Supporting Information

Sc(OTf)₃ Catalyzed [3 + 2]-Annulation Reaction of Donor–Acceptor Aziridines with Methylene exo-Glycals: Synthesis of Chiral Carbohydrate-spiro-heterocycles

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1. General information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. The $^1$H NMR spectra was recorded on 400 MHz spectrometers, and the $^{13}$C NMR was recorded on 100 MHz spectrometer. The spectra were recorded in CDCl$_3$ at room temperature. $^1$H and $^{13}$C NMR chemical shifts are reported in ppm relative to either the residual solvent peak ($^{13}$C) (δ = 77.00 ppm) or TMS ($^1$H) (δ = 0 ppm) as an internal standard. Data for $^1$H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double of doublet, td = triplet of doublet, m = multiplet), integration, coupling constant (Hz) and assignment. HRMS were performed on FT–ICRMS mass instrument (ESI). Optical rotation was measured on the Perkin Elmer 341 polarimeter with [α]$_D$ values reported in degrees. Concentration (c) is in g/100 mL.

2. Procedure for the Sc(OTf)$_3$ catalyzed [3 + 2]-annulation reaction of aziridine 1 with exo-glycal 2a and 2c

Under an atmosphere of dry nitrogen, activated 4 Å molecular sieves (100 mg), aziridine 1$^1$ (0.20 mmol, 1.0 equiv), exo-glycal 2$^2$ (0.24 mmol, 1.2 equiv) and 2mL of

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(2) (a) W. M. Li, Y. H. Niu, D. C. Xiong, X. P. Cao, and X. S. Ye, *J. Med. Chem.* 2015, **58**, 52
anhydrous DCM were added into an over-dried reaction tube equipped with a stir bar, and the solution was stirred at -20 °C for 15 min. Subsequently, the 0.01 mmol of Sc(OTf)₃ (4.9 mg, 0.05 eq) was added. The reaction mixture was stirred at the indicated temperature until the aziridine was completely exhausted (monitored by TLC). Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give the corresponding product.

3. General procedure for the Sc(OTf)₃ catalyzed [3 + 2]-annulation reaction of aziridine 1 with exo-glycal 2b

Under an atmosphere of dry nitrogen, activated 4 Å molecular sieves (100 mg), aziridine 1 (0.20 mmol, 1.0 equiv), exo-glycal 2b (0.6 mmol, 3 equiv) and 2 mL of anhydrous DCM were added into an over-dried reaction tube equipped with a stir bar, and the solution was stirred at -20 °C for 15 min. Subsequently, the 0.01 mmol of Sc(OTf)₃ (4.9 mg, 0.05 eq) was added. The reaction mixture was stirred at the indicated temperature until the aziridine was completely exhausted (monitored by TLC). Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give the corresponding product.


4. Procedure for the gram-scale reaction of aziridine 1l with exo-glycal 2a

Under an atmosphere of dry nitrogen, activated 4 Å molecular sieves (1.5 g), aziridine 1l (3 mmol, 1.0 equiv, 1.29 g), exo-glycal 2a (3.6 mmol, 1.2 equiv, 0.67 g) and 30 mL of anhydrous DCM were added into an over-dried reaction tube equipped with a stir bar, and the solution was stirred at -20 °C for 15 min. Subsequently, the 0.15 mmol of Sc(OTf)³ (74 mg, 0.05 eq) was added. The reaction mixture was stirred at the indicated temperature until the aziridine was completely exhausted (monitored by TLC). Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give the corresponding products (8R)-3la (1.06 g, 1.66 mmol, 58%) and (8S)-3la (0.62 g, 0.97 mmol, 34%).

5. Procedure for the desylation of the annulation product (8S)-3aa

According to the previous report on the method for desylation,⁴ compound (8S)-3aa (63.7 mg, 0.1 mmol) in anhydrous MeOH (2 mL) was treated with Mg powder (48.6 mg, 2 mmol) and the mixture was sonicated for 1 h. After removal of the solvent

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under vacuum, the residue was diluted with CH$_2$Cl$_2$ and filtrated with Celite pad. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel directly (petroleum ether/EtOAc = 4:1, $R_f = 0.37$) to afford 7 (42.1 mg, 87% isolated yield).

6. Procedure for the hydrolysis of annulation product (8R)-3la

Hydrolysis of the product (8R)-3la was carried out according to the literature.$^5$ To a solution of (8R)-3la (185.3 mg, 0.3 mmol) in dioxane (2 ml) was added 0.1 M HCl (1 ml) and the reaction mixture was refluxed for 4 h. The solution was neutralized with 0.5 M NaOH, the solvent were removed in vacuo and the residue was dissolved in EtOAc. The combined organic layer was dried and concentrated in vacuo to afford the crude product, which was purified by column chromatography on silica gel (EtOAc/petroleum ether = 2:1, $R_f = 0.4$) to afford 8 (105.4 mg, 68% isolated yield).

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7. Characterization data of Products

**Diethyl 3-(3-chlorophenyl)-1-tosylaziridine-2,2-dicarboxylate (1k)**

[Chemical structure image]

Colorless liquid (petroleum ether/EtOAc = 5:1, 72% isolated yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.97 (d, \(J = 8.4\) Hz, 2H), 7.37 (d, \(J = 8.0\) Hz, 2H), 7.33 (d, \(J = 7.6\) Hz, 1H), 7.24—7.20 (m, 1H), 7.12-7.09 (m, 2H), 5.05 (s, 1H), 4.44—4.38 (q, \(J = 7.2\) Hz, 2H), 3.99—3.87 (m, 2H), 2.46 (s, 3H), 1.38 (t, \(J = 7.2\) Hz, 3H), 0.86 (t, \(J = 7.2\) Hz, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 162.8, 162.3, 145.1, 136.2, 134.1, 130.1, 129.9, 129.4, 129.2, 128.5, 127.9, 126.7, 63.4, 62.2, 56.7, 48.1, 21.8, 13.8, 13.6; HRMS calcd for C\(_{21}\)H\(_{23}\)ClNO\(_6\)S [M+H]\(^+\) 452.0929, found 452.0928.

**Diethyl 3-(o-tolyl)-1-tosylaziridine-2,2-dicarboxylate (1l)**

[Chemical structure image]

White solid (petroleum ether/EtOAc = 5:1, 66% isolated yield); mp:90–93 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.99 (d, \(J = 8.4\) Hz, 2H), 7.37 (d, \(J = 8.0\) Hz, 2H), 7.19—7.14 (m, 1H), 7.11 (d, \(J = 6.8\) Hz, 1H), 7.03 (d, \(J = 4.0\) Hz, 2H), 4.85 (s, 1H), 4.44—4.38 (m, 2H), 3.93—3.85 (m, 2H), 2.47 (s, 3H), 2.43 (s, 3H), 1.38 (t, \(J = 7.0\) Hz, 3H), 0.80 (t, \(J = 7.2\) Hz, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 163.3, 162.7, 145.0, 137.2, 136.2, 129.9, 129.8, 129.3, 128.8, 128.0, 126.7, 125.8, 63.5, 62.2, 56.7, 48.8, 21.9, 18.9, 13.9, 13.6; HRMS calcd for C\(_{22}\)H\(_{26}\)NO\(_6\)S [M+H]\(^+\) 432.1475, found 432.1472.

**Dimethyl 3-(4-chlorophenyl)-1-tosylaziridine-2,2-dicarboxylate (1p)**

[Chemical structure image]

White solid (petroleum ether/EtOAc = 5:1, 75% isolated yield); mp:115–118 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.93 (d, \(J = 8.4\) Hz, 2H), 7.36 (d, \(J = 8.0\) Hz, 2H), 7.25 (d, \(J = 8.4\) Hz, 2H), 7.18 (d, \(J = 8.8\) Hz, 2H), 4.84 (s, 3H), 3.93 (s, 3H), 3.52 (s, 3H), 2.46 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 163.5, 162.9, 145.2, 136.1, 135.1, 130.0, 129.6, 128.9, 128.5, 127.9, 57.4, 54.2, 53.3, 49.0, 21.8; HRMS calcd for C\(_{10}\)H\(_{10}\)ClNO\(_6\)S[M+H]\(^+\) 424.0616, found 424.0617.
(2R,3R,4S,5R,8R)-diethyl 8-(4-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3aa)

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.45$, 54% isolated yield); mp: 129–131 °C; $[\alpha]_D^{20} = -43$ (c 1.0, CH$_2$Cl$_2$);

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.98 (dd, $J = 16.0$, 8.0 Hz, 4H), 5.53 (d, $J = 10.4$ Hz, 2H), 6.98 (dd, $J = 16.0$, 8.0 Hz, 4H), 5.33 (dd, $J = 13.6$, 10.4 Hz, 1H), 3.11 (s, 3H), 2.52 (s, 3H), 1.82 (d, $J = 14.4$ Hz, 1H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.42 (s, 3H), 1.38 (t, $J = 7.2$ Hz, 3H), 1.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.8, 165.5, 143.0, 138.8, 136.6, 133.6, 130.2, 128.7, 128.1, 127.8, 113.3, 110.0, 95.8, 85.6, 81.3, 81.2, 62.7, 62.5, 61.9, 56.9, 42.6, 26.2, 24.9, 21.6, 14.2, 14.1; HRMS calcd for C$_{30}$H$_{37}$ClNO$_{10}$S [M+H]$^+$: 638.1822, found for: 638.1824.

(2R,3R,4S,5R,8R)-diethyl 8-(4-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3aa)

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.37$, 45% isolated yield); mp: 150–152 °C; $[\alpha]_D^{20} = -30$ (c 1.0, CH$_2$Cl$_2$);

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 (d, $J = 8.4$ Hz, 2H), 7.01–6.98 (m, 4H), 6.92 (d, $J = 8.4$ Hz, 2H), 5.05 (t, $J = 7.4$ Hz, 1H), 5.00 (d, $J = 6.4$ Hz, 1H), 4.93 (d, $J = 1.2$ Hz, 1H), 4.56 (dd, $J = 6.4$, 1.2 Hz, 1H), 4.52–4.42 (m, 2H), 4.39–4.27 (m, 2H), 3.41 (s, 3H), 2.72 (dd, $J = 13.2$, 7.2 Hz, 1H), 2.42 (dd, $J = 13.2$, 7.6 Hz, 1H), 2.35 (s, 3H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.41 (t, $J = 7.2$, 3H), 1.33 (s, 3H), 1.21 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.8, 165.5, 143.0, 138.8, 136.6, 133.6, 130.2, 128.7, 128.1, 127.8, 113.3, 110.0, 95.8, 85.6, 81.3, 81.2, 62.7, 62.5, 61.9, 56.9, 42.6, 26.2, 24.9, 21.6, 14.2, 14.1; HRMS calcd for C$_{30}$H$_{37}$ClNO$_{10}$S [M+H]$^+$: 638.1822, found for: 638.1821.

(2R,3R,4S,5R,8S)-diethyl 8-phenyl-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3aa)

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.45$, 62% isolated yield); mp: 110–112 °C; $[\alpha]_D^{20} = -27$ (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 8.4$ Hz, 2H), 7.01–6.98 (m, 4H), 6.92 (d, $J = 8.4$ Hz, 2H), 5.05 (t, $J = 7.4$ Hz, 1H), 5.00 (d, $J = 6.4$ Hz, 1H), 4.93 (d, $J = 1.2$ Hz, 1H), 4.56 (dd, $J = 6.4$, 1.2 Hz, 1H), 4.52–4.42 (m, 2H), 4.39–4.27 (m, 2H), 3.41 (s, 3H), 2.72 (dd, $J = 13.2$, 7.2 Hz, 1H), 2.42 (dd, $J = 13.2$, 7.6 Hz, 1H), 2.35 (s, 3H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.41 (t, $J = 7.2$, 3H), 1.33 (s, 3H), 1.21 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.8, 165.5, 143.0, 138.8, 136.6, 133.6, 130.2, 128.7, 128.1, 127.8, 113.3, 110.0, 95.8, 85.6, 81.3, 81.2, 62.7, 62.5, 61.9, 56.9, 42.6, 26.2, 24.9, 21.6, 14.2, 14.1; HRMS calcd for C$_{30}$H$_{37}$ClNO$_{10}$S [M+H]$^+$: 638.1822, found for: 638.1821.
Hz, 2H), 7.17 (d, J = 6.8 Hz, 2H), 7.05–6.99 (m, 3H), 6.94 (d, J = 8.0 Hz, 2H), 5.60 (d, J = 10.4 Hz, 1H), 5.00 (d, J = 7.2 Hz, 1H), 4.62 (d, J = 2.0 Hz, 1H), 4.53–4.47 (m, 2H), 4.42–4.14 (m, 2H), 4.20–4.14 (m, 1H), 3.34 (dd, J = 13.6, 10.8 Hz, 1H), 3.11 (s, 3H), 2.28 (s, 3H), 1.88 (d, J = 7.2 Hz, 3H), 1.42 (s, 3H), 1.40–1.36 (t, J = 7.2 Hz, 3H), 1.28 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 167.5, 165.8, 142.9, 141.6, 137.6, 128.8, 128.3, 127.7, 127.5, 126.6, 114.5, 108.9, 97.9, 85.1, 83.5, 80.4, 63.8, 62.9, 62.5, 56.6, 42.9, 26.2, 24.8, 21.5, 14.1; HRMS calcd for C30H38NO10S [M+H]+: 604.2212, found for: 604.2213.

(2R,3R,4S,5R,8S)-diethyl 8-phenyl-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ba)

White solid (petroleum ether/EtOAc = 5:1, Rf = 0.36, 37% isolated yield); mp: 99–101 °C; [α]D20 = -50 (c 1.0, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.28 (d, J = 8.0 Hz, 2H), 7.10–7.07 (m, 3H), 7.00–6.93 (m, 4H), 5.09 (t, J = 7.6 Hz, 1H), 5.01 (d, J = 6.4 Hz, 1H), 4.93 (s, 1H), 4.55 (d, J = 1.2 Hz, 1H), 4.54–4.42 (m, 2H), 4.38–4.28 (m, 2H), 3.41 (s, 3H), 2.77 (dd, J = 13.2, 7.2 Hz, 1H), 2.43 (dd, J = 12.8, 7.6 Hz, 1H), 2.31 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.32 (s, 3H), 1.18 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 167.8, 165.6, 142.5, 138.8, 138.0, 128.8, 128.6, 128.1, 127.7, 127.5, 113.2, 110.0, 95.8, 85.5, 81.4, 81.2, 62.6, 62.6, 62.4, 56.9, 42.8, 26.2, 24.8, 21.5, 14.2, 14.0; HRMS calcd for C30H38NO10S [M+H]+: 604.2212, found for: 604.2213.

(2R,3R,4S,5R,8R)-diethyl 8-(4-fluorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3ca)

White solid (petroleum ether/EtOAc = 4:1, Rf = 0.46, 53% isolated yield); mp: 118–120 °C; [α]D20 = -26 (c 1.0, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.47 (d, J = 8.4 Hz, 2H), 7.13 (dd, J = 8.8, 5.6 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.69 (t, J = 8.8 Hz, 2H), 5.57 (d, J = 10.4 Hz, 1H), 4.99 (d, J = 6.8 Hz, 1H), 4.62 (d, J = 2.0 Hz, 1H), 4.20–4.14 (m, 2H), 4.20–4.14 (m, 1H), 3.34 (dd, J = 13.6, 10.8 Hz, 1H), 3.11 (s, 3H), 2.28 (s, 3H), 1.88 (d, J = 7.2 Hz, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.42 (s, 3H), 1.40–1.36 (t, J = 7.2 Hz, 3H), 1.28 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 167.5, 165.8, 142.9, 141.6, 137.6, 128.8, 128.3, 127.7, 127.5, 126.6, 114.5, 108.9, 97.9, 85.1, 83.5, 80.4, 63.8, 62.9, 62.5, 56.6, 42.9, 26.2, 24.8, 21.5, 14.1; HRMS calcd for C30H38NO10S [M+H]+: 604.2212, found for: 604.2213.
1H), 4.54–4.47 (m, 2H), 4.46–4.38 (m, 2H), 4.18–4.14 (m, 1H), 3.33 (dd, $J = 13.6, 10.4$ Hz, 1H), 3.12 (s, 3H), 2.30 (s, 3H), 1.83 (d, $J = 14.0$ Hz, 1H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.41 (s, 3H), 1.38 (t, $J = 7.2$ Hz, 3H), 1.28 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -116.72; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.4, 165.8, 161.7 (d, $J = 14.0$ Hz), 160.5, 143.2, 137.5, 137.4, 129.3 (d, $J = 8.0$ Hz), 128.6 (d, $J = 39.5$ Hz), 114.2 (d, $J = 21.2$ Hz), 114.1, 109.0, 98.0, 85.1, 83.5, 80.3, 63.1, 62.6, 56.7, 43.0, 26.2, 24.8, 21.6, 14.1; HRMS calcd for C$_{30}$H$_{37}$FNO$_{10}$S [M+H]$^+$: 622.2117, found for: 622.2119.

$^{(2R,3R,4S,5R,8S)}$-diethyl 8-(4-fluorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ($^{(8S)}$-3ca)

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.37$, 36% isolated yield); mp:145–147 °C; $[\alpha]_D^{20} = -46$ (c 1.0, CH$_2$Cl$_2$);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, $J = 8.4$ Hz, 2H), 7.04 (dd, $J = 8.4, 5.2$ Hz, 2H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.66 (t, $J = 8.8$ Hz, 2H), 5.07 (t, $J = 7.2$ Hz, 1H), 5.02 (d, $J = 6.4$ Hz, 1H), 4.94 (d, $J = 1.2$ Hz, 1H), 4.56 (dd, $J = 6.4, 1.2$ Hz, 1H), 4.53–4.43 (m, 2H), 3.41 (s, 3H), 2.73 (dd, $J = 12.8, 7.2$ Hz, 1H), 2.41 (dd, $J = 12.8, 7.6$ Hz, 1H), 2.33 (s, 3H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.41 (t, $J = 7.2$, 3H), 1.33 (s, 3H), 1.21 (s, 3H); $^{19}$F NMR (376 MHz, CDCl$_3$) δ -114.97; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.8, 165.6, 162.3 (d, $J = 244.9$ Hz), 142.8, 138.8, 133.6 (d, $J = 2.9$ Hz), 130.4 (d, $J = 8.3$ Hz), 128.6, 128.0, 114.4 (d, $J = 21.3$ Hz), 113.2, 109.9, 95.7, 85.5, 81.3, 81.1, 62.7, 62.4, 61.8, 56.9, 42.6, 26.2, 24.8, 21.5, 14.1, 14.0; HRMS calcd for C$_{30}$H$_{37}$FNO$_{10}$S [M+H]$^+$: 622.2117, found for: 622.2119.

$^{(2R,3R,4S,5R,8R)}$-diethyl 8-(4-bromophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ($^{(8R)}$-3da)

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.46$, 62% isolated yield); mp:102–110 °C; $[\alpha]_D^{20} = -23$ (c 1.0, CH$_2$Cl$_2$);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.01 (t, $J = 8.8$ Hz, 4H), 5.51 (d, $J = 10.4$ Hz, 1H), 4.99 (d, $J = 7.2$ Hz, 1H), 4.62 (d, $J = 2.0$ Hz, 1H), 4.54–4.46 (m, 2H), 4.46–4.38 (m, 2H), 4.20–4.12 (m, 1H), 3.33 (dd, $J = 13.6, 10.4$ Hz, 1H), 3.12 (s, 3H),
2.33 (s, 3H), 1.82 (d, J = 14.0 Hz, 1H), 1.42 (t, J = 7.2 Hz, 3H), 1.42 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H), 1.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 167.3, 165.7, 143.4, 140.8, 137.3, 130.5, 129.5, 128.8, 128.5, 120.4, 114.5, 109.1, 98.1, 85.2, 83.5, 80.4, 63.1, 63.0, 62.6, 56.7, 43.0, 26.2, 24.8, 21.6, 14.1, 14.1; HRMS calcd for C\(_{30}\)H\(_{37}\)BrNO\(_{10}\)S [M+H]\(^+\): 682.1316, found for: 682.1319.

\((2R,3R,4S,5R,8R)\)-diethyl 8-(4-bromophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate (\((8S)\)-3da)

White solid (petroleum ether/EtOAc = 4:1, R\(_f\) = 0.37, 36% isolated yield); mp: 133–136 °C; \([\alpha]_D^{20} = -25\) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.28 (d, J = 5.6 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 5.01 (d, J = 6.8 Hz, 2H), 4.93 (s, 1H), 4.55 (d, J = 6.0 Hz, 1H), 4.52–4.42 (m, 2H), 4.39–4.27 (m, 2H), 4.27–4.25 (m, 2H), 4.39–4.27 (m, 2H), 3.41 (s, 3H), 2.71 (dd, J = 12.8, 7.2 Hz, 1H), 2.40 (dd, J = 12.8, 7.6 Hz, 1H), 2.36 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.2, 3H), 1.34 (s, 3H), 1.21 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 167.8, 165.5, 143.0, 138.8, 136.9, 130.7, 130.5, 128.7, 128.0, 121.8, 113.3, 109.9, 95.7, 85.6, 81.3, 81.2, 62.7, 62.5, 61.9, 56.9, 42.5, 26.2, 24.9, 21.6, 14.2, 14.0; HRMS calcd for C\(_{30}\)H\(_{37}\)BrNO\(_{10}\)S [M+H]\(^+\): 682.1316, found for: 682.1318.

\((2R,3R,4S,5R,8R)\)-diethyl 8-(4-cyanophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate (\((8R)\)-3ea)

White solid (petroleum ether/EtOAc = 4:1, R\(_f\) = 0.34, 71% isolated yield); mp: 212–214 °C; \([\alpha]_D^{20} = -52\) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.54 (d, J = 8.4 Hz, 2H), 7.29–7.22 (m, 4H), 7.01 (d, J = 8.4 Hz, 2H), 5.59 (d, J = 10.4 Hz, 1H), 4.98 (d, J = 7.2 Hz, 1H), 4.55 (d, J = 2.4 Hz, 1H), 4.55–4.47 (m, 2H), 4.45–4.39 (m, 2H), 4.18–4.14 (m, 1H), 3.38 (dd, J = 13.6, 10.4 Hz, 1H), 3.06 (s, 3H), 2.33 (s, 3H), 1.83 (d, J = 14.0 Hz, 1H), 1.42 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 167.1, 165.8, 147.4, 143.7, 137.0, 131.2, 128.8, 128.6, 128.2, 119.1, 114.5, 110.1, 109.1, 98.2, 85.1, 83.5, 80.2, 63.1, 63.0, 62.7, 56.6, 43.3, 26.1, 24.7, 21.6, 14.0, 14.0; HRMS calcd for...
C$_{31}$H$_{37}$N$_2$O$_{10}$S [M+H]$^+$: 629.2163, found for: 629.2167.

(2R,3R,4S,5R,8R)-diethyl 8-(4-cyanophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ea)

White solid (petroleum ether/EtOAc = 4:1, $R_f$ = 0.31, 25% isolated yield); mp: 170–172 °C; [α]$_{D}^{20}$ = -42 (c 1.0, CH$_2$Cl$_2$);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 5.19 (dd, $J = 8.0$, 1.2 Hz, 1H), 4.91 (d, $J = 1.2$ Hz, 1H), 4.86 (d, $J = 6.30$ Hz, 1H), 4.56–4.42 (m, 3H), 4.36–4.28 (m, 2H), 3.39 (s, 3H), 2.56–2.42 (m, 2H), 2.36 (s, 3H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.41 (t, $J = 7.2$, 3H), 1.27 (s, 3H), 1.11 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.7, 165.5, 144.7, 143.5, 138.1, 131.4, 128.9, 128.8, 128.3, 118.8, 113.1, 111.0, 110.2, 96.2, 85.8, 81.4, 81.2, 62.8, 62.6, 61.6, 56.8, 42.2, 26.1, 24.7, 21.6, 14.1, 14.0;

HRMS calcd for C$_{31}$H$_{37}$N$_2$O$_{10}$S [M+H]$^+$: 629.2163, found for: 629.2165.

(2R,3R,4S,5R,8R)-diethyl 8-(4-nitrophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3fa)

White solid (petroleum ether/EtOAc = 4:1, $R_f$ = 0.36, 70% isolated yield); mp: 121–125 °C; [α]$_{D}^{20}$ = -26 (c 1.0, CH$_2$Cl$_2$);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 8.8$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 5.63 (d, $J = 10.4$ Hz, 1H), 4.99 (d, $J = 6.8$ Hz, 1H), 4.57–4.48 (m, 3H), 4.46–4.40 (m, 2H), 4.21–4.13 (m, 1H), 3.41 (dd, $J = 13.6$, 10.4 Hz, 1H), 3.07 (s, 3H), 2.30 (s, 3H), 1.85 (d, $J = 14.0$ Hz, 1H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.41 (s, 3H), 1.41 (t, $J = 7.2$ Hz, 3H), 1.29 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.1, 165.8, 149.5, 146.5, 143.9, 137.0, 128.9, 128.7, 128.3, 122.6, 114.5, 109.2, 98.4, 85.2, 83.5, 80.3, 63.1, 62.9, 62.8, 56.6, 43.4, 26.2, 24.7, 21.6, 14.1, 14.1; HRMS calcd for C$_{30}$H$_{37}$N$_2$O$_{12}$S [M+H]$^+$: 649.2062, found for: 649.2064.

(2R,3R,4S,5R,8R)-diethyl 8-(4-nitrophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3fa)

White solid (petroleum ether/EtOAc = 4:1, $R_f$ = 0.31, 27% isolated yield); mp: 146–151 °C; [α]$_{D}^{20}$ = -42 (c 1.0, CH$_2$Cl$_2$);

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 5.19 (dd, $J = 8.0$, 1.2 Hz, 1H), 4.91 (d, $J = 1.2$ Hz, 1H), 4.86 (d, $J = 6.30$ Hz, 1H), 4.56–4.42 (m, 3H), 4.36–4.28 (m, 2H), 3.39 (s, 3H), 2.56–2.42 (m, 2H), 2.36 (s, 3H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.41 (t, $J = 7.2$, 3H), 1.27 (s, 3H), 1.11 (s, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.7, 165.5, 144.7, 143.5, 138.1, 131.2, 128.9, 128.8, 128.3, 118.8, 113.1, 111.0, 110.2, 96.2, 85.8, 81.4, 81.2, 62.8, 62.6, 61.6, 56.8, 42.2, 26.1, 24.7, 21.6, 14.1, 14.0; HRMS calcd for C$_{31}$H$_{37}$N$_2$O$_{10}$S [M+H]$^+$: 629.2163, found for: 629.2165.
148 °C; [α]D 20 = -44 (c 1.0, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.84 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 5.22 (dd, J = 8.0, 5.6 Hz, 1H), 4.92 (d, J = 6.4 Hz, 2H), 4.56–4.43 (m, 3H), 4.38–4.29 (m, 2H), 3.40 (s, 3H), 2.74–2.61 (m, 2H), 2.34 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.27 (s, 3H), 1.13 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 167.8, 165.4, 147.1, 146.6, 143.7, 138.1, 129.1, 128.8, 128.3, 122.8, 113.2, 110.2, 96.2, 85.8, 62.9, 62.7, 61.4, 56.9, 42.3, 26.2, 24.8, 21.6, 14.2, 14.0; HRMS calcd for C30H37N2O12S [M+H]+: 649.2062, found for: 649.2064.

(2R,3R,4S,5R,8R)-diethyl 8-(4-trifluoromethylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3ga)

White solid (petroleum ether/EtOAc = 4:1, Rf = 0.45, 60% isolated yield); mp: 120–124°C; [α]D 20 = -16 (c 1.0, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.50 (d, J = 6.8 Hz, 2H), 7.26–7.20 (m, 4H), 6.94 (d, J = 7.2 Hz, 2H), 5.58 (d, J = 10.4 Hz, 1H), 5.00–4.99 (m, 1H), 4.61 (s, 1H), 4.54–4.40 (m, 4H), 4.24–4.13 (m, 1H), 3.37 (t, J = 12.4 Hz, 1H), 3.11 (d, J = 1.6 Hz, 3H), 2.27 (s, 3H), 1.86 (d, J = 13.6 Hz, 1H), 1.43 (t, J = 7.2 Hz, 3H), 1.42 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.28 (s, 3H); 19F NMR (376 MHz, CDCl3) δ -62.48; 13C NMR (100 MHz, CDCl3) δ 167.2, 165.7, 145.8, 143.5, 137.1, 128.8, 128.5, 128.4, 128.0, 124.3 (q, J = 3.7 Hz), 114.5, 109.1, 98.2, 85.2, 83.5, 80.3, 63.1, 63.0, 62.6, 56.6, 43.0, 26.2, 24.8, 21.4, 14.1, 14.1; HRMS calcd for C31H37F3NO10S [M+H]+: 672.2085, found for: 672.2086.

(2R,3R,4S,5R,8R)-diethyl 8-(4-trifluoromethylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ga)

White solid (petroleum ether/EtOAc = 4:1, Rf = 0.38, 26% isolated yield); mp: 128–130 °C; [α]D 20 = -34 (c 1.0, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.28 (d, J = 8.8 Hz, 2H), 7.21–7.16 (m, 4H), 6.93 (d, J = 8.0 Hz, 2H), 5.15 (t, J = 7.2 Hz, 1H), 5.00 (d, J = 6.4 Hz, 1H), 4.94 (d, J = 1.2 Hz, 1H), 4.56 (dd, J = 6.4, 1.2
Hz, 1H), 4.54–4.43 (m, 2H), 4.39–4.29 (m, 2H), 3.41 (s, 3H), 2.74 (dd, J = 13.2, 6.4 Hz, 1H), 2.50 (dd, J = 13.2, 8.0 Hz, 1H), 2.31 (s, 3H), 1.43 (t, J = 7.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.31 (s, 3H), 1.18 (s, 3H); 19F NMR (376 MHz, CDCl3) δ -62.66; 13C NMR (100 MHz, CDCl3) δ 167.8, 165.5, 143.1, 142.3, 138.5, 129.0, 128.7, 128.0, 124.5, 124.5, 113.3, 110.1, 95.9, 85.6, 81.4, 81.2, 62.8, 62.5, 61.8, 56.9, 42.4, 26.2, 24.8, 21.4, 14.2, 14.0; HRMS calcd for C31H37F3NO10 [M+H]+: 672.2085, found for: 672.2089.

(2R,3R,4S,5R,8R)-diethyl 8-(4-methylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3ha)

White solid (petroleum ether/EtOAc = 4:1, Rf = 0.46, 55% isolated yield); mp:130–132 °C; [α]D20 = -32 (c 1.0, CH2Cl2);

1H NMR (400 MHz, CDCl3) δ 7.41 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 7.6 Hz, 2H), 6.55 (d, J = 10.4 Hz, 2H), 5.00 (d, J = 6.8 Hz, 1H), 4.66 (d, J = 1.6 Hz, 1H), 4.53–4.47 (m, 2H), 4.45–4.39 (m, 2H), 4.19–4.11 (m, 1H), 3.32 (dd, J = 13.6, 10.8 Hz, 1H), 3.15 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 1.86 (d, J = 13.6 Hz, 1H), 1.42 (t, J = 7.2 Hz, 3H), 1.40 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H), 1.28 (s, 3H); 13C NMR (400 MHz, CDCl3) δ 167.6, 165.7, 142.1, 138.9, 137.4, 134.2, 128.9, 128.3, 128.2, 127.8, 114.4, 109.0, 97.9, 85.1, 83.5, 80.4, 63.7, 62.8, 62.4, 56.6, 42.9, 29.8, 26.2, 24.8, 21.5, 21.1, 14.1; HRMS calcd for C30H40F3NO10S [M+H]+: 618.2367, found for: 618.2369.

(2R,3R,4S,5R,8R)-diethyl 8-(4-methylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ha)

White solid (petroleum ether/EtOAc = 4:1, Rf = 0.33, 43% isolated yield); mp:162–174 °C; [α]D20 = -34 (c 1.0, CH2Cl2);

1H NMR (400 MHz, CDCl3) δ 7.23 (d, J = 7.6 Hz, 2H), 6.92 (dd, J = 10.8, 6.8 Hz, 4H), 6.77 (d, J = 6.4 Hz, 2H), 5.07 (d, J = 6.0 Hz, 1H), 4.97 (t, J = 7.4 Hz, 1H), 4.94 (s, 1H), 4.54 (d, J = 6.4 Hz, 1H), 4.49–4.41 (m, 2H), 4.39–4.26 (m, 2H), 3.41 (s, 3H), 2.81–2.76 (m, 1H), 2.32 (s, 4H), 2.24 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.41 (s, 3H), 1.35 (s, 3H), 1.24 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 167.7, 165.4, 142.1, 138.9, 137.4, 134.2, 128.9, 128.3, 128.2,
127.8, 113.2, 109.5, 95.4, 85.3, 81.1, 81.0, 62.5, 62.5, 62.2, 56.8, 42.9, 29.7, 26.0, 24.7, 21.4, 21.1, 14.0, 13.9; HRMS calcd for C\textsubscript{30}H\textsubscript{40}NO\textsubscript{10}S [M+H]\textsuperscript{+}: 618.2367, found for: 618.2369.

\((2R,3R,4S,5R,8R)\)-diethyl 8-(4-methoxyphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3ia)

White solid (petroleum ether/EtOAc = 4:1, \(R_f = 0.45\), 58% isolated yield); mp:102–104 °C; \([\alpha]_D^{20} = -34\) (c 1.0, CH\textsubscript{2}Cl\textsubscript{2});

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.41 (d, \(J = 8.4\) Hz, 2H), 7.07 (d, \(J = 8.0\) Hz, 2H), 6.94 (d, \(J = 8.0\) Hz, 2H), 5.54 (d, \(J = 10.8\) Hz, 1H), 5.00 (d, \(J = 6.8\) Hz, 1H), 4.66 (d, \(J = 1.6\) Hz, 1H), 4.51–4.47 (m, 2H), 4.45–4.39 (m, 2H), 3.35 (dd, \(J = 13.2, 10.8\) Hz, 1H), 3.15 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), 1.86 (d, \(J = 13.6\) Hz, 1H), 1.42 (t, \(J = 7.2\) Hz, 3H), 1.40 (s, 3H), 1.37 (t, \(J = 7.2\) Hz, 3H), 1.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 167.6, 165.7, 142.8, 138.7, 137.8, 136.2, 128.8, 128.2, 127.8, 114.5, 109.0, 98.0, 85.2, 83.5, 80.5, 63.8, 62.9, 62.4, 56.7, 42.9, 26.2, 24.9, 21.5, 21.1, 14.1; HRMS calcd for C\textsubscript{31}H\textsubscript{40}NO\textsubscript{11}S [M+H]\textsuperscript{+}: 634.2317, found for: 634.2321.

\((2R,3R,4S,5R,8R)\)-diethyl 8-(2-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ia)

White solid (petroleum ether/EtOAc = 4:1, \(R_f = 0.37\), 41% isolated yield); mp:120–122 °C; \([\alpha]_D^{20} = -37\) (c 1.0, CH\textsubscript{2}Cl\textsubscript{2});

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.23 (d, \(J = 8.4\) Hz, 2H), 6.95 (dd, \(J = 17.2, 8.0\) Hz, 4H), 5.07 (d, \(J = 6.4\) Hz, 1H), 4.99 (t, \(J = 7.6\) Hz, 1H), 4.94 (d, \(J = 1.2\) Hz, 1H), 4.56 (dd, \(J = 6.8, 1.6\) Hz, 1H), 4.51–4.22 (m, 2H), 4.41–4.26 (m, 2H), 3.41 (s, 3H), 2.78 (dd, \(J = 13.2, 8.4\) Hz, 1H), 2.32 (s, 3H), 2.31–2.28 (m, 1H), 2.24 (s, 3H), 1.42 (t, \(J = 7.2\) Hz, 3H), 1.40 (t, \(J = 7.2\) Hz, 3H), 1.35 (s, 3H), 1.24 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 167.8, 165.5, 142.2, 139.0, 137.5, 134.3, 129.0, 128.4, 128.3, 127.9, 113.3, 109.6, 95.6, 85.4, 81.2, 81.1, 62.6, 62.6, 62.3, 56.9, 43.0, 26.2, 24.8, 21.5, 21.2, 14.1, 14.0; HRMS calcd for C\textsubscript{31}H\textsubscript{40}NO\textsubscript{11}S [M+H]\textsuperscript{+}: 634.2317, found for: 634.2318.

\((2R,3R,4S,5R,8R)\)-diethyl 8-(2-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-
7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3ja)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.45 \), 34% isolated yield); mp:169–171 °C; \([\alpha]_D^{20} = -8 \) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (d, \( J = 8.0 \) Hz, 2H), 7.21 (dd, \( J = 7.6 \), 0.8 Hz, 1H), 7.14 (dd, \( J = 8.0 \), 1.2 Hz, 1H), 7.00 (d, \( J = 8.0 \) Hz, 2H), 6.95 (td, \( J = 7.6 \), 1.6 Hz, 1H), 6.60 (td, \( J = 8.0 \), 0.8 Hz, 1H), 5.86 (d, \( J = 10.0 \) Hz, 1H), 4.98 (d, \( J = 6.8 \) Hz, 1H), 4.56–4.50 (m, 2H), 4.48–4.41 (m, 3H), 4.21–4.13 (m, 1H), 3.35 (dd, \( J = 13.6 \), 10.0 Hz, 1H), 3.01 (s, 3H), 2.29 (s, 3H), 1.90 (d, \( J = 13.6 \) Hz, 1H), 1.43 (d, \( J = 7.2 \) Hz, 1H), 1.42 (d, \( J = 7.2 \) Hz, 1H), 1.40 (t, \( J = 7.2 \) Hz, 3H), 1.28 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.2, 166.1, 143.3, 138.5, 137.0, 131.6, 130.4, 128.9, 128.5, 127.7, 125.2, 114.6, 108.9, 98.0, 85.1, 83.6, 80.4, 63.0, 62.6, 61.1, 56.5, 41.8, 26.2, 24.8, 21.6, 14.1, 14.1; HRMS calcd for C\(_{30}\)H\(_{37}\)ClNO\(_{10}\)S\([\text{M+H}]^+\): 638.1822, found for: 638.1823.

(2R,3R,4S,5R,8R)-diethyl 8-(2-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ja)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.39 \), 61% isolated yield); mp:100–102 °C; \([\alpha]_D^{20} = -80 \) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (d, \( J = 8.0 \) Hz, 1H), 7.05 (d, \( J = 8.0 \) Hz, 2H), 7.00 (t, \( J = 7.8 \) Hz, 2H), 6.70 (t, \( J = 7.6 \) Hz, 1H), 5.66 (d, \( J = 7.2 \) Hz, 1H), 4.86 (s, 1H), 4.62–4.50 (m, 1H), 4.50–4.40 (m, 3H), 4.38–4.23 (m, 2H), 3.35 (s, 3H), 2.99 (dd, \( J = 12.4 \), 9.6 Hz, 1H), 2.75 (dd, \( J = 12.8 \), 2.4 Hz, 1H), 2.32 (s, 3H), 1.43 (t, \( J = 7.2 \) Hz, 3H), 1.42 (t, \( J = 7.2 \) Hz, 3H), 1.19 (s, 3H), 0.90 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.9, 165.8, 143.3, 138.5, 137.0, 131.6, 130.4, 128.9, 128.5, 127.7, 125.2, 114.6, 108.9, 98.0, 85.1, 83.6, 80.4, 63.0, 62.6, 61.1, 56.5, 41.8, 26.2, 24.8, 21.6, 14.1, 14.1; HRMS calcd for C\(_{30}\)H\(_{37}\)ClNO\(_{10}\)S\([\text{M+H}]^+\): 638.1822, found for: 638.1828.

(2R,3R,4S,5R,8R)-diethyl 8-(3-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ja)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.45 \), 75% isolated yield); mp:168–170 °C; \([\alpha]_D^{20} = -8 \) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.57 (d, \( J = 8.4 \) Hz, 1H), 7.42 (d, \( J = 8.4 \) Hz, 2H), 7.22 (d, \( J = 8.8 \) Hz, 2H), 6.97 (d, \( J = 8.8 \) Hz, 2H), 6.88 (d, \( J = 8.8 \) Hz, 2H), 6.70 (t, \( J = 7.6 \) Hz, 1H), 5.66 (d, \( J = 7.2 \) Hz, 1H), 4.86 (s, 1H), 4.62–4.50 (m, 1H), 4.50–4.40 (m, 3H), 4.38–4.23 (m, 2H), 3.35 (s, 3H), 2.99 (dd, \( J = 12.4 \), 9.6 Hz, 1H), 2.75 (dd, \( J = 12.8 \), 2.4 Hz, 1H), 2.32 (s, 3H), 1.43 (t, \( J = 7.2 \) Hz, 3H), 1.42 (t, \( J = 7.2 \) Hz, 3H), 1.19 (s, 3H), 0.90 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.9, 165.8, 143.3, 137.6, 137.5, 132.2, 129.1, 128.7, 128.7, 128.0, 125.6, 112.6, 110.7, 97.1, 86.0, 82.1, 81.3, 62.6, 62.6, 56.4, 40.5, 26.2, 24.5, 21.6, 14.1, 14.0; HRMS calcd for C\(_{30}\)H\(_{37}\)ClNO\(_{10}\)S\([\text{M+H}]^+\): 638.1822, found for: 638.1828.
2H), 7.21 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.15 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 2H), 6.95 (td, $J = 7.6, 1.6$ Hz, 1H), 6.63–6.59 (m, 1H), 5.86 (d, $J = 10.0$ Hz, 1H), 4.98 (d, $J = 6.8$ Hz, 1H), 4.56–4.41 (m, 5H), 4.21–4.15 (m, 1H), 3.35 (dd, $J = 13.6, 10.0$ Hz, 1H), 3.01 (s, 3H), 2.29 (s, 3H), 1.90 (d, $J = 14.0$ Hz, 1H), 1.44 (s, 3H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.2, 166.1, 143.3, 138.5, 137.1, 131.6, 130.4, 128.9, 128.6, 128.5, 127.7, 125.2, 114.6, 109.0, 98.1, 85.1, 83.6, 80.4, 63.0, 62.6, 61.1, 56.5, 41.9, 24.8, 21.6, 14.1, 14.1; HRMS calcd for C$_{30}$H$_{37}$ClNO$_{10}$S [M+H]$^+$: 638.1822, found for: 638.1825.

(2R,3R,4S,5R,8R)-diethyl 8-(3-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ka)

White solid (petroleum ether/EtOAc = 4:1, $R_f$ = 0.37, 24% isolated yield); mp:122–124 °C; [α]$_D^{20}$ = -71 (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 2H), 7.02–6.97 (m, 2H), 6.70 (t, $J = 7.2$ Hz, 1H), 5.66 (dd, $J = 9.2, 2.0$ Hz, 1H), 4.86 (d, $J = 1.6$ Hz, 1H), 4.60–4.56 (m, 1H), 4.50–4.39 (m, 3H), 4.38–4.25 (m, 2H), 3.35 (s, 3H), 3.02–2.96 (m, 1H), 2.75 (dd, $J = 12.8, 2.4$ Hz, 1H), 2.33 (s, 3H), 1.43 (t, $J = 7.2$, 3H), 1.42 (t, $J = 7.2$, 3H), 1.19 (s, 3H), 0.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 165.8, 143.4, 137.6, 137.5, 132.3, 129.1, 128.8, 128.7, 128.0, 125.6, 112.6, 110.7, 97.1, 86.1, 82.1, 81.3, 62.6, 62.6, 59.1, 56.5, 40.5, 26.2, 24.5, 21.6, 14.2, 14.0; HRMS calcd for C$_{30}$H$_{37}$ClNO$_{10}$S [M+H]$^+$: 638.1822, found for: 638.1828.

(2R,3R,4S,5R,8R)-diethyl 8-(2-methylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3la)

White solid (petroleum ether/EtOAc = 4:1, $R_f$ = 0.46, 58% isolated yield); mp:165–168 °C; [α]$_D^{20}$ = -7 (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 8.2$ Hz, 2H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.96–6.90 (m, 3H), 6.57 (t, $J = 7.4$ Hz, 1H), 5.77 (d, $J = 10.4$ Hz, 1H), 5.00 (d, $J = 6.8$ Hz, 1H), 4.59 (d, $J = 1.6$ Hz, 1H), 4.26–4.11 (m, 5H), 4.10–4.05 (m, 1H), 3.73 (dd, $J = 13.6, 10.0$ Hz, 1H), 3.01 (s, 3H), 2.33 (t, $J = 7.2$ Hz, 3H), 1.42 (t, $J = 7.2$, 3H), 1.19 (s, 3H), 0.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.9, 165.8, 143.4, 137.6, 137.5, 132.3, 129.1, 128.8, 128.7, 128.0, 125.6, 112.6, 110.7, 97.1, 86.1, 82.1, 81.3, 62.6, 62.6, 59.1, 56.5, 40.5, 26.2, 24.5, 21.6, 14.2, 14.0; HRMS calcd for C$_{30}$H$_{37}$ClNO$_{10}$S [M+H]$^+$: 638.1822, found for: 638.1828.
(2R,3R,4S,5R,8R)-diethyl 8-(2-methylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3la)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.28 \), 39% isolated yield); mp:110–112 °C; \([\alpha]_D^{20} = -26 \) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.29 (d, \( J = 8.0 \) Hz, 2H), 7.02 (d, \( J = 7.6 \) Hz, 1H), 6.95 (d, \( J = 8.0 \) Hz, 3H), 6.84 (d, \( J = 7.6 \) Hz, 1H), 6.54 (t, \( J = 7.4 \) Hz, 1H), 5.46 (t, \( J = 6.8 \) Hz, 1H), 4.91 (d, \( J = 6.4 \) Hz, 1H), 4.86 (d, \( J = 6.4 \) Hz, 1H), 4.57–4.51 (m, 2H), 4.49–4.43 (m, 1H), 4.37–4.28 (m, 2H), 3.40 (s, 3H), 2.69–2.55 (m, 2H), 2.36 (s, 3H), 2.30 (s, 3H), 1.42 (t, \( J = 7.2 \) Hz, 3H), 1.42 (t, \( J = 7.2 \) Hz, 3H), 1.26 (s, 3H), 1.09 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 167.8, 165.7, 142.8, 141.4, 137.6, 138.4, 136.4, 135.7, 129.9, 128.5, 128.2, 127.9, 126.9, 125.1, 112.9, 110.2, 96.3, 85.6, 81.6, 81.2, 62.5, 62.4, 58.4, 56.7, 41.7, 26.2, 24.6, 21.5, 19.7, 14.2, 14.0; HRMS calcd for C\(_{30}\)H\(_{40}\)NO\(_{10}\)S [M+H]\(^+\): 618.2367, found for: 618.2367.

(2R,3R,4S,5R,8R)-diethyl 8-(3-methylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3ma)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.46 \), 65% isolated yield); mp:167–169 °C; \([\alpha]_D^{20} = -13 \) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 (d, \( J = 8.4 \) Hz, 2H), 6.96–6.92 (m, 5H), 6.85 (d, \( J = 6.4 \) Hz, 1H), 5.57 (d, \( J = 10.8 \) Hz, 1H), 5.00 (d, \( J = 7.2 \) Hz, 1H), 4.65 (s, 1H), 4.54–4.48 (m, 2H), 4.46–4.39 (m, 2H), 4.20–4.12 (m, 1H), 3.33 (dd, \( J = 13.6, 10.8 \) Hz, 1H), 3.13 (s, 3H), 2.28 (s, 3H), 2.03 (s, 3H), 1.88 (d, \( J = 14.0 \) Hz, 1H), 1.43 (t, \( J = 7.2 \) Hz, 1H), 1.41 (s, 3H), 1.38 (t, \( J = 7.2 \) Hz, 3H), 1.28 (s, 3H); \(^{13}\)C NMR (100 MHz,CDCl\(_3\)) \( \delta \) 167.6, 165.7, 142.8, 141.4, 137.6, 137.0, 128.8, 128.7, 128.1, 127.5, 127.2, 124.6, 114.4, 109.0, 98.1, 85.2, 83.5,
80.5, 63.8, 62.9, 62.4, 56.5, 42.9, 26.2, 24.8, 21.5, 21.2, 14.1; HRMS calcd for C₃₀H₄₀NO₁₀S [M+H]⁺: 618.2367, found for: 618.2371.

(2R,3R,4S,5R,8R)-diethyl 8-(3-methylphenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8S)-3ma)

White solid (petroleum ether/EtOAc = 4:1, Rᵣ = 0.36, 34% isolated yield); mp: 120–123 °C; [α]D²⁰ = -55 (c 1.0, CH₂Cl₂);

¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 8.4 Hz, 2H), 6.94 (dd, J = 10.4, 6.0 Hz, 4H), 6.88 (d, J = 6.4 Hz, 1H), 6.77(s, 1H), 5.11 (d, J = 6.4, 1.6 Hz, 1H), 5.03 (t, J = 7.6 Hz, 1H), 4.93 (d, J = 1.6 Hz, 1H), 4.56 (dd, J = 13.2, 7.6 Hz, 1H), 2.35 (dd, J = 13.2, 7.6 Hz, 1H), 2.31 (s, 3H), 2.01 (s, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.42 (t, J = 7.2 Hz, 3H), 1.34 (s, 3H), 1.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 165.6, 142.2, 139.0, 137.1, 129.4, 128.3, 127.8, 126.6, 113.1, 109.9, 95.4, 85.3, 81.2, 80.9, 62.5, 62.5, 62.3, 56.8, 42.4, 26.2, 24.8, 21.4, 21.0, 14.1, 14.0; HRMS calcd for C₃₀H₄₀NO₁₀S [M+H]⁺: 618.2367, found for: 618.2371.

(2R,3R,4S,5R,8R)-diethyl 8-(naphthalen-1-yl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ((8R)-3na)

White solid (petroleum ether/EtOAc = 4:1, Rᵣ = 0.42, 63% isolated yield); mp: 150–152 °C; [α]D²⁰ = -8 (c 1.0, CH₂Cl₂);

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.58–7.53 (m, 2H), 7.51–7.47 (m, 3H), 7.27 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 8.0 Hz, 2H), 6.84 (t, J = 7.8 Hz, 1H), 6.36 (d, J = 10.0 Hz, 1H), 5.00 (d, J = 6.8 Hz, 1H), 4.60–4.52 (m, 1H), 4.51 – 4.44 (m, 3H), 4.39 (d, J = 2.4 Hz, 1H), 4.23 - 4.15 (m, 1H), 3.53 (dd, J = 13.6, 10.4 Hz, 1H), 2.97 (s, 3H), 2.28 (s, 3H), 2.01 (d, J = 13.6 Hz, 1H), 1.47 (t, J = 7.2 Hz, 3H), 1.41 (t, J = 7.0 Hz, 3H), 1.37 (s, 3H), 1.26 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.6, 166.2, 143.2, 137.4, 135.6, 133.5, 130.1, 129.0, 129.0, 128.4, 126.9, 126.4, 126.0, 125.1, 124.6, 122.9, 114.5, 109.0, 98.0, 85.0, 83.7, 80.6, 63.0, 62.6, 60.9, 56.5, 42.1, 26.2, 24.8, 21.5, 14.1, 14.1; HRMS calcd for C₃₄H₄₀NO₁₀S [M+H]⁺: 654.2367, found for: 654.2368.

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White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.36 \), 22\% isolated yield); mp: 168–170 °C; \([\alpha]_D^{20} = -46 \) (c 1.0, CH\( _2 \)Cl\(_2 \));

\(^1\)H NMR (400 MHz, CDCl\(_3 \)) \( \delta \) 7.94 (d, \( J = 8.4 \) Hz, 1H), 7.80 (d, \( J = 8.0 \) Hz, 1H), 7.56–7.45 (m, 5H), 7.06 (d, \( J = 7.2 \) Hz, 1H), 6.97 (d, \( J = 8.0 \) Hz, 2H), 6.85 (t, \( J = 7.6 \) Hz, 1H), 6.18 (d, \( J = 8.8 \) Hz, 1H), 4.81 (s, 1H), 4.66–4.58 (m, 1H), 4.53–4.37 (m, 4H), 4.31–4.23 (m, 1H), 3.36 (s, 3H), 3.20 (dd, \( J = 12.0 \) Hz, 1H), 2.84 (d, \( J = 12.0 \) Hz, 1H), 2.30 (s, 3H), 1.47 (t, \( J = 7.2 \) Hz, 3H), 1.44 (t, \( J = 7.2 \) Hz, 3H), 0.85 (s, 3H), 0.73 (s, 3H); \(^{13}\)C NMR (400 MHz, CDCl\(_3 \)) \( \delta \) 168.0, 166.3, 143.2, 137.7, 135.1, 133.7, 130.8, 128.8, 128.7, 128.5, 127.3, 125.9, 125.2, 124.7, 124.4, 123.2, 112.3, 110.9, 97.3, 86.0, 82.4, 81.4, 62.6, 62.5, 58.6, 56.4, 41.1, 29.8, 25.9, 24.3, 21.6, 14.2, 14.1; HRMS calcd for C\(_{34}\)H\(_{40}\)NO\(_{10}\)S [M+H]\(^+\): 654.2367, found for: 654.2369.

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.45 \), 50\% isolated yield); mp: 138–142 °C; \([\alpha]_D^{20} = -32 \) (c 1.0, CH\( _2 \)Cl\(_2 \));

\(^1\)H NMR (400 MHz, CDCl\(_3 \)) \( \delta \) 7.51 (d, \( J = 8.4 \) Hz, 2H), 7.30 (d, \( J = 8.4 \) Hz, 2H), 5.47 (d, \( J = 10.8 \) Hz, 1H), 5.01 (d, \( J = 6.8 \) Hz, 1H), 4.81 (d, \( J = 1.2 \) Hz, 1H), 4.55 (dd, \( J = 6.8 \), 1.2 Hz, 1H), 4.53–4.45 (m, 1H), 4.38–4.32 (m, 2H), 4.23–4.15 (m, 1H), 3.32 (s, 3H), 3.30–3.27 (m, 1H), 2.94 (s, 3H), 1.83 (d, \( J = 14.0 \) Hz, 1H), 1.42(s, 3H), 1.39 (t, \( J = 6.8 \) Hz, 3H), 1.37 (t, \( J = 6.6 \) Hz, 3H), 1.29 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3 \)) \( \delta \) 167.4, 166.2, 140.5, 133.4, 129.5, 128.5, 114.4, 109.3, 98.4, 85.4, 83.4, 80.2, 63.1, 63.0, 62.8, 56.7, 43.6, 42.5, 26.2, 24.8, 14.0; HRMS calcd for C\(_{24}\)H\(_{33}\)ClNO\(_{10}\)S [M+H]\(^+\): 562.1508, found for: 562.1508.

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.38 \), 45\% isolated yield); mp: 110–
112 °C; [α]$_D^{20}$ = -58 (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (dd, J = 8.4, 6.0 Hz, 4H), 5.16 (dd, J = 8.4, 6.0 Hz, 1H), 4.94 (d, J = 24.4, 8.4 Hz, 4H), 4.86 (d, J = 6.4 Hz, 1H), 4.56 (dd, J = 6.4, 1.6 Hz, 1H), 4.52–4.18 (m, 4H), 3.37 (s, 3H), 2.97 (s, 3H), 2.79–2.62 (m, 2H), 1.40 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.34 (s, 3H), 1.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.9, 165.6, 139.1, 133.7, 129.2, 128.5, 113.4, 110.1, 96.7, 86.1, 81.5, 81.4, 62.8, 62.6, 62.0, 56.6, 42.8, 42.6, 26.2, 24.8, 14.1, 14.0; HRMS calcd for C$_{24}$H$_{33}$ClNO$_{10}$S [M+H]$^+$: 562.1508, found for: 562.1508.

(2R,3R,4S,5R,8R)-dimethyl 8-(4-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ([8R]-3pa)

White solid (petroleum ether/EtOAc = 4:1, R$_f$ = 0.33, 52% isolated yield); mp: 118–120 °C; [α]$_D^{20}$ = -43 (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.99 (dd, J = 14.4, 8.0 Hz, 4H), 5.55 (d, J = 10.4 Hz, 1H), 4.94 (d, J = 6.8 Hz, 1H), 4.65 (d, J = 1.6 Hz, 1H), 4.49 (dd, J = 6.8, 2.0 Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.33 (dd, J = 13.6, 10.8 Hz, 1H), 3.14 (s, 3H), 2.32 (s, 3H), 1.84 (d, J = 13.6 Hz, 1H), 1.41 (s, 3H), 1.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.1, 166.2, 143.5, 140.1, 137.2, 132.4, 129.1, 128.8, 128.4, 127.6, 114.4, 109.4, 98.5, 85.3, 83.7, 80.5, 63.1, 56.6, 53.8, 53.2, 43.1, 26.2, 24.8, 21.5; HRMS calcd for C$_{28}$H$_{33}$ClNO$_{10}$S [M+H]$^+$: 610.1508, found for: 610.1509.

(2R,3R,4S,5R,8R)-Dimethyl 8-(4-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-7-tosyl-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate ([8S]-3pa)

White solid (petroleum ether/EtOAc = 4:1, R$_f$ = 0.26, 47% isolated yield); mp: 144–146 °C; [α]$_D^{20}$ = -25 (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, J = 6.8 Hz, 2H), 7.01–6.99 (m, 4H), 6.93 (d, J = 8.4 Hz, 2H), 5.03 (t, J = 6.4 Hz, 2H), 4.93 (d, J = 1.2 Hz, 1H), 4.55 (dd, J = 6.4, 1.2 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.41 (s, 3H), 2.72 (dd, J = 13.2, 7.2 Hz, 1H), 2.39 (dd, J = 13.2, 8.0 Hz, 1H), 2.35 (s, 3H), 1.34 (s, 3H), 1.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.3,
166.2, 143.0, 138.6, 136.2, 133.6, 130.2, 128.7, 127.9, 127.8, 127.8, 113.3, 110.0, 95.8, 85.5, 81.2, 81.2, 61.8, 56.9, 53.4, 53.2, 42.4, 26.2, 24.9, 21.6; HRMS calcd for C$_{28}$H$_{33}$ClNO$_{10}$S [M+H]$^+$: 610.1508, found for: 610.1508.

(3S,5R,7S,8R,9S,10R)-diethyl 7,8:9,10-di-O-isopropylidene-3-(4-chlorophenyl)-2-tosyl-6-oxa-2-azaspiro[4.5]decane-1,1-dicarboxylate ((5R)-5ab)

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.35$, 20% isolated yield); mp: 186–190 $^\circ$C; $[\alpha]_{D}^{20} = -61$ (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.00 (dd, $J = 11.8$, 8.6 Hz, 4H), 5.59 (d, $J = 10.0$ Hz, 1H), 4.92 (d, $J = 6.8$ Hz, 1H), 4.60–4.50 (m, 2H), 4.41–4.26 (m, 3H), 4.19–4.11 (m, 1H), 4.00 (d, $J = 2.4$ Hz, 1H), 3.22 (dd, $J = 14.0$, 10.4 Hz, 1H), 2.32 (s, 3H), 1.99 (d, $J = 14.4$ Hz, 1H), 1.44 (s, 3H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.37 (d, $J = 7.2$ Hz, 3H), 1.33 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.1, 165.3, 143.3, 139.4, 137.9, 132.8, 129.2, 128.9, 128.5, 128.1, 110.8, 109.1, 93.5, 89.3, 83.8, 75.7, 75.1, 68.5, 62.9, 62.9, 62.4, 34.5, 27.7, 26.2, 26.0, 25.3, 21.7, 14.3, 14.1. HRMS calcd for C$_{33}$H$_{41}$ClNO$_{11}$S [M+H]$^+$: 694.2083, found for: 694.2093.

(3S,5R,7S,8R,9S,10R)-diethyl 7,8:9,10-di-O-isopropylidene-3-(4-chlorophenyl)-2-tosyl-6-oxa-2-azaspiro[4.5]decane-1,1-dicarboxylate ((5S)-5ab)

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.24$, 64% isolated yield); mp: 180–182 $^\circ$C; $[\alpha]_{D}^{20} = -16$ (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (d, $J = 8.0$ Hz, 2H), 7.01 (dd, $J = 21.2$, 8.4 Hz, 4H), 6.90 (d, $J = 8.0$ Hz, 2H), 5.56 (d, $J = 3.2$ Hz, 1H), 5.16 (t, $J = 7.4$ Hz, 1H), 4.51–4.39 (m, 3H), 4.37–4.25 (m, 2H), 4.23 (d, $J = 5.2$ Hz, 1H), 3.88 (d, $J = 3.2$ Hz, 1H), 2.84 (dd, $J = 12.8$, 6.8 Hz, 1H), 2.35 (s, 3H), 2.20 (dd, $J = 12.8$, 8.4 Hz, 1H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H), 1.29 (s, 3H), 1.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 165.6, 143.0, 138.7, 135.5, 133.8, 130.0, 128.7, 128.1, 127.9, 109.7, 109.7, 95.9, 84.5, 82.7, 73.5, 72.3, 62.5, 62.1, 62.0, 46.4, 27.4, 26.9, 25.4, 25.3, 21.5, 14.2, 14.0. HRMS calcd for C$_{33}$H$_{41}$ClNO$_{11}$S [M+H]$^+$: 694.2083,
found for: 694.2083.

(3S,5R,7S,8R,9S,10R)-diethyl 7,8:9,10-di-O-isopropylidene-3-phenyl-2-tosyl-6-oxa-2-azaspiro[4.5]decane-1,1-dicarboxylate ((5R)-5bb)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.38 \), 15% isolated yield); mp: 172–174 °C; [\( \alpha \rbrack_{D}^{20} = -59 \) (c 1.0, CH\(_2\)Cl\(_2\));

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.39 (d, \( J = 8.4 \) Hz, 2H), 7.20–7.18 (m, 2H), 7.09–7.04 (m, 3H), 6.94 (d, \( J = 8.0 \) Hz, 2H), 5.66 (d, \( J = 10.4 \) Hz, 1H), 4.94 (d, \( J = 6.8 \) Hz, 1H), 4.60–4.53 (m, 1H), 4.50 (d, \( J = 6.8 \) Hz, 1H), 4.44–4.36 (m, 2H), 4.34–4.26 (m, 1H), 4.18–4.10 (m, 1H), 3.99 (d, \( J = 3.2 \) Hz, 1H), 2.29 (s, 3H), 2.02 (d, \( J = 14.0 \) Hz, 1H), 1.45 (s, 3H), 1.42 (t, \( J = 7.2 \) Hz, 3H), 1.35 (t, \( J = 7.2 \) Hz, 3H), 1.33 (s, 3H), 1.31 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 166.2, 165.2, 142.8, 140.6, 138.0, 128.8, 128.2, 127.9, 127.7, 127.0, 110.5, 109.0, 93.5, 89.2, 83.6, 75.6, 75.1, 68.4, 63.5, 62.8, 62.2, 34.5, 27.6, 26.2, 25.9, 25.2, 21.6, 14.2, 14.0. HRMS calcd for C\(_{33}\)H\(_{42}\)NO\(_{11}\)S [M+H]\(^{+}\): 660.2473, found for: 660.2473.

(3S,5S,7S,8R,9S,10R)-diethyl 7,8:9,10-di-O-isopropylidene-3-phenyl-2-tosyl-6-oxa-2-azaspiro[4.5]decane-1,1-dicarboxylate ((5S)-5bb)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.26 \), 66% isolated yield); mp: 166–170 °C; [\( \alpha \rbrack_{D}^{20} = -37 \) (c 1.0, CH\(_2\)Cl\(_2\));

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.21 (d, \( J = 8.4 \) Hz, 2H), 7.12–7.06 (m, 3H), 6.95 (dd, \( J = 13.6 \), 7.8 Hz, 4H), 5.57 (d, \( J = 3.2 \) Hz, 1H), 5.24 (t, \( J = 7.4 \) Hz, 1H), 4.52–4.42 (m, 5H), 4.18 (d, \( J = 5.2 \) Hz, 1H), 3.87 (d, \( J = 3.2 \) Hz, 1H), 2.91 (dd, \( J = 12.8 \), 7.2 Hz, 1H), 2.31 (s, 3H), 2.22 (dd, \( J = 12.4 \), 7.6 Hz, 1H), 1.42 (t, \( J = 7.2 \) Hz, 3H), 1.41 (t, \( J = 7.2 \) Hz, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 168.2, 165.8, 142.6, 138.6, 137.5, 128.6, 128.6, 128.3, 127.9, 127.8, 109.7, 109.7, 96.0, 84.6, 82.5, 73.4, 72.5, 62.9, 62.4, 61.9, 46.6, 29.8, 27.5, 26.9, 25.5, 25.3, 21.5, 14.2, 14.1. HRMS calcd for C\(_{33}\)H\(_{42}\)NO\(_{11}\)S [M+H]\(^{+}\): 660.2473, found for: 660.2473.

(3S,5R,7S,8R,9S,10R)-diethyl 7,8:9,10-di-O-isopropylidene-3-(4-methylphenyl)-2-tosyl-6-oxa-2-azaspiro[4.5]decane-1,1-dicarboxylate ((5R)-5hb)
White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.36, 16\%\) isolated yield); mp: 190–192 °C; \([\alpha]_D^{20} = -48\) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (d, \( J = 8.4\) Hz, 2H), 7.09 (d, \( J = 8.4\) Hz, 2H), 6.93 (d, \( J = 8.0\) Hz, 2H), 6.87 (d, \( J = 8.0\) Hz, 2H), 6.87 (d, \( J = 10.4\) Hz, 1H), 4.94 (d, \( J = 6.4\) Hz, 1H), 4.59–4.53 (m, 1H), 4.52–4.50 (m, 2H), 4.43–4.35 (m, 1H), 4.34–4.26 (m, 1H), 4.16–4.08 (m, 1H), 4.01 (d, \( J = 3.2\) Hz, 1H), 3.29 (s, 3H), 2.26 (s, 3H), 1.98 (s, 3H), 1.42 (t, \( J = 7.2\) Hz, 3H), 1.34 (s, 3H), 1.20 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.2, 165.2, 142.7, 138.1, 137.7, 136.5, 128.8, 128.6, 128.2, 127.6, 110.6, 108.9, 93.6, 89.1, 83.5, 75.6, 75.2, 68.5, 63.5, 62.7, 62.1, 34.3, 27.6, 26.2, 25.9, 25.2, 21.5, 21.2, 14.2, 14.0. HRMS calcd for C\(_{34}\)H\(_{44}\)NO\(_{11}\)S\([\text{M+H}]^+\): 674.2630, found for: 674.2630.

(3S, 5R, 7S, 8R, 9S, 10R)-diethyl 7,8:9,10-di O-isopropylidene-3-(4-methylphenyl)-2-tosyl-6-oxa-2-azaspiro[4.5]decane-1,1-dicarboxylate ([5R]-5hb)

White solid (petroleum ether/EtOAc = 4:1, \( R_f = 0.25, 76\%\) isolated yield); mp: 180–182 °C; \([\alpha]_D^{20} = -49\) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.19 (d, \( J = 8.4\) Hz, 2H), 6.95 (dLd, \( J = 21.6, 8.0\) Hz, 4H), 5.56 (d, \( J = 2.8\) Hz, 1H), 4.49–4.45 (m, 1H), 4.34–4.27 (m, 2H), 4.22 (d, \( J = 5.2\) Hz, 1H), 3.87 (d, \( J = 2.8\) Hz, 1H), 2.81 (dd, \( J = 12.4, 6.4\) Hz, 1H), 2.32 (s, 3H), 2.28–2.18 (m, 4H), 1.41–1.40 (m, 12H), 1.28 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.3, 165.8, 142.4, 138.9, 137.6, 133.9, 128.7, 128.5, 128.4, 128.2, 109.8, 109.6, 95.9, 84.5, 82.7, 73.6, 72.5, 62.7, 62.4, 61.9, 46.6, 27.5, 27.0, 25.5, 25.3, 21.5, 21.2, 14.1. HRMS calcd for C\(_{34}\)H\(_{44}\)NO\(_{11}\)S\([\text{M+H}]^+\): 674.2630, found for: 674.2630.

Compound (8R)-3hc

White solid (petroleum ether/EtOAc = 1:1, \( R_f = 0.36, 47\%\) isolated yield); mp: 100–102 °C; \([\alpha]_D^{20} = +38\) (c 1.0, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, \( J = 8.4\) Hz, 2H), 7.97–7.95 (m, 2H), 7.66 (t, \( J = 7.4\) Hz, 1H), 7.50 (dd, \( J = 17.2, 8.4\) Hz, 3H),
7.29 (d, $J = 8.0$ Hz, 2H), 7.08 (dd, $J = 8.4$, $J = 1.0$ Hz, 1H), 6.32 (s, 1H), 6.05 (d, $J = 8.4$ Hz, 1H), 5.55 (d, $J = 10.8$ Hz, 1H), 5.27 (d, $J = 11.6$ Hz, 1H), 4.81 (d, $J = 6.0$ Hz, 1H), 4.50 (s, 1H), 4.32–4.18 (m, 4H), 2.39 (s, 3H), 2.27 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.29 (t, $J = 7.2$, 3H), 1.28 (t, $J = 7.2$, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.5, 167.6, 166.2, 161.9, 159.3, 149.0, 144.1, 139.8, 137.9, 136.8, 135.3, 134.5, 131.5, 130.6, 129.7, 129.3, 129.2, 128.6, 127.2, 114.4, 103.5, 101.8, 90.9, 83.3, 76.3, 62.6, 62.5, 61.5, 57.6, 26.8, 25.9, 21.6, 21.0, 14.1, 13.9. HRMS calcd for C$_{41}$H$_{44}$N$_3$O$_{12}$S [M+H]$^+$: 802.2640, found for: 802.2644.

**Compound (8S)-3hc**

White solid (petroleum ether/EtOAc = 1:1, $R_f = 0.31$, 20% isolated yield); mp: 126–130 °C; [α]$_D^{20}$ = +133 (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, $J = 7.2$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.00 (s, 4H), 5.92 (d, $J = 8.4$ Hz, 2H), 5.76 (d, $J = 9.2$ Hz, 1H), 5.28 (d, $J = 6.0$ Hz, 1H), 5.14 (d, $J = 9.2$ Hz, 1H), 5.01 (d, $J = 5.6$ Hz, 1H), 4.44 (s, 1H), 4.19–4.04 (m, 4H), 2.39 (s, 3H), 2.26 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H), 1.16 (t, $J = 7.2$ Hz, 3H), 1.15 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.9, 167.1, 166.4, 162.2, 156.9, 149.3, 143.8, 138.1, 137.5, 135.4, 134.2, 131.4, 131.0, 129.5, 129.4, 129.3, 128.6, 127.9, 114.2, 103.2, 82.9, 79.4, 62.5, 62.2, 61.7, 56.9, 27.0, 25.9, 21.7, 21.2, 14.0, 13.9. HRMS calcd for C$_{41}$H$_{44}$N$_3$O$_{12}$S [M+H]$^+$: 802.2640, found for: 802.2643.

**Uncyclized product 4**

White solid (petroleum ether/EtOAc = 4:1, $R_f = 0.21$); mp: 132–136 °C; [α]$_D^{20}$ = -16 (c 1.0, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 4.8$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.16 (d, $J = 8.4$ Hz, 2H), 5.78 (d, $J = 8.4$ Hz, 1H), 5.08 (s, 1H), 5.02 (d, $J = 8.8$ Hz, 1H), 4.96 (d, $J = 6.0$ Hz, 1H), 4.58 (s, 1H), 4.45 (d, $J = 5.6$ Hz, 2H), 4.32–4.18 (m, 2H), 4.14–4.10 (m, 2H), 3.40 (s, H)
3H), 2.40 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H), 1.30 (t, J = 7.2, 3H), 1.21 (t, J = 7.2, 3H);
13C NMR (100 MHz, CDCl3) δ 166.8, 166.4, 156.5, 143.5, 137.7, 136.3, 133.9, 130.1, 129.2, 128.3, 128.3, 113.2, 109.1, 100.2, 82.2, 78.7, 62.5, 62.2, 62.0, 57.1, 56.2, 27.0, 25.9, 21.7, 14.0, 14.0; HRMS calcd for C30H37ClNO10S [M+H]+: 638.1822, found for: 638.1816.

Uncyclized product 6

White solid (petroleum ether/EtOAc = 1:1, Rf = 0.26, 26% isolated yield); mp: 102–104 °C; [α]D20 = -24 (c 1.0, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 8.01 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 7.2 Hz, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 7.30 (dd, J = 8.2, 3.4 Hz, 1H), 7.25 (s, 2H), 6.92 (d, J = 6.8 Hz, 2H), 6.64 (s, 2H), 5.86 (d, J = 8.0 Hz, 1H), 5.65 (d, J = 8.0 Hz, 1H), 5.57 (s, 1H), 5.29 (d, J = 8.0 Hz, 1H), 4.90 (dd, J = 36.4, 6.0 Hz, 2H), 4.36–4.22 (m, 3H), 4.05–3.99 (m, 2H), 2.41 (s, 3H), 2.16 (s, 3H), 1.50 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 168.1, 167.1, 166.3, 161.9, 158.5, 149.3, 143.4, 137.9, 137.4, 135.6, 133.8, 131.4, 130.6, 129.4, 129.2, 129.1, 128.9, 114.1, 102.9, 100.3, 97.7, 83.2, 78.1, 62.5, 61.9, 61.7, 57.5, 26.7, 25.8, 21.7, 21.1, 14.1, 13.9. HRMS calcd for C41H44N3O12S [M+Na]+: 824.2460, found for: 824.2459.

(2R,3R,4S,5R,8S)-diethyl 8-(4-chlorophenyl)-3,4-O-isopropylidene-2-methoxy-1-oxa-7-azaspiro[4.4]nonane-6,6-dicarboxylate (7)

White solid (petroleum ether/EtOAc = 3:1, Rf = 0.47, 87% isolated yield); mp: 102–106 °C; [α]D20 = -75 (c 1.0, CH2Cl2); 1H NMR (400 MHz, CDCl3) δ 7.25 (d, J = 1.6 Hz, 4H), 5.27 (d, J = 6.8 Hz, 1H), 4.98 (s, 1H), 4.62 (dd, J = 11.2, 6.0 Hz, 1H), 4.57 (d, J = 6.8 Hz, 1H), 4.42–4.36 (m, 1H), 4.34–4.18 (m, 2H), 4.12–4.04 (m, 1H), 3.63 (s, 1H), 3.31 (s, 3H), 2.48 (dd, J = 13.2, 11.2 Hz, 1H), 2.24 (dd, J = 13.2, 6.0 Hz, 1H), 1.48 (s, 3H), 1.35 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 170.4, 168.2, 143.1, 132.6, 128.5,
128.1, 113.1, 108.5, 99.1, 86.2, 80.8, 77.7, 62.3, 61.7, 59.4, 56.5, 46.2, 26.3, 24.8, 14.1, 14.0. HRMS calcd for C\textsubscript{23}H\textsubscript{31}ClNO\textsubscript{8} [M+H]\textsuperscript{+}: 484.1732, found for: 484.1732.

**Ethyl-2,3-dihydroxy-5-oxo-7-(o-tolyl)-6-tosyloctahydrofuro[2',3':4,5]furo[3,4-b]pyrrole-5a-carboxylate (8)**

White solid (petroleum ether/EtOAc = 1:2, \(R_f\) = 0.4, 68% isolated yield); mp: 228–230 °C; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.31 (d, \(J = 8.4\) Hz, 2H), 7.12 (d, \(J = 7.6\) Hz, 1H), 7.01 (dd, \(J = 10.8, 8.0\) Hz, 3H), 6.56 (t, \(J = 7.6\) Hz, 1H), 6.26 (d, \(J = 8.0\) Hz, 1H), 5.82 (d, \(J = 10.4\) Hz, 1H), 5.43 (t, \(J = 3.8\) Hz, 1H), 4.62 (d, \(J = 3.2\) Hz, 1H), 4.51–4.42 (m, 2H), 4.40 (d, \(J = 5.2\) Hz, 1H), 4.06–4.04 (m, 1H), 3.44 (d, \(J = 12.0\) Hz, 1H), 3.17–3.11 (m, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.98 (d, \(J = 12.8\) Hz, 1H), 1.46 (t, \(J = 7.2\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 168.0, 166.0, 144.0, 137.1, 137.1, 134.7, 131.0, 129.2, 128.0, 127.4, 125.7, 124.7, 95.4, 95.2, 80.6, 75.0, 72.3, 63.0, 60.5, 40.3, 21.6, 19.6, 14.2. HRMS calcd for C\textsubscript{25}H\textsubscript{27}NO\textsubscript{8}SNa [M+Na]\textsuperscript{+}: 540.1299, found for: 540.1297.
8. X-ray crystallographic data of the compounds

**X-ray Crystallographic Data of Compound (8R)-3aa**

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<td>gamma</td>
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<td>Calculated Volume</td>
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<tr>
<td>Space group</td>
<td>P 21</td>
</tr>
<tr>
<td>Hall group</td>
<td>P 2yb</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C₃₀H₃₅ClNO₁₀S</td>
</tr>
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<td>C₃₀H₃₅ClNO₁₀S</td>
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<td>Moiety formula Calculated</td>
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<td>MR</td>
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<td>Mu (mm⁻¹)</td>
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<td>Correction method</td>
<td># Reported T Limits:</td>
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<td>AbsCorr</td>
<td>MULTI-SCAN</td>
</tr>
<tr>
<td>Data completeness</td>
<td>1.93/1.00</td>
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<tr>
<td>Theta(max)</td>
<td>66.590</td>
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<td>R(reflections)</td>
<td>0.0330 ( 5312)</td>
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<td>wR2(reflections)</td>
<td>0.0921( 5634)</td>
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<tr>
<td>S</td>
<td>1.038</td>
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<td>Npar</td>
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X-ray Crystallographic Data of Compound (8S)-3aa

<table>
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<tr>
<th>Bond precision:</th>
<th>C-C = 0.0076 Å</th>
<th>Wavelength=1.54184</th>
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<td>b=13.4972(5)</td>
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<td>alpha=90</td>
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<td>Temperature:</td>
<td>293 K</td>
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<tr>
<td>Volume</td>
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<td>Space group</td>
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<td>Hall group</td>
<td>-P 2ybc</td>
<td>-P 2ybc</td>
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<tr>
<td>Moiety formula</td>
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<td>C$<em>{30}$ H$</em>{36}$ Cl N O$_{10}$ S</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C$<em>{30}$ H$</em>{36}$ Cl N O$_{10}$ S</td>
<td>C$<em>{30}$ H$</em>{36}$ Cl N O$_{10}$ S</td>
</tr>
<tr>
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<td>638.11</td>
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<td>Mu (mm-1)</td>
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<td>13, 16, 25</td>
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<td>4959</td>
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<td>Correction method= # Reported T Limits: Tmin=0.414 Tmax=1.000</td>
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<tr>
<td>AbsCorr = MULTI-SCAN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data completeness= 1.54/0.87</td>
<td>Theta(max)= 66.596</td>
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<td>R(reflections)= 0.0487( 4323)</td>
<td>wR2(reflections)= 0.1345( 4959)</td>
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X-ray Crystallographic Data of Compound (5R)-5bb

Bond precision:  
C-C = 0.0050 Å  

Wavelength=1.54184

Cell:  
a=10.7929(2)  
b=14.1343(3)  
c=22.1643(5)  

Cell parameters:  
alpha=90  
beta=90  
gamma=90

Temperature:  
295 K

Volume:  
3381.17(12)  

Calculated

Reported

Space group:  
P 21 21 21

Hall group:  
P 2ac 2ab

Moiety formula:  
C₃₃H₄₁ClNO₁₁S

Sum formula:  
C₃₃H₄₁ClNO₁₁S

Mr:  
659.73  

Dₙ,g cm⁻³:  
1.296  

Z:  
4

Mu (mm⁻¹):  
1.358  

F000:  
1400.0  

F000’:  
1405.86

h,k,lmax:  
12, 16, 26  

Nref:  
5977[3366]

Tmin,Tmax:  
0.805, 0.850  

0.593, 1.000

Correction method= # Reported T Limits: Tmin=0.593 Tmax=1.000

AbsCorr = MULTI-SCAN

CCDC 2025967
X-ray Crystallographic Data of Compound (5S)-5bb

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<td>Hall group</td>
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<td>P 2ac 2ab</td>
</tr>
<tr>
<td>Moiety formula</td>
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<td>C₃₃ H₄₁ Cl N O₁₁ S</td>
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<tr>
<td>Sum formula</td>
<td>C₃₃ H₄₁ Cl N O₁₁ S</td>
<td>C₃₃ H₄₁ Cl N O₁₁ S</td>
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<td>Mr</td>
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<td>Dx,g cm⁻³</td>
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Correction method= # Reported T Limits: Tmin=0.663 Tmax=1.000  
AbsCorr = MULTI-SCAN  
Data completeness= 1.56/0.88  
Theta(max)= 66.578
X-ray Crystallographic Data of Compound 6

Bond precision: C-C = 0.0091 Å

Wavelength: 1.5418 Å

Cell:
- a = 11.6704(12) Å
- b = 19.5166(19) Å
- c = 11.8028(11) Å
- α = 90°
- β = 99.959(10)°
- γ = 90°

Temperature: 293 K

Volume: 2647.8(5) Å³

Space group: P 21

Hall group: P 2yb

Moiety formula: C₄₁H₄₃ClNO₁₂S

Sum formula: C₄₁H₄₃ClNO₁₂S

Mr: 801.84

Dx, g cm⁻³: 1.006

Z: 2

Mu (mm⁻¹): 0.971

F₀₀₀: 844.0

F₀₀₀': 847.41

h,k,lmax: 13, 23, 14

Nref: 9337 [4818]

Tmin, Tmax: 0.954, 0.971

Tmin': 0.916

Correction method: # Reported T Limits: Tmin=0.306 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.66/0.85

Theta(max) = 66.597
X-ray Crystallographic Data of Compound 8

Bond precision: \( C-C = 0.0081 \) A  
Wavelength: 0.71073
Cell:  
\( a = 7.633(3) \)  
\( b = 14.652(5) \)  
\( c = 31.395222.078(8) \)  
\( \alpha = 90 \)  
\( \beta = 90 \)  
\( \gamma = 90 \)
Temperature: 296 K
Volume: 2469.2(16)  
2469.1(15)
Space group: P 21 21 21  
P 21 21 21
Hall group: P 2ac 2ab  
P 2ac 2ab
Moiety formula: \( C_{25}H_{27}ClN_9O_9S \)  
\( C_{25}H_{27}ClN_9O_9S \)
Sum formula: \( C_{25}H_{27}ClN_9O_9S \)  
\( C_{25}H_{27}ClN_9O_9S \)
Mr: 571.54  
571.53
Dx,g cm\(^{-3}\): 1.392  
1.392
Z: 4  
4
Mu (mm\(^{-1}\)): 0.186  
0.186
F000: 1088.0  
1088.0
F000": 1089.11
h,k,lmax: 9, 17, 26  
9, 17, 26
Nref: 4363[2505]  
4345
Tmin,Tmax: 0.956, 0.963  
0.647, 0.745
Tmin": 0.946
Correction method= # Reported T Limits: Tmin=0.647 Tmax=0.745
AbsCorr = MULTI-SCAN
Data completeness: 1.73/1.00  
Theta(max)= 25.028
$R(\text{reflections}) = 0.0468(3039)$

$wR^2(\text{reflections}) = 0.1225(4345)$

$S = 0.998$

$N_{\text{par}} = 331$
9. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of the compounds

$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (1k)

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (1k)
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (1l)

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (1l)
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (1p)

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (1p)
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3aa

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3aa
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3aa

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3aa
$^{1}$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3ba

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3ba
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3ba

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ba
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3ca

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3ca
$^{19}$F-NMR (376 MHz, CDCl$_3$) spectra of compound (8$R$)-3ca

[Diagram of compound (8$R$)-3ca]

$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$S$)-3ca

[Diagram of compound (8$S$)-3ca]
$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ca

$^{19}$F-NMR (376 MHz, CDCl$_3$) spectra of compound (8S)-3ca
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3da

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3da
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3da

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3da
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3ea

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3ea
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3ea

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ea
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3fa

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3fa
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3fa

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3fa
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3ga

![H-NMR Spectra](image1)

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3ga

![C-NMR Spectra](image2)
$^{19}$F-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3ga

![$^{19}$F-NMR spectrum of (8$R$)-3ga](image)

$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$S$)-3ga

![$^1$H-NMR spectrum of (8$S$)-3ga](image)
$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ga

![C-NMR Spectra](image)

$^{19}$F-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ga

![F-NMR Spectra](image)
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3ha

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3ha
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3ha

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ha
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3ia

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3ia
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3ia

![H-NMR Spectra of (8S)-3ia](image)

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ia

![C-NMR Spectra of (8S)-3ia](image)
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3ja

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3ja
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3ja

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ja
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3ka

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3ka
$^{1}$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3ka

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ka
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3la

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3la
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$S$)-3la

\[ \text{(8$S$)-3la} \]

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$S$)-3la

\[ \text{(8$S$)-3la} \]
$^{1}H$-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3ma

$^{13}C$-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3ma
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3ma

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3ma
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3na

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3na
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3na

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3na
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8R)-3oa

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8R)-3oa
$^{1}$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3oa

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3oa
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3pa

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3pa
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3pa

![H-NMR spectrum of (8S)-3pa](image)

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3pa

![C-NMR spectrum of (8S)-3pa](image)
$^{1}H$-NMR (400 MHz, CDCl$_3$) spectra of compound (5R)-5ab

![H-NMR spectrum of (5R)-5ab](image)

$^{13}C$-NMR (100 MHz, CDCl$_3$) spectra of compound (5R)-5ab

![C-NMR spectrum of (5R)-5ab](image)
$^{1}H$-NMR (400 MHz, CDCl$_3$) spectra of compound (5S)-5ab

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (5S)-5ab
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (5R)-5bb

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (5R)-5bb
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (5$S$)-5bb

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (5$S$)-5bb
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (5$R$)-5hb

1$^3$C-NMR (100 MHz, CDCl$_3$) spectra of compound (5$R$)-5hb
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (5$\text{S}$)-5hb

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (5$\text{S}$)-5hb
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8$R$)-3hc

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8$R$)-3hc
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound (8S)-3hc

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound (8S)-3hc
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound 4

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound 4
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound 6

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound 6
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound 7

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound 7
$^1$H-NMR (400 MHz, CDCl$_3$) spectra of compound 8

$^{13}$C-NMR (100 MHz, CDCl$_3$) spectra of compound 8