Supporting information for

Solvation of the Boc-Val-Phe-*n*Pr peptide characterized by VCD spectroscopy and DFT calculations

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1. Conformational analysis

Table S1. Conformations and relative energies of LL-**2** obtained at B3LYP/6-31G+(2d,p)/IEFPCM($CHCl_3$) level of theory. Relative zero-point corrected and Gibbs Free energies, ΔE_{ZPC} and ΔG_{298K}, are given in kcal/mol and the corresponding Boltzmann weights χ in percentage.

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C^{α}-C(H)-$C(H_3)$	Phe Side N-C^{α}-$C(H_2)$-C_{Ar}	Boc	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
(γ,β)	79.0	-58.5	-144.1	157.7	-174.6	67.2	T	5.32	7.18	0.00	0.00
	84.0	-60.0	-145.4	157.4	-144.9	65.9	C	7.71	10.22	0.00	0.00
	77.1	-59.7	-114.5	113.9	-178.2	-173.6	T	3.06	4.03	0.07	0.04
	82.3	-59.9	-147.4	134.4	-145.4	-174.4	C	5.75	7.28	0.00	0.00
	64.2	-24.9	-137.2	157.2	-56.1	67.9	T	8.46	10.28	0.00	0.00
	73.8	-31.0	-153.9	160.2	-34.0	62.4	C	12.04	15.45	0.00	0.00
	64.6	-31.4	-120.6	117.8	-55.5	-174.5	T	5.75	6.23	0.00	0.00
	64.4	-25.9	-139.8	156.8	-55.9	69.8	T	8.52	10.86	0.00	0.00
(γ,γ')	62.8	-55.5	-85.0	54.9	70.7	46.5	T	9.70	12.90	0.00	0.00
	66.5	-42.9	-84.6	83.3	80.9	-166.3	T	6.39	7.92	0.00	0.00
	89.0	-6.1	-85.0	84.8	153.7	-166.4	C	10.35	12.24	0.00	0.00
	64.2	-44.6	-82.8	74.0	74.4	-67.0	T	6.40	7.83	0.00	0.00
	63.5	-47.8	-85.8	58.0	-58.5	44.4	T	9.01	11.54	0.00	0.00
	63.2	-36.8	-85.6	82.9	-56.7	-165.4	T	5.53	7.32	0.00	0.00
	62.4	-37.2	-84.1	73.9	-58.4	-66.9	T	5.47	7.68	0.00	0.00
	75.5	-67.7	-84.8	55.3	-177.0	45.0	T	5.03	7.51	0.00	0.00
	76.0	-60.3	-83.6	83.4	-178.6	-165.4	T	2.54	4.38	0.16	0.02
	81.3	-63.5	-85.2	84.0	-143.4	-165.1	C	6.34	9.62	0.00	0.00
	75.8	-61.0	-83.6	72.1	-178.4	-64.7	T	2.21	4.00	0.27	0.04
(β,γ')	-103.7	123.4	-83.0	53.8	177.2	44.7	T	2.30	3.64	0.24	0.08
	-116.2	125.2	-83.0	55.6	-172.9	43.6	C	4.23	5.68	0.01	0.00
	-105.9	121.1	-85.9	85.7	176.9	-166.2	T	1.26	2.08	1.37	1.07
	-104.3	121.5	-85.6	86.5	-173.8	-166.4	C	2.91	3.36	0.08	0.12
	-118.5	125.8	-84.5	75.0	177.2	-63.0	T	1.13	2.39	1.70	0.64
	-120.6	127.3	-84.0	75.8	-172.9	-62.2	C	2.99	4.21	0.07	0.03
	-140.9	146.3	-84.4	56.2	63.1	43.4	T	3.21	4.98	0.05	0.01
	-149.1	149.0	-84.1	56.0	93.6	43.3	C	4.73	6.56	0.00	0.00
	-143.9	149.7	-85.9	89.2	64.8	-167.5	T	1.86	2.49	0.50	0.54
	-150.0	148.1	-87.3	89.4	93.9	-167.5	C	3.49	4.39	0.03	0.02
	-143.6	149.9	-85.7	75.8	64.9	-60.7	T	1.68	2.62	0.68	0.43
	-117.6	155.3	-84.4	56.4	-67.3	43.3	T	2.66	4.12	0.13	0.03
	-119.8	154.9	-83.8	56.5	-93.8	43.1	C	4.59	5.98	0.00	0.00
	-120.8	156.8	-86.3	90.4	-66.1	-168.2	T	1.45	2.36	1.00	0.67
	-119.4	153.5	-87.0	90.6	-93.6	-168.6	C	3.19	3.90	0.05	0.05
	-121.1	157.1	-85.8	75.9	-66.1	-61.2	T	1.27	2.36	1.34	0.68
	-120.3	156.0	-85.3	77.2	-94.2	-60.2	C	3.06	4.29	0.07	0.03
(β,β)	-146.0	149.9	-153.8	162.8	65.1	61.8	T	1.81	2.85	0.55	0.29
	-146.1	150.9	-153.1	143.7	65.4	-173.5	T	0.66	1.57	3.75	2.54

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C^{α}-C(H)-$C(H_3)$	Phe Side N-C^{α}-$C(H_2)$-C_{Ar}	Boc	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-149.5	149.1	-154.4	147.6	93.0	-173.0	C	2.08	3.18	0.34	0.17
	-121.6	159.5	-151.0	162.3	-65.4	61.7	T	1.23	1.86	1.44	1.56
	-124.3	157.5	-152.8	164.3	-74.4	61.4	C	3.03	4.25	0.07	0.03
	-120.8	159.2	-151.5	144.9	-65.5	-173.4	T	0.05	0.00	10.54	36.09
	-122.7	157.7	-152.0	146.6	-75.6	-173.3	C	1.93	3.04	0.44	0.21
	-121.4	156.9	-121.1	139.5	-65.9	-64.0	T	1.21	1.60	1.48	2.43
	-124.6	156.8	-124.7	143.2	-85.5	-62.8	C	2.97	3.32	0.08	0.13
	-118.1	128.6	-150.1	162.3	175.7	63.6	T	1.42	2.30	1.05	0.75
	-123.2	127.8	-150.7	162.9	-166.1	61.9	C	2.92	3.94	0.08	0.05
	-111.2	126.2	-150.9	144.2	175.9	-173.1	T	0.07	0.30	10.21	21.82
	-111.6	123.7	-153.2	146.7	-166.9	-172.7	C	1.47	1.09	0.97	5.76
	-150.7	147.2	-155.6	163.4	93.6	60.8	C	3.16	4.26	0.06	0.03
(α',β)	61.0	35.3	-150.0	145.2	-24.8	-173.4	C	7.30	8.89	0.00	0.00
(α',γ')	60.0	36.8	-85.4	85.9	-35.6	-168.0	C	7.87	10.07	0.00	0.00
(δ,γ')	-81.9	-31.8	-83.8	52.0	170.2	45.2	C	3.41	5.10	0.04	0.01
	-83.9	-31.7	-83.4	53.6	-151.6	44.0	T	4.64	6.96	0.00	0.00
	-82.8	-31.6	-85.0	83.3	171.0	-165.7	C	2.34	3.32	0.22	0.13
	-83.1	-29.9	-84.7	72.8	170.5	-62.4	T	1.96	3.47	0.42	0.10
	-84.8	-29.0	-84.5	72.2	-152.0	-62.6	C	3.14	5.53	0.06	0.00
	-108.9	-2.6	-84.0	54.6	-65.0	44.0	T	2.14	4.12	0.31	0.03
	-106.2	-3.2	-83.1	53.0	14.2	45.0	C	3.45	5.50	0.03	0.00
	-111.4	-0.9	-85.6	81.7	-65.1	-165.1	T	0.91	2.19	2.47	0.89
	-100.7	-5.9	-85.2	83.7	13.5	-165.9	C	2.04	3.20	0.37	0.16
	-112.6	2.6	-84.4	71.6	-65.3	-61.7	T	0.34	1.65	6.51	2.24
	-107.0	-0.2	-84.4	73.2	7.7	-62.4	C	1.66	2.75	0.70	0.34
	-91.2	-17.4	-84.0	54.7	70.3	43.9	T	3.72	5.89	0.02	0.00
	-89.9	-18.0	-83.3	53.9	121.6	44.2	C	4.91	7.29	0.00	0.00
	-94.6	-15.3	-85.7	81.7	71.3	-165.1	T	2.56	4.17	0.15	0.03
	-90.2	-17.5	-84.9	84.4	120.5	-165.4	C	3.64	5.82	0.02	0.00
	-103.0	-7.8	-83.9	71.4	72.0	-62.4	T	2.20	3.64	0.28	0.08
	-92.5	-13.2	-83.4	73.0	121.8	-62.2	C	3.20	4.72	0.05	0.01
(δ,β)	-80.3	-31.3	-145.6	160.8	173.0	62.9	T	2.87	4.41	0.09	0.02
	-82.0	-32.3	-146.2	162.4	-154.2	63.1	C	3.96	5.29	0.01	0.00
	-80.1	-31.0	-146.6	143.7	171.4	-173.4	T	1.42	1.97	1.05	1.31
	-80.0	-32.8	-148.2	142.6	-154.5	-172.9	C	2.41	2.51	0.20	0.52
	-84.3	-30.8	-114.1	130.4	171.2	-62.8	T	2.65	3.15	0.13	0.18
	-84.1	-30.8	-100.7	128.5	-152.8	-62.4	C	3.73	4.66	0.02	0.01
	-113.1	4.4	-145.0	161.4	-65.2	62.9	T	1.40	2.45	1.07	0.58
	-109.9	2.8	-143.0	161.3	-0.3	64.6	C	3.11	4.28	0.06	0.03
	-108.7	-0.1	-149.8	142.0	-65.5	-173.2	T	0.00	0.86	11.52	8.38
	-101.4	-4.1	-148.8	140.6	16.5	-173.8	C	1.44	1.48	1.01	2.97
	-113.4	0.9	-108.8	125.6	-65.5	-61.8	T	1.26	1.81	1.37	1.71
	-106.9	-4.8	-143.9	161.0	73.3	65.2	T	3.40	4.82	0.04	0.01
	-97.6	-10.4	-139.5	161.1	112.4	66.3	C	4.82	5.87	0.00	0.00

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C^{α}-C(H)-$C(H_3)$	Phe Side N-C^{α}-$C(H_2)$-C_{Ar}	Boc	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-89.9	-16.8	-150.0	144.1	70.3	-173.3	T	1.66	2.54	0.70	0.50
	-85.4	-20.4	-148.6	143.2	108.4	-173.6	C	2.72	3.34	0.12	0.13
	-96.4	-15.3	-111.3	126.5	69.6	-63.3	T	3.23	4.03	0.05	0.04
	-89.1	-16.3	-90.0	122.5	119.4	-62.1	C	4.17	5.40	0.01	0.00
	-108.2	-0.7	-99.2	126.3	8.8	-62.4	C	2.41	3.05	0.20	0.21
(γ',β)	-88.4	65.5	-147.7	134.3	-73.7	-173.7	T	2.28	3.04	0.24	0.21
	-94.3	62.8	-149.2	140.7	-38.8	-173.4	C	4.01	4.69	0.01	0.01
	-88.7	54.8	-113.7	122.8	-71.2	-65.4	T	3.27	3.99	0.05	0.04
	-96.7	65.8	-154.7	162.2	61.5	62.7	T	5.60	6.82	0.00	0.00
	-90.3	68.6	-124.7	134.9	60.7	-66.1	T	4.45	5.20	0.01	0.01
	-94.0	73.2	-128.1	138.4	89.0	-65.3	C	6.25	8.01	0.00	0.00
	-86.1	56.5	-86.5	82.7	-71.5	-165.4	T	2.38	3.76	0.21	0.06
	-88.7	46.5	-85.7	72.3	-69.4	-67.4	T	2.63	4.54	0.14	0.02
	-86.6	70.7	-88.2	82.4	60.4	-165.7	T	3.49	4.91	0.03	0.01
	-91.3	55.3	-87.1	74.0	65.6	-69.3	T	4.28	6.66	0.01	0.00
(δ,δ)	-77.5	-11.4	-84.2	-7.8	60.4	-63.3	T	0.04	2.30	10.75	0.75
	-68.5	-28.2	-79.9	-7.1	-66.5	-62.9	T	0.04	2.77	10.82	0.34
	-77.7	-11.3	-73.6	-22.1	60.6	-170.1	T	1.19	3.64	1.54	0.08
	-68.0	-30.2	-88.0	3.0	-66.8	56.3	T	1.16	3.24	1.63	0.15
	-78.0	-11.7	-93.4	1.5	60.5	56.5	T	2.48	4.16	0.18	0.03
	-73.4	-19.9	-90.0	1.0	-163.3	56.6	T	1.01	3.63	2.09	0.08
	-73.2	-19.0	-80.9	-8.5	-164.6	-63.9	T	1.16	3.65	1.64	0.08
	-72.7	-19.7	-69.7	-23.9	-163.8	-171.2	T	3.72	6.37	0.02	0.00
	-68.8	-28.4	-71.9	-19.6	-65.9	-168.1	T	4.12	7.06	0.01	0.00
(β,δ)	-120.8	119.2	-100.2	-7.3	-60.5	-65.8	T	2.07	2.75	0.35	0.35
	-89.2	112.4	-108.3	0.6	-59.4	58.5	T	1.46	2.76	0.98	0.34
	-119.6	157.6	-110.2	3.2	59.5	55.7	T	1.77	3.38	0.58	0.12
	-121.8	159.0	-103.1	-4.8	58.8	-63.7	T	2.05	2.99	0.36	0.23
	-133.7	136.6	-116.0	2.3	-173.1	56.6	T	2.85	3.93	0.09	0.05
	-120.2	158.2	-83.5	-28.1	59.7	-171.7	T	4.30	5.05	0.01	0.01
	-143.6	150.7	-101.2	-6.3	-164.9	-63.0	T	2.99	4.50	0.07	0.02
(γ',δ)	-85.2	84.5	-79.4	-30.5	-54.0	-173.4	T	3.52	4.52	0.03	0.02

Table S2. Conformations and relative energies of LL-**2**·(DMSO-d_6) obtained at B3LYP/6-31G+(2d,p)/ IEFPCM(DMSO) level of theory. Relative zero-point corrected and Gibbs Free energies, ΔE_{ZPC} and ΔG_{298K}, are given in kcal/mol and the corresponding Boltzmann weights χ in percentage. Only trans-Boc structures.

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C$^{\alpha}$-C(H)-C(H$_3$)	Phe Side N-C$^{\alpha}$-C(H$_2$)-C$_{Ar}$	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
(β,β)	-121.9	158.4	-127.3	140.7	59.6	-63.9	0.49	0.59	4.62	4.27
	-112.3	124.6	-148.2	130.7	-59.9	-175.9	0.55	0.63	4.13	3.97
	-120.1	158.1	-148.6	129.5	59.8	-175.9	0.59	0.69	3.89	3.60
	-121.8	160.4	-146.9	130.2	60.2	-175.7	0.60	0.62	3.79	4.01
	-120.9	127.3	-127.3	141.4	-60.0	-64.6	0.63	0.74	3.64	3.29
	-120.7	127.4	-128.7	140.3	-60.4	-64.3	0.78	0.89	2.82	2.54
	-117.9	128.7	-150.9	161.0	-60.4	64.1	0.88	0.93	2.39	2.40
	-117.7	125.4	-99.7	119.0	-60.5	-174.2	1.10	0.83	1.64	2.84
	-145.4	149.3	-129.7	141.8	-167.2	-63.6	1.14	1.24	1.54	1.41
	-146.2	150.9	-147.5	129.5	-166.8	-176.1	1.14	1.18	1.52	1.56
	-145.9	151.1	-148.0	130.2	-166.7	-175.9	1.16	1.17	1.48	1.59
	-146.0	150.5	-128.4	139.6	-166.5	-63.7	1.21	1.25	1.35	1.39
	-145.0	149.2	-154.4	161.8	-167.4	63.2	1.26	1.24	1.26	1.42
	-116.5	125.9	-101.4	118.6	-60.7	-173.7	1.37	1.51	1.04	0.89
	-121.1	155.9	-108.5	117.5	59.6	-173.8	1.57	1.74	0.74	0.61
	-120.9	155.4	-115.5	126.7	59.9	-65.1	1.64	1.92	0.66	0.45
	-121.1	126.8	-107.7	125.8	-60.8	-67.2	1.64	1.88	0.65	0.48
	-120.9	155.4	-115.5	126.7	59.9	-65.1	1.65	1.92	0.65	0.45
	-95.8	115.0	-151.0	139.2	-58.9	-174.2	1.83	2.05	0.48	0.36
	-110.0	120.2	-124.9	140.0	-59.4	-66.1	2.28	2.61	0.22	0.14
	-110.3	121.8	-124.8	142.8	-59.6	-65.7	2.44	2.71	0.17	0.12
	-143.7	143.0	-123.4	118.3	-171.1	-174.4	2.45	2.61	0.17	0.14
	-141.4	141.0	-109.2	117.8	-171.7	-173.9	2.58	2.73	0.13	0.11
	-145.2	141.1	-116.8	128.1	-172.1	-66.6	2.63	2.95	0.12	0.08
	-105.9	121.8	-150.0	160.3	-59.7	64.7	2.65	2.87	0.12	0.09
	-110.3	156.1	-125.6	142.8	64.5	-64.5	3.29	3.56	0.04	0.03
	-100.9	158.3	-149.3	139.6	66.8	-174.8	3.30	3.38	0.04	0.04
	-103.7	160.7	-148.8	139.9	64.6	-174.7	3.48	3.62	0.03	0.03
	-107.2	139.8	-150.2	139.1	-165.7	-174.4	3.89	4.05	0.01	0.01
	-125.5	130.6	-144.1	158.4	-60.9	63.7	3.95	4.22	0.01	0.01
	-145.1	138.9	-150.3	157.1	-173.1	63.4	4.06	4.24	0.01	0.01
	-94.0	142.5	-150.3	138.3	-163.2	-175.0	4.19	4.27	0.01	0.01
	-116.0	139.2	-126.7	141.1	-166.3	-65.0	4.43	4.60	0.01	0.00
	-117.8	137.4	-152.8	162.0	-167.2	64.2	4.54	4.69	0.00	0.00
(β,δ)	-119.3	120.0	-110.0	-37.6	-59.1	-66.1	0.56	0.71	4.04	3.49
	-121.0	155.7	-109.1	-37.4	59.6	-65.3	0.59	0.67	3.86	3.73
	-120.9	123.0	-110.5	-35.9	-60.1	-65.0	0.62	0.78	3.69	3.08
	-107.0	118.0	-117.3	-51.5	-59.5	-176.1	1.15	1.27	1.51	1.34
	-121.0	158.1	-109.5	-49.0	59.6	-175.9	1.20	1.18	1.38	1.55
	-111.6	123.4	-114.1	-49.2	-60.5	-175.5	1.21	1.29	1.36	1.31
	-121.3	157.8	-107.4	-49.2	59.6	-175.6	1.29	1.28	1.19	1.31

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C^{α}-C(H)-$C(H_3)$	Phe Side N-C^{α}-$C(H_2)$-C_{Ar}	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-112.2	120.9	-135.6	-14.8	-60.6	62.7	1.51	1.57	0.82	0.81
	-143.1	139.8	-115.7	-41.9	-171.0	-65.5	1.72	1.76	0.57	0.58
	-115.8	121.4	-129.9	-15.9	-60.7	63.5	1.77	1.87	0.53	0.49
	-120.2	154.2	-132.9	-15.3	59.5	62.2	1.78	1.76	0.52	0.58
	-120.4	153.9	-131.8	-16.4	59.8	63.0	1.92	1.88	0.41	0.48
	-145.0	143.9	-119.2	-51.1	-169.9	-175.0	2.15	2.11	0.28	0.32
	-145.0	143.7	-118.4	-51.4	-169.9	-175.0	2.23	2.19	0.24	0.28
	-91.9	100.3	-99.4	-6.4	-57.3	60.4	2.56	2.70	0.14	0.12
	-141.8	135.1	-138.1	-18.0	-174.9	64.0	3.05	3.08	0.06	0.06
	-87.1	82.1	-76.5	-33.4	-53.4	-174.4	3.18	3.29	0.05	0.04
	-134.5	130.5	-140.1	-17.7	-175.1	62.2	3.36	3.33	0.04	0.04
	-122.3	156.7	-112.3	-99.1	59.5	-67.0	3.71	3.97	0.02	0.01
	-99.7	155.5	-106.8	-2.4	65.3	57.4	4.05	4.08	0.01	0.01
	-107.7	157.0	-105.4	-2.1	62.9	57.0	4.33	4.32	0.01	0.01
	-142.8	141.0	-113.5	-97.8	-172.1	-68.7	4.70	4.98	0.00	0.00
	-112.8	120.3	-108.7	-88.5	-59.0	-68.3	5.16	5.35	0.00	0.00
	-112.6	123.8	-106.0	-3.8	-171.9	57.5	5.22	5.21	0.00	0.00
	-105.8	158.7	-76.6	-34.5	62.9	-173.5	5.32	5.37	0.00	0.00
	-109.1	157.1	-107.9	-87.8	64.1	-66.6	6.19	6.44	0.00	0.00
	-145.9	154.4	-92.7	-18.1	-162.4	58.6	6.48	6.59	0.00	0.00
	-112.2	141.7	-109.1	-95.2	-164.7	-68.0	7.59	7.74	0.00	0.00
	-95.0	142.4	-126.6	-73.3	-163.5	-174.1	7.81	7.87	0.00	0.00
	-120.4	153.9	-131.8	-16.4	59.8	63.0	1.92	1.88	0.41	0.48
(δ,β)	-100.9	-27.7	-130.2	116.6	-162.6	-174.4	3.30	3.48	0.04	0.03
	-110.0	0.2	-119.1	137.8	60.4	-64.8	0.53	0.53	4.31	4.68
	-111.2	2.4	-145.3	160.6	61.7	66.1	0.71	0.65	3.15	3.81
	-93.1	-47.3	-126.5	119.9	-61.0	-174.4	1.04	1.16	1.82	1.60
	-78.2	-34.2	-137.2	126.7	-64.4	-176.2	1.04	1.15	1.81	1.63
	-94.4	-50.4	-116.6	118.5	-60.9	-174.6	1.27	1.40	1.22	1.08
	-81.2	-32.6	-116.6	135.3	-63.9	-64.3	1.31	1.36	1.16	1.16
	-112.6	2.6	-146.0	136.7	64.6	-174.7	1.70	1.85	0.60	0.51
	-79.3	-33.4	-145.6	161.3	-63.8	65.0	1.74	1.72	0.56	0.62
	-113.6	3.1	-145.3	139.2	64.4	-174.4	1.81	1.98	0.50	0.40
	-85.1	-19.7	-143.4	129.5	-163.4	-175.8	1.85	2.01	0.46	0.38
	-93.4	-51.3	-97.9	124.3	-60.5	-65.4	1.89	2.16	0.43	0.30
	-89.4	-19.1	-116.9	134.9	-164.4	-66.2	2.00	2.06	0.36	0.35
	-110.7	1.8	-117.9	138.4	65.1	-67.1	2.33	2.57	0.20	0.15
	-111.2	1.3	-122.6	142.9	64.6	-67.0	2.37	2.56	0.19	0.15
	-80.1	-33.3	-116.0	138.2	-63.4	-64.8	2.60	2.91	0.13	0.08
	-95.1	-12.6	-140.4	160.0	-160.6	67.9	2.61	2.55	0.13	0.15
	-78.9	-33.3	-144.6	160.3	-63.8	65.3	2.86	3.12	0.08	0.06
	-78.9	-33.5	-144.5	160.6	-63.7	65.4	2.90	3.12	0.08	0.06
	-102.5	-2.1	-145.4	160.1	67.4	68.0	2.96	3.14	0.07	0.06
	-102.5	-2.1	-145.4	160.1	67.4	68.0	2.96	3.14	0.07	0.06
	-78.6	-23.3	-147.1	138.3	-160.2	-174.7	2.99	3.10	0.07	0.06

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C^{α}-C(H)-$C(H_3)$	Phe Side N-C^{α}-$C(H_2)$-C_{Ar}	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-106.6	-32.3	-105.0	132.6	-166.8	-67.3	3.75	3.97	0.02	0.01
	-87.5	-18.2	-90.1	133.3	-157.5	-64.5	3.97	4.14	0.01	0.01
	-86.4	-16.4	-139.5	158.6	-156.2	68.6	4.31	4.45	0.01	0.01
	-106.6	-26.0	-141.0	156.7	-162.3	69.9	5.03	5.19	0.00	0.00
	-104.5	-3.1	-138.6	125.6	61.5	-175.8	0.00	0.00	10.49	11.47
(δ,γ)	-110.6	-48.3	72.4	-54.0	-60.8	-62.4	2.85	2.85	0.09	0.09
	-114.7	-19.0	71.9	-51.9	61.7	-61.4	2.95	2.96	0.07	0.08
	-114.3	-17.3	72.2	-52.0	61.9	-61.4	3.02	3.03	0.06	0.07
	-92.9	-50.7	74.3	-58.9	-61.1	-170.6	3.10	3.07	0.06	0.06
	-91.9	-48.4	74.1	-59.6	-61.3	-170.8	3.20	3.15	0.05	0.06
	-120.2	-30.0	72.7	-52.5	-163.8	-61.1	4.04	4.07	0.01	0.01
	-96.7	-11.8	73.2	-58.5	61.6	-170.7	4.17	4.24	0.01	0.01
	-111.8	0.6	73.6	-58.3	65.1	-171.2	4.21	4.06	0.01	0.01
	-116.5	-26.0	73.0	-52.5	-162.4	-61.0	4.39	4.43	0.01	0.01
	-98.6	-29.5	74.1	-59.2	-162.9	-170.2	4.81	4.84	0.00	0.00
	-79.5	-22.5	74.0	-58.8	-159.9	-171.3	5.38	5.24	0.00	0.00
	-98.7	-49.9	57.1	-32.5	-61.3	69.2	6.70	6.63	0.00	0.00
	-99.3	-49.0	56.7	-32.1	-61.2	68.8	6.74	6.65	0.00	0.00
	-107.8	-18.6	55.6	-31.5	62.2	67.3	6.77	6.73	0.00	0.00
	-114.7	3.4	55.4	-30.3	64.7	66.7	7.26	7.19	0.00	0.00
	-113.5	-32.2	57.2	-31.5	-165.3	68.0	8.14	8.02	0.00	0.00
	-82.2	-20.9	55.3	-31.1	-158.9	69.7	8.84	8.61	0.00	0.00
	-110.9	-49.1	72.1	-53.3	-61.1	-63.0	2.81	2.85	0.09	0.09
(β,γ')	-119.0	154.3	74.3	-58.8	59.0	-170.7	2.74	2.70	0.10	0.12
	-116.0	126.4	73.5	-59.0	-60.6	-170.9	2.83	2.81	0.09	0.10
	-93.0	111.4	72.8	-58.8	-58.3	-171.4	4.64	4.64	0.00	0.00
	-106.1	146.5	71.3	-51.0	57.9	-63.9	5.75	5.85	0.00	0.00
	-116.9	148.8	56.6	-31.8	55.0	70.9	6.73	6.61	0.00	0.00
	-116.0	124.3	59.3	-35.1	-56.7	75.5	6.74	6.64	0.00	0.00
	-106.1	146.5	57.1	-31.9	58.4	71.0	10.07	10.06	0.00	0.00
	-116.8	147.5	71.0	-51.1	54.7	-63.7	2.77	2.80	0.10	0.10
(γ',γ)	-87.1	79.2	69.0	-50.9	-54.0	-63.0	4.25	4.20	0.01	0.01
	-87.4	80.4	53.6	-31.8	-52.8	68.9	8.03	7.90	0.00	0.00
(δ,δ)	-74.6	-14.1	-81.5	-9.4	63.9	-64.6	1.06	0.99	1.75	2.17
	-70.2	-21.4	-77.0	-12.1	-161.8	-64.8	1.49	1.37	0.85	1.13
	-67.4	-27.9	-79.6	-6.8	-68.2	-64.4	1.49	1.47	0.85	0.96
	-74.4	-15.0	-87.0	-2.7	63.7	58.2	1.52	1.47	0.81	0.95
	-69.5	-23.2	-84.9	-3.0	-162.3	57.4	1.83	1.75	0.47	0.59
	-101.9	-62.0	-116.5	-14.4	-58.7	62.1	1.98	1.96	0.37	0.42
	-67.6	-29.0	-83.5	-1.9	-69.0	57.6	2.01	1.92	0.35	0.45
	-96.0	-49.0	-75.4	-31.7	-61.4	-172.5	2.11	2.25	0.30	0.26
	-111.5	-6.2	-102.0	-48.5	61.0	-66.6	2.41	2.50	0.18	0.17
	-103.7	-9.2	-113.9	-56.1	61.7	-175.8	2.52	2.56	0.15	0.15
	-109.8	-13.6	-72.9	-33.6	62.9	-172.1	2.65	2.90	0.12	0.09

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side $N\text{-}C^{\alpha}\text{-}C(H)\text{-}C(H_3)$	Phe Side $N\text{-}C^{\alpha}\text{-}C(H_2)\text{-}C_{Ar}$	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-69.2	-22.4	-68.6	-25.2	-162.4	-171.2	3.08	2.92	0.06	0.08
	-110.3	1.3	-75.0	-32.0	65.6	-172.3	3.11	2.64	0.05	0.13
	-67.6	-27.0	-66.0	-25.8	-67.5	-171.4	3.20	3.12	0.05	0.06
	-68.5	-24.4	-68.5	-26.0	-160.7	-172.3	4.38	4.53	0.01	0.01
(δ,γ')	-110.0	-33.4	-123.2	11.5	-165.8	62.5	5.77	5.81	0.00	0.00
	-97.5	-55.9	-86.4	73.5	-60.4	-67.6	1.44	1.55	0.93	0.84
	-94.2	-51.1	-86.3	83.1	-61.2	-166.7	1.50	1.54	0.83	0.86
	-92.1	-49.5	-86.3	83.6	-61.2	-166.0	1.77	1.84	0.52	0.51
	-110.0	-22.1	-88.2	83.8	61.9	-166.6	2.34	2.40	0.20	0.20
	-111.9	0.4	-86.1	82.8	65.7	-166.4	2.41	2.45	0.18	0.18
	-96.6	-7.2	-84.6	72.2	67.2	-65.8	2.49	2.58	0.16	0.15
	-64.8	-37.1	-93.7	7.6	-65.1	-69.2	2.52	2.67	0.15	0.13
	-108.4	-24.9	-87.3	75.2	59.9	-72.9	2.75	2.73	0.10	0.11
	-78.5	-34.3	-85.3	72.5	-65.2	-36.6	2.79	2.90	0.09	0.09
	-78.5	-34.3	-85.3	72.5	-65.2	-67.5	2.79	2.90	0.09	0.09
	-71.1	-25.5	-91.9	3.2	-165.9	-70.9	3.25	3.38	0.04	0.04
	-106.7	-34.7	-88.2	83.9	-166.0	-166.4	3.43	3.40	0.03	0.04
	-81.7	-19.9	-83.6	72.4	-159.3	-65.4	3.52	3.55	0.03	0.03
	-124.5	-41.0	-88.0	78.2	-170.7	-68.3	3.52	3.59	0.03	0.03
	-81.4	-22.0	-86.1	82.8	-159.3	-166.6	3.73	3.68	0.02	0.02
	-110.5	-35.6	-86.2	74.9	-167.9	-70.4	3.86	3.89	0.02	0.02
	-91.6	-10.0	-83.5	50.0	67.2	47.5	4.67	4.70	0.00	0.00
	-94.5	-8.1	-83.3	48.9	68.0	47.8	4.90	4.87	0.00	0.00
	-97.5	-55.9	-86.4	73.5	-60.4	-36.8	1.44	1.55	0.93	0.84

Table S3. Conformations and relative energies of LL-**2**·(DMSO-d_6)$_2$ obtained at B3LYP/6-31G+(2d,p)/IEFPCM(DMSO) level of theory. Relative zero-point corrected and Gibbs Free energies, ΔE_{ZPC} and ΔG_{298K}, are given in kcal/mol and the corresponding Boltzmann weights χ in percentage.

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C$^{\alpha}$-C(H)-C(H$_3$)	Phe Side N-C$^{\alpha}$-C(H$_2$)-C$_{Ar}$	Boc	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
(β,β)	-121.9	156.9	-116.1	131.1	60.0	-64.4	T	0.21	0.33	12.47	11.77
	-119.2	130.1	-131.8	117.4	-61.2	-174.3	T	0.91	1.04	3.88	3.50
	-121.8	156.8	-115.7	130.5	59.9	-65.4	T	0.94	1.12	3.68	3.05
	-113.8	118.4	-107.7	-35.6	-59.3	-66.7	T	1.02	1.25	3.20	2.48
	-94.0	118.9	-148.2	130.1	-59.8	-175.4	T	1.06	1.26	2.99	2.41
	-121.1	157.4	-125.1	115.4	60.2	-174.0	T	1.23	1.39	2.22	1.95
	-136.6	141.1	-126.6	117.9	-171.7	-174.5	T	1.49	1.56	1.45	1.47
	-103.4	123.3	-150.3	161.1	-60.2	65.8	T	1.49	1.61	1.44	1.34
	-121.0	128.5	-106.9	140.5	-61.3	-66.8	T	1.50	1.78	1.42	1.02
	-112.1	119.7	-126.1	146.7	-59.1	-67.0	T	1.59	1.77	1.23	1.03
	-122.8	156.1	-114.5	130.8	59.1	-64.9	C	1.67	1.81	1.07	0.95
	-120.4	156.0	-136.8	116.6	60.1	-173.2	T	1.73	1.89	0.97	0.83
	-144.6	141.1	-121.1	133.3	-172.0	-64.5	T	2.02	2.16	0.59	0.53
	-122.1	158.0	-136.9	118.3	59.4	-174.7	C	2.10	2.22	0.51	0.48
	-114.9	153.3	-109.5	-35.7	63.2	-64.8	T	2.10	2.17	0.51	0.52
	-126.6	128.2	-113.0	132.5	-60.8	-65.0	C	2.27	2.44	0.39	0.33
	-88.7	123.2	-147.6	128.7	-60.6	-175.2	C	2.33	2.49	0.35	0.30
	-125.7	131.2	-126.8	118.5	-61.4	-174.5	C	2.35	2.48	0.34	0.31
	-150.1	143.7	-134.8	118.4	-171.3	-174.4	C	2.35	2.40	0.34	0.35
	-124.2	156.6	-114.2	130.9	59.3	-64.5	C	2.35	2.60	0.34	0.25
	-122.9	157.2	-133.0	117.9	59.4	-174.3	C	2.36	2.40	0.33	0.36
	-108.5	158.7	-125.1	140.5	65.2	-64.0	T	2.37	2.59	0.33	0.26
	-91.6	126.8	-118.5	117.5	-61.5	-173.9	T	2.38	2.59	0.32	0.26
	-104.9	159.4	-147.9	128.7	65.3	-175.4	T	2.41	2.54	0.31	0.28
	-110.7	124.2	-102.8	121.9	-60.3	-67.9	T	2.76	3.01	0.17	0.13
	-151.2	141.2	-120.1	131.1	-172.2	-64.6	C	2.77	2.93	0.17	0.15
	-96.9	125.3	-116.1	117.2	-61.2	-173.8	T	2.98	3.19	0.12	0.09
	-116.2	121.2	-151.5	161.8	-59.7	65.9	C	3.00	3.09	0.11	0.11
	-109.9	121.7	-126.3	134.6	-60.1	-65.6	C	3.00	3.26	0.11	0.08
	-115.7	153.2	-111.8	128.4	63.2	-65.0	T	3.08	3.41	0.10	0.06
	-119.8	119.6	-104.3	-35.0	-60.2	-67.3	C	3.12	3.18	0.09	0.09
	-130.2	138.0	-153.3	161.2	-169.3	63.8	T	3.24	3.27	0.08	0.08
	-123.3	139.2	-149.6	129.9	-167.9	-175.1	T	3.32	3.42	0.07	0.06
	-131.7	141.2	-127.0	138.9	-167.5	-64.0	T	3.33	3.53	0.06	0.05
	-108.7	150.4	-114.3	116.3	63.6	-174.2	T	3.36	3.56	0.06	0.05
	-83.9	157.1	-149.4	129.1	65.8	-175.4	C	3.46	3.53	0.05	0.05
	-106.8	154.5	-127.4	119.1	64.6	-173.8	T	3.55	3.70	0.04	0.04
	-110.7	157.1	-125.1	141.3	63.3	-64.8	C	3.58	3.68	0.04	0.04
	-116.0	155.9	-104.4	-36.9	62.9	-64.7	C	3.77	3.88	0.03	0.03
	-81.1	133.2	-114.8	115.7	-63.5	-173.6	C	3.78	3.89	0.03	0.03
	-82.5	132.6	-112.7	116.6	-63.4	-173.9	C	3.87	4.05	0.03	0.02

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side $N\text{-}C^{\alpha}\text{-}C(H)\text{-}C(H_3)$	Phe Side $N\text{-}C^{\alpha}\text{-}C(H_2)\text{-}C_{Ar}$	Boc	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-126.4	133.3	-106.4	116.0	-171.7	-173.8	T	3.91	4.09	0.02	0.02
	-102.1	157.3	-148.7	129.5	64.3	-175.8	C	4.00	4.04	0.02	0.02
	-123.6	125.3	-108.5	129.2	-61.0	-66.7	C	4.09	3.85	0.02	0.03
	-141.7	139.5	-153.5	161.3	-169.1	63.1	C	4.58	4.52	0.01	0.01
	-131.9	142.0	-146.9	129.2	-168.0	-176.1	C	4.63	4.71	0.01	0.01
	-124.7	133.1	-105.5	118.0	-171.3	-174.2	T	4.72	4.94	0.01	0.00
	-139.2	144.4	-126.9	140.2	-167.0	-63.5	C	4.76	4.86	0.01	0.01
	-126.7	132.8	-110.7	121.8	-171.7	-67.4	T	4.79	5.07	0.01	0.00
	-102.7	156.0	-127.5	118.8	64.3	-173.9	C	4.89	5.11	0.00	0.00
	-90.5	156.8	-105.1	118.1	66.4	-174.1	C	4.96	5.20	0.00	0.00
	-144.7	141.0	-120.5	129.6	-172.2	-65.3	T	5.25	5.71	0.00	0.00
	-142.3	132.6	-113.4	126.9	-173.6	-64.5	C	5.61	5.90	0.00	0.00
	-142.8	135.6	-105.4	118.1	-171.8	-173.4	C	5.62	5.83	0.00	0.00
	-151.0	141.8	-120.3	128.4	-172.1	-65.1	C	6.42	6.80	0.00	0.00
(β,δ)	-103.1	117.1	-114.5	-49.9	-59.1	-175.7	T	1.18	1.20	2.42	2.71
	-108.8	117.8	-126.6	-16.7	-60.0	64.1	T	2.26	2.35	0.39	0.39
	-111.3	144.9	-129.4	-50.4	61.9	-175.5	T	2.98	2.93	0.12	0.14
	-132.2	129.6	-110.3	-36.8	-173.2	-65.3	T	3.01	3.19	0.11	0.09
	-106.1	156.9	-108.5	-48.8	63.9	-176.1	T	3.01	3.10	0.11	0.11
	-119.1	130.7	-123.5	-50.6	-171.4	-176.1	T	3.50	3.43	0.05	0.06
	-110.7	152.1	-131.1	-17.2	63.7	63.5	T	3.73	3.76	0.03	0.04
	-90.0	126.0	-100.3	-51.1	-61.0	-175.9	C	3.75	3.81	0.03	0.03
	-122.5	126.3	-112.7	-92.5	-59.8	-66.6	T	3.76	3.95	0.03	0.03
	-136.3	131.7	-114.7	-50.6	-171.7	-175.6	T	3.76	3.78	0.03	0.03
	-116.9	122.6	-121.2	-15.9	-61.7	64.1	C	4.32	4.33	0.01	0.01
	-113.0	157.8	-106.5	-48.9	63.4	-175.3	C	4.41	4.44	0.01	0.01
	-119.3	124.7	-140.6	-84.0	-61.0	-171.9	T	4.48	4.67	0.01	0.01
	-117.5	150.5	-136.5	-87.2	59.7	-169.7	T	4.54	4.58	0.01	0.01
	-147.0	134.9	-109.2	-38.0	-172.7	-65.6	C	4.71	4.82	0.01	0.01
	-107.8	151.1	-130.9	-15.8	63.5	63.4	C	5.32	5.38	0.00	0.00
	-148.0	135.7	-110.2	-50.5	-172.0	-175.2	C	5.33	5.34	0.00	0.00
	-148.0	135.7	-110.2	-50.5	-172.0	-175.2	C	5.33	5.33	0.00	0.00
	-137.1	139.6	-117.4	-86.6	-172.4	-170.5	T	5.74	5.88	0.00	0.00
	-126.3	132.7	-110.6	-108.0	-60.9	-65.0	C	5.84	5.99	0.00	0.00
	-121.2	154.4	-138.6	-84.7	59.1	-171.0	C	5.91	6.08	0.00	0.00
	-122.0	127.3	-139.7	-85.3	-62.0	-171.2	C	6.19	6.34	0.00	0.00
	-151.0	139.9	-139.2	-84.9	-173.8	-166.7	C	6.56	6.59	0.00	0.00
	-128.7	126.4	-105.8	-3.6	-173.7	57.4	T	7.70	7.76	0.00	0.00
	-150.8	144.6	-70.2	-27.7	-166.8	75.6	C	8.81	8.84	0.00	0.00
(β,γ)	-96.2	121.8	73.0	-58.9	-60.2	-171.4	T	3.43	3.46	0.05	0.06
	-113.0	153.8	74.6	-58.2	63.2	-170.3	T	4.25	4.27	0.01	0.01
	-109.7	147.0	71.1	-50.5	58.3	-63.9	T	4.39	4.45	0.01	0.01
	-86.5	130.7	73.4	-59.1	-62.2	-171.3	C	5.20	5.20	0.00	0.00
	-110.2	156.8	74.5	-58.8	63.4	-170.9	C	5.89	5.90	0.00	0.00

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side N-C^{α}-C(H)-$C(H_3)$	Phe Side N-C^{α}-$C(H_2)$-C_{Ar}	Boc	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-106.9	150.0	71.0	-50.6	58.1	-64.8	C	6.12	6.15	0.00	0.00
	-104.5	117.3	58.5	-34.2	-56.9	75.2	T	7.54	7.50	0.00	0.00
	-110.3	144.4	56.8	-31.4	59.4	71.7	T	8.14	8.09	0.00	0.00
	-89.9	129.2	59.5	-35.0	-58.4	76.0	C	9.47	9.41	0.00	0.00
	-101.6	148.8	57.0	-32.5	59.8	71.9	C	10.02	10.08	0.00	0.00
(δ,β)	-93.0	-46.7	-132.0	120.1	-60.7	-174.9	T	0.00	0.00	17.90	20.39
	-90.9	-46.5	-129.2	117.3	-60.7	-174.3	T	0.32	0.34	10.46	11.52
	-96.3	-52.1	-97.4	129.4	-60.1	-65.4	T	4.46	5.00	0.01	0.00
	-98.0	-51.5	-102.5	129.9	-59.8	-64.6	T	0.38	0.46	9.41	9.30
	-87.8	-47.7	-99.2	132.2	-61.0	-64.8	C	1.40	1.40	1.69	1.91
	-86.1	-45.9	-133.0	117.1	-61.4	-174.5	C	1.47	1.49	1.50	1.66
	-85.1	-45.1	-130.7	120.3	-61.2	-175.0	C	1.17	1.19	2.50	2.74
	-78.2	-37.4	-149.3	161.9	-62.0	66.4	T	1.82	1.89	0.83	0.84
	-76.6	-36.7	-148.3	161.4	-62.8	66.4	C	3.09	3.05	0.10	0.12
	-81.6	-32.2	-115.4	135.3	-63.0	-64.3	T	1.37	1.57	1.78	1.44
	-81.4	-31.5	-113.8	133.8	-63.4	-64.4	C	2.57	2.70	0.23	0.21
	-73.7	-30.0	-115.3	113.9	-161.2	-173.4	T	5.84	6.24	0.00	0.00
	-112.0	-29.1	-129.5	120.4	-162.7	-175.2	T	2.17	1.66	0.45	1.24
	-77.2	-28.6	-110.7	117.4	-162.0	-173.4	C	6.80	6.96	0.00	0.00
	-97.0	-26.5	-125.3	119.3	-162.3	-175.3	C	3.27	3.12	0.07	0.11
	-81.5	-20.8	-137.1	125.1	-158.7	-175.6	T	2.11	2.09	0.51	0.60
	-83.7	-19.8	-134.3	125.4	-160.0	-175.8	C	2.84	2.87	0.15	0.16
	-87.6	-19.6	-114.6	135.2	-160.9	-66.3	C	3.56	3.60	0.04	0.05
	-87.3	-15.7	-140.8	159.6	-156.0	68.6	T	3.45	3.44	0.05	0.06
	-87.8	-15.5	-139.9	159.6	-158.4	68.9	C	4.20	4.18	0.01	0.02
	-93.5	-14.4	-117.0	139.2	-156.8	-66.9	T	3.09	3.16	0.10	0.10
	-100.0	-4.1	-144.6	127.6	64.7	-176.0	C	2.00	2.08	0.61	0.61
	-99.3	-3.5	-144.5	160.2	65.4	67.5	C	2.75	2.73	0.17	0.20
	-101.5	-2.8	-145.9	160.2	67.4	66.7	T	1.97	2.03	0.65	0.66
	-111.2	0.2	-124.5	141.8	64.3	-67.1	T	1.35	1.44	1.82	1.81
	-110.3	2.3	-143.5	127.2	65.3	-175.5	T	1.02	1.13	3.22	3.02
(δ,γ')	-66.1	-33.3	-95.9	9.4	-70.3	-67.2	T	3.65	3.83	0.04	0.03
	-88.1	-49.2	-86.0	73.5	-61.7	-36.8	C	4.80	4.95	0.01	0.00
	-81.3	-39.6	-89.2	79.9	-67.2	-165.1	T	4.88	4.98	0.00	0.00
	-92.9	-54.2	-86.3	73.2	-60.7	-68.5	C	5.00	5.22	0.00	0.00
	-78.4	-40.7	-89.8	80.7	-67.5	-163.8	T	5.58	5.63	0.00	0.00
	-83.0	-35.5	-88.6	79.7	-66.8	-165.1	C	5.63	5.64	0.00	0.00
	-80.2	-38.3	-89.0	84.1	-67.5	-165.3	C	6.63	6.69	0.00	0.00
	-99.8	-56.3	-86.2	73.4	-59.9	-37.6	T	3.95	4.20	0.02	0.02
(δ,δ)	-84.8	-17.9	-113.4	-56.0	62.4	-175.8	C	4.47	4.48	0.01	0.01
	-70.0	-22.9	-85.7	-2.8	-162.2	57.6	T	4.64	4.11	0.01	0.02
	-80.7	-35.0	-93.6	-52.3	-67.8	-175.5	C	5.09	5.25	0.00	0.00
	-87.8	-31.7	-98.1	-2.7	-66.7	-66.2	C	5.64	5.85	0.00	0.00
	-61.5	-34.3	-68.3	-24.4	-71.8	-169.3	T	5.72	5.78	0.00	0.00

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side $N\text{-}C^{\alpha}\text{-}C(H)\text{-}C(H_3)$	Phe Side $N\text{-}C^{\alpha}\text{-}C(H_2)\text{-}C_{Ar}$	Boc	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
	-67.0	-31.7	-85.8	-0.4	-66.2	56.6	T	6.99	7.38	0.00	0.00
	-85.1	-17.3	-110.3	-56.4	63.6	-175.2	T	3.91	4.05	0.02	0.02

Table S2. Conformations and relative energies of LL-**2**·$(DMSO\text{-}d_6)_3$ obtained at B3LYP/6-31G+(2d,p)/IEFPCM(DMSO) level of theory. Relative zero-point corrected and Gibbs Free energies, ΔE_{ZPC} and ΔG_{298K}, are given in kcal/mol and the corresponding Boltzmann weights χ in percentage. Only trans-Boc structures.

	Val ϕ	Val ψ	Phe ϕ	Phe ψ	Val-Side $N\text{-}C^{\alpha}\text{-}C(H)\text{-}C(H_3)$	Phe Side $N\text{-}C^{\alpha}\text{-}C(H_2)\text{-}C_{Ar}$	ΔE_{ZPC}	ΔG_{298K}	χ(ΔE)	χ(ΔG)
(δ,β)	-91.5	-49.4	-108.3	118.8	-61.3	-174.4	1.95	2.26	1.80	1.22
	-78.8	-41.9	-102.9	130.7	-67.2	-65.2	3.34	3.30	0.17	0.21
	-73.8	-30.2	-118.8	118.1	-161.3	-173.9	3.97	4.09	0.06	0.06
(β,β)	-94.8	127.8	-121.9	118.5	-61.1	-174.6	0.00	0.00	48.01	55.13
	-130.8	133.8	-115.6	134.4	-171.3	-65.0	2.26	2.42	1.06	0.93
	-114.9	137.1	-133.2	118.4	-168.9	-174.2	1.91	1.99	1.91	1.93
	-107.2	123.2	-140.2	-82.6	-61.3	-172.1	3.70	3.79	0.09	0.09
	-116.3	123.2	-111.6	138.4	-60.1	-66.0	0.25	0.42	31.36	27.23
	-121.6	156.4	-111.0	-128.7	59.6	-63.2	5.05	5.38	0.01	0.01
	-114.3	153.4	-137.6	-84.7	63.5	-167.6	4.39	4.37	0.03	0.03
	-107.1	155.8	-107.5	135.6	65.2	-64.3	1.09	1.25	7.65	6.66
	-105.8	157.1	-136.1	118.2	65.3	-174.4	1.07	1.27	7.85	6.51

2. Additional figures

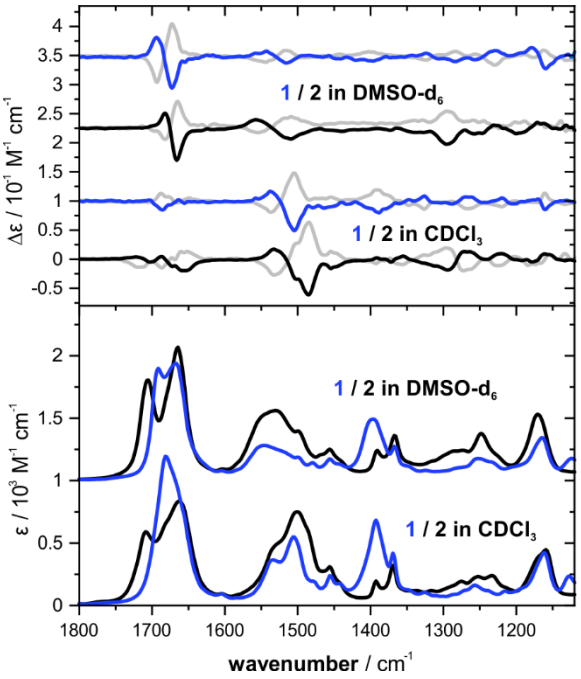

Fig. S1. Comparison of the experimental IR and VCD spectra of **1** and **2** recorded in $CDCl_3$ and DMSO-d_6.

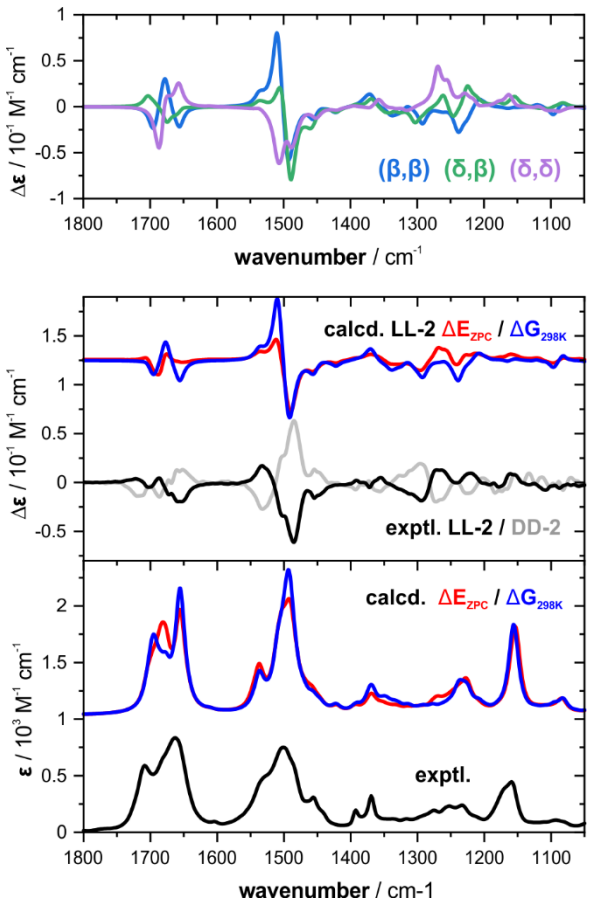

Fig. S2. Spectra of the (β,β)-, (δ,β)- and (δ,δ)- conformer families of LL-**2** compared to those simulated based on ΔE_{ZPC}- and ΔG_{298K}. For the ΔG_{298K}-based VCD, the increased contribution of the (β,β)-family and the decrease in population of the (δ,δ)-family can be noted in the amide III region, where it leads to a worse match than the DEZPC-based spectrum.

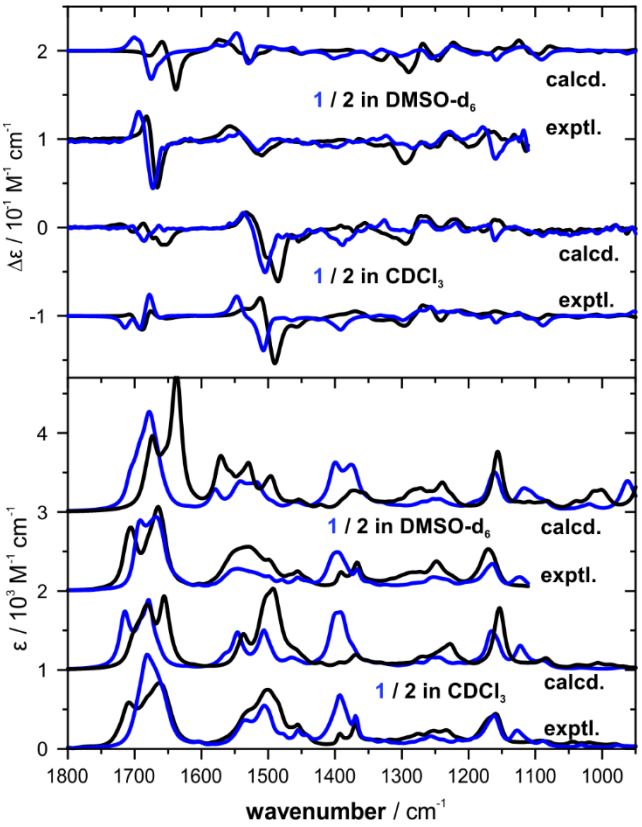

Fig. S3 Comparison of experimental IR and VCD spectra of **1** and **2** recorded in $CDCl_3$ and DMSO-d_6 with the corresponding computed spectra.

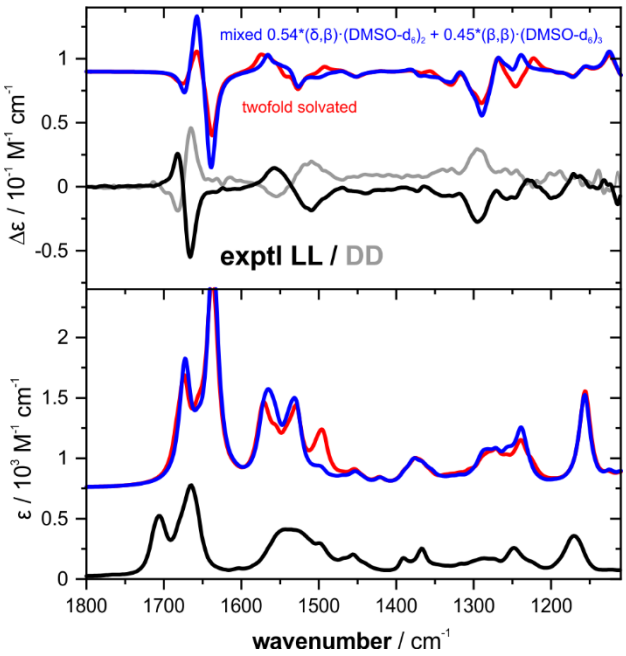

Fig. S4. Comparison of the twofold solvated **2** and the mixed spectrum generated through the shown formula.

3. Cartesian coordinates of selected structures

(β,β)-LL-2

C	-2.13597800	-0.46305800	0.00453200
H	-2.22141200	-0.37346400	1.09015700
C	-3.10979400	-1.52088400	-0.53093000
N	-4.22637700	-1.72421400	0.19087200
H	-4.38263400	-1.15900600	1.01170700
C	-5.28451900	-2.62397800	-0.24723900
H	-4.87783500	-3.61887700	-0.44446000
H	-6.03111100	-2.69289100	0.54472600
H	-5.76287500	-2.25717500	-1.16108800
O	-2.86392800	-2.12666400	-1.57543700
N	-0.79407500	-0.92905900	-0.30090400
H	-0.70696000	-1.51103800	-1.12495400
C	0.28858400	-0.61205700	0.44046900
O	0.23233600	0.12181600	1.42742900
C	1.60762300	-1.26525700	-0.00743700
H	1.67535000	-1.21779200	-1.09801700
N	2.70862200	-0.48501400	0.52496300
H	2.53645100	-0.03146700	1.41311100
C	3.64347400	0.09432300	-0.28292400
O	3.79271600	-0.16164700	-1.46725700
O	4.38287600	0.96488600	0.43745500
C	5.50939900	1.71075300	-0.15727700
C	6.02523300	2.52823300	1.02885800
H	6.87562700	3.14110000	0.71566000
H	5.24299700	3.19059100	1.41183900
H	6.35210000	1.87046100	1.83995000
C	5.00216400	2.63504800	-1.26706800
H	5.82186700	3.27875500	-1.60286500
H	4.63231600	2.06765000	-2.12186100
H	4.19894300	3.27718500	-0.89143200
C	6.58541100	0.73975300	-0.64966300
H	6.23589300	0.15317000	-1.50005200
H	7.46980200	1.30785700	-0.95648500
H	6.88252000	0.05899000	0.15466300
C	-2.40210900	0.92912700	-0.64095400
H	-1.57240000	1.57265600	-0.33265100
H	-2.34573500	0.81750600	-1.72843600
C	1.66495000	-2.76548700	0.41290300
H	0.76850100	-3.23455200	-0.01339000
C	2.89175000	-3.45173300	-0.20165500
H	2.89519500	-3.36745900	-1.29328800
H	3.81998900	-3.00800100	0.17393000
H	2.89960000	-4.51581500	0.05735900
C	1.62606400	-2.95702600	1.93510600
H	0.73270000	-2.51304600	2.38557400
H	1.62989400	-4.02432500	2.17919400
H	2.50421900	-2.50540100	2.41020100
C	-3.71749700	1.55935000	-0.24242400
C	-3.87604400	2.13149000	1.02823500
C	-4.80382200	1.58628900	-1.12569800
C	-5.08946100	2.70598900	1.40839800
H	-3.03893100	2.13729700	1.72128800
C	-6.01889300	2.16329500	-0.75083000
H	-4.69655200	1.15637600	-2.11767900
C	-6.16654400	2.72256900	0.51922600
H	-5.19056400	3.14831900	2.39463900
H	-6.84693400	2.17857300	-1.45271600
H	-7.10914800	3.17426200	0.81156600

(δ,β)-LL-2

C	-1.73217200	0.02645000	0.32538400
H	-2.08306100	0.36312000	1.30435100

C	-1.73640900	-1.50494100	0.24262500
N	-2.58639700	-2.14447500	1.06585200
H	-3.17322600	-1.59855000	1.67798500
C	-2.76083400	-3.58975300	1.03632600
H	-1.80696400	-4.09400900	1.21242300
H	-3.46395500	-3.86986200	1.82135100
H	-3.15348000	-3.91851100	0.06900500
O	-1.00352600	-2.09241400	-0.55491500
N	-0.35534700	0.46041900	0.17247600
H	0.26937700	-0.15539000	-0.33247700
C	0.13151100	1.57985600	0.74487900
O	-0.56061600	2.35086400	1.41039400
C	1.63575100	1.86134700	0.55319800
H	2.05772400	1.80480500	1.56109500
N	2.32432600	0.85142800	-0.23381300
H	2.37681600	0.96124700	-1.23628000
C	3.21096900	-0.03238500	0.32122000
O	3.37021600	-0.18282700	1.52022600
O	3.84969100	-0.70194500	-0.65845000
C	4.82772000	-1.77210800	-0.36372300
C	5.24231800	-2.23137500	-1.76268700
H	5.98137400	-3.03414300	-1.68515500
H	4.37861100	-2.60838000	-2.31857800
H	5.68668000	-1.40535300	-2.32631900
C	4.14743600	-2.91139200	0.39836700
H	4.84359300	-3.75234800	0.48218100
H	3.85281100	-2.60260300	1.40202300
H	3.26085000	-3.25745900	-0.14233100
C	6.02561100	-1.19245400	0.39191600
H	5.74410300	-0.85787400	1.39105600
H	6.79843500	-1.96234900	0.48605600
H	6.45358600	-0.34872600	-0.15901500
C	-2.63895300	0.65052400	-0.77582900
H	-2.45329500	1.72876000	-0.75111700
H	-2.29956300	0.27887700	-1.74792300
C	1.86157700	3.29926400	0.01707600
H	1.25998400	3.93795000	0.67153600
C	3.33126600	3.71676600	0.15371400
H	3.67457700	3.63376600	1.19051800
H	3.98685400	3.09703500	-0.46886600
H	3.46161400	4.75698400	-0.16268500
C	1.35380200	3.49040800	-1.42046000
H	0.30222100	3.20332000	-1.52522700
H	1.44024000	4.54223500	-1.71121600
H	1.93903300	2.91342600	-2.14779600
C	-4.11502400	0.37902100	-0.59244200
C	-4.85194100	1.07888700	0.37403400
C	-4.77855200	-0.57383600	-1.37524200
C	-6.21184300	0.82709600	0.55860000
H	-4.35854300	1.83414700	0.98002200
C	-6.14013300	-0.82693300	-1.19625600
H	-4.22590900	-1.11953000	-2.13497400
C	-6.86086800	-0.12881200	-0.22630100
H	-6.76569400	1.38286100	1.30890700
H	-6.63652000	-1.56635100	-1.81708500
H	-7.91986700	-0.32190300	-0.08751200

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C	2.07914200	-1.59798400	0.54339600
H	2.23803300	-2.63092500	0.86510100
C	2.42609100	-0.74114100	1.78142400
N	1.43420000	-0.03698800	2.35333900
H	0.49407500	-0.07861600	1.97681100
C	1.65487500	0.74557300	3.55936100
H	2.40028900	1.52811200	3.38729400
H	0.71001300	1.20800100	3.84788300

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H     2.00865200    0.11112900    4.37804900
O     3.58081100   -0.74601200    2.21292100
N     0.69192100   -1.49950200    0.12875100
H     0.41095200   -0.72492600   -0.45786600
C    -0.27125100   -2.35794800    0.53842500
O    -0.04920500   -3.34943200    1.22764800
C    -1.71776000   -2.03381400    0.12139300
H    -2.27804600   -2.09208000    1.06105100
N    -1.88493700   -0.69529400   -0.43501200
H    -2.30470900   -0.59636800   -1.34787900
C    -1.93865100    0.40640100    0.37297000
O    -1.56417000    0.40099400    1.53804400
O    -2.42326500    1.45784400   -0.30351000
C    -2.52206100    2.81007800    0.30012300
C    -3.09261000    3.63867300   -0.85148700
H    -3.22150800    4.67650400   -0.53111300
H    -2.41723600    3.62364400   -1.71210500
H    -4.06630800    3.24987200   -1.16423900
C    -1.13183000    3.31285100    0.69199600
H    -1.20454800    4.36168700    0.99722300
H    -0.71579600    2.74025700    1.52165300
H    -0.44758300    3.25502800   -0.16018900
C    -3.49336700    2.78075100    1.48148400
H    -3.09897400    2.19195200    2.31051800
H    -3.66347700    3.80421800    1.83093100
H    -4.45756500    2.36329600    1.17452900
C     3.04817200   -1.31353700   -0.63064100
H     4.06120100   -1.39084900   -0.22836200
H     2.92002100   -2.11580000   -1.36364900
C    -2.27315200   -3.12705600   -0.82607300
H    -2.04132700   -4.06707800   -0.31478800
C    -1.57994200   -3.15564600   -2.19706700
H    -0.49493200   -3.26471800   -2.10244300
H    -1.94942700   -4.00350300   -2.78226300
H    -1.77785000   -2.25087600   -2.78472400
C    -3.79962400   -3.03254300   -0.96355700
H    -4.28839500   -3.04518600    0.01638000
H    -4.11525200   -2.12118000   -1.48495000
H    -4.17773800   -3.88271300   -1.54038100
C     2.85381200    0.02820200   -1.30593200
C     2.10855900    0.13283200   -2.48840600
C     3.41638400    1.19620500   -0.76909200
C     1.91984700    1.36744600   -3.11441200
H     1.68588300   -0.76383200   -2.93377800
C     3.23008100    2.43075000   -1.39118000
H     4.01097500    1.13306700    0.13706500
C     2.47902100    2.52166700   -2.56553300
H     1.34485300    1.42350500   -4.03360900
H     3.67933900    3.32152700   -0.96299800
H     2.34033100    3.48162700   -3.05267600
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