Supporting Information

Silver(I)-catalysed domino alkyne-annulation/Diels-Alder reaction: A mild synthetic approach to tetrahydrospiro[carbazole-4,3'-indoline] scaffolds

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Experimental Section

General Information: All reactions were performed at room temperature under nitrogen atmosphere and stirred magnetically. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ or DMSO–d$_6$ on a 500 MHz and 125 MHz spectrometer respectively by using tetramethyl silane (TMS) as the internal standard. All chemical shift values were reported in ppm relative to resonance in TMS at δ 0.00 or CDCl$_3$ at 7.26 for $^1$H NMR and δ 77.0 for $^{13}$C NMR. Spin multiplicities were described as s (singlet), d (doublet), dd (double doublet), t (triplet), and m (multiplet). Coupling constant ($J$) values were expressed in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on ESI-QTOF mass spectrometer. All the melting points were recorded on micromelting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on MERCK precoated silica gel 60f–254 (0.5 mm) aluminum plates. TLC spot visualization was achieved UV light. Solvents and reagents of reagent grade were purchased from commercial resources and were used without additional purification. Column chromatography was performed using silica gel 100-200.

Reaction procedure for the synthesis of 3a:

To a mixture of 1a (50 mg, 0.230 mmol, 1.0 equiv.) with 2b (88 mg, 0.299 mmol, 1.3 equiv.) in DCE (5 mL) under nitrogen, was added AgOTf (10 mol%) and the reaction mixture was stirred for 72 h. Evaporation of the DCE gave a crude residue which was further purified by column chromatography on silica gel ($\text{SiO}_2$, ethyl acetate/hexane as eluent) to obtain 3a in 73% yield. All the compounds 3b–z were prepared according to the same procedure as described for 3a.

**Ethyl 2'-ox-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3a):**

Reaction of 1a (50 mg, 0.230 mmol) with 2b (88 mg, 0.299 mmol); Yield: 73% (86 mg); white solid; m.p. 128–130 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.73 (s, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.24–7.14 (m, 4H), 7.03 (d, $J = 7.0$ Hz, 1H), 6.96–6.85 (m, 4H), 3.81–3.77 (m, 2H), 3.61–3.56 (m, 1H), 3.42–3.39 (m, 1H), 3.11–3.04 (m, 1H), 2.54–2.50 (m, 1H), 2.39–2.33 (m, 4H), 0.87 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 179.9, 170.9, 144.9, 140.7, 137.4, 136.5, 135.9, 130.2, 129.9, 128.9, 127.0,
126.4, 125.0, 124.3, 123.6, 122.9, 118.1, 115.9, 114.3, 109.8, 60.8, 51.1, 47.6, 23.5, 22.3, 21.6, 13.6; HRMS (ESI): calcd for C_{29}H_{28}N_{2}O_{5}S[M+H]^+ 515.1635, found: 515.1641.

**Ethyl 5'-fluoro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3b):** Reaction of 1b (50 mg, 0.213 mmol) with 2b (82 mg, 0.277 mmol); Yield: 75% (84 mg); white solid; m.p. 119–121 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.81 (s, 1H), 8.12 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 8.2 Hz, 2H), 7.26–7.24 (m, 2H), 7.18 (t, $J$ = 7.6 Hz, 1H), 6.97 (t, $J$ = 7.8 Hz, 1H), 6.90–6.85 (m, 3H), 6.74–6.72 (m, 1H), 3.86–3.81 (m, 2H), 3.59–3.55 (m, 1H), 3.42–3.39 (m, 1H), 3.13–3.06 (m, 1H), 2.56–2.52 (m, 1H), 2.37 (s, 3H), 2.31–2.23 (m, 1H), 0.91 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.9, 170.6, 159.9 (d, $J_{C-F}$ = 241.6 Hz), 145.1, 137.5, 136.7 (d, $J_{C-F}$ = 1.8 Hz), 136.5, 135.9, 131.9 (d, $J_{C-F}$ = 7.3 Hz), 130.0, 126.8, 126.4, 124.5, 123.7, 117.9, 115.5, 115.4 (d, $J_{C-F}$ = 1.8 Hz), 114.5, 113.2 (d, $J_{C-F}$ = 24.5 Hz), 110.4 (d, $J_{C-F}$ = 8.2 Hz), 60.9, 51.5, 47.6, 23.4, 22.2, 21.6, 13.7; HRMS (ESI): calcd for C_{29}H_{28}FN_{2}O_{5}S [M+H]^+ 533.1546, found: 533.1545.

**Ethyl 5'-chloro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3c):** Reaction of 1c (50 mg, 0.199 mmol) with 2b (77 mg, 0.258 mmol); Yield: 70% (76 mg); white solid; m.p. 120–122 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.90 (s, 1H), 8.12 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 8.4 Hz, 2H), 7.32–7.30 (m, 1H), 7.26–7.25 (m, 2H), 7.19–7.14 (m, 2H), 6.98–6.95 (m, 2H), 6.87–6.84 (m, 2H), 3.86–3.82 (m, 2H), 3.59–3.55 (m, 1H), 3.42–3.38 (m, 1H), 3.13–3.05 (m, 1H), 2.56–2.53 (m, 1H), 2.37 (s, 3H), 2.34–2.26 (m, 1H), 0.91 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.7, 170.6, 145.1, 139.4, 137.5, 136.5, 135.9, 132.0, 129.0, 128.1, 126.8, 126.4, 125.4, 124.5, 123.7, 117.9, 115.3, 114.5, 110.8, 60.9, 51.3, 47.7, 23.5, 22.2, 21.6, 13.7; HRMS (ESI): calcd for C_{29}H_{26}ClN_{2}O_{5}S [M+H]^+ 549.1251, found: 549.1244.

**Ethyl 5'-bromo-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3d):** Reaction of 1d (50 mg, 0.170 mmol) with 2b (65 mg, 0.221 mmol); Yield: 68% (68 mg); white solid; m.p. 141–143°C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.86 (s, 1H), 8.12 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 8.4 Hz, 2H), 7.32–7.30 (m, 1H), 7.26–7.25 (m, 2H), 7.19
Ethyl 5'-methyl-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3e): Reaction of 1e (50 mg, 0.216 mmol) with 2b (83 mg, 0.281 mmol); Yield: 70% (80 mg); white solid; m.p. 174–176 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.48 (s, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.16 (t, $J = 7.3$ Hz, 1H), 6.99–6.94 (m, 2H), 6.89 (d, $J = 7.8$ Hz, 1H), 6.82–6.81 (m, 2H), 3.83–3.78 (m, 2H), 3.63–3.58 (m, 1H), 3.40–3.37 (m, 1H), 3.09–3.01 (m, 1H), 2.53–2.48 (m, 1H), 2.40–2.32 (m, 4H), 2.16 (s, 3H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.9, 171.0, 144.9, 138.1, 137.3, 136.5, 135.9, 132.3, 130.2, 129.9, 129.3, 127.1, 126.4, 125.8, 124.3, 123.6, 118.2, 116.2, 114.3, 109.4, 60.7, 51.1, 47.5, 23.4, 22.3, 21.6, 21.1, 13.6; HRMS (ESI): calcd for C$_{30}$H$_{29}$BrN$_2$O$_5$S [M+H]$^+$ 529.1792, found: 529.1792.

Methyl 2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3f): Reaction of 1f (50 mg, 0.246 mmol) with 2b (95 mg, 0.320 mmol); Yield: 71% (87 mg); white solid; m.p. 119–121 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.59 (s, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.21–7.14 (m, 2H), 7.02 (d, $J = 7.5$ Hz, 1H), 6.96–6.93 (m, 2H), 6.91–6.84 (m, 2H), 3.62–3.58 (m, 1H), 3.45–3.42 (m, 1H), 3.30 (s, 3H), 3.12–3.04 (m, 1H), 2.53–2.50 (m, 1H), 2.40–2.33 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.9, 171.4, 144.9, 140.5, 137.3, 136.4, 135.9, 130.1, 130.0, 129.0, 127.0, 126.4, 125.0, 124.4, 123.6, 122.9, 118.0, 115.8, 114.4, 109.8, 51.1, 47.8, 23.4, 22.2, 21.6; HRMS (ESI): calcd for C$_{28}$H$_{25}$N$_2$O$_5$S [M+H]$^+$ 501.1484, found: 501.1479.
Methyl 5'-fluoro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3g): Reaction of 1g (50 mg, 0.226 mmol) with 2b (87 mg, 0.294 mmol); Yield: 70% (82 mg); white solid; m.p. 128–130 °C; \( ^1 \)H NMR (500 MHz, CDCl\(_3 \)): \( \delta \) 8.99 (s, 1H), 8.12 (d, \( J = 8.4 \) Hz, 1H), 7.69 (d, \( J = 8.4 \) Hz, 2H), 7.26–7.24 (m, 2H), 7.18 (t, \( J = 7.2 \) Hz, 1H), 6.96 (t, \( J = 7.0 \) Hz, 1H), 6.91–6.84 (m, 3H), 6.72–6.70 (m, 1H), 3.60–3.56 (m, 1H), 3.46–3.43 (m, 1H), 3.34 (s, 3H), 3.14–3.08 (m, 1H), 2.56–2.52 (m, 1H), 2.37(s, 3H), 2.33–2.29 (m, 1H); \( ^{13} \)C NMR (125 MHz, CDCl\(_3 \)): \( \delta \) 180.1, 171.1, 159.9 (d, \( J_{CF} = 241.6 \) Hz), 145.2, 137.4, 136.6 (d, \( J_{CF} = 14.5 \) Hz), 135.8, 131.8 (d, \( J_{CF} = 7.3 \) Hz), 130.0, 126.8, 126.4, 124.5, 123.7, 117.8, 115.6, 115.4, 114.5, 113.1 (d, \( J_{CF} = 24.5 \) Hz), 110.5 (d, \( J_{CF} = 8.2 \) Hz), 51.7, 51.5, 47.7, 23.4, 22.1, 21.6; HRMS (ESI): calcd for C\(_{28}\)H\(_{24}\)FN\(_2\)O\(_5\)S [M+H]\(^+\) 519.1390, found: 519.1388.

Methyl 5'-chloro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3h): Reaction of 1h (50 mg, 0.209 mmol) with 2b (80 mg, 0.272 mmol); Yield: 75% (83.7 mg); white solid; m.p. 141–143 °C; \( ^1 \)H NMR (500 MHz, CDCl\(_3 \)): \( \delta \) 8.71(s, 1H), 8.12 (d, \( J = 8.5 \) Hz, 1H), 7.69 (d, \( J = 8.2 \) Hz, 2H), 7.26–7.24 (m, 2H), 7.21–7.15 (m, 2H), 6.99–6.93 (m, 2H), 6.88–6.83 (m, 2H), 3.60–3.56 (m, 1H), 3.45–3.42 (m, 1H), 3.36 (s, 3H), 3.12–3.06 (m, 1H), 2.59–2.52 (m, 1H), 2.37 (s, 3H), 2.35–2.26 (s, 1H); \( ^{13} \)C NMR (125 MHz, CDCl\(_3 \)): \( \delta \) 179.6, 171.1, 145.2, 139.1, 137.4, 136.5, 135.8, 131.9, 130.1, 129.0, 128.1, 126.8, 126.4, 124.5, 124.6, 123.7, 117.8, 115.6, 115.4, 114.5, 110.8, 51.9, 51.2, 47.8, 23.4, 22.1, 21.6; HRMS (ESI): calcd for C\(_{28}\)H\(_{24}\)ClN\(_2\)O\(_5\)S [M+H]\(^+\) 535.1094, found: 535.1086.

Methyl 5'-bromo-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3i): Reaction of 1i (50 mg, 0.179 mmol) with 2b (69 mg, 0.232 mmol); Yield: 78% (80.5 mg); white solid; m.p. 126–128 °C; \( ^1 \)H NMR (500 MHz, CDCl\(_3 \)): \( \delta \) 8.72 (s, 1H), 8.12 (d, \( J = 8.5 \) Hz, 1H), 7.68 (d, \( J = 8.2 \) Hz, 2H), 7.32–7.30 (m, 1H), 7.26–7.25 (m, 2H), 7.19 (t, \( J = 7.8 \) Hz, 1H), 7.07 (s, 1H), 6.97 (t, \( J = 7.8 \) Hz, 1H), 6.84 (t, \( J = 7.6 \) Hz, 2H), 3.60–3.56 (m, 1H), 3.44–3.42 (m, 1H), 3.37 (s, 3H), 3.13–3.07 (m, 1H), 2.56–2.52 (m, 1H), 2.37(s, 3H), 2.33–2.34 (m, 1H); \( ^{13} \)C NMR (125 MHz, CDCl\(_3 \)): \( \delta \) 179.4, 171.1,
Methyl 5'-methyl-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3j): Reaction of 1j (50 mg, 0.230 mmol) with 2b (88 mg, 0.300 mmol); Yield: 62% (73.4 mg); white solid; m.p. 125–127 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.41 (s, 1H), 8.09 (d, $J$ = 8.4 Hz, 1H), 7.69 (d, $J$ = 8.2 Hz, 2H), 7.25 (d, $J$ = 8.2 Hz, 2H), 7.16 (t, $J$ = 7.5 Hz, 1H), 6.99–6.94 (m, 2H), 6.88–6.80 (m, 3H), 3.63–3.59 (m, 1H), 3.43–3.40 (m, 1H), 3.32 (s, 3H), 3.11–3.00 (m, 1H), 2.52–2.48 (m, 1H), 2.41–2.28 (m, 4H), 2.16 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 179.8, 171.5, 144.9, 137.9, 137.2, 136.5, 135.9, 132.3, 130.1, 129.9, 129.4, 127.1, 126.4, 125.8, 124.3, 123.6, 118.2, 116.1, 114.3, 109.4, 51.6, 51.1, 47.7, 23.4, 22.2, 21.6, 21.1; HRMS (ESI): calcd for C$_{29}$H$_{27}$N$_2$O$_5$S [M+H]$^+$ 515.1641, found: 515.1638.

tert-Butyl 2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3k): Reaction of 1k (50 mg, 0.204 mmol) with 2b (78 mg, 0.265 mmol); Yield: 78% (86 mg); white solid; m.p. 129–131 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.98 (s, 1H), 8.08 (d, $J$ = 8.4 Hz, 1H), 7.67 (d, $J$ = 8.4 Hz, 2H), 7.24–7.18 (m, 3H), 7.14 (t, $J$ = 7.8 Hz, 1H), 7.05 (d, $J$ = 7.5 Hz, 1H), 6.98 (d, $J$ = 7.8 Hz, 1H), 6.94–6.86 (m, 3H), 3.58–3.53 (m, 1H), 3.34–3.31 (m, 1H), 3.08–3.00 (m, 1H), 2.50–2.46 (m, 1H), 2.36 (s, 3H), 2.29–2.21 (m, 1H), 1.04 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 180.3, 170.0, 144.9, 141.0, 137.6, 136.5, 135.9, 130.5, 129.9, 128.9, 127.1, 126.4, 125.0, 124.2, 123.6, 122.9, 118.1, 116.1, 114.3, 109.9, 81.5, 51.1, 47.9, 27.3, 23.6, 22.5, 21.6; HRMS (ESI): calcd for C$_{31}$H$_{31}$N$_2$O$_5$S [M+H]$^+$ 543.1954, found: 543.1948.

 tert-Butyl 5'-fluoro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3l): Reaction of 1l (50 mg, 0.190 mmol) with 2b (73 mg, 0.247 mmol); Yield: 76% (80 mg); white solid; m.p. 127–129 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.62 (s, 1H), 8.11 (d, $J$ = 8.4 Hz, 1H), 7.67 (d, $J$ = 8.2 Hz, 2H), 7.25–7.23 (m, 2H), 7.17 (t, $J$ = 7.8 Hz,
1H), 6.98–6.91 (m, 3H), 6.87 (d, J = 7.8 Hz, 1H), 6.77 (d, J = 8.7 Hz, 1H), 3.56–3.52 (m, 1H), 3.34–3.30 (m, 1H), 3.07–3.00 (m, 1H), 2.51–2.47 (m, 1H), 2.37 (s, 3H), 2.21–2.12 (m, 1H), 1.10 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 179.9, 170.1, 159.9 (d, JCF = 240.7 Hz), 145.3, 138.3, 137.7, 136.7, 136.1, 132.3 (d, JCF = 7.3 Hz), 130.3, 127.3, 126.5, 124.6, 123.8, 118.4, 116.3, 115.5 (d, JCF = 22.7 Hz), 114.6, 113.52, 110.7, 81.7, 51.8, 48.0, 27.6, 23.7, 22.7, 21.8; HRMS (ESI): calcd for C31H30FN2O5S [M+H]+ 561.1859, found: 561.1853.

**tert-Butyl 5'-chloro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate** (**3m**): Reaction of **1m** (50 mg, 0.179 mmol) with **2b** (69 mg, 0.233 mmol); Yield: 78% (80 mg); white solid; m.p. 124–126 °C; 1H NMR (500 MHz, CDCl3): δ 8.85 (s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.26–7.24 (m, 2H), 7.18 (t, J = 7.9 Hz, 2H), 6.96–6.94 (m, 2H), 6.91 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.56–3.52 (m, 1H), 3.33–3.30 (m, 1H), 3.08–3.01 (m, 1H), 2.51–2.47 (m, 1H), 2.37 (s, 3H), 2.23–2.17 (m, 1H), 1.09 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 179.7, 169.7, 145.1, 139.6, 137.7, 136.5, 135.9, 132.3, 130.0, 128.8, 128.1, 126.8, 126.4, 125.5, 124.4, 123.7, 117.9, 115.4, 114.5, 110.8, 81.8, 51.3, 48.1, 27.1, 23.5, 22.4, 21.6; HRMS (ESI): calcd for C31H30ClN2O5S [M+H]+ 577.1564, found: 577.1558.

**tert-Butyl 5'-bromo-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate** (**3n**): Reaction of **1n** (50 mg, 0.154 mmol) with **2b** (59 mg, 0.200 mmol); Yield: 76% (72 mg); white solid; m.p. 166–168 °C; 1H NMR (500 MHz, CDCl3): δ 9.08 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.34–7.32 (m, 1H), 7.26–7.24 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 1.7 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.1 Hz, 2H), 3.56–3.52 (m, 1H), 3.33–3.30 (m, 1H), 3.09–3.02 (m, 1H), 2.51–2.48 (m, 1H), 2.37 (s, 3H), 2.23–2.16 (m, 1H), 1.08 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 179.8, 169.7, 145.1, 140.1, 137.7, 136.5, 135.9, 132.7, 131.7, 130.1, 130.0, 128.2, 126.8, 124.4, 123.7, 117.9, 114.5, 114.5, 111.4, 81.8, 51.3, 48.1, 27.4, 23.5, 22.4, 21.6; HRMS (ESI): calcd for C31H30BrN2O5S [M+2]+ 623.1038, found: 623.1038.
tert-Butyl 5'-methyl-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3o): Reaction of 1o (50 mg, 0.193 mmol) with 2b (74 mg, 0.251 mmol); Yield: 77% (84 mg); white solid; m.p. 144–146 °C; 1H NMR (500 MHz, CDCl3): δ 8.50 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.15 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.85 (t, J = 4.0 Hz, 2H), 3.59–3.55 (m, 1H), 3.32–3.29 (m, 1H), 3.05–2.99 (m, 1H), 2.49–2.45 (m, 1H), 2.36 (s, 3H), 2.30–2.23 (m, 1H), 2.16 (s, 3H), 1.05 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 179.9, 170.1, 144.9, 138.4, 137.5, 136.5, 136.0, 132.4, 130.6, 129.9, 129.2, 127.2, 126.4, 125.8, 124.2, 123.6, 118.3, 116.4, 114.3, 109.4, 81.4, 51.2, 47.9, 27.3, 23.5, 22.5, 21.6, 21.0; HRMS (ESI): calcd for C32H33N2O5S [M+H]+ 557.2110, found: 557.2107.

Ethyl 6',7'-dimethyl-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3p): Reaction of 1p (50 mg, 0.204 mmol) with 2b (78 mg, 0.265 mmol); Yield: 53% (48 mg); white solid; m.p. 130–132 °C; 1H NMR (500 MHz, CDCl3): δ 8.95 (s, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.12 (t, J = 7.0 Hz, 1H), 6.91–6.86 (m, 2H), 6.75 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 3.87–3.77 (m, 2H), 3.58–3.54 (m, 1H), 3.38–3.35 (m, 1H), 3.10–3.03 (m, 1H), 2.50–2.42 (m, 1H), 2.38–2.30 (m, 4H), 2.17 (s, 3H), 1.95 (s, 3H), 0.87 (t, J = 7.2 Hz, 3H); 13C NMR (125 MHz, CDCl3): δ 180.9, 171.1, 145.0, 139.5, 137.7, 137.4, 136.6, 136.2, 130.1, 127.5, 126.5, 124.4, 124.3, 123.7, 122.1, 118.2, 117.9, 116.5, 114.5, 60.7, 51.9, 47.8, 23.6, 22.3, 21.7, 19.9, 13.7, 13.2; HRMS (ESI): calcd for C31H33N2O5S [M+H]+ 543.1954, found: 543.1961.

tert-Butyl 6',7'-dimethyl-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3q): Reaction of 1q (50 mg, 0.183 mmol) with 2b (71 mg, 0.238 mmol); Yield: 50% (52 mg); white solid; m.p. 245–247 °C; 1H NMR (500 MHz, CDCl3): δ 9.25 (s, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.13–7.09 (m, 1H), 6.92–6.87 (m, 2H), 6.77 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 3.55–3.50 (m, 1H), 3.31–3.28 (m, 1H), 3.07–3.00 (m, 1H), 2.50–2.42 (m, 1H), 2.36 (s, 3H), 2.29–2.14 (m, 4H), 1.91 (s, 3H), 1.04 (s, 9H); 13C NMR (125 MHz, CDCl3): δ 181.1, 170.1,
144.0, 139.6, 137.5, 136.5, 136.0, 130.0, 127.6, 127.4, 126.3, 124.1, 124.0, 123.5, 122.0, 118.0, 117.7, 116.6, 114.4, 81.2, 51.8, 48.0, 27.3, 23.6, 22.3, 21.6, 19.7, 13.0; HRMS (ESI): calcd for C$_{33}$H$_{35}$N$_2$O$_5$S [M+H]$^+$ 571.2267, found: 571.2270.

Ethyl 7'-fluoro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3r): Reaction of 1r (50 mg, 0.213 mmol) with 2b (82 mg, 0.276 mmol); Yield: 78% (88 mg); white solid; m.p. 177–179 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.44 (s, 1H), 8.10 (d, $J$ = 8.4 Hz, 1H), 7.69 (d, $J$ = 8.4 Hz, 2H), 7.25 (d, $J$ = 7.9 Hz, 2H), 7.20–7.16 (m, 1H), 7.04–6.98 (m, 2H), 6.89–6.84 (m, 3H), 3.90–3.79 (m, 2H), 3.64–3.57 (m, 1H), 3.43–3.39 (m, 1H), 3.10–3.01 (m, 1H), 2.56–2.50 (m, 1H), 2.39–2.27 (m, 4H), 1.26 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 178.9, 170.8, 148.1 (d, $J_{CF}$ = 244.3 Hz), 145.2, 137.7, 136.6, 136.0, 133.0 (d, $J_{CF}$ = 2.7 Hz), 130.2, 128.2 (d, $J_{CF}$ = 12.7 Hz), 127.0, 126.5, 124.6, 123.9, 123.6 (d, $J_{CF}$ = 5.4 Hz), 120.9 (d, $J_{CF}$ = 2.7 Hz), 118.0, 116.2, (d, $J_{CF}$ = 16.3 Hz), 115.5, 114.6, 61.0, 51.5 (d, $J_{CF}$ = 2.7 Hz), 47.8, 23.5, 22.3, 21.7, 13.7 ; HRMS (ESI): calcd for C$_{29}$H$_{26}$FN$_2$O$_5$S [M+H]$^+$ 533.1546, found: 533.1552.

tert-Butyl 7'-fluoro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3s): Reaction of 1s (50 mg, 0.190 mmol) with 2b (73 mg, 0.247 mmol); Yield: 70% (74 mg); white solid; m.p. 126–128 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.32–8.25 (m, 1H), 8.10 (d, $J$ = 8.4 Hz, 1H), 7.66 (d, $J$ = 8.4 Hz, 2H), 7.24 (d, $J$ = 7.9 Hz, 2H), 7.18 (t, $J$ = 7.6 Hz, 1H), 7.05–6.98 (m, 2H), 6.88–6.86 (m, 3H), 3.60–3.55 (m, 1H), 3.34–3.30 (m, 1H), 3.04–2.97 (m, 1H), 2.52–2.43 (m, 1H), 2.36(s, 3H), 2.26–2.14 (m, 1H), 1.10 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 178.9, 169.9, 148.1 (d, $J_{CF}$ = 243.4 Hz), 145.2, 137.9, 136.7, 136.0, 133.4 (d, $J_{CF}$ = 2.7 Hz), 130.2, 128.4 (d, $J_{CF}$ = 12.7 Hz), 127.1, 126.5, 124.6, 123.9, 123.7 (d, $J_{CF}$ = 6.4 Hz), 120.9 (d, $J_{CF}$ = 3.6 Hz), 118.0, 116.1 (d, $J_{CF}$ = 16.3 Hz), 115.7, 114.6, 81.9, 51.5 (d, $J_{CF}$ = 2.7 Hz), 48.3, 27.5, 23.6, 22.5, 21.7; HRMS (ESI): calcd for C$_{31}$H$_{30}$FN$_2$O$_5$S [M+H]$^+$ 561.1859, found: 561.1857.
Methyl 7'-fluoro-2'-oxo-9-tosyl-1,2,3,9-tetrahydros piro[carbazole-4,3'-indoline]-3-carboxylate (3t): Reaction of 1t (50 mg, 0.226 mmol) with 2b (80 mg, 0.271 mmol); Yield: 73% (85 mg); white solid; m.p. 150–152 °C; 1H NMR (500 MHz, CDCl3): δ 8.28 (s, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.20–7.17 (m, 1H), 7.04–6.99 (m, 2H), 6.89–6.83 (m, 3H), 3.63–3.58 (m, 1H), 3.46–3.42 (m, 1H), 3.09–3.02 (m, 1H), 2.55–2.50 (m, 1H), 2.38–2.30 (m, 4H); 13C NMR (125 MHz, CDCl3): δ 178.7, 171.3, 148.0 (d, J_{CF} = 244.3 Hz), 145.2, 137.6, 136.6, 136.1, 133.0 (d, J_{CF} = 2.7 Hz), 130.2, 128.1 (d, J_{CF} = 11.8 Hz), 127.0, 126.5, 124.7, 123.9, 123.7 (d, J_{CF} = 5.4 Hz), 120.9, 118.0, 116.3 (d, J_{CF} = 17.3 Hz), 115.5, 114.6, 51.8, 51.5, 48.1, 23.5, 22.3, 21.7; HRMS (ESI): calcd for C_{28}H_{24}FN_{2}O_{5}S [M+H]+ 519.1390, found: 519.1392.

Ethyl-1'-benzyl-2'-oxo-9-tosyl-1,2,3,9-tetrahydros piro[carbazole-4,3'-indoline]-3-carboxylate (3u): Reaction of 1u (50 mg, 0.163 mmol) with 2b (62 mg, 0.211 mmol); Yield: 65% (63 mg); white solid; m.p. 103–105 °C; 1H NMR (500 MHz, CDCl3): δ 8.06 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 6.9 Hz, 2H), 7.38–7.32 (m, 3H), 7.25–7.19 (m, 3H), 7.10 (t, J = 8.1 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 6.99 (d, J = 7.9 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.73 (t, J = 7.8 Hz, 1H), 6.37 (d, J = 7.9 Hz, 1H), 5.18 (d, J = 15.0 Hz, 1H), 4.85 (d, J = 15.0 Hz, 1H), 3.72–3.58 (m, 3H), 3.45–3.42 (m, 1H), 3.09–3.02 (m, 1H), 2.55–2.50 (m, 1H), 2.40–2.32 (m, 4H), 0.75 (t, J = 7.2 Hz, 3H); 13C NMR (125 MHz, CDCl3): δ 177.9, 171.3, 144.9, 143.0, 137.4, 136.3, 136.0, 135.7, 130.0, 129.8, 128.9, 128.8, 128.7, 128.0, 126.9, 126.4, 124.8, 124.2, 123.3, 122.8, 118.3, 116.2, 114.2, 108.8, 60.6, 50.6, 47.8, 45.0, 23.4, 22.6, 21.6. 13.7; HRMS (ESI): calcd for C_{36}H_{32}N_{2}O_{5}S[M+H]^+ 605.2105, found: 605.2107.

Ethyl 5'-bromo-1'-ethyl-2'-oxo-9-tosyl-1,2,3,9-tetrahydros piro[carbazole-4,3'-indoline]-3-carboxylate (3v): Reaction of 1v (50 mg, 0.155 mmol) with 2b (59 mg, 0.201 mmol); Yield: 57% (54 mg); white solid; m.p. 105–107 °C; 1H NMR (500 MHz, CDCl3): δ 8.11 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.41–7.39 (m, 1H), 7.25–7.24 (m, 2H), 7.18–7.12 (m, 2H), 6.96 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 7.8 Hz, 1H), 3.98–3.93 (m, 1H), 3.86–3.79 (m, 3H), 3.60–3.55 (m, 1H), 3.39–3.36 (m,
1H), 3.09–3.03 (m, 1H), 2.54–2.50 (m, 1H), 2.37 (s, 3H), 2.32–2.23 (m, 1H), 1.40 (t, \( J = 7.3 \) Hz, 3H), 0.90 (t, \( J = 7.2 \) Hz, 3H), \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 176.7, 170.5, 145.1, 142.1, 137.5, 136.6, 135.9, 132.1, 131.7, 130.0, 128.1, 126.9, 126.3, 124.4, 123.5, 117.8, 115.7, 115.1, 114.6, 109.4, 60.7, 50.5, 47.8, 35.5, 23.5, 22.4, 21.6, 13.8, 12.3; HRMS (ESI) calcd for C\(_{31}\)H\(_{30}\)BrN\(_2\)O\(_5\)S[\text{M+2}\]+ 623.1042, found: 623.1043.

**Ethyl 1’-benzyl-5’-fluoro-2’-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3w):** Reaction of 1w (50 mg, 0.154 mmol) with 2b (59 mg, 0.198 mmol); Yield: 58% (55 mg); white solid; m.p. 147–149 \( ^\circ \)C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.10 (d, \( J = 8.4 \) Hz, 1H), 7.69 (d, \( J = 8.4 \) Hz, 2H), 7.53 (d, \( J = 6.9 \) Hz, 2H), 7.39–7.33 (m, 3H), 7.26–7.24 (m, 1H), 7.14 (t, \( J = 7.6 \) Hz, 2H), 6.91–6.90 (m, 2H), 6.78–6.75 (m, 2H), 6.38 (d, \( J = 7.9 \) Hz, 1H), 5.18 (d, \( J = 15.1 \) Hz, 1H), 4.86 (d, \( J = 15.0 \) Hz, 1H), 3.78–3.73 (m, 2H), 3.62–3.57 (m, 1H), 3.48–3.44 (m, 1H), 3.12–3.05 (m, 1H), 2.56–2.53 (m, 1H), 2.37 (s, 3H), 2.32–2.23 (m, 1H), 0.82 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 177.6, 170.7, 159.9 (d, \( J_{CF} = 241.6 \) Hz), 145.1, 139.1 (d, \( J_{CF} = 1.8 \) Hz), 137.5, 136.4, 135.9, 135.4, 131.6 (d, \( J_{CF} = 8.2 \) Hz), 130.0, 128.8, 128.7, 128.1, 126.8, 126.4, 124.3, 123.8, 118.2, 115.7, 115.2 (d, \( J_{CF} = 23.6 \) Hz), 114.4, 113.2 (d, \( J_{CF} = 25.4 \) Hz), 109.3 (d, \( J_{CF} = 7.3 \) Hz), 60.7, 50.8, 47.7, 45.2, 23.4, 22.5, 21.5. 13.7; HRMS (ESI): calcd for C\(_{36}\)H\(_{32}\)F\(_2\)N\(_2\)O\(_5\)S[\text{M+H}\]+ 623.2016, found: 623.2017.

**Ethyl 1’-benzyl-5’-chloro-2’-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3x):** Reaction of 1x (50 mg, 0.146 mmol) with 2b (56 mg, 0.191 mmol); Yield: 63% (58 mg); white solid; m.p. 153–155 \( ^\circ \)C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.09 (d, \( J = 8.4 \) Hz, 1H), 7.68 (d, \( J = 8.4 \) Hz, 2H), 7.52 (d, \( J = 6.6 \) Hz, 2H), 7.38–7.34 (m, 3H), 7.26–7.24 (m, 2H), 7.18–7.12 (m, 2H), 6.98 (s, 1H), 6.90 (d, \( J = 8.4 \) Hz, 1H), 6.76 (t, \( J = 7.5 \) Hz, 1H), 6.36 (d, \( J = 7.8 \) Hz, 1H), 5.17 (d, \( J = 15.1 \) Hz, 1H), 4.84 (d, \( J = 15.0 \) Hz, 1H), 3.78–3.73 (m, 2H), 3.61–3.57 (m, 1H), 3.45–3.42 (m, 1H), 3.11–3.04 (m, 1H), 2.56–2.52 (m, 1H), 2.37–2.25 (m, 4H), 0.83 (t, \( J = 7.0 \) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 177.4, 170.6, 145.1, 141.7, 137.5, 136.5, 135.9, 135.2, 131.7, 130.1, 128.8, 128.7, 128.2, 128.1, 127.4, 126.8, 126.4, 125.3, 124.4, 123.4, 118.2, 115.6, 114.4, 109.7, 60.8, 50.7, 47.8, 45.1, 23.4, 22.5, 21.6. 13.8; HRMS (ESI): calcd for C\(_{36}\)H\(_{32}\)ClN\(_2\)O\(_5\)S[\text{M+H}\]^+ 639.1720, found: 639.1718.
Ethyl 1'-benzyl-5'-bromo-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3y): Reaction of 1y (50 mg, 0.129 mmol) with 2b (50 mg, 0.169 mmol); Yield: 62% (54 mg); white solid; m.p. 137–139 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.09 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 8.2$ Hz, 2H), 7.51 (d, $J = 7.2$ Hz, 2H), 7.37–7.31 (m, 4H), 7.26–7.24 (m, 2H), 7.15–7.10 (m, 2H), 6.86 (d, $J = 8.4$ Hz, 1H), 6.75 (t, $J = 7.8$ Hz, 1H), 6.36 (d, $J = 7.8$ Hz, 1H), 5.16 (d, $J = 15.0$ Hz, 1H), 4.84 (d, $J = 15.0$ Hz, 1H), 3.78–3.74 (m, 2H), 3.61–3.56 (m, 1H), 3.45–3.41 (m, 1H), 3.10–3.04 (m, 1H), 2.56–2.52 (m, 1H), 2.37 (s, 3H), 232–2.24 (m, 1H), 0.83 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 177.3, 170.6, 145.1, 142.2, 137.5, 136.5, 135.9, 135.2, 132.0, 131.7, 130.1, 129.6, 128.8, 128.2, 127.9, 126.8, 126.4, 124.4, 123.4, 118.2, 115.6, 115.4, 114.4, 110.2, 60.8, 50.6, 47.9, 45.1, 23.4, 22.5, 21.6. 13.8; HRMS (ESI): calcd for C$_{36}$H$_{32}$BrN$_2$O$_5$S $\left[\text{M+2}\right]^+$ 685.1195, found: 685.1196.

Ethyl 1'-(4-bromobenzyl)-5'-fluoro-2'-oxo-9-tosyl-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (3z): Reaction of 1z (50 mg, 0.124 mmol) with 2b (48 mg, 0.161 mmol); Yield: 69% (59 mg); white solid; m.p. 113–115 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.09 (d, $J = 8.5$ Hz, 1H), 7.68 (d, $J = 8.2$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.26–7.24 (m, 2H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.93–6.89 (m, 1H), 6.83–6.76 (m, 3H), 6.31 (d, $J = 7.8$ Hz, 1H), 5.09 (d, $J = 15.1$ Hz, 1H), 4.82 (d, $J = 15.1$ Hz, 1H), 4.82 (d, $J = 15.1$ Hz, 1H), 3.79–3.75 (m, 2H), 3.60–3.56 (m, 1H), 3.45–3.42 (m, 1H), 3.11–3.04 (m, 1H), 2.56–2.52 (m, 1H), 2.37 (s, 3H), 2.31–2.24 (m, 1H), 0.85 (t, $J = 14.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 177.6, 170.6, 160.0 (d, $J_{C-F} = 242.5$ Hz), 145.1, 138.8 (d, $J_{C-F} = 1.8$ Hz), 137.6, 136.4, 135.9, 134.4, 131.9, 131.6 (d, $J_{C-F} = 8.2$ Hz), 130.4, 130.1, 126.7, 126.4, 124.5, 123.3, 122.2, 117.9, 115.3, 115.3 (d, $J_{C-F} = 23.6$ Hz), 114.5, 113.3 (d, $J_{C-F} = 25.4$ Hz), 109.1 (d, $J_{C-F} = 8.2$ Hz), 60.8, 50.9, 47.8, 44.5, 23.4, 22.7, 21.6, 13.8; HRMS (ESI): calcd for C$_{36}$H$_{32}$BrFN$_2$O$_5$S $\left[\text{M+2}\right]^+$ 703.1101, found: 703.1102.

Detosylation procedure for 3h:

To a solution of 3h (0.06 mmol) in THF (2 mL), TBAF (1M in THF, 0.30 mmol) was added and the reaction mixture was refluxed at 80 °C for 14 h. After completion of the reaction,
crushed ice was added and extracted with 2 x 15 mL of ethyl acetate. The organic layers were collected and dried over anhydrous Na$_2$SO$_4$ and evaporated to obtain as crude residue, which was further purified by column chromatography to obtain 4 in 87% yield.

Methyl 5'-chloro-2'-oxo-1,2,3,9-tetrahydrospiro[carbazole-4,3'-indoline]-3-carboxylate (4): Yield: 87% (24 mg); white solid; m.p. 133–135 °C; $^1$H NMR (500 MHz, CDCl$_3$ + 2 drops of DMSO-$d_6$): $\delta$ 10.34 (s, 1H), 9.98 (s, 1H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.14–7.10 (m, 1H), 7.01–6.88 (m, 4H), 6.80 (t, $J = 7.5$ Hz, 1H), 3.48–3.45 (m, 1H), 3.38 (s, 3H), 3.04–2.92 (m, 2H), 2.49–2.34 (m, 2H), $^{13}$C NMR (125 MHz, CDCl$_3$ + 2 drops of DMSO-$d_6$): $\delta$ 180.4, 171.5, 139.9, 135.8, 135.6, 133.4, 127.6, 126.3, 124.4, 123.2, 120.6, 118.6, 116.8, 110.5, 110.1, 106.4, 51.0, 50.9, 47.6, 21.9, 21.6; HRMS (ESI): calcd for C$_{21}$H$_{18}$ClN$_2$O$_3$ [M+H]$^+$ 381.1006, found: 381.1011.

Procedure for the preparation of 2-(but-3-en-1-yn-1-yl) aniline (2a)

To an oven dried 100 mL 2-neck round bottom flask dried at 120 °C for 2 h, solution of 2-iodoaniline (1.837 g, 8.4 mmol) and Et$_3$N (10 mL) in dry THF (10 mL) was degassed with nitrogen for 30 minutes. PdCl$_2$(PPh$_3$)$_2$ (235 mg, 4 mol%), copper iodide (32 mg, 2 mol%), and O-tosyl-alkyne (1.978 g, 8.8 mmol) were added successively under nitrogen atmosphere at room temperature. The mixture was stirred for 8 h. After completion of the reaction, as monitored by TLC, the mixture was filtered through a Celite pad, the solvent was evaporated under reduced pressure, and the resulting crude product was purified by column chromatography (silica gel, 100–200 mesh) using an ethyl acetate/n-hexane gradient mixture to afford the pure product 2a as a light green thick mass in 70% yield.

2-(but-3-en-1-yn-1-yl)aniline (2a): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.28–7.26 (m, 1H), 7.13–7.09 (m, 1H), 6.69–6.66 (m, 2H), 6.08–6.03 (m, 1H), 5.73–5.69 (m, 1H), 5.53–5.51 (m, 1H), 4.20 (brs, 2H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 146.5, 131.5, 129.8, 127.3, 122.3, 116.9, 115.5, 109.3, 94.4, 85.3 ppm. HRMS (ESI): calcd for C$_{10}$H$_{10}$N [M + H]$^+$: 144.0808; found: 144.0832.
Procedure for the preparation of N-(2-(but-3-en-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (2b)

The aniline 2a (930 mg, 6.5 mmol) was dissolved in dry DCM (10 mL) and to this pyridine (1.2 mL, 13.0 mmol) was added at 0 °C followed by 4-toluenesulfonyl chloride (1.483 g, 7.8 mmol). The mixture was stirred at room temperature for overnight. After completion of reaction as determine by TLC, reaction mixture was diluted with H₂O (10 mL) and extracted with dichloromethane (3 x 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The resulting crude product was purified by column chromatography (silica gel, 100–2000 mesh) using an ethyl acetate/n-hexane (5-10%) mixture to afford the pure product 2b in 92% yields.

N-(2-(but-3-en-1-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (2b): ¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 1H), 7.30–7.24 (m, 2H), 7.22–7.18 (m, 2H), 7.12 (s, 1H), 7.02 (t, J = 8.5 Hz, 1H), 6.01–5.94 (m, 1H), 5.75 (dd, J = 1.8, 17.5 Hz, 1H), 5.63 (dd, J = 1.8, 11.3 Hz, 1H), 2.36 (s, 3H), ¹³C NMR (125 MHz, CDCl₃): δ 144.0, 137.5, 136.0, 132.0, 129.6, 129.5, 128.2, 127.2, 124.4, 120.0, 116.2, 114.3, 94.7, 84.2, 21.5; HRMS (ESI): calcd for C₁₇H₁₆NO₂S [M+H]^+ 298.0902, found: 298.0907.

1-Tosyl-2-vinyl-1H-indole (B): ¹H NMR (500 MHz, CDCl₃): δ 8.20 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.2 Hz, 2H), 7.45–7.27 (m, 3H), 7.25–7.13 (m, 3H), 6.72 (s, 1H), 5.72 (dd, J = 1.4, 17.4 Hz, 1H), 5.40 (dd, J = 1.4, 11.1 Hz, 1H), 2.31 (s, 3H), ¹³C NMR (125 MHz, CDCl₃): δ 144.7, 139.8, 137.2, 135.4, 129.8, 129.6, 127.7, 126.6, 124.7, 123.9, 120.7, 117.8, 115.1, 108.8, 21.5; HRMS (ESI): calcd for C₁₇H₁₆NO₂S [M+H]^+ 298.0902, found: 298.0896.
General procedure for the synthesis of 3-ylideneoxindoles 1a–z

To a stirred solution of methyl-2 (triphenylphosphoranylidene) acetate (1.3 mmol) or ethyl-2 (triphenylphosphoranylidene) acetate (1.3 mmol) or tert-butyl-2 (triphenylphosphoranylidene) acetate (1.3 mmol) in dry THF (10 mL) at 0 °C was added corresponding isatins (1 mmol) and the reaction mixture was stirred at same temperature for 2-3 h. After completion of reaction as determined by TLC, the crude was directly purified by column chromatography by using silica gel (100-200, ethyl acetate:hexane) to obtain 3-ylideneoxindoles 1 as red coloured solids. All the isatins 1a-z were prepared in a similar manner using the above mentioned procedure.¹

X-ray crystallography information and data

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.² Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program.¹ The structure was solved by direct methods using SHELXS³ and refinement was carried out by full-matrix least-squares technique using SHELXL.³ Anisotropic displacement parameters were included for all non-hydrogen atoms. The N-bound H atom was located in difference Fourier maps and their positions and isotropic displacement parameters were located and refined. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and Uiso(H) = 1.2U eq(c) for H atoms].

Crystal Data for 3a: C29H26N2O5S (M = 514.58): triclinic, space group P-1 (no. 2), a = 8.3151(7) Å, b = 8.6250(7) Å, c = 18.7838(16) Å, α = 99.7400(10)°, β = 96.6860(10)°, γ = 104.0170(10)°, V = 1270.61(18) Å³, Z = 2, T = 294.15 K, μ(MoKα) = 0.171 mm-1, Dcalc = 1.345 g/mm³, 14660 reflections measured (4.462 ≤ 2θ ≤ 56.594), 5910 unique (Rint = 0.0177) which were used in all calculations. The final R1 was 0.0494 (I > 2σ(I)) and wR2 was 0.1503 (all data). CCDC 1496246 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].
References


2D $^1$H–$^1$H DQFCOSY spectrum of compound 3s recorded at 500 MHz NMR spectrometer in CDCl$_3$ at 25 °C
Expansion of 2D $^1$H-$^1$H DQFCOSY spectrum of compound 3s recorded at 500 MHz NMR spectrometer in CDCl$_3$ at 25 °C
$^{1}$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3a

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3a
$^{1}H$ NMR (500 MHz, CDCl$_3$) spectrum of compound 3b

$^{13}C$ NMR (125 MHz, CDCl$_3$) spectrum of compound 3b
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3c

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3c
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3d

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3d
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3e

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3e
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3f

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3f
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3g

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3g
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3h

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3h
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3i

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3i
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3j

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3j
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3k

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3k
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3l

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3l
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound $3m$

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound $3m$
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3n

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3n
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3o

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3o
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3p

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3p
$^1$H NMR (125 MHz, CDCl$_3$) spectrum of compound 3q

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3q
$^1$H NMR (125 MHz, CDCl$_3$) spectrum of compound 3r

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3r
$^1$H NMR (125 MHz, CDCl$_3$) spectrum of compound 3s

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3s
$^1$H NMR (125 MHz, CDCl$_3$) spectrum of compound $3t$

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound $3t$
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3u

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3u
$^1\text{H NMR (500 MHz, CDCl}_3$) spectrum of compound 3v

$^{13}\text{C NMR (125 MHz, CDCl}_3$) spectrum of compound 3v
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3w

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3w
$^{1}H$ NMR (500 MHz, CDCl$_3$) spectrum of compound 3x

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3x
$^1\text{H NMR (500 MHz, CDCl}_3\text{)}$ spectrum of compound $3y$

$^{13}\text{C NMR (125 MHz, CDCl}_3\text{)}$ spectrum of compound $3y$
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 3z

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound 3z
$^1$H NMR (500 MHz, CDCl$_3$ + DMSO-$d_6$) spectrum of compound 4

$^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO-$d_6$) spectrum of compound 4
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 2a

$^{13}$C NMR (500 MHz, CDCl$_3$) spectrum of compound 2a
H NMR (500 MHz, CDCl₃) spectrum of compound 2b

13C NMR (125 MHz, CDCl₃) spectrum of compound 2b
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound B

$^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of compound B