Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPLEMENTARY INFORMATION

Catalytic properties of 4,5-bridged proline methano- and ethanologues in the Hajos-Parrish intramolecular aldol reaction

Sofiane Hocine,[1,ǂ] Gilles Berger,[2,ǂ] Ken N. Houk,[3] Stephen Hanessian[1,*]

[1] Department of Chemistry, Université de Montréal, Station Centre-Ville, C.P. 6128, Montreal, QC, H3C 3J7, Canada

[2] Microbiology, Bioorganic & Macromolecular Chemistry, Faculty of Pharmacy, Université Libre de Bruxelles, Bd du Triomphe, 1050 Brussels, Belgium.

[3] Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095-1569, U.S.A.

[*] Corresponding author

[ǂ] These authors contributed equally

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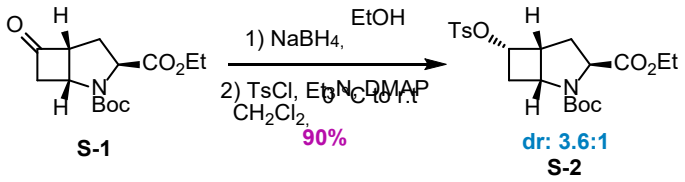
1. GENERAL INFORMATION

Physical Data and Spectroscopic Measurements NMR spectra were recorded on a Bruker 300 spectrometer (75 MHz for ^{13}C), a Bruker AVANCE™ 400 RG spectrometer (400 MHz for ^{1}H) and a Bruker AVANCE™ 500 Ultrashield Plus spectrometer (500 MHz for ^{1}H, 126 MHz for ^{13}C and 471 MHz for ^{19}F) in chloroform-*d* or methanol-*d4*. Data are reported as fellows: chemical shifts (δ) reported in parts per million (ppm), multiplicity, coupling constants (J) reported in Hertz (Hz) and integration. Accurate mass measurements were performed on a LC-TOF instrument from Agilent Technologies in positive electrospray mode. Protonated molecular ions $(M+H)^+$ and/or sodium adducts $(M+Na)^+$ were used for empirical formula confirmation. Infrared spectra (IR) were obtained on a PERKIN-ELMER Spectrum One ATR-FTIR system and are reported in terms of frequency of absorption (cm^{-1}). Melting points were determined on a Büchi B-540 melting point apparatus. Thin Layer Chromatography (TLC) was performed on pre-coated Silicycle silica gel (250 µM, 60 Å) plates with F-254 indicator. Visualizing was performed with a UV light (254 nm) or with stains ($KMnO_4$, *p*-anisaldehyde or ninhydrin). ZEO prep 60 (0.040-0.063 mm) silica gel was used for all column chromatography. Chiral SFC were performed on a 1260 SFC system coupled to a 6120 single quadrupole mass spectrometer detector both from Agilent technologies.

2. EXPERIMENTAL PROCEDURES

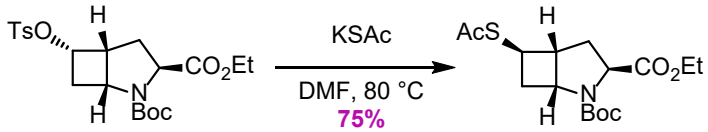
ETHANOPROLINE SYNTHESIS

Figure 1.Synthesis of cis and trans-ethanoprolines



2-(tert-Butyl) 3-ethyl (1R,3S,5R,6S)-6-(tosyloxy)-2-azabicyclo[3.2.0]heptane-2,3-dicarboxylate (S-2). To solution of ketone S-11 (3.3 g, 11.6 mmol) in ethanol (240 ml, 0.05 M) was added sodium borohydride (1.32 g, 34.9 mmol) portionwise at 0 ºC. The solution was then stirred for 30min at 0 ºC, monitoring by TLC. After completion, the methanol was removed under vacuum and the residue was diluted with DCM, then poured into water. The aqueous layer was then extracted 3 times with DCM. The organic layers were then combined, dried over MgSO4, filtered, and concentrated under reduced pressure to give the crude alcohol as a colorless oil, which was dissolved in DCM (23 ml). At 0 ºC was added triethylamine (0.82 ml, 34.9 mmol) and 4-Diméthylaminopyridine (2.4mg, 0.12 mmol). To the resulting mixture was added p-toluene sulfonyl chloride (5g, 26.2 mmol). The solution was then stirred for 24 hours at room temperature. After completion the reaction was mixed with water and extracted 3 times with DCM. The combined organic layers were then washed with water and brine, then dried over Mg2SO4, filtered, and concentrated,1H NMR indicate >3.6:1 dr. The resulting crude mixture was purified by flash chromatography (silica gel; 20% EtOAc/ Hexane) to give a mixture of the major tosylate S-2 and the minor diastereoisomer (4.6g, 90%) as a colorless oil. Data

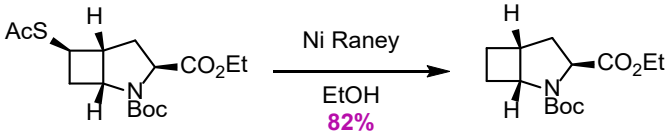
for S-2: [□]D25°C= -117 (c= 0.54, CHCl3); 1H NMR (500 MHz, CDCl3, mixture of rotamers) δ 7.77 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 4.77 – 4.67 (m, 1H), 4.50 (d, J = 8.1 Hz, 0.4H, minor Boc conformer), 4.39 (d, J = 8.6 Hz, 0.6H, major Boc conformer), 4.21 – 4.10 (m, 2H), 4.06 (m, 0.6H, major Boc conformer), 3.93 (m, 1H, mimor Boc conformer), 3.31 – 3.18 (m, 1H), 2.80 – 2.68 (m, 1.6H), 2.66 – 2.56 (m, 0.4H), 2.45 (s, 3H), 2.08 – 1.90 (m, 2H), 1.40 (s, 9H), 1.29 – 1.19 (m, 3H); 13C NMR (126 MHz, CDCl3, mixture of rotamers) δ 172.85, (172.63 minor conformer), 153.66, (153.50 minor conformer), 145.23, (133.57 minor conformer), 133.49, (130.07 minor conformer), 127.98, 80.68, (80.35 minor conformer), 69.59, (69.13 minor conformer), 61.60, (61.27 minor conformer), 61.20, 51.54, (51.05 minor conformer), (44.23 minor conformer), 43.34, 38.05, 37.78, 29.97, (29.06 minor conformer), (28.44 minor conformer), 28.34, 21.79, 14.37, (14.24 minor conformer). IR: □max 2977, 1741, 1697, 1391, 1365, 1175 cm- 1. HRMS (ESI+) : Calc. for C21H29NO7S (M+Na)+ : 462.1557; found 462.1564



dr: 3.6:1

S-2 **S-3**

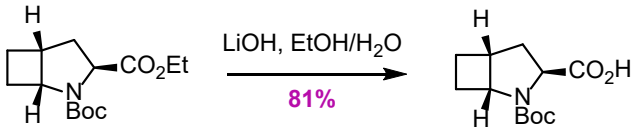
2-(*tert*-Butyl) 3-ethyl (1*R*,3*S*,5*R*,6*R*)-6-(acetylthio)-2-azabicyclo[3.2.0]heptane-2,3-dicarboxylate (S-3). To a solution of tosylate **S-2** (4.5 g, 10.21 mmol) in DMF (22 mL), was added KSAc (2.9 g, 25.7 mmol) and the resulting mixture was then heated at 90°C for 16 h in a sealed tube. The resulting dark brown solution was taken up in 50 mL of EtOAc and washed with 50 mL of water. The aqueous phase was extracted twice with 30mL of EtOAc, and the organic layers were combined, dried over $MgSO_4$, and concentrated to give the crude dithioacetate as a brown oil. The major impurities were removed by flash chromatography (silica gel; 10% EtOAc/ Hexane), The thioacetate was not obtained pure, but the major isomer **S-3** was characterised quickly by NMR and the both isomers were used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 4.64 – 4.58 (m, 0.5H, minor Boc conformer), 4.58 – 4.51 (m, 0.6H), 4.49 – 4.42 (m, 0.6H), 4.39 – 4.33 (m, 0.5H, minor Boc conformer), 4.31 – 4.13 (m, 2H), 3.88 – 3.76 (m, 1H), 3.07 – 2.96 (m, 1H), 2.60 – 2.34 (m, 2H), 2.32 (s, 3H), 2.28 – 2.17 (m, 1H), 2.09 – 1.99 (m, 1H), 1.46 (s, 4H, minor Boc conformer), 1.45 (s, 5H), 1.36 – 1.23 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, mixture of rotamers) δ 195.88, (195.77 minor conformer), 173.06, (172.63 minor conformer), (154.25 minor conformer), 153.55, 80.75, (80.31 minor conformer), (61.23 minor conformer), (61.21 minor conformer), 61.15, 61.04, 56.64, (56.13 minor conformer), (48.10 minor conformer), 47.54, 39.00, (38.86 minor conformer), 35.21, (34.48 minor conformer), (33.51 minor conformer), 32.50, (28.52 minor conformer), 28.36, 14.33, (14.25 minor conformer).



S-3 **S-4**

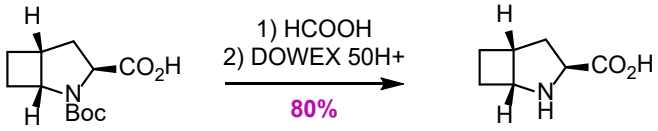
2-(*tert*-Butyl) 3-ethyl (1*R*,3*S*,5*R*)-2-azabicyclo[3.2.0]heptane-2,3-dicarboxylate (S-4). The crude mixture of thioacetate **S-3** was dissolved in no anhydrous EtOH (60 ml), two Raney Nickel teaspoons were added. The suspension was refluxed 30min to 1h until total consummation of the starting material by TLC checking. The mixture was then cooled to rt and filtered through Celite pad to remove the Nickel. The filtrate was rotaevaporated to give a colorless oil which was purified by chromatography (silica gel; 5-10% EtOAc/ Hexane) to afford **S-4** (1.7g, 62%) as colorless oil. $[\alpha]_D^{25°C}$= -148 (c= 0.50, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$,

mixture of rotamers) δ 4.57 – 4.50 (m, 0.5H, Boc conformer), 4.46 (dd, *J* = 7.9, 6.7 Hz, 0.5H, Boc conformer), 4.39 – 4.32 (m, 0.5H, Boc conformer), 4.27 – 4.09 (m, 3H), 3.04 – 2.94 (m, 1H), 2.35 – 1.99 (m, 4H), 1.92 – 1.84 (m, 0.5H, Boc conformer), 1.84 – 1.76 (m, 0.5H, Boc conformer), 1.73 – 1.62 (m, 1H), 1.43 (s, 4.5H, Boc conformer), 1.41 (s, 4.5H, Boc conformer), 1.26 (q, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers) δ (173.44 minor Boc conformer), 173.02, 154.46, (153.58 minor Boc conformer), (80.25 minor Boc conformer), 79.79, (61.48 minor Boc conformer), 61.18, 61.06, (60.99 minor Boc conformer), (58.86 minor Boc conformer), 58.42, (37.92 minor Boc conformer), 37.01, (36.80 minor Boc conformer), 35.92, (28.54 minor Boc conformer), 28.41, 26.92, (26.33 minor Boc conformer), 23.40, (23.08 minor Boc conformer), (14.35 minor Boc conformer), 14.27; IR: υ_{max} 2976, 1742, 1698, 1386, 1366, 1184, 1135 cm^{-1}. HRMS (ESI+): Calc. for $C_{14}H_{23}NO_4$ $(M+Na)^+$: 292.1519; found 292.1519



S-4 **S-5**

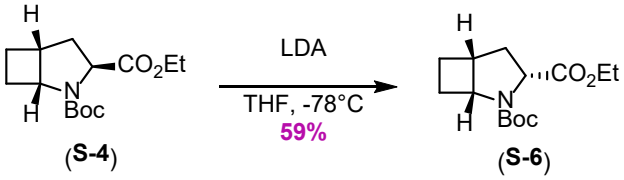
(1R,3S,5R)-2-(tert-butoxycarbonyl)-2-azabicyclo[3.2.0]heptane-3-carboxylic acid (S-5). A solution of ethyl ester **S-4** (400 mg, 1.49 mmol) in EtOH/H_2O (1:1, 10 mL) was treated with solid LiOH (142 mg, 5.94 mmol) and stirred vigorously overnight. The mixture was washed with dichloromethane and the organic layer was discarded. The aqueous layer was acidified to pH 4 using a solution of 10% $KHSO_4$. The aqueous layer was then extracted with dichloromethane twice. The organic layers were combined, dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give 291 mg (81%) of the carboxylic acid **S-5** as a colorless oil. $[\alpha]_D^{25^\circ C}$= -196 (c= 0.55, $CHCl_3$); ^{1}H NMR (500 MHz, MeOD, mixture of rotamers) δ 4.88 (br s, 2H), 4.48 (ddd, *J* = 15.1, 10.5, 6.8 Hz, 1H), 4.32 – 4.25 (m, 0.6H, major Boc conformer), 4.25 – 4.19 (m, 0.4H, minor Boc conformer), 3.04 (s, 1H), 2.33 – 2.21 (m, 2H), 2.18 – 2.03 (m, 2H), 1.87 – 1.78 (m, 1H), 1.78 – 1.67 (m, 1H), 1.43 (s, 4H, minor Boc conformer), 1.43 (s, 5H, major Boc conformer); ^{13}C NMR (126 MHz, MeOD, mixture of rotamers) δ 175.46, (175.04 minor Boc conformer), (154.64 minor Boc conformer), 154.14 , 80.45, (79.75 minor Boc conformer), 61.32, (61.06 minor Boc conformer), 58.73, (58.39 minor Boc conformer), (37.68 minor Boc conformer), 37.05, 35.99, (35.54 minor Boc conformer), (27.33 minor Boc conformer), 27.13, (26.40 minor Boc conformer), 25.61 , 22.60, (22.32 minor Boc conformer); IR: υ_{max} 2975, 1673, 1390, 1366, 1138 cm^{-1}. HRMS (ESI+): Calc. for $C_{12}H_{19}NO_4$ $(M+Na)^+$: 264.1206; found 264.1208.



(**S-5**) (**7**)

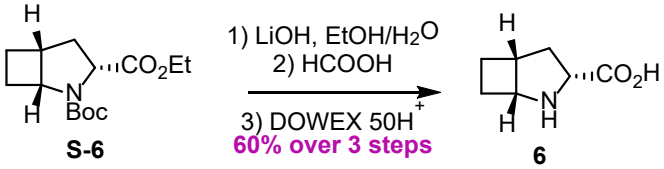
(1R,3S,5R)-2-azabicyclo[3.2.0]heptane-3-carboxylic acid (7). The Carboxylic acid **S-5** (200 mg, 0.83 mmol) was dissolved in formic acid (97%, 1mL) and stirred for 14h. After evaporation of the volatiles and dissolution and evaporation twice from water under reduced pressure, the resultant oil was further purified by elution, using water then NH_4OH sol. (1M) through an ion exchange chromatography column (Dowex 50WX8, mesh 200, freshly regenerated with 1N hydrochloric acid and water). Lyophilization afforded the amino acid **7** (94 mg, 80%) as white amorphous powder. $[\alpha]_D^{25^\circ C}$= -38 (c= 0.51, H_2O); ^{1}H NMR (500 MHz, D_2O) δ 4.58 (dd, *J* = 12.0, 6.6 Hz, 1H), 4.37 – 4.29 (m, 1H), 3.26 – 3.16 (m, 1H), 2.55 – 2.44 (m, 1H), 2.36 – 2.24 (m, 2H), 2.08 – 1.94 (m, 2H), 1.84 – 1.74 (m, 1H); ^{13}C NMR (126 MHz, D_2O) δ 173.98, 61.26, 57.49, 37.17, 34.88, 21.80, 21.58. IR: υ_{max} 2948, 1590, 1394, 1347, 1314, 1286 cm^{-1}. HRMS (ESI+): Calc.

for $C_7H_{11}NO_2$ $(M+H)^+$: 142.0863; found 142.0863. Some crystals of the corresponding HCl salt were then obtained after slow evaporation in EtOH.



(**S-4**) (**S-6**)

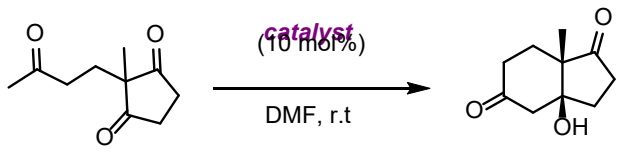
2-(tert-Butyl) 3-ethyl (1R,3R,5R)-2-azabicyclo[3.2.0]heptane-2,3-dicarboxylate (S-6). A solution of ethyl ester **S-4** (495 mg, 1.84 mmol) in THF (15 mL) was treated with LDA solution in hexane (2.76 mL, 2.76 mmol) at -78°C, stirred for 2h, poured into water and extracted with dichloromethane twice. The combined organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure to give the crude mixture, which was purified by chromatography (silica gel; 5-10% EtOAc/ Hexane) to afford the epimer **S-6** (290 mg, 59%) as colorless oil. $[\alpha]_D^{25°C}$= -66 (c=0.57, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, mixture of rotamers) δ 4.58 (dd, *J* = 10.3, 2.3 Hz, 0.4H, minor Boc conformer), 4.48 (dd, *J* = 10.3, 2.7 Hz, 0.6H, major Boc conformer), 4.35 – 4.29 (m, 0.6H, major Boc conformer), 4.28 – 4.13 (m, 2.4H), 3.07 – 2.97 (m, 1H), 2.38 – 1.98 (m, 4H), 1.98 – 1.90 (m, 1H), 1.73 – 1.60 (m, 1H), 1.42 (s, 4H), 1.40 (s, 5H), 1.31 – 1.24 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers) δ 173.79, (173.40, minor Boc conformer), (153.92, minor Boc conformer), 153.32, 79.84, (79.52, minor Boc conformer), 61.45, (61.14, minor Boc conformer), (61.00, minor Boc conformer, 60.98, 58.66, (58.52, minor Boc conformer), (38.42, minor Boc conformer), 37.47, 35.60, (34.56, minor boc conformer), (28.44, minor Boc conformer), 28.32, (26.28, minor Boc conformer), 25.95, 23.44, (23.26, minor Boc conformer), 14.25, (14.13, minor Boc conformer); IR: υ_{max} 2977, 1745, 1698, 1386, 1247, 1159, 1126, 752 cm; ^{1}HRMS (ESI+) : Calc. for $C_{14}H_{23}NO_4$ $(M+Na)^+$: 292.1519; found 292.1526



S-6 **6**

(1R,3R,5R)-2-azabicyclo[3.2.0]heptane-3-carboxylic acid (6): The compound was synthesized following the procedures used for **7**, using 280 mg (1.04 mmol) of ethyl ester **S-6**. The aminoacid **6** (88mg, 60%) was obtained as a white amorphous powder. $[\alpha]_D^{25}$ +58 (c 0.36, H_2O); ^{1}H NMR (500 MHz, D_2O) δ 4.62 (dd, *J* = 9.1, 5.3 Hz, 1H), 4.33 – 4.25 (m, 1H), 3.23 – 3.14 (m, 1H), 2.57 – 2.43 (m, 2H), 2.37 (ddd, *J* = 14.2, 5.3, 3.5 Hz, 1H), 2.26 – 2.13 (m, 2H), 1.68 – 1.58 (m, 1H); ^{13}C NMR (126 MHz, D_2O) δ 172.08, 62.45, 59.53, 37.83, 34.46, 22.18, 21.74; IR: υ_{max} 2956, 1615, 1562, 1377, 1340, 1308, 808 cm^{-1}; HRMS (ESI+) : Calc. for $C_7H_{11}NO_2$ $(M+H)^+$: 142.0863; found 142.0863. Some crystals of **6** and the N-Boc aminoacid intermediate were individually obtained after slow evaporation in EtOH.

TYPICAL PROCEDURE FOR HAJOS PARISH KETONE



1 **2**

Catalyst (11-16 mg, 0.1 mmol, 0.1 equiv.) was mixed respectively with 0.5 mL of DMF and stirred at 15°C for 15 min. A solution of triketone **1** (0.182 mg, 1 mmol, 1 equiv.) in 1 mL of DMF was added and stirred for 140 h at 15°C in a reaction tube, immersed in a water bath and protected from light. DMF was removed under reduced pressure and the residual dark oil was chromatographed using 1 : 1 EtOAc:hexanes. to give the bicyclic compound **2**. The enantiomeric excess was determined using chiral SFC [Chiralcel AD-H 25 cm, 5 µm, 10% i-PrOH, 3 mL/min, 35 °C, 150 bar; t_r (R)= 4.4 min and t_r (S)= 7.6 min] on an average of 2 tests

NMR TRACKING PROCEDURE

In an NMR tube equipped with stir bar, 5-8 mg of catalyst (0.05 mmol, 0.1 equiv.) were mixed respectively with 0.25 mL of DMSO-*d6* and stirred at r.t for 15 min. A solution of triketone **1** (0.91 mg, 0.5 mmol, 1 equiv.) in 0.5 mL of DMSO-*d6* was then added and stirred for 140 h at r.t protected from light. The stir bar is removed before each ^{1}H NMR analysis, then replaced in the tube. The conversion was determined by integrating the singlets corresponding to the methyl group of the starting product **1** at 1 ppm and the one of the formed bicycle compound **2** at 1.1ppm.

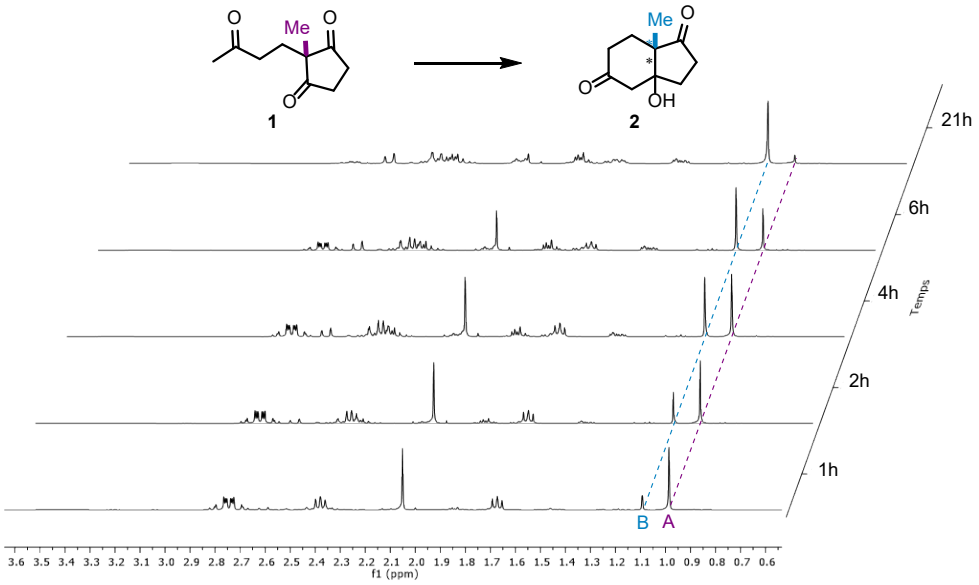


Figure 2.Evolution of the reaction by 1H NMR monitoring

3. **NMR SPECTRA**

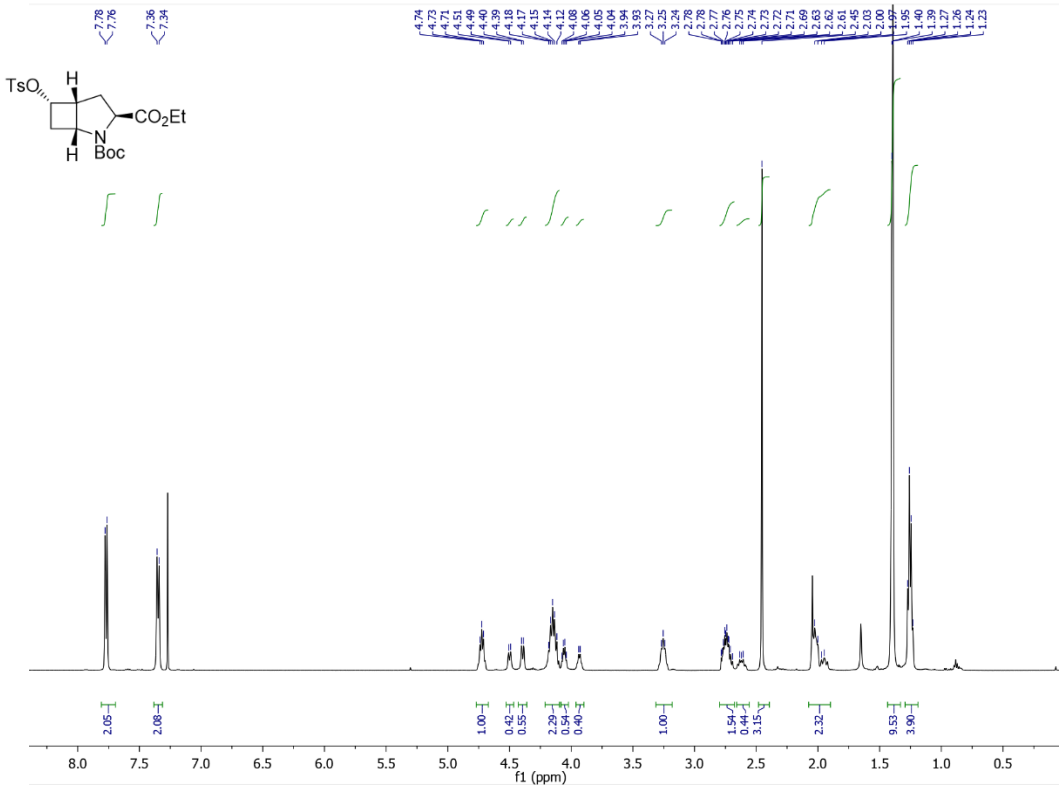


Figure 3.^{1}H Spectrum of **S-2** in $CDCl_3$ (500MHz)

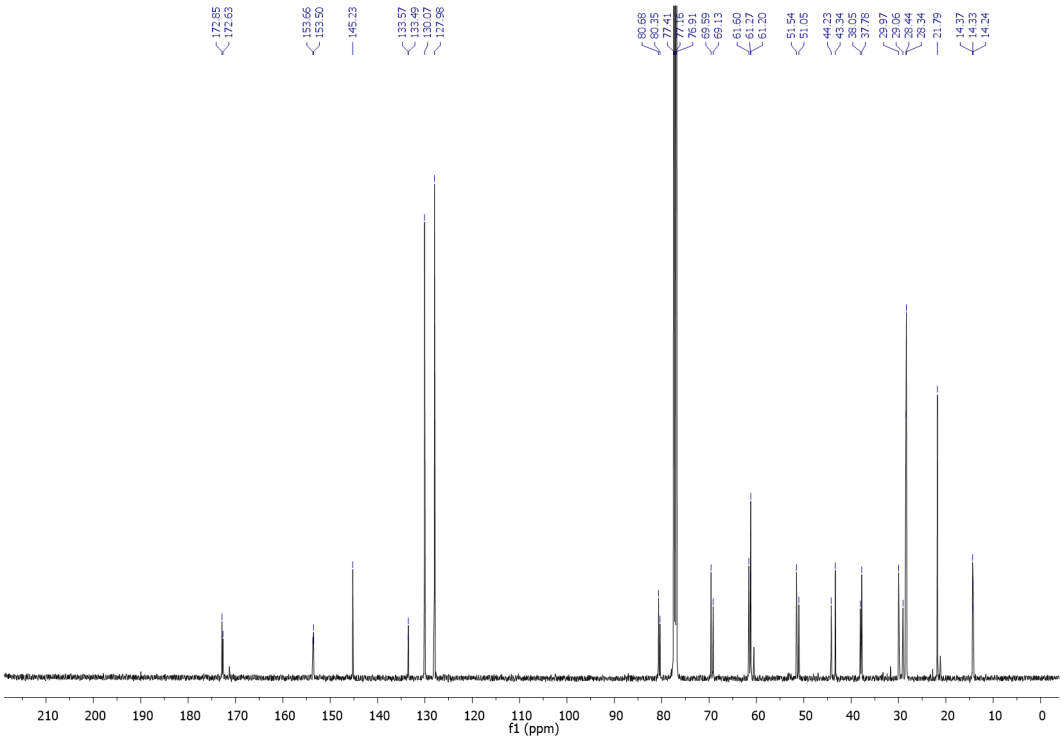


Figure 4.^{13}C Spectrum of **S-2** in $CDCl_3$ (126MHz)

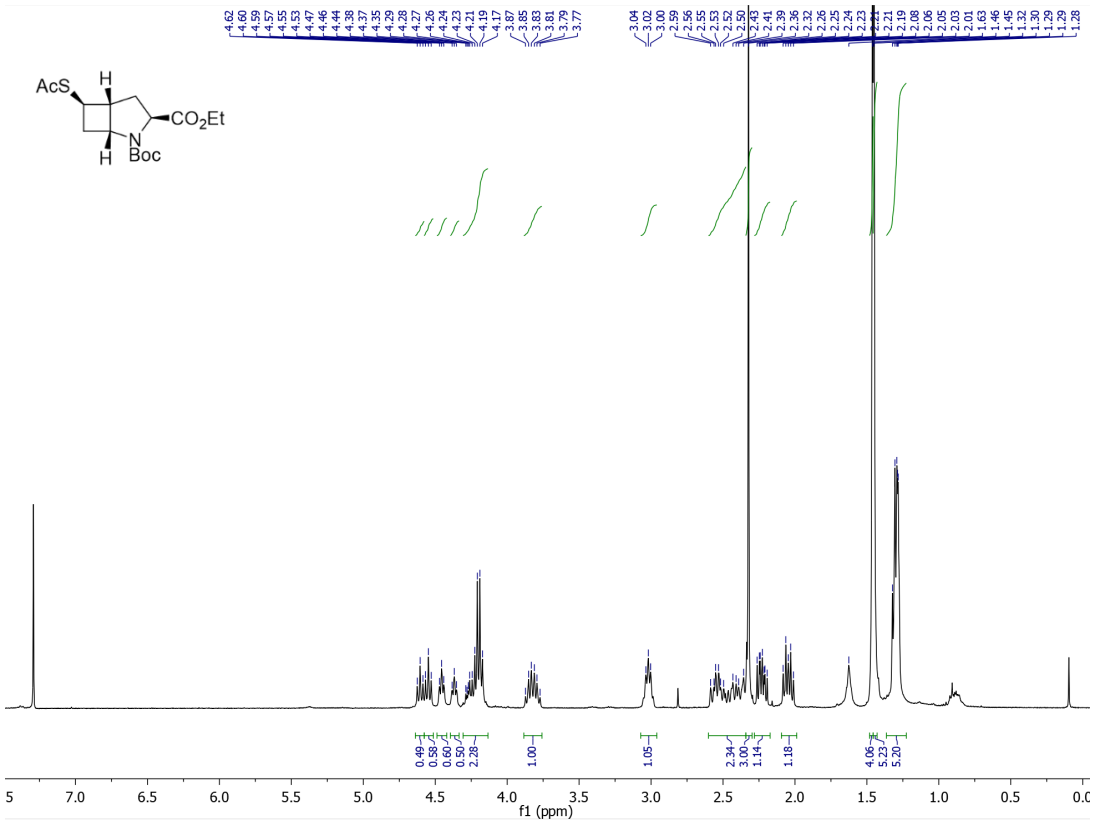


Figure 5.^{1}H Spectrum of **S-3** in $CDCl_3$ (400MHz)

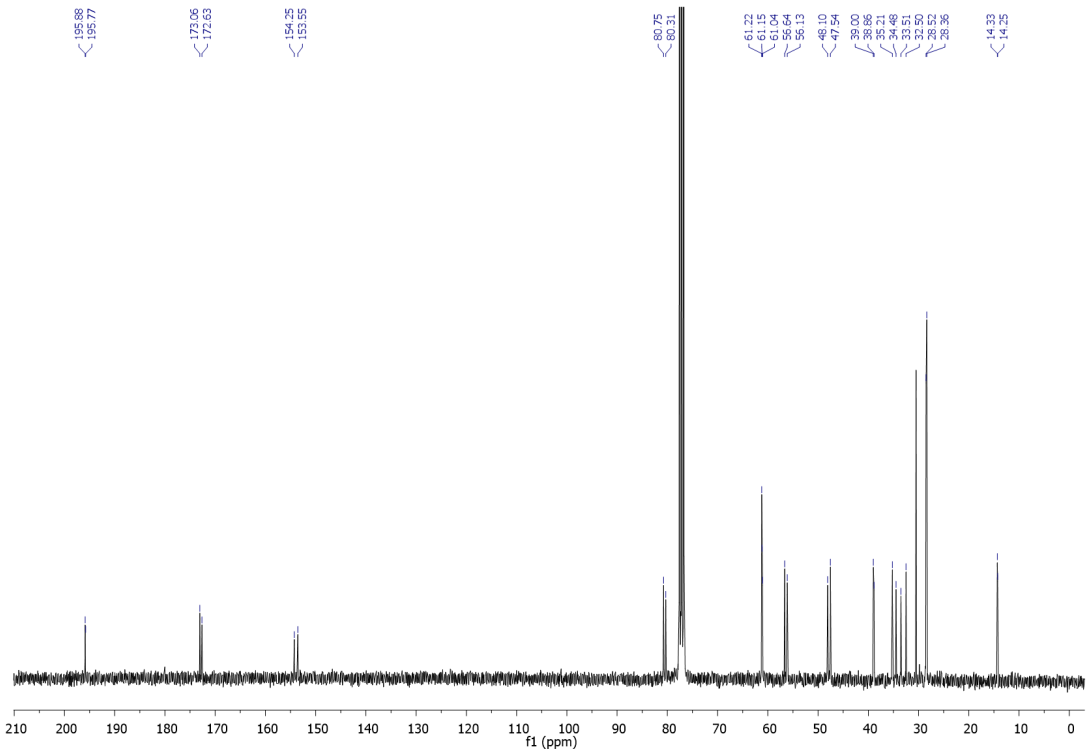


Figure 6.^{13}C Spectrum of **S-3** in $CDCl_3$ (75MHz)

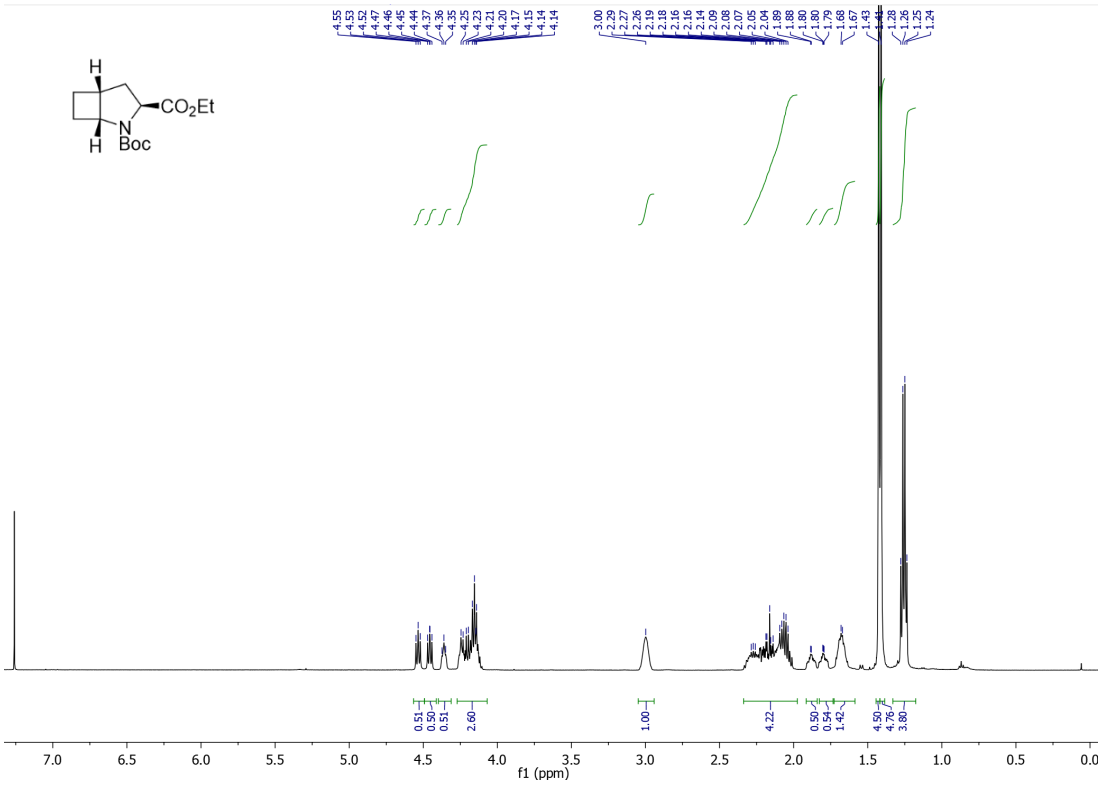


Figure 7.^{1}H Spectrum of **S-4** in $CDCl_3$ (500MHz)

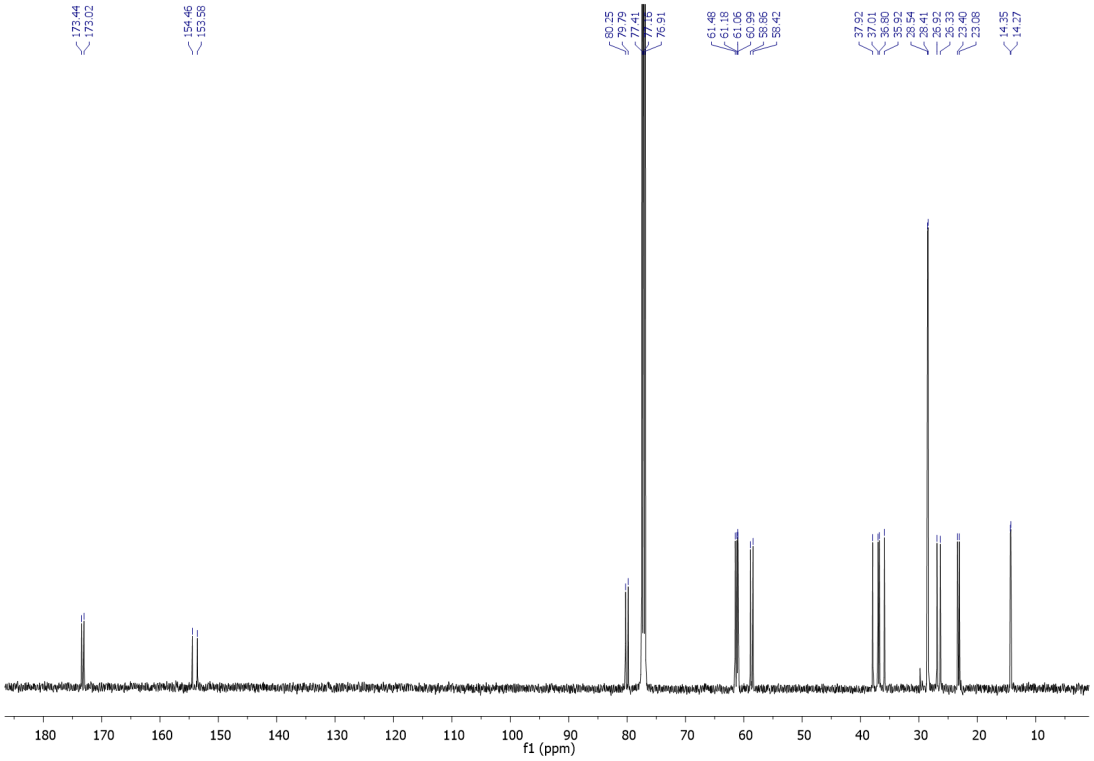


Figure 8.^{13}C Spectrum of **S-4** in $CDCl_3$ (126MHz)

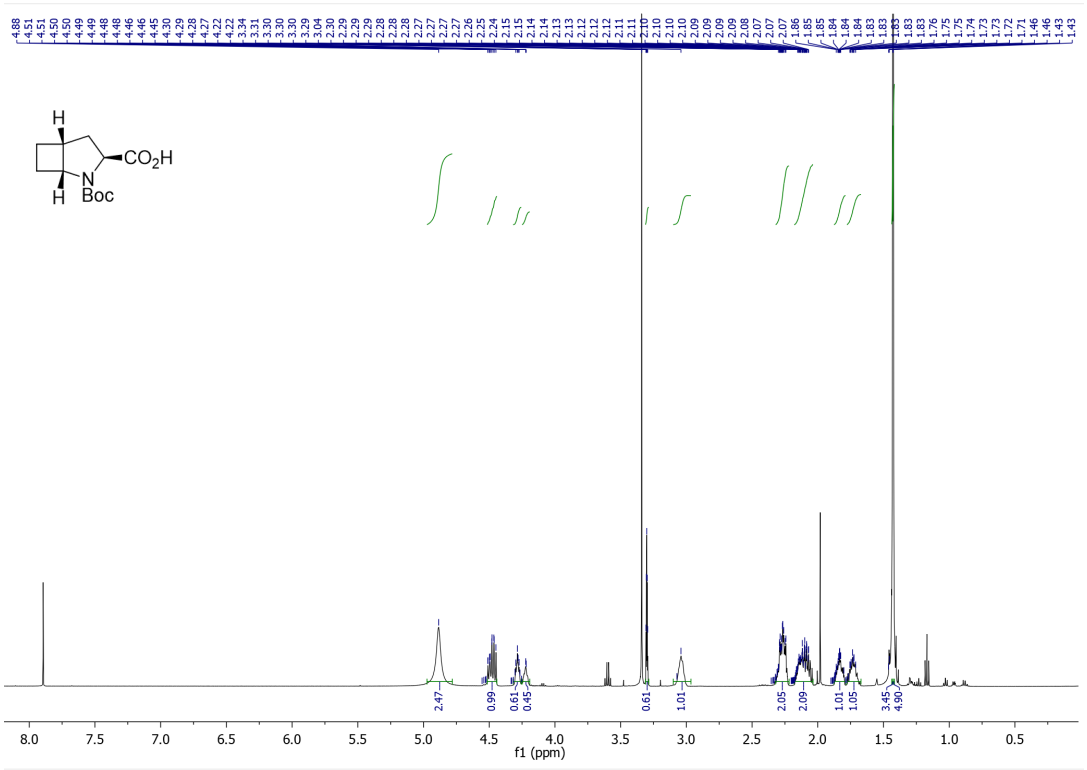


Figure 9.^{1}H Spectrum of **S-5** in MeOD (500MHz)

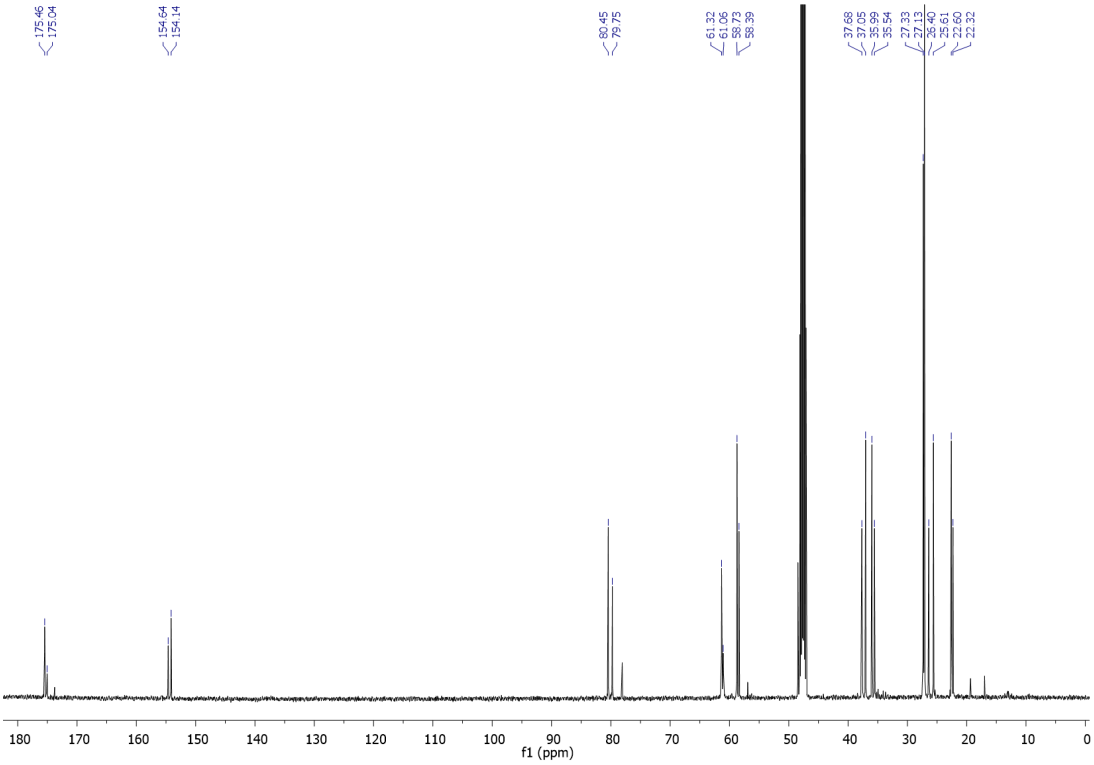


Figure 10. ^{13}C Spectrum of **S-5** in MeOD (126MHz)

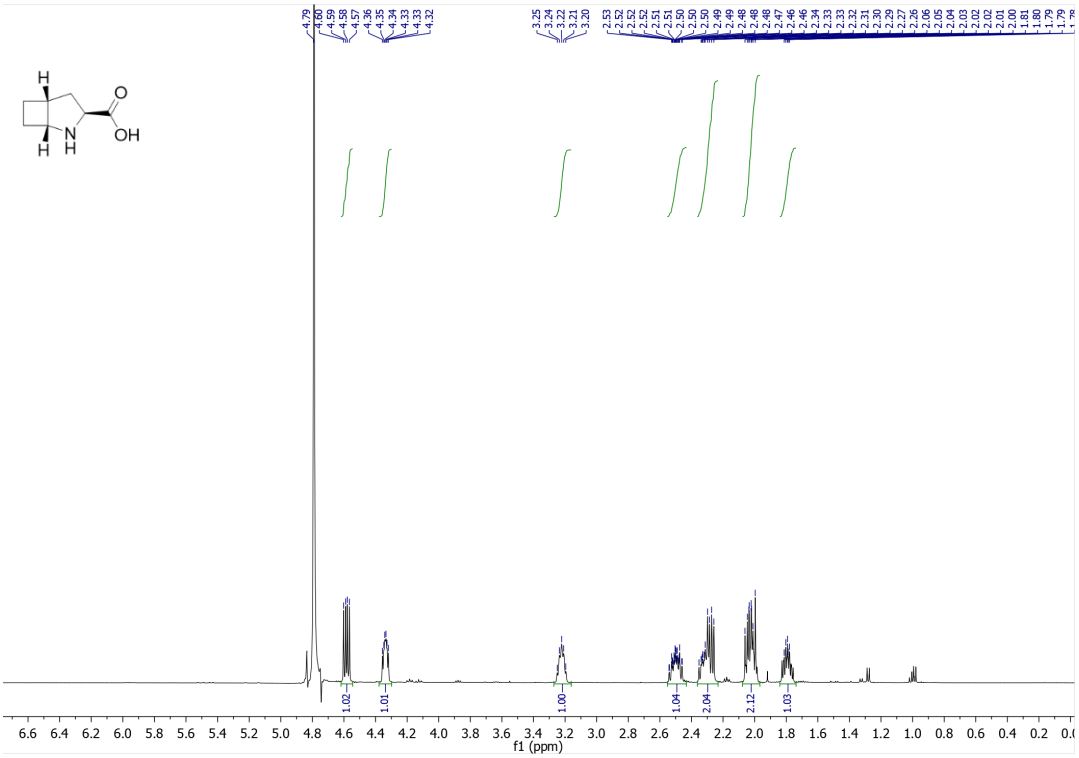


Figure 11. ^{1}H Spectrum of **7** in D_2O (500MHz)

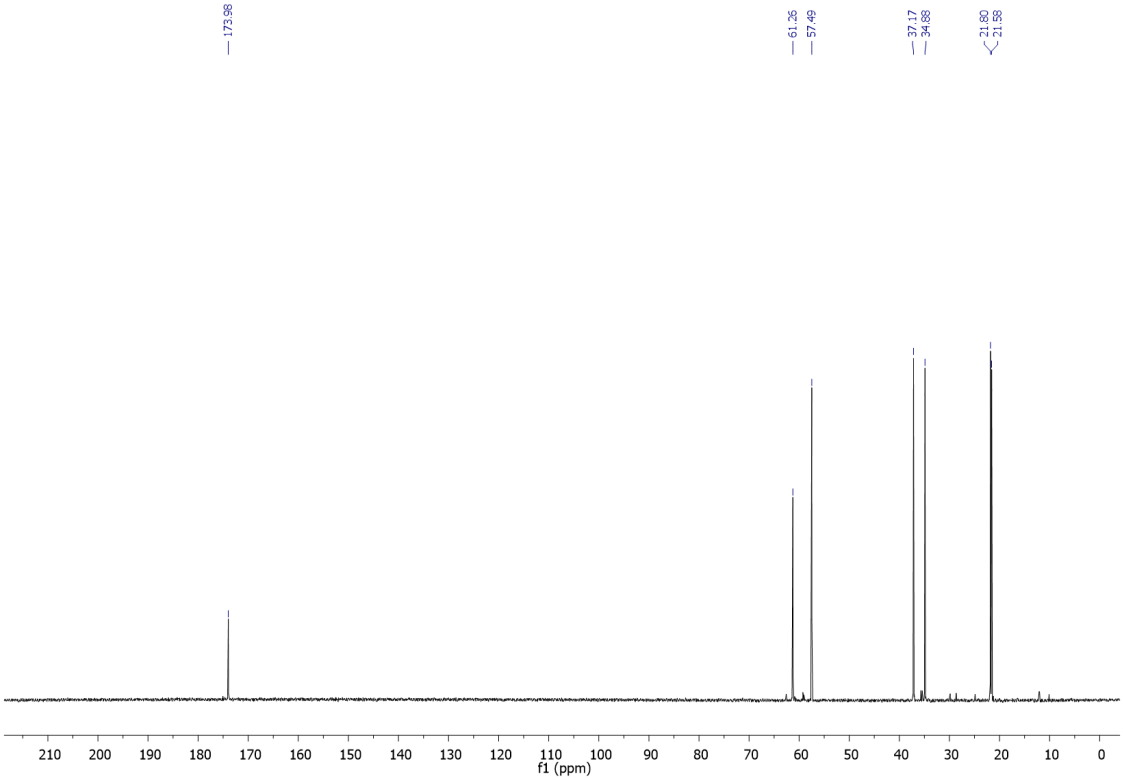


Figure 12. ^{13}C Spectrum of **7** in D_2O (126MHz)

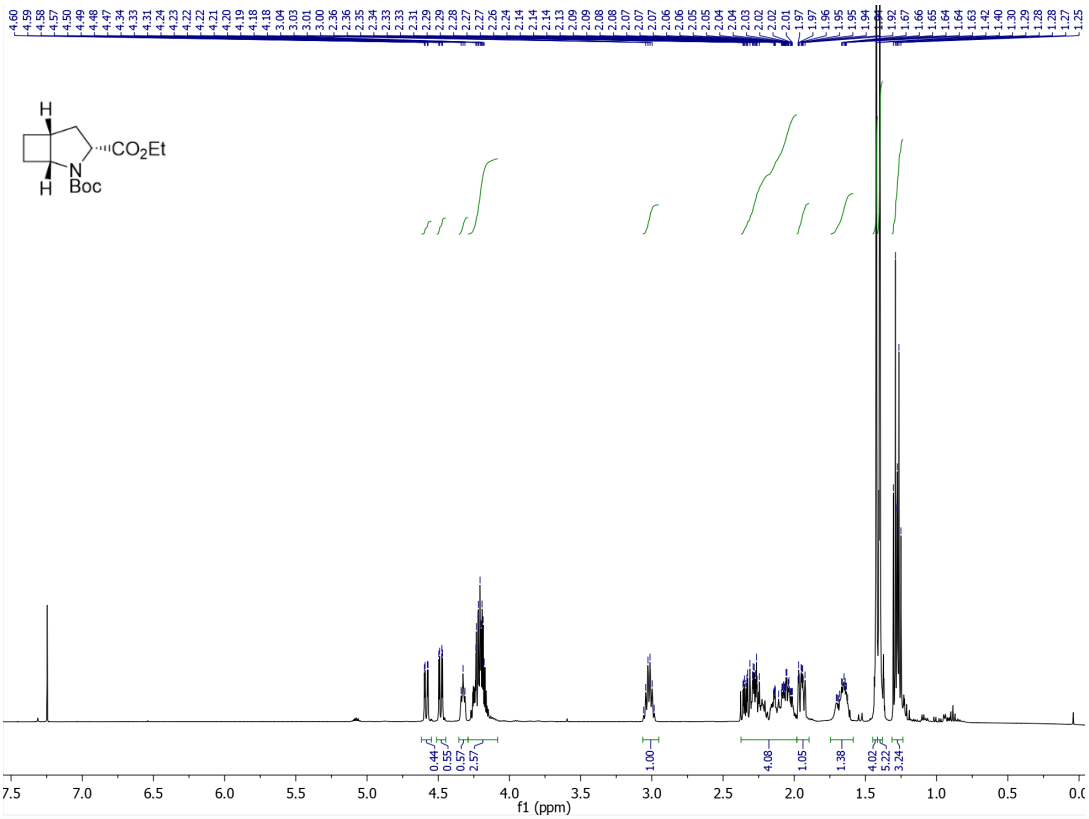


Figure 13. ^{1}H Spectrum of **S-6** in $CDCl_3$ (500MHz)

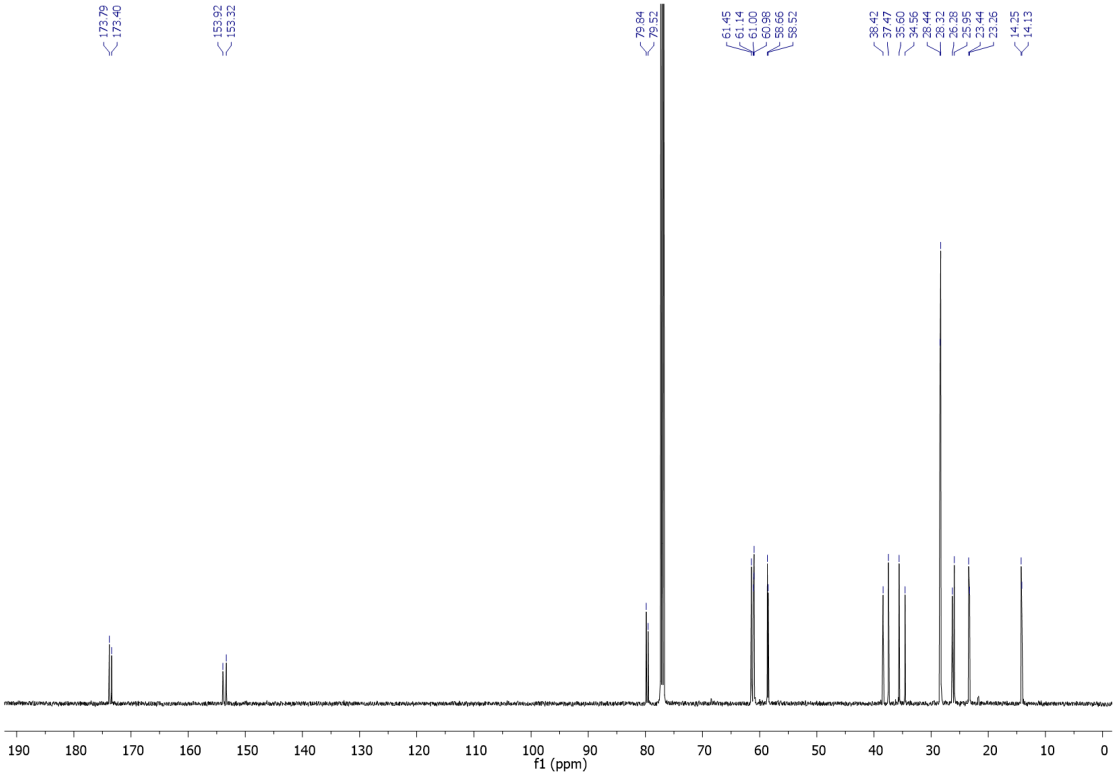


Figure 14. ^{13}C Spectrum of **S-6** in $CDCl_3$ (126MHz)

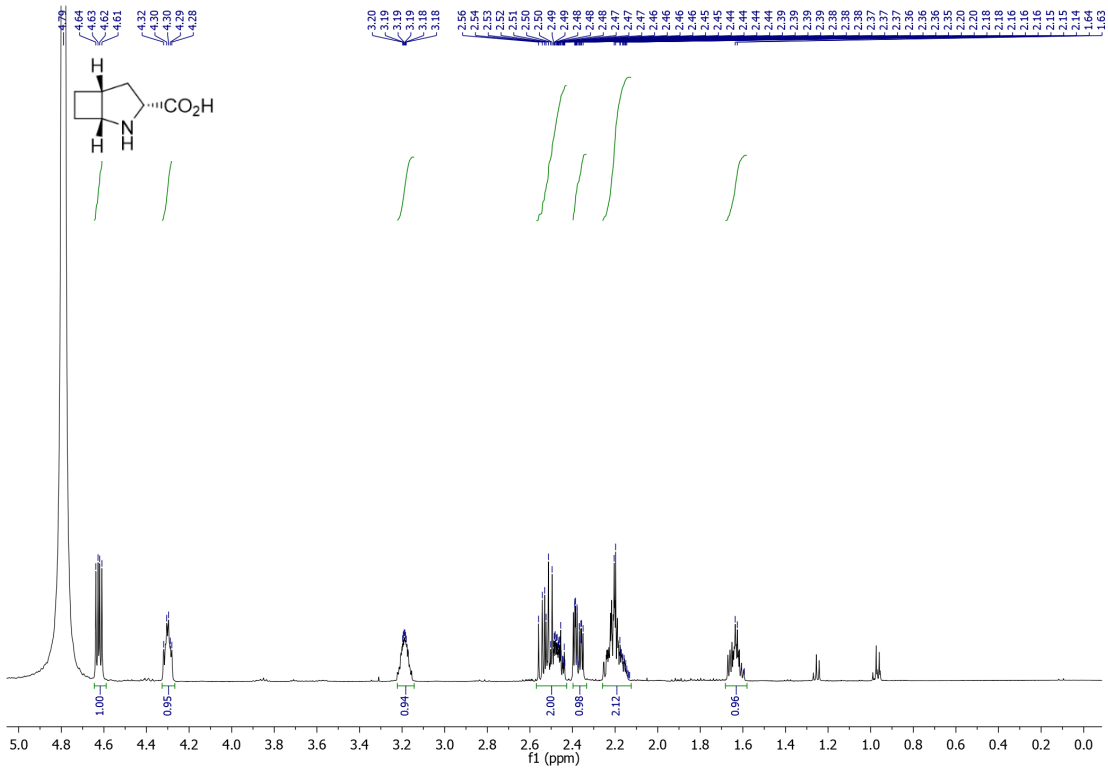


Figure 15. ^{1}H Spectrum of **6** in $CDCl_3$ (500MHz)

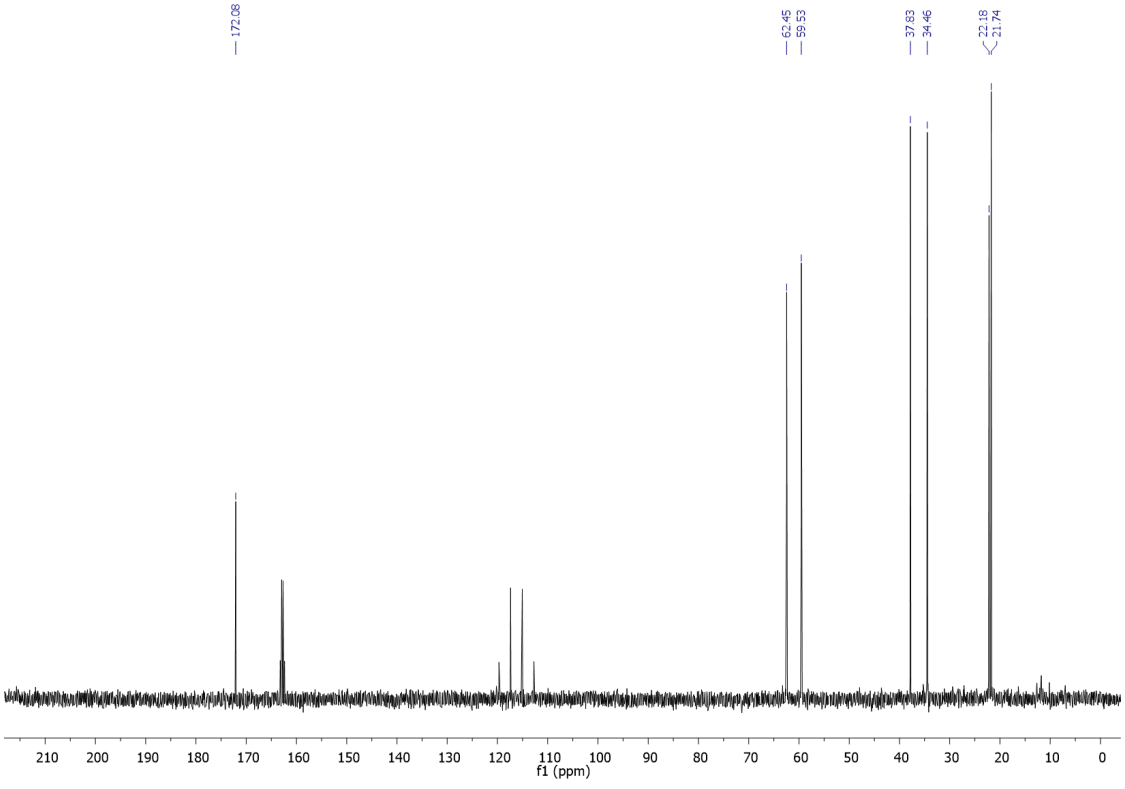
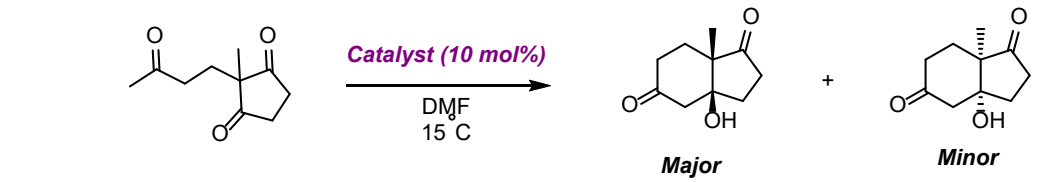


Figure 16. ^{13}C Spectrum of **6** in $CDCl_3$ (126MHz)

4. **SFC spectra for Hydroxy Hajos Parrish ketone:**



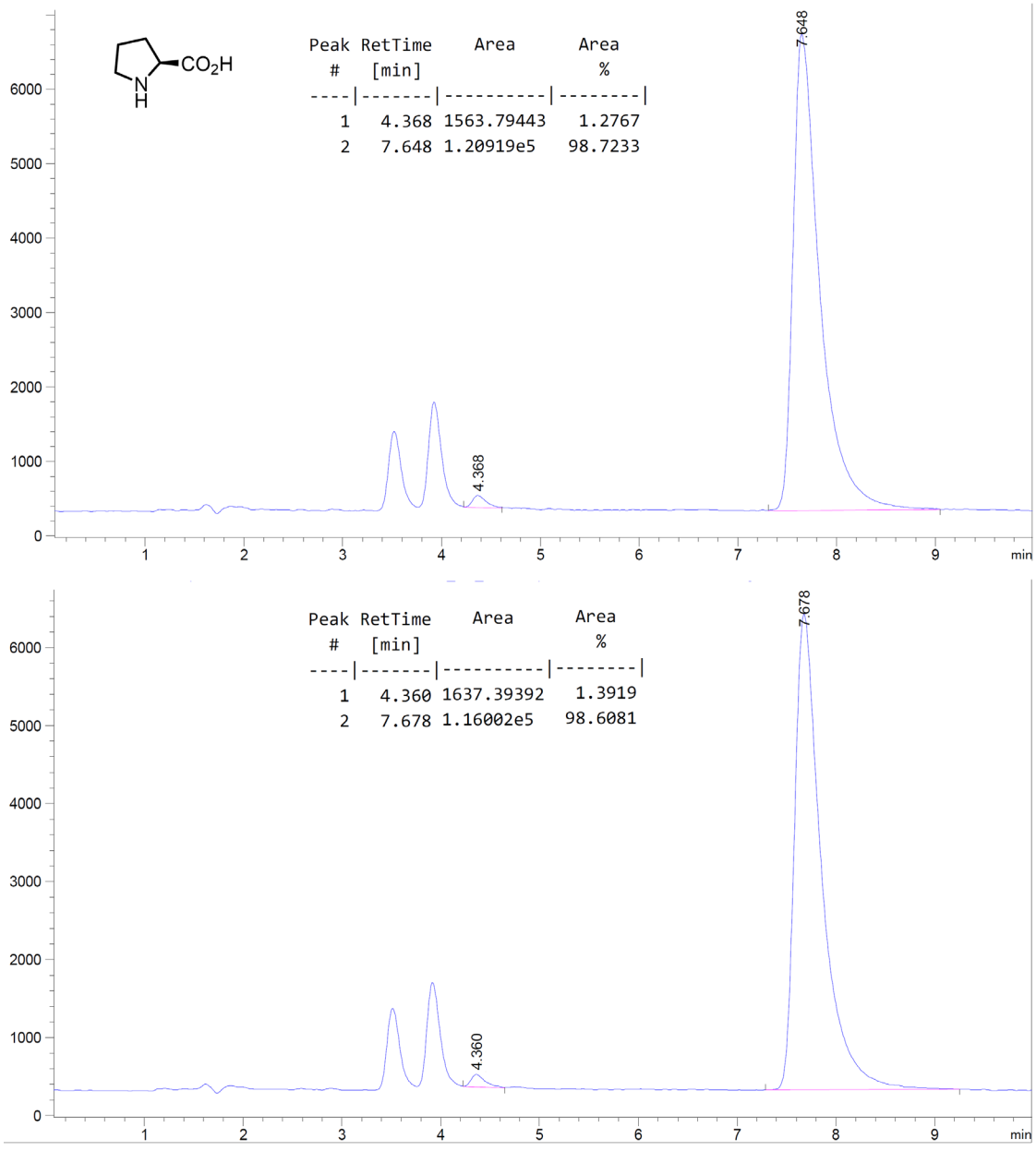


Figure 17. SCF spectra for the hydroxy Hajos Parrish ketone using proline as catalyst

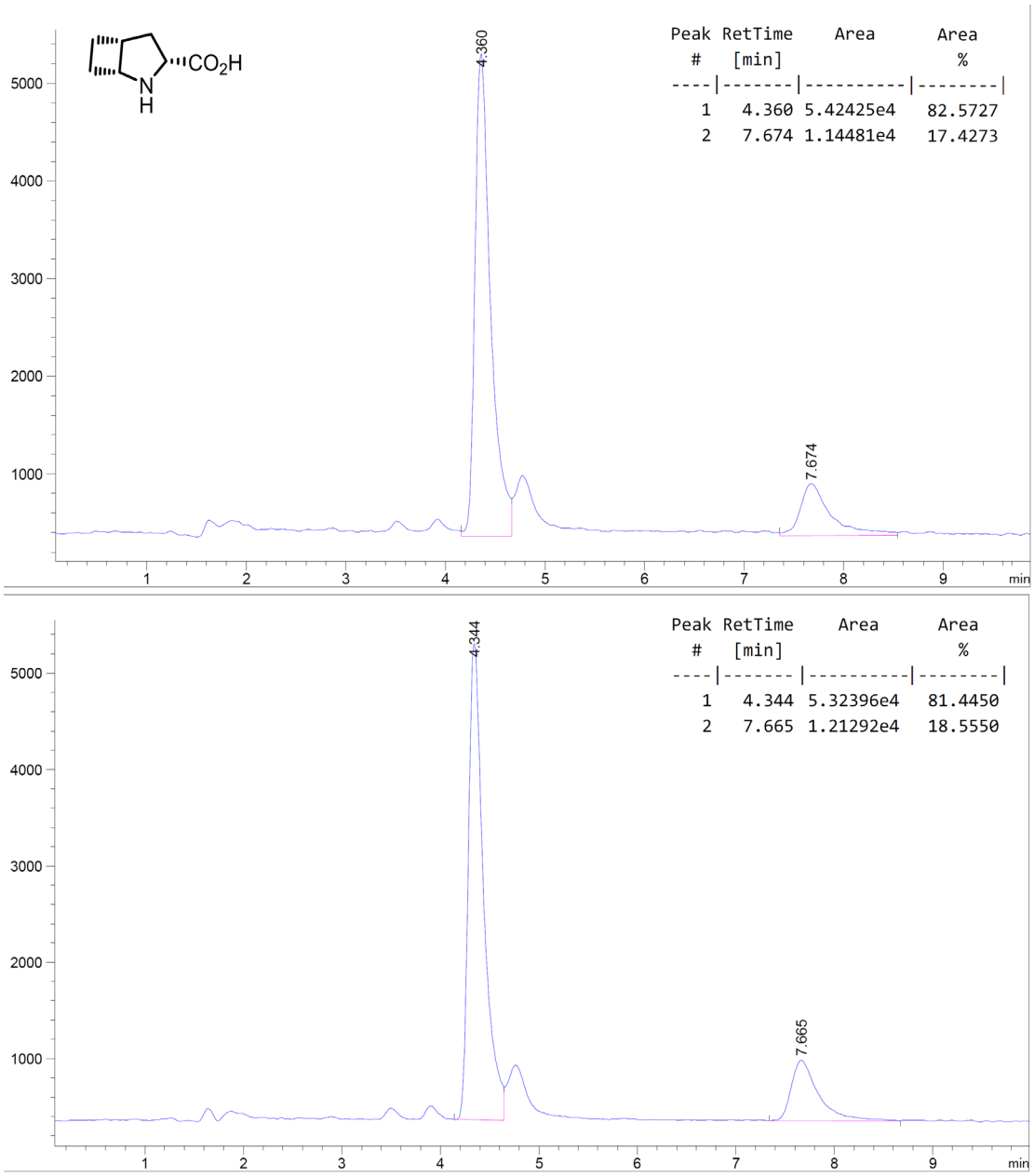


Figure 18. SCF spectra for hydroxy Hajos Parrish ketone using cis-4,5-ethano-R-proline (**6**) as catalyst

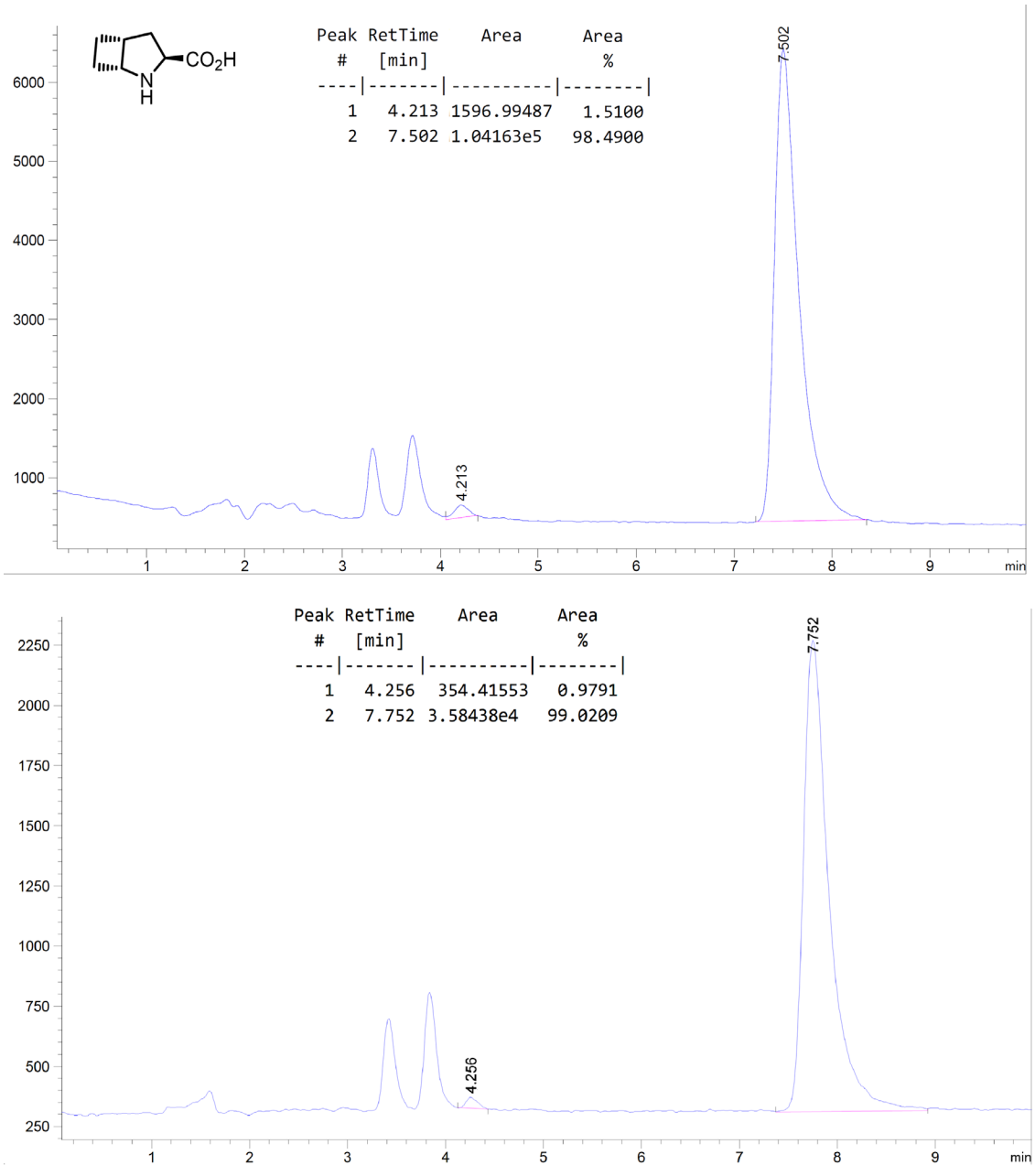


Figure 19. SCF spectra for the hydroxy Hajos Parrish ketone using trans-4,5-ethano-L-proline (**7**) as catalyst.

5. X-RAY CRYSTALLOGRAPHY DATA

X-Ray analysis of (1R,3S,5R)-2-(tert-butoxycarbonyl)-2-azabicyclo[3.2.0]heptane-3-carboxylic acid (N-Boc-6)

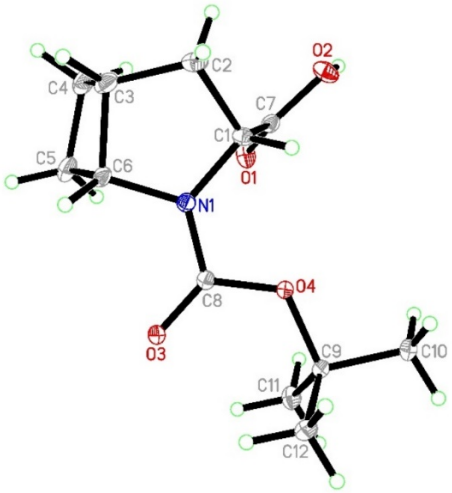
Experimental

A suitable crystal of $C_{12}H_{19}NO_4$ han528, was selected and mounted on a cryoloop on a Bruker Smart APEX diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of N-Boc-6

Crystal Data for $C_{12}H_{19}NO_4$ (M =241.28 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.64820(10) Å, b = 13.0584(2) Å, c = 14.8798(2) Å, V = 1291.79(3) Å^3, Z = 4, T = 100 K, μ(CuKα) = 0.768 mm^{-1}, *Dcalc* = 1.241 g/cm^3, 35128 reflections measured (13.698° ≤ 2Θ ≤ 144.478°), 2502 unique (R_{int} = 0.0233, R_{sigma} = 0.0086) which were used in all calculations. The final R_1 was 0.0265 (I > 2σ(I)) and wR_2 was 0.0689 (all data).



Crystallographic parameters and data are provided in the CIF file which can be retrieved from the Cambridge Crystallographic Data Centre using deposition number **2100195** at the following URL:

http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/Requestastructure.aspx

X-Ray analysis of (1R,3S,5R)-2-azabicyclo[3.2.0]heptane-3-carboxylic acid (6).

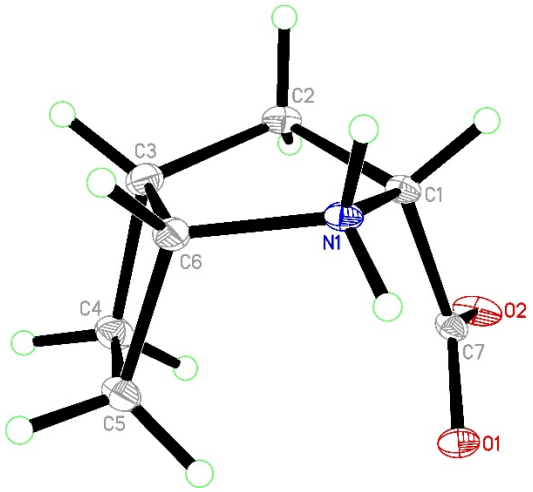
Experimental

A suitable crystal of $C_7H_{11}NO_2$ han526 was selected and mounted on a cryoloop on a Bruker Smart APEX diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 6

Crystal Data for $C_7H_{11}NO_2$ (*M* =141.17 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 5.28430(7) Å, *b* = 9.55030(13) Å, *c* = 6.61740(9) Å, *β* = 99.1230(4)°, *V* = 329.734(8) Å^3, *Z* = 2, *T* = 100 K, μ(CuKα) = 0.860 mm^{-1}, *Dcalc* = 1.422 g/cm^3, 13824 reflections measured (13.552° ≤ 2Θ ≤ 144.672°), 1296 unique (R_{int} = 0.0142, R_{sigma} = 0.0065) which were used in all calculations. The final R_1 was 0.0286 (I > 2σ(I)) and wR_2 was 0.0762 (all data).



Crystallographic parameters and data are provided in the CIF file which can be retrieved from the Cambridge Crystallographic Data Centre using deposition number **2100196** at the following URL:

http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/Requestastructure.aspx

X-Ray analysis of (1R,3R,5R)-2-azabicyclo[3.2.0]heptane-3-carboxylic acid (7)(hydrochlorate salt):

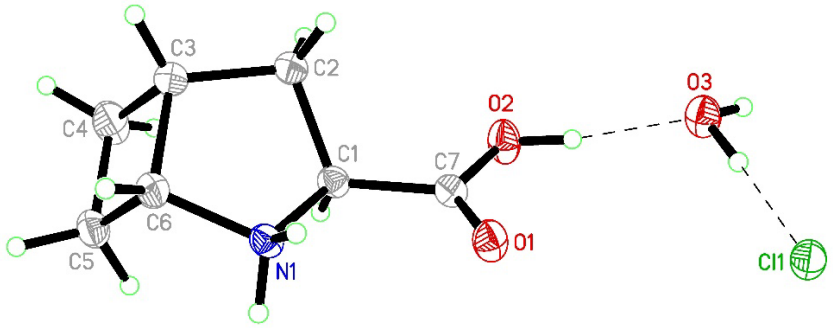
Experimental

A suitable crystal of $C_7H_{14}ClNO_3$ han527, was selected and mounted on a cryoloop on a Bruker Venture Metaljet diffractometer. The crystal was kept at 150 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 7.HCl

Crystal Data for $C_7H_{14}ClNO_3$ (M =195.64 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.2340(6) Å, b = 10.1941(8) Å, c = 13.0701(10) Å, V = 963.84(13) Å^3, Z = 4, T = 150 K, μ(GaKα) = 2.155 mm^{-1}, *Dcalc* = 1.348 g/cm^3, 10311 reflections measured (9.572° ≤ 2Θ ≤ 121.448°), 2213 unique (R_{int} = 0.0574, R_{sigma} = 0.0387) which were used in all calculations. The final R_1 was 0.0301 (I > 2σ(I)) and wR_2 was 0.0789 (all data).



Crystallographic parameters and data are provided in the CIF file which can be retrieved from the Cambridge Crystallographic Data Centre using deposition number **2100197** at the following URL:

http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/Requestastructure.aspx

X-Ray analysis of (1R,3S,5R)-2-azabicyclo[3.1.0]hexane-3-carboxylic acid (5):

Experimental

Some crystals of **5**[2,3] was obtained after slow evaporation in EtOH. A suitable crystal of $C_6H_9NO_2$ han525 (**5**) was selected and mounted on a cryoloop on a Bruker Venture Metaljet diffractometer. The crystal was kept at 150 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

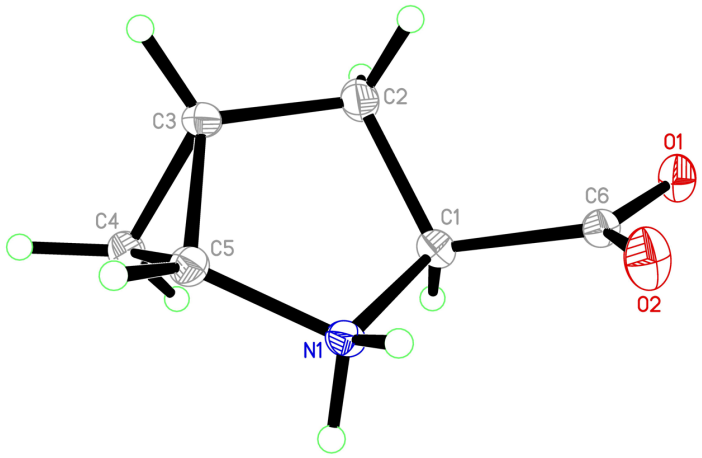
Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of han525

Crystal Data for $C_6H_9NO_2$ (*M* =127.14 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 4.8817(2) Å, *b* = 8.1667(4) Å, *c* = 14.6054(6) Å, *V* = 582.28(4) Å^3, *Z* = 4, *T* = 150 K, μ(GaKα) = 0.584 mm^{-1}, *Dcalc* = 1.450 g/cm^3, 4745 reflections measured (10.54° ≤ 2Θ ≤ 120.9°), 1329 unique (R_{int} = 0.0534, R_{sigma} = 0.0420) which were used in all calculations. The final R_1 was 0.0357 (I > 2σ(I)) and wR_2 was 0.0990 (all data).



Crystallographic parameters and data are provided in the CIF file which can be retrieved from the Cambridge Crystallographic Data Centre using deposition number **2100194** at the following URL:

http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/Requestastructure.aspx

6. COMPUTATIONAL DETAILS

6.1. Computational procedures

All quantum mechanical calculations have been achieved using Gaussian16 rev A.03 or Orca 4.1.2. Geometries of the investigated systems were fully optimized at the spin-restricted density functional theory level using the dispersion-corrected ωB97x-D exchange-correlation functional,[4] and the MN15 global hybrid functional from Truhlar and co-workers.[5] The balanced polarized triple-zeta basis set def2-TZVP from Ahlrichs and co-workers[6,7] has been used for all atoms. Alternatively, geometries were optimized at the spin-restricted Hartree-Fock level of theory followed by a Møller-Plesset perturbative correction, truncated at the second order,[8] using the frozen core approximation and the resolution of identity (RI-MP2) to speed up the calculations,[9,10] and an appropriate auxiliary basis sets.[11] DLPNO-CCSD(T) calculations have been performed as implemented in Orca 4.1.2, as single points from the DFT geometries, using the cc-pVTZ basis set (and its corresponding auxiliary basis) and the tight PNO settings.

Potential energy surface minima found upon optimization were confirmed by frequency calculations and free energies were corrected to account for the zero-point energy. Optimized geometries were verified as minima (i.e. zero imaginary frequencies). The Synchronous Transit-Guided Quasi-Newton (STQN) method[12,13] was used for locating transition structures. These structures were further verified as first-order saddle points by frequency calculations (i.e. one imaginary frequency). The bulk solvent effects have been included through the Integral Equation Formalism version of the Polarizable Continuum Model (IEF-PCM).[14] Natural Bond Orbital (NBO) analysis was performed using the latest version of the program from Weinhold and co-workers (NBOPro 7.0).[15] When necessary, conformers search was achieved using Avogadro 1.2.0, by systematic rotor search.

6.2. Cartesian coordinates of transition states for the Hajos-Parish reaction at the ωB97x-D level (in the gas phase)

L-Proline *syn*-(*R*,*R*) TS

C	2.7759850	0.0623660	-0.6390040
C	4.4905250	-0.0938890	1.1725900
H	4.7404840	2.0114560	0.6406280
H	5.5606340	-0.2057720	0.9995520
H	4.2720820	-0.5569170	2.1367810
C	-1.3423180	-2.0726970	1.4342650
C	1.3833100	-0.5140350	-0.8700920
C	0.6745680	-0.9219770	0.4154320
H	0.8057800	0.2313500	-1.4140860
H	1.4704730	-1.3801370	-1.5263440
H	0.7601470	-0.1501040	1.1836020
H	1.1706900	-1.8037020	0.8319920
C	3.4521980	0.4026740	-1.9856320
H	4.4496010	0.8244200	-1.8499620
H	3.5399430	-0.5059140	-2.5813600
H	2.8403480	1.1264950	-2.5244260
C	4.0001760	1.3522620	1.1005450
C	2.7836020	1.3341750	0.1973220
O	1.9486950	2.2012400	0.1384150
C	-0.7892890	-1.3226880	0.2355430

C	3.7221600	-0.8632890	0.1140120
O	3.8444290	-2.0410320	-0.1057290
H	3.7388430	1.7839870	2.0650100
H	-2.4094480	-2.2625580	1.3330380
H	-0.8358860	-3.0390630	1.4683360
N	-1.6764190	0.3452460	0.5046950
C	-1.4682600	1.3028050	-0.6097100
C	-3.1311960	0.3733610	0.7982920
C	-2.6562510	2.2828400	-0.5691830
H	-0.5033250	1.7870750	-0.4813690
C	-3.4562880	1.8636260	0.6689780
C	-4.0515660	-0.4530030	-0.1213700
H	-3.3008370	-0.0022400	1.8063800
H	-2.3251220	3.3173220	-0.5098980
H	-3.0943570	2.3806400	1.5587140
H	-4.5244240	2.0400460	0.5799140
O	-3.5646280	-1.2936240	-0.9884550
O	-5.2470640	-0.2924490	0.0041730
H	-2.5246700	-1.4835980	-0.9696770
H	-3.2622390	2.1799230	-1.4693260
H	-1.4473980	0.7260150	-1.5339390
O	-1.1490810	-1.6978330	-0.9278600
H	-1.2217550	0.7140980	1.3333240
H	-1.1475780	-1.5551290	2.3739560

L-Proline *anti*-(*S*,*S*) TS

C	-1.8576660	0.7161310	-0.1360840
C	-3.6160710	-1.0328200	-0.2826560
H	-2.7125990	-1.0681830	-2.2686560
H	-4.5503890	-0.7825770	-0.7876860
H	-3.8505980	-1.8238240	0.4304590
C	-0.7388370	-1.6100250	0.7421930
C	-0.9483140	1.4458190	0.8428020
C	-0.2516630	0.5134770	1.8544130
H	-0.2008780	2.0025790	0.2781060
H	-1.5422860	2.1734230	1.3981120
H	-0.9785230	0.1874240	2.5979130
H	0.5340910	1.0566040	2.3749230
C	-2.2674450	1.6938010	-1.2547650
H	-2.9987460	1.2580010	-1.9370580
H	-2.7034710	2.5940580	-0.8197690
H	-1.3850440	1.9656270	-1.8338270
C	-2.4850240	-1.3862660	-1.2495200
C	-1.2671500	-0.5567060	-0.8044670
O	-0.2630980	-0.4725500	-1.5806800
C	0.2474490	-0.6982590	1.1348250

C	-3.1369490	0.1883910	0.4935470
O	-3.6816440	0.6468360	1.4621030
H	-2.2573080	-2.4491530	-1.2915030
H	-0.4506030	-2.5396360	0.2731940
H	-1.5963720	-1.6887970	1.3983380
N	1.4642820	-0.7541340	0.6310060
C	1.9849570	-1.9405930	-0.0798240
C	2.4741600	0.2976630	0.7088860
C	3.4034390	-1.5465980	-0.4797900
H	1.9729020	-2.7877450	0.6113220
C	3.7825320	-0.4760780	0.5391340
C	2.3686330	1.4010640	-0.3704320
H	2.4345130	0.8075940	1.6678760
H	4.0779050	-2.4005500	-0.4743140
H	4.0595150	-0.9313570	1.4922280
H	4.5909780	0.1759380	0.2190420
O	1.5331690	1.2628720	-1.3639850
O	3.1064310	2.3460260	-0.2566570
H	0.8347840	0.4979750	-1.3579780
H	3.4023140	-1.1231920	-1.4851310
H	1.3586680	-2.1647510	-0.9384430

Cis-methano proline _syn_-(_R_,_R_) TS 4b

C	2.3234330	-0.4269590	0.5439860
C	3.4307470	1.3943900	-0.7140580
H	1.6930460	2.7421170	-0.4920670
H	3.4122860	1.6076120	-1.7832160
H	4.3947970	1.7476740	-0.3443600
C	0.5299280	0.4971550	-1.3230970
C	1.6395300	-1.7777690	0.4241480
C	0.7610650	-1.8875280	-0.8304750
H	2.3898880	-2.5695210	0.4026520
H	1.0222530	-1.9208450	1.3145060
H	1.4052890	-1.9033770	-1.7100270
H	0.1985890	-2.8187020	-0.8255100
C	3.0323720	-0.3409060	1.9092150
H	3.6145020	0.5753760	2.0169250
H	2.2821570	-0.3580840	2.6994810
H	3.7095840	-1.1876050	2.0299670
C	2.2424470	1.9798020	0.0560550
C	1.3581540	0.7748580	0.4287550
O	0.4305180	0.8678120	1.2901370
C	-0.1174900	-0.6809600	-0.9376290
C	3.3585870	-0.1187160	-0.5207250
O	4.0081860	-0.9259890	-1.1307110
H	2.5566110	2.4310200	0.9992890

H	-0.0412100	1.4115330	-1.4187250
H	1.3315770	0.3907840	-2.0427310
N	-1.3417230	-0.6632120	-0.4439240
C	-1.9455320	-1.7346770	0.3126000
C	-2.3750740	0.3171770	-0.8317220
C	-3.4254690	-1.6483450	0.1230370
H	-1.3961900	-2.6591760	0.3608950
C	-3.6725180	-0.5186670	-0.8489640
C	-2.5756110	1.6252090	-0.0188650
H	-2.1340080	0.6671790	-1.8351390
H	-4.0187150	-2.5469620	0.0327080
H	-3.8310620	-0.9348000	-1.8449640
H	-4.5231960	0.1104880	-0.6014800
O	-1.6864510	2.0380120	0.8309550
O	-3.5790270	2.2458590	-0.2692970
H	-0.8142800	1.4951330	0.9792440
C	-2.8191030	-1.3090600	1.4550740
H	-2.7768280	-0.2807260	1.7881300
H	-2.9416320	-2.0322050	2.2492240

Cis-methano proline _anti_-(_S_,_S_) TS 4a

C	-2.0220980	0.6753020	-0.1605880
C	-3.6730630	-1.1821540	-0.2314890
H	-2.7700800	-1.2526030	-2.2165580
H	-4.6207920	-1.0112640	-0.7445570
H	-3.8588800	-1.9544610	0.5156100
C	-0.7585170	-1.5579480	0.8271770
C	-1.1616390	1.4928870	0.7923920
C	-0.4307710	0.6389700	1.8452090
H	-0.4397590	2.0657110	0.2107520
H	-1.8003130	2.2090620	1.3118300
H	-1.1534280	0.2944860	2.5847890
H	0.3082880	1.2447620	2.3655410
C	-2.4870910	1.5850440	-1.3151810
H	-3.1832900	1.0784790	-1.9852720
H	-2.9843490	2.4688200	-0.9133700
H	-1.6205730	1.8952630	-1.8989950
C	-2.5223490	-1.5073260	-1.1841790
C	-1.3610650	-0.5827650	-0.7839740
O	-0.3579390	-0.4864720	-1.5510110
C	0.1579990	-0.5690640	1.1883100
C	-3.2699250	0.0980040	0.4900650
O	-3.8449120	0.5661050	1.4360910
H	-2.2259840	-2.5537980	-1.1784960
H	-0.4155570	-2.4650850	0.3519040
H	-1.6144680	-1.6779050	1.4788770

N	1.3982390	-0.5682480	0.7267230
C	2.0686950	-1.7543240	0.2381070
C	2.3125750	0.5753530	0.7143580
C	3.5340670	-1.4590420	0.1944560
C	3.7233270	-0.0524060	0.7126460
C	2.1547580	1.5778400	-0.4553950
H	2.1709790	1.1766010	1.6088820
H	4.1066250	-0.0963350	1.7325510
H	4.4082360	0.5540900	0.1239180
O	1.2965040	1.3568470	-1.4103670
O	2.8677740	2.5482520	-0.4218930
H	0.6417490	0.5446940	-1.3667990
C	2.7670190	-1.6621070	-1.0814580
H	1.6649500	-2.6878330	0.5959350
H	4.2452610	-2.2138160	0.4984570
H	2.5505900	-0.8202500	-1.7238310
H	2.9201780	-2.5963400	-1.6035260

***Trans*-methano proline *syn*-(*R*,*R*) TS 5b**

C	2.3311060	-0.3717810	0.5838750
C	3.4798950	1.1757240	-0.9665030
H	1.8362480	2.6506190	-0.8756970
H	3.4265880	1.2387920	-2.0537300
H	4.4791040	1.5127290	-0.6854500
C	0.5180350	0.3825630	-1.3160250
C	1.5652150	-1.6770750	0.7000160
C	0.5984840	-1.9210810	-0.4702700
H	2.2650730	-2.5120270	0.7578160
H	1.0011870	-1.6490700	1.6351580
H	1.1789150	-2.1549710	-1.3635970
H	-0.0478520	-2.7680480	-0.2503970
C	3.1126650	-0.1313270	1.8898260
H	3.7561330	0.7476640	1.8323000
H	2.4038870	0.0231470	2.7031450
H	3.7404550	-0.9954740	2.1116980
C	2.3649620	1.9398810	-0.2440780
C	1.4289280	0.8587830	0.3310830
O	0.5507490	1.1335140	1.2060080
C	-0.1881650	-0.6809540	-0.7473780
C	3.3260090	-0.2877550	-0.5566880
O	3.8920370	-1.2143560	-1.0733080
H	2.7480440	2.4986260	0.6119680
H	-0.0037880	1.3047930	-1.5378400
H	1.2852950	0.1165460	-2.0318900
N	-1.3937080	-0.5212080	-0.2305600
C	-2.0007190	-1.4576980	0.6850480

C	-2.3982470	0.4479450	-0.7025810
C	-3.4749660	-1.3865980	0.4592640
C	-3.7065850	-0.3605600	-0.6402850
C	-2.5585920	1.8010340	0.0458150
H	-2.1494020	0.7254180	-1.7275950
H	-3.9027150	-0.8457550	-1.5972350
H	-4.5355080	0.3055750	-0.4217410
O	-1.5889020	2.2866370	0.7570650
O	-3.5953930	2.3908660	-0.1339190
H	-0.7188750	1.7473230	0.8890880
H	-4.1502850	-1.4137710	1.3014810
H	-1.5498990	-1.5105250	1.6657780
C	-2.7252920	-2.6315950	0.0898420
H	-2.8394970	-3.5033530	0.7199280
H	-2.5714710	-2.8401210	-0.9617960

Trans-methano proline _anti_-(_S_,_S_) TS 5a

C	-2.0542100	0.6813070	-0.0157510
C	-3.6562510	-1.1807120	-0.3854750
H	-2.8285350	-0.8374870	-2.3752020
H	-4.6271570	-0.9451970	-0.8243130
H	-3.7940230	-2.0874000	0.2046150
C	-0.6933300	-1.6406120	0.4614820
C	-1.1753480	1.3342030	1.0419790
C	-0.3871440	0.3200600	1.8941690
H	-0.4840690	2.0187940	0.5495530
H	-1.8047370	1.9289920	1.7057570
H	-1.0725520	-0.1848880	2.5741100
H	0.3551530	0.8386810	2.4970800
C	-2.5881620	1.7737630	-0.9622800
H	-3.3013140	1.3790910	-1.6874240
H	-3.0869380	2.5539900	-0.3858030
H	-1.7544680	2.2101240	-1.5122430
C	-2.5356110	-1.2805280	-1.4215120
C	-1.3793820	-0.4167370	-0.8852240
O	-0.4171380	-0.1234630	-1.6617780
C	0.2042480	-0.7054260	0.9830760
C	-3.2577950	-0.0502220	0.5559340
O	-3.8040140	0.2058600	1.5957770
H	-2.2166820	-2.2997000	-1.6285890
H	-0.3166120	-2.4410670	-0.1596790
H	-1.5152010	-1.9195140	1.1086980
N	1.3999920	-0.5453680	0.4458510
C	2.0024230	-1.5008510	-0.4654420
C	2.3219460	0.5656170	0.6715130
C	3.4735800	-1.2551970	-0.4183870

C	3.7107260	-0.0784360	0.5178710
C	2.1633410	1.7493930	-0.3146730
H	2.1853320	0.9881290	1.6636630
H	4.0894110	-0.4072280	1.4865460
H	4.4152910	0.6418770	0.1105240
O	1.2627070	1.6996540	-1.2563940
O	2.9029100	2.6869160	-0.1586940
H	0.6177790	0.8953770	-1.3262420
C	2.9057770	-2.5164300	0.1689820
H	4.0523950	-1.3216660	-1.3275630
H	1.4641210	-1.6883360	-1.3805780
H	3.0601470	-3.4411840	-0.3700430
H	2.8781430	-2.6106980	1.2473140

***Cis*-ethano proline *syn*-(*R*,*R*) TS 6b**

C	2.4202170	-0.5090260	0.4975030
C	3.6508600	1.4161030	-0.4570610
H	1.9508290	2.7910220	-0.1341090
H	3.6902980	1.7665250	-1.4888650
H	4.6076550	1.6803320	-0.0036310
C	0.7486360	0.7272480	-1.3070230
C	1.6982800	-1.8018750	0.1619130
C	0.8924120	-1.7061950	-1.1412210
H	2.4211880	-2.6141890	0.0730040
H	1.0256780	-2.0386370	0.9901960
H	1.5866430	-1.6198810	-1.9775420
H	0.3097420	-2.6117700	-1.2919520
C	3.0618970	-0.6364840	1.8924340
H	3.6655540	0.2343270	2.1520340
H	2.2731550	-0.7334710	2.6381740
H	3.7057500	-1.5164550	1.9255740
C	2.4476800	1.9426490	0.3314480
C	1.5057930	0.7364610	0.5046890
O	0.5436180	0.7584380	1.3310210
C	0.0499460	-0.4694170	-1.1220510
C	3.5190840	-0.1050640	-0.4671770
O	4.1741100	-0.8515160	-1.1449010
H	2.7311600	2.2540790	1.3387840
H	0.2098270	1.6658230	-1.3008640
H	1.5867780	0.6937390	-1.9912830
N	-1.2040600	-0.4870930	-0.7026350
C	-1.8605150	-1.6442040	-0.0908690
C	-2.1785950	0.5811090	-0.9936650
C	-3.3714300	-1.3768090	-0.2505610
H	-1.4584580	-2.5685950	-0.4934530
C	-3.4800840	-0.2043980	-1.2091230

C	-2.4053620	1.7492060	0.0050820
H	-1.8662480	1.0750910	-1.9140610
H	-3.9512810	-2.2386680	-0.5736980
H	-3.5149850	-0.5698930	-2.2371910
H	-4.3436490	0.4323460	-1.0371160
O	-1.5535820	2.0109300	0.9504110
O	-3.3883380	2.4218790	-0.1849620
H	-0.6981030	1.4454100	1.0450270
C	-2.0019670	-1.5558970	1.4455970
C	-3.4694810	-1.0948450	1.2717730
H	-3.6351060	-0.0455360	1.5141130
H	-4.2133760	-1.6866150	1.8013380
H	-1.3155410	-0.8604320	1.9247630
H	-1.9097720	-2.5341150	1.9165400

Cis-ethano proline _anti_-(_S_,_S_) TS 6a

C	2.2516510	0.6363760	0.2554770
C	3.7837340	-1.3110180	0.1099080
H	2.8411110	-1.5682280	2.0621670
H	4.7300740	-1.2605970	0.6508610
H	3.9392330	-1.9969140	-0.7235780
C	0.8571780	-1.3752050	-0.9785060
C	1.4466880	1.6168070	-0.5823520
C	0.7162310	0.9406260	-1.7543240
H	0.7262890	2.1215410	0.0633290
H	2.1179440	2.3784330	-0.9820390
H	1.4528220	0.6314360	-2.4961620
H	0.0435560	1.6466200	-2.2363930
C	2.7532820	1.3559850	1.5225050
H	3.4134510	0.7270090	2.1214030
H	3.3023400	2.2567070	1.2448580
H	1.8981840	1.6306280	2.1399420
C	2.5985960	-1.6804600	1.0038830
C	1.4988500	-0.6452640	0.7040690
O	0.5031930	-0.5584740	1.4870610
C	0.0223180	-0.2896840	-1.2641870
C	3.4694480	0.0697340	-0.4548560
O	4.0829420	0.6107230	-1.3359020
H	2.2436240	-2.6994780	0.8657200
H	0.4186860	-2.2981230	-0.6239350
H	1.7194360	-1.4984370	-1.6220980
N	-1.2386810	-0.2751170	-0.8656950
C	-2.0204630	-1.5048800	-0.6521780
C	-2.0786910	0.9153280	-0.7472390
C	-3.4922500	-1.0308510	-0.6443730
C	-3.4823570	0.4162830	-1.1063630

C	-2.0578360	1.6259900	0.6307840
H	-1.7520900	1.6800200	-1.4483370
H	-3.6159310	0.4663160	-2.1883910
H	-4.2436640	1.0346920	-0.6364340
O	-1.1956280	1.2760090	1.5440070
O	-2.8454500	2.5237920	0.7870200
H	-0.5265680	0.5053100	1.3848620
C	-3.5618000	-1.3182010	0.8763760
C	-2.1865640	-2.0190380	0.7942240
H	-4.3971410	-1.9375780	1.1969280
H	-3.5527280	-0.4154350	1.4871220
H	-2.2690470	-3.1061870	0.8022210
H	-1.4144500	-1.7131940	1.4942790
H	-1.7118150	-2.2352710	-1.3978900
H	-4.1610920	-1.6550330	-1.2331410

Trans-ethano proline _syn_-(_R_,_R_) TS 7b

C	2.4499960	-0.5527180	0.5629510
C	3.7637600	1.0371110	-0.8010760
H	2.2456670	2.6304140	-0.5901440
H	3.7456370	1.2141600	-1.8767190
H	4.7795060	1.2568260	-0.4679400
C	0.7644920	0.5339130	-1.3017890
C	1.5689550	-1.7876860	0.5375430
C	0.6132140	-1.8294800	-0.6652170
H	2.1897970	-2.6847790	0.5238530
H	0.9878810	-1.7986560	1.4626120
H	1.1923010	-2.0325260	-1.5670150
H	-0.1029800	-2.6373100	-0.5409330
C	3.2169670	-0.5112440	1.8989710
H	3.9347170	0.3091870	1.9400770
H	2.5046430	-0.3766430	2.7127100
H	3.7628120	-1.4448060	2.0425710
C	2.6972260	1.8181440	-0.0247160
C	1.6623360	0.7677190	0.4196000
O	0.7814660	1.0214500	1.2981330
C	-0.0550560	-0.5023830	-0.8457580
C	3.4768460	-0.4418230	-0.5465870
O	3.9760610	-1.3574220	-1.1450430
H	3.1031070	2.2545680	0.8900630
H	0.3383020	1.5176020	-1.4517960
H	1.5288140	0.2611660	-2.0181630
N	-1.2585190	-0.2750010	-0.3563990
C	-1.9935470	-1.2042120	0.4993280
C	-2.1306750	0.8436860	-0.7604610
C	-3.4355700	-0.6779180	0.5722990

C	-3.5241840	0.2138700	-0.6665770
C	-2.1064070	2.1900260	0.0160150
H	-1.8843740	1.1134370	-1.7879420
H	-3.7102190	-0.3892470	-1.5578980
H	-4.2909630	0.9795840	-0.6030650
O	-1.1534020	2.4799510	0.8459700
O	-3.0058160	2.9532360	-0.2387600
H	-0.3724580	1.8171270	0.9923010
H	-3.7232290	-0.1440210	1.4762560
H	-1.4774210	-1.3211870	1.4507670
C	-3.9524340	-2.1191720	0.3922980
C	-2.5419080	-2.5314230	-0.0878920
H	-4.7773490	-2.2590120	-0.3048390
H	-4.2117860	-2.5848510	1.3419350
H	-2.4550070	-2.5626990	-1.1737070
H	-2.1282980	-3.4495130	0.3258190

***Trans*-ethano proline *anti*-(*S*,*S*) TS 7a**

C	-2.3022460	0.5714420	-0.0482530
C	-3.6854680	-1.4634780	-0.3909080
H	-2.8687200	-1.0804920	-2.3777770
H	-4.6692090	-1.3471850	-0.8485130
H	-3.7321920	-2.3648850	0.2210830
C	-0.7048220	-1.5799530	0.5122940
C	-1.5158560	1.3411830	1.0034190
C	-0.6409090	0.4390600	1.8948730
H	-0.8918480	2.0815630	0.5018040
H	-2.2159250	1.8840300	1.6403960
H	-1.2815850	-0.1196420	2.5765230
H	0.0298680	1.0493240	2.4959220
C	-2.9363790	1.5764900	-1.0294200
H	-3.5901660	1.0894300	-1.7543970
H	-3.5265420	2.3108350	-0.4796220
H	-2.1459530	2.0881540	-1.5783720
C	-2.5441460	-1.4647940	-1.4089100
C	-1.4988640	-0.4658300	-0.8808630
O	-0.5614360	-0.0887500	-1.6500000
C	0.0768320	-0.5383400	1.0216110
C	-3.4283980	-0.2729640	0.5255920
O	-4.0173880	-0.0520930	1.5500440
H	-2.1118870	-2.4473270	-1.5850940
H	-0.2370830	-2.3501190	-0.0847560
H	-1.5038100	-1.9311780	1.1527990
N	1.2612250	-0.2695550	0.5080680
C	1.9993350	-1.2000360	-0.3535630
C	2.0450780	0.9460160	0.7088640

C	3.4060300	-0.6057930	-0.5287240
C	3.4887040	0.4514670	0.5749870
C	1.7697180	2.0849560	-0.3027770
H	1.8616200	1.3721470	1.6919880
H	3.8003700	-0.0004370	1.5192430
H	4.1653810	1.2715220	0.3495600
O	0.9167170	1.9053850	-1.2737090
O	2.3832690	3.1094630	-0.1471660
H	0.3585980	1.0379850	-1.3265770
C	4.0071300	-1.9901560	-0.2005020
C	2.6214520	-2.4477730	0.3167620
H	3.6338620	-0.1847450	-1.5059630
H	1.4485160	-1.3919640	-1.2690310
H	2.5345340	-2.4141630	1.4024600
H	2.2595850	-3.4123300	-0.0339460
H	4.8312590	-2.0047700	0.5117610
H	4.3103150	-2.5299000	-1.0962010

6.3. Cartesian coordinates of transition states for the formation of enamines at the *ω*B97x-D level (in DMF)

L-Proline TS1^{syn}

C	-2.7759970	0.0625450	0.6391810
C	-4.4875320	-0.0942190	-1.1753200
H	-4.7411250	2.0093040	-0.6389100
H	-5.5582180	-0.2081070	-1.0074450
H	-4.2636010	-0.5562650	-2.1387810
C	1.3422290	-2.0727980	-1.4343400
C	-1.3834490	-0.5143560	0.8701670
C	-0.6747510	-0.9224630	-0.4153270
H	-0.8056800	0.2306930	1.4143590
H	-1.4710490	-1.3805300	1.5262700
H	-0.7604880	-0.1508370	-1.1837110
H	-1.1707600	-1.8043910	-0.8316120
C	-3.4519280	0.4027300	1.9859320
H	-4.4491620	0.8249290	1.8504440
H	-3.5400330	-0.5060070	2.5813760
H	-2.8397370	1.1261190	2.5249200
C	-3.9996260	1.3525860	-1.1005070
C	-2.7832720	1.3344650	-0.1970150
O	-1.9483750	2.2015140	-0.1377120
C	0.7891700	-1.3229680	-0.2355130
C	-3.7221710	-0.8629590	-0.1141150
O	-3.8462870	-2.0402200	0.1071760
H	-3.7392530	1.7869380	-2.0640220

H	2.4094040	-2.2624620	-1.3332330
H	0.8359840	-3.0392610	-1.4684150
N	1.6760870	0.3450910	-0.5045690
C	1.4679930	1.3025610	0.6099230
C	3.1308380	0.3733600	-0.7982880
C	2.6557770	2.2828420	0.5691430
H	0.5029380	1.7866520	0.4818260
C	3.4557650	1.8636630	-0.6690670
C	4.0513680	-0.4528690	0.1213500
H	3.3004420	-0.0022770	-1.8063700
H	4.5238870	2.0401940	-0.5800810
O	3.5646100	-1.2939140	0.9881250
O	5.2468290	-0.2918910	-0.0039920
H	2.5246700	-1.4839270	0.9694680
O	1.1490450	-1.6981950	0.9278360
H	1.2213220	0.7139910	-1.3331240
H	1.1472950	-1.5552150	-2.3739810
H	3.0937210	2.3806040	-1.5588000
H	2.3244090	3.3172430	0.5097660
H	3.2618890	2.1801730	1.4692300
H	1.4474740	0.7257250	1.5341330

L-Proline TS2^{anti}

C	-2.3618860	-0.3921230	0.4496500
C	-3.6109810	-0.9529660	-1.6253250
H	-5.3163720	0.1576640	-0.7696010
H	-4.2170410	-1.8486100	-1.4681140
H	-3.4141720	-0.8792710	-2.6932400
C	1.1972020	3.0439690	-0.6649410
C	-1.0244410	0.2154740	0.8573150
C	-0.4983790	1.2412410	-0.1366590
H	-1.1321240	0.6785300	1.8386000
H	-0.3308760	-0.6141350	0.9800880
H	-1.1681570	2.1068950	-0.1328090
H	-0.5224510	0.8534760	-1.1574760
C	-2.8510030	-1.3901290	1.5229390
H	-3.8038700	-1.8493160	1.2546350
H	-2.1089850	-2.1791390	1.6475220
H	-2.9759830	-0.8637330	2.4691480
C	-4.2638590	0.2895590	-1.0192410
C	-3.4800840	0.6196060	0.2375590
O	-3.7097770	1.5475530	0.9697410
C	0.8879680	1.8150120	0.1695000
C	-2.3113770	-1.1459000	-0.8718610
O	-1.3759270	-1.8039310	-1.2522720
H	-4.1975590	1.1548200	-1.6816490

H	2.2299180	3.3560480	-0.5251410
H	0.9889560	2.9011620	-1.7257800
N	1.9975180	0.5586080	-0.7353580
C	3.4336590	0.9361060	-0.6981180
C	1.9562460	-0.8981880	-0.4438360
C	3.1537380	-1.4144690	-1.2448160
C	2.1079670	-1.3132090	1.0305000
H	1.0039260	-1.3061290	-0.7850690
H	2.8933160	-1.4269170	-2.3040790
H	3.4388380	-2.4198860	-0.9488360
O	2.0464620	-0.4278420	1.9867860
O	2.2842310	-2.4882730	1.2682410
H	1.7149540	0.5299890	1.7295780
O	1.2989030	1.8342730	1.3748410
H	1.6730840	0.6512190	-1.6925160
H	0.5512760	3.8450900	-0.3009180
C	4.2275910	-0.3594180	-0.9549160
H	3.6195460	1.7009570	-1.4467030
H	4.9267550	-0.2474640	-1.7805250
H	4.8012410	-0.6336570	-0.0694650
H	3.6378670	1.3605170	0.2846560

Cis-methano L-Proline TS1^{syn}

C	-2.8169710	0.0889860	0.6143740
C	-4.6417400	-0.2641880	-1.0559320
H	-4.8772910	1.8882640	-0.7476740
H	-5.6929450	-0.3555910	-0.7827350
H	-4.5018200	-0.8246180	-1.9819200
C	1.2395940	-2.2557420	-1.3590360
C	-1.4090410	-0.4501770	0.8414240
C	-0.7362420	-0.9572460	-0.4280550
H	-0.8148150	0.3359380	1.3063050
H	-1.4665070	-1.2624090	1.5661830
H	-0.8181720	-0.2356920	-1.2440670
H	-1.2560740	-1.8543040	-0.7774330
C	-3.4347350	0.5612100	1.9503910
H	-4.4446500	0.9541820	1.8214850
H	-3.4773490	-0.2806360	2.6414450
H	-2.8101220	1.3451700	2.3790540
C	-4.1595970	1.1819100	-1.1715530
C	-2.8926930	1.2671450	-0.3449010
O	-2.0712040	2.1458930	-0.4234410
C	0.7197560	-1.3750260	-0.2367390
C	-3.7856830	-0.9201510	0.0114720
O	-3.8632960	-2.0752660	0.3427270
H	-3.9556060	1.5033460	-2.1914220

H	2.3105930	-2.4296240	-1.2719280
H	0.7368660	-3.2202140	-1.2675420
N	1.6394250	0.2267800	-0.7035260
C	1.2612320	1.3988090	0.0856450
C	3.1320650	0.2449570	-0.8327980
C	2.4116340	2.3528140	0.1172000
H	0.2350960	1.7115380	-0.0359010
C	3.5101110	1.7401830	-0.7197550
C	3.9988810	-0.6127450	0.1148680
H	3.3761440	-0.1387970	-1.8219710
H	4.5078690	1.8524830	-0.3023940
O	3.4806510	-1.4369690	0.9694710
O	5.2010470	-0.4857650	-0.0089310
H	2.3988800	-1.5553670	0.9774490
O	1.0799330	-1.6470350	0.9575100
H	1.2857610	0.3883130	-1.6417450
H	1.0122810	-1.8485980	-2.3445130
H	3.5022480	2.1969120	-1.7099780
H	2.2395550	3.4167770	0.0456830
H	1.4596610	2.2027410	2.1107050
H	2.6191100	0.8467450	1.7763060
C	1.9931410	1.6274480	1.3671650

Cis-methano L-Proline TS1^{anti}

C	-2.5255370	-0.3859870	0.4129600
C	-3.7772340	-0.7912590	-1.6981140
H	-5.4767880	0.2006090	-0.7039030
H	-4.3825920	-1.6988420	-1.6424980
H	-3.5633770	-0.6117690	-2.7504320
C	1.1185760	3.0088910	-0.5178200
C	-1.1748730	0.1586280	0.8611140
C	-0.6308290	1.2484260	-0.0523460
H	-1.2652300	0.5427560	1.8775800
H	-0.5031430	-0.6953430	0.9097870
H	-1.2622580	2.1354940	0.0527480
H	-0.7067510	0.9577880	-1.1028290
C	-3.0427510	-1.4421190	1.4159710
H	-4.0026470	-1.8629890	1.1122190
H	-2.3177680	-2.2528680	1.4920950
H	-3.1636210	-0.9770810	2.3942880
C	-4.4410380	0.3891230	-0.9872090
C	-3.6233700	0.6572970	0.2632050
O	-3.8183450	1.5613270	1.0342850
C	0.7886200	1.7429290	0.2498390
C	-2.4843980	-1.0543840	-0.9538030
O	-1.5580490	-1.7013120	-1.3735750

H	-4.4350620	1.2979590	-1.5907140
H	2.1489570	3.3074720	-0.3386430
H	0.9327580	2.9213800	-1.5888220
N	1.8056470	0.5021350	-0.7234440
C	3.1953260	0.8973600	-0.9718710
C	1.8287200	-0.9635570	-0.3980290
C	3.0420660	-1.5011490	-1.1868550
C	1.9024220	-1.4088630	1.0768110
H	0.8958010	-1.3915420	-0.7653570
H	2.7340130	-1.7702650	-2.1978560
H	3.4481780	-2.3879350	-0.7068670
O	1.7808770	-0.5623450	2.0521510
O	2.0546040	-2.5972950	1.2729770
H	1.5077700	0.4480800	1.7965980
O	1.2102270	1.7080200	1.4583160
H	1.3411320	0.5593850	-1.6255920
H	0.4680960	3.7933310	-0.1276460
C	3.9985800	-0.3326970	-1.2536330
C	4.2374560	0.4582830	0.0033240
H	3.3100140	1.8116110	-1.5305130
H	4.7511460	-0.3243160	-2.0282970
H	3.9483680	0.0601760	0.9652540
H	5.1285480	1.0692740	0.0290160

Trans-methano L-Proline TS1^{syn}

C	-2.8235990	0.3033000	0.5162150
C	-4.6573400	-0.9020860	-0.6823720
H	-5.2762770	1.1546360	-1.0771440
H	-5.6632920	-1.0791680	-0.3031880
H	-4.4225900	-1.7222360	-1.3643430
C	1.2091930	-2.0957920	-1.3799500
C	-1.3269500	0.0563020	0.6851260
C	-0.7185360	-0.7813100	-0.4303480
H	-0.8465800	1.0331910	0.7367600
H	-1.1633490	-0.4397800	1.6425580
H	-0.7874340	-0.2674130	-1.3915660
H	-1.2923870	-1.7076380	-0.5420780
C	-3.3613480	1.1549130	1.6863760
H	-4.4305690	1.3528500	1.5940760
H	-3.1883820	0.6249550	2.6230980
H	-2.8338310	2.1086940	1.7117310
C	-4.4718500	0.4637970	-1.3417600
C	-3.1858230	1.0289490	-0.7729300
O	-2.5490830	1.9309340	-1.2546730
C	0.7097510	-1.2715510	-0.2032590
C	-3.6598490	-0.9688670	0.4586200

O	-3.5423890	-1.8970980	1.2169020
H	-4.4165910	0.4329650	-2.4283630
H	2.2436880	-2.4068280	-1.2493410
H	0.5977100	-2.9989970	-1.4179050
N	1.7139720	0.2979220	-0.4577280
C	1.6693090	1.1802070	0.7142860
C	3.1561880	0.1973960	-0.8191340
C	2.8831990	2.0571330	0.6707280
C	3.6773600	1.6240630	-0.5540870
C	3.9963590	-0.8005940	0.0017890
H	3.2507100	-0.1004160	-1.8620700
H	4.7493440	1.6208540	-0.3778900
O	3.4623670	-1.5272010	0.9404580
O	5.1811070	-0.8548340	-0.2523260
H	2.4017090	-1.5898120	0.9892020
O	1.0154550	-1.6592940	0.9758640
H	1.2422750	0.7431620	-1.2388120
H	1.0993110	-1.5733300	-2.3302330
H	3.4775910	2.2617800	-1.4161060
H	3.4112980	2.2950790	1.5821980
H	1.3031350	0.7102570	1.6140450
C	1.5160700	2.6420760	0.4512900
H	1.2472050	2.9575750	-0.5501120
H	1.0870550	3.2365050	1.2462280

Trans-methano L-Proline TS1^{anti}

C	2.5590690	-0.3927990	-0.3437980
C	3.7576640	-0.6208450	1.8225840
H	5.4390180	0.4453730	0.8696210
H	4.4100220	-1.4972920	1.8079930
H	3.5151870	-0.4164510	2.8638360
C	-1.1759740	2.9772730	0.2200030
C	1.2076030	0.0804770	-0.8664020
C	0.5934580	1.1921320	-0.0280020
H	1.3249480	0.4201790	-1.8958350
H	0.5654610	-0.7975990	-0.8986140
H	1.2316400	2.0781530	-0.1010970
H	0.5774030	0.9241620	1.0307800
C	3.1410220	-1.4885530	-1.2647250
H	4.1056130	-1.8546480	-0.9094250
H	2.4472350	-2.3283630	-1.3101840
H	3.2744720	-1.0797540	-2.2662490
C	4.3759450	0.5634120	1.0785000
C	3.6149950	0.6980010	-0.2277040
O	3.8187580	1.5433950	-1.0605820
C	-0.7945680	1.6748670	-0.4626290

C	2.4981300	-0.9775780	1.0603660
O	1.5837310	-1.6334590	1.4918730
H	4.2590350	1.5014980	1.6242810
H	-2.2228550	3.2185830	0.0472880
H	-0.9700740	2.9684850	1.2911720
N	-1.9051260	0.5144870	0.4864230
C	-3.3252000	0.8275810	0.2804440
C	-1.8145790	-0.9718860	0.3893410
C	-3.0908750	-1.4273020	1.1210080
C	-1.8200070	-1.5539990	-1.0357800
H	-0.8944030	-1.3112190	0.8672000
H	-2.9237660	-1.4284330	2.1989960
H	-3.3760690	-2.4312080	0.8202360
O	-1.7419750	-0.7767740	-2.0773010
O	-1.9063190	-2.7584970	-1.1440380
H	-1.4703130	0.2312070	-1.9173240
O	-1.1323610	1.5628770	-1.6910450
H	-1.6518110	0.7504130	1.4410500
H	-0.5683470	3.7617940	-0.2338260
C	-4.1130480	-0.3756260	0.7042700
H	-4.9793180	-0.6823720	0.1369740
H	-3.5360950	1.4002100	-0.6105210
C	-4.1826440	0.8968920	1.5008090
H	-3.6968090	0.9249380	2.4693170
H	-5.0849030	1.4883110	1.4283880

Cis-ethano L-Proline TS1*syn*

C	2.8988610	0.1980580	-0.6021480
C	4.7613770	-0.2869930	0.9938360
H	4.9370620	1.8886850	0.9026700
H	5.8182310	-0.3296670	0.7320390
H	4.6150100	-0.9536060	1.8461310
C	-0.9542050	-2.5292570	1.2843320
C	1.5059780	-0.3779220	-0.8365920
C	0.9140190	-1.0624950	0.3874530
H	0.8637770	0.4334630	-1.1758250
H	1.5632700	-1.0925660	-1.6574860
H	0.9854450	-0.4287800	1.2744880
H	1.4993630	-1.9581600	0.6163540
C	3.4361150	0.8473410	-1.8966230
H	4.4315170	1.2735150	-1.7610150
H	3.4879360	0.0917950	-2.6805340
H	2.7585080	1.6421340	-2.2094340
C	4.2475850	1.1252170	1.2714920
C	2.9589370	1.2603680	0.4862440
O	2.1113750	2.0947810	0.6811110

C	-0.5207000	-1.5524250	0.2026690
C	3.9292130	-0.8302880	-0.1526250
O	4.0633440	-1.9216040	-0.6438360
H	4.0649710	1.3364420	2.3235450
H	-2.0075820	-2.7867430	1.1857850
H	-0.3749820	-3.4422660	1.1369120
N	-1.5057250	-0.0538150	0.7731050
C	-1.2609120	1.2510110	0.1094300
C	-2.9813810	-0.1632140	0.9764500
C	-2.4848310	2.1464380	0.4401900
H	-0.2751190	1.6072130	0.3949940
C	-3.3948990	1.2790050	1.3024070
C	-3.8332080	-0.7813470	-0.1528880
H	-3.1545790	-0.8211400	1.8283850
H	-4.4532670	1.4373540	1.1115230
O	-3.2974830	-1.5699650	-1.0337690
O	-5.0274390	-0.5628480	-0.1330000
H	-2.2299560	-1.7162950	-1.0068960
O	-0.8886110	-1.8088600	-0.9951820
H	-1.1263630	0.0439180	1.7101830
H	-0.7561330	-2.1634210	2.2925000
H	-3.2030430	1.4696530	2.3592150
H	-2.2578770	3.0998170	0.9105810
C	-2.8221280	2.2291280	-1.0684070
C	-1.5940630	1.3474190	-1.3938580
H	-2.7754000	3.2352380	-1.4800420
H	-3.7840730	1.7915130	-1.3358750
H	-0.8137620	1.8634080	-1.9511380
H	-1.7969150	0.4029040	-1.8895530

Trans-ethano L-Proline TS1^{syn}

C	-2.9212280	0.2197680	0.5548720
C	-4.7007050	-0.7609890	-0.9050730
H	-5.1941930	1.3543370	-1.0988610
H	-5.7474700	-0.9458110	-0.6678010
H	-4.3985870	-1.5133170	-1.6379270
C	1.0130780	-2.3870060	-1.2682930
C	-1.4628460	-0.1727940	0.7847250
C	-0.8528600	-0.9424160	-0.3758200
H	-0.9062250	0.7428240	0.9758040
H	-1.4077030	-0.7776680	1.6900230
H	-0.8847120	-0.3620910	-1.3002960
H	-1.4520100	-1.8395090	-0.5666270
C	-3.4625270	1.0054890	1.7667310
H	-4.5039920	1.3023930	1.6313930
H	-3.3946780	0.3813060	2.6578080

H	-2.8623220	1.9040580	1.9124020
C	-4.4068560	0.6557130	-1.3940640
C	-3.1391160	1.0824100	-0.6818760
O	-2.4169740	1.9822250	-1.0275170
C	0.5566880	-1.4775390	-0.1392760
C	-3.8406340	-0.9749260	0.3254030
O	-3.8724890	-1.9537680	1.0263510
H	-4.2813300	0.7441430	-2.4714050
H	2.0432810	-2.7125960	-1.1390090
H	0.3817430	-3.2768390	-1.2347200
N	1.6377850	0.0493810	-0.5224090
C	1.6458330	1.0662540	0.5560370
C	3.0684410	-0.1615500	-0.8752180
C	3.0056450	1.8010980	0.4840330
C	3.6445720	1.2579150	-0.7946900
C	3.8839530	-1.0930480	0.0425060
H	3.1352560	-0.5836970	-1.8763590
H	4.7310490	1.2549150	-0.7799190
O	3.3241020	-1.7356510	1.0281090
O	5.0715970	-1.1860990	-0.1834520
H	2.2684460	-1.7659490	1.0639740
O	0.8697690	-1.7924180	1.0551890
H	1.2001570	0.4473770	-1.3472740
H	0.8929380	-1.9244600	-2.2481830
H	3.3147020	1.8235520	-1.6686580
C	0.9145320	2.3979190	0.2833310
C	2.2618430	3.1515140	0.3952830
H	2.5322070	3.7788990	-0.4530770
H	2.3405730	3.7413730	1.3062710
H	0.4439330	2.4443640	-0.6987830
H	0.1674130	2.6690730	1.0261700
H	3.6587320	1.6731570	1.3454050
H	1.4033770	0.5733300	1.4954040

Cis-ethano L-Proline TS1^{anti}

C	2.7609360	-0.3580300	-0.4592140
C	3.9554990	-0.9637870	1.6355550
H	5.6750230	0.1771310	0.8518660
H	4.5729190	-1.8510520	1.4755700
H	3.7263280	-0.9172910	2.6985540
C	-0.9181130	2.9638250	0.6474690
C	1.4296560	0.2482400	-0.8876280
C	0.8700880	1.2518040	0.1127430
H	1.5589270	0.7324850	-1.8558600
H	0.7433100	-0.5812060	-1.0482460
H	1.4891220	2.1532710	0.0857090

H	0.9443270	0.8774020	1.1365180
C	3.2900690	-1.3220220	-1.5445800
H	4.2380770	-1.7819020	-1.2607470
H	2.5584110	-2.1125290	-1.7132190
H	3.4388960	-0.7686360	-2.4717230
C	4.6162050	0.2980990	1.0795780
C	3.8622720	0.6580640	-0.1872380
O	4.1009340	1.6099770	-0.8848750
C	-0.5556700	1.7408830	-0.1740720
C	2.6801810	-1.1474620	0.8396110
O	1.7395540	-1.8222500	1.1760340
H	4.5301390	1.1448350	1.7631790
H	-1.9613970	3.2327380	0.4945220
H	-0.7159410	2.8388180	1.7119180
N	-1.5557600	0.4496010	0.7257700
C	-2.9597220	0.8088130	1.0530430
C	-1.5621300	-0.9922270	0.3193310
C	-2.6245920	-1.6040320	1.2431390
C	-1.8219070	-1.3384630	-1.1604400
H	-0.5712410	-1.3995570	0.5288570
H	-2.1740100	-1.8025820	2.2164920
H	-3.0026000	-2.5408300	0.8420410
O	-1.6287350	-0.4556390	-2.0934520
O	-2.1454540	-2.4792100	-1.4197720
H	-1.2870410	0.5107940	-1.7908370
O	-0.9454780	1.7606600	-1.3947240
H	-1.0650090	0.4530200	1.6150920
H	-0.3002960	3.7854310	0.2814070
C	-3.6888320	-0.5209030	1.3717350
C	-4.6186940	-0.2894940	0.1541490
C	-3.9096470	1.0553660	-0.1351020
H	-4.5193150	-1.0369020	-0.6330220
H	-5.6722820	-0.1992830	0.4102550
H	-3.4285190	1.1466630	-1.1044270
H	-4.5364630	1.9312800	0.0206090
H	-2.9523090	1.5764120	1.8199770
H	-4.1989010	-0.5560630	2.3309680

Trans-ethano L-Proline TS1^{anti}

C	-2.8078770	0.3946430	-0.2357320
C	-3.8644240	0.3704390	2.0148270
H	-5.5800040	-0.6683580	1.0906000
H	-4.5376010	1.2249320	2.1195410
H	-3.5543290	0.0783950	3.0164010
C	1.0359180	-2.9160180	-0.2113860
C	-1.4868830	-0.0082040	-0.8818530

C	-0.8092220	-1.1825340	-0.1907790
H	-1.6664790	-0.2529240	-1.9291300
H	-0.8546810	0.8776330	-0.8731360
H	-1.4307190	-2.0741220	-0.3222700
H	-0.7426850	-1.0234370	0.8878270
C	-3.4497220	1.5692170	-1.0063310
H	-4.3954490	1.8842920	-0.5625900
H	-2.7664120	2.4187930	-1.0054490
H	-3.6369580	1.2614980	-2.0350640
C	-4.4993410	-0.7558640	1.1989990
C	-3.8438150	-0.7199260	-0.1690620
O	-4.1050720	-1.4644100	-1.0786790
C	0.5633510	-1.5751050	-0.7427260
C	-2.6645250	0.8334970	1.2149590
O	-1.7348560	1.4631860	1.6530760
H	-4.2985720	-1.7390640	1.6294560
H	2.0749320	-3.0956090	-0.4811110
H	0.9085920	-3.0152830	0.8670540
N	1.6975800	-0.4498590	0.2845190
C	3.1318000	-0.7124190	0.0247200
C	1.5690270	1.0335470	0.3126350
C	2.8384730	1.4558850	1.0648850
C	1.5261530	1.7436300	-1.0514170
H	0.6507050	1.3049370	0.8351280
H	2.7137280	1.2303390	2.1258470
H	3.0356250	2.5193700	0.9624180
O	1.4033210	1.0633580	-2.1577900
O	1.6128510	2.9521940	-1.0588490
H	1.1508760	0.0527200	-2.0736120
O	0.8366650	-1.3241500	-1.9613340
H	1.4826070	-0.7589210	1.2274190
H	0.4257330	-3.6813380	-0.6943980
C	3.9081920	0.5616070	0.4317130
H	4.4309950	1.0733920	-0.3741970
H	3.2433510	-1.0501480	-1.0040890
C	4.7932100	-0.2917090	1.3691800
C	3.8978940	-1.5236520	1.0884160
H	3.2765630	-1.8264200	1.9323020
H	4.4101800	-2.4046340	0.7079840
H	4.8353170	0.0426350	2.4049490
H	5.8091030	-0.4133030	0.9988140

L-Proline TS2^{syn}

C	-0.5716700	-0.5567680	-0.5470290
C	1.3738560	-1.7996620	-1.5963330
H	0.7303050	-2.6757980	-1.5640220

H	1.2779480	-1.3445940	-2.5843840
C	0.9331620	-0.7952780	-0.5610710
H	-0.7265670	0.3358200	-1.1598010
N	1.7276980	0.2715510	-0.3910000
C	1.3538330	1.4363300	0.4232090
C	3.1478030	0.3111070	-0.7387230
C	2.6069710	2.3145360	0.4389260
H	0.4966300	1.9421440	-0.0241990
C	3.4323000	1.8101940	-0.7409550
C	4.0805390	-0.4648940	0.2262370
H	3.3060240	-0.1118710	-1.7302300
H	2.3620780	3.3720230	0.3658410
H	3.0714010	2.2420960	-1.6756820
H	4.4948040	2.0167300	-0.6479830
O	3.5538200	-1.2546300	1.0808090
O	5.2880620	-0.2891280	0.0934740
H	2.2823260	-1.5462080	1.0411850
O	1.1907590	-1.7511750	0.9534660
H	-1.0305760	-1.3850630	-1.0865390
H	1.0450960	-2.6930950	0.8217450
C	-1.2878520	-0.4059950	0.7930230
C	-2.7512720	-0.0056420	0.6346330
H	-0.8107400	0.3431220	1.4209330
H	-1.2488810	-1.3484710	1.3365480
C	-3.4296390	0.0925250	2.0201470
C	-2.9660650	1.3335920	-0.0561130
C	-3.5860310	-0.9714540	-0.1955730
H	-4.4802750	0.3769010	1.9433250
H	-3.3695450	-0.8752020	2.5181110
H	-2.9122450	0.8389270	2.6231480
C	-4.2047730	1.2743550	-0.9279800
O	-2.2608530	2.2998670	0.0845800
C	-4.5246120	-0.2094170	-1.1120420
O	-3.5138590	-2.1715830	-0.1258320
H	-5.0032680	1.8060160	-0.4055440
H	-4.0206550	1.8066530	-1.8597490
H	-5.5544200	-0.4675020	-0.8640500
H	-4.3459690	-0.5534680	-2.1319210
H	2.4033260	-2.1189820	-1.4551070
H	3.1566990	2.1622770	1.3690370
H	1.0798780	1.1286940	1.4322290

L-Proline TS2^{anti}

C	2.4411710	0.0842270	0.7139260
C	4.1532200	-0.3959130	-1.0345230
H	4.1956570	-2.3452590	-0.0321260
H	5.2117740	-0.3283180	-0.7807350
H	4.0684830	-0.2026030	-2.1042580
C	-1.1109320	2.8972880	0.0234620
C	1.1043870	0.8035010	0.8303420
C	0.3228680	0.8530020	-0.4851770
H	0.5155860	0.3007780	1.5999550
H	1.2939040	1.8180360	1.1849630
H	0.2481100	-0.1401880	-0.9274910
H	0.8526470	1.4850320	-1.1975700
C	3.1705820	0.0769510	2.0771640
H	4.1313040	-0.4374990	2.0242190
H	3.3459930	1.1041020	2.3970530
H	2.5485280	-0.4279560	2.8163920
C	3.5155340	-1.7224260	-0.6168090
C	2.3360050	-1.3665010	0.2656930
O	1.4490130	-2.1185290	0.5796790
C	-1.0618620	1.4251650	-0.2762530
C	3.4031850	0.6959310	-0.2953730
O	3.5487720	1.8779680	-0.4716230
H	3.1685300	-2.3258180	-1.4543020
H	-2.1044220	3.3066300	-0.1369560
H	-0.8345850	3.0558600	1.0677000
N	-1.9420820	0.6490000	0.3693820
C	-3.2220380	1.1617520	0.8805240
C	-1.8919860	-0.8144880	0.4237890
C	-3.9972120	-0.0918130	1.2773350
C	-2.9030940	-1.1258950	1.5247000
C	-2.2357040	-1.5469070	-0.8975140
H	-0.8945290	-1.1551190	0.7041860
H	-2.4374960	-0.9649640	2.4987400
H	-3.2506130	-2.1535880	1.4693030
O	-2.3327010	-0.8696890	-1.9772030
O	-2.3734900	-2.7644040	-0.8306250
H	-1.9985080	0.3747850	-2.0136900
O	-1.6869480	1.4524920	-1.9740960
H	-0.4042730	3.4305840	-0.6084800
H	-0.9971790	1.6203180	-2.6235000
H	-4.6354340	-0.4151830	0.4529540
H	-3.7413260	1.7412000	0.1164090
H	-4.6303080	0.0796010	2.1453650
H	-3.0391680	1.8106210	1.7394280

Cis-methano L-Proline TS2^{syn}

C	-0.6545430	-0.7671290	-0.5695280
C	1.3300290	-2.0380730	-1.5236540
H	0.7108330	-2.9263210	-1.4241560
H	1.2311240	-1.6678420	-2.5463150
C	0.8548590	-0.9610960	-0.5809000
H	-0.8559050	0.0172160	-1.3045710
N	1.6179920	0.1420300	-0.5162610
C	1.1828640	1.3928890	0.0611790
C	3.0630570	0.1739240	-0.7921290
C	2.2981970	2.3664690	-0.0791870
H	0.1547860	1.6712060	-0.1089830
C	3.4041950	1.6770200	-0.8414130
C	3.9834280	-0.5861060	0.1978170
H	3.2553330	-0.2788810	-1.7645320
H	2.0805130	3.3976770	-0.3171660
H	3.3900870	2.0264370	-1.8739570
H	4.3994990	1.8543220	-0.4400420
O	3.4657750	-1.3000120	1.1193660
O	5.1897260	-0.4623660	0.0091690
H	2.1939480	-1.5756320	1.1009560
O	1.1072390	-1.7825240	1.0124680
H	-1.1018020	-1.6788740	-0.9643180
H	0.9644230	-2.7327040	0.9578320
C	1.9184350	1.8576310	1.2869660
H	1.3972570	2.5453700	1.9387320
H	2.5658090	1.1506170	1.7896460
C	-1.3225180	-0.4405060	0.7668350
C	-2.7685870	0.0171070	0.6117510
H	-0.7774360	0.3315120	1.3080520
H	-1.3155950	-1.3267820	1.3987070
C	-3.3920690	0.2935350	1.9995160
C	-2.9516390	1.2839690	-0.2101870
C	-3.6766420	-0.9885920	-0.0841160
H	-4.4308260	0.6191610	1.9258850
H	-3.3577280	-0.6183840	2.5955590
H	-2.8196640	1.0727430	2.5030820
C	-4.2324600	1.1988450	-1.0154610
O	-2.1932320	2.2205710	-0.2090990
C	-4.6280300	-0.2783080	-1.0285550
O	-3.6452380	-2.1784570	0.0979720
H	-4.9795080	1.8218090	-0.5185230
H	-4.0685770	1.6218640	-2.0052160
H	-5.6532780	-0.4570160	-0.7035570
H	-4.5215630	-0.7325520	-2.0146660
H	2.3667080	-2.3163410	-1.3512390

Cis-methano L-Proline TS2^{anti}

C	2.5855830	-0.1330400	-0.7312120
C	4.3020240	0.3492740	1.0140270
H	4.4051840	2.2515670	-0.0669810
H	5.3654970	0.2493300	0.7949310
H	4.1797270	0.1852720	2.0853900
C	-1.0122240	-2.8644440	0.0567310
C	1.2333960	-0.8270700	-0.8208450
C	0.4663930	-0.8374770	0.5040460
H	0.6466490	-0.3250660	-1.5923540
H	1.3976570	-1.8513180	-1.1598360
H	0.4184480	0.1638380	0.9309070
H	0.9907940	-1.4683150	1.2211840
C	3.3017820	-0.1708850	-2.1004980
H	4.2737120	0.3235300	-2.0674870
H	3.4522070	-1.2083790	-2.3989240
H	2.6836740	0.3308630	-2.8451790
C	3.7074880	1.6798670	0.5488410
C	2.5114840	1.3286610	-0.3126540
O	1.6341550	2.0896610	-0.6322590
C	-0.9317160	-1.3854680	0.3190320
C	3.5424770	-0.7426100	0.2845820
O	3.6760190	-1.9240950	0.4735880
H	3.3900930	2.3299990	1.3624900
H	-2.0045460	-3.2530200	0.2675960
H	-0.7700990	-3.0594060	-0.9895210
N	-1.7931290	-0.5978500	-0.3420460
C	-3.0587090	-1.0624150	-0.8614130
C	-1.7292950	0.8723240	-0.3851160
C	-3.7129600	0.0882120	-1.5429650
H	-3.0699930	-2.0586170	-1.2726700
C	-2.7535440	1.2530080	-1.4709010
C	-1.9905000	1.6243660	0.9454070
H	-0.7310710	1.1892520	-0.6892850
H	-4.2567940	-0.0707720	-2.4628970
H	-2.2514030	1.3555290	-2.4333880
H	-3.2240570	2.2040230	-1.2319130
O	-2.0678740	0.9688110	2.0375640
O	-2.0761050	2.8456520	0.8624410
H	-1.7968980	-0.3041330	2.0751530
O	-1.5385010	-1.3825800	2.0254780
H	-0.2926820	-3.3881600	0.6821650
H	-0.8476830	-1.5807330	2.6655830
C	-4.2980110	-0.4546450	-0.2660700
H	-4.1998910	0.1130090	0.6500570

H	-5.2101860	-1.0288710	-0.3511580

Trans-methano L-Proline TS2^{syn}

C	-0.6142250	-0.3214080	-0.6375560
C	1.2147700	-1.5578960	-1.8448880
H	0.4548660	-2.3220310	-1.9895350
H	1.2501400	-0.9379090	-2.7425580
C	0.8584290	-0.6838450	-0.6666700
H	-0.7462540	0.4039110	-1.4464660
N	1.7748660	0.2331770	-0.3217250
C	1.5735430	1.2480730	0.6872930
C	3.2026930	0.1551560	-0.6560660
C	2.7500540	2.1600540	0.6115930
C	3.6869770	1.5981440	-0.4468010
C	4.0003450	-0.8674880	0.1949170
H	3.3301730	-0.1446820	-1.6953330
H	3.6226990	2.1605960	-1.3788890
H	4.7230240	1.6027820	-0.1191820
O	3.3514050	-1.7206440	0.8873640
O	5.2246640	-0.8123900	0.1246050
H	2.0419270	-1.8412140	0.8068380
O	0.9422980	-1.8782250	0.6870160
H	-1.1444860	-1.2242130	-0.9421800
H	0.6692300	-2.7616710	0.4204860
C	-1.2491160	0.2084190	0.6456990
C	-2.7729150	0.2258100	0.5796350
H	-0.9250160	1.2265240	0.8490140
H	-0.9534320	-0.4149690	1.4895040
C	-3.3557530	0.7981850	1.8924590
C	-3.3433520	1.0642830	-0.5554180
C	-3.4186010	-1.1370920	0.3735060
H	-4.4465950	0.8232790	1.8815260
H	-3.0325940	0.1782720	2.7288710
H	-2.9883340	1.8143160	2.0364340
C	-4.5699040	0.3910740	-1.1415370
O	-2.8897810	2.1173030	-0.9240940
C	-4.6228770	-1.0143870	-0.5404930
O	-3.0332460	-2.1614690	0.8759400
H	-5.4445560	0.9933710	-0.8904270
H	-4.4825350	0.3926830	-2.2278600
H	-5.5220900	-1.1870920	0.0534690
H	-4.5769600	-1.8065610	-1.2873880
H	2.1775560	-2.0465650	-1.7184300
H	3.1718480	2.5565540	1.5233070
H	1.1618020	0.9248290	1.6318150
C	1.3914520	2.6494040	0.1869020

H	1.2003950	2.7743210	-0.8714840
H	0.8832860	3.3477090	0.8384530

Trans-methano L-Proline TS2^{anti}

C	2.5065920	-0.2427490	-0.7205970
C	4.3676750	0.4566050	0.7810600
H	4.3482260	2.2631970	-0.4678300
H	5.3835880	0.3119930	0.4101040
H	4.4194910	0.4380250	1.8694190
C	-1.1099320	-2.7337800	0.6395130
C	1.1445740	-0.9163170	-0.6302900
C	0.4581070	-0.7227780	0.7245280
H	0.5176080	-0.5179470	-1.4306390
H	1.2761920	-1.9814030	-0.8279850
H	0.4606310	0.3282840	1.0135420
H	1.0067080	-1.2700600	1.4905660
C	3.1402960	-0.4947600	-2.1083360
H	4.1180930	-0.0206810	-2.2054880
H	3.2603770	-1.5675750	-2.2592900
H	2.4841020	-0.0949880	-2.8815970
C	3.7066130	1.7215430	0.2296450
C	2.4708340	1.2656550	-0.5199640
O	1.5881470	1.9873250	-0.9089830
C	-0.9625450	-1.2395570	0.6903670
C	3.5180850	-0.7109250	0.3165480
O	3.6296460	-1.8465780	0.7001690
H	3.4079380	2.4280320	1.0033270
H	-2.1176500	-3.0454700	0.8992450
H	-0.8952110	-3.0726710	-0.3756170
N	-1.8442110	-0.5297950	-0.0256400
C	-3.1517100	-1.0291940	-0.3810330
C	-1.7488410	0.9015760	-0.3365230
C	-3.7170410	-0.0631300	-1.3656550
C	-2.7031860	1.0606240	-1.5302450
C	-2.1071970	1.8388840	0.8444010
H	-0.7297770	1.1636790	-0.6231590
H	-2.1561560	0.9695880	-2.4695440
H	-3.1722730	2.0403610	-1.5059460
O	-2.1294930	1.3520810	2.0245860
O	-2.3106640	3.0190210	0.5758960
H	-1.7809970	0.1181940	2.2657110
O	-1.4794070	-0.9450830	2.4009550
H	-0.4059750	-3.2035360	1.3226750
H	-0.7549090	-1.0020540	3.0316670
H	-4.7675930	0.1842170	-1.3270660
H	-3.7445210	-1.4652740	0.4110260

C	-3.3264760	-1.4463600	-1.8111160
H	-2.4287360	-1.5546240	-2.4071830
H	-4.1206010	-2.1468720	-2.0312400

Cis-ethano L-Proline TS2^{syn}

C	0.8055490	-0.8673630	0.5138160
C	-1.0676320	-2.3646770	1.3385240
H	-0.3859100	-3.1841910	1.1235430
H	-0.9772300	-2.1168280	2.3982890
C	-0.6889400	-1.1490510	0.5289540
H	0.9779820	-0.1719730	1.3406130
N	-1.5189960	-0.0962710	0.6044420
C	-1.1779790	1.2499140	0.1483200
C	-2.9418240	-0.1977720	0.9486600
C	-2.4056450	2.1143330	0.5127540
H	-0.2120350	1.5503600	0.5464730
C	-3.3051810	1.2319900	1.3606160
C	-3.8623170	-0.7659110	-0.1626710
H	-3.0682520	-0.8682530	1.7980590
H	-2.1638830	3.0573790	0.9970840
H	-3.0744520	1.3703810	2.4176140
H	-4.3652540	1.4236370	1.2105510
O	-3.3284510	-1.3623300	-1.1570760
O	-5.0721180	-0.6415630	0.0044370
H	-2.0475850	-1.6155790	-1.1843420
O	-0.9517420	-1.7965690	-1.1489180
H	1.3105870	-1.7950320	0.7812230
H	-0.7785660	-2.7414700	-1.2050130
C	1.4305990	-0.3332760	-0.7735800
C	2.8738950	0.1226260	-0.5875450
H	0.8681680	0.5076300	-1.1729320
H	1.4127420	-1.1123210	-1.5336380
C	3.4595730	0.5981280	-1.9366890
C	3.0507320	1.2706730	0.3959640
C	3.8118790	-0.9513540	-0.0523050
H	4.4923830	0.9367450	-1.8398570
H	3.4316930	-0.2256960	-2.6498470
H	2.8591060	1.4238720	-2.3189960
C	4.3408610	1.0943190	1.1715370
O	2.2831150	2.1903120	0.5239700
C	4.7509760	-0.3668740	0.9861190
O	3.8097860	-2.1010050	-0.4108650
H	5.0762470	1.7842770	0.7514710
H	4.1854610	1.3832250	2.2096750
H	5.7805910	-0.4927590	0.6508660
H	4.6390300	-0.9515250	1.9006680

H	-2.0831230	-2.6985080	1.1415370
C	-2.7468300	2.2561220	-0.9908250
C	-1.4170470	1.5573870	-1.3520310
H	-1.4825460	0.6891330	-2.0044440
H	-0.6654250	2.2419350	-1.7448230
H	-3.6333200	1.6946350	-1.2872100
H	-2.8521700	3.2787820	-1.3477410

Trans-ethano L-Proline TS2^{syn}

C	0.7193870	-0.4595620	0.6054910
C	-1.0263540	-1.8825570	1.7474940
H	-0.2425960	-2.6341890	1.8044470
H	-1.0464180	-1.3386380	2.6941130
C	-0.7349200	-0.9027110	0.6366420
H	0.8006060	0.3331980	1.3551540
N	-1.6934480	-0.0004910	0.3828430
C	-1.5313540	1.1576430	-0.4906930
C	-3.1139540	-0.1858900	0.7062440
C	-2.9073050	1.8371290	-0.5808930
C	-3.6711940	1.2339980	0.5975130
C	-3.8711460	-1.1815560	-0.2102020
H	-3.2250580	-0.5594800	1.7235340
H	-3.4472780	1.7772930	1.5175090
H	-4.7485880	1.2253060	0.4584900
O	-3.1974810	-1.9252410	-0.9991410
O	-5.0936510	-1.2100170	-0.1020710
H	-1.8951100	-1.9966090	-0.9200410
O	-0.7904930	-2.0062080	-0.8005740
H	1.2950970	-1.3040020	0.9846870
H	-0.4896390	-2.8961060	-0.5925540
C	1.3505170	-0.0052630	-0.7092880
C	2.8663460	0.1358990	-0.6091000
H	0.9624140	0.9592100	-1.0270690
H	1.1266670	-0.7273700	-1.4927430
C	3.4439120	0.6301960	-1.9548550
C	3.3370870	1.1141370	0.4580760
C	3.6013500	-1.1514440	-0.2620150
H	4.5289180	0.7400770	-1.9201880
H	3.1930100	-0.0846110	-2.7386890
H	3.0068990	1.5985040	-2.1991180
C	4.5514730	0.5651320	1.1829870
O	2.8206540	2.1780810	0.6855980
C	4.7740110	-0.8511270	0.6513390
O	3.3011220	-2.2444500	-0.6687500
H	5.3975400	1.2309060	1.0097730
H	4.3427030	0.5864850	2.2533640

H	5.6880700	-0.9334470	0.0593390
H	4.8276480	-1.6103700	1.4302540
H	-1.9800980	-2.3867630	1.6140420
H	-3.4478390	1.7131800	-1.5178180
H	-1.1006110	0.8777290	-1.4497070
C	-2.2305250	3.2018690	-0.3345630
C	-0.9509400	2.4589510	0.1167780
H	-2.7079270	3.8544560	0.3954680
H	-2.0779100	3.7571800	-1.2587940
H	-0.8616250	2.3853840	1.2002550
H	-0.0042890	2.8097500	-0.2898230

Cis-ethano L-Proline TS2^{anti}

C	2.8104310	-0.1156350	-0.7300370
C	4.5449060	0.2737580	1.0202160
H	4.6692460	2.2172640	0.0163550
H	5.6040560	0.1657580	0.7843700
H	4.4326010	0.0712930	2.0860200
C	-0.8386470	-2.8190690	-0.0102670
C	1.4460050	-0.7820870	-0.8404880
C	0.6875690	-0.8374150	0.4882980
H	0.8632070	-0.2361190	-1.5849340
H	1.5895420	-1.7931620	-1.2253650
H	0.6597400	0.1450770	0.9587990
H	1.2053870	-1.5083510	1.1730250
C	3.5225670	-0.1133200	-2.1020060
H	4.5028150	0.3631010	-2.0527990
H	3.6549000	-1.1410470	-2.4401500
H	2.9112370	0.4266770	-2.8252230
C	3.9668140	1.6300140	0.6117670
C	2.7620070	1.3303300	-0.2568350
O	1.8958170	2.1168700	-0.5433820
C	-0.7211100	-1.3508090	0.2881480
C	3.7608030	-0.7780330	0.2583740
O	3.8734520	-1.9676240	0.4053890
H	3.6616850	2.2505740	1.4527820
H	-1.8483800	-3.1809290	0.1644450
H	-0.5779860	-2.9949420	-1.0558320
N	-1.5783050	-0.5351030	-0.3417810
C	-2.8392020	-1.0031160	-0.9167650
C	-1.4861930	0.9311830	-0.3448450
C	-3.4818830	0.2607470	-1.5234960
H	-2.6566880	-1.8468200	-1.5778400
C	-2.4078630	1.3342830	-1.5003870
C	-1.8459730	1.6393600	0.9862350
H	-0.4631100	1.2421830	-0.5602290

H	-3.9096790	0.1134080	-2.5122760
H	-1.8434890	1.3146180	-2.4339530
H	-2.7994170	2.3385720	-1.3557710
O	-1.9374730	0.9466840	2.0551640
O	-1.9843830	2.8580190	0.9382240
H	-1.6078340	-0.3070680	2.0698730
O	-1.3092140	-1.3799350	2.0118920
H	-0.1508330	-3.3803910	0.6177670
H	-0.6016020	-1.5539620	2.6403570
C	-4.0308620	-1.1356700	0.0615300
C	-4.5381010	0.2538290	-0.3895170
H	-5.5746580	0.2960420	-0.7183670
H	-4.3801950	1.0377550	0.3515660
H	-4.6965310	-1.9473400	-0.2294620
H	-3.7690710	-1.2486900	1.1114580

Trans-ethano L-Proline TS2^{anti}

C	2.6609140	-0.4275510	-0.7609950
C	4.5467770	0.4559880	0.6169270
H	4.6428610	1.8831450	-1.0387500
H	5.5919190	0.2331390	0.4020630
H	4.4732950	0.6416030	1.6897600
C	-0.9700420	-2.4936510	1.1657630
C	1.2795570	-1.0119310	-0.4956600
C	0.6842430	-0.5780170	0.8466150
H	0.6232600	-0.7105640	-1.3146560
H	1.3562580	-2.0998720	-0.5306980
H	0.7482960	0.5036120	0.9672360
H	1.2544730	-1.0286810	1.6587970
C	3.2118780	-0.9402820	-2.1104140
H	4.1985800	-0.5311890	-2.3326620
H	3.2887700	-2.0270520	-2.0770290
H	2.5300690	-0.6531960	-2.9111360
C	3.9806710	1.6078260	-0.2146400
C	2.6893270	1.0936900	-0.8165000
O	1.8143780	1.7789050	-1.2813180
C	-0.7568840	-1.0184790	0.9719980
C	3.6990450	-0.7620230	0.3026750
O	3.8247270	-1.8438110	0.8159930
H	3.7837540	2.5133210	0.3565840
H	-1.9805220	-2.7104110	1.5024530
H	-0.8051800	-3.0037220	0.2151410
N	-1.6502430	-0.3820250	0.2040690
C	-3.0195740	-0.8517370	0.0223160
C	-1.5123640	0.9856660	-0.3096620
C	-3.7322500	0.2078220	-0.8331620

C	-2.5760780	1.0292300	-1.4081100
C	-1.7086260	2.1071180	0.7411520
H	-0.5187100	1.1401770	-0.7320810
H	-2.1784830	0.5532450	-2.3067910
H	-2.8499230	2.0511720	-1.6546020
O	-1.7186130	1.7957760	1.9799360
O	-1.8167070	3.2526520	0.3138410
H	-1.4150940	0.5973100	2.3753170
O	-1.1474620	-0.4513040	2.6484480
H	-0.2637670	-2.8808930	1.8964960
H	-0.3798830	-0.4510690	3.2285330
H	-4.4576980	0.8377850	-0.3210530
H	-3.4943190	-1.0770260	0.9768510
C	-4.2914850	-0.9178070	-1.7303350
C	-3.2894420	-1.9026820	-1.0812790
H	-5.3245480	-1.1620830	-1.4875740
H	-4.2081080	-0.7648660	-2.8057560
H	-3.6840400	-2.8605270	-0.7474490
H	-2.4041260	-2.0760120	-1.6928040

L-Proline TS3^{syn}

C	-2.4328050	-0.1877340	0.6352220
C	-4.4920400	0.0561890	-0.7506550
H	-4.7155390	1.8807180	0.4436500
H	-5.4576130	-0.2401250	-0.3390070
H	-4.5631800	-0.0421500	-1.8342690
C	1.4431230	-2.0839550	-1.1770950
C	-0.9866210	-0.6248060	0.4512270
C	-0.4659320	-0.4483220	-0.9831320
H	-0.3700220	-0.0518070	1.1468990
H	-0.8996940	-1.6742620	0.7372740
H	2.0618970	-2.0840870	0.0513060
H	-0.9881130	-1.1307090	-1.6515590
C	-2.8827030	-0.4224340	2.0956020
H	-3.9164680	-0.1147940	2.2603170
H	-2.7962550	-1.4828770	2.3322470
H	-2.2409120	0.1484770	2.7668040
C	-4.0490940	1.4518900	-0.3076480
C	-2.6833910	1.2813870	0.3265650
O	-1.9089980	2.1730320	0.5636120
C	1.0012690	-0.7535040	-1.0380340
C	-3.4326410	-0.9110840	-0.2566750
O	-3.3885420	-2.0845320	-0.5217660
H	-3.9802740	2.1706370	-1.1228850
H	2.3727300	-2.2463340	-1.7178150
N	1.8477950	0.2160170	-0.7555980

C	1.4895950	1.6279220	-0.5298410
C	3.2946430	-0.0039020	-0.5715070
C	2.7599290	2.2363930	0.0471940
H	4.8095470	1.4519140	-0.0509220
C	3.8680520	1.4044100	-0.5899340
C	3.5906450	-0.7842680	0.7407550
H	-0.6513810	0.5669220	-1.3335100
H	4.0339180	1.7174530	-1.6218880
H	3.6819570	-0.6063770	-1.3959670
O	2.8269370	-1.7958310	0.9916690
O	4.5210790	-0.4437890	1.4496680
H	0.6718770	-2.8075540	-1.4078610
H	2.8359970	3.2980460	-0.1768220
H	1.2286830	2.0868230	-1.4859970
H	2.7758230	2.1132860	1.1315460
H	0.6364550	1.7145430	0.1399310

L-Proline TS3^{anti}

C	-2.7834360	0.5533120	-0.0198080
C	-3.2241300	-1.8443920	0.5380880
H	-4.7735770	-1.5330150	-0.9671300
H	-4.0001730	-2.2373730	1.1937190
H	-2.3838200	-2.5414450	0.5802070
C	1.1440470	2.5962600	-0.1680840
C	-1.5023530	1.3763710	-0.1320960
C	-0.2799600	0.5228770	-0.4402420
H	-1.6492070	2.1264910	-0.9109080
H	-1.3671480	1.9041590	0.8135220
H	-0.4172090	0.0136430	-1.3978690
H	-0.1873410	-0.2623370	0.3156280
C	-3.9841900	1.4696100	0.2957330
H	-4.9152630	0.9075220	0.3837630
H	-3.8034880	1.9864400	1.2383400
H	-4.0981340	2.2052280	-0.5006650
C	-3.6844460	-1.5928100	-0.8969770
C	-3.1324400	-0.2337130	-1.2767300
O	-3.0018140	0.1775950	-2.4009030
C	1.0374270	1.2488330	-0.5046810
C	-2.7224710	-0.5152380	1.0669140
O	-2.3234940	-0.3227510	2.1866680
H	-3.3543050	-2.3434740	-1.6124080
H	1.4646890	2.1416480	1.2021980
H	2.0465660	3.1363150	-0.4240990
N	2.1142230	0.5036740	-0.7206300
C	3.4665620	1.0669480	-0.8029960
C	2.1414790	-0.9548240	-0.7072990

C	4.3862850	-0.1506540	-0.8617450
H	3.5411720	1.6894810	-1.6973400
C	3.4810240	-1.2674830	-1.3742050
C	2.0625410	-1.5651350	0.7184580
H	1.3125380	-1.3667000	-1.2792360
H	5.2492010	0.0245200	-1.5004430
H	3.3677660	-1.2029140	-2.4575570
H	3.8329270	-2.2647790	-1.1226580
O	2.0897860	-0.7895940	1.7260930
O	1.9899950	-2.7906950	0.7717180
H	1.9732570	0.5642970	1.9363770
H	4.7495650	-0.3913880	0.1381430
H	3.6746950	1.6946580	0.0646310
O	1.8732230	1.6088820	2.1793170
H	0.2418860	3.1898870	-0.1568700
H	1.2386420	1.7061520	2.8959470

Cis-methano L-Proline TS3^{syn}

C	-2.4658840	-0.0723850	0.6302430
C	-4.6110640	-0.2779170	-0.6227540
H	-4.8778000	1.7938310	0.0488470
H	-5.5174820	-0.4934110	-0.0552140
H	-4.7687710	-0.6572940	-1.6323980
C	1.3691300	-2.2113410	-1.2553940
C	-1.0040370	-0.4691340	0.4795440
C	-0.5522740	-0.5998110	-0.9807680
H	-0.3991800	0.2788770	0.9934500
H	-0.8477920	-1.4211010	0.9901350
H	1.9684620	-2.2261070	-0.0229350
H	-1.0926410	-1.4093590	-1.4672630
C	-2.8396590	0.0376380	2.1267060
H	-3.8838060	0.3206920	2.2686740
H	-2.6740970	-0.9253240	2.6098830
H	-2.2095410	0.7900120	2.6012750
C	-4.2213520	1.2012280	-0.5911930
C	-2.8216070	1.2610930	-0.0118000
O	-2.0961490	2.2219700	-0.0450530
C	0.9167190	-0.8903100	-1.0757880
C	-3.4580500	-1.0410040	0.0014700
O	-3.3444320	-2.2394680	0.0103460
H	-4.2203690	1.6733760	-1.5728090
H	2.3045240	-2.3556280	-1.7909440
N	1.7663140	0.0818800	-0.8014040
C	1.4163610	1.4470390	-0.4857050
C	3.2145960	-0.1342820	-0.6067480
C	2.6838240	2.2152350	-0.3324290

H	4.6429260	1.3355190	0.0825140
C	3.8259300	1.2706280	-0.6322290
C	3.5136970	-0.9454000	0.6865590
H	-0.7764970	0.3162100	-1.5295530
H	4.2168570	1.4866260	-1.6260420
H	3.5992670	-0.7339970	-1.4338030
O	2.7286680	-1.9405510	0.9306340
O	4.4689690	-0.6441840	1.3798530
H	0.6060840	-2.9375020	-1.5015160
H	2.7451220	3.2295980	-0.6983150
H	0.5368890	1.8431220	-0.9667530
C	1.8328810	1.9363910	0.8739770
H	2.1713740	1.2120430	1.6039050
H	1.2605560	2.7585190	1.2802980

Cis-methano L-Proline TS3^{anti}

C	-2.6910160	0.0416500	-0.7475720
C	-4.2934620	0.0423420	1.1604420
H	-4.4437250	-2.1028920	0.7106930
H	-5.3547290	0.0839480	0.9096210
H	-4.1836230	0.4700690	2.1566630
C	1.2853840	2.6885540	-0.2479730
C	-1.3314030	0.6249800	-1.1058000
C	-0.4603310	0.9427090	0.1155470
H	-0.8225680	-0.0903190	-1.7553080
H	-1.4816730	1.5361000	-1.6876380
H	2.2564120	0.9327980	1.9914720
H	-0.8995970	1.7647230	0.6779350
C	-3.5273380	-0.2031180	-2.0243890
H	-4.5038030	-0.6342290	-1.7980990
H	-3.6794150	0.7437950	-2.5424230
H	-2.9907370	-0.8889150	-2.6802350
C	-3.7085130	-1.3661260	1.0390700
C	-2.6156960	-1.2869150	-0.0083070
O	-1.8063280	-2.1498460	-0.2343320
C	0.9203300	1.3477300	-0.3168440
C	-3.5362830	0.9102390	0.1732380
O	-3.6013000	2.1109930	0.1135440
H	-3.2769380	-1.7375520	1.9680480
H	2.1777510	3.0388000	-0.7518110
N	1.7703600	0.3863650	-0.6586600
C	3.0625150	0.6464320	-1.2424070
C	1.6229120	-1.0312770	-0.3143600
C	3.6946760	-0.6697480	-1.5385200
H	3.1300000	-2.5763200	-0.6166220
C	2.6960770	-1.7420260	-1.1644540

C	1.7744080	-1.3545350	1.1971560
H	-0.4125750	0.0843000	0.7860850
H	2.2446010	-2.1369850	-2.0745620
H	0.6301930	-1.3864790	-0.5879660
O	2.0458400	-0.4271880	2.0220870
O	1.6030850	-2.5342510	1.4956210
H	0.4842230	3.4091700	-0.1460570
O	2.4133200	1.9935300	2.0372140
H	1.9981760	2.3383370	2.8339160
H	1.8576220	2.4079860	1.0864210
H	4.2645520	-0.7969090	-2.4474440
H	3.1102840	1.4876130	-1.9166050
C	4.2654400	0.2037690	-0.4557530
H	5.1960430	0.7094620	-0.6727960
H	4.1238740	-0.0749300	0.5798090

transM syn TS3

C	-2.5328300	-0.3712170	0.6088290
C	-4.4901430	0.3062450	-0.7836270
H	-4.7020650	1.7801970	0.8212750
H	-5.5059760	-0.0056380	-0.5399550
H	-4.4551470	0.4661830	-1.8622660
C	1.3544650	-2.0211830	-1.4357090
C	-1.1045580	-0.8418560	0.3723930
C	-0.5276680	-0.3992040	-0.9806110
H	-0.4858840	-0.4596470	1.1869730
H	-1.0785950	-1.9308230	0.4354390
H	1.9565300	-2.2511340	-0.2198350
H	-1.0462220	-0.9122590	-1.7888920
C	-3.0535760	-0.8924340	1.9675260
H	-4.0750000	-0.5648020	2.1673950
H	-3.0351420	-1.9822320	1.9646830
H	-2.4095850	-0.5248490	2.7666170
C	-4.0194970	1.5284910	0.0063760
C	-2.6906280	1.1428970	0.6230810
O	-1.8784890	1.9125540	1.0694100
C	0.9311260	-0.7316300	-1.0611480
C	-3.5300790	-0.8203780	-0.4510800
O	-3.5512880	-1.9169700	-0.9473480
H	-3.8953710	2.4255810	-0.5977940
H	2.2909360	-2.1009360	-1.9830930
N	1.7858100	0.1502990	-0.5799290
C	1.4359900	1.4518570	-0.0579920
C	3.2309180	-0.1090790	-0.4322900
C	2.7104820	2.1928120	0.1573850
H	4.5884510	1.2061320	0.5918880

C	3.8600950	1.2705800	-0.2124630
C	3.5000340	-1.1223200	0.7177440
H	-0.6639790	0.6737590	-1.1211600
H	4.3738430	1.6097720	-1.1116050
H	3.6064850	-0.5712440	-1.3469660
O	2.7151090	-2.1475910	0.7649500
O	4.4265920	-0.9388380	1.4857910
H	0.5757090	-2.6747600	-1.8071370
C	1.7741510	2.6214030	-0.9366010
H	2.8133380	2.8290030	1.0238250
H	0.6069540	1.4950290	0.6331540
H	2.0545220	2.4121700	-1.9612350
H	1.2004480	3.5252720	-0.7851120

Trans-methano L-Proline TS3^{anti}

C	-2.6316000	0.1233440	-0.7681020
C	-4.3434800	-0.0717700	1.0313440
H	-4.4304430	-2.1784810	0.4082950
H	-5.3837880	-0.0207350	0.7050100
H	-4.3172240	0.2620580	2.0681080
C	1.3077410	2.6760910	0.2669550
C	-1.2565290	0.7416790	-0.9789120
C	-0.4552780	0.9052720	0.3185010
H	-0.7105990	0.1107450	-1.6834420
H	-1.3790190	1.7177950	-1.4515590
H	2.2331380	0.5751930	2.2549950
H	-0.9289200	1.6543590	0.9508130
C	-3.3864530	0.0124740	-2.1120850
H	-4.3733140	-0.4370460	-1.9914470
H	-3.5098770	1.0076440	-2.5393760
H	-2.8078760	-0.6042920	-2.7999850
C	-3.7256070	-1.4554080	0.8217540
C	-2.5898110	-1.2738900	-0.1653150
O	-1.7696100	-2.1120430	-0.4408720
C	0.9445460	1.3557870	0.0183290
C	-3.5348490	0.8931150	0.1854400
O	-3.6026550	2.0936020	0.2454230
H	-3.3227800	-1.8899580	1.7364970
H	2.2121190	3.0742200	-0.1776980
N	1.8292100	0.4405730	-0.3536100
C	3.1933540	0.7577530	-0.6995620
C	1.6477000	-1.0101410	-0.2880840
C	3.7733750	-0.4696600	-1.3162780
H	3.0971760	-2.4987770	-0.9154020
C	2.7022430	-1.5501040	-1.2698420
C	1.8451570	-1.5784800	1.1431410

H	-0.4386020	-0.0290710	0.8813900
H	2.2599850	-1.7166790	-2.2526370
H	0.6432920	-1.2939820	-0.5975900
O	2.0898110	-0.7789390	2.1007800
O	1.7341020	-2.7974700	1.2516980
H	0.5032630	3.3831020	0.4222930
O	2.3574120	1.6282070	2.4573020
H	1.9285900	1.8439920	3.2908970
H	1.8268180	2.2018020	1.5679310
H	4.7971960	-0.7390930	-1.1036710
H	3.7415900	1.3801280	-0.0061850
C	3.5149080	0.7446310	-2.1647380
H	2.6812690	0.7169500	-2.8552220
H	4.3685540	1.3250990	-2.4866720

Cis-ethano L-Proline TS3^{syn}

C	-2.7790860	-0.2462000	0.6015030
C	-4.7003740	0.1958740	-0.9206480
H	-4.8875200	2.0927270	0.1793620
H	-5.6762200	-0.0474670	-0.4957490
H	-4.7966870	0.1265950	-2.0033550
C	0.9356030	-2.3760780	-0.7535070
C	-1.3419460	-0.7450230	0.5199260
C	-0.6693800	-0.4459770	-0.8268510
H	-0.7720420	-0.2823620	1.3275760
H	-1.3457020	-1.8201150	0.7020810
H	1.6255300	-2.2353800	0.4325040
H	-1.2285190	-0.9315970	-1.6284110
C	-3.3821740	-0.5762680	1.9857910
H	-4.4133490	-0.2307480	2.0752220
H	-3.3643040	-1.6552660	2.1396830
H	-2.7876430	-0.0930340	2.7611720
C	-4.1714230	1.5461940	-0.4356420
C	-2.9382930	1.2541870	0.3979880
O	-2.1939120	2.0871690	0.8467560
C	0.7300870	-0.9879500	-0.8664070
C	-3.7103810	-0.8478450	-0.4420700
O	-3.6699450	-1.9909420	-0.8181670
H	-3.8817010	2.2080480	-1.2522980
H	1.7843900	-2.7996880	-1.2844900
N	1.7485260	-0.1480250	-0.8428080
C	1.6380830	1.3153160	-0.8661200
C	3.1451530	-0.5974680	-0.6732480
C	3.0927300	1.8145040	-0.7704190
H	4.9140060	0.6345710	-0.4879850
C	3.9849530	0.6182640	-1.0530600

C	3.4154660	-1.1557070	0.7530100
H	-0.6826500	0.6258910	-1.0107420
H	4.2245270	0.5752470	-2.1158260
H	3.3391430	-1.4254190	-1.3587260
O	2.4923330	-1.9048330	1.2592210
O	4.4716010	-0.9105060	1.3081920
H	0.0423940	-2.9857540	-0.8038450
H	3.3081010	2.6620020	-1.4162340
H	1.0444190	1.6310490	-1.7205620
C	2.8401990	2.2204510	0.7034130
C	1.3290120	1.9703140	0.4979690
H	3.3013890	1.5373130	1.4160550
H	3.1229090	3.2379940	0.9647520
H	0.8259790	1.3389950	1.2276570
H	0.7538710	2.8859490	0.3740360

Trans-ethano L-Proline TS3^{syn}

C	-2.6424490	-0.4020490	0.6027640
C	-4.6137970	0.4221980	-0.6787680
H	-4.6218810	2.0084190	0.8409780
H	-5.5970680	0.1572100	-0.2865080
H	-4.7292870	0.5777540	-1.7510740
C	1.1247650	-2.2389890	-1.4750290
C	-1.2515230	-0.9612510	0.3405830
C	-0.6503130	-0.5074520	-0.9979450
H	-0.6049270	-0.6540470	1.1651130
H	-1.3009790	-2.0509740	0.3622350
H	1.7059990	-2.5139610	-0.2565360
H	-1.2006290	-0.9596180	-1.8214610
C	-3.1861120	-0.9236980	1.9528020
H	-4.1797190	-0.5308880	2.1735470
H	-3.2435830	-2.0117140	1.9215250
H	-2.5101130	-0.6230000	2.7533780
C	-3.9885250	1.6178630	0.0425550
C	-2.6984440	1.1178450	0.6615670
O	-1.8406800	1.8164810	1.1382290
C	0.7861470	-0.9266300	-1.0917560
C	-3.6794790	-0.7518870	-0.4555370
O	-3.7500710	-1.8122990	-1.0209440
H	-3.7592620	2.4519660	-0.6199770
H	2.0558440	-2.3758980	-2.0201020
N	1.6964330	-0.1005910	-0.6172560
C	1.4355560	1.2171170	-0.0410400
C	3.1157370	-0.4642540	-0.4537940
C	2.7799200	1.7442010	0.4808120
H	4.7307200	0.7477630	0.3228650

C	3.8118000	0.8739490	-0.2427780
C	3.2972670	-1.4774370	0.7093100
H	-0.7264320	0.5751870	-1.1012550
H	4.0610870	1.3037950	-1.2142680
H	3.4745120	-0.9555170	-1.3603820
O	2.4603270	-2.4623460	0.7381210
O	4.2050040	-1.3314560	1.5081800
H	0.3065240	-2.8384220	-1.8532160
H	2.9222870	1.7280480	1.5594200
H	0.6315480	1.1791520	0.6903710
C	2.4694900	3.1089250	-0.1728020
C	1.3443260	2.4329400	-0.9930170
H	3.2797390	3.5740910	-0.7325220
H	2.0767280	3.8266050	0.5456200
H	1.6489480	2.1766140	-2.0071360
H	0.3820720	2.9401920	-1.0260640

Cis-ethano L-Proline TS3^{anti}

C	-2.8865960	-0.0295180	-0.7627170
C	-4.4992820	0.0870380	1.1362400
H	-4.6840020	-2.0592950	0.7258250
H	-5.5684610	0.1407900	0.9273420
H	-4.3388000	0.5631310	2.1039390
C	1.0666750	2.6804240	-0.3061890
C	-1.5264470	0.5459170	-1.1323830
C	-0.6809900	0.9460060	0.0822210
H	-0.9997550	-0.1996620	-1.7313690
H	-1.6763630	1.4195170	-1.7692870
H	1.8332480	0.9880180	2.0676700
H	-1.1394860	1.7958220	0.5852380
C	-3.6960970	-0.3645700	-2.0361720
H	-4.6746400	-0.7857720	-1.8005320
H	-3.8431990	0.5451650	-2.6183020
H	-3.1433340	-1.0884800	-2.6351750
C	-3.9428000	-1.3366890	1.0733590
C	-2.8131060	-1.3056320	0.0639780
O	-1.9798960	-2.1644030	-0.0749610
C	0.7064920	1.3377230	-0.3426630
C	-3.7565110	0.8890150	0.0843040
O	-3.8459510	2.0798030	-0.0692510
H	-3.5619650	-1.7015070	2.0261890
H	1.9952870	3.0065460	-0.7591830
N	1.5728280	0.3737340	-0.6291660
C	2.8763320	0.6405900	-1.2322510
C	1.4124870	-1.0342730	-0.2656550
C	3.4913840	-0.7554340	-1.4668740

H	2.7314660	-2.6899630	-0.7687210
C	2.3795210	-1.7591990	-1.2082400
C	1.6726760	-1.3409690	1.2361440
H	-0.6345470	0.1314870	0.8060440
H	1.8644190	-1.9932730	-2.1409070
H	0.3908880	-1.3651450	-0.4503180
O	1.8289660	-0.3819130	2.0559990
O	1.6728450	-2.5313280	1.5422380
H	0.2639490	3.4065850	-0.2818300
O	1.8611690	2.0616380	2.1446000
H	1.2670770	2.3472580	2.8455030
H	1.4649570	2.4425050	1.0974990
H	3.9545300	-0.8819370	-2.4423930
H	2.7449870	1.3039960	-2.0856560
C	4.5093860	-0.4860060	-0.3307170
C	4.0370160	0.9837660	-0.2675430
H	5.5543090	-0.6372350	-0.5942650
H	4.2967990	-1.0495680	0.5780750
H	4.7373930	1.6781830	-0.7297410
H	3.7575420	1.3671930	0.7104690

Trans-ethano L-Proline TS3^{anti}

C	2.7861360	-0.3089310	-0.8113940
C	4.6250150	0.1919430	0.7937160
H	4.7351960	2.0845470	-0.3155560
H	5.6450470	0.0244900	0.4441260
H	4.6390790	0.0937220	1.8789490
C	-1.1183410	-2.4816630	0.9621220
C	1.3877230	-0.9099000	-0.8033920
C	0.6762200	-0.7894990	0.5496630
H	0.8053880	-0.4116810	-1.5813550
H	1.4567330	-1.9633900	-1.0803410
H	-1.9007340	-0.0078770	2.5453790
H	1.1797220	-1.4129840	1.2866100
C	3.4487570	-0.5030390	-2.1944730
H	4.4518580	-0.0754880	-2.2319150
H	3.5192640	-1.5686000	-2.4130320
H	2.8383080	-0.0198860	-2.9575660
C	4.0431460	1.5234460	0.3149430
C	2.8184840	1.1829190	-0.5105790
O	1.9900580	1.9739320	-0.8834170
C	-0.7485370	-1.2470450	0.4337710
C	3.7388050	-0.8972310	0.2198790
O	3.7863530	-2.0614740	0.5227280
H	3.7452110	2.1840470	1.1285460
H	-2.0543140	-2.9359100	0.6597600

N	-1.6399320	-0.4031060	-0.0631370
C	-3.0394640	-0.7534710	-0.2633270
C	-1.4385890	1.0269070	-0.2876270
C	-3.7147600	0.4833330	-0.8773830
H	-2.7670060	2.4283180	-1.2941600
C	-2.5366520	1.3661150	-1.2989970
C	-1.5595930	1.8716670	1.0085170
H	0.7140690	0.2380680	0.9141940
H	-2.1940170	1.0960980	-2.2998840
H	-0.4513480	1.2275330	-0.7008720
O	-1.7865920	1.2841400	2.1137470
O	-1.4175360	3.0845460	0.8717160
H	-0.3185800	-3.1680120	1.2083240
O	-2.0018770	-0.9978180	2.9674440
H	-1.5032560	-1.0444090	3.7888000
H	-1.5436350	-1.7462470	2.1718710
H	-4.4104730	1.0189790	-0.2344780
H	-3.4878560	-1.1290780	0.6563670
C	-3.3970410	-1.5707270	-1.5274050
C	-4.3334910	-0.4189670	-1.9688160
H	-5.3815780	-0.6418150	-1.7758120
H	-4.2306510	-0.0693810	-2.9953840
H	-3.8631800	-2.5385180	-1.3544550
H	-2.5338610	-1.7025330	-2.1792040

Cis-ethano TSoxa^{endo}

C	-2.7115700	-0.1647190	0.6095830
C	-4.5161720	0.2323410	-1.0610910
H	-4.7914970	2.1516730	-0.0204870
H	-5.5201530	-0.0065650	-0.7046570
H	-4.5312020	0.1382070	-2.1461170
C	0.8319320	-2.4765090	-0.9775590
C	-1.2713860	-0.6595490	0.6522420
C	-0.4990950	-0.3630670	-0.6346270
H	-0.7654960	-0.1902630	1.4948230
H	-1.2904900	-1.7318490	0.8489220
H	-0.4275050	0.7119210	-0.7761140
H	-1.0497060	-0.7681120	-1.4887930
C	-3.4184040	-0.4639930	1.9513010
H	-4.4534530	-0.1186820	1.9550400
H	-3.4115270	-1.5392210	2.1307190
H	-2.8840830	0.0377340	2.7580730
C	-4.0298650	1.5961010	-0.5690870
C	-2.8597920	1.3297160	0.3590460
O	-2.1533110	2.1776770	0.8403090
C	0.8599770	-1.0054020	-0.6846000

C	-3.5595880	-0.7942180	-0.4866180
O	-3.4846560	-1.9445370	-0.8350690
H	-3.6840770	2.2416530	-1.3769120
H	1.7887750	-2.9700550	-0.8481300
H	0.0960550	-2.9702080	-0.3477660
N	1.9164410	-0.2800790	-1.0550580
C	1.9252410	1.1919640	-1.0544470
C	3.1639570	-0.7842190	-0.4944180
C	3.4015550	1.5982860	-0.8221480
C	4.2008390	0.3020150	-0.7341500
C	2.8027750	-1.1066650	0.9928040
H	3.4684790	-1.7239950	-0.9529580
H	4.7218700	0.1073540	-1.6713580
H	4.9373620	0.3143340	0.0683550
O	1.5518990	-1.2251050	1.1860430
O	3.6993940	-1.2489770	1.8196400
H	0.5180990	-2.5908870	-2.0184620
H	3.8088200	2.2838570	-1.5609780
H	1.4410540	1.5523530	-1.9590630
C	3.0065310	2.2684560	0.5145540
C	1.5245580	1.9254990	0.2532200
H	3.4313420	1.7775480	1.3903980
H	3.2280010	3.3323310	0.5709680
H	1.0490640	1.3044930	1.0084300
H	0.8896140	2.7882290	0.0600590

Trans-ethano TSoxa*endo*

C	-2.5305570	-0.1692440	0.6687880
C	-4.4822700	0.2538060	-0.8294550
H	-4.6017490	2.0806770	0.3718370
H	-5.5038810	0.0560200	-0.5040250
H	-4.4678050	0.1526050	-1.9155330
C	1.1709840	-2.1865470	-1.8875180
C	-1.1270110	-0.7481820	0.5447820
C	-0.5601390	-0.6447440	-0.8740580
H	-0.4816290	-0.2333870	1.2559440
H	-1.1499200	-1.7939890	0.8478610
H	-0.6730250	0.3724990	-1.2543630
H	-1.1323270	-1.2948150	-1.5349740
C	-3.0511200	-0.3382330	2.1145570
H	-4.0553610	0.0696310	2.2403050
H	-3.0753760	-1.3987950	2.3648420
H	-2.3798730	0.1769300	2.8019090
C	-3.9421560	1.6043730	-0.3570090
C	-2.6254930	1.3123090	0.3337700
O	-1.7779460	2.1292130	0.5909340

C	0.8960200	-1.0192350	-0.9919650
C	-3.5635600	-0.8063090	-0.2513060
O	-3.6403850	-1.9859260	-0.4799440
H	-3.7802050	2.3214090	-1.1602200
H	2.2127160	-2.4905830	-1.9079260
H	0.5534220	-3.0310340	-1.5898560
N	1.8248180	-0.0763540	-0.8317110
C	1.5701420	1.2335680	-0.2242270
C	3.0948060	-0.5974100	-0.3297860
C	2.7595000	1.5643320	0.6921040
C	3.8545320	0.6048290	0.2123370
C	2.6754180	-1.6463410	0.7510570
H	3.6642560	-1.1231910	-1.0951840
H	4.4477790	1.0568480	-0.5841280
H	4.5330040	0.2983070	1.0051900
O	1.4570860	-1.9927390	0.6749660
O	3.5183340	-2.0580060	1.5446730
H	0.8737720	-1.8889180	-2.8975950
H	0.5971080	1.2933560	0.2511650
H	2.5886510	1.4808420	1.7639780
C	2.7932020	2.9845310	0.0869610
C	1.9030900	2.4792750	-1.0747130
H	3.7737970	3.3808490	-0.1738150
H	2.2742080	3.7066800	0.7156180
H	2.4788070	2.2147740	-1.9611740
H	1.0608710	3.1027560	-1.3688390

Cis-ethano TSoxa^{exo}

C	2.6402910	-0.0570990	-0.6357880
C	4.4885110	-0.5523860	0.9578290
H	5.3918010	1.2798490	0.1420670
H	5.3450600	-1.0672210	0.5183190
H	4.4761890	-0.8002750	2.0185000
C	-1.5886090	0.6788930	2.0390870
C	1.1176960	-0.0362240	-0.6710870
C	0.4854500	0.2454360	0.6833700
H	0.7957610	0.7224480	-1.3865150
H	0.7868130	-1.0024930	-1.0525450
H	0.8831130	1.1704750	1.1115480
H	0.7302230	-0.5347750	1.4118170
C	3.2044670	-0.3591030	-2.0433680
H	4.2953490	-0.3789050	-2.0537400
H	2.8381310	-1.3297350	-2.3780670
H	2.8665200	0.4103280	-2.7376470
C	4.5014270	0.9521900	0.6806940
C	3.2838420	1.2439430	-0.1758780

O	2.8843880	2.3432840	-0.4607820
C	-0.9961430	0.4260850	0.6871950
C	3.2303200	-1.0949020	0.3087190
O	2.7643780	-2.1885590	0.5016170
H	4.4372350	1.5548480	1.5866800
H	-2.6568610	0.8715090	2.0185140
H	-1.4230150	-0.2467170	2.6037350
N	-1.7004140	-0.0614240	-0.3376450
C	-1.7711920	-1.4256360	-0.8596370
C	-2.9595060	0.5814670	-0.6502920
C	-3.2730890	-1.7654690	-0.5532690
C	-4.0206800	-0.4441080	-0.2530210
C	-2.8522880	2.0357470	-0.1725570
H	-2.9824030	0.6518090	-1.7461070
H	-4.9345430	-0.3339540	-0.8326400
H	-4.2763550	-0.3713570	0.8050840
O	-1.6601330	2.3669350	0.1382500
O	-3.8441400	2.7606750	-0.1818850
H	-1.0800080	1.4878460	2.5570000
C	-2.7874800	-2.6355250	0.6329690
C	-1.3424430	-2.5516030	0.0938740
H	-2.9125710	-2.1305860	1.5914000
H	-3.2153280	-3.6329160	0.7082060
H	-0.5423340	-2.3435780	0.8022940
H	-1.0649490	-3.4344300	-0.4794010
H	-1.4325880	-1.4703050	-1.8942410
H	-3.7417150	-2.3508200	-1.3413830

Trans-ethano TSoxa^{exo}

C	2.5727980	-0.0075140	-0.7004580
C	4.4023270	-1.3730990	0.2953160
H	5.5031610	0.5293880	0.4061090
H	5.1742510	-1.6801010	-0.4131520
H	4.4002680	-2.1045570	1.1024460
C	-1.1804100	-0.6534910	2.5510470
C	1.0638040	0.1754360	-0.5625280
C	0.5649520	-0.1346060	0.8400390
H	0.8360950	1.2070170	-0.8320420
H	0.5882240	-0.4840860	-1.2903720
H	1.0237440	0.5375210	1.5659430
H	0.8962270	-1.1447720	1.1144400
C	3.0231450	0.3456220	-2.1365310
H	4.0995280	0.2257830	-2.2693530
H	2.5127570	-0.3063700	-2.8455710
H	2.7624450	1.3822310	-2.3501340
C	4.5854000	0.0680020	0.7729150

C	3.4008750	0.8537980	0.2435850
O	3.1519360	1.9990910	0.5187450
C	-0.9028060	-0.1732650	1.1631760
C	3.0664440	-1.4201470	-0.4198890
O	2.4827130	-2.4249380	-0.7357840
H	4.5953680	0.1581860	1.8594890
H	-2.0085910	-0.1019170	2.9910950
H	-1.4510350	-1.7112940	2.5260920
N	-1.8661280	-0.2767650	0.2569760
C	-3.2180860	-0.7329400	0.6128020
C	-1.9306500	0.7932210	-0.7367800
C	-4.0339950	-0.4081730	-0.6452720
C	-3.3124760	0.7045980	-1.3941290
C	-1.6508730	2.1047910	0.0704650
H	-1.1411610	0.7126990	-1.4777850
H	-3.2327760	0.4843600	-2.4579600
H	-3.8211100	1.6620160	-1.2917420
O	-1.1376500	1.9069480	1.2078390
O	-1.9149220	3.1829390	-0.4626690
H	-0.3003260	-0.5379620	3.1776260
H	-5.0735540	-0.1756540	-0.4277950
H	-3.5452000	-0.3202710	1.5654140
C	-3.4165130	-2.2356920	0.3455080
C	-3.8461150	-1.8789210	-1.0970670
H	-4.7251520	-2.3854510	-1.4901680
H	-3.0280720	-1.9840400	-1.8106440
H	-4.2418050	-2.6285600	0.9375960
H	-2.5439430	-2.8748450	0.4733940

1.1. Hajos-Parish calculations for L-proline

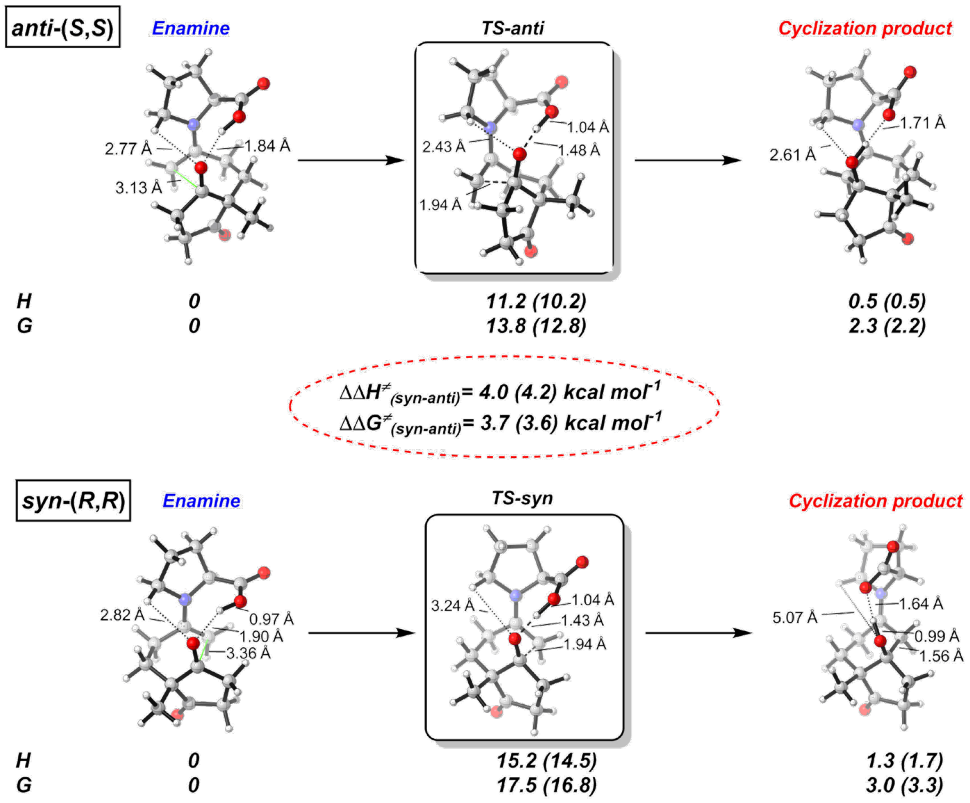


Figure 20. Thermochemical parameters (in kcal.mol^{-1}) of the proline-catalyzed reaction for diastereomeric transition states, calculated in the gas phase by DFT at the ωB97x-D/def2-TZVP level of theory. Results were consolidated using the M06-2X functional, for which values are found between brackets.

Table 1. DLPNO-CCSD(T) energies for the HPESW reaction using the different catalysts. Geometries and thermochemical corrections were extracted from the ωB97x-D and MN15 calculations.

Entry		DLPNO-CCSD(T) $\Delta G^{\neq}$ ($\Delta H^{\neq}$)		$\Delta\Delta G^{\neq}$ ($\Delta\Delta H^{\neq}$)	
		Geometries			
		ωB97x-D	*MN15*	*ωB97x-D*	*MN15*
L-Proline	*syn*	14.2 (11.9)	17.0 (15.0)	3.6 (3.8)	2.9 (3.7)
	anti	10.7 (8.2)	14.1 (11.4)		
cis-methano	*syn*	16.6 (13.3)	16.0 (12.8)	4.5 (4.8)	4.4 (3.8)
	anti	12.1 (9.0)	11.7 (9.0)		
trans-methano	*syn*	19.4 (17.0)	19.2 (17.1)	4.9 (5.6)	5.1 (5.6)
	anti	14.5 (11.5)	14.0 (11.5)		
cis-ethano	*syn*	15.0 (12.4)	13.8 (10.8)	1.9 (2.5)	2.9 (2.7)
	anti	13.1 (9.9)	10.9 (8.2)		
trans-ethano	*syn*	18.5 (16.4)	16.6 (14.3)	5.3 (5.9)	5.5 (5.4)
	anti	13.3 (10.5)	11.1 (8.9)		

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