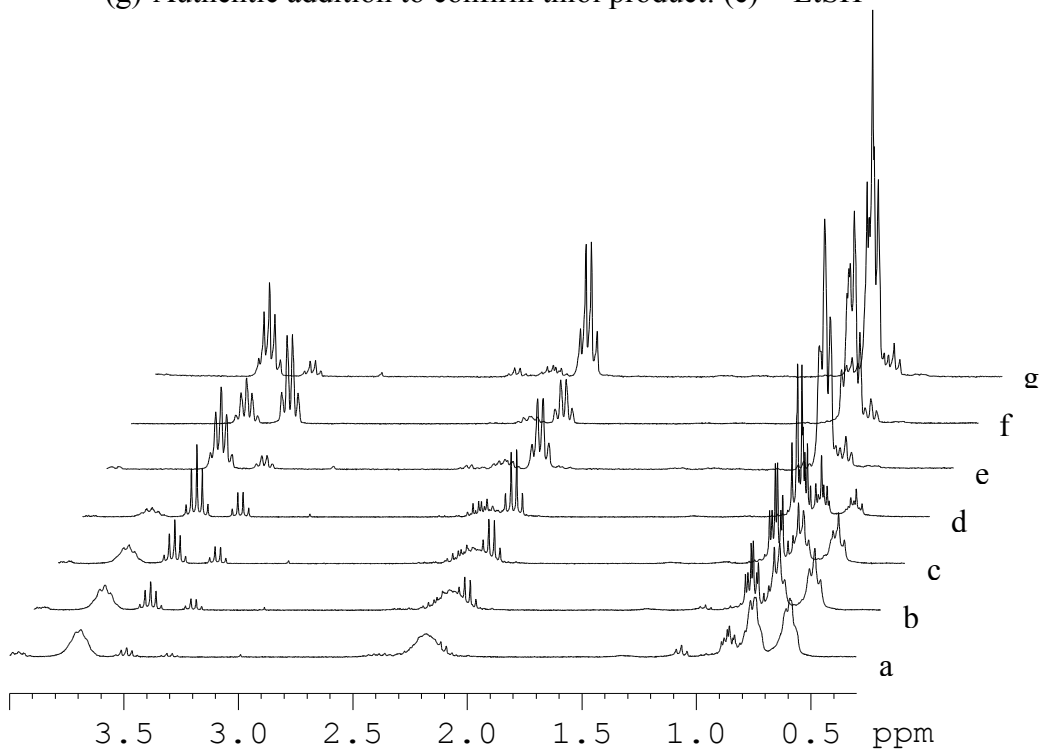


SUPPORTING INFORMATION

S1: ^1H NMR of DEPP alkaline hydrolysis (0.1 M NaOH in D_2O) showing the production of both EtOH (quartet at 3.4 ppm) and EtSH (quartet at 2.2 ppm)

- (a) 10°C , $t=0$ min
- (b) 10°C , $t=20$ min
- (c) 10°C , $t=100$ min
- (d) 20°C , $t=280$ min
- (e) 20°C , $t=8$ days
- (f) Authentic addition to confirm alcohol product: (e) + EtOH
- (g) Authentic addition to confirm thiol product: (e) + EtSH



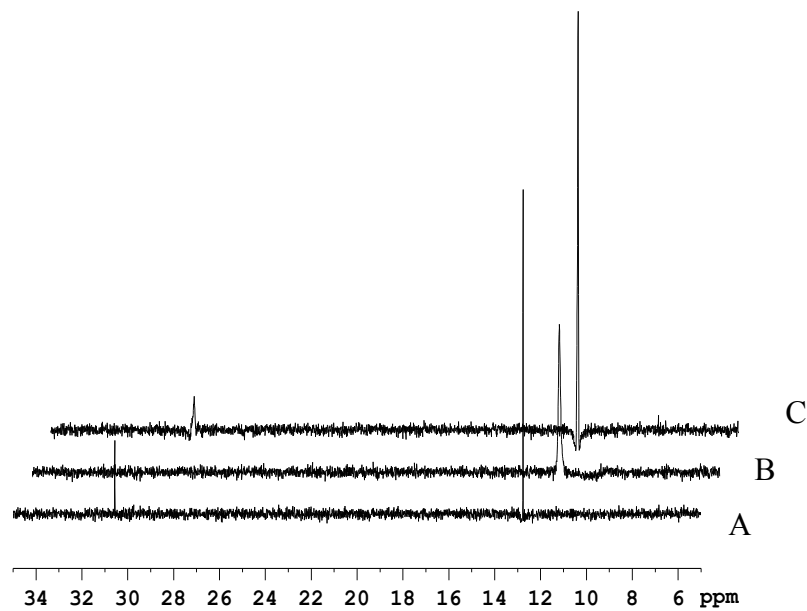


Figure S2: Stacked ^{31}P NMR confirming only P-S cleavage in the hydrolysis of DEPP, 25 °C. (A) DEPP in 0.1 M NaOH with both P-S and P-O scission products at 13 and 31.5 ppm respectively. (B) DEPP with Cp_2MoCl_2 in MOPS (pH 7.2)/THF buffer with only one signal at 12 ppm; last spectrum from Fig 2. (C) Combined samples from (A) and (B) showing only one enhanced the upfield signal at 12 ppm.

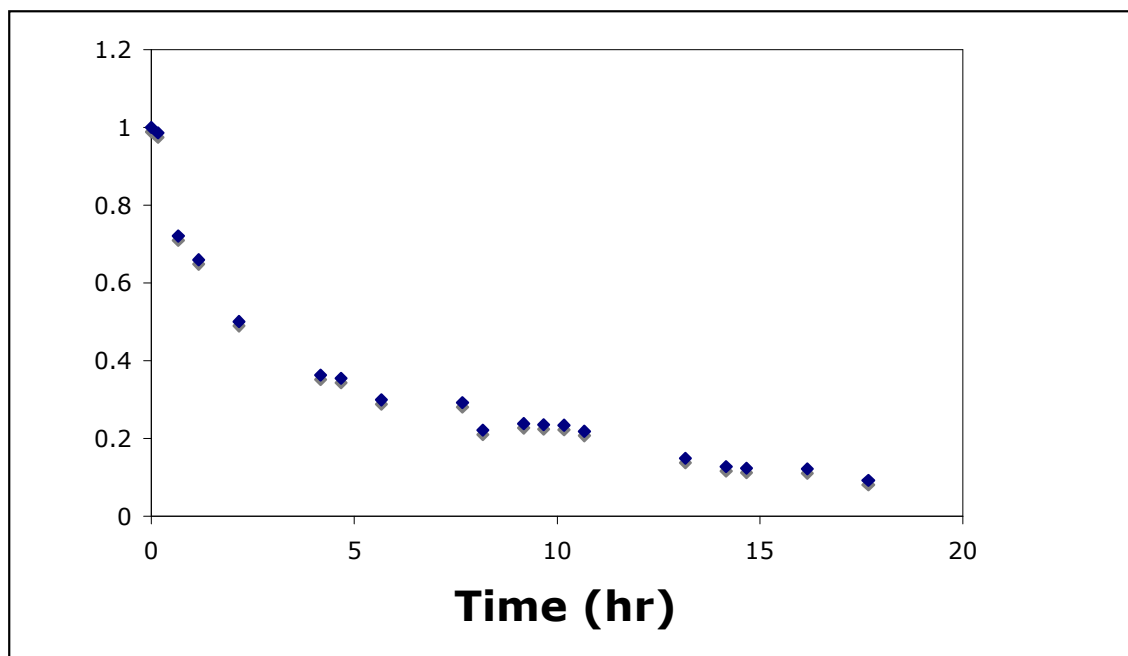
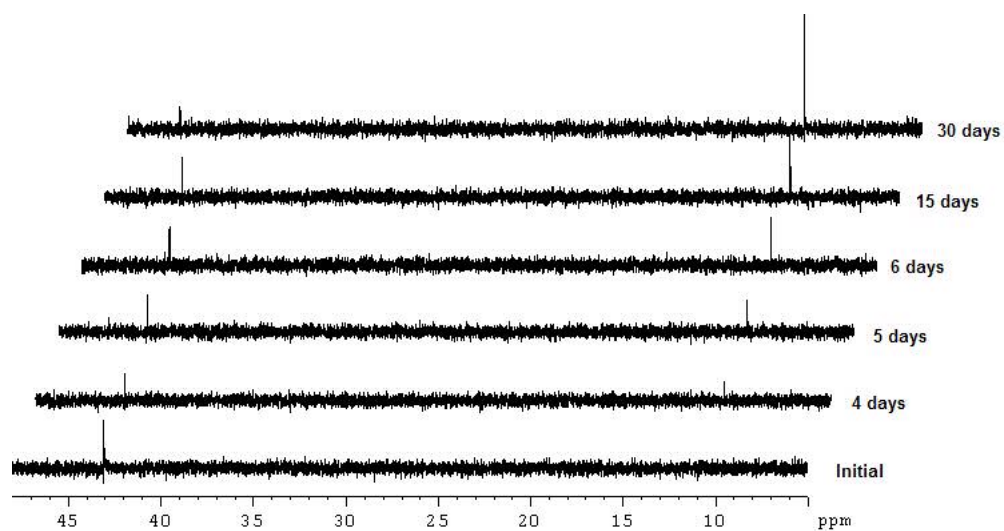


Figure S3: Kinetics plot of DEPP hydrolysis by Cp_2MoCl_2 at 35 °C used in the Arrhenius plot in Figure 4.



S4: ^{31}P NMR of DEPP (17 mM) + *ansa*-CMe₂-Cp₂MoCl₂ (33 mM) in 135 mM mM MOPS (pH 7.2) and THF

TABLE I
Bond Lengths and Angles for Cp₂Mo(SEt)₂

Mo(1)-C(3)	2.294(4)
Mo(1)-C(3)#1	2.294(4)
Mo(1)-C(2)	2.312(3)
Mo(1)-C(2)#1	2.312(3)
Mo(1)-C(4)	2.312(4)
Mo(1)-C(4)#1	2.312(4)
Mo(1)-C(5)	2.356(4)
Mo(1)-C(5)#1	2.356(4)
Mo(1)-C(1)	2.371(3)
Mo(1)-C(1)#1	2.371(3)
Mo(1)-S(1)#1	2.4725(9)
Mo(1)-S(1)	2.4725(9)
S(1)-C(6)	1.827(4)
C(1)-C(5)	1.383(5)
C(1)-C(2)	1.401(5)
C(1)-H(1)	0.95(4)
C(2)-C(3)	1.417(5)
C(2)-H(2)	0.83(3)
C(3)-C(4)	1.406(5)
C(3)-H(3)	0.84(3)
C(4)-C(5)	1.403(6)
C(4)-H(4)	0.81(4)
C(5)-H(5)	0.97(3)
C(6)-C(7)	1.510(5)
C(6)-H(6A)	0.95(4)
C(6)-H(6B)	0.94(3)
C(7)-H(7A)	0.96(4)
C(7)-H(7B)	0.97(4)
C(7)-H(7C)	0.92(4)
C(3)-Mo(1)-C(3)#1	145.4(2)
C(3)-Mo(1)-C(2)	35.84(13)
C(3)#1-Mo(1)-C(2)	152.53(13)

C(3)-Mo(1)-C(2)#1	152.53(13)
C(3)#1-Mo(1)-C(2)#1	35.84(13)
C(2)-Mo(1)-C(2)#1	165.18(19)
C(3)-Mo(1)-C(4)	35.55(14)
C(3)#1-Mo(1)-C(4)	110.84(16)
C(2)-Mo(1)-C(4)	58.41(14)
C(2)#1-Mo(1)-C(4)	136.26(14)
C(3)-Mo(1)-C(4)#1	110.84(16)
C(3)#1-Mo(1)-C(4)#1	35.55(14)
C(2)-Mo(1)-C(4)#1	136.26(14)
C(2)#1-Mo(1)-C(4)#1	58.41(14)
C(4)-Mo(1)-C(4)#1	79.3(2)
C(3)-Mo(1)-C(5)	58.90(14)
C(3)#1-Mo(1)-C(5)	98.27(14)
C(2)-Mo(1)-C(5)	57.78(14)
C(2)#1-Mo(1)-C(5)	134.01(14)
C(4)-Mo(1)-C(5)	34.97(14)
C(4)#1-Mo(1)-C(5)	81.62(14)
C(3)-Mo(1)-C(5)#1	98.27(14)
C(3)#1-Mo(1)-C(5)#1	58.90(14)
C(2)-Mo(1)-C(5)#1	134.01(14)
C(2)#1-Mo(1)-C(5)#1	57.78(14)
C(4)-Mo(1)-C(5)#1	81.62(14)
C(4)#1-Mo(1)-C(5)#1	34.97(14)
C(5)-Mo(1)-C(5)#1	102.4(2)
C(3)-Mo(1)-C(1)	58.76(13)
C(3)#1-Mo(1)-C(1)	117.78(13)
C(2)-Mo(1)-C(1)	34.79(12)
C(2)#1-Mo(1)-C(1)	147.57(13)
C(4)-Mo(1)-C(1)	57.56(13)
C(4)#1-Mo(1)-C(1)	113.61(13)
C(5)-Mo(1)-C(1)	34.03(12)
C(5)#1-Mo(1)-C(1)	135.89(14)
C(3)-Mo(1)-C(1)#1	117.78(13)
C(3)#1-Mo(1)-C(1)#1	58.76(13)
C(2)-Mo(1)-C(1)#1	147.57(13)

C(2)#1-Mo(1)-C(1)#1	34.79(12)
C(4)-Mo(1)-C(1)#1	113.61(13)
C(4)#1-Mo(1)-C(1)#1	57.56(13)
C(5)-Mo(1)-C(1)#1	135.89(14)
C(5)#1-Mo(1)-C(1)#1	34.03(12)
C(1)-Mo(1)-C(1)#1	169.87(18)
C(3)-Mo(1)-S(1)#1	122.31(10)
C(3)#1-Mo(1)-S(1)#1	86.06(11)
C(2)-Mo(1)-S(1)#1	86.83(10)
C(2)#1-Mo(1)-S(1)#1	81.57(10)
C(4)-Mo(1)-S(1)#1	134.47(10)
C(4)#1-Mo(1)-S(1)#1	120.37(12)
C(5)-Mo(1)-S(1)#1	103.06(10)
C(5)#1-Mo(1)-S(1)#1	139.08(10)
C(1)-Mo(1)-S(1)#1	77.03(9)
C(1)#1-Mo(1)-S(1)#1	111.27(9)
C(3)-Mo(1)-S(1)	86.06(11)
C(3)#1-Mo(1)-S(1)	122.31(10)
C(2)-Mo(1)-S(1)	81.57(10)
C(2)#1-Mo(1)-S(1)	86.83(10)
C(4)-Mo(1)-S(1)	120.37(12)
C(4)#1-Mo(1)-S(1)	134.47(10)
C(5)-Mo(1)-S(1)	139.08(10)
C(5)#1-Mo(1)-S(1)	103.06(10)
C(1)-Mo(1)-S(1)	111.27(9)
C(1)#1-Mo(1)-S(1)	77.03(9)
S(1)#1-Mo(1)-S(1)	76.91(4)
C(6)-S(1)-Mo(1)	108.24(13)
C(5)-C(1)-C(2)	108.2(3)
C(5)-C(1)-Mo(1)	72.4(2)
C(2)-C(1)-Mo(1)	70.27(19)
C(5)-C(1)-H(1)	123(2)
C(2)-C(1)-H(1)	129(2)
Mo(1)-C(1)-H(1)	120(2)
C(1)-C(2)-C(3)	108.7(3)
C(1)-C(2)-Mo(1)	74.9(2)

C(3)-C(2)-Mo(1)	71.4(2)
C(1)-C(2)-H(2)	124(2)
C(3)-C(2)-H(2)	128(2)
Mo(1)-C(2)-H(2)	117(2)
C(4)-C(3)-C(2)	106.1(4)
C(4)-C(3)-Mo(1)	72.9(2)
C(2)-C(3)-Mo(1)	72.8(2)
C(4)-C(3)-H(3)	127(3)
C(2)-C(3)-H(3)	127(3)
Mo(1)-C(3)-H(3)	121(2)
C(5)-C(4)-C(3)	109.0(3)
C(5)-C(4)-Mo(1)	74.3(2)
C(3)-C(4)-Mo(1)	71.5(2)
C(5)-C(4)-H(4)	131(3)
C(3)-C(4)-H(4)	120(3)
Mo(1)-C(4)-H(4)	116(3)
C(1)-C(5)-C(4)	108.1(4)
C(1)-C(5)-Mo(1)	73.6(2)
C(4)-C(5)-Mo(1)	70.8(2)
C(1)-C(5)-H(5)	129(2)
C(4)-C(5)-H(5)	123(2)
Mo(1)-C(5)-H(5)	120(2)
C(7)-C(6)-S(1)	111.4(3)
C(7)-C(6)-H(6A)	108(2)
S(1)-C(6)-H(6A)	110(2)
C(7)-C(6)-H(6B)	110(2)
S(1)-C(6)-H(6B)	108(2)
H(6A)-C(6)-H(6B)	110(3)
C(6)-C(7)-H(7A)	110(2)
C(6)-C(7)-H(7B)	110(2)
H(7A)-C(7)-H(7B)	110(3)
C(6)-C(7)-H(7C)	111(2)
H(7A)-C(7)-H(7C)	108(3)
H(7B)-C(7)-H(7C)	107(3)