Supporting information

for

Highly Regio- and Chemoselective Ring Opening of Oxa-Bridged Piperidinones toward Functionalized Furanones and Piperidines

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General Procedure. All reactions were carried out under an argon atmosphere (except Amberlyst-15[®] mediated reactions) and glasswares were dried in an oven before using for ring opening reaction. Dry dichloromethane (dried over phosphorous pentoxide) has freshly been prepared for every reaction. Analytical thin layer chromatography (TLC) was performed on alumina plates and components were visualized by observation under iodine and UV-Light. Column chromatography was performed on a silica gel (100-200 mesh) column. The melting points are uncorrected. The FT-IR spectra were recorded using KBr method. ¹H NMR and ¹³C NMR spectra (200 MHz and 50.3 MHz, respectively) were referenced to TMS. Carbon types were determined from DEPT ¹³C NMR experiments. Mass spectra were determined on a high resolution liquid chromatography/mass spectrometer with ESI⁺ method.

Compound 4a: To a solution of oxa-bridged piperidinone **3a** (200 mg, 0.5 mmol) in CH₂Cl₂ (10 mL) at room temperature was added Amberlyst-15[®] (250 mg) and stirred for 60 minutes, during which time the progress of the reaction was monitored by

TLC. The reaction mixture was filtered and the solvent was removed under reduced pressure. The resulting residue purified using silica gel column chromatography (EtOAc/hexanes 3:7) to afford **4a** (198 mg, 95 %) as a single diastereomer. Colorless solid: mp 175-177 °C (CHCl₃/hexane). R_f 0.50 (3:7 EtOAc/hexanes).

ν_{max} (KBr)/cm⁻¹ 3467, 3273, 2919, 2851, 1752, 1457, 1329, 1159, 1091, 1055, 700.

¹H NMR (200 MHz, CDCl₃) δ 7.47 (d, 2H, Arom-*H*, *J* = 8.0 Hz), 7.16-7.07 (m, 7H, Arom-*H*), 6.04 (d, 1H, NH, *J* = 4.0 Hz), 4.70 (t, 1H, CH, *J* = 4.0 Hz), 4.48 (d, 1H, CH, *J* = 6.0 Hz), 2.49 (broad-s, 1H, OH), 2.34 (s, 3H, CH₃), 1.87 (d, 1H, *J* = 10.0 Hz), 1.57-1.26 (m, 7H), 0.98 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, CDCl₃) δ 215.2 (C=O), 143.0 (*quat-C*), 136.9 (*quat-C*), 136.6 (*quat-C*), 129.1 (=CH), 128.3 (=CH), 127.9 (=CH), 127.7 (=CH), 104.4 (*quat-C*), 79.1 (CH), 59.8 (CH), 52.0 (*quat-C*), 33.2 (CH₂), 33.0 (CH₃), 22.6 (CH₂), 21.3 (CH₂), 20.3 (CH₂), 13.3 (CH₃).

HRMS (ESI⁺) calcd for C₂₃H₂₇NO₅SN_a (M+Na)⁺: 452.1563, found 452.1540.

Figure S1. ORTEP view of compound **4a**

Crystal data for the compound **4a**: $C_{23}H_{27}NO_5S$, $M = 429.52$, $0.32 \times 0.25 \times 0.20 \text{ mm}^3$, Orthorhombic, space group $P212121$ with $a = 24.290(5) \text{ \AA}$, $b = 10.813(2) \text{ \AA}$, $c = 8.2719(16) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2172.6(7) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $R_1 = 0.0489$, $wR_2 = 0.1163$ on observed data, $z = 4$, $D_{\text{calcd}} = 1.313 \text{ g cm}^{-3}$, $F(000) = 912$, Absorption coefficient $= 0.183 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, 10425 reflections were collected on a smart apex CCD single crystal diffractometer, 3814 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole $= 0.454$ and $-0.245 \text{ e \AA}^{-3}$, respectively.

Compound 4b: To a solution of oxa-bridged piperidinone **3b** (300 mg, 0.8 mmol) in CH_2Cl_2 (15 mL) at room temperature was added Amberlyst-15[®] (350 mg) and stirred for 50 minutes. The reaction was followed as prescribed above and afforded **4b**

(273 mg, 87 %) as a single diastereomer. Colorless solid: mp $163\text{--}165^\circ\text{C}$ ($\text{CHCl}_3/\text{hexane}$). R_f 0.53 (3:7 EtOAc/hexanes).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3459, 3240, 2919, 2851, 1762, 1455, 1334, 1323, 1159, 1082, 939, 699.

^1H NMR (200 MHz, CDCl_3) δ 7.60 (d, 2H, Arom- H , $J = 8.2 \text{ Hz}$), 7.21–7.13 (m, 7H, Arom- H), 6.17 (d, 1H, NH, $J = 8.2 \text{ Hz}$), 4.84 (dd, 1H, CH, $J_1 = 8.2 \text{ Hz}$, $J_2 = 3.2 \text{ Hz}$), 4.57 (d, 1H, CH, $J = 3.2 \text{ Hz}$), 3.17 (broad s, 1H, OH), 2.37 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 0.98 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, CDCl_3) δ 216.4 ($\text{C}=\text{O}$), 143.2 (*quat-C*), 137.1 (*quat-C*), 135.6 (*quat-C*), 129.3 ($=\text{CH}$), 128.5 ($=\text{CH}$), 128.0 ($=\text{CH}$), 127.8 ($=\text{CH}$), 127.1 ($=\text{CH}$), 105.9

(*quat-C*), 80.9 (CH), 57.7 (CH), 50.8 (*quat-C*), 22.1 (CH₃), 21.3 (CH₃), 19.3 (CH₃), 17.4 (CH₃).

HRMS (ESI⁺) calcd for C₂₁H₂₅NO₅SNa (M+Na)⁺: 426.1388, found 426.1351.

Compound 4c: To a solution of oxa-bridged piperidinone **3c** (200 mg, 0.46 mmol) in CH₂Cl₂ (12 mL) at room temperature was added Amberlyst-15[®] (250 mg) and stirred for 60 minutes. The reaction was followed as prescribed above and afforded **4c** (187 mg, 90 %) as a single diastereomer. Colorless solid:

mp 178-180 °C (CHCl₃/hexane). R_f 0.50 (3:7 EtOAc/hexanes).

¹H NMR (200 MHz, CDCl₃+CD₃OD) δ 7.44 (d, 2H, Arom-*H*, *J* = 8.2 Hz), 7.18-7.09 (m, 4H, Arom-*H*), 6.80 (t, 2H, Arom-*H*, *J* = 8.6 Hz), 6.66 (d, 1H, NH, *J* = 1.6 Hz), 4.69-4.64 (m, 1H), 4.38 (d, 1H, *J* = 6.2 Hz), 2.35 (s, 3H, CH₃), 2.10-2.04 (broad s, 1H, OH), 1.93 (d, 1H, *J* = 11.2 Hz), 1.63-1.25 (m, 7H), 1.00 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, CDCl₃+CD₃OD) δ 215.4 (C=O), 164.6 (*quat-C*), 159.7 (*quat-C*), 143.2 (*quat-C*), 136.8 (*quat-C*), 132.2 (*quat-C*), 130.2 (=CH), 130.0 (=CH), 129.0 (=CH), 127.3 (=CH), 114.8 (=CH), 114.4 (=CH), 104.2 (*quat-C*), 78.5 (CH), 59.2 (CH), 52.0 (*quat-C*), 33.2 (CH₃), 32.6 (CH₂), 22.6 (CH₂), 21.3 (CH₂), 20.3 (CH₂), 13.2 (CH₃).

Compound 7a: To a solution of oxa-bridged piperidinone **3a** (200 mg, 0.5 mmol) in CH₂Cl₂ (15 mL) at 0 °C was added Et₃SiH (0.155 mL, 1.0 mmol) and stirred for two min. BF₃•OEt₂ (0.120 mL, 1.0 mmol) was added and stirred for 2 h at 0

°C, and allowed to gradually warm to rt. The reaction was quenched by the addition of sat'd NaHCO₃, and diluted with H₂O. The aqueous phase was extracted with DCM (2 x 20 ml) then ethyl acetate (1 x 20 ml). The combined organic extracted were washed with brine, desiccated with Na₂SO₄, and the solvents removed under reduced pressure. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 4:6) to

afford **7a** (170 mg, 85 %) as a single diastereomer. Colorless solid: mp 169-171 °C (CHCl₃/hexane). R_f 0.45 (4:6 EtOAc/hexanes).

$\nu_{\max}$ (KBr)/cm⁻¹ 3280, 2927, 2856, 1752, 1453, 1437, 1303, 1161, 1082, 1021, 671.

¹H NMR (200 MHz, CDCl₃) δ 7.32 (d, 2H, *J* = 8.0 Hz, Arom-*H*), 6.91-6.84 (m, 7H, Arom-*H*), 5.61 (d, 1H, *J* = 8.6 Hz, *OH*), 4.54 (dd, 1H, *J*₁ = 8.6 Hz, *J*₂ = 3.2 Hz, *CH*), 4.35 (d, 1H, *J* = 3.2 Hz, *CH*), 2.79 (d, 1H, *J* = 3.0 Hz, *CH*), 2.10 (s, 3H, CH₃), 1.56-1.50 (m, 1H), 1.21-0.89 (m, 7H), 0.37 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, CDCl₃) δ 216.1 (C=O), 143.0 (*quat-C*), 137.3 (*quat-C*), 136.0 (*quat-C*), 129.2 (=CH), 128.0 (=CH), 127.8 (=CH), 127.7 (=CH), 126.9 (=CH), 82.0 (CH), 80.9 (CH), 58.1 (CH), 45.8 (*quat-C*), 29.7 (CH₂), 25.4 (CH₂), 21.3 (CH₃), 20.5 (CH₂), 19.5 (CH₂), 15.6 (CH₃).

HRMS (ESI⁺) calcd for C₂₃H₂₇NO₄SNa (M+Na)⁺: 436.4033, found 436.4057.

Figure S2. ORTEP view of compound **7a**

Crystal data for the compound **7a**: C₂₃H₂₇NO₄S, *M* = 413.52, 0.20 x 0.14 x 0.08 mm³, Triclinic, space group P-1 with *a* = 10.3837(11) Å, *b* = 10.6240(11) Å, *c* = 11.7950(12) Å, α = 114.394(2)°, β = 97.555(2)°, γ = 111.069(2)°, *V* = 1044.08(19) Å³, *T* = 273(2) K, *R*_i = 0.0612, *wR*₂ = 0.1385 on observed data, *z* = 2, *D*_{calcd} = 1.315 g cm⁻³, *F*(000) = 440, Absorption coefficient = 0.184 mm⁻¹, λ = 0.71073 Å, 6102 reflections were collected on a smart apex CCD single crystal diffractometer, 4506 observed reflections (*I* ≥ 2σ(*I*)). The largest difference peak and hole = 0.687 and -0.337 e Å⁻³, respectively.

Compound 7b: To a solution of oxa-bridged piperidinone **3b** (200 mg, 0.5 mmol) in CH₂Cl₂ (20 mL) at 0 °C was added Et₃SiH (0.165 mL, 1.0 mmol) and stirred for two min. BF₃•OEt₂ (0.130 mL, 1.0 mmol) was added and stirred for 90 min.

Further, the reaction was followed as prescribed in **7a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 4:6) to afford **7b** (164 mg, 82 %) as a single diastereomer. Colorless solid: mp 153-155 °C (CHCl₃/hexane). R_f 0.45 (4:6 EtOAc/hexanes).

ν_{max} (KBr)/cm⁻¹ 3286, 2976, 2859, 1754, 1455, 1438, 1325, 1158, 1089, 1069, 933, 667.

¹H NMR (200 MHz, CDCl₃) δ 7.93 (d, 2H, *J* = 8.2 Hz, Arom-*H*), 7.55-7.40 (m, 7H, Arom-*H*), 6.21 (d, 1H, *J* = 8.8 Hz, OH), 5.19 (dd, 1H, *J*₁ = 8.8 Hz, *J*₂ = 3.2 Hz, CH), 4.55 (d, 1H, *J* = 3.2 Hz, CH), 4.15 (q, 1H, *J* = 6.2 Hz, CH), 2.72 (s, 3H, CH₃), 1.48 (d, 3H, *J* = 6.2 Hz, CH₃), 1.27 (s, 3H, CH₃), 0.33 (s, 3H, CH₃),.

¹³C NMR (50.3 MHz, CDCl₃) δ 217.2 (C=O), 142.9 (*quat-C*), 137.2 (*quat-C*), 135.4 (*quat-C*), 129.1 (=CH), 128.5 (=CH), 127.6 (=CH), 126.9 (=CH), 83.7 (CH), 81.3 (CH), 57.9 (CH), 46.7 (*quat-C*), 21.2 (CH₃), 20.0 (CH₃), 15.5 (CH₃), 13.8 (CH₃).

HRMS (ESI⁺) calcd for C₂₁H₂₅NO₄Sn (M+Na)⁺: 410.1507, found 410.1517

Compounds 7a and 7b: Following the above procedure, the compounds **7a** and **7b** were synthesized using other Lewis acids (SnCl₄, TBSiOTf and Cu(II)-triflate) with triethyl silylhydride instead of BF₃•OEt₂.

Compound 7c: To a solution of oxa-bridged piperidinone **3c** (180 mg, 0.4 mmol) in CH₂Cl₂ (15 mL) at 0 °C was added Et₃SiH (0.135 mL, 0.8 mmol) and stirred for 2 min. BF₃•OEt₂ (0.105 mL, 0.8 mmol) was added and stirred for 1.5 h. Further, the reaction was followed as prescribed in **7a**. The

crude product was purified by column chromatography (silica gel; EtOAc/hexanes 4:6) to afford **7c** (160 mg, 89 %) as a single diastereomer. Colorless solid: mp 182-184 °C (CHCl₃/hexane). R_f 0.45 (4:6 EtOAc/hexanes).

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3269, 2960, 2928, 2869, 1753, 1512, 1430, 1328, 1231, 1161, 1065, 675.
 ^1H NMR (200 MHz, CDCl_3) δ 7.54 (d, 2H, $J = 8.2$ Hz, Arom- H), 7.12-7.01 (m, 4H, Arom- H), 6.83-6.74 (m, 2H, Arom- H), 5.98 (d, 1H, $J = 8.4$ Hz, NH), 4.77 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 3.2$ Hz, CH), 4.54 (d, 1H, $J = 3.2$ Hz, CH), 3.07 (d, 1H, $J = 3.2$ Hz, CH), 2.33 (s, 3H, CH_3), 1.77-1.70 (m, 1H), 1.42-1.09 (m, 7H), 00 (s, 3H, CH_3),.
 ^{13}C NMR (50.3 MHz, CDCl_3) δ 216.0 (C=O), 164.6 (*quat-C*), 159.7 (*quat-C*), 143.1 (*quat-C*), 137.2 (*quat-C*), 132.2 (*quat-C*), 129.7 (=CH), 129.6 (=CH), 129.2 (=CH), 126.9 (=CH), 115.1 (=CH), 114.7 (=CH), 81.7 (CH), 81.0 (CH), 57.5 (CH), 45.9 (*quat-C*), 29.7 (CH_2), 25.4 (CH_2), 21.2 (CH_3), 20.5 (CH_2), 19.5 (CH_2), 15.7 (CH_3).
 HRMS (ESI^+) calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_4\text{SFNa}$ ($\text{M}+\text{Na}$) $^+$: 454.1571, found 454.1545.

Compound 7d: To a solution of oxa-bridged piperidinone **3d** (200 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added Et_3SiH (0.155 mL, 1.0 mmol) and stirred for 2 min. $\text{BF}_3\cdot\text{OEt}_2$ (0.120 mL, 1.0 mmol) was added and stirred for 2 h. Further, the reaction was followed as prescribed in **7a**. The

crude product was purified by column chromatography (silica gel; EtOAc/hexanes 4:6) to afford **7d** (176 mg, 88 %) as a single diastereomer. Colorless solid: mp 168-170 °C (CHCl_3 /hexane). R_f 0.50 (4:6 EtOAc/hexanes).

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3267, 2969, 2830, 1753, 1511, 1451, 1426, 1413, 1330, 1163, 1090, 1069, 929, 671.

^1H NMR (200 MHz, CDCl_3) δ 7.72 (d, 2H, $J = 8.2$ Hz, Arom- H), 7.32-7.20 (m, 4H, Arom- H), 6.98 (t, 2H, $J = 8.6$ Hz, Arom- H), 5.93 (d, 1H, $J = 8.6$ Hz, NH), 4.97 (dd, 1H, $J_1 = 8.6$ Hz, $J_2 = 3.2$ Hz, CH), 4.31 (d, 1H, $J = 3.2$ Hz, CH), 3.99 (q, 1H, $J = 6.2$ Hz, CH), 2.55 (s, 3H, CH_3), 1.29 (d, 3H, $J = 6.2$ Hz, CH_3), 1.08 (s, 3H, CH_3), 0.20 (s, 3H, CH_3),.

^{13}C NMR (50.3 MHz, CDCl_3) δ 217.1 (C=O), 164.7 (*quat-C*), 159.8 (*quat-C*), 143.2 (*quat-C*), 137.2 (*quat-C*), 131.5 (*quat-C*), 130.4 (=CH), 130.2 (=CH), 129.2 (=CH), 127.0 (=CH), 114.8 (=CH), 114.6 (=CH), 114.3 (=CH), 83.5 (CH), 81.4 (CH), 57.2 (CH), 46.7 (*quat-C*), 21.3 (CH_3), 20.0 (CH_3), 15.8 (CH_3), 13.8 (CH_3).

HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_4\text{SFNa}$ ($\text{M}+\text{Na}$) $^+$: 428.1408, found 428.1434.

Compound 7e: To a solution of oxa-bridged piperidinone **3e** (150 mg, 0.35 mmol) in CH₂Cl₂ (12 mL) at 0 °C was added Et₃SiH (0.100 mL, 0.6 mmol) and stirred for 3 min. BF₃•OEt₂ (0.080 mL, 0.6 mmol) was added and stirred for 2 h. Further,

the reaction was followed as prescribed in **7a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 3:7) to afford **7e** (112 mg, 75 %) as a single diastereomer. Colorless solid: mp 139-141 °C (CHCl₃/hexane). R_f 0.55 (3:7 EtOAc/hexanes).

ν_{max} (KBr)/cm⁻¹ 3317, 2962, 2929, 1747, 1458, 1432, 1342, 1229, 1165, 1095, 1030, 677.

¹H NMR (200 MHz, CDCl₃) δ 7.42 (d, 2H, *J* = 8.2 Hz, Arom-*H*), 7.10-6.95 (m, 4H, Arom-*H*), 5.71 (d, 1H, *J* = 10.6 Hz, NH), 5.31 (d, 1H, CH, *J* = 10.6 Hz), 4.19 (q, 2H, OCH₂, *J* = 7.0 Hz), 2.84 (s, 1H, CH), 2.26 (s, 3H, CH₃), 1.96 (d, 1H, *J* = 14.6 Hz), 1.64-1.49 (m, 4H), 1.32 (t, 3H, CH₃, *J* = 7.0 Hz), 1.25-1.07 (m, 3H), 0.53 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, CDCl₃) δ 208.9 (C=O), 166.2 (*quat-C*), 142.8 (*quat-C*), 137.6 (*quat-C*), 134.7 (*quat-C*), 128.9 (=CH), 128.3 (=CH), 128.0 (=CH), 127.8 (=CH), 126.8 (=CH), 89.4 (*quat-C*), 80.1 (CH), 62.7 (OCH), 60.7 (CH), 45.5 (*quat-C*), 29.1 (CH₂), 25.3 (CH₂), 21.2 (CH₃), 20.3 (CH₂), 19.1 (CH₂), 15.6 (CH₃), 13.9 (CH₃).

HRMS (ESI⁺) calcd for C₂₆H₃₁NO₆SN⁺ (M+Na)⁺: 508.1874, found 508.1868.

Compound 7f: To a solution of appropriate cycloadduct **3f** (175 mg, 0.45 mmol) in CH₂Cl₂ (15 mL) at 0 °C was added Et₃SiH (0.140 mL, 0.9 mmol) and stirred for 2 min. BF₃•OEt₂ (0.110 mL, 0.9 mmol) was added and stirred for 2.5 h. Further, the reaction was followed as prescribed in **7a**. The

crude product was purified by column chromatography (silica gel; EtOAc/hexanes 4:6) to afford **7f** (135 mg, 77 %) as a single diastereomer. Colorless solid: mp 134-136 °C (CHCl₃/hexane). R_f 0.53 (4:6 EtOAc/hexanes).

ν_{max} (KBr)/cm⁻¹ 3275, 2969, 2865, 1753, 1450, 1421, 1327, 1162, 1066, 929, 673.

^1H NMR (200 MHz, CDCl_3) δ 7.85 (d, 2H, J = 8.2 Hz, Arom- H), 7.41 (d, 2H, J = 8.0 Hz, Arom- H), 7.29-7.19 (m, 4H, Arom- H), 5.99 (d, 1H, J = 8.6 Hz, NH), 5.04 (dd, 1H, J_1 = 8.6 Hz, J_2 = 3.4 Hz, CH), 4.45 (d, 1H, J = 3.4 Hz, CH), 4.08 (q, 1H, J = 6.4 Hz, CH), 2.67 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 1.42 (d, 3H, J = 6.4 Hz, CH_3), 1.20 (s, 3H, CH_3), 0.32 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, CDCl_3) δ 217.4 (C=O), 142.9 (*quat-C*), 137.4 (*quat-C*), 132.6 (*quat-C*), 129.1 (=CH), 128.4 (=CH), 128.3 (=CH), 127.0 (=CH), 83.7 (CH), 81.3 (CH), 57.7 (CH), 46.7 (*quat-C*), 21.3 (CH_3), 20.9 (CH_3), 20.0 (CH_3), 15.7 (CH_3), 13.8 (CH_3).

HRMS (ESI^+) calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_4\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 424.1423, found 424.1440.

Compound 9a: To a solution of oxa-bridged piperidinone **3a** (200 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C were added Et_3SiH (0.310 mL, 1.9 mmol) and TiCl_4 (0.110 mL, 0.96 mmol). The reaction mixture was stirred for 4 h. and allowed to gradually warm to rt. The reaction was quenched by the addition of sat'd NaHCO_3 , and diluted with H_2O . The aqueous phase was extracted with DCM (3 x 20 mL) then ethyl acetate

(1 x 20 mL). The combined organic extracted were washed with brine, desiccated with Na_2SO_4 , and the solvents removed under reduced pressure. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5) to afford **9a** (127 mg, 63 %) as a single diastereomer. Colorless solid: mp 183-185 °C (CHCl_3 /hexane). Rf 0.35 (5:5 EtOAc/hexanes).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3463, 2947, 1450, 1326, 1153, 1084, 1031, 663.

^1H NMR (200 MHz, $\text{CDCl}_3+\text{CD}_3\text{OD}$) δ 7.45-7.21 (m, 5H, Arom- H), 7.11-7.01 (m, 4H, Arom- H), 4.60 (d, 1H, CH, J = 8.6 Hz), 4.42 (dd, 1H, CH, J_1 = 8.6 Hz, J_2 = 3.0 Hz), 3.96 (brod s, 2H, OH), 3.64 (dd, 1H, CH, J_1 = 11.5 Hz, J_2 = 3.2 Hz), 3.45 (d, 1H, CH, J = 2.8 Hz), 2.33 (s, 3H, CH_3), 2.21-2.14 (m, 1H), 1.96-1.81 (m, 2H), 1.52-1.26 (m, 5H), 1.10 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, $\text{CDCl}_3+\text{CD}_3\text{OD}$) δ 141.8 (*quat-C*), 138.8 (*quat-C*), 137.9 (*quat-C*), 129.4 (=CH), 128.4 (=CH), 127.0 (=CH), 126.7 (=CH), 126.4 (=CH), 75.0 (CH), 69.3

(CH), 64.3 (CH), 62.7 (CH), 39.7 (*quat*-C), 34.2 (CH₂), 27.4 (CH₂), 26.2 (CH₂), 20.8 (CH₃), 20.2 (CH₂), 16.7 (CH₃).

HRMS (ESI⁺) calcd for C₂₃H₂₉NO₄SNa (M+Na)⁺: 438.2296, found 438.2201.

Compound 9b: To a solution of oxa-bridged piperidinone **3g** (200 mg, 0.5 mmol) in CH₂Cl₂ (20 mL) at 0 °C were added Et₃SiH (0.300 mL, 1.8 mmol) and TiCl₄ (0.105 mL, 0.93 mmol). The reaction was stirred for 3 hr. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5) to afford **9b** (151 mg, 75 %) as a single diastereomer.

Colorless solid: mp 190-192 °C (CHCl₃/hexane). R_f 0.38 (5:5 EtOAc/hexanes).

ν_{max} (KBr)/cm⁻¹ 3450, 2927, 2854, 1591, 1492, 1453, 1303, 1145, 1087, 1051, 1028, 781.

¹H NMR (CD₃OD+CDCl₃, 200 MHz) δ 1.04 (s, 3H, CH₃), 1.50-1.35 (m, 3H), 1.85-1.51 (m, 3H), 2.20-2.01 (m, 2H), 2.33 (s, 3H, CH₃), 3.30 (broad s, 1H, OH), 3.40 (d, 1H, *J* = 3.2 Hz), 3.57 (dd, 1H, *J*₁ = 11.5 Hz, *J*₂ = 3.0 Hz), 4.34-4.28 (m, 1H), 4.57 (d, 1H, *J* = 8.2 Hz), 6.83-6.76 (m, 1H, Arom-*H*) 7.09-6.85 (m, 5H, Arom-*H*), 7.31 (d, 2H, *J* = 8.0 Hz).

¹³C NMR (CD₃OD+CDCl₃, 50.3 MHz) δ 164.4 (*quat*-C), 159.9 (*quat*-C), 142.3 (*quat*-C), 141.5 (*quat*-C), 141.4 (*quat*-C), 138.4 (*quat*-C), 129.6 (=CH), 128.7 (=CH), 128.5 (=CH), 126.7 (=CH), 124.8 (=CH), 116.4 (=CH), 116.0 (=CH), 113.8 (=CH), 113.4 (=CH), 75.0 (CH), 69.6 (CH), 63.9 (CH), 62.3 (CH), 39.6 (*quat*-C), 34.3 (CH₂), 27.5 (CH₂), 26.2 (CH₂), 21.0 (CH₃), 20.2 (CH₂), 16.7 (CH₃).

HRMS (ESI⁺) calcd for C₂₃H₂₈NO₄SFNa (M+Na)⁺: 456.2088, found 456.2121.

Compound 9c: To a solution of oxa-bridged piperidinone **3c** (200 mg, 0.5 mmol) in CH₂Cl₂ (20 mL) at 0 °C were added Et₃SiH (0.300 mL, 1.8 mmol) and TiCl₄ (0.105 mL, 0.93 mmol). The reaction was stirred for 3 hr. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5) to afford **9c** (141 mg, 70 %) as a single diastereomer. Colorless solid: mp 187-189 °C (CHCl₃/hexane). R_f 0.38 (5:5 EtOAc/hexanes).

^1H NMR (200 MHz, $\text{CD}_3\text{OD}+\text{CDCl}_3$) δ 7.22-7.15 (m, 4H, Arom-*H*), 7.02 (d, 2H, $J = 8.0$ Hz), 6.72 (t, 2H, $J = 8.8$ Hz), 4.56-4.45 (m, 2H), 3.65 (dd, 1H, $J_1 = 11.0$ Hz, $J_2 = 4.6$ Hz), 3.49 (d, 2H, $J = 2.2$ Hz), 3.40 (s, 1H), 2.33 (s, 3H, CH_3), 2.29-2.24 (m, 2H), 2.01-1.82 (m, 2H), 1.56-1.38 (m, 2H), 1.30-1.26 (m, 2H), 1.15 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, $\text{CD}_3\text{OD}+\text{CDCl}_3$) δ 164.1 (*quat-C*), 159.2 (*quat-C*), 141.9 (*quat-C*), 139.5 (*quat-C*), 132.0 (=CH), 131.9 (=CH), 128.5 (=CH), 126.3 (=CH), 113.9 (=CH), 113.5 (=CH), 75.5 (CH), 68.5 (CH), 64.0 (CH), 63.8 (CH), 40.2 (*quat-C*), 34.2 (CH_2), 27.5 (CH_2), 26.5 (CH_2), 21.0 (CH_3), 20.4 (CH_2), 17.0 (CH_3).

HRMS (ESI^+) calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_4\text{SFNa}$ ($\text{M}+\text{Na}$) $^+$: 456.6004, found 456.6015

Compound 9d: To a solution of oxa-bridged piperidinone **3h** (150 mg, 0.37 mmol) in CH_2Cl_2 (15 mL) at 0 °C were added Et_3SiH (0.240 mL, 1.5 mmol) and TiCl_4 (0.080 mL, 0.74 mmol). The reaction was stirred for 3 hr. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5) to afford **9d** (107 mg, 71 %) as a single diastereomer. Colorless solid: mp 202-204 °C (CHCl_3 /hexane). R_f 0.45 (5:5 EtOAc/hexanes).

^1H NMR (200 MHz, CDCl_3) δ 7.78 (d, 2H, $J = 8.2$ Hz), 7.36-7.23 (m, 5H, Arom-*H*), 6.94 (t, 1H, $J = 8.0$ Hz), 5.47 (s, 1H, CH), 4.58 (s, 1H, CH), 3.76-3.66 (m, 1H), 3.23 (s, 1H), 2.40 (s, 3H, CH_3), 0.85 (d, 3H, $J = 7.4$ Hz), 0.82 (s, 3H, CH_3), 0.53 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, CDCl_3) δ 165.0 (*quat-C*), 160.2 (*quat-C*), 143.2 (*quat-C*), 143.0 (*quat-C*), 137.4 (*quat-C*), 129.7 (=CH), 129.5 (=CH), 129.0 (=CH), 127.9 (=CH), 123.0 (=CH), 114.8 (=CH), 114.8 (=CH), 114.4 (=CH), 114.2 (=CH), 113.8 (=CH), 69.5 (CH), 69.4 (CH), 60.8 (CH), 59.4 (CH), 38.0 (*quat-C*), 25.3, (CH_3), 22.2, (CH_3), 21.2 (CH_3), 18.4 (CH_3).

HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_4\text{SFNa}$ ($\text{M}+\text{Na}$) $^+$: 430.1657, found 430.1685.

Compound 9e: To a solution of oxa-bridged piperidinone **3i** (180 mg, 0.38 mmol) in CH_2Cl_2 (25 mL) at 0 °C were added Et_3SiH (0.250 mL, 1.54 mmol) and TiCl_4 (0.85 mL,

0.77 mmol). The reaction was stirred for 4 hr. Further, the reaction was followed as prescribed above in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5) to afford **9e** (144 mg, 80 %) as a single diastereomer. Colorless solid: mp 206-208 °C (CHCl₃/hexane). Rf 0.44 (5:5 EtOAc/hexanes).

¹H NMR (200 MHz, CDCl₃) δ 7.76 (d, 2H, *J* = 8.0 Hz), 7.45-7.10 (m, 6H, Arom-*H*), 5.42 (s, 1H, *CH*), 4.59 (s, 1H, *CH*), 3.82 (q, 1H, *J* = 7.2 Hz), 3.74 (d, 1H, *J* = 2.8 Hz), 2.84 (brod s, 1H, OH), 2.40 (s, 3H, CH₃), 0.84 (s, 3H, CH₃), 0.82 (d, 3H, *J* = 7.2 Hz), 0.67 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, CDCl₃) δ 143.5 (*quat-C*), 142.1 (*quat-C*), 137.6 (*quat-C*), 130.5 (=CH), 130.3 (=CH), 129.8 (=CH), 129.4 (=CH), 127.8 (=CH), 126.3 (=CH), 122.5 (*quat-C*), 69.2 (CH), 69.7 (CH), 60.5 (CH), 59.3 (CH), 38.3 (*quat-C*), 25.5, (CH₃), 22.6, (CH₃), 21.5 (CH₃), 18.6 (CH₃).

HRMS (ESI⁺) calcd for C₂₁H₂₆NO₄SBrNa ((M+2)+Na)⁺: 492.2728, found 492.2714.

Compound 9f: To a solution of oxa-bridged piperidinone **3d** (160 mg, 0.39 mmol) in CH₂Cl₂ (18 mL) at 0 °C were added Et₃SiH (0.250 mL, 1.58 mmol) and TiCl₄ (0.090 mL, 0.79 mmol). The reaction was stirred for 4 hr. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5) to afford **9f** (109 mg, 68 %) as a single diastereomer. Colorless solid: mp 192-194 °C (CHCl₃/hexane). Rf 0.47 (5:5 EtOAc/hexanes).

¹H NMR (200 MHz, CDCl₃) δ 7.80 (d, 2H, Arom-*H*, *J* = 7.8 Hz), 7.50-7.44 (m, 2H, Arom-*H*), 7.25 (d, 2H, Arom-*H*, *J* = 7.8 Hz), 7.06-6.93 (m, 2H, Arom-*H*), 5.48 (s, 1H, *CH*), 4.63 (s, 1H, *CH*), 3.76-3.62 (m, 2H), 2.42 (s, 3H, CH₃), 0.82 (s, 3H, CH₃), 0.78 (d, 3H, CH₃, *J* = 7.4 Hz), 0.55 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, CDCl₃+CD₃OD) δ 164.2, (*quat-C*), 159.3 (*quat-C*), 143.1 (*quat-C*), 137.6 (*quat-C*), 135.7 (*quat-C*), 129.3 (=CH), 129.1 (=CH), 127.9 (=CH), 115.2

(=CH), 114.8 (=CH), 69.7 (CH), 69.5 (CH), 60.5 (CH), 59.4 (CH), 38.1 (*quat*-C), 25.5 (CH₃), 22.4 (CH₃), 21.4 (CH₃), 18.5 (CH₃).

HRMS (ESI⁺) calcd for C₂₁H₂₆NO₄SFNa (M+Na)⁺: 430.1685, found 430.1698.

Compound 9g: To a solution of oxa-bridged piperidinone **3b** (250 mg, 0.64 mmol) in CH₂Cl₂ (25 mL) at 0 °C were added Et₃SiH (0.415 mL, 2.58 mmol) and TiCl₄ (0.145 mL, 1.29 mmol). The reaction was stirred for 4 hr. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica

gel; EtOAc/hexanes 5:5) to afford **9g** (168 mg, 67 %) as a single diastereomer. Colorless solid: mp 181-183 °C (CHCl₃/hexane). R_f 0.35 (5:5 EtOAc/hexanes).

¹H NMR (200 MHz, CDCl₃) δ 7.79 (d, 2H, Arom-*H*, *J* = 8.4 Hz), 7.43 (dd, 2H, Arom-*H*, *J*₁ = 7.0 Hz, *J*₂ = 1.8 Hz), 7.30-7.23 (m, 5H, Arom-*H*), 5.52 (s, 1H, *CH*), 4.71-4.68 (m, 1H, *CH*), 3.86-3.75 (m, 2H), 2.40 (s, 3H, CH₃), 0.82 (s, 3H, CH₃), 0.78 (d, 3H, CH₃, *J* = 7.4 Hz), 0.61 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, CDCl₃+CD₃OD) δ 142.9 (*quat*-C), 139.9 (*quat*-C), 137.5 (*quat*-C), 128.9 (=CH), 128.0 (=CH), 127.8 (=CH), 127.2 (=CH), 127.0 (=CH), 69.3 (CH), 61.2 (CH), 59.4 (CH), 38.0 (*quat*-C), 25.3 (CH₃), 22.1 (CH₃), 21.1 (CH₃), 18.2 (CH₃).

HRMS (ESI⁺) calcd for C₂₁H₂₇NO₄SNa (M+Na)⁺: 412.1763, found 412.1785.

Compound 12: To a solution of oxa-bridged piperidinone **3e** (150 mg, 0.3 mmol) in CH₂Cl₂ (15 mL) at 0 °C were added Et₃SiH (0.200 mL, 1.23 mmol) and TiCl₄ (0.70 mL, 0.61 mmol). The reaction was stirred for 2 hr. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 4:6) to afford **12** (92 mg, 61 %) as a single diastereomer. Colorless

solid: mp 139-141 °C (CHCl₃/hexane). R_f 0.57 (4:6 EtOAc/hexanes).

ν_{max} (KBr)/cm⁻¹ 3442, 2938, 1756, 1712, 1452, 1321, 1223, 1155, 698, 565.

^1H NMR (200 MHz, CDCl_3) δ 7.15-7.00 (m, 9H, Arom-*H*), 4.99 (s, 1H, *CH*), 4.38 (dd, 1H, $J_1 = 12.4$ Hz, $J_2 = 3.6$ Hz), 4.13 (s, 1H, *CH*), 3.82-3.55 (m, 1H), 2.52 (d, 1H, $J = 10.2$ Hz), 2.36 (s, 3H, CH_3), 2.18 (d, 1H, $J = 10.2$ Hz), 2.01-1.82 (m, 2H), 1.64 (s, 3H, CH_3), 1.58-1.14 (m, 4H), 1.00 (t, 3H, CH_3 , $J = 7.2$ Hz). ^{13}C NMR (50.3 MHz, CDCl_3) δ 209.5 ($\text{C}=\text{O}$), 169.6 ($\text{C}=\text{O}$), 142.9 (*quat-C*), 139.2 (*quat-C*), 133.6 (*quat-C*), 130.5 ($=\text{CH}$), 128.9 ($=\text{CH}$), 128.1 ($=\text{CH}$), 127.2 ($=\text{CH}$), 126.8 ($=\text{CH}$), 80.8 (*quat-C*), 68.7 (*CH*), 64.0 (*CH*), 62.4 (OCH_2), 50.8 (*quat-C*), 35.8, (CH_2), 29.1, (CH_2), 26.1 (CH_3), 25.4, (CH_2), 22.1 (CH_2), 21.3 (CH_3), 13.3 (CH_3).

$\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3442, 2938, 1756, 1712, 1452, 1321, 1223, 1155, 698, 565.

HRMS (ESI^+) calcd for $\text{C}_{26}\text{H}_{31}\text{NO}_6\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 508.2292, found 508.2297.

Compound 13: To a solution of oxa-bridged piperidinone **3a** (200 mg, 0.48 mmol) in CH_3OH (15 mL) at 0 °C (ice bath) was added NaBH_4 (0.045 mg, 1.5 mmol) and the reaction was stirred for 60 minutes, during which time the progress of the reaction was monitored by TLC. Reaction mixture was concentrated and quenched with saturated aqueous NaHCO_3 (20 ml) and then the resulting phases were separated. The

organic extracts were washed with water and brine, and then dried (Na_2SO_4). The solvent was removed under reduced pressure. The resulting residue was purified using silica gel column chromatography (silica gel; EtOAc /hexanes) to afford mixture of two diastereomers in 5:1 ratio of **13** (150 mg, 75%) and **7a** (30 mg, 15%).

Compound **13**: ^1H NMR (200 MHz, CDCl_3) δ 7.73 (d, 2H, Arom-*H*, $J = 8.0$ Hz), 7.56 (d, 2H, Arom-*H*, $J = 7.0$ Hz), 7.37-7.22 (m, 5H, Arom-*H*), 5.21 (d, 1H, *CH*, $J = 4.2$ Hz), 4.81 (t, 1H, $J = 4.6$ Hz), 3.74-3.69 (m, 1H, *CH*), 2.47 (s, 3H, CH_3), 2.16 (d, 1H, $J = 13.8$ Hz), 1.68-1.30 (m, 7H), 1.26 (s, 3H, CH_3).

^{13}C NMR (50.3 MHz, CDCl_3) δ 143.5 (*quat-C*), 137.5 (*quat-C*), 136.2 (*quat-C*), 129.3 ($=\text{CH}$), 128.3 ($=\text{CH}$), 127.9 ($=\text{CH}$), 126.7 ($=\text{CH}$), 106.3 (*quat-C*), 82.1 (*CH*), 80.8 (*CH*), 67.4 (*CH*), 46.7 (*quat-C*), 41.4 (CH_2), 26.3 (CH_2), 23.2 (CH_2), 21.3 (CH_3), 21.1 (CH_2), 15.0 (CH_3).

HRMS (ESI^+) calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_4\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 436.1761, found 436.1775.

Compound 14: To a solution of alcohol **13** (130 mg, 0.3 mmol) in CH₂Cl₂ (15 mL) at 0 °C were added Et₃SiH (0.100 mL, 0.62 mmol) and TiCl₄ (0.070 mL, 0.62 mmol). The reaction was stirred for 2 hr. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5) to afford **14** (94 mg, 72 %) as a single diastereomer. Colorless solid: mp 175-177 °C (CHCl₃/hexane). R_f 0.40 (5:5 EtOAc/hexanes).

¹H NMR (200 MHz, Acetone-d₆) δ 7.52-7.38 (m, 4H, Arom-H), 7.21-7.15 (m, 5H), 4.83 (d, 1H, CH, J = 6.0 Hz), 4.13-4.06 (m, 1H), 3.23 (dd, 1H, J_1 = 12.0 Hz, J_2 = 3.0 Hz), 3.02 (broad s, 1H, OH), 2.80 (d, 1H, J = 8.4 Hz), 2.37 (s, 3H, CH₃), 2.08-2.02 (m, 1H), 1.88-1.83 (m, 2H), 1.46-1.42 (m, 4H), 1.12-0.97 (m, 1H), 0.86 (s, 3H, CH₃).

¹³C NMR (50.3 MHz, Acetone-d₆) δ 142.3 (quat-C), 140.5 (quat-C), 138.1 (quat-C), 128.9 (=CH), 128.1 (=CH), 127.2 (=CH), 126.4 (=CH), 81.0 (CH), 75.4 (CH), 67.6 (CH), 67.0 (CH), 39.6 (quat-C), 36.9 (CH₂), 28.0 (CH₂), 26.1 (CH₂), 20.4 (CH₃), 20.0 (CH₂), 11.7 (CH₃).

HRMS (ESI⁺) calcd for C₂₃H₂₉NO₄SNa (M+Na)⁺: 438.2416, found 438.2427.

Compound 15: To a solution of oxa-bridged piperidinone **3b** (200 mg, 0.51 mmol) in CH₃OH (15 mL) at 0 °C was added NaBH₄ (0.050 mg, 1.5 mmol) and the reaction was stirred for 60 minutes, during which time the progress of the reaction was monitored by TLC. Reaction mixture was concentrated and quenched with saturated aqueous

NaHCO₃ (20 ml) and then the resulting phases were separated. The organic extracts were washed with water and brine, and then dried (Na₂SO₄). The solvent was removed under reduced pressure. The resulting residue purified using silica gel column chromatography (silica gel; EtOAc/hexanes) to afford the mixture of two diastereomers in 5:1 ratio of *endo*-alcohol **15** (153 mg, 76%) and **7b** (31 mg, 16%).

Compound **15**: ¹H NMR (CDCl₃, 200 MHz) δ 7.77 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 7.2 Hz), 7.38-7.20 (m, 5H, Arom-H), 5.25 (d, 1H, J = 4.4 Hz), 4.74 (t, 1H, J = 4.8 Hz),

3.74 (t, 1H, $J = 4.4$ Hz), 2.41 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 0.99 (s, 3H, CH_3).

^{13}C NMR (CDCl_3 , 50.3 MHz) δ 143.7 (*quat-C*), 136.9 (*quat-C*), 135.8 (*quat-C*), 129.5 (=CH), 129.1 (=CH), 128.3 (=CH), 128.1 (=CH), 127.4 (=CH), 126.9 (=CH), 106.7 (*quat-C*), 81.0 (CH), 79.7 (CH), 67.5 (CH), 47.1 (*quat-C*), 28.3 (CH_3), 21.4 (CH_3), 17.9 (CH_3), 14.4 (CH_3).

HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_4\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 410.2834, found 410.2856.

Compound 16: To a solution of alcohol **15** (150 mg, 0.38 mmol) in CH_2Cl_2 (15 mL) at 0 °C were added Et_3SiH (0.125 mL, 0.76 mmol) and TiCl_4 (0.085 mL, 0.77 mmol). The reaction was stirred for 3 hrs. Further, the reaction was followed as prescribed in **9a**. The crude product was purified by column chromatography (silica gel; EtOAc/hexanes 5:5)

to afford **16** (114 mg, 76 %) as a single diastereomer. Colorless solid: mp 180-182 °C (CHCl_3 /hexane). R_f 0.45 (5:5 EtOAc/hexanes).

^1H NMR (Acetone- d_6 , 200 MHz) δ 7.58 (d, 2H, Arom- H , $J = 7.6$ Hz), 7.50 (d, 2H, Arom- H , $J = 8.4$ Hz), 7.32-7.20 (m, 5H, Arom- H), 5.18 (d, 1H, CH , $J = 4.6$ Hz), 4.42 (broad s, 1H, OH), 4.06-3.96 (m, 1H, CH), 3.71 (q, 1H, CH , $J = 6.8$ Hz), 3.15 (broad s, 1H, OH), 2.69 (d, 1H, CH , $J = 8.6$ Hz), 2.39 (s, 3H, CH_3), 1.20 (d, 3H, CH_3 , $J = 6.8$ Hz), 0.86 (s, 3H, CH_3), 0.61 (s, 3H, CH_3).

^{13}C NMR (Acetone- d_6 , 50.3 MHz) δ 142.9 (*quat-C*), 142.2 (*quat-C*), 135.9 (*quat-C*), 129.2 (=CH), 128.9 (=CH), 127.8 (=CH), 127.5 (=CH), 126.6 (=CH), 126.5 (=CH), 76.7 (CH), 75.5 (CH), 63.8 (CH), 59.5 (CH), 37.6 (*quat-C*), 27.9 (CH_3), 20.5 (CH_3), 18.7 (CH_3), 16.8 (CH_3).

HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{27}\text{NO}_4\text{SNa}$ ($\text{M}+\text{Na}$) $^+$: 412.1763, found 412.1774.

X-ray data for compound 4a

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **4a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
S(14)	1622(1)	1789(1)	4967(1)	53(1)
O(28)	1471(1)	2022(2)	3319(3)	76(1)
O(27)	1368(1)	804(2)	5816(3)	76(1)
O(1)	1143(1)	4394(2)	9873(2)	42(1)
N(13)	1507(1)	3088(2)	5887(3)	48(1)
O(11)	705(1)	2567(2)	10574(3)	53(1)
C(15)	2338(1)	1550(2)	5068(4)	44(1)
C(21)	2125(1)	3368(3)	8228(3)	42(1)
C(9)	645(1)	3851(2)	10511(3)	41(1)
O(30)	385(1)	3809(3)	6359(3)	76(1)
C(3)	550(1)	4003(3)	7709(3)	46(1)
C(2)	1152(1)	4236(3)	8177(3)	43(1)
C(4)	213(1)	4134(3)	9226(3)	45(1)
C(12)	1539(1)	3165(3)	7663(3)	41(1)
C(18)	3464(1)	1170(3)	5220(4)	54(1)
C(6)	-80(1)	5984(3)	10964(4)	62(1)
C(5)	66(1)	5545(3)	9274(4)	53(1)
C(8)	539(1)	4401(3)	12162(3)	49(1)
C(17)	3106(2)	483(3)	6114(5)	73(1)
C(26)	2354(2)	2634(4)	9386(4)	68(1)
C(10)	-298(1)	3331(3)	9256(4)	62(1)
C(23)	2990(2)	4405(4)	7969(5)	77(1)
C(24)	3216(1)	3643(4)	9087(5)	77(1)
C(22)	2448(1)	4263(3)	7533(4)	61(1)
C(20)	2685(2)	2252(4)	4165(5)	77(1)
C(7)	391(1)	5754(3)	12116(4)	62(1)
C(19)	3240(1)	2042(4)	4253(5)	83(1)
C(25)	2906(2)	2775(5)	9805(5)	87(1)
C(29)	4073(1)	938(4)	5305(6)	92(1)
C(16)	2545(1)	664(3)	6054(5)	67(1)

Table S2. Bond lengths [Å] and angles [°] for compound **4a**.

S(14)-O(27)	1.417(3)	C(6)-H(6A)	0.9700
S(14)-O(28)	1.433(2)	C(6)-H(6B)	0.9700
S(14)-N(13)	1.621(2)	C(5)-H(5A)	0.9700
S(14)-C(15)	1.761(3)	C(5)-H(5B)	0.9700
O(1)-C(2)	1.414(3)	C(8)-C(7)	1.508(5)
O(1)-C(9)	1.446(3)	C(8)-H(8A)	0.9700
N(13)-C(12)	1.473(3)	C(8)-H(8B)	0.9700
N(13)-H(13)	0.8600	C(17)-C(16)	1.377(5)
O(11)-C(9)	1.397(3)	C(17)-H(17)	0.9300
O(11)-H(11)	0.8200	C(26)-C(25)	1.394(5)
C(15)-C(16)	1.355(4)	C(26)-H(26)	0.9300
C(15)-C(20)	1.358(4)	C(10)-H(10A)	0.9600
C(21)-C(26)	1.363(4)	C(10)-H(10B)	0.9600
C(21)-C(22)	1.372(4)	C(10)-H(10C)	0.9600
C(21)-C(12)	1.512(3)	C(23)-C(24)	1.355(6)
C(9)-C(8)	1.512(4)	C(23)-C(22)	1.374(5)
C(9)-C(4)	1.524(4)	C(23)-H(23)	0.9300
O(30)-C(3)	1.205(3)	C(24)-C(25)	1.341(6)
C(3)-C(4)	1.504(4)	C(24)-H(24)	0.9300
C(3)-C(2)	1.534(4)	C(22)-H(22)	0.9300
C(2)-C(12)	1.552(4)	C(20)-C(19)	1.370(5)
C(2)-H(2)	0.9800	C(20)-H(20)	0.9300
C(4)-C(10)	1.516(4)	C(7)-H(7A)	0.9700
C(4)-C(5)	1.569(4)	C(7)-H(7B)	0.9700
C(12)-H(12)	0.9800	C(19)-H(19)	0.9300
C(18)-C(19)	1.350(5)	C(25)-H(25)	0.9300
C(18)-C(17)	1.361(5)	C(29)-H(29A)	0.9600
C(18)-C(29)	1.503(4)	C(29)-H(29B)	0.9600
C(6)-C(7)	1.510(4)	C(29)-H(29C)	0.9600
C(6)-C(5)	1.518(5)	C(16)-H(16)	0.9300
O(27)-S(14)-O(28)	119.51(16)	C(4)-C(5)-H(5A)	109.1
O(27)-S(14)-N(13)	110.12(13)	C(6)-C(5)-H(5B)	109.1
O(28)-S(14)-N(13)	104.52(14)	C(4)-C(5)-H(5B)	109.1
O(27)-S(14)-C(15)	107.14(14)	H(5A)-C(5)-H(5B)	107.9
O(28)-S(14)-C(15)	108.86(14)	C(7)-C(8)-C(9)	113.5(3)
N(13)-S(14)-C(15)	105.94(12)	C(7)-C(8)-H(8A)	108.9
C(2)-O(1)-C(9)	109.0(2)	C(9)-C(8)-H(8A)	108.9
C(12)-N(13)-S(14)	120.5(2)	C(7)-C(8)-H(8B)	108.9
C(12)-N(13)-H(13)	119.7	C(9)-C(8)-H(8B)	108.9
S(14)-N(13)-H(13)	119.7	H(8A)-C(8)-H(8B)	107.7
C(9)-O(11)-H(11)	109.5	C(18)-C(17)-C(16)	122.2(3)
C(16)-C(15)-C(20)	119.7(3)	C(18)-C(17)-H(17)	118.9

C(16)-C(15)-S(14)	120.0(2)	C(16)-C(17)-H(17)	118.9
C(20)-C(15)-S(14)	120.3(2)	C(21)-C(26)-C(25)	120.3(4)
C(26)-C(21)-C(22)	118.1(3)	C(21)-C(26)-H(26)	119.9
C(26)-C(21)-C(12)	121.1(3)	C(25)-C(26)-H(26)	119.9
C(22)-C(21)-C(12)	120.7(3)	C(4)-C(10)-H(10A)	109.5
O(11)-C(9)-O(1)	109.2(2)	C(4)-C(10)-H(10B)	109.5
O(11)-C(9)-C(8)	112.0(2)	H(10A)-C(10)-H(10B)	109.5
O(1)-C(9)-C(8)	108.2(2)	C(4)-C(10)-H(10C)	109.5
O(11)-C(9)-C(4)	107.3(2)	H(10A)-C(10)-H(10C)	109.5
O(1)-C(9)-C(4)	103.9(2)	H(10B)-C(10)-H(10C)	109.5
C(8)-C(9)-C(4)	115.7(2)	C(24)-C(23)-C(22)	120.0(4)
O(30)-C(3)-C(4)	127.5(3)	C(24)-C(23)-H(23)	120.0
O(30)-C(3)-C(2)	125.4(3)	C(22)-C(23)-H(23)	120.0
C(4)-C(3)-C(2)	107.0(2)	C(25)-C(24)-C(23)	120.0(3)
O(1)-C(2)-C(3)	104.8(2)	C(25)-C(24)-H(24)	120.0
O(1)-C(2)-C(12)	111.8(2)	C(23)-C(24)-H(24)	120.0
C(3)-C(2)-C(12)	112.7(2)	C(21)-C(22)-C(23)	121.1(3)
O(1)-C(2)-H(2)	109.1	C(21)-C(22)-H(22)	119.4
C(3)-C(2)-H(2)	109.1	C(23)-C(22)-H(22)	119.4
C(12)-C(2)-H(2)	109.1	C(15)-C(20)-C(19)	119.3(3)
C(3)-C(4)-C(10)	113.9(2)	C(15)-C(20)-H(20)	120.4
C(3)-C(4)-C(9)	100.9(2)	C(19)-C(20)-H(20)	120.4
C(10)-C(4)-C(9)	115.9(2)	C(8)-C(7)-C(6)	110.8(3)
C(3)-C(4)-C(5)	103.7(2)	C(8)-C(7)-H(7A)	109.5
C(10)-C(4)-C(5)	111.7(2)	C(6)-C(7)-H(7A)	109.5
C(9)-C(4)-C(5)	109.6(2)	C(8)-C(7)-H(7B)	109.5
N(13)-C(12)-C(21)	111.5(2)	C(6)-C(7)-H(7B)	109.5
N(13)-C(12)-C(2)	106.4(2)	H(7A)-C(7)-H(7B)	108.1
C(21)-C(12)-C(2)	112.1(2)	C(18)-C(19)-C(20)	122.9(3)
N(13)-C(12)-H(12)	108.9	C(18)-C(19)-H(19)	118.6
C(21)-C(12)-H(12)	108.9	C(20)-C(19)-H(19)	118.6
C(2)-C(12)-H(12)	108.9	C(24)-C(25)-C(26)	120.4(4)
C(19)-C(18)-C(17)	116.6(3)	C(24)-C(25)-H(25)	119.8
C(19)-C(18)-C(29)	122.7(3)	C(26)-C(25)-H(25)	119.8
C(17)-C(18)-C(29)	120.8(3)	C(18)-C(29)-H(29A)	109.5
C(7)-C(6)-C(5)	110.6(2)	C(18)-C(29)-H(29B)	109.5
C(7)-C(6)-H(6A)	109.5	H(29A)-C(29)-H(29B)	109.5
C(5)-C(6)-H(6A)	109.5	C(18)-C(29)-H(29C)	109.5
C(7)-C(6)-H(6B)	109.5	H(29A)-C(29)-H(29C)	109.5
C(5)-C(6)-H(6B)	109.5	H(29B)-C(29)-H(29C)	109.5
H(6A)-C(6)-H(6B)	108.1	C(15)-C(16)-H(17)	119.3(3)
C(6)-C(5)-C(4)	112.4(3)	C(15)-C(16)-H(16)	120.3
C(6)-C(5)-H(5A)	109.1	C(17)-C(16)-H(16)	120.3

X-ray data for compound 7a

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **7a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
S(16)	8267(1)	4124(1)	3190(1)	20(1)
O(1)	9672(2)	307(2)	2812(2)	22(1)
O(18)	9415(2)	5643(2)	4178(2)	24(1)
O(26)	7957(2)	-1226(2)	-558(2)	29(1)
O(17)	7670(2)	3841(2)	1893(2)	27(1)
N(15)	8978(2)	2943(2)	3034(2)	21(1)
C(3)	8481(3)	-1003(3)	522(2)	21(1)
C(10)	5550(3)	-763(3)	1143(2)	21(1)
C(2)	9217(3)	586(3)	1784(2)	20(1)
C(19)	6813(3)	3699(3)	3830(2)	21(1)
C(9)	6838(2)	351(2)	2204(2)	18(1)
C(22)	4519(3)	3059(3)	4836(3)	26(1)
C(8)	8154(3)	1307(3)	1980(2)	19(1)
C(14)	6894(3)	510(3)	3443(2)	21(1)
C(20)	5374(3)	2894(3)	2994(2)	25(1)
C(24)	7121(3)	4182(3)	5164(2)	24(1)
C(13)	5713(3)	-437(3)	3613(2)	24(1)
C(21)	4249(3)	2573(3)	3501(3)	27(1)
C(12)	4450(3)	-1555(3)	2554(3)	28(1)
C(7A)	8830(3)	-1349(3)	2368(2)	22(1)
C(5)	10456(3)	-3073(3)	1336(2)	27(1)
C(4)	9897(3)	-2413(3)	575(2)	24(1)
C(3A)	8561(3)	-2193(3)	886(2)	22(1)
C(23)	5977(3)	3862(3)	5655(2)	26(1)
C(7)	9632(3)	-1793(3)	3183(3)	29(1)
C(11)	4372(3)	-1714(3)	1316(3)	28(1)
C(25)	3283(3)	2740(3)	5382(3)	31(1)
C(6)	10934(3)	-1967(3)	2809(2)	28(1)
C(27)	7144(3)	-3731(3)	130(3)	35(1)

Table S4. Bond lengths [Å] and angles [°] for compound **7a**.

S(16)-O(17)	1.4323(18)	C(13)-C(12)	1.383(4)
S(16)-O(18)	1.4430(17)	C(13)-H(13)	0.9300
S(16)-N(15)	1.631(2)	C(21)-H(21)	0.9300
S(16)-C(19)	1.772(2)	C(12)-C(11)	1.387(4)
O(1)-C(2)	1.424(3)	C(12)-H(12)	0.9300
O(1)-C(7A)	1.465(3)	C(7A)-C(7)	1.513(3)
O(26)-(3)	1.205(3)	C(7A)-C(3A)	1.527(3)
N(15)-C(8)	1.472(3)	C(7A)-H(7A)	0.9800
N(15)-(15)	0.84(3)	C(5)-C(4)	1.520(4)
C(3)-C(3A)	1.519(3)	C(5)-C(6)	1.521(3)
C(3)-C(2)	1.532(3)	C(5)-H(5A)	0.9700
C(10)-C(11)	1.380(3)	C(5)-H(5B)	0.9700
C(10)-C(9)	1.397(3)	C(4)-C(3A)	1.552(3)
C(10)-H(10)	0.9300	C(4)-H(4A)	0.9700
C(2)-C(8)	1.545(3)	C(4)-H(4B)	0.9700
C(2)-H(2)	0.9800	C(3A)-C(27)	1.534(3)
C(19)-C(24)	1.387(3)	C(23)-H(23)	0.9300
C(19)-C(20)	1.390(3)	C(7)-C(6)	1.525(4)
C(9)-C(14)	1.390(3)	C(7)-H(7B)	0.9700
C(9)-C(8)	1.514(3)	C(7)-H(7C)	0.9700
C(22)-C(21)	1.390(4)	C(11)-H(11)	0.9300
C(22)-C(23)	1.400(4)	C(25)-H(25A)	0.9600
C(22)-C(25)	1.504(4)	C(25)-H(25B)	0.9600
C(8)-H(8)	0.9800	C(25)-H(25C)	0.9600
C(14)-C(13)	1.379(3)	C(6)-H(6A)	0.9700
C(14)-H(14)	0.9300	C(6)-H(6B)	0.9700
C(20)-C(21)	1.380(4)	C(27)-H(27A)	0.9600
C(20)-H(20)	0.9300	C(27)-H(27B)	0.9600
C(24)-C(23)	1.384(4)	C(27)-H(27C)	0.9600
C(24)-H(24)	0.9300		
O(17)-S(16)-O(18)	119.51(10)	O(1)-C(7A)-C(7)	109.5(2)
O(17)-S(16)-N(15)	106.92(11)	O(1)-C(7A)-C(3A)	105.44(18)
O(18)-S(16)-N(15)	104.97(10)	C(7)-C(7A)-C(3A)	116.4(2)
O(17)-S(16)-C(19)	107.86(11)	O(1)-C(7A)-H(7A)	108.4
O(18)-S(16)-C(19)	107.14(11)	C(7)-C(7A)-H(7A)	108.4
N(15)-S(16)-C(19)	110.28(11)	C(3A)-C(7A)-H(7A)	108.4
C(2)-O(1)-C(7A)	108.65(17)	C(4)-C(5)-C(6)	109.7(2)
C(8)-N(15)-S(16)	119.38(16)	C(4)-C(5)-H(5A)	109.7
C(8)-N(15)-H(15)	116(2)	C(6)-C(5)-H(5A)	109.7
S(16)-N(15)-H(15)	111(2)	C(4)-C(5)-H(5B)	109.7
O(26)-C(3)-C(3A)	127.4(2)	C(6)-C(5)-H(5B)	109.7
O(26)-C(3)-C(2)	124.6(2)	H(5A)-C(5)-H(5B)	108.2

C(3A)-C(3)-C(2)	107.92(19)	C(5)-C(4)-C(3A)	112.0(2)
C(11)-C(10)-C(9)	120.6(2)	C(5)-C(4)-H(4A)	109.2
C(11)-C(10)-H(10)	119.7	C(3A)-C(4)-H(4A)	109.2
C(9)-C(10)-H(10)	119.7	C(5)-C(4)-H(4B)	109.2
O(1)-C(2)-C(3)	105.52(18)	C(3A)-C(4)-H(4B)	109.2
O(1)-C(2)-C(8)	114.41(18)	H(4A)-C(4)-H(4B)	107.9
C(3)-C(2)-C(8)	110.06(19)	C(3)-C(3A)-C(7A)	101.40(18)
O(1)-C(2)-H(2)	108.9	C(3)-C(3A)-C(27)	111.6(2)
C(3)-C(2)-H(2)	108.9	C(7A)-C(3A)-C(27)	113.0(2)
C(8)-C(2)-H(2)	108.9	C(3)-C(3A)-C(4)	106.43(19)
C(24)-C(19)-C(20)	120.5(2)	C(7A)-C(3A)-C(4)	112.0(2)
C(24)-C(19)-S(16)	119.65(19)	C(27)-C(3A)-C(4)	111.8(2)
C(20)-C(19)-S(16)	119.86(18)	C(24)-C(23)-C(22)	121.5(2)
C(14)-C(9)-C(10)	118.7(2)	C(24)-C(23)-H(23)	119.3
C(14)-C(9)-C(8)	121.3(2)	C(22)-C(23)-H(23)	119.3
C(10)-C(9)-C(8)	119.9(2)	C(7A)-C(7)-C(6)	114.0(2)
C(21)-C(22)-C(23)	117.9(2)	C(7A)-C(7)-H(7B)	108.8
C(21)-C(22)-C(25)	121.0(2)	C(6)-C(7)-H(7B)	108.8
C(23)-C(22)-C(25)	121.1(2)	C(7A)-C(7)-H(7C)	108.8
N(15)-C(8)-C(9)	114.19(18)	C(6)-C(7)-H(7C)	108.8
N(15)-C(8)-C(2)	108.59(19)	H(7B)-C(7)-H(7C)	107.7
C(9)-C(8)-C(2)	111.53(18)	C(10)-C(11)-C(12)	120.1(2)
N(15)-C(8)-H(8)	107.4	C(10)-C(11)-H(11)	120.0
C(9)-C(8)-H(8)	107.4	C(12)-C(11)-H(11)	120.0
C(2)-C(8)-H(8)	107.4	C(22)-C(25)-H(25A)	109.5
C(13)-C(14)-C(9)	120.5(2)	C(22)-C(25)-H(25B)	109.5
C(13)-C(14)-H(14)	119.7	H(25A)-C(25)-H(25B)	109.5
C(9)-C(14)-H(14)	119.7	C(22)-C(25)-H(25C)	109.5
C(21)-C(20)-C(19)	119.5(2)	H(25A)-C(25)-H(25C)	109.5
C(21)-C(20)-H(20)	120.3	H(25B)-C(25)-H(25C)	109.5
C(19)-C(20)-H(20)	120.3	C(5)-C(6)-C(7)	109.7(2)
C(23)-C(24)-C(19)	119.2(2)	C(5)-C(6)-H(6A)	109.7
C(23)-C(24)-H(24)	120.4	C(7)-C(6)-H(6A)	109.7
C(19)-C(24)-H(24)	120.4	C(5)-C(6)-H(6B)	109.7
C(14)-C(13)-C(12)	120.5(2)	C(7)-C(6)-H(6B)	109.7
C(14)-C(13)-H(13)	119.7	H(6A)-C(6)-H(6B)	108.2
C(12)-C(13)-H(13)	119.7	C(3A)-C(27)-H(27A)	109.5
C(20)-C(21)-C(22)	121.5(2)	C(3A)-C(27)-H(27B)	109.5
C(20)-C(21)-H(21)	119.2	H(27A)-C(27)-H(27B)	109.5
C(22)-C(21)-H(21)	119.2	C(3A)-C(27)-H(27C)	109.5
C(13)-C(12)-C(11)	119.6(2)	H(27A)-C(27)-H(27C)	109.5
C(13)-C(12)-H(12)	120.2	H(27B)-C(27)-H(27C)	109.5
C(11)-C(12)-H(12)	120.2		

X-ray data for compound 9a

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **9a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
S(36)	8465(1)	6740(1)	8844(1)	12(1)
O(37)	8051(2)	6277(2)	8403(1)	17(1)
O(38)	7831(2)	7182(2)	9213(1)	16(1)
C(35)	8763(2)	5528(3)	9951(1)	16(1)
C(31)	11139(2)	5327(3)	9244(1)	13(1)
N(28)	9122(2)	5555(3)	9060(1)	11(1)
C(35A)	9505(2)	5773(3)	9557(1)	11(1)
C(39)	9257(2)	8012(3)	8701(1)	12(1)
C(41)	10148(2)	9854(3)	8961(1)	16(1)
C(47)	9607(3)	3098(3)	8098(1)	17(1)
C(44)	9716(2)	8066(3)	8259(1)	16(1)
C(46)	9232(2)	3662(3)	8505(1)	12(1)
C(45)	11420(2)	10886(3)	8450(2)	23(1)
C(50)	8053(3)	1958(3)	8539(1)	18(1)
C(32)	10862(2)	5527(3)	10124(1)	15(1)
C(54)	10301(3)	3557(3)	9685(1)	15(1)
C(29)	9702(2)	4898(3)	8677(1)	12(1)
C(51)	8441(2)	3093(3)	8722(1)	15(1)
C(30)	10790(2)	4699(3)	8782(1)	14(1)
C(31A)	10440(2)	5032(3)	9648(1)	13(1)
C(40)	9458(2)	8917(3)	9051(1)	16(1)
C(49)	8444(3)	1401(3)	8130(1)	20(1)
C(48)	9222(2)	1976(3)	7909(1)	19(1)
C(34)	9176(2)	6064(4)	10417(1)	19(1)
C(42)	10643(2)	9897(3)	8533(2)	19(1)
C(43)	10410(2)	9007(3)	8180(1)	18(1)
C(33)	10146(2)	5455(3)	10543(1)	19(1)
S(9)	6177(1)	1817(1)	6441(1)	12(1)
O(11)	5737(2)	1348(2)	6874(1)	16(1)
O(10)	5560(2)	2271(2)	6066(1)	18(1)
N(1)	6832(2)	621(2)	6224(1)	12(1)
C(4)	8844(2)	327(3)	6045(1)	14(1)
C(12)	6973(2)	3072(3)	6596(1)	16(1)
C(21)	5822(2)	-3037(3)	6703(1)	18(1)
C(13)	7244(2)	3956(3)	6248(2)	19(1)
C(8)	6475(2)	595(3)	5336(1)	16(1)

C(24)	7239(3)	-1784(3)	7211(1)	18(1)
C(19)	6911(2)	-1245(3)	6792(1)	14(1)
C(8A)	7213(2)	831(3)	5729(1)	13(1)
C(17)	7348(3)	3146(3)	7053(2)	21(1)
C(5)	8574(2)	565(3)	5162(1)	16(1)
C(2)	7401(2)	-25(3)	6613(1)	13(1)
C(3)	8484(2)	-300(3)	6500(1)	14(1)
C(27)	7991(2)	-1401(3)	5595(1)	16(1)
C(4A)	8152(2)	60(3)	5634(1)	13(1)
C(7)	6899(2)	1120(3)	4868(1)	17(1)
C(22)	6161(2)	-3577(3)	7118(1)	17(1)
C(20)	6187(2)	-1882(3)	6535(1)	15(1)
C(14)	7918(3)	4881(3)	6356(2)	25(1)
C(18)	9103(3)	5937(4)	6915(2)	41(1)
C(16)	8034(2)	4079(3)	7156(2)	25(1)
C(6)	7871(2)	505(3)	4744(1)	18(1)
C(23)	6868(3)	-2938(3)	7375(1)	19(1)
C(15)	8337(2)	4949(3)	6806(2)	26(1)
O(25)	9009(2)	151(2)	6904(1)	19(1)
O(52)	11297(2)	5231(3)	8383(1)	21(1)
O(53)	11209(2)	6686(2)	9182(1)	18(1)
O(26)	8937(2)	1680(2)	6111(1)	17(1)

Table S6. Bond lengths [Å] and angles [°] for compound **9a**.

S(36)-O(38)	1.432(3)	S(9)-N(1)	1.656(3)
S(36)-O(37)	1.446(3)	S(9)-C(12)	1.764(3)
S(36)-N(28)	1.647(3)	N(1)-C(8A)	1.499(4)
S(36)-C(39)	1.765(3)	N(1)-C(2)	1.504(4)
C(35)-C(35A)	1.528(5)	C(4)-O(26)	1.426(4)
C(35)-C(34)	1.531(5)	C(4)-C(3)	1.516(5)
C(35)-H(35A)	0.9700	C(4)-C(4A)	1.524(5)
C(35)-H(35B)	0.9700	C(4)-H(4)	0.9800
C(31)-O(53)	1.428(4)	C(12)-C(17)	1.383(5)
C(31)-C(31A)	1.519(5)	C(12)-C(13)	1.391(5)
C(31)-C(30)	1.527(5)	C(21)-C(22)	1.373(5)
C(31)-H(31)	0.9800	C(21)-C(20)	1.386(5)
N(28)-C(29)	1.502(4)	C(21)-H(21)	0.9300
N(28)-C(35A)	1.507(4)	C(13)-C(14)	1.374(5)
C(35A)-C(31A)	1.529(4)	C(13)-H(13)	0.9300
C(35A)-H(35C)	0.9800	C(8)-C(8A)	1.519(5)
C(39)-C(40)	1.387(5)	C(8)-C(7)	1.537(5)
C(39)-C(44)	1.393(5)	C(8)-H(8A)	0.9700
C(41)-C(42)	1.382(5)	C(8)-H(8B)	0.9700
C(41)-C(40)	1.388(5)	C(24)-C(19)	1.377(5)
C(41)-H(41)	0.9300	C(24)-C(23)	1.385(5)
C(47)-C(46)	1.384(5)	C(24)-H(24)	0.9300
C(47)-C(48)	1.388(5)	C(19)-C(20)	1.401(5)
C(47)-H(47)	0.9300	C(19)-C(2)	1.525(4)
C(44)-C(43)	1.389(5)	C(8A)-C(4A)	1.551(4)
C(44)-H(44)	0.9300	C(8A)-H(8A1)	0.9800
C(46)-C(51)	1.385(5)	C(17)-C(16)	1.388(5)
C(46)-C(29)	1.520(4)	C(17)-H(17)	0.9300
C(45)-C(42)	1.507(5)	C(5)-C(6)	1.524(5)
C(45)-H(45A)	0.9600	C(5)-C(4A)	1.537(5)
C(45)-H(45B)	0.9600	C(5)-H(5A)	0.9700
C(45)-H(45C)	0.9600	C(5)-H(5B)	0.9700
C(50)-C(49)	1.393(5)	C(2)-C(3)	1.558(4)
C(50)-C(51)	1.395(5)	C(2)-H(2)	0.9800
C(50)-H(50)	0.9300	C(3)-O(25)	1.422(4)
C(32)-C(33)	1.538(5)	C(3)-H(3)	0.9800
C(32)-C(31A)	1.544(5)	C(27)-C(4A)	1.541(4)
C(32)-H(32A)	0.9700	C(27)-H(27A)	0.9600
C(32)-H(32B)	0.9700	C(27)-H(27B)	0.9600
C(54)-C(31A)	1.550(4)	C(27)-H(27C)	0.9600
C(54)-H(54A)	0.9600	C(7)-C(6)	1.530(5)
C(54)-H(54B)	0.9600	C(7)-H(7A)	0.9700
C(54)-H(54C)	0.9600	C(7)-H(7B)	0.9700
C(29)-C(30)	1.548(4)	C(22)-C(23)	1.386(5)

C(29)-H(29)	0.9800	C(22)-H(22)	0.9300
C(51)-H(51)	0.9300	C(20)-H(20)	0.9300
C(30)-O(52)	1.431(4)	C(14)-C(15)	1.387(6)
C(30)-H(30)	0.9800	C(14)-H(14)	0.9300
C(40)-H(40)	0.9300	C(18)-C(15)	1.508(5)
C(49)-C(48)	1.379(5)	C(18)-H(18A)	0.9600
C(49)-H(49)	0.9300	C(18)-H(18B)	0.9600
C(48)-H(48)	0.9300	C(18)-H(18C)	0.9600
C(34)-C(33)	1.526(5)	C(16)-C(15)	1.398(6)
C(34)-H(34A)	0.9700	C(16)-H(16)	0.9300
C(34)-H(34B)	0.9700	C(6)-H(6A)	0.9700
C(42)-C(43)	1.393(5)	C(6)-H(6B)	0.9700
C(43)-H(43)	0.9300	C(23)-H(23)	0.9300
C(33)-H(33A)	0.9700	O(25)-H(25)	0.8200
C(33)-H(33B)	0.9700	O(52)-H(52)	0.8200
S(9)-O(10)	1.433(3)	O(53)-H(53)	0.8200
S(9)-O(11)	1.444(3)	O(26)-H(26)	0.8200
O(38)-S(36)-O(37)	118.75(14)	O(11)-S(9)-N(1)	106.61(14)
O(38)-S(36)-N(28)	108.34(15)	O(10)-S(9)-C(12)	107.98(16)
O(37)-S(36)-N(28)	106.44(14)	O(11)-S(9)-C(12)	107.82(17)
O(38)-S(36)-C(39)	107.67(15)	N(1)-S(9)-C(12)	107.76(14)
O(37)-S(36)-C(39)	107.59(16)	C(8A)-N(1)-C(2)	123.5(2)
N(28)-S(36)-C(39)	107.59(14)	C(8A)-N(1)-S(9)	115.0(2)
C(35A)-C(35)-C(34)	107.7(3)	C(2)-N(1)-S(9)	110.9(2)
C(35A)-C(35)-H(35A)	110.2	O(26)-C(4)-C(3)	110.2(3)
C(34)-C(35)-H(35A)	110.2	O(26)-C(4)-C(4A)	109.6(3)
C(35A)-C(35)-H(35B)	110.2	C(3)-C(4)-C(4A)	110.5(3)
C(34)-C(35)-H(35B)	110.2	O(26)-C(4)-H(4)	108.8
H(35A)-C(35)-H(35B)	108.5	C(3)-C(4)-H(4)	108.8
O(53)-C(31)-C(31A)	109.6(3)	C(4A)-C(4)-H(4)	108.8
O(53)-C(31)-C(30)	110.0(3)	C(17)-C(12)-C(13)	120.7(3)
C(31A)-C(31)-C(30)	110.0(3)	C(17)-C(12)-S(9)	120.2(3)
O(53)-C(31)-H(31)	109.1	C(13)-C(12)-S(9)	119.0(3)
C(31A)-C(31)-H(31)	109.1	C(22)-C(21)-C(20)	121.2(3)
C(30)-C(31)-H(31)	109.1	C(22)-C(21)-H(21)	119.4
C(29)-N(28)-C(35A)	122.6(2)	C(20)-C(21)-H(21)	119.4
C(29)-N(28)-S(36)	112.0(2)	C(14)-C(13)-C(12)	119.4(4)
C(35A)-N(28)-S(36)	114.8(2)	C(14)-C(13)-H(13)	120.3
N(28)-C(35A)-C(35)	113.9(3)	C(12)-C(13)-H(13)	120.3
N(28)-C(35A)-C(31A)	112.0(3)	C(8A)-C(8)-C(7)	107.6(3)
C(35)-C(35A)-C(31A)	111.4(3)	C(8A)-C(8)-H(8A)	110.2
N(28)-C(35A)-H(35C)	106.3	C(7)-C(8)-H(8A)	110.2
C(35)-C(35A)-H(35C)	106.3	C(8A)-C(8)-H(8B)	110.2
C(31A)-C(35A)-H(35C)	106.3	C(7)-C(8)-H(8B)	110.2

C(40)-C(39)-C(44)	120.6(3)	H(8A)-C(8)-H(8B)	108.5
C(40)-C(39)-S(36)	118.3(3)	C(19)-C(24)-C(23)	120.9(3)
C(44)-C(39)-S(36)	121.0(3)	C(19)-C(24)-H(24)	119.5
C(42)-C(41)-C(40)	121.4(3)	C(23)-C(24)-H(24)	119.5
C(42)-C(41)-H(41)	119.3	C(24)-C(19)-C(20)	118.8(3)
C(40)-C(41)-H(41)	119.3	C(24)-C(19)-C(2)	118.2(3)
C(46)-C(47)-C(48)	121.8(3)	C(20)-C(19)-C(2)	122.9(3)
C(46)-C(47)-H(47)	119.1	N(1)-C(8A)-C(8)	114.1(3)
C(48)-C(47)-H(47)	119.1	N(1)-C(8A)-C(4A)	112.2(3)
C(43)-C(44)-C(39)	119.0(3)	C(8)-C(8A)-C(4A)	110.8(3)
C(43)-C(44)-H(44)	120.5	N(1)-C(8A)-H(8A1)	106.4
C(39)-C(44)-H(44)	120.5	C(8)-C(8A)-H(8A1)	106.4
C(47)-C(46)-C(51)	118.5(3)	C(4A)-C(8A)-H(8A1)	106.4
C(47)-C(46)-C(29)	117.4(3)	C(12)-C(17)-C(16)	119.2(4)
C(51)-C(46)-C(29)	124.1(3)	C(12)-C(17)-H(17)	120.4
C(42)-C(45)-H(45A)	109.5	C(16)-C(17)-H(17)	120.4
C(42)-C(45)-H(45B)	109.5	C(6)-C(5)-C(4A)	113.8(3)
H(45A)-C(45)-H(45B)	109.5	C(6)-C(5)-H(5A)	108.8
C(42)-C(45)-H(45C)	109.5	C(4A)-C(5)-H(5A)	108.8
H(45A)-C(45)-H(45C)	109.5	C(6)-C(5)-H(5B)	108.8
H(45B)-C(45)-H(45C)	109.5	C(4A)-C(5)-H(5B)	108.8
C(49)-C(50)-C(51)	120.2(3)	H(5A)-C(5)-H(5B)	107.7
C(49)-C(50)-H(50)	119.9	N(1)-C(2)-C(19)	112.2(3)
C(51)-C(50)-H(50)	119.9	N(1)-C(2)-C(3)	116.0(3)
C(33)-C(32)-C(31A)	113.5(3)	C(19)-C(2)-C(3)	110.0(2)
C(33)-C(32)-H(32A)	108.9	N(1)-C(2)-H(2)	105.9
C(31A)-C(32)-H(32A)	108.9	C(19)-C(2)-H(2)	105.9
C(33)-C(32)-H(32B)	108.9	C(3)-C(2)-H(2)	105.9
C(31A)-C(32)-H(32B)	108.9	O(25)-C(3)-C(4)	111.0(3)
H(32A)-C(32)-H(32B)	107.7	O(25)-C(3)-C(2)	105.6(3)
C(31A)-C(54)-H(54A)	109.5	C(4)-C(3)-C(2)	114.0(3)
C(31A)-C(54)-H(54B)	109.5	O(25)-C(3)-H(3)	108.7
H(54A)-C(54)-H(54B)	109.5	C(4)-C(3)-H(3)	108.7
C(31A)-C(54)-H(54C)	109.5	C(2)-C(3)-H(3)	108.7
H(54A)-C(54)-H(54C)	109.5	C(4A)-C(27)-H(27A)	109.5
H(54B)-C(54)-H(54C)	109.5	C(4A)-C(27)-H(27B)	109.5
N(28)-C(29)-C(46)	112.5(2)	H(27A)-C(27)-H(27B)	109.5
N(28)-C(29)-C(30)	116.4(3)	C(4A)-C(27)-H(27C)	109.5
C(46)-C(29)-C(30)	111.3(2)	H(27A)-C(27)-H(27C)	109.5
N(28)-C(29)-H(29)	105.1	H(27B)-C(27)-H(27C)	109.5
C(46)-C(29)-H(29)	105.1	C(4)-C(4A)-C(5)	110.4(3)
C(30)-C(29)-H(29)	105.1	C(4)-C(4A)-C(27)	108.8(3)
C(46)-C(51)-C(50)	120.4(3)	C(5)-C(4A)-C(27)	109.5(3)
C(46)-C(51)-H(51)	119.8	C(4)-C(4A)-C(8A)	107.6(3)
C(50)-C(51)-H(51)	119.8	C(5)-C(4A)-C(8A)	106.8(3)
O(52)-C(30)-C(31)	109.9(2)	C(27)-C(4A)-C(8A)	113.7(3)

O(52)-C(30)-C(29)	106.1(3)	C(6)-C(7)-C(8)	112.4(3)
C(31)-C(30)-C(29)	114.3(3)	C(6)-C(7)-H(7A)	109.1
O(52)-C(30)-H(30)	108.8	C(8)-C(7)-H(7A)	109.1
C(31)-C(30)-H(30)	108.8	C(6)-C(7)-H(7B)	109.1
C(29)-C(30)-H(30)	108.8	C(8)-C(7)-H(7B)	109.1
C(31)-C(31A)-C(35A)	108.2(3)	H(7A)-C(7)-H(7B)	107.9
C(31)-C(31A)-C(32)	109.6(3)	C(21)-C(22)-C(23)	119.0(3)
C(35A)-C(31A)-C(32)	107.1(3)	C(21)-C(22)-H(22)	120.5
C(31)-C(31A)-C(54)	109.2(3)	C(23)-C(22)-H(22)	120.5
C(35A)-C(31A)-C(54)	113.9(3)	C(21)-C(20)-C(19)	119.8(3)
C(32)-C(31A)-C(54)	108.7(3)	C(21)-C(20)-H(20)	120.1
C(39)-C(40)-C(41)	119.2(3)	C(19)-C(20)-H(20)	120.1
C(39)-C(40)-H(40)	120.4	C(13)-C(14)-C(15)	121.3(4)
C(41)-C(40)-H(40)	120.4	C(13)-C(14)-H(14)	119.4
C(48)-C(49)-C(50)	119.5(3)	C(15)-C(14)-H(14)	119.4
C(48)-C(49)-H(49)	120.2	C(15)-C(18)-H(18A)	109.5
C(50)-C(49)-H(49)	120.2	C(15)-C(18)-H(18B)	109.5
C(49)-C(48)-C(47)	119.6(3)	H(18A)-C(18)-H(18B)	109.5
C(49)-C(48)-H(48)	120.2	C(15)-C(18)-H(18C)	109.5
C(47)-C(48)-H(48)	120.2	H(18A)-C(18)-H(18C)	109.5
C(33)-C(34)-C(35)	112.0(3)	H(18B)-C(18)-H(18C)	109.5
C(33)-C(34)-H(34A)	109.2	C(17)-C(16)-C(15)	120.8(4)
C(35)-C(34)-H(34A)	109.2	C(17)-C(16)-H(16)	119.6
C(33)-C(34)-H(34B)	109.2	C(15)-C(16)-H(16)	119.6
C(35)-C(34)-H(34B)	109.2	C(5)-C(6)-C(7)	111.7(3)
H(34A)-C(34)-H(34B)	107.9	C(5)-C(6)-H(6A)	109.3
C(41)-C(42)-C(43)	118.7(3)	C(7)-C(6)-H(6A)	109.3
C(41)-C(42)-C(45)	120.6(3)	C(5)-C(6)-H(6B)	109.3
C(43)-C(42)-C(45)	120.7(4)	C(7)-C(6)-H(6B)	109.3
C(44)-C(43)-C(42)	121.0(3)	H(6A)-C(6)-H(6B)	107.9
C(44)-C(43)-H(43)	119.5	C(24)-C(23)-C(22)	120.3(3)
C(42)-C(43)-H(43)	119.5	C(24)-C(23)-H(23)	119.8
C(34)-C(33)-C(32)	111.7(3)	C(22)-C(23)-H(23)	119.8
C(34)-C(33)-H(33A)	109.3	C(14)-C(15)-C(16)	118.5(3)
C(32)-C(33)-H(33A)	109.3	C(14)-C(15)-C(18)	120.8(4)
C(34)-C(33)-H(33B)	109.3	C(16)-C(15)-C(18)	120.7(4)
C(32)-C(33)-H(33B)	109.3	C(3)-O(25)-H(25)	109.5
H(33A)-C(33)-H(33B)	107.9	C(30)-O(52)-H(52)	109.5
O(10)-S(9)-O(11)	118.46(14)	C(31)-O(53)-H(53)	109.5
O(10)-S(9)-N(1)	107.79(15)	C(4)-O(26)-H(26)	109.5

X-ray data for compound 14

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
C(18)	9352(4)	10384(4)	2871(1)	71(1)
S(36)	2320(1)	8472(1)	1311(1)	30(1)
S(9)	7432(1)	7821(1)	1428(1)	36(1)
O(37)	1918(2)	7145(2)	1342(1)	41(1)
N(28)	3453(2)	8457(2)	1087(1)	28(1)
O(53)	3731(2)	8679(2)	-74(1)	41(1)
N(1)	8432(2)	7999(2)	1148(1)	32(1)
O(26)	7917(2)	7971(2)	-20(1)	46(1)
C(31A)	3573(2)	7271(3)	477(1)	29(1)
C(30)	3595(2)	9821(3)	520(1)	31(1)
O(10)	6470(2)	8583(2)	1298(1)	48(1)
O(38)	1549(2)	9447(2)	1153(1)	41(1)
O(11)	7278(2)	6436(2)	1495(1)	52(1)
C(29)	3932(2)	9726(3)	943(1)	29(1)
C(35A)	3936(2)	7267(3)	904(1)	28(1)
O(52)	4117(2)	10975(2)	372(1)	41(1)
C(4A)	8448(2)	6712(3)	550(1)	31(1)
O(25)	8307(2)	10421(2)	365(1)	46(1)
C(8A)	9003(2)	6906(3)	950(1)	31(1)
C(4)	8488(2)	8057(3)	346(1)	34(1)
C(46)	3751(2)	10932(3)	1183(1)	31(1)
C(35)	3819(3)	5924(3)	1095(1)	38(1)
C(12)	7970(3)	8546(3)	1857(1)	38(1)
C(2)	8592(2)	9303(3)	957(1)	33(1)
C(31)	3998(2)	8593(3)	322(1)	30(1)
C(3)	8033(2)	9230(3)	558(1)	35(1)
C(39)	2766(3)	9001(3)	1773(1)	36(1)
C(54)	2301(2)	7137(3)	400(1)	38(1)
C(5)	9147(3)	5700(3)	342(1)	42(1)
C(32)	4161(3)	6108(3)	291(1)	39(1)
C(51)	2871(3)	11826(3)	1118(1)	40(1)
C(33)	4073(3)	4782(3)	489(1)	48(1)
C(8)	9205(3)	5610(3)	1164(1)	41(1)
C(44)	2181(3)	9964(4)	1950(1)	54(1)
C(47)	4485(2)	11147(3)	1493(1)	37(1)

C(34)	4505(3)	4898(3)	900(1)	44(1)
C(13)	9048(3)	8263(3)	1993(1)	45(1)
C(15)	8847(3)	9709(4)	2522(1)	50(1)
C(42)	3450(4)	9772(4)	2502(1)	59(1)
C(48)	4332(3)	12167(3)	1741(1)	49(1)
C(27)	7239(2)	6228(3)	554(1)	39(1)
C(19)	8342(3)	10544(3)	1182(1)	37(1)
C(14)	9474(3)	8836(3)	2323(1)	49(1)
C(7)	9923(3)	4688(3)	945(1)	48(1)
C(50)	2710(3)	12844(3)	1370(1)	49(1)
C(17)	7325(3)	9390(4)	2054(1)	55(1)
C(40)	3679(3)	8420(4)	1957(1)	55(1)
C(20)	9145(3)	10989(3)	1448(1)	48(1)
C(49)	3435(3)	13003(3)	1683(1)	52(1)
C(6)	9366(3)	4412(3)	555(1)	50(1)
C(24)	7363(3)	11281(3)	1126(1)	56(1)
C(43)	2540(3)	10336(4)	2315(1)	64(1)
C(16)	7765(3)	9958(4)	2384(1)	63(1)
C(41)	4015(4)	8804(4)	2318(1)	66(1)
C(23)	7205(4)	12416(4)	1338(1)	71(1)
C(22)	8001(4)	12803(4)	1608(1)	74(1)
C(45)	3863(4)	10219(5)	2894(1)	90(2)
C(21)	8979(4)	12092(4)	1663(1)	67(1)
O(55)	574(3)	1086(4)	487(1)	83(1)

Table S8. Bond lengths [Å] and angles [°] for compound **14**.

C(18)-C(15)	1.508(5)	C(46)-C(47)	1.378(4)
C(18)-H(18A)	0.9600	C(46)-C(51)	1.394(4)
C(18)-H(18B)	0.9600	C(35)-C(34)	1.516(4)
C(18)-H(18C)	0.9600	C(35)-H(35B)	0.9700
S(36)-O(37)	1.424(2)	C(35)-H(35C)	0.9700
S(36)-O(38)	1.436(2)	C(12)-C(17)	1.375(4)
S(36)-N(28)	1.625(2)	C(12)-C(13)	1.379(4)
S(36)-C(39)	1.776(3)	C(2)-C(19)	1.523(4)
S(9)-O(11)	1.425(2)	C(2)-C(3)	1.531(4)
S(9)-O(10)	1.435(2)	C(2)-H(2)	0.9800
S(9)-N(1)	1.624(2)	C(31)-H(31)	0.9800
S(9)-C(12)	1.772(3)	C(3)-H(3)	0.9800
N(28)-C(35A)	1.496(3)	C(39)-C(40)	1.366(4)
N(28)-C(29)	1.503(3)	C(39)-C(44)	1.374(4)
O(53)-C(31)	1.429(3)	C(54)-H(54A)	0.9600
O(53)-H(53)	0.8200	C(54)-H(54B)	0.9600
N(1)-C(2)	1.495(3)	C(54)-H(54C)	0.9600
N(1)-C(8A)	1.497(3)	C(5)-C(6)	1.513(4)
O(26)-C(4)	1.432(3)	C(5)-H(5A)	0.9700
O(26)-H(26)	0.8200	C(5)-H(5B)	0.9700
C(31A)-C(54)	1.538(4)	C(32)-C(33)	1.514(4)
C(31A)-C(31)	1.538(4)	C(32)-H(32A)	0.9700
C(31A)-C(32)	1.539(4)	C(32)-H(32B)	0.9700
C(31A)-C(35A)	1.554(4)	C(51)-C(50)	1.381(4)
C(30)-O(52)	1.435(3)	C(51)-H(51)	0.9300
C(30)-C(31)	1.516(4)	C(33)-C(34)	1.524(4)
C(30)-C(29)	1.535(4)	C(33)-H(33A)	0.9700
C(30)-H(30)	0.9800	C(33)-H(33B)	0.9700
C(29)-C(46)	1.508(4)	C(8)-C(7)	1.518(4)
C(29)-H(29)	0.9800	C(8)-H(8B)	0.9700
C(35A)-C(35)	1.520(4)	C(8)-H(8C)	0.9700
C(35A)-H(35A)	0.9800	C(44)-C(43)	1.392(5)
O(52)-H(52)	0.8200	C(44)-H(44)	0.9300
C(4A)-C(27)	1.531(4)	C(47)-C(48)	1.373(4)
C(4A)-C(4)	1.536(4)	C(47)-H(47)	0.9300
C(4A)-C(5)	1.539(4)	C(34)-H(34A)	0.9700
C(4A)-C(8A)	1.542(4)	C(34)-H(34B)	0.9700
O(25)-C(3)	1.429(3)	C(13)-C(14)	1.375(4)
O(25)-H(25)	0.8200	C(13)-H(13)	0.9300
C(8A)-C(8)	1.519(4)	C(15)-C(16)	1.378(5)
C(8A)-H(8A)	0.9800	C(15)-C(14)	1.383(4)
C(4)-C(3)	1.521(4)	C(42)-C(43)	1.362(5)
C(4)-H(4)	0.9800	C(42)-C(41)	1.376(5)

C(42)-C(45)	1.516(5)	C(20)-H(20)	0.9300
C(48)-C(49)	1.369(5)	C(49)-H(49)	0.9300
C(48)-H(48)	0.9300	C(6)-H(6A)	0.9700
C(27)-H(27A)	0.9600	C(6)-H(6B)	0.9700
C(27)-H(27B)	0.9600	C(24)-C(23)	1.387(5)
C(27)-H(27C)	0.9600	C(24)-H(24)	0.9300
C(19)-C(20)	1.376(4)	C(43)-H(43)	0.9300
C(19)-C(24)	1.392(5)	C(16)-H(16)	0.9300
C(14)-H(14)	0.9300	C(41)-H(41)	0.9300
C(7)-C(6)	1.523(4)	C(23)-C(22)	1.363(6)
C(7)-H(7A)	0.9700	C(23)-H(23)	0.9300
C(7)-H(7B)	0.9700	C(22)-C(21)	1.376(6)
C(50)-C(49)	1.377(5)	C(22)-H(22)	0.9300
C(50)-H(50)	0.9300	C(45)-H(45A)	0.9600
C(17)-C(16)	1.378(5)	C(45)-H(45B)	0.9600
C(17)-H(17)	0.9300	C(45)-H(45C)	0.9600
C(40)-C(41)	1.377(5)	C(21)-H(21)	0.9300
C(40)-H(40)	0.9300	O(55)-H(55A)	0.79(6)
C(20)-C(21)	1.370(5)	O(55)-H(55B)	0.86(5)
C(15)-C(18)-H(18A)	109.5	C(4)-O(26)-H(26)	109.5
C(15)-C(18)-H(18B)	109.5	C(54)-C(31A)-C(31)	111.2(2)
H(18A)-C(18)-H(18B)	109.5	C(54)-C(31A)-C(32)	109.7(2)
C(15)-C(18)-H(18C)	109.5	C(31)-C(31A)-C(32)	109.0(2)
H(18A)-C(18)-H(18C)	109.5	C(54)-C(31A)-C(35A)	112.3(2)
H(18B)-C(18)-H(18C)	109.5	C(31)-C(31A)-C(35A)	106.0(2)
O(37)-S(36)-O(38)	117.09(13)	C(32)-C(31A)-C(35A)	108.4(2)
O(37)-S(36)-N(28)	109.16(12)	O(52)-C(30)-C(31)	108.9(2)
O(38)-S(36)-N(28)	110.63(12)	O(52)-C(30)-C(29)	108.6(2)
O(37)-S(36)-C(39)	106.93(13)	C(31)-C(30)-C(29)	109.6(2)
O(38)-S(36)-C(39)	107.70(14)	O(52)-C(30)-H(30)	109.9
N(28)-S(36)-C(39)	104.52(13)	C(31)-C(30)-H(30)	109.9
O(11)-S(9)-O(10)	117.62(14)	C(29)-C(30)-H(30)	109.9
O(11)-S(9)-N(1)	108.73(13)	N(28)-C(29)-C(46)	114.4(2)
O(10)-S(9)-N(1)	110.80(12)	N(28)-C(29)-C(30)	107.9(2)
O(11)-S(9)-C(12)	107.47(14)	C(46)-C(29)-C(30)	118.0(2)
O(10)-S(9)-C(12)	107.21(14)	N(28)-C(29)-H(29)	105.1
N(1)-S(9)-C(12)	104.10(13)	C(46)-C(29)-H(29)	105.1
C(35A)-N(28)-C(29)	111.03(19)	C(30)-C(29)-H(29)	105.1
C(35A)-N(28)-S(36)	125.75(18)	N(28)-C(35A)-C(35)	117.6(2)
C(29)-N(28)-S(36)	120.89(17)	N(28)-C(35A)-C(31A)	109.5(2)
C(31)-O(53)-H(53)	109.5	C(35)-C(35A)-C(31A)	114.3(2)
C(2)-N(1)-C(8A)	110.5(2)	N(28)-C(35A)-H(35A)	104.7
C(2)-N(1)-S(9)	120.03(18)	C(35)-C(35A)-H(35A)	104.7
C(8A)-N(1)-S(9)	126.31(18)	C(31A)-C(35A)-H(35A)	104.7

C(30)-O(52)-H(52)	109.5	C(4)-C(3)-C(2)	110.4(2)
C(27)-C(4A)-C(4)	110.2(2)	O(25)-C(3)-H(3)	110.2
C(27)-C(4A)-C(5)	110.1(2)	C(4)-C(3)-H(3)	110.2
C(4)-C(4A)-C(5)	108.5(2)	C(2)-C(3)-H(3)	110.2
C(27)-C(4A)-C(8A)	112.4(2)	C(40)-C(39)-C(44)	120.0(3)
C(4)-C(4A)-C(8A)	107.5(2)	C(40)-C(39)-S(36)	119.6(2)
C(5)-C(4A)-C(8A)	108.2(2)	C(44)-C(39)-S(36)	120.4(3)
C(3)-O(25)-H(25)	109.5	C(31A)-C(54)-H(54A)	109.5
N(1)-C(8A)-C(8)	116.9(2)	C(31A)-C(54)-H(54B)	109.5
N(1)-C(8A)-C(4A)	110.3(2)	H(54A)-C(54)-H(54B)	109.5
C(8)-C(8A)-C(4A)	113.5(2)	C(31A)-C(54)-H(54C)	109.5
N(1)-C(8A)-H(8A)	105.0	H(54A)-C(54)-H(54C)	109.5
C(8)-C(8A)-H(8A)	105.0	H(54B)-C(54)-H(54C)	109.5
C(4A)-C(8A)-H(8A)	105.0	C(6)-C(5)-C(4A)	113.9(2)
O(26)-C(4)-C(3)	109.4(2)	C(6)-C(5)-H(5A)	108.8
O(26)-C(4)-C(4A)	110.4(2)	C(4A)-C(5)-H(5A)	108.8
C(3)-C(4)-C(4A)	114.9(2)	C(6)-C(5)-H(5B)	108.8
O(26)-C(4)-H(4)	107.2	C(4A)-C(5)-H(5B)	108.8
C(3)-C(4)-H(4)	107.2	H(5A)-C(5)-H(5B)	107.7
C(4A)-C(4)-H(4)	107.2	C(33)-C(32)-C(31A)	114.6(2)
C(47)-C(46)-C(51)	117.9(3)	C(33)-C(32)-H(32A)	108.6
C(47)-C(46)-C(29)	118.1(3)	C(31A)-C(32)-H(32A)	108.6
C(51)-C(46)-C(29)	124.1(3)	C(33)-C(32)-H(32B)	108.6
C(34)-C(35)-C(35A)	109.2(2)	C(31A)-C(32)-H(32B)	108.6
C(34)-C(35)-H(35B)	109.8	H(32A)-C(32)-H(32B)	107.6
C(35A)-C(35)-H(35B)	109.8	C(50)-C(51)-C(46)	120.5(3)
C(34)-C(35)-H(35C)	109.8	C(50)-C(51)-H(51)	119.8
C(35A)-C(35)-H(35C)	109.8	C(46)-C(51)-H(51)	119.8
H(35B)-C(35)-H(35C)	108.3	C(32)-C(33)-C(34)	110.6(3)
C(17)-C(12)-C(13)	119.7(3)	C(32)-C(33)-H(33A)	109.5
C(17)-C(12)-S(9)	120.7(3)	C(34)-C(33)-H(33A)	109.5
C(13)-C(12)-S(9)	119.6(2)	C(32)-C(33)-H(33B)	109.5
N(1)-C(2)-C(19)	116.1(2)	C(34)-C(33)-H(33B)	109.5
N(1)-C(2)-C(3)	108.6(2)	H(33A)-C(33)-H(33B)	108.1
C(19)-C(2)-C(3)	116.0(2)	C(7)-C(8)-C(8A)	109.8(2)
N(1)-C(2)-H(2)	104.9	C(7)-C(8)-H(8B)	109.7
C(19)-C(2)-H(2)	104.9	C(8A)-C(8)-H(8B)	109.7
C(3)-C(2)-H(2)	104.9	C(7)-C(8)-H(8C)	109.7
O(53)-C(31)-C(30)	110.8(2)	C(8A)-C(8)-H(8C)	109.7
O(53)-C(31)-C(31A)	110.4(2)	H(8B)-C(8)-H(8C)	108.2
C(30)-C(31)-C(31A)	114.2(2)	C(39)-C(44)-C(43)	118.8(4)
O(53)-C(31)-H(31)	107.0	C(39)-C(44)-H(44)	120.6
C(30)-C(31)-H(31)	107.0	C(43)-C(44)-H(44)	120.6
C(31A)-C(31)-H(31)	107.0	C(48)-C(47)-C(46)	121.6(3)
O(25)-C(3)-C(4)	107.8(2)	C(48)-C(47)-H(47)	119.2
O(25)-C(3)-C(2)	107.9(2)	C(46)-C(47)-H(47)	119.2

C(35)-C(34)-C(33)	109.5(3)	C(21)-C(20)-C(19)	121.7(4)
C(35)-C(34)-H(34A)	109.8	C(21)-C(20)-H(20)	119.1
C(33)-C(34)-H(34A)	109.8	C(19)-C(20)-H(20)	119.1
C(35)-C(34)-H(34B)	109.8	C(48)-C(49)-C(50)	119.7(3)
C(33)-C(34)-H(34B)	109.8	C(48)-C(49)-H(49)	120.1
H(34A)-C(34)-H(34B)	108.2	C(50)-C(49)-H(49)	120.2
C(14)-C(13)-C(12)	119.9(3)	C(5)-C(6)-C(7)	110.6(3)
C(14)-C(13)-H(13)	120.1	C(5)-C(6)-H(6A)	109.5
C(12)-C(13)-H(13)	120.1	C(7)-C(6)-H(6A)	109.5
C(16)-C(15)-C(14)	117.8(3)	C(5)-C(6)-H(6B)	109.5
C(16)-C(15)-C(18)	121.7(3)	C(7)-C(6)-H(6B)	109.5
C(14)-C(15)-C(18)	120.4(3)	H(6A)-C(6)-H(6B)	108.1
C(43)-C(42)-C(41)	117.7(3)	C(23)-C(24)-C(19)	120.4(4)
C(43)-C(42)-C(45)	121.7(4)	C(23)-C(24)-H(24)	119.8
C(41)-C(42)-C(45)	120.5(4)	C(19)-C(24)-H(24)	119.8
C(49)-C(48)-C(47)	120.0(3)	C(42)-C(43)-C(44)	122.0(4)
C(49)-C(48)-H(48)	120.0	C(42)-C(43)-H(43)	119.0
C(47)-C(48)-H(48)	120.0	C(44)-C(43)-H(43)	119.0
C(4A)-C(27)-H(27A)	109.5	C(15)-C(16)-C(17)	121.5(3)
C(4A)-C(27)-H(27B)	109.5	C(15)-C(16)-H(16)	119.2
H(27A)-C(27)-H(27B)	109.5	C(17)-C(16)-H(16)	119.2
C(4A)-C(27)-H(27C)	109.5	C(42)-C(41)-C(40)	121.4(4)
H(27A)-C(27)-H(27C)	109.5	C(42)-C(41)-H(41)	119.3
H(27B)-C(27)-H(27C)	109.5	C(40)-C(41)-H(41)	119.3
C(20)-C(19)-C(24)	118.0(3)	C(22)-C(23)-C(24)	120.1(4)
C(20)-C(19)-C(2)	118.3(3)	C(22)-C(23)-H(23)	119.9
C(24)-C(19)-C(2)	123.7(3)	C(24)-C(23)-H(23)	119.9
C(13)-C(14)-C(15)	121.3(3)	C(23)-C(22)-C(21)	120.2(4)
C(13)-C(14)-H(14)	119.3	C(23)-C(22)-H(22)	119.9
C(15)-C(14)-H(14)	119.3	C(21)-C(22)-H(22)	119.9
C(8)-C(7)-C(6)	110.5(3)	C(42)-C(45)-H(45A)	109.5
C(8)-C(7)-H(7A)	109.5	C(42)-C(45)-H(45B)	109.5
C(6)-C(7)-H(7A)	109.5	H(45A)-C(45)-H(45B)	109.5
C(8)-C(7)-H(7B)	109.5	C(42)-C(45)-H(45C)	109.5
C(6)-C(7)-H(7B)	109.5	H(45A)-C(45)-H(45C)	109.5
H(7A)-C(7)-H(7B)	108.1	H(45B)-C(45)-H(45C)	109.5
C(49)-C(50)-C(51)	120.2(3)	C(20)-C(21)-C(22)	119.6(4)
C(49)-C(50)-H(50)	119.9	C(20)-C(21)-H(21)	120.2
C(51)-C(50)-H(50)	119.9	C(22)-C(21)-H(21)	120.2
C(12)-C(17)-C(16)	119.8(3)	H(55A)-O(55)-H(55B)	108(5)
C(12)-C(17)-H(17)	120.1		
C(16)-C(17)-H(17)	120.1		
C(39)-C(40)-C(41)	119.9(3)		
C(39)-C(40)-H(40)	120.0		
C(41)-C(40)-H(40)	120.0		