Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Material for:

Synthesis and pharmacological effects of the enantiomers of the *N*-phenethyl analogues of the *ortho* and *para* e- and f-oxide-bridged phenylmorphans‡

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‡ Probes for Narcotic Receptor Mediated Phenomena. Part 36.[1]

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Chemistry: Experimental Section

Experimental data for **22** to **26**, **30, 36** to **43**, and **49** to **51.**

(1*R,4a*R**,9a*R**)-2-(6-Nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridyl)-ethylcarboxylate (22).** Compound **22** was prepared using the same procedure as carbamate **16** in 78% yield. Mp ((±-**22**) 125-128.0 ^{o}C (2-propanol:H_2O). Optical rotations: (1*S*,4a*S*,9a*S*)-(+)-**22**: $[\alpha]_D^{24}$ +34.8 (*c* 1.0, $CHCl_3$) (from the (+)-amine), (1*R*,4a*R*,9a*R*)-(-)-**22**: $[\alpha]_D^{25}$ – 33.9 (*c* 1.0, $CHCl_3$) (from the (-)-amine). ^{1}H-NMR: 8.16 (dd, 1H, *J* = 8.7, 2.1), 7.98 (d, 1H, *J* = 2.4), 6.98 (d, 1H, *J* = 8.7), 4.90, 4.78 (bs, 1H), 4.18 (m, 3H), 4.04 (m, 1H), 3.65 (m, 1H), 2.38 (m, 1H), 2.19 (m, 1H), 2.20-1.96 (m, 1H), 1.90-1.55 (m, 5H), 1.44 (m, 1H), 1.30 (t, 3H, *J* = 7.2). ^{13}C-NMR: 164.6, 156.4, 142.7, 140.6, 125.7, 117.9, 111.2, 88.2, 87.9, 61.9, 61.8, 49.3, 49.1, 42.2, 41.9, 41.0, 33.8, 31.2, 30.9, 25.5, 24.1, 23.4, 19.6, 19.5, 14.8. HRMS: $[MH]^+$ calcd $C_{17}H_{21}N_2O_5$: 333.1450, found 333.1432. $C_{17}H_{20}N_2O_5$ requires: C, 61.44; H, 6.07; N, 8.43; found: C, 61.31; H, 6.22; N, 8.31%.

(1*R,4a*R**,9a*R**)-6-Nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (23).** Compound **23** was prepared in 79% yield using the same procedure as for compound **17**. Mp ((-)-**23**) 167-168 ^{o}C. Optical rotations: (1*S*,4a*S*,9a*S*))-(+)-**23**: $[\alpha]_D^{23}$ +79.4 (*c* 1.0, $CHCl_3$) (from the (+)-carbamate), (1*R*,4a*R*,9a*R*)-(-)-**23**: $[\alpha]_D^{23}$ –79.8 (*c* 1.0, $CHCl_3$) (from the (-)-carbamate). ^{1}H-NMR: 8.14 (dd, 1H, *J* = 8.7, 2.4), 7.96 (d, 1H, *J* = 2.7), 6.95 (d, 1H, *J* = 8.7), 4.27 (d, 1H, *J* = 3.9), 3.57 (m, 1H), 3.49 (ddd, 1H, *J* =

14.1, 12.6, 5.4), 3.04 (dd, 1H, *J* = 14.4, 7.5), 2.35 (dd, 1H, *J* = 12.6, 5.1), 2.20-1.60 (m, 7H), 1.50-1.36 (m, 1H). ^{13}C-NMR: 164.5, 142.4, 141.9, 125.6, 117.8, 111.0, 91.3, 48.9, 42.0, 41.5, 35.9, 33.7 25.8, 20.9. HRMS: $[MH]^+$ calcd $C_{14}H_{17}N_2O_3$: 261.1239, found 261.1258. $C_{14}H_{16}N_2O_3$•0.1MeOH requires: C, 64.27; H, 6.27; N, 10.63; found: C, 64.16; H, 6.25; N, 10.43%.

(1*R,4a*R**,9a*R**)-6-Nitro-2-(2-phenethyl)-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (24).** Compound **24** was prepared using the same procedure as for compound **18** in 83% yield. Mp ((±)-**24**) 114-116 °C. Optical rotations: (1*S*,4a*S*,9a*S*)-(+)-**24**: $[\alpha]_D^{24}$ +56.6 (*c* 1.0, $CHCl_3$) (from the (+)-amine), (1*R*,4a*R*,9a*R*)-(-)-**24**: $[\alpha]_D^{24}$ –55.4 (*c* 1.0, $CHCl_3$) (from the (-)-amine). ^{1}H-NMR: 8.14 (dd, 1H, *J* = 9.0, 2.7), 7.97 (d, 1H, *J* = 2.4), 7.34-7.16 (m, 5H), 6.95 (d, 1H, *J* = 8.7), 4.29 (d, 1H, *J* = 3.3), 3.53 (m, 1H), 3.18-3.03 (m, 2H), 2.97-2.79 (m, 4H), 2.34-2.09 (m, 3H), 1.90-1.40 (m, 4H). ^{13}C-NMR: 165.0, 142.4, 141.6, 140.4, 128.9, 128.6, 126.3, 125.5, 117.9, 111.0, 90.5, 56.8, 53.0, 48.9, 41.2, 34.8, 33.8, 32.3, 20.9, 20.8. HRMS: $[MH]^+$ calcd $C_{22}H_{25}N_2O_3$: 365.1865, found 365.1869. $C_{22}H_{24}N_2O_3$ requires: C, 72.50; H, 6.64; N, 7.69; found: C, 72.50; H, 6.72; N, 7.60%.

(1*R,4a*R**,9a*R**)-6-Amino-2-(2-phenethyl)-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (25).** Compound **25** was prepared using the same procedure as for **19** in 94% yield. Optical rotations: (1*S*,4a*S*,9a*S*)-(+)-**25**: $[\alpha]_D^{23}$ +15.6 (*c* 1.0, $CHCl_3$) (from the (+)-amine), (1*R*,4a*R*,9a*R*)-(-)-**25**: $[\alpha]_D^{23}$ –16.1 (*c* 1.0, $CHCl_3$)

(from the (-)-amine). ^{1}H-NMR: 7.31-7.18 (m, 5H), 6.71 (d, 1H, *J* = 7.8), 6.48 (d, 1H, *J* = 2.4), 6.46 (dd, 1H, *J* = 8.1, 2.4), 4.09 (d, 1H, *J* = 3.6), 3.47 (bs, 1H), 3.42 (bs, 2H), 3.14-2.96 (m, 2H), 2.96-2.76 (m, 4H), 2.22-1.98 (m, 3H), 1.76-1.40 (m, 5H). ^{13}C-NMR: 152.4, 141.4, 140.7, 140.5, 128.9, 128.5, 126.2, 113.9, 111.2, 109.8, 88.5, 57.0, 53.4, 49.4, 41.5, 34.9, 33.9, 32.7, 21.2, 21.1. HRMS: $[MH]^+$ calcd $C_{22}H_{27}N_2O$: 335.2123, found 335.2114. $C_{22}H_{26}N_2O \cdot 0.25H_2O$ requires: C, 77.96; H, 7.88; N, 8.26; found: C, 77.97; H, 7.76; N, 8.15%.

(1*R,4a*R**,9a*R**)-6-Hydroxy-2-(2-phenethyl)-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (26).** Compound **26** was prepared using the same procedure as for **20** in 89% yield. Optical rotations (oxalates): (1*S*,4a*S*,9a*S*)-(+)-**26**: $[\alpha]_D^{24}$ +15.3 (*c* 1.0, 90% EtOH), (1*R*,4a*R*,9a*R*)-(-)-**26**: $[\alpha]_D^{24}$ –15.5 (*c* 1.0, 90% EtOH). Optical rotations (free bases): (1*S*,4a*S*,9a*S*)-(+)-**26**: α_D^{24} +12.5^{o} (c = 1.0, $CHCl_3$), (1*R*,4a*R*,9a*R*)-(-)-**26**: α_D^{24} –12.5^{o} (c = 1.0, $CHCl_3$). ^{1}H-NMR: 7.31-7.18 (m, 5H), 6.74 (d, 1H, *J* = 8.1), 6.60 (d, 1H, *J* = 2.7), 6.56 (dd, 1H, *J* = 8.4, 2.7), 4.14 (d, 1H, *J* = 3.3), 3.52 (bs, 1H), 3.06 (m, 2H), 2.95-2.81 (m, 4H), 2.20-2.00 (m, 3H), 1.80-1.40 (m, 5H). ^{13}C-NMR: 153.0, 150.6, 141.4, 140.3, 128.9, 128.6, 126.4, 113.9, 111.2, 109.8, 88.4, 56.9, 53.4, 49.5, 41.5, 34.5, 33.7, 32.4, 21.1, 20.9. HRMS: $[MH]^+$ calcd $C_{22}H_{26}NO_2$: 336.1963, found 336.1964. $C_{22}H_{25}NO_2 \cdot C_2H_2O_4$ requires: C, 67.75; H, 6.40; N, 3.29; found: C, 67.81; H, 6.41; N, 3.30%.

(1*S,4a*S**)-5-(2-Fluorophenyl)-2-methyl-2-azabicyclo[3.3.1]nonan-9-one (30).** Quaternary salt **12**[3] (24.65 g, split into 6 batches) was dry-distilled at ca. 240-250 ^{o}C and

high vacuum (0.050-0.200 mm Hg). The tertiary amine distilled out and condensed at room temperature to give **30** as a yellow oil, which crystallized on standing to give 14.97 g of white solid (84%). The spectral data were identical to those previously published.[3]

(1*R,4a*R**,9a*S**)-6-Amino-2-methyl-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (36).** Amine **36** was prepared from compound **15** according to the published procedure.[3]

(1*R,4a*R**,9a*S**)-6-Chloro-2-methyl-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (37).** Compound **37** was prepared in 79% yield using the same procedure as for **47**. Mp ((±)-**37**) 120-122 ^{o}C (2-propanol:H_2O). ^{1}H-NMR: 7.07 (dd, 1H, *J* = 8.4, 2.1), 7.03 (d, 1H, *J* = 2.1), 6.82 (d, 1H, *J* = 8.4), 4.07 (d, 1H, *J* = 3.0), 3.43 (m, 1H), 2.85-2.66 (m, 2H), 2.51 (s, 3H), 2.36-2.26 (m, 2H), 1.97-1.50 (m, 6H), 1.45 (m, 1H). ^{13}C-NMR: 157.8, 141.6, 127.6, 125.6, 121.9, 112.4, 90.1, 56.1, 49.5, 43.7, 40.5, 34.1, 33.4, 23.5, 22.3. HRMS: $[MH]^+$ calcd $C_{15}H_{19}ClNO$: 264.1155, found 264.1163. $C_{15}H_{18}ClNO$ requires: C, 68.30; H, 6.88; N, 5.31; found: C, 68.17; H, 6.94; N, 5.33%.

(1*R,4a*R**,9a*S**)-6-Chloro-2-methyl-8-nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (38).** Compound **38** was prepared in 84% yield using the same procedure as for **48**. Mp ((±)-**38**) 187-188 ^{o}C (2-propanol:H_2O). ^{1}H-NMR: 7.90 (d, 1H, *J* = 2.1), 7.28 (d, 1H, *J* = 2.1), 4.30 (d, 1H, *J* = 3.0), 3.58 (m, 1H), 2.90-2.68 (m, 2H), 2.55 (s, 3H), 2.35 (m, 2H), 2.00-1.77 (m, 5H), 1.45 (m, 1H). ^{13}C-NMR: 153.1, 145.9, 134.0, 127.7, 125.9, 123.1, 92.4, 55.7, 49.0, 43.6, 40.2, 33.9, 33.5, 23.8, 22.0.

HRMS: $[MH]^+$ calcd $C_{15}H_{18}N_2O_3Cl$: 309.1006, found 309.0993. $C_{15}H_{17}ClN_2O_3$ requires: C, 58.35; H, 5.55; N, 9.07; found: C, 58.34; H, 5.58; N, 9.04%.

(1*R,4a*R**,9a*S**)-6-Chloro-2-methyl-8-nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridyl ethylcarboxylate (39).** Compound **39** was prepared in 88% yield using the same procedure as for **16**. Mp ((±)-**39**) 139-140 ^oC. ^1H-NMR: 7.94 (d, 1H, J = 1.8), 7.32 (d, 1H, J = 2.1), 4.88 and 4.84 (bs, 1H), 4.35 and 4.31 (bs, 1H), 4.25-4.15 (m, 2H), 3.78-3.48 (m, 2H), 2.29-1.58 (m, 8H), 1.33 (m, 3H). ^{13}C-NMR: 156.3, 156.1, 152.6, 145.1, 145.0, 134.1, 127.9, 126.8, 126.8, 123.5, 92.2, 91.9, 61.8, 61.7, 49.0, 48.9, 41.2, 38.9, 38.6, 34.3, 34.1, 33.3, 30.4, 29.9, 18.5, 18.4, 14.9, 14.8. HRMS: $[M-Na]^+$ calcd $C_{17}H_{19}N_2O_5NaCl$: 389.0880, found 389.0862. $C_{17}H_{19}ClN_2O_5$ requires: C, 55.67; H, 5.22; N, 7.64; found: C, 55.57; H, 5.21; N, 7.54%.

(1*R,4a*R**,9a*S**)-6-Chloro-8-nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (40).** Compound **40** was prepared in 85% yield using the same procedure as for **17**. ^1H-NMR: 7.92 (d, 1H, J = 2.1), 7.27 (d, 1H, J = 2.1), 4.12 (d, 1H, J = 3.9), 3.79 (m, 1H), 3.28 (ddd, 1H, J = 12.6, 9.4, 4.8), 2.89 (dd, 1H, J = 14.4, 7.5), 2.39 (dd, 1H, J = 12.9, 7.2), 2.20-2.07 (m, 2H), 1.98-1.80 (m, 5H), 1.70 (dd, 1H, J = 14.4, 4.2), 1.54-1.42 (m, 1H). ^{13}C-NMR: 153.2, 146.3, 133.9, 127.5, 126.0, 122.9, 90.4, 48.5, 41.0, 40.4, 33.7, 33.1, 30.9, 21.6. HRMS: $[MH]^+$ calcd $C_{14}H_{16}N_2O_3Cl$: 295.0849, found 295.0829. $C_{14}H_{15}ClN_2O_3$ requires: C, 57.05; H, 5.13; N, 9.50; found: C, 57.09; H, 5.17; N, 9.33%.

(1*R,4a*R**,9a*S**)-6-Chloro-2-(2-phenylethyl)-8-nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (41).** Compound **41** was prepared in 78% yield using the same procedure as for **51**. ^{1}H-NMR: 7.92 (d, 1H, *J* = 2.1), 7.32-7.20 (m, 6H), 4.30 (d, 1H, *J* = 3.0), 3.77 (m, 1H), 2.89 (m, 6H), 2.32 (m, 2H), 2.05-1.80 (m, 5H), 1.50 (m, 1H). ^{13}C-NMR: 153.1, 145.9, 140.3, 133.8, 128.9, 128.5, 127.6, 126.1, 125.8, 122.9, 92.3, 57.8, 53.6, 47.5, 40.7, 34.5, 33.8, 33.3, 25.2, 21.6. HRMS: $[MH]^+$ calcd $C_{22}H_{24}N_2O_3Cl$: 399.1475, found 399.1495. $C_{22}H_{23}ClN_2O_3$ requires: C, 66.24; H, 5.81; N, 7.02; found: C, 66.31; H, 5.79; N, 6.93%.

(1*R,4a*R**,9a*S**)-8-Amino-2-(2-phenylethyl)-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (42).** Compound **42** was prepared using same procedure as for **52** in 86% yield. ^{1}H-NMR: 7.32-7.20 (m, 5H), 6.73 (dd, 1H, *J* = 8.1, 7.2), 6.58 (dd, 1H, *J* = 5.4, 1.5), 6.55 (dd, 1H, *J* = 4.2, 1.5), 4.08 (d, 1H, *J* = 3.0), 3.67 (m, 3H), 2.89 (m, 6H), 2.30 (m, 2H), 2.00-1.70 (m, 5H), 1.45 (m, 1H). ^{13}C-NMR: 146.5, 140.7, 139.9, 132.0, 129.0, 128.6, 126.3, 121.8, 115.3, 111.6, 90.1, 58.3, 53.9, 48.5, 41.1, 34.5, 34.0, 33.8, 25.2, 22.1. HRMS: $[MH]^+$ calcd $C_{22}H_{27}N_2O$: 335.2123, found 335.2112. $C_{22}H_{26}N_2O{\cdot}0.25H_2O$ requires: C, 77.96; H, 7.88; N, 8.26; found: C, 78.00; H, 7.77; N, 8.20%.

(*1*R**,4a*R**,9a*S**)-8-Hydroxy-2-(2-phenylethyl)-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (43). Compound **43** was prepared in 35% yield using the same procedure as for **53**. ^{1}H-NMR: 7.33-7.18 (m, 5H), 6.83-6.75 (m, 2H), 6.68 (dd, 1H, *J* = 6.3, 1.8), 4.13 (d, 1H, *J* = 3.0), 3.7 (m, 1H), 2.91 (m, 6H), 2.33 (m, 2H), 1.94-

1.70 (m, 6H), 1.49 (m, 1H). ^{13}C-NMR: 145.8, 141.8, 140.7, 140.5, 128.9, 128.6, 126.2, 122.0, 115.7, 113.2, 90.5, 58.3, 54.3, 48.2, 41.2, 34.4, 33.9, 33.6, 25.0, 22.0. HRMS: $[MH]^+$ calcd $C_{22}H_{26}NO_2$: 336.1964, found 336.1962. $C_{22}H_{25}NO_2 \cdot C_2H_2O_4 \cdot 0.25H_2O$ requires: C, 67.04; H, 6.45; N, 3.26; found: C, 67.00; H, 6.43; N, 3.33%.

Separation of enantiomers: The racemic compound **43** was prepared in larger quantity (ca. 0.150 g) and the enantiomers were separated on a chiral phase (Daicel's Chiralcel OD column (20 x 50 mm Guard plus 20 x 250 mm) using isocratic elution with hexanes:2-propanol:Et_2NH (80:20:0.2) mixture (8 mL/min, detection at 254 nm). Racemate was injected dissolved in 2-propanol (150 mg/1.5 mL, three runs, 500 μL each). Retention times of the enantiomers were around 15 and 23 minutes, (-) and (+) respectively. Corresponding fractions were pooled together, evaporated and analyzed on an analytical column of the same type. For better handling, the oily products were converted into their corresponding oxalate salts in acetone. Optical rotations: 1*S*,4a*S*,9a*R*-**(-)-43** (base): $[\alpha]_D^{21}$ – 34.8 (*c* 1.0, $CHCl_3$), oxalate: $[\alpha]_D^{23}$ – 37.9 (*c* 1.0, 90% EtOH); 1*R*,4a*R*,9a*S*-**(+)-43** (base): $[\alpha]_D^{21}$ + 28.5 (*c* 1.0, $CHCl_3$), oxalate: $[\alpha]_D^{23}$ + 36.2 (*c* 1.0, 90% EtOH).

(1*R,4a*R**,9a*R**)-2-(6-Chloro-2-methyl-8-nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridyl)-ethylcarboxylate (49).** Compound **49** was obtained in 75% yield using the same procedure as for **16**. Mp 166-168 ^oC (2-propanol:H_2O). The mother liquor was evaporated and dried to give 0.069 g (18%) of slightly impure product. ^{1}H-NMR: 7.94 (d, 1H, *J* = 1.5), 7.29 (d, 1H, *J* = 1.2), 5.01 and 4.93 (bs, 1H), 4.25 (m, 1H), 4.19 (q, 2H, *J* = 7.2), 4.10-3.90 (m, 1H), 3.64 (m, 1H), 2.39-1.40 (m, 9H), 1.29 (t,

1H, *J* = 7.2). ^{13}C-NMR: 156.2, 153.0, 145.4, 134.1, 127.8, 127.6, 123.3, 89.0, 88.7, 62.0, 49.1, 49.0, 42.1, 41.9, 41.4, 33.7, 31.3, 31.0, 25.6, 24.0, 23.3, 19.6, 14.8. HRMS: $[MH]^+$ calcd $C_{17}H_{20}ClN_2O_5$: 367.1061, found 367.1077. $C_{17}H_{19}ClN_2O_5$ requires: C, 55.67, H, 5.22; N, 7.64; found: C, 55.58; H, 5.34; N, 7.43%.

(1*R,4a*R**,9a*R**)-6-Chloro-8-nitro-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (50).** Compound **50** was prepared in 93% yield the using same procedure as for **17**. ^{1}H-NMR: 7.92 (d, 1H, *J* = 2.1), 7.26 (d, 1H, *J* = 2.1), 4.34 (d, 1H, *J* = 3.9), 3.67 (m., 1H), 3.48 (ddd, 1H, *J* = 14.3, 14.0, 5.1), 3.04 (dd, 1H, *J* = 14.1, 7.2), 2.31 (dd, 1H, *J* = 12.6, 5.1), 2.15-1.90 (m, 5H), 1.80 (dd, 1H, *J* = 15.3, 4.5), 1.67 (m, 1H), 1.48 (m, 1H). ^{13}C-NMR: 152.7, 146.7, 133.6, 127.4, 125.8, 122.7, 91.9, 48.5, 41.6, 41.5, 35.8, 33.3, 25.3, 20.6. HRMS: $[MH]^+$ calcd $C_{14}H_{16}ClN_2O_3$: 295.0849, found 295.0855. $C_{14}H_{15}ClN_2O_3$ requires: C, 57.05; H, 5.13; N, 9.50; found: C, 56.89; H, 5.21; N, 9.44%.

(1*R,4a*R**,9a*R**)-6-Chloro-8-nitro-2-(2-phenylethyl)-1,3,4,9a-tetrahydro-2*H*-1,4a-propanobenzofuro[2,3-c]pyridine (51).** Compound **51** was prepared in 78% yield using the same procedure as for **18**. Mp ((±)-**51**) 213-214 ^{o}C (acetone). ^{1}H-NMR: 7.92 (d, 1H, *J* = 2.1), 7.32-7.20 (m, 6H), 4.36 (d, 1H, *J* = 3.6), 3.64 (m, 1H), 3.18-3.00 (m, 2H), 3.00-2.77 (m, 4H), 2.29-2.10 (m, 3H), 1.90-1.40 (m, 6H). ^{13}C-NMR: 153.3, 146.4, 140.2, 133.8, 128.7, 128.4, 127.5, 126.2, 125.9, 122.7, 91.1, 56.5, 52.4, 48.6, 41.3, 34.6, 33.6, 32.1, 20.7, 20.6. HRMS: $[MH]^+$ calcd $C_{22}H_{24}N_2O_3Cl$: 399.1475, found 399.1455. $C_{22}H_{23}ClN_2O_3$ requires: C, 66.24; H, 5.81; N, 7.02; found: C, 66.25; H, 5.78; N, 6.92%.

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Table 1. Crystal data and structure refinement for 1*R*,4a*R*,9a*S*-(+)-**15**.[(1*S*)-(endo,anti)]-(-)-3-bromocamphor-8-sulfonate

Empirical formula	$C_{25}H_{33}BrN_2O_7S$	
Formula weight	585.50	
Temperature	93(2)°K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P\,2_12_12_1$	
Unit cell dimensions	a = 7.719(3) Å	α= 90°
	b = 13.922(5) Å	β= 90°
	c = 24.899(12) Å	γ = 90°
Volume	2675.7(18) Å^3	
Z	4	
Density (calculated)	1.453 Mg/m^3	
Absorption coefficient	1.660 mm^{-1}	
F(000)	1216	
Crystal size	0.65 x 0.35 x 0.14 mm^3	
Theta range for data collection	1.68 to 28.51°	
Index ranges	-10<=h<=8, -18<=k<=18, -32<=l<=32	
Reflections collected	18485	
Independent reflections	6212 [R(int) = 0.0508]	
Completeness to theta = 28.51°	91.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.793 and 0.430	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6212 / 0 / 331	
Goodness-of-fit on F^2	0.939	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1069	
R indices (all data)	R1 = 0.0508, wR2 = 0.1159	
Absolute structure parameter	0.090(8)	
Largest diff. peak and hole	0.551 and -0.348 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(+)-15**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	10294(4)	-268(2)	928(1)	23(1)
N(2)	11027(4)	-1013(2)	539(1)	21(1)
C(2)	12220(4)	-1705(2)	814(1)	24(1)
C(3)	9614(4)	-1505(2)	228(1)	20(1)
C(4)	8509(4)	-769(2)	-76(1)	20(1)
C(4A)	7920(4)	136(2)	262(1)	19(1)
C(4B)	7796(4)	975(2)	-134(1)	21(1)
C(5)	6505(4)	1279(2)	-485(1)	21(1)
C(6)	6955(5)	2020(2)	-849(1)	22(1)
N(6)	5598(4)	2405(2)	-1206(1)	24(1)
O(6A)	4061(3)	2162(2)	-1115(1)	31(1)
O(6B)	6013(4)	2963(2)	-1573(1)	38(1)
C(7)	8614(5)	2421(2)	-884(1)	26(1)
C(8)	9919(5)	2106(2)	-528(2)	27(1)
C(9)	9463(4)	1405(2)	-157(1)	23(1)
O(9)	10578(3)	1045(2)	234(1)	27(1)
C(9A)	9432(5)	530(2)	608(1)	24(1)
C(10)	6427(4)	-70(2)	656(1)	24(1)
C(11)	7014(5)	-805(2)	1094(1)	27(1)
C(12)	8883(5)	-653(3)	1320(1)	30(1)
C(1')	3035(5)	-230(2)	2694(1)	24(1)
C(1A')	1605(5)	-943(3)	2557(1)	31(1)
C(2')	3680(4)	377(2)	2219(1)	22(1)
O(2')	3582(3)	188(2)	1739(1)	30(1)
C(3')	4539(4)	1279(2)	2463(1)	24(1)
C(4')	4527(4)	1057(2)	3076(1)	19(1)
C(5')	5748(5)	196(3)	3183(1)	29(1)
C(6')	4781(4)	-674(2)	2917(2)	27(1)
C(7')	2656(4)	588(2)	3121(1)	18(1)
C(7A')	1152(4)	1253(3)	2940(2)	26(1)
C(8')	2263(4)	150(2)	3685(1)	22(1)
S(8')	1694(1)	988(1)	4212(1)	21(1)
O(8A')	1828(4)	406(2)	4711(1)	28(1)
O(8B')	2990(3)	1768(2)	4194(1)	26(1)
O(8C')	-80(3)	1316(2)	4114(1)	31(1)
Br(3')	6801(1)	1540(1)	2127(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for **(+)-15**.

C(1)-C(9A)	1.520(5)	C(1)-N(2)	1.527(4)
C(1)-C(12)	1.558(5)	C(1)-H(1A)	1.0000
N(2)-C(2)	1.498(4)	N(2)-C(3)	1.504(4)
N(2)-H(2)	0.95(4)	C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800	C(2)-H(2C)	0.9800
C(3)-C(4)	1.532(4)	C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900	C(4)-C(4A)	1.581(4)
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(4A)-C(4B)	1.529(4)	C(4A)-C(10)	1.541(5)
C(4A)-C(9A)	1.552(4)	C(4B)-C(5)	1.392(5)
C(4B)-C(9)	1.420(4)	C(5)-C(6)	1.416(4)
C(5)-H(5A)	0.9500	C(6)-C(7)	1.400(5)
C(6)-N(6)	1.475(4)	N(6)-O(6B)	1.242(4)
N(6)-O(6A)	1.253(4)	C(7)-C(8)	1.411(5)
C(7)-H(7A)	0.9500	C(8)-C(9)	1.390(5)
C(8)-H(8A)	0.9500	C(9)-O(9)	1.393(4)
O(9)-C(9A)	1.471(4)	C(9A)-H(9AA)	1.0000
C(10)-C(11)	1.564(4)	C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900	C(11)-C(12)	1.563(5)
C(11)-H(11A)	0.9900	C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900	C(12)-H(12B)	0.9900
C(1')-C(1A')	1.523(5)	C(1')-C(2')	1.536(5)
C(1')-C(7')	1.586(4)	C(1')-C(6')	1.583(5)
C(1A')-H(1AA)	0.9800	C(1A')-H(1AB)	0.9800
C(1A')-H(1AC)	0.9800	C(2')-O(2')	1.226(4)
C(2')-C(3')	1.545(5)	C(3')-C(4')	1.558(5)
C(3')-Br(3')	1.970(3)	C(3')-H(3'A)	1.0000
C(4')-C(5')	1.547(5)	C(4')-C(7')	1.589(4)
C(4')-H(4'A)	1.0000	C(5')-C(6')	1.569(5)
C(5')-H(5'A)	0.9900	C(5')-H(5'B)	0.9900
C(6')-H(6'A)	0.9900	C(6')-H(6'B)	0.9900
C(7')-C(8')	1.561(4)	C(7')-C(7A')	1.552(4)
C(7A')-H(7AA)	0.9800	C(7A')-H(7AB)	0.9800
C(7A')-H(7AC)	0.9800	C(8')-S(8')	1.809(3)
C(8')-H(8'A)	0.9900	C(8')-H(8'B)	0.9900
S(8')-O(8C')	1.464(3)	S(8')-O(8B')	1.476(2)
S(8')-O(8A')	1.488(2)		

C(9A)-C(1)-N(2)	109.1(3)	C(9A)-C(1)-C(12)	105.9(3)
N(2)-C(1)-C(12)	115.0(3)	C(9A)-C(1)-H(1A)	108.9
N(2)-C(1)-H(1A)	108.9	C(12)-C(1)-H(1A)	108.9
C(2)-N(2)-C(3)	112.9(2)	C(2)-N(2)-C(1)	112.0(3)
C(3)-N(2)-C(1)	111.6(2)	C(2)-N(2)-H(2)	108(3)
C(3)-N(2)-H(2)	107(2)	C(1)-N(2)-H(2)	105(2)
N(2)-C(2)-H(2A)	109.5	N(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5	N(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5
N(2)-C(3)-C(4)	110.7(2)	N(2)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3A)	109.5	N(2)-C(3)-H(3B)	109.5
C(4)-C(3)-H(3B)	109.5	H(3A)-C(3)-H(3B)	108.1
C(3)-C(4)-C(4A)	115.5(3)	C(3)-C(4)-H(4A)	108.4
C(4A)-C(4)-H(4A)	108.4	C(3)-C(4)-H(4B)	108.4

Table 3. (continued).

C(4A)-C(4)-H(4B)	108.4	H(4A)-C(4)-H(4B)	107.5
C(4B)-C(4A)-C(10)	120.3(3)	C(4B)-C(4A)-C(9A)	97.8(2)
C(10)-C(4A)-C(9A)	105.9(3)	C(4B)-C(4A)-C(4)	106.5(2)
C(10)-C(4A)-C(4)	113.9(2)	C(9A)-C(4A)-C(4)	111.2(2)
C(5)-C(4B)-C(9)	119.6(3)	C(5)-C(4B)-C(4A)	132.9(3)
C(9)-C(4B)-C(4A)	106.9(3)	C(4B)-C(5)-C(6)	116.6(3)
C(4B)-C(5)-H(5A)	121.7	C(6)-C(5)-H(5A)	121.7
C(7)-C(6)-C(5)	123.7(3)	C(7)-C(6)-N(6)	117.9(3)
C(5)-C(6)-N(6)	118.4(3)	O(6B)-N(6)-O(6A)	123.0(3)
O(6B)-N(6)-C(6)	119.2(3)	O(6A)-N(6)-C(6)	117.8(3)
C(6)-C(7)-C(8)	119.3(3)	C(6)-C(7)-H(7A)	120.3
C(8)-C(7)-H(7A)	120.3	C(9)-C(8)-C(7)	117.1(3)
C(9)-C(8)-H(8A)	121.5	C(7)-C(8)-H(8A)	121.5
C(8)-C(9)-O(9)	124.1(3)	C(8)-C(9)-C(4B)	123.6(3)
O(9)-C(9)-C(4B)	112.3(3)	C(9)-O(9)-C(9A)	104.3(2)
O(9)-C(9A)-C(1)	115.1(3)	O(9)-C(9A)-C(4A)	105.7(3)
C(1)-C(9A)-C(4A)	111.2(3)	O(9)-C(9A)-H(9AA)	108.2
C(1)-C(9A)-H(9AA)	108.2	C(4A)-C(9A)-H(9AA)	108.2
C(4A)-C(10)-C(11)	110.5(3)	C(4A)-C(10)-H(10A)	109.6
C(11)-C(10)-H(10A)	109.6	C(4A)-C(10)-H(10B)	109.6
C(11)-C(10)-H(10B)	109.6	H(10A)-C(10)-H(10B)	108.1
C(12)-C(11)-C(10)	115.5(3)	C(12)-C(11)-H(11A)	108.4
C(10)-C(11)-H(11A)	108.4	C(12)-C(11)-H(11B)	108.4
C(10)-C(11)-H(11B)	108.4	H(11A)-C(11)-H(11B)	107.5
C(1)-C(12)-C(11)	117.8(3)	C(1)-C(12)-H(12A)	107.9
C(11)-C(12)-H(12A)	107.9	C(1)-C(12)-H(12B)	107.8
C(11)-C(12)-H(12B)	107.9	H(12A)-C(12)-H(12B)	107.2
C(1A')-C(1')-C(2')	114.8(3)	C(1A')-C(1')-C(7')	119.0(3)
C(2')-C(1')-C(7')	100.4(2)	C(1A')-C(1')-C(6')	116.2(3)
C(2')-C(1')-C(6')	102.0(3)	C(7')-C(1')-C(6')	101.7(2)
C(1')-C(1A')-H(1AA)	109.5	C(1')-C(1A')-H(1AB)	109.5
H(1AA)-C(1A')-H(1AB)	109.5	C(1')-C(1A')-H(1AC)	109.5
H(1AA)-C(1A')-H(1AC)	109.5	H(1AB)-C(1A')-H(1AC)	109.5
O(2')-C(2')-C(1')	127.8(3)	O(2')-C(2')-C(3')	125.7(3)
C(1')-C(2')-C(3')	106.5(3)	C(4')-C(3')-C(2')	102.8(3)
C(4')-C(3')-Br(3')	117.3(2)	C(2')-C(3')-Br(3')	111.4(2)
C(4')-C(3')-H(3'A)	108.4	C(2')-C(3')-H(3'A)	108.4
Br(3')-C(3')-H(3'A)	108.4	C(3')-C(4')-C(5')	108.5(3)
C(3')-C(4')-C(7')	99.0(2)	C(5')-C(4')-C(7')	102.9(2)
C(3')-C(4')-H(4'A)	114.9	C(5')-C(4')-H(4'A)	114.9
C(7')-C(4')-H(4'A)	114.9	C(4')-C(5')-C(6')	103.6(3)
C(4')-C(5')-H(5'A)	111.0	C(6')-C(5')-H(5'A)	111.0
C(4')-C(5')-H(5'B)	111.0	C(6')-C(5')-H(5'B)	111.0
H(5'A)-C(5')-H(5'B)	109.0	C(5')-C(6')-C(1')	104.6(2)
C(5')-C(6')-H(6'A)	110.8	C(1')-C(6')-H(6'A)	110.8
C(5')-C(6')-H(6'B)	110.8	C(1')-C(6')-H(6'B)	110.8
H(6'A)-C(6')-H(6'B)	108.9	C(8')-C(7')-C(7A')	110.5(3)
C(8')-C(7')-C(1')	111.0(2)	C(7A')-C(7')-C(1')	111.8(3)
C(8')-C(7')-C(4')	113.6(3)	C(7A')-C(7')-C(4')	114.5(3)
C(1')-C(7')-C(4')	94.6(2)	C(7')-C(7A')-H(7AA)	109.5
C(7')-C(7A')-H(7AB)	109.5	H(7AA)-C(7A')-H(7AB)	109.5
C(7')-C(7A')-H(7AC)	109.5	H(7AA)-C(7A')-H(7AC)	109.5
H(7AB)-C(7A')-H(7AC)	109.5	C(7')-C(8')-S(8')	116.5(2)

Table 3. (continued).

C(7')-C(8')-H(8'A)	108.2	S(8')-C(8')-H(8'A)	108.1
C(7')-C(8')-H(8'B)	108.2	S(8')-C(8')-H(8'B)	108.2
H(8'A)-C(8')-H(8'B)	107.3	O(8C')-S(8')-O(8B')	113.58(15)
O(8C')-S(8')-O(8A')	111.95(16)	O(8B')-S(8')-O(8A')	112.20(14)
O(8C')-S(8')-C(8')	107.89(16)	O(8B')-S(8')-C(8')	106.77(14)
O(8A')-S(8')-C(8')	103.72(14)		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **(+)-15**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(2)	20(2)	25(2)	-8(1)	-9(1)	3(1)
N(2)	22(1)	19(1)	21(1)	-2(1)	-3(1)	2(1)
C(2)	23(2)	23(2)	27(2)	2(1)	-4(1)	4(1)
C(3)	21(1)	17(1)	22(2)	-2(1)	-4(1)	0(1)
C(4)	22(2)	20(1)	20(2)	-3(1)	-3(1)	-1(1)
C(4A)	17(2)	18(1)	22(2)	1(1)	-4(1)	1(1)
C(4B)	23(2)	17(1)	22(2)	-2(1)	3(1)	-3(1)
C(5)	25(2)	18(1)	20(2)	-3(1)	1(1)	1(1)
C(6)	27(2)	17(1)	21(2)	-1(1)	0(1)	3(1)
N(6)	29(2)	19(1)	24(2)	0(1)	-3(1)	2(1)
O(6A)	31(1)	26(1)	37(1)	7(1)	-8(1)	0(1)
O(6B)	49(2)	37(1)	29(1)	16(1)	1(1)	-4(1)
C(7)	31(2)	21(2)	26(2)	2(1)	6(1)	-4(1)
C(8)	26(2)	21(2)	33(2)	-1(1)	4(2)	-6(1)
C(9)	19(1)	19(2)	32(2)	-5(1)	-2(1)	-1(1)
O(9)	23(1)	22(1)	36(1)	-3(1)	-8(1)	-3(1)
C(9A)	25(2)	18(1)	30(2)	-4(1)	-6(1)	1(1)
C(10)	26(2)	24(2)	23(2)	3(1)	-2(1)	3(1)
C(11)	30(2)	31(2)	19(2)	2(1)	5(1)	10(1)
C(12)	38(2)	33(2)	18(2)	-2(1)	-8(2)	10(2)
C(1')	26(2)	28(2)	17(1)	-4(1)	-4(1)	1(1)
C(1A')	39(2)	31(2)	24(2)	-5(1)	-5(2)	-7(2)
C(2')	19(1)	28(2)	19(2)	-2(1)	0(1)	6(1)
O(2')	25(1)	47(1)	18(1)	-5(1)	-3(1)	2(1)
C(3')	22(2)	28(2)	22(2)	1(1)	7(1)	1(1)
C(4')	19(1)	22(1)	17(1)	-2(1)	2(1)	-1(1)
C(5')	22(2)	45(2)	20(2)	1(2)	-5(1)	3(2)
C(6')	28(2)	26(2)	26(2)	-5(1)	0(2)	10(1)
C(7')	16(1)	23(1)	15(2)	-1(1)	2(1)	1(1)
C(7A')	19(1)	34(2)	25(2)	3(1)	2(1)	6(1)
C(8')	29(2)	17(1)	18(2)	0(1)	1(1)	1(1)
S(8')	24(1)	21(1)	19(1)	-2(1)	3(1)	1(1)
O(8A')	37(1)	30(1)	17(1)	0(1)	3(1)	-6(1)
O(8B')	32(1)	21(1)	24(1)	-2(1)	3(1)	-4(1)
O(8C')	21(1)	41(1)	32(1)	-3(1)	3(1)	7(1)
Br(3')	28(1)	37(1)	28(1)	-2(1)	9(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **(+)-15**.

	x	y	z	U(eq)
H(1A)	11267	11	1142	28
H(2)	11700(60)	-650(30)	291(16)	31
H(2A)	12895	-2056	545	37
H(2B)	11538	-2161	1027	37
H(2C)	13008	-1351	1051	37
H(3A)	8870	-1875	477	24
H(3B)	10135	-1961	-32	24
H(4A)	7460	-1098	-212	24
H(4B)	9174	-542	-391	24
H(5A)	5379	1004	-480	25
H(7A)	8860	2900	-1145	31
H(8A)	11059	2362	-542	32
H(9AA)	8946	1007	868	29
H(10A)	5423	-332	457	29
H(10B)	6060	536	830	29
H(11A)	6186	-773	1397	32
H(11B)	6941	-1459	940	32
H(12A)	8805	-201	1626	35
H(12B)	9291	-1276	1465	35
H(1AA)	2001	-1371	2269	47
H(1AB)	573	-593	2437	47
H(1AC)	1319	-1324	2876	47
H(3'A)	3764	1842	2396	29
H(4'A)	4722	1626	3313	23
H(5'A)	5907	91	3573	34
H(5'B)	6894	300	3014	34
H(6'A)	4541	-1182	3185	32
H(6'B)	5479	-951	2621	32
H(7AA)	41	940	3015	39
H(7AB)	1250	1378	2554	39
H(7AC)	1216	1862	3137	39
H(8'A)	3295	-216	3803	26
H(8'B)	1301	-315	3646	26

Table 6. Torsion angles [°] for **(+)-15**.

C(9A)-C(1)-N(2)-C(2)	167.6(3)	C(12)-C(1)-N(2)-C(2)	-73.6(3)
C(9A)-C(1)-N(2)-C(3)	-64.7(3)	C(12)-C(1)-N(2)-C(3)	54.0(4)
C(2)-N(2)-C(3)-C(4)	-176.2(3)	C(1)-N(2)-C(3)-C(4)	56.6(3)
N(2)-C(3)-C(4)-C(4A)	-46.4(4)	C(3)-C(4)-C(4A)-C(4B)	148.7(3)
C(3)-C(4)-C(4A)-C(10)	-76.2(3)	C(3)-C(4)-C(4A)-C(9A)	43.3(4)
C(10)-C(4A)-C(4B)-C(5)	-48.0(5)	C(9A)-C(4A)-C(4B)-C(5)	-161.6(3)
C(4)-C(4A)-C(4B)-C(5)	83.5(4)	C(10)-C(4A)-C(4B)-C(9)	140.3(3)
C(9A)-C(4A)-C(4B)-C(9)	26.7(3)	C(4)-C(4A)-C(4B)-C(9)	-88.2(3)
C(9)-C(4B)-C(5)-C(6)	-0.4(4)	C(4A)-C(4B)-C(5)-C(6)	-171.2(3)
C(4B)-C(5)-C(6)-C(7)	2.6(5)	C(4B)-C(5)-C(6)-N(6)	-176.4(3)
C(7)-C(6)-N(6)-O(6B)	10.1(4)	C(5)-C(6)-N(6)-O(6B)	-170.8(3)
C(7)-C(6)-N(6)-O(6A)	-168.5(3)	C(5)-C(6)-N(6)-O(6A)	10.6(4)
C(5)-C(6)-C(7)-C(8)	-2.4(5)	N(6)-C(6)-C(7)-C(8)	176.6(3)
C(6)-C(7)-C(8)-C(9)	-0.1(5)	C(7)-C(8)-C(9)-O(9)	-177.5(3)
C(7)-C(8)-C(9)-C(4B)	2.4(5)	C(5)-C(4B)-C(9)-C(8)	-2.2(5)
C(4A)-C(4B)-C(9)-C(8)	170.8(3)	C(5)-C(4B)-C(9)-O(9)	177.7(3)
C(4A)-C(4B)-C(9)-O(9)	-9.3(4)	C(8)-C(9)-O(9)-C(9A)	165.7(3)
C(4B)-C(9)-O(9)-C(9A)	-14.1(3)	C(9)-O(9)-C(9A)-C(1)	154.9(3)
C(9)-O(9)-C(9A)-C(4A)	31.7(3)	N(2)-C(1)-C(9A)-O(9)	-59.6(3)
C(12)-C(1)-C(9A)-O(9)	176.1(3)	N(2)-C(1)-C(9A)-C(4A)	60.6(4)
C(12)-C(1)-C(9A)-C(4A)	-63.7(3)	C(4B)-C(4A)-C(9A)-O(9)	-35.3(3)
C(10)-C(4A)-C(9A)-O(9)	-160.0(2)	C(4)-C(4A)-C(9A)-O(9)	75.9(3)
C(4B)-C(4A)-C(9A)-C(1)	-160.9(3)	C(10)-C(4A)-C(9A)-C(1)	74.4(3)
C(4)-C(4A)-C(9A)-C(1)	-49.8(4)	C(4B)-C(4A)-C(10)-C(11)	-167.7(3)
C(9A)-C(4A)-C(10)-C(11)	-58.5(3)	C(4)-C(4A)-C(10)-C(11)	64.0(3)
C(4A)-C(10)-C(11)-C(12)	41.1(4)	C(9A)-C(1)-C(12)-C(11)	43.1(4)
N(2)-C(1)-C(12)-C(11)	-77.4(4)	C(10)-C(11)-C(12)-C(1)	-34.2(4)
C(1A')-C(1')-C(2')-O(2')	-22.9(5)	C(7')-C(1')-C(2')-O(2')	-151.9(3)
C(6')-C(1')-C(2')-O(2')	103.7(4)	C(1A')-C(1')-C(2')-C(3')	158.6(3)
C(7')-C(1')-C(2')-C(3')	29.6(3)	C(6')-C(1')-C(2')-C(3')	-74.8(3)
O(2')-C(2')-C(3')-C(4')	-171.6(3)	C(1')-C(2')-C(3')-C(4')	6.9(3)
O(2')-C(2')-C(3')-Br(3')	-45.3(4)	C(1')-C(2')-C(3')-Br(3')	133.3(2)
C(2')-C(3')-C(4')-C(5')	66.4(3)	Br(3')-C(3')-C(4')-C(5')	-56.1(3)
C(2')-C(3')-C(4')-C(7')	-40.6(3)	Br(3')-C(3')-C(4')-C(7')	-163.1(2)
C(3')-C(4')-C(5')-C(6')	-68.9(3)	C(7')-C(4')-C(5')-C(6')	35.4(3)
C(4')-C(5')-C(6')-C(1')	-1.8(3)	C(1A')-C(1')-C(6')-C(5')	-163.2(3)
C(2')-C(1')-C(6')-C(5')	71.1(3)	C(7')-C(1')-C(6')-C(5')	-32.3(3)
C(1A')-C(1')-C(7')-C(8')	63.3(4)	C(2')-C(1')-C(7')-C(8')	-170.5(3)
C(6')-C(1')-C(7')-C(8')	-65.8(3)	C(1A')-C(1')-C(7')-C(7A')	-60.6(4)
C(2')-C(1')-C(7')-C(7A')	65.6(3)	C(6')-C(1')-C(7')-C(7A')	170.3(3)
C(1A')-C(1')-C(7')-C(4')	-179.2(3)	C(2')-C(1')-C(7')-C(4')	-53.0(3)
C(6')-C(1')-C(7')-C(4')	51.7(3)	C(3')-C(4')-C(7')-C(8')	172.9(3)
C(5')-C(4')-C(7')-C(8')	61.3(3)	C(3')-C(4')-C(7')-C(7A')	-58.9(3)
C(5')-C(4')-C(7')-C(7A')	-170.5(3)	C(3')-C(4')-C(7')-C(1')	57.5(3)
C(5')-C(4')-C(7')-C(1')	-54.0(3)	C(7A')-C(7')-C(8')-S(8')	-52.3(3)
C(1')-C(7')-C(8')-S(8')	-177.0(2)	C(4')-C(7')-C(8')-S(8')	77.9(3)
C(7')-C(8')-S(8')-O(8C')	74.5(3)	C(7')-C(8')-S(8')-O(8B')	-47.9(3)
C(7')-C(8')-S(8')-O(8A')	-166.6(2)		

Table 7. Crystal data and structure refinement for (1*R*,4a*R*,9a*R*)-(+)-**29**.(-)-di-O,O'-*p*-toluoyl-D-tartaric acid

Empirical formula	$C_{36.50}H_{43}FN_2O_{12.50}$	
Formula weight	728.73	
Temperature	93(2)°K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P\ 2_12_12_1$	
Unit cell dimensions	a = 8.7028(11) Å	α= 90°
	b = 13.9149(15) Å	β= 90°
	c = 30.493(3) Å	γ = 90°
Volume	3692.7(7) Å^3	
Z	4	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	1540	
Crystal size	0.50 x 0.46 x 0.14 mm^3	
Theta range for data collection	1.34 to 28.34°	
Index ranges	-10<=h<=11, -18<=k<=17, -40<=l<=40	
Reflections collected	29850	
Independent reflections	8982 [R(int) = 0.0474]	
Completeness to theta = 28.34°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.986 and 0.821	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8982 / 0 / 495	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0621, wR2 = 0.1270	
R indices (all data)	R1 = 0.0747, wR2 = 0.1312	
Absolute structure parameter	0.5(8)	
Largest diff. peak and hole	0.344 and -0.359 e.Å^{-3}	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(+)-29**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1837(3)	2127(2)	1157(1)	21(1)
N(2)	3074(3)	2265(1)	1497(1)	21(1)
C(2)	3310(4)	1400(2)	1783(1)	31(1)
C(3)	4579(3)	2580(2)	1305(1)	22(1)
C(4)	4365(3)	3421(2)	991(1)	22(1)
C(4A)	3033(3)	3345(2)	652(1)	20(1)
C(4B)	2909(3)	4328(2)	429(1)	21(1)
C(5)	1587(3)	4893(2)	448(1)	22(1)
C(6)	1567(3)	5797(2)	258(1)	26(1)
N(6)	142(3)	6358(2)	281(1)	30(1)
O(6A)	193(3)	7204(1)	172(1)	42(1)
O(6B)	-1036(2)	5950(2)	394(1)	40(1)
C(7)	2812(3)	6192(2)	44(1)	31(1)
C(8)	4122(3)	5643(2)	13(1)	30(1)
C(9)	4137(3)	4736(2)	204(1)	26(1)
F(9)	5462(2)	4235(1)	162(1)	34(1)
C(9A)	1592(3)	3100(2)	921(1)	17(1)
O(9)	292(2)	3010(1)	646(1)	25(1)
C(10)	3241(3)	2565(2)	293(1)	25(1)
C(11)	3338(3)	1541(2)	473(1)	28(1)
C(12)	2128(3)	1325(2)	823(1)	26(1)
O(1')	7819(2)	31(1)	2038(1)	21(1)
C(2')	9035(3)	516(2)	2261(1)	18(1)
C(2")	8969(3)	1601(2)	2170(1)	18(1)
O(2')	10132(2)	2033(1)	2342(1)	28(1)
O(2")	7953(2)	1967(1)	1957(1)	27(1)
C(3')	8828(3)	304(2)	2747(1)	18(1)
C(3")	8784(3)	-788(2)	2830(1)	21(1)
O(3')	7647(2)	-1159(1)	2998(1)	24(1)
O(3")	10011(2)	-1206(1)	2707(1)	35(1)
O(4')	7417(2)	748(1)	2870(1)	21(1)
C(5')	7169(3)	846(2)	3309(1)	20(1)
O(5')	8125(2)	655(1)	3581(1)	28(1)
C(6')	5603(3)	1223(2)	3396(1)	22(1)
C(7')	5189(3)	1404(2)	3831(1)	24(1)
C(8')	3751(3)	1780(2)	3923(1)	28(1)
C(9')	2713(3)	1981(2)	3590(1)	29(1)
C(9A')	1150(3)	2394(2)	3690(1)	39(1)
C(10')	3126(3)	1786(2)	3159(1)	31(1)
C(11')	4570(3)	1411(2)	3062(1)	27(1)
C(12')	7924(3)	-6(2)	1596(1)	23(1)
O(12')	9027(2)	261(1)	1394(1)	34(1)
C(13')	6504(3)	-412(2)	1406(1)	25(1)
C(14')	6212(3)	-298(2)	963(1)	33(1)
C(15')	4853(4)	-643(2)	784(1)	39(1)
C(16')	3779(4)	-1119(2)	1041(1)	39(1)
C(16A)	2317(4)	-1501(2)	839(1)	54(1)
C(17')	4079(3)	-1235(2)	1480(1)	37(1)
C(18')	5424(3)	-882(2)	1667(1)	31(1)
C(1S)	8059(4)	4404(2)	1327(1)	55(1)

Table 8. (continued).

	x	y	z	U(eq)
O(1S)	8109(2)	3378(1)	1279(1)	34(1)
C(2S)	4008(6)	9068(4)	2680(2)	30(1)
O(2S)	2818(5)	9577(3)	2466(1)	36(1)

Table 9. Bond lengths [Å] and angles [°] for (+)-**29**.

C(1)-N(2)	1.507(3)	C(1)-C(12)	1.531(3)
C(1)-C(9A)	1.547(3)	C(1)-H(1A)	1.0000
N(2)-C(2)	1.500(3)	N(2)-C(3)	1.501(3)
N(2)-H(2)	0.93(3)	C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800	C(2)-H(2C)	0.9800
C(3)-C(4)	1.522(3)	C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900	C(4)-C(4A)	1.558(3)
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(4A)-C(4B)	1.531(3)	C(4A)-C(9A)	1.537(3)
C(4A)-C(10)	1.551(3)	C(4B)-C(9)	1.392(4)
C(4B)-C(5)	1.395(4)	C(5)-C(6)	1.386(3)
C(5)-H(5A)	0.9500	C(6)-C(7)	1.378(4)
C(6)-N(6)	1.467(3)	N(6)-O(6B)	1.221(3)
N(6)-O(6A)	1.225(3)	C(7)-C(8)	1.376(4)
C(7)-H(7A)	0.9500	C(8)-C(9)	1.390(4)
C(8)-H(8A)	0.9500	C(9)-F(9)	1.353(3)
C(9A)-O(9)	1.414(3)	C(9A)-H(9AA)	1.0000
O(9)-H(9)	0.88(3)	C(10)-C(11)	1.528(3)
C(10)-H(10A)	0.9900	C(10)-H(10B)	0.9900
C(11)-C(12)	1.531(4)	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900	O(1')-C(12')	1.354(3)
O(1')-C(2')	1.427(3)	C(2')-C(3')	1.522(3)
C(2')-C(2")	1.535(3)	C(2')-H(2'A)	1.0000
C(2")-O(2")	1.209(3)	C(2")-O(2')	1.289(3)
O(2')-H(2')	0.8400	C(3')-O(4')	1.425(3)
C(3')-C(3")	1.540(3)	C(3')-H(3'A)	1.0000
C(3")-O(3')	1.229(3)	C(3")-O(3")	1.272(3)
O(4')-C(5')	1.362(3)	C(5')-O(5')	1.204(3)
C(5')-C(6')	1.485(4)	C(6')-C(11')	1.384(4)
C(6')-C(7')	1.395(3)	C(7')-C(8')	1.386(4)
C(7')-H(7'A)	0.9500	C(8')-C(9')	1.388(4)
C(8')-H(8'A)	0.9500	C(9')-C(10')	1.390(4)
C(9')-C(9A')	1.508(4)	C(9A')-H(9AB)	0.9800
C(9A')-H(9AC)	0.9800	C(9A')-H(9AD)	0.9800
C(10')-C(11')	1.392(4)	C(10')-H(10C)	0.9500
C(11')-H(11C)	0.9500	C(12')-O(12')	1.199(3)
C(12')-C(13')	1.476(4)	C(13')-C(14')	1.384(4)
C(13')-C(18')	1.394(4)	C(14')-C(15')	1.388(4)
C(14')-H(14A)	0.9500	C(15')-C(16')	1.388(5)
C(15')-H(15A)	0.9500	C(16')-C(17')	1.373(5)
C(16')-C(16A)	1.511(4)	C(16A)-H(16A)	0.9800
C(16A)-H(16B)	0.9800	C(16A)-H(16C)	0.9800
C(17')-C(18')	1.391(4)	C(17')-H(17A)	0.9500
C(18')-H(18A)	0.9500	C(1S)-O(1S)	1.437(4)
C(1S)-H(1SA)	0.9800	C(1S)-H(1SB)	0.9800
C(1S)-H(1SC)	0.9800	O(1S)-H(1S)	0.8400
C(2S)-O(2S)	1.414(6)	C(2S)-H(2SA)	0.9800
C(2S)-H(2SB)	0.9800	C(2S)-H(2SC)	0.9800
O(2S)-H(2S)	0.8400		
N(2)-C(1)-C(12)	115.6(2)	N(2)-C(1)-C(9A)	107.87(18)
C(12)-C(1)-C(9A)	110.6(2)	N(2)-C(1)-H(1A)	107.5
C(12)-C(1)-H(1A)	107.5	C(9A)-C(1)-H(1A)	107.5

Table 9. (continued).

C(2)-N(2)-C(3)	110.0(2)	C(2)-N(2)-C(1)	113.32(19)
C(3)-N(2)-C(1)	113.07(18)	C(2)-N(2)-H(2)	102.2(18)
C(3)-N(2)-H(2)	110.5(19)	C(1)-N(2)-H(2)	107.2(19)
N(2)-C(2)-H(2A)	109.5	N(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5	N(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5
N(2)-C(3)-C(4)	111.3(2)	N(2)-C(3)-H(3A)	109.4
C(4)-C(3)-H(3A)	109.4	N(2)-C(3)-H(3B)	109.4
C(4)-C(3)-H(3B)	109.4	H(3A)-C(3)-H(3B)	108.0
C(3)-C(4)-C(4A)	117.1(2)	C(3)-C(4)-H(4A)	108.0
C(4A)-C(4)-H(4A)	108.0	C(3)-C(4)-H(4B)	108.0
C(4A)-C(4)-H(4B)	108.0	H(4A)-C(4)-H(4B)	107.3
C(4B)-C(4A)-C(9A)	112.2(2)	C(4B)-C(4A)-C(10)	108.65(19)
C(9A)-C(4A)-C(10)	108.49(19)	C(4B)-C(4A)-C(4)	106.66(19)
C(9A)-C(4A)-C(4)	105.52(19)	C(10)-C(4A)-C(4)	115.4(2)
C(9)-C(4B)-C(5)	115.1(2)	C(9)-C(4B)-C(4A)	122.0(2)
C(5)-C(4B)-C(4A)	122.9(2)	C(6)-C(5)-C(4B)	120.3(2)
C(6)-C(5)-H(5A)	119.9	C(4B)-C(5)-H(5A)	119.9
C(7)-C(6)-C(5)	123.4(3)	C(7)-C(6)-N(6)	118.4(2)
C(5)-C(6)-N(6)	118.2(2)	O(6B)-N(6)-O(6A)	123.6(2)
O(6B)-N(6)-C(6)	118.5(2)	O(6A)-N(6)-C(6)	117.9(2)
C(8)-C(7)-C(6)	117.6(2)	C(8)-C(7)-H(7A)	121.2
C(6)-C(7)-H(7A)	121.2	C(7)-C(8)-C(9)	118.9(3)
C(7)-C(8)-H(8A)	120.6	C(9)-C(8)-H(8A)	120.6
F(9)-C(9)-C(8)	115.9(2)	F(9)-C(9)-C(4B)	119.4(2)
C(8)-C(9)-C(4B)	124.7(3)	O(9)-C(9A)-C(4A)	110.79(19)
O(9)-C(9A)-C(1)	107.96(18)	C(4A)-C(9A)-C(1)	109.23(19)
O(9)-C(9A)-H(9AA)	109.6	C(4A)-C(9A)-H(9AA)	109.6
C(1)-C(9A)-H(9AA)	109.6	C(9A)-O(9)-H(9)	105(2)
C(11)-C(10)-C(4A)	114.0(2)	C(11)-C(10)-H(10A)	108.8
C(4A)-C(10)-H(10A)	108.8	C(11)-C(10)-H(10B)	108.8
C(4A)-C(10)-H(10B)	108.8	H(10A)-C(10)-H(10B)	107.7
C(10)-C(11)-C(12)	113.3(2)	C(10)-C(11)-H(11A)	108.9
C(12)-C(11)-H(11A)	108.9	C(10)-C(11)-H(11B)	108.9
C(12)-C(11)-H(11B)	108.9	H(11A)-C(11)-H(11B)	107.7
C(11)-C(12)-C(1)	115.7(2)	C(11)-C(12)-H(12A)	108.3
C(1)-C(12)-H(12A)	108.3	C(11)-C(12)-H(12B)	108.3
C(1)-C(12)-H(12B)	108.3	H(12A)-C(12)-H(12B)	107.4
C(12')-O(1')-C(2')	116.22(19)	O(1')-C(2')-C(3')	106.45(18)
O(1')-C(2')-C(2")	110.59(19)	C(3')-C(2')-C(2")	111.17(18)
O(1')-C(2')-H(2'A)	109.5	C(3')-C(2')-H(2'A)	109.5
C(2")-C(2')-H(2'A)	109.5	O(2")-C(2")-O(2')	126.5(2)
O(2")-C(2")-C(2')	122.6(2)	O(2')-C(2")-C(2')	110.9(2)
C(2")-O(2')-H(2')	109.5	O(4')-C(3')-C(2')	105.98(18)
O(4')-C(3')-C(3")	111.28(19)	C(2')-C(3')-C(3")	110.72(19)
O(4')-C(3')-H(3'A)	109.6	C(2')-C(3')-H(3'A)	109.6
C(3")-C(3')-H(3'A)	109.6	O(3')-C(3")-O(3")	127.3(2)
O(3')-C(3")-C(3')	120.2(2)	O(3")-C(3")-C(3')	112.5(2)
C(5')-O(4')-C(3')	116.04(18)	O(5')-C(5')-O(4')	123.0(2)
O(5')-C(5')-C(6')	126.1(2)	O(4')-C(5')-C(6')	110.9(2)
C(11')-C(6')-C(7')	119.8(2)	C(11')-C(6')-C(5')	122.1(2)
C(7')-C(6')-C(5')	118.1(2)	C(8')-C(7')-C(6')	119.6(2)
C(8')-C(7')-H(7'A)	120.2	C(6')-C(7')-H(7'A)	120.2

Table 9. (continued).

C(7')-C(8')-C(9')	121.0(2)	C(7')-C(8')-H(8'A)	119.5
C(9')-C(8')-H(8'A)	119.5	C(8')-C(9')-C(10')	119.0(2)
C(8')-C(9')-C(9A')	121.0(3)	C(10')-C(9')-C(9A')	120.0(3)
C(9')-C(9A')-H(9AB)	109.5	C(9')-C(9A')-H(9AC)	109.5
H(9AB)-C(9A')-H(9AC)	109.5	C(9')-C(9A')-H(9AD)	109.5
H(9AB)-C(9A')-H(9AD)	109.5	H(9AC)-C(9A')-H(9AD)	109.5
C(9')-C(10')-C(11')	120.5(3)	C(9')-C(10')-H(10C)	119.8
C(11')-C(10')-H(10C)	119.8	C(6')-C(11')-C(10')	120.1(2)
C(6')-C(11')-H(11C)	120.0	C(10')-C(11')-H(11C)	120.0
O(12')-C(12')-O(1')	123.5(2)	O(12')-C(12')-C(13')	126.1(2)
O(1')-C(12')-C(13')	110.4(2)	C(14')-C(13')-C(18')	119.1(3)
C(14')-C(13')-C(12')	119.4(2)	C(18')-C(13')-C(12')	121.4(2)
C(13')-C(14')-C(15')	120.0(3)	C(13')-C(14')-H(14A)	120.0
C(15')-C(14')-H(14A)	120.0	C(14')-C(15')-C(16')	121.1(3)
C(14')-C(15')-H(15A)	119.5	C(16')-C(15')-H(15A)	119.5
C(17')-C(16')-C(15')	118.6(3)	C(17')-C(16')-C(16A)	121.1(3)
C(15')-C(16')-C(16A)	120.3(3)	C(16')-C(16A)-H(16A)	109.5
C(16')-C(16A)-H(16B)	109.5	H(16A)-C(16A)-H(16B)	109.5
C(16')-C(16A)-H(16C)	109.5	H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5	C(16')-C(17')-C(18')	121.1(3)
C(16')-C(17')-H(17A)	119.4	C(18')-C(17')-H(17A)	119.4
C(17')-C(18')-C(13')	120.0(3)	C(17')-C(18')-H(18A)	120.0
C(13')-C(18')-H(18A)	120.0	O(1S)-C(1S)-H(1SA)	109.5
O(1S)-C(1S)-H(1SB)	109.5	H(1SA)-C(1S)-H(1SB)	109.5
O(1S)-C(1S)-H(1SC)	109.5	H(1SA)-C(1S)-H(1SC)	109.5
H(1SB)-C(1S)-H(1SC)	109.5	C(1S)-O(1S)-H(1S)	109.5
O(2S)-C(2S)-H(2SA)	109.5	O(2S)-C(2S)-H(2SB)	109.5
H(2SA)-C(2S)-H(2SB)	109.5	O(2S)-C(2S)-H(2SC)	109.5
H(2SA)-C(2S)-H(2SC)	109.5	H(2SB)-C(2S)-H(2SC)	109.5
C(2S)-O(2S)-H(2S)	109.5		

Table 10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (+)-**29**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	17(1)	19(1)	26(1)	-1(1)	2(1)	-1(1)
N(2)	23(1)	18(1)	22(1)	-1(1)	1(1)	5(1)
C(2)	36(2)	26(1)	31(1)	9(1)	3(1)	7(1)
C(3)	16(1)	25(1)	25(1)	0(1)	-4(1)	3(1)
C(4)	14(1)	26(1)	25(1)	-1(1)	-2(1)	-1(1)
C(4A)	16(1)	20(1)	23(1)	0(1)	2(1)	0(1)
C(4B)	22(1)	25(1)	16(1)	0(1)	0(1)	-2(1)
C(5)	19(1)	26(1)	22(1)	1(1)	-2(1)	-2(1)
C(6)	29(1)	25(1)	23(1)	2(1)	-6(1)	3(1)
N(6)	34(1)	27(1)	27(1)	3(1)	-6(1)	8(1)
O(6A)	49(1)	24(1)	54(1)	4(1)	-12(1)	8(1)
O(6B)	31(1)	40(1)	47(1)	9(1)	6(1)	11(1)
C(7)	37(2)	28(1)	28(1)	8(1)	-3(1)	-6(1)
C(8)	27(2)	35(1)	28(1)	4(1)	5(1)	-8(1)
C(9)	21(1)	30(1)	27(1)	-1(1)	2(1)	0(1)
F(9)	23(1)	39(1)	40(1)	6(1)	10(1)	2(1)
C(9A)	15(1)	17(1)	20(1)	-2(1)	-2(1)	0(1)
O(9)	18(1)	29(1)	28(1)	-1(1)	-5(1)	-1(1)
C(10)	25(1)	29(1)	21(1)	-4(1)	3(1)	2(1)
C(11)	33(2)	22(1)	31(1)	-10(1)	0(1)	2(1)
C(12)	28(1)	18(1)	32(1)	-5(1)	-2(1)	-2(1)
O(1')	21(1)	17(1)	27(1)	-3(1)	1(1)	-5(1)
C(2')	15(1)	14(1)	26(1)	-2(1)	1(1)	-1(1)
C(2")	19(1)	14(1)	22(1)	0(1)	6(1)	0(1)
O(2')	26(1)	13(1)	45(1)	4(1)	-10(1)	-2(1)
O(2")	27(1)	17(1)	36(1)	4(1)	-8(1)	-1(1)
C(3')	14(1)	14(1)	28(1)	2(1)	-1(1)	0(1)
C(3")	24(1)	14(1)	24(1)	1(1)	-4(1)	1(1)
O(3')	25(1)	17(1)	32(1)	5(1)	2(1)	-4(1)
O(3")	24(1)	15(1)	66(1)	5(1)	7(1)	4(1)
O(4')	20(1)	17(1)	24(1)	2(1)	2(1)	5(1)
C(5')	20(1)	15(1)	25(1)	2(1)	-2(1)	-3(1)
O(5')	23(1)	34(1)	28(1)	0(1)	-5(1)	5(1)
C(6')	23(1)	16(1)	27(1)	-2(1)	-1(1)	-2(1)
C(7')	23(1)	24(1)	24(1)	1(1)	-2(1)	-6(1)
C(8')	29(2)	26(1)	29(1)	-4(1)	10(1)	-6(1)
C(9')	23(1)	23(1)	41(2)	-1(1)	5(1)	-2(1)
C(9A')	22(2)	39(2)	55(2)	-1(1)	8(1)	2(1)
C(10')	25(2)	32(1)	36(2)	1(1)	-5(1)	3(1)
C(11')	25(1)	32(1)	25(1)	-1(1)	-3(1)	3(1)
C(12')	25(1)	18(1)	27(1)	-3(1)	4(1)	2(1)
O(12')	30(1)	41(1)	31(1)	-6(1)	6(1)	-6(1)
C(13')	25(1)	17(1)	34(1)	-7(1)	-2(1)	3(1)
C(14')	33(2)	29(1)	38(2)	-10(1)	1(1)	5(1)
C(15')	43(2)	35(1)	39(2)	-15(1)	-14(2)	10(1)
C(16')	31(2)	22(1)	63(2)	-15(1)	-15(2)	6(1)
C(16A)	39(2)	42(2)	81(3)	-17(2)	-28(2)	6(2)
C(17')	29(2)	22(1)	59(2)	-4(1)	-5(1)	-3(1)
C(18')	27(2)	21(1)	45(2)	-3(1)	-8(1)	-2(1)

Table 10. (continued).

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1S)	37(2)	44(2)	84(3)	-12(2)	-17(2)	7(2)
O(1S)	25(1)	36(1)	41(1)	10(1)	5(1)	3(1)
C(2S)	19(3)	46(3)	25(3)	0(2)	5(2)	10(2)
O(2S)	22(2)	42(2)	44(2)	16(2)	4(2)	-4(2)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (+)-**29**.

	x	y	z	U(eq)
H(1A)	864	1969	1315	25
H(2)	2720(40)	2720(20)	1696(10)	31
H(2A)	2332	1218	1918	46
H(2B)	4061	1551	2012	46
H(2C)	3692	865	1604	46
H(3A)	5054	2036	1146	26
H(3B)	5283	2772	1544	26
H(4A)	5337	3510	827	26
H(4B)	4199	4008	1168	26
H(5A)	696	4657	592	27
H(7A)	2766	6820	-78	37
H(8A)	5002	5880	-137	36
H(9AA)	1405	3615	1144	21
H(9)	-500(40)	3080(20)	821(10)	37
H(10A)	2367	2604	86	30
H(10B)	4191	2705	127	30
H(11A)	4373	1439	600	34
H(11B)	3211	1083	227	34
H(12A)	2448	741	985	31
H(12B)	1146	1176	674	31
H(2'A)	10045	255	2160	22
H(2')	10041	2629	2306	42
H(3'A)	9693	597	2916	22
H(7'A)	5889	1270	4062	28
H(8'A)	3472	1903	4219	34
H(9AB)	1218	2808	3950	58
H(9AC)	425	1870	3747	58
H(9AD)	792	2773	3440	58
H(10C)	2418	1909	2928	37
H(11C)	4846	1284	2766	33
H(14A)	6943	16	781	40
H(15A)	4655	-552	481	47
H(16A)	2408	-1491	519	81
H(16B)	1450	-1097	929	81
H(16C)	2143	-2162	938	81
H(17A)	3355	-1562	1659	44
H(18A)	5606	-962	1972	38
H(1SA)	7304	4575	1553	82
H(1SB)	7764	4699	1048	82
H(1SC)	9076	4640	1415	82
H(1S)	8156	3119	1527	51
H(2SA)	3848	9095	2998	45
H(2SB)	5000	9359	2607	45
H(2SC)	3999	8396	2583	45
H(2S)	1965	9408	2569	54

Table 12. Torsion angles [°] for (+)-**29**.

C(12)-C(1)-N(2)-C(2)	-61.7(3)	C(9A)-C(1)-N(2)-C(2)	173.9(2)
C(12)-C(1)-N(2)-C(3)	64.3(3)	C(9A)-C(1)-N(2)-C(3)	-60.1(2)
C(2)-N(2)-C(3)-C(4)	176.6(2)	C(1)-N(2)-C(3)-C(4)	48.8(3)
N(2)-C(3)-C(4)-C(4A)	-45.9(3)	C(3)-C(4)-C(4A)-C(4B)	171.5(2)
C(3)-C(4)-C(4A)-C(9A)	51.9(3)	C(3)-C(4)-C(4A)-C(10)	-67.8(3)
C(9A)-C(4A)-C(4B)-C(9)	173.7(2)	C(10)-C(4A)-C(4B)-C(9)	-66.4(3)
C(4)-C(4A)-C(4B)-C(9)	58.6(3)	C(9A)-C(4A)-C(4B)-C(5)	-4.1(3)
C(10)-C(4A)-C(4B)-C(5)	115.8(3)	C(4)-C(4A)-C(4B)-C(5)	-119.2(2)
C(9)-C(4B)-C(5)-C(6)	-1.1(3)	C(4A)-C(4B)-C(5)-C(6)	176.9(2)
C(4B)-C(5)-C(6)-C(7)	-0.2(4)	C(4B)-C(5)-C(6)-N(6)	179.2(2)
C(7)-C(6)-N(6)-O(6B)	166.3(2)	C(5)-C(6)-N(6)-O(6B)	-13.1(3)
C(7)-C(6)-N(6)-O(6A)	-11.2(4)	C(5)-C(6)-N(6)-O(6A)	169.4(2)
C(5)-C(6)-C(7)-C(8)	1.4(4)	N(6)-C(6)-C(7)-C(8)	-178.0(2)
C(6)-C(7)-C(8)-C(9)	-1.2(4)	C(7)-C(8)-C(9)-F(9)	-179.8(2)
C(7)-C(8)-C(9)-C(4B)	-0.1(4)	C(5)-C(4B)-C(9)-F(9)	-179.0(2)
C(4A)-C(4B)-C(9)-F(9)	3.0(4)	C(5)-C(4B)-C(9)-C(8)	1.2(4)
C(4A)-C(4B)-C(9)-C(8)	-176.7(2)	C(4B)-C(4A)-C(9A)-O(9)	64.3(2)
C(10)-C(4A)-C(9A)-O(9)	-55.7(2)	C(4)-C(4A)-C(9A)-O(9)	-179.91(17)
C(4B)-C(4A)-C(9A)-C(1)	-176.88(18)	C(10)-C(4A)-C(9A)-C(1)	63.1(2)
C(4)-C(4A)-C(9A)-C(1)	-61.1(2)	N(2)-C(1)-C(9A)-O(9)	-171.94(18)
C(12)-C(1)-C(9A)-O(9)	60.7(3)	N(2)-C(1)-C(9A)-C(4A)	67.5(2)
C(12)-C(1)-C(9A)-C(4A)	-59.8(3)	C(4B)-C(4A)-C(10)-C(11)	-178.5(2)
C(9A)-C(4A)-C(10)-C(11)	-56.2(3)	C(4)-C(4A)-C(10)-C(11)	61.8(3)
C(4A)-C(10)-C(11)-C(12)	44.8(3)	C(10)-C(11)-C(12)-C(1)	-41.2(3)
N(2)-C(1)-C(12)-C(11)	-74.1(3)	C(9A)-C(1)-C(12)-C(11)	48.9(3)
C(12')-O(1')-C(2')-C(3')	-169.66(18)	C(12')-O(1')-C(2')-C(2")	69.5(2)
O(1')-C(2')-C(2")-O(2")	3.7(3)	C(3')-C(2')-C(2")-O(2")	-114.3(3)
O(1')-C(2')-C(2")-O(2')	-175.04(19)	C(3')-C(2')-C(2")-O(2')	66.9(3)
O(1')-C(2')-C(3')-O(4')	-65.2(2)	C(2")-C(2')-C(3')-O(4')	55.3(2)
O(1')-C(2')-C(3')-C(3")	55.6(2)	C(2")-C(2')-C(3')-C(3")	176.1(2)
O(4')-C(3')-C(3")-O(3')	-2.5(3)	C(2')-C(3')-C(3")-O(3')	-120.1(2)
O(4')-C(3')-C(3")-O(3")	177.6(2)	C(2')-C(3')-C(3")-O(3")	60.0(3)
C(2')-C(3')-O(4')-C(5')	-165.18(18)	C(3")-C(3')-O(4')-C(5')	74.4(2)
C(3')-O(4')-C(5')-O(5')	6.5(3)	C(3')-O(4')-C(5')-C(6')	-174.17(17)
O(5')-C(5')-C(6')-C(11')	-179.1(2)	O(4')-C(5')-C(6')-C(11')	1.6(3)
O(5')-C(5')-C(6')-C(7')	1.9(3)	O(4')-C(5')-C(6')-C(7')	-177.4(2)
C(11')-C(6')-C(7')-C(8')	-0.7(4)	C(5')-C(6')-C(7')-C(8')	178.3(2)
C(6')-C(7')-C(8')-C(9')	0.0(4)	C(7')-C(8')-C(9')-C(10')	1.0(4)
C(7')-C(8')-C(9')-C(9A')	-179.8(2)	C(8')-C(9')-C(10')-C(11')	-1.2(4)
C(9A')-C(9')-C(10')-C(11')	179.6(2)	C(7')-C(6')-C(11')-C(10')	0.5(4)
C(5')-C(6')-C(11')-C(10')	-178.5(2)	C(9')-C(10')-C(11')-C(6')	0.5(4)
C(2')-O(1')-C(12')-O(12')	7.2(3)	C(2')-O(1')-C(12')-C(13')	-172.66(18)
O(12')-C(12')-C(13')-C(14')	-15.6(4)	O(1')-C(12')-C(13')-C(14')	164.2(2)
O(12')-C(12')-C(13')-C(18')	166.5(3)	O(1')-C(12')-C(13')-C(18')	-13.7(3)
C(18')-C(13')-C(14')-C(15')	0.5(4)	C(12')-C(13')-C(14')-C(15')	-177.5(2)
C(13')-C(14')-C(15')-C(16')	-1.1(4)	C(14')-C(15')-C(16')-C(17')	0.7(4)
C(14')-C(15')-C(16')-C(16A)	-179.2(3)	C(15')-C(16')-C(17')-C(18')	0.3(4)
C(16A)-C(16')-C(17')-C(18')	-179.8(3)	C(16')-C(17')-C(18')-C(13')	-0.8(4)
C(14')-C(13')-C(18')-C(17')	0.4(4)	C(12')-C(13')-C(18')-C(17')	178.3(2)

Table 13. Crystal data and structure refinement for (1*S**,4a*S**,9a*S**)-**21**.

Empirical formula	$C_{15}H_{18}N_2O_3$	
Formula weight	274.31	
Temperature	93(2)°K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P\,2_12_12_1$	
Unit cell dimensions	a = 7.4315(16) Å	α= 90°
	b = 8.4430(18) Å	β= 90°
	c = 21.576(5) Å	γ = 90°
Volume	1353.7(5) Å^3	
Z	4	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	584	
Crystal size	0.64 x 0.36 x 0.28 mm^3	
Theta range for data collection	2.59 to 28.05°	
Index ranges	-9<=h<=9, -11<=k<=11, -25<=l<=27	
Reflections collected	9044	
Independent reflections	3138 [R(int) = 0.0409]	
Completeness to theta = 28.05°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.974 and 0.582	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3138 / 0 / 181	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1064	
R indices (all data)	R1 = 0.0459, wR2 = 0.1085	
Absolute structure parameter	1.1(11)	
Largest diff. peak and hole	0.290 and -0.228 e.Å^{-3}	

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **21**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8771(2)	901(2)	8273(1)	16(1)
N(2)	8895(2)	-32(2)	8857(1)	15(1)
C(2)	9981(2)	-1476(2)	8773(1)	19(1)
C(3)	9449(2)	801(2)	9437(1)	17(1)
C(4B)	7138(2)	4753(2)	8865(1)	14(1)
C(4A)	8417(2)	3346(2)	8929(1)	14(1)
C(4)	8459(2)	2398(2)	9538(1)	16(1)
C(5)	6757(2)	6040(2)	9240(1)	15(1)
C(6)	5682(2)	7251(2)	8982(1)	16(1)
N(6)	5280(2)	8642(2)	9367(1)	20(1)
O(6A)	4342(2)	9715(2)	9142(1)	26(1)
O(6B)	5886(2)	8679(2)	9903(1)	26(1)
C(7)	5033(2)	7209(2)	8375(1)	18(1)
C(8)	5415(2)	5901(2)	7995(1)	18(1)
C(9A)	7515(2)	2256(2)	8449(1)	15(1)
O(9)	6950(2)	3328(1)	7941(1)	18(1)
C(9)	6450(2)	4690(2)	8252(1)	16(1)
C(10)	10323(2)	3929(2)	8699(1)	18(1)
C(11)	11594(2)	2640(2)	8426(1)	23(1)
C(12)	10567(3)	1521(2)	7989(1)	22(1)

Table 15. Bond lengths [Å] and angles [°] for **21**.

C(1)-N(2)	1.489(2)	C(1)-C(9A)	1.525(2)
C(1)-C(12)	1.559(2)	C(1)-H(1A)	1.0000
N(2)-C(2)	1.473(2)	N(2)-C(3)	1.493(2)
C(2)-H(2A)	0.9800	C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800	C(3)-C(4)	1.551(2)
C(3)-H(3A)	0.9900	C(3)-H(3B)	0.9900
C(4B)-C(5)	1.385(2)	C(4B)-C(9)	1.418(2)
C(4B)-C(4A)	1.528(2)	C(4A)-C(4)	1.538(2)
C(4A)-C(9A)	1.540(2)	C(4A)-C(10)	1.579(2)
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(5)-C(6)	1.412(2)	C(5)-H(5A)	0.9500
C(6)-C(7)	1.396(2)	C(6)-N(6)	1.470(2)
N(6)-O(6A)	1.2420(19)	N(6)-O(6B)	1.242(2)
C(7)-C(8)	1.404(2)	C(7)-H(7A)	0.9500
C(8)-C(9)	1.394(2)	C(8)-H(8A)	0.9500
C(9A)-O(9)	1.4821(19)	C(9A)-H(9AA)	1.0000
O(9)-C(9)	1.382(2)	C(10)-C(11)	1.557(2)
C(10)-H(10A)	0.9900	C(10)-H(10B)	0.9900
C(11)-C(12)	1.537(3)	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900	N(2)-C(1)-C(9A)	102.94(12)
N(2)-C(1)-C(12)	117.20(14)	C(9A)-C(1)-C(12)	111.71(14)
N(2)-C(1)-H(1A)	108.2	C(9A)-C(1)-H(1A)	108.2
C(12)-C(1)-H(1A)	108.2	C(2)-N(2)-C(1)	111.55(13)
C(2)-N(2)-C(3)	110.00(13)	C(1)-N(2)-C(3)	118.48(13)
N(2)-C(2)-H(2A)	109.5	N(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5	N(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5
N(2)-C(3)-C(4)	113.35(13)	N(2)-C(3)-H(3A)	108.9
C(4)-C(3)-H(3A)	108.9	N(2)-C(3)-H(3B)	108.9
C(4)-C(3)-H(3B)	108.9	H(3A)-C(3)-H(3B)	107.7
C(5)-C(4B)-C(9)	120.11(15)	C(5)-C(4B)-C(4A)	133.14(15)
C(9)-C(4B)-C(4A)	106.25(14)	C(4B)-C(4A)-C(4)	119.69(14)
C(4B)-C(4A)-C(9A)	97.63(13)	C(4)-C(4A)-C(9A)	105.77(13)
C(4B)-C(4A)-C(10)	106.69(13)	C(4)-C(4A)-C(10)	114.35(14)
C(9A)-C(4A)-C(10)	111.41(13)	C(4A)-C(4)-C(3)	110.04(13)
C(4A)-C(4)-H(4A)	109.7	C(3)-C(4)-H(4A)	109.7
C(4A)-C(4)-H(4B)	109.7	C(3)-C(4)-H(4B)	109.7
H(4A)-C(4)-H(4B)	108.2	C(4B)-C(5)-C(6)	116.90(15)
C(4B)-C(5)-H(5A)	121.5	C(6)-C(5)-H(5A)	121.5
C(7)-C(6)-C(5)	123.18(15)	C(7)-C(6)-N(6)	118.76(14)
C(5)-C(6)-N(6)	118.03(15)	O(6A)-N(6)-O(6B)	123.35(15)
O(6A)-N(6)-C(6)	118.38(15)	O(6B)-N(6)-C(6)	118.27(15)
C(6)-C(7)-C(8)	119.85(15)	C(6)-C(7)-H(7A)	120.1
C(8)-C(7)-H(7A)	120.1	C(9)-C(8)-C(7)	117.17(15)
C(9)-C(8)-H(8A)	121.4	C(7)-C(8)-H(8A)	121.4
O(9)-C(9A)-C(1)	116.58(13)	O(9)-C(9A)-C(4A)	104.83(13)
C(1)-C(9A)-C(4A)	110.48(13)	O(9)-C(9A)-H(9AA)	108.2
C(1)-C(9A)-H(9AA)	108.2	C(4A)-C(9A)-H(9AA)	108.2
C(9)-O(9)-C(9A)	103.01(12)	O(9)-C(9)-C(8)	124.45(15)
O(9)-C(9)-C(4B)	112.77(14)	C(8)-C(9)-C(4B)	122.76(15)
C(11)-C(10)-C(4A)	116.45(13)	C(11)-C(10)-H(10A)	108.2
C(4A)-C(10)-H(10A)	108.2	C(11)-C(10)-H(10B)	108.2

Table 15. Bond lengths [Å] and angles [°] for **21**.

C(4A)-C(10)-H(10B)	108.2	H(10A)-C(10)-H(10B)	107.3
C(12)-C(11)-C(10)	111.13(15)	C(12)-C(11)-H(11A)	109.4
C(10)-C(11)-H(11A)	109.4	C(12)-C(11)-H(11B)	109.4
C(10)-C(11)-H(11B)	109.4	H(11A)-C(11)-H(11B)	108.0
C(11)-C(12)-C(1)	113.01(14)	C(11)-C(12)-H(12A)	109.0
C(1)-C(12)-H(12A)	109.0	C(11)-C(12)-H(12B)	109.0
C(1)-C(12)-H(12B)	109.0	H(12A)-C(12)-H(12B)	107.8

Table 16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **21**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	18(1)	15(1)	15(1)	-1(1)	-1(1)	2(1)
N(2)	15(1)	11(1)	18(1)	0(1)	0(1)	1(1)
C(2)	16(1)	13(1)	28(1)	0(1)	1(1)	3(1)
C(3)	17(1)	15(1)	18(1)	1(1)	-2(1)	1(1)
C(4B)	11(1)	13(1)	19(1)	1(1)	0(1)	0(1)
C(4A)	13(1)	14(1)	15(1)	-1(1)	-1(1)	1(1)
C(4)	17(1)	15(1)	16(1)	0(1)	-1(1)	2(1)
C(5)	13(1)	14(1)	19(1)	0(1)	1(1)	-1(1)
C(6)	13(1)	12(1)	24(1)	1(1)	4(1)	0(1)
N(6)	15(1)	16(1)	28(1)	-1(1)	6(1)	1(1)
O(6A)	18(1)	17(1)	44(1)	-2(1)	0(1)	6(1)
O(6B)	35(1)	21(1)	23(1)	-2(1)	7(1)	2(1)
C(7)	12(1)	16(1)	27(1)	5(1)	0(1)	2(1)
C(8)	15(1)	18(1)	21(1)	1(1)	-3(1)	1(1)
C(9A)	15(1)	14(1)	16(1)	1(1)	-2(1)	0(1)
O(9)	23(1)	15(1)	16(1)	0(1)	-5(1)	4(1)
C(9)	13(1)	14(1)	20(1)	-1(1)	0(1)	-2(1)
C(10)	14(1)	16(1)	24(1)	1(1)	-1(1)	1(1)
C(11)	16(1)	20(1)	33(1)	2(1)	7(1)	1(1)
C(12)	24(1)	18(1)	24(1)	1(1)	9(1)	4(1)

Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **21**.

	x	y	z	U(eq)
H(1A)	8153	234	7954	19
H(2A)	9609	-2015	8392	29
H(2B)	9800	-2183	9128	29
H(2C)	11256	-1189	8744	29
H(3A)	10761	1001	9422	20
H(3B)	9209	101	9796	20
H(4A)	7214	2195	9680	19
H(4B)	9086	3019	9861	19
H(5A)	7199	6105	9653	18
H(7A)	4335	8063	8219	22
H(8A)	4986	5844	7581	22
H(9AA)	6409	1792	8641	18
H(10A)	10135	4752	8378	21
H(10B)	10945	4439	9052	21
H(11A)	12583	3158	8195	27
H(11B)	12131	2020	8768	27
H(12A)	11346	606	7888	26
H(12B)	10300	2087	7598	26

Table 18. Torsion angles [°] for **21**.

C(9A)-C(1)-N(2)-C(2)	176.49(13)	C(12)-C(1)-N(2)-C(2)	-60.51(18)
C(9A)-C(1)-N(2)-C(3)	-54.26(18)	C(12)-C(1)-N(2)-C(3)	68.74(18)
C(2)-N(2)-C(3)-C(4)	176.08(13)	C(1)-N(2)-C(3)-C(4)	46.12(19)
C(5)-C(4B)-C(4A)-C(4)	47.8(3)	C(9)-C(4B)-C(4A)-C(4)	-140.61(15)
C(5)-C(4B)-C(4A)-C(9A)	160.92(17)	C(9)-C(4B)-C(4A)-C(9A)	-27.52(16)
C(5)-C(4B)-C(4A)-C(10)	-84.0(2)	C(9)-C(4B)-C(4A)-C(10)	87.60(15)
C(4B)-C(4A)-C(4)-C(3)	165.02(14)	C(9A)-C(4A)-C(4)-C(3)	56.36(16)
C(10)-C(4A)-C(4)-C(3)	-66.60(17)	N(2)-C(3)-C(4)-C(4A)	-44.89(18)
C(9)-C(4B)-C(5)-C(6)	-0.3(2)	C(4A)-C(4B)-C(5)-C(6)	170.31(16)
C(4B)-C(5)-C(6)-C(7)	-1.0(2)	C(4B)-C(5)-C(6)-N(6)	-179.11(14)
C(7)-C(6)-N(6)-O(6A)	1.5(2)	C(5)-C(6)-N(6)-O(6A)	179.69(14)
C(7)-C(6)-N(6)-O(6B)	-178.98(15)	C(5)-C(6)-N(6)-O(6B)	-0.8(2)
C(5)-C(6)-C(7)-C(8)	1.3(2)	N(6)-C(6)-C(7)-C(8)	179.35(15)
C(6)-C(7)-C(8)-C(9)	-0.1(2)	N(2)-C(1)-C(9A)-O(9)	-173.62(12)
C(12)-C(1)-C(9A)-O(9)	59.77(18)	N(2)-C(1)-C(9A)-C(4A)	66.88(16)
C(12)-C(1)-C(9A)-C(4A)	-59.72(17)	C(4B)-C(4A)-C(9A)-O(9)	38.25(14)
C(4)-C(4A)-C(9A)-O(9)	162.11(12)	C(10)-C(4A)-C(9A)-O(9)	-73.08(16)
C(4B)-C(4A)-C(9A)-C(1)	164.62(13)	C(4)-C(4A)-C(9A)-C(1)	-71.52(16)
C(10)-C(4A)-C(9A)-C(1)	53.29(17)	C(1)-C(9A)-O(9)-C(9)	-158.20(14)
C(4A)-C(9A)-O(9)-C(9)	-35.71(15)	C(9A)-O(9)-C(9)-C(8)	-163.54(16)
C(9A)-O(9)-C(9)-C(4B)	17.79(17)	C(7)-C(8)-C(9)-O(9)	-179.74(15)
C(7)-C(8)-C(9)-C(4B)	-1.2(2)	C(5)-C(4B)-C(9)-O(9)	-179.85(14)
C(4A)-C(4B)-C(9)-O(9)	7.27(18)	C(5)-C(4B)-C(9)-C(8)	1.5(2)
C(4A)-C(4B)-C(9)-C(8)	-171.43(15)	C(4B)-C(4A)-C(10)-C(11)	-152.21(15)
C(4)-C(4A)-C(10)-C(11)	73.10(18)	C(9A)-C(4A)-C(10)-C(11)	-46.76(19)
C(4A)-C(10)-C(11)-C(12)	43.6(2)	C(10)-C(11)-C(12)-C(1)	-48.03(19)
N(2)-C(1)-C(12)-C(11)	-60.52(19)	C(9A)-C(1)-C(12)-C(11)	57.87(18)

Table 19. Crystal data and structure refinement for (1*S*,4a*S*,9a*S*)-(+)-**53**.HBr

Empirical formula	$C_{22}H_{26}BrNO_2$	
Formula weight	416.35	
Temperature	298(2)°K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P\,2_12_12_1$	
Unit cell dimensions	a = 7.5366(2) Å	α= 90°
	b = 11.9922(4) Å	β= 90°
	c = 21.9804(11) Å	γ = 90°
Volume	1986.60(13) Å^3	
Z	4	
Density (calculated)	1.392 Mg/m^3	
Absorption coefficient	2.085 mm^{-1}	
F(000)	864	
Crystal size	0.84 x 0.54 x 0.30 mm^3	
Theta range for data collection	1.85 to 30.32°	
Index ranges	-8<=h<=10, -16<=k<=16, -30<=l<=30	
Reflections collected	22724	
Independent reflections	5648 [R(int) = 0.0247]	
Completeness to theta = 30.32°	97.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.535 and 0.348	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5648 / 0 / 241	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0750	
R indices (all data)	R1 = 0.0436, wR2 = 0.0787	
Absolute structure parameter	0.019(7)	
Largest diff. peak and hole	0.833 and -0.327 e.Å^{-3}	

Table 20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (+)-**53**.HBr. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	5186(1)	7657(1)	797(1)	48(1)
C(1)	9174(3)	8502(2)	1743(1)	31(1)
N(2)	9325(2)	8202(1)	1069(1)	31(1)
C(3)	9997(4)	9116(2)	656(1)	42(1)
C(4)	9145(4)	10261(2)	771(1)	43(1)
C(4A)	8974(3)	10518(2)	1452(1)	31(1)
C(4B)	7667(3)	11408(2)	1654(1)	34(1)
C(5)	7305(3)	12481(2)	1462(1)	46(1)
C(6)	6082(4)	13094(2)	1798(1)	55(1)
C(7)	5279(3)	12662(2)	2305(1)	57(1)
C(8)	5649(3)	11597(2)	2512(1)	48(1)
O(8)	4883(4)	11108(2)	3006(1)	78(1)
C(9)	6848(3)	10985(2)	2170(1)	36(1)
O(9)	7342(2)	9897(1)	2306(1)	39(1)
C(9A)	8008(3)	9522(2)	1725(1)	30(1)
C(10)	10748(3)	10733(2)	1780(1)	42(1)
C(11)	11958(4)	9699(2)	1860(1)	56(1)
C(12)	10904(4)	8685(2)	2066(1)	50(1)
C(13)	10326(3)	7142(2)	937(1)	39(1)
C(14)	9612(4)	6124(2)	1265(1)	46(1)
C(15)	10123(3)	5088(2)	913(1)	38(1)
C(16)	9246(4)	4831(2)	377(1)	55(1)
C(17)	9746(5)	3907(2)	41(1)	67(1)
C(18)	11084(5)	3239(2)	233(1)	63(1)
C(19)	11969(4)	3481(2)	759(1)	59(1)
C(20)	11497(4)	4409(2)	1101(1)	49(1)

Table 21. Bond lengths [Å] and angles [°] for (+)-**53**.HBr.

C(1)-C(12)	1.501(3)	C(1)-C(9A)	1.506(3)
C(1)-N(2)	1.528(2)	C(1)-H(1A)	0.9800
N(2)-C(13)	1.506(3)	N(2)-C(3)	1.511(3)
N(2)-H(2)	0.86(3)	C(3)-C(4)	1.537(3)
C(3)-H(3A)	0.9700	C(3)-H(3B)	0.9700
C(4)-C(4A)	1.534(3)	C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700	C(4A)-C(4B)	1.518(3)
C(4A)-C(9A)	1.523(3)	C(4A)-C(10)	1.540(3)
C(4B)-C(5)	1.381(3)	C(4B)-C(9)	1.388(3)
C(5)-C(6)	1.391(4)	C(5)-H(5A)	0.9300
C(6)-C(7)	1.370(4)	C(6)-H(6A)	0.9300
C(7)-C(8)	1.384(4)	C(7)-H(7A)	0.9300
C(8)-O(8)	1.362(3)	C(8)-C(9)	1.387(3)
O(8)-H(8)	0.65(4)	C(9)-O(9)	1.390(3)
O(9)-C(9A)	1.443(2)	C(9A)-H(9AA)	0.9800
C(10)-C(11)	1.549(3)	C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700	C(11)-C(12)	1.522(4)
C(11)-H(11A)	0.9700	C(11)-H(11B)	0.9700
C(12)-H(12A)	0.9700	C(12)-H(12B)	0.9700
C(13)-C(14)	1.517(3)	C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700	C(14)-C(15)	1.514(3)
C(14)-H(14A)	0.9700	C(14)-H(14B)	0.9700
C(15)-C(20)	1.380(3)	C(15)-C(16)	1.384(3)
C(16)-C(17)	1.385(4)	C(16)-H(16A)	0.9300
C(17)-C(18)	1.355(5)	C(17)-H(17A)	0.9300
C(18)-C(19)	1.367(4)	C(18)-H(18A)	0.9300
C(19)-C(20)	1.389(3)	C(19)-H(19A)	0.9300
C(20)-H(20A)	0.9300		
C(12)-C(1)-C(9A)	113.61(16)	C(12)-C(1)-N(2)	115.40(18)
C(9A)-C(1)-N(2)	102.10(15)	C(12)-C(1)-H(1A)	108.5
C(9A)-C(1)-H(1A)	108.5	N(2)-C(1)-H(1A)	108.5
C(13)-N(2)-C(3)	109.19(15)	C(13)-N(2)-C(1)	114.97(15)
C(3)-N(2)-C(1)	115.87(14)	C(13)-N(2)-H(2)	107.3(16)
C(3)-N(2)-H(2)	109.0(16)	C(1)-N(2)-H(2)	99.6(16)
N(2)-C(3)-C(4)	114.15(17)	N(2)-C(3)-H(3A)	108.7
C(4)-C(3)-H(3A)	108.7	N(2)-C(3)-H(3B)	108.7
C(4)-C(3)-H(3B)	108.7	H(3A)-C(3)-H(3B)	107.6
C(4A)-C(4)-C(3)	112.07(16)	C(4A)-C(4)-H(4A)	109.2
C(3)-C(4)-H(4A)	109.2	C(4A)-C(4)-H(4B)	109.2
C(3)-C(4)-H(4B)	109.2	H(4A)-C(4)-H(4B)	107.9
C(4B)-C(4A)-C(9A)	97.27(16)	C(4B)-C(4A)-C(4)	118.70(17)
C(9A)-C(4A)-C(4)	105.47(16)	C(4B)-C(4A)-C(10)	108.05(16)
C(9A)-C(4A)-C(10)	111.26(17)	C(4)-C(4A)-C(10)	114.62(19)
C(5)-C(4B)-C(9)	120.2(2)	C(5)-C(4B)-C(4A)	134.0(2)
C(9)-C(4B)-C(4A)	105.65(17)	C(4B)-C(5)-C(6)	117.5(2)
C(4B)-C(5)-H(5A)	121.3	C(6)-C(5)-H(5A)	121.3
C(7)-C(6)-C(5)	121.6(2)	C(7)-C(6)-H(6A)	119.2
C(5)-C(6)-H(6A)	119.2	C(6)-C(7)-C(8)	121.9(2)
C(6)-C(7)-H(7A)	119.1	C(8)-C(7)-H(7A)	119.1
O(8)-C(8)-C(7)	125.0(2)	O(8)-C(8)-C(9)	118.8(2)
C(7)-C(8)-C(9)	116.2(2)	C(8)-O(8)-H(8)	109(4)

Table 21. (continued).

C(4B)-C(9)-C(8)	122.7(2)	C(4B)-C(9)-O(9)	113.61(17)
C(8)-C(9)-O(9)	123.7(2)	C(9)-O(9)-C(9A)	101.25(14)
O(9)-C(9A)-C(1)	115.66(15)	O(9)-C(9A)-C(4A)	105.67(14)
C(1)-C(9A)-C(4A)	111.59(17)	O(9)-C(9A)-H(9AA)	107.9
C(1)-C(9A)-H(9AA)	107.9	C(4A)-C(9A)-H(9AA)	107.9
C(4A)-C(10)-C(11)	115.51(18)	C(4A)-C(10)-H(10A)	108.4
C(11)-C(10)-H(10A)	108.4	C(4A)-C(10)-H(10B)	108.4
C(11)-C(10)-H(10B)	108.4	H(10A)-C(10)-H(10B)	107.5
C(12)-C(11)-C(10)	111.5(2)	C(12)-C(11)-H(11A)	109.3
C(10)-C(11)-H(11A)	109.3	C(12)-C(11)-H(11B)	109.3
C(10)-C(11)-H(11B)	109.3	H(11A)-C(11)-H(11B)	108.0
C(1)-C(12)-C(11)	115.36(19)	C(1)-C(12)-H(12A)	108.4
C(11)-C(12)-H(12A)	108.4	C(1)-C(12)-H(12B)	108.4
C(11)-C(12)-H(12B)	108.4	H(12A)-C(12)-H(12B)	107.5
N(2)-C(13)-C(14)	114.22(17)	N(2)-C(13)-H(13A)	108.7
C(14)-C(13)-H(13A)	108.7	N(2)-C(13)-H(13B)	108.7
C(14)-C(13)-H(13B)	108.7	H(13A)-C(13)-H(13B)	107.6
C(15)-C(14)-C(13)	109.09(17)	C(15)-C(14)-H(14A)	109.9
C(13)-C14)-H(14A)	109.9	C(15)-C(14)-H(14B)	109.9
C(13)-C(14)-H(14B)	109.9	H(14A)-C(14)-H(14B)	108.3
C(20)-C(15)-C(16)	118.8(2)	C(20)-C(15)-C(14)	121.5(2)
C(16)-C(15)-C(14)	119.7(2)	C(15)-C(16)-C(17)	120.1(3)
C(15)-C(16)-H(16A)	119.9	C(17)-C(16)-H(16A)	119.9
C(18)-C(17)-C(16)	120.7(3)	C(18)-C(17)-H(17A)	119.7
C(16)-C(17)-H(17A)	119.7	C(17)-C(18)-C(19)	120.1(2)
C(17)-C(18)-H(18A)	120.0	C(19)-C(18)-H(18A)	120.0
C(18)-C(19)-C(20)	120.1(3)	C(18)-C(19)-H(19A)	119.9
C(20)-C(19)-H(19A)	119.9	C(15)-C(20)-C(19)	120.2(2)
C(15)-C(20)-H(20A)	119.9	C(19)-C(20)-H(20A)	119.9

Table 22. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (+)-**53**.HBr. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	37(1)	65(1)	40(1)	-3(1)	-3(1)	-9(1)
C(1)	38(1)	27(1)	29(1)	-2(1)	3(1)	1(1)
N(2)	32(1)	29(1)	34(1)	-5(1)	3(1)	1(1)
C(3)	57(1)	34(1)	36(1)	-1(1)	16(1)	-1(1)
C(4)	65(2)	32(1)	33(1)	3(1)	8(1)	5(1)
C(4A)	35(1)	27(1)	32(1)	-1(1)	5(1)	3(1)
C(4B)	35(1)	29(1)	39(1)	-8(1)	-3(1)	3(1)
C(5)	59(1)	34(1)	45(1)	-4(1)	-11(1)	7(1)
C(6)	59(2)	35(1)	72(2)	-14(1)	-24(1)	14(1)
C(7)	33(1)	50(1)	89(2)	-35(1)	1(1)	4(1)
C(8)	36(1)	45(1)	64(1)	-25(1)	11(1)	-7(1)
O(8)	85(2)	62(1)	89(1)	-34(1)	54(1)	-23(1)
C(9)	32(1)	32(1)	44(1)	-12(1)	4(1)	-4(1)
O(9)	50(1)	31(1)	38(1)	-6(1)	16(1)	-3(1)
C(9A)	32(1)	29(1)	29(1)	-4(1)	3(1)	0(1)
C(10)	35(1)	37(1)	54(1)	-3(1)	3(1)	-6(1)
C(11)	36(1)	52(1)	81(2)	-15(1)	-17(1)	3(1)
C(12)	54(2)	41(1)	56(1)	-4(1)	-21(1)	10(1)
C(13)	38(1)	31(1)	49(1)	-6(1)	11(1)	5(1)
C(14)	55(2)	34(1)	50(1)	-2(1)	13(1)	9(1)
C(15)	44(1)	29(1)	41(1)	0(1)	4(1)	1(1)
C(16)	60(2)	45(1)	60(1)	3(1)	-13(1)	-2(1)
C(17)	92(2)	55(2)	53(1)	-11(1)	-7(2)	-27(2)
C(18)	87(2)	38(1)	63(2)	-11(1)	22(2)	-7(1)
C(19)	64(2)	41(1)	73(2)	1(1)	12(2)	16(1)
C(20)	54(2)	44(1)	49(1)	-3(1)	-5(1)	8(1)

Table 23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (+)-**53**.HBr.

	x	y	z	U(eq)
H(1A)	8529	7904	1951	38
H(2)	8230(40)	8080(20)	989(10)	41
H(3A)	9775	8902	237	51
H(3B)	11271	9182	708	51
H(4A)	9861	10834	579	52
H(4B)	7977	10279	586	52
H(5A)	7858	12782	1121	55
H(6A)	5801	13815	1675	66
H(7A)	4463	13096	2516	69
H(8)	4890(70)	11460(40)	3230(20)	118
H(9AA)	6986	9354	1465	36
H(10A)	10496	11039	2179	50
H(10B)	11399	11294	1553	50
H(11A)	12539	9534	1476	68
H(11B)	12870	9864	2158	68
H(12A)	11636	8027	2011	60
H(12B)	10666	8758	2498	60
H(13A)	11558	7247	1052	47
H(13B)	10292	7004	503	47
H(14A)	10101	6088	1673	55
H(14B)	8330	6172	1298	55
H(16A)	8320	5281	243	66
H(17A)	9157	3743	-320	80
H(18A)	11401	2616	6	75
H(19A)	12890	3022	889	71
H(20A)	12108	4574	1457	59

Table 24. Torsion angles [°] for (+)-**53**.HBr.

C(12)-C(1)-N(2)-C(13)	60.6(2)	C(9A)-C(1)-N(2)-C(3')	-175.68(17)
C(12)-C(1)-N(2)-C(3)	-68.4(2)	C(9A)-C(1)-N(2)-C(3)	55.4(2)
C(13)-N(2)-C(3)-C(4)	-176.79(19)	C(1)-N(2)-C(3)-C(4)	-45.1(3)
N(2)-C(3)-C(4)-C(4A)	42.6(3)	C(3)-C(4)-C(4A)-C(4B)	-160.6(2)
C(3)-C(4)-C(4A)-C(9A)	-53.1(2)	C(3)-C(4)-C(4A)-C(10)	69.7(2)
C(9A)-C(4A)-C(4B)-C(5)	-159.5(2)	C(4)-C(4A)-C(4B)-C(5)	-47.4(3)
C(10)-C(4A)-C(4B)-C(5)	85.3(3)	C(9A)-C(4A)-C(4B)-C(9)	26.3(2)
C(4)-C(4A)-C(4B)-C(9)	138.42(19)	C(10)-C(4A)-C(4B)-C(9)	-88.9(2)
C(9)-C(4B)-C(5)-C(6)	-1.1(3)	C(4A)-C(4B)-C(5)-C(6)	-174.6(2)
C(4B)-C(5)-C(6)-C(7)	0.9(4)	C(5)-C(6)-C(7)-C(8)	0.4(4)
C(6)-C(7)-C(8)-O(8)	-178.9(3)	C(6)-C(7)-C(8)-C(9)	-1.4(4)
C(5)-C(4B)-C(9)-C(8)	0.1(3)	C(4A)-C(4B)-C(9)-C(8)	175.2(2)
C(5)-C(4B)-C(9)-O(9)	179.99(19)	C(4A)-C(4B)-C(9)-O(9)	-4.9(2)
O(8)-C(8)-C(9)-C(4B)	178.9(2)	C(7)-C(8)-C(9)-C(4B)	1.2(3)
O(8)-C(8)-C(9)-O(9)	-1.1(4)	C(7)-C(8)-C(9)-O(9)	-178.7(2)
C(4B)-C(9)-O(9)-C(9A)	-20.5(2)	C(8)-C(9)-O(9)-C(9A)	159.4(2)
C(9)-O(9)-C(9A)-C(1)	161.77(17)	C(9)-O(9)-C(9A)-C(4A)	37.8(2)
C(12)-C(1)-C(9A)-O(9)	-66.0(2)	N(2)-C(1)-C(9A)-O(9)	169.07(16)
C(12)-C(1)-C(9A)-C(4A)	54.8(2)	N(2)-C(1)-C(9A)-C(4A)	-70.11(19)
C(4B)-C(4A)-C(9A)-O(9)	-39.55(19)	C(4)-C(4A)-C(9A)-O(9)	-162.07(17)
C(10)-C(4A)-C(9A)-O(9)	73.1(2)	C(4B)-C(4A)-C(9A)-C(1)	-166.04(15)
C(4)-C(4A)-C(9A)-C(1)	71.4(2)	C(10)-C(4A)-C(9A)-C(1)	-53.4(2)
C(4B)-C(4A)-C(10)-C(11)	155.0(2)	C(9A)-C(4A)-C(10)-C(11)	49.4(3)
C(4)-C(4A)-C(10)-C(11)	-70.1(3)	C(4A)-C(10)-C(11)-C(12)	-43.9(3)
C(9A)-C(1)-C(12)-C(11)	-50.8(3)	N(2)-C(1)-C(12)-C(11)	66.7(3)
C(10)-C(11)-C(12)-C(1)	43.9(3)	C(3)-N(2)-C(13)-C(14)	-172.48(19)
C(1)-N(2)-C(13)-C(14)	55.3(3)	N(2)-C(13)-C(14)-C(15)	155.47(19)
C(13)-C(14)-C(15)-C(20)	102.9(3)	C(13)-C(14)-C(15)-C(16)	-74.6(3)
C(20)-C(15)-C(16)-C(17)	0.2(4)	C(14)-C(15)-C(16)-C(17)	177.8(2)
C(15)-C(16)-C(17)-C(18)	0.5(4)	C(16)-C(17)-C(18)-C(19)	-0.7(5)
C(17)-C(18)-C(19)-C(20)	0.2(4)	C(16)-C(15)-C(20)-C(19)	-0.7(4)
C(14)-C(15)-C(20)-C(19)	-178.2(2)	C(18)-C(19)-C(20)-C(15)	0.5(4)