IR: (Film)

2932 (s), 2865 (m), 1453 (m), 1375 (m), 1325 (m), 1294 (m), 1219 (s), 1125 (m), 1063 (m), 1036 (m), 990 (s), 922 (m), 764 (s)

MS: (70 eV)

260 (M^++1, 31), 259 (M^+, 100), 258 (22), 244 (72), 216 (49), 215 (41), 214 (38), 201 (70), 169 (31), 167 (15), 125 (13), 124 (14)

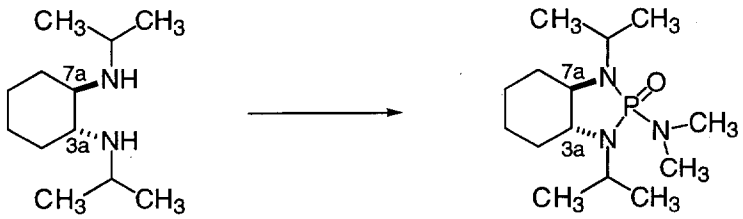
TLC: R_f 0.22 (EtOAc/*i*-PrOH, 10/1)

Optical Rotation: $[\alpha]_D^{22}$ = -94.58° (c = 1.13, $CHCl_3$)

Analysis: $C_{12}H_{26}N_3OP$ (259.33)

Calcd:	C, 55.58;	H, 10.11;	N, 16.20;	P, 11.94.
Found:	C, 55.50;	H, 10.16;	N, 16.15;	P, 11.79.

(3a*R*,7a*R*)-2-Amino-1,3-bis(1'-methylethyl)-*N*,*N*-dimethyloctahydro-2*H*-1,3,2-benzo-diazaphosphole 2-Oxide (9d)



9d

Data for **9d**:

^{1}H NMR: (400 MHz, $CDCl_3$)

3.40 - 3.20 (m, 2H, 2 x HC(1')), 2.99 - 2.90 (m, 1H, HC((3a or 7a)), 2.84 - 2.76 (m, 1H, HC((3a or 7a)), 2.63 (d, J = 9.3, 6H, $(CH_3)_2N$), 2.05 - 1.96 (br m , 2H, HC(3), HC(7)), 1.84 - 1.70 (br m , 2H, HC(3), HC(7)), 1.45 - 1.08 (m, 16H, $H_2C(5)$, $H_2C(6)$, 4 x CH_3C)

^{13}C NMR: (100 MHz, $CDCl_3$)

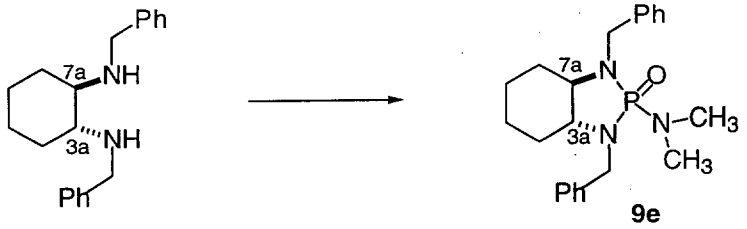
61.01 (d, J = 9.9), 59.09 (d, J = 9.9), 42.23 (d, J = 3.1), 43.65 (d, J = 4.6), 37.20 (d, J = 4.6), 29.90 (d, J = 8.4), 29.58 (d, J = 10.7), 24.35, 22.01, 21.20, 21.16, 20.68, 20.65, 20.03

^{31}P NMR: (162 MHz, $CDCl_3$)

24.42

TLC: R_f 0.36 (EtOAc/*i*-PrOH, 10/1)

(3a*R*,7a*R*)-2-Amino-1,3-dibenzyl-*N*,*N*-dimethyloctahydro-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9e)



9e

Data for **9e**:

mp: 135 - 136 °C

^{1}H NMR: (400 MHz, $CDCl_3$)

7.43 - 7.18 (m, 10H, CH(Ph)), 4.27 (dd, J = 15.9, 12.5, 1H, HCPh), 4.18 (dd, J = 14.9, 11.2, 1H, HCPh), 3.86 (dd, J = 14.2, 14.2, 1H, HCPh), 3.75 (dd, J = 16.1, 8.3, 1H, HCPh), 2.95 - 2.82 (m, 2H, HC(3a), HC(7a)), 2.40 (d, J = 9.5, 6H, $(CH_3)_2N$), 1.90 - 1.58 (m, 4H, $H_2C(3)$, $H_2C(7)$), 1.28 - 0.94 (m, 4H, $H_2C(5)$, $H_2C(6)$)

^{13}C NMR: (100 MHz, $CDCl_3$)

140.36 (d, J = 3.8, C(Ph)), 139.50 (d, J = 4.6, C(Ph)), 128.37 (CH(Ph)), 128.12 (CH(Ph)), 128.06 (CH(Ph)), 127.48 (CH(Ph)), 126.81 (CH(Ph)), 126.70 (CH(Ph)), 65.60 (d, J = 9.9) and 63.01 (d, J = 9.2) (C(3a), C(7a)), 47.31 (d, J = 2.3, CH_2Ph),

46.63 (d, J = 4.6, CH_2Ph), 36.23 (d, J = 4.6, CH_3N), 30.19 (d, J = 7.6) and 29.49 (d, J = 10.7) (C(3), C(7)), 24.40 (C(5), C(6))

^{31}P NMR: (162 MHz, $CDCl_3$)

30.25

IR: (KBr)

2930 (m), 1495 (m), 1453 (s), 1325 (m), 1296 (s), 1271 (m), 1211 (m),, 1175 (s), 1111 (m), 1067 (s), 1053 (s), 1028 (m), 995 (s), 968 (s), 816 (s), 797 (s)

MS: (70 eV)

383 (M^+, 17), 292 (10), 106 (9), 92 (17), 91 (100), 65 (10)

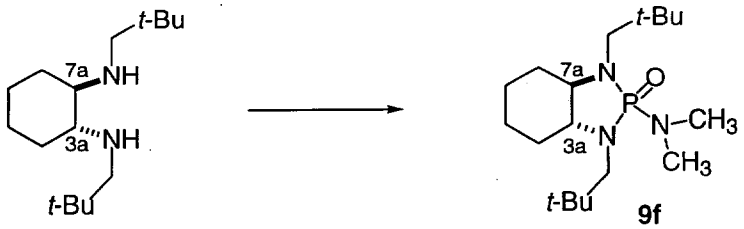
TLC: R_f 0.14 (EtOAc/hexane, 2/1)

Optical Rotation: $[\alpha]_D^{22}$ = -94.19° (c = 1.05, $CHCl_3$)

Analysis: $C_{22}H_{30}N_3OP$ (383.23)

Calcd:	C, 68.91;	H, 7.89;	N, 10.96;	P, 8.08.
Found:	C, 68.88;	H, 7.88;	N, 10.95;	P, 8.05.

(3a*R*,7a*R*)-2-Amino-1,3-*bis*(2',2'-dimethylpropyl)-*N*,*N*'-dimethyloctahydro-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9f)



Data for **9f**:

^{1}H NMR: (400 MHz, $CDCl_3$)

3.26 (dd, J = 14.4, 14.4, 1H, HCHN), 2.75 - 2.55 (m, 9H, HCHN, HC(3a), HC(7a), $(CH_3)_2N$), 2.36 (dd, J = 17.6, 14.4, 1H, HCHN), 2.18 (dd, J = 14.2, 14.2, 1H,

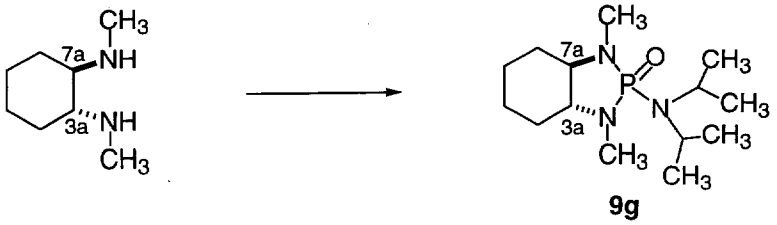
HCHN), 2.00 - 1.85 (br m , 2H, HC(3), HC(7)), 1.80 - 1.70 (br m , 2H, HC(3), HC(7)), 1.30 - 1.15 (m, 4H, $H_2C(5)$, $H_2C(6)$), 0.92, 0.85 (each s, 18H, 2 x $(CH_3)_3C$)

^{31}P NMR: (162 MHz, $CDCl_3$)

35.64

TLC: R_f 0.36 (hexane/EtOAc, 1/1)

(3a*R*,7a*R*)-2-Amino-1,3-dimethyl--*N*,*N*-*bis*(1'-methylethyl)-octahydro-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9g)



9g

Data for **9g**:

^{1}H NMR: (400 MHz, $CDCl_3$)

3.28 - 3.12 (m, 2H, HC(1')), 2.65 - 2.50 (m, 2H, HC(3a), HC(7a)), 2.48 (d, J = 10.5, 3H, CH_3N), 2.43 (d, J = 11.7, 3H, CH_3N), 2.00 - 1.90 (br m, 2H, HC(3), HC(7)), 1.83 - 1.75 (br m, 2H, HC(3), HC(7)), 1.40 - 1.05 (m, 16H, 2 x $(CH_3)_2C$, $H_2C(5)$, $H_2C(6)$)

^{13}C NMR: (100 MHz, $CDCl_3$)

65.31 (d, J = 9.2), 63.00 (d, J = 8.4), 45.29, 45.25, 45.24, 28.85 (d, J = 8.4), 28.76 (d, J = 2.3), 28.52 (d, J = 3.8), 28.50, 28.41, 24.35, 24.30 (d, J = 1.5), 22.90 (d, J = 13.7)

^{31}P NMR: (162 MHz, $CDCl_3$)

29.81

TLC: R_f 0.17 (EtOAc)

(3a*R*,7a*R*,1'*S*)-1,3-dimethyloctahydro-2-(*N*-methyl-1'-benzenethanamino)-2*H*-1,3,2-benzodiazaphosphole 2-Oxide (9h)

9h

Data for **9h**:

mp: 107 - 108 °C (hexane)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.45 - 7.42 (m, 2H, CH(Ph)), 7.35 - 7.29 (m, 2H, CH(Ph)), 7.26 - 7.21 (m, 1H, CH(Ph)), 5.11 (dq, *J*= 8.3, 7.3, CH(1')), 2.72 - 2.64 (m 1H, HC(3a or 7a)), 2.59 - 2.51 (m, 1H, HC(3a or 7a)), 2.45 (d, *J* = 11.7 CH_3N), 2.36 (d, *J* = 10.5, CH_3N), 2.23 (d, *J* = 10.0, CH_3N), 2.03 - 1.90 (br m, 2H, HC(3), HC(7)), 1.84 - 1.76 (br m, 2H, HC(3), HC(7)), 1.51 (d, *J* = 7.1 $CH_3C(1')$), 1.42 - 1.06 (m, 4H, $H_2C(5)$, $H_2C(6)$)

^{13}C NMR: (100 MHz, $CDCl_3$)

142.28 (d, *J* = 4.6, C(Ph)), 128.02 (CH(Ph)), 127.70 (CH(Ph)), 126.84 (CH(Ph), 65.07 (d, *J* = 9.2) and 63.65 (d, *J* = 8.4) (C(3a), C(7a)), 53.13 (CH(1')), 28.96 (d, *J* = 1.5, CH_3N), 28.67 (d, *J* = 7.6, CH_2), 28.34 (d, *J* = 10.7, CH_2), 28.00 (d, *J* = 3.8, CH_3N), 26.43 (d, *J* = 4.6, CH_3N), 24.32 (d, *J* = 1.5) and 24.24 (d, *J* = 1.5) (C(5), C(6)), 17.34 (d, *J* = 1.5, $CH_3C(1')$)

^{31}P NMR: (162 MHz, $CDCl_3$)

31.11

IR: (Film)

2940 (s), 2869 (s), 2813 (s), 1451 (s), 1370 (m), 1300 (m), 1208 (s), 1173 (s), 1059 (m), 1042 (m), 1026 (s), 994 (s), 945 (s), 924 (s), 891 (m), 808 (s), 781 (s), 706 (s)

MS: (70 eV)

644 ($2M^+$+2, 26), 643 ($2M^+$+1, 63), 642 ($2M^+$, 20), 508 (42), 455 (40), 322 (M^++1, 100), 321 (M^+, 25), 187 (23), 134 (72), 118 (19), 105 (18)

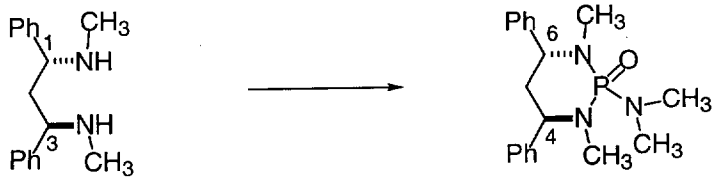
TLC: R_f 0.16 (EtOAc), 0.39 (EtOAc/*i*-PrOH, 15/1)

Optical Rotation: $[\alpha]_D^{22}$ = -52.96° (c = 1.06, $CHCl_3$)

Analysis: $C_{17}H_{28}N_3OP$ (321.40)

Calcd:	C, 63.53;	H, 8.78;	N, 13.07;	P, 9.64.
Found:	C, 63.57;	H, 8.82;	N, 13.04;	P, 9.56.

(4*R*,6*R*)-2-Amino-4,6-diphenyl-*N*,*N*,1,3-tetramethyl-1,3,2-diazaphosphorinane 2-Oxide (10)



10

Data for **10**:

mp: 122 - 123 °C (hexane)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.56 - 7.52 (m, 2H, CH(Ph)), 7.41 - 7.19 (m, 8H, CH(Ph)), 4.28 (ddd, *J* = 15.4, 4.9, 4.9, HCPh), 3.95 (ddd, *J* = 10.0, 3.2, 3.2, HCPh), 2.84 (d, *J* = 9.8, 6H, $(CH_3)_2N$), 2.56 (d, *J* = 8.8, CH_3N), 2.46 - 2.38 (d overlapping m, *J* = 10.0, CH_3N, HC(5)), 2.19 - 2.12 (m, 1H, HC(5))

^{13}C NMR: (100 MHz, $CDCl_3$)

142.44 (d, *J* = 6.9, C(Ph)), 141.28 (C(Ph)), 128.65 (CH(Ph)), 128.52 (CH(Ph)), 127.40 (CH(Ph)), 127.11 (CH(Ph)), 127.01 (CH(Ph)), 126.86 (CH(Ph)), 62.90 (d, *J* = 2.3) and

60.02 (C(3), C(6)), 42.14 (d, J = 6.1, C(5)), 37.19 (d, J = 4.6, $(CH_3)_2N$), 33.50 (d, J = 4.6) and 33.20 (d, J = 2.3) (2 x CH_3N)

^{31}P NMR: (162 MHz, $CDCl_3$)

19.00

IR: (Film)

2921 (m), 1495 (w), 1455 (m), 1300 (m), 1270 (m), 1204 (s), 1183 (s), 1146 (m), 1084 (w), 1063 (s), 990 (s), 901 (m), 768 (s), 708 (s)

MS: (70 eV)

344 (M^++1, 24), 343 (M^+, 40), 298 (21), 135 (17), 133 (19), 120 (20), 118 (18), 99 (20), 97 (31), 87 (22), 86 (50), 85 (77), 84 (71), 83 (100)

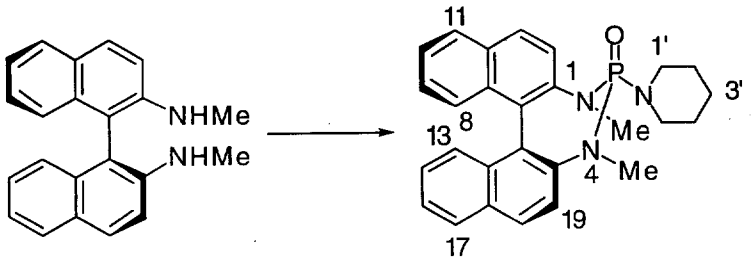
TLC: R_f 0.16 (EtOAc)

Optical Rotation: $[\alpha]_D^{22}$ = +16.87° (c = 1.12, $CHCl_3$)

Analysis: $C_{19}H_{26}N_3OP$ (343.41)

Calcd:	C, 66.45;	H, 7.63;	N, 12.24;	P, 9.02.
Found:	C, 66.46;	H, 7.66;	N, 12.23;	P, 8.98.

(*R*)-2,4-Dimethyl-3,4-dihydro-3-piperidinyl-dinaphtho[2,1-d:1'2'-f]-1H-[1,3,2]diazaphosphepine 3-Oxide (11).



27 11

Analytical Data for (–)-**11**

mp: 276-277 °C (toluene/hexane)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.96 (d, 1H, J = 9.0, H(18)); 7.94 (d, 1H, J = 9.0, H(12)); 7.89 (d, 1H, J = 8.1, H(11)); 7.86 (d, 1H, J = 8.1, H(17)); 7.74 (d, 1H, J = 8.8, H(19)); 7.64 (d, 1H, J = 8.8, H(13)); 7.40 (ddd, 1H, J = 8.1, 6.5, 1.5, H(10)); 7.35 (ddd, 1H, J = 8.1, 7.5, 0.7, H(16)); 7.25 (d, 1H, J = 7.1, H(16)); 7.25 (d, 1H, J = 7.1, H(8)); 7.21 (ddd, 1H, J = 8.5, 6.3, 1.2, H(9)); 7.13 (ddd, 1H, J = 8.3, 6.8, 1.2, H(15)); 7.05 (d, 1H, J = 8.3, H(14)); 3.10 (d, 3H, J = 9.0, H_3CN); 3.08 (d, 3H, J = 10.3, H_3CN); 3.10-2.78 (m, 4H, H_2CN); 1.58-1.38 (m, 6H, H_2CC)

^{13}C NMR: (100.6 MHz, $CDCl_3$)

143.26 (s, C(1/5)); 141.54 (s, C(5/1)); 132.57, 132.36 (s, C(6a, 7a, 11a, 17a)); 131.10, 130.78 (s, C(6, 7)); 129.58, 128.82 (s, C(18, 12); 127.93, 127.79 (s, C(11, 17)); 127.83, 127.29 (s, C(8, 14)); 126.00, 125.81 (s, C(9, 15)); 124.88, 124.72 (s, C(10, 16)); 122.59, 122.36 (s, C(19, 13)); 45.91 (s, C(1')); 35.56 (d, J = 6.1, CH_3)); 35.22 (d, J = 4.6, CH_3)); 26.58 (d, J = 4.6, C(2')); 24.50 (s, C(3'))

^{31}P NMR: (162 MHz, $CDCl_3$)

27.38

IR: (KBr)

3064 (w), 3055 (w), 3039 (w), 2962 (w), 2936 (m), 2913 (m), 2839 (m), 1647 (m), 1618 (m), 1507 (s), 1470 (m), 1455 (m), 1373 (w), 1340 (m), 1280 (m), 1222 (s), 1163 (s), 1149 (m), 1091 (m), 1060 (s), 1026 (m), 962 (s), 933 (s), 833 (m), 825 (m), 815 (s), 748 (s), 707 (m)

MS: (EI, 70 eV)

442 (M^++1, 19), 441 (M^+, 60), 358 (59), 311 (30), 281 (100), 265 (14), 141 (10), 84 (13)

TLC: R_f 0.34 (EtOAc/*i*-PrOH, 95/5)

Optical Rotation: $[\alpha]_D^{22}$ = -472° (c = 1.18, $CHCl_3$)

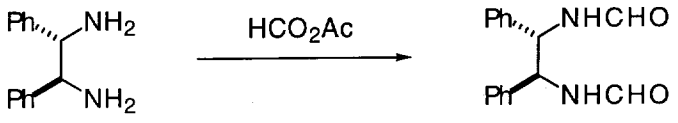
HPLC: t_R (*R*)-**11**, 21.21 min (99.76%), t_R (*S*)-**11**, 14.85 min (0.24%)(ß-GEM-1, hexane/*i*-PrOH, 65/35, 0.6 mL/min)

Analysis: $C_{27}H_{28}N_3OP$ (441.52)

Calcd:	C, 73.45%;	H, 6.39%;	N, 9.52%;	P, 7.02%.
Found:	C, 73.71%;	H, 6.42%;	N, 9.44%;	P, 6.81%.

Synthesis of Enantiomerically Pure Diamines

(1*S*,2*S*) *N*,*N*'-Diformyl-1,2-diphenyl-1,2-ethanediamine ((*S*,*S*)-13)



(*S*,*S*)-12 (*S*,*S*)-13

To a cold (ice-bath, 0 °C) solution of diamine **12** (4.0 g, 18.8 mmol, 1.0 equiv) in CH_2Cl_2 (40 ml) was added acetic formic anhydride (4.3 mL, 2.5 equiv) dropwise over 5 min. A white solid immediately precipated and the mixture turned to a thick cake. The cold bath was removed and the reaction mixture was stirred at rt for 30 min. The solvent and other volatiles evaporated and the residue was dried under vacuum for 10 h to remove residual AcOH. Recrystallization of the residue from MeOH afforded 4.6 g (91%) of bisformamide (*S*,*S*)-**13** as white plates.

Data for (*S*,*S*)-**13**:

mp: 231-233 °C (MeOH)

^{1}H NMR: (DMSO-d_6, 500 MHz)

mixture of rotamers: [8.68, d, J = 6.6; 8.64, d, J = 9.7; 8.43, d, J = 9.0; 8.35, t, J = 10.6 (2H, *H*NCO)], [8.07, s; 8.05, s; 7.93, d, J = 11.2; 7.90, d, J = 11.2 (2H, *H*CO)], 7.11-7.26 (m, 10H, 2(C_6H_5)), [5.15- 5.27, m; 4.82-4.86, m (2H, *H*CPh)]

^{13}C NMR: (DMSO-d_6, 125.7 MHz)

160.66 (C=O), 139.86 (Ar-ipso), 128.00, 127.38, 127.06, 55.51 (*C*HPh)

IR: (KBr)

3321 (b), 3040 (w), 3037 (w), 2876 (w), 1658 (s), 1605 (s), 1519 (w), 1495 (w), 1456(w), 1387 (w), 1348 (w), 1333 (w), 1289 (w), 1278 (w), 1239 (w)

MS: (70eV)

268 (M^+), 148 (7), 135 (11), 134 (100), 107 (7), 106 (53), 79(13)

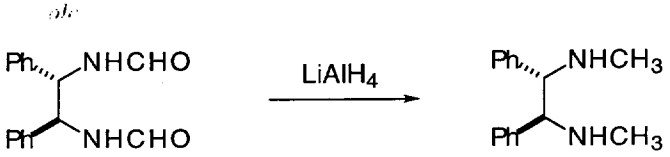
TLC: R_f 0.50 (CH_2Cl_2/MeOH, 19/1)

Optical Rotation: $[\alpha]_D^{22} = +111.6°$ (c = 0.45, MeOH)

Anal. $C_{16}H_{16}N_2O_2$(268.34)

Calcd.:	C, 71.62;	H, 6.01;	N, 10.44.
Found:	C, 71.90;	H, 6.10;	N, 10.37.

(1*S*,2*S*)-*N*,*N'*-Dimethyl-1,2-diphenyl-1,2-ethanediamine ((*S*,*S*)-14)



(*S*,*S*)-**13** (*S*,*S*)-**14**

To a solution of bisformamide **13** (4.0 g, 14.9 mmol) in dry THF (150 mL) slowly added $LiAlH_4$ (12.82 g, 74.8 mmol, 5 equiv) in a small portions over 5 min. The reaction mixture was heated to reflux for 4 h, then was cooled to rt and quenched with the succesive addition of H_2O (8 mL), 2N NaOH (18 mL) and H_2O (120 mL). The mixture was filtered through Celite and the filtrate was extracted with EtOAc (3 X 150 mL) and then the combioned organic extracts were washed with brine (120 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by Kugelohr distillation (ABT, 155-160 °C/0.01 mmHg) to afford 3.22 g (90%) of diamine (*S*,*S*)-**14** as a white solid.[10]

Data for (*S*,*S*)-**14**:

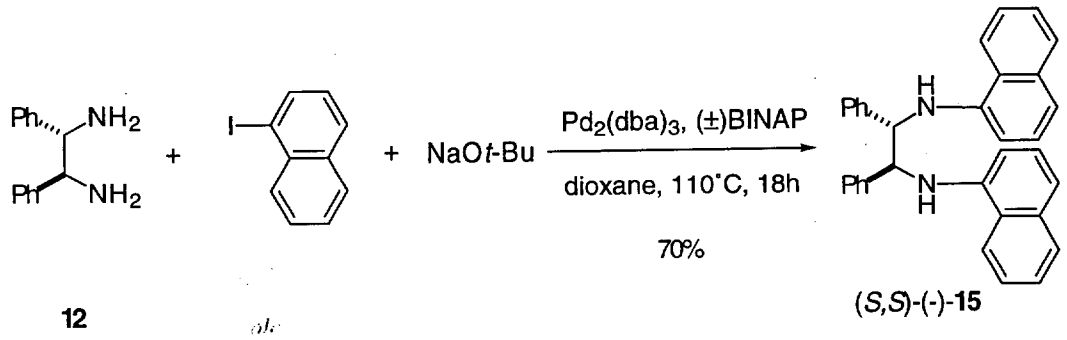
^{1}H NMR: ($CDCl_3$, 500 MHz)

δ 7.03-7.17 (m, 10H, 2(C_6H_5)), 3.53 (s, 2H, 2*H*CPh), 2.25 (s, 6H, 2(CH_3), 1.99 (b, 2H, 2*H*N)

^{13}C NMR: ($CDCl_3$, 125.7 MHz)

140.91 (Ar-ipso), 127.91, 127.89, 126.83, 71.11 (*C*HPh), 34.54 (CH_3)

(–)-(1*S*,2*S*)-*N*,*N*′-Di-(1-naphthyl)-1,2-diphenyl-1,2-ethanediamine (15)



A mixture of the (*S*,*S*)-1,2-diphenyl-1,2-ethanediamine (485 mg, 2.28 mmol), sodium *t*-butoxide (530 mg, 5.48 mmol, 2.4 equiv), (±)-BINAP (427 mg, 0.685 mmol, 0.3 equiv), and $Pd_2(dba)_3$ (105 mg, 0.114 mmol, 0.05 equiv) was purged with argon in a Carrius tube. Dioxane (15 mL) was added followed by 1-naphthyl iodide (735 µl, 5.03 mmol, 2.2 equiv). The dark brown mixture was sealed then heated to 110 °C for 18 h with stirring. After being cooled to rt the mixture was filtered through a layer of Celite and washed with THF. The filtrate was concentrated in vacuo and the residue was filtered through a plug of silica gel (hexane/EtOAc, 3/1). The column eluent was concentrated to about 10 mL and the crystals (BINAP) were collected and washed with EtOAc. The filtrate was then concentrated and purified by column chromatography (SiO_2, hexane/EtOAc, 20/1) to give 744 mg (70%) of **15** as a yellowish foam, which was recrystallized from hexane to give white amorphous solid (582 mg, 55%).

Data for (–)-(1*S*,2*S*)-**15**

mp: 151-152 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

7.91 (d, J = 7.7, 2 H, HC(5")), 7.80 (dd, J = 7.7, 1.6, 2 H, HC(4")), 7.48-7.40 (m, 4 H, HC(6", 7")), 7.37-7.33 (m, 4 H, HC(2')), 7.31-7.27 (m, 4 H, HC(3')), 7.27-7.20 (m, 4 H, HC(4', 4")), 7.17 (dt, J =7.9, 1.6, 2 H, HC (3")), 6.40 (d, J = 7.5, 2 H, HC (2")), 5.42 (br, 2 H, HN), 4.96 (s, 2 H, HC (1))

^{13}C NMR: (125 MHz, $CDCl_3$)

141.90 (C(10")), 139.59 (C(1')), 134.19 (C(9")), 128.74 (C(5")), 128.69 (C(3')), 127.82 (C(4')), 127.24 (C(2')), 126.32 (C(3"), 125.78 (C(7")), 124.10 (C(6")), 119.89 (C(8")), 118.23 (C(4")), 107.10 (C(2")), 64.00 (C(1))

IR: ($CHCl_3$)

3405 (w), 3064 (w), 3006 (w), 1627 (w), 1581 (s), 1524 (s), 1476 (s), 1454 (m), 1407 (s), 1371 (w), 1344 (s), 1314 (w), 1282 (m), 1252 (w), 1118 (m), 1075 (w), 702 (w)

MS: (FAB)

465 (M^++1, 20), 323 (10), 322 (41), 234 (12), 233 (25), 232 (100)

TLC: R_f 0.17 (hexane/EtOAc, 20/1)

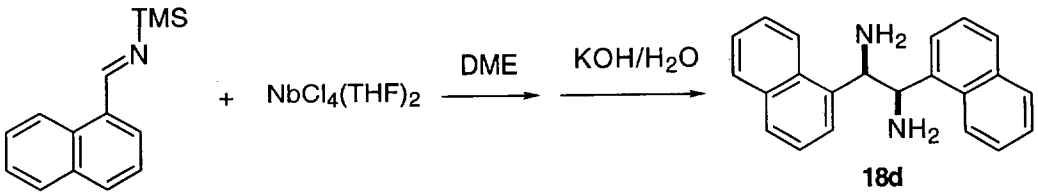
Optical Rotation: $[\alpha]_D^{22}$ = -175° (c = 1.11, $CHCl_3$)

HPLC: t_R (1*S*,2*S*)-**15**, 3.20 min (Daicel ChiralCel AS, CO_2/MeOH, 70/30, 3.5 mL/min, 40°C, 150 psi)

Analysis: $C_{34}H_{28}N_2$ (464.62)

Calcd:	C, 87.90%;	H, 6.07%;	N, 6.03%.
Found:	C, 87.83%;	H, 6.04%;	N, 6.17%.

General Procedure IV: Coupling of *N* -Silylimines. Preparation of 1,2-Di-(1-naphthyl)-1,2-ethanediamine (±)-18d



18d

The niobium reagent[4] (12.1g, 31.9 mmol) was transferred into a 1 liter 2-necked round bottomed flask under a gentle stream of dry nitrogen. DME (500 mL) was added and the mixture was stirred at rt for about 10 min. The solution turned light brown and almost all the solid was

dissolved. The silylimine in 10 mL of DME was then added dropwise over about 30 min. The dark solution was then stirred overnight to give light brown solution. The solvent was removed under vacuum and the brown residue was stirred with 150 mL of 10% aqueous KOH solution. The white precipitate was filtered and washed with methylene chloride. The phases of the filtrate were separated and the aqueous phase was extracted with methylene chloride (2×100 mL). The combined organic extracts were dried (K_2CO_3) and concentrated in vacuo to give yellowish solid, which was recrystallized from toluene/hexane to give 2.57 g (52%) of **18d** white crystals.

Analytical Data for (±)-**18d**

mp: 140-142 (toluene)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.33 (d, J = 8.4, 2 H, HC(8')), 7.89 (d, J =8.1, 2 H, HC(5')), 7.81 (d, J = 7.1, 2 H, HC(4')), 7.78 (d, J = 8.1, 2 H, HC(2')), 7.59 (ddd, J = 8.4, 6.8, 1.3, 2 H, HC (7')), 7.52 (ddd, J = 8.1, 7.0, 0.9, 2 H, HC (6')), 7.49 (dd, J = 7.9, 7.1, 2 H, HC(3')), 5.13 (s, 2 H, HC(1)), 1.66 (br, 4 H, H_2N)

^{13}C NMR: (125 MHz, $CDCl_3$)

139.65 (C(1')), 133.95 (C(10')), 130.85 (C(9')), 129.15 (C(5')), 127.65 (C(4')), 125.98 (C(3')), 125.46 (C(7')), 125.43 (C(6')), 124.17 (C(8')), 122.87 (C(2')), 54.33 (C(1))

IR: ($CHCl_3$)

3380 (w), 3320 (w), 3005 (m), 2955 (s), 1597 (s), 1511 (m), 1396 (m), 1365 (w), 1341 (w), 1256 (w), 1168 (w), 1143 (w), 1086 (w), 1069 (w), 1030 (w), 995 (w), 950 (s), 941 (s), 904 (s), 860 (s), 842 (m), 803 (w), 659 (w), 649 (w)

MS: (CI)

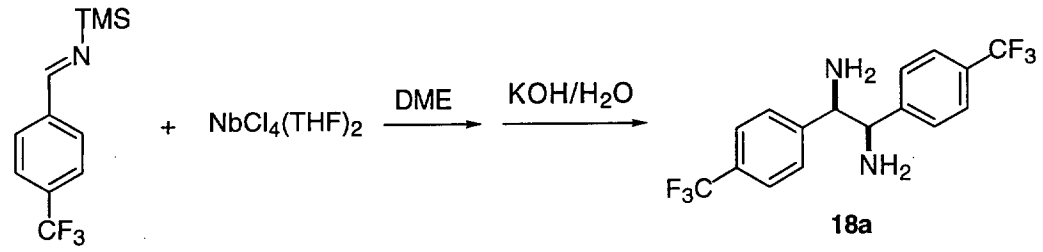
313 (M^++1, 2), 297 (13), 296 (52), 156 (14), 156 (100)

TLC: R_f 0.51 (TBME/MeOH/NH_3•H_2O, 80/20/1)

Analysis: $C_{22}H_{20}N_2$ (312.42)

Calcd:	C, 84.58%;	H, 6.45%;	N, 8.97%.
Found:	C, 84.57%;	H, 6.39%;	N, 8.99%.

1,2-Bis-(4-trifluoromethylphenyl)-1,2-ethanediamine (18a)



18a

Following General Procedure IV from 10.75 g (43.8 mmol) of the *N*-silyl imine and 16.6 g (43.8 mmol) of the niobium reagent was obtained 3.77 g (49%) of (±)-**18a** after recrystallization (hexane) along with the meso diastereomer (0.97g, 13%).

Analytical Data for (±)-**18a**

M.W.: 348.29

^{1}H NMR: (500 MHz, $CDCl_3$)

7.55 (d, J = 8.2, 4 H, HC(3')), 7.39 (d, J = 8.2, 4 H, HC(2')), 4.17 (s, 2 H, H(1)), 1.77 (br, 4 H, H_2N)

^{19}F NMR: (470 MHz, $CDCl_3$)

−63.69

Analytical Data for *meso* -**18a**

M.W.: 348.29

mp: 115-117 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

7.60 (d, J = 8.1, 4 H, HC(3')), 7.45 (d, J = 8.1, 4 H, HC(2')), 4.13 (s, 2 H, H(1)), 1.37 (br, 4 H, H_2N)

^{13}C NMR: (125 MHz, $CDCl_3$)

146.36 (C(1')), 129.97 (q, J = 32.5, C(4')), 127.93 (C(2'), 125.33 (q, J = 3.8, C(3')), 124.05 (q, J = 271.4, CF_3), 62.20 (C(1))

^{19}F NMR: (470 MHz, $CDCl_3$)

−63.65

IR: ($CHCl_3$)

3381 (w), 3320 (w), 2987 (w), 2961 (w), 2876 (w), 1620 (m), 2588 (w), 1420 (w), 1325 (s), 1168 (s), 1130 (s), 1109 (m), 1069 (s), 1017 (m), 900 (w), 849 (m), 601 (w)

MS: (CI)

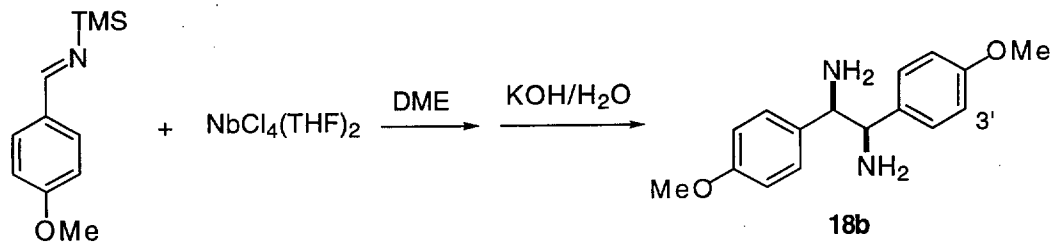
349 (M^++1, 12), 330 (13), 329 (63), 175 (12), 174 (100)

TLC: R_f 0.39 (TBME/MeOH/NH_3•H_2O, 100/5/1)

Analysis: $C_{16}H_{24}F_6N$

Calcd:	C, 55.18%;	H, 4.05%;	N, 8.04%;	F, 32.73%.
Found:	C, 55.35%;	H, 4.08%;	N, 7.92%;	F, 32.42%.

(±)-1,2-Di-(4-methoxyphenyl)-1,2-ethanediamine (18b)



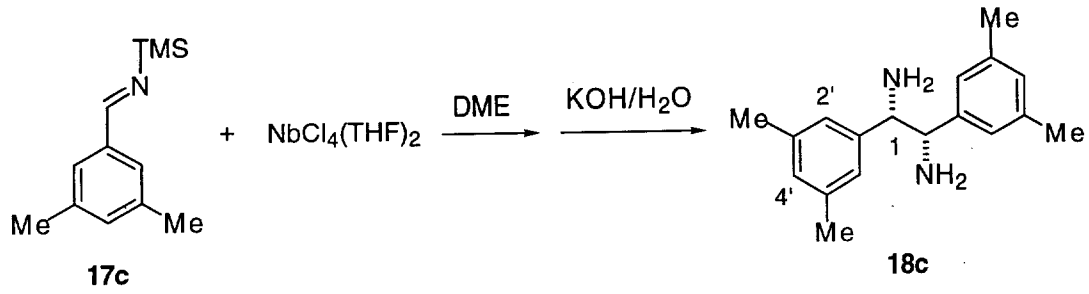
18b

Following General Procedure IV from 8.47 g (42.1 mmol) of the *N*-silyl imine **17b** and 15.9 g (42.0 mmol, 1.0 equiv) of the niobium reagent was obtained 2.59 g (45%) of **18b** as a white solid after recrystallization (hexane).[5]

^{1}H NMR: (500 MHz, $CDCl_3$)

7.16 (d, J = 8.8, 4 H, HC(2')), 6.81 (d, J = 8.8, 4 H, HC(3')), 4.01 (s, 2 H, HC(1)), 3.78 (s, 6 H, Me), 1.50 (br, 4 H, H_2N)

(±)-1,2-Bis-(3,5-dimethylphenyl)-1,2-ethanediamine (18c)



Following General Procedure IV from 4.45 g (21.7 mmol) of the *N*-silyl imine **17c** and 8.22 g (21.7 mmol, 1.0 mmol) of the niobium reagent was obtained 1.95 g (67%) of **18c** as a white solid after recrystallization (hexane).[5]

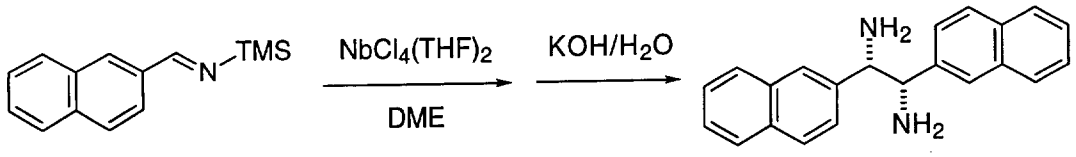
^{1}H NMR: (500 MHz, $CDCl_3$)

6.98 (s, 4 H, HC(4')), 6.89 (s, 2 H, HC(2')), 4.09 (s, 2 H, HC(1)), 2.32 (s, 12 H, Me), 1.39 (br, 4 H, H_2N)

^{13}C NMR: (125 MHz, $CDCl_3$)

143.48 (C(1')), 137.70 (C(3')), 128.54 (C(4')), 124.58 (C(2')), 61.03 (C(1)), 21.32 (Me)

1,2-Di-(2-naphthyl)-1,2-ethanediamine (18e)



17e **18e**

Following General Procedure IV, from 14.0 g (61.6 mmol) imine and 24.5 g (64.7 mmol) of the niobium reagent was obtained 4.59 g (48%) of **18e** as pale yellow solid after recrystallization (toluene/hexane).

Analytical Data for (±)-**18e**

mp: 124-128 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

7.85 (s, 2 H, HC(1')), 7.83-7.78 (m, 8 H, Ar), 7.50-7.43 (m, 4 H, Ar), 4.43 (s, 2 H, HC(1)), 1.65 (br, 4 H, H_2N)

^{13}C NMR: (125 MHz, $CDCl_3$)

140.78 (C(2')), 133.29 (C(9')), 132.69 (C(10')), 127.96 (C(8')), 127.89 (C(5')), 127.58 (C(4')), 126.04 (C(7')), 125.65 (C(6')), 125.43 (C(3')), 125.34 (C(1')), 61.42 (C(1))

IR: ($CHCl_3$)

3379 (w), 3313 (w), 3005 (m), 2960 (m), 2861 (w), 1633 (w), 1602 (m), 1508 (m), 1373 (w), 1310 (w), 1272 (w), 1246 (w), 1144 (w), 1124 (w), 1056 (w), 1018 (w), 964 (w), 950 (m), 892 (s), 858 (s), 822 (s), 660 (w)

MS: (CI)

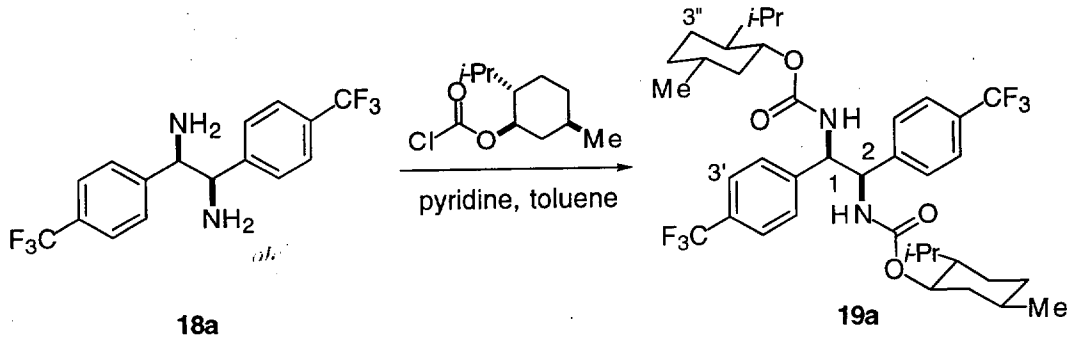
313 (M^++1, 4), 297 (11), 296 (40), 158 (12), 157 (18), 156 (100), 141 (10), 129 (10)

TLC: R_f 0.45 (TBME/MeOH/NH_3•H_2O, 80/20/1)

Analysis: $C_{22}H_{20}N_2$ (312.42)

Calcd:	C, 84.58%;	H, 6.45%;	N, 8.97%.
Found:	C, 84.60%;	H, 6.42%;	N, 8.54%.

General Procedure V: Resolution of Diamines via Biscarbamates: *N,N'*-Bis-((−)-menthoxycarbonyl)-1,2-bis-(4-trifluoromethylphenyl)-1,2-ethanediamine (19a)



18a **19a**

To a solution of the diamine **18a** (3.50 g, 10.05 mmol) and pyridine (2.85 mL, 35.18 mmol, 3.5 equiv) in DMF (100 mL) was added (−)-menthyl chloroformate (Aldrich, 4.74 mL, 22.11 mmol, 2.2 equiv) at rt. The turbid solution was then stirred at rt for 2 h and TLC showed no starting material left. The solvent was then removed in vacuo and the residue passed through a layer of silica gel (CH_2Cl_2/CH_3CN, 10/1) to give 3.4 g of the less polar and 3.2 g (92% combined yield) of the more polar components **19a** as white solids. The less polar component was then purified by column chromatography (SiO_2, toluene/CH_3CN, 20/1) to give (1*R*,2*R*)-**19a** as a white amorphous solid.

Analytical Data for (1*R*,2*R*)-**19a**

^{1}H NMR: (400 MHz, $CDCl_3$)

7.50 (d, J = 7.6, 4 H, HC(3')), 7.21 (d, J = 7.6, 4 H, HC(2')), 5.67 (br, 2 H, HN), 5.02 (br, 2 H, HC(1, 2), 4.51 (dt, J = 10.7, 4.2, 2 H, HC(1")), 2.10-0.74 (m, 30 H), 0.67 (d, J = 6.8, 6 H, Me)

^{19}F NMR: (376 MHz, $CDCl_3$)

−63.86

TLC: R_f 0.25 (toluene/CH_3CN, 50/1).

Analytical Data for (1*S*,2*S*)-**19a**

^{1}H NMR: (400 MHz, $CDCl_3$)

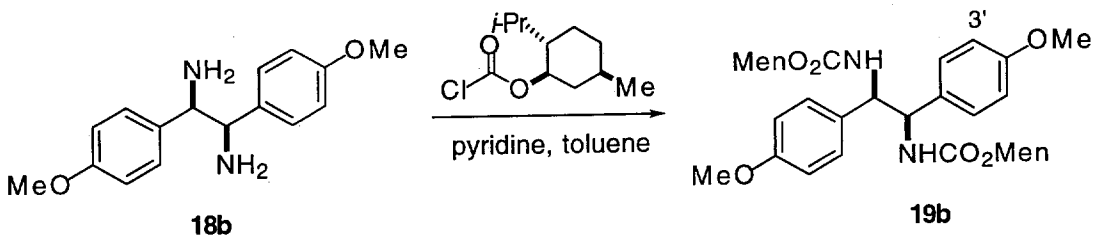
7.62-7.38 (m, 4 H, HC(3')), 7.38-7.04 (m, 4 H, HC(2')), 6.04-5.58 (m, 2 H, HN), 5.16-4.90 (m, 2 H, HC(1, 2)), 4.42 (br, 2 H, HC–O), 2.00-0.36 (m, 36 H)

^{19}F NMR: (376 MHz, $CDCl_3$)

mixture of rotamers: –63.80, –63.84 (major), –63.54, –63.56 (minor)

TLC: R_f 0.12 (toluene/CH_3CN, 50/1).

_N,N'_-Bis-((–)menthoxycarbonyl)-1,2-bis-(4-methoxyphenyl)-1,2-ethanediamine (19b)



18b **19b**

Following General Procedure V from 2.59 g (9.51 mmol) of the (±)-**18b** and 5.1 mL (23.8 mmol, 2.5 mmol) of (–)-menthyl chloroformate was obtained 1.98 g of the less polar, 1.61 g of the more polar and 0.63 g of mixed carbamates (total yield 69%) as white solids after column chromatography (SiO_2, CH_2Cl_2/CH_3CN, 20/1).

Analytical Data for (1*R*,2*R*)-**19b**

^{1}H NMR: (500 MHz, $CDCl_3$)

6.97 (br, d, J = 8.2, 4 H, HC(2')), 6.73 (d, J = 8.6, 4 H, HC(3')), 5.54 (br, 2 H, HN), 4.85 (br, AB, 2 H, HC(1,2)), 4.51 (dt, J = 10.9, 4.4, 2 H, HC(1")), 3.74 (s, 6 H, MeO), 2.12-0.80 (m, 18 H), 0.92 (d, J = 8.0, 6 H, Me), 0.83 (d, J = 7.0, 6 H, Me), 0.69 (d, J = 6.6, 6 H, Me)

TLC: R_f 0.25 (CH_2Cl_2/CH_3CN, 20/1)

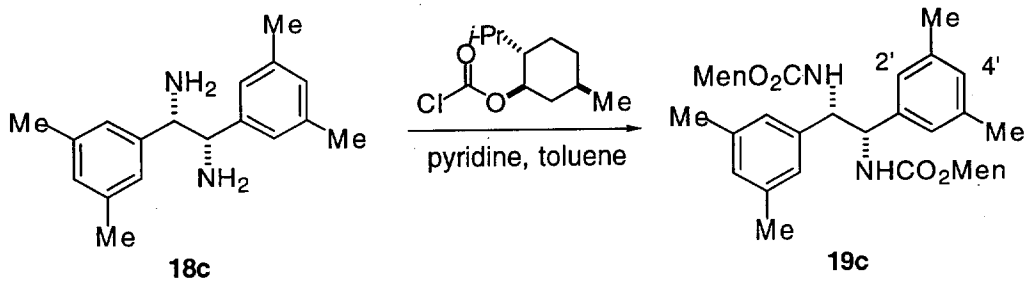
Analytical Data for (1*S*,2*S*)-**19b**

^{1}H NMR: (500 MHz, $CDCl_3$)

6.96 (br, 4 H, HC(2')), 6.73 (br, 4 H, HC(3')), 6.20-5.42 (br, 2 H, HN), 4.84 (br, 2 H, HC(1,2)), 4.48 (br, 2 H, HC(1")), 3.74 (s, br, 6 H, MeO), 2.20-0.40 (m, 36 H)

TLC: R_f 0.13 (CH_2Cl_2/CH_3CN, 20/1)

_N,N'_-Bis-((−)menthoxycarbonyl)-1,2-bis-(3,5-dimethylphenyl)-1,2-ethanediamine (19c)



Following General Procedure V from 2.14 g (7.97 mmol) of the diamine (±)-**18c**, 4.27 mL (19.9 mmol, 2.5 equiv) of (−)-menthyl chloroformate and pyridine (1.93 mL, 23.9 mmol, 3.0 equiv) was obtained 4.36 g (92%) of **19c** as a white solid after column chromatography (SiO_2, hexane/EtOAc, 3/1), which was separated with column chromatography (SiO_2, CH_2Cl_2/Et_2O, 39/1) to give 1.15 g (23%) of the more polar diastereomer (1*S*,2*S*)-**19c** as a white solid.

Analytical Data for (1*S*,2*S*)-**19c**

^{1}H NMR: (500 MHz, $CDCl_3$)

6.84 (br, 2 H, HC(4')), 6.58 (br, 4 H, HC(2')), 5.44-4.38 (m, 6 H, HC(1,2,1"), HN), 2.21 (s, 12 H, Me(Ar)), 2.10-0.36 (m, 36 H)

TLC: R_f 0.21 (CH_2Cl_2/Et_2O, 39/1)

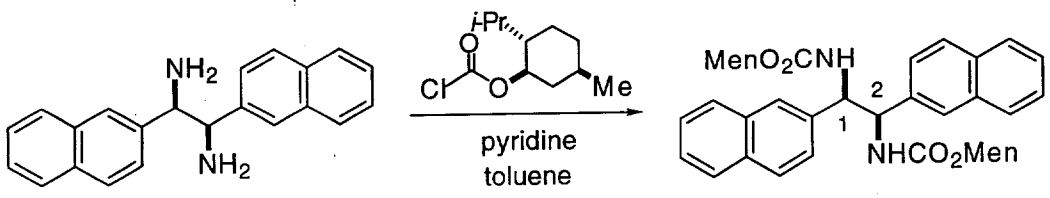
Analytical Data for (1*R*,2*R*)-**19c**

^{1}H NMR: (500 MHz, $CDCl_3$)

6.82 (S, 2 H, HC(4')), 6.64 (S, 4 H, HC(2')), 5.44 (br, 2 H, HN), 4.85 (br, AB, 2H, HC(1,2)), 4.52 (dt, J = 10.5, 4.2, 2 H, HC(1")), 2.20 (s, 12 H, Me(Ar)), 2.16-0.80 (m, 30 H), 0.68 (d, 6 H, J = 6.8, Me)

TLC: R_f 0.35 (CH_2Cl_2/Et_2O, 39/1)

N,N'-Bis-((−)menthoxycarbonyl)-1,2-di-(2-naphthyl)-1,2-ethanediamine (19e).



(±)**18e** **19e**

Following General Procedure V from 4.50 g (14.4 mmol) of (±)-**18e**, 7.72 mL (36.0 mmol, 2.5 mmol) of (−)-menthyl chloroformate and pyridine (3.34 mL, 43.2 mmol, 3.0 equiv) in toluene (70 mL) was obtained 7.31 g (75%) of the crude biscarbamates as a pale yellow solid, which were separated and purified by column chromatography (SiO_2, CH_2Cl_2/Et_2O, 40/1) to give 1.42 g (15%) of the less polar diastereomer (1*R*,2*R*)-**19e**.

Analytical Data for (1*R*,2*R*)-**19e**

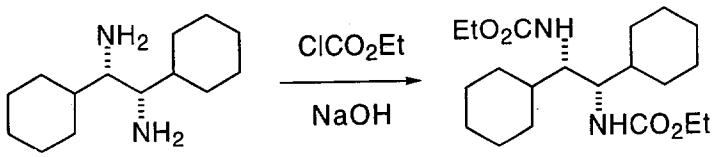
^{1}H NMR: (500 MHz, $CDCl_3$)

7.84-7.16 (m, 14 H, Ar), 5.68 (br, 2 H, HN), 5.24 (m, 2 H, HC(1,2)), 4.52 (dt, J = 10.2, 3.9, 2 H, HCO), 2.16-0.80 (m, 30 H), 0.65 (d, J = 7.1, 6 H, Me)

TLC: R_f 0.52 (SiO_2, CH_2Cl_2/Et_2O, 40/1)

(R_f 0.38 (SiO_2, CH_2Cl_2/Et_2O, 40/1) for diastereomer, ((*1S*,*2S*)-**19e**)

(1*S*,2*S*)-(–)-*N*,*N*'-Bis-(ethoxycarbonyl)-1,2-dicyclohexyl-1,2-ethanediamine-(19f)



18f **19f**

To a mixture of the diamine **18f** (1.55g, 6.91 mmol)[6] in benzene (30 mL) and aqueous sodium hydroxide solution (6 M, 10 mL) was added ethyl chloroformate (1.4 mL, 14.7 mmol, 2.1 equiv) and the mixture was stirred at rt for 5 h. Another portion of ethyl chloroformate (1.4 mL, 14.7 mmol, 2.1 equiv) was added and mixture stirred for 5 h. The layers were separated and aqueous layer extracted with ether (2×20 mL). The combined organic solution was washed (brine, 20 mL), dried (Na_2SO_4), and concentrated in vacuo. The resulting white foam was run through a plug of silica gel and recrystallized from hexane to give 2.05 g (80%) of **19f** as colorless needles.

Analytical Data for (–)-(1*S*, 2*S*)-**19f**

M.W. 368.52

mp: 123-125 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

major rotamer: 4.73 (d, J = 8.6, 2 H, HN), 4.18-4.00 (m, 4 H, H(1")), 3.60-3.48 (m, 2 H, HC(1)), 1.80-1.60 (m, 10 H, HC(1', 2')), 1.22 (t, J = 7.0, 6 H, Me), 1.38-0.90 (m, 12 H, HC(3', 4'));

minor rotamer: 5.40-5.20, 5.16-5.05, 4.24-4.18, 1.96-1.80, 1.46-1.38

^{13}C NMR: (125 MHz, $CDCl_3$)

major conformer: 157.41 (C=O), 60.77 (C(1")), 56.66 (C(1)), 39.04 (C1')), 30.56 (CH_2), 27.38 (CH_2), 26.27 (CH_2), 26.14 (CH_2), 26.08 (CH_2), 14.15 (Me);

minor conformer: 61.29, 55.90, 39.64, 30.18, 28.98, 28.82, 25.93

IR: ($CHCl_3$)

3436 (m), 3363 (w), 2985 (m), 2930 (s), 2855 (s), 1712 (s), 1519 (m), 1503 (m), 1480 (m), 1451 (m), 1417 (w), 1380 (m), 1370 (w), 1343 (m), 1338 (m), 1320 (m), 1300 (m), 1279 (m), 1247 (m), 1215 (w), 1201 (w), 1190 (w), 1172 (w), 1144 (w), 1106 (m), 1097 (m), 1079 (m), 1073 (m), 1062 (m), 1038 (w)

MS: (EI, 70 eV)

369 (M^++1, 5), 185 (16), 184 (100), 183 (22), 102 (27), 95 (15)

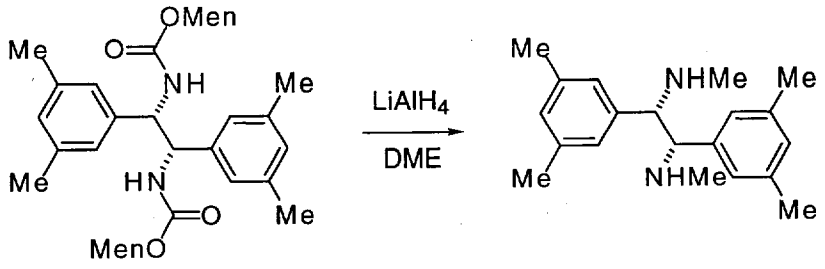
TLC: R_f 0.58 (TBME/MeOH, 49/1)

Optical Rotation: $[\alpha]_D^{22}$ = -27.5° (c = 1.23, $CHCl_3$)

Analysis: $C_{20}H_{36}N_2O_4$

Calcd:	C, 65.19%;	H, 9.85%;	N, 7.60%.
Found:	C, 65.18%;	H, 9.90%;	N, 7.54%.

General Procedure VI: Reduction of Carbamates. Preparation of (*S,S*)- (–)-*N,N'*-Dimethyl-1,2-bis-(3,5-dimethylphenyl)-1,2-ethanediamine (20c).



19c (–)-**20c**

To a solution of the biscarbamate **19c** (1.0 g, 1.58 mmol) in DME (60 mL) was added $LiAlH_4$ (600 mg, 15.8 mmol) portionwise at 0 °C. The reaction mixture was then heated to reflux for 20 hours before it was cooled to 0 °C. Water (1.7 mL) was added slowly and then the mixture was heated back to reflux. The white precipitate was filtered through a layer of Celite and washed

with fresh THF (3×20 mL). The filtrate was concentrated in vacuo and the residue was purified by column chromatography (SiO_2, TBME/MeOH/NH_3•H_2O, 95/5/0.5) to give 224 mg (48%) of (–)-**20c** as white crystals. An analytical sample was obtained by crystallization from hexane to give colorless needles.

Analytical Data for (–)- (**20c**)

mp: 126-127 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

6.80 (s, 2 H, HC(4')), 6.71 (s, 4 H, HC(2')), 3.51 (s, 2 H, HC(1)), 2.23, (s, 12 H, MeC(3')), 2.22 (s, 6 H, MeN), 1.71 (s, br, 2 H, HN)

^{13}C NMR: (125 MHz, $CDCl_3$)

140.70 (C(1)), 137.21 (C(3')), 128.49 (C(4)), 125.82 (C(2)), 70.55 (C(1)), 34.79 (MeN), 21.25 (Me-Ar)

IR: (KBr)

3294 (m), 3239 (m), 3006 (m), 2972 (m), 2960 (m), 2949 (m), 2926 (s), 2917 (s), 2881 (s), 2969 (m), 2847 (m), 2810 (w), 2789 (m), 1608 (s), 1493 (m), 1468 (m), 1447 (m), 1428 (s), 1412 (m), 1385 (w), 1376 (w), 1335 (w0, 1317 (w), 1156 (m), 1135 (m), 1114 (m), 1101 (m), 1037 (w), 949 (w), 934 (w), 918 (w), 908 (w), 893 (w), 885 (w), 871 (m), 846 (s), 713 (s), 703 (s), 691 (m), 671 (m), 619 (w)

MS: (CI)

297 (M^++1, 30), 296 (M^+, 9), 295 (M^+-1, 33), 267 (13), 266 (48), 149 (16), 148 (100)

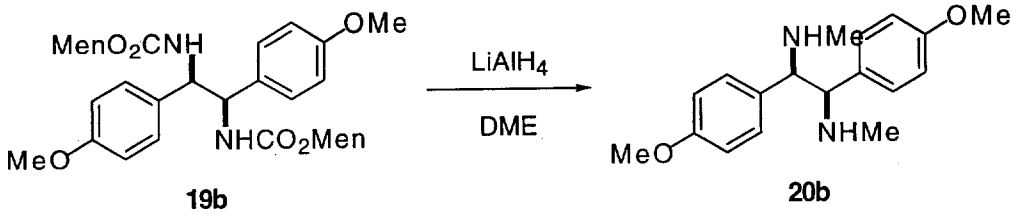
TLC: R_f 0.50 (TBME/MeOH/NH_3•H_2O, 90/10/1)

Optical Rotation: $[\alpha]_D^{22}$ = -6.3° (c = 1.00, $CHCl_3$)

Analysis: $C_{20}H_{28}N_2$ (296.48)

Calcd:	C, 81.03%;	H, 9.52%;	N, 9.45%.
Found:	C, 81.26%;	H, 9.58%;	N, 9.52%.

(+)-(1*R*,2*R*)-*N*,*N*'-Dimethyl-1,2-bis-4-methoxyphenyl)-1,2-ethanediamine (20b)



19b **20b**

Following General Procedure VI from the less polar carbamate **19b** (1.79 g, 2.81 mmol) and 1.07 g of $LiAlH_4$ the title compound was obtained in 586 mg (69%) of yield after recrystallization (hexane).

Analytical Data for **20b**

mp: 118-120 °C

^{1}H NMR: (500 MHz, $CDCl_3$)

6.93 (d, 4 H, J = 8.8, HC (2')), 6.71 (d, 4 H, HC(3')), 3.74 (s, 6 H, MeO), 3.46 (s, 2 H, HC(1)), 2.23 (s, 6 H, MeN), 1.83 (br, 2H, NH)

^{13}C NMR: (125 MHz, $CDCl_3$)

158.34 (C(4')), 133.03 (C(1')), 128.90 (C(2')), 113.28 (C(3')), 70.42 (C(1)), 55.05 (MeO), 34.48 (MeN)

IR: ($CHCl_3$)

3307 (w), 3001 (w), 2951 (s), 2939 (s),2912 (m), 2878 (m), 2853 (m), 2838 (m), 2797 (m), 2489 (w), 1611 (s), 1586 (m), 1511 (s), 1465 (m), 1457 (m), 1442 (m), 1417 (w), 1348 (w), 1332 (w), 1303 (m), 1280 (m), 1251 (s), 1176 (m), 1137 (m), 1109 (m), 1097 (m), 1036 (s), 886 (w), 857 (m), 831 (s), 660 (w)

MS: (EI, 70 eV)

300 (M^+, 3), 299 (M^+-1, 15), 271 (21), 270 (100), 162 (12), 151 (10), 150 (94)

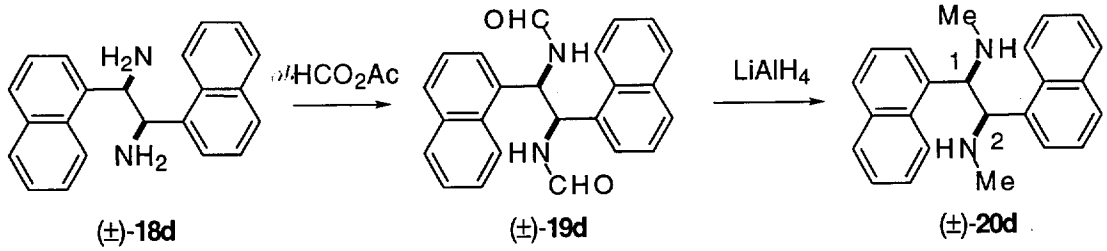
TLC: R_f 0.48 (TBME/MeOH/NH_3•H_2O, 100/5/1)

Optical Rotation: $[\alpha]_D^{22}$ = +36.4° (c = 1.01, $CHCl_3$)

Analysis: $C_{18}H_{24}N_2O_2$ (300.40)

Calcd:	C, 71.97%;	H, 8.05%;	N, 9.33%.
Found:	C, 71.69%;	H, 8.11%;	N, 9.22%.

(±)-*N,N'*-Dimethyl-1,2-di-(1-naphthyl)-1,2-ethanediamine (20d)



(±)-**18d** (±)-**19d** (±)-**20d**

To a solution of the diamine (±)-**18d** (410 mg, 1.312 mmol) in CH_2Cl_2 (10 mL) was added acetic formic anhydride[7] at 0 °C. White precipitate was generated immediately. The mixture was then allowed to warm to rt and was stirred for 4 h before it was poured into a separatory funnel containing 5% aqueous HCl (20 mL). The layers were separated and the organic layer washed with saturated aqueous $NaHCO_3$ (10 mL), brine (10 mL) and dried (Na_2SO_4). The solvent was removed in vacuo to give 474 mg (98%) of (±)-**19d** as a white solid, which was used directly for the following reduction step without further purification.

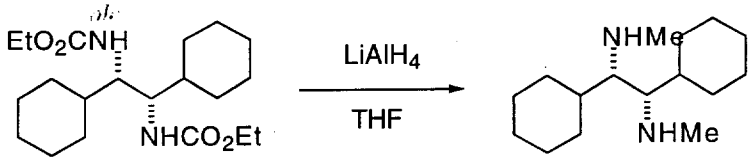
To a solution of the bisformamide (±)-**19d** (560 mg, 1.52 mmol) in DME (50 mL) was added $LiAlH_4$ (490 mg, 12.9 mmol, 8.5 equiv) in portions at 0 °C and the mixture was then heated to reflux for 1 h. The greenish mixture was cooled to 0 °C and quenched by adding H_2O (0.5 mL), 15% aqueous NaOH (0.5 mL) and H_2O (1.5 mL) in that order. The mixture was heated back to reflux and then was filtered and washed with THF (3×10 mL). The solvent was removed in vacuo and the white residue was recrystallized from hexane to give 370 mg (71%) of (±)-**20d** as a white solid.

Analytical Data for (±)-**20d**

^{1}H NMR: (500 MHz, $CDCl_3$)

8.21 (br, 2 H, Ar), 7.74-7.58 (m, 6 H, Ar), 7.40-7.28 (m, 6 H, Ar), 4.69 (s, 2 H, HC(1,2)), 2.22 (s, 6 H, Me), 2.08 (br, 2 H, HN)

Synthesis of (1*S*,2*S*)-*N*,*N*′-Dimethyl-1,2-dicyclohexyl-1,2-ethanediamine (20f)



19f **20f**

To a solution of the biscarbamate **19f** (2.32 g, 6.3 mmol) in THF (100 mL) was added lithium aluminum hydride and the mixture was heated to reflux for 52 h. The mixture was cooled to 0°C and water (2.4 mL), 15% NaOH (2.4 mL), and water (7.2 mL) were added in that order. The mixture was heated to reflux and filtered. The filtrate was concentrated and residue purified by column chromatography (SiO_2, TBME/MeOH/NH_3•H_2O, 40/20/1) to give 610 mg (38%) of **20f** as an oil, which was distilled (Kugelrohr) to give 488 mg (30%) colorless oil.

Analytical Data for (+)-**20f**

bp: 175-180 °C (ABT, 0.01 mmHg)

^{1}H NMR: (500 MHz, $CDCl_3$)

2.36 (s, 6 H, Me), 2.08 (d, J = 3.8, 2 H, HC(1)), 1.78-1.68 (m, 6 H, HC(1', 2')), 1.68-1.58 (m, 4 H), 1.42-1.38 (m, 2 H), 1.26 -0.92 (m, 12 H)

^{13}C NMR: (125 MHz, $CDCl_3$)

64.85 (C(1)), 41.54 (C(1')), 36.64 (C(2')), 29.84 (Me), 29.23 (C(3')), 26.77 (C(4'))

IR: ($CHCl_3$)

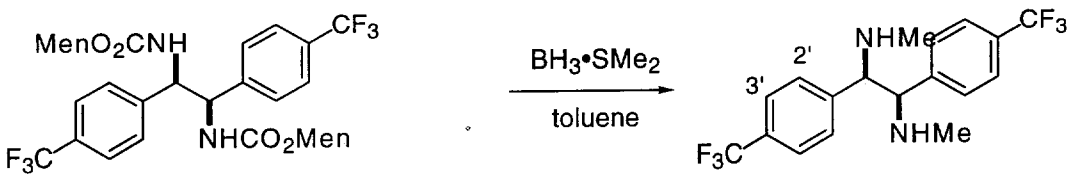
2927 (s), 2854 (s), 2796 (w), 1604 (w), 1449 (m), 1265 (w), 1349 (w), 1325 (w), 1300 (w), 1264 (w), 1130 (w), 1096 (w), 949 (w), 892 (w), 869 (w), 658 (w)

MS: (CI)

253 (M^++1, 40), 251 (M^+-1, 31), 222 (21), 169 (16), 127 (11), 126 (100), 86 (25), 84 (40)

Optical Rotation: $[\alpha]_D^{22} = +33.4°$ (c = 1.58, $CHCl_3$)

General Procedure VII: Reduction of Biscarbamates with Borane-Dimethylsulfide. (*R,R*)-(–)-*N,N'*-Dimethyl-1,2-bis-(4-trifluoromethyl-phenyl)-1,2-ethanediamine (20a)



19a **20a**

A solution of (1*R*,2*R*)-**19a** (468 mg, 0.657 mmol) and borane-dimethyl sulfide (10 M, 0.66 mL, 6.57 mmol, 10 equiv) in toluene (60 mL) was heated to reflux under nitrogen for three days. The reaction was quenched by adding aqueous HCl (6 M, 5 mL) at rt and heated back to reflux. The mixture was basified with aqueous NaOH (12 M, 5 mL) at rt and the phases were separated. The aqueous phase was extracted with ether (3×10 mL) and the organic phases were washed with brine (20 mL) and dried (K_2CO_3). The solvent was removed in vacuo and the residue purified by column chromatography (SiO_2, Et_2O saturated with aqueous ammonia) to give 125 mg (51%) of (1*R*,2*R*)-**20a** as a colorless oil .

Analytical Data for (1*R*,2*R*)-**20a**

^{1}H NMR: (500 MHz, $CDCl_3$)

7.43 (d, J = 8.1, 4 H, HC(3')), 7.13 (d, J = 8.1, 4 H, HC(2')), 3.57 (s, 2 H, HC(1)), 2.24 (s, 6 H, Me), 1.90 (br, 2 H, HN)

^{13}C NMR: (125 MHz, $CDCl_3$)

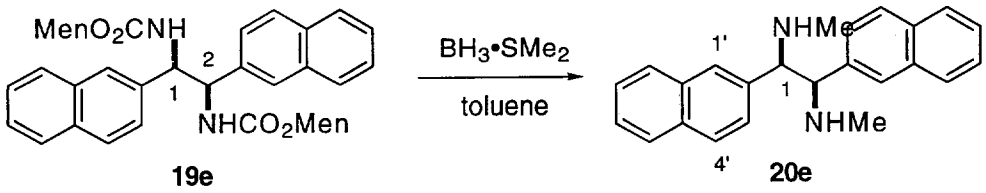
128.17 (C(2')), 125.07 (d, J = 3.7, C(3')), 70.17 (C(1)), 34.47 (Me)

^{19}F NMR: (125 MHz, $CDCl_3$)

–64.10

TLC: R_f 0.26 (Et_2O (saturated with 37% $NH_3 \cdot H_2O$))

(*R,R*)-(–)-*N,N'*-Dimethyl-1,2-bis-(4-trifluoromethyl-phenyl)-1,2-ethanediamine (20e)



According to General Procedure VII from (1*R*,2*R*)-**19e** (1.40 g, 2.07 mmol) and borane-dimethyl sulfide (10 M, 2.1 mL, 20.7 mmol, 10 equiv) in toluene (50 mL), refluxing under nitrogen for two days, was obtained 488 mg (69%) of (1*R*,2*R*)-**20e** as off-white solid after column chromatography (SiO_2, CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$, 95/5/1).

Analytical Data for (1*R*,2*R*)-**20e**

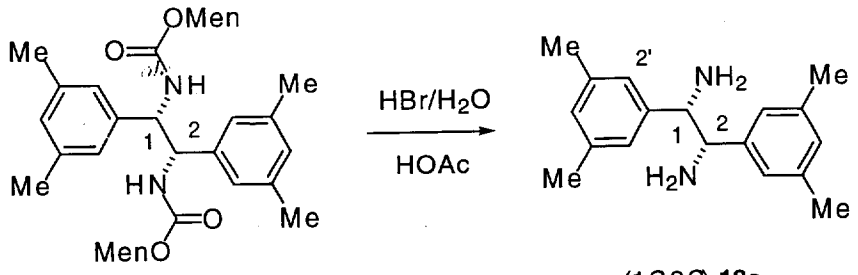
^{1}H NMR: (500 MHz, $CDCl_3$)

7.76-7.66 (m, 4 H, Ar), 7.65 (d, J = 8.6, 2 H, HC(4')), 7.58 (s, 2 H, HC(1')), 7.41-7.37 (m, 4 H, Ar), 7.25 (d, J = 1.8, 2 H, Ar), 3.87 (s, HC(1)), 2.27 (s, 6 H, Me), 2.0 (br, 2 H, HN)

TLC: R_f 0.21 (SiO_2, CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$, 97/3/1)

Miscellaneous Reactions

Hydrolysis of (1*S*,2*S*)-*N*,*N*'-Bis-((−)menthoxycarbonyl)-1,2-bis-(3,5-dimethylphenyl)-1,2-ethanediamine (19c): Confirmation of the Absolute Configuration of the Diamine 18c.



19c (1*S*,2*S*)-**18c**

A mixture of the biscarbamate **19c** (the more polar diastereomer, 63.3 mg, 0.1 mmol), glacial acetic acid (2 mL) and 48% hydrobromic acid (2 mL) was heated to reflux overnight (23 h) under nitrogen. The solvent was then removed in vacuo and the residue partition between ether (10 mL) and water (10 mL). The layers were separated and the ethereal phase was extracted with 5% aqueous HCl. The combined aqueous solution was washed with ether (2 mL) and then basified with 12 M aqueous NaOH and extracted with CH_2Cl_2 (3×3 mL). The organic phase was washed with brine, dried (K_2CO_3) and concentrated in vacuo to give 20 mg (75%) of white crystals: $[\alpha]_D^{22} = -55°$ (c = 2.0, $CHCl_3$) (lit. $[\alpha]_D^{22} = -75.4°$ (c = 0.94, $CHCl_3$),[8] $[\alpha]_D^{22} = -43.4°$(c = 0.82, $CHCl_3$).[5] Since the absolute configuration of (−)-**18c** was established to be (1*S*,2*S*) by *X*-ray of its derivative,[9] the absolute configuration of **19c** is established to be (1*S*,2*S*) by this experiment. The absolute configuration of other diamines resolved by the biscarbamate method are deduced from the comparison of the ^{1}H NMR spectra and *Rf* values of their biscarbamate to those of (1*R*,2*R*)-**19c** and (1*S*,2*S*)-**19c**.

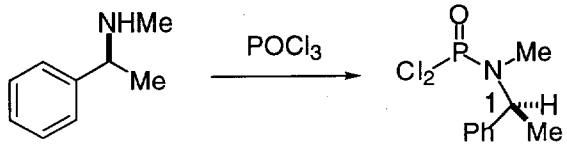
Analytical Data for (1*S*,2*S*)-**18c**

^{1}H NMR: (500 MHz, $CDCl_3$)

6.98 (s, 4 H, HC(2')), 6.89 (s, 2 H, HC(4')), 4.09 (s, 2 H, HC(1,2), 2.32 (s, 12 H, Me), 1.61 (br, 4 H, H_2N)

Optical Rotation: $[\alpha]_D^{22} = -55^\circ$ (c = 2.0, $CHCl_3$)

Preparation of *N*-Methyl-1-Benzenethanaminophosphoramic Dichloride



(*S*)-α-Methylbenzylamine (0.90 g, 6.65 mmol) was added dropwise to phosphorus oxychloride (2.48 mL, 4.08 g, 26.62 mmol) at 0 °C under an atmosphere of nitrogen. The white suspension was heated at reflux for 18 h the excess phosphorus oxychloride was removed by distillation at atmospheric pressure. The residue was distilled (Kugelrohr) to afford 0.80 g (48%) of the title compound as a white solid.

Analytical data for **50**:

bp: 170-175 °C (ABT, 0.1 mmHg)

^{1}H NMR: (400 MHz, $CDCl_3$)

7.40 - 7.30 (m, 5H, CH(Ar)), 5.39 (dq, *J* = 11.0, 6.8, 1H, HC(1)), 2.55 (d, *J* = 16.1, 3H, MeN), 1.63 (d, *J* = 7.1 MeC(1))

^{13}C NMR: (100 MHz, $CDCl_3$)

138.70 (d, *J* = 6.1, C(Ar)), 128.59 (CH(Ar)), 127.95 (CH(Ar)), 127.45 (CH(Ar)), 55.00 (d, *J* = 3.8, CHN), 28.02 (d, *J* = 5.3, CH_3N), 16.32 (d, *J* = 3.1, MeC(1))

^{31}P NMR: (162 MHz, $CDCl_3$)

18.36

IR: (Film)

3033 (w). 2979 (m), 1495 (m), 1453 (m), 1381 (m), 1287 (s), 1219 (m), 1202 (m), 1142 (m), 1046 (m), 1028 (m), 994 (s), 945 (s), 785 (m)

MS: (70 eV)

254 (M^+(^{37}Cl, ^{35}Cl), 31), 252 (M^+(^{35}Cl), 46), 238 (28), 236 (42), 134 (73), 133 (75), 132 (28), 118 (93), 105 (100), 104 (20), 77 (20)

Optical Rotation: $[\alpha]_D^{22} = -24.37°$ (c = 1.06, $CHCl_3$)

Analysis: $C_9H_{12}Cl_2NOP$ (252.08)

Calcd:	C, 42.88;	H, 4.80;	N, 5.56;	Cl, 12.29;	P, 28.10.
Found:	C, 43.03;	H, 4.86;	N, 5.55;	Cl, 12.18;	P, 27.96.

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