Noncovalent Interactions Underlying Binary Mixtures of Amino Acid based Ionic Liquids: Insights from Theory.

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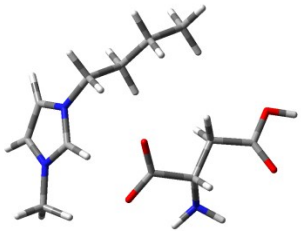
Supporting Information

Figure S11 Infrared spectra of (a) [Bmim][Asp] (b) [Bmim][Asn] (c) [MBmim][Glu] and (d) [Bmim][Gln] ion pairs.

Figure S12 A comparison of selected vibrational frequencies (ν = Stretching and δ = Bending) in (a) $[Bmim]_2[Asp][Asn]$ and (b) $[Bmim]_2[Glu][Gln]$ complexes. See text for details.



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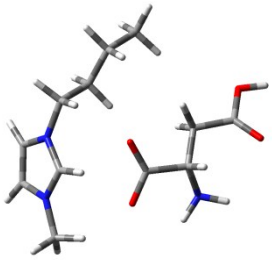

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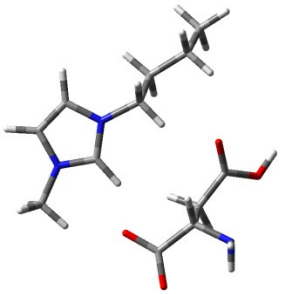

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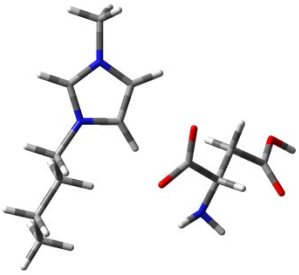
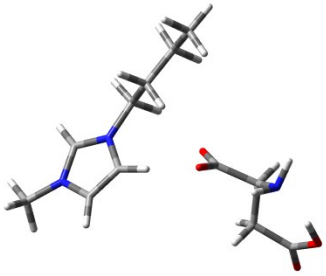


C4 (71.4)



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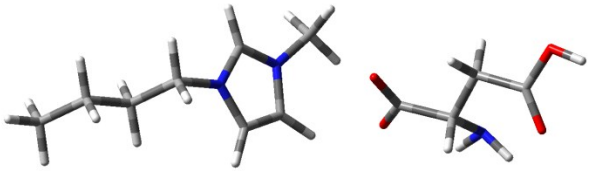
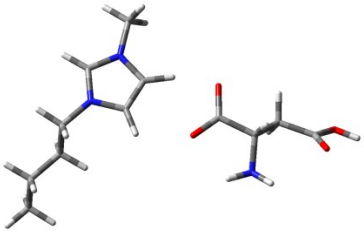
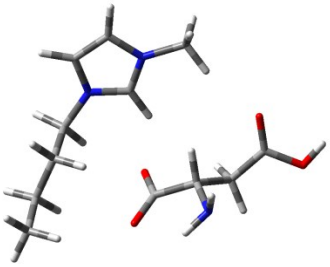


C6 (62.2)



C7 (76.5)



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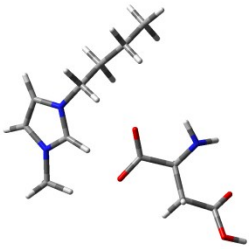

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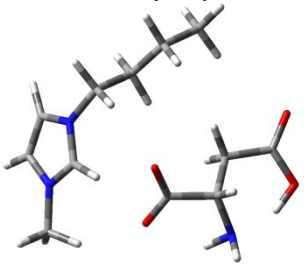

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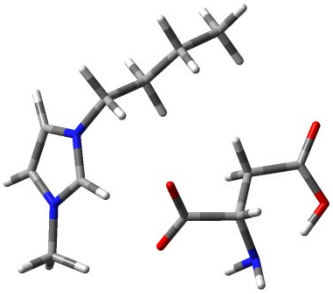

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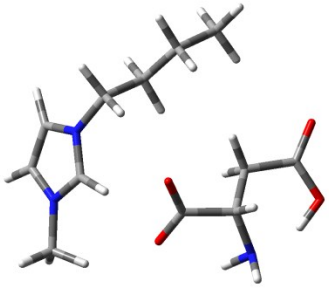

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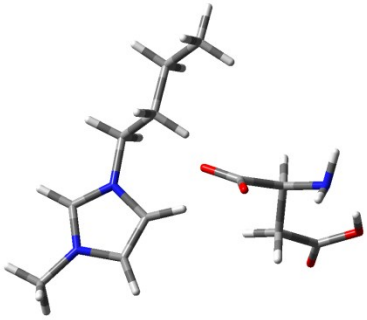

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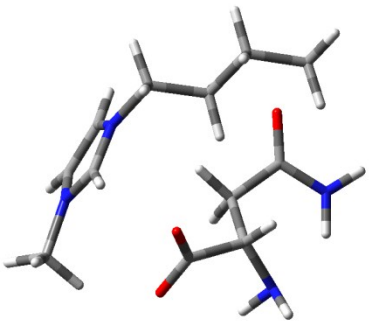
Figure S1



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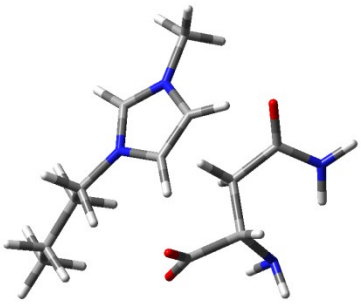

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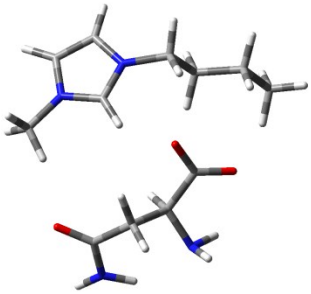

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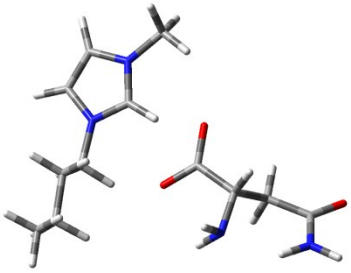

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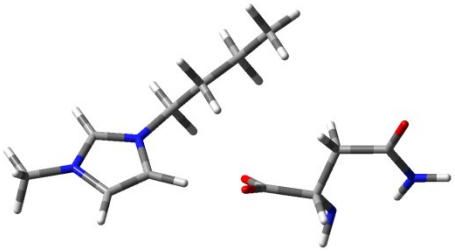

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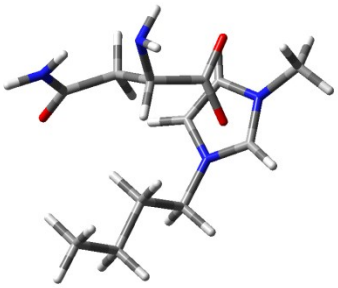

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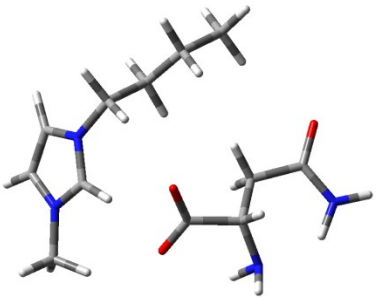

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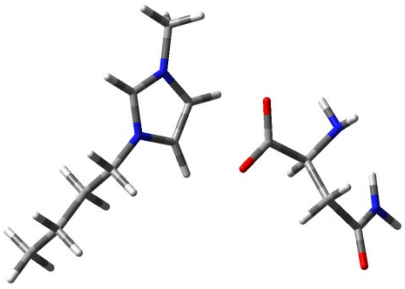

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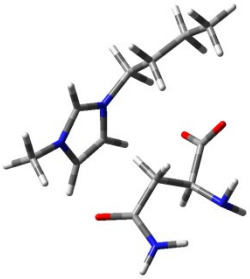

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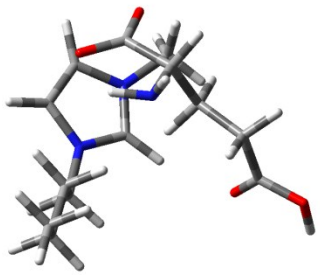
Figure S2



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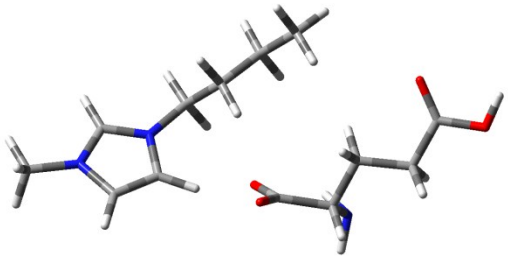

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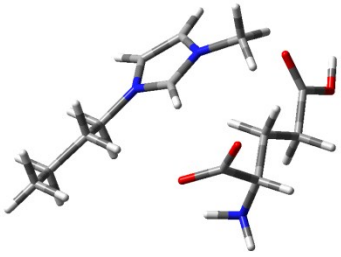

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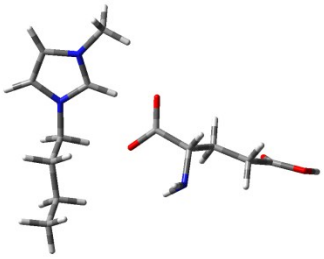

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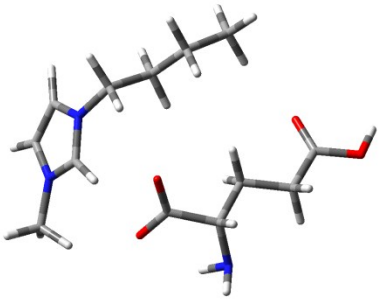

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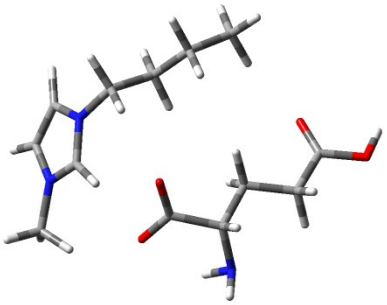

C6 (0.72)

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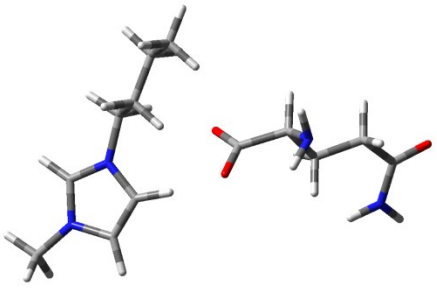

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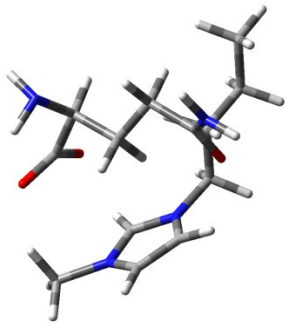

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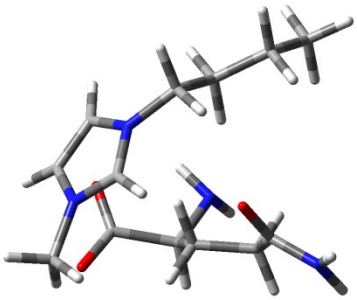

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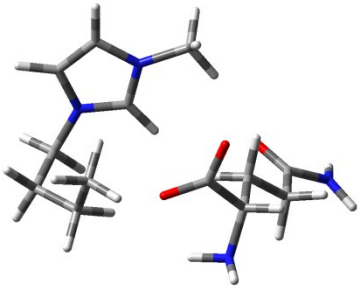

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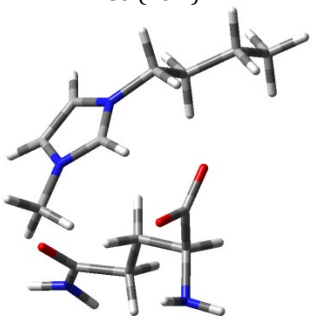

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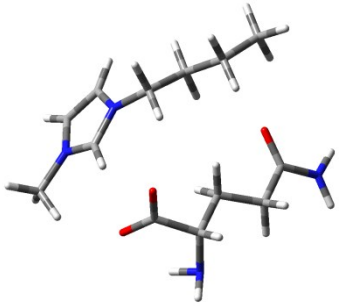
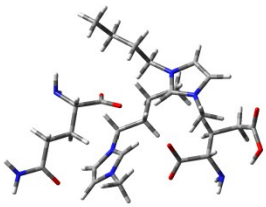


C6 (5.8)

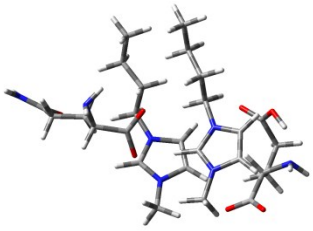
Figure S4

Table S1

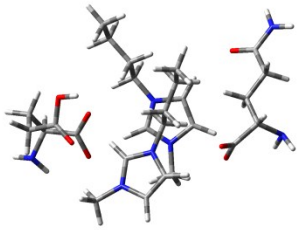
[Bmim][Asp]			[Bmim][Asn]		
	BE-M05	BE-D3		BE_M05	BE_D3
C14	-419.611	-427.572	C7	-398.342	-406.344
C10	-419.611	-427.572	C4	-390.132	-395.566
C11	-419.611	-427.572	C6	-388.329	-398.204
C1	-403.346	-410.984	C1	-388.328	-398.203
C2	-403.345	-410.983	C3	-383.005	-391.112
C9	-399.909	-405.461	C2	-378.763	-387.811
C5	-379.467	-384.777	C9	-378.762	-387.81
C13	-379.467	-384.777	C5	-355.825	-362.506
C8	-376.914	-387.008	C8	-335.242	-338.28
C3	-370.199	-377.547			
C12	-365.811	-369.847			
C6	-357.371	-405.48			
C4	-348.172	-365.314			
C7	-343.105	-346.128			
[Bmim][Glu]			[Bmim][Gln]		
	BE_M05	BE_D3		BE_M05	BE_D3
C3	-411.805	-420.66	C5	-411.767	-421.448
C6	-411.689	-419.936	C6	-406.295	-415.608
C5	-411.688	-419.936	C2	-396.731	-407.717
C4	-403.646	-409.264	C4	-391.29	-397.77
C1	-383.434	-397.623	C3	-385.624	-397.686
C2	-370.693	-377.926	C1	-354.608	-360.452



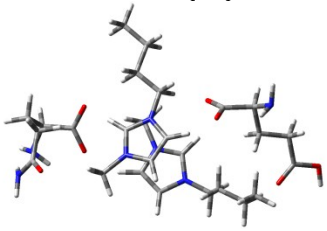
II_T_C4_fn (0.0)



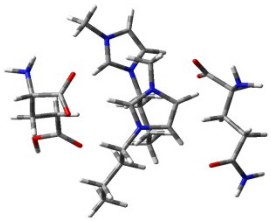
II_P_mf_C2 (3.30**)**



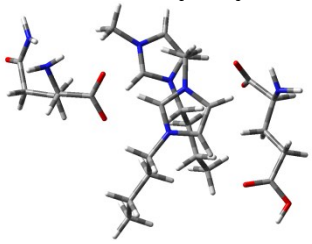
II_P_mn_C2 (12.67**)**



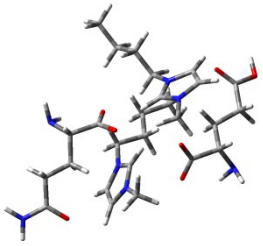
II_A_C21_nn (13.67**)**



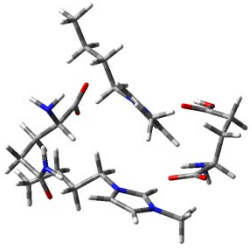
II_P_nn_C6 (17.76**)**



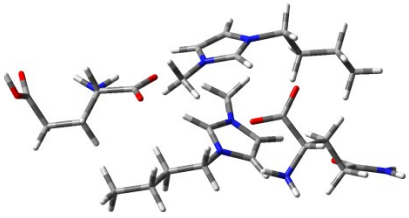
II_P_mm_C4 (18.55**)**



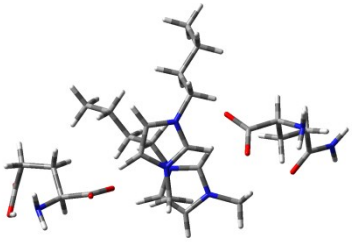
II_T_C5_ff (18.64**)**



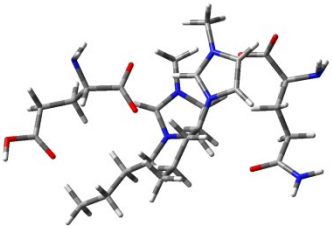
II_T_C2_fn (19.57**)**



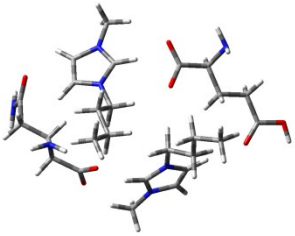
II_A_C7_mf (20.08**)**



II_P_mm_C3 (21.68**)**



II_P_ff_C11 (25.00**)**



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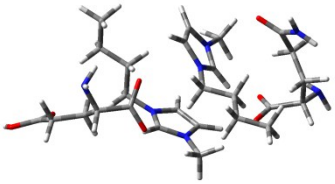
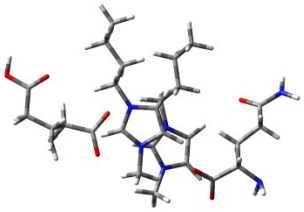
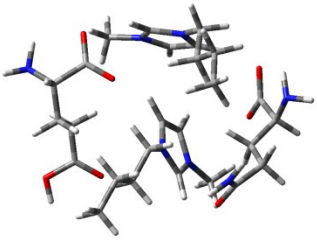


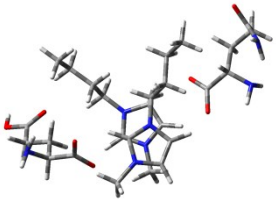
II_A_C1_mn (25.78**)**



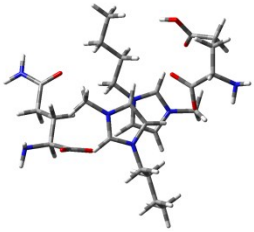
II_P_ff_C12 (26.45**)**



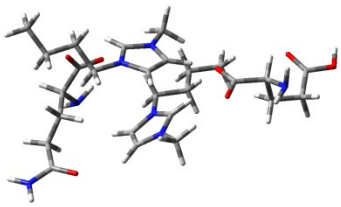
II_P_nn_C5 (26.74**)**



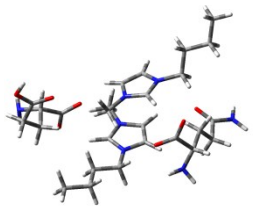
II_P_mf_C1 (27.12**)**



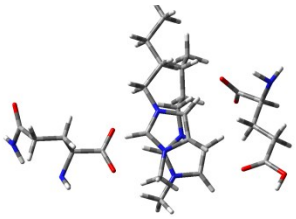
II_A_C16_fn (27.25**)**



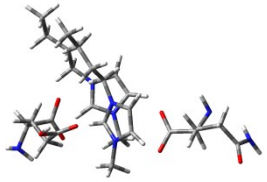
II_A_C10_ff (28.51**)**



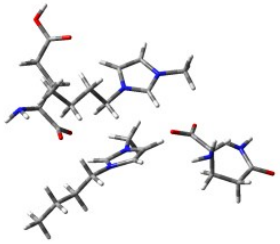
II_A_C6_mf (29.36**)**



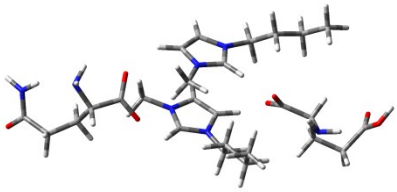
II_P_ff_C13 (30.12**)**



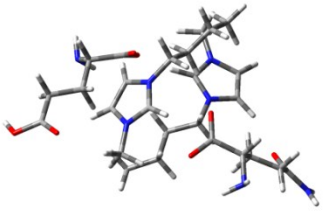
II_P_mf_C15 (30.97**)**



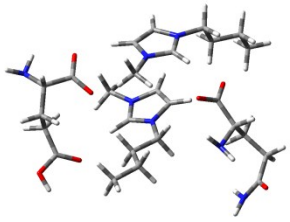
II_T_C3_fn (31.16**)**



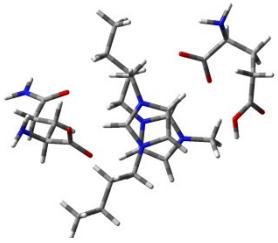
II_A_C15_mm (31.87**)**



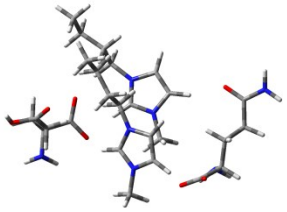
II_DA_C1_nn (32.04**)**



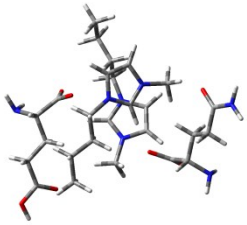
II_A_C2_mn (34.01**)**



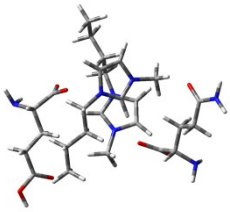
II_A_C14_mm (34.98**)**



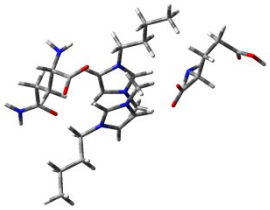
II_P_fn_C10 (35.13**)**



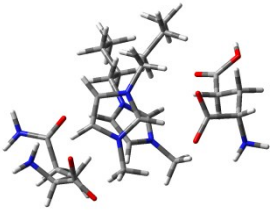
II_A_C22_nn (35.22**)**



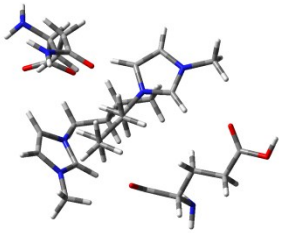
II_A_C23_nn (35.22**)**



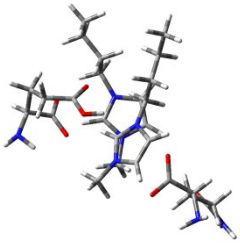
II_A_C8_mf (35.64**)**



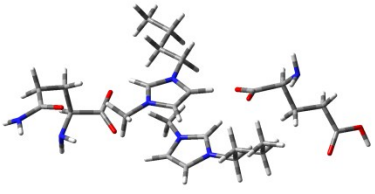
II_P_fm_C17 (35.85**)**



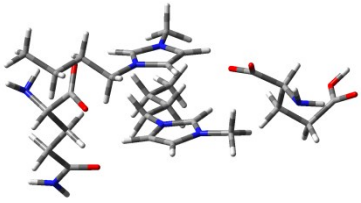
II_DP_C2_nn (36.67**)**



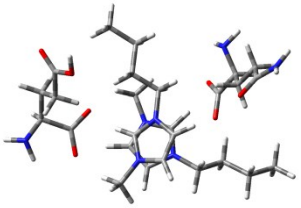
II_P_fm_C8 (36.70**)**



II_A_C19_fm (36.95**)**

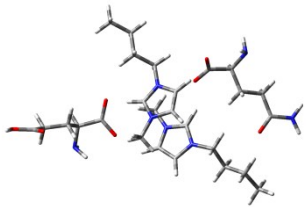


II_A_C5_mf (37.47**)**

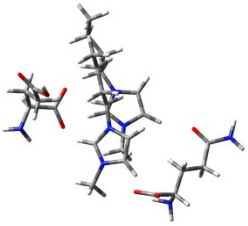


II_A_C17_mn (38.04**)**

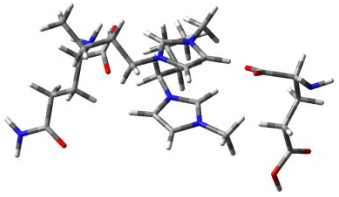
Figure S5 contd.



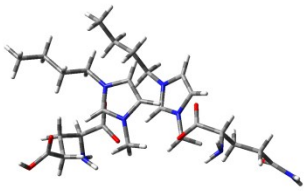
II_A_C13_mn (38.20**)**



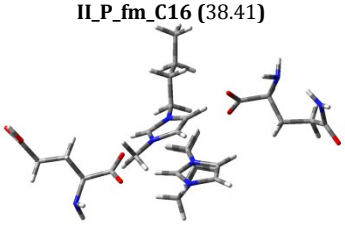
II_P_fm_C16 (38.41**)**



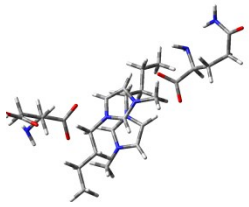
II_A_C18_mn (40.61**)**



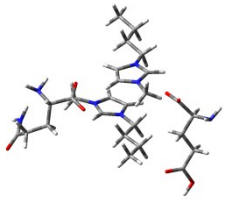
II_P_fn_C9 (40.66**)**



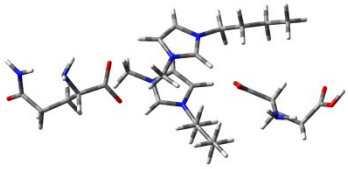
II_P_ff_C14 (40.85**)**



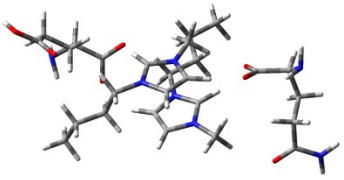
II_A_C12_ff (42.65**)**



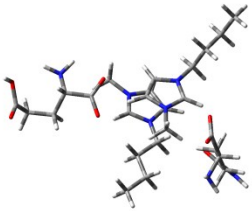
II_A_ff_C9 (44.62)



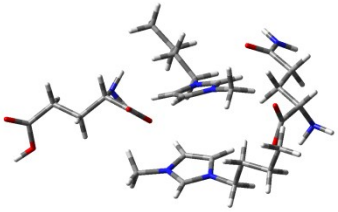
II_A_C3_mm (46.38)



II_A_C20_mn (48.02**)**



II_A_C4_mm (55.50**)**



II_A_C11_ff (64.42**)**

Figure S5

Table S2

Conformers	R.S.E (kJ mol^{-1})	Conformers	R.S.E (kJ mol^{-1})	Conformers	R.S.E (kJ mol^{-1})	Conformers	R.S.E (kJ mol^{-1})
I_T_ff_C1	0	I_P_mf_C7	42.9671	II_T_C4_fn	0.0000	II_A_C2_mn	36.1321
I_T_fn_C4	7.293639	I_A_fn_C16	43.10887	II_P_mf_C2	1.3374	II_A_C14_mm	37.9634
I_T_ff_C5	7.293902	I_P_nn_C5	43.55311	II_P_mn_C2	11.5821	II_P_fn_C10	38.4266
I_DA_nn_C1	8.780722	I_T_fn_C3	45.1074	II_A_C21_nn	16.8570	II_A_C22_nn	35.7336
I_DP_nn_C2	12.96262	I_P_mn_C2	50.21164	II_P_nn_C6	14.3426	II_A_C23_nn	35.7336
I_P_nn_C6	13.97055	I_P_fm_C17	50.27675	II_P_mm_C4	20.1670	II_A_C8_mf	38.7154
I_P_fm_C15	17.16421	I_A_mn_C13	52.8886	II_T_C5_ff	17.6357	II_P_fm_C17	34.2465
I_A_mn_C18	19.61432	I_P_mn_C1	53.00071	II_T_C2_fn	25.2476	II_DP_C2_nn	37.5756
I_A_mn_C17	19.81281	I_A_mm_C3	55.25155	II_A_C7_mf	21.7801	II_P_fm_C8	37.8361
I_A_mn_C2	19.8984	I_A_ff_C9	55.25155	II_P_mm_C3	24.4429	II_A_C19_fm	36.1576
I_A_mm_C14	24.28614	I_A_mf_C5	56.5068	II_P_ff_C11	26.9683	II_A_C5_mf	42.9148
I_P_fm_C8	26.34742	I_A_ff_C10	56.50706	II_T_C1_ff	28.2695	II_A_C17_mn	7.4155
I_P_fn_C9	29.33104	I_P_ff_C13	57.18208	II_A_C1_mn	23.7466	II_A_C13_mn	48.4686
I_P_fm_C16	29.3355	I_A_mf_C8	57.84712	II_P_ff_C12	28.6306	II_P_fm_C16	39.8719
I_P_mm_C4	31.33167	I_A_mf_C6	58.17609	II_P_nn_C5	22.3464	II_A_C18_mn	46.5139
I_P_fn_C10	38.36512	I_P_ff_C11	61.34665	II_P_mf_C1	31.1634	II_P_fn_C9	46.3272
I_A_mn_C1	38.46305	I_P_ff_C14	67.07627	II_A_C16_fn	28.9973	II_P_ff_C14	51.2842
I_P_mm_C3	40.78452	I_A_mm_C4	70.82155	II_A_C10_ff	33.5213	II_A_C12_ff	45.0685
I_T_fn_C1	42.12037	I_P_ff_C12	74.65268	II_A_C6_mf	33.2008	II_A_C9_ff	48.8094
I_A_fn_C15	42.55909	I_A_ff_C11	77.15452	II_P_ff_C13	35.2153	II_A_C3_mm	52.2306
I_A_mf_C7	42.68013	I_A_ff_C12	80.07486	II_P_mf_C15	33.8905	II_A_C20_mn	52.6229
				II_T_C3_fn	37.9217	II_A_C4_mm	63.5649
				II_A_C15_mm	36.1371	II_A_C11_ff	58.7261
				II_DA_C1_nn	33.1230		

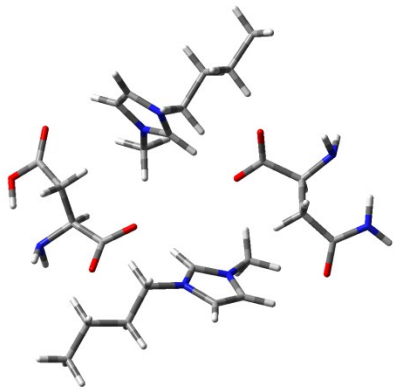
Table S3

Conformers@B3LYP	B3LYP	Conformers@B3LYP-D3	B3LYP-D3
I_T_fn_C4	-868.53	**I_A_mn_C1**	-292.86
I_A_mn_C1	-843.05	**I_T_fn_C5**	-284.32
I_T_fn_C5	-842.44	**I_DA_nn_C1**	-282.22
I_A_mn_C17	-841.60	**I_A_mn_C17**	-281.63
I_T_fn_C3	-838.76	**I_DP_nn_C2**	-280.55
I_DA_nn_C1	-836.69	**I_T_fn_C4**	-278.69
I_P_mn_C2	-836.52	**I_P_nn_C6**	-276.59
I_T_ff_C5	-836.10	**I_T_fn_C1**	-276.18
I_P_fn_C10	-835.07	**I_P_mn_C2**	-275.83
I_P_fn_C9	-835.07	**I_A_mn_C2**	-273.46
I_DP_nn_C2	-831.45	**I_A_fn_C15**	-271.71
I_A_fn_C16	-831.07	**I_P_fm_C8**	-270.67
I_T_ff_C1	-830.39	**I_P_mf_C7**	-270.42
I_A_mn_C18	-824.76	**I_P_fm_C15**	-270.23
I_P_mm_C1	-824.30	**I_P_fn_C9**	-270.00
I_P_fm_C17	-823.35	**I_A_fn_C16**	-267.02
I_P_fm_C8	-822.99	**I_P_fn_C10**	-266.53
I_A_mm_C14	-822.43	**I_P_mm_C1**	-266.04
I_P_fm_C16	-820.93	**I_A_mn_C18**	-265.37
I_A_mn_C2	-820.15	**I_T_ff_C1**	-260.49
I_P_fm_C15	-818.98	**I_P_mm_C3**	-259.53
I_P_nn_C6	-818.24	**I_P_fm_C17**	-259.03
I_P_ff_C12	-817.57	**I_A_mm_C14**	-258.09
I_P_ff_C11	-816.35	**I_P_ff_C13**	-253.39
I_A_mf_C6	-815.00	**I_P_fm_C16**	-247.98
I_P_ff_C13	-814.65	**I_T_fn_C3**	-246.55
I_P_mf_C7	-813.03	**I_P_ff_C12**	-245.98
I_A_fn_C15	-810.02	**I_P_ff_C11**	-243.37
I_P_nn_C5	-807.42	**I_P_nn_C5**	-242.05
I_P_mm_C3	-804.87	**I_A_mf_C6**	-241.09
I_A_mf_C8	-804.31	**I_A_mf_C7**	-240.47
I_A_mf_C7	-802.93	**I_A_mn_C13**	-235.99
I_A_ff_C10	-801.60	**I_A_mf_C8**	-231.36
I_P_ff_C14	-800.51	**I_A_ff_C10**	-231.27
I_A_mm_C4	-794.123	**I_A_mm_C3**	-228.01
I_A_mn_C13	-794.026	**I_A_ff_C9**	-228.01
I_P_mm_C4	-792.28	**I_A_mm_C4**	-227.78
I_A_mf_C5	-790.23	**I_A_mf_C5**	-226.82
I_A_mm_C3	-786.82	**I_P_mm_C4**	-222.61

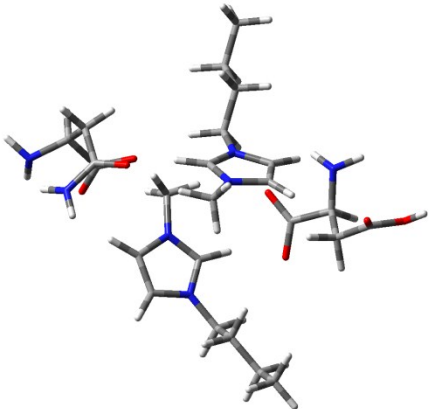
I_A_ff_C9	-786.82	**I_P_ff_C14**	-222.25
I_A_ff_C11	-786.66	**I_A_ff_C11**	-208.31
I_A_ff_C12	-776.23	**I_A_ff_C12**	-202.86

Table S4 Calculated interaction energies (in kJ mol^{-1}) using B3LYP and B3LYP-D3 level of theory for $[Bmim]_2[Glu][Gln]$ mixed IL*s*.

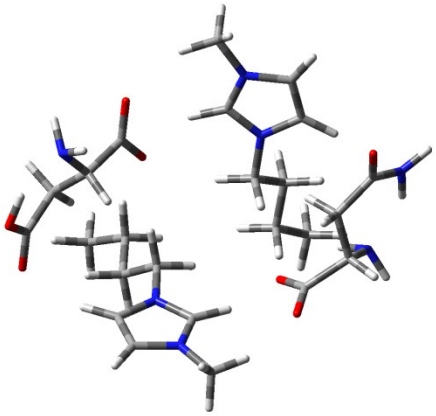
Conformers@B3LYP	B3LYP	Conformers@B3LYP-D3	B3LYP-D3
II_P_mf_C1	-849.46	II_A__nn_C21	-298.13
II_A__nn C21	-849.41	II_P_mf_C1	-282.99
II_P_mm_C3	-834.86	II_DA__nn C1	-279.52
II_A__nn C22	-829.97	II_A__mm C15	-269.32
II_A__nn C23	-829.97	II_A__nn C22	-268.83
II_A__mm C15	-827.54	II_A__nn C23	-268.83
II_A__fm C19	-820.88	II_DP__nn C2	-267.23
II_DP__nn C2	-820.34	II_A__fm C19	-261.31
II_A__mn C20	-815.77	II_A__mn C20	-257.21
II_DA__nn C1	-815.72		



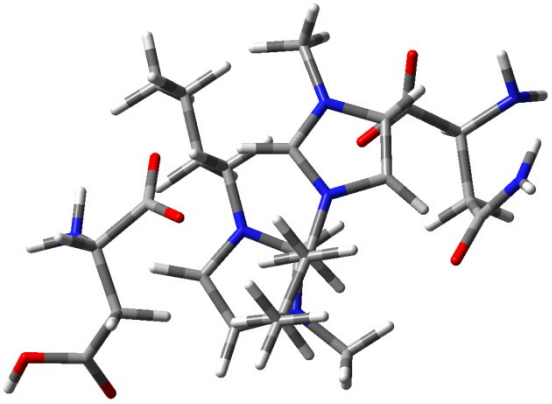
I_T_fn_C4 (0.0)



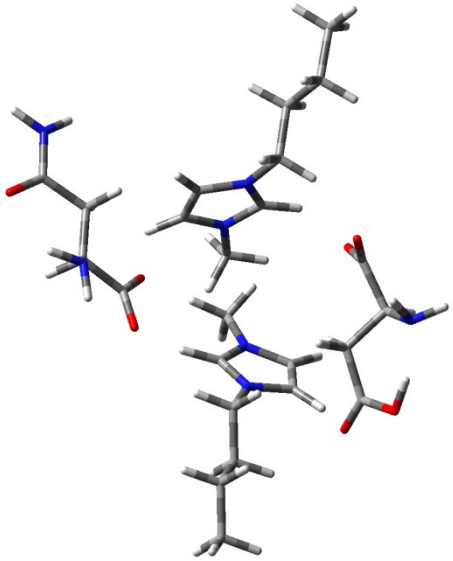
I_A_mn_C1 (25.4)



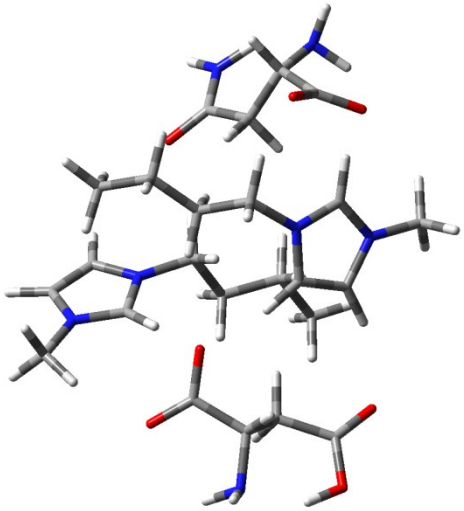
I_T_fn_C1 (26.1)



I_A_mn_C17 (26.9)

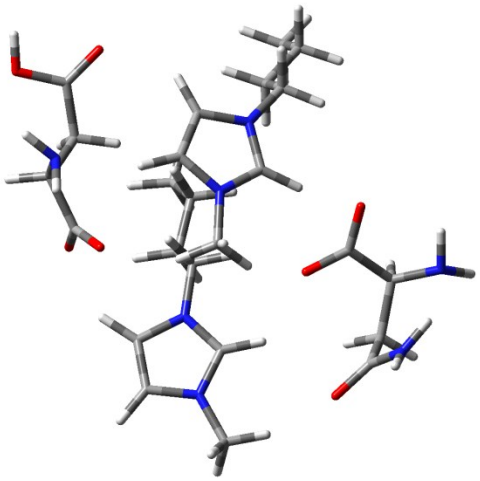


I_T_fn_C3 (29.7)

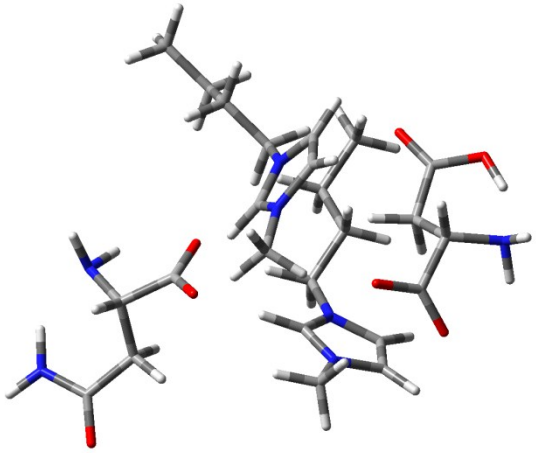


I_DA_nn_C1 (31.8)

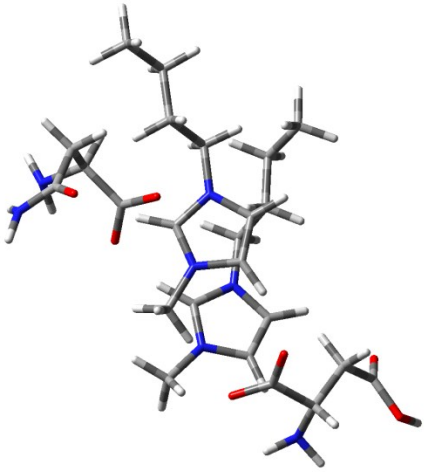
Figure S6 contd.



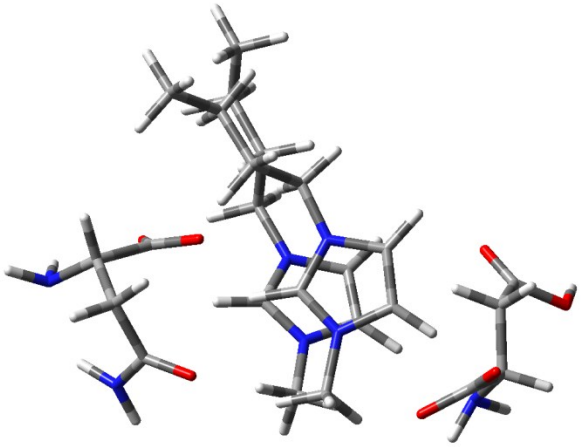
I_P_mn_C2 (32.0)



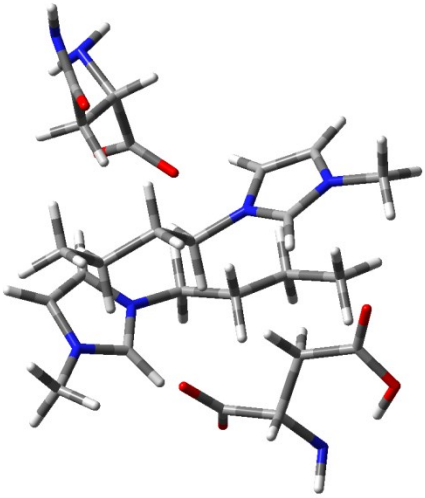
I_T_fn_C5 (32.4)



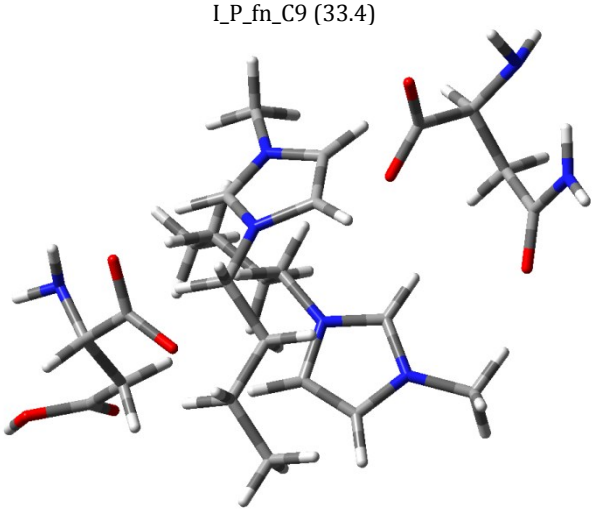
I_P_fn_C10 (33.4)



I_P_fn_C9 (33.4)

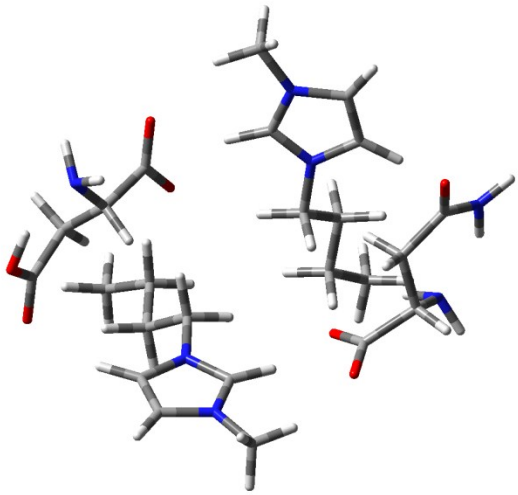


I_DP_nn_C2 (37.08)

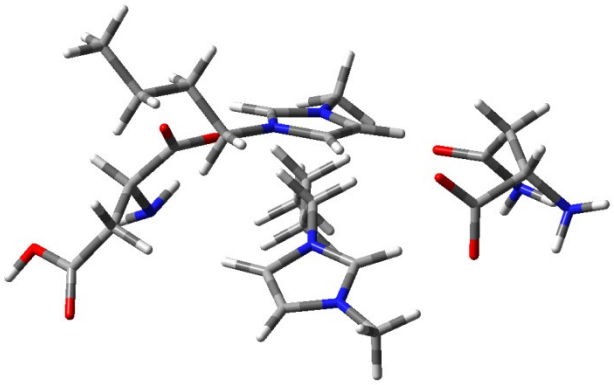


I_A_fn_C16 (37.4)

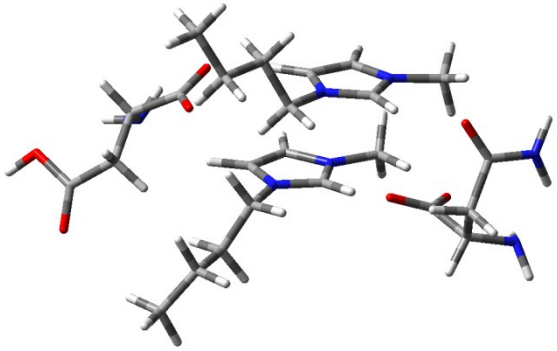
Figure S6 contd.



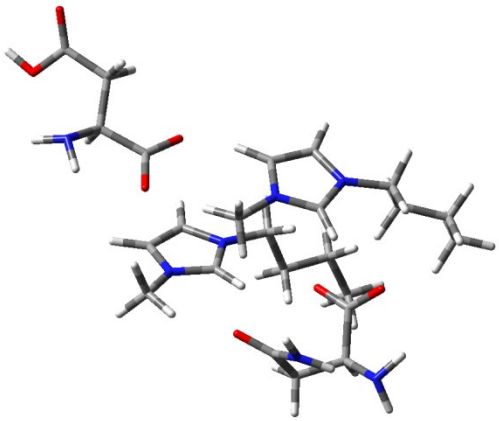
I_T_ff_C1 (38.1)



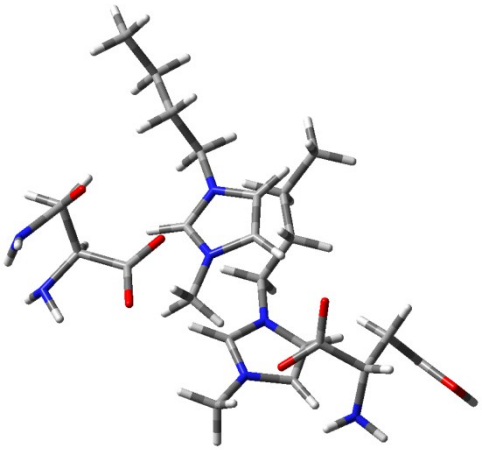
I_A_mn_C18 (43.7)



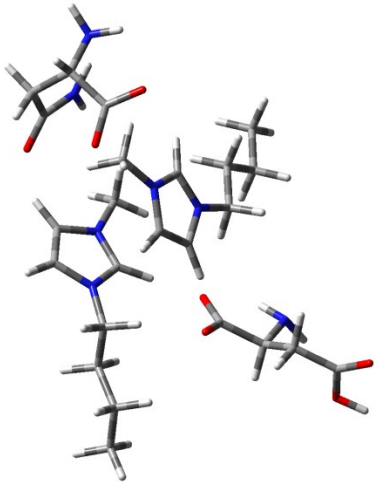
I_P_mn_C1 (44.2)



I_P_fm_C17 (45.1)

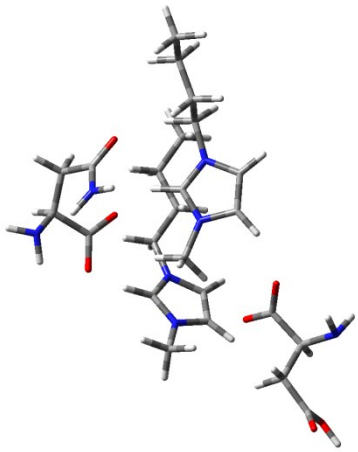


I_P_fm_C8 (45.5)

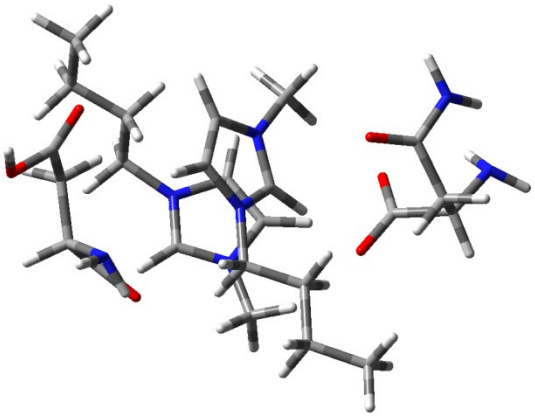


I_A_mm_C14 (46.0)

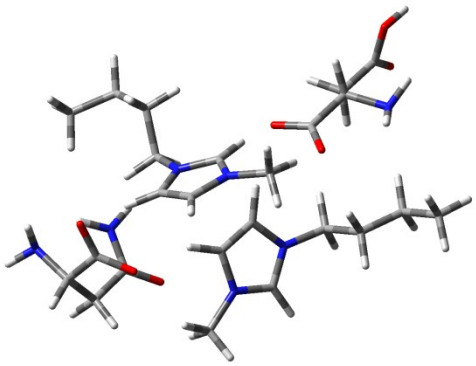
Figure S6 contd.



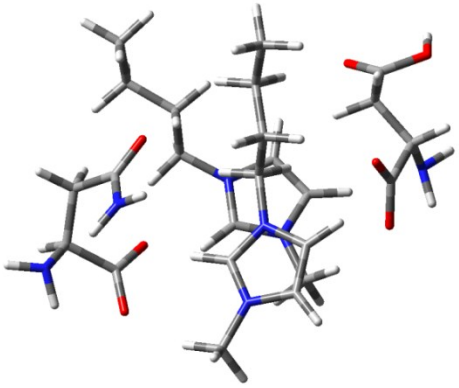
I_P_fm_C16 (47.6)



I_A_mn_C2 (48.3)

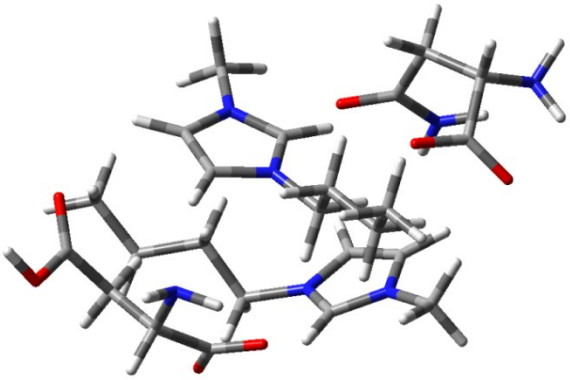


I_P_fm_C15 (49.5)

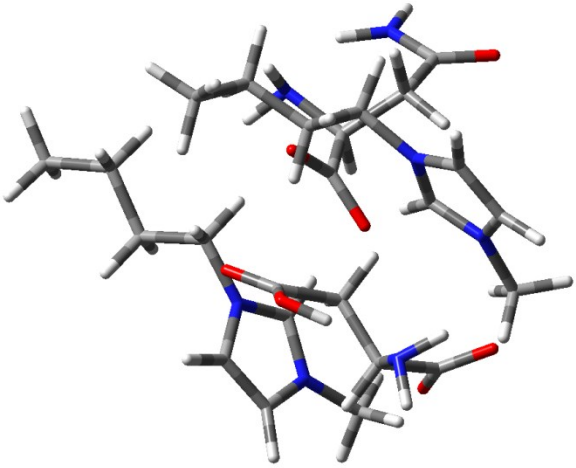


I_P_nn_C6 (50.2)

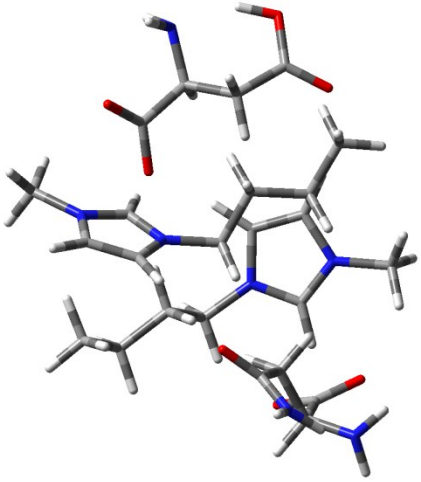
Figure S6



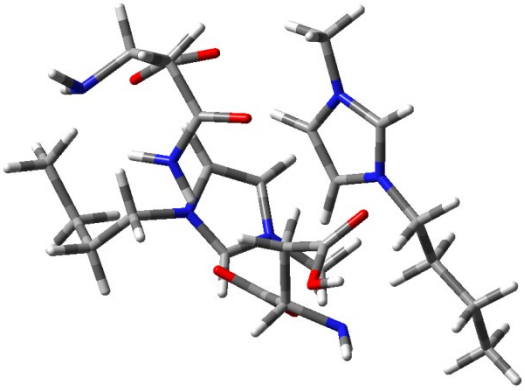
I_A_mn_C1 (0.0)



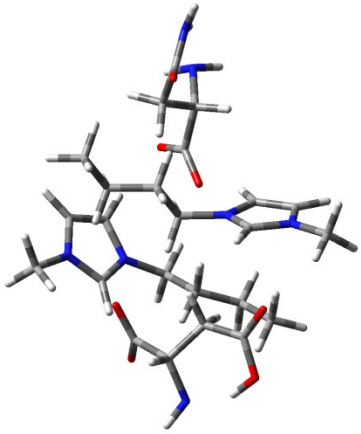
I_T_fn_C5 (8.5)



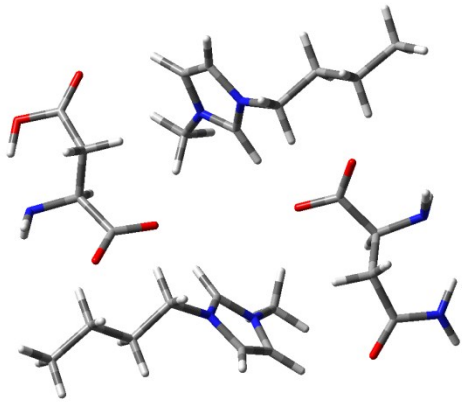
I_DA_nn_C1 (10.6)



I_A_mn_C17 (11.2)

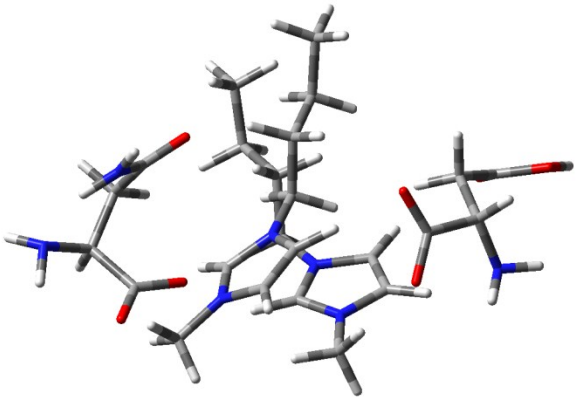


I_DP_nn_C2 (12.3)

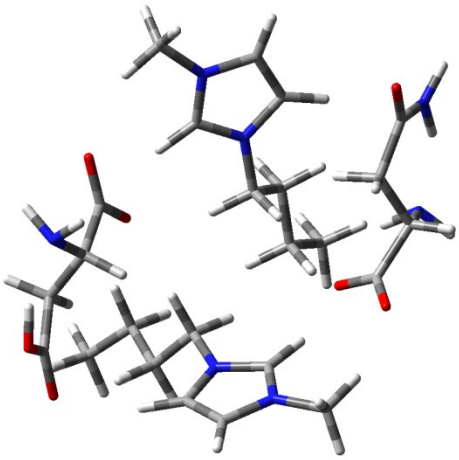


I_T_fn_C4 (14.1)

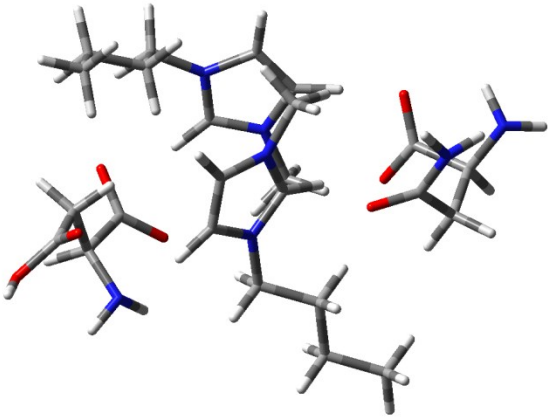
Figure S7 contd.



I_P_nn_C6 (16.2)



I_T_fn_C1 (16.6)



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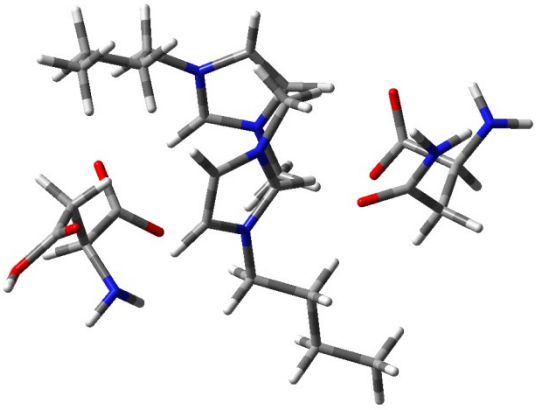
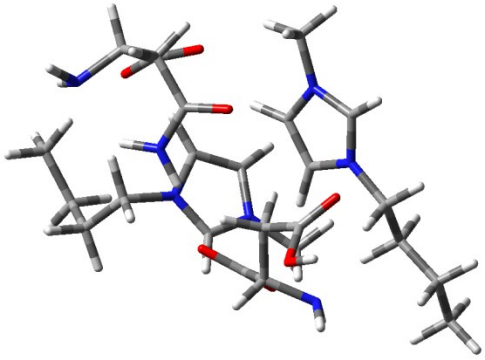
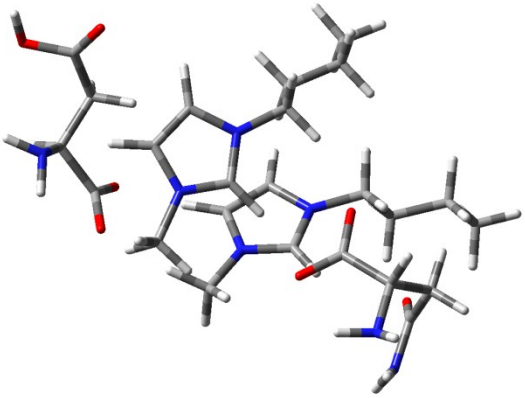


I_A_mn_C2 (19.4)

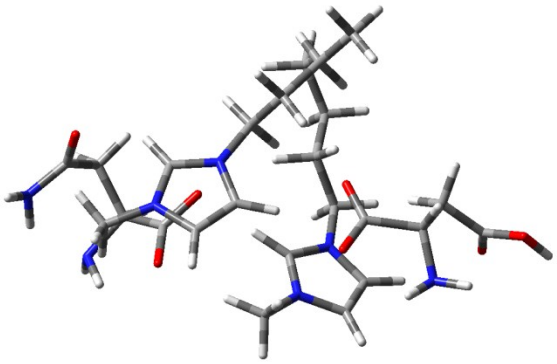


I_A_fn_C15 (21.1)

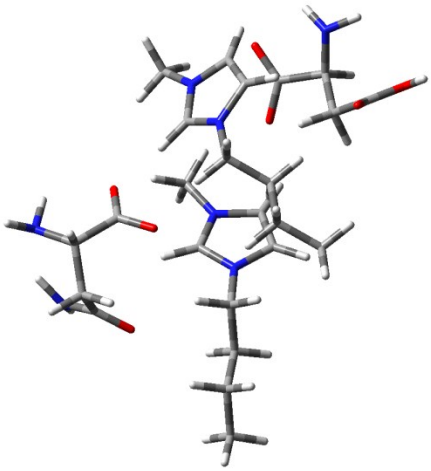


I_P_fm_C8 (22.1)

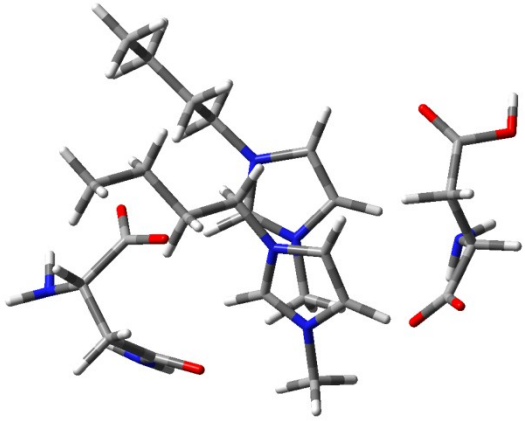
Figure S7 contd.



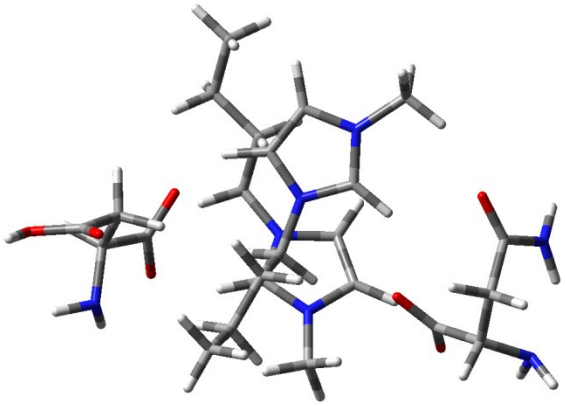
I_P_mf_C7 (22.4)



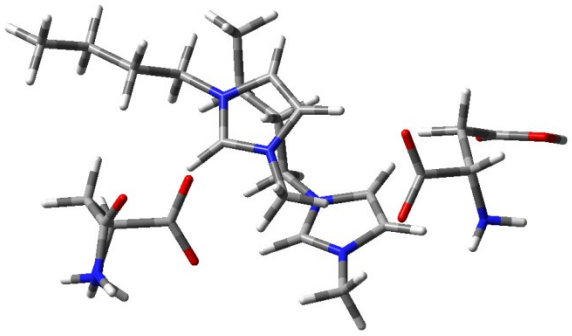
I_P_fm_C15 (22.6)



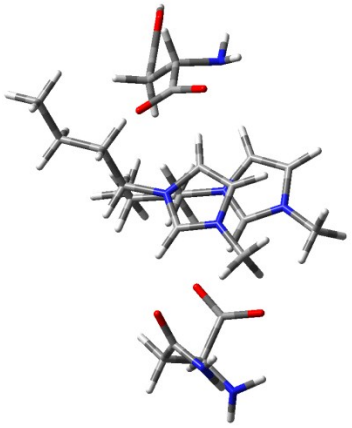
I_P_fn_C9 (22.8)



I_A_fn_C16 (25.8)

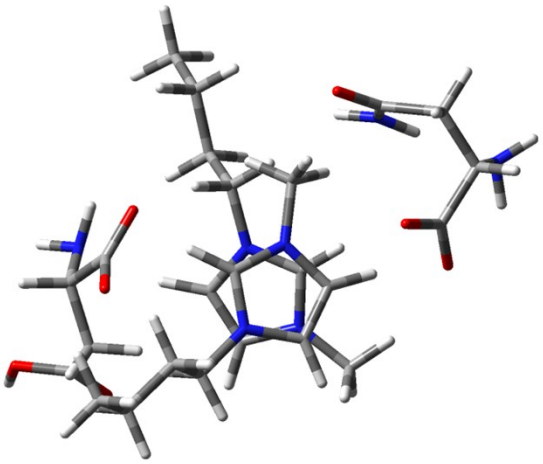


I_P_fn_C10 (26.3)

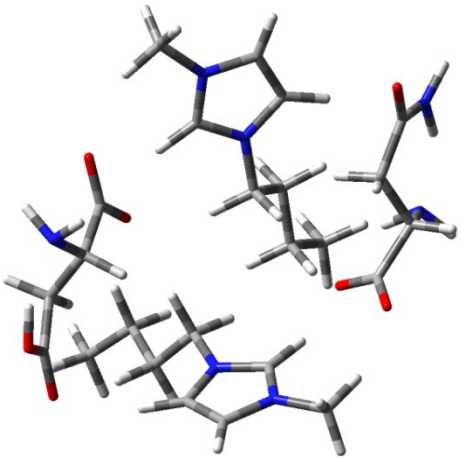


I_P_mn_C1 (26.8)

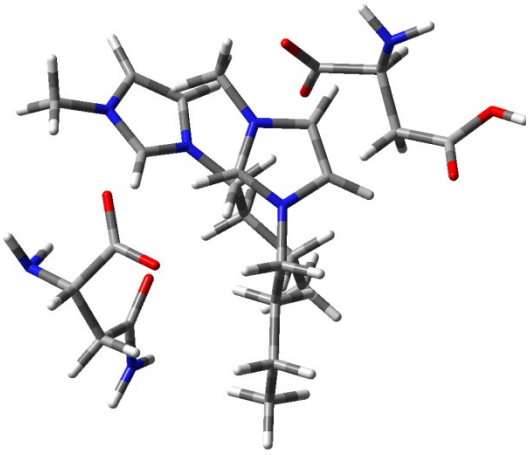
Figure S7 contd.



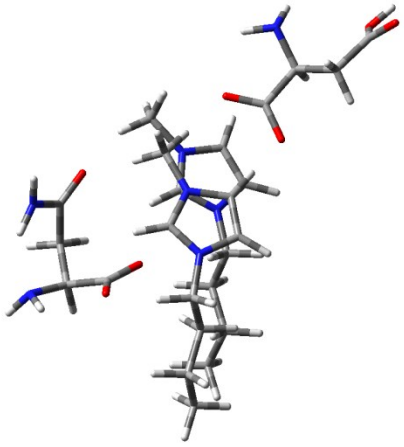
I_A_mn_C18 (27.4)



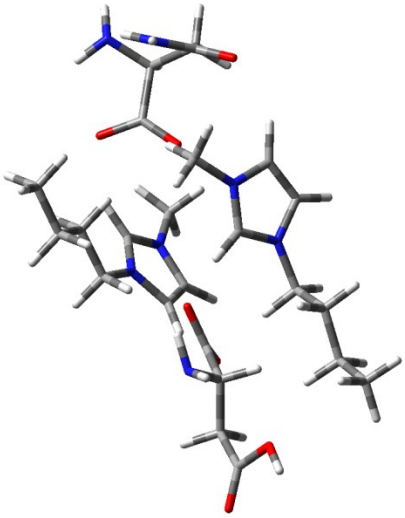
I_T_ff_C1 (32.3)



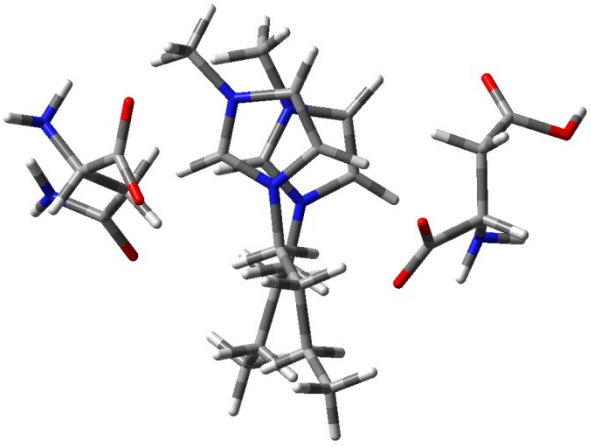
I_P_mm_C3 (33.3)



I_P_fm_C17 (33.8)



I_A_mm_C14 (34.7)



I_P_ff_C13 (39.4)

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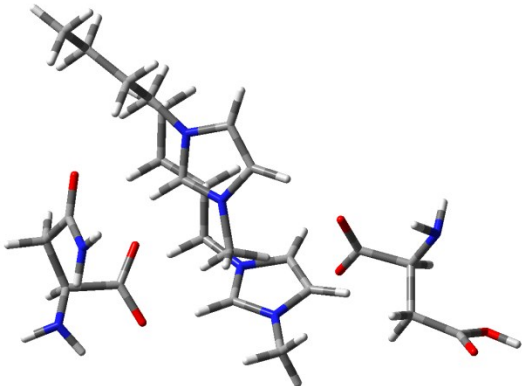
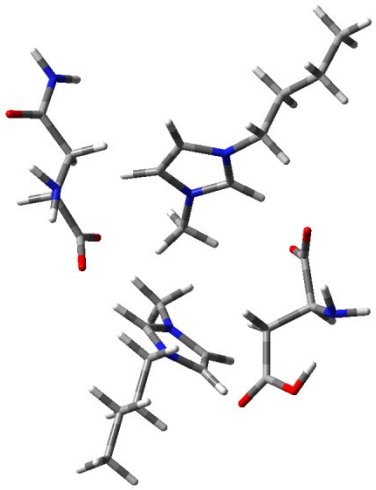
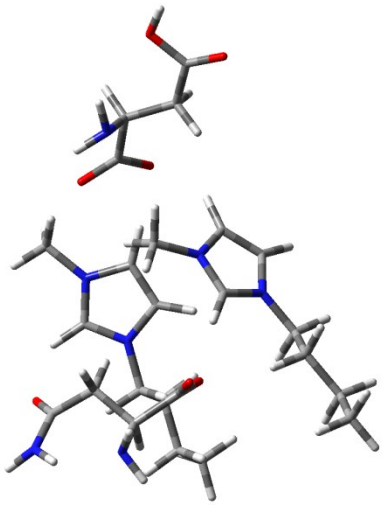


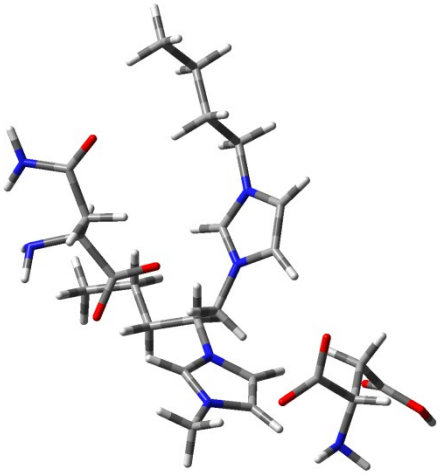
I_P_fm_C16 (44.8)



I_T_fn_C3 (46.3)

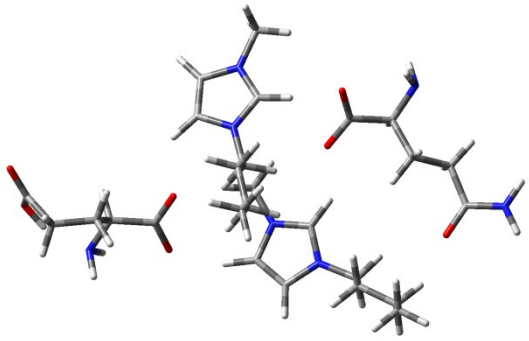


I_P_ff_C12 (46.8)

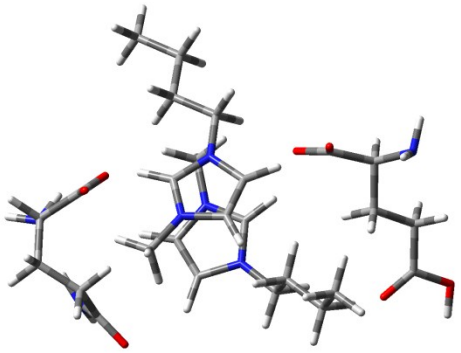


I_P_ff_C11 (49.4)

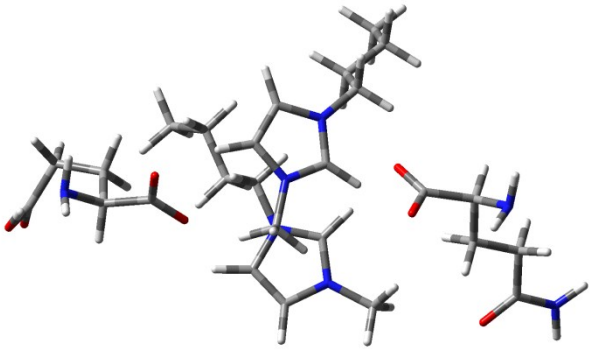
Figure S7



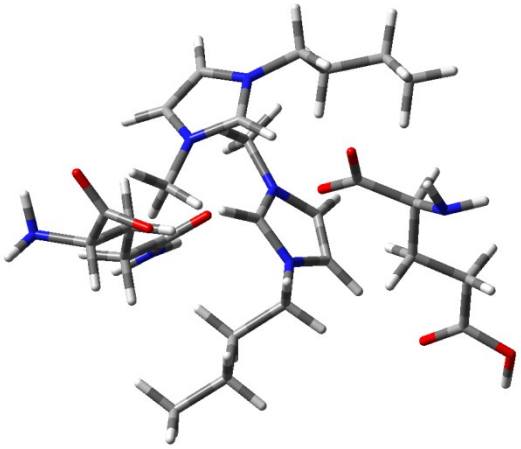
II_P_mf_C1 (0.0)



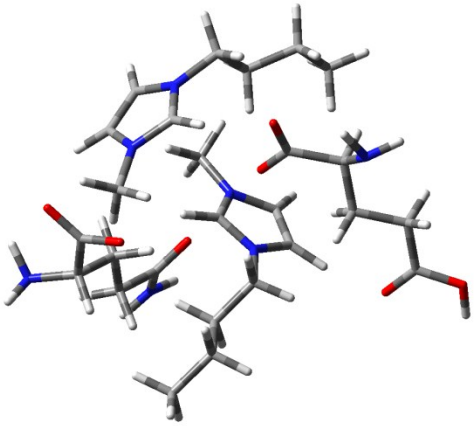
II_A _nn_C21(0.05)



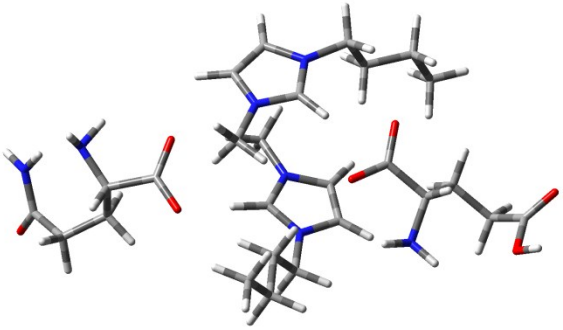
II_P_mm_C3 (14.6)



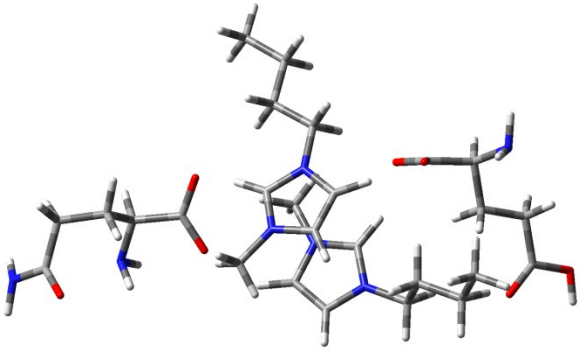
II_A _nn_C22 (19.4)

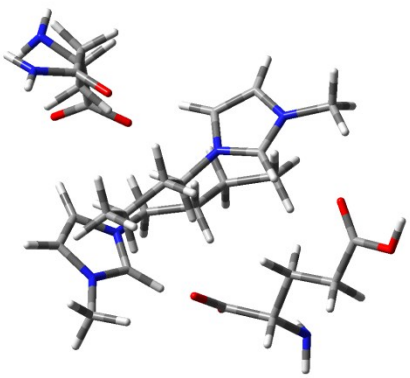


II_A _nn_C23 (19.4)

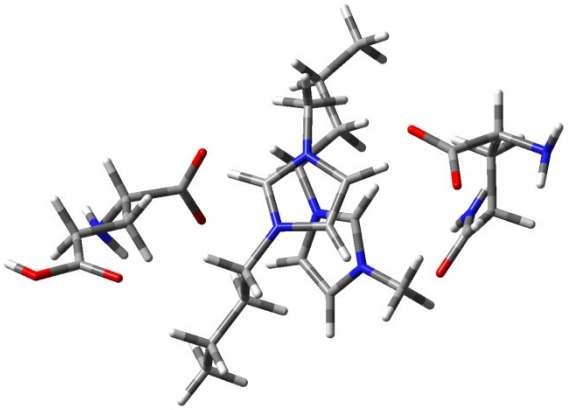


II_A_mm_C15 (21.9)

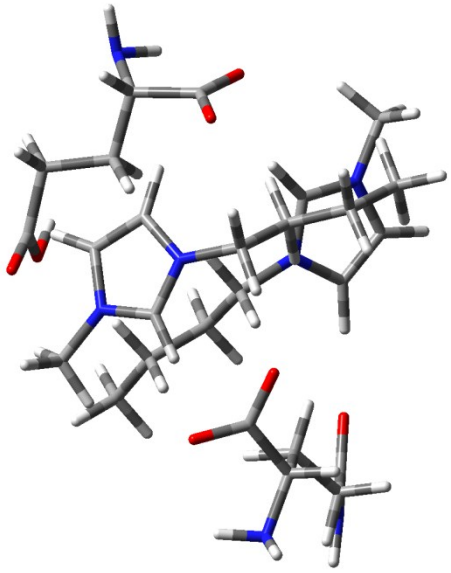




II_A _fm_C19 (28.5)



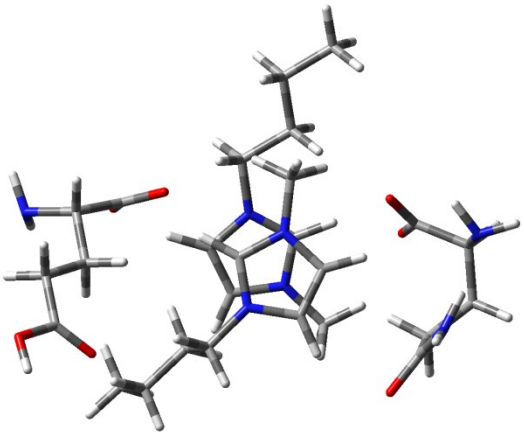
II_DP _nn_C2 (29.11)



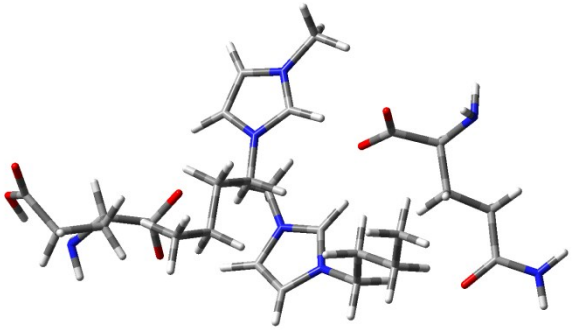
II_A _mn_C20 (33.6)

II_DA _nn_C1 (33.7)

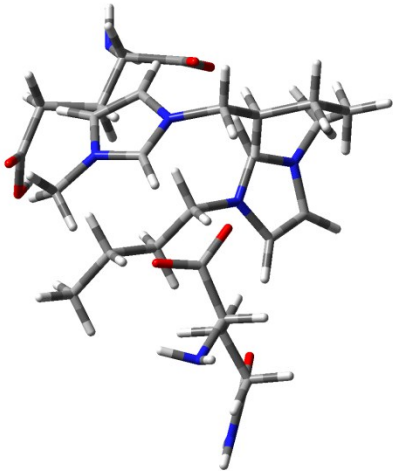
Figure S8



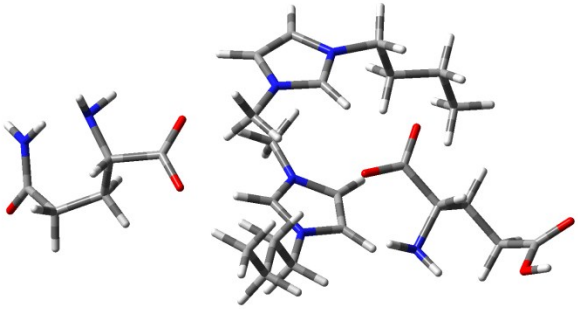
II_A _nn_C21 (0.0)



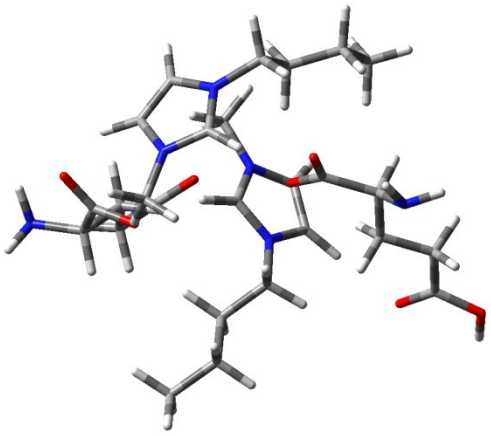
II_P_mf_C1 (15.13)



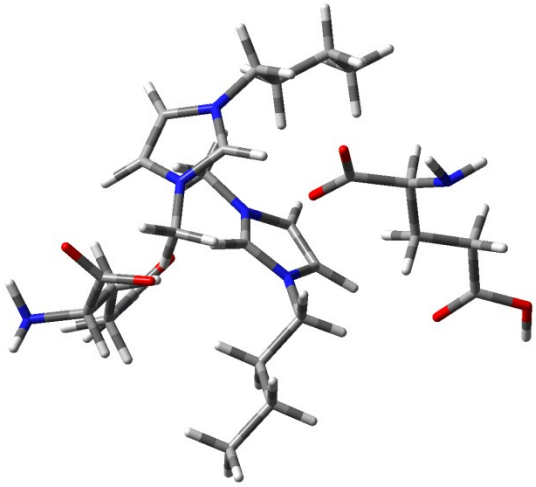
II_DA _nn_C1 (18.6)



II_A _mm_C15 (28.8)

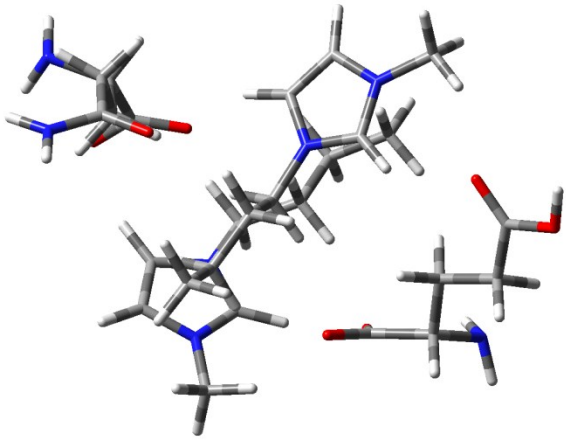


II_A _nn_C22 (29.29)

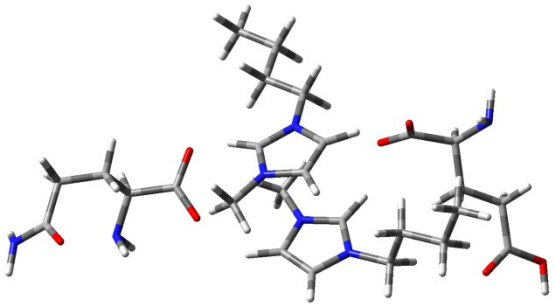


II_A _nn_C23 (29.29)

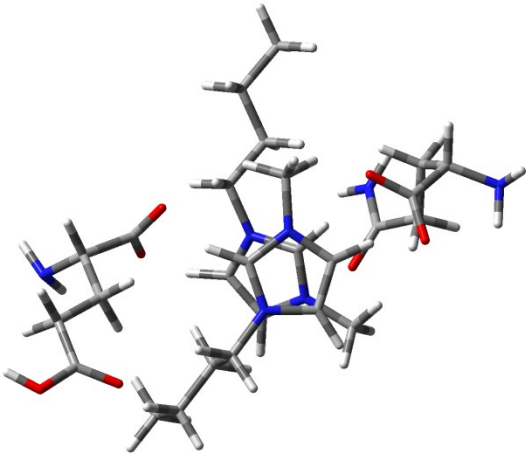
Figure S9 contd.



II_DP _nn_C2 (30.8)



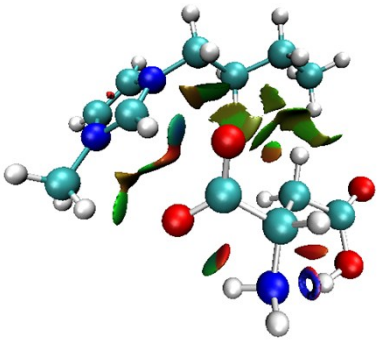
II_A _fm_C19 (36.8)

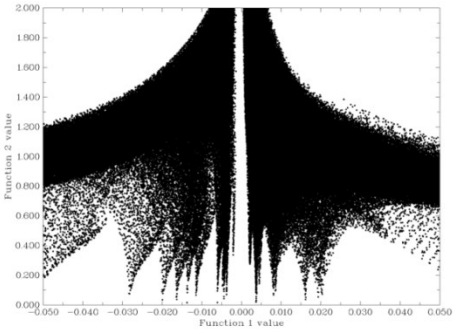


II_A _mn_C20 (40.92)

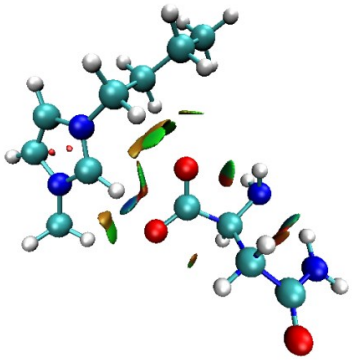
Figure S9

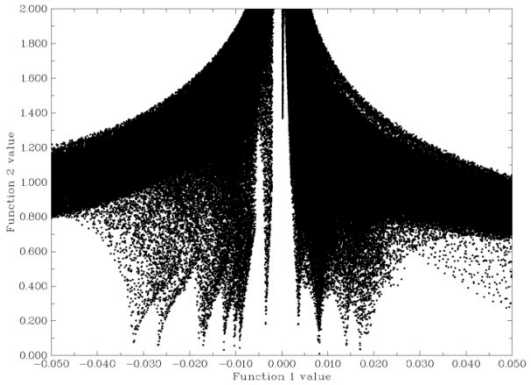
(a)



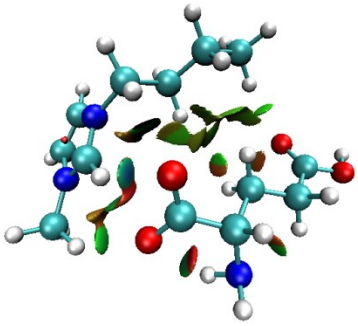


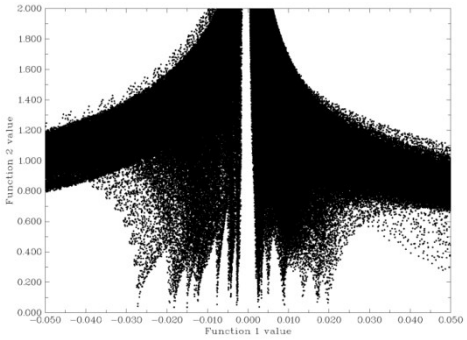
(b)



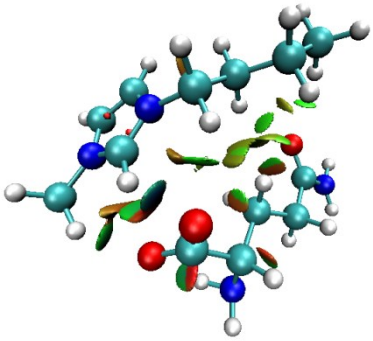


(c)





(d)



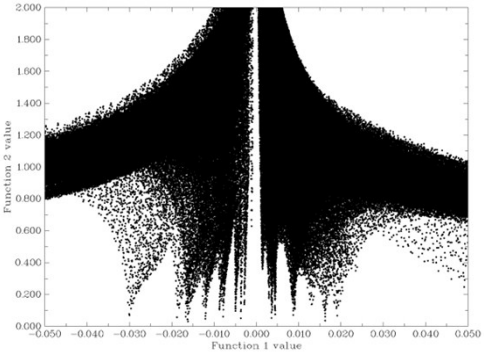
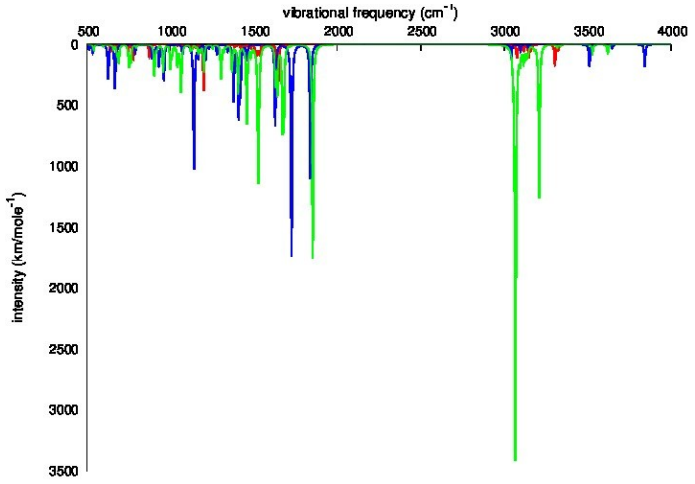
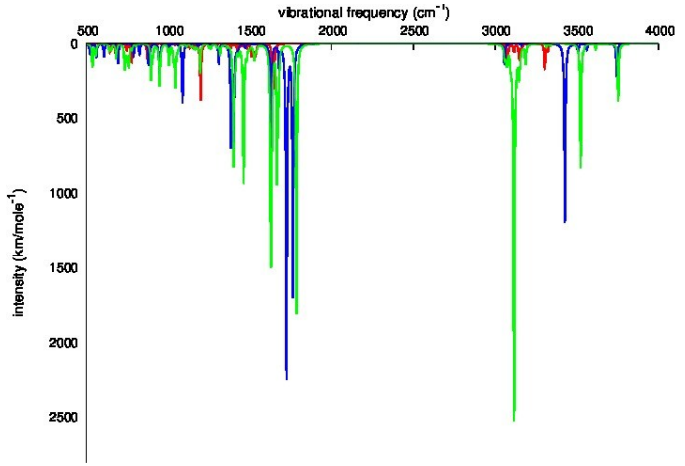


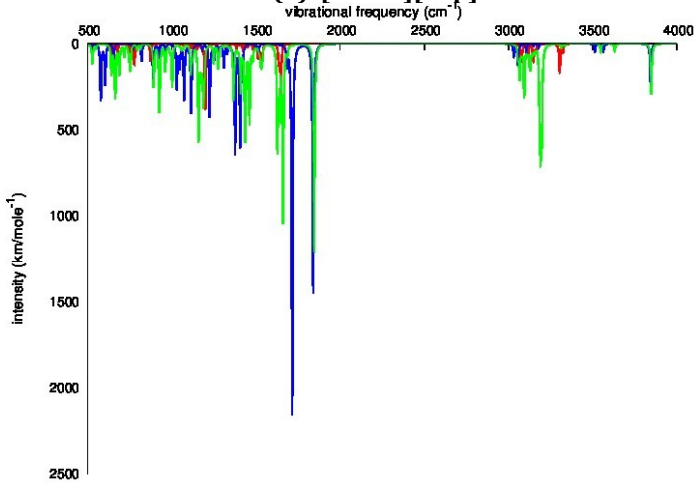
Figure S10



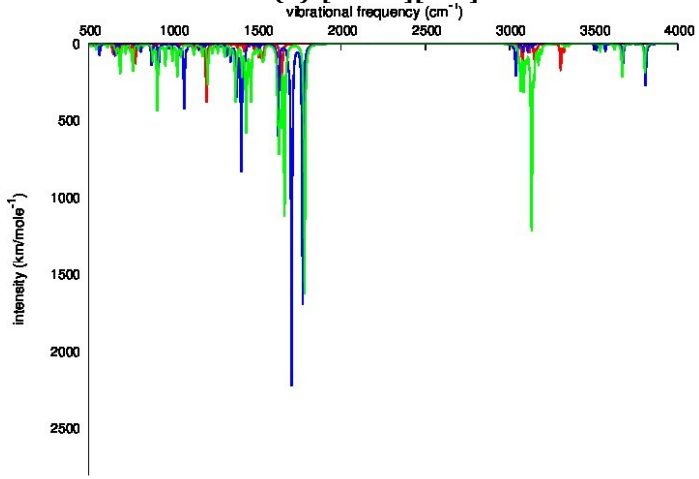
(a) [Bmim][Asp]



(b) [Bmim][Asn]



(a) [Bmim][Glu]



(b) [Bmim][Gln]

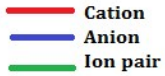
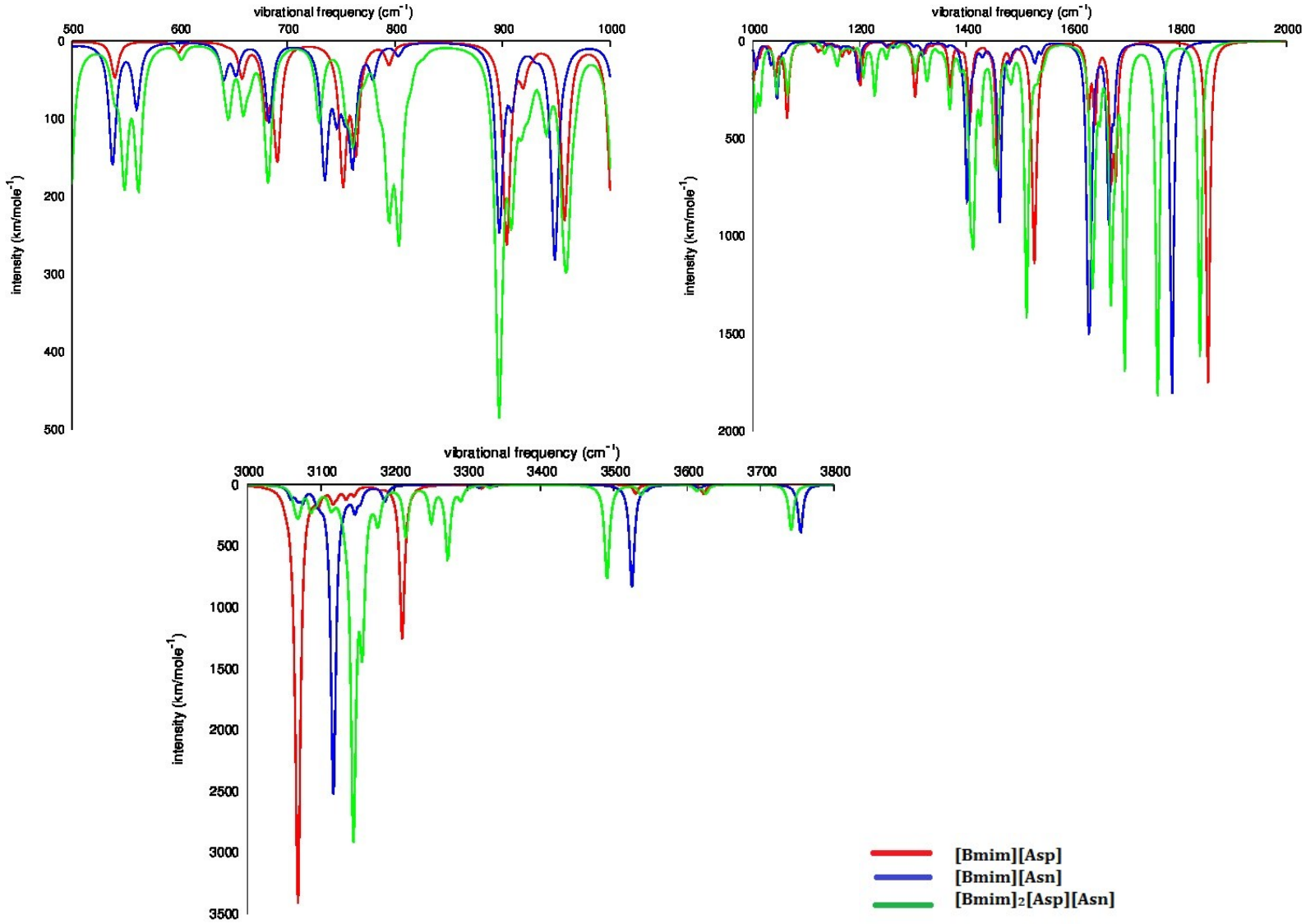
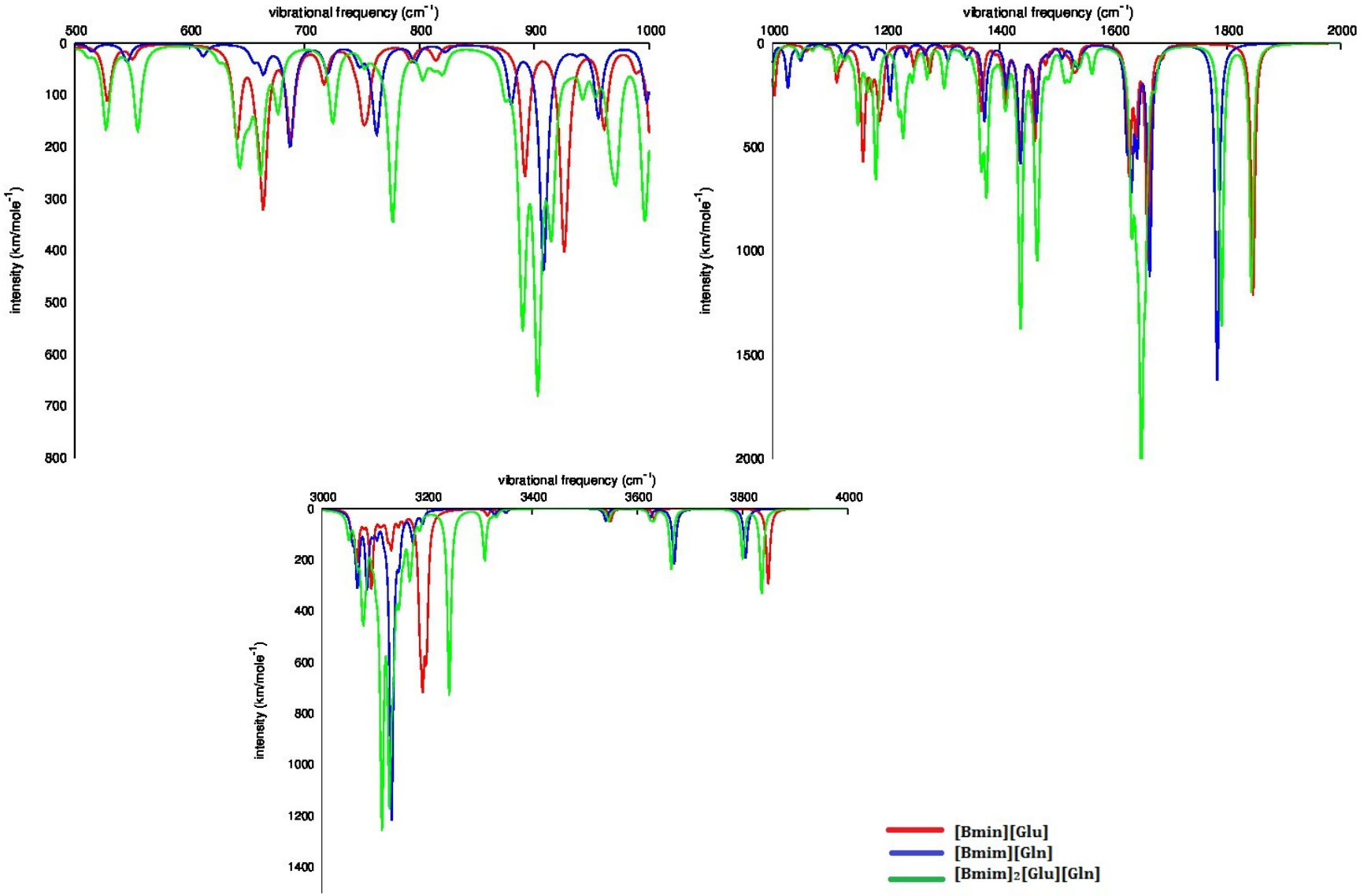


Figure S11



(a) $[Bmim]_2[Asp][Asn]$

Figure S12 contd.



(b) [Bmim]$_2$[Glu][Gln]

Figure S12