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Supporting Information

Puckering transition of proline residue along the pseudorotational path: revisited

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Table S1 Torsion angles and thermodynamic properties of local minima for Ac-Pro-OH optimized at the M06-2X/6-31+G(d) level of theory in the gas phase[a]

Conf.[b]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	ΔE^c	ΔH^d	ΔG^e
*t*Cd	-171.6	-80.1	63.5	-2.7	31.8	-39.9	32.0	-12.5	-12.2	0.00	0.00	0.00
*t*Cu	-171.2	-77.4	64.4	-4.6	-19.3	35.5	-37.8	27.1	-4.9	1.64	1.79	1.97
*t*Fd	174.3	-64.7	156.7	178.5	32.7	-37.8	28.2	-7.9	-15.7	2.47	2.51	1.81
*t*Ad	175.4	-62.5	-24.0	179.9	31.9	-37.8	28.8	-9.0	-14.5	3.11	3.17	2.52
*t*Fu	176.3	-55.0	146.0	178.9	-23.3	37.1	-36.3	23.0	0.1	3.24	3.22	2.36
*t*Au	177.0	-52.5	-34.8	-179.7	-24.2	37.5	-36.1	22.1	1.3	3.43	3.44	2.90
*c*Fd	-2.2	-73.6	170.4	178.5	34.0	-38.3	27.8	-6.3	-17.6	3.75	3.65	2.59
*c*Ad	-3.8	-72.2	-18.7	-178.0	33.8	-37.6	26.7	-5.4	-18.0	4.02	3.90	2.75
*c*Au	-2.2	-56.7	-35.6	-176.5	-25.7	38.2	-35.7	20.6	3.2	4.46	4.50	3.85
*c*Fu	-1.6	-59.0	165.1	177.0	-25.1	37.6	-35.4	20.6	2.9	4.48	4.46	3.84

[a] Torsion angles (°) are defined in Fig. 1c. [b] See the text for definition. For example, the first conformational letter code *t*Cd denotes that the backbone conformation of the Pro residue is C with the *trans* prolyl peptide bond and the down puckering. [c] Relative electronic energies in kcal mol^{-1}. [d] Relative enthalpies in kcal mol^{-1} at 25 °C. [e] Relative Gibbs free energies in kcal mol^{-1} at 25 °C and 1 atm.

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

Conf.[b]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	ΔE^c	ΔH^d	ΔG^e
*t*Cd	-169.0	-78.8	59.1	-1.8	-10.6	31.1	-40.2	33.1	-14.2	0.00	0.00	0.38
*t*Fd	176.4	-65.7	162.0	177.0	-13.2	31.4	-38.3	30.0	-10.5	0.38	0.43	0.00
*t*Fu	-179.8	-54.8	148.1	176.5	7.6	-29.0	39.6	-34.6	17.0	0.56	0.72	0.56
*t*Au	175.8	-51.2	-36.5	-176.6	0.9	-24.0	37.8	-36.6	22.6	0.78	1.09	1.19
*t*Ad	176.1	-60.7	-27.2	-177.5	-11.1	29.8	-37.5	30.4	-12.1	0.80	1.05	0.87
*c*Fd	-4.2	-74.2	168.2	177.9	-18.3	34.3	-38.1	27.0	-5.4	1.18	1.25	0.71
*t*Cu	-168.3	-72.6	53.8	-1.1	1.9	-25.2	38.7	-37.0	22.1	1.23	1.25	1.82
*c*Ad	-6.6	-72.8	-12.7	-178.4	-21.9	35.7	-37.1	23.9	-1.1	1.77	1.92	1.48
*c*Fu	-2.5	-58.2	163.3	176.3	5.5	-27.1	38.5	-34.8	18.4	1.93	2.08	1.44
*c*Au	-9.1	-53.4	-31.9	-176.6	-0.7	-22.6	37.0	-36.9	23.7	2.45	2.50	0.71

[a] Torsion angles (°) are defined in Fig. 1c. [b] See the text for definition. For example, the first conformational letter code *t*Cd denotes that the backbone conformation of the Pro residue is C with the *trans* prolyl peptide bond and the down puckering. [c] Relative electronic energies in kcal mol^{-1}. [d] Relative enthalpies in kcal mol^{-1} at 25 °C. [e] Relative Gibbs free energies in kcal mol^{-1} at 25 °C and 1 atm.

Table S3 Torsion angles and electronic energies of Ac-*trans*-Pro-OH along the pseudorotation phase angle optimized at the M06-2X/6-31+G(d) level of theory in the gas phase[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	-169.9	-72.8	62.0	-5.8	-31.2	38.6	-31.1	12.2	11.8	-553.6106979	2.68
18	E^{γ}	-170.7	-76.5	63.8	-4.8	-22.7	36.7	-36.4	23.4	-0.5	-553.6122676	1.69
36	${}^{\gamma}\mathrm{T}_{\delta}$	-172.4	-78.6	65.0	-4.2	-11.9	31.2	-38.4	32.7	-13.1	-553.6120941	1.80
54	E_{δ}	-175.7	-78.6	65.0	-3.0	0.0	22.7	-36.6	38.7	-24.4	-553.6108072	2.61
72	${}_{\delta}\mathrm{T}^{N}$	-179.2	-78.0	65.1	-1.8	11.9	11.9	-31.1	40.8	-33.2	-553.6094298	3.47
90	E^{N}	178.6	-78.0	65.9	-1.3	22.7	0.0	-22.6	38.8	-38.9	-553.6087782	3.88
108	${}^{N}\mathrm{T}_{\alpha}$	178.2	-78.3	66.2	-1.0	31.2	-11.9	-11.8	32.9	-40.6	-553.6091800	3.63
126	E_{α}	179.2	-78.4	65.3	-0.8	36.7	-22.7	0.2	24.0	-38.5	-553.6103477	2.90
144	${}_{\alpha}\mathrm{T}^{\beta}$	-178.5	-78.6	63.9	-0.8	38.6	-31.2	11.9	13.1	-32.8	-553.6121195	1.78
162	E^{β}	-175.4	-79.2	63.3	-1.4	36.7	-36.7	22.3	0.9	-23.8	-553.6140020	0.60
180	${}^{\beta}\mathrm{T}_{\gamma}$	-171.7	-80.1	63.8	-2.8	31.2	-38.6	30.6	-11.4	-12.5	-553.6149614	0.00
198	E_{γ}	-167.9	-80.7	64.7	-4.1	22.7	-36.7	36.0	-22.7	0.0	-553.6138537	0.70
216	${}_{\gamma}\mathrm{T}^{\delta}$	-165.6	-79.6	65.9	-5.9	11.9	-31.2	38.2	-32.1	12.6	-553.6103224	2.91
234	E^{δ}	-165.4	-75.5	65.9	-8.4	0.0	-22.7	36.7	-38.2	23.8	-553.6058747	5.70
252	${}^{\delta}\mathrm{T}_{N}$	-165.8	-69.3	61.7	-9.2	-11.9	-11.9	31.3	-40.3	32.3	-553.6022796	7.96
270	E_{N}	-166.5	-63.0	55.4	-8.4	-22.7	0.0	22.8	-38.5	37.9	-553.6004668	9.10
288	${}_{N}\mathrm{T}^{\alpha}$	-167.4	-59.4	51.9	-7.8	-31.2	11.9	12.0	-32.6	39.6	-553.6004023	9.14
306	E^{α}	-168.9	-59.9	54.1	-8.6	-36.7	22.7	-0.1	-23.6	37.5	-553.6015982	8.39
324	${}^{\alpha}\mathrm{T}_{\beta}$	-168.5	-64.2	58.0	-8.8	-38.6	31.2	-12.1	-12.4	31.7	-553.6041400	6.79
342	E_{β}	-168.9	-68.5	59.7	-7.0	-36.7	36.7	-22.7	-0.1	22.9	-553.6076669	4.58
360	${}_{\beta}\mathrm{T}^{\gamma}$	-169.9	-72.8	62.0	-5.8	-31.2	38.6	-31.1	12.2	11.8	-553.6106979	2.68

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S4 Torsion angles and electronic energies of Ac-*cis*-Pro-OH along the pseudorotation phase angle optimized at the M06-2X/6-31+G(d) level of theory in the gas phase[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	4.6	-59.8	159.1	176.3	-31.2	38.6	-31.2	11.9	12.1	-553.6075455	0.84
18	E^{γ}	-3.3	-59.1	166.5	177.1	-22.7	36.7	-36.5	23.4	-0.5	-553.6077915	0.69
36	${}^{\gamma}\mathrm{T}_{\delta}$	-10.7	-61.2	169.9	177.4	-11.9	31.2	-38.4	32.9	-13.3	-553.6070954	1.13
54	E_{δ}	-15.9	-63.4	173.6	178.4	0.0	22.7	-36.6	39.0	-24.6	-553.6060775	1.76
72	${}_{\delta}\mathrm{T}^{N}$	-19.8	-66.2	177.3	179.9	11.9	11.9	-30.9	40.9	-33.3	-553.6050692	2.40
90	E^{N}	-21.5	-67.5	-178.9	-178.9	22.7	0.0	-22.3	38.9	-39.0	-553.6044816	2.77
108	${}^{N}\mathrm{T}_{\alpha}$	-20.8	-69.8	-178.0	-179.0	31.2	-11.9	-11.4	33.0	-40.7	-553.6048945	2.51
126	E_{α}	-18.5	-71.3	179.2	179.9	36.7	-22.7	0.7	24.0	-38.5	-553.6062243	1.67
144	${}_{\alpha}\mathrm{T}^{\beta}$	-13.9	-72.3	175.1	179.1	38.6	-31.2	12.3	13.1	-32.8	-553.6077145	0.74
162	E^{β}	-7.0	-72.8	171.2	178.8	36.7	-36.7	22.7	0.9	-23.8	-553.6087544	0.08
180	${}^{\beta}\mathrm{T}_{\gamma}$	1.4	-73.8	168.9	178.0	31.2	-38.6	30.9	-11.6	-12.5	-553.6088888	0.00
198	E_{γ}	8.5	-69.0	161.6	176.7	22.7	-36.7	36.2	-23.2	0.3	-553.6077625	0.71
216	${}_{\gamma}\mathrm{T}^{\delta}$	16.4	-69.2	157.4	175.9	11.9	-31.2	38.3	-32.7	13.1	-553.6055199	2.11
234	E^{δ}	21.9	-68.2	156.0	175.5	0.0	-22.7	36.6	-38.8	24.3	-553.6028206	3.81
252	${}^{\delta}\mathrm{T}_{N}$	25.2	-65.4	152.6	175.0	-11.9	-11.9	31.1	-40.8	33.0	-553.6007573	5.10
270	E_{N}	26.1	-61.9	147.9	175.0	-22.7	0.0	22.5	-38.8	38.5	-553.5997495	5.74
288	${}_{N}\mathrm{T}^{\alpha}$	25.2	-60.2	146.0	175.1	-31.2	11.9	11.5	-32.8	40.2	-553.6000218	5.56
306	E^{α}	22.0	-59.5	147.7	175.0	-36.7	22.7	-0.7	-23.8	38.0	-553.6013978	4.70
324	${}^{\alpha}\mathrm{T}_{\beta}$	17.5	-59.7	150.5	175.0	-38.6	31.2	-12.4	-12.7	32.3	-553.6035956	3.32
342	E_{β}	11.8	-60.2	154.3	175.6	-36.7	36.7	-22.9	-0.5	23.4	-553.6059293	1.86
360	${}_{\beta}\mathrm{T}^{\gamma}$	4.6	-59.8	159.1	176.3	-31.2	38.6	-31.2	11.9	12.1	-553.6075455	0.84

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S5 Torsion angles and electronic energies of Ac-*trans*-Pro-OH along the pseudorotation phase angle optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	-177.9	-54.9	147.1	176.5	-31.2	38.6	-30.8	11.5	12.5	-553.6357941	0.33
18	E^{γ}	176.1	-55.2	152.6	176.0	-22.7	36.7	-36.1	23.0	-0.2	-553.6357651	0.34
36	${}^{\gamma}\mathrm{T}_{\delta}$	172.2	-58.5	161.9	175.7	-11.9	31.2	-38.3	32.5	-13.0	-553.6348619	0.91
54	E_{δ}	168.9	-60.5	167.1	176.7	0.0	22.7	-36.5	38.5	-24.2	-553.6333486	1.86
72	${}_{\delta}\mathrm{T}^{N}$	165.2	-61.1	169.0	178.2	11.9	11.9	-30.8	40.4	-32.9	-553.6316995	2.89
90	E^{N}	164.9	-63.7	173.2	179.9	22.7	0.0	-22.2	38.4	-38.5	-553.6306818	3.53
108	${}^{N}\mathrm{T}_{\alpha}$	165.6	-66.0	174.6	179.8	31.2	-11.9	-11.3	32.6	-40.2	-553.6308972	3.40
126	E_{α}	166.8	-67.4	172.6	178.6	36.7	-22.7	0.7	23.6	-38.1	-553.6322807	2.53
144	${}_{\alpha}\mathrm{T}^{\beta}$	168.1	-66.6	168.7	178.2	38.6	-31.2	12.4	12.7	-32.4	-553.6341118	1.38
162	E^{β}	172.0	-65.6	163.8	177.5	36.7	-36.7	22.6	0.8	-23.7	-553.6355926	0.45
180	${}^{\beta}\mathrm{T}_{\gamma}$	176.7	-65.7	162.1	176.9	31.2	-38.6	30.7	-11.4	-12.5	-553.6363123	0.00
198	E_{γ}	-178.9	-64.1	157.5	175.8	22.7	-36.7	36.0	-22.9	0.1	-553.6356780	0.40
216	${}_{\gamma}\mathrm{T}^{\delta}$	-172.7	-62.6	151.4	174.8	11.9	-31.2	38.1	-32.4	12.9	-553.6337471	1.61
234	E^{δ}	-168.5	-62.5	148.8	175.2	0.0	-22.7	36.5	-38.5	24.2	-553.6314979	3.02
252	${}^{\delta}\mathrm{T}_{N}$	-166.6	-59.5	143.9	175.9	-11.9	-11.9	30.9	-40.4	32.9	-553.6297641	4.11
270	E_{N}	-167.0	-55.9	140.6	176.2	-22.7	0.0	22.4	-38.6	38.6	-553.6286791	4.79
288	${}_{N}\mathrm{T}^{\alpha}$	-167.5	-53.5	137.4	176.5	-31.2	11.9	11.5	-32.8	40.3	-553.6287795	4.73
306	E^{α}	-168.9	-53.1	138.6	176.4	-36.7	22.7	-0.5	-23.8	38.2	-553.6299159	4.01
324	${}^{\alpha}\mathrm{T}_{\beta}$	-171.0	-53.8	141.0	176.5	-38.6	31.2	-12.2	-12.9	32.5	-553.6319550	2.73
342	E_{β}	-173.3	-55.1	144.4	176.5	-36.7	36.7	-22.7	-0.7	23.7	-553.6343066	1.26
360	${}_{\beta}\mathrm{T}^{\gamma}$	-177.9	-54.9	147.1	176.5	-31.2	38.6	-30.8	11.5	12.5	-553.6357941	0.33

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S6 Torsion angles and electronic energies of Ac-*cis*-Pro-OH along the pseudorotation phase angle optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	1.7	-59.0	160.5	175.5	-31.2	38.6	-31.1	11.8	12.2	-553.6335272	0.79
18	E^{γ}	-8.1	-56.5	166.1	176.8	-22.7	36.7	-36.3	23.1	-0.3	-553.6336854	0.69
36	${}^{\gamma}\mathrm{T}_{\delta}$	-15.6	-56.7	168.1	176.0	-11.9	31.2	-38.4	32.6	-13.0	-553.6330895	1.06
54	E_{δ}	-20.9	-60.5	170.7	177.6	0.0	22.7	-36.6	38.6	-24.3	-553.6319087	1.80
72	${}_{\delta}\mathrm{T}^{N}$	-22.4	-65.3	176.2	-179.9	11.9	11.9	-30.9	40.6	-33.1	-553.6307109	2.55
90	E^{N}	-24.4	-66.4	-178.4	-178.6	22.7	0.0	-22.3	38.6	-38.7	-553.6301918	2.88
108	${}^{N}\mathrm{T}_{\alpha}$	-23.4	-69.0	-178.0	-178.6	31.2	-11.9	-11.5	32.8	-40.5	-553.6305985	2.62
126	E_{α}	-20.9	-69.1	178.5	179.5	36.7	-22.7	0.6	23.8	-38.3	-553.6321134	1.67
144	${}_{\alpha}\mathrm{T}^{\beta}$	-15.3	-71.4	173.5	178.7	38.6	-31.2	12.2	13.0	-32.6	-553.6336955	0.68
162	E^{β}	-9.1	-71.8	168.3	178.5	36.7	-36.7	22.6	1.0	-23.8	-553.6347708	0.01
180	${}^{\beta}\mathrm{T}_{\gamma}$	-0.6	-74.6	168.2	177.2	31.2	-38.6	30.7	-11.3	-12.6	-553.6347792	0.00
198	E_{γ}	7.8	-71.9	160.7	175.5	22.7	-36.7	36.1	-22.8	0.1	-553.6334120	0.86
216	${}_{\gamma}\mathrm{T}^{\delta}$	15.5	-69.7	156.9	174.9	11.9	-31.2	38.2	-32.3	12.8	-553.6310476	2.34
234	E^{δ}	21.9	-71.5	155.8	174.7	0.0	-22.7	36.6	-38.4	24.0	-553.6282039	4.13
252	${}^{\delta}\mathrm{T}_{N}$	24.1	-68.2	155.9	173.9	-11.9	-11.9	31.1	-40.3	32.6	-553.6259756	5.52
270	E_{N}	24.2	-64.8	155.3	173.6	-22.7	0.0	22.4	-38.3	38.1	-553.6248252	6.25
288	${}_{N}\mathrm{T}^{\alpha}$	22.3	-63.1	154.0	174.1	-31.2	11.9	11.4	-32.4	39.8	-553.6250540	6.10
306	E^{α}	18.9	-60.7	152.8	174.4	-36.7	22.7	-0.7	-23.4	37.7	-553.6265566	5.16
324	${}^{\alpha}\mathrm{T}_{\beta}$	14.9	-60.7	154.3	174.7	-38.6	31.2	-12.5	-12.5	32.1	-553.6290264	3.61
342	E_{β}	8.3	-60.0	156.6	175.1	-36.7	36.7	-22.9	-0.5	23.4	-553.6316800	1.94
360	${}_{\beta}\mathrm{T}^{\gamma}$	1.7	-59.0	160.5	175.5	-31.2	38.6	-31.1	11.8	12.2	-553.6335272	0.79

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S7 Torsion angles and electronic energies of Ac-*trans*-Pro-OMe along the pseudorotation phase angle optimized at the M06-2X/6-31+G(d) level of theory in the gas phase[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	-179.6	-52.6	137.4	-178.4	-31.2	38.6	-30.8	11.7	12.3	-592.8940220	0.96
18	E^{γ}	175.8	-53.4	141.8	-179.0	-22.7	36.7	-36.2	23.3	-0.5	-592.8944971	0.66
36	${}^{\gamma}\mathrm{T}_{\delta}$	171.7	-56.0	148.8	179.8	-11.9	31.2	-38.3	32.8	-13.3	-592.8939175	1.02
54	E_{δ}	168.4	-60.3	158.7	178.5	0.0	22.7	-36.6	38.9	-24.6	-592.8928909	1.67
72	${}_{\delta}\mathrm{T}^{N}$	166.8	-63.4	163.9	178.9	11.9	11.9	-30.9	40.8	-33.3	-592.8918366	2.33
90	E^{N}	166.1	-66.3	167.5	179.6	22.7	0.0	-22.3	38.8	-38.9	-592.8910787	2.80
108	${}^{N}\mathrm{T}_{\alpha}$	166.7	-68.6	167.8	179.6	31.2	-11.9	-11.4	32.9	-40.6	-592.8913796	2.61
126	E_{α}	168.4	-69.7	165.5	179.2	36.7	-22.7	0.6	24.0	-38.5	-592.8926675	1.81
144	${}_{\alpha}\mathrm{T}^{\beta}$	169.2	-67.8	161.2	179.2	38.6	-31.2	12.2	13.0	-32.7	-592.8941926	0.85
162	E^{β}	171.6	-65.8	158.1	179.2	36.7	-36.7	22.6	0.8	-23.8	-592.8952807	0.17
180	${}^{\beta}\mathrm{T}_{\gamma}$	175.1	-63.7	153.6	179.0	31.2	-38.6	30.8	-11.6	-12.4	-592.8955457	0.00
198	E_{γ}	178.6	-60.1	146.2	179.9	22.7	-36.7	36.1	-23.1	0.3	-592.8944920	0.66
216	${}_{\gamma}\mathrm{T}^{\delta}$	-176.4	-59.7	141.6	-179.4	11.9	-31.2	38.1	-32.7	13.2	-592.8921851	2.11
234	E^{δ}	-172.7	-58.3	137.6	-178.7	0.0	-22.7	36.5	-39.0	24.6	-592.8897000	3.67
252	${}^{\delta}\mathrm{T}_{N}$	-171.2	-54.9	134.1	-178.0	-11.9	-11.9	31.1	-41.0	33.4	-592.8878502	4.83
270	E_{N}	-170.7	-51.7	130.3	-176.7	-22.7	0.0	22.6	-39.2	39.0	-592.8871167	5.29
288	${}_{N}\mathrm{T}^{\alpha}$	-171.2	-50.5	130.2	-176.8	-31.2	11.9	11.7	-33.3	40.7	-592.8873107	5.17
306	E^{α}	-172.9	-49.8	130.9	-177.2	-36.7	22.7	-0.3	-24.3	38.6	-592.8884034	4.48
324	${}^{\alpha}\mathrm{T}_{\beta}$	-174.6	-50.2	132.4	-177.6	-38.6	31.2	-12.0	-13.2	32.8	-592.8902271	3.34
342	E_{β}	-176.2	-52.1	134.9	-178.1	-36.7	36.7	-22.5	-0.8	23.7	-592.8923665	1.99
360	${}_{\beta}\mathrm{T}^{\gamma}$	-179.6	-52.6	137.4	-178.4	-31.2	38.6	-30.8	11.7	12.3	-592.8940220	0.96

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S8 Torsion angles and electronic energies of Ac-*cis*-Pro-OMe along the pseudorotation phase angle optimized at the M06-2X/6-31+G(d) level of theory in the gas phase[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	3.9	-58.2	152.3	176.5	-31.2	38.6	-31.0	11.9	12.2	-592.8920809	0.77
18	E^{γ}	-3.2	-58.5	157.9	176.6	-22.7	36.7	-36.4	23.4	-0.4	-592.8922473	0.66
36	${}^{\gamma}\mathrm{T}_{\delta}$	-11.2	-60.1	168.5	177.1	-11.9	31.2	-38.4	32.9	-13.3	-592.8915072	1.13
54	E_{δ}	-16.0	-64.0	172.8	178.2	0.0	22.7	-36.6	39.0	-24.6	-592.8903855	1.83
72	${}_{\delta}\mathrm{T}^{N}$	-20.0	-65.5	177.8	179.5	11.9	11.9	-31.0	40.9	-33.3	-592.8893587	2.48
90	E^{N}	-21.3	-68.0	-177.7	-179.5	22.7	0.0	-22.3	39.0	-39.0	-592.8888643	2.79
108	${}^{N}\mathrm{T}_{\alpha}$	-20.9	-69.6	-177.0	-179.2	31.2	-11.9	-11.4	33.0	-40.7	-592.8892904	2.52
126	E_{α}	-18.2	-71.3	177.7	179.7	36.7	-22.7	0.6	24.0	-38.6	-592.8906455	1.67
144	${}_{\alpha}\mathrm{T}^{\beta}$	-14.1	-71.6	174.2	179.2	38.6	-31.2	12.3	13.1	-32.8	-592.8921711	0.71
162	E^{β}	-7.4	-72.7	168.7	178.3	36.7	-36.7	22.6	0.9	-23.9	-592.8931719	0.08
180	${}^{\beta}\mathrm{T}_{\gamma}$	-0.2	-69.0	160.8	177.3	31.2	-38.6	30.9	-11.6	-12.4	-592.8933038	0.00
198	E_{γ}	8.2	-69.5	156.4	176.3	22.7	-36.7	36.2	-23.1	0.3	-592.8922475	0.66
216	${}_{\gamma}\mathrm{T}^{\delta}$	16.1	-68.5	151.7	176.2	11.9	-31.2	38.3	-32.7	13.1	-592.8900126	2.07
234	E^{δ}	21.6	-66.7	148.0	176.3	0.0	-22.7	36.6	-38.9	24.4	-592.8873519	3.73
252	${}^{\delta}\mathrm{T}_{N}$	24.4	-63.3	143.1	176.8	-11.9	-11.9	31.1	-40.9	33.1	-592.8854094	4.95
270	E_{N}	25.9	-59.3	135.1	178.1	-22.7	0.0	22.6	-38.9	38.7	-592.8845449	5.50
288	${}_{N}\mathrm{T}^{\alpha}$	25.0	-57.7	135.5	177.8	-31.2	11.9	11.6	-33.0	40.3	-592.8848724	5.29
306	E^{α}	21.7	-57.1	137.0	177.6	-36.7	22.7	-0.5	-23.9	38.1	-592.8862324	4.44
324	${}^{\alpha}\mathrm{T}_{\beta}$	17.0	-57.4	139.5	177.3	-38.6	31.2	-12.3	-12.9	32.4	-592.8883334	3.12
342	E_{β}	11.2	-58.6	148.8	176.4	-36.7	36.7	-22.8	-0.6	23.5	-592.8905424	1.73
360	${}_{\beta}\mathrm{T}^{\gamma}$	3.9	-58.2	152.3	176.5	-31.2	38.6	-31.0	11.9	12.2	-592.8920809	0.77

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S9 Torsion angles and electronic energies of Ac-*trans*-Pro-OMe along the pseudorotation phase angle optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	-178.4	-53.3	143.4	176.7	-31.2	38.6	-30.7	11.5	12.5	-592.9153091	0.25
18	E^{γ}	177.8	-54.8	147.1	176.6	-22.7	36.7	-36.1	22.9	-0.1	-592.9150953	0.38
36	${}^{\gamma}\mathrm{T}_{\delta}$	172.3	-58.3	160.6	176.3	-11.9	31.2	-38.2	32.5	-13.0	-592.9142667	0.90
54	E_{δ}	169.0	-60.5	165.6	176.8	0.0	22.7	-36.4	38.5	-24.2	-592.9127248	1.87
72	${}_{\delta}\mathrm{T}^{N}$	167.4	-63.1	170.6	-179.9	11.9	11.9	-30.8	40.5	-33.0	-592.9110555	2.92
90	E^{N}	163.8	-64.6	176.4	-179.3	22.7	0.0	-22.2	38.5	-38.5	-592.9100493	3.55
108	${}^{N}\mathrm{T}_{\alpha}$	164.2	-66.3	177.7	-178.6	31.2	-11.9	-11.3	32.6	-40.3	-592.9100756	3.53
126	E_{α}	166.4	-66.9	171.0	178.2	36.7	-22.7	0.7	23.6	-38.1	-592.9114724	2.65
144	${}_{\alpha}\mathrm{T}^{\beta}$	168.7	-66.2	168.3	177.6	38.6	-31.2	12.3	12.8	-32.4	-592.9134484	1.41
162	E^{β}	171.7	-64.6	162.1	177.5	36.7	-36.7	22.6	0.8	-23.6	-592.9151117	0.37
180	${}^{\beta}\mathrm{T}_{\gamma}$	175.9	-63.1	158.2	176.4	31.2	-38.6	30.7	-11.5	-12.4	-592.9157025	0.00
198	E_{γ}	179.4	-59.3	149.5	176.5	22.7	-36.7	36.0	-22.9	0.2	-592.9150662	0.40
216	${}_{\gamma}\mathrm{T}^{\delta}$	-174.2	-61.4	149.2	174.5	11.9	-31.2	38.0	-32.3	12.9	-592.9132621	1.53
234	E^{δ}	-170.6	-59.6	146.8	174.9	0.0	-22.7	36.4	-38.5	24.2	-592.9110640	2.91
252	${}^{\delta}\mathrm{T}_{N}$	-168.0	-58.1	143.0	176.5	-11.9	-11.9	30.9	-40.5	32.9	-592.9091902	4.09
270	E_{N}	-166.8	-55.7	139.7	177.2	-22.7	0.0	22.4	-38.5	38.6	-592.9082321	4.69
288	${}_{N}\mathrm{T}^{\alpha}$	-166.2	-54.2	136.8	177.8	-31.2	11.9	11.5	-32.7	40.3	-592.9084549	4.55
306	E^{α}	-167.9	-53.3	136.8	177.8	-36.7	22.7	-0.5	-23.8	38.2	-592.9096059	3.83
324	${}^{\alpha}\mathrm{T}_{\beta}$	-170.4	-53.4	138.9	177.1	-38.6	31.2	-12.2	-12.9	32.5	-592.9116219	2.56
342	E_{β}	-174.2	-52.7	140.4	177.1	-36.7	36.7	-22.6	-0.9	23.8	-592.9138166	1.18
360	${}_{\beta}\mathrm{T}^{\gamma}$	-178.4	-53.3	143.4	176.7	-31.2	38.6	-30.7	11.5	12.5	-592.9153091	0.25

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S10 Torsion angles and electronic energies of Ac-*cis*-Pro-OMe along the pseudorotation phase angle optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	0.2	-57.4	150.2	176.2	-31.2	38.6	-30.9	11.7	12.3	-592.9129655	0.82
18	E^{γ}	-8.1	-56.8	162.5	175.7	-22.7	36.7	-36.3	23.1	-0.3	-592.9131962	0.68
36	${}^{\gamma}\mathrm{T}_{\delta}$	-15.6	-55.6	165.4	175.3	-11.9	31.2	-38.4	32.5	-13.0	-592.9125586	1.08
54	E_{δ}	-20.3	-61.0	170.6	176.2	0.0	22.7	-36.6	38.6	-24.3	-592.9112604	1.89
72	${}_{\delta}\mathrm{T}^{N}$	-23.2	-63.5	175.8	-179.7	11.9	11.9	-30.9	40.6	-33.0	-592.9101438	2.59
90	E^{N}	-24.9	-66.0	-177.1	-179.1	22.7	0.0	-22.4	38.6	-38.7	-592.9094237	3.04
108	${}^{N}\mathrm{T}_{\alpha}$	-23.9	-68.1	-175.6	-178.2	31.2	-11.9	-11.5	32.8	-40.5	-592.9099341	2.72
126	E_{α}	-20.6	-70.2	177.4	179.3	36.7	-22.7	0.5	23.9	-38.3	-592.9113770	1.82
144	${}_{\alpha}\mathrm{T}^{\beta}$	-15.0	-71.8	173.7	177.9	38.6	-31.2	12.2	13.0	-32.7	-592.9133203	0.60
162	E^{β}	-8.6	-73.8	170.0	177.2	36.7	-36.7	22.5	1.0	-23.8	-592.9142724	0.00
180	${}^{\beta}\mathrm{T}_{\gamma}$	-1.1	-72.7	164.0	176.1	31.2	-38.6	30.7	-11.4	-12.5	-592.9142094	0.04
198	E_{γ}	7.7	-69.7	156.7	175.2	22.7	-36.7	36.1	-22.9	0.1	-592.9129176	0.85
216	${}_{\gamma}\mathrm{T}^{\delta}$	13.6	-69.2	154.2	175.0	11.9	-31.2	38.2	-32.3	12.8	-592.9105793	2.32
234	E^{δ}	20.3	-70.0	151.9	175.2	0.0	-22.7	36.6	-38.4	24.0	-592.9077325	4.10
252	${}^{\delta}\mathrm{T}_{N}$	23.1	-66.2	147.3	176.2	-11.9	-11.9	31.1	-40.4	32.6	-592.9054936	5.51
270	E_{N}	24.0	-64.4	146.9	176.0	-22.7	0.0	22.5	-38.3	38.1	-592.9044028	6.19
288	${}_{N}\mathrm{T}^{\alpha}$	22.9	-61.0	143.9	176.6	-31.2	11.9	11.5	-32.5	39.9	-592.9047248	5.99
306	E^{α}	20.4	-59.6	144.1	176.4	-36.7	22.7	-0.6	-23.6	37.8	-592.9062029	5.06
324	${}^{\alpha}\mathrm{T}_{\beta}$	14.7	-59.5	146.3	175.9	-38.6	31.2	-12.3	-12.7	32.2	-592.9085607	3.58
342	E_{β}	7.4	-58.8	147.9	176.1	-36.7	36.7	-22.8	-0.6	23.5	-592.9111014	1.99
360	${}_{\beta}\mathrm{T}^{\gamma}$	0.2	-57.4	150.2	176.2	-31.2	38.6	-30.9	11.7	12.3	-592.9129655	0.82

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S11 Torsion angles and electronic energies of Ac-*trans*-Pro-NHMe along the pseudorotation phase angle optimized at the M06-2X/6-31+G(d) level of theory in the gas phase[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	-173.2	-76.2	85.9	-18.7	-31.2	38.6	-31.1	12.3	11.7	-573.0362798	3.24
18	E^{γ}	-173.2	-80.7	80.5	-13.3	-22.7	36.7	-36.5	23.6	-0.6	-573.0382484	2.00
36	${}^{\gamma}\mathrm{T}_{\delta}$	-174.6	-82.9	78.4	-10.8	-11.9	31.2	-38.5	32.8	-13.2	-573.0386145	1.77
54	E_{δ}	-178.0	-82.5	76.9	-9.1	0.0	22.7	-36.7	38.8	-24.5	-573.0377993	2.28
72	${}_{\delta}\mathrm{T}^{N}$	178.5	-81.8	76.5	-7.9	11.9	11.9	-31.1	40.8	-33.3	-573.0368375	2.89
90	E^{N}	176.4	-81.6	76.1	-6.9	22.7	0.0	-22.6	38.9	-39.0	-573.0364287	3.14
108	${}^{N}\mathrm{T}_{\alpha}$	176.3	-82.1	74.1	-4.9	31.2	-11.9	-11.8	33.1	-40.8	-573.0369604	2.81
126	E_{α}	177.8	-82.6	73.4	-4.8	36.7	-22.7	0.2	24.2	-38.6	-573.0379898	2.16
144	${}_{\alpha}\mathrm{T}^{\beta}$	-179.3	-83.2	71.5	-4.6	38.6	-31.2	11.8	13.2	-32.8	-573.0393114	1.33
162	E^{β}	-176.2	-83.9	70.5	-4.8	36.7	-36.7	22.3	1.0	-23.9	-573.0408263	0.38
180	${}^{\beta}\mathrm{T}_{\gamma}$	-173.2	-84.7	71.7	-6.3	31.2	-38.6	30.6	-11.4	-12.5	-573.0414363	0.00
198	E_{γ}	-169.9	-84.9	74.2	-8.4	22.7	-36.7	36.0	-22.7	0.0	-573.0398938	0.97
216	${}_{\gamma}\mathrm{T}^{\delta}$	-168.8	-82.5	81.9	-14.2	11.9	-31.2	38.2	-32.1	12.6	-573.0362117	3.28
234	E^{δ}	-169.4	-76.8	91.4	-21.3	0.0	-22.7	36.6	-38.3	23.9	-573.0317591	6.07
252	${}^{\delta}\mathrm{T}_{N}$	-170.1	-64.0	112.5	-29.4	-11.9	-11.9	31.1	-40.7	33.0	-573.0286630	8.02
270	E_{N}	-170.9	-57.2	117.8	-28.8	-22.7	0.0	22.6	-39.0	38.8	-573.0274411	8.78
288	${}_{N}\mathrm{T}^{\alpha}$	-171.6	-55.0	119.1	-28.4	-31.2	11.9	11.8	-33.1	40.5	-573.0274550	8.77
306	E^{α}	-172.9	-54.6	119.9	-28.4	-36.7	22.7	-0.3	-24.1	38.3	-573.0285347	8.10
324	${}^{\alpha}\mathrm{T}_{\beta}$	-174.2	-56.1	119.0	-28.9	-38.6	31.2	-12.0	-13.0	32.5	-573.0305822	6.81
342	E_{β}	-172.5	-69.3	99.4	-27.3	-36.7	36.7	-22.7	-0.3	23.1	-573.0332008	5.17
360	${}_{\beta}\mathrm{T}^{\gamma}$	-173.2	-76.2	85.9	-18.7	-31.2	38.6	-31.1	12.3	11.7	-573.0362798	3.24

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S12 Torsion angles and electronic energies of Ac-*cis*-Pro-NHMe along the pseudorotation phase angle optimized at the M06-2X/6-31+G(d) level of theory in the gas phase[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	10.3	-69.3	-27.9	7.4	-31.2	38.6	-30.9	11.7	12.2	-573.0349028	1.25
18	E^{γ}	5.3	-75.7	-19.6	6.9	-22.7	36.7	-36.3	23.3	-0.4	-573.0350690	1.15
36	${}^{\gamma}\mathrm{T}_{\delta}$	-0.3	-79.4	-11.0	3.6	-11.9	31.2	-38.3	32.7	-13.2	-573.0339928	1.82
54	E_{δ}	-4.5	-83.4	0.0	-1.6	0.0	22.7	-36.6	38.9	-24.5	-573.0325036	2.76
72	${}_{\delta}\mathrm{T}^{N}$	-8.1	-86.4	10.0	-6.6	11.9	11.9	-31.0	40.9	-33.4	-573.0312667	3.53
90	E^{N}	-15.0	-83.5	14.3	-8.8	22.7	0.0	-22.4	39.0	-39.1	-573.0306181	3.94
108	${}^{N}\mathrm{T}_{\alpha}$	-16.1	-84.3	15.6	-8.6	31.2	-11.9	-11.6	33.1	-40.9	-573.0310917	3.64
126	E_{α}	-14.4	-83.8	10.0	-4.0	36.7	-22.7	0.4	24.1	-38.7	-573.0326858	2.64
144	${}_{\alpha}\mathrm{T}^{\beta}$	-6.8	-87.2	5.4	-1.9	38.6	-31.2	12.1	13.2	-32.9	-573.0347487	1.35
162	E^{β}	0.3	-87.5	-0.2	0.3	36.7	-36.7	22.5	1.0	-23.9	-573.0364367	0.29
180	${}^{\beta}\mathrm{T}_{\gamma}$	9.3	-88.8	-5.6	1.3	31.2	-38.6	30.8	-11.5	-12.5	-573.0368966	0.00
198	E_{γ}	14.7	-84.4	-16.0	6.8	22.7	-36.7	36.1	-22.9	0.1	-573.0359375	0.60
216	${}_{\gamma}\mathrm{T}^{\delta}$	19.5	-78.7	-26.5	10.5	11.9	-31.2	38.2	-32.4	12.9	-573.0337383	1.98
234	E^{δ}	25.0	-72.9	-34.1	12.5	0.0	-22.7	36.6	-38.7	24.2	-573.0312908	3.52
252	${}^{\delta}\mathrm{T}_{N}$	26.4	-70.7	-33.5	4.8	-11.9	-11.9	31.1	-40.6	32.8	-573.0286240	5.19
270	E_{N}	26.9	-66.8	-38.0	11.1	-22.7	0.0	22.6	-38.7	38.4	-573.0274560	5.92
288	${}_{N}\mathrm{T}^{\alpha}$	25.6	-65.1	-37.8	10.3	-31.2	11.9	11.6	-32.7	40.0	-573.0273836	5.97
306	E^{α}	23.0	-64.9	-37.1	10.3	-36.7	22.7	-0.5	-23.7	37.8	-573.0287176	5.13
324	${}^{\alpha}\mathrm{T}_{\beta}$	19.6	-65.4	-35.3	10.2	-38.6	31.2	-12.2	-12.7	32.2	-573.0310005	3.70
342	E_{β}	14.9	-66.3	-32.8	9.9	-36.7	36.7	-22.7	-0.6	23.5	-573.0333960	2.20
360	${}_{\beta}\mathrm{T}^{\gamma}$	10.3	-69.3	-27.9	7.4	-31.2	38.6	-30.9	11.7	12.2	-573.0349028	1.25

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S13 Torsion angles and electronic energies of Ac-*trans*-Pro-NHMe along the pseudorotation phase angle optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	-178.8	-53.7	142.9	-5.8	-31.2	38.6	-30.7	11.5	12.4	-573.0639490	0.00
18	E^{γ}	177.2	-55.5	144.5	-5.0	-22.7	36.7	-36.0	23.0	-0.2	-573.0639139	0.02
36	${}^{\gamma}\mathrm{T}_{\delta}$	169.9	-54.2	146.8	-4.9	-11.9	31.2	-38.1	32.4	-12.9	-573.0628628	0.68
54	E_{δ}	167.3	-57.2	151.8	-4.4	0.0	22.7	-36.4	38.5	-24.2	-573.0608506	1.94
72	${}_{\delta}\mathrm{T}^{N}$	165.8	-60.6	162.0	-1.1	11.9	11.9	-30.8	40.5	-32.9	-573.0586963	3.30
90	E^{N}	164.4	-64.3	170.3	2.0	22.7	0.0	-22.3	38.6	-38.6	-573.0573853	4.12
108	${}^{N}\mathrm{T}_{\alpha}$	164.8	-66.7	172.5	1.6	31.2	-11.9	-11.4	32.8	-40.4	-573.0576251	3.97
126	E_{α}	165.6	-66.6	169.8	1.0	36.7	-22.7	0.5	23.8	-38.2	-573.0592460	2.95
144	${}_{\alpha}\mathrm{T}^{\beta}$	168.0	-64.7	158.8	-1.5	38.6	-31.2	12.1	12.9	-32.5	-573.0615067	1.53
162	E^{β}	171.4	-63.9	155.5	-1.6	36.7	-36.7	22.4	0.9	-23.7	-573.0632355	0.45
180	${}^{\beta}\mathrm{T}_{\gamma}$	175.5	-61.7	149.2	-4.6	31.2	-38.6	30.6	-11.4	-12.4	-573.0638671	0.05
198	E_{γ}	179.4	-59.5	145.6	-6.4	22.7	-36.7	36.0	-22.9	0.2	-573.0634447	0.32
216	${}_{\gamma}\mathrm{T}^{\delta}$	-174.8	-60.1	144.8	-6.9	11.9	-31.2	38.0	-32.4	12.9	-573.0615962	1.48
234	E^{δ}	-171.1	-58.8	144.7	-5.7	0.0	-22.7	36.4	-38.6	24.2	-573.0594362	2.83
252	${}^{\delta}\mathrm{T}_{N}$	-168.2	-57.8	143.3	-6.4	-11.9	-11.9	31.0	-40.6	32.9	-573.0577047	3.92
270	E_{N}	-168.1	-55.1	141.9	-6.6	-22.7	0.0	22.4	-38.7	38.6	-573.0567692	4.51
288	${}_{N}\mathrm{T}^{\alpha}$	-168.0	-53.8	140.7	-6.8	-31.2	11.9	11.6	-32.8	40.3	-573.0569059	4.42
306	E^{α}	-168.9	-53.3	140.2	-6.8	-36.7	22.7	-0.4	-23.9	38.1	-573.0580036	3.73
324	${}^{\alpha}\mathrm{T}_{\beta}$	-171.1	-53.4	141.3	-6.9	-38.6	31.2	-12.1	-12.9	32.4	-573.0600688	2.43
342	E_{β}	-174.6	-52.8	141.6	-6.5	-36.7	36.7	-22.5	-0.9	23.7	-573.0623621	1.00
360	${}_{\beta}\mathrm{T}^{\gamma}$	-178.8	-53.7	142.9	-5.8	-31.2	38.6	-30.7	11.5	12.4	-573.0639490	0.00

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S14 Torsion angles and electronic energies of Ac-*cis*-Pro-NHMe along the pseudorotation phase angle optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

P (°)[b]	Letter code[c]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	E[d]	ΔE[e]
0	${}_{\beta}\mathrm{T}^{\gamma}$	2.2	-57.8	-32.8	6.4	-31.2	38.6	-30.8	11.6	12.3	-573.0598503	1.87
18	E^{γ}	-5.7	-57.4	-32.3	4.8	-22.7	36.7	-36.1	23.0	-0.2	-573.0605220	1.45
36	${}^{\gamma}\mathrm{T}_{\delta}$	-5.9	-73.5	-18.3	4.9	-11.9	31.2	-38.2	32.5	-13.0	-573.0603833	1.53
54	E_{δ}	-10.2	-76.0	-10.9	3.1	0.0	22.7	-36.4	38.6	-24.3	-573.0588159	2.52
72	${}_{\delta}\mathrm{T}^{N}$	-10.9	-81.3	-1.6	0.1	11.9	11.9	-30.8	40.7	-33.2	-573.0571562	3.56
90	E^{N}	-12.3	-83.6	7.1	-3.1	22.7	0.0	-22.4	38.9	-38.9	-573.0561252	4.20
108	${}^{N}\mathrm{T}_{\alpha}$	-13.0	-84.3	6.1	-0.9	31.2	-11.9	-11.6	33.1	-40.7	-573.0568472	3.75
126	E_{α}	-11.2	-85.1	2.4	1.8	36.7	-22.7	0.4	24.2	-38.5	-573.0590832	2.35
144	${}_{\alpha}\mathrm{T}^{\beta}$	-7.4	-84.5	0.4	0.9	38.6	-31.2	12.0	13.3	-32.8	-573.0615618	0.79
162	E^{β}	-0.7	-86.7	-4.0	1.3	36.7	-36.7	22.3	1.2	-23.9	-573.0628262	0.00
180	${}^{\beta}\mathrm{T}_{\gamma}$	3.3	-80.8	-14.6	3.1	31.2	-38.6	30.5	-11.2	-12.6	-573.0626322	0.12
198	E_{γ}	9.6	-78.2	-22.1	4.7	22.7	-36.7	35.8	-22.7	0.0	-573.0612270	1.00
216	${}_{\gamma}\mathrm{T}^{\delta}$	15.7	-71.2	-31.4	8.2	11.9	-31.2	38.1	-32.3	12.8	-573.0584760	2.73
234	E^{δ}	20.1	-70.1	-33.3	8.6	0.0	-22.7	36.5	-38.3	24.0	-573.0554532	4.63
252	${}^{\delta}\mathrm{T}_{N}$	23.5	-66.9	-30.3	11.8	-11.9	-11.9	31.1	-40.3	32.6	-573.0526409	6.39
270	E_{N}	24.2	-63.9	-37.0	8.4	-22.7	0.0	22.6	-38.4	38.1	-573.0512442	7.27
288	${}_{N}\mathrm{T}^{\alpha}$	23.5	-62.8	-34.3	9.9	-31.2	11.9	11.6	-32.4	39.7	-573.0513047	7.23
306	E^{α}	20.0	-61.1	-34.9	9.6	-36.7	22.7	-0.5	-23.5	37.6	-573.0528362	6.27
324	${}^{\alpha}\mathrm{T}_{\beta}$	14.5	-59.2	-34.9	9.4	-38.6	31.2	-12.2	-12.7	32.2	-573.0552399	4.76
342	E_{β}	10.3	-60.5	-30.9	8.7	-36.7	36.7	-22.7	-0.6	23.4	-573.0580599	2.99
360	${}_{\beta}\mathrm{T}^{\gamma}$	2.2	-57.8	-32.8	6.4	-31.2	38.6	-30.8	11.6	12.3	-573.0598503	1.87

[a] Torsion angles (°) are defined in Fig. 1c. Each structure was optimized with torsion angles χ_1 and χ_2 fixed at the initial values in Table 1. [b] Phase angle of the pseudorotation. [c] Letter code for each puckered Pro ring. "T" and "E" stand for twist and envelop forms, respectively. Depending on the position of atoms against the mean, the superscript and subscript were assigned. For example, "${}_{\beta}\mathrm{T}^{\gamma}$" represents the "T" structure with C^{β} and C^{γ} atoms below and above the mean plane, respectively. [d] Electronic energies in hartrees. [e] Relative electronic energies in kcal mol^{-1}.

Table S15 Absolute electronic energies, enthalpies, and Gibbs free energies of local minima and transition states for puckering transitions of Ac-Pro-OH, Ac-Pro-OMe, and Ac-Pro-NHMe at M06-2X/6-31+G(d) level of theory in the gas phase and SMD M06-2X/6-31+G(d) level of theory in water[a]

		Conf.	Gas phase			Water		
			E_e	H	G	E_e	H	G
Ac-Pro-OH	*trans*	*t*Cu	-553.6123763	-553.425482	-553.473668	-553.636031	-553.449898	-553.498819
		t-ts1	-553.6097807	-553.423534	-553.470639	-553.6319574	-553.446771	-553.495060
		*t*Cd	-553.6149917	-553.428328	-553.476807	-553.636318	-553.450394	-553.499732
		t-ts2	-553.6004668	-553.414793	-553.462399	-553.6300675	-553.444824	-553.495236
	cis	*c*Fu	-553.6078574	-553.421258	-553.470858	-553.6338243	-553.447544	-553.496884
		c-ts1	-553.6050557	-553.419355	-553.467855	-553.6309157	-553.446070	-553.494519
		*c*Fd	-553.6090174	-553.422505	-553.472676	-553.6350335	-553.449082	-553.498439
		c-ts2	-553.5997495	-553.414057	-553.462486	-553.6248252	-553.439713	-553.487381
Ac-Pro-OMe	*trans*	*t*Fu	-592.8945002	-592.679248	-592.733466	-592.9154308	-592.700661	-592.753525
		t-ts1	-592.8919236	-592.677289	-592.729298	-592.9113468	-592.697289	-592.749322
		*t*Fd	-592.8956178	-592.680241	-592.733537	-592.9157064	-592.700876	-592.754480
		t-ts2	-592.8871167	-592.672662	-592.724322	-592.9095434	-592.695105	-592.746609
	cis	*c*Fu	-592.8923434	-592.676979	-592.730512	-592.9132199	-592.698065	-592.750580
		c-ts1	-592.8893705	-592.675271	-592.730587	-592.9103914	-592.696549	-592.748453
		*c*Fd	-592.8933314	-592.678231	-592.733191	-592.9143729	-592.699586	-592.753316
		c-ts2	-592.8845449	-592.670155	-592.722469	-592.9044028	-592.690625	-592.742567
Ac-Pro-NHMe	*trans*	*t*Cu	-573.0386639	-572.810990	-572.864711	-573.0641152	-572.837178	-572.890844
		t-ts1	-573.0370793	-572.810205	-572.862283	-573.0595836	-572.833376	-572.886032
		*t*Cd	-573.0414786	-572.814025	-572.867273	-573.0639108	-572.836787	-572.890516
		t-ts2	-573.0274411	-572.801072	-572.853565	-573.0580929	-572.831447	-572.883385
	cis	*c*Au	-573.0351368	-572.807944	-572.862081	-573.0607181	-572.833680	-572.886562
		c-ts1	-573.0317047	-572.805245	-572.858695	-573.0581416	-572.831717	-572.884510
		*c*Ad	-573.0369309	-572.809757	-572.864140	-573.062979	-572.836249	-572.890579
		c-ts2	-573.027456	-572.801366	-572.854225	-573.0512442	-572.825521	-572.878458

[a] Optimized torsion angles are listed in Tables 2 and 4. Absolute electronic energies, enthalpies, and Gibbs free energies are in hartrees.

Table S16 Absolute single-point energies of local minima and transition states for puckering transitions of Ac-Pro-OH, Ac-Pro-OMe, and Ac-Pro-NHMe at CCSD(T) and MP2 levels of theory in the gas phase[a]

		Conf.	CCSD(T)	MP2				
			CBS-limit	aDZ	aDZ	aTZ	aQZ	CBS-limit
Ac-Pro-OH	*trans*	*t*Cu	-553.269239	-552.523240	-552.385853	-552.864522	-553.019072	-553.131852
		t-ts1	-553.266410	-552.520499	-552.382846	-552.861299	-553.015924	-553.128757
		*t*Cd	-553.271407	-552.525677	-552.388488	-552.867030	-553.021498	-553.134218
		t-ts2	-553.258086	-552.512312	-552.374102	-552.852620	-553.007127	-553.119875
	cis	*c*Fu	-553.263236	-552.518179	-552.381414	-552.859470	-553.013830	-553.126472
		c-ts1	-553.260841	-552.515885	-552.378566	-552.856412	-553.010835	-553.123522
		*c*Fd	-553.264511	-552.519453	-552.382721	-552.860782	-553.015140	-553.127779
		c-ts2	-553.255890	-552.511280	-552.373877	-552.851437	-553.005825	-553.118487
Ac-Pro-OMe	*trans*	*t*Fu	-592.513356	-591.710596	-591.553641	-592.070565	-592.235814	-592.356401
		t-ts1	-592.510792	-591.708307	-591.550728	-592.067275	-592.232583	-592.353214
		*t*Fd	-592.514154	-591.711541	-591.554601	-592.071482	-592.236671	-592.357214
		t-ts2	-592.506509	-591.704006	-591.546537	-592.063078	-592.228400	-592.349040
	cis	*c*Fu	-592.510987	-591.708397	-591.551726	-592.068573	-592.233769	-592.354317
		c-ts1	-592.508396	-591.705836	-591.548511	-592.065163	-592.230454	-592.351072
		*c*Fd	-592.512133	-591.709505	-591.552808	-592.069678	-592.234882	-592.355436
		c-ts2	-592.503722	-591.701620	-591.544304	-592.060725	-592.225884	-592.346406
Ac-Pro-NHMe	*trans*	*t*Cu	-572.656616	-571.876922	-571.715212	-572.217589	-572.377913	-572.494906
		t-ts1	-572.654842	-571.875378	-571.713503	-572.215646	-572.375972	-572.492967
		*t*Cd	-572.658947	-571.879494	-571.717933	-572.220204	-572.380450	-572.497386
		t-ts2	-572.645680	-571.867081	-571.704516	-572.206063	-572.366233	-572.483114
	cis	*c*Au	-572.652108	-571.873390	-571.712393	-572.214348	-572.374352	-572.491111
		c-ts1	-572.648927	-571.869865	-571.708431	-572.210352	-572.370574	-572.487492
		*c*Ad	-572.653722	-571.875012	-571.714124	-572.216053	-572.376067	-572.492834
		c-ts2	-572.644742	-571.866495	-571.704675	-572.206229	-572.366192	-572.482921

[a] Optimized torsion angles are listed in Table 2. Absolute single-point energies are in hartrees.

Table S17 Absolute single-point energies of local minima and transition states for puckering transitions of Ac-Pro-OH, Ac-Pro-OMe, and Ac-Pro-NHMe at DSD-PBEP86-D3BJ and M06-2X levels of theory in the gas phase[a]

		Conf.	DSD-PBEP86-D3BJ			M06-2X		
			TZ	dTZ	dQZ	TZ	dTZ	dQZ
Ac-Pro-OH	*trans*	*t*Cu	-553.076067	-553.073735	-553.193264	-553.815523	-553.822979	-553.870863
		t-ts1	-553.072907	-553.070678	-553.190235	-553.812687	-553.820278	-553.868151
		*t*Cd	-553.078360	-553.076029	-553.195478	-553.818225	-553.825581	-553.873429
		t-ts2	-553.064594	-553.062047	-553.181742	-553.803917	-553.811218	-553.859233
	cis	*c*Fu	-553.070142	-553.068280	-553.187545	-553.810302	-553.817932	-553.865578
		c-ts1	-553.067369	-553.065456	-553.184757	-553.807616	-553.815186	-553.862863
		*c*Fd	-553.071452	-553.069572	-553.188774	-553.811673	-553.819220	-553.866880
		c-ts2	-553.062167	-553.060252	-553.179594	-553.802200	-553.809780	-553.857518
Ac-Pro-OMe	*trans*	*t*Fu	-592.306064	-592.302253	-592.431192	-593.106341	-593.114261	-593.165388
		t-ts1	-592.303111	-592.299237	-592.428233	-593.103710	-593.111598	-593.162734
		*t*Fd	-592.307024	-592.303145	-592.432014	-593.107554	-593.115397	-593.166476
		t-ts2	-592.298811	-592.294904	-592.423942	-593.098900	-593.106802	-593.157988
	cis	*c*Fu	-592.303974	-592.300056	-592.429017	-593.104341	-593.112274	-593.163350
		c-ts1	-592.300948	-592.296936	-592.425967	-593.101400	-593.109251	-593.160374
		*c*Fd	-592.305101	-592.301156	-592.430074	-593.105481	-593.113338	-593.164421
		c-ts2	-592.296183	-592.292144	-592.421190	-593.096514	-593.104364	-593.155515
Ac-Pro-NHMe	*trans*	*t*Cu	-572.457140	-572.449539	-572.578302	-573.242168	-573.248972	-573.299865
		t-ts1	-572.455188	-572.447666	-572.576434	-573.240614	-573.247433	-573.298331
		*t*Cd	-572.459608	-572.451969	-572.580690	-573.245215	-573.251869	-573.302743
		t-ts2	-572.445623	-572.438220	-572.566913	-573.230902	-573.237741	-573.288685
	cis	*c*Au	-572.452799	-572.445660	-572.574293	-573.238151	-573.245299	-573.296155
		c-ts1	-572.449216	-572.442045	-572.570805	-573.234895	-573.242042	-573.292934
		*c*Ad	-572.454486	-572.447315	-572.575920	-573.239952	-573.247007	-573.297861
		c-ts2	-572.445082	-572.437668	-572.566221	-573.230605	-573.237539	-573.288308

[a] Optimized torsion angles are listed in Table 2. Absolute single-point energies are in hartrees.

Table S18 Absolute single-point energies of local minima and transition states for puckering transitions of Ac-Pro-OH, Ac-Pro-OMe, and Ac-Pro-NHMe at CCSD(T) and MP2 levels of theory in water[a]

		Conf.	CCSD(T)	MP2				
			CBS-limit	aDZ	aDZ	aTZ	aQZ	CBS-limit
Ac-Pro-OH	*trans*	*t*Cu	-553.263637	-552.519191	-552.382515	-552.860159	-553.014404	-553.126961
		t-ts1	-553.261267	-552.516955	-552.379553	-552.856994	-553.011279	-553.123865
		*t*Cd	-553.264739	-552.520361	-552.383647	-552.861279	-553.015492	-553.128025
		t-ts2	-553.257794	-552.513267	-552.375828	-552.853375	-553.007722	-553.120354
	cis	*c*Fu	-553.261222	-552.516987	-552.380419	-552.857992	-553.012156	-553.124654
		c-ts1	-553.259178	-552.515077	-552.377990	-552.855328	-553.009550	-553.122091
		*c*Fd	-553.262912	-552.518652	-552.382168	-552.859739	-553.013919	-553.126428
		c-ts2	-553.254182	-552.510340	-552.373103	-552.850341	-553.004471	-553.116945
Ac-Pro-OMe	*trans*	*t*Fu	-592.511606	-591.709634	-591.552917	-592.069359	-592.234430	-592.354888
		t-ts1	-592.509198	-591.707314	-591.549890	-592.066069	-592.231242	-592.351773
		*t*Fd	-592.512598	-591.710691	-591.553932	-592.070368	-592.235406	-592.355839
		t-ts2	-592.505542	-591.703528	-591.546132	-592.062416	-592.227603	-592.348145
	cis	*c*Fu	-592.509314	-591.707518	-591.550984	-592.067333	-592.232357	-592.352781
		c-ts1	-592.506965	-591.705288	-591.548191	-592.064324	-592.229404	-592.349868
		*c*Fd	-592.510638	-591.708836	-591.552301	-592.068643	-592.233674	-592.354102
		c-ts2	-592.502280	-591.700975	-591.543757	-592.059725	-592.224685	-592.345062
Ac-Pro-NHMe	*trans*	*t*Cu	-572.648635	-571.870258	-571.708956	-572.210499	-572.370543	-572.487332
		t-ts1	-572.646952	-571.868762	-571.706696	-572.208013	-572.368080	-572.484886
		*t*Cd	-572.649917	-571.871636	-571.710245	-572.211825	-572.371793	-572.488526
		t-ts2	-572.642004	-571.863590	-571.701622	-572.203043	-572.363180	-572.480037
	cis	*c*Au	-572.649736	-571.871745	-571.711021	-572.212493	-572.372355	-572.489012
		c-ts1	-572.646893	-571.868640	-571.707414	-572.208860	-572.368889	-572.485667
		*c*Ad	-572.651641	-571.873710	-571.713130	-572.214577	-572.374419	-572.491061
		c-ts2	-572.642714	-571.865120	-571.703656	-572.204814	-572.364629	-572.481250

[a] Optimized torsion angles are listed in Table 4. Absolute single-point energies are in hartrees.

Table S19 Absolute single-point energies of local minima and transition states for puckering transitions of Ac-Pro-OH, Ac-Pro-OMe, and Ac-Pro-NHMe at DSD-PBEP86-D3BJ and M06-2X levels of theory in water[a]

		Conf.	DSD-PBEP86-D3BJ			M06-2X		
			TZ	dTZ	dQZ	TZ	dTZ	dQZ
Ac-Pro-OH	*trans*	*t*Cu	-553.070237	-553.068691	-553.187919	-553.809723	-553.817490	-553.865192
		t-ts1	-553.067550	-553.065863	-553.185166	-553.807480	-553.815151	-553.862872
		*t*Cd	-553.071502	-553.069824	-553.188963	-553.811241	-553.818842	-553.866486
		t-ts2	-553.063923	-553.062377	-553.181764	-553.803548	-553.811400	-553.859170
	cis	*c*Fu	-553.068224	-553.066429	-553.185628	-553.807930	-553.815584	-553.863176
		c-ts1	-553.065735	-553.063916	-553.183157	-553.805580	-553.813182	-553.860803
		*c*Fd	-553.069916	-553.068136	-553.187280	-553.809645	-553.817226	-553.864843
		c-ts2	-553.060581	-553.058753	-553.178027	-553.800295	-553.807870	-553.855579
Ac-Pro-OMe	*trans*	*t*Fu	-592.304336	-592.300616	-592.429563	-593.104026	-593.111999	-593.163142
		t-ts1	-592.301563	-592.297750	-592.426747	-593.101687	-593.109609	-593.160758
		*t*Fd	-592.305467	-592.301656	-592.430524	-593.105459	-593.113322	-593.164401
		t-ts2	-592.297839	-592.294119	-592.423205	-593.097618	-593.105679	-593.156880
	cis	*c*Fu	-592.302313	-592.298432	-592.427372	-593.102144	-593.110060	-593.161124
		c-ts1	-592.299558	-592.295625	-592.424626	-593.099540	-593.107409	-593.158502
		*c*Fd	-592.303651	-592.299735	-592.428639	-593.103531	-593.111382	-593.162447
		c-ts2	-592.294756	-592.290805	-592.419804	-593.094559	-593.102393	-593.153540
Ac-Pro-NHMe	*trans*	*t*Cu	-572.448745	-572.441779	-572.570561	-573.233537	-573.240648	-573.291759
		t-ts1	-572.446684	-572.439688	-572.568500	-573.231889	-573.238978	-573.290084
		*t*Cd	-572.450195	-572.443134	-572.571820	-573.235251	-573.242259	-573.293287
		t-ts2	-572.441705	-572.434714	-572.563641	-573.226550	-573.233741	-573.284913
	cis	*c*Au	-572.450339	-572.443410	-572.572041	-573.235185	-573.242456	-573.293312
		c-ts1	-572.447091	-572.440160	-572.568906	-573.232191	-573.239491	-573.290401
		*c*Ad	-572.452365	-572.445378	-572.573954	-573.237236	-573.244405	-573.295240
		c-ts2	-572.443131	-572.435840	-572.564400	-573.228104	-573.235103	-573.285870

[a] Optimized torsion angles are listed in Table 4. Absolute single-point energies are in hartrees.

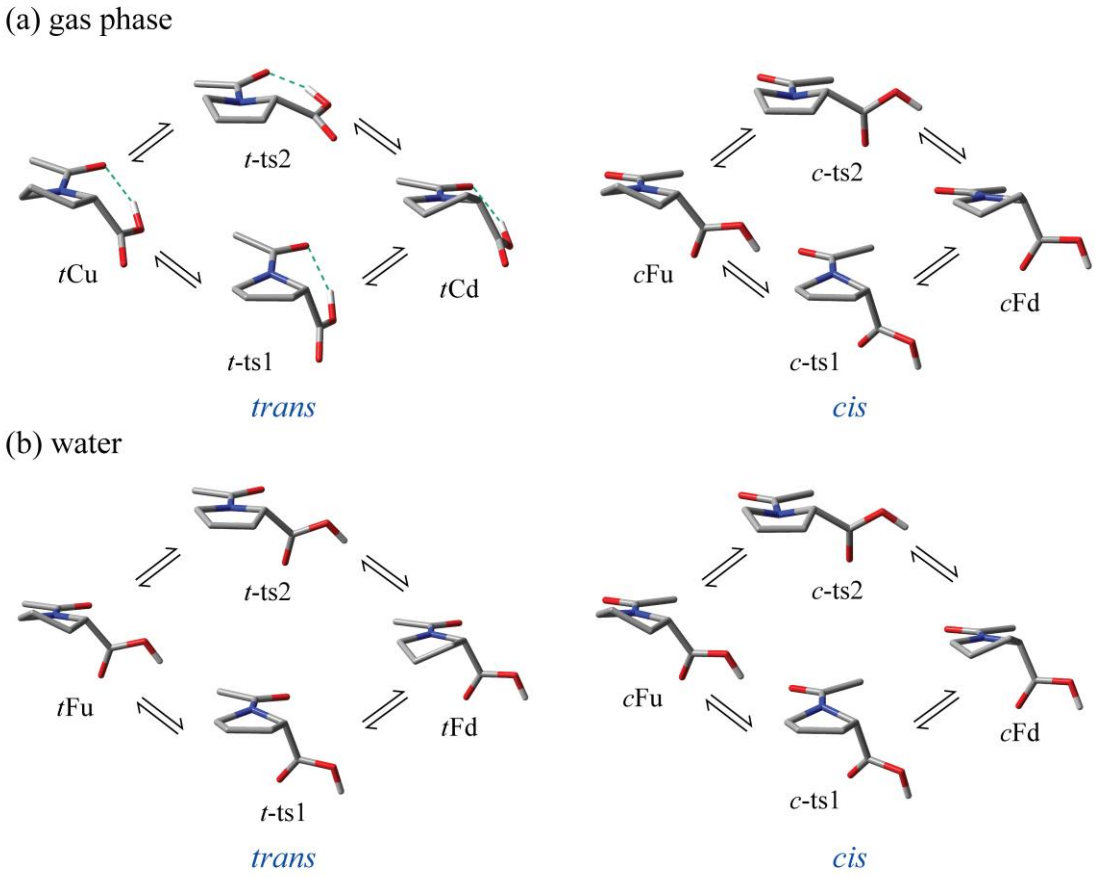

Fig. S1 Puckering transitions of local minima and transition states of Ac-Pro-OH with *trans* and *cis* prolyl peptide bonds in (a) the gas phase and (b) water. For clarity, all hydrogen atoms are omitted. All H-bonds are represented by dotted lines.

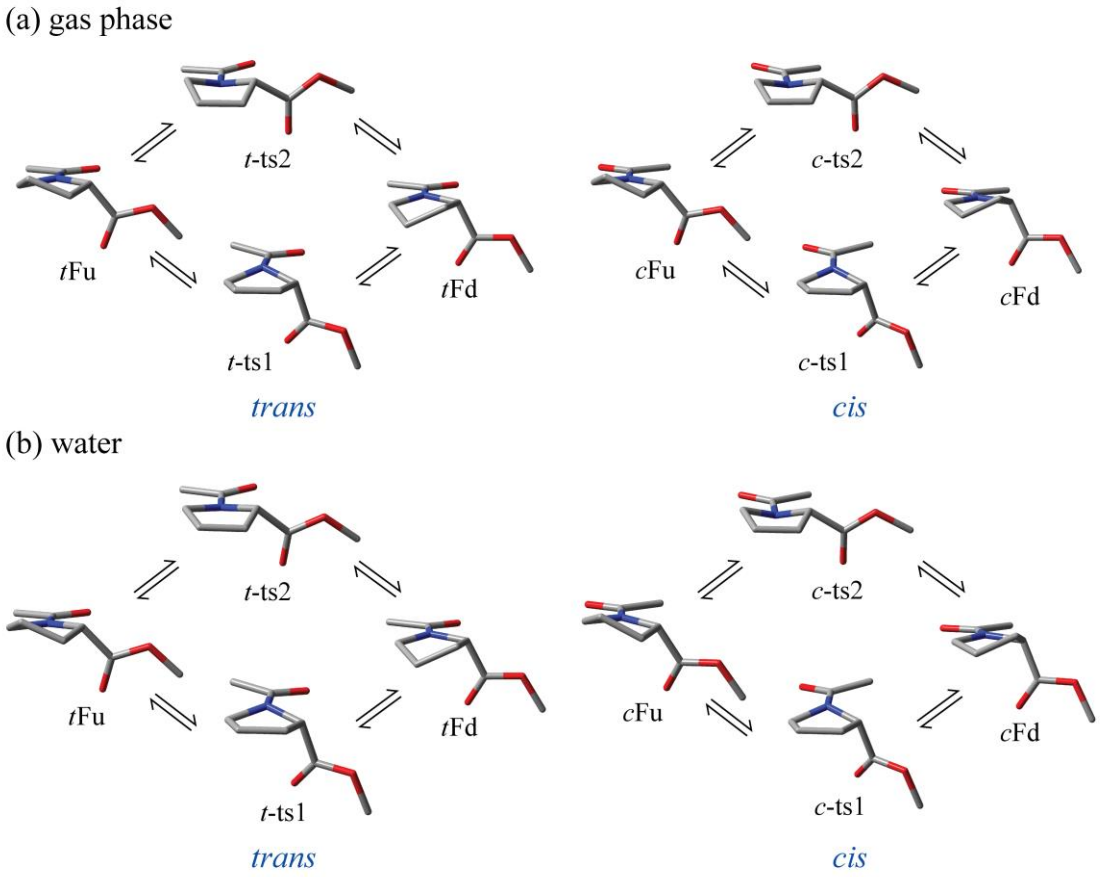

Fig. S2 Puckering transitions of local minima and transition states of Ac-Pro-OMe with *trans* and *cis* prolyl peptide bonds in (a) the gas phase and (b) water. For clarity, all hydrogen atoms are omitted. All H-bonds are represented by dotted lines.

Table S20 Torsion angles and relative electronic energies of Ac-*trans*-X-OMe optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

	Conf.[b]	ω'	ϕ	ψ	ω	χ_1	χ_2	χ_3	χ_4	χ_5	P[c]	χ_m[d]	ΔE_e[e]
Hyp	*t*Fu-t	179.2	-54.6	146.8	175.7	-27.7	38.7	-34.4	17.8	6.1	8.9	39.0	0.00
	t-ts1	169.6	-64.8	168.3	176.4	21.5	-6.7	-10.4	25.6	-29.7	103.3	29.3	3.26
	*t*Fd-g	174.7	-59.7	153.6	177.1	29.5	-37.3	30.3	-12.2	-10.9	181.1	37.2	1.06
hyp	*t*Fu-gm	-179.5	-53.2	143.8	176.7	-28.9	39.1	-33.7	16.2	8.0	6.2	39.1	1.79
	t-ts1	170.1	-63.0	163.3	177.0	14.7	1.0	-16.3	27.4	-26.7	87.9	27.9	4.04
	*t*Fd-gm	175.1	-55.1	142.8	176.4	25.2	-36.5	33.3	-18.6	-4.1	191.5	37.1	0.00
Flp	*t*Fu	179.4	-55.0	147.3	175.7	-26.1	36.8	-32.7	16.6	6.0	8.7	37.0	0.00
	t-ts1	167.7	-64.7	170.3	178.1	23.6	-8.1	-10.4	27.0	-32.0	104.9	31.5	3.02
	*t*Fd	173.8	-59.3	153.0	177.1	30.0	-36.8	28.9	-10.1	-12.6	178.2	36.6	2.15
flp	*t*Fu	-179.6	-52.8	142.9	177.1	-28.6	38.7	-33.1	15.3	8.4	5.5	38.6	2.51
	t-ts1	170.6	-62.8	164.8	176.5	10.6	5.8	-19.8	28.4	-24.8	78.2	28.0	3.68
	*t*Fd	177.3	-67.4	172.1	178.3	30.7	-36.8	28.2	-8.7	-13.9	176.0	36.7	0.00
mep	*t*Fu	179.5	-54.4	146.2	176.0	-28.6	38.9	-34.0	17.1	7.2	7.4	39.1	0.62
	t-ts1	169.5	-63.0	164.6	175.5	12.8	3.6	-18.4	28.5	-26.0	82.8	28.3	3.27
	*t*Fd	175.5	-61.5	155.9	176.9	30.0	-37.7	30.7	-12.6	-10.9	181.3	37.6	0.00
Mep	*t*Fu	179.7	-52.0	143.6	176.9	-29.7	39.6	-34.0	16.2	8.4	5.7	39.7	0.00
	t-ts1	169.4	-62.9	162.9	177.0	18.5	-3.7	-12.3	25.6	-27.8	97.8	27.8	2.79
	*t*Fd	-177.6	-67.2	168.4	178.4	24.2	-34.2	30.8	-16.9	-4.6	190.4	34.7	1.21
Clp	*t*Fu	177.0	-54.2	148.0	176.0	-25.0	37.1	-34.4	19.5	3.4	12.8	37.8	0.00
	t-ts1	167.5	-64.5	168.3	176.9	24.3	-9.5	-8.7	25.6	-31.8	108.0	31.1	3.66
	*t*Fd	175.4	-59.9	155.5	176.1	30.6	-39.9	33.2	-14.1	-10.4	182.9	39.7	1.00
clp	*t*Fu	-179.3	-56.7	149.1	176.7	-28.7	40.8	-36.5	18.8	6.2	9.3	41.1	0.98
	t-ts1	168.2	-62.9	166.0	176.9	16.5	1.1	-18.0	30.3	-29.8	88.2	31.0	3.58
	*t*Fd	-178.5	-74.4	-173.5	-179.2	30.0	-36.9	29.0	-10.4	-12.3	178.5	36.7	0.00
mpc	*t*Fu-t	177.4	-54.8	148.5	175.8	-25.2	37.0	-34.3	19.7	3.5	12.7	37.9	0.91
	t-ts1	167.4	-64.3	168.2	177.1	22.2	-6.6	-11.2	26.9	-31.2	102.7	30.7	3.79
	*t*Fd-g	175.8	-60.7	156.1	176.4	30.4	-39.1	32.4	-13.7	-10.5	182.4	39.0	0.00
Mpc	*t*Fu-gm	-179.4	-56.0	148.7	176.4	-29.0	40.0	-35.2	17.6	7.2	7.7	40.2	0.00
	t-ts1	168.7	-63.2	163.1	177.4	19.6	-4.4	-12.3	26.4	-29.3	98.9	29.1	3.13
	*t*Fd-gm	-177.9	-66.4	167.2	177.5	23.3	-35.6	33.8	-20.5	-1.7	195.2	36.8	0.58
mop	*t*Fu-t	-179.8	-55.8	147.1	176.8	-27.4	38.7	-34.5	18.0	5.8	15.2	36.8	1.35
	t-ts1	169.6	-63.1	164.3	177.8	15.0	1.0	-16.6	27.9	-27.2	88.0	28.4	3.22
	*t*Fd-g	177.3	-75.2	-166.6	178.0	37.9	-42.2	30.1	-6.3	-20.0	170.5	42.7	0.00

[a] Torsion angles (°) are defined in Fig. 1c. [b] The structures of local minima for Ac-*trans*-X-OMe optimized at the SMD M06-2X/6-31+G(d) level of theory were taken from ref. 42. [c] The phase angle of pseudorotation in degrees. [d] The amplitude of pseudorotation in degrees. [e] Relative electronic energies in in kcal mol^{-1}.

Table S21 Absolute electronic energies, enthalpies, Gibbs free energies, and single-point energies of local minima and transition states for puckering transitions of Ac-*trans*-X-OMe optimized at the SMD M06-2X/6-31+G(d) level of theory in water[a]

	Conf.	E_e	H	G	$E_{e,sp}$[b]	$E_{e,sp}$[c]	$E_{e,sp}$[d]
Hyp	*t*Fu-t	-668.117274	-667.897081	-667.952613	-668.084054	-667.585163	-668.395889
	t-ts1	-668.112083	-667.892914	-667.947386	-668.080734	-667.581611	-668.392556
	*t*Fd-g	-668.115585	-667.894821	-667.949964	-668.083762	-667.584605	-668.395709
hyp	*t*Fu-gm	-668.115420	-667.894791	-667.950885	-668.082782	-667.583933	-668.394780
	t-ts1	-668.111839	-667.892422	-667.947429	-668.081253	-667.581661	-668.392948
	*t*Fd-gm	-668.118267	-667.897777	-667.952510	-668.091894	-667.591791	-668.402914
Flp	*t*Fu	-692.131626	-691.923264	-691.978182	-692.106154	-691.601089	-692.423235
	t-ts1	-692.126806	-691.919559	-691.973710	-692.103362	-691.597849	-692.420344
	*t*Fd	-692.128201	-691.919718	-691.974503	-692.105449	-691.600030	-692.422458
flp	*t*Fu	-692.127768	-691.919460	-691.975515	-692.103323	-691.598373	-692.420464
	t-ts1	-692.125891	-691.918243	-691.970900	-692.102035	-691.596538	-692.418925
	*t*Fd	-692.131762	-691.923661	-691.978983	-692.103907	-691.598378	-692.420773
mep	*t*Fu	-632.210201	-631.967267	-632.023348	-632.188374	-631.688706	-632.476437
	t-ts1	-632.205986	-631.964078	-632.018414	-632.185496	-631.685531	-632.473528
	*t*Fd	-632.211194	-631.968526	-632.025330	-632.190063	-631.690170	-632.478131
Mep	*t*Fu	-632.211013	-631.968238	-632.025003	-632.188756	-631.689245	-632.476928
	t-ts1	-632.206562	-631.964503	-632.019446	-632.186180	-631.686076	-632.474177
	*t*Fd	-632.209087	-631.966246	-632.022203	-632.187201	-631.687309	-632.475351
Clp	*t*Fu	-1052.488723	-1052.281392	-1052.338190	-1052.463789	-1051.747087	-1052.781674
	t-ts1	-1052.482895	-1052.276574	-1052.331644	-1052.459788	-1051.742813	-1052.777672
	*t*Fd	-1052.487125	-1052.279549	-1052.335842	-1052.464215	-1051.747248	-1052.781957
clp	*t*Fu	-1052.486784	-1052.279651	-1052.336616	-1052.462269	-1051.745791	-1052.780152
	t-ts1	-1052.482663	-1052.276250	-1052.330163	-1052.459263	-1051.742358	-1052.777021
	*t*Fd	-1052.488501	-1052.281415	-1052.337653	-1052.460290	-1051.743111	-1052.778125
mpc	*t*Fu-t	-991.068710	-990.852812	-990.911533	-991.042782	-990.343028	-991.362708
	t-ts1	-991.064116	-990.849036	-990.904909	-991.039965	-990.339994	-991.359986
	*t*Fd-g	-991.070121	-990.854079	-990.911430	-991.045574	-990.345162	-991.365159
Mpc	*t*Fu-gm	-991.069816	-990.853699	-990.911382	-991.044042	-990.343964	-991.363670
	t-ts1	-991.064821	-990.849417	-990.904481	-991.041511	-990.340897	-991.360987
	*t*Fd-gm	-991.068893	-990.853751	-990.907749	-991.045273	-990.344130	-991.364168
mop	*t*Fu-t	-707.394243	-707.144863	-707.204039	-707.367862	-706.825234	-707.692460
	t-ts1	-707.391256	-707.143073	-707.200460	-707.365987	-706.823021	-707.690513
	*t*Fd-g	-707.396388	-707.148467	-707.204472	-707.366532	-706.822970	-707.690539

[a] Optimized torsion angles are listed in Table S20 (ESI‡). Absolute electronic energies, enthalpies, Gibbs free energies, and single-point energies are in hartrees. [b] Single-point energies at the M06-2X/6-31+G(d) level of theory. [c] Single-point energies at the DSD-PBEP86-D3BJ/def2-QZVP level of theory. [c] Single-point energies at the M06-2X/def2-QZVP level of theory.

Cartesian coordinates of local minima and transition states for puckering transitions of Ac-Pro-OH, Ac-Pro-OMe, and Ac-Pro-NHMe optimized at M06-2X/6-31+G(d) level of theory in the gas phase and SMD M06-2X/6-31+G(d) level of theory in water**:**

A. Gas phase

(1) Ac-Pro-OH

(a) *t*Cu

N	0.595215	0.272503	-0.091598
C	-0.731363	0.160509	0.549984
C	0.806788	1.621283	-0.628831
C	-1.30143	1.583842	0.491138
C	-1.643068	-0.864695	-0.15942
O	-2.676682	-0.551343	-0.693345
C	-0.079438	2.480534	0.271978
C	1.546038	-0.667775	0.111553
O	1.283514	-1.722931	0.701381
C	2.93975	-0.395037	-0.404288
H	3.514895	-1.315696	-0.311924
H	3.424646	0.387507	0.18905
H	2.926227	-0.072719	-1.449132
H	-0.576109	-0.189045	1.579567
H	0.473219	1.666254	-1.673415
H	1.861884	1.895022	-0.586514
H	-1.990801	1.648496	-0.35537
H	-1.861789	1.829205	1.395646
H	-0.333464	3.440407	-0.184024
H	0.439455	2.672738	1.217873
O	-1.223537	-2.125825	-0.118689
H	-0.334693	-2.18086	0.311968

(b) *t*-ts1

N	0.539229	0.423003	0.09814
C	-0.6955	-0.073372	0.712423
C	0.275791	1.612774	-0.710392
C	-1.569244	1.175472	0.871374
C	-1.335985	-1.143419	-0.195349
O	-2.389573	-0.989871	-0.758386
C	-0.948188	2.26229	-0.040402
C	1.697861	-0.271915	0.174995
O	1.740385	-1.378798	0.724057
C	2.930463	0.358616	-0.428208
H	3.769892	-0.31503	-0.259575
H	3.142653	1.329668	0.02978
H	2.799511	0.512398	-1.504199
H	-0.438279	-0.543701	1.66758
H	0.053649	1.318463	-1.744323
H	1.149485	2.267756	-0.719601
H	-2.596941	0.942859	0.589126
H	-1.562487	1.498921	1.914539
H	-1.657654	2.612843	-0.792633
H	-0.639414	3.127292	0.551748
O	-0.620507	-2.261672	-0.327105
H	0.231359	-2.192444	0.165412

(c) *t*Cd

N	0.581509	0.38902	0.077323
C	-0.674933	-0.037286	0.719724
C	0.51057	1.772697	-0.413529
C	-1.444568	1.271449	0.880184
C	-1.426798	-1.054913	-0.161717
O	-2.51621	-0.834646	-0.627567
C	-0.983661	2.092683	-0.32852
C	1.694368	-0.376622	0.128988
O	1.655415	-1.532462	0.567586
C	2.97539	0.231634	-0.387429
H	3.791473	-0.45643	-0.169242
H	3.174542	1.203307	0.074483
H	2.912799	0.38066	-1.470693
H	-0.435616	-0.522199	1.673809
H	0.907221	1.845258	-1.430013
H	1.096243	2.435066	0.238045
H	-2.521645	1.101054	0.894433
H	-1.142085	1.759598	1.813168
H	-1.497458	1.738594	-1.227954
H	-1.168854	3.163735	-0.220141
O	-0.788208	-2.205268	-0.365745
H	0.102625	-2.190636	0.062449

(d) *t*-ts2

N	0.649265	0.246767	-0.129826
C	-0.713227	0.276277	0.454307
C	1.224206	1.591425	0.116993
C	-1.205765	1.696471	0.125391
C	-1.755841	-0.752373	-0.070225
O	-2.844324	-0.374695	-0.428536
C	0.056102	2.552274	-0.094125
C	1.48113	-0.832169	-0.008294
O	1.093901	-1.941223	0.361922
C	2.935401	-0.629774	-0.365652
H	3.406742	-1.611105	-0.40971
H	3.43842	-0.027411	0.398238

H	3.044533	-0.121938	-1.327487
H	-0.630882	0.115124	1.541617
H	2.058568	1.782528	-0.559549
H	1.594965	1.640336	1.151384
H	-1.820795	1.654659	-0.773069
H	-1.843146	2.072458	0.928401
H	0.074023	2.95169	-1.1112
H	0.119994	3.398219	0.594153
O	-1.451814	-2.038089	-0.022241
H	-0.501408	-2.162649	0.236474

(e) *c*Fu

N	-0.764575	0.221975	-0.077256
C	0.617036	0.349775	-0.498601
C	-1.326356	1.480743	0.414963
C	0.970027	1.818576	-0.155086
C	1.563327	-0.574805	0.245636
O	1.343337	-1.125303	1.292931
C	-0.388515	2.523348	-0.19019
C	-1.532424	-0.909275	-0.113739
O	-2.684514	-0.897532	0.294224
C	-0.900637	-2.166796	-0.67362
H	-1.703309	-2.801941	-1.049779
H	-0.383363	-2.695578	0.132626
H	-0.182591	-1.972531	-1.476286
H	0.735805	0.171295	-1.575407
H	-1.309875	1.501815	1.512546
H	-2.364687	1.567177	0.089362
H	1.383724	1.864511	0.859267
H	1.709575	2.226483	-0.846757
H	-0.38634	3.465109	0.363869
H	-0.680244	2.732019	-1.225563
O	2.739629	-0.666735	-0.40577
H	3.330962	-1.225031	0.129653

(f) *c*-ts1

N	0.666437	0.469975	0.221031
C	-0.618336	-0.013283	0.667014
C	0.504605	1.65407	-0.618648
C	-1.478477	1.269938	0.79532
C	-1.232518	-0.982573	-0.339362
O	-0.77532	-1.257451	-1.418866
C	-0.740759	2.344948	-0.040818
C	1.806753	-0.288524	0.123922
O	2.774151	0.10519	-0.50596
C	1.809533	-1.607171	0.870455
H	2.805317	-2.040654	0.780632
H	1.081126	-2.299703	0.435285
H	1.566902	-1.469831	1.929126
H	-0.54676	-0.538125	1.624942
H	0.358575	1.34757	-1.662751
H	1.410056	2.260062	-0.567852
H	-2.5018	1.092427	0.45633
H	-1.530929	1.56198	1.846287
H	-1.37378	2.744855	-0.836298
H	-0.450474	3.181951	0.598884
O	-2.380558	-1.508857	0.131405
H	-2.734274	-2.105845	-0.551734

(g) *c*Fd

N	-0.717142	0.387448	-0.193021
C	0.589589	0.014647	-0.686289
C	-0.76233	1.752232	0.34169
C	1.291415	1.378233	-0.854641
C	1.356177	-0.85114	0.308335
O	1.04548	-1.058344	1.452818
C	0.702683	2.197083	0.299842
C	-1.808874	-0.427663	-0.091121
O	-2.861276	-0.011429	0.369018
C	-1.644649	-1.849457	-0.588672
H	-2.592349	-2.367127	-0.442596
H	-0.859678	-2.37048	-0.030922
H	-1.384256	-1.870234	-1.652259
H	0.538391	-0.529366	-1.635514
H	-1.187839	1.741399	1.348178
H	-1.406646	2.375214	-0.290072
H	2.380371	1.29269	-0.836041
H	0.992584	1.803322	-1.818374
H	1.200686	1.933448	1.2392
H	0.809065	3.273947	0.149445
O	2.471983	-1.355291	-0.256362
H	2.936095	-1.878048	0.421442

(h) *c*-ts2

N	0.793731	-0.050425	0.079822
C	-0.477775	-0.503203	-0.457671
C	1.758984	-1.142017	-0.10865
C	-0.53264	-1.997785	-0.042829
C	-1.685896	0.190325	0.141486
O	-1.803717	0.545759	1.285157
C	0.942431	-2.404513	0.18325
C	1.278045	1.24026	-0.020183
O	2.477193	1.455441	0.04019
C	0.277911	2.367493	-0.164694
H	0.837577	3.27565	-0.387819
H	-0.278306	2.50038	0.767254
H	-0.442339	2.183063	-0.969772
H	-0.515317	-0.40305	-1.552072

H	2.60804	-0.997765	0.559312
H	2.136957	-1.126604	-1.141417
H	-1.101365	-2.096936	0.88524
H	-1.032154	-2.589313	-0.813368
H	1.088801	-2.720069	1.218862
H	1.244799	-3.23264	-0.462211
O	-2.675816	0.296762	-0.767174
H	-3.450456	0.673193	-0.312402

(2) Ac-Pro-OMe

(a) *t*Fu

N	1.103212	0.058112	-0.176187
C	-0.089361	-0.684178	-0.561506
C	2.135352	-0.789443	0.413648
C	0.245293	-2.136049	-0.161176
C	-1.30103	-0.17277	0.206638
O	-1.284392	0.107015	1.380613
C	1.778227	-2.167119	-0.145099
C	1.085134	1.418346	-0.242048
O	0.112509	2.008058	-0.69635
C	2.318493	2.136471	0.2595
H	2.133966	3.209005	0.204864
H	3.191327	1.888794	-0.353767
H	2.541231	1.854574	1.293807
H	-0.280414	-0.573603	-1.633944
H	2.07037	-0.777836	1.511114
H	3.133076	-0.45521	0.116633
H	-0.136046	-2.327508	0.848075
H	-0.200214	-2.861908	-0.844615
H	2.180412	-2.984263	0.458929
H	2.169387	-2.26359	-1.163895
O	-2.394296	-0.143591	-0.559954
C	-3.572725	0.346775	0.082543
H	-4.358388	0.300385	-0.669957
H	-3.823173	-0.275298	0.944886
H	-3.410873	1.375622	0.411699

(b) *t*-ts1

N	-1.142869	0.150553	-0.298512
C	0.186443	0.475684	-0.771757
C	-1.602465	1.138895	0.676291
C	0.243523	2.017625	-0.706883
C	1.233392	-0.145532	0.147154
O	1.031869	-0.486814	1.287989
C	-0.910258	2.441236	0.235728
C	-1.525567	-1.166457	-0.319717
O	-0.86541	-2.00359	-0.917392
C	-2.802843	-1.506292	0.414276
H	-3.035676	-2.554466	0.228344
H	-3.635439	-0.878876	0.081193
H	-2.670196	-1.350143	1.49051
H	0.342141	0.084878	-1.779086
H	-1.288912	0.848349	1.687296
H	-2.692359	1.219265	0.655111
H	1.219371	2.36277	-0.355361
H	0.096471	2.428576	-1.707972
H	-0.546836	2.997588	1.102751
H	-1.613424	3.08631	-0.297192
O	2.426881	-0.211011	-0.454213
C	3.48369	-0.75762	0.338688
H	3.239768	-1.781868	0.628418
H	4.368622	-0.736088	-0.295091
H	3.63434	-0.154083	1.236904

(c) *t*Fd

N	-1.145064	0.113942	-0.307387
C	0.173941	0.470389	-0.795168
C	-1.828216	1.221382	0.366934
C	0.152359	2.007865	-0.753748
C	1.244993	-0.07616	0.142902
O	1.092211	-0.257881	1.3268
C	-0.745231	2.304375	0.454067
C	-1.482215	-1.206856	-0.25003
O	-0.733121	-2.064431	-0.699285
C	-2.808941	-1.538768	0.395449
H	-3.062098	-2.569569	0.147873
H	-3.606851	-0.868036	0.062917
H	-2.720065	-1.448516	1.483943
H	0.348642	0.066215	-1.794894
H	-2.185845	0.918227	1.355186
H	-2.688828	1.558327	-0.226476
H	1.153818	2.438111	-0.669894
H	-0.304274	2.380845	-1.676757
H	-0.177132	2.177529	1.380533
H	-1.164023	3.313617	0.437228
O	2.402507	-0.262356	-0.50118
C	3.476351	-0.757269	0.302093
H	4.320737	-0.872972	-0.375482
H	3.711923	-0.047065	1.098294
H	3.19842	-1.716715	0.74357

(d) *t*-ts2

N	-1.073756	-0.111616	-0.010223
C	0.026262	0.724663	-0.468592
C	-2.319182	0.61837	-0.247795
C	-0.410043	2.138813	-0.033744
C	1.330267	0.316245	0.203642

O	1.471172	0.224021	1.397651
C	-1.951063	2.065887	0.110475
C	-0.94629	-1.476311	-0.057095
O	0.13249	-2.002645	-0.286608
C	-2.197443	-2.279183	0.226054
H	-1.921241	-3.332254	0.272852
H	-2.938002	-2.136634	-0.568469
H	-2.653583	-1.975486	1.173091
H	0.146013	0.642272	-1.557307
H	-3.127395	0.221036	0.370076
H	-2.615909	0.534365	-1.304761
H	0.050559	2.372362	0.929088
H	-0.087246	2.887995	-0.760429
H	-2.242912	2.283444	1.140627
H	-2.466425	2.777174	-0.539595
O	2.311989	0.149216	-0.68703
C	3.549083	-0.307352	-0.138093
H	4.2338	-0.386854	-0.981022
H	3.923675	0.40351	0.601919
H	3.400197	-1.281156	0.334281

(e) *c*Fu

N	-1.159017	-0.040645	-0.079478
C	0.07614	0.584998	-0.518114
C	-2.146232	0.924088	0.406311
C	-0.132748	2.076454	-0.163745
C	1.304677	0.06195	0.209635
O	1.317433	-0.376285	1.332276
C	-1.655033	2.237107	-0.199997
C	-1.446069	-1.376151	-0.097292
O	-2.517854	-1.796045	0.314709
C	-0.379991	-2.306091	-0.640607
H	-0.869213	-3.228691	-0.954073
H	0.332801	-2.539646	0.157002
H	0.172329	-1.878945	-1.483761
H	0.232437	0.46361	-1.597594
H	-2.141625	0.951828	1.50379
H	-3.142711	0.622297	0.077959
H	0.232525	2.258109	0.853861
H	0.406628	2.733822	-0.849101
H	-1.997507	3.114843	0.353547
H	-2.00273	2.324199	-1.235528
O	2.399139	0.202684	-0.552605
C	3.629055	-0.190207	0.063732
H	4.400782	-0.018209	-0.684495
H	3.812448	0.410951	0.957114
H	3.588414	-1.245379	0.343049

(f) *c*-ts1

N	1.175105	0.182276	0.191761
C	-0.145947	0.38052	0.741635
C	1.518996	1.268251	-0.722358
C	-0.293241	1.921388	0.815704
C	-1.224067	-0.230732	-0.152415
O	-1.033408	-0.724224	-1.236278
C	0.794046	2.48712	-0.13157
C	1.811803	-1.028198	0.079657
O	2.794673	-1.160337	-0.631108
C	1.254097	-2.167056	0.90879
H	1.933029	-3.014414	0.815555
H	0.266121	-2.46117	0.538014
H	1.159737	-1.890614	1.9637
H	-0.245676	-0.073232	1.732615
H	1.163034	1.025421	-1.732189
H	2.603587	1.377129	-0.763537
H	-1.303876	2.230715	0.538793
H	-0.124138	2.250812	1.843248
H	0.362708	3.10938	-0.919229
H	1.492939	3.110155	0.432141
O	-2.429686	-0.14627	0.429403
C	-3.518262	-0.677728	-0.332214
H	-3.347348	-1.735313	-0.544528
H	-4.403319	-0.545272	0.287863
H	-3.619705	-0.134265	-1.274276

(g) *c*Fd

N	-1.177958	0.138271	-0.183765
C	0.135343	0.343462	-0.755734
C	-1.739187	1.350142	0.42139
C	0.210411	1.878607	-0.886735
C	1.247013	-0.154727	0.164468
O	1.125105	-0.397314	1.339223
C	-0.588316	2.356921	0.331231
C	-1.821902	-1.058135	-0.050465
O	-2.91597	-1.128299	0.489471
C	-1.117643	-2.274917	-0.616987
H	-1.75903	-3.140666	-0.45356
H	-0.15814	-2.439923	-0.115284
H	-0.929506	-2.163053	-1.689966
H	0.248394	-0.148084	-1.727154
H	-2.055123	1.139656	1.446163
H	-2.62194	1.670731	-0.144802
H	1.239679	2.24454	-0.920021
H	-0.290971	2.172504	-1.814873
H	0.030267	2.297249	1.232857
H	-0.940355	3.385875	0.22597
O	2.404786	-0.259045	-0.505455
C	3.530581	-0.672917	0.274748

H	4.368859	-0.716298	-0.418503
H	3.722544	0.049702	1.071003
H	3.341848	-1.65348	0.717117

(h) *c*-ts2

N	1.13829	0.141891	0.058933
C	0.022694	-0.646618	-0.446742
C	2.362812	-0.630274	-0.182408
C	0.407601	-2.095197	-0.056589
C	-1.310423	-0.299626	0.197461
O	-1.496527	-0.179255	1.382181
C	1.944839	-2.073777	0.1145
C	1.230666	1.51713	0.001421
O	2.319318	2.067853	0.028961
C	-0.058384	2.310395	-0.053736
H	0.206275	3.360455	-0.176654
H	-0.624701	2.182801	0.873426
H	-0.692647	1.998571	-0.891397
H	-0.07362	-0.545568	-1.537216
H	3.161911	-0.257605	0.458385
H	2.681233	-0.501495	-1.227474
H	-0.077446	-2.352256	0.888179
H	0.068877	-2.800801	-0.81904
H	2.210891	-2.342051	1.139559
H	2.444811	-2.77846	-0.554451
O	-2.279853	-0.194748	-0.723292
C	-3.583707	0.087724	-0.206799
H	-4.243486	0.111173	-1.072228
H	-3.889128	-0.690627	0.495786
H	-3.581107	1.053293	0.30515

(3) Ac-Pro-NHMe

(a) *t*Cu

N	0.941522	0.149412	0.078479
C	-0.024016	-0.687393	-0.657667
C	1.931284	-0.681801	0.765982
C	0.569989	-2.103724	-0.59098
C	-1.416124	-0.610773	0.006015
O	-1.838354	-1.491304	0.744997
C	2.024647	-1.902821	-0.148808
C	1.012648	1.485241	-0.146079
O	0.209842	2.057894	-0.884947
C	2.119181	2.251303	0.548709
H	1.91568	3.314689	0.425516
H	3.089441	2.02428	0.093701
H	2.176075	2.007046	1.613154
H	-0.093275	-0.298316	-1.679795
H	1.561267	-0.962114	1.76095
H	2.878225	-0.151791	0.878903
H	0.014316	-2.674827	0.158196
H	0.483265	-2.620986	-1.549165
H	2.437734	-2.777832	0.359465
H	2.66545	-1.665078	-1.005468
N	-2.118765	0.502665	-0.291108
H	-1.622171	1.256939	-0.758241
C	-3.394496	0.751514	0.351589
H	-3.824163	1.663341	-0.065099
H	-4.072062	-0.085932	0.167979
H	-3.279662	0.864063	1.43533

(b) *t*-ts1

N	0.987245	-0.111377	0.083299
C	-0.029793	0.634384	0.82814
C	1.634135	0.762493	-0.893127
C	0.51327	2.068734	0.868374
C	-1.368743	0.541313	0.071477
O	-1.788988	1.452444	-0.631375
C	1.615788	2.143497	-0.216718
C	1.120444	-1.455183	0.208035
O	0.398957	-2.107728	0.964139
C	2.20547	-2.115564	-0.615554
H	2.183409	-3.184396	-0.405183
H	3.192686	-1.716872	-0.360966
H	2.040721	-1.951315	-1.685307
H	-0.135466	0.179236	1.816783
H	1.055401	0.773044	-1.826398
H	2.644469	0.412576	-1.114635
H	-0.294881	2.774779	0.672328
H	0.929696	2.27945	1.856137
H	1.416494	2.930617	-0.946881
H	2.588045	2.348136	0.239831
N	-2.012301	-0.636618	0.224859
H	-1.517055	-1.386626	0.700234
C	-3.222985	-0.916309	-0.522808
H	-3.638249	-1.862927	-0.174847
H	-3.951371	-0.118635	-0.358873
H	-3.023762	-0.979015	-1.598348

(c) *t*Cd

N	1.003415	-0.018076	0.047887
C	-0.092561	0.59098	0.821044
C	1.825062	0.988868	-0.637161
C	0.30092	2.066022	0.872047
C	-1.445303	0.386361	0.10858
O	-2.043315	1.310044	-0.431056
C	1.016093	2.2773	-0.466791
C	1.307146	-1.333334	0.171038

O	0.605086	-2.102185	0.830702
C	2.544924	-1.8126	-0.554906
H	2.691322	-2.866527	-0.320399
H	3.429953	-1.243108	-0.254142
H	2.425439	-1.695785	-1.637194
H	-0.132027	0.113354	1.805929
H	1.981908	0.719991	-1.686103
H	2.806356	1.071736	-0.150281
H	-0.571427	2.71045	0.989206
H	0.9908	2.23064	1.70746
H	0.269807	2.36532	-1.261734
H	1.653242	3.164828	-0.482365
N	-1.906917	-0.880611	0.131068
H	-1.303561	-1.600773	0.520668
C	-3.132892	-1.228302	-0.559974
H	-3.367897	-2.272763	-0.351689
H	-3.952604	-0.59472	-0.211189
H	-3.031294	-1.086479	-1.641279

(d) *t*-ts2

N	1.054519	0.160572	0.042266
C	0.032577	-0.729962	-0.50114
C	2.360259	-0.46065	-0.212914
C	0.572823	-2.128622	-0.154171
C	-1.329003	-0.494586	0.173025
O	-1.497557	-0.755388	1.351843
C	2.099048	-1.951742	0.034769
C	0.854772	1.515965	-0.008993
O	-0.228877	1.98931	-0.325122
C	2.033001	2.386365	0.370964
H	1.683629	3.415345	0.45244
H	2.812468	2.333013	-0.397209
H	2.470822	2.06653	1.320919
H	-0.050968	-0.58159	-1.589591
H	3.123513	-0.046325	0.449499
H	2.66729	-0.278143	-1.254554
H	0.105771	-2.455845	0.776655
H	0.325357	-2.848119	-0.938638
H	2.385549	-2.218203	1.055015
H	2.683943	-2.572525	-0.648377
N	-2.328009	-0.071784	-0.648883
H	-2.017045	0.463839	-1.450003
C	-3.582509	0.346267	-0.046093
H	-4.310471	0.535953	-0.836599
H	-3.949292	-0.454054	0.598182
H	-3.45047	1.249022	0.562124

(e) *c*Au

N	0.988105	-0.091023	-0.105274
C	0.007496	0.653318	0.686313
C	1.878611	0.79392	-0.866745
C	0.274274	2.125069	0.29876
C	-1.450851	0.299603	0.402032
O	-2.328072	0.584077	1.204388
C	1.744401	2.124235	-0.127374
C	1.323115	-1.407634	0.094259
O	2.234822	-1.931688	-0.528316
C	0.503171	-2.168189	1.116924
H	0.849783	-3.201222	1.122197
H	-0.565816	-2.142608	0.882616
H	0.633109	-1.739229	2.116219
H	0.163502	0.505529	1.761341
H	1.540083	0.878909	-1.908345
H	2.88577	0.373138	-0.871193
H	-0.36083	2.397803	-0.552829
H	0.042699	2.801986	1.122996
H	2.007129	2.983726	-0.749113
H	2.395757	2.124197	0.753924
N	-1.703276	-0.270614	-0.799172
H	-0.92101	-0.528534	-1.385429
C	-3.06152	-0.601198	-1.188125
H	-3.04532	-1.035654	-2.188248
H	-3.500305	-1.31753	-0.486863
H	-3.684527	0.297101	-1.190989

(f) *c*-ts1

N	1.017061	0.092842	-0.003357
C	-0.072264	0.604231	0.81077
C	1.343146	1.005864	-1.095822
C	0.028994	2.140518	0.661149
C	-1.463664	0.106828	0.38894
O	-2.457176	0.475847	0.998918
C	0.963566	2.391449	-0.547605
C	1.62795	-1.124719	0.117052
O	2.441135	-1.511844	-0.711065
C	1.247119	-1.958232	1.324861
H	1.768468	-2.91221	1.250569
H	0.167126	-2.134888	1.368476
H	1.544189	-1.456668	2.251827
H	0.045688	0.303997	1.855811
H	0.761992	0.754362	-1.99454
H	2.399613	0.898536	-1.347345
H	-0.966089	2.571048	0.531724
H	0.451281	2.571615	1.571339
H	0.48113	2.999913	-1.316203
H	1.861919	2.924595	-0.226257
N	-1.523895	-0.740573	-0.663915
H	-0.672392	-1.006556	-1.13826

C	-2.803715	-1.254721	-1.116734
H	-2.635164	-1.928525	-1.957268
H	-3.302433	-1.79615	-0.308234
H	-3.455955	-0.434283	-1.429223

(g) *c*Ad

N	1.003259	0.141456	-0.037193
C	-0.091785	0.497562	0.861479
C	1.429688	1.266297	-0.881618
C	-0.097646	2.034981	0.80423
C	-1.460103	-0.055506	0.44017
O	-2.440581	0.127325	1.148345
C	0.347583	2.320487	-0.634411
C	1.790627	-0.974627	0.05033
O	2.775834	-1.102965	-0.662234
C	1.37771	-2.024929	1.061867
H	1.943045	-2.933409	0.854849
H	0.305028	-2.239019	1.02457
H	1.61776	-1.684763	2.075437
H	0.085349	0.136206	1.87888
H	1.510326	0.95162	-1.925898
H	2.423438	1.603923	-0.562554
H	-1.077222	2.442087	1.06296
H	0.641778	2.422857	1.513149
H	-0.491884	2.17152	-1.323514
H	0.721446	3.337552	-0.773214
N	-1.514747	-0.72208	-0.734665
H	-0.664064	-0.835092	-1.268437
C	-2.769719	-1.273756	-1.210078
H	-2.59407	-1.784569	-2.157338
H	-3.173128	-1.982908	-0.481842
H	-3.507547	-0.479562	-1.354732

(h) *c*-ts2

N	-1.003786	0.142855	-0.162909
C	-0.103684	-0.653795	0.676406
C	-2.266851	-0.61278	-0.270135
C	-0.397615	-2.107184	0.233227
C	1.378145	-0.34863	0.470196
O	2.175447	-0.401561	1.394236
C	-1.814958	-2.071035	-0.384976
C	-1.144246	1.518863	-0.006034
O	-2.17418	2.074138	-0.345317
C	0.021595	2.293051	0.572474
H	-0.301612	3.32585	0.70133
H	0.885851	2.265367	-0.097845
H	0.342372	1.885845	1.537098
H	-0.317233	-0.515524	1.744937
H	-2.841759	-0.255972	-1.124752
H	-2.868239	-0.439337	0.633519
H	0.341042	-2.425386	-0.50729
H	-0.319318	-2.784742	1.086298
H	-1.779723	-2.377239	-1.433882
H	-2.508249	-2.7413	0.128755
N	1.743172	-0.09914	-0.81127
H	1.008251	0.038019	-1.493452
C	3.119069	0.22141	-1.138022
H	3.227699	0.253354	-2.222877
H	3.413859	1.188656	-0.714121
H	3.782497	-0.543606	-0.728636

B. Water

(1) Ac-Pro-OH

(a) *t*Fu

N	-0.726877	0.164203	-0.101274
C	0.654858	0.422687	-0.485893
C	-1.423244	1.376493	0.356449
C	0.877797	1.888337	-0.065771
C	1.614506	-0.501344	0.2342
O	1.471049	-0.909652	1.368953
C	-0.525555	2.490534	-0.177048
C	-1.24396	-1.070723	-0.220579
O	-0.548923	-2.006714	-0.662878
C	-2.678473	-1.258809	0.190033
H	-2.910811	-2.323961	0.196772
H	-3.338333	-0.751358	-0.522187
H	-2.862517	-0.833132	1.18093
H	0.785209	0.289409	-1.564922
H	-1.474298	1.391268	1.451509
H	-2.436453	1.411617	-0.048074
H	1.218057	1.92327	0.975389
H	1.620494	2.377764	-0.697742
H	-0.632845	3.415913	0.392456
H	-0.766476	2.692179	-1.226057
O	2.692636	-0.771397	-0.509234
H	3.31243	-1.323334	0.007767

(b) *t*-ts1

N	-0.674794	0.366087	-0.320824
C	0.707016	0.104049	-0.677371
C	-0.805783	1.576395	0.50216
C	1.401044	1.483431	-0.614079
C	1.334751	-0.858963	0.315253
O	0.911926	-1.081157	1.432125
C	0.432551	2.414891	0.151397
C	-1.561312	-0.654443	-0.322196
O	-1.257347	-1.759327	-0.805455

C	-2.913137	-0.390043	0.279681
H	-3.55942	-1.24894	0.097316
H	-3.366987	0.511285	-0.142063
H	-2.809861	-0.236978	1.36018
H	0.774623	-0.343498	-1.671028
H	-0.818118	1.30212	1.563209
H	-1.738767	2.091458	0.26614
H	2.375536	1.407878	-0.125693
H	1.567924	1.843833	-1.630415
H	0.890325	2.812974	1.058898
H	0.151856	3.262065	-0.477908
O	2.449299	-1.413127	-0.172731
H	2.854653	-1.98782	0.506558

(c) *t*Fd

N	-0.701614	0.315311	-0.288858
C	0.673821	0.099854	-0.707022
C	-0.927813	1.666117	0.259213
C	1.267295	1.521015	-0.71052
C	1.408037	-0.785931	0.285159
O	1.072115	-0.978381	1.436242
C	0.489766	2.220398	0.408005
C	-1.569718	-0.711272	-0.250654
O	-1.227364	-1.849396	-0.624876
C	-2.950619	-0.423559	0.271479
H	-3.602424	-1.266401	0.039695
H	-3.360314	0.49361	-0.160826
H	-2.90929	-0.292453	1.358789
H	0.721674	-0.375472	-1.689862
H	-1.459983	1.610335	1.211259
H	-1.522247	2.260187	-0.443533
H	2.348905	1.519444	-0.55835
H	1.051601	1.982106	-1.678977
H	0.898163	1.938646	1.384102
H	0.514874	3.308575	0.32216
O	2.517153	-1.306538	-0.251449
H	2.990503	-1.830969	0.424246

(d) *t*-ts2

N	-0.725577	0.155303	-0.081575
C	0.638485	0.385978	-0.526096
C	-1.500574	1.392819	0.07659
C	0.915498	1.875075	-0.21782
C	1.614705	-0.498316	0.224068
O	1.524341	-0.801194	1.396778
C	-0.449297	2.51071	0.133428
C	-1.2503	-1.083529	-0.164657
O	-0.541276	-2.049246	-0.504733
C	-2.704771	-1.235868	0.183437
H	-2.983149	-2.287019	0.105899
H	-3.323682	-0.641734	-0.49705
H	-2.89455	-0.880584	1.201344
H	0.733444	0.170884	-1.595704
H	-2.103838	1.343292	0.985708
H	-2.175523	1.517124	-0.776996
H	1.604264	1.964559	0.626294
H	1.384146	2.349371	-1.081062
H	-0.412903	2.948211	1.132938
H	-0.704862	3.307032	-0.56809
O	2.652034	-0.849698	-0.54312
H	3.292424	-1.358368	-0.00736

(e) *c*Fu

N	-0.7637	0.235509	-0.072909
C	0.629638	0.345852	-0.494656
C	-1.306709	1.519549	0.39645
C	1.007832	1.801606	-0.134622
C	1.545741	-0.608212	0.240818
O	1.278893	-1.191727	1.270693
C	-0.332842	2.533513	-0.194847
C	-1.518897	-0.87798	-0.11464
O	-2.679437	-0.875453	0.339685
C	-0.942748	-2.131618	-0.720692
H	-1.744023	-2.638936	-1.262262
H	-0.605246	-2.793761	0.083005
H	-0.109108	-1.951161	-1.40256
H	0.734684	0.174548	-1.571184
H	-1.311261	1.548924	1.492562
H	-2.330851	1.638176	0.038528
H	1.406995	1.836084	0.885473
H	1.760364	2.194179	-0.819888
H	-0.322781	3.472014	0.36311
H	-0.600874	2.744663	-1.235307
O	2.732036	-0.694546	-0.369795
H	3.323969	-1.275751	0.147363

(f) *c*-ts1

N	0.655364	0.502926	0.249161
C	-0.631392	-0.020175	0.67609
C	0.468215	1.695315	-0.584179
C	-1.543857	1.228046	0.759826
C	-1.173844	-1.014335	-0.341379
O	-0.683183	-1.234575	-1.430204
C	-0.812788	2.335061	-0.036048
C	1.773946	-0.252472	0.139395
O	2.743913	0.141719	-0.528124
C	1.811038	-1.560807	0.887085
H	1.565046	-1.417746	1.943469

H	2.812367	-1.98347	0.800459
H	1.091932	-2.271628	0.465898
H	-0.55946	-0.531043	1.639512
H	0.360143	1.394323	-1.6335
H	1.34062	2.344917	-0.501446
H	-2.535976	1.012349	0.357684
H	-1.664539	1.510789	1.806777
H	-1.429074	2.725374	-0.848087
H	-0.564267	3.167665	0.625904
O	-2.277574	-1.620621	0.105291
H	-2.617499	-2.228002	-0.581238

(g) *c*Fd

N	-0.718303	0.386868	-0.183072
C	0.588458	-0.001789	-0.69039
C	-0.736111	1.763127	0.34091
C	1.295379	1.354031	-0.882888
C	1.346799	-0.852539	0.315695
O	1.040024	-0.998324	1.481477
C	0.72958	2.194684	0.26484
C	-1.78991	-0.422336	-0.084816
O	-2.857354	-0.004922	0.401207
C	-1.656419	-1.827835	-0.611924
H	-2.593852	-2.357343	-0.440368
H	-0.843855	-2.366648	-0.113985
H	-1.442301	-1.812167	-1.685526
H	0.513772	-0.559684	-1.627465
H	-1.134491	1.771789	1.35852
H	-1.381388	2.383822	-0.290186
H	2.383296	1.259949	-0.867063
H	0.990325	1.762573	-1.850648
H	1.243568	1.948312	1.199813
H	0.832215	3.267438	0.089604
O	2.427346	-1.41248	-0.237463
H	2.914044	-1.924374	0.438482

(h) *c*-ts2

N	0.796152	-0.101008	0.108603
C	-0.511062	-0.439278	-0.451834
C	1.656174	-1.289174	-0.085689
C	-0.706016	-1.927489	-0.064074
C	-1.662591	0.333731	0.149369
O	-1.705651	0.771342	1.280607
C	0.720497	-2.469992	0.172376
C	1.372711	1.129725	-0.027341
O	2.599757	1.258527	0.083804
C	0.491411	2.326244	-0.271075
H	1.126673	3.165724	-0.555065
H	-0.05384	2.587185	0.640567
H	-0.236465	2.144872	-1.068275
H	-0.514718	-0.312943	-1.540309
H	2.503347	-1.253331	0.598658
H	2.037459	-1.285736	-1.114444
H	-1.300901	-1.999954	0.850463
H	-1.239086	-2.451006	-0.859243
H	0.82431	-2.818513	1.20227
H	0.955046	-3.304609	-0.491287
O	-2.692204	0.399954	-0.701798
H	-3.45685	0.814178	-0.254859

(2) Ac-Pro-OMe

(a) *t*Fu

N	-1.102612	-0.04316	-0.118166
C	0.11114	0.67082	-0.500321
C	-2.175217	0.858291	0.331553
C	-0.173245	2.115766	-0.051121
C	1.327156	0.103681	0.205357
O	1.342927	-0.260129	1.36563
C	-1.695956	2.217869	-0.173528
C	-1.163179	-1.381961	-0.210157
O	-0.187159	-2.031188	-0.635955
C	-2.445835	-2.043953	0.212132
H	-2.305392	-3.125086	0.212762
H	-3.248688	-1.785697	-0.486813
H	-2.750141	-1.710169	1.208877
H	0.270865	0.607855	-1.581649
H	-2.25149	0.838731	1.424909
H	-3.132903	0.556222	-0.097201
H	0.124943	2.236604	0.996558
H	0.369183	2.841112	-0.659765
H	-2.111513	3.043337	0.408096
H	-1.982095	2.347485	-1.222498
O	2.4017	0.113344	-0.580114
C	3.628957	-0.33876	0.017178
H	4.378365	-0.268796	-0.768903
H	3.893781	0.305971	0.857447
H	3.5207	-1.372182	0.35231

(b) *t*-ts1

N	-1.135986	0.140057	-0.287755
C	0.196177	0.47459	-0.756232
C	-1.647941	1.156229	0.643412
C	0.258698	2.015139	-0.675081
C	1.245511	-0.170205	0.136667
O	1.038506	-0.592842	1.258089
C	-0.901944	2.441125	0.253797
C	-1.543442	-1.149101	-0.306512

O	-0.874536	-2.020923	-0.888717
C	-2.838811	-1.467191	0.387421
H	-3.087497	-2.514549	0.215377
H	-3.64746	-0.830615	0.015613
H	-2.739996	-1.288652	1.463845
H	0.3512	0.112087	-1.774403
H	-1.421591	0.858642	1.673656
H	-2.730315	1.250957	0.538986
H	1.230966	2.351197	-0.307123
H	0.125023	2.42629	-1.677035
H	-0.535896	2.95252	1.146172
H	-1.57056	3.126329	-0.271648
O	2.441207	-0.185363	-0.448968
C	3.524671	-0.717722	0.333322
H	3.325246	-1.762975	0.576918
H	4.408202	-0.634008	-0.296497
H	3.645632	-0.13178	1.246439

(c) *t*Fd

N	-1.141172	0.11715	-0.290717
C	0.187308	0.459489	-0.774993
C	-1.831135	1.257547	0.33998
C	0.200686	1.997766	-0.707623
C	1.255633	-0.128863	0.132555
O	1.093296	-0.417708	1.302532
C	-0.721767	2.301467	0.475987
C	-1.529732	-1.170073	-0.240023
O	-0.78971	-2.074706	-0.672613
C	-2.878148	-1.459406	0.360647
H	-3.15946	-2.48655	0.126437
H	-3.639965	-0.770983	-0.015572
H	-2.825237	-1.343005	1.449111
H	0.349639	0.083257	-1.78771
H	-2.254783	0.96393	1.302685
H	-2.639833	1.609877	-0.309903
H	1.210324	2.398485	-0.590848
H	-0.223403	2.387832	-1.637653
H	-0.186878	2.154924	1.420073
H	-1.114402	3.320167	0.454432
O	2.420721	-0.244842	-0.502174
C	3.528483	-0.716814	0.283969
H	4.374279	-0.756849	-0.399824
H	3.728026	-0.019551	1.099997
H	3.307465	-1.710217	0.678845

(d) *t*-ts2

N	-1.097758	-0.03938	-0.067245
C	0.114018	0.62716	-0.516055
C	-2.240943	0.879014	0.015468
C	-0.099947	2.112336	-0.150467
C	1.335995	0.079335	0.193695
O	1.37622	-0.22107	1.371341
C	-1.611765	2.275062	0.131258
C	-1.19208	-1.382506	-0.141393
O	-0.2055	-2.070656	-0.462161
C	-2.525412	-1.993924	0.188975
H	-2.442846	-3.079795	0.13886
H	-3.28321	-1.652602	-0.524468
H	-2.851415	-1.695198	1.190138
H	0.248412	0.491278	-1.594776
H	-2.862499	0.627149	0.876949
H	-2.851041	0.787548	-0.890068
H	0.479777	2.363767	0.741852
H	0.245064	2.751018	-0.964769
H	-1.764966	2.680738	1.133211
H	-2.076223	2.961283	-0.579267
O	2.394915	0.047178	-0.612859
C	3.636058	-0.365573	-0.016067
H	4.371919	-0.324857	-0.81694
H	3.906879	0.319856	0.789396
H	3.543828	-1.383561	0.367539

(e) *c*Fu

N	-1.169925	0.001909	-0.102008
C	0.100383	0.559999	-0.557716
C	-2.056095	1.028849	0.463347
C	-0.009934	2.063637	-0.205844
C	1.288918	-0.03319	0.172397
O	1.237411	-0.587534	1.252523
C	-1.518961	2.309024	-0.16548
C	-1.499927	-1.303209	-0.102423
O	-2.560743	-1.693428	0.421879
C	-0.563532	-2.283255	-0.761164
H	-1.160872	-3.104492	-1.161783
H	0.120007	-2.692713	-0.009956
H	0.026773	-1.841449	-1.567494
H	0.233559	0.419233	-1.634863
H	-1.968501	1.043936	1.556793
H	-3.091734	0.809399	0.198609
H	0.422449	2.240465	0.785708
H	0.521932	2.678627	-0.933226
H	-1.783215	3.198129	0.410702
H	-1.914383	2.416916	-1.1809
O	2.418618	0.188375	-0.495034
C	3.631377	-0.244068	0.147904
H	4.434106	0.018718	-0.538208
H	3.752141	0.277316	1.099365
H	3.601548	-1.323469	0.308235

(f) *c*-ts1

N	1.188963	0.162904	0.209056
C	-0.137155	0.40163	0.75504
C	1.572591	1.249939	-0.698432
C	-0.263831	1.94394	0.790613
C	-1.208712	-0.203739	-0.142178
O	-1.00923	-0.668958	-1.247684
C	0.858437	2.480199	-0.128325
C	1.744487	-1.065914	0.090063
O	2.717906	-1.25431	-0.658329
C	1.162675	-2.178969	0.922383
H	1.806165	-3.054823	0.83563
H	0.160227	-2.441935	0.566497
H	1.082491	-1.886377	1.97325
H	-0.247252	-0.03334	1.751287
H	1.235726	1.013088	-1.715247
H	2.658297	1.353808	-0.712832
H	-1.256536	2.25993	0.462881
H	-0.128777	2.289487	1.816868
H	0.461663	3.104782	-0.930898
H	1.557298	3.086519	0.452283
O	-2.408147	-0.145673	0.431055
C	-3.511852	-0.633738	-0.352423
H	-3.36796	-1.692188	-0.577185
H	-4.394214	-0.491465	0.268512
H	-3.593948	-0.056375	-1.275212

(g) *c*Fd

N	1.178643	0.168052	0.178627
C	-0.139401	0.314851	0.777123
C	1.638592	1.40326	-0.480106
C	-0.271873	1.841891	0.927525
C	-1.228595	-0.216692	-0.145707
O	-1.070509	-0.501284	-1.317015
C	0.462265	2.369327	-0.308627
C	1.851606	-0.990669	0.048462
O	2.937017	-1.02915	-0.560373
C	1.259125	-2.221154	0.686475
H	1.952199	-3.052428	0.555097
H	0.302212	-2.47912	0.219839
H	1.082337	-2.060538	1.754319
H	-0.212158	-0.198776	1.738592
H	1.875997	1.201208	-1.527778
H	2.545903	1.763419	0.016076
H	-1.313568	2.163543	0.990827
H	0.244529	2.141729	1.844186
H	-0.19345	2.324704	-1.184278
H	0.797313	3.401248	-0.186895
O	-2.397618	-0.299837	0.484426
C	-3.51991	-0.716646	-0.313445
H	-4.371994	-0.722815	0.363465
H	-3.680577	-0.005352	-1.125907
H	-3.341217	-1.716036	-0.71443

(h) *c*-ts2

N	1.156915	0.086945	0.110492
C	-0.021421	-0.58757	-0.436964
C	2.305109	-0.813744	-0.130713
C	0.209357	-2.077106	-0.085927
C	-1.322647	-0.147269	0.201436
O	-1.461933	0.126622	1.377384
C	1.736057	-2.211904	0.112053
C	1.366457	1.431168	-0.013371
O	2.511358	1.895333	0.074479
C	0.180815	2.335764	-0.225405
H	0.550401	3.338372	-0.442336
H	-0.441483	2.374738	0.67344
H	-0.439641	1.997147	-1.06199
H	-0.081768	-0.443594	-1.521478
H	3.126587	-0.562305	0.53975
H	2.64555	-0.683148	-1.16565
H	-0.320332	-2.329443	0.836379
H	-0.177743	-2.712022	-0.884652
H	1.954965	-2.538235	1.131293
H	2.175812	-2.936421	-0.576054
O	-2.324742	-0.171675	-0.673873
C	-3.628819	0.142887	-0.153727
H	-4.308156	0.054111	-0.999189
H	-3.896724	-0.565946	0.632052
H	-3.63278	1.162536	0.236788

(3) Ac-Pro-NHMe

(a) *t*Fu

N	-1.111651	-0.043674	-0.124136
C	0.107785	0.666086	-0.506314
C	-2.172117	0.86199	0.344557
C	-0.177728	2.113378	-0.068384
C	1.333656	0.107718	0.205441
O	1.298501	-0.22455	1.400938
C	-1.700734	2.218153	-0.175043
C	-1.191378	-1.380525	-0.217198
O	-0.237073	-2.047377	-0.665686
C	-2.475307	-2.026816	0.229029
H	-2.346353	-3.109446	0.229314
H	-3.287519	-1.76246	-0.456705
H	-2.75919	-1.688869	1.230338

H	0.251909	0.602236	-1.591471
H	-2.224275	0.84795	1.439834
H	-3.139953	0.560602	-0.061084
H	0.131485	2.243654	0.975129
H	0.359507	2.834159	-0.687685
H	-2.111375	3.047452	0.404841
H	-1.999362	2.339126	-1.22182
N	2.457614	0.070686	-0.516426
H	2.422161	0.326488	-1.496288
C	3.718836	-0.364922	0.059929
H	4.487605	-0.304539	-0.709358
H	3.998854	0.276356	0.90001
H	3.645264	-1.396752	0.41476

(b) *t*-ts1

N	-1.147676	0.043033	-0.310214
C	0.149353	0.532	-0.75818
C	-1.827683	1.006666	0.568511
C	0.03492	2.068649	-0.662195
C	1.257269	0.01212	0.154538
O	1.070943	-0.139207	1.373581
C	-1.21407	2.364134	0.199774
C	-1.381773	-1.286888	-0.287133
O	-0.583993	-2.084924	-0.812559
C	-2.64251	-1.750756	0.388635
H	-2.76464	-2.821266	0.221717
H	-3.516647	-1.216062	0.005796
H	-2.578337	-1.557296	1.465478
H	0.337295	0.202643	-1.783311
H	-1.63422	0.750097	1.615722
H	-2.905802	0.976039	0.397873
H	0.942216	2.500185	-0.23179
H	-0.080448	2.482224	-1.665817
H	-0.957234	2.921958	1.102358
H	-1.928991	2.963186	-0.368512
N	2.441216	-0.208689	-0.423928
H	2.525932	-0.103647	-1.4282
C	3.605693	-0.612774	0.346849
H	3.451116	-1.596829	0.798213
H	4.462954	-0.658521	-0.32361
H	3.809223	0.111029	1.140107

(c) *t*Fd

N	-1.149299	0.051462	-0.294675
C	0.153218	0.507606	-0.766779
C	-1.960124	1.133752	0.292144
C	0.03347	2.041116	-0.696224
C	1.268093	-0.005122	0.142397
O	1.105167	-0.141532	1.365694
C	-0.955608	2.275817	0.44931
C	-1.420279	-1.262726	-0.226167
O	-0.595491	-2.105257	-0.633237
C	-2.745375	-1.665494	0.361683
H	-2.922232	-2.720855	0.151893
H	-3.563631	-1.064695	-0.045389
H	-2.724949	-1.515933	1.447115
H	0.331385	0.158227	-1.788071
H	-2.390991	0.816246	1.244045
H	-2.773597	1.402617	-0.391153
H	1.00245	2.522089	-0.540636
H	-0.384178	2.402834	-1.640866
H	-0.447456	2.194637	1.414872
H	-1.43817	3.253941	0.392481
N	2.440981	-0.241116	-0.45445
H	2.510204	-0.146977	-1.460909
C	3.61429	-0.648891	0.300121
H	4.459011	-0.710892	-0.384846
H	3.83929	0.080877	1.082112
H	3.457588	-1.626568	0.764669

(d) *t*-ts2

N	-1.10696	-0.04529	-0.071691
C	0.105986	0.629423	-0.513982
C	-2.255108	0.867973	0.000089
C	-0.123773	2.111548	-0.14918
C	1.344014	0.09488	0.194564
O	1.340971	-0.176709	1.405679
C	-1.635147	2.265574	0.135534
C	-1.205402	-1.387672	-0.139863
O	-0.224952	-2.086569	-0.45653
C	-2.542832	-1.993114	0.190227
H	-2.461936	-3.079527	0.148579
H	-3.297152	-1.656909	-0.529363
H	-2.873833	-1.687103	1.187464
H	0.225556	0.501414	-1.597274
H	-2.889895	0.607908	0.849382
H	-2.851177	0.780942	-0.915542
H	0.456405	2.366949	0.741846
H	0.215457	2.754016	-0.963543
H	-1.7905	2.655015	1.143763
H	-2.105058	2.959569	-0.563996
N	2.45065	0.028321	-0.552086
H	2.388403	0.235944	-1.541803
C	3.726385	-0.381576	0.010549
H	4.477157	-0.346954	-0.777901
H	4.022763	0.291533	0.819516
H	3.665094	-1.400005	0.404479

(e) *c*Au

N	1.027134	-0.059986	-0.038526
C	-0.001156	0.631351	0.741515
C	1.75928	0.859294	-0.920687
C	0.202294	2.127429	0.387727
C	-1.431055	0.231764	0.402458
O	-2.341985	0.491062	1.207284
C	1.618717	2.191402	-0.190816
C	1.361217	-1.360309	0.098582
O	2.237911	-1.878114	-0.616586
C	0.642923	-2.152278	1.161786
H	1.025685	-3.172962	1.155776
H	-0.437252	-2.176885	0.985538
H	0.810202	-1.706591	2.147839
H	0.142605	0.453715	1.811341
H	1.290358	0.887207	-1.912473
H	2.790895	0.521826	-1.028628
H	-0.526023	2.428774	-0.373014
H	0.060212	2.760395	1.265154
H	1.759124	3.046895	-0.855138
H	2.358297	2.247995	0.614511
N	-1.659584	-0.315204	-0.793943
H	-0.871778	-0.526318	-1.396375
C	-3.004059	-0.660514	-1.227331
H	-3.640244	0.228329	-1.24517
H	-2.943341	-1.077964	-2.231597
H	-3.447962	-1.400494	-0.555477

(f) *c*-ts1

N	1.037487	0.086916	0.002173
C	-0.064072	0.563653	0.82786
C	1.394414	1.045847	-1.048015
C	-0.005101	2.10484	0.69239
C	-1.439518	0.046468	0.408757
O	-2.415652	0.277835	1.143196
C	0.952005	2.40303	-0.484627
C	1.61672	-1.128878	0.095298
O	2.477779	-1.490989	-0.726131
C	1.207677	-2.011875	1.246767
H	1.708206	-2.97463	1.142298
H	0.125074	-2.169443	1.275214
H	1.504413	-1.551033	2.195143
H	0.073119	0.253742	1.866789
H	0.87329	0.795954	-1.980392
H	2.467725	0.99116	-1.236695
H	-1.004637	2.512612	0.525653
H	0.374641	2.534994	1.620691
H	0.46713	3.003488	-1.256792
H	1.82193	2.959148	-0.128171
N	-1.55527	-0.603576	-0.751235
H	-0.724718	-0.795739	-1.299315
C	-2.839729	-1.109573	-1.209076
H	-3.558358	-0.292107	-1.308333
H	-2.696538	-1.581776	-2.180056
H	-3.23819	-1.845598	-0.505245

(g) *c*Ad

N	-1.024408	0.17188	0.008789
C	0.087342	0.474722	-0.889884
C	-1.343897	1.293037	0.910988
C	0.135953	2.011993	-0.847447
C	1.42658	-0.117526	-0.450245
O	2.403049	-0.035906	-1.215711
C	-0.26065	2.328178	0.597954
C	-1.795684	-0.932837	-0.032685
O	-2.762311	-1.057339	0.741391
C	-1.46729	-1.985756	-1.059684
H	-2.039679	-2.885772	-0.833798
H	-0.401185	-2.227514	-1.082221
H	-1.750051	-1.623506	-2.054694
H	-0.106316	0.102921	-1.899066
H	-1.333004	0.957771	1.951705
H	-2.348346	1.6641	0.679136
H	1.116207	2.401019	-1.131089
H	-0.611934	2.401819	-1.544857
H	0.59753	2.192485	1.264083
H	-0.628704	3.348762	0.720396
N	1.504712	-0.679619	0.757791
H	0.665178	-0.739634	1.323043
C	2.746296	-1.253355	1.251888
H	2.569374	-1.646213	2.252295
H	3.081963	-2.065373	0.600874
H	3.52903	-0.491471	1.297384

(h) *c*-ts2

N	1.025842	0.16636	0.142056
C	0.113745	-0.669675	-0.650396
C	2.298751	-0.584369	0.243535
C	0.430506	-2.106004	-0.172031
C	-1.367617	-0.388897	-0.440424
O	-2.166533	-0.524193	-1.382058
C	1.859524	-2.039146	0.409911
C	1.11246	1.523894	-0.015314
O	2.137265	2.126941	0.329313
C	-0.064192	2.271524	-0.587583
H	0.247955	3.296525	-0.789699
H	-0.895931	2.289602	0.123526
H	-0.416929	1.8135	-1.517153

H	0.32303	-0.554411	-1.720361	N	-1.760523	-0.079233	0.798168
H	2.887807	-0.212652	1.081886	H	-1.050307	0.081372	1.503414
H	2.870528	-0.432958	-0.680756	C	-3.143161	0.248359	1.101007
H	-0.28361	-2.411955	0.596252	H	-3.219695	0.459992	2.167098
H	0.343309	-2.803109	-1.007613	H	-3.467992	1.127176	0.534248
H	1.849825	-2.313141	1.467421	H	-3.797263	-0.592202	0.85554
H	2.546095	-2.713736	-0.105639				

Cartesian coordinates of transition state ts1 for puckering transition of Ac-*trans*-X-OMe optimized at SMD M06-2X/6-31+G(d) level of theory in water**:**

(a) Ac-Hyp-OMe

N	0.899842	0.471636	-0.269353
C	-0.236833	-0.295161	-0.746442
C	1.666342	-0.291762	0.723429
C	0.230424	-1.756745	-0.632854
C	-1.462237	-0.030354	0.11854
O	-1.442957	0.525373	1.199585
C	1.377558	-1.765689	0.392504
C	0.863542	1.824745	-0.321054
O	-0.029788	2.413188	-0.951433
C	1.95673	2.561728	0.40098
H	1.864024	3.628625	0.197175
H	2.942013	2.209022	0.081409
H	1.873028	2.389417	1.479761
H	-0.485779	-0.028117	-1.775272
H	1.323237	-0.043871	1.734472
H	2.734319	-0.074644	0.64695
H	-0.584528	-2.429342	-0.358613
H	0.629859	-2.079012	-1.597806
H	1.10132	-2.305165	1.302597
O	-2.564035	-0.52008	-0.443563
C	-3.77786	-0.401677	0.319544
H	-4.003282	0.651209	0.498261
H	-4.552079	-0.860311	-0.292429
H	-3.672102	-0.933132	1.267391
O	2.491446	-2.415882	-0.214685
H	3.187741	-2.517433	0.454467

(b) Ac-hyp-OMe

N	-1.052458	-0.360353	-0.392846
C	0.230113	0.111042	-0.890642
C	-1.757532	0.691047	0.341562
C	0.044045	1.633791	-1.051163
C	1.335117	-0.200065	0.107024
O	1.156546	-0.45746	1.281872
C	-1.240887	2.002315	-0.274218
C	-1.236865	-1.68698	-0.190426
O	-0.405605	-2.51108	-0.604918
C	-2.486785	-2.101098	0.534804
H	-2.554997	-3.189077	0.537203
H	-3.374658	-1.676633	0.05669
H	-2.455765	-1.737012	1.567777
H	0.47917	-0.375015	-1.835718
H	-1.49488	0.659073	1.407466
H	-2.838219	0.578617	0.240658
H	0.898408	2.189791	-0.654069
H	-0.055063	1.883219	-2.108803
H	-1.983476	2.420362	-0.954984
O	2.53624	-0.11288	-0.458476
C	3.66471	-0.320955	0.409284
H	3.624944	-1.326128	0.833016
H	4.543164	-0.20677	-0.222814
H	3.662925	0.427504	1.204225
O	-1.041267	3.006757	0.709841
H	-0.363145	2.697264	1.335378

(c) Ac-Flp-OMe

N	0.924678	0.431857	-0.278586
C	-0.235364	-0.300675	-0.756354
C	1.630108	-0.34616	0.747741
C	0.196904	-1.772926	-0.646468
C	-1.452043	0.004295	0.10974
O	-1.415682	0.599816	1.168502
C	1.302368	-1.800033	0.415826
C	0.928654	1.788029	-0.33087
O	0.071826	2.399076	-0.986902
C	2.016539	2.493631	0.428126
H	1.985438	3.557587	0.192829
H	3.001039	2.086925	0.17895
H	1.859698	2.355625	1.504138
H	-0.476756	-0.02671	-1.785058
H	1.254988	-0.088134	1.744484
H	2.707451	-0.172495	0.715483
H	-0.636837	-2.434671	-0.406045
H	0.629971	-2.092416	-1.597415
H	1.047143	-2.376646	1.304307
O	-2.5647	-0.486614	-0.427936
C	-3.774244	-0.29442	0.327605
H	-3.971805	0.772644	0.445395
H	-4.560899	-0.767799	-0.256488
H	-3.680442	-0.773181	1.304192
F	2.439909	-2.421378	-0.132893

(d) Ac-flp-OMe

N	1.030242	-0.37338	0.37219
C	-0.239822	0.138329	0.861617
C	1.776986	0.649655	-0.35842

C	-0.023852	1.663816	0.977006
C	-1.360545	-0.183039	-0.115923
O	-1.197926	-0.507442	-1.275629
C	1.308787	1.958286	0.276716
C	1.194303	-1.70794	0.205594
O	0.348049	-2.505411	0.63905
C	2.440468	-2.160383	-0.503006
H	2.476439	-3.249833	-0.50009
H	3.333748	-1.761115	-0.012925
H	2.435271	-1.798966	-1.53721
H	-0.489257	-0.311614	1.824466
H	1.50629	0.649182	-1.42211
H	2.851944	0.495598	-0.25915
H	-0.825251	2.226743	0.490885
H	0.010161	1.960823	2.025569
H	2.048725	2.375758	0.959971
O	-2.552782	-0.020339	0.450968
C	-3.695947	-0.220275	-0.39927
H	-3.701566	-1.243061	-0.780099
H	-4.563098	-0.042747	0.233854
H	-3.671313	0.493843	-1.224806
F	1.132803	2.917099	-0.731632

(e) Ac-mep-OMe

N	0.849375	0.508672	-0.225256
C	-0.214495	-0.365065	-0.684035
C	1.680267	-0.154915	0.788049
C	0.326639	-1.792931	-0.450666
C	-1.480413	-0.129441	0.124847
O	-1.523134	0.431204	1.203153
C	1.581485	-1.652394	0.449335
C	0.703426	1.848425	-0.336436
O	-0.226734	2.334032	-1.004047
C	1.715717	2.70878	0.367787
H	2.733377	2.449347	0.060405
H	1.64542	2.55734	1.450717
H	1.517591	3.755378	0.135661
H	-0.444063	-0.177714	-1.734913
H	1.282829	0.058842	1.787659
H	2.708151	0.212408	0.736359
H	-0.435488	-2.432324	0.002262
H	0.596092	-2.236177	-1.413015
H	1.442028	-2.215961	1.375805
O	-2.543273	-0.661934	-0.47441
C	-3.786184	-0.590982	0.246102
H	-4.050534	0.451793	0.431009
H	-4.524236	-1.063104	-0.399452
H	-3.697682	-1.132355	1.190182
C	2.834876	-2.161523	-0.258173
H	3.714825	-2.074046	0.387744
H	2.720878	-3.214082	-0.538916
H	3.0224	-1.586205	-1.173144

(f) Ac-Mep-OMe

N	-1.078489	-0.344997	-0.420189
C	0.2239	0.057394	-0.922334
C	-1.73642	0.760425	0.28979
C	0.095914	1.5785	-1.143771
C	1.30615	-0.254544	0.099381
O	1.108107	-0.456569	1.282241
C	-1.129147	2.040122	-0.314499
C	-1.311025	-1.653858	-0.16571
O	-0.512759	-2.527053	-0.547225
C	-2.57298	-1.993315	0.577493
H	-2.691519	-3.076687	0.605726
H	-3.44515	-1.538256	0.098835
H	-2.514315	-1.608491	1.601901
H	0.46723	-0.474904	-1.843932
H	-1.51711	0.694478	1.363815
H	-2.818695	0.707903	0.155179
H	1.009697	2.099722	-0.841969
H	-0.058234	1.77007	-2.207406
H	-1.859885	2.489008	-0.993538
O	2.51641	-0.242835	-0.455498
C	3.625379	-0.460006	0.434662
H	3.537723	-1.442789	0.901563
H	4.515345	-0.411606	-0.18977
H	3.647189	0.321409	1.196943
C	-0.767766	3.053249	0.766276
H	-0.361721	3.969014	0.324479
H	-1.646407	3.324628	1.361926
H	-0.012825	2.635334	1.44371

(g) Ac-Clp-OMe

N	0.366355	0.886525	-0.27224
C	-0.377157	-0.2659	-0.746761
C	1.328349	0.493102	0.764191
C	0.623066	-1.427675	-0.618379
C	-1.616826	-0.489799	0.110838
O	-1.822908	0.047141	1.181512
C	1.620405	-0.98397	0.46819
C	-0.204487	2.117057	-0.338924
O	-1.234295	2.299422	-1.005284
C	0.470409	3.225542	0.418145
H	-0.0037	4.173019	0.16148

H	1.538972	3.271638	0.188995
H	0.365513	3.049217	1.494964
H	-0.698957	-0.127039	-1.780426
H	0.875585	0.585792	1.757851
H	2.222021	1.117101	0.72551
H	0.136067	-2.370307	-0.36076
H	1.133045	-1.555379	-1.574938
H	1.540009	-1.583618	1.372424
O	-2.437682	-1.374563	-0.447324
C	-3.613696	-1.717743	0.308789
H	-4.227926	-0.828752	0.463501
H	-4.14465	-2.449721	-0.296542
H	-3.322858	-2.149708	1.268267
Cl	3.329475	-1.224565	-0.09073

(h) Ac-clp-OMe

N	0.034414	-1.192515	0.451176
C	-0.398657	0.096369	0.962654
C	1.344782	-1.083471	-0.195447
C	0.913599	0.830771	1.306781
C	-1.193597	0.850123	-0.094963
O	-1.210903	0.571942	-1.277968
C	2.025777	0.056235	0.573958
C	-0.901647	-2.113659	0.10293
O	-2.088133	-1.958214	0.426829
C	-0.427589	-3.313408	-0.66792
H	-1.256154	-4.012038	-0.784597
H	0.403393	-3.808621	-0.156959
H	-0.074754	-3.001768	-1.657674
H	-1.034464	-0.028016	1.841031
H	1.228022	-0.82715	-1.254949
H	1.902415	-2.01727	-0.111951
H	0.878428	1.881712	1.012725
H	1.086408	0.787889	2.383303
H	2.759273	-0.330622	1.278291
O	-1.845454	1.8796	0.437046
C	-2.579246	2.712615	-0.478521
H	-3.354262	2.1253	-0.974282
H	-3.025355	3.49374	0.134015
H	-1.898121	3.143985	-1.214385
Cl	2.97645	1.10473	-0.552757

(i) Ac-mpc-OMe

N	0.361422	0.879991	-0.261327
C	-0.373685	-0.279995	-0.728572
C	1.316168	0.500709	0.787418
C	0.62018	-1.444189	-0.567429
C	-1.624825	-0.491318	0.114633
O	-1.847151	0.059348	1.175095
C	1.644035	-0.973173	0.49314
C	-0.211371	2.106974	-0.35014
O	-1.234977	2.280097	-1.030087
C	0.451102	3.227265	0.401185
H	-0.031155	4.168428	0.136545
H	1.519623	3.281876	0.17355
H	0.346448	3.05784	1.479066
H	-0.683455	-0.155085	-1.767821
H	0.846255	0.59036	1.774041
H	2.194499	1.147798	0.758791
H	0.123616	-2.369744	-0.269418
H	1.102523	-1.619829	-1.532962
H	1.555412	-1.561039	1.406589
O	-2.439026	-1.383052	-0.443532
C	-3.62765	-1.713109	0.298055
H	-4.243922	-0.821549	0.427878
H	-4.148902	-2.454711	-0.304029
H	-3.354138	-2.129638	1.269428
S	3.32802	-1.234598	-0.18242
H	4.000437	-0.791214	0.894808

(j) Ac-Mpc-OMe

N	0.023368	1.212213	0.460001
C	0.401224	-0.08981	0.980765
C	-1.311895	1.174218	-0.147145
C	-0.937296	-0.748707	1.365328
C	1.123483	-0.901066	-0.085295
O	1.07363	-0.675172	-1.279117
C	-2.028011	0.020714	0.581317
C	0.996844	2.075244	0.075832
O	2.184811	1.854524	0.358936
C	0.567233	3.2939	-0.691389
H	1.42329	3.957402	-0.815377
H	-0.240623	3.823661	-0.178761
H	0.196762	2.993872	-1.678453
H	1.066335	0.012739	1.840001
H	-1.229174	0.979975	-1.222945
H	-1.82935	2.124501	-0.002601
H	-0.936575	-1.818601	1.145236
H	-1.099495	-0.628886	2.438355
H	-2.757146	0.428705	1.283378
O	1.786929	-1.920978	0.45117
C	2.465233	-2.797546	-0.465798
H	3.238464	-2.244352	-1.002209
H	2.911709	-3.574231	0.152127
H	1.750238	-3.229812	-1.168108

S	-3.041563	-1.006182	-0.539999
H	-2.016855	-1.440242	-1.300259

(k) Ac-mop-OMe

N	-0.196115	1.07723	0.470241
C	0.519367	-0.093043	0.948959
C	-1.492829	0.711022	-0.101556
C	-0.592028	-1.102363	1.303239
C	1.430513	-0.63943	-0.140097
O	1.336651	-0.371312	-1.32205
C	-1.881215	-0.578915	0.645695
C	0.502595	2.184389	0.12065
O	1.709385	2.283514	0.3954
C	-0.252096	3.272937	-0.589574
H	0.40882	4.127451	-0.735952
H	-1.130081	3.578828	-0.012538
H	-0.600862	2.911845	-1.563317
H	1.13592	0.158688	1.813587
H	-1.39246	0.496002	-1.174103
H	-2.214855	1.517576	0.034815
H	-0.363851	-2.1053	0.932521
H	-0.705013	-1.160625	2.386475
H	-2.641733	-0.363116	1.406407
O	2.330064	-1.482958	0.359794
C	3.217935	-2.103286	-0.587435
H	3.787382	-1.337392	-1.117143
H	3.879802	-2.732109	0.004738
H	2.645054	-2.707431	-1.293585
O	-2.392331	-1.566276	-0.234057
C	-3.668974	-1.218799	-0.749826
H	-3.621641	-0.302687	-1.352067
H	-3.995829	-2.046025	-1.381937
H	-4.387604	-1.075137	0.067394