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Supplementary information

Which DFT levels of theory are appropriate in predicting the prolyl *cis–trans* isomerization in solution?

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Page	Contents

Table S1 Torsion angles (°) of local minima for Ac-Pro-NHMe optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform[a]

Conf.	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4
cAd	9	-89	-6	-179	-14	33	-39	30	-10
cAu	5	-73	-23	-177	3	-25	38	-36	21
cFd	-2	-71	155	176	-15	32	-38	28	-8
cFu	-3	-55	145	177	5	-27	38	-35	19
tAd	-172	-86	-4	177	-12	32	-40	32	-12
tAu	-173	-69	-23	-180	5	-27	38	-35	19
tCd	-173	-85	67	-178	-14	33	-40	31	-10
tCu	-174	-83	78	-176	-9	-16	34	-38	30
tFd	177	-66	144	180	-12	30	-37	30	-11
tFu	178	-57	138	-179	2	-25	38	-36	21

[a] Torsion angles are defined in Fig. 1c.

Table S2 Torsion angles (°) of local minima for Ac-Pro-NHMe optimized at the SMD M06-2X/6-31+G(d) level of theory in chloroform[a]

Conf.	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4
cAd	7	-89	-6	-179	-16	34	-39	30	-9
cAu	4	-73	-22	-177	1	-24	37	-36	22
cFd	-2	-71	154	176	-16	32	-38	28	-8
cFu	-4	-56	148	176	3	-26	38	-35	20
tAd	-172	-84	-5	177	-13	32	-40	32	-12
tAu	-174	-69	-22	-180	5	-27	39	-35	19
tCd	-172	-85	66	-179	-14	33	-40	31	-11
tCu	-174	-82	79	-176	-8	-17	34	-38	29
tFd	178	-67	142	180	-11	30	-37	30	-12
tFu	178	-58	137	-178	1	-24	38	-36	22

[a] Torsion angles are defined in Fig. 1c.

Table S3 Torsion angles (°) of local minima for Ac-Pro-NHMe optimized at the PCM M06-2X/6-31+G(d) level of theory in water[a]

Conf.	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4
cAd	9	-89	-8	-179	-14	33	-39	30	-10
cAu	6	-68	-27	-177	6	-28	39	-34	18
cFd	-2	-73	158	177	-16	33	-38	28	-7
cFu	-3	-56	147	177	5	-27	38	-35	19
tAd	-173	-81	-12	-179	-10	30	-39	33	-14
tAu	-174	-67	-27	-177	6	-27	39	-35	18
tCd	-172	-85	65	-179	-14	33	-40	31	-10
tCu	-173	-83	76	-176	-8	-17	34	-39	30
tFd	178	-67	150	176	-11	30	-38	31	-13
tFu	179	-57	143	178	4	-26	38	-35	20

[a] Torsion angles are defined in Fig. 1c.

Table S4 Torsion angles (°) of local minima for Ac-Pro-NHMe optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

Conf.	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4
cAd	2	-86	-9	-179	-19	35	-38	26	-4
cAu	-2	-71	-22	-177	-5	-19	34	-37	26
cFd	-4	-68	154	176	-15	32	-37	28	-8
cFu	-6	-55	150	177	4	-26	38	-36	20
tAd	-178	-76	-12	-179	-13	32	-39	30	-10
tAu	-178	-67	-21	-176	-1	-23	37	-37	24
tCd	-171	-86	64	-180	-13	33	-41	32	-12
tCu	-172	-83	80	-177	-5	-20	36	-39	27
tFd	176	-61	149	176	-11	29	-37	30	-12
tFu	179	-53	143	176	7	-29	39	-34	17

[a] Torsion angles are defined in Fig. 1c.

Table S5 Relative free energies (kcal mol^{-1}) of local minima for Ac-Pro-NHMe optimized at the PCM M06-2X/6-31+G(d) level of theory depending on single-point energies in chloroform[a]

Level of theory	Basis set	cAd	cAu	cFd	cFu	tAd	tAu	tCd	tCu	tFd	tFu
M06-2X	6-311++G(d,p)	0.76	2.11	2.65	2.93	1.36	2.43	0.00	2.52	1.45	1.93
	cc-pVTZ	1.30	2.63	2.82	3.04	1.76	2.77	0.00	2.61	1.62	2.07
	def2-TZVP	1.05	2.32	2.60	2.85	1.54	2.48	0.00	2.51	1.41	1.82
	def2-QZVP	1.06	2.34	2.55	2.76	1.49	2.45	0.00	2.50	1.33	1.72
ωB97X-D	6-311++G(d,p)	0.40	1.77	2.62	3.08	1.07	2.34	0.00	2.24	1.53	2.04
	cc-pVTZ	0.87	2.23	2.68	3.12	1.38	2.60	0.00	2.30	1.65	2.15
	def2-TZVP	0.61	1.94	2.44	2.87	1.16	2.32	0.00	2.23	1.39	1.83
	def2-QZVP	0.53	1.85	2.32	2.75	1.04	2.20	0.00	2.25	1.28	1.71
DSD-PBEP86-D3BJ	cc-pVTZ	1.20	2.49	2.87	3.12	1.63	2.57	0.00	2.25	1.65	1.96

[a] Torsion angles are listed in Table S1.

Table S6 Relative free energies (kcal mol^{-1}) of local minima for Ac-Pro-NHMe optimized at the SMD M06-2X/6-31+G(d) level of theory depending on single-point energies in chloroform[a]

Level of theory	Basis set	cAd	cAu	cFd	cFu	tAd	tAu	tCd	tCu	tFd	tFu
M06-2X	6-311++G(d,p)	0.07	1.48	0.87	2.17	0.52	1.53	0.00	1.86	0.28	0.90
	cc-pVTZ	0.61	2.02	1.05	2.29	0.91	1.86	0.00	1.96	0.46	1.04
	def2-TZVP	0.35	1.69	0.83	2.09	0.69	1.57	0.00	1.87	0.24	0.79
	def2-QZVP	0.37	1.71	0.78	2.00	0.64	1.54	0.00	1.87	0.17	0.70
ωB97X-D	6-311++G(d,p)	0.00	1.38	1.07	2.54	0.50	1.71	0.26	1.86	0.62	1.24
	cc-pVTZ	0.53	1.75	2.38	3.00	1.09	2.00	0.00	1.66	1.48	1.79
	def2-TZVP	0.26	1.45	2.15	2.74	0.88	1.71	0.00	1.59	1.21	1.48
	def2-QZVP	0.20	1.35	2.02	2.62	0.76	1.60	0.00	1.61	1.11	1.36
DSD-PBEP86-D3BJ	cc-pVTZ	0.50	1.86	1.06	2.33	0.78	1.67	0.00	1.62	0.48	0.90

[a] Torsion angles are listed in Table S2.

Table S7 Relative free energies (kcal mol^{-1}) of local minima for Ac-Pro-NHMe optimized at the PCM M06-2X/6-31+G(d) level of theory depending on single-point energies in water[a]

Level of theory	Basis set	cAd	cAu	cFd	cFu	tAd	tAu	tCd	tCu	tFd	tFu
M06-2X	6-311++G(d,p)	0.07	1.48	0.87	2.17	0.52	1.54	0.00	1.86	0.28	0.26
	cc-pVTZ	0.61	2.02	1.06	2.29	0.91	1.88	0.00	1.96	0.46	0.40
	def2-TZVP	0.57	2.05	0.43	0.98	0.00	0.69	0.34	2.33	0.08	0.54
	def2-QZVP	0.37	1.71	0.78	2.00	0.64	1.55	0.00	1.87	0.17	0.06
ωB97X-D	6-311++G(d,p)	0.00	1.54	1.27	2.72	1.01	2.25	0.26	1.85	1.39	1.52
	cc-pVTZ	0.22	1.71	1.05	2.51	1.04	2.23	0.00	1.66	1.20	1.36
	def2-TZVP	0.00	1.49	0.86	2.30	0.87	2.00	0.04	1.64	1.00	1.07
	def2-QZVP	0.00	1.47	0.81	2.25	0.83	1.95	0.12	1.73	0.93	0.98
DSD-PBEP86-D3BJ	cc-pVTZ	0.65	2.24	0.59	1.14	0.00	0.67	0.27	2.01	0.26	0.60

[a] Torsion angles are listed in Table S3.

Table S8 Relative free energies (kcal mol^{-1}) of local minima for Ac-Pro-NHMe optimized at the SMD M06-2X/6-31+G(d) level of theory depending on single-point energies in water[a]

Level of theory	Basis set	cAd	cAu	cFd	cFu	tAd	tAu	tCd	tCu	tFd	tFu
M06-2X	6-311++G(d,p)	0.23	2.69	0.73	1.27	0.33	1.77	1.58	3.78	0.07	0.00
	cc-pVTZ	0.67	3.13	0.77	1.27	0.55	2.00	1.47	3.81	0.09	0.00
	def2-TZVP	0.64	3.03	0.73	1.34	0.56	1.94	1.73	3.97	0.15	0.00
	def2-QZVP	0.81	3.18	0.93	1.41	0.70	2.07	1.88	4.11	0.21	0.00
ωB97X-D	6-311++G(d,p)	0.00	2.41	0.80	1.53	0.16	1.79	1.72	3.70	0.34	0.29
	cc-pVTZ	0.15	2.55	0.52	1.23	0.06	1.72	1.37	3.45	0.04	0.00
	def2-TZVP	0.17	2.54	0.63	1.31	0.15	1.73	1.70	3.69	0.13	0.00
	def2-QZVP	0.27	2.61	0.69	1.36	0.21	1.79	1.86	3.88	0.16	0.00
DSD-PBEP86-D3BJ	cc-pVTZ	0.73	3.16	0.87	1.41	0.61	1.96	1.65	3.66	0.25	0.00

[a] Torsion angles are listed in Table S4.

Table S9 Populations (%) of the backbone conformations of local minima for Ac-Pro-NHMe optimized at the PCM M06-2X/6-31+G(d) level of theory depending on single-point energies in chloroform[a]

Level of theory	Basis set	C	A	tF	cF	*cis*
M06-2X	6-311++G(d,p)	64.2	26.8	7.9	1.2	20.5
	cc-pVTZ	77.5	14.1	7.3	1.1	10.5
	def2-TZVP	69.7	19.3	9.6	1.4	14.5
	def2-QZVP	68.5	19.1	10.8	1.6	14.1
ωB97X-D	6-311++G(d,p)	54.1	39.4	5.6	0.9	30.6
	cc-pVTZ	68.5	24.5	6.0	1.1	18.2
	def2-TZVP	58.6	31.9	8.2	1.4	24.1
	def2-QZVP	54.6	34.6	9.2	1.6	25.6
DSD-PBEP86-D3BJ	cc-pVTZ	75.3	16.4	7.3	1.0	11.7

[a] Torsion angles are listed in Table S1. The population of each conformer was calculated using its ΔG value at 25 °C listed in Table S5. The *cis* population was calculated by summing the populations of cAd, cAu, cFd, and cFu conformers at each level of theory.

Table S10 Populations (%) of the backbone conformations of local minima for Ac-Pro-NHMe optimized at the SMD M06-2X/6-31+G(d) level of theory depending on single-point energies in chloroform

Level of theory	Basis set	C	A	tF	cF	*cis*
M06-2X	6-311++G(d,p)	28.9	40.8	23.3	7.1	34.1
	cc-pVTZ	41.3	25.8	25.3	7.5	23.1
	def2-TZVP	32.2	30.7	28.7	8.5	27.3
	def2-QZVP	30.7	29.5	30.9	8.9	26.2
ωB97X-D	6-311++G(d,p)	23.4	54.2	16.3	6.1	43.6
	cc-pVTZ	56.7	34.9	7.0	1.3	26.0
	def2-TZVP	45.8	43.5	9.1	1.6	33.0
	def2-QZVP	42.1	46.0	10.1	1.8	34.2
DSD-PBEP86-D3BJ	cc-pVTZ	39.2	29.4	24.6	6.9	24.3

[a] Torsion angles are listed in Table S2. The population of each conformer was calculated using its ΔG value at 25 °C listed in Table S6. The *cis* population was calculated by summing the populations of cAd, cAu, cFd, and cFu conformers at each level of theory.

Table S11 Populations (%) of the backbone conformations of local minima for Ac-Pro-NHMe optimized at the PCM M06-2X/6-31+G(d) level of theory depending on single-point energies in water

Level of theory	Basis set	C	A	tF	cF	*cis*
M06-2X	6-311++G(d,p)	25.8	36.4	31.4	6.3	30.5
	cc-pVTZ	36.4	22.7	34.2	6.7	20.3
	def2-TZVP	13.6	40.5	30.1	15.9	25.6
	def2-QZVP	26.1	25.0	41.3	7.6	22.3
ωB97X-D	6-311++G(d,p)	30.3	56.4	7.6	5.6	53.0
	cc-pVTZ	43.8	39.0	9.6	7.6	38.5
	def2-TZVP	33.7	45.8	11.9	8.6	45.4
	def2-QZVP	30.0	46.9	13.6	9.5	46.7
DSD-PBEP86-D3BJ	cc-pVTZ	17.3	43.4	26.0	13.3	22.4

[a] Torsion angles are listed in Table S3. The population of each conformer was calculated using its ΔG value at 25 °C listed in Table S7. The *cis* population was calculated by summing the populations of cAd, cAu, cFd, and cFu conformers at each level of theory.

Table S12 Populations (%) of the backbone conformations of local minima for Ac-Pro-NHMe optimized at the SMD M06-2X/6-31+G(d) level of theory depending on single-point energies in water

Level of theory	Basis set	C	A	tF	cF	*cis*
M06-2X	6-311++G(d,p)	1.9	35.6	51.4	11.0	29.7
	cc-pVTZ	2.8	24.4	60.3	12.6	23.1
	def2-TZVP	1.8	25.7	59.2	13.2	24.8
	def2-QZVP	1.6	22.5	64.5	11.4	21.1
ωB97X-D	6-311++G(d,p)	1.7	54.0	34.6	9.8	39.8
	cc-pVTZ	2.4	40.5	44.7	12.5	30.7
	def2-TZVP	1.5	40.8	46.1	11.7	31.2
	def2-QZVP	1.2	38.5	48.8	11.4	29.2
DSD-PBEP86-D3BJ	cc-pVTZ	2.4	25.3	60.5	11.9	22.8

[a] Torsion angles are listed in Table S4. The population of each conformer was calculated using its ΔG value at 25 °C listed in Table S8. The *cis* population was calculated by summing the populations of cAd, cAu, cFd, and cFu conformers at each level of theory.

Table S13 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Pro-OMe in chloroform

Conf.	Torsion angles[a]									DSD-PBEP86-D3BJ/cc-pVTZ[b]				M06-2X/def2-TZVP[c]			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-3	-75	-11	-179	-19	35	-38	27	-5	1.31	1.20	1.04	4.4	1.45	1.34	1.10	4.0
cAu	-2	-56	-32	-178	4	-26	38	-35	20	1.83	1.90	2.48	0.4	1.78	1.85	2.36	0.5
cFd	-1	-76	169	178	-18	34	-38	27	-6	0.95	0.82	0.13	20.1	1.00	0.87	0.12	21.0
cFu	-3	-59	162	176	3	-25	38	-36	21	1.72	1.81	2.03	0.8	1.77	1.86	2.01	0.9
tAd	178	-63	-27	-179	-11	30	-38	31	-12	0.57	0.44	0.00	25.1	0.71	0.58	0.07	22.7
tAu	179	-53	-37	-179	5	-27	39	-35	19	0.57	0.52	0.83	6.2	0.67	0.61	0.85	6.1
tFd	177	-67	157	178	-13	31	-38	30	-11	0.00	0.00	0.07	22.4	0.00	0.00	0.00	25.6
tFu	179	-55	144	178	5	-27	39	-35	19	0.25	0.18	0.12	20.5	0.37	0.30	0.17	19.2
ts1	113	-103	71	-176	11	16	-36	43	-34	20.05	18.85	18.96		20.59	19.38	19.42	
ts2	114	-96	72	-177	17	-37	41	-32	9	21.05	20.12	21.56		21.50	20.57	21.94	
ts3	-65	-100	77	-174	10	16	-36	42	-33	22.07	20.96	21.52		22.48	21.37	21.87	
ts4	-65	-83	-77	175	24	-40	40	-26	2	23.53	22.40	23.08		23.90	22.77	23.38	
cis%													25.7				26.4

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S14 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Pro-OMe in water

Conf.	Torsion angles[a]									DSD-PBEP86-D3BJ/cc-pVTZ[b]				M06-2X/def2-TZVP[c]			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-8	-70	-13	-179	-21	35	-37	25	-3	1.30	1.26	1.41	3.0	1.43	1.39	1.54	2.7
cAu	-8	-52	-33	-180	2	-24	38	-36	22	1.96	2.09	2.51	0.5	1.82	1.96	2.38	0.6
cFd	-6	-74	169	176	-21	35	-37	25	-2	0.64	0.62	0.58	12.2	0.72	0.70	0.65	11.8
cFu	-7	-57	162	176	1	-24	38	-36	22	1.47	1.68	2.36	0.6	1.54	1.74	2.43	0.6
tAd	176	-62	-23	-177	-13	31	-38	30	-10	0.61	0.54	0.07	28.9	0.68	0.61	0.14	28.0
tAu	178	-52	-36	-177	6	-28	39	-35	18	0.45	0.54	0.79	8.5	0.53	0.62	0.87	8.2
tFd	176	-63	158	176	-13	31	-38	30	-11	0.00	0.00	0.00	32.3	0.00	0.00	0.00	35.6
tFu	180	-53	143	177	9	-30	40	-34	16	0.06	0.03	0.50	14.0	0.19	0.15	0.62	12.5
ts1	116	-99	80	-173	16	11	-34	44	-38	22.15	21.33	23.24		22.69	21.87	23.78	
ts2	115	-101	43	178	13	-35	42	-35	13	23.17	22.03	23.53		23.42	22.29	23.78	
ts3	-62	-110	76	-178	5	21	-38	41	-29	21.90	20.94	21.99		22.26	21.30	22.34	
ts4	-58	-85	-91	177	26	-42	42	-27	1	22.85	21.99	23.21		23.29	22.43	23.65	
cis%													16.3				15.7

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S15 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Hyp-OMe in chloroform

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]
cAd-g	-3	-72	-18	-178	-18	33	-37	26	-5	59	2.66	2.50	1.66	1.1	2.68	2.51	1.68	1.0
cAd-gm	-4	-71	-15	-179	-18	34	-38	27	-6	-75	2.61	2.37	1.90	0.8	2.67	2.44	1.97	0.6
cAd-t	-4	-70	-19	-178	-16	33	-38	28	-7	-171	2.61	2.36	1.58	1.3	2.63	2.38	1.60	1.2
cAu-g	-6	-57	-32	-178	-4	-22	38	-39	27	72	2.40	2.35	2.00	0.6	2.21	2.15	1.81	0.8
cAu-gm	0	-58	-33	-177	7	-29	39	-35	17	-67	1.57	1.61	1.85	0.8	1.48	1.52	1.76	0.9
cAu-t	1	-58	-33	-177	6	-28	39	-35	19	176	1.38	1.40	1.62	1.2	1.22	1.24	1.46	1.5
cFd-g	-1	-75	166	177	-16	33	-38	28	-7	60	2.34	2.24	1.52	1.4	2.27	2.16	1.44	1.5
cFd-gm	-1	-75	166	177	-16	33	-38	29	-8	-78	2.24	2.04	1.01	3.4	2.23	2.04	1.00	3.2
cFd-t	-1	-74	166	177	-15	33	-38	29	-8	-170	2.15	1.94	1.01	3.4	2.07	1.86	0.92	3.6
cFu-g	-6	-60	164	177	-4	-21	37	-39	27	72	2.16	2.19	1.77	0.9	2.02	2.05	1.63	1.1
cFu-gm	0	-60	159	176	7	-28	39	-34	17	-68	1.44	1.57	1.56	1.3	1.39	1.52	1.51	1.3
cFu-t	1	-61	160	176	6	-28	39	-35	18	175	1.16	1.29	1.24	2.3	1.02	1.15	1.10	2.7
tAd-g	177	-60	-30	-179	-10	29	-37	31	-13	55	1.67	1.62	1.59	1.3	1.71	1.66	1.63	1.1
tAd-gm	177	-61	-29	-179	-11	30	-38	31	-13	-75	1.56	1.51	1.35	1.9	1.61	1.55	1.40	1.6
tAd-t	177	-60	-30	-179	-10	29	-38	31	-14	-166	1.64	1.58	1.44	1.6	1.73	1.67	1.53	1.3
tAu-g	177	-53	-36	-179	-2	-22	38	-38	26	61	1.09	1.07	1.17	2.6	1.01	0.99	1.09	2.7
tAu-gm	-179	-54	-36	-180	7	-28	39	-34	18	-65	0.34	0.32	0.53	7.6	0.35	0.33	0.54	6.9
tAu-t	-180	-53	-37	-179	7	-28	39	-34	17	-179	0.54	0.52	0.81	4.7	0.56	0.54	0.84	4.2
tFd-g	177	-65	154	177	-11	30	-38	30	-12	55	1.14	1.06	0.65	6.2	1.03	0.95	0.53	6.9
tFd-gm	177	-65	153	177	-11	30	-38	31	-13	-78	0.98	0.89	0.27	11.8	0.86	0.78	0.15	13.2
tFu-g	176	-56	146	179	-3	-22	38	-39	26	64	0.69	0.66	0.32	10.8	0.57	0.55	0.21	12.1
tFu-gm	-179	-57	143	179	6	-28	39	-34	18	-66	0.00	0.00	0.00	18.5	0.00	0.00	0.00	17.1
tFu-t	-180	-56	143	179	6	-28	39	-35	18	180	0.11	0.11	0.15	14.5	0.10	0.10	0.14	13.5
ts1	120	-106	68	-177	8	-31	42	-38	19	77	18.12	17.05	18.47		18.48	17.41	18.83	
ts2	112	-82	75	-177	31	-43	38	-19	-8	-66	20.88	19.63	20.22		21.22	19.97	20.56	
ts3	-68	-88	80	-174	23	-39	40	-26	2	-66	21.50	20.32	21.18		21.71	20.53	21.38	
ts4	-64	-102	76	-174	9	17	-36	42	-32	-77	22.94	21.80	22.32		23.15	22.01	22.53	
cis%														18.6				19.3

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using Δ*G* values.

Table S16 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Hyp-OMe in water

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]
cAd-gm [h]	-8	-70	-16	-178	-22	35	-36	23	0	-72	2.84	3.14	3.69	0.1	2.84	3.14	3.69	0.1
cAd-g	-8	-70	-17	-178	-22	35	-36	23	-1	58	2.46	2.91	3.51	0.1	2.41	2.85	3.46	0.1
cAd-t	-8	-70	-16	-178	-22	35	-36	23	0	-168	2.92	3.22	3.74	0.1	2.88	3.17	3.70	0.1
cAu-gm	-4	-54	-33	180	6	-28	39	-35	18	-64	1.91	1.99	2.21	0.7	1.72	1.80	2.02	0.9
cAu-g	-5	-54	-33	-180	5	-26	37	-34	19	54	3.09	3.12	3.19	0.1	2.77	2.79	2.87	0.2
cAu-t	-4	-54	-32	180	5	-27	39	-35	19	176	2.03	2.08	2.04	0.9	1.74	1.79	1.75	1.5
cFd-gm	-4	-73	165	178	-17	33	-38	27	-6	-74	2.28	2.36	1.37	2.9	2.28	2.35	1.37	2.8
cFd-g	-3	-72	164	178	-16	33	-38	28	-7	59	1.91	2.23	1.63	1.9	1.84	2.16	1.56	2.0
cFd-t	-4	-72	163	177	-16	33	-38	28	-7	-171	2.40	2.55	1.74	1.6	2.30	2.45	1.64	1.8
cFu-gm	-4	-57	164	175	5	-26	38	-34	18	-63	1.36	1.51	1.72	1.6	1.28	1.42	1.64	1.8
cFu-g	-5	-58	166	175	2	-24	37	-35	20	58	2.59	2.78	3.19	0.1	2.40	2.58	3.01	0.2
cFu-t	-5	-58	165	175	3	-25	38	-35	20	175	1.46	1.59	1.93	1.1	1.27	1.40	1.75	1.5
tAd-gm	176	-56	-32	-179	-10	29	-37	31	-14	-75	2.06	2.36	2.83	0.2	2.04	2.34	2.82	0.2
tAd-g	176	-56	-33	-179	-9	28	-37	31	-14	57	1.52	1.85	2.40	0.5	1.50	1.83	2.39	0.5
tAd-t	176	-56	-32	-179	-9	29	-37	31	-14	-171	1.91	2.26	2.84	0.2	1.95	2.30	2.90	0.2
tAu-gm	176	-48	-39	-178	8	-28	38	-33	16	-62	0.45	0.52	0.77	8.0	0.47	0.54	0.79	7.5
tAu-g	178	-50	-38	-178	7	-28	39	-34	17	58	1.62	1.55	1.23	3.7	1.51	1.44	1.13	4.2
tAu-t	178	-50	-39	-178	6	-28	39	-34	17	177	0.42	0.43	0.45	13.8	0.45	0.46	0.48	12.6
tFd-gm	175	-61	155	177	-12	30	-38	30	-12	-74	1.60	1.75	1.78	1.5	1.45	1.59	1.63	1.8
tFd-g	175	-60	154	177	-11	30	-37	30	-12	57	1.10	1.46	1.75	1.5	0.95	1.31	1.62	1.9
tFu-gm	179	-54	146	176	6	-28	38	-34	17	-63	0.05	0.02	0.00	29.3	0.04	0.02	0.00	28.6
tFu-g	179	-54	146	176	6	-27	38	-34	18	56	1.19	1.20	1.27	3.5	1.08	1.10	1.17	4.0
tFu-t	179	-55	147	176	6	-28	39	-34	18	177	0.00	0.00	0.05	26.7	0.00	0.00	0.06	25.7
ts1	119	-106	56	180	9	-32	41	-37	17	77	21.64	20.51	21.84		21.91	20.77	22.11	
ts2	-69	-86	22	177	26	-40	39	-23	-2	-63	22.01	21.33	22.23		22.40	21.72	22.63	
ts3	119	-88	-10	-178	27	-41	40	-24	-2	-64	23.09	21.72	22.76		23.06	21.69	22.73	
ts4	-60	-109	72	-175	6	20	-38	42	-30	-73	23.44	22.43	22.58		23.64	22.63	22.78	
cis%														11.2				12.9

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c]

Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using Δ*G* values. [h] "gm" stands for the gauche- for χ^{OH}.

Table S17 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-hyp-OMe in chloroform

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd-g[h]	-3	-82	15	-178	-23	38	-40	27	-2	66	3.02	2.76	2.28	1.3	2.85	2.58	2.11	1.7
cAd-gm[i]	5	-67	-30	-177	-4	25	-36	33	-18	-63	3.34	3.30	2.76	0.6	3.30	3.25	2.71	0.6
cAd-t	-3	-80	9	-178	-20	37	-40	28	-5	-171	3.24	2.99	2.65	0.7	3.03	2.78	2.44	1.0
cAu-g	-3	-57	-32	-177	3	-25	38	-35	21	76	5.46	5.15	4.07	0.1	5.36	5.06	3.97	0.1
cAu-gm	-3	-56	-33	-178	3	-25	37	-35	20	-62	5.59	5.27	4.13	0.1	5.38	5.06	3.92	0.1
cAu-t	-3	-58	-32	-177	1	-24	38	-36	22	171	5.37	5.11	4.12	0.1	5.24	4.98	3.99	0.1
cFd-g	-3	-80	-164	-178	-23	38	-40	26	-2	68	3.37	2.97	2.13	1.7	3.24	2.84	2.00	2.0
cFd-gm	5	-69	144	177	-5	26	-37	34	-18	-58	2.08	1.98	0.83	15.3	1.99	1.89	0.74	16.9
cFd-t	-3	-78	-169	-180	-21	37	-40	28	-4	-167	3.06	2.70	2.03	2.0	2.75	2.39	1.72	3.2
cFu-g	-1	-60	163	177	3	-25	38	-36	21	76	5.33	5.18	3.77	0.1	5.28	5.12	3.72	0.1
cFu-gm	-2	-60	158	176	3	-25	37	-35	20	-60	5.28	5.13	3.88	0.1	5.14	5.00	3.74	0.1
cFu-t	-2	-61	164	177	1	-25	38	-37	22	172	5.20	5.03	3.62	0.1	5.12	4.94	3.53	0.2
tAd-g	179	-81	12	-180	-21	37	-40	28	-4	65	3.04	2.74	2.14	1.7	2.89	2.59	1.99	2.0
tAd-gm	-180	-55	-37	-179	2	21	-36	36	-25	-54	1.76	1.77	1.75	3.3	1.84	1.86	1.84	2.7
tAd-t	179	-77	5	180	-18	35	-40	29	-7	-174	3.46	3.16	2.62	0.8	3.34	3.04	2.50	0.9
tAu-g[h]	178	-53	-36	-179	3	-25	38	-36	21	75	4.02	3.80	2.41	1.1	3.98	3.77	2.37	1.1
tAu-gm[h]	178	-53	-36	-179	2	-25	37	-35	21	-56	4.17	4.08	3.12	0.3	4.07	3.99	3.02	0.4
tAu-t[h]	178	-53	-36	-179	1	-24	38	-36	22	167	4.09	3.96	2.91	0.5	4.09	3.96	2.91	0.4
tFd-g[h]	177	-76	-176	-179	-19	35	-38	27	-5	68	3.44	3.17	2.20	1.5	3.45	3.18	2.21	1.4
tFd-gm	179	-57	139	178	0	24	-37	36	-23	-51	0.00	0.00	0.00	62.6	0.00	0.00	0.00	59.0
tFd-t[h]	177	-76	-178	-180	-18	35	-39	28	-6	-171	3.38	3.14	2.31	1.3	3.27	3.04	2.21	1.4
tFu-g[h]	179	-55	143	179	5	-27	39	-35	19	74	3.74	3.51	2.17	1.6	3.73	3.50	2.16	1.5
tFu-gm[h]	179	-55	143	179	4	-26	38	-35	20	-55	3.70	3.53	2.39	1.1	3.61	3.45	2.30	1.2
tFu-t[h]	179	-56	144	178	2	-25	38	-36	21	168	3.79	3.53	1.99	2.2	3.82	3.56	2.02	1.9
ts1	115	-109	34	176	3	23	-39	41	-27	-173	23.31	21.87	21.60		23.50	22.06	21.80	
ts2	117	-104	68	-177	10	-32	41	-36	16	171	24.17	22.85	22.29		24.54	23.22	22.66	
ts3	-65	-113	16	178	-5	29	-41	39	-22	-168	25.78	24.27	23.75		25.77	24.25	23.73	
ts4	-69	-86	79	-175	24	-39	40	-25	1	171	26.70	25.33	24.83		26.94	25.58	25.08	
cis%														22.2				26.0

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine. [i] "gm" stands for the gauche- for χ^{OH}.

Table S18 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-hyp-OMe in water

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]
cAd-g	-3	-81	9	179	-21	37	-40	27	-4	61	1.79	1.59	2.76	0.2	1.81	1.60	2.90	0.1
cAd-gm [h]	-6	-67	-23	-177	-17	31	-34	24	-5	-66	2.32	1.04	0.39	8.3	2.20	0.91	0.39	9.2
cAd-t	-4	-78	6	179	-20	36	-39	27	-4	-173	1.78	1.33	0.69	5.0	1.62	1.16	0.65	5.9
cAu-g	-6	-53	-32	-178	3	-25	38	-36	21	74	3.89	3.49	2.57	0.2	3.66	3.25	2.46	0.3
cAu-gm	-7	-53	-32	-178	2	-24	37	-35	21	-57	3.70	3.73	2.99	0.1	3.57	3.59	2.98	0.1
cAu-t	-7	-53	-31	-178	1	-24	37	-36	22	170	4.01	3.76	2.58	0.2	3.84	3.58	2.53	0.2
cFd-g	-7	-76	-174	-179	-22	37	-38	25	-1	64	1.30	1.45	1.46	1.4	1.23	1.38	1.52	1.4
cFd-gm	0	-68	149	175	-9	28	-36	30	-14	-60	1.43	0.65	0.58	6.0	1.43	0.64	0.70	5.4
cFd-t	-7	-75	-174	-180	-22	37	-39	26	-2	-172	1.40	0.97	0.91	3.4	1.16	0.73	0.80	4.6
cFu-g	-5	-58	161	176	4	-26	38	-36	20	74	3.45	3.10	2.68	0.2	3.29	2.94	2.65	0.2
cFu-gm	-6	-57	164	176	3	-25	38	-35	21	-58	3.17	2.58	2.85	0.1	3.17	2.57	2.98	0.1
cFu-t	-6	-59	163	176	2	-25	38	-36	22	173	3.55	3.42	2.62	0.2	3.49	3.35	2.68	0.2
tAd-g	179	-75	6	180	-19	36	-40	29	-6	62	1.64	1.08	1.49	1.3	1.76	1.20	1.74	0.9
tAd-gm	176	-53	-37	-176	-2	23	-35	33	-20	-54	0.98	0.89	0.98	3.1	0.81	0.72	0.94	3.6
tAd-t	-180	-74	5	-179	-15	34	-40	31	-10	-174	1.39	0.83	0.00	15.9	1.27	0.69	0.00	17.7
tAu-g	179	-52	-38	-179	5	-27	39	-36	19	72	2.45	1.94	1.10	2.5	2.39	1.88	1.17	2.5
tAu-gm	178	-52	-38	-179	5	-27	39	-35	19	-58	2.29	2.28	1.22	2.0	2.28	2.26	1.33	1.9
tAu-t	178	-52	-37	-179	4	-26	39	-36	20	170	2.48	2.18	1.09	2.5	2.52	2.21	1.25	2.1
tFd-g	179	-71	-180	179	-13	32	-39	31	-11	63	0.87	0.00	0.03	15.0	0.88	0.00	0.17	13.3
tFd-gm	175	-55	143	176	-4	25	-37	33	-19	-54	0.00	0.26	0.39	8.2	0.00	0.25	0.52	7.4
tFd-t	180	-71	-179	179	-13	32	-39	31	-11	-175	0.79	0.39	0.29	9.8	0.72	0.31	0.35	9.9
tFu-g	-179	-54	145	176	8	-29	40	-34	16	74	2.01	1.49	0.68	5.1	1.94	1.42	0.73	5.1
tFu-gm	-179	-53	144	177	8	-29	39	-34	16	-57	1.78	1.77	0.68	5.0	1.78	1.77	0.81	4.5
tFu-t	180	-53	143	177	8	-29	40	-35	17	171	2.04	1.78	0.79	4.2	2.09	1.82	0.97	3.4
ts1	118	-116	27	177	-3	28	-42	40	-24	-172	23.14	21.41	21.65		23.28	21.53	21.91	
ts2	119	-90	-7	-179	24	-40	41	-27	2	173	24.66	23.26	23.54		24.99	23.58	24.00	
ts3	-64	-114	30	176	-3	27	-40	39	-23	-174	22.78	21.30	21.96		22.84	21.34	22.14	
ts4	-67	-91	54	179	22	-39	40	-27	3	175	24.16	22.94	23.57		24.27	23.03	23.80	
cis%														25.3				27.7

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] "gm" stands for the gauche- for χ^{OH}.

Table S19 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Flp-OMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-10	-67	-16	-180	-22	34	-35	21	1	3.58	3.58	3.17	0.3	3.54	3.54	3.14	0.3
cAu	-5	-53	-33	-180	5	-25	36	-32	17	1.98	1.99	1.94	2.5	1.75	1.76	1.71	3.6
cFd	-11	-70	167	178	-25	35	-33	19	4	3.05	3.01	2.72	0.7	3.00	2.96	2.66	0.7
cFu	-5	-57	165	175	4	-25	36	-33	18	1.40	1.50	1.78	3.2	1.27	1.37	1.65	4.0
tAd	175	-55	-34	-178	-10	28	-37	30	-13	2.75	2.89	3.07	0.4	2.77	2.90	3.09	0.3
tAu	178	-50	-39	-178	7	-27	37	-32	16	0.41	0.41	0.50	27.6	0.45	0.45	0.54	25.7
tFd	174	-59	153	177	-13	30	-37	29	-10	2.31	2.38	2.47	1.0	2.18	2.25	2.34	1.2
tFu	179	-55	147	176	6	-26	37	-33	17	0.00	0.00	0.00	64.4	0.00	0.00	0.00	64.1
ts1'	118	-92	-169	-178	22	-38	39	-27	3	21.47	20.33	21.23		21.59	20.45	21.36	
ts2	117	-87	75	-174	27	-41	39	-23	-2	21.64	20.66	21.85		21.95	20.97	22.15	
ts4	-65	-90	52	180	23	-38	38	-24	0	21.88	20.87	21.74		22.01	21.00	21.87	
cis%													6.6				8.6

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S20 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-flp-OMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-8	-75	-1	-178	-25	37	-36	21	3	1.08	1.10	1.35	6.0	0.98	1.00	1.24	6.9
cAu	-7	-53	-32	-178	2	-24	37	-35	21	4.29	4.50	3.94	0.1	4.12	4.33	3.78	0.1
cFd	-2	-76	177	179	-17	33	-37	26	-5	0.50	0.53	0.66	19.2	0.47	0.49	0.62	19.5
cFu	-7	-57	165	176	2	-24	37	-35	21	3.87	4.24	4.69	0.0	3.78	4.16	4.60	0.0
tAd	175	-67	-7	-179	-18	33	-37	25	-4	0.71	0.71	0.83	14.3	0.64	0.64	0.77	15.3
tAu	178	-53	-36	-179	3	-25	38	-36	20	2.88	3.05	2.85	0.5	2.87	3.05	2.85	0.5
tFd	177	-67	172	178	-14	31	-37	28	-9	0.00	0.00	0.00	58.2	0.00	0.00	0.00	56.0
tFu	-180	-53	143	177	8	-29	39	-33	15	2.42	2.55	2.09	1.7	2.42	2.55	2.09	1.7
ts2	116	-75	69	-173	41	-20	-8	33	-47	21.29	20.39	21.89		21.46	20.56	22.06	
ts3	-62	-106	65	-177	7	17	-35	39	-29	21.68	20.82	21.84		21.95	21.09	22.11	
ts4'	-60	-111	173	179	2	21	-37	38	-25	21.46	20.54	21.40		21.84	20.93	21.79	
cis%													25.3				26.5

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S21 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-mep-OMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-4	-72	-16	-178	-17	34	-38	28	-7	1.27	1.45	2.05	1.5	1.36	1.54	2.14	1.4
cAu	-5	-53	-32	-180	5	-28	39	-35	19	2.48	2.64	3.04	0.3	2.33	2.49	2.88	0.4
cFd[h]	-2	-75	169	178	-16	33	-38	28	-8	0.70	0.74	0.17	36.4	0.74	0.78	0.21	35.5
cFu	-4	-56	161	176	6	-27	38	-34	18	1.95	2.21	2.99	0.3	1.94	2.20	2.99	0.3
tAd	177	-58	-30	-179	-10	29	-37	31	-14	0.38	0.72	1.44	4.2	0.49	0.82	1.55	3.7
tAu	178	-50	-39	-178	9	-29	39	-33	16	1.00	1.23	1.75	2.5	1.06	1.28	1.80	2.4
tFd	175	-61	156	177	-11	30	-38	31	-13	0.00	0.00	0.00	48.3	0.00	0.00	0.00	50.5
tFu	180	-54	146	176	7	-29	39	-34	17	0.57	0.74	1.20	6.4	0.65	0.82	1.27	5.9
ts1'	119	-75	65	-174	41	-18	-10	35	-47	22.28	21.50	22.87		22.59	21.81	23.18	
ts2	116	-86	77	-174	27	-41	39	-23	-2	23.17	22.35	24.05		23.48	22.66	24.37	
ts3	-62	-110	72	-175	5	21	-38	42	-29	21.91	20.93	21.64		22.26	21.27	21.98	
ts4	-65	-77	-88	176	32	-42	36	-17	-9	23.99	23.19	24.57		24.29	23.49	24.87	
cis%													38.5				37.6

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S22 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Mep-OMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-3	-79	6	-179	-20	34	-35	23	-2	2.44	2.41	2.44	0.8	2.26	2.23	2.26	1.0
cAu	-8	-52	-31	-179	3	-25	38	-35	21	1.84	1.97	2.43	0.8	1.63	1.76	2.22	1.1
cFd	-1	-77	-176	-179	-17	32	-35	25	-5	2.03	2.00	1.76	2.5	1.78	1.75	1.51	3.7
cFu	-4	-59	161	176	4	-26	39	-36	21	1.34	1.43	1.59	3.4	1.30	1.39	1.55	3.4
tAd	-178	-75	5	-179	-14	31	-37	28	-9	1.96	1.90	1.91	1.9	1.73	1.68	1.69	2.8
tAu	178	-50	-39	-179	6	-27	39	-35	19	0.44	0.41	0.13	39.2	0.44	0.41	0.13	37.8
tFd	-178	-67	168	178	-5	24	-34	31	-17	1.24	1.28	1.79	2.4	1.17	1.21	1.72	2.6
tFu	180	-52	144	177	8	-30	40	-34	16	0.00	0.00	0.00	49.0	0.00	0.00	0.00	47.5
ts1	115	-93	76	-172	21	6	-30	44	-41	22.99	22.00	23.23		23.39	22.39	23.63	
ts2	118	-97	70	-174	18	-38	43	-32	9	22.80	21.83	23.17		23.11	22.15	23.49	
ts3	-63	-106	45	179	4	22	-38	41	-29	22.94	21.80	22.83		22.93	21.79	22.81	
ts4	-59	-91	-60	-180	22	-39	41	-28	4	23.05	21.94	22.42		23.39	22.29	22.76	
cis%													7.5				9.3

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S23 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Clp-OMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-9	-68	-12	180	-19	36	-40	28	-5	2.61	2.69	3.01	0.4	2.66	2.74	3.06	0.4
cAu	-4	-55	-32	180	4	-26	38	-35	20	1.56	1.65	1.96	2.4	1.42	1.51	1.82	3.1
cFd	-4	-74	168	178	-18	34	-39	29	-7	1.87	2.10	2.29	1.4	1.85	2.08	2.26	1.4
cFu[h]	-2	-59	159	176	4	-25	37	-34	19	1.17	1.27	1.77	3.3	1.11	1.21	1.71	3.7
tAd	173	-58	-29	-179	-14	32	-39	30	-10	1.68	1.82	2.67	0.7	1.82	1.97	2.82	0.6
tAu	178	-52	-38	-179	4	-26	38	-34	19	0.28	0.32	0.66	21.6	0.34	0.37	0.72	19.8
tFd	175	-60	156	176	-10	31	-40	33	-14	1.13	1.28	1.60	4.4	1.07	1.23	1.54	4.9
tFu	177	-54	148	176	3	-25	37	-34	20	0.00	0.00	0.00	65.7	0.00	0.00	0.00	66.2
ts1'	121	-75	65	-176	43	-20	-9	35	-48	22.32	21.39	22.24		22.63	21.70	22.55	
ts2	117	-85	74	-174	28	-41	38	-21	-4	21.91	20.86	22.34		22.05	21.00	22.48	
ts3	-60	-104	76	-177	10	18	-38	44	-34	22.36	21.51	22.50		22.76	21.91	22.90	
ts4	-62	-83	-180	-179	30	-41	36	-19	-7	21.67	20.78	22.38		21.74	20.85	22.45	
cis%													7.5				8.6

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S24 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-clp-OMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	2	-83	10	-180	-16	33	-37	27	-7	0.88	0.84	0.94	7.5	0.87	0.83	0.93	8.1
cAu	-6	-55	-33	-178	0	-24	39	-38	24	2.60	3.03	3.09	0.2	2.76	3.19	3.25	0.2
cFd	1	-80	-172	-178	-17	32	-37	26	-6	0.54	0.42	0.25	24.1	0.47	0.36	0.18	28.4
cFu	-6	-58	168	177	3	-26	39	-37	22	2.24	2.44	1.70	2.1	2.51	2.70	1.96	1.4
tAd	-178	-76	7	-179	-13	31	-38	30	-11	0.45	0.50	0.89	8.1	0.32	0.38	0.76	10.7
tAu	179	-54	-35	-179	2	-26	40	-38	23	1.12	1.42	1.55	2.7	1.45	1.75	1.88	1.6
tFd	-179	-74	-173	-179	-12	30	-37	29	-10	0.00	0.00	0.00	36.5	0.00	0.00	0.00	38.7
tFu	-179	-57	149	177	6	-29	41	-37	19	0.76	0.92	0.39	18.9	1.12	1.28	0.75	10.9
ts1	119	-73	65	-174	44	-24	-4	30	-46	21.30	20.51	21.31		21.89	21.11	21.90	
ts2	118	-103	42	177	11	-34	43	-37	16	22.49	21.70	22.79		23.01	22.22	23.30	
ts3	-62	-105	38	176	6	19	-36	40	-29	21.11	19.44	21.62		21.50	19.82	22.00	
ts4	-62	-84	-96	175	26	-42	43	-28	1	23.07	22.37	23.06		23.77	23.07	23.76	
cis%													33.8				38.1

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S25 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-mpc-OMe in chloroform

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd-gm[h]	-8	-70	-10	180	-20	36	-39	27	-4	-72	2.13	2.09	2.63	0.6	2.31	2.27	2.68	0.5
cAd-g	-8	-69	-12	-180	-19	35	-39	28	-5	57	1.50	1.48	2.59	0.6	1.60	1.59	2.56	0.6
cAd-t	-8	-69	-11	-180	-19	35	-39	28	-5	-180	2.22	2.16	2.55	0.7	2.39	2.33	2.59	0.6
cAu-gm	-4	-55	-30	-179	4	-26	38	-35	19	-63	2.13	2.08	3.34	0.2	2.13	2.07	3.20	0.2
cAu-g	-5	-55	-32	-180	2	-26	39	-37	22	60	2.43	2.48	4.04	0.1	2.39	2.44	3.86	0.1
cAu-t	-4	-55	-31	-180	3	-26	38	-35	20	171	2.19	2.23	3.70	0.1	2.19	2.24	3.57	0.1
cFd-gm	-3	-75	169	178	-18	35	-39	28	-6	-69	1.40	0.81	2.45	0.8	1.51	0.92	2.43	0.8
cFd-g	-2	-75	168	178	-16	34	-39	29	-8	58	0.75	0.76	1.68	2.8	0.79	0.80	1.60	3.3
cFd-t	-1	-76	168	178	-16	34	-39	30	-8	-175	1.48	1.59	2.90	0.4	1.57	1.67	2.86	0.4
cFu-gm[h,i]	-3	-58	160	176	5	-27	38	-34	18	-57	1.68	1.88	1.05	8.3	1.79	1.98	1.03	8.5
cFu-g	-4	-58	161	176	3	-26	38	-36	21	61	2.02	2.12	3.46	0.1	2.10	2.20	3.41	0.2
cFu-t	-4	-58	161	176	3	-25	36	-34	19	167	1.84	1.91	2.64	0.6	1.93	1.99	2.59	0.6
tAd-gm	176	-55	-35	-179	-7	28	-38	34	-17	-72	1.43	0.86	2.82	0.4	1.66	1.08	2.92	0.3
tAd-g	176	-55	-35	-179	-7	27	-38	34	-17	57	0.55	0.58	1.95	1.8	0.71	0.74	1.98	1.7
tAd-t	176	-54	-36	-179	-5	27	-39	35	-19	179	1.21	1.25	2.39	0.9	1.45	1.49	2.50	0.7
tAu-gm	179	-52	-37	-179	4	-26	38	-35	20	-62	0.86	0.86	2.24	1.1	1.04	1.05	2.29	1.0
tAu-g	178	-53	-37	-179	2	-25	39	-37	22	56	1.13	0.51	2.62	0.6	1.23	0.62	2.59	0.6
tAu-t	178	-52	-37	-179	3	-25	37	-35	20	170	0.83	0.88	2.20	1.2	1.02	1.07	2.26	1.1
tFd-gm	176	-61	157	176	-11	31	-39	32	-13	-73	0.86	0.22	2.00	1.7	0.93	0.28	1.94	1.8
tFd-g	176	-61	156	176	-11	30	-39	32	-14	57	0.00	0.00	1.16	6.8	0.00	0.00	1.03	8.5
tFu-gm	178	-55	151	175	5	-27	38	-34	18	-55	0.61	0.42	0.00	48.6	0.74	0.55	0.00	48.1
tFu-g	177	-55	150	176	2	-25	38	-36	22	52	0.76	0.71	1.60	3.2	0.86	0.81	1.57	3.4
tFu-t	177	-55	149	176	3	-25	37	-34	20	170	0.53	0.37	0.57	18.6	0.71	0.55	0.62	17.0
ts1'	114	-93	66	-175	20	-38	41	-29	6	76	22.41	21.50	24.47		22.73	21.82	24.66	
ts2	118	-84	-5	-180	30	-42	37	-20	-6	-62	22.94	21.99	24.66		23.36	22.41	24.95	
ts4	-73	-87	47	177	22	-37	38	-25	2	-61	23.51	22.46	24.25		23.51	22.46	24.11	
ts3	-60	-106	76	-177	8	19	-38	43	-32	-68	22.40	21.43	22.54		22.88	21.91	22.89	
cis%														15.1				15.9

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ

method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using Δ*G* values. [h] "gm" stands for the gauche- for χ^{OH}. [i] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S26 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Mpc-OMe in chloroform

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd-gm[h]	0	-79	2	-177	-16	33	-38	27	-7	-82	2.21	2.31	3.51	0.1	1.94	2.03	3.23	0.1
cAd-g	0	-82	12	-180	-18	34	-37	26	-5	60	1.65	1.60	2.18	0.9	1.32	1.27	1.85	1.5
cAd-t	0	-83	15	179	-18	34	-37	26	-5	-165	2.03	1.99	2.77	0.3	1.73	1.69	2.47	0.5
cAu-gm	-5	-55	-33	-178	1	-25	38	-37	23	-58	1.83	2.08	2.75	0.3	1.66	1.91	2.58	0.4
cAu-g	-5	-55	-33	-177	2	-25	39	-37	22	67	2.62	2.98	3.51	0.1	2.50	2.86	3.39	0.1
cAu-t	-6	-55	-33	-178	0	-24	39	-38	24	175	2.47	2.68	3.01	0.2	2.37	2.58	2.92	0.2
cFd-gm	1	-78	-176	179	-15	32	-38	29	-9	-85	1.95	1.88	2.41	0.6	1.48	1.42	1.95	1.3
cFd-g	0	-81	-170	-177	-19	34	-36	25	-4	60	1.23	1.08	1.33	3.8	0.89	0.73	0.98	6.4
cFd-t	1	-82	-168	-177	-18	33	-36	25	-4	-165	1.78	1.80	2.14	1.0	1.45	1.47	1.81	1.6
cFu-gm	-5	-57	165	176	5	-27	39	-36	19	-61	1.48	1.62	1.38	3.5	1.39	1.53	1.29	3.8
cFu-g	-5	-56	165	176	6	-28	40	-36	19	68	2.19	2.37	2.27	0.8	2.19	2.38	2.28	0.7
cFu-t	-5	-57	166	177	3	-26	40	-37	21	176	2.12	2.23	1.20	4.7	2.11	2.22	1.19	4.5
tAd-gm	-178	-72	-1	-178	-10	29	-37	31	-14	-76	1.60	1.56	1.92	1.4	1.44	1.39	1.76	1.7
tAd-g	-177	-79	14	-179	-14	32	-38	30	-10	60	1.29	1.27	2.03	1.2	0.89	0.87	1.63	2.1
tAd-t	-176	-80	15	-179	-13	31	-38	30	-11	-164	1.53	1.64	2.82	0.3	1.19	1.30	2.49	0.5
tAu-gm	179	-53	-35	-179	3	-26	39	-37	21	-58	0.36	0.53	0.87	8.2	0.37	0.55	0.88	7.6
tAu-g	-180	-53	-35	-179	7	-29	41	-36	19	72	1.23	1.34	1.48	2.9	1.29	1.40	1.54	2.5
tAu-t	179	-53	-35	-179	3	-27	40	-38	22	174	0.93	1.17	1.85	1.6	1.00	1.24	1.92	1.3
tFd-gm	-178	-66	167	178	-2	23	-36	34	-21	-67	0.93	0.31	2.63	0.4	0.86	0.24	2.56	0.4
tFd-g	-179	-75	-170	-179	-15	32	-37	28	-8	57	0.93	0.86	1.69	2.1	0.64	0.58	1.40	3.2
tFd-t	-179	-75	-171	-178	-14	31	-36	28	-8	-165	1.28	1.15	1.63	2.3	1.07	0.94	1.41	3.1
tFu-gm	-179	-56	149	176	7	-29	40	-35	18	-59	0.00	0.00	0.00	35.6	0.00	0.00	0.00	33.6
tFu-g	-180	-56	148	177	7	-29	40	-35	18	70	0.82	0.81	0.67	11.5	0.90	0.90	0.75	9.4
tFu-t	-179	-56	149	177	6	-29	41	-37	19	178	0.63	0.64	0.47	16.2	0.71	0.72	0.55	13.3
ts1	117	-111	30	177	1	24	-39	40	-26	-164	22.39	21.18	22.70		22.47	21.27	22.78	
ts2	117	-103	42	177	11	-34	43	-37	16	-178	22.65	21.67	23.15		22.90	21.92	23.40	
ts3	-62	-107	36	176	4	21	-37	40	-27	-166	22.23	21.16	22.10		22.24	21.17	22.11	
ts4	-67	-92	65	-178	21	-39	42	-30	6	-177	22.48	21.51	22.16		22.76	21.79	22.44	
cis%														16.3				21.3

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] "gm" stands for the gauche- for χ^{OH}.

Table S27 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-mop-OMe in chloroform

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	$\chi^{OM\varepsilon}$	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]
cAd-g	-3	-83	17	-178	-23	39	-42	28	-3	72	0.00	0.19	0.52	9.9	0.00	0.00	0.28	11.9
cAd-gm[h]	0	-79	7	-180	-17	24	-22	12	4	-57	4.99	5.56	6.92	0.0	4.10	4.48	5.79	0.0
cAd-t	-3	-80	9	-178	-21	38	-40	27	-4	172	0.44	0.60	0.71	7.2	0.67	0.64	0.70	5.9
cAu-g	-3	-56	-32	-178	3	-25	37	-35	20	70	2.68	2.86	2.14	0.7	2.58	2.57	1.80	0.9
cAu-gm	-1	-56	-34	-178	6	-28	39	-35	18	-48	5.26	5.72	5.89	0.0	5.01	5.28	5.41	0.0
cAu-t	-2	-57	-32	-177	3	-25	37	-35	20	177	2.57	2.77	2.66	0.3	2.47	2.48	2.31	0.4
cFd-g	-2	-82	-159	-180	-24	39	-41	27	-2	74	0.34	0.39	0.71	7.3	0.36	0.23	0.50	8.3
cFd-gm	1	-76	-172	-178	-14	23	-23	15	0	-56	4.74	5.17	6.09	0.0	3.65	3.89	4.76	0.0
cFd-t	-4	-77	-169	-179	-22	38	-39	26	-2	171	0.38	0.53	0.40	12.2	0.46	0.42	0.24	12.8
cFu-g	-1	-60	163	177	3	-25	37	-35	20	69	2.56	2.80	1.87	1.0	2.54	2.59	1.61	1.3
cFu-gm	-1	-59	158	176	5	-27	39	-36	19	-47	5.08	5.50	5.29	0.0	4.92	5.15	4.89	0.0
cFu-t	-2	-60	162	176	2	-24	37	-35	21	177	2.41	2.82	2.87	0.2	2.31	2.52	2.53	0.3
tAd-g	179	-83	16	-179	-21	38	-42	29	-5	70	0.10	0.27	0.57	9.2	0.09	0.07	0.32	11.2
tAd-gm	-174	-52	-39	180	24	-7	-11	24	-31	-64	4.98	4.59	6.40	0.0	4.71	4.14	5.90	0.0
tAd-t	179	-76	3	-179	-18	35	-39	28	-6	171	0.57	0.59	0.53	9.8	0.86	0.68	0.57	7.3
tAu-g	179	-54	-35	-180	4	-25	37	-35	20	70	1.20	1.37	0.79	6.4	1.20	1.18	0.54	7.7
tAu-gm	180	-53	-37	-180	7	-29	40	-35	18	-46	3.75	4.21	4.62	0.0	3.64	3.92	4.27	0.0
tAu-t	178	-53	-36	-179	3	-25	38	-35	20	176	1.32	1.60	1.71	1.3	1.29	1.38	1.44	1.7
tFd-g	178	-82	-165	-179	-22	38	-41	27	-3	73	0.50	0.00	1.05	4.1	0.71	0.02	1.01	3.5
tFd-gm	-179	-71	177	-179	-8	18	-22	17	-6	-56	4.42	4.80	4.82	0.0	3.50	3.69	3.66	0.0
tFd-t	176	-73	179	-180	-20	35	-37	25	-3	169	0.62	0.66	0.00	24.0	0.86	0.71	0.00	19.2
tFu-g	179	-56	145	178	4	-26	38	-35	20	69	0.93	1.21	1.05	4.1	0.94	1.04	0.82	4.8
tFu-gm	180	-56	143	178	5	-28	39	-36	19	-46	3.37	3.81	3.91	0.0	3.26	3.51	3.56	0.0
tFu-t	179	-57	145	178	3	-25	37	-35	21	177	1.00	1.39	1.42	2.2	0.97	1.16	1.15	2.8
ts1	114	-106	40	177	6	21	-39	43	-30	177	20.61	19.56	20.09		21.15	19.92	20.40	
ts2	115	-99	68	-178	14	-35	41	-32	11	176	21.50	20.62	20.93		21.85	20.78	21.04	
ts3	-64	-112	20	177	-3	28	-41	40	-23	180	23.13	22.26	23.02		23.45	22.39	23.11	
ts4	-69	-85	80	-175	24	-39	39	-25	0	176	23.78	22.93	23.19		24.00	22.96	23.17	
cis%														38.7				41.8

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] "gm" stands for the gauche- for $\chi^{\mathrm{OM\varepsilon}}$.

Table S28 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-mop-OMe in water

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	$\chi^{OM\varepsilon}$	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]	ΔE_e [d]	ΔH [e]	ΔG [f]	w [g]
cAd-gm[h]	-8	-75	2	-177	-23	26	-20	6	12	-56	4.92	5.84	6.94	0.0	3.95	4.87	5.80	0.0
cAd-g	-3	-82	11	-176	-23	39	-41	28	-3	72	0.61	1.19	1.74	3.1	0.54	1.12	1.49	4.0
cAd-t	-6	-77	6	-180	-23	37	-39	25	-1	169	1.02	1.57	1.40	5.4	1.14	1.69	1.35	5.1
cAu-gm	-4	-52	-32	-179	8	-29	40	-34	16	-47	5.56	6.73	7.04	0.0	5.15	6.32	6.46	0.0
cAu-g	-2	-56	-31	-179	5	-26	38	-35	19	68	3.26	4.06	3.53	0.1	3.03	3.83	3.13	0.3
cAu-t	-7	-52	-31	-179	3	-25	37	-35	20	177	3.26	4.29	4.39	0.0	2.94	3.96	3.90	0.1
cFd-gm	-10	-72	-176	-179	-22	25	-20	7	10	-55	4.57	5.43	6.44	0.0	3.51	4.37	5.20	0.0
cFd-g	-3	-82	-163	178	-21	39	-42	29	-5	71	0.21	0.75	1.35	5.9	0.12	0.67	1.09	7.9
cFd-t	-3	-77	-175	180	-18	35	-39	28	-6	168	0.64	1.23	1.29	6.5	0.71	1.30	1.19	6.7
cFu-gm	-6	-56	164	177	5	-27	40	-36	20	-46	5.06	6.19	6.14	0.0	4.80	5.92	5.70	0.0
cFu-g	-5	-56	164	176	4	-26	37	-34	19	68	2.87	3.85	3.74	0.1	2.73	3.71	3.43	0.2
cFu-t	-7	-56	163	176	3	-25	38	-35	20	177	2.68	3.74	3.65	0.1	2.49	3.55	3.28	0.2
tAd-gm	-179	-72	2	-176	-13	22	-23	15	-1	-57	4.69	5.55	6.17	0.0	3.59	4.46	4.91	0.0
tAd-g	178	-76	8	-174	-20	38	-42	30	-7	72	0.45	1.03	1.54	4.3	0.32	0.89	1.23	6.3
tAd-t	178	-73	2	-179	-17	34	-40	29	-8	168	0.60	1.17	1.22	7.3	0.75	1.32	1.21	6.5
tAu-gm	179	-50	-38	-177	8	-29	40	-35	17	-46	4.00	5.17	5.39	0.0	3.79	4.95	5.01	0.0
tAu-g	180	-53	-37	-179	6	-28	39	-34	18	69	1.79	1.95	2.68	0.6	1.68	1.83	2.40	0.9
tAu-t	176	-50	-38	-178	3	-25	38	-35	20	176	1.72	2.49	1.87	2.4	1.60	2.38	1.59	3.4
tFd-gm	-178	-70	-180	180	-8	19	-22	17	-5	-56	4.13	4.88	4.96	0.0	3.13	3.88	3.78	0.1
tFd-g	177	-75	-167	178	-20	38	-42	30	-6	71	0.00	0.00	1.80	2.7	0.00	0.00	1.63	3.2
tFd-t	179	-70	177	179	-14	32	-38	29	-10	166	0.16	0.77	0.00	57.4	0.33	0.94	0.00	49.9
tFu-gm	-179	-54	146	175	11	-31	40	-34	14	-46	3.50	4.49	4.51	0.0	3.32	4.31	4.16	0.0
tFu-g	179	-52	142	178	7	-27	37	-33	17	69	1.41	2.28	2.03	1.9	1.35	2.22	1.79	2.4
tFu-t	-180	-56	147	177	6	-27	39	-34	18	178	1.24	2.16	1.97	2.0	1.13	2.05	1.69	2.9
ts1	118	-73	65	-175	45	-26	-1	29	-46	166	21.58	21.29	22.39		21.94	21.65	22.58	
ts2	117	-84	73	-174	31	-43	38	-20	-6	174	23.42	23.19	24.05		23.62	23.39	24.08	
ts3	-62	-109	56	179	4	21	-38	40	-28	168	22.06	21.70	21.21		22.48	22.11	21.46	
ts4	-64	-68	68	-177	46	-26	-2	30	-47	166	21.98	21.55	21.74		22.70	22.27	22.29	
cis%														21.3				24.4

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] "gm" stands for the gauche- for $\chi^{\mathrm{OM\varepsilon}}$.

Table S29 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(2-Mep)-NHMe in chloroform

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	10	-76	-18	-178	-4	26	-38	35	-19	2.33	1.63	2.23	1.2	1.84	1.14	1.73	2.0
cAu	1	-60	-29	-176	11	-31	39	-32	13	2.43	2.54	2.07	1.5	1.90	2.01	1.54	2.8
cFd	-3	-66	155	176	-10	29	-38	32	-14	4.24	3.65	4.35	0.0	3.68	3.09	3.79	0.1
cFu	-5	-46	137	-180	12	-31	39	-31	12	4.06	4.08	3.59	0.1	3.50	3.51	3.03	0.2
tAd[h]	-173	-70	-21	178	-1	24	-38	36	-22	1.56	1.52	0.71	15.1	1.38	1.34	0.53	15.5
tAu[h]	-175	-59	-30	179	11	-31	39	-32	13	1.54	1.47	0.85	11.9	1.26	1.20	0.58	14.4
tCd	-172	-80	55	178	-13	33	-42	33	-13	0.00	0.00	0.00	50.2	0.00	0.00	0.00	38.1
tCu[h]	-174	-71	53	176	1	-25	40	-38	23	1.71	1.81	1.52	3.9	1.91	2.00	1.72	2.1
tFd	177	-58	141	-179	-4	25	-36	33	-19	1.94	1.94	1.28	5.8	1.50	1.50	0.85	9.1
tFu	176	-52	133	-176	5	-27	39	-35	19	1.57	1.53	0.94	10.2	1.16	1.11	0.53	15.6
ts1	125	-129	9	179	-13	34	-42	34	-13	19.24	18.10	18.61		19.33	18.19	18.70	
ts2	126	-159	24	177	-36	24	-2	-20	35	18.98	17.79	18.08		19.13	17.95	18.23	
ts3	-57	-119	12	178	-10	32	-41	35	-15	21.05	19.99	20.65		20.70	19.64	20.30	
ts4	-61	-69	-15	-177	41	-41	28	-3	-25	21.97	21.06	21.69		21.57	20.67	21.30	
cis%													2.8				5.2

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S30 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(2-Mep)-NHMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	3	-74	-17	-178	-10	29	-38	31	-13	2.39	2.38	2.50	0.8	2.15	2.14	2.26	1.3
cAu	-5	-57	-30	-176	6	-28	39	-35	18	2.77	2.70	2.29	1.1	2.57	2.50	2.09	1.7
cFd	-4	-67	160	175	-12	31	-38	29	-11	2.30	1.74	3.36	0.2	2.15	1.58	3.21	0.3
cFu	-6	-47	148	178	14	-33	40	-31	11	1.95	2.24	3.34	0.2	1.90	2.19	3.29	0.2
tAd	-178	-64	-27	-176	-3	24	-37	34	-20	0.78	0.79	0.81	13.9	0.90	0.91	0.93	11.9
tAu	179	-53	-38	180	7	-29	40	-35	17	0.67	0.54	0.74	15.8	0.79	0.66	0.86	13.5
tCd	-171	-81	42	175	-14	34	-42	33	-12	1.97	1.89	2.47	0.8	2.18	2.10	2.68	0.6
tFd	178	-56	146	178	-2	24	-36	34	-20	0.50	0.55	0.88	12.3	0.48	0.53	0.87	13.3
tFu	176	-51	143	178	8	-29	40	-34	17	0.00	0.00	0.00	54.8	0.00	0.00	0.00	57.3
ts1	124	-118	10	177	-4	29	-42	39	-22	21.39	20.33	22.19		21.86	20.80	22.65	
ts2	127	-157	18	178	-35	23	-2	-19	34	21.54	20.49	21.95		21.97	20.92	22.38	
ts3	-51	-136	10	180	-18	36	-40	29	-7	22.32	21.38	23.30		22.50	21.56	23.48	
ts4	-60	-71	-10	-178	43	-41	26	0	-27	23.26	22.38	23.76		23.19	22.31	23.69	
cis%													2.3				3.4

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S31 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(3-mep)-NHMe in chloroform

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd-add	7	-87	-6	180	-16	34	-40	30	-8	0.60	0.46	0.50	15.7	0.70	0.57	0.61	15.7
cAu	8	-70	-21	-175	7	-28	39	-35	17	1.53	1.53	2.00	1.3	1.57	1.56	2.03	1.4
cFd	-2	-73	146	174	-17	33	-38	28	-7	1.09	0.98	0.64	12.4	1.16	1.05	0.71	13.2
cFu	-2	-56	158	175	6	-27	39	-35	18	2.89	2.81	3.12	0.2	2.80	2.72	3.03	0.3
tAd	-173	-76	-24	179	-7	28	-38	34	-17	0.32	0.25	0.49	16.0	0.51	0.43	0.68	13.9
tAu	-172	-69	-20	-179	8	-29	39	-35	16	1.32	1.22	1.49	3.0	1.38	1.29	1.56	3.2
tCd	-175	-84	85	-173	-18	35	-39	28	-6	0.39	0.39	0.62	13.0	0.89	0.88	1.11	6.7
tFd	176	-67	143	179	-14	32	-38	29	-9	0.00	0.00	0.00	36.8	0.00	0.00	0.00	43.8
tFu	179	-59	151	180	2	-25	38	-36	21	2.02	2.01	1.84	1.7	2.05	2.05	1.87	1.9
ts1	118	-101	-21	-178	11	16	-36	43	-34	17.85	16.60	17.32		18.59	17.34	18.06	
ts2	119	-94	-14	-174	20	-38	41	-30	6	18.28	17.21	18.69		18.88	17.81	19.29	
ts3	-62	-95	-19	179	12	15	-35	42	-34	18.94	17.75	17.50		19.52	18.33	18.07	
ts4	-63	-85	-9	-178	24	-40	41	-27	2	18.64	17.51	18.76		18.85	17.72	18.97	
cis%													29.6				30.5

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S32 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(3-mep)-NHMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	3	-87	-9	180	-19	35	-39	27	-4	2.02	1.95	1.49	3.2	2.05	1.98	1.53	3.2
cAu	0	-65	-25	-176	2	-24	38	-37	22	4.02	4.04	3.65	0.1	3.93	3.95	3.56	0.1
cFd	-3	-69	149	174	-17	33	-38	27	-6	0.72	0.68	0.13	31.4	0.83	0.79	0.24	28.3
cFu	-3	-55	154	176	7	-28	39	-35	18	2.25	2.19	1.84	1.8	2.26	2.20	1.85	1.9
tAd	178	-67	-28	-178	-13	30	-37	29	-10	0.61	0.60	0.74	11.3	0.64	0.63	0.77	11.6
tAu	-174	-66	-19	-178	9	-30	40	-34	16	2.39	2.19	1.93	1.5	2.41	2.21	1.95	1.6
tFd	175	-62	146	175	-14	31	-37	29	-9	0.00	0.00	0.00	39.4	0.00	0.00	0.00	42.6
tFu	-180	-55	150	176	8	-29	40	-35	16	1.01	1.04	0.74	11.3	1.10	1.13	0.82	10.6
ts1	118	-96	-18	178	16	11	-34	44	-38	21.76	20.62	21.76		22.54	21.39	22.54	
ts2	118	-99	-9	-179	16	-36	42	-33	10	22.03	20.64	20.76		22.63	21.24	21.36	
ts3	-60	-94	-15	-180	15	12	-34	44	-37	21.75	20.53	21.16		22.31	21.09	21.72	
ts4	-62	-88	-5	-178	25	-41	41	-27	2	21.30	20.16	20.65		21.47	20.32	20.82	
cis%													36.4				33.5

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S33 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(3-Mep)-NHMe in chloroform

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd[h]	7	-90	-5	-179	-18	34	-39	29	-7	1.11	1.17	1.19	7.8	0.88	0.95	0.97	10.6
cAu[h]	5	-68	-26	-177	6	-27	38	-34	18	1.69	1.71	1.62	3.8	1.52	1.54	1.45	4.7
cFd[h]	-2	-72	152	176	-17	33	-38	28	-6	2.95	2.95	1.99	2.0	2.66	2.66	1.70	3.1
cFu[h]	-3	-55	143	178	7	-28	39	-35	18	2.66	2.72	2.67	0.6	2.44	2.49	2.45	0.9
tAd	-171	-89	-2	178	-17	34	-40	30	-8	1.45	0.94	2.06	1.8	1.39	0.88	2.01	1.8
tAu	-173	-69	-23	179	6	-28	39	-34	18	1.62	1.64	1.50	4.6	1.56	1.58	1.44	4.8
tCd	-173	-85	68	-178	-17	34	-39	29	-8	0.00	0.00	0.00	58.1	0.00	0.00	0.00	54.3
tCu	-172	-82	71	-178	-6	-19	36	-39	28	0.97	1.11	1.37	5.8	1.31	1.45	1.71	3.0
tFd	177	-68	144	180	-15	32	-38	29	-9	1.94	2.15	2.24	1.3	1.66	1.87	1.96	2.0
tFu	179	-56	137	-178	5	-27	38	-35	19	1.37	1.46	0.83	14.2	1.31	1.39	0.77	14.8
ts1	117	-112	-6	-179	0	24	-39	40	-25	18.99	17.43	19.75		19.34	17.78	20.11	
ts2	120	-101	-15	-176	13	-34	41	-34	13	19.22	18.24	19.30		19.68	18.69	19.76	
ts3	-66	-103	-1	178	0	24	-39	39	-25	20.11	18.63	20.82		20.13	18.65	20.84	
ts4	-64	-88	-13	-179	22	-38	40	-27	3	19.87	18.85	19.61		19.89	18.86	19.63	
cis%													14.2				19.3

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S34 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(3-Mep)-NHMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd[h]	2	-87	-7	-180	-20	35	-38	26	-4	1.93	1.80	1.69	2.5	1.75	1.62	1.51	3.1
cAu[h]	-3	-56	-33	178	4	-26	38	-35	19	2.75	2.56	1.88	1.8	2.40	2.21	1.53	3.0
cFd[h]	-6	-67	155	177	-17	33	-37	27	-6	1.53	1.59	0.96	8.7	1.39	1.45	0.82	10.0
cFu[h]	-7	-55	149	174	3	-25	38	-35	20	1.11	1.23	1.36	4.4	1.04	1.16	1.28	4.6
tAd[h]	-179	-75	-14	-179	-13	31	-38	29	-10	1.31	1.27	1.38	4.2	1.24	1.20	1.31	4.3
tAu[h]	-176	-65	-25	-178	3	-25	38	-36	21	1.32	1.00	0.45	20.3	1.31	1.00	0.45	18.7
tCd[h]	-172	-86	60	179	-16	34	-40	30	-9	2.53	2.47	2.66	0.5	2.53	2.46	2.65	0.5
tCu[h]	-170	-83	54	179	-3	-21	37	-39	26	3.41	3.30	3.27	0.2	3.69	3.58	3.56	0.1
tFd[h]	177	-62	148	176	-10	29	-37	31	-13	0.85	0.18	0.69	13.6	0.70	0.03	0.54	16.0
tFu[h]	178	-53	143	176	6	-27	39	-35	18	0.00	0.00	0.00	43.7	0.00	0.00	0.00	39.8
ts1	117	-109	-1	178	3	22	-38	40	-27	21.73	20.39	20.05		22.15	20.81	20.47	
ts2	119	-105	-9	-180	11	-32	41	-35	15	21.85	20.39	20.54		22.40	20.93	21.08	
ts3	-60	-97	-4	180	14	12	-33	42	-35	21.60	20.69	21.81		21.72	20.81	21.93	
ts4	-63	-90	-12	-180	23	-39	40	-27	3	21.36	20.12	20.79		21.45	20.22	20.89	
cis%													17.4				20.7

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S35 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(5-mep)-NHMe in chloroform

Conf.	Torsion angles[a]									DSD-PBEP86-D3BJ/cc-pVTZ[b]				M06-2X/def2-TZVP[c]			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-2	-76	-14	-178	-12	31	-39	32	-13	0.36	0.21	0.04	33.1	0.12	0.00	0.00	34.6
cAu[h]	-11	-51	-33	-178	9	-28	38	-32	14	3.54	3.31	2.81	0.3	3.03	2.83	2.39	0.6
cFd	-7	-64	152	176	-14	32	-38	30	-10	1.73	0.89	0.89	7.8	1.53	0.72	0.79	9.1
cFu	-17	-42	143	177	9	-28	38	-32	14	3.82	3.56	2.98	0.2	3.58	3.35	2.83	0.3
tAd	-177	-75	-16	178	-7	28	-39	34	-17	1.23	1.29	1.16	4.9	1.18	1.26	1.20	4.6
tAu	175	-56	-32	179	14	-32	38	-29	9	4.22	4.09	3.82	0.1	3.94	3.84	3.63	0.1
tCd[h]	-178	-81	70	-177	-13	33	-41	32	-12	0.00	0.00	0.00	35.3	0.00	0.03	0.09	29.7
tFd[h]	171	-58	143	180	-7	27	-38	33	-16	1.09	0.96	0.39	18.2	0.91	0.81	0.30	20.8
tFu	170	-48	135	-177	12	-30	38	-30	12	3.24	3.21	3.42	0.1	2.96	2.97	3.35	0.1
ts1	107	-93	-20	-177	14	14	-35	43	-35	20.25	19.01	19.54		20.38	19.19	19.88	
ts2	118	-146	16	178	-31	13	9	-29	38	19.23	17.94	18.03		19.40	18.16	18.41	
ts3	-78	-84	-9	178	12	16	-36	42	-34	21.76	20.50	20.81		21.64	20.43	20.90	
cis%													41.4				44.7

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C. [g] Population (%) of *cis* conformers calculated by ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S36 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(5-mep)-NHMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-7	-75	-14	-178	-15	33	-39	30	-9	1.21	1.19	1.93	2.2	1.07	1.05	1.79	2.8
cAu[h]	-15	-49	-35	177	2	-24	37	-35	21	4.55	4.56	4.81	0.0	4.12	4.13	4.38	0.0
cFd	-7	-63	151	176	-13	31	-38	30	-10	0.51	0.40	0.37	29.7	0.56	0.45	0.42	28.1
cFu	-18	-44	149	177	10	-29	38	-32	14	2.50	2.25	2.01	1.9	2.51	2.27	2.02	1.9
tAd	-179	-69	-22	180	-7	27	-38	33	-16	0.85	0.95	1.08	9.0	0.93	1.03	1.16	8.1
tAu	172	-56	-33	-177	5	-26	38	-34	18	3.65	3.73	4.27	0.0	3.46	3.54	4.08	0.1
tCd[h]	-178	-82	68	-177	-12	32	-41	33	-13	2.52	2.44	3.19	0.3	2.64	2.56	3.32	0.2
tFd[h]	171	-56	146	174	-6	27	-37	33	-17	0.00	0.00	0.00	55.8	0.00	0.00	0.00	57.4
tFu	171	-47	143	177	13	-31	39	-30	11	1.71	1.76	2.32	1.1	1.61	1.67	2.22	1.4
ts1	107	-92	-21	-178	15	13	-35	43	-37	23.15	21.96	23.22		23.41	22.22	23.48	
ts2	116	-145	10	179	-30	13	9	-28	36	22.04	21.00	22.24		22.30	21.26	22.50	
ts3	-76	-80	-13	179	22	6	-31	43	-41	23.86	22.79	23.81		23.84	22.76	23.78	
cis%													33.8				32.9

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C. [g] Population (%) of *cis* conformers calculated by ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S37 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(5-Mep)-NHMe in chloroform

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	17	-99	0	180	-18	34	-39	28	-6	0.55	0.38	0.40	15.4	0.45	0.37	0.34	15.2
cAu	6	-71	-24	-177	5	-26	38	-34	18	1.27	1.05	0.41	15.0	0.89	0.76	0.07	24.0
cFd	10	-90	148	176	-20	34	-36	24	-2	2.84	2.67	1.88	1.3	2.69	2.60	1.76	1.4
cFu	0	-59	143	177	3	-25	37	-35	20	2.42	1.44	1.98	1.1	2.08	1.18	1.67	1.6
tAd	-168	-95	7	176	-19	35	-39	27	-5	1.67	1.56	1.38	2.9	1.48	1.45	1.23	3.4
tAu	-170	-73	-19	180	3	-25	38	-35	20	1.28	1.13	1.01	5.5	1.01	0.94	0.77	7.4
tCd	-170	-89	65	-179	-22	35	-37	23	0	0.09	0.00	0.05	27.8	0.00	0.00	0.00	27.1
tCu	-173	-83	71	-177	-11	-13	32	-37	31	0.00	0.02	0.00	30.2	0.18	0.29	0.22	18.7
tFd	-173	-82	138	-180	-20	33	-35	22	-1	2.75	2.70	2.17	0.8	2.42	2.45	1.87	1.2
ts1	119	-107	-9	-179	7	20	-38	42	-31	17.28	15.85	16.04		17.64	16.30	16.43	
ts2	118	-100	-14	-176	14	-34	40	-32	11	18.67	17.31	17.75		19.00	17.72	18.11	
ts3	-63	-107	0	178	2	23	-39	40	-27	18.05	16.59	16.82		18.23	16.86	17.04	
ts4	-67	-86	-9	-179	23	-38	39	-26	2	19.10	17.75	18.03		19.15	17.89	18.13	
cis%													32.7				42.2

[a] Torsion angles are defined in Fig. 1. Optimized at the PCM M06-2X/6-31+G(d) level of theory in chloroform. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S38 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(5-Mep)-NHMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	11	-96	-1	180	-19	35	-38	26	-4	0.66	0.76	1.33	4.8	0.87	0.97	1.54	3.5
cAu	1	-66	-26	-179	2	-24	37	-35	21	1.34	1.17	1.20	6.0	1.18	1.01	1.04	8.2
cFd	11	-89	154	175	-19	33	-36	25	-3	1.01	1.06	1.07	7.5	1.24	1.30	1.30	5.3
cFu	-4	-59	153	176	0	-23	37	-36	23	0.12	0.16	0.36	24.7	0.18	0.22	0.41	23.7
tAd	-169	-85	-4	179	-17	34	-38	28	-6	0.86	1.01	1.82	2.1	0.94	1.09	1.91	1.9
tAu	-173	-69	-21	-177	0	-23	37	-36	22	0.00	0.00	0.00	45.1	0.00	0.00	0.00	47.6
tCd	-171	-89	58	-179	-25	37	-36	21	3	1.77	1.63	2.03	1.5	1.97	1.83	2.22	1.1
tCu	-174	-82	65	-179	-12	-13	32	-38	31	2.22	2.16	1.75	2.3	2.66	2.60	2.20	1.2
tFd	-173	-74	148	176	-16	31	-36	26	-6	1.25	1.32	1.20	6.0	1.15	1.21	1.09	7.5
ts1	117	-98	-14	180	17	10	-33	43	-38	19.38	18.16	19.46		20.05	18.83	20.13	
ts2	119	-111	-6	-177	4	-26	38	-36	20	20.80	19.55	20.57		21.44	20.19	21.22	
ts3	-60	-100	-5	178	11	16	-36	42	-34	19.25	17.97	18.33		19.81	18.53	18.89	
ts4	-66	-88	-8	-178	25	-40	40	-25	0	20.19	19.18	20.39		20.57	19.56	20.78	
cis%													43.0				40.7

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S39 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(5-tbp)-NHMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd	-19	-50	-34	179	-5	23	-33	29	-15	1.58	1.40	1.68	3.4	1.41	1.10	1.36	5.3
cAu	-24	-38	-40	178	14	-32	39	-30	9	8.01	7.68	7.24	0.0	8.07	7.60	7.15	0.0
cFd	-20	-48	148	177	-4	23	-33	30	-16	0.11	0.00	0.00	58.5	0.26	0.02	0.00	52.3
cFu	-30	-23	145	175	29	-35	29	-11	-12	4.61	4.19	3.09	0.3	5.11	4.55	3.44	0.2
tAd	167	-52	-37	-178	6	15	-30	32	-24	1.11	1.02	1.26	7.0	1.24	1.02	1.24	6.5
tAu	160	-34	-50	176	35	-36	25	-4	-20	5.38	5.36	5.20	0.0	5.78	5.63	5.46	0.0
tFd	167	-51	145	176	3	17	-30	32	-22	0.00	0.14	0.38	30.8	0.00	0.00	0.23	35.8
ts1	106	-136	13	178	-32	40	-33	14	11	25.57	23.92	23.59		26.43	24.65	24.30	
ts2	112	-148	10	-179	-34	16	9	-30	40	21.60	20.13	20.43		22.10	20.49	20.78	
cis%													62.2				57.8

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values.

Table S40 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-(5-Tbp)-NHMe in water

Conf.	Torsion angles									DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cDd[h]	25	-122	48	-173	-31	40	-36	17	8	2.13	2.04	2.67	0.7	2.15	2.05	2.68	0.7
cAu	12	-83	-9	-177	2	-22	34	-32	18	0.51	0.38	0.67	19.0	0.55	0.42	0.72	18.2
cFd[h]	33	-110	146	174	-16	32	-36	26	-6	4.21	4.15	3.74	0.1	4.55	4.50	4.08	0.1
cFu[h]	13	-75	160	176	3	-23	34	-32	18	0.00	0.00	0.00	59.0	0.00	0.00	0.00	60.8
tAu	-160	-82	-4	-179	-1	-20	33	-33	21	0.89	0.92	0.77	16.0	0.97	1.00	0.85	14.4
tCd	-156	-98	63	-174	-29	35	-30	13	10	2.14	1.91	2.32	1.2	1.95	1.72	2.13	1.7
tCu	-161	-87	43	178	-11	-10	26	-32	27	1.29	1.24	1.57	4.2	1.29	1.24	1.57	4.3
ts1	134	-112	4	180	-4	28	-42	39	-21	18.63	17.25	17.75		19.01	17.63	18.13	
ts2	120	-97	-13	-177	18	-33	37	-26	5	18.29	16.96	17.83		18.56	17.24	18.10	
ts3	-49	-111	3	178	-3	26	-39	37	-21	17.47	16.21	16.97		17.84	16.58	17.34	
ts4	-60	-89	-12	-178	23	-37	37	-23	0	16.98	15.37	15.38		17.13	15.52	15.53	
cis%													78.7				79.7

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S41 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-Hyp-NHMe in water

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd-gm[h]	1	-85	-8	-178	-19	34	-38	26	-4	-75	3.01	2.93	2.96	0.3	2.89	2.81	2.84	0.3
cAd-g	2	-86	-7	-179	-20	34	-36	24	-3	57	2.51	2.69	3.29	0.1	2.60	2.77	3.38	0.1
cAd-t	1	-85	-7	-178	-19	34	-37	25	-4	-169	3.04	3.04	3.38	0.1	2.98	2.98	3.32	0.1
cAu-gm	-1	-74	-21	-176	-3	-20	35	-36	25	-61	2.62	2.42	2.63	0.5	2.39	2.19	2.40	0.6
cAu-g	3	-80	-17	-178	-7	-18	35	-39	29	62	3.55	3.38	3.77	0.1	3.39	3.21	3.61	0.1
cAu-t	-2	-70	-23	-177	-3	-20	34	-36	24	176	2.62	2.55	2.71	0.4	2.41	2.34	2.50	0.5
cFd-gm	-5	-66	152	177	-16	32	-37	27	-7	-74	2.41	2.48	3.11	0.2	2.54	2.61	3.24	0.2
cFd-g	-5	-66	151	177	-16	32	-37	27	-7	58	1.95	2.14	2.87	0.3	2.15	2.34	3.07	0.2
cFd-t	-5	-66	151	177	-16	32	-37	27	-7	-169	2.48	2.59	3.25	0.2	2.55	2.67	3.33	0.1
cFu-gm[h,i]	-6	-56	148	176	4	-26	38	-35	20	-64	1.19	1.01	0.66	12.7	1.01	0.83	0.48	16.2
cFu-g	-7	-57	148	177	1	-24	37	-35	22	58	2.32	2.30	2.89	0.3	2.19	2.16	2.76	0.3
cFu-t[h]	-6	-56	148	177	3	-25	37	-35	20	175	1.26	1.19	1.45	3.3	1.06	0.99	1.25	4.4
tAd-gm	-178	-73	-15	-179	-12	31	-38	30	-11	-71	2.45	2.48	2.70	0.4	2.46	2.49	2.71	0.4
tAd-g	-179	-72	-17	-178	-11	30	-38	30	-12	56	1.90	2.06	2.33	0.7	2.05	2.22	2.49	0.5
tAd-t	-178	-72	-16	-179	-11	30	-38	31	-12	-171	2.25	2.27	2.22	0.9	2.33	2.35	2.30	0.7
tAu-gm	-176	-68	-23	-177	0	-23	37	-36	23	-62	1.34	1.34	1.84	1.7	1.40	1.39	1.90	1.5
tAu-g	-176	-69	-22	-177	-1	-22	37	-37	24	56	2.35	2.35	3.00	0.2	2.37	2.36	3.02	0.2
tAu-t	-176	-69	-23	-177	0	-23	37	-36	23	177	1.18	1.14	1.72	2.1	1.30	1.26	1.84	1.6
tCd-gm	-172	-86	63	-179	-15	34	-41	31	-10	-74	3.08	3.33	3.96	0.0	3.38	3.62	4.26	0.0
tCd-g	-173	-86	63	-179	-15	34	-40	31	-10	56	2.47	2.84	3.70	0.1	2.96	3.32	4.19	0.0
tCu-gm	-169	-86	64	-180	-5	-20	37	-39	28	-62	3.02	2.87	3.30	0.1	3.16	3.01	3.45	0.1
tCu-g	-170	-88	75	-177	-8	-18	36	-39	30	57	3.72	3.12	4.83	0.0	3.40	2.80	4.51	0.0
tCu-t	-169	-87	76	-177	-6	-19	36	-39	29	177	2.72	2.13	3.93	0.1	2.56	1.96	3.76	0.1
tFd-gm	175	-61	148	175	-11	30	-37	30	-12	-75	1.78	1.72	2.05	1.2	1.60	1.54	1.87	1.5
tFd-g	175	-60	148	175	-11	29	-37	30	-12	56	1.23	1.37	1.97	1.4	1.27	1.42	2.02	1.2
tFu-gm	177	-53	144	177	5	-26	38	-34	19	-63	0.04	0.04	0.15	29.9	0.05	0.04	0.15	28.0
tFu-g	176	-54	144	177	4	-26	38	-34	19	55	1.16	1.20	1.28	4.4	1.11	1.14	1.22	4.6
tFu-t	177	-54	144	177	5	-27	38	-35	19	176	0.00	0.00	0.00	38.3	0.00	0.00	0.00	36.2
ts1	120	-108	-1	180	8	-31	41	-37	18	75	20.02	18.68	19.60		19.26	17.92	18.84	

ts2	116	-108	1	176	6	20	-39	43	-30	-72	22.58	21.84	23.81		22.39	21.65	23.62	
ts3	-64	-89	-6	-178	24	-39	39	-25	0	-64	21.12	19.99	21.05		20.06	18.93	19.99	
ts4	-60	-107	6	179	5	21	-38	41	-29	-74	22.58	21.82	23.09		21.97	21.20	22.47	
cis%														18.4				23.2

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] "gm" stands for the gauche- for χ^{OH}. [i] Vibrational frequencies were calculated with the option Int = Ultrafine.

Table S42 Torsion angles (°) and thermodynamic properties (kcal mol^{-1}) of local minima and transition states of Ac-hyp-NHMe in water

Conf.	Torsion angles										DSD-PBEP86-D3BJ/cc-pVTZ				M06-2X/def2-TZVP			
	ω'	ϕ	ψ	ω	χ^0	χ^1	χ^2	χ^3	χ^4	χ^{OH}	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]	ΔE_e[d]	ΔH[e]	ΔG[f]	w[g]
cAd-gm[h]	2	-84	-8	-177	-19	33	-35	24	-3	-62	4.41	4.41	4.26	0.0	4.16	4.15	4.01	0.0
cAd-g	2	-90	5	-178	-22	35	-36	23	0	63	3.01	2.80	1.87	1.2	2.71	2.51	1.58	1.7
cAd-t	4	-88	3	-178	-20	35	-37	24	-2	-174	3.05	2.75	1.91	1.1	2.79	2.49	1.65	1.5
cAu-gm	-4	-72	-20	-176	-7	-17	33	-37	28	-58	5.06	5.19	4.52	0.0	4.71	4.83	4.17	0.0
cAu-g	-4	-71	-20	-176	-7	-17	34	-37	28	72	5.50	5.46	4.57	0.0	5.22	5.17	4.28	0.0
cAu-t	-4	-72	-20	-176	-8	-16	33	-37	28	171	5.38	5.36	4.59	0.0	5.08	5.06	4.29	0.0
cFd-gm[h,i]	1	-68	144	176	-9	28	-36	30	-13	-54	1.13	1.07	0.68	8.8	1.15	1.09	0.70	7.6
cFd-g	-2	-75	174	177	-17	34	-38	27	-6	62	2.63	2.35	0.95	5.6	2.60	2.32	0.92	5.2
cFd-t	-8	-74	-177	180	-23	37	-38	24	-1	-173	2.94	2.73	1.84	1.2	2.58	2.37	1.48	2.0
cFu-gm	-6	-56	149	176	3	-26	38	-35	20	-57	3.57	3.89	3.05	0.2	3.32	3.64	2.80	0.2
cFu-g	-5	-56	149	176	4	-26	39	-36	20	73	3.93	4.09	3.17	0.1	3.84	4.00	3.08	0.1
cFu-t	-6	-56	149	176	2	-25	38	-37	22	173	3.96	4.11	3.01	0.2	3.79	3.94	2.84	0.2
tAd-gm	-176	-78	-8	-179	-12	30	-36	28	-10	-57	3.88	3.65	2.32	0.5	3.70	3.47	2.14	0.7
tAd-g	-175	-82	3	180	-13	32	-39	30	-10	61	2.40	2.23	1.44	2.4	2.15	1.97	1.18	3.3
tAd-t	-175	-81	3	180	-13	32	-39	30	-11	-176	2.34	2.23	1.86	1.2	2.20	2.10	1.72	1.4
tAu-gm	-176	-67	-22	-178	0	-23	37	-36	23	-56	3.64	3.94	3.26	0.1	3.39	3.69	3.01	0.2
tAu-g	-176	-67	-22	-178	1	-24	38	-37	23	74	4.16	4.21	3.18	0.1	3.94	4.00	2.97	0.2
tAu-t	-176	-67	-22	-178	-1	-23	37	-37	23	172	3.92	3.97	2.88	0.2	3.80	3.85	2.76	0.2
tCd-gm	-173	-84	86	-175	-10	28	-36	29	-12	-29	1.93	1.95	2.03	0.9	2.03	2.05	2.13	0.7
tCu-gm	-172	-83	79	-176	-6	-19	35	-38	27	-55	5.43	5.69	4.82	0.0	5.51	5.77	4.90	0.0
tCu-g	-172	-82	78	-176	-5	-20	36	-38	27	72	6.00	6.17	5.20	0.0	6.14	6.31	5.34	0.0
tCu-t	-172	-83	78	-176	-5	-20	36	-39	28	172	5.60	5.85	5.15	0.0	5.85	6.10	5.40	0.0
tFd-gm	175	-58	143	177	-6	27	-37	32	-17	-52	0.00	0.00	0.00	27.6	0.00	0.00	0.00	24.6
tFd-g	180	-63	158	177	-6	26	-35	31	-16	60	2.15	1.97	0.67	8.9	2.15	1.98	0.67	7.9
tFd-t	180	-63	158	177	-7	26	-35	31	-15	-178	2.18	1.98	0.62	9.7	2.19	2.00	0.63	8.4
tFu-gm	179	-54	145	175	6	-28	39	-34	18	-57	2.40	2.47	0.81	7.0	2.17	2.24	0.58	9.2
tFu-g	180	-55	146	175	7	-28	40	-35	18	73	2.84	2.81	1.16	3.9	2.71	2.68	1.03	4.3
tFu-t	178	-54	145	175	4	-27	39	-36	20	172	2.78	2.63	0.22	19.0	2.68	2.52	0.11	20.3
ts1	117	-116	12	176	-3	27	-40	39	-23	-173	22.25	20.98	21.31		22.55	21.28	21.62	

ts2	121	-109	-1	-180	6	-29	40	-37	19	173	23.75	22.72	23.27		24.12	23.10	23.65	
ts3	-62	-112	16	178	-1	25	-39	39	-23	-175	22.11	20.86	20.89		22.05	20.81	20.84	
ts4	-60	-92	-2	180	21	-38	40	-28	4	173	23.61	22.52	22.00		23.60	22.50	21.98	
cis%														18.4				18.7

[a] Torsion angles are defined in Fig. 1. Optimized at the SMD M06-2X/6-31+G(d) level of theory in water. [b] Single-point energies by the DSD-PBEP86-D3BJ/cc-pVTZ method. [c] Single-point energies by the M06-2X/def2-TZVP method. [d] Relative electronic energies. [e] Relative enthalpies at 25 °C. [f] Relative Gibbs free energies at 25 °C and 1 atm. [g] Population (%) of *cis* conformers calculated using ΔG values. [h] "gm" stands for the gauche- for χ^{OH}. [i] Vibrational frequencies were calculated with the option Int = Ultrafine.