Supporting Information

Diastereoselective desymmetrization reaction of prochiral para-quinamines with in situ generated cyclopropenes: access to fused-hydroindol-5-one scaffolds

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**General Information:** All reactions were carried out either under inert atmosphere or air and monitored by TLC using Merck 60 F254 pre coated silica gel plates (0.25 mm thickness) and the products were visualized by UV detection. Flash chromatography was carried out with silica gel (200-300 mesh). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance (III) 400 and 500 MHz spectrometers. Data for $^1$H NMR are reported as a chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant $J$ (Hz), integration, and assignment, data for $^{13}$C are reported as a chemical shift ($\delta$ ppm). High resolutions mass spectral analyses (HRMS) were carried out using ESI-TOF-MS. Melting points were recorded on an electrothermal melting points apparatus and are uncorrected.

**Preparation of starting materials:** The para-quinamines (1a-h)$^1$ and ethyl 1-chloro-2-aroylcyclopropanecarboxylates (2a-j)$^2$ were prepared according to the literature procedures. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated.

**Representative procedure for the synthesis of ethyl 6b-benzoyl-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3aa):** To a stirred solution of compounds 1a (0.2 mmol) and 2a (0.26 mmol) in dry MeCN (2.0 mL) was added Cs$_2$CO$_3$ (0.4 mmol) at room temperature, followed by heating at 80 °C for 16 h under N$_2$-atmosphere. Upon completion of the reaction (monitored by TLC), the reaction mixture was extracted three times with ethyl acetate (3 × 10 mL), washed with water and brine, respectively, and dried over Na$_2$SO$_4$. The combined organic phases were evaporated under reduced pressure to afford the crude residue. Finally, the product 3aa was isolated in a pure form (68 mg; 62% yield) through column chromatography over silica gel using a mixture of EtOAc/hexane (25:75, v/v) as the eluent. The product was fully characterized by its spectroscopic data ($^1$HNMR, $^{13}$C NMR, and HRMS). Moreover, the relative configuration was assigned by its single crystal X-ray diffraction data. The minor isomer was unable to isolate.

All the prepared products in Table 2 were followed the above procedure and characterized by their corresponding spectroscopic data ($^1$H NMR, $^{13}$C NMR, and HRMS).
(±)-(cis-trans-cis)-Ethyl 6b-benzoyl-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3aa): Colorless solid; mp 185-187 °C; yield 62% (68 mg); dr = 90:10; $R_f = 0.32$ (EtOAc/hexane = 25:75); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95 (d, $J = 7.5$ Hz, 2H), 7.60 (t, $J = 7.3$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.25-7.19 (m, 3H), 7.09 – 7.04 (m, 6H), 6.30 (d, $J = 10.5$ Hz, 1H), 4.34-4.28 (m, 2H), 3.47 (br s, 1H), 2.69 (d, $J = 5.6$ Hz, 1H), 2.40 (s, 3H), 2.30-2.16 (m, 2H), 2.10 – 1.99 (m, 1H), 1.34 (br s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.3, 192.0, 168.3, 148.1, 143.4, 138.7, 135.8, 134.2, 132.9, 129.2(2C), 129.0(3C), 127.9, 127.6(2C), 78.5, 77.4, 77.0, 76.7, 62.0, 55.3, 55.1, 44.2, 35.2, 33.8, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{32}$H$_{29}$NNaO$_6$S$^+$ 578.1608, found 578.1605.

Crystallographic data: Single crystal X-ray structural of compound 3aa was measured on the Bruker D8 Quest Single Crystal-XRD at 150(2) K using graphite monochromated Mo Kα radiation ($\lambda_{\alpha} = 0.71073$ Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structure was solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on $F^2$. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2$U_{eq}$ of their parent atoms. The crystal data are summarized in Table S1. The CCDC number of compound 3aa (2094494) can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre,12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
Figure S1. ORTEP diagram of compound 3aa (CCDC 2094494), thermal ellipsoids drawn at the 50% probability level.

Table S1. Crystal data for compound 3aa.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3aa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{32}$ H$</em>{29}$ NO$_6$ S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>555.62</td>
</tr>
<tr>
<td>Temperature</td>
<td>293 K</td>
</tr>
<tr>
<td>Wave length (Å )</td>
<td>1.54184 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic P1 21/n1</td>
</tr>
<tr>
<td>a (Å )</td>
<td>a = 10.7889(3) Å</td>
</tr>
</tbody>
</table>
\[ b (\text{Å}) = 23.8675(5) \text{ Å} \]
\[ c (\text{Å}) = 11.6684(5) \text{ Å} \]
\[ \alpha (°) = 90 \text{ deg.} \]
\[ \beta (°) = 113.658(4) \text{ deg.} \]
\[ \gamma (°) = 90 \text{ deg.} \]

Volume (Å³)
\[ 2752.14(17) \text{ Å³} \]

Z, Calculated density (mg/m³)
\[ 4, 1.266 \text{ Mg/m³} \]

Absorption coefficient (mm⁻¹)
\[ 1.433 \text{ mm}^{-1} \]

F(000)
\[ 1108 \]

\( \Theta \) range (deg)
\[ 3.704 \text{ to 71.223 deg.} \]

Limiting indices
\[ -13\leq h\leq 13, -28\leq k\leq 28, -14\leq l\leq 14 \]

Reflections collected / unique
\[ 12957 / 5159 \text{ [R(int) = 0.0799]} \]

Completeness to \( \Theta \)
\[ 96.6 \% \]

Max. and min. transmission
\[ 0.846 \text{ and 1.0} \]

Absorption correction
none

Data / restraints / parameters
\[ 5159 / 0 / 363 \]

Goodness-of-fit on \( F^2 \)
\[ 1.640 \]

Final R indices [I>2sigma(I)]
\[ R1 = 0.1249, \text{ wR2 = 0.2615} \]

R indices (all data)
\[ R1 = 0.1028, \text{ wR2 = 0.3020} \]

Extinction coefficient
n/a

Largest diff. peak and hole (e.Å⁻³)
\[ 0.387 \text{ and -1.205 e.Å}^{-3} \]

CCDC
\[ 2094494 \]

(±)-(cis-trans-cis)-Ethyl 6b-(4-methylbenzoyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ab):

Colorless solid; mp 195-197 °C; yield = 59% (67 mg); dr = 91:9; 
\( R_f = 0.32 \) (EtOAc/hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl₃) δ 7.85 (d, \( J = 7.7 \) Hz, 2H), 7.57 (d, \( J = 11.5 \) Hz, 1H), 7.37-7.23 (m, 4H), 7.21 (d, \( J = 7.9 \) Hz, 2H), 7.06-7.05 (m, 5H), 6.29 (d, \( J = 10.6 \) Hz, 1H), 4.34-4.27 (m, 2H), 3.45 (br s, 1H), 2.68 (d, \( J = 5.3 \) Hz, 1H), 2.41 (d, \( J = 6.5 \) Hz, 6H), 2.25-2.18 (m, 2H), 2.06-2.01 (m, 2H), 1.33 (br s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl₃) δ 193.3, 191.5, 168.3, 148.1, 145.2, 143.3, 138.6, 133.4, 132.9, 129.7, 129.3, 129.2, 129.0 (2C), 128.9, 127.8, 127.6, 78.4, 61.9, 55.2, 54.9, 44.2, 35.2, 33.8, 21.7, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C₂₃H₁₇NNaO₆S⁺ 592.1764, found 592.1772.

(±)-(cis-trans-cis)-Ethyl 6b-(4-methoxybenzoyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ac):

Colorless solid; mp 183-185 °C; yield = 60% (70 mg); dr =
88:12; \( R_f = 0.31 \) (EtOAc/hexane = 25:75); \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.94 (d, \( J = 8.3 \) Hz, 2H), 7.57 (d, \( J = 11.5 \) Hz, 1H), 7.26 – 7.20 (m, 4H), 7.06-7.05 (m, 5H), 6.94 (d, \( J = 7.9 \) Hz, 2H), 6.29 (d, \( J = 9.6 \) Hz, 1H), 4.32-4.27 (m, 2H), 3.88 (s, 3H), 3.44 (br s, 1H), 2.68 (d, \( J = 4.6 \) Hz, 1H), 2.40 (s, 3H), 2.23 – 2.17 (m, 2H), 2.06-2.02 (m, 1H), 1.34 (br s, 3H) ppm; \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 193.3, 190.3, 168.4, 164.3, 148.0, 143.3, 138.7, 131.4, 130.6, 129.3, 129.0, 128.97, 128.92, 128.3, 127.8, 127.6, 114.2, 78.4, 61.9, 55.6, 55.3, 54.9, 44.2, 35.2, 33.8, 21.5, 21.4 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{33}\)H\(_{31}\)NNaO\(_7\)S\(^+\) 608.1713, found 608.1727.

Ethyl 2-(4-methoxybenzoyl)-1-tosylcyclopropanecarboxylate (byproduct): Colorless solid; mp 85-90 °C; \( R_f = 0.41 \) (ethyl acetate/hexane = 25:75); \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.96 (d, \( J = 8.7 \) Hz, 1H), 7.85 (d, \( J = 8.1 \) Hz, 1H), 7.37 (d, \( J = 8.0 \) Hz, 1H), 6.92 (d, \( J = 8.7 \) Hz, 1H), 3.97 (dd, \( J = 7.0, 2.3 \) Hz, 1H), 3.88 (s, 1H), 3.62 (dd, \( J = 9.1, 7.8 \) Hz, 1H), 2.47 (s, 1H), 2.32 (dd, \( J = 7.1, 5.5 \) Hz, 1H), 2.17 (dd, \( J = 9.4, 5.3 \) Hz, 1H), 0.98 (t, \( J = 7.1 \) Hz, 1H) ppm; \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 190.6, 164.1, 163.5, 145.3, 135.3, 131.0, 129.7, 129.5, 129.2, 113.9, 62.4, 55.5, 29.9, 21.7, 18.3, 13.5 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{21}\)H\(_{22}\)NaO\(_6\)S\(^+\) 425.1029, found 425.1034.

(±)-(cis-trans-cis)-Ethyl 6b-(2,4-dimethylbenzoyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ad): Colorless solid; mp 190-192 °C; yield = 52% (61 mg); dr = 90:10; \( R_f = 0.32 \) (EtOAc/hexane = 25:75); \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.78 (d, \( J = 7.1 \) Hz, 1H), 7.60 (d, \( J = 9.7 \) Hz, 1H), 7.60 (d, \( J = 7.1 \) Hz, 1H), 7.26-7.17 (m, 3H), 7.08-7.05 (m, 8H), 6.34 (d, \( J = 10.4 \) Hz, 1H), 4.38 – 4.26 (m, 2H), 3.41 (br s, 1H), 2.66 (d, \( J = 4.3 \) Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 2.24-2.20 (m, 2H), 2.06-2.02 (m, 1H), 1.36 (br s, 3H) ppm; \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 193.7, 193.5, 168.5, 148.0, 143.6, 143.3, 143.2, 142.0, 138.8, 133.8, 133.2, 132.2, 130.7, 129.4, 129.0, 128.9, 127.8, 127.5, 126.2, 78.4, 62.0, 55.9, 55.8, 45.7, 35.3, 34.4, 21.7, 21.5 (2C), 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{34}\)H\(_{33}\)NNaO\(_6\)S\(^+\) 606.1921, found 606.1935.

(±)-(cis-trans-cis)-Ethyl 6b-(4-(tert-butyl) benzoyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ae): Colorless solid; mp 170 -172 °C; yield = 54% (66 mg); dr = 89:11; \( R_f = 0.32 \) (EtOAc/hexane = 25:75); \( ^1\)H
NMR (400 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 9.2$ Hz, 1H), 7.48 (d, $J = 8.3$ Hz, 2H), 7.23 – 7.20 (m, 3H), 7.08 – 7.05 (m, 6H), 6.30 (d, $J = 10.5$ Hz, 1H), 4.30 (q, $J = 6.8$ Hz, 2H), 3.47 (br s, 1H), 2.69 (d, $J = 5.5$ Hz, 1H), 2.40 (s, 3H), 2.26-2.21 (m, 2H), 2.07 – 2.01 (m, 1H), 1.34 (br s, 12H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.4, 191.4, 168.3, 158.1, 148.0, 143.3, 138.6, 133.2, 132.9, 129.3, 129.1(2C), 128.9, 127.8, 127.6(2C), 126.0, 78.4, 61.9, 55.2, 54.9, 44.2, 35.2, 35.1, 33.8, 31.0, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{36}$H$_{37}$NNaO$_6$S$^+$ 634.2234, found 634.2211.

(±)-(cis-trans-cis)-Ethyl 6b-([1,1'-biphenyl]-4-carbonyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3af): Colorless solid; mp 190-192 °C; yield = 61% (77 mg); dr = 92:8; $R_f = 0.32$ (EtOAc/hexane = 25:75); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.03 (d, $J = 7.2$ Hz, 2H), 7.69 (d, $J = 7.4$ Hz, 2H), 7.61 (d, $J = 6.2$ Hz, 3H), 7.48 – 7.41 (m, 3H), 7.24 – 7.21 (m, 3H), 7.09-7.07 (m, 6H), 6.32 (d, $J = 10.0$ Hz, 1H), 4.35-4.29 (m, 2H), 3.51 (br s, 1H), 2.74 (d, $J = 4.7$ Hz, 1H), 2.41 (s, 3H), 2.30 – 2.25 (m, 2H), 2.10-2.06 (m, 1H), 1.36 (br s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.3, 191.5, 168.3, 148.1, 146.9, 143.4, 139.6, 138.6, 134.5, 132.9, 129.7, 129.4, 129.1 (2C), 129.0, 128.5, 127.9, 127.7, 127.6(2C), 127.3, 78.4, 62.0, 55.2, 55.0, 44.2, 35.2, 33.8, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{38}$H$_{33}$NNaO$_6$S$^+$ 654.1921, found 654.1915.

(±)-(cis-trans-cis)-Ethyl 6b-(4-chlorobenzoyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ag): Colorless solid; mp 210-212 °C; yield = 69% (81 mg); dr = 90:10; $R_f = 0.32$ (ethyl acetate/hexane = 25:75); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.90 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 9.0$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.26-7.22 (m, 1H), 7.19 (d, $J = 7.8$ Hz, 2H), 7.07–7.04 (m, 6H), 6.29 (d, $J = 10.5$ Hz, 1H), 4.34-4.25 (m, 2H), 3.46 (br s, 1H), 2.67 (d, $J = 5.6$ Hz, 1H), 2.40 (s, 3H), 2.27 (d, $J = 4.1$ Hz, 1H), 2.17 – 2.04 (m, 2H), 1.34 (br s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.1, 190.9, 168.1, 148.1, 143.4, 140.8, 138.5, 134.1, 132.7, 130.4, 129.4, 129.3, 129.1,
129.0, 127.9, 127.5 (2C), 78.4, 62.1, 55.1 (2C), 43.9, 35.2, 33.6, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C₃₂H₂₈ClNNaO₆S⁺ 612.1218, found 612.1236.

(±)-(cis-trans-cis)-Ethyl 6b-(4-bromobenzoyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ah):

Colorless solid; mp 220-222 °C; yield = 70% (88 mg); dr = 89:11; 
Rₛ = 0.32 (ethyl acetate/hexane = 25:75); ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 3H), 7.25-7.22 (m, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.25-7.22 (m, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.07 – 7.04 (m, 6H), 6.29 (d, J = 10.5 Hz, 1H), 4.33-4.25 (m, 2H), 3.46 (br s, 1H), 2.67 (d, J = 5.6 Hz, 1H), 2.40 (s, 3H), 2.26-2.25 (m, 1H), 2.17-2.13 (m, 1H), 2.07 (dd, J = 5.4, 17.8 Hz, 1H), 1.34 (br s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 193.1, 191.1, 168.1, 148.1, 143.4, 138.5, 134.5, 132.7, 132.4, 130.4, 129.6, 129.3, 129.1, 129.0, 127.9, 127.5 (2C), 78.4, 62.1, 55.0 (2C), 43.9, 35.2, 33.6, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C₃₂H₂₈ClNNaO₆S⁺ 656.0713, found 656.0724.

(±)-(cis-trans-cis)-Ethyl 6b-(1-naphthoyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ai):

Colorless solid; mp 200-202 °C; yield = 55% (66 mg); dr = 93:7; 
Rₛ = 0.32 (EtOAc/hexane = 25:75); ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 6.9 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.62-7.48 (m, 4H), 7.25-7.19 (m, 3H), 7.12-7.05 (m, 6H), 6.42 (d, J = 10.4 Hz, 1H), 4.43-4.23 (m, 2H), 3.55 (br s, 1H), 2.74 (d, J = 5.1 Hz, 1H), 2.40 (s, 3H), 2.33 – 2.29 (m, 2H), 2.14-2.09 (m, 1H), 1.33 (t, J = 6.3 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 194.8, 193.1, 168.1, 147.6, 143.3, 138.7, 134.8, 134.2, 133.3, 132.7, 131.0, 130.7, 129.6, 129.14, 129.12, 128.9, 128.8, 128.4, 127.9, 127.6, 126.9, 126.2, 123.8, 78.4, 62.1, 56.4, 56.0, 46.0, 35.3, 34.8, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C₃₆H₃₁NNaO₆S⁺ 628.1764, found 628.1760.

(±)-(cis-trans-cis)-Ethyl 6b-(5-methylthiophene-2-carbonyl)-5-oxo-2a-phenyl-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3aj):
carboxylate (3aj): Colorless solid; mp 192-194 °C; yield = 57% (65 mg); \( R_f = 0.32 \) (EtOAc /hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta 7.64 \) (d, \( J = 3.55 \) Hz, 1H), 7.52 (d, \( J = 7.65 \) Hz, 1H), 7.24-7.19 (m, 3H), 7.06-7.04(m, 6H), 6.82 (d, \( J = 3.5 \) Hz, 1H), 6.30 (d, \( J = 10.5 \) Hz, 1H), 4.28-4.25 (m, 2H), 3.41 (br s, 1H), 2.81 (d, \( J = 5.5 \) Hz, 1H), 2.54 (s, 3H), 2.40 (s, 3H), 2.37-2.32 (m, 1H), 2.21 (br s, 1H), 2.09-2.04 (m, 1H), 1.32 (s , 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 193.2, 183.9, 168.1, 152.0, 147.7, 143.3, 140.8, 138.6, 134.3, 133.0, 129.5, 129.12, 128.9, 127.8, 127.6, 127.2, 78.2, 62.0, 55.1, 54.7, 44.6, 35.0, 33.7, 21.5, 16.1, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{31}\)H\(_{29}\)NNaO\(_6\)S\(_2\)+ 598.1329, found 598.1314.

(\(\pm\)-(cis-trans-cis)-Ethyl 6b-benzoyl-5-oxo-2a-(p-tolyl)-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ba): Colorless solid; mp 177-179 °C; yield = 61% (69 mg); \( R_f = 0.32 \) (EtOAc/hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.96 \) (d, \( J = 7.4 \) Hz, 2H), 7.60 (t, \( J = 7.4 \) Hz, 2H), 7.52 (d, \( J = 7.7 \) Hz, 2H), 7.21 (d, \( J = 7.9 \) Hz, 2H), 7.05 (d, \( J = 8.1 \) Hz, 2H), 6.97 (d, \( J = 7.6 \) Hz, 2H), 6.85 (d, \( J = 7.8 \) Hz, 2H), 6.28 (d, \( J = 10.5 \) Hz, 1H), 4.37 – 4.25 (m, 2H), 3.47 (br s,1H), 2.69 (d, \( J = 5.6 \) Hz, 1H), 2.10 (dd, \( J = 5.5, 18.0 \) Hz, 1H), 1.33 (br s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta 193.2, 183.9, 168.1, 152.0, 147.7, 143.3, 140.8, 138.6, 134.3, 133.0, 129.5, 129.12, 128.9, 127.8, 127.6, 127.2, 78.2, 62.0, 55.1, 54.7, 44.6, 35.0, 33.7, 21.5, 16.1, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{33}\)H\(_{31}\)NNaO\(_6\)S\(_2\)+ 592.1764, found 592.1766.

(\(\pm\)-(cis-trans-cis)-Ethyl 6b-(4-methylbenzoyl)-5-oxo-2a-(p-tolyl)-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3bb): Colorless solid; mp 183-185 °C; yield = 60% (70 mg); \( R_f = 0.32 \) (EtOAc/hexane = 25:75); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.85 \) (d, \( J = 8.0 \) Hz, 2H), 7.57 (d, \( J = 8.8 \) Hz, 1H), 7.27-7.25 (m, 2H), 7.21 (d, \( J = 7.7 \) Hz, 2H), 7.05 (d, \( J = 8.0 \) Hz, 2H), 6.97 (d, \( J = 7.5 \) Hz, 2H), 6.84 (d, \( J = 7.6 \) Hz, 2H), 6.27 (d, \( J = 10.5 \) Hz, 1H), 4.30 (q, \( J = 7.5 \) Hz, 2H), 3.44 (br s, 1H), 2.67 (d, \( J = 5.5 \) Hz, 1H), 2.41 (s, 6H), 2.30 (s, 3H), 2.24 – 2.17 (m, 2H), 2.07-2.02 (m, 1H), 1.33 (br s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 193.4, 191.6, 168.4, 148.3, 145.2, 143.2, 139.0, 138.7, 133.4, 129.8, 129.7, 129.24,
129.2, 128.9, 128.92, 128.4, 127.6, 78.2, 61.9, 54.9, 54.8, 44.2, 35.2, 33.8, 21.7, 21.5, 21.1, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{34}H_{33}NNaO_{6}S^+ 606.1921, found 606.1900.

(±)-(cis-trans-cis)-Ethyl 6b-(4-methoxybenzoyl)-5-oxo-2a-(p-tolyl)-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopenta[b]indole-1a-carboxylate (3bc): Colorless solid; mp 184-186 °C; yield = 62% (74 mg); dr = 89:11; R_f = 0.31 (EtOAc/hexane = 25:75); ^1H NMR (500 MHz, CDCl_3) δ 7.94 (d, J = 8.8 Hz, 2H), 7.56 (br s, 1H), 7.21 (d, J = 7.4 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.97-6.93 (m, 4H), 6.85 (d, J = 8.0 Hz, 2H), 6.27 (d, J = 10.5 Hz, 1H), 4.32-4.26 (m, 2H), 3.87 (s, 3H), 3.43 (br s, 1H), 2.67 (d, J = 5.5 Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 2.22-2.18 (m, 2H), 2.05 (dd, J = 5.4, 17.7 Hz, 1H), 1.33 (br s, 3H) ppm; ^13C NMR (125 MHz, CDCl_3) δ 193.4, 190.3, 168.4, 164.2, 148.2, 143.2, 139.0, 138.7, 131.4, 129.8, 129.2, 129.0, 128.94, 128.91, 128.4, 127.6, 114.2, 78.2, 61.9, 55.6, 55.0, 54.8, 44.2, 35.2, 33.9, 21.5, 21.1, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{34}H_{33}NNaO_{6}S^+ 622.1870, found 622.1868.

(±)-(cis-trans-cis)-Ethyl 6b-([1,1'-biphenyl]-4-carbonyl)-5-oxo-2a-(p-tolyl)-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopenta[b]indole-1a-carboxylate (3bf): Colorless solid; mp 175-177 °C; yield = 64% (82 mg); dr = 92:8; R_f = 0.32 (ethyl acetate/hexane = 25:75); ^1H NMR (500 MHz, CDCl_3) δ 8.03 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 7.4 Hz, 3H), 7.48 (t, J = 7.3 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.2 Hz, 2H), 6.86 (d, J = 7.5 Hz, 2H), 6.29 (d, J = 10.5 Hz, 1H), 4.34-4.28 (m, 2H), 3.50 (br s, 1H), 2.73 (d, J = 5.5 Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 2.28-2.24 (m, 2H), 2.10 (dd, J=5.5, 17.8 Hz, 1H), 1.35 (br s, 3H) ppm; ^13C NMR (100 MHz, CDCl_3) δ 193.4, 191.5, 168.3, 148.3, 146.9, 143.3, 139.6, 139.1, 138.7, 134.5, 129.8, 129.7, 129.2, 129.0(2C), 128.9, 128.5, 127.7(2C), 127.6, 127.3, 78.2, 62.0, 54.9(2C), 44.2, 35.2, 33.9, 21.5, 21.1, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{39}H_{35}NNaO_{6}S^+ 668.2077, found 668.2058.
(±)-(cis-trans-cis)-Ethyl 6b-(4-bromobenzoyl)-5-oxo-2a-(p-tolyl)-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3bh):

Colorless solid; mp 210-212 °C; yield = 71% (92 mg); dr = 90:10; \( R_f = 0.32 \) (EtOAc/hexane = 25:75); \(^1^H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.82 (d, \( J = 8.3 \) Hz, 2H), 7.62 (d, \( J = 8.3 \) Hz, 2H), 7.58 (d, \( J = 10.0 \) Hz, 1H), 7.20 (d, \( J = 7.9 \) Hz, 2H), 7.05 (d, \( J = 8.0 \) Hz, 2H), 6.96 (d, \( J = 7.5 \) Hz, 2H), 6.85 (d, \( J = 7.6 \) Hz, 2H), 6.27 (d, \( J = 10.5 \) Hz, 1H), 4.33-4.24 (m, 2H), 3.44 (br s, 1H), 2.66 (d, \( J = 5.5 \) Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 2.25 (d, \( J = 4.7 \) Hz, 1H), 2.17 – 2.04 (m, 2H), 1.34 (br s, 3H) ppm; \(^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 193.2, 191.2, 168.2, 148.3, 143.3, 139.1, 138.6, 134.6, 132.4, 130.4, 129.65, 129.6, 129.1, 128.5, 128.5, 127.6, 78.2, 64.9, 54.8, 43.9, 35.2, 33.7, 21.5, 21.1 ppm; HRMS (ESI-TOF) m/z [M + Na\(^+\)] calcld for C\(_{33}\)H\(_{30}\)BrNNaO\(_6\)S\(_6\) 670.0869, found 670.0882.

(±)-(cis-trans-cis)-Ethyl 6b-(1-naphthoyl)-5-oxo-2a-(p-tolyl)-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3bi):

Colorless solid; mp 190-194 °C; yield = 52% (64 mg); dr = 92:8; \( R_f = 0.32 \) (ethyl acetate/hexane = 25:75); \(^1^H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.68 (d, \( J = 8.5 \) Hz, 1H), 8.13 (d, \( J = 7.2 \) Hz, 1H), 8.05 (d, \( J = 8.1 \) Hz, 1H), 8.05 (d, \( J = 8.0 \) Hz, 2H), 7.21 (d, \( J = 8.0 \) Hz, 2H), 7.00 (d, \( J = 7.8 \) Hz, 2H), 6.86 (d, \( J = 7.7 \) Hz, 2H), 6.39 (d, \( J = 10.4 \) Hz, 1H), 4.44-4.20 (m, 2H), 3.54 (d, \( J = 5.2 \) Hz, 1H), 2.73 (d, \( J = 5.6 \) Hz, 1H), 2.41 (s, 3H), 2.37-2.33 (m, 1H), 2.31 (s, 3H), 2.28 (d, \( J = 5.6 \) Hz, 1H), 2.13 (dd, \( J = 5.7, 17.8 \) Hz, 1H), 1.33 (t, \( J = 7.0 \) Hz, 3H) ppm; \(^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 194.9, 193.2, 168.3, 147.7, 143.2, 139.0, 138.7, 134.7, 134.2, 132.7, 130.9, 130.7, 130.1, 129.4, 129.0, 128.9, 128.8, 128.5, 128.4, 127.6, 126.9, 126.2, 123.8, 78.1, 62.1, 56.4, 55.7, 46.0, 35.3, 34.8, 21.5, 21.1, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na\(^+\)] calcld for C\(_{37}\)H\(_{33}\)NNaO\(_6\)S\(_6\) 642.1921, found 642.1942.

(±)-(cis-trans-cis)-Ethyl 6b-benzoyl-2a-(4-methoxyphenyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ca):

Colorless solid; mp 197-199 °C; yield = 65% (76 mg); dr =
89:11; $R_f = 0.30$ (EtOAc/hexane = 25:75); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.5$ Hz, 2H), 7.64 – 7.52 (m, 2H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.56 (d, $J = 8.3$ Hz, 2H), 6.27 (d, $J = 10.5$ Hz, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 3.79 (s, 3H), 3.45 (br s, 1H), 2.69 (d, $J = 5.6$ Hz, 1H), 2.40 (s, 3H), 2.26-2.18 (m, 2H), 2.12-2.02 (m, 1H), 1.33 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.3, 192.0, 168.4, 159.9, 148.3, 143.3, 138.7, 135.8, 134.1, 130.5, 129.2, 129.1, 129.0, 127.6(2C), 124.5, 113.1, 78.0, 62.0, 55.3, 54.8, 54.7, 44.2, 35.2, 33.9, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{33}$H$_{31}$NNaO$_7$S$^+$ 608.1713, found 608.1717.

(±)-(cis-trans-cis)-Ethyl 2a-(4-methoxyphenyl)-6b-(4-methylbenzoyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3cb): Colorless solid; mp 180-182 °C; yield = 60% (72 mg); $R_f = 0.31$ (EtOAc/hexane = 25:75); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 9.1$ Hz, 1H), 7.27-7.24 (m, 4H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.00 (d, $J = 7.8$ Hz, 2H), 6.56 (d, $J = 8.3$ Hz, 2H), 6.25 (d, $J = 10.5$ Hz, 1H), 4.29 (q, $J = 7.5$ Hz, 2H), 3.78 (s, 3H), 3.42 (br s, 1H), 2.68 (d, $J = 5.1$ Hz, 1H), 2.41 (s, 3H), 2.40 (s, 3H), 2.24 – 2.16 (m, 2H), 2.07-2.03 (m, 1H), 1.30 (br s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.3, 191.5, 168.4, 159.9, 148.3, 145.2, 143.2, 138.7, 133.4, 130.5, 129.7, 129.2, 129.1, 129.0, 127.6, 124.5, 113.1, 78.0, 61.9, 55.3, 54.7, 54.6, 44.3, 35.2, 34.0, 21.7, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{34}$H$_{33}$NNaO$_7$S$^+$ 622.1870, found 622.1896.

(±)-(cis-trans-cis)-Ethyl 6b-(4-methoxybenzoyl)-2a-(4-methoxyphenyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3cc): Colorless solid; mp 183-185°C; yield = 59% (73 mg); $R_f = 0.30$ (EtOAc/hexane = 25:75); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.9$ Hz, 2H), 7.07 (d, $J = 7.2$ Hz, 2H), 7.00 (d, $J = 6.32$ Hz, 2H), 6.94 (d, $J = 7.9$Hz, 2H), 6.56 (d, $J = 7.1$ Hz, 2H), 6.25 (d, $J = 10.2$ Hz, 1H), 4.29 (br s, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 3.41 (br s, 1H), 2.68 (d, $J = 4.3$ Hz, 1H), 2.40 (s, 3H), 2.23-2.19 (m, 2H), 2.08-2.03 (m, 1H), 1.33 (br s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.3, 190.4, 168.5, 164.3, 159.9, 148.3, 143.2,
138.7, 131.4, 130.5, 129.2, 129.0, 128.9, 127.6, 124.6, 114.2, 113.1, 78.0, 61.9, 55.6, 55.3, 54.9, 54.6, 44.2, 35.2, 34.0, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C_{34}H_{33}NNaO_{8}S⁺ 638.1819, found 638.1820.

(±)-(cis-trans-cis)-Ethyl 6b-(2,4-dimethylbenzoyl)-2a-(4-methoxyphenyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3cd): Colorless solid; mp 180-182 °C; yield = 49% (60 mg); dr = 91:9; R_f = 0.32 (EtOAc/hexane = 25:75); ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 10.5 Hz, 1H), 7.23 (d, J = 8.1 Hz, 2H), 7.08-7.05 (m, 4H), 7.00 (d, J = 8.1 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 6.30 (d, J = 10.5 Hz, 1H), 4.39-4.22 (m, 2H), 3.78 (s, 3H), 3.39 (br s, 1H), 2.65 (d, J = 5.5 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H), 2.24-2.17 (m, 2H), 2.08-2.03 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 193.7, 193.5, 168.5, 159.8, 148.3, 143.6, 143.1, 142.0, 138.8, 133.8, 132.2, 130.7, 130.4, 129.2, 129.0, 127.5, 126.2, 124.7, 113.1, 77.9, 61.9, 55.6, 55.3, 45.7, 35.3, 34.5, 21.7, 21.5, 21.52, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C_{35}H_{35}NNaO_{7}S⁺ 636.2026, found 636.2053.

(±)-(cis-trans-cis)-Ethyl 6b-(4-chlorobenzoyl)-2a-(4-methoxyphenyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3cg): Colorless solid; yield 70% (87 mg); dr = 92:8; mp 205-207 °C; R_f = 0.32 (EtOAc/hexane = 25:75); ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 6.56 (d, J = 8.0 Hz, 2H), 6.26 (d, J = 10.5 Hz, 1H), 4.32-4.25 (m, 2H), 3.78 (s, 3H), 3.43 (br s, 1H), 2.67 (d, J = 5.6 Hz, 1H), 2.40 (s, 3H), 2.26 (d, J = 3.8 Hz, 1H), 2.17-2.04 (m, 2H), 1.33 (br s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 193.1, 191.0, 168.2, 159.9, 148.3, 143.3, 140.7, 138.6, 134.2, 130.4, 129.4, 129.1, 129.0, 127.6(2C), 124.3, 113.1, 78.0, 62.0, 55.3, 54.7, 54.6, 44.0, 35.2, 33.8, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C_{35}H_{36}ClNNaO_{7}S⁺ 642.1324, found 642.1312.

(±)-(cis-trans-cis)-Ethyl 6b-(4-bromobenzoyl)-2a-(4-methoxyphenyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3dg): Colorless solid; yield 70% (87 mg); dr = 92:8; mp 205-207 °C; R_f = 0.32 (EtOAc/hexane = 25:75); ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 7.7 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 6.56 (d, J = 8.0 Hz, 2H), 6.26 (d, J = 10.5 Hz, 1H), 4.32-4.25 (m, 2H), 3.78 (s, 3H), 3.43 (br s, 1H), 2.67 (d, J = 5.6 Hz, 1H), 2.40 (s, 3H), 2.26 (d, J = 3.8 Hz, 1H), 2.17-2.04 (m, 2H), 1.33 (br s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 193.1, 191.0, 168.2, 159.9, 148.3, 143.3, 140.7, 138.6, 134.2, 130.4, 129.4, 129.1, 129.0, 127.6(2C), 124.3, 113.1, 78.0, 62.0, 55.3, 54.7, 54.6, 44.0, 35.2, 33.8, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for C_{35}H_{36}ClNNaO_{7}S⁺ 642.1324, found 642.1312.
**carboxylate (3ch):** Colorless solid; yield = 68% (90 mg); \( \text{mp 222-224}^\circ \text{C}; \) \( R_f = 0.31 \) (EtOAc/hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.82 \) (d, \( J = 8.5 \) Hz, 2H), 7.63 (d, \( J = 8.5 \) Hz, 2H), 7.55 (d, \( J = 8.8 \) Hz, 1H), 7.24 (d, \( J = 8.0 \) Hz, 2H), 7.08 (d, \( J = 8.1 \) Hz, 2H), 7.00 (d, \( J = 7.7 \) Hz, 2H), 6.56 (d, \( J = 8.2 \) Hz, 2H), 6.25 (d, \( J = 10.5 \) Hz, 1H), 4.41 – 4.15 (m, 2H), 3.78 (s, 3H), 3.42 (d, \( J = 0.8 \) Hz, 1H), 2.67 (d, \( J = 5.6 \) Hz, 1H), 2.39 (s, 3H), 2.28-2.12 (m, 2H), 2.11-2.04 (m, 1H), 1.33 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 190.6, 188.6, 165.7, 157.4, 145.8, 140.8, 136.1, 132.0, 129.9, 127.9, 127.0, 126.6, 126.5(2C), 125.0, 121.7, 110.6, 75.5, 59.5, 52.8, 52.2, 52.1, 41.4, 32.7, 31.2, 19.0, 11.4 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{33}\)H\(_{30}\)BrNNaO\(_7\)S\(^+\) 686.0819, found 686.0797.

(±)-(cis-trans-cis)-Ethyl 2a-(4-methoxyphenyl)-6b-(5-methylthiophene-2-carbonyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopenta[b]indole-1a-carboxylate (3cj): Colorless solid; mp 200-202 \(^\circ\)C; yield = 60% (73 mg); \( \text{dr} = 88:12 \); \( R_f = 0.31 \) (EtOAc/hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 7.82 \) (d, \( J = 6.6 \) Hz, 1H), 7.49 (d, \( J = 7.1 \) Hz, 2H), 7.07 (d, \( J = 7.0 \) Hz, 2H), 6.99 (d, \( J = 6.8 \) Hz, 1H), 6.55 (d, \( J = 8.0 \) Hz, 2H), 6.26 (d, \( J = 10.5 \) Hz, 1H), 4.30-4.24 (m, 2H), 3.78 (s, 3H), 3.38 (br s, 1H), 2.67(d, \( J = 4.4 \) Hz, 1H), 2.54 (s, 3H), 2.40 (s, 3H), 2.38-2.32 (m, 1H), 2.20 (d, \( J = 0.8 \) Hz, 1H), 2.12-2.06 (m, 1H), 1.31 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta 193.2, 184.0, 168.2, 159.9, 152.0, 147.9, 143.3, 140.9, 138.7, 134.3, 130.5, 129.3, 129.0, 127.6, 127.2, 124.5, 113.1, 77.8, 62.0, 55.3, 54.7, 54.4, 44.7, 35.0, 33.8, 21.5, 16.1, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{32}\)H\(_{31}\)NNaO\(_7\)S\(^+\) 628.1434, found 628.1432.

(±)-(cis-trans-cis)-Ethyl 2a-([1,1’-biphenyl]-4-yl)-6b-benzoyl-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopenta[b]indole-1a-carboxylate (3da): Colorless solid; mp 180-182 \(^\circ\)C; yield = 56% (71 mg); \( \text{dr} = 91:9 \); \( R_f = 0.32 \) (EtOAc/hexane = 25:75); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.98 \) (d, \( J = 7.6 \) Hz, 2H), 7.68 (d, \( J = 9.8 \) Hz, 1H), 7.61 (t, \( J = 7.2 \) Hz, 1H), 7.52 – 7.45 (m, 6H), 7.40 (t, \( J = 6.8 \) Hz, 1H), 7.26-7.23 (m, 4H), 7.15 (d, \( J = 7.4 \) Hz, 2H), 7.04 (d, \( J = 7.8 \) Hz, 2H), 6.34 (d, \( J = 10.5 \) Hz, 1H), 4.33
(q, J = 7.2 Hz, 2H), 3.53 (br s, 1H), 2.72 (d, J = 5.5 Hz, 1H), 2.39 (s, 3H), 2.31-2.21 (m, 2H), 2.13 (dd, J = 5.2, 17.8 Hz, 1H), 1.36 (br s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.2, 192.0, 168.3, 148.0, 143.3, 141.7, 139.8, 138.7, 135.8, 134.2, 131.7, 129.4, 129.1, 129.10, 129.06(2C), 129.0, 127.9, 127.5, 126.9, 126.3, 78.1, 62.0, 55.1, 54.9, 44.2, 35.2, 33.9, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{38}$H$_{33}$NNaO$_6$S$^+$ 654.1921, found 654.1910.

(±)-(cis-trans-cis)-Ethyl 6b-([1,1'-biphenyl]-4-carbonyl)-2a-([1,1'-biphenyl]-4-yl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3df): Colorless solid; mp 197-199 °C; yield = 51% (72 mg); dr = 94:6; $R_f$ = 0.32 (EtOAc/hexane = 25:75); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.05 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.1 Hz, 3H), 7.61 (d, J = 7.4 Hz, 2H), 7.52 – 7.46 (m, 6H), 7.43 – 7.38 (m, 2H), 7.25-7.17 (m, 4H), 7.04 (d, J = 7.9 Hz, 2H), 6.35 (d, J = 10.5 Hz, 1H), 4.36-4.31 (m, 2H), 3.57 (br s, 1H), 2.76 (d, J = 5.5 Hz, 2H), 2.39 (s, 3H), 2.32-2.29 (m, 2H), 2.16(dd, J = 5.5, 17.8 Hz, 1H), 1.37 ( br s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.2, 191.5, 168.3, 148.0, 146.9, 143.3, 141.8, 139.8, 139.6, 138.7, 134.5, 131.7, 129.7, 129.5, 129.1, 129.0, 128.9, 128.5, 128.0, 127.7(2C), 127.6, 127.3, 126.9, 126.4, 78.1, 62.0, 55.1, 55.9, 44.3, 35.3, 33.9, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{44}$H$_{37}$NNaO$_6$S$^+$ 730.2234, found 730.2205.

(±)-(cis-trans-cis)-Ethyl 2a-([1,1'-biphenyl]-4-yl)-6b-(4-bromobenzoyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3dh): Colorless solid; mp 202-204 °C; yield = 63% (89 mg); dr = 93:7; $R_f$ = 0.33 (ethyl acetate/hexane = 25:75); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 10.0 Hz, 1H), 7.63 (d, J = 8.1 Hz, 2H), 7.52-7.45 (m, 4H), 7.40 (t, J = 6.8 Hz, 1H), 7.26-7.22 (m, 4H), 7.14 (d, J = 6.8 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 6.33 (d, J = 10.5 Hz, 1H), 4.32 (q, J = 7.5 Hz, 2H), 3.51 (br s, 1H), 2.69 (d, J = 5.4 Hz, 1H), 2.39 (s, 3H), 2.29 (d, J = 4.2 Hz, 1H), 2.21 – 2.10 (m, 2H), 1.35 ( br s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 193.1, 191.5, 168.1, 148.0, 143.4, 141.8, 139.7, 138.6, 134.5, 132.4, 131.5, 130.5, 129.6, 129.4, 129.1, 129.0, 128.0, 127.5(2C), 126.9,
126.4, 78.1, 62.1, 55.1, 54.8, 43.9, 35.3, 33.7, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{38}H_{32}BrNNaO_6S^+ 732.1026, found 732.1004.

(±)-(cis-trans-cis)-Ethyl 6b-(2-naphthoyl)-2a-([1,1'-biphenyl]-4-yl)-5-oxo-2-tosyl-1,1a,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3di): Colorless solid; mp 188-190°C; yield = 52% (71 mg); dr = 95:5; R_f = 0.32 (EtOAc/hexane = 25:75); ^1H NMR (500 MHz, CDCl_3) δ 8.69 (d, J = 7.9 Hz, 1H), 8.15 (d, J = 5.2 Hz, 1H), 8.06 (d, J = 6.6 Hz, 1H), 7.87 (d, J = 6.7 Hz, 1H), 7.71 (d, J = 9.9 Hz, 1H), 7.61-7.40 (m, 8H), 7.25-7.18 (m, 6H), 7.03 (d, J = 6.2 Hz, 2H), 6.45 (d, J = 9.7 Hz, 1H), 4.43-4.26 (m, 2H), 3.61 (br s, 1H), 2.77 (br s, 1H), 2.41-2.33 (m, 5H), 2.21-2.16 (m, 1H), 1.34 (br s, 3H) ppm; ^13C NMR (125 MHz, CDCl_3) δ 194.8, 193.1, 168.2, 147.4, 143.3, 141.7, 139.8, 138.8, 134.8, 134.2, 132.7, 132.1, 131.0, 130.7, 129.7, 129.5, 129.1, 128.9, 128.8, 128.4, 127.9, 127.5, 126.98, 126.9, 126.3, 126.2, 123.8, 78.0, 62.1, 56.5, 55.7, 46.1, 35.4, 34.9, 21.5, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{42}H_{35}BrNNaO_6S^+ 704.2077, found 704.2091.

(±)-(cis-trans-cis)-Ethyl 6b-(4-bromobenzoyl)-5-oxo-2-tosyl-2a-(4-(trifluoromethyl) phenyl)-1,1a,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3eh): Colorless solid; mp 228-230 °C; yield = 58% (81 mg); dr = 92:8; R_f = 0.34 (EtOAc /hexane = 25:75); ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, J = 7.4 Hz, 2H), 7.69 (d, J = 9.3 Hz, 1H), 7.63 (d, J = 7.4 Hz, 2H), 7.26 – 7.16 (m, 6H), 7.05 (d, J = 7.0 Hz, 2H), 6.36 (d, J = 10.2 Hz, 1H), 4.34-4.28 (m, 2H), 3.44 (br s, 1H), 2.70 (d, J = 4.2 Hz, 1H), 2.40 (s, 3H), 2.27-2.17 (m, 2H), 2.06-2.01 (dd, J = 3.85, 17.5 Hz, 1H), 1.35 (br s, 3H) ppm; ^13C NMR (100 MHz, CDCl_3) δ 192.5, 190.9, 167.8, 146.7, 143.9, 138.5, 137.0, 134.4, 132.5, 131.3, 131.0, 130.4, 130.1, 129.8, 129.3(2C), 127.2, 125.0 – 124.6 (q, 1C), 77.7, 62.2, 55.5, 55.1, 43.8, 35.1, 33.8, 21, 14.0 ppm; ^19F NMR (470 MHz, CDC_3) δ -63.0 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{33}H_{27}BrNNaO_6S^+ 724.0587, found 724.0607.
(±)-(cis-trans-cis)-Ethyl 6b-benzoyl-2a-(3-chlorophenyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3fa): Colorless solid; mp 225-227 °C; yield = 54% (64 mg); dr = 91:9; \( R_f = 0.31 \) (ethyl acetate/hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.96 (d, \( J = 7.2 \) Hz, 2H), 7.66-7.58 (m, 2H), 7.48 (t, \( J = 7.7 \) Hz, 2H), 7.24-7.20 (m, 3H), 7.19-7.14 (m, 2H), 6.78 (br s, 1H), 6.34 (d, \( J = 10.5 \) Hz, 1H), 4.36-4.27 (m, 2H), 3.39 (br s, 1H), 2.70 (d, \( J = 10.2 \) Hz, 1H), 2.42 (s, 3H), 2.25-2.20 (m, 2H), 1.33 (br s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 192.8, 191.8, 168.1, 147.1, 144.0, 138.4, 135.7, 135.1, 134.2, 134.1, 129.7, 129.4, 129.3, 129.1(2C), 129.0, 127.7(2C), 127.1, 77.8, 62.1, 55.2(2C), 43.9, 35.1, 33.8, 21.6, 14.0 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^{+}\) calcld for C\(_{32}\)H\(_{28}\)ClNNaO\(_6\)S\(^+\) 612.1218, found 612.1207.

(±)-(cis-trans-cis)-Ethyl 6b-benzoyl-2a-methyl-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ga): Colorless solid; mp 170-172 °C; yield 65% (64 mg); dr = 86:14; \( R_f = 0.34 \) (EtOAc/hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.08 (d, \( J = 7.8 \) Hz, 2H), 7.95 (d, \( J = 7.4 \) Hz, 2H), 7.61 (t, \( J = 7.4 \) Hz, 1H), 7.49 (t, \( J = 7.7 \) Hz, 2H), 7.37 (d, \( J = 8.0 \) Hz, 2H), 6.66 (d, \( J = 10.2 \) Hz, 1H), 5.97 (d, \( J = 10.0 \) Hz, 1H), 4.20-4.17 (m, 2H), 2.94 (d, \( J = 5.2 \) Hz, 1H), 2.63 (d, \( J = 5.7 \) Hz, 1H), 2.47 (s, 3H), 2.41 (d, \( J = 6.0 \) Hz, 1H), 2.36-2.33 (m, 1H), 2.19-2.16 (m, 1H), 1.25 (s, 3H), 1.24 (t, \( J = 7.0 \) Hz, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 192.7, 192.1, 168.1, 149.7, 144.3, 138.6, 135.8, 134.1, 129.7, 129.1, 129.0, 128.4, 127.8, 73.6, 61.8, 53.5, 53.4, 46.2, 35.5, 34.3, 21.6, 21.3, 13.9 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^{+}\) calcld for C\(_{27}\)H\(_{27}\)NNaO\(_6\)S\(^+\) 516.1451, found 516.1435.

(±)-(cis-trans-cis)-Ethyl 6b-benzoyl-2a-butyl-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ha): Colorless solid; mp 145-147 °C; yield = 60% (64 mg), dr = 85:15; \( R_f = 0.33 \) (ethyl acetate/hexane = 25:75); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.04 (d, \( J = 5.8 \) Hz, 2H), 7.95 (d, \( J = 7.4 \) Hz, 2H), 7.61 (t, \( J = 7.4 \) Hz, 1H), 7.48 (t, \( J = 7.7 \) Hz, 2H), 7.36 (d, \( J = 8.0 \) Hz, 2H), 6.68 (br s, 1H), 6.10 (d, \( J = 10.4 \) Hz, 1H), 4.20-4.17 (m, 2H), 3.08 (d, \( J = 5.4 \) Hz, 1H), 2.57 (d, \( J = 5.6 \) Hz, 1H), 1.34 (t, \( J = 6.0 \) Hz, 3H), 1.25 (s, 3H), 1.24 (t, \( J = 7.0 \) Hz, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 192.7, 192.1, 168.1, 149.7, 144.3, 138.6, 135.8, 134.1, 129.7, 129.0, 128.4, 127.8, 73.6, 61.8, 53.5, 53.4, 46.2, 35.5, 34.3, 21.6, 21.3, 13.9 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^{+}\) calcld for C\(_{32}\)H\(_{32}\)NNaO\(_6\)S\(^+\) 634.1578, found 634.1566.
Hz, 1H), 2.49 – 2.44 (m, 4H), 2.34-2.30 (m, 1H), 2.07-2.04 (m, 2H), 1.91-1.86 (m, 1H), 1.27 – 1.14 (m, 7H), 0.77 (t, J = 7.0 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ (major isomer) 193.3, 192.3, 168.5, 148.3, 144.2, 139.1, 135.8, 134.1, 129.6, 129.1, 129.0, 128.7, 128.3, 77.3, 61.8, 53.8, 50.9, 45.8, 37.0, 35.4, 33.5, 27.3, 23.1, 21.6, 13.9, 13.6 ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for C$_{30}$H$_{33}$NNaO$_6$S$^+$ 558.1921, found 558.1937.

(±)-Ethyl 6b-benzoyl-2a-butyl-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3ha', minor isomer): Colorless solid; $R_f$ = 0.34 (ethyl acetate/hexane = 25:75); Whit solid; mp 140-145 °C; $R_f$ = 0.32 (ethyl acetate/hexane = 25:75); $^1$H NMR (500 MHz, CDCl$_3$) δ (minor isomer) 7.90 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 7.5 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.32 (d, J = 7.7 Hz, 2H), 6.75 (d, J = 10.4 Hz, 1H), 6.05 (d, J = 10.5 Hz, 1H), 4.24 – 4.13 (m, 2H), 2.99 (dd, J = 11.9, 5.8 Hz, 1H), 2.51-2.47 (m, 3H), 2.45 (s, 3H), 2.41 (d, J = 6.4 Hz, 1H), 2.12 – 2.01 (m, 2H), 1.34 – 1.24 (m, 7H), 0.88 (t, J = 6.6 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ (minor isomer) 197.3, 194.5, 168.5, 145.1, 144.5, 137.3, 135.3, 134.0, 129.9, 129.5, 129.1, 128.9, 128.6, 75.4, 62.0, 53.3, 48.2, 45.7, 39.7, 37.2, 27.3, 26.4, 22.7, 21.6, 14.0 (2C) ppm; HRMS (ESI-TOF) m/z[M + Na]$^+$ calcd for C$_{30}$H$_{33}$NNaO$_6$S$^+$ 558.1921, found 558.1938.

(±)-(cis-trans-cis)-Ethyl 2a-butyl-6b-(4-chlorobenzoyl)-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3hg): Colorless solid; mp 150-152 °C; yield = 65% (74 mg); dr = 85:15; $R_f$ = 0.33 (ethyl acetate/hexane = 25:75); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.02 (br s, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 7.7 Hz, 2H), 6.68 (d, J = 7.9 Hz, 1H), 6.10 (d, J = 10.2 Hz, 1H), 4.19 – 4.17 (m, 2H), 3.06 (br s, 1H), 2.55 (d, J = 5.3 Hz, 1H), 2.50 – 2.46 (m, 4H), 2.29-2.25 (m, 1H), 2.17-2.04 (m, 2H), 1.90 – 1.86 (m, 1H), 1.23 – 1.05 (m, 7H), 0.76 (t, J = 7.1 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 193.1, 191.2, 168.3, 148.3, 144.3, 140.8, 139.1, 134.2, 130.4, 129.7, 129.4, 128.7, 128.2, 77.3, 61.9, 53.8, 50.8, 45.6, 37.0, 35.3, 33.4,
27.3, 23.1, 21.6, 13.9, 13.6 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{30}H_{32}ClINaO_6S^+ 592.1531, found 592.1543.

(±)-(cis-trans-cis)-Ethyl 6b-(4-bromobenzoyl)-2a-butyl-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3hh):

Colorless solid; mp 160-162 °C; yield = 64% (78 mg); dr = 84:16; R_f = 0.33 (ethyl acetate/hexane = 25:75); 1^H NMR (500 MHz, CDCl_3) δ 8.02 (d, J = 6.6 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 6.68 (d, J = 6.7 Hz, 1H), 6.09 (d, J = 10.4 Hz, 1H), 4.20-4.15 (m, 2H), 3.06 (d, J = 5.8 Hz, 1H), 2.54 (d, J = 5.6 Hz, 1H), 2.50 (d, J = 6.4 Hz, 1H), 2.47 (s, 3H), 2.28-2.25 (m, 1H), 2.06-2.04 (m, 2H), 1.90-1.86 (m, 1H), 1.27 – 1.04 (m, 7H), 0.76 (t, J = 7.0 Hz, 3H) ppm; 13^C NMR (125 MHz, CDCl_3) δ 193.1, 191.5, 168.3, 148.2, 144.3, 139.1, 134.6, 132.4, 130.4, 129.7, 129.6, 128.6, 128.2, 77.3, 61.9, 53.8, 50.7, 45.6, 37.0, 35.3, 33.4, 27.3, 23.1, 21.6, 13.9, 13.6 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{30}H_{32}BrINaO_6S^+ 636.1026, found 636.1040.

(±)-(cis-trans-cis)-Ethyl 6b-(1-naphthoyl)-2a-butyl-5-oxo-2-tosyl-1,1a,2,2a,5,6,6a,6b-octahydrocyclopropa[b]indole-1a-carboxylate (3hi):

Colorless solid; mp 180-182 °C; yield = 57% (66 mg); dr = 91:9; R_f = 0.32 (ethyl acetate/hexane = 25:75); 1^H NMR (500 MHz, CDCl_3) δ 8.69 (d, J = 8.5 Hz, 1H), 8.10 – 8.03 (m, 4H), 7.87 (d, J = 7.7 Hz, 1H), 7.60-7.50 (m, 3H), 7.36 (d, J = 7.5 Hz, 2H), 6.70 (d, J = 9.9 Hz, 1H), 6.20 (d, J = 10.2 Hz, 1H), 4.32-4.11 (m, 2H), 3.15 (br s, 1H), 2.59 (d, J = 5.3 Hz, 1H), 2.54-2.51 (m, 2H), 2.46 (s, 3H), 2.08 – 2.04 (m, 2H), 1.95 – 1.90 (m, 1H), 1.27 – 1.10 (m, 7H), 0.78 (t, J = 6.6 Hz, 3H) ppm; 13^C NMR (125 MHz, CDCl_3) δ 195.1, 193.2, 168.5, 147.7, 144.2, 139.2, 134.8, 134.2, 132.7, 131.0, 130.9, 129.6, 129.0, 128.8, 128.4, 128.3, 126.9, 126.1, 123.9, 77.2 (merging with CDCl_3 peaks), 61.9, 55.2, 51.5, 47.9, 37.3, 35.7, 34.4, 27.3, 23.1, 21.6, 13.9, 13.6 ppm; HRMS (ESI-TOF) m/z [M + Na]^+ calcd for C_{34}H_{35}NNaO_6S^+ 608.2077, found 608.2099.
The compound 3ha (81.0 mg, 0.15 mmol) in EtOH (10 mL, degassed) was taken in a two-neck round-bottom flask. Afterward, 5 mol% of Pd/C (10 mg) was added to the above reaction mixture. Then, the reaction was stirred at 10 °C under H₂-ballon for 1h. After completion of the reaction, it was filtered through short-pad celite-545 and washed with EtOAc (20 mL). Next, evaporation of solvent left the crude materials which was purified, leading to the pure product 5 in 88% yield.

\((\pm)-(\text{cis-trans-cis})\)-Ethyl 6b-benzoyl-2a-butyl-5-oxo-2-tosyldecahydrocyclopropa[b]indole-1a-carboxylate (5): Colorless solid; mp 78-80 °C; \(R_f=0.33\) (ethyl acetate/hexane = 25:75); yield = 88% (71 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92-7.91 (m, 4H), 7.59 (t, \(J=7.2\) Hz, 1H), 7.46 (t, \(J=7.5\) Hz, 2H), 7.32 (d, \(J=7.9\) Hz, 2H), 4.35-4.22 (m, 2H), 3.34-3.28 (m, 1H), 3.06 (d, \(J=4.8\) Hz, 1H), 2.45 (s, 4H), 2.36 – 2.29 (m, 3H), 2.23-2.10 (m, 2H), 1.95-1.90 (m, 1H), 1.64 (br s, 2H), 1.35 – 1.25 (m, 7H), 0.87 (t, \(J=6.7\) Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 208.4, 192.3, 168.3, 143.9, 138.6, 135.4, 134.0, 129.4, 129.0, 128.5, 125.2, 76.8, 62.1, 55.1, 47.9, 44.7, 40.1, 39.3, 34.6, 31.3, 27.6, 23.1, 21.5, 13.9, 13.8 ppm; HRMS (ESI-TOF) m/z [M + Na]\(^+\) calcd for C\(_{30}\)H\(_{35}\)NNaO\(_6\)S\(^+\) 560.2077, found 560.2066.

A mixture of compound 5 (54.0 mg, 0.1 mmol), ortho-aminoacetophenone (20.0 mg, 0.15 mmol) and PTSA (20 mol%) was taken in sealed tube and heated at 100 °C for 16h. After completion of the reaction, the reaction mixture was concentrated and added aqueous NaHCO₃ solution, followed by extraction with ethyl acetate, dried over Na₂SO₄. Next, the solvent was evaporated under
reduced pressure to give the crude mass, which was purified by column chromatography over silica-gel to afford the pure product 6 in 75% yield.

\[ (+)-(cis-trans-cis)-Ethyl \ 10b-benzoyl-2a-butyl-4-methyl-2-tosyl-1,1a,2,2a,3,10,10a,10b-octahydrocyclopropa[4,5]pyrrolo[2,3-b]acridine-1a-carboxylate \] (6): Colorless solid; mp 88-90 °C; yield = 75% (47 mg); \( R_f = 0.3 \) (ethyl acetate/hexane = 25:75); \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.04 (d, \( J = 7.7 \) Hz, 2H), 8.00 (d, \( J = 7.6 \) Hz, 1H), 7.95-7.87 (m, 1H), 7.58 (t, \( J = 7.5 \) Hz, 1H), 7.50 (d, \( J = 8.3 \) Hz, 1H), 7.46 (d, \( J = 7.5 \) Hz, 2H), 7.36 – 7.30 (m, 3H), 7.15 (t, \( J = 7.4 \) Hz, 2H), 4.35-4.15 (m, 2H), 4.12 (s, 1H), 3.84-3.78 (m, 1H), 3.22-2.98 (m, 2H), 2.85 – 2.76 (m, 2H), 2.47 (s, 3H), 2.44-2.34 (m, 1H), 2.21 (s, 3H), 1.75 – 1.65 (m, 2H), 1.33-1.25 (m, 5H), 1.12-1.07 (m, 2H), 0.66 (t, \( J = 7.1 \) Hz, 3H) ppm; \( ^{13}C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 192.9, 168.8, 160.2, 143.8, 139.2, 136.2, 133.1, 129.5, 129.2, 128.98, 128.93, 128.8, 128.6, 128.4, 128.1, 126.3, 125.5, 125.2, 123.5, 80.0, 62.0, 55.6, 53.8, 46.7, 37.7, 33.3, 32.5, 31.5, 27.2, 23.0, 21.6, 14.7, 13.9, 13.7 ppm; HRMS (ESI-TOF) \( m/z \) [M + Na]\(^+\) calcd for C\(_{38}\)H\(_{40}\)N\(_2\)NaO\(_5\)S\(^+\) 659.2550, found 659.2540.

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