Chiral Phosphoramide Catalyzed Aldol Additions of Ketone Trichlorosilyl Enolates. Mechanistic Aspects

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SUPPORTING INFORMATION

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General Experimental

^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz, respectively. Spectra are referenced to residual chloroform (δ 7.26, ^{1}H; δ 77.0, ^{13}C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz. ^{1}H and ^{13}C NMR assignments are corroborated by 2D experiments (HETCOR and COSY). Purity criteria for new compounds was established by microanalysis where possible. Otherwise, HRMS was obtained for elemental formula and P-31 NMR (>60/1 S/N) H-1 NMR (>100/1 S/N) data for purity (>98%). This criterion also applies to all the products of allylation which are known compounds (purity also assured by SFC and GC analysis). Spectra

are available on request from denmark@scs.uiuc.edu.

Mass spectrometric data are reported in the form of *m*/*z* (intensity relative to base peak = 100). Infrared spectra (IR) are reported in cm^{-1} with the indicated relative intensities: br (broad); s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Optical rotations are reported as follows: $[\alpha]_D^T$ temperature (T), concentration (c = g/100 mL) and solvent. Analytical supercritical fluid chromatography (SFC) was performed on packed-column SFC with a built-in photometric detector (λ = 220 nm) using a Daicel Chiralpak AD, AS, OD or OJ column, as indicated. Kugelrohr (bulb-to-bulb) distillation boiling points (bp) correspond to uncorrected air-bath temperatures (ABT). All temperatures correspond to internal reaction temperatures measured by Teflon-coated thermocouples unless otherwise noted.

^1H NMR spectra for all kinetic runs were recorded at 500 MHz using a 5 mm ^{15}N – ^{31}P broad band (BB) probe, in methylene chloride-d_2 unless otherwise stated. Tredicator temperatures were calibrated using standard methods involving ethylene glycol and methanol as needed. Analytical gas chromatography (GC) was performed using a flame ionization detector and a Hewlett-Packard HP-5 (50 meter) column or a Hewlett-Packard Ultra-2 (50 meter) column. The injector temperature was 225 °C (set to 160 °C for all kinetic experiments). The detector temperature was 300 °C with a split ratio of approximately 100:1.

All reactions were performed using oven (140 °C) and/or flame-dried glassware under an atmosphere of dry nitrogen, unless otherwise stated. Solvents and commercial reagents were purified using established procedures prior to use, with the exception of methylene chloride-d_2, which was used directly from the ampoule.

Fourier transform IR analysis was performed using a ReactIR™ 1000 fitted with a ⅝" DiComp™ Probe. Mettler-Toledo AutoChem Inc., 7075 Samuel Morse Drive, Columbia, MD, 21046 USA, or visit http://us.mt.com. Acquisitions were recorded using software version 2.1a. Small-volume, flat-bottomed reaction vessels fitted with multiple side arms were designed to mount tightly around the IR probe. In this manner, the mounted reaction vessel could be carefully flame-dried under vacuum and purged with an inert gas, in our case dry nitrogen. 1,2-Dichloroethane was then carefully introduced via syringe. The appropriate background scans were taken following thermal equilibration.

Rapid Injection NMR (RINMR) analysis was performed on a home-built apparatus. For details contact denmark@scs.uiuc.edu. Samples were prepared for RINMR analysis in the

following manner. A carefully dried NMR tube was charged with the desired amount of catalyst and fitted with a small septum. The tube was then placed under vacuum and purged several times with dry nitrogen. Dichloromethane-d_2 was then added via syringe followed by **4**. The NMR tube was quickly vortexed to ensure homogeneity and placed into a short Dewar flask at -78 ºC. Several tubes could be prepared and stored in this manner to allow sequential collection of the desired kinetic data. The septum is then removed from the cooled NMR tube and it is quickly lowered into a precooled NMR magnet. The RINMR injection probe is then carefully lowered into the open, spinning NMR tube and the entire apparatus is allowed to equilibrate for several minutes. After equilibration, the desired amount of benzaldehyde in $CDCl_3$ is rapidly injected and is followed immediately by data collection.

Natural abundance ^{13}C NMR experiments were performed at 500 MHz spectrometer. To obtain the highest quality NMR data, the 90º pulse width (pw90) was determined by measuring the 360º pulse width and dividing by 4. Using this value, T1 was accurately measured and the NMR delay (d1) was set to 8× the longest T1. To assure an integration accuracy of ≤1%, a sufficient number of transients were collected to achieve a signal-to-noise of not less than 250:1 as measured using the shortest peak. Integration was standardized by selecting a region 20× the peak width at half-height, centered about the peak in question.

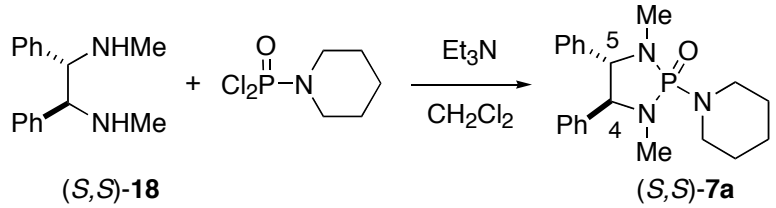
Literature Preparations. The following compounds were prepared following the literature methods.

(*S,S*)- and (*R,R*)-1,2-Diphenyl-1,2-ethanediamine,[1] (*S,S*)-*N,N′*-dimethyl-1,2-diphenyl-1,2-ethanediamine and all other chiral diamines not listed,[2] (*S,S*)-*N,N′*-diethyl-1,2-diphenyl-1,2-ethanediamine,[3] (*R,R*)- and (*S,S*)-*N,N*'-1,2-tetraphenylethylene diamine,[4] 1-piperidinophosphoric dichloride,[5] 1-pyrrolidinylphosphoramic dichloride,[5] 1-piperidinophosphorus dichloride,[5] di-*iso*-propylaminophosphorus dichloride,[5] diphenylaminophosphamic dichloride.[6]

Procedures.

Preparation of Phosphoramide Promoters.

Representative Procedure I: Synthesis of Phosphoramides from Aminophosphoryl Dichlorides. (4*S*,5*S*)-(+)-1,3-Dimethyl-4,5-diphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide ((*S*,*S*)-7a)



(*S*,*S*)-**18** (*S*,*S*)-**7a**

To a solution of (*S*,*S*)-*N*,*N*'-dimethyl-1,2-diphenyl-1,2-ethanediamine (*S*,*S*)-**18**[2] (3.53 g, 14.7 mmol) and triethylamine (5.2 mL, 37.1 mmol, 2.5 equiv) in CH_2Cl_2 (300 mL) was added *N*-piperidinophosphoric dichloride (2.4 mL, 15.6 mmol, 1.05 equiv). The solution was heated to reflux under nitrogen for 44 h and then was cooled to rt. The solution was washed with 5% aq. HCl (2 X 50 mL) and sat. aq. $NaHCO_3$ solution (60 mL) and was dried (Na_2SO_4), filtered and concentrated on a rotavap. The residue was purified by column chromatography (SiO_2, EtOAc/*i*-PrOH, 19/1) and was recrystallized from hexane to afford 3.15 g (58%) of (*S*,*S*)-**7a** as white needles.

Analytical Data for (*S*,*S*)-**7a**:

mp: 110-111 ˚C (hexane)

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

7.30-7.26 (m, 6 H, 2 X *m*-, *p*-Ph), 7.13-7.10 (m, 2 H, *o*-Ph), 7.07-7.02 (m, 2 H, *o*-Ph), 3.94 (d, *J* = 8.8, 1 H, HC(4)), 3.89 (d, *J* = 9.0, 1 H, HC(5)), 3.33-3.24 (m, 4 H, HC(1')), 2.38 (d, *J* = 9.5, 3 H, NMe), 2.37 (d, *J* = 9.2, 3 H, NMe), 1.72-1.54 (m, 6 H, (HC(2',3'))

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

138.5 (d, *J* = 9.9, *ipso*-Ph), 138.3 (d, *J* = 6.1, *ipso*-Ph), 128.4 (*m*-Ph), 127.96 (*m*-Ph), 127.89 (*o*-Ph), 127.6 (*o*-Ph), 72.4 (d, *J* = 11.5, C(4)), 70.5 (d, *J* = 10.7, C(5)), 45.4 (d, *J* = 3.1, C(1')), 30.1 (d, *J* = 2.3, NMe), 29.5 (d, *J* = 4.6, NMe), 26.8 (d, *J* = 3.8, C(2')), 24.8 (C(3'))

^{31}P NMR: (122 MHz, $CDCl_3$)

27.35

IR: ($CHCl_3$)

3067 (w, CH), 3036 (w, CH), 3020 (w, CH), 3012 (w, CH), 2979 (m, CH), 2959 (m, CH), 2939 (s, CH), 2853 (m, CH), 2818 (w, CH), 1497 (w), 1469 (w), 1456 (m), 1446 (w), 1376 (w), 1359 (w), 1339 (w), 1294 (w), 1280 (w), 1241 (s), 1221 (w), 1207 (m), 1180 (s), 1162 (s), 1125 (w), 1071 (m), 1039 (w), 1019 (m), 998 (m), 962 (s), 833 (w), 810 (w), 775 (w), 768 (w), 700 (s)

MS: (EI, 70 eV)

369 (M^+, 26), 250 (23), 166 (15), 165 (12), 120 (32), 119 ($C_8H_9N^+$, 36), 118 (87), 84 ($C_5H_{10}N^+$, 100), 60 (19), 43 (17), 42 (12)

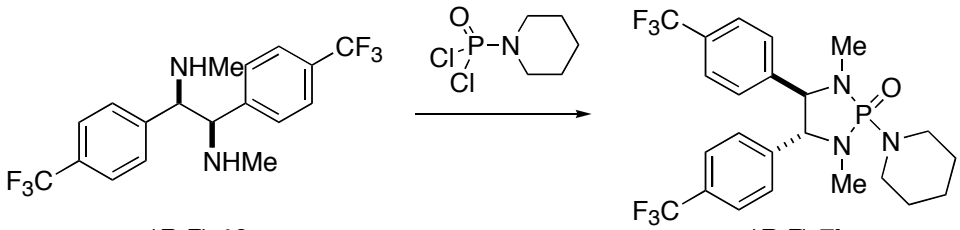
TLC: R_f 0.42 (EtOAc/*i*-PrOH, 9/1)

Opt. Rot.: $[\alpha]_D^{22}$ +18.2 (c = 1.3, $CHCl_3$)

Analysis: Calcd for $C_{21}H_{28}N_3OP$ (369.45)

Calculated:	C, 68.27%;	H, 7.64%;	N, 11.37%;	P, 8.38%
Found:	C, 68.00%;	H, 7.68%;	N, 11.31%;	P, 8.23%

(+)-(4*R*,5*R*)-1,3-Dimethyl-4,5-bis-(4-trifluoromethyl-phenyl)-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*R*,*R*)-7b.



(*R*,*R*)-**19** (*R*,*R*)-**7b**

Following Representative Procedure I from triethylamine (230 μL, 1.64 mmol, 4.5 equiv), (*R*,*R*)-**19**[2] (137 mg, 0.364 mmol) and piperidinophosphoric dichloride (61 μL, 0.4 mmol, 1.1 equiv) in 70 mL of CH_2Cl_2 was obtained 75 mg (41%) of (*R*,*R*)-**7b** as white needles after column chromatography (SiO_2, TBME/MeOH, 19/1) and recrystallization (hexane).

Analytical Data for (+)-(*R*,*R*)-**7b**:

M.W.: 505.45

mp: 138-139 ˚C (hexane)

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

7.58 (d, *J* = 8.0, 2 H, HC(3')), 7.57 (d, *J* = 7.8, 2 H, HC(3')), 7.26 (d, *J* = 7.8, 2 H, HC(2')), 7.17 (d, *J* = 8.1, 2 H, HC(2')), 3.98 (d, *J* = 8.7, 1 H, HC(4)), 3.92 (d, *J* = 8.7, 1 H, HC(5)), 3.32-3.22 (m, 4 H, HC(1")), 3.38 (d, *J* = 10.4, 3 H, Me), 3.37 (d, *J* = 9.2, 3 H, Me), 1.73-1.63 (m, 2 H, HC(3")), 1.63-1.56 (m, 4 H, HC(2")).

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

142.3 (d, *J* = 10.3 (C(1')), 142.2 (d, *J* = 6.6, C(1')), 130.7 (q, *J* = 32.2, C(4')), 128.2 (C(2')), 127.9 (C(2')), 125.7 (br, C(3')), 123.98 (q, *J* = 272.6, CF_3), 123.90 (q, *J* = 271.7, CF_3), 71.7 (d, *J* = 11.0, C(4)), 70.0 (d, *J* = 11.1, C(5)), 45.6 (d, *J* =2.8, C(1")), 30.4 (d, *J* = 2.8, Me), 29.6 (d, *J* = 4.6, Me), 26.8 (d, *J* = 3.7, C(2")), 24.7 (C(3")).

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

–64.18, –64.22.

^{31}P NMR: (202 MHz, $CDCl_3$)

29.54

IR: ($CHCl_3$)

2981 (w), 2940 (w), 2880 (w), 2842 (w), 2820 (w), 1620 (w), 1467 (w), 1447 (w), 1419 (w), 1368 (w), 1325 (s), 1310 (w), 1300 (w), 1288 (w), 1244 (w), 1167 (m), 1132 (s), 1107 (m), 1068 (s), 1038 (w), 1017 (w), 1002 (w), 962 (m), 856 (w), 836 (w).

MS: (CI)

534 (M^++29, 29), 507 (M^++2, 24), 506 (M^++1, 95), 505 (M^+, 17), 504 (M^+-1, 14), 487 (26), 486 (M^+-F, 100), 84 (35).

HRMS: (CI)

Calcd. for ($C_{23}H_{27}F_6N_3OP$)	506.1796
Found:	506.1790

Opt. Rot.: $[\alpha]_D^{22}$ +0.6 ($CHCl_3$, c = 2.10) (+24.2 at 405 nm.)

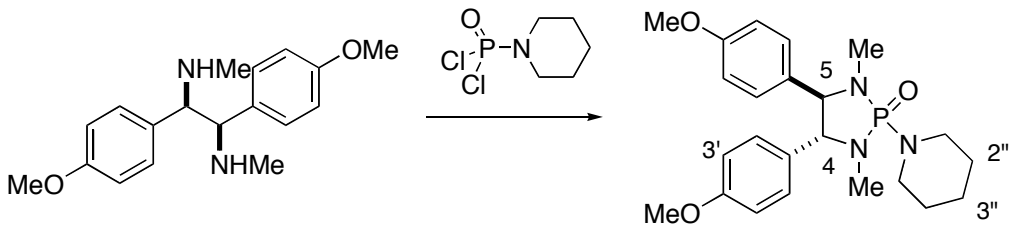
TLC: R_f 0.38 (TBME / MeOH, 20/1)

HPLC: t_R ((4*R*,5*R*)-**134a**) 20.73 min (Daicel ChiralCel AD, hexane/EtOH, 97/3, 0.5 mL/min)

Analysis: $C_{23}H_{26}F_6N_3OP$

Calcd:	C,	54.66%;	H,	5.18%; N,	8.31%.
Found:	C,	54.75%;	H,	5.22%; N,	7.84%.

(+)-(4*R*,5*R*)-1,3-Dimethyl-4,5-bis(4-methoxyphenyl)-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*R,R*)-7c.



(*R,R*)-**20** (*R,R*)-**7c**

To a solution of the diamine (*R,R*)-**20**[2] (523 mg, 1.74 mmol) and triethylamine (610 μL, 4.35 mmol, 2.5 equiv) in CH_2Cl_2 (160 mL) was added piperidinophosphoryl dichloride (280 μL, 1.83 mmol, 1.05 equiv) at 0 ˚C. The solution was then heated to reflux for 37 h and another portion of the dichloride (140 μL, 0.9 mmol, 0.52 equiv) was added. The reaction mixture was heated to reflux for 8 h further and then was poured into 5% aq. HCl (20 mL). The phases were separated and the organic phase was washed with sat. aq. $NaHCO_3$ solution (20 mL) and brine (20 mL), and then was dried (Na_2SO_4) filtered and concentrated on a rotovap. The residue was purified by column chromatography (EtOAc/*i*-PrOH, 9/1) to afford 560 mg (75%) of a white foam, which was recrystallized (hexane) to give 251 mg (34%) of (*R,R*)-**7c** as white crystals.

Analytical Data for (+)-(*R,R*)-**7c**:

M.W.: 429.50

mp: 115-117 ˚C (hexane)

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

7.03 (d, *J* = 8.1, 2 H, HC(2')), 6.95 (d, *J* = 8.8, 2 H, HC(2')), 6.80 (d, *J* = 8.8, 2 H, HC(3')), 6.79 (d, *J* = 8.8, 2 H, HC(3')), 3.85 (d, *J* = 9.0, 1 H, HC(4)), 3.79 (d, 1 H, HC(5)), 3.78 (s, 3 H, MeO), 3.78 (s, 3 H, MeO), 3.26-3.20 (m, 4 H, HC(1")), 2.34 (d, *J* = 10.2, 3 H, MeN), 2.33 (d, *J* = 9.5, 3 H, MeN), 1.68-1.54 (m, 6 H, HC (2", 3")).

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

159.23 (C(4')), 159.21 (C(4')), 130.4 (d, *J* =9.9, C(1')), 130.3 (d, *J* = 5.9, C(1')), 129.0 (C(2')), 128.7 (C(2')), 113.72 (C(3')), 113.62 (C(3')), 72.1 (d, *J* = 10.7 C(4)), 70.2 (d, *J* = 10.7, C(5)), 55.2 (MeO), 45.6 (d, *J* = 2.3, C(1")), 30.0 (d, *J* = 3.1, MeN), 29.4 (d, *J* = 4.6, MeN), 26.8 (d, *J* = 3.1, C(2")), 24.8 (C(3")).

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

27.11

IR: ($CHCl_3$)

3020 (w), 2958 (m), 2938 (m), 2879 (w), 2851 (m), 2840 (m), 2817 (w), 1613 (m), 1587 (w), 1513 (s), 1464 (m), 1443 (m), 1303 (w), 1289 (w), 1246 (s), 1213 (w), 1173 (s), 1160 (s), 1070 (w), 1037 (m), 1022 (w), 997 (m), 961 (s), 849 (w), 839 (w), 833 (w), 796 (m), 747 (w), 773 (w).

MS: (EI, 70 eV)

429 (M^+, 8), 280 (5), 184 (10), 149 (26), 148 (12), 89 (28), 73 (100), 69 (12), 62 (46), 61 (12), 58 (46), 57 (12), 55 (17).

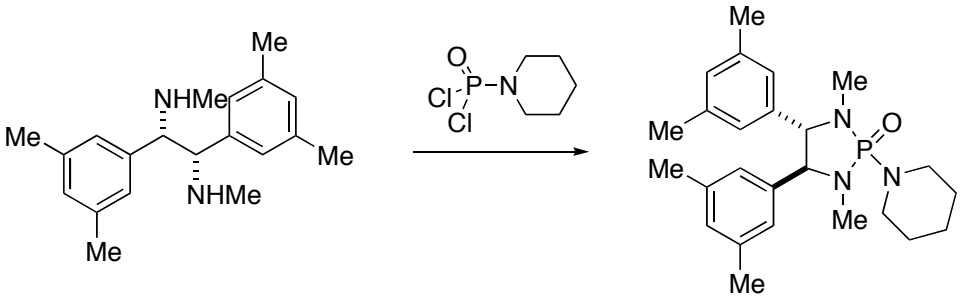
Opt. Rot.: $[\alpha]_D^{22}$ +49.9 ($CHCl_3$, c = 1.12)

TLC: R_f 0.32 (TBME/MeOH, 20/1)

Analysis: $C_{23}H_{32}N_3O_3P$

Calcd:	C,	64.32%;	H,	7.51%;	N, 9.78%;	P, 7.21%.
Found:	C,	64.18%;	H,	7.68%;	N, 9.66%;	P, 6.96%.

(+)-(4*S*,5*S*)-1,3-Dimethyl-4,5-bis(3,5-dimethylphenyl)-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*S*,*S*)-7d.



(*S*,*S*)-**21** (*S*,*S*)-**7d**

Following Representative Procedure I from triethylamine (185 μL, 1.33 mmol, 2.4 equiv), the diamine (*S*,*S*)-**21**[2] (164 mg, 0.55 mmol) and piperidinophosphoryl dichloride (86 μL, 0.56 mmol, 1.02 equiv) in 65 mL of CH_2Cl_2 was obtained 145 mg (62%) of (*S*,*S*)-**7d** as a white foam after column chromatography (SiO_2, TBME/MeOH, 19/1). An analytical sample was obtained by recrystallization from hexane.

Analytical Data for (*S*,*S*)-**7d**:

M.W.: 425.56

mp: 149-150 ˚C

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

6.91 (s, 1 H, HC (4')), 6.89 (s, 1 H, HC(4')), 6.74 (br, 2 H, HC(2')), 6.64 (s, 2 H, H(2')), 3.83 (d, *J* = 8.6, 1 H, HC(4)), 3.78 (d, *J* = 8.6, 1 H, HC(5)), 3.28-3.20 (m, 4 H, HC(1")), 2.37 (d, *J* = 10.2, 3 H, MeN), 2.36 (d, *J* = 9.1, 3 H, MeN), 2.25 (s, 3 H, Me-Ar), 2.24 (s, 3 H, Me-Ar), 1.70-1.56 (m, 6 H, HC(2", 3").

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

138.9 (d, *J* = 10.1 C(1')), 138.6 (d, *J* = 6.4, C(1')), 137.7 (C(3')), 129.52 (C(4')), 129.47 (C(4')), 125.6 (C(2')), 125.4 (C(2')), 72.1 (d, *J* = 11.0, C(4)), 70.3 (d, *J* = 11.0, C(5)), 45.6 (d, *J* = 2.8, C(1")), 30.2 (d, *J* = 3.7, MeN), 29.6 (d, *J* = 4.6, MeN), 26.8 (d, *J* = 3.7, C(2")), 24.8 (C(3")), 21.3 (Me-Ar), 21.2 (Me-Ar).

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

27.48

IR: ($CHCl_3$)

2981 (m), 2938 (s), 2853 (m), 2816 (w), 1609 (m), 1463 (m), 1446 (m), 1376 (m), 1359 (w), 1339 (m), 1305 (w), 1281 (w), 1258 (m), 1244 (w), 1156 (s), 1124 (w), 1071 (m), 1033 (w), 1022 (m), 998 (m), 961 (s), 923 (w), 857 (w), 822 (w), 701 (w), 660 (w), 608 (w).

MS: (EI, 70 eV)

426 (M^++1, 36), 425 (M^+, 97), 424 (M^+–1, 13), 410 (15), 344 (11), 340 (10), 320 (10), 279 (15), 278 (65), 263 (16), 194 (43), 193 (47), 148 (68), 147 (47), 146 (93), 132 (61), 119 (17), 84 (100), 60 (26).

Opt. Rot.: $[\alpha]_D^{22}$ +7.2 ($CHCl_3$, c = 1.00)

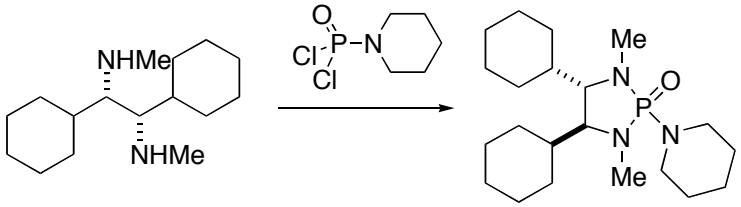
TLC: R_f 0.47 (TBME/MeOH, 20/1)

HPLC: t_R ((4*S*,5*S*)-**7d**) 9.93 min (Daicel ChiralCel AD, hexane/EtOH, 97/3, 0.5 mL/min)

Analysis: $C_{25}H_{36}N_3OP$

Calcd:	C,	70.56%;	H,	8.53%;	N, 9.87%.
Found:	C,	70.74%;	H,	8.63%;	N, 9.82%.

(+)-(4*S*,5*S*)-1,3-Dimethyl-4,5-dicyclohexyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*S*,*S*)-7e.



(*S*,*S*)-**22** (*S*,*S*)-**7e**

Following Representative Procedure I, to a solution of the diamine (*S*,*S*)-**22**[2] (230 mg, 0.911 mmol) and triethylamine (305 μL, 2.19 mmol, 2.4 equiv) in CH_2Cl_2 (100 mL) was added piperidinophosphoryl dichloride (153 μL, 0.929 mmol, 1.02 equiv) dropwise at 0 ˚C. The

solution was then heated to reflux for 66 h and then was poured into 5% aq. HCl solution. The phases were separated and the organic layer was washed with sat. aq. $NaHCO_3$ solution and brine then was dried (Na_2SO_4) and concentrated on a rotavap. The residue was purified by column chromatography (SiO_2, EtOAc/*i*-PrOH 19/1) to give 172 mg (49%) of (*S,S*)-**7e** as a white foam.

Analytical Data for (*S,S*)-**7e**

M.W.: 381.55

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

3.18-2.98 (m, 4 H, H(1")), 2.64 (d, *J* = 16.1, 1 H, HC(4)), 2.52 (d, *J* = 9.1, 3 H, Me), 2.51 (d, *J* = 2.7, 3 H, Me), 2.35 (dd, *J* = 7.3, 7.1, 1 H, HC(5)), 1.97 (d, *J* = 12.8, 1 H), 1.86 (d, *J* = 12.3, 1 H), 1.80-0.90 (m, 26 H, CH_2).

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

66.9 (d, *J* = 15.7, C(4)), 66.0 (d, *J* = 11.0, C(5)), 45.4 (d, *J* = 2.8, C(1")), 45.0 (d, *J* = 2.8, C(1')), 41.0 (C(1')), 33.7 (d, *J* = 5.5, Me), 30.6 (d, *J* = 6.4, Me), 30.1, 29.6, 29.1, 27.7, 26.8 (d, *J* = 3.7, C(2")), 26.52, 26.45 (d, *J* = 3.7, C(2")), 26.3, 26.2, 24.9 (C(3")).

^{31}P NMR: (202 MHz, $CDCl_3$)

27.48

IR: ($CHCl_3$)

2931 (s), 2854 (s), 1450 (m), 1374 (w), 1358 (w), 1338 (w), 1301 (w), 1260 (w), 1249 (w), 1161 (s), 1124 (w), 1070 (m), 1027 (w), 1008 (w), 977 (w), 961 (m), 896 (w).

MS: (CI)

410 (M^++29, 16), 383 (M+2, 24), 382 (M+1, 100), 381 (M+, 11), 380 (M-1, 45), 299 (15), 298 (87).

HRMS: (CI)

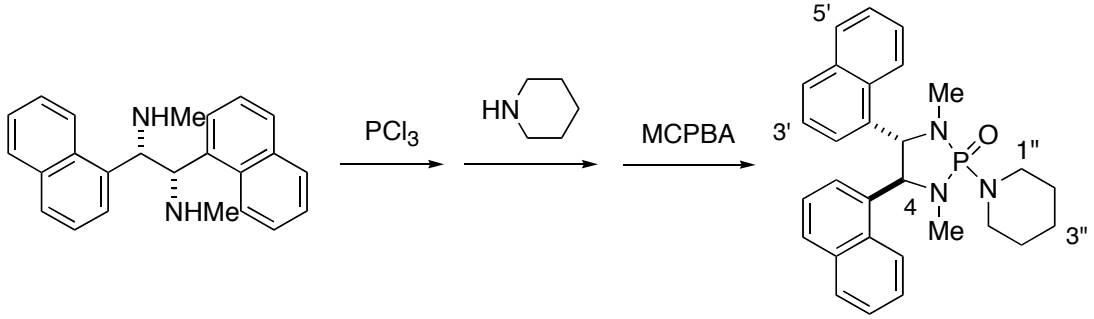
Calcd. for ($C_{21}H_{41}N_3OP$) 382.2987

Found: 382.2991

Opt. Rot.: $[\alpha]_D^{22}$ +1.5 ($CHCl_3$, c = 2.31)

TLC: R_f 0.52 (EtOAc/*i*-PrOH, 19/1)

Representative Procedure II: Synthesis of Phosphoramides from Phosphorus Trichloride. (±)-1,3-Dimethyl-4,5-bis(1-naphthyl)-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (±)-7f



(±)-**23** (±)-**7f**

To a stirred cold (–78 °C) solution of PCl_3 (97 μL, 1.11 mmol, 1.02 equiv) in 3 mL of CH_2Cl_2 was added (±)-*N*,*N*'-dimethyl-1,2-bis(1-naphthyl)-1,2-ethanediamine (±)-**23**[2] (370 mg, 1.09 mmol) in 3 mL of CH_2Cl_2 via a syringe under nitrogen. Then triethylamine (318 μL, 2.28 mmol, 2.1 equiv) was added at the same temperature. The mixture was warmed to room temperature, was stirred for 5 h, and then was evaporated under reduced pressure to remove the excess reagents (PCl_3 and triethylamine).

The residue was suspended in 4 mL of CH_2Cl_2 and piperidine (269 μL, 2.72 mmol, 2.5 equiv) at room temperature and the mixture was stirred under nitrogen, for 18 h and then was concentrated under reduced pressure to remove excess piperidine.

The residue was dissolved in 5 mL of CH_2Cl_2 and a solution of MCPBA (70 %, 563 mg, 2.28 mmol, 2.1 equiv) in 5 mL of CH_2Cl_2 was added dropwise at 0° C. The mixture was allowed to warm to room temperature and was stirred for 24 h. Then, sat. aq. $NaHCO_3$ solution (10 mL) was added with stirring. The aqueous layer was separated and was extracted with CH_2Cl_2 (2 X 10 mL). The combined organic solutions were washed with sat. aq. $NaHCO_3$, (10 mL) dried ($MgSO_4$), filtered, and evaporated to give a residue, which was purified by column chromatography (SiO_2, EtOAc/*i*-PrOH, 19/1 to 9/1) to afford 196 mg (38%) of (±)-**7f**. An analytical sample was obtained by recrystallization from hexane.

Analytical Data for (±)-**7f**:

M.W.: 469.57

mp: 183-186 ˚C (hexane)

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

mixture of rotamers: 9.33 (d, *J* = 8.6), 8.12 (d, *J* = 5.1), 7.90 (d, *J* = 8.1), 7.87 (d, *J* = 7.1), 7.78-7.52 (m), 7.16 (dd, *J* = 7.7, 7.5), 7.10-6.92 (br), 6.83 (dd, *J* = 8.1, 7.1), 6.74-6.58(br), 6.48 (d, *J* = 6.8), 6.37 (d, *J* = 8.8), 5.54 (d, *J* = 9.1), 5.08-4.92 (br), 4.33 (d, *J* = 9.3), 3.46-3.32 (br, HC(1")), 2.48 (d, *J* =10.4), 2.44 (d, *J* = 9.0, Me), 2.43 (d, *J* = 10.5, Me), 1.82-1.62 (br, HC(2", 3")).

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

mixture of rotamers: 136.1, 135.0, 133.3, 132.4, 132.2, 131.7, 131.4, 129,6, 129.2, 128.9, 128.1, 127.2, 126.0, 125.8, 125.4, 125.3, 125.1, 124.7, 124.4, 124.2, 123.2, 122.1, 121.5, 61.2, 46-45 (br, C(1")), 31-29 (br, Me), 26.89 (d, *J* = 2.8, C(2")), 24.85 (C(3")).

^{31}P NMR: (202 MHz, $CDCl_3$)

28.20 (br), 26.21, 25.63 (minor).

IR: ($CHCl_3$)

3059 (w), 3018 (w), 2981 (m), 2970 (m), 2958 (m), 2939 (m), 2883 (w), 2853 (m), 2822 (w), 1597 (w), 1512 (w), 1466 (w), 1446 (w), 1396 (w), 1376 (w), 1362 (w), 1352 (w), 1339 (m), 1326 (w), 1289 (m), 1257 (w), 1243 (m), 1165 (s), 1150 (m), 1124 (w), 1071 (w), 1048 (w), 1020 (m), 981 (m), 962 (s), 865 (w), 852 (w), 834 (w), 815 (w), 804 (w), 661 (w), 647 (w).

MS: (FAB)

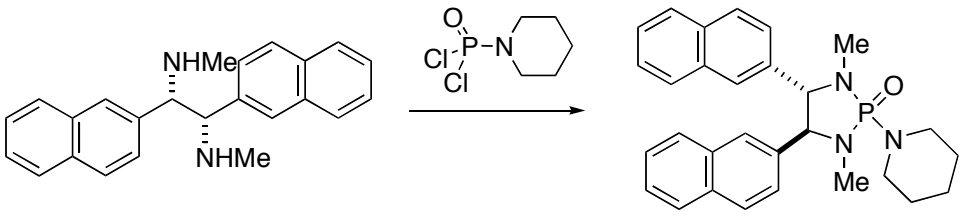
471 (M^++2, 34), 470 (M^++1, 100), 469 (M^+, 11), 468 (M^+–1, 13), 216 (18), 170 (10), 168 (14).

TLC: R_f 0.40 (TBME/MeOH, 20/1)

Analysis: $C_{29}H_{32}N_3OP$

Calcd:	C,	74.18%;	H,	6.87%;	N, 8.95%.
Found:	C,	74.10%;	H,	6.75%;	N, 8.88%.

(+)-(4*S*,5*S*)-1,3-Dimethyl-4,5-bis-(2-naphthyl)-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*S*,*S*)-7g.



(*S*,*S*)-**24** (*S*,*S*)-**7g**

Following Representative Procedure I from triethylamine (185 μL, 1.32 mmol, 3.5 equiv), the diamine (*S*,*S*)-**24**[2] (180 mg, 0.529 mmol) and piperidinophosphoryl dichloride (89 μL, 0.582 mmol, 1.1 equiv) in 50 mL of CH_2Cl_2 was obtained 75 mg (30%) of (*S*,*S*)-**7g** as white crystals after column chromatography (SiO_2, EtOAc/*i*-PrOH, 9/1) and recrystallization (hexane).

Analytical Data for (*S*,*S*)-**7g**:

M.W.: 469.59

mp: 205-206 ˚C (hexane)

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

7.86-7.78 (m, 4 H, Ar), 7.69 (d, *J* = 7.7, 1 H, Ar), 7.66 (d, *J* = 7.9, 1 H, Ar), 7.54 (br, 1 H, HC(1')), 7.50-7.40 (m, 5 H, Ar), 7.37 (br, 1 H, HC(1')), 7.32 (dd, *J* = 8.5, 1.5, 1 H, HC(3')), 4.24 (d, *J* = 8.6, 1 H, HC(4)), 4.19 (d, *J* = 8.6, 1 H, HC(5)), 3.40-3.38 (m, 4 H, HC(1")), 2.43 (d, *J* = 10.4, Me), 2.42 (d, *J* = 9.1 3 H, Me), 1.72-1.60 (m, 6 H, HC (2", 3")).

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

136.1 (d, *J* = 10.2, C(2')), 136.0 (d, *J* = 7.5, C(2')), 133.29 (C(9')), 133.27 (C(9')), 133.14 (C(10')), 133.11 (C(10')), 128.5 (Ar), 128.4 (Ar), 127.9 (Ar), 127.9 (Ar), 127.7 (Ar), 127.4 (Ar), 127.2 (Ar), 126.2 (Ar), 126.08 (Ar), 126.02 (Ar), 125.5 (Ar), 124.7 (Ar), 72.2 (d, *J* = 12.0, C(4)), 70.6 (d, *J* = 11.0, C(5)), 45.7 (C(1")), 30.3 (Me), 29.6 (d, *J* = 3.7, Me), 26.8 (d, *J* = 3.7, C(2")), 24.8 (C(3")).

^{31}P NMR: (202 MHz, $CDCl_3$)

27.38

IR: ($CHCl_3$)

3059 (w), 2982 (m), 2973 (m), 2963 (m), 2939 (m), 2904 (w), 2882 (w), 2852 (m), 2822 (w), 1602 (w), 1509 (w), 1467 (w), 1445 (w), 1375 (m, 1361 (w), 1339 (m), 1326 (w), 1319 (w), 1289 (m), 1269 (w), 1244 (m), 1162 (w), 1150 (m), 1123 (m), 1071 (m), 1026 (m), 1019 (m), 1005 (m), 961 (s), 953 (m), 896 (w), 883 (w), 962 (w), 832 (w), 660 (w).

MS: (EI, 70 eV)

470 (M^++1), 469 (M^+, 70), 301 (10), 300 (42), 216 (21), 215 (17), 170 (33), 169 (81), 168 (100), 153 (14), 141 (23), 128 (11), 60 (18).

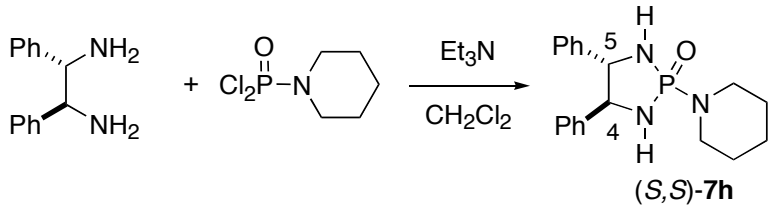
Opt. Rot.: $[\alpha]_D^{22}$ +80.7 ($CHCl_3$, c = 1.38)

TLC: R_f 0.39 (TBME / MeOH, 20 / 1)

Analysis: $C_{29}H_{32}N_3OP$

Calcd: C,	74.18%;	H,	6.87%;	N,	8.95%;	P, 6.60%.
Found: C,	74.12%;	H,	6.75%;	N,	8.68%;	P, 6.72%.

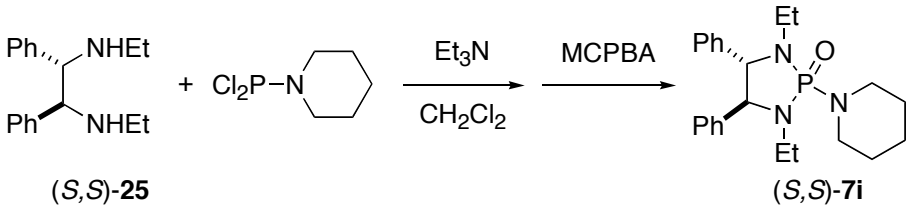
(4*S*,5*S*)-4,5-Diphenyl-2-(1-piperidinyl)-1,3,2-diazaphospholidine 2-Oxide (*S,S*)-7h.



(*S,S*)-**7h**

Following Representative Procedure I, from triethylamine (0.63 mL, 4.5 mmol, 3.0 equiv), (*S,S*)-1,2-diphenyl-1,2-ethanediamine[1] (0.318 g, 1.5 mmol) and 1-piperidinylphosphoric dichloride (0.23 mL, 1.5 mmol, 1.0 equiv) in CH_2Cl_2 (14+8+8 mL) was obtained 0.301 g (59%) of (*S,S*)-**7h** as white crystals after column chromatography (SiO_2, EtOAc/*i*-PrOH 10/1) and recrystallization ($CHCl_3$/hexane). Anal. Calcd for $C_{19}H_{24}N_3OP$ (341,37): C, 66.85; H, 7.09; N, 12.31. Found: C, 66.52; H, 6.90; N, 12.13.

Representative Procedure III: Synthesis of Phosphoramides from Aminophosphorus Dichloride. (4*S*,5*S*)-(+)-1,3-Diethyl-4,5-diphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*S*,*S*)-7i)



To a solution of triethylamine (0.66 mL, 4.73 mmol, 2.2 equiv) in 80 mL of CH_2Cl_2 at reflux was added a solution of *N*,*N*'-diethyl-1,2-diphenyl-1,2-ethanediamine (*S*,*S*)-**25**[3] (578 mg, 2.15 mmol)in 5 mL of CH_2Cl_2 and a solution of piperidinophosphorus dichloride (0.33 mL, 2.15 mmol, 1.0 equiv) in 5 mL of CH_2Cl_2 simultaneously via a syringe pump over 2 h. After addition the solution was heated to reflux for an additional 30 min and then was cooled back to 0° C. A solution of MCPBA (85%, 480 mg, 2.37 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was then added via syringe and the solution was stirred at rt overnight. The slightly yellow solution was poured into a separatory funnel and washed with water (20 mL), sat. aq. $NaHCO_3$ solution (2 X 20 mL) and brine (20 mL). The organic layer was dried (Na_2SO_4), and concentrated in vacuo to afford a crude product that was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 19/1) to give 549 mg (64%) of (*S*,*S*)-**7i** as a white solid. Recrystallization from hexane afforded 255 mg (30%) analytically pure sample as white prisms.

Analytical Data for (*S*,*S*)-**7i**:

mp: 150-152 °C (hexane)

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

7.32-7.20 (m, 6 H, Ph), 7.20-7.12 (m, 2 H, Ph), 7.06-7.00 (m, 2 H, Ph), 4.12 (d, *J* = 8.5, 1 H, HC(4)), 4.04 (d, *J* = 8.5, 1 H, HC(5)), 3.36-3.20 (m, 4 H, HC(1')), 2.88-2.70 (m, 4 H, H_2C(Et)), 1.68-1.58 (m, 6 H, HC(2', 3')), 1.07 (t, *J* =7.2, 3H, Me), 0.97 (t, *J* = 7.1, Me).

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

139.2 (d, *J* = 10.1, C(1")), 138.9 (d, *J* = 6.4, C(1")), 128.4 (C(3")), 128.3 (C(3")),

128.1 (C(2")), 127.90 (C(2")), 127.87 (C(4")), 127.6 (C(4")), 69.5 (d, *J* = 12.0, C(4)), 68.1 (d, *J* = 11.0, C(5)), 45.9 (d, *J* = 2.8, C(1')), 38.0 (d, *J* = 2.8, C(Et)), 37.1 (d, *J* = 4.6, C(Et)), 26.6 (d, *J* = 4.6, C(2')), 24,8 (C(3')), 13.6 (Me), 13.4 (Me).

^{31}P NMR: (202 MHz, $CDCl_3$)

28.12

IR: ($CHCl_3$)

2973 (m), 2938 (s), 2902 (w), 2872 (m), 2853 (m), 1602 (w), 1492 (w), 1463 (w), 1455 (m), 1444 (m), 1377 (m), 1357 (m), 1338 (m), 1310 (w), 1278 (w), 1258 (w), 1161 (s), 1123 (m), 1071 (s), 1054 (m), 1022 (m), 961 (s), 917 (w), 912 (w), 901 (w), 879 (w), 854 (w), 838 (w), 700 (w), 659 (w), 613 (w).

MS: (EI, 70 eV)

397 (M^+, 34), 264 (21), 235 (13), 180 (14), 179 (11), 134 (39), 133 (40), 132 (53), 118 (25), 104 (20), 91 (13), 84 (100), 74 (13), 55 (11).

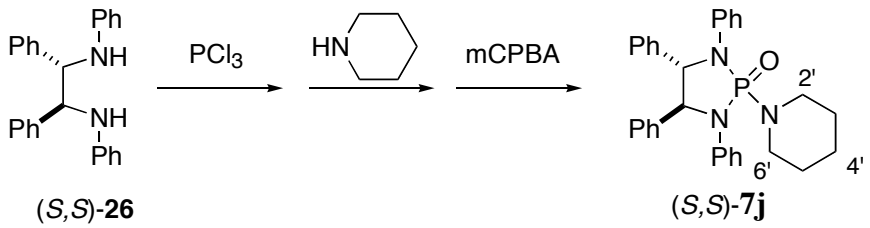
Opt. Rot.: $[\alpha]_D^{22}$ +6.2 ($CHCl_3$, c = 1.20)

TLC: R_f 0.33 (CH_2Cl_2/MeOH, 19/1)

Analysis: Calcd for $C_{23}H_{32}N_3OP$ (397.50)

Calcd:	C,	69.50%;	H,	8.11%;	N,	10.57%;	P,	7.79%.
Found:	C,	69.48%;	H,	8.08%;	N,	10.55%;	P,	8.04%.

(*S,S*)-1,3,4,5-Tetraphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*S,S*)-7j.



(*S,S*)-**26** (*S,S*)-**7j**

Following Representative Procedure II, to a stirred cold (–78 ˚C) solution of PCl_3 (69 mL, 0.79 mmol, 1.04 equiv) in 3 mL of CH_2Cl_2 was added (*S,S*)-*N*,*N*',1,2-tetraphenyl-1,2-ethanediamine (*S,S*)-**26**[4] (261 mg, 0.716 mmol, 1.0 equiv) in 3 mL of CH_2Cl_2 via a syringe under nitrogen. Then triethylamine (0.22 mL, 1.57 mmol, 2.2 equiv) was added at the same temperature. The mixture was warmed to room temperature, was stirred for 5 h, and then was evaporated under reduced pressure to remove the excess reagents (PCl_3 and triethylamine).

The residue was suspended in 4 mL of CH_2Cl_2 and piperidine (0.21 mL, 2.15 mmol, 3.0 equiv) at room temperature and the mixture was stirred under nitrogen, for 18 h and then was concentrated under reduced pressure to remove excess piperidine.

The residue was dissolved in 5 mL of CH_2Cl_2 and a solution of MCPBA (50%, 250 mg; 0.72 mmol, 1.0 mmol) in 5 mL of CH_2Cl_2 was added dropwise at 0˚ C. The mixture was allowed to warm to room temperature and was stirred for 24 h. Then, sat. aq. $NaHCO_3$ solution (10 mL) was added with stirring. The aqueous layer was separated and was extracted with CH_2Cl_2 (2 X 10 mL). The combined organic solutions were washed with sat. aq. $NaHCO_3$, (10 mL) dried ($MgSO_4$), filtered, and evaporated to give a residue, which was purified by column chromatography (SiO_2, CH_2Cl_2 then CH_2Cl_2/*i*-PrOH, 100/1 as eluents). Recrystallization from hexane afforded 196 mg (55 %) of (*S,S*)-**7j** as a colorless amorphous solid.

Analytical Data for (–)-(***S,S*)-7j**:

M.W.: 493.59

mp: 195-197˚ C (hexane)

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

7.25-7.20 (m, 8H), 7.19-7.13 (m, 6H), 7.103-7.06 (m, 2H), 7.00 (dd, *J* = 7.7, 0.9,

2H), 6.94 (t, *J* = 7.3, 1H), 6.91 (t, *J* = 6.4, 1H), 4.93 (d, *J* = 8.1, 1H, HC(4/5)), 4.88 (dd, *J* = 8.3, 6.8, 1H, H(5/4)), 3.40-3.32 (m, 2H, HC(1')), 3.18-3.08 (m, 2H, HC(1')), 1.46-1.38 (m, 4H, HC(2')H_2), 1.18-1.06 (m, 2H, HC(3'))

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

140.30 (d, *J* = 3.7, C(1")), 140.29 (d, *J* = 6.6, (C1")), 138.38 (d, *J* = 8.3,C(1'")), 138.30 (d, *J* = 4.6,(C1'")), 129.0, 128.6, 128.52, 128.1, 127.7, 127.5, 123.2, 122.2, 121.9, 121.8, 119.6, 119.5, 67.7 (d, *J* = 10.1, C(4/5)), 66.7 (d, *J* = 12.0, C(5/4)), 45.4 (d, *J* = 2.8, C(1')), 25.4 (d, *J* = 4.6, C(2')), 24.4 (C(3'))

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

17.30

IR: ($CHCl_3$)

2989(w), 2940(m), 2899(w), 2854(w), 1599(m), 1493(s), 1456(m), 1385(m), 1377(m), 1361(w), 1353(w), 1341(w), 1308(w), 1294(m), 1279(w), 1262(m), 124(w), 1165(w), 1120(m), 1069(m), 1029 (w), 1001(w), 967(s), 917 (w), 836(w), 699(w)

MS: (EI, 70 eV)

494 (M^++1, 21), 493 (M^+, 50), 182 (43), 181 (100), 180 (39), 104 (10), 84 (25), 77 (18)

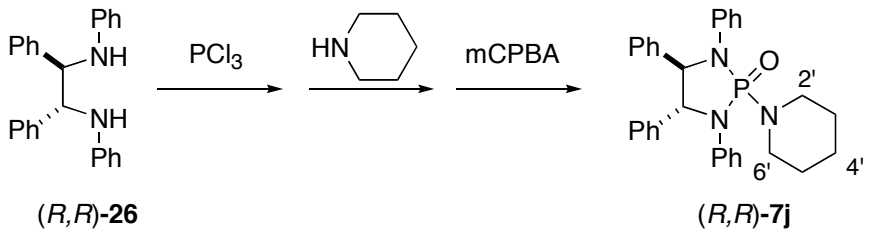
Opt. Rot.: $[\alpha]_D^{22}$ –194 ($CHCl_3$, *c* = 1.01)

TLC: R_f 0.49 (EtOAc)

Analysis: $C_{31}H_{32}N_3OP$

Calcd:	C,	75.44%;	H,	6.53%;	N,	8.51%;	P,	6.28%.
Found:	C,	75.31%;	H,	6.30%;	N,	8.46%;	P,	6.09%.

(*R*,*R*)-1,3,4,5-Tetraphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*R*,*R*)-7j.



(*R*,*R*)-**26** (*R*,*R*)-**7j**

Following Representative Procedure II, to a stirred cold (-78 °C) solution of PCl_3 (69 mL, 0.79 mmol) in 3 mL of dry CH_2Cl_2 was added (*R*,*R*)-**26**[4] (261 mg, 0.716 mmol) in 3 mL of dry CH_2Cl_2 via a syringe under nitrogen. Then triethylamine (0.22 mL, 1.57 mmol) was added at the same temperature. The mixture was warmed to room temperature, stirred for 5 h, and then condensed under reduced pressure to remove the excess reagents (PCl_3 and triethylamine).

The residue was suspended in 4 mL of dry CH_2Cl_2 and stirred, to which was added piperidine (0.21 mL, 2.15 mmol) at room temperature under nitrogen. The mixture was stirred for 18 h and condensed under reduced pressure to remove excess piperidine.

The residue was dissolved in 5 mL of CH_2Cl_2. *m*-Chloroperbenzoic acid (50%, 250 mg; 0.72 mmol) in 5 mL of CH_2Cl_2 was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 24 h. Then saturated aqueous $NaHCO_3$ was added with stirring. The aqueous layer was separated and extracted with CH_2Cl_2 twice. The combined organic solutions were washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated to give a crude material, which was chromatographed on silica gel (CH_2Cl_2 then CH_2Cl_2/2-propanol = 100/1 as eluents) and recrystalized from hexane to afford 196 mg (55%) of (*R*,*R*)-**7j** as a colorless amorphous solid.

Analytical Data for (*R*,*R*)-**7j :**

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

7.24-7.20 (m, 8H), 7.18-7.13 (m, 6H), 7.10 (m, 2H), 7.00 (d, *J* = 8.1, 2H), 6.94 (t, *J* = 7.3, 1H), 6.91 (t, *J* = 6.6, 1H), 4.93 (d, *J* = 8.2, 1H, NCH), 4.88 (dd, *J* = 8.2, 1.4, 1H, NCH), 3.36 (m, 2H, C(2'/6')H_2), 3.14 (m, 2H, C(2'/6')H_2), 1.43 (m, 4H, C(3', 5')H_2), 1.13 (m, 2H, C(4')H_2).

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

140.24 (d, *J* = 3.1, *ipso*-Ph), 140.22 (d, *J* = 6.1, *ipso*-Ph), 138.3 (d, *J* = 8.8, *ipso*-Ph), 138.2 (d, *J* = 6.1, *ipso*-Ph), 128.9, 128.6, 128.5, 128.0, 127.7, 127.5, 123.2, 122.2, 121.8 (d, *J* = 3.8, *o*-Ph), 119.5 (d, *J* = 4.6, *o*-Ph), 67.7 (d, *J* = 9.9, CH), 66.7 (d, *J* = 11.4, CH), 45.3 (d, *J* = 3.1, C(2', 6')), 25.4 (d, *J* = 4.6, C(3', 5')), 24.3 (C(4')).

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

17.25

IR: (KBr)

3063 (w), 3029 (w), 3010 (w), 2934 (m), 2851 (m), 1630 (w), 1599 (s), 1494 (s), 1455 (m), 1401 (s), 1385 (m), 1340 (m), 1259 (s), 1236 (s), 1165 (m), 1120 (m), 1067 (m), 1030 (m), 965 (s), 917 (w), 793 (w), 757 (m), 734 (m), 698 (m)

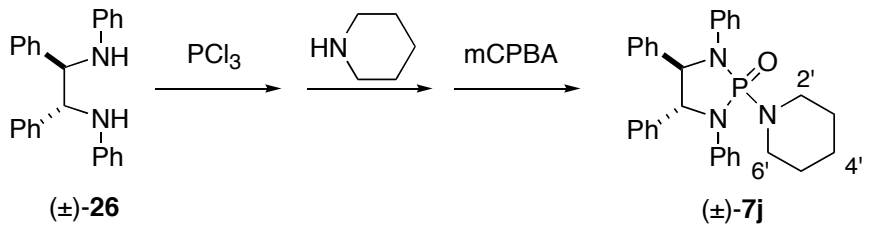
MS: (EI, 70 eV)

494 (M^++1, 22), 493 (M^+, 57), 182 (48), 181 (100), 180 (34), 104 (9), 84 (22), 77 (17).

TLC: *Rf* 0.89 (EtOAc)

Opt. Rot.: $[\alpha]_D^{22}$ +174.8 (*c* = 1.05, $CHCl_3$)

(±)-1,3,4,5-Tetraphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (±)-(7j)



(±)-**26** (±)-**7j**

Following Representative Procedure II, from (±)-**26**[4] (1.09 g, 3.0 mmol), PCl_3 (294 mL, 3.3 mmol, 1.1 equiv), triethylamine (0.92 mL, 6.6 mmol, 2.2 equiv), piperidine (0.89 mL, 9.0 mmol, 3.0 equiv) and MCPBA (50%, 1.14 g, 3.3 mmol, 1.1 equiv) in CH_2Cl_2 (15+15+15 mL) was obtained 0.62 g (42%) of (±)-**7j** as a colorless amorphous solid after column chromatography (SiO_2, CH_2Cl_2/*i*-PrOH, 20/1) and recrystallization (toluene/hexane).

Analytical Data for (±)-**7j**:

M.W.: 493.59

mp: 196-197 ˚C (toluene/hexane)

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

17.30

MS: (EI, 70 eV)

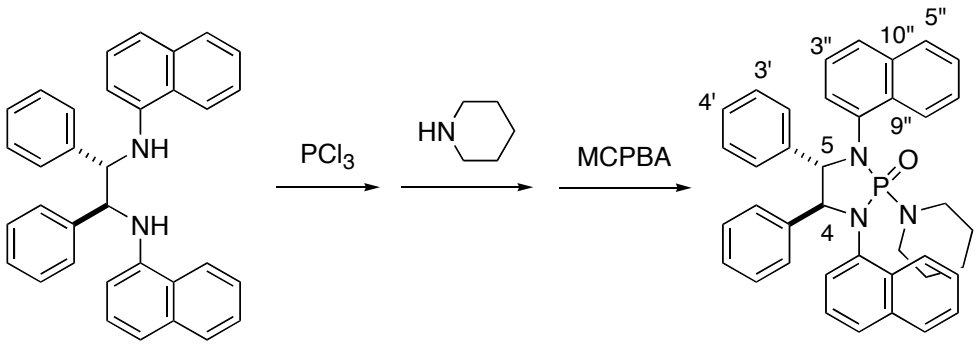
494 (M+1, 21), 493 (M^+, 50), 182 (100), 180 (39), 104 (10), 84 (25), 77 (18).

TLC: R_f 0.49 (EtOAc)

Analysis: $C_{31}H_{32}N_3OP$

Calcd:	C,	75.44%;	H,	6.53%;	N,	8.51%;	P, 6.28%.
Found:	C,	75.68%;	H,	6.51%;	N,	8.49%;	P, 6.25%.

(+)-(4*S*,5*S*)-1,3-Bis-(1-naphthyl)-4,5-diphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*S,S*)-7k.



(*S,S*)-**27** (*S,S*)-**7k**

Following Representative Procedure II, to a solution of phosphorus trichloride (100 μL, 1.14 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was added the solution of the diamine (*S,S*)-**27**[4] (482 mg, 1.04 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) via a cannula at –78 ˚C followed by triethylamine (363 μL, 3.12 mmol, 3.0 equiv). The colorless solution was then slowly warmed to rt and the solution turned light green-yellow. The solution was stirred at rt for 6 h and then was cooled back to –78 ˚C. Piperidine (310 μL, 3.12 mmol, 3.0 equiv) was added and then the solution was allowed to warm to rt and was stirred overnight. A solution of MCPBA (50%, 431 mg, 1.25 mmol, 1.2 equiv) in CH_2Cl_2 (2 mL) was added and the mixture stirred at rt for 5 h. The red-orange solution was then poured into sat. aq. $NaHCO_3$ solution (30 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 X 20 mL) and combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), and concentrated on a rotavap. The oily residue was then purified by column chromatography (SiO_2, hexane/EtOAc, 3/1 to 1/1) to give 309 mg (50%) of (*S,S*)-**7k** as an off-white foam, which was recrystallized from toluene/hexane to give white amorphous powder.

Analytical Data for (*S,S*)-**7k**:

M.W.: 593.72

mp: 188-190 ˚C(toluene/hexane)

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

mixture of rotamers: 9.54 (d, J = 8.4), 8.82-8.38 (br), 8.32-8.06 (br), 7.96-6.92

(br), 5.64-5.52 (br), 5.57 (d, J = 9.2), 5.24-5.12 (br), 3.36 -2.72 (br), 1.74-1.62 (br), 1.32-0.36 (br).

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

mixture of rotamers: 138.8, 137.8, 134.5, 132.6, 131.1, 129.0, 128.6, 128.2, 128.0, 127.8, 127.6, 127.4, 126.6, 126.2, 125.6, 125.0, 124.6, 123.6, 118.1, 71.76, 69.9, 46.2, 45.7, 26.0, 25.0, 24.0, 14.1.

^{31}P NMR: (202 MHz, $CDCl_3$)

mixture of rotamers: 21.29 (br), 20.25 (br), 14.02 (minor).

IR: ($CHCl_3$)

3091 (w), 3065 (w), 2986 (m), 2968 (m), 2941 (m), 2903 (w), 2884 (w), 2879 (w), 2854 (m), 1596 (m), 1575 (m), 1510 (w), 1497 (w), 1465 (w), 1456 (w), 1444 (w), 1393 (s), 1376 (w), 1363 (w), 1342 (w), 1307 (w), 1281 (m), 1266 (m), 1251 (w), 1237 (w), 1192 (w), 1166 (m), 1151 (w), 1116 (m), 1097 (s), 1072 (s), 1049 (m), 1034 (w), 1026 (m), 967 (s), 945 (m), 915 (w), 854 (w), 839 (w), 820 (w), 699 (w), 605 (w).

MS: (EI, 70 eV)

594 (M+1, 10), 593 (M^+, 23), 446 (17), 232 (24), 231 (100), 230 (13), 91 (14), 84 (10), 57 (16), 56 (12).

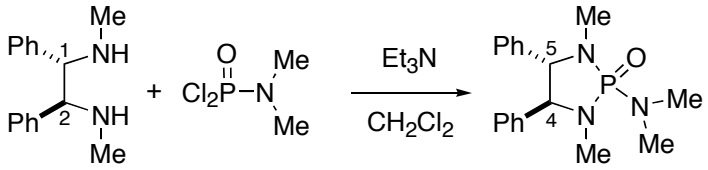
Opt. Rot.: $[\alpha]_D^{22}$ –356 ($CHCl_3$, c = 1.01)

TLC: R_f 0.33 (hexane / EtOAc, 1/1).

Analysis: $C_{39}H_{36}N_3OP$

Calcd:	C,	78.90%;	H,	6.11%;	N, 7.08%;	P, 5.22%.
Found:	C,	78.86%;	H,	6.26%;	N, 6.91%;	P, 5.18%.

(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-2-dimethylamino-1,3,2-diazaphospholidine 2-Oxide (*S*,*S*)-7m



(*S,S*)-**18** (*S,S*)-**7m**

Following Representative Procedure I, from triethylamine (0.21 mL, 0.154 g, 1.53 mmol), (*S,S*)-**18**[2] (0.146 g, 0.61 mmol) and *N,N*-dimethylphosphoramic dichloride (0.073 mL, 0.099 g, 0.61 mmol) in CH_2Cl_2 (5+1+1 mL), was obtained 0.121 g (60%) of (*S,S*)-**7m** as a white solid after chromatography (SiO_2, EtOAc/*i*-PrOH 10/1). An analytical sample was obtained by recrystallization from hexane.

Analytical data for (*S,*S)-**7m**:

mp: 161 - 163 ˚C (hexane)

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

7.30 - 7.25 (m, 6H, CH(Ar)), 7.14 - 7.10 (m, 2H, CH(Ar)), 7.08 - 7.05 (m, 2H, CH(Ar)), 3.94 (dm J = 9.0, HCPh), 3.90 (d, J = 8.8, HCPh), 2.88 (d, J = 9.5, 6H, $(CH_3)_2N$), 2.37 (d, J = 9.0, CH_3N), 2.35 (d, J = 10.3, CH_3N)

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

138.3 (C(Ar)), 138.2(C(Ar)), 128.4 (CH(Ar)), 128.4 (CH(Ar)), 128.0 (CH(Ar)), 128.0 (CH(Ar)), 127.9 (CH(Ar)), 127.7 (CH(Ar)), 72.3 (d, J = 11.4) and 70.7 (d, J = 10.7) ((C(4), C(5)), 37.0 (d, J = 4.6, $(CH_3)_2N$), 30.2 (d, J = 2.3, CH_3N), 29.2(d, J = 4.6, CH_3N)

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

29.61

IR: (KBr)

3470 (w), 3210 (w), 3027 (w), 2940 (w), 2805 (w), 1491 (m), 1455 (m), 1291 (m), 1244 (s), 1202 (s), 1152 (s), 1071 (m), 984 (s), 791 (s), 745 (s)

MS: (70 eV)

329 (M^+, 85), 210 (38), 166 (27), 165 (28), 120 (28), 119 (56), 118 (100)

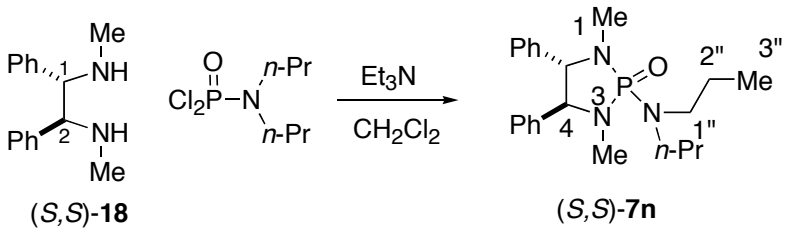
TLC: R_f 0.23 (EtOAc/*i*-PrOH, 10/1)

Opt. Rot.: $[\alpha]_D^{22}$ -5.10 (c = 1.02, $CHCl_3$)

Analysis: Calcd for $C_{18}H_{24}N_3OP$

Calcd:	C, 65.64;	H, 7.34;	N, 12.76;	P, 9.40.
Found:	C, 65.68;	H, 7.30;	N, 12.65;	P, 9.34.

(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-2-di-*n*-propylamino-1,3,2-diazaphospholidine 2-Oxide (*S,S*)-7n



(*S,S*)-**18** (*S,S*)-**7n**

Following Representative Procedure I, from triethylamine (0.42 mL, 3.0 mmol, 3.0 equiv), (*S,S*)-**18**[2] (0.248 g, 1.0 mmol) and *N,N*-dipropylphosphoramic dichloride (0.218 mL, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was obtained 0.179 g (46%) of **7n** as a thick oil after column chromatography (SiO_2, EtOAc/*i*-PrOH 10/1).

Analytical Data for (*S,S*)-**7n**:

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

7.28-7.20 (m, 6 H, Ar), 7.18-7.12 (d, 2 H, Ar), 7.04-6.98 (d, Ar), 3.94 (d, *J* = 8.6, 1H, HC(4)), 3.90 (d, *J* = 8.6, 1H, HC(5)), 3.22-3.12 (m, 2 H, H_2C(1")), 3.04-2.96 (m, 2 H, H_2C(1")), 2.35 (d, *J* = 9.3, 3 H, MeN(1)), 2.32 (d, *J* = 11.5, 3 H, MeN(3)), 1.76-1.58 (m, 4 H, H_2C(2")), 0.97 (t, *J* = 7.3, 6 H, Me(3"))

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

27.74

MS: (EI, 70 eV)

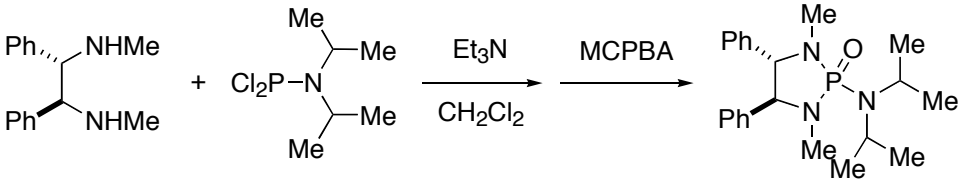
386 (M^++1, 13), 385 (M^+, 34), 357 (29), 356 (100), 286 (22), 285 (96), 251 (14),

166 (40), 165 (10), 133 (53), 132 (63), 120 (24), 119 (20), 118 (54), 100 (39), 91 (18), 60 (23)

Analysis: Calcd for $C_{22}H_{32}N_3OP$ (385.49)

Calcd:	C, 68.55%;	H, 8.37%;	N, 10.90%.
Found:	C, 68.52%;	H, 8.07%;	N, 10.98%.

(4*S*,5*S*)-1,3-Di-(2-propyl)-4,5-diphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (*S*,*S*)-7o)



(*S,S*)-**18** (*S,S*)-**7o**

Following Representative Procedure III, from (*S,S*)-**18**[2] (483 mg, 2.01 mmol), triethylamine (0.62 mL, 4.42 mmol, 2.2 equiv) and dimethylaminophosphoric dichloride (0.414 mL, 2.01 mmol, 1.0 equiv) in CH_2Cl_2 (80+10+10 mL) was obtained 549 mg (71%) of (*S,S*)-**7o** as a white foam after chromatography (SiO_2, TBME/MeOH, 49/1).

Analytical Data for (*S,S*)-**7o**:

M.W.: 385.49

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

7.28-7.22 (m, 6 H, Ph), 7.18-7.04 (m, 2 H, Ph), 7.00-6.96 (m, 2 H, Ph), 3.92 (d, *J* = 8.8, 1 H, HC(4)), 3.87 (d, *J* = 8.8, HC(5)), 3.50-3.88 (m, 2 H, HC(1')), 2.35 (d, *J* = 9.2, 3 H, MeN), 2.35 (d, *J* = 10.3, 3 H, MeN), 1.42-1.32 (m, 12 H, Me-CH).

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

138.8 (d, *J* = 10.1, C(1")), 138.7 (d, *J* = 5.5, C(1")), 128.4 (C(3")), 128.3 (C(3")), 128.0 (C(2")), 127.9 (C(2")), 127.8 (C(4")), 127.5 (C(4")), 72.1 (d, *J* = 11.0, C(4)), 70.9 (d, *J* = 11.0, C(5)), 45.8 (br, C(1')), 30.0 (d, *J* = 2.8, MeN), 29.4 (d, *J* = 5.5, MeN), 24.0 (br, C(2')).

^{31}P NMR: (202 MHz, $CDCl_3$)

28.12

MS: (EI, 70 eV)

385 (M^+, 20), 371 (12), 370 (44), 343 (15), 342 (60), 286 (26), 285 (100), 266 (11), 167 (11), 166 (56), 165 (11), 120 (30), 119 (30), 118 (77), 105 (24), 100 (61), 91 (12), 77(21), 73 (83), 60 (30), 59 (17), 57 (36)

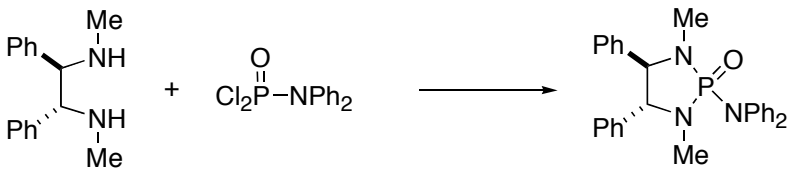
HRMS (EI)

Calcd. for $C_{22}H_{32}N_3OP$ 385.2283;

Found: 385.2284.

TLC: R_f 0.42 (TBME / MeOH, 19/1)

(*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-diphenylamino-1,3,2-diazaphospholidine 2-Oxide (*R*,*R*)-7p.



(*R*,*R*)- **18** (*R*,*R*)- **7p**

Following Representative Procedure I, to a solution of triethylamine (0.44 mL, 3.16 mmol) in 30 mL of dry CH_2Cl_2 were added solutions of (*R*,*R*)-**18**[7] (314 mg, 1.31 mmol) in 15 mL of dry CH_2Cl_2 and diphenylaminophosphorus dichloride (450 mg, 1.57 mmol) in 15 mL of dry CH_2Cl_2 simultaneously and dropwise over 30 min at reflux under nitrogen. The solution was heated to reflux for 36 h then was concentrated under reduced pressure to give a residue, which was purified by column chromatography on silica gel (CH_2Cl_2, CH_2Cl_2/2-propanol, 100/2 then 100/4) affording 372 mg (63%) of (*R*,*R*)-**7p** as a colorless amorphous solid.

Data for (*R*,*R*)-**7p**:

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

7.44-7.35 (m, 8H, *o*, *m*-Ph), 7.27-7.17 (m, 6H, *m*, *p*-Ph', *p*-Ph, *p*-Ph"), 7.12-7.08

(m, 4H, *o*-Ph', *m*-Ph"), 6.44 (d, *J* = 8.3, 2H, *o*-Ph"), 3.99 (d, *J* = 8.9, 1H, NCH), 3.71 (d, *J* = 8.9, 1H, NCH), 2.56 (d, *J* = 9.5, 3H, CH_3), 2.46 (d, *J* = 10.3, 3H, CH_3).

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

145.3 (d, *J* = 4.6, *ipso*-Ph), 137.7 (*ipso*-Ph), 137.6 (d, *J* = 4.6, *ipso*-Ph), 129.1, 128.5, 128.23, 128.16, 128.09, 127.99 (d, *J* = 2.8), 127.95, 127.87, 125.4, 71.2 (d, *J* = 10.0, NCH), 71.0 (d, *J* = 11.0, NCH), 29.6 (d, *J* = 3.7, CH_3), 29.1 (d, *J* = 5.5, CH_3)

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

20.76

IR: (KBr)

3088 (w), 3062 (w), 3032 (w), 2974 (w), 2930 (m), 2904 (m), 2856 (m), 2815 (w), 1590 (m), 1489 (s), 1455 (m), 1401 (m), 1339 (w), 1300 (m), 1280 (m), 1257 (s), 1211 (s), 1166 (s), 1074 (m), 1033 (s), 1016 (s), 991 (s), 915 (w), 901 (w), 891 (w), 830 (w), 814 (w), 777 (m), 746 (s), 700 (s), 632 (m), 626 (w), 613 (w), 555 (s)

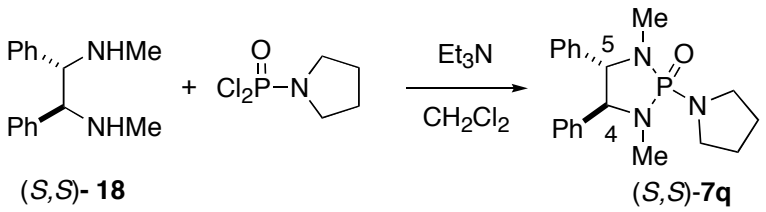
Opt. Rot.: $[\alpha]_D^{22}$ +25.7 (*c* = 0.65, $CHCl_3$)

TLC: *Rf* 0.73 (EtOAc)

Analysis: $C_{28}H_{28}N_3OP$ (453.52)

Calcd.: C, 74.15;	H, 6.22;	N, 9.27;	P, 6.83
Found: C, ;	H, ;	N, ;	P,

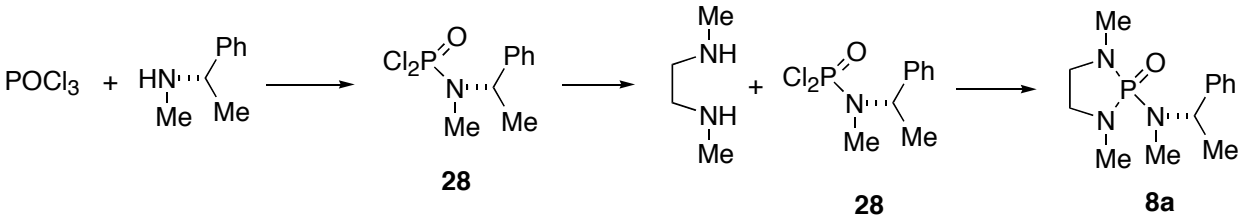
(4*S*,5*S*)-1,3-Dimethyl-4,5-diphenyl-2-(1-pyrrolidinyl)-1,3,2-diazaphospholidine 2-Oxide (*S,S*)-7q.



(*S,S*)- **18** (*S,S*)-**7q**

Following Representative Procedure I, from triethylamine (0.55 mL, 3.93 mmol, 2.5 equiv), (*S,S*)-**18**[2] (0.377 g, 1.57 mmol) and 1-pyrrolidinylphosphoramic dichloride (0.295 g, 1.57 mmol, 1.0 equiv) in CH_2Cl_2 (20+8+8 mL) was obtained 0.34 g (61%) of (*S,S*)-**7q** as white crystals after column chromatography (SiO_2, EtOAc/*i*-PrOH 9/1) and recrystallization (hexane), mp: 105-106 ˚C (hexane); TLC R_f = 0.32 (EtOAc/*i*-PrOH, 10/1). Anal. Calcd for $C_{20}H_{26}N_3OP$ (355.42): C, 67.5; H, 7.37; N, 11.82. Found: C, 67.36; H, 7.13; N, 11.78.

(*S*)-1,3-Dimethyl-2-methyl(1-phenylethyl)amino-1,3,2-diazaphospholidine 2-Oxide (8a)



A solution of (*S*)-1-methylamino-1-phenylethane (7.3 mL, 50 mmol) in 15 mL of dry diethyl ether was added to a solution of $POCl_3$ (14 mL, 150 mmol) in 25 mL of dry diethyl ether, dropwise through an addition funnel at 0 °C under nitrogen. After completion of the addition, the mixture was stirred at rt overnight. The solvent was distilled off, the mixture was heated at 130-140 °C (bath temperature) to reflux for 20 h, the $POCl_3$ was distilled off under atmospheric pressure then the product was distilled under reduced pressure to give 9.35 g (74%) of **28** as a colorless liquid (bp 150 °C/1.1 mmHg; ABT) which solidified upon cooling.

Data for **28**:

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

7.37-7.31 (m, 5H, Ph), 5.39 (dq, J = 11.0, 7.1, C*H*CH_3), 2.55 (d, J_{PH} = 16.1, NC*H*$_3$), 1.63 (d, J = 6.8, CHC*H*$_3$)

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

18.19

To a solution of triethylamine (3.5 mL, 25 mmol) in 200 mL of dry CH_2Cl_2 were added solutions of *N*,*N*'-dimethylethylenediamine (1.06 mL, 10 mmol) in 25 mL of dry CH_2Cl_2 and (*S*)-methyl(1-phenylethyl)aminophosphorus dichloride **18** (2.52 g, 10 mmol) in 25 mL of dry CH_2Cl_2 simultaneously over 2 h using a syringe pump at reflux under nitrogen. The solution was heated to reflux for 42 h then was concentrated under reduced pressure to give a residue, which was purified by column chromatography on silica gel (ethyl acetate/2-propanol, 10/1, 10/2, then 10/3). Distillation under reduced pressure (bp 160-165 °C/0.1 mmHg; ABT) afforded 2.139g (80%) of **8a** as hygroscopic colorless crystals. Analytical sample was obtained by further recrystalization from hexane.

Analytical Data for **8a**:

mp: 51-52 °C (hexane)

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

7.41 (d, J = 7.1, 2H, *o*-Ph), 7.32 (t, J = 7.5, 2H, *m*-Ph), 7.23 (t, J = 7.3, *p*-Ph), 5.05 (dq, J = 8.8, 7.1, C*H*CH_3), 3.18 (m, 2H, CH_2), 3.11 (m, 2H, CH_2), 2.57 (d, J = 9.7, 3H, NCH_3), 2.49 (d, J = 9.7, 3H, NCH_3), 2.27 (d, J = 10.2, 3H, NCH_3), 1.52 (d, J = 7.1, 3H, CHC*H*$_3$).

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

142.3 (d, J = 4.6, *ipso*-Ph), 128.0 (*o*/*m*-Ph), 127.5 (*o*/*m*-Ph), 126.8 (*p*-Ph), 53.2 (d, J = 4.6, *C*HCH_3), 47.3 (d, J = 12.2, CH_2), 31.43 (d, J = 6.9, NCH_3), 31.38 (d, J = 6.9, NCH_3), 26.6 (d, J = 5.3, NCH_3), 17.5 (d, J = 1.5, CH*C*H_3)

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

27.93

IR: ($CHCl_3$)

3104 (w), 3088 (w), 3017 (w), 2979 (s), 2943 (m), 2854 (w), 2819 (w), 1494 (w), 1481 (w), 1470 (w), 1452 (w), 1376 (m), 1352 (s), 1265 (m), 1229 (s), 1211 (s), 1196 (s), 1167 (s), 1038 (m), 1027 (m), 1005 (m), 995 (m), 948 (s), 889 (w), 702 (m), 662 (m), 518 (m)

MS: (EI, 70 eV)

267 (M^+, 38), 252 (22), 135 (13), 134 (100), 133 (91), 105 (13), 90 (8), 77 (8)

Opt. Rot.: $[\alpha]_D^{22}$ -1.6 (*c* = 1.1, $CHCl_3$)

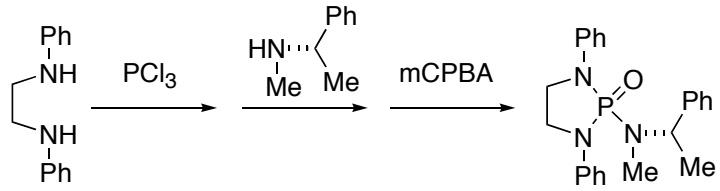
TLC: *Rf* 0.58 (EtOAc/*i*-PrOH, 9/1)

Analysis: $C_{13}H_{22}N_3OP$ (267.31)

Calcd.: C, 58.41%; H, 8.30%; N, 15.72%; P, 11.59%.

Found: C, 58.39%; H, 8.38%; N, 15.77%; P, 11.37%.

(*S*)-1,3-Diphenyl-2-methyl(1-phenylethyl)amino-1,3,2-diazaphospholidine 2-Oxide (8b)



8b

Following Representative Procedure II, to a stirred cold (-78 °C) solution of PCl_3 (0.95 mL; 11 mmol) in 20 mL of dry CH_2Cl_2 was added a solution of *N*,*N*'-diphenylethylenediamine (2.12 g, 10 mmol) in 20 mL of dry CH_2Cl_2 through a dropping funnel under nitrogen. Then triethylamine (3.5 mL; 25 mmol) was added at the same temperature. The mixture was warmed to room temperature and was stirred for 24 h. To this mixture was added 40 mL of dry diethyl ether and the precipitates were filtered off and washed with dry ether (40 mL). The combined filtrate and washings were concentrated under reduced pressure to remove the excess reagents (PCl_3 and triethylamine).

The residue was dissolved in 10 mL of dry CH_2Cl_2 and stirred, to which was added a mixture of (*S*)-1-methylamino-1-phenylethane (1.45 mL, 10 mmol) and triethylamine (4.2 mL, 30 mmol) at 0 °C, and the mixture was stirred for 18 h at rt under nitrogen. After addition of dry

ether (30 mL), the suspension was filtered to remove the precipitates and condensed under reduced pressure.

The residue was dissolved in 10 mL of CH_2Cl_2, and a solution of *m*-chloroperbenzoic acid (50%, 3.45 g, 10 mmol) in 15 mL of CH_2Cl_2 was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 24 h. Then sat. aq. $NaHCO_3$ solution (25 mL) was added with stirring. The aqueous layer was separated and extracted with CH_2Cl_2 (2 X 25 mL). The combined organic solutions were washed with sat. aq. $NaHCO_3$ solution (25 mL) than was dried over $MgSO_4$, filtered, and evaporated to give a crude material, which was purified by column chromatography on silica gel (benzene/CH_2Cl_2/2-propanol, 30/20/1 as eluent). Recrystallization from CH_2Cl_2/hexane afforded 1.96 g (50%) of **8b** as colorless fine needles. An analytical sample was obtained by sublimation at 0.05 mmHg.

Analytical Data for **8b**:

mp: 204-205 °C (sublimation)

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

7.32 (t, *J* = 7.8, 2H, *m*-Ph), 7.25 (t, *J* = 7.8, 2H, *m*-Ph'), 7.22 (d, *J* = 7.8, 2H, *o*-Ph), 7.16 (d, *J* = 7.6, 2H, *o*-Ph'), 7.13-7.07 (m, 3H, *m*, *p*-Ph"), 7.04-6.97 (m, 4H, *p*-Ph, *o*-Ph", *p*-Ph'), 4.84 (dq, *J* = 10.0, 7.1, C*H*CH_3), 3.94-3.76 (m, 4H, CH_2CH_2), 2.51 (d, *J* = 10.5, 3H, NCH_3), 1.20 (d, *J* = 7.1, 3H, CHC*H3*).

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

141.6 (d, *J* = 6.6, *ipso*-Ph), 140.7 (d, *J* = 4.6, *ipso*-Ph'), 129.18 (*m*-Ph), 129.15 (*m*-Ph), 127.9 (*o*/*m*-Ph'), 127.5 (*o*/*m*-Ph'), 126.9 (*p*-Ph'), 121.74 (*p*-Ph), 121.68 (*p*-Ph), 117.1 (d, *J* = 4.6, *o*-PhN), 117.0 (d, *J* = 4.6, *o*-PhN), 54.0 (d, *J* = 5.3, *C*HCH_3), 43.04 (d, *J* = 12.2, CH_2), 43.00 (d, *J* = 12.2, CH_2), 27.9 (d, *J* = 5.3, NCH_3), 16.8 ($CHCH_3$)

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

15.31

IR: (KBr)

3057 (w), 3030 (w), 2981 (w), 2941 (w), 2883 (w), 2811 (w), 1599 (s), 1581 (m), 1499 (s), 1482 (s), 1453 (m), 1400 (m), 1384 (m), 1379 (s), 1363 (m), 1348 (m),

1317 (m), 1281 (s), 1231 (s), 1207 (s), 1190 (m), 1165 (s), 1135 (s), 1102 (w), 1066 (w), 1048 (m), 1033 (m), 994 (s), 949 (s), 877 (w), 777 (m), 749 (s), 734 (m), 702 (s), 688 (s), 616 (m), 586 (w), 530 (m)

MS: (EI, 70 eV)

391 (M^+, 29), 376 (13), 258 (14), 257 (46), 152 (23), 135 (10), 134 (100), 119 (13), 106 (42), 105 (37), 104 (20), 77 (19).

Opt. Rot.: $[\alpha]_D^{22}$ +1.7 (*c* = 1.1, $CHCl_3$)

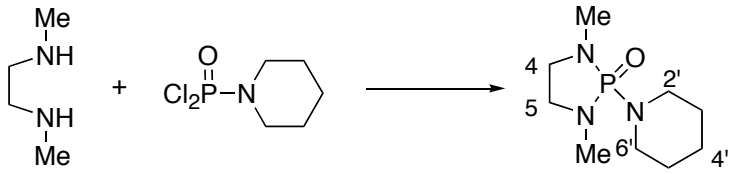
TLC: R_f 0.87 (EtOAc)

Analysis: $C_{23}H_{26}N_3OP$ (391.45)

Calcd.: C, 70.57%; H, 6.69%; N, 10.73%; P, 7.91%.

Found: C, 70.35%; H, 6.56%; N, 10.79%; P, 7.86%.

1,3-Dimethyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (11a)



11a

Following Representative Procedure I, to a solution of triethylamine (2.3 mL, 17 mmol) in 150 mL of dry CH_2Cl_2 were added solutions of *N*,*N*'-dimethylethylenediamine (0.71 mL; 6.7 mmol) in 30 mL of dry CH_2Cl_2 and piperidinophosphorus dichloride (1.02 mL; 6.7 mmol) in 30 mL of dry CH_2Cl_2 simultaneously over 2 h using a syringe pump at reflux under nitrogen. The solution was heated to reflux for 40 h then was concentrated under reduced pressure to give a colorless residue, which was purified by column chromatography on silica gel (ethyl acetate, ethyl acetate/2-propanol, 9/1, and then ethyl acetate/2-propanol, 7/3 as eluents). Distillation of the product, (bp 120-125 °C/0.05 mmHg; ABT) afforded 1.45 g (100%) of **11a** as colorless hygroscopic crystals. An analytical sample was prepared by further recrystalization from hexane.

Analytical Data for **11a**:

mp: 55-56 °C (hexane)

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

3.11 (m, 2H, C(4/5)H_2), 3.05-2.96 (m, 6H, C(4/5)H_2, C(2', 6')H_2), 2.49 (d, J = 9.8, 6H, CH_3), 1.51 (m, 2H, C(4')H_2), 1.41 (m, 4H, C(3', 5')H_2).

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

47.2 (d, J = 12.2, C(4, 5)), 45.3 (d, J = 3.1, C(2', 6')), 31.5 (d, J = 4.6, CH_3), 26.7 (d, J = 3.8, C(3', 5')), 24.7 (C(4')).

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

26.44

IR: ($CHCl_3$)

2979 (m), 2938 (s), 2852 (m), 1493 (w), 1482 (w), 1470 (w), 1445 (w), 1376 (w), 1351 (w), 1338 (w), 1264 (m), 1230 (m), 1191 (m), 1166 (s), 1122 (w), 1068 (m), 1040 (m), 1026 (w), 961 (s), 943 (m), 863 (w), 853 (w), 834 (w), 670 (w), 665 (w), 547 (w)

MS: (EI, 70 eV)

217 (M^+, 30), 133 (44), 131 (8), 90 (8), 85 (11), 84 (100)

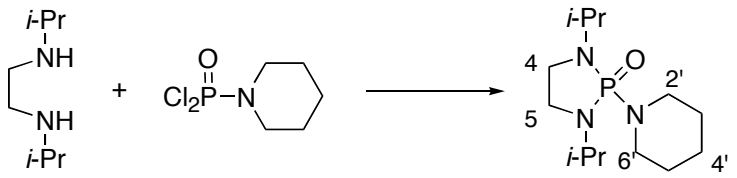
TLC: R_f 0.20 (EtOAc/*i*-PrOH, 9/1)

Analysis: $C_9H_{20}N_3OP$ (217.25)

Calcd.: C, 49.76%; H, 9.28%; N, 19.34%; P, 14.26%.

Found: C, 49.56%; H, 9.22%; N, 19.46%; P, 14.34%.

1,3-Diisopropyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (11b)



11b

Following Representative Procedure I, to a solution of triethylamine (2.4 mL, 17.5 mmol) in 150 mL of dry CH_2Cl_2 were added solutions of *N*,*N*'-diisopropylethylenediamine (1.27 mL, 7.0 mmol) in 30 mL of dry CH_2Cl_2 and piperidinophosphorus dichloride[5] (1.07 mL; 7.0 mmol)

in 30 mL of dry CH_2Cl_2 simultaneously over 2 h using a syringe pump at reflux under nitrogen. The solution was heated to reflux for 36 h then was concentrated under reduced pressure to give a colorless residue, which was purified by column chromatography on silica gel (ethyl acetate, ethyl acetate/2-propanol, 95/5 then ethyl acetate/2-propanol, 9/1 as eluents). Distillation of the product (bp 145 °C/0.05 mmHg; ABT) afforded 949 mg (50%) of **11b** as hygroscopic colorless crystals. The analytical sample was prepared by further recrystalization from hexane.

Analytical Data for **11b**:

mp: 52-53 °C (hexane)

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

3.34 (d sep, *J* = 8.2Hz, 6.6, 2H, CH), 3.09 (m, 2H, C(4/5)H_2), 2.97 (m, 6H, C(4/5)H_2, C(2', 6')H_2), 1.49 (m, 2H, C(4')H_2), 1.41 (m, 4H, C(3' 5')H_2), 1.13 (d, *J* = 6.6Hz, 6H, CH_3), 1.08 (d, *J* = 6.6Hz, 6H, CH_3).

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

45.6 (d, *J* = 3.1, C(2', 6')), 44.1 (d, *J* = 5.3, CH), 39.0 (d, *J* = 13.0, C(4, 5)), 26.7 (d, *J* = 4.6, C(3', 5')), 24.8 (C(4')), 21.4 (d, *J* =2.3, CH_3), 21.2 (d, *J* = 4.6, CH_3).

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

22.44

IR: ($CDCl_3$)

2970 (s), 2937 (s), 2851 (m), 1477 (w), 1464 (w), 1452 (w), 1443 (w), 1401 (w), 1390 (w), 1365 (w), 1336 (w), 1230 (m), 1222 (m), 1212 (m), 1179 (s), 1167 (m), 1112 (m), 1064 (m), 1027 (w), 960 (s), 862 (w), 698 (w), 669 (w), 561 (w)

MS: (EI, 70 eV)

273 (M^+, 34), 259 (10), 258 (70), 189 (15), 175 (79), 147 (8), 133 (17), 105 (17), 85 (10), 84 (100), 72 (12)

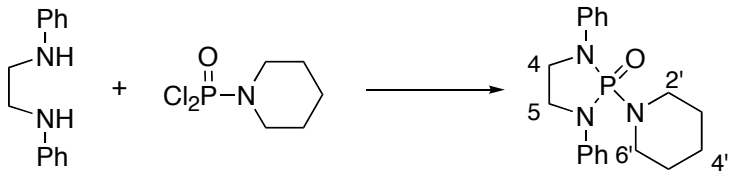
TLC: R_f 0.71 (EtOAc/*i*-PrOH, 9/1)

Analysis: $C_{13}H_{28}N_3OP$ (273.36)

Calcd.: C, 57.12%; H, 10.32%; N, 15.37%; P, 11.33%.

Found: C, 56.82%; H, 10.46%; N, 15.56%; P, 11.21%.

1,3-Diphenyl-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (11c)



11c

Following Representative Procedure I, to a solution of *N*,*N*'-diphenylethylene diamine (2.12 g, 10 mmol) in 20 mL of dry 1,2-dichloroethane were added triethylamine (3.5 mL, 25 mmol) and piperidinophosphorus dichloride[5] (1.53 mL, 10 mmol) at r.t. under nitrogen. The mixture was heated to reflux for 19 h when the mixture solidified. The mixture was filtered with help of CH_2Cl_2 (50 mL) and was washed with CH_2Cl_2 (100 mL). The filtrate and the washings were combined and concentrated under reduced pressure to give tan solid which was purified by column chromatography on silica gel (CH_2Cl_2 then CH_2Cl_2/2-propanol, 20/1 as eluents). Recrystalization from benzene/hexane afforded 1.741 g (51%) of **11c** as colorless fine needles.

Analytical Data for **11c**:

mp: 169-171 °C (benzene-hexane)

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

7.33 (t, *J* = 7.9, 4H, *m*-Ph), 7.17 (d, *J* = 7.9Hz, 4H, *o*-Ph), 7.00 (t, *J* = 7.3Hz, 2H, *p*-Ph), 3.81 (m, 4H, C(4, 5)H_2), 3.08 (m, 4H, C(2', 6')H_2), 1.40 (m, 2H, C(4')H_2), 1.26 (m, 4H, C(3', 5')H_2).

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

141.7 (d, *J* = 7.4Hz, *ipso*-Ph), 129.2 (*m*-Ph), 121.3 (*p*-Ph), 116.2 (d, *J* = 4.6Hz, *o*-Ph), 45.0 (d, *J* = 2.8Hz, C(2', 6')), 42.5 (d, *J* = 11.0Hz, C(4, 5)), 25.5 (d, *J* = 4.6Hz, C(3', 5')), 24.3 (C(4')).

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

13.32.

IR: (KBr)

2950 (m), 2933 (s), 2873 (m), 2853 (m), 2836 (s), 1598 (s), 1491 (s), 1465 (m), 1452 (m), 1438 (m), 1400 (m), 1383 (s), 1342 (s), 1325 (m), 1286 (s), 1249 (s), 1219 (s), 1187 (s), 1166 (s), 1147 (m), 1121 (s), 1072 (s), 1033 (s), 997 (s), 962

(s), 863 (m), 831 (m), 754 (s), 737 (m), 708 (s), 691 (s), 591 (m), 526 (s)

MS: (EI, 70 eV)

342 (M^++1, 22), 341 (M^+, 91), 258 (58), 257 (34), 153 (23), 152 (32), 119 (36), 107 (10), 106 (100), 105 (41), 104 (30), 84 (89), 77 (28).

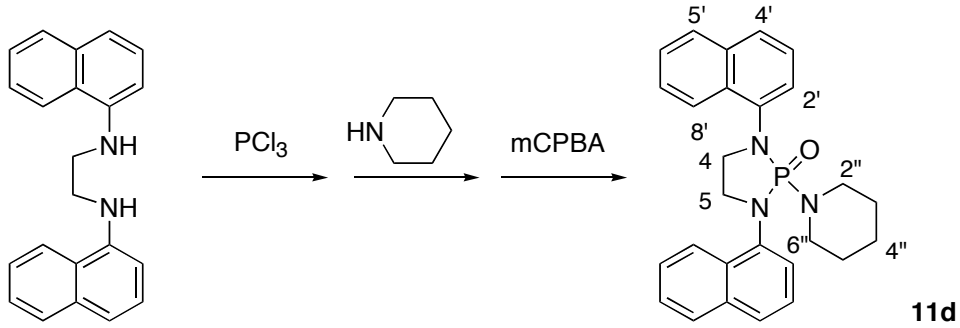
TLC: R_f 0.83 (EtOAc)

Analysis: $C_{19}H_{24}N_3OP$ (341.39)

Calcd.: C, 66.85%; H, 7.09%; N, 12.31%; P, 9.07%.

Found: C, 66.66%; H, 7.04%; N, 12.19%; P, 8.88%.

1,3-Di(1-naphthyl)-2-piperidino-1,3,2-diazaphospholidine 2-Oxide (11d)



11d

Following Representative Procedure II, to a stirred cold (-78 °C) solution of PCl_3 (0.61 mL, 7.0 mmol) in 10 mL of dry CH_2Cl_2 was added a solution of 1,2-di(1-naphthylamino)ethane[8] (2.0 g, 6.4 mmol) in 10 mL of dry CH_2Cl_2 through a dropping funnel under nitrogen. Then triethylamine (2.2 mL, 16 mmol) was added at the same temperature. The mixture was warmed to room temperature and was stirred for 24 h. After filtration of the precipitates, the filtrate was concentrated under reduced pressure to remove the excess reagents (PCl_3 and triethylamine).

The residue was suspended in 13 mL of dry CH_2Cl_2 and was stirred, to which was added piperidine (2.3 mL, 2.3 mmol) at room temperature. The mixture was stirred for 20 h, filtered to remove the precipitates, and was concentrated under reduced pressure to remove excess piperidine.

The residue was dissolved in 10 mL of CH_2Cl_2 and a solution of *m*-chloroperbenzoic acid (50%, 2.21 g, 6.4 mmol) in 10 mL of CH_2Cl_2 was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 24 h. Then sat. aq. $NaHCO_3$ solution

(25 mL) was added with stirring. The aqueous layer was separated and extracted with CH_2Cl_2 (2 X 10 mL). The combined organic solutions were washed with sat. aq. $NaHCO_3$ solution, then were dried over $MgSO_4$, filtered, and evaporated to give a residue that was chromatographed (SiO_2, benzene then benzene/ethyl acetate, 4/1). Recrystalized from diethyl ether/hexane gave 1.29 g (46%) of **11d** as slightly tan crystals.

Analytical Data for **11d**:

mp: 170-171 °C (Et_2O-hexane)

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

8.44 (d, *J* = 8.4, 2H, C(8')H), 7.93 (d, *J* = 7.3, 2H, C(2'/4')H), 7.91 (d, *J* = 8.1, 2H, C(5')H), 7.77 (d, *J* = 8.2, 2H, C(2'/4')H), 7.60 (ddd, *J* = 8.4, 6.8, 1.3, 2H, C(7')H), 7.53 (ddd, *J* = 8.2, 7.0, 1.1, 2H, C(6')H), 7.50 (t, *J* = 7.9, 2H, C(3')H), 4.19 (m, 2H, C(4/5)H_2), 3.82 (m, 2H, C(4/5)H_2), 3.06 (m, 4H, C(2", 6")H_2), 1.14 (m, 2H, C(4")H_2), 0.92 (m, 4H, C(3", 5")H_2).

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

138.0 (d, *J* = 4.6), 134.8, 131.3 (d, *J* = 5.3), 128.5, 126.6, 126.1, 126.0, 125.9, 124.5 (d, *J* = 3.0), 123.5 (br), 49.3 (d, *J* = 12.2, C(4, 5)), 45.7 (d, *J* = 3.1, C(2", 6")), 26.0 (d, *J* = 4.6, C(3", 5")), 24.1 (C(4")).

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

16.56.

IR: (KBr)

3037 (w), 3010 (w), 2964 (m), 2931 (s), 2846 (s), 1591 (s), 1574 (s), 1509 (m), 1478 (w), 1462 (s), 1441 (m), 1394 (s), 1372 (s), 1341 (s), 1276 (s), 1237 (s), 1219 (s), 1205 (s), 1180 (s), 1168 (s), 1116 (s), 1100 (s), 1080 (s), 1071 (s), 1028 (s), 1017 (m), 966 (s), 936 (m), 804 (s), 797 (s), 775 (s), 731 (s), 680 (m), 646 (m), 623 (m), 605 (w),

MS: (EI, 70 eV)

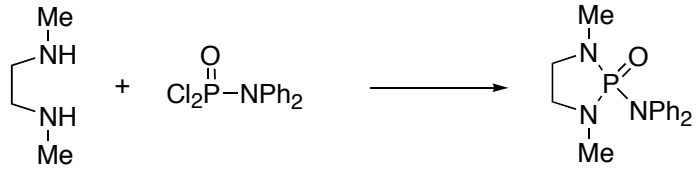
442 (M^++1, 51), 441 (M^+, 100), 359 (25), 358 (77), 357 (18), 291 (33), 272 (16), 203 (20), 188 (16), 186 (18), 170 (11), 169 (32), 168 (18), 167 (11), 157 (21), 156 (92), 155 (40), 154 (51), 143 (10), 130 (10), 129 (15), 128 (23), 127 (28), 115 (18), 84 (35).

TLC: R_f 0.83 (EtOAc)

Analysis: $C_{27}H_{28}N_3OP$ (441.51)

Calcd.:	C, 73.45%;	H, 6.39%;	N, 9.52%;	P, 7.02%.
Found:	C, 73.32%;	H, 6.42%;	N, 9.61%;	P, 6.74%.

1,3-Dimethyl-2-diphenylamino-1,3,2-diazaphospholidine 2-Oxide (12a)



12a

Following Representative Procedure I, to a solution of triethylamine (1.74 mL, 12.5 mmol) in 150 mL of dry CH_2Cl_2 were added solutions of *N*,*N*'-dimethylethylenediamine (0.53 mL, 5.0 mmol) in 15 mL of dry CH_2Cl_2 and diphenylaminophosphorus dichloride (1.43 g, 5.0 mmol) in 15 mL of dry CH_2Cl_2 simultaneously and dropwise at reflux under nitrogen. The solution was heated to reflux for 15 h then was concentrated under reduced pressure to give a residue, which was purified by column chromatography on silica gel (ethyl acetate then ethyl acetate/2-propanol, 10/1 as eluents). Recrystalization from CH_2Cl_2/hexane afforded 1.32 g (87%) of **12a** as colorless needles.

Analytical Data for **12a**:

mp: 115-116 °C (CH_2Cl_2-hexane)

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

7.28 (m, 8H, *o*, *m*-Ph), 7.11 (m, 2H, *p*-Ph), 3.12 (m, 2H, CH_2), 2.79 (m, 2H, CH_2), 2.64 (d, J_{PH} = 9.5, 6H, CH_3).

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

145.2 (d, J_{PC} = 4.6, *ipso*-Ph), 128.8 (*m*-Ph), 127.2 (d, J_{PC} = 3.1, *o*-Ph), 124.9 (*p*-Ph), 46.6 (d, J_{PC} = 13.7, CH_2), 31.2 (d, J_{PC} = 6.1, CH_3).

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

19.39.

IR: (KBr)

3090 (w), 3059 (w), 3020 (w), 3000 (w), 2987 (w), 2969 (w), 2987 (m), 2969 (m), 2934 (m), 2912 (s), 2898 (s), 2861 (s), 2820 (m), 1584 (s), 1485 (s), 1454 (s), 1444 (s), 1427 (m), 1400 (m), 1381 (s), 1355 (s), 1336 (m), 1311 (m), 1254 (s), 1203 (s), 1173 (s), 1088 (m), 1074 (s), 1040 (s), 1033 (s), 1005 (s), 981 (s), 945 (s), 925 (s), 894 (s), 862 (m), 851 (m), 762 (s), 733 (s), 721 (s), 713 (s), 696 (s), 667 (s), 610 (m), 604 (m), 541 (s), 516 (m)

MS: (EI, 70 eV)

302 (M^++1, 9), 301 (M^+, 51), 169 (5), 168 (5), 167 (9), 134 (5), 133 (100), 90 (6), 69 (9).

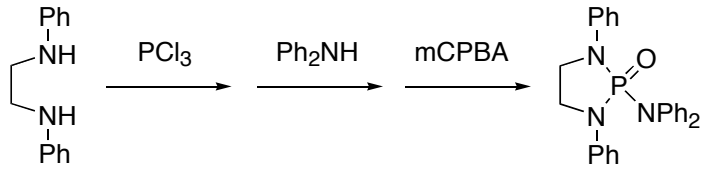
TLC: R_f 0.61 (EtOAc/*i*-PrOH, 9/1)

Analysis: $C_{16}H_{20}N_3OP$ (301.33)

Calcd.: C, 63.78%; H, 6.69%; N, 13.95%; P, 10.28%.

Found: C, 63.73%; H, 6.79%; N, 14.21%; P, 9.97%.

1,3-Diphenyl-2-diphenylamino-1,3,2-diazaphospholidine 2-Oxide (12b)



12b

Following Representative Procedure II, to a stirred cold (-78 °C) solution of PCl_3 (0.5 mL, 5.73 mmol) in 20 mL of dry CH_2Cl_2 was added a solution of *N*,*N*'-diphenylethylene diamide (1.10 g, 5.17 mmol) in 5 mL of dry CH_2Cl_2 immediately followed by addition of triethylamine (1.8 mL, 13 mmol). The mixture was warmed to rt and stirring was continued overnight. Solvent, excess PCl_3 and triethylamine were removed under reduced pressure.

The residue was suspended in 10 mL of dry CH_2Cl_2 and a solution of diphenylamine (0.875 g, 5.17 mmol) dissolved in triethylamine (2.2 mL, 15.5 mmol) was added to it via a syringe, which was washed with 5 mL of dry CH_2Cl_2. The mixture was stirred at rt for 36 h and then was concentrated under reduced pressure to remove excess triethylamine.

The residue was suspended in CH_2Cl_2 (25 mL) and was treated with *m*CPBA (50 %, 1.78 g, 5.17 mmol) at 0 °C. The mixture was stirred at 0 °C-rt for 20 h, then sat. aq. $NaHCO_3$ solution (25 mL) was added with stirring. The aqueous layer was separated and extracted with CH_2Cl_2 (2 X 10 mL). The combined organic solutions were washed with sat. aq. $NaHCO_3$ (10 mL), dried over $MgSO_4$, filtered, and evaporated to give a crude material. The product was purified by column chromatography on silica gel (CH_2Cl_2/hexane, 1/2 then CH_2Cl_2/hexane/2-propanol, 1/2/0.03) and recrystallization from benzene/hexane to give 1.59 g (72 %) of **12b** as colorless needles.

Analytical Data for **12b**:

mp: 210-211 °C (benzene/hexane)

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

7.35 (t, *J* = 7.8, 4H, *m*-Ph), 7.23 (d, *J* = 7.8, 4H, *o*-Ph), 7.21 (t, *J* = 7.8, 4H, *m*-Ph'), 7.13 (t, *J* = 7.3, 2H, *p*-Ph'), 7.08-7.03 (m, 6H, *o*-Ph', *p*-Ph), 3.62 (m, 2H, CH_2), 3.14 (m, 2H, CH_2).

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

143.6 (d, *J* = 5.3, *ipso*-Ph), 141.1 (d, *J* = 7.6, *ipso*-Ph), 129.3 (*m*-Ph), 129.0 (*m*-Ph), 127.4 (d, *J* = 2.3, *o*-Ph), 125.8 (*p*-Ph), 121.8 (*p*-Ph), 116.6 (d, *J* = 5.3, *o*-Ph), 42.2 (d, *J* = 12.2, CH_2)

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

7.43

IR: (KBr)

3064 (m), 3055 (m), 3036 (m), 2970 (w), 2946 (m), 2888 (m), 2874 (m), 1597 (s), 1492 (s), 1467 (s), 1451 (m), 1401 (m), 1383 (m), 1362 (s), 1353 (s), 1310 (s), 1267 (s), 1255 (s), 1231 (s), 1213 (s), 1149 (m), 1127 (s), 1106 (s), 1077 (s), 1031 (s), 1019 (s), 996 (s), 958 (s), 935 (m), 751 (s), 701 (s), 691 (s), 586 (s), 531 (s)

MS: (EI, 70 eV)

426 (M^++1, 44), 425 (M^+, 90), 258 (38), 257 (100), 169 (10), 168 (15), 167 (22), 152 (64), 106 (16), 105 (46), 104 (37), 91 (10), 77 (38).

TLC: R_f 0.90 (EtOAc)

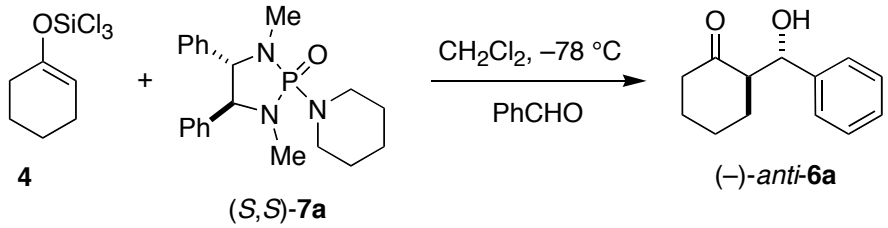
Analysis: $C_{26}H_{24}N_3OP$ (425.47)

Calcd.: C, 73.40%; H, 5.69%; N, 9.88%; P, 7.28%

Found: C, 73.48%; H, 5.63%; N, 9.92%; P, 6.98%

2. Catalyzed Aldol Additions of Trichlorosilyl Enolates

General Procedure for Catalyzed Aldol Additions of Trichlorosilyl Enolates 4 and (*Z*)-9 with Fast Addition of Aldehyde: (–)-(2*R*,1'*S*)-2-(Hydroxyphenylmethyl)cyclohexanone (*anti*-6a)



4 (*S*,*S*)-**7a** (–)-*anti*-**6a**

Catalyst (*S*,*S*)-**7a** (7.3 mg, 0.02 mmol, 0.1 equiv) was dissolved in CH_2Cl_2 (2 mL) and was cooled to –78 °C. Trichlorosilyl enolate **4b** (40 μL, 0.22 mmol, 1.1 equiv) was added dropwise over 1 min Benzaldehyde (20.3 μL, 1.0 mmol) was then added neat, over 20 sec. The reaction mixture was stirred at –78 °C for 2 h, then sat. aq. $NaHCO_3$ solution (5 mL)was added quickly and the mixture was allowed to warm to rt. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 X 10 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The syn/anti ratio was determined by ^{1}H NMR (400 MHz) analysis to be 1/28. The crude material was purified by column chromatography (SiO_2, hexane/EtOAc, 6/1) to give 1.3 mg of (–)-*syn*-**6a** as an oil and 35.3 mg (90% total) of (–)-*anti*-**6a** as a clear oil.

Analytical Data for (–)-*anti*-**6a:**

mp: 41-42 °C

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

7.36-7.26 (m, 5 H, Ph), 4.78 (dd, *J* = 9.2 and 2.4, 1 H, PhC*H*OH), 3.98 (d, *J* =2.4, 1 H, OH), 2.64-2.58 (m, 1 H, C(2)H_{ax}), 2.50-2.44 (m, 1 H, C(6)H_{eq}), 2.39-2.31

(m, 1 H, C(6)H_{ax}), 2.11-2.03 (m, 1 H, C(5)H_{eq}), 1.80-1.74 (m, 1 H, C(4)H_{eq}), 1.71-1.47 (m, 3 H, C(5)H_{ax}, C(3)H_{eq}, C(4)H_{ax}), 1.34-1.23 (m, 1 H, C(3)H_{ax})

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

215.53 (C=O), 140.84 (*ipso*-Ph), 128.30 (*m*-Ph), 127.81 (*p*-Ph), 126.95 (*o*-Ph), 74.64 (CHOH), 57.35 (C(2)), 42.60 (C(6)), 30.76 (C(3)), 27.74 (C(5)), 24.63 (C(4))

IR: ($CHCl_3$)

3536 (m, OH), 3066 (m), 3033 (m), 2945 (s), 2904 (m), 2868 (m), 1697 (s, C=O), 1497 (m), 1450 (s), 1426 (m), 1400 (m), 1322 (m), 1312 (m), 1297(m), 1226 (s), 1201(s), 1191 (m), 1130 (s, C-O), 1101 (m), 1064 (m), 1041 (s), 1029 (m), 1016 (m), 846 (m), 777 (m), 731 (m), 724 (m), 707(m)

MS: (EI, 70 eV)

204 (M^+, 6), 186 ($M^+ - H_2O$, 21), 106 ($M^+ - C_6H_{10}O$, 40), 98 ($M^+ - C_7H_6O$, 100), 70 (48), 55 (33)

TLC: R_f 0.24 (hexane/EtOAc, 3/1)

Opt. Rot.: $[\alpha]_D^{24}$ –24.2° (*c* =1.03, $CHCl_3$)

HPLC: t_R (2*R*,1'*S*)-**6a** 16.2 min (4.6%); t_R (2*S*,1'*R*)-**6a** 19.6 min (95.4%) (Chiracel OJ, 90/10 hexane/*i*-PrOH, 0.5 mL min^{-1})

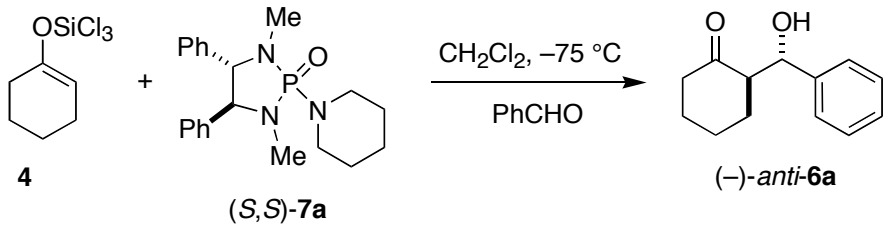
HPLC: t_R (2*S*,1'*S*)-**6a** 16.8 min (40.5%); t_R (2*R*,1'*R*)-**6a** 22.3 min (59.5%) (Chiracel OJ, 90/10 hexane/*i*-PrOH, 0.5 mL min^{-1})

Analysis: $C_{13}H_{16}O_2$ (204.27)

Calcd.: C, 76.44%; H, 7.90%

Found: C, 76.45%; H, 7.80%

General Procedure for Catalyzed Aldol Additions of 4 with Slow Addition of Aldehyde: (–)-(2*R*,1'*S*)-2-(Hydroxyphenylmethyl)cyclohexanone (*anti*-6a)



4 (*S*,*S*)-**7a** (–)-*anti*-**6a**

Catalyst (*S*,*S*)-**7a** (37.6 mg, 0.1 mmol, 0.1 equiv) was dried under vacuum (0.05 mmHg) for 12 at rt, CH_2Cl_2 (5 mL) was added and the solution was cooled to –75 °C (internal). Trichlorosilyl enolate **4** (200 μL, 1.1 mmol, 1.1 equiv) was added dropwise over 2 min A solution of benzaldehyde (102.0 μL, 1.0 mmol) in CH_2Cl_2 (5 mL) was then added to the first solution, dropwise, via cannula over 45 min During the addition the temperature remained at –75 °C. The reaction mixture was stirred at –75 °C for 30 min, then it was quickly poured into cold (0 °C) sat. aq. $NaHCO_3$ solution (10 mL) and the slurry was stirred for 15 min The two-phase mixture was filtered through Celite, the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 X 50 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated. The syn/anti ratio was determined by ^1H NMR (500 MHz) analysis to be 1/>50. The crude material was purified by column chromatography (SiO_2, hexane/EtOAc, 6/1) to give 2.4 mg of (–)-*syn*-**6a** as an oil and 189.8 mg (94% total) of (–)-*anti*-**6a** as a clear oil .

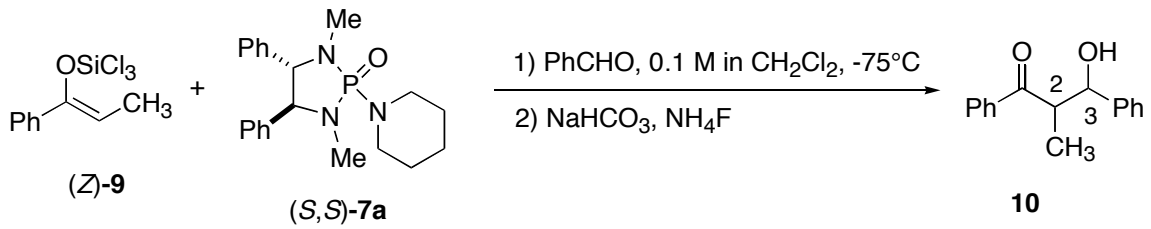
Analytical Data for (–)-*syn*-**6a**:

SFC: t_R (2*S*,1'*S*)-**6a** 2.62 min (41.0%); t_R (2*R*,1'*R*)-**6a** 3.26 min (59.0%) (Chiralcel OJ, 150 bar, 40 °C, 6% CH_3OH in CO_2, 2.5 mL min^{-1})

Analytical Data for (–)-*anti*-**6a**:

SFC: t_R (2*S*,1'*R*)-**6a** 2.23 min (4.5%); t_R (2*R*,1'*S*)-**6a** 2.54 min (95.5%) (Chiralcel OJ, 150 bar, 40 °C, 6% CH_3OH in CO_2, 2.5 mL min^{-1})

Reaction between (*Z*)-9 and Benzaldehyde Promoted by Phosphoramide (*S,S*)-7a



Phosphoramide (*S,S*)**-7a** (34.7 mg, 0.079 mmol) was dried at room temperature under high vacuum (ca. 0.05 mmHg) for 3 h in a two-necked round-bottomed flask. To this were added trichlorosilyl enolate (*Z*)**-9** (113 mL, 0.55 mmol) and 5 mL of dry CH_2Cl_2 successively under nitrogen. After the solution was cooled to -75 °C (internal temperature, dry ice-2-propanol bath), benzaldehyde (50 mL, 0.49 mmol) was added dropwise and the mixture was stirred at -75 °C for 6 h.

The reaction mixture was poured into a mixture of 5 mL of sat. aq. $NaHCO_3$ solution and 8 mL of 20% aqueous NH_4F solution at 0 °C and was stirred for 1 h at room temperature. After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (2 X 10mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the crude products.

By the ^1H NMR analysis of of the crude products (comparison of the integrarions of C(3)*H* of **10**; d 5.25 (br) for *syn*-**10** and d 5.00 (dd) for *anti*-**10**), the diastereomeric ratio was determined to be syn/anti = 1/1.4. The crude mixture was chromatographed on silica gel (hexane/ethyl acetate = 20/1.5) to give *syn*-**10** (26.6 mg, 0.111 mmol) and *anti*-**10** (42.0 mg, 0.173 mmol). Total yield was 58 %.

Reaction in 8 min

Reactions were performed as mentioned above but the reaction time was 8 min In the reactions of the promoters **11a**, **11b**, **11c**, and **HMPA**, 0.20 mL (1.1 mmol) of **4** and 0.10 mL (0.98 mmol) of benzaldehyde were used. In the reactions of **11d**, **12a**, and **12b**, 100 mL (0.55 mmol) of enolate **4** and 50 mL (0.49 mmol) of benzaldehyde were used.

Conversion was determined by comparison of ^1H NMR integrations of the aromatic

signal of remained benzaldehyde (d 7.88 (d, 2H, *o*-Ph)) and the C(1')H signals of **6a**.

Reaction for Loading Effect

According to the general method, most of the reactions for loading effect were performed in 0.5 mmol scale; i.e. using 50 mL (0.49 mmol) of benzaldehyde and 100 mL (0.55 mmol) of enolate **4** or 113 mL of enolate (*Z*)**-9** in 5 mL of dry CH_2Cl_2. Other procedure was the same.

When the loading of the promoter was more than 40 mol%, the reaction scale was 0.25 mmol; i.e. using 25 mL (0.25 mmol) of benzaldehyde and 50 mL (0.28 mmol) of enolate **4** in 2.5 mL of dry CH_2Cl_2.

Concentration Effect

(1 M reaction) Phosphoramide **12a** (15.6 mg, 0.052 mmol) was dried at room temperature under high vacuum (ca. 0.05 mmHg) for 3 h in a two-necked round-bottomed flask. To this were added trichlorosilyl enolate **4** (0.10 mL, 0.55 mmol) and 0.5 mL of dry CH_2Cl_2 successively under nitrogen. After the solution was cooled to -75 °C (internal temperature, dry ice-2-propanol bath), benzaldehyde (50 mL, 0.49 mmol) was added dropwise and the mixture was stirred at -75 °C for 1.5 h.

(0.01 M reaction) Procedure was the same as above except using 50 mL of dry CH_2Cl_2 as the solvent and the reaction time extended to 6 h.

Quenching procedure, determination of the product ratio, and isolation of the product were the same in both cases as those of the general method.

Loading Effect of Aldehyde

Phosphoramide **11c** (18.5 mg, 0.054 mmol) was dried at room temperature under high vacuum (ca. 0.05 mmHg) for 3 h in a two-necked round-bottomed flask. To this were added trichlorosilyl enolate **4** (0.10 mL, 0.55 mmol) and 5 mL of dry CH_2Cl_2 successively under nitrogen. After the solution was cooled to -75 °C (internal temperature, dry ice-2-propanol bath), benzaldehyde (0.20 mL, 1.97 mmol) was added dropwise and the mixture was stirred at -75 °C for 3 h. Quenching procedure and determination of the product ratio were the same as those of the general method.

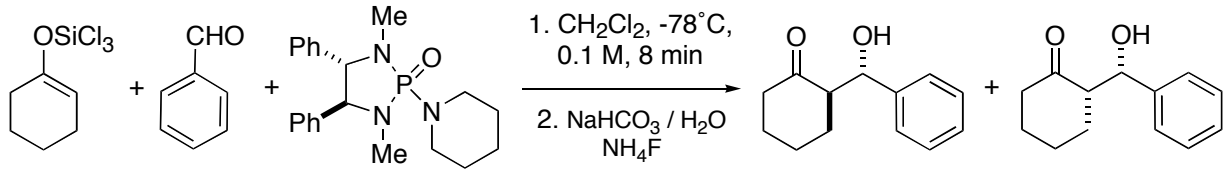
Phosphoramide-Promoted Reaction in the Presence of Acid

Phosphoramide **12a** (3.4 mg, 0.011 mmol) was dried at room temperature under high vacuum (ca. 0.05 mmHg) for 3 h in a two-necked round-bottomed flask. To this were added trichlorosilyl enolate **4** (100 mL, 0.55 mmol) and 4 mL of dry CH_2Cl_2 successively under nitrogen. After the solution was cooled to -75 °C (dry ice-2-propanol bath), benzoic acid (1.4 mg, 0.011 mmol) in 1 mL of dry CH_2Cl_2 and benzaldehyde (50 mL, 0.49 mmol) were added successively and the mixture was stirred at -75 °C for 3 h. The cold reaction mixture was poured into a mixture of 5 mL of saturated aqueous $NaHCO_3$ and 8 mL of 20 % aqueous NH_4F at 0 °C with vigorous stirring, which was continued for 30 min at rt. Then insoluble material was filtered through a celite pad and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic solutions were dried ($MgSO_4$) and condensed to give white solid.

The product ratio was determined by ^1H NMR as metioned above. The product **6a** was isolated (86.8 mg, 87 %) by column chromatography.

Other experiments in Tables 13 and 14 were performed in a similar way. For triflic acid, a CH_2Cl_2 solution (0.113 M) was prepared in advance by diluting 20 mL (0.226 mmol) of triflic acid with 2 mL of dry CH_2Cl_2 under nitrogen.

Aldol Addition Reactions of Trichlorosilyl Enolate 4 to Benzaldehyde Catalyzed by (*S,S*)-7a



4 **5a** (*S,S*)-**7a** *anti*-**6a** *syn*-**6a**

The phosphoramide (*S,S*)-**7a** (36.9 mg, 0.1 mmol, 0.1 equiv) was weighed into a dry flask and dried under high vacuum for 4 h and then CH_2Cl_2 (10 mL) was added under argon. The solution was then cooled to –78˚ C and trichlorosilyl enolate **4** (201 μL, 1.1 mmol, 1.1 equiv) was added neat and the solution stirred for 10 min Benzaldehyde (167 μL, 1.0 mmol, 1.0 equiv) was added into the reaction mixture via a syringe along the wall of the flask and the reaction mixture was stirred at –78 ˚C for 8 min and then poured into a mixture of sat. aq. $NaHCO_3$ (10

mL) solution and 20% aq. NH_4F (10 mL) solution at 0 ˚C with vigorous stirring. The mixture was then allowed to stir at rt for 30 min Layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 X 10 mL). The organic extracts were washed (brine), dried (Na_2SO_4) and concentrated in vacuo to give an oil. ^1H NMR analysis showed a syn/anti ratio of 1/35. The crude product was then separated by column chromatography (SiO_2, hexane/EtOAc 9/1 to 3/1) to give 6.3 mg (3%) *syn*-**6a**, and 196.1 mg of *anti*-**6a** (96%) (total yield 99%). Analysis of the products by chiral HPLC revealed syn er of 1.2/1 and anti er of 21/1.

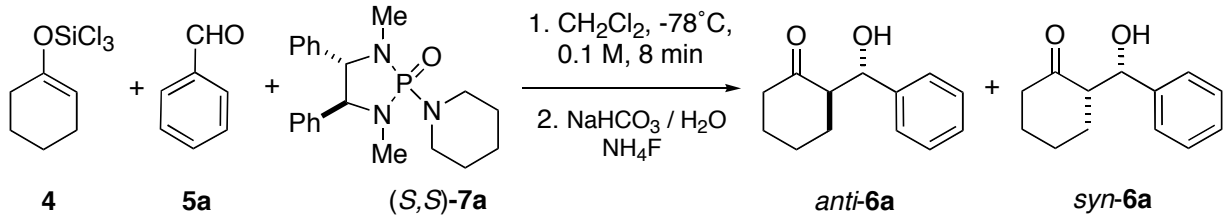
Analytical Data for *anti*-**6a**:

HPLC: t_R ((2*S*,1'*R*)-**6a**) 14.36 min (4.5%), and t_R ((2*R*,1'*S*)-**6a**) 17.52 min (95.5%) (Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min) (er 21/1)

Analytical Data for *syn*-**6a**

HPLC: t_R (2*R*,1'*R*-**6a**) 15.22 min (45.4%), and t_R (2*S*,1'*S*-**6a**) 20.82 min (54.6%) (Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min) (er 1.2/1)

Aldol Addition Reactions of Trichlorosilyl Enolate 4 to Benzaldehyde Catalyzed by (*S,S*)-7a (One Equivalent)



4 **5a** (*S,S*)-**7a** *anti*-**6a** *syn*-**6a**

Following the procedure described above from the phosphormide (*S,S*)-**7a** (369.3 mg, 1.0 mmol, 1.0 equiv), the trichlorosilyl enolate **4** (201 μL, 1.1 mmol, 1.1 equiv) and benzaldehyde (101.6 μL, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was obtained 2.1 mg (1%) *syn*-**6a**, and 199.1 mg of *anti*-**6a** (97%) (total yield 98%). Diastereomeric ratio was determined on the crude product mixture by ^1H NMR analysis (syn/anti, 1/95).

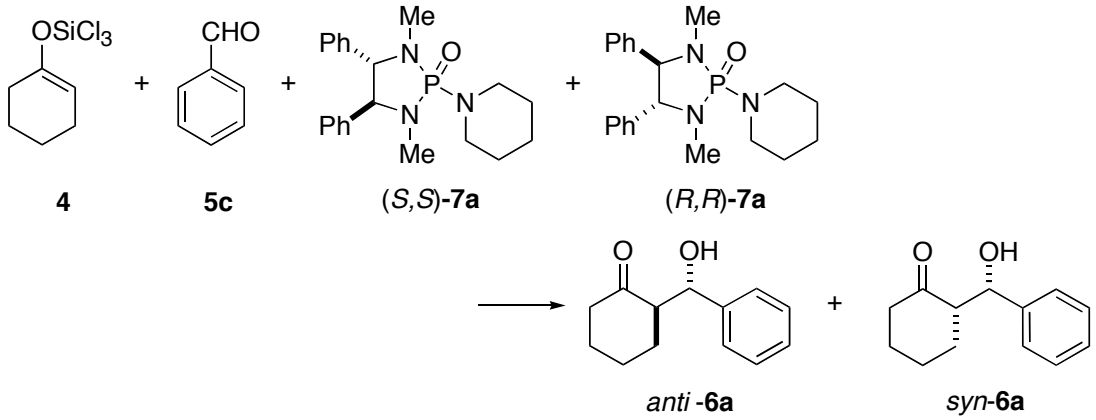
Analytical Data for *anti*-**6a**:

HPLC: t_R ((2*S*,1'*R*)-**6a**) 13.33 min (4.15%), and t_R ((2*R*,1'*S*)-**6a**) 16.28 min (95.85%) (Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min) (er 23/1)

Analytical Data for *syn*-**6a**

HPLC: t_R (2*R*,1'*R*-**6a**) 13.96 min (15.3%), and t_R (2*S*,1'*S*-**6a**) 18.10 min (84.7%) (Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min) (er 5.5/1)

Nonlinear Effect Studies: **Phosphoramide (*S,S*)-7a.**

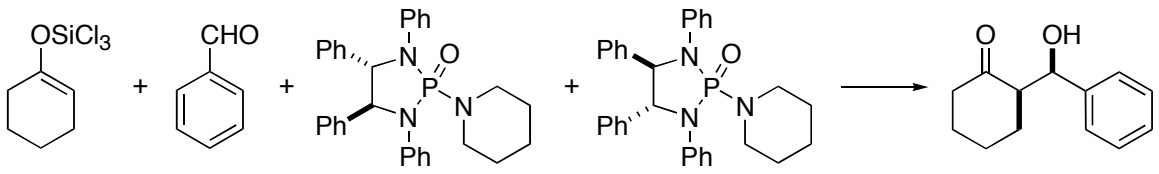


Phosphoramide (*S,S*)-**7a** (25.89 mg, 0.07008 mmol) and (*R,R*)-**7a** (11.11 mg, 0.03007 mmol) was weighed into a round bottomed flask and dried under high vacuums for 4 h. The phosphoramide (39.95% e.e. based on the weights) was then dissolved in CH_2Cl_2 (10 mL) under argon and the solution cooled to –78 ˚C. The trichlorosilyl enolate **4** (201 μL, 1.1 mmol) was then added via a syringe and solution stirred for 5 min Benzaldehyde (102 μL, 1.0 mmol) was then added and the solution stirred at –78˚ C for 8 min The reaction mixture was then poured into a mixture of sat. aq. $NaHCO_3$ solution and 20% aq. NH_4F solution at 0˚ C with vigorous stirring. The mixture was then stirred at rt for 30 min The layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 X 20 mL). The combined organic solution was washed with brine, dried ($MgSO_4$) and concentrated to give oily residue, which was then purified by column chromatography (SiO_2, hexane/EtOAc, 9/1 to 3/1) to give *anti*-**6a** (189 mg, 93%) along with *syn*-**6a** (9.2 mg, 5%).

Analytical Data for *anti*-**6a**

HPLC: t_R ((2*S*,1'*R*)-**6a**) 13.65 min (23.4%), and t_R ((2*R*,1'*S*)-**6a**) 16.87 min (76.6%) (Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min) (53.3% e.e.)

Nonlinear Effect Studies: **Phosphoramide (*S,S*)-7j.**



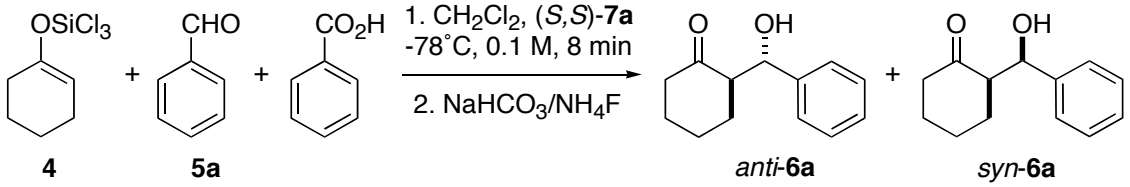
4 **5a** (*S,S*)-**7j** (±)-**7j** *syn*-**6a**

A mixture of (*S,S*)-**7j** (4.96 mg, 0.01005 mmol) and (±)-**7j** (19.69 mg, 0.03989 mmol) was dried under high vacuums over night and then dissolved in CH_2Cl_2 (5 mL) under argon (20.1% e.e. of phosphoramide **7j** based on weights). The solution was cooled to –78° C and enolate **4** (100.3 μL, 0.55 mmol) was added. After the solution was stirred for 5 min at –78° C benzaldehyde (50.8 μL, 0.50 mmol) was added and the solution was stirred at –78° C for 2 h. The reaction was then quenched by pouring into a mixture of sat. aq. $NaHCO_3$ solution (6 mL) and 20% aq. NH_4F solution (6 mL) solution at 0° C with vigorous stirring. The mixture was then stirred at rt for 1 h and then filtered through a layer of Celite. The layers of the filtrate were separated and the aqueous layer extracted with CH_2Cl_2 (2 X 10 mL). The combined organic solution was washed with brine, dried ($MgSO_4$) and concentrated to give solid residue (syn/anti >100/1), which was then purified by column chromatography (SiO_2, hexane/EtOAc, 9/1) to give *syn*-**6a** (86.7 mg, 85%). HPLC analysis showed 11.3% e.e. for *syn*-**6a**.

Analytical Data for *syn*-**6a**

HPLC: t_R (2*R*,1'*R*)-**6a**)13.35 min (55.65%), and t_R ((2*S*,1'*S*)-**6a**) 17.87 min (44.35%)
(Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min)

Benzoic Acid Effects on the Phosphoramide (*S,S,*)-7a Catalyzed Reactions



4 **5a** *anti*-**6a** *syn*-**6a**

To a solution of the phosphoramide (*S,S,*)**-7a** (36.9 mg, 0.1 mmol, 0.1 equiv) and benzoic acid (12.2 mg, 0.1 mmol, 0.1 equiv) in CH_2Cl_2 (10 mL) was added **4** (201 μL, 1.1 mmol, 1.1 equiv) via a syringe at –78 ˚C. The solution was stirred for 5 min before benzaldehyde (102 μL, 1.0 mmol, 1.0 equiv) was added along the side wall of the flask at –78 ˚C. The reaction mixture was then stirred for 8 min at this temperature and poured into a mixture of sat. aq. $NaHCO_3$ solution (10 mL) and 20 % aq. NH_4F solution (10 mL) at 0 ˚C with rapid stirring. The mixture was then warmed to rt and stirred for 30 min The layers were separated and aqueous layer was extracted with CH_2Cl_2 (2 X 10 mL). The combined extracts were washed with brine (10 mL) and dried (MgSO4). Solvent was removed in vacuo to give the crude product as an oil. ^1H NMR analysis showed conversion of 24% with syn/anti ratio of 4.1/1. The crude product was then separated by column chromatography (SiO_2, hexane/EtOAc 9/1 to 3/1) to give the syn product *syn*-**6a** (28.7 mg, 1.0/1 er) as white crystals, anti product *anti*-**6a** (6.5 mg, er, 8.1/1) as an oil and 1.4 mg of mixed product (total yield 18%).

Analytical Data for *syn*-**6a**

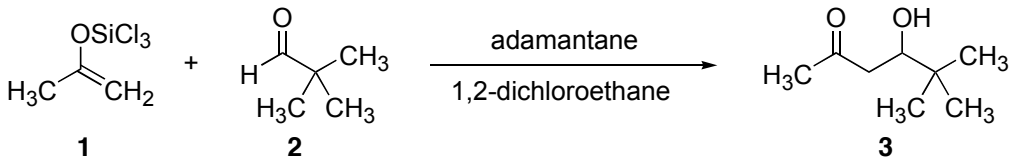
HPLC: t_R ((2*R*,1'*R*)-**138**) 13.92 min (51.0%), and t_R ((2*S*,1'*S*)-**138**) 18.50 min (49.0%)
(Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min)

Analytical Data for *anti*-**6a**

HPLC: t_R ((2*S*,1'*R*)-**6a**) 13.50 min (10.8%), and t_R ((2*R*,1'*S*)-**6a**) 16.34 min (89.2%)
(Daicel ChiralCel OJ, hexane/*i*-PrOH, 90/10, 0.8 mL/min)

Kinetics: General Procedures.

General Procedure 1a, GC Kinetics using zeroth order aldehyde:



Pivalaldehyde (**2**) (1.16 mL, 10.4 mmol, 10 equiv.) was added rapidly to a solution of enolate, **1** (150 μL, 1.04 mmol) and adamantane (22.3 mg, 0.16 mmol) in 1,2-dichloroethane (8 mL) at room temperature. Small aliquots were removed via cannula directly into a cold (0 °C) solution of concentrated KF and 1.0 M phosphate buffer (1/1, v/v). The mixture was vigorously vortexed and then was extracted with EtOAc. The mixture was passed through Florisil (plug) and quickly eluted with EtOAc. The sample was then analyzed by GC.

General Procedure 1b, GC Kinetics using zeroth order enolate:

Pivalaldehyde (**2**) (29 μL, 0.26 mmol) was added rapidly to a solution of enolate**, 1** (380 μL, 2.6 mmol, 10 equiv.) and adamantane (6.8 mg, 0.05 mmol) in dichloroethane (2 mL) at room temperature. Small aliquots were removed via cannula directly into a cold (0 °C) solution of concentrated KF and 1.0 M phosphate buffer (1/1, v/v). The mixture was vigorously vortexed and then was extracted with EtOAc. The mixture was passed through Florisil (plug) and quickly eluted with EtOAc. The sample was then analyzed by GC.

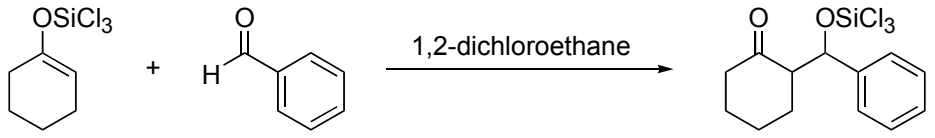
GC:

Instrument: Hewlett-Packard 5890, Hewlett-Packard 3396 Series III Integrator

Conditions: Hewlett-Packard HP-5, 50 m 150 °C, 15 psi, 4 μL.

Retention Times (t_R): **3** = 5.8 min; Adamantane = 7.0 min

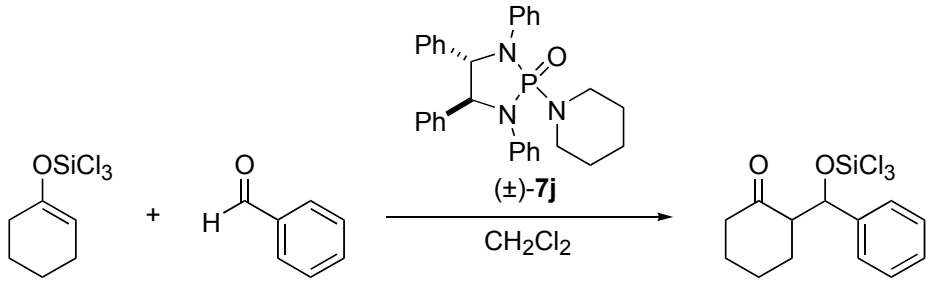
General Procedure 2a, Uncatalyzed ReactIR Kinetics:



4 **5a** **i**

A dry reaction vessel was assembled onto the IR probe and vented for several minutes with dry nitrogen. 1,2-dichloroethane (1.5 mL) was then added to the reaction vessel and a *background* file was collected. Enolate **1** (82 μL, 0.45 mmol) was then added and allowed to fully mix and the solution was left to equilibrate before beginning data collection. Benzaldehyde (46 μL, 0.45 mmol) was added quickly to the enolate solution. IR spectra were collected at 3 min intervals for 180 min at 30 °C by internal monitoring. Recorded disappearance of peak at 1679 cm^{-1} (enolate C=C).

General Procedure 2b, Catalyzed ReactIR Kinetics:



4 **5a** **i**

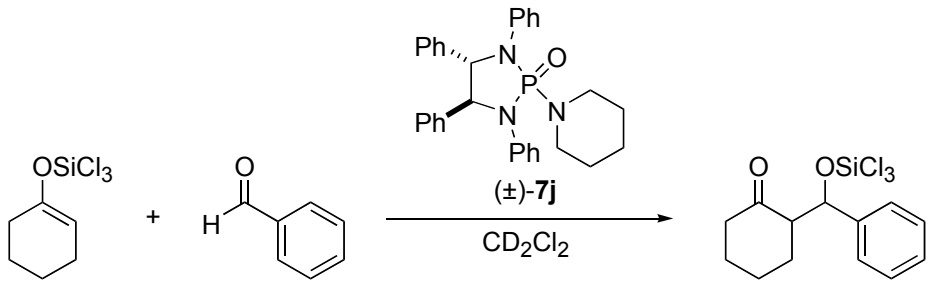
15 mg of (±)-**7j** was added to a dry reaction vessel. The vessel was assembled onto the IR probe and vented for several minutes with dry nitrogen. Dry methylene chloride (2.3 mL) was then added to the reaction vessel. The vessel was then submerged into a chilled isopropanol bath and the contents were allowed to equilibrate prior to collecting a *background* file. Enolate **4**(111 μL, 0.61 mmol) was then added and allowed to fully mix. Benzaldehyde (62 μL, 0.61 mmol) was added quickly to the reaction solution. IR spectra were collected at 30 s intervals for 240 min at -49 °C by internal monitoring. Recorded disappearance of peak at 1679 cm^{-1} (enolate C=C).

IR:

Instrument: ASI ReactIR 1000

Probe and Detector: 5/8" DiComp Probe using an MCT detector operating at –195 °C

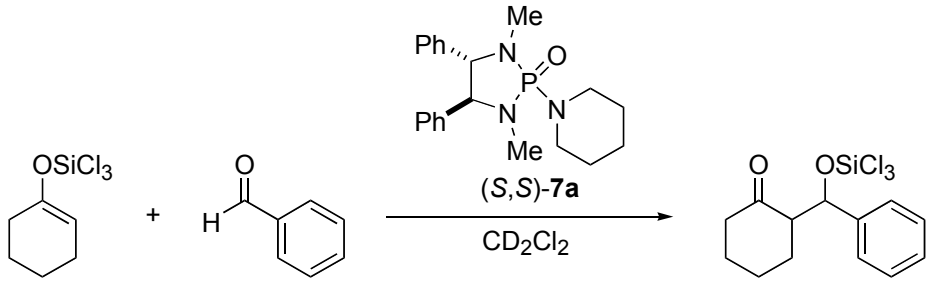
General Procedure 3a, Rapid Injection NMR Kinetics Using (±)-7j:



4 **5a** **i**

To a dry NMR tube was added phosphoramide (±)-**7j** (8.6 mg, 0.017 mmol) of, CD_2Cl_2 (600 μL) and enolate **4** (65 mL, 0.35 mmol). The tube was vigorously mixed using a vortex shaker and stored in a short dewar at –78 °C. Following proper positioning into spinner, the cap was carefully removed and the tube was quickly lowered into a precooled spectrometer under dry nitrogen. The fully primed RINMR injection apparatus was then carefully lowered into the spinning tube and the entire setup was allowed to equilibrate for several minutes. After equilibration, a benzaldehyde solution (85 μL, 0.35 mmol) was then rapidly injected.

General Procedure 3b, Rapid Injection NMR Kinetics Using (*S,S*)-7a:



4 **5a** **i**

To a dry NMR tube was added 3.2 mg (0.009 mmol) of phosphoramide, 600 μL of CD_2Cl_2, 50 μL of a stock solution of 1% TMS in $CDCl_3$ followed by 16 μL (0.086 mmol) of enolate (*S,S*)-**7a**. The tube was vigorously mixed using a vortex shaker and stored in a short dewar at –78 °C. Following proper positioning into spinner, the cap was carefully removed and the tube was quickly lowered into a precooled spectrometer under dry nitrogen. The fully primed RINMR injection apparatus was then carefully lowered into the spinning tube and the entire setup was allowed to equilibrate for several minutes. After equilibration a benzaldehyde solution (42 μL, 0.086 mmol) was then rapidly injected.

Raw Data. GC Kinetics of Addition of 1 to 2.

Temperature: 20 °C, Run #1:

Using General Procedure 1, pivalaldehyde (380 μL, 2.6 mmol) was added to a solution of enolate **1** (29 μL, 0.26 mmol) and adamantane (6.9 mg, 0.051 mmol) in 1,2-dichloroethane (2.0 mL) at 20 °C as internally monitored. The reaction was monitored every 5 minutes for 90 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.014$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	1441	5925	0.10	0.10	0.09
10	1854	4396	0.16	0.10	0.15
15	2660	4334	0.22	0.09	0.23
20	3339	4400	0.27	0.08	0.30
25	3644	4073	0.32	0.08	0.36
30	4609	4334	0.38	0.07	0.45
37	3023	2398	0.44	0.06	0.56
40	5023	3583	0.49	0.06	0.65
45	5957	4114	0.51	0.06	0.68
50	5320	3400	0.55	0.05	0.76
55	7074	4210	0.59	0.05	0.85
60	8078	4575	0.61	0.04	0.92

Temperature: 20 °C, Run #2:

Using General Procedure 1, pivalaldehyde (380 μL, 2.6 mmol) was added to a solution of enolate **1** (29 μL, 0.26 mmol) and adamantane (7.5 mg, 0.055 mmol) in 1,2-dichloroethane (2.0 mL) at 20 °C as internally monitored. The reaction was monitored every 5 minutes for 90 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.015$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	0	0	-	-	-
10	1446	3637	0.15	0.09	0.16
15	2360	4030	0.21	0.09	0.24
20	3124	4234	0.27	0.08	0.32
25	3808	4184	0.32	0.07	0.41
30	3966	3980	0.35	0.07	0.46
35	5387	4594	0.41	0.06	0.57
40	4413	3348	0.46	0.06	0.67
45	4436	3162	0.49	0.05	0.73
50	6356	4226	0.53	0.05	0.81
55	6257	3944	0.55	0.05	0.88
60	5901	3527	0.58	0.04	0.96

Temperature: 20 °C, Run #3:

Using General Procedure 1, pivalaldehyde (380 μL, 2.6 mmol) was added to a solution of enolate **1** (29 μL, 0.26 mmol) and adamantane (6.9 mg, 0.051 mmol) in 1,2-dichloroethane (2.0 mL) at 20 °C as internally monitored. The reaction was monitored every 5 minutes for 90 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.022$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	1433	2876	0.18	0.10	0.14
10	2732	2914	0.33	0.08	0.29
15	4211	3102	0.48	0.07	0.45
20	4417	2625	0.59	0.06	0.59
25	5700	2897	0.68	0.05	0.74
30	6000	2731	0.76	0.05	0.88

Temperature: 30 °C, Run #1:

Using General Procedure 1, pivalaldehyde (380 μL, 2.6 mmol) was added to a solution of enolate **1** (29 μL, 0.26 mmol) and adamantane (5.4 mg, 0.040 mmol) in 1,2-dichloroethane (8.0 mL) at 30 °C as internally monitored. The reaction was monitored every 5 minutes for 90 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.022$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	1527	3550	0.16	0.10	0.12
10	2561	3237	0.28	0.09	0.24
15	3852	3395	0.40	0.08	0.36
20	4421	3123	0.48	0.07	0.47
25	5203	3101	0.58	0.06	0.59
30	5564	2949	0.64	0.06	0.70
35	7145	3315	0.75	0.05	0.85

Temperature: 30 °C, Run #2:

Using General Procedure 1, pivalaldehyde (1.16 mL, 10.4 mmol) was added to a solution of enolate **1** (150 μL, 1.03 mmol) and adamantane (22 mg, 0.16 mmol) in 1,2-dichloroethane (8.0 mL) at 30 °C as internally monitored. The reaction was monitored every 5 minutes for 90 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.026$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	3698	8134	0.17	0.10	0.14
10	9981	11970	0.30	0.08	0.27
15	9753	8239	0.42	0.07	0.41
20	11317	7846	0.50	0.07	0.53
25	16531	9866	0.58	0.06	0.64
30	20130	10449	0.67	0.05	0.79

Temperature: 30 °C, Run #3:

Using General Procedure 1, pivalaldehyde (1.16 mL, 10.4 mmol) was added to a solution of enolate **1** (150 μL, 1.03 mmol) and adamantane (22 mg, 0.15 mmol) in 1,2-dichloroethane (8.0 mL) at 30 °C as internally monitored. The reaction was monitored every 5 minutes for 90 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.025$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	4071	7921	0.19	0.10	0.14
10	7399	7945	0.33	0.08	0.27
15	10888	8526	0.45	0.07	0.40
20	14008	8708	0.56	0.07	0.53
25	13471	7268	0.64	0.06	0.65
30	18727	8974	0.72	0.05	0.77

Temperature: 40 °C, Run #1:

Using General Procedure 1, pivalaldehyde (380 μL, 2.6 mmol) was added to a solution of enolate **1** (29 μL, 0.26 mmol) and adamantane (7.1 mg, 0.052 mmol) in 1,2-dichloroethane (2.0 mL) at 40 °C as internally monitored. The reaction was monitored every 5 minutes for 100 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.035$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	1595	3093	0.19	0.09	0.20
10	2842	3424	0.30	0.08	0.34
18	6117	4420	0.48	0.06	0.66
22	7056	4488	0.55	0.05	0.80
26	11330	6468	0.61	0.04	0.95
30	10167	5380	0.66	0.04	1.08
35	9355	4549	0.71	0.03	1.27

Temperature: 40 °C, Run #2:

Using General Procedure 1, pivalaldehyde (380 μL, 2.6 mmol) was added to a solution of enolate **1** (29 μL, 0.26 mmol) and adamantane (6.7 mg, 0.049 mmol) in 1,2-dichloroethane (2.0 mL) at 40 °C as internally monitored. The reaction was monitored every 5 minutes for 90 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.026$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	1326	4711	0.11	0.10	0.10
10	1776	3092	0.21	0.09	0.21
18	3695	4074	0.32	0.08	0.36
22	4210	3474	0.43	0.07	0.51
26	5539	3832	0.51	0.06	0.65
30	5972	3633	0.57	0.05	0.78
35	6005	3338	0.63	0.05	0.90
40	6595	3457	0.66	0.04	0.99
45	5750	2710	0.73	0.03	1.20

Temperature: 40 °C, Run #3:

Using General Procedure 1, pivalaldehyde (380 μL, 2.6 mmol) was added to a solution of enolate **1** 29 μL, 0.26 mmol) and adamantane (22 mg, 0.15 mmol) in 1,2-dichloroethane (2.0 mL) at 40 °C as internally monitored. The reaction was monitored every 3 minutes for 60 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.025$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
4	1739	3834	0.17	0.10	0.13
7	3354	4104	0.29	0.09	0.25
11	5481	4499	0.43	0.07	0.40
14	6249	4244	0.51	0.07	0.51
17	3327	1901	0.61	0.06	0.65
21	16019	7914	0.70	0.05	0.80

Temperature: 65 °C, Run #1:

Using General Procedure 1, pivalaldehyde (760 μL, 5.2 mmol) was added to a solution of enolate **1** (58 μL, 0.52 mmol) and adamantane (9.1 mg, 0.07 mmol) in 1,2-dichloroethane (8.0 mL) at 65 °C as internally monitored. The reaction was monitored every 4 minutes for 60 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.085$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
7	6365	3494	0.45	0.06	0.60
14	7716	2770	0.69	0.03	1.18
19	9388	2930	0.80	0.02	1.59
23	7015	2028	0.86	0.02	1.96

Temperature: 65 °C, Run #2:

Using General Procedure 1, pivalaldehyde (760 μL, 5.2 mmol) was added to a solution of enolate **1** (58 μL, 0.52 mmol) and adamantane (13 mg, 0.10 mmol) in 1,2-dichloroethane (8.0 mL) at 63 °C as internally monitored. The reaction was monitored every 4 minutes for 60 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.055$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
5	4637	5759	0.29	0.08	0.30
10	7577	4104	0.49	0.05	0.88
18	8830	4145	0.74	0.04	1.13
23	10224	4333	0.82	0.03	1.38

Temperature: 65 °C, Run #3:

Using General Procedure 1, pivalaldehyde (760 μL, 5.2 mmol) was added to a solution of enolate **1** (58 μL, 0.52 mmol) and adamantane (6.8 mg, 0.05 mmol) in 1,2-dichloroethane (8.0 mL) at 63 °C as internally monitored. The reaction was monitored every 4 minutes for 60 minutes, and then incrementally thereafter until complete conversion. $k_{obs} = 0.062$ min^{-1}.

Time (min)	Aldolate Area	Adamantane Area	Conversion	[Enolate]	ln([Enolate]/[Enolate]$_o$)
7	6365	3494	0.41	0.07	0.52
14	7716	2770	0.62	0.04	0.98
19	9388	2930	0.72	0.03	1.26
23	7015	2028	0.77	0.03	1.49

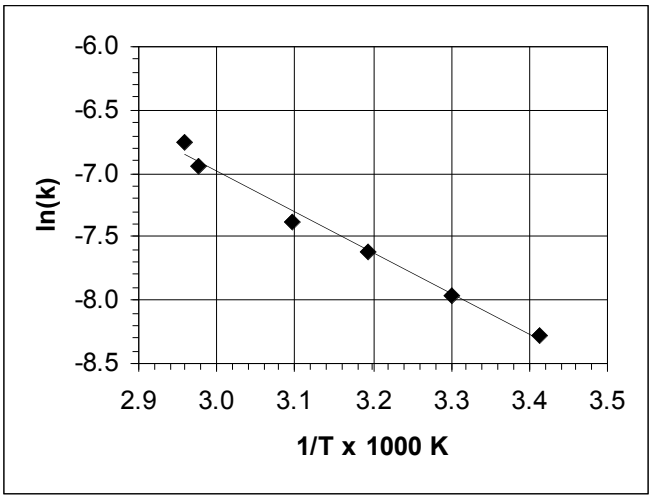


Figure I. Arrhenius Plot. The graph depicts a linear fit, $f(x) = mx + b$ ($m = -3.22$, $R^2 = 0.99$).

Raw Data. ReactIR Kinetics of Addition of 1 to 2. Uncatalyzed.

Temperature: 30 °C, Run #1:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 30 °C as internally monitored. The reaction was monitored every 3 minutes until complete conversion. $k = 0.021\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0314	0.203	0.00	1.59	0.00
3.00	0.0288	0.182	0.10	1.70	0.11
6.00	0.0255	0.157	0.23	1.85	0.25
9.00	0.0229	0.136	0.33	1.99	0.40
12.00	0.0205	0.118	0.42	2.14	0.54
15.00	0.0187	0.104	0.49	2.26	0.67
18.00	0.0167	0.089	0.56	2.42	0.82
21.00	0.0155	0.080	0.61	2.53	0.93
24.00	0.0144	0.071	0.65	2.64	1.05
27.00	0.0131	0.061	0.70	2.80	1.21

Temperature: 30 °C, Run #2:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 30 °C as internally monitored. The reaction was monitored every 3 minutes until complete conversion. $k = 0.021\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0274	0.203	0.00	1.59	0.00
3.00	0.0244	0.176	0.13	1.74	0.14
6.00	0.0219	0.154	0.24	1.87	0.27
9.00	0.0195	0.133	0.34	2.02	0.42
12.00	0.0173	0.114	0.44	2.17	0.58
15.00	0.0160	0.102	0.50	2.28	0.69
18.00	0.0143	0.087	0.57	2.44	0.84
21.00	0.0133	0.079	0.61	2.54	0.94
24.00	0.0123	0.070	0.66	2.66	1.07
27.00	0.0113	0.061	0.70	2.79	1.20

Temperature: 30 °C, Run #3:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 30 °C as internally monitored. The reaction was monitored every 3 minutes until complete conversion. $k = 0.0211\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0353	0.203	0.00	1.595	0.00
3.00	0.0314	0.177	0.13	1.731	0.14
6.00	0.0279	0.154	0.24	1.870	0.28
9.00	0.0249	0.134	0.34	2.012	0.42
12.00	0.0226	0.118	0.42	2.133	0.54
15.00	0.0207	0.105	0.48	2.249	0.65
18.00	0.0187	0.092	0.54	2.381	0.79
21.00	0.0169	0.081	0.60	2.517	0.92
24.00	0.0156	0.072	0.65	2.632	1.04
27.00	0.0143	0.063	0.69	2.766	1.17

Temperature: 40 °C, Run #1:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 40 °C as internally monitored. The reaction was monitored every 3 minutes until complete conversion. $k = 0.027\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0342	0.203	0.00	1.59	0.00
3.00	0.0291	0.168	0.17	1.78	0.19
6.00	0.0251	0.141	0.31	1.96	0.37
9.00	0.0219	0.119	0.42	2.13	0.54
12.00	0.0192	0.099	0.51	2.31	0.71
15.00	0.0169	0.084	0.59	2.48	0.88
18.00	0.0153	0.073	0.64	2.62	1.02
21.00	0.0137	0.062	0.69	2.78	1.19

Temperature: 40 °C, Run #2:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 40 °C as internally monitored. The reaction was monitored every 2 minutes until complete conversion. $k = 0.028\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0306	0.203	0.00	1.59	0.00
2.00	0.0276	0.180	0.11	1.72	0.12
4.00	0.0252	0.161	0.21	1.83	0.23
6.00	0.0229	0.143	0.30	1.95	0.35
8.00	0.0208	0.127	0.38	2.07	0.47
10.00	0.0190	0.113	0.44	2.18	0.59
12.00	0.0174	0.101	0.50	2.30	0.70
14.00	0.0160	0.090	0.56	2.41	0.81
16.00	0.0148	0.081	0.60	2.52	0.92
18.00	0.0136	0.071	0.65	2.64	1.05
20.00	0.0128	0.065	0.68	2.729	1.134

Temperature: 40 °C, Run #3:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 40 °C as internally monitored. The reaction was monitored every 2 minutes until complete conversion. $k = 0.0266\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0321	0.203	0.00	1.59	0.00
2.00	0.0291	0.181	0.11	1.71	0.11
4.00	0.0262	0.160	0.21	1.83	0.24
6.00	0.0239	0.143	0.30	1.94	0.35
8.00	0.0215	0.125	0.38	2.08	0.48
10.00	0.0197	0.112	0.45	2.19	0.60
12.00	0.0181	0.100	0.51	2.30	0.70
14.00	0.0166	0.089	0.56	2.42	0.82
16.00	0.0154	0.081	0.60	2.52	0.92
18.00	0.0145	0.074	0.64	2.60	1.01
20.00	0.0134	0.065	0.68	2.72	1.13
22.00	0.0128	0.061	0.70	2.79	1.19

Temperature: 50 °C, Run #1:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 50 °C as internally monitored. The reaction was monitored every 2 minutes until complete conversion. $k = 0.0407\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0369	0.203	0.00	1.59	0.00
2.00	0.0302	0.160	0.21	1.84	0.24
4.00	0.0263	0.134	0.34	2.01	0.42
6.00	0.0231	0.113	0.44	2.18	0.58
8.00	0.0206	0.097	0.52	2.33	0.73
10.00	0.0183	0.082	0.60	2.50	0.90
12.00	0.0166	0.071	0.65	2.65	1.05
14.00	0.0148	0.059	0.71	2.82	1.23

Temperature: 50 °C, Run #2:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 50 °C as internally monitored. The reaction was monitored every 2 minutes until complete conversion. $k = 0.0385\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0321	0.203	0.00	1.59	0.00
2.00	0.0282	0.173	0.15	1.76	0.16
4.00	0.0244	0.144	0.29	1.94	0.34
6.00	0.0217	0.124	0.39	2.09	0.49
8.00	0.0194	0.106	0.48	2.24	0.65
10.00	0.0172	0.090	0.56	2.41	0.81
12.00	0.0155	0.077	0.62	2.56	0.97
14.00	0.0141	0.067	0.67	2.71	1.11

Temperature: 50 °C, Run #3:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 50 °C as internally monitored. The reaction was monitored every 2 minutes until complete conversion. $k = 0.0417\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0338	0.203	0.00	1.59	0.00
2.00	0.0300	0.175	0.14	1.74	0.15
4.00	0.0265	0.150	0.26	1.90	0.30
6.00	0.0231	0.125	0.38	2.08	0.49
8.00	0.0204	0.105	0.48	2.25	0.66
10.00	0.0180	0.088	0.57	2.43	0.84
12.00	0.0160	0.073	0.64	2.61	1.02
14.00	0.0144	0.062	0.70	2.79	1.19

Temperature: 60 °C, Run #1:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 60 °C as internally monitored. The reaction was monitored every 2 minutes until complete conversion. $k = 0.0550\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0292	0.203	0.00	1.59	4.93
2.00	0.0246	0.164	0.19	1.81	6.11
4.00	0.0207	0.131	0.36	2.03	7.65
6.00	0.0179	0.107	0.47	2.24	9.38
8.00	0.0153	0.085	0.58	2.47	11.83
10.00	0.0131	0.066	0.68	2.72	15.18

Temperature: 60 °C, Run #2:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 60 °C as internally monitored. The reaction was monitored every 1 minutes until complete conversion. $k = 0.0545\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0004	0.000	0.00		
0.00	0.0005	0.000	0.00		
0.00	0.0229	0.203	0.00	1.59	0.00
1.00	0.0208	0.184	0.09	1.69	0.10
2.00	0.0184	0.162	0.20	1.82	0.22
3.00	0.0167	0.147	0.28	1.92	0.32
4.00	0.0147	0.129	0.36	2.05	0.45
5.00	0.0132	0.115	0.43	2.16	0.56
6.00	0.0120	0.104	0.49	2.26	0.66
7.00	0.0105	0.091	0.55	2.39	0.80
8.00	0.0093	0.080	0.61	2.52	0.93
9.00	0.0087	0.075	0.63	2.59	0.99
10.00	0.0079	0.067	0.67	2.70	1.11
11.00	0.0069	0.058	0.71	2.84	1.25

Temperature: 60 °C, Run #3:

Using General Procedure 2a, pivalaldehyde (300 μL, 2.7 mmol) was added to a solution of enolate **1** (38 μL, 0.27 mmol) in 1,2-dichloroethane (1.0 mL) at 60 °C as internally monitored. The reaction was monitored every 1 minutes until complete conversion. $k = 0.0532\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	ln([Enolate])	ln([Enolate]/[Enolate]$_o$)
0.00	0.0287	0.203	0.00	1.59	0.00
1.00	0.0263	0.183	0.10	1.70	0.10
2.00	0.0238	0.161	0.21	1.83	0.23
3.00	0.0216	0.142	0.30	1.95	0.36
4.00	0.0201	0.129	0.36	2.05	0.45
5.00	0.0182	0.113	0.44	2.18	0.59
6.00	0.0172	0.104	0.49	2.26	0.67
7.00	0.0161	0.094	0.53	2.36	0.77
8.00	0.0149	0.084	0.58	2.47	0.88
9.00	0.0139	0.075	0.63	2.59	0.99
10.00	0.0132	0.069	0.66	2.67	1.08
11.00	0.0121	0.060	0.70	2.81	1.22

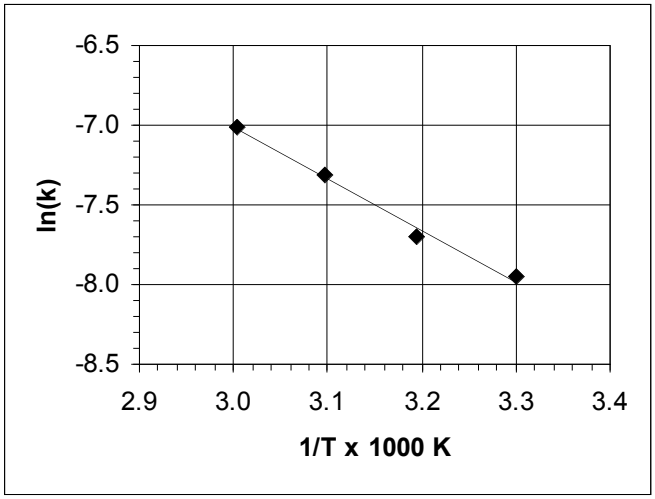


Figure II. Arrhenius Plot. The graph depicts a linear fit, $f(x) = mx + b$ (m = -3.25, R^2 = 0.99).

Raw Data. ReactIR Kinetics of Addition of 4 to 5a. Uncatalyzed.

Temperature: 30 °C, Run #1:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 30 °C as internally monitored. The reaction was monitored every 1 minute until complete conversion. $k = 1.741\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0325	0.276	0.00	3.62
1.00	0.0241	0.192	0.31	5.22
2.00	0.0191	0.142	0.49	7.05
3.00	0.0163	0.113	0.59	8.81
4.00	0.0130	0.080	0.71	12.54
5.00	0.0127	0.077	0.72	13.04

Temperature: 30 °C, Run #2:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 30 °C as internally monitored. The reaction was monitored every 1 minute until complete conversion. $k = 1.732\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0352	0.276	0.00	3.62
1.00	0.0264	0.195	0.29	5.13
2.00	0.0208	0.144	0.48	6.97
3.00	0.0176	0.114	0.59	8.78
4.00	0.0151	0.091	0.67	11.03
5.00	0.0135	0.077	0.72	13.07

Temperature: 30 °C, Run #3:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 30 °C as internally monitored. The reaction was monitored every 1 minute until complete conversion. $k = 1.662\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0336	0.276	0.00	3.62
1.00	0.0259	0.200	0.28	5.00
2.00	0.0205	0.146	0.47	6.83
3.00	0.0175	0.117	0.58	8.55
4.00	0.0153	0.095	0.66	10.50
5.00	0.0131	0.074	0.73	13.54

Temperature: 40 °C, Run #1:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 40 °C as internally monitored. The reaction was monitored every 1 minute until complete conversion. $k = 1.816\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0290	0.276	0.00	3.62
1.00	0.0273	0.258	0.07	3.87
2.00	0.0196	0.178	0.36	5.63
3.00	0.0153	0.132	0.52	7.56
4.00	0.0130	0.108	0.61	9.28
5.00	0.0112	0.089	0.68	11.20
6.00	0.0102	0.078	0.72	12.78

Temperature: 40 °C, Run #2:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 40 °C as internally monitored. The reaction was monitored every 1 minute until complete conversion. $k = 1.807\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0317	0.276	0.00	3.62
1.00	0.0297	0.257	0.07	3.90
2.00	0.0219	0.181	0.35	5.54
3.00	0.0171	0.134	0.52	7.48
4.00	0.0145	0.108	0.61	9.27
5.00	0.0124	0.087	0.68	11.44
6.00	0.0110	0.074	0.73	13.57

Temperature: 40 °C, Run #3:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 40 °C as internally monitored. The reaction was monitored every 1 minute until complete conversion. $k = 1.807\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0296	0.276	0.00	3.62
1.00	0.0284	0.263	0.05	3.80
2.00	0.0210	0.184	0.33	5.42
3.00	0.0162	0.135	0.51	7.42
4.00	0.0134	0.105	0.62	9.53
5.00	0.0109	0.079	0.72	12.70
6.00	0.0102	0.071	0.74	14.09

Temperature: 50 °C, Run #1:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 50 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 1.811\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0375	0.276	0.00	3.62
0.50	0.0326	0.222	0.19	4.50
1.00	0.0294	0.187	0.32	5.36
1.50	0.0269	0.159	0.42	6.28
2.00	0.0250	0.139	0.50	7.20
2.50	0.0236	0.123	0.55	8.12
3.00	0.0222	0.108	0.61	9.22
3.50	0.0215	0.100	0.64	9.96
4.00	0.0209	0.093	0.66	10.72
4.50	0.0198	0.082	0.70	12.21

Temperature: 50 °C, Run #2:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 50 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 2.062\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0288	0.276	0.00	3.62
0.50	0.0276	0.264	0.05	3.79
1.00	0.0225	0.212	0.23	4.72
1.50	0.0191	0.177	0.36	5.65
2.00	0.0161	0.146	0.47	6.87
2.50	0.0142	0.127	0.54	7.88
3.00	0.0128	0.113	0.59	8.88
3.50	0.0117	0.101	0.64	9.95
4.00	0.0102	0.086	0.69	11.65
4.50	0.0096	0.079	0.71	12.63

Temperature: 50 °C, Run #3:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 50 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 2.227\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0291	0.276	0.00	3.62
0.50	0.0277	0.262	0.05	3.82
1.00	0.0227	0.210	0.24	4.75
1.50	0.0190	0.172	0.38	5.80
2.00	0.0160	0.143	0.48	7.02
2.50	0.0139	0.121	0.56	8.25
3.00	0.0126	0.107	0.61	9.32
3.50	0.0114	0.095	0.66	10.55
4.00	0.0099	0.079	0.71	12.58

Temperature: 60 °C, Run #1:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 60 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 2.541\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0239	0.276	0.00	3.62
0.50	0.0194	0.210	0.24	4.75
1.00	0.0166	0.171	0.38	5.86
1.50	0.0143	0.137	0.51	7.32
2.00	0.0128	0.115	0.58	8.69
2.50	0.0113	0.093	0.66	10.70
3.00	0.0107	0.086	0.69	11.69

Temperature: 60 °C, Run #2:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 60 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 2.627\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0281	0.276	0.00	3.62
0.50	0.0255	0.249	0.10	4.02
1.00	0.0197	0.186	0.33	5.37
1.50	0.0160	0.146	0.47	6.84
2.00	0.0129	0.114	0.59	8.78
2.50	0.0111	0.095	0.66	10.57
3.00	0.0100	0.082	0.70	12.12

Temperature: 60 °C, Run #3:

Using General Procedure 2a, benzaldehyde (46 μL, 0.45 mmol) was added to a solution of enolate **4** (82 μL, 0.45 mmol) in 1,2-dichloroethane (1.5 mL) at 60 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 2.956\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0276	0.276	0.00	3.62
0.50	0.0248	0.247	0.11	4.05
1.00	0.0194	0.189	0.31	5.28
1.50	0.0151	0.144	0.48	6.94
2.00	0.0127	0.119	0.57	8.43
2.50	0.0104	0.095	0.66	10.57
3.00	0.0093	0.083	0.70	12.06

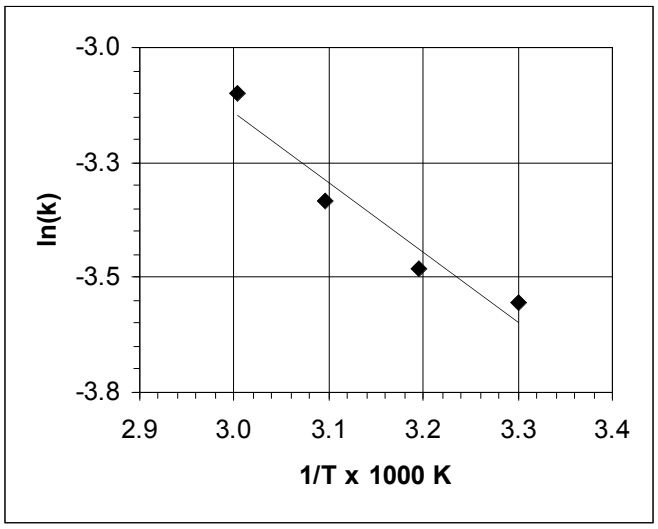


Figure III. Arrhenius Plot. The graph depicts a linear fit, $f(x) = mx + b$ ($m = -1.52$, $R^2 = 0.94$).

Raw Data. ReactIR Kinetics of Addition of 4 to 5a. Catalyzed by (±)-7j.

Temperature: -49 °C, Run #1:

Using General Procedure 2b, benzaldehyde (62 μL, 0.61 mmol) was added to a solution of enolate **4** (111 μL, 0.61 mmol) and phosphoramide **(±)-7j** (15 mg, 0.031 mmol) in methylene chloride (2.3 mL) at -49 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 55.57\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0325	0.246	0.00	4.06
0.5	0.2473	0.000	0.00	0.00
1.0	0.0750	0.000	0.00	0.00
1.5	0.0292	0.219	0.11	4.56
2.0	0.0275	0.205	0.17	4.87
2.5	0.0258	0.191	0.22	5.24
3.0	0.0246	0.181	0.26	5.52
3.5	0.0232	0.170	0.31	5.89
4.0	0.0218	0.158	0.36	6.33
4.5	0.0204	0.147	0.40	6.82
5.0	0.0197	0.141	0.43	7.10
5.5	0.0188	0.134	0.46	7.47
6.0	0.0183	0.130	0.47	7.71
6.5	0.0177	0.125	0.49	8.02
7.0	0.0166	0.115	0.53	8.67
7.5	0.0162	0.112	0.55	8.93
8.0	0.0154	0.105	0.57	9.49
8.5	0.0149	0.101	0.59	9.86
9.0	0.0144	0.097	0.61	10.29
9.5	0.0138	0.093	0.62	10.81
10.0	0.0138	0.093	0.62	10.81
10.5	0.0133	0.089	0.64	11.26
11.0	0.0130	0.086	0.65	11.65
11.5	0.0126	0.083	0.66	12.04
12.0	0.0122	0.080	0.68	12.58
12.5	0.0119	0.077	0.69	12.95
13.0	0.0117	0.076	0.69	13.22
13.5	0.0115	0.073	0.70	13.64

Temperature: -49 °C, Run #2:

Using General Procedure 2b, benzaldehyde (67 μL, 0.66 mmol) was added to a solution of enolate **4** (120 μL, 0.66 mmol) and phosphoramide (**±)-7j** (16 mg, 0.033 mmol) in methylene chloride (2.5 mL) at -49 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 77.96\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0347	0.245	0.00	4.08
0.5	0.0305	0.215	0.12	4.65
1.0	0.0278	0.196	0.20	5.11
1.5	0.0255	0.179	0.27	5.58
2.0	0.0240	0.168	0.31	5.94
2.5	0.0219	0.153	0.37	6.53
3.0	0.0205	0.144	0.41	6.96
3.5	0.0193	0.135	0.45	7.42
4.0	0.0180	0.125	0.49	8.00
4.5	0.0170	0.118	0.52	8.45
5.0	0.0161	0.112	0.54	8.95
5.5	0.0155	0.108	0.56	9.29
6.0	0.0145	0.100	0.59	9.98
6.5	0.0139	0.096	0.61	10.43
7.0	0.0128	0.088	0.64	11.33
7.5	0.0126	0.087	0.65	11.54
8.0	0.0119	0.082	0.67	12.20
8.5	0.0115	0.079	0.68	12.70
9.0	0.0109	0.074	0.70	13.46
9.5	0.0103	0.071	0.71	14.16

Temperature: -49 °C, Run #3:

Using General Procedure 2b, benzaldehyde (60 μL, 0.59 mmol) was added to a solution of enolate **1** (107 μL, 0.59 mmol) and phosphoramide **(±)-7j** (15 mg, 0.030 mmol) in methylene chloride (2.2 mL) at -49 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 50.93\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0325	0.248	0.00	4.03
0.5	0.0311	0.237	0.04	4.22
1.0	0.0294	0.223	0.10	4.47
1.5	0.0276	0.209	0.16	4.79
2.0	0.0263	0.198	0.20	5.05
2.5	0.0247	0.185	0.25	5.41
3.0	0.0234	0.174	0.30	5.73
3.5	0.0227	0.169	0.32	5.93
4.0	0.0212	0.157	0.37	6.39
4.5	0.0201	0.148	0.40	6.76
5.0	0.0194	0.143	0.42	7.01
5.5	0.0187	0.137	0.45	7.31
6.0	0.0178	0.129	0.48	7.74
6.5	0.0171	0.124	0.50	8.07
7.0	0.0167	0.121	0.51	8.29
7.5	0.0160	0.115	0.54	8.69
8.0	0.0154	0.110	0.56	9.11
8.5	0.0147	0.104	0.58	9.63
9.0	0.0144	0.102	0.59	9.79
9.5	0.0141	0.099	0.60	10.11
10.0	0.0139	0.098	0.61	10.22
10.5	0.0133	0.093	0.62	10.74
11.0	0.0131	0.091	0.63	10.94
11.5	0.0126	0.087	0.65	11.51
12.0	0.0123	0.085	0.66	11.80
12.5	0.0118	0.081	0.67	12.34
13.0	0.0115	0.078	0.68	12.74
13.5	0.0113	0.077	0.69	13.06
14.0	0.0113	0.076	0.69	13.10
14.5	0.0107	0.072	0.71	13.90

Temperature: -32 °C, Run #1:

Using General Procedure 2b, benzaldehyde (62 μL, 0.61 mmol) was added to a solution of enolate **4** (111 μL, 0.61 mmol) and phosphoramide (**±)-7j** (15 mg, 0.031 mmol) in methylene chloride (2.3 mL) at -32 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 72.30\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0325	0.276	0.00	3.62
0.00	0.0340	0.246	0.00	4.06
0.50	0.0308	0.223	0.09	4.48
1.00	0.0281	0.203	0.17	4.92
1.50	0.0256	0.185	0.25	5.40
2.00	0.0236	0.171	0.30	5.84
2.50	0.0222	0.161	0.35	6.23
3.00	0.0204	0.147	0.40	6.78
3.50	0.0193	0.140	0.43	7.16
4.00	0.0182	0.131	0.47	7.61
4.50	0.0171	0.124	0.50	8.08
5.00	0.0163	0.118	0.52	8.46
5.50	0.0155	0.112	0.55	8.94
6.00	0.0146	0.106	0.57	9.47
6.50	0.0142	0.103	0.58	9.74
7.00	0.0133	0.096	0.61	10.42
7.50	0.0127	0.092	0.63	10.90
8.00	0.0124	0.090	0.63	11.12
8.50	0.0119	0.086	0.65	11.68
9.00	0.0115	0.083	0.66	12.01
9.50	0.0110	0.080	0.68	12.54
10.00	0.0105	0.076	0.69	13.12
10.50	0.0104	0.075	0.69	13.27
11.00	0.0099	0.072	0.71	13.92

Temperature: -32 °C, Run #2:

Using General Procedure 2b, benzaldehyde (78 μL, 0.77 mmol) was added to a solution of enolate **4** (140 μL, 0.77 mmol) and phosphoramide (**±)-7j** (19 mg, 0.038 mmol) in methylene chloride (2.9 mL) at -32 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 63.05\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0327	0.246	0.00	4.06
0.50	0.0302	0.226	0.08	4.42
1.00	0.0277	0.208	0.16	4.82
1.50	0.0257	0.191	0.22	5.22
2.00	0.0240	0.178	0.28	5.60
2.50	0.0224	0.166	0.33	6.02
3.00	0.0211	0.156	0.37	6.40
3.50	0.0199	0.147	0.40	6.82
4.00	0.0191	0.141	0.43	7.12
4.50	0.0179	0.131	0.47	7.63
5.00	0.0173	0.126	0.49	7.92
5.50	0.0165	0.120	0.51	8.30
6.00	0.0157	0.114	0.54	8.77
6.50	0.0151	0.109	0.56	9.14
7.00	0.0143	0.103	0.58	9.69
7.50	0.0139	0.100	0.59	10.03
8.00	0.0134	0.096	0.61	10.41
8.50	0.0128	0.091	0.63	10.93
9.00	0.0123	0.088	0.64	11.43
9.50	0.0123	0.087	0.65	11.44
10.00	0.0118	0.083	0.66	12.00
10.50	0.0112	0.079	0.68	12.71
11.00	0.0110	0.078	0.69	12.90
11.50	0.0107	0.075	0.69	13.28
12.00	0.0106	0.074	0.70	13.54
12.50	0.0102	0.071	0.71	14.06

Temperature: -32 °C, Run #3:

Using General Procedure 2b, benzaldehyde (58 μL, 0.57 mmol) was added to a solution of enolate **4** (103 μL, 0.57 mmol) and phosphoramide (**±)-7j** (14 mg, 0.029 mmol) in methylene chloride (2.1 mL) at -32 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 61.46\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.00	0.0319	0.250	0.00	4.00
0.50	0.0292	0.228	0.09	4.38
1.00	0.0270	0.210	0.16	4.76
1.50	0.0250	0.194	0.22	5.16
2.00	0.0232	0.180	0.28	5.57
2.50	0.0218	0.169	0.33	5.93
3.00	0.0206	0.159	0.37	6.31
3.50	0.0195	0.150	0.40	6.68
4.00	0.0183	0.140	0.44	7.12
4.50	0.0174	0.133	0.47	7.50
5.00	0.0168	0.128	0.49	7.79
5.50	0.0159	0.121	0.52	8.27
6.00	0.0149	0.113	0.55	8.83
6.50	0.0143	0.108	0.57	9.25
7.00	0.0137	0.103	0.59	9.71
7.50	0.0131	0.098	0.61	10.17
8.00	0.0122	0.091	0.63	10.96
8.50	0.0118	0.088	0.65	11.36
9.00	0.0115	0.085	0.66	11.75
9.50	0.0113	0.084	0.66	11.91
10.00	0.0108	0.080	0.68	12.57
10.50	0.0103	0.076	0.70	13.15

Temperature: -26 °C, Run #1:

Using General Procedure 2b, benzaldehyde (63 μL, 0.61 mmol) was added to a solution of enolate **4** (113 μL, 0.62 mmol) and phosphoramide (**±)-7j** (15.3 mg, 0.031 mmol) in methylene chloride (2.3 mL) at -26 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 61.77\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0300	0.250	0.00	4.00
0.5	0.0281	0.234	0.07	4.28
1.0	0.0266	0.220	0.12	4.54
1.5	0.0246	0.203	0.19	4.93
2.0	0.0227	0.186	0.26	5.37
2.5	0.0218	0.178	0.29	5.62
3.0	0.0202	0.164	0.34	6.09
3.5	0.0192	0.155	0.38	6.44
4.0	0.0179	0.144	0.43	6.96
4.5	0.0171	0.137	0.45	7.32
5.0	0.0164	0.130	0.48	7.66
5.5	0.0155	0.122	0.51	8.17
6.0	0.0149	0.117	0.53	8.55
6.5	0.0144	0.113	0.55	8.88
7.0	0.0136	0.106	0.58	9.47
7.5	0.0132	0.102	0.59	9.80
8.0	0.0125	0.097	0.61	10.36
8.5	0.0123	0.094	0.62	10.63
9.0	0.0117	0.089	0.64	11.18
9.5	0.0115	0.087	0.65	11.49
10.0	0.0110	0.083	0.67	12.11
10.5	0.0106	0.079	0.68	12.65
11.0	0.0105	0.078	0.69	12.80
11.5	0.0102	0.076	0.70	13.16
12.0	0.0101	0.075	0.70	13.27
12.5	0.0097	0.071	0.72	14.06

Temperature: -26 °C, Run #2:

Using General Procedure 2b, benzaldehyde (64 μL, 0.63 mmol) was added to a solution of enolate **4** (115 μL, 0.63 mmol) and phosphoramide (**±)-7j** (15.6 mg, 0.032 mmol) in methylene chloride (2.3 mL) at -26 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 59.54\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0353	0.254	0.00	3.93
0.5	0.0323	0.232	0.09	4.31
1.0	0.0299	0.214	0.16	4.68
1.5	0.0283	0.202	0.21	4.96
2.0	0.0267	0.190	0.25	5.26
2.5	0.0242	0.171	0.33	5.85
3.0	0.0228	0.161	0.37	6.21
3.5	0.0233	0.164	0.35	6.09
4.0	0.0208	0.146	0.43	6.85
4.5	0.0196	0.137	0.46	7.31
5.0	0.0190	0.132	0.48	7.57
5.5	0.0175	0.121	0.52	8.25
6.0	0.0170	0.118	0.54	8.49
6.5	0.0166	0.114	0.55	8.75
7.0	0.0158	0.109	0.57	9.21
7.5	0.0158	0.108	0.57	9.25
8.0	0.0151	0.103	0.60	9.72
8.5	0.0146	0.100	0.61	10.02
9.0	0.0140	0.095	0.63	10.49
9.5	0.0135	0.091	0.64	10.94
10.0	0.0137	0.093	0.64	10.80
10.5	0.0126	0.085	0.67	11.79
11.0	0.0126	0.085	0.67	11.80
11.5	0.0120	0.080	0.68	12.44
12.0	0.0122	0.081	0.68	12.28
12.5	0.0115	0.076	0.70	13.09
13.0	0.0114	0.075	0.70	13.25
13.5	0.0113	0.075	0.71	13.34

Temperature: -26 °C, Run #3:

Using General Procedure 2b, benzaldehyde (63 μL, 0.61 mmol) was added to a solution of enolate **4** (113 μL, 0.62 mmol) and phosphoramide (**±)-7j** (15.6 mg, 0.032 mmol) in methylene chloride (2.3 mL) at -26 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 69.57\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0274	0.250	0.00	4.00
0.5	0.0249	0.226	0.10	4.42
1.0	0.0233	0.211	0.16	4.74
1.5	0.0212	0.191	0.24	5.24
2.0	0.0199	0.179	0.29	5.59
2.5	0.0187	0.167	0.33	5.98
3.0	0.0175	0.155	0.38	6.44
3.5	0.0165	0.146	0.41	6.83
4.0	0.0156	0.137	0.45	7.28
4.5	0.0144	0.126	0.50	7.92
5.0	0.0136	0.118	0.53	8.45
5.5	0.0134	0.116	0.53	8.59
6.0	0.0126	0.109	0.56	9.14
6.5	0.0119	0.102	0.59	9.80
7.0	0.0117	0.100	0.60	9.99
7.5	0.0112	0.095	0.62	10.49
8.0	0.0107	0.091	0.64	11.01
8.5	0.0101	0.086	0.66	11.67
9.0	0.0098	0.083	0.67	12.08
9.5	0.0095	0.079	0.68	12.60
10.0	0.0090	0.075	0.70	13.31
10.5	0.0087	0.072	0.71	13.92

Temperature: -10 °C, Run #1:

Using General Procedure 2b, benzaldehyde (63 μL, 0.61 mmol) was added to a solution of enolate **4** (112 μL, 0.61 mmol) and phosphoramide (**±)-7j** (15.2 mg, 0.031 mmol) in methylene chloride (2.3 mL) at -10 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 73.48\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0304	0.248	0.00	4.03
0.5	0.0278	0.225	0.09	4.44
1.0	0.0256	0.207	0.17	4.83
1.5	0.0235	0.189	0.24	5.28
2.0	0.0215	0.173	0.30	5.79
2.5	0.0204	0.163	0.34	6.12
3.0	0.0188	0.150	0.40	6.67
3.5	0.0178	0.141	0.43	7.09
4.0	0.0166	0.132	0.47	7.60
4.5	0.0157	0.123	0.50	8.10
5.0	0.0148	0.116	0.53	8.60
5.5	0.0139	0.108	0.56	9.24
6.0	0.0137	0.107	0.57	9.37
6.5	0.0127	0.098	0.60	10.18
7.0	0.0123	0.095	0.62	10.49
7.5	0.0116	0.089	0.64	11.24
8.0	0.0113	0.087	0.65	11.54
8.5	0.0105	0.080	0.68	12.53
9.0	0.0102	0.078	0.69	12.89
9.5	0.0100	0.075	0.70	13.28
10.0	0.0095	0.071	0.71	14.09

Temperature: -10 °C, Run #2:

Using General Procedure 2b, benzaldehyde (54 μL, 0.54 mmol) was added to a solution of enolate **4** (98 μL, 0.54 mmol) and phosphoramide (**±)-7j** (13.2 mg, 0.027 mmol) in methylene chloride (2.0 mL) at -10 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 71.19\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0302	0.250	0.00	4.00
0.5	0.0274	0.225	0.10	4.44
1.0	0.0253	0.207	0.17	4.83
1.5	0.0237	0.192	0.23	5.20
2.0	0.0213	0.172	0.31	5.83
2.5	0.0202	0.161	0.35	6.19
3.0	0.0190	0.151	0.39	6.60
3.5	0.0180	0.142	0.43	7.03
4.0	0.0169	0.133	0.47	7.52
4.5	0.0162	0.127	0.49	7.90
5.0	0.0152	0.118	0.53	8.47
5.5	0.0146	0.113	0.55	8.88
6.0	0.0139	0.106	0.57	9.40
6.5	0.0134	0.103	0.59	9.76
7.0	0.0126	0.096	0.62	10.46
7.5	0.0124	0.094	0.62	10.65
8.0	0.0119	0.089	0.64	11.22
8.5	0.0113	0.084	0.66	11.88
9.0	0.0110	0.081	0.67	12.32
9.5	0.0106	0.078	0.69	12.81
10.0	0.0101	0.073	0.71	13.65

Temperature: -10 °C, Run #3:

Using General Procedure 2b, benzaldehyde (62 μL, 0.61 mmol) was added to a solution of enolate **4** (111 μL, 0.61 mmol) and phosphoramide (**±**)**-7j** (15 mg, 0.030 mmol) in methylene chloride (2.0 mL) at -10 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k = 70.97\ M^{-2}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0321	0.246	0.00	4.06
0.5	0.0293	0.224	0.09	4.46
1.0	0.0270	0.206	0.16	4.86
1.5	0.0245	0.186	0.24	5.38
2.0	0.0232	0.175	0.29	5.70
2.5	0.0217	0.163	0.34	6.13
3.0	0.0203	0.152	0.38	6.57
3.5	0.0189	0.141	0.43	7.07
4.0	0.0179	0.133	0.46	7.51
4.5	0.0171	0.126	0.49	7.91
5.0	0.0161	0.118	0.52	8.44
5.5	0.0157	0.116	0.53	8.63
6.0	0.0149	0.109	0.56	9.17
6.5	0.0144	0.105	0.57	9.54
7.0	0.0136	0.099	0.60	10.13
7.5	0.0128	0.093	0.62	10.79
8.0	0.0126	0.091	0.63	10.96
8.5	0.0120	0.086	0.65	11.60
9.0	0.0118	0.085	0.66	11.81
9.5	0.0112	0.080	0.68	12.52
10.0	0.0107	0.076	0.69	13.21
11.0	0.0101	0.075	0.71	14.10

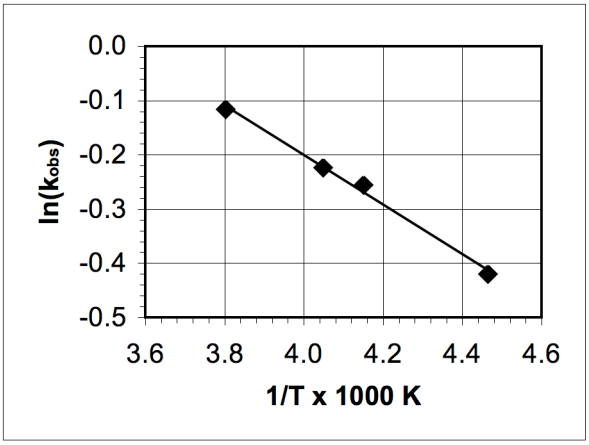


Figure IV. Arrhenius Plot. The graph depicts a linear fit, $f(x) = mx + b$ (m = -0.46, R^2 = 0.99).

Raw Data. ReactIR Loading Studies on Addition of 4 to 5a Catalyzed by (±)-7j, Temperature: -34 °C, 1 mol %:

Using General Procedure 2b, benzaldehyde (66 μL, 0.65 mmol) was added to a solution of enolate **4** (118 μL, 0.65 mmol) and phosphoramide **(±)-7j** (3.2 mg, 0.007 mmol) in methylene chloride (2.4 mL) at -34 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k_{obs} = 0.513\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0344	0.250	0.00	3.99
0.5	0.0326	0.238	0.05	4.21
1.0	0.0309	0.225	0.10	4.44
1.5	0.0295	0.215	0.14	4.65
2.0	0.0276	0.201	0.20	4.98
2.5	0.0265	0.193	0.23	5.17
3.0	0.0253	0.184	0.26	5.43
3.5	0.0240	0.175	0.30	5.73
4.0	0.0234	0.170	0.32	5.87
4.5	0.0221	0.161	0.36	6.22
5.0	0.0210	0.153	0.39	6.53
5.5	0.0206	0.150	0.40	6.68
6.0	0.0197	0.144	0.43	6.95
6.5	0.0186	0.135	0.46	7.38
7.0	0.0184	0.134	0.46	7.44
7.5	0.0177	0.129	0.48	7.74
8.0	0.0170	0.124	0.51	8.07
8.5	0.0167	0.122	0.51	8.23
9.0	0.0159	0.116	0.54	8.64
9.5	0.0156	0.113	0.55	8.82
10.0	0.0152	0.111	0.56	9.00
10.5	0.0149	0.109	0.57	9.20
11.0	0.0143	0.104	0.58	9.61
11.5	0.0140	0.102	0.59	9.81
12.0	0.0137	0.100	0.60	9.98
12.5	0.0132	0.096	0.62	10.40
13.0	0.0125	0.091	0.64	10.97
13.5	0.0128	0.093	0.63	10.71
14.0	0.0122	0.089	0.64	11.24
14.5	0.0121	0.088	0.65	11.31
15.0	0.0118	0.086	0.66	11.67
15.5	0.0115	0.083	0.67	11.98
16.0	0.0113	0.082	0.67	12.15
16.5	0.0110	0.080	0.68	12.50
17.0	0.0109	0.079	0.68	12.60
17.5	0.0108	0.079	0.68	12.67

18.0	0.0102	0.074	0.70	13.44
18.5	0.0104	0.076	0.70	13.15
19.0	0.0102	0.074	0.70	13.49

Temperature: -34 °C, 10 mol %:

Using General Procedure 2b, benzaldehyde (66 μL, 0.65 mmol) was added to a solution of enolate **4** (119 μL, 0.65 mmol) and phosphoramide (**±)-7j** (32 mg, 0.065 mmol) in methylene chloride (2.4 mL) at -34 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. $k_{obs} = 0.778\ M^{-1}\ min^{-1}$.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0342	0.252	0.00	3.96
0.5	0.0313	0.230	0.09	4.34
1.0	0.0289	0.212	0.16	4.71
1.5	0.0267	0.196	0.23	5.11
2.0	0.0249	0.182	0.28	5.50
2.5	0.0235	0.172	0.32	5.83
3.0	0.0217	0.158	0.38	6.34
3.5	0.0207	0.150	0.40	6.66
4.0	0.0196	0.142	0.44	7.07
4.5	0.0187	0.135	0.46	7.40
5.0	0.0178	0.128	0.49	7.82
5.5	0.0170	0.122	0.52	8.18
6.0	0.0161	0.115	0.54	8.68
6.5	0.0152	0.109	0.57	9.19
7.0	0.0148	0.106	0.58	9.48
7.5	0.0141	0.100	0.60	10.01
8.0	0.0134	0.095	0.62	10.53
8.5	0.0130	0.092	0.64	10.88
9.0	0.0127	0.089	0.65	11.20
9.5	0.0119	0.083	0.67	12.00
10.0	0.0116	0.081	0.68	12.32
10.5	0.0115	0.080	0.68	12.48
11.0	0.0112	0.078	0.69	12.85
11.5	0.0107	0.075	0.70	13.41

Temperature: -34 °C, 20 mol %:

Using General Procedure 2b, benzaldehyde (67 μL, 0.66 mmol) was added to a solution of enolate **4** (120 μL, 0.66 mmol) and phosphoramide (**±)-7j** (65 mg, 0.131 mmol) in methylene chloride (2.4 mL) at -34 °C as internally monitored. The reaction was monitored every 30 seconds until complete conversion. k_{obs} = 1.048 M^{-1} min^{-1}.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0344	0.254	0.00	3.93
0.3	0.0318	0.234	0.08	4.27
0.7	0.0293	0.215	0.16	4.66
1.0	0.0274	0.200	0.21	5.00
1.3	0.0258	0.187	0.26	5.34
1.7	0.0241	0.175	0.31	5.73
2.0	0.0231	0.166	0.35	6.01
2.3	0.0219	0.157	0.38	6.36
2.7	0.0211	0.151	0.41	6.64
3.0	0.0198	0.140	0.45	7.13
3.3	0.0190	0.134	0.47	7.44
3.7	0.0181	0.128	0.50	7.84
4.0	0.0177	0.124	0.51	8.03
4.3	0.0168	0.117	0.54	8.53
4.7	0.0163	0.113	0.55	8.83
5.0	0.0155	0.107	0.58	9.35
5.3	0.0153	0.106	0.58	9.47
5.7	0.0144	0.099	0.61	10.13
6.0	0.0142	0.097	0.62	10.28
6.3	0.0142	0.097	0.62	10.29
6.7	0.0135	0.092	0.64	10.92
7.0	0.0130	0.088	0.65	11.38
7.3	0.0130	0.088	0.66	11.40
7.7	0.0129	0.087	0.66	11.56
8.0	0.0121	0.081	0.68	12.35
8.3	0.0119	0.079	0.69	12.72
8.7	0.0116	0.076	0.70	13.10
9.0	0.0115	0.076	0.70	13.13

Temperature: -34 °C, 30 mol %:

Using General Procedure 2b, benzaldehyde (63 μL, 0.62 mmol) was added to a solution of enolate **4** (112 μL, 0.61 mmol) and phosphoramide (**±)-7j** (88 mg, 0.179 mmol) in methylene chloride (2.3 mL) at -34 °C as internally monitored. The reaction was monitored every 20 seconds until complete conversion. k_{obs} = 1.305 M^{-1} min^{-1}.

Time (min)	Absorbance	[Enolate]	Conversion	1/[Enolate]
0.0	0.0344	0.254	0.00	3.93
0.3	0.0318	0.234	0.08	4.27
0.7	0.0293	0.215	0.16	4.66
1.0	0.0274	0.200	0.21	5.00
1.3	0.0258	0.187	0.26	5.34
1.7	0.0241	0.175	0.31	5.73
2.0	0.0231	0.166	0.35	6.01
2.3	0.0219	0.157	0.38	6.36
2.7	0.0211	0.151	0.41	6.64
3.0	0.0198	0.140	0.45	7.13
3.3	0.0190	0.134	0.47	7.44
3.7	0.0181	0.128	0.50	7.84
4.0	0.0177	0.124	0.51	8.03
4.3	0.0168	0.117	0.54	8.53
4.7	0.0163	0.113	0.55	8.83
5.0	0.0155	0.107	0.58	9.35
5.3	0.0153	0.106	0.58	9.47
5.7	0.0144	0.099	0.61	10.13
6.0	0.0142	0.097	0.62	10.28
6.3	0.0142	0.097	0.62	10.29
6.7	0.0135	0.092	0.64	10.92
7.0	0.0130	0.088	0.65	11.38
7.3	0.0130	0.088	0.66	11.40
7.7	0.0129	0.087	0.66	11.56
8.0	0.0121	0.081	0.68	12.35
8.3	0.0119	0.079	0.69	12.72
8.7	0.0116	0.076	0.70	13.10
9.0	0.0115	0.076	0.70	13.13

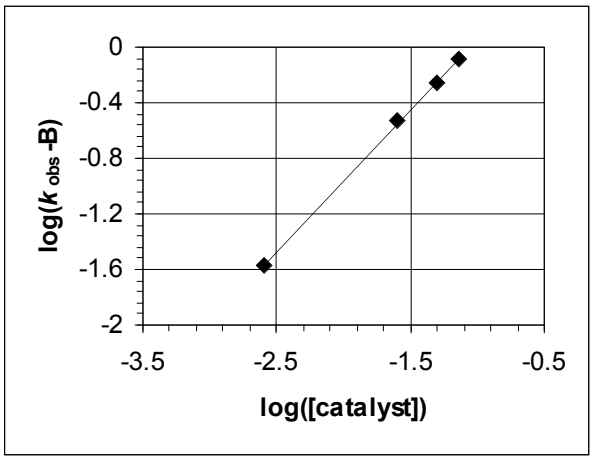


Figure V. Plot of log(k_{obs}-B) versus log([catalyst]) for the addition of **4** to **5a** catalyzed by **7j** at T = –35 °C. The graph depicts the linear fit to $f(x) = mx + b$ (m = 1.014, R^2 = 1.000).

Raw Data. RINMR kinetics of Addition of 4 to 5a Catalyzed by (±)-7j

Temperature: -27 °C:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide **(±)-7j** (8.6 mg, 0.018 mmol) in methylene chloride-d_2 (0.6 mL) at -27 °C as internally monitored. The reaction was monitored every 37 seconds until complete conversion. k = 0.4373 M^{-2} s^{-1}.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	0.00	0.00	0.437	2.289
11	97.17	2.83	0.425	2.355
48	84.61	15.39	0.370	2.705
85	75.20	24.80	0.329	3.043
122	67.69	32.31	0.296	3.381
159	60.95	39.05	0.266	3.755
196	55.60	44.40	0.243	4.116
233	50.65	49.35	0.221	4.519

Temperature: -37 °C:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide, **(±)-7j** (8.6 mg, 0.018 mmol) in methylene chloride-d_2 (0.6 mL) at -37 °C as internally monitored. The reaction was monitored every 37 seconds until complete conversion. k = 0.353 M^{-2} s^{-1}.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	0.00	0.00	0.437	2.289
11	97.59	2.41	0.426	2.345
48	86.84	13.16	0.379	2.635
85	78.23	21.77	0.342	2.925
122	70.82	29.18	0.309	3.232
159	64.70	35.30	0.283	3.537
196	59.85	40.15	0.262	3.824
233	55.83	44.17	0.244	4.099
270	52.66	47.34	0.230	4.346
307	49.60	50.40	0.217	4.614

Temperature: -49 °C:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide (**±**)**-7j** (8.6 mg, 0.018 mmol) in methylene chloride-d_2 (0.6 mL) at -49 °C as internally monitored. The reaction was monitored every 37 seconds until complete conversion. $k = 0.300\ M^{-2}\ s^{-1}$.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.437	2.289
180	92.84	7.16	0.406	2.465
217	78.84	21.16	0.345	2.903
254	66.58	33.42	0.291	3.437
291	57.47	42.53	0.251	3.982
328	50.49	49.51	0.221	4.532
365	45.32	54.68	0.198	5.050

Temperature: -58 °C:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide (**±**)**-7j** (8.6 mg, 0.018 mmol) in methylene chloride-d_2 (0.6 mL) at -58 °C as internally monitored. The reaction was monitored every 67 seconds until complete conversion. $k = 0.247\ M^{-2}\ s^{-1}$.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.437	2.289
90	83.68	16.32	0.366	2.735
157	73.16	26.84	0.320	3.128
224	64.85	35.15	0.283	3.529
291	58.84	41.16	0.257	3.889
358	54.19	45.81	0.237	4.223
425	50.35	49.65	0.220	4.546

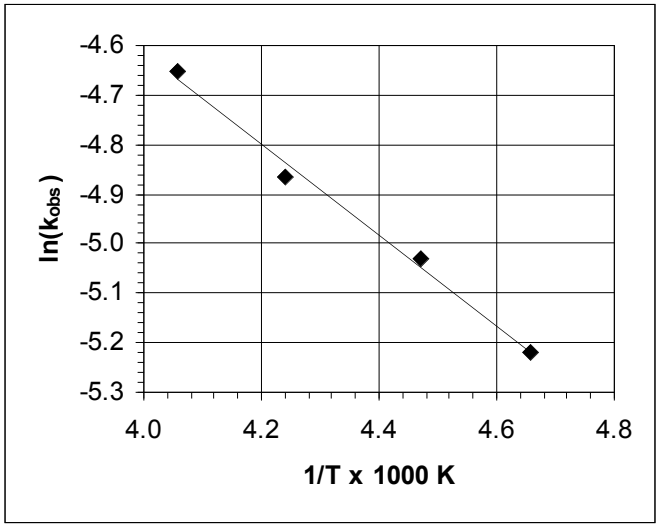


Figure VI. Arrhenius Plot. The graph depicts a linear fit, $f(x) = mx + b$ (m = -0.92, R^2 = 0.99).

Raw Data. RINMR Loading Studies on the Addition of 4 to 5a Catalyzed by (±)-7j.

Temperature: -53 °C, 5 mol %:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide **(±)-7j** (8.6 mg, 0.018 mmol) in methylene chloride-d_2 (0.6 mL) at -53 °C as internally monitored. The reaction was monitored every 10 seconds until complete conversion. $k_{obs} = 0.012\ M^{-1}\ s^{-1}$.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.470	2.129
4	-	-	-	-
14	86.68	13.32	0.407	2.456
24	83.62	16.38	0.393	2.545
34	80.66	19.34	0.379	2.639
44	77.70	22.30	0.365	2.739
54	75.11	24.89	0.353	2.834
64	72.67	27.33	0.341	2.929
74	70.50	29.50	0.331	3.019
84	68.46	31.54	0.322	3.109
94	66.53	33.47	0.313	3.199
104	64.76	35.24	0.304	3.287
114	63.02	36.98	0.296	3.378
124	61.49	38.51	0.289	3.462
134	60.28	39.72	0.283	3.531

Temperature: -53 °C, 3 mol %:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide (**±)-7j** (5.1 mg, 0.010 mmol) in methylene chloride-d_2 (0.6 mL) at -53 °C as internally monitored. The reaction was monitored every 10 seconds until complete conversion. $k_{obs} = 0.011\ M^{-1}\ s^{-1}$.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.470	2.129
4	-	-	-	-
14	91.65	8.35	0.431	2.323
24	88.08	11.92	0.414	2.417
34	84.75	15.25	0.398	2.512
44	81.54	18.46	0.383	2.611
54	76.14	23.86	0.358	2.795
64	73.51	26.49	0.345	2.896
74	71.22	28.78	0.335	2.989
84	68.95	31.05	0.324	3.087
94	66.99	33.01	0.315	3.177
104	65.08	34.92	0.306	3.270
114	63.33	36.67	0.298	3.361
124	61.70	38.30	0.290	3.450
134	60.26	39.74	0.283	3.532
144	58.77	41.23	0.276	3.622
154	57.54	42.46	0.270	3.699
164	56.30	43.70	0.264	3.781

Temperature: -53 °C, 2 mol %:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide (**±)-7j** (3.4 mg, 0.007 mmol) in methylene chloride-d_2 (0.6 mL) at -53 °C as internally monitored. The reaction was monitored every 10 seconds until complete conversion. $k_{obs} = 0.009\ M^{-1}\ s^{-1}$.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.470	2.129
4	-	-	-	-
14	93.08	6.92	0.437	2.287
24	89.15	10.85	0.419	2.388
34	85.93	14.07	0.404	2.477
44	82.78	17.22	0.389	2.571
54	79.17	20.83	0.372	2.689
64	77.15	22.85	0.362	2.759
74	74.59	25.41	0.350	2.854
84	72.24	27.76	0.339	2.946
94	70.11	29.89	0.329	3.036
104	68.10	31.90	0.320	3.126
114	66.20	33.80	0.311	3.215
124	64.45	35.55	0.303	3.303
134	62.86	37.14	0.295	3.386
144	61.35	38.65	0.288	3.469
154	59.97	40.03	0.282	3.550
164	57.52	42.48	0.270	3.700
174	56.32	43.68	0.265	3.779
184	55.19	44.81	0.259	3.857
194	54.06	45.94	0.254	3.937
204	53.00	47.00	0.249	4.016
214	52.01	47.99	0.244	4.093
224	50.22	49.78	0.236	4.239
234	49.33	50.67	0.232	4.315

Temperature: -53 °C, 1 mol %:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide (**±)-7j** (1.7 mg, 0.004 mmol) in methylene chloride-d_2 (0.6 mL) at -53 °C as internally monitored. The reaction was monitored every 10 seconds until complete conversion. $k_{obs} = 0.007\ M^{-1}\ s^{-1}$.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.470	2.129
4	-	-	-	-
14	91.60	8.40	0.430	2.324
24	89.15	10.85	0.419	2.388
34	86.86	13.14	0.408	2.450
44	84.72	15.28	0.398	2.513
54	82.65	17.35	0.388	2.575
64	80.57	19.43	0.379	2.642
74	78.65	21.35	0.369	2.707
84	76.81	23.19	0.361	2.771
94	75.14	24.86	0.353	2.833
104	73.50	26.50	0.345	2.896
114	71.98	28.02	0.338	2.957
124	70.57	29.43	0.332	3.016
134	69.13	30.87	0.325	3.079
144	67.84	32.16	0.319	3.138
154	66.67	33.33	0.313	3.193
164	65.45	34.55	0.307	3.252
174	64.30	35.70	0.302	3.310
184	63.20	36.80	0.297	3.368
194	62.28	37.72	0.293	3.418
204	59.39	40.61	0.279	3.584
214	58.52	41.48	0.275	3.637
224	57.74	42.26	0.271	3.687
234	56.91	43.09	0.267	3.740

Temperature: -53 °C, 0.5 mol %:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) and phosphoramide (**±)-7j** (0.9 mg, 0.002 mmol) in methylene chloride-d_2 (0.6 mL) at -53 °C as internally monitored. The reaction was monitored every 10 seconds until complete conversion. $k_{obs} = 0.006\ M^{-1}\ s^{-1}$.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.470	2.129
4	-	-	-	-
14	95.35	4.65	0.448	2.232
24	92.96	7.04	0.437	2.290
34	90.65	9.35	0.426	2.348
44	88.45	11.55	0.416	2.407
54	86.37	13.63	0.406	2.464
64	84.43	15.57	0.397	2.521
74	82.53	17.47	0.388	2.579
84	80.79	19.21	0.380	2.635
94	79.04	20.96	0.371	2.693
104	77.45	22.55	0.364	2.748
114	75.88	24.12	0.356	2.805
124	71.10	28.90	0.334	2.994
134	69.76	30.24	0.328	3.051
144	68.45	31.55	0.322	3.110
154	67.16	32.84	0.316	3.169
164	65.88	34.12	0.310	3.231
174	64.72	35.28	0.304	3.289
184	63.59	36.41	0.299	3.347
194	62.51	37.49	0.294	3.405
204	61.46	38.54	0.289	3.463
214	59.49	40.51	0.279	3.578
224	61.20	38.80	0.288	3.478
234	60.36	39.64	0.284	3.526

Temperature: -53 °C, 0.0 mol %:

Using General Procedure 3a, a solution of benzaldehyde in chloroform (85 μL, 0.35 mmol) was injected into an NMR tube containing enolate **4** (65 μL, 0.65 mmol) in methylene chloride-d_2 (0.6 mL) at -53 °C as internally monitored. The reaction was monitored every 10 seconds for several minutes. k = 0.001 M^{-1} s^{-1}.

Time (s)	% Enolate	% Aldolate	[Enolate]	1/[Enolate]
0	100.00	0.00	0.437	2.289
4	97.49	2.51	0.426	2.348
14	97.42	2.58	0.426	2.349
24	96.97	3.03	0.424	2.360
34	96.59	3.41	0.422	2.369
44	96.16	3.84	0.420	2.380
54	95.81	4.19	0.419	2.389
64	95.40	4.60	0.417	2.399
74	95.03	4.97	0.415	2.408
84	94.64	5.36	0.414	2.418
94	94.23	5.77	0.412	2.429
104	93.89	6.11	0.410	2.437
114	93.50	6.50	0.409	2.448
124	93.16	6.84	0.407	2.456
134	92.80	7.20	0.405	2.466
144	92.40	7.60	0.404	2.477
154	92.05	7.95	0.402	2.486
164	91.70	8.30	0.401	2.496
174	91.36	8.64	0.399	2.505
184	91.01	8.99	0.398	2.515

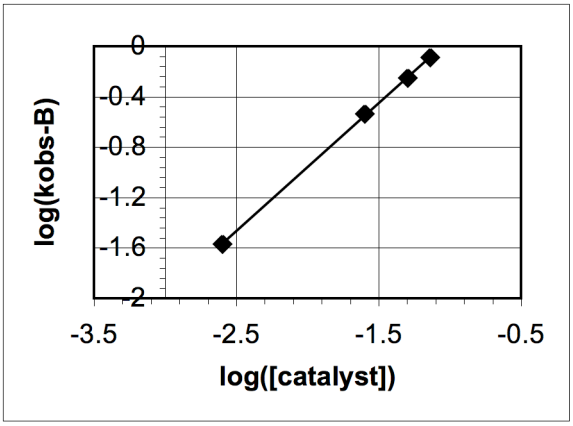


Figure VI. Plot of log(k_{obs}-B versus log([catalyst]) for the addition of **4** to benzaldehyde catalyzed by **(±)-7j** at T = -35 °C. The graph depicts the linear fit to $f(x) = mx + b$(m = 1.01, R^2 = 0.99).

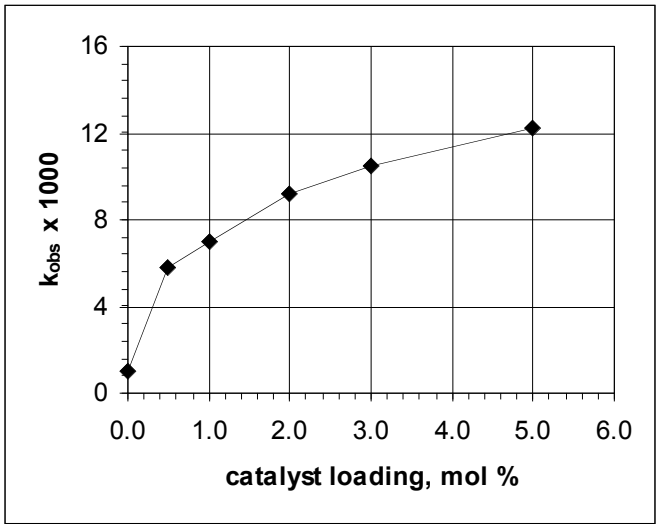


Figure VII. Plot of k_{obs} versus catalyst loading for the addition of **4** to benzaldehyde catalyzed by **(±)-7j**.

Raw Data. RINMR Kinetics of the Addition of 4 to 5a Catalyzed by (*S,S*)-7a

Series #1, Temperature: -96 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL)at -96 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. k = 48.07 M^{-2} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	1.00	0.075	13.338
14	0.90	0.067	14.953
19	0.81	0.060	16.603
24	0.73	0.054	18.374
29	0.69	0.052	19.377
34	0.65	0.049	20.603
39	0.63	0.047	21.428

† Area of aldehydic proton relative to internal standard

Series #1, Temperature: -91 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL)at -91 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. k = 55.68 M^{-2} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	0.90	0.067	14.883
14	0.93	0.070	14.378
19	0.91	0.068	14.790
24	0.86	0.065	15.493

† Area of aldehydic proton relative to internal standard

Series #1, Temperature: -85 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in

chloroform-*d* (0.05 mL) at -85 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. k = 64.05 M^{-2} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	0.87	0.065	15.402
14	0.75	0.056	17.957
19	0.64	0.048	20.802
24	0.58	0.043	23.106
29	0.53	0.040	25.244
34	0.47	0.035	28.656
39	0.44	0.033	30.701

† Area of aldehydic proton relative to internal standard

Series #1, Temperature: -80 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -85 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. k = 70.78 M^{-2} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	0.84	0.062	16.036
14	0.71	0.053	18.947
19	0.61	0.045	21.996
24	0.55	0.041	24.542
29	0.50	0.037	26.936
34	0.44	0.033	30.580
39	0.40	0.030	33.195

† Area of aldehydic proton relative to internal standard

Series #2, Temperature: -85 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -85 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. k = 29.72 M^{-2} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	1.24	0.093	10.784
14	1.15	0.086	11.631
19	1.12	0.083	11.999
24	1.04	0.078	12.894
29	0.98	0.074	13.603
34	0.93	0.070	14.369
39	0.92	0.069	14.593

† Area of aldehydic proton relative to internal standard

Series #2, Temperature: -80 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at –80 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. $k = 36.24\ M^{-2}\ s^{-1}$.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
5	1.02	0.076	13.169
10	1.02	0.076	13.074
15	1.00	0.075	13.385
20	0.98	0.073	13.720
25	0.95	0.071	14.105
30	0.92	0.069	14.583
35	0.89	0.067	14.970

† Area of aldehydic proton relative to internal standard

Series #2, Temperature: -75 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at –75 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. $k = 44.06\ M^{-2}\ s^{-1}$.

Time (s)	Integral †	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	1.10	0.082	12.194
14	0.94	0.070	14.236
19	0.85	0.063	15.831
24	0.77	0.057	17.441
29	0.68	0.051	19.674
34	0.62	0.046	21.759
39	0.58	0.043	23.262

† Area of aldehydic proton relative to internal standard

Series #3, Temperature: -70 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at –70 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. $k = 56.46\ M^{-2}\ s^{-1}$.

Time (s)	Integral †	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	1.08	0.081	12.390
14	1.00	0.075	13.362
19	0.94	0.070	14.254
24	0.86	0.064	15.511
29	0.80	0.060	16.688
34	0.76	0.057	17.515
39	0.73	0.055	18.323

† Area of aldehydic proton relative to internal standard

Series #3, Temperature: -75 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at –75 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. $k = 46.53\ M^{-2}\ s^{-1}$.

Time (s)	Integral †	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	1.30	0.097	10.336
14	1.20	0.089	11.181
19	1.13	0.084	11.904
24	1.05	0.079	12.709
29	0.99	0.074	13.497
34	0.95	0.071	14.142
39	0.90	0.067	14.842

† Area of aldehydic proton relative to internal standard

Series #3, Temperature: -75 °C:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at –75 °C as internally monitored. The reaction was monitored every 5 seconds until complete conversion. $k = 16.47\ M^{-2}\ s^{-1}$.

Time (s)	Integral †	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
9	1.15	0.086	11.636
14	1.17	0.087	11.472
19	1.14	0.085	11.779
24	1.14	0.085	11.785
29	1.12	0.083	11.978

† Area of aldehydic proton relative to internal standard

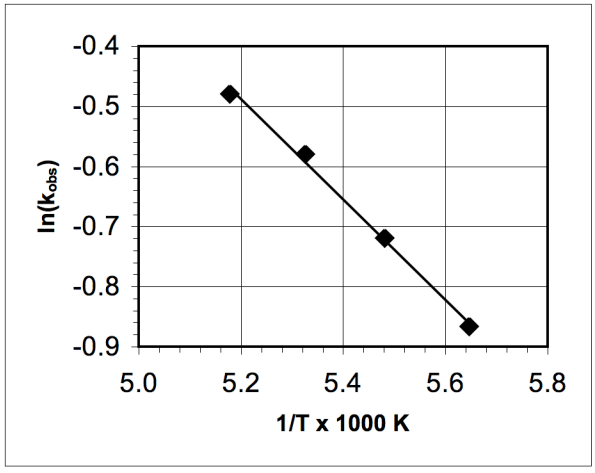


Figure VIII. Arrhenius Plot. The graph depicts a linear fit, $f(x) = mx + b$ (m = -0.84, R^2 = 1.00).

Raw Data. RINMR Loading Studies on the Addition of 4 to 5a Catalyzed by (*S,S*)-7a, Temperature: -80 °C, 10 mol %:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (3.2 mg, 0.009 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -80 °C as internally monitored. The reaction was monitored every 2 seconds until complete conversion. $k_{obs} = 0.513\ M^{-1}\ s^{-1}$.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
5	1.20	0.071	14.041
7	1.16	0.069	14.526
9	1.12	0.066	15.103
11	1.06	0.063	15.835
13	1.03	0.061	16.388
15	0.97	0.058	17.303
17	0.94	0.056	17.887

† Area of aldehydic proton relative to internal standard

Temperature: -80 °C, 13 mol %:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (4.1 mg, 0.011 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -80 °C as internally monitored. The reaction was monitored every 1 second until complete conversion. $k_{obs} = 0.810\ M^{-1}\ s^{-1}$.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
5	1.11	0.083	12.085
6	1.03	0.077	12.944
7	1.00	0.074	13.442
8	0.95	0.071	14.071
9	0.92	0.069	14.506
10	0.87	0.065	15.334

† Area of aldehydic proton relative to internal standard

Temperature: -80 °C, 15 mol %:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-

7a (4.8 mg, 0.013 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -80 °C as internally monitored. The reaction was monitored every 1 second until complete conversion. k_{obs} = 1.133 M^{-1} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
5	1.02	0.076	13.156
6	0.88	0.066	15.195
7	0.80	0.059	16.846
8	0.69	0.052	19.402
9	0.65	0.048	20.711
10	0.59	0.044	22.756

† Area of aldehydic proton relative to internal standard

Temperature: -80 °C, 16 mol %:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (5.2 mg, 0.014 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -80 °C as internally monitored. The reaction was monitored every 1 second until complete conversion. k_{obs} = 1.314 M^{-1} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
5	1.08	0.081	12.409
6	0.92	0.069	14.513
7	0.79	0.059	17.021
8	0.71	0.053	18.991
9	0.60	0.045	22.250
10	0.54	0.040	25.019

† Area of aldehydic proton relative to internal standard

Temperature: -80 °C, 17 mol %:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (5.5 mg, 0.015 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -80 °C as internally monitored. The reaction was monitored every 1 second until complete conversion. k_{obs} = 1.502 M^{-1} s^{-1}.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
5	0.97	0.072	13.854
6	0.81	0.061	16.484
7	0.69	0.052	19.281
8	0.61	0.045	22.129
9	0.54	0.040	24.817
10	0.46	0.035	28.944

† Area of aldehydic proton relative to internal standard

Temperature: -80 °C, 18 mol %:

Using General Procedure 3b, a solution of benzaldehyde in chloroform (44 μL, 0.086 mmol) was injected into an NMR tube containing enolate **4** (16 μL, 0.086 mmol) and phosphoramide (*S,S*)-**7a** (5.9 mg, 0.016 mmol) in methylene chloride-d_2 (0.6 mL) with a standard solution of TMS in chloroform-*d* (0.05 mL) at -80 °C as internally monitored. The reaction was monitored every 1 second until complete conversion. $k_{obs} = 1.803\ M^{-1}\ s^{-1}$.

Time (s)	Integral	[PhCHO]	1/[PhCHO]
0	-	0.124	8.069
5	1.05	0.078	12.757
6	0.85	0.064	15.722
7	0.72	0.054	18.570
8	0.63	0.047	21.312
9	0.54	0.040	24.916
10	0.48	0.036	27.915

† Area of aldehydic proton relative to internal standard

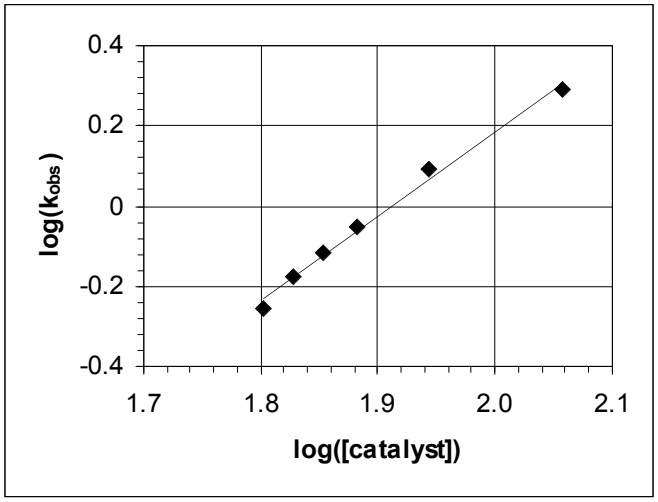
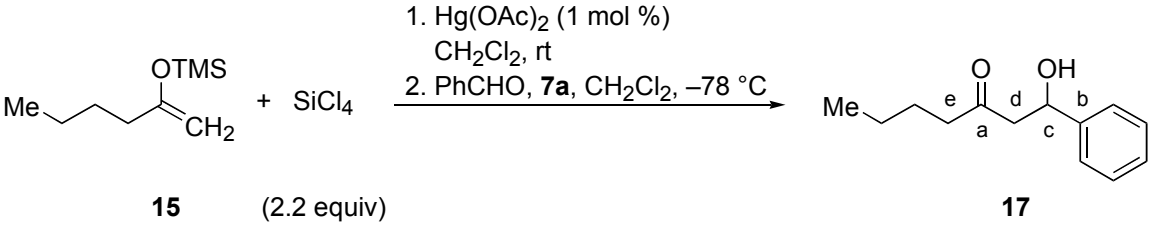


Figure IX. Plot of $\log(k_{obs})$ versus log([catalyst]) for the addition of **4** to benzaldehyde catalyzed by (*S,S*)-**7a** at T = -80 °C. The graph depicts the linear fit to $f(x) = mx + b$ ($m = 2.11$, $R^2 = 0.99$).

Natural Abundance ^{13}C NMR Kinetic Isotope Effects Studies
Limiting Aldehyde

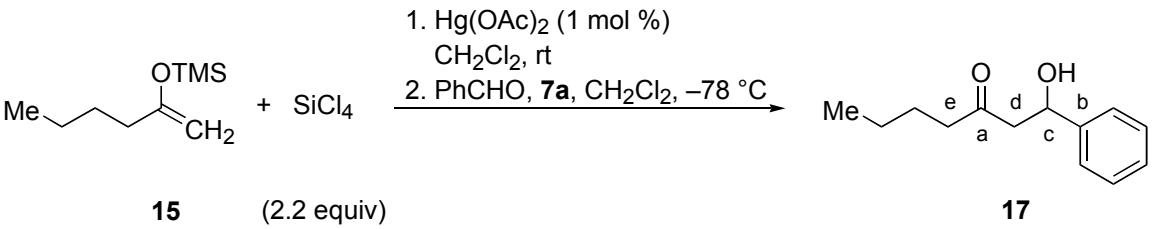


15 (2.2 equiv) **17**

Silyl enol ether **15** (862 mg, 5.0 mmol) was added quickly to a stirred suspension of silicon tetrachloride (1.1 mL, 10.0 mmol, 2.0 equiv) and mercuric acetate (16 mg, 0.05 mmol, 0.01 equiv) in CH_2Cl_2 (5 mL) at room temperature. After addition, the mixture was stirred at room temperature for 2 h. The volatile components were then removed under reduced pressure (0.1 mmHg) to give a cloudy oil. A solution of catalyst **7a** (184 mg, 0.5 mmol, 0.10 equiv) in CH_2Cl_2 (10 mL) was then added via cannula and the mixture was cooled to –78 °C. Benzaldehyde (25 μL, 0.25 mmol, 0.05 equiv) was then added dropwise via syringe and the reaction mixture was allowed to stir at –78 °C for 6 h. The reaction mixture was then poured into a rapidly stirring sat. aq. $NaHCO_3$ solution (30 mL) submerged in an ice bath and was allowed to stir at room temperature for 6 h. The heterogeneous mixture was then filtered through Celite, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated to give a crude oil. Purification by silica gel chromatography (SiO_2, pentane/Et_2O, 6/1) afforded 35 mg (95%) of **17** as a clear, colorless oil. Parameters for ^{13}C NMR analysis are as follows: T1 = 6 s; pw90 = 8. Spectra suitable for integration were obtained using a d1 = 8 × T1 and a final signal-to-noise exceeding 250:1.

Peak	δ	Run 1	Run 2	Run 3	Run 4	Run 5	Average	Standard	Ratio	KIE
a	211.74	1.004	1.005	1.005	1.000	1.003	1.003	1.003	1.000	1.000
b	142.82	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
c	69.89	1.988	1.992	1.987	1.979	1.993	1.988	1.988	1.000	0.997
d	50.94	1.927	1.927	1.926	1.920	1.926	1.925	1.929	0.998	0.963
e	43.37	1.886	1.889	1.890	1.878	1.889	1.886	1.886	1.000	1.003

Limiting Enolate



15 (2.2 equiv) **17**

Silyl enol ether **15** (86 mg, 0.50 mmol, 0.05 equiv) was added quickly to a stirred suspension of silicon tetrachloride (115 μL, 1.0 mmol, 0.10 equiv) and mercuric acetate (1.6 mg, 0.005 mmol, 0.0005 equiv) in CH_2Cl_2 (0.5 mL) at room temperature. After addition, the mixture was stirred at room temperature for 2 h. The volatile components were then removed under reduced pressure (0.1 mmHg) to give a cloudy oil. A solution of **7a** (368 mg, 1.0 mmol, 0.10 equiv) in CH_2Cl_2 (10 mL) was then added via cannula and the mixture was cooled to –78 °C. Benzaldehyde (1.0 mL, 10.0 mmol) was then added dropwise via syringe and the reaction mixture was allowed to stir at –78 °C for 10 h. The reaction mixture was then poured into a rapidly stirring sat. aq. $NaHCO_3$ solution (30 mL) submerged in an ice bath and was allowed to stir at room temperature for 6 h. The heterogeneous mixture was then filtered through Celite, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated to give a crude oil. Purification by silica gel chromatography (SiO_2, pentane/Et_2O, 6/1) afforded 68 mg (92%) of **17** as a clear, colorless oil. Parameters for ^{13}C NMR analysis are as follows: T1 = 6 s; pw90 = 8. Spectra suitable for integration were obtained using a d1 = 8 × T1 and a final signal-to-noise exceeding 250:1.

Peak	δ	Run 1	Run 2	Run 3	Run 4	Run 5	Average	Standard	Ratio	KIE
a	211.74	1.005	1.002	1.002	1.004	1.004	1.003	1.003	1.000	1.002
b	142.82	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
c	69.89	1.995	1.984	1.979	1.982	1.985	1.985	1.988	0.998	0.969
d	50.94	1.931	1.930	1.925	1.928	1.930	1.929	1.929	1.000	0.995
e	43.37	1.894	1.885	1.881	1.884	1.886	1.886	1.886	1.000	1.001

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