Supplementary Information
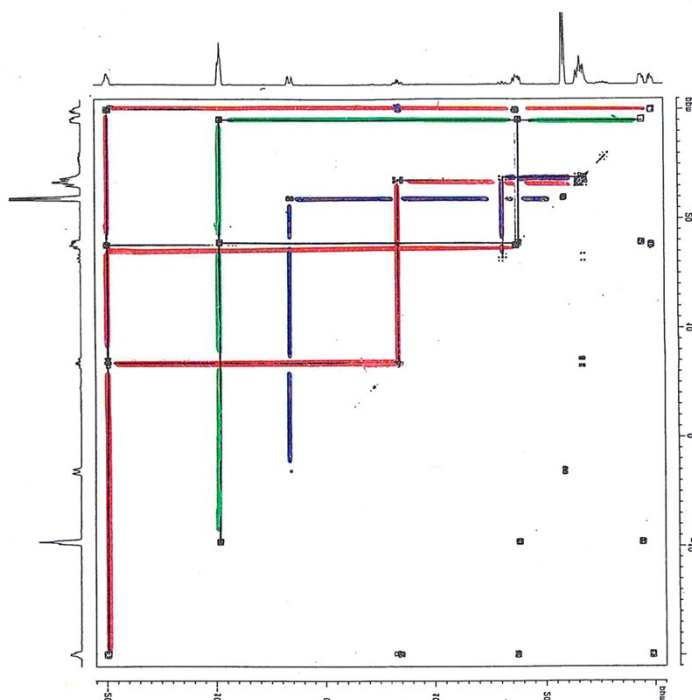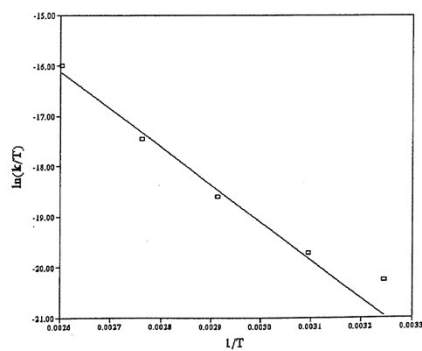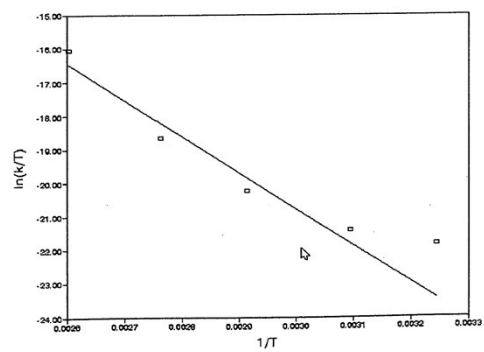

Figure S1. ^{31}P COSY NMR sectrum of the reaaranged mixture after themolysis of **8** at 111^{0}C for ten hours.

^{31}P NMR Data for wet Samples

^{31}P NMR Data for Dry Samples

^{1}H NMR Data for Dry Samples
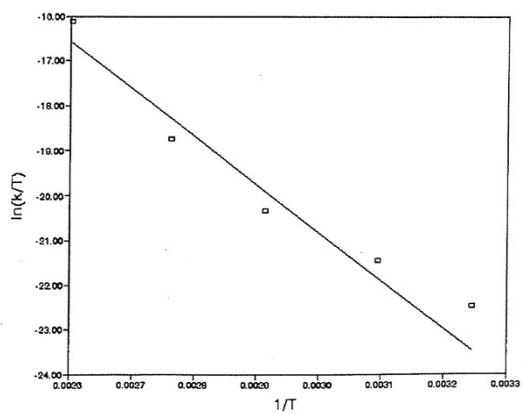
Figure S2. Eyring Plots

Table S1. NMR Data for Compounds 14 and 15.

Data	14	14
^{1}H NMR		
Vinyl (cis)	6.28 (m)	6.28 (m)
Vinyl (trans)	5.42 (m)	5.42 (m)
Methyl	1.96 (m)	1.36 (m)
α-CH$_2$	4.603, 4.599 (AB)	4.68 (m)
β-CH$_2$	3.7 (m)	3.7 (m)
		-19.9 (m)
^{31}P NMR		
P(O)O	-19.9 (m)	
P(CL)O-	-10.7 (m)	7.0 (d of t), $^2J_{pp}$ = 26.1, 66.8
4-PCl$_2$	17.6 (d of d); $^2J_{pp}$ 24.6, 48.0	17.5 (d of d) $^2J_{pp}$ = 33.2, 49.6
PCl$_2$	-	23.6 (d), $^2J_{pp}$ = 66.8
6-PCl$_2$	29.2 (m)	30.1 (m)
^{31}C NMR		
=$\underline{C}$(CH$_3$)C(O)O	137.1	137.1
H$_2$C=	127.1	127.1
C=O	167.4	167.4

CH$_3$	19.1	19.1
α=CH$_2$	62.5	62.5
β=CH$_2$	46.6	46.6

Table S2. ^{31}P NMR Kinetic Data for Dry Samples and Reaction Order Fit

111^0 C

		First order kinetic fit		Second order kinetic fit	
Time (hours)	integration	ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0	1.00	0.00	0.08	0.00	-0.64
2	0.83	-0.18	-0.22	0.20	0.15
4	0.62	-0.48	-0.52	0.62	0.93
6	0.45	-0.79	-0.81	1.20	1.72
8	0.35	-1.06	-1.11	1.88	2.50
10.2	0.23	-1.47	-1.44	3.35	3.37
12.2	0.17	-1.78	-1.74	4.91	4.15

Regression Output:				Regression Output:	
Constant			0.08	Constant	-0.64
Std Err of Y Est			0.05	Std Err of Y Est	0.59
R Squared			0.99	R Squared	0.91
No. of Observations			7	No. of Observations	7
Degrees of Freedom			5	Degrees of Freedom	5

X Coefficient(s)	-1.49e-01		X Coefficient(s)	3.93e-01
Std Err of Coef.	5.07e-03		Std Err of Coef.	5.48e-02

Half-life   4.65e+00 hours

90^0 C

| | | First order kinetic fit | | Second order kinetic fit | |
Time (hours)	integration	ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0	1.00	0.00	0.05	0.00	-0.35
9.25	0.95	-0.05	-0.05	0.06	-0.14
35.42	0.82	-0.20	-0.32	0.22	0.47
44.5	0.64	-0.45	-0.41	0.57	0.68
67.5	0.53	-0.64	-0.65	0.90	1.22
87.5	0.40	-0.91	-0.86	1.49	1.69
151.5	0.22	-1.51	-1.52	3.52	3.18
1126.83*	0.00	-5.82	-11.59	335.70	25.97

Regression Output:				Regression Output:	
Constant			0.05	Constant	-0.35
Std Err of Y Est			0.07	Std Err of Y Est	0.32
R Squared			0.99	R Squared	0.95
No. of Observations			7	No. of Observations	7
Degrees of Freedom			5	Degrees of Freedom	5
X Coefficient(s)	-1.03e-02			X Coefficient(s)	2.34e-02
Std Err of Coef.	5.15e-04			Std Err of Coef.	2.48e-03

Half-life 6.71e+01 hours

70° C

| | | First order kinetic fit | | Second order kinetic fit | |
Time (hours)	integration	ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0	1.00	0.00	0.01	0.00	-0.08
30.25	0.97	-0.03	-0.05	0.04	0.02
68.75	0.91	-0.10	-0.13	0.10	0.15
100	0.82	-0.20	-0.19	0.22	0.25
155	0.69	-0.37	-0.31	0.44	0.43
290.33	0.57	-0.57	-0.58	0.77	0.87
463.33	0.40	-0.92	-0.93	1.51	1.44
959.33*	0.05	-3.04	-1.93	19.83	3.06

Regression Output:				Regression Output:	
Constant			0.01	Constant	-0.08
Std Err of Y Est			0.03	Std Err of Y Est	0.07
R Squared			0.99	R Squared	0.99
No. of Observations			7	No. of Observations	7
Degrees of Freedom			5	Degrees of Freedom	5
X Coefficient(s)	-2.02e-03			X Coefficient(s)	3.27e-03
Std Err of Coef.	8.02e-05			Std Err of Coef.	1.79e-04

Half-life 3.43e+02 hours

50° C

Time (hours)	integration	First order kinetic fit		Second order kinetic fit	
		ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0*	1.00	0.00	0.18	0.00	-0.28
120	1.05	0.05	0.11	-0.05	-0.17
218	1.02	0.02	0.05	-0.02	-0.09
475	0.95	-0.06	-0.10	0.06	0.14
855.83	0.81	-0.21	-0.32	0.24	0.48
1695	0.43	-0.85	-0.80	1.35	1.22

Regression Output:			Regression Output:	
Constant		0.18	Constant	-0.28
Std Err of Y Est		0.08	Std Err of Y Est	0.18
R Squared		0.96	R Squared	0.93
No. of Observations		5	No. of Observations	5
Degrees of Freedom		3	Degrees of Freedom	3
X Coefficient(s)	-5.74e-04		X Coefficient(s)	8.85e-04
Std Err of Coef.	6.32e-05		Std Err of Coef.	1.44e-04

Half-life   1.21e+03 hours

35^{0}C

Table S3. ^{31}P NMR Kinetic Data and Reaction Order Fit

111^{0}C

Time (hours)	integration	First order kinetic fit		Second order kinetic fit	
		ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0*	1.00	0.00	0.11	0.00	-2.82
3	0.64	-0.45	-0.36	0.57	-0.67
6	0.44	-0.82	-0.83	1.26	1.48
9	0.31	-1.18	-1.30	2.26	3.64
12	0.19	-1.66	-1.77	4.25	5.79
15	0.09	-2.38	-2.24	9.84	7.94
18*	0.06	-2.89	-2.71	17.01	10.09

Regression Output:			Regression Output:	
Constant		0.11	Constant	-2.82
Std Err of Y Est		0.14	Std Err of Y Est	1.78
R Squared		0.98	R Squared	0.83
No. of Observations		5	No. of Observations	5
Degrees of Freedom		3	Degrees of Freedom	3
X Coefficient(s)	-1.57e-01		X Coefficient(s)	7.18e-01
Std Err of Coef.	1.45e-02		Std Err of Coef.	1.88e-01

Half-life   4.42e+00 hours

89^0

Time (hours)	integration	First order kinetic fit		Second order kinetic fit	
		ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0*	1.00	0.00	0.07	0.00	-0.84
9	0.75	-0.29	-0.23	0.33	-0.03
18	0.59	-0.53	-0.54	0.70	0.78
27	0.46	-0.79	-0.85	1.20	1.59
36	0.33	-1.11	-1.16	2.03	2.40
46	0.21	-1.56	-1.50	3.78	3.30
57*	0.11	-2.22	-1.87	8.23	4.29

		Regression Output:				Regression Output:	
		Constant	0.07			Constant	-0.84
		Std Err of Y Est	0.07			Std Err of Y Est	0.47
		R Squared	0.99			R Squared	0.91
		No. of Observations	5			No. of Observations	5
		Degrees of Freedom	3			Degrees of Freedom	3
		X Coefficient(s)	-3.42e-02			X Coefficient(s)	9.01e-02
		Std Err of Coef.	2.29e-03			Std Err of Coef.	1.61e-02

Half-life   2.03e+01   hours

$70^{\circ}C$

		First order kinetic fit		Second order kinetic fit	
Time (hours)	integration	$\ln(I/I_o)$	Regression fit	$1/I - 1/I_o$	Regression fit
0	1.00	0.00	0.05	0.00	-0.20
336	0.63	-0.46	-0.55	0.58	0.97
672	0.30	-1.20	-1.16	2.33	2.14
1008*	0.11	-2.22	-1.76	8.21	3.30

	Regression Output:		Regression Output:	
Constant		0.05	Constant	-0.20
Std Err of Y Est		0.12	Std Err of Y Est	0.48
R Squared		0.98	R Squared	0.92
No. of Observations		3	No. of Observations	3
Degrees of Freedom		1	Degrees of Freedom	1
X Coefficient(s)		-1.79e-03	X Coefficient(s)	3.47e-03
Std Err of Coef.		2.49e-04	Std Err of Coef.	1.01e-03

Half-Life   3.87e+02   hours

50^0C

Time (hours)	integration	First order kinetic fit		Second order kinetic fit	
		ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0*	1.00	0.00	0.13	0.00	-0.80
96	0.75	-0.28	-0.18	0.33	-0.04
216	0.64	-0.45	-0.56	0.56	0.90
336	0.42	-0.87	-0.95	1.38	1.84
456	0.24	-1.43	-1.34	3.19	2.77
588*	0.07	-2.68	-1.76	13.62	3.81

Regression Output:

			Regression Output:	
Constant		0.13	Constant	-0.80
Std Err of Y Est		0.14	Std Err of Y Est	0.56
R Squared		0.95	R Squared	0.88
No. of Observations		4	No. of Observations	4
Degrees of Freedom		2	Degrees of Freedom	2
X Coefficient(s)		-3.22e-03	X Coefficient(s)	7.83e-03
Std Err of Coef.		5.32e-04	Std Err of Coef.	2.08e-03

Half-Life   2.15e+02   hours

35^0

Time (hours)	integration	First order kinetic fit		Second order kinetic fit	
		ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0	1.00	0.00	0.05	0.00	-0.20
336	0.63	-0.46	-0.55	0.58	0.97
672	0.30	-1.20	-1.16	2.33	2.14
1008*	0.11	-2.22	-1.76	8.21	3.30

Regression Output:

			Regression Output:	
Constant		0.05	Constant	-0.20
Std Err of Y Est		0.12	Std Err of Y Est	0.48
R Squared		0.98	R Squared	0.92
No. of Observations		3	No. of Observations	3
Degrees of Freedom		1	Degrees of Freedom	1
X Coefficient(s)		-1.79e-03	X Coefficient(s)	3.47e-03
Std Err of Coef.		2.49e-04	Std Err of Coef.	1.01e-03

Half-Life   3.87e+02   hours

^{31}P signal from the PCl(OCH$_2$CH$_2$OC(O)CMe=CH$_2$ center followed. * Data point not included in regression analyses.

Table S4. ^{1}H NMR Kinetic Data for Dry Samples and Reaction Order Fit

111^0 C

Time (hours)	integration	First order kinetic fit ln(I/Io)	Regression fit	Second order kinetic fit 1/I - 1/Io	Regression fit
0	1.00	0.00	-0.02	0.00	-0.39
2	0.74	-0.30	-0.30	0.35	0.31
4	0.57	-0.57	-0.57	0.77	1.01
6	0.41	-0.89	-0.85	1.44	1.71
8	0.32	-1.14	-1.12	2.13	2.41
10.2	0.25	-1.38	-1.42	2.99	3.18
12.2	0.18	-1.69	-1.70	4.43	3.88

Regression Output:			Regression Output:	
Constant		-0.02	Constant	-0.39
Std Err of Y Est		0.03	Std Err of Y Est	0.37
R Squared		1.00	R Squared	0.95
No. of Observations		7	No. of Observations	7
Degrees of Freedom		5	Degrees of Freedom	5
X Coefficient(s)	-1.37e-01		X Coefficient(s)	3.50e-01
Std Err of Coef.	2.74e-03		Std Err of Coef.	3.48e-02

Half-life   5.06e+00 hours

90^0 C

Time (hours)	integration	First order kinetic fit ln(I/Io)	Regression fit	Second order kinetic fit 1/I - 1/Io	Regression fit
0	1.00	0.00	0.04	0.00	-0.26
9.25	0.96	-0.04	-0.05	0.04	-0.08
35.42	0.84	-0.18	-0.30	0.20	0.42
44.5	0.66	-0.41	-0.38	0.51	0.60
67.5	0.54	-0.61	-0.60	0.84	1.05
87.5	0.42	-0.86	-0.78	1.37	1.43
151.5	0.26	-1.36	-1.39	2.88	2.67
1126.83	0.02	-3.76	-10.55	41.75	21.59

Regression Output:			Regression Output:	
Constant		0.04	Constant	-0.26
Std Err of Y Est		0.07	Std Err of Y Est	0.22
R Squared		0.98	R Squared	0.96
No. of Observations		7	No. of Observations	7
Degrees of Freedom		5	Degrees of Freedom	5
X Coefficient(s)	-9.40e-03		X Coefficient(s)	1.94e-02
Std Err of Coef.	5.33e-04		Std Err of Coef.	1.70e-03

Half-life   7.38e+01 hours

70° C

Time (hours)	integration	First order kinetic fit		Second order kinetic fit	
		ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0	1.00	0.00	-0.02	0.00	-0.04
30.25	0.93	-0.07	-0.07	0.07	0.05
68.75	0.86	-0.16	-0.14	0.17	0.16
100	0.84	-0.18	-0.20	0.19	0.25
155	0.70	-0.35	-0.30	0.43	0.41
290.33	0.59	-0.53	-0.55	0.69	0.81
463.33	0.42	-0.87	-0.87	1.39	1.32
959.33*	0.06	-2.79	-1.78	15.36	2.77

	Regression Output:			Regression Output:	
Constant			-0.02	Constant	-0.04
Std Err of Y Est			0.03	Std Err of Y Est	0.07
R Squared			0.99	R Squared	0.98
No. of Observations			7	No. of Observations	7
Degrees of Freedom			5	Degrees of Freedom	5

X Coefficient(s)   -1.84e-03   X Coefficient(s)   2.93e-03
Std Err of Coef.   7.30e-05   Std Err of Coef.   1.74e-04

Half-life   3.76e+02 hours

50° C

Time (hours)	integration	First order kinetic fit		Second order kinetic fit	
		ln(I/Io)	Regression fit	1/I - 1/Io	Regression fit
0	1.00	0.00	-0.02	0.00	-0.04
30.25	0.93	-0.07	-0.07	0.07	0.05
68.75	0.86	-0.16	-0.14	0.17	0.16
100	0.84	-0.18	-0.20	0.19	0.25
155	0.70	-0.35	-0.30	0.43	0.41
290.33	0.59	-0.53	-0.55	0.69	0.81
463.33	0.42	-0.87	-0.87	1.39	1.32
959.33*	0.06	-2.79	-1.78	15.36	2.77

	Regression Output:			Regression Output:	
Constant			-0.02	Constant	-0.04
Std Err of Y Est			0.03	Std Err of Y Est	0.07
R Squared			0.99	R Squared	0.98
No. of Observations			7	No. of Observations	7
Degrees of Freedom			5	Degrees of Freedom	5

X Coefficient(s)   -1.84e-03   X Coefficient(s)   2.93e-03
Std Err of Coef.   7.30e-05   Std Err of Coef.   1.74e-04

Half-life   3.76e+02 hours

Table S5. Eryring Plot of Kinetic Data and Calcualtions

³¹P NMR Data

Temp(C)	Temp(K)	1/T	Rate Const.(hours)	Rate Const.(seconds)	ln(k/T)	Reg. fit	Calc. S
111	384	2.60e-03	1.57e-01	4.35e-05	-16.0	-16.3	-187
89	362	2.76e-03	3.42e-02	9.50e-06	-17.5	-17.3	-190
70	343	2.91e-03	1.03e-02	2.86e-06	-18.6	-18.3	-191
50	323	3.09e-03	3.22e-03	8.95e-07	-19.7	-19.5	-191
35*	308	3.25e-03	1.80e-03	5.00e-07	-20.2	-20.5	-187

Regression Output:

Constant	3.46
Std Err of Y Est	0.19
R Squared	0.99
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s)	-7525
Std Err of Coef.	514

$\Delta H^{\ddagger}$	62.6 KJ/mol
$\Delta S^{\ddagger}$	-169 J/mol K

³¹P NMR Data for Dry Samples

Temp(C)	Temp(K)	1/T	Rate Const.(hours)	Rate Const.(seconds)	ln(k/T)	Reg. fit	Calc. S
111	384	2.60e-03	1.49e-01	4.14e-05	-16.0	-16.8	-139
89	362	2.76e-03	1.03e-02	2.86e-06	-18.7	-18.2	-149
70	343	2.91e-03	2.02e-03	5.61e-07	-20.2	-19.6	-151
50	323	3.09e-03	5.74e-04	1.59e-07	-21.4	-21.2	-147
35*	308	3.25e-03	3.58e-04	9.94e-08	-21.9	-22.5	-140

Regression Output:

Constant	11.71
Std Err of Y Est	0.59
R Squared	0.96
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s)	-10834
Std Err of Coef.	1614

$\Delta H^{\ddagger}$	90.1 KJ/mol
$\Delta S^{\ddagger}$	-100 J/mol K

¹H NMR Data for Dry Samples

Temp(C)	Temp(K)	1/T	Rate Const.(hours)	Rate Const.(seconds)	ln(k/T)	Reg. fit	Calc. S
111	384	2.60e-03	1.37e-01	3.81e-05	-16.1	-16.8	-126
89	362	2.76e-03	9.40e-03	2.61e-06	-18.7	-18.3	-135
70	343	2.91e-03	1.84e-03	5.11e-07	-20.3	-19.7	-136
50	323	3.09e-03	5.66e-04	1.50e-07	-21.5	-21.5	-131
35*	308	3.25e-03	1.92e-04	5.33e-08	-22.5	-22.9	-127

Regression Output:

Constant	11.27
Std Err of Y Est	0.62
R Squared	0.95
No. of Observations	4
Degrees of Freedom	2

X Coefficient(s)	-10701
Std Err of Coef.	1692

$\Delta H^{\ddagger}$	89.0 KJ/mol
$\Delta S^{\ddagger}$	-104 J/mol K

- Labeled data not included in analysis