Electronic Supplementary Information

Elucidation of Ac-Gly-NHMe conformational preferences in solution

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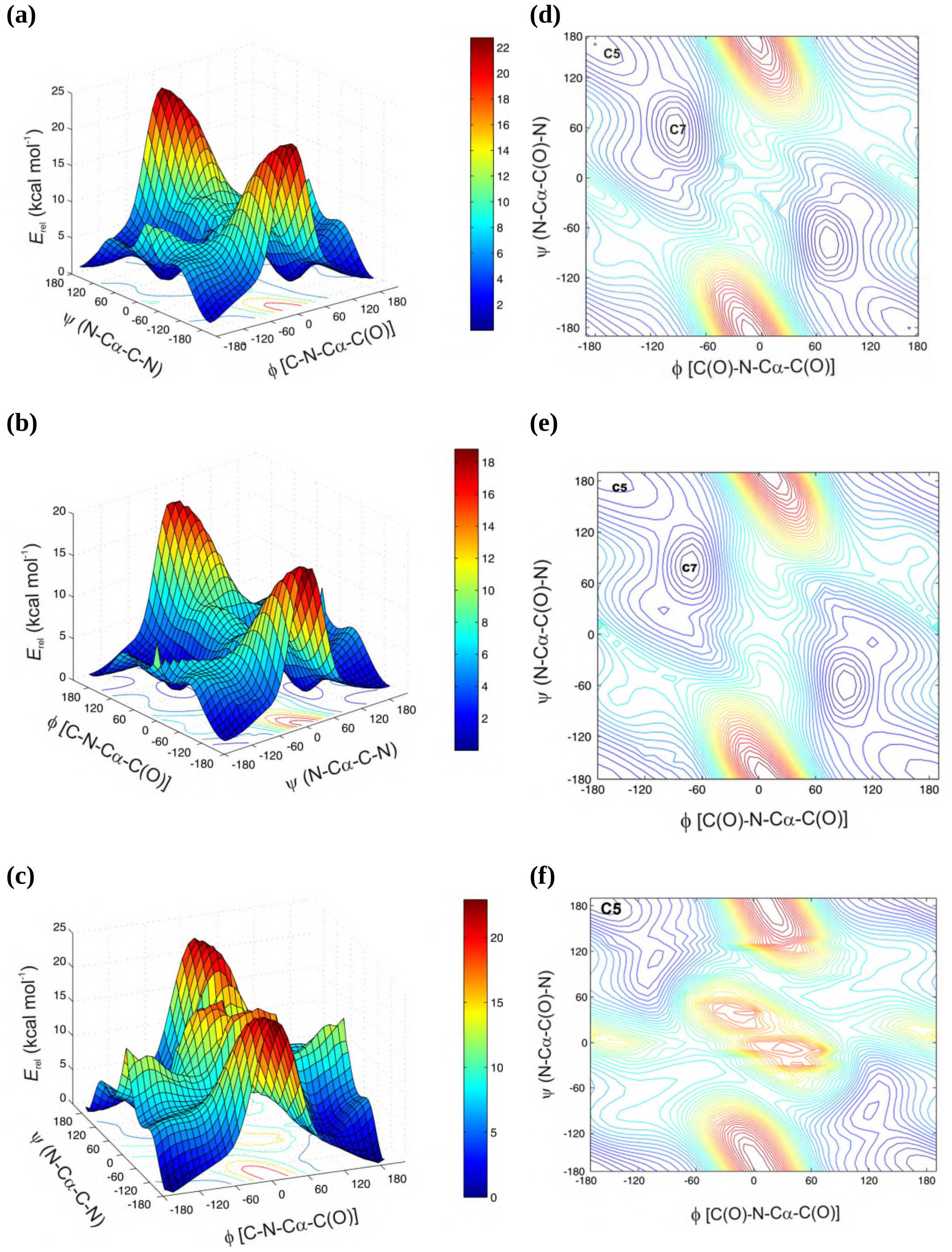
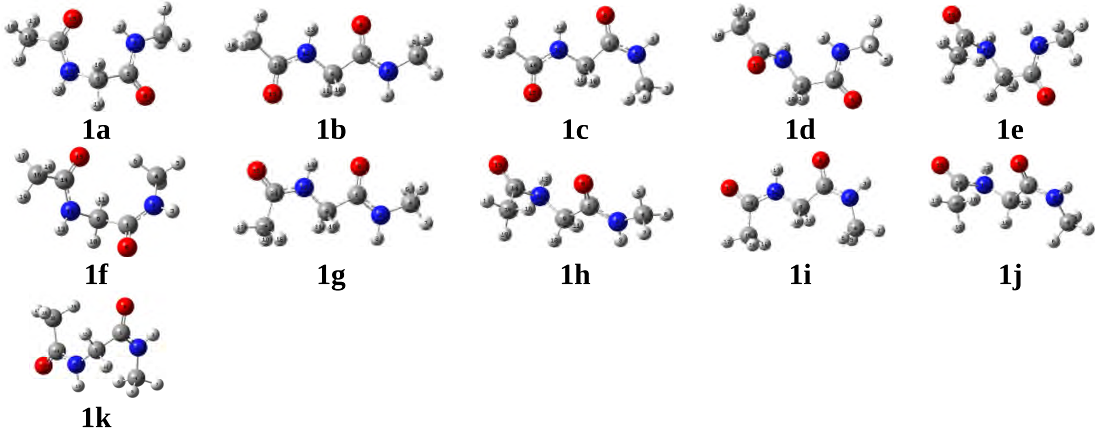


Figure S1: Potential energy surface of (a) Ac-Gly-NHMe, (**b**) CF_3-C(O)-Gly-NHMe and (**c**) Ac-Gly-N(Me)$_2$, built by scanning its ψ and ϕ dihedral angles at the B3LYP/cc-pVDZ level**.** PES Ramachandran-like ψ and ϕ dihedral angles projection of (d) Ac-Gly-NHMe, (**e**) CF_3-C(O)-Gly-NHMe and (**f**) Ac-Gly-N(Me)$_2$.

Ac-Gly-NHMe

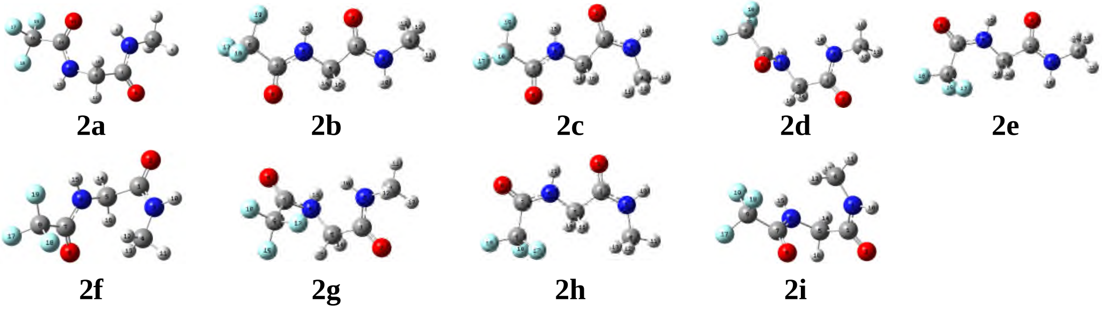


1a **1b** **1c** **1d** **1e**

1f **1g** **1h** **1i** **1j**

1k

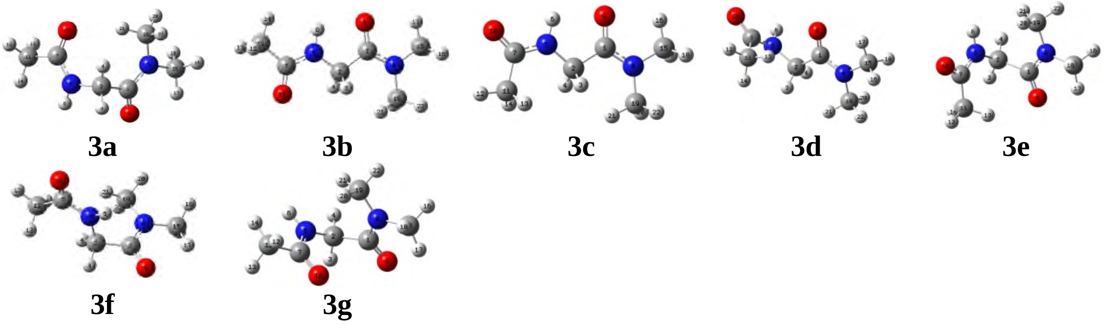
CF$_3$-C(O)-Gly-NHMe



2a **2b** **2c** **2d** **2e**

2f **2g** **2h** **2i**

Ac-Gly-N(Me)$_2$



3a **3b** **3c** **3d** **3e**

3f **3g**

Figure S2: Compounds **1**, **2** and **3** conformer geometrical representations.

Table S1: Relative energies and mean absolute deviation (MAD) from the CCSD(T)-F12a/VDZ-F12//B3LYP/aug-cc-pVDZ in kcal mol^{-1} for compound **1** conformers optimised geometries at different levels. DFT and DFT-D3 (showed in parenthesis) functionals used the aug-cc-pVDZ basis set. MP2/aug-cc-pVDZ level was the only *ab initio* optimisation. A*b initio* single point calculations were calculated on B3LYP/aug-cc-pVDZ optimised geometries.

		1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**	**MAD**
Semiepirical	**AM1**	0.00	1.88	2.04	---	2.99	2.21	5.29	---	4.87	4.98	3.56	3.13
	PM3	2.61	0.63	2.59	2.92	3.90	0.00	2.68	---	3.37	2.19	2.03	3.97
	PM6	0.00	2.05	2.22	---	3.12	1.08	5.64	3.12	5.82	3.73	3.73	3.19
DFT (DFT-D3)	**B3LYP**	0.00 (0.00)	0.28 (1.27)	1.90 (2.53)	2.21 (2.77)	3.84 (3.52)	4.50 (4.33)	4.89 (5.48)	6.43 (6.38)	6.63 (6.83)	8.78 (8.26)	9.40 (8.29)	1.38 (1.30)
	BLYP	0.00 (0.00)	1.59 (1.74)	2.08 (2.81)	2.17 (1.54)	3.80 (3.41)	4.35 (4.13)	4.85 (5.53)	6.33 (6.38)	6.49 (6.71)	8.69 (8.08)	9.15 (7.75)	1.38 (1.54)
	BP86	0.00 (0.00)	0.50 (1.89)	2.09 (2.87)	2.06 (---)	3.62 (3.24)	4.59 (4.42)	4.93 (5.67)	6.50 (6.51)	6.42 (6.72)	8.85 (8.30)	9.40 (8.00)	1.37 (1.37)
	B97-D	0.00 (0.00)	1.84 (1.48)	2.57 (2.46)	--- (---)	2.86 (2.96)	3.77 (4.15)	5.34 (5.22)	5.90 (6.14)	6.13 (6.30)	7.32 (7.76)	6.96 (7.59)	2.04 (1.85)
	M06	0.00 (0.00)	0.25 (0.40)	1.40 (1.50)	--- (---)	3.12 (2.99)	4.02 (3.93)	4.35 (4.47)	5.66 (5.64)	5.60 (5.64)	7.50 (7.44)	7.71 (7.41)	2.22 (2.23)
Ab initio	**MP2/aug-cc-pVDZ***	0.00 (0.00)	1.75 (1.37)	3.18 (2.99)	---	3.46 (3.70)	4.33 (4.79)	6.12 (5.93)	6.38 (6.72)	7.64 (7.66)	8.45 (8.94)	8.28 (9.11)	1.40 (0.92)
	RHF	0.73	0.00	2.09	2.40	4.64	4.90	5.35	6.53	7.86	9.12	10.41	1.04
	DF-MP2	0.00	1.51	3.05	2.67	3.99	4.89	5.88	6.78	7.69	9.06	9.43	0.87
	DF-MP2-F12	0.00	1.24	2.84	2.61	3.97	4.88	5.82	6.82	7.61	9.19	9.66	0.85
	SCS-DF-MP2	0.00	1.29	2.89	2.59	4.02	4.67	5.59	6.54	7.54	8.79	9.21	0.99
	SCS-DF-MP2-F12/3C(FIX)	0.00	1.02	2.68	2.52	3.99	4.64	5.54	6.59	7.47	8.93	9.44	1.02
	CCSD-F12a	0.00	0.72	2.42	2.50	4.07	4.61	5.41	6.42	7.34	8.81	9.51	1.11
	CCSD(T)-F12a	0.00	1.26	3.89	3.76	5.26	5.75	6.88	7.74	8.68	10.15	10.65	---

* MP2/aug-cc-pVTZ//MP2/aug-cc-pVDZ energy and MAD values are showed in parenthesis.

Table S2: Compounds **1**, **2** and **3** relative energies (Δ*E*) in kcal mol^{-1} and corresponding populations (%P) obtained at the B3LYP-D3/aug-cc-pVDZ level for the isolated compounds and by using the IEF-PCM implicit solvent model with dichloromethane, acetone, acetonitrile, DMSO, methanol and water dielectric constants.

		1a		**1b**		**1c**		**1d**		**1e**		**1f**		**1g**		**1h**		**1i**		**1j**		**1k**	
		Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P	Δ*E*	%P
	Isolated	0.00	87.4	1.27	10.3	2.53	1.2	2.77	0.8	3.52	0.2	4.33	0.1	5.48	0.0	6.38	0.0	6.83	0.0	8.26	0.0	8.29	0.0
	CH_2Cl_2	0.00	56.2	0.65	18.9	1.77	2.8	0.64	19.2	1.88	2.4	4.19	0.0	3.12	0.3	3.48	0.2	4.22	0.0	5.03	0.0	6.26	0.0
	Acetone	0.00	44.7	0.57	17.1	1.72	2.4	0.20	31.9	1.66	2.7	2.96	0.3	2.74	0.4	3.00	0.3	3.88	0.1	4.56	0.0	6.03	0.0
1	**Acetonitrile**	0.00	39.9	0.54	16.0	1.71	2.2	0.03	37.9	1.59	2.7	2.85	0.3	2.61	0.5	2.82	0.3	3.77	0.1	4.39	0.0	5.95	0.0
	DMSO	0.03	38.3	0.56	15.6	1.73	2.1	0.00	40.0	1.59	2.7	2.83	0.3	2.59	0.5	2.79	0.4	3.75	0.1	4.37	0.0	5.95	0.0
	Methanol	0.00	40.5	0.54	16.2	1.71	2.3	0.05	37.1	1.60	2.7	2.86	0.3	2.63	0.5	2.85	0.3	3.78	0.1	4.42	0.0	5.96	0.0
	Water	0.10	36.1	0.62	15.0	1.80	2.0	0.00	42.8	1.63	2.7	2.85	0.3	2.61	0.5	2.79	0.4	3.78	0.1	4.37	0.0	5.99	0.0
		2a		**2b**		**2c**		**2d**		**2e**		**2f**		**2g**		**2h**		**2i**					
	Isolated	0.00	47.7	0.01	47.3	1.35	4.9	---	---	4.10	0.0	4.04	0.1	5.13	0.0	5.37	0.0	7.84	0.0	---	---	---	---
	CH_2Cl_2	0.95	13.7	0.00	68.0	1.24	8.4	1.16	9.6	3.92	0.1	4.07	0.1	4.40	0.0	5.04	0.0	5.42	0.0	---	---	---	---
	Acetone	1.06	11.1	0.00	66.2	1.29	7.5	0.88	14.9	3.88	0.1	4.05	0.1	4.26	0.1	5.03	0.0	4.94	0.0	---	---	---	---
2	**Acetonitrile**	1.10	10.2	0.00	64.7	1.31	7.1	0.76	17.8	3.87	0.1	4.04	0.1	4.20	0.1	5.03	0.0	4.75	0.0	---	---	---	---
	DMSO	1.11	9.8	0.00	64.1	1.31	7.0	0.72	18.8	3.86	0.1	4.04	0.1	4.18	0.1	5.03	0.0	4.68	0.0	---	---	---	---
	Methanol	1.09	10.3	0.00	64.9	1.30	7.2	0.78	17.4	3.87	0.1	4.04	0.1	4.21	0.1	5.03	0.0	4.77	0.0	---	---	---	---
	Water	1.13	9.4	0.00	63.2	1.32	6.8	0.67	20.4	3.86	0.1	4.04	0.1	4.15	0.1	5.03	0.0	4.59	0.0	---	---	---	---
		3a		**3b**		**3c**		**3d**		**3e**		**3f**		**3g**									
	Isolated	1.86	4.2	0.00	95.8	4.42	0.1	5.78	0.0	5.60	0.0	6.66	0.0	6.85	0.0	---	---	---	---	---	---	---	---
	CH_2Cl_2	1.83	4.3	0.00	93.9	2.58	1.2	3.34	0.3	4.27	0.1	5.27	0.0	3.57	0.2	---	---	---	---	---	---	---	---
	Acetone	1.74	4.8	0.00	91.8	2.29	1.9	2.92	0.7	4.07	0.1	5.07	0.0	2.89	0.7	---	---	---	---	---	---	---	---
3	**Acetonitrile**	1.71	5.1	0.00	90.6	2.18	2.3	2.76	0.9	3.99	0.1	4.99	0.0	2.63	1.1	---	---	---	---	---	---	---	---
	DMSO	1.69	5.2	0.00	90.1	2.14	2.4	2.71	0.9	3.97	0.1	4.96	0.0	2.54	1.2	---	---	---	---	---	---	---	---
	Methanol	1.71	5.0	0.00	90.8	2.19	2.2	2.78	0.8	4.00	0.1	5.00	0.0	2.66	1.0	---	---	---	---	---	---	---	---
	Water	1.68	5.3	0.00	89.5	2.10	2.6	2.64	1.0	3.94	0.1	4.93	0.0	2.43	1.5	---	---	---	---	---	---	---	---

Table S3: Compounds **1**, **2** and **3** relative enthalpy energies (ΔH) in kcal mol^{-1} and corresponding populations (%P) obtained at the B3LYP-D3/aug-cc-pVDZ level for the isolated compounds and by using the IEF-PCM implicit solvent model with dichloromethane, acetone, acetonitrile, DMSO, methanol and water dielectric constants.

		1a		**1b**		**1c**		**1d**		**1e**		**1f**		**1g**		**1h**		**1i**		**1j**		**1k**	
		ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P	ΔH	%P
	Isolated	0.00	61.1	0.31	36.4	2.21	1.5	2.57	0.8	3.45	0.2	4.39	0.0	4.47	0.0	6.19	0.0	6.39	0.0	8.03	0.0	8.22	0.0
	CH_2Cl_2	0.00	46.1	0.31	27.3	1.52	3.6	0.51	19.6	1.81	2.2	4.27	0.0	2.25	1.0	3.38	0.2	3.90	0.1	4.93	0.0	6.35	0.0
	Acetone	0.00	36.5	0.23	24.8	1.46	3.1	0.08	31.9	1.59	2.5	2.88	0.3	2.49	0.5	2.92	0.3	3.58	0.1	4.47	0.0	6.11	0.0
1	**Acetonitrile**	0.09	32.4	0.29	23.1	1.53	2.9	0.00	37.7	1.60	2.5	2.86	0.3	2.45	0.6	2.84	0.3	3.56	0.1	4.39	0.0	6.11	0.0
	DMSO	0.14	31.2	0.33	22.6	1.57	2.8	0.00	39.5	1.64	2.5	2.87	0.3	2.45	0.6	2.83	0.3	3.57	0.1	4.39	0.0	6.13	0.0
	Methanol	0.07	33.0	0.27	23.4	1.51	2.9	0.00	36.9	1.59	2.5	2.85	0.3	2.44	0.6	2.84	0.3	3.55	0.1	4.39	0.0	6.10	0.0
	Water	0.23	29.2	0.41	21.5	1.65	2.6	0.00	42.7	1.68	2.5	2.90	0.3	2.48	0.6	2.84	0.4	3.61	0.1	4.40	0.0	6.18	0.0
		2a		**2b**		**2c**		**2d**		**2e**		**2f**		**2g**		**2h**		**2i**					
	Isolated	0.97	15.8	0.00	81.1	1.95	3.03	---	---	4.10	0.1	5.02	0.0	5.94	0.0	5.98	0.0	8.58	0.0	---	---	---	---
	CH_2Cl_2	1.29	8.4	0.00	74.5	1.23	9.3	1.35	7.6	3.87	0.1	4.45	0.0	4.62	0.0	4.45	0.0	5.69	0.0	---	---	---	---
	Acetone	1.40	6.8	0.00	72.2	1.28	8.3	1.04	12.5	3.84	0.1	4.46	0.0	4.48	0.0	5.06	0.0	5.21	0.0	---	---	---	---
2	**Acetonitrile**	1.43	6.4	0.00	70.7	1.29	8.0	0.93	14.8	3.82	0.1	4.45	0.0	4.44	0.0	5.06	0.0	5.02	0.0	---	---	---	---
	DMSO	1.43	6.2	0.00	70.2	1.29	7.9	0.89	15.5	3.81	0.1	4.45	0.0	4.43	0.0	5.06	0.0	4.97	0.0	---	---	---	---
	Methanol	1.42	6.4	0.00	70.9	1.29	8.0	0.94	14.5	3.82	0.1	4.46	0.0	4.45	0.0	5.06	0.0	5.04	0.0	---	---	---	---
	Water	1.45	6.0	0.00	69.4	1.30	7.8	0.85	16.5	3.80	0.1	4.44	0.0	4.41	0.0	5.06	0.0	4.91	0.0	---	---	---	---
		3a		**3b**		**3c**		**3d**		**3e**		**3f**		**3g**									
	Isolated	2.26	2.1	0.00	97.7	3.73	0.2	5.86	0.0	5.88	0.0	6.90	0.0	6.79	0.0	---	---	---	---	---	---	---	---
	CH_2Cl_2	2.12	2.6	0.00	93.6	1.99	3.2	3.47	0.3	4.57	0.0	5.52	0.0	3.66	0.2	---	---	---	---	---	---	---	---
	Acetone	2.03	3.0	0.00	91.0	1.72	5.0	3.07	0.5	4.38	0.1	5.39	0.0	3.08	0.5	---	---	---	---	---	---	---	---
3	**Acetonitrile**	1.98	3.1	0.00	89.6	1.62	5.8	2.92	0.6	4.31	0.1	5.32	0.0	2.85	0.7	---	---	---	---	---	---	---	---
	DMSO	1.97	3.2	0.00	89.1	1.58	6.1	2.87	0.7	4.29	0.1	5.30	0.0	2.76	0.8	---	---	---	---	---	---	---	---
	Methanol	1.99	3.1	0.00	89.8	1.63	5.7	2.94	0.6	4.32	0.1	5.33	0.0	2.88	0.7	---	---	---	---	---	---	---	---
	Water	1.95	3.3	0.00	88.3	1.54	6.6	2.81	0.8	4.25	0.1	5.27	0.0	2.66	1.0	---	---	---	---	---	---	---	---

Table S4: Compounds **1**, **2** and **3** relative Gibbs free energies (ΔG) in kcal mol^{-1} and corresponding populations (%P) obtained at the B3LYP-D3/aug-cc-pVDZ level for the isolated compounds and by using the IEF-PCM implicit solvent model with dichloromethane, acetone, acetonitrile, DMSO, methanol and water dielectric constants.

		1a		**1b**		**1c**		**1d**		**1e**		**1f**		**1g**		**1h**		**1i**		**1j**		**1k**	
		ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P	ΔG	%P
1	**Isolated**	0.51	24.0	0.77	15.4	1.64	3.5	0.00	56.5	2.97	0.4	5.32	0.0	4.05	0.1	4.26	0.0	4.91	0.0	6.51	0.0	7.76	0.0
	CH_2Cl_2	1.08	11.0	0.00	68.8	2.30	1.4	0.79	18.0	2.88	0.5	5.04	0.0	3.63	0.1	4.17	0.1	4.58	0.0	6.41	0.0	8.14	0.0
	Acetone	1.11	8.9	0.00	58.1	2.14	1.6	0.41	29.0	2.57	0.8	3.34	0.2	2.25	1.3	3.75	0.1	4.32	0.0	5.86	0.0	7.77	0.0
	Acetonitrile	1.13	7.3	0.00	49.4	2.06	1.5	0.13	39.9	2.46	0.8	3.32	0.2	2.51	0.7	3.56	0.1	4.23	0.0	5.65	0.0	7.61	0.0
	DMSO	1.16	7.2	0.00	51.5	2.07	1.6	0.18	37.9	2.46	0.8	3.35	0.2	2.58	0.7	3.52	0.1	4.22	0.0	5.60	0.0	7.59	0.0
	Methanol	1.13	7.6	0.00	50.9	2.07	1.5	0.17	38.1	2.48	0.8	3.34	0.2	2.49	0.8	3.58	0.1	4.24	0.0	5.68	0.0	7.64	0.0
	Water	1.35	5.6	0.22	37.6	2.20	1.3	0.00	54.1	2.62	0.6	3.49	0.1	2.80	0.5	3.60	0.1	4.35	0.0	5.68	0.0	7.68	0.0
		2a		**2b**		**2c**		**2d**		**2e**		**2f**		**2g**		**2h**		**2i**					
2	**Isolated**	0.46	27.0	0.00	58.9	0.85	14.0	---	---	4.64	0.0	4.97	0.0	5.52	0.0	3.92	0.1	8.04	0.0	---	---	---	---
	CH_2Cl_2	2.03	2.7	0.00	82.4	1.72	4.5	1.23	10.3	3.58	0.2	5.50	0.0	5.37	0.0	6.52	0.0	6.89	0.0	---	---	---	---
	Acetone	2.28	1.7	0.00	80.8	1.96	2.9	1.02	14.4	3.79	0.1	5.92	0.0	5.54	0.0	5.08	0.0	6.52	0.0	---	---	---	---
	Acetonitrile	2.43	1.4	0.00	84.6	2.00	2.9	1.21	11.0	3.92	0.1	6.03	0.0	5.62	0.0	5.33	0.0	5.74	0.0	---	---	---	---
	DMSO	2.44	1.4	0.00	84.8	1.97	3.0	1.23	10.7	3.92	0.1	6.01	0.0	5.63	0.0	5.35	0.0	6.05	0.0	---	---	---	---
	Methanol	2.43	1.4	0.00	84.5	2.02	2.8	1.20	11.2	3.92	0.1	6.04	0.0	5.62	0.0	5.32	0.0	5.44	0.0	---	---	---	---
	Water	2.44	1.4	0.00	84.7	1.91	3.3	1.24	10.5	3.92	0.1	6.00	0.0	5.62	0.0	5.38	0.0	6.24	0.0	---	---	---	---
		3a		**3b**		**3c**		**3d**		**3e**		**3f**		**3g**									
3	**Isolated**	2.92	0.7	0.00	99.3	5.80	0.0	6.94	0.0	7.35	0.0	7.72	0.0	7.12	0.0	---	---	---	---	---	---	---	---
	CH_2Cl_2	2.93	0.7	0.00	98.9	3.72	0.2	4.15	0.1	5.52	0.0	4.71	0.0	4.25	0.1	---	---	---	---	---	---	---	---
	Acetone	2.90	0.7	0.00	98.7	3.54	0.2	3.69	0.2	5.42	0.0	6.33	0.0	4.07	0.1	---	---	---	---	---	---	---	---
	Acetonitrile	2.85	0.8	0.00	98.5	3.48	0.3	3.59	0.2	5.30	0.0	6.31	0.0	3.88	0.1	---	---	---	---	---	---	---	---
	DMSO	2.82	0.8	0.00	98.4	3.44	0.3	3.55	0.2	5.24	0.0	6.30	0.0	3.81	0.2	---	---	---	---	---	---	---	---
	Methanol	2.86	0.8	0.00	98.6	3.49	0.3	3.61	0.2	5.33	0.0	6.31	0.0	3.92	0.1	---	---	---	---	---	---	---	---
	Water	2.76	0.9	0.00	98.3	3.39	0.3	3.47	0.3	5.18	0.0	6.27	0.0	3.69	0.2	---	---	---	---	---	---	---	---

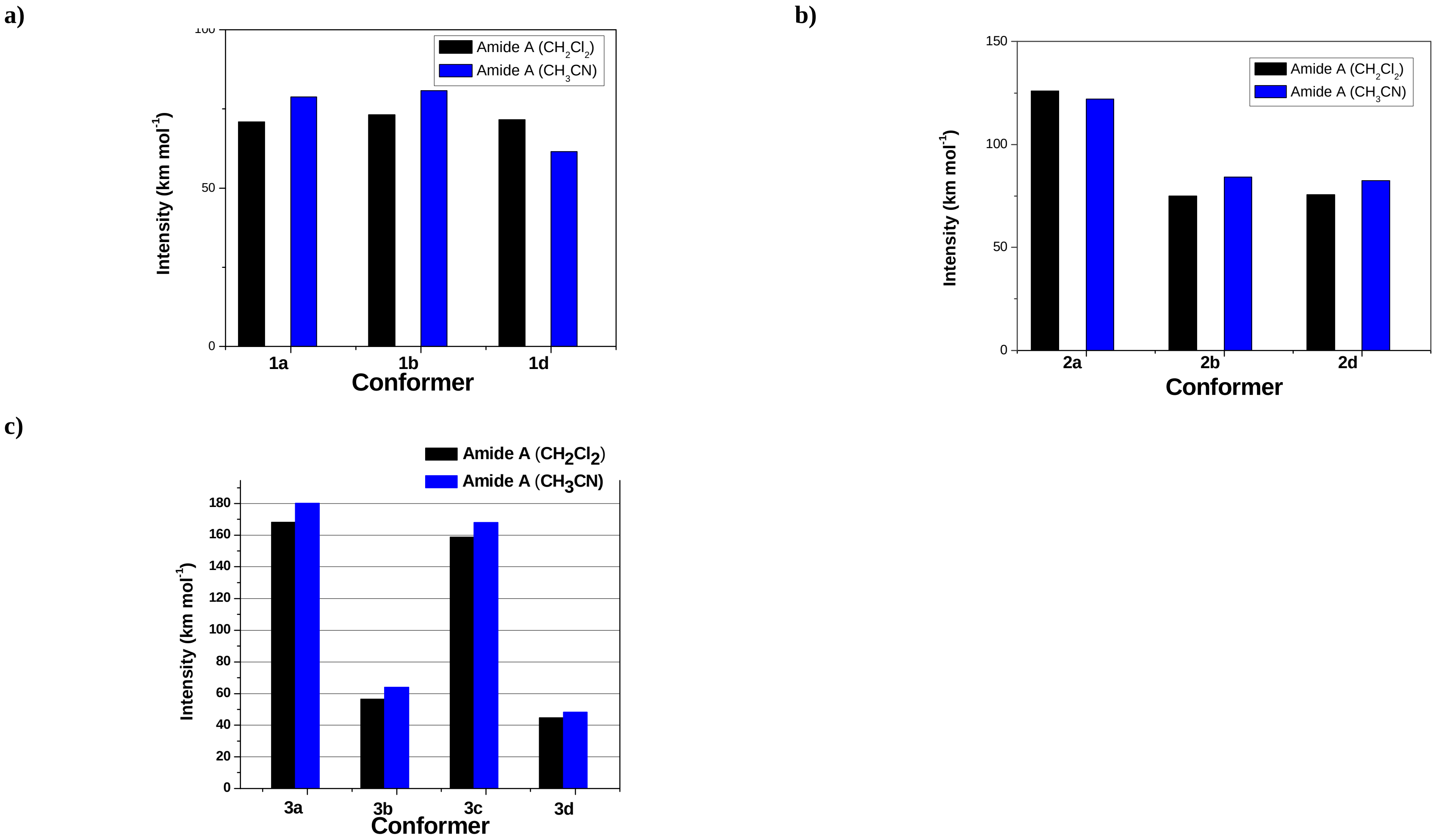
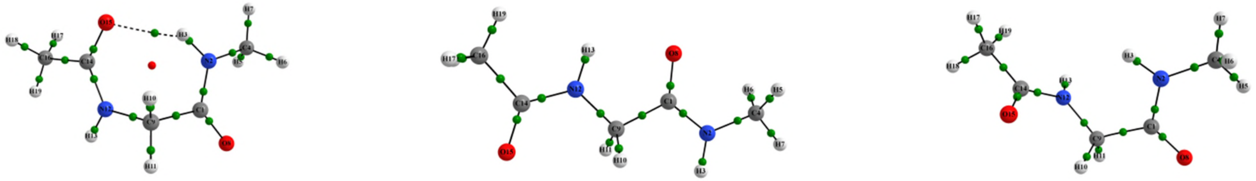


Figure S3: Ac-Gly-NHMe calculated (B3LYP-D3/aug-cc-pVDZ) IR intensities for **a)** Amide A and Amide B absorptions for conformers **1a**, **1b** and **1d** in CH_2Cl_2 and acetonitrile**. b)** Amide A and Amide B absorptions for conformers **2a**, **2b** and **2d** in CH_2Cl_2 and acetonitrile and c). Amide A and Amide B absorptions for conformers **3a**, **3b** and **3d** in CH_2Cl_2 and acetonitrile

Ac-Gly-NHMe

1a **1b** **1d**



ρ = 0.022 au
$\nabla^2\rho$ = +0.066 au
ε = 0.034 au

CF_3-C(O)-Gly-NHMe

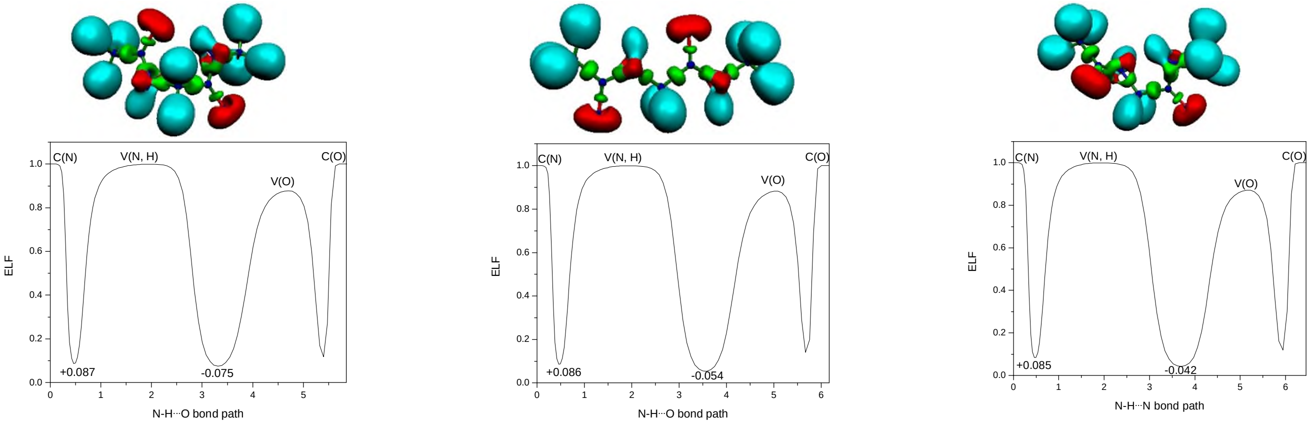
2a **2b** **2c** **2d**

ρ = 0.017
$\nabla^2\rho$ = +0.052
ε = 0.029 au

Figure S4: QTAIM molecular graphs of compounds **1** and **2** most stable conformers obtained from B3LYP-D3/aug-cc-pVDZ optimisations. Electron density (ρ), Laplacian of the electron density ($\nabla^2\rho$) and ellipticity values (ε, au) in the intramolecular hydrogen bond bond critical point (BCP) are indicated for each case. Green points represent BCPs and red points represent ring critical points (RCPs).

Ac-Gly-NHMe

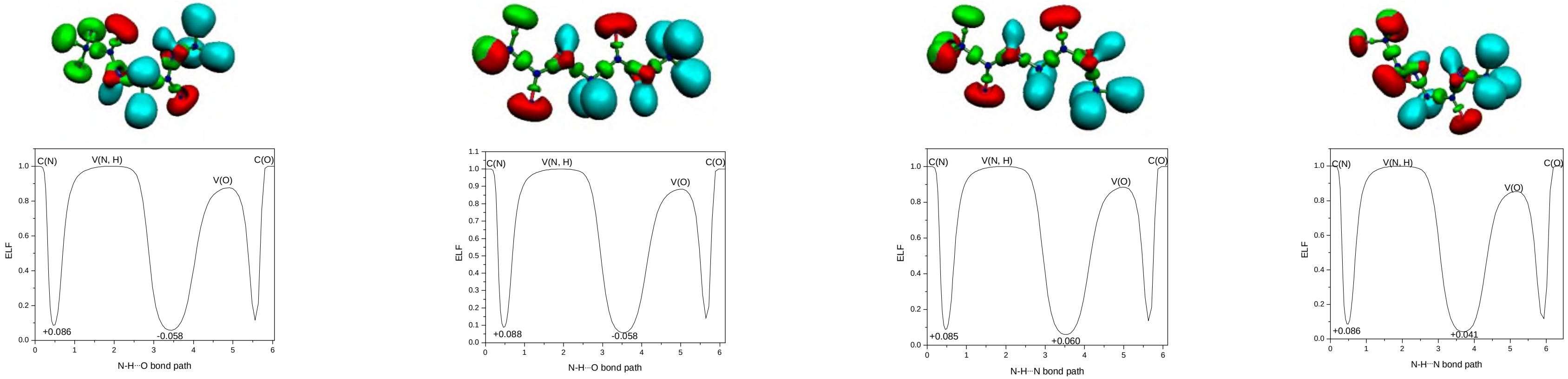
1a **1b** **1d**



CVBI = +0.012 CVBI = +0.032 CVBI = +0.042

CF_3-C(O)-Gly-NHMe

2a **2b** **2c** **2d**

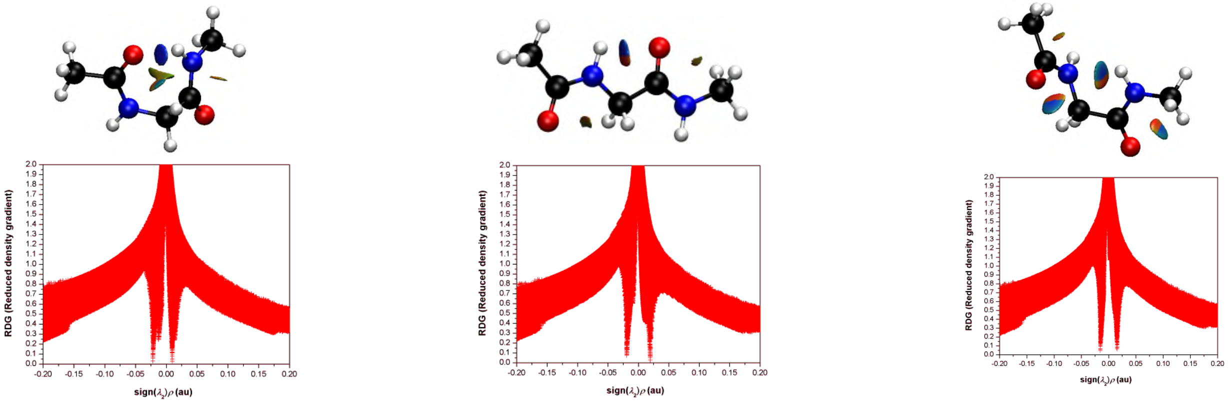


CVBI = +0.027 CVBI = +0.030 CVBI = +0.030 CVBI = +0.045

Figure S5: ELF localization domains (0.8 au isodensity value) of compounds **1** and **2** main conformers obtained from B3LYP-D3/aug-cc-pVDZ optimisations. Graphs of ELF value along the bond path of the IHB are given for each case. Core valence bifurcation index (CVBI) values (au) for each case obtained from those graphs are also indicated.

Ac-Gly-NHMe

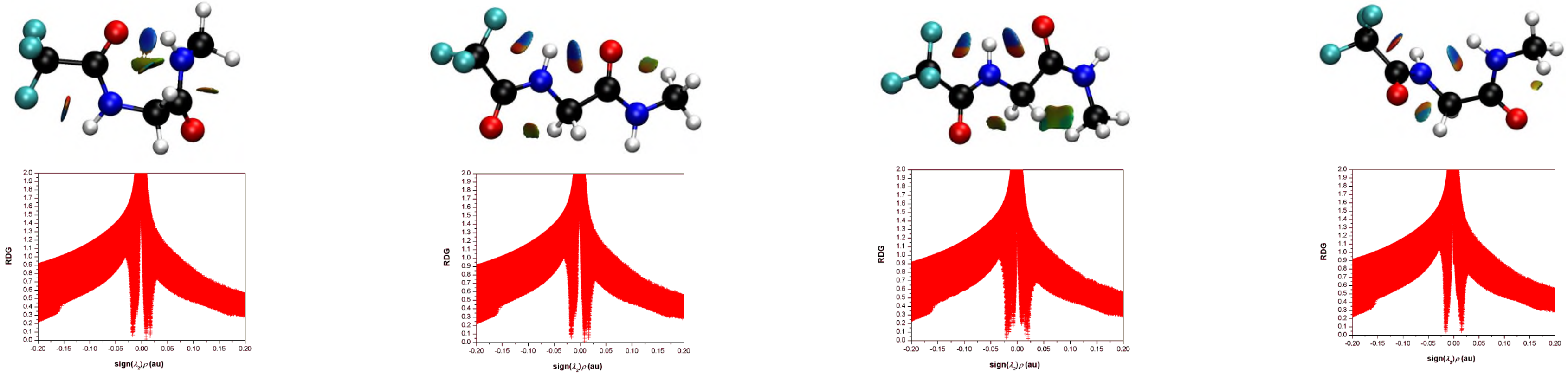
1a **1b** **1d**



sign(λ_2)ρ = -0.022 sign(λ_2)ρ = -0.019 sign(λ_2)ρ = -0.016

CF$_3$-C(O)-Gly-NHMe

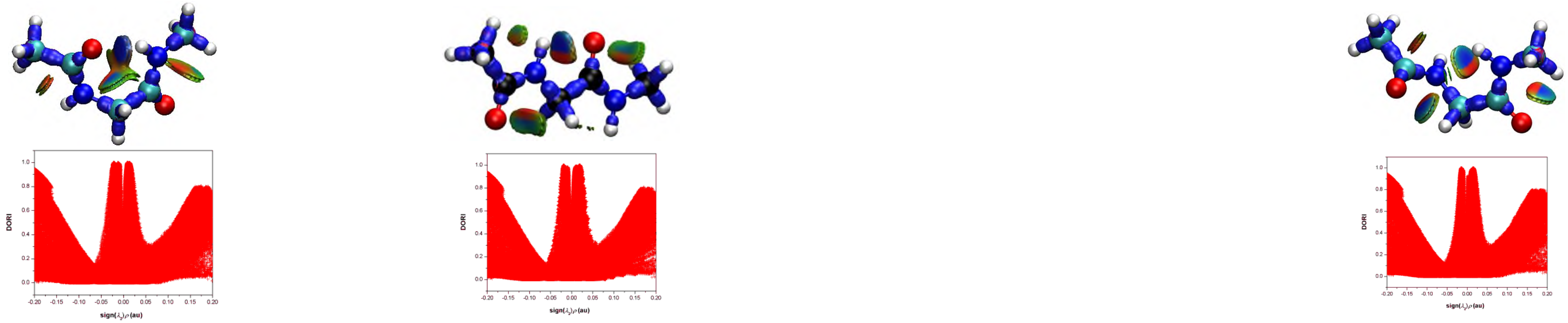
2a **2b** **2c** **2d**



sign(λ_2)ρ = -0.017 sign(λ_2)ρ = -0.020 sign(λ_2)ρ = -0.020 sign(λ_2)ρ = -0.015

Figure S6: NCI isosurface plots of compounds **1** and **2** main conformers obtained from B3LYP-D3/aug-cc-pVDZ optimisations. The figures were obtained with a reduced density gradient (RDG) value of 0.6 and the blue-green-red values ranging from -0.02 to 0.02 au. Graph of the RDG *vs* sign(λ_2)ρ are given for each case. Values of sign(λ_2)ρ (au) corresponding to IHBs peaks in the (RDG) *vs* sign(λ_2)ρ graphs are given for each case.

Ac-Gly-NHMe

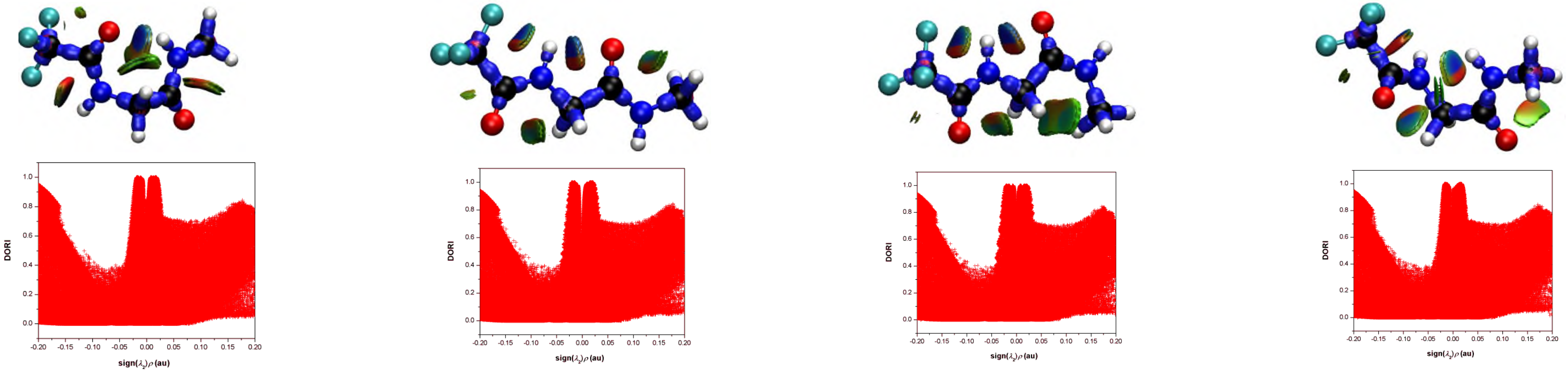


1a sign(λ_2)ρ = -0.022

1b sign(λ_2)ρ = -0.019

1d sign(λ_2)ρ = -0.015

CF$_3$-C(O)-Gly-NHMe



2a sign(λ_2)ρ =

2b sign(λ_2)ρ = -0.020

2c sign(λ_2)ρ = -0.020

2d sign(λ_2)ρ = -0.015

Figure S7: DORI isosurface plots of compounds **1** and **2** main conformers obtained from B3LYP-D3/aug-cc-pVDZ optimisations. The figures were obtained with a DORI value of 0.9 au and the blue-green-red values ranging from -0.02 to 0.02 au. Values of sign(λ_2)ρ (au) corresponding to IHBs peaks in the DORI vs sign(λ_2)ρ graphs are given for each case.

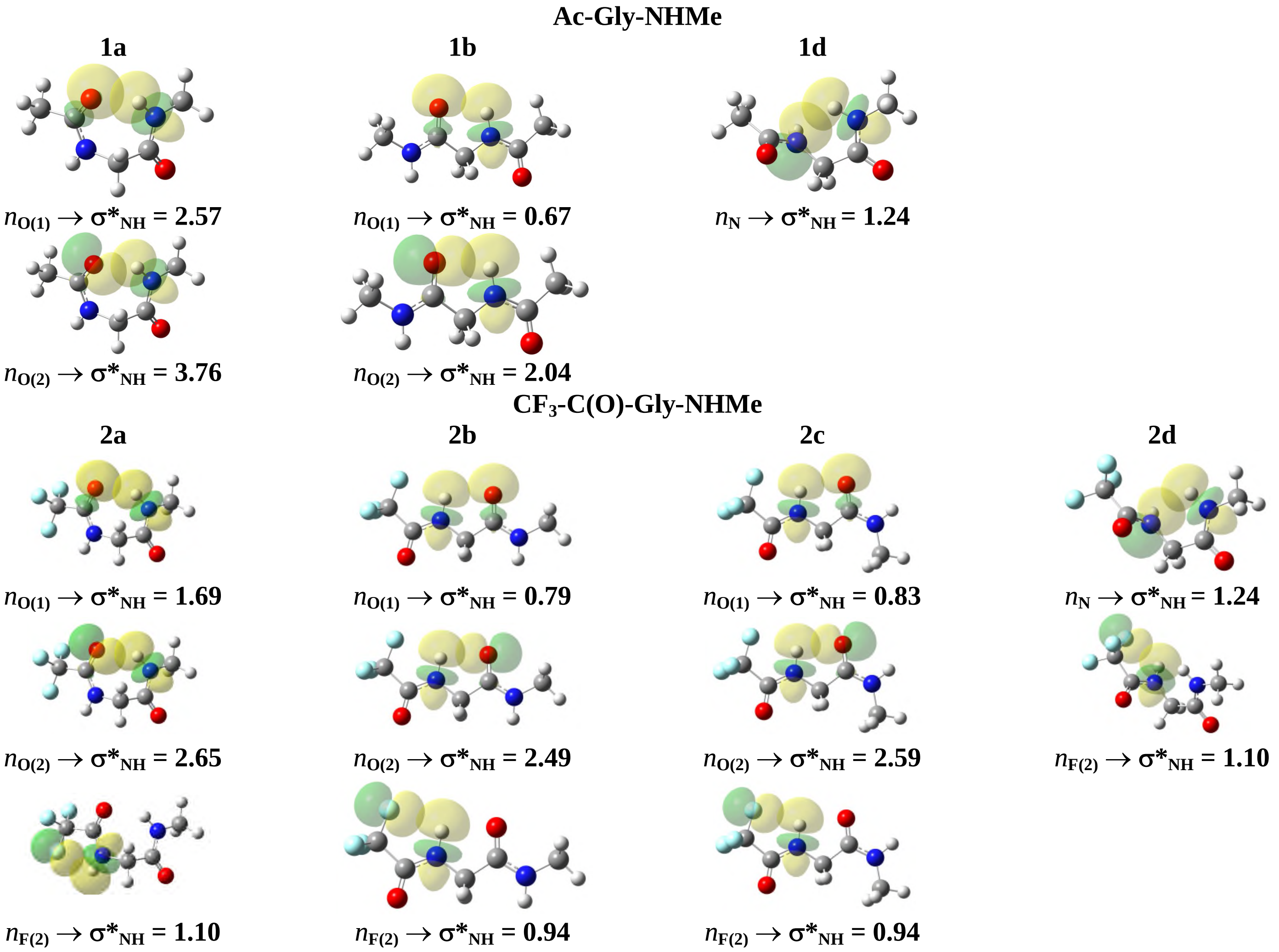


Figure S8: NBO plots of $n \rightarrow \sigma^*_{NH}$ interactions for main conformers of **1** and **2**. Figures were obtained at the B3LYP-D3/aug-cc-pVDZ level with an isovalue of 0.04 au. $n \rightarrow \sigma^*_{NH}$ energy values are given in kcal mol^{-1}.

Table S5: Compounds **1**, **2** and **3** $^{3}J_{\mathrm{HH}}$ calculated SSCCs (in Hz) at the BHandH/EPR-III and SOPPA(CCSD)/EPR-III on B3LYP-D3/aug-cc-pVDZ optimised geometries for the isolated compounds.

		1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**
1	**$^{3}J_{\mathrm{H10H13}}$ (BHand/EPR-III)**	7.01	2.76	3.07	9.73	7.82	3.81	3.12	11.35	3.54	10.56	8.37
	$^{3}J_{\mathrm{H11H13}}$ (BHand/EPR-III)	6.47	2.79	2.71	4.61	7.71	10.23	3.12	5.22	3.00	5.72	8.17
	($^{3}J_{\mathrm{H10H11}}$ + $^{3}J_{\mathrm{H11H13}}$)/2	6.74	2.78	2.89	7.17	7.77	7.02	3.12	8.29	3.27	8.14	8.27
	$^{3}J_{\mathrm{H10H13}}$ [SOPPA(CCSD)/EPR-III]	6.01	1.76	2.04	8.33	6.64	3.22	2.16	10.04	2.55	9.42	7.63
	$^{3}J_{\mathrm{H11H13}}$ [SOPPA(CCSD)/EPR-III]	5.66	1.78	1.72	4.00	7.02	8.73	2.16	4.53	2.04	5.10	6.95
	($^{3}J_{\mathrm{H10H11}}$ + $^{3}J_{\mathrm{H11H13}}$)/2	5.84	1.77	1.88	6.17	6.83	5.98	2.16	7.29	2.30	7.26	7.29
		2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**	**2i**		
2	**$^{3}J_{\mathrm{H14H15}}$ (BHand/EPR-III)**	8.15	3.01	2.57	6.65	2.60	2.30	5.40	2.80	8.45	---	---
	$^{3}J_{\mathrm{H15H16}}$ (BHand/EPR-III)	6.62	2.57	3.24	8.07	2.59	12.08	9.74	2.75	3.90	---	---
	($^{3}J_{\mathrm{H14H15}}$ + $^{3}J_{\mathrm{H15H16}}$)/2	7.39	2.79	2.91	7.36	2.60	7.19	7.57	2.78	6.18	---	---
	$^{3}J_{\mathrm{H14H15}}$ [SOPPA(CCSD)/EPR-III]	6.65	2.43	2.00	5.86	2.62	1.95	5.38	2.76	7.58	---	---
	$^{3}J_{\mathrm{H15H16}}$ [SOPPA(CCSD)/EPR-III]	5.83	1.99	2.64	6.58	2.60	10.07	9.97	2.72	3.11	---	---
	($^{3}J_{\mathrm{H14H15}}$ + $^{3}J_{\mathrm{H15H16}}$)/2	6.24	2.21	2.32	6.22	2.61	6.01	7.68	2.74	5.35		
		3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**				
3	**$^{3}J_{\mathrm{H3H6}}$ (BHand/EPR-III)**	3.28	2.57	2.98	10.29	8.96	0.03	1.39		---	---	---
	$^{3}J_{\mathrm{H4H6}}$ (BHand/EPR-III)	10.25	2.66	2.98	5.77	7.69	11.80	7.87		---	---	---
	($^{3}J_{\mathrm{H3H6}}$ + $^{3}J_{\mathrm{H4H6}}$)/2	6.77	2.62	2.98	8.03	8.33	5.92	4.63		---	---	---
	$^{3}J_{\mathrm{H3H6}}$ [SOPPA(CCSD)/EPR-III]	2.70	1.84	2.28	9.40	7.92	-0.41	0.81		---	---	---
	$^{3}J_{\mathrm{H4H6}}$ [SOPPA(CCSD)/EPR-III]	8.98	1.92	2.28	5.09	6.88	10.61	7.13		---	---	---
	($^{3}J_{\mathrm{H3H6}}$ + $^{3}J_{\mathrm{H4H6}}$)/2	5.84	1.88	2.28	7.25	7.40	5.10	3.97		---	---	---

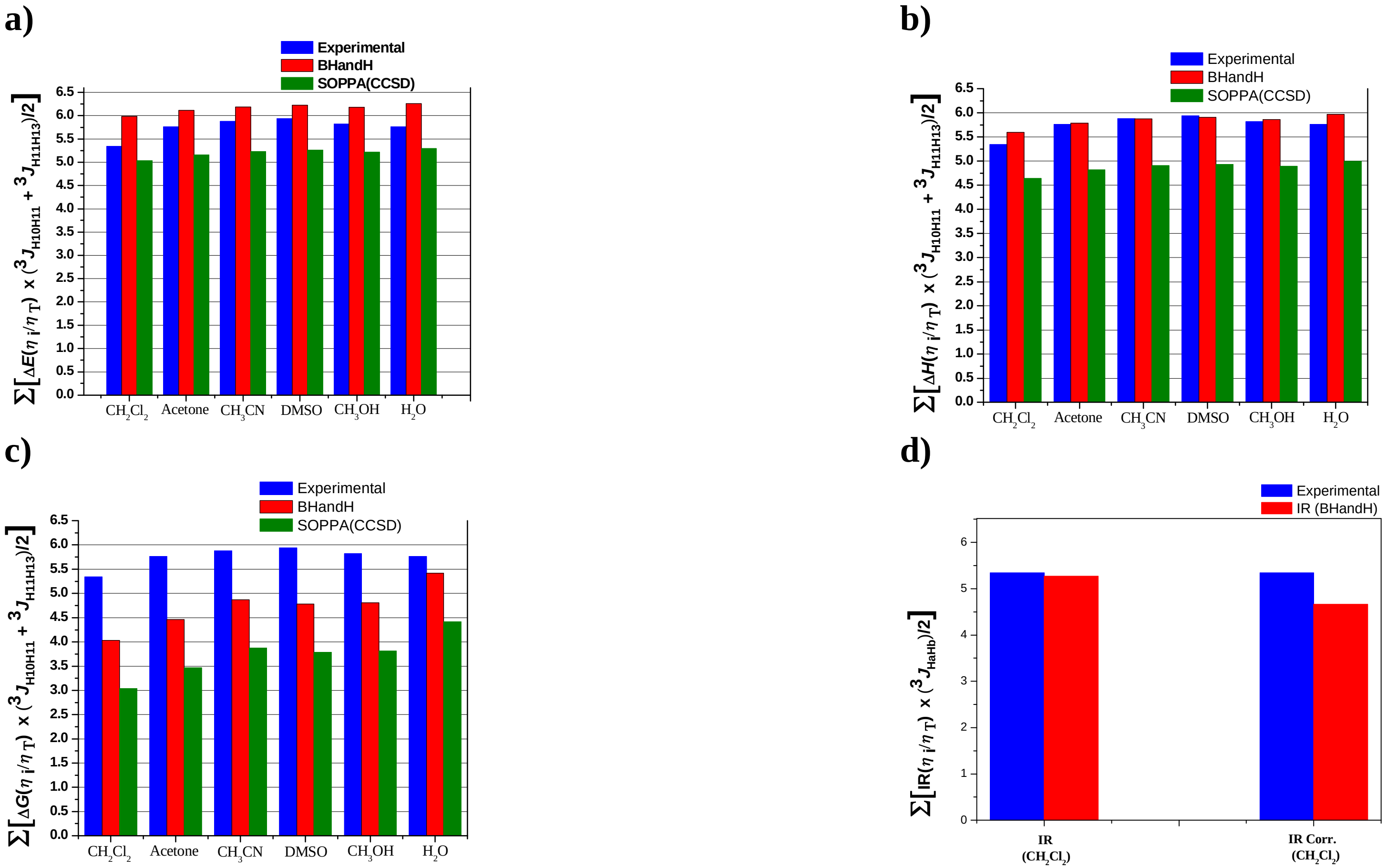


Figure S9: Sum of all Ac-Gly-NHMe conformers contributions [(n_i/n_T) x J] for the $^3J_{H10H11}$ and $^3J_{H11H13}$ SSCCs average values ($^3J_{H10H11}$ + $^3J_{H11H13}/2$) obtained in different solvents (B3LYP-D3/aug-cc-pVDZ level) by using the IEF-PCM model. Conformer contributions (n_i/n_T) values to $^3J_{HH}$ from **a)** ΔE; **b)** ΔH; **c)** ΔG; **d)** Experimental IR (using BHandH calculated $^3J_{HH}$) uncorrected and corrected (IR Corr.) by conformers calculated infrared intensities.

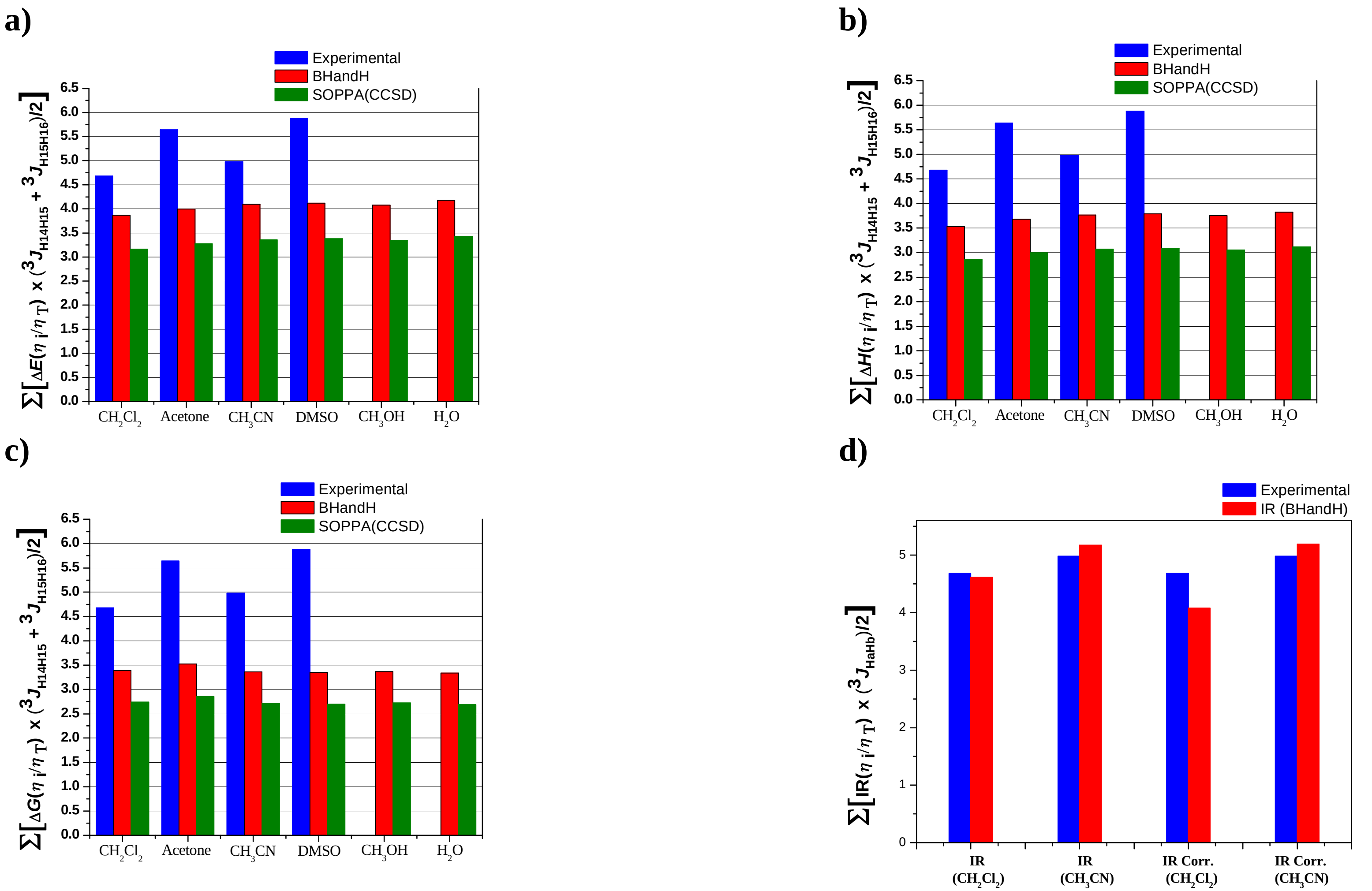


Figure S10: Sum of all CF_3-C(O)-Gly-NHMe conformers contributions [(n_i/n_T) x J] for the $^3J_{H14H15}$ and $^3J_{H15H16}$ SSCCs average values ($^3J_{H14H15}$ + $^3J_{H15H16}$)/2 obtained in different solvents (B3LYP-D3/aug-cc-pVDZ level) by using the IEF-PCM model. Conformer contributions (n_i/n_T) values to $^3J_{HH}$ from **a)** ΔE; **b)** ΔH; **c)** ΔG; **d)** Experimental IR (using BHandH calculated $^3J_{HH}$) and corrected IR (IR Corr.) with calculated infrared intensities.

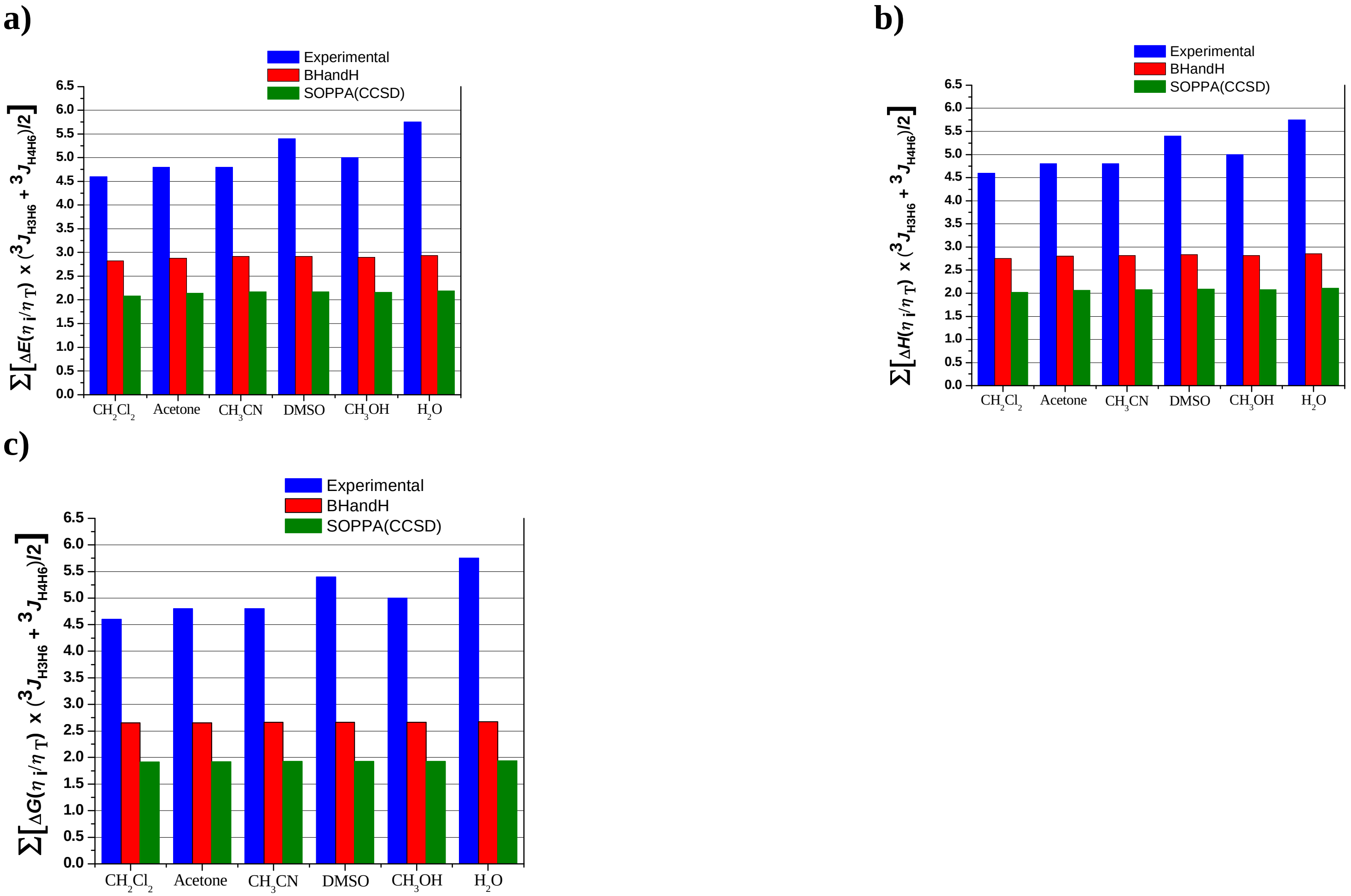
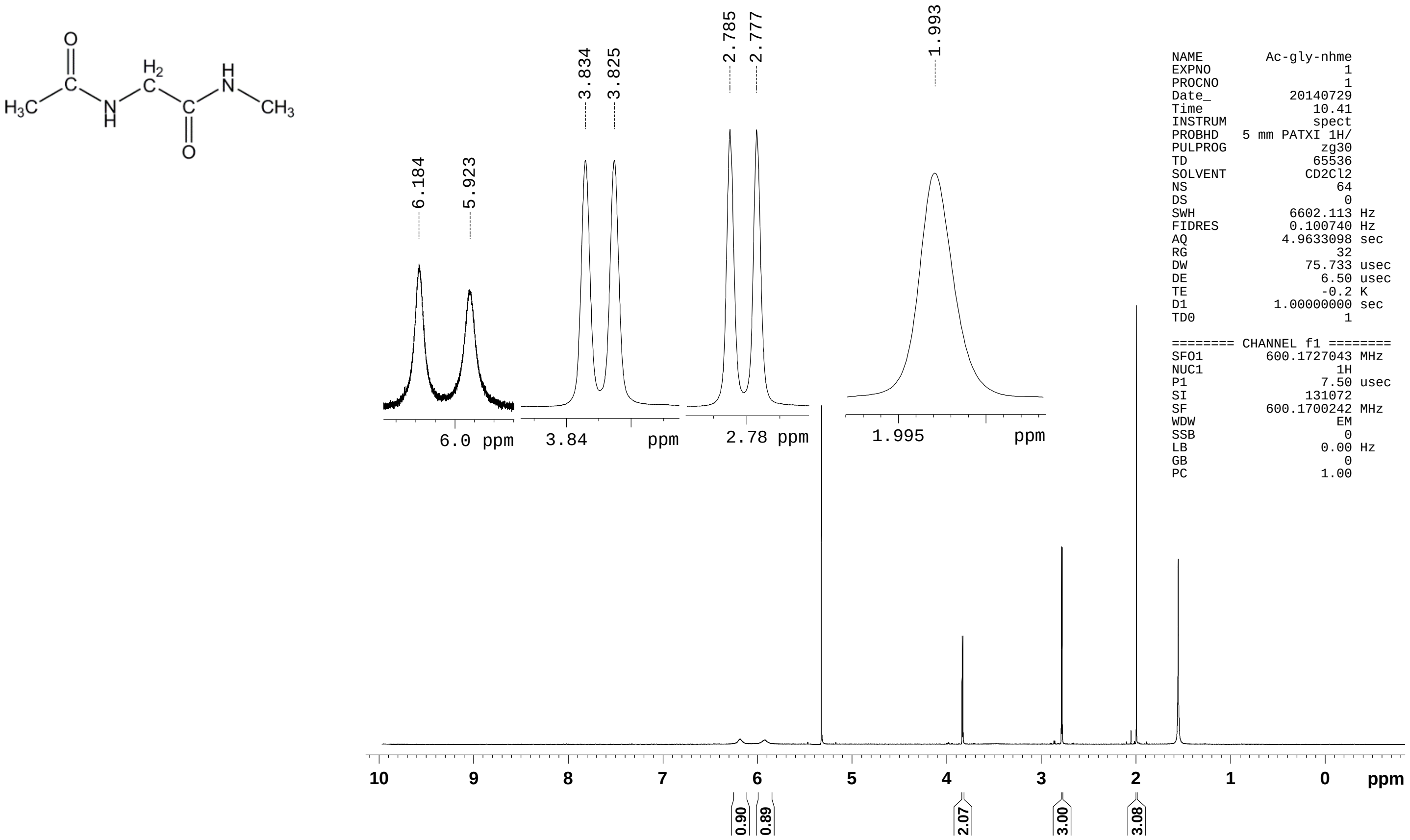


Figure S11: Sum of all Ac-Gly-N(Me)$_2$ conformers contributions [(n_i/n_T) x J] for the $^3J_{H3H6}$ and $^3J_{H4H6}$ SSCCs average values $(^3J_{H3H6} + {}^3J_{H4H6})/2$ obtained in different solvents (B3LYP-D3/aug-cc-pVDZ level) by using the IEF-PCM model. Conformer contributions (n_i/n_T) values to $^3J_{HH}$ from **a)** ΔE; **b)** ΔH and **c)** ΔG

^{1}H NMR Spectra (Bruker avance III 600 MHz)

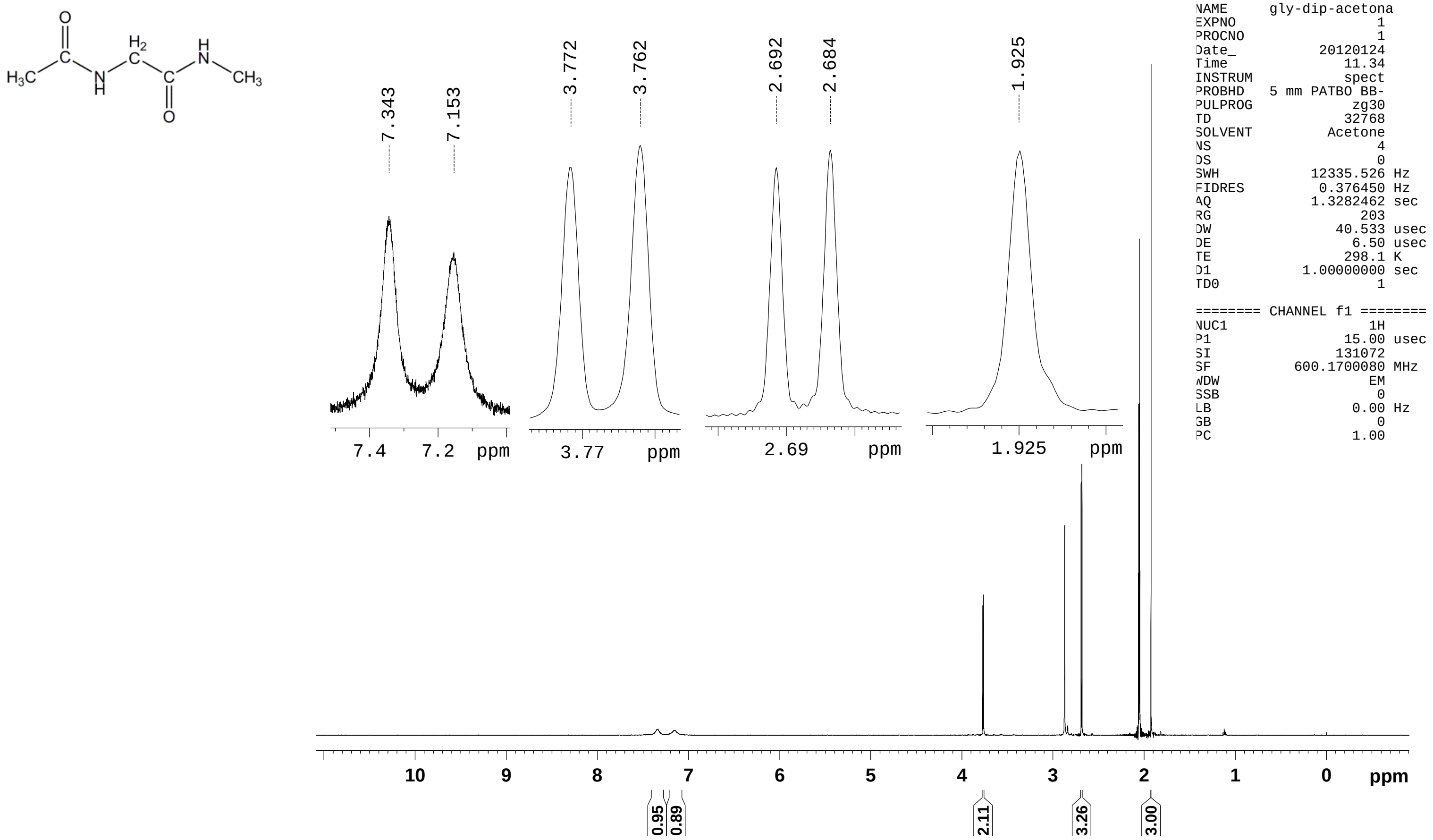
1. Ac-Gly-NHMe



```
NAME        Ac-gly-nhme
EXPNO                 1
PROCNO                1
Date_          20140729
Time              10.41
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG            zg30
TD                65536
SOLVENT          CD2Cl2
NS                   64
DS                    0
SWH            6602.113 Hz
FIDRES         0.100740 Hz
AQ            4.9633098 sec
RG                   32
DW               75.733 usec
DE                 6.50 usec
TE                 -0.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1727043 MHz
NUC1                 1H
P1                 7.50 usec
SI               131072
SF          600.1700242 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

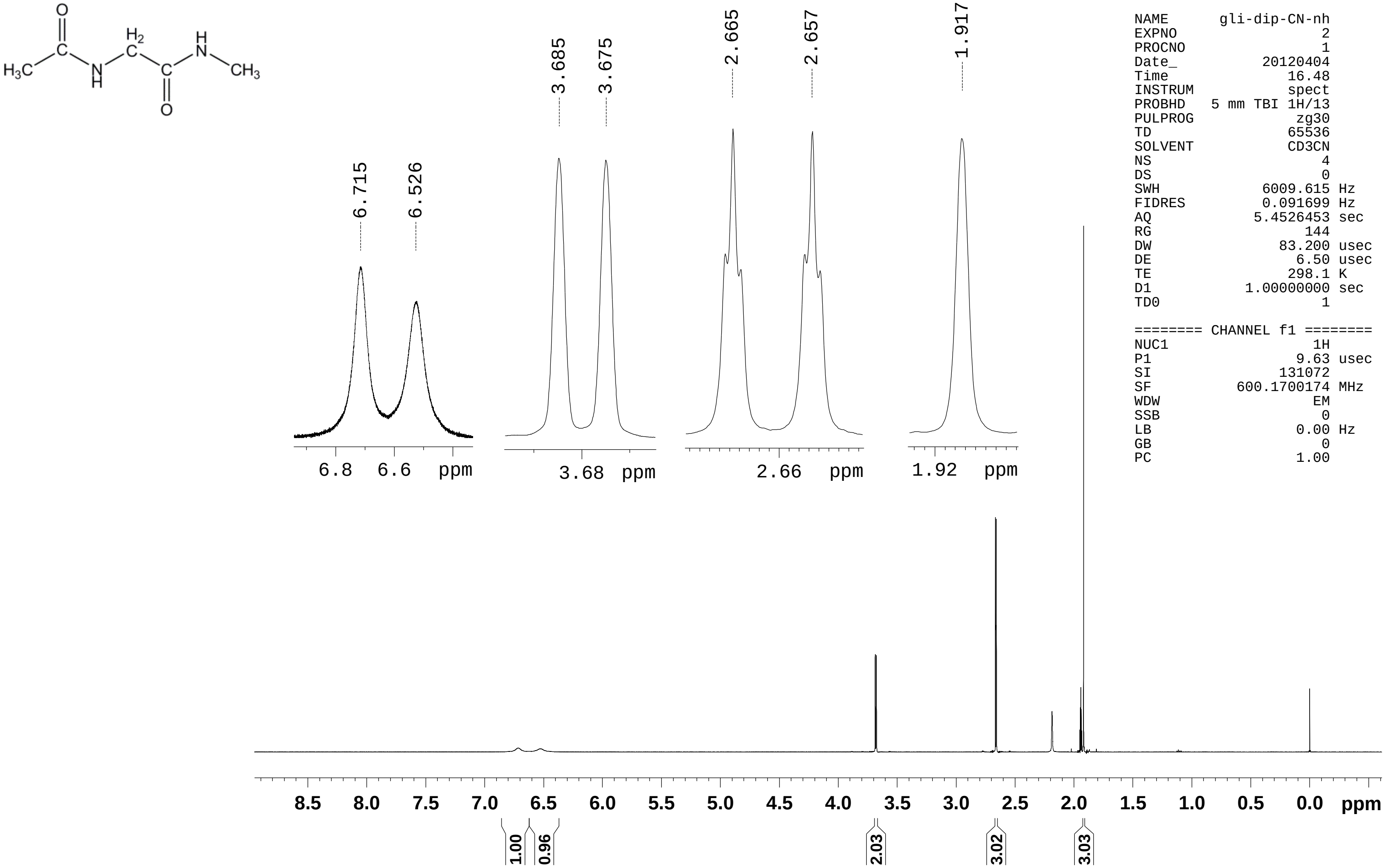
Spectrum S1: Ac-Gly-NHMe ^{1}H NMR Spectrum in CD_2Cl_2.



```
NAME     gly-dip-acetona
EXPNO                  1
PROCNO                 1
Date_           20120124
Time               11.34
INSTRUM            spect
PROBHD   5 mm PATBO BB-
PULPROG             zg30
TD                 32768
SOLVENT          Acetone
NS                     4
DS                     0
SWH           12335.526 Hz
FIDRES         0.376450 Hz
AQ            1.3282462 sec
RG                   203
DW               40.533 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
SI                131072
SF           600.1700080 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

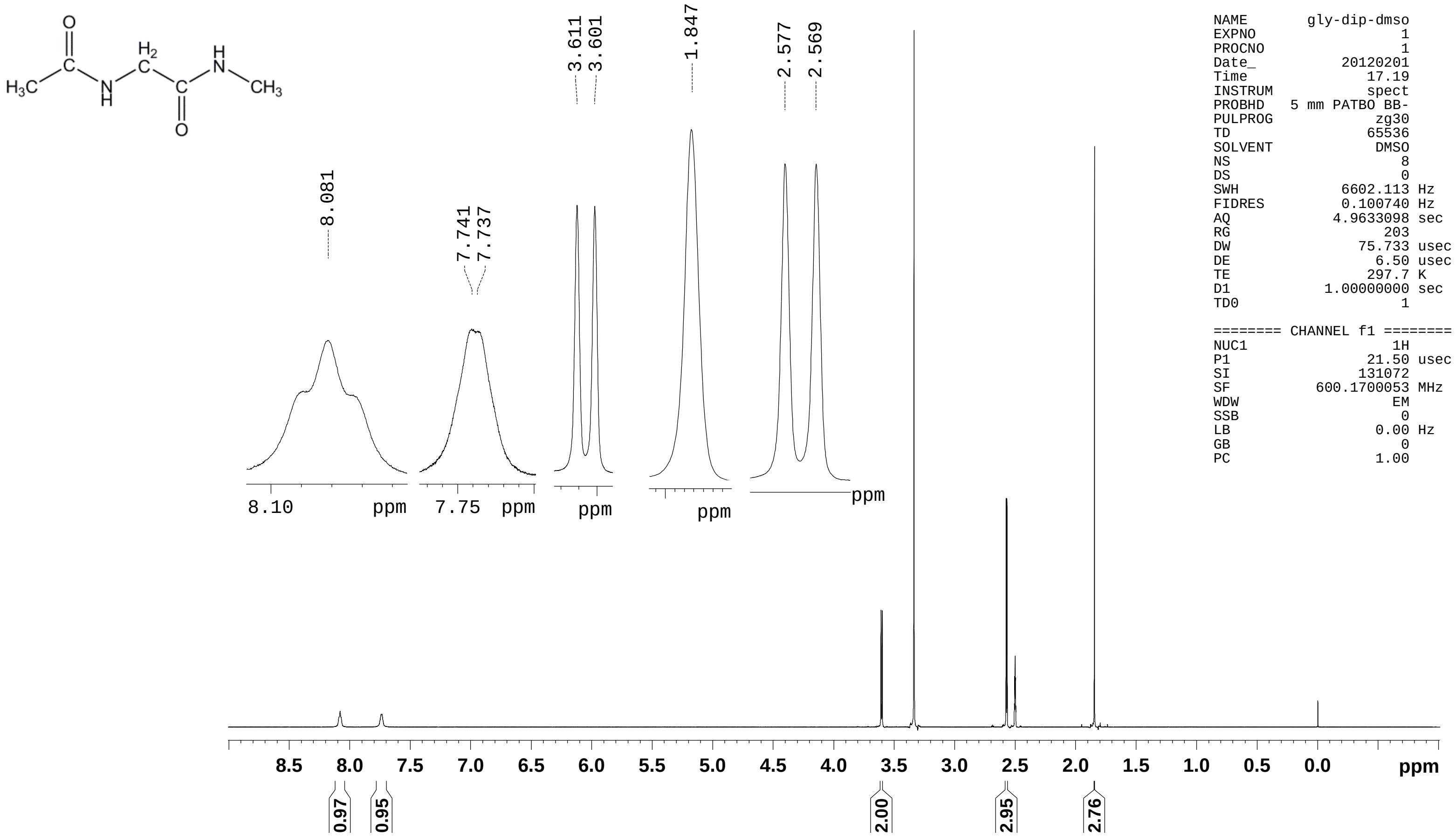
Spectrum S2: Ac-Gly-NHMe ^{1}H NMR Spectrum in acetone-d_6.



```
NAME      gli-dip-CN-nh
EXPNO                 2
PROCNO                1
Date_          20120404
Time              16.48
INSTRUM           spect
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                65536
SOLVENT            CD3CN
NS                    4
DS                    0
SWH            6009.615 Hz
FIDRES         0.091699 Hz
AQ            5.4526453 sec
RG                  144
DW               83.200 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 9.63 usec
SI               131072
SF          600.1700174 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

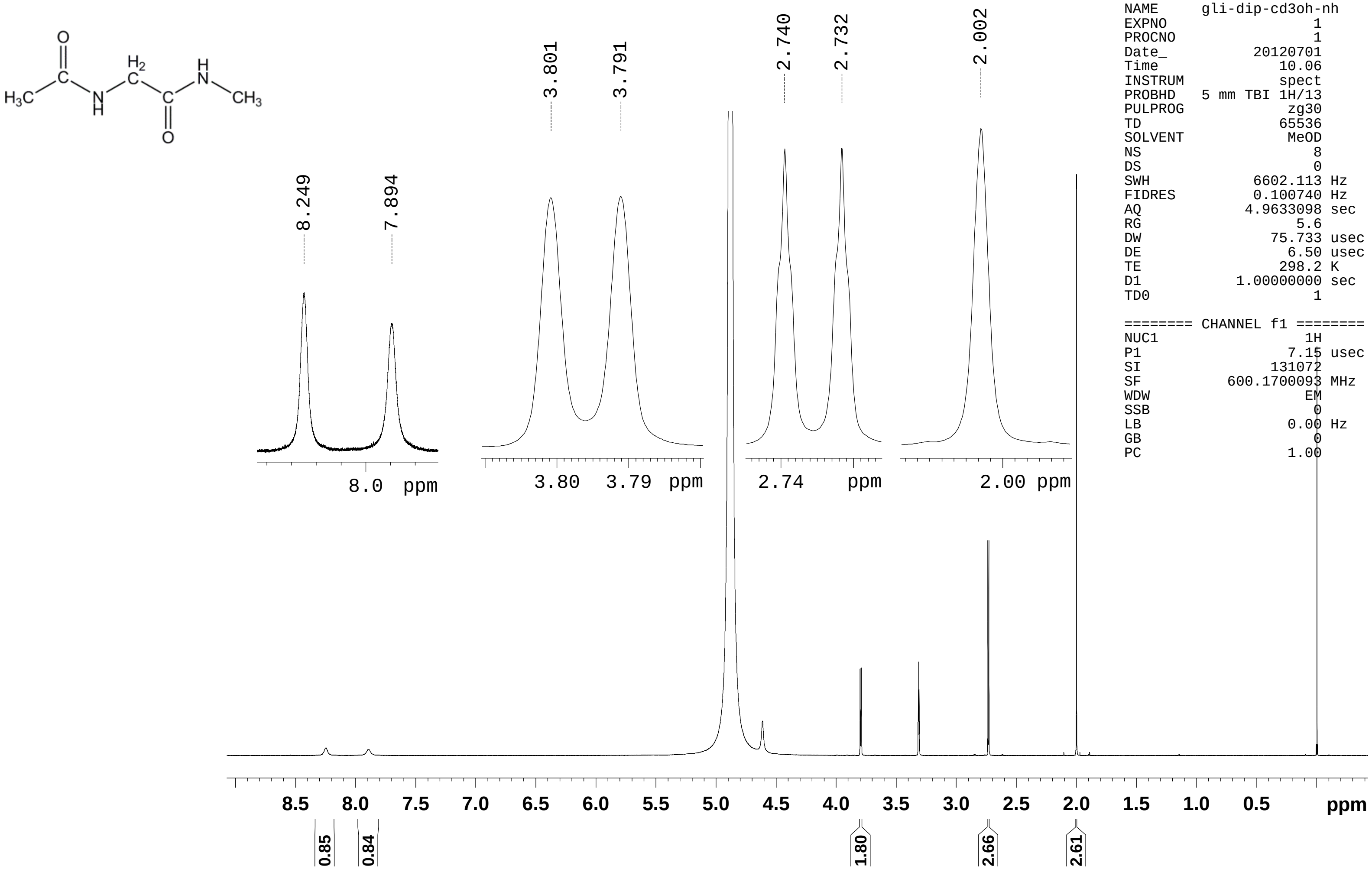
Spectrum S3: Ac-Gly-NHMe ^{1}H NMR Spectrum in CD_3CN.



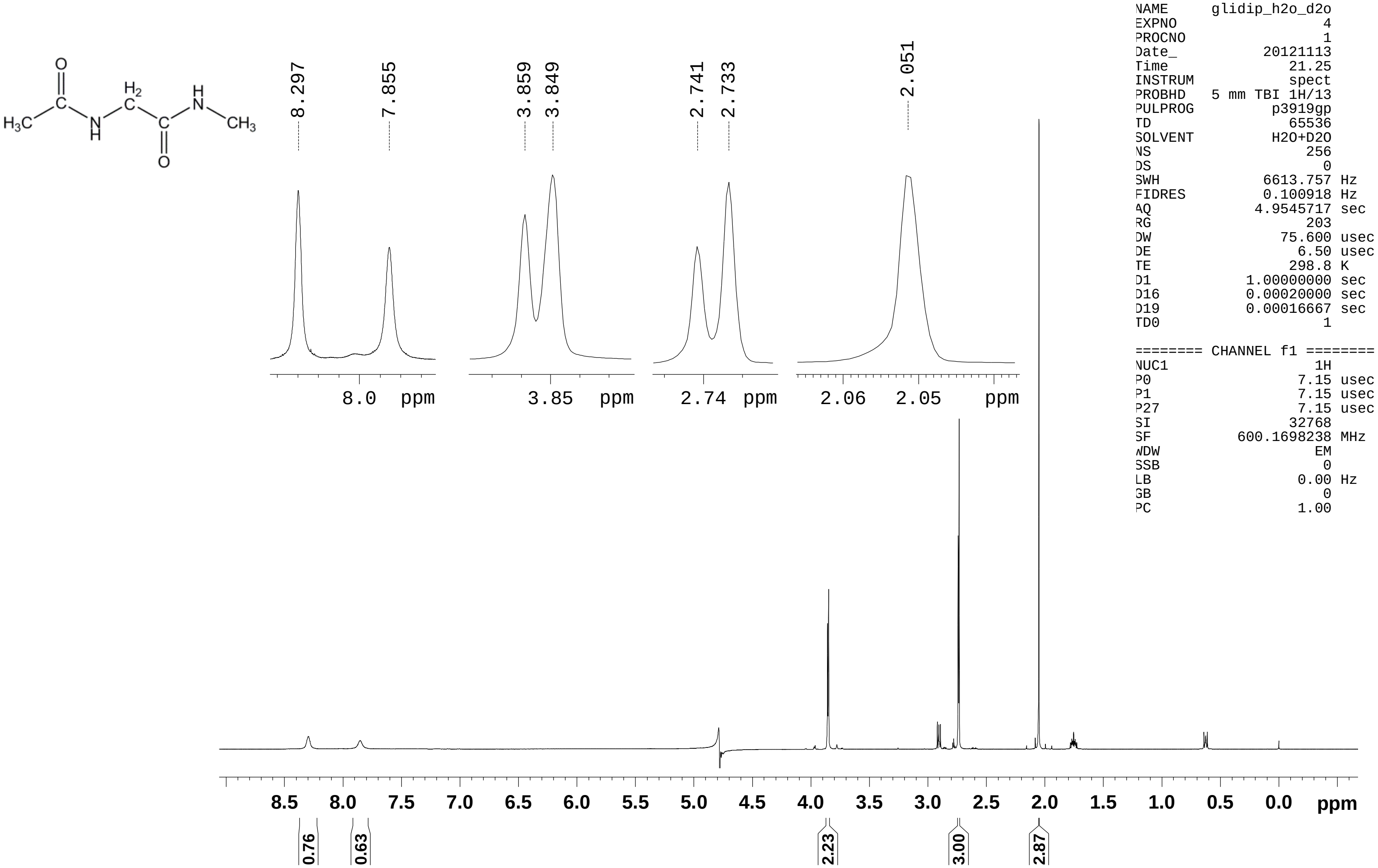
```
NAME       gly-dip-dmso
EXPNO                 1
PROCNO                1
Date_          20120201
Time              17.19
INSTRUM           spect
PROBHD   5 mm PATBO BB-
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                    8
DS                    0
SWH            6602.113 Hz
FIDRES         0.100740 Hz
AQ            4.9633098 sec
RG                  203
DW               75.733 usec
DE                 6.50 usec
TE                297.7 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                21.50 usec
SI               131072
SF          600.1700053 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

Spectrum S4: Ac-Gly-NHMe ^{1}H NMR Spectrum in DMSO-d_6.



Spectrum S5: Ac-Gly-NHMe ^{1}H NMR Spectrum in CD_3OH.

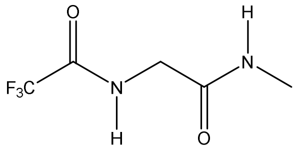


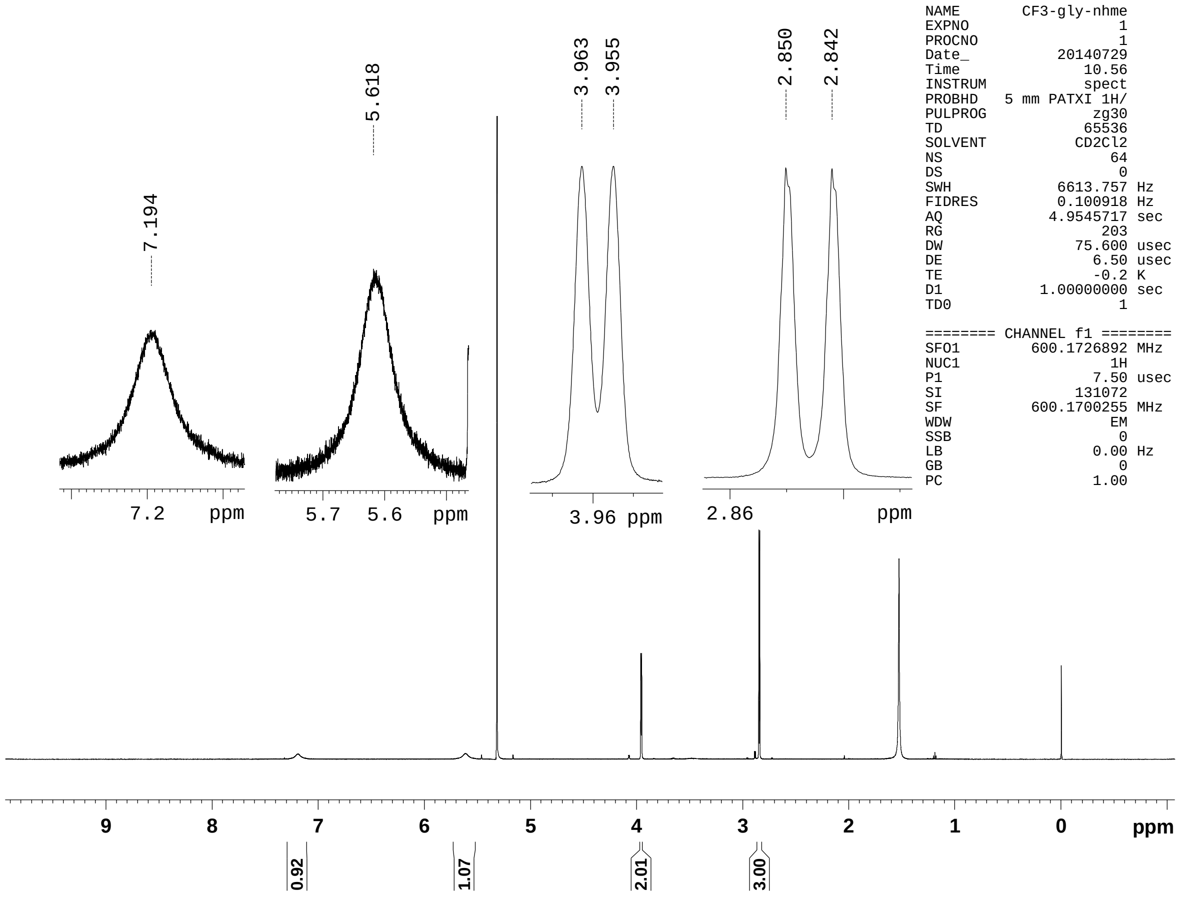
```
NAME      glidip_h2o_d2o
EXPNO                  4
PROCNO                 1
Date_           20121113
Time               21.25
INSTRUM            spect
PROBHD   5 mm TBI 1H/13
PULPROG          p3919gp
TD                 65536
SOLVENT          H2O+D2O
NS                   256
DS                     0
SWH             6613.757 Hz
FIDRES          0.100918 Hz
AQ             4.9545717 sec
RG                   203
DW                75.600 usec
DE                  6.50 usec
TE                 298.8 K
D1            1.00000000 sec
D16           0.00020000 sec
D19           0.00016667 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P0                  7.15 usec
P1                  7.15 usec
P27                 7.15 usec
SI                 32768
SF           600.1698238 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

Spectrum S6: Ac-Gly-NHMe ^{1}H NMR Spectrum in H_2O. WATERGATE solvent suppression was used.

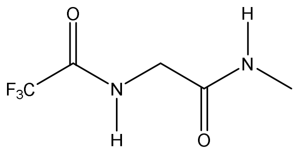
2. CF_3-C(O)-Gly-NHMe

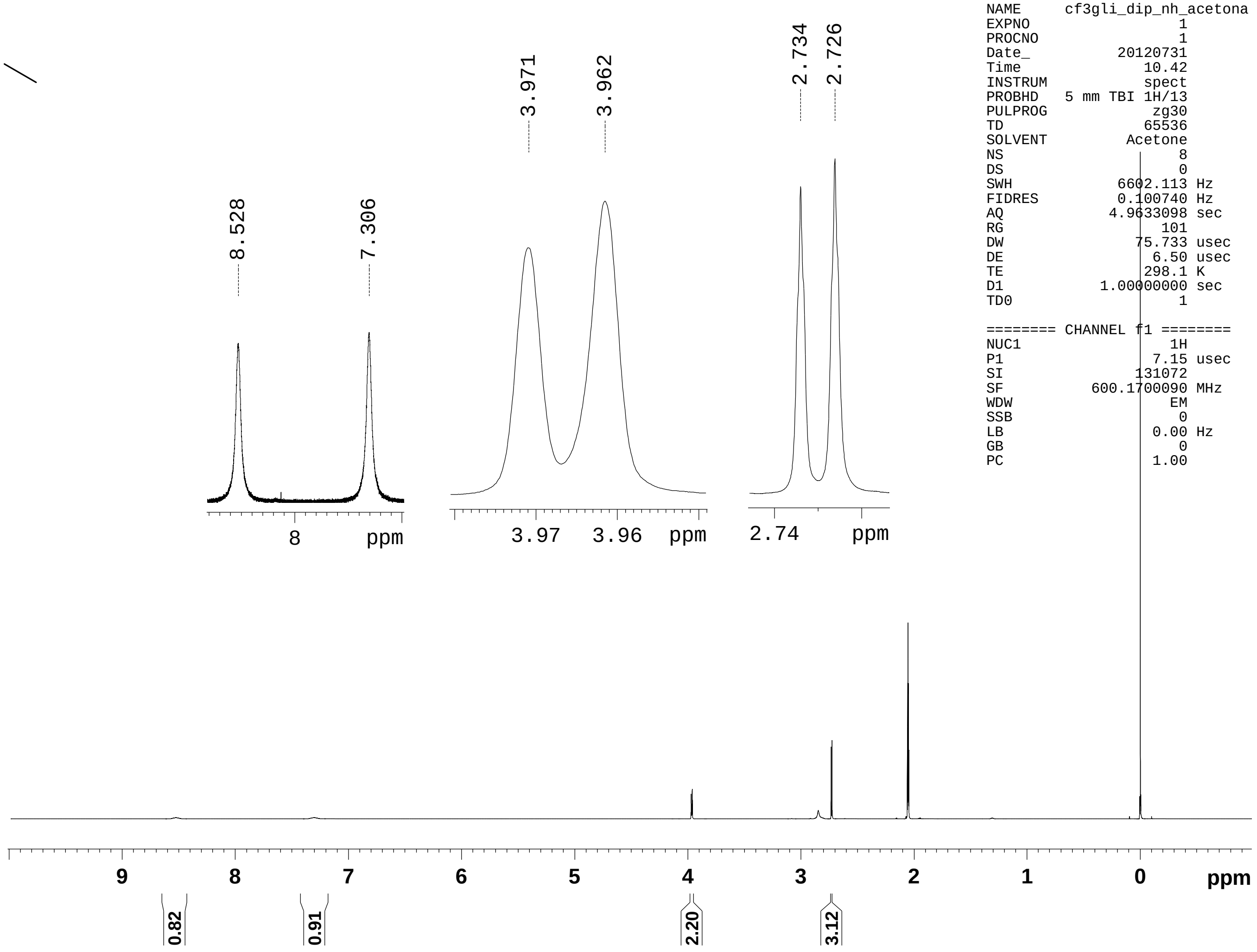



```
NAME        CF3-gly-nhme
EXPNO                  1
PROCNO                 1
Date_           20140729
Time               10.56
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG             zg30
TD                 65536
SOLVENT           CD2Cl2
NS                    64
DS                     0
SWH             6613.757 Hz
FIDRES          0.100918 Hz
AQ             4.9545717 sec
RG                   203
DW                75.600 usec
DE                  6.50 usec
TE                  -0.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         600.1726892 MHz
NUC1                  1H
P1                  7.50 usec
SI                131072
SF           600.1700255 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

Spectrum S7: CF_3-C(O)-Gly-NHMe ^{1}H NMR Spectrum in CD_2Cl_2.

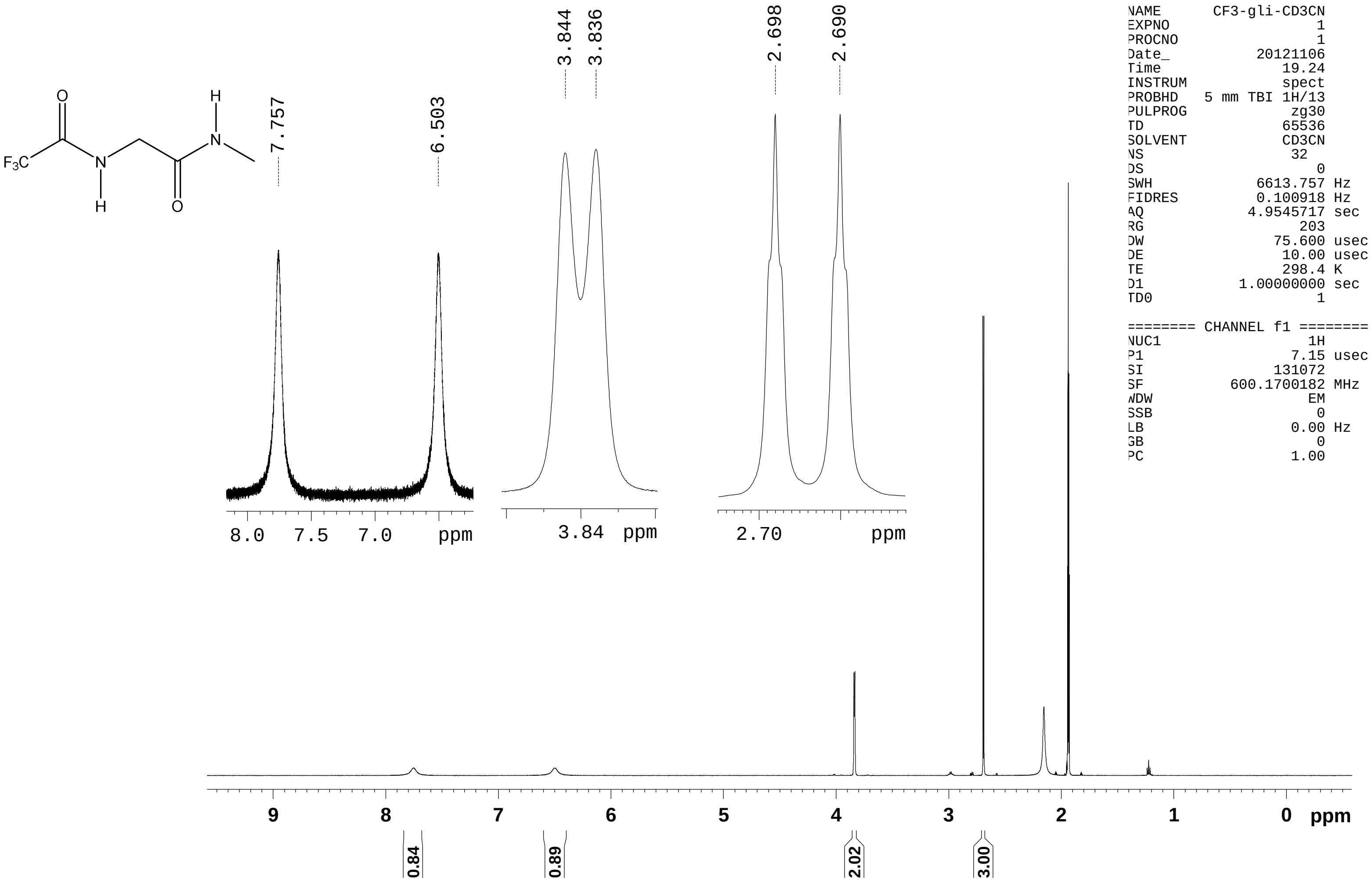




```
NAME     cf3gli_dip_nh_acetona
EXPNO                    1
PROCNO                   1
Date_             20120731
Time                 10.42
INSTRUM              spect
PROBHD   5 mm TBI 1H/13
PULPROG               zg30
TD                   65536
SOLVENT            Acetone
NS                       8
DS                       0
SWH            6602.113 Hz
FIDRES         0.100740 Hz
AQ            4.9633098 sec
RG                     101
DW               75.733 usec
DE                 6.50 usec
TE                 298.1 K
D1           1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.15 usec
SI                  131072
SF          600.1700090 MHz
WDW                     EM
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```

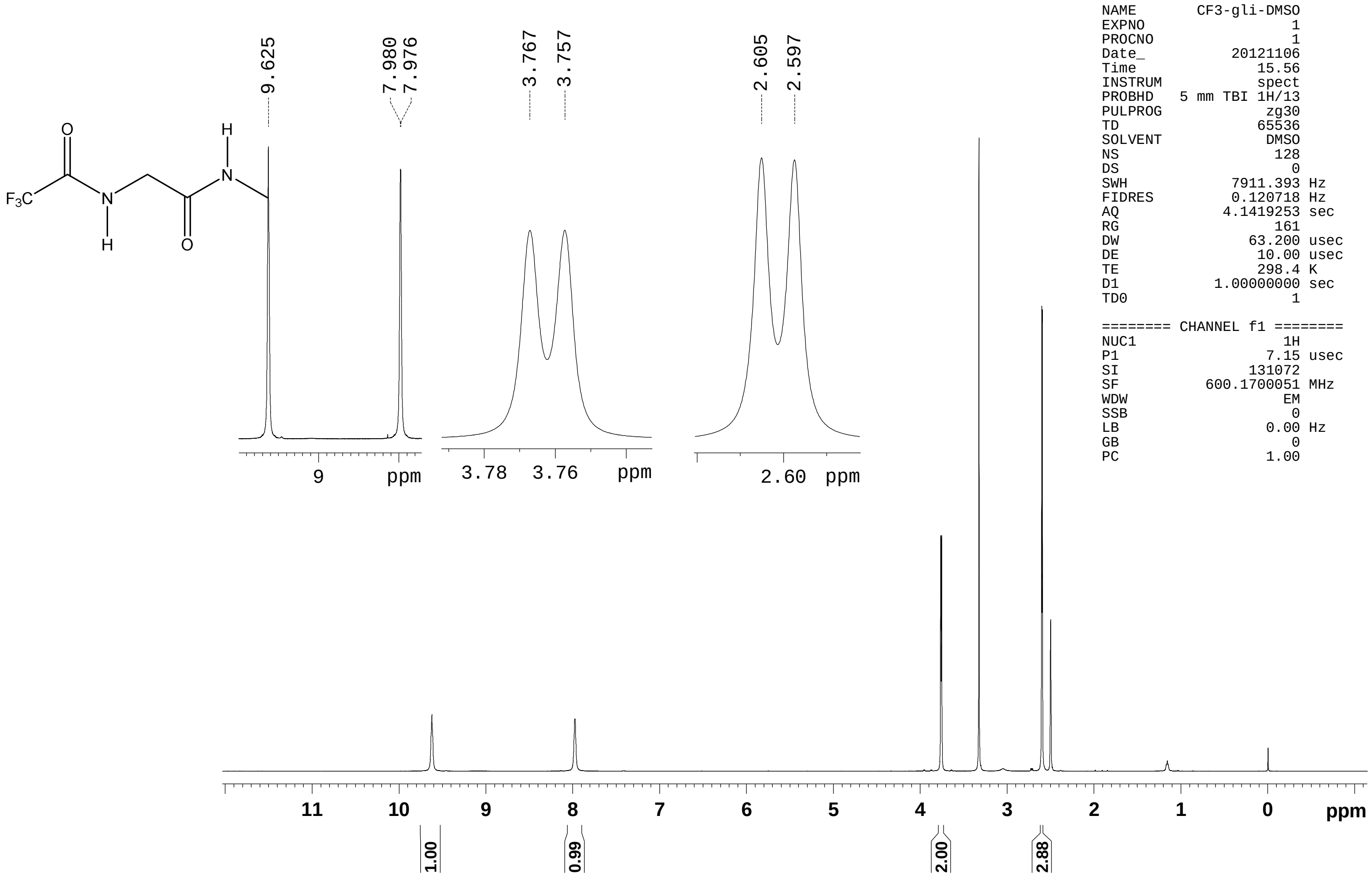
Spectrum S8: CF_3-C(O)-Gly-NHMe ^{1}H NMR Spectrum in acetone-d_6.



```
NAME      CF3-gli-CD3CN
EXPNO                 1
PROCNO                1
Date_          20121106
Time              19.24
INSTRUM           spect
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                65536
SOLVENT           CD3CN
NS                   32
DS                    0
SWH            6613.757 Hz
FIDRES         0.100918 Hz
AQ            4.9545717 sec
RG                  203
DW               75.600 usec
DE                10.00 usec
TE                298.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.15 usec
SI               131072
SF          600.1700182 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

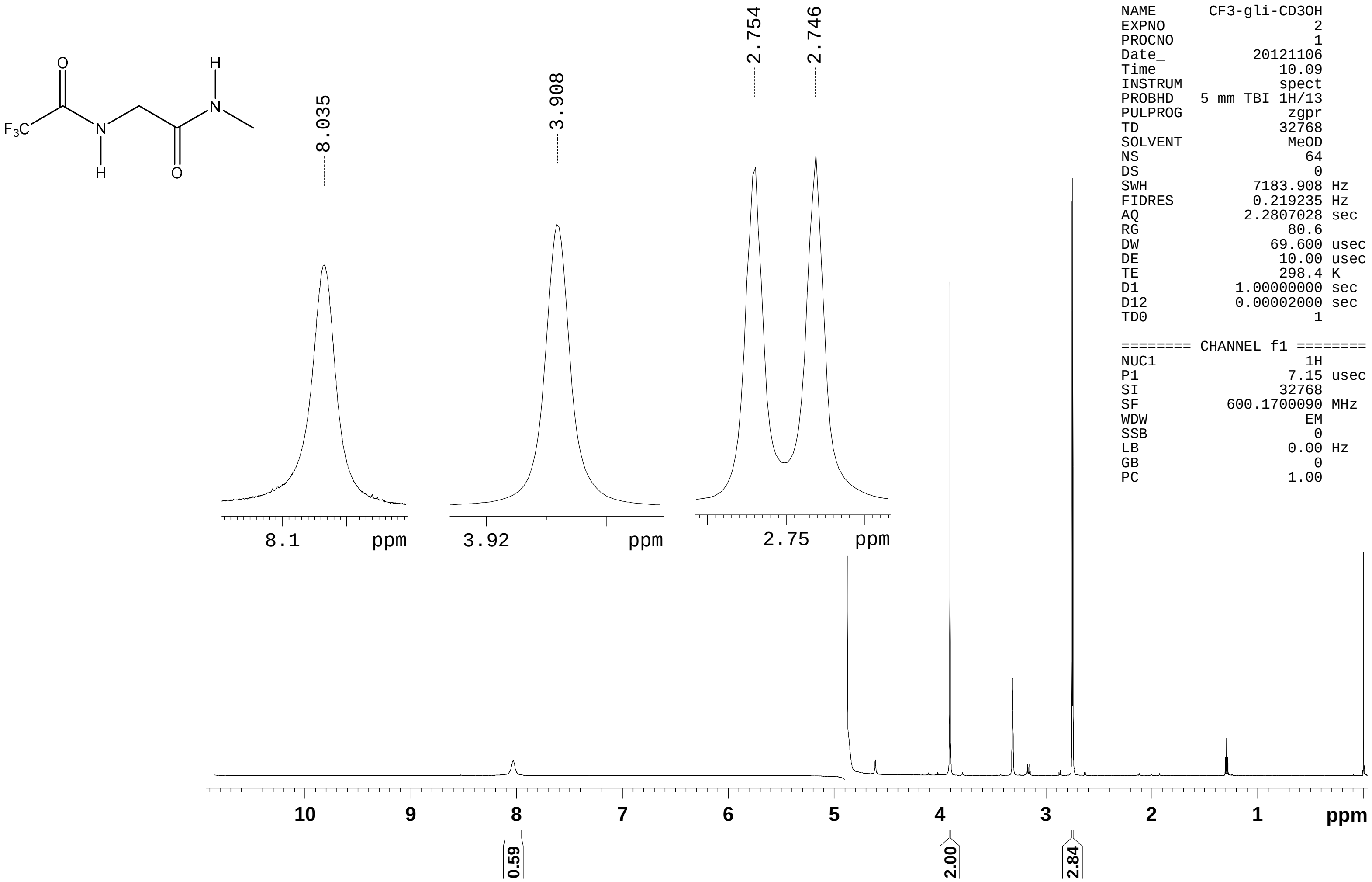
Spectrum S9: CF_3-C(O)-Gly-NHMe ^{1}H NMR Spectrum in CD_3CN.



```
NAME       CF3-gli-DMSO
EXPNO                 1
PROCNO                1
Date_          20121106
Time              15.56
INSTRUM           spect
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                65536
SOLVENT            DMSO
NS                  128
DS                    0
SWH            7911.393 Hz
FIDRES         0.120718 Hz
AQ            4.1419253 sec
RG                  161
DW               63.200 usec
DE                10.00 usec
TE                298.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.15 usec
SI               131072
SF          600.1700051 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

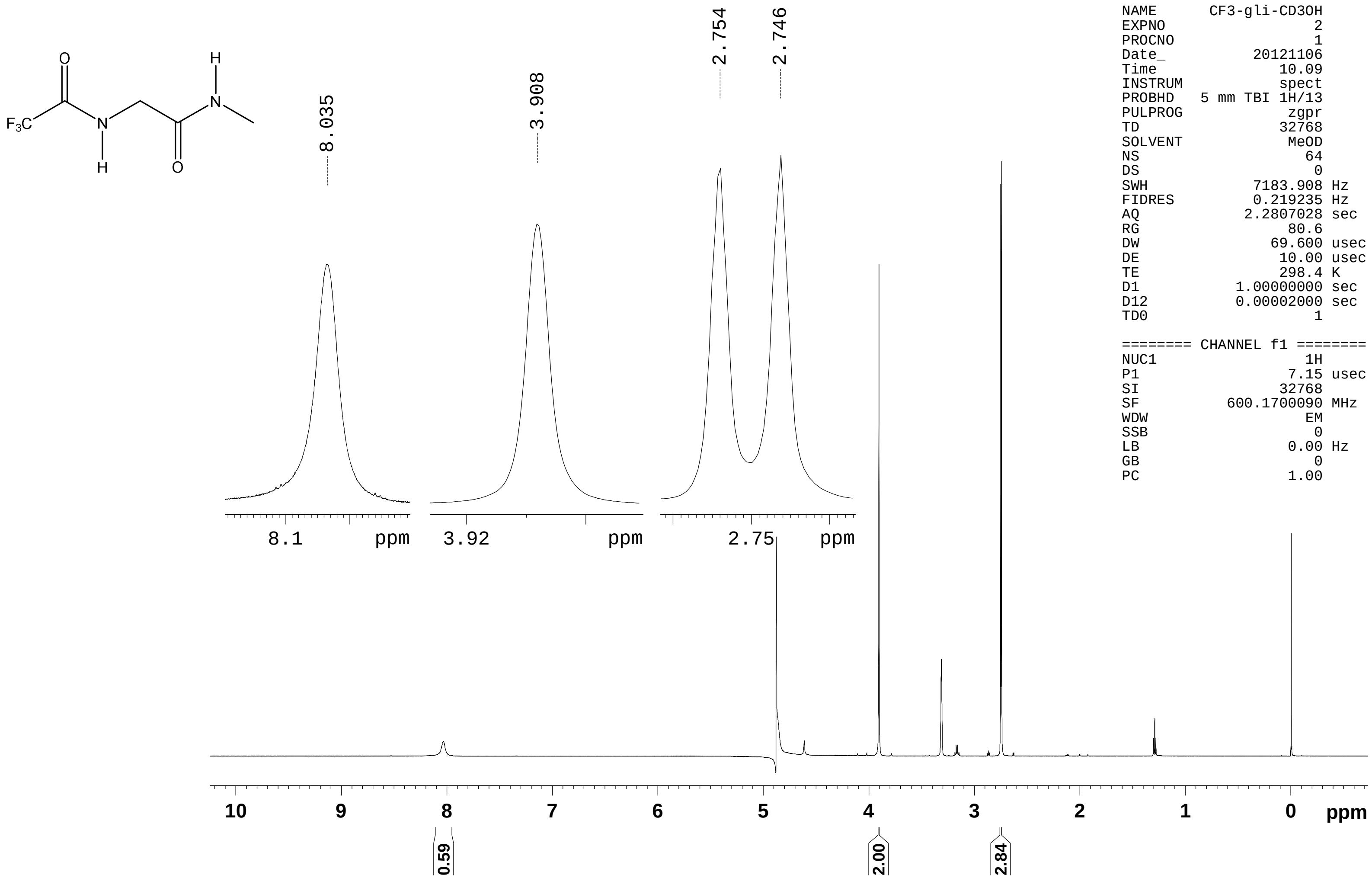
Spectrum S10: CF_3-C(O)-Gly-NHMe ^{1}H NMR Spectrum in DMSO-d_6.



```
NAME       CF3-gli-CD3OH
EXPNO                  2
PROCNO                 1
Date_           20121106
Time               10.09
INSTRUM            spect
PROBHD   5 mm TBI 1H/13
PULPROG             zgpr
TD                 32768
SOLVENT             MeOD
NS                    64
DS                     0
SWH             7183.908 Hz
FIDRES          0.219235 Hz
AQ             2.2807028 sec
RG                  80.6
DW                69.600 usec
DE                 10.00 usec
TE                 298.4 K
D1            1.00000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.15 usec
SI                 32768
SF           600.1700090 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

Spectrum S11: CF_3-C(O)-Gly-NHMe ^{1}H NMR Spectrum in CD_3OH. Solvent presaturation experiment was used.

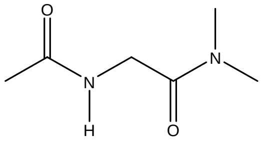


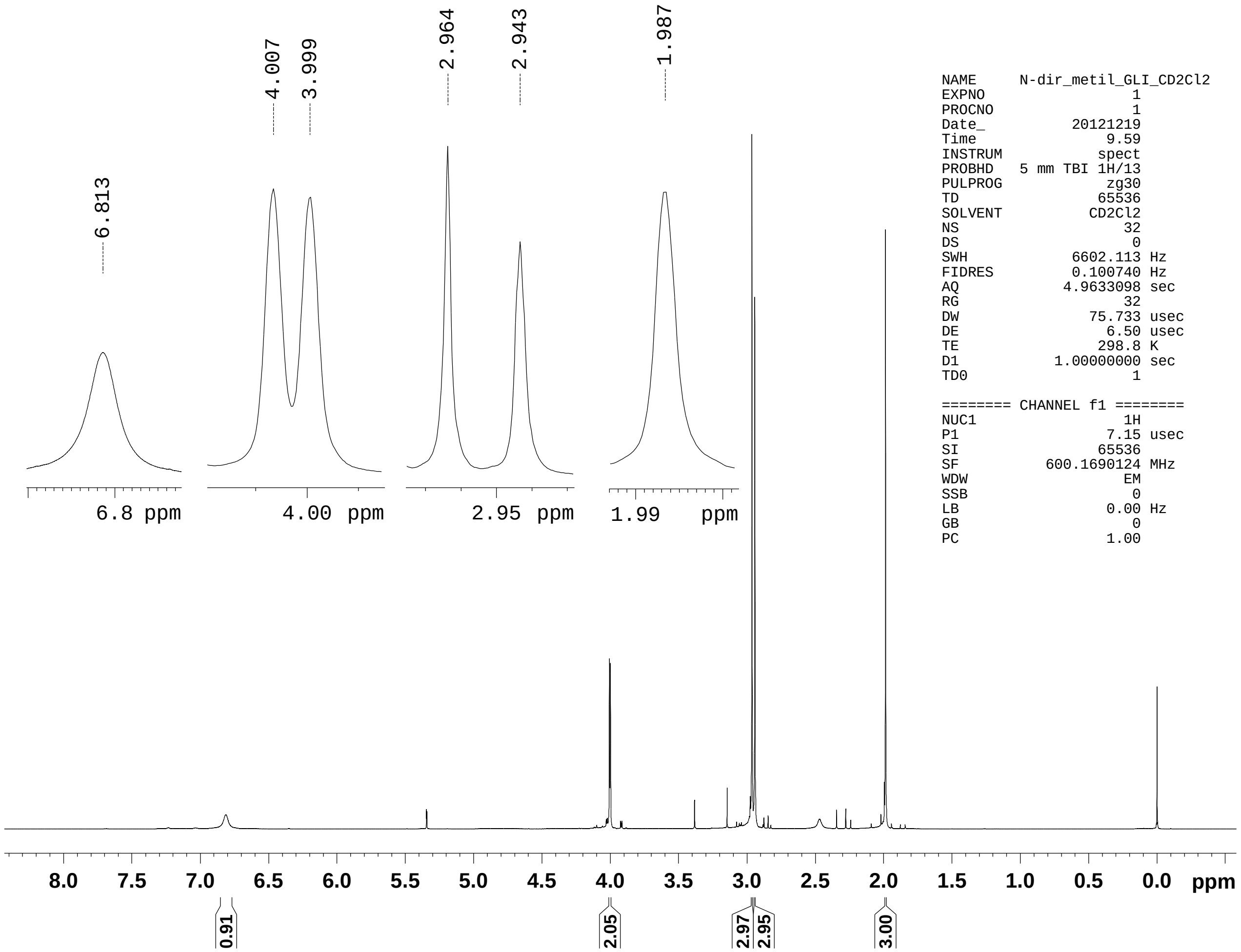
```
NAME       CF3-gli-CD3OH
EXPNO                  2
PROCNO                 1
Date_           20121106
Time               10.09
INSTRUM            spect
PROBHD   5 mm TBI 1H/13
PULPROG             zgpr
TD                 32768
SOLVENT             MeOD
NS                    64
DS                     0
SWH             7183.908 Hz
FIDRES          0.219235 Hz
AQ             2.2807028 sec
RG                  80.6
DW                69.600 usec
DE                 10.00 usec
TE                 298.4 K
D1            1.00000000 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.15 usec
SI                 32768
SF           600.1700090 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

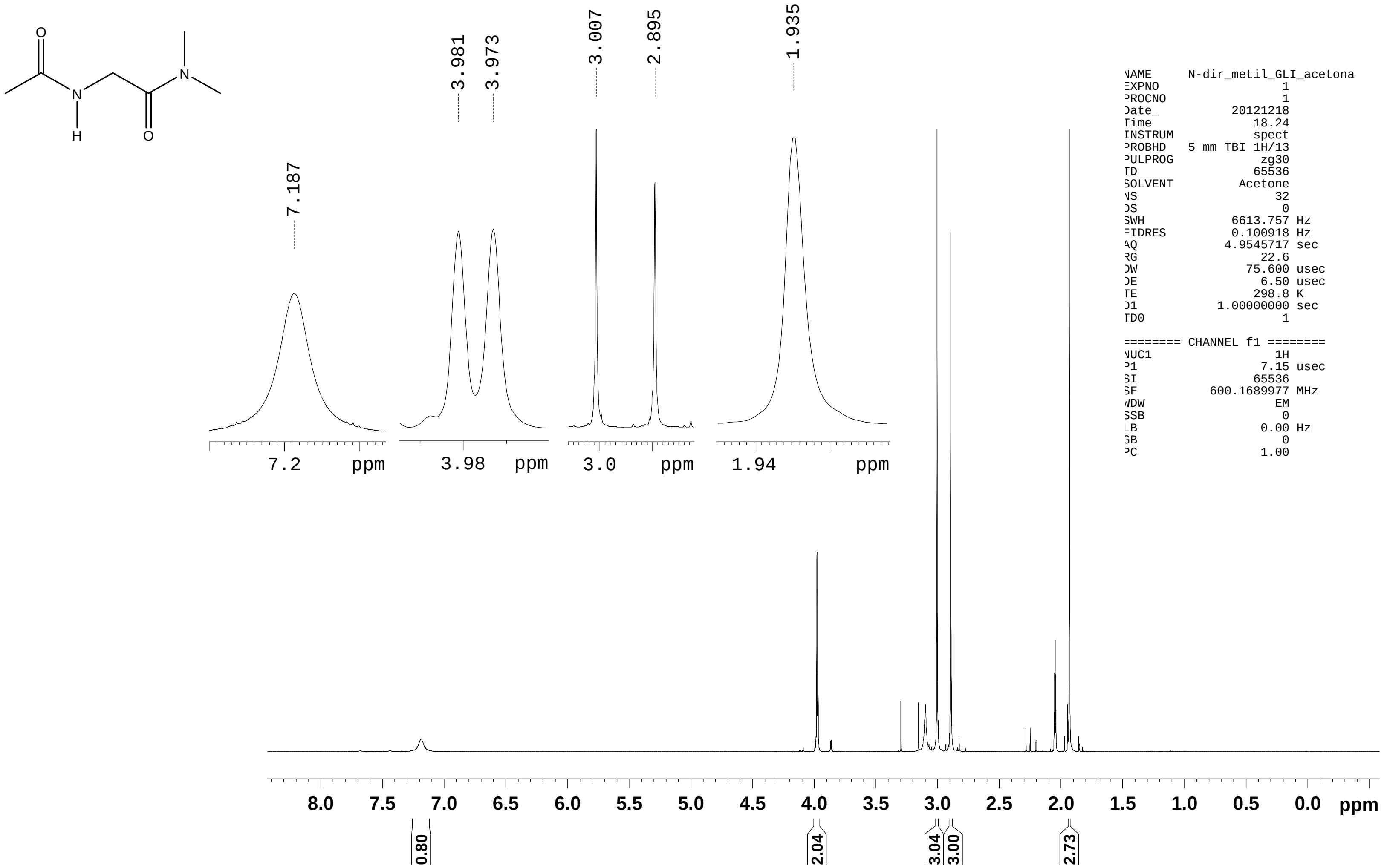
Spectrum S12: CF_3-C(O)-Gly-NHMe ^{1}H NMR Spectrum in H_2O. Solvent presaturation experiment was used.

3. Ac-Gly-N(Me)$_2$

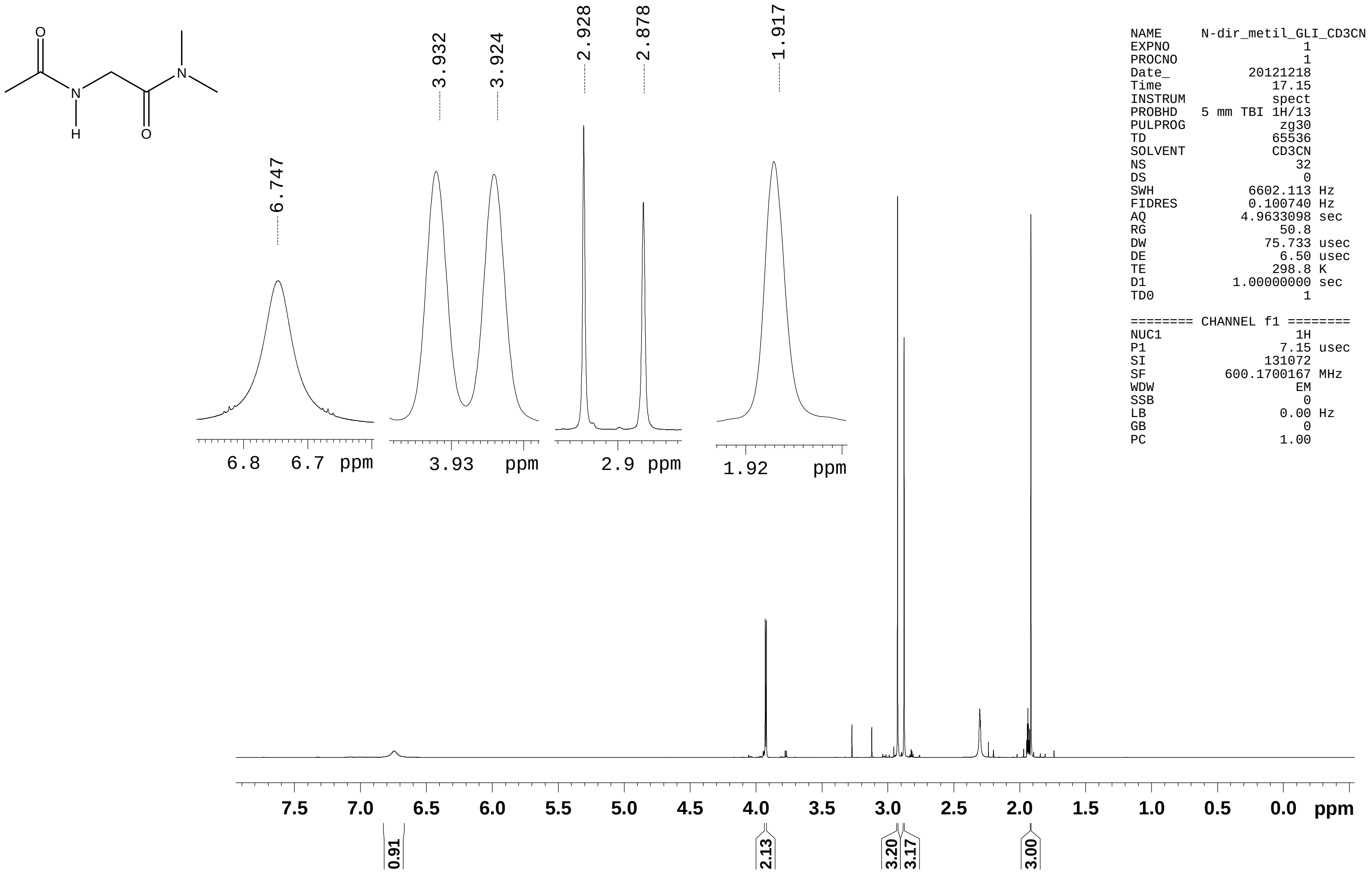




Spectrum S13: Ac-Gly-N(Me)$_2$ ^{1}H NMR Spectrum in CD$_2$Cl$_2$.



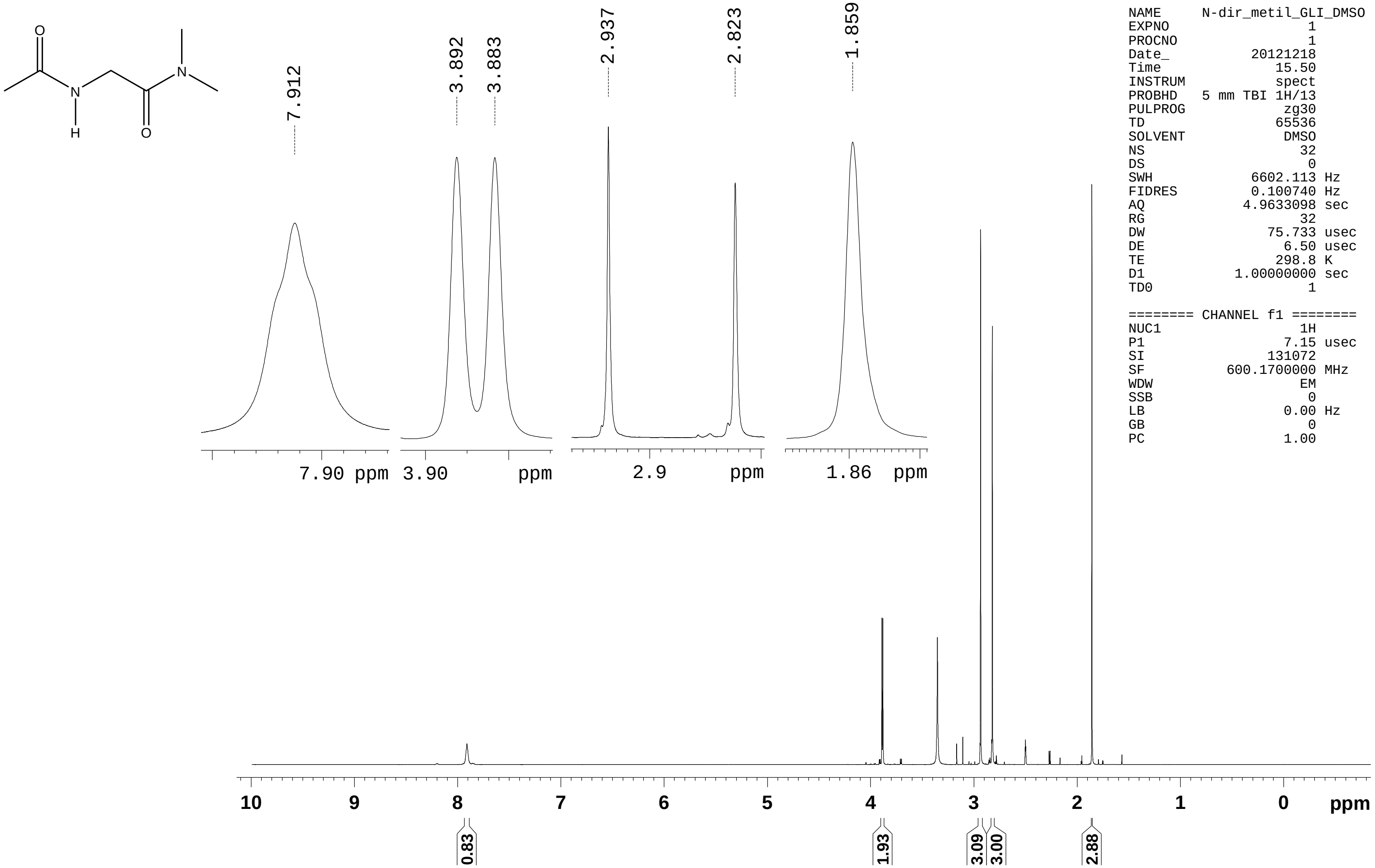
Spectrum S14: Ac-Gly-N(Me)$_2$ ^{1}H NMR Spectrum in acetone-d$_6$.



```
NAME     N-dir_metil_GLI_CD3CN
EXPNO                   1
PROCNO                  1
Date_            20121218
Time                17.15
INSTRUM             spect
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CD3CN
NS                     32
DS                      0
SWH              6602.113 Hz
FIDRES           0.100740 Hz
AQ              4.9633098 sec
RG                   50.8
DW                 75.733 usec
DE                   6.50 usec
TE                  298.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.15 usec
SI                 131072
SF            600.1700167 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

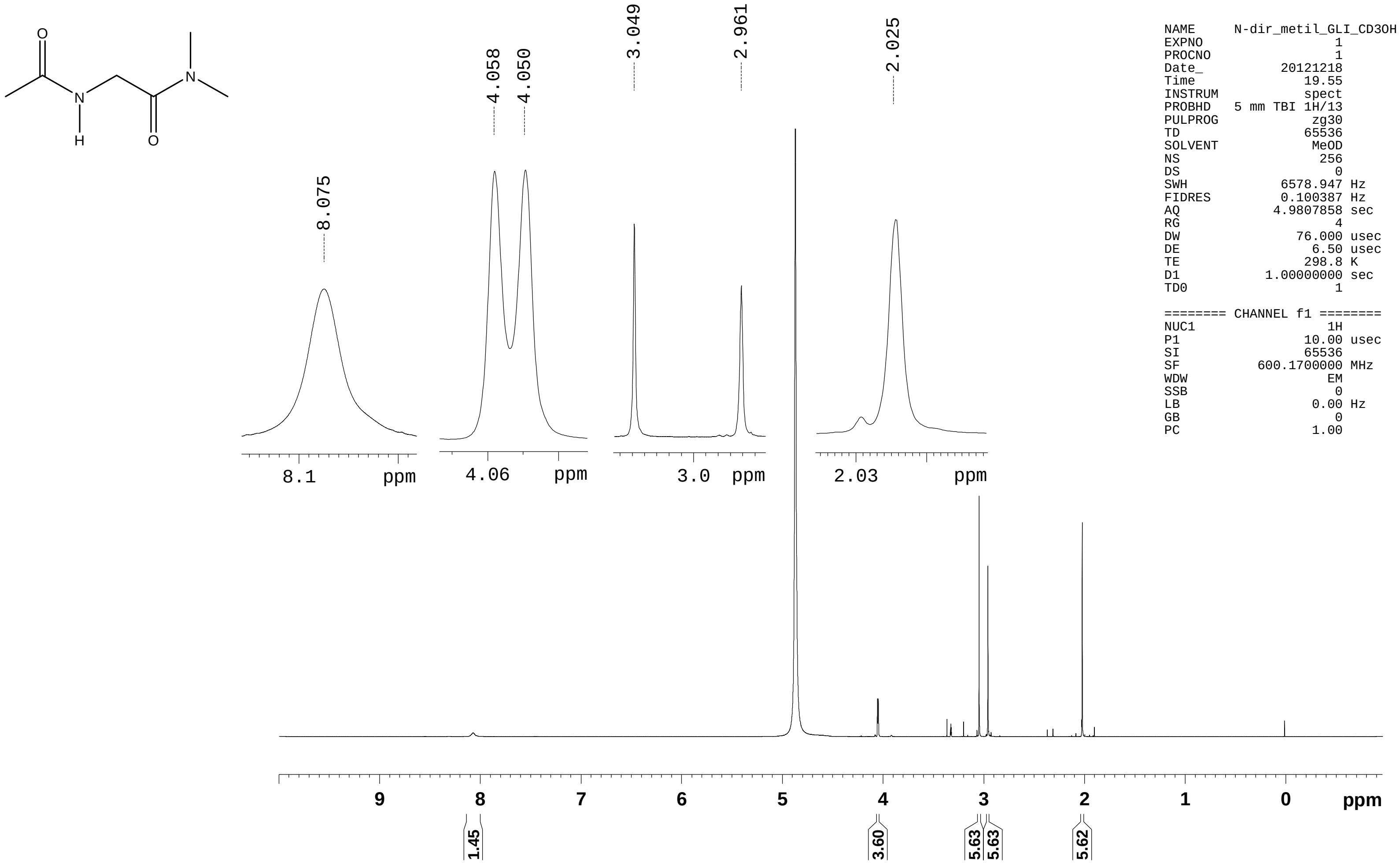
Spectrum S15: Ac-Gly-N(Me)$_2$ ^{1}H NMR Spectrum in CD$_3$CN.



```
NAME     N-dir_metil_GLI_DMSO
EXPNO                   1
PROCNO                  1
Date_            20121218
Time                15.50
INSTRUM             spect
PROBHD   5 mm TBI 1H/13
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     32
DS                      0
SWH              6602.113 Hz
FIDRES           0.100740 Hz
AQ              4.9633098 sec
RG                     32
DW                 75.733 usec
DE                   6.50 usec
TE                  298.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.15 usec
SI                 131072
SF            600.1700000 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

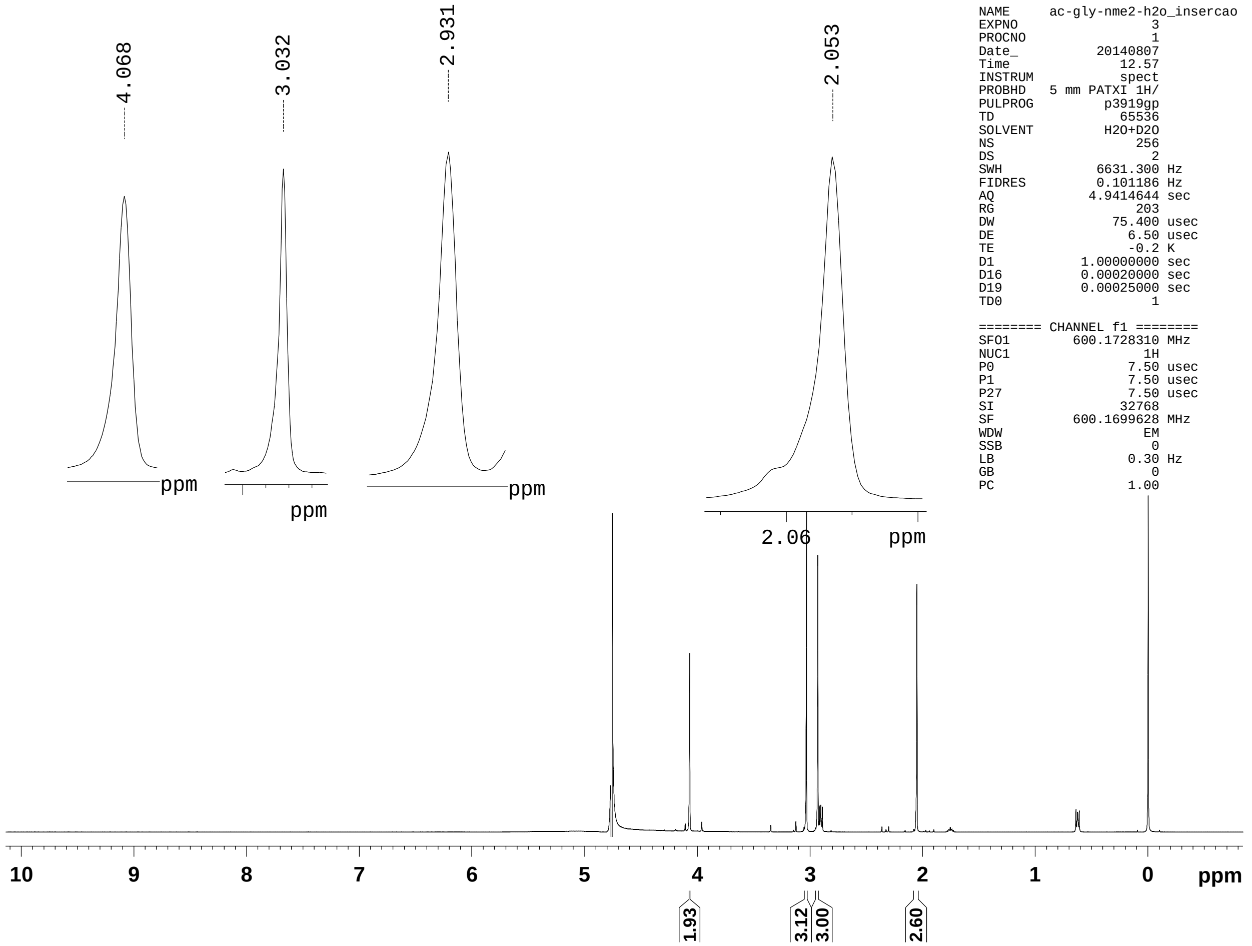
Spectrum S16: Ac-Gly-N(Me)$_2$ ^{1}H NMR Spectrum in DMSO-d$_6$.



```
NAME      N-dir_metil_GLI_CD3OH
EXPNO                 1
PROCNO                1
Date_          20121218
Time              19.55
INSTRUM           spect
PROBHD   5 mm TBI 1H/13
PULPROG            zg30
TD                65536
SOLVENT            MeOD
NS                  256
DS                    0
SWH            6578.947 Hz
FIDRES         0.100387 Hz
AQ            4.9807858 sec
RG                    4
DW               76.000 usec
DE                 6.50 usec
TE                298.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
SI                65536
SF          600.1700000 MHz
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

Spectrum S17: Ac-Gly-N(Me)$_2$ ^{1}H NMR Spectrum in CD$_3$OH.



```
NAME     ac-gly-nme2-h2o_insercao
EXPNO                       3
PROCNO                      1
Date_                20140807
Time                    12.57
INSTRUM                 spect
PROBHD   5 mm PATXI 1H/
PULPROG               p3919gp
TD                      65536
SOLVENT               H2O+D2O
NS                        256
DS                          2
SWH                  6631.300 Hz
FIDRES               0.101186 Hz
AQ                  4.9414644 sec
RG                        203
DW                     75.400 usec
DE                       6.50 usec
TE                       -0.2 K
D1                 1.00000000 sec
D16                0.00020000 sec
D19                0.00025000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1              600.1728310 MHz
NUC1                       1H
P0                       7.50 usec
P1                       7.50 usec
P27                      7.50 usec
SI                      32768
SF                600.1699628 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

Spectrum S18: Ac-Gly-N(Me)$_2$ ^{1}H NMR Spectrum in H_2O. WATERGATE solvent suppression was used.

Infrared spectra

Ac-Gly-NHMe N-H in CH_2Cl_2

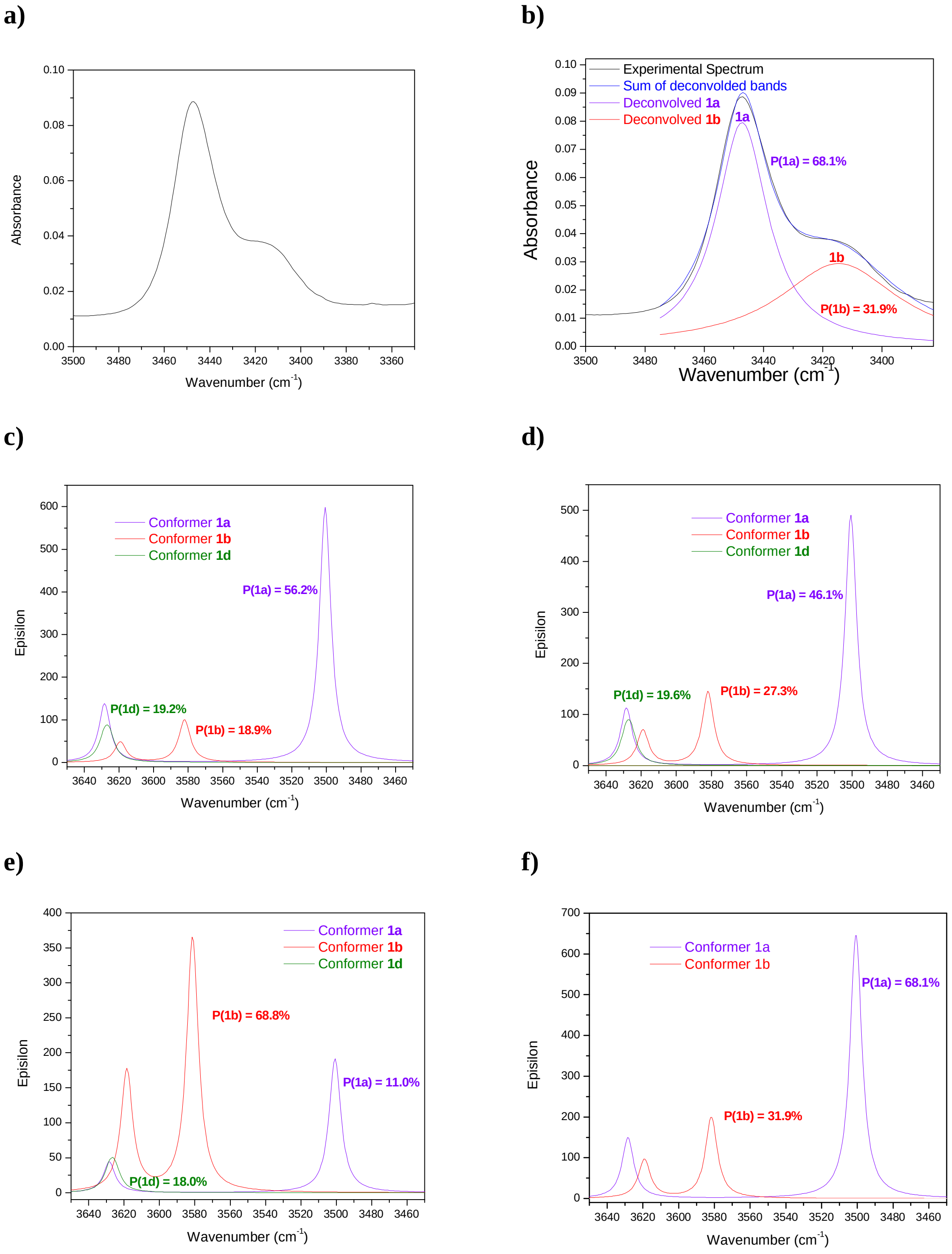


Figure S12: Ac-Gly-NHMe N-H stretchings region in CH_2Cl_2 of: **a)** IR experimental spectrum **b)** Deconvolved experimental Spectrum. Each conformer N-H stretchings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **c)** ΔE populations; **d)** ΔH populations and **e)** ΔG populations. **f)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum.

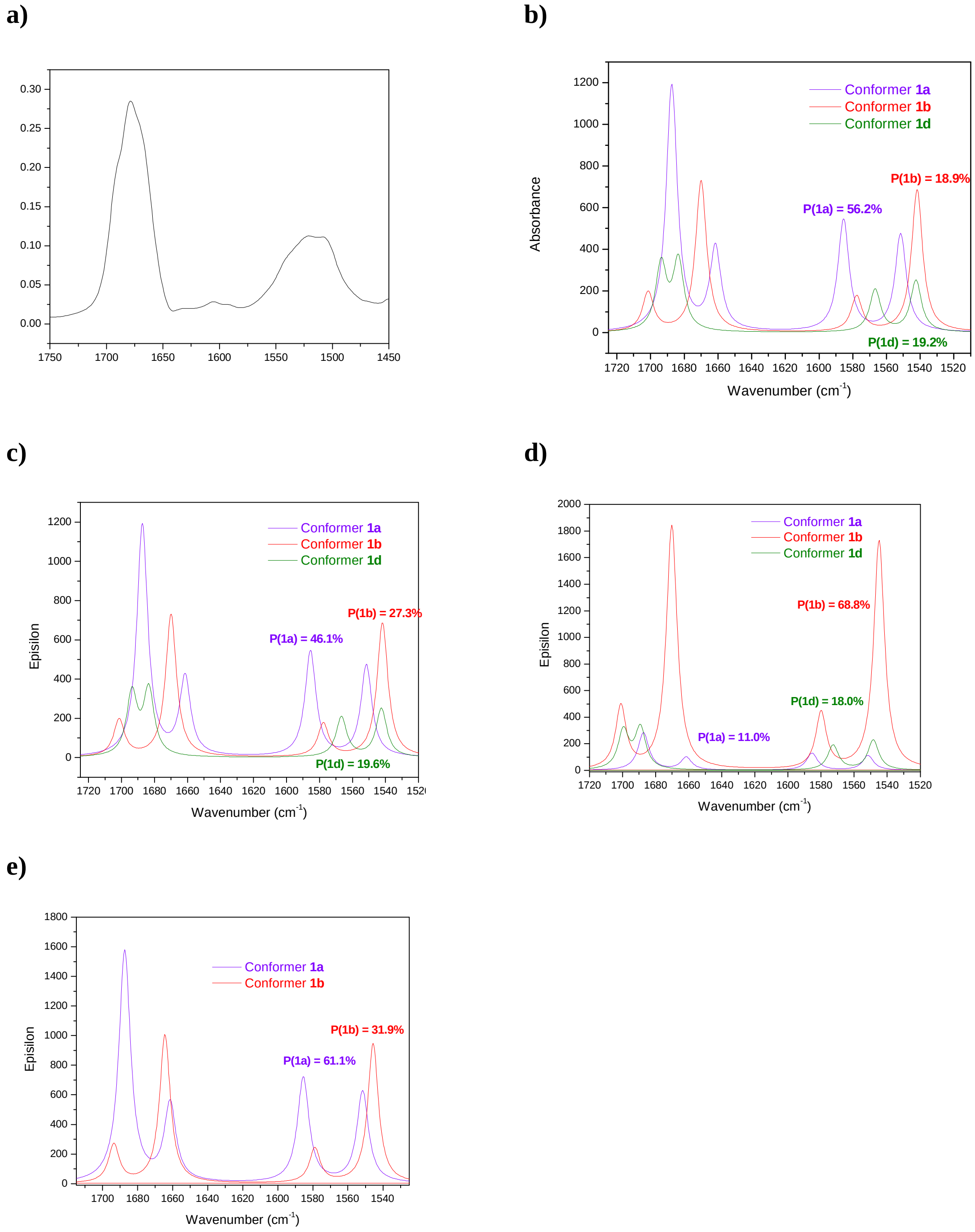


Figure S13: Ac-Gly-NHMe C=O stretchings region (~1700 cm^{-1}; Amide I bands) and mix of C(O)-N-H bond angle deformation/C-N bond stretching (~1550 cm^{-1}; Amide II) in CH_2Cl_2 of: **a)** IR experimental spectrum. Each conformer C=O bond stretchings/angular bending weighted by its B3LYP-D3/aug-cc-pVDZ populations for **b)** Δ*E* populations; **c)** Δ*H* populations and **d)** Δ*G* populations. **e)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum.

Ac-Gly-NHMe in Acetonitrile

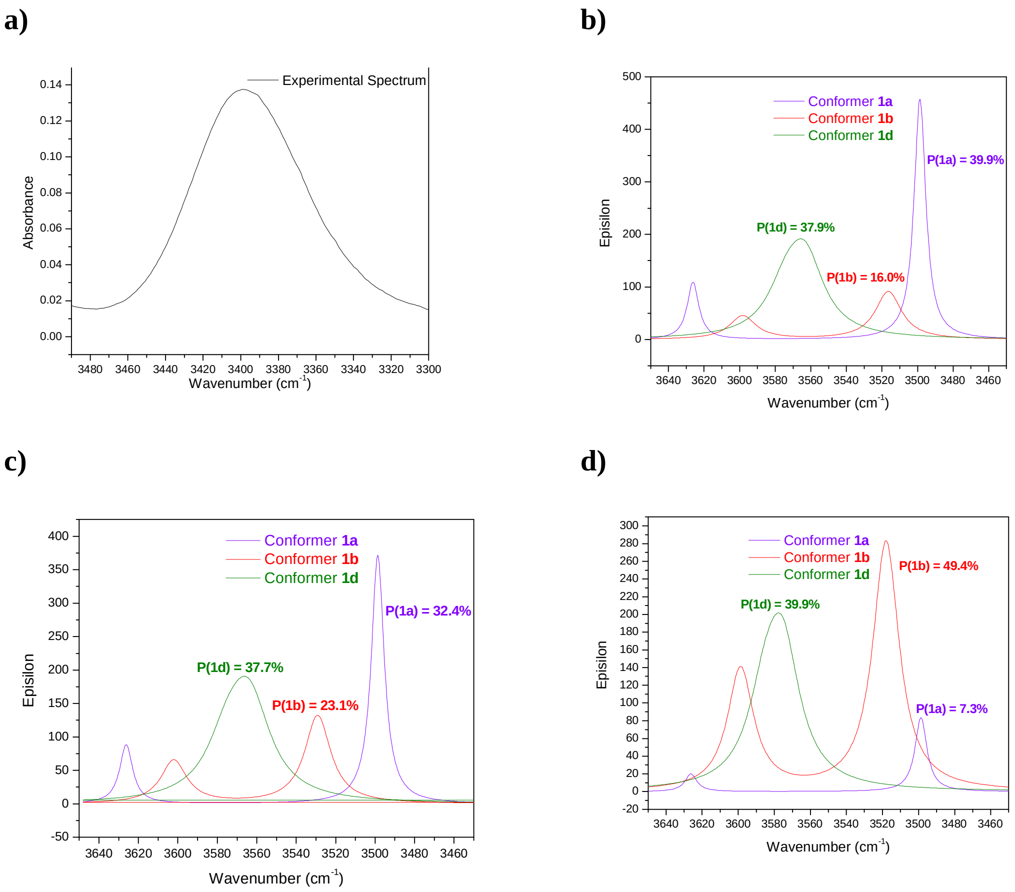


Figure S14: Ac-Gly-NHMe N-H stretchings region (Amide A and B bands) in acetonitrile of: **a)** IR experimental spectrum **b)** Δ*E* populations; **c)** Δ*H* populations and **d)** Δ*G* populations.

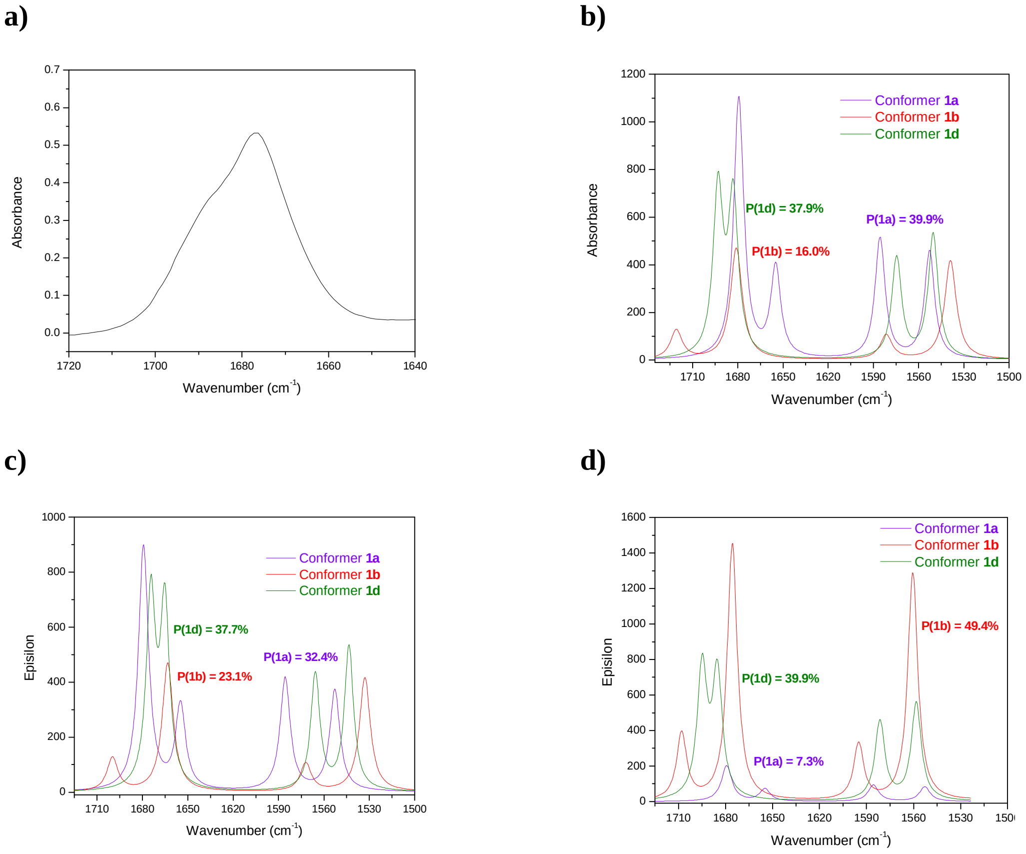


Figure S15: Ac-Gly-NHMe C=O stretchings region (~1700 cm^{-1}; Amide I bands) and mix of C(O)-N-H bond angle deformation/C-N bond stretching (~1550 cm^{-1}; Amide II) in acetonitrile of: **a)** IR experimental spectrum. Each conformer bond stretchings/angular bendings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **b)** ΔE populations; **c)** ΔH populations and **d)** ΔG populations.

CF_3-C(O)-Gly-NHMe in CH_2Cl_2

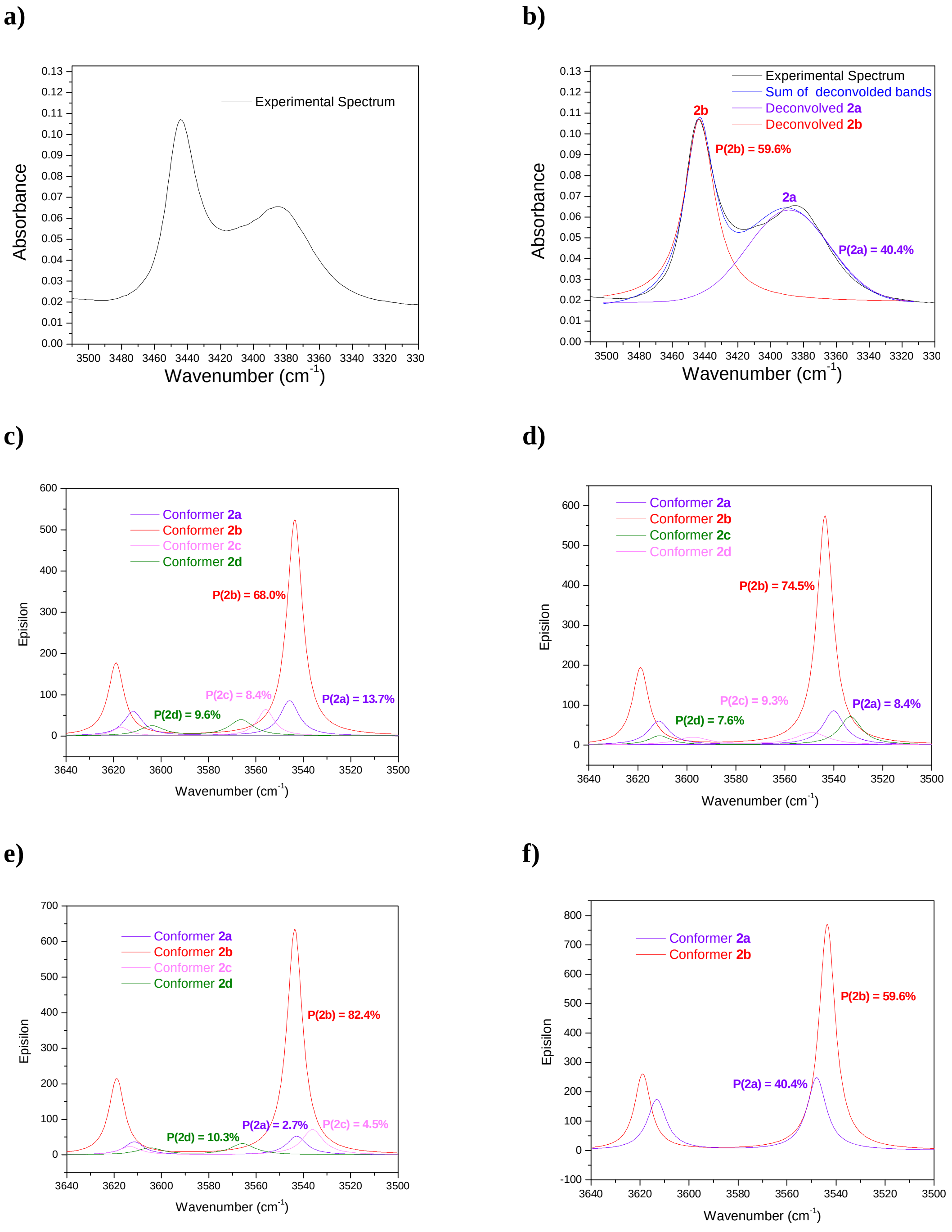


Figure S16: CF_3-C(O)-Gly-NHMe N-H stretchings region (Amide A and B bands) in CH_2Cl_2 of: **a)** IR experimental spectrum **b)** Deconvolved experimental Spectrum. Each conformer N-H stretchings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **c)** Δ*E* populations; **d)** Δ*H* populations and **e)** Δ*G* populations. **f)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum.

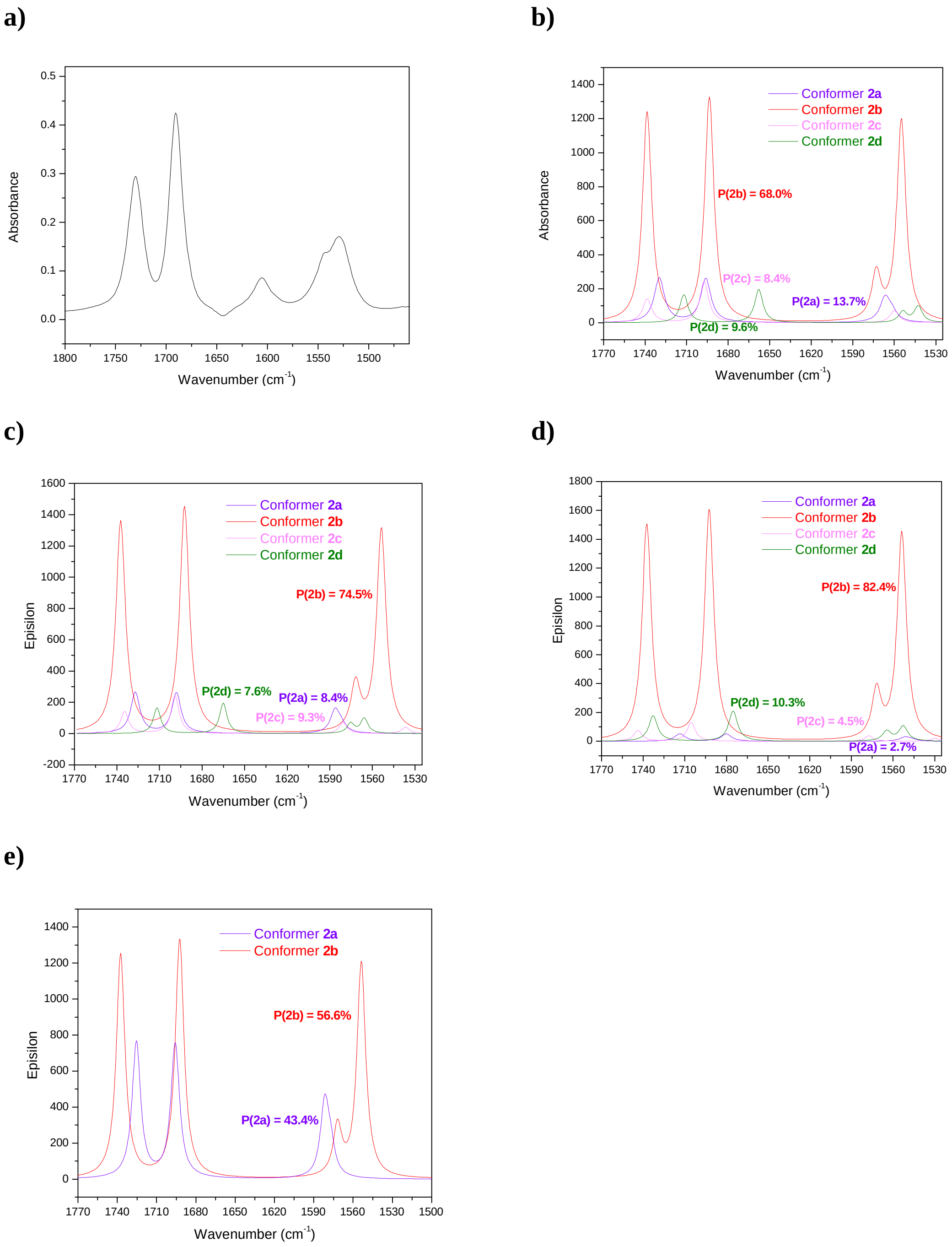


Figure S17: CF_3-C(O)-Gly-NHMe C=O stretchings region (~1700 cm^{-1}; Amide I bands) and mix of C(O)-N-H bond angle deformation/C-N bond stretching (~1550 cm^{-1}; Amide II) in CH_2Cl_2 of: **a)** IR experimental spectrum. Each conformer bond stretchings/angular bendings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **b)** Δ*E* populations; **c)** Δ*H* populations and d**)** Δ*G* populations. **e)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum.

CF_3-C(O)-Gly-NHMe in Acetonitrile

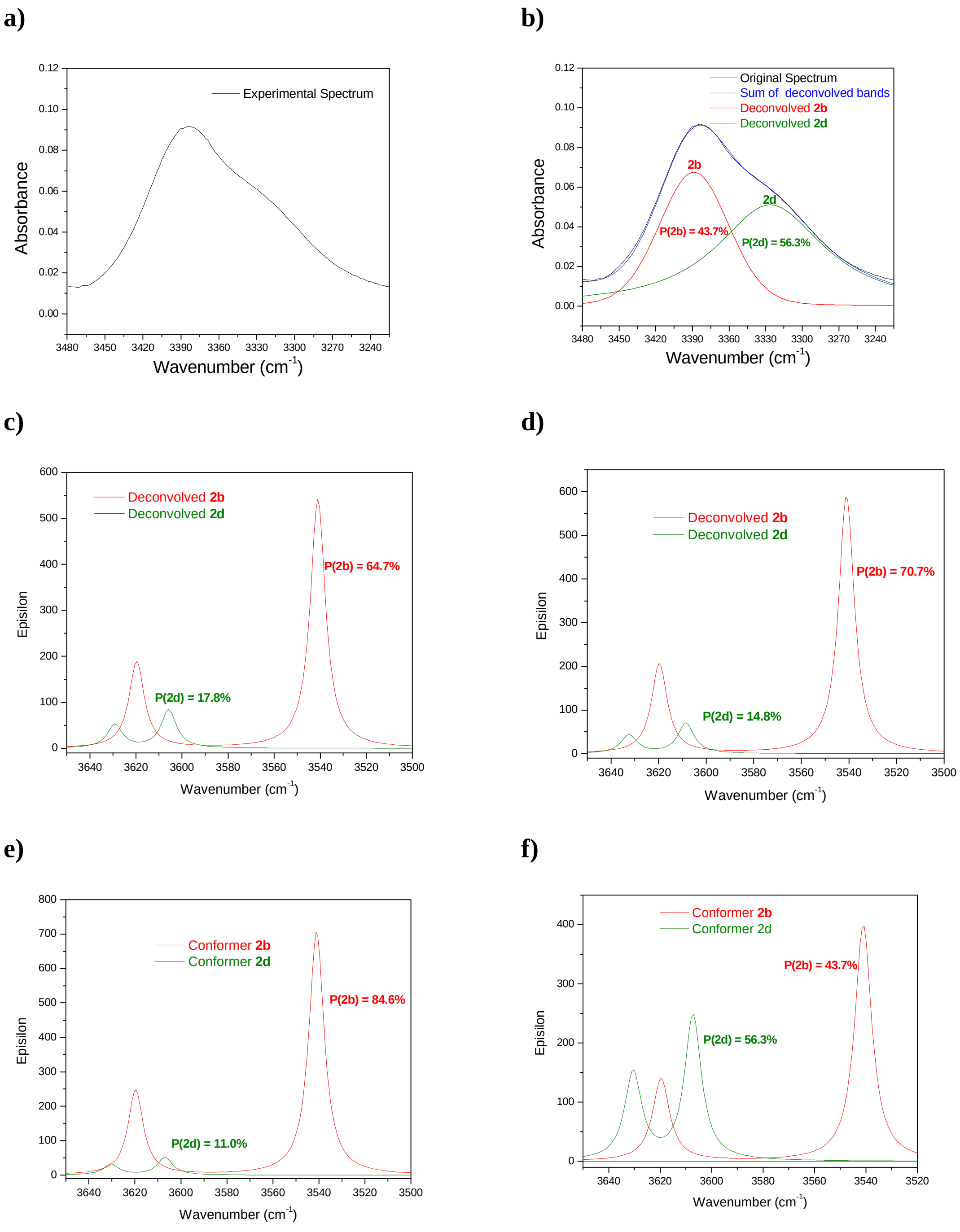


Figure S18: CF_3-C(O)-Gly-NHMe N-H stretchings region (Amide A and B bands) in acetonitrile of: **a)** IR experimental spectrum **b)** Deconvolved experimental Spectrum. Each conformer N-H stretchings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **c)** ΔE populations; **d)** ΔH populations and **e)** ΔG populations. **f)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum..

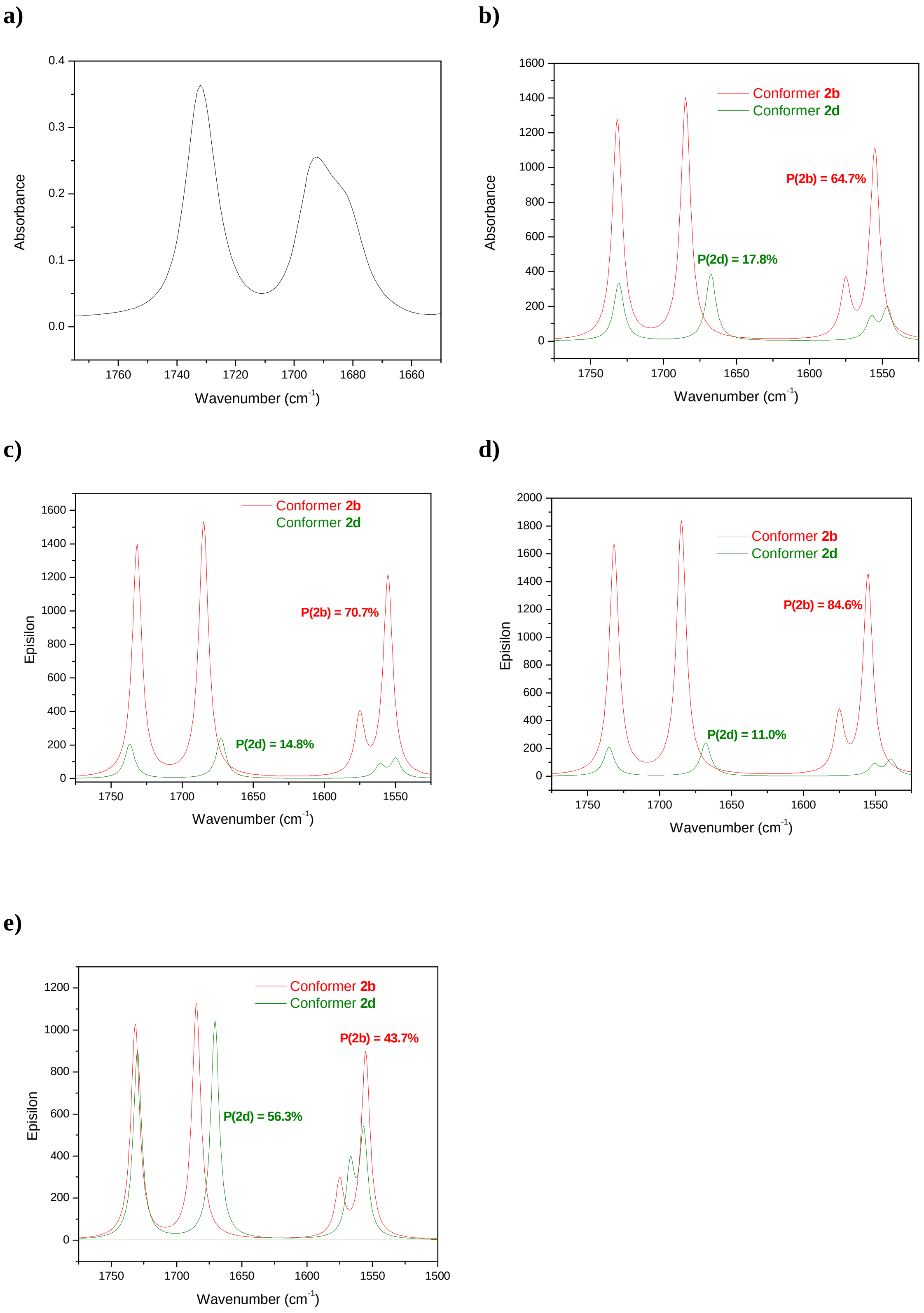


Figure S19: CF_3-C(O)-Gly-NHMe C=O stretchings region (~1700 cm^{-1}; Amide I bands) and mix of C(O)-N-H bond angle deformation/C-N bond stretching (~1550 cm^{-1}; Amide II) in acetonitrile of: **a)** IR experimental spectrum. Each conformer bond stretchings/angular bendings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **b)** ΔE populations; **c)** ΔH populations and **d)** ΔG populations. **e)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum.

Ac-Gly-N(Me)$_2$ in CH$_2$Cl$_2$

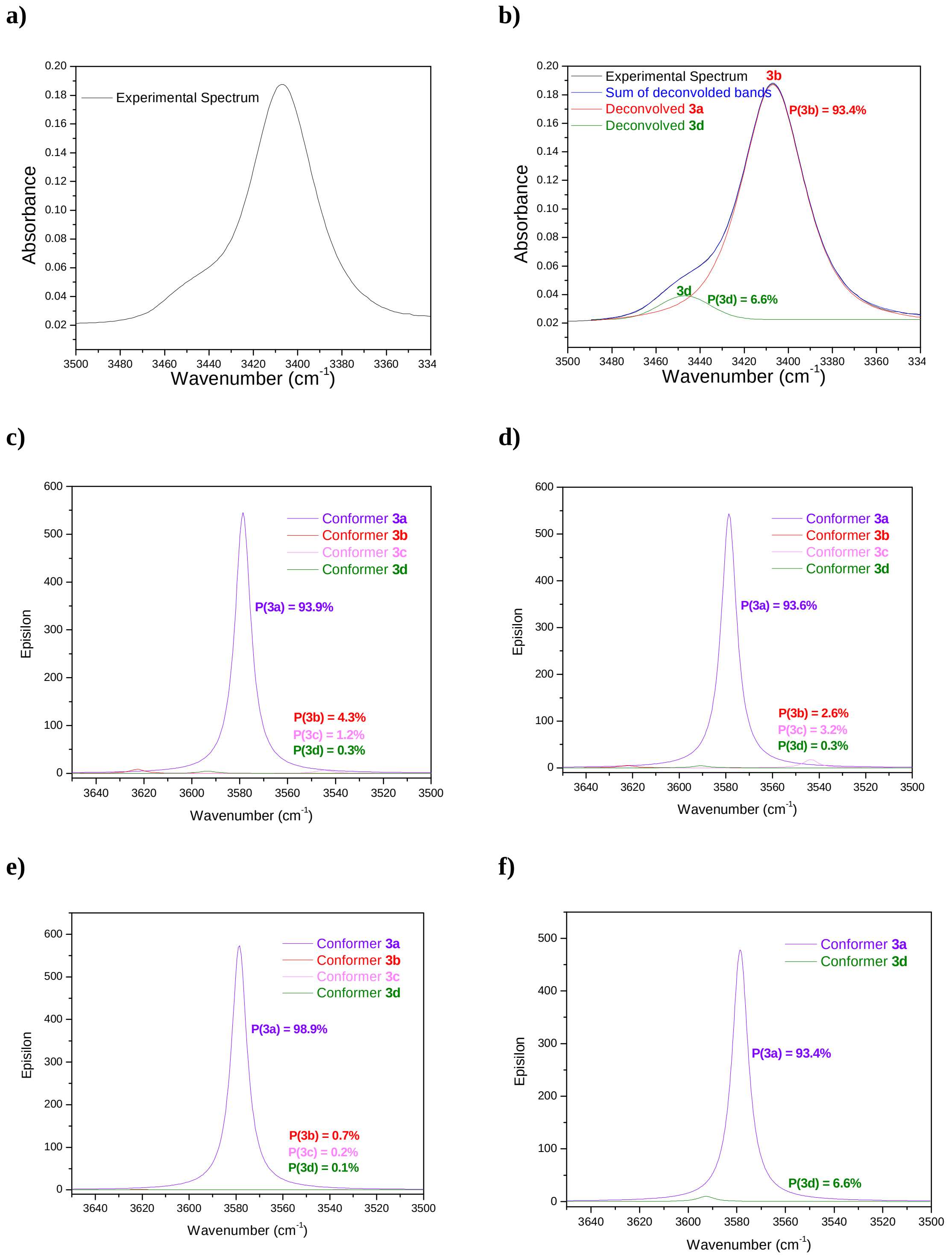


Figure S20: Ac-Gly-(NMe)$_2$ N-H stretchings region (Amide A and B bands) in CH$_2$Cl$_2$ of: **a)** IR experimental spectrum **b)** Deconvolved experimental Spectrum. Each conformer N-H stretchings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **c)** Δ*E* populations; **d)** Δ*H* populations and **e)** Δ*G* populations. **f)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum

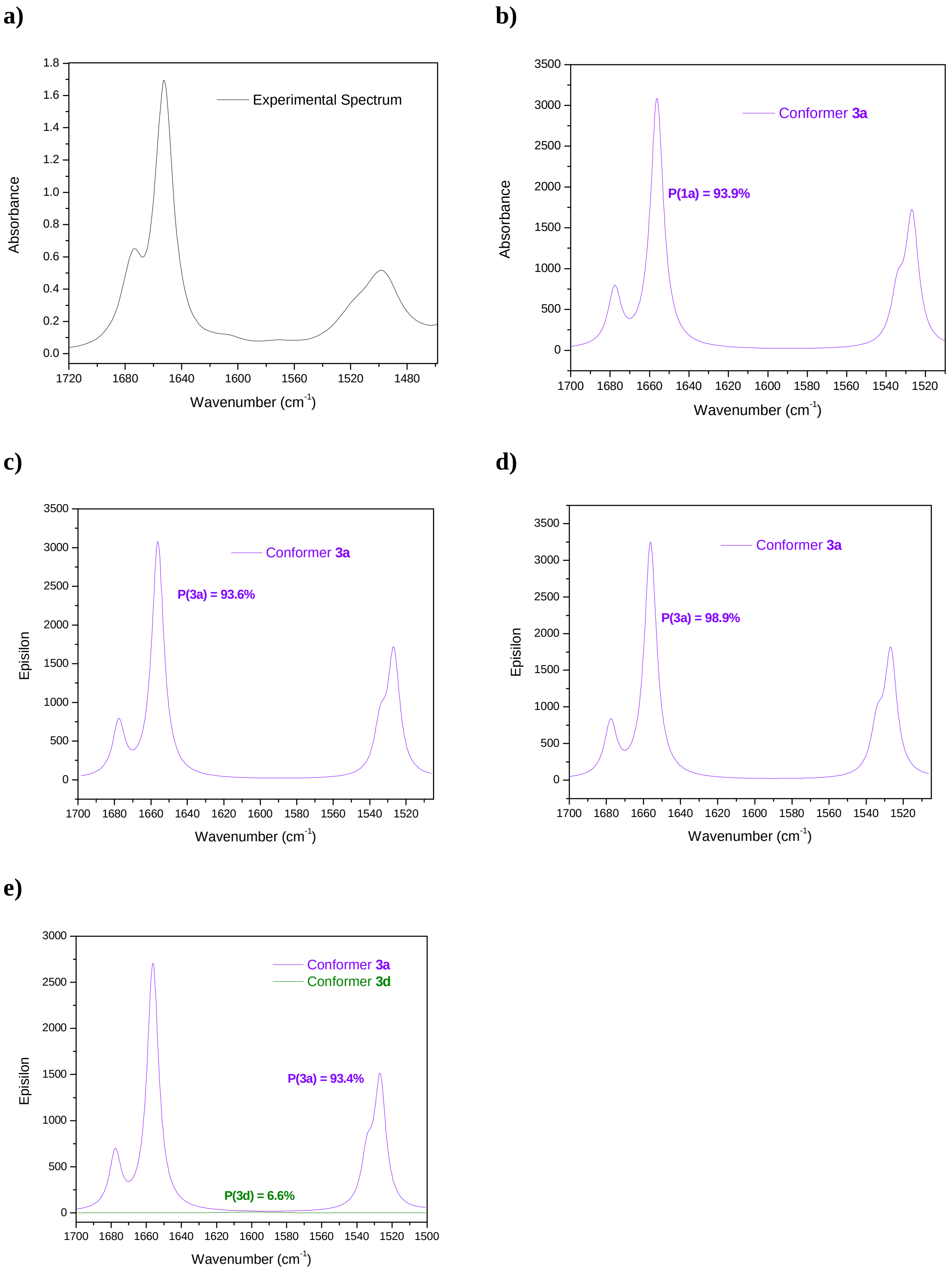


Figure S21: Ac-Gly-(NMe)$_2$ C=O stretchings region (~1700 cm^{-1}; Amide I bands) and mix of C(O)-N-H bond angle deformation/C-N bond stretching (~1550 cm^{-1}; Amide II) in CH_2Cl_2 of: **a)** IR experimental spectrum. Each conformer bond stretchings/angular bendings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **b)** ΔE populations; **c)** ΔH populations and **d)** ΔG populations. **e)** Theoretical spectrum using B3LYP-D3/aug-cc-pVDZ geometries and populations obtained from the deconvolved experimental spectrum.

Ac-Gly-N(Me)$_2$ in Acetonitrile

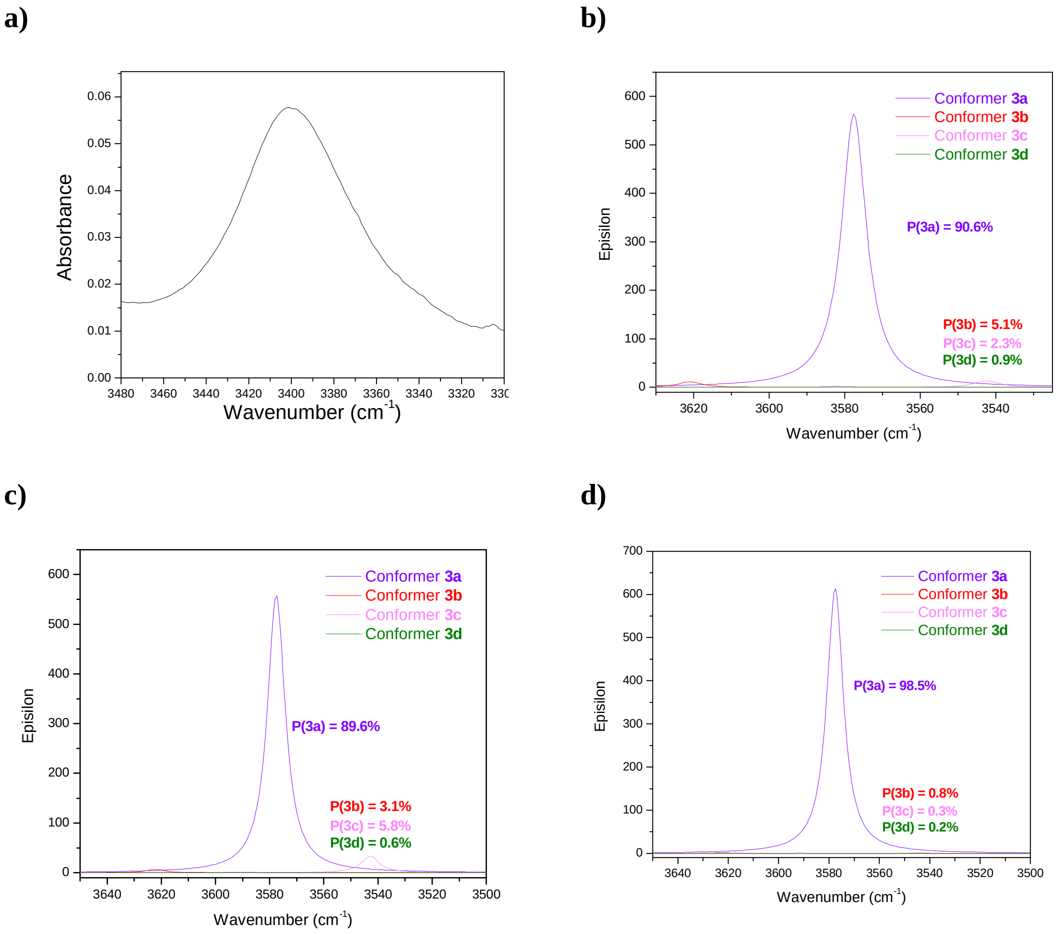


Figure S22: Ac-Gly-(NMe)$_2$ N-H stretchings region in acetonitrile of: **a)** IR experimental spectrum **b)** ΔE populations; **c)** ΔH populations and **d)** ΔG populations.

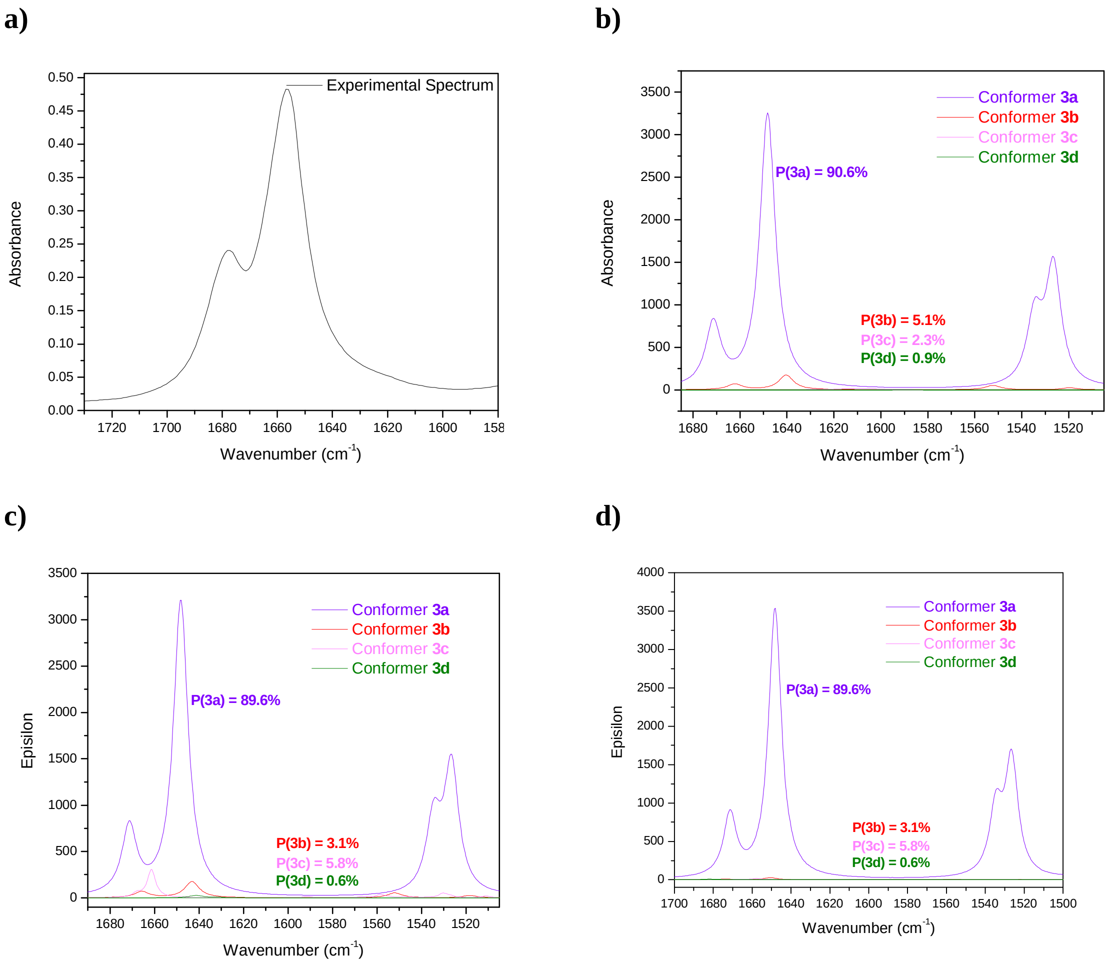


Figure S23: Ac-Gly-(NMe)$_2$ C=O stretchings region (~1700 cm^{-1}; Amide I bands) and mix of C(O)-N-H bond angle deformation/C-N bond stretching (~1550 cm^{-1}; Amide II) in acetonitrile of: **a)** IR experimental spectrum. Each conformer bond stretchings/angular bendings were weighted by its B3LYP-D3/aug-cc-pVDZ populations for **b)** ΔE populations; **c)** ΔH populations and **d)** ΔG populations.