Supporting Information for:

Mechanism and Activity of Ruthenium Olefin Metathesis Catalysts

Melanie S. Sanford, Jennifer A. Love, and Robert H. Grubbs

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125 (U.S.A.)

Table S1. Rate Constants for and T_1 values for Phosphine Exchange in **1–14**.

Complex	k_{obs}/s^{-1}	eq PR_3	T/K	T_{1F}/s	T_{1C}/s
1	0.116 ± 0.002	3 eq	313	9.2	2.3
	0.381 ± 0.010	3 eq	323	9.8	2.7
	1.21 ± 0.02	3 eq	333	8.9	3.1
	3.56 ± 0.06	3 eq	343	7.8	3.6
	9.57 ± 0.06	3 eq	353	7.3	4.3
	1.22 ± 0.04	1.5 eq	333	8.3	3.3
	1.13 ± 0.04	10 eq	333	10.0	2.7
	1.11 ± 0.03	20 eq	333	9.0	2.3
2	0.40 ± 0.01	3 eq	313	8.3	2.1
	11.4 ± 0.2	3 eq	343	13.0	2.5
	30.3 ± 0.11	3 eq	353	11.4	2.6
	0.45 ± 0.03	10 eq	313	3.7	2.3
	0.34 ± 0.04	20 eq	313	5.3	1.8
3	0.46 ± 0.02	3 eq	273	5.7	1.1
	1.56 ± 0.08	3 eq	283	6.9	1.4
	8.3 ± 0.5	3 eq	297	10	1.6
	16.5 ± 0.5	3 eq	303	10	1.7
	28 ± 1	3 eq	308	15	1.5
	44 ± 2	3 eq	313	5.8	3.0
	15.9 ± 0.8	10 eq	303	11	0.84
	15.5 ± 0.6	20 eq	303	8	0.74
5	0.202 ± 0.008	3 eq	313	6.3	2.3
	2.18 ± 0.04	3 eq	333	9.6	3.0
	6.55 ± 0.14	3 eq	343	3.9	3.5
	19.4 ± 0.6	3 eq	353	5.4	2.4
	1.94 ± 0.06	10 eq	333	12.1	2.1

	1.81 ± 0.08	20 eq	333	10.4	1.9
6	0.037 ± 0.003	3 eq	333	8.7	3.0
	0.090 ± 0.004	3 eq	343	11.1	2.9
	0.326 ± 0.015	3 eq	353	10.6	3.3
	0.838 ± 0.016	3 eq	363	7.7	3.2
	2.16 ± 0.02	3 eq	373	7.0	2.9
	0.47 ± 0.02	10 eq	353	10.5	3.4
	0.41 ± 0.01	20 eq	353	9.5	2.7
7	0.163 ± 0.006	3 eq	333	7.8	5.2
	0.50 ± 0.01	3 eq	343	6.9	5.3
	1.42 ± 0.04	3 eq	353	5.8	5.2
	3.68 ± 0.12	3 eq	363	4.4	5.1
	0.43 ± 0.02	10 eq	343	10.8	4.7
	0.41 ± 0.06	20 eq	343	11.6	2.4
8	0.04 ± 0.01	1.5 eq	343	4.9	3.4
	0.126 ± 0.006	1.5 eq	353	8.4	3.6
	0.355 ± 0.016	1.5 eq	363	7.4	3.9
	1.02 ± 0.06	1.5 eq	373	12.6	3.4
	0.121 ± 0.008	5 eq	353	10.5	3.7
	0.12 ± 0.02	10 eq	353	9.2	3.3
9	0.52 ± 0.03	1.5 eq	353	9.6	3.8
	1.8 ± 0.1	1.5 eq	363	9.5	3.7
	4.3 ± 0.2	1.5 eq	373	13.5	4.0
	10.9 ± 0.5	1.5 eq	383	6.0	1.3
	0.52 ± 0.02	5 eq	353	8.3	3.7
	0.50 ± 0.02	10 eq	353	8.3	3.1
10	1.2 ± 0.1	1.5 eq	323	11.0	1.6
	5.0 ± 0.6	1.5 eq	333	11.6	1.9
	10 ± 1	1.5 eq	343	18.5	1.6
	30 ± 3	1.5 eq	353	12.4	1.7
	30 ± 3	5 eq	353	13.0	1.8
	29 ± 3	10 eq	353	13.2	2.0
11	0.049 ± 0.008	1.5 eq	303	17.8	4.1
	0.138 ± 0.005	1.5 eq	313	18.5	4.2
	0.420 ± 0.008	1.5 eq	323	20.0	4.5
	1.22 ± 0.02	1.5 eq	333	16.7	5.5

	0.11 ± 0.05	5 eq	313	20.0	3.5
	0.14 ± 0.04	10 eq	313	19.2	3.3
12	0.165 ± 0.006	1.5 eq	353	6.4	3.6
	0.47 ± 0.01	1.5 eq	363	7.1	3.9
	1.26 ± 0.04	1.5 eq	373	7.7	4.0
	3.37 ± 0.12	1.5 eq	383	12.5	4.3
	0.17 ± 0.05	5 eq	353	9.6	2.9
	0.18 ± 0.06	10 eq	353	8.5	3.8
14	0.09 ± 0.01	1.5 eq	363	7.1	1.8
	0.21 ± 0.02	1.5 eq	373	8.3	3.0
	0.54 ± 0.03	1.5 eq	383	6.2	3.9
	1.41 ± 0.08	1.5 eq	393	5.2	3.7
	1.2 ± 0.1	5 eq	393	5.1	3.2
	1.0 ± 0.2	10 eq	393	4.7	3.1

Table S2. T_1 Analysis for complexes **1-14** in C_7D_8 solution.

Complex	T_1 (s^{-1})
PCy_3	11.1 ± 0.2
PPh_3	23.7 ± 0.6
PBn_3	3.60 ± 0.09
1	2.46 ± 0.02
2	2.31 ± 0.02
3	1.91 ± 0.11
5	2.82 ± 0.02
6	2.78 ± 0.04
7	4.06 ± 0.03
8	3.07 ± 0.06
9	2.09 ± 0.03
10	1.58 ± 0.09
11	3.5 ± 0.2
12	1.6 ± 0.1
14	1.81 ± 0.02

Table S3. Values of k_1 from $1/k_{obs}$ versus $[PR_3]/[olefin]$.

Complex	k_1 (s^{-1})	k_1 (predicted) (s^{-1})
1	2.2×10^{-1}	7.7×10^{-1}
2	-7.0×10^{-3}	2.6
3	-1.0×10^{-1}	2.4×10^{2}
6	2.7×10^{-2}	2.3×10^{-2}
8	3.1×10^{-2}	3.2×10^{-2}
10	1.7×10^{-2}	1.4
11	1.3×10^{-2}	2.5×10^{-2}
12	5.0×10^{-3}	4.3×10^{-3}

Note: k_{-1} values are from 1/intercept and therefore have a significant amount of error associated with them. The negative values for catalysts **2** and **3** reflect the fact that $1/k_1$ in these systems is very close to zero, and the error inherent in the intercept is relatively large.

Figure S1. Eyring Plot for Phosphine Exchange in Catalyst 1

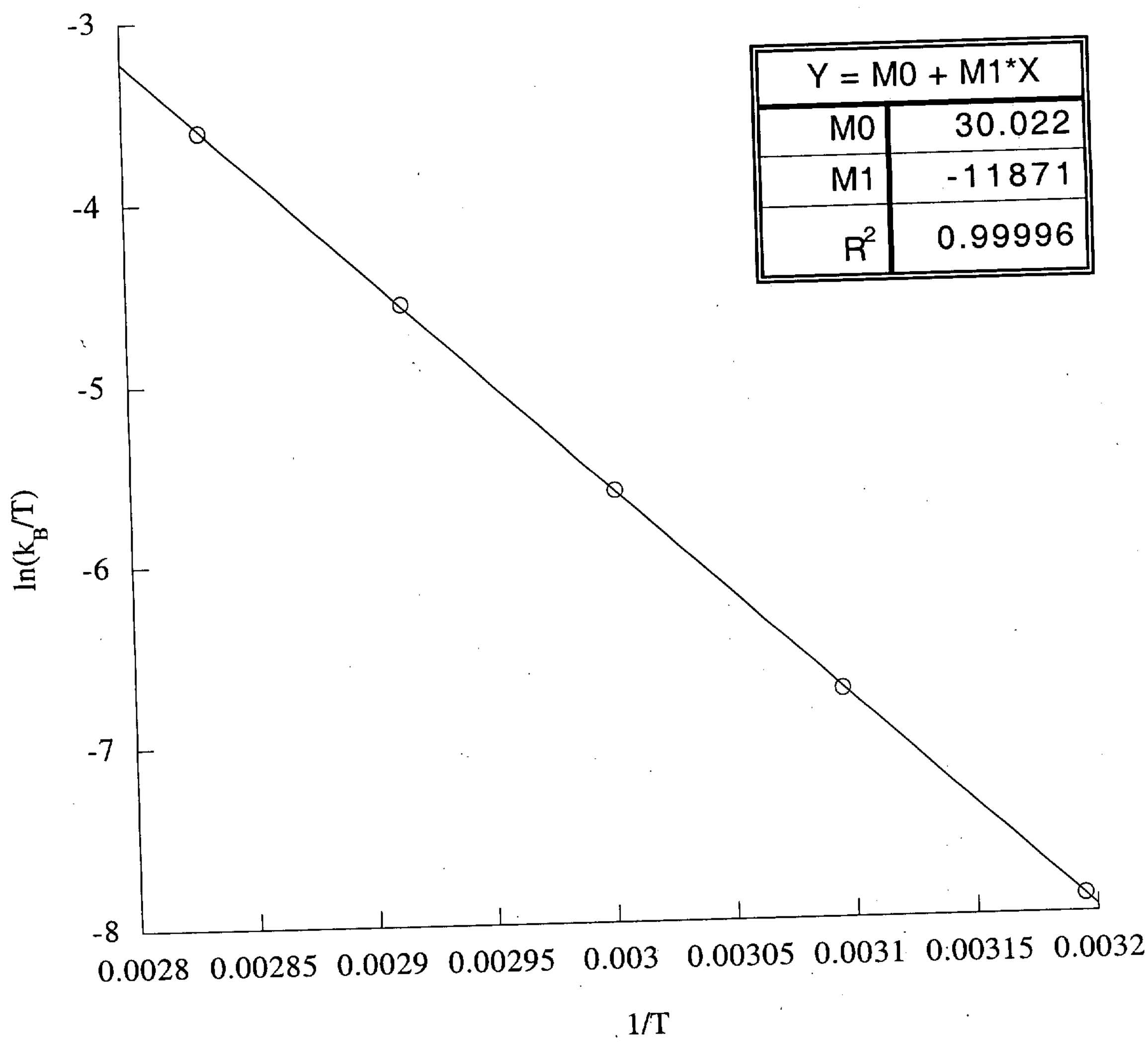

Figure S2. Eyring Plot for Phosphine Exchange in Catalyst 2

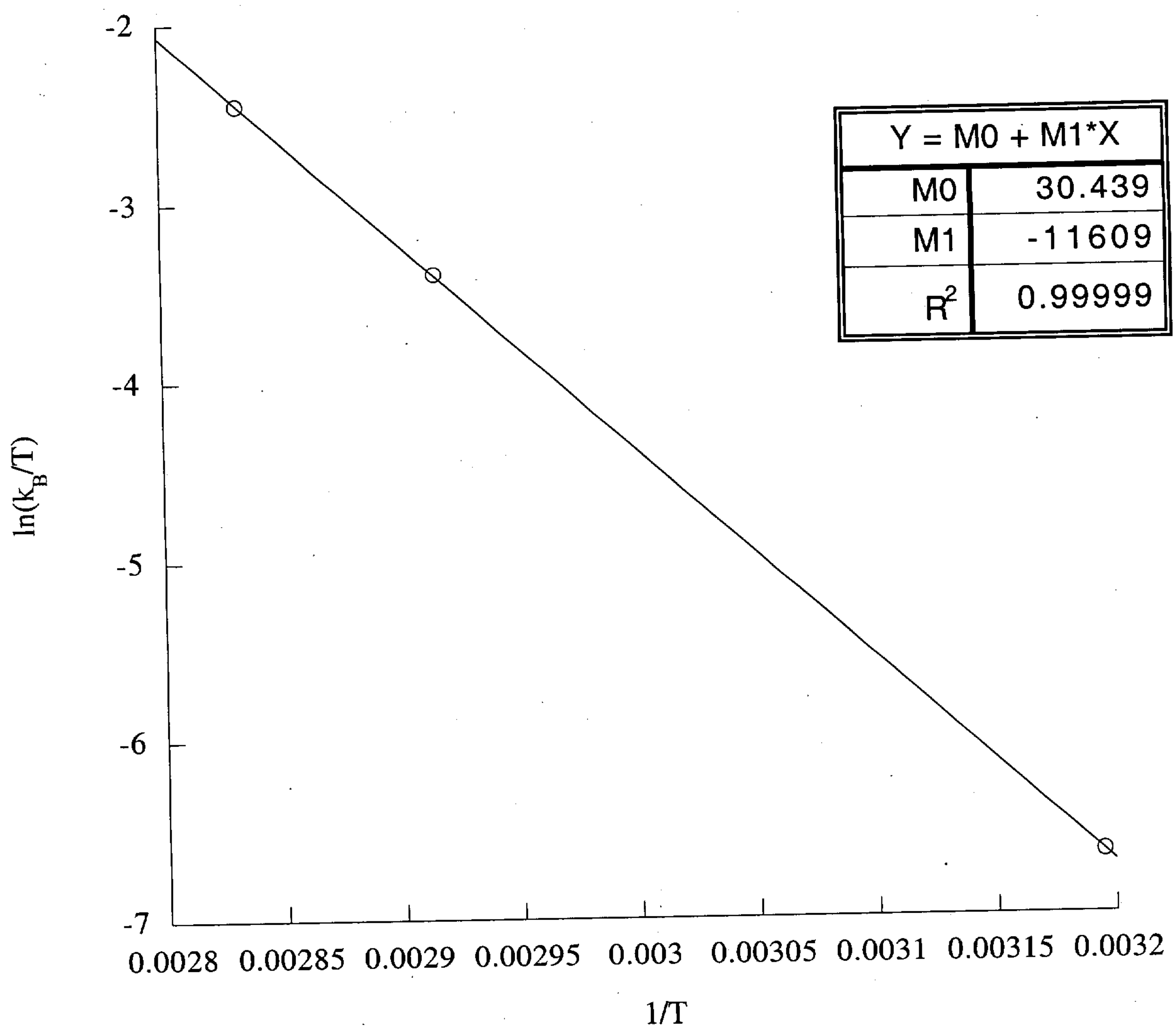

Figure S3. Eyring Plot for Phosphine Exchange in Catalyst 3

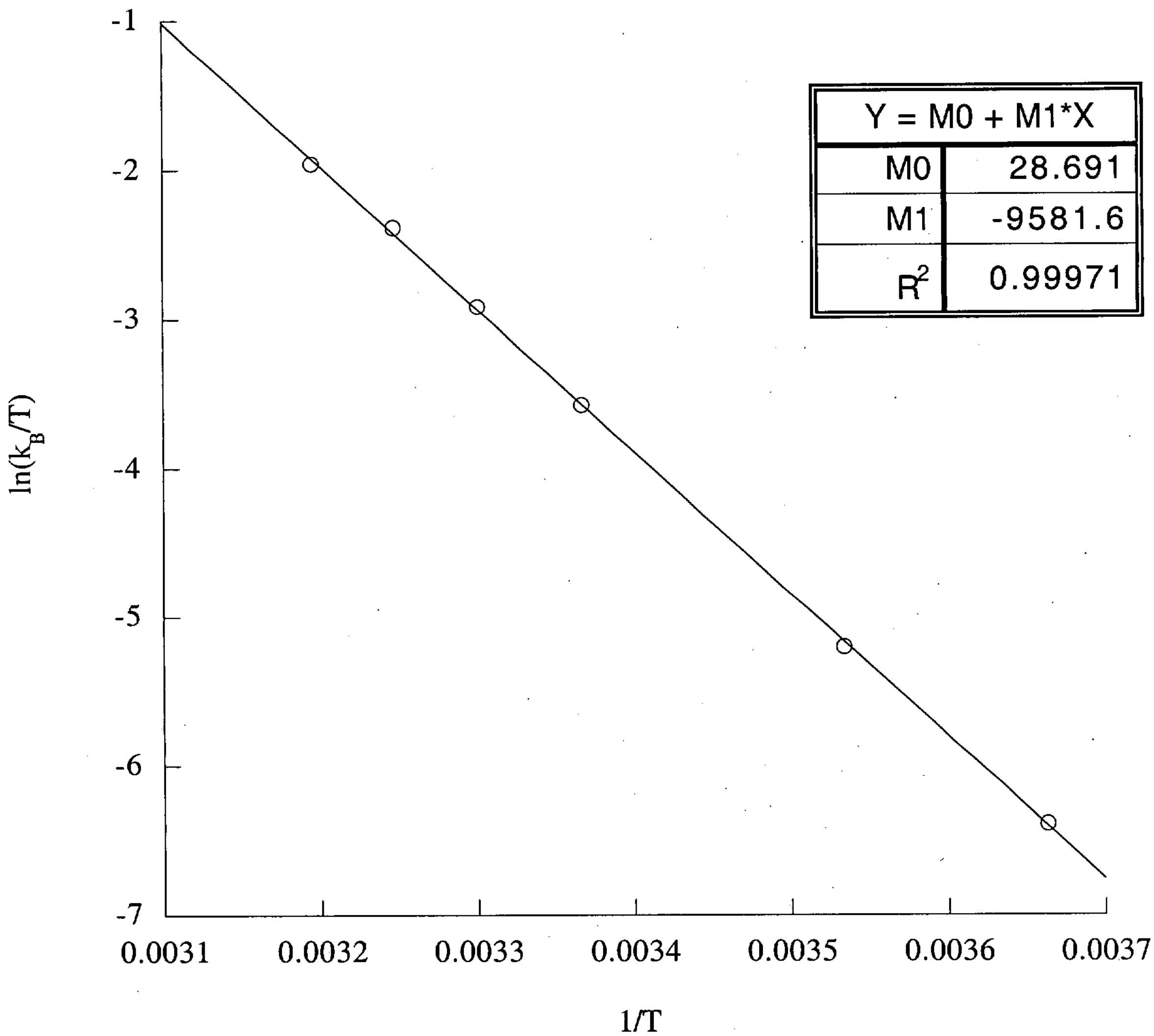

Figure S4. Eyring Plot for Phosphine Exchange in Catalyst 5

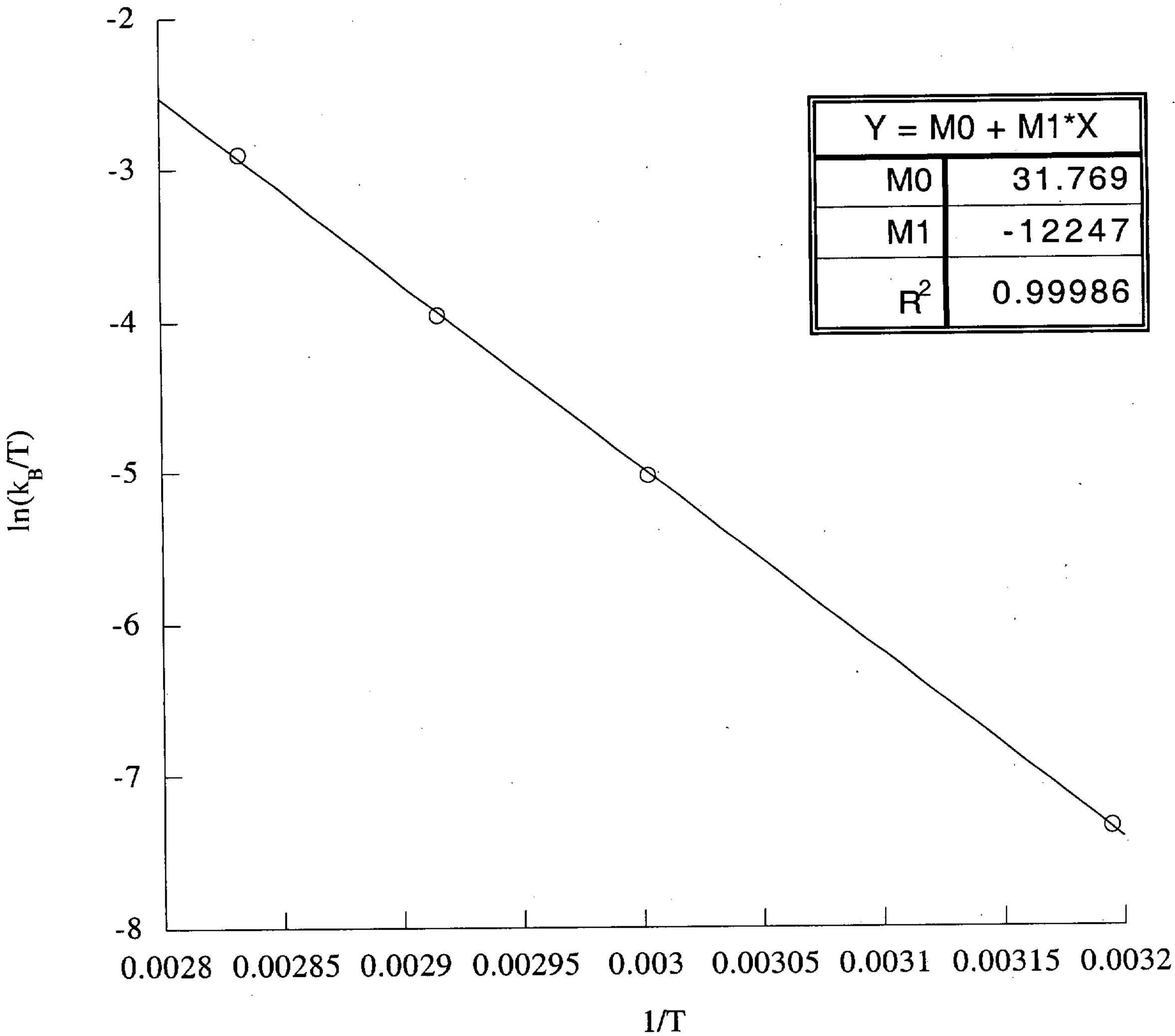

Figure S5. Eyring Plot for Phosphine Exchange in Catalyst 7.

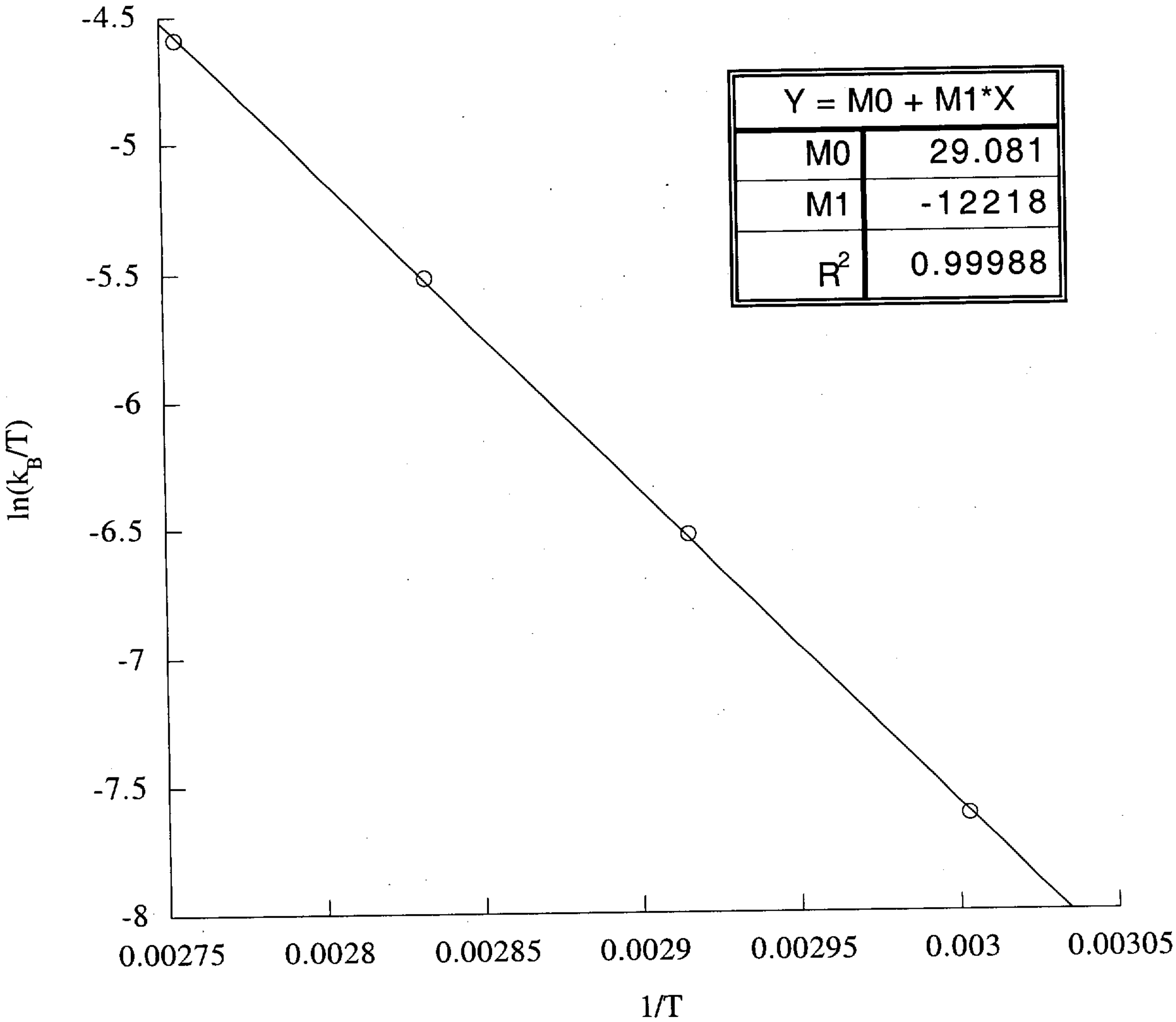

Figure S6. Eyring Plot for Phosphine Exchange in Catalyst 8.

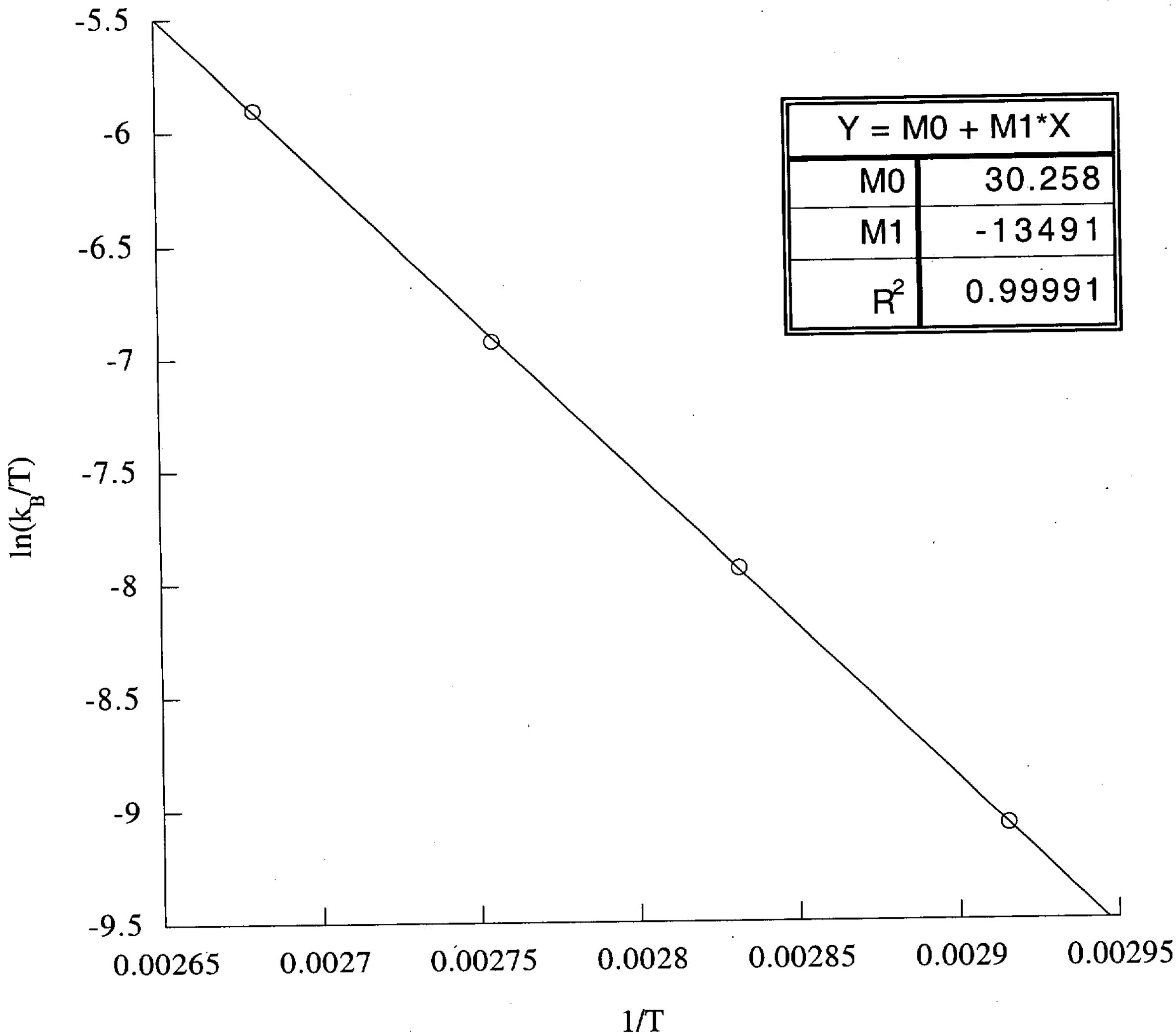

Figure S7. Eyring Plot for Phosphine Exchange in Catalyst 9.

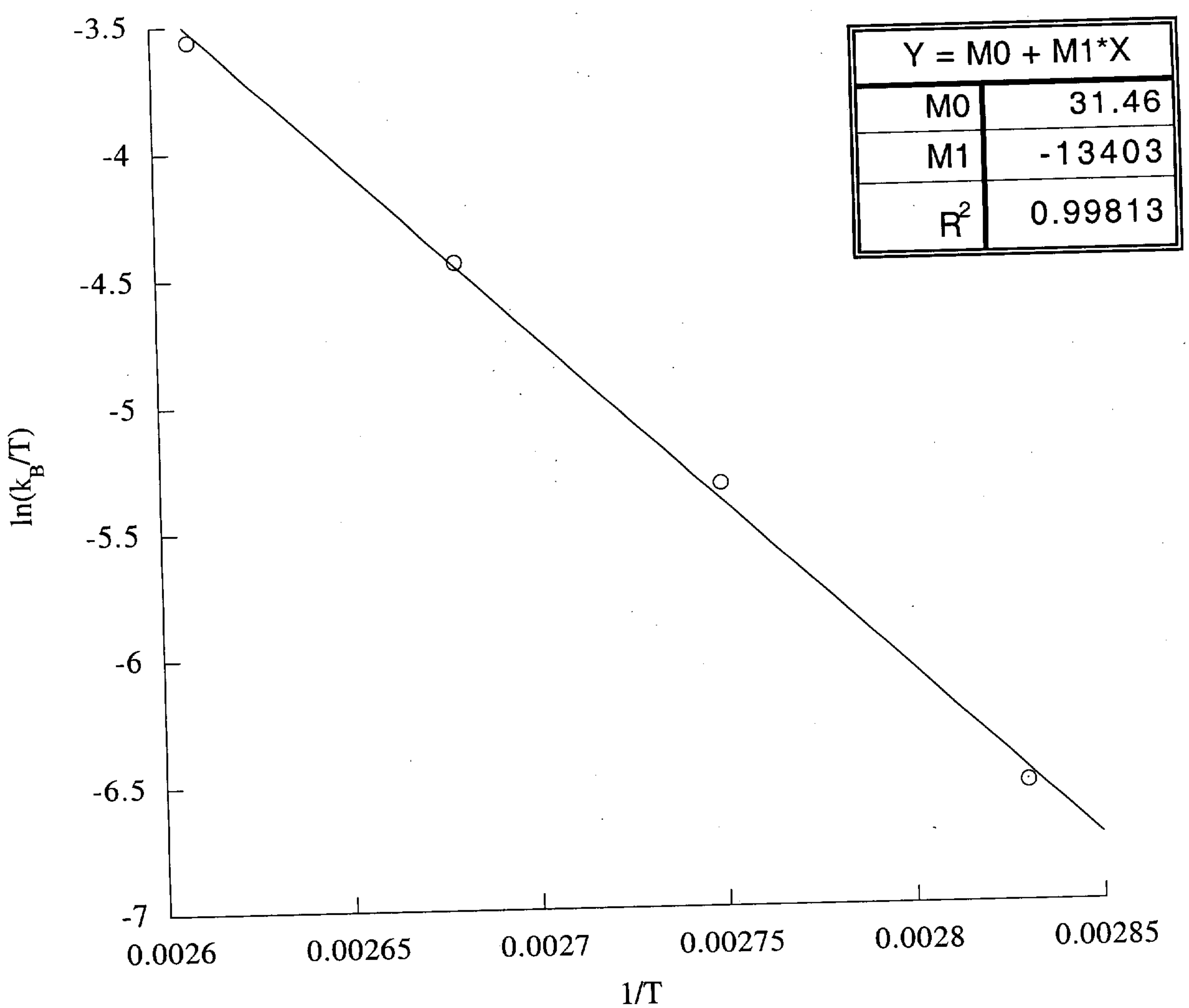

Figure S8. Eyring Plot for Phosphine Exchange in Catalyst 10

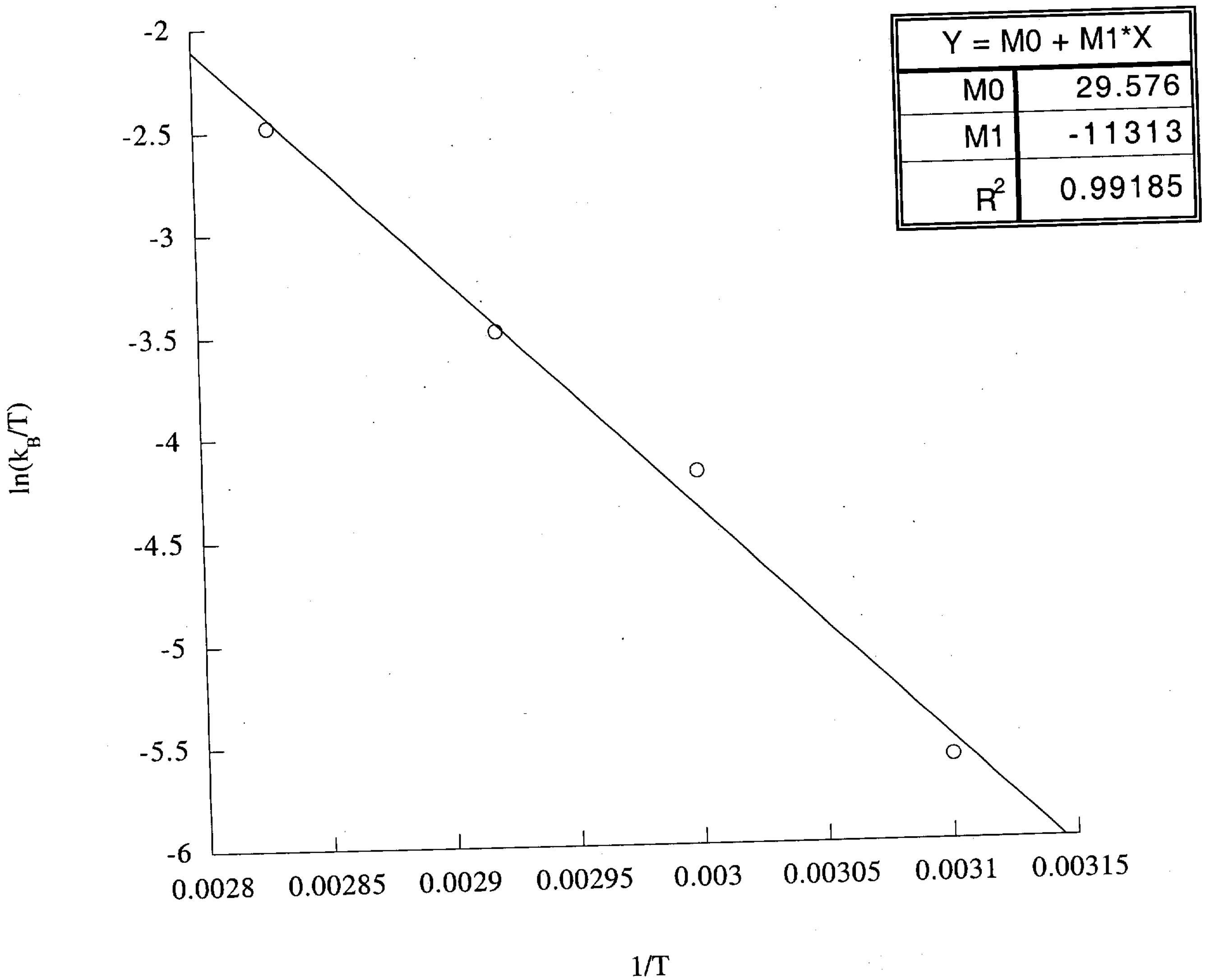

Figure S9. Eyring Plot for Phosphine Exchange in Catalyst 11

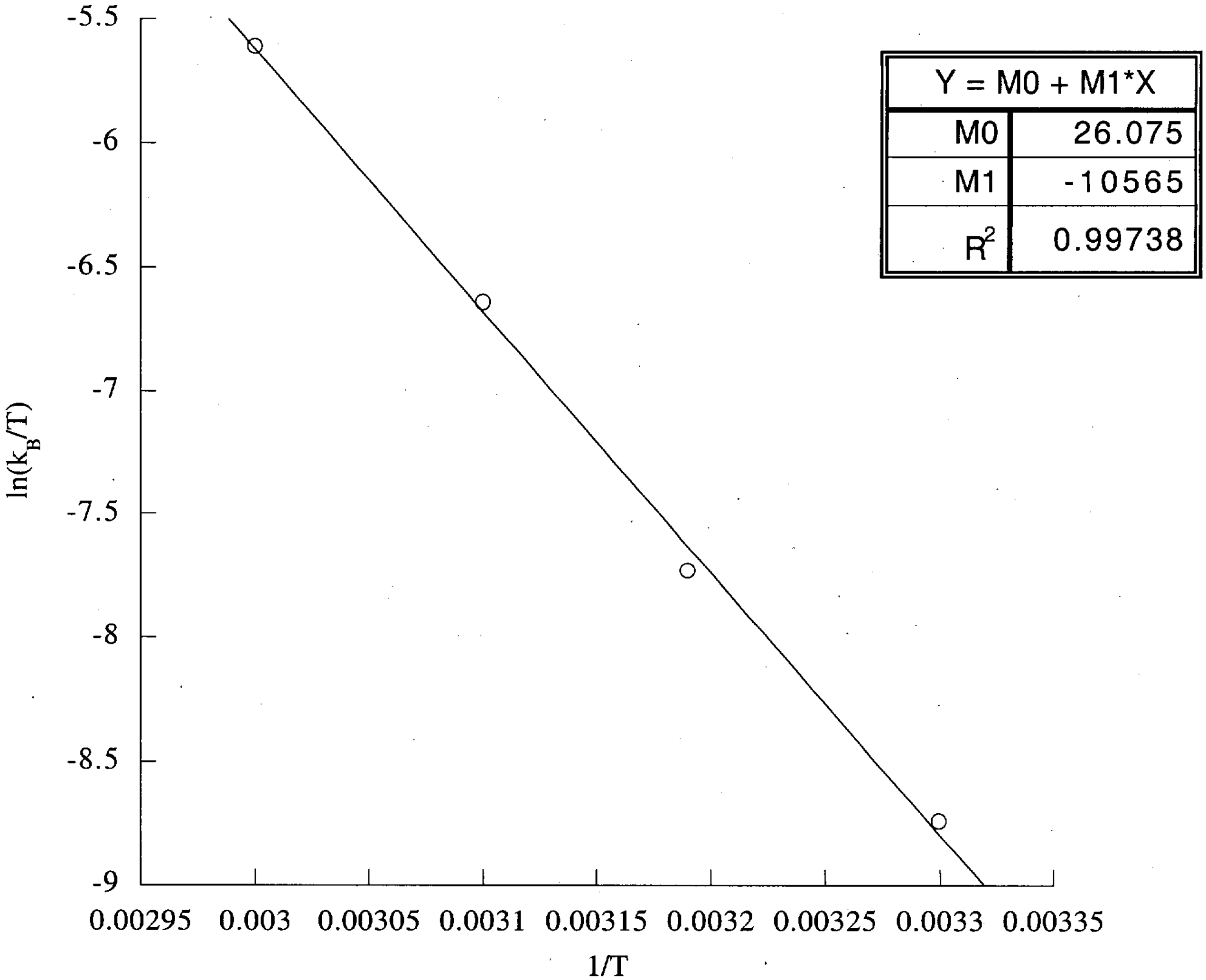

Figure S10. Eyring Plot for Phosphine Exchange in Catalyst 12

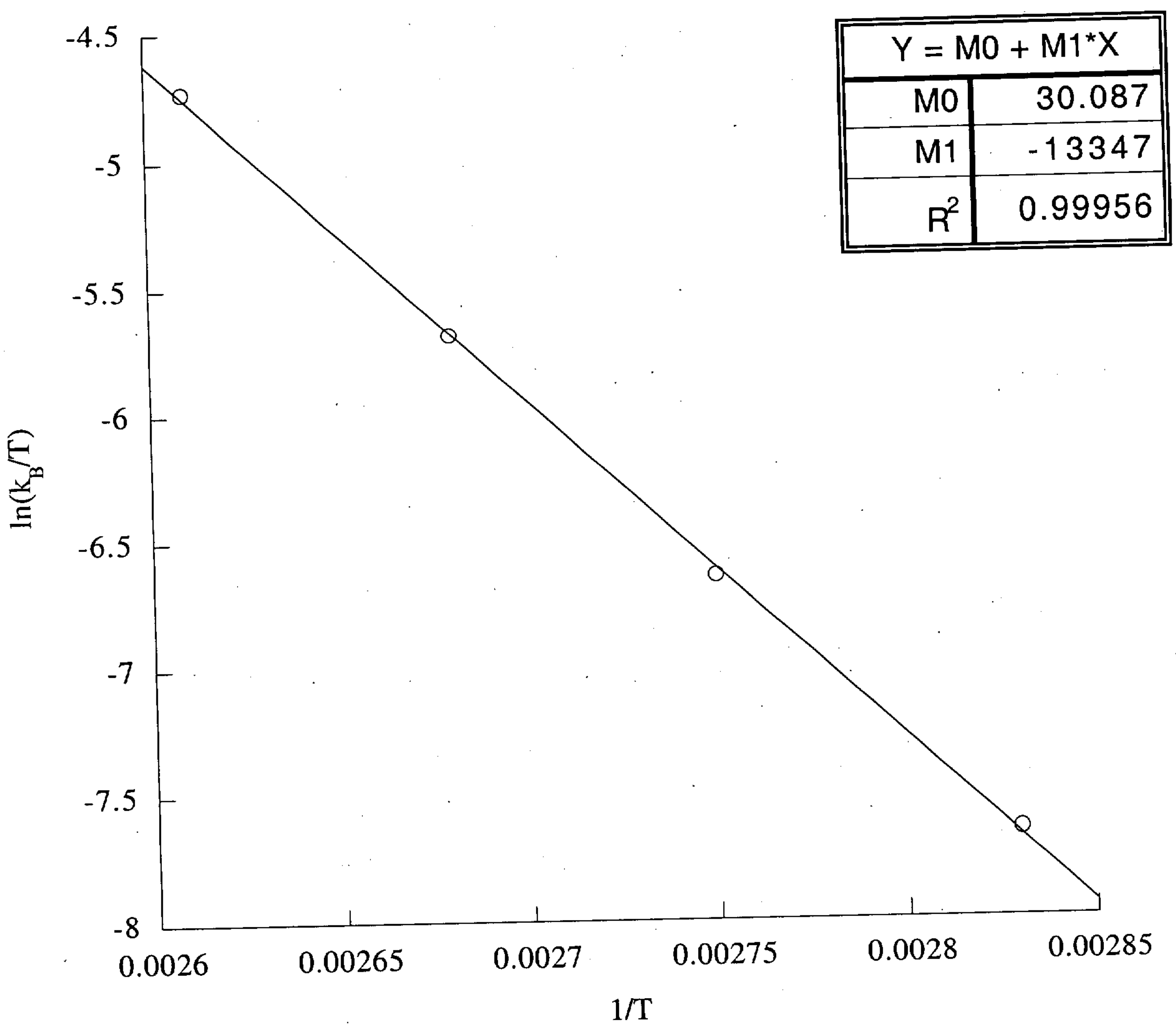

Figure S11. Eyring Plot for Phosphine Exchange in Catalyst 14.

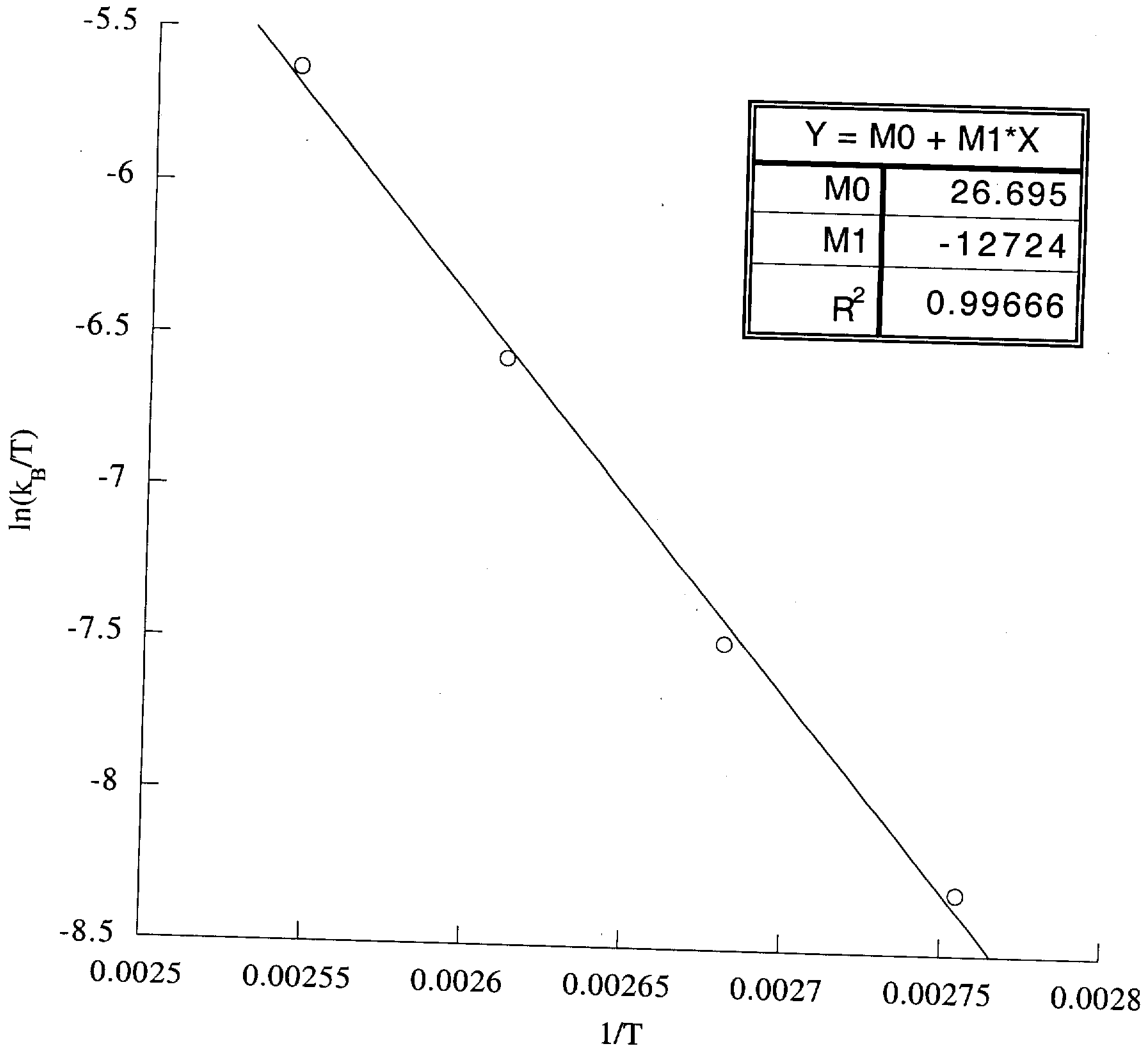

Figure S12. k_{Init} versus [olefin] for Catalyst 2

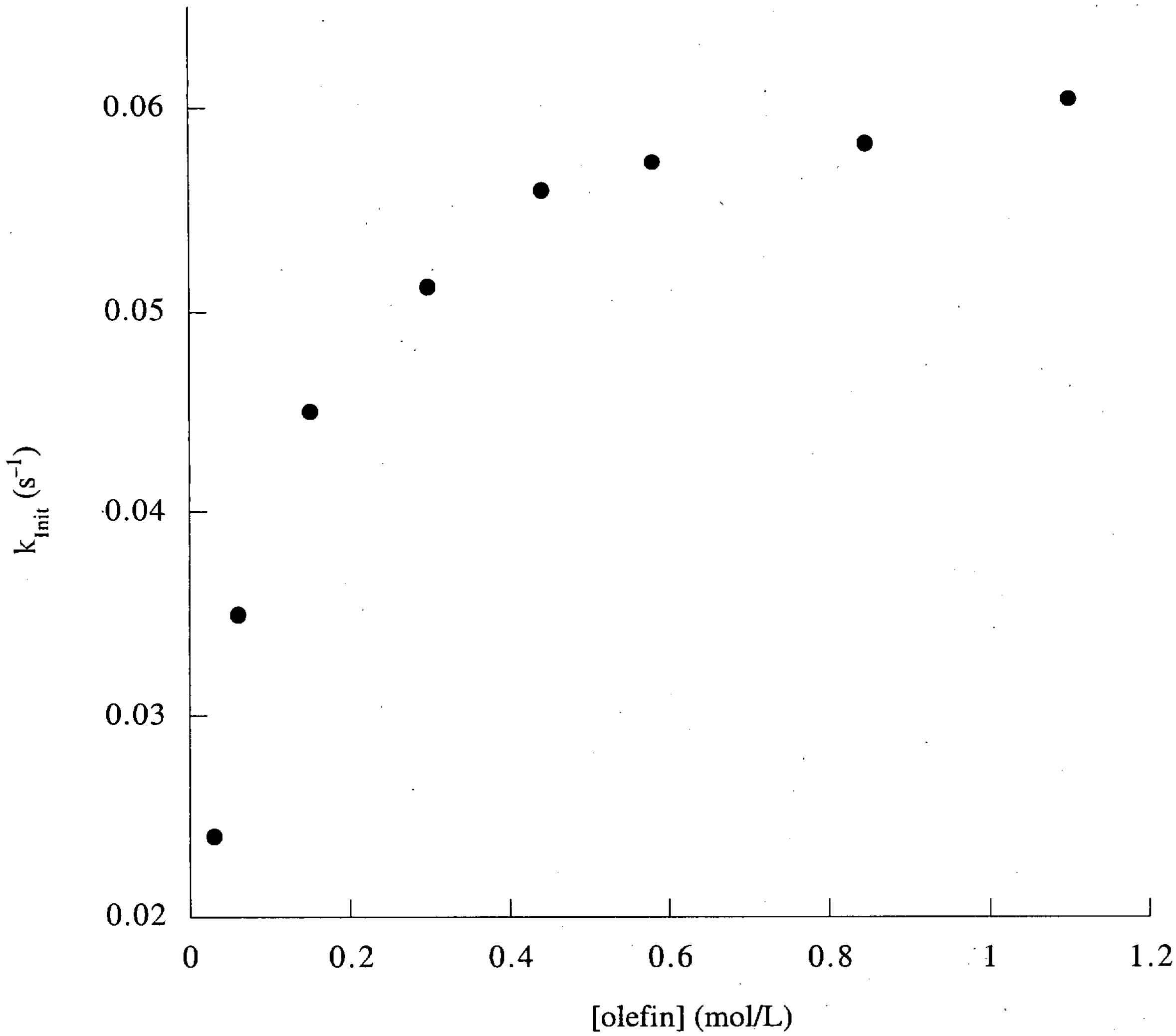

Figure S13. k_{Init} versus [olefin] for Catalyst 5.

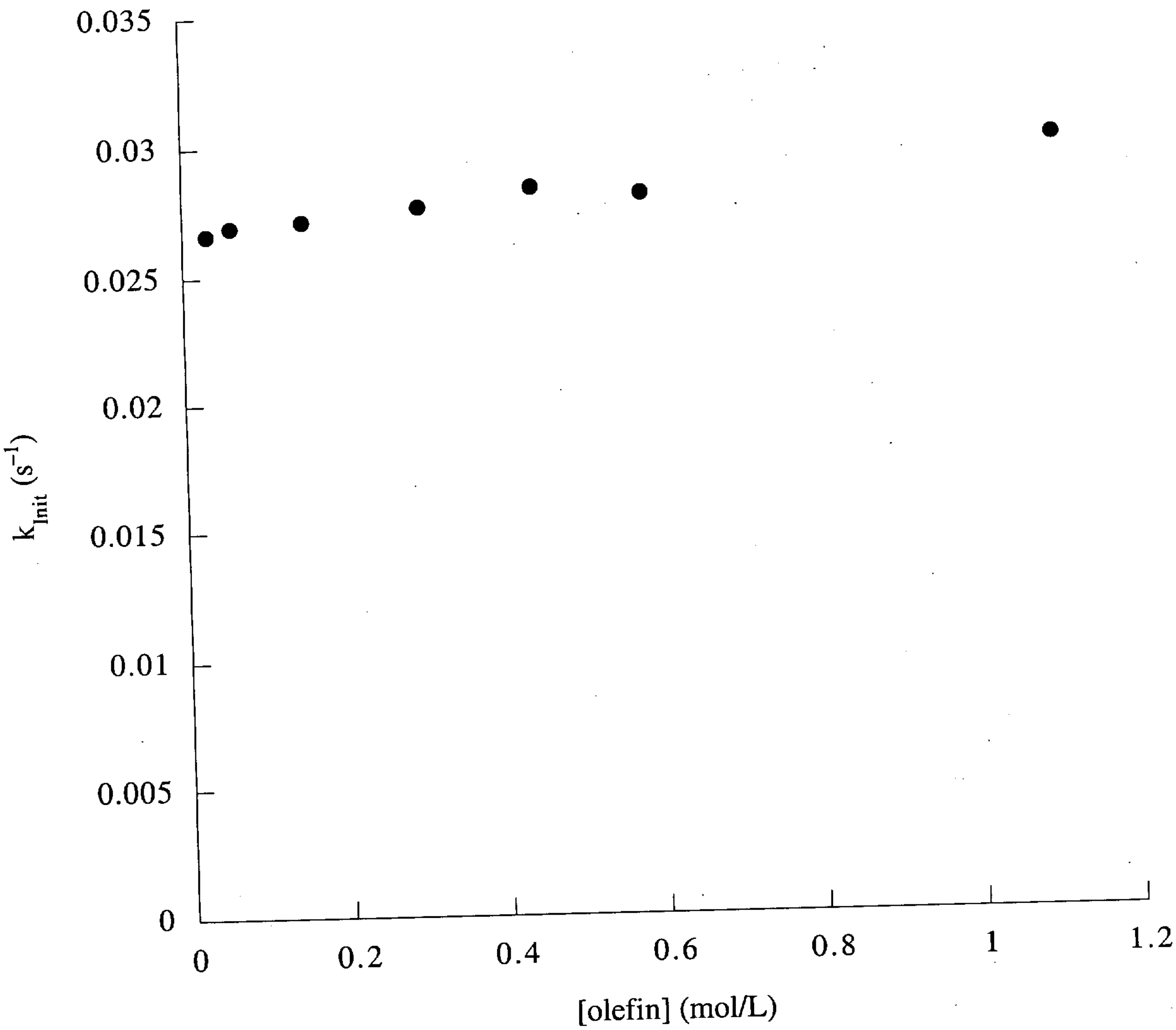

Figure S14. k_{Init} versus [olefin] for Catalyst 7.

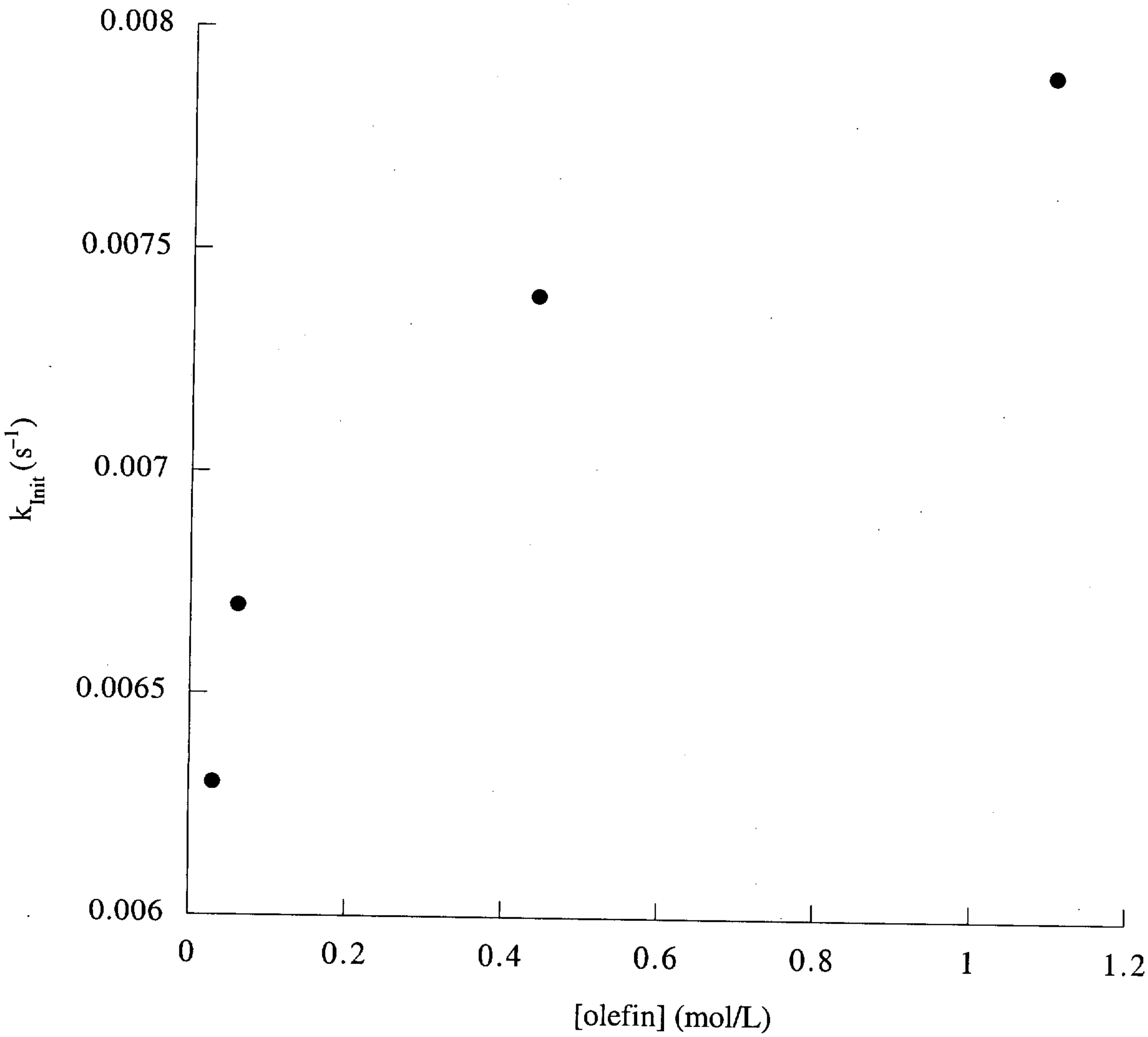

Figure S15. $1/k_{obs}$ versus $[PCy_3]/[Olefin]$ for Catalyst 1

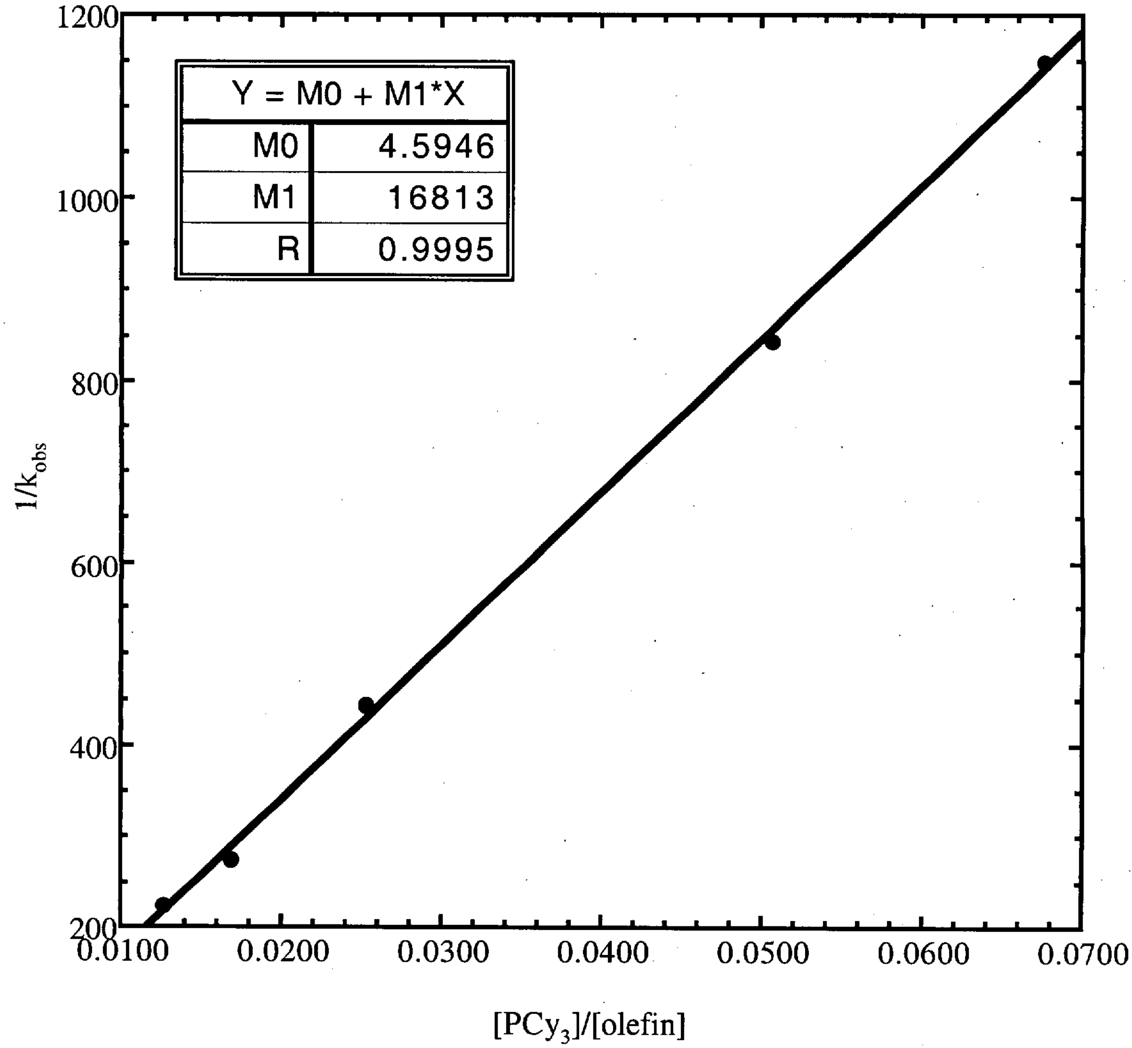

Figure S16. $1/k_{obs}$ versus $[PCy_3]/[Olefin]$ for Catalyst 2

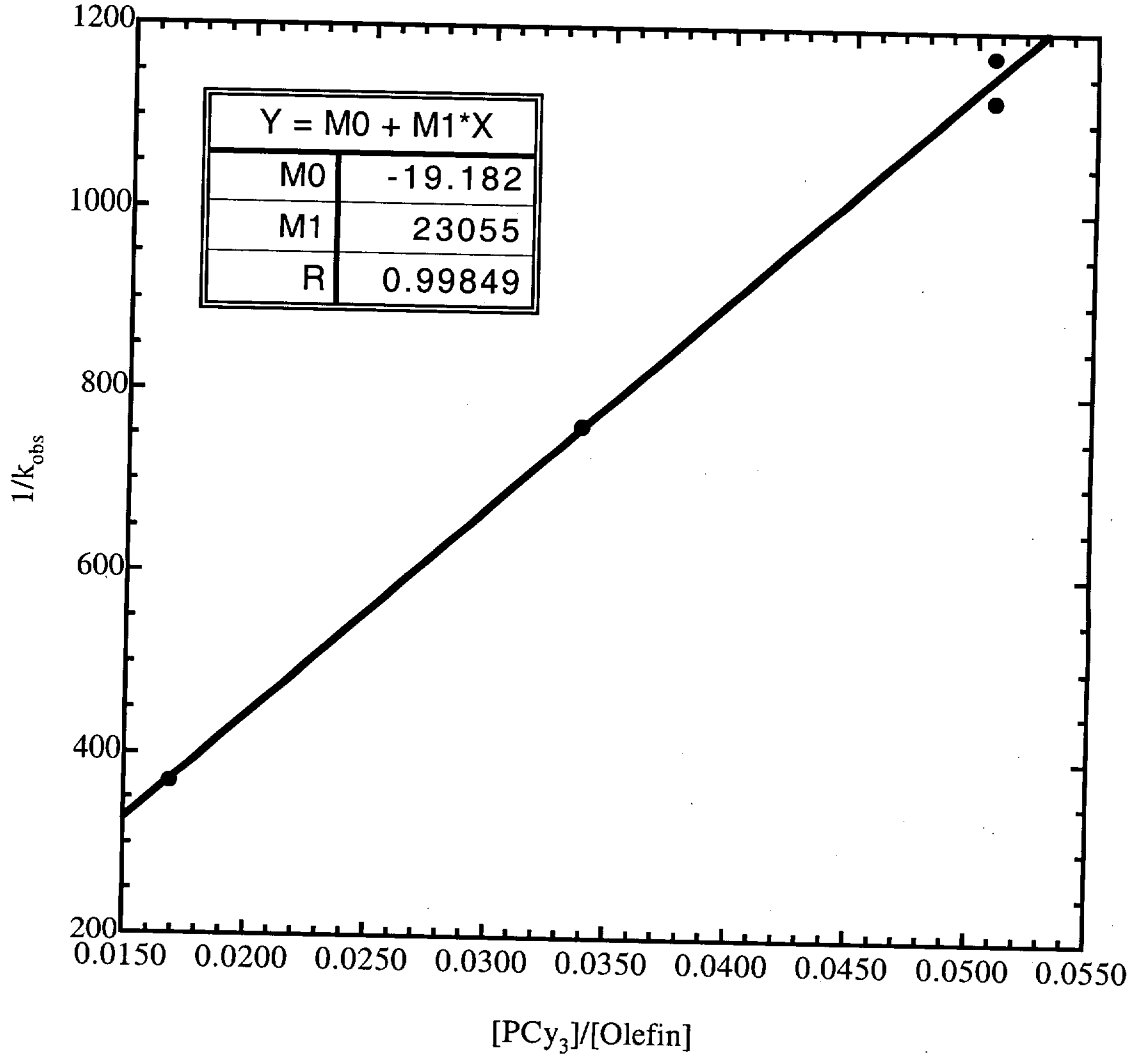

Figure S17. $1/k_{obs}$ versus $[PCy_3]/[Olefin]$ for Catalyst 3

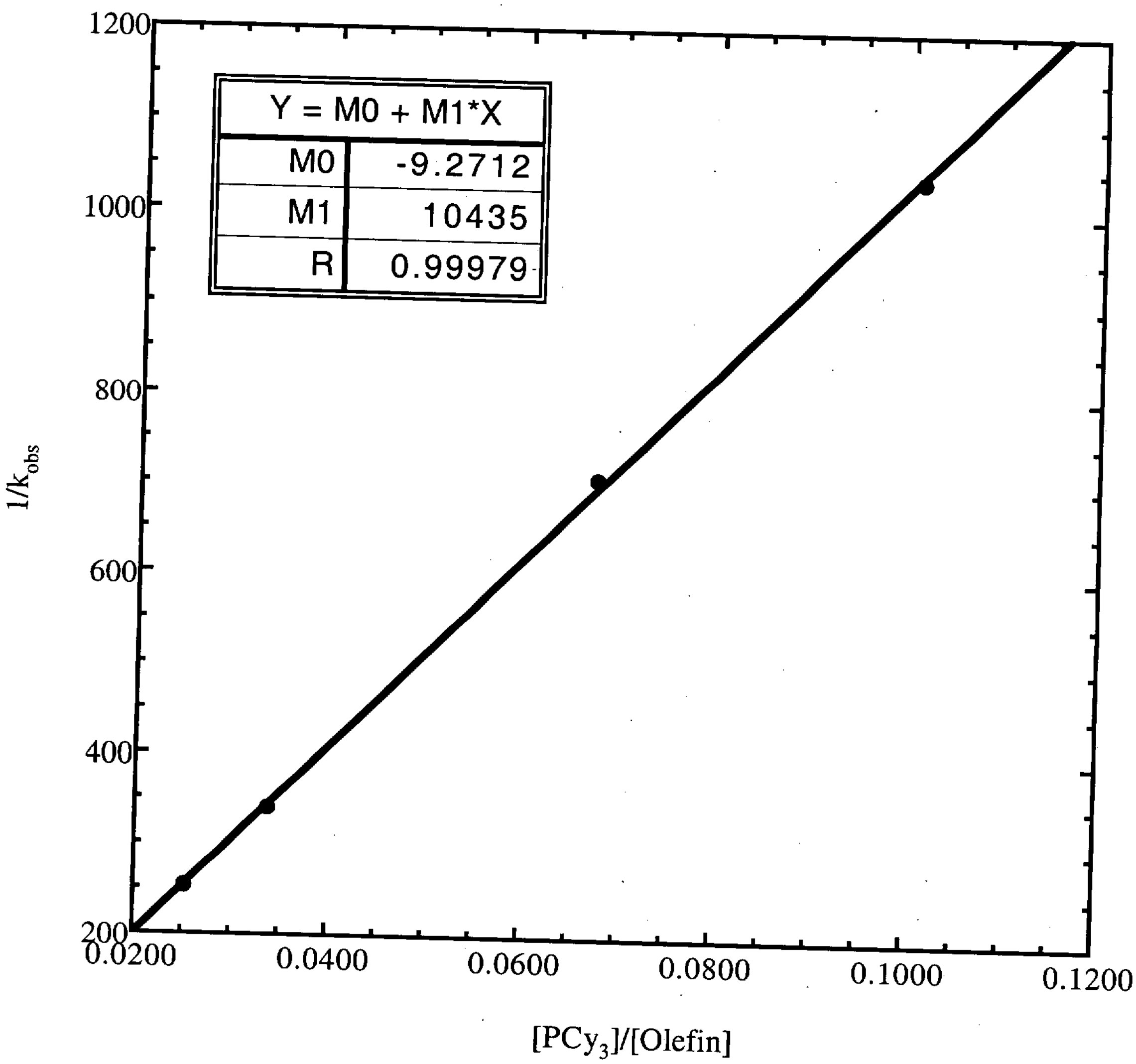

Figure S18. $1/k_{obs}$ versus $[PCy_3]/[Olefin]$ for Catalyst 6

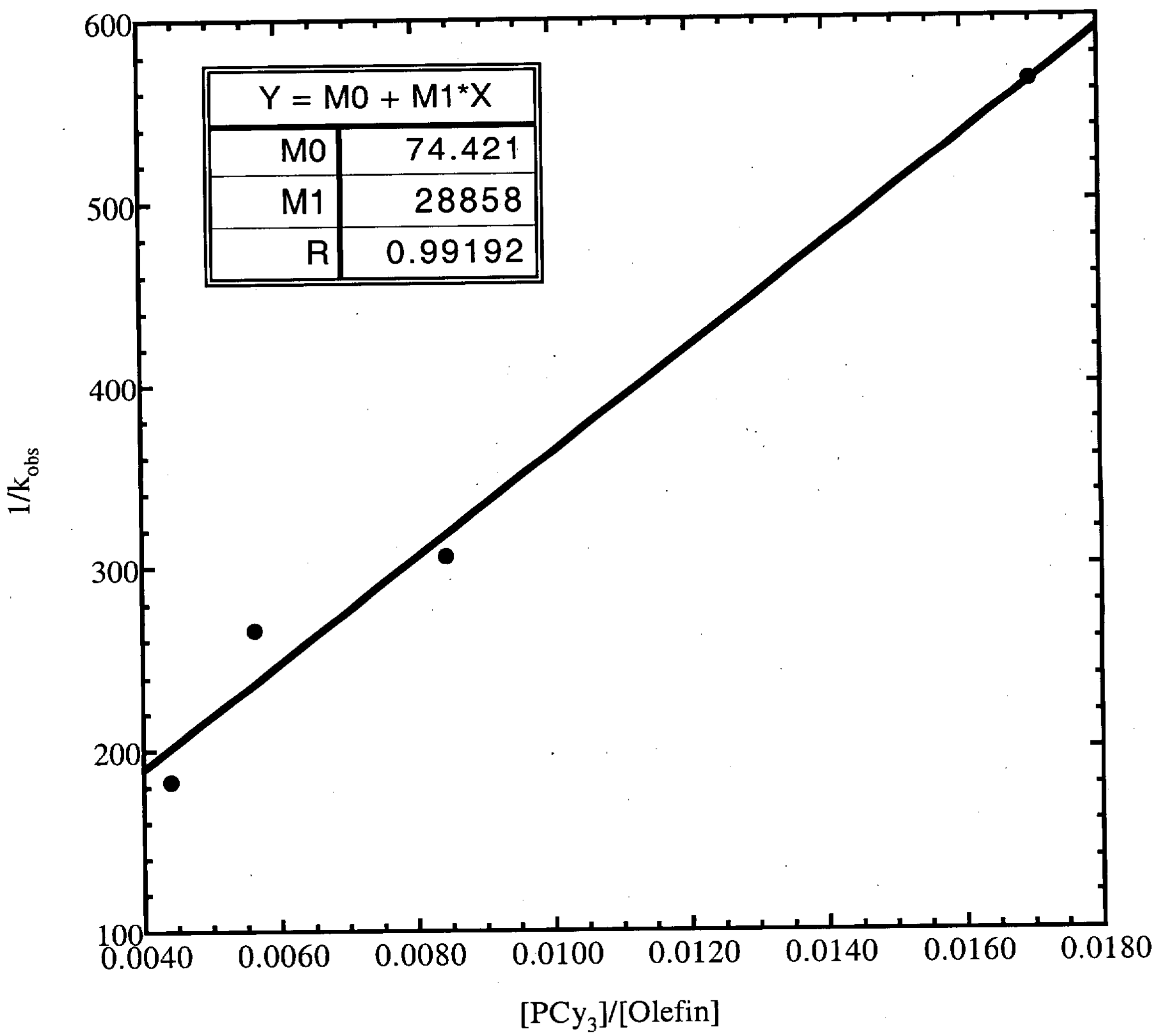

Figure S19. $1/k_{obs}$ versus $[PCy_3]/[Olefin]$ for Catalyst 8

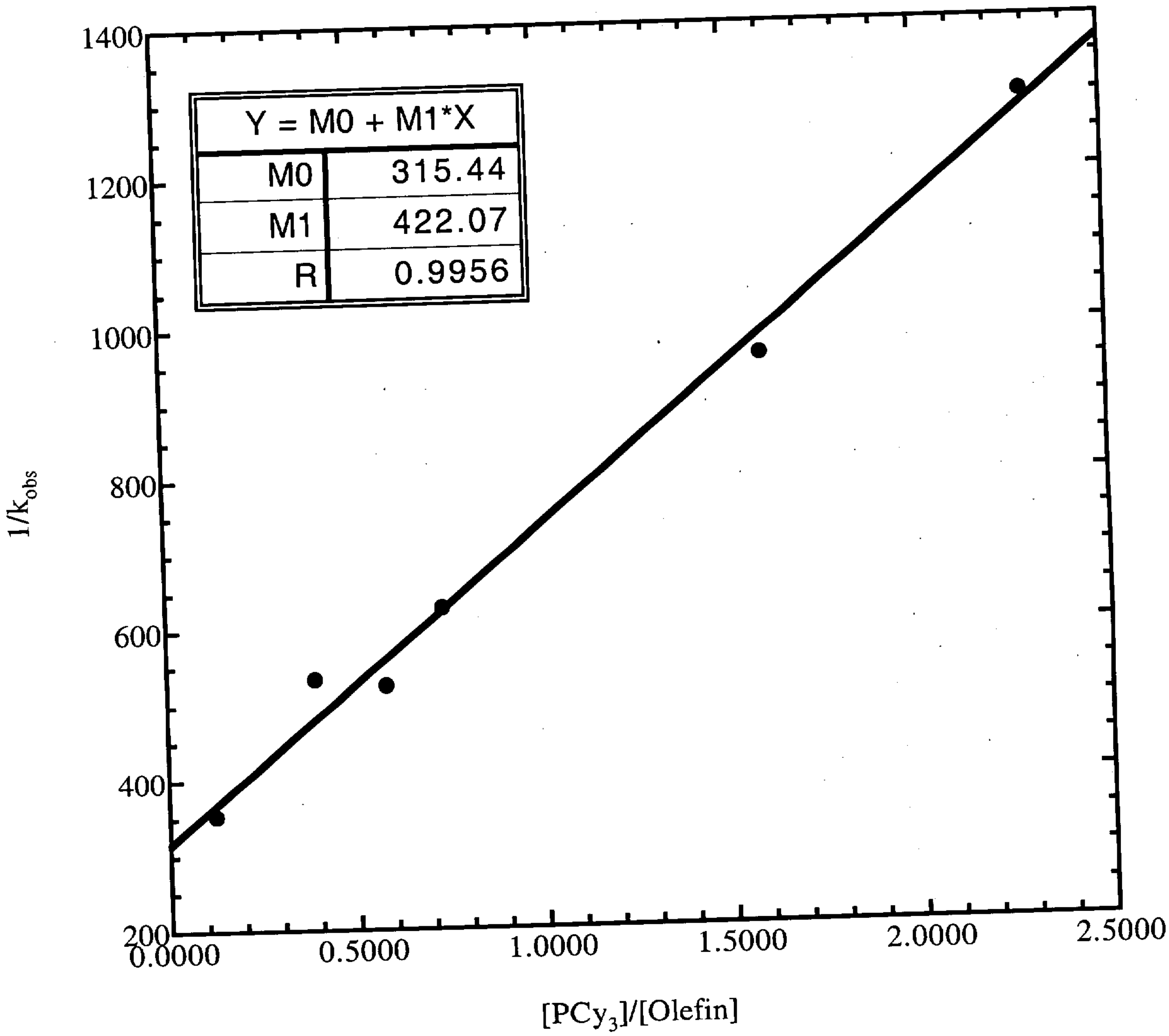

Figure S20. $1/k_{obs}$ versus $[PCy_3]$/[olefin]for Catalyst 10

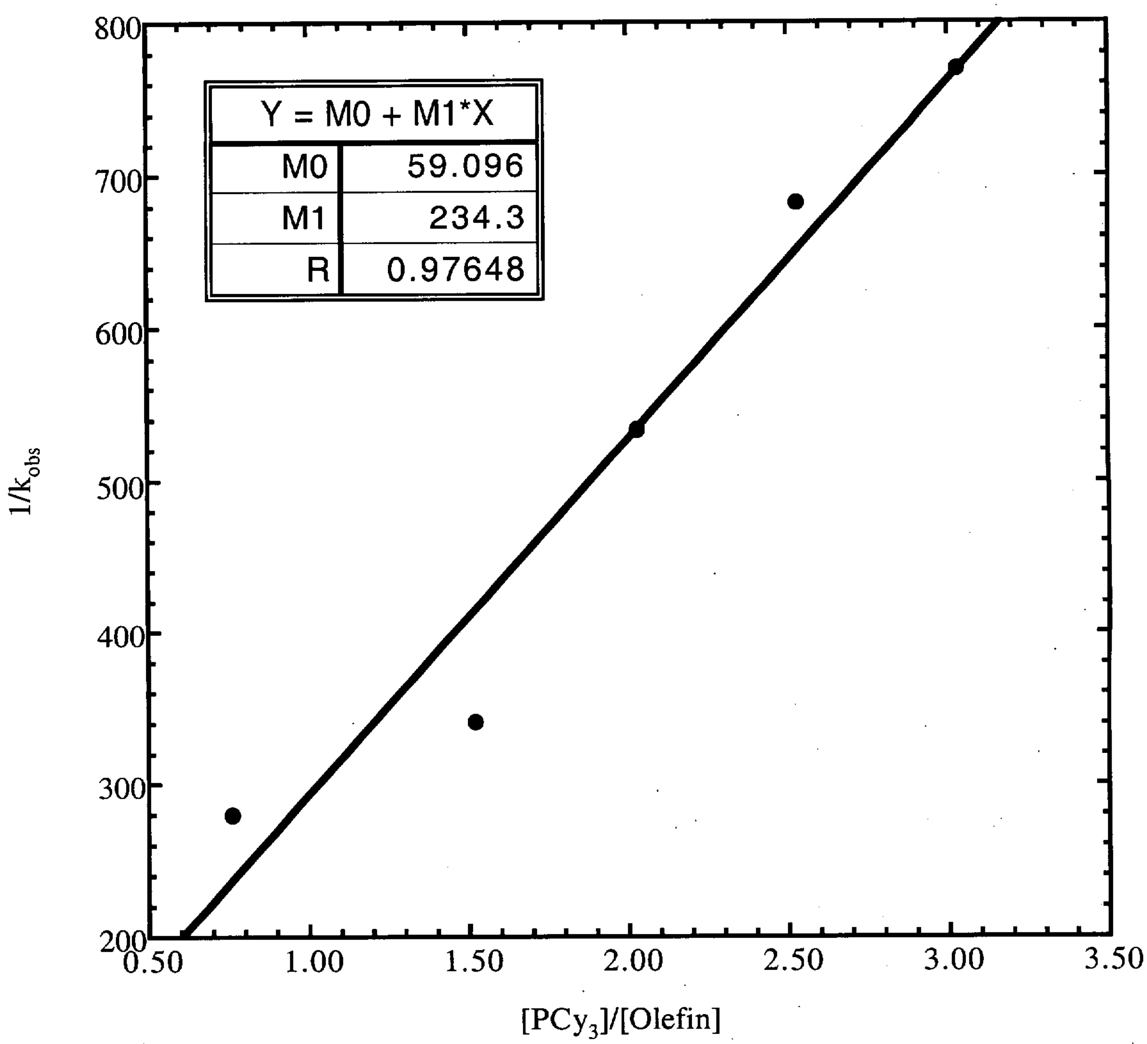

Figure S21. $1/k_{obs}$ versus $[PPh_3]/[Olefin]$ for Catalyst 11

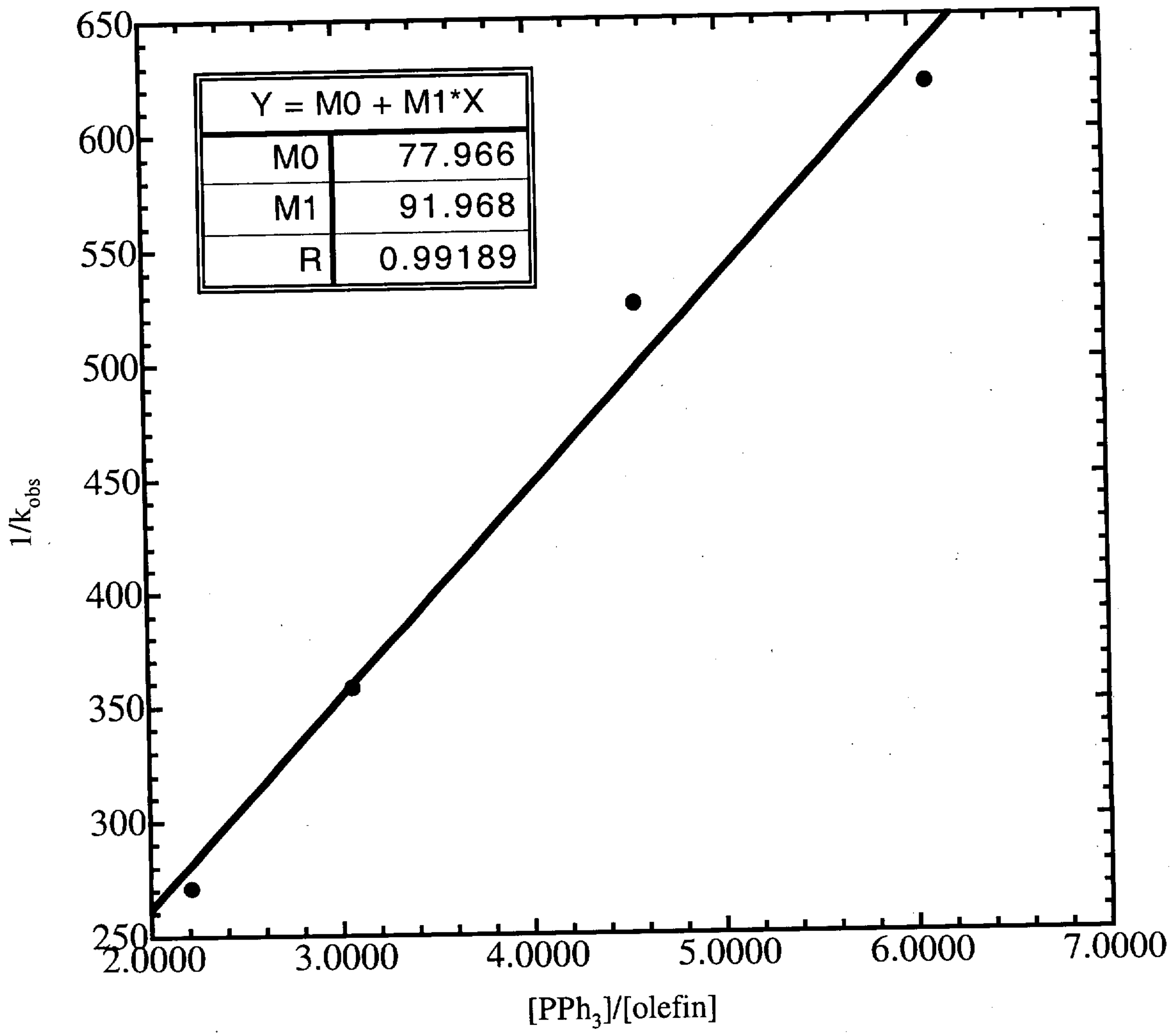

Figure S22. $1/k_{obs}$ versus $[PBn_3]/[Olefin]$ for Catalyst 12