

Table 1 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of substituted triphenylphosphines (**2a-g**) for reaction with **1a** in acetonitrile at 25 °C.

$c(\text{Ph}_3\text{P})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}$ ( <b>2a</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2b</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2c</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2d</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2e</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2f</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2g</b> ) ( $\text{s}^{-1}$ )
0.0020	86.15	60.39	29.30	–	–	–	–
0.0025	–	–	–	24.93	15.14	8.658	0.5765
0.0040	205.9	129.3	65.99	–	–	–	–
0.0050	–	–	–	55.91	34.9	18.74	1.355
0.0060	324.9	206.2	102.3	–	–	–	–
0.0075	–	–	–	88.40	54.01	29.43	1.918
0.0080	439.3	276.0	140.3	–	–	–	–
0.0100	557.3	338.4	171.1	117.3	72.55	39.96	2.582
0.0120	685.0	397.5	207.5	–	–	–	–
0.0125	–	–	–	150.2	92.55	50.32	3.259
0.0150	–	–	–	189.9	115.0	60.15	3.976
0.0175	–	–	–	221.4	131.7	69.79	4.472
0.0200	–	–	–	255.5	153.1	–	5.052

Notes: Triphenyl phosphines **2a-c** are sparingly soluble in acetonitrile. Quoted values of  $k_{\text{obs}}$  are average values from six kinetic runs.

Table 2 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of substituted triphenylphosphines (**2a-g**) for reaction with **1b** in acetonitrile at 25 °C.

$c(\text{Ph}_3\text{P})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}$ ( <b>2a</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2b</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2c</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2d</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2e</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2f</b> ) ( $\text{s}^{-1}$ )	$k_{\text{obs}}$ ( <b>2g</b> ) ( $\text{s}^{-1}$ )
0.0020	66.01	39.97	20.87	–	–	–	–
0.0025	–	–	–	23.96	10.36	4.891	0.3028
0.0040	159.9	94.65	46.58	–	–	–	–
0.0050	–	–	–	52.41	23.76	11.12	0.685
0.0060	246.5	150.4	73.37	–	–	–	–
0.0075	–	–	–	80.24	36.67	17.46	1.035
0.0080	335.9	209.8	100.5	–	–	–	–
0.0100	427.7	261.5	126.8	110.2	49.88	23.88	1.404
0.0120	512.5	318.7	154.2	–	–	–	–
0.0125	–	–	–	140.1	62.39	30.24	1.764
0.0150	–	–	–	174.3	75.19	36.46	2.148
0.0175	–	–	–	202.1	88.39	42.4	2.505
0.0200	–	–	–	238.3	101.7	–	2.835

Note: Triphenyl phosphines **2a-c** are sparingly soluble in acetonitrile. Quoted values of  $k_{\text{obs}}$  are average values from six kinetic runs.

Table 3 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of triphenylphosphine (**2d**) for reaction with **1a** and **1b** in acetonitrile at 30°, 35° and 40 °C.

$c(\mathbf{2d})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}(\mathbf{1a})$ ( $\text{s}^{-1}$ )	$k_{\text{obs}}(\mathbf{1a})$ ( $\text{s}^{-1}$ )	$k_{\text{obs}}(\mathbf{1a})$ ( $\text{s}^{-1}$ )	$k_{\text{obs}}(\mathbf{1b})$ ( $\text{s}^{-1}$ )	$k_{\text{obs}}(\mathbf{1b})$ ( $\text{s}^{-1}$ )	$k_{\text{obs}}(\mathbf{1b})$ ( $\text{s}^{-1}$ )
	30 °C	35 °C	40 °C	30 °C	35 °C	40 °C
0.0025	28.50	32.49	39.42	27.12	29.72	33.04
0.0050	64.98	72.38	79.50	59.44	63.84	67.97
0.0075	102.1	104.9	128.4	90.99	99.69	107.0
0.0100	139.9	154.9	173.3	124.3	137.0	146.4
0.0125	177.1	195.1	220.8	156.4	174.4	189.5
0.0150	211.9	225.9	268.3	196.0	211.2	229.8
0.0175	246.4	269.6	300.2	225.8	248.9	269.1
0.0200	278.3	314.9	349.2	260.3	284.2	312.0

Note: Quoted values of  $k_{\text{obs}}$  are average values from six kinetic runs.

Table 4 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of triphenyl phosphite (**3d**) for reaction with **1a** in acetonitrile at 25°, 30°, 35° and 40 °C.

$c(\mathbf{3d})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}(\text{s}^{-1})$ 25 °C	$k_{\text{obs}}(\text{s}^{-1})$ 30 °C	$k_{\text{obs}}(\text{s}^{-1})$ 35 °C	$k_{\text{obs}}(\text{s}^{-1})$ 40 °C
	0.005	0.01332	0.01887	0.02114
0.010	0.02622	0.03258	0.04102	0.05069
0.015	0.04150	0.05012	0.06496	0.07763
0.020	0.05401	0.06526	0.08465	0.1050
0.025	0.06738	0.08136	0.1036	0.1332
0.030	0.08021	0.0965	0.1258	0.1590
0.035	0.09366	0.1153	0.1462	0.1850
0.040	0.1055	0.1334	0.1711	0.2143

Note: Quoted values of  $k_{\text{obs}}$  are average values from six kinetic runs.

Table 5 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of triphenyl phosphine (**2d**) for reaction with **1a** in ethanol at 25°, 30°, 35° and 40 °C.

$c(\mathbf{2d})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) 25 °C	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) 30 °C	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) 35 °C	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) 40 °C
0.0025	8.816	10.69	12.7	14.89
0.0050	19.06	22.65	27.71	31.31
0.0075	30.02	35.06	41.83	47.77
0.0100	38.83	46.05	53.33	61.00
0.0125	48.85	56.65	66.28	76.35
0.0150	58.19	67.92	79.88	91.11
0.0175	68.55	81.02	95.26	108.2
0.0200	78.21	92.96	111.5	125.2

Note: Quoted values of  $k_{\text{obs}}$  are average values from six kinetic runs.

Table 6 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of triphenyl phosphine (**2d**) for reaction with **1b** in ethanol and dichloromethane at 25 °C and for reaction with **10** in acetonitrile

$c(\mathbf{2d})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}$ ( <b>1b</b> ) ( $\text{s}^{-1}$ ) (ethanol)	$k_{\text{obs}}$ ( <b>1b</b> ) ( $\text{s}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ )	$k_{\text{obs}}$ ( <b>10</b> ) ( $\text{s}^{-1}$ ) (acetonitrile)
0.0025	30.62	22.78	–
0.0050	70.63	47.88	2.207
0.0075	116.0	75.68	3.148
0.0100	146.9	103.4	4.153
0.0125	191.8	126.0	5.268
0.0150	232.5	161.8	6.490
0.0175	276.8	193.7	7.313
0.0200	319.3	227.3	8.254

Note: Quoted values of  $k_{\text{obs}}$  are average values from six kinetic runs.

Table 7 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of substituted triphenylphosphites (**3a-e**) for reaction with **1a** in acetonitrile at 30 °C.

$c(\text{PhO}_3\text{P})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}\cdot 10^2$ ( $\text{s}^{-1}$ ) ( <b>3a</b> )	$k_{\text{obs}}\cdot 10^2$ ( $\text{s}^{-1}$ ) ( <b>3b</b> )	$k_{\text{obs}}\cdot 10^2$ ( $\text{s}^{-1}$ ) ( <b>3c</b> )	$k_{\text{obs}}\cdot 10^2$ ( $\text{s}^{-1}$ ) ( <b>3e</b> )
0.00043	0.934	–	–	–
0.00086	2.072	–	–	–
0.00215	5.100	–	–	–
0.00258	6.334	–	–	–
0.00344	9.005	–	–	–
0.00120	–	0.8208	–	–
0.00204	–	1.583	–	–
0.00409	–	3.041	–	–
0.00613	–	4.438	–	–
0.00730	–	5.243	–	–
0.01022	–	7.135	–	–
0.01460	–	9.932	–	–
0.00101	–	–	0.4565	–
0.00203	–	–	0.8813	–
0.00406	–	–	1.698	–
0.00608	–	–	2.487	–
0.00845	–	–	3.417	–
0.01099	–	–	4.430	–
0.01352	–	–	5.385	–
0.00063	–	–	–	0.0282
0.00189	–	–	–	0.0810
0.00315	–	–	–	0.1340
0.00441	–	–	–	0.2292
0.00630	–	–	–	0.3143
0.00819	–	–	–	0.4120

Notes: Quoted values of  $k_{\text{obs}}$  are average values from three kinetic runs.

Table 8 – Measured observed rate constant  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) on the concentration of substituted triphenylphosphites (**4a-f**) for reaction with **1a** in acetonitrile at 30 °C.

$\alpha(\text{PhO}_3\text{P})$ ( $\text{mol}\cdot\text{l}^{-1}$ )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) ( <b>4a</b> )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) ( <b>4b</b> )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) ( <b>4c</b> )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) ( <b>4d</b> )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) ( <b>4e</b> )	$k_{\text{obs}}$ ( $\text{s}^{-1}$ ) ( <b>4f</b> )
0.00064	1.39	–	–	–	–	–
0.00128	2.90	–	–	–	–	–
0.00256	6.61	–	–	–	–	–
0.00384	10.80	–	–	–	–	–
0.00512	14.90	–	–	–	–	–
0.00640	18.50	–	–	–	–	–
0.00090	–	2.36	–	–	–	–
0.00270	–	6.70	–	–	–	–
0.00540	–	15.28	–	–	–	–
0.00720	–	21.10	–	–	–	–
0.00900	–	27.50	–	–	–	–
0.00083	–	–	2.42	–	–	–
0.00166	–	–	5.65	–	–	–
0.00332	–	–	11.60	–	–	–
0.00498	–	–	18.28	–	–	–
0.00664	–	–	24.60	–	–	–
0.00830	–	–	29.20	–	–	–
0.00093	–	–	–	2.83	–	–
0.00186	–	–	–	6.11	–	–
0.00372	–	–	–	13.40	–	–
0.00558	–	–	–	21.00	–	–
0.00744	–	–	–	29.10	–	–
0.00930	–	–	–	34.30	–	–
0.00221	–	–	–	–	0.0056	–
0.00332	–	–	–	–	0.0115	–
0.00443	–	–	–	–	0.0164	–
0.00553	–	–	–	–	0.0208	–
0.00664	–	–	–	–	0.0328	–
0.00774	–	–	–	–	0.0367	–
0.00885	–	–	–	–	0.0416	–
0.00102	–	–	–	–	–	0.50
0.00204	–	–	–	–	–	0.95
0.00306	–	–	–	–	–	1.70
0.00408	–	–	–	–	–	2.43
0.00510	–	–	–	–	–	3.19
0.00612	–	–	–	–	–	4.00

Notes: Quoted values of  $k_{\text{obs}}$  are average values from three kinetic runs.