Supporting Information

Gold(I)-Catalyzed Enantioselective Synthesis of Polycyclic Indoline Skeletons and Enantiomerically Enriched β-Substituted Tryptamine-Allenes by Kinetic Resolution

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CONTENTS

1. General remarks.................................................................................................................. S2
2. General procedure for synthesis of 1.................................................................................. S3
3. Conditions screening for kinetic resolution of racemic indole-allenes 1.......................... S5
4. General procedure for the gold(I)-catalyzed kinetic resolution of racemic indole-allenes 1... S6
5. Proposed reaction mechanism................................................................................................ S7-S8
6. Characterization and spectra charts for compounds 1...................................................... S9-S65
7. Characterization and spectra charts for compounds 2..................................................... S66-S126
8. Characterization and spectra charts for compounds 3 and 4........................................... S127-S131
9. Transformations and the characterization and spectra charts........................................... S132-S142
10. X-ray crystallographic information of products 2f, 6, 7 and 2r'...................................... S143-S146
11. References....................................................................................................................... S147
1. **General remarks.** Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. Unless otherwise noted, all reaction mixtures were stirred with a magnetic stir bar in flame-dried glassware under argon atmosphere. All the temperatures were referred to the used oil baths. Extracts were dried over MgSO₄ or Na₂SO₄ and solvents were removed in a rotary evaporator. TLC analysis of reaction mixtures was performed on Huanghai GF₉₅₄ silica gel coated plates. Flash column chromatography was performed using 300-400 mesh silica gel (Huanghai GF254) and 250-400 mesh silica gel (Silicycle UltraPure silica gels). MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. Infra-red spectra were measured on a spectrometer. ¹H NMR spectra were recorded for solution in CDCl₃ with tetramethylsilane (TMS) as an internal standard. ¹⁹F NMR spectra were recorded for a solution in CDCl₃ with CFCl₃ as the external reference. J-values are in Hz. Mass and HRMS spectra were recorded by ESI method.
2. General procedure for synthesis of 1.

The compounds S1 are prepared according to known procedures.\textsuperscript{[1]}

The compounds S2 and S3 are prepared according to known procedures.\textsuperscript{[2]}

To an oven-dried reaction bottle was sequentially added S1 or S3 (4.00 mmol), K$_2$CO$_3$ (8.00 mmol), KI (0.40 mmol) and S4 (4.80 mmol) in acetone (20.00 mL). The resulting mixture was stirred under reflux. When the reaction was complete as monitored by TLC, it was cooled to room temperature. The solution was filtered through a short column of silica gel eluting with ethyl acetate, and then the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 15/1) to give the corresponding product 1.
3. Conditions screening for kinetic resolution of racemic indole-allenes 1.

Table S1 Conditions screening for kinetic resolution of racemic indole-allenes 1.a,b,c,d

<table>
<thead>
<tr>
<th>entry</th>
<th>Au cat.</th>
<th>solvent</th>
<th>T (°C)</th>
<th>yield (%)</th>
<th>ee (%)</th>
<th>s-factor</th>
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<tr>
<td>1</td>
<td>L1Au(MeCN)SbF6</td>
<td>toluene</td>
<td>0</td>
<td>48</td>
<td>&gt;99</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>L2AuSbF6</td>
<td>toluene</td>
<td>0</td>
<td>48</td>
<td>&gt;99</td>
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<td>0</td>
<td>48</td>
<td>95</td>
<td>-</td>
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<td>toluene</td>
<td>0</td>
<td>48</td>
<td>94</td>
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<td>-</td>
</tr>
<tr>
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<td>toluene</td>
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<td>33</td>
<td>91</td>
<td>87</td>
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<td>89</td>
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<td>30</td>
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<td>toluene</td>
<td>-10</td>
<td>31</td>
<td>46</td>
<td>92</td>
</tr>
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</table>

a The reaction conditions: 0.1 M in solvent. b The yield was determined by 1H NMR spectroscopic data using 1,3,5-trimethoxybenzene as an internal standard. c Determined by HPLC on a chiral stationary phase. d Selectivity (s-factor) calculated as $s = \frac{\ln[(1-C)(1-\text{eeSM})]}{\ln[(1-C)(1+\text{eeSM})]}$. 

Our studies were initiated by examining the reactivity of racemic indole-allene 1a in the presence of a series of gold complexes derived from chiral ligands L1-L6 (Table S1). It was found that, chiral phosphine ligands L1 and L2 coordinated gold catalysts had no catalytic activities for the reaction (entries 1-2). When Feringa phosphoramidite-based ligand (L3) and biaryl bispophine ligand (R)-DM-Segphos (L4) incorporated gold catalyst were employed, only trace of cyclization product 2a was detected by 1H NMR analysis (entries 3-4). Further examination of chiral phosphine ligands revealed that sterically more demanding (R)-DTBM-Segphos (L5) furnished 2a in 31% yield along with 92% ee value at 0 °C (entry 5). Next, we investigated the counterion effect by pre-preparing cationic gold catalysts and found
that NTf₂ was the better counterion, giving the cycloadduct 2a in 33% yield along with 91% ee and enantiomerically enriched 1a in 40% yield along with 87% ee (s-factor = 10.1) at 0 °C (entry 6). The reaction conditions with regard to temperature and concentration were then examined. We found that when 4Å molecular sieves (50 mg) was added into the reaction mixture or concentration of the reaction solution was deceased to 0.05 M in toluene, the s-factor could be dramatically improved to 32.0 or 35.7 at 0 °C (entries 7-10). Carrying out the reaction in DCM or using (R)-DTBM-MeO-BIPHEP(AuNTf₂)₂ (L6) as the catalyst did not further enhance the kinetic resolution efficiency (entries 11-12). The optimal conditions shown in entry 10 of Table S1 could afford 2a in 49% yield and 91% ee as well as 1a in 45% yield and 97% ee along with a s-factor of 35.7. This synthetic strategy could provide a convenient and highly efficient method to prepare diversified enantiomerically enriched polycyclic indolines and β-substituted tryptamine-allene motifs.

To a flame dried Schlenk tube was added unsymmetrical indole-allene 1 (0.1 mmol), (R)-DTBMSegphos(AuNTf₂)₂ (5.0 mol %) and the tube was evacuated and backfilled with argon for three times. Then, anhydrous toluene (2.0 mL) was added into tube under argon atmosphere. The reaction mixture was allowed to stir at 0 °C. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography on silica gel to give the enantiomerically enriched compound 1 and desired product 2.
5. Proposed reaction mechanism.

A plausible reaction mechanism for this gold(I)-catalyzed tandem intramolecular cyclization is outlined in Figure S1 on the basis of the previous literature. Coordination of gold(I) complex with allene moiety in 1a generates intermediate A, which then initiates a nucleophilic attack from C3 position of indole to allene moiety, resulting in the cyclized intermediate B. Intermediate B undergoes a further intramolecular cyclization to give a Au-carbenoid intermediate C, which follows a 1,2-hydrogen migration to afford intermediate D. The release of gold(I) catalyst produces the cycloaddition product 2a and restarts the next catalytic cycle.

Figure S1 Proposed reaction mechanism.
Proposed key transition states for stereochemical control are illustrated in Figure S2. The intermediate **A** can undergo a nucleophilic attack from C3 position of indole to allene moiety via *re*-face or *si*-face to generate intermediate **B**. Probably due to the steric repulsion between the benzene ring moiety and chiral phosphine ligand (TS1*re*), the *si*-face attack is preferred in this step. Subsequently, the olefinic moiety of intermediate **B** attacks the C2 position of indole via *re*-face or *si*-face to form intermediate **C**. In this step, *re*-face attack is probably the dominated pathway since the *si*-face attack is disfavored due to the steric repulsion between the benzene ring and indole moiety (TS2*si*).
6. Characterization and spectra charts for compounds 1.

\[(R)-N-(\text{buta-2,3-dien-1-yl})-4\text{-methyl-N-(2-(1-methyl-1H-indol-3-yl)-2-phenylethyl)benzenesulfonamide 1a}\]

A white solid, 45% yield (20.5 mg). M.p.: 53-56 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.38 (s, 3H), 3.53-3.61 (m, 1H), 3.62-3.69 (m, 1H), 3.73 (s, 3H), 3.82-3.90 (m, 1H), 3.99-4.06 (m, 1H), 4.60-4.71 (m, 4H), 7.00-7.06 (m, 2H), 7.16-7.22 (m, 4H), 7.25-7.34 (m, 5H), 7.47 (d, \(J = 8.0\) Hz, 1H), 7.60 (d, \(J = 8.0\) Hz, 2H). \(^1\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.4, 32.7, 41.4, 46.2, 50.8, 76.1, 85.2, 109.1, 114.6, 118.8, 119.1, 121.5, 126.6, 126.9, 127.1, 127.2, 128.2, 128.4, 129.5, 136.9, 137.1, 142.0, 143.1, 209.2. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 2920, 1949, 1599, 1474, 1334, 1160, 1093, 1010, 903, 858, 750, 659 cm\(^{-1}\). MS (ESI) \(m/\text{z}\) (%): 457.19 (100) [M+H]\(^+\); HRMS (DART) Calcd. For C\(_{28}\)H\(_{29}\)N\(_2\)O\(_2\)S\(^{+1}\) [M+H]\(^+\) requires 457.1944, found: 457.1941. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [\(\lambda = 254\) nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 23.35\) min, \(t_{\text{major}} = 26.05\) min; ee\% = 97%; [\(\alpha\)]\(_D\)\(^{25}\) = -23.0 (c 0.70, CH\(_2\)Cl\(_2\))].
Translation: Chiralcel IC column \( [\lambda = 254 \text{ nm}; \text{ eluent: Hexane/Isopropanol} = 86/14; \text{ Flow rate:} \ 0.70 \ \text{mL/min; } t_{\text{minor}} = 23.35 \ \text{min, } t_{\text{major}} = 26.05 \ \text{min; } \text{ee\%} = 97\%]. \)

\[
(R)-\text{N-(2-(1-benzyl-1H-indol-3-yl)-2-phenylethyl)-N-}(\text{buta-2,3-dien-1-yl})-4\text{-methylbenzenesulfonamide} \ 1b
\]

A white solid, 48\% yield (25.5 mg). M.p.: 65-68 \degree C. \(^1\)H NMR (CD\(_3\)Cl, TMS, 400 MHz) \( \delta \) 2.38 (s, 3H), 3.51-3.58 (m, 1H), 3.66 (dd, \( J = 14.0, 8.0 \, \text{Hz, 1H})\), 3.79-3.87 (m, 1H), 4.03 (dd, \( J = 14.0, 8.0 \, \text{Hz, 1H})\), 4.62-4.68 (m, 4H), 5.28 (s, 2H), 7.00-7.05 (m, 1H), 7.09-7.15 (m, 4H), 7.19-7.33 (m, 11H), 7.48 (d, \( J = 8.0 \, \text{Hz, 1H})\), 7.60 (d, \( J = 8.0 \, \text{Hz, 2H})\). \(^13\)C NMR (CD\(_3\)Cl, 100 MHz, TMS) \( \delta \) 21.4, 41.6, 46.3, 50.0, 50.9, 76.1, 85.3, 109.7, 115.2, 119.1, 119.3, 121.8, 126.4, 126.5, 126.6, 127.1, 127.4, 127.6, 128.3, 128.4, 128.6, 129.5, 136.6, 137.1, 137.5, 142.0, 143.1, 209.2. IR (CH\(_2\)Cl\(_2\)) \( \nu \) 3028, 2918, 2850, 1952, 1598, 1466, 1331, 1155, 1092, 936, 897, 846, 738, 657 cm\(^{-1}\). MS (ESI) \( m/z \) (%): 533.22 (100) [M+H]\(^+\); HRMS (DART) Calcd. For C\(_{34}\)H\(_{33}\)N\(_2\)O\(_2\)S\(^+\) [M+H]\(^+\) requires 533.2257, found: 533.2253. Enantiomeric excess was determined by HPLC with a Chiralcel IC column \([\lambda = 254 \, \text{nm}; \text{ eluent: Hexane/Isopropanol} = 86/14; \text{ Flow rate:} \ 0.70 \ \text{mL/min; } t_{\text{minor}} = 21.38 \ \text{min, } t_{\text{major}} = 22.70 \ \text{min; } \text{ee\%} = 84\%; [\alpha]_D^{25} = -68.5 \, \text{(c 0.16, CH}_2\text{Cl}_2)\).
Translation: Chiralcel IC column [\(\lambda = 254\) nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 21.38\) min, \(t_{\text{major}} = 22.70\) min; ee\% = 84\%].

\[
\text{(R)-N-}(2-(1\text{-allyl-1H-indol-3-yl})\text{-2-phenylethyl)-N-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1c}
\]

A white solid, 46\% yield (22.2 mg). M.p.: 60-63 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.39 (s, 3H), 3.52-3.59 (m, 1H), 3.63-3.69 (m, 1H), 3.80-3.88 (m, 1H), 3.99-4.05 (m, 1H), 4.61-4.70 (m, 6H), 5.08 (d, \(J = 17.2\) Hz, 1H), 5.19 (d, \(J = 10.4\) Hz, 1H), 5.93-6.03 (m, 1H), 7.01-7.06 (m, 2H), 7.14-7.19 (m, 1H), 7.21-7.33 (m, 8H), 7.48 (d, \(J = 8.0\) Hz, 1H), 7.60 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.4, 41.5, 46.3, 48.8, 50.8, 76.1, 85.3, 109.6, 115.0, 117.1, 119.0, 119.3, 121.6, 125.9, 126.6, 127.2, 127.5, 128.3, 128.5, 129.6, 133.4, 136.4, 137.1, 142.0, 143.1, 209.2. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 3064, 2902, 1960, 1595, 1462, 1330, 1154, 1089, 858, 741, 673 cm\(^{-1}\). MS (ESI) \(m/z\) (%): 483.21 (100) [M+H]\(^+\); HRMS (DART) Calcd. For C\(_{30}\)H\(_{31}\)N\(_2\)O\(_2\)S\(^{+}\) [M+H]\(^+\) requires 483.2101, found: 483.2102. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [\(\lambda = 214\) nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 12.78\) min, \(t_{\text{major}} = 13.73\) min; ee\% =
97%; $[\alpha]_D^{25} = -78.0$ (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t<sub>minor</sub> = 12.78 min, t<sub>major</sub> = 13.73 min; ee% = 97%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
(R)-N-(buta-2,3-dien-1-yl)-N-(2-(1,5-dimethyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonylamide 1d

A white solid, 48% yield (22.5 mg). M.p.: 83-86 °C. 1H NMR (CDCl₃, TMS, 400 MHz) δ 2.39 (s, 3H), 2.40 (s, 3H), 3.54-3.61 (m, 1H), 3.65 (dd, J = 13.6, 8.4 Hz, 1H), 3.70 (s, 3H), 3.81-3.89 (m, 1H), 3.97 (dd, J = 14.0, 7.6 Hz, 1H), 4.60 (t, J = 8.0 Hz, 1H), 4.64-4.72 (m, 3H), 6.94 (s, 1H), 7.01 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.20-7.24 (m, 3H), 7.26-7.34 (m, 5H), 7.60 (d, J = 8.0 Hz, 2H). 13C NMR (CDCl₃, 100 MHz, TMS) δ 21.47, 21.49, 32.8, 41.3, 46.2, 50.8, 76.1, 85.3, 108.9, 114.0, 118.8, 123.2, 126.6, 127.0, 127.2, 127.4, 128.0, 128.3, 128.5, 129.6, 135.4, 137.2, 142.1, 143.1, 209.3. IR (CH₂Cl₂) ν 2921, 2850, 1698, 1608, 1510, 1450, 1335, 1273, 1159, 1015, 941, 769, 656 cm⁻¹. MS (ESI) m/z (%): 471.20 (100) [M+H]+; HRMS (ESI) Calcd. For C₂₉H₃₁N₂O₂S⁺ [M+H]+ requires 471.2101, found: 471.2097. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.50 mL/min; t_minor = 24.61 min, t_major = 27.33 min; ee% = 96%; [α]D^25 = -25.0 (c 0.20, CH₂Cl₂)].
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.50 mL/min; t_{minor} = 24.61 min, t_{major} = 27.33 min; ee% = 96%].

(R)-N-(buta-2,3-dien-1-yl)-N-(2-(4-fluoro-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzesulfonamide 1e

A white solid, 50% yield (23.8 mg). M.p.: 117-120 °C. 1H NMR (CDCl3, TMS, 400 MHz) δ 2.39 (s, 3H), 3.60-3.72 (m, 2H), 3.74 (s, 3H), 3.85-3.93 (m, 1H), 4.00 (dd, J = 13.6, 8.8 Hz, 1H), 4.68-4.73 (m, 3H), 4.82 (t, J = 8.0 Hz, 1H), 6.62-6.68 (m, 1H), 7.01-7.10 (m, 3H), 7.18-7.31 (m, 7H), 7.59 (d, J = 8.0 Hz, 2H). 13C NMR (CDCl3, 100 MHz, TMS) δ 21.5, 33.2, 41.1, 46.0, 51.1, 76.1, 85.1, 104.2 (d, J = 19.7 Hz), 105.3 (d, J = 3.5 Hz), 113.1 (d, J = 3.6 Hz), 115.9 (d, J = 19.5 Hz), 121.9 (d, J = 8.0 Hz), 126.5, 127.1, 127.3, 128.2, 128.4, 129.6, 137.0, 139.7 (d, J = 11.9 Hz), 142.4, 143.1, 156.8 (d, J = 245.0 Hz), 209.2. 19F NMR (CDCl3, 376 MHz, CFCl3) δ -121.7. IR (CH2Cl2) ν 2914, 2861, 1956, 1627, 1498, 1331, 1236, 1152, 1091, 984, 844, 771, 658 cm⁻¹. MS (ESI) m/z (%): 475.18 (100) [M+H]+; HRMS (ESI) Calcd. For C28H28N2O2FS+1 [M+H]+ requires 475.1850, found: 475.1844.

Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 30.62 min, t_{major} = 50.90 min; ee% =
68%; [α]D^25 = -47.1 (c 0.08, CH2Cl2).
Translation: Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 30.62$ min, $t_{\text{major}} = 50.90$ min; ee% = 68%].
(R)-N-(buta-2,3-dien-1-yl)-N-(2-(5-fluoro-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 1f

A white solid, 46% yield (21.8 mg). M.p.: 104-107 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.36 (s, 3H), 3.54-3.65 (m, 2H), 3.69 (s, 3H), 3.82-3.88 (m, 1H), 4.00 (dd, $J = 13.6$, 8.0 Hz, 1H), 4.54 (t, $J = 8.0$ Hz, 1H), 4.63-4.72 (m, 3H), 6.87-6.93 (m, 1H), 7.06-7.16 (m, 3H), 7.19-7.31 (m, 7H), 7.59 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.4, 32.9, 41.3, 46.2, 50.7, 76.2, 85.2, 103.9 (d, $J = 23.9$ Hz), 109.7, 109.8, 109.9, 110.0, 114.4 (d, $J = 4.8$ Hz), 126.7, 127.1, 127.4 (d, $J = 9.7$ Hz), 128.1, 128.5, 129.6, 133.6, 137.0, 141.8, 143.2, 157.4 (d, $J = 232.6$ Hz), 209.2. $^{19}$F NMR (CDCl$_3$, 376 MHz, CFCl$_3$) $\delta$ -125.2. IR (CH$_2$Cl$_2$) $\nu$ 3034, 1954, 1597, 1489, 1339, 1157, 1098, 953, 848, 770, 661 cm$^{-1}$. MS (ESI) m/z (%): 475.18 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{28}$H$_{28}$N$_2$O$_2$FS$^+$ [M+H]$^+$ requires 475.1850, found: 475.1846. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 20.34$ min, $t_{\text{major}} = 22.40$ min; ee% = 92%; $[\alpha]$$_D^{25}$ = -162.5 (c 0.08, CH$_2$Cl$_2$)].
Chiralcel IC column \([\lambda = 214 \text{ nm}]\); eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 20.34 \text{ min}\), \(t_{\text{major}} = 22.40 \text{ min}\); ee\% = 92\%. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
(R)-N-(buta-2,3-dien-1-yl)-N-(2-(5-chloro-1-methyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonamide 1g

A white solid, 46% yield (22.5 mg). M.p.: 112-115 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.40 (s, 3H), 3.57-3.63 (m, 2H), 3.73 (s, 3H), 3.82-3.89 (m, 1H), 3.98 (dd, $J = 13.6$, 8.4 Hz, 1H), 4.54 (t, $J = 8.0$ Hz, 1H), 4.60-4.68 (m, 1H), 4.72-4.75 (m, 2H), 7.10-7.13 (m, 2H), 7.16-7.19 (m, 1H), 7.22-7.25 (m, 3H), 7.28-7.30 (m, 4H), 7.37 (d, $J = 2.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.5, 33.0, 41.0, 46.2, 50.7, 76.3, 85.1, 110.3, 114.1, 118.5, 121.9, 124.7, 126.8, 127.2, 128.2, 128.3, 128.4, 128.6, 129.7, 135.4, 137.0, 141.7, 143.3, 209.2. IR (CH$_2$Cl$_2$) $\nu$ 3028, 2922, 1953, 1598, 1478, 1336, 1155, 941, 852, 795, 701, 656 cm$^{-1}$. MS (ESI) $m/z$ (%): 491.15 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{28}$H$_{28}$N$_2$O$_2$ClS$^+$ [M+H]$^+$ requires 491.1555, found: 491.1552. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 10.30$ min, $t_{\text{major}} = 11.34$ min; ee% = 92%; $[\alpha]_D^{25} = 37.33$ (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column [\(\lambda = 254 \text{ nm}\); eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 10.30 \text{ min}\), \(t_{\text{major}} = 11.34 \text{ min}\); ee\% = 92\%].

(R)-N-(2-(5-bromo-1-methyl-1H-indol-3-yl)-2-phenylethyl)-N-(buta-2,3-dien-1-yl)-4-methylbenzenesulfonamide 1h

A white solid, 48% yield (25.6 mg). M.p.: 101-104 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.40 (s, 3H), 3.57-3.63 (m, 2H), 3.73 (s, 3H), 3.82-3.88 (m, 1H), 3.97 (dd, \(J = 13.6, 8.4 \text{ Hz}\), 1H), 4.54 (t, \(J = 8.0 \text{ Hz}\), 1H), 4.60-4.77 (m, 3H), 7.08 (s, 1H), 7.12-7.15 (m, 1H), 7.22-7.30 (m, 8H), 7.54 (d, \(J = 2.0 \text{ Hz}\), 1H), 7.60 (d, \(J = 8.0 \text{ Hz}\), 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.5, 33.0, 41.0, 46.2, 50.7, 76.3, 85.2, 110.7, 112.3, 114.1, 121.6, 124.4, 126.8, 127.2, 128.2, 128.3, 128.6, 129.0, 129.7, 135.7, 137.0, 141.7, 143.3, 209.2. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 2913, 1952, 1597, 1475, 1335, 1157, 1061, 946, 842, 794, 708, 663 cm\(^{-1}\). MS (ESI) \(m/z\) (%): 535.10 (100) [M+H]\(^+\); HRMS (DART) Calcd. For C\(_{28}\)H\(_{28}\)N\(_2\)O\(_2\)BrS\(^+\) [M+H]\(^+\) requires 535.1049, found: 535.1046. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [\(\lambda = 214 \text{ nm}\); eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 14.19 \text{ min}\), \(t_{\text{major}} = 16.03 \text{ min}\); ee\% = 80\%; [\(\alpha\)]\(_D\)^{25} = -30.0 (c 0.10, CH\(_2\)Cl\(_2\))].
**Translation:** Chiralcel IC column \([\lambda = 214 \text{ nm}]; \text{eluent: Hexane/Isopropanol} = 70/30; \text{Flow rate:} 0.70 \, \text{mL/min}; \, t_{\text{minor}} = 14.19 \, \text{min}, \, t_{\text{major}} = 16.03 \, \text{min}; \, \text{ee\%} = 80\%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(R)-Methyl 3-(2-(N-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-1-phenylethyl)-1-methyl-1H-indole-6-carboxylate 1i

A white solid, 50\% yield (25.7 mg). M.p.: 170-173 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.40 (s, 3H), 3.54-3.63 (m, 2H), 3.83 (s, 3H), 3.84-3.90 (m, 1H), 3.93 (s, 3H), 4.03 (dd, \(J = 13.6, 8.4\) Hz, 1H), 4.61-4.72 (m, 4H), 7.22-7.26 (m, 4H), 7.29 (d, \(J = 8.4\) Hz, 4H), 7.45 (d, \(J = 8.4\) Hz, 1H), 7.60 (d, \(J = 8.4\) Hz, 2H), 7.69-7.73 (m, 1H), 8.05 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.5, 33.0, 41.2, 46.3, 50.9, 51.9, 76.2, 85.2, 111.7, 115.1, 118.8, 120.0, 123.2, 126.3, 127.2, 128.2, 128.6, 129.7, 130.4, 130.8, 136.4, 137.0, 141.8, 143.3, 168.1, 209.3. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 2923, 2860, 1948, 1703, 1478, 1341, 1160, 1106, 979, 882, 748, 659 cm\(^{-1}\). MS (ESI) \(m/z\) (%): 515.19 (100) [M+H]\(^+\); HRMS (DART) Calcd. For C\(_{30}\)H\(_{31}\)N\(_2\)O\(_4\)S\(^+\) [M+H]\(^+\) requires 515.1999, found: 515.1993. Enantiomeric excess was determined by HPLC with a Chiralcel IA column \([\lambda = 214 \text{ nm}]; \text{eluent: Hexane/Isopropanol} = 90/10; \text{Flow rate:} 0.70 \, \text{mL/min}; \, t_{\text{minor}} = 35.63 \, \text{min}, \, t_{\text{major}} = 44.09 \, \text{min}; \, \text{ee\%} = 80\%; [\alpha]_{D}^{25} = -17.8 \, (c 0.12, \text{CH}_2\text{Cl}_2)]\).
Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_minor = 35.63 min, t_major = 44.09 min; ee% = 80%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(R)-N-(buta-2,3-dien-1-yl)-N-(2-(1,7-dimethyl-1H-indol-3-yl)-2-phenylethyl)-4-methylbenzenesulfonyl amide 1j

A white solid, 46% yield (21.7 mg). M.p.: 102-105 °C. 1H NMR (CDCl₃, TMS, 400 MHz) δ 2.39 (s, 3H), 2.74 (s, 3H), 3.53-3.65 (m, 2H), 3.84-3.92 (m, 1H), 3.98 (dd, J = 13.6, 7.6 Hz, 1H), 4.01 (s, 3H), 4.58 (t, J = 8.0 Hz, 1H), 4.64-4.72 (m, 3H), 6.87-6.91 (m, 3H), 7.19-7.31 (m, 8H), 7.60 (d, J = 8.0 Hz, 2H). 13C NMR (CDCl₃, 100 MHz, TMS) δ 19.7, 21.5, 36.8, 41.1, 46.2, 50.7, 76.2, 85.3, 114.2, 117.2, 119.2, 121.2, 124.3, 126.6, 127.2, 128.30, 128.34, 128.5, 128.7, 129.6, 135.7, 137.2, 142.1, 143.1, 209.3. IR (CH₂Cl₂) ν 2923, 2867, 1956, 1451, 1156, 959, 808, 769, 660 cm⁻¹. MS (ESI) m/z (%): 471.20 (100) [M+H]+; HRMS (DART) Calcd. For C₂₉H₃₁N₂O₂S⁺ [M+H]+ requires 471.2101, found: 471.2097. Enantiomeric excess was determined by HPLC with a Chiralcel ID3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_minor = 13.29 min, t_major = 14.58 min; ee% = 97%; [α]D²⁵ = -119.6 (c 0.6, CH₂Cl₂)].
Translation: Chiralcel ID3 column \([\lambda = 214 \text{ nm}; \text{eluent: Hexane/Isopropanol} = 80/20; \text{Flow rate: 0.70 mL/min}; t_{\text{minor}} = 13.29 \text{ min}, t_{\text{major}} = 14.58 \text{ min}; ee\% = 97\%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

\[
\text{BnN} \overset{\text{O}}{\text{NTs}} \overset{\text{O}}{\text{N}}(\text{R})-\text{N}-2-(1\text{-benzyl}-4\text{-methoxy}-1H\text{-indol}-3\text{-yl})-2\text{-phenylethyl})-\text{N}(\text{buta-2,3-dien-1-yl})-4\text{-methylbenzenesulfonamide 1k}
\]

A white solid, 47% yield (26.4 mg). M.p.: 107-110 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.37 (s, 3H), 3.63-3.71 (m, 2H), 3.77 (s, 3H), 3.89-4.00 (m, 2H), 4.68-4.78 (m, 3H), 5.07 (t, \(J = 8.0 \text{ Hz}, 1\text{H})\), 5.24 (s, 2H), 6.40 (d, \(J = 8.0 \text{ Hz}, 1\text{H})\), 6.80 (d, \(J = 8.0 \text{ Hz}, 1\text{H})\), 6.98-7.30 (m, 14H), 7.56 (d, \(J = 8.0 \text{ Hz}, 2\text{H})\). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.5, 41.3, 45.9, 50.3, 51.5, 54.9, 76.0, 85.7, 99.5, 103.2, 115.8, 117.6, 122.5, 125.6, 126.2, 126.6, 127.3, 127.5, 128.2, 128.6, 128.7, 129.6, 137.3, 137.6, 138.2, 143.0, 143.1, 154.6, 209.1. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 3027, 2925, 1954, 1578, 1497, 1338, 1257, 1156, 1091, 940, 850, 730, 699 cm\(^{-1}\). MS (ESI) \(m/z\) (%): 563.23 (100) [M+\(\text{H}\)]\(^+\); HRMS (DART) Calcd. For C\(_{35}\)H\(_{35}\)N\(_2\)O\(_3\)S\(^{+}\) [M+\(\text{H}\)]\(^+\) requires 563.2363, found: 563.2355. Enantiomeric excess was determined by HPLC with a Chiralcel IA column \([\lambda = 214 \text{ nm}; \text{eluent: Hexane/Isopropanol} = 90/10; \text{Flow rate: 0.70 mL/min}; t_{\text{minor}} = 21.02 \text{ min}, t_{\text{major}} = 18.78 \text{ min}; ee\% = 96\%; [\alpha]'D = -80.0 (c 0.10, CH\(_2\)Cl\(_2\))].\]
Translation: Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 21.02$ min, $t_{\text{major}} = 18.78$ min; ee% = 96%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(R)-N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)-2-(p-tolyl)ethyl)benzenesulfonylamide 11

A white solid, 48% yield (22.6 mg). M.p.: 66-69 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.30 (s, 3H), 2.39 (s, 3H), 3.56-3.66 (m, 2H), 3.74 (s, 3H), 3.83-3.91 (m, 1H), 4.00 (dd, $J = 13.6$, 7.6 Hz, 1H), 4.58 (t, $J = 8.0$ Hz, 1H), 4.64-4.71 (m, 3H), 7.00 (s, 1H), 7.02-7.09 (m, 3H), 7.16-7.26 (m, 6H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.0, 21.5, 32.8, 40.9, 46.2, 50.8, 76.1, 85.3, 109.2, 114.9, 118.8, 119.2, 121.6, 126.9, 127.2, 127.3, 128.1, 129.2, 129.6, 136.1, 137.0, 137.2, 139.0, 143.1, 209.3. IR (CH$_2$Cl$_2$) $\nu$ 2923, 1953, 1325, 1155, 1092, 739, 656 cm$^{-1}$. MS (ESI) $m/z$ (%): 471.20 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{29}$H$_{31}$N$_2$O$_2$S$^+$ [M+H]$^+$ requires 471.2101, found: 471.2096. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 24.13$ min, $t_{\text{major}} = 21.33$ min; ee% = 98%; $[\alpha]_D^{25} = -35.3$ (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 24.13$ min, $t_{\text{major}} = 21.33$ min; ee% = 98%]. (Note: In the 5-minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(R)-N-(buta-2,3-dien-1-yl)-N-(2-(4-fluorophenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzencesulfonamide 1m

A white solid, 44% yield (20.9 mg). M.p.: 109-112 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.40 (s, 3H), 3.55-3.66 (m, 2H), 3.75 (s, 3H), 3.80-3.88 (m, 1H), 3.96 (dd, $J = 13.6$, 7.2 Hz, 1H), 4.62 (t, $J = 8.0$ Hz, 1H), 4.65-4.71 (m, 3H), 6.93-6.98 (m, 3H), 7.01-7.06 (m, 1H), 7.17-7.30 (m, 6H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.5, 32.8, 40.7, 46.4, 50.9, 76.2, 85.3, 109.3, 114.6, 115.2 (d, $J = 21.2$ Hz), 119.0 (d, $J = 16.9$ Hz), 121.8, 126.8, 127.1, 127.2, 129.6, 129.7 (d, $J = 7.9$ Hz), 137.1, 137.7 (d, $J = 3.0$ Hz), 143.2, 161.6 (d, $J = 243.3$ Hz), 209.3. $^{19}$F NMR (CDCl$_3$, 376 MHz, CFCl$_3$) $\delta$ -116.3. IR (CH$_2$Cl$_2$) $\nu$ 2920, 2854, 1951, 1599, 1503, 1336, 1154, 1100, 1090, 969, 837, 747, 658 cm$^{-1}$. MS (ESI) $m/z$ (%): 475.18 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{28}$H$_{26}$N$_2$O$_2$FS$^{11}$ [M+H]$^+$ requires 475.1850, found: 475.1846. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 49.95$ min, $t_{\text{major}} = 44.47$ min; ee% = 98%; [$\alpha$]$_D^{25} = -41.5$ (c 0.20, 1% MeCN).
Translation: Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t<sub>minor</sub> = 49.95 min, t<sub>major</sub> = 44.47 min; ee% = 98%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(R)-N-(buta-2,3-dien-1-yl)-N-(2-(4-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide 1n

A white solid, 46% yield (22.3 mg). M.p.: 61-64 °C. 1H NMR (CDCl<sub>3</sub>, TMS, 400 MHz) δ 2.40 (s, 3H), 3.54-3.63 (m, 2H), 3.75 (s, 3H), 3.78 (s, 3H), 3.83-3.91 (m, 1H), 3.98 (dd, J = 14.0, 7.6 Hz, 1H), 4.57 (t, J = 8.0 Hz, 1H), 4.62-4.70 (m, 3H), 6.81 (d, J = 8.0 Hz, 2H), 6.98-7.06 (m, 2H), 7.17-7.29 (m, 6H), 7.47 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H). 13C NMR (CDCl<sub>3</sub>, 100 MHz, TMS) δ 21.4, 32.7, 40.5, 46.2, 50.9, 55.1, 76.1, 85.3, 109.1, 113.8, 115.0, 118.8, 119.2, 121.5, 126.8, 127.1, 127.2, 129.2, 129.6, 134.1, 137.0, 137.1, 143.1, 158.2, 209.2. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν 2931, 1953, 1610, 1510, 1325, 1248, 1154, 1092, 814, 739, 656 cm<sup>-1</sup>. MS (ESI) m/z (%): 487.20 (100) [M+H]<sup>+</sup>; HRMS (ESI) Calcd. For C<sub>29</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> requires 487.2050, found: 487.2046. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t<sub>minor</sub> = 25.87 min, t<sub>major</sub> = 22.80 min; ee% = 97%; [α]<sub>D</sub><sup>25</sup> = -71.6 (c 0.70, CH<sub>2</sub>Cl<sub>2</sub>).
Translation: Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 25.87$ min, $t_{\text{major}} = 22.80$ min; ee% = 97%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(R)-methyl 4-(2-(N-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-1-(1-methyl-1H-indol-3-yl) ethyl)benzoate 1o

A white solid, 44% yield (22.8 mg). M.p.: 152-155 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.56-3.62 (m, 1H), 3.65-3.72 (m, 1H), 3.75 (s, 3H), 3.84 (dd, $J = 15.6$, 6.8 Hz, 1H), 3.90 (s, 3H), 3.99 (dd, $J = 14.0$, 7.2 Hz, 1H), 4.63-4.72 (m, 4H), 6.98 (s, 1H), 7.01-7.06 (m, 1H), 7.18-7.24 (m, 3H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.94 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.5, 32.8, 41.6, 46.5, 50.6, 52.0, 76.3, 85.3, 109.3, 114.0, 119.0, 119.1, 121.8, 126.8, 127.0, 127.2, 128.4, 128.6, 129.7, 129.8, 136.97, 137.02, 143.3, 147.5, 166.9, 209.3. IR (CH$_2$Cl$_2$) ν 2948, 2954, 1716, 1610, 1435, 1328, 1278, 1158, 1018, 936, 852, 741, 658 cm$^{-1}$. MS (ESI) $m/z$ (%): 515.19 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{30}$H$_{31}$N$_2$O$_4$S$^{+1}$ [M+H]$^+$ requires 515.1999, found: 515.1993. (Note: compound 3o was reduced to the corresponding alcohol 3o’ to determine enantiomeric excess.)
To an oven-dried reaction tube was added LiAlH₄ (3.3 mg, 0.088 mmol) and anhydrous THF (0.8 mL). The tube was cooled to 0 °C, and 3o (22.8 mg, 0.044 mmol) was added into tube at 0 °C. The resulting mixture was stirred at room temperature for 2 h. The solution was filtered through a short column of silica gel eluting with ethyl acetate, and then the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 4/1) to give the corresponding product 3o'.

(R)-N-(buta-2,3-dien-1-yl)-N-(2-(4-(hydroxymethyl)phenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide 1o'

A white liquid, 86% yield (18.4 mg). ¹H NMR (CDCl₃, TMS, 400 MHz) δ 2.39 (s, 3H), 3.56-3.63 (m, 1H), 3.63-3.69 (m, 1H), 3.74 (s, 3H), 3.82-3.89 (m, 1H), 3.99 (dd, J = 14.0, 7.2 Hz, 1H), 4.61-4.71 (m, 6H), 6.99-7.05 (m, 2H), 7.16-7.33 (m, 9H), 7.46 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 32.8, 41.1, 46.3, 50.8, 65.1, 76.2, 85.3, 109.2, 114.6, 118.9, 119.1, 121.6, 126.9, 127.2, 127.21, 127.24, 128.5, 129.6, 137.0, 137.1, 139.2, 141.6, 143.2, 209.3. MS (ESI) m/z (%): 504.23 (100) [M+NH₄]+; HRMS (ESI) Calcd. For C₂₉H₃₄N₃O₃S⁺ [M+NH₄]+ requires 504.2315, found: 504.2308. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 23.41 min, t_{major} = 26.74 min; ee% = 96%; [α]D²⁵ = -81.5 (c 0.10, CH₂Cl₂)].
Translation: Chiralcel IC column \([\lambda = 214 \text{ nm}}; \text{eluent: Hexane/Isopropanol = 70/30}; \text{Flow rate: 0.70 mL/min}; \text{t}_{\text{minor}} = 23.41 \text{ min}, \text{t}_{\text{major}} = 26.74 \text{ min}; \text{ee\% = 96\%}]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

\((R)-N-(2-((1,1'\text{-biphenyl})-4-yl)-2-(1\text{-methyl-1H-indol-3-yl})\text{ethyl})-N-(\text{buta-2,3-dien-1-yl})-4\text{-methyl benzenesulfonamide 1p}\)

A white solid, 44\% yield (25.4 mg). M.p.: 43-46 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.37 (s, 3H), 3.61-3.74 (m, 2H), 3.76 (s, 3H), 3.84-3.92 (m, 1H), 4.04 (dd, \(J = 13.6, 7.6 \text{ Hz}, 1\text{H})\), 4.65-4.72 (m, 4H), 7.03-7.08 (m, 2H), 7.18-7.24 (m, 3H), 7.27-7.34 (m, 2H), 7.37-7.44 (m, 4H), 7.49-7.53 (m, 3H), 7.56 (d, \(J = 8.0 \text{ Hz}, 2\text{H})\), 7.61 (d, \(J = 8.0 \text{ Hz}, 2\text{H})\). \(^1\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.5, 32.8, 41.0, 46.3, 50.7, 76.2, 85.3, 109.2, 114.6, 118.9, 119.2, 121.7, 126.9, 127.0, 127.10, 127.17, 127.19, 127.2, 128.7, 129.6, 137.0, 137.1, 139.4, 140.8, 141.2, 143.2, 209.3. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 3027, 2923, 1954, 1598, 1485, 1326, 1154, 936, 814, 738, 656 cm\(^{-1}\). MS (ESI) \(m/\text{z}\) (%): 533.22 (100) \([\text{M+H}]^+\); HRMS (DART) Calcd. For C\(_{34}\)H\(_{33}\)N\(_2\)O\(_2\)S\(^{1+}\) \([\text{M+H}]^+\) requires 533.2257, found: 533.2252. Enantiomeric excess was determined by HPLC with a Chiralcel IA column \([\lambda = 214 \text{ nm}}; \text{eluent: Hexane/Isopropanol = 70/30}; \text{Flow rate: 0.70 mL/min}; \text{t}_{\text{minor}} = 16.43 \text{ min}, \text{t}_{\text{major}} = 12.29 \text{ min}; \text{ee\% = 89\%}; [\alpha]_D^{25} = -12.7 \text{ (c 0.10, CH}_2\text{Cl}_2)\).
Translation: Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 16.43$ min, $t_{\text{major}} = 12.29$ min; ee% = 89%]. (*Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring.*)

(R)-N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)-2-(naphthalen-2-yl)ethyl)benzenesulfonamide 1q

A white solid, 50% yield (25.3 mg). M.p.: 80-83 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.35 (s, 3H), 3.57-3.65 (m, 1H), 3.74 (s, 3H), 3.78 (dd, $J = 13.6$, 8.4 Hz, 1H), 3.84-3.92 (m, 1H), 4.10 (dd, $J = 13.6$, 7.2 Hz, 1H), 4.70-4.74 (m, 3H), 4.79 (t, $J = 8.0$ Hz, 1H), 6.99-7.04 (m, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.16-7.28 (m, 2H), 7.42-7.57 (m, 6H), 7.72-7.80 (m, 4H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.4, 32.8, 41.5, 46.3, 50.7, 76.2, 85.4, 109.2, 114.7, 118.9, 119.2, 121.7, 125.5, 125.9, 126.6, 126.9, 127.0, 127.1, 127.3, 127.5, 127.7, 128.2, 129.5, 132.4, 133.4, 137.0, 137.2, 139.5, 143.1, 209.3. IR (CH$_2$Cl$_2$) $\nu$ 3051, 2923, 1952, 1598, 1328, 1155, 1092, 934, 813, 739, 657 cm$^{-1}$. MS (ESI) $m/z$ (%): 507.20 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{32}$H$_{31}$N$_2$O$_2$S$^{-1}$ [M+H]$^+$ requires 507.2101, found: 507.2095.

Enantiomeric excess was determined by HPLC with a Chiralcel IG column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 21.60$ min, $t_{\text{major}} = 18.32$ min; ee% = 80%; $[\alpha]_D^{25} = -86.3$ (c 0.08, CH$_2$Cl$_2$)].
Translation: Chiralcel IG column [$\lambda = 214 \text{ nm}$; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 21.60 \text{ min}$, $t_{\text{major}} = 18.32 \text{ min}$; ee% = 80%]. *(Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring)*.

![Graph](image)

(S)-N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)-2-(thiophen-3-yl)ethyl)benzenesulfonamide 1r

A white solid, 48% yield (22.2 mg). M.p.: 101-104 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 2.39 (s, 3H), 3.56-3.64 (m, 1H), 3.71 (s, 3H), 3.74-3.82 (m, 2H), 3.88 (dd, $J = 13.6, 6.8$ Hz, 1H), 4.64-4.68 (m, 3H), 4.74 (t, $J = 8.0$ Hz, 1H), 6.87 (s, 1H), 7.03-7.13 (m, 3H), 7.18-7.29 (m, 5H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.5, 32.7, 37.2, 46.6, 51.0, 76.1, 85.4, 109.3, 114.8, 118.9, 119.2, 121.55, 121.63, 125.4, 126.9, 127.0, 127.2, 127.8, 129.6, 137.0, 137.2, 142.7, 143.1, 209.2. IR (CH$_2$Cl$_2$) ν 2919, 2858, 1952, 1455, 1337, 1155, 1098, 837, 747, 667 cm$^{-1}$. MS (ESI) $m/z$ (%): 463.15 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{26}$H$_{27}$N$_2$O$_2$S$_2$ requires 463.1508, found: 463.1507. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [$\lambda = 214 \text{ nm}$; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 35.81$ min, $t_{\text{major}} = 39.73$ min; ee% = 95%; [α]$_{D}^{25}$ = -115.3 (c 0.12, CH$_2$Cl$_2$)].
Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; t_{minor} = 35.81 min, t_{major} = 39.73 min; ee% = 95%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(R)-N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)but-3-en-1-yl)benzenesulfonamide 1s
A white liquid, 48% yield (19.4 mg). $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 2.40 (s, 3H), 3.55-3.58 (m, 2H), 3.75 (s, 3H), 3.77-4.05 (m, 3H), 4.62-4.79 (m, 3H), 5.12-5.21 (m, 2H), 6.03-6.13 (m, 1H), 6.92 (s, 1H), 7.07-7.12 (m, 1H), 7.20-7.31 (m, 4H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.5, 32.7, 40.1, 46.7, 50.6, 76.1, 85.5, 109.3, 114.0, 116.2, 118.9, 119.3, 121.7, 126.3, 126.9, 127.2, 129.6, 137.0, 137.4, 138.7, 143.1, 209.3. IR (CH$_2$Cl$_2$) ν 2924, 1954, 1597, 1328, 1155, 1090, 848, 739, 657 cm$^{-1}$. MS (ESI) m/z (%): 407.17 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{24}$H$_{27}$N$_2$O$_2$S$^+$/[M+H]$^+$ requires 407.1788, found: 407.1782. Enantiomeric excess was determined by HPLC with a Chiralcel IB column [λ = 214 nm; eluent: Hexane/Isopropanol = 96/4; Flow rate: 0.70 mL/min; t_{minor} = 21.41 min, t_{major} = 19.79 min; ee% = 84%; $[\alpha]_D^{25} = -23.0$ (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel IB column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 96/4; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 21.41$ min, $t_{\text{major}} = 19.79$ min; ee% = 84%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

\[
\text{(R,E)-ethyl 5-[(N-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-4-(1-methyl-1H-indol-3-yl)}\text{pent-2-enoate 1t}
\]

A white liquid, 44% yield (20.9 mg). $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 1.27 (t, $J = 7.2$ Hz, 3H), 2.40 (s, 3H), 3.55-3.67 (m, 2H), 3.69-3.89 (m, 5H), 4.13-4.24 (m, 3H), 4.66-4.80 (m, 3H), 5.89 (d, $J = 15.6$ Hz, 1H), 6.94 (s, 1H), 7.08-7.22 (m, 2H), 7.24-7.32 (m, 4H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 14.2, 21.5, 32.8, 39.0, 47.3, 50.2, 60.3, 76.3, 85.4, 109.5, 111.9, 119.0, 119.2, 121.9, 122.4, 126.6, 127.2, 129.7, 136.9, 137.0, 143.3, 148.0, 166.4, 209.4. IR (CH$_2$Cl$_2$) $\nu$ 2924, 1954, 1712, 1597, 1470, 1328, 1155, 1090, 981, 853, 741, 657 cm$^{-1}$. MS (ESI) $m/z$ (%): 496.22 (100) [M+NH$_4$]$^+$; HRMS (ESI) Caled. For C$_{27}$H$_{34}$N$_3$O$_4$S$^+$ [M+NH$_4$]$^+$ requires 496.2265, found: 496.2254. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 27.91$ min, $t_{\text{major}} = 24.09$ min; ee% = 91%; $[\alpha]_D^{25} = 3.5$ (c 0.08, CH$_2$Cl$_2$)].
Translation: Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 27.91$ min, $t_{\text{major}} = 24.09$ min; ee% = 91%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

\[
(R)-N-(\text{buta-2,3-dien-1-yl})-4\text{-methyl-N-}(2-(1\text{-methyl-1H-indol-3-yl})\text{hexyl})\text{benzenesulfonamide 1u}
\]
A white liquid, 43% yield (18.8 mg). $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 0.82 (t, $J = 7.2$ Hz, 3H), 1.16-1.30 (m, 4H), 1.62-1.72 (m, 1H), 1.85-1.94 (m, 1H), 2.38 (s, 3H), 3.19-3.27 (m, 1H), 3.31 (dd, $J = 13.2$, 6.8 Hz, 1H), 3.52 (dd, $J = 13.6$, 8.8 Hz, 1H), 3.74 (s, 3H), 3.74-3.78 (m, 1H), 3.81-3.89 (m, 1H), 4.64-4.68 (m, 2H), 4.73-4.80 (m, 1H), 6.84 (s, 1H), 7.04-7.09 (m, 1H), 7.18-7.22 (m, 3H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 1.0, 14.0, 21.4, 22.8, 29.7, 32.3, 32.7, 35.3, 46.9, 52.2, 76.0, 85.7, 109.3, 115.4, 118.6, 119.1, 121.4, 126.3, 127.1, 127.4, 129.5, 137.0, 137.3, 143.0, 209.2. IR (CH$_2$Cl$_2$) $\nu$ 3288, 2954, 2921, 2851, 1735, 1597, 1494, 1349, 1185, 1161, 1092, 929, 898, 750, 658 cm$^{-1}$. MS (ESI) $m/z$ (%): 437.22 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{26}$H$_{33}$N$_2$O$_2$S$^+$ [M+H]$^+$ requires 437.2257, found: 437.2256. Enantiomeric excess was determined by HPLC with a Chiralcel AD column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 100/1; Flow rate: 0.30 mL/min; $t_{\text{minor}} = 93.49$ min, $t_{\text{major}} = 99.29$ min; ee% = 94%; $[\alpha]_D^{25} = 9.1$ (c 0.15, CH$_2$Cl$_2$)].

\[
\begin{align*}
\text{(R)-N-(buta-2,3-dien-1-yl)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)hexyl)benzenesulfonamide 1u} \\
\end{align*}
\]
Translation: Chiralcel AD column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 100/1; Flow rate: 0.30 mL/min; $t_{minor} = 93.49$ min, $t_{major} = 99.29$ min; ee% = 94%].

(R)-ethyl 5-(N-(buta-2,3-dien-1-yl)-4-methylphenylsulfonamido)-4-(1-methyl-1H-indol-3-yl) Pentanoate 1v

A white liquid, 43% yield (20.5 mg). $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 1.87 (t, $J = 7.2$ Hz, 3H), 1.91-2.01 (m, 1H), 2.16-2.33 (m, 3H), 2.38 (s, 3H), 3.28-3.37 (m, 2H), 3.52-3.60 (m, 1H), 3.74 (s, 3H), 3.76-3.81 (m, 1H), 3.86-3.93 (m, 1H), 4.03 (q, $J = 7.2$ Hz, 2H), 4.64-4.79 (m, 3H), 6.87 (s, 1H), 7.05-7.10 (m, 1H), 7.19-7.30 (m, 4H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 14.1, 21.4, 27.6, 32.2, 32.7, 34.8, 46.9, 51.8, 60.1, 76.1, 85.4, 109.3, 113.9, 118.8, 119.1, 121.6, 126.6, 127.1, 127.2, 129.5, 137.08, 137.11, 143.1, 173.5, 209.3. IR (CH$_2$Cl$_2$) $\nu$ 2929, 1954, 1727, 1327, 1155, 1090, 971, 852, 739, 658 cm$^{-1}$. MS (ESI) m/z (%): 498.24 (100) [M+NH$_4^+$]; HRMS (ESI) Calcd. For C$_{27}$H$_{36}$N$_3$O$_4$S$^+$ [M+NH$_4^+$] requires 498.2421, found: 498.2410. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; $t_{minor} = 51.95$ min, $t_{major} = 48.65$ min; ee% = 99%; $[\alpha]_D^{25} = 10.0$ (c 0.08, CH$_2$Cl$_2$)].
Translation: Chiralcel IE3 column [\( \lambda = 214 \text{ nm} \); eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 51.95 \text{ min} \), \( t_{\text{major}} = 48.65 \text{ min} \); ee\% = 99\%]. (Note: In the 5-minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

\[
(R)-N-(\text{buta-2,3-dien-1-yl})-4\text{-methyl-N-(2-(1-methyl-1H-indol-3-yl)-5-oxohexyl)}\text{benzenesulfonamide 1w}
\]

A white liquid, 42\% yield (18.8 mg). \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \( \delta \) 1.25-1.30 (m, 1H), 1.83-1.93 (m, 1H), 2.01 (s, 3H), 2.20-2.29 (m, 1H), 2.35-2.39 (m, 5H), 3.26-3.36 (m, 2H), 3.50-3.57 (m, 1H), 3.74-3.81 (m, 4H), 3.85-3.92 (m, 1H), 4.60-4.77 (m, 3H), 6.86 (s, 1H), 7.06-7.11 (m, 1H), 7.20-7.31 (m, 5H), 7.55 (d, \( J = 8.0 \text{ Hz} \), 1H), 7.62 (d, \( J = 8.0 \text{ Hz} \), 2H). \(^13\)C NMR (CDCl\(_3\), 100 MHz, TMS) \( \delta \) 21.5, 26.4, 29.9, 32.7, 34.7, 41.4, 47.0, 51.9, 76.0, 85.4, 109.4, 114.2, 118.9, 119.0, 121.6, 126.5, 127.1, 127.3, 129.5, 137.07, 137.12, 143.1, 208.9, 209.3. IR (CH\(_2\)Cl\(_2\)) \( \nu \) 2921, 1954, 1711, 1597, 1471, 1327, 1155, 1089, 964, 897, 740, 657 cm\(^{-1}\). MS (ESI) \( m/z \) (%): 468.23 (100) [M+NH\(_4\)]\(^+\); HRMS (ESI) Calcd. For C\(_{26}\)H\(_{34}\)N\(_3\)O\(_3\)S\(^{+1}\) [M+NH\(_4\)]\(^+\) requires 468.2315, found: 468.2305. Enantiomeric excess was determined by HPLC with a Chiralcel IF3 column [\( \lambda = 286 \text{ nm} \); eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 65.64 \text{ min} \), \( t_{\text{major}} = 62.59 \text{ min} \); ee\% = 80\%; [\( \alpha \)]\(_D\)\(^{25}\) = -6.0 (c 0.05, CH\(_2\)Cl\(_2\)].
Translation: Chiralcel IF3 column [\(\lambda = 286 \text{ nm}\); eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; \(t_{\text{min}} = 65.64 \text{ min}\), \(t_{\text{maj}} = 62.59 \text{ min}\); ee\% = 80\%].

\[
(R)-N-(\text{buta-2,3-dien-1-yl})-N-(5-((7\text{-tert-butyldimethylsilyl})oxy)-2-(1-methyl-1H-indol-3-yl)pentyl)-4\text{-methylbenzenesulfonamide 1x}
\]

A white liquid, 43\% yield (23.9 mg). \(^1\text{H} \text{NMR (CDCl}_3, \text{TMS, 400 MHz)} \delta 0.15 (s, 3\text{H}), 0.16 (s, 3\text{H}), 1.01 (s, 9\text{H}), 1.56-1.71 (m, 2\text{H}), 1.80-1.91 (m, 1\text{H}), 2.07-2.17 (m, 1\text{H}), 2.53 (s, 3\text{H}), 3.35-3.51 (m, 2\text{H}), 3.63-3.73 (m, 3\text{H}), 3.87-3.93 (m, 4\text{H}), 3.97-4.04 (m, 1\text{H}), 4.79-4.94 (m, 3\text{H}), 7.00 (s, 1\text{H}), 7.19-7.23 (m, 1\text{H}), 7.32-7.44 (m, 4\text{H}), 7.71 (d, \(J = 8.0 \text{ Hz}\), 1\text{H}), 7.75 (d, \(J = 8.0 \text{ Hz}\), 2\text{H}). \(^{13}\text{C} \text{NMR (CDCl}_3, 100 \text{ MHz, TMS)} \delta -5.3, 18.3, 21.5, 26.0, 28.6, 30.8, 32.7, 35.3, 47.0, 52.3, 63.2, 76.0, 85.7, 109.3, 115.0, 118.7, 119.1, 121.4, 126.5, 127.1, 127.4, 129.5, 137.1, 137.3, 143.0, 209.3. IR (CH\text{_2Cl}_2) \nu 2927, 2855, 1954, 1598, 1471, 1327, 1158, 1090, 834, 737, 658 cm\(^{-1}\). MS (ESI) \text{m/z} (%) 553.29 (100) [M+H\text{]}^+; \text{HRMS (ESI) Calcd. For C}_{31}\text{H}_{45}\text{N}_2\text{O}_3\text{SSi}^{17} \text{[M+H]}^+ \text{requires 553.2915, found: 553.2900. Enantiomeric excess was determined by HPLC with a Chiralcel PC1 column [\(\lambda = 214 \text{ nm}\); eluent: CO}_2 / \text{MeOH = 95/5; Flow rate: 2.20 mL/min; \(t_{\text{min}} = 17.44 \text{ min}\), \(t_{\text{maj}} = 14.00 \text{ min}\); ee\% = 98\%; [\(\alpha\text{]}_D^{25} = 31.8 (c 0.3, \text{CH}_2\text{Cl}_2).}
Translation: Chiralcel PC1 column [λ = 214 nm; eluent: CO₂ / MeOH = 95/5; Flow rate: 2.20 mL/min; t_{minor} = 17.44 min, t_{major} = 14.00 min; ee% = 98%].

(R)-N-(buta-2,3-dien-1-yl)-N-(5-(1,3-dioxoisindolin-2-yl)-2-(1-methyl-1H-indol-3-yl)pentyl)-4-methylbenzenesulfonamide 1y

A white solid, 42% yield (23.2 mg). M.p.: 88-91 °C. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 1.61-1.79 (m, 3H), 1.91-2.00 (m, 1H), 2.38 (s, 3H), 3.23-3.35 (m, 2H), 3.49-3.65 (m, 3H), 3.67-3.73 (m, 4H), 3.81-3.87 (m, 1H), 4.60-4.66 (m, 2H), 4.70-4.78 (m, 1H), 6.85 (s, 1H), 6.99-7.04 (m, 1H), 7.14-7.24 (m, 4H), 7.52 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.66-7.69 (m, 2H), 7.78-7.81 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 26.6, 29.8, 32.7, 35.3, 37.9, 47.0, 52.1, 76.1, 85.6, 109.3, 114.5, 118.7, 119.0, 121.5, 123.1, 126.5, 127.1, 127.2, 129.5, 132.1, 133.8, 137.0, 137.2, 143.0, 168.3, 209.3. IR (CH₂Cl₂) ν 3242, 2933, 1953, 1706, 1395, 1185, 1155, 1090, 852, 741, 656 cm⁻¹. MS (ESI) m/z (%): 568.22 (100) [M+H]+. HRMS (ESI) Calcd. For C₃₃H₃₄N₃O₄S⁺ [M+H]+ requires 568.2265, found: 568.2257. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 77.92 min, t_{major} = 84.36 min; ee% = 91%; [α]D²⁵ = 36.0 (c 1.1, CH₂Cl₂)].
Translation: Chiralcel IE3 column \([\lambda = 214 \text{ nm}];\) eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 77.92 \text{ min}, t_{\text{major}} = 84.36 \text{ min};\) ee\% = 91\%. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
7. Characterization and spectra charts for compounds 2.

(1S,4aR,6aR,11bS)-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2a

A white solid, 49% yield (22.3 mg). M.p.: 183-186 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 2.38 (s, 3H), 2.40-2.44 (m, 1H), 2.46 (s, 3H), 3.02 (dd, $J = 12.0$, 12.0 Hz, 1H), 3.21-3.29 (m, 2H), 3.68 (dd, $J = 11.2$, 4.8 Hz, 1H), 3.93 (dd, $J = 12.4$, 6.0 Hz, 1H), 4.45 (s, 1H), 5.69 (d, $J = 6.0$ Hz, 1H), 5.83-5.86 (m, 1H), 5.95 (d, $J = 7.6$ Hz, 1H), 6.60-6.64 (m, 1H), 6.69-6.72 (m, 2H), 6.95-7.09 (m, 5H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.5, 32.0, 47.71, 47.73, 50.4, 50.7, 57.4, 72.8, 106.0, 116.4, 122.8, 126.8, 127.3, 127.6, 127.7, 128.6, 129.0, 129.8, 133.8, 134.7, 134.9, 138.6, 143.6, 149.9. IR (CH$_2$Cl$_2$) ν 3054, 2920, 2852, 1604, 1494, 1339, 1161, 937, 860, 733, 662 cm$^{-1}$. MS (ESI) m/z (%): 457.19 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{28}$H$_{29}$N$_2$O$_2$S$^+$[M+H]$^+$ requires 457.1944, found: 457.1940. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 41.05$ min, $t_{\text{major}} = 37.92$ min; ee% = 91%; $[\alpha]_D^{25} = -162.9$ (c 0.1, CH$_2$Cl$_2$)].
(1S,4aR,6aR,11bS)-7-benzyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2b

A white solid, 34% yield (18.1 mg). M.p.: 117-120 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.21 (dd, \(J = 12.0, 9.6\) Hz, 1H), 2.43 (s, 3H), 2.85 (dd, \(J = 12.0, 12.0\) Hz, 1H), 3.28-3.33 (m, 2H), 3.75 (dd, \(J = 11.6, 4.4\) Hz, 1H), 3.84 (d, \(J = 15.2\) Hz, 1H), 3.90 (d, \(J = 15.2\) Hz, 1H), 4.00 (dd, \(J = 12.0, 6.0\) Hz, 1H), 4.42 (s, 1H), 5.61 (d, \(J = 6.0\) Hz, 1H), 5.83 (dd, \(J = 6.0, 2.4\) Hz, 1H), 5.94 (d, \(J = 7.6\) Hz, 1H), 6.65-6.73 (m, 5H), 6.92-6.97 (m, 1H), 7.07-7.11 (m, 2H), 7.16-7.19 (m, 5H), 7.32 (d, \(J = 8.0\) Hz, 2H), 7.66 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.5, 47.8, 47.9, 50.7, 50.8, 51.1, 57.4, 71.3, 107.3, 117.4, 123.0, 126.7, 127.3, 127.5, 127.7, 127.8, 128.1, 128.6, 129.0, 129.8, 133.5, 135.0, 135.3, 138.0, 138.9, 143.6, 149.7. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 3058, 2920, 1600, 1484, 1344, 1162, 1089, 936, 859, 729, 659 cm\(^{-1}\). MS (ESI) \(m/z\) (%) 533.22 (100) [M+H]\(^+\); HRMS (DART) Calcd. For C\(_{34}\)H\(_{35}\)N\(_2\)O\(_2\)S\(^+\) [M+H]\(^+\) requires 533.2257, found: 533.2251. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [\(\lambda = 254\) nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 41.05\) min, \(t_{\text{major}} = 37.92\) min; ee\% = 91%].

Translation: Chiralcel IC column [\(\lambda = 254\) nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 41.05\) min, \(t_{\text{major}} = 37.92\) min; ee\% = 91%].
mL/min; \( t_{\text{minor}} = 39.86 \text{ min} \), \( t_{\text{major}} = 34.48 \text{ min} \); ee\% = 94\%; \( [\alpha]_D^{25} = -129.4 \text{ (c 0.4, CH}_2\text{Cl}_2)\].
Translation: Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 39.86$ min, $t_{\text{major}} = 34.48$ min; ee% = 94%].
(1S,4aR,6aR,11bS)-7-allyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2c

A white solid, 45% yield (21.7 mg). M.p.: 107-110 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.34 (dd, $J = 12.0$, 8.8 Hz, 1H), 2.46 (s, 3H), 2.95 (dd, $J = 12.0$, 12.0 Hz, 1H), 3.21-3.33 (m, 4H), 3.73 (dd, $J = 11.6$, 4.8 Hz, 1H), 3.98 (dd, $J = 12.0$, 5.6 Hz, 1H), 4.47 (s, 1H), 4.82 (d, $J = 17.2$ Hz, 1H), 4.94 (d, $J = 10.0$ Hz, 1H), 5.34-5.45 (m, 1H), 5.62 (d, $J = 6.0$ Hz, 1H), 5.83 (dd, $J = 6.0$, 2.4 Hz, 1H), 6.01 (d, $J = 8.0$ Hz, 1H), 6.64-6.69 (m, 3H), 6.95-7.14 (m, 5H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.6, 47.7, 47.8, 49.1, 50.5, 50.8, 57.4, 71.2, 106.6, 116.3, 116.9, 123.0, 126.8, 127.5, 127.6, 127.8, 128.6, 129.6, 129.8, 133.7, 134.7, 134.8, 134.9, 138.7, 143.6, 149.2.

IR (CH$_2$Cl$_2$) $\nu$ 3053, 2921, 2850, 1601, 1485, 1343, 1161, 1089, 934, 858, 730, 659 cm$^{-1}$. MS (ESI) $m/z$ (%): 483.20 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{30}$H$_{31}$N$_2$O$_2$S$^+$ [M+H]$^+$ requires 483.2101, found: 483.2092. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 16.34$ min, $t_{\text{major}} = 14.46$ min; ee% = 94%; $[\alpha]_D^{25} = -102.5$ (c 0.08, CH$_2$Cl$_2$)].
Translation: Chiralcel IA column \[ \lambda = 214 \text{ nm} \]; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 16.34 \text{ min} \), \( t_{\text{major}} = 14.46 \text{ min} \); ee\% = 94\%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

\[
\text{(1S,4aR,6aR,11bS)-7,10-dimethyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2d}
\]
A white solid, 49% yield (23.0 mg). M.p.: 89-92 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \( \delta \) 2.26 (s, 3H), 2.33 (s, 3H), 2.37 (dd, \( J = 12.0, 8.8 \text{ Hz}, 1\)H), 2.47 (s, 3H), 2.97 (dd, \( J = 12.0, 12.0 \text{ Hz}, 1\)H), 3.20-3.28 (m, 2H), 3.71 (dd, \( J = 11.6, 4.8 \text{ Hz}, 1\)H), 3.97 (dd, \( J = 12.4, 6.0 \text{ Hz}, 1\)H), 4.40 (s, 1H), 5.68 (d, \( J = 5.6 \text{ Hz}, 1\)H), 5.82-5.85 (m, 1H), 5.89 (d, \( J = 8.0 \text{ Hz}, 1\)H), 6.68-6.71 (m, 2H), 6.79 (d, \( J = 8.0 \text{ Hz}, 1\)H), 6.91 (s, 1H), 7.00-7.09 (m, 3H), 7.35 (d, \( J = 8.0 \text{ Hz}, 2\)H), 7.69 (d, \( J = 8.0 \text{ Hz}, 2\)H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \( \delta \) 20.9, 21.6, 32.6, 47.7, 47.9, 50.5, 50.7, 57.5, 73.0, 106.1, 123.6, 125.7, 126.7, 127.3, 127.6, 127.7, 129.0, 129.8, 133.8, 134.8, 135.0, 138.8, 143.6, 147.9. IR (CH\(_2\)Cl\(_2\)) \( \nu \) 2962, 2852, 1496, 1341, 1259, 1016, 865, 795, 696 cm\(^{-1}\). MS (ESI) \( m/z \) (%): 471.20 (100) [M+H\(^+\)]; HRMS (ESI) Calcd. For C\(_{29}\)H\(_{31}\)N\(_2\)O\(_2\)S\(^+\) [M+H\(^+\)] requires 471.2101, found: 471.2092. Enantiomeric excess was determined by HPLC with a Chiralcel IA column \([\lambda = 214 \text{ nm}]\); eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 7.65 \text{ min} \), \( t_{\text{major}} = 7.02 \text{ min} \); ee\% = 92\%; \([\alpha]_D^{25} = -132.5 \text{ (c 0.12, CH}_2\text{Cl}_2)]\).
Translation: Chiralcel IA column [\( \lambda = 214 \) nm; eluent: Hexane/Isopropanol = 50/50; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 7.65 \) min, \( t_{\text{major}} = 7.02 \) min; ee\% = 92\%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(1S,4aR,6aR,11bS)-11-fluoro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2e

A white solid, 46\% yield (21.9 mg). M.p.: 176-179 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \( \delta \) 2.43 (s, 3H), 2.53 (s, 3H), 3.10 (dd, \( J = 12.0, 4.0 \) Hz, 1H), 3.38-3.52 (m, 3H), 3.56-3.63 (m, 2H), 4.72 (s, 1H), 5.73 (d, \( J = 8.0 \) Hz, 1H), 5.84-5.88 (m, 2H), 6.18-6.24 (m, 1H), 6.82-6.89 (m, 1H), 6.91-6.94 (m, 2H), 7.03-7.08 (m, 3H), 7.31 (d, \( J = 8.0 \) Hz, 2H), 7.67 (d, \( J = 8.0 \) Hz, 2H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \( \delta \) 21.5, 32.3, 43.2, 46.3, 46.8, 51.5, 56.69, 56.71, 73.9, 101.8 (d, \( J = 2.3 \) Hz), 103.4 (d, \( J = 21.0 \) Hz), 118.3 (d, \( J = 16.4 \) Hz), 127.1, 127.4, 127.5, 127.9, 129.2, 129.7, 130.1 (d, \( J = 9.6 \) Hz), 134.0, 135.1, 138.2, 143.4, 152.0 (d, \( J = 9.6 \) Hz), 159.8 (d, \( J = 241.1 \) Hz). \(^{19}\)F NMR (CDCl\(_3\), 376 MHz, CFCl\(_3\)) \( \delta \) -122.4. IR (CH\(_2\)Cl\(_2\)) \( \nu \) 3059, 2901, 1913, 1627, 1467, 1159, 1087, 958, 860, 782, 661 cm\(^{-1}\). MS (ESI) \( m/z \) (%): 475.18 (100) [M+H]\(^+\); HRMS (ESI) Calcd. For C\(_{28}\)H\(_{28}\)N\(_2\)O\(_2\)FS\(^-\) [M+H]\(^+\) requires 475.1850, found: 475.1841. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [\( \lambda = 254 \) nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 44.07 \) min,
$t_{major} = 47.53 \text{ min; ee}\% = 95\%; [\alpha]_D^{25} = -62.3 \ (c \ 0.10, \text{CH}_2\text{Cl}_2)$. 
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 44.07 min, t_{major} = 47.53 min; ee% = 95%].

(1S,4aR,6aR,11bS)-10-fluoro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2f

A white solid, 49% yield (23.3 mg). M.p.: 142-145 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 2.45 (dd, $J = 12.0$, 8.8 Hz, 1H), 2.46 (s, 3H), 3.04 (dd, $J = 12.0$, 12.0 Hz, 1H), 3.14-3.21 (m, 2H), 3.68 (dd, $J = 12.0$, 4.8 Hz, 1H), 3.92 (dd, $J = 12.0$, 6.0 Hz, 1H), 4.48 (s, 1H), 5.71 (d, $J = 5.6$ Hz, 1H), 5.82-5.87 (m, 2H), 6.63-6.78 (m, 1H), 7.02-7.11 (m, 3H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.68 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.5, 32.7, 47.5, 47.6, 50.2, 50.6, 57.5, 73.3, 106.2 (d, $J = 8.0$ Hz), 110.2 (d, $J = 23.8$ Hz), 114.5 (d, $J = 22.8$ Hz), 126.9, 127.5, 127.6, 127.7, 129.0, 129.8, 133.9, 136.2 (d, $J = 7.1$ Hz), 138.3, 143.7, 146.3, 155.4 (d, $J = 232.3$ Hz). $^{19}$F NMR (CDCl$_3$, 376 MHz, CFCl$_3$) δ -128.3. IR (CH$_2$Cl$_2$) ν 3029, 2920, 2849, 1646, 1492, 1337, 1164, 988, 960, 860, 771, 658 cm$^{-1}$. MS (ESI) m/z (%): 475.18 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{28}$H$_{28}$N$_2$O$_2$FS$^{+}$ [M+H]$^+$ requires 475.1850, found: 475.1846. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 87.93 min, t_{major} = 53.11 min; ee% = 99%; [α]$_D^{25}$ = -80.1 (c 0.20, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 86/14; Flow rate: 0.70 mL/min; t_{minor} = 87.93 min, t_{major} = 53.11 min; ee% = 99%].
(1S,4aR,6aR,11bS)-10-chloro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2g

A white solid, 45% yield (22.1 mg). M.p.: 183-186 °C. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 2.36 (s, 3H), 2.42-2.47 (m, 4H), 3.05 (dd, J = 12.0, 12.0 Hz, 1H), 3.12-3.21 (m, 2H), 3.69 (dd, J = 11.2, 4.4 Hz, 1H), 3.94 (dd, J = 12.4, 6.0 Hz, 1H), 4.48 (s, 1H), 5.68 (d, J = 6.0 Hz, 1H), 5.82-5.88 (m, 2H), 6.72-6.75 (m, 2H), 6.88-6.95 (m, 2H), 7.02-7.11 (m, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.6, 32.0, 47.5, 47.6, 50.2, 50.3, 57.5, 73.1, 106.6, 120.6, 123.0, 126.9, 127.48, 127.52, 127.6, 128.3, 128.7, 129.8, 134.0, 134.9, 136.7, 138.2, 143.7, 148.4. IR (CH₂Cl₂) ν 2923, 1597, 1492, 1342, 1153, 935, 814, 730, 658 cm⁻¹. MS (ESI) m/z (%): 491.15 (100) [M+H]⁺; HRMS (ESI) Calcd. For C₂₈H₂₈N₂O₂ClS⁺[M+H]⁺ requires 491.1555, found: 491.1552. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_minor = 45.89 min, t_major = 35.44 min; ee% = 98%; [α]D²⁵ = -111.1 (c 0.12, CH₂Cl₂)].
Translation: Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 45.89$ min, $t_{\text{major}} = 35.44$ min; ee% = 98%].

(1S,4aR,6aR,11bS)-10-bromo-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2h
A white solid, 47% yield (24.9 mg). M.p.: 199-202 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.37 (s, 3H), 2.44-2.50 (m, 4H), 3.06 (dd, $J = 12.0, 12.0$ Hz, 1H), 3.12-3.22 (m, 2H), 3.69 (dd, $J = 10.8, 4.0$ Hz, 1H), 3.93 (dd, $J = 12.0, 6.0$ Hz, 1H), 4.48 (s, 1H), 5.69 (d, $J = 6.0$ Hz, 1H), 5.81 (d, $J = 8.0$ Hz, 1H), 5.86-5.89 (m, 1H), 6.72-6.75 (m, 2H), 7.02-7.11 (m, 5H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.6, 31.9, 47.5, 47.6, 50.2, 50.4, 57.5, 73.1, 107.3, 107.5, 125.8, 127.0, 127.5, 127.6, 127.7, 128.7, 129.9, 131.3, 134.1, 135.0, 137.2, 138.2, 143.7, 148.8. IR (CH$_2$Cl$_2$) $\nu$ 2918, 2852, 1595, 1481, 1343, 1169, 938, 861, 730, 658 cm$^{-1}$. MS (ESI) $m/z$ (%): 535.10 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{28}$H$_{28}$N$_2$O$_2$BrS$^{+}$[M+H]$^+$ requires 535.1049, found: 535.1048. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 30.13$ min, $t_{\text{major}} = 24.97$ min; ee% = 91%; $[\alpha]_D^{25} = -111.1$ (c 0.30, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column [\(\lambda = 214\) nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 30.13\) min, \(t_{\text{major}} = 24.97\) min; ee\% = 91\%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

\[
(1S,4aR,6aR,11bS)-\text{-methyl 7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido}
\]

\[(4',3';2,3]cyclopenta[1,2-b]indole-9-carboxylate 2i\]

A white solid, 48% yield (24.6 mg). M.p.: 142-145 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.40-2.44 (m, 1H), 2.45 (s, 3H), 2.46 (s, 3H), 3.02 (dd, \(J = 12.0, 12.0\) Hz, 1H), 3.20-3.29 (m, 2H), 3.67 (dd, \(J = 11.6, 4.8\) Hz, 1H), 3.83 (s, 3H), 3.93 (dd, \(J = 12.4, 6.0\) Hz, 1H), 4.53 (s, 1H), 5.69-5.72 (m, 1H), 5.86-5.89 (m, 1H), 6.58-6.59 (m, 1H), 6.70-6.72 (m, 2H), 6.99-7.14 (m, 4H), 7.33-7.37 (m, 3H), 7.68 (d, \(J = 8.0\) Hz, 2H). \(^13\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.5, 31.8, 47.6, 47.7, 50.3, 50.5, 51.8, 57.5, 73.0, 106.3, 118.6, 122.5, 127.0, 127.53, 127.55, 127.57, 128.7, 129.8, 130.6, 133.7, 135.0, 138.1, 140.3, 143.7, 149.9, 167.5. IR (CH\(_2\)Cl\(_2\)) v 2918, 2847, 1712, 1496, 1345, 1164, 1090, 931, 859, 730, 662 cm\(^{-1}\). MS (ESI) \(m/z\) (%): 515.19 (100) [M+H]\(^+\); HRMS (ESI) Calcd. For C\(_{30}\)H\(_{31}\)N\(_2\)O\(_4\)S\(^+\)[M+H]\(^+\) requires 515.1999, found: 515.1990. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [\(\lambda = 214\) nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 39.07\) min, \(t_{\text{major}} = 35.57\) min; ee\% = 98\%; [\(\alpha\)]\(_D\)\(^{25}\) = -43.0 (c 0.10, CH\(_2\)Cl\(_2\))].
Translation: Chiralcel IA column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; tminor = 39.07 min, tmajor = 35.57 min; ee% = 98%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(1S,4aR,6aR,11bS)-7,8-dimethyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2j

A white solid, 46% yield (21.6 mg). M.p.: 85-88 °C. 1H NMR (CDCl₃, TMS, 400 MHz) δ 2.01 (s, 3H), 2.07 (s, 3H), 2.36 (dd, J = 12.0, 8.8 Hz, 1H), 2.46 (s, 3H), 2.94 (dd, J = 12.0, 12.0 Hz, 1H), 3.24-3.30 (m, 2H), 3.75 (dd, J = 11.6, 4.8 Hz, 1H), 3.99 (dd, J = 12.0, 6.0 Hz, 1H), 4.12 (s, 1H), 5.62 (d, J = 5.6 Hz, 1H), 5.71-5.74 (m, 1H), 6.60-6.63 (m, 2H), 6.71-6.76 (m, 1H), 6.80-6.82 (m, 1H), 6.98-7.01 (m, 1H), 7.04-7.07 (m, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H). 13C NMR (CDCl₃, 100 MHz, TMS) δ 18.8, 21.5, 37.9, 47.6, 47.7, 50.5, 51.0, 58.8, 75.6, 119.4, 120.9, 121.2, 126.9, 127.6, 127.9, 129.8, 131.2, 132.0, 133.5, 133.7, 136.9, 139.3, 143.6, 149.2. IR (CH₂Cl₂) ν 2920, 1598, 1467, 1343, 1162, 1089, 937, 855, 744, 659 cm⁻¹. MS (ESI) m/z (%): 471.20 (100) [M+H]⁺; HRMS (DART) Calcd. For C₂₉H₃₁N₂O₂S⁺[M+H]⁺ requires 471.2101, found: 471.2097. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.50 mL/min; tminor = 78.59 min, tmajor = 85.21 min; ee% = 97%; [α]D²⁵ = -77.7 (c 0.20,
$\text{CH}_2\text{Cl}_2$].
Translation: Chiralcel IC column [\( \lambda = 254 \) nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.50 mL/min; \( t_{\text{minor}} = 78.59 \) min, \( t_{\text{major}} = 85.21 \) min; ee\% = 97\%].
(1S,4aR,6aR,11bS)-7-benzyl-11-methoxy-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4', 3':2,3]cyclopenta[1,2-b]indole 2k
A white solid, 46% yield (25.9 mg). M.p.: 90-93 °C. 1H NMR (CDCl3, TMS, 400 MHz) δ 2.43 (s, 3H), 3.02 (dd, J = 12.0, 4.8 Hz, 1H), 3.31 (dd, J = 12.0, 12.0 Hz, 1H), 3.50 (dd, J = 11.2, 5.2 Hz, 1H), 3.59-3.63 (m, 1H), 3.69 (dd, J = 12.0, 5.2 Hz, 1H), 3.85-4.01 (m, 6H), 4.59 (s, 1H), 5.65-5.68 (m, 2H), 5.75-5.77 (m, 1H), 6.22 (d, J = 8.4 Hz, 1H), 6.81-6.83 (m, 4H), 6.86-6.91 (m, 1H), 7.08-7.13 (m, 2H), 7.15-7.22 (m, 4H), 7.30 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H). 13C NMR (CDCl3, 100 MHz, TMS) δ 21.5, 41.2, 45.8, 47.1, 50.7, 51.2, 55.1, 57.0, 72.3, 100.1, 100.7, 118.7, 126.7, 126.8, 127.3, 127.5, 127.7, 128.1, 128.3, 129.61, 129.64, 134.3, 135.8, 138.3, 139.1, 143.3, 151.2, 156.3. IR (CH2Cl2) ν 3028, 2919, 2842, 1599, 1494, 1338, 1166, 941, 859, 729, 662 cm⁻¹. MS (ESI) m/z (%): 563.23 (100) [M+H]+; HRMS (DART) Calcd. For C35H35N2O3S+[M+H]+ requires 563.2363, found: 563.2358. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; tminor = 42.29 min, tmajor = 45.30 min; ee% = 99%; [α]D25 = -25.0 (c 0.70, CH2Cl2)].
Translation: Chiralcel IC column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 42.29$ min, $t_{\text{major}} = 45.30$ min; ee% = 99%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
(1S,4aR,6aR,11bS)-7-methyl-1-(p-tolyl)-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2l

A white solid, 47% yield (22.1 mg). M.p.: 50-53 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.17 (s, 3H), 2.40 (s, 3H), 2.43-2.50 (m, 4H), 3.01 (dd, $J = 12.0, 12.0$ Hz, 1H), 3.18-3.26 (m, 2H), 3.62 (dd, $J = 11.6, 4.8$ Hz, 1H), 3.89 (dd, $J = 12.0, 6.0$ Hz, 1H), 4.46 (s, 1H), 5.70 (d, $J = 5.6$ Hz, 1H), 5.81-5.84 (m, 1H), 5.97 (d, $J = 8.0$ Hz, 1H), 6.59-6.61 (m, 3H), 6.80-6.83 (m, 2H), 6.94-6.98 (m, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 20.8, 21.4, 32.1, 47.2, 47.7, 50.0, 50.9, 57.3, 72.8, 106.0, 116.3, 122.7, 127.5, 128.0, 128.4, 129.0, 129.7, 133.7, 134.7, 134.8, 135.5, 136.1, 143.5, 149.9. IR (CH$_2$Cl$_2$) $\nu$ 2921, 2851, 1603, 1489, 1341, 1159, 1089, 933, 815, 719, 657 cm$^{-1}$. MS (ESI) $m/z$ (%): 471.20 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{29}$H$_{31}$N$_2$O$_2$S$^+$[M+H]$^+$ requires 471.2101, found: 471.2098. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 54.57$ min, $t_{\text{major}} = 49.77$ min; ee% = 90%; $[\alpha]_D^{25} = -22.0$ (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column \([\lambda = 254 \text{ nm}}; \text{eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 \text{ mL/min}; t_{\text{minor}} = 54.57 \text{ min, } t_{\text{major}} = 49.77 \text{ min; } \text{ee}\% = 90\%].

(1S,4aR,6aR,11bS)-1-(4-fluorophenyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2m

A white solid, 46% yield (21.8 mg). M.p.: 91-94 °C. \(^1\)H NMR (CDCl\(_3\), TMS, 400 MHz) \(\delta\) 2.36 (dd, \(J = 12.4, 8.8 \text{ Hz, } 1H\)), 2.43 (s, 3H), 2.46 (s, 3H), 2.93 (dd, \(J = 12.0, 12.0 \text{ Hz, } 1H\)), 3.19-3.29 (m, 2H), 3.67 (dd, \(J = 12.0, 4.8 \text{ Hz, } 1H\)), 3.94 (dd, \(J = 12.0, 6.0 \text{ Hz, } 1H\)), 4.41 (s, 1H), 5.69 (d, \(J = 5.6 \text{ Hz, } 1H\)), 5.84-5.87 (m, 1H), 5.98 (d, \(J = 7.6 \text{ Hz, } 1H\)), 6.60-6.73 (m, 5H), 6.96-7.01 (m, 1H), 7.07-7.09 (m, 1H), 7.35 (d, \(J = 8.0 \text{ Hz, } 2H\)), 7.68 (d, \(J = 8.0 \text{ Hz, } 2H\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 21.5, 31.9, 47.1, 47.8, 50.5, 50.6, 57.3, 72.6, 106.0, 114.1 (d, \(J = 20.9 \text{ Hz, } 1H\)), 116.5, 122.7, 127.6, 128.6 (d, \(J = 15.7 \text{ Hz, } 1H\)), 129.0 (d, \(J = 7.8 \text{ Hz, } 1H\)), 129.8, 133.6, 134.4 (d, \(J = 3.3 \text{ Hz, } 1H\)), 134.5, 135.0, 143.7, 149.8, 161.6 (d, \(J = 243.5 \text{ Hz, } 1H\)). \(^{19}\)F NMR (CDCl\(_3\), 376 MHz, CFC\(_13\)) \(\delta\) -115.9. IR (CH\(_2\)Cl\(_2\)) \(\nu\) 3049, 2919, 1602, 1510, 1341, 1158, 935, 833, 770, 657 cm\(^{-1}\). MS (ESI) \(m/z\) (%): 475.18 (100) [M+H]\(^+\); HRMS (ESI) Calcd. For C\(_{28}\)H\(_{28}\)N\(_2\)O\(_2\)FS\(^{+1}\) [M+H]\(^+\) requires 475.1850, found: 475.1839. Enantiomeric excess was determined by HPLC with a Chiralcel IC column \([\lambda = 254 \text{ nm}}; \text{eluent: Hexane/Isopropanol = 94/6;}}\)
Flow rate: 0.70 mL/min; $t_{\text{minor}} = 100.31$ min, $t_{\text{major}} = 83.00$ min; ee% = 87%; $[\alpha]_D^{25} = -106.2$ (c 0.50, CH$_2$Cl$_2$).
Translation: Chiralcel IC column [λ = 254 nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; tminor = 100.31 min, tmajor = 83.00 min; ee% = 87%].

(1S,4aR,6aR,11bS)-1-(4-methoxyphenyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2n

A white solid, 46% yield (22.5 mg). M.p.: 77-80 °C. 1H NMR (CDCl3, TMS, 400 MHz) δ 2.43 (s, 3H), 2.45-2.48 (m, 4H), 2.99 (dd, J = 12.0, 12.0 Hz, 1H), 3.17-3.27 (m, 2H), 3.63 (dd, J = 11.6, 4.8 Hz, 1H), 3.68 (s, 3H), 3.89 (dd, J = 12.0, 6.0 Hz, 1H), 4.45 (s, 1H), 5.71 (d, J = 6.0 Hz, 1H), 5.82-5.85 (m, 1H), 5.98 (d, J = 8.0 Hz, 1H), 6.54-6.65 (m, 5H), 6.95-7.00 (m, 1H), 7.05-7.08 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H). 13C NMR (CDCl3, 100 MHz, TMS) δ 21.5, 32.2, 46.8, 47.8, 50.1, 50.9, 55.0, 57.4, 72.9, 106.1, 112.7, 116.4, 122.7, 127.6, 128.5, 128.6, 129.0, 129.7, 130.7, 133.7, 134.8, 134.9, 143.5, 150.0, 158.2. IR (CH2Cl2) ν 2920, 2852, 1602, 1514, 1340, 1161, 935, 833, 729, 658 cm⁻¹. MS (ESI) m/z (%): 487.20 (100) [M+H]+; HRMS (ESI) Calcd. For C29H31N2O3S+1[M+H]+ requires 487.2050, found: 487.2042. Enantiomeric excess was determined by HPLC with a Chiralcel IA column [λ = 314 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; tminor = 35.52
$t_{\text{major}} = 26.75 \text{ min;} \quad \text{ee\%} = 91\%; \quad \left[\alpha\right]_{D}^{25} = -118.4 \, (c \, 0.70, \, \text{CH}_2\text{Cl}_2)$. 

![Chemical structure diagram]

![NMR spectrum graph]
Translation: Chiralcel IA column $[\lambda = 314 \text{ nm}; \text{eluent: Hexane/Isopropanol} = 90/10; \text{Flow rate: 0.70 mL/min; } t_{\text{minor}} = 35.52 \text{ min, } t_{\text{major}} = 26.75 \text{ min; } \text{ee\%} = 91\%]$. 
Methyl 4-((1S,4aR,6aR,11bS)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indol-1-yl)benzoate 2o

A white solid, 45% yield (23.3 mg). M.p.: 88-92 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 2.33 (dd, $J$ = 12.4, 8.8 Hz, 1H), 2.37 (s, 3H), 2.47 (s, 3H), 2.96 (dd, $J$ = 12.0, 12.0 Hz, 1H), 3.27-3.32 (m, 2H), 3.71 (dd, $J$ = 11.6, 4.8 Hz, 1H), 3.84 (s, 3H), 3.98 (dd, $J$ = 12.0, 6.0 Hz, 1H), 4.42 (s, 1H), 5.67 (d, $J$ = 6.0 Hz, 1H), 5.85-5.88 (m, 1H), 5.95 (d, $J$ = 8.0 Hz, 1H), 6.62-6.66 (m, 1H), 6.76 (d, $J$ = 8.0 Hz, 2H), 6.96-7.01 (m, 1H), 7.09-7.12 (m, 1H), 7.36 (d, $J$ = 8.0 Hz, 2H), 7.67-7.70 (m, 4H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.5, 31.9, 47.6, 48.0, 50.3, 50.8, 51.9, 57.3, 72.5, 106.2, 116.6, 122.7, 127.6, 127.7, 128.5, 128.6, 128.9, 129.8, 133.5, 134.2, 135.0, 143.7, 144.2, 149.7, 166.9. IR (CH$_2$Cl$_2$) $\nu$ 2923, 2852, 1717, 1603, 1488, 1208, 1164, 935, 779, 674 cm$^{-1}$. MS (ESI) $m/z$ (%): 515.19 (100) [M+H]$^+$; HRMS (DART) Calcd. for C$_{30}$H$_{31}$N$_2$O$_4$S$^+$ [M+H]$^+$ requires 515.1999, found: 515.1994. Enantiomeric excess was determined by HPLC with a Chiralcel IF3 column [λ = 317 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; $t_{\text{minor}}$ = 37.91 min, $t_{\text{major}}$ = 33.82 min; ee% = 88%; $[\alpha]_D^{25}$ = -108.1 (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel IF3 column [λ = 317 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 37.91 \text{ min} \), \( t_{\text{major}} = 33.82 \text{ min} \); ee% = 88%].

\[
\text{NTs} \quad \text{N} \quad \text{H} \quad \text{H} \quad \text{Ph} \\
\begin{align*}
&\text{(1S,4aR,6aR,11bS)-1-[(1,1'-biphenyl)-4-yl]-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2p}\\
\text{A white solid, 45% yield (23.9 mg). M.p.: 124-127 °C.} \\
&\text{\(^1\)H NMR (CDCl}_3, \text{TMS, 400 MHz) \delta 2.38 (s, 3H), 2.41-2.46 (m, 4H), 3.03 (dd, } J = 12.0, 12.0 \text{ Hz, 1H), 3.26-3.31 (m, 2H), 3.71 (dd, } J = 11.6, 4.8 \text{ Hz, 1H), 3.95 (dd, } J = 12.0, 6.0 \text{ Hz, 1H), 4.47 (s, 1H), 5.70 (d, } J = 6.0 \text{ Hz, 1H), 5.84-5.87 (m, 1H), 5.96 (d, } J = 8.0 \text{ Hz, 1H), 6.62-6.66 (m, 1H), 6.76 (d, } J = 8.0 \text{ Hz, 2H), 6.96-7.01 (m, 1H), 7.09-7.12 (m, 1H), 7.23-7.50 (m, 7H), 7.48 (d, } J = 8.0 \text{ Hz, 2H), 7.69 (d, } J = 8.0 \text{ Hz, 2H).} \\
&\text{\(^13\)C NMR (CDCl}_3, \text{100 MHz, TMS) \delta 21.6, 32.1, 47.5, 47.7, 50.5, 50.6, 57.5, 72.8, 106.1, 116.5, 122.8, 125.9, 126.8, 127.1, 127.6, 128.1, 128.6, 128.7, 129.8, 133.7, 134.7, 134.9, 137.8, 139.3, 140.6, 143.6, 149.9. IR (CH}_2\text{Cl}_2) \\
&\text{v 3051, 2920, 1602, 1488, 1340, 1160, 929, 838, 722, 659 cm}^{-1}. \text{ MS (ESI) } m/z (\%) : 533.22 (100) \text{[M+H]}^++; \text{HRMS (DART) Calcd. For } C_{34}H_{33}N_2O_2S^{+}[M+H]^+ \text{ requires 533.2257, found: 533.2256.} \\
&\text{Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; } t_{\text{minor}} = 32.91 \text{ min, } t_{\text{major}} = 22.85 \text{ min; ee% =} 
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91%; $[\alpha]_D^{25} = -63.8$ (c 0.08, CH$_2$Cl$_2$).
Translation: Chiralcel IE3 column ($\lambda = 214$ nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 32.91$ min, $t_{\text{major}} = 22.85$ min; ee% = 91%). (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
(1S,4aR,6aR,11bS)-7-methyl-1-(naphthalen-2-yl)-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3 ' :2,3]cyclopenta[1,2-b]indole 2q

A white solid, 49% yield (24.7 mg). M.p.: 153-156 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 2.27 (s, 3H), 2.46 (s, 3H), 2.51 (dd, $J = 12.0, 8.8$ Hz, 1H), 3.17 (dd, $J = 12.0, 12.0$ Hz, 1H), 3.30-3.34 (m, 1H), 3.40 (dd, $J = 12.0, 4.8$ Hz, 1H), 3.74 (dd, $J = 12.8, 5.2$ Hz, 1H), 3.96 (dd, $J = 12.0, 6.0$ Hz, 1H), 4.56 (s, 1H), 5.71 (d, $J = 6.0$ Hz, 1H), 5.85-5.88 (m, 2H), 6.63-6.67 (m, 1H), 6.75-6.78 (m, 1H), 6.92-6.97 (m, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.23-7.24 (m, 1H), 7.34-7.37 (m, 4H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.57-7.72 (m, 4H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.6, 32.1, 47.79, 47.81, 50.3, 50.9, 57.5, 72.9, 106.2, 116.5, 122.8, 125.4, 125.6, 126.1, 126.5, 126.6, 127.3, 127.55, 127.61, 128.7, 129.0, 129.8, 132.3, 132.8, 133.8, 134.7, 134.9, 136.4, 143.6, 149.9. IR (CH$_2$Cl$_2$) ν 3050, 2920, 1602, 1489, 1338, 1158, 934, 816, 723, 657 cm$^{-1}$. MS (ESI) $m/z$ (%): 507.20 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{32}$H$_{31}$N$_2$O$_2$S$^+$[M+H]$^+$ requires 507.2101, found: 507.2094. Enantiomeric excess was determined by HPLC with a Chiralcel IC column ($\lambda = 254$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 68.13$ min, $t_{\text{major}} = 62.80$ min; ee% = 90%; $\left[\alpha\right]_D^{25} = -187.7$ (c 2.00, CH$_2$Cl$_2$)].
(1R,4aR,6aR,11bS)-7-methyl-1-(thiophen-3-yl)-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2r

A white solid, 48% yield (22.1 mg). M.p.: 145-148 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 2.44 (s, 3H), 2.46 (s, 3H), 2.54 (dd, $J = 12.0, 8.0$ Hz, 1H), 2.99 (dd, $J = 12.0, 12.0$ Hz, 1H), 3.22-3.27 (m, 1H), 3.39 (dd, $J = 12.4, 5.2$ Hz, 1H), 3.70 (dd, $J = 11.6, 5.2$ Hz, 1H), 3.87 (dd, $J = 12.4, 5.6$ Hz, 1H), 4.32 (s, 1H), 5.71 (d, $J = 6.0$ Hz, 1H), 5.81-5.84 (m, 1H), 6.07 (d, $J = 8.0$ Hz, 1H), 6.29 (dd, $J = 4.8, 1.6$ Hz, 1H), 6.57-6.66 (m, 2H), 6.96-7.09 (m, 3H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.5, 32.5, 43.3, 47.4, 49.7, 50.9, 57.2, 73.5, 116.6, 120.7, 122.7, 123.8, 127.2, 127.5, 128.8, 129.3, 129.8, 133.9, 134.98, 135.03, 139.2, 143.6, 150.2. IR (CH$_2$Cl$_2$) $\nu$ 3047, 2922, 1600, 1493, 1335, 1161, 935, 812, 732, 657 cm$^{-1}$. MS (ESI) $m/z$ (%): 463.15 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{26}$H$_{27}$N$_2$O$_2$S$_2$+$^+$[M+H]$^+$ requires 463.1508, found: 463.1505.

Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda$ = 254 nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 133.59$ min, $t_{\text{major}} = 121.45$ min; ee% = 95%; $[\alpha]_D^{25} = -104.7$ (c 0.15, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column [\(\lambda = 254\) nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 133.59\) min, \(t_{\text{major}} = 121.45\) min; ee\% = 95\%].

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\text{(1S,4aR,6aR,11bR)-7-methyl-3-tosyl-1-vinyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 2s}
\]

A white solid, 48% yield (19.4 mg). M.p.: 92-95 °C. \(^1\)H NMR (CDCl, TMS, 400 MHz) \(\delta 2.45\) (s, 3H), 2.55-2.61 (m, 1H), 2.68-2.76 (m, 2H), 2.82 (s, 3H), 3.11-3.15 (m, 1H), 3.46-3.54 (m, 1H), 3.66-3.71 (m, 1H), 4.42 (s, 1H), 4.75-4.87 (m, 2H), 5.42-5.52 (m, 1H), 5.81 (s, 2H), 6.31 (d, \(J = 7.6\) Hz, 1H), 6.61-6.65 (m, 1H), 6.94-7.10 (m, 2H), 7.34 (d, \(J = 8.0\) Hz, 2H), 7.67 (d, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (CDCl, 100 MHz, TMS) \(\delta 21.6, 32.6, 45.3, 46.9, 48.8, 51.5, 55.5, 73.2, 106.4, 116.6, 117.1, 122.6, 127.5, 128.6, 128.8, 129.7, 133.9, 135.1, 135.4, 135.5, 143.5, 150.4. IR (CH2Cl2) \(\nu 2922, 2852, 2360, 1747, 1463, 1382, 1089, 937, 815, 747, 658\) cm\(^{-1}\). MS (ESI) \(m/z\) (%): 407.17 (100) [M+H]\(^+\); HRMS (ESI) Calcd. For C\(_{24}\)H\(_{27}\)N\(_2\)O\(_2\)S\(^+\) [M+H]\(^+\) requires 407.1788, found: 407.1775. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [\(\lambda = 214\) nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 29.53\) min, \(t_{\text{major}} = 27.93\) min; ee\% = 95\%; \([\alpha\]\(_D\)\(^{25}\) = 17.3 (c 0.10, CH2Cl2)].
Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 29.53 min, t_{major} = 27.93 min; ee% = 95%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(E)-ethyl 3-((1S,4aR,6aR,11bS)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4′,3′:2,3]cyclopenta[1,2-b]indol-1-yl)acrylate 2t

A white solid, 43% yield (20.8 mg). M.p.: 66-69 °C. ^1H NMR (CDCl₃, TMS, 400 MHz) δ 1.21 (t, J = 7.2 Hz, 3H), 2.27 (dd, J = 12.0, 8.8 Hz, 1H), 2.46 (s, 3H), 2.55 (dd, J = 12.0, 12.0 Hz, 1H), 2.80 (s, 3H), 2.81-2.87 (m, 1H), 3.14-3.20 (m, 1H), 3.61 (dd, J = 12.0, 5.2 Hz, 1H), 3.85 (dd, J = 12.0, 5.6 Hz, 1H), 4.08 (q, J = 7.2 Hz, 2H), 4.33 (s, 1H), 5.45-5.50 (m, 1H), 5.72-5.74 (m, 1H), 5.83-5.86 (m, 1H), 6.30 (d, J = 8.0 Hz, 1H), 6.54-6.66 (m, 2H), 6.96-6.99 (m, 1H), 7.06-7.11 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H). ^13C NMR (CDCl₃, 100 MHz, TMS) δ 14.1, 21.5, 32.5, 44.8, 46.8, 50.2, 55.7, 60.2, 72.8, 106.7, 117.3, 122.2, 122.4, 127.6, 128.3, 129.0, 129.8, 133.5, 134.2, 135.5, 143.8, 145.5, 150.1, 165.9. IR (CH₂Cl₂) ν 3052, 2933, 1721, 1601, 1342, 1168, 1011, 932, 822, 750, 662 cm⁻¹. MS (ESI) m/z (%): 479.19 (100) [M+H]+; HRMS (ESI) Calcd. For C₂₇H₃₁N₂O₄S⁺ [M+H]+ requires 479.1999, found: 479.1985. Enantiomeric excess was determined by HPLC with a Chiralcel
IE3 column [$\lambda = 325$ nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 82.44$ min, $t_{\text{major}} = 62.63$ min; ee% = 99%; $[\alpha]_D^{25} = -31.2$ (c 0.08, CH$_2$Cl$_2$)].
Translation: Chiralcel IE3 column [λ = 325 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; t_{minor} = 84.44 min, t_{major} = 62.63 min; ee% = 99%].
(1S,4aR,6aR,11bR)-1-butyl-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cycloptenta[1,2-b]indole 2u

A white solid, 44% yield (19.2 mg). M.p.: 43-46 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ 0.72 (t, $J = 7.2$ Hz, 3H), 0.89-1.19 (m, 6H), 1.96 (br, 1H), 2.45 (s, 3H), 2.54 (dd, $J = 12.0$, 12.0 Hz, 1H), 2.65 (dd, $J = 12.4$, 6.4 Hz, 1H), 2.82 (s, 3H), 3.07 (br, 1H), 3.49-3.61 (m, 2H), 4.40 (s, 1H), 5.76-5.83 (m, 2H), 6.31 (d, $J = 8.0$ Hz, 1H), 6.60-6.65 (m, 1H), 6.91 (d, $J = 7.2$ Hz, 1H), 7.06-7.11 (m, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 13.8, 21.6, 22.4, 28.4, 29.4, 32.6, 40.6, 47.4, 48.4, 52.4, 55.8, 73.2, 106.3, 117.1, 122.5, 127.5, 128.5, 129.0, 129.7, 134.0, 135.5, 135.6, 143.4, 150.6. IR (CH$_2$Cl$_2$) ν 2920, 1794, 1601, 1407, 1169, 1090, 965, 871, 712, 661 cm$^{-1}$. MS (ESI) $m/z$ (%): 437.22 (100) [M+H]$^+$; HRMS (DART) Calcd. For C$_{26}$H$_{33}$N$_2$O$_2$S$^+$ [M+H]$^+$ requires 437.2257, found: 437.2254. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 64.48$ min, $t_{\text{major}} = 78.27$ min; ee% = 92%; $[\alpha]_D^{25} = -12.3$ (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column [$\lambda = 254$ nm; eluent: Hexane/Isopropanol = 94/6; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 64.48$ min, $t_{\text{major}} = 78.27$ min; ee% = 92%].

ethyl 3-((1S,4aR,6aR,11bR)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indol-1-yl)propanoate 2v

A white solid, 43% yield (20.8 mg). M.p.: 55-58 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 1.18 (t, $J = 7.2$ Hz, 3H), 1.36-1.52 (m, 1H), 1.95-2.15 (m, 4H), 2.45 (s, 3H), 2.52-2.63 (m, 2H), 2.82 (s, 3H), 3.07 (br, 1H), 3.47 (dd, $J = 12.0$, 5.6 Hz, 1H), 3.58 (dd, $J = 12.0$, 5.6 Hz, 1H), 4.02 (q, $J = 7.2$ Hz, 2H), 4.43 (s, 1H), 5.78-5.83 (m, 2H), 6.32 (d, $J = 8.0$ Hz, 1H), 6.61-6.66 (m, 1H), 6.91-6.93 (m, 1H), 7.07-7.12 (m, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 14.1, 21.6, 24.3, 32.2, 32.5, 40.6, 47.3, 48.5, 52.2, 55.7, 60.3, 73.1, 106.6, 117.3, 122.6, 127.5, 128.7, 128.8, 129.7, 133.9, 135.1, 135.4, 143.5, 150.5, 173.1. IR (CH$_2$Cl$_2$) $\nu$ 2922, 2852, 1730, 1602, 1486, 1344, 1160, 1089, 930, 816, 739, 659 cm$^{-1}$. MS (ESI) $m/z$ (%): 481.21 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{27}$H$_{33}$N$_2$O$_4$S$^+$ [M+H]$^+$ requires 481.2156, found: 481.2145. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [$\lambda = 309$ nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 65.21$ min, $t_{\text{major}} = 58.03$ min; ee% = 93%; [$\alpha$]$_D^{25} = -58.8$ (c
[0.08, CH$_2$Cl$_2$].
Translation: Chiralcel IE3 column [λ = 309 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 65.21 \text{ min} \), \( t_{\text{major}} = 58.03 \text{ min} \); ee% = 93%].
4-((1S,4aR,6aR,11bR)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indol-1-yl)butan-2-one 2w

A white liquid, 43% yield (19.4 mg). ¹H NMR (CDCl₃, TMS, 400 MHz) δ 1.31-1.50 (m, 2H), 1.94 (s, 3H), 1.98-2.24 (m, 3H), 2.45 (s, 3H), 2.48-2.56 (m, 2H), 2.83 (s, 3H), 3.05-3.09 (m, 1H), 3.45 (dd, J = 11.6, 5.6 Hz, 1H), 3.61 (dd, J = 12.4, 5.6 Hz, 1H), 4.43 (s, 1H), 5.78-5.82 (m, 2H), 6.34 (d, J = 7.6 Hz, 1H), 6.63-6.67 (m, 1H), 6.92-6.95 (m, 1H), 7.08-7.13 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 23.1, 29.7, 32.6, 40.7, 41.6, 47.6, 48.8, 52.1, 55.7, 73.0, 106.7, 117.3, 122.6, 127.5, 128.6, 128.8, 129.7, 133.8, 135.4, 135.5, 143.5, 150.5, 208.4.

IR (CH₂Cl₂) ν 2921, 1716, 1485, 1340, 1164, 1091, 937, 815, 786, 660 cm⁻¹. MS (ESI) m/z (%): 451.20 (100) [M+H]⁺; HRMS (ESI) Calcd. For C₂₆H₃₁N₂O₃S⁺ [M+H]⁺ requires 451.2050, found: 451.2035. Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 311 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_minor = 57.19 min, t_major = 51.27 min; ee% = 94%; [α]D²⁵ = -17.8 (c 1.10, CH₂Cl₂)].
Translation: Chiralcel IE3 column [λ = 311 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; tminor = 57.19 min, tmajor = 51.27 min; ee% = 94%].

(1S,4aR,6aR,11bR)-1-((tert-butyldimethylsilyl)oxy)propyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4′,3′:2,3]cyclopenta[1,2-b]indole 2x
A white liquid, 44% yield (24.2 mg). $^1$H NMR (CDCl$_3$, TMS, 400 MHz) δ -0.07 (s, 6H), 0.80 (s, 9H), 0.98-1.22 (m, 3H), 1.38-1.48 (m, 1H), 1.94-2.02 (m, 1H), 2.45 (s, 3H), 2.54 (dd, $J = 11.6$, 11.6 Hz, 1H), 2.63 (dd, $J = 12.0$, 6.4 Hz, 1H), 2.81 (s, 3H), 3.05-3.09 (m, 1H), 3.34-3.44 (m, 2H), 3.48-3.60 (m, 2H), 4.41 (s, 1H), 5.77-5.83 (m, 2H), 6.29 (d, $J = 8.0$ Hz, 1H), 6.59-6.64 (m, 1H), 6.90-6.92 (m, 1H), 7.05-7.09 (m, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ -5.46, -5.41, 18.2, 21.5, 25.5, 25.9, 30.5, 32.5, 40.9, 47.5, 48.4, 52.2, 55.8, 63.0, 73.2, 106.4, 117.1, 122.5, 127.5, 128.6, 128.9, 129.7, 133.9, 135.4, 135.5, 143.4, 150.5. IR (CH$_2$Cl$_2$) ν 3041, 2927, 2853, 1603, 1491, 1346, 1248, 1157, 1090, 945, 833, 737, 668 cm$^{-1}$. MS (ESI) m/z (%): 553.28 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{31}$H$_{45}$N$_2$O$_3$SSi$^{15}$ [M+H]$^+$ requires 553.2915, found: 553.2898. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; tminor = 28.29 min, tmajor = 26.32 min; ee% =
90%; [α]D<sup>25</sup> = -183.1 (c 0.12, CH₂Cl₂).
Translation: Chiralcel IG column [λ = 214 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t_{minor} = 28.29 min, t_{major} = 26.32 min; ee% = 90%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
2-(3-((1S,4aR,6aR,11bR)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indol-1-yl)propyl)isoindoline-1,3-dione 2y

A white solid, 44% yield (24.9 mg). M.p.: 163-166 °C. \( ^1 \)H NMR (CDCl\textsubscript{3}, TMS, 400 MHz) \( \delta 1.01-1.22 \) (m, 2H), 1.26-1.35 (m, 2H), 1.95-2.05 (m, 1H), 2.45 (s, 3H), 2.52-2.63 (m, 2H), 2.76 (s, 3H), 3.03-3.07 (m, 1H), 3.41-3.49 (m, 3H), 3.57 (dd, \( J = 12.4, 5.6 \) Hz, 1H), 4.38 (s, 1H), 5.76-5.80 (m, 2H), 6.17 (d, \( J = 7.6 \) Hz, 1H), 6.51-6.56 (m, 1H), 6.86-6.89 (m, 1H), 6.94-6.98 (m, 1H), 7.33 (d, \( J = 8.0 \) Hz, 2H), 7.66 (d, \( J = 8.0 \) Hz, 2H), 7.79-7.82 (m, 2H). \( ^13 \)C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) \( \delta 21.5, 26.1, 26.4, 32.4, 37.7, 40.7, 47.4, 48.5, 52.0, 55.8, 73.1, 106.3, 117.2, 122.5, 123.1, 127.5, 128.6, 128.8, 129.7, 132.0, 133.8, 134.0, 135.1, 135.4, 143.4, 150.4, 168.2. \( \text{IR (CH}_2\text{Cl}_2) \nu 2924, 2849, 1770, 1601, 1397, 1161, 1090, 934, 877, 786, 660 \) cm\(^{-1}\). MS (ESI) \( m/z \) (%): 568.22 (100) [M+H]\(^+\); HRMS (ESI) Calcd. For C\textsubscript{33}H\textsubscript{34}N\textsubscript{3}O\textsubscript{4}S\textsuperscript{+1} [M+H]\(^+\) requires 568.2265, found: 568.2252. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [\( \lambda = 214 \) nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 79.14 \) min, \( t_{\text{major}} = 66.33 \) min; ee\% = 91%; \( [\alpha]_{D}^{25} = -15.1 \) (c 0.5, CH\textsubscript{2}Cl\textsubscript{2})].
Translation: Chiralcel IG column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 79.14$ min, $t_{\text{major}} = 66.33$ min; ee$\% = 91\%$]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
8. Characterization and spectra charts for compounds 3 and 4

\[
N-\text{(buta-2,3-dien-1-yl)}-N-\text{((R)-5-((R)-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yloxy)-2-(1-methyl-1H-indol-3-yl)pentyl)-4-methylbenzenesulfonamide 3}
\]

A white liquid, 43% yield (35.6 mg). $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 0.83-0.88 (m, 12H), 1.02-1.16 (m, 8H), 1.24-1.56 (m, 16H), 1.64-1.84 (m, 5H), 2.04-2.12 (m, 4H), 2.37 (s, 3H), 2.65-2.70 (m, 2H), 3.26-3.37 (m, 2H), 3.52-3.58 (m, 1H), 3.72 (s, 3H), 3.76-3.89 (m, 4H), 4.63-4.66 (m, 2H), 4.73-4.80 (m, 1H), 6.37 (d, $J = 3.2$ Hz, 1H), 6.50 (d, $J = 3.2$ Hz, 1H), 6.86 (s, 1H), 7.04-7.09 (m, 1H), 7.18-7.23 (m, 3H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 16.2, 19.6, 19.7, 21.0, 21.5, 22.6, 22.7, 24.1, 24.4, 24.8, 27.4, 28.0, 28.8, 31.4, 32.68, 32.7, 32.8, 35.3, 37.3, 37.4, 37.5, 39.3, 40.0, 47.1, 52.3, 68.3, 75.5, 76.1, 85.7, 109.3, 111.8, 114.8, 115.4, 118.7, 119.1, 120.9, 121.5, 126.5, 127.0, 127.1, 127.3, 129.5, 137.1, 137.2, 143.0, 146.0, 151.4, 209.3. IR (CH$_2$Cl$_2$) $\nu$ 2924, 2866, 1954, 1599, 1469, 1327, 1156, 1090, 1055, 850, 737, 659 cm$^{-1}$. MS (ESI) $m/z$ (%): 823.54 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{52}$H$_{75}$N$_2$O$_4$S$^{+1}$ [M+H]$^+$ requires 823.5442, found: 823.5442. Enantiomeric excess was determined by HPLC with a Chiralcel IF3 column [$\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; $t_{\text{minor}} = 19.95$ min, $t_{\text{major}} = 18.56$ min; ee% = 96%; [$\alpha$]$_D^{25} = 35.3$ (c 0.1, CH$_2$Cl$_2$)].
Translation: Chiralcel IF3 column $\lambda = 214$ nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t$_{\text{minor}}$ = 19.95 min, t$_{\text{major}}$ = 18.56 min; ee% = 96%. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).

(1S,4aR,6aR,11bR)-1-(3-(((S)-2,8-dimethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propyl)-7-methyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indenol 4

A white solid, 43% yield (35.5 mg). M.p.: 127-130 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 0.83-0.88 (m, 12H), 1.01-1.16 (m, 8H), 1.23-1.82 (m, 22H), 1.98-2.07 (m, 1H), 2.11 (s, 3H), 2.45 (s, 3H), 2.57-2.70 (m, 4H), 2.81 (s, 3H), 3.07 (br, 1H), 3.52-3.69 (m, 4H), 4.43 (s, 1H), 5.78-5.85 (m, 2H), 6.29-6.33 (m, 2H), 6.41-6.42 (m, 1H), 6.60-6.64 (m, 1H), 6.89-6.92 (m, 1H), 7.06-7.11 (m, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 16.2, 19.6, 19.7, 21.0, 21.5, 22.6, 22.7, 24.1, 24.4, 24.8, 25.6, 27.3, 28.0, 31.3, 32.6, 32.7, 32.8, 37.3, 37.42, 37.45, 39.4, 40.0, 40.8, 47.5, 48.4, 52.4, 55.8, 68.1, 73.2, 75.5, 106.4, 111.7, 115.4, 117.2, 120.8, 122.5, 127.0, 127.5, 128.6, 128.9, 129.7, 134.0, 135.4, 143.4, 146.0, 150.6, 151.2. IR (CH$_2$Cl$_2$) $\nu$ 2922, 2849, 1603, 1486, 1468, 1338, 1260, 1156, 1012, 935, 812, 738, 659 cm$^{-1}$. MS (ESI) $m/z$ (%): 823.54 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{52}$H$_{75}$N$_2$O$_4$S$^+$ [M+H]$^+$ requires 823.5442, found: 823.5445.
Enantiomeric excess was determined by HPLC with a Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{\text{minor}} = 39.94 min, t_{\text{major}} = 36.70 min; ee% = 92%; [\alpha]_D^{25} = -153.8 (c 0.20, CH₂Cl₂)].
Translation: Chiralcel IE3 column [λ = 214 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; t_{minor} = 39.94 min, t_{major} = 36.70 min; ee% = 92%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
9. General procedure for the synthesis of 5, 6, 7 and 8 and their characterization and spectra

**Charts**

To an oven-dried reaction tube was sequentially added [Rh(COD)Cl]₂ (0.005 mmol), (+)-DIOP (0.01 mmol) and benzoic acid (0.1 mmol), and the tube was evacuated and backfilled with argon for three times. Then, 1a (0.10 mmol) in 1,2-dichloroethane (1.00 mL) was added into tube under an argon atmosphere. The resulting mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1) to give the corresponding product 5.

\[(R,E)-N-(buta-1,3-dien-1-yl)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)-2-phenylethyl)benzenesulfonamide 5\]

A white liquid, 51% yield (23.2 mg). \(^1\)H NMR (CDCl₃, TMS, 400 MHz) δ 2.37 (s, 3H), 3.77 (s, 3H), 3.88 (dd, J = 14.0, 8.0 Hz, 1H), 4.04 (dd, J = 14.0, 8.0 Hz, 1H), 4.71 (t, J = 7.6 Hz, 1H), 4.90-5.00 (m, 2H), 5.57 (dd, J = 14.0, 10.0 Hz, 1H), 6.17-6.27 (m, 1H), 6.67 (d, J = 14.0 Hz, 1H), 6.98-7.03 (m, 1H), 7.11 (s, 1H), 7.15-7.22 (m, 4H), 7.26-7.39 (m, 6H), 7.52 (d, J = 8.0 Hz, 1H). \(^1\)C NMR (CDCl₃, 100 MHz, TMS) δ 21.5, 32.8, 40.3, 50.8, 109.2, 114.4, 114.7, 115.2, 118.9, 119.4, 121.7, 126.6, 126.7, 126.9, 127.4, 128.3, 128.4, 129.7, 129.9, 134.6, 135.6, 137.1, 141.9, 143.7. IR (CH₂Cl₂) ν 2920, 1949, 1599, 1474, 1334, 1160, 1093, 1010, 903, 858, 750, 659 cm⁻¹. MS (ESI) m/z (%): 457.19 (100) [M+H]⁺; HRMS (ESI) Calcd. For C₂₈H₂₉N₂O₂S⁺ [M+H]⁺ requires 457.1944, found: 457.1941.
To an oven-dried reaction tube was sequentially added Pd(OAc)$_2$ (0.005 mmol), dppe (0.005 mmol), 1a and acetonitrile (1.00 mL). Then, iodobenzene (0.125 mmol) and pyrrolidine (0.6 mmol) were added into tube under an argon atmosphere. The resulting mixture was stirred at 95 °C. When the reaction was complete as monitored by TLC, the solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1-5/1) to give the corresponding product 6.

(R,Z)-4-methyl-N-(2-(1-methyl-1H-indol-3-yl)-2-phenylethyl)-N-(3-phenyl-4-(pyrrolidin-1-yl)but-2-en-1-yl)benzenesulfonamide 6

A white solid, 73% yield (44.1 mg). M.p.: 111-114 °C. $^1$H NMR (CDCl$_3$, TMS, 400 MHz) $\delta$ 1.64-1.68 (m, 4H), 2.37-2.40 (m, 7H), 3.27-3.35 (m, 2H), 3.59-3.65 (m, 1H), 3.72 (s, 3H), 3.88-4.13 (m, 3H), 4.66 (t, $J$ = 8.0 Hz, 1H), 5.33 (t, $J$ = 6.4 Hz, 1H), 6.96-7.02 (m, 2H), 7.09-7.12 (m, 2H), 7.18-7.32 (m, 12H), 7.41 (d, $J$ = 8.0 Hz, 1H), 7.64 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.5, 23.4, 32.7, 42.2, 46.5, 52.4, 53.9, 109.2, 114.8, 118.9, 119.3, 121.6, 126.3, 126.6, 127.0, 127.1, 127.2, 127.3, 128.0, 128.3, 128.5, 129.6, 137.0, 137.1, 141.8, 142.2, 143.2. IR (CH$_2$Cl$_2$) $\nu$ 3394, 2922, 2851, 1646, 1454, 1327, 1155, 1090, 922, 814, 738, 699, 653 cm$^{-1}$. MS (ESI) m/z (%): 604.29 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{38}$H$_{42}$N$_3$O$_2$S$^+$ [M+H]$^+$ requires 604.2992, found: 604.2978. Enantiomeric excess was determined by HPLC with a Chiralcel ID3 column [$\lambda$ = 254 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.70 mL/min; t$_{minor}$ = 30.71 min, t$_{major}$ = 32.46 min; ee% = 99%; [$\alpha$]$_D^{25}$ = -106.5 (c 0.10, CH$_2$Cl$_2$)].
Translation: Chiralcel ID3 column \([\lambda = 254 \text{ nm}}; \text{ eluent: Hexane/Isopropanol} = 95/5; \text{ Flow rate: 0.70 mL/min}}; t_{\text{minor}} = 30.71 \text{ min}, t_{\text{major}} = 32.46 \text{ min}; \text{ ee}\% = 99\%].

To an oven-dried reaction tube was sequentially added \(2a\) (0.10 mmol), PyHBr\(_3\) (0.01 mmol), and Chloramine-T (0.20 mmol) in acetonitrile (1.00 mL) under an argon atmosphere. The resulting mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, water (5.00 mL) and ethyl acetate (5.00 mL) were added and then the aqueous solution was separated and extracted with ethyl acetate (3 × 5 mL). The organic layer was then washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). The solution was concentrated under reduced pressure and the crude residue was purified via a silica gel flash column chromatography (PE/EA = 10/1) to give the corresponding product 7.

\[
\begin{align*}
\text{NTs} & \text{N} \\
\text{H} & \text{Ph} \\
\text{Cl} & \text{Cl}
\end{align*}
\]

\((1S,4aR,6aR,11bS)-8,10\text{-dichloro-7-methyl-1-phenyl-3-tosyl-2,3,4,4a,6a,7-hexahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole} 7\)

A white solid, 52% yield (27.1 mg). M.p.: 166–169 °C. \(^1\text{H} \text{NMR (CDCl}_3, \text{TMS, 400 MHz}) \delta 2.36 \text{ (s,} \)
3H), 2.42-2.47 (m, 4H), 3.05 (dd, J = 12.0, 12.0 Hz, 1H), 3.12-3.21 (m, 2H), 3.69 (dd, J = 11.2, 4.4 Hz, 1H), 3.94 (dd, J = 12.4, 6.0 Hz, 1H), 4.48 (s, 1H), 5.68 (d, J = 6.0 Hz, 1H), 5.82-5.88 (m, 2H), 6.72-6.75 (m, 2H), 6.88-6.95 (m, 2H), 7.02-7.11 (m, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H). $^1$H NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 21.6, 36.1, 47.4, 47.8, 50.1, 50.7, 58.8, 75.6, 115.7, 122.1, 122.3, 127.50, 127.59, 127.6, 127.9, 129.7, 129.9, 130.6, 134.1, 134.2, 138.2, 140.5, 143.8, 144.7. IR (CH$_2$Cl$_2$) $\nu$ 2923, 1597, 1492, 1342, 1153, 1058, 935, 814, 730, 658 cm$^{-1}$. MS (ESI) $m/z$ (%): 525.11 (100) [M+H]$^+$; HRMS (ESI) Calcd. For C$_{28}$H$_{27}$N$_2$O$_2$Cl$_2$S$^+$[M+H]$^+$ requires 525.1165, found: 525.1165. Enantiomeric excess was determined by HPLC with a Chiralcel IC column [\(\lambda = 214\) nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; $t_{\text{minor}}$ = 23.42 min, $t_{\text{major}}$ = 20.54 min; ee% = 95%; $[\alpha]_D^{25} = -263.8$ (c 0.20, CH$_2$Cl$_2$)].
Translation: Chiralcel IC column [λ = 214 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_{minor} = 23.42 min, t_{major} = 20.54 min; ee% = 95%]. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
To an oven-dried reaction tube was sequentially added 2b (0.10 mmol) and Pd/C (0.01 mmol) in ethyl acetate (2.00 mL). The resulting mixture was stirred at room temperature under H₂ atmosphere. When the reaction was complete as monitored by TLC, the Pd/C was removed, and then the solution was concentrated under reduced pressure to give the crude residue. Then, ACE-Cl (0.2 mmol) in DCE (1.0 mL) was added into crude residue. The resulting mixture was stirred at room temperature for 12 h. After that, DCE was removed under reduced pressure and MeOH (1.0 mL) was added into bottle. The bottle was stirred at reflux for 2 h. When the reaction was complete as monitored by TLC, the mixture was based with saturated NaHCO₃ solution, and extracted with ethyl acetate (3 × 5 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give the residue. Then, the crude residue was purified via a silica gel flash column chromatography (PE/EA = 6/1) to give the corresponding product 8.

(1S,4aR,6aR,11bS)-1-phenyl-3-tosyl-2,3,4,4a,5,6a,7-octahydro-1H-pyrido[4',3':2,3]cyclopenta[1,2-b]indole 8

A white solid, 57% yield for two steps (25.3 mg). M.p.: 59-62 °C. ¹H NMR (CDCl₃, TMS, 400 MHz) δ 1.35-1.47 (m, 2H), 1.56-1.67 (m, 1H), 1.95-2.07 (m, 1H), 2.18-2.25 (m, 1H), 2.49 (s, 3H), 2.67-2.80 (m, 2H), 3.27-3.32 (m, 1H), 3.86-3.94 (m, 3H), 6.24 (d, J = 7.6 Hz, 1H), 6.64-6.67 (m, 2H), 6.76-6.80 (m, 1H), 6.92-6.97 (m, 1H), 6.99-7.04 (m, 2H), 7.07-7.13 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.6, 28.8, 35.6, 44.9, 47.3, 48.1, 48.7, 60.5, 61.7, 109.6, 119.0, 122.9, 126.7, 127.5, 127.68, 127.70, 128.1, 129.8, 133.7, 133.8, 138.7, 143.6, 151.2. IR (CH₂Cl₂) ν 3380, 3030, 2967, 1603, 1344, 1161, 1089, 934, 815, 700, 662 cm⁻¹. MS (ESI) m/z (%): 445.19 (100) [M+H]+; HRMS (ESI) Calcd. For C₂₇H₂₉N₂O₂S⁺[M+H]+ requires 445.1944, found: 445.1940. Enantiomeric excess was determined by HPLC with a Chiralcel IG column [λ = 214 nm;
eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; \( t_{\text{minor}} = 105.67 \text{ min} \), \( t_{\text{major}} = 81.33 \text{ min} \);
ee\% = 99\%; \([\alpha]_D^{25} = -42.1 \text{ (c 0.20, CH}_2\text{Cl}_2)\].
Translation: Chiralcel IG column \([\lambda = 214 \text{ nm}];\) eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.70 mL/min; \(t_{\text{minor}} = 105.67 \text{ min}, t_{\text{major}} = 81.33 \text{ min};\) ee\% = 99\%. (Note: In the 5 minute position, there is the peak of dichloromethane, due to that the sample was dissolved in dichloromethane for measuring).
To a flame dried Schlenk tube was added chiral compound 1r (0.1 mmol), tBuBrettphosAuNTf$_2$ (2.0 mol %) and the tube was evacuated and backfilled with argon for three times. Then, anhydrous toluene (1.0 mL) was added into tube under argon atmosphere. The reaction mixture was allowed to stir at 70 °C. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography on silica gel to give the desired product 2r'.

\[
\text{1r (95% ee)} \xrightarrow{\text{BuBrettPhosAuNTf}_2 (2 \text{ mol } \%)} \text{2r', 82% yield (30% ee)}
\]
10. X-ray crystallographic information of products 2f, 6, 7 and 2r'.

The crystal data of 2f have been deposited in CCDC with number 1816191. Empirical Formula: C_{28}H_{27}FN_{2}O_{2}S; Formula Weight: 474.57; Crystal Color, colorless; Crystal Dimensions: 0.180 x 0.140 x 0.100 mm³; Crystal System: Monoclinic; Lattice Parameters: a = 9.8347(3)Å, b = 10.2954(3)Å, c = 12.0508(4)Å, α = 90°, β = 105.0320(10)°, γ = 90°, V = 1178.42(6)Å³; Space group: P 21; Z = 2; D_{calc} = 1.337 g/cm³; F_{000} = 500; Final R indices [I>2σ(I)] R1 = 0.0321, wR2 = 0.0830.
The crystal data of 6 have been deposited in CCDC with number 1851028. Empirical Formula: C₃₈H₄₁N₃O₂S; Formula Weight: 603.80; Crystal Color, colorless; Crystal Dimensions: 0.1 x 0.03 x 0.02 mm³; Crystal System: Orthorhombic; Lattice Parameters: a = 9.7314(4)Å, b = 11.3674(5)Å, c = 29.2938(12)Å, α = 90°, β = 90°, γ = 90°, V = 3240.5(2)Å³; Space group: P2₁2₁2₁; Z = 4; D_{calc} = 1.238 g/cm³; F₀₀₀ = 1288; Final R indices [I>2\sigma(I)] R₁ = 0.0459, wR₂ = 0.1111.
The crystal data of 7 have been deposited in CCDC with number 1846480. Empirical Formula: C_{28}H_{26}Cl_2N_2O_2S; Formula Weight: 525.47; Crystal Color, colorless; Crystal Dimensions: 0.160 x 0.130 x 0.080 mm³; Crystal System: Monoclinic; Lattice Parameters: a = 8.5142(5) Å, b = 11.8312(8) Å, c = 13.0004(8) Å, α = 90°, β = 106.969(3)°, γ = 90°, V = 1252.56(14) Å³; Space group: P 21; Z = 2; D_{calc} = 1.393 g/cm³; F_{000} = 548; Final R indices [I>2σ(I)] R1 = 0.0862, wR2 = 0.2346.
The crystal data of 2r' have been deposited in CCDC with number 1838571. Empirical Formula: C_{26}H_{26}N_{2}O_{2}S_{2}; Formula Weight: 462.61; Crystal Color, colorless; Crystal Dimensions: 0.1 x 0.08 x 0.05 mm³; Crystal System: Triclinic; Lattice Parameters: a = 6.42400(10)Å, b = 8.1480(2)Å, c = 11.8965(3)Å, α = 108.3570(10)°, β = 103.5550(10)°, γ = 93.6680(10)°, V = 568.10(2)Å³; Space group: P1; Z = 1; D_{calc} = 1.352 g/cm³; F_{000} = 244; Final R indices [I>2σ(I)] R1 = 0.0369, wR2 = 0.1009.
11. References
