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

Supporting Information

Conformation-specific IR Spectroscopic Signature for C=O…C=O n→π* Interaction in capped 4*R*-Hydroxyproline

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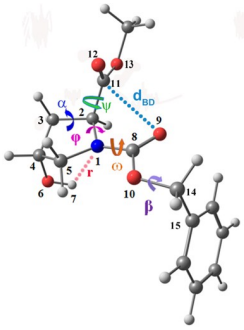
Table S1: Important geometrical parameters[a] of all the conformers of Cbz-Hyp-OMe in groups P, Q and R calculated at the M05-2X/aVDZ level of theory. "*c*" and "*t*" after the conformer number represent *cis* and *trans* conformations, respectively. 2[nd] order perturbative energies for C=O…C=O and O…C=O n→π^* interactions obtained from NBO calculations performed at the M05-2X/aVDZ level of theory



Conformers	**φ (º)**	**Ψ (º)**	**ω (º)**	**α (º)**	**β (º)**	**$r_{O\text{-}H..N}$ (Å)**	$E^{(2)}_{n\rightarrow\pi^*}$ (C8=O9…C11=O12) **(kcal/mol)**	$E^{(2)}_{n\rightarrow\pi^*}$ (O10…C11=O12) **(kcal/mol)**

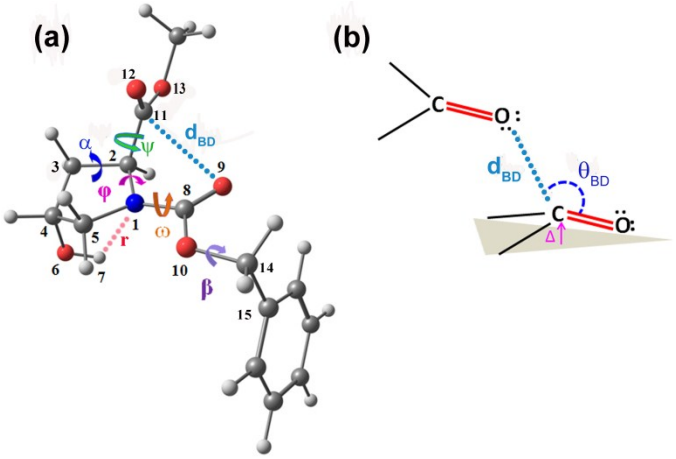
	I-*t*	-63.49	152.38	174.48	31.89	-84.83	-		0.69		-	
	I-*c*	-52.75	141.64	-16.64	31.08	-105.07	-		-		2.43	
	II-*t*	-58.26	153.16	171.71	32.19	94.03	-		1.20		-	
	II-*c*	-63.72	155.30	-6.06	31.72	86.10	-		-		0.98	
P (endo)	I′-*t*	-55.61	140.37	177.93	-25.63	-87.24	-		1.92		-	
	I′-*c*	-51.26	135.49	-9.91	-25.14	-112.44	-		-		2.90	
	II′-*t*	-48.41	140.32	172.65	-25.76	93.91	-		2.73		-	
	II′-*c*	-63.02	144.60	4.38	-28.11	84.20	-		-		1.68	
Q (exo)	I″-*t*	-50.84	146.24	170.54	-17.25	-83.96	2.51		1.39		-	
	I″-*c*	-48.11	138.73	-19.64	-16.17	-105.30	2.50		-		2.58	
	II″-*t*	-50.30	146.33	167.87	-16.69	95.14	2.51		1.88		-	
R (exo)	II″-*c*	-57.38	151.06	-8.95	-17.50	84.85	2.52		-		1.4	

	d_{BD} ($O_9…C_{11}$) (Å)	d_{BD} ($O_{10}…C_{11}$) (Å)	θ_{BD} ($\angle O_9…C_{11}=O_{12}$) (°)	θ_{BD} ($\angle O_{10}…C_{11}=O_{12}$) (°)	Δ_{BD} (Å)	$E^{(2)}_{n\rightarrow\pi^*}$ ($C_8=O_9…C_{11}=O_{12}$) (kcal/mol)		$E^{(2)}_{n\rightarrow\pi^*}$ ($O_{10}…C_{11}=O_{12}$) (kcal/mol)	
I-*t*	2.97	96.16		0.022		0.69		-	
I-*c*	-	2.75	-	101.8	0.013	-		2.43	
I′-*t*	2.89	93.08		0.022		1.20		-	
I′-*c*	-	2.90	-	95.96	0.020	-		0.98	
II-*t*	2.83	98.06		0.023		1.92		-	
II-*c*	-	2.71	-	102.4	0.013	-		2.90	
II′-*t*	2.75	94.54		0.024		2.73		-	
II′-*c*	-	2.81	-	99.30	0.020	-		1.68	
I″-*t*	2.86	95.76		0.022		1.39		-	
I″-*c*	-	2.74	-	101.27	0.013	-		2.58	

[a]Dihedral angles φ (C8-N1-C2-C-11) and ψ (N1-C2-C11-O13) represent the Ramachandran angles. Dihedral angle ω (O10-C8-N1-C2) represents the orientation of the amide bond. α (N1-C2-C3-C4) represents the puckering angle of the pyrrolidine ring. Torsional angle β (C8-O10-C14-C15) represents the orientation of the benzyl group and $r_{O\text{-}H..N}$ represents the H…N hydrogen bond distance. C8=O9…C11=O12 n→π* interaction is present only in the trans conformers while O10…C11=O12 interaction is present in the cis conformers only.

$II^{//}$-*t*	2.80		93.36	-	0.023	1.88	-
$II^{//}$-*c*	-	2.90	-	95.63	0.020	-	1.4

Table S2. Burgi-Dunitz parameters for the C8=O9…C11=O12 and O10…C11=O12 n→π* interactions present in the *trans* and *cis* conformers of Cbz-Hyp-OMe, respectively, calculated at the M05-2X/aVDZ level of theory



d_{BD} (O9…C11) represents distance between the donor oxygen (O9) and carbon atom (C11) of the acceptor carbonyl group for C8=O9…C11=O12 n→π* interaction in the trans conformers of Cbz-Hyp-OMe. On the other hand, d_{BD} (O10…C11) stands for distance between the donor oxygen (O10) and carbon atom (C11) of the acceptor carbonyl group for O10…C11=O12 n→π* interaction in the trans conformers of Cbz-Hyp-OMe. θ_{BD} (**∠O9…C11=O12)** and θ_{BD} (**∠O10…C11=O12)** are Burgi-Dunitz angles for C8=O9…C11=O12 and O10…C11=O12 n→π* interactions, respectively. "*Δ*"represents degree of pyramidalization of the acceptor carbonyl carbon from the plane of its three substituents.

C8=O9…C11=O12 n→π* interaction is present only in the trans conformers. Although the *cis* conformers of Cbz-Hyp-OMe does not have any C=O…C=O n→π* interaction, these conformers have completely different type of n→π* interaction (O10…C11=O12) involving the ether oxygen atom (O10) of the Cbz group and the ester C11=O12 group of the C-terminal.

	Experimental frequency (cm^{-1})	Calculated frequency[c] (cm^{-1})	Scaling factor
C=O (amide) group of proline dipeptide	1691[a]	1791	0.9441
C=O (ester) group of proline dipeptide	1748[a]	1831	0.9546
OH group of benzyl alcohol	3649[b]	3882	0.9400

Table S3. Determination of scaling factors for the amide C=O, ester C=O and –OH stretching frequencies of Cbz-Hyp-OMe calculated with harmonic approximation at the M05-2X/aug-cc-pVDZ level theory

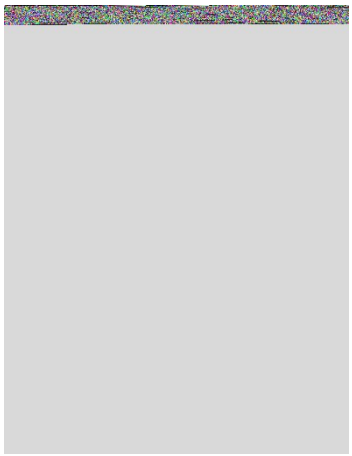
[a]Experimental amide and ester C=O stretching frequencies are taken from the reported FTIR spectrum of terminally protected proline dipeptide [(R)-tert-butyl 2-((S)-2-(methoxycarbonyl)pyrrolidine-1-carbonyl)-pyrrolidine-1-carboxylate] in the solid state. Reference: Das, S. *et al., J. Phys. Chem. A* **2016**, *120*, 9829-9840.

[b]Experimental OH stretching frequency is taken from the reported resonance ion dip infrared (RIDIR) spectrum of benzyl alcohol studied in supersonic jet. Reference: M. Mons *et al., J. Phys. Chem. A* **2000**, *104,* 1430-1437.

[c]Geometry optimization and frequency calculations of proline dipeptide as well as benzyl alcohol are performed at the M05-2X/aug-cc-pVDZ level of theory.

Detailed description on hyperconjugation effect in the amide C8=O9 and the ester C11=O12 groups in Cbz-Hyp-OMe:

The second-order perturbative energy values of all the possible orbital interactions (denoted as R1 and R2 interactions) in the amide and ester parts of Cbz-Hyp-OMe, which involve lone pairs (N1, O10, and O9, O12, O13 atoms), π^* and σ^* NBOs of the donor C8=O9 as well as the acceptor C11=O12 and σ^* NBOs of C8-N1, C8-O10 and C11-O13 bonds in the conformers of P, Q, and R groups are shown as bar diagram in Figure 5 in the main text. The second order perturbative energy values for the n→π^* interaction are not included in the bar diagram.



In general, there are two opposing hyperconjugation effects (resonance and inductive) that determine the C=O stretching frequency in esters and amides. In Cbz-Hyp-OMe, the overlap between the π^* as well as the σ^* orbital of the amide C8=O9 with the lone pair (n) orbitals of the neighboring nitrogen atom (N1) in the proline ring and ether oxygen (O10) decreases the amide C8=O9 streching frequency. These orbital interactions, denoted as $R1_N$ ($n_{N1} \rightarrow \pi^*_{C8=O9,}$ $n_{N1} \rightarrow \sigma^*_{C8=O9}$) and $R1_O$ ($n_{O10} \rightarrow \pi^*_{C8=O9,}$ $n_{O10} \rightarrow \sigma^*_{C8=O9}$), can be called resonance effect as these interactions involve delocalization of lone pair orbital of neighbouring electronegative atom into

the π^* orbital of the carbonyl group. The $R1_N$ and $R1_O$ interactions are together called $R1_{amide}$ interaction. The reduction in the C=O streching frequency will be more as the overlap between the lone pair orbital of the electronagetive atom and the π^* orbital of the carbonyl group increases. On the other hand, overlap between the lone pair orbitals (p-type and s-type) of the carbonyl oxygen (O9) with the σ^* orbital of C8-N1 bond as well as C8-O10 bond increases the C8=O9 stretching frequency. These orbital interactions, marked as $R2_N$ ($n_{O9} \rightarrow \sigma^*_{C8\text{-}N1}$) and $R2_O$ ($n_{O9} \rightarrow \sigma^*_{C8\text{-}O10}$) are termed as inductive effect. A combined values for $R2_N$ and $R2_O$ interactions are called $R2_{amide}$ interaction.

NBO views of $R1_{amide}$, $R2_{amide}$ interactions and C=O…C=O n→π^* interaction in group Q conformers of CbZ-Hyp-OMe are provided below.

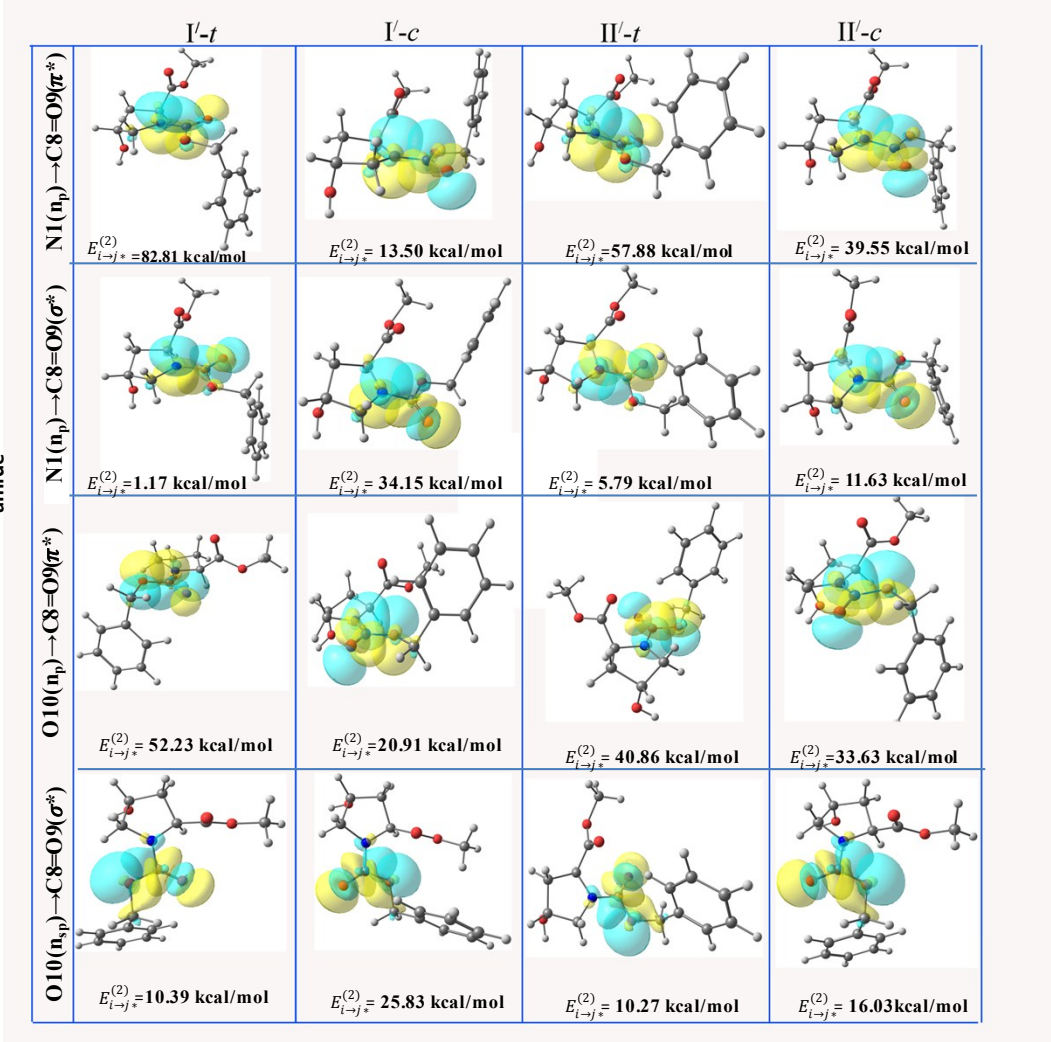


Figure S1a: NBO views of $R1_{amide}$ interactions in group Q conformers of Cbz-Hyp-OMe. The $R1_{amide}$ interaction represents delocalization of lone pair electrons of neighboring electronegative atoms (N1 and O10) into the π^* and σ^* orbitals of the amide C8=O9 group.

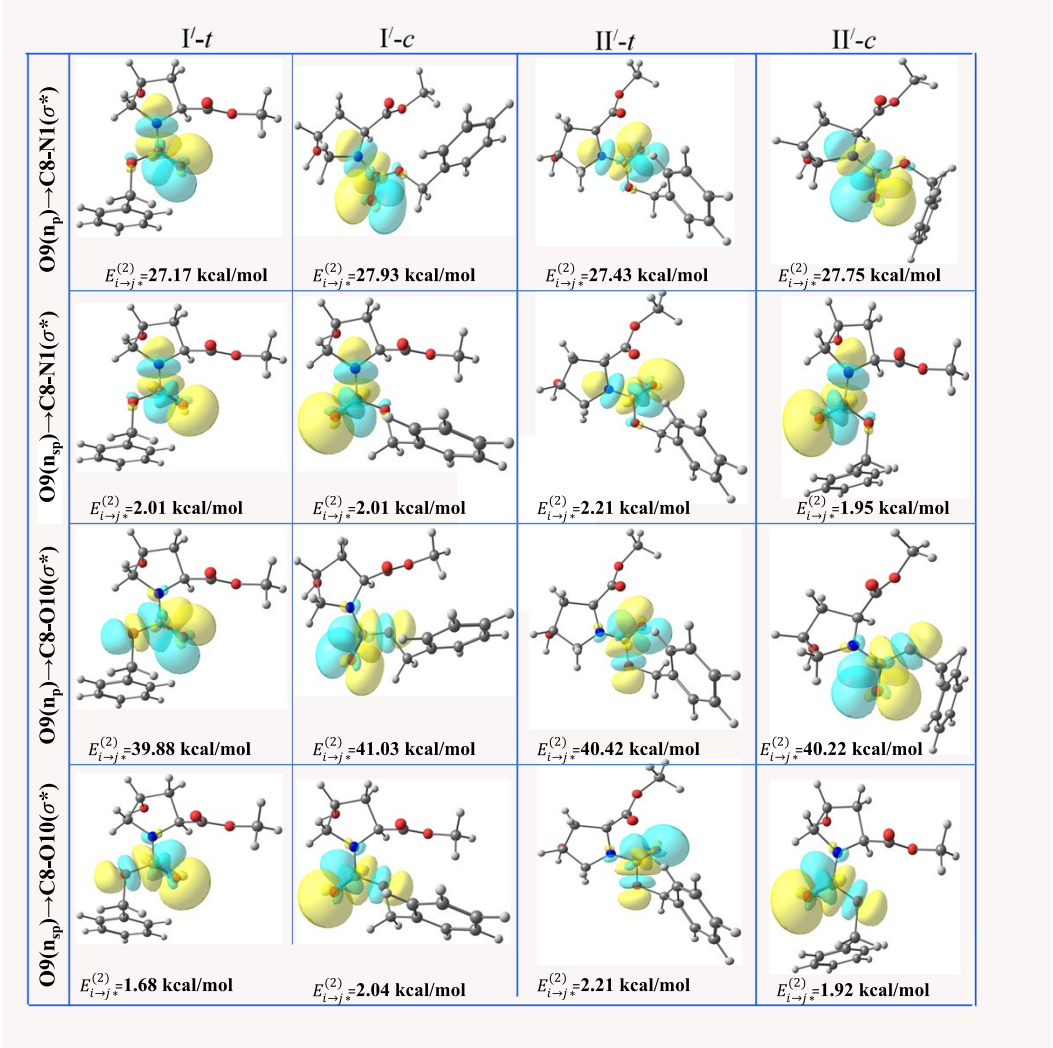


Figure S1b: NBO views of $R2_{amide}$ interactions in group Q conformers of Cbz-Hyp-OMe. The $R2_{amide}$ interaction represents delocalization of lone pair electrons of the amide carbonyl oxygen (O9) into the σ^* orbitals of C-N bond (C8-N1) and C-O bond (C8-O10).

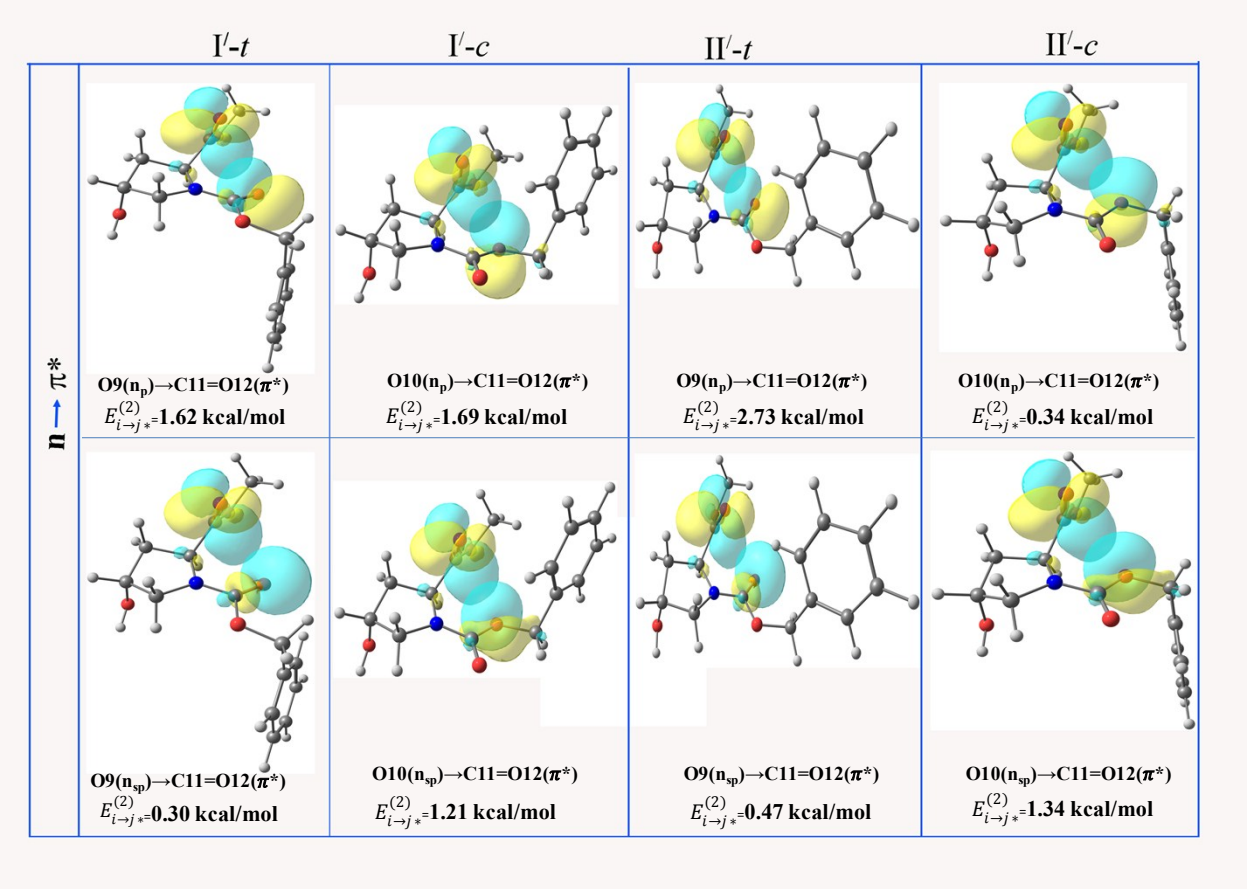


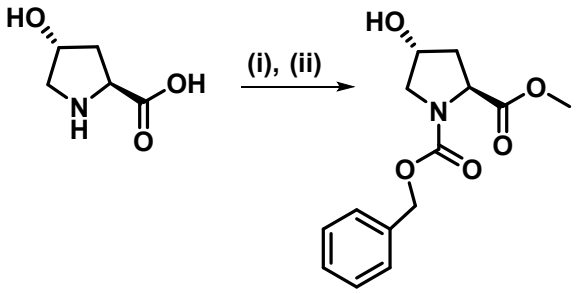
Figure S1c: NBO views of C=O…C=O n→π^* interactions of the *trans* conformers as well as O…C=O n→π^* interactions of the *cis* conformers in group Q conformers of Cbz-Hyp-OMe.

Experimental and computational methods:

Synthesis of Cbz-Hyp-OMe. (2*S*,4*R*)-N[1]–(benzyloxycarbonyl)-4-hydroxyproline methyl ester (Cbz-Hyp-OMe) was synthesized from commercially available 4R-hydroxyproline using previously reported method.[1, 2] The compound Cbz-Hyp-OMe was characterized using HRMS, ^{1}H NMR, and ^{13}C NMR.

Synthesis procedure of Cbz-Hyp-OMe

Scheme: (2*S*, 4*R*)-N[1]–(benzyloxycarbonyl)-4-hydroxyproline methyl ester



Reagents and conditions: (i) 50% Cbz-Cl in toluene, $NaHCO_3$, 1,4-dioxan:H_2O (1:1) **(ii)** Anhydrous K_2CO_3, dimethylsulphate, acetone, reflux.

Synthesis: (2*S*, 4*R*)-N[1]–(benzyloxycarbonyl)-4-hydroxyproline methyl ester

(i) (2*S*, 4*R*)-N[1]–(benzyloxycarbonyl)-4-hydroxyproline: Commercially available *trans*-4-hydroxyproline (4g, 30.5 mmol) was dissolved in 1:1 mixture of 10% aq. $NaHCO_3$ and 1,4-dioxan (40mL) and cooled in an ice bath for 30 min. 50% solution of Cbz-Cl in toluene was added to the resulting solution. The reaction mixture was stirred for 12 h at room temperature. After completion of the reaction, solvent was removed under vacuum. The residual aqueous solution was cooled to 0 ^{o}C and washed with diethyl ether to remove excess reagent. The aq. portion was acidified to pH 3 with saturated $KHSO_4$ and then extracted with ethyl acetate (10X3 mL). The combined organic layer was washed with water followed by brine solution and dried

over anhydrous Na_2SO_4. The resulting organic layer was concentrated under reduced pressure to afford white solid compound which was taken for the next step without further purification.

(ii) (2*S*, 4*R*)-N^1–(benzyloxycarbonyl)-4-hydroxyproline methyl ester.

Anhydrous K_2CO_3 (16.9g, 122.mmol) and dimethylsulphate (5.6ml, 58.8mmol) were added in in the stirred solution of the compound (2*S*, 4*R*)-N^1–(benzyloxycarbonyl)-4-hydroxyproline **(**13g, 49 mmol) in anhydrous acetone (75ml). The mixture was then refluxed under nitrogen for 4 hrs. Acetone was removed under reduced pressure and the resulting residue was dissolved in water and then extracted three times with ethyl acetate. The combined organic layer was washed with water, followed by saturated brine solution, and dried over Na_2SO_4 under vacuum. The crude material was purified by silica gel chromatography (40% ethyl acetate/hexane elute) to afford (2*S*, 4*R*)-N^1–(benzyloxycarbonyl)-4-hydroxyproline methyl ester as colourless viscous liquid with yield 13.52g; 98%.

^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.0-1.88 (1H, m), 2.21-2.09 (1H, m), 3.36-3.64 (5H, m), 4.28-4.38 (2H, m), 4.94-5.08 (2H, m), 5.06 (1H, s), 7.38-7.27 (5H, m).

^{13}C NMR δ: 37.91, 51.92, 51.90, 55.03, 54.59, 57.84, 57.41, 66.17, 66.13, 67.80, 68.58, 127.52, 127.3, 127.87, 127.78, 128.42, 128.32, 136.78, 136.62, 154.26, 153.7, 172.95, 172.61

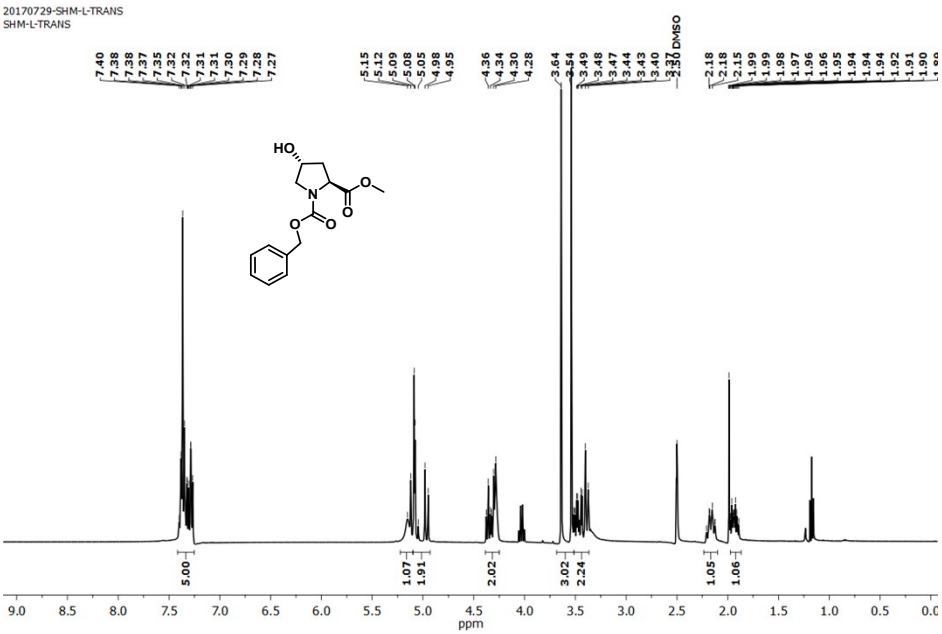
HRMS (ESI-TOF) (m/z): $[M+Na]^+$ calculated for ($C_{14}H_{17}NO_5Na$) 302.1004, found 302.1005.

Specific rotation: $[\alpha]_D^{25}$ -40 (c 2.0, in CH_2Cl_2)

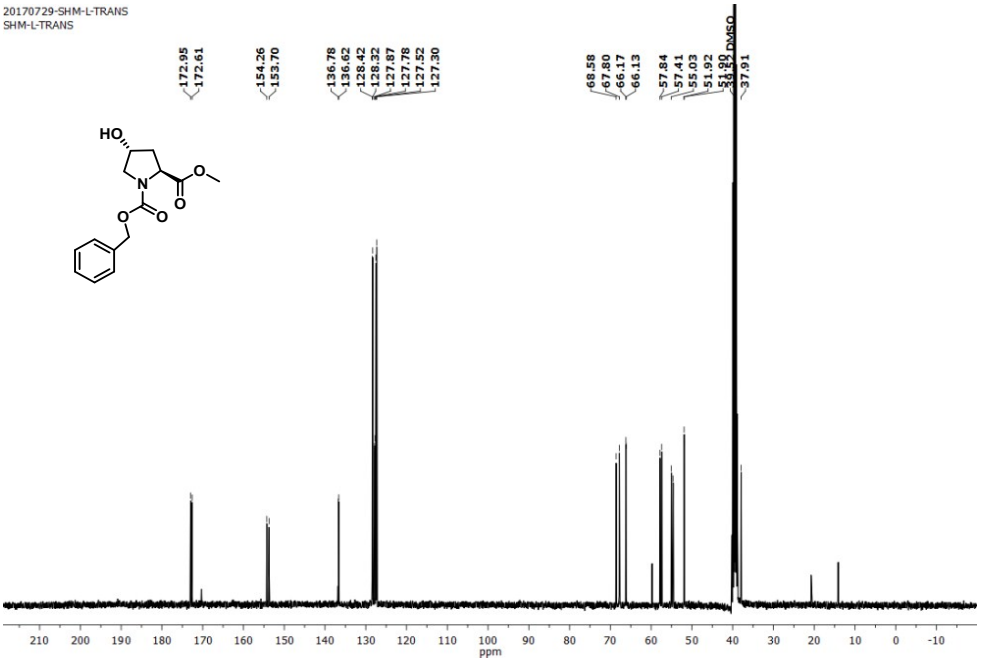
IR (Neat cm^{-1}) υ: 3437.64 (Broad), 2952.22, 1742.08, 1683.14, 1420.53, 1354.3, 1276.84, 1205.18, 1169.62, 1129.05, 1085.53, 997.87.

Characterization of cbz-Hyp-OMe

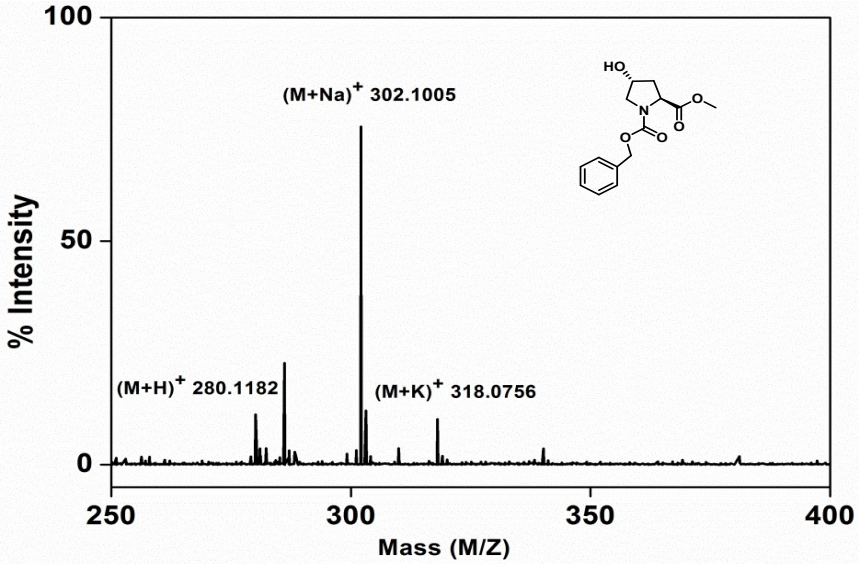
^{1}H NMR of (2*S*, 4*R*)-N^{1}–(benzyloxycarbonyl)-4-hydroxyproline methyl ester



^{13}C NMR of (2*S*, 4*R*)-N^{1}–(benzyloxycarbonyl)-4-hydroxyproline methyl ester



HRMS of (2*S*, 4*R*)-N^1–(benzyloxycarbonyl)-4-hydroxyproline methyl ester



Cartesian co-ordinates of the optimized structures of all the 16 conformers of Cbz-Hyp-OMe obtained at the M05-2X/aVDZ level of theory

I-t

C	2.073984362	0.281092319	-0.590564543
H	1.744441866	-0.061730743	-1.572685336
N	0.949516997	0.655656619	0.245737817
C	-0.008322129	-0.265491462	0.492765824
O	-0.035059208	-1.366774761	-0.029898599
C	2.885877324	-0.828113838	0.063884573
O	3.006725784	-0.976384351	1.255549436
O	3.507902893	-1.576451536	-0.852350376
C	4.329628298	-2.625808153	-0.313842796
H	5.117273069	-2.197914729	0.310685369
H	3.714141417	-3.300351712	0.285289035
H	4.748677829	-3.13963593	-1.17794912
O	-0.921790211	0.187634595	1.376902346
C	-2.03718116	-0.702678773	1.615191456
H	-2.396203241	-0.41996563	2.606243279
H	-1.66887284	-1.729572738	1.6225059
C	-3.113806527	-0.51184451	0.580284901
C	-4.061033663	0.502232758	0.740292241
C	-3.168108576	-1.329280964	-0.550921879
C	-5.05054731	0.702623651	-0.218870506
H	-4.021659272	1.138039788	1.622639959

C	-4.159477522	-1.131553188	-1.510023005
H	-2.418402109	-2.104956254	-0.67978759
C	-5.100545769	-0.116458848	-1.346052893
H	-5.785303465	1.492599368	-0.08560627
H	-4.197457857	-1.771166975	-2.38813379
H	-5.874150829	0.035418797	-2.094625736
C	2.632501721	2.215217814	0.717800208
H	3.251761423	1.735792781	1.483455307
C	1.150728142	1.901659362	0.979586369
H	0.923979197	1.764201861	2.038905494
H	0.530663297	2.709250479	0.574319047
C	2.897584333	1.575884027	-0.643133226
H	2.497965282	2.238131818	-1.417497734
H	3.958217427	1.40137582	-0.834416223
O	2.909777166	3.603747026	0.642326207
H	2.94972796	3.9675317	1.529137395

I-c

C	1.801167256	0.702906278	0.502773982
H	1.731945289	0.712490227	1.591165521
N	1.935834581	-0.653124767	-0.020590439
C	0.920209381	-1.547957199	0.055196209
O	0.845669661	-2.580290398	-0.580498111
C	0.55463165	1.359592414	-0.077194191
O	0.202210643	1.231595845	-1.226125269

O	-0.077929974	2.113486015	0.821711649
C	-1.297115977	2.716595785	0.346408378
H	-1.68865244	3.278957115	1.192752705
H	-1.079996644	3.374453912	-0.49773692
H	-1.991900617	1.932280324	0.037437172
O	0.001149822	-1.128444983	0.963402191
C	-1.228936135	-1.877293549	1.04247411
H	-1.426511193	-2.015973093	2.107292936
H	-1.074915061	-2.843438309	0.558560454
C	-2.336774456	-1.092720229	0.391261864
C	-2.312878521	-0.873628029	-0.989317654
C	-3.377020435	-0.560458726	1.152707649
C	-3.319584024	-0.130040638	-1.597099355
H	-1.494881538	-1.277102039	-1.581459783
C	-4.392124138	0.178150828	0.543686468
H	-3.393736494	-0.723060268	2.228307108
C	-4.363490681	0.393970967	-0.83224938
H	-3.290536018	0.043066845	-2.669394064
H	-5.201726879	0.585866457	1.143542271
H	-5.151756629	0.970549249	-1.309378988
C	2.96072177	-0.77423626	-1.053944418
H	2.553844724	-1.306170431	-1.916669671
H	3.840465645	-1.308975565	-0.678517897
C	3.065333031	1.394802354	-0.024940837
H	3.904745656	1.197608974	0.649286526

H	2.944424366	2.47415485	-0.137622256
C	3.341266062	0.684021627	-1.347892478
H	2.69453098	1.086680114	-2.133643103
O	4.709276434	0.852468619	-1.683434931
H	4.847482622	0.578109324	-2.592330557

II-t

C	2.362969627	0.081390556	0.341694724
H	2.785466053	0.178303582	1.343016212
N	1.313789537	-0.92123562	0.296888231
C	0.208346853	-0.709134535	1.049192171
O	0.114836218	0.187350227	1.868359041
C	1.817991833	1.437751631	-0.087128326
O	0.912169514	1.59416148	-0.871616903
O	2.513771017	2.434792529	0.461699022
C	2.07638245	3.752839853	0.087432538
H	2.166486253	3.880950443	-0.993580065
H	1.035535842	3.889194309	0.388297785
H	2.732692609	4.438762585	0.621031976
O	-0.756757863	-1.614999301	0.781539964
C	-2.031549594	-1.369851484	1.398150975
H	-1.86779287	-0.823365026	2.329979539
H	-2.445647183	-2.35642554	1.6147999
C	-2.950305986	-0.606890073	0.475682152
C	-4.315897316	-0.894830663	0.484505595

C	-2.467562692	0.400167043	-0.363047796
C	-5.196422815	-0.180008286	-0.325226204
H	-4.695109154	-1.687796828	1.126552412
C	-3.347461871	1.107914894	-1.178731382
H	-1.408799298	0.644925145	-0.387884877
C	-4.7124117	0.824028291	-1.160939794
H	-6.257891577	-0.414042367	-0.310022024
H	-2.96158319	1.888554136	-1.829281237
H	-5.394951953	1.379827295	-1.798758612
C	2.482708492	-1.126892514	-1.728886849
H	2.03367383	-0.383131128	-2.39584996
C	1.386785608	-1.788493685	-0.878241242
H	0.419122572	-1.830087648	-1.381997297
H	1.701866446	-2.802102757	-0.606454895
C	3.369004061	-0.435817952	-0.695581928
H	4.01728698	-1.190484136	-0.239458894
H	3.987864271	0.355773635	-1.122497981
O	3.262726395	-2.055169967	-2.463579148
H	2.769104071	-2.344638397	-3.233746773

II-c

C	-1.829343879	-0.087926791	-0.58131365
H	-1.193538688	0.231020257	-1.408764059
N	-1.109212511	-0.920148896	0.364826561
C	0.006536922	-0.523103243	1.018059785

O	0.56398634	-1.166309044	1.886846046
C	-2.406398055	1.14853137	0.092918197
O	-2.719650723	1.219558074	1.255306455
O	-2.584233647	2.136876584	-0.792858337
C	-3.192496341	3.323233051	-0.254863214
H	-4.182338694	3.085707105	0.141511161
H	-2.568073339	3.726303647	0.545487119
H	-3.260603779	4.019918931	-1.089308325
O	0.422411738	0.686091248	0.570432464
C	1.670453709	1.154284355	1.131946567
H	1.714872058	0.853123428	2.179467318
H	1.610051464	2.240899461	1.050437963
C	2.844873608	0.622749398	0.35444159
C	3.482091344	-0.557865829	0.744006785
C	3.294581193	1.303441154	-0.779251438
C	4.555530796	-1.049947183	0.004173021
H	3.11854769	-1.092193526	1.617421566
C	4.366230868	0.811588034	-1.520461264
H	2.801445179	2.22519415	-1.082005418
C	4.998472653	-0.367247907	-1.127628799
H	5.048136685	-1.968681577	0.312175916
H	4.711694882	1.348871488	-2.40003415
H	5.837369338	-0.75202683	-1.702152471
C	-2.973644546	-1.010483162	-1.03138661
H	-2.623281457	-1.672760659	-1.82906727

H	-3.851251214	-0.462999374	-1.38101071
C	-1.846809535	-2.10609096	0.785245377
H	-1.828504316	-2.191308136	1.874193145
H	-1.42384711	-3.015678344	0.343418334
C	-3.247653421	-1.858915778	0.20822181
H	-3.849887861	-1.291635887	0.926492616
O	-3.917691488	-3.044981389	-0.183718096
H	-4.229063886	-3.505508153	0.598403374

I'-t

C	2.275824785	-0.006439514	0.353064181
H	1.967195317	0.378035994	1.327983582
C	1.275438389	-2.029553014	-0.56226303
H	0.320717966	-2.52968616	-0.38094156
H	1.611338763	-2.258894051	-1.581267111
C	2.343235786	-2.409744512	0.462675307
C	3.256887671	-1.189246398	0.470532905
H	3.86136972	-1.142839759	1.377285576
H	3.903674366	-1.211352678	-0.412126681
N	1.152404096	-0.593354153	-0.355699641
C	0.133779502	0.190511092	-0.760881506
O	0.073679696	1.388973892	-0.542699953
C	2.894406216	1.120225252	-0.458100884
O	3.094721958	1.065331576	-1.64618827
O	3.249024416	2.147398738	0.318317639

C	3.8451914	3.248328664	-0.386299069
H	4.753328994	2.917313218	-0.895420491
H	3.135187819	3.636469848	-1.120031428
H	4.070241801	3.993968156	0.375172513
O	1.798801898	-2.514084279	1.773845444
H	1.095558661	-3.167678332	1.77466394
H	2.871887726	-3.328654078	0.185713691
O	-0.797719288	-0.515995169	-1.440296758
C	-1.978377019	0.228177365	-1.821158084
H	-2.347608148	-0.28883503	-2.708500579
H	-1.681171207	1.247662326	-2.07063298
C	-3.006739915	0.205334972	-0.72170304
C	-3.946303708	-0.826485186	-0.667317544
C	-3.020220704	1.198253223	0.261468293
C	-4.887889005	-0.872506402	0.358299586
H	-3.940882542	-1.597635548	-1.435273355
C	-3.961880555	1.153271253	1.287417271
H	-2.279458037	1.992173769	0.221933354
C	-4.89569712	0.1192545	1.337781297
H	-5.618111858	-1.677153115	0.390956011
H	-3.96808165	1.928639043	2.049246359
H	-5.63122812	0.088125414	2.137727683

I'-c

C	1.841218046	0.751270409	0.43814068

H	1.821612356	0.718990628	1.52936091
C	3.110064625	-0.829155442	-0.912242743
H	3.47110186	-1.848430068	-0.750740043
H	2.921704309	-0.686068261	-1.983874505
C	4.057115488	0.239927209	-0.374277131
C	3.122718283	1.415130419	-0.108246448
H	3.557589754	2.124018156	0.597613802
H	2.893828412	1.917991869	-1.05260123
N	1.90815779	-0.588942414	-0.129547475
C	0.892070273	-1.476179477	-0.104645688
O	0.876443153	-2.532670232	-0.707235703
C	0.606629209	1.480098057	-0.073166672
O	0.277060463	1.495745784	-1.234793449
O	-0.03805629	2.122453445	0.900580038
C	-1.245007785	2.788657807	0.483305557
H	-1.630094461	3.273768575	1.379018455
H	-1.014360173	3.520369788	-0.293811717
H	-1.952836806	2.050306058	0.099365082
O	4.610519662	-0.131212649	0.884109606
H	5.076221327	-0.965585124	0.790328908
H	4.848468474	0.489298823	-1.089705126
O	-0.1011574	-1.025212449	0.704141345
C	-1.341722256	-1.758331079	0.695926009
H	-1.573348499	-1.986787387	1.738602643
H	-1.189742043	-2.682978092	0.135836452

C	-2.415082761	-0.897530801	0.085200736
C	-2.310432629	-0.509319987	-1.253577187
C	-3.501155525	-0.461665663	0.843138915
C	-3.282667892	0.305317713	-1.824525424
H	-1.453542986	-0.831402253	-1.840631176
C	-4.481501605	0.349764185	0.270422609
H	-3.579723239	-0.754093412	1.888092842
C	-4.372515694	0.733842028	-1.064017392
H	-3.189342776	0.610903641	-2.863015352
H	-5.32612118	0.684118759	0.867368334
H	-5.132939607	1.368553377	-1.511635749

II'-t

C	-2.333071675	0.29032257	0.057809007
H	-2.937118861	0.451662494	-0.83759836
C	-1.407004584	-1.885535113	0.640374134
H	-1.161763829	-2.780138538	0.062500234
H	-0.74932494	-1.835380236	1.517025761
C	-2.876967094	-1.83800184	1.052782846
C	-3.138838142	-0.344269563	1.20978859
H	-4.203270937	-0.113277327	1.152536618
H	-2.73198691	-0.003174855	2.166697899
N	-1.285860025	-0.688424929	-0.181515522
C	-0.219766024	-0.347247841	-0.933848721
O	-0.128637879	0.705060135	-1.541532317

C	-1.725403017	1.612411779	0.501344232
O	-0.820959404	1.702624481	1.296878289
O	-2.35415148	2.653584935	-0.043298369
C	-1.815341146	3.935154108	0.322060476
H	-1.877474412	4.070700696	1.40415532
H	-0.772298909	3.991599761	0.003119757
H	-2.426741698	4.667821099	-0.202795536
O	-3.730961247	-2.291090875	0.007845988
H	-3.504485421	-3.196739075	-0.216301604
H	-3.063128817	-2.395105786	1.977572712
O	0.724283848	-1.316198466	-0.920173939
C	1.975512614	-0.973873215	-1.541930749
H	1.782933716	-0.237141365	-2.325167662
H	2.344821982	-1.900266681	-1.985843432
C	2.9632984	-0.447881495	-0.530139005
C	4.299309601	-0.842320236	-0.609357199
C	2.57055691	0.447665814	0.468244744
C	5.241019956	-0.342119102	0.288518196
H	4.607411276	-1.549836614	-1.376937649
C	3.510193268	0.938601002	1.37114964
H	1.535961119	0.771624997	0.549194189
C	4.846727821	0.54965535	1.282898369
H	6.27904093	-0.656955986	0.21684879
H	3.194547365	1.632417467	2.146018538
H	5.576426098	0.936774279	1.989524667

II'-c

C	1.915066858	0.476927416	0.354685322
H	1.230716346	0.714739974	1.172420209
C	2.263447141	-1.832098222	-0.327710752
H	1.637064964	-2.724611291	-0.248191164
H	2.916901166	-1.935670935	-1.202783831
C	3.077152676	-1.549134365	0.932767168
C	3.273956824	-0.038496245	0.874546584
H	3.529734494	0.37621257	1.850450077
H	4.056531541	0.200402489	0.147548706
N	1.429384266	-0.644041224	-0.431129788
C	0.246925973	-0.66534929	-1.081578147
O	-0.196904807	-1.626777756	-1.682314957
C	2.123616549	1.713817594	-0.500593985
O	2.562245362	1.704720039	-1.623025387
O	1.819309174	2.828343865	0.176418218
C	2.045602275	4.047448124	-0.549341235
H	3.099648713	4.126425042	-0.82503462
H	1.43309164	4.05576889	-1.453806431
H	1.755983338	4.848964471	0.129065495
O	2.326247396	-1.810256876	2.113743228
H	2.014299555	-2.718154303	2.096117422
H	4.026777517	-2.095543413	0.945025161
O	-0.379071704	0.531574283	-0.981276237

C	-1.696349484	0.584406654	-1.573696192
H	-1.686770808	0.00673346	-2.499078877
H	-1.84991472	1.643508096	-1.787748898
C	-2.739862221	0.07154405	-0.617273921
C	-3.223799769	-1.233726637	-0.721864963
C	-3.219324924	0.902584031	0.398131905
C	-4.179641708	-1.700205244	0.179011287
H	-2.831351855	-1.883273677	-1.499506192
C	-4.170490395	0.43656656	1.301820094
H	-2.841839423	1.919996833	0.480631563
C	-4.653356097	-0.867020227	1.190806146
H	-4.554316234	-2.716892069	0.091921897
H	-4.539788973	1.089546147	2.088496681
H	-5.399283514	-1.232137891	1.892372143

I''-t

C	2.122773676	0.320452824	-0.609445598
H	1.829550819	0.049461911	-1.626222958
C	1.138452348	1.950707023	0.893482584
H	0.182324339	2.454433234	1.037399836
H	1.632556802	1.796082687	1.860705754
C	2.04422242	2.692756825	-0.084754684
C	3.006246869	1.591805997	-0.549114864
H	3.457601877	1.832660329	-1.512250494
H	3.792520947	1.456616537	0.200343972

N	0.959982117	0.684021051	0.18679745
C	0.0385916	-0.268122672	0.470275446
O	0.032546229	-1.371272524	-0.046650347
C	2.854780557	-0.854428665	0.016822813
O	2.979863111	-1.010894873	1.206466033
O	3.397921829	-1.647120153	-0.909878883
C	4.128453494	-2.768364727	-0.384104521
H	4.952315182	-2.415288776	0.240326453
H	3.45818639	-3.391315665	0.212101842
H	4.497755351	-3.3090244	-1.254432689
O	1.298568231	3.230480362	-1.167659522
H	0.674260557	2.560972723	-1.466408418
H	2.564231969	3.534045034	0.376174543
O	-0.86235752	0.16284777	1.37549068
C	-1.968437744	-0.74020493	1.614674072
H	-2.323047472	-0.466915248	2.609735209
H	-1.590195983	-1.763352994	1.612787884
C	-3.049742525	-0.548998781	0.585027006
C	-3.982609741	0.479171093	0.740550869
C	-3.120529131	-1.376184869	-0.537965597
C	-4.974488953	0.683368358	-0.215107085
H	-3.930128604	1.122619447	1.616686787
C	-4.115079326	-1.175064369	-1.493423961
H	-2.381827583	-2.163008678	-0.663788389
C	-5.041646989	-0.146153587	-1.33396706

H	-5.69810039	1.484151011	-0.085778625
H	-4.166456943	-1.822797305	-2.364863887
H	-5.817610953	0.008308559	-2.079536301

I''-c

C	1.817062452	0.726706641	0.529791982
H	1.778050031	0.752055694	1.620443949
C	2.996065179	-0.775381713	-0.9654409
H	3.403578846	-1.787096154	-0.965356486
H	2.617476693	-0.526445332	-1.964453352
C	3.990266499	0.265462246	-0.464984362
C	3.074861369	1.423545986	-0.047391719
H	3.55998391	2.075744944	0.679831122
H	2.796035436	2.002898314	-0.932841869
N	1.941535568	-0.646040515	0.03847355
C	0.909049825	-1.528330899	0.075485953
O	0.842602625	-2.546849037	-0.580921023
C	0.555684089	1.366833634	-0.029371034
O	0.207634104	1.242913524	-1.179395996
O	-0.089919995	2.095059049	0.880050657
C	-1.318628099	2.686040474	0.412598644
H	-1.709427129	3.245329129	1.261259493
H	-1.112935785	3.34491354	-0.433513082
H	-2.008368043	1.895340437	0.109037093
O	4.746030813	-0.228599058	0.632438566

H	4.147751298	-0.700811388	1.220541186
H	4.713122572	0.561197612	-1.226825149
O	-0.019228495	-1.119092912	0.975544111
C	-1.249925182	-1.87135866	1.033640057
H	-1.455630849	-2.02427128	2.09489184
H	-1.088855925	-2.830625191	0.538647033
C	-2.353547682	-1.081486361	0.38261657
C	-2.314051216	-0.839128708	-0.993666335
C	-3.4064299	-0.569304691	1.140476816
C	-3.317953945	-0.091396335	-1.600874432
H	-1.486444208	-1.226616179	-1.583026839
C	-4.418696209	0.173362698	0.531674058
H	-3.435120998	-0.750341448	2.212866437
C	-4.374363328	0.412976975	-0.839913041
H	-3.276800166	0.10028007	-2.669560676
H	-5.238123153	0.565588663	1.128444849
H	-5.160181044	0.992997823	-1.316883104

II''-t

C	2.428517166	0.117963459	0.267759011
H	2.92860832	0.184989231	1.236371453
C	1.481383528	-1.803239097	-0.869625387
H	1.095105189	-2.792863812	-0.625196716
H	0.941761504	-1.392202818	-1.731726033
C	2.988719654	-1.811175734	-1.101971344

C	3.370016332	-0.34303767	-0.873320027
H	4.423992263	-0.237567853	-0.613613085
H	3.157391099	0.232907152	-1.779457175
N	1.391528607	-0.905586714	0.282930149
C	0.269698856	-0.669614893	1.009610546
O	0.173204838	0.23364605	1.819539841
C	1.829483824	1.474542002	-0.065832185
O	0.929789397	1.634537029	-0.856088748
O	2.461555636	2.462719951	0.565709341
C	1.949464601	3.778032761	0.287649901
H	2.035755545	3.992012183	-0.779919301
H	0.901480569	3.829208152	0.590297085
H	2.562389729	4.458457396	0.876848794
O	3.645740434	-2.673913145	-0.184380063
H	3.285027856	-2.511666986	0.693405874
H	3.259878756	-2.162383447	-2.098710329
O	-0.699033483	-1.563882245	0.726566495
C	-1.972135674	-1.331357855	1.355396641
H	-1.804014742	-0.790749941	2.28965305
H	-2.377381306	-2.322461158	1.567776251
C	-2.902649814	-0.568001858	0.445928128
C	-4.262342166	-0.882206383	0.444937444
C	-2.436195027	0.464800584	-0.370271772
C	-5.153974373	-0.167039512	-0.352335068
H	-4.628270543	-1.695517004	1.068926408

C	-3.326991418	1.172489121	-1.173828225
H	-1.381616562	0.727059635	-0.388229069
C	-4.686539113	0.862936063	-1.165429776
H	-6.210844502	-0.421345635	-0.345576354
H	-2.953986878	1.972250294	-1.808408939
H	-5.377702152	1.418510975	-1.794073116

II''-c

C	-1.877163886	-0.074374613	-0.597584866
H	-1.275585661	0.200658532	-1.466847524
C	-1.841821217	-2.11956323	0.704983975
H	-1.141424446	-2.92274847	0.936987097
H	-2.492748403	-1.933500726	1.56838304
C	-2.650159361	-2.380081199	-0.561485117
C	-3.089098921	-0.968477014	-0.971287348
H	-3.333145358	-0.914390951	-2.032731663
H	-3.961458366	-0.672267295	-0.379831133
N	-1.121189262	-0.90916325	0.323411926
C	-0.018138609	-0.493596599	0.992626771
O	0.541210941	-1.128248126	1.86487316
C	-2.371191062	1.192805217	0.076399387
O	-2.675444948	1.271154713	1.240180637
O	-2.490514324	2.195137995	-0.801917411
C	-3.020215314	3.413418336	-0.251358457
H	-4.019458466	3.234569296	0.151954357

H	-2.365410071	3.771176486	0.546248652
H	-3.051741845	4.118452004	-1.080912242
O	-1.853394026	-2.990849595	-1.566517964
H	-0.988384261	-2.567897345	-1.565246195
H	-3.498104538	-3.04600438	-0.39365427
O	0.387423405	0.716310728	0.541224002
C	1.630008396	1.196551463	1.106621624
H	1.662566064	0.917661648	2.160723391
H	1.569640942	2.280967578	1.000790927
C	2.811362052	0.646296795	0.353228661
C	3.476734819	-0.494982579	0.80632046
C	3.238478034	1.269029433	-0.822032386
C	4.556809524	-1.006138458	0.089132827
H	3.129775358	-0.986145463	1.711239589
C	4.315704559	0.757496549	-1.541150269
H	2.722743619	2.160270518	-1.174487083
C	4.976924183	-0.381893519	-1.084134537
H	5.071866234	-1.893933687	0.447009678
H	4.643693422	1.24936444	-2.453371409
H	5.820643713	-0.781089704	-1.64148611

I’’’-t

C	-4.732304167	0.520410042	2.560919271
H	-5.598739528	0.830390384	1.977429325
C	-4.002095281	-1.802656622	2.501692593

H	-4.117142158	-2.609355013	1.773628041
H	-3.077560106	-1.958222567	3.071210399
C	-5.202971439	-1.673535329	3.437646485
C	-5.152236822	-0.20780387	3.85316845
H	-6.117035173	0.134081821	4.231527143
H	-4.377573483	-0.066505792	4.611403726
N	-4.000946365	-0.507811619	1.836437558
C	-3.403344625	-0.195700007	0.672785882
O	-3.470002175	0.911693314	0.158772475
C	-3.789359302	1.683911818	2.89676349
O	-2.754613775	1.476938943	3.475923952
O	-4.157963374	2.93962525	2.613495889
C	-5.253604529	3.201484796	1.724119157
H	-5.109308658	2.659131026	0.787391536
H	-6.20609429	2.940962157	2.195128423
H	-5.220656622	4.276359442	1.546716958
O	-6.431622207	-1.854394268	2.740202651
H	-6.442988333	-2.725921122	2.337563926
H	-5.13554447	-2.354399615	4.293253335
O	-2.724061552	-1.240533324	0.156183113
C	-2.143464035	-1.010345803	-1.149643527
H	-1.320229585	-1.724555111	-1.203191189
H	-1.76317472	0.011316101	-1.187222834
C	-3.149446882	-1.265023659	-2.240207134
C	-3.375287071	-2.568735696	-2.688187869
C	-3.874711307	-0.21162487	-2.801028441
C	-4.318115274	-2.820993245	-3.681538456

H	-2.80624571	-3.389905532	-2.256458125
C	-4.816275039	-0.462125361	-3.797395393
H	-3.7060622	0.79849559	-2.438134244
C	-5.039753396	-1.765463476	-4.237839279
H	-4.485266886	-3.837892974	-4.027470323
H	-5.376578174	0.36179382	-4.23192806
H	-5.773121291	-1.959089628	-5.016618904

I'''-c

C	-4.710658993	0.538796503	2.536105434
H	-5.714917237	0.660382605	2.130912337
C	-3.729673975	-1.688252017	2.643183251
H	-3.891780479	-2.604062106	2.068223054
H	-2.694645938	-1.675225047	3.006846756
C	-4.71808056	-1.514401268	3.793780989
C	-4.755979636	-0.001579633	3.98059167
H	-5.651076957	0.315234783	4.518662539
H	-3.859321832	0.325497839	4.51409004
N	-4.012779232	-0.521417279	1.823109143
C	-3.604213938	-0.425907755	0.541482735
O	-2.97354036	-1.268957106	-0.065018799
C	-3.896094971	1.835998567	2.492381149
O	-2.723962952	1.837758223	2.766632871
O	-4.512465771	2.994249134	2.214177549
C	-5.833000241	3.020820668	1.652063407

H	-6.006341859	4.064547023	1.391155228
H	-5.873753914	2.40645143	0.750269038
H	-6.574551904	2.697320247	2.387861525
O	-6.035205671	-1.907379012	3.419054138
H	-6.023630412	-2.82713854	3.143625622
H	-4.397056075	-2.039103174	4.700150476
O	-4.009406461	0.755262272	0.009799572
C	-3.500125345	1.04563912	-1.309144679
H	-3.952303422	0.357398832	-2.027478031
H	-2.418303264	0.88997997	-1.300396903
C	-3.866082438	2.474724656	-1.594796387
C	-3.332754028	3.492479778	-0.797959746
C	-4.751905719	2.79744004	-2.621068147
C	-3.68959049	4.817503578	-1.025086611
H	-2.654484322	3.240547898	0.014501156
C	-5.103596795	4.127313518	-2.856048027
H	-5.170733589	2.006058303	-3.238954403
C	-4.574765166	5.137259112	-2.056672763
H	-3.276232585	5.603250919	-0.398181646
H	-5.792129313	4.372120274	-3.660718161
H	-4.849054156	6.173587646	-2.237035374

II’’’-t

C	-4.972137611	0.528603428	2.378458164
H	-5.978722812	0.424344037	1.97559364

C	-3.540097427	-1.398204441	2.783664256
H	-3.482682418	-2.41241355	2.381189366
H	-2.539909805	-1.077294793	3.099880644
C	-4.543461571	-1.272796782	3.928363236
C	-4.924991585	0.202913083	3.886326966
H	-5.879645215	0.381966139	4.383471109
H	-4.137828402	0.796827943	4.357825314
N	-4.100834262	-0.482847679	1.799075581
C	-3.700104595	-0.336251154	0.52227728
O	-4.146379683	0.522508727	-0.223870647
C	-4.365897744	1.917212439	2.126148583
O	-3.219928119	2.138558813	2.427333379
O	-5.135003696	2.902087849	1.651482105
C	-6.389668776	2.607380527	1.018987045
H	-6.244462479	1.849661539	0.246026817
H	-7.131943278	2.291136397	1.75765815
H	-6.705415761	3.548123199	0.568458335
O	-5.734127923	-2.008547267	3.664608296
H	-5.51651032	-2.9384754	3.566019501
H	-4.109708032	-1.564344919	4.891036135
O	-2.760762395	-1.242548656	0.183041389
C	-2.131047699	-1.044594967	-1.097244104
H	-2.838867309	-0.536960739	-1.756178453
H	-1.922544121	-2.04635204	-1.477068087
C	-0.85101229	-0.258736043	-0.958665613
C	0.270067973	-0.643171368	-1.694949509
C	-0.77503127	0.862251928	-0.127827263

C	1.454422667	0.087774451	-1.616344715
H	0.219584072	-1.523459711	-2.333108001
C	0.41158549	1.585631264	-0.041956717
H	-1.634230537	1.184020349	0.455285028
C	1.527157203	1.20439317	-0.787256188
H	2.321324381	-0.221139685	-2.194959079
H	0.460602455	2.454723709	0.60880196
H	2.450512896	1.773820204	-0.718183901

II'''-c

C	-4.681207744	0.606484113	2.613925508
H	-5.599940531	0.974050238	2.157948608
C	-4.150753724	-1.750646151	2.305123658
H	-4.423853999	-2.463758998	1.522678746
H	-3.188833467	-2.049168583	2.73904714
C	-5.218159462	-1.602993956	3.387087824
C	-4.985121455	-0.186450357	3.899327837
H	-5.856158773	0.198210461	4.432895427
H	-4.104645375	-0.166318647	4.547506724
N	-4.080898095	-0.405020796	1.754566561
C	-3.630222397	-0.163677078	0.507858133
O	-3.208415395	-1.009050716	-0.25954103
C	-3.675664222	1.723774425	2.90896995
O	-2.573538015	1.470421769	3.316385644
O	-4.053710009	3.00513423	2.765311181
C	-5.311121505	3.347300702	2.168324325
H	-5.388197006	2.922051343	1.164498182

H	-6.144547539	3.017819516	2.795432847
H	-5.310003067	4.435903191	2.11411887
O	-6.531114168	-1.619093664	2.833873826
H	-6.666833467	-2.446642557	2.366264155
H	-5.117107045	-2.356090726	4.176088553
O	-3.708844081	1.16240046	0.227990371
C	-3.282295562	1.560124884	-1.095189655
H	-2.527658166	0.852538487	-1.440749879
H	-2.842203794	2.549542336	-0.957502659
C	-4.461730727	1.617926934	-2.027850913
C	-4.921013372	0.457060974	-2.656959723
C	-5.123256281	2.826870481	-2.250194034
C	-6.033719955	0.509441246	-3.492716006
H	-4.403380835	-0.481950628	-2.477718695
C	-6.236275144	2.880296973	-3.087608319
H	-4.76047627	3.733617321	-1.769517452
C	-6.692825579	1.719702433	-3.708803639
H	-6.385693337	-0.395097757	-3.982141673
H	-6.742882163	3.826518328	-3.259720035
H	-7.558698275	1.758469769	-4.364910358

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