Supplementary Material for Synthesis, Characterisation and Protonation Studies of [(triphos)Fe(CO)H_2]

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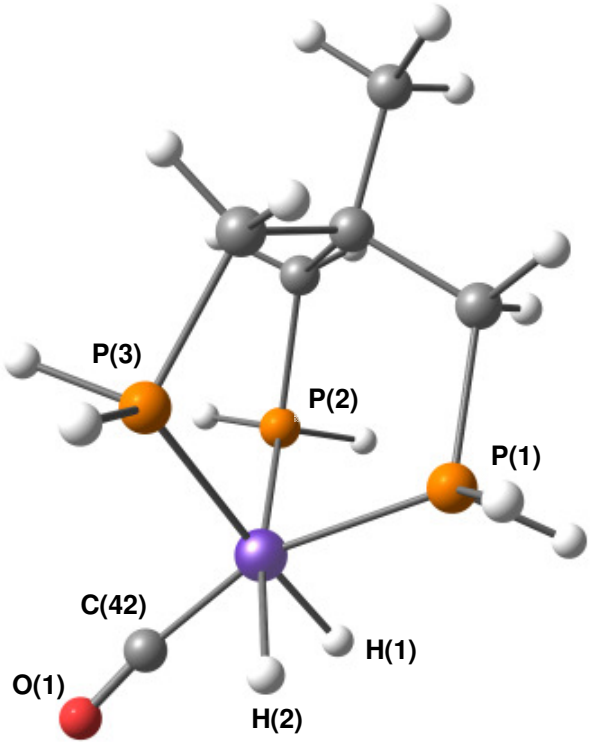


Figure S1. DFT structure of [(triphos′)Fe(CO)H_2] (**1'**) calculated at the B3LYP level of theory with a 6-31G(d,p) basis set. Selected bond lengths (in Å): Fe–H(1) 1.52, Fe–H(2) 1.52. Fe–P(1) 2.190, Fe–P(2) 2.185, Fe–P(3) 2.188. Selected angles (in degrees): H(1)–Fe–H(2) 84.5, C(42)–Fe–H(1) 81.3, C(42)–Fe–H(2) 81.3, Fe–C(42)–O(1) 173.9, P(3)–Fe–H(1) 175.1, P(2)–Fe–H(2) 172.1, P(1)–Fe–C(42) 161.2.

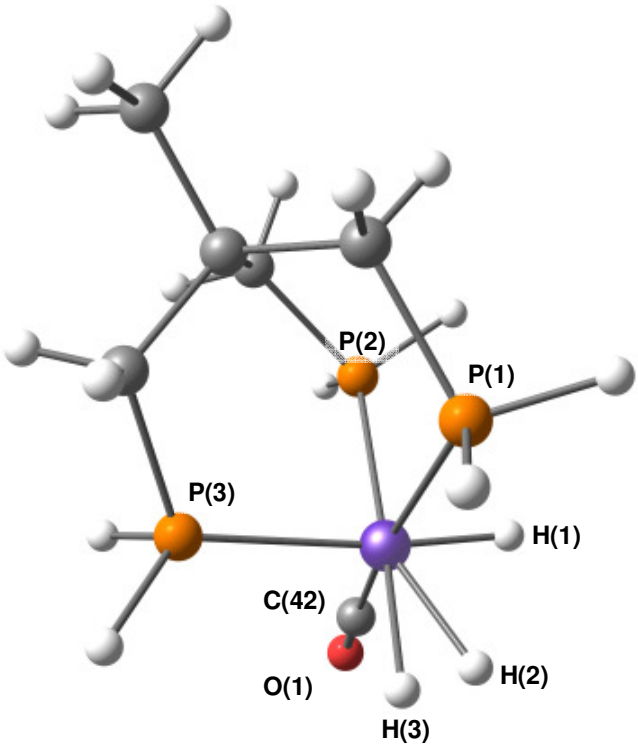
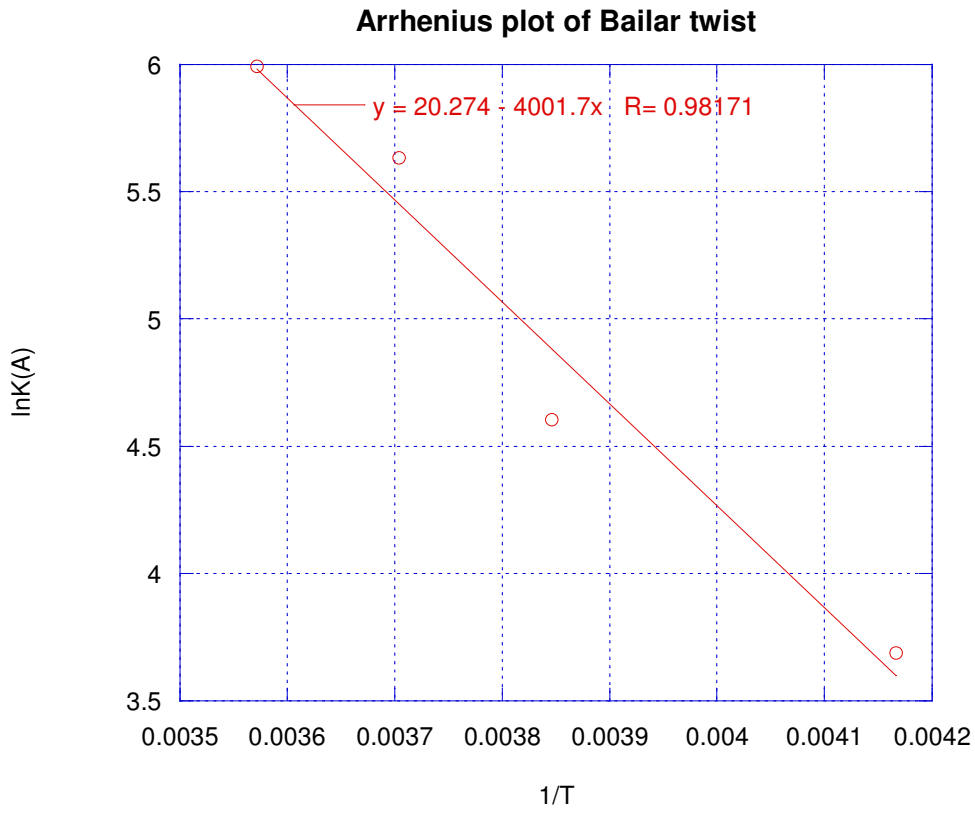


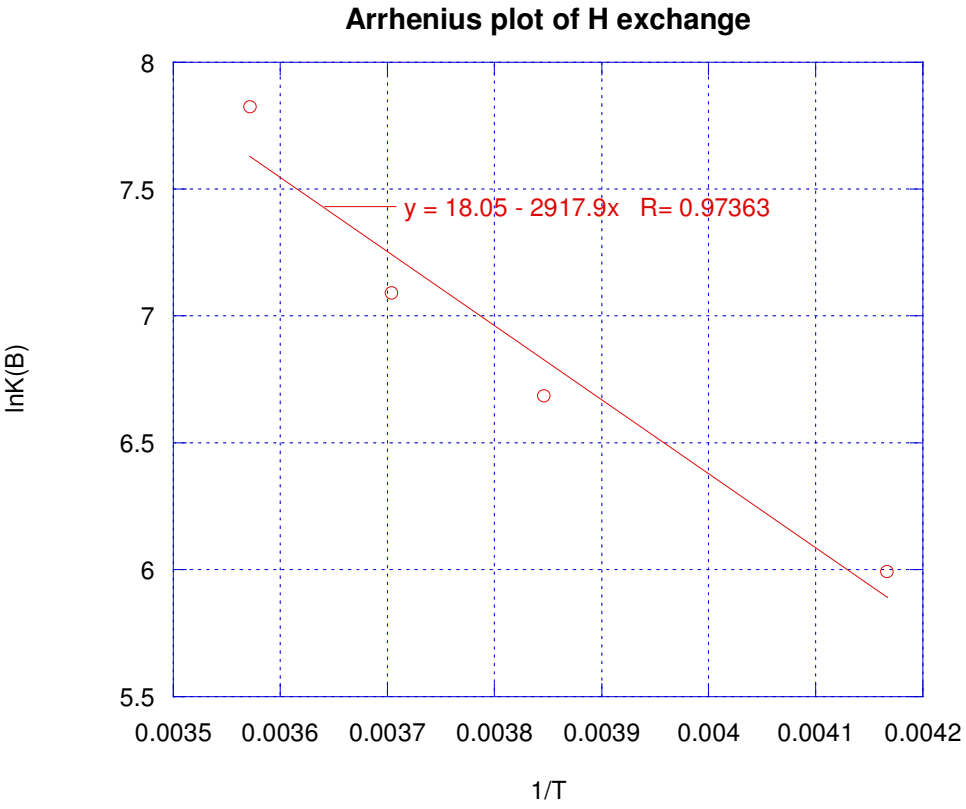
Figure S2. DFT structure of [(triphos′)Fe(CO)(η^2-H_2)H]$^+$ (**2′**) calculated at the B3LYP level of theory with a 6-31G(d,p) basis set. Selected bond lengths (in Å): Fe–H(1) 1.51, Fe–H(2) 1.59, Fe-H(3) 1.62, H(1)-H(2) 1.74, H(2)-H(3) 0.85, Fe–P(1) 2.323, Fe–P(2) 2.235, Fe–P(3) 2.274. Selected angles (in degrees): H(1)–Fe–H(2) 68.6, H(1)–Fe–H(3) 99.2, H(2)–Fe–H(3) 30.6, C(42)–Fe–H(1) 84.9, C(42)–Fe–H(2) 89.0, C(42)–Fe–H(3) 90.6, Fe–C(42)–O(1) 176.2, P(3)–Fe–H(1) 173.4, P(2)–Fe–H(2) 152.8, P(2)–Fe–H(3) 174.8, P(1)–Fe–C(42) 169.6.

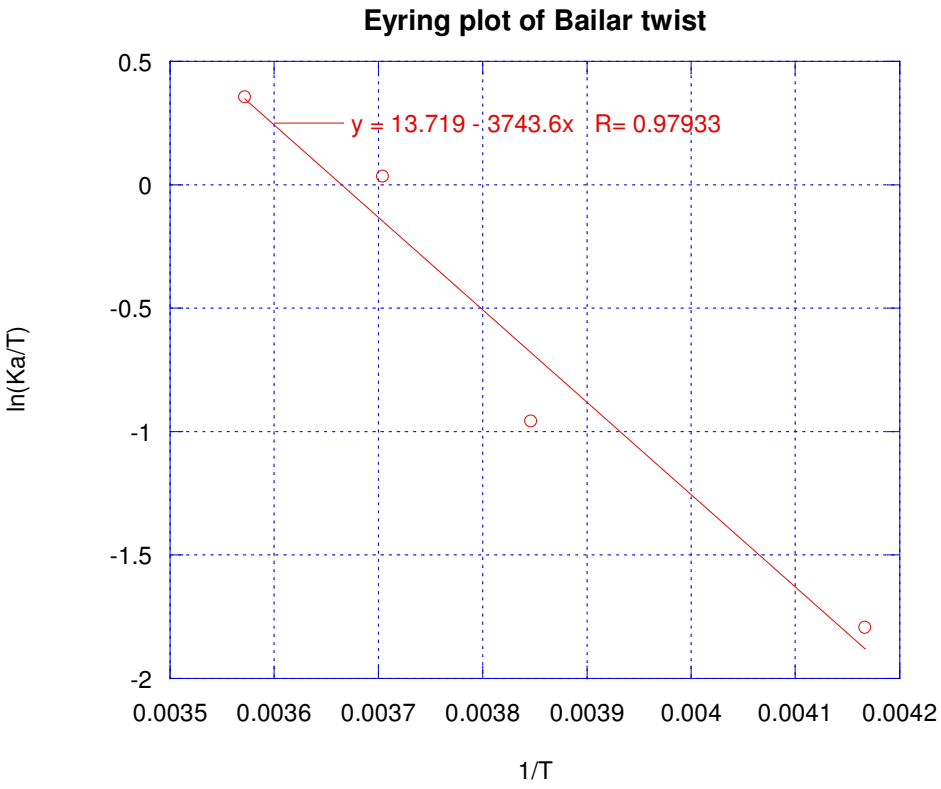
Arrhenius and Eyring Plots for Processes A and B in the ^{1}H NMR Spectrum of Complex 1

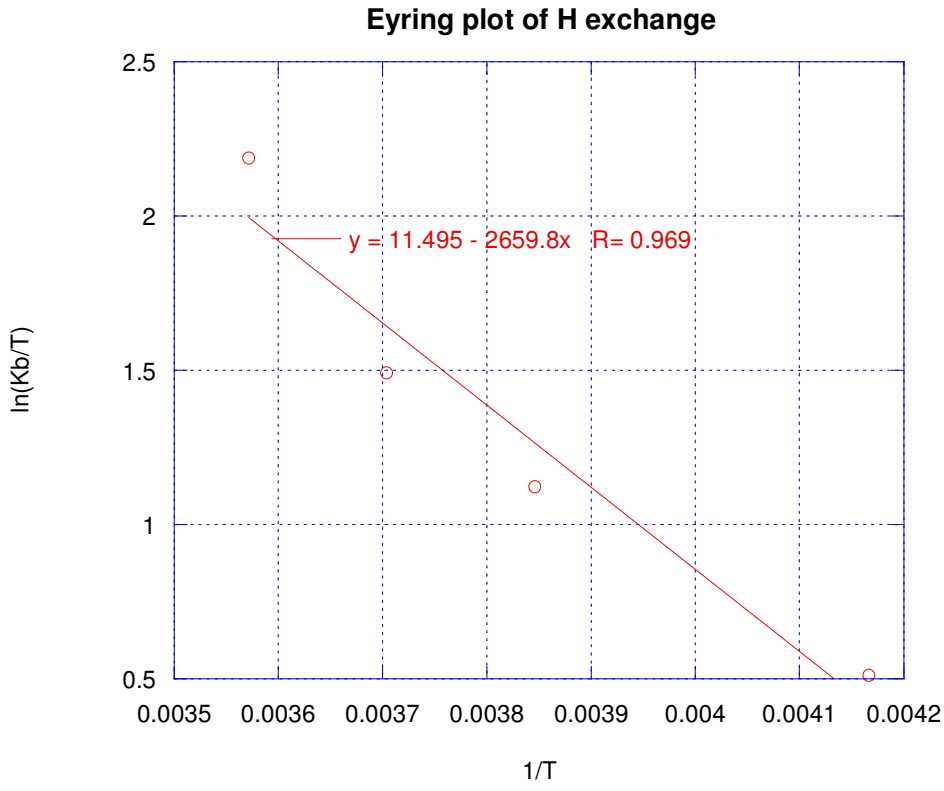
Data for Processes A and B

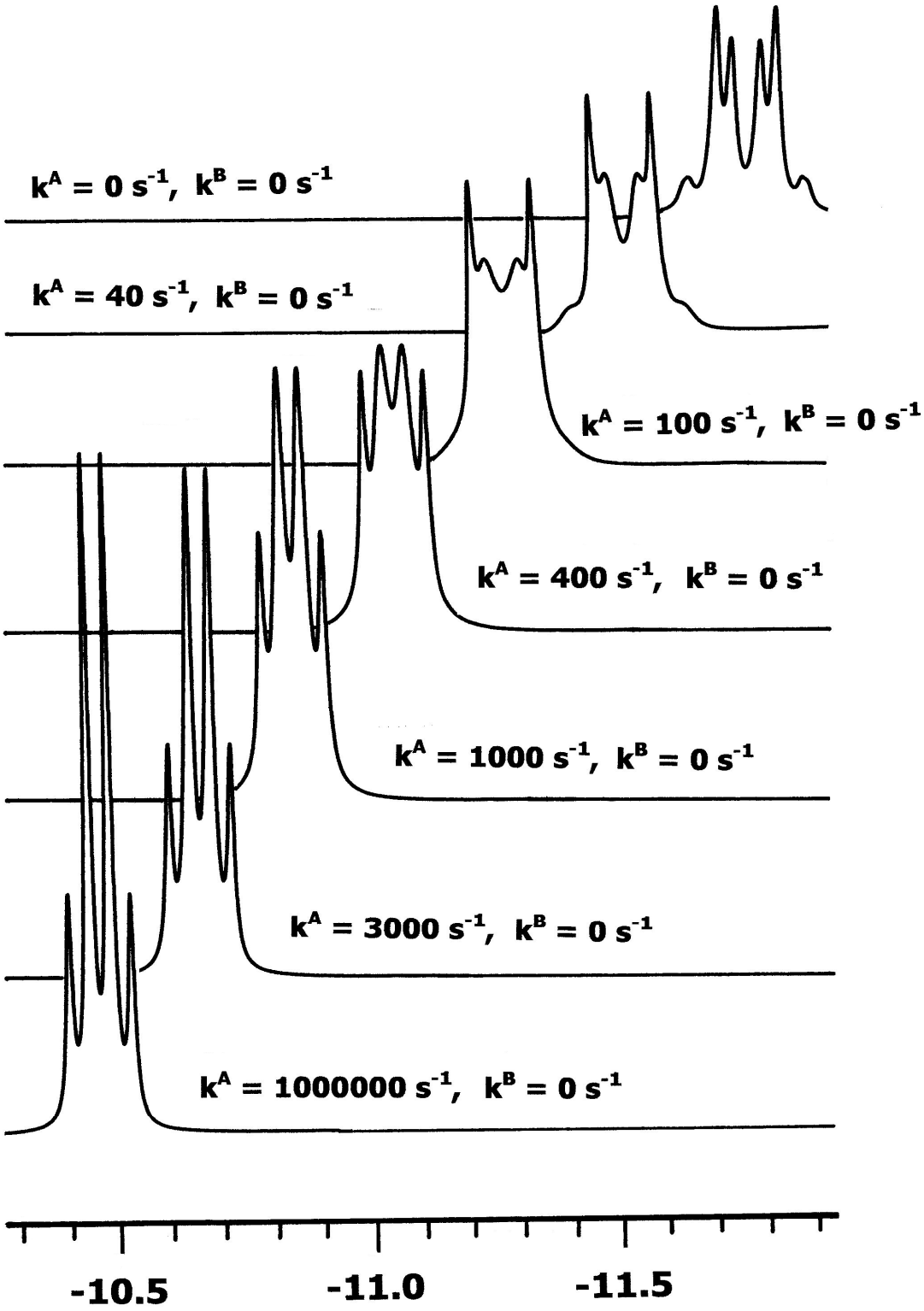
T	K(A)	K(B)	lnK(A)	lnK(B)	$\ln(K_A/T)$	$\ln(K_B/T)$	1/T
280	400	2500	5.9915	7.824	0.35667	2.1893	0.003571
270	280	1200	5.6348	7.0901	0.036368	1.4917	0.003704
260	100	800	4.6052	6.6846	-0.95551	1.1239	0.003846
240	40	400	3.6889	5.9915	-1.7918	0.51083	0.004167


Arrhenius plot of Bailar twist
y = 20.274 - 4001.7x R= 0.98171
lnK(A)
1/T
6
5.5
5
4.5
4
3.5
0.0035
0.0036
0.0037
0.0038
0.0039
0.004
0.0041
0.0042

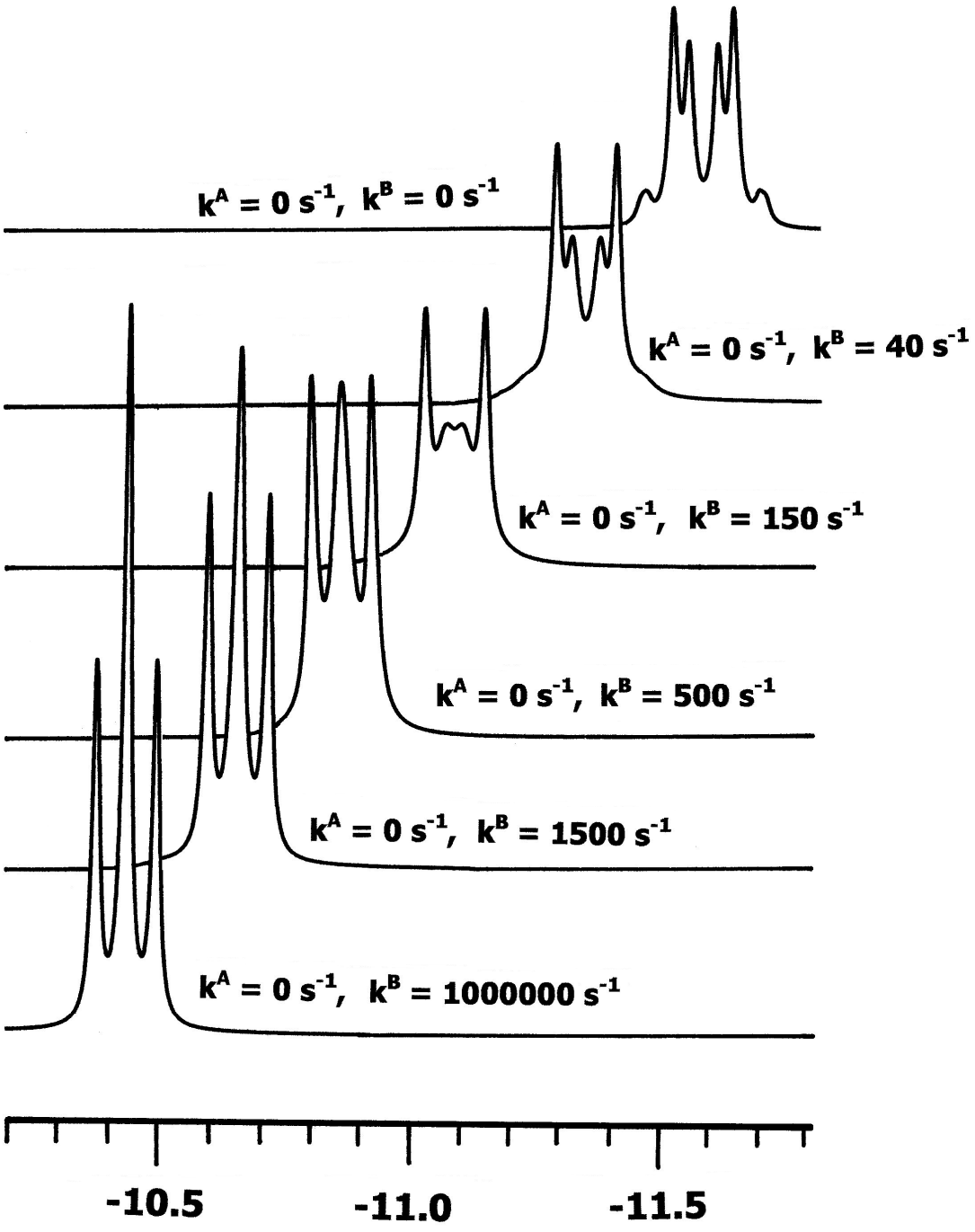

Arrhenius plot of H exchange
y = 18.05 - 2917.9x R= 0.97363
lnK(B)
1/T
8
7.5
7
6.5
6
5.5
0.0035
0.0036
0.0037
0.0038
0.0039
0.004
0.0041
0.0042







Simulated ^{1}H-NMR spectra for 1 based on Bailar rotation mechanism A with rotation of the $Fe(CO)H_2$ group with respect to the triphos ligand (rate of process A/s^{-1} = k^A).



Simulated ^{1}H-NMR spectra of 1 based on mechanism B with pairwise exchange of the two hydride ligands with the Fe(triphos)(CO) group remaining rigid (rate of process B/s^{-1} = k^B).