Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

On the interaction between imidazolium cation and aromatic amino acids. A computational study

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Table S1. Complexation energies (kJ/mol) obtained for the most stable minima of the imidazolium···phenylalanine complex. Zwitterionic minima in italics.

	M06-2X/ 6-31+G*	MP2/CBS	MP2.X	SAPT	$E_{def,MP2/CBS}$
Phe-A	-127.6	-133.5	-122.3	-123.3	34.4
Phe-B	*-113.3*	*-118.7*	*-118.4*	*-110.8*	*84.0*
Phe-C	-123.5	-130.3	-118.4	-119.5	34.7
Phe-D	-115.2	-119.2	-117.7	-116.8	7.0
Phe-E	*-111.0*	*-114.9*	*-114.9*	*-107.4*	*94.3*
Phe-F	*-108.5*	*-116.1*	*-114.5*	*-108.1*	*86.8*
Phe-G	-112.0	-115.5	-114.0	-113.8	10.0
Phe-H	-110.5	-114.7	-112.9	-113.2	10.7
Phe-I	-114.8	-117.0	-111.6	-114.2	29.5
Phe-J	*-106.7*	*-112.5*	*-111.1*	*-105.0*	*98.4*
Phe-K	-114.7	-114.9	-111.0	-112.5	31.0
Phe-L	-111.1	-115.6	-110.6	-109.7	23.0
Phe-M	-112.3	-113.9	-110.6	-110.1	24.2
Phe-N	-113.3	-112.5	-108.2	-110.0	32.6
Phe-O	*-103.8*	*-109.4*	*-108.1*	*-99.6*	*83.9*
Phe-P	-108.7	-111.7	-107.4	-107.2	27.2
Phe-Q	*-105.9*	*-105.1*	*-105.5*	*-96.1*	*97.2*
Phe-R	-108.4	-110.5	-105.3	-107.3	30.1
Phe-S	*-100.6*	*-104.8*	*-103.6*	*-95.1*	*93.1*
Phe-T	-103.4	-105.9	-102.3	-100.8	16.1

Table S2. Complexation energies (kJ/mol) obtained for the most stable minima of the imidazolium···tyrosine complex. Zwitterionic minima in italics.

	M06-2X/ 6-31+G*	MP2/CBS	MP2.X	SAPT	$E_{def,MP2/CBS}$
Tyr-A	-131.3	-137.7	-124.6	-125.3	39.0
Tyr-B	-130.9	-136.7	-123.4	-123.5	40.9
Tyr-C	-126.5	-128.2	-122.9	-121.5	29.4
Tyr-D	-124.9	-126.1	-121.1	-119.6	29.2
Tyr-E	-128.3	-135.0	-120.4	-121.0	41.8
Tyr-F	*-114.1*	*-119.8*	*-119.1*	*-112.5*	*85.9*
Tyr-G	-115.9	-120.2	-118.3	-116.9	8.8
Tyr-H	*-113.4*	*-119.1*	*-118.3*	*-111.8*	*84.5*
Tyr-I	-122.7	-126.5	-118.2	-116.5	29.7
Tyr-J	-113.8	-118.9	-116.6	-115.6	9.4
Tyr-K	-113.6	-117.9	-116.0	-114.6	7.6
Tyr-L	*-112.2*	*-115.9*	*-115.8*	*-107.5*	*82.9*
Tyr-M	*-111.2*	*-115.6*	*-115.1*	*-109.1*	*96.4*
Tyr-N	-116.9	-119.1	-115.0	-115.0	23.9
Tyr-O	*-110.9*	*-115.3*	*-114.9*	*-108.8*	*96.4*
Tyr-P	*-108.7*	*-116.3*	*-114.2*	*-109.0*	*88.2*
Tyr-Q	-118.8	-121.0	-113.8	-112.0	33.5
Tyr-R	-111.6	-115.6	-113.7	-114.0	11.6
Tyr-S	-118.4	-122.3	-113.7	-112.1	30.8
Tyr-T	-119.1	-120.1	-113.3	-111.4	36.1

Table S3. Complexation energies (kJ/mol) obtained for the most stable minima of the imidazolium···tryptophan complex. Zwitterionic minima in italics.

	M06-2X/ 6-31+G*	MP2/CBS	MP2.X	SAPT	$E_{def,MP2/CBS}$
Trp-A	-138.2	-147.6	-131.5	-132.2	44.6
Trp-B	-131.2	-138.2	-130.8	-129.6	23.7
Trp-C	*-121.4*	*-127.4*	*-126.8*	*-119.2*	*84.4*
Trp-D	-123.9	-132.7	-126.6	-126.1	30.5
Trp-E	-131.9	-140.5	-125.9	-125.6	38.7
Trp-F	-123.2	-132.5	-124.8	-123.9	24.0
Trp-G	*-120.2*	*-125.1*	*-123.8*	*-117.2*	*87.8*
Trp-H	-122.9	-133.7	-123.3	-122.5	24.8
Trp-I	*-118.4*	*-123.4*	*-122.8*	*-116.6*	*98.7*
Trp-J	*-116.3*	*-124.3*	*-122.4*	*-116.3*	*89.0*
Trp-K	-127.7	-139.0	-121.1	-121.5	45.6
Trp-L	-125.6	-135.5	-119.7	-120.7	50.0
Trp-M	-122.1	-126.8	-119.4	-121.3	40.0
Trp-N	-116.6	-120.7	-119.1	-116.9	8.5
Trp-O	*-111.1*	*-121.8*	*-119.1*	*-113.8*	*92.3*
Trp-P	*-113.8*	*-120.6*	*-118.8*	*-113.8*	*103.1*
Trp-Q	-117.2	-126.2	-118.2	-116.8	22.2
Trp-R	*-114.9*	*-117.7*	*-117.8*	*-109.2*	*92.2*
Trp-S	*-113.0*	*-119.4*	*-117.5*	*-112.6*	*103.3*
Trp-T	-117.4	-125.7	-117.4	-116.1	35.0

Table S4. Complexation energies (kJ/mol) obtained for the most stable minima of the imidazolium···histidine complex. Zwitterionic minima in italics.

	M06-2X/ 6-31+G*	MP2/CBS	MP2.X	SAPT	$E_{def,MP2/CBS}$
His-A	*-143.7*	*-146.0*	*-145.5*	*-140.7*	*81.0*
His-B	*-144.4*	*-144.2*	*-143.6*	*-139.0*	*88.6*
His-C	*-141.6*	*-142.5*	*-142.4*	*-135.9*	*77.3*
His-D	-135.3	-137.5	-142.2	-186.0	333.3
His-E	*-138.2*	*-142.5*	*-140.6*	*-137.6*	*88.3*
His-F	*-142.2*	*-140.4*	*-140.3*	*-134.0*	*83.7*
His-G	*-139.3*	*-140.8*	*-138.9*	*-135.9*	*95.9*
His-H	-131.1	-132.7	-137.6	-181.7	346.4
His-I	-132.0	-133.0	-136.7	-180.2	329.7
His-J	*-134.1*	*-137.2*	*-135.5*	*-130.1*	*81.7*
His-K	-130.0	-126.4	-134.6	-154.3	375.8
His-L	-126.3	-122.4	-130.3	-146.9	365.4
His-M	-122.2	-123.9	-128.4	-171.8	338.4
His-N	-119.2	-123.9	-127.9	-171.0	311.9
His-O	-124.3	-118.7	-127.2	-144.3	401.3
His-P	-127.7	-127.9	-126.4	-126.3	25.3
His-Q	-119.7	-119.0	-125.9	-143.3	331.2
His-R	-128.4	-130.6	-125.5	-126.1	46.1
His-S	-130.6	-129.0	-125.2	-127.1	35.4
His-T	-128.7	-127.4	-125.1	-125.6	29.8
His-U	-125.8	-126.9	-124.8	-125.5	26.7
His-V	-113.1	-111.7	-124.7	-180.7	513.0
His-W	-127.7	-129.0	-124.3	-125.3	35.2
His-X	-127.4	-125.5	-123.9	-124.9	25.9
His-Y	-116.8	-115.4	-121.7	-139.2	324.6
His-Z	-121.1	-122.7	-121.1	-121.5	41.0
His-AA	-123.7	-124.7	-120.9	-122.6	30.7
His-AB	-117.6	-111.4	-120.1	-139.4	421.5
His-AC	-111.9	-115.6	-119.2	-169.7	368.5
His-AD	-124.4	-123.1	-119.1	-119.4	60.5
His-AE	-118.3	-119.0	-118.2	-115.2	156.5

His-AF	-123.1	-118.5	-118.0	-111.0	22.0
His-AG	-120.4	-116.8	-115.9	-106.9	29.1
His-AH	-107.9	-112.8	-114.8	-102.7	316.8
His-AI	-107.4	-112.8	-114.7	-98.5	337.7

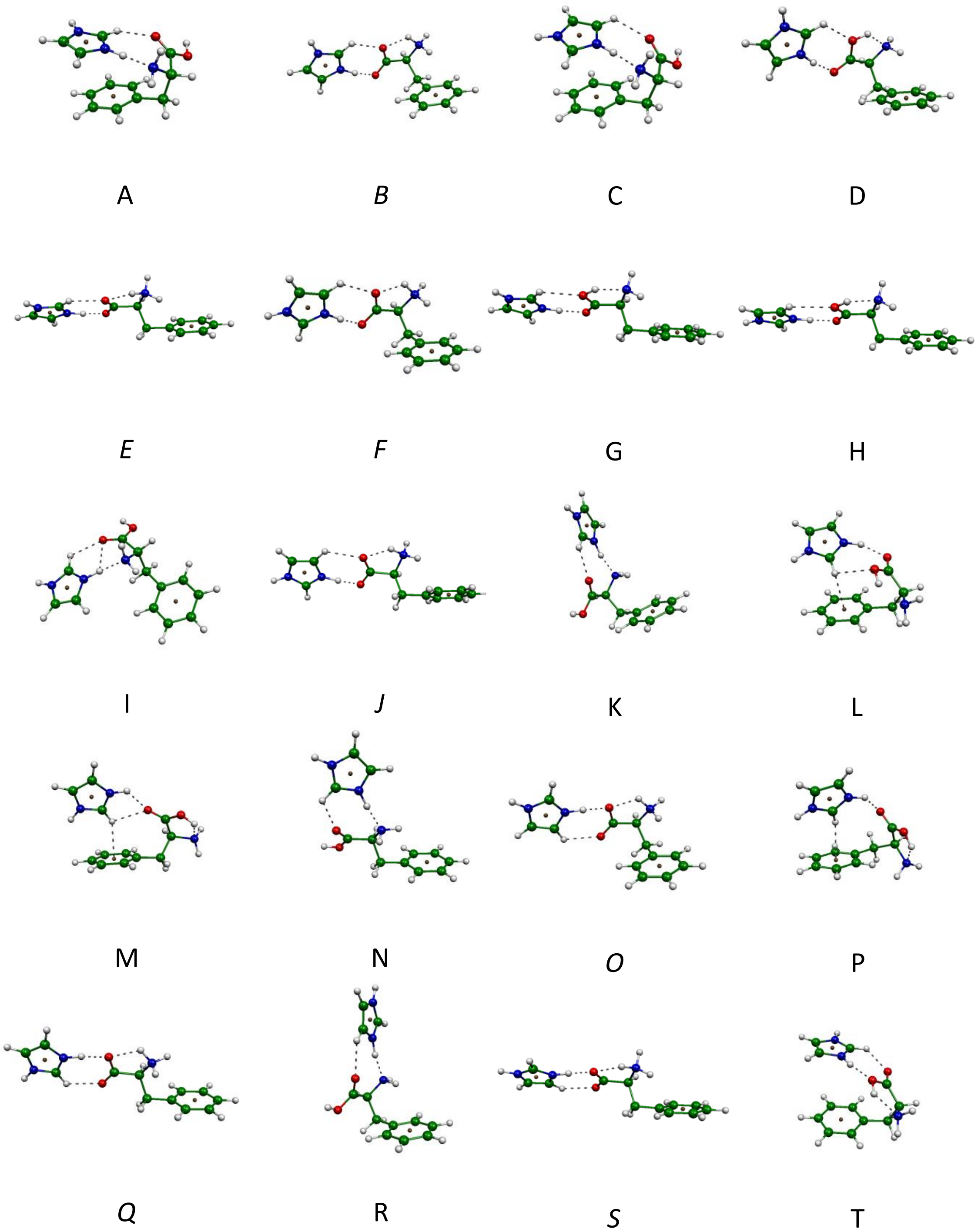


Figure S1. Structures of the most stable minima of Imz···Phe complex as obtained at the M06-2X/6-31+G* level. Zwitterionic minima in italics.

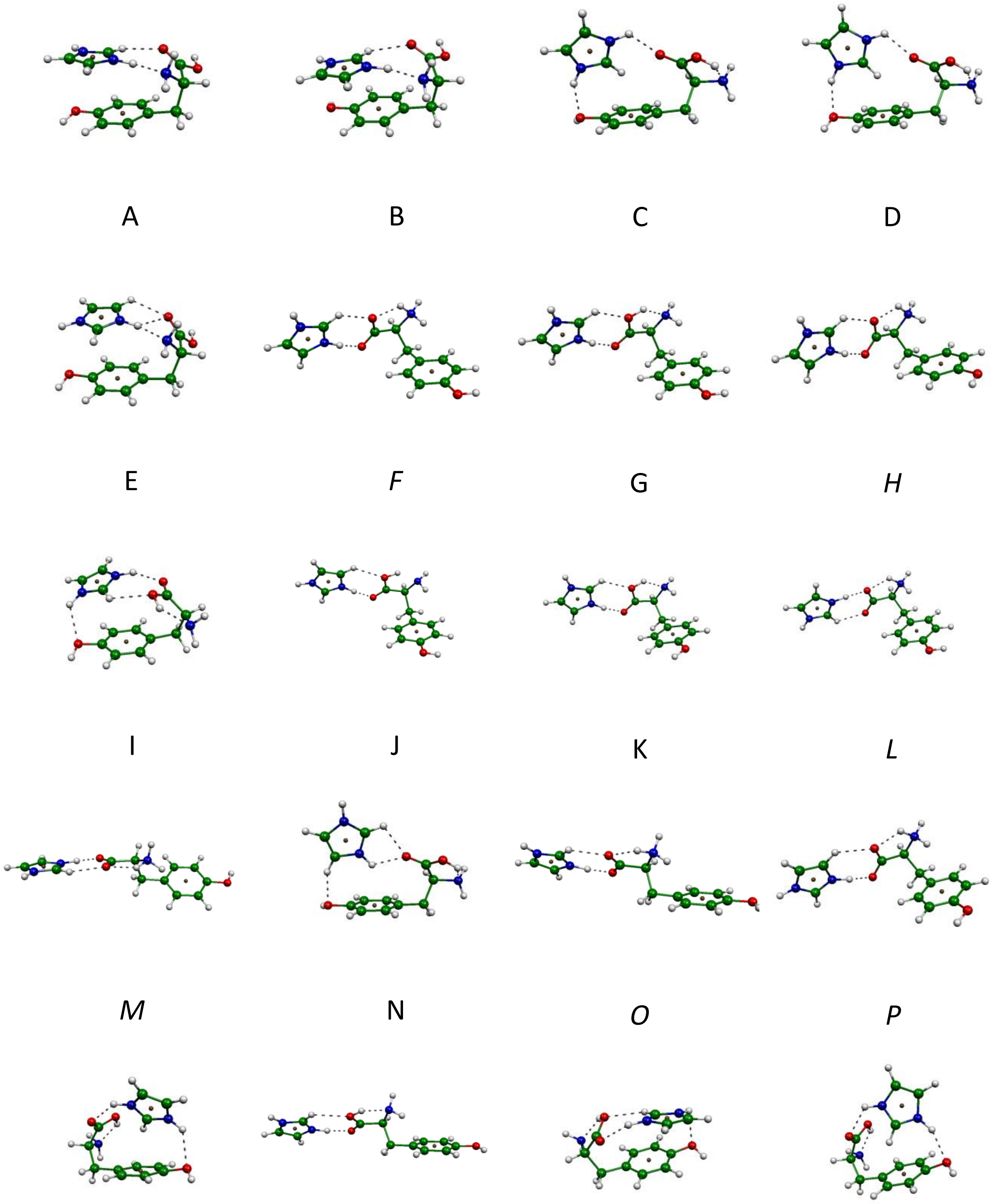


Figure S2. Structures of the most stable minima of Imz···Tyr complex as obtained at the M06-2X/6-31+G* level. Zwitterionic minima in italics.

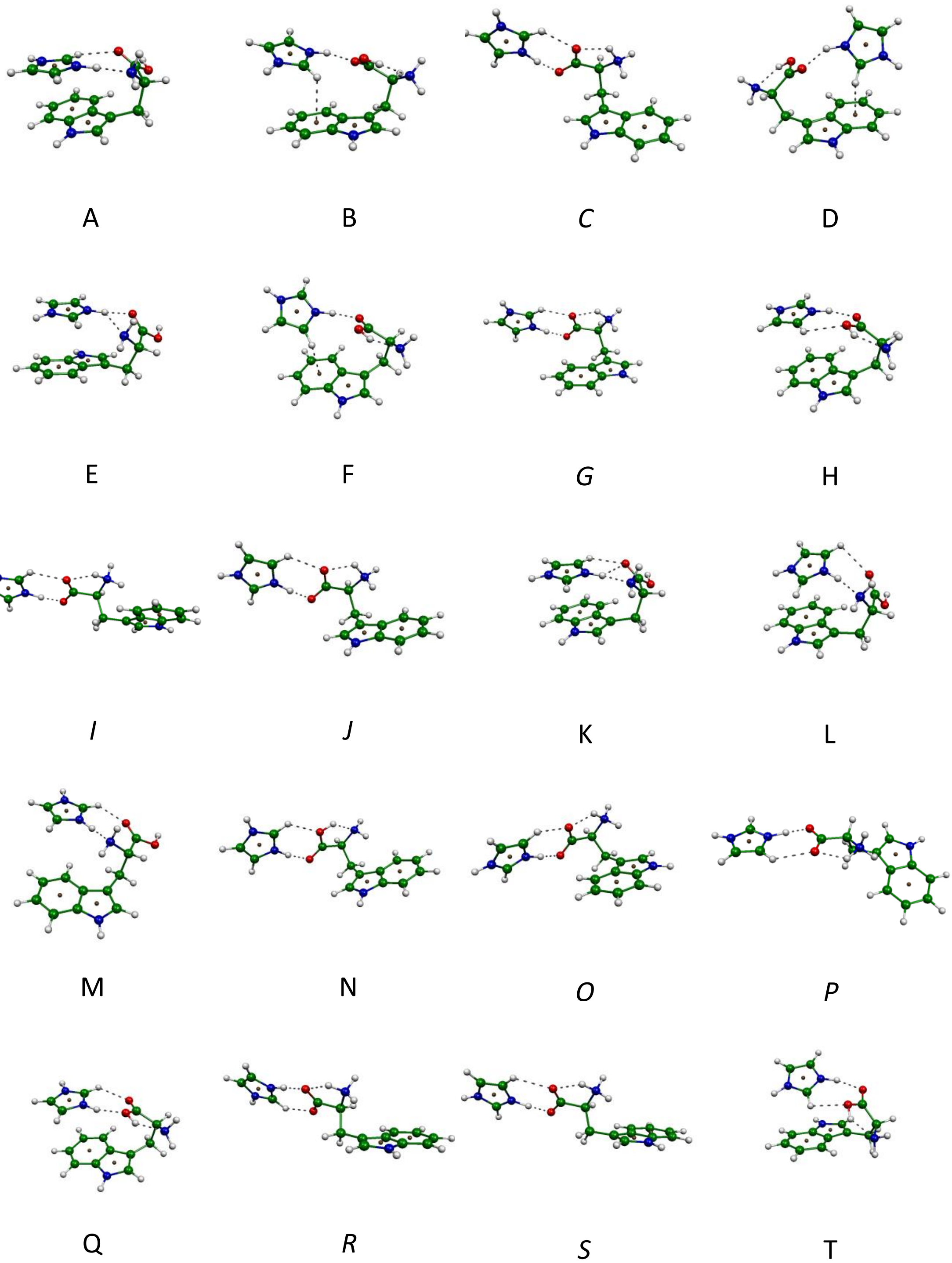


Figure S3. Structures of the most stable minima of Imz···Trp complex as obtained at the M06-2X/6-31+G* level. Zwitterionic minima in italics.

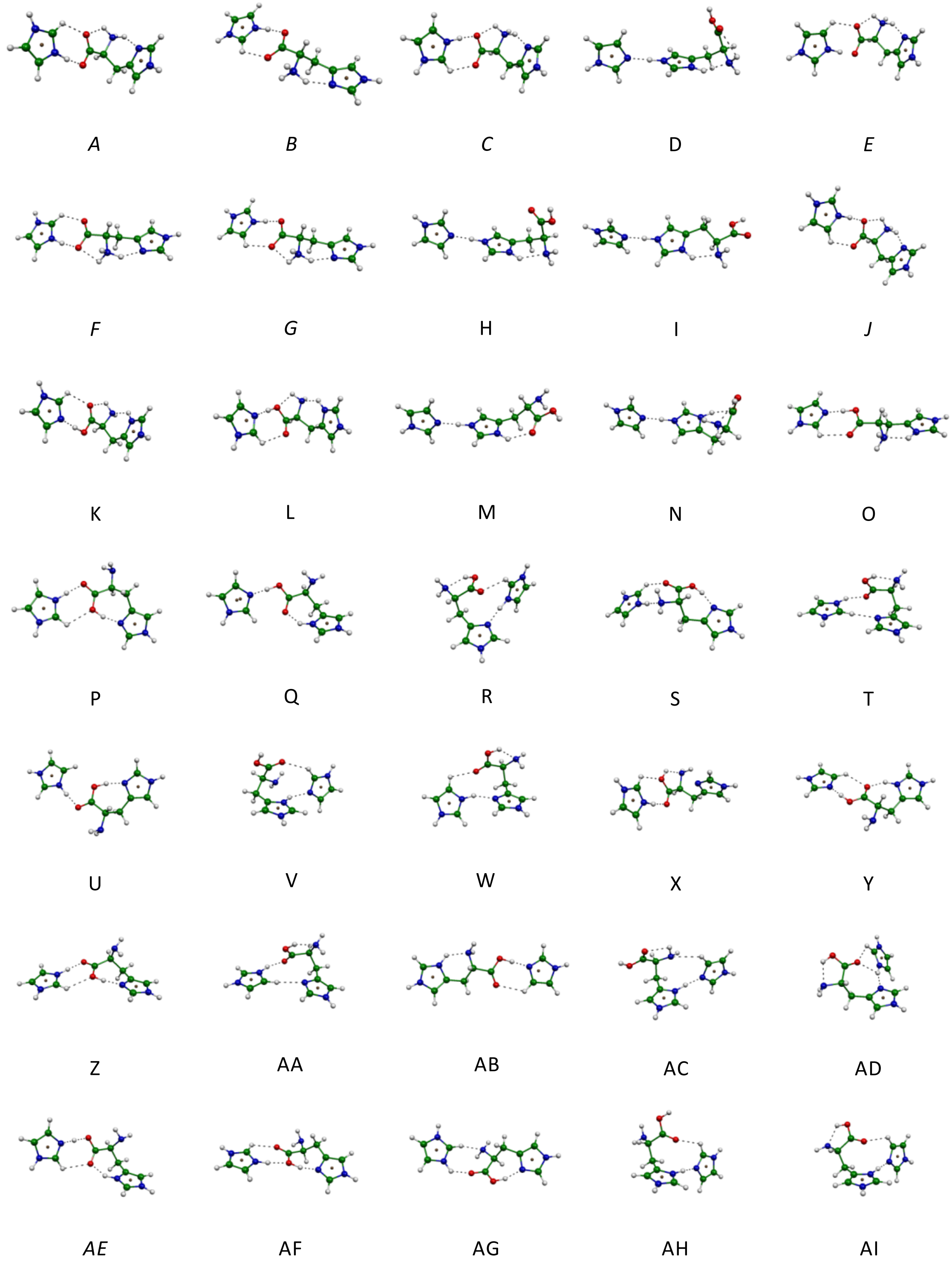
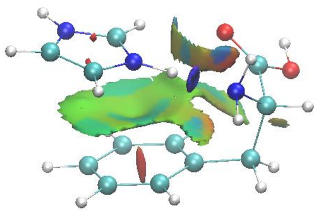
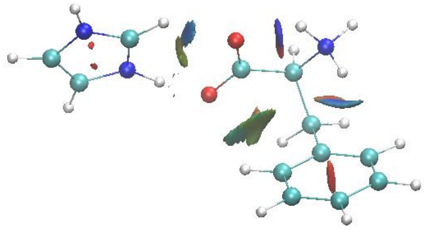


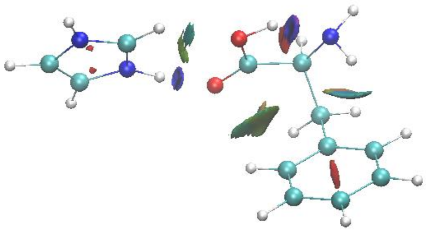
Figure S4. Structures of the most stable minima of Imz···His complex as obtained at the M06-2X/6-31+G* level. Zwitterionic minima in italics.



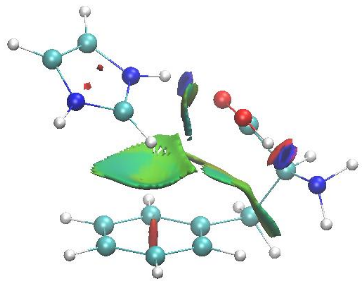
Phe-A (P)



Phe-B (Z)

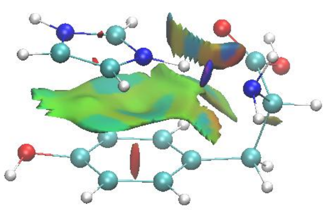


Phe-D (E)

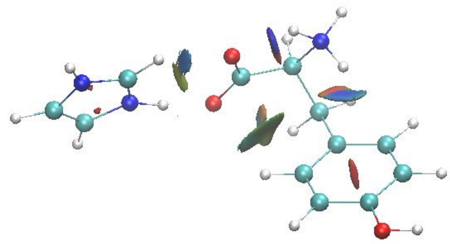


Phe-L (T)

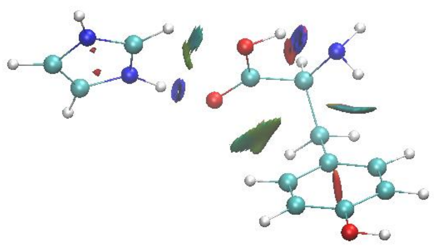
Figure S5. Non covalent interaction (NCI) plots for selected complexes of Imz with Phe. The reduced gradient density isosurface amounts to 0.5 a.u. and the color scale runs from 0.02 a.u. (red) to 0.02 a.u. (blue). Zwitterionic minima in italics.



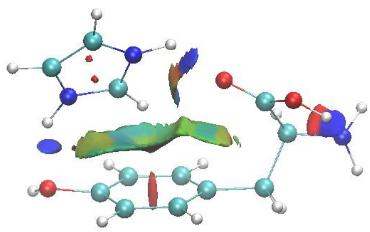
Tyr-A (P)



Tyr-F (Z)



Tyr-G (E)



Tyr-C (T)

Figure S6. Non covalent interaction (NCI) plots for selected complexes of Imz with Tyr. The reduced gradient density isosurface amounts to 0.5 a.u. and the color scale runs from 0.02 a.u. (red) to 0.02 a.u. (blue). Zwitterionic minima in italics.

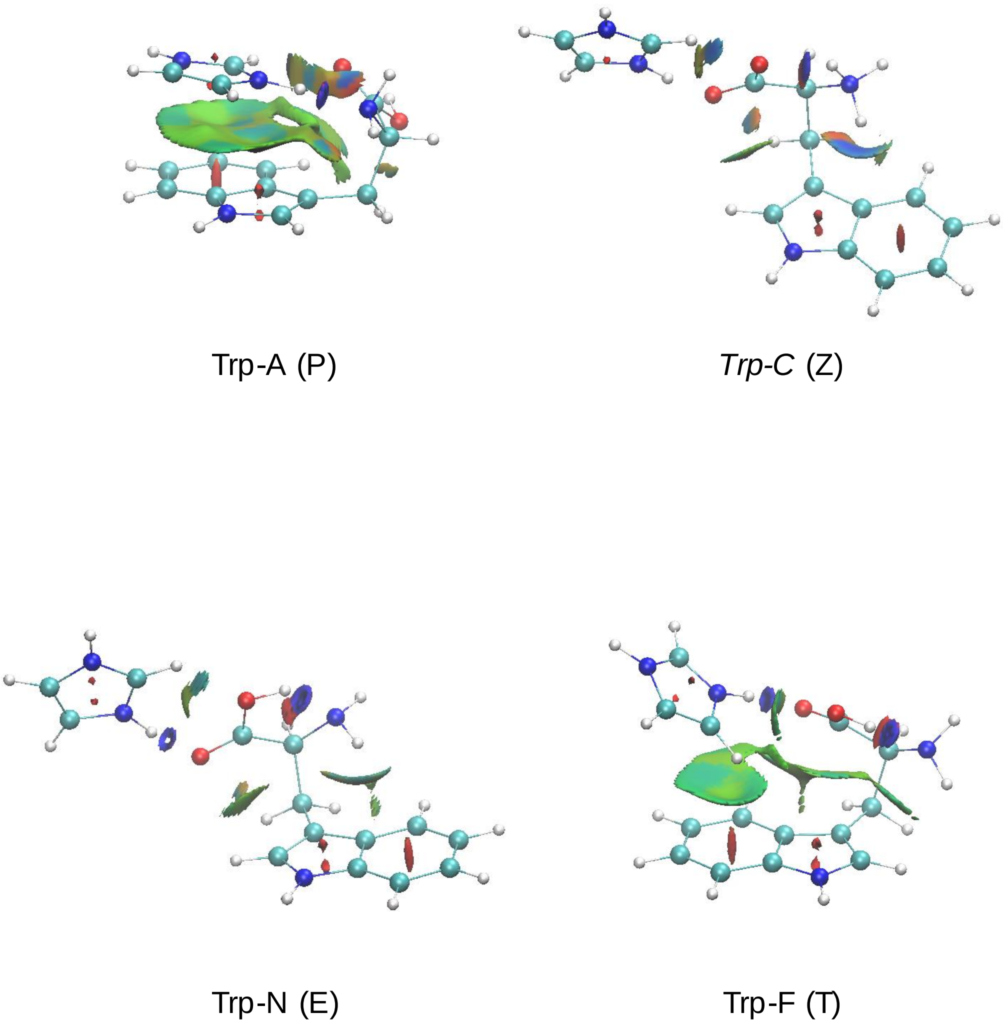
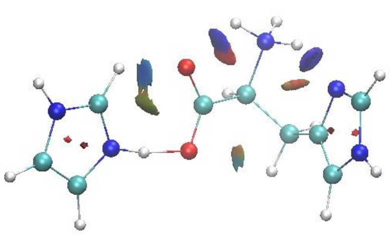
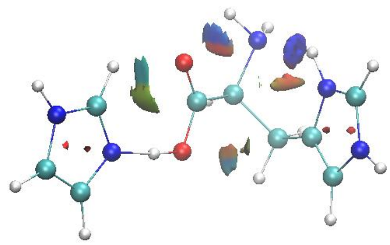


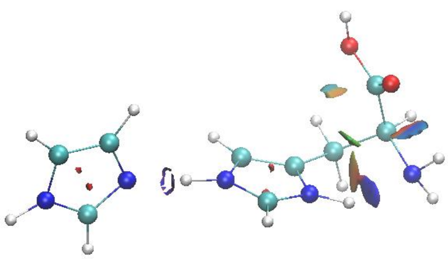
Figure S7. Non covalent interaction (NCI) plots for selected complexes of Imz with Trp. The reduced gradient density isosurface amounts to 0.5 a.u. and the color scale runs from 0.02 a.u. (red) to 0.02 a.u. (blue). Zwitterionic minima in italics.



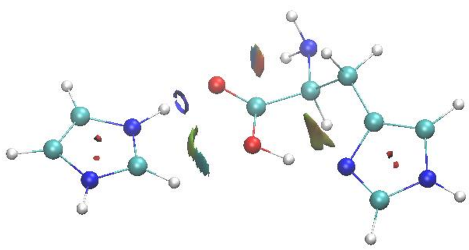
His-A



His-K

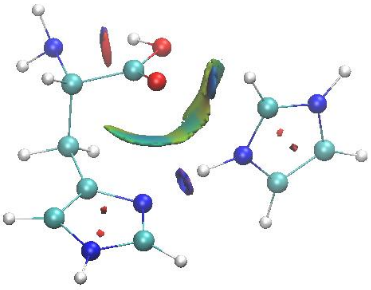


His-D

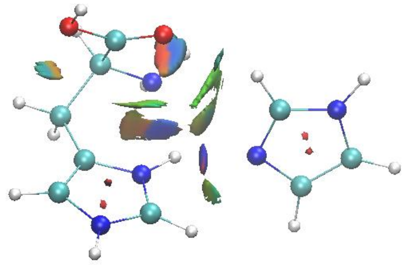


His-P

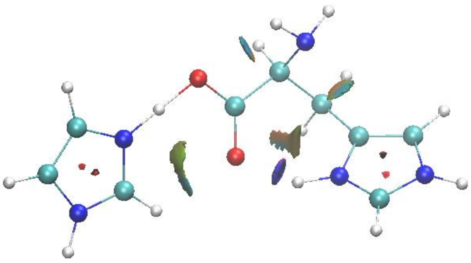
Figure S8a. Non covalent interaction (NCI) plots for selected complexes of Imz with His. The reduced gradient density isosurface amounts to 0.5 a.u. and the color scale runs from 0.02 a.u. (red) to 0.02 a.u. (blue). Zwitterionic minima in italics.



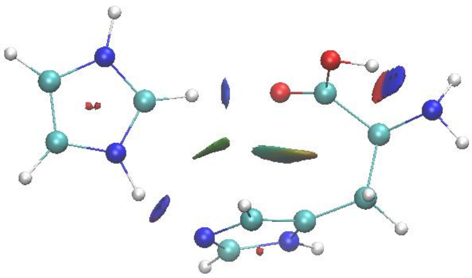
His-R



His-V



His-AE



His-AL

Figure S8b. Non covalent interaction (NCI) plots for selected complexes of Imz with His. The reduced gradient density isosurface amounts to 0.5 a.u. and the color scale runs from 0.02 a.u. (red) to 0.02 a.u. (blue).

Table S5. SAPT(DFT) contributions in mE_h to the interaction energy in Imz···Phe complexes as obtained employing PBE0 with the aug-cc-pVDZ basis set. Zwitterionic minima in italics.

	E_{ele}	E_{rep}	E_{ind}	$E_{exch-ind}$	E_{dis}	$E_{exch-dis}$	δ_{HF}
Phe-A	-59.84	54.14	-38.58	20.10	-25.04	3.97	-10.78
Phe-B	*-81.96*	*60.91*	*-45.64*	*22.80*	*-16.50*	*3.29*	*-14.52*
Phe-C	-58.59	53.17	-38.02	19.91	-24.72	3.91	-10.39
Phe-D	-50.13	38.09	-28.64	13.32	-11.86	2.01	-8.04
Phe-E	*-84.56*	*61.66*	*-46.80*	*23.21*	*-16.38*	*3.31*	*-14.78*
Phe-F	*-81.52*	*63.80*	*-47.47*	*23.20*	*-16.61*	*3.29*	*-16.33*
Phe-G	-50.22	37.42	-28.27	13.09	-11.44	1.96	-7.89
Phe-H	-50.08	37.83	-28.54	13.11	-11.27	1.93	-8.37
Phe-I	-59.46	53.71	-40.19	19.78	-17.02	3.02	-11.85
Phe-J	*-84.77*	*65.65*	*-49.43*	*23.95*	*-16.58*	*3.33*	*-17.08*
Phe-K	-59.12	48.94	-36.62	17.76	-15.41	2.76	-10.52
Phe-L	-48.77	39.54	-29.64	14.26	-18.46	2.74	-7.15
Phe-M	-47.91	33.80	-25.56	10.98	-17.30	2.46	-4.77
Phe-N	-59.60	51.50	-38.21	18.65	-15.66	2.84	-11.32
Phe-O	*-75.86*	*55.07*	*-41.54*	*20.51*	*-15.69*	*3.05*	*-13.02*
Phe-P	-47.12	34.70	-26.95	11.79	-16.93	2.37	-6.23
Phe-Q	*-80.21*	*54.38*	*-41.92*	*21.06*	*-15.64*	*3.10*	*-11.95*
Phe-R	-55.89	46.07	-34.70	16.79	-14.88	2.64	-10.00
Phe-S	*-77.41*	*54.64*	*-41.81*	*20.59*	*-15.53*	*3.05*	*-12.79*
Phe-T	-41.85	29.86	-23.29	10.83	-15.23	2.13	-4.43

Table S6. SAPT(DFT) contributions in mE_h to the interaction energy in Imz···Tyr complexes as obtained employing PBE0 with the aug-cc-pVDZ basis set. Zwitterionic minima in italics.

	E_{ele}	E_{rep}	E_{ind}	$E_{exch\text{-}ind}$	E_{dis}	$E_{exch\text{-}dis}$	δ_{HF}
Tyr-A	-62.22	56.64	-39.64	21.22	-27.64	4.36	-10.81
Tyr-B	-63.62	57.91	-40.89	22.49	-28.29	4.55	-10.19
Tyr-C	-56.34	42.03	-29.87	13.43	-21.02	3.04	-5.27
Tyr-D	-54.70	41.28	-28.96	12.36	-20.83	2.93	-5.31
Tyr-E	-63.46	58.31	-40.64	22.65	-28.80	4.63	-10.01
Tyr-F	*-83.29*	*61.43*	*-46.08*	*22.87*	*-16.56*	*3.30*	*-14.71*
Tyr-G	-50.68	38.12	-28.65	13.25	-11.92	2.01	-8.07
Tyr-H	*-82.68*	*62.28*	*-46.63*	*23.18*	*-16.67*	*3.33*	*-15.00*
Tyr-I	-55.99	46.04	-33.38	17.89	-23.59	3.58	-6.38
Tyr-J	-50.19	38.41	-28.91	13.25	-11.69	1.96	-8.58
Tyr-K	-49.49	38.39	-28.79	13.37	-11.96	2.02	-8.14
Tyr-L	*-78.81*	*53.84*	*-41.12*	*20.57*	*-15.72*	*3.07*	*-11.91*
Tyr-M	*-86.08*	*62.52*	*-47.40*	*23.44*	*-16.51*	*3.34*	*-15.06*
Tyr-N	-49.09	31.64	-23.76	9.72	-16.90	2.25	-3.99
Tyr-O	*-85.92*	*62.44*	*-47.34*	*23.40*	*-16.50*	*3.34*	*-15.04*
Tyr-P	*-82.48*	*65.58*	*-48.82*	*23.69*	*-16.78*	*3.34*	*-17.04*
Tyr-Q	-54.03	43.72	-31.31	15.44	-22.71	3.33	-6.11
Tyr-R	-50.84	37.72	-28.49	13.15	-11.53	1.97	-7.99
Tyr-S	-53.76	45.48	-32.40	16.99	-23.72	3.53	-6.62
Tyr-T	-52.81	40.76	-30.40	14.51	-22.31	3.16	-5.37

Table S7. SAPT(DFT) contributions in mE_h to the interaction energy in Imz···Trp complexes as obtained employing PBE0 with the aug-cc-pVDZ basis set. Zwitterionic minima in italics.

	E_{ele}	E_{rep}	E_{ind}	$E_{exch-ind}$	E_{dis}	$E_{exch-dis}$	δ_{HF}
Trp-A	-65.96	60.99	-42.83	22.69	-30.50	4.77	-11.53
Trp-B	-55.41	43.61	-33.60	16.49	-21.22	3.22	-7.99
Trp-C	*-85.98*	*65.88*	*-49.50*	*24.63*	*-17.23*	*3.50*	*-16.21*
Trp-D	-56.26	42.20	-32.95	15.10	-19.48	2.92	-7.99
Trp-E	-58.57	50.86	-37.45	20.12	-28.88	4.39	-8.32
Trp-F	-53.89	42.89	-31.90	15.23	-19.57	2.93	-8.85
Trp-G	*-85.11*	*63.99*	*-48.35*	*23.89*	*-17.67*	*3.44*	*-15.52*
Trp-H	-54.37	45.32	-33.57	17.50	-22.70	3.47	-8.03
Trp-I	*-90.41*	*66.76*	*-50.48*	*24.99*	*-17.10*	*3.50*	*-16.63*
Trp-J	*-86.14*	*70.15*	*-52.26*	*25.37*	*-17.51*	*3.54*	*-18.62*
Trp-K	-62.57	59.84	-41.42	22.19	-30.44	4.76	-11.09
Trp-L	-66.39	62.52	-44.15	24.02	-29.96	4.77	-10.98
Trp-M	-64.96	59.39	-43.98	21.41	-20.46	3.45	-13.02
Trp-N	-50.88	39.45	-29.77	13.86	-12.15	2.08	-8.45
Trp-O	*-85.15*	*68.24*	*-51.15*	*24.69*	*-17.88*	*3.47*	*-17.95*
Trp-P	*-90.59*	*70.81*	*-53.09*	*25.67*	*-17.34*	*3.54*	*-18.95*
Trp-Q	-48.75	35.62	-27.58	14.10	-20.93	3.03	-4.99
Trp-R	*-83.52*	*55.94*	*-43.18*	*21.73*	*-15.97*	*3.20*	*-12.43*
Trp-S	*-90.13*	*71.04*	*-53.27*	*25.68*	*-17.35*	*3.53*	*-19.06*
Trp-T	-52.94	43.29	-32.57	15.50	-22.27	3.18	-8.04

Table S8. SAPT(DFT) contributions in mE_h to the interaction energy in Imz···His complexes as obtained employing PBE0 with the aug-cc-pVDZ basis set. Zwitterionic minima in italics.

	E_{ele}	E_{rep}	E_{ind}	$E_{exch-ind}$	E_{dis}	$E_{exch-dis}$	δ_{HF}
His-A	*-94.54*	*70.49*	*-52.35*	*26.51*	*-17.89*	*3.74*	*-17.68*
His-B	*-96.76*	*71.01*	*-52.98*	*26.70*	*-17.77*	*3.74*	*-17.92*
His-C	*-90.39*	*63.42*	*-47.60*	*24.42*	*-17.10*	*3.53*	*-14.88*
His-D	-109.76	170.50	-171.33	49.54	-30.58	4.14	-105.23
His-E	*-95.60*	*77.40*	*-57.00*	*27.94*	*-18.50*	*3.85*	*-21.32*
His-F	*-91.79*	*62.35*	*-47.33*	*24.28*	*-16.88*	*3.50*	*-14.44*
His-G	*-97.86*	*77.60*	*-57.34*	*28.01*	*-18.35*	*3.84*	*-21.37*
His-H	-112.07	170.47	-171.78	49.51	-30.60	4.15	-105.73
His-I	-108.00	170.22	-170.23	49.42	-30.46	4.12	-104.18
His-J	*-89.23*	*66.78*	*-49.58*	*24.79*	*-17.31*	*3.55*	*-16.99*
His-K	-148.93	176.99	-169.25	63.47	-32.33	6.53	-93.37
His-L	-147.24	174.92	-164.47	62.44	-31.82	6.39	-90.46
His-M	-109.32	169.96	-168.75	48.99	-30.39	4.14	-103.90
His-N	-103.94	169.41	-165.84	48.88	-30.20	4.10	-101.29
His-O	-156.38	176.03	-167.64	62.88	-32.01	6.49	-92.25
His-P	-62.66	46.03	-34.38	16.54	-13.24	2.42	-10.33
His-Q	-139.31	170.00	-156.05	59.49	-30.41	6.00	-85.78
His-R	-70.09	55.48	-40.37	19.76	-18.92	3.24	-11.64
His-S	-66.02	47.35	-35.53	17.32	-15.75	2.82	-9.58
His-T	-61.29	40.42	-30.35	14.33	-15.10	2.49	-7.26
His-U	-62.70	46.89	-34.91	16.64	-13.18	2.41	-11.03
His-V	-130.42	191.47	-218.49	66.19	-41.17	5.70	-130.67
His-W	-60.92	39.60	-30.31	13.27	-15.12	2.44	-7.66
His-X	-61.70	43.45	-32.30	15.35	-12.83	2.28	-9.65
His-Y	-135.25	168.14	-153.80	58.23	-29.93	5.84	-85.27
His-Z	-67.20	47.31	-35.25	16.99	-13.28	2.46	-10.84
His-AA	-60.69	42.75	-31.40	14.77	-15.11	2.48	-8.75
His-AB	-152.48	174.68	-173.13	63.39	-31.78	6.29	-95.65
His-AC	-111.02	174.52	-176.11	51.93	-35.23	4.78	-108.01
His-AD	-71.13	50.91	-37.23	16.55	-16.88	2.86	-10.91
His-AE	-113.49	106.76	-79.49	37.06	-22.30	4.73	-34.13
His-AF	-54.73	31.80	-25.31	12.20	-11.73	2.01	-5.19
His-AG	-58.13	34.80	-25.34	11.47	-12.97	2.16	-5.61
His-AH	-113.56	172.19	-157.49	48.64	-34.19	4.63	-94.28
His-AI	-114.69	174.22	-163.96	50.43	-34.92	4.74	-98.80