Electronic Supplementary Information

Combined dual substituent constant and activation parameter analysis assigns a concerted mechanism to alkaline ethanolysis at phosphorus of Y-substituted phenyl diphenylphosphinates

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Table S1. Kinetic data for the reaction of phenyl diphenylphosphinate (**1a**) with EtO^-K^+ in the presence of excess 18C6 in anhydrous EtOH at $25.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 [EtO^-K^+]/ M$	$10^4 k_{obsd}/ s^{-1}$
4.37	0.253
9.83	0.631
16.9	1.13
26.2	1.77
46.2	3.47
59.0	4.27

$k_{EtO^-} = (7.51 \pm 0.16) \times 10^{-3} M^{-1} s^{-1}$
$R^2 = 0.9990$

Table S2. Kinetic data for the reaction of 4-chlorophenyl diphenylphosphinate (**1b**) with EtO^-K^+ in the presence of excess 18C6 in anhydrous EtOH at $25.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 [EtO^-K^+]/M$	$10^3 k_{obsd}/s^{-1}$
11.7	0.493
19.3	0.767
26.8	1.07
34.2	1.41
44.4	1.85

$k_{EtO^-} = (4.19 \pm 0.10) \times 10^{-2} M^{-1} s^{-1}$
$R^2 = 0.9991$

Table S3. Kinetic data for the reaction of 3-acetylphenyl diphenylphosphinate (**1c**) with EtO$^-$K$^+$ in the presence of excess 18C6 in anhydrous EtOH at 25.0 ± 0.1°C. ([18C6]/[EtO$^-$K$^+$] = 5.0)

10^3 [EtO$^-$K$^+$]/M	$10^3 \, k_{obsd}/s^{-1}$
5.05	0.307
15.9	1.09
24.7	1.58
34.2	2.19
44.4	2.86

k_{EtO-} = (6.41±0.13) x 10^{-2} M^{-1}s^{-1}
R^2 = 0.9993

Table S4. Kinetic data for the reaction of 4-acetylphenyl diphenylphosphinate (**1d**) with EtO$^-$K$^+$ in the presence of excess 18C6 in anhydrous EtOH at 25.0 ± 0.1°C. ([18C6]/[EtO$^-$K$^+$] = 5.0)

10^3 [EtO$^-$K$^+$]/M	$10^3 \, k_{obsd}/s^{-1}$
4.55	0.711
11.5	1.71
20.0	3.14
30.8	4.98
40.0	6.72

k_{EtO-} = (1.70±0.04) x 10^{-1} M^{-1}s^{-1}
R^2 = 0.9991

Table S5. Kinetic data for the reaction of 4-cyanophenyl diphenylphosphinate (**1e**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at $25.0 \pm 0.1°C$. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3\, k_{obsd}/s^{-1}$
12.8	6.64
19.3	10.0
27.8	14.7
35.7	19.0
44.4	24.5

$k_{EtO-} = (5.63\pm0.12) \times 10^{-1}\, M^{-1}s^{-1}$
$R^2 = 0.9993$

Table S6. Kinetic data for the reaction of 4-formylphenyl diphenylphosphinate (**1f**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at $25.0 \pm 0.1°C$. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3\, k_{obsd}/s^{-1}$
10.5	2.62
25.0	6.15
29.2	7.50
40.0	10.2
50.0	13.1

$k_{EtO-} = (2.65\pm0.06) \times 10^{-1}\, M^{-1}s^{-1}$
$R^2 = 0.9993$

Table S7. Kinetic data for the reaction of 4-nitrophenyl diphenylphosphinate (**1g**) with EtO^- K^+ in the presence of excess 18C6 in anhydrous EtOH at $25.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 [EtO^-K^+]/M$	$10^3 k_{obsd}/s^{-1}$
4.55	4.45
8.33	8.48
11.5	12.1
14.3	15.0
16.7	17.7

$k_{EtO-} = 1.09 \pm 0.01\ M^{-1}s^{-1}$
$R^2 = 0.9999$

Table S8. Kinetic data for the reaction of 3,4-dinitrophenyl diphenylphosphinate (**1h**) with EtO^-K^+ in the presence of excess 18C6 in anhydrous EtOH at $25.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 [EtO^-K^+]/M$	$10^3 k_{obsd}/s^{-1}$
0.495	9.30
0.980	19.8
1.46	30.0
1.92	40.0
2.38	49.6

$k_{EtO-} = 21.4 \pm 0.1\ M^{-1}s^{-1}$
$R^2 = 0.9999$

Table S9. Kinetic data for the reaction of phenyl diphenylphosphinate (**1a**) with EtO^-K^+ in the presence of excess 18C6 in anhydrous EtOH at $15.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 \, [EtO^-K^+]/M$	$10^4 \, k_{obsd}/s^{-1}$
9.83	0.314
16.9	0.544
26.2	0.909
36.3	1.27
46.2	1.69

$k_{EtO^-} = (3.78 \pm 0.08) \times 10^{-3} \, M^{-1} s^{-1}$
$R^2 = 0.9992$

Table S10. Kinetic data for the reaction of phenyl diphenylphosphinate (**1a**) with EtO^-K^+ in the presence of excess 18C6 in anhydrous EtOH at $20.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 \, [EtO^-K^+]/M$	$10^3 \, k_{obsd}/s^{-1}$
16.9	0.080
26.2	0.128
36.3	0.187
46.2	0.241
59.0	0.325

$k_{EtO^-} = (5.80 \pm 0.15) \times 10^{-3} \, M^{-1} s^{-1}$
$R^2 = 0.9990$

Table S11. Kinetic data for the reaction of phenyl diphenylphosphinate (**1a**) with EtO^-K^+ in the presence of excess 18C6 in anhydrous EtOH at $35.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 [EtO^-K^+]/M$	$10^4 k_{obsd}/s^{-1}$
4.37	0.517
9.83	1.20
16.9	2.16
26.2	3.60
36.3	4.94

$k_{EtO^-} = (1.41 \pm 0.03) \times 10^{-2} M^{-1}s^{-1}$
$R^2 = 0.9995$

Table S12. Kinetic data for the reaction of phenyl diphenylphosphinate (**1a**) with EtO^-K^+ in the presence of excess 18C6 in anhydrous EtOH at $45.0 \pm 0.1°C$. ($[18C6]/[EtO^-K^+] = 5.0$)

$10^3 [EtO^-K^+]/M$	$10^4 k_{obsd}/s^{-1}$
4.37	0.873
9.83	2.24
16.9	4.04
26.2	6.99
46.2	12.3
59.0	16.5

$k_{EtO^-} = (2.85 \pm 0.05) \times 10^{-2} M^{-1}s^{-1}$
$R^2 = 0.9993$

Table S13. Kinetic data for the reaction of 4-nitrophenyl diphenylphosphinate (**1g**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at 15.0 ± 0.1°C. ([18C6]/[EtO⁻ K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3 k_{obsd}/s^{-1}$
5.36	2.78
9.83	5.30
13.6	7.58
16.9	9.78
19.7	11.1

$k_{EtO-} = (5.91 \pm 0.14) \times 10^{-1} \, M^{-1} s^{-1}$
$R^2 = 0.9992$

Table S14. Kinetic data for the reaction of 4-nitrophenyl diphenylphosphinate (**1g**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at 20.0 ± 0.1°C. ([18C6]/[EtO⁻ K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3 k_{obsd}/s^{-1}$
5.36	3.84
9.83	7.23
13.6	10.7
16.9	13.6
19.7	15.7

$k_{EtO-} = (8.41 \pm 0.17) \times 10^{-1} \, M^{-1} s^{-1}$
$R^2 = 0.9993$

Table S15. Kinetic data for the reaction of 4-nitrophenyl diphenylphosphinate (**1g**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at $35.0 \pm 0.1°C$. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3 k_{obsd}/s^{-1}$
5.36	9.26
9.83	16.8
13.6	23.8
16.9	28.3
19.7	33.8

$k_{EtO-} = 1.69 \pm 0.04\ M^{-1}s^{-1}$
$R^2 = 0.9991$

Table S16. Kinetic data for the reaction of 4-nitrophenyl diphenylphosphinate (**1g**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at $45.0 \pm 0.1°C$. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3 k_{obsd}/s^{-1}$
5.36	14.3
9.83	26.3
13.6	37.1
16.9	45.6
19.7	53.4

$k_{EtO-} = 2.73 \pm 0.02\ M^{-1}s^{-1}$
$R^2 = 0.9999$

Table S17. Kinetic data for the reaction of 3,4-dinitrophenyl diphenylphosphinate (**1h**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at 15.0 ± 0.1°C. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3 \, k_{obsd}/s^{-1}$
0.468	5.06
0.929	11.4
1.38	18.9
1.83	25.7
2.27	31.2

k_{EtO-} = 14.8±0.4 M⁻¹s⁻¹
R^2 = 0.9990

Table S18. Kinetic data for the reaction of 3,4-dinitrophenyl diphenylphosphinate (**1h**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at 20.0 ± 0.1°C. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3 \, k_{obsd}/s^{-1}$
0.584	8.38
1.16	18.7
1.72	27.7
2.27	37.8
2.81	47.9

k_{EtO-} = 17.6±0.2 M⁻¹s⁻¹
R^2 = 0.9997

Table S19. Kinetic data for the reaction of 3,4-dinitrophenyl diphenylphosphinate (**1h**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at 35.0 ± 0.1°C. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3\ k_{obsd}/s^{-1}$
0.584	17.7
1.16	37.4
1.72	56.5
2.27	72.0
2.81	91.7

k_{EtO^-} = 32.8±0.6 M⁻¹s⁻¹
R^2 = 0.9994

Table S20. Kinetic data for the reaction of 3,4-dinitrophenyl diphenylphosphinate (**1h**) with EtO⁻K⁺ in the presence of excess 18C6 in anhydrous EtOH at 45.0 ± 0.1°C. ([18C6]/[EtO⁻K⁺] = 5.0)

10^3 [EtO⁻K⁺]/M	$10^3\ k_{obsd}/s^{-1}$
0.468	18.4
0.929	41.0
1.38	61.4
1.83	82.4
2.27	103

k_{EtO^-}= 46.8±0.3 M⁻¹s⁻¹
R^2 = 0.9999