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1. General Information

The $^1$H NMR and $^{13}$C NMR spectra were recorded at Bruker AV 400 MHz or 600 MHz. $^1$H and $^{13}$C NMR Chemical shifts were calibrated to tetramethylsilane as an internal reference. Chemical shifts are given in (ppm) and coupling constants ($J$) in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; High resolution mass spectrometric (HRMS) analyses spectrum was determined on the Varian 7.0T FTMS instrument.

2. Synthesis of the arylalkynols 1.

To a solution of 2-bromobenzaldehyde or its derivatives S1 (20 mmol, 1 equiv.), PdCl$_2$(PPh$_3$)$_2$ (702.0 mg, 5 mol %), and CuI (76.0 mg, 2 mol %) in Et$_3$N (40.0 mL) was added under N$_2$ atmosphere. After being stirred for 10 mins at room temperature, terminal acetylene (1.5 equiv.) was added to the mixture. The resulting mixture was heated under N$_2$ atmosphere at 50 °C for 6-18 h. After the reaction was completed, the reaction mixture was quenched with distilled water and extracted with CH$_2$Cl$_2$ (100 mL × 3). The combined organic layer was washed with brine, dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product 2-((trimethylsilyl)ethynyl)benzaldehyde derivatives S2.

S2 (10 mmol, 1.0 equiv.) was dissolved in the mixture solution of MeOH, and treated with K$_2$CO$_3$ (2.764 g, 20 mmol, 2.0 equiv.). After stirring at ambient temperature for 2 h, the mixture was diluted with Et$_2$O, partitioned with H$_2$O, dried over Na$_2$SO$_4$ and concentrated in vacuo, purified by flash column chromatography to
give the arylalkynyl benzaldehyde derivatives product S3.

S3 (8 mmol, 1.0 equiv.) was added to round-bottomed flask and dissolved by MeOH. At 0 °C, NaBH₄ (605.3 mg, 16 mmol, 2.0 equiv.) was added to the flask in batches. After 30 min, the mixture was quenched with saturated NH₄Cl aqueous solution, and then was washed three times with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product 1.

![Chemical structures](image)


A mixture of benzylamine (7.26 g, 66.0 mmol), ethyl acrylate (7.2 mL, 66.0 mmol) in EtOH (15 mL) was stirred at room temperature for 16 h. Diethyl oxalate (9.0 mL, 66 mmol) and freshly-made sodium ethoxide solution in EtOH (generated from 2.0 g of sodium metal, 80.0 mmol, in 15 mL EtOH) was added. The mixture was heated at reflux for 1 h and solidified. The volatiles were removed in vacuo. The crude product was diluted with H₂O (80 mL) and the pH of the mixture was adjusted to 1 by adding conc.HCl. The mixture was subjected to filtration to afford S4 as a white solid.

A mixture of S4 (2.6 g, 9.8 mmol), aromatic aldehyde (9.8 mmol) in EtOH (20 mL)/ 20% aq. HCl (50 mL) was heated at reflux for 4 h. After cooling down to
ambient temperature, the aqueous layer was decanted. The obtained chunky solid was collected and further recrystallized from EtOAc to afford 2 as a bright yellow solid.


To a shlenck tube, dioxopyrrolidienes 2 (0.2 mmol), Ni(OTf)$_2$ (13 mg, 0.04 mmol, 20% mol), 4Å MS (40 mg) and a magnetic stir was sequentially added under nitrogen atmosphere. The mixture was stirred at room temperature for 2 h, then Ph$_3$PAuCl (5 mg, 5 mol%) and arylalkynols 1 (0.3 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at 50 ºC until complete disappearance of 2 observed by TLC. After completion, the mixture was cooled to room temperature, filtered through silica soil and the solvent was removed in vacuo. The product was purified by silica gel column chromatography (petroleum ether/EtOAc = 2:1) to afford the compound 3.
White solid, 72 mg, yield 88%, m.p. 164-165 °C, dr = 14:1, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.43 – 7.17 (m, 16H), 5.37 (d, $J$ = 12.5 Hz, 1H), 5.11 (d, $J$ = 12.6 Hz, 1H), 4.76 (d, $J$ = 14.9 Hz, 1H), 4.44 (d, $J$ = 14.9 Hz, 1H), 4.10 (dd, $J$ = 12.0, 5.8 Hz, 1H), 3.57 (d, $J$ = 18.2 Hz, 1.26H), 3.48 (d, $J$ = 18.3 Hz, 0.94H), 2.53 (t, $J$ = 12.7 Hz, 1H), 2.37 (dd, $J$ = 13.3, 5.8 Hz, 1H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.7, 144.7, 141.1, 140.2, 138.6, 137.2, 130.0, 129.2, 128.9, 128.3, 128.0, 127.7, 127.6, 123.6, 122.6, 121.3, 110.6, 72.7, 47.7, 46.7, 39.9, 36.7. HRMS (ESI+) calculated for C$_{27}$H$_{24}$NO$_3$ (M+H$^+$) 410.1751; found 410.1754.

Yellow solid, 74 mg, yield 76%, m.p. 139-140 °C, dr = 12:1, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.68 – 6.97 (m, 15H), 5.36 (d, $J$ = 12.6 Hz, 1H), 5.11 (d, $J$ = 12.6 Hz, 1H), 4.74 (d, $J$ = 14.9 Hz, 1H), 4.45 (d, $J$ = 14.9 Hz, 1H), 4.08 (dd, $J$ = 12.0, 5.7 Hz, 1H), 3.56 (dd, $J$ = 18.2, 1.7 Hz, 1H), 3.45 (d, $J$ = 18.2 Hz, 1H), 2.48 (t, $J$ = 12.7 Hz, 1H), 2.35 (dd, $J$ = 13.3, 5.7 Hz, 1H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.5, 145.0, 140.14, 140.09, 138.4, 137.1, 132.4, 130.1, 129.7, 128.9, 128.3, 128.0, 127.8, 122.7, 122.5, 121.43, 121.35, 110.5, 72.8, 47.5, 46.7, 39.7, 36.3. HRMS (ESI+) calculated for C$_{27}$H$_{23}$BrNO$_3$ (M+H$^+$) 488.0856; found 488.0859.
6'-benzyl-4'-(4-chlorophenyl)-5',6'-dihydro-3'H,3'H-spiro[isobenzofuran-1,2'-pyrano]

[2,3-c]pyrrol]-7'(4'H)-one

White solid, 74 mg, yield 84\%, m.p. 168-169 °C, \( dr = 11:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta 7.39 - 7.28 \) (m, 3H), 7.25 (dt, \( J = 7.3, 2.8 \) Hz, 5H), 7.23 - 7.18 (m, 2H), 7.18 - 7.09 (m, 4H), 5.30 (d, \( J = 12.6 \) Hz, 1H), 5.05 (d, \( J = 12.6 \) Hz, 1H), 4.69 (d, \( J = 14.9 \) Hz, 1H), 4.40 (d, \( J = 15.0 \) Hz, 1H), 4.04 (dd, \( J = 12.1, 5.7 \) Hz, 1H), 3.51 (dd, \( J = 18.1, 1.7 \) Hz, 1H), 3.40 (d, \( J = 18.2 \) Hz, 1H), 2.43 (t, \( J = 12.7 \) Hz, 1H), 2.30 (dd, \( J = 13.4, 5.8 \) Hz, 1H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 165.4, 144.9, 140.1, 139.5, 138.4, 137.1, 133.3, 130.0, 129.4, 129.3, 128.9, 128.3, 128.0, 127.8, 122.8, 122.5, 121.3, 110.5, 72.7, 47.5, 46.7, 39.9, 36.2. HRMS (ESI+) calculated for C\(_{27}\)H\(_{23}\)ClNO\(_3\) (M+H\(^+\)) 444.1361; found 444.1355.

6'-benzyl-4'-(4-fluorophenyl)-5',6'-dihydro-3'H,3'H-spiro[isobenzofuran-1,2'-pyrano]

[2,3-c]pyrrol]-7'(4'H)-one

Yellow solid, 54 mg, yield 63\%, m.p. 143-144 °C, \( dr = 12:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta 7.61 - 7.15 \) (m, 12H), 7.04 (t, \( J = 8.3 \) Hz, 2H), 5.39 (d, \( J = 12.6 \) Hz, 1H), 5.13 (d, \( J = 12.6 \) Hz, 1H), 4.77 (d, \( J = 14.9 \) Hz, 1H), 4.47 (d, \( J = 14.9 \) Hz, 1H), 4.12 (dd, \( J = 12.0, 5.7 \) Hz, 1H), 3.59 (dd, \( J = 18.2, 1.7 \) Hz, 1H), 3.47 (d, \( J = 18.2 \) Hz, 1H), 2.51 (t, \( J = 12.7 \) Hz, 1H), 2.38 (dd, \( J = 13.3, 5.8 \) Hz, 1H). \(^13\)C NMR (101 MHz,
CDCl$_3$ δ 165.6, 163.4, 161.0, 144.8, 140.2, 138.5, 137.2, 136.8, 136.7, 130.1, 129.6, 129.5, 128.9, 128.3, 128.0, 127.8, 123.2, 122.6, 121.4, 116.3, 116.0, 110.6, 72.8, 47.6, 46.7, 39.9, 36.1. HRMS (ESI+) calculated for C$_{27}$H$_{23}$FNO$_3$ (M+H$^+$) 428.1656; found 428.1652.

![Chemical Structure](image_url)

6'-benzyl-4'-(p-tolyl)-5',6'-dihydro-3H,3'H-spiro[isobenzofuran-1,2'-pyrano[2,3-c]pyrrol]-7'(4'H)-one

Yellow solid, 79 mg, yield 94%, m.p. 174-175°C, dr = 16:1, $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.45 – 7.32 (m, 3H), 7.32 – 7.22 (m, 4H), 7.23 – 7.16 (m, 2H), 7.16 – 7.07 (m, 4H), 5.36 (d, J = 12.6 Hz, 1H), 5.10 (d, J = 12.6 Hz, 1H), 4.74 (d, J = 15.0 Hz, 1H), 4.44 (d, J = 15.0 Hz, 1H), 4.06 (dd, J = 12.1, 5.8 Hz, 1H), 3.56 (dd, J = 18.2, 1.7 Hz, 1H), 3.48 (dd, J = 18.2, 1.2 Hz, 1H), 2.51 (dd, J = 13.5, 12.1 Hz, 1H), 2.38 – 2.29 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.7, 144.6, 140.2, 138.6, 137.9, 137.2, 129.93, 129.85, 128.8, 128.3, 128.0, 127.9, 127.7, 123.8, 122.5, 121.3, 110.6, 72.7, 47.6, 46.67, 39.9, 36.3, 21.2. HRMS (ESI+) calculated for C$_{28}$H$_{26}$NO$_3$ (M+H$^+$) 424.1907; found 424.1910.

![Chemical Structure](image_url)

6'-benzyl-4'-(4-methoxyphenyl)-5',6'-dihydro-3H,3'H-spiro[isobenzofuran-1,2'-pyrano[2,3-c]pyrrol]-7'(4'H)-one
Colorless oil, 79 mg, yield 90%, \( dr = 16:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.65 – 7.14 (m, 12H), 7.04 – 6.80 (m, 2H), 5.46 (d, \( J = 12.6 \) Hz, 1H), 5.21 (d, \( J = 12.6 \) Hz, 1H), 4.85 (d, \( J = 15.0 \) Hz, 1H), 4.54 (d, \( J = 15.0 \) Hz, 1H), 4.16 (dd, \( J = 12.1, 5.7 \) Hz, 1H), 3.88 (s, 3H), 3.67 (dd, \( J = 18.3, 1.7 \) Hz, 1H), 3.57 (dd, \( J = 18.2, 1.3 \) Hz, 1H), 2.60 (dd, \( J = 13.4, 12.1 \) Hz, 1H), 2.45 (dd, \( J = 13.4, 5.8 \) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\( _3 \)) \( \delta \) 165.7, 158.9, 144.5, 140.2, 138.6, 137.2, 132.9, 130.0, 129.0, 128.8, 128.3, 128.0, 127.7, 124.0, 122.5, 121.3, 114.6, 110.6, 72.7, 55.5, 47.7, 46.7, 40.0, 35.9. HRMS (ESI+) calculated for C\(_{28}\)H\(_{26}\)NO\(_4\) (M+H\(^+\)) 440.1856; found 424.1853.

![3ag]

6'-benzyl-4'-(4-(trifluoromethyl)phenyl)-5',6'-dihydro-3H,3'H-spiroisobenzofuran-1,2'-pyrano[2,3-c]pyrrol]-7'(4'H)-one

White solid, 81 mg, yield 85%, m.p. 194-195 °C, \( dr = 16:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.52 (d, \( J = 8.0 \) Hz, 2H), 7.39 – 7.25 (m, 5H), 7.25 – 7.16 (m, 5H), 7.16 – 7.11 (m, 2H), 5.29 (d, \( J = 12.6 \) Hz, 1H), 5.04 (d, \( J = 12.6 \) Hz, 1H), 4.68 (d, \( J = 15.0 \) Hz, 1H), 4.37 (d, \( J = 15.0 \) Hz, 1H), 4.10 (dd, \( J = 12.1, 5.8 \) Hz, 1H), 3.38 (dd, \( J = 12.1, 1.2 \) Hz, 1H), 2.44 (dd, \( J = 13.4, 1.2 \) Hz, 1H), 2.30 (dd, \( J = 13.4, 5.8 \) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\( _3 \)) \( \delta \) 165.4, 145.2, 140.1, 138.2, 137.1, 130.1, 128.9, 128.4, 128.3, 128.1, 127.8, 126.24, 126.20, 122.5, 122.2, 121.4, 110.4, 72.8, 47.5, 46.7, 39.7, 36.7. HRMS (ESI+) calculated for C\(_{28}\)H\(_{23}\)F\(_3\)NO\(_3\) (M+H\(^+\)) 478.1625; found 478.1627.

![3ah]
3-(6'-benzyl-7'-oxo-4',5',6',7'-tetrahydro-3H,3'H-spiroisobenzofuran-1,2'-pyrano)[2,3-c]pyrrol-4'-yl)benzonitrile

Yellow oil, 63 mg, yield 72.5%, $dr = 25:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.59 – 7.50 (m, 2H), 7.49 – 7.44 (m, 1H), 7.44 – 7.32 (m, 4H), 7.32 – 7.22 (m, 5H), 7.21 – 7.16 (m, 2H), 5.34 (d, $J = 12.6$ Hz, 1H), 5.09 (d, $J = 12.6$ Hz, 1H), 4.75 (d, $J = 15.0$ Hz, 1H), 4.43 (d, $J = 15.0$ Hz, 1H), 4.20 – 4.03 (m, 1H), 3.55 (dd, $J = 18.2$, 1.8 Hz, 1H), 3.39 (dd, $J = 18.2$, 1.2 Hz, 1H), 2.47 (dd, $J = 13.3$, 12.0 Hz, 1H), 2.35 (dd, $J = 13.4$, 5.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.3, 145.4, 142.7, 140.1, 138.1, 137.0, 132.5, 131.6, 131.4, 130.2, 128.9, 128.3, 128.1, 127.9, 122.5, 121.6, 121.4, 118.6, 113.4, 110.4, 72.9, 47.3, 46.7, 39.7, 36.6. HRMS (ESI+) calculated for C$_{28}$H$_{23}$N$_2$O$_3$ (M+H$^+$) 435.1703; found 424.1710.

6'-benzyl-4'-(naphthalen-1-yl)-5',6'-dihydro-3H,3'H-spiroisobenzofuran-1,2'-pyrano [2,3-c]pyrrol-7'(4'H)-one

Yellow oil, 41 mg, yield 45%, $dr = 2:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.18 – 7.98 (m, 1H), 7.89 – 7.74 (m, 3H), 7.52 – 7.42 (m, 5H), 7.41 – 7.24 (m, 10H), 7.23 – 7.08 (m, 5H), 5.41 (d, $J = 12.6$ Hz, 1.41H), 5.17 (d, $J = 12.5$ Hz, 1.55H), 5.07 (dd, $J = 11.6$, 6.2 Hz, 1H), 4.69 (t, $J = 16.1$ Hz, 1.70H), 4.57 – 4.43 (m, 1.91H), 3.68 – 3.52 (m, 2.49H), 3.34 (d, $J = 18.3$ Hz, 0.48H), 3.10 (s, 0.48H), 2.66 – 2.48 (m, 2H), 2.33 (d, $J = 10.0$ Hz, 0.48H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.7, 145.6, 140.2, 138.6, 137.5, 137.3, 137.2, 134.2, 131.8, 130.0, 129.8, 129.3, 129.0, 128.93, 128.85, 128.3, 128.0, 127.9, 127.8, 127.7, 126.7, 126.2, 125.9, 125.7, 124.7, 123.7, 122.6, 122.5, 121.3, 110.7, 72.8, 47.8, 46.7, 39.8, 31.1. HRMS (ESI+) calculated for C$_{31}$H$_{26}$NO$_3$ (M+H$^+$) 460.1907; found 460.1907.
6'-benzyl-4'-(thiophen-2-yl)-5',6'-dihydro-3H,3'H-spiroisobenzofuran-1,2'-pyran

[2,3-c]pyrrolo]-7'(4'H)-one

White solid, 36 mg, yield 43%, m.p. 184–185 °C, $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.45 – 7.39 (m, 2H), 7.37 (dd, $J = 6.8$, 1.1 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 (s, 2H), 7.24 – 7.19 (m, 3H), 7.07 – 6.65 (m, 2H), 5.36 (d, $J = 12.6$ Hz, 1H), 5.11 (d, $J = 12.6$ Hz, 1H), 4.75 (d, $J = 15.0$ Hz, 1H), 4.62 – 4.25 (m, 2H), 3.66 (dd, $J = 18.2$, 1.8 Hz, 1H), 3.58 (dd, $J = 18.2$, 1.4 Hz, 1H), 2.61 (dd, $J = 13.3$, 12.0 Hz, 1H), 2.47 (dd, $J = 13.3$, 5.7 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.5, 144.1, 143.9, 140.2, 138.4, 137.3, 130.1, 128.9, 128.3, 128.1, 127.8, 127.3, 125.5, 124.7, 123.1, 122.7, 121.4, 110.6, 72.8, 47.7, 46.7, 40.2, 32.0. HRMS (ESI+) calculated for C$_{25}$H$_{22}$NO$_3$S (M+H$^+$) 416.1315; found 416.1319.

6'-benzyl-4'-chloro-4'-(p-tolyl)-5',6'-dihydro-3H,3'H-spiroisobenzofuran-1,2'-pyran

[2,3-c]pyrrolo]-7'(4'H)-one

White solid, 84 mg, yield 92%, m.p. 209-210 °C, $dr = 16:1$, $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.37 (dq, $J = 3.7$, 1.9 Hz, 2H), 7.32 – 7.17 (m, 7H), 7.12 (q, $J = 8.0$ Hz, 4H), 5.31 (d, $J = 12.8$ Hz, 1H), 5.07 (d, $J = 12.7$ Hz, 1H), 4.75 (d, $J = 15.0$ Hz, 1H), 4.43 (d, $J = 15.0$ Hz, 1H), 4.04 (dd, $J = 12.0$, 5.8 Hz, 1H), 3.56 (dd, $J = 18.3$, 1.7 Hz, 1H), 3.48 (d, $J = 18.4$ Hz, 1H), 2.46 (dd, $J = 13.4$, 12.0 Hz, 1H), 2.38 – 2.28 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.5, 144.3, 140.5, 138.6, 137.6, 137.4, 137.2,
133.9, 130.2, 129.9, 128.9, 128.3, 127.8, 127.7, 124.0, 123.1, 122.6, 110.1, 72.4, 47.6, 46.7, 39.7, 36.2, 21.2. HRMS (ESI+) calculated for C$_{28}$H$_{25}$ClNO$_3$ (M+H$^+$) 458.1517; found 458.1509.

6'-benzyl-6-chloro-4'-(4-methoxyphenyl)-5',6'-dihydro-3H,3'H-spiro[isobenzofuran-1,2'-pyrano[2,3-c]pyrrol]-7'(4'H)-one

White solid, 68 mg, yield 72%, m.p. 179-181 °C, $dr = 12:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.37 (dd, $J = 4.6$, 2.6 Hz, 2H), 7.34 – 7.17 (m, 7H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 7.9$ Hz, 2H), 5.31 (d, $J = 12.7$ Hz, 1H), 5.07 (d, $J = 12.7$ Hz, 1H), 4.75 (d, $J = 14.8$ Hz, 1H), 4.43 (d, $J = 14.9$ Hz, 1H), 4.03 (dd, $J = 12.0$, 5.7 Hz, 1H), 3.78 (s, 3H), 3.56 (d, $J = 18.5$ Hz, 1H), 3.47 (d, $J = 18.3$ Hz, 1H), 2.45 (t, $J = 12.7$ Hz, 1H), 2.34 (dd, $J = 13.3$, 5.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.5, 159.1, 144.3, 140.5, 138.6, 137.2, 133.9, 132.6, 130.3, 129.0, 128.9, 128.3, 127.8, 124.2, 123.1, 122.6, 114.6, 110.1, 72.4, 55.5, 47.7, 46.7, 39.8, 35.8. HRMS (ESI+) calculated for C$_{28}$H$_{25}$ClNO$_4$ (M+H$^+$) 474.1467; found 474.1461.

6'-benzyl-6-fluoro-4'-(p-tolyl)-5',6'-dihydro-3H,3'H-spiro[isobenzofuran-1,2'-pyrano[2,3-c]pyrrol]-7'(4'H)-one

Colorless oil, 57 mg, yield 65%, $dr = 16:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.37 (dq, $J = 3.6$, 1.8 Hz, 2H), 7.32 – 7.17 (m, 6H), 7.12 (q, $J = 8.1$ Hz, 4H), 5.31 (d, $J = 5.8$ Hz, 2H), 3.56 (d, $J = 18.5$ Hz, 1H), 3.47 (d, $J = 18.3$ Hz, 1H), 2.45 (t, $J = 12.7$ Hz, 1H), 2.34 (dd, $J = 13.3$, 5.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.5, 159.1, 144.3, 140.5, 138.6, 137.2, 133.9, 132.6, 130.3, 129.0, 128.9, 128.3, 127.8, 124.2, 123.1, 122.6, 114.6, 110.1, 72.4, 55.5, 47.7, 46.7, 39.8, 35.8. HRMS (ESI+) calculated for C$_{28}$H$_{25}$ClNO$_4$ (M+H$^+$) 474.1467; found 474.1461.
12.8 Hz, 1H), 5.07 (d, J = 12.8 Hz, 1H), 4.75 (d, J = 15.0 Hz, 1H), 4.43 (d, J = 14.9 Hz, 1H), 4.04 (dd, J = 12.0, 5.8 Hz, 1H), 3.56 (dd, J = 18.2, 1.7 Hz, 1H), 3.51 – 3.43 (dd, J = 18.1, 1.5 Hz, 1H), 2.46 (dd, J = 13.4, 12.0 Hz, 1H), 2.38 – 2.29 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 165.6, 165.3, 162.9, 144.5, 142.7, 142.6, 137.8, 137.3, 137.2, 134.5, 129.9, 128.8, 128.2, 127.8, 127.7, 124.2, 124.1, 123.9, 115.5, 115.3, 110.1, 108.7, 108.5, 72.2, 47.6, 46.7, 40.0, 36.3, 21.2. HRMS (ESI+) calculated for C28H25FNO3 (M+H+) 442.1813; found 442.1814.

[2,3-c]pyrrol-7′(4'H)-one

Colorless oil, 63 mg, yield 71%, dr = 16:1. 1H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.16 (m, 6H), 7.13 (t, J = 6.3 Hz, 4H), 7.07 – 6.92 (m, 2H), 5.32 (d, J = 12.9 Hz, 1H), 5.06 (d, J = 12.9 Hz, 1H), 4.75 (d, J = 14.8 Hz, 1H), 4.43 (d, J = 14.9 Hz, 1H), 4.05 (dd, J = 11.9, 5.6 Hz, 1H), 3.56 (d, J = 18.2 Hz, 1H), 3.48 (d, J = 18.4 Hz, 1H), 2.47 (t, J = 12.7 Hz, 1H), 2.32 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 165.6, 165.3, 162.9, 144.5, 142.7, 142.6, 137.8, 137.3, 137.2, 134.5, 129.9, 128.8, 128.2, 127.8, 127.7, 124.2, 124.1, 123.9, 115.5, 115.27, 110.1, 108.7, 108.5, 72.1, 47.6, 46.7, 39.9, 36.3, 21.2. HRMS (ESI+) calculated for C28H25FNO3 (M+H+) 442.1813; found 442.1810.
6'-benzyl-6-methoxy-4'-(p-tolyl)-5',6'-dihydro-3H,3'H-spiro[isobenzofuran-1,2'-pyrano][2,3-c]pyrrol]-7'(4'H)-one

White solid, 75 mg, yield 83%, m.p. 220-221 °C, ¹H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.04 (m, 10H), 6.95 (dd, J = 8.3, 2.3 Hz, 1H), 6.88 (d, J = 2.3 Hz, 1H), 5.30 (d, J = 11.9 Hz, 1H), 5.05 (d, J = 12.0 Hz, 1H), 4.75 (d, J = 15.0 Hz, 1H), 4.44 (d, J = 15.0 Hz, 1H), 4.15 – 3.93 (m, 1H), 3.80 (s, 3H), 3.56 (dd, J = 18.2, 1.7 Hz, 1H), 3.48 (dd, J = 18.2, 1.3 Hz, 1H), 2.47 (dd, J = 13.4, 12.0 Hz, 1H), 2.40 – 2.27 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 165.7, 160.0, 144.6, 140.0, 138.0, 137.3, 132.0, 129.9, 128.8, 128.3, 127.9, 127.7, 123.8, 122.1, 117.2, 110.5, 106.9, 72.5, 55.8, 47.7, 46.7, 40.0, 36.3, 21.2. HRMS (ESI+) calculated for C₂₉H₂₈NO₄ (M+H⁺) 454.2013; found 454.2011.

6'-benzyl-6-methyl-4'-(p-tolyl)-5',6'-dihydro-3H,3'H-spiro[isobenzofuran-1,2'-pyrano][2,3-c]pyrrol]-7'(4'H)-one

White solid, 62 mg, yield 71%, m.p. 146-147 °C, dr = 11:1, ¹H NMR (400 MHz, Chloroform-d) δ 7.48 – 6.81 (m, 13H), 5.31 (d, J = 12.3 Hz, 1H), 5.06 (d, J = 12.3 Hz, 1H), 4.75 (d, J = 15.0 Hz, 1H), 4.43 (d, J = 14.9 Hz, 1H), 4.05 (dd, J = 12.1, 5.8 Hz, 1H), 3.55 (dd, J = 18.2, 1.7 Hz, 1H), 3.47 (d, J = 18.2 Hz, 1H), 2.50 (t, J = 12.8 Hz, 1H), 2.42 – 2.22 (m, 7H). ¹³C NMR (101 MHz, CDCl₃) δ 165.7, 144.6, 138.8, 138.0, 137.8, 137.3, 137.2, 137.2, 130.8, 129.8, 128.8, 128.3, 127.9, 127.7, 123.7, 123.0, 121.0, 110.6, 72.6, 47.6, 46.7, 39.9, 36.3, 21.4, 21.2. HRMS (ESI+) calculated for C₂₉H₂₈NO₃ (M+H⁺) 438.2064; found 438.2069.
6'-benzyl-3,6-dimethyl-4'-(p-tolyl)-5',6'-dihydro-3H,3'H-spiro[isobenzofuran-1,2'-pyrano[2,3-c]pyrrol]-7'(4'H)-one

Colorless oil, 82 mg, yield 91%, dr = 11:6:3:1, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.60 – 6.80 (m, 22.6H), 5.59 (d, $J$ = 6.5 Hz, 0.65H), 5.40 (d, $J$ = 6.5 Hz, 1H), 4.73 (dd, $J$ = 15.0, 6.0 Hz, 1.64H), 4.45 (dd, $J$ = 14.9, 12.6 Hz, 1.66H), 4.06 (dd, $J$ = 11.8, 5.7 Hz, 1.66H), 3.56 (dd, $J$ = 18.2, 1.7 Hz, 1.58H), 3.47 (d, $J$ = 18.2 Hz, 1.50H), 2.68 – 2.37 (m, 1.71H), 2.39 – 2.12 (m, 6.5H), 1.63 (d, $J$ =6.6 Hz, 3H), 1.35 (d, $J$ = 6.5 Hz, 1.7H), 1.35 (d, $J$ = 6.4 Hz, 0.26H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.7, 144.6, 144.4, 138.5, 138.1, 137.3, 137.2, 130.02, 129.97, 129.8, 128.8, 128.3, 128.12, 128.07, 127.9, 127.7, 123.7, 123.6, 122.7, 122.4, 121.2, 121.1, 109.9, 109.4, 81.1, 79.5, 47.70, 47.65, 46.7, 40.4, 40.3, 36.4, 36.1, 23.7, 21.2, 21.1. HRMS (ESI+) calculated for C$_{29}$H$_{28}$NO$_3$ (M+H$^+$) 438.2064; found 438.2059.

6'-benzyl-4'-(p-tolyl)-5',6'-dihydro-3H,3'H-spiro[naphtho[1,2-c]furan-1,2'-pyrano[2,3-c]pyrrol]-7'(4'H)-one

White solid, 44 mg, yield 46%, m.p. 180-181 °C, 3he : 4he = 2.5:1, $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.68 – 8.62 (m, 0.11H), 8.34 (dd, $J$ = 8.4, 1.1 Hz, 0.28H), 8.10 – 7.98 (m, 0.76H), 7.90 (dd, $J$ = 8.1, 1.8 Hz, 1.75H), 7.81 – 7.67 (m, 0.34H), 7.67 – 7.04 (m, 16H), 6.76 (d, $J$ = 7.5 Hz, 0.56H), 6.25 (d, $J$ = 8.3 Hz, 0.27H), 5.59 – 5.41 (m, 1H), 5.30 (d, $J$ = 12.8 Hz, 0.72H), 5.09 (d, $J$ = 6.0 Hz, 0.27H), 4.78 (dd, $J$ = 15.1, 2.1 Hz, 1H), 4.59 (d, $J$ = 6.0 Hz, 0.28H), 4.45 (d, $J$ = 15.0 Hz, 0.73H), 4.16 (dd, $J$ = 11.9, 5.7 Hz, 0.72H), 4.03 (d, $J$ = 15.0 Hz, 0.28H), 3.60 (dd, $J$ = 18.3, 1.7 Hz, 0.77H), 3.54 (dd, $J$ = 18.2, 1.3 Hz, 0.76H), 3.32 (d, $J$ = 17.8 Hz, 0.28H), 3.19 (dd, $J$ = 17.9, 1.1 Hz, 0.28H), 2.98 (dd, $J$ = 13.5, 12.0 Hz, 0.73H), 2.44 (dd, $J$ = 13.5, 5.7 Hz, 0.74H), 2.36 (s, 0.81H), 2.34 (s, 0.87H), 2.32 (s, 2.11H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.5, 165.7, 144.6, 138.2, 138.0, 137.9, 137.3, 137.1, 134.6, 134.5, 134.4, 133.9, 133.1, 132.6, 132.1, 131.9, 131.4, 130.3, 129.9, 129.5, 129.4, 129.3, 129.1, 128.9, 128.8, 128.4, 128.2, 128.0, 127.8, 127.6, 127.5, 127.4, 126.6, 126.4, 126.0, 125.9, 124.4, 123.9, 123.5, 121.3, 119.1, 118.8, 112.5, 112.4, 85.0, 73.4, 65.6, 55.7, 49.0, 47.8, 46.8, 46.7, 40.9, 36.5, 26.4, 21.4, 21.3. HRMS (ESI+) calculated for C$_{32}$H$_{28}$NO$_3$ (M+H$^+$) 474.2064; found 474.2059.


To a shlenck tube, a magnetic stir, dioxopyrrolidiens 2 (0.2 mmol), (rac)-PA (12 mg, 20% mol), 4Å MS (40 mg) and toluene (2 mL) were sequentially added under nitrogen atmosphere. The mixture was stirred for 2 h at room temperature, then Ph$_3$PAuCl (5 mg, 5 mol%) and arylalkynols 1 (0.3 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at 50 ºC until complete disappearance of 2 observed by TLC. The mixture was cooled to room temperature, filtered through kieselguhr and the solvent was removed in vacuo. The product was purified by silica gel column chromatography (petrol ether/EtOAc = 2 :1) to afford the compound 4.
2-benzyl-5-methyl-11-phenyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino

[2,3-c]pyrrol-3(5H)-one

Colorless oil, 77 mg, yield 94%, $dr = 10:1$, $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 7.46 (d, $J = 7.5$ Hz, 1H), 7.39 – 7.28 (m, 5H), 7.27 – 7.09 (m, 7H), 7.08 – 6.91 (m, 2H), 6.14 (d, $J = 7.6$ Hz, 1H), 5.35 (d, $J = 5.9$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.58 (d, $J = 6.0$ Hz, 1H), 4.11 (d, $J = 15.0$ Hz, 1H), 3.42 (d, $J = 17.8$ Hz, 1H), 3.24 (d, $J = 17.8$ Hz, 1H), 2.07 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.6, 141.9, 139.2, 138.6, 137.0, 135.0, 130.3, 129.1, 128.8, 128.6, 128.2, 128.13, 128.07, 127.6, 123.7, 122.1, 118.6, 111.3, 85.0, 54.9, 48.9, 46.7, 24.6. HRMS (ESI+) calculated for C$_{27}$H$_{24}$NO$_3$ (M+H$^+$) 410.1751; found 410.1755.

2-benzyl-11-(4-bromophenyl)-5-methyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7] oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 78 mg, yield 80%, m.p. 125-126 °C, $dr = 6:1$, $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 7.65 – 6.99 (m, 13H), 6.84 (d, $J = 7.9$ Hz, 2H), 6.21 (d, $J = 7.6$ Hz, 1H), 5.33 (d, $J = 6.1$ Hz, 1.15H), 4.82 (d, $J = 14.9$ Hz, 1H), 4.54 (d, $J = 5.9$ Hz, 1H), 4.43 (d, $J = 7.1$ Hz, 0.32H), 4.11 (d, $J = 15.0$ Hz, 1H), 3.77 (s, 0.16H), 3.34 (d, $J = 17.7$ Hz, 1H), 3.26 – 3.18 (m, 1.31H), 2.08 (d, $J = 13.3$ Hz, 3.48H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.4, 142.1, 138.9, 138.6, 136.9, 134.1, 132.2, 132.0, 131.8, 130.0,
129.3, 128.8, 128.3, 128.1, 127.7, 123.5, 122.3, 122.2, 117.8, 111.4, 84.6, 54.4, 48.8, 46.7, 24.6. HRMS (ESI+) calculated for C$_{27}$H$_{23}$BrNO$_3$ (M+H$^+$) 488.0856; found 488.0858.

![Structural formula of 4ac](image)

**2-benzyl-11-(4-chlorophenyl)-5-methyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one**

Colorless oil, 74 mg, yield 84%, dr = 2.5:1, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.52 – 7.34 (m, 3H), 7.35 – 7.14 (m, 9H), 7.12 (dd, $J$ = 7.8, 1.7 Hz, 2H), 7.10 – 7.01 (m, 0.78H), 6.90 (d, $J$ = 7.9 Hz, 2H), 6.21 (d, $J$ = 7.5 Hz, 1H), 5.56 – 5.18 (m, 1.39H), 4.81 (d, $J$ = 15.0 Hz, 1H), 4.56 (d, $J$ = 5.9 Hz, 1H), 4.43 (d, $J$ = 5.0 Hz, 0.81H), 4.12 (d, $J$ = 15.0 Hz, 1H), 3.78 (s, 0.38H), 3.34 (d, $J$ = 17.8 Hz, 1H), 3.27 – 3.16 (m, 1.76H), 2.08 (d, $J$ = 13.7 Hz, 4.17H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.4, 142.1, 138.94, 138.6, 136.9, 134.1, 133.6, 131.6, 129.6, 129.28, 129.25, 128.8, 128.24, 128.19, 128.1, 127.7, 123.5, 122.3, 117.9, 111.4, 84.7, 54.4, 48.8, 46.7, 24.6. HRMS (ESI+) calculated for C$_{27}$H$_{23}$ClNO$_3$ (M+H$^+$) 444.1361; found 444.1369.

![Structural formula of 4ad](image)

**4ad 2-benzyl-11-(4-fluorophenyl)-5-methyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one**

White solid, 64 mg, yield 75%, m.p. 128-129 °C, dr = 4:1, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.47 (d, $J$ = 7.6 Hz, 1.21H), 7.43 – 7.28 (m, 2.70H), 7.28 – 7.09 (m,
7.47H), 7.08 – 6.97 (m, 3.17H), 6.92 (t, J = 6.7 Hz, 1.89H), 6.18 (d, J = 7.5 Hz, 1H),
5.52 – 5.32 (m, 1.26H), 4.82 (d, J = 15.0 Hz, 1H), 4.57 (d, J = 6.0 Hz, 1H), 4.43 (d, J
= 4.1 Hz, 0.53H), 4.12 (d, J = 15.0 Hz, 1H), 3.79 (s, 0.26H), 3.35 (d, J = 17.8 Hz, 1H),
3.23 (d, J = 17.9 Hz, 1.5H), 2.08 (d, J = 14.6 Hz, 3.79H).\[^{13}\text{C}\] NMR (101 MHz, CDCl\(_3\))
d 166.5, 163.8, 161.3, 141.9, 139.0, 138.6, 136.9, 131.9, 131.8, 129.2, 128.8, 128.2,
128.1, 127.7, 123.5, 122.3, 118.2, 115.7, 115.5, 111.4, 84.9, 54.2, 48.9, 46.7, 24.7.
HRMS (ESI+) calculated for C\(_{27}\)H\(_{23}\)FNO\(_3\) (M+H\(^+\)) 428.1656; found 428.1653.

![4ae](image)

\textbf{2-benzyl-5-methyl-11-(p-tolyl)-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino
[2,3-c]pyrrol-3(5H)-one}

White solid, 67 mg, yield 79%, m.p. 153-154 °C, \(d_r = 8:1\), \[^{1}\text{H}\] NMR (400 MHz,
Chloroform-d) \(\delta\) 7.69 – 6.97 (m, 13H), 6.84 (d, J = 7.6 Hz, 2H), 6.21 (d, J = 7.5 Hz,
1H), 5.32 (d, J = 5.8 Hz, 1.13H), 4.82 (d, J = 15.0 Hz, 1H), 4.54 (d, J = 5.9 Hz, 1H),
4.42 (q, J = 15.0 Hz, 0.26H), 4.10 (d, J = 15.0 Hz, 1H), 3.79 (s, 0.13H), 3.41 (d, J
= 17.8 Hz, 1H), 3.32 (d, J = 17.5 Hz, 0.14H), 3.22 (d, J = 18.0 Hz, 1.12H), 2.36 (s,
3.39H), 2.06 (s, 3.39H).\[^{13}\text{C}\] NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.5, 141.6, 139.2, 138.4,
137.7, 136.9, 131.8, 130.1, 129.7, 129.1, 128.9, 128.6, 127.99, 127.97, 127.9, 127.5,
123.6, 121.9, 118.9, 111.0, 84.9, 54.4, 48.8, 46.5, 24.5, 21.2. HRMS (ESI+) calculated for C\(_{28}\)H\(_{26}\)NO\(_3\) (M+H\(^+\)) 424.1908; found 424.1909.

![4af](image)
2-benzyl-11-(4-methoxyphenyl)-5-methyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 76 mg, yield 87%, m.p. 96-97 °C, $dr = 10:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.46 (d, $J = 7.5$ Hz, 1H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.30 – 7.07 (m, 7H), 6.85 (d, $J = 3.5$ Hz, 4H), 6.24 (d, $J = 7.5$ Hz, 1H), 5.32 (d, $J = 5.9$ Hz, 1.10H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.53 (d, $J = 6.0$ Hz, 1.31H), 4.10 (d, $J = 15.0$ Hz, 1H), 3.82 (s, 3.30H), 3.39 (d, $J = 17.8$ Hz, 1.07H), 3.23 (d, $J = 17.8$ Hz, 1.14H), 2.07 (s, 3.30H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.7, 159.4, 141.7, 139.4, 138.6, 137.1, 131.4, 129.0, 128.8, 128.2, 128.1, 127.7, 127.0, 123.7, 122.2, 119.1, 113.9, 111.2, 85.1, 55.5, 54.1, 49.0, 46.7, 24.7. HRMS (ESI+) calculated for C$_{28}$H$_{26}$NO$_4$ (M+H$^+$) 440.1856; found 440.1863.

2-benzyl-5-methyl-11-(4-(trifluoromethyl)phenyl)-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 76 mg, yield 80%, m.p. 105-106 °C, $dr = 10:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.60 (d, $J = 7.9$ Hz, 2H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.39 (s, 1H), 7.30 – 7.16 (m, 5H), 7.17 – 7.03 (m, 4H), 6.13 (d, $J = 7.5$ Hz, 1H), 5.37 (d, $J = 5.8$ Hz, 1.10H), 4.84 (d, $J = 15.0$ Hz, 1H), 4.66 (d, $J = 5.9$ Hz, 1H), 4.57 – 4.31 (m, 0.20H), 4.11 (d, $J = 15.0$ Hz, 1H), 3.88 (s, 0.11H), 3.35 (d, $J = 17.7$ Hz, 1.04H), 3.23 (d, $J = 17.8$ Hz, 1.14H), 2.07 (s, 3.28H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.3, 142.3, 138.7, 138.6, 136.8, 130.7, 129.4, 128.8, 128.4, 128.2, 127.8, 125.59, 125.55, 123.3, 122.4, 117.3, 111.5, 84.6, 54.8, 48.8, 46.7, 24.6. HRMS (ESI+) calculated for C$_{28}$H$_{23}$F$_3$NO$_3$ (M+H$^+$) 478.1625; found 478.1634.
3-(2-benzyl-5-methyl-3-oxo-1,2,3,5,10,11-hexahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-11-yl)benzonitrile

Colorless oil, 56 mg, yield 65%, $dr = 14:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.63 (dd, $J = 8.2$, 3.9 Hz, 1H), 7.57 – 7.26 (m, 3H), 7.32 – 6.91 (m, 9H), 6.05 (dd, $J = 7.8$, 4.0 Hz, 1H), 5.33 (t, $J = 5.2$ Hz, 1.07H), 4.85 (dd, $J = 15.1$, 3.9 Hz, 1H), 4.61 (t, $J = 5.0$ Hz, 1H), 4.43 (d, $J = 4.0$ Hz, 0.14H), 4.09 (dd, $J = 15.1$, 4.0 Hz, 1H), 3.81 (d, $J = 3.8$ Hz, 0.07H), 3.23 (dd, $J = 7.5$, 4.1 Hz, 2.15H), 2.05 (d, $J = 4.4$ Hz, 3.24H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.2, 142.5, 138.6, 138.5, 136.9, 136.8, 134.7, 133.7, 132.0, 129.63, 129.55, 128.9, 128.4, 128.2, 127.8, 123.1, 122.7, 118.4, 116.5, 113.0, 111.7, 84.5, 54.6, 48.7, 46.8, 24.7. HRMS (ESI+) calculated for C$_{28}$H$_{23}$N$_2$O$_3$ (M+H$^+$) 435.1703; found 435.1705.

2-benzyl-11-(2-bromophenyl)-5-methyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 71 mg, yield 73%, m.p. 175-176 °C, $dr = 6:1$, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.64 (dd, $J = 7.7$, 1.6 Hz, 1.22H), 7.48 (d, $J = 7.6$ Hz, 1.19H), 7.42 (d, $J = 9.7$ Hz, 0.64H), 7.41 – 7.29 (m, 1.76H), 7.29 – 7.18 (m, 4.70H), 7.20 – 7.02 (m, 5H), 6.50 (dd, $J = 7.4$, 2.0 Hz, 1H), 6.02 (d, $J = 7.5$ Hz, 1H), 5.56 (d, $J = 6.0$ Hz, 1H), 5.44 (s, 0.16H), 5.14 (d, $J = 6.1$ Hz, 1H), 4.83 (d, $J = 15.0$ Hz, 1H), 4.60 – 4.38 (m, 0.49H), 4.14 (d, $J = 15.0$ Hz, 1H), 3.36 (d, $J = 17.6$ Hz, 1H), 3.26 (d, $J = 18.0$ Hz, 1.32H), 2.08 (s, 3.48H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.3, 142.1, 138.9, 138.6,
136.7, 134.3, 133.1, 132.6, 129.6, 129.0, 128.7, 128.6, 128.03, 127.9, 127.9, 127.6, 126.9, 125.2, 123.5, 122.1, 117.4, 111.3, 82.0, 53.5, 48.8, 46.6, 24.5. HRMS (ESI+) calculated for C_{27}H_{23}BrNO_3 (M+H^+) 488.0856; found 488.0858.

2-benzyl-5-methyl-11-(naphthalen-1-yl)-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrrol-3(5H)-one

White solid, 59 mg, yield 64%, m.p. 145-146 °C, d.r = 4:1, \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.30 (d, \(J = 8.4\) Hz, 1H), 8.17 (d, \(J = 8.4\) Hz, 0.29H), 8.05 – 7.81 (m, 3.11H), 7.74 – 7.48 (m, 5.25H), 7.39 (td, \(J = 7.5, 4.2\) Hz, 1.44H), 7.24 (dq, \(J = 8.0, 6.1\) Hz, 4.22H), 7.19 – 7.07 (m, 3.20H), 6.73 (d, \(J = 7.0\) Hz, 1H), 5.83 (d, \(J = 7.5\) Hz, 1H), 5.63 (d, \(J = 5.9\) Hz, 1H), 5.53 (d, \(J = 5.6\) Hz, 1.27H), 4.89 (d, \(J = 14.9\) Hz, 1.27H), 4.49 (s, 0.55H), 4.17 (d, \(J = 14.8\) Hz, 1H), 3.60 (d, \(J = 17.7\) Hz, 1H), 3.28 (d, \(J = 17.8\) Hz, 1.61H), 2.15 (d, \(J = 6.3\) Hz, 3.81H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.6, 142.6, 139.5, 138.5, 136.9, 133.9, 131.8, 130.7, 129.5, 129.2, 129.0, 128.8, 128.7, 128.2, 128.1, 127.9, 127.7, 127.3, 126.3, 124.8, 123.9, 122.03, 121.98, 118.7, 111.4, 83.2, 49.8, 49.0, 46.8, 24.7. HRMS (ESI+) calculated for C_{31}H_{26}NO_3 (M+H^+) 460.1907; found 460.1911.

2-benzyl-5-methyl-11-(thiophen-2-yl)-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrrol-3(5H)-one

White solid, 63 mg, yield 76%, m.p. 189-191 °C, \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.42 (s, 1H), 7.41 – 7.33 (m, 1H), 7.29 – 7.15 (m, 5H), 7.17 – 7.04 (m, 2H), 6.97 (dd,
$J = 5.2$, 3.5 Hz, 1H), 6.59 (d, $J = 3.4$ Hz, 1H), 6.37 (d, $J = 7.5$ Hz, 1H), 5.36 (d, $J = 5.7$ Hz, 1H), 5.02–4.65 (m, 2H), 4.11 (d, $J = 15.0$ Hz, 1H), 3.56 (d, $J = 17.9$ Hz, 1H), 3.29 (dd, $J = 17.8$, 1.3 Hz, 1H), 2.04 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.4, 141.4, 139.3, 138.4, 137.3, 137.0, 129.3, 128.8, 128.4, 128.2, 127.9, 127.7, 127.3, 125.2, 123.5, 122.1, 118.2, 111.4, 84.9, 49.6, 49.0, 46.7, 24.5. HRMS (ESI+) calculated for C$_{25}$H$_{22}$NO$_3$S (M+H$^+$) 416.1315; found 416.1315.

![Image of chemical structure](chart1.png)

**4be**

2-benzyl-7-chloro-5-methyl-11-(p-tolyl)-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7] oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 83 mg, yield 91%, m.p. 200–201 °C, dr = 25:1, $^1$H NMR (400 MHz, Chloroform-d) δ 7.43 (d, $J = 1.8$ Hz, 1.04H), 7.35–7.18 (m, 3.57H), 7.22–6.95 (m, 5.05H), 6.83 (d, $J = 7.6$ Hz, 2.10H), 6.11 (d, $J = 8.0$ Hz, 1H), 5.30 (d, $J = 5.9$ Hz, 1.04H), 4.82 (d, $J = 15.0$ Hz, 1H), 4.53 (d, $J = 6.0$ Hz, 1.04H), 4.14 (d, $J = 15.0$ Hz, 1.04H), 3.43 (d, $J = 17.8$ Hz, 1.04H), 3.23 (d, $J = 17.9$ Hz, 1.04H), 2.36 (s, 3.12H), 2.04 (s, 3.12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.4, 141.8, 140.6, 138.1, 137.8, 137.0, 135.0, 131.7, 130.1, 129.4, 128.8, 128.5, 128.2, 127.7, 125.0, 119.0, 110.7, 84.9, 54.4, 49.0, 46.6, 24.5, 21.3. HRMS (ESI+) calculated for C$_{28}$H$_{25}$ClNO$_3$ (M+H$^+$) 458.1517; found 458.1526.

![Image of chemical structure](chart2.png)

**4bf**

2-benzyl-7-chloro-11-(4-methoxyphenyl)-5-methyl-1,2,10,11-tetrahydro-5,10-
epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 68 mg, yield 72%, m.p. 91-92 °C, \( d_r = 33:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.43 (d, \( J = 1.8 \) Hz, 1H), 7.24 – 7.06 (m, 6H), 6.85 (s, 4H), 6.14 (d, \( J = 8.0 \) Hz, 1H), 5.29 (d, \( J = 5.9 \) Hz, 1.02H), 4.82 (d, \( J = 15.0 \) Hz, 1.04H), 4.51 (d, \( J = 5.9 \) Hz, 1H), 4.14 (d, \( J = 14.9 \) Hz, 1H), 3.82 (s, 3.08H), 3.41 (d, \( J = 17.8 \) Hz, 1H), 3.24 (d, \( J = 17.8 \) Hz, 1.04H), 2.04 (s, 3.09H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.4, 159.5, 141.6, 140.6, 137.8, 137.0, 134.9, 131.3, 128.8, 128.5, 128.2, 127.7, 126.7, 124.9, 122.6, 119.1, 114.0, 110.7, 84.9, 55.5, 53.9, 49.0, 46.7, 24.5. HRMS (ESI+) calculated for C\(_{28}H_{25}ClNO\(_4\) (M+H\(^{+}\)) 474.1467; found 474.1470.

\[ 4cc \]

2-benzyl-11-(4-chlorophenyl)-7-fluoro-5-methyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one

Colorless oil, 71 mg, yield 77%, \( d_r = 33:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.42 (dd, \( J = 8.3, 4.7 \) Hz, 1.03H), 7.37 – 7.29 (m, 2H), 7.29 – 7.19 (m, 3.56H), 7.17 – 7.02 (m, 3.07H), 6.92 (d, \( J = 7.9 \) Hz, 2H), 5.89 (dd, \( J = 8.3, 2.3 \) Hz, 1H), 5.28 (d, \( J = 6.0 \) Hz, 1.03H), 4.81 (d, \( J = 15.0 \) Hz, 1.03H), 4.56 (d, \( J = 5.9 \) Hz, 1.03H), 4.14 (d, \( J = 15.0 \) Hz, 1.03H), 3.37 (d, \( J = 17.7 \) Hz, 1.02H), 3.23 (dd, \( J = 17.7, 1.2 \) Hz, 1.04H), 2.05 (s, 3.09H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.3, 162.5, 142.1, 141.5, 136.9, 134.4, 133.2, 131.5, 129.0, 128.9, 128.2, 127.8, 124.0, 117.7, 116.8, 110.9, 110.6, 84.26, 54.2, 48.8, 46.8, 24.7. HRMS (ESI+) calculated for C\(_{27}H_{22}ClFNO\(_3\) (M+H\(^{+}\)) 462.1267; found 462.1270.
2-benzyl-8-fluoro-5-methyl-11-(p-tolyl)-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]-oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 63 mg, yield 71%, m.p. 144-145 °C, \( dr = 6:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.41 (dd, \( J = 8.3, 4.6 \) Hz, 1.23H), 7.30 – 7.18 (m, 4.22H), 7.13 (dd, \( J = 9.8, 7.3 \) Hz, 4.45H), 7.10 – 7.01 (m, 1.52H), 6.85 (d, \( J = 7.6 \) Hz, 1.88H), 5.87 (dd, \( J = 8.4, 2.2 \) Hz, 1H), 5.28 (d, \( J = 5.8 \) Hz, 1.17H), 4.82 (d, \( J = 14.9 \) Hz, 1H), 4.54 (d, \( J = 6.1 \) Hz, 1.18H), 4.39 (d, \( J = 15.0 \) Hz, 0.17H), 4.13 (d, \( J = 14.9 \) Hz, 1H), 3.75 (s, 0.16H), 3.45 (d, \( J = 17.8 \) Hz, 1H), 3.24 (d, \( J = 17.8 \) Hz, 1.34H), 2.35 (d, \( J = 15.8 \) Hz, 3.52H), 2.06 (d, \( J = 10.3 \) Hz, 3.52H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.50, 162.4, 161.2, 141.8, 138.2, 137.0, 131.6, 130.1, 129.9, 129.4, 128.8, 128.2, 128.0, 127.7, 123.6, 118.8, 116.4, 111.1, 110.8, 84.6, 54.4, 49.0, 46.7, 24.8, 21.3. HRMS (ESI+) calculated for C\(_{28}\)H\(_{25}\)FNO\(_3\) (M+H\(^+\)) 442.1813; found 442.1820.

2-benzyl-11-(4-chlorophenyl)-7-methoxy-5-methyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]-oxocino[2,3-c]pyrrol-3(5H)-one

Colorless oil, 73 mg, yield 77%, \( dr = 14:1 \), \(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta \) 7.33 – 7.18 (m, 6.19H), 7.17 – 7.07 (m, 2.14H), 7.01 – 6.83 (m, 3.15H), 6.72 (dd, \( J = 8.3, 2.3 \) Hz, 1H), 6.10 (d, \( J = 8.3 \) Hz, 1H), 5.27 (d, \( J = 5.8 \) Hz, 1.07H), 4.81 (d, \( J = 15.0 \) Hz, 1H), 4.60 (d, \( J = 6.5 \) Hz, 0.07H), 4.52 (d, \( J = 5.8 \) Hz, 1H), 4.45 (s, 0.07H), 4.14 (d, \( J = \).
15.0 Hz, 1.06H), 3.82 (s, 3.22H), 3.35 (d, J = 17.7 Hz, 1H), 3.22 (d, J = 17.8 Hz, 1.14H), 2.05 (s, 3.21H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.5, 160.8, 142.0, 140.2, 136.9, 134.0, 133.8, 131.6, 130.8, 128.8, 128.19, 128.16, 127.7, 124.4, 118.1, 115.5, 111.3, 106.4, 84.5, 55.7, 54.5, 48.8, 46.7, 24.5. HRMS (ESI+) calculated for C$_{28}$H$_{25}$ClNO$_4$ (M+H$^+$) 474.1467; found 474.1468.

![Image of 4fc](image)

2-benzyl-11-(4-chlorophenyl)-5,7-dimethyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one

White solid, 65 mg, yield 71%, m.p. 190-191 °C, $^1$H NMR (400 MHz, Chloroform-$_d$) δ 7.31 – 7.16 (m, 7H), 7.12 – 7.07 (m, 2H), 6.96 (dd, J = 7.8, 1.4 Hz, 1H), 6.87 (d, J = 7.9 Hz, 2H), 6.08 (d, J = 7.7 Hz, 1H), 5.26 (d, J = 5.9 Hz, 1H), 4.79 (d, J = 15.0 Hz, 1H), 4.51 (d, J = 5.8 Hz, 1H), 4.09 (d, J = 15.0 Hz, 1H), 3.31 (d, J = 17.8 Hz, 1H), 3.19 (d, J = 17.8 Hz, 1H), 2.35 (s, 3H), 2.02 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.5, 142.0, 139.3, 138.8, 136.9, 136.0, 134.0, 133.7, 131.7, 129.2, 128.80, 128.76, 128.2, 127.7, 123.2, 122.8, 118.0, 111.3, 84.6, 54.4, 48.8, 46.7, 24.6, 21.5. HRMS (ESI+) calculated for C$_{28}$H$_{25}$ClNO$_3$ (M+H$^+$) 458.1517; found 458.1523.

![Image of 4ga](image)

2-benzyl-5,10-dimethyl-11-phenyl-1,2,10,11-tetrahydro-5,10-epoxybenzo[6,7]oxocino[2,3-c]pyrrol-3(5H)-one

s25
White solid, 73 mg, yield 86%, m.p. 183-184 °C, $dr = 33:1$, $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.47 (dt, $J = 7.6$, 0.9 Hz, 1H), 7.43 – 7.15 (m, 10H), 7.14 – 6.99 (m, 2H), 6.51 (dt, $J = 7.9$, 1.5 Hz, 1H), 6.31 (dt, $J = 7.6$, 0.9 Hz, 1H), 4.83 (d, $J = 15.1$ Hz, 1H), 4.26 (s, 1H), 4.04 (d, $J = 15.1$ Hz, 1H), 3.17 (dd, $J = 11.0$, 1.1 Hz, 2.07H), 2.06 (s, 3.09H), 1.53 (s, 3.09H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.7, 142.4, 141.6, 138.9, 137.1, 136.5, 131.4, 130.5, 129.0, 128.71, 128.69, 128.5, 128.3, 128.1, 128.0, 127.7, 127.6, 123.5, 122.3, 119.8, 110.2, 89.4, 61.0, 49.5, 46.5, 25.4, 25.2. HRMS (ESI+) calculated for C$_{28}$H$_{26}$NO$_3$ (M+H$^+$) 424.1907; found 424.1915.
HPLC analysis condition: the er value was determined by HPLC analysis using a chiral IC column (2-propanol/n-hexane = 30:70, 1.0 mL/min, λ = 254 nm), retention time $t_{\text{minor}} = 31.118$ min; $t_{\text{major}} = 46.285$ min.
HPLC analysis condition: the \( er \) value was determined by HPLC analysis using a chiral OD-H column (2-propanol/n-hexane = 30:70, 1.0 mL/min, \( \lambda = 254 \) nm), retention time \( t_{\text{minor}} = 9.282 \) min; \( t_{\text{major}} = 11.603 \) min.