Ag-Catalyzed Diastereo- and Enantioselective Vinylogous Mannich Reactions of α–Ketoimine Esters. Development of a Method and Investigation of its Mechanism

Laura C. Wieland, Erika Vieira, Marc L. Snapper*, and Amir H. Hoveyda*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

SUPPORTING INFORMATION, PART 1

Table of Contents ***Page***

General. Infrared (IR) spectra are recorded on a Perkin Elmer 781 spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m) or weak (w). ^{1}H NMR spectra are recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuteration as the internal standard ($CDCl_3$: δ 7.26). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants. ^{13}C NMR spectra are recorded on a Varian Unity INOVA 400 (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). ^{31}P NMR spectra are recorded on a Varian Unity INOVA 400 (162 MHz) with complete proton decoupling. Chemical shifts are reported in ppm (H_3PO_4: δ 0.00 ppm). Enantiomeric ratios were determined by analytical liquid chromatography (HPLC) Shimazu chromatograph (Chiral Technologies Chiralpak AS (4.6 x 250 mm), Chiral Technologies Chiralcel OD (4.6 x 250 mm) or Chiral Technologies Chiralpak AD (4.6 x 250 mm)) in comparison with authentic racemic materials. High-resolution mass spectrometry is performed on a Micromass LCT ESI-MS (positive mode)) at the Mass Spectrometry Facility (Boston College). Optical rotation values are recorded on a Rudolph Research Analytical Autopol IV polarimeter. Unless otherwise stated, all reactions are conducted under an inert atmosphere of nitrogen. Tetrahydrofuran is purified by distillation from sodium benzophenone ketal immediately prior to use. All work-up and purification procedures are carried out with reagent solvents in air. All solvents are purchased from Doe and Ingalls. 2-(Trimethylsilyloxy)furan and AgOAc were purchased from Aldrich and used as received. α–Ketoesters were purchased from commercial sources or synthesized from commercially available starting materials through known methods.[1] The corresponding ketoimines are synthesized using known methods.[2] EDC•HCl, HOBt•H_2O, trifluroacetic acid, *p*-anisidine, Boc-protected amino acids and 2-(diphenylphosphino)benzaldehyde are purchased from commercial sources and used without further purification. Phosphino amino-acid based ligand **1** was prepared as previously reported.[3]

Analytical Data for Substrates 4a-m, 15:

4a: 10:1 mixture of *E*/*Z* isomers. mp = 106–107 °C. IR (neat): 3101 (w), 3008 (w), 2945 (w), 2911 (w), 2865 (w, br), 2835 (w), 1729 (s), 1623 (s), 1585 (s), 1514 (s), 1484 (m), 1451 (m), 1409 (m), 1350 (s), 1336 (m), 1303 (s), 1260 (s), 1231 (s), 1181 (m), 1096 (m), 1020 (m), 1007 (m), 797 (m), 687 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.90 (2H, d, J = 7.3

---

(1) a) Wasserman, H. H.; Ho, W. B. *J. Org. Chem.* **1994**, 59, 4364-4366; b) Babudri, F.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron* **1996**, *52*, 13513–13520; c) Rodriguez, A.; Nomen, M.; Spur, B. W. *Tetrahedron Lett*, **1998**, *39*, 8563–8566; d) Domagala, J. M. *Tetrahedron Lett.* **1980**, *21*, 4997–5000.

(2) (a) Palacios, F.; Vicario, J.; Aparicio, D. *J. Org. Chem.* **2006**, 71, 7690-7696; b) Niwa, Y.; Shimizu, M. *J. Am. Chem. Soc.* **2003**, *125*, 3720–3721.

(3) Carswell, E. L.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem. Int., Ed.* **2006**, *45*, 7230–7233.

Hz), 7.85 (1H, dd, *J* = 8.8, 2.2 Hz), 7.77 (1H, d, *J* = 2.2 Hz), 7.55 (1 H, t, *J* = 7.3 Hz), 7.48 (2H, t, *J* = 7.3 Hz), 6.89 (1H, d, *J* = 8.4 Hz), 3.89 (3H, s), 3.66 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 161.8, 150.1, 145.9, 145.6, 133.3, 132.8, 129.1, 128.8, 119.5, 117.0, 106.7, 56.5, 52.4. HRMS Calcd for $C_{16}H_{15}N_2O_5$ (M + H): 315.09810; Found: 315.09849.

4b: 5:1 mixture of *E*/*Z* isomers. mp = 104–105 °C. IR (neat): 3084 (w, br), 3008 (w, br), 2957 (w, br), 2839 (w, br), 1742 (s), 1641 (m), 1585 (m), 1523 (s), 1354 (s), 1320 (m), 1253 (s), 1096 (m), 1028 (m), 796 (m), 670 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.86 (1H, dd, *J* = 8.4, 2.0 Hz), 7.77 (1H, d, *J* = 2.0 Hz), 7.51 (1H, s), 7.38 (2 H, d, *J* = 4.8 Hz), 7.13-7.08 (1H, m), 6.90 (1H, d, *J* = 8.4 Hz), 3.91 (3H, s), 3.87 (3H, s), 3.66 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 161.7, 160.2, 150.1, 145.9, 145.6, 134.6, 130.0, 121.7, 119.5, 119.3, 117.0, 112.8, 106.7, 56.5, 55.7, 52.4. HRMS Calcd for $C_{17}H_{17}N_2O_6$ (M + H): 345.10866; Found: 345.10892.

4c: 13:1 mixture of *E*/*Z* isomers. mp = 106–108 °C. IR (neat): 3111 (w, br), 3015 (w), 2955 (w), 2843 (w), 1725 (s), 1615 (s), 1579 (s), 1507 (s), 1487 (m), 1450 (m), 1412 (m), 1342 (s), 1318 (s), 1276 (m), 1250 (s), 1223 (s), 1175 (s), 1091 (m), 1024 (s), 938 (m), 866 (m), 830 (m), 794 (m), 714 (m), 682 (m), 665 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.94 (1H, s), 7.87 (1H, dd, *J* = 8.4, 2.2 Hz), 7.78 (1H, d, *J* = 2.2 Hz), 7.74 (1 H, d, *J* = 7.7 Hz), 7.53 (1H, d, *J* = 8.4 Hz), 7.42 (1H, t, *J* = 8.4 Hz), 6.89 (1H, d, *J* = 8.4 Hz), 3.91 (3H, s), 3.67 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 160.4, 150.0, 145.8, 145.4, 135.3, 135.1, 132.7, 130.3, 128.6, 127.1, 119.4, 117.0, 106.7, 56.5, 52.6. HRMS Calcd for $C_{16}H_{14}ClN_2O_5$ (M + H): 349.05912; Found: 349.05871.

4d: 10:1 mixture of *E*/*Z* isomers. mp = 154–155 °C. IR (neat): 3352 (w), 3088 (w), 3007 (w), 2971 (w), 2834 (w), 2657 (w, br), 1732 (s), 1626 (s), 1581 (s), 1566 (m), 1505 (s), 1489 (m), 1462 (m), 1400 (m), 1309 (s), 1253 (m), 1224 (s), 1176 (m), 1123 (m), 1091 (m), 1069 (m), 1028 (m), 1005 (m), 859 (m), 687 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.86 (1H, dd, *J* = 8.4, 2.2 Hz), 7.78-7.76 (3H, m), 7.63 (2H, d, *J* = 8.8 Hz), 6.88 (1H, d, *J* = 8.4 Hz), 3.90 (3H, s), 3.66 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 160.5, 150.0, 145.7, 145.6, 139.1, 131.9, 130.2, 129.3, 119.4, 117.0, 106.7, 56.5, 52.6. HRMS Calcd for $C_{16}H_{14}BrN_2O_5$ (M + H): 393.00861; Found: 393.00875.

4e: 10:1 mixture of *E*/*Z* isomers. mp = 166–169 °C. IR (neat): 3070 (w), 3004 (w), 2959 (w), 2915 (w), 2833 (w, br), 2655 (w), 1730 (s), 1624 (m), 1579 (m), 1504 (s), 1487 (m), 1462 (m), 1395 (m), 1309 (s), 1251 (m), 1223 (s), 1175 (s), 1123 (m), 1092 (m), 1056 (m), 1026 (m), 1001 (s), 859 (m), 841 (m), 829 (m), 794 (m), 743 (m), 721 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.88-7.84 (3H, m), 7.78 (1H, d, *J* = 2.2 Hz), 7.62 (2H, d, *J* = 8.4 Hz), 6.88 (1 H, d, *J* = 8.4 Hz), 3.90 (3H, s), 3.66 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 160.9, 150.0, 145.7, 145.6, 138.3, 132.9, 130.2, 119.4, 117.0, 106.8, 100.2, 56.5, 52.5. HRMS Calcd for $C_{16}H_{14}IN_2O_5$ (M + H): 440.99474; Found: 440.99559.

4f: 10:1 mixture of *E*/*Z* isomers. mp = 148–151 °C. IR (neat): 3101 (w), 3006 (w, br), 2866 (w), 2835 (w), 1730 (s), 1601 (m), 1578 (m), 1561 (m), 1488 (s), 1410 (m), 1312 (s), 1231 (m), 1191(m), 1173 (m), 1128 (m), 1091 (m), 1022 (m), 1005 (m), 873 (m), 843 (m), 793 (m), 736 (m), 536 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.87-7.77 (4H, m), 7.51 (2H, d, *J* = 8.1 Hz), 6.88 (1H, d, *J* = 8.4 Hz), 3.90 (3H, s), 3.66 (3H, s), 1.35 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 161.6, 156.6, 150.2, 146.2, 145.4, 130.6, 128.7, 126.1, 119.5, 117.0, 106.7, 56.5, 52.3, 35.3, 31.3. HRMS Calcd for $C_{20}H_{23}N_2O_5$ (M + H): 371.16070; Found: 371.16194.

4g: 11:1 mixture of *E*/*Z* isomers. mp = 128–130 °C. IR (neat): 3118(w), 3012 (w), 2958 (w), 2839 (w), 2653 (w, br), 2514 (w), 1742 (s), 1641 (s), 1582 (s), 1523 (s), 1489 (m), 1464 (m), 1417 (m), 1328 (s), 1316 (m), 1256 (s), 1223 (s), 1181 (m), 1131 (m), 1067 (m), 1028 (m), 1007 (m), 910 (m), 873 (m), 856 (m), 801 (m), 742 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 8.02 (2H, d, *J* = 8.4 Hz), 7.86 (1H, dd, *J* = 8.4, 2.0 Hz), 7.78 (1H, d, *J* = 2.0 Hz), 7.73 (2H, d, *J* = 8.4 Hz), 6.90 (1H, d, *J* = 8.4 Hz), 3.90 (3H, s), 3.69 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 160.4, 149.8, 145.9, 145.3, 136.6, 133.5 (q, *J* = 32.6 Hz), 129.2, 125.9 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 217 Hz), 119.4, 117.0, 106.8, 56.5, 52.6. HRMS Calcd for $C_{17}H_{14}F_3N_2O_5$ (M + H): 383.08548; Found: 383.08515.

4h: 20:1 mixture of *E*/*Z* isomers. mp = 128–129 °C. IR (neat): 3109 (w), 3063 (w), 3017 (w), 2953 (w), 2854 (w, br), 2839 (w), 1742 (s), 1619 (s), 1582 (s), 1518 (s), 1493 (m), 1468 (m), 1412 (m), 1350 (s), 1312 (m), 1257 (s), 1223 (m), 1168 (m), 1126 (m), 1096 (m), 1033 (m), 1016 (m), 868 (m), 797 (m), 733 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 8.25 (1H, s), 8.12 (1H, dd, *J* = 8.6, 1.4 Hz), 7.94-7.87 (4H, m), 7.80 (1H, d, *J* = 2.0 Hz), 7.61-7.53 (2H, m), 6.95 (1H, d, *J* = 8.4 Hz), 3.91 (3H, s), 3.72 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 161.8, 150.2, 146.1, 145.6, 135.5, 132.9, 130.8, 129.5, 129.1, 128.7, 128.1, 127.2, 124.1, 119.5, 117.0, 106.8, 56.5, 52.5. HRMS Calcd for $C_{20}H_{17}N_2O_5$ (M + H): 365.11375; Found: 365.11481.

4i: 5:1 mixture of *E*/*Z* isomers. mp = 102–106 °C. IR (neat): 3097 (w), 3012 (w), 2953 (w), 2939 (w), 1738 (s), 1653 (m), 1581 (m), 1518 (s), 1489 (m), 1463 (m), 1409 (m), 1354 (s), 1253 (s), 1215 (m), 1092 (m), 1058 (m), 1025 (m), 915 (m), 860 (m), 810 (m), 742 (m), 645 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.77 (1H, dd, *J* = 8.8, 2.4 Hz), 7.63 (1H, d, *J* = 2.4 Hz), 7.53 (1H, dd, *J* = 8.0, 1.6 Hz), 7.21-7.13 (2H, m), 6.93 (1H, dd, *J* = 7.2, 2.0 Hz), 6.81 (1H, d, *J* = 8.4 Hz), 3.97 (3H, s), 3.84 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 162.4, (161.5), (161.2), 149.0, (148.3), 145.9, (145.4), 144.1, (137.2), 135.2, (133.3), 132.8, (132.4), (132.0), 131.5, 129.2, (128.0), 127.4, (122.3), 121.4, 119.4, (117.2), 116.8, (106.8), 106.7, (56.5), 56.3, 53.9, (53.0). HRMS Calcd for $C_{16}H_{14}N_2O_5Br$ (M + H): 393.00861; Found: 393.01005.

4j: 2.5:1 mixture of *E*/*Z* isomers. mp = 98–100 °C. IR (neat): 3147 (w), 3118 (w), 2953 (w), 2835 (w), 1742 (s), 1628 (m), 1518 (s), 1472 (s), 1354 (s), 1337 (s), 1257 (s), 1239 (m), 1096 (m), 1045 (s), 1016 (m), 1155 (m), 805 (m), 762 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, mixture of isomers): δ 7.84-7.81 (1 + [0.4]H, m), [7.72 (0.4H, s)], 7.71 (1H, m), 7.65 (1H, s), [7.28 (0.4H, s)], 7.12 (1H, d, *J* = 3.2 Hz), [7.03 (0.4H, d, *J* = 2.2 Hz)], 6.92 (1H, d, *J* = 8.8 Hz), [6.86 (0.4H, d, *J* = 8.4 Hz)], 6.56 (1H, t, *J* = 1.6 Hz), [6.41 (0.4H, s)], [3.97 (1.2H, s)], 3.84 (3H, s), [3.75 (1.2H, s)], 3.65 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$, mixture of isomers): δ [163.7], 161.8, 150.2, 149.5, 149.2, [148.6], [147.9], 147.5, [146.8], [146.5], [145.9], 145.4, 145.3, [145.1], [120.6], 120.3, 119.3, [118.8], [117.2], 117.1, 112.9, [112.5], 106.6, [106.6], 56.4, [56.4], [53.7], 52.7. HRMS Calcd for $C_{14}H_{13}N_2O_6$ (M + H): 305.07736; Found: 305.07696.

4k: 8:1 mixture of *E*/*Z* isomers. mp = 153–154 °C. IR (neat): 3085 (w), 2960 (w), 2916 (w), 2848 (w), 1734 (s), 1617 (s), 1581 (m), 1511 (s), 1486 (m), 1465 (m), 1406 (m), 1345 (s), 1288 (m), 1226 (s), 1170 (s), 1125 (m), 1091 (m), 1023 (s), 860 (m), 803 (m), 731 (m), 687 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.96 (1H, s), 7.86 (1H, dd, *J* = 8.4, 2.2 Hz), 7.77 (1H, d, *J* = 2.2 Hz), 7.69 (1H, d, *J* = 4.8 Hz), 7.42-7.38 (1H, m), 6.90 (1H, d, *J* = 8.8 Hz), 3.89 (3H, s), 3.65 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5, 156.0, 149.7, 145.9, 145.4, 137.3, 131.8, 127.1, 127.0, 119.8, 117.1, 106.7, 56.4, 52.5. HRMS Calcd for $C_{14}H_{13}N_2O_5S$ (M + H): 321.05452; Found: 321.05540.

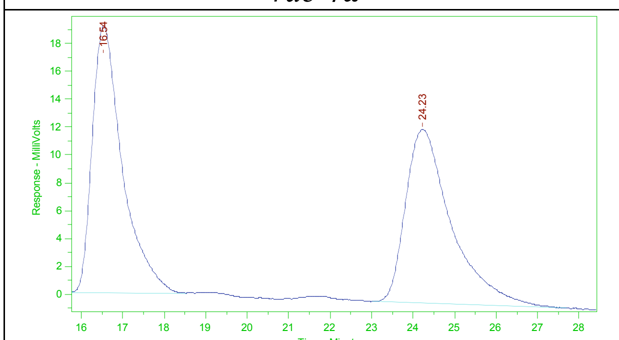
4m: 11:1 mixture of *E*/*Z* isomers. mp=132–134 °C. IR (neat): 3354 (w), 3091 (w), 3009 (w), 2957 (w), 2835 (w, br), 1734 (s), 1629 (s), 1581 (s), 1507 (s), 1493 (m), 1461 (m), 1405 (m), 1339 (s), 1310 (m), 1253 (m), 1224 (s), 1176 (m), 1090 (s), 1029 (m), 1008 (m), 858 (m), 842 (m), 796 (m), 766 (m), 744 (m), 727 (m), 671 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.85-7.77 (4H, m), 7.44 (2H, d, *J* = 8.4 Hz), 6.88 (1 H, d, *J* = 8.4 Hz), 3.89 (3H, s), 3.66 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 160.6, 149.9, 145.7, 145.6, 132.32, 132.26, 130.2, 127.7, 119.4, 117.0, 106.7, 56.5, 52.5. HRMS Calcd for $C_{16}H_{14}ClN_2O_5$ (M + H): 349.05912; Found: 349.05911.

15: IR (neat): 3001 (w), 2951 (w), 2837 (w), 1722 (s), 1656 (m), 1591 (m), 1506 (m), 1489 (s), 1454 (m), 1436 (m), 1367 (w), 1314 (m), 1275 (m), 1244 (s), 1224 (m), 1193 (m), 1138 (s), 1113 (s), 944 (m), 853 (m), 812 (m), 77 (m), 744 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$), major isomer: δ 7.05 (1H, ddd, *J* = 7.6, 7.6, 1.6 Hz), 6.90-6.85 (2H, m), 6.89 (1H, dd, *J* = 7.6, 1.6 Hz), 3.85 (3H, s), 3.72 (3H, s), 1.98 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 162.1, 148.3, 138.1, 126.0, 120.9, 120.2, 111.6, 55.7, 53.2, 17.6. HRMS Calcd for $C_{11}H_{14}NO_3$: 208.09737; Found: 208.09785.

Representative experimental procedure for gram-scale Ag-catalyzed addition of vinylogous silyl enol ether 2 to an α-ketoimine ester: A flame-dried 100 mL round bottom flask was charged with AgOAc (117 mg, 0.700 mmol), **1** (320 mg, 0.636 mmol), and **4a** (2.00 g, 6.36 mmol). The flask was sealed with a septum and purged with a N_2 atmosphere. Freshly distilled THF was added (64 mL) through a syringe, followed by *i*-PrOH (487 μL, 0.636 mmol), and the resulting homogenous yellow solution was allowed to cool to –78 °C (dry ice/acetone) with stirring. 2-Trimethylsiloxyfuran (**2**) (2.66 mL, 13.4 mmol) was added, and the resulting solution was kept at –78 ^oC for 15 h before addition of HOAc (765 μL, 13.4 mmol) in MeOH (10 mL). The resulting solution was allowed to stir at –78 ^oC for an additional three hours, after which it was allowed to warm to 22 ^oC. A saturated aqueous solution of $NaHCO_3$ was added, after which the aqueous layer was washed with EtOAc (3 x 100 mL), dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The unpurified residue (typically yellow oil) was a 20:1 mixture of **7a:8a** by ^1H NMR analysis, which can be separated by silica gel chromatography (3:1 petroleum ether:EtOAc) to furnish pure **7a** as a yellow solid (2.24 g, 5.62 mmol, 88% yield, 92% ee of **7a**), which was recrystallized from MeOH to afford **7a** (yellow crystals) in >98% ee (1.53 g, 3.84 mmol, 68% yield, >98% ee).

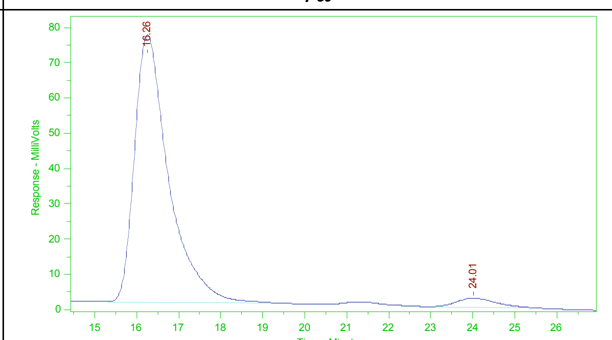
7a: IR (neat): 3396 (w, br), 1791 (m), 1766 (s), 1595 (m), 1532 (m), 1501 (m), 1338 (m), 1293 (s), 1256 (m), 1231 (m), 1092 (m), 734 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (1H, d, J = 2.4 Hz), 7.52 (1H, ddd, J = 6.8, 2.4, 0.4 Hz), 7.50 (1H, dd, J = 5.8, 1.6 Hz), 7.46-7.39 (5 H, m), 6.21 (1H, br s), 6.11 (1H, dd, J = 2.0, 1.6 Hz), 6.04 (1H, dd, J = 5.6, 2.0 Hz), 5.84 (1H, d, J = 8.8 Hz), 3.98 (3H, s), 3.80 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.6, 152.4, 146.4, 140.6, 138.7, 133.5, 129.7, 129.6, 127.0, 124.0, 118.1, 111.4, 105.1, 84.7, 68.6, 56.4, 54.1. HRMS Calcd for $C_{20}H_{18}N_2O_7$ [M + H]: 399.11923; Found: 399.11946. $[\alpha]^{26}_D$ = +165.45 (c = 1.00, $CHCl_3$) for a 92% ee sample. The enantiomeric purity of this compound was determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7a**: 16 min (major) and 24 min (minor); t_R of **8a**: 19 min and 21 min.

rac-**7a**



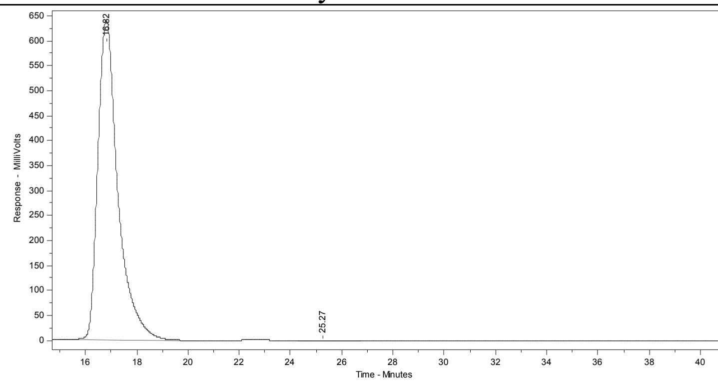
Peak #	Ret. Time	Area	Area %
1	16.54	967379	50.226
2	24.23	958669	49.774

7a



Peak #	Ret. Time	Area	Area %
1	16.26	4274050	96.33
2	24.01	162829	3.67

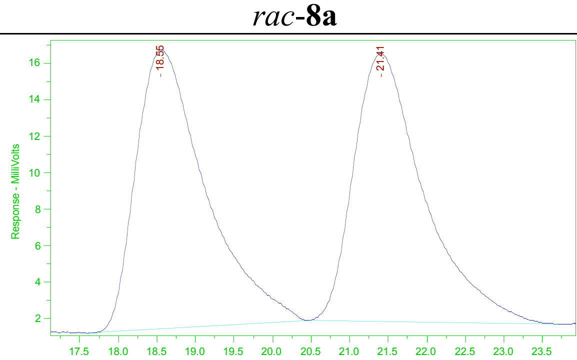
Recrystallized **7a**



Peak #	Ret. Time	Area	Area %
1	16.82	35044100	99.858
2	25.27	49883	0.142

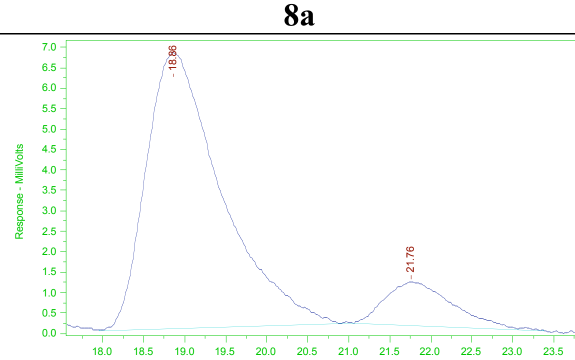
8a: IR (neat): 3390 (w, br), 3100 (w, br), 2961 (w, br), 1791 (m), 1766 (s), 1596 (m), 1527 (m), 1501 (m), 1338 (m), 1294 (s), 1262 (m), 1161 (m), 1098 (m), 733 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (1H, d, J = 2.4 Hz), 7.53-7.50 (2H, m), 7.49 (1H, dd, J = 9.2, 2.4 Hz), 7.41-7.39 (3H, m), 7.30 (1H, dd, J = 6.0, 1.6 Hz), 6.26 (1H, br s), 6.17 (1H, dd, J = 6.0, 2.0 Hz), 6.05 (1H, d, J = 9.2 Hz), 5.93 (1H, dd, J = 1.8, 1.8 Hz), 3.89 (3H, s), 3.77 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 170.2, 152.4, 146.4, 140.5, 138.8, 134.0, 129.54, 129.49, 127.6, 123.9, 118.3, 112.6, 104.9, 85.9, 69.2, 56.4, 54.0. HRMS Calcd for $C_{20}H_{18}N_2O_7Na$: [M + Na] 421.1012; Found: 421.1009. $[\alpha]^{26}_{D}$ = +34.99 (c = 1.00, $CHCl_3$) for a 75% ee sample. The enantiomeric purity of the compound is determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **8a**: 19 min and 21 min; t_R of **7a**: 16 min (major) and 24 min (minor).

rac-**8a**



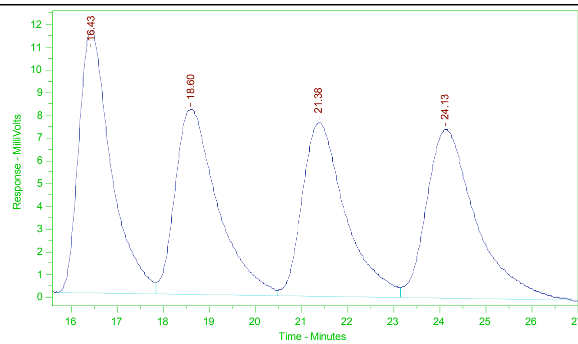
Peak #	Ret. Time	Area	Area %
1	18.55	960705	50.794
2	21.41	930684	49.206

8a



Peak #	Ret. Time	Area	Area %
1	18.86	432036	87.415
2	21.76	62198	12.585

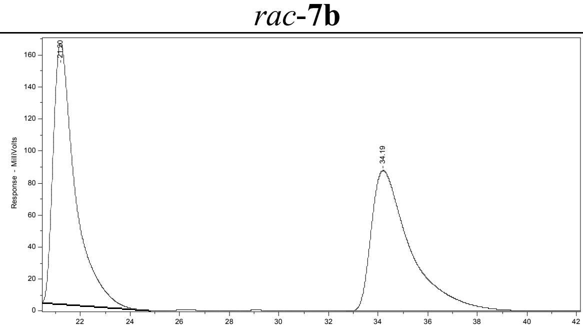
***rac*-7a and 8a**



Peak #	Ret. Time	Area	Area %
1	16.43	565621	26.445
2	18.60	525228	24.557
3	21.38	498033	23.285
4	24.13	549947	25.713

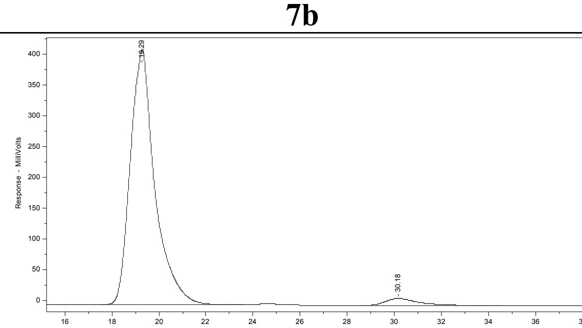
7b: IR (neat): 3389 (w, br), 3096 (w, br), 2954 (w, br), 2835 (w, br), 1795 (m), 1758 (s), 1596 (s), 1521 (s), 1503 (m), 1334 (m), 1303 (s), 1260 (m), 1228 (m), 1153 (w), 1098 (m), 1029 (w), 736 (w), 662 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (1H, d, *J* = 2.2 Hz), 7.53 (1H, dd, *J* = 8.8, 2.4 Hz), 7.50 (1H, dd, *J* = 5.7, 1.7 Hz), 7.34 (1H, t, *J* = 7.9 Hz), 7.02 (1H, ddd, *J* = 7.7, 1.1, 0.7 Hz), 6.98 (1H, t, *J* = 2.2 Hz), 6.93 (1H, ddd, *J* = 8.3, 2.5, 0.7 Hz), 6.19 (1H, br s), 6.10 (1H, t, *J* = 1.8 Hz), 6.03 (1H, dd, *J* = 5.9, 2.2 Hz), 5.86 (1H, d, *J* = 8.8 Hz), 3.98 (3H, s), 3.80 (3H, s), 3.77 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.5, 160.5, 152.4, 146.4, 140.7, 138.7, 135.2, 130.8, 123.9, 119.0, 118.1, 114.3, 113.5, 111.4, 105.1, 84.7, 68.5, 56.5, 55.6, 54.1. HRMS Calcd for $C_{21}H_{21}N_2O_8$ [M + H]: 429.1297; Found: 429.1302. $[\alpha]^{23}_{D}$ = +75.26 (*c* = 1.00, $CHCl_3$) for a 93% ee sample. The enantiomeric purity of the compound was determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7b**: 19 min (major) and 30 min (minor); t_R of **8b:** 22 min (major) and 28 min (minor).

***rac*-7b**



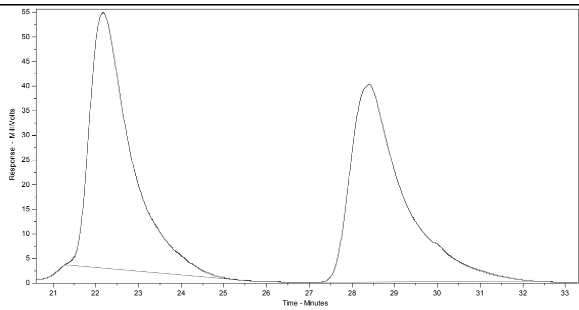
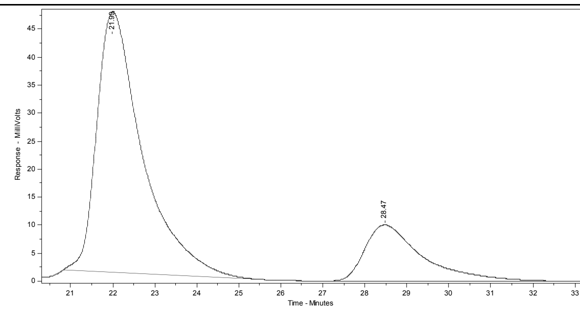
Peak #	Ret. Time	Area	Area %
1	21.20	9968915	50.844

7b



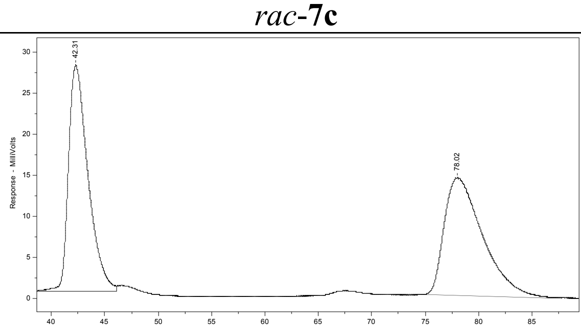
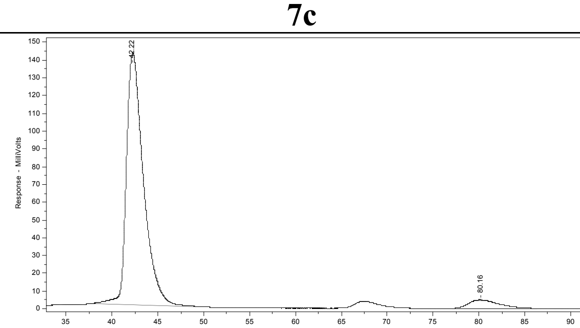
Peak #	Ret. Time	Area	Area %
1	19.29	29958420	96.254

2	34.19	9638127	49.156	2	30.18	1165924	3.746

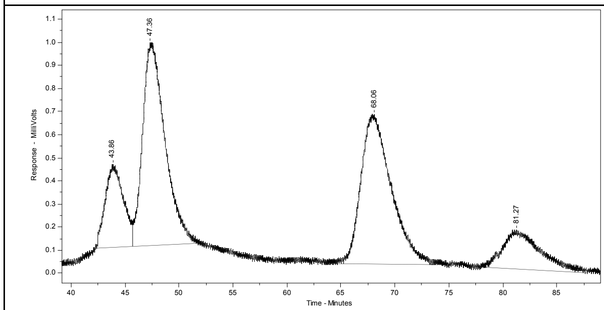
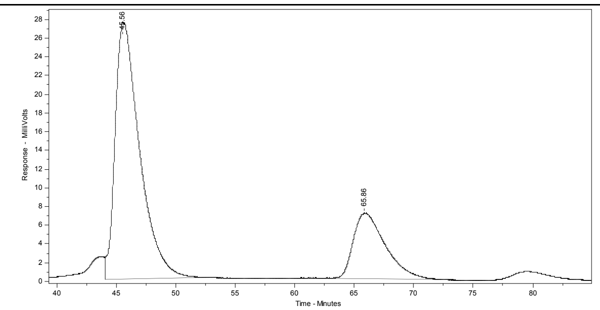
rac-**8b**	**8b**
	

Peak #	Ret. Time	Area	Area %	Peak #	Ret. Time	Area	Area %
1	22.17	3506655	50.345	1	21.99	3503242	78.338
2	28.39	3458649	49.655	2	28.47	968738	21.662

7c: IR (neat): 3383 (w, br), 3100 (w, br), 3018 (w, br), 2955 (w, br), 2943 (w, br), 2848 (w, br), 1784 (s), 1759 (s), 1590 (s), 1527 (s), 1507 (m), 1338 (m), 1239 (s), 1256 (m), 1231 (m), 1092 (m), 1029 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (1H, d, J = 2.6 Hz), 7.56 (1H, dd, J = 9.2, 2.6 Hz), 7.52-7.50 (1H, m), 7.46 (1H, dd, J = 5.9, 1.5 Hz), 7.41-7.33 (3H, m), 6.18 (1H, br s), 6.10 (1H, dd, J = 5.7, 1.8 Hz), 6.01 (1H, t, J = 1.8 Hz), 5.85 (1H, d, J = 9.2 Hz), 4.00 (3H, s), 3.80 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.0, 152.0, 146.5, 140.1, 139.0, 135.70, 135.67, 130.8, 129.9, 127.5, 125.5, 124.3, 118.0, 111.4, 105.2, 84.4, 68.3, 56.5, 54.3. HRMS Calcd for $C_{20}H_{17}N_2O_7ClNa$ [M + Na]: 455.0609; Found: 455.0622. $[\alpha]^{25}_{D}$ = +106.65 (c = 1.00, $CHCl_3$) for an 88% ee sample. The enantiomeric purity of the compound was determined by chiral HPLC analysis (OD, 90:10 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7c**: 42 min (major) and 80 min (minor); t_R of **8c**: 46 min (major) and 66 min (minor).

rac-**7c**	**7c**
	

Peak #	Ret. Time	Area	Area %	Peak #	Ret. Time	Area	Area %
1	42.31	3496745	49.405	1	42.22	18325730	94.174
2	78.02	3581021	50.595	2	80.16	1133718	5.826

rac-**7c** and **8c**	**8c**
	

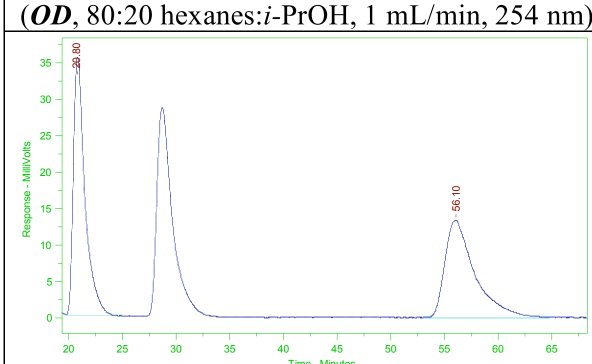
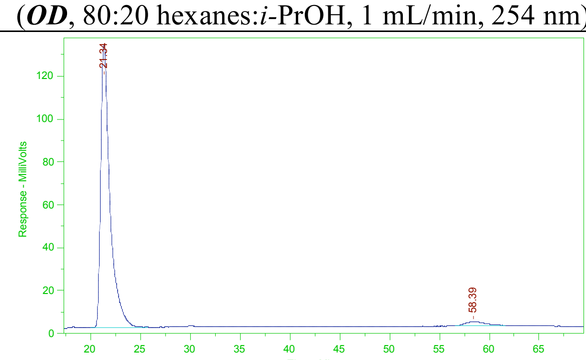
rac-**7c** and **8c**

Peak #	Ret. Time	Area	Area %
1	43.86	42012	12.522
2	47.36	126276	37.636
3	68.06	127110	37.884
4	81.27	40123	11.958

8c

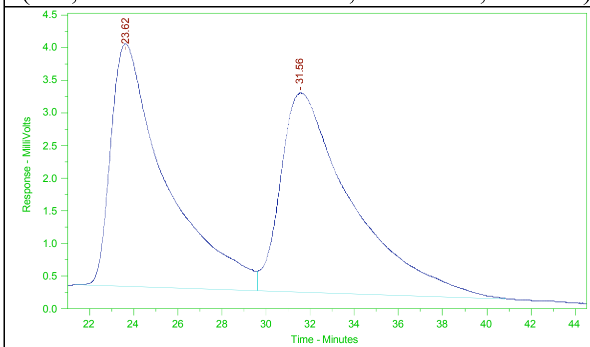
Peak #	Ret. Time	Area	Area %
1	45.56	3955760	75.204
2	65.86	1304255	24.796

7d: IR (neat): 3386 (w, br), 3094 (w, br), 3019 (w, br), 2926 (w, br), 2846 (w, br), 1791 (m), 1753 (m), 1591 (m), 1523 (m), 1505 (m), 1338 (m), 1288 (s), 1232 (m), 1095 (m), 741 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (1H, d, *J* = 2.6 Hz), 7.56-7.52 (3H, m), 7.46 (1H, dd, *J* = 5.9, 1.5 Hz), 7.35 (2 H, ddd, *J* = 9.2, 2.3, 2.3 Hz), 6.17 (1H, br s), 6.08 (1H, dd, *J* = 5.8, 1.8 Hz), 6.00 (1H, t, *J* = 1.8 Hz), 5.86 (1H, d, *J* = 9.2 Hz), 3.99 (3H, s), 3.79 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.1, 152.1, 146.5, 140.1, 139.0, 132.8, 132.5, 129.0, 124.3, 124.0, 118.1, 111.5, 105.2, 84.3, 68.3, 56.5, 54.2. HRMS Calcd for $C_{20}H_{17}N_2O_7BrNa$ [M + Na]: 499.0117; Found: 499.0121. $[\alpha]^{26}_D$ = +67.8 (*c* = 1.00, $CHCl_3$) for a 94% ee sample. The enantiomeric purity of the compound was determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7d**: 21 min (major) and 57 min (minor).

rac-**7d** and **8d** (***OD***, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm)	**7d** (***OD***, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm)
	
Peak # Ret. Time Area Area %	**Ret.**

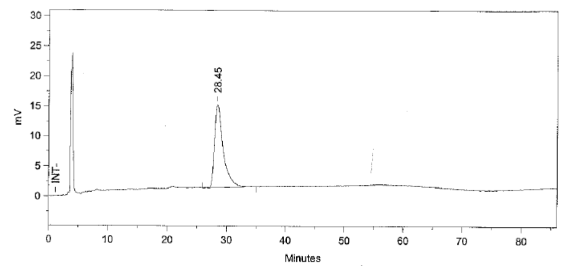
1	20.8	2641062	50.596	Time			
2	56.1	2578827	49.404	1	21.34	8461288	96.822
*peak at 28 min is rac-syn-**8d***				2	58.39	277741	3.178

rac-**8d**
(***AD***, 90:10 hexanes:*i*-PrOH, 1 mL/min, 254 nm)



Peak #	Ret. Time	Area	Area %
1	23.62	645454	48.541
2	31.56	684247	51.459

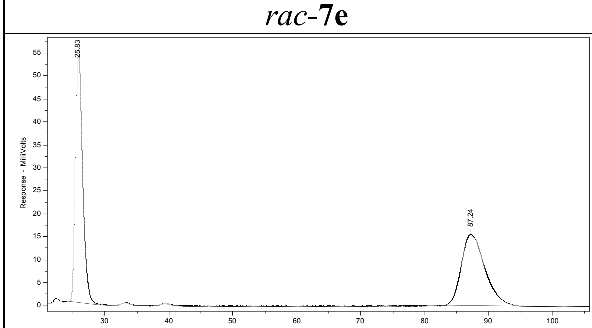
rac-**8d**
(***OD***, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm)



PK#	Ret Time	Name	Amount	Amount%	Area	Area%	Type	Width	Height	Height%
1	28.449		0.0000	0.000	1411421.0	100.000	BB	1.704	13802.20	100.000

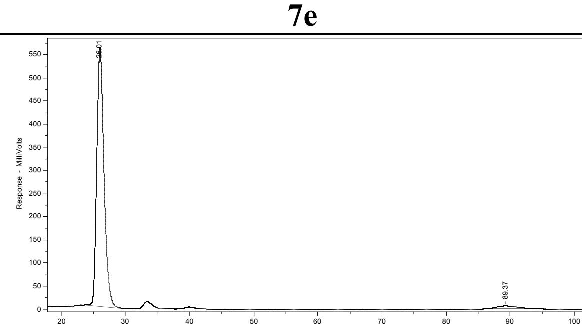
7e: IR (neat): 3387 (w, br), 1789 (m), 1758 (s), 1593 (m), 1526 (m), 1295 (s), 1231 (m), 1096 (m), 1028 (m), 746 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (2H, ddd, J = 8.8, 2.2, 2.2 Hz), 7.63 (1H, d, J = 2.6 Hz), 7.55 (1H, dd, J = 8.8, 2.6 Hz), 7.45 (1H, dd, J = 5.8, 1.5 Hz), 7.21 (2H, ddd, J = 8.4, 2.2, 2.2 Hz), 6.16 (1H, br s), 6.08 (1H, dd, J = 5.9, 2.2 Hz), 6.00 (1H, dd, J = 1.8, 1.8 Hz), 5.86 (1H, d, J = 8.8 Hz), 3.98 (3H, s), 3.78 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.1, 152.1, 146.5, 140.1, 138.9, 138.7, 133.2, 129.1, 124.3, 118.1, 111.5, 105.2, 95.8, 84.3, 68.4, 56.5, 54.2. HRMS Calcd for $C_{20}H_{18}N_2O_7I$ [M + H]: 525.01587; Found: 525.01710. $[\alpha]^{24}_D$ = +69.9 (c = 1.00, $CHCl_3$) for a 94% ee sample. The enantiomeric purity of the compound was determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7e**: 26 min (major) and 89 min (minor); t_R of **8e**: 33 min and 39 min.

rac-**7e**



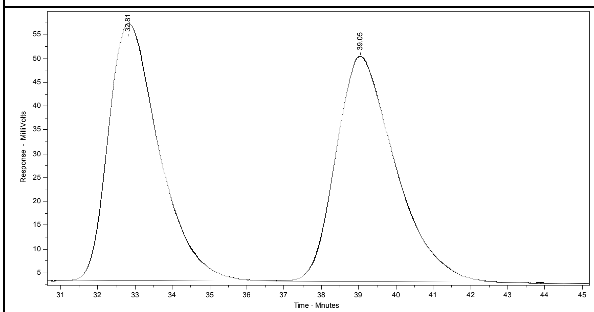
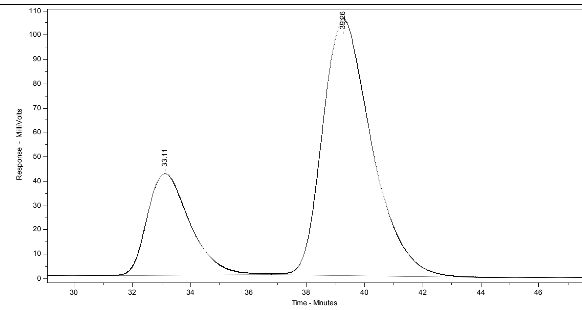
Peak #	Ret. Time	Area	Area %

7e



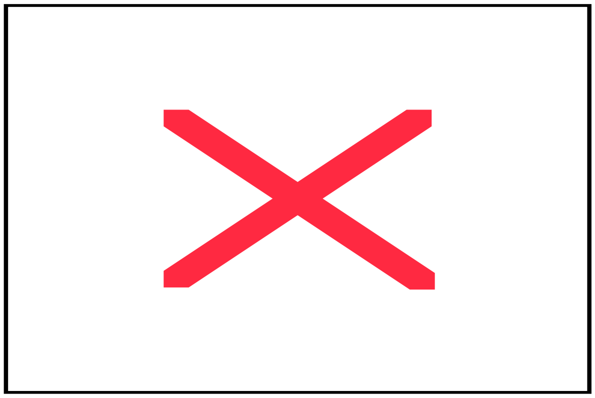
Peak #	Ret. Time	Area	Area %

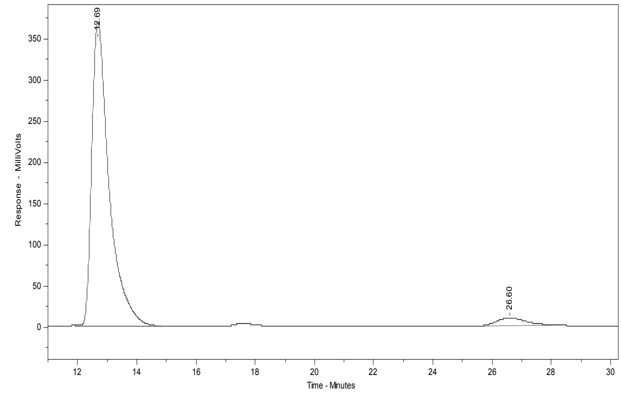
2	87.24	3957386	49.287	2	89.37	1409877	3.032

rac-**8e**				**8e**			
							
Peak #	**Ret. Time**	**Area**	**Area %**	**Peak #**	**Ret. Time**	**Area**	**Area %**
1	32.81	5117000	49.346	1	33.11	4254926	25.684
2	39.05	5252693	50.654	2	39.26	12311430	74.316

7f: IR (neat): 3387 (w, br), 3099 (w, br), 3019 (w, br), 2961 (w, br), 2870 (w, br), 1788 (m), 1755 (m), 1592 (m), 1526 (m), 1504 (m), 1321 (m), 1292 (s), 1229 (m), 1093 (m), 1026 (m), 817 (m), 797 (m), 744 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (1H, d, J = 2.2 Hz), 7.54 (1H, dd, J = 8.8, 2.2 Hz), 7.48 (1H, dd, J = 5.9, 1.8 Hz), 7.43-7.33 (4 H, m), 6.15 (1H, br s), 6.11 (1H, t, J = 1.8 Hz), 6.03 (1H, dd, J = 5.9, 2.2 Hz), 5.86 (1H, d, J = 9.2 Hz), 3.97 (3H, s), 3.79 (3H, s), 1.31 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 170.8, 152.8, 152.5, 146.4, 140.8, 138.6, 130.4, 126.62, 126.58, 124.0, 118.1, 111.4, 105.1, 84.9, 68.4, 56.5, 54.0, 34.9, 31.4. HRMS Calcd for $C_{24}H_{27}N_2O_7$ [M + H]: 455.18183; Found: 455.18032. $[\alpha]^{23}_{D}$ = +90.6 (c = 0.500, $CHCl_3$) for a 90% ee sample. The enantiomeric purity of the compound was determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7f**: 12 min (major) and 26 min (minor); t_R of **8f**: 15 min and 17 min

rac-**7f** and **8f**	**7f**



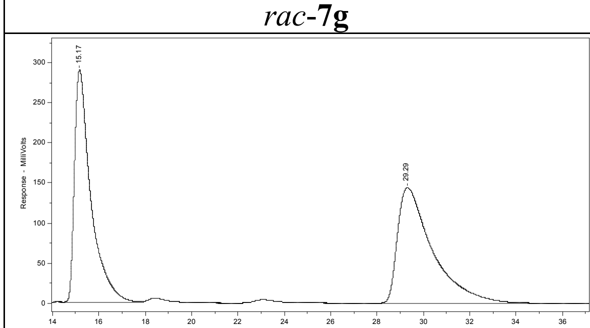


Peak #	Ret. Time	Area	Area %
1	11.95	253446	13.634
2	14.48	674813	36.301
3	16.81	679463	36.551
4	23.99	251214	13.514

Peak #	Ret. Time	Area	Area %
1	12.69	14923210	94.871
2	26.60	806859	5.129

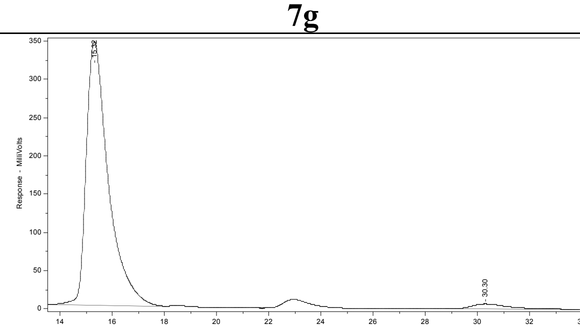
7g: IR (neat): 3389 (w, br), 3106 (w, br), 2986 (w, br), 2873 (w, br), 1791 (m), 1759 (m), 1589 (m), 1527 (m), 1508 (m), 1325 (s), 1294 (s), 1256 (m), 1237 (m), 1167 (m), 1130 (m), 1099 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.63 (5H, m), 7.53 (1H, dd, *J* = 8.8, 2.4 Hz), 7.46 (1H, dd, *J* = 5.8, 1.8 Hz), 6.24 (1H, br s), 6.10 (1H, dd, *J* = 6.0, 2.0 Hz), 6.03 (1H, t, *J* = 1.8 Hz), 5.82 (1H, d, *J* = 9.2 Hz), 4.00 (3H, s), 3.80 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 169.9, 151.9, 146.5, 139.9, 139.1, 137.6, 131.8 (q, *J* = 33.0 Hz), 128.0, 126.5 (q, *J* = 3.8 Hz), 125.4 (q, *J* = 202 Hz), 124.4, 118.1, 111.3, 105.3, 84.2, 68.5, 56.5, 54.3. HRMS Calcd for $C_{21}H_{17}N_2O_7F_3Na$ [M + Na]: 489.0886; Found: 489.0882. $[\alpha]^{25}_{D}$ = +43.5 (*c* = 0.630, $CHCl_3$) for a 91% ee sample. The enantiomeric purity of the compound was determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7g**: 15 min (major) and 30 min (minor).

rac-**7g**



Peak #	Ret. Time	Area	Area %
1	15.17	14290790	48.836
2	29.29	14971950	51.164

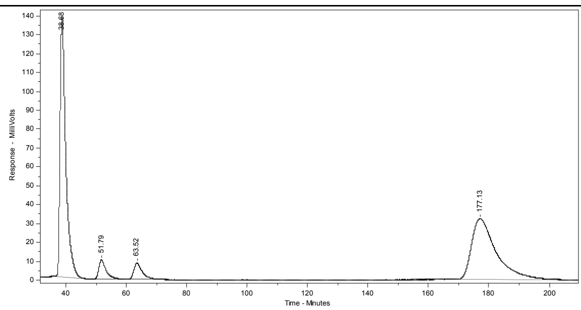
7g



Peak #	Ret. Time	Area	Area %
1	15.32	20258000	96.862
2	30.3	656256	3.138

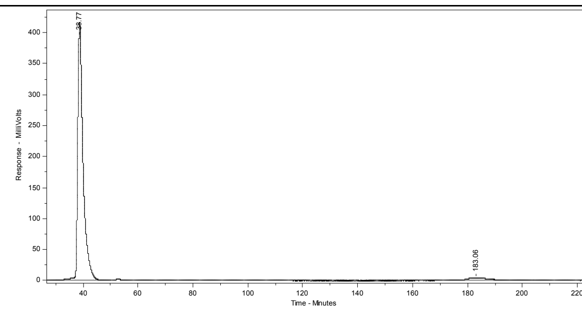
7h: IR (neat): 3382 (w, br), 3102 (w, br), 2953 (w, br), 1788 (m), 1759 (s), 1587 (s), 1527 (m), 1331 (m), 1301 (s), 1230 (m), 1093 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (1H, d, *J* = 2.2 Hz), 7.89-7.85 (2H, m), 7.85 (1H, d, *J* = 8.4 Hz), 7.62 (1 H, d, *J* = 2.6 Hz), 7.58-7.54 (3H, m), 7.44 (2H, ddd, *J* = 10.4, 6.0, 2.0 Hz), 6.33 (1H, br s), 6.24 (1H, dd, *J* = 1.8, 1.8 Hz), 6.05 (1H, dd, *J* = 5.6, 2.0 Hz), 5.85 (1H, d, *J* = 8.8 Hz), 4.01 (3H, s), 3.80 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.6, 152.3, 146.5, 140.7, 138.7, 133.5, 133.4, 131.2, 129.7, 128.7, 128.0, 127.7, 127.3, 126.7, 124.1, 124.0, 118.1, 111.5, 105.1, 84.9, 68.8, 56.5, 54.2. HRMS Calcd for $C_{24}H_{20}N_2O_7Na$ [M + Na]: 471.1168; Found: 471.1164. $[\alpha]^{26}_{D}$ = +114.7 (*c* = 1.00, $CHCl_3$) for a 90% ee sample. The optical purity of the compound is determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7h**: 39 min (major) and 183 min (minor); t_R of **8h**: 52 min and 64 min.

rac-**7h** and **8h**



Peak #	Ret. Time	Area	Area %
1	38.68	18403890	45.821
2	51.79	1812002	4.511
3	63.52	1719289	4.281
4	177.13	18229490	45.387

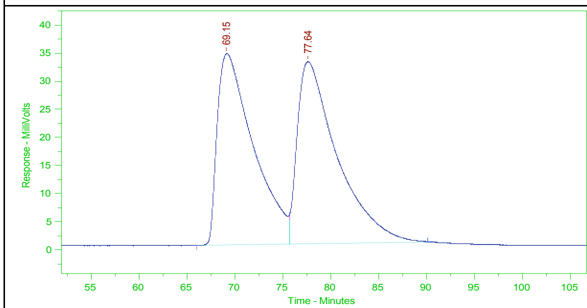
7h



Peak #	Ret. Time	Area	Area %
1	38.77	56347020	95.269
2	183.06	2798026	4.731

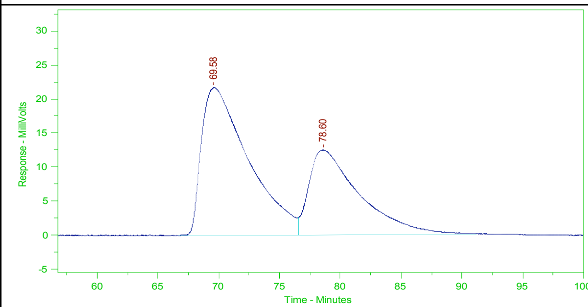
8i: IR (neat): 3365 (w, br), 3083 (w), 2953 (w), 2833 (w), 1787 (m), 1760 (m), 1744 (m), 1592 (m), 1526 (m), 1503 (m), 1476 (m), 1439 (m), 1333 (m), 1292 (s), 1257 (m), 1228 (m), 1197 (m), 1159 (m), 1100 (m), 1029 (m), 889 (m), 823 (m), 800 (m), 746 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (1H, dd, *J* = 8.4, 1.6 Hz), 7.56 (1H, d, *J* = 2.8 Hz), 7.52-7.41 (3H, m), 7.34 (1H, dd, *J* = 6.0, 1.6 Hz), 7.25 (1H, dt, *J* = 7.6, 1.6 Hz), 6.44 (1H, br s), 6.29 (1H, dd, *J* = 4.0, 1.6 Hz), 6.18 (1H, d, *J* = 9.2 Hz), 6.11 (1H, t, *J* =1.6 Hz), 3.94 (3H, s), 3.86 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 170.5, 151.9, 146.6, 140.2, 138.7, 135.2, 134.4, 131.7, 130.7, 128.0, 124.7, 123.0, 118.2, 111.5, 104.9, 84.4, 70.3, 56.4, 54.6. HRMS Calcd for $C_{20}H_{18}N_2O_7$ [M + H]: 477.02974; Found: 477.02861 $[\alpha]^{24}_{D}$ = -25.11 (*c* = 1.00, $CHCl_3$) for a 24% ee sample. The enantiomeric purity of the compound is determined by chiral HPLC analysis (OD, 90:10 hexanes:*i*-PrOH, 0.7 mL/min, 254 nm): t_R of **8i**: 69 min and 78 min.

rac-**8i**



Peak #	Ret. Time	Area	Area %
1	69.15	8933499	48.769
2	77.64	9384385	51.231

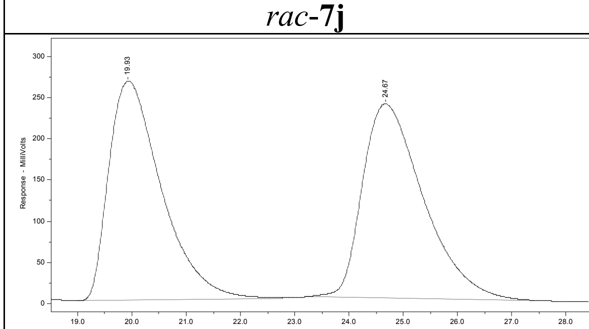
8i



Peak #	Ret. Time	Area	Area %
1	69.58	5831568	62.215
2	78.60	3541722	37.785

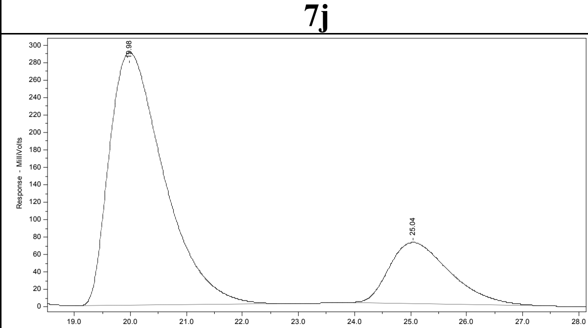
7j: IR (neat): 3375 (w, br), 3105 (w), 2957 (w), 2919 (w), 2847 (w), 1792 (m), 1755 (m), 1595 (m), 1531 (m), 1509 (m), 1337 (m), 1299 (s), 1265 (m), 1236 (m), 1159 (m), 1101 (m), 1025 (m), 906 (m), 797 (m), 733 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (2H, m), 7.45 (1H, dd, J = 6.0, 1.4 Hz), 7.42 (1H, dd, J = 2.0, 0.80 Hz), 6.70 (1H, dd, J = 3.6, 0.80 Hz), 6.45 (1H, dd, J = 3.4, 1.6 Hz), 6.27 (1H, br s), 6.24 (1H, d, J = 9.2 Hz), 6.19 (1H, dd, J = 5.8, 2.2 Hz), 5.87 (1H, dd, J = 1.4, 1.4 Hz), 3.98 (3H, s), 3.78 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 168.4, 152.2, 147.1, 146.6, 143.8, 140.7, 139.3, 123.8, 118.6, 112.0, 111.4, 110.7, 105.1, 84.1, 65.9, 56.4, 54.2. HRMS Calcd for $C_{18}H_{16}N_2O_8Na$ [M + Na]: 411.0804; Found: 411.0793. $[\alpha]^{24}_D$ = +3.49 (c = 0.230, $CHCl_3$) for a 58% ee sample. The enantiomeric purity of the compound is determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7j**: 20 min and 25 min.

rac-**7j**



Peak #	Ret. Time	Area	Area %
1	19.93	17917710	49.454
2	24.67	18313550	50.546

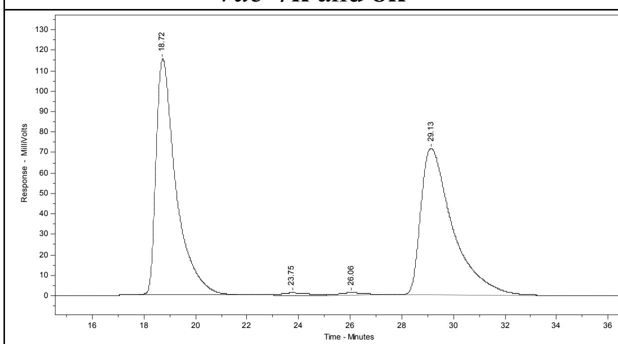
7j

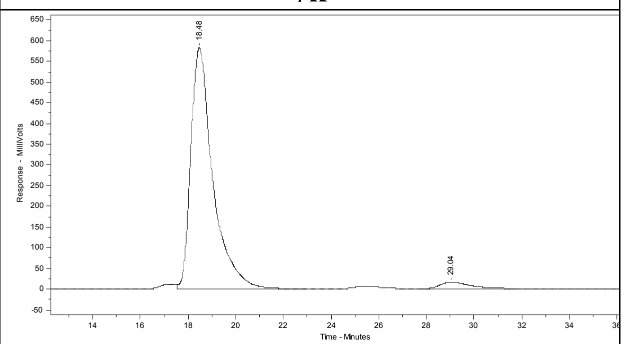


Peak #	Ret. Time	Area	Area %
1	19.98	19664200	78.665
2	25.04	5333194	21.335

7k: IR (neat): 3384(w, br), 3104 (w, br), 2926 (w), 2852 (w), 1789 (m), 1732 (s), 1592 (s), 1525 (m), 1505 (m), 1323 (m), 1292 (s), 1229 (s), 1155 (m), 1095 (m), 1043 (m), 1026 (m), 890 (m), 798 (m), 745 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ 7.63 (1H, d, J = 2.2 Hz), 7.58 (1H, m), 7.54 (1H, dd, J = 2.9, 1.5 Hz), 7.44 (1 H, dd, J = 5.9, 1.5 Hz), 7.35 (1H, dd, J = 5.1, 2.9 Hz), 7.04 (1H, dd, J = 5.1, 1.5 Hz), 6.13 (1H, dd, J = 5.8, 2.2 Hz), 6.03 (1H, s), 5.95 (1H, d, J = 8.8 Hz), 5.88 (1H, t, J = 2.2 Hz), 3.97 (3H, s), 3.80 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 170.2, 152.2, 146.3, 140.6, 138.9, 134.6, 127.4, 126.8, 124.8, 124.0, 118.1, 111.0, 105.1, 85.0, 66.4, 56.4, 54.0. HRMS Calcd for $C_{18}H_{17}N_2O_7S$ [M + H]: 405.07565; Found: 405.07530. $[\alpha]^{23}_{D}$ = +107.9 (c = 1.00, $CHCl_3$) for a 92% ee sample. The enantiomeric purity of the compound is determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7k**: 18 min (major) and 29 min (minor).

rac-**7k** and **8k**	**7k**

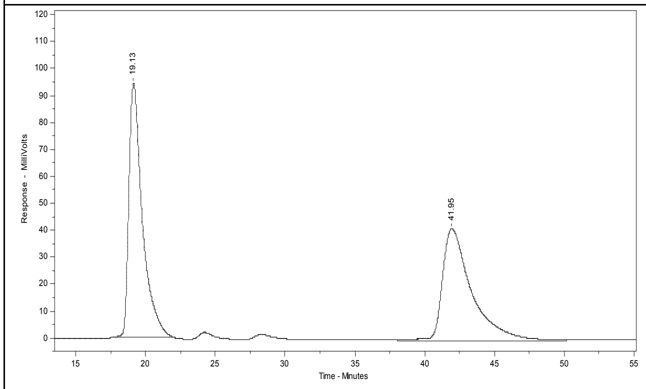
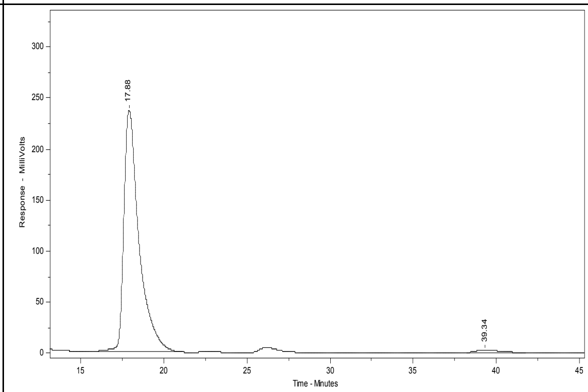




Peak #	Ret. Time	Area	Area %
1	18.72	6209680	49.379
2	23.75	99198	0.789
3	26.06	94179	0.749
4	29.13	6172575	49.084

Peak #	Ret. Time	Area	Area %
1	18.48	37587020	96.053
2	29.04	1544582	3.947

7m: IR (neat): 3381(w, br), 3094 (w, br), 2953 (w, br), 2846 (w, br), 1787 (m), 1754 (m), 1592 (m), 1523 (m), 1493 (m), 1324 (m), 1292 (s), 1228 (m), 1093 (m), 1026 (m), 816 (m), 796 (m), 744 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (1H, d, J = 2.6 Hz), 7.56-7.53 (1H, dd, J = 8.8, 2.6 Hz), 7.47-7.45 (1H, dd, J = 5.9, 1.5 Hz), 7.43-7.36 (4 H, m), 6.18 (1H, br s), 6.09-6.07 (1H, dd, J = 5.9, 1.8 Hz), 6.01 (1H, t, J = 1.8 Hz), 5.86 (1H, d, J = 8.8 Hz), 3.99 (3H, s), 3.79 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.4, 152.3, 146.7, 140.3, 139.2, 136.0, 132.2, 130.0, 129.0, 124.5, 118.3, 111.7, 105.4, 84.6, 68.5, 56.7, 54.4. HRMS Calcd for $C_{20}H_{18}N_2O_7Cl$ (M + H): 433.08025; Found: 433.07983. $[\alpha]^{25}_{D}$ = 67.6 (c = 1.0, $CHCl_3$) for a 96% ee sample. The enantiomeric purity of the compound is determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **7m**: 18 min and 41 min.

rac-**7m**	**7m**
	

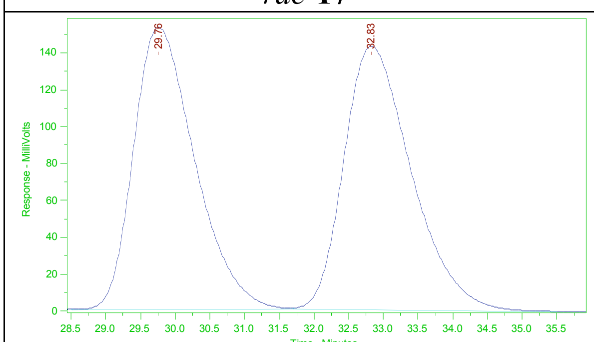
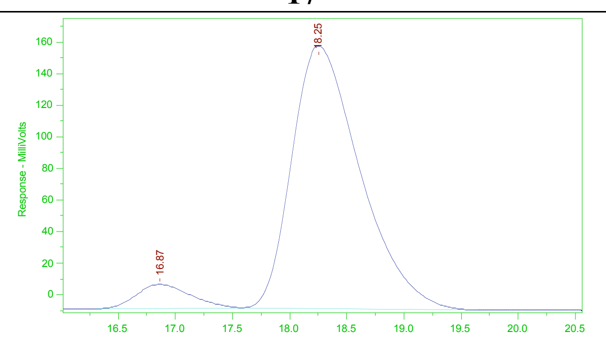
rac-**7m**

Peak #	Ret. Time	Area	Area %
1	19.1	2641062	50.596
2	41.9	2578827	49.404

7m

Peak #	Ret. Time	Area	Area %
1	17.88	15232200	97.901
2	39.34	326651	2.099

17: IR (neat): 3396 (w, br), 3006 (w), 2949 (w), 2829 (w), 1761 (m), 1759 (s), 1757 (m), 1595 (m), 1520 (m), 1464 (m), 1250 (m), 1224 (m), 1162 (m), 1092 (m), 1048 (m), 1029 (m), 746 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (1H, dd, J = 5.6, 1.6 Hz), 6.76-7.72 (3H, m), 6.52-6.48 (1H, m), 6.03 (1 H, dd, J = 6.0, 2.0 Hz), 5.56 (1H, dd, J = 1.8, 1.8 Hz), 4.66 (1H, br s), 3.81 (3H, s), 3.76 (3H, s), 1.59 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 172.7, 153.7, 148.4, 134.5, 122.8, 120.9, 119.8, 114.3, 110.3, 85.5, 62.9, 55.8, 53.1, 21.4. HRMS Calcd for $C_{15}H_{17}NO_5$ [M + H]: 291.11067; Found: 291.11070. $[\alpha]^{26}_{D}$ = 135.73 (c = 1.00, $CHCl_3$) for an 87% ee sample. The optical purity of the compound is determined by chiral HPLC analysis (OD, 80:20 hexanes:*i*-PrOH, 1 ml/min, 254 nm): t_R of **17:** 17 min (minor) and 18 min (major).

rac-**17**	**17**
	

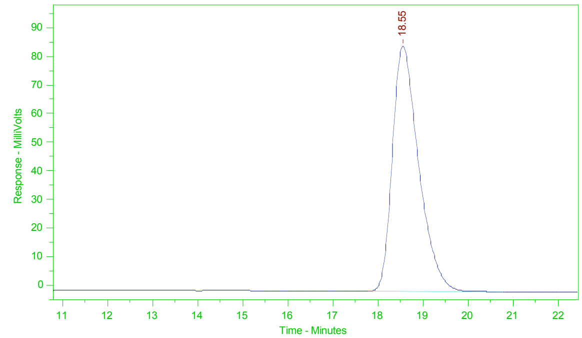
rac-**17**

Peak #	Ret. Time	Area	Area %
1	29.76	9370419	49.250
2	32.83	9655780	50.750

17

Peak #	Ret. Time	Area	Area %
1	16.87	498065	6.677
2	18.25	6960887	93.323

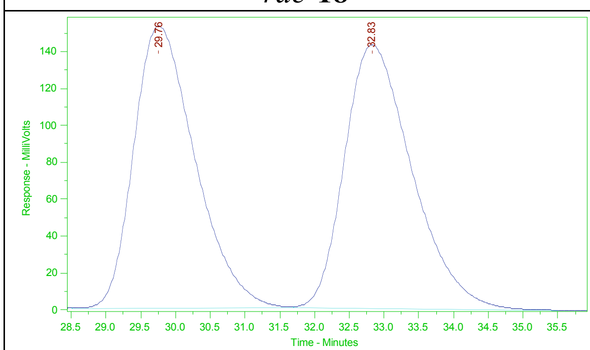
17 (recrystallized to optical purity)



Peak #	Ret. Time	Area	Area %
1	18.55	3476269.0	100.000

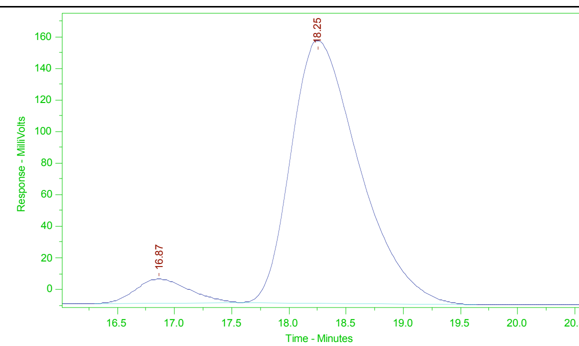
18: IR (neat): 3367 (w, br), 3105 (w), 2952 (w), 2839 (w), 2141 (w), 1761 (m), 1756 (s), 1738 (s), 1721 (s), 1641 (m), 1600 (m), 1516 (m), 1488 (m), 1459 (m), 1263 (s), 1223 (s), 1181 (m), 1162 (m), 1153 (m), 1108 (m), 1047 (m), 1025 (m), 905 (m), 745 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (3H, t, J = 4.5 Hz), 5.88-5.87 (1H, m), 5.45 (1 H, s), 4.72 (1H, br s), 3.81 (3H, s), 3.74 (3H, s), 2.11 (3H, s), 1.48 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 167.0, 153.7, 149.0, 134.1, 121.1, 120.0, 119.8, 115.8, 110.3, 86.2, 63.0, 55.9, 53.1, 18.7, 16.0. HRMS Calcd for $C_{16}H_{20}NO_5$ [M + H]: 306.13415; Found: 306.13391. $[\alpha]^{24}_D$ = +16.464 (c = 1.00, $CHCl_3$) for a 72% ee sample. The optical purity of the compound is determined by chiral HPLC analysis (OD, 95:5 hexanes:*i*-PrOH, 1 ml/min, 254 nm): t_R of **18:** 28 min (major) and 40 min (minor).

rac-**18**



Peak #	Ret. Time	Area	Area %
1	27.70	2949347	50.887
2	40.28	2846474	49.113

18



Peak #	Ret. Time	Area	Area %
1	27.23	7470072	86.245
2	40.25	1191339	13.755

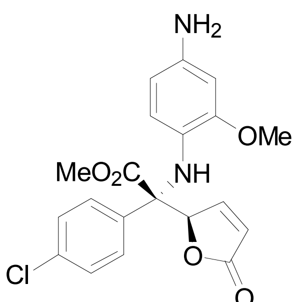
16: IR (neat): 3262 (w, br), 3052 (w), 2952 (w, br), 2838 (w, br), 1736 (m), 1675 (s), 1592 (m), 1557 (s), 1510 (m), 1462 (m), 1435 (m), 1338 (m), 1264 (s), 1242 (s), 1169 (m), 1058 (m), 828 (m), 784 (m), 745 (m), 697 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (1H, s br), 8.39 (1H, d, J = 2.8 Hz), 7.62-7.58 (2H, m), 7.38-7.18 (11H, m), 6.87-6.83 (2H, m), 6.36 (1H, d, J = 4.4 Hz), 3.98 (3H, s), 3.78 (3H, s), 3.52 (1H, d, J = 1.6 Hz), 3.47 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$):

δ 169.5, 161.22, 161.17, 156.2, 150.5, 149.3, 140.1, 138.5, 138.4, 137.1, 137.0, 134.6, 134.4, 133.1, 133.0, 132.2, 132.1, 131.2, 129.2, 129.1, 128.83, 128.76, 128.65, 128.61, 128.5, 121.6, 117.4, 114.3, 114.2, 114.1, 85.5, 56.2, 55.6, 55.5, 35.5, 27.1. HRMS Calcd for $C_{34}H_{38}N_2O_4P$ [M + H]: 569.25692; Found: 569.25454. $[\alpha]^{23}_D$ = +70.1 (*c* = 1.00, $CHCl_3$) for a >98% ee sample.

Experimental procedure for $SnCl_2$-mediated reduction of 7a followed by $PhI(OAc)_2$-mediated deprotection: A 50 mL round bottom flask was charged with catalytic AVM product **7a** (200 mg, 0.502 mmol), $SnCl_2$ (476 mg, 2.51 mmol), and ethanol (10.0 mL). The round bottom flask was fitted with a reflux condensor, and the mixture was allowed to warm to 65 °C with stirring. The resulting homogeneous solution was kept at 65 °C for 15 h before careful addition of a saturated solution of $NaHCO_3$. The aqueous layer was washed with EtOAc (3 x 50 mL). The organic layers were combined, dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The residue was redissolved in EtOAc and the solution was passed through a plug of SiO_2 (EtOAc). The volatiles were again removed *in vacuo*, and the resulting brown oil residue was analyzed by ^1H NMR spectroscopy. The residue was dissolved in MeCN (5.00 mL). The resulting homogeneous solution was allowed to cool to 0 °C with stirring. $PhI(OAc)_2$ (322 mg, 1.00 mmol) was added as a solid, and the homogeneous mixture was kept at 0 °C for 30 min before addition of 1M H_2SO_4 (10.0 equiv, 5.00 mL). The aqueous layer was washed with dichloromethane (3 x 5 mL). The organic layers were combined and set aside. The aqueous layer was basified (pH = 10) by dropwise addition of a saturated solution of Na_2CO_3, and was subsequently washed with dichloromethane (6 x 5 mL). The organic layers were combined, dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The dark brown oil was purified by silica gel chromatography (2:1 petroleum ether:EtOAc) to deliver **11** as an off-white oil (100 mg, 0.404 mmol, 81% yield over two steps). IR (neat): 3384 (w), 3321 (w), 2953 (w), 2924 (w), 1784 (m), 1759 (s),, 1734 (m), 1601 (m), 1489 (m), 145 (s), 1434 (m), 1244 (m), 1144 (m), 1096 (m), 1050 (m), 1024 (m), 890 (m), 834 (m), 704 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.59 (2H, m), 7.44-7.36 (3H, m), 6.97 (1H, dd, *J* = 5.8, 1.4 Hz), 6.14 (1H, dd, *J* = 6.0, 2.0 Hz), 5.89 (1H, dd, *J* = 2.0, 1.6 Hz), 3.82 (3H, s), 1.89 (2H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 172.8, 153.4, 137.1, 129.3, 129.2, 125.7, 123.5 86.7, 65.2, 53.6. HRMS Calcd for $C_{13}H_{14}NO_4$ [M + H]: 248.09228; Found: 248.09293. $[\alpha]^{26}_D$ = +94.45 (*c* = 0.733, $CDCl_3$) for a >98% ee sample.

Experimental procedure for $SnCl_2$-mediated reduction of 7a: A 100 mL round bottom flask was charged with **6a** (398 mg, 1.00 mmol), $SnCl_2$ (1.14 g, 6.00 mmol), and ethanol (20.0 mL). The round bottom flask was fitted with a reflux condensor, and the mixture was allowed to warm to 65 °C with stirring. The resulting homogeneous solution was kept at 65 °C for 15 h before careful addition of a saturated solution of $NaHCO_3$. The aqueous layer was washed with EtOAc (3 x 100 mL). The organic layers were combined, dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The dark brown oil residue was purified by silica gel chromatography (1:1 petroleum ether:EtOAc) to afford **10a** as an off-white solid (285 mg, 0.771 mmol, 77% yield).

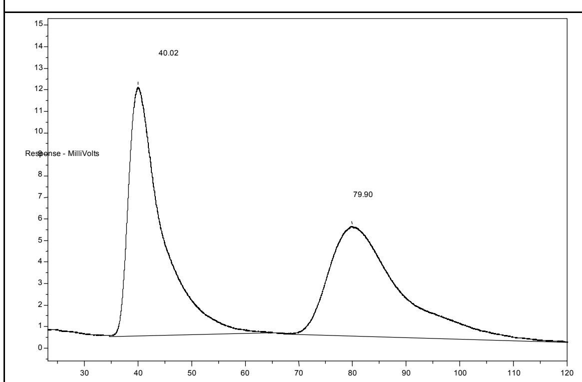
10a: IR (neat): 3445 (w), 3356 (w), 2951 (w), 1785 (w), 1735 (s), 1616 (m), 1592 (m), 1512 (s), 1458 (m), 1429 (m), 1283 (m), 1238 (s), 1199 (s), 1166 (m), 1095 (m), 1061 (m), 1031 (m), 1004 (m), 948 (m), 906 (m), 836 (m), 826 (m), 795 (m), 725 (s), 696 (s), 612 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (2H, dd, *J* = 8.0, 1.5 Hz), 7.46 (1H, dd, *J* = 5.8, 1.5 Hz), 7.36-7.29 (3H, m), 6.19 (1H, d, *J* = 2.2 Hz), 5.98 (1H, d, *J* = 4.8 Hz), 5.96 (1H, d, *J* = 1.8 Hz), 5.90 (1H, dd, *J* = 8.4, 2.6 Hz), 5.83 (1H, dd, *J* = 5.9, 2.2 Hz), 5.10 (1H, br s), 3.76 (3H, s), 3.69 (3H, s), 3.37 (2H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 172.2, 154.1, 150.1, 140.2, 136.5, 128.9, 128.8, 127.6, 126.2, 122.3, 117.4, 106.8, 99.8, 84.5, 69.9, 55.8, 53.4. HRMS Calcd for $C_{20}H_{21}N_2O_5$ [M + H]: 369.14505; Found: 369.14474. $[\alpha]^{25}_{D}$ = +76.25 (*c* = 1.00, $CHCl_3$) for a >98% ee sample.



10m

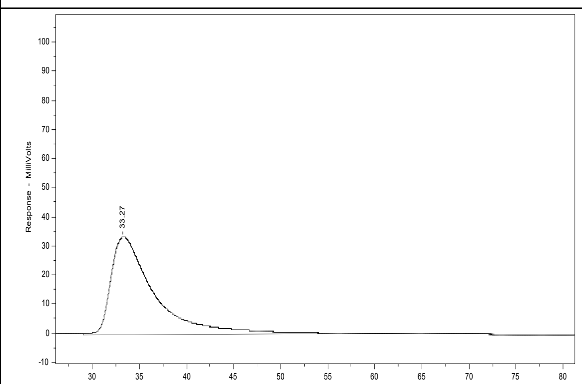
10m: IR (neat): 3444 (w, br), 3363 (w, br), 3098 (w, br), 3010 (w, br), 2850 (w, br), 2846 (w, br), 1763 (m), 1737 (m), 1515 (m), 1523 (m), 1463 (m), 1250 (s), 1201 (m), 1090 (m), 1026 (m), 947(m), 892(m), 821 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (2H, m), 7.45 (1H, dd, *J* = 5.9, 1.8 Hz), 7.35-7.32 (2 H, m), 6.23 (1H, d, *J* = 2.2 Hz), 6.01-5.94 (3H, m), 5.90 (1H, t, *J* = 1.8 Hz), 5.10 (1H, br s), 3.82 (3H, s), 3.72 (3H, s), 3.38 (2H, br s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 171.5, 153.6, 150.0, 140.1, 135.0, 134.6, 129.3, 128.9, 125.6, 122.7, 117.5, 106.8, 99.6, 84.2, 69.3, 55.7, 53.4. HRMS Calcd for $C_{20}H_{20}N_2O_5Cl$ [M + H]: 403.10607; Found: 403.10422. $[\alpha]^{23}_{D}$ = +41.8 (*c* = 0.500, $CHCl_3$) for a >98% ee sample. The enantiomeric purity of the compound was determined by chiral HPLC analysis (OJ, 70:30 hexanes:*i*-PrOH, 1 mL/min, 254 nm): t_R of **10m**: 40.0 min (major) and 79.9 min (minor)

***rac*-10m**



Peak #	Ret. Time	Area	Area %
1	40.02	4940318	51.877
2	79.90	4582752	48.123

10m



Peak #	Ret. Time	Area	Area %
1	40.06	12910630	100.000

Experimental procedure for $PhI(OAc)_2$ mediated deprotection of 10a: A 13x100 mm test tube was charged with aniline **10a** (36.8 mg, 0.100 mmol) and acetonitrile (1.00 mL). The resulting homogeneous solution was allowed to cool to 0 °C with stirring. $PhI(OAc)_2$ (64.4 mg, 0.200 mmol) was added as a solid, and the resulting homogeneous solution was kept at 0 °C for 30 min before addition of 1M H_2SO_4 (10.0 equiv, 1.00 mL). The aqueous layer was washed with dichloromethane (3 x 2 mL). The organic layers were combined and set aside. The aqueous layer was basified (pH = 10) by dropwise addition of a saturated solution of Na_2CO_3, and was subsequently washed with dichloromethane (6 x 2 mL). The organic layers were combined, dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The resulting brown oil residue was purified by silica gel chromatography (2:1 petroleum ether:EtOAc) to furnish **11** as an off-white oil (21.0 mg, 0.0849 mmol, 85% yield).

Experimental procedure for synthesis of Ag-based complex 12: A 50 mL round bottom flask was charged with **1** (203 mg, 0.400 mmol), AgOAc (66.8 mg, 0.400 mmol), and THF (5.0 mL). The mixture was allowed to stir at 25 °C for 5 min, and was then filtered through a pad of Celite® into a vial. Petroleum ether was added dropwise to the resulting homogeneous solution until the solution became slightly cloudy. At this point, THF was added dropwise until the solution was again clear, and the vial was sealed and stored in the dark for 12 hours. The resulting colorless crystals were isolated through filtration (193 mg, 0.325 mmol, 81% yield). mp = 128–132 °C. IR (neat): 3249 (w), 3057 (w), 2954 (m), 2865 (w), 1687 (m), 1627 (w), 1545 (m), 1508 (s), 1479 (m), 1460 (m), 1436 (m), 1409 (m), 1292 (m), 1236 (s), 1160 (s), 1097 (m), 1068 (m), 1031 (m), 826 (s), 798 (m), 756 (s) 690 (s), 505 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.03 (1H, br s), 9.12 (1H, br s), 8.20 (1H, d, J = 6.0 Hz), 7.59-7.47 (5H, m), 7.42-7.20 (7H, m), 7.14 (2H, t, J = 7.6 Hz), 6.89 (1H, t, J = 7.6 Hz), 6.79 (2H, ddd, J = 9.2, 3.2, 2.2 Hz), 3.79 (1H, br s), 3.69 (3H, s), 2.08 (1.5H, s, *AgOAc*), 0.73 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 178.0, 167.9, 160.3, 160.2, 155.7, 138.8, 138.7, 135.0, 134.8, 134.3, 134.1, 133.3, 132.8, 132.5, 132.2, 131.0, 130.7, 130.5, 130.4, 130.3, 129.6, 129.3, 129.2, 129.16, 129.1, 120.7, 113.4, 82.5, 54.7, 34.9, 26.3. $[\alpha]^{23}_D$ = –54.26 (c = 1.00, $CHCl_3$).

Experimental procedure for synthesis of powder Ag-ligand complex: A 50 mL round bottom flask was charged with **1** (200 mg, 0.393 mmol), AgOAc (65.6 mg, 0.393 mmol), and THF (5.0 mL). The mixture was allowed to stir at 25 °C for 5 min, and was subsequently filtered through a pad of Celite®. Volatiles were removed *in vacuo* to give a white powder (258.5 mg, 0.277 mmol, 71% yield). mp = 148-153 °C. IR (neat): 3119 (w), 2951 (w), 2833 (w), 1648 (w), 1545 (m), 1509 (s), 1478 (m), 1462 (m), 1435 (m), 1400 (m), 1362 (m), 1234 (s), 1163 (m), 1095 (m), 1032 (m), 828 (m), 744 (m), 693 (s), 658 (s), 484 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.14 (1H, br s), 9.17 (1H, br s), 8.18 (1H, d, J = 6.4 Hz), 7.57-7.55 (3H, m), 7.50 (2H, dd, J = 7.4, 3.6 Hz), 7,41-7.27 (7H, m), 7.19 (2H, t, J = 6.6 Hz), 6.86 (1H, t, J = 8.2 Hz), 6.72 (2H, d, J = 8.8 Hz), 3.93 (1H, br s), 3.69 (3H, s), 2.03 (2H, s, *AgOAc*), 0.72 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 168.0, 160.3, 160.1, 155.7, 138.7, 138.67, 135.1, 134.9, 134.4, 134.2, 133.3, 132.9, 132.4, 132.45, 132.2, 131.8, 130.9, 130.8, 130.6, 130.5, 129.8, 129.4, 129.3, 129.15, 120.8, 113.4, 82.3, 54.7, 34.9, 26.4, 23.0. $[\alpha]^{23}_{D}$ = –69.25 (*c* =1.00, $CHCl_3$).

■ **X-ray crystal structure of α-ketoimine ester 4a:**

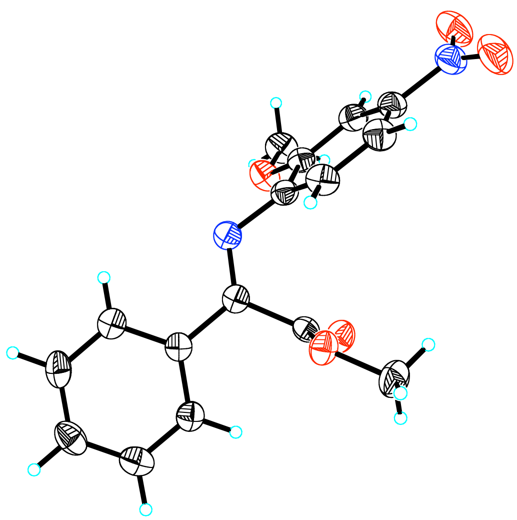


Table 1. Crystal data and structure refinement for **4a**

Identification code	lcw07	
Empirical formula	C16 H14 N2 O5	
Formula weight	314.29	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Trilinic	
Space group	P -1	
Unit cell dimensions	a = 8.595(2) Å	α= 71.928(5)°.
	b = 9.799(3) Å	β= 85.027(5)°.
	c = 10.014(3) Å	γ = 68.533(5)°.
Volume	745.9(3) $Å^3$	
Z	2	
Density (calculated)	1.399 Mg/m^3	

Absorption coefficient	0.106 mm^{-1}
F(000)	328
Crystal size	0.16 x 0.12 x 0.09 mm^3
Theta range for data collection	2.14 to 28.38°.
Index ranges	-11<=h<=8, -13<=k<=13, -13<=l<=13
Reflections collected	5715
Independent reflections	3706 [R(int) = 0.0241]
Completeness to theta = 28.38°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9905 and 0.9833
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3706 / 0 / 264
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1048
R indices (all data)	R1 = 0.0898, wR2 = 0.1220
Extinction coefficient	noref
Largest diff. peak and hole	0.193 and -0.225 e.$Å^{-3}$

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

	x	y	z	U(eq)
O(1)	1737(2)	5641(1)	4945(1)	35(1)
O(2)	3939(2)	5382(1)	3545(1)	39(1)
O(3)	-1708(2)	10323(2)	-1104(2)	60(1)
O(4)	-202(2)	9249(2)	-2610(2)	56(1)
O(5)	3282(2)	3972(1)	370(1)	38(1)
N(1)	1872(2)	3621(2)	2895(1)	31(1)
N(2)	-696(2)	9209(2)	-1416(2)	43(1)
C(1)	2546(2)	3578(2)	4003(2)	27(1)
C(2)	3142(2)	2171(2)	5203(2)	27(1)
C(3)	2748(2)	894(2)	5276(2)	33(1)
C(4)	3346(3)	-426(2)	6390(2)	40(1)
C(5)	4352(3)	-503(2)	7431(2)	42(1)
C(6)	4747(2)	754(2)	7368(2)	39(1)
C(7)	4143(2)	2086(2)	6265(2)	32(1)
C(8)	2839(2)	4967(2)	4119(2)	27(1)
C(9)	1886(3)	7004(2)	5123(3)	44(1)
C(10)	1243(2)	5045(2)	1828(2)	29(1)
C(11)	-111(2)	6247(2)	2049(2)	36(1)
C(12)	-756(2)	7621(2)	998(2)	38(1)
C(13)	-44(2)	7752(2)	-288(2)	34(1)
C(14)	1296(2)	6565(2)	-565(2)	34(1)
C(15)	1945(2)	5204(2)	494(2)	30(1)
C(16)	4072(3)	4118(3)	-960(2)	43(1)

Table 3. Bond lengths [Å] and angles [°]

O(1)-C(8)	1.3276(19)
O(1)-C(9)	1.452(2)
O(2)-C(8)	1.196(2)
O(3)-N(2)	1.231(2)
O(4)-N(2)	1.227(2)
O(5)-C(15)	1.359(2)
O(5)-C(16)	1.432(2)
N(1)-C(1)	1.278(2)
N(1)-C(10)	1.415(2)
N(2)-C(13)	1.467(2)
C(1)-C(2)	1.473(2)
C(1)-C(8)	1.512(2)
C(2)-C(7)	1.390(2)
C(2)-C(3)	1.391(2)
C(3)-C(4)	1.378(3)
C(3)-H(3)	0.918(19)
C(4)-C(5)	1.378(3)
C(4)-H(4)	0.954(19)
C(5)-C(6)	1.375(3)
C(5)-H(5)	0.96(2)
C(6)-C(7)	1.379(3)
C(6)-H(6)	0.98(2)
C(7)-H(7)	0.956(18)
C(9)-H(9A)	0.98(2)
C(9)-H(9B)	0.996(19)
C(9)-H(9C)	0.95(2)
C(10)-C(11)	1.380(2)
C(10)-C(15)	1.405(2)
C(11)-C(12)	1.380(3)
C(11)-H(11)	0.956(19)
C(12)-C(13)	1.366(3)
C(12)-H(12)	0.949(19)
C(13)-C(14)	1.386(2)
C(14)-C(15)	1.376(2)
C(14)-H(14)	0.941(18)

C(16)-H(16A)	0.98(2)
C(16)-H(16B)	1.01(2)
C(16)-H(16C)	0.99(2)
C(8)-O(1)-C(9)	116.16(15)
C(15)-O(5)-C(16)	117.08(15)
C(1)-N(1)-C(10)	118.58(14)
O(4)-N(2)-O(3)	123.85(17)
O(4)-N(2)-C(13)	118.39(17)
O(3)-N(2)-C(13)	117.76(17)
N(1)-C(1)-C(2)	122.37(15)
N(1)-C(1)-C(8)	121.16(15)
C(2)-C(1)-C(8)	116.42(15)
C(7)-C(2)-C(3)	118.90(17)
C(7)-C(2)-C(1)	120.37(15)
C(3)-C(2)-C(1)	120.71(16)
C(4)-C(3)-C(2)	120.00(19)
C(4)-C(3)-H(3)	121.0(12)
C(2)-C(3)-H(3)	118.9(12)
C(5)-C(4)-C(3)	120.65(19)
C(5)-C(4)-H(4)	119.9(11)
C(3)-C(4)-H(4)	119.4(12)
C(6)-C(5)-C(4)	119.73(19)
C(6)-C(5)-H(5)	119.4(13)
C(4)-C(5)-H(5)	120.8(13)
C(5)-C(6)-C(7)	120.2(2)
C(5)-C(6)-H(6)	120.3(12)
C(7)-C(6)-H(6)	119.5(12)
C(6)-C(7)-C(2)	120.50(18)
C(6)-C(7)-H(7)	120.3(11)
C(2)-C(7)-H(7)	119.2(11)
O(2)-C(8)-O(1)	125.09(16)
O(2)-C(8)-C(1)	123.67(15)
O(1)-C(8)-C(1)	111.23(14)
O(1)-C(9)-H(9A)	112.3(12)
O(1)-C(9)-H(9B)	105.1(11)
H(9A)-C(9)-H(9B)	113.6(16)

O(1)-C(9)-H(9C)	109.5(13)
H(9A)-C(9)-H(9C)	105.0(18)
H(9B)-C(9)-H(9C)	111.4(16)
C(11)-C(10)-C(15)	119.41(16)
C(11)-C(10)-N(1)	121.18(15)
C(15)-C(10)-N(1)	119.30(15)
C(10)-C(11)-C(12)	121.28(17)
C(10)-C(11)-H(11)	119.8(11)
C(12)-C(11)-H(11)	119.0(11)
C(13)-C(12)-C(11)	118.17(18)
C(13)-C(12)-H(12)	118.8(12)
C(11)-C(12)-H(12)	123.0(12)
C(12)-C(13)-C(14)	122.52(17)
C(12)-C(13)-N(2)	119.09(17)
C(14)-C(13)-N(2)	118.38(16)
C(15)-C(14)-C(13)	118.94(17)
C(15)-C(14)-H(14)	123.8(10)
C(13)-C(14)-H(14)	117.2(10)
O(5)-C(15)-C(14)	124.72(15)
O(5)-C(15)-C(10)	115.59(15)
C(14)-C(15)-C(10)	119.66(16)
O(5)-C(16)-H(16A)	106.0(12)
O(5)-C(16)-H(16B)	109.2(11)
H(16A)-C(16)-H(16B)	109.2(16)
O(5)-C(16)-H(16C)	110.3(12)
H(16A)-C(16)-H(16C)	108.9(16)
H(16B)-C(16)-H(16C)	113.1(17)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	37(1)	32(1)	38(1)	-17(1)	10(1)	-13(1)
O(2)	42(1)	43(1)	38(1)	-13(1)	11(1)	-24(1)
O(3)	51(1)	39(1)	70(1)	-7(1)	-8(1)	0(1)
O(4)	62(1)	54(1)	38(1)	6(1)	-1(1)	-20(1)
O(5)	41(1)	37(1)	29(1)	-11(1)	9(1)	-8(1)
N(1)	34(1)	34(1)	26(1)	-10(1)	6(1)	-15(1)
N(2)	36(1)	40(1)	48(1)	-2(1)	-8(1)	-14(1)
C(1)	25(1)	31(1)	26(1)	-12(1)	9(1)	-12(1)
C(2)	25(1)	29(1)	28(1)	-12(1)	8(1)	-8(1)
C(3)	32(1)	34(1)	35(1)	-14(1)	7(1)	-13(1)
C(4)	47(1)	26(1)	46(1)	-11(1)	10(1)	-14(1)
C(5)	45(1)	31(1)	36(1)	-6(1)	3(1)	-2(1)
C(6)	35(1)	42(1)	33(1)	-13(1)	1(1)	-6(1)
C(7)	34(1)	32(1)	33(1)	-13(1)	7(1)	-12(1)
C(8)	29(1)	29(1)	21(1)	-5(1)	2(1)	-10(1)
C(9)	47(1)	34(1)	54(1)	-22(1)	3(1)	-11(1)
C(10)	32(1)	34(1)	25(1)	-9(1)	1(1)	-15(1)
C(11)	32(1)	44(1)	32(1)	-12(1)	7(1)	-14(1)
C(12)	28(1)	40(1)	42(1)	-14(1)	3(1)	-8(1)
C(13)	30(1)	35(1)	34(1)	-6(1)	-4(1)	-13(1)
C(14)	35(1)	41(1)	27(1)	-9(1)	4(1)	-19(1)
C(15)	29(1)	34(1)	28(1)	-12(1)	1(1)	-12(1)
C(16)	45(1)	50(1)	32(1)	-18(1)	12(1)	-13(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

	x	y	z	U(eq)
H(3)	2060(20)	960(20)	4590(20)	37(5)
H(4)	3100(20)	-1310(20)	6415(19)	39(5)
H(5)	4800(30)	-1430(30)	8190(20)	58(6)
H(6)	5460(20)	710(20)	8100(20)	49(6)
H(7)	4450(20)	2950(20)	6202(18)	33(5)
H(9A)	3010(30)	6820(20)	5440(20)	48(6)
H(9B)	1000(30)	7330(20)	5790(20)	44(5)
H(9C)	1710(30)	7780(30)	4240(20)	58(7)
H(11)	-620(20)	6130(20)	2950(20)	39(5)
H(12)	-1670(20)	8470(20)	1127(19)	48(6)
H(14)	1710(20)	6747(19)	-1479(19)	32(5)
H(16A)	5020(30)	3160(20)	-850(20)	53(6)
H(16B)	4500(20)	5000(20)	-1180(20)	50(6)
H(16C)	3300(30)	4240(20)	-1690(20)	52(6)

Table 6. Torsion angles [°]

C(10)-N(1)-C(1)-C(2)	176.19(14)
C(10)-N(1)-C(1)-C(8)	-6.5(2)
N(1)-C(1)-C(2)-C(7)	167.75(16)
C(8)-C(1)-C(2)-C(7)	-9.7(2)
N(1)-C(1)-C(2)-C(3)	-10.6(2)
C(8)-C(1)-C(2)-C(3)	171.92(15)
C(7)-C(2)-C(3)-C(4)	0.2(2)
C(1)-C(2)-C(3)-C(4)	178.58(15)
C(2)-C(3)-C(4)-C(5)	-0.9(3)
C(3)-C(4)-C(5)-C(6)	0.9(3)
C(4)-C(5)-C(6)-C(7)	-0.3(3)
C(5)-C(6)-C(7)-C(2)	-0.4(3)
C(3)-C(2)-C(7)-C(6)	0.5(2)
C(1)-C(2)-C(7)-C(6)	-177.95(15)
C(9)-O(1)-C(8)-O(2)	1.3(3)
C(9)-O(1)-C(8)-C(1)	-179.37(16)
N(1)-C(1)-C(8)-O(2)	-75.9(2)
C(2)-C(1)-C(8)-O(2)	101.57(19)
N(1)-C(1)-C(8)-O(1)	104.73(17)
C(2)-C(1)-C(8)-O(1)	-77.80(18)
C(1)-N(1)-C(10)-C(11)	-66.5(2)
C(1)-N(1)-C(10)-C(15)	117.43(18)
C(15)-C(10)-C(11)-C(12)	-2.1(3)
N(1)-C(10)-C(11)-C(12)	-178.15(17)
C(10)-C(11)-C(12)-C(13)	1.6(3)
C(11)-C(12)-C(13)-C(14)	-0.4(3)
C(11)-C(12)-C(13)-N(2)	-179.23(17)
O(4)-N(2)-C(13)-C(12)	-170.46(18)
O(3)-N(2)-C(13)-C(12)	9.7(3)
O(4)-N(2)-C(13)-C(14)	10.6(3)
O(3)-N(2)-C(13)-C(14)	-169.19(16)
C(12)-C(13)-C(14)-C(15)	-0.4(3)
N(2)-C(13)-C(14)-C(15)	178.50(16)
C(16)-O(5)-C(15)-C(14)	0.6(3)
C(16)-O(5)-C(15)-C(10)	-177.48(17)

C(13)-C(14)-C(15)-O(5)	-178.08(16)
C(13)-C(14)-C(15)-C(10)	-0.1(3)
C(11)-C(10)-C(15)-O(5)	179.44(15)
N(1)-C(10)-C(15)-O(5)	-4.4(2)
C(11)-C(10)-C(15)-C(14)	1.3(3)
N(1)-C(10)-C(15)-C(14)	177.44(16)

Symmetry transformations used to generate equivalent atoms:

■ X-ray crystal structure of 10m:

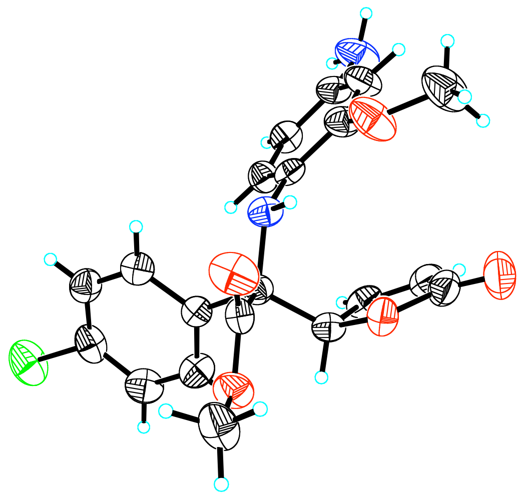


Table 1. Crystal data and structure refinement for **10m**

Identification code	emv01	
Empirical formula	C20 H19 Cl N2 O5	
Formula weight	402.82	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.8375(16) Å	α= 90°.
	b = 11.630(2) Å	β= 90°.
	c = 18.584(3) Å	γ = 90°.
Volume	1910.2(6) $Å^3$	
Z	4	
Density (calculated)	1.401 Mg/m^3	
Absorption coefficient	0.235 mm^{-1}	
F(000)	840	
Crystal size	0.1 x 0.1 x 0.05 mm^3	
Theta range for data collection	2.07 to 28.31°.	
Index ranges	-11<=h<=10, -11<=k<=15, -24<=l<=18	
Reflections collected	14569	
Independent reflections	4754 [R(int) = 0.0728]	
Completeness to theta = 28.31°	100.0 %	

Absorption correction	Empirical
Max. and min. transmission	none and none
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4754 / 0 / 329
Goodness-of-fit on F^2	0.995
Final R indices [I>2sigma(I)]	R1 = 0.0615, wR2 = 0.1043
R indices (all data)	R1 = 0.1139, wR2 = 0.1226
Absolute structure parameter	0.05(9)
Largest diff. peak and hole	0.247 and -0.171 e.$Å^{-3}$

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

	x	y	z	U(eq)
Cl(1)	-66(1)	2810(1)	119(1)	70(1)
O(2)	6754(2)	5252(2)	2680(1)	41(1)
O(5)	3296(3)	5135(2)	2927(1)	46(1)
O(4)	3827(3)	6925(2)	2592(1)	56(1)
C(9)	5920(4)	4578(3)	2162(2)	38(1)
N(2)	5285(3)	6322(2)	1433(1)	36(1)
C(15)	3491(3)	4680(3)	1411(2)	33(1)
C(8)	4672(3)	5354(3)	1836(2)	33(1)
O(3)	9175(3)	5670(3)	2898(2)	65(1)
C(13)	3873(3)	5914(3)	2491(2)	35(1)
C(10)	7112(4)	4125(3)	1672(2)	42(1)
C(12)	8272(4)	5191(3)	2528(2)	46(1)
C(3)	6020(4)	5485(3)	255(2)	38(1)
C(20)	2579(4)	5263(3)	916(2)	42(1)
C(4)	6281(3)	6185(3)	841(2)	33(1)
O(1)	7816(3)	7506(2)	1442(1)	63(1)
C(6)	8558(5)	6842(3)	255(2)	50(1)
C(17)	2152(4)	2940(3)	1109(2)	50(1)
C(1)	8281(4)	6123(3)	-332(2)	43(1)
C(16)	3237(4)	3522(3)	1500(2)	45(1)
C(18)	1313(4)	3529(3)	618(2)	46(1)
C(5)	7588(4)	6862(3)	831(2)	42(1)
C(19)	1511(4)	4688(4)	516(2)	44(1)
C(14)	2593(5)	5574(5)	3577(2)	57(1)
C(11)	8438(4)	4475(3)	1895(2)	48(1)
C(2)	7014(4)	5451(3)	-320(2)	40(1)
N(1)	9333(4)	6057(4)	-887(2)	64(1)
C(7)	9313(6)	7873(5)	1603(3)	73(2)

Table 3. Bond lengths [Å] and angles [°]

Cl(1)-C(18)	1.745(3)
O(2)-C(12)	1.373(4)
O(2)-C(9)	1.445(4)
O(5)-C(13)	1.318(4)
O(5)-C(14)	1.451(5)
O(4)-C(13)	1.192(4)
C(9)-C(10)	1.489(5)
C(9)-C(8)	1.549(4)
N(2)-C(4)	1.418(4)
N(2)-C(8)	1.456(4)
C(15)-C(16)	1.375(5)
C(15)-C(20)	1.399(4)
C(15)-C(8)	1.526(4)
C(8)-C(13)	1.550(4)
O(3)-C(12)	1.192(4)
C(10)-C(11)	1.307(5)
C(12)-C(11)	1.448(5)
C(3)-C(4)	1.378(4)
C(3)-C(2)	1.385(4)
C(20)-C(19)	1.375(5)
C(4)-C(5)	1.398(4)
O(1)-C(5)	1.374(4)
O(1)-C(7)	1.423(5)
C(6)-C(5)	1.372(5)
C(6)-C(1)	1.396(5)
C(17)-C(18)	1.361(5)
C(17)-C(16)	1.381(5)
C(1)-C(2)	1.366(5)
C(1)-N(1)	1.391(5)
C(18)-C(19)	1.372(5)
C(12)-O(2)-C(9)	109.5(3)
C(13)-O(5)-C(14)	115.8(3)
O(2)-C(9)-C(10)	103.8(3)
O(2)-C(9)-C(8)	107.9(3)
C(10)-C(9)-C(8)	118.1(3)

C(4)-N(2)-C(8)	123.0(3)
C(16)-C(15)-C(20)	117.4(3)
C(16)-C(15)-C(8)	123.5(3)
C(20)-C(15)-C(8)	119.0(3)
N(2)-C(8)-C(15)	112.6(2)
N(2)-C(8)-C(9)	112.8(3)
C(15)-C(8)-C(9)	112.9(3)
N(2)-C(8)-C(13)	104.4(3)
C(15)-C(8)-C(13)	108.1(2)
C(9)-C(8)-C(13)	105.2(2)
O(4)-C(13)-O(5)	124.6(3)
O(4)-C(13)-C(8)	123.6(3)
O(5)-C(13)-C(8)	111.7(3)
C(11)-C(10)-C(9)	109.3(3)
O(3)-C(12)-O(2)	120.7(3)
O(3)-C(12)-C(11)	132.0(3)
O(2)-C(12)-C(11)	107.2(3)
C(4)-C(3)-C(2)	121.4(3)
C(19)-C(20)-C(15)	121.0(4)
C(3)-C(4)-C(5)	117.5(3)
C(3)-C(4)-N(2)	125.1(3)
C(5)-C(4)-N(2)	117.4(3)
C(5)-O(1)-C(7)	118.3(3)
C(5)-C(6)-C(1)	120.7(3)
C(18)-C(17)-C(16)	119.0(4)
C(2)-C(1)-N(1)	121.9(3)
C(2)-C(1)-C(6)	118.3(3)
N(1)-C(1)-C(6)	119.7(3)
C(15)-C(16)-C(17)	122.0(4)
C(17)-C(18)-C(19)	121.1(3)
C(17)-C(18)-Cl(1)	119.8(3)
C(19)-C(18)-Cl(1)	119.1(3)
C(6)-C(5)-O(1)	124.2(3)
C(6)-C(5)-C(4)	121.1(3)
O(1)-C(5)-C(4)	114.7(3)
C(20)-C(19)-C(18)	119.4(4)

C(10)-C(11)-C(12)	110.2(3)
C(1)-C(2)-C(3)	121.0(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for EMV01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	61(1)	85(1)	65(1)	-23(1)	-11(1)	-21(1)
O(2)	35(1)	52(2)	36(1)	-4(1)	-2(1)	5(1)
O(5)	50(1)	56(2)	33(1)	-1(1)	10(1)	-2(1)
O(4)	65(2)	42(2)	60(2)	-16(1)	18(1)	0(1)
C(9)	40(2)	38(2)	34(2)	2(2)	3(2)	-1(2)
N(2)	46(2)	29(2)	32(1)	-2(1)	1(1)	-1(1)
C(15)	35(2)	34(2)	30(2)	-4(1)	4(1)	4(2)
C(8)	35(2)	33(2)	31(2)	0(1)	-1(1)	0(1)
O(3)	42(1)	87(2)	66(2)	0(2)	-15(1)	-4(2)
C(13)	28(2)	38(2)	38(2)	-5(2)	-3(1)	0(2)
C(10)	53(2)	40(2)	34(2)	4(2)	2(2)	13(2)
C(12)	38(2)	54(2)	45(2)	9(2)	-3(2)	9(2)
C(3)	37(2)	40(2)	38(2)	-4(2)	-2(2)	-4(2)
C(20)	43(2)	41(2)	41(2)	-1(2)	2(2)	1(2)
C(4)	38(2)	30(2)	33(2)	6(1)	-2(1)	7(1)
O(1)	66(2)	68(2)	55(2)	-21(1)	10(1)	-28(2)
C(6)	52(2)	45(2)	52(2)	3(2)	7(2)	-16(2)
C(17)	59(2)	33(2)	56(2)	-8(2)	0(2)	-8(2)
C(1)	50(2)	44(2)	35(2)	8(2)	7(2)	-4(2)
C(16)	53(2)	37(2)	43(2)	-4(2)	-4(2)	4(2)
C(18)	39(2)	60(3)	38(2)	-17(2)	-2(2)	-5(2)
C(5)	52(2)	34(2)	39(2)	-2(2)	0(2)	-6(2)
C(19)	43(2)	52(2)	37(2)	2(2)	-1(2)	3(2)
C(14)	49(2)	84(4)	39(2)	-14(3)	6(2)	-8(3)
C(11)	39(2)	58(3)	46(2)	13(2)	11(2)	15(2)
C(2)	49(2)	41(2)	31(2)	-6(2)	-1(2)	1(2)
N(1)	76(2)	69(3)	46(2)	-4(2)	18(2)	-25(2)
C(7)	75(3)	84(4)	61(3)	-19(3)	-2(3)	-36(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)

	x	y	z	U(eq)
H(3)	2730(30)	6080(30)	871(14)	27(8)
H(2)	5220(40)	5050(30)	230(14)	37(9)
H(1)	6850(30)	3650(30)	1272(16)	35(9)
H(8)	5650(30)	6840(30)	1769(17)	41(9)
H(11)	1940(30)	2170(30)	1207(14)	32(8)
H(5)	9780(40)	8290(30)	1244(19)	53(11)
H(9)	9380(40)	4290(30)	1758(17)	56(11)
H(10)	5460(30)	4010(30)	2463(15)	32(8)
H(6)	6780(30)	4970(30)	-706(16)	36(9)
H(7)	8990(50)	5630(40)	-1230(20)	73(15)
H(12)	3770(40)	3110(30)	1834(17)	46(10)
H(4)	9450(40)	7280(30)	287(15)	41(9)
H(14)	1710(50)	6120(40)	3450(20)	74(13)
H(16)	950(40)	5090(30)	229(16)	35(9)
H(13)	3220(40)	6160(30)	3807(19)	64(12)
H(15)	2450(60)	5030(40)	3850(20)	81(18)
H(17)	10080(50)	7180(40)	1690(20)	95(17)
H(18)	9240(50)	8280(40)	2100(20)	97(15)
H(19)	9810(50)	6720(40)	-1009(19)	73(14)

Table 6. Torsion angles [°]

C(12)-O(2)-C(9)-C(10)	-1.2(3)
C(12)-O(2)-C(9)-C(8)	-127.2(3)
C(4)-N(2)-C(8)-C(15)	-71.6(4)
C(4)-N(2)-C(8)-C(9)	57.7(4)
C(4)-N(2)-C(8)-C(13)	171.4(2)
C(16)-C(15)-C(8)-N(2)	150.1(3)
C(20)-C(15)-C(8)-N(2)	-31.8(4)
C(16)-C(15)-C(8)-C(9)	20.9(4)
C(20)-C(15)-C(8)-C(9)	-161.0(3)
C(16)-C(15)-C(8)-C(13)	-95.1(4)
C(20)-C(15)-C(8)-C(13)	83.0(3)
O(2)-C(9)-C(8)-N(2)	63.9(3)
C(10)-C(9)-C(8)-N(2)	-53.2(4)
O(2)-C(9)-C(8)-C(15)	-167.0(2)
C(10)-C(9)-C(8)-C(15)	75.9(4)
O(2)-C(9)-C(8)-C(13)	-49.3(3)
C(10)-C(9)-C(8)-C(13)	-166.4(3)
C(14)-O(5)-C(13)-O(4)	-1.2(5)
C(14)-O(5)-C(13)-C(8)	176.8(3)
N(2)-C(8)-C(13)-O(4)	0.3(4)
C(15)-C(8)-C(13)-O(4)	-119.9(3)
C(9)-C(8)-C(13)-O(4)	119.2(3)
N(2)-C(8)-C(13)-O(5)	-177.8(2)
C(15)-C(8)-C(13)-O(5)	62.1(3)
C(9)-C(8)-C(13)-O(5)	-58.8(3)
O(2)-C(9)-C(10)-C(11)	1.3(4)
C(8)-C(9)-C(10)-C(11)	120.6(3)
C(9)-O(2)-C(12)-O(3)	-178.6(3)
C(9)-O(2)-C(12)-C(11)	0.7(4)
C(16)-C(15)-C(20)-C(19)	-2.4(5)
C(8)-C(15)-C(20)-C(19)	179.4(3)
C(2)-C(3)-C(4)-C(5)	0.1(5)
C(2)-C(3)-C(4)-N(2)	176.3(3)
C(8)-N(2)-C(4)-C(3)	51.7(4)
C(8)-N(2)-C(4)-C(5)	-132.0(3)

C(5)-C(6)-C(1)-C(2)	0.5(5)
C(5)-C(6)-C(1)-N(1)	-175.5(4)
C(20)-C(15)-C(16)-C(17)	1.4(5)
C(8)-C(15)-C(16)-C(17)	179.6(3)
C(18)-C(17)-C(16)-C(15)	0.3(5)
C(16)-C(17)-C(18)-C(19)	-1.2(5)
C(16)-C(17)-C(18)-Cl(1)	-179.9(3)
C(1)-C(6)-C(5)-O(1)	177.1(3)
C(1)-C(6)-C(5)-C(4)	-1.4(5)
C(7)-O(1)-C(5)-C(6)	-21.4(6)
C(7)-O(1)-C(5)-C(4)	157.1(4)
C(3)-C(4)-C(5)-C(6)	1.0(5)
N(2)-C(4)-C(5)-C(6)	-175.5(3)
C(3)-C(4)-C(5)-O(1)	-177.5(3)
N(2)-C(4)-C(5)-O(1)	5.9(4)
C(15)-C(20)-C(19)-C(18)	1.6(5)
C(17)-C(18)-C(19)-C(20)	0.3(5)
Cl(1)-C(18)-C(19)-C(20)	179.0(3)
C(9)-C(10)-C(11)-C(12)	-1.0(4)
O(3)-C(12)-C(11)-C(10)	179.4(4)
O(2)-C(12)-C(11)-C(10)	0.2(4)
N(1)-C(1)-C(2)-C(3)	176.6(3)
C(6)-C(1)-C(2)-C(3)	0.6(5)
C(4)-C(3)-C(2)-C(1)	-0.9(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for EMV01 [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(8)...O(1)	0.93(3)	2.15(3)	2.627(4)	111(2)
N(1)-H(7)...O(2)#1	0.86(4)	2.36(4)	3.215(5)	169(4)
N(1)-H(19)...N(2)#2	0.91(5)	2.44(5)	3.322(5)	162(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,-y+1,z-1/2   #2 x+1/2,-y+3/2,-z

■ X-ray crystal structure of AgOAc-1 complex 12:

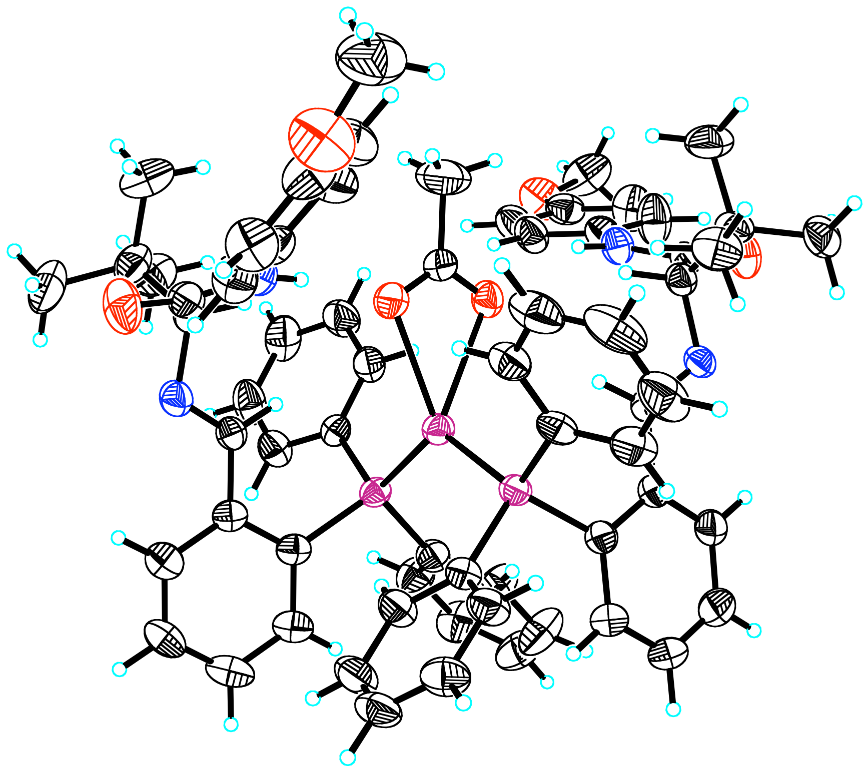


Table 1. Crystal data and structure refinement for AgOAc-**1** complex **12**

Identification code	bc106	
Empirical formula	C70 H79 Ag N4 O7 P2	
Formula weight	1258.18	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 17.451(4) Å	α= 90°.
	b = 17.675(5) Å	β= 90°.
	c = 21.505(6) Å	γ = 90°.
Volume	6633(3) Å^3	
Z	4	
Density (calculated)	1.260 Mg/m^3	
Absorption coefficient	0.406 mm^{-1}	

F(000)	2640
Crystal size	0.12 x 0.10 x 0.10 mm^3
Theta range for data collection	1.49 to 25.00°.
Index ranges	-14<=h<=20, -18<=k<=21, -25<=l<=25
Reflections collected	42921
Independent reflections	11670 [R(int) = 0.0218]
Completeness to theta = 25.00°	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.9605 and 0.9528
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11670 / 2 / 740
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0316, wR2 = 0.0861
R indices (all data)	R1 = 0.0352, wR2 = 0.0895
Absolute structure parameter	-0.024(14)
Largest diff. peak and hole	0.936 and -0.350 e.$Å^{-3}$

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

	x	y	z	U(eq)
Ag(1)	2286(1)	3664(1)	502(1)	32(1)
P(1)	1851(1)	2422(1)	838(1)	30(1)
P(2)	2558(1)	4084(1)	-551(1)	30(1)
O(1)	1963(1)	4614(1)	1264(1)	41(1)
O(2)	3193(1)	4342(1)	1256(1)	39(1)
O(3)	5525(1)	3198(1)	2099(1)	49(1)
O(4)	6799(2)	6206(2)	619(1)	66(1)
O(5)	-586(1)	5670(2)	933(1)	60(1)
O(6)	-1202(2)	4128(2)	3532(2)	80(1)
N(1)	4078(1)	2416(1)	1734(1)	33(1)
N(2)	4783(2)	4140(1)	1702(1)	39(1)
N(3)	574(1)	5452(2)	-70(1)	41(1)
N(4)	393(1)	5097(2)	1447(1)	40(1)
C(1)	2630(2)	4683(2)	1479(1)	37(1)
C(2)	2762(3)	5181(3)	2039(2)	86(2)
C(3)	2605(2)	1741(2)	655(1)	35(1)
C(4)	3338(2)	1822(2)	921(1)	34(1)
C(5)	3934(2)	1351(2)	725(1)	43(1)
C(6)	3812(2)	810(2)	270(2)	58(1)
C(7)	3098(2)	724(2)	17(2)	57(1)
C(8)	2495(2)	1187(2)	202(2)	47(1)
C(9)	3489(2)	2412(2)	1387(1)	31(1)
C(10)	4143(2)	3060(2)	2154(1)	33(1)
C(11)	4899(2)	3467(2)	1991(1)	35(1)
C(12)	4086(2)	2829(2)	2846(1)	39(1)
C(13)	3281(2)	2521(2)	2948(2)	55(1)
C(14)	4667(2)	2243(2)	3041(2)	52(1)
C(15)	4188(2)	3557(2)	3228(2)	59(1)
C(16)	5341(2)	4630(2)	1444(1)	40(1)
C(17)	5081(2)	5220(2)	1083(2)	46(1)
C(18)	5581(2)	5726(2)	813(2)	52(1)

C(19)	6355(2)	5658(2)	909(2)	47(1)
C(20)	6624(2)	5082(2)	1251(2)	63(1)
C(21)	6127(2)	4556(2)	1527(2)	64(1)
C(22)	7586(2)	6248(2)	773(2)	70(1)
C(23)	1603(2)	2256(2)	1649(1)	36(1)
C(24)	1721(2)	1563(2)	1931(2)	49(1)
C(25)	1472(2)	1456(2)	2542(2)	62(1)
C(26)	1120(2)	2025(3)	2858(2)	64(1)
C(27)	1000(2)	2714(3)	2579(2)	61(1)
C(28)	1254(2)	2836(2)	1977(2)	44(1)
C(29)	1020(2)	2075(2)	420(1)	35(1)
C(30)	842(2)	2404(2)	-152(1)	43(1)
C(31)	230(2)	2143(2)	-497(2)	53(1)
C(32)	-218(2)	1565(2)	-273(2)	49(1)
C(33)	-47(2)	1236(2)	284(2)	49(1)
C(34)	564(2)	1486(2)	638(2)	44(1)
C(35)	1692(2)	4137(2)	-1031(1)	32(1)
C(36)	1083(2)	4614(2)	-856(1)	31(1)
C(37)	441(2)	4671(2)	-1243(1)	40(1)
C(38)	390(2)	4236(2)	-1773(2)	46(1)
C(39)	964(2)	3732(2)	-1922(2)	50(1)
C(40)	1619(2)	3691(2)	-1559(1)	42(1)
C(41)	1113(2)	5043(2)	-268(1)	31(1)
C(42)	708(2)	5810(2)	530(2)	39(1)
C(43)	99(2)	5519(2)	982(2)	41(1)
C(44)	735(2)	6683(2)	478(2)	50(1)
C(45)	818(3)	7007(2)	1131(2)	70(1)
C(46)	37(3)	6998(2)	144(2)	73(1)
C(47)	1459(2)	6893(2)	110(2)	61(1)
C(48)	-9(2)	4836(2)	1977(2)	41(1)
C(49)	355(2)	4830(2)	2539(2)	56(1)
C(50)	-15(3)	4601(2)	3080(2)	63(1)
C(51)	-770(2)	4362(2)	3040(2)	57(1)
C(52)	-1130(2)	4344(2)	2470(2)	61(1)
C(53)	-764(2)	4585(2)	1945(2)	54(1)
C(54)	-902(4)	4230(3)	4120(2)	87(2)

C(55)	3205(2)	3482(2)	-996(1)	39(1)
C(56)	3590(2)	3728(2)	-1516(2)	50(1)
C(57)	4075(2)	3246(2)	-1839(2)	62(1)
C(58)	4165(3)	2522(2)	-1649(2)	68(1)
C(59)	3800(3)	2269(2)	-1129(2)	71(1)
C(60)	3310(2)	2742(2)	-800(2)	54(1)
C(61)	2956(2)	5042(2)	-623(1)	31(1)
C(62)	2806(2)	5503(2)	-1125(2)	43(1)
C(63)	3113(2)	6221(2)	-1153(2)	55(1)
C(64)	3570(2)	6478(2)	-673(2)	59(1)
C(65)	3718(2)	6031(2)	-172(2)	53(1)
C(66)	3411(2)	5306(2)	-146(2)	40(1)
O(1S)	6925(8)	3438(7)	3279(7)	314(6)
C(1S)	6727(6)	4760(5)	3235(4)	159(3)
C(2S)	6705(7)	4140(6)	3731(5)	198(5)
C(3S)	6820(9)	2876(8)	3890(6)	245(6)
C(4S)	6947(10)	2135(9)	3497(8)	299(8)

Table 3. Bond lengths [Å] and angles [°]

Ag(1)-O(1)	2.413(2)	Ag(1)-P(2)	2.4306(9)
Ag(1)-P(1)	2.4328(9)	Ag(1)-O(2)	2.562(2)
P(1)-C(29)	1.813(3)	P(1)-C(23)	1.820(3)
P(1)-C(3)	1.826(3)	P(2)-C(55)	1.824(3)
P(2)-C(35)	1.831(3)	P(2)-C(61)	1.836(3)
O(1)-C(1)	1.257(4)	O(2)-C(1)	1.248(4)
O(3)-C(11)	1.213(4)	O(4)-C(19)	1.389(4)
O(4)-C(22)	1.413(5)	O(5)-C(43)	1.229(4)
O(6)-C(51)	1.362(5)	O(6)-C(54)	1.381(6)
N(1)-C(9)	1.271(4)	N(1)-C(10)	1.457(4)
N(2)-C(11)	1.358(4)	N(2)-C(16)	1.416(4)
N(2)-H(2)	0.8800	N(3)-C(41)	1.260(4)
N(3)-C(42)	1.456(4)	N(4)-C(43)	1.349(4)
N(4)-C(48)	1.416(4)	N(4)-H(4)	0.8800
C(1)-C(2)	1.510(5)	C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800	C(2)-H(2C)	0.9800
C(3)-C(8)	1.396(4)	C(3)-C(4)	1.408(4)
C(4)-C(5)	1.397(4)	C(4)-C(9)	1.470(4)
C(5)-C(6)	1.384(5)	C(5)-H(5)	0.9500
C(6)-C(7)	1.368(6)	C(6)-H(6)	0.9500
C(7)-C(8)	1.391(5)	C(7)-H(7)	0.9500
C(8)-H(8)	0.9500	C(9)-H(9)	0.9500
C(10)-C(11)	1.543(4)	C(10)-C(12)	1.546(4)
C(10)-H(10)	1.0000	C(12)-C(14)	1.509(5)
C(12)-C(13)	1.521(5)	C(12)-C(15)	1.537(5)
C(13)-H(13A)	0.9800	C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800	C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800	C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800	C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800	C(16)-C(17)	1.377(5)
C(16)-C(21)	1.389(5)	C(17)-C(18)	1.377(5)
C(17)-H(17)	0.9500	C(18)-C(19)	1.372(5)
C(18)-H(18)	0.9500	C(19)-C(20)	1.340(5)
C(20)-C(21)	1.403(5)	C(20)-H(20)	0.9500

C(21)-H(21)	0.9500	C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800	C(22)-H(22C)	0.9800
C(23)-C(24)	1.382(5)	C(23)-C(28)	1.385(5)
C(24)-C(25)	1.396(5)	C(24)-H(24)	0.9500
C(25)-C(26)	1.361(6)	C(25)-H(25)	0.9500
C(26)-C(27)	1.373(6)	C(26)-H(26)	0.9500
C(27)-C(28)	1.387(5)	C(27)-H(27)	0.9500
C(28)-H(28)	0.9500	C(29)-C(34)	1.391(4)
C(29)-C(30)	1.395(4)	C(30)-C(31)	1.381(5)
C(30)-H(30)	0.9500	C(31)-C(32)	1.375(5)
C(31)-H(31)	0.9500	C(32)-C(33)	1.363(5)
C(32)-H(32)	0.9500	C(33)-C(34)	1.383(5)
C(33)-H(33)	0.9500	C(34)-H(34)	0.9500
C(35)-C(40)	1.388(4)	C(35)-C(36)	1.409(4)
C(36)-C(37)	1.398(4)	C(36)-C(41)	1.475(4)
C(37)-C(38)	1.378(5)	C(37)-H(37)	0.9500
C(38)-C(39)	1.378(5)	C(38)-H(38)	0.9500
C(39)-C(40)	1.386(5)	C(39)-H(39)	0.9500
C(40)-H(40)	0.9500	C(41)-H(41)	0.9500
C(42)-C(43)	1.530(5)	C(42)-C(44)	1.548(4)
C(42)-H(42)	1.0000	C(44)-C(45)	1.525(5)
C(44)-C(46)	1.519(6)	C(44)-C(47)	1.536(5)
C(45)-H(45A)	0.9800	C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800	C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800	C(46)-H(46C)	0.9800
C(47)-H(47A)	0.9800	C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800	C(48)-C(49)	1.366(5)
C(48)-C(53)	1.392(5)	C(49)-C(50)	1.390(5)
C(49)-H(49)	0.9500	C(50)-C(51)	1.387(6)
C(50)-H(50)	0.9500	C(51)-C(52)	1.378(6)
C(52)-C(53)	1.365(5)	C(52)-H(52)	0.9500
C(53)-H(53)	0.9500	C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800	C(54)-H(54C)	0.9800
C(55)-C(56)	1.374(5)	C(55)-C(60)	1.387(5)
C(56)-C(57)	1.388(5)	C(56)-H(56)	0.9500
C(57)-C(58)	1.351(6)	C(57)-H(57)	0.9500

C(58)-C(59)	1.363(6)	C(58)-H(58)	0.9500
C(59)-C(60)	1.390(5)	C(59)-H(59)	0.9500
C(60)-H(60)	0.9500	C(61)-C(62)	1.378(4)
C(61)-C(66)	1.380(4)	C(62)-C(63)	1.378(5)
C(62)-H(62)	0.9500	C(63)-C(64)	1.382(5)
C(63)-H(63)	0.9500	C(64)-C(65)	1.362(5)
C(64)-H(64)	0.9500	C(65)-C(66)	1.390(5)
C(65)-H(65)	0.9500	C(66)-H(66)	0.9500
O(1S)-C(2S)	1.622(13)	O(1S)-C(3S)	1.657(14)
C(1S)-C(2S)	1.530(11)	C(1S)-H(1S1)	0.9800
C(1S)-H(1S2)	0.9800	C(1S)-H(1S3)	0.9800
C(2S)-H(2S1)	0.9900	C(2S)-H(2S2)	0.9900
C(3S)-C(4S)	1.574(14)	C(3S)-H(3S1)	0.9900
C(3S)-H(3S2)	0.9900	C(4S)-H(4S1)	0.9800
C(4S)-H(4S2)	0.9800	C(4S)-H(4S3)	0.9800

O(1)-Ag(1)-P(2)	117.79(6)	O(1)-Ag(1)-P(1)	110.69(6)
P(2)-Ag(1)-P(1)	127.81(2)	O(1)-Ag(1)-O(2)	52.37(7)
P(2)-Ag(1)-O(2)	109.06(5)	P(1)-Ag(1)-O(2)	115.26(5)
C(29)-P(1)-C(23)	103.34(13)	C(29)-P(1)-C(3)	104.21(13)
C(23)-P(1)-C(3)	105.75(13)	C(29)-P(1)-Ag(1)	114.08(10)
C(23)-P(1)-Ag(1)	120.28(10)	C(3)-P(1)-Ag(1)	107.81(10)
C(55)-P(2)-C(35)	104.18(13)	C(55)-P(2)-C(61)	105.01(13)
C(35)-P(2)-C(61)	102.55(12)	C(55)-P(2)-Ag(1)	115.58(10)
C(35)-P(2)-Ag(1)	112.35(9)	C(61)-P(2)-Ag(1)	115.72(9)
C(1)-O(1)-Ag(1)	95.73(17)	C(1)-O(2)-Ag(1)	88.98(17)
C(19)-O(4)-C(22)	118.3(3)	C(51)-O(6)-C(54)	117.6(4)
C(9)-N(1)-C(10)	115.6(2)	C(11)-N(2)-C(16)	127.8(3)
C(11)-N(2)-H(2)	116.1	C(16)-N(2)-H(2)	116.1
C(41)-N(3)-C(42)	115.3(2)	C(43)-N(4)-C(48)	126.0(3)
C(43)-N(4)-H(4)	117.0	C(48)-N(4)-H(4)	117.0
O(2)-C(1)-O(1)	122.8(3)	O(2)-C(1)-C(2)	117.9(3)
O(1)-C(1)-C(2)	119.3(3)	C(1)-C(2)-H(2A)	109.1
C(1)-C(2)-H(2B)	110.7	H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	108.6	H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5	C(8)-C(3)-C(4)	118.6(3)

C(8)-C(3)-P(1)	121.0(2)	C(4)-C(3)-P(1)	120.0(2)
C(5)-C(4)-C(3)	119.6(3)	C(5)-C(4)-C(9)	119.6(3)
C(3)-C(4)-C(9)	120.8(3)	C(6)-C(5)-C(4)	120.6(3)
C(6)-C(5)-H(5)	119.7	C(4)-C(5)-H(5)	119.7
C(7)-C(6)-C(5)	119.9(3)	C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0	C(6)-C(7)-C(8)	120.6(3)
C(6)-C(7)-H(7)	119.7	C(8)-C(7)-H(7)	119.7
C(7)-C(8)-C(3)	120.6(3)	C(7)-C(8)-H(8)	119.7
C(3)-C(8)-H(8)	119.7	N(1)-C(9)-C(4)	123.4(3)
N(1)-C(9)-H(9)	118.3	C(4)-C(9)-H(9)	118.3
N(1)-C(10)-C(11)	106.8(2)	N(1)-C(10)-C(12)	112.6(2)
C(11)-C(10)-C(12)	113.4(2)	N(1)-C(10)-H(10)	107.9
C(11)-C(10)-H(10)	107.9	C(12)-C(10)-H(10)	107.9
O(3)-C(11)-N(2)	124.4(3)	O(3)-C(11)-C(10)	123.0(3)
N(2)-C(11)-C(10)	112.6(2)	C(14)-C(12)-C(13)	109.6(3)
C(14)-C(12)-C(15)	110.3(3)	C(13)-C(12)-C(15)	109.2(3)
C(14)-C(12)-C(10)	113.9(3)	C(13)-C(12)-C(10)	107.0(3)
C(15)-C(12)-C(10)	106.6(3)	C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5	H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5	H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5	C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5	H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5	H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5	C(17)-C(16)-C(21)	117.9(3)
C(17)-C(16)-N(2)	117.2(3)	C(21)-C(16)-N(2)	124.8(3)
C(16)-C(17)-C(18)	121.4(3)	C(16)-C(17)-H(17)	119.3
C(18)-C(17)-H(17)	119.3	C(19)-C(18)-C(17)	120.2(3)
C(19)-C(18)-H(18)	119.9	C(17)-C(18)-H(18)	119.9
C(20)-C(19)-C(18)	119.6(3)	C(20)-C(19)-O(4)	125.4(3)
C(18)-C(19)-O(4)	114.9(3)	C(19)-C(20)-C(21)	121.2(4)
C(19)-C(20)-H(20)	119.4	C(21)-C(20)-H(20)	119.4
C(16)-C(21)-C(20)	119.6(3)	C(16)-C(21)-H(21)	120.2
C(20)-C(21)-H(21)	120.2	O(4)-C(22)-H(22A)	109.5

O(4)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
O(4)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	C(24)-C(23)-C(28)	119.8(3)
C(24)-C(23)-P(1)	121.9(2)	C(28)-C(23)-P(1)	118.2(2)
C(23)-C(24)-C(25)	119.2(4)	C(23)-C(24)-H(24)	120.4
C(25)-C(24)-H(24)	120.4	C(26)-C(25)-C(24)	120.6(4)
C(26)-C(25)-H(25)	119.7	C(24)-C(25)-H(25)	119.7
C(25)-C(26)-C(27)	120.5(3)	C(25)-C(26)-H(26)	119.8
C(27)-C(26)-H(26)	119.8	C(26)-C(27)-C(28)	119.8(4)
C(26)-C(27)-H(27)	120.1	C(28)-C(27)-H(27)	120.1
C(23)-C(28)-C(27)	120.1(3)	C(23)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0	C(34)-C(29)-C(30)	118.8(3)
C(34)-C(29)-P(1)	122.9(2)	C(30)-C(29)-P(1)	118.3(2)
C(31)-C(30)-C(29)	120.5(3)	C(31)-C(30)-H(30)	119.8
C(29)-C(30)-H(30)	119.8	C(32)-C(31)-C(30)	119.9(3)
C(32)-C(31)-H(31)	120.0	C(30)-C(31)-H(31)	120.0
C(33)-C(32)-C(31)	120.1(3)	C(33)-C(32)-H(32)	120.0
C(31)-C(32)-H(32)	120.0	C(32)-C(33)-C(34)	121.0(3)
C(32)-C(33)-H(33)	119.5	C(34)-C(33)-H(33)	119.5
C(33)-C(34)-C(29)	119.7(3)	C(33)-C(34)-H(34)	120.2
C(29)-C(34)-H(34)	120.2	C(40)-C(35)-C(36)	119.3(3)
C(40)-C(35)-P(2)	120.5(2)	C(36)-C(35)-P(2)	120.2(2)
C(37)-C(36)-C(35)	119.2(3)	C(37)-C(36)-C(41)	120.1(3)
C(35)-C(36)-C(41)	120.6(3)	C(38)-C(37)-C(36)	120.3(3)
C(38)-C(37)-H(37)	119.9	C(36)-C(37)-H(37)	119.9
C(39)-C(38)-C(37)	120.4(3)	C(39)-C(38)-H(38)	119.8
C(37)-C(38)-H(38)	119.8	C(38)-C(39)-C(40)	120.2(3)
C(38)-C(39)-H(39)	119.9	C(40)-C(39)-H(39)	119.9
C(35)-C(40)-C(39)	120.4(3)	C(35)-C(40)-H(40)	119.8
C(39)-C(40)-H(40)	119.8	N(3)-C(41)-C(36)	123.8(3)
N(3)-C(41)-H(41)	118.1	C(36)-C(41)-H(41)	118.1
N(3)-C(42)-C(43)	107.8(2)	N(3)-C(42)-C(44)	112.0(3)
C(43)-C(42)-C(44)	113.6(3)	N(3)-C(42)-H(42)	107.7
C(43)-C(42)-H(42)	107.7	C(44)-C(42)-H(42)	107.7
O(5)-C(43)-N(4)	123.6(3)	O(5)-C(43)-C(42)	123.2(3)
N(4)-C(43)-C(42)	113.1(3)	C(45)-C(44)-C(46)	111.9(3)

C(45)-C(44)-C(47)	107.7(3)	C(46)-C(44)-C(47)	109.2(3)
C(45)-C(44)-C(42)	108.1(3)	C(46)-C(44)-C(42)	112.1(3)
C(47)-C(44)-C(42)	107.7(3)	C(44)-C(45)-H(45A)	109.5
C(44)-C(45)-H(45B)	109.5	H(45A)-C(45)-H(45B)	109.5
C(44)-C(45)-H(45C)	109.5	H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5	C(44)-C(46)-H(46A)	109.5
C(44)-C(46)-H(46B)	109.5	H(46A)-C(46)-H(46B)	109.5
C(44)-C(46)-H(46C)	109.5	H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5	C(44)-C(47)-H(47A)	109.5
C(44)-C(47)-H(47B)	109.5	H(47A)-C(47)-H(47B)	109.5
C(44)-C(47)-H(47C)	109.5	H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5	C(49)-C(48)-C(53)	118.8(3)
C(49)-C(48)-N(4)	119.0(3)	C(53)-C(48)-N(4)	122.2(3)
C(48)-C(49)-C(50)	121.8(4)	C(48)-C(49)-H(49)	119.1
C(50)-C(49)-H(49)	119.1	C(51)-C(50)-C(49)	118.6(4)
C(51)-C(50)-H(50)	120.7	C(49)-C(50)-H(50)	120.7
O(6)-C(51)-C(52)	115.6(4)	O(6)-C(51)-C(50)	124.7(4)
C(52)-C(51)-C(50)	119.7(4)	C(53)-C(52)-C(51)	121.0(4)
C(53)-C(52)-H(52)	119.5	C(51)-C(52)-H(52)	119.5
C(52)-C(53)-C(48)	120.2(4)	C(52)-C(53)-H(53)	119.9
C(48)-C(53)-H(53)	119.9	O(6)-C(54)-H(54A)	109.5
O(6)-C(54)-H(54B)	109.5	H(54A)-C(54)-H(54B)	109.5
O(6)-C(54)-H(54C)	109.5	H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5	C(56)-C(55)-C(60)	118.8(3)
C(56)-C(55)-P(2)	123.0(2)	C(60)-C(55)-P(2)	118.2(2)
C(55)-C(56)-C(57)	120.7(4)	C(55)-C(56)-H(56)	119.7
C(57)-C(56)-H(56)	119.7	C(58)-C(57)-C(56)	120.0(4)
C(58)-C(57)-H(57)	120.0	C(56)-C(57)-H(57)	120.0
C(57)-C(58)-C(59)	120.4(4)	C(57)-C(58)-H(58)	119.8
C(59)-C(58)-H(58)	119.8	C(58)-C(59)-C(60)	120.5(4)
C(58)-C(59)-H(59)	119.8	C(60)-C(59)-H(59)	119.8
C(59)-C(60)-C(55)	119.6(3)	C(59)-C(60)-H(60)	120.2
C(55)-C(60)-H(60)	120.2	C(62)-C(61)-C(66)	119.4(3)
C(62)-C(61)-P(2)	122.7(2)	C(66)-C(61)-P(2)	117.8(2)
C(61)-C(62)-C(63)	120.4(3)	C(61)-C(62)-H(62)	119.8
C(63)-C(62)-H(62)	119.8	C(62)-C(63)-C(64)	119.7(3)

C(62)-C(63)-H(63)	120.2	C(64)-C(63)-H(63)	120.2
C(65)-C(64)-C(63)	120.6(3)	C(65)-C(64)-H(64)	119.7
C(63)-C(64)-H(64)	119.7	C(64)-C(65)-C(66)	119.6(3)
C(64)-C(65)-H(65)	120.2	C(66)-C(65)-H(65)	120.2
C(61)-C(66)-C(65)	120.3(3)	C(61)-C(66)-H(66)	119.9
C(65)-C(66)-H(66)	119.9	C(2S)-O(1S)-C(3S)	87.6(10)
C(2S)-C(1S)-H(1S1)	107.3	C(2S)-C(1S)-H(1S2)	109.8
H(1S1)-C(1S)-H(1S2)	109.5	C(2S)-C(1S)-H(1S3)	111.3
H(1S1)-C(1S)-H(1S3)	109.5	H(1S2)-C(1S)-H(1S3)	109.5
C(1S)-C(2S)-O(1S)	97.1(9)	C(1S)-C(2S)-H(2S1)	109.6
O(1S)-C(2S)-H(2S1)	117.3	C(1S)-C(2S)-H(2S2)	111.5
O(1S)-C(2S)-H(2S2)	112.7	H(2S1)-C(2S)-H(2S2)	108.1
C(4S)-C(3S)-O(1S)	93.3(11)	C(4S)-C(3S)-H(3S1)	111.3
O(1S)-C(3S)-H(3S1)	112.9	C(4S)-C(3S)-H(3S2)	113.1
O(1S)-C(3S)-H(3S2)	116.1	H(3S1)-C(3S)-H(3S2)	109.3
C(3S)-C(4S)-H(4S1)	107.8	C(3S)-C(4S)-H(4S2)	109.5
H(4S1)-C(4S)-H(4S2)	109.5	C(3S)-C(4S)-H(4S3)	111.1
H(4S1)-C(4S)-H(4S3)	109.5	H(4S2)-C(4S)-H(4S3)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for bc106. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ag(1)	37(1)	29(1)	30(1)	0(1)	0(1)	0(1)
P(1)	33(1)	30(1)	28(1)	0(1)	-4(1)	-2(1)
P(2)	33(1)	29(1)	28(1)	-1(1)	4(1)	0(1)
O(1)	35(1)	44(1)	45(1)	-6(1)	-2(1)	7(1)
O(2)	31(1)	44(1)	43(1)	1(1)	-3(1)	6(1)
O(3)	31(1)	57(1)	60(1)	14(1)	-4(1)	2(1)
O(4)	64(2)	70(2)	62(2)	12(1)	0(1)	-26(1)
O(5)	34(1)	87(2)	58(2)	11(1)	5(1)	16(1)
O(6)	76(2)	94(2)	70(2)	13(2)	11(2)	-18(2)
N(1)	33(1)	40(1)	26(1)	-1(1)	-2(1)	5(1)
N(2)	31(1)	44(1)	43(1)	4(1)	-3(1)	0(1)
N(3)	33(1)	51(2)	39(1)	-5(1)	-3(1)	8(1)
N(4)	30(1)	47(1)	42(1)	-4(1)	4(1)	6(1)
C(1)	42(2)	35(1)	33(1)	-3(1)	-1(1)	3(1)
C(2)	76(3)	109(4)	73(3)	-49(3)	-18(3)	14(3)
C(3)	44(2)	31(1)	30(1)	2(1)	-4(1)	1(1)
C(4)	42(2)	33(1)	28(1)	3(1)	-3(1)	1(1)
C(5)	46(2)	45(2)	39(2)	-3(1)	-6(1)	13(2)
C(6)	71(2)	52(2)	50(2)	-12(2)	-8(2)	23(2)
C(7)	75(3)	46(2)	50(2)	-20(2)	-14(2)	16(2)
C(8)	58(2)	39(2)	45(2)	-10(1)	-12(2)	4(1)
C(9)	29(1)	35(1)	30(1)	0(1)	3(1)	3(1)
C(10)	29(1)	37(2)	33(1)	-1(1)	-3(1)	3(1)
C(11)	34(2)	39(2)	32(1)	1(1)	-3(1)	1(1)
C(12)	41(2)	47(2)	29(1)	-7(1)	2(1)	2(1)
C(13)	51(2)	69(2)	45(2)	-3(2)	14(2)	-7(2)
C(14)	64(2)	58(2)	32(2)	9(1)	1(2)	9(2)
C(15)	72(2)	62(2)	43(2)	-19(2)	4(2)	3(2)
C(16)	37(2)	43(2)	39(2)	2(1)	-2(1)	-8(1)
C(17)	42(2)	47(2)	50(2)	5(2)	-12(2)	-7(2)
C(18)	59(2)	49(2)	48(2)	7(2)	-11(2)	-12(2)

C(19)	56(2)	45(2)	42(2)	-3(1)	-2(2)	-14(2)
C(20)	38(2)	69(2)	81(3)	7(2)	5(2)	-4(2)
C(21)	41(2)	63(2)	87(3)	26(2)	-6(2)	-1(2)
C(22)	53(2)	54(2)	104(3)	-12(2)	22(2)	-20(2)
C(23)	34(2)	44(2)	30(1)	-2(1)	-3(1)	-12(1)
C(24)	62(2)	47(2)	38(2)	4(1)	-2(2)	-16(2)
C(25)	77(3)	65(2)	44(2)	20(2)	-12(2)	-27(2)
C(26)	51(2)	110(4)	33(2)	1(2)	5(2)	-27(2)
C(27)	47(2)	95(3)	39(2)	-14(2)	0(2)	-4(2)
C(28)	39(2)	56(2)	38(2)	-5(2)	-5(1)	-2(2)
C(29)	36(2)	36(1)	34(1)	-4(1)	-5(1)	-1(1)
C(30)	43(2)	45(2)	40(2)	3(1)	-8(1)	-6(1)
C(31)	53(2)	65(2)	40(2)	-6(2)	-15(2)	-1(2)
C(32)	35(2)	63(2)	48(2)	-17(2)	-9(1)	-6(2)
C(33)	42(2)	52(2)	52(2)	-8(2)	2(1)	-14(2)
C(34)	46(2)	45(2)	40(2)	0(1)	-7(1)	-11(1)
C(35)	38(2)	29(1)	30(1)	2(1)	3(1)	-8(1)
C(36)	32(1)	29(1)	33(1)	2(1)	4(1)	-8(1)
C(37)	34(2)	45(2)	40(2)	4(1)	2(1)	-9(1)
C(38)	37(2)	64(2)	38(2)	2(2)	-6(1)	-13(2)
C(39)	51(2)	63(2)	36(2)	-12(2)	1(1)	-20(2)
C(40)	43(2)	46(2)	36(1)	-7(1)	3(1)	-8(2)
C(41)	27(1)	34(1)	33(1)	2(1)	-1(1)	-1(1)
C(42)	32(1)	48(2)	36(1)	-5(1)	0(1)	10(1)
C(43)	34(2)	50(2)	40(2)	-8(1)	1(1)	7(1)
C(44)	53(2)	44(2)	53(2)	-4(2)	9(2)	13(1)
C(45)	84(3)	56(2)	69(3)	-22(2)	16(2)	-1(2)
C(46)	74(3)	58(2)	88(3)	4(2)	5(2)	30(2)
C(47)	71(3)	52(2)	61(2)	0(2)	10(2)	1(2)
C(48)	38(2)	37(2)	48(2)	-5(1)	7(1)	3(1)
C(49)	51(2)	68(2)	50(2)	-2(2)	2(2)	-17(2)
C(50)	73(3)	71(3)	45(2)	4(2)	-2(2)	-10(2)
C(51)	59(2)	48(2)	64(2)	0(2)	24(2)	-4(2)
C(52)	54(2)	64(2)	65(2)	4(2)	5(2)	-8(2)
C(53)	44(2)	52(2)	66(2)	2(2)	0(2)	-4(2)
C(54)	131(5)	75(3)	56(2)	0(2)	4(3)	-16(3)

C(55)	37(2)	44(2)	34(1)	-5(1)	2(1)	5(1)
C(56)	54(2)	49(2)	47(2)	-2(2)	13(2)	6(2)
C(57)	54(2)	76(3)	55(2)	-9(2)	21(2)	6(2)
C(58)	64(3)	59(2)	80(3)	-22(2)	22(2)	11(2)
C(59)	87(3)	42(2)	83(3)	-2(2)	25(2)	15(2)
C(60)	68(2)	39(2)	56(2)	-2(2)	21(2)	8(2)
C(61)	26(1)	32(1)	35(1)	0(1)	4(1)	1(1)
C(62)	40(2)	45(2)	43(2)	8(1)	-5(1)	-6(2)
C(63)	45(2)	51(2)	68(2)	23(2)	-10(2)	-7(2)
C(64)	46(2)	40(2)	92(3)	14(2)	-11(2)	-12(2)
C(65)	49(2)	48(2)	62(2)	0(2)	-17(2)	-9(2)
C(66)	38(2)	38(2)	44(2)	5(1)	-5(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)

	x	y	z	U(eq)
H(2)	4304	4289	1671	47
H(4)	880	4972	1418	48
H(2A)	3229	5016	2252	128
H(2B)	2327	5152	2326	128
H(2C)	2826	5704	1896	128
H(5)	4428	1401	906	52
H(6)	4223	500	133	69
H(7)	3013	344	-288	68
H(8)	2004	1125	17	57
H(9)	3127	2810	1431	38
H(10)	3711	3414	2062	40
H(13A)	3227	2036	2731	83
H(13B)	2905	2882	2784	83
H(13C)	3194	2447	3394	83
H(14A)	4583	2108	3478	77
H(14B)	5184	2450	2992	77
H(14C)	4611	1791	2781	77
H(15A)	3797	3926	3107	89
H(15B)	4698	3769	3150	89
H(15C)	4135	3440	3672	89
H(17)	4546	5279	1019	55
H(18)	5389	6123	559	63
H(20)	7161	5030	1308	75
H(21)	6326	4152	1768	77
H(22A)	7642	6299	1224	105
H(22B)	7815	6688	567	105
H(22C)	7845	5787	633	105
H(24)	1967	1165	1712	59
H(25)	1550	981	2739	75
H(26)	957	1945	3274	77
H(27)	742	3105	2799	73
H(28)	1189	3318	1789	53

H(30)	1145	2811	-304	51
H(31)	119	2363	-890	63
H(32)	-647	1394	-506	58
H(33)	-353	828	430	59
H(34)	672	1257	1028	52
H(37)	39	5011	-1140	48
H(38)	-43	4284	-2038	56
H(39)	910	3411	-2274	60
H(40)	2021	3356	-1673	50
H(41)	1565	5008	-24	38
H(42)	1219	5635	684	46
H(45A)	910	7553	1105	105
H(45B)	1251	6763	1341	105
H(45C)	347	6912	1367	105
H(46A)	56	7552	151	110
H(46B)	-429	6825	355	110
H(46C)	34	6820	-287	110
H(47A)	1420	6693	-313	92
H(47B)	1910	6675	316	92
H(47C)	1510	7445	95	92
H(49)	875	4987	2562	68
H(50)	244	4608	3469	76
H(52)	-1641	4161	2441	73
H(53)	-1024	4581	1558	65
H(54A)	-486	3868	4189	131
H(54B)	-1305	4149	4430	131
H(54C)	-703	4747	4158	131
H(56)	3523	4234	-1655	60
H(57)	4344	3424	-2194	74
H(58)	4483	2189	-1880	81
H(59)	3882	1765	-990	85
H(60)	3049	2559	-442	65
H(62)	2490	5326	-1454	51
H(63)	3010	6537	-1501	65
H(64)	3784	6972	-694	71
H(65)	4029	6213	158	64

H(66)	3515	4991	202	48
H(1S1)	7058	5164	3392	239
H(1S2)	6209	4959	3167	239
H(1S3)	6932	4568	2842	239
H(2S1)	6193	4130	3930	237
H(2S2)	7092	4228	4060	237
H(3S1)	7229	2943	4204	294
H(3S2)	6315	2892	4098	294
H(4S1)	6491	1817	3545	449
H(4S2)	7397	1864	3654	449
H(4S3)	7022	2254	3056	449

Table 6. Torsion angles [°]

O(1)-Ag(1)-P(1)-C(29)	106.45(12)
P(2)-Ag(1)-P(1)-C(29)	-51.05(11)
O(2)-Ag(1)-P(1)-C(29)	163.53(11)
O(1)-Ag(1)-P(1)-C(23)	-17.16(13)
P(2)-Ag(1)-P(1)-C(23)	-174.67(12)
O(2)-Ag(1)-P(1)-C(23)	39.92(13)
O(1)-Ag(1)-P(1)-C(3)	-138.34(10)
P(2)-Ag(1)-P(1)-C(3)	64.16(10)
O(2)-Ag(1)-P(1)-C(3)	-81.26(10)
O(1)-Ag(1)-P(2)-C(55)	152.20(12)
P(1)-Ag(1)-P(2)-C(55)	-51.67(12)
O(2)-Ag(1)-P(2)-C(55)	95.44(12)
O(1)-Ag(1)-P(2)-C(35)	-88.44(11)
P(1)-Ag(1)-P(2)-C(35)	67.70(10)
O(2)-Ag(1)-P(2)-C(35)	-145.20(11)
O(1)-Ag(1)-P(2)-C(61)	28.87(11)
P(1)-Ag(1)-P(2)-C(61)	-174.99(9)
O(2)-Ag(1)-P(2)-C(61)	-27.89(11)
P(2)-Ag(1)-O(1)-C(1)	-95.56(17)
P(1)-Ag(1)-O(1)-C(1)	104.42(17)
O(2)-Ag(1)-O(1)-C(1)	-2.13(16)
O(1)-Ag(1)-O(2)-C(1)	2.13(16)
P(2)-Ag(1)-O(2)-C(1)	113.02(16)
P(1)-Ag(1)-O(2)-C(1)	-95.30(17)
Ag(1)-O(2)-C(1)-O(1)	-3.9(3)
Ag(1)-O(2)-C(1)-C(2)	174.6(3)
Ag(1)-O(1)-C(1)-O(2)	4.1(3)
Ag(1)-O(1)-C(1)-C(2)	-174.3(3)
C(29)-P(1)-C(3)-C(8)	9.1(3)
C(23)-P(1)-C(3)-C(8)	117.7(2)
Ag(1)-P(1)-C(3)-C(8)	-112.4(2)
C(29)-P(1)-C(3)-C(4)	-178.1(2)
C(23)-P(1)-C(3)-C(4)	-69.5(2)
Ag(1)-P(1)-C(3)-C(4)	60.4(2)
C(8)-C(3)-C(4)-C(5)	0.1(4)

P(1)-C(3)-C(4)-C(5)	-172.8(2)
C(8)-C(3)-C(4)-C(9)	178.2(3)
P(1)-C(3)-C(4)-C(9)	5.3(4)
C(3)-C(4)-C(5)-C(6)	0.5(5)
C(9)-C(4)-C(5)-C(6)	-177.6(3)
C(4)-C(5)-C(6)-C(7)	-1.4(6)
C(5)-C(6)-C(7)-C(8)	1.6(6)
C(6)-C(7)-C(8)-C(3)	-1.0(6)
C(4)-C(3)-C(8)-C(7)	0.1(5)
P(1)-C(3)-C(8)-C(7)	172.9(3)
C(10)-N(1)-C(9)-C(4)	178.0(2)
C(5)-C(4)-C(9)-N(1)	-17.1(4)
C(3)-C(4)-C(9)-N(1)	164.8(3)
C(9)-N(1)-C(10)-C(11)	-120.4(3)
C(9)-N(1)-C(10)-C(12)	114.5(3)
C(16)-N(2)-C(11)-O(3)	3.7(5)
C(16)-N(2)-C(11)-C(10)	-174.5(3)
N(1)-C(10)-C(11)-O(3)	-70.0(4)
C(12)-C(10)-C(11)-O(3)	54.7(4)
N(1)-C(10)-C(11)-N(2)	108.3(3)
C(12)-C(10)-C(11)-N(2)	-127.0(3)
N(1)-C(10)-C(12)-C(14)	56.4(4)
C(11)-C(10)-C(12)-C(14)	-65.1(3)
N(1)-C(10)-C(12)-C(13)	-64.9(3)
C(11)-C(10)-C(12)-C(13)	173.6(3)
N(1)-C(10)-C(12)-C(15)	178.3(3)
C(11)-C(10)-C(12)-C(15)	56.8(3)
C(11)-N(2)-C(16)-C(17)	169.4(3)
C(11)-N(2)-C(16)-C(21)	-10.2(5)
C(21)-C(16)-C(17)-C(18)	-0.3(5)
N(2)-C(16)-C(17)-C(18)	-180.0(3)
C(16)-C(17)-C(18)-C(19)	-1.2(6)
C(17)-C(18)-C(19)-C(20)	2.1(6)
C(17)-C(18)-C(19)-O(4)	-179.2(3)
C(22)-O(4)-C(19)-C(20)	-11.2(5)
C(22)-O(4)-C(19)-C(18)	170.2(3)

C(18)-C(19)-C(20)-C(21)	-1.5(6)
O(4)-C(19)-C(20)-C(21)	179.9(4)
C(17)-C(16)-C(21)-C(20)	0.9(6)
N(2)-C(16)-C(21)-C(20)	-179.5(4)
C(19)-C(20)-C(21)-C(16)	0.0(7)
C(29)-P(1)-C(23)-C(24)	84.0(3)
C(3)-P(1)-C(23)-C(24)	-25.2(3)
Ag(1)-P(1)-C(23)-C(24)	-147.4(2)
C(29)-P(1)-C(23)-C(28)	-92.9(3)
C(3)-P(1)-C(23)-C(28)	157.9(2)
Ag(1)-P(1)-C(23)-C(28)	35.8(3)
C(28)-C(23)-C(24)-C(25)	1.1(5)
P(1)-C(23)-C(24)-C(25)	-175.8(3)
C(23)-C(24)-C(25)-C(26)	-0.1(6)
C(24)-C(25)-C(26)-C(27)	0.4(6)
C(25)-C(26)-C(27)-C(28)	-1.5(6)
C(24)-C(23)-C(28)-C(27)	-2.2(5)
P(1)-C(23)-C(28)-C(27)	174.7(3)
C(26)-C(27)-C(28)-C(23)	2.4(5)
C(23)-P(1)-C(29)-C(34)	-30.4(3)
C(3)-P(1)-C(29)-C(34)	80.0(3)
Ag(1)-P(1)-C(29)-C(34)	-162.7(2)
C(23)-P(1)-C(29)-C(30)	151.0(2)
C(3)-P(1)-C(29)-C(30)	-98.7(3)
Ag(1)-P(1)-C(29)-C(30)	18.6(3)
C(34)-C(29)-C(30)-C(31)	-0.8(5)
P(1)-C(29)-C(30)-C(31)	177.9(3)
C(29)-C(30)-C(31)-C(32)	1.3(5)
C(30)-C(31)-C(32)-C(33)	-1.6(5)
C(31)-C(32)-C(33)-C(34)	1.5(5)
C(32)-C(33)-C(34)-C(29)	-1.0(5)
C(30)-C(29)-C(34)-C(33)	0.6(5)
P(1)-C(29)-C(34)-C(33)	-178.0(3)
C(55)-P(2)-C(35)-C(40)	7.5(3)
C(61)-P(2)-C(35)-C(40)	116.7(2)
Ag(1)-P(2)-C(35)-C(40)	-118.4(2)

C(55)-P(2)-C(35)-C(36)	-174.6(2)
C(61)-P(2)-C(35)-C(36)	-65.3(2)
Ag(1)-P(2)-C(35)-C(36)	59.6(2)
C(40)-C(35)-C(36)-C(37)	-4.8(4)
P(2)-C(35)-C(36)-C(37)	177.2(2)
C(40)-C(35)-C(36)-C(41)	174.5(3)
P(2)-C(35)-C(36)-C(41)	-3.5(3)
C(35)-C(36)-C(37)-C(38)	3.3(4)
C(41)-C(36)-C(37)-C(38)	-176.0(3)
C(36)-C(37)-C(38)-C(39)	1.1(5)
C(37)-C(38)-C(39)-C(40)	-3.9(5)
C(36)-C(35)-C(40)-C(39)	2.0(4)
P(2)-C(35)-C(40)-C(39)	180.0(2)
C(38)-C(39)-C(40)-C(35)	2.4(5)
C(42)-N(3)-C(41)-C(36)	178.2(3)
C(37)-C(36)-C(41)-N(3)	2.6(4)
C(35)-C(36)-C(41)-N(3)	-176.7(3)
C(41)-N(3)-C(42)-C(43)	-118.4(3)
C(41)-N(3)-C(42)-C(44)	115.8(3)
C(48)-N(4)-C(43)-O(5)	-7.5(5)
C(48)-N(4)-C(43)-C(42)	171.1(3)
N(3)-C(42)-C(43)-O(5)	-67.3(4)
C(44)-C(42)-C(43)-O(5)	57.4(5)
N(3)-C(42)-C(43)-N(4)	114.1(3)
C(44)-C(42)-C(43)-N(4)	-121.2(3)
N(3)-C(42)-C(44)-C(45)	175.9(3)
C(43)-C(42)-C(44)-C(45)	53.4(4)
N(3)-C(42)-C(44)-C(46)	52.1(4)
C(43)-C(42)-C(44)-C(46)	-70.4(4)
N(3)-C(42)-C(44)-C(47)	-68.0(4)
C(43)-C(42)-C(44)-C(47)	169.5(3)
C(43)-N(4)-C(48)-C(49)	-141.3(3)
C(43)-N(4)-C(48)-C(53)	38.8(5)
C(53)-C(48)-C(49)-C(50)	-1.9(6)
N(4)-C(48)-C(49)-C(50)	178.2(3)
C(48)-C(49)-C(50)-C(51)	1.0(6)

C(54)-O(6)-C(51)-C(52)	-171.6(4)
C(54)-O(6)-C(51)-C(50)	9.0(6)
C(49)-C(50)-C(51)-O(6)	-179.5(4)
C(49)-C(50)-C(51)-C(52)	1.1(6)
O(6)-C(51)-C(52)-C(53)	178.1(4)
C(50)-C(51)-C(52)-C(53)	-2.4(6)
C(51)-C(52)-C(53)-C(48)	1.6(6)
C(49)-C(48)-C(53)-C(52)	0.6(5)
N(4)-C(48)-C(53)-C(52)	-179.5(3)
C(35)-P(2)-C(55)-C(56)	75.4(3)
C(61)-P(2)-C(55)-C(56)	-32.0(3)
Ag(1)-P(2)-C(55)-C(56)	-160.8(3)
C(35)-P(2)-C(55)-C(60)	-104.4(3)
C(61)-P(2)-C(55)-C(60)	148.1(3)
Ag(1)-P(2)-C(55)-C(60)	19.3(3)
C(60)-C(55)-C(56)-C(57)	0.0(5)
P(2)-C(55)-C(56)-C(57)	-179.8(3)
C(55)-C(56)-C(57)-C(58)	0.9(6)
C(56)-C(57)-C(58)-C(59)	-2.1(7)
C(57)-C(58)-C(59)-C(60)	2.4(7)
C(58)-C(59)-C(60)-C(55)	-1.4(7)
C(56)-C(55)-C(60)-C(59)	0.2(6)
P(2)-C(55)-C(60)-C(59)	-180.0(3)
C(55)-P(2)-C(61)-C(62)	83.8(3)
C(35)-P(2)-C(61)-C(62)	-24.9(3)
Ag(1)-P(2)-C(61)-C(62)	-147.5(2)
C(55)-P(2)-C(61)-C(66)	-97.4(2)
C(35)-P(2)-C(61)-C(66)	154.0(2)
Ag(1)-P(2)-C(61)-C(66)	31.3(3)
C(66)-C(61)-C(62)-C(63)	0.5(5)
P(2)-C(61)-C(62)-C(63)	179.3(3)
C(61)-C(62)-C(63)-C(64)	-0.2(6)
C(62)-C(63)-C(64)-C(65)	-0.3(6)
C(63)-C(64)-C(65)-C(66)	0.6(6)
C(62)-C(61)-C(66)-C(65)	-0.2(5)
P(2)-C(61)-C(66)-C(65)	-179.1(3)

C(64)-C(65)-C(66)-C(61)	-0.4(5)
C(3S)-O(1S)-C(2S)-C(1S)	-177.3(10)
C(2S)-O(1S)-C(3S)-C(4S)	175.0(12)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for bc106 [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(2)	0.88	2.14	2.958(3)	155.2
N(4)-H(4)...O(1)	0.88	2.02	2.897(3)	173.4

Symmetry transformations used to generate equivalent atoms:

■ X-ray crystal structure of 17:

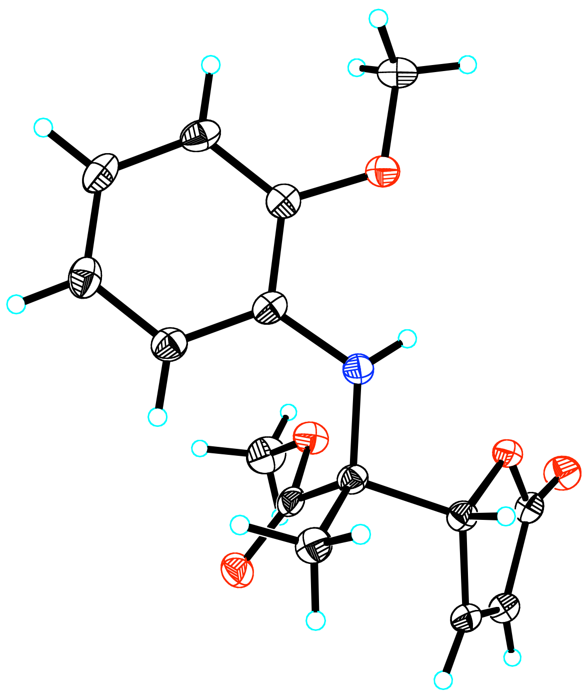


Table 1. Crystal data and structure refinement for **17**

Identification code	d08002	
Empirical formula	C15 H17 N O5	
Formula weight	291.30	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.4323(2) Å	α= 90°.
	b = 9.5882(2) Å	β= 90°.
	c = 23.5349(6) Å	γ = 90°.
Volume	1451.50(7) Å^3	
Z	4	
Density (calculated)	1.333 Mg/m^3	
Absorption coefficient	0.841 mm^{-1}	
F(000)	616	
Crystal size	0.45 x 0.15 x 0.15 mm^3	
Theta range for data collection	3.76 to 67.56°.	

Index ranges	-7<=h<=7, -11<=k<=10, -27<=l<=28
Reflections collected	19525
Independent reflections	2610 [R(int) = 0.0193]
Completeness to theta = 67.56°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8842 and 0.7033
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2610 / 1 / 196
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0241, wR2 = 0.0628
R indices (all data)	R1 = 0.0242, wR2 = 0.0629
Absolute structure parameter	0.05(12)
Largest diff. peak and hole	0.169 and -0.161 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d08002. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(3)	4092(1)	-1303(1)	7898(1)	18(1)
O(1)	2313(1)	2902(1)	8285(1)	20(1)
O(5)	4054(1)	-901(1)	9116(1)	21(1)
O(4)	7338(1)	-1421(1)	9365(1)	24(1)
N(1)	5459(2)	1152(1)	8400(1)	17(1)
O(2)	1862(1)	-3095(1)	7901(1)	26(1)
C(12)	3621(2)	-2681(1)	7951(1)	19(1)
C(7)	5166(2)	2147(1)	8830(1)	18(1)
C(8)	6711(2)	-100(1)	8497(1)	16(1)
C(13)	6112(2)	-874(1)	9050(1)	17(1)
C(1)	382(2)	3648(1)	8255(1)	23(1)
C(9)	6288(2)	-1105(1)	7992(1)	17(1)
C(10)	7104(2)	-2554(1)	8083(1)	19(1)
C(15)	9056(2)	195(1)	8480(1)	21(1)
C(6)	6396(2)	2269(1)	9315(1)	21(1)
C(11)	5545(2)	-3451(1)	8066(1)	20(1)
C(5)	6074(2)	3336(1)	9707(1)	24(1)
C(2)	3515(2)	3111(1)	8761(1)	18(1)
C(4)	4491(2)	4286(1)	9626(1)	25(1)
C(3)	3201(2)	4167(1)	9153(1)	22(1)
C(14)	3306(2)	-1668(1)	9606(1)	29(1)

Table 3. Bond lengths [Å] and angles [°] for d08002

O(3)-C(12)	1.3613(15)
O(3)-C(9)	1.4421(14)
O(1)-C(2)	1.3761(14)
O(1)-C(1)	1.4347(15)
O(5)-C(13)	1.3327(15)
O(5)-C(14)	1.4496(15)
O(4)-C(13)	1.2025(15)
N(1)-C(7)	1.4029(15)
N(1)-C(8)	1.4634(15)
N(1)-H(1)	0.870(13)
O(2)-C(12)	1.2053(15)
C(12)-C(11)	1.4664(17)
C(7)-C(6)	1.3939(17)
C(7)-C(2)	1.4172(17)
C(8)-C(15)	1.5356(16)
C(8)-C(13)	1.5479(15)
C(8)-C(9)	1.5535(15)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(9)-C(10)	1.5007(16)
C(9)-H(9)	1.0000
C(10)-C(11)	1.3212(18)
C(10)-H(10)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(6)-C(5)	1.3941(17)
C(6)-H(6)	0.9500
C(11)-H(11)	0.9500
C(5)-C(4)	1.3791(19)
C(5)-H(5)	0.9500
C(2)-C(3)	1.3842(17)
C(4)-C(3)	1.3946(19)
C(4)-H(4)	0.9500

C(3)-H(3)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(12)-O(3)-C(9)	109.37(9)
C(2)-O(1)-C(1)	116.94(9)
C(13)-O(5)-C(14)	115.63(10)
C(7)-N(1)-C(8)	121.29(9)
C(7)-N(1)-H(1)	110.5(10)
C(8)-N(1)-H(1)	114.7(10)
O(2)-C(12)-O(3)	121.34(11)
O(2)-C(12)-C(11)	130.13(12)
O(3)-C(12)-C(11)	108.53(10)
C(6)-C(7)-N(1)	124.84(11)
C(6)-C(7)-C(2)	117.67(10)
N(1)-C(7)-C(2)	117.48(10)
N(1)-C(8)-C(15)	112.67(10)
N(1)-C(8)-C(13)	112.80(9)
C(15)-C(8)-C(13)	110.77(10)
N(1)-C(8)-C(9)	107.08(9)
C(15)-C(8)-C(9)	105.44(9)
C(13)-C(8)-C(9)	107.60(9)
O(4)-C(13)-O(5)	124.80(11)
O(4)-C(13)-C(8)	124.38(11)
O(5)-C(13)-C(8)	110.77(10)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(3)-C(9)-C(10)	104.03(9)
O(3)-C(9)-C(8)	111.72(9)
C(10)-C(9)-C(8)	113.84(9)
O(3)-C(9)-H(9)	109.0

C(10)-C(9)-H(9)	109.0
C(8)-C(9)-H(9)	109.0
C(11)-C(10)-C(9)	109.46(11)
C(11)-C(10)-H(10)	125.3
C(9)-C(10)-H(10)	125.3
C(8)-C(15)-H(15A)	109.5
C(8)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(8)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(7)-C(6)-C(5)	121.35(12)
C(7)-C(6)-H(6)	119.3
C(5)-C(6)-H(6)	119.3
C(10)-C(11)-C(12)	108.55(11)
C(10)-C(11)-H(11)	125.7
C(12)-C(11)-H(11)	125.7
C(4)-C(5)-C(6)	120.16(12)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
O(1)-C(2)-C(3)	124.55(11)
O(1)-C(2)-C(7)	114.80(10)
C(3)-C(2)-C(7)	120.66(11)
C(5)-C(4)-C(3)	119.73(11)
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-H(4)	120.1
C(2)-C(3)-C(4)	120.38(11)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
O(5)-C(14)-H(14A)	109.5
O(5)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
O(5)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$)for d08002. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(3)	16(1)	18(1)	19(1)	-1(1)	-2(1)	2(1)
O(1)	20(1)	20(1)	21(1)	0(1)	0(1)	3(1)
O(5)	22(1)	22(1)	20(1)	6(1)	4(1)	0(1)
O(4)	29(1)	21(1)	21(1)	2(1)	-5(1)	2(1)
N(1)	19(1)	16(1)	17(1)	0(1)	-1(1)	0(1)
O(2)	17(1)	27(1)	33(1)	-2(1)	0(1)	-3(1)
C(12)	20(1)	19(1)	17(1)	-2(1)	2(1)	0(1)
C(7)	21(1)	13(1)	18(1)	2(1)	5(1)	-2(1)
C(8)	18(1)	14(1)	17(1)	0(1)	1(1)	0(1)
C(13)	22(1)	13(1)	16(1)	-3(1)	-1(1)	0(1)
C(1)	21(1)	20(1)	30(1)	3(1)	2(1)	3(1)
C(9)	15(1)	18(1)	17(1)	-1(1)	2(1)	-1(1)
C(10)	17(1)	20(1)	19(1)	-3(1)	1(1)	3(1)
C(15)	19(1)	20(1)	24(1)	-2(1)	1(1)	-2(1)
C(6)	24(1)	17(1)	21(1)	2(1)	2(1)	0(1)
C(11)	21(1)	18(1)	21(1)	-2(1)	0(1)	2(1)
C(5)	31(1)	21(1)	19(1)	0(1)	0(1)	-5(1)
C(2)	20(1)	17(1)	18(1)	3(1)	4(1)	-3(1)
C(4)	35(1)	18(1)	21(1)	-4(1)	6(1)	-2(1)
C(3)	26(1)	16(1)	24(1)	2(1)	7(1)	2(1)
C(14)	35(1)	27(1)	24(1)	7(1)	9(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d08002.

	x	y	z	U(eq)
H(1)	4300(20)	1010(15)	8216(6)	20
H(1A)	661	4648	8217	35
H(1B)	-419	3480	8603	35
H(1C)	-416	3324	7926	35
H(9)	6928	-709	7640	20
H(10)	8520	-2790	8144	22
H(15A)	9426	830	8790	31
H(15B)	9418	626	8115	31
H(15C)	9822	-682	8523	31
H(6)	7475	1611	9379	25
H(11)	5653	-4431	8119	24
H(5)	6948	3410	10032	28
H(4)	4281	5018	9892	30
H(3)	2100	4813	9099	27
H(14A)	3770	-1203	9955	43
H(14B)	3857	-2620	9596	43
H(14C)	1783	-1699	9599	43

Table 6. Torsion angles [°] for d08002.

C(9)-O(3)-C(12)-O(2)	178.67(11)
C(9)-O(3)-C(12)-C(11)	-1.85(12)
C(8)-N(1)-C(7)-C(6)	17.83(17)
C(8)-N(1)-C(7)-C(2)	-163.14(10)
C(7)-N(1)-C(8)-C(15)	-77.21(13)
C(7)-N(1)-C(8)-C(13)	49.13(14)
C(7)-N(1)-C(8)-C(9)	167.31(10)
C(14)-O(5)-C(13)-O(4)	-0.54(17)
C(14)-O(5)-C(13)-C(8)	176.79(9)
N(1)-C(8)-C(13)-O(4)	-141.54(11)
C(15)-C(8)-C(13)-O(4)	-14.19(16)
C(9)-C(8)-C(13)-O(4)	100.58(13)
N(1)-C(8)-C(13)-O(5)	41.11(13)
C(15)-C(8)-C(13)-O(5)	168.46(9)
C(9)-C(8)-C(13)-O(5)	-76.77(11)
C(12)-O(3)-C(9)-C(10)	2.47(11)
C(12)-O(3)-C(9)-C(8)	-120.75(10)
N(1)-C(8)-C(9)-O(3)	-50.61(12)
C(15)-C(8)-C(9)-O(3)	-170.82(9)
C(13)-C(8)-C(9)-O(3)	70.91(12)
N(1)-C(8)-C(9)-C(10)	-168.07(9)
C(15)-C(8)-C(9)-C(10)	71.71(12)
C(13)-C(8)-C(9)-C(10)	-46.56(12)
O(3)-C(9)-C(10)-C(11)	-2.26(12)
C(8)-C(9)-C(10)-C(11)	119.57(11)
N(1)-C(7)-C(6)-C(5)	176.36(11)
C(2)-C(7)-C(6)-C(5)	-2.67(17)
C(9)-C(10)-C(11)-C(12)	1.21(13)
O(2)-C(12)-C(11)-C(10)	179.79(13)
O(3)-C(12)-C(11)-C(10)	0.37(13)
C(7)-C(6)-C(5)-C(4)	1.18(19)
C(1)-O(1)-C(2)-C(3)	-12.97(16)
C(1)-O(1)-C(2)-C(7)	167.18(10)
C(6)-C(7)-C(2)-O(1)	-177.66(10)

N(1)-C(7)-C(2)-O(1)	3.24(15)
C(6)-C(7)-C(2)-C(3)	2.49(17)
N(1)-C(7)-C(2)-C(3)	-176.61(10)
C(6)-C(5)-C(4)-C(3)	0.58(19)
O(1)-C(2)-C(3)-C(4)	179.33(11)
C(7)-C(2)-C(3)-C(4)	-0.83(18)
C(5)-C(4)-C(3)-C(2)	-0.74(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for d08002 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(3)	0.870(13)	2.344(15)	2.7764(13)	110.9(11)

Symmetry transformations used to generate equivalent atoms: