Electronic Supplementary Information

Kinetics and Mechanism of the Aminolysis of Aryl Ethyl Chloro and Chlorothio Phosphates with Anilines

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Table S1. Second-order rate constants ($k_H \times 10^4/M^{-1} s^{-1}$, $k_D \times 10^4/M^{-1} s^{-1}$) and kinetic isotope effects, k_H/k_D , for the aminolyses of ethyl Y-phenyl chloro-(1) and chlorothio-(2) phosphates with $XC_6H_4ND_2$ in acetonitrile at 55.0 °C

	X	Y	k_H	k_D	k_H/k_D
	4-MeO	4-MeO	113 ± 7[a]	104 ± 1[a]	1.09 ± 0.07[a]
	4-MeO	H	182 ± 9	153 ± 4	1.19 ± 0.07
	4-MeO	4-Cl	328 ± 27	268 ± 10	1.22 ± 0.11
	H	4-Me	16.2 ± 1.1	15.4 ± 0.8	1.10 ± 0.09
	H	H	20.0 ± 0.8	15.6 ± 1.4	1.28 ± 0.13
	H	4-Cl	37.4 ± 0.9	20.8 ± 1.0	1.80 ± 0.10
1	4-Cl	4-Me	3.00 ± 0.30	2.80 ± 0.28	1.07 ± 0.15
	4-Cl	H	3.60 ± 0.56	3.40 ± 0.20	1.10 ± 0.18
	4-Cl	4-Cl	6.00 ± 0.60	4.80 ± 0.23	1.25 ± 0.14
	4-MeO	4-MeO	16.7 ± 0.8	15.8 ± 1.2	1.06 ± 0.10
	4-MeO	H	25.9 ± 1.4	22.7 ± 2.1	1.14 ± 1.20
	4-MeO	4-Cl	53.7 ± 0.8	42.2 ± 0.1	1.27 ± 0.02
	H	4-Me	2.53 ± 0.11	2.33 ± 0.08	1.09 ± 0.04
	H	H	2.80 ± 0.05	2.51 ± 0.10	1.12 ± 0.05
	H	4-Cl	5.31 ± 0.20	4.54 ± 0.34	1.17 ± 0.10
2	4-Cl	4-Me	0.333 ± 0.020	0.308 ± 0.020	1.08 ± 0.10
	4-Cl	H	0.410 ± 0.010	0.370 ± 0.030	1.11 ± 0.10
	4-Cl	4-Cl	1.35 ± 0.10	1.10 ± 0.15	1.23 ± 0.20

[a] Standard deviation.

Table S2. Activation parameters[a] of the anilinolysis of (EtO)(YPhO)P(O)Cl (1), (EtO)(YPhO)P(S)Cl (2), (PhO)(YPhO)P(S)Cl (4), and (4-ClPhO)(YPhO)P(S)Cl (4′) in acetonitrile at 55.0 °C

	X	Y	$k_2 \times 10^4/M^{-1} s^{-1}$, (°C)	$\Delta H^{\neq}$ [c]	$-\Delta S^{\neq}$ [d]
	4-MeO	H	159 (45.0), 182 (55.0), 216 (65.0)	2.7 ± 0.2[b]	58 ± 1[b]
	4-MeO	4-Cl	285 (45.0), 328 (55.0), 363 (65.0)	1.9 ± 0.2	60 ± 1
	4-Me	4-Me	43.4 (45.0), 57.0 (55.0), 71.4 (65.0)	4.7 ± 0.2	55 ± 1
1	H	H	13.8 (45.0), 20.0 (55.0), 27.6 (65.0)	6.8 ± 0.2	51 ± 1
	H	4-Cl	25.6 (45.0), 37.4 (55.0), 54.8 (65.0)	7.5 ± 0.2	47 ± 1
	4-Cl	4-Cl	4.79 (45.0), 6.00 (55.0), 7.20 (65.0)	3.7 ± 0.2	62 ± 1
	3-Cl	H	1.29 (45.0), 1.60 (55.0), 2.01 (65.0)	4.1 ± 0.2	64 ± 1
	4-MeO	H	19.2 (45.0), 25.9 (55.0), 33.4 (65.0)	5.0 ± 0.4	64 ± 1
2	H	H	2.17 (45.0), 2.80 (55.0), 3.78 (65.0)	5.4 ± 0.4	59 ± 1
	3-Cl	H	0.226 (45.0), 0.240 (55.0), 0.377 (65.0)	5.4 ± 0.3	54 ± 1
	4-MeO	4-MeO	6.40 (45.0), 7.61 (50.0), 9.20 (55.0)	7.0 ± 0.3	52 ± 1
4	4-MeO	H	6.51 (45.0), 8.92 (50.0), 12.6 (55.0)	13.0 ± 0.3	32 ± 1
	H	H	0.690 (45.0), 0.823 (50.0), 1.01 (55.0)	7.7 ± 0.2	54 ± 1
	4-Me	4-Me	3.60 (45.0), 4.40 (55.0), 5.60 (65.0)	4.2 ± 0.2	61 ± 1
	4-Me	4-Cl	9.01 (45.0), 13.4 (55.0), 19.2 (65.0)	7.7 ± 0.2	49 ± 1
4′	H	H	1.00 (45.0), 1.48 (55.0), 2.01(65.0)	6.9 ± 0.4	55 ± 1
	3-Cl	4-Cl	0.0573 (45.0), 0.0954 (55.0), 0.164 (65.0)	10.9 ± 0.2	48 ± 1

[a] Calculated by Eyring equation. [b] Standard deviation. [c] kcal mol^{-1}. [d] cal mol^{-1} K^{-1}.

Substrates

The substrates were prepared by the following one-step synthesis. ethyl dichlorophosphate (for **1**) and ethyl dichlorothiophosphate (for **2**) were treated with substituted phenols in the presence of triethylamine in methylene chloride for 2 h on ice. All the compounds were identified by TLC, IR, ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, GC-MS and elemental analysis. The physical constants after column chromatography (silica gel 60 (0.063-0.200 mm)/ethyl acetate + n-hexane) were as follows:

Ethyl 4-methoxyphenyl chlorophosphate. Yellowish Liquid; IR (neat) 3078 (C–H, aromatic), 2994 (CH_3), 2912 (CH_2), 1597, 1506, 1305, 1194 (P-O-C_6H_4), 1444 (CH_3O), 835 (P=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.37 (m, 2H, CH_2), 3.78 (s, 3H, OCH_3), 1.45 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.6, 114.7, 115.9, 121.2, 143.2, 157.4 (C=C, aromatic), 66.7 (CH_2), 55.6 (OCH_3), 15.8 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.68 (P=O, 1P, s); m/z, 250 (M^+); Anal. Calcd. for $C_9H_{12}O_4PCl$: C, 43.1; H, 4.8. Found: C, 43.2; H, 5.0.

Ethyl 4-methylphenyl chlorophosphate.[1] Yellowish Liquid; IR (neat) 3039 (C–H, aromatic), 2990 (CH_3), 2926 (CH_2), 1607, 1509, 1394 (P-O-C_6H_4), 823 (P=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (m, 4H, C_6H_4), 4.33−4.39 (m, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.43 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.0, 119.9, 129.7, 130.2, 135.7, 147.4 (C=C, aromatic), 66.6 (CH_2), 20.8 (CH_3), 15.8 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.20 (P=O, 1P, s); m/z, 250 (M^+); Anal. Calcd. for $C_9H_{12}O_3PCl$: C, 46.1; H, 5.2. Found: C, 46.4; H, 5.5.

Ethyl phenyl chlorophosphate.[1a,2] Liquid, Colourless; IR (neat) 3077 (C–H, aromatic), 2989 (CH_3), 2912 (CH_2), 1593, 1193 (P-O-C_6H_4), 793 (P=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.26 (m, 5H, C_6H_5), 4.39 (m, 2H, CH_2), 1.38 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.9, 125.2, 129.7, 150.5 (C=C, aromatic), 65.5 (CH_2), 16.1 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ –12.40 (P=O, 1P, s); m/z, 220 (M^+); Anal. Calcd. for $C_8H_{10}O_3PCl$: C, 43.6; H, 4.6. Found: C, 44.0; H, 4.7.

Ethyl 3-methoxyphenyl chlorophosphate.[1b] Yellowish Liquid; IR (neat) 3080 (C–H, aromatic), 2988 (CH_3), 2912 (CH_2), 1608, 1592, 1492, 1193 (P-O-C_6H_4), 1450 (CH_3-O), 862 (P=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 1H, C_6H_4), 6.85 (m, 1H, C_6H_4), 6.77 (m, 2H, C_6H_4), 4.37 (m, 2H, CH_2), 3.77 (s, 3H, OCH_3), 1.43 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.3, 111.8, 112.2, 130.1, 150.4, 160.6 (C=C, aromatic), 66.7 (CH_2), 55.4 (OCH_3), 15.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.76 (P=O, 1P, s); m/z, 250 (M^+); Anal. Calcd. for $C_9H_{12}O_4PCl$: C, 43.1; H, 4.8. Found: C, 43.1; H, 5.0.

Ethyl 4-chlorophenyl chlorophosphate.[3] Yellowish Liquid; IR (neat) 3100 (C–H, aromatic), 2988 (CH_3), 2915 (CH_2), 1589, 1488, 1302, 1199 (P-O-C_6H_4), 835 (P=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 2H, C_6H_4), 7.19 (m, 2H, C_6H_4), 4.40 (m, 2H, CH_2), 1.47 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.3, 129.7, 130.8, 148.8 (C=C, aromatic), 65.9 (CH_2), 16.1 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.00 (P=O, 1P, s); m/z, 254 (M^+); Anal. Calcd. for $C_8H_9O_3PCl_2$: C, 37.7; H, 3.6. Found: C, 38.0; H, 3.9.

Ethyl 4-methoxyphenyl chlorothiophosphate.[4] Liquid, Colourless; IR (neat) 3098 (C–H, aromatic), 2995 (CH_3), 2910 (CH_2), 1602, 1191 (P-O-C_6H_4), 1465 (CH_3O), 816 (P=S); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (m, 2H, C_6H_4), 6.84−6.87 (m, 2H, C_6H_4), 4.38 (m, 2H, CH_2), 3.77 (s, 3H, OCH_3), 1.42−1.45 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.5, 122.0, 143.6, 157.4 (C=C, aromatic), 66.8 (CH_2), 55.6 (OCH_3), 15.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 70.37 (P=S, 1P, s); m/z, 266 (M^+); Anal. Calcd. for $C_9H_{12}O_3PSCl$: C, 40.5; H, 4.5; S, 12.0.Found: C, 40.7; H, 4.4; S, 11.9.

Ethyl 4-methylphenyl chlorothiophosphate.[5] Liquid, Colourless; IR (neat) 3037 (C–H, aromatic), 2989 (CH_3), 2925 (CH_2), 1602, 1195 (P-O-C_6H_4), 825 (P=S); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.17 (m, 4H, C_6H_4), 4.38−4.44 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 1.45−1.48 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.8, 130.1, 135.9, 148.0 (C=C, aromatic), 66.8 (CH_2), 20.9 (CH_3), 15.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 69.64 (P=S, 1P, s); m/z, 250 (M^+); Anal. Calcd. for $C_9H_{12}O_2PSCl$: C, 43.1; H, 4.8; S, 12.8. Found: C, 43.5; H, 4.6; S, 12.7.

Ethyl phenyl chlorothiophosphate.[6] Liquid, Colourless; IR (neat) 3072 (C–H, aromatic), 2989 (CH_3), 2908 (CH_2), 1592, 1194 (P-O-C_6H_4), 814 (P=S); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.36 (m, 2H, C_6H_5), 7.23−7.26 (m, 3H, C_6H_5), 4.38−4.42 (m, 2H, CH_2), 1.42−1.46 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.1, 126.1, 129.6, 150.0 (C=C, aromatic), 66.8 (CH_2), 15.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 69.09 (P=S, 1P, s); m/z, 236 (M^+); Anal. Calcd. for $C_8H_{10}O_2PSCl$: C, 40.6; H, 4.3; S, 13.6. Found: C, 41.0; H, 4.3; S, 14.0.

Ethyl 4-chlorophenyl chlorothiophosphate.[4,5d] Liquid, Colourless; IR (neat) 3097 (C–H, aromatic), 2989 (CH_3), 2908 (CH_2), 1590, 1162 (P-O-C_6H_4), 835 (P=S); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.36 (m, 2H, C_6H_4), 7.21 (m, 2H, C_6H_4), 4.40−4.43 (m, 2H, CH_2), 1.44−1.49 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.5, 122.6, 129.7 (C=C, aromatic), 67.0 (CH_2), 15.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 69.10 (P=S, 1P, s); m/z, 270 (M^+); Anal. Calcd. for $C_8H_9O_2PSCl_2$: C, 35.4; H, 3.4; S, 11.8. Found: C, 35.7; H, 3.4; S, 12.2.

Ethyl 4-cyanophenyl chlorothiophosphate.[7] White solid; mp 42−44 ^{o}C; IR (neat) 3102 (C–H, aromatic), 2992 (CH_3), 2942 (CH_2), 2234 (C≡N), 1600, 1212 (P-O-C_6H_4), 850 (P=S); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.72 (m, 2H, C_6H_4), 7.38−7.41 (m, 2H, C_6H_4), 4.38 (m, 2H, CH_2), 1.46−1.50 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.8, 122.2, 133.9, 153.0 (C=C, aromatic), 110.2 (4-CN), 67.4 (CH_2), 15.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 67.60 (P=S, 1P, s); m/z, 261 (M^+); Anal. Calcd. for $C_9H_9O_2NPSCl$: C, 41.3; H, 3.5; N, 5.4; S, 12.3. Found: C, 40.9; H, 3.5; N, 5.3; S, 12.7.

Product analysis. Ethyl 4-methylphenyl chlorophosphate was treated with excess aniline (for **1**) and ethyl 4-chlorophenyl chlorothiophosphate was treated with excess 4-methylaniline, for more than 15 half-lives at 55.0 °C in acetonitrile. The physical constants after column chromatography (silica gel/ethyl acetate + n-hexane) were:

(CH_3-CH_2O)(4-CH_3-C_6H_4O)P(=O)NH-C_6H_5.[8] Yellowish Liquid; IR (neat) 3173 (NH), 3094 (C–H, aromatic), 2986 (CH_3), 2912 (CH_2), 1605, 1504, 1166 (P-O-C_6H_4), 826 (P=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, 2H, C_6H_4), 7.26 (m, 7H, Ar), 6.46 (d, J = 9.6 Hz, 1H, NH), 4.38−4.51 (m, 2H, CH_2), 2.49 (s, 3H, CH_3), 1.57 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.6, 120.1, 129.2, 129.9, 134.5, 139.2, 148.0 (C=C, aromatic), 63.4 (CH_2), 20.8 (CH_3), 16.2 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.39 (d, J = 8.0 Hz, 1P, P=O); m/z, 291 (M^+); Anal. Calcd. for $C_{15}H_{18}NO_3P$: C, 61.9; H, 6.2; N, 4.8. Found: C, 61.5; H, 6.5; N, 5.1.

(CH_3-CH_2O)(4-Cl-C_6H_4O)P(=S)NH-(4-CH_3-C_6H_4). Brownish Liquid; IR (neat) 3269 (NH), 3030 (C–H, aromatic), 2985 (CH_3), 2920 (CH_2), 1617, 1515, 1163 (P-O-C_6H_4), 814 (P=S); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 2H, C_6H_4), 7.06−7.11 (m, 4H, C_6H_4), 6.97 (m, 2H, C_6H_4), 5.38 (d, J = 16.0 Hz, 1H, NH), 4.15−4.32 (m, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.38 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.0, 122.7, 129.4, 129.9, 130.6, 132.2, 136.3, 148.8 (C=C, aromatic), 64.0 (CH_2), 20.7 (CH_3), 15.8 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 67.0 (s, 1P, P=S); m/z, 341 (M^+); Anal. Calcd. for $C_{15}H_{17}NO_2PSCl$: C, 52.7; H, 5.0; N, 4.1, S, 9.4. Found: C, 52.8; H, 5.2; N, 4.5, S, 9.0.

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Reactant - Ethyl phenyl chlorophosphate (1) (gas-phase)

N-N= 1.037283355046D+03 E-N=-5.234139730459D+03 KE= 1.334660676058D+03
1\1\GINC-GOM6_1\FOpt\RB3LYP\6-311+G(d,p)\C8H10Cl1O3P1\GAUSS\02-Feb-200
7\1\\# B3LYP/6-311+G(d,p) opt=(z-matrix) optcyc=100 # freq=noraman\\PO
-BACK-FULL\\0,1\P\O,1,op2\Cl,1,clp3,2,clpo3\O,1,op4,2,opo4,3,dih4,0\O,
1,op5,2,opo5,3,dih5,0\C,4,co6,1,cop6,2,dih6,0\C,6,cc7,4,cco7,1,dih7,0\
C,7,cc8,6,ccc8,4,dih8,0\C,8,cc9,7,ccc9,6,dih9,0\C,9,cc10,8,ccc10,7,dih
10,0\C,10,cc11,9,ccc11,8,dih11,0\H,7,hc12,6,hcc12,8,dih12,0\H,8,hc13,7
,hcc13,9,dih13,0\H,9,hc14,8,hcc14,10,dih14,0\H,10,hc15,9,hcc15,8,dih15
,0\H,11,hc16,10,hcc16,9,dih16,0\C,2,co17,1,cop17,3,dih17,0\C,17,cc18,2
,cco18,1,dih18,0\H,17,hc19,2,hco19,18,dih19,0\H,17,hc20,2,hco20,18,dih
20,0\H,18,hc21,17,hcc21,2,dih21,0\H,18,hc22,17,hcc22,21,dih22,0\H,18,h
c23,17,hcc23,21,dih23,0\\op2=1.58805421\clp3=2.04304443\clpo3=100.9152
5222\op4=1.61429931\opo4=101.24322661\dih4=-107.1337549\op5=1.4734841\
opo5=118.08093014\dih5=125.05448989\co6=1.40303125\cop6=125.90168126\d
ih6=179.83887708\cc7=1.38997158\cco7=116.28611854\dih7=226.27763443\cc
8=1.39269798\ccc8=118.98346599\dih8=182.96596845\cc9=1.39435651\ccc9=1
20.25965781\dih9=-0.25369613\cc10=1.39368978\ccc10=119.78476119\dih10=
0.15575389\cc11=1.39444234\ccc11=120.7026201\dih11=0.16118915\hc12=1.0
8279644\hcc12=119.32953593\dih12=179.8271833\hc13=1.08388625\hcc13=119
.51594855\dih13=180.17358722\hc14=1.08368425\hcc14=120.1097375\dih14=1
79.98987177\hc15=1.0839165\hcc15=120.10870309\dih15=179.968294\hc16=1.
08209722\hcc16=121.42519487\dih16=180.19365693\co17=1.46452386\cop17=1
20.93176296\dih17=190.5255768\cc18=1.51260256\cco18=107.4566855\dih18=
167.17588805\hc19=1.09274114\hco19=107.79224722\dih19=120.5812591\hc20
=1.09184766\hco20=108.42220459\dih20=238.73991556\hc21=1.09357062\hcc2
1=109.39307924\dih21=179.10972734\hc22=1.09160819\hcc22=110.80273471\d
ih22=119.58612034\hc23=1.09171263\hcc23=110.86403592\dih23=240.4522533
6\\Version=IA32L-G03RevD.02\State=1-A\HF=-1338.3813309\RMSD=6.663e-09\
RMSF=3.822e-05\Thermal=0.\Dipole=-0.5190389,0.8235936,0.5306036\PG=C01
[X(C8H10Cl1O3P1)]\\@

Reactant - Ethyl phenyl chlorothiophosphate (2) (gas-phase)

N-N= 1.147250253658D+03 E-N=-6.223269369153D+03 KE= 1.657282898454D+031\1\GINC-GOM6_1\FOpt\RB3LYP\6-311+G(d,p)\C8H10Cl1O2P1S1\GAUSS\05-Feb-2 007\1\\# B3LYP/6-311+G(d,p) opt=z-matrix freq=noraman optcyc=200\\PO-B
ACK-FULL\\0,1\P\O,1,op2\Cl,1,clp3,2,clpo3\O,1,op4,2,opo4,3,dih4,0\S,1,
sp5,2,opo5,3,dih5,0\C,4,co6,1,cop6,2,dih6,0\C,6,cc7,4,cco7,1,dih7,0\C,
7,cc8,6,ccc8,4,dih8,0\C,8,cc9,7,ccc9,6,dih9,0\C,9,cc10,8,ccc10,7,dih10
,0\C,10,cc11,9,ccc11,8,dih11,0\H,7,hc12,6,hcc12,8,dih12,0\H,8,hc13,7,h
cc13,9,dih13,0\H,9,hc14,8,hcc14,10,dih14,0\H,10,hc15,9,hcc15,8,dih15,0
\H,11,hc16,10,hcc16,9,dih16,0\C,2,co17,1,cop17,3,dih17,0\C,17,cc18,2,c
co18,1,dih18,0\H,17,hc19,2,hco19,18,dih19,0\H,17,hc20,2,hco20,18,dih20
,0\H,18,hc21,17,hcc21,2,dih21,0\H,18,hc22,17,hcc22,21,dih22,0\H,18,hc2
3,17,hcc23,21,dih23,0\\op2=1.59645516\clp3=2.06330856\clpo3=98.8181504
7\op4=1.6258663\opo4=99.9173564\dih4=-105.38747635\sp5=1.92599696\opo5
118.98796882\dih5=125.47438385\co6=1.40081259\cop6=126.17473246\dih6=
179.81939924\cc7=1.39004586\cco7=118.16165107\dih7=257.33020292\cc8=1.
9331856\ccc8=118.85515154\dih8=183.52473009\cc9=1.39425663\ccc9=120.3
327389\dih9=0.13207854\cc10=1.39408152\ccc10=119.89956121\dih10=0.103
88901\cc11=1.39361386\ccc11=120.42261615\dih11=-
0.07620007\hc12=1.08261609\hcc12=119.59063194\dih12=179.78696613\hc13=1.08385596\hc
c13=119.5095396\dih13=179.81621678\hc14=1.08372641\hcc14=120.0492187\dih14=179.833
07897\hc15=1.08384927\hcc15=120.15383591\dih15=179.81960459\hc16=1.08196613\hcc16=
121.41607857\dih16=180.10134874\co17=1.46061648\cop17=122.19793932\dih17=183.40146
26\cc18=1.51298275\cco18=107.36368023\dih18=171.24678448\hc19=1.09271639\hco19=107.
93439403\dih19=120.67730404\hc20=1.092421\hco20=108.46373486\dih20=238.9116452\hc2
1=1.09357082\hcc21=109.36020471\dih21=179.41335017\hc22=1.09161119\hcc22=110.79052
886\dih22=119.55986876\hc23=1.09168495\hcc23=110.9014693\dih23=240.43515724\\Version
=IA32L-G03RevD.02\State=1-A\HF=-1661.3390485\RMSD=2.496e-09\RM SF=7.680e-
05\Thermal=0.\Dipole=-0.6068972,0.8497042,0.417119\PG=C01 [X (C8H10Cl1O2P1S1)]\\@

Reactant - 4-Nitrophenyl diphenylphosphinate (5) (gas-phase)

N-N= 2.080625494124D+03 E-N=-7.421693545515D+03 KE= 1.386859546989D+03
1\1\GINC-GOM2_10\FOpt\RB3LYP\6-311+G(d,p)\C18H14N1O4P1\GAUSS\24-May-20
07\0\\# B3LYP/6-311+G(d,p) opt optcyc=200 freq=noraman\\### 2-ph-oph-n
o2-rea ###\\0,1\C,-0.0008363444,-0.0036326104,0.0005362944\C,0.0024384
262,0.0004558415,1.3997028377\C,1.2198585805,0.008222337,2.0928116477\
C,2.4208504041,0.0048211159,1.3903738844\C,2.4136541635,-0.0034738042,
-0.0051575041\C,1.2050471269,-0.0069779617,-0.6981269903\P,-1.60441029
32,0.0092485934,2.2528739554\O,-1.4987408597,-1.2632270636,3.312962409
9\C,-1.6667118446,1.3679779746,3.4485502451\C,-1.1220093077,1.28957983
96,4.7359476097\C,-1.189798556,2.390051936,5.5865944877\C,-1.798646812
5,3.5694739495,5.1591468809\C,-2.3495806462,3.6475137239,3.8811646352\
C,-2.2880842984,2.5499067574,3.0264927305\O,-2.7451001968,-0.027121012
2,1.2959440288\H,-0.6696532826,0.3678478059,5.0793201078\H,-0.77405900
34,2.3241544197,6.5855940745\H,-1.8504723009,4.4237574656,5.8246909308
\H,-2.8349022937,4.5590916467,3.5519847191\H,-2.7344920811,2.597747512
1,2.0400301085\H,1.2343172415,0.0212602474,3.1767024196\H,3.3615169433
,0.0099692862,1.9290947788\H,3.351012386,-0.0057196079,-0.5500057807\H
,1.1993284354,-0.0122969594,-1.7820760089\H,-0.9481397763,-0.004635736
5,-0.5253187072\C,-1.5021818417,-2.5966693734,2.9666022888\C,-0.670530
3818,-3.4392950004,3.7078526445\C,-0.6593723779,-4.8010392707,3.445979
7037\C,-1.4829052901,-5.2997045942,2.4397089984\C,-2.3176930893,-4.468
5524255,1.6986774726\C,-2.3352862939,-3.1054579201,1.9656648757\H,-0.0
437315079,-3.0165036406,4.4825322405\H,-0.0254829694,-5.4768043702,4.0
030512788\N,-1.4689864594,-6.7447927886,2.1538230312\H,-2.9482239701,-
4.8934763758,0.9299348461\H,-2.9822608237,-2.4370289102,1.4130808803\O
,-2.1976724758,-7.1571899232,1.2588047901\O,-0.7278889262,-7.452558599
9,2.8273793512\\Version=IA32L-G03RevD.02\State=1-A\HF=-1391.6064034\RM
SD=1.852e-09\RMSF=2.004e-05\Thermal=0.\Dipole=1.4117619,2.6665272,0.80
07091\PG=C01 [X(C18H14N1O4P1)]\\@

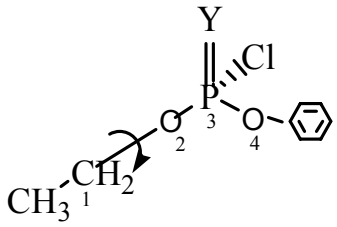
Reactant - 4-Nitrophenyl methylphenylphosphinate (6) (gas-phase)

N-N= 1.478497787190D+03 E-N=-5.772514064087D+03 KE= 1.195939703971D+03
1\1\GINC-GOM6_1\FOpt\RB3LYP\6-311+G(d,p)\C13H12N1O4P1\GAUSS\22-May-200
7\1\\# b3lyp/6-311+G(d,p) opt=z-matrix optcyc=200 # freq=noraman geom=
check guess=check\\-- ph-po-me-phno2 --\\0,1\P\C,1,cp2\O,1,op3,2,opc3\
C,1,cp4,2,cpc4,3,dih4,0\O,1,op5,2,opc5,3,dih5,0\C,2,cc6,1,ccp6,3,dih6,
0\C,6,cc7,2,ccc7,1,dih7,0\C,7,cc8,6,ccc8,2,dih8,0\C,8,cc9,7,ccc9,6,dih
9,0\C,9,cc10,8,ccc10,7,dih10,0\H,6,hc11,2,hcc11,7,dih11,0\H,7,hc12,6,h
cc12,8,dih12,0\H,8,hc13,7,hcc13,9,dih13,0\H,9,hc14,8,hcc14,7,dih14,0\H
,10,hc15,9,hcc15,8,dih15,0\H,4,hc16,1,hcp16,2,dih16,0\H,4,hc17,1,hcp17
,16,dih17,0\H,4,hc18,1,hcp18,16,dih18,0\C,3,co19,1,cop19,5,dih19,0\C,1
9,cc20,3,cco20,1,dih20,0\C,20,cc21,19,ccc21,3,dih21,0\C,21,cc22,20,ccc
22,19,dih22,0\C,22,cc23,21,ccc23,20,dih23,0\C,23,cc24,22,ccc24,21,dih2
4,0\H,20,hc25,19,hcc25,21,dih25,0\H,21,hc26,20,hcc26,22,dih26,0\N,22,n
c27,21,ncc27,23,dih27,0\H,23,hc28,22,hcc28,21,dih28,0\H,24,hc29,23,hcc
29,22,dih29,0\O,27,on30,22,onc30,21,dih30,0\O,27,on31,30,ono31,22,dih3
1,0\\cp2=1.80968537\op3=1.66278173\opc3=99.65999806\cp4=1.81796268\cpc
4=108.93707064\dih4=-107.16419607\op5=1.48849351\opc5=114.37396384\dih
5=124.01025146\cc6=1.39892458\ccp6=117.39224115\dih6=226.63758092\cc7=
1.39359899\ccc7=119.85636611\dih7=181.31321409\cc8=1.39322287\ccc8=120
.08162602\dih8=-0.07927515\cc9=1.39555751\ccc9=120.1670205\dih9=-0.083
44387\cc10=1.39148713\ccc10=120.02400533\dih10=0.15121216\hc11=1.08377
824\hcc11=119.29850084\dih11=180.53560183\hc12=1.08389999\hcc12=119.77
718582\dih12=180.26109686\hc13=1.08418661\hcc13=119.96304568\dih13=180
.1872313\hc14=1.08396261\hcc14=120.11322139\dih14=180.43687415\hc15=1.
08403401\hcc15=119.70360389\dih15=180.93342576\hc16=1.09183949\hcp16=1
09.00885147\dih16=171.74512525\hc17=1.0913289\hcp17=108.373285\dih17=1
18.24354391\hc18=1.09101564\hcp18=111.4061026\dih18=238.85898205\co19=
1.37558211\cop19=126.39023993\dih19=50.9976034\cc20=1.39824544\cco20=1
16.20670372\dih20=150.36964909\cc21=1.38618967\ccc21=119.8751643\dih21
=178.45675172\cc22=1.39307765\ccc22=118.93940642\dih22=0.14845297\cc23
=1.39143694\ccc23=121.63233944\dih23=-0.46738314\cc24=1.38954775\ccc24
=119.51668517\dih24=0.10555041\hc25=1.08255896\hcc25=119.11947778\dih2
5=180.29180912\hc26=1.08115396\hcc26=121.37536984\dih26=179.84253877\n
c27=1.47277576\ncc27=119.10285209\dih27=180.17641533\hc28=1.08131128\h
cc28=119.5783755\dih28=180.63391878\hc29=1.08217912\hcc29=120.90605011
\dih29=181.17813781\on30=1.22563001\onc30=117.78971923\dih30=180.16604
373\on31=1.22630489\ono31=124.49978182\dih31=180.08165871\\Version=IA3
2L-G03RevD.02\State=1-A\HF=-1199.8299133\RMSD=7.126e-09\RMSF=2.708e-05
\Thermal=0.\Dipole=-0.9244963,1.3293022,2.711793\PG=C01 [X(C13H12N1O4P
1)]\\@

Reactant - 4-Nitrophenyl dimethylphosphinate (7) (gas-phase)

N-N= 9.968329823284D+02 E-N=-4.364494510914D+03 KE= 1.005017513639D+03
1\1\GINC-GOM6_9\FOpt\RB3LYP\6-311+G(d,p)\C8H10N1O4P1\GAUSS\20-May-2007
\1\\# b3lyp/6-311+G(d,p) opt=z-matrix optcyc=200 # freq=noraman geom=c
heck guess=check\\-- 2me-po-phno2 --\\0,1\P\C,1,cp2\O,1,op3,2,opc3\C,1
,cp4,2,cpc4,3,dih4,0\O,1,op5,2,opc5,3,dih5,0\H,2,hc6,1,hcp6,3,dih6,0\H
,2,hc7,1,hcp7,6,dih7,0\H,2,hc8,1,hcp8,6,dih8,0\H,4,hc9,1,hcp9,2,dih9,0
\H,4,hc10,1,hcp10,9,dih10,0\H,4,hc11,1,hcp11,9,dih11,0\C,3,co12,1,cop1
2,2,dih12,0\C,12,cc13,3,cco13,1,dih13,0\C,13,cc14,12,ccc14,3,dih14,0\C
,14,cc15,13,ccc15,12,dih15,0\C,15,cc16,14,ccc16,13,dih16,0\C,16,cc17,1
5,ccc17,14,dih17,0\H,13,hc18,12,hcc18,14,dih18,0\H,14,hc19,13,hcc19,15
,dih19,0\N,15,nc20,14,ncc20,16,dih20,0\H,16,hc21,15,hcc21,14,dih21,0\H
,17,hc22,16,hcc22,15,dih22,0\O,20,on23,15,onc23,14,dih23,0\O,20,on24,2
3,ono24,15,dih24,0\\cp2=1.80926527\op3=1.66331166\opc3=98.37308854\cp4
=1.81792837\cpc4=108.50774184\dih4=-107.10494814\op5=1.4877565\opc5=11
5.73415053\dih5=123.36434902\hc6=1.09169115\hcp6=108.66715153\dih6=174
.2059151\hc7=1.09097655\hcp7=108.4022979\dih7=118.10733231\hc8=1.09072
771\hcp8=111.44877662\dih8=238.77887027\hc9=1.09159379\hcp9=108.809072
35\dih9=171.07131646\hc10=1.09173329\hcp10=108.789816\dih10=117.845736
55\hc11=1.09128745\hcp11=111.52262225\dih11=239.080856\co12=1.37618688
\cop12=126.6800926\dih12=172.36892882\cc13=1.39803342\cco13=116.174675
69\dih13=148.98548214\cc14=1.38634695\ccc14=119.85381031\dih14=178.335
58467\cc15=1.39299302\ccc15=118.9287931\dih15=0.21858976\cc16=1.391447
54\ccc16=121.65167667\dih16=-0.40098506\cc17=1.38965114\ccc17=119.5105
3632\dih17=0.06044135\hc18=1.0825921\hcc18=119.11247939\dih18=180.2899
9751\hc19=1.08114209\hcc19=121.38965612\dih19=179.79300966\nc20=1.4731
6012\ncc20=119.09184388\dih20=180.10950036\hc21=1.08129324\hcc21=119.5
8991385\dih21=180.55255147\hc22=1.08203582\hcc22=120.97998067\dih22=18
0.95415938\on23=1.22555215\onc23=117.7747698\dih23=180.11145777\on24=1
.22624554\ono24=124.52318125\dih24=180.07733688\\Version=IA32L-G03RevD
.02\State=1-A\HF=-1008.053353\RMSD=1.763e-09\RMSF=2.949e-05\Thermal=0.
\Dipole=-0.9445544,1.4575176,2.3645589\PG=C01 [X(C8H10N1O4P1)]\\@

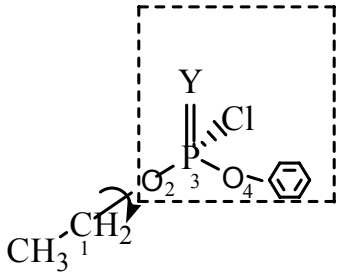
Table S3. Rotation barriers for ∠1234 in kcal mol^{-1} (calculated at the RHF/6-31G* level)



Y / Relative Tortional Angle (∠1234)	O	S
0°[a]	0.0	0.0
30°	0.1	0.5
60°	0.2	0.6
90°	0.4	0.2
120°	1.2	0.3
150°	3.1	2.6
180°	3.0	3.4
210°	1.1	1.9
240°	0.3	0.4
270°	1.4	1.1
300°	1.7	1.8
330°	0.7	0.8

[a] Real tortional angle is 109.5° in the optimized structure.

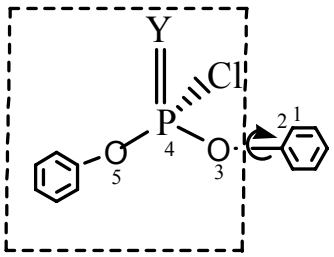
Table S4. Rotation barriers for ∠1234 in kcal mol^{-1}[a] (calculated at the RHF/6-31G* level)



Relative Tortional Angle (∠1234) \ Y	O	S
0°[b]	0.0	0.0
30°	0.6	1.1
60°	0.4	1.2
90°	0.3	0.3
120°	2.7	1.1
150°	6.2	4.5
180°	5.5	5.6
210°	2.4	3.1
240°	1.7	1.2
270°	3.0	2.1
300°	2.7	2.6
330°	1.1	1.2

[a] All geometrical parameters in dashed area are fixed at equilibrium geometries. [b] Real tortional angle is 109.5° in the optimized structure.

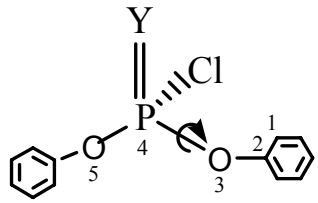
Table S5. Rotation barriers for ∠1234 in kcal mol^{-1}[a] (calculated at the RHF/6-31G* level)



Y / Relative Tortional Angle (∠1234)	O	S
0°[b]	0.0	0.0
30°	0.6	1.0
60°	2.6	5.0
90°	4.4	11.3
120°	8.5	28.0
150°	18.8	45.4
180°	16.1	23.9
210°	8.2	8.9
240°	10.3	5.2
270°	6.1	5.0
300°	5.3	3.2
330°	2.0	0.7

[a] All geometrical parameters in dashed area are fixed at equilibrium .geometries. [b] Real tortional angle is 231.1° in the optimized structure.

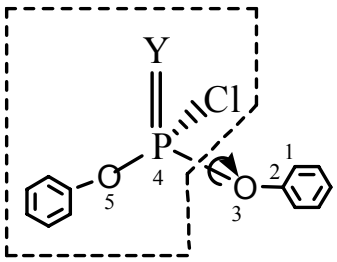
Table S6. Rotation barriers for ∠2345 in kcal mol^{-1} (calculated at the RHF/6-31G* level)



Y / Relative Tortional Angle (∠2345)	O	S
0°[a]	0.0	0.0
60°	1.8	1.6
120°	0.2	0.2
180°	2.0	2.0
240°	0.7	2.1
300°	2.9	3.0

[a] Real tortional angle is 183.2° in the optimized structure.

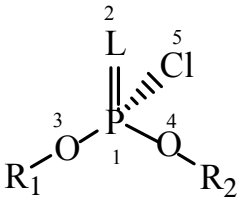
Table S7. Rotation barriers for ∠2345 in kcal mol^{-1}[a] (calculated at the RHF/6-31G* level)



Y / Relative Tortional Angle(∠2345)	O	S
0°[b]	0.0	0.0
30°	0.5	1.2
60°	1.2	2.2
90°	1.3	2.2
120°	0.9	1.6
150°	0.2	0.4
180°	0.4	0.9
210°	0.4	1.6
240°	1.2	2.2
270°	1.3	2.2
300°	0.9	1.5
330°	0.1	1.6

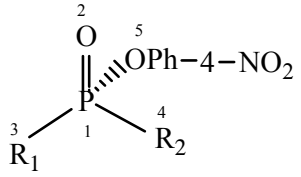
[a] All geometrical parameters in dashed area are fixed at equilibrium geometries. [b] Real tortional angle is 183.2° in the optimized structure.

Table S8. Bond angles of 1, 2, 3, and 4 (calculated at the B3LYP/6-311+G(d,p) level)



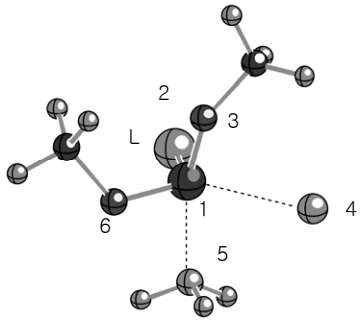
substrate	L	R_1	R_2	∠213	∠214	∠215	∠314	∠415	∠315
1	O	Et	Ph	118.1	116.0	114.1	101.2	104.3	100.9
2	S	Et	Ph	119.0	117.4	115.3	99.9	103.4	98.8
3	O	Ph	Ph	118.5	116.7	113.9	100.7	104.8	99.8
4	S	Ph	Ph	119.4	117.9	115.8	99.4	103.4	97.5

Table S9. Bond angles of 5, 6, and 7 (calculated at the B3LYP/6-311+G(d,p) level)



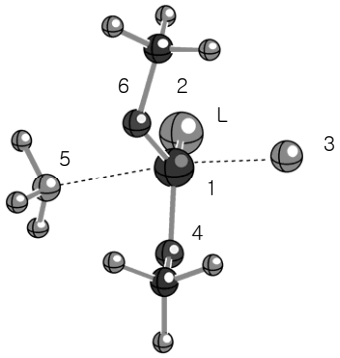
substrate	R_1	R_2	∠213	∠214	∠215	∠314	∠415	∠315
5	Ph	Ph	114.6	112.0	116.1	110.1	103.9	99.0
6	Ph	Me	114.4	114.0	115.7	108.9	120.8	99.7
7	Me	Me	115.7	113.9	115.3	108.5	103.3	98.4

Table S10. Bond angles of 9f and 10f in acetonitrile (calculated at the CPCM−MP2/6−31+G* level)



substrate	L	∠216	∠214	∠614	∠312	∠314	∠316	∠512	∠514	∠516
position		e,e	e,e	e,e	a,e	a,e	a,e	a,e	a,e	a,e
9f	O	119.0	103.6	135.0	112.4	84.1	92.1	100.6	76.4	81.8
10f	S	115.8	105.3	136.5	113.3	84.7	91.2	103.4	76.4	80.9

Table S11. Bond angles of 9b and 10b in acetonitrile (calculated at the CPCM−MP2/6−31+G* level)



substrate	L	∠216	∠214	∠614	∠312	∠314	∠316	∠512	∠514	∠516
position		e,e	e,e	e,e	a,e	a,e	a,e	a,e	a,e	a,e
9b	O	125.9	120.9	108.4	100.3	95.6	95.3	85.8	81.4	80.7
10b	S	125.4	119.4	109.3	103.0	95.0	95.5	88.0	79.6	77.4