Catalytic Asymmetric Aldol Reactions in Aqueous Media Using Chiral Bis-pyridino-18-crown-6–Rare Earth Metal Triflate Complexes

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Supporting Information 1

Experimental Section

General: Melting points were uncorrected. IR spectra were measured with JASCO FT/IR-610 spectrometers. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, or JNM-LA500 spectrometer in CDCl₃ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ¹H NMR and CDCl₃ as internal standard ($\delta = 77.0$) for ¹³C NMR. X-ray crystal structure analysis were performed on a Rigaku R-Axis RAPID AUTO. Preparative thin-layer chromatography was carried out using Wakogel B-5F.

Synthesis of Crown Ethers:

Crown ethers **1**, **3**, **4**, **7**, **8**, and **9** were synthesized as shown in Eqs. 1, 5, 6, 2, 3, and 4, respectively. Although crown ether **1** is a known compound¹, we have developed a new modified procedure for the synthesis of **1** as shown in Eq. 1.

(4)

(5)

(6)

10: A solution of (2*R*,3*R*)-2,3-butanediol (56.8 mmol), *p*-anisaldehyde (86.4 mmol), and *p*-toluenesulfonic acid monohydrate (TsOH•H₂O) (0.568 mmol) in benzene (250 mL) was refluxed in a Dean-Stark apparatus. After 30 h, the solution was washed with 10% NaOH (200 mL), and the aqueous layer was extracted with dichloromethane (2 x 250 mL). The combined organic phases were dried over MgSO₄ and concentrated *in vacuo*. To the residue was added dichloromethane (43 mL) under argon, and the solution was stirred at –78 °C. To the solution was added DIBAL (209 mL, 199 mmol, 0.95 M in *n*-hexane), and the reaction mixture was stirred at –78 °C. After 3 h, the reaction mixture was gradually allowed to warm to room temperature with stirring. Methanol (15 mL) was added, and the resultant solution was washed with 10% Rochelle salt (270 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 x 250 mL). The combined organic phases were washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (4/1)) to afford **10** (86% yield) as a colorless oil: ¹H NMR (CDCl₃) δ 1.13 (d, 3H, *J* = 6.4 Hz), 1.15 (d, 3H, *J* = 6.2 Hz), 2.61 (brs), 3.28 (dq, 1H, *J* = 6.6, 6.5 Hz), 3.58 (quin, 1H, *J* = 6.6 Hz), 3.79 (s, 3H), 4.36 (d, 1H, *J* = 11.2 Hz), 4.59 (d, 1H, *J* = 11.2 Hz), 6.84-6.91 (m, 2H), 7.22-7.29 (m, 2H); ¹³C NMR (CDCl₃) δ 15.4, 18.5, 55.2, 70.7, 71.1, 79.9, 113.9, 129.4, 130.3, 159.2; IR (neat) 2975, 2874, 1613, 1514, 1246, 1083, 1037, 825 cm⁻¹; HRMS calcd for C₁₂H₁₈O₃: 210.1256, found: 210.1268; [α]_D²³ –26.8 (*c* 1.00, EtOH).

12: Under argon, sodium hydride (7.67 mmol) was suspended in THF (11 mL) after being washed with petroleum ether. A solution of **10** (5.90 mmol) in THF (30 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 1.5 h, the mixture was cooled to 0 °C, and **11**¹ (2.95 mmol) was added. The reaction mixture was stirred for 10 min at 0 °C, stirred for 20 min at room temperature, and refluxed for 7 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (90 mL) and water (90 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 90 mL). The combined organic phases were washed with water, brine, and water, dried over MgSO₄, and concentrated *in vacuo*. The residue was passed through a flash column (silica gel, hexane/ethyl acetate (2/1)) to afford a mixture of a coupling adduct and **10**. To the mixture were added dichloromethane (54 mL), water (3 mL), and 2,3-dichloro-5,6-dicyanoquinone (DDQ) (5.34 mmol) at 0 °C. After stirred for 20 h at 0 °C, the reaction was quenched with saturated aqueous NaHCO₃ (30 mL). The organic layer was separated, and the aqueous layer

was extracted with dichloromethane (2 x 50 mL). The combined organic phases were dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (1/6)) to afford **12** (41% yield) as a colorless oil: ^1H NMR (CDCl_3) δ 1.15 (d, 6H, $J = 6.3$ Hz), 1.19 (d, 6H, $J = 6.3$ Hz), 3.36 (dq, 2H, $J = 7.6, 6.3$ Hz), 3.72 (dq, 2H, $J = 7.6, 6.3$ Hz), 4.61 (d, 2H, $J = 13.2$ Hz), 4.83 (d, 2H, $J = 13.4$ Hz), 5.50 (brs), 7.19 (d, 2H, $J = 7.8$ Hz), 7.67 (t, 1H, $J = 7.7$ Hz); ^{13}C NMR (CDCl_3) δ 16.0, 18.8, 71.1, 71.2, 82.8, 120.4, 137.5, 157.9; IR (neat) 3410, 1597, 1579, 1459, 1380, 1113 cm^{-1} ; MS m/z 195 ($\text{M}^+-(\text{CH}_3\text{COCH}(\text{CH}_3)\text{OH})+\text{H}$), 238 ($\text{M}^+-(\text{CH}_3\text{CHOH})$); Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_4$: C, 63.58; H, 8.89; N, 4.94. Found: C, 63.30; H, 8.87; N, 4.95; $[\alpha]_D^{23}$ -60.2 (c 0.50, EtOH).

1: Under argon, sodium hydride (7.67 mmol) was suspended in THF (5 mL) after being washed with petroleum ether. A solution of **12** (0.519 mmol) in THF (8 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 2 h, **11** (0.519 mmol) was added. The reaction mixture was stirred for 4.5 h at room temperature, and refluxed for 16 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (20 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic phases were washed with water, brine, and water again, dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (1/2)) to afford **1** (50% yield) as a white solid. **1** was used in the asymmetric aldol reactions, after being recrystallized from heptane: ^1H NMR (CDCl_3) δ 1.17 (d, 12H, $J = 6.2$ Hz), 3.64 (dq, 4H, $J = 6.8, 3.6$ Hz), 4.57 (d, 4H, $J = 13.8$ Hz), 4.63 (d, 4H, $J = 13.8$ Hz), 7.24 (d, 4H, $J = 7.7$ Hz), 7.62 (t, 2H, $J = 7.7$ Hz); ^{13}C NMR (CDCl_3) δ 15.0, 72.0, 76.7, 119.9, 136.8, 158.4; Mp 102-105 $^\circ\text{C}$ (lit.¹ 100-101 $^\circ\text{C}$).

13: A solution of (3*R*,4*R*)-3,4-hexanediol² (2.16 mmol), *p*-anisaldehyde (27.8 mmol), and $\text{TsOH}\cdot\text{H}_2\text{O}$ (0.183 mmol) in benzene (130 mL) was refluxed in a Dean-Stark apparatus. After 23 h, the solution was washed with 10% NaOH (70 mL), and the aqueous layer was extracted with dichloromethane (2 x 100 mL). The combined organic phases were washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. To the residue was added dichloromethane (19 mL) under argon, and the solution was stirred at -78 $^\circ\text{C}$. To the solution was added DIBAL (49 mL, 46 mmol, 0.93 M in *n*-hexane), and the reaction mixture was stirred at -78 $^\circ\text{C}$. After 1 h, the reaction mixture was allowed to warm to 4 $^\circ\text{C}$, and stirred for 60 h at 4 $^\circ\text{C}$. The reaction mixture was poured into a solution of methanol (3.6 mL) in diethyl ether (95 mL) at 0 $^\circ\text{C}$. Rochelle salt (10%, 65 mL) was added, and the

mixture was allowed to warm to room temperature with stirring. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 x 150 mL). The combined organic phases were dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (3/1)) to afford **13** (67% yield) as a colorless oil: ¹H NMR (CDCl₃) δ 0.86 (d, 3H, *J* = 7.5 Hz), 0.91 (d, 3H, *J* = 7.2 Hz), 1.28-1.71 (m, 4H), 2.20 (brs), 3.14 (q, 1H, *J* = 5.6 Hz), 3.39 (dq, 1H, *J* = 5.6, 4.2 Hz), 3.73 (s, 3H), 4.34 (d, 1H, *J* = 11.0 Hz), 4.52 (d, 1H, *J* = 11.0 Hz), 6.78-6.84 (m, 2H), 7.16-7.23 (m, 2H); ¹³C NMR (CDCl₃) δ 9.3, 10.1, 22.8, 26.3, 55.2, 72.0, 73.5, 82.7, 113.8, 129.4, 130.5, 159.2; IR (neat) 3459, 2963, 2876, 1613, 1515, 1252, 1075, 1034 cm⁻¹; MS *m/z* 238 (M⁺); Anal. Calcd for C₁₄H₂₂O₃: C, 70.56; H, 9.30. Found: C, 70.65; H, 9.22; [α]_D²³ +15.2 (*c* 1.00, EtOH).

14: Under argon, sodium hydride (3.16 mmol) was suspended in THF (7.2 mL) after being washed with petroleum ether. A solution of **13** (2.36 mmol) in THF (10 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 1 h, **11** (1.18 mmol) was added. The reaction mixture was stirred for 20 min at room temperature, and refluxed for 14 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (40 mL) and water (40 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 40 mL). The combined organic phases were washed with water, brine, and water, dried over MgSO₄, and concentrated *in vacuo*. The residue was passed through a flash column (silica gel, hexane/ethyl acetate (3/1)) to afford a mixture of a coupling adduct and **13**. To the mixture were added dichloromethane (47 mL), water (2.6 mL), and DDQ (1.85 mmol) at 0 °C. After stirring for 12 h at 0 °C, the reaction was quenched with saturated aqueous NaHCO₃ (15 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic phases were dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (1/6)) to afford **14** (19% yield) as a colorless oil: ¹H NMR (CDCl₃) δ 1.00 (t, 6H, *J* = 7.3 Hz), 1.02 (t, 6H, *J* = 7.3 Hz), 1.37-1.80 (m, 8H), 3.28 (dt, 2H, *J* = 6.7, 4.6 Hz), 3.58 (dt, 2H, *J* = 7.3, 3.5 Hz), 4.68 (d, 2H, *J* = 13.0 Hz), 4.87 (d, 2H, *J* = 13.2 Hz), 5.32 (brs), 7.18 (d, 2H, *J* = 7.7 Hz), 7.66 (t, 1H, *J* = 7.7 Hz); ¹³C NMR (CDCl₃) δ 9.7, 9.9, 23.8, 26.0, 73.2, 74.2, 86.5, 120.3, 137.5, 158.0; IR (neat) 3401, 2965, 2932, 2877, 1597, 1579, 1462, 1156, 1111, 976 cm⁻¹; HRMS calcd for C₁₉H₃₃NO₄: 339.2410, found: 339.2422; [α]_D²⁶ +7.4 (*c* 1.00, EtOH).

7: Under argon, sodium hydride (0.587 mmol) was suspended in THF (2 mL) after being washed with petroleum ether. A solution of **14** (0.219 mmol) in THF (3.5 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 45 min, **11** (0.219 mmol) was added. The reaction mixture was stirred for 15 min at room temperature, and refluxed for 16 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (20 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic phases were washed with water, brine, and water, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate/diisopropylamine (10/20/1)) to afford **7** (50% yield) as a colorless oil: ¹H NMR (CDCl₃) δ 0.95 (t, 12H, *J* = 7.4 Hz), 1.34-1.52 (m, 4H), 1.53-1.73 (m, 4H), 3.42 (dt, 4H, *J* = 8.3, 5.5 Hz), 4.63 (d, 4H, *J* = 13.3 Hz), 4.76 (d, 4H, *J* = 13.3 Hz), 7.27 (d, 4H, *J* = 7.6 Hz), 7.62 (t, 2H, *J* = 7.6 Hz); ¹³C NMR (CDCl₃) δ 10.5, 23.0, 73.3, 81.5, 120.3, 136.8, 158.2; IR (neat) 2964, 2873, 1593, 1578, 1460, 1104, 761 cm⁻¹; MS *m/z* 442 (M⁺); Anal. Calcd for C₂₆H₃₈N₂O₄: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.29; H, 8.62; N, 6.26; [α]_D²⁵ +31.5 (*c* 1.00, CHCl₃).

15: A solution of (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediol³ (43.4 mmol), *p*-anisaldehyde (65.9 mmol), and TsOH•H₂O (0.434 mmol) in toluene (370 mL) was refluxed in a Dean-Stark apparatus. After 16 h, the solution was washed with 10% NaOH (150 mL), and the aqueous layer was extracted with dichloromethane (1 x 200 mL, 1 x 150 mL). The combined organic phases were dried over MgSO₄, and concentrated *in vacuo*. To the residue was added dichloromethane (45 mL) under argon, and the solution was stirred at -78 °C. To the solution was added DIBAL (115 mL, 109 mmol, 0.95 M in *n*-hexane), and the reaction mixture was stirred at -78 °C. After 3 h, the reaction mixture was gradually allowed to warm to room temperature. The reaction mixture was poured into a solution of methanol (8.6 mL) in diethyl ether (200 mL) at 0 °C. Rochelle salt (10%, 155 mL) was added, and the mixture was allowed to warm to room temperature with stirring. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (1 x 200 mL, 1 x 150 mL). The combined organic phases were dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (2/1)) to afford **15** (99% yield) as a white solid: ¹H NMR (CDCl₃) δ 3.53 (d, *J* = 1.5 Hz), 3.81 (s, 3H), 4.26 (d, 1H, *J* = 11.0 Hz), 4.33 (d, 1H, *J* = 8.3 Hz), 4.46 (d, 1H, *J* = 11.0 Hz), 4.70 (d, 1H, *J* = 8.3 Hz), 6.89 (d, 2H, *J* = 8.8 Hz), 6.96-7.10 (m, 4H), 7.11-7.34 (m, 8H); ¹³C NMR (CDCl₃) δ

55.3, 70.5, 78.5, 86.6, 113.9, 127.3, 127.6, 127.8, 127.9, 128.0, 128.1, 129.6, 129.8, 137.6, 139.1, 159.3; IR (KBr) 3523, 2869, 1512, 1245, 1082, 1063, 1024, 1011, 754, 700 cm^{-1} ; MS m/z 334 (M^+); Mp 85 $^{\circ}\text{C}$; Anal. Calcd for $\text{C}_{22}\text{H}_{22}\text{O}_3$: C, 79.02; H, 6.63. Found: C, 78.88; H, 6.79; $[\alpha]_{\text{D}}^{23}$ -34.7 (c 1.00, EtOH).

16: Under argon, sodium hydride (41.0 mmol) was suspended in THF (59 mL) after being washed with petroleum ether. A solution of **15** (30.6 mmol) in THF (150 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 2 h, **11** (15.3 mmol) was added. The reaction mixture was stirred for 10 min at room temperature, and refluxed for 14 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (200 mL) and water (200 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 200 mL). The combined organic phases were washed with water, brine, and water again, dried over MgSO_4 , and concentrated *in vacuo*. The residue was passed through a flash column (silica gel, hexane/ethyl acetate (2/1)) to afford a mixture of a coupling adduct and **15**. To the mixture were added dichloromethane (195 mL), water (10.8 mL), and DDQ (24.7 mmol) at 0 $^{\circ}\text{C}$. After stirred for 12 h at 0 $^{\circ}\text{C}$, the reaction was quenched with saturated aqueous NaHCO_3 (150 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 200 mL). The combined organic phases were dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (1/6)) to afford **16** (36% yield) as a white solid: ^1H NMR (CDCl_3) δ 4.43 (d, 2H, J = 8.5 Hz), 4.62 (d, 2H, J = 13.9 Hz), 4.75 (d, 2H, J = 13.9 Hz), 4.83 (d, 2H, J = 8.5 Hz), 5.70 (brs), 6.97-7.35 (m, 22H), 7.70 (t, 1H, J = 7.7 Hz); ^{13}C NMR (CDCl_3) δ 71.1, 78.9, 89.0, 120.4, 127.4, 127.4, 127.7, 127.8, 128.0, 128.0, 137.6, 137.9, 139.7, 157.7; IR (KBr) 3366, 3029, 2871, 1451, 1254, 1199, 1124, 1048, 757, 700 cm^{-1} ; MS m/z 531 (M^+); Mp 134-138 $^{\circ}\text{C}$; Anal. Calcd for $\text{C}_{35}\text{H}_{33}\text{NO}_4$: C, 79.07; H, 6.26; N, 2.63. Found: C, 78.94; H, 6.37; N, 2.65; $[\alpha]_{\text{D}}^{25}$ -47.1 (c 1.00, EtOH).

8: To a solution of **16** (4.70 mmol) in THF (53 mL) was added KHMDS (22.0 mL, 11.0 mmol, 0.5 M in toluene) at room temperature under argon. After stirred for 2 h, **11** (4.70 mmol) was added. The reaction mixture was stirred for 50 min at room temperature, and refluxed for 24 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (80 mL) and water (80 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 80 mL). The combined organic phases were dried over MgSO_4 , and

concentrated *in vacuo*. The residue was purified by chromatography (silica gel, chloroform/methanol (9/1), then acetone) to afford **8** as a white solid, which was recrystallized from acetone (4% yield): ^1H NMR (CDCl_3) δ 4.71 (d, 4H, $J = 12.8$ Hz), 4.75 (s, 4H), 4.80 (d, 4H, $J = 12.8$ Hz), 7.00-7.22 (m, 24H), 7.57 (t, 2H, $J = 7.7$ Hz); ^{13}C NMR (CDCl_3) δ 72.3, 84.9, 120.9, 127.4, 127.6, 128.0, 136.7, 138.3, 158.0; IR (KBr) 3064, 3029, 2871, 1593, 1577, 1083, 759, 698 cm^{-1} ; Mp 174–177 $^\circ\text{C}$; HRMS calcd for $\text{C}_{42}\text{H}_{38}\text{O}_4\text{N}_2$: 634.2832, found: 634.2854; $[\alpha]_{\text{D}}^{23} -133.5$ (c 0.05, acetone).

17: Under argon, sodium hydride (1.01 mmol) was suspended in THF (1.0 mL) after being washed with petroleum ether. A solution of (1*R*,2*R*)-1,2-cyclohexanediol (0.777 mmol) in THF (2.9 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 30 min, *p*-methoxybenzyl chloride (1.17 mmol) and tetrabutylammonium iodide (0.155 mmol) were added. The reaction mixture was stirred for 15 min at room temperature, and refluxed for 24 h. The reaction mixture was allowed to cool to room temperature, and dichloromethane (10 mL) and water (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic phases were dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (2/1)) to afford a mixture of a coupling adduct and **17** (58% yield) as a colorless oil: ^1H NMR (CDCl_3) δ 1.10-1.37 (m, 4H), 1.59-1.82 (m, 2H), 1.90-2.07 (m, 1H), 2.07-2.20 (m, 1H), 2.30 (brs), 3.10-3.22 (m, 1H), 3.39-3.52 (m, 1H), 3.81 (s, 3H), 4.40 (d, 1H, $J = 11.1$ Hz), 4.63 (d, 1H, $J = 11.1$ Hz), 6.89 (d, 2H, $J = 8.6$ Hz), 7.27 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR (CDCl_3) δ 23.9, 24.2, 29.2, 32.0, 55.3, 70.5, 73.8, 83.2, 113.9, 129.3, 130.7, 159.2; IR (neat) 3442, 2934, 2863, 1613, 1514, 1250, 1081, 1035 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3$: 236.1412, found: 236.1434; $[\alpha]_{\text{D}}^{24} -37.5$ (c 1.20, EtOH).

18: Under argon, sodium hydride (5.29 mmol) was suspended in THF (10 mL) after being washed with petroleum ether. A solution of **17** (3.95 mmol) in THF (18 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 45 min, **11** (1.97 mmol) was added. The reaction mixture was stirred for 3 min at room temperature, and refluxed for 14 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (60 mL) and water (60 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 60 mL). The combined organic phases were washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. The residue was passed through a flash column

(silica gel, hexane/ethyl acetate (2/1)) to afford a mixture of a coupling adduct and **17**. To the mixture were added dichloromethane (82 mL), water (4.5 mL), and DDQ (3.26 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature with stirring. After 24 h, the reaction was quenched with saturated aqueous NaHCO₃ (60 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 80 mL). The combined organic phases were dried over MgSO₄, and concentrated *in vacuo*. The residue was passed through a flash column (silica gel, hexane/ethyl acetate (1/6)) to afford crude **18**, which was purified by preparative TLC (silica gel, chloroform/methanol (19/1)) to afford pure **18** (30% yield) as a white solid: ¹H NMR (CDCl₃) δ 1.09-1.45 (m, 8H), 1.55-1.84 (m, 4H), 1.95-2.23 (m, 4H), 3.15-3.35 (m, 2H), 3.47-3.67 (m, 2H), 4.65 (d, 2H, *J* = 13.0 Hz), 4.87 (d, 2H, *J* = 13.0 Hz), 6.65 (brs), 7.15 (d, 2H, *J* = 7.7 Hz), 7.67 (t, 1H, *J* = 7.7 Hz); ¹³C NMR (CDCl₃) δ 23.9, 24.5, 30.1, 32.7, 71.2, 73.6, 86.1, 120.8, 137.8, 158.0; IR (KBr) 3401, 3144, 2925, 2852, 1597, 1579, 1469, 1455, 1144, 1114, 1090, 1013, 999, 851, 803 cm⁻¹; MS *m/z* 335 (M⁺); Mp 68-70 °C; Anal. Calcd for C₁₉H₂₉NO₄: C, 68.03; H, 8.71; N, 4.18. Found: C, 67.77; H, 8.58; N, 4.21; [α]_D²⁰ -93.4 (c 1.00, EtOH).

9: Under argon, sodium hydride (1.25 mmol) was suspended in THF (3.7 mL) after being washed with petroleum ether. A solution of **18** (0.467 mmol) in THF (8.0 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 75 min, **11** (0.467 mmol) was added. The reaction mixture was stirred for 30 min at room temperature, and refluxed for 20 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (40 mL) and water (20 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 40 mL). The combined organic phases were washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by preparative TLC (silica gel, hexane/ethyl acetate/diisopropylamine (10/15/1)) to afford **9** (53% yield) as a white solid: ¹H NMR (CDCl₃) δ 1.16-1.56 (m, 8H), 1.60-1.83 (m, 4H), 1.94-2.16 (m, 4H), 3.46 (ddd, 4H, *J* = 9.8, 5.7, 5.7 Hz), 4.65 (d, 4H, *J* = 13.2 Hz), 4.77 (d, 4H, *J* = 13.2 Hz), 7.19 (d, 4H, *J* = 7.6 Hz), 7.58 (t, 2H, *J* = 7.6 Hz); ¹³C NMR (CDCl₃) δ 23.3, 30.0, 72.2, 80.1, 119.8, 136.7, 158.3; IR (KBr) 2930, 2859, 1593, 1577, 1455, 1100, 1070, 806 cm⁻¹; MS *m/z* 438 (M⁺); Mp 163-165 °C; Anal. Calcd for C₂₆H₃₄N₂O₄: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.02; H, 7.94; N, 6.35; [α]_D¹⁷ -70.1 (c 0.50, CHCl₃).

19: To a solution of 2,6-bis(hydroxymethyl)-4-methoxypyridine⁴ (27.3 mmol) in THF (124 mL) was added KOH (78.1 mmol) followed by *p*-toluenesulfonyl chloride (62.5 mmol) at 0

$^{\circ}\text{C}$. The reaction mixture was allowed to warm to room temperature with stirring. After stirred for 12 h at room temperature, the reaction was filtered through Celite, and the solvent was removed *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (1/1)) to afford **19** (94% yield) as a white solid: ^1H NMR (CDCl_3) δ 2.44 (s, 6H), 3.82 (s, 3H), 4.99 (s, 4H), 6.81 (s, 2H), 7.33 (d, 4H, $J = 8.2$ Hz), 7.80 (d, 4H, $J = 8.2$ Hz); ^{13}C NMR (CDCl_3) δ 21.6, 55.5, 71.2, 107.3, 128.0, 129.9, 132.7, 145.1, 155.1, 167.3; IR (KBr) 3087, 3034, 2985, 2948, 1603, 1573, 1465, 1363, 1194, 1174, 1036 cm^{-1} ; MS m/z 477 (M^+); Mp 79-80 $^{\circ}\text{C}$; Anal. Calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_7\text{S}_2$: C, 55.33; H, 4.85; N, 2.93. Found: C, 55.13; H, 5.02; N, 2.85.

20: Under argon, sodium hydride (22.8 mmol) was suspended in THF (30 mL) after being washed with petroleum ether. A solution of **10** (17.0 mmol) in THF (90 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 2.5 h, **19** (8.52 mmol) was added. The reaction mixture was refluxed for 12 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (250 mL) and water (100 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 250 mL). The combined organic phases were dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (2/1)) to afford **20** (56% yield) as a colorless oil: ^1H NMR (CDCl_3) δ 1.17 (d, 6H, $J = 6.1$ Hz), 1.19 (d, 6H, $J = 6.2$ Hz), 3.57-3.69 (m, 4H), 3.75 (s, 3H), 3.79 (s, 6H), 4.49 (d, 2H, $J = 11.4$ Hz), 4.56 (d, 2H, $J = 11.4$ Hz), 4.58 (d, 2H, $J = 13.9$ Hz), 4.67 (d, 2H, $J = 13.9$ Hz), 6.85 (d, 4H, $J = 8.8$ Hz), 6.93 (s, 2H), 7.26 (d, 4H, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3) δ 14.8, 14.9, 55.0, 55.2, 71.0, 71.8, 76.6, 77.9, 105.5, 113.7, 129.2, 131.0, 159.0, 160.3, 167.2; IR (neat) 2975, 2935, 1601, 1513, 1462, 1248, 1114, 1054 cm^{-1} ; HRMS calcd for $\text{C}_{32}\text{H}_{43}\text{NO}_7$: 553.3040, found: 553.3073; $[\alpha]_{\text{D}}^{23}$ -28.3 (c 1.00, EtOH).

21: To a solution of **20** (0.476 mmol) in dichloromethane (13.3 mL) and water (0.74 mL) was added DDQ (3.43 mmol) at room temperature. After stirred for 12 h, the reaction was quenched with saturated aqueous NaHCO_3 (10 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 20 mL). The combined organic phases were dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate/diisopropylamine (3/18/1)) to afford **21** (65% yield) as a colorless oil: ^1H NMR (CDCl_3) δ 1.15 (d, 6H, $J = 8.4$ Hz), 1.17 (d, 6H, $J = 8.4$ Hz), 3.20-3.37 (m, 2H), 3.56-3.73 (m, 2H), 3.85 (s, 3H), 4.55 (d, 2H, $J = 13.4$ Hz), 4.76

(d, 2H, $J = 13.4$ Hz), 5.50 (brs), 6.70 (s, 2H); ^{13}C NMR (CDCl_3) δ 16.1, 18.8, 55.3, 71.2, 71.2, 82.8, 106.3, 159.7, 167.0; IR (neat) 3409, 2975, 2931, 2877, 1604, 1577, 1465, 1116, 1056 cm^{-1} ; HRMS calcd for $\text{C}_{16}\text{H}_{28}\text{NO}_5$: 314.1967, found: 314.1968; $[\alpha]_{\text{D}}^{23} -70.0$ (c 1.02, EtOH).

3: Under argon, sodium hydride (9.07 mmol) was suspended in THF (19 mL) after being washed with petroleum ether. A solution of **21** (2.62 mmol) in THF (40 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 1 h, **19** (2.62 mmol) was added. The reaction mixture was refluxed for 12 h. The reaction mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (120 mL) and water (40 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 120 mL). The combined organic phases were washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate/diisopropylamine (3/18/1)) to afford **3** (42% yield) as a white solid: ^1H NMR (CDCl_3) δ 1.17 (d, 12H, $J = 6.1$ Hz), 3.58-3.70 (m, 4H), 3.84 (s, 6H), 4.54 (s, 8H), 6.77 (s, 4H); ^{13}C NMR (CDCl_3) δ 14.9, 55.0, 71.8, 76.6, 106.0, 160.2, 166.8; IR (KBr) 2982, 2921, 2897, 2863, 1598, 1574, 1465, 1121, 1048 cm^{-1} ; MS m/z 446 (M^+); Mp 110-112 $^\circ\text{C}$; Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_6$: C, 64.55; H, 7.67; N, 6.27. Found: C, 64.33; H, 7.69; N, 6.17; $[\alpha]_{\text{D}}^{25} -13.7$ (c 0.50, CHCl_3).

23: Under argon, sodium hydride (55.0 mmol) was suspended in THF (65 mL) after being washed with petroleum ether. A solution of **10** (36.7 mmol) in THF (200 mL) was added to the mixture, and the whole mixture was stirred at room temperature. After 30 min, compound **22**⁵ (18.4 mmol) was added. The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was concentrated *in vacuo*. To the residue was added water (100 mL), and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic phases were dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (2/1)) to afford **23** (83% yield) as a colorless oil: ^1H NMR (CDCl_3) δ 1.10-1.27 (m, 12H), 3.55-3.70 (m, 4H), 3.80 (s, 6H), 4.48 (d, 2H, $J = 11.5$ Hz), 4.57 (d, 2H, $J = 11.5$ Hz), 4.59 (d, 2H, $J = 14.0$ Hz), 4.67 (d, 2H, $J = 14.0$ Hz), 6.86 (d, 4H, $J = 8.5$ Hz), 7.26 (d, 4H, $J = 8.5$ Hz), 7.56 (s, 2H); ^{13}C NMR (CDCl_3) δ 15.0, 15.0, 55.2, 70.9, 71.5, 76.6, 78.3, 113.7, 112.8, 129.2, 130.8, 134.2, 159.0, 160.0; IR (neat) 2976, 2872, 1613, 1568, 1513, 1461, 1248, 1115, 822 cm^{-1} ; HRMS calcd for $\text{C}_{31}\text{H}_{40}\text{BrNO}_6$: 601.2080, found: 601.2039; $[\alpha]_{\text{D}}^{18} -38.9$ (c 1.00, EtOH).

24: To a solution of **23** (10.6 mmol) in acetonitrile (94.5 mL) and water (10.5 mL) was added

cerium ammonium nitrate (58.3 mmol) in small portions at room temperature. After stirred for 3 h, the reaction was quenched with saturated aqueous NaHCO₃ (300 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 x 250 mL). The combined organic phases were dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate/diisopropylamine (3/18/1)) to afford **24** (84% yield) as a white solid: ¹H NMR (CDCl₃) δ 1.10-1.24 (m, 12H), 3.26-3.44 (m, 2H), 3.62-3.80 (m, 2H), 4.57 (d, 2H, *J* = 13.6 Hz), 4.78 (d, 2H, *J* = 13.6 Hz), 4.93 (brs), 7.39 (s, 2H); ¹³C NMR (CDCl₃) δ 15.9, 18.7, 70.6, 71.2, 82.7, 123.5, 134.2, 159.5; IR (neat) 3426, 2977, 2880, 1575, 1459, 1116 cm⁻¹; Mp 33-34 °C; Anal. Calcd for C₁₅H₂₄BrNO₄: C, 49.73; H, 6.68; N, 3.87. Found: C, 49.44; H, 6.68; N, 3.80; [α]_D²¹ -49.9 (*c* 0.50, EtOH).

4: Under argon, sodium hydride (10.5 mmol) was suspended in THF (200 mL) after being washed with petroleum ether. Then, **24** (4.36 mmol) was added to the mixture, and the whole mixture was stirred at room temperature. After 20 min, **25**⁵ was added, and the mixture was refluxed for 8 h. The mixture was allowed to cool to room temperature, and concentrated *in vacuo*. To the residue were added dichloromethane (60 mL) and water (120 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 x 60 mL). The combined organic phases were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. The residue was purified by chromatography (silica gel, hexane/ethyl acetate (1/2)) to afford **4** (27% yield) as a white solid: ¹H NMR (CDCl₃) δ 1.18 (d, 12H, *J* = 6.1 Hz), 3.56-3.75 (m, 4H), 4.58 (d, 4H, *J* = 13.8 Hz), 4.62 (d, 4H, *J* = 13.8 Hz), 7.38 (s, 4H); ¹³C NMR (CDCl₃) δ 15.6, 71.7, 78.0, 123.1, 133.7, 159.9; IR (KBr) 2977, 2928, 2896, 1569, 1456, 1119 cm⁻¹; MS *m/z* 542 (M⁺); Mp 103-105 °C; Anal. Calcd for C₂₂H₂₈Br₂N₂O₄: C, 48.55; H, 5.19; N, 5.15. Found: C, 48.47; H, 5.38; N, 5.10; [α]_D¹⁸ -30.0 (*c* 0.50, CHCl₃).

Characterization Data of the Aldol Adducts

3-Hydroxy-2-methyl-1, 3-diphenyl-propan-1-one⁶: ¹H NMR (CDCl₃) δ 1.20 (d, *J* = 7.3 Hz), 3.66 (brs), 3.71 (dq, *J* = 7.2, 3.1 Hz), 5.00 (d, 0.09H, *anti*, *J* = 8.1 Hz), 5.24 (d, 0.91H, *syn*, *J* = 3.2 Hz), 7.21-7.63 (m, 8H), 7.90-7.99 (m, 2H); HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 30/1, flow rate = 1.0 mL/min) *syn* isomer: *t*_R = 19.7 min (major), *t*_R = 25.2 min (minor), *anti* isomer: *t*_R = 36.5 min (minor), *t*_R = 41.3 min (major).

3-Hydroxy-3-(4-methoxy-phenyl)-2-methyl-1-phenyl-propan-1-one⁷: ¹H NMR (CDCl₃) δ

1.21 (d, $J = 7.2$ Hz), 3.54 (d, $J = 1.8$ Hz), 3.68 (dq, $J = 7.2, 3.6$ Hz), 3.79 (s), 4.95 (dd, 0.08H, *anti*, $J = 8.2, 3.8$ Hz), 5.17 (d, 0.92H, *syn*, $J = 1.8$ Hz), 6.80-6.94 (m, 2H), 7.27-7.37 (m, 2H), 7.39-7.63 (m, 3H), 7.85-8.02 (m, 2H); HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min) *syn* isomer: $t_R = 11.4$ min (major), $t_R = 19.4$ min (minor), *anti* isomer: $t_R = 31.8$ min (minor), $t_R = 35.5$ min (major).

3-Hydroxy-3-(2-methoxy-phenyl)-2-methyl-1-phenyl-propan-1-one⁸: ^1H NMR (CDCl_3) *syn* isomer: δ 1.14 (d, 3H, $J = 7.3$ Hz), 3.54 (brd, $J = 2.8$ Hz), 3.86 (s, 3H), 3.95 (dq, 1H, $J = 7.2, 3.0$ Hz), 5.42 (s, 1H), 6.86 (d, 1H, $J = 8.3$ Hz), 6.93-7.05 (m, 1H), 7.18-7.31 (m, 1H), 7.41-7.63 (m, 4H), 7.95-8.06 (m, 2H), *anti* isomer: δ 1.13 (d, 3H, $J = 7.2$ Hz), 3.44 (brs), 3.87 (s, 3H), 4.07 (quin, 1H, $J = 7.2$ Hz), 5.25 (d, 1H, $J = 7.3$ Hz), 6.87 (d, 1H, $J = 8.3$ Hz), 6.91-6.98 (m, 1H), 7.18-7.28 (m, 1H), 7.34-7.58 (m, 4H), 7.89-7.97 (m, 2H); HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 19/1, flow rate = 1.0 mL/min) *syn* isomer: $t_R = 17.1$ min (major), $t_R = 24.5$ min (minor); HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 19/1, flow rate = 1.0 mL/min) *anti* isomer: $t_R = 19.0$ min (major), $t_R = 37.1$ min (minor).

3-(4-Chloro-phenyl)-3-hydroxy-2-methyl-1-phenyl-propan-1-one⁹: ^1H NMR (CDCl_3) δ 1.17 (d, $J = 7.3$ Hz), 3.65 (dq, $J = 7.2, 3.0$ Hz), 3.83 (brs), 4.97 (d, 0.10H, *anti*, $J = 8.1$ Hz), 5.21 (d, 0.90H, *syn*, $J = 2.9$ Hz), 7.28-7.39 (m, 4H), 7.43-7.65 (m, 3H), 7.87-8.01 (m, 2H); HPLC (Daicel Chiralcel OD, hexane/*i*-PrOH = 60/1, flow rate = 1.0 mL/min) *syn* isomer: $t_R = 19.9$ min (major), $t_R = 24.3$ min (minor), *anti* isomer: $t_R = 52.8$ min (major), $t_R = 60.0$ min (minor).

3-Hydroxy-2-methyl-3-naphthalen-1-yl-1-phenyl-propan-1-one¹⁰: ^1H NMR (CDCl_3) *syn* isomer: δ 1.17 (d, 3H, $J = 7.3$ Hz), 3.91 (dq, 1H, $J = 7.2, 2.2$ Hz), 4.07 (d, $J = 1.8$ Hz), 6.05 (s, 1H), 7.40-7.66 (m, 6H), 7.74-8.02 (m, 6H), *anti* isomer: δ 1.11 (d, 3H, $J = 7.2$ Hz), 3.31 (d, $J = 5.0$ Hz), 4.20 (quin, $J = 7.3$ Hz), 5.80 (dd, 1H, $J = 7.6, 4.9$ Hz), 7.37-7.67 (m, 6H), 7.74-8.03 (m, 5H), 8.34 (d, 1H, $J = 8.4$ Hz); HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 30/1, flow rate = 1.0 mL/min) *syn* isomer: $t_R = 21.2$ min (major), $t_R = 28.2$ min (minor); HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 30/1, flow rate = 1.0 mL/min) *anti* isomer: $t_R = 34.9$ min (minor), $t_R = 53.6$ min (major).

3-Hydroxy-2-methyl-1-phenyl-3-thiophen-2-yl-propan-1-one¹¹: ^1H NMR (CDCl_3) δ 1.32 (d, $J = 7.2$ Hz), 3.65 (brd, $J = 2.2$ Hz), 3.80 (dq, $J = 7.2, 3.9$ Hz), 5.25 (dd, 0.09H, *anti*, $J = 7.6, 4.9$ Hz), 5.47 (s, 0.91H, *syn*), 6.92-7.05 (m, 2H), 7.19-7.28 (m, 1H), 7.42-7.63 (m, 3H), 7.89-8.04 (m, 2H); HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 60/1, flow rate = 1.0 mL/min) *syn* isomer: $t_R = 18.7$ min (major), $t_R = 22.8$ min (minor).

3-Hydroxy-2-methyl-1-phenyl-3-pyridin-2-yl-propan-1-one¹²: ¹H NMR (CDCl₃) *syn* isomer: δ 1.15 (d, 3H, J = 7.3 Hz), 4.08 (dq, 1H, J = 7.2, 3.9 Hz), 4.24 (brs), 5.24 (s, 1H), 7.17 (dd, 1H, J = 7.1, 5.4 Hz), 7.39-7.61 (m, 4H), 7.63-7.72 (m, 1H), 7.90-8.02 (m, 2H), 8.55 (d, 1H, J = 4.9 Hz), *anti* isomer: ¹H NMR (CDCl₃) δ 1.25 (d, 3H, J = 7.3 Hz), 4.20 (dq, 1H, J = 6.7, 4.3 Hz), 4.28 (d, J = 8.3 Hz), 5.01 (t, 1H, J = 6.7 Hz), 7.17 (dd, 1H, J = 7.6, 4.9 Hz), 7.38-7.49 (m, 3H), 7.51-7.60 (m, 1H), 7.67 (dt, 1H, J = 10.8, 3.8 Hz), 7.90-8.01 (m, 2H), 8.52 (d, 1H, J = 4.9 Hz); HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min) *syn* isomer: t_R = 8.1 min (major), t_R = 11.2 min (minor), *anti* isomer: t_R = 12.6 min (major), t_R = 15.0 min (minor).

3-Hydroxy-2-methyl-1, 5-diphenyl-pent-4-en-1-one¹⁰: ¹H NMR (CDCl₃) δ 1.31 (d, J = 7.2 Hz), 3.35 (brs), 3.64 (dq, J = 7.2, 3.5 Hz), 4.60 (dd, 0.22H, *anti*, J = 10.8, 6.6 Hz), 4.79 (s, 0.78H, *syn*), 6.19-6.34 (m, 1H), 6.62-6.78 (m, 1H), 7.17-7.66 (m, 8H), 7.88-8.06 (m, 2H); HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 30/1, flow rate = 1.0 mL/min) *syn* isomer: t_R = 19.1 min (major), t_R = 33.5 min (minor), *anti* isomer: t_R = 43.1 min (major), t_R = 58.7 min (minor).

3-Hydroxy-2-methyl-1-phenyl-hex-4-en-1-one¹⁰: ¹H NMR (CDCl₃) δ 1.27 (d, J = 7.2 Hz), 1.62-1.84 (m, 3H), 2.86 (brs), 3.46-3.65 (m, 1H), 4.36 (t, 0.19H, *anti*, J = 7.2 Hz), 4.47-4.55 (m, 0.81H, *syn*), 5.45-5.63 (m, 1H), 5.68-5.86 (m, 1H), 7.40-7.72 (m, 3H), 7.88-8.04 (m, 2H); HPLC (Daicel Chiralcel OD, hexane/*i*-PrOH = 200/1, flow rate = 0.8 mL/min) *syn* isomer: t_R = 32.9 min (major), t_R = 48.8 min (minor); HPLC (Daicel Chiralcel OC, hexane/*i*-PrOH = 30/1, flow rate = 1.0 mL/min) *anti* isomer: t_R = 23.7 min (minor), t_R = 30.5 min (major).

3-Hydroxy-2-methyl-1, 5-diphenyl-pentan-1-one¹³: ¹H NMR (CDCl₃) δ 1.27 (d, J = 7.2 Hz), 1.62-2.04 (m, 2H), 2.62-2.79 (m, 1H), 2.82-2.98 (m, 1H), 3.44 (dq, J = 7.2, 2.8 Hz), 3.83-3.93 (m, 0.33H, *anti*), 4.08 (dt, 0.67H, *syn*, J = 9.2, 3.3 Hz), 7.12-7.34 (m, 5H), 7.41-7.52 (m, 2H), 7.53-7.63 (m, 1H), 7.86-7.97 (m, 2H); HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 60/1, flow rate = 1.0 mL/min) *syn* isomer: t_R = 15.8 min (major), t_R = 24.8 min (minor), *anti* isomer: t_R = 17.7 min (minor), t_R = 40.4 min (major).

1-Hydroxy-2-methyl-1-phenyl-pentan-3-one¹²: ¹H NMR (CDCl₃) δ 1.00 (t, J = 7.2 Hz), 1.08 (d, J = 7.2 Hz), 2.26-2.62 (m, 2H), 2.78-2.99 (m, 1H), 3.15 (d, J = 2.4 Hz), 4.75 (dd, 0.19H, *anti*, J = 8.2, 4.1 Hz), 5.05 (dd, 0.81H, *syn*, J = 3.9, 1.8 Hz), 7.19-7.40 (m, 5H); HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 30/1, flow rate = 1.0 mL/min) *syn* isomer: t_R = 12.8 min (major), t_R = 14.7 min (minor), *anti* isomer: t_R = 16.1 min (major), t_R = 23.9 min

(minor).

S-tert-Butyl 3-hydroxy-2-methyl-3-phenylpropanethioate¹⁴: ¹H NMR (CDCl₃) δ 1.01 (d, 0.15H, *anti*, *J* = 7.1 Hz), 1.14 (d, 2.85 H, *syn*, *J* = 7.1 Hz), 1.43 (s, 8.55H, *syn*), 1.46 (s, 0.45H, *anti*), 2.76-2.92 (m, 1H), 2.95 (brs), 4.77 (d, 0.05H, *anti*, *J* = 8.1 Hz), 5.07 (d, 0.95H, *syn*, *J* = 3.9 Hz), 7.22-7.36 (m, 5H); ¹³C NMR (CDCl₃) δ 11.4, 15.5, 29.7, 29.7, 48.2, 55.1, 55.6, 73.9, 126.1, 126.6, 127.4, 128.0, 128.2, 128.4, 141.3, 141.9, 205.0; HPLC (Daicel Chiralcel OD, hexane/*i*-PrOH = 100/1, flow rate = 1.0 mL/min) *syn* isomer: *t*_R = 13.3 min (major), *t*_R = 16.6 min (minor), *anti* isomer: *t*_R = 20.4 min (major), *t*_R = 27.0 min (minor).

S-tert-Butyl 3-hydroxy-2-methyl-3-pyridin-2-yl-propanthioate: ¹H NMR (CDCl₃) *syn* isomer: δ 1.13 (d, 3H, *J* = 7.0 Hz), 1.44 (s, 9H), 3.01 (dq, 1H, *J* = 4.8, 7.0 Hz), 5.08 (d, 1H, *J* = 4.8 Hz), 7.22 (ddd, 1H, *J* = 1.1, 5.0, 7.5 Hz), 7.36 (d, 1H, *J* = 7.9 Hz), 7.70 (ddd, 1H, *J* = 1.7, 7.5, 7.9 Hz), 8.52-8.60 (m, 1H), *anti* isomer: δ 1.13 (d, 3H, *J* = 7.2 Hz), 1.42 (s, 9H), 3.09 (dq, 1H, *J* = 6.1, 7.2 Hz), 4.88 (d, 1H, *J* = 6.1 Hz), 7.22 (ddd, 1H, *J* = 1.2, 4.9, 7.6 Hz), 7.31 (d, 1H, *J* = 7.8 Hz), 7.69 (ddd, 1H, *J* = 1.8, 7.6, 7.8 Hz), 8.52-8.60 (m, 1H); ¹³C NMR (CDCl₃) *syn* isomer: δ 11.9, 29.7, 48.1, 54.8, 73.7, 121.4, 122.6, 136.8, 148.2, 159.6, 203.9, *anti* isomer: δ 14.5, 29.6, 48.1, 54.7, 75.7, 121.6, 122.7, 136.6, 148.5, 159.9, 203.6; IR (neat) 3422, 2967, 1675, 1594 cm⁻¹; HRMS Calcd for C₁₃H₁₉NO₂S: 253.1137, Found: 253.1091; HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 19/1, flow rate = 1.0 mL/min) *syn* isomer: *t*_R = 10.4 min (major), *t*_R = 12.9 min (minor), *anti* isomer: *t*_R = 20.4 min (major), *t*_R = 21.6 min (minor).

S-tert-Butyl 3-hydroxy-3-(4-methoxy-phenyl)-2-methyl-propanthioate: ¹H NMR (CDCl₃) δ 0.97 (d, 0.12H, *anti*, *J* = 7.1 Hz), 1.15 (d, 2.88 H, *syn*, *J* = 7.1 Hz), 1.41 (s, 8.64H, *syn*), 1.47 (s, 0.36H, *anti*), 2.70-2.89 (m, 1H), 2.91 (brs), 3.79 (s, 2.88H, *syn*), 3.79(s, 0.12H, *anti*), 4.72 (dd, 0.04H, *anti*, *J* = 2.6, 8.2 Hz), 4.97 (d, 0.96H, *syn*, *J* = 4.4 Hz), 6.81-6.91 (m, 2H), 7.18-7.29 (m, 2H); ¹³C NMR (CDCl₃) δ 11.8, 15.4, 29.6, 29.7, 48.1, 48.2, 55.2, 55.3, 55.7, 73.7, 76.2, 113.5, 113.8, 127.3, 127.8, 133.6, 134.0, 158.9, 159.3, 204.4, 204.8; IR (neat) 3487, 2960, 1671, 1613, 1514, 1251, 1037cm⁻¹; MS *m/z* 282 (M⁺); Anal. Calcd for C₁₅H₂₂O₃S: C, 63.80; H, 7.85. Found: C, 63.57; H, 7.85; HPLC (Daicel Chiralcel OD, hexane/*i*-PrOH = 19/1, flow rate = 0.75 mL/min) *syn* isomer: *t*_R = 16.2 min (major), *t*_R = 26.2 min (minor), *anti* isomer: *t*_R = 18.1 min (minor), *t*_R = 20.7 min (major).

S-tert-Butyl 3-hydroxy-2-methyl-5-phenyl-4-pentenethioate¹⁴: ¹H NMR (CDCl₃) δ 1.22 (d, 0.39H, *anti*, *J* = 7.1 Hz), 1.24 (d, 2.61 H, *syn*, *J* = 7.1 Hz), 1.45 (s, 7.83H, *syn*), 1.46 (s, 1.17H, *anti*), 2.54 (d, OH, *anti*, *J* = 5.9 Hz), 2.66 (d, OH, *syn*, *J* = 3.4 Hz), 2.71-2.82 (m, 1H),

4.35-4.43 (m, 0.13H, *anti*), 4.54-4.61(m, 0.87H, *syn*), 6.15 (dd, 0.87H, *syn*, $J = 6.1, 15.9$ Hz), 6.18 (dd, 0.13H, *anti*, $J = 6.6, 15.9$ Hz), 6.63 (d, 0.13H, *anti*, $J = 15.9$ Hz), 6.64 (d, 0.87H, *syn*, $J = 15.9$ Hz), 7.18-7.42 (m, 5H); ^{13}C NMR (CDCl_3) δ 12.1, 15.0, 29.7, 48.3, 53.7, 54.0, 73.2, 75.0, 126.5, 126.5, 127.6, 127.8, 128.5, 128.5, 128.7, 129.5, 131.4, 131.9, 136.5, 136.6, 204.3; HPLC (Daicel Chiralcel OD, hexane/*i*-PrOH = 19/1, flow rate = 0.75 mL/min) *syn* isomer: $t_{\text{R}} = 16.2$ min (major), $t_{\text{R}} = 26.2$ min (minor), *anti* isomer: $t_{\text{R}} = 18.1$ min (minor), $t_{\text{R}} = 20.7$ min (major).

Binding Studies

The binding constants were calculated by comparison of signal areas of a crown ether complexed with a rare earth metal cation and free one by ^1H NMR analysis.

The chemical shifts and J constants of the pyridine rings' protons were shown below. The residual proton signal of the methyl group of $\text{C}_2\text{D}_5\text{OD}$ served as a standard ($\delta = 1.10$ ppm) for ^1H NMR in both $\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9) and $\text{C}_2\text{D}_5\text{OD}$, and the signal of CD_2Cl_2 served as a standard ($\delta = 5.30$ ppm) for ^1H NMR in CD_2Cl_2 .

1: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.29 (d, 4H, $J = 7.6$ Hz), 7.74 (t, 2H, $J = 7.6$ Hz).

1–La³⁺: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.52 (d, 4H, $J = 7.9$ Hz), 8.03 (t, 2H, $J = 7.9$ Hz).

1: ^1H NMR ($\text{C}_2\text{D}_5\text{OD}$) δ 7.29 (d, 4H, $J = 7.6$ Hz), 7.73 (t, 2H, $J = 7.6$ Hz).

1–La³⁺: ^1H NMR ($\text{C}_2\text{D}_5\text{OD}$) δ 7.50 (d, 4H, $J = 7.9$ Hz), 8.04 (t, 2H, $J = 7.9$ Hz).

1: ^1H NMR (CD_2Cl_2) δ 7.21 (d, 4H, $J = 7.7$ Hz), 7.63 (t, 2H, $J = 7.7$ Hz).

1–La³⁺: ^1H NMR (CD_2Cl_2) δ 7.28 (d, 4H, $J = 7.8$ Hz), 7.91 (t, 2H, $J = 7.8$ Hz).

1–Y³⁺: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.51 (d, 4H, $J = 7.9$ Hz), 8.03 (t, 2H, $J = 7.9$ Hz).

3: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 6.92 (s, 4H).

3–La³⁺: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.04 (s, 4H).

3–Y³⁺: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.03 (s, 4H).

4: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.37 (s, 4H).

4–La³⁺: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.80 (s, 4H).

4–Y³⁺: ^1H NMR ($\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ (1/9)) δ 7.78 (s, 4H).

Kinetic Studies

The aldol reaction of benzaldehyde with **2** in $\text{H}_2\text{O}/\text{EtOH}$ (1/9) was carried out as described in the general procedure for aldol reactions in the presence of acetophenone (40

mol %) as an internal standard. At the times as given in Figure 4 or 9, a small portion of the reaction mixture was taken in a mixture of ethyl acetate, a saturated aqueous NaHCO_3 solution, and brine. Yields of the products in the hexane layer were measured by the comparison of the peak areas of the products and acetophenone by HPLC analysis (R-SIL-5A-06, YMC; hexane/ethyl acetate = 12/1; flow rate = 1.0 mL/min; acetophenone: t_R = 5.4 min, aldol product (*syn*): t_R = 22.6 min, aldol product (*anti*): t_R = 30.4 min).

Crystallization of $\text{RE}(\text{NO}_3)_3$ –crown ether complexes

Crystallization of $[\text{Pr}(\text{NO}_3)_2 \cdot \mathbf{1}]_3[\text{Pr}(\text{NO}_3)_6]$ was carried out as follows: To a solution of $\text{Pr}(\text{NO}_3)_3$ (6.2 mg) in ethanol (0.11 mL) was added a solution of **1** (5.2 mg) in ethanol (0.24 mL) at room temperature. A white precipitate was immediately formed, and dissolved by addition of water (80 μL) at 80 $^\circ\text{C}$ (oil bath temperature). The resulting solution was allowed to stand at 5 $^\circ\text{C}$ under ethanol vapor to give the crystals.

The crystals of the other complexes were prepared by the similar procedure.

For ORTEP structures of the complexes, see Supporting Information 2.

Intramolecular Distances Involving the Nonhydrogen Atoms and Intramolecular Bond Angles Involving the Nonhydrogen Atoms of [Pr(NO₃)₂•1]₃[Pr(NO₃)₆]

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
Pr(1)	O(1)	2.517(6)	1	O(3)	C(15)	1.42(1)	1
Pr(1)	O(2)	2.562(6)	1	O(3)	C(16)	1.47(1)	1
Pr(1)	O(3)	2.550(6)	1	O(4)	C(17)	1.47(1)	1
Pr(1)	O(4)	2.529(6)	1	O(4)	C(18)	1.44(1)	1
Pr(1)	O(5)	2.507(7)	1	O(5)	N(3)	1.30(1)	1
Pr(1)	O(6)	2.522(8)	1	O(6)	N(3)	1.26(1)	1
Pr(1)	O(8)	2.594(7)	1	O(7)	N(3)	1.18(1)	1
Pr(1)	O(9)	2.544(9)	1	O(8)	N(4)	1.26(1)	1
Pr(1)	N(1)	2.658(9)	1	O(9)	N(4)	1.30(1)	1
Pr(1)	N(2)	2.647(8)	1	O(10)	N(4)	1.22(1)	1
Pr(2)	O(11)	2.597(8)	1	O(11)	N(5)	1.29(1)	1
Pr(2)	O(11)	2.597(8)	65502	O(12)	N(5)	1.26(1)	1
Pr(2)	O(11)	2.597(8)	66503	O(13)	N(5)	1.23(1)	1
Pr(2)	O(12)	2.681(7)	1	O(14)	N(6)	1.28(1)	1
Pr(2)	O(12)	2.681(7)	65502	O(15)	N(6)	1.26(1)	1
Pr(2)	O(12)	2.681(7)	66503	O(16)	N(6)	1.21(1)	1
Pr(2)	O(14)	2.647(7)	1	N(1)	C(1)	1.34(1)	1
Pr(2)	O(14)	2.647(7)	65502	N(1)	C(5)	1.35(1)	1
Pr(2)	O(14)	2.647(7)	66503	N(2)	C(10)	1.35(1)	1
Pr(2)	O(15)	2.608(7)	1	N(2)	C(14)	1.32(1)	1
Pr(2)	O(15)	2.608(7)	65502	C(1)	C(2)	1.38(1)	1
Pr(2)	O(15)	2.608(7)	66503	C(1)	C(18)	1.49(1)	1
O(1)	C(6)	1.44(1)	1	C(2)	C(3)	1.38(1)	1
O(1)	C(7)	1.44(1)	1	C(3)	C(4)	1.39(1)	1
O(2)	C(8)	1.45(1)	1	C(4)	C(5)	1.37(1)	1
O(2)	C(9)	1.42(1)	1	C(5)	C(6)	1.52(1)	1

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms cont

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
C(7)	C(8)	1.51(1)	1				
C(7)	C(19)	1.53(2)	1				
C(8)	C(20)	1.50(2)	1				
C(9)	C(10)	1.49(1)	1				
C(10)	C(11)	1.36(1)	1				
C(11)	C(12)	1.39(2)	1				
C(12)	C(13)	1.40(2)	1				
C(13)	C(14)	1.38(1)	1				
C(14)	C(15)	1.54(1)	1				
C(16)	C(17)	1.50(1)	1				
C(16)	C(21)	1.50(1)	1				
C(17)	C(22)	1.52(1)	1				

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Pr(1)	O(2)	60.7(2)	O(4)	Pr(1)	O(8)	114.7(2)
O(1)	Pr(1)	O(3)	164.4(2)	O(4)	Pr(1)	O(9)	83.1(2)
O(1)	Pr(1)	O(4)	123.5(2)	O(4)	Pr(1)	N(1)	60.6(2)
O(1)	Pr(1)	O(5)	77.8(2)	O(4)	Pr(1)	N(2)	119.1(2)
O(1)	Pr(1)	O(6)	111.4(2)	O(5)	Pr(1)	O(6)	50.4(2)
O(1)	Pr(1)	O(8)	91.0(2)	O(5)	Pr(1)	O(8)	168.0(2)
O(1)	Pr(1)	O(9)	76.8(2)	O(5)	Pr(1)	O(9)	129.4(2)
O(1)	Pr(1)	N(1)	63.1(2)	O(5)	Pr(1)	N(1)	65.7(2)
O(1)	Pr(1)	N(2)	117.4(2)	O(5)	Pr(1)	N(2)	116.2(3)
O(2)	Pr(1)	O(3)	121.1(2)	O(6)	Pr(1)	O(8)	132.7(2)
O(2)	Pr(1)	O(4)	158.5(2)	O(6)	Pr(1)	O(9)	170.1(2)
O(2)	Pr(1)	O(5)	85.5(2)	O(6)	Pr(1)	N(1)	114.2(2)
O(2)	Pr(1)	O(6)	72.1(2)	O(6)	Pr(1)	N(2)	67.6(2)
O(2)	Pr(1)	O(8)	85.2(2)	O(8)	Pr(1)	O(9)	50.1(2)
O(2)	Pr(1)	O(9)	117.5(2)	O(8)	Pr(1)	N(1)	113.1(3)
O(2)	Pr(1)	N(1)	120.8(2)	O(8)	Pr(1)	N(2)	65.1(2)
O(2)	Pr(1)	N(2)	60.3(2)	O(9)	Pr(1)	N(1)	63.8(2)
O(3)	Pr(1)	O(4)	61.4(2)	O(9)	Pr(1)	N(2)	114.3(3)
O(3)	Pr(1)	O(5)	117.4(2)	N(1)	Pr(1)	N(2)	178.0(3)
O(3)	Pr(1)	O(6)	82.9(2)	O(11)	Pr(2)	O(11)	67.7(3)
O(3)	Pr(1)	O(8)	74.1(2)	O(11)	Pr(2)	O(11)	67.7(3)
O(3)	Pr(1)	O(9)	89.7(2)	O(11)	Pr(2)	O(12)	48.8(2)
O(3)	Pr(1)	N(1)	118.0(2)	O(11)	Pr(2)	O(12)	65.2(2)
O(3)	Pr(1)	N(2)	60.9(2)	O(11)	Pr(2)	O(12)	110.7(3)
O(4)	Pr(1)	O(5)	75.8(2)	O(11)	Pr(2)	O(14)	113.1(2)
O(4)	Pr(1)	O(6)	87.6(2)	O(11)	Pr(2)	O(14)	67.5(2)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(11)	Pr(2)	O(14)	130.0(2)	O(12)	Pr(2)	O(14)	69.0(2)
O(11)	Pr(2)	O(15)	111.7(2)	O(12)	Pr(2)	O(14)	178.1(3)
O(11)	Pr(2)	O(15)	110.8(2)	O(12)	Pr(2)	O(15)	68.2(2)
O(11)	Pr(2)	O(15)	178.5(3)	O(12)	Pr(2)	O(15)	114.0(2)
O(11)	Pr(2)	O(11)	67.7(3)	O(12)	Pr(2)	O(15)	132.4(2)
O(11)	Pr(2)	O(12)	110.7(3)	O(12)	Pr(2)	O(12)	110.5(2)
O(11)	Pr(2)	O(12)	48.8(2)	O(12)	Pr(2)	O(14)	178.1(3)
O(11)	Pr(2)	O(12)	65.2(2)	O(12)	Pr(2)	O(14)	68.2(2)
O(11)	Pr(2)	O(14)	130.0(2)	O(12)	Pr(2)	O(14)	69.0(2)
O(11)	Pr(2)	O(14)	113.1(2)	O(12)	Pr(2)	O(15)	132.4(2)
O(11)	Pr(2)	O(14)	67.5(2)	O(12)	Pr(2)	O(15)	68.2(2)
O(11)	Pr(2)	O(15)	178.5(3)	O(12)	Pr(2)	O(15)	114.0(2)
O(11)	Pr(2)	O(15)	111.7(2)	O(12)	Pr(2)	O(14)	69.0(2)
O(11)	Pr(2)	O(15)	110.8(2)	O(12)	Pr(2)	O(14)	178.1(3)
O(11)	Pr(2)	O(12)	65.2(2)	O(12)	Pr(2)	O(14)	68.2(2)
O(11)	Pr(2)	O(12)	110.7(3)	O(12)	Pr(2)	O(15)	114.0(2)
O(11)	Pr(2)	O(12)	48.8(2)	O(12)	Pr(2)	O(15)	132.4(2)
O(11)	Pr(2)	O(14)	67.5(2)	O(12)	Pr(2)	O(15)	68.2(2)
O(11)	Pr(2)	O(14)	130.0(2)	O(14)	Pr(2)	O(14)	112.3(2)
O(11)	Pr(2)	O(14)	113.1(2)	O(14)	Pr(2)	O(14)	112.3(2)
O(11)	Pr(2)	O(15)	110.8(2)	O(14)	Pr(2)	O(15)	48.8(2)
O(11)	Pr(2)	O(15)	178.5(3)	O(14)	Pr(2)	O(15)	113.5(3)
O(11)	Pr(2)	O(15)	111.7(2)	O(14)	Pr(2)	O(15)	67.6(2)
O(12)	Pr(2)	O(12)	110.5(2)	O(14)	Pr(2)	O(14)	112.3(2)
O(12)	Pr(2)	O(12)	110.5(2)	O(14)	Pr(2)	O(15)	67.6(2)
O(12)	Pr(2)	O(14)	68.2(2)	O(14)	Pr(2)	O(15)	48.8(2)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(14)	Pr(2)	O(15)	113.5(3)	Pr(2)	O(15)	N(6)	98.3(5)
O(14)	Pr(2)	O(15)	113.5(3)	Pr(1)	N(1)	C(1)	123.8(6)
O(14)	Pr(2)	O(15)	67.6(2)	Pr(1)	N(1)	C(5)	119.2(6)
O(14)	Pr(2)	O(15)	48.8(2)	C(1)	N(1)	C(5)	116.8(8)
O(15)	Pr(2)	O(15)	69.8(3)	Pr(1)	N(2)	C(10)	121.5(6)
O(15)	Pr(2)	O(15)	69.8(3)	Pr(1)	N(2)	C(14)	120.0(6)
O(15)	Pr(2)	O(15)	69.8(3)	C(10)	N(2)	C(14)	117.9(8)
Pr(1)	O(1)	C(6)	123.5(5)	O(5)	N(3)	O(6)	113.4(9)
Pr(1)	O(1)	C(7)	122.0(5)	O(5)	N(3)	O(7)	120.3(9)
C(6)	O(1)	C(7)	112.0(7)	O(6)	N(3)	O(7)	126.2(9)
Pr(1)	O(2)	C(8)	122.8(5)	O(8)	N(4)	O(9)	116.4(8)
Pr(1)	O(2)	C(9)	123.4(5)	O(8)	N(4)	O(10)	122.2(8)
C(8)	O(2)	C(9)	112.4(7)	O(9)	N(4)	O(10)	121.4(8)
Pr(1)	O(3)	C(15)	120.9(6)	O(11)	N(5)	O(12)	117.7(8)
Pr(1)	O(3)	C(16)	122.0(5)	O(11)	N(5)	O(13)	120.9(9)
C(15)	O(3)	C(16)	112.4(7)	O(12)	N(5)	O(13)	121.4(9)
Pr(1)	O(4)	C(17)	120.9(5)	O(14)	N(6)	O(15)	117.0(8)
Pr(1)	O(4)	C(18)	127.2(5)	O(14)	N(6)	O(16)	120.7(9)
C(17)	O(4)	C(18)	111.8(7)	O(15)	N(6)	O(16)	122.2(9)
Pr(1)	O(5)	N(3)	97.9(6)	N(1)	C(1)	C(2)	124.2(9)
Pr(1)	O(6)	N(3)	98.2(6)	N(1)	C(1)	C(18)	116.2(8)
Pr(1)	O(8)	N(4)	96.1(5)	C(2)	C(1)	C(18)	119.6(8)
Pr(1)	O(9)	N(4)	97.4(6)	C(1)	C(2)	C(3)	117.7(9)
Pr(2)	O(11)	N(5)	98.3(6)	C(2)	C(3)	C(4)	119.8(9)
Pr(2)	O(12)	N(5)	95.3(6)	C(3)	C(4)	C(5)	118.1(9)
Pr(2)	O(14)	N(6)	95.8(5)	N(1)	C(5)	C(4)	123.3(9)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	C(5)	C(6)	118.3(9)	O(4)	C(18)	C(1)	111.8(8)
C(4)	C(5)	C(6)	118.4(9)				
O(1)	C(6)	C(5)	110.0(8)				
O(1)	C(7)	C(8)	106.3(8)				
O(1)	C(7)	C(19)	109.6(9)				
C(8)	C(7)	C(19)	112.0(8)				
O(2)	C(8)	C(7)	104.9(8)				
O(2)	C(8)	C(20)	111.9(8)				
C(7)	C(8)	C(20)	114.3(9)				
O(2)	C(9)	C(10)	107.4(8)				
N(2)	C(10)	C(9)	116.8(9)				
N(2)	C(10)	C(11)	123(1)				
C(9)	C(10)	C(11)	119.7(9)				
C(10)	C(11)	C(12)	117(1)				
C(11)	C(12)	C(13)	121.5(9)				
C(12)	C(13)	C(14)	115.6(9)				
N(2)	C(14)	C(13)	124.4(9)				
N(2)	C(14)	C(15)	117.6(8)				
C(13)	C(14)	C(15)	117.9(9)				
O(3)	C(15)	C(14)	108.5(7)				
O(3)	C(16)	C(17)	104.4(7)				
O(3)	C(16)	C(21)	110.9(8)				
C(17)	C(16)	C(21)	113.8(8)				
O(4)	C(17)	C(16)	106.0(7)				
O(4)	C(17)	C(22)	110.4(7)				
C(16)	C(17)	C(22)	114.4(8)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms and Intramolecular Bond Angles Involving the Nonhydrogen Atoms of [Ce(NO₃)₂•1]₃[Ce(NO₃)₆]

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
Ce (1)	O (1)	2.547 (4)	1	O (3)	C (17)	1.442 (7)	1
Ce (1)	O (2)	2.552 (4)	1	O (3)	C (18)	1.461 (7)	1
Ce (1)	O (3)	2.581 (5)	1	O (4)	C (20)	1.459 (7)	1
Ce (1)	O (4)	2.528 (4)	1	O (4)	C (22)	1.433 (7)	1
Ce (1)	O (5)	2.603 (6)	1	O (5)	N (3)	1.278 (6)	1
Ce (1)	O (6)	2.564 (8)	1	O (6)	N (3)	1.285 (7)	1
Ce (1)	O (8)	2.549 (6)	1	O (7)	N (3)	1.221 (7)	1
Ce (1)	O (9)	2.586 (7)	1	O (8)	N (4)	1.288 (7)	1
Ce (1)	N (1)	2.666 (5)	1	O (9)	N (4)	1.278 (6)	1
Ce (1)	N (2)	2.676 (5)	1	O (10)	N (4)	1.208 (7)	1
Ce (2)	O (11)	2.640 (6)	1	O (11)	N (6)	1.281 (6)	1
Ce (2)	O (11)	2.637 (6)	2	O (12)	N (6)	1.270 (7)	1
Ce (2)	O (11)	2.637 (6)	3	O (13)	N (6)	1.234 (7)	1
Ce (2)	O (12)	2.686 (5)	1	O (14)	N (5)	1.265 (7)	1
Ce (2)	O (12)	2.683 (5)	2	O (15)	N (5)	1.263 (7)	1
Ce (2)	O (12)	2.686 (5)	3	O (16)	N (5)	1.235 (7)	1
Ce (2)	O (14)	2.654 (5)	1	N (1)	C (1)	1.351 (7)	1
Ce (2)	O (14)	2.655 (5)	2	N (1)	C (5)	1.335 (7)	1
Ce (2)	O (14)	2.652 (5)	3	N (2)	C (12)	1.338 (7)	1
Ce (2)	O (15)	2.593 (6)	1	N (2)	C (16)	1.345 (8)	1
Ce (2)	O (15)	2.596 (6)	2	C (1)	C (2)	1.410 (8)	1
Ce (2)	O (15)	2.592 (6)	3	C (1)	C (22)	1.480 (8)	1
O (1)	C (6)	1.435 (7)	1	C (2)	C (3)	1.376 (9)	1
O (1)	C (7)	1.467 (6)	1	C (3)	C (4)	1.380 (9)	1
O (2)	C (9)	1.472 (7)	1	C (4)	C (5)	1.400 (8)	1
O (2)	C (11)	1.432 (7)	1	C (5)	C (6)	1.489 (8)	1

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms cont

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
C(7)	C(8)	1.502(9)	1				
C(7)	C(9)	1.517(8)	1				
C(9)	C(10)	1.517(9)	1				
C(11)	C(12)	1.509(9)	1				
C(12)	C(13)	1.382(7)	1				
C(13)	C(14)	1.39(1)	1				
C(14)	C(15)	1.38(1)	1				
C(15)	C(16)	1.393(8)	1				
C(16)	C(17)	1.494(9)	1				
C(18)	C(19)	1.514(9)	1				
C(18)	C(20)	1.51(1)	1				
C(20)	C(21)	1.53(1)	1				

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Ce(1)	O(2)	61.7(1)	O(4)	Ce(1)	O(8)	77.3(2)
O(1)	Ce(1)	O(3)	158.3(3)	O(4)	Ce(1)	O(9)	109.7(2)
O(1)	Ce(1)	O(4)	122.5(1)	O(4)	Ce(1)	N(1)	62.3(1)
O(1)	Ce(1)	O(5)	114.2(2)	O(4)	Ce(1)	N(2)	118.2(1)
O(1)	Ce(1)	O(6)	84.1(2)	O(5)	Ce(1)	O(6)	49.6(2)
O(1)	Ce(1)	O(8)	74.9(2)	O(5)	Ce(1)	O(8)	169.5(2)
O(1)	Ce(1)	O(9)	88.2(2)	O(5)	Ce(1)	O(9)	132.7(1)
O(1)	Ce(1)	N(1)	60.6(1)	O(5)	Ce(1)	N(1)	113.1(2)
O(1)	Ce(1)	N(2)	119.1(1)	O(5)	Ce(1)	N(2)	65.5(1)
O(2)	Ce(1)	O(3)	120.7(1)	O(6)	Ce(1)	O(8)	129.9(2)
O(2)	Ce(1)	O(4)	166.5(2)	O(6)	Ce(1)	O(9)	171.8(1)
O(2)	Ce(1)	O(5)	74.2(2)	O(6)	Ce(1)	N(1)	64.0(2)
O(2)	Ce(1)	O(6)	91.5(2)	O(6)	Ce(1)	N(2)	114.5(2)
O(2)	Ce(1)	O(8)	115.7(2)	O(8)	Ce(1)	O(9)	49.7(2)
O(2)	Ce(1)	O(9)	82.5(2)	O(8)	Ce(1)	N(1)	66.0(1)
O(2)	Ce(1)	N(1)	118.7(1)	O(8)	Ce(1)	N(2)	115.5(2)
O(2)	Ce(1)	N(2)	60.5(1)	O(9)	Ce(1)	N(1)	114.1(2)
O(3)	Ce(1)	O(4)	60.9(1)	O(9)	Ce(1)	N(2)	67.2(2)
O(3)	Ce(1)	O(5)	85.9(1)	N(1)	Ce(1)	N(2)	178.5(3)
O(3)	Ce(1)	O(6)	116.5(2)	O(11)	Ce(2)	O(11)	67.6(2)
O(3)	Ce(1)	O(8)	85.9(2)	O(11)	Ce(2)	O(11)	67.6(2)
O(3)	Ce(1)	O(9)	71.5(2)	O(11)	Ce(2)	O(12)	48.2(1)
O(3)	Ce(1)	N(1)	120.6(1)	O(11)	Ce(2)	O(12)	110.2(2)
O(3)	Ce(1)	N(2)	60.4(1)	O(11)	Ce(2)	O(12)	65.3(2)
O(4)	Ce(1)	O(5)	92.9(2)	O(11)	Ce(2)	O(14)	113.7(2)
O(4)	Ce(1)	O(6)	76.8(2)	O(11)	Ce(2)	O(14)	130.0(2)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(11)	Ce(2)	O(14)	67.8(2)	O(12)	Ce(2)	O(14)	178.0(3)
O(11)	Ce(2)	O(15)	111.5(1)	O(12)	Ce(2)	O(14)	68.4(1)
O(11)	Ce(2)	O(15)	178.1(2)	O(12)	Ce(2)	O(15)	68.4(1)
O(11)	Ce(2)	O(15)	110.5(1)	O(12)	Ce(2)	O(15)	133.3(2)
O(11)	Ce(2)	O(11)	67.7(2)	O(12)	Ce(2)	O(15)	113.9(2)
O(11)	Ce(2)	O(12)	65.2(2)	O(12)	Ce(2)	O(12)	110.2(1)
O(11)	Ce(2)	O(12)	48.3(1)	O(12)	Ce(2)	O(14)	68.4(1)
O(11)	Ce(2)	O(12)	110.2(2)	O(12)	Ce(2)	O(14)	69.5(1)
O(11)	Ce(2)	O(14)	67.9(2)	O(12)	Ce(2)	O(14)	178.0(3)
O(11)	Ce(2)	O(14)	113.8(2)	O(12)	Ce(2)	O(15)	113.8(2)
O(11)	Ce(2)	O(14)	129.9(2)	O(12)	Ce(2)	O(15)	68.4(1)
O(11)	Ce(2)	O(15)	110.4(1)	O(12)	Ce(2)	O(15)	133.2(2)
O(11)	Ce(2)	O(15)	111.5(1)	O(12)	Ce(2)	O(14)	178.0(3)
O(11)	Ce(2)	O(15)	178.1(2)	O(12)	Ce(2)	O(14)	68.4(1)
O(11)	Ce(2)	O(12)	110.1(2)	O(12)	Ce(2)	O(14)	69.4(1)
O(11)	Ce(2)	O(12)	65.4(2)	O(12)	Ce(2)	O(15)	133.3(2)
O(11)	Ce(2)	O(12)	48.2(1)	O(12)	Ce(2)	O(15)	113.8(2)
O(11)	Ce(2)	O(14)	130.0(2)	O(12)	Ce(2)	O(15)	68.4(1)
O(11)	Ce(2)	O(14)	67.9(2)	O(14)	Ce(2)	O(14)	111.9(1)
O(11)	Ce(2)	O(14)	113.6(2)	O(14)	Ce(2)	O(14)	111.9(1)
O(11)	Ce(2)	O(15)	178.1(2)	O(14)	Ce(2)	O(15)	48.5(1)
O(11)	Ce(2)	O(15)	110.5(1)	O(14)	Ce(2)	O(15)	67.1(2)
O(11)	Ce(2)	O(15)	111.5(1)	O(14)	Ce(2)	O(15)	113.6(2)
O(12)	Ce(2)	O(12)	110.2(1)	O(14)	Ce(2)	O(14)	111.9(1)
O(12)	Ce(2)	O(12)	110.1(1)	O(14)	Ce(2)	O(15)	113.6(2)
O(12)	Ce(2)	O(14)	69.5(1)	O(14)	Ce(2)	O(15)	48.6(1)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(14)	Ce(2)	O(15)	67.1(2)	Ce(2)	O(15)	N(5)	98.7(3)
O(14)	Ce(2)	O(15)	67.2(2)	Ce(1)	N(1)	C(1)	118.8(4)
O(14)	Ce(2)	O(15)	113.6(2)	Ce(1)	N(1)	C(5)	122.4(4)
O(14)	Ce(2)	O(15)	48.6(1)	C(1)	N(1)	C(5)	118.6(5)
O(15)	Ce(2)	O(15)	70.3(2)	Ce(1)	N(2)	C(12)	119.8(4)
O(15)	Ce(2)	O(15)	70.4(2)	Ce(1)	N(2)	C(16)	120.9(4)
O(15)	Ce(2)	O(15)	70.3(2)	C(12)	N(2)	C(16)	118.6(5)
Ce(1)	O(1)	C(6)	127.9(3)	O(5)	N(3)	O(6)	115.5(5)
Ce(1)	O(1)	C(7)	120.5(3)	O(5)	N(3)	O(7)	122.1(5)
C(6)	O(1)	C(7)	111.5(4)	O(6)	N(3)	O(7)	122.3(5)
Ce(1)	O(2)	C(9)	121.6(3)	O(8)	N(4)	O(9)	114.6(5)
Ce(1)	O(2)	C(11)	121.3(3)	O(8)	N(4)	O(10)	122.0(5)
C(9)	O(2)	C(11)	112.5(4)	O(9)	N(4)	O(10)	123.4(5)
Ce(1)	O(3)	C(17)	122.8(3)	O(14)	N(5)	O(15)	117.2(5)
Ce(1)	O(3)	C(18)	122.7(3)	O(14)	N(5)	O(16)	121.0(5)
C(17)	O(3)	C(18)	112.9(4)	O(15)	N(5)	O(16)	121.8(6)
Ce(1)	O(4)	C(20)	121.0(3)	O(11)	N(6)	O(12)	116.9(5)
Ce(1)	O(4)	C(22)	122.4(3)	O(11)	N(6)	O(13)	120.1(5)
C(20)	O(4)	C(22)	112.4(4)	O(12)	N(6)	O(13)	122.9(5)
Ce(1)	O(5)	N(3)	96.6(3)	N(1)	C(1)	C(2)	121.8(5)
Ce(1)	O(6)	N(3)	98.3(4)	N(1)	C(1)	C(22)	118.5(5)
Ce(1)	O(8)	N(4)	98.5(3)	C(2)	C(1)	C(22)	119.7(5)
Ce(1)	O(9)	N(4)	97.0(3)	C(1)	C(2)	C(3)	118.7(5)
Ce(2)	O(11)	N(6)	98.4(3)	C(2)	C(3)	C(4)	119.5(5)
Ce(2)	O(12)	N(6)	96.5(3)	C(3)	C(4)	C(5)	118.8(5)
Ce(2)	O(14)	N(5)	95.6(3)	N(1)	C(5)	C(4)	122.5(5)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
N(1)	C(5)	C(6)	118.6(5)	O(4)	C(22)	C(1)	110.3(5)
C(4)	C(5)	C(6)	118.9(5)				
O(1)	C(6)	C(5)	109.9(5)				
O(1)	C(7)	C(8)	110.9(5)				
O(1)	C(7)	C(9)	105.6(5)				
C(8)	C(7)	C(9)	113.9(5)				
O(2)	C(9)	C(7)	104.7(4)				
O(2)	C(9)	C(10)	109.6(5)				
C(7)	C(9)	C(10)	114.1(5)				
O(2)	C(11)	C(12)	109.6(5)				
N(2)	C(12)	C(11)	117.5(5)				
N(2)	C(12)	C(13)	122.8(6)				
C(11)	C(12)	C(13)	119.7(5)				
C(12)	C(13)	C(14)	118.3(6)				
C(13)	C(14)	C(15)	119.7(5)				
C(14)	C(15)	C(16)	118.2(6)				
N(2)	C(16)	C(15)	122.4(5)				
N(2)	C(16)	C(17)	117.9(5)				
C(15)	C(16)	C(17)	119.7(5)				
O(3)	C(17)	C(16)	107.2(5)				
O(3)	C(18)	C(19)	111.0(5)				
O(3)	C(18)	C(20)	104.4(5)				
C(19)	C(18)	C(20)	114.8(5)				
O(4)	C(20)	C(18)	106.0(5)				
O(4)	C(20)	C(21)	110.6(6)				
C(18)	C(20)	C(21)	112.8(5)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms and Intramolecular Bond Angles Involving the Nonhydrogen Atoms of [Gd(NO₃)₂•1](NO₃)

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	atom	atom	distance
Gd(1)	O(1)	2.450(6)	O(12)	N(5)	1.25(3)
Gd(1)	O(2)	2.483(8)	O(13)	N(5)	1.25(2)
Gd(1)	O(3)	2.495(9)	N(1)	C(1)	1.32(2)
Gd(1)	O(4)	2.467(6)	N(1)	C(5)	1.30(2)
Gd(1)	O(5)	2.501(9)	N(2)	C(12)	1.37(2)
Gd(1)	O(6)	2.496(8)	N(2)	C(16)	1.39(2)
Gd(1)	O(8)	2.499(7)	C(1)	C(2)	1.32(3)
Gd(1)	O(9)	2.511(9)	C(1)	C(22)	1.53(2)
Gd(1)	N(1)	2.600(8)	C(2)	C(3)	1.41(3)
Gd(1)	N(2)	2.590(7)	C(3)	C(4)	1.34(3)
O(1)	C(6)	1.42(1)	C(4)	C(5)	1.45(2)
O(1)	C(7)	1.48(1)	C(5)	C(6)	1.55(2)
O(2)	C(9)	1.47(1)	C(7)	C(8)	1.48(2)
O(2)	C(11)	1.45(2)	C(7)	C(9)	1.52(2)
O(3)	C(17)	1.46(2)	C(9)	C(10)	1.36(3)
O(3)	C(18)	1.43(1)	C(11)	C(12)	1.49(2)
O(4)	C(20)	1.45(1)	C(12)	C(13)	1.40(2)
O(4)	C(22)	1.46(1)	C(13)	C(14)	1.36(3)
O(5)	N(3)	1.26(2)	C(14)	C(15)	1.39(3)
O(6)	N(3)	1.30(1)	C(15)	C(16)	1.38(1)
O(7)	N(3)	1.20(2)	C(16)	C(17)	1.49(2)
O(8)	N(4)	1.29(1)	C(18)	C(19)	1.57(2)
O(9)	N(4)	1.25(2)	C(18)	C(20)	1.48(2)
O(10)	N(4)	1.20(2)	C(20)	C(21)	1.63(2)
O(11)	N(5)	1.27(2)			

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Gd(1)	O(2)	61.7(3)	O(4)	Gd(1)	O(8)	80.1(3)
O(1)	Gd(1)	O(3)	157.1(3)	O(4)	Gd(1)	O(9)	118.8(3)
O(1)	Gd(1)	O(4)	124.3(2)	O(4)	Gd(1)	N(1)	62.4(5)
O(1)	Gd(1)	O(5)	118.8(3)	O(4)	Gd(1)	N(2)	118.2(5)
O(1)	Gd(1)	O(6)	80.0(3)	O(5)	Gd(1)	O(6)	50.7(4)
O(1)	Gd(1)	O(8)	78.4(3)	O(5)	Gd(1)	O(8)	161.2(3)
O(1)	Gd(1)	O(9)	83.9(3)	O(5)	Gd(1)	O(9)	133.1(4)
O(1)	Gd(1)	N(1)	61.9(5)	O(5)	Gd(1)	N(1)	113.3(5)
O(1)	Gd(1)	N(2)	117.4(5)	O(5)	Gd(1)	N(2)	67.5(5)
O(2)	Gd(1)	O(3)	123.6(4)	O(6)	Gd(1)	O(8)	133.1(3)
O(2)	Gd(1)	O(4)	156.9(2)	O(6)	Gd(1)	O(9)	161.3(3)
O(2)	Gd(1)	O(5)	75.3(2)	O(6)	Gd(1)	N(1)	66.7(3)
O(2)	Gd(1)	O(6)	81.0(3)	O(6)	Gd(1)	N(2)	113.9(3)
O(2)	Gd(1)	O(8)	122.2(3)	O(8)	Gd(1)	O(9)	51.2(4)
O(2)	Gd(1)	O(9)	82.9(3)	O(8)	Gd(1)	N(1)	66.4(3)
O(2)	Gd(1)	N(1)	118.3(5)	O(8)	Gd(1)	N(2)	113.0(3)
O(2)	Gd(1)	N(2)	61.4(5)	O(9)	Gd(1)	N(1)	113.6(5)
O(3)	Gd(1)	O(4)	61.0(3)	O(9)	Gd(1)	N(2)	65.6(5)
O(3)	Gd(1)	O(5)	83.0(4)	N(1)	Gd(1)	N(2)	179.1(9)
O(3)	Gd(1)	O(6)	122.0(3)	Gd(1)	O(1)	C(6)	124.1(7)
O(3)	Gd(1)	O(8)	81.1(3)	Gd(1)	O(1)	C(7)	123.4(7)
O(3)	Gd(1)	O(9)	75.3(2)	C(6)	O(1)	C(7)	111.4(8)
O(3)	Gd(1)	N(1)	118.1(5)	Gd(1)	O(2)	C(9)	124.7(8)
O(3)	Gd(1)	N(2)	62.3(5)	Gd(1)	O(2)	C(11)	122.1(7)
O(4)	Gd(1)	O(5)	83.5(3)	C(9)	O(2)	C(11)	111.1(9)
O(4)	Gd(1)	O(6)	78.7(3)	Gd(1)	O(3)	C(17)	120.2(7)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
Gd(1)	O(3)	C(18)	124.7(9)	C(2)	C(1)	C(22)	117(2)
C(17)	O(3)	C(18)	113.2(9)	C(1)	C(2)	C(3)	119(2)
Gd(1)	O(4)	C(20)	122.8(7)	C(2)	C(3)	C(4)	120(1)
Gd(1)	O(4)	C(22)	124.9(7)	C(3)	C(4)	C(5)	114(1)
C(20)	O(4)	C(22)	111.4(8)	N(1)	C(5)	C(4)	126(1)
Gd(1)	O(5)	N(3)	98.0(8)	N(1)	C(5)	C(6)	114(2)
Gd(1)	O(6)	N(3)	97.4(7)	C(4)	C(5)	C(6)	119(1)
Gd(1)	O(8)	N(4)	95.7(7)	O(1)	C(6)	C(5)	110(1)
Gd(1)	O(9)	N(4)	96.2(8)	O(1)	C(7)	C(8)	109(1)
Gd(1)	N(1)	C(1)	121(1)	O(1)	C(7)	C(9)	106.2(8)
Gd(1)	N(1)	C(5)	123(1)	C(8)	C(7)	C(9)	115(1)
C(1)	N(1)	C(5)	115.4(9)	O(2)	C(9)	C(7)	103(1)
Gd(1)	N(2)	C(12)	121.0(8)	O(2)	C(9)	C(10)	114(1)
Gd(1)	N(2)	C(16)	120.9(9)	C(7)	C(9)	C(10)	113(1)
C(12)	N(2)	C(16)	118.0(9)	O(2)	C(11)	C(12)	107.5(8)
O(5)	N(3)	O(6)	113.2(9)	N(2)	C(12)	C(11)	116(1)
O(5)	N(3)	O(7)	126(2)	N(2)	C(12)	C(13)	121(1)
O(6)	N(3)	O(7)	121(1)	C(11)	C(12)	C(13)	123(1)
O(8)	N(4)	O(9)	117(1)	C(12)	C(13)	C(14)	119(1)
O(8)	N(4)	O(10)	123(1)	C(13)	C(14)	C(15)	121(1)
O(9)	N(4)	O(10)	121(2)	C(14)	C(15)	C(16)	118(1)
O(11)	N(5)	O(12)	119(2)	N(2)	C(16)	C(15)	123(1)
O(11)	N(5)	O(13)	121(1)	N(2)	C(16)	C(17)	115(1)
O(12)	N(5)	O(13)	120(2)	C(15)	C(16)	C(17)	122(1)
N(1)	C(1)	C(2)	125(2)	O(3)	C(17)	C(16)	108.7(9)
N(1)	C(1)	C(22)	118(2)	O(3)	C(18)	C(19)	107(1)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(3)	C(18)	C(20)	105.1(9)				
C(19)	C(18)	C(20)	118(1)				
O(4)	C(20)	C(18)	107.3(8)				
O(4)	C(20)	C(21)	108(1)				
C(18)	C(20)	C(21)	116(1)				
O(4)	C(22)	C(1)	108(1)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms and Intramolecular Bond Angles Involving the Nonhydrogen Atoms of [Y(NO₃)₂•**1**](NO₃)(EtOH)

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
Y(1)	O(1)	2.424(3)	1	O(7)	N(4)	1.258(4)	1
Y(1)	O(1)	2.424(3)	75604	O(8)	C(14)	1.302(9)	1
Y(1)	O(2)	2.439(5)	1	N(1)	C(3)	1.335(5)	1
Y(1)	O(2)	2.439(5)	75604	N(1)	C(3)	1.335(5)	75604
Y(1)	O(3)	2.444(3)	1	N(2)	C(10)	1.356(5)	1
Y(1)	O(3)	2.444(3)	75604	N(2)	C(10)	1.356(5)	75604
Y(1)	O(4)	2.465(4)	1	C(1)	C(2)	1.371(5)	1
Y(1)	O(4)	2.465(4)	75604	C(1)	C(2)	1.371(5)	75604
Y(1)	N(1)	2.568(5)	1	C(2)	C(3)	1.404(6)	1
Y(1)	N(2)	2.599(5)	1	C(3)	C(4)	1.491(6)	1
O(1)	C(4)	1.450(5)	1	C(5)	C(6)	1.546(7)	1
O(1)	C(5)	1.456(5)	1	C(5)	C(7)	1.519(7)	1
O(2)	C(7)	1.472(6)	1	C(7)	C(8)	1.503(9)	1
O(2)	C(9)	1.448(7)	1	C(9)	C(10)	1.505(7)	1
O(3)	N(3)	1.268(5)	1	C(10)	C(11)	1.372(6)	1
O(4)	N(3)	1.257(6)	1	C(11)	C(12)	1.368(6)	1
O(5)	N(3)	1.215(6)	1	C(14)	C(14)	1.52(1)	56602
O(6)	N(4)	1.244(9)	1				

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Y(1)	O(1)	124.7(1)	O(2)	Y(1)	O(4)	83.8(1)
O(1)	Y(1)	O(2)	62.7(1)	O(2)	Y(1)	O(4)	73.69(9)
O(1)	Y(1)	O(2)	154.6(1)	O(2)	Y(1)	N(1)	118.6(1)
O(1)	Y(1)	O(3)	80.3(1)	O(2)	Y(1)	N(2)	61.4(1)
O(1)	Y(1)	O(3)	78.1(1)	O(3)	Y(1)	O(3)	132.3(2)
O(1)	Y(1)	O(4)	120.0(1)	O(3)	Y(1)	O(4)	52.1(1)
O(1)	Y(1)	O(4)	82.9(1)	O(3)	Y(1)	O(4)	160.5(1)
O(1)	Y(1)	N(1)	62.33(7)	O(3)	Y(1)	N(1)	66.17(8)
O(1)	Y(1)	N(2)	117.67(7)	O(3)	Y(1)	N(2)	113.83(8)
O(1)	Y(1)	O(2)	154.6(1)	O(3)	Y(1)	O(4)	160.5(1)
O(1)	Y(1)	O(2)	62.7(1)	O(3)	Y(1)	O(4)	52.1(1)
O(1)	Y(1)	O(3)	78.1(1)	O(3)	Y(1)	N(1)	66.17(8)
O(1)	Y(1)	O(3)	80.3(1)	O(3)	Y(1)	N(2)	113.83(8)
O(1)	Y(1)	O(4)	82.9(1)	O(4)	Y(1)	O(4)	132.1(2)
O(1)	Y(1)	O(4)	120.0(1)	O(4)	Y(1)	N(1)	114.0(1)
O(1)	Y(1)	N(1)	62.33(7)	O(4)	Y(1)	N(2)	66.0(1)
O(1)	Y(1)	N(2)	117.67(7)	O(4)	Y(1)	N(1)	114.0(1)
O(2)	Y(1)	O(2)	122.9(2)	O(4)	Y(1)	N(2)	66.0(1)
O(2)	Y(1)	O(3)	79.7(1)	N(1)	Y(1)	N(2)	180.00
O(2)	Y(1)	O(3)	124.4(1)	Y(1)	O(1)	C(4)	125.2(3)
O(2)	Y(1)	O(4)	73.69(9)	Y(1)	O(1)	C(5)	121.9(2)
O(2)	Y(1)	O(4)	83.8(1)	C(4)	O(1)	C(5)	111.8(3)
O(2)	Y(1)	N(1)	118.6(1)	Y(1)	O(2)	C(7)	124.8(3)
O(2)	Y(1)	N(2)	61.4(1)	Y(1)	O(2)	C(9)	123.6(3)
O(2)	Y(1)	O(3)	124.4(1)	C(7)	O(2)	C(9)	110.6(4)
O(2)	Y(1)	O(3)	79.7(1)	Y(1)	O(3)	N(3)	95.3(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
Y(1)	O(4)	N(3)	94.6(3)	N(2)	C(10)	C(9)	115.9(4)
Y(1)	N(1)	C(3)	121.3(3)	N(2)	C(10)	C(11)	121.2(5)
Y(1)	N(1)	C(3)	121.3(3)	C(9)	C(10)	C(11)	122.9(5)
C(3)	N(1)	C(3)	117.4(5)	C(10)	C(11)	C(12)	120.5(5)
Y(1)	N(2)	C(10)	120.8(3)	C(11)	C(12)	C(11)	118.3(6)
Y(1)	N(2)	C(10)	120.8(3)	O(8)	C(14)	C(14)	112.0(4)
C(10)	N(2)	C(10)	118.4(5)				
O(3)	N(3)	O(4)	117.2(4)				
O(3)	N(3)	O(5)	121.7(5)				
O(4)	N(3)	O(5)	121.1(5)				
O(6)	N(4)	O(7)	119.8(3)				
O(6)	N(4)	O(7)	119.8(3)				
O(7)	N(4)	O(7)	120.4(6)				
C(2)	C(1)	C(2)	118.9(6)				
C(1)	C(2)	C(3)	118.9(5)				
N(1)	C(3)	C(2)	122.9(4)				
N(1)	C(3)	C(4)	117.5(4)				
C(2)	C(3)	C(4)	119.6(4)				
O(1)	C(4)	C(3)	107.9(3)				
O(1)	C(5)	C(6)	109.3(4)				
O(1)	C(5)	C(7)	106.5(3)				
C(6)	C(5)	C(7)	116.3(4)				
O(2)	C(7)	C(5)	103.1(4)				
O(2)	C(7)	C(8)	111.1(4)				
C(5)	C(7)	C(8)	114.0(5)				
O(2)	C(9)	C(10)	106.9(4)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms and Intramolecular Bond Angles Involving the Nonhydrogen Atoms of [Pr(NO₃)₂•3]₃[Pr(NO₃)₆]

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
Pr(1)	O(1)	2.509(9)	1	Pr(3)	O(23)	2.677(9)	1
Pr(1)	O(2)	2.550(8)	1	Pr(3)	O(23)	2.677(9)	2
Pr(1)	O(3)	2.515(8)	1	Pr(3)	O(25)	2.63(1)	1
Pr(1)	O(4)	2.555(7)	1	Pr(3)	O(25)	2.63(1)	2
Pr(1)	O(7)	2.568(9)	1	Pr(3)	O(26)	2.60(2)	1
Pr(1)	O(8)	2.554(9)	1	Pr(3)	O(26)	2.60(2)	2
Pr(1)	O(10)	2.577(8)	1	Pr(3)	O(25')	2.49(2)	1
Pr(1)	O(11)	2.587(8)	1	Pr(3)	O(25')	2.49(2)	2
Pr(1)	N(1)	2.63(1)	1	Pr(3)	O(26')	2.68(2)	1
Pr(1)	N(2)	2.615(9)	1	Pr(3)	O(26')	2.68(2)	2
Pr(2)	O(13)	2.553(7)	1	O(1)	C(6)	1.48(2)	1
Pr(2)	O(13)	2.553(7)	56502	O(1)	C(7)	1.44(1)	1
Pr(2)	O(14)	2.594(7)	1	O(2)	C(8)	1.42(2)	1
Pr(2)	O(14)	2.594(7)	56502	O(2)	C(9)	1.42(2)	1
Pr(2)	O(16)	2.553(8)	1	O(3)	C(15)	1.45(2)	1
Pr(2)	O(16)	2.553(8)	56502	O(3)	C(16)	1.46(2)	1
Pr(2)	O(17)	2.551(9)	1	O(4)	C(17)	1.49(2)	1
Pr(2)	O(17)	2.551(9)	56502	O(4)	C(18)	1.41(1)	1
Pr(2)	N(5)	2.650(9)	1	O(5)	C(3)	1.32(2)	1
Pr(2)	N(5)	2.650(9)	56502	O(5)	C(19)	1.46(2)	1
Pr(3)	O(19)	2.64(1)	1	O(6)	C(12)	1.36(2)	1
Pr(3)	O(19)	2.64(1)	2	O(6)	C(22)	1.40(3)	1
Pr(3)	O(20)	2.560(8)	1	O(6)	C(22')	1.31(3)	1
Pr(3)	O(20)	2.560(8)	2	O(7)	N(3)	1.29(1)	1
Pr(3)	O(22)	2.561(9)	1	O(8)	N(3)	1.28(1)	1
Pr(3)	O(22)	2.561(9)	2	O(9)	N(3)	1.21(1)	1

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms cont

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
O(10)	N(4)	1.28(1)	1	C(1)	C(2)	1.36(2)	1
O(11)	N(4)	1.26(1)	1	C(1)	C(18)	1.49(2)	1
O(12)	N(4)	1.227(9)	1	C(2)	C(3)	1.36(2)	1
O(13)	C(30)	1.56(3)	1	C(3)	C(4)	1.41(2)	1
O(13)	C(30')	1.48(2)	1	C(4)	C(5)	1.37(2)	1
O(13)	C(31)	1.48(1)	1	C(5)	C(6)	1.50(2)	1
O(14)	C(32)	1.48(1)	1	C(7)	C(8)	1.45(2)	1
O(14)	C(33)	1.48(1)	1	C(7)	C(20)	1.59(2)	1
O(15)	C(27)	1.41(2)	1	C(8)	C(21)	1.54(2)	1
O(15)	C(34)	1.46(2)	1	C(9)	C(10)	1.52(2)	1
O(16)	N(6)	1.18(2)	1	C(10)	C(11)	1.36(2)	1
O(17)	N(6)	1.39(2)	1	C(11)	C(12)	1.38(2)	1
O(18)	N(6)	1.26(1)	1	C(12)	C(13)	1.37(2)	1
O(19)	N(8)	1.30(1)	1	C(13)	C(14)	1.39(2)	1
O(20)	N(8)	1.28(1)	1	C(14)	C(15)	1.46(2)	1
O(21)	N(8)	1.27(1)	1	C(16)	C(17)	1.51(2)	1
O(22)	N(7)	1.38(1)	1	C(16)	C(23)	1.46(2)	1
O(23)	N(7)	1.27(2)	1	C(17)	C(24)	1.52(2)	1
O(24)	N(7)	1.30(1)	1	C(25)	C(26)	1.43(2)	1
N(1)	C(1)	1.35(2)	1	C(25)	C(33)	1.55(2)	1
N(1)	C(5)	1.34(2)	1	C(26)	C(27)	1.40(2)	1
N(2)	C(10)	1.37(2)	1	C(27)	C(28)	1.31(3)	1
N(2)	C(14)	1.35(2)	1	C(27)	C(28')	1.52(3)	1
N(5)	C(25)	1.30(2)	1	C(28)	C(28')	0.73(3)	1
N(5)	C(29)	1.40(2)	1	C(28)	C(29)	1.38(3)	1
N(5)	C(29')	1.34(2)	1	C(28)	C(29')	1.69(3)	1

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms cont

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
C(28')	C(29)	1.36(3)	1	N(9')	O(25')	1.25(2)	1
C(28')	C(29')	1.35(3)	1	N(9')	O(26')	1.25(2)	1
C(29)	C(29')	0.67(3)	1	N(9')	O(27')	1.25(2)	1
C(29)	C(30)	1.42(4)	1				
C(29)	C(30')	1.82(3)	1				
C(29')	C(30)	1.57(4)	1				
C(29')	C(30')	1.47(3)	1				
C(30)	C(30')	1.21(4)	1				
C(31)	C(31)	1.61(2)	56502				
C(31)	C(35)	1.54(2)	1				
C(32)	C(32)	1.54(2)	56502				
C(32)	C(36)	1.55(1)	1				
N(9)	O(25)	1.25(2)	1				
N(9)	O(26)	1.25(2)	1				
N(9)	O(27)	1.25(2)	1				
N(9)	N(9')	0.88(2)	1				
N(9)	O(26')	0.59(2)	1				
N(9)	O(27')	1.66(2)	1				
O(25)	N(9')	0.63(2)	1				
O(25)	O(25')	0.78(2)	1				
O(25)	O(26')	1.55(2)	1				
O(25)	O(27')	1.70(2)	1				
O(26)	O(26')	0.76(2)	1				
O(27)	N(9')	1.64(2)	1				
O(27)	O(26')	1.66(2)	1				
O(27)	O(27')	1.33(2)	1				

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Pr(1)	O(2)	60.9(3)	O(4)	Pr(1)	O(10)	86.3(2)
O(1)	Pr(1)	O(3)	162.1(3)	O(4)	Pr(1)	O(11)	75.7(2)
O(1)	Pr(1)	O(4)	122.3(3)	O(4)	Pr(1)	N(1)	60.0(3)
O(1)	Pr(1)	O(7)	75.6(3)	O(4)	Pr(1)	N(2)	119.2(3)
O(1)	Pr(1)	O(8)	86.9(3)	O(7)	Pr(1)	O(8)	50.5(3)
O(1)	Pr(1)	O(10)	116.3(3)	O(7)	Pr(1)	O(10)	167.2(3)
O(1)	Pr(1)	O(11)	81.2(3)	O(7)	Pr(1)	O(11)	133.0(3)
O(1)	Pr(1)	N(1)	62.4(3)	O(7)	Pr(1)	N(1)	67.8(3)
O(1)	Pr(1)	N(2)	118.4(3)	O(7)	Pr(1)	N(2)	114.8(3)
O(2)	Pr(1)	O(3)	123.3(3)	O(8)	Pr(1)	O(10)	131.0(3)
O(2)	Pr(1)	O(4)	158.4(3)	O(8)	Pr(1)	O(11)	165.3(2)
O(2)	Pr(1)	O(7)	117.2(3)	O(8)	Pr(1)	N(1)	116.5(3)
O(2)	Pr(1)	O(8)	82.4(3)	O(8)	Pr(1)	N(2)	66.2(3)
O(2)	Pr(1)	O(10)	74.5(3)	O(10)	Pr(1)	O(11)	49.8(2)
O(2)	Pr(1)	O(11)	84.3(2)	O(10)	Pr(1)	N(1)	112.5(3)
O(2)	Pr(1)	N(1)	118.4(3)	O(10)	Pr(1)	N(2)	64.8(3)
O(2)	Pr(1)	N(2)	61.3(3)	O(11)	Pr(1)	N(1)	65.2(3)
O(3)	Pr(1)	O(4)	61.2(3)	O(11)	Pr(1)	N(2)	112.2(3)
O(3)	Pr(1)	O(7)	88.0(3)	N(1)	Pr(1)	N(2)	177.3(3)
O(3)	Pr(1)	O(8)	77.0(3)	O(13)	Pr(2)	O(13)	61.2(3)
O(3)	Pr(1)	O(10)	80.6(3)	O(13)	Pr(2)	O(14)	121.6(2)
O(3)	Pr(1)	O(11)	115.8(3)	O(13)	Pr(2)	O(14)	164.7(3)
O(3)	Pr(1)	N(1)	118.1(3)	O(13)	Pr(2)	O(16)	78.6(3)
O(3)	Pr(1)	N(2)	62.0(3)	O(13)	Pr(2)	O(16)	83.8(3)
O(4)	Pr(1)	O(7)	83.0(3)	O(13)	Pr(2)	O(17)	119.8(3)
O(4)	Pr(1)	O(8)	118.3(3)	O(13)	Pr(2)	O(17)	79.3(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(13)	Pr(2)	N(5)	61.4(3)	O(16)	Pr(2)	N(5)	65.4(3)
O(13)	Pr(2)	N(5)	118.7(3)	O(16)	Pr(2)	N(5)	114.7(3)
O(13)	Pr(2)	O(14)	164.7(3)	O(16)	Pr(2)	O(17)	132.7(3)
O(13)	Pr(2)	O(14)	121.6(2)	O(16)	Pr(2)	O(17)	52.2(3)
O(13)	Pr(2)	O(16)	83.8(3)	O(16)	Pr(2)	N(5)	114.7(3)
O(13)	Pr(2)	O(16)	78.6(3)	O(16)	Pr(2)	N(5)	65.4(3)
O(13)	Pr(2)	O(17)	79.3(3)	O(17)	Pr(2)	O(17)	159.1(5)
O(13)	Pr(2)	O(17)	119.8(3)	O(17)	Pr(2)	N(5)	112.7(3)
O(13)	Pr(2)	N(5)	118.7(3)	O(17)	Pr(2)	N(5)	67.3(3)
O(13)	Pr(2)	N(5)	61.4(3)	O(17)	Pr(2)	N(5)	67.3(3)
O(14)	Pr(2)	O(14)	60.3(3)	O(17)	Pr(2)	N(5)	112.7(3)
O(14)	Pr(2)	O(16)	82.2(3)	N(5)	Pr(2)	N(5)	179.9(5)
O(14)	Pr(2)	O(16)	116.2(3)	O(19)	Pr(3)	O(19)	133.0(4)
O(14)	Pr(2)	O(17)	87.1(3)	O(19)	Pr(3)	O(20)	49.8(3)
O(14)	Pr(2)	O(17)	74.8(3)	O(19)	Pr(3)	O(20)	172.5(3)
O(14)	Pr(2)	N(5)	60.4(3)	O(19)	Pr(3)	O(22)	68.7(3)
O(14)	Pr(2)	N(5)	119.5(3)	O(19)	Pr(3)	O(22)	72.3(3)
O(14)	Pr(2)	O(16)	116.2(3)	O(19)	Pr(3)	O(23)	63.2(3)
O(14)	Pr(2)	O(16)	82.2(3)	O(19)	Pr(3)	O(23)	109.7(3)
O(14)	Pr(2)	O(17)	74.8(3)	O(19)	Pr(3)	O(25)	98.2(4)
O(14)	Pr(2)	O(17)	87.1(3)	O(19)	Pr(3)	O(25)	114.9(4)
O(14)	Pr(2)	N(5)	119.5(3)	O(19)	Pr(3)	O(26)	59.2(4)
O(14)	Pr(2)	N(5)	60.4(3)	O(19)	Pr(3)	O(26)	120.8(4)
O(16)	Pr(2)	O(16)	159.6(5)	O(19)	Pr(3)	O(25')	107.3(4)
O(16)	Pr(2)	O(17)	52.2(3)	O(19)	Pr(3)	O(25')	114.1(4)
O(16)	Pr(2)	O(17)	132.7(3)	O(19)	Pr(3)	O(26')	67.8(4)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(19)	Pr(3)	O(26')	127.1(5)	O(20)	Pr(3)	O(26')	59.9(5)
O(19)	Pr(3)	O(20)	172.5(3)	O(20)	Pr(3)	O(26')	104.9(4)
O(19)	Pr(3)	O(20)	49.8(3)	O(20)	Pr(3)	O(22)	117.4(3)
O(19)	Pr(3)	O(22)	72.3(3)	O(20)	Pr(3)	O(22)	105.5(3)
O(19)	Pr(3)	O(22)	68.7(3)	O(20)	Pr(3)	O(23)	123.7(3)
O(19)	Pr(3)	O(23)	109.7(3)	O(20)	Pr(3)	O(23)	64.4(3)
O(19)	Pr(3)	O(23)	63.2(3)	O(20)	Pr(3)	O(25)	75.1(3)
O(19)	Pr(3)	O(25)	114.9(4)	O(20)	Pr(3)	O(25)	69.0(3)
O(19)	Pr(3)	O(25)	98.2(4)	O(20)	Pr(3)	O(26)	113.3(4)
O(19)	Pr(3)	O(26)	120.8(4)	O(20)	Pr(3)	O(26)	66.7(4)
O(19)	Pr(3)	O(26)	59.2(4)	O(20)	Pr(3)	O(25')	67.2(4)
O(19)	Pr(3)	O(25')	114.1(4)	O(20)	Pr(3)	O(25')	67.6(4)
O(19)	Pr(3)	O(25')	107.3(4)	O(20)	Pr(3)	O(26')	104.9(4)
O(19)	Pr(3)	O(26')	127.1(5)	O(20)	Pr(3)	O(26')	59.9(5)
O(19)	Pr(3)	O(26')	67.8(4)	O(22)	Pr(3)	O(22)	66.3(4)
O(20)	Pr(3)	O(20)	128.5(3)	O(22)	Pr(3)	O(23)	51.7(3)
O(20)	Pr(3)	O(22)	105.5(3)	O(22)	Pr(3)	O(23)	112.5(3)
O(20)	Pr(3)	O(22)	117.4(3)	O(22)	Pr(3)	O(25)	164.7(4)
O(20)	Pr(3)	O(23)	64.4(3)	O(22)	Pr(3)	O(25)	102.8(4)
O(20)	Pr(3)	O(23)	123.7(3)	O(22)	Pr(3)	O(26)	115.8(3)
O(20)	Pr(3)	O(25)	69.0(3)	O(22)	Pr(3)	O(26)	64.2(3)
O(20)	Pr(3)	O(25)	75.1(3)	O(22)	Pr(3)	O(25')	172.5(4)
O(20)	Pr(3)	O(26)	66.7(4)	O(22)	Pr(3)	O(25')	119.1(4)
O(20)	Pr(3)	O(26)	113.3(4)	O(22)	Pr(3)	O(26')	130.9(4)
O(20)	Pr(3)	O(25')	67.6(4)	O(22)	Pr(3)	O(26')	79.6(4)
O(20)	Pr(3)	O(25')	67.2(4)	O(22)	Pr(3)	O(23)	112.5(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(22)	Pr(3)	O(23)	51.7(3)	O(25)	Pr(3)	O(25)	89.8(6)
O(22)	Pr(3)	O(25)	102.8(4)	O(25)	Pr(3)	O(26)	48.9(4)
O(22)	Pr(3)	O(25)	164.7(4)	O(25)	Pr(3)	O(26)	131.1(4)
O(22)	Pr(3)	O(26)	64.2(3)	O(25)	Pr(3)	O(25')	17.2(5)
O(22)	Pr(3)	O(26)	115.8(3)	O(25)	Pr(3)	O(25')	72.8(5)
O(22)	Pr(3)	O(25')	119.1(4)	O(25)	Pr(3)	O(26')	33.9(4)
O(22)	Pr(3)	O(25')	172.5(4)	O(25)	Pr(3)	O(26')	115.5(4)
O(22)	Pr(3)	O(26')	79.6(4)	O(25)	Pr(3)	O(26)	131.1(4)
O(22)	Pr(3)	O(26')	130.9(4)	O(25)	Pr(3)	O(26)	48.9(4)
O(23)	Pr(3)	O(23)	163.7(4)	O(25)	Pr(3)	O(25')	72.8(5)
O(23)	Pr(3)	O(25)	130.6(4)	O(25)	Pr(3)	O(25')	17.2(5)
O(23)	Pr(3)	O(25)	63.3(4)	O(25)	Pr(3)	O(26')	115.5(4)
O(23)	Pr(3)	O(26)	120.0(4)	O(25)	Pr(3)	O(26')	33.9(4)
O(23)	Pr(3)	O(26)	60.0(4)	O(26)	Pr(3)	O(26)	180.0(5)
O(23)	Pr(3)	O(25')	121.0(4)	O(26)	Pr(3)	O(25')	65.2(4)
O(23)	Pr(3)	O(25')	74.7(4)	O(26)	Pr(3)	O(25')	114.8(4)
O(23)	Pr(3)	O(26')	121.4(5)	O(26)	Pr(3)	O(26')	16.4(4)
O(23)	Pr(3)	O(26')	63.9(5)	O(26)	Pr(3)	O(26')	163.6(4)
O(23)	Pr(3)	O(25)	63.3(4)	O(26)	Pr(3)	O(25')	114.8(4)
O(23)	Pr(3)	O(25)	130.6(4)	O(26)	Pr(3)	O(25')	65.2(4)
O(23)	Pr(3)	O(26)	60.0(4)	O(26)	Pr(3)	O(26')	163.6(4)
O(23)	Pr(3)	O(26)	120.0(4)	O(26)	Pr(3)	O(26')	16.4(4)
O(23)	Pr(3)	O(25')	74.7(4)	O(25')	Pr(3)	O(25')	56.0(8)
O(23)	Pr(3)	O(25')	121.0(4)	O(25')	Pr(3)	O(26')	49.3(5)
O(23)	Pr(3)	O(26')	63.9(5)	O(25')	Pr(3)	O(26')	98.8(5)
O(23)	Pr(3)	O(26')	121.4(5)	O(25')	Pr(3)	O(26')	98.8(5)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(25')	Pr(3)	O(26')	49.3(5)	C(30)	O(13)	C(31)	112(1)
O(26')	Pr(3)	O(26')	147.2(6)	C(30')	O(13)	C(31)	112(1)
Pr(1)	O(1)	C(6)	120.7(7)	Pr(2)	O(14)	C(32)	123.2(5)
Pr(1)	O(1)	C(7)	122.4(7)	Pr(2)	O(14)	C(33)	128.9(7)
C(6)	O(1)	C(7)	115(1)	C(32)	O(14)	C(33)	107.8(8)
Pr(1)	O(2)	C(8)	121.5(7)	C(27)	O(15)	C(34)	118(1)
Pr(1)	O(2)	C(9)	124.7(7)	Pr(2)	O(16)	N(6)	95.6(7)
C(8)	O(2)	C(9)	112.6(9)	Pr(2)	O(17)	N(6)	90.6(7)
Pr(1)	O(3)	C(15)	120.5(7)	Pr(3)	O(19)	N(8)	94.5(7)
Pr(1)	O(3)	C(16)	123.9(7)	Pr(3)	O(20)	N(8)	98.8(6)
C(15)	O(3)	C(16)	113.6(9)	Pr(3)	O(22)	N(7)	96.0(7)
Pr(1)	O(4)	C(17)	119.7(6)	Pr(3)	O(23)	N(7)	93.4(6)
Pr(1)	O(4)	C(18)	124.2(7)	Pr(1)	N(1)	C(1)	121.8(9)
C(17)	O(4)	C(18)	112.9(9)	Pr(1)	N(1)	C(5)	120.0(7)
C(3)	O(5)	C(19)	121(1)	C(1)	N(1)	C(5)	117(1)
C(12)	O(6)	C(22)	120(1)	Pr(1)	N(2)	C(10)	122.3(8)
C(12)	O(6)	C(22')	122(2)	Pr(1)	N(2)	C(14)	121.3(7)
C(22)	O(6)	C(22')	114(2)	C(10)	N(2)	C(14)	115(1)
Pr(1)	O(7)	N(3)	95.7(6)	O(7)	N(3)	O(8)	116.8(8)
Pr(1)	O(8)	N(3)	96.5(6)	O(7)	N(3)	O(9)	121(1)
Pr(1)	O(10)	N(4)	96.3(6)	O(8)	N(3)	O(9)	123(1)
Pr(1)	O(11)	N(4)	96.3(6)	O(10)	N(4)	O(11)	117.3(8)
Pr(2)	O(13)	C(30)	118(1)	O(10)	N(4)	O(12)	120(1)
Pr(2)	O(13)	C(30')	121(1)	O(11)	N(4)	O(12)	123(1)
Pr(2)	O(13)	C(31)	122.8(6)	Pr(2)	N(5)	C(25)	122.7(8)
C(30)	O(13)	C(30')	47(1)	Pr(2)	N(5)	C(29)	121(1)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
Pr(2)	N(5)	C(29')	119(1)	O(1)	C(7)	C(20)	108(1)
C(25)	N(5)	C(29)	112(1)	C(8)	C(7)	C(20)	114(1)
C(25)	N(5)	C(29')	118(1)	O(2)	C(8)	C(7)	108(1)
C(29)	N(5)	C(29')	28(1)	O(2)	C(8)	C(21)	110(1)
O(16)	N(6)	O(17)	121.6(9)	C(7)	C(8)	C(21)	111(1)
O(16)	N(6)	O(18)	119(1)	O(2)	C(9)	C(10)	111(1)
O(17)	N(6)	O(18)	119(2)	N(2)	C(10)	C(9)	116(1)
O(22)	N(7)	O(23)	119(1)	N(2)	C(10)	C(11)	124(1)
O(22)	N(7)	O(24)	113(1)	C(9)	C(10)	C(11)	120(1)
O(23)	N(7)	O(24)	128(1)	C(10)	C(11)	C(12)	119(1)
O(19)	N(8)	O(20)	116.5(9)	O(6)	C(12)	C(11)	121(1)
O(19)	N(8)	O(21)	122(1)	O(6)	C(12)	C(13)	120(1)
O(20)	N(8)	O(21)	121(1)	C(11)	C(12)	C(13)	119(1)
N(1)	C(1)	C(2)	122(1)	C(12)	C(13)	C(14)	119(1)
N(1)	C(1)	C(18)	117(1)	N(2)	C(14)	C(13)	123(1)
C(2)	C(1)	C(18)	121(1)	N(2)	C(14)	C(15)	116(1)
C(1)	C(2)	C(3)	122(1)	C(13)	C(14)	C(15)	121(1)
O(5)	C(3)	C(2)	120(1)	O(3)	C(15)	C(14)	110(1)
O(5)	C(3)	C(4)	123(1)	O(3)	C(16)	C(17)	103(1)
C(2)	C(3)	C(4)	117(1)	O(3)	C(16)	C(23)	111(1)
C(3)	C(4)	C(5)	118(1)	C(17)	C(16)	C(23)	115(1)
N(1)	C(5)	C(4)	124(1)	O(4)	C(17)	C(16)	106(1)
N(1)	C(5)	C(6)	117(1)	O(4)	C(17)	C(24)	112(1)
C(4)	C(5)	C(6)	119(1)	C(16)	C(17)	C(24)	117(1)
O(1)	C(6)	C(5)	107(1)	O(4)	C(18)	C(1)	111(1)
O(1)	C(7)	C(8)	108(1)	N(5)	C(25)	C(26)	128(1)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
N(5)	C(25)	C(33)	122(1)	C(28)	C(29)	C(28')	31(1)
C(26)	C(25)	C(33)	109(1)	C(28)	C(29)	C(29')	106(3)
C(25)	C(26)	C(27)	110(1)	C(28)	C(29)	C(30)	117(2)
O(15)	C(27)	C(26)	118(1)	C(28)	C(29)	C(30')	120(2)
O(15)	C(27)	C(28)	113(1)	C(28')	C(29)	C(29')	75(3)
O(15)	C(27)	C(28')	120(1)	C(28')	C(29)	C(30)	114(2)
C(26)	C(27)	C(28)	128(1)	C(28')	C(29)	C(30')	97(2)
C(26)	C(27)	C(28')	120(1)	C(29')	C(29)	C(30)	90(3)
C(28)	C(27)	C(28')	29(1)	C(29')	C(29)	C(30')	48(2)
C(27)	C(28)	C(28')	92(3)	C(30)	C(29)	C(30')	41(1)
C(27)	C(28)	C(29)	113(2)	N(5)	C(29')	C(28)	109(2)
C(27)	C(28)	C(29')	108(2)	N(5)	C(29')	C(28')	122(2)
C(28')	C(28)	C(29)	73(2)	N(5)	C(29')	C(29)	81(3)
C(28')	C(28)	C(29')	51(2)	N(5)	C(29')	C(30)	111(2)
C(29)	C(28)	C(29')	22(1)	N(5)	C(29')	C(30')	121(2)
C(27)	C(28')	C(28)	59(2)	C(28)	C(29')	C(28')	25(1)
C(27)	C(28')	C(29)	102(2)	C(28)	C(29')	C(29)	52(2)
C(27)	C(28')	C(29')	116(2)	C(28)	C(29')	C(30)	94(2)
C(28)	C(28')	C(29)	76(2)	C(28)	C(29')	C(30')	124(2)
C(28)	C(28')	C(29')	104(3)	C(28')	C(29')	C(29)	76(3)
C(29)	C(28')	C(29')	29(1)	C(28')	C(29')	C(30)	106(2)
N(5)	C(29)	C(28)	127(2)	C(28')	C(29')	C(30')	117(2)
N(5)	C(29)	C(28')	117(2)	C(29)	C(29')	C(30)	65(3)
N(5)	C(29)	C(29')	71(3)	C(29)	C(29')	C(30')	112(3)
N(5)	C(29)	C(30)	116(2)	C(30)	C(29')	C(30')	47(1)
N(5)	C(29)	C(30')	98(1)	O(13)	C(30)	C(29)	113(2)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(13)	C(30)	C(29')	98(2)	O(26)	N(9)	O(27')	164(1)
O(13)	C(30)	C(30')	63(2)	O(27)	N(9)	N(9')	99(1)
C(29)	C(30)	C(29')	25(1)	O(27)	N(9)	O(26')	125(2)
C(29)	C(30)	C(30')	88(2)	O(27)	N(9)	O(27')	52.1(9)
C(29')	C(30)	C(30')	62(2)	N(9')	N(9)	O(26')	115(2)
O(13)	C(30')	C(29)	97(1)	N(9')	N(9)	O(27')	47(1)
O(13)	C(30')	C(29')	106(2)	O(26')	N(9)	O(27')	144(2)
O(13)	C(30')	C(30)	70(2)	Pr(3)	O(25)	N(9)	94.7(9)
C(29)	C(30')	C(29')	20(1)	Pr(3)	O(25)	N(9')	118(2)
C(29)	C(30')	C(30)	51(2)	Pr(3)	O(25)	O(25')	72(2)
C(29')	C(30')	C(30)	71(2)	Pr(3)	O(25)	O(26')	75.0(9)
O(13)	C(31)	C(31)	102.6(7)	Pr(3)	O(25)	O(27')	154.4(9)
O(13)	C(31)	C(35)	110.0(9)	N(9)	O(25)	N(9')	41(1)
C(31)	C(31)	C(35)	114(1)	N(9)	O(25)	O(25')	153(2)
O(14)	C(32)	C(32)	105.1(5)	N(9)	O(25)	O(26')	21.0(9)
O(14)	C(32)	C(36)	109.9(8)	N(9)	O(25)	O(27')	66.7(9)
C(32)	C(32)	C(36)	114(1)	N(9')	O(25)	O(25')	125(3)
O(14)	C(33)	C(25)	103.9(9)	N(9')	O(25)	O(26')	51(2)
O(25)	N(9)	O(26)	120(1)	N(9')	O(25)	O(27')	37(2)
O(25)	N(9)	O(27)	120(1)	O(25')	O(25)	O(26')	135(2)
O(25)	N(9)	N(9')	28(1)	O(25')	O(25)	O(27')	117(2)
O(25)	N(9)	O(26')	109(2)	O(26')	O(25)	O(27')	84(1)
O(25)	N(9)	O(27')	70(1)	Pr(3)	O(26)	N(9)	96.2(9)
O(26)	N(9)	O(27)	120(1)	Pr(3)	O(26)	O(26')	88(2)
O(26)	N(9)	N(9')	136(1)	N(9)	O(26)	O(26')	19(2)
O(26)	N(9)	O(26')	25(2)	N(9)	O(27)	N(9')	31.9(7)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
N(9)	O(27)	O(26')	16.9(8)	Pr(3)	O(26')	O(27)	155(1)
N(9)	O(27)	O(27')	80(1)	Pr(3)	O(26')	N(9')	91(1)
N(9')	O(27)	O(26')	44.5(8)	N(9)	O(26')	O(25)	50(2)
N(9')	O(27)	O(27')	48.3(9)	N(9)	O(26')	O(26)	136(4)
O(26')	O(27)	O(27')	92(1)	N(9)	O(26')	O(27)	38(2)
N(9)	N(9')	O(25)	111(2)	N(9)	O(26')	N(9')	40(2)
N(9)	N(9')	O(27)	49(1)	O(25)	O(26')	O(26)	137(2)
N(9)	N(9')	O(25')	135(2)	O(25)	O(26')	O(27)	85(1)
N(9)	N(9')	O(26')	25(1)	O(25)	O(26')	N(9')	23.0(8)
N(9)	N(9')	O(27')	101(1)	O(26)	O(26')	O(27)	123(2)
O(25)	N(9')	O(27)	140(2)	O(26)	O(26')	N(9')	160(3)
O(25)	N(9')	O(25')	31(2)	O(27)	O(26')	N(9')	67(1)
O(25)	N(9')	O(26')	106(2)	N(9)	O(27')	O(25)	43.7(7)
O(25)	N(9')	O(27')	126(2)	N(9)	O(27')	O(27)	47.8(8)
O(27)	N(9')	O(25')	166(1)	N(9)	O(27')	N(9')	31.3(7)
O(27)	N(9')	O(26')	69(1)	O(25)	O(27')	O(27)	90(1)
O(27)	N(9')	O(27')	53(1)	O(25)	O(27')	N(9')	17.5(8)
O(25')	N(9')	O(26')	120(2)	O(27)	O(27')	N(9')	79(1)
O(25')	N(9')	O(27')	120(1)				
O(26')	N(9')	O(27')	120(1)				
Pr(3)	O(25')	O(25)	91(2)				
Pr(3)	O(25')	N(9')	100(1)				
O(25)	O(25')	N(9')	24(1)				
Pr(3)	O(26')	N(9)	118(2)				
Pr(3)	O(26')	O(25)	71.1(9)				
Pr(3)	O(26')	O(26)	75(2)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms and Intramolecular Bond Angles Involving the Nonhydrogen Atoms of $[\text{Pr}(\text{NO}_3)_2 \cdot \mathbf{4}]_3[\text{Pr}(\text{NO}_3)_6](\text{EtOH})$

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
Pr(1)	O(1)	2.558(4)	1	O(2)	C(8)	1.469(8)	1
Pr(1)	O(2)	2.555(7)	1	O(2)	C(9)	1.43(1)	1
Pr(1)	O(3)	2.607(4)	1	O(3)	C(15)	1.422(9)	1
Pr(1)	O(4)	2.575(7)	1	O(3)	C(16)	1.45(1)	1
Pr(1)	O(5)	2.551(5)	1	O(4)	C(17)	1.459(8)	1
Pr(1)	O(6)	2.528(5)	1	O(4)	C(18)	1.45(1)	1
Pr(1)	O(8)	2.524(6)	1	O(5)	N(3)	1.281(8)	1
Pr(1)	O(9)	2.519(5)	1	O(6)	N(3)	1.296(7)	1
Pr(1)	N(1)	2.622(7)	1	O(7)	N(3)	1.227(8)	1
Pr(1)	N(2)	2.664(7)	1	O(8)	N(4)	1.261(9)	1
Pr(2)	O(11)	2.605(4)	1	O(9)	N(4)	1.29(1)	1
Pr(2)	O(11)	2.605(4)	67503	O(10)	N(4)	1.216(8)	1
Pr(2)	O(11)	2.605(4)	76502	O(11)	N(5)	1.258(9)	1
Pr(2)	O(12)	2.636(6)	1	O(12)	N(5)	1.274(7)	1
Pr(2)	O(12)	2.636(6)	67503	O(13)	N(5)	1.232(9)	1
Pr(2)	O(12)	2.636(6)	76502	O(14)	N(6)	1.251(9)	1
Pr(2)	O(14)	2.644(6)	1	O(15)	N(6)	1.28(1)	1
Pr(2)	O(14)	2.644(6)	67503	O(16)	N(6)	1.237(8)	1
Pr(2)	O(14)	2.644(6)	76502	O(17)	C(24)	1.51(2)	1
Pr(2)	O(15)	2.620(5)	1	N(1)	C(1)	1.37(1)	1
Pr(2)	O(15)	2.620(5)	67503	N(1)	C(5)	1.348(8)	1
Pr(2)	O(15)	2.620(5)	76502	N(2)	C(10)	1.35(1)	1
Br(1)	C(3)	1.890(8)	1	N(2)	C(14)	1.332(8)	1
Br(2)	C(12)	1.884(9)	1	C(1)	C(2)	1.39(1)	1
O(1)	C(6)	1.439(9)	1	C(1)	C(18)	1.511(9)	1
O(1)	C(7)	1.47(1)	1	C(2)	C(3)	1.386(9)	1

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms cont

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
C(3)	C(4)	1.37(1)	1				
C(4)	C(5)	1.40(1)	1				
C(5)	C(6)	1.50(1)	1				
C(7)	C(8)	1.51(1)	1				
C(7)	C(19)	1.52(1)	1				
C(8)	C(20)	1.530(9)	1				
C(9)	C(10)	1.500(9)	1				
C(10)	C(11)	1.40(1)	1				
C(11)	C(12)	1.384(9)	1				
C(12)	C(13)	1.39(1)	1				
C(13)	C(14)	1.42(1)	1				
C(14)	C(15)	1.52(1)	1				
C(16)	C(17)	1.54(1)	1				
C(16)	C(21)	1.51(1)	1				
C(17)	C(22)	1.52(1)	1				
C(23)	C(24)	1.53(2)	1				

Distances are in angstroms. Estimated standard deviations in

the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Pr(1)	O(2)	61.1(2)	O(4)	Pr(1)	O(8)	74.8(2)
O(1)	Pr(1)	O(3)	160.1(1)	O(4)	Pr(1)	O(9)	115.8(2)
O(1)	Pr(1)	O(4)	124.5(2)	O(4)	Pr(1)	N(1)	63.4(2)
O(1)	Pr(1)	O(5)	77.8(2)	O(4)	Pr(1)	N(2)	116.1(2)
O(1)	Pr(1)	O(6)	112.1(2)	O(5)	Pr(1)	O(6)	51.2(2)
O(1)	Pr(1)	O(8)	86.7(2)	O(5)	Pr(1)	O(8)	130.8(2)
O(1)	Pr(1)	O(9)	87.6(1)	O(5)	Pr(1)	O(9)	164.9(2)
O(1)	Pr(1)	N(1)	61.1(2)	O(5)	Pr(1)	N(1)	64.6(2)
O(1)	Pr(1)	N(2)	119.5(2)	O(5)	Pr(1)	N(2)	116.9(2)
O(2)	Pr(1)	O(3)	121.8(2)	O(6)	Pr(1)	O(8)	159.5(2)
O(2)	Pr(1)	O(4)	161.2(2)	O(6)	Pr(1)	O(9)	134.3(2)
O(2)	Pr(1)	O(5)	88.4(2)	O(6)	Pr(1)	N(1)	114.1(2)
O(2)	Pr(1)	O(6)	74.4(2)	O(6)	Pr(1)	N(2)	67.2(2)
O(2)	Pr(1)	O(8)	123.9(2)	O(8)	Pr(1)	O(9)	50.8(2)
O(2)	Pr(1)	O(9)	81.2(2)	O(8)	Pr(1)	N(1)	67.0(2)
O(2)	Pr(1)	N(1)	119.8(2)	O(8)	Pr(1)	N(2)	111.4(2)
O(2)	Pr(1)	N(2)	61.2(2)	O(9)	Pr(1)	N(1)	111.5(2)
O(3)	Pr(1)	O(4)	60.2(2)	O(9)	Pr(1)	N(2)	67.2(2)
O(3)	Pr(1)	O(5)	120.9(2)	N(1)	Pr(1)	N(2)	178.4(2)
O(3)	Pr(1)	O(6)	86.7(2)	O(11)	Pr(2)	O(11)	113.24(9)
O(3)	Pr(1)	O(8)	75.8(2)	O(11)	Pr(2)	O(11)	113.24(9)
O(3)	Pr(1)	O(9)	74.1(2)	O(11)	Pr(2)	O(12)	48.9(2)
O(3)	Pr(1)	N(1)	118.2(2)	O(11)	Pr(2)	O(12)	114.5(2)
O(3)	Pr(1)	N(2)	60.7(2)	O(11)	Pr(2)	O(12)	69.3(2)
O(4)	Pr(1)	O(5)	76.4(2)	O(11)	Pr(2)	O(14)	66.9(2)
O(4)	Pr(1)	O(6)	87.4(2)	O(11)	Pr(2)	O(14)	66.6(2)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(11)	Pr(2)	O(14)	179.8(2)	O(12)	Pr(2)	O(14)	65.6(2)
O(11)	Pr(2)	O(15)	65.6(2)	O(12)	Pr(2)	O(14)	131.1(2)
O(11)	Pr(2)	O(15)	110.2(2)	O(12)	Pr(2)	O(15)	110.4(2)
O(11)	Pr(2)	O(15)	131.6(2)	O(12)	Pr(2)	O(15)	109.7(2)
O(11)	Pr(2)	O(11)	113.24(9)	O(12)	Pr(2)	O(15)	179.4(2)
O(11)	Pr(2)	O(12)	69.3(2)	O(12)	Pr(2)	O(12)	69.9(2)
O(11)	Pr(2)	O(12)	48.9(2)	O(12)	Pr(2)	O(14)	131.1(2)
O(11)	Pr(2)	O(12)	114.5(2)	O(12)	Pr(2)	O(14)	110.9(2)
O(11)	Pr(2)	O(14)	179.8(2)	O(12)	Pr(2)	O(14)	65.6(2)
O(11)	Pr(2)	O(14)	66.9(2)	O(12)	Pr(2)	O(15)	179.4(2)
O(11)	Pr(2)	O(14)	66.6(2)	O(12)	Pr(2)	O(15)	110.4(2)
O(11)	Pr(2)	O(15)	131.6(2)	O(12)	Pr(2)	O(15)	109.7(2)
O(11)	Pr(2)	O(15)	65.6(2)	O(12)	Pr(2)	O(14)	65.6(2)
O(11)	Pr(2)	O(15)	110.2(2)	O(12)	Pr(2)	O(14)	131.1(2)
O(11)	Pr(2)	O(12)	114.5(2)	O(12)	Pr(2)	O(14)	110.9(2)
O(11)	Pr(2)	O(12)	69.3(2)	O(12)	Pr(2)	O(15)	109.7(2)
O(11)	Pr(2)	O(12)	48.9(2)	O(12)	Pr(2)	O(15)	179.4(2)
O(11)	Pr(2)	O(14)	66.6(2)	O(12)	Pr(2)	O(15)	110.4(2)
O(11)	Pr(2)	O(14)	179.8(2)	O(14)	Pr(2)	O(14)	113.17(9)
O(11)	Pr(2)	O(14)	66.9(2)	O(14)	Pr(2)	O(14)	113.17(9)
O(11)	Pr(2)	O(15)	110.2(2)	O(14)	Pr(2)	O(15)	48.4(2)
O(11)	Pr(2)	O(15)	131.6(2)	O(14)	Pr(2)	O(15)	114.4(2)
O(11)	Pr(2)	O(15)	65.6(2)	O(14)	Pr(2)	O(15)	69.7(2)
O(12)	Pr(2)	O(12)	69.9(2)	O(14)	Pr(2)	O(14)	113.17(9)
O(12)	Pr(2)	O(12)	69.9(2)	O(14)	Pr(2)	O(15)	69.7(2)
O(12)	Pr(2)	O(14)	110.9(2)	O(14)	Pr(2)	O(15)	48.4(2)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
O(14)	Pr(2)	O(15)	114.4(2)	Pr(2)	O(15)	N(6)	97.2(4)
O(14)	Pr(2)	O(15)	114.4(2)	Pr(1)	N(1)	C(1)	119.1(4)
O(14)	Pr(2)	O(15)	69.7(2)	Pr(1)	N(1)	C(5)	122.4(6)
O(14)	Pr(2)	O(15)	48.4(2)	C(1)	N(1)	C(5)	117.5(7)
O(15)	Pr(2)	O(15)	70.0(2)	Pr(1)	N(2)	C(10)	119.4(4)
O(15)	Pr(2)	O(15)	70.0(2)	Pr(1)	N(2)	C(14)	121.9(6)
O(15)	Pr(2)	O(15)	70.0(2)	C(10)	N(2)	C(14)	118.6(7)
Pr(1)	O(1)	C(6)	125.5(5)	O(5)	N(3)	O(6)	116.7(5)
Pr(1)	O(1)	C(7)	122.1(4)	O(5)	N(3)	O(7)	122.4(6)
C(6)	O(1)	C(7)	110.3(5)	O(6)	N(3)	O(7)	120.9(6)
Pr(1)	O(2)	C(8)	122.8(5)	O(8)	N(4)	O(9)	115.9(6)
Pr(1)	O(2)	C(9)	119.8(4)	O(8)	N(4)	O(10)	122.9(8)
C(8)	O(2)	C(9)	112.0(6)	O(9)	N(4)	O(10)	121.2(7)
Pr(1)	O(3)	C(15)	122.6(5)	O(11)	N(5)	O(12)	117.9(6)
Pr(1)	O(3)	C(16)	124.5(4)	O(11)	N(5)	O(13)	122.2(6)
C(15)	O(3)	C(16)	112.2(5)	O(12)	N(5)	O(13)	119.9(7)
Pr(1)	O(4)	C(17)	121.9(5)	O(14)	N(6)	O(15)	117.2(6)
Pr(1)	O(4)	C(18)	118.6(4)	O(14)	N(6)	O(16)	121.8(8)
C(17)	O(4)	C(18)	112.9(7)	O(15)	N(6)	O(16)	121.0(7)
Pr(1)	O(5)	N(3)	95.7(3)	N(1)	C(1)	C(2)	123.1(6)
Pr(1)	O(6)	N(3)	96.4(4)	N(1)	C(1)	C(18)	117.8(7)
Pr(1)	O(8)	N(4)	96.3(5)	C(2)	C(1)	C(18)	119.1(8)
Pr(1)	O(9)	N(4)	95.7(4)	C(1)	C(2)	C(3)	117.6(8)
Pr(2)	O(11)	N(5)	97.4(3)	Br(1)	C(3)	C(2)	118.6(7)
Pr(2)	O(12)	N(5)	95.4(4)	Br(1)	C(3)	C(4)	120.2(5)
Pr(2)	O(14)	N(6)	96.8(5)	C(2)	C(3)	C(4)	121.2(7)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
C(3)	C(4)	C(5)	117.9(6)	C(17)	C(16)	C(21)	116.7(8)
N(1)	C(5)	C(4)	122.8(9)	O(4)	C(17)	C(16)	107.2(6)
N(1)	C(5)	C(6)	118.4(7)	O(4)	C(17)	C(22)	108.7(6)
C(4)	C(5)	C(6)	118.8(6)	C(16)	C(17)	C(22)	111.7(7)
O(1)	C(6)	C(5)	109.6(5)	O(4)	C(18)	C(1)	108.9(7)
O(1)	C(7)	C(8)	107.0(6)	O(17)	C(24)	O(17)	115.8(6)
O(1)	C(7)	C(19)	109.6(7)	O(17)	C(24)	O(17)	115.8(6)
C(8)	C(7)	C(19)	113.9(7)	O(17)	C(24)	C(23)	102.1(9)
O(2)	C(8)	C(7)	105.3(6)	O(17)	C(24)	O(17)	115.8(6)
O(2)	C(8)	C(20)	109.9(6)	O(17)	C(24)	C(23)	102.1(9)
C(7)	C(8)	C(20)	112.4(6)	O(17)	C(24)	C(23)	102.1(9)
O(2)	C(9)	C(10)	109.1(7)				
N(2)	C(10)	C(9)	117.4(7)				
N(2)	C(10)	C(11)	122.5(6)				
C(9)	C(10)	C(11)	120.0(8)				
C(10)	C(11)	C(12)	117.8(9)				
Br(2)	C(12)	C(11)	120.0(8)				
Br(2)	C(12)	C(13)	118.6(5)				
C(11)	C(12)	C(13)	121.3(8)				
C(12)	C(13)	C(14)	116.2(6)				
N(2)	C(14)	C(13)	123.5(9)				
N(2)	C(14)	C(15)	118.1(7)				
C(13)	C(14)	C(15)	118.3(6)				
O(3)	C(15)	C(14)	109.1(5)				
O(3)	C(16)	C(17)	104.5(6)				
O(3)	C(16)	C(21)	111.0(7)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

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