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Supporting Information

69451 Weinheim, Germany

Short Synthesis of (+)-Cylindricine C Using Catalytic Asymmetric Michael Reaction with a Newly Designed Two-Center Organocatalyst

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01. General;

NMR spectra were measured on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H, 126 MHz for ^{13}C. For ^{1}H and ^{13}C NMR, chemical shifts are reported in ppm on the δ scale relative to TMS (d = 0 for ^{1}H NMR) or residual solvent as internal reference. Infrared (IR) spectra were recorded on a JASCO FT/IR-410 diffraction grating infrared spectrophotometer. ESI mass spectra were measured on Waters-ZQ4000. FAB mass spectra were measured on a JEOL JMS-700V. Optical rotations were measured on a JASCO P-1010 polarimeter. The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, PU980; detector; UVIDEC-100-IV, measured at 245 nm; column, DAICEL CHIRALPAK AD-H and DAICEL CHIRALCEL OD-H; mobil phase, hexane–2-propanol. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise mentioned.

02. The preparation method for TaDiAS 6b and spectral data;

02.1. Concept of a Newly Designed TaDiAS 6b

For the conformational analysis of catalyst, X-ray crystallographic analysis of **6a** was examined (Figure 1). A tetrafluoroborate anion is situated very close to each of the ammonium cations, thus creating an attractive C_2-symmetrical chiral-environment. Another interesting fact is that the alkyl chains of the acetal moiety snake up to in a direction perpendicular to the dioxolane ring. A previous examination of substituent effects in asymmetric phase-transfer catalysis revealed that both the aromatic and acetal moieties strongly affected enantioselectivity. This unexpected strong substituent effect of the acetal moiety can be understood by the close proximity between the counter anions and acetal side-chains, especially the C2- and C3-positions (Figure 1b).

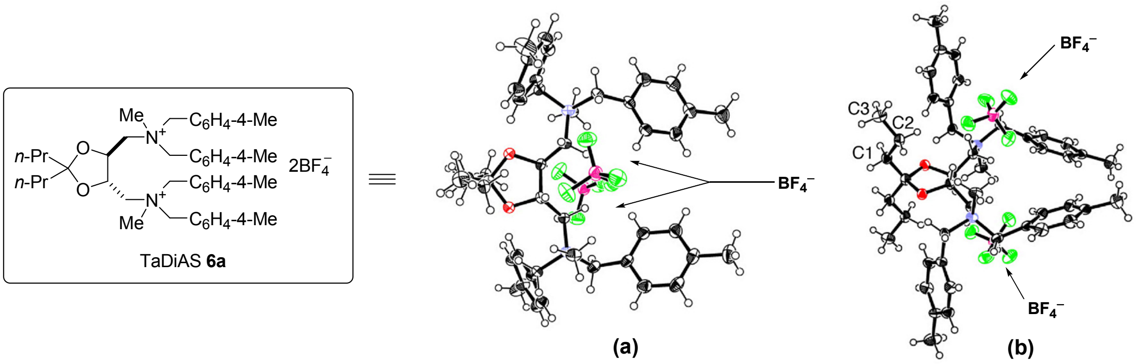
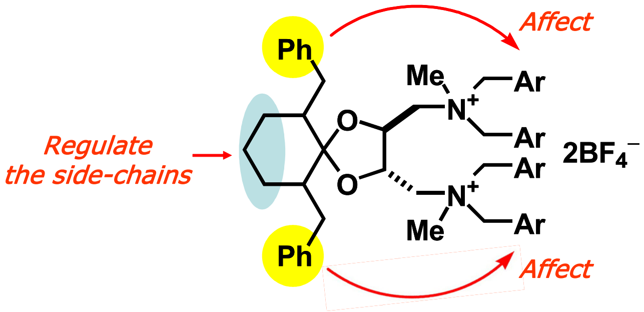


Figure 1. X-ray cryptographic analysis of TaDiAS **6a**. a) Top view and b) side view.

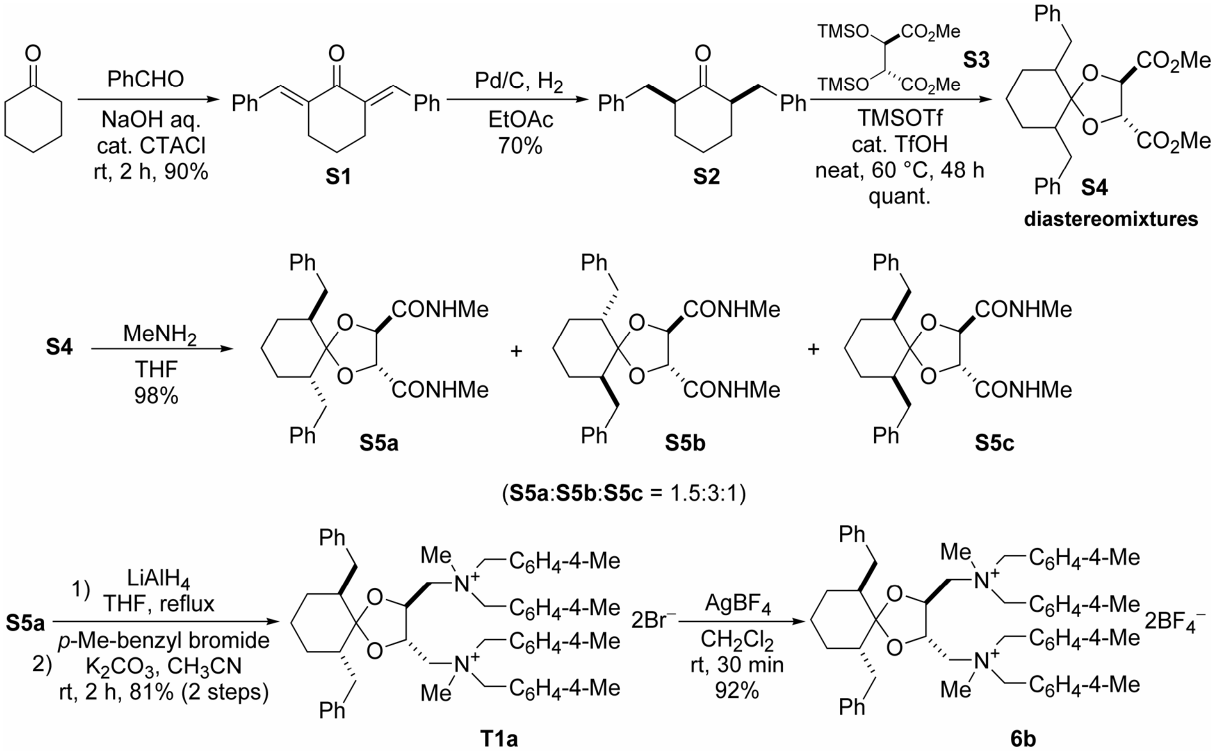
To affect chiral-environment more strongly, we designed a new catalyst **6b** that had 2,6-disubstituted cyclohexane structure and bulky substituents on acetal side-chains (Scheme 1).



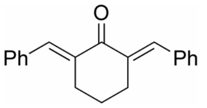
Scheme 1. Concept of a New TaDiAS **6b**.

02.2. The preparation method for TaDiAS 6b

Scheme 2. Preparation Method for TaDiAS **6b** (Overall)

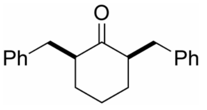


(*E*,*E*)-2,6-bis(phenylmethylene)cyclohexanone (S1);



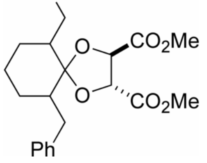
Known compound[1]; **S1** was obtained from cyclohexanone in 90% yield according to the literature.[1]

cis-2,6-bis(phenylmethyl)cyclohexanone (*cis*-S2);



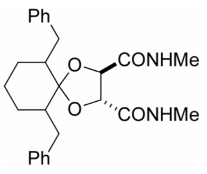
Known compound[2]; Pd on charcoal (10%, 200 mg) was added to a solution of **S1** (12.1 g, 44 mmol) in EtOAc (200 mL) at room temperature. The reaction mixture was stirred at the same temperature under H_2 atmosphere for 4 hours. Pd and charcoal were filtered off and the mixture was concentrated. The obtained solid was recrystallized from MeOH to give *cis*-**S2** as white crystal (8.5 g, 31 mmol, 70%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.26 (m, 4H), 7.20-7.15 (m, 6H), 3.24 (dd, J = 14.1 Hz, 4.9 Hz, 2H), 2.60-2.56 (m, 2H), 2.43 (dd, J = 14.1 Hz, 8.9 Hz, 2H), 2.07-2.05 (m, 2H), 1.79-1.76 (m, 1H), 1.56-1.51 (m, 1H), 1.39-1.30 (m; 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 212.7, 140.6, 129.1, 128.2, 125.9, 52.8, 35.5, 34.8, 25.3.

6,10-Bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*R* ,3*R*)-dicarboxylic acid dimethyl ester (S4);



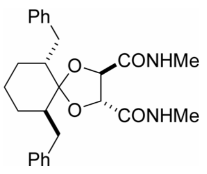
To a mixture of *cis*-**S2** (10.0 g, 35.9 mmol) and **S3** (12.7 ml, 39.5 mmol) were added freshly distilled TMSOTf (6.5 mL, 35.9 mmol) and TfOH (0.32 mL, 3.59 mmol). The mixture was stirred for 48 h at 60 °C. The reaction mixture was quenched with Et_3N (4.98 mL, 35.9 mmol) and aqueous $NaHCO_3$ solution (5 mL). The mixture was extracted with Et_2O (20 mL), washed with brine (20 mL), and dried over Na_2SO_4. After evaporation, the residue was purified by flash chromatography (silica gel, hexane/EtOAc = 10/1) and gave **S4** (15.7g, 35.9 mmol, quant.) as diastereomixtures (colorless oil).

Preparation of S5a-S5c;



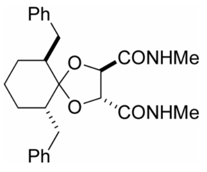
Methylamine (8.85 mL, 114 mmol, 40% in MeOH) was added to a solution of **S4** (12.5 g, 28.5 mmol) in THF (50 mL) at room temperature. The reaction mixture was stirred for 5 h, and then evaporated. The residue was purified by Lober^{TM} column chromatography (silica gel, hexane/EtOAc = 1:1) to gave **S5a** (6.7g, 15.4 mmol), **S5b** (3.34g, 7.6 mmol), and **S5c** (2.17g, 4.9 mmol) as colorless amorphous (total y. 98%);

N,*N*'-Dimethyl-(6*S*,10*S*)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*R*,3*R*)-dicarboxamide (S5a);



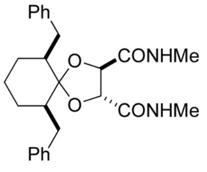
R_f = 0.37 (silica gel, 30% hexane in EtOAc); $[\alpha]^{22}_D$= +10.1° (*c* = 1.0, $CHCl_3$); FT-IR (KBr) ν_{max} 3322, 2937, 1663, 1542, 1118, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31-7.28 (m, 4H), 7.21-7.18 (m, 6H), 6.92 (bs, 2H), 4.51 (s, 2H), 3.12 (d, *J* = 13.4 Hz, 1H), 3.11 (d, *J* = 13.4 Hz, 1H), 2.88 (s, 3H), 2.87 (s, 3H), 2.47 (d, *J* = 13.2 Hz, 1H), 2.45 (d, *J* = 13.2 Hz, 1H), 2.12-2.10 (m, 2H), 1.67-1.66 (m, 2H), 1.56-1.55 (m, 2H), 1.44-1.43 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.8, 141.0, 129.2, 128.3, 125.9, 116.8, 77.7, 43.3, 34.3, 27.3, 26.1, 19.1; LR-MS [ESI(+)] *m/z* 459 $[M+Na]^+$; HR-MS [FAB(+)] calcd for $C_{26}H_{33}N_2O_4^+$ $[M+H]^+$: 437.2435. Found: 437.2429.

N,*N*'-Dimethyl-(6*R*,10*R*)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*R*,3*R*)-dicarboxamide (S5b);



R_f = 0.35 (silica gel, 30% hexane in EtOAc); $[\alpha]^{22}_D$= +35.7 (*c* = 1.08, $CHCl_3$); FT-IR (KBr) ν_{max} 3320, 2937, 1663, 1542, 1125, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.29-7.26 (m, 4H), 7.21-7.14 (m, 6H), 6.87 (bs, 2H), 4.48 (s, 2H), 3.05 (dd, J = 13.8, 4.0 Hz, 2H), 2.84 (s, 3H), 2.83 (s, 3H), 2.46 (dd, J = 13.5, 10.1 Hz, 2H), 2.19 (m, 2H), 1.67 (m, 2H), 1.56 (m, 2H), 1.48 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.7, 140.8, 129.2, 129.0, 128.3, 125.8, 116.2, 77.2, 42.2, 34.4, 27.2, 26.0, 19.2; LR-MS [ESI(+)] *m/z* 459 $[M+Na]^+$; HR-MS [FAB(+)] calcd for $C_{26}H_{33}N_2O_4^+$ $[M+H]^+$: 437.2435. Found: 437.2429.

N,*N*'-Dimethyl-(6*R*,10*S*)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*R*,3*R*)-dicarboxamide (S5c);

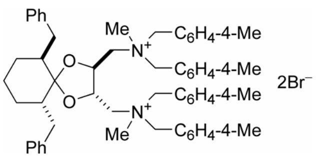


R_f = 0.46 (silica gel, 30% hexane in EtOAc); $[\alpha]^{22}_D$= +40.1° (*c* = 1.14, $CHCl_3$); FT-IR (KBr) ν_{max} 3316, 2936, 1656, 1542, 1189, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 (bs, 1H), 7.28-7.25 (m, 5H), 7.19-7.13 (m, 6H), 4.63 (d, *J* = 9.2 Hz, 1H), 4.61 (d, *J* = 9.2 Hz, 1H), 3.25 (d, *J* = 12.2 Hz, 1H), 2.97 (d, *J* = 4.9 Hz, 3H), 2.94 (d, *J* = 12.2 Hz, 1H), 2.88 (d, *J* = 4.9 Hz, 3H), 2.27 (t, *J* = 11.6 Hz, 1H), 2.07 (t, *J* = 11.6 Hz, 1H), 1.97-1.93 (m, 2H), 1.58-1.53 (m, 3H), 1.33-1.25 (m, 2H), 0.98-0.95 (m, 1H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 169.6, 168.7, 140.4, 140.1, 129.2, 128.2, 125.9, 125.8, 117.5, 79.0, 78.8, 60.3, 49.4, 49.3, 35.6, 35.5, 28.9, 28.5, 26.1, 26.0, 24.7, 21.0, 14.1; LR-MS [ESI(+)] *m/z* 459 [M+Na]$^+$; HR-MS [FAB(+)] calcd for $C_{26}H_{33}N_2O_4^+$ [M+H]$^+$: 437.2435. Found: 437.2429.

Preparation of T1a;

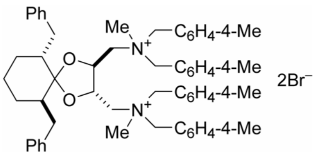
A solution of **S5a** (2.05g, 4.7 mmol)) in THF (10 mL) was slowly added to a suspension of $LiAlH_4$ (624 mg, 16.5 mmol) in THF (40 mL) at 4 °C. The reaction mixture was then heated to reflux. After 2 h, the reaction mixture was cooled to 4 °C, and quenched with H_2O (0.62 mL), 4 N NaOH aq. (0.62 mL), H_2O (1.86 mL). The mixture was stirred until gray color was turned to white suspension. Then, the mixture was filtered off and evaporated. Obtained colorless oil (diamine) was used for following reaction without further purification. *p*-Methylbenzyl bromide (5.22 g, 28.2 mmol) was added to a mixture of obtained diamine and K_2CO_3 (5.20 g, 37.6 mmol) in CH_3CN (16 mL, 0.3 M) at 4 °C and stirred for 2 h at room temperature. Then the reaction mixture was quenched by the addition of H_2O and extracted with EtOAc (10 mL x 3), washed with brine (15 mL), and dried over Na_2SO_4. After the evaporation of solvent, the residue was purified by flash chromatography (silica gel, EtOAc/MeOH = 1/0 to 5/1) to give **T1a** (3.76 g, 3.8 mmol, 81% from **S5a**) as colorless amorphous.

***N,N'*-Dimethyl-*N,N,N',N'*-tetrakis[(4-methylphenyl)methyl]-(6*R*,10*R*)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*S*,3*S*)-dimethanaminium dibromide (T1a)**;



R_f = 0.34 (silica gel, 10% MeOH in EtOAc); $[\alpha]^{20}_D$= −14.2° (*c* = 0.86, CHCl$_3$) ; FT-IR (KBr) ν_{max} 3407, 2935, 1614, 1516, 1454, 1128, 805, 702 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.59 (d, *J* = 7.9 Hz, 4H), 7.49 (d, *J* = 7.9 Hz, 4H), 7.31-7.26 (m, 10H), 7.23-7.15 (m, 10H), 5.65 (bs, 2H), 5.27 (d, *J* = 12.5 Hz, 2H), 5.19-5.16 (m, 4H), 4.74 (d, *J* = 12.2 Hz, 2H), 4.48 (d, *J* = 12.2 Hz, 2H), 3.94 (bs, 2H), 2.96 (s, 6H), 2.95-2.88 (m, 2H), 2.45 (bs, 2H), 2.39-2.28 (m, 2H), 2.34 (s, 6H), 2.32 (s, 6H), 1.68 (bs 2H), 1.49 (bs, 2H), 1.35-1.25 (m, 4H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 141.1, 141.0, 140.1, 133.4, 133.3, 129.9, 129.3, 128.2, 125.7, 123.6, 123.5, 117.2, 66.6, 65.5, 62.8, 46.0, 42.9, 35.0, 21.2, 19.0; LR-MS [ESI(+)] *m/z* 905 [M−Br$^-$]$^+$; HR-MS [FAB(+)] calcd for $C_{58}H_{70}BrN_2O_2^+$ [M−Br$^-$]$^+$: 905.4615. Found: 905.4626.

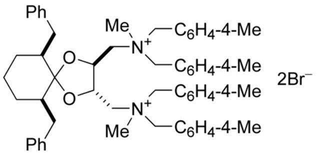
***N,N'*-Dimethyl-*N,N,N',N'*-tetrakis[(4-methylphenyl)methyl]-(6*S*,10*S*)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*S*,3*S*)-dimethanaminium dibromide (T1b)**;



R_f = 0.34 (silica gel, 10% MeOH in EtOAc); $[\alpha]^{20}_D$= −23.9° (*c* = 0.98, CHCl$_3$); FT-IR (KBr) ν_{max} 3398, 2935, 1615, 1516, 1454, 1128, 805, 703 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.56 (d, *J* = 7.9 Hz, 4H), 7.51 (d, J = 7.9 Hz, 4H), 7.29-7.24 (m, 12H), 7.18-7.12 (m, 6H), 5.29 (bs, 2H), 5.16-5.12 (m, 4H), 5.11 (d, *J* = 12.5 Hz, 2H), 4.66 (d, *J* = 12.5 Hz, 2H), 4.44 (bs, 2H), 3.96 (dd; *J* = 7.6, 7.6 Hz, 2H), 2.88 (s, 6H), 2.82 (dd, *J* = 14.0, 4.9 Hz, 2H), 2.59 (bs, 2H), 2.42 (dd, *J* = 14.0, 5.2

Hz, 2H), 2.38 (s, 6H), 2.28 (s, 6H), 1.77 (m, 2H), 1.58-1.55 (m, 2H), 1.38-1.34 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.0, 140.9, 140.2, 133.4, 133.3, 129.9, 129.8, 128.9, 128.2, 125.7, 123.8, 123.7, 117.2, 73.2, 66.8, 65.5, 62.5, 46.2, 42.3, 34.5, 21.2, 21.1, 19.0; LR-MS [ESI(+)] *m/z* 905 $[M-Br^-]^+$; HR-MS [FAB(+)] calcd for $C_{58}H_{70}BrN_2O_2^+$ $[M-Br^-]^+$: 905.4615. Found: 905.4626.

_N,N'_-Dimethyl-_N,N,N',N'_-tetrakis[(4-methylphenyl)methyl]-(6_R_,10_S_)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2_S_,3_S_)- dimethanaminium dibromide (T1c);

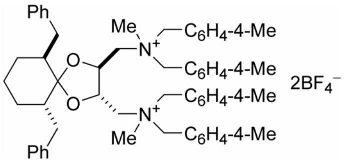


R_f = 0.18 (silica gel, 10% MeOH in EtOAc); $[\alpha]^{22}_D$= +1.7° (*c* = 1.0, $CHCl_3$); FT-IR (KBr) ν_{max} 3408, 2928, 1614, 1454, 1190, 822, 701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.27-7.11 (m, 12H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 5.41 (d, *J* = 12.8 Hz, 1H), 5.38 (d, *J* = 13.8 Hz, 1H), 5.26 (d, *J* = 13.8 Hz, 1H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.05 (d, *J* = 12.8 Hz, 1H), 5.03 (d, *J* = 12.2 Hz, 1H), 5.00 (d, *J* = 12.6 Hz, 1H), 4.86 (d, *J* = 12.5 Hz, 1H), 4.72 (d, *J* = 12.6 Hz, 1H), 4.67 (dd, *J* = 9.5, 7.9 Hz, 1H), 4.43 (dd, *J* = 9.5, 8.8 Hz, 1H), 4.32 (d, *J* = 12.2 Hz, 1H), 3.75 (dd, *J* = 13.7, 9.2 Hz, 1H), 3.50 (dd, *J* = 14.4, 9.2 Hz, 1H), 3.27 (s, 3H), 2.92 (s, 3H), 2.50 (m, 2H), 2.43 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 1.95-1.89 (m, 2H), 1.82 (bs, 1H), 1.65 (bs, 1H), 1.53 (d, *J* = 13.1 Hz, 1H), 1.45 (d, *J* = 11.3 Hz, 1H), 1.36 (d, *J* = 11.3 Hz, 1H), 1.09-1.05 (m, 1H), 0.96-0.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.0, 140.95, 140.87, 140.8, 139.1, 138.9, 133.5, 133.2, 133.0, 129.6, 129.5, 128.60, 128.57, 127.9, 127.8, 125.7, 125.6, 125.1, 124.6, 124.0, 123.6, 117.2, 74.5, 74.3, 69.2, 68.9, 67.3, 67.0, 61.6, 61.2, 47.8, 47.4, 46.0, 45.8, 35.3, 35.0, 28.6, 28.3, 24.0, 21.0, 20.9, 20.8, 20.5; LR-MS [ESI(+)] *m/z* 905 $[M-Br^-]^+$; HR-MS [FAB(+)] calcd for $C_{58}H_{70}BrN_2O_2^+$ $[M-Br^-]^+$: 905.4615. Found: 905.4593.

Preparation of (_S,S_)-6b;

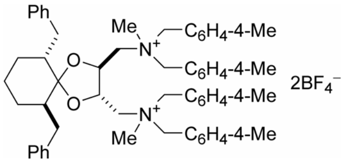
$AgBF_4$ (146 mg, 0.75 mmol) was added to a solution of **T1a** (296 mg, 0.3 mmol) in CH_2Cl_2 (1.0 mL) at room temperature, and stirred for 30 min. After filtration of the precipitate (AgBr), solvent was evaporated. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 1/1 to 0/1) to give **(_S,S_)-6b** (277mg, 0.28 mmol, 92%) as colorless amorphous.

_N,N'_-Dimethyl-_N,N,N',N'_-tetrakis[(4-methylphenyl)methyl]-(6_R_,10_R_)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2_S_,3_S_)-dimethanaminium bistetrafluoroborate ((_S,S_)-6b)



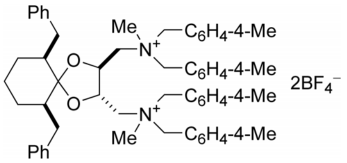
R_f = 0.59 (silica gel, EtOAc); $[\alpha]^{20}_D$= −3.7° (*c* = 0.95, $CHCl_3$); FT-IR (KBr) ν_{max} 2935, 1468, 1058 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.13 (m, 26H), 4.82 (d, *J* = 5.5 Hz, 2H), 4.73 (d, *J* = 12.5 Hz, 2H), 4.63 (d, *J* = 12.5 Hz, 2H), 4.40 (d, *J* = 12.5 Hz, 2H), 4.21 (d, *J* = 12.5 Hz, 2H), 3.94-3.83 (m, 4H), 2.81 (s, 6H), 2.72 (d, *J* = 15.5 Hz, 2H), 2.38-2.30 (m, 18H), 1.41-1.22 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.4, 140.2, 133.2, 133.1, 130.1, 129.1, 128.9, 128.4, 125.9, 123.4, 123.2, 118.0, 73.3, 67.6, 67.1, 63.1, 45.6, 42.6, 34.9, 21.3, 21.2, 19.0; LR-MS [ESI(+)] *m/z* 913 $[M–BF_4^-]^+$; HR-MS [FAB(+)] calcd for $C_{58}H_{70}BF_4N_2O_2^+$ $[M–BF_4^-]^+$: 913.5461. Found: 913.5463.

***N*,*N'*-Dimethyl-*N*,*N*,*N'*,*N'*-tetrakis[(4-methylphenyl)methyl]-(6*S*,10*S*)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*S*,3*S*)- dimethanaminium bistetrafluoroborate ((*S*,*S*)-6c);**



R_f = 0.59 (silica gel, EtOAc); $[\alpha]^{20}_D$= −14.2° (*c* = 1.0, CHCl$_3$); FT-IR (KBr) ν_{max} 2933, 1468, 1059 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.38 (d, *J* = 8.0 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 4H), 7.32-7.27 (m, 8H), 7.21-7.13 (m, 10H), 4.63-4.57 (m, 4H), 4.58 (d, *J* = 12.5 Hz, 2H), 4.35 (d, *J* = 12.5 Hz, 2H), 4.16 (d, *J* = 12.5 Hz, 2H), 3.89-3.82 (m, 4H), 2.73 (s, 6H), 2.70 (d, *J* = 9.0 Hz, 2H), 2.43-2.33 (m, 4H), 2.38 (s, 6H), 2.34 (s, 6H), 1.56-1.54 (m, 2H), 1.38-1.36 (m, 2H), 1.29-1.26 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 141.3, 140.2, 133.2, 133.1, 130.1, 130.0, 128.9, 128.4, 125.9, 123.4, 123.3, 117.6, 72.8, 68.0, 67.0, 62.8, 45.9, 42.3, 34.4, 21.23, 21.16, 19.0; LR-MS [ESI(+)] *m/z* 913 $[M–BF_4^-]^+$; HR-MS [FAB(+)] calcd for $C_{58}H_{70}BF_4N_2O_2^+$ $[M–BF_4^-]^+$: 913.5461. Found: 913.5463.

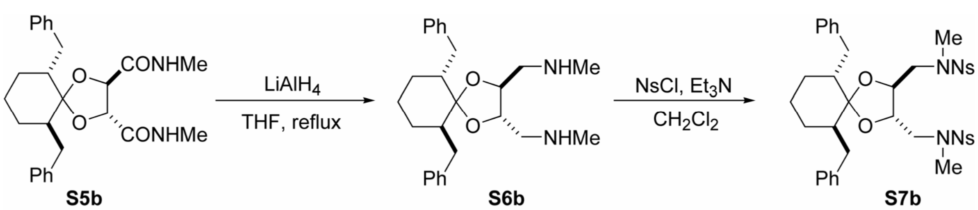
***N*,*N'*-Dimethyl-*N*,*N*,*N'*,*N'*-tetrakis[(4-methylphenyl)methyl]-(6*R*,10*S*)-bis(phenylmethyl)-1,4-dioxaspiro[4.5]decane-(2*S*,3*S*)-dimethanaminium bistetrafluoroborate ((*S*,*S*)-6d);**



R_f = 0.59 (silica gel, EtOAc); $[\alpha]^{21}_D$= +14.3° (*c* = 1.0, CHCl$_3$); FT-IR (KBr) ν_{max} 2929, 1469, 1058 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.40-7.11 (m, 18H), 7.01 (d, *J* = 7.0 Hz, 2H), 6.94 (d, *J* = 7.0 Hz, 2H), 4.88 (d, *J* = 13.0 Hz, 1H), 4.74 (d, *J* = 12.5 Hz, 1H), 4.61 (d, *J* = 13.0 Hz, 1H), 4.55-4.49 (m, 1H), 4.48 (d, *J* = 13.5 Hz, 2H), 4.39 (d, *J* = 12.5 Hz, 1H), 4.36-4.33 (m, 1H), 4.19-4.16 (m, 1H), 4.13 (d, *J* = 13.5 Hz, 2H), 4.05 (d, *J* = 14.0 Hz, 1H), 3.92 (d, *J* = 14.0 Hz, 1H), 3.76-3.71 (m, 1H), 3.58-3.53 (m, 1H), 3.06 (s, 3H), 2.75 (s, 3H), 2.49-2.37 (m, 3H), 2.42 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 1.90-1.85 (m, 3H), 1.66-1.38 (m, 4H), 1.06-0.90 (m, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 141.7, 141.5, 141.4, 139.7, 139.5, 133.5, 133.2, 133.0, 130.2, 130.15, 129.0, 128.9, 128.4, 128.2, 126.1, 125.9, 124.1, 123.7, 123.2, 118.4, 111.9, 74.6, 74.4, 69.4, 69.0, 68.2, 68.0, 62.3, 62.0, 48.2, 47.6, 46.0, 45.8, 35.5, 29.2, 29.1, 24.4, 21.3, 21.2, 21.17, 21.0; LR-MS [ESI(+)] *m/z* 913 $[M–BF_4^-]^+$; HR-MS [FAB(+)] calcd for $C_{58}H_{70}BF_4N_2O_2^+$ $[M–BF_4^-]^+$: 913.5461. Found: 913.5505.

02.3. Determination of the diastereochemistries of TaDiAS 6b

02.3.1. Transformation to S7b.



A solution of **S5b** (360 mg, 0.82 mmol) in THF (3 mL) was slowly added to a suspension of $LiAlH_4$ (109 mg, 2.87 mmol) in THF (7 mL) at 4 °C. The reaction mixture was then heated to reflux. After 8 h, the reaction mixture was cooled to 4 °C, and quenched with H_2O (0.11 mL), 4 N NaOH aq. (0.11 mL), H_2O (0.33 mL). The mixture was stirred until gray color was turned to white suspension. Then, the mixture was filtered off and evaporated. Obtained colorless oil (**S6b**) was used for the following reaction without further purification.

To a stirred solution of **S6b** (209 mg, 0.512 mmol) and Et_3N (1.40 mL, 10.2 mmol) in CH_2Cl_2 (5.0 mL) was added NsCl (1.70 g, 7.67 mmol) at room temperature. The mixture was stirred for 15 hours at the same temperature. The reaction was quenched with saturated $NaHCO_3$ solution (2.0 mL). The organic layer was separated, and the aqueous layer was extracted twice with EtOAc (15 min). The combined organic layer was washed with saturated NH_4Cl and brine, dried over Na_2SO_4, and concentrated to give a pale yellow solid (1.22 g), which was purified twice by silica gel column chromatography (SiO_2 40 g, EtOAc / hexane = 1/2) to give **S7b** (120 mg, 0.154 mmol, 30% yield) as a pale yellow solid. It was recrystallized from EtOAc-hexane to give a slightly yellow needle crystal, which was filtrated and recrystallized again from acetone-hexane to give a white crystal; FT-IR (neat) ν_{max} 3314, 2934, 1699, 1543, 1366, 1162 cm^{-1}; ^1H NMR ($(CD_3)_2CO$, 500 MHz) δ 8.11 (m, 2H), 7.86 (m, 6H), 7.23 (m, 4H), 7.20 (m, 4H), 7.13 (t, J = 7.0 Hz, 2H), 4.21 (br s, 1H), 3.67 (br s, 1H), 3.12 (s, 6H), 2.99 (dd, J = 12.9, 3.1 Hz, 2H), 2.47 (t, J = 12.9 Hz, 2H), 2.01 (m, 2H), 1.48 (m, 2H), 1.36 (m, 2H), 1.23 (m, 2H).; ^{13}C NMR ($(CD_3)_2CO$, 125 MHz) δ 145.5, 138.3, 131.3, 129.1, 128.5, 127.4, 126.1, 125.1, 122.6, 121.2, 112.7, 112.6, 110.9, 74.7, 48.6, 40.9, 33.1, 30.7, 26.7, 15.9.; LR-MS [ESI(+)] *m/z* 801 $[M + Na]^+$.

02.3.2. X-ray crystallographic analysis of S7b.

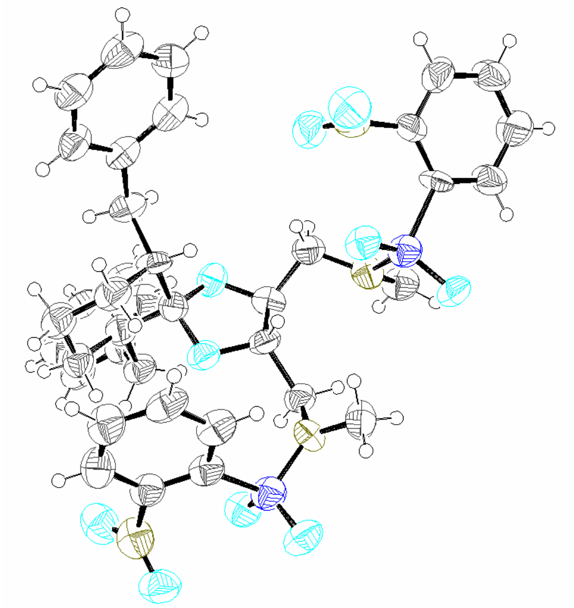
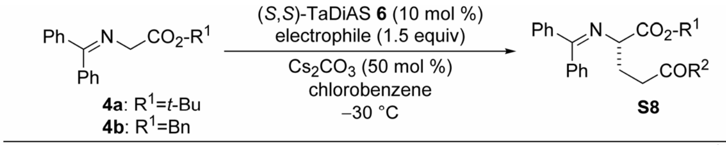


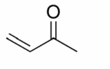
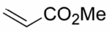
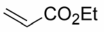
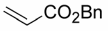
Figure 2. X-ray crystallographic analysis of **S7b**.

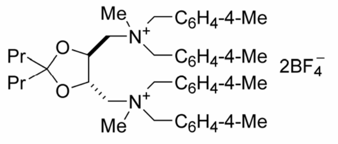
03. General Procedure for Catalytic Asymmetric Phase-Transfer Michael Reaction

03.1. Catalytic asymmetric Michael reaction using Newly designed TaDiAS

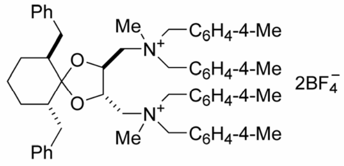
Table 03-1. Catalytic asymmetric Michael reaction using Newly designed TaDiAS 6



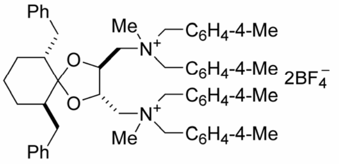
entry	catalyst	glycine Schiff base	electrophile	time (h)	yield[a] (%)	ee[b] (%)
1[c,d]	**6a**	**4a**		48	87	33
2	**6a**	**4a**		48	74	62
3[e]	**6b**	**4a**		24	92	71
4[e]	**6c**	**4a**		24	91	66
5[e]	**6d**	**4a**		24	46	28
6	**6b**	**4b**		12	95	73
7[f,g]	**6b**	**4b**		48	93	80
8	**6c**	**4b**		12	96	88
9	**6c**	**4b**		13	92	88
10	**6c**	**4b**		11	96	87



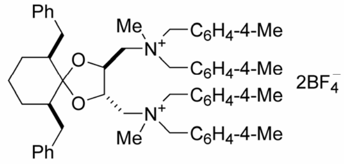
6a



6b



6c



6d

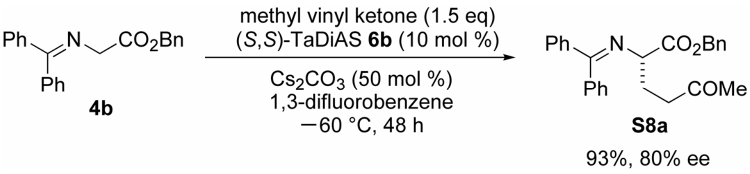
a) Isolated yield. b) Determined by chiral HPLC. c) Counter anions of **6a** were 2I. d) 10 equiv of Cs$_2$CO$_3$ were used. e) 1 equiv of Cs$_2$CO$_3$ was used. f) 1,3-difluorobenzene was used as solvent. g) Reaction was performed at −60 °C.

In contrast to the asymmetric phase-transfer Michael reaction to α,β-unsaturated esters, there is much room for improvement in the Michael reaction of **4a** using α,β-unsaturated ketones (enone) as electrophiles. We examined reaction conditions based on our previous results (Table 03-1). First, the reaction was performed using 10 mol % of (*S*,*S*)-**6a** (the best catalyst for the Michael reaction to α,β-unsaturated esters). Although replacement of the soft counter anion (I^-) by a hard counter anion (BF_4^-) improved enantioselectivity, the obtained result was still unsatisfactory (entries 1, 2). Previous conformation analysis of **6a** suggested that the acetal moiety regulated the chiral-environment around two ammonium cations. To affect the chiral-environment more strongly, we designed a new catalyst **6b-d** that had a 2,6-disubstituted cyclohexane structure on the acetal moiety. Thus, we synthesized three diastereomers (**6b-d**) and found that C_2-symmetric **6b** improved the selectivity to 71% ee (entry

3). Because of the decreased reactivity of the reaction with **6b-d**, 1 equiv of Cs_2CO_3 was needed to complete the reaction. By changing *tert*-butyl ester **4a** to benzyl ester **4b** of the glycine Schiff base, the reaction was completed with 0.5 equiv of Cs_2CO_3 without a loss of enantioselectivity (entry 6). The use of 1,3-difluorobenzene as a solvent allowed us to decrease the reaction temperature, and selectivity was increased to 80% ee at –60 °C (entry 7). When acrylates were used as the substrate (entry 8-10), **6c** was the most effective catalyst.

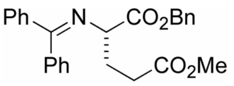
03.2. General Procedure for Catalytic Asymmetric Phase-Transfer Michael Reaction

***N*-Diphenylmethylene-L-norleucine benzyl ester (S8a);**



To a solution of **4b** (49.4 mg, 0.15 mmol) in chlorobenzene (1mL, 0.15 M), TaDiAS **6b** (15.0 mg, 0.015 mmol), methyl vinyl ketone (18.8 mL, 0.225 mmol) was added under Ar atmosphere. The mixture was cooled to –60 °C and then Cs_2CO_3 (24.4 mg, 0.075 mmol) was added. The reaction mixture was stirred at this temperature until **4b** was consumed, then quenched by the addition of water (3 mL), extracted with Et_2O (5 mL x 2), washed with brine (5 mL x 1), and dried over Na_2SO_4. After evaporation of solvent, the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 5/1) to give **S8a** (55.8 mg, 0.14 mmol, 93%, 80% ee) as colorless oil; R_f = 0.35 (silica gel, 30% EtOAc in hexane); $[\alpha]^{22}_{D}$= –63.6° (*c* = 1.10, $CHCl_3$, 80% ee); FT-IR (neat) ν_{max} 1738, 1160, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.42-7.31 (m, 11H), 7.11-1.09 (m, 2H), 5.17 (d, *J* = 12.5 Hz, 1H), 5.12 (d, *J* = 12.5 Hz, 1H), 4.13 (t, *J* = 6.0 Hz, 1H), 2.55-2.46 (m, 2H), 2.18 (dd, *J* = 14.0, 7.0 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 207.8, 171.5, 171.0, 139.2, 136.1, 135.8, 130.4, 128.7, 128.6, 128.5, 128.4, 128.13, 128.10, 128.0, 127.6, 66.4, 64.0, 39.5, 29.8, 27.5; LR-MS [ESI(+)] *m/z* 422 $[M+Na]^+$; HR-MS [FAB(+)] calcd for $C_{26}H_{26}NO_3^+$ $[M+H]^+$: 400.1907. Found: 400.1902.; HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol 20/1, 1.0 mL/min) t_R: 13.6 min (minor) and 15.6 min (major).

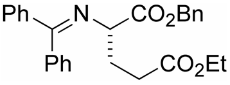
***N*-Diphenylmethylene-L-glutamic acid 1-benzy-5-methyl ester (S8b);**



Colorless oil; R_f = 0.53 (silica gel, 30% EtOAc in hexane); $[\alpha]^{21}_{D}$= –87.0° (*c* = 0.89, $CHCl_3$, 88% ee); FT-IR (neat) ν_{max} 2950, 1739, 1171, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.41-7.31 (m, 11H), 7.12-7.10 (m, 2H), 5.18 (d, *J* = 12.2 Hz, 1H), 5.13 (d, *J* = 12.2 Hz, 1H), 4.14 (dd, *J* = 5.8, 5.8 Hz, 1H), 3.57 (s, 3H), 2.37 (m, 2H), 2.28 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 171.3, 139.2, 136.1, 135.8, 130.5, 128.8, 128.6, 128.5, 128.2, 128.1, 128.0, 127.7, 66.6, 64.1, 51.5, 30.3, 28.5; LR-MS [ESI(+)] *m/z* 438 $[M+Na]^+$; HR-MS [FAB(+)] calcd for $C_{26}H_{26}NO_4^+$ $[M+H]^+$: 416.1856. Found: 416.1855.; HPLC

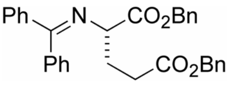
(DAICEL CHIRALPAK OD-H, hexane/2-propanol 100/1, 1.0 mL/min) t_R: 25.3 min (minor) and 32.1 min (major).

N-Diphenylmethylene-L-glutamic acid 1-benzy-5-ethyl ester (S8c);



Colorless oil; $R_f = 0.58$ (silica gel, 30% EtOAc in hexane); $[\alpha]^{22}_{D} = -85.4°$ (c = 1.09, $CHCl_3$, 88% ee); FT-IR (neat) ν_{max} 2979, 1731, 1445, 1177, 1028, 697; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.40-7.31 (m, 11H), 7.11 (dd, J = 8.0, 1.8 Hz, 2H), 5.18 (d, J = 12.5 Hz, 1H), 5.13 (d, J = 12.5 Hz, 1H), 4.14 (dd, J = 6.7, 5.8 Hz, 1H), 4.03 (q, J = 7.0 Hz, 2H), 2.37-2,33 (m, 2H), 2.29-2.27 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.9, 171.4, 171.3, 139.2, 136.1, 135.8, 130.4, 128.8, 128.6, 128.5, 128.2, 128.1, 128.0, 127.7, 66.5, 64.2, 60.3, 30.6, 28.5, 14.1; LR-MS [ESI(+)] *m/z* 430 [M+H]$^+$; HR-MS [FAB(+)] calcd for $C_{27}H_{28}NO_4^+$ [M+H]$^+$: 430.2013. Found: 430.2007.; HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol 100/1, 1.0 mL/min) t_R: 19.2 min (minor) and 24.6 min (major).

N-Diphenylmethylene-L-glutamic acid dibenzyl ester (S8d);



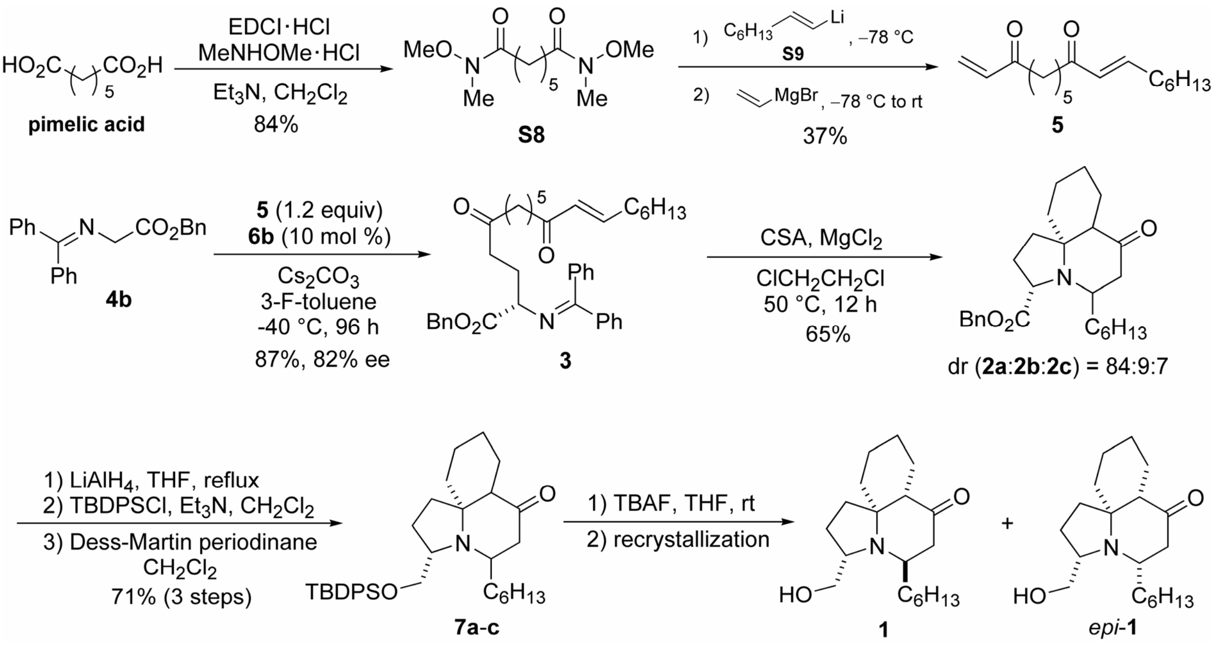
Colorless oil; $R_f = 0.58$ (silica gel, 30% EtOAc in hexane); $[\alpha]^{22}_{D} = -61.6°$ (c = 0.81, $CHCl_3$, 87% ee) ; FT-IR (neat) ν_{max} 2948, 1731, 1446, 1159, 1081, 696 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 7.0 Hz, 2H), 7.39-7.27 (m, 16H), 7.08 (d, J = 7.0 Hz, 2H), 5.17 (d, J = 12.2 Hz, 1H), 5.12 (d, J = 12.5 Hz, 1H), 5.02 (s, 2H), 4.14 (dd, J = 5.2, 5.2 Hz, 1H), 2.43-2.40 (m, 2H), 2.33-2.29 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.7, 171.4, 139.2, 136.1, 135.9, 135.8, 130.5, 128.8, 128.6, 128.5, 128.2, 128.1, 128.0, 127.7, 66.6, 66.2, 64.1, 30.6, 28.5; LR-MS [ESI(+)] *m/z* 492 [M+H]$^+$; HR-MS [FAB(+)] calcd for $C_{32}H_{30}NO_4^+$ [M+H]$^+$: 492.2169. Found: 492.2164. HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol 20/1, 1.0 mL/min) t_R: 16.1 min (minor) and 19.9 min (major).

04. The synthetic route of (+)-cylindricine C

04.1. General scheme of the total synthesis of (+)-cylindricine C

We synthesized (+)-cylindricine C using catalytic asymmetric Michael reaction and tandem cyclization as shown in Scheme 3.

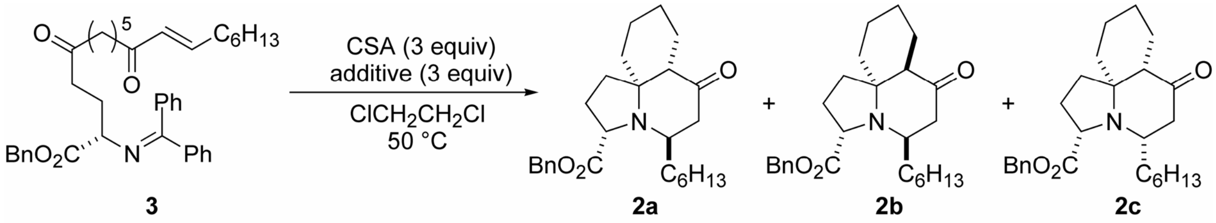
Scheme 3. The total synthesis of (+)-cylindricine C (Overall)



04.2. $MgCl_2$ Effects (tandem cyclization)

In the presence of $MgCl_2$, the reactivity of tandem cyclization was increased and selectivity was dramatically improved. Several metal salts also showed such effects (Scheme 4).

Scheme 4. Additive Effects on Tandem Cyclization

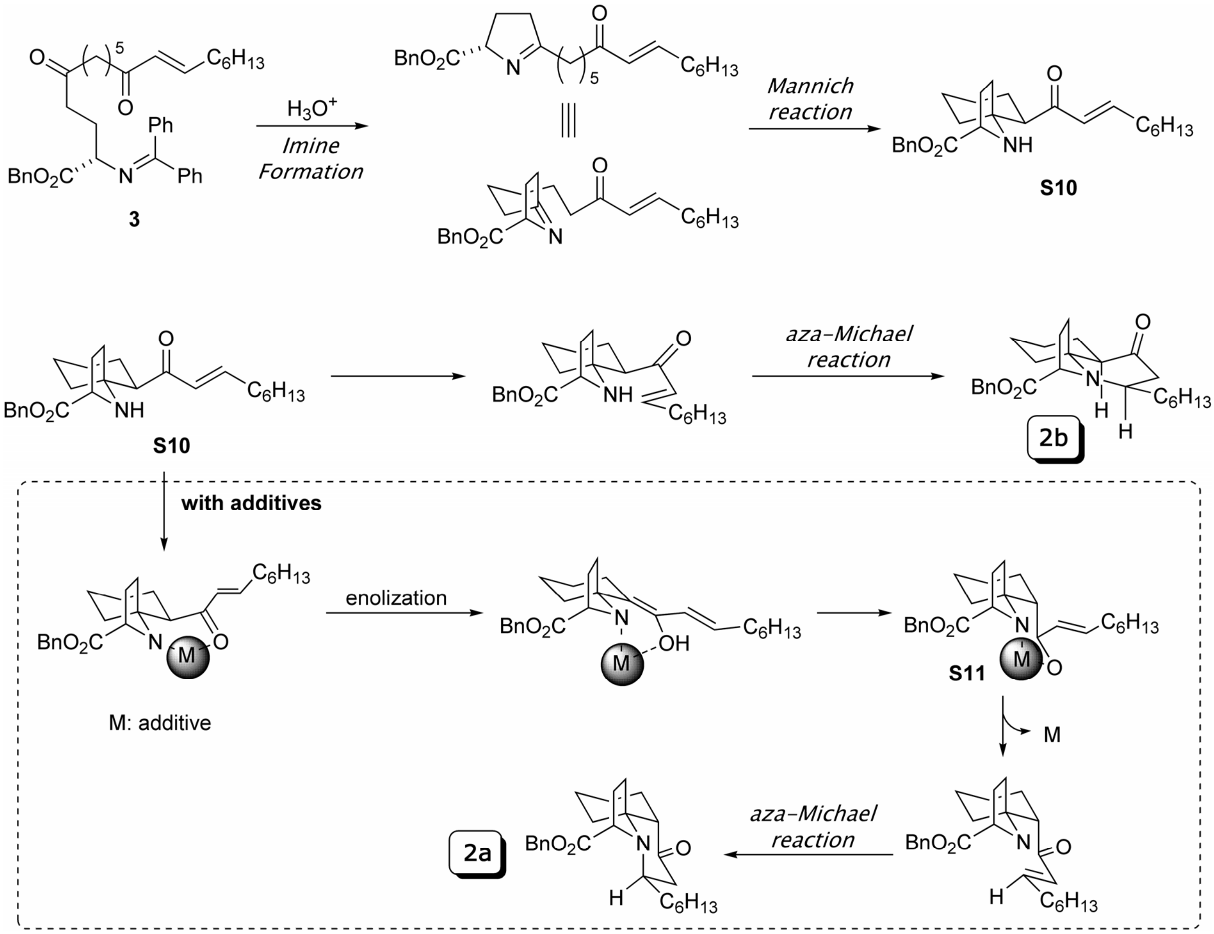


Representative Results

entry	additive	time (h)	dr (**2a**:**2b**:**2c**)	yield (%)
1	none	18	33:63:4	47
2	$AlCl_3$	24	87:13:trace	47
3	$MgCl_2$	12	84:9:7	65
4	$MgBr_2 \cdot (Et_2O)_2$	18	82:13:5	61
5	LiCl	18	89:6:5	57
6	$La(OTf)_3$	12	27:65:8	57

Now we consider that these additives affect on aza-Michael reaction (Scheme 5). After Mannich reaction proceeds, **S10** would be formed. In the absence of additive, aza-Michael reaction would proceed directly because the side chain possessed equatorial position, and **2b** would be obtained as major diastereomer. On the other hand, in the presence of additive, carbonyl group on C7 would be activated by additives and enolization would occur easily (Lewis acid effects). Following protonation would give C7a-epimerized compound because intermediate **S11** would be stabilized by additives (chelation effects). After additives from **S11** leave, aza-Michael reaction proceeds and desired **2a** would be obtained as major diastereomer.

Scheme 5. Proposed Mechanism of Additive Effects

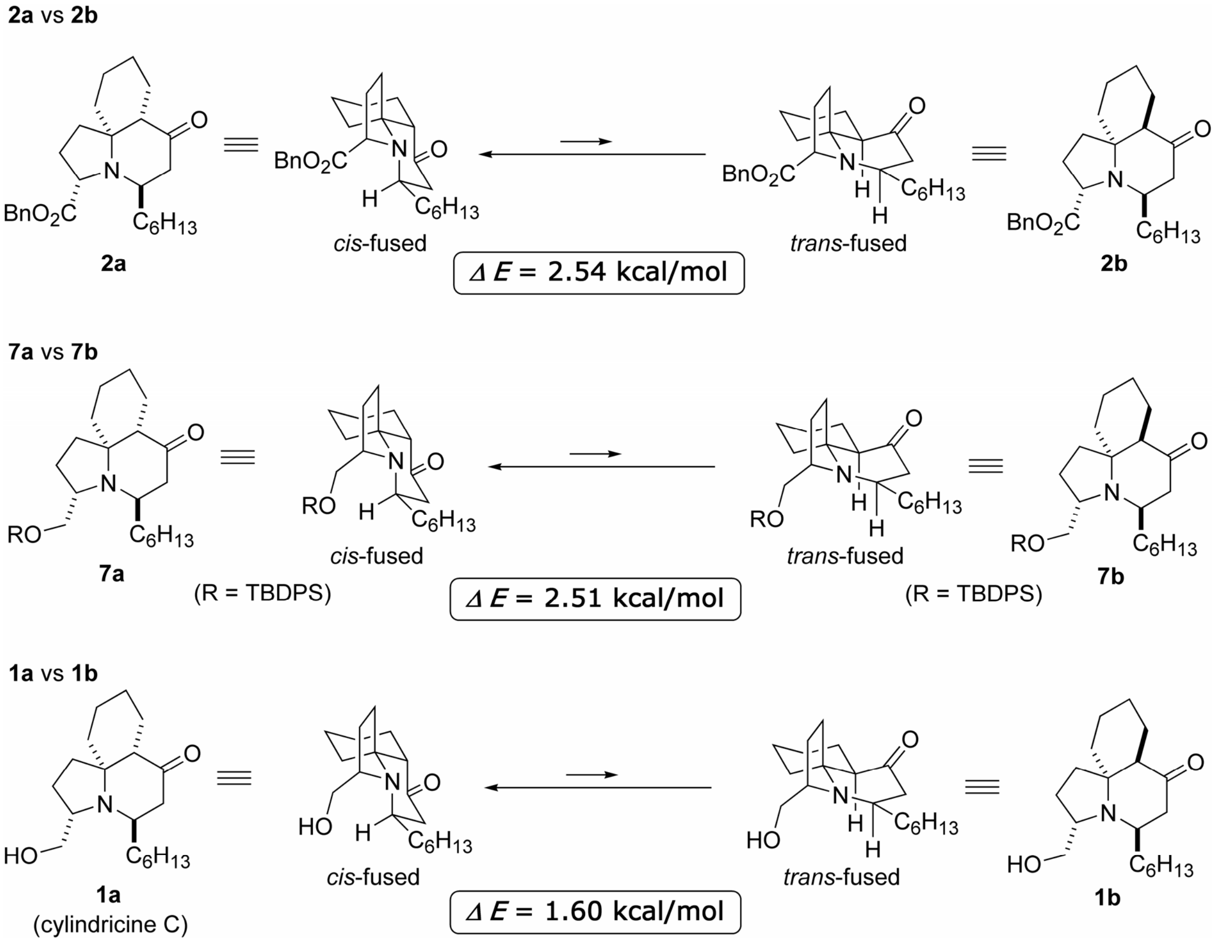


04.3. Computational Analysis of tricyclic compounds (2a, 2b, 7a, 7b, 1a, and 1b)

To find a possible explanation of such isomerization, we performed several computational studies (Scheme 6). First, conformational analysis was performed for all isomers (**2a**, **2b**, **7a**, **7b**, **1a**, and **1b**) by CONFLEX5[3]/MMFF94s[4]. Then, all the geometries of the global minimum (lowest energy structure) were further optimized with Gaussian03[5] at B3LYP[6]/6-31G(d) level followed by frequency calculations to determine the nature of the stationary points. Energies shown below include zero-point energy corrections at the same level of the geometry (B3LYP/6-31G(d)) scaled by 0.9806.[7]

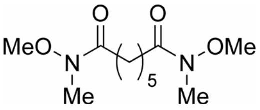
The computational results suggested that *cis*-fused isomers are thermodynamically more stable than *trans*-fused isomers.

Scheme 6. Computational Analysis of *cis*-Fused Compounds and *trans*-Fused Compounds



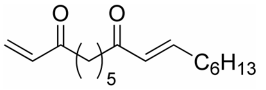
04.4. The synthetic procedures and spectral data

Synthesis of *N,N'*-Dimethoxy-*N,N'*-dimethyl-pimelic amide (S8);



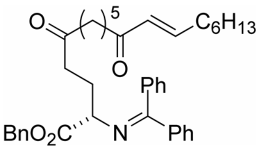
A mixture of pimelic acid (4.8 g, 30 mmol), *N,O*-dimethylhydroxylamine hydrochloride (6.4 g, 66 mmol), EDCI (12.6 g, 66 mmol), triethylamine (12.6 mL, 90 mmol), and CH_2Cl_2 (75 mL) was stirred 22 h. The reaction mixture was quenched by water (50 ml), and extracted with CH_2Cl_2 (50 ml x 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel, EtOAc) to yield **S8** (6.17 g, 84%) as colorless oil; R_f= 0.31 (silica gel, EtOAc); FT-IR (neat) ν_{max} 2934, 1665, 1415, 1385, 1178, 1117, 999 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.67 (s, OMe, 6H), 3.17 (s, NMe, 6H), 2.42 (t, *J* = 7.3 Hz, 4H), 1.66 (m, 4H), 1.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 174.6, 61.2, 53.4, 32.1, 31.7, 29.1, 24.3; LR-MS [ESI(+)] *m/z* 269 [$M+Na^+$]; HR-MS [FAB(+)] Calcd for $C_{11}H_{23}N_2O_4^+$ [$M+H^+$]: 247.1652.; Found 247.1652.

Synthesis of Heptadeca-1,10-diene-3,9-dione (5);



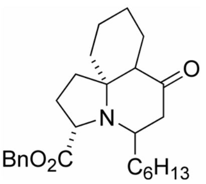
To a solution of *trans*-1-iodo-1-octene (476 mg, 2.0 mmol) in THF (10 mL) was added *t*-BuLi (1.46 M, 2.74 mL, 4.0 mmol) at −78 °C. After stirring for 2 h at this temperature, the reaction mixture was added to a solution of **S8** (492 mg, 2.0 mmol) and THF (10 mL) at −78 °C. The reaction mixture was stirred for 2 h at same temperature, and then vinylmagnesium bromide (1.0 M, 4.0 mL, 4.0 mmol) was added. After the mixture was allowed to warm to rt, the reaction mixture was stirred for 12 h. The mixture was quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O (30 ml x 3). The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel, 10% EtOAc in hexane) to yield **7** (195.5 mg, 37%) as pale yellow oil; R_f = 0.55 (silica gel, 25% EtOAc in hexane); FT-IR (neat) ν_{max} 2929, 2857, 1680, 1677, 1628, 1403, 981 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 6.82 (dt, *J* = 15.9, 7.0 Hz, 1H), 6.34 (dd, *J* =17.7 , 10.7 Hz, 1H), 6.21 (dd, *J* =17.7 , 1.2 Hz, 1H), 6.08 (dt, *J* =15.9 , 1.5 Hz, 1H), 5.81 (dd, *J* =10.7 , 1.2 Hz, 1H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.20 (dd, *J* = 14.7, 1.6 Hz, 2H) 1.67-1.1.60 (m, 4H), 1.46 (m, *J* = 7.6 Hz, 2H), 1.37-1.26 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 126 MHz) δ 200.8, 200.7, 147.5, 136.5, 130.2, 128.0, 39.7, 39.3, 32.4, 31.5, 28.82, 28.77, 28.0, 23.9, 23.6, 22.5, 14.0; LR-MS [ESI(+)] *m/z* 287; [$M+Na^+$]; HR-MS [FAB(+)] Calcd for $C_{17}H_{29}O_2^+$ [$M+H^+$]: 265.2162; Found 265.2162.

Synthesis of 2-(Diphenylmethylene)amino-5,11-dioxo-12-nonadecenoic acid benzyl ester (3).



A mixture of **4b** (35.2 mg, 0.107 mmol), **5** (33.9 mg 0.128 mmol) and (*S,S*)-TaDiAS **6b** (10.7 mg, 0.0107 mmol) in 3-fluorotoluene (0.71 mL) was stirred for 1 h at −60 °C, and then Cs_2CO_3 (52.1 mg, 0.160 mmol) was added. The mixture was stirred vigorously for 96 h at this temperature. The reaction was quenched with water (2 mL) and extracted with Et_2O (5 mL x 3). The combined organic layer were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel, 10% EtOAc in hexane) to yield **3** (55.4 mg, 87%) as pale yellow oil; R_f = 0.29 (silica gel, 25% EtOAc in hexane); $[\alpha]^{23}_{D}$ = –44° (c = 1.62, $CHCl_3$) (82% ee); FT-IR (neat) ν_{max} 2929, 2857, 1739, 1713, 1626, 1173, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.61 (m, 2H), 7.41-7.24 (m, 11H), 7.09 (m, 2H), 6.81 (dt, J = 15.9, 6.9 Hz, 1H), 6.07 (dt, J = 15.9, 1.5 Hz, 1H), 5.14 (dd, J = 27.8, 12.1 Hz, 2H), 4.12 (t, J = 6.1 Hz, 1H), 2.51-2.33 (m, 6H), 2.19 (m, 4H), 1.60-1.42 (m, 6H), 1.34-1.22 (m, 8H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 210.0, 200.6, 171.6, 171.0, 147.4, 139.3, 136.1, 135.8, 130.4, 130.2, 128.8, 128.7, 128.51, 128.46, 128.2, 128.1, 128.0, 127.6, 66.5, 64.1, 42.5, 39.7, 38.6, 32.4, 31.5, 28.8, 28.7, 28.0, 27.6, 23.9, 23.4, 22.5, 14.0; LR-MS[ESI(+)] m/z 616 $[M+Na^+]$; HR-MS [FAB(+)] calcd for $C_{39}H_{48}NO_4^+$ $[M+H^+]$: 594.3578; Found 594.3575; HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol = 9/1, 1.0 mL/min) t_R: 14.9 min (minor) and 16.6 min (major).

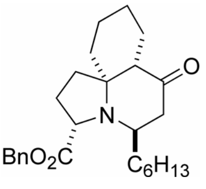
Synthesis of tricyclic compound 2a-c;



To a solution of **3** (6.7 mg, 0.0113 mmol) in 1,2-dichloroethane (0.28 mL) was added CSA (7.9 mg, 0.0339 mmol). After mixture was stirred for 1 h at rt, $MgCl_2$ (3.2 mg, 0.0339 mmol) was added, then the mixture was warmed to 50 °C. The mixture was stirred for 18 h at this temperature. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (5 mL), and extracted with EtOAc (5 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel, 10% EtOAc in hexane) to yield **2a-2c** (3.3 mg, 71 %) as pale yellow oil as diastereomixtures. They were used for the following reaction without further purification.

To determine their conformations, they were separated by HPLC. HPLC separation was performed on JASCO HPLC systems (PU-2086 Plus Pump, UV-2075-Plus Detector, 254 nm.) (DAICEL CHIRALPAK AS-H, hexane/2-propanol = 50/1, 20 mL/min) $t_{R,}$ 11.5 min (**2c**, major), 12.5 min (**2a**, major), 13.0 min (**2c**, minor), 13.0 min (**2a**, minor), 15.0 min (**2b** minor), and after 20 min solvent was changed to hexane/2-propanol = 4/1, flow rate 20 mL/min, t_R 10 min (**2b**, major).

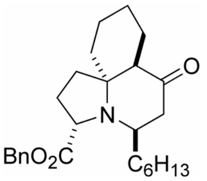
(3*S*,5*R*,7a*S*,11a*S*)-5-Hexyloctahydro-pyrrolo-1*H*-[2,1-*j*]quinoline-7-one-3-carboxylic acid benzyl ester (2a);



R_f = 0.55 (silica gel, 10% Et_2O in toluene); FT-IR (neat) ν_{max} 2931, 2859, 1747, 1706, 1455, 1145, 698.1 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.32 (m, 5H), 5.13 (dd, J = 69.9, 12.2 Hz, 2H), 3.99 (dd, J = 10.7, 2.7 Hz, 1H), 3.34 (m, 1H), 2.29-2.10 (m, 6H), 1.93-1.86 (m, 2H), 1.70 (m, 1H), 1.62-1.14 (m, 16H), 0.86, (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 210.5, 176.1, 135.9, 128.5, 128.33, 128.27, 69.5, 66.4, 58.4, 54.1, 50.9, 42.6, 35.6, 34.6, 34.4, 31.7, 29.2, 27.6, 26.4, 24.3, 23.0, 22.5, 21.6, 14.0; LR-MS [ESI(+)] m/z 434 $[M+Na^+]$; HR-MS [FAB(+)] calcd for $C_{26}H_{38}NO_3^+$ $[M+H]^+$: 412.2846. Found:

412.2851.

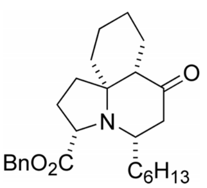
(3*S*,5*R*,7a*R*,11a*S*)-5-Hexyloctahydro-pyrrolo-1*H*-[2,1-*j*]quinoline-7-one-3-carboxylic acid benzyl ester (2b);



R_f = 0.43 (silica gel, 10% Et_2O in toluene); FT-IR (neat) ν_{max} 2930, 2857, 1749, 1715, 1454, 1152, 697.1 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36-7.29 (m, 5H), 5.14 (dd, *J* = 93.7, 12.3 Hz, 2H), 3.73-3.66 (m, 2H), 2.70 (dd, *J* = 11, 2.8 Hz, 1H), 2.24 (t, *J* = 5.1 Hz, 2H), 2.07-1.97 (m, 2H), 1.92 (d, *J* = 8.9 Hz, 1H), 1.82-1.70 (m, 4H), 1.62 (dt, *J* = 13.3, 2.8 Hz, 1H), 1.53 (m, 1H), 1.38-1.05 (m, 14H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 212.3, 176.3, 135.9, 128.5, 128.3, 128.2, 68.3, 66.4, 61.5, 54.9, 53.9, 40.9, 39.2, 32.9, 31.9, 31.7, 29.3, 28.8, 27.0, 24.8, 24.1, 22.5, 22.4, 14.0; LR-MS [ESI(+)] *m/z* 434 [M+Na$^+$]; HR-MS [FAB(+)] calcd for $C_{26}H_{38}NO_3^+$ [M+H]$^+$: 412.2846. Found: 412.2849.

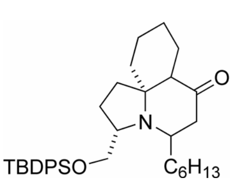
Based on NOE measurement, **2b** had *trans*-fused AB ring, and A ring had boat type conformation.

(3*S*,5*S*,7a*S*,11a*S*)-5-Hexyloctahydro-pyrrolo-1*H*-[2,1-*j*]quinoline-7-one-3-carboxylic acid benzyl ester (2c);



R_f = 0.55 (silica gel, 10% Et_2O in toluene); FT-IR (neat) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.31 (m, 5H), 5.15 (dd, *J* = 41.5, 12.2 Hz, 2H), 3.67 (t, *J* = 7.5 Hz, 1H), 3.18 (m, 1H), 2.50 (dd, *J* = 17.4, 3.7 Hz, 1H), 2.48 (m, 1H), 2.30-2.14 (m, 4H), 1.95 (m, 1H), 1.78 (dd, *J* = 12.2, 6.7 Hz, 1H), 1.75 (d, *J* = 11.9 Hz, 1H), 1.47-1.41 (m, 2H), 1.37-1.07 (m, 14H), 0.87 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 211.8, 175.9, 136.1, 128.6, 128.3,128.2, 67.8, 67.0, 66.5, 57.9, 52.6, 43.4, 39.6, 36.7, 36.1, 31.9, 29.4, 28.8, 25.2, 24.3, 23.0, 22.7, 21.4, 14.2; LR-MS [ESI(+)] *m/z* 434 [M+Na$^+$]; HR-MS [FAB(+)] calcd for $C_{26}H_{38}NO_3^+$ [M+H]$^+$: 412.2846. Found: 412.2849.

Synthesis of 7a-c

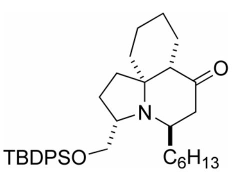


A solution of **2** (48.9 mg, 0.0824 mmol, diastereomixtures (**2a**:**2b**:**2c** = 84:9:7)) in THF (0.8 mL) was added to lithium aluminum hydride (6.3 mg, 0.165 mmol) in THF (0.8 mL) at 0 °C. Then the mixture was heated at reflux, and stirred for 2 h. The mixture was added H_2O (6.3 μL), 4N NaOH (6.3 μL), and H_2O (18.9 μL) at 0 °C. The mixture was warmed to rt, and stirred over night, diluted with water (3.0 mL) and extracted with 20% MeOH in CH_2Cl_2 (5.0 ml x 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The obtained residue was dissolved in CH_2Cl_2 (0.8 mL) and TBDPSCl (64.3 μL, 0.247 mmol), triethylamine (41.4μL, 0.297 mmol), and DMAP (1.0 mg, 0.00824 mmol) were added and stirred for 6 h. The reaction was quenched with water (3.0 mL) and extracted CH_2Cl_2 (3.0 mL x 3). The combined organic layer were washed with brine, dried over Na_2SO_4, and concentrated.

The obtained residue was dissolved in CH_2Cl_2 (0.8 mL) and DMP (69.9 mg, 0.165 mmol) was added. The reaction mixture was stirred for 12 h and then quenched with water (3.0 mL) and extracted CH_2Cl_2

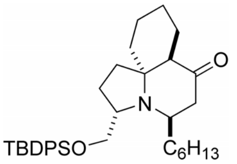
(5.0 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel, 7.5% to 10% EtOAc in hexane) to yield **7** (32 mg, 71 %, diastereomixtures (**7a**:**7b**:**7c** = 90:3:7)) as brown oil.

(3*S*,5*R*,7a*S*,11a*S*)-3-[[(*tert*-Butyldiphenylsilyl)oxy]methyl]-5-hexyloctahydro-1-*H*-pyrrolo[2,1,*j*]-quinolin-7(7a*H*)-one (7a);



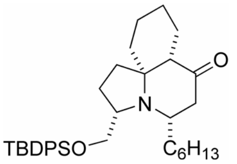
R_f = 0.71 (silica gel, 25% EtOAc in hexane); $[\alpha]^{20}_D$ = +8.5° (c = 0.71, $CHCl_3$) (78% ee); FT-IR (neat) ν_{max} 2930, 2856, 1707, 1427, 1111, 702, 505 cm^{-1};^1H NMR ($CDCl_3$, 500 MHz) δ 7.70-7.66 (m, 4H), 7.43-7.35 (m, 6H), 3.61 (dd, J = 9.2, 3.1 Hz, 1H), 3.33 (m,1H), 3.29 (dd, J = 18.5, 9.3Hz, 1H), 3.08 (m, 1H), 2.27 (m, 1H), 2.22-2.05 (m, 6H), 1.62-1.45 (m, 4H),1.32-1.18 (m, 9H) 1.07(s, 9H) 1.07-1.03 (m, 5H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 211.4, 135.6, 133.9,129.6, 127.6, 70.2, 68.4, 57.8, 55.3, 51.0, 43.0, 35.9, 34.9, 34.8, 31.7, 29.1, 27.0, 26.9, 25.9, 24.4, 22.9, 22.5, 21.9, 19.3, 14.0; LR-MS [ESI(+)] *m*/*z* 568 $[M+Na]^+$; HR-MS [FAB(+)] calcd for $C_{35}H_{52}NO_2Si^+$ $[M+H]^+$: 546.3762. Found: 546.3771.

(3*S*,5*R*,7a*R*,11a*S*)-3-[[(*tert*-Butyldiphenylsilyl)oxy]methyl]-5-hexyloctahydro-1-*H*-pyrrolo[2,1,*j*]-quinolin-7(7a*H*)-one (7b);



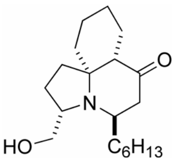
R_f = 0.67 (silica gel, 25% EtOAc in hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.71-7.63 (m, 4H), 7.43-7.27 (m, 6H), 3.73 (dd, J = 9.6, 4.1 Hz, 1H), 3.46 (m, 1H), 3.28 (t, J = 9.2 Hz, 1H), 3.18 (m, 1H), 2.61 (dd, J = 11.6, 3.1 Hz, 1H), 2.15 (d, J = 8.0 Hz, 2H), 1.95-1.89 (m, 2H), 1.81-1.75 (m, 2H), 1.72-1.51 (m, 5H), 1.41 (m, 1H), 1.32-1.06 (m, 12H), 1.04 (s, 9H), 0.86 (t, J = 6.7 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 126 MHz) δ 213.5, 135.6, 134.0, 129.6, 127.6, 70.4, 68.3, 60.2, 54.7, 54.0, 41.5, 40.7, 33.3, 31.8, 31.5, 29.7, 28.3, 27.3, 26.9, 24.9, 24.1, 22.6, 22.5, 19.2, 14.0; LR-MS [ESI(+)] *m*/*z* 568 $[M+Na^+]$; HR-MS [FAB(+)] calcd for $C_{35}H_{52}NO_2Si^+$ $[M+H]^+$: 546.3762. Found: 546.3770.

(3*S*,5*S*,7a*S*,11*S*)-3-[[(*tert*-Butyldiphenylsilyl)oxy]methyl]-5-hexyloctahydro-1-*H*-pyrrolo[2,1,*j*]-quinolin-7(7a*H*)-one (7c);



R_f = 0.71 (silica gel, 25% EtOAc in hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.69-7.63 (m, 4H), 7.44-7.35 (m, 6H), 3.57 (dd, J = 10.1, 4.3 Hz, 1H), 3.40 (t, J = 9.5 Hz, 1H) 3.12 (m, 1H), 3.00 (m, 1H), 2.48 (dd, J = 15.4, 5.4 Hz, 1H), 2.43 (m, 1H), 2.23 (m, 1H), 2.07 (dd, J = 15.4, 7.0 Hz, 1H), 2.00 (m, 2H), 1.88 (m, 1H), 1.73 (m,1H), 15.2 (m, 1H), 1.43-1.39 (m, 4H), 1.38-1.05 (m, 12H), 1.04 (s, 9H), 0.88 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 212.5, 135.6, 133.9, 129.6, 127.6, 68.1, 66.2, 58.6, 50.9, 43.1, 40.5, 36.9, 36.2, 31.8, 29.7, 29.2, 26.9, 26.0, 25.7, 24.3, 23.1, 22.6, 21.7, 19.2, 14.0; LR-MSMS [ESI(+)] *m*/*z* 568 $[M+Na^+]$; HR-MS [FAB(+)] calcd for $C_{35}H_{52}NO_2Si^+$ $[M+H]^+$: 546.3762. Found: 546.3772.

Synthesis of (+)-cylindricine C (1);



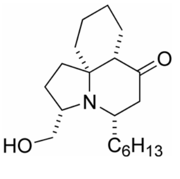
To a solution of **7** (16.9 mg, 0.0299 mmol, diastereomixtures (**7a**:**7b**:**7c** = 90:3:7)) in THF (1.5 mL) was added TBAF (90 µL, 0.0897 mmol) at 0 °C. The mixture was stirred for 6 h at rt. The reaction was quenched with water (3.0 mL) and extracted CH_2Cl_2 (5.0 mL x 3). The combined organic layer were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (silica gel, 7.5% to 10% EtOAc in hexane) to give **1** (7.4 mg, 0.024 mmol, 80%) and *epi*-**1** (0.73 mg, 0.0023 mmol, 8%).

Recrystallization of picrate of 1.

Picric acid (31.1 mg, 0.136 mmol) was added to a solution of **1** (41.6 mg, 0.136 mmol, 82% ee) in EtOH (1.0 mL). After picric acid was dissolved completely, solvent was removed *in vacuo* and yellow solid was obtained. This solid was recrystallized from EtOH (3 times, 43.0 mg, 59%).

This solid was dissolved in EtOAc (5 mL) and the organic layer was washed with saturated aqueous $NaHCO_3$ solution (5 mL). The aqueous layer was extracted with EtOAc (5 mL x 3) and the combined organic layer was washed with brine, dried over Na_2SO_4. After solvent was evaporated, the residue was purified by flash column chromatography (silica gel, 7.5% to 10% EtOAc in hexane) to yield optically pure **1** (>99% ee) as pale yellow oil; R_f = 0.53 (silica gel, 50% EtOAc in hexane); $[\alpha]^{21}_{D}$ = +63.6° (*c* = 0.44, CH_2Cl_2, >99% ee); FT-IR (neat) ν_{max} 3425, 2931, 2859, 1704, 1448, 1078, 407; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.50-3.55 (m, 2H), 3.42 (d, *J* = 9.8 Hz, 1H), 3.28 (m, 1H), 2.91 (br, 1H), 2.30 (t, *J* = 12.4 Hz, 2H), 2.23 (dd, *J* = 13.1, 1.9 Hz, 2H), 2.12 (dd, *J* = 12.2, 8.0 Hz, 1H), 1.83 (m, 1H), 1.71-1.60 (m, 5H), 1.48 (m, 1H), 1.43-1.26 (m, 13H), 0.87 (t, *J* = 7.7 Hz, 3H);^{13}C NMR ($CDCl_3$, 126 MHz) δ 210.6, 70.7, 66.4, 56.5, 55.3, 50.2, 42.5, 36.4, 35.9, 35.2, 31.7, 29.3, 28.7, 27.1, 24.2, 22.7, 22.6, 21.8, 14.0; LR-MS [ESI(+)] *m/z* 308 [$M+H^+$]; HR-MS [FAB(+)] calcd for $C_{19}H_{34}NO_2^+$ [$M+H^+$]: 308.2584; Found 308.2591.; HPLC (DAICEL CHIRALPAK OD-H, hexane/2-propanol = 50/1, 1.0 mL/min) t_R: 16.8 min (minor) and 18.9 min (major).

***epi*-cylindricine C (*epi*-1);**



Pale yellow oil; R_f= 0.40 (silica gel, 50% EtOAc in hexane); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.56 (dd, *J* = 10.5, 4.1 Hz, 1H), 3.34 (dd, *J* = 10.7, 2.8 Hz, 1H), 3.31 (m, 1H), 3.22 (m, 1H), 2.80 (m, 1H), 2.66 (dd, *J* = 15.4, 5.6 Hz, 1H), 2.52 (m, 1H), 2.26 (m, 1H), 2.16 (dd, *J* = 15.6, 6.1 Hz, 1H), 2.07- 2.02 (m, 2H), 1.83-1.25 (m, 19H), 0.87 (t, *J* = 6.9 Hz, 3H); LR-MS [ESI(+)] *m/z* 308 [$M+H^+$]; HR-MS [FAB(+)] calcd for $C_{19}H_{34}NO_2^+$ $[M+H]^+$: 308.2584. Found: 308.2585.

A shorter approach to (+)-cylindricine C from 2a;

To a solution of **2a** (17.2 mg, 0.0418 mmol) in MeOH (0.42 mL), Pd on charcoal (10%, 4.4 mg, 0.0042 mmol) was added at room temperature. The reaction mixture was stirred at the same temperature under H_2 atmosphere for 12 h. Pd and charcoal were filtered off and the mixture was concentrated.

The obtained residue was dissolved in THF (0.42 mL). To this solution were *N*-methyl morpholine (4.6 μL, 0.0418 mmol) and ethyl chloroformate (4.0 μL, 0.0418 mmol) at −10 °C and stirred for 2 h. Then $NaBH_4$ (4.7 mg, 0.125 mmol) and MeOH (0.42 mL) were added and stirred for 2 h at room temperature. The reaction mixture was quenched with 1N HCl (9.4 μL), washed with saturated $NaHCO_3$ (5 mL), and extracted with CH_2Cl_2 (5 mL x 3). The combined organic layer was washed with brine, dried over Na_2SO_4. After evaporation of solvent, the residue was purified by flash column chromatography (silica gel, 7.5% to 10% EtOAc in hexane) to give **1** (4.0 mg, 0.013 mmol, 31%) as pale yellow oil.

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Experimental

Data Collection

A colorless needle crystal of $C_{38}H_{42}N_{4}O_{10}S_{2}$ having approximate dimensions of 0.18 x 0.02 x 0.02 mm was mounted in a loop. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-Kα radiation.

Indexing was performed from 13 oscillations that were exposed for 3600 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$a = 12.9756(3)$ Å
$b = 10.5186(3)$ Å $\quad\beta = 110.0170(15)^{\circ}$
$c = 14.4500(7)$ Å
$V = 1853.07(11)$ Å^{3}

For Z = 2 and F.W. = 778.89, the calculated density is 1.396 g/cm^{3}. Based on the systematic absences of:

0k0: $k \pm 2n$

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P2_{1}$ (#4)

The data were collected at a temperature of -180 ± 1°C to a maximum 2θ value of 136.4°. A total of 67 oscillation images were collected. A sweep of data was done using ω scans from 80.0 to 260.0° in 10.0° step, at χ=0.0° and ϕ = 0.0°. The exposure rate was 360.0 [sec./$^{\circ}$]. A second sweep was performed using ω scans from 80.0 to

260.0° in 10.0° step, at χ=54.0° and ϕ = 0.0°. The exposure rate was 360.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 10.0° step, at χ=54.0° and ϕ = 90.0°. The exposure rate was 360.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 210.0° in 10.0° step, at χ=54.0° and ϕ = 180.0°. The exposure rate was 360.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 16048 reflections that were collected, 5986 were unique (R_{int} = 0.076); equivalent reflections were merged.

The linear absorption coefficient, μ, for Cu-Kα radiation is 18.484 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.694 to 0.964. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction[1] was applied (coefficient = 0.001520).

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques[3]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 5986 observed reflections and 492 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \,||Fo| - |Fc|| \,/\, \Sigma\, |Fo| = 0.0766 \quad (I>2.00\sigma(I))$$

$$wR2 = [\,\Sigma\,(\,w\,(Fo^2 - Fc^2)^2\,)/\,\Sigma\, w(Fo^2)^2]^{1/2} = 0.2085$$

The standard deviation of an observation of unit weight[5] was 1.05. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.36 and -0.36 e$^-$/Å^3, respectively. The absolute structure was deduced based on Flack parameter 0.02(3), refined using Friedel pair 2416.[6]

Neutral atom scattering factors were taken from Cromer and Waber[7]. Anomalous dispersion effects were included in Fcalc[8]; the values for Δf' and Δf" were those of Creagh and McAuley[9]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[10]. All calculations were performed using the CrystalStructure[11] crystallographic software package except for refinement, which was performed using SHELXL-97[12].

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(4) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2-F_c^2)^2 \qquad \text{where w = Least Squares weights.}$$

(5) Standard deviation of an observation of unit weight:

$$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$$

where: N_o = number of observations
N_v = number of variables

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EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{38}H_{42}N_4O_{10}S_2$
Formula Weight	778.89
Crystal Color, Habit	colorless, needle
Crystal Dimensions	0.18 X 0.02 X 0.02 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	13 oscillations @ 3600.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 12.9756(3) Å b = 10.5186(3) Å c = 14.4500(7) Å β = 110.0170(15) ^{o} V = 1853.07(11) Å^3
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.396 g/cm^3
F_{000}	820.00
$\mu(CuK\alpha)$	18.484 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	CuKα (λ = 1.54187 Å) graphite monochromated
Detector Aperture	460 mm x 256 mm
Data Images	67 exposures
ω oscillation Range (χ=0.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	360.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	360.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	80.0 - 260.0^{o}
Exposure Rate	360.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	80.0 - 210.0^{o}
Exposure Rate	360.0 sec./^{o}
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	136.4^{o}
No. of Reflections Measured	Total: 16048 Unique: 5986 (R_{int} = 0.076) Friedel pairs: 2416
Corrections	Lorentz-polarization Absorption (trans. factors: 0.694 - 0.964)

Secondary Extinction
(coefficient: 1.52000e-003)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$\sigma^2(Fo^2) + (0.0775 \cdot P)^2$ + 0.0000 · P] where P = $(Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.4°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5986
No. Variables	492
Reflection/Parameter Ratio	12.17
Residuals: R1 ($I>2.00\sigma(I)$)	0.0766
Residuals: R (All reflections)	0.1765
Residuals: wR2 (All reflections)	0.2085
Goodness of Fit Indicator	1.053
Flack Parameter (Friedel pairs = 2416)	0.02(3)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.36 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.36 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S(1)	0.35364(18)	0.2112(2)	0.12864(16)	4.48(5)
S(2)	0.50290(19)	-0.3065(2)	0.35191(17)	4.81(5)
O(1)	0.6918(4)	0.1880(6)	0.4143(3)	4.57(12)
O(2)	0.6750(5)	-0.0268(5)	0.3841(4)	4.46(13)
O(3)	0.4369(4)	0.1549(5)	0.0971(3)	4.67(13)
O(4)	0.2497(4)	0.1487(5)	0.1084(3)	4.71(13)
O(5)	0.5761(5)	0.3978(7)	0.1258(5)	6.36(18)
O(6)	0.5181(4)	0.3394(7)	-0.0279(4)	6.40(17)
O(7)	0.5393(4)	-0.2899(6)	0.4576(3)	5.12(13)
O(8)	0.4270(5)	-0.4075(6)	0.3040(4)	5.76(15)
O(9)	0.6597(6)	-0.5174(7)	0.4871(5)	6.30(17)
O(10)	0.7941(6)	-0.3853(7)	0.5576(5)	6.54(18)
N(1)	0.4065(5)	0.2296(7)	0.2484(4)	4.51(16)
N(2)	0.5048(7)	0.3858(8)	0.0451(7)	5.7(2)
N(3)	0.4524(5)	-0.1725(7)	0.3026(5)	4.16(15)
N(4)	0.7231(8)	-0.4349(10)	0.4851(7)	5.9(2)
C(1)	0.7522(7)	0.0754(9)	0.4066(6)	4.12(18)
C(2)	0.8027(7)	0.0930(8)	0.3272(6)	4.16(18)
C(3)	0.8614(7)	-0.0302(9)	0.3170(7)	5.1(2)
C(4)	0.9500(7)	-0.0668(10)	0.4153(6)	5.5(2)
C(5)	0.9040(7)	-0.0737(9)	0.4999(6)	4.7(2)
C(6)	0.8403(7)	0.0489(9)	0.5080(6)	4.6(2)
C(7)	0.8760(7)	0.2133(9)	0.3447(5)	4.64(19)
C(8)	0.9030(7)	0.2571(9)	0.2553(6)	4.5(2)
C(9)	0.9886(6)	0.2064(10)	0.2301(6)	4.88(19)
C(10)	1.0057(7)	0.2437(10)	0.1447(7)	5.4(2)
C(11)	0.9374(8)	0.3346(11)	0.0831(6)	5.7(2)
C(12)	0.8531(7)	0.3888(9)	0.1087(6)	4.8(2)
C(13)	0.8350(7)	0.3479(9)	0.1937(6)	4.9(2)
C(14)	0.7913(7)	0.0393(8)	0.5910(6)	4.6(2)
C(15)	0.8420(8)	0.1339(11)	0.6716(7)	4.7(2)
C(16)	0.9163(8)	0.0989(12)	0.7624(8)	6.2(2)
C(17)	0.9700(8)	0.1908(14)	0.8361(7)	6.2(2)
C(18)	0.9466(8)	0.3171(13)	0.8157(8)	5.9(2)
C(19)	0.8716(8)	0.3547(12)	0.7267(8)	6.4(2)
C(20)	0.8221(8)	0.2646(12)	0.6559(8)	5.5(2)
C(21)	0.5767(7)	0.1613(8)	0.3728(5)	4.21(19)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C(22)	0.5696(7)	0.0264(8)	0.3344(6)	3.98(18)
C(23)	0.5243(7)	0.2606(8)	0.2935(6)	4.7(2)
C(24)	0.3333(6)	0.2852(10)	0.2981(6)	5.3(2)
C(25)	0.3233(7)	0.3642(7)	0.0728(5)	3.79(17)
C(26)	0.3939(7)	0.4285(9)	0.0356(6)	4.24(19)
C(27)	0.3656(7)	0.5440(11)	-0.0101(6)	5.5(2)
C(28)	0.2658(8)	0.5972(11)	-0.0196(7)	6.0(2)
C(29)	0.1967(8)	0.5354(11)	0.0198(7)	6.1(2)
C(30)	0.2238(8)	0.4196(10)	0.0636(7)	5.5(2)
C(31)	0.4801(6)	-0.0527(8)	0.3562(6)	4.28(19)
C(32)	0.3713(6)	-0.1671(10)	0.2026(5)	5.2(2)
C(33)	0.6240(7)	-0.3325(8)	0.3238(6)	4.4(2)
C(34)	0.7199(8)	-0.3831(9)	0.3898(7)	4.5(2)
C(35)	0.8141(7)	-0.3948(9)	0.3664(7)	5.5(2)
C(36)	0.8138(8)	-0.3618(9)	0.2728(7)	5.6(2)
C(37)	0.7182(8)	-0.3160(9)	0.2049(7)	5.2(2)
C(38)	0.6246(7)	-0.3004(9)	0.2297(6)	5.0(2)
H(1)	0.7422	0.1056	0.2650	4.99
H(2)	0.8951	-0.0189	0.2671	6.17
H(3)	0.8082	-0.0985	0.2958	6.17
H(4)	0.9808	-0.1487	0.4082	6.61
H(5)	1.0086	-0.0045	0.4313	6.61
H(6)	0.9640	-0.0866	0.5614	5.64
H(7)	0.8552	-0.1462	0.4896	5.64
H(8)	0.8922	0.1199	0.5235	5.58
H(9)	0.8392	0.2820	0.3656	5.57
H(10)	0.9441	0.1962	0.3981	5.57
H(11)	1.0349	0.1466	0.2712	5.86
H(12)	1.0629	0.2083	0.1283	6.46
H(13)	0.9482	0.3587	0.0251	6.79
H(14)	0.8091	0.4518	0.0694	5.82
H(15)	0.7769	0.3816	0.2095	5.90
H(16)	0.7129	0.0539	0.5638	5.50
H(17)	0.8030	-0.0459	0.6184	5.50
H(18)	0.9318	0.0132	0.7758	7.41
H(19)	1.0197	0.1654	0.8966	7.44
H(20)	0.9818	0.3781	0.8625	7.08

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
H(21)	0.8543	0.4403	0.7145	7.71
H(22)	0.7737	0.2917	0.5954	6.56
H(23)	0.5435	0.1659	0.4243	5.05
H(24)	0.5555	0.0277	0.2633	4.78
H(25)	0.5331	0.3448	0.3226	5.63
H(26)	0.5592	0.2593	0.2439	5.63
H(27)	0.3307	0.3758	0.2902	6.38
H(28)	0.3613	0.2646	0.3670	6.38
H(29)	0.2608	0.2508	0.2692	6.38
H(30)	0.4139	0.5862	-0.0346	6.64
H(31)	0.2451	0.6743	-0.0523	7.20
H(32)	0.1307	0.5732	0.0164	7.37
H(33)	0.1750	0.3775	0.0874	6.56
H(34)	0.5045	-0.0708	0.4262	5.14
H(35)	0.4141	-0.0015	0.3404	5.14
H(36)	0.4009	-0.1199	0.1607	6.27
H(37)	0.3059	-0.1260	0.2043	6.27
H(38)	0.3539	-0.2518	0.1774	6.27
H(39)	0.8782	-0.4249	0.4133	6.59
H(40)	0.8769	-0.3706	0.2566	6.67
H(41)	0.7164	-0.2954	0.1418	6.28
H(42)	0.5612	-0.2681	0.1831	6.05

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0591(14)	0.0590(16)	0.0601(13)	0.0018(14)	0.0308(11)	0.0004(13)
S(2)	0.0619(15)	0.0648(18)	0.0673(15)	0.0009(16)	0.0366(12)	0.0033(15)
O(1)	0.051(3)	0.069(4)	0.060(3)	-0.000(3)	0.026(2)	-0.005(3)
O(2)	0.057(4)	0.053(4)	0.069(4)	-0.004(3)	0.033(3)	0.002(3)
O(3)	0.061(3)	0.057(4)	0.071(3)	0.003(3)	0.038(3)	-0.005(3)
O(4)	0.052(3)	0.064(4)	0.069(3)	-0.012(3)	0.029(3)	0.004(3)
O(5)	0.059(4)	0.112(6)	0.073(4)	0.001(4)	0.026(3)	0.019(4)
O(6)	0.090(4)	0.098(5)	0.074(4)	0.015(4)	0.051(4)	0.002(4)
O(7)	0.073(3)	0.072(4)	0.063(3)	0.008(4)	0.042(3)	0.003(3)
O(8)	0.068(4)	0.063(4)	0.094(4)	-0.020(4)	0.034(3)	-0.014(4)
O(9)	0.092(5)	0.067(5)	0.097(5)	-0.000(4)	0.055(4)	0.010(4)
O(10)	0.090(5)	0.084(6)	0.082(5)	0.021(4)	0.038(4)	0.004(4)
N(1)	0.061(4)	0.077(6)	0.041(3)	0.011(4)	0.028(3)	0.006(3)
N(2)	0.071(6)	0.079(7)	0.080(6)	0.006(5)	0.042(5)	0.018(5)
N(3)	0.057(4)	0.047(5)	0.051(4)	0.011(4)	0.014(3)	0.005(4)
N(4)	0.076(7)	0.086(8)	0.066(6)	0.010(6)	0.031(5)	-0.002(5)
C(1)	0.050(5)	0.050(6)	0.066(6)	0.009(5)	0.031(5)	0.007(5)
C(2)	0.068(6)	0.041(5)	0.064(5)	-0.006(5)	0.044(5)	0.008(4)
C(3)	0.066(6)	0.060(7)	0.080(7)	-0.006(5)	0.040(5)	-0.006(5)
C(4)	0.063(6)	0.084(8)	0.073(6)	0.001(6)	0.036(5)	0.005(6)
C(5)	0.053(5)	0.066(7)	0.065(5)	0.006(5)	0.028(4)	-0.002(5)
C(6)	0.056(5)	0.072(7)	0.055(5)	0.001(5)	0.026(5)	0.009(5)
C(7)	0.069(5)	0.060(6)	0.058(5)	-0.014(5)	0.035(4)	-0.005(5)
C(8)	0.054(5)	0.066(7)	0.056(5)	-0.016(5)	0.025(4)	-0.011(5)
C(9)	0.049(5)	0.083(7)	0.059(5)	-0.007(6)	0.024(4)	-0.003(5)
C(10)	0.064(6)	0.083(8)	0.067(6)	-0.011(6)	0.036(5)	-0.007(6)
C(11)	0.077(7)	0.101(9)	0.047(5)	-0.029(7)	0.035(5)	-0.013(6)
C(12)	0.072(6)	0.053(6)	0.060(5)	-0.005(5)	0.024(5)	-0.006(4)
C(13)	0.060(6)	0.070(7)	0.064(6)	-0.014(6)	0.030(5)	-0.020(5)
C(14)	0.060(5)	0.059(6)	0.064(6)	-0.002(5)	0.033(5)	-0.002(5)
C(15)	0.059(6)	0.070(8)	0.056(6)	0.003(6)	0.027(5)	0.001(6)
C(16)	0.072(7)	0.102(9)	0.080(7)	0.003(7)	0.051(6)	0.008(7)
C(17)	0.086(7)	0.106(10)	0.057(6)	-0.000(8)	0.041(5)	0.013(7)
C(18)	0.075(7)	0.084(9)	0.082(8)	-0.025(7)	0.049(6)	-0.008(7)
C(19)	0.089(8)	0.096(10)	0.076(7)	-0.009(7)	0.051(7)	-0.003(8)
C(20)	0.082(8)	0.075(8)	0.070(7)	0.002(7)	0.050(6)	-0.005(6)
C(21)	0.068(6)	0.047(6)	0.048(5)	0.001(5)	0.025(4)	-0.001(4)

Table 2. Anisotropic displacement parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(22)	0.051(5)	0.042(6)	0.068(6)	-0.006(5)	0.033(5)	0.004(5)
C(23)	0.060(6)	0.051(6)	0.072(6)	-0.001(5)	0.028(5)	0.006(5)
C(24)	0.078(6)	0.076(7)	0.062(6)	0.001(5)	0.042(5)	-0.000(5)
C(25)	0.068(6)	0.028(5)	0.054(5)	0.008(4)	0.029(4)	0.015(4)
C(26)	0.055(6)	0.055(6)	0.051(5)	0.006(5)	0.019(4)	0.015(5)
C(27)	0.052(6)	0.096(9)	0.068(6)	-0.002(6)	0.029(5)	0.009(6)
C(28)	0.080(7)	0.083(8)	0.084(7)	0.023(6)	0.053(6)	0.033(6)
C(29)	0.067(6)	0.084(8)	0.102(8)	0.015(6)	0.053(6)	0.013(7)
C(30)	0.068(6)	0.067(7)	0.086(7)	0.016(6)	0.043(5)	0.025(6)
C(31)	0.051(5)	0.050(6)	0.069(6)	0.001(5)	0.030(4)	0.003(5)
C(32)	0.049(5)	0.086(8)	0.061(6)	0.005(5)	0.015(5)	0.004(5)
C(33)	0.062(6)	0.052(7)	0.067(5)	-0.000(5)	0.041(5)	-0.004(5)
C(34)	0.061(6)	0.057(6)	0.068(6)	0.003(5)	0.039(5)	0.000(5)
C(35)	0.062(6)	0.077(7)	0.071(6)	0.007(6)	0.025(5)	-0.008(6)
C(36)	0.068(7)	0.077(8)	0.079(7)	0.010(6)	0.043(6)	-0.008(6)
C(37)	0.075(6)	0.067(7)	0.077(6)	-0.015(6)	0.052(5)	-0.012(6)
C(38)	0.071(5)	0.064(6)	0.067(5)	-0.008(6)	0.038(4)	-0.014(5)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S(1)	O(3)	1.436(6)	S(1)	O(4)	1.438(6)
S(1)	N(1)	1.640(6)	S(1)	C(25)	1.783(8)
S(2)	O(7)	1.446(5)	S(2)	O(8)	1.453(6)
S(2)	N(3)	1.614(7)	S(2)	C(33)	1.774(10)
O(1)	C(1)	1.445(11)	O(1)	C(21)	1.435(10)
O(2)	C(1)	1.428(11)	O(2)	C(22)	1.423(10)
O(5)	N(2)	1.223(10)	O(6)	N(2)	1.226(13)
O(9)	N(4)	1.203(14)	O(10)	N(4)	1.248(11)
N(1)	C(23)	1.479(10)	N(1)	C(24)	1.492(13)
N(2)	C(26)	1.469(14)	N(3)	C(31)	1.458(11)
N(3)	C(32)	1.469(9)	N(4)	C(34)	1.469(15)
C(1)	C(2)	1.515(15)	C(1)	C(6)	1.544(10)
C(2)	C(3)	1.536(14)	C(2)	C(7)	1.550(13)
C(3)	C(4)	1.539(11)	C(4)	C(5)	1.535(14)
C(5)	C(6)	1.557(14)	C(6)	C(14)	1.540(14)
C(7)	C(8)	1.521(14)	C(8)	C(9)	1.388(14)
C(8)	C(13)	1.395(12)	C(9)	C(10)	1.384(14)
C(10)	C(11)	1.397(13)	C(11)	C(12)	1.391(16)
C(12)	C(13)	1.395(14)	C(14)	C(15)	1.501(13)
C(15)	C(16)	1.386(13)	C(15)	C(20)	1.403(17)
C(16)	C(17)	1.430(16)	C(17)	C(18)	1.37(2)
C(18)	C(19)	1.379(14)	C(19)	C(20)	1.381(16)
C(21)	C(22)	1.515(12)	C(21)	C(23)	1.527(11)
C(22)	C(31)	1.547(13)	C(25)	C(26)	1.385(14)
C(25)	C(30)	1.381(14)	C(26)	C(27)	1.372(14)
C(27)	C(28)	1.374(15)	C(28)	C(29)	1.379(17)
C(29)	C(30)	1.362(15)	C(33)	C(34)	1.389(12)
C(33)	C(38)	1.404(13)	C(34)	C(35)	1.380(16)
C(35)	C(36)	1.395(16)	C(36)	C(37)	1.379(13)
C(37)	C(38)	1.389(15)			

Table 4. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C(2)	H(1)	0.980	C(3)	H(2)	0.970
C(3)	H(3)	0.970	C(4)	H(4)	0.970
C(4)	H(5)	0.970	C(5)	H(6)	0.970
C(5)	H(7)	0.970	C(6)	H(8)	0.980
C(7)	H(9)	0.970	C(7)	H(10)	0.970
C(9)	H(11)	0.930	C(10)	H(12)	0.930
C(11)	H(13)	0.930	C(12)	H(14)	0.930
C(13)	H(15)	0.930	C(14)	H(16)	0.970
C(14)	H(17)	0.970	C(16)	H(18)	0.930
C(17)	H(19)	0.930	C(18)	H(20)	0.930
C(19)	H(21)	0.930	C(20)	H(22)	0.930
C(21)	H(23)	0.980	C(22)	H(24)	0.980
C(23)	H(25)	0.970	C(23)	H(26)	0.970
C(24)	H(27)	0.960	C(24)	H(28)	0.960
C(24)	H(29)	0.960	C(27)	H(30)	0.930
C(28)	H(31)	0.930	C(29)	H(32)	0.930
C(30)	H(33)	0.930	C(31)	H(34)	0.970
C(31)	H(35)	0.970	C(32)	H(36)	0.960
C(32)	H(37)	0.960	C(32)	H(38)	0.960
C(35)	H(39)	0.930	C(36)	H(40)	0.930
C(37)	H(41)	0.930	C(38)	H(42)	0.930

Table 5. Bond angles (^{o})

atom	atom	atom	angle	atom	atom	atom	angle
O(3)	S(1)	O(4)	120.2(3)	O(3)	S(1)	N(1)	107.2(3)
O(3)	S(1)	C(25)	107.6(4)	O(4)	S(1)	N(1)	107.0(3)
O(4)	S(1)	C(25)	105.9(3)	N(1)	S(1)	C(25)	108.6(3)
O(7)	S(2)	O(8)	121.0(4)	O(7)	S(2)	N(3)	107.3(4)
O(7)	S(2)	C(33)	105.4(3)	O(8)	S(2)	N(3)	108.7(3)
O(8)	S(2)	C(33)	106.7(4)	N(3)	S(2)	C(33)	106.9(4)
C(1)	O(1)	C(21)	108.8(6)	C(1)	O(2)	C(22)	107.3(6)
S(1)	N(1)	C(23)	119.2(6)	S(1)	N(1)	C(24)	116.7(4)
C(23)	N(1)	C(24)	115.6(6)	O(5)	N(2)	O(6)	125.4(9)
O(5)	N(2)	C(26)	117.0(9)	O(6)	N(2)	C(26)	117.7(7)
S(2)	N(3)	C(31)	122.1(5)	S(2)	N(3)	C(32)	120.9(6)
C(31)	N(3)	C(32)	116.9(7)	O(9)	N(4)	O(10)	126.5(10)
O(9)	N(4)	C(34)	119.4(8)	O(10)	N(4)	C(34)	114.1(10)
O(1)	C(1)	O(2)	106.2(6)	O(1)	C(1)	C(2)	110.1(7)
O(1)	C(1)	C(6)	108.6(7)	O(2)	C(1)	C(2)	111.8(7)
O(2)	C(1)	C(6)	108.3(7)	C(2)	C(1)	C(6)	111.6(7)
C(1)	C(2)	C(3)	109.1(7)	C(1)	C(2)	C(7)	112.1(7)
C(3)	C(2)	C(7)	114.1(8)	C(2)	C(3)	C(4)	111.1(7)
C(3)	C(4)	C(5)	112.1(7)	C(4)	C(5)	C(6)	112.5(8)
C(1)	C(6)	C(5)	108.5(7)	C(1)	C(6)	C(14)	112.5(7)
C(5)	C(6)	C(14)	112.1(7)	C(2)	C(7)	C(8)	114.6(7)
C(7)	C(8)	C(9)	122.9(8)	C(7)	C(8)	C(13)	118.1(9)
C(9)	C(8)	C(13)	118.9(9)	C(8)	C(9)	C(10)	120.8(8)
C(9)	C(10)	C(11)	120.1(10)	C(10)	C(11)	C(12)	119.7(10)
C(11)	C(12)	C(13)	119.5(8)	C(8)	C(13)	C(12)	120.9(9)
C(6)	C(14)	C(15)	111.9(8)	C(14)	C(15)	C(16)	122.5(10)
C(14)	C(15)	C(20)	121.1(8)	C(16)	C(15)	C(20)	116.3(9)
C(15)	C(16)	C(17)	122.0(11)	C(16)	C(17)	C(18)	118.6(9)
C(17)	C(18)	C(19)	120.7(11)	C(18)	C(19)	C(20)	119.7(11)
C(15)	C(20)	C(19)	122.6(9)	O(1)	C(21)	C(22)	105.1(7)
O(1)	C(21)	C(23)	108.2(7)	C(22)	C(21)	C(23)	114.2(6)
O(2)	C(22)	C(21)	104.8(6)	O(2)	C(22)	C(31)	110.2(6)
C(21)	C(22)	C(31)	112.6(8)	N(1)	C(23)	C(21)	107.9(7)
S(1)	C(25)	C(26)	122.9(7)	S(1)	C(25)	C(30)	118.6(7)
C(26)	C(25)	C(30)	118.5(8)	N(2)	C(26)	C(25)	124.8(8)
N(2)	C(26)	C(27)	114.0(9)	C(25)	C(26)	C(27)	121.1(9)
C(26)	C(27)	C(28)	119.7(10)	C(27)	C(28)	C(29)	119.4(10)

Table 5. Bond angles (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(28)	C(29)	C(30)	120.8(10)	C(25)	C(30)	C(29)	120.4(10)
N(3)	C(31)	C(22)	115.0(8)	S(2)	C(33)	C(34)	123.9(8)
S(2)	C(33)	C(38)	118.9(6)	C(34)	C(33)	C(38)	117.2(9)
N(4)	C(34)	C(33)	121.1(10)	N(4)	C(34)	C(35)	117.0(8)
C(33)	C(34)	C(35)	121.8(9)	C(34)	C(35)	C(36)	120.4(8)
C(35)	C(36)	C(37)	118.7(11)	C(36)	C(37)	C(38)	120.8(10)
C(33)	C(38)	C(37)	121.0(7)				

Table 6. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	C(2)	H(1)	107.0	C(3)	C(2)	H(1)	107.0
C(7)	C(2)	H(1)	107.1	C(2)	C(3)	H(2)	109.4
C(2)	C(3)	H(3)	109.4	C(4)	C(3)	H(2)	109.4
C(4)	C(3)	H(3)	109.4	H(2)	C(3)	H(3)	108.0
C(3)	C(4)	H(4)	109.2	C(3)	C(4)	H(5)	109.2
C(5)	C(4)	H(4)	109.2	C(5)	C(4)	H(5)	109.2
H(4)	C(4)	H(5)	107.9	C(4)	C(5)	H(6)	109.1
C(4)	C(5)	H(7)	109.1	C(6)	C(5)	H(6)	109.1
C(6)	C(5)	H(7)	109.1	H(6)	C(5)	H(7)	107.8
C(1)	C(6)	H(8)	107.9	C(5)	C(6)	H(8)	107.9
C(14)	C(6)	H(8)	107.9	C(2)	C(7)	H(9)	108.6
C(2)	C(7)	H(10)	108.6	C(8)	C(7)	H(9)	108.6
C(8)	C(7)	H(10)	108.6	H(9)	C(7)	H(10)	107.6
C(8)	C(9)	H(11)	119.6	C(10)	C(9)	H(11)	119.6
C(9)	C(10)	H(12)	119.9	C(11)	C(10)	H(12)	119.9
C(10)	C(11)	H(13)	120.2	C(12)	C(11)	H(13)	120.1
C(11)	C(12)	H(14)	120.2	C(13)	C(12)	H(14)	120.2
C(8)	C(13)	H(15)	119.6	C(12)	C(13)	H(15)	119.6
C(6)	C(14)	H(16)	109.2	C(6)	C(14)	H(17)	109.2
C(15)	C(14)	H(16)	109.2	C(15)	C(14)	H(17)	109.2
H(16)	C(14)	H(17)	107.9	C(15)	C(16)	H(18)	119.0
C(17)	C(16)	H(18)	119.0	C(16)	C(17)	H(19)	120.7
C(18)	C(17)	H(19)	120.7	C(17)	C(18)	H(20)	119.6
C(19)	C(18)	H(20)	119.6	C(18)	C(19)	H(21)	120.1
C(20)	C(19)	H(21)	120.2	C(15)	C(20)	H(22)	118.7
C(19)	C(20)	H(22)	118.7	O(1)	C(21)	H(23)	109.7
C(22)	C(21)	H(23)	109.7	C(23)	C(21)	H(23)	109.7
O(2)	C(22)	H(24)	109.7	C(21)	C(22)	H(24)	109.7
C(31)	C(22)	H(24)	109.7	N(1)	C(23)	H(25)	110.1
N(1)	C(23)	H(26)	110.1	C(21)	C(23)	H(25)	110.1
C(21)	C(23)	H(26)	110.1	H(25)	C(23)	H(26)	108.4
N(1)	C(24)	H(27)	109.5	N(1)	C(24)	H(28)	109.5
N(1)	C(24)	H(29)	109.5	H(27)	C(24)	H(28)	109.5
H(27)	C(24)	H(29)	109.5	H(28)	C(24)	H(29)	109.5
C(26)	C(27)	H(30)	120.1	C(28)	C(27)	H(30)	120.1
C(27)	C(28)	H(31)	120.3	C(29)	C(28)	H(31)	120.3
C(28)	C(29)	H(32)	119.6	C(30)	C(29)	H(32)	119.6

Table 6. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C(25)	C(30)	H(33)	119.8	C(29)	C(30)	H(33)	119.8
N(3)	C(31)	H(34)	108.5	N(3)	C(31)	H(35)	108.5
C(22)	C(31)	H(34)	108.5	C(22)	C(31)	H(35)	108.5
H(34)	C(31)	H(35)	107.5	N(3)	C(32)	H(36)	109.5
N(3)	C(32)	H(37)	109.5	N(3)	C(32)	H(38)	109.5
H(36)	C(32)	H(37)	109.5	H(36)	C(32)	H(38)	109.5
H(37)	C(32)	H(38)	109.5	C(34)	C(35)	H(39)	119.8
C(36)	C(35)	H(39)	119.8	C(35)	C(36)	H(40)	120.7
C(37)	C(36)	H(40)	120.7	C(36)	C(37)	H(41)	119.6
C(38)	C(37)	H(41)	119.6	C(33)	C(38)	H(42)	119.5
C(37)	C(38)	H(42)	119.5				

Table 7. Torsion Angles(°)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O(3)	S(1)	N(1)	C(23)	34.3(7)	O(3)	S(1)	N(1)	C(24)	-179.0(6)
O(3)	S(1)	C(25)	C(26)	-19.5(7)	O(3)	S(1)	C(25)	C(30)	158.5(6)
O(4)	S(1)	N(1)	C(23)	164.4(6)	O(4)	S(1)	N(1)	C(24)	-48.9(7)
O(4)	S(1)	C(25)	C(26)	-149.2(6)	O(4)	S(1)	C(25)	C(30)	28.9(7)
N(1)	S(1)	C(25)	C(26)	96.2(7)	N(1)	S(1)	C(25)	C(30)	-85.8(7)
C(25)	S(1)	N(1)	C(23)	-81.6(7)	C(25)	S(1)	N(1)	C(24)	65.1(7)
O(7)	S(2)	N(3)	C(31)	21.0(8)	O(7)	S(2)	N(3)	C(32)	-155.7(6)
O(7)	S(2)	C(33)	C(34)	26.1(9)	O(7)	S(2)	C(33)	C(38)	-153.9(7)
O(8)	S(2)	N(3)	C(31)	153.5(7)	O(8)	S(2)	N(3)	C(32)	-23.2(8)
O(8)	S(2)	C(33)	C(34)	-103.7(8)	O(8)	S(2)	C(33)	C(38)	76.4(8)
N(3)	S(2)	C(33)	C(34)	140.1(7)	N(3)	S(2)	C(33)	C(38)	-39.9(8)
C(33)	S(2)	N(3)	C(31)	-91.7(7)	C(33)	S(2)	N(3)	C(32)	91.7(7)
C(1)	O(1)	C(21)	C(22)	-2.6(9)	C(1)	O(1)	C(21)	C(23)	-125.0(7)
C(21)	O(1)	C(1)	O(2)	-14.5(8)	C(21)	O(1)	C(1)	C(2)	106.7(7)
C(21)	O(1)	C(1)	C(6)	-130.7(7)	C(1)	O(2)	C(22)	C(21)	-28.2(9)
C(1)	O(2)	C(22)	C(31)	-149.6(7)	C(22)	O(2)	C(1)	O(1)	26.9(9)
C(22)	O(2)	C(1)	C(2)	-93.2(8)	C(22)	O(2)	C(1)	C(6)	143.4(8)
S(1)	N(1)	C(23)	C(21)	-125.2(7)	C(24)	N(1)	C(23)	C(21)	87.8(9)
O(5)	N(2)	C(26)	C(25)	-74.6(12)	O(5)	N(2)	C(26)	C(27)	102.3(10)
O(6)	N(2)	C(26)	C(25)	104.4(11)	O(6)	N(2)	C(26)	C(27)	-78.7(11)
S(2)	N(3)	C(31)	C(22)	98.7(8)	C(32)	N(3)	C(31)	C(22)	-84.5(8)
O(9)	N(4)	C(34)	C(33)	55.8(14)	O(9)	N(4)	C(34)	C(35)	-120.0(11)
O(10)	N(4)	C(34)	C(33)	-123.8(10)	O(10)	N(4)	C(34)	C(35)	60.4(13)
O(1)	C(1)	C(2)	C(3)	-177.2(6)	O(1)	C(1)	C(2)	C(7)	55.5(8)
O(1)	C(1)	C(6)	C(5)	179.2(7)	O(1)	C(1)	C(6)	C(14)	54.6(10)
O(2)	C(1)	C(2)	C(3)	-59.4(8)	O(2)	C(1)	C(2)	C(7)	173.2(6)
O(2)	C(1)	C(6)	C(5)	64.3(10)	O(2)	C(1)	C(6)	C(14)	-60.3(10)
C(2)	C(1)	C(6)	C(5)	-59.2(10)	C(2)	C(1)	C(6)	C(14)	176.3(7)
C(6)	C(1)	C(2)	C(3)	62.0(9)	C(6)	C(1)	C(2)	C(7)	-65.3(9)
C(1)	C(2)	C(3)	C(4)	-58.0(9)	C(1)	C(2)	C(7)	C(8)	-163.7(7)
C(3)	C(2)	C(7)	C(8)	71.6(9)	C(7)	C(2)	C(3)	C(4)	68.2(10)
C(2)	C(3)	C(4)	C(5)	53.6(11)	C(3)	C(4)	C(5)	C(6)	-51.9(10)
C(4)	C(5)	C(6)	C(1)	53.4(9)	C(4)	C(5)	C(6)	C(14)	178.2(6)
C(1)	C(6)	C(14)	C(15)	-122.4(8)	C(5)	C(6)	C(14)	C(15)	115.0(8)
C(2)	C(7)	C(8)	C(9)	-83.9(10)	C(2)	C(7)	C(8)	C(13)	92.9(10)
C(7)	C(8)	C(9)	C(10)	175.9(8)	C(7)	C(8)	C(13)	C(12)	-177.8(8)
C(9)	C(8)	C(13)	C(12)	-0.9(13)	C(13)	C(8)	C(9)	C(10)	-0.8(14)

Table 7. Torsion angles (^{o}) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C(8)	C(9)	C(10)	C(11)	0.7(14)	C(9)	C(10)	C(11)	C(12)	1.0(14)
C(10)	C(11)	C(12)	C(13)	-2.6(14)	C(11)	C(12)	C(13)	C(8)	2.6(13)
C(6)	C(14)	C(15)	C(16)	-106.0(12)	C(6)	C(14)	C(15)	C(20)	69.4(12)
C(14)	C(15)	C(16)	C(17)	175.5(11)	C(14)	C(15)	C(20)	C(19)	-176.7(11)
C(16)	C(15)	C(20)	C(19)	-1.1(18)	C(20)	C(15)	C(16)	C(17)	-0.1(17)
C(15)	C(16)	C(17)	C(18)	0.0(18)	C(16)	C(17)	C(18)	C(19)	1.1(19)
C(17)	C(18)	C(19)	C(20)	-2(2)	C(18)	C(19)	C(20)	C(15)	2(2)
O(1)	C(21)	C(22)	O(2)	18.7(9)	O(1)	C(21)	C(22)	C(31)	138.5(6)
O(1)	C(21)	C(23)	N(1)	177.8(7)	C(22)	C(21)	C(23)	N(1)	61.2(10)
C(23)	C(21)	C(22)	O(2)	137.2(8)	C(23)	C(21)	C(22)	C(31)	-103.1(9)
O(2)	C(22)	C(31)	N(3)	-76.6(8)	C(21)	C(22)	C(31)	N(3)	166.8(6)
S(1)	C(25)	C(26)	N(2)	-5.8(12)	S(1)	C(25)	C(26)	C(27)	177.5(6)
S(1)	C(25)	C(30)	C(29)	-178.8(7)	C(26)	C(25)	C(30)	C(29)	-0.7(12)
C(30)	C(25)	C(26)	N(2)	176.1(8)	C(30)	C(25)	C(26)	C(27)	-0.5(11)
N(2)	C(26)	C(27)	C(28)	-177.1(8)	C(25)	C(26)	C(27)	C(28)	-0.1(11)
C(26)	C(27)	C(28)	C(29)	2.0(14)	C(27)	C(28)	C(29)	C(30)	-3.2(15)
C(28)	C(29)	C(30)	C(25)	2.6(14)	S(2)	C(33)	C(34)	N(4)	8.1(13)
S(2)	C(33)	C(34)	C(35)	-176.2(7)	S(2)	C(33)	C(38)	C(37)	178.4(7)
C(34)	C(33)	C(38)	C(37)	-1.5(14)	C(38)	C(33)	C(34)	N(4)	-171.9(9)
C(38)	C(33)	C(34)	C(35)	3.7(13)	N(4)	C(34)	C(35)	C(36)	172.4(9)
C(33)	C(34)	C(35)	C(36)	-3.4(14)	C(34)	C(35)	C(36)	C(37)	0.8(13)
C(35)	C(36)	C(37)	C(38)	1.4(15)	C(36)	C(37)	C(38)	C(33)	-1.0(15)

The sign is positive if when looking from atom 2 to atom 3 a clock-wise motion of atom 1 would superimpose it on atom 4.

Table 8. Distances beyond the asymmetric unit out to 3.60 Å

atom	atom	distance	atom	atom	distance
O(1)	O(9)$^{1)}$	3.344(10)	O(3)	O(6)$^{2)}$	3.570(9)
O(3)	C(27)$^{2)}$	3.422(12)	O(4)	C(10)$^{3)}$	3.526(12)
O(5)	C(37)$^{1)}$	3.511(12)	O(5)	C(38)$^{1)}$	3.475(12)
O(6)	C(27)$^{2)}$	3.415(13)	O(6)	C(32)$^{4)}$	3.304(12)
O(6)	C(38)$^{4)}$	3.224(10)	O(7)	C(21)$^{5)}$	3.326(12)
O(7)	C(24)$^{5)}$	3.439(9)	O(8)	C(24)$^{6)}$	3.445(12)
O(9)	C(20)$^{6)}$	3.482(12)	O(9)	C(31)$^{5)}$	3.372(13)
O(10)	C(9)$^{7)}$	3.517(10)	O(10)	C(19)$^{6)}$	3.575(14)
O(10)	C(24)$^{5)}$	3.557(13)	C(11)	C(28)$^{2)}$	3.517(15)
C(12)	C(28)$^{2)}$	3.476(14)	C(13)	C(28)$^{2)}$	3.569(14)
C(13)	C(36)$^{1)}$	3.305(14)			

Symmetry Operators:

(1) X,Y+1,Z
(2) -X+1,Y+1/2-1,-Z
(3) X-1,Y,Z
(4) -X+1,Y+1/2,-Z
(5) -X+1,Y+1/2-1,-Z+1
(6) X,Y-1,Z
(7) -X+2,Y+1/2-1,-Z+1

Table 9. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S(2)	H(23)$^{1)}$	3.498	O(3)	H(30)$^{2)}$	2.507
O(3)	H(41)$^{3)}$	3.384	O(4)	H(12)$^{4)}$	2.614
O(4)	H(14)$^{2)}$	3.183	O(4)	H(19)$^{5)}$	3.472
O(5)	H(30)$^{2)}$	3.553	O(6)	H(30)$^{2)}$	2.854
O(6)	H(31)$^{2)}$	3.371	O(6)	H(36)$^{3)}$	2.519
O(6)	H(38)$^{3)}$	3.285	O(6)	H(41)$^{3)}$	3.248
O(6)	H(42)$^{3)}$	2.406	O(7)	H(16)$^{1)}$	3.579
O(7)	H(23)$^{1)}$	2.354	O(7)	H(28)$^{1)}$	2.486
O(7)	H(34)$^{1)}$	3.540	O(7)	H(35)$^{1)}$	3.554
O(8)	H(16)$^{1)}$	3.079	O(8)	H(25)$^{6)}$	2.916
O(8)	H(27)$^{6)}$	2.574	O(9)	H(21)$^{6)}$	3.418
O(9)	H(22)$^{6)}$	2.661	O(9)	H(25)$^{6)}$	2.789
O(9)	H(34)$^{1)}$	2.873	O(9)	H(35)$^{1)}$	2.965
O(10)	H(5)$^{7)}$	2.806	O(10)	H(10)$^{7)}$	3.347
O(10)	H(11)$^{7)}$	2.720	O(10)	H(21)$^{6)}$	2.811
O(10)	H(22)$^{6)}$	3.466	O(10)	H(28)$^{1)}$	3.040
O(10)	H(29)$^{1)}$	3.169	N(2)	H(30)$^{2)}$	3.344
N(2)	H(36)$^{3)}$	3.581	N(2)	H(42)$^{3)}$	3.506
N(4)	H(5)$^{7)}$	3.351	N(4)	H(21)$^{6)}$	3.427
N(4)	H(22)$^{6)}$	3.244	N(4)	H(28)$^{1)}$	3.431
C(4)	H(10)$^{7)}$	3.584	C(4)	H(39)$^{8)}$	3.090
C(5)	H(9)$^{7)}$	3.571	C(5)	H(10)$^{7)}$	3.151
C(5)	H(39)$^{8)}$	3.096	C(6)	H(39)$^{8)}$	3.446
C(7)	H(6)$^{8)}$	2.942	C(8)	H(6)$^{8)}$	3.093
C(8)	H(18)$^{8)}$	3.566	C(8)	H(31)$^{2)}$	3.033
C(9)	H(6)$^{8)}$	3.595	C(9)	H(18)$^{8)}$	3.398
C(9)	H(21)$^{7)}$	3.394	C(9)	H(29)$^{9)}$	3.413
C(9)	H(31)$^{2)}$	3.252	C(10)	H(18)$^{8)}$	3.061
C(10)	H(29)$^{9)}$	3.181	C(10)	H(31)$^{2)}$	3.151
C(10)	H(32)$^{2)}$	2.992	C(10)	H(33)$^{9)}$	2.955
C(11)	H(18)$^{8)}$	2.864	C(11)	H(19)$^{8)}$	3.520
C(11)	H(20)$^{10)}$	3.458	C(11)	H(31)$^{2)}$	2.815
C(11)	H(32)$^{2)}$	3.088	C(11)	H(33)$^{9)}$	3.095
C(12)	H(18)$^{8)}$	3.017	C(12)	H(19)$^{8)}$	3.359
C(12)	H(31)$^{2)}$	2.582	C(12)	H(40)$^{11)}$	3.259
C(13)	H(18)$^{8)}$	3.385	C(13)	H(31)$^{2)}$	2.672
C(13)	H(40)$^{11)}$	3.091	C(14)	H(27)$^{1)}$	3.206

Table 9. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C(15)	H(40)$^{8)}$	3.434	C(16)	H(32)$^{1)}$	3.464
C(16)	H(40)$^{8)}$	2.807	C(17)	H(13)$^{12)}$	3.345
C(17)	H(32)$^{1)}$	3.112	C(17)	H(40)$^{8)}$	2.825
C(18)	H(2)$^{8)}$	3.211	C(18)	H(13)$^{12)}$	3.050
C(18)	H(37)$^{13)}$	3.244	C(18)	H(40)$^{8)}$	3.446
C(19)	H(2)$^{8)}$	3.280	C(19)	H(4)$^{8)}$	3.166
C(19)	H(5)$^{8)}$	3.501	C(19)	H(11)$^{8)}$	3.298
C(19)	H(37)$^{13)}$	2.811	C(20)	H(4)$^{8)}$	3.138
C(20)	H(37)$^{13)}$	3.233	C(24)	H(17)$^{13)}$	3.034
C(25)	H(41)$^{3)}$	3.407	C(26)	H(41)$^{3)}$	3.414
C(27)	H(1)$^{3)}$	3.523	C(27)	H(38)$^{11)}$	3.501
C(28)	H(1)$^{3)}$	3.512	C(28)	H(38)$^{11)}$	3.114
C(29)	H(20)$^{5)}$	3.367	C(29)	H(38)$^{11)}$	3.344
C(30)	H(12)$^{4)}$	3.393	C(30)	H(13)$^{4)}$	3.486
C(30)	H(20)$^{5)}$	3.500	C(33)	H(25)$^{6)}$	3.592
C(35)	H(5)$^{7)}$	3.250	C(35)	H(6)$^{7)}$	3.375
C(35)	H(8)$^{7)}$	3.595	C(35)	H(9)$^{6)}$	3.415
C(35)	H(15)$^{6)}$	3.187	C(36)	H(14)$^{6)}$	3.516
C(36)	H(15)$^{6)}$	2.837	C(37)	H(14)$^{6)}$	3.574
C(37)	H(15)$^{6)}$	3.266	H(1)	H(30)$^{2)}$	3.257
H(1)	H(31)$^{2)}$	3.216	H(2)	H(20)$^{7)}$	3.046
H(2)	H(21)$^{7)}$	3.199	H(4)	H(8)$^{7)}$	2.915
H(4)	H(9)$^{7)}$	3.383	H(4)	H(10)$^{7)}$	3.095
H(4)	H(21)$^{7)}$	3.345	H(4)	H(22)$^{7)}$	3.264
H(4)	H(39)$^{8)}$	3.508	H(5)	H(21)$^{7)}$	3.241
H(5)	H(39)$^{8)}$	2.375	H(6)	H(9)$^{7)}$	2.775
H(6)	H(10)$^{7)}$	2.550	H(6)	H(39)$^{8)}$	2.590
H(6)	H(40)$^{8)}$	3.554	H(7)	H(10)$^{7)}$	3.045
H(8)	H(39)$^{8)}$	2.841	H(8)	H(40)$^{8)}$	3.545
H(9)	H(39)$^{11)}$	3.161	H(10)	H(39)$^{8)}$	3.173
H(11)	H(20)$^{7)}$	3.386	H(11)	H(21)$^{7)}$	2.572
H(11)	H(29)$^{9)}$	3.138	H(12)	H(18)$^{8)}$	3.485
H(12)	H(19)$^{10)}$	3.232	H(12)	H(20)$^{7)}$	3.531
H(12)	H(21)$^{7)}$	3.549	H(12)	H(29)$^{9)}$	2.712
H(12)	H(32)$^{2)}$	3.017	H(12)	H(33)$^{9)}$	2.495
H(13)	H(18)$^{8)}$	3.205	H(13)	H(19)$^{10)}$	3.102
H(13)	H(19)$^{8)}$	3.396	H(13)	H(20)$^{10)}$	2.541

Table 9. Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H(13)	H(31)$^{2)}$	3.298	H(13)	H(32)$^{9)}$	3.304
H(13)	H(32)$^{2)}$	3.163	H(13)	H(33)$^{9)}$	2.774
H(14)	H(18)$^{8)}$	3.402	H(14)	H(19)$^{8)}$	3.079
H(14)	H(31)$^{2)}$	2.993	H(14)	H(36)$^{3)}$	3.584
H(14)	H(40)$^{11)}$	3.154	H(14)	H(41)$^{11)}$	3.237
H(15)	H(31)$^{2)}$	3.091	H(15)	H(39)$^{11)}$	3.449
H(15)	H(40)$^{11)}$	2.888	H(15)	H(41)$^{11)}$	3.548
H(16)	H(27)$^{1)}$	3.017	H(16)	H(28)$^{1)}$	3.443
H(17)	H(27)$^{1)}$	2.647	H(17)	H(28)$^{1)}$	2.979
H(17)	H(29)$^{1)}$	2.970	H(18)	H(27)$^{1)}$	3.518
H(18)	H(32)$^{1)}$	3.427	H(18)	H(33)$^{1)}$	3.121
H(18)	H(40)$^{8)}$	2.944	H(19)	H(32)$^{1)}$	2.830
H(19)	H(33)$^{14)}$	3.583	H(19)	H(40)$^{8)}$	2.980
H(20)	H(32)$^{14)}$	3.154	H(20)	H(33)$^{14)}$	3.357
H(20)	H(37)$^{13)}$	3.521	H(21)	H(35)$^{13)}$	3.353
H(21)	H(37)$^{13)}$	2.802	H(22)	H(37)$^{13)}$	3.498
H(24)	H(30)$^{2)}$	3.515	H(28)	H(34)$^{13)}$	3.377
H(30)	H(42)$^{11)}$	3.433	H(31)	H(38)$^{11)}$	3.225
H(32)	H(38)$^{11)}$	3.547			

Symmetry Operators:

(1) -X+1,Y+1/2-1,-Z+1
(2) -X+1,Y+1/2-1,-Z
(3) -X+1,Y+1/2,-Z
(4) X-1,Y,Z
(5) X-1,Y,Z-1
(6) X,Y-1,Z
(7) -X+2,Y+1/2-1,-Z+1
(8) -X+2,Y+1/2,-Z+1
(9) X+1,Y,Z
(10) X,Y,Z-1
(11) X,Y+1,Z
(12) X,Y,Z+1
(13) -X+1,Y+1/2,-Z+1
(14) X+1,Y,Z+1