Asymmetric Synthesis of Quaternary α-Amino Phosphonates using Sulfinimines

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Supporting Information

General Procedure. Column chromatography was performed on silica gel, Merck grade 60 (230-400 mesh). Analytical and preparative thin-layer chromatography was performed on precoated silica gel plates (250 and 1000 microns) purchased from Analtech Inc. TLC plates were visualized with UV, in an iodine chamber, or with phosphomolybdic acid unless noted otherwise. THF was freshly distilled under argon from a purple solution of sodium and benzophenone. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. IR spectra were recorded using NaCl plates or as KBr discs. ^{1}H, ^{13}C, and ^{31}P NMR were measured at 500, 125, and 202 MHz, respectively, on a General Electric Omega 500. ^{31}P NMR spectra were referenced externally to 85% H_3PO_4. HRMS data were collected using a Fission ZAB HF double-focusing mass spectrometer at the Department of Chemistry, Drexel University, Philadelphia, PA. Elemental analyses were performed at the Department of Chemistry, University of Pennsylvania, Philadelphia, PA.

Unless otherwise stated, all reagents were purchased from commercial sources and used without additional purification. The keto sulfinimines were prepared by condensing commercially available (*S*)-(+)-*p*-toluenesulfinamide with the appropriate ketone as previously descried.[1,2]

(*S*S,*R*)-(+)-*O*,*O*-Diethyl *N*-(*p*-toluenesulfinyl)-2-amino-2,3,3-trimethylpropiophosphonate (2f). Typical Procedure. In an oven-dried 100-mL two-necked round-bottom flask fitted with a rubber septum and a magnetic stir bar under an argon balloon was placed a solution of sulfinimine (*S*)-(+)-**1f** (0.24 g, 1.0 mmol) in THF (15 mL) and cooled to -78 °C. In a separate 50-mL single-necked round-bottom flask fitted with a magnetic stir bar and a rubber septum under an argon balloon was placed a solution of diethyl phosphite (0.26 mL, 2.0 mmol) in THF (15 mL). The solution was cooled to -78 °C and LiHMDS (2.0 mL, 2.0 mmol) was slowly added. The reaction mixture was stirred for 0.25 h, cannulated to the solution of (+)-**2f**, stirred for 1 h at -78 °C, and quenched with sat. NH_4Cl (1 mL). The organic phase was extracted with EtOAc (20 mL), washed with H_2O (10 mL), and brine (5 mL), dried ($MgSO_4$), and concentrated to give the crude phosphonate **2f** (dr >99:1). Flash chromatography (CH_2Cl_2:MeOH, 95:5) afforded 0.36 g (97%) of (+)-**2f** as a solid; mp 51-52 °C; $[\alpha]^{20}_D$ +139 (*c* 0.7 $CHCl_3$); IR (KBr) 3484, 2978, 1240, 1068 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H), 1.36 (m, 6 H), 1.77 (d, J_{HP} = 16.6 Hz, 3 H), 2.41 (s, 3 H), 4.25 (m, 4 H), 4.62 (d, J_{HP} = 6.8 Hz, 1 H), 7.30 (d, J = 7.8 Hz, 2 H), 7.63 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.1 (d, J_{CP} = 4.1 Hz), 16.8 (d, J_{CP} = 6.1 Hz), 17.0 (d, J_{CP} = 4.1 Hz), 21.7, 27.0 (d, J_{CP} = 6.1 Hz), 38.0 (d, J_{CP} = 6.1 Hz), 62.6 (d, J_{CP} = 8.1 Hz), 63.5 (d, J_{CP} = 146 Hz), 64.5 (d, J_{CP} = 6.1 Hz), 125.7, 130.6, 141.7, 144.3; ^{31}P NMR ($CDCl_3$) δ 26.53. Anal. Calcd for $C_{17}H_{30}NO_4PS$: C, 54.38; H, 8.05; N, 3.73. Found: C, 54.47; H, 8.32; N, 3.51.

(*S*S,*R*)-(-)-*O*,*O*-Diethyl-*N*-(*p*-toluenesulfinyl)-2-amino-2-(*p*-methoxyphenyl)-ethylphosphonate (2a): dr 99:1; flash chromatography (CH_2Cl_2:EtOAc, 2:1); yield 73%; oil; $[\alpha]_D^{20}$ -14.6 (*c* 1.0, $CHCl_3$); IR (neat), 3159, 1512, 1253, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (t, J = 7.1 Hz, 3 H), 1.22 (t, J = 7.1 Hz, 3 H), 2.13 (d, J_{HP} = 15.8 Hz, 3 H), 2.41 (s, 3 H), 3.83 (s, 3 H), 3.88 (m, 4 H), 4.68 (d, J_{HP} = 4.7 Hz, 1 H), 6.95 (d, J = 9.2 Hz, 2 H), 7.31 (d, J = 8.5 Hz, 2 H),

7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.9, 21.9, 25.0, 55.8, 61.2 (d, J_{CP} = 155 Hz), 64.0 (d, J_{CP} = 8.1 Hz), 64.3 (d, J_{CP} = 6.1 Hz), 114.1, 125.9, 129.0, 130.2, 130.8, 142.0, 143.6, 160.0; ^{31}P NMR ($CDCl_3$) δ 22.95; HRMS Calcd for $C_{20}H_{28}NO_5PSNa$ (M+Na): 448.1323; Found: 448.1335; Anal. Calcd for $C_{20}H_{28}NO_5PS$: C, 56.46; H, 6.63; N, 3.29. Found: C, 56.27; H, 6.59; N, 2.97.

(S_S,*R*)-(-)-*O*,*O*-Diethyl *N*-(*p*-toluenesulfinyl)-2-amino-2-(*p*-toluene)ethyl-phosphonate (2b): dr 99:1; flash chromatography (CH_2Cl_2:EtOAc, 5:1); yield 91%; oil; $[\alpha]_D^{20}$ -5.8 (c 1.2, $CHCl_3$); IR (neat), 3152, 1238, 1020 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.0 Hz, 3 H), 2.16 (d, J_{HP} = 16.1 Hz, 3 H), 2.37 (s, 3H), 2.42 (s, 3 H), 3.90 (m, 4 H), 4.69 (d, J_{HP} = 4.8 Hz, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 16.9 (d, J_{CP} = 4.1 Hz), 21.7, 21.9, 24.9, 61.5(d, J_{CP} = 154 Hz), 64.0 (d, J_{CP} = 7.9 Hz), 64.2 (d, J_{CP} = 8.1 Hz), 125.9, 129.3, 129.5, 130.2, 134.5, 138.6, 142.0, 143.8; ^{31}P NMR ($CHCl_3$) δ 22.91; HRMS Calcd for $C_{20}H_{28}NO_4PSNa$ (M+Na): 432.1374. Found: 432.1384.

(S_S,*R*)-(+)-*O*,*O*-Diethyl *N*-(*p*-toluenesulfinyl)-2-amino-2-phenylethyl-phosphonate (2c): oil; dr 99:1; flash chromatography (EtOAc:hexane, 9:1), yield 92%; $[\alpha]_D^{20}$ +5.6 (*c* 1.0 $CHCl_3$); IR (neat) 3482, 2982, 1238, 1021 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (t, *J* = 7.0 Hz, 3 H), 1.22 (t, *J* = 7.0 Hz, 3 H), 2.19 (d, J_{HP} = 15.8, 3 H), 2.43 (s, 3 H), 3.83 (m, 1 H), 3.96 (m, 3 H), 4.74 (d, J_{HP} = 5.1 Hz, 1 H), 7.41 (m, 5 H), 7.63 (m, 2 H), 7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.2, 16.3, 21.3, 24.1, 61.1 (d, J_{CP} = 153 Hz), 63.4 (d, J_{CP} = 6.1 Hz), 63.6 (d, J_{CP} = 6.1 Hz), 125.7, 128.1, 128.8, 129.1, 129.6, 137.0, 137.1, 141.4, 143.0; ^{31}P NMR ($CDCl_3$) δ 22.66. Anal. Calcd for $C_{19}H_{26}NO_4PS$: C, 57.71; H, 6.63; N, 3.54. Found: C, 57.47; H, 6.89; N, 3.86.

(S_S,*R*)-(-)-*O*,*O*-Diethyl *N*-(*p*-toluenesulfinyl)-2-amino-2-phenyl-propyl-phosphonate (2d): mp 88-89 °C; dr 99:1; crystallization (EtOAc:pentane, 1:9), yield 93%; $[\alpha]_D^{20}$ -2.9 (*c* 0.8 $CHCl_3$); IR (KBr) 3457, 3137, 1226, 1067 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (m, 6 H), 1.26 (t, *J* = 7.0 Hz, 3 H), 2.44 (s, 3 H), 2.51 (m, 1 H), 2.72 (m, 1 H), 3.74 (m, 1 H), 3.87 (m, 1H), 4.02 (m, 2 H), 4.79 (d, J_{HP} = 6.6 Hz, 1 H), 7.37 (m, 5 H), 7.71 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 9.2, 16.8, (d, J_{CP} = 6.1 Hz), 17.0 (d, J_{CP} = 1.1 Hz), 21.9, 29.6, 63.6 (d, J_{CP} = 6.1 Hz), 63.7 (d, J_{CP} = 6.1 Hz), 64.7 (d, J_{CP} = 151 Hz), 126.1, 128.4, 128.6, 129.2, 130.3, 137.6, 141.9, 144.6; ^{31}P NMR ($CDCl_3$) δ 22.55. Anal. Calcd for $C_{20}H_{28}NO_4PS$: C, 58.66; H, 6.89; N, 3.42. Found: C, 58.95; H, 7.11; N, 3.03.

(S_S,*R*)-(-)-*O*,*O*-Diethyl *N*-(*p*-toluenesulfinyl)-2-amino-2-(*p*-nitrophenyl)ethyl-phosphonate (2e): glassy solid, dr 99:1; flash chromatography (CH_2Cl_2:EtOAc, 5:1); yield 92%; $[\alpha]_D^{20}$ -45.7 (*c* 1.2, $CHCl_3$); IR (KBr), 3149, 1349, 1019 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (m, 6 H), 2.23 (d, J_{HP} = 15.8 Hz, 3 H), 2.44 (s, 3 H), 3.99 (m, 4 H), 4.79 (d, J_{HP} = 5.9 Hz, 1 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.60 (d, *J* = 8.1 Hz, 2 H), 7.89 (d, *J* = 9.0 Hz, 2 H), 8.28 (d, *J* = 8.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.8, 21.8, 24.6, 61.8 (d, J_{CP}= 152 Hz), 64.5 (d, J_{CP} = 8.1 Hz), 123.6, 125.7, 130.3, 142.3, 143.2, 143.3, 146.1, 148.0; ^{31}P NMR δ 21.36; HRMS Calcd for $C_{19}H_{25}N_2O_6PSNa$ (M+Na): 463.1068. Found: 463.1082. Anal. Calcd for $C_{19}H_{25}N_2O_6PS$: C, 51.81; H, 5.72; N, 6.36. Found: C, 51.54; H, 5.36; N, 6.38.

(S_S,*R*)-(+)-*O*,*O*-Diethyl *N*-(*p*-toluenesulfinyl)-2-amino-2-*n*-butylethylphosphonate (2g): oil; dr 82:12; flash chromatography (EtOAc:hexane, 9:1), yield 71%; $[\alpha]_D^{20}$ +70.3 (*c* 1.5 $CHCl_3$); IR (neat) 3481, 3157, 1238, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3 H), 1.34 (m, 8 H), 1.47 (m, 1 H), 1.55 (m, 1 H), 1.58 (d, J_{HP} = 15.8 Hz, 3 H), 1.94 (m, 2 H), 2.39 (s, 3 H), 4.17 (m, 4 H), 4.26 (d, J_{HP} = 4.4 Hz, 1 H), 7.27 (d, *J* = 7.7 Hz, 2 H), 7.60 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.6, 17.2, 22.0, 22.2, 23.7, 25.9, 36.8, 58.5 (d, J_{CP} = 157 Hz), 63.3 (d, J_{CP} = 6.17 Hz), 63.8 (d, J_{CP} = 8.1 Hz), 63.9, 126.1, 130.2, 141.9, 144.1; ^{31}P NMR ($CDCl_3$) δ

26.66. Anal. Calcd for $C_{17}H_{30}NO_4PS$: C, 54.38; H, 8.05; N, 3.73. Found: C, 54.58; H, 8.37; N, 3.37.

(*R*)-(+)-*O*,*O*-Diethyl-2-amino-2,3,3-trimethylpropiophosphonate (4f). Typical Procedure. In an oven-dried 25-mL single-necked round-bottom flask fitted with a rubber septum and a magnetic stir bar, under an argon balloon, was placed a solution of (+)-**2f** (0.050 g, 0.13 mmol) in MeOH (5 mL) and the reaction mixture was cooled to 0 ^{o}C. Trifluoroacetic acid (0.050 mL, 0.65 mmol) was added slowly added at 0 ^{o}C, and the reaction mixture was warmed to rt and stirred for 3 h. The solution was concentrated, the residue was dissolved in CH_2Cl_2 (5 mL), cooled to 0 ^{o}C and neutralized to pH 7 with sat. $NaHCO_3$ (5 mL). The aqueous phase was washed with CH_2Cl_2 (10 mL) and the combined organic phases were washed with H_2O (5 mL), and brine (5 mL), dried ($MgSO_4$), and concentrated. Purification by flash chromatography (CH_2Cl_2:MeOH, 1:1) afforded 0.025 g (82%) of (+)-**4f** as an oil; $[\alpha]^{20}_D$ +11.0 (*c* 0.5 $CHCl_3$); IR (neat) 3394, 2950 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 9H), 1.25 (d, J_{HP} = 16.1 Hz, 3 H), 1.33 (m, 6 H), 1.62 (b, 2 H), 4.14 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.2 (d, J_{CP} = 4.1 Hz), 20.7, 26.8, 37.0, 58.9, (d, J_{CP} = 142 Hz), 62.6 (d, J_{CP} = 8.1 Hz), 62.7 (d, J_{CP} = 8.1 Hz); ^{31}P ($CDCl_3$) δ 31.8. LRMS Calcd for $C_6H_{16}NO_3P$ (M+H) 238. Found (M+H) 238.

(*R*)-(+)-(+)-*O*,*O*-Diethyl-2-amino-2-(*p*-tolyl)ethylphosphonate (4b). Flash chromatography (CH_2Cl_2:MeOH, 10:1); oil; yield 81%; $[\alpha]_D^{20}$ +36.8 (*c* 0.9, $CHCl_3$); IR (neat) 2979, 1236, 1026 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (t, *J* = 7.0 Hz, 3 H), 1.26 (t, *J* = 7.0 Hz, 3 H), 1.70 (d, J_{HP} = 15.8 Hz, 3 H), 1.84 (b, 2 H), 2.33 (s, 3 H), 3.90 (m, 4 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.8 (d, J_{CP} = 5.9 Hz), 21.4, 26.5, 55.3 (d, J_{CP} = 146 Hz), 63.0 (d, J_{CP} = 7.4 Hz), 63.4 (d, J_{CP} = 7.3 Hz), 126.8, 129.2, 137.2, 138.5; ^{31}P NMR ($CDCl_3$) δ 28.24. HRMS Calcd for $C_{13}H_{22}NO_3PNa$ (M+Na): 294.1235. Found: 294.1247.

(*R*)-(+)-*O*,*O*-Diethyl-2-amino-2-(*p*-nitrophenyl)ethylphosphonate (4e) Flash chromatography (CH_2Cl_2:MeOH, 50:1); mp 76-77 ^{o}C; yield 78%; $[\alpha]_D^{20}$ +57.7 (*c* 1.1, $CHCl_3$); IR (KBr) 3360, 2986, 1511, 1345, 1232, 1015, 960 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (t, *J* = 7.3 Hz, 3 H), 1.28 (t, *J* = 7.0 Hz, 3 H), 1.72 (d, J_{HP} = 15.7 Hz, 3 H), 1.89 (Br, 3 H), 4.00 (m, 4 H), 7.84 (m, 2 H), 8.19 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.0 (d, J_{CP} = 6.1 Hz), 26.9, 56.3 (d, J_{CP} = 146 Hz), 64.7 (d, J_{CP} = 6.1 Hz), 63.9 (d, J_{CP} = 8.2 Hz), 123.7, 128.3, 147.6, 149.8; ^{31}P NMR ($CDCl_3$) δ 26.25. HRMS Calcd for $C_{12}H_{19}N_2O_5PNa$ (M+Na): 325.0929. Found: 325.0926.

(*R*)-(+)-(1-Amino-1,2,2-trimethylpropyl)phosphonic acid (5f). Typical Procedure. In an oven-dried 25-mL single-necked round-bottom flask equipped with a magnetic stir bar and a reflux condenser was placed (+)-**2f** (0.10 g, 0.27 mmol) in 10 N HCl (10 mL). The solution was cooled to rt after refluxing for 18 h, concentrated, and placed under high vacuum for 3 h. The residue was dissolved in a minimum amount of hot ethanol (ca 5 mL), cooled to rt, and excess propylene oxide (1 mL) was added. After being stirred for 3 h the white solid was filtered to afford 0.041 g (84%) of (+)-**5f**, mp 207-208 ^{o}C; $[\alpha]^{20}_D$ +16.5 (*c* 0.5 1 N NaOH); IR (KBr) 3424, 2980, 1163 cm^{-1}; ^{1}H NMR (D_2O) δ 1.12 (s, 9 H), 1.42 (d, J_{HP} = 13.2 Hz, 3 H); ^{13}C NMR (D_2O, $CDCl_3$) δ 18.1, 25.2, 34.8, 61.6 (d, J_{CP} = 140 Hz); ^{31}P NMR (D_2O) δ 15.8. HMRS Calcd for $C_6H_{16}NO_3P$ (M+2Na-H) 226.0585. Found (M+2Na-H): 226.0579. Anal. Calcd for $C_6H_{16}NO_3P{\cdot}3/2\ H_2O$: C, 34.61; H, 9.20; N, 6.73. Found: C, 34.70; H, 8.81; N, 6.36.

(*R*)-(+)-(1-Amino-1-*p*-tolylethyl)phosphonic acid (5b); yield 70%; mp 211-213 ^{o}C; $[\alpha]_D^{20}$ +52.0 (*c* 0.6, 0.5 N NaOH); IR (KBr), 3415, 2923, 1519, 1175 cm^{-1};^{1}H NMR (D_2O, 0.5 N NaOH) δ 1.36 (d, J_{HP} = 12.9 Hz, 2 H), 2.14 (s, 3 H), 7.03 (d, *J* = 8.1 Hz, 2 H), 7.23 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR (D_2O, 0.5 N NaOH) δ 20.3, 25.5, 55.2 (d, J_{CP} = 133 Hz), 126.6, 128.5, 135.8,

142.9; ^{31}P NMR (D_2O, 0.5 N NaOH) δ 21.77. Anal. Calcd for $C_9H_{14}NO_3P \cdot 9/10H_2O$: C, 46.71; H, 6.88; N, 6.05. Found: C, 46.97; H, 7.32 ; N 5.93.

(*R*)-(+)-(1-Amino-1-*p*-nitrophenyl)ethylphosphonic acid (5e) yield 68%; mp 235-240 °C (dec); $[\alpha]_D^{20}$ +82.4° (c 0.6, 0.5 N NaOH); IR (KBr) 3418, 2936, 1606, 1352, 1090 cm^{-1}; ^{1}H NMR (D_2O, 0.5 N NaOH) δ 1.49 (d, J_{HP} = 12.9 Hz, 3H), 7.58 (d, J = 7.7 Hz, 2 H), 8.07 (d, J = 8.7 Hz, 2 H); ^{13}C NMR (D_2O, 0.5 N NaOH) δ 25.2, 56.5 (d, J_{CP} = 128.6 Hz), 123.0, 127.5, 145.7, 154.8; ^{31}P NMR (D_2O, 0.5 N NaOH) δ 19.86; Anal. Calcd for $C_8H_{11}N_2O_5P \cdot H_2O$: C, 36.37; H, 4.96; N, 10.60. Found: C, 36.78; H, 4.90; N, 10.19.

(S_S,*R*)-(+)-*O*,*O*-Dimethyl *N*-(*p*-toluenesulfinyl)-2-amino-2-(*p*-toluene)-ethylphosphonate (3). Prepared from (*S*)-(+)-**1b** and lithium dimethyl phosphite; (dr >99:1); flash chromatography (EtOAc); yield 64%; mp 83-84 °C; $[\alpha]_D^{20}$ +0.8 (*c* 1.0, $CHCl_3$); IR (KBr), 3171, 2953, 1240, 1094, 1027cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.16 (d, J_{HP} = 16.2 Hz, 3 H), 2.37 (s, 3 H), 2.42 (s, 3 H), 3.58 (d, J_{HP} = 10.3 Hz, 3 H), 3.62 (d, J_{HP} = 10.7 Hz, 3 H), 4.71 (d, J_{HP} = 5.1 Hz, 1 H), 7.24 (d, J = 8.5 Hz, 2 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 22.0, 24.8, 54.7 (d, J_{CP} = 8.1 Hz), 54.9 (d, J_{CP} = 6.1 Hz), 61.6 (d, J_{CP} = 152 Hz), 125.9, 129.2, 129.7, 130.2, 134.3, 138.8, 142.1, 143.6; ^{31}P NMR δ 25.27. HRMS Calcd for $C_{18}H_{24}NO_4PSNa$ (M+Na): 404.1061. Found: 404.1061. Anal. Calcd for $C_{18}H_{24}NO_4PS$: C, 56.68; H, 6.34; N, 3.67. Found: C, 57.03; H, 5.85; N, 3.93.

(S_S,*R*)-(+)-*O*,*O*-Dimethyl 2-amino-2-(*p*-toluene)ethylphosphonate (6): Flash chromatography (CH_2Cl_2:MeOH, 10:1); oil; yield 85%; $[\alpha]_D^{20}$ +35.1 (*c* 0.9, $CHCl_3$); IR (neat) 3369, 3304, 2952, 1238, 1028 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70 (d, J_{HP} = 16.1 Hz, 3 H), 1.84 (br, 2 H), 2.33 (s, 3 H), 3.55 (d, J_{HP} = 10.3 Hz, 3 H), 3.68 (d, J_{HP} = 10.3 Hz, 3 H), 7.17 (d, J = 8.4 Hz, 2 H), 7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.3, 26.6, 54.0 (d, J_{CP} = 6.8 Hz), 54.3 (d, J_{CP} = 6.9 Hz), 55.5 (d, J_{CP} = 147 Hz), 126.6, 129.3, 137.4, 138.3; ^{31}P NMR ($CDCl_3$) δ 30.42. HRMS Calcd for $C_{11}H_{18}NO_3PNa$ (M+Na): 266.0922. Found: 266.0932. Anal. Calcd. For $C_{11}H_{18}NO_3P$: C, 54.32, H 7.46; N 5.76. Found: C, 53.85; H, 2.68, N, 5.54.

Preparation of (*R*)-(+)-6 from (+)-5b. In an oven -dried 25-mL single-necked round-bottom flask equipped with a magnetic stir bar was placed (+)-**5b** (0.020 g, 0.08 mmol) in EtOH (3 mL). An ethereal solution of diazomethane[3] (3 mL), prepared prior to use, was slowly added at rt until a yellow color persisted. The excess diazomethane was quenched with a few drops of acetic acid, the solvent was evaporated, and EtOAc (5 mL) and sat. $NaHCO_3$ (5 mL) were added. The organic phase was separated, the aqueous phase was washed with EtOAc (5 mL), and the combined organic phases were washed with H_2O (5 mL), and brine (5 mL), dried ($MgSO_4$), and concentrated. The crude phosphonate ester was purified by preparative TLC (EtOAc:MeOH, 95:5) affording 0.0050 g (27%) (*R*)-(+)-**6** as an oil and identical in all respects to that prepared from the (S_S,*R*)-(+)-**3**; $[\alpha]^{20}_D$ = +36.0 (*c* 0.2, $CHCl_3$).

Bis(diethylamido) phosphorous acid.[4] In a 500-mL round-bottom flask equipped with magnetic stir bar under argon atmosphere was placed phosphorous trichloride 5.0 mL, 57.3 mmol) in Et_2O (200 mL). The solution was cooled in an ice bath and a mixture of Et_3N (24.0 mL, 172 mmol) and Et_2NH (11.86 mL, 115 mmol) was slowly added. After stirring for 5 h at rt H_2O (10.3 mL, 57.3 mmol) was added at 0°C and the reaction mixture was stirred for 0.5 h at rt. The phases were separated and the aqueous phase was washed with Et_2O (2 x 25 mL). The combined organic phases were washed it with brine (2 x 25 mL), dried ($MgSO_4$) and concentrated. Flash chromatography (EtOAc:hexane: MeOH, 5:5 :1) afforded 4.64 g (42%) of an oil; ^{1}H NMR ($CDCl_3$) δ 1.12 (t, J = 7.1 Hz, 12 H), 3.05 (m, 8 H), 6.76 (d, J_{HP} = 570.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.6, 38.0 (d, J_{CP} = 6.2 Hz); ^{31}P NMR ($CDCl_3$) δ 20.5.

(-)-***N,N*-Diethyl *N*-(*p*-toluenesulfinyl)-2-amino-2-(*p*-toluene)ethylphosphamide (7)**. In an oven-dried 100-mL two-necked round-bottom flask fitted with a rubber septum and a magnetic stir bar under an argon balloon was placed a solution of (*S*)-(+)-**1b** (0.27 g, 1.0 mmol) in THF (15 mL) and the mixture was cooled to -78 ^{o}C. In a separate 50 mL single-necked round-bottom flask fitted with a magnetic stir bar and a rubber septum under an argon balloon was placed a solution of bis(diethylamido)phosphorous acid (0.038 g, 2.0 mmol) in THF (15 mL). The solution was cooled to -78 ^{o}C and LiHMDS (2.0 mL, 2.0 mmol) was added dropwise. The reaction mixture was stirred for 8 h, cannulated to the solution of (+)-**1b**, stirred for 8 h and quenched at -78 ^{o}C with sat. NH_4Cl (5 mL). The reaction mixture was warmed to rt, H_2O (5 mL) was added, the phases separated and the aqueous phase was washed with EtOAc (2 x 20 mL). The combined organic phases were dried ($MgSO_4$), concentrated purified by flash chromatography (EtOAc) to give 0.38 g (78%) of an oil, dr 99:1; $[\alpha]_D^{20}$ -17.8 (*c* 0.9, $CHCl_3$); IR (neat) 3263, 1380, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 6 H), 1.03 (t, *J* = 7.3 Hz, 6 H), 2.15 (d, J_{HP} = 15.4 Hz, 3 H), 2.35 (s, 3 H), 2.40 (s, 3 H), 2.91 (m, 8 H), 5.33 (d, J_{HP} = 5.5 Hz, 1 H), 7.17 (d, J_{HP} = 8.1 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 7.55 (d, *J* = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 14.4, 14.5, 14.6, 21.9, 24.9, 40.0, 40.6, 63.9 (d, J_{CP} = 115 Hz), 125.9, 129.0, 129.3, 130.2, 137.8, 138.7, 141.8, 144.2; ^{31}P NMR δ 34.97; HRMS Calcd for $C_{24}H_{38}N_3O_2PSNa$ (M+Na): 486.2320. Found: 486.2334.

Hydrolysis of (-)-7. In 10-mL round-bottom flask equipped with magnetic stir bar under argon atmosphere was placed (-)-**7** (0.023 g, 0.05 mmol) in 6 N HCl (1 mL). After stirring for 16 h at rt the solution was washed with EtOAc (3 x 5 mL), the aqueous phase was concentrated and azeotropically dried with toluene (3 x 5 mL). The residue was dissolved in a minimum amount of hot ethanol (ca. 1 mL), cooled to rt, and treated with propylene oxide (2.0 mL). After 0.5 h the white precipitate was collected and washed ethanol to afford 0.0018 g (44%) of phosphorous acid, ^{1}H NMR (0.5 N NaOH, D_2O) δ 6.55 (d, *J* = 566.4 Hz, 1 H); ^{31}P NMR (0.5 N NaOH, D_2O) δ 3.25.

The EtOAc phase was concentrated to give 0.0034 g (51%) of 4'-methylacetophenone (8) identified by comparison with literature values.

(*S*$_s$,*R*)-(+)-*O,O*-Diethyl-*N*-(*p*-toluenesulfinyl)-2-amino-2-phenyl-methylphosphonate (10). In an oven-dried 100-mL two-necked round-bottom flask fitted with a rubber septum and a magnetic stir bar under an argon balloon was placed sulfinimine (*S*)-(+)-**9** (0.24 g, 1.0 mmol) in THF (15 mL) and the mixture was cooled to -78 ^{o}C. In a separate 50-mL single-necked round-bottom flask fitted with a magnetic stir bar and a rubber septum under an argon balloon was placed a solution of diethyl phosphite (0.26 mL, 2.0 mmol) in THF (15 mL). The solution was cooled to -78 ^{o}C and LiHMDS (2.0 mL, 2.0 mmol) was slowly added. The solution was stirred for 0.25 h and cannulated to the solution of (+)-**9**. After stirring for 1 h the reaction mixture was quenched at -78 ^{o}C by addition of sat. NH_4Cl (1 mL). The organic phase was separated and the aqueous phase was washed with EtOAc (20 mL). The combined organic phases were washed with H_2O (10 mL), and brine (5 mL), dried ($MgSO_4$), and concentrated to give the **10** (dr 12:1). Crystallization (EtOAc:pentane, 5:95) afforded 0.29 g (76%) of (+)-**10**; mp 118-119 ^{o}C; $[\alpha]^{20}_D$ +128 (*c* 0.9 $CHCl_3$). Spectral properties were in agreement with literature values.[5]

(*R*)-(+)-*O,O*-Diethyl-2-amino-2-phenylmethylphosphonate (11). In an oven dried 25-mL single-necked round-bottom flask fitted with a rubber septum and a magnetic stir bar under an argon balloon was placed a solution of (+)-**10** (0.10 g, 0.26 mmol) in MeOH (5 mL) and the mixture was cooled to 0 ^{o}C. Trifluoroacetic acid (0.040 mL, 0.52 mmol) was slowly added, the reaction mixture was warmed to rt, stirred for 3 h and concentrated. The resulting residue was

dissolved in CH_2Cl_2 (5 mL), cooled to 0 °C and neutralized to pH 7 with sat. $NaHCO_3$ (5 mL). The organic phase was separated and the aqueous phase was washed with CH_2Cl_2 (10 mL). The combined organic phases were washed with H_2O (5 mL), and brine (5 mL), dried ($MgSO_4$), and concentrated. Flash chromatography (CH_2Cl_2:MeOH, 95:5) afforded 0.049 g (79%) of (+)-**12** as an oil; $[\alpha]^{20}_D$ +17.2 (*c* 1.0 $CHCl_3$), [lit.[5] $[\alpha]^{20}_D$ +16.45 (*c* 1.9, $CHCl_3$)]. Smith et. al. reports a value $[\alpha]^{20}_D$ -13 (*c* 1.9 $CHCl_3$) for the (*R*)-enantiomer which was in error.[6] Spectral properties were in agreement with literature values.[6]

(*R*)-(+)-2-Amino-2-phenylmethylphosphonic acid (12). In an oven-dried 25-mL single-necked round-bottom flask equipped with a magnetic stir bar and a condenser was placed a solution of (+)-**11** (0.10 g, 0.26 mmol) in 8 N HCl (10 mL). After the solution was refluxed for 9 h, it was cooled to rt, concentrated, and dried under high vacuum at rt for 3 h. The residue was dissolved in a minimum amount of hot ethanol (ca. 5 mL), cooled to rt, and treated with propylene oxide. After stirring for 3 h the white solid was collected to yield 0.030 g (61%) of (+)-**12** as a white solid; mp 284-285 °C, [lit.[6] mp 282-284 °C]; $[\alpha]^{20}_D$ +18.2 (*c* 0.7, 1 N NaOH), [lit.[7] $[\alpha]^{20}_D$ +18.1 (*c* 2.0, 1 N NaOH)]. Spectral properties were in agreement with literature values.[8]

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X-ray Structure Determination of a -amino phosphonate (-)-2d

The α-amino phosphonate (-)-**2d**, $C_{20}H_{28}NO_4PS$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences: h00: h = odd; *0k0*: *k* = odd; 00l: l = odd) with a = 9.751(3)Å, b = 12.074(7)Å, c = 18.64(1)Å, and V = 2194(3) Å^3 . Intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo-*K* (=0.7107Å) radiation with *-2* scans. X-ray data were processed and the structure was solved and refined using the MolEN package[1].

The intensity data were corrected for Lorentz and polarization effects, and for absorption using psi scan techniques. Of the 2550 unique reflections measured, 1628 with $F^2>3$ (F^2) were used during subsequent structure refinement.

The structure was solved by direct methods (SIR92)[2]. Refinement was by full-matrix least squares techniques based on F to minimize the quantity $w(|F_o|-|F_c|)^2$ with w = 4 F_o^2 / $^2(F_o^2)$ + 0.0064 F_o^4 . Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined. The hydrogen atom attached to nitrogen (H01) was refined isotropically. Refinement converged to R_1= 0.052 and R_2 = 0.071.

Table 1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic displacement parameters are given in Table 2. Tables 3 and 4 list bond angles and distances; Table 5 gives general displacement parameters for the anisotropically-refined atoms. Figure 1 is an ORTEP[3] drawing (30% probability ellipsoids) of the molecule.

References

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3. ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, C.K. Johnson (1976) ORNL-5138.

Table 1. Summary of Structure Determination of a-amino phosphonate (-)-2d

Formula:	$C_{20}H_{28}NO_4PS$
Formula weight:	409.49
Crystal class:	orthorhombic
Space Group:	$P2_1\,2_12_1$
Z	4
Cell constants:	
a	9.751(3)Å
b	12.074(7)Å
c	18.64(1)Å
V	2194(3) $Å^3$
μ	0.235 cm^{-1}
crystal size, mm	0.30 x 0.32 x 0.61
D_{calc}	1.24
F(000)	872
Radiation:	Mo-*K* (λ=0.7107Å)
θ range:	2.5 - 26.3θ
h, *k*, *l* collected:	0 to 12, 0 to 15, 0 to 23
No. reflections measured:	2550
No. reflections used in refinement:	1628 (F^2 >3.0σ)
No. of parameters:	248
Data/parameter ratio:	6.56
R_1	0.052
R_2	0.071
GOF:	1.50

Table 2. Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B_{eq}(Å^2)
S1	-0.0038(1)	0.9453(1)	0.89711(7)	0.0669(6)
P2	0.0602(1)	0.7062(1)	0.82038(8)	0.0639(6)
O3	0.1689(4)	0.7230(3)	0.8812(2)	0.079(2)
O4	0.0893(4)	0.6111(3)	0.7750(2)	0.081(2)
N5	-0.0241(4)	0.9213(3)	0.8112(2)	0.059(2)
O6	0.0933(4)	1.0384(3)	0.9137(2)	0.093(2
O7	-0.0799(4)	0.7015(3)	0.8608(2)	0.078(2
C8	0.0506(5)	0.8367(4)	0.7701(3)	0.060(2
C9	-0.1675(5)	1.0032(4)	0.9119(3)	0.066(3)
C10	0.2016(5)	0.8706(4)	0.7503(3)	0.066(3
C11	-0.4270(6)	1.0856(4)	0.9479(3)	0.076(3)
C12	-0.2891(5)	0.9474(4)	0.8904(3)	0.068(3)
C13	0.2537(5)	0.9686(4)	0.7697(3)	0.074(3)
C14	-0.0293(6)	0.8183(4)	0.6999(3)	0.076(3)
C15	-0.3118(6)	1.1397(4)	0.9684(4)	0.088(3)
C16	-0.1797(6)	1.0986(5)	0.9504(3)	0.085(3)
C17	-0.4148(5)	0.9888(4)	0.9082(3)	0.073(3)
C18	-0.5684(6)	1.1339(5)	0.9648(4)	0.098(4)
C19	0.3873(6)	0.9984(5)	0.7496(4)	0.094(4)
C20	-0.1778(6)	0.7923(6)	0.7056(4)	0.095(4)
C21	0.2808(7)	0.7992(5)	0.7092(4)	0.104(4)
C22	0.4687(6)	0.9295(6)	0.7106(4)	0.109(5)
C23	0.4100(8)	0.8284(7)	0.6897(5)	0.138(6)
C24	-0.1083(8)	0.6136(6)	0.9106(4)	0.124(5)
C25	-0.2493(9)	0.6189(7)	0.9359(5)	0.137(6)
C26	0.287(1)	0.6542(8)	0.8895(7)	0.257(7)
C27	0.390(1)	0.662(1)	0.9086(8)	0.25(1)
H01	-0.041(3)	0.962(2)	0.792(2)	0.021(7)
H1	-0.1003	1.1398	0.9663	0.1103
H2	-0.3156	1.2111	0.9937	0.1164
H3	-0.2828	0.8781	0.8632	0.0883
H4	-0.4979	0.9483	0.8933	0.0932
H5	-0.5611	1.2013	0.9905	0.1307
H6	-0.6162	1.1515	0.9193	0.1307
H7	-0.6244	1.0834	0.9898	0.1307
H8	-0.2174	0.7799	0.6607	0.1218
H9	-0.1887	0.7242	0.7342	0.1218
H10	-0.2244	0.8493	0.7306	0.1218
H11	0.0160	0.7583	0.6751	0.0991
H12	-0.0197	0.8834	0.6716	0.0991

Table 2. Positional Parameters and Their Estimated Standard Deviations (continued)

Atom	x	y	z	B_{eq}(Å^2)
H13	0.4401	0.5973	0.9122	0.3604
H14	0.4330	0.7184	0.8847	0.3604
H15	0.3803	0.6895	0.9610	0.3604
H16	0.3105	0.6204	0.8459	0.2661
H17	0.2577	0.5915	0.9222	0.2661
H18	0.2419	0.7288	0.6937	0.1372
H19	0.4665	0.7734	0.6632	0.1712
H20	0.5598	0.9503	0.6947	0.1513
H21	0.4228	1.0701	0.7650	0.1369
H22	0.1987	1.0202	0.7986	0.0939
H23	-0.2698	0.5589	0.9679	0.1765
H24	-0.2732	0.6860	0.9558	0.1765
H25	-0.3111	0.6063	0.8936	0.1765
H26	-0.0512	0.6238	0.9522	0.1712
H27	-0.0892	0.5441	0.8900	0.1712

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

(4/3) [$a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12}(\cos\gamma) + ac\beta_{13}(\cos\beta) + bc\beta_{23}(\cos\alpha)$]

Table 3. Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N5	S1	O6	114.2(2)	N5	S1	C9	96.5(2)
O6	S1	C9	104.0(2)	O3	P2	O4	113.1(2)
O3	P2	O7	104.4(2)	O3	P2	C8	107.0(2)
O4	P2	O7	115.0(2)	O4	P2	C8	113.0(2)
O7	P2	C8	103.5(2)	P2	O3	C26	123.3(5)
S1	N5	C8	124.9(3)	S1	N5	H01	117
C8	N5	H01	111	P2	O7	C24	120.5(4)
P2	C8	N5	110.9(3)	P2	C8	C10	107.2(3)
P2	C8	C14	109.7(3)	N5	C8	C10	113.9(4)
N5	C8	C14	107.0(4)	C10	C8	C14	108.2(4)
S1	C9	C12	121.5(4)	S1	C9	C16	119.8(4)
C12	C9	C16	118.5(5)	C8	C10	C13	121.5(5)
C8	C10	C21	119.3(5)	C13	C10	C21	119.1(5)
C15	C11	C17	119.0(5)	C15	C11	C18	120.4(5)
C17	C11	C18	120.5(5)	C9	C12	C17	120.5(5)
C10	C13	C19	120.5(5)	C8	C14	C20	117.5(5)
C11	C15	C16	121.2(6)	C9	C16	C15	119.9(5)
C11	C17	C12	121.0(5)	C13	C19	C22	121.9(6)
C10	C21	C23	120.2(6)	C19	C22	C23	116.2(6)
C21	C23	C22	122.0(7)	O7	C24	C25	111.0(6)
O3	C26	C27	137(1)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4. Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	N5	1.639(4)	S1	O6	1.502(4)
S1	C9	1.764(5)	P2	O3	1.566(4)
P2	O4	1.454(4)	P2	O7	1.561(4)
P2	C8	1.835(5)	O3	C26	1.43(1)
N5	C8	1.470(6)	N5	H01	0.6
O7	C24	1.437(8)	C8	C10	1.572(7)
C8	C14	1.539(7)	C9	C12	1.422(7)
C9	C16	1.363(7)	C10	C13	1.338(7)
C10	C21	1.388(9)	C11	C15	1.354(8)
C11	C17	1.389(7)	C11	C18	1.529(9)
C12	C17	1.365(7)	C13	C19	1.402(8)
C14	C20	1.485(8)	C15	C16	1.421(8)
C19	C22	1.36(1)	C21	C23	1.36(1)
C22	C23	1.40(1)	C24	C25	1.46(1)
C26	C27	1.07(1)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 5. General Displacement Parameters - *U's*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0632(6)	0.0700(7)	0.0678(6)	0.0115(7)	-0.0042(7)	-0.0097(6)
P2	0.0679(7)	0.0491(5)	0.0781(7)	0.0056(7)	-0.0017(7)	-0.0024(6)
O3	0.087(2)	0.070(2)	0.082(2)	0.027(2)	-0.017(2)	-0.007(2)
O4	0.091(3)	0.054(2)	0.107(3)	0.002(2)	-0.002(2)	-0.014(2)
N5	0.060(2)	0.047(2)	0.073(2)	0.011(2)	-0.005(2)	0.003(2)
O6	0.078(2)	0.106(2)	0.097(2)	-0.007(2)	-0.012(2)	-0.034(2)
O7	0.074(2)	0.067(2)	0.097(2)	0.001(2)	0.016(2)	0.017(2)
C8	0.063(3)	0.052(2)	0.065(3)	0.002(2)	0.006(2)	-0.004(2)
C9	0.070(3)	0.058(3)	0.072(3)	0.008(3)	-0.001(3)	-0.009(3)
C10	0.056(3)	0.060(3)	0.086(3)	0.006(3)	0.007(3)	0.007(3)
C11	0.076(3)	0.067(3)	0.086(3)	0.005(3)	0.009(3)	-0.009(3)
C12	0.063(3)	0.059(3)	0.083(3)	-0.005(3)	0.002(3)	-0.014(3)
C13	0.056(3)	0.072(3)	0.101(4)	-0.000(3)	-0.000(3)	0.004(3)
C14	0.081(4)	0.075(3)	0.073(3)	0.008(3)	-0.006(3)	-0.007(3)
C15	0.065(3)	0.079(3)	0.131(4)	0.010(3)	0.008(4)	-0.046(3)
C16	0.087(4)	0.073(3)	0.097(4)	-0.011(3)	0.005(3)	-0.032(3)
C17	0.062(3)	0.071(3)	0.089(3)	-0.000(3)	0.000(3)	-0.014(3)
C18	0.070(3)	0.104(4)	0.129(5)	0.017(4)	0.019(4)	-0.020(4)
C19	0.072(3)	0.088(4)	0.131(5)	-0.012(3)	0.005(4)	0.009(4)
C20	0.082(4)	0.111(4)	0.093(4)	-0.005(4)	-0.018(3)	-0.001(4)
C21	0.089(4)	0.088(4)	0.142(5)	-0.004(4)	0.044(4)	-0.017(4)
C22	0.078(4)	0.109(4)	0.152(6)	0.001(4)	0.029(4)	0.018(5)
C23	0.108(5)	0.128(5)	0.192(7)	0.026(5)	0.069(5)	-0.006(6)
C24	0.147(5)	0.099(4)	0.131(5)	0.022(5)	0.069(4)	0.031(4)
C25	0.124(5)	0.139(6)	0.148(7)	0.007(6)	0.039(5)	0.033(5)
C26	0.229(6)	0.240(8)	0.309(9)	0.151(6)	-0.195(5)	-0.164(7)
C27	0.140(7)	0.58(3)	0.20(1)	0.13(1)	-0.041(8)	-0.11(2)

The form of the anisotropic displacement parameter is:

$\exp [-2B^2(h^2\boldsymbol{a}^{*2}\boldsymbol{U_{11}} + k^2\boldsymbol{b}^{*2}\boldsymbol{U_{22}} + l^2\boldsymbol{c}^{*2}\boldsymbol{U_{33}} + 2hk\boldsymbol{a}^*\boldsymbol{b}^*\boldsymbol{U_{12}} + 2hl\boldsymbol{a}^*\boldsymbol{c}^*\boldsymbol{U_{13}} + 2kl\boldsymbol{b}^*\boldsymbol{c}^*\boldsymbol{U_{23}})]$.

Molecular Structure of a-amino phosphonate (-)-2d