Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Improving the accuracy of solid-state nuclear magnetic resonance chemical shift prediction with a simple molecular correction

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Electronic Supplementary Information

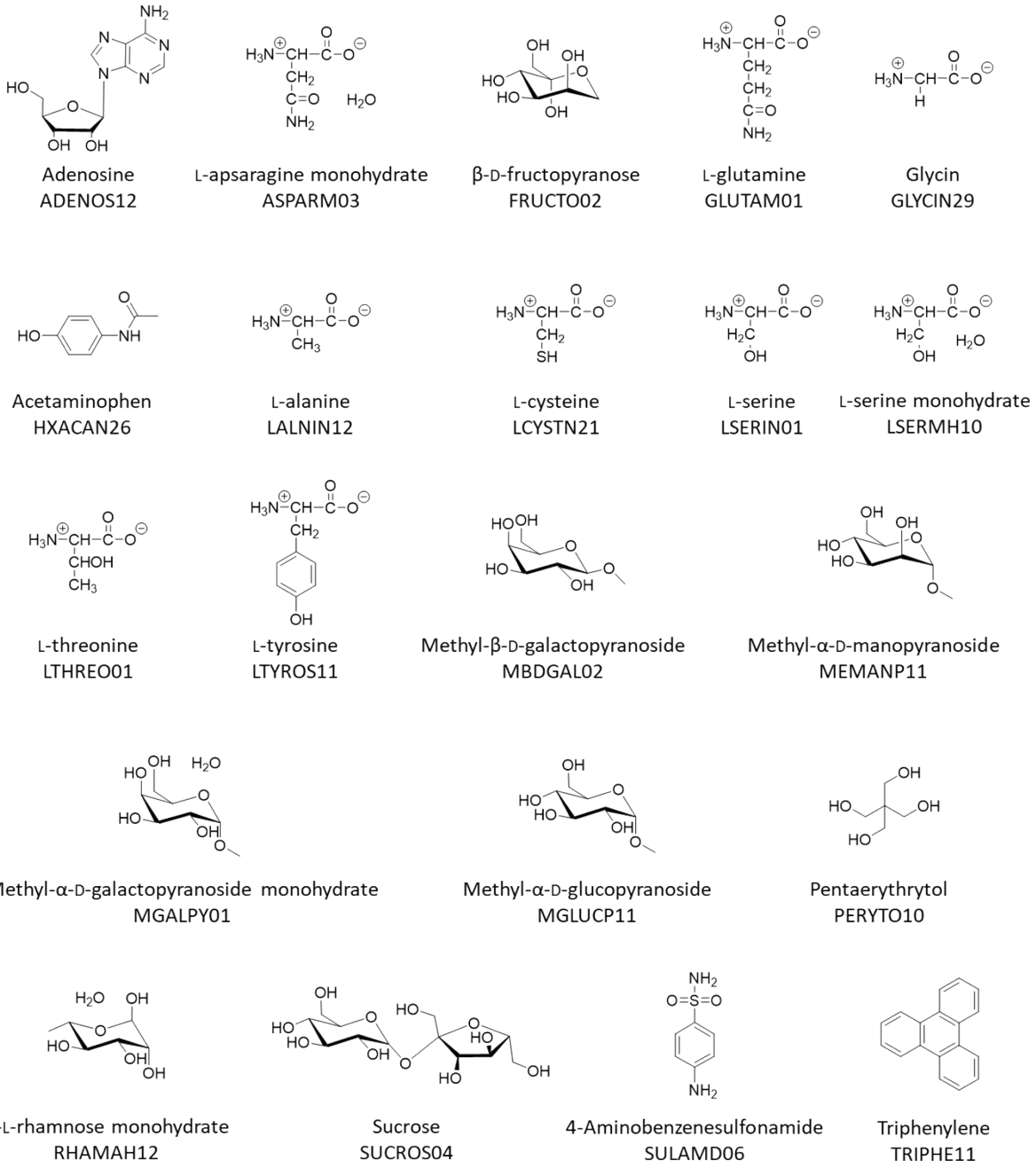


Figure S1. Crystal structures and corresponding CSD reference codes included in the ^{13}C benchmark set.

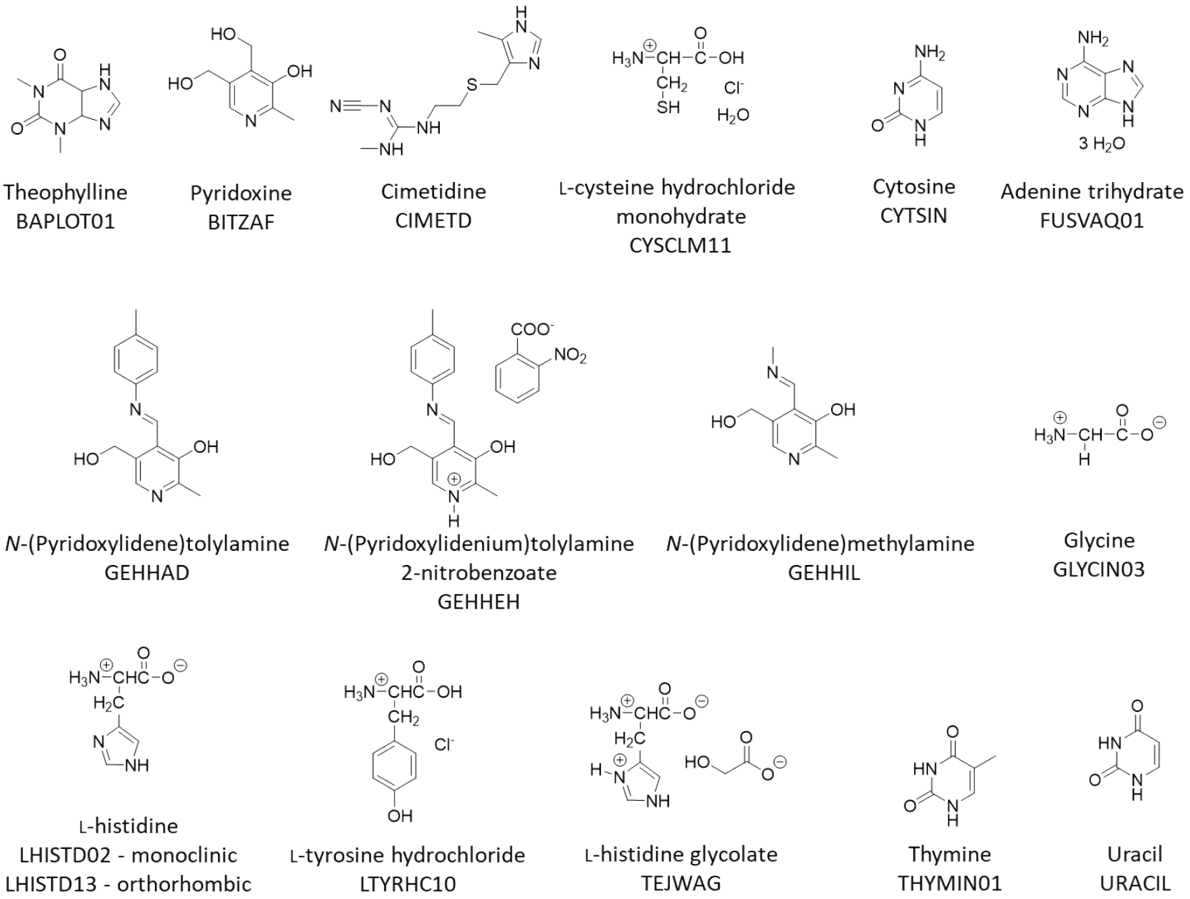
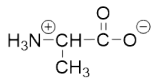
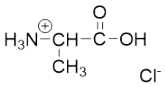


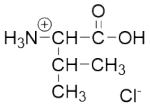
Figure S2. Crystal structures and corresponding CSD reference codes included in the ^{15}N benchmark set.



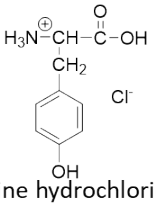
L-alanine
LALNIN12



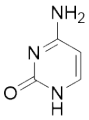
L-alanine hydrochloride
ALAHCL



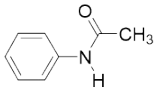
L-valine hydrochloride
VALEHC11



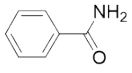
L-tyrosine hydrochloride
LTYRHC10



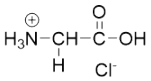
Cytosine
CYTSIN



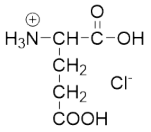
acetanilide
ACANIL03



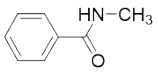
benzamide
BZAMID07



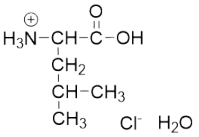
glycine hydrochloride
GLYHCL01



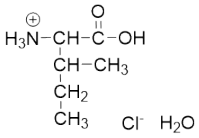
L-glutamic acid hydrochloride
VALEHC11



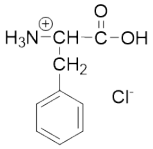
N-methylbenzamide
MBNZAM10



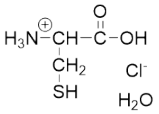
L-leucine hydrochloride monohydrate
FEQYUW



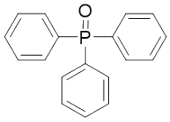
L-isoleucine hydrochloride monohydrate
LILEUC10



L-phenylalanine hydrochloride
PHALNC01



L-cysteine hydrochloride monohydrate
CYSCLM11



triphenylphosphine oxide
TPEPHO02

Figure S3. Crystal structures and corresponding CSD reference codes included in the ^{17}O benchmark set.

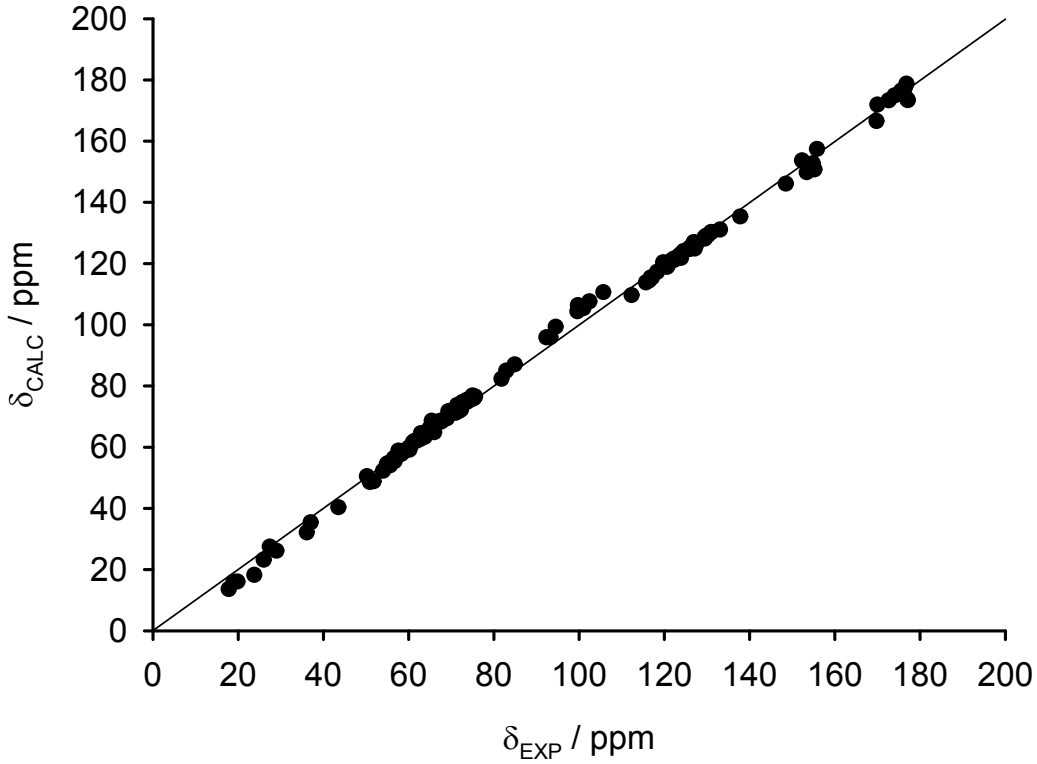


Figure S4. The correlation between the uncorrected GIPAW-calculated and experimental chemical shifts in the carbon benchmark set.

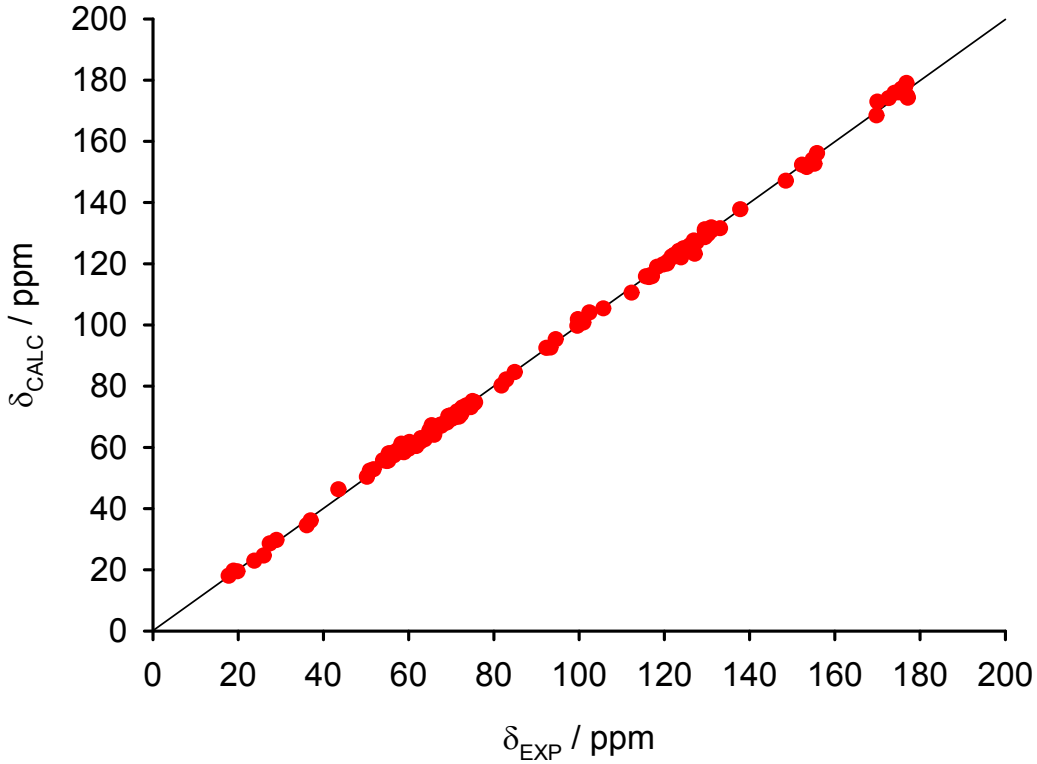
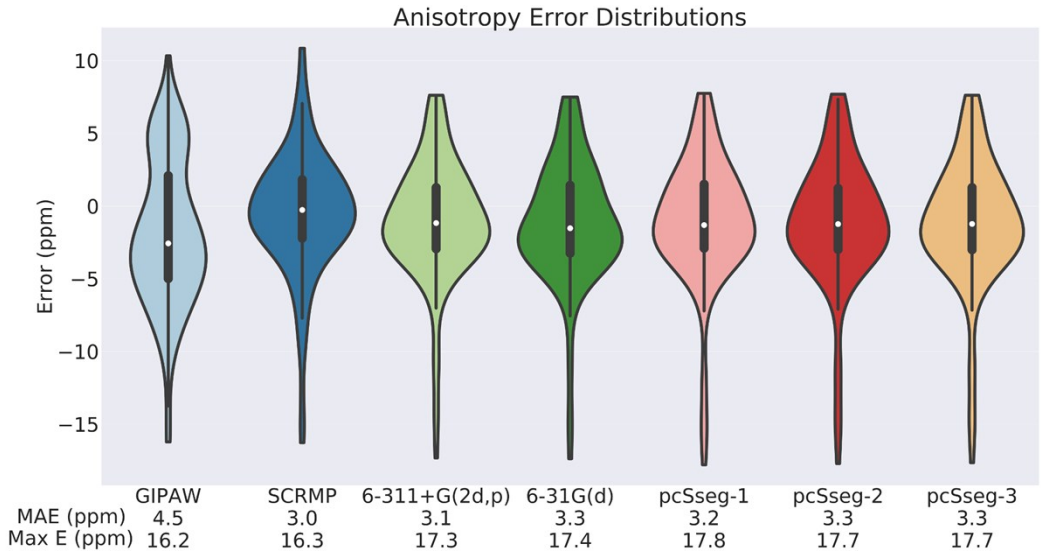


Figure S5. The correlation between PBE0-corrected and experimental chemical shifts in the carbon benchmark set.

Table S1. The parameters of the linear correlation between experimental chemical shifts and calculated shieldings (GIPAW, SCRMP and GIPAW calculations corrected with monomer corrections calculated with various basis sets).

	^{13}C		^{15}N		^{17}O	
Method	Slope	Intercept	Slope	Intercept	Slope	Intercept
GIPAW	-1.004	170.443	-0.970	180.160	-0.927	232.940
SCRMP	-1.034	185.711	-0.985	193.429	-0.958	257.794
PBE0/6-311+G(2d,p)	-1.062	180.005	-1.025	189.954	-1.024	261.767
PBE0/6-31G(p)	-1.067	179.615	-1.031	190.177	-1.028	262.963
PBE0/pcSseg1	-1.066	180.948	-1.025	190.304	-1.026	263.197
PBE0/pcSseg2	-1.061	181.045	-1.023	191.020	-1.022	263.152
PBE0/pcSseg3	-1.061	180.838	-1.024	191.016	-1.021	262.216



Figue S6. Errors in reproducing the experimental ^{13}C anisotropy calculated from the principal components.

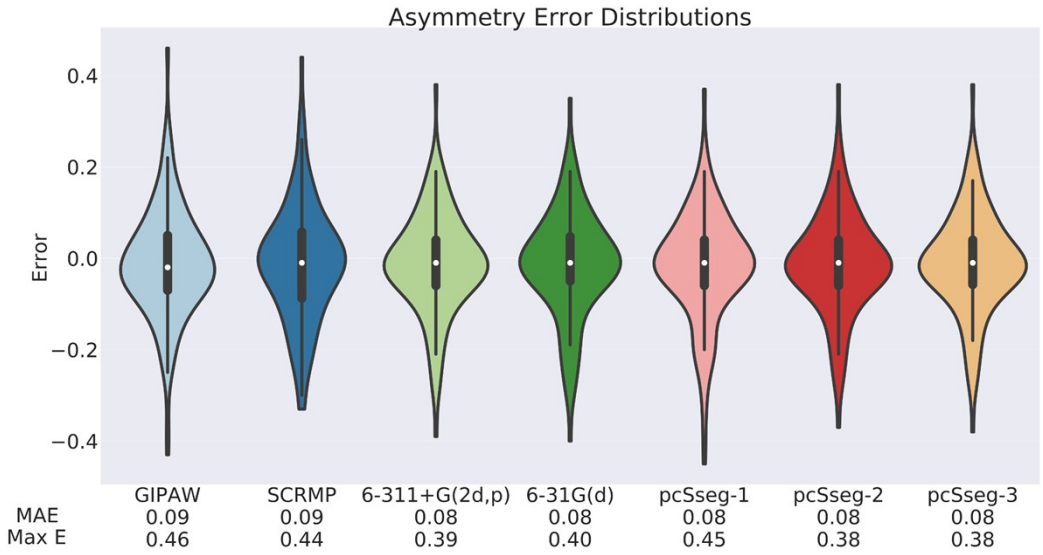


Figure S7. Errors in reproducing the experimental ^{13}C asymmetry calculated from the principal components.

To complement Figure 2 in the main paper, Figures S6 and S7 plot the error distributions for the chemical shielding anisotropy and asymmetry relative to experiment. These were computed from the principal components of the shielding tensor according to the Haeberlen convention:

$$|\delta zz-\delta iso| \geq |\delta xx-\delta iso| \geq |\delta yy-\delta iso|$$

$$\text{Isotropic: } \delta iso = (\delta 11 + \delta 22 + \delta 33)/3$$

$$\text{Anisotropy: } \delta = 3(\delta zz-\delta iso)/2$$

$$\text{Asymmetry: } \eta = (\delta yy - \delta xx) / \delta$$

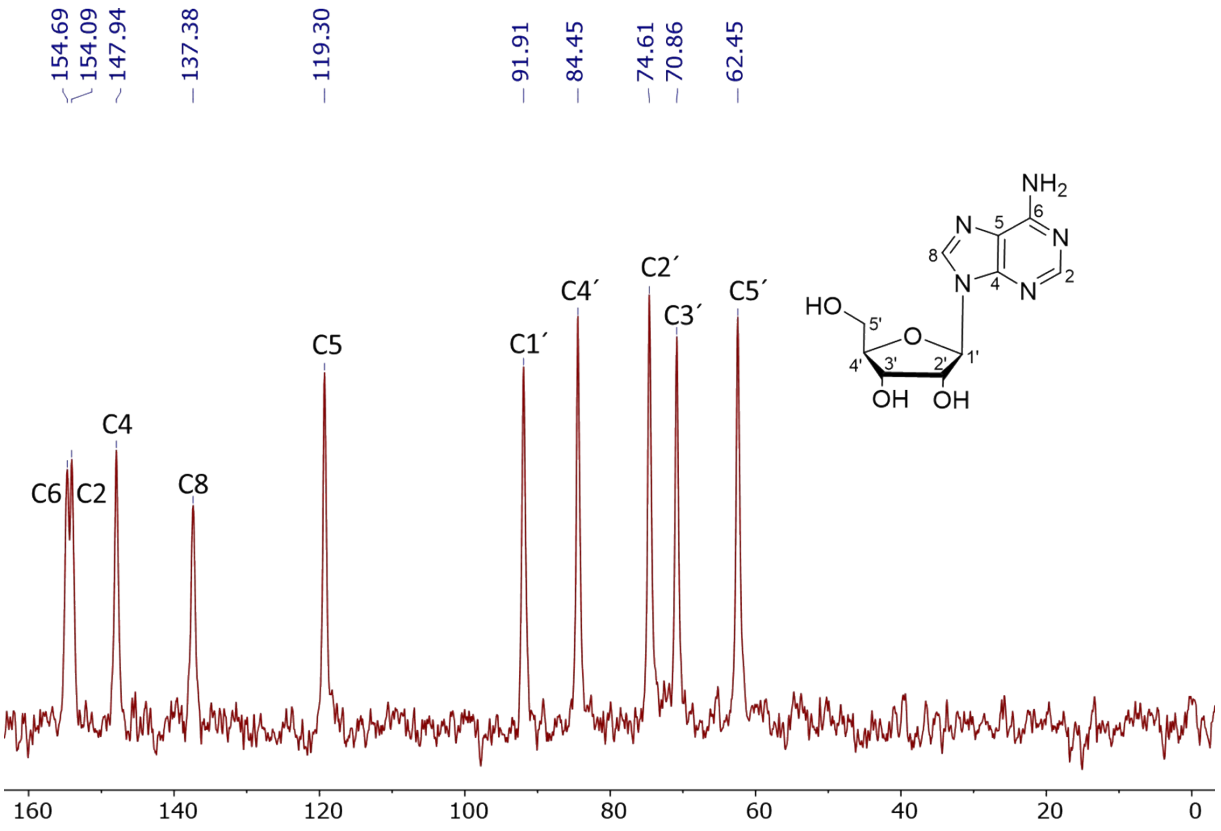


Figure S8. ^{13}C CP-MAS spectrum of adenosine.

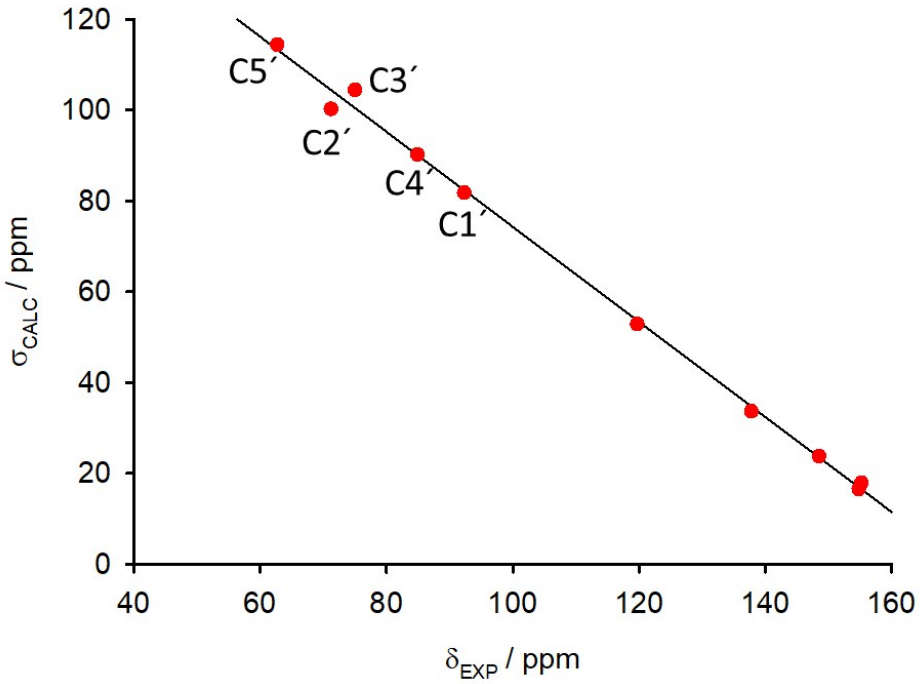


Figure S9. The correlation between calculated NMR shieldings and experimental shifts in adenosine. The original signal assignment of C2' and C3' is used in this plot.

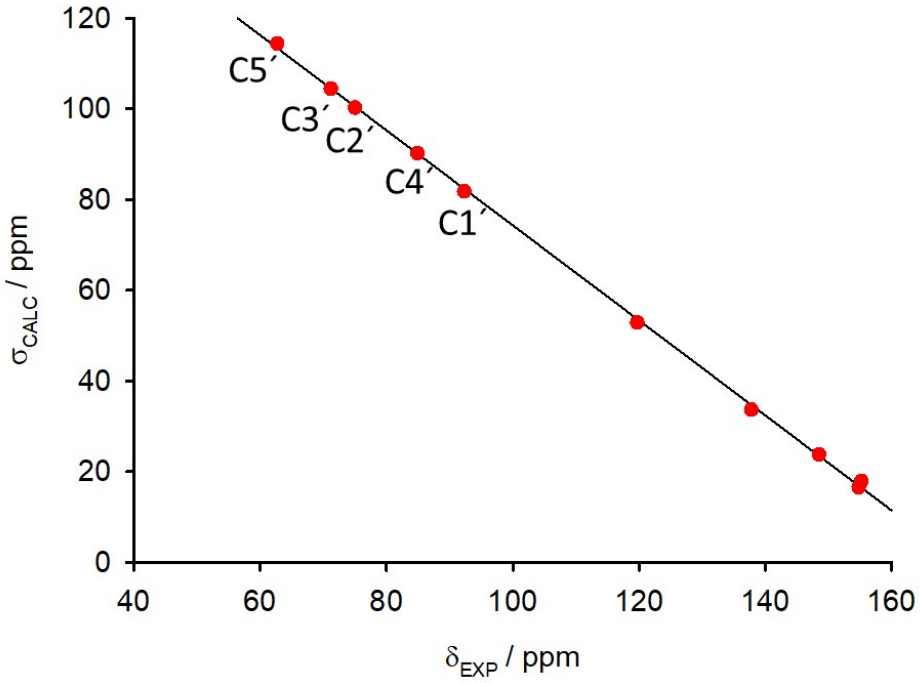


Figure S10. The correlation between calculated NMR shieldings and experimental shifts in adenosine. The new signal assignment of C2' and C3' is used in this plot.

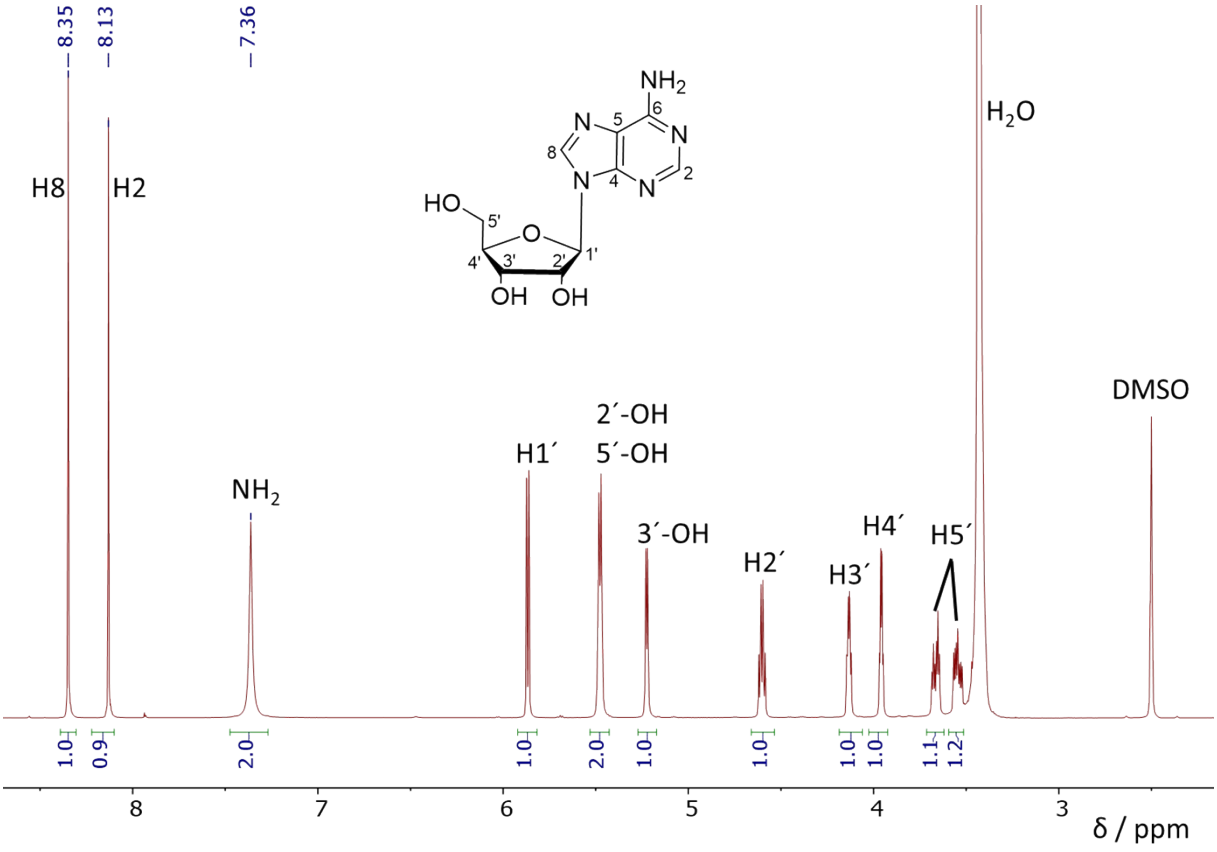


Figure S11. ^{1}H NMR spectrum of adenosine in DMSO-d_6 with signal assignment.

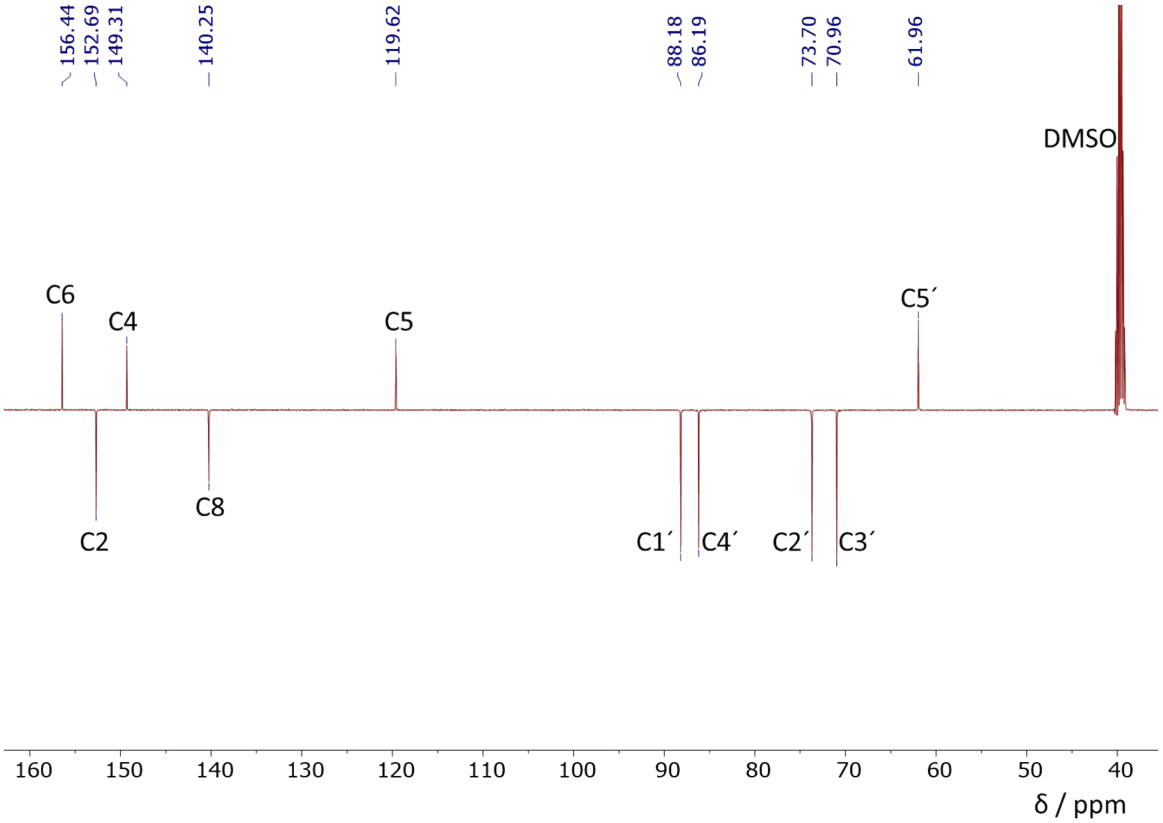


Figure S12. ^{13}C attached proton test (APT) NMR spectrum of adenosine in DMSO-d_6 with signal assignment. Negative signals correspond to CH and CH_3 groups, positive signals correspond to CH_2 and quaternary carbons.

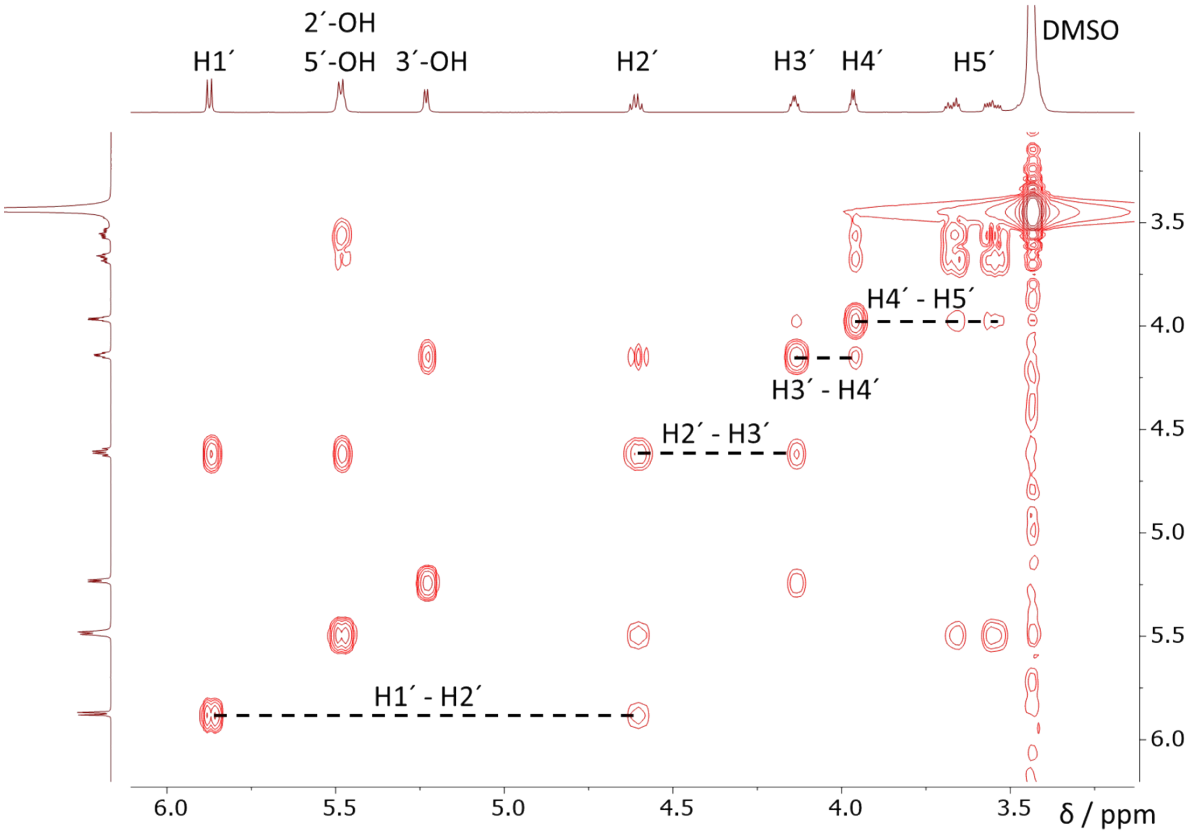


Figure S13. H,H-COSY spectrum of adenosine in DMSO-d_6 with signal assignment.

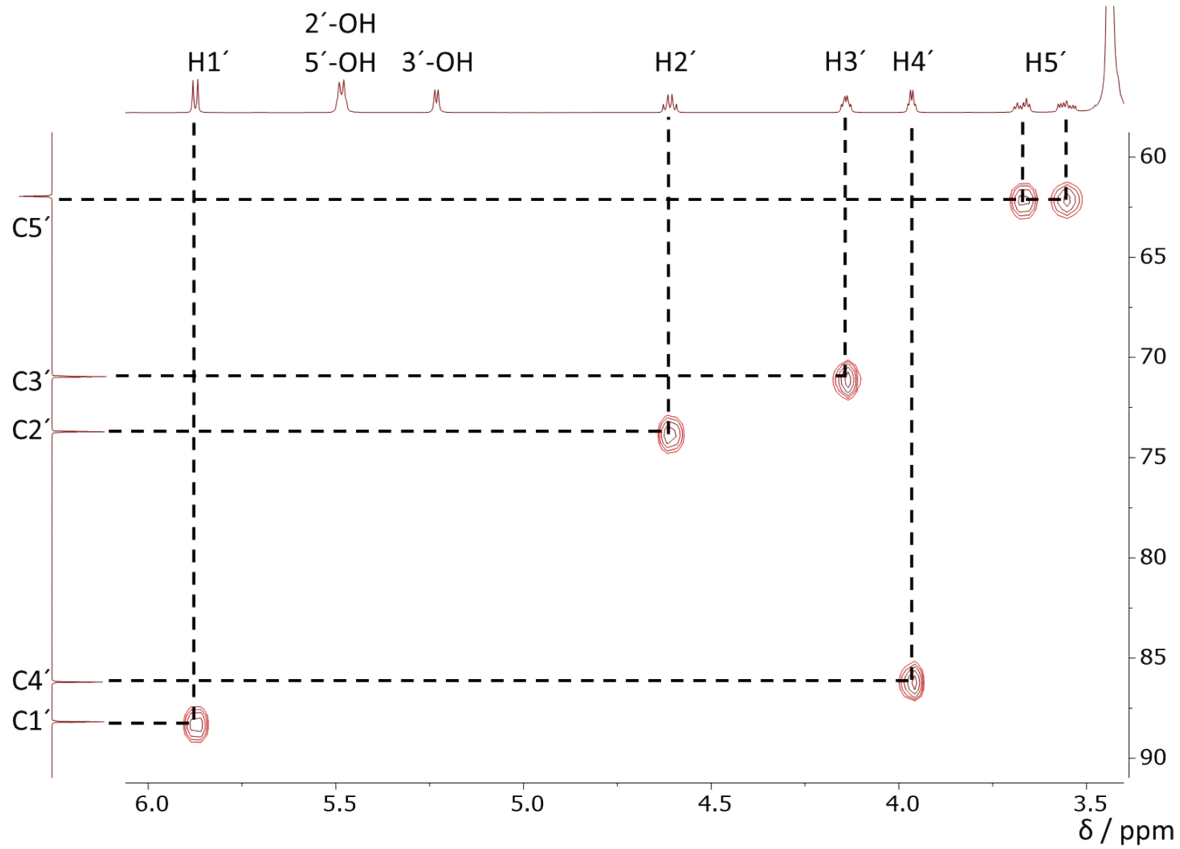


Figure S14. H,C-HSQC spectrum of adenosine in DMSO-d_6 with signal assignment.

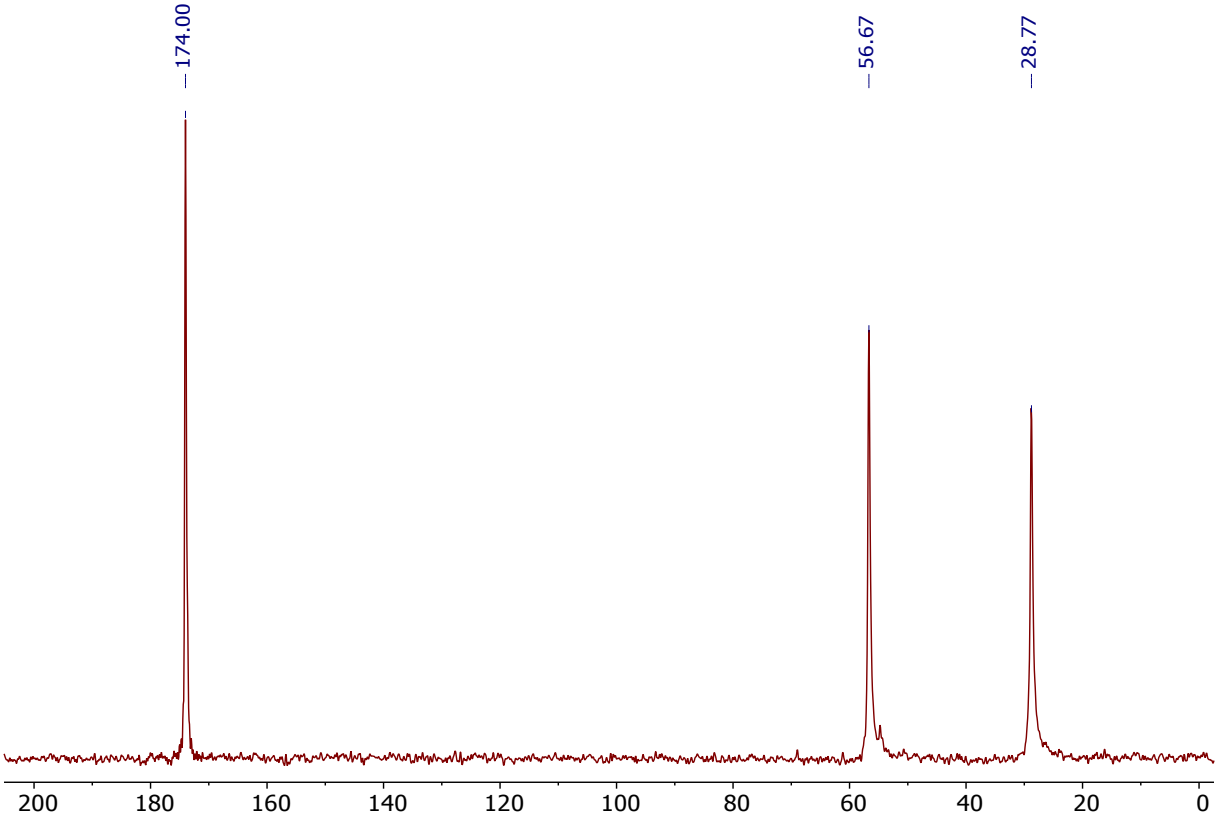


Figure S15. ^{13}C CP-MAS spectrum of L-cysteine.

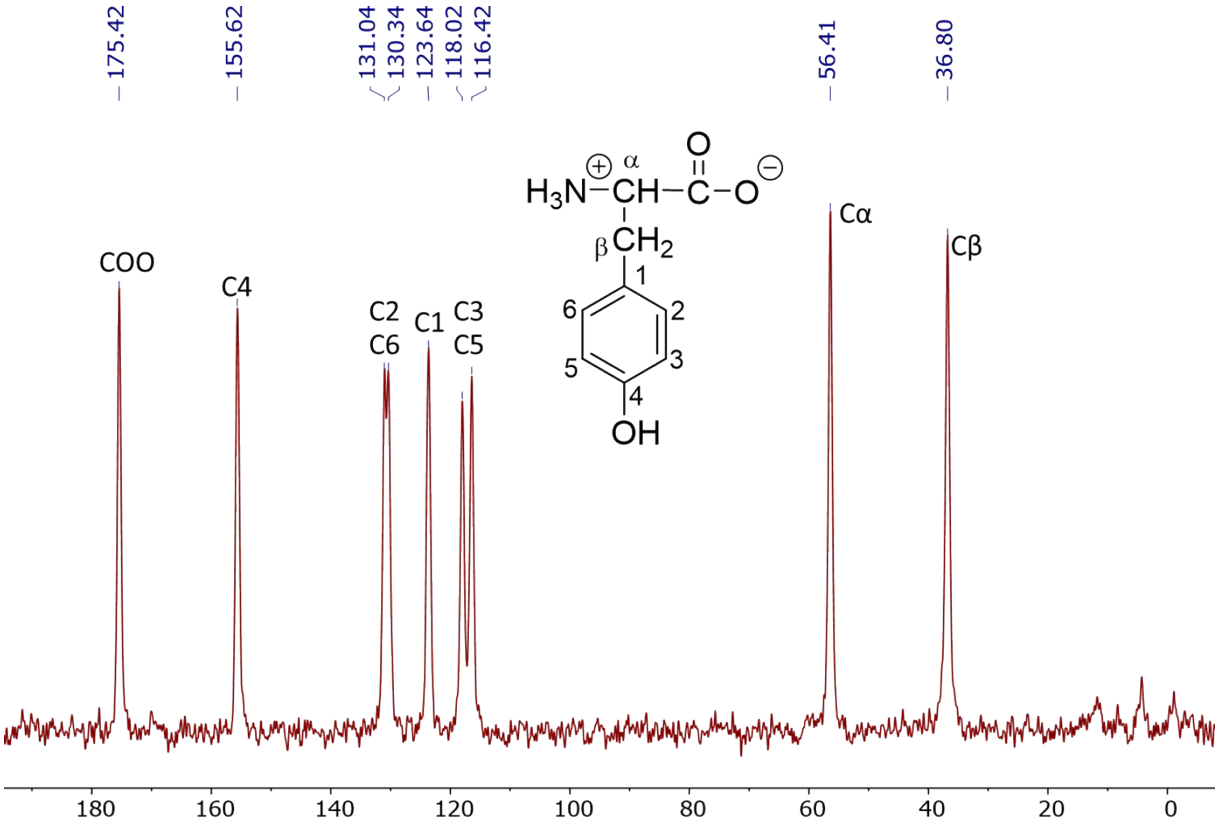


Figure S16. ^{13}C CP-MAS spectrum of L-tyrosine

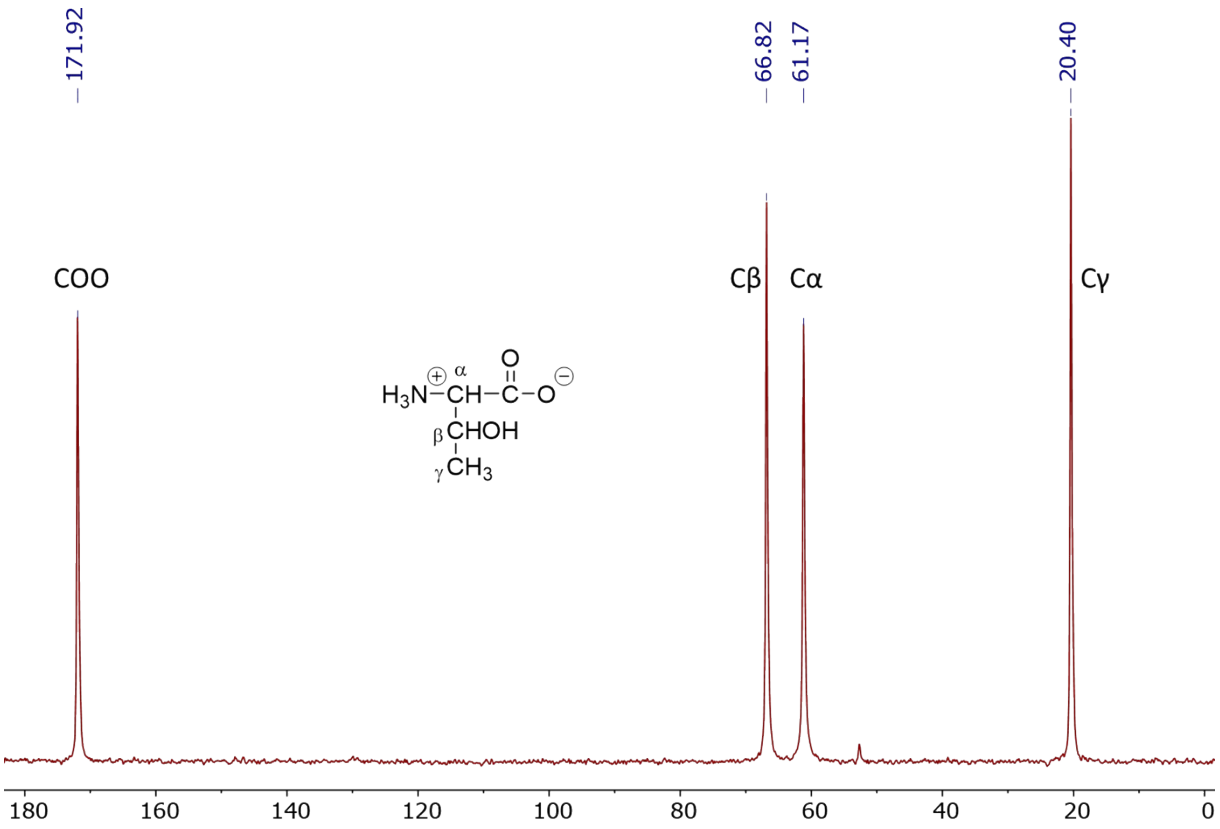


Figure S17. ^{13}C CP-MAS spectrum of L-threonine.

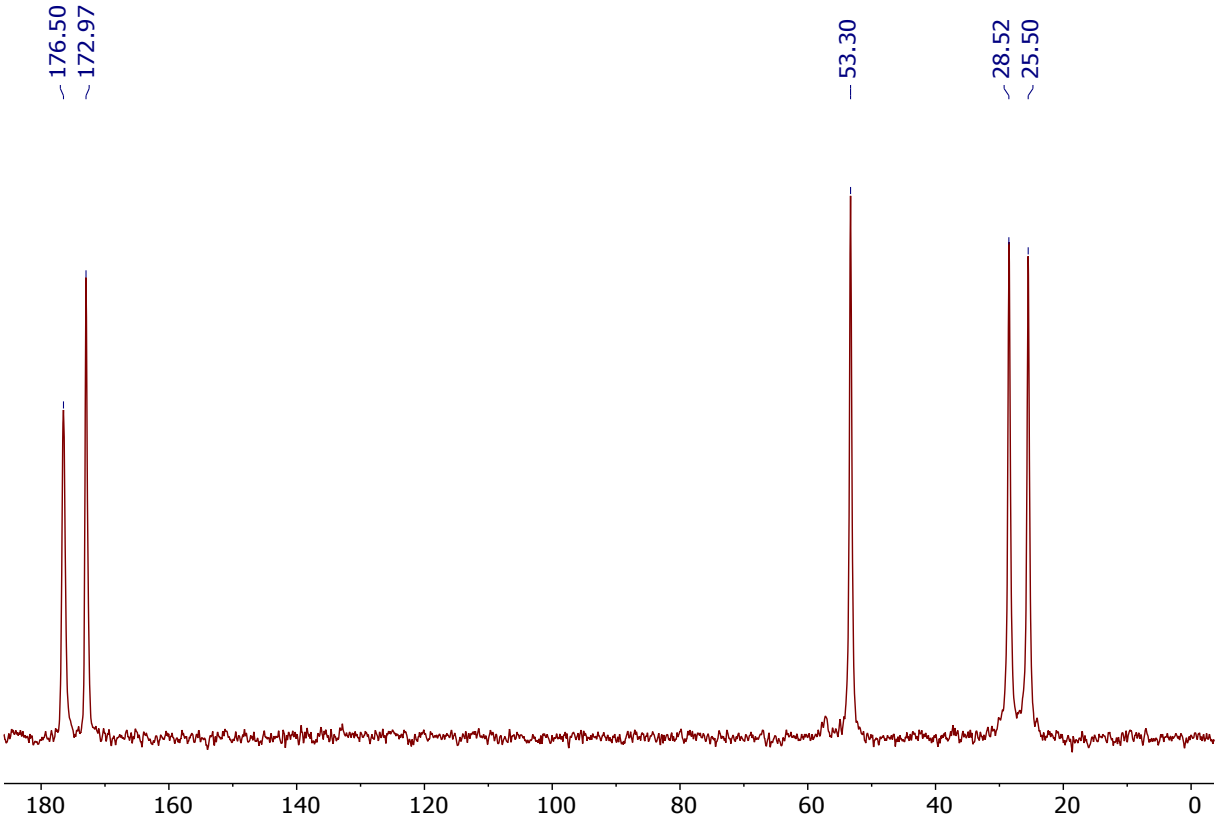


Figure S18. ^{13}C CP-MAS spectrum of L-glutamine

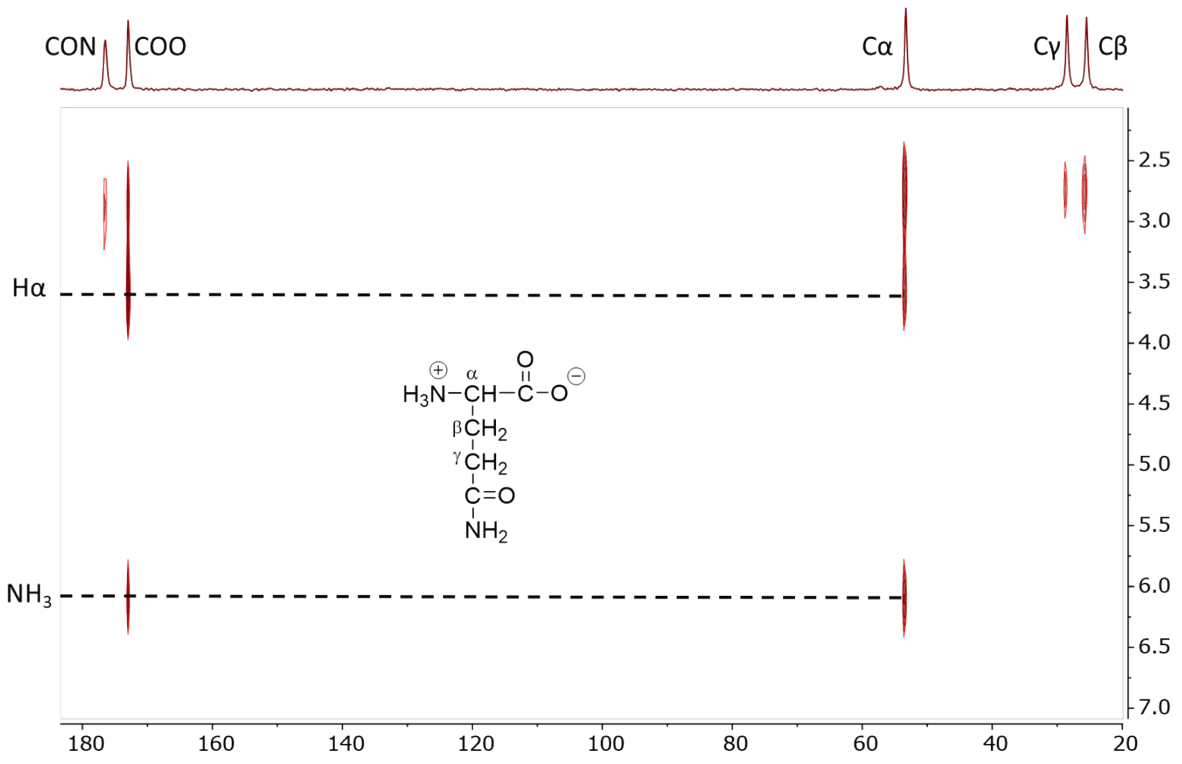


Figure S19. C,H-HETCOR spectrum of L-glutamine

Table S2: Mean absolute difference (MAD) and max difference in the predicted chemical shielding for corrections computed on the single molecule only versus the entire asymmetric unit and how those differences impact the agreement between predicted and experimental chemical shifts. Results here reflect only the multi-component crystals from the test sets. All values are in ppm.

	Shielding Correction		**Error vs Experiment**			
			Molecule Only		**Asymmetric Unit**	
	MAD	**Max Diff**	**MAE**	**Max Error**	**MAE**	**Max Error**
Carbon shift	0.02	0.08	1.8	2.9	1.8	2.9
Carbon CSA	0.04	0.16	--	--	--	--
Nitrogen shift	1.8	6.9	3.1	8.3	3.4	9.1
Oxygen shift	1.66	6.25	3.3	6.3	4.0	11.4