hydroxy-11-methoxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2e): white solid (59.6 mg, 81%). M.p. 250 – 252 °C. 1H NMR (400 MHz, DMSO-δ) δ 10.77 (s, 1H), 7.80 (s, 1H), 7.57 (d, J = 9.0 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.34 (d, J = 7.7 Hz, 2H), 7.13 – 7.10 (m, 1H), 4.49 – 4.46 (m, 2H), 3.85 (s, 3H), 2.81 – 2.78 (m, 2H), 2.11 (s, 2H), 1.93 – 1.90 (m, 2H). 13C NMR (101 MHz, DMSO-δ) δ 155.4, 154.3, 145.4, 140.7, 139.1, 136.3, 130.2, 128.7, 128.3, 121.9, 118.3, 118.2, 114.8, 111.9 110.9, 105.8, 91.8, 56.1, 43.8, 27.7, 27.0, 26.4. HRMS (ESI) calcd for C24H21N2O2+ [M+H]+ 369.1603, found 369.1592.

11-Fluoro-1-hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2f): white solid (60.5 mg, 85%). M.p. 290 – 292 °C. 1H NMR (400 MHz, DMSO-δ) δ 11.01 (s, 1H), 7.96 – 7.99 (m, 1H), 7.72 – 7.68 (m, 1H), 7.53 – 7.46 (m, 3H), 7.34 (d, J = 6.4 Hz, 3H), 4.53 (s, 2H), 2.82 – 2.79 (m, 2H), 2.12 (s, 2H), 1.92 (s, 2H). 13C NMR (101 MHz, DMSO-δ) δ 157.4 (d, J = 234.0 Hz), 155.6, 145.7, 141.4, 138.9, 137.9, 130.1, 128.7, 128.3, 121.7 (d, J = 10.5 Hz), 118.2 (d, J = 29.2 Hz), 113.5 (d, J = 25.2 Hz), 111.8, 111.3 (d, J = 9.3 Hz), 107.6 (J = 24.6 Hz), 92.2, 43.9, 27.6, 26.9, 26.3. 19F NMR (376
MHz, DMSO-\textit{d}_6) \& 118.33. HRMS (ESI) calcd for C\textsubscript{23}H\textsubscript{18}FN\textsubscript{2}O\textsuperscript{+} [M+H]\textsuperscript{+} 357.1403, found 357.1392.

11-Chloro-1-hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-\textit{jk}]carbazole-2-carbonitrile (2g): white solid (57.3 mg, 77%). M.p. 267 – 269 °C. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \& 11.07 (s, 1H), 8.24 (d, \textit{J} = 2.0 Hz, 1H), 7.72 (d, \textit{J} = 8.8 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.36 – 7.34 (m, 2H), 4.54 – 4.52 (m, 2H), 2.82 – 2.79 (m, 2H), 2.12 (s, 2H), 1.94 – 1.91 (m, 2H). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) \& 154.9, 144.9, 141.2, 139.3, 138.3, 129.6, 128.3, 127.9, 125.3, 124.2, 122.0, 121.3, 118.0, 117.5, 111.4, 110.8, 92.1, 43.3, 27.0, 26.3, 25.7. HRMS (ESI) calcd for C\textsubscript{23}H\textsubscript{18}ClN\textsubscript{2}O\textsuperscript{+} [M+H]\textsuperscript{+} 373.1108, found 373.1097.

11-Bromo-1-hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-\textit{jk}]carbazole-2-carbonitrile (2h): white solid (70.2 mg, 84%). M.p. 276 – 278 °C. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \& 11.11 (s, 1H), 8.38 (d, \textit{J} = 1.4 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.53 – 7.45 (m, 3H), 7.35 (d, \textit{J} = 6.9 Hz, 2H), 4.54 – 4.51 (m, 2H), 2.82 – 2.79 (m, 2H), 2.12 (s, 2H), 1.94 – 1.91 (m, 2H). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) \& 155.0, 144.8, 141.2, 139.6, 138.4, 129.6, 128.3, 127.9, 124.3, 122.7, 118.0, 117.5, 112.1, 112.0, 111.9, 110.7, 92.2, 43.3, 27.0, 26.3, 25.7. C\textsubscript{23}H\textsubscript{18}BrN\textsubscript{2}O\textsuperscript{+} [M+H]\textsuperscript{+} 417.0603, found 417.0597.

Methyl 2-cyano-1-hydroxy-3-phenyl-5,6-dihydro-4H-pyrido[3,2,1-\textit{jk}]carbazole-10-carboxylate (2i): white solid (56.2 mg, 71%). M.p. 285 – 286 °C. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \& 11.13 (s, 1H), 8.91 (s, 1H), 8.08 (d, \textit{J} = 4.9 Hz, 1H), 7.74 – 7.76 (m, 1H), 7.51 (d, \textit{J} = 5.6 Hz, 3H), 7.36 (s, 2H), 4.58 (s, 2H), 3.92 (d, \textit{J} = 3.1 Hz, 3H), 2.82 (s, 2H), 2.14 (s, 2H), 1.97 (d, \textit{J} = 21.6 Hz, 2H). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6) \& 167.2, 155.5, 145.6, 143.9, 141.9, 138.7, 130.1, 128.8, 128.5, 127.1, 124.7, 121.7, 121.3, 118.8, 118.0, 112.2, 110.1, 93.2,
52.4, 43.7, 27.3, 26.6, 26.2. **HRMS (ESI)** calcd for C_{25}H_{21}N_{2}O_{3}^{+} [M+H]^{+} 397.1552, found 397.1546.

1-Hydroxy-11-nitro-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2j): yellow solid (67.4 mg, 88%). M.p. >300 °C. **^1H NMR** (400 MHz, DMSO-d$_6$) δ 11.45 (s, 1H), 9.09 (s, 1H), 8.36 (d, $J = 9.1$ Hz, 1H), 7.88 (d, $J = 9.3$ Hz, 1H), 7.53 – 7.49 (m, 3H), 7.37 (d, $J = 7.1$ Hz, 2H), 4.64 (s, 2H), 2.84 (s, 2H), 2.15 (s, 2H), 1.94 (s, 2H). **^13C NMR** (101 MHz, DMSO-d$_6$) δ 155.0, 145.6, 143.9, 142.3, 140.5, 138.0, 129.5, 128.3, 128.1, 121.0, 120.5, 118.6, 118.2, 117.2, 111.5, 110.0, 93.3, 43.5, 26.6, 25.9, 25.5. **HRMS (ESI)** calcd for C$_{23}$H$_{18}$N$_{3}$O$_{3}$^{+} [M+H]^{+} 384.1348, found 384.1340.

1-Hydroxy-10-methyl-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2k): white solid (64.8 mg, 92%). M.p. 264 – 266 °C. **^1H NMR** (400 MHz, DMSO-d$_6$) δ 10.73 (s, 1H), 8.14 (d, $J = 7.9$ Hz, 1H), 7.52 – 7.43 (m, 4H), 7.34 (d, $J = 6.8$ Hz, 2H), 7.09 (d, $J = 7.9$ Hz, 1H), 4.50 – 4.48 (m, 2H), 2.82 – 2.79 (m, 2H), 2.51 (s, 3H), 2.11 (s, 2H), 1.92 (s, 2H). **^13C NMR** (101 MHz, DMSO-d$_6$) δ 154.9, 144.9, 141.7, 140.5, 139.1, 135.7, 130.2, 128.7, 128.3, 122.5, 122.0, 119.2, 118.3, 118.2, 112.3, 110.2, 92.3, 43.4, 27.6, 26.8, 26.4, 22.2. **HRMS (ESI)** calcd for C$_{23}$H$_{18}$N$_{3}$O$_{3}$^{+} [M+H]^{+} 384.1348, found 384.1340.

10-Bromo-1-hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2l): white solid (70.2 mg, 84%). M.p. 278 – 279 °C. **^1H NMR** (400 MHz, DMSO-d$_6$) δ 11.01 (s, 1H), 8.18 (d, $J = 8.3$ Hz, 1H), 7.96 (s, 1H), 7.53 – 7.46 (m, 3H), 7.41 (d, $J = 8.2$ Hz, 1H), 7.34 (d, $J = 7.0$ Hz, 2H), 4.53 (s, 2H), 2.81 (s, 2H), 2.11 (s, 2H), 1.92 (s, 2H). **^13C NMR** (101 MHz, DMSO-d$_6$) δ 154.8, 144.7, 141.8, 141.1, 138.4, 129.6, 128.3, 127.9, 123.8, 122.8, 120.1, 118.6, 118.0, 117.5, 112.7, 111.3, 92.4, 43.2, 26.9, 26.2, 25.7. **HRMS (ESI)** calcd for C$_{23}$H$_{18}$BrN$_{3}$O$_{3}$^{+} [M+H]^{+} 417.0603, found 417.0591.
1-Hydroxy-9-methyl-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2m): white solid (58.4 mg, 83%). M.p. 279 – 280 °C. 1H NMR (400 MHz, DMSO-\textit{d}_6) \(\delta\) 10.79 (s, 1H), 8.13 (d, \(J = 7.5\) Hz, 1H), 7.51 – 7.46 (m, 5H), 7.22 – 7.13 (m, 2H), 4.62 (s, 2H), 2.77 (s, 2H), 2.74 (s, 3H), 2.10 (s, 2H), 1.90 (s, 2H). 13C NMR (101 MHz, DMSO-\textit{d}_6) \(\delta\) 154.6, 146.6, 140.8, 138.5, 129.7, 128.8, 128.2, 127.8, 122.2, 120.8, 120.4, 117.9, 117.7, 112.3, 92.3, 45.2, 27.7, 26.4, 25.2, 19.9. HRMS (ESI) calcd for C_{24}H_{21}N_2O + [M+H]^+ 353.1654, found 353.1655.

9-Chloro-1-hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2n): white solid (59.5 mg, 80%). M.p. >300 °C. 1H NMR (400 MHz, DMSO-\textit{d}_6) \(\delta\) 11.15 (s, 1H), 8.26 (d, \(J = 7.7\) Hz, 1H), 7.54 – 7.47 (m, 4H), 7.38 (d, \(J = 7.2\) Hz, 2H), 7.25 – 7.29 (m, 1H), 4.84 (s, 2H), 2.77 (s, 2H), 2.12 (s, 2H), 1.90 (s, 2H). 13C NMR (101 MHz, DMSO-\textit{d}_6) \(\delta\) 154.8, 146.6, 140.8, 138.2, 136.8, 129.7, 128.3, 128.0, 127.4, 124.8, 121.5, 118.4, 117.4, 115.4, 111.8, 93.1, 44.9, 27.3, 26.3, 24.9. HRMS (ESI) calcd for C_{24}H_{18}ClN_2O + [M+H]^+ 373.1108, found 373.1097.

3-(4-Fluorophenyl)-1-hydroxy-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile(2o): white solid (62.6 mg, 88%). M.p. >300 °C. 1H NMR (400 MHz, DMSO-\textit{d}_6) \(\delta\) 10.87 (s, 1H), 8.28 (d, \(J = 7.7\) Hz, 1H), 7.66 (d, \(J = 8.3\) Hz, 1H), 7.50 – 7.25 (m, 6H), 4.53 (s, 2H), 2.81 (d, \(J = 5.1\) Hz, 2H), 2.13 (s, 2H), 1.94 (s, 2H). 13C NMR (101 MHz, DMSO-\textit{d}_6) \(\delta\) 161.8 (d, \(J = 244.6\) Hz), 154.8, 144.4, 140.8, 139.3, 134.8, 131.78 (d, \(J = 8.3\) Hz), 125.6 (s), 122.4, 120.9, 120.1, 118.0, 117.7, 115.1 (d, \(J = 21.5\) Hz), 111.74, 109.7, 91.8, 43.0, 27.1, 26.4, 25.8. 19F NMR (376 MHz, DMSO-\textit{d}_6) \(\delta\) -109.27. HRMS (ESI) calcd for C_{24}H_{18}FN_2O + [M+H]^+ 357.1403, found 357.1397.
3-(4-Chlorophenyl)-1-hydroxy-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2p): white solid (52.1 mg, 70%). M.p. >300 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.92 (s, 1H), 8.28 (d, \(J = 7.8\) Hz, 1H), 7.67 (d, \(J = 8.3\) Hz, 1H), 7.58 (d, \(J = 8.3\) Hz, 2H), 7.48 (t, \(J = 7.7\) Hz, 1H), 7.39 (d, \(J = 8.3\) Hz, 2H), 7.27 (t, \(J = 7.5\) Hz, 1H), 4.54 – 4.52 (m, 2H), 2.83 – 2.80 (m, 2H), 2.13 (s, 2H), 1.99 – 1.94 (m, 2H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 154.9, 144.4, 140.8, 139.0, 137.4, 132.8, 131.6, 128.3, 125.6, 122.4, 120.9, 120.1, 117.9, 117.7, 111.8, 109.7, 91.5, 43.0, 27.1, 26.4, 25.8. HRMS (ESI) calcd for C\(_{23}\)H\(_{18}\)ClN\(_2\)O\(_2\) \([M+H]^+\) 373.1108, found 373.1101.

1-Hydroxy-3-(p-tolyl)-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2q): white solid (50.1 mg, 71%). M.p. 286 – 288 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.81 (s, 1H), 8.28 (d, \(J = 7.7\) Hz, 1H), 7.66 (d, \(J = 8.3\) Hz, 1H), 7.47 (t, \(J = 7.4\) Hz, 1H), 7.32 – 7.22 (m, 5H), 4.54 – 4.51 (m, 2H), 2.84 – 2.81 (m, 2H), 2.40 (s, 3H), 2.13 (s, 2H), 1.94 – 1.91 (m, 2H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 154.8, 144.5, 140.8, 139.0, 137.0, 135.6, 129.5, 128.8, 125.5, 122.3, 121.0, 120.0, 117.8, 111.6, 109.6, 92.0, 43.1, 27.1, 26.4, 25.9, 20.8. HRMS (ESI) calcd for C\(_{24}\)H\(_{21}\)N\(_2\)O\(_2\) \([M+H]^+\) 353.1654, found 353.1653.

1-Hydroxy-3-(4-methoxyphenyl)-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2r): white solid (65.5 mg, 89%). M.p. 294 – 296 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.79 (s, 1H), 8.29 (d, \(J = 7.7\) Hz, 1H), 7.64 (d, \(J = 8.2\) Hz, 1H), 7.46 (t, \(J = 7.5\) Hz, 1H), 7.26 (d, \(J = 6.6\) Hz, 3H), 7.05 (d, \(J = 6.7\) Hz, 2H), 4.51 (s, 2H), 3.83 (s, 3H), 2.84 (s, 2H), 2.12 (s, 2H), 1.96 (d, \(J = 26.2\) Hz, 2H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 159.3, 155.3, 145.02, 141.3, 140.7, 131.4, 131.1, 125.9, 122.8, 121.5, 120.5, 118.5, 118.4, 112.1, 110.1, 92.8, 55.6, 43.5, 27.6, 26.8, 26.4. HRMS (ESI) calcd for C\(_{24}\)H\(_{20}\)N\(_2\)O\(_2\) \([M+H]^+\) 369.1603, found 369.1599.
1-Hydroxy-3-(naphthalen-2-yl)-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazole-2-carbonitrile (2s): White solid (52.0 mg, 67%). M.p. 297 – 298 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.90 (s, 1H), 8.31 (d, $J$ = 7.6 Hz, 1H), 8.04 (d, $J$ = 8.9 Hz, 3H), 7.92 (s, 1H), 7.68 (d, $J$ = 7.9 Hz, 1H), 7.60 (s, 2H), 7.49 (s, 2H), 7.29 (d, $J$ = 7.2 Hz, 1H), 4.55 (s, 2H), 2.85 (s, 2H), 2.14 (s, 2H), 1.95 (s, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 154.9, 144.5, 140.9, 140.3, 136.1, 132.6, 132.3, 128.5, 128.1, 127.7, 127.6, 126.5, 125.6, 122.4, 121.0, 120.1, 118.0, 117.9, 111.7, 109.7, 91.9, 43.1, 27.1, 26.5, 25.8. HRMS (ESI) calcd for C$_{27}$H$_{21}$N$_2$O$^+$ [M+H]$^+$ 389.1654, found 389.1651.

7-Hydroxy-5-phenyl-1,2-dihydro-4H-[1,4]oxazepino[6,5,4-jk]carbazole-6-carbonitrile (2t): White solid (36.1 mg, 53%). M.p. 272 – 274 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.10 (s, 1H), 8.35 (d, $J$ = 7.7 Hz, 1H), 7.69 (d, $J$ = 8.3 Hz, 1H), 7.55 – 7.47 (m, 4H), 7.35 – 7.32 (m, 3H), 4.69 (s, 2H), 4.53 – 4.51 (m, 2H), 4.24 – 4.21 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 155.2, 143.2, 140.8, 139.7, 137.6, 129.3, 128.4, 128.2, 125.9, 122.4, 121.3, 120.7, 117.2, 116.4, 112.5, 110.1, 92.3, 70.1, 69.9, 47.5. HRMS (ESI) calcd for C$_{22}$H$_{17}$N$_2$O$_2^+$ [M+H]$^+$ 341.1290, found 341.1284.

2-Ethyl-1,1,3-triphenyl-1H-phosphindol-1-ium tetrafluoroborate (2u): White solid (57.6 mg, 89%). M.p. 272 – 273 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.81 (s, 1H), 8.32 (d, $J$ = 7.8 Hz, 1H), 7.62 – 7.41 (m, 7H), 7.29 (t, $J$ = 7.5 Hz, 1H), 4.24 (t, $J$ = 5.4 Hz, 2H), 2.69 (t, $J$ = 5.8 Hz, 2H), 2.12 – 2.10 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 155.0, 140.6, 139.5, 138.8, 137.2, 129.6, 128.2, 127.9, 125.4, 122.5, 120.7, 119.9, 118.1, 112.5, 109.2, 108.9, 91.0, 40.6, 22.9, 21.7. HRMS (ESI) calcd for C$_{22}$H$_{17}$N$_2$O$^+$ [M+H]$^+$ 325.1341, found 325.1340.
1-Hydroxy-3-phenyl-5,6,7,8-tetrahydro-4H-azocino[3,2,1-jk]carbazole-2-carbonitrile (2v): White solid (31.1 mg, 44%). M.p. 292 – 293 °C. \( ^1H \) NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 10.88 (s, 1H), 8.34 (d, \( J = 7.7 \) Hz, 1H), 7.69 (d, \( J = 8.3 \) Hz, 1H), 7.51 – 7.46 (m, 4H), 7.30 – 7.26 (m, 3H), 4.80 (s, 2H), 2.99-2.73 (m, 2H), 1.94 (s, 2H), 1.66 (s, 2H), 1.29 (s, 2H). \( ^{13}C \) NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 154.6, 144.3, 142.0, 140.0, 139.1, 129.2, 128.1, 127.8, 125.5, 122.4, 120.7, 120.0, 117.6, 115.6, 111.1, 109.0, 92.1, 42.5, 29.1, 28.8, 26.6, 21.0. HRMS (ESI) calcd for \( C_{24}H_{21}N_2O^+ \) [M+H]^+ 353.1654, found 353.1648.

Ethyl (E)-3-(2-cyano-1-hydroxy-3-phenyl-4,5,6,7-tetrahydroazepino[3,2,1-jk]carbazol-12-yl)acrylate (8): Yellow solid (33.2 mg, 38%). M.p. 199 – 200 °C. \( ^1H \) NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 11.25 (s, 1H), 9.50 (d, \( J = 15.8 \) Hz, 1H), 7.77 (d, \( J = 8.2 \) Hz, 1H), 7.66 (d, \( J = 7.6 \) Hz, 1H), 7.54 – 7.45 (m, 4H), 7.37 (d, \( J = 6.6 \) Hz, 2H), 6.52 (d, \( J = 15.7 \) Hz, 1H), 4.61 – 4.58 (m, 2H), 4.24 (q, \( J = 7.1 \) Hz, 2H), 2.86 – 2.83 (m, 2H), 2.13 (s, 2H), 1.94 (d, \( J = 5.4 \) Hz, 2H), 1.31 (t, \( J = 7.1 \) Hz, 3H). \( ^{13}C \) NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 166.4, 154.0, 147.1, 145.3, 141.8, 141.3, 138.3, 129.6, 129.4, 128.3, 127.9, 125.9, 120.1, 119.5, 118.0, 117.9, 117.8, 112.3, 111.3, 93.3, 59.8, 42.9, 26.8, 25.9, 25.6, 14.3. HRMS (ESI) calcd for \( C_{28}H_{25}N_2O^+ \) [M+H]^+ 437.1865, found 437.1862.

2,3,12-Triphenyl-8,9,10,11-tetrahydroazepino[3,2,1-jk]oxepino[5,4,3,2-def]carbazole-13-carbonitrile (10): Yellow solid (89.5 mg, 87%). M.p. 290 – 291 °C. \( ^1H \) NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 7.52 – 7.41 (m, 4H), 7.34 – 7.10 (m, 13H), 6.13 (d, \( J = 7.6 \) Hz, 1H), 4.44 – 4.42 (m, 2H), 2.78 – 2.75 (m, 2H), 2.14 (d, \( J = 5.5 \) Hz, 2H), 1.94 – 1.92 (m, 2H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 155.0, 151.6, 143.1, 142.4, 140.4, 139.5, 138.4, 138.1, 133.5, 132.1,
129.8, 129.8, 129.7, 129.7, 129.6, 128.4, 128.1, 128.1, 127.7, 127.3, 126.9, 126.7, 123.1, 121.7, 120.8, 120.6, 116.1, 113.9, 109.5, 93.1, 45.2, 28.6, 28.1, 26.6. HRMS (ESI) calcd for C_{37}H_{27}N_{2}O^{+} [M+H]^+ 515.2123, found 515.2118.
7. Copies of $^1$H, $^{13}$C and $^{19}$F NMR Spectra for Compounds

$^1$H NMR spectrum of 1a (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1a (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1b (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1b (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1c (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1c (CDCl$_3$, 101 MHz)
\(^1\)H NMR spectrum of 1d (CDCl\(_3\), 400 MHz)

\(^{13}\)C NMR spectrum of 1d (CDCl\(_3\), 101 MHz)
$^1$H NMR spectrum of 1e (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1e (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1f (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1f (CDCl$_3$, 101 MHz)
$^{19}$F NMR spectrum of $\mathbf{1f}$ (CDCl$_3$, 376 MHz)

$^1$H NMR spectrum of $\mathbf{1g}$ (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of $1g$ (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of $1h$ (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of $1h$ (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of $1i$ (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of 1i (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of 1j (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of 1j (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of 1k (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of $\textbf{1k}$ (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of $\textbf{1l}$ (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of 1l (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of 1m (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of 1m (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of 1n (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of 1n (CDCl$_3$, 101 MHz)

$^1$H NMR spectrum of 1o (CDCl$_3$, 400 MHz)
$^{13}$C NMR spectrum of 1o (CDCl$_3$, 101 MHz)

$^{19}$F NMR spectrum of 1o (CDCl$_3$, 376 MHz)
$^{1}$H NMR spectrum of 1p (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1p (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1q (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1q (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1r (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1r (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1s (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1s (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1t (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1t (CDCl$_3$, 101 MHz)
$^{1}H$ NMR spectrum of 1u (CDCl$_3$, 400 MHz)

$^{13}C$ NMR spectrum of 1u (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 1v (CDCl$_3$, 400 MHz)

$^{13}$C NMR spectrum of 1v (CDCl$_3$, 101 MHz)
$^1$H NMR spectrum of 2a (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2a (DMSO-$d_6$, 101 MHz)
$^1$H NMR spectrum of 2b (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2b (DMSO-$d_6$, 101 MHz)
\(^1\)H NMR spectrum of 2c (DMSO-\(d_6\), 400 MHz)

\(^{13}\)C NMR spectrum of 2c (DMSO-\(d_6\), 101 MHz)
$^1$H NMR spectrum of 2d (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2d (DMSO-$d_6$, 101 MHz)
$^1$H NMR spectrum of 2e (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2e (DMSO-$d_6$, 101 MHz)
$^1$H NMR spectrum of 2f (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2f (DMSO-$d_6$, 101 MHz)
$^{19}$F NMR spectrum of 2f (DMSO-$d_6$, 376 MHz)

$^1$H NMR spectrum of 2g (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2g (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of 2h (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2h (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of 2i (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2i (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of 2j (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2j (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of 2k (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2k (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of 2l (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2l (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of 2m (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of $2m$ (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of $2n$ (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2n (DMSO-$d_6$, 101 MHz)

$^1$H NMR spectrum of 2o (DMSO-$d_6$, 400 MHz)
$^{13}$C NMR spectrum of 2o (DMSO-$d_6$, 101 MHz)

$^{19}$F NMR spectrum of 2o (DMSO-$d_6$, 376 MHz)
\(^1\text{H NMR spectrum of } 2p \text{ (DMSO-}d_6, \text{ 400 MHz)}

\(^{13}\text{C NMR spectrum of } 2p \text{ (DMSO-}d_6, \text{ 101 MHz)}

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$^1$H NMR spectrum of 2q (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2q (DMSO-$d_6$, 101 MHz)
$^1$H NMR spectrum of $2r$ (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of $2r$ (DMSO-$d_6$, 101 MHz)
$^1$H NMR spectrum of 2s (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2s (DMSO-$d_6$, 101 MHz)
$^1$H NMR spectrum of 2t (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 2t (DMSO-$d_6$, 101 MHz)
¹H NMR spectrum of 2u (DMSO-\textit{d}_6, 400 MHz)

¹³C NMR spectrum of 2u (DMSO-\textit{d}_6, 101 MHz)
$^1$H NMR spectrum of 2v (DMSO-\textit{d}_6, 400 MHz)

$^{13}$C NMR spectrum of 2v (DMSO-\textit{d}_6, 101 MHz)
$^1$H NMR spectrum of 8 (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 8 (DMSO-$d_6$, 101 MHz)
$^1$H NMR spectrum of 10 (DMSO-$d_6$, 400 MHz)

$^{13}$C NMR spectrum of 10 (CDCl$_3$, 101 MHz)
11. References

