

Table S1. Table of relative Gibbs Energies and Enthalpies (298 K, in kJ mol^{-1}) for the different proton-bound proline dimer isomers.

Structure	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP/ 6-311+G(3df,3pd)// B3LYP/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ MP2/ 6-311+G(3df,3pd)// B3LYP/6- 31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP/ 6-311+G(3df,3pd)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ MP2/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ MP2/ 6-311+G(3df,3pd)// MP2/6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP-D3/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP-D3/ 6-311+G(3df,3pd)// B3LYP-D3/ 6-31+G(d,p)
ZW1	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
ZW2	1.9(-0.1)	1.7(-1.4)	1.3(-0.7)	1.7(-0.4)	2.6(0.5)	1.8(-0.3)	1.7(-0.1)	1.7(-0.1)
ZW3	2.1(3.7)	2.0(3.6)	2.7(4.3)	-0.3(1.7)	1.6(3.6)	1.3(3.3)	4.8(3.5)	4.9(3.7)
ZW4	7.3(9.6)	7.3(9.6)	3.7(6.0)	7.4(9.7)	0.8(3.1)	0.6(2.8)	9.9(5.6)	9.8(5.5)
ZW5	2.3(3.0)	2.4(3.1)	4.9(5.6)	2.4(3.1)	4.0(4.7)	5.4(6.1)	5.2(4.7)	4.9(4.4)
ZW6	3.4(5.4)	3.3(5.2)	6.8(8.8)	3.2(5.2)	6.6(8.6)	7.8(9.8)	6.5(7.5)	6.5(7.5)
CS7	7.2(8.6)	4.9(6.4)	7.5(9.0)	4.9(6.3)	13.6(15.1)	8.0(9.4)	9.6(9.2)	11.6(11.1)
ZW8	9.9(9.8)	10.6(10.4)	9.5(9.3)	10.5(10.4)	6.1(5.9)	7.3(7.2)	10.7(7.6)	10.2(7.1)
CS9	8.1(10.8)	5.6(8.3)	9.7(12.4)	5.5(8.2)	15.6(18.3)	10.6(13.3)	12.4(12.1)	14.7(14.3)
ZW10	9.9(9.7)	10.6(10.4)	9.9(9.7)	10.7(10.4)	6.1(5.8)	7.4(7.1)	10.7(7.6)	10.2(7.1)
CS11	8.4(10.3)	5.8(7.6)	10.0(11.9)					
ZW12	8.7(11.9)	9.4(12.6)	10.0(13.3)					
CS13	7.4(11.0)	5.1(8.7)	10.2(13.7)					
CS14	8.6(10.8)	6.0(8.2)	10.4(12.6)					

CS15	11.2(12.3)	11.7(12.8)	10.5(11.6)					
CS16	7.4(11.7)	4.9(9.2)	11.0(15.3)					
ZW17	14.4(15.9)	14.8(16.3)	12.4(13.9)					
ZW18	12.1(13.0)	12.9(13.9)	15.2(16.2)					
ZW19	13.7(15.0)	14.6(16.0)						
ZW20	18.0(16.9)	19.2(18.1)						
ZW21	12.9(19.6)	13.8(20.8)						
ZW22	15.0(14.8)							
CS23	18.4(24.8)							
CS24	21.9(27.0)							
CS25	21.6(27.9)							
ZW26	21.6(27.9)							
CS27	22.0(29.3)							
CS28	22.2(27.1)							
CS29	23.5(27.2)							
CS30	24.0(28.8)							
ZW31	25.3(26.1)							
CS32	25.7(30.5)							

ZW33	25.8(29.4)							
ZW34	26.9(29.2)							
ZW35	30.1(28.4)							
ZW36	32.1(29.8)							
CS37	32.3(37.9)							
ZW38	35.1(32.3)							
ZW39	40.5(38.4)							
ZW40	42.6(42.0)							
ZW41	49.1(52.0)							
ZW42	55.6(51.9)							

Table S2. Table of relative Gibbs Energies and Enthalpies (298 K, in kJ mol⁻¹) for the different sodium-bound proline dimer isomers.

Structure	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP/ 6-311+G(3df,3pd)// B3LYP/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP/ 6-311+G(3df,3pd)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ MP2/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ MP2/ 6-311+G(3df,3pd)// MP2/6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP-D3/ 6-31+G(d,p)	$\Delta_{\text{rel}}G(\Delta_{\text{rel}}H)$ B3LYP-D3/ 6-311+G(3df,3pd)// B3LYP-D3/ 6-31+G(d,p)
ZW-CS1	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	3.4(5.8)	2.9(5.3)
ZW-ZW2	-1.0(-5.9)	1.6(-3.3)	1.6(-3.3)	-9.0(-13.9)	2.2(-0.6)	4.4(2.0)	1.5(-0.9)
ZW-CS3	1.9(3.8)	2.5(4.5)	0.6(2.5)	2.2(4.1)	3.6(5.5)	7.8(10.0)	7.2(9.5)
ZW-CS4	3.5(-0.8)	3.1(-1.2)	3.1(-1.2)	1.0(-3.3)	4.9(0.6)	0.0(0.0)	0.0(0.0)
ZW-CS5	2.9(-1.6)	3.6(-0.9)	1.6(-3.3)	1.0(-3.5)	1.9(-2.6)	2.0(2.7)	1.4(2.1)
ZW-CS6	6.1(0.4)	3.7(-1.9)	7.7(2.1)	4.2(-1.4)	8.1(2.5)	1.3(1.9)	1.5(2.1)
ZW-ZW7	1.3(-6.5)	3.8(-3.8)	3.8(-3.9)	-6.6(-14.4)	0.8(-6.9)	6.6(1.3)	3.8(-1.6)
ZW-ZW8	6.1(0.4)	4.9(-0.7)	8.2(2.8)	-3.0(-8.4)	6.0(0.5)	7.8(7.0)	4.7(3.9)
ZW-ZW9	2.5(-3)	5.3(-0.2)	7.5(2.0)	-3.7(-9.2)	5.3(-0.2)	2.3(-0.6)	2.5(-0.4)
ZW-CS10	6.8(1.5)	6.2(0.9)				7.6(4.0)	4.5(3.0)
ZW-CS11	7.4(6.3)	6.8(5.7)					
ZW-CS12	8.2(2.7)	7.9(2.4)	10.1(4.6)	7.1(1.6)	12.5(6.9)		
ZW-CS13	8.3(3.7)	8.0(3.4)					
ZW-CS14	9.3(4.8)	8.9(4.3)					

ZWZW15	6.5(0.9)	9.4(3.9)					
ZWZW16	8.0(1.6)	10.9(4.5)	13.1(6.7)	3.5(-2.8)	14.1(7.7)		
ZW-CS17	12.0(0.8)	11.2(0.0)					
CS-CS18	12.4(11.1)	11.5(10.1)					
CS-CS19	14.2(13.4)	13.1(12.2)					
CS-CS20	19.8(16.1)	16.3(12.7)					
ZW-CS21	19.7(16.0)	19.3(15.7)					
ZW-CS22	20.0(15.9)	19.6(15.5)					
CS-CS23	23.9(18.2)	19.9(14.1)					
ZW-CS24	23.2(19.3)	23.0(19.1)					
ZW-CS25	19.5(19.2)	23.1(19.1)					
ZW-CS26	28.0(24.6)	23.6(20.2)					
ZW-CS27	27.9(24.5)	24.0(20.7)					
CS-CS28	28.9(27.7)	26.6(25.5)					
ZW-CS29	32.0(33.7)	30.2(31.5)					
ZW-CS30	33.9(33.9)	31.6(31.6)					
ZW-CS31	31.2(28.5)	32.8(30.1)					
ZW-CS32	42.3(37.2)	39.3(34.2)					

CS-CS33	43.5(47.6)	40.3(44.4)						
ZW-CS34	46.9(48.3)	41.2(42.6)						
ZW-CS35	39.8(38.7)	41.6(40.5)						
ZW-CS36	40.3(38.6)	42.0(40.3)						

Figure S1a.

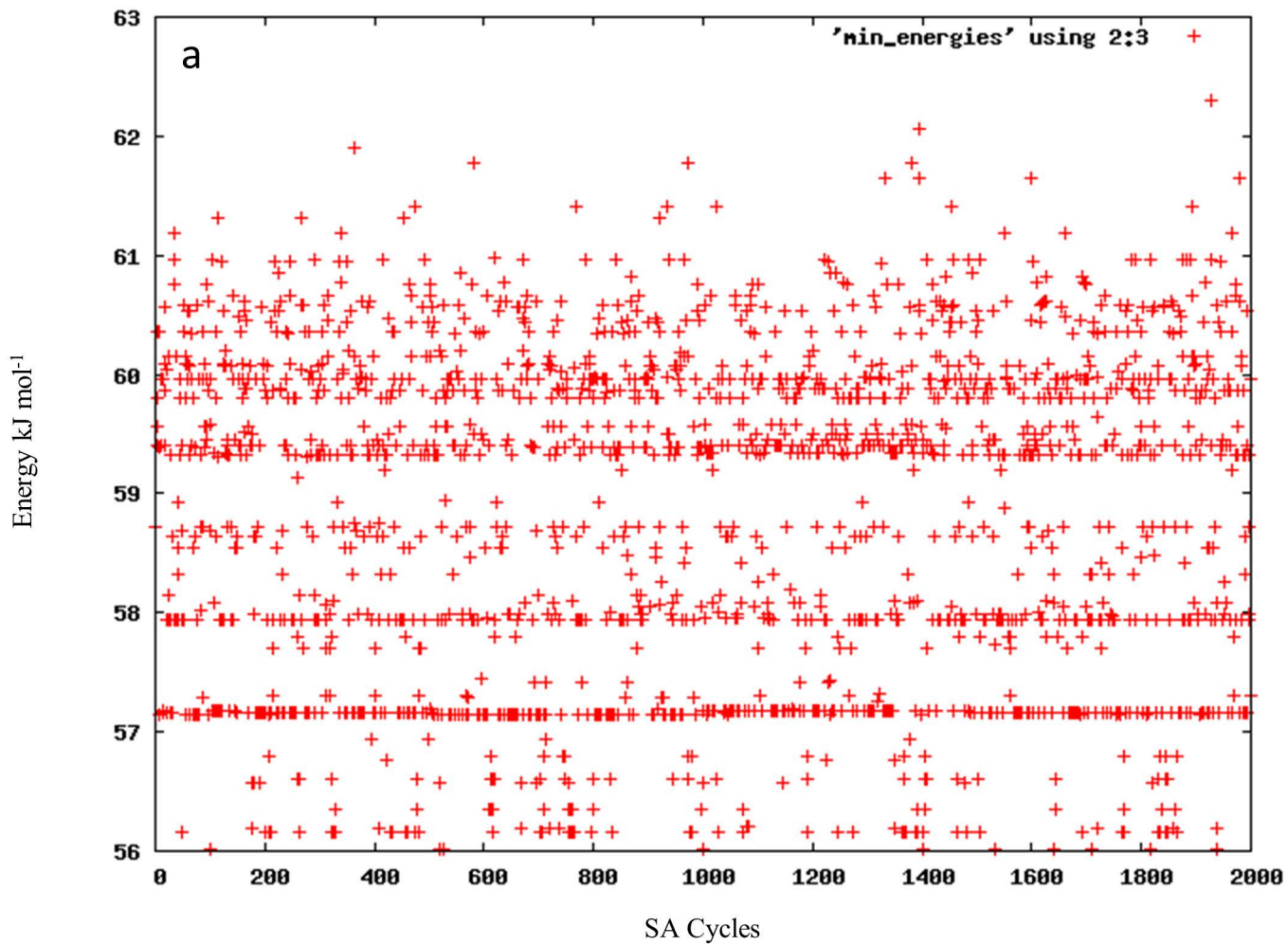
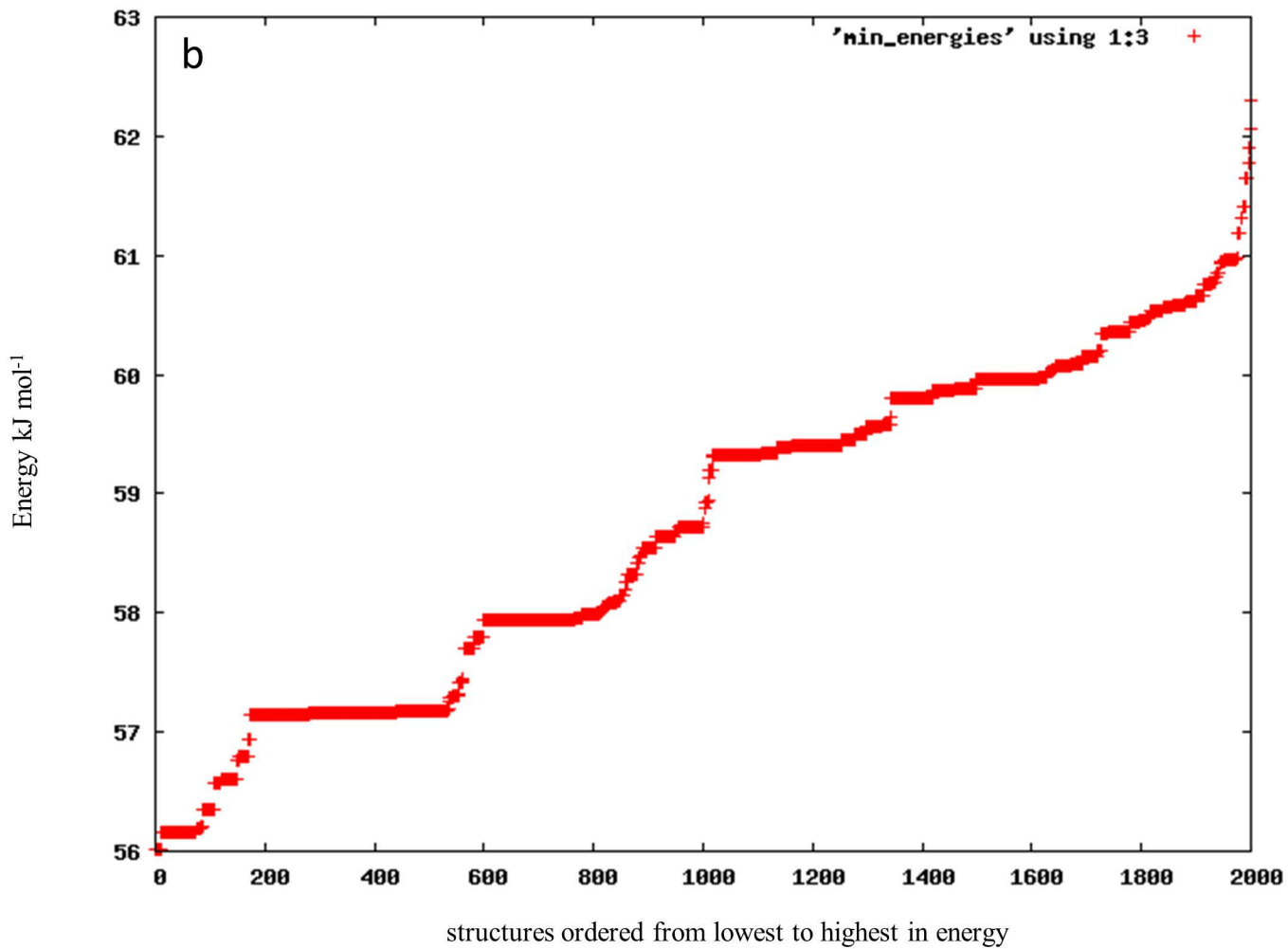


Figure S1b.



SA Cycles

Figure S2

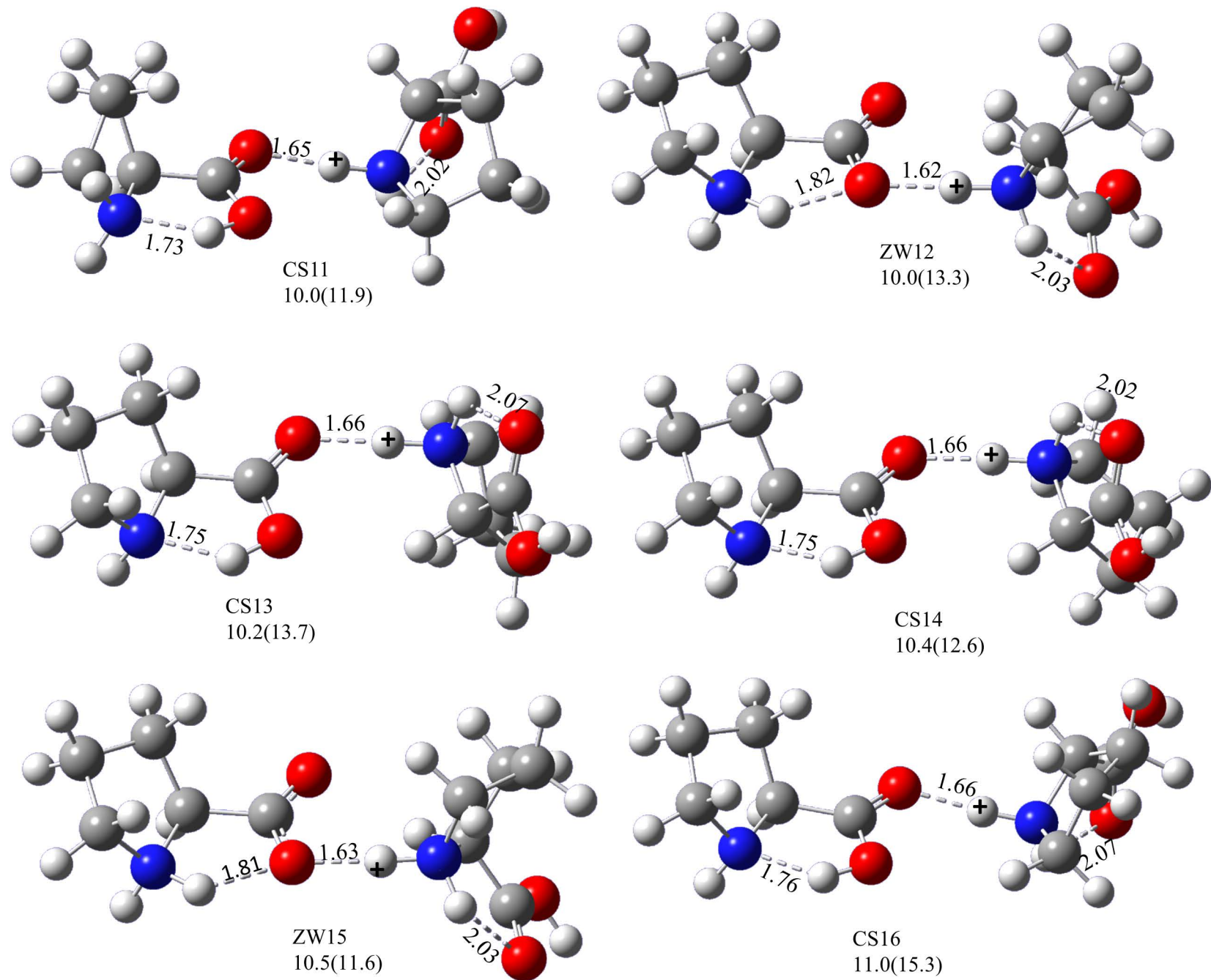


Figure S2 (cont'd)

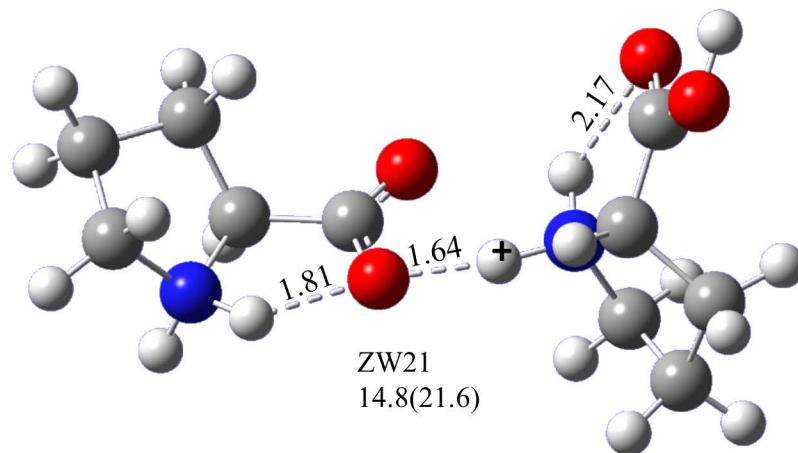
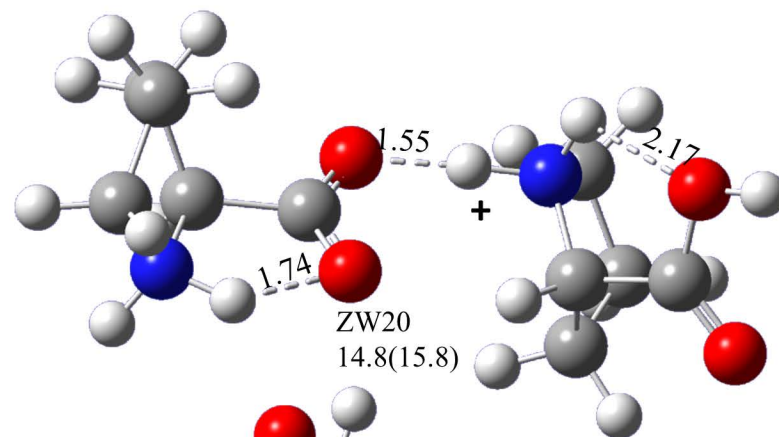
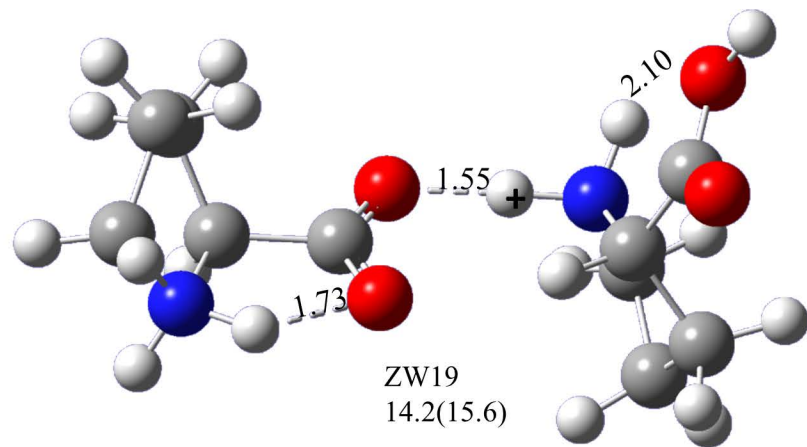
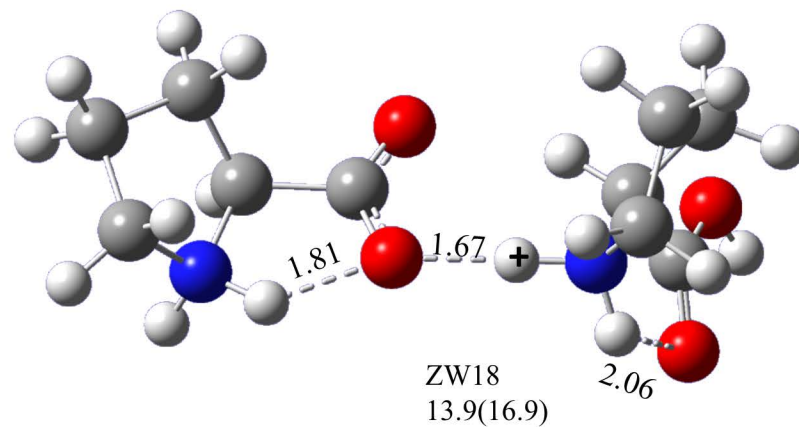
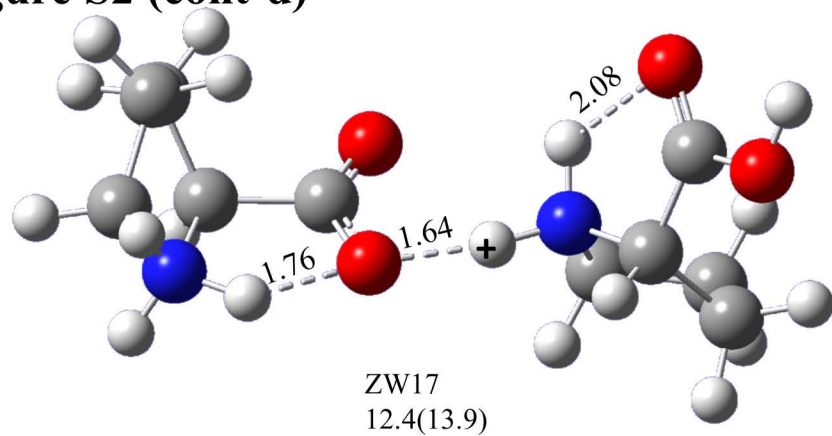


Figure S3. IRMPD spectrum of $(\text{Pro})_2\text{H}^+$ investigated by McMahon and Wu in $(1000\text{-}2000\text{cm}^{-1})$ compared with the B3LYP/6-3+G(d,p) predicted spectra for ZW1, ZW4.

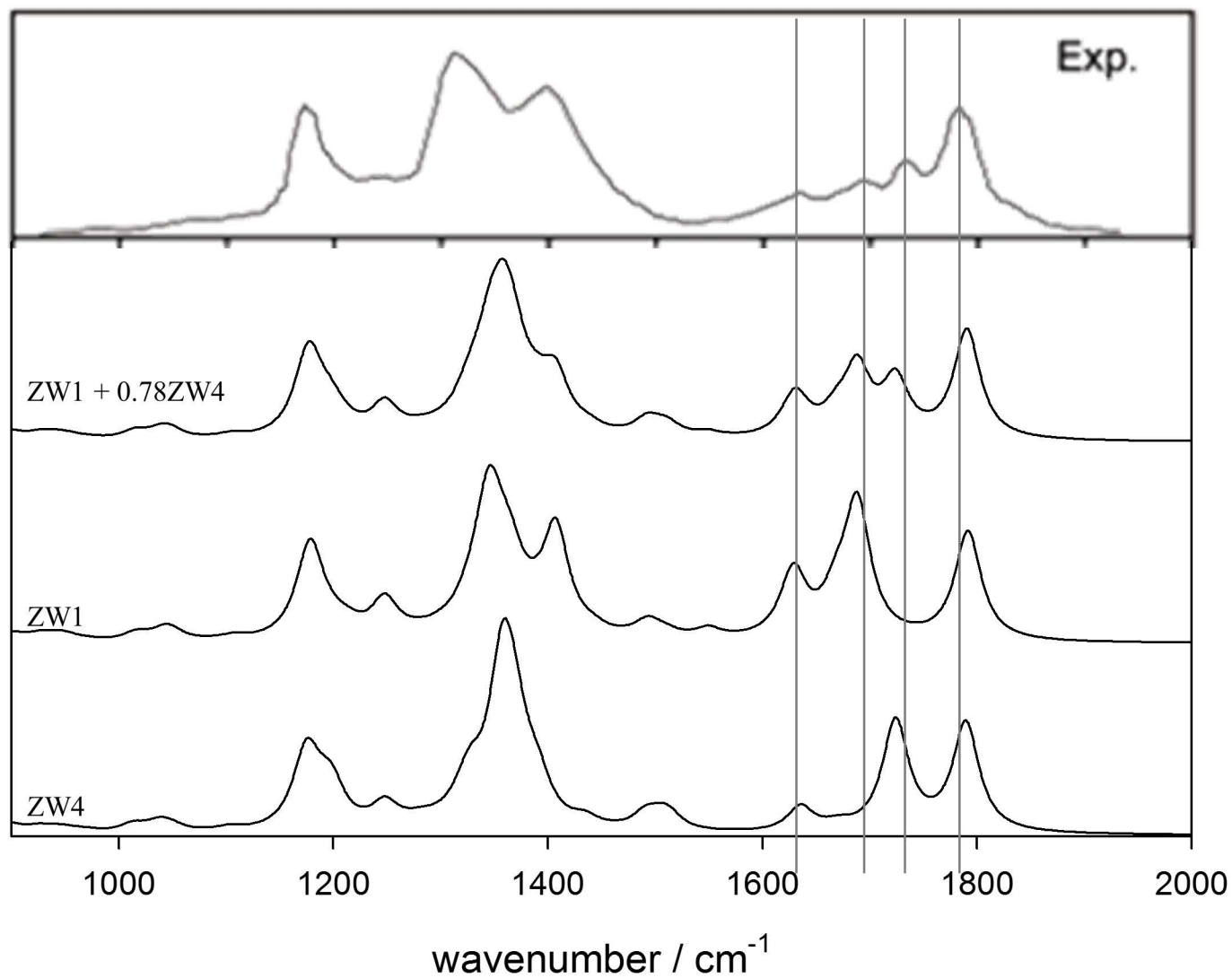
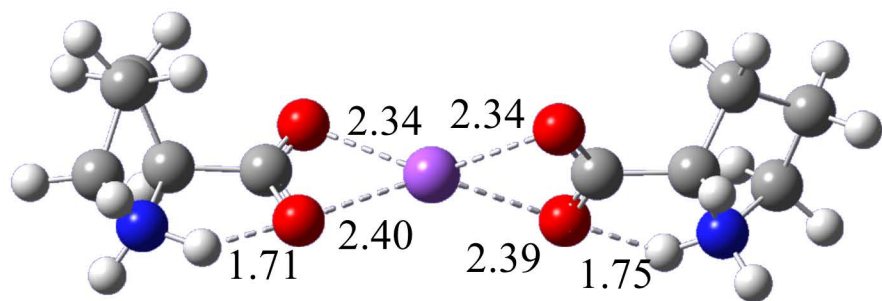
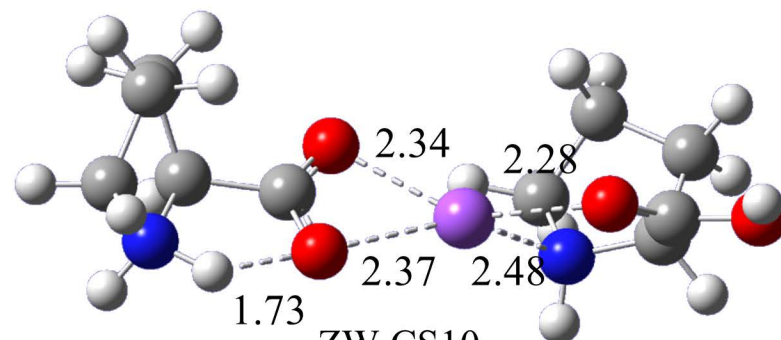


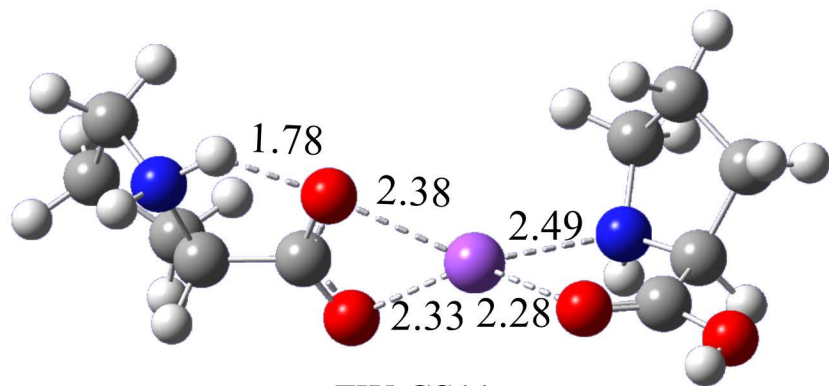
Figure S4



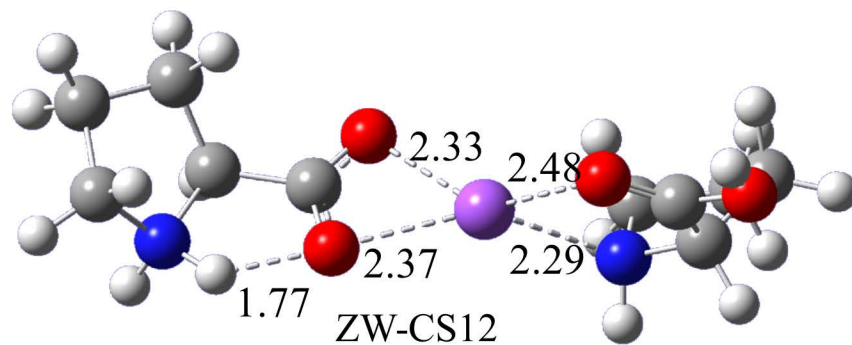
ZW-ZW9
5.3(-0.2)



ZW-CS10
6.2(0.9)

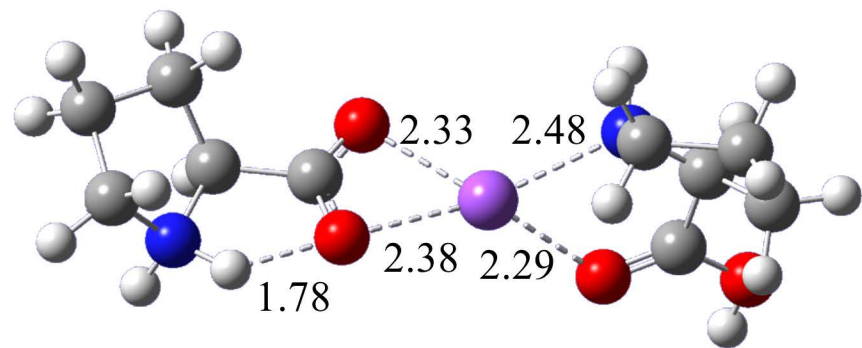


ZW-CS11
6.8(5.7)

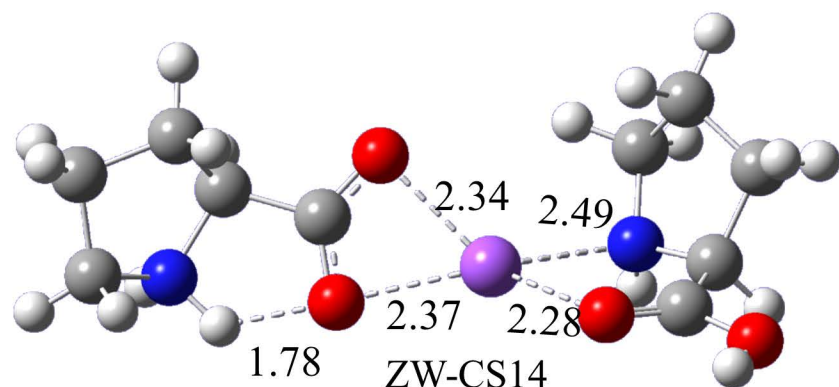


ZW-CS12
7.9(2.4)

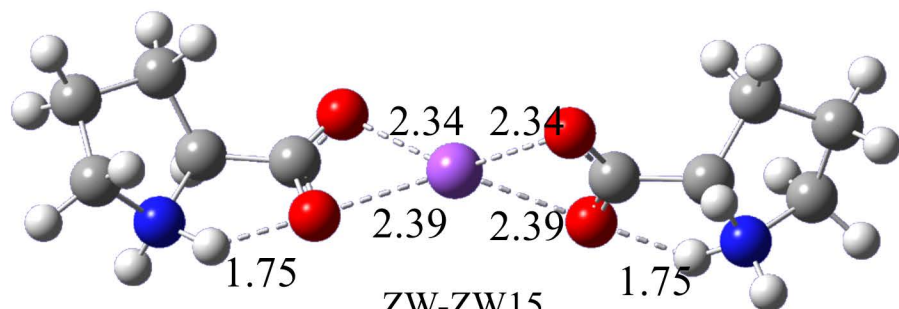
Figure S4.



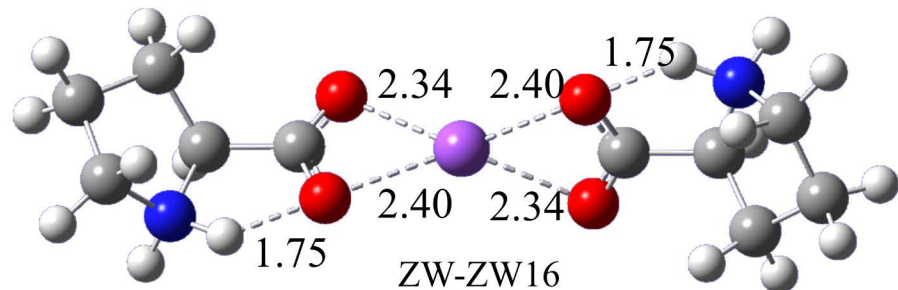
ZW-CS13
8.0(3.4)



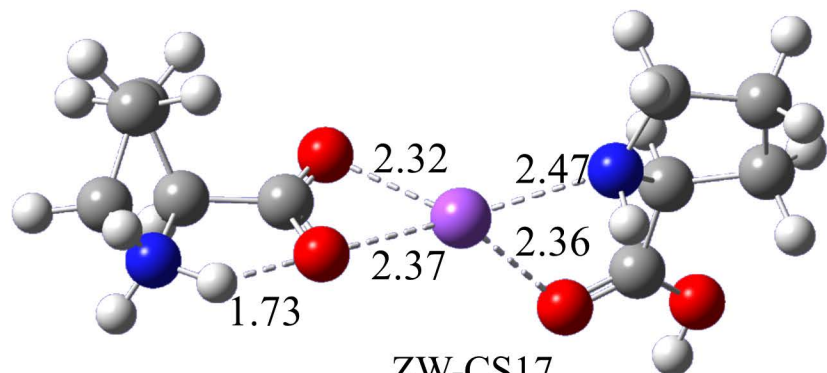
ZW-CS14
8.9(4.3)



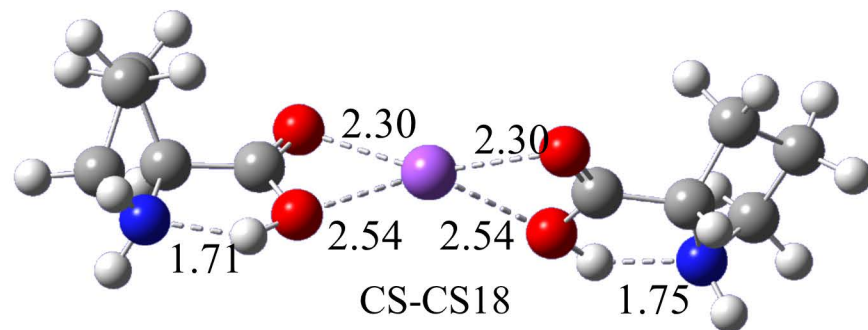
ZW-ZW15
9.4(3.9)



ZW-ZW16
10.9 (4.5)

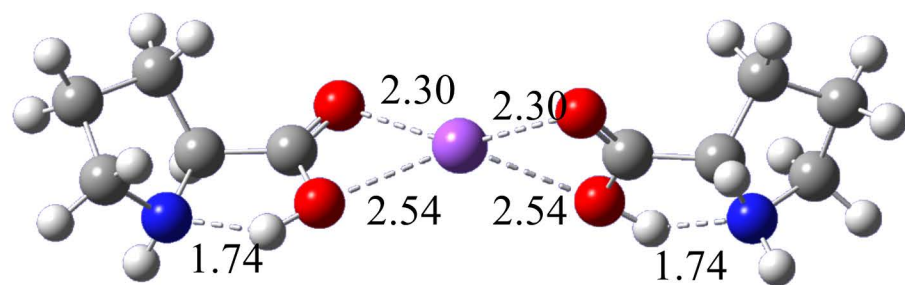


ZW-CS17
11.2(0.0)

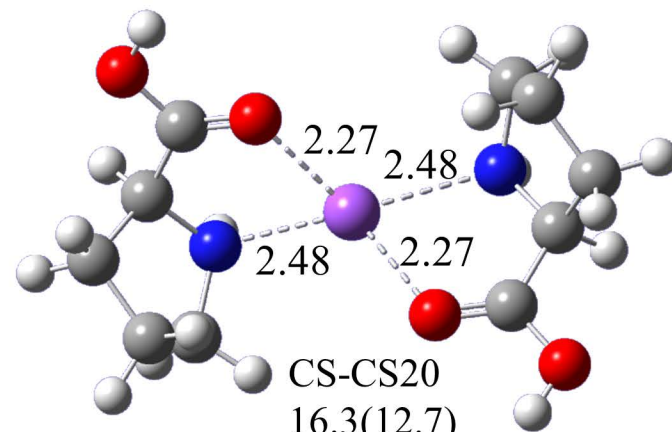


CS-CS18
11.5(10.1)

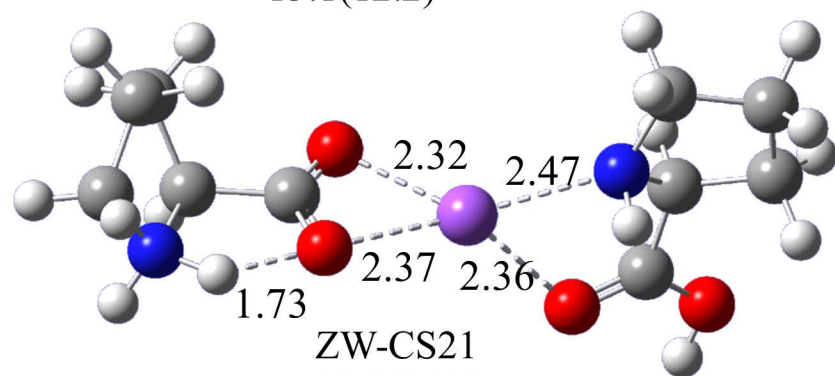
Figure S4 (cont'd)



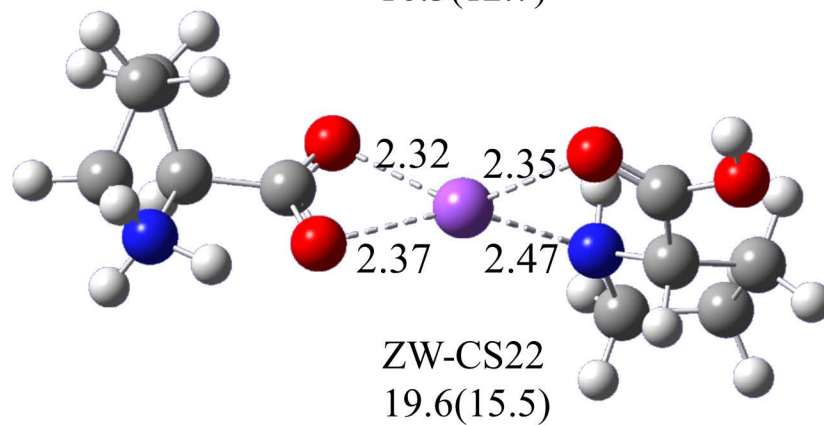
CS-CS19
13.1(12.2)



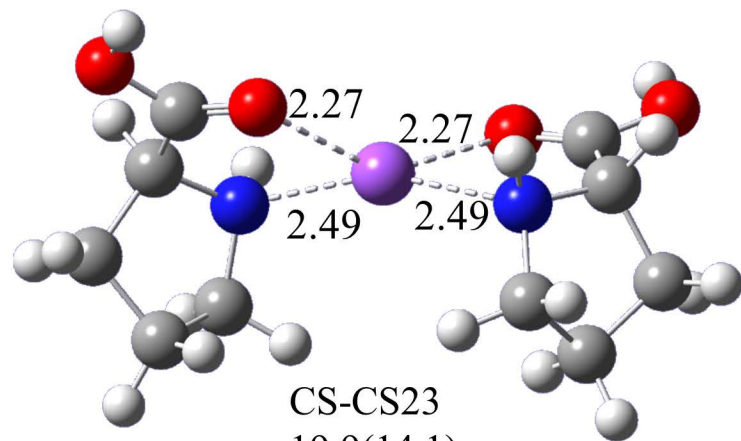
CS-CS20
16.3(12.7)



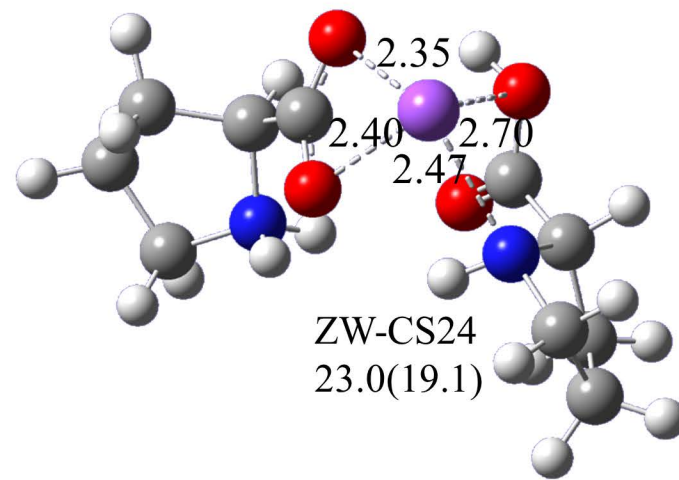
ZW-CS21
19.3(15.7)



ZW-CS22
19.6(15.5)

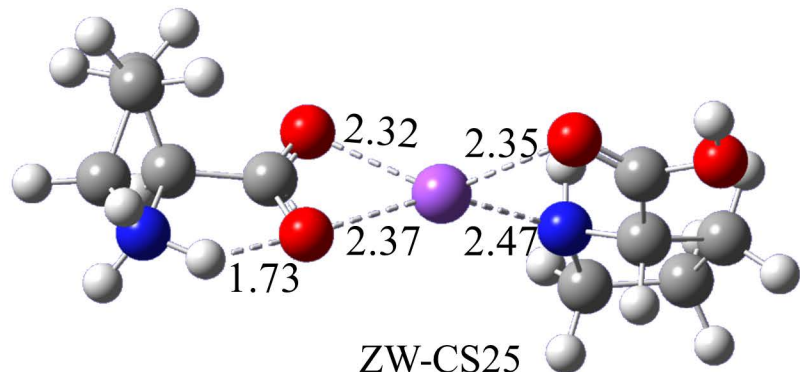


CS-CS23
19.9(14.1)

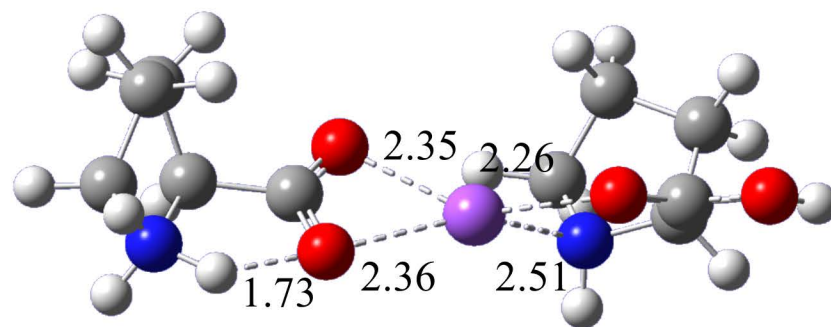


ZW-CS24
23.0(19.1)

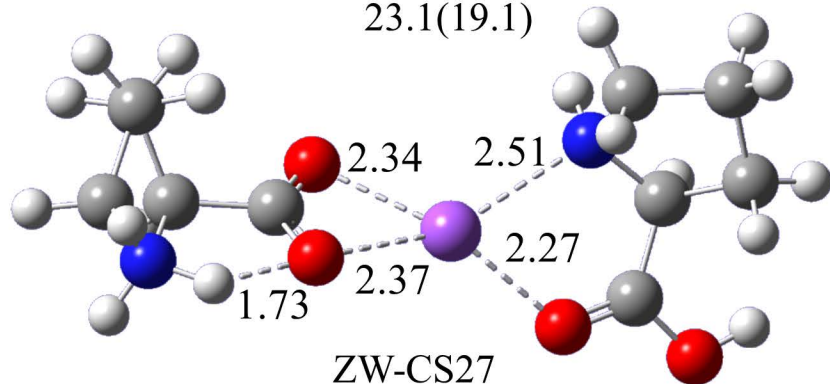
Figure S4 (cont'd)



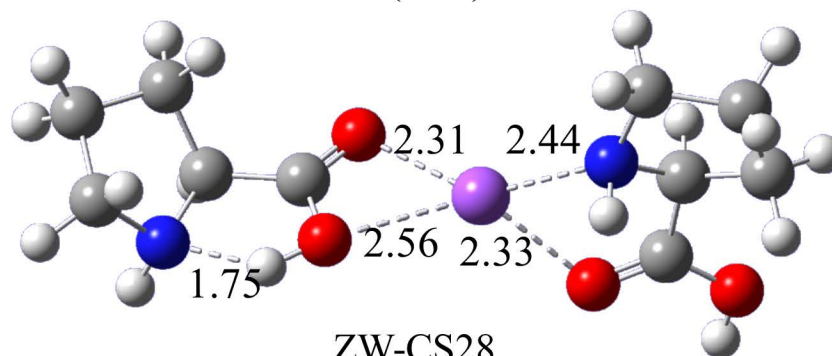
ZW-CS25
23.1(19.1)



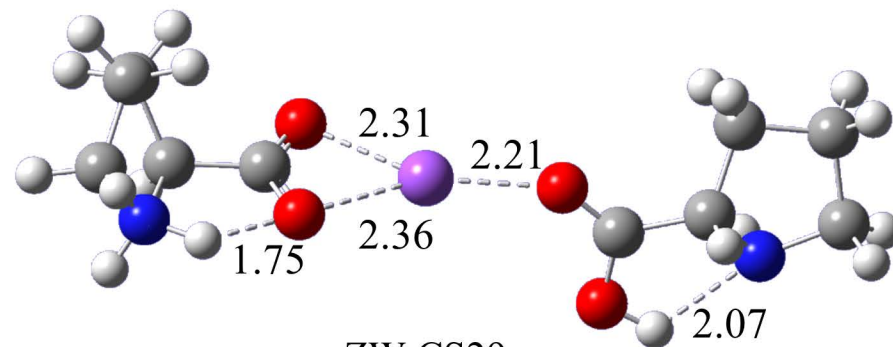
ZW-CS26
23.6(20.2)



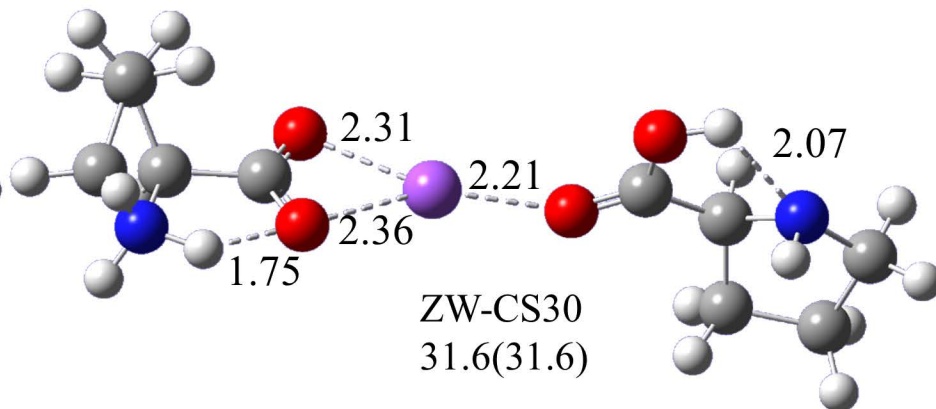
ZW-CS27
24.0(20.7)



ZW-CS28
26.6(25.5)

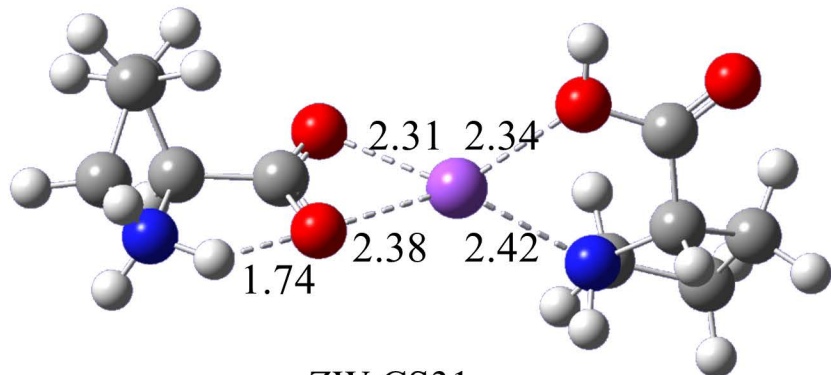


ZW-CS29
30.2(31.5)

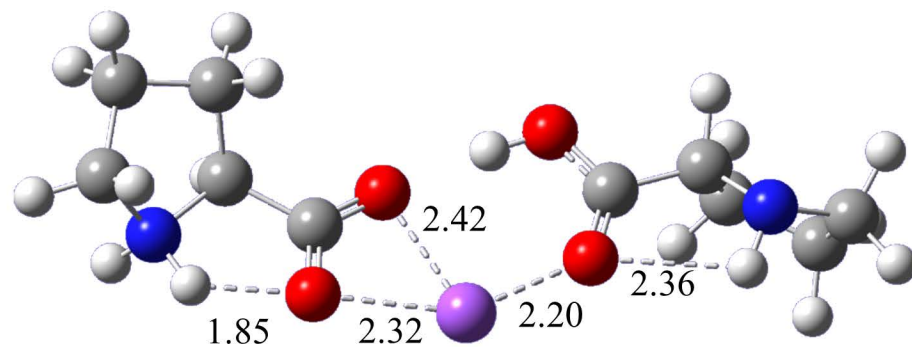


ZW-CS30
31.6(31.6)

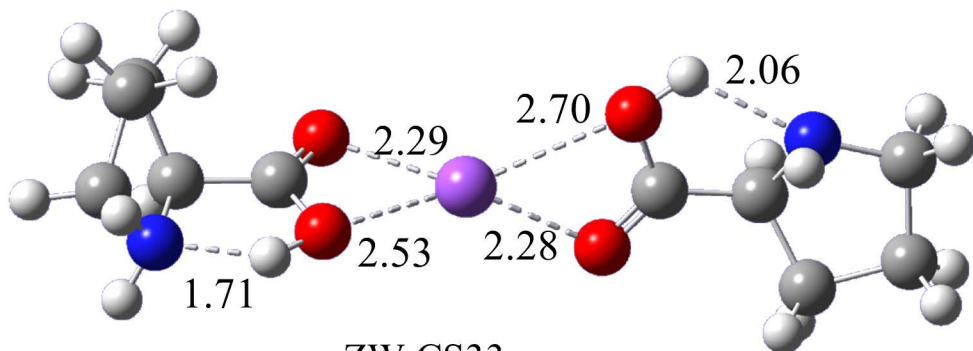
Figure S4 (cont'd)



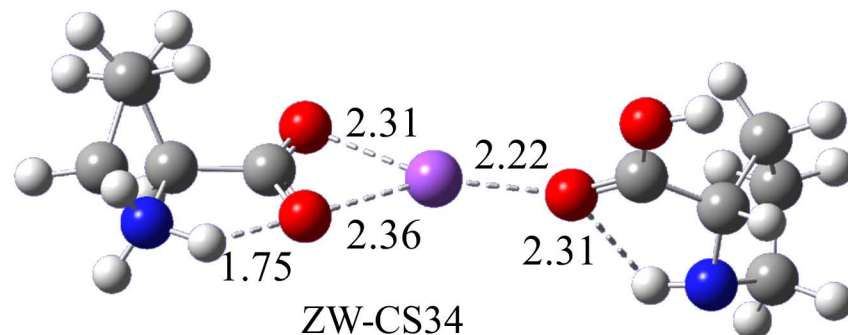
ZW-CS31
32.8(30.1)



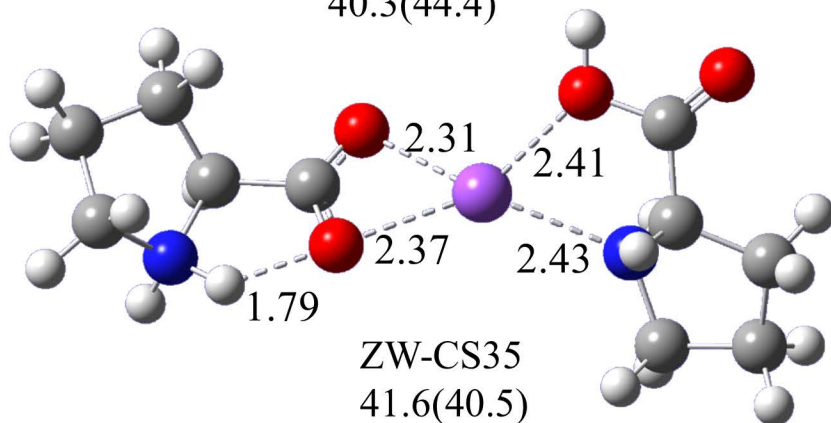
ZW-CS32
39.3(34.2)



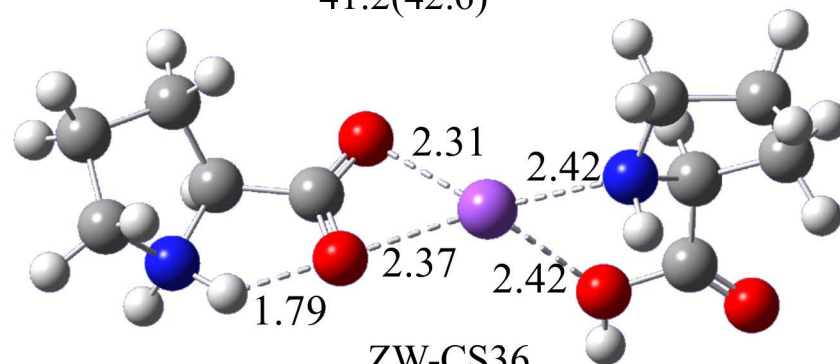
ZW-CS33
40.3(44.4)



ZW-CS34
41.2(42.6)



ZW-CS35
41.6(40.5)



ZW-CS36
42.0(40.3)