Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Conformational Analysis of Helical Aminoisobutyric Acid (Aib) Oligomers Bearing C-Terminal Schellman Motifs

Sarah J. Pike,[†] James Raftery,[†] Simon J. Webb,*[‡†] Jonathan Clayden,*[†]

[†] School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.

[‡] Manchester Institute of Biotechnology and School of Chemistry, University of Manchester, 131 Princess St., Manchester, M1 7DN, UK.

Email: s.webb@manchester.ac.uk, clayden@manchester.ac.uk

Content 2

General Experimental Section

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Ultrashield 300 and 400 MHz spectrometer. ^{1}H and ^{13}C spectra were referenced relative to the solvent residual peaks and chemical shifts (δ) reported in ppm downfield of tetramethylsilane ($CDCl_3$ δ H: 7.26 ppm, δ C: 77.0 ppm). Coupling constants (J) are reported in Hertz and rounded to 0.1 Hz. Splitting patterns are abbreviated as follows: singlet (s) and broad (br).

Low and high resolution mass spectra were recorded by staff at the University of Manchester. Electrospray (ES) spectra were recorded on a Waters Platform II and high resolution mass spectra (HRMS) were recorded on a Thermo Finnigan MAT95XP and are accurate to ± 0.001 Da. Infrared spectra were recorded on an Ati Mason Genesis Series FTIR spectrometer as thin films on a sodium chloride plate. Melting points were determined on a GallenKamp apparatus and are uncorrected. Thin layer chromatography (TLC) was performed using commercially available pre-coated plates (Macherey-Nagel alugram. Sil G/UV254) and visualized with UV light at 254 nm; phosphomolybdic acid dip was used to reveal the products. Flash column chromatography was carried out using Fluorochem Davisil 40-63m 60Å.

All reactions were conducted under a nitrogen atmosphere in oven-dried glassware unless stated otherwise. Dichloromethane was obtained by distillation over calcium hydride under a nitrogen atmosphere. Anhydrous acetonitrile was purchased from Sigma-Aldrich. Triethylamine was distilled over calcium hydride under nitrogen atmosphere. Petrol refers to the fraction of light petroleum ether boiling between 40 and 60 °C. All other solvents and commercially available reagents were used as received.

Procedures for the synthesis of $N_3Aib_nO^tBu$ where n = 2-4 have been reported previously.[1]

NOE Spectra

Partial NOE spectra for $N_3Aib_3O^tBu$.

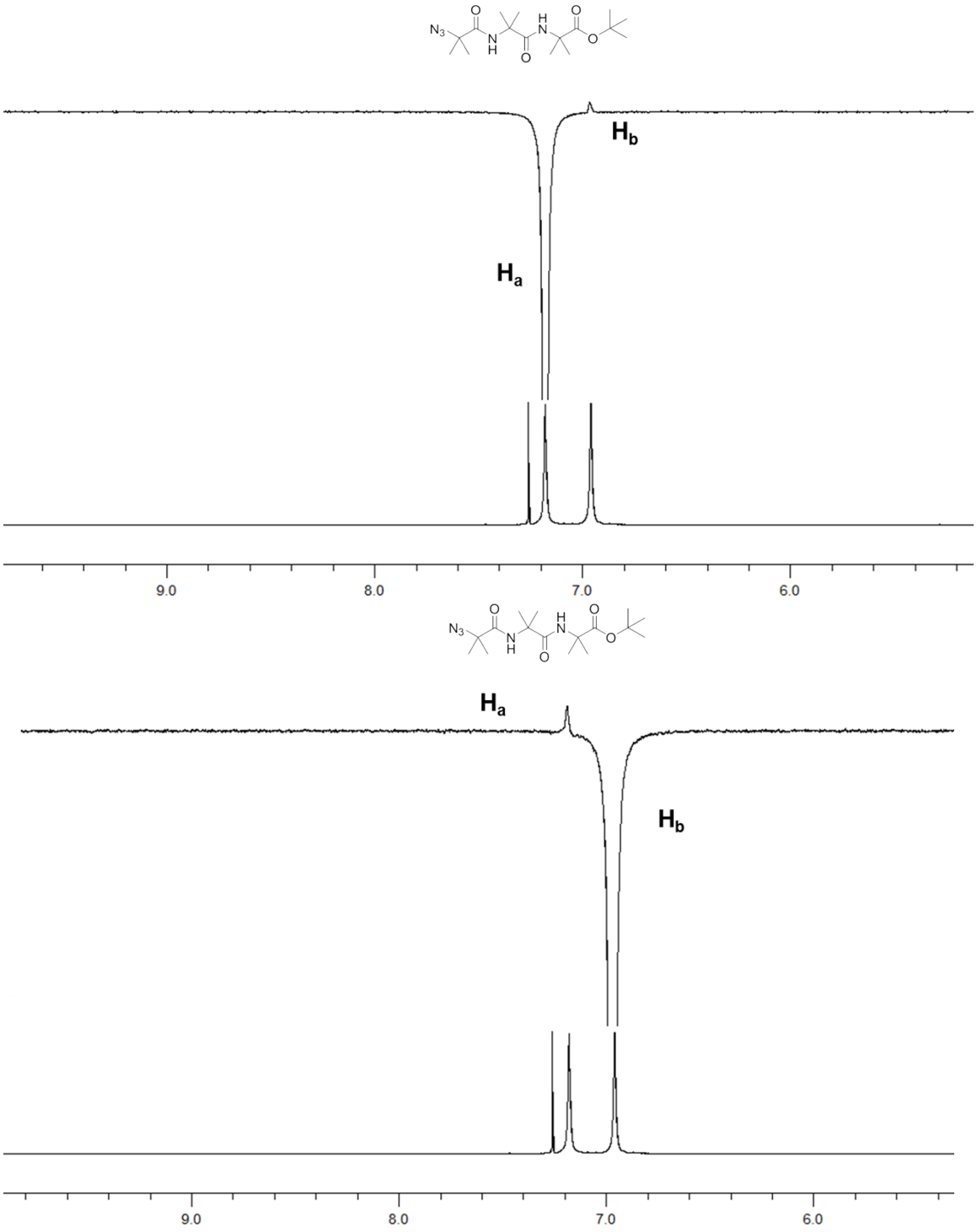


Figure 1. Partial NOE spectra for $N_3Aib_3O^tBu$ showing through-space coupling between NH protons with selective irradiation of each NH peak.

NOE spectra for $N_3Aib_4O^tBu$.

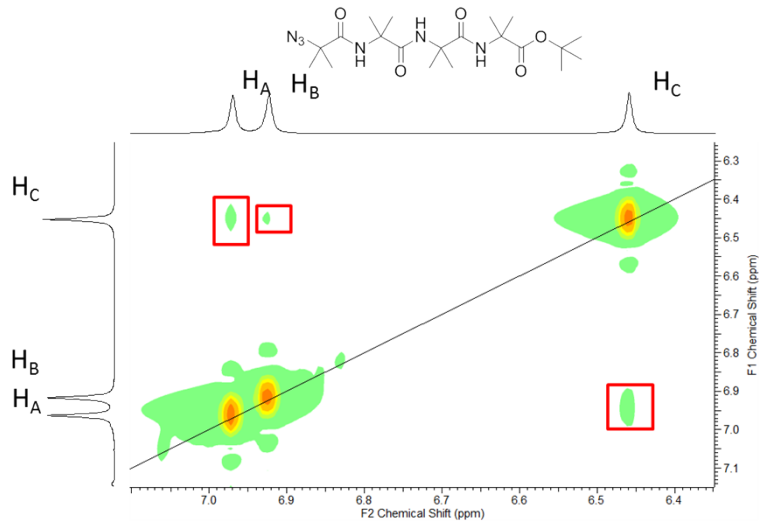


Figure 2. Partial NOE spectra for $N_3Aib_4O^tBu$ showing through-space coupling between NH protons.

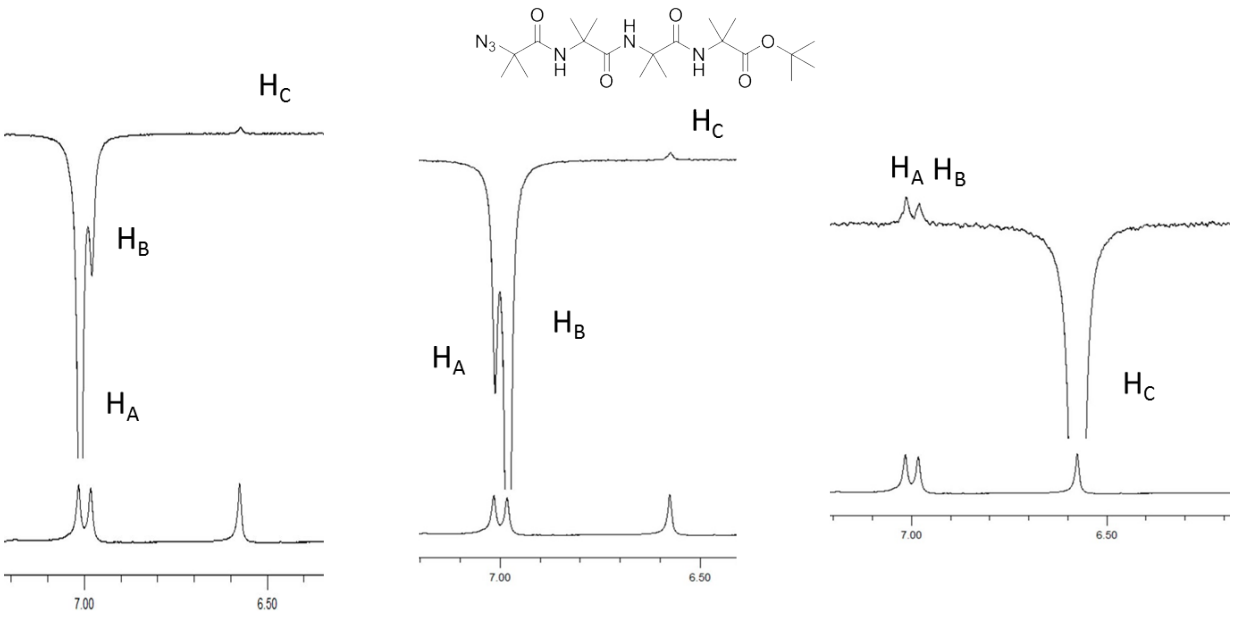


Figure 4. Partial NOE spectra for $N_3Aib_4O^tBu$ showing through-space coupling between NH protons with selective irradiation of each NH peak.

Partial NOE spectra for N_3Aib_4OMe

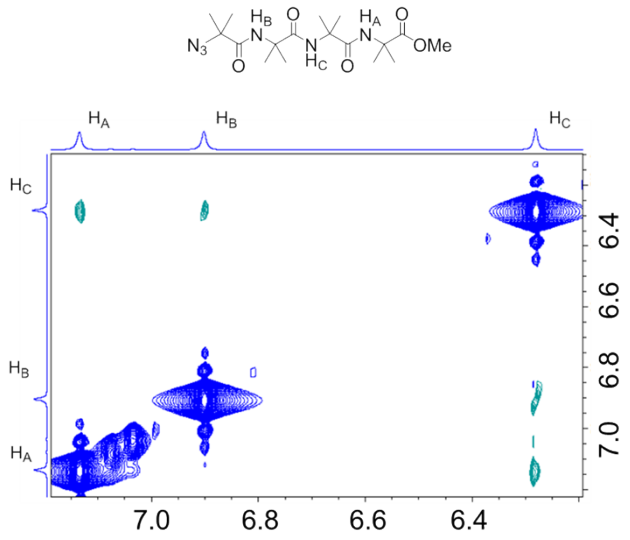


Figure 3. Partial NOE spectra for N_3Aib_4OMe showing through-space coupling between NH protons.

Partial NOE spectra for $N_3Aib_5O^tBu$.

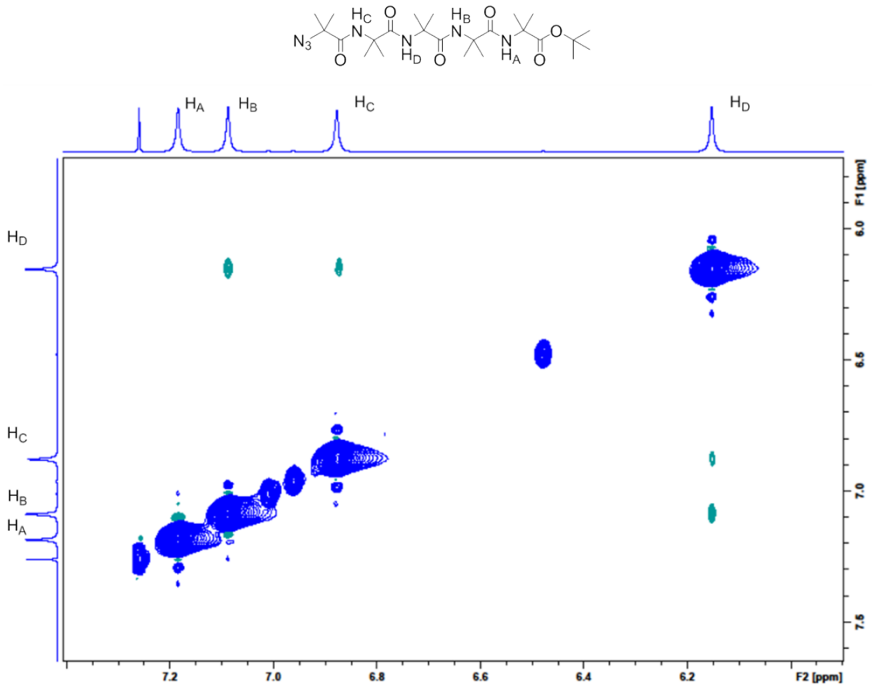


Figure 5. Partial NOE spectra for $N_3Aib_5O^tBu$ showing through-space coupling between NH protons with selective irradiation of each NH peak.

NOE spectra for N_3Aib_5OMe.

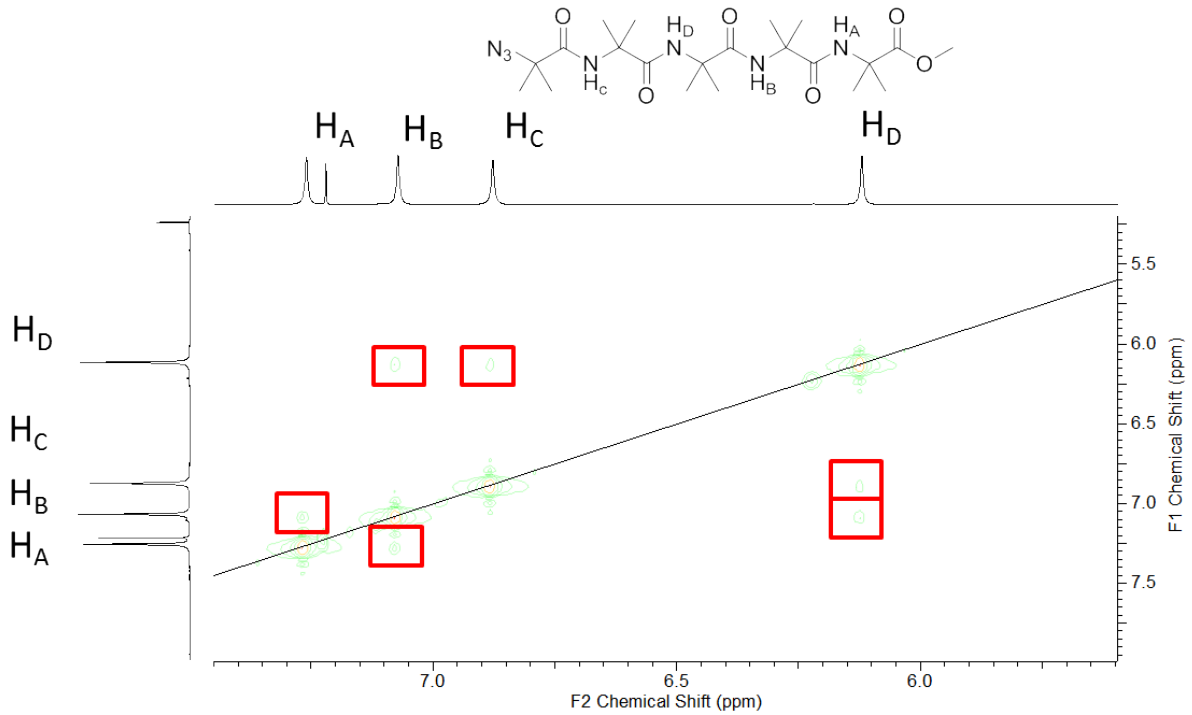
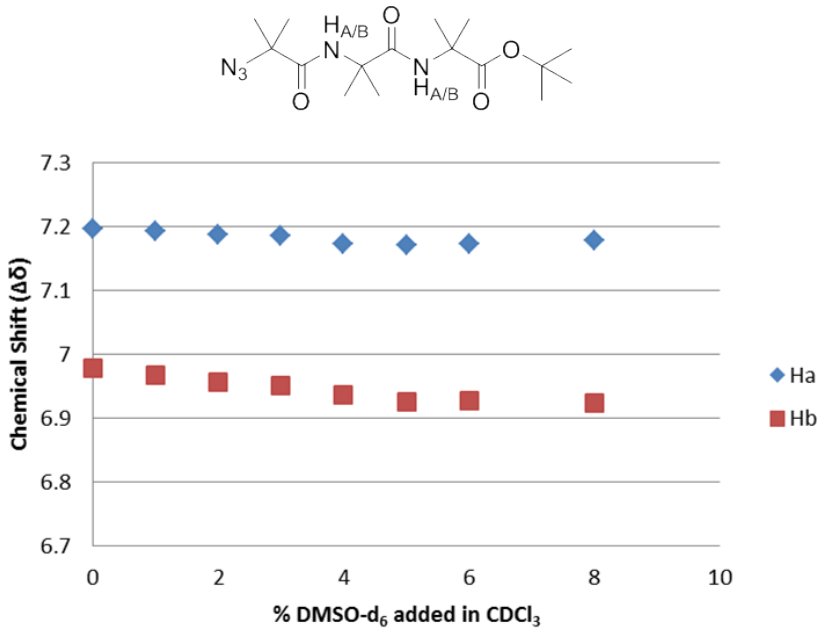


Figure 6. Partial NOE spectra for N_3Aib_5OMe showing through-space coupling between NH protons.

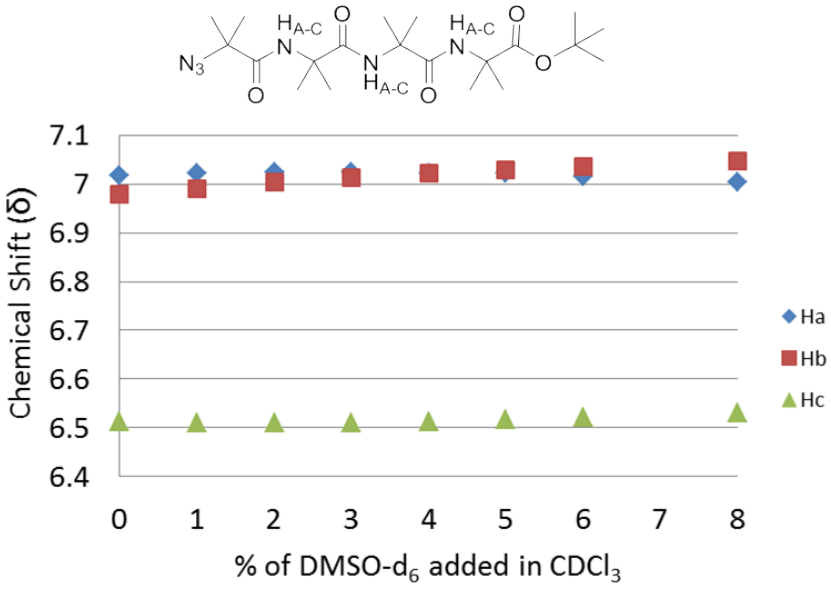
DMSO-d_6 titrations

DMSO-d_6 Titration for $N_3Aib_3O^tBu$



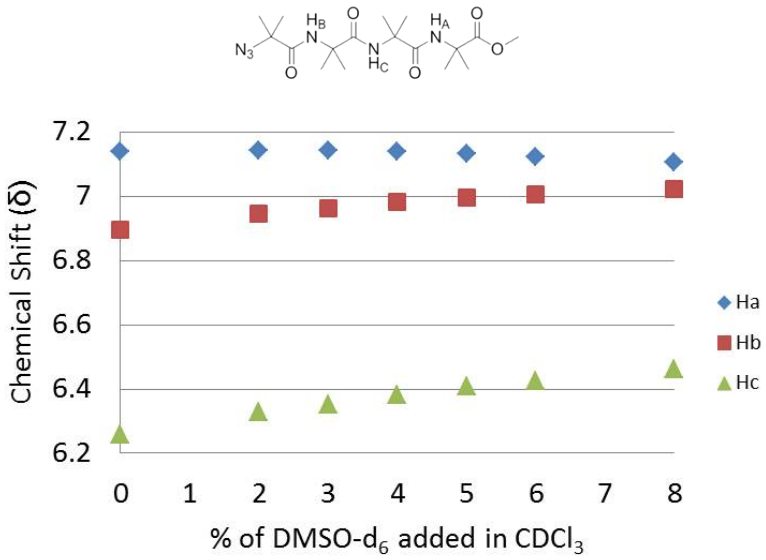
Graph 1. A graph to show the plot of % DMSO *vs* chemical shift for the NH protons of a 0.005M solution of $N_3Aib_3O^tBu$.

DMSO-d_6 Titration for $N_3Aib_4O^tBu$



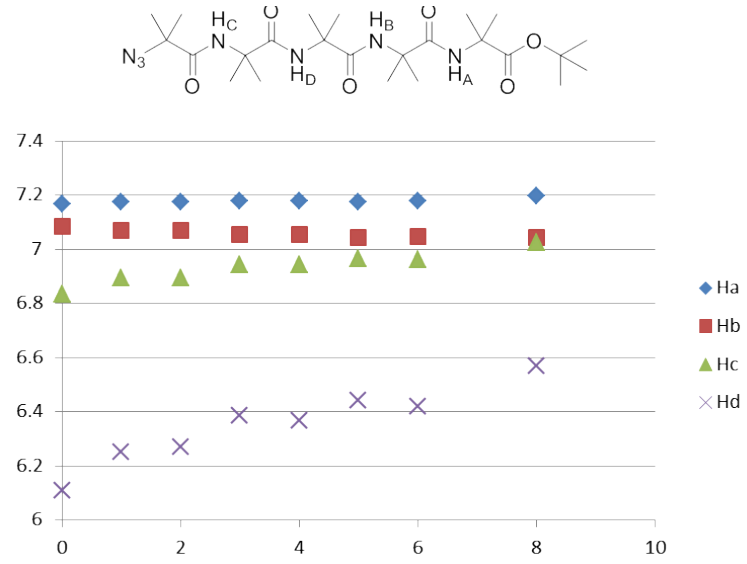
Graph 2. A graph to show the plot of % DMSO *vs* chemical shift for the NH protons of a 0.005M solution of $N_3Aib_4O^tBu$.

DMSO-d_6 Titration for N_3Aib_4OMe



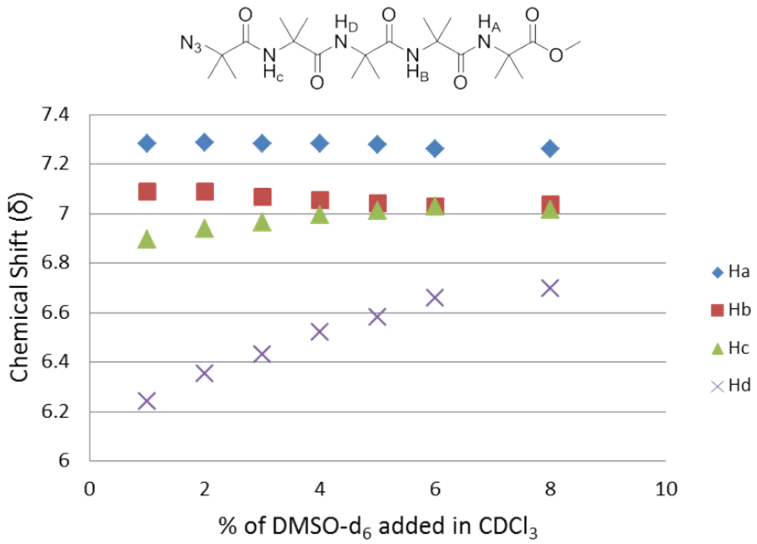
Graph 3. A graph to show the plot of % DMSO *vs* chemical shift for the NH protons of a 0.005M solution of N_3Aib_4OMe.

DMSO-d_6 Titration for $N_3Aib_5O^tBu$



Graph 4. A graph to show the plot of % DMSO *vs* chemical shift for the NH protons of a 0.005M solution of $N_3Aib_5O^tBu$.

DMSO-d_6 Titration for N_3Aib_5OMe



Graph 5. A graph to show the plot of % DMSO *vs* chemical shift for the NH protons of a 0.005M solution of N_3Aib_5OMe.

X-ray Structures

$N_3Aib_2O^tBu$

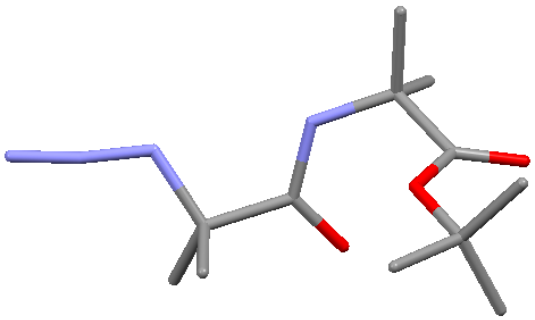


Table 1. Crystal data and structure refinement for $N_3Aib_2O^tBu$.

Identification code	$N_3Aib_2O^tBu$	
Empirical formula	C12 H22 N4 O3	
Formula weight	270.34	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.23450(10) Å	a= 90°.
	b = 10.44030(10) Å	b= 90°.
	c = 15.8938(2) Å	g = 90°.
Volume	1532.34(3) $Å^3$	
Z	4	
Density (calculated)	1.172 Mg/m^3	
Absorption coefficient	0.704 mm^{-1}	
F(000)	584	
Crystal size	0.28 x 0.25 x 0.22 mm^3	
Theta range for data collection	5.07 to 72.42°.	
Index ranges	-7<=h<=11, -12<=k<=12, -19<=l<=19	
Reflections collected	8405	
Independent reflections	2966 [R(int) = 0.0191]	
Completeness to theta = 66.60°	99.4 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8605 and 0.794158
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2966 / 0 / 183
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0261, wR2 = 0.0674
R indices (all data)	R1 = 0.0265, wR2 = 0.0677
Absolute structure parameter	-0.01(14)
Largest diff. peak and hole	0.244 and -0.247 e.Å^{-3}

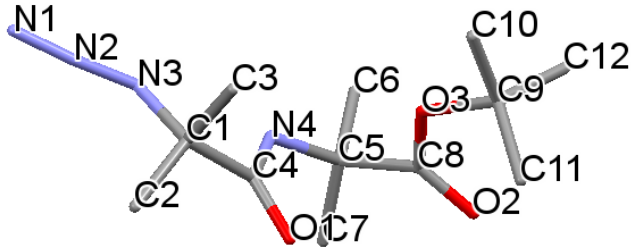


Table 2. Torsion angles [°] for $N_3Aib_2O^tBu$.

N(3)-C(1)-C(4)-O(1)	-162.28(10)
C(2)-C(1)-C(4)-O(1)	-40.87(14)
C(3)-C(1)-C(4)-O(1)	80.56(13)
N(3)-C(1)-C(4)-N(4)	21.88(13)
C(2)-C(1)-C(4)-N(4)	143.29(10)
C(3)-C(1)-C(4)-N(4)	-95.27(11)
N(4)-C(5)-C(8)-O(2)	150.62(10)
C(7)-C(5)-C(8)-O(2)	26.69(15)
C(6)-C(5)-C(8)-O(2)	-91.90(12)
N(4)-C(5)-C(8)-O(3)	-34.77(12)
C(7)-C(5)-C(8)-O(3)	-158.71(9)
C(6)-C(5)-C(8)-O(3)	82.70(11)
N(1)-N(2)-N(3)-C(1)	172.5(11)
C(2)-C(1)-N(3)-N(2)	46.93(15)
C(3)-C(1)-N(3)-N(2)	-76.62(14)
C(4)-C(1)-N(3)-N(2)	168.15(11)
O(1)-C(4)-N(4)-C(5)	-4.19(16)
C(1)-C(4)-N(4)-C(5)	171.51(9)

C(7)-C(5)-N(4)-C(4)	70.76(12)
C(8)-C(5)-N(4)-C(4)	-52.16(13)
C(6)-C(5)-N(4)-C(4)	-168.11(10)
O(2)-C(8)-O(3)-C(9)	2.23(16)
C(5)-C(8)-O(3)-C(9)	-172.19(9)
C(12)-C(9)-O(3)-C(8)	65.78(12)
C(11)-C(9)-O(3)-C(8)	-59.28(13)
C(10)-C(9)-O(3)-C(8)	-176.96(10)

Table 3. Hydrogen bonds for $N_3Aib_2O^tBu$. [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4)...O(2)#1	0.864(16)	2.164(16)	2.9995(12)	162.5(14)

$N_3Aib_3O^tBu$

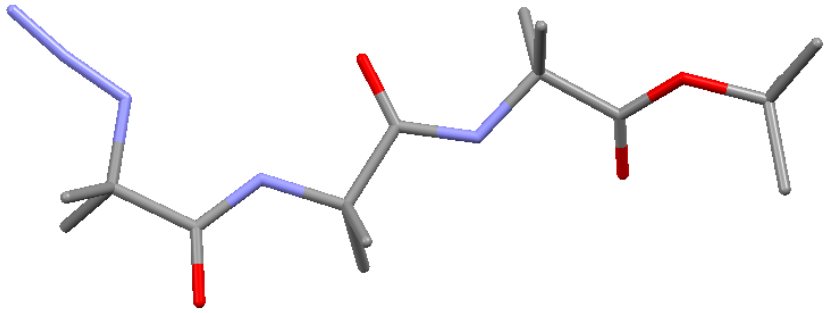


Table 4. Crystal data and structure refinement for $N_3Aib_3O^tBu$

Identification code	$N_3Aib_3O^tBu$	
Empirical formula	C16 H29 N5 O4	
Formula weight	355.44	
Temperature	150.06(15) K	
Wavelength	0.7107 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.2430(2) Å	a= 90°.
	b = 10.7344(2) Å	b= 97.2641(19)°.
	c = 17.9400(4) Å	g = 90°.
Volume	1956.72(7) $Å^3$	
Z	4	
Density (calculated)	1.207 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	768	
Crystal size	0.2500 x 0.2200 x 0.1700 mm^3	
Theta range for data collection	2.76 to 29.45°.	
Index ranges	-14<=h<=13, -14<=k<=12, -23<=l<=23	
Reflections collected	20582	
Independent reflections	4895 [R(int) = 0.0283]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.90394	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4895 / 0 / 243	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.0888	
R indices (all data)	R1 = 0.0587, wR2 = 0.0987	

Largest diff. peak and hole 0.338 and -0.254 e.Å^{-3}

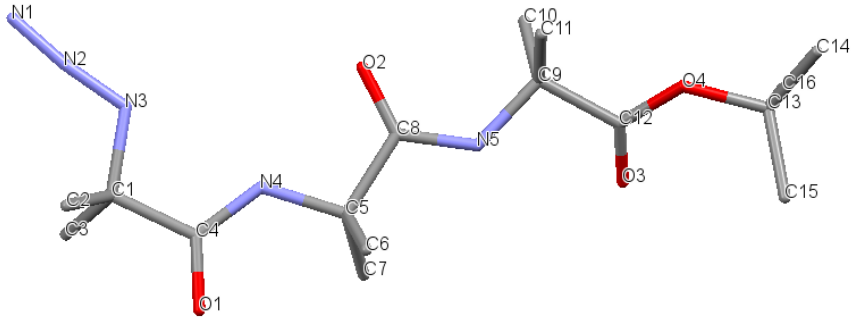


Table 5. Torsion angles [°] for $N_3Aib_3O^tBu$

N(3)-C(1)-C(4)-O(1)	-177.68(10)
C(2)-C(1)-C(4)-O(1)	62.69(13)
C(3)-C(1)-C(4)-O(1)	-59.41(14)
N(3)-C(1)-C(4)-N(4)	2.36(14)
C(2)-C(1)-C(4)-N(4)	-117.27(11)
C(3)-C(1)-C(4)-N(4)	120.63(11)
N(4)-C(5)-C(8)-O(2)	5.04(15)
C(7)-C(5)-C(8)-O(2)	123.77(12)
C(6)-C(5)-C(8)-O(2)	-112.80(12)
N(4)-C(5)-C(8)-N(5)	-175.23(10)
C(7)-C(5)-C(8)-N(5)	-56.50(13)
C(6)-C(5)-C(8)-N(5)	66.93(13)
N(5)-C(9)-C(12)-O(3)	35.56(15)
C(11)-C(9)-C(12)-O(3)	155.75(12)
C(10)-C(9)-C(12)-O(3)	-82.47(14)
N(5)-C(9)-C(12)-O(4)	-147.79(10)
C(11)-C(9)-C(12)-O(4)	-27.61(14)
C(10)-C(9)-C(12)-O(4)	94.18(11)
N(1)-N(2)-N(3)-C(1)	176.5(16)
C(2)-C(1)-N(3)-N(2)	-52.41(15)
C(3)-C(1)-N(3)-N(2)	71.54(14)
C(4)-C(1)-N(3)-N(2)	-170.78(11)
O(1)-C(4)-N(4)-C(5)	1.75(19)

C(1)-C(4)-N(4)-C(5)	-178.29(10)
C(7)-C(5)-N(4)-C(4)	60.55(15)
C(6)-C(5)-N(4)-C(4)	-63.53(14)
C(8)-C(5)-N(4)-C(4)	179.62(11)
O(2)-C(8)-N(5)-C(9)	6.6(2)
C(5)-C(8)-N(5)-C(9)	-173.10(10)
C(11)-C(9)-N(5)-C(8)	66.70(15)
C(10)-C(9)-N(5)-C(8)	-57.54(16)
C(12)-C(9)-N(5)-C(8)	-170.90(11)
O(3)-C(12)-O(4)-C(13)	6.67(17)
C(9)-C(12)-O(4)-C(13)	-169.83(9)
C(16)-C(13)-O(4)-C(12)	63.58(13)
C(14)-C(13)-O(4)-C(12)	-178.82(10)
C(15)-C(13)-O(4)-C(12)	-60.18(14)

Table 6. Bond lengths [Å] and angles [°] for $N_3Aib_3O^tBu$

C(1)-N(3)	1.4946(14)
C(1)-C(2)	1.5190(17)
C(1)-C(3)	1.5238(17)
C(1)-C(4)	1.5375(15)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-O(1)	1.2323(13)
C(4)-N(4)	1.3338(15)
C(5)-N(4)	1.4633(14)
C(5)-C(7)	1.5264(16)
C(5)-C(6)	1.5320(16)
C(5)-C(8)	1.5516(15)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800

C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-O(2)	1.2270(13)
C(8)-N(5)	1.3359(15)
C(9)-N(5)	1.4707(14)
C(9)-C(11)	1.5258(17)
C(9)-C(10)	1.5346(17)
C(9)-C(12)	1.5361(16)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-O(3)	1.2039(14)
C(12)-O(4)	1.3297(14)
C(13)-O(4)	1.4843(13)
C(13)-C(16)	1.5120(18)
C(13)-C(14)	1.5156(18)
C(13)-C(15)	1.5190(17)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
N(1)-N(2)	1.1275(16)
N(2)-N(3)	1.2250(14)
N(4)-H(4)	0.856(14)
N(5)-H(5)	0.849(15)

N(3)-C(1)-C(2)	110.70(9)
N(3)-C(1)-C(3)	109.58(10)
C(2)-C(1)-C(3)	111.95(10)
N(3)-C(1)-C(4)	107.03(9)

C(2)-C(1)-C(4)	108.75(9)
C(3)-C(1)-C(4)	108.69(9)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
O(1)-C(4)-N(4)	124.57(10)
O(1)-C(4)-C(1)	118.47(10)
N(4)-C(4)-C(1)	116.96(9)
N(4)-C(5)-C(7)	110.25(9)
N(4)-C(5)-C(6)	110.28(10)
C(7)-C(5)-C(6)	111.91(10)
N(4)-C(5)-C(8)	104.56(8)
C(7)-C(5)-C(8)	110.74(10)
C(6)-C(5)-C(8)	108.84(9)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
O(2)-C(8)-N(5)	124.58(11)
O(2)-C(8)-C(5)	120.66(10)
N(5)-C(8)-C(5)	114.76(9)

N(5)-C(9)-C(11)	110.08(10)
N(5)-C(9)-C(10)	111.81(10)
C(11)-C(9)-C(10)	111.28(10)
N(5)-C(9)-C(12)	104.89(9)
C(11)-C(9)-C(12)	113.46(10)
C(10)-C(9)-C(12)	105.08(10)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(3)-C(12)-O(4)	126.12(11)
O(3)-C(12)-C(9)	122.67(10)
O(4)-C(12)-C(9)	111.11(9)
O(4)-C(13)-C(16)	109.08(9)
O(4)-C(13)-C(14)	101.94(9)
C(16)-C(13)-C(14)	111.14(11)
O(4)-C(13)-C(15)	110.72(10)
C(16)-C(13)-C(15)	112.06(11)
C(14)-C(13)-C(15)	111.44(11)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N(1)-N(2)-N(3)	173.23(14)
N(2)-N(3)-C(1)	114.57(10)
C(4)-N(4)-C(5)	125.45(10)
C(4)-N(4)-H(4)	119.4(9)
C(5)-N(4)-H(4)	115.1(9)
C(8)-N(5)-C(9)	125.50(10)
C(8)-N(5)-H(5)	118.9(10)
C(9)-N(5)-H(5)	113.9(10)
C(12)-O(4)-C(13)	121.35(9)

Table 7. Hydrogen bonds for $N_3Aib_3O^tBu$ [Å and °].[2]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4)...O(2)	0.856(14)	2.099(14)	2.5731(13)	114.4(11)
N(4)-H(4)...N(3)	0.856(14)	2.159(14)	2.5916(13)	111.0(11)
N(5)-H(5)...O(1)#1	0.849(15)	2.282(15)	3.0237(12)	146.0(13)

$N_3Aib_4O^tBu$

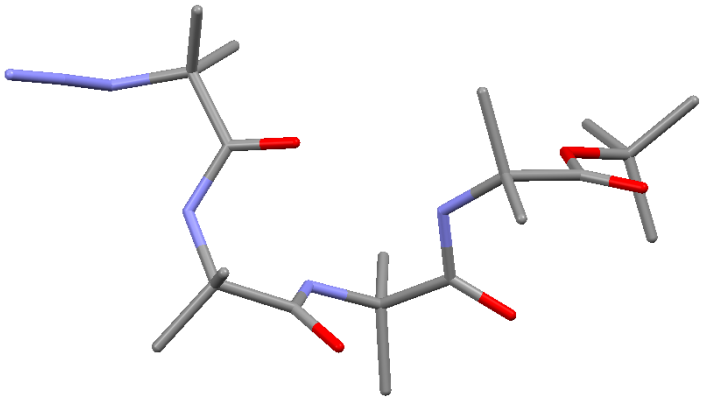


Table 8. Crystal data and structure refinement for $N_3Aib_4O^tBu$

Identification code	s3770ma	
Empirical formula	C20 H36 N6 O5	
Formula weight	440.55	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.2952(7) Å	a= 108.580(3)°.
	b = 12.9363(9) Å	b= 96.720(3)°.
	c = 18.6722(12) Å	g = 104.173(3)°.
Volume	2450.3(3) $Å^3$	
Z	4	
Density (calculated)	1.194 Mg/m^3	
Absorption coefficient	0.715 mm^{-1}	
F(000)	952	
Crystal size	0.25 x 0.22 x 0.19 mm^3	
Theta range for data collection	2.55 to 72.36°.	
Index ranges	-13<=h<=13, -15<=k<=15, -22<=l<=23	
Reflections collected	20090	
Independent reflections	9107 [R(int) = 0.0457]	
Completeness to theta = 66.60°	95.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8761 and 0.653006	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9107 / 0 / 605	
Goodness-of-fit on F^2	1.097	

Final R indices [I>2sigma(I)]	R1 = 0.0690, wR2 = 0.1838
R indices (all data)	R1 = 0.0733, wR2 = 0.1897
Largest diff. peak and hole	0.666 and -0.476 e.Å^{-3}

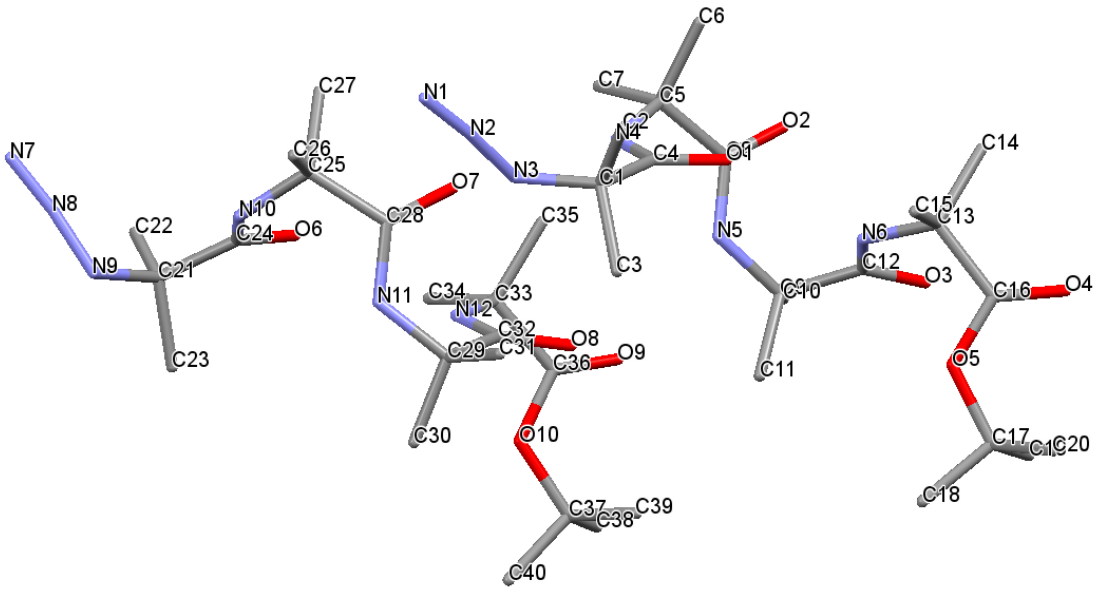


Table 9. Torsion angles [°] for $N_3Aib_4O^tBu$

N(3)-C(1)-C(4)-O(1)	178.5(2)
C(3)-C(1)-C(4)-O(1)	-63.5(3)
C(2)-C(1)-C(4)-O(1)	56.2(3)
N(3)-C(1)-C(4)-N(4)	-0.9(3)
C(3)-C(1)-C(4)-N(4)	117.0(3)
C(2)-C(1)-C(4)-N(4)	-123.2(2)
N(4)-C(5)-C(8)-O(2)	-156.4(2)
C(6)-C(5)-C(8)-O(2)	-33.8(3)
C(7)-C(5)-C(8)-O(2)	85.5(3)
N(4)-C(5)-C(8)-N(5)	23.6(3)
C(6)-C(5)-C(8)-N(5)	146.1(2)
C(7)-C(5)-C(8)-N(5)	-94.6(3)
N(5)-C(9)-C(12)-O(3)	-149.1(2)
C(10)-C(9)-C(12)-O(3)	-25.4(3)

C(11)-C(9)-C(12)-O(3)	95.2(3)
N(5)-C(9)-C(12)-N(6)	37.1(3)
C(10)-C(9)-C(12)-N(6)	160.8(2)
C(11)-C(9)-C(12)-N(6)	-78.6(3)
N(6)-C(13)-C(16)-O(4)	141.5(3)
C(14)-C(13)-C(16)-O(4)	18.3(4)
C(15)-C(13)-C(16)-O(4)	-100.9(3)
N(6)-C(13)-C(16)-O(5)	-44.4(3)
C(14)-C(13)-C(16)-O(5)	-167.6(2)
C(15)-C(13)-C(16)-O(5)	73.2(3)
N(9)-C(21)-C(24)-O(6)	-176.0(2)
C(23)-C(21)-C(24)-O(6)	67.9(3)
C(22)-C(21)-C(24)-O(6)	-52.9(3)
N(9)-C(21)-C(24)-N(10)	4.8(3)
C(23)-C(21)-C(24)-N(10)	-111.3(3)
C(22)-C(21)-C(24)-N(10)	127.9(2)
N(10)-C(25)-C(28)-O(7)	153.3(2)
C(26)-C(25)-C(28)-O(7)	-87.9(3)
C(27)-C(25)-C(28)-O(7)	31.5(3)
N(10)-C(25)-C(28)-N(11)	-28.3(3)
C(26)-C(25)-C(28)-N(11)	90.5(2)
C(27)-C(25)-C(28)-N(11)	-150.0(2)
N(11)-C(29)-C(32)-O(8)	147.2(2)
C(31)-C(29)-C(32)-O(8)	24.0(3)
C(30)-C(29)-C(32)-O(8)	-96.5(3)
N(11)-C(29)-C(32)-N(12)	-39.3(3)
C(31)-C(29)-C(32)-N(12)	-162.5(2)
C(30)-C(29)-C(32)-N(12)	77.0(3)
N(12)-C(33)-C(36)-O(9)	-140.3(3)
C(35)-C(33)-C(36)-O(9)	-17.6(3)
C(34)-C(33)-C(36)-O(9)	102.3(3)
N(12)-C(33)-C(36)-O(10)	44.4(3)
C(35)-C(33)-C(36)-O(10)	167.1(2)
C(34)-C(33)-C(36)-O(10)	-73.0(3)
N(1)-N(2)-N(3)-C(1)	-173(2)
C(3)-C(1)-N(3)-N(2)	116.0(3)
C(2)-C(1)-N(3)-N(2)	-6.0(3)
C(4)-C(1)-N(3)-N(2)	-125.1(2)

O(1)-C(4)-N(4)-C(5)	-10.5(4)
C(1)-C(4)-N(4)-C(5)	168.9(2)
C(6)-C(5)-N(4)-C(4)	-58.9(3)
C(7)-C(5)-N(4)-C(4)	-179.4(2)
C(8)-C(5)-N(4)-C(4)	62.3(3)
O(2)-C(8)-N(5)-C(9)	2.9(4)
C(5)-C(8)-N(5)-C(9)	-177.1(2)
C(10)-C(9)-N(5)-C(8)	-69.0(3)
C(11)-C(9)-N(5)-C(8)	169.8(2)
C(12)-C(9)-N(5)-C(8)	54.4(3)
O(3)-C(12)-N(6)-C(13)	-2.2(4)
C(9)-C(12)-N(6)-C(13)	171.5(2)
C(14)-C(13)-N(6)-C(12)	73.4(3)
C(15)-C(13)-N(6)-C(12)	-165.7(2)
C(16)-C(13)-N(6)-C(12)	-48.3(3)
N(7)-N(8)-N(9)-C(21)	175(2)
C(23)-C(21)-N(9)-N(8)	-154.4(2)
C(22)-C(21)-N(9)-N(8)	-32.8(3)
C(24)-C(21)-N(9)-N(8)	87.9(3)
O(6)-C(24)-N(10)-C(25)	8.0(4)
C(21)-C(24)-N(10)-C(25)	-172.9(2)
C(26)-C(25)-N(10)-C(24)	-178.3(2)
C(27)-C(25)-N(10)-C(24)	61.5(3)
C(28)-C(25)-N(10)-C(24)	-59.9(3)
O(7)-C(28)-N(11)-C(29)	-2.2(4)
C(25)-C(28)-N(11)-C(29)	179.4(2)
C(31)-C(29)-N(11)-C(28)	69.9(3)
C(30)-C(29)-N(11)-C(28)	-169.1(2)
C(32)-C(29)-N(11)-C(28)	-53.1(3)
O(8)-C(32)-N(12)-C(33)	-1.5(4)
C(29)-C(32)-N(12)-C(33)	-174.8(2)
C(35)-C(33)-N(12)-C(32)	-71.8(3)
C(34)-C(33)-N(12)-C(32)	166.9(2)
C(36)-C(33)-N(12)-C(32)	49.1(3)
O(4)-C(16)-O(5)-C(17)	-5.8(4)
C(13)-C(16)-O(5)-C(17)	-179.6(2)
C(19)-C(17)-O(5)-C(16)	-60.9(3)
C(18)-C(17)-O(5)-C(16)	-179.0(2)

C(20)-C(17)-O(5)-C(16)	63.6(3)
O(9)-C(36)-O(10)-C(37)	10.9(4)
C(33)-C(36)-O(10)-C(37)	-173.9(2)
C(39)-C(37)-O(10)-C(36)	63.8(3)
C(40)-C(37)-O(10)-C(36)	-179.6(2)
C(38)-C(37)-O(10)-C(36)	-62.8(3)

Table 10. Hydrogen bonds for $N_3Aib_4O^tBu$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6)...O(1)	0.86(4)	2.15(4)	2.987(3)	164(3)
N(5)-H(5)...O(8)	0.82(3)	2.61(3)	3.212(3)	132(3)
N(4)-H(4)...O(7)	0.84(3)	2.31(3)	3.107(3)	157(2)
N(10)-H(10)...O(2)#1	0.85(3)	2.29(3)	3.054(3)	149(3)
N(12)-H(12)...O(6)	0.78(3)	2.25(3)	2.996(3)	162(3)

N_3Aib_4OMe

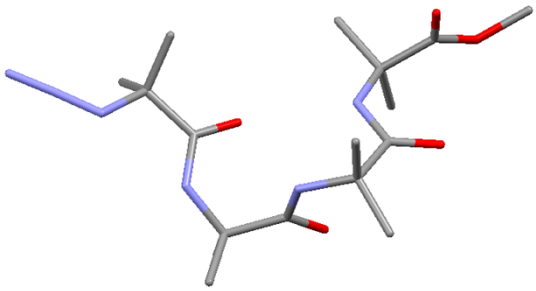


Table 11. Crystal data and structure refinement for $N_3Aib_3O^tBu$

Identification code	N_3Aib_4OMe	
Empirical formula	C17 H30 N6 O5	
Formula weight	398.47	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.6156(4) Å	a= 90°.
	b = 10.7583(3) Å	b= 114.8690(10)°.
	c = 15.9339(5) Å	g = 90°.
Volume	2117.58(11) $Å^3$	
Z	4	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.776 mm^{-1}	
F(000)	856	
Crystal size	0.23 x 0.19 x 0.11 mm^3	
Theta range for data collection	5.12 to 72.23°.	
Index ranges	-16<=h<=16, -13<=k<=13, -19<=l<=19	
Reflections collected	11781	
Independent reflections	4094 [R(int) = 0.0238]	
Completeness to theta = 66.60°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9195 and 0.7305	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4094 / 0 / 274	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0981	
R indices (all data)	R1 = 0.0394, wR2 = 0.0995	

Largest diff. peak and hole	0.352 and -0.289 e.Å^{-3}

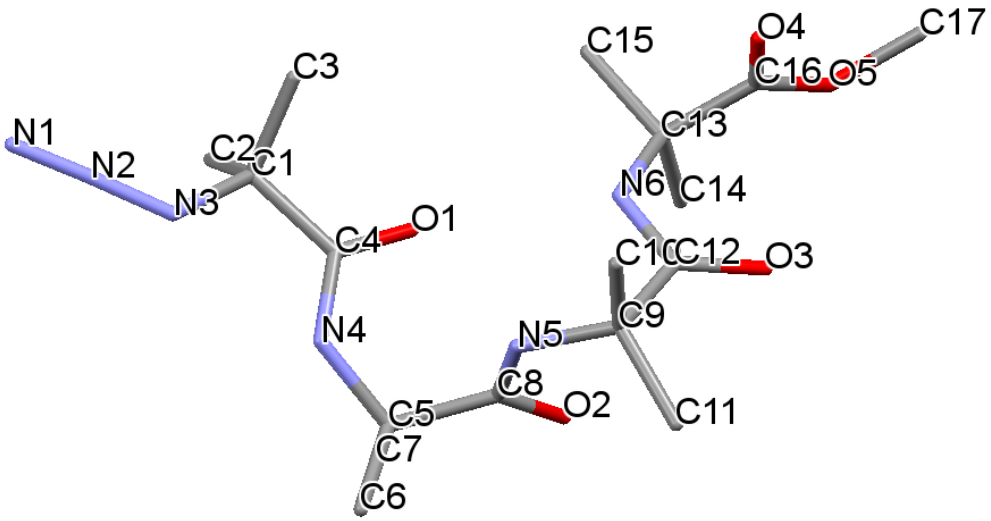


Table 12. Torsion angles [°] for N_3Aib_4OMe

N(3)-C(1)-C(4)-O(1)	-172.76(11)
C(2)-C(1)-C(4)-O(1)	66.66(14)
C(3)-C(1)-C(4)-O(1)	-54.50(14)
N(3)-C(1)-C(4)-N(4)	8.15(14)
C(2)-C(1)-C(4)-N(4)	-112.43(12)
C(3)-C(1)-C(4)-N(4)	126.42(11)
N(4)-C(5)-C(8)-O(2)	-134.32(11)
C(7)-C(5)-C(8)-O(2)	-13.21(15)
C(6)-C(5)-C(8)-O(2)	107.46(12)
N(4)-C(5)-C(8)-N(5)	47.82(12)
C(7)-C(5)-C(8)-N(5)	168.93(10)
C(6)-C(5)-C(8)-N(5)	-70.41(12)
N(5)-C(9)-C(12)-O(3)	-152.41(10)
C(11)-C(9)-C(12)-O(3)	-28.89(14)
C(10)-C(9)-C(12)-O(3)	90.36(12)
N(5)-C(9)-C(12)-N(6)	33.98(12)
C(11)-C(9)-C(12)-N(6)	157.50(9)
C(10)-C(9)-C(12)-N(6)	-83.24(11)
N(6)-C(13)-C(16)-O(4)	-47.66(14)
C(14)-C(13)-C(16)-O(4)	-170.69(11)
C(15)-C(13)-C(16)-O(4)	67.83(13)
N(6)-C(13)-C(16)-O(5)	138.04(9)
C(14)-C(13)-C(16)-O(5)	15.02(13)

C(15)-C(13)-C(16)-O(5)	-106.46(11)
N(1)-N(2)-N(3)-C(1)	-159.7(18)
C(4)-C(1)-N(3)-N(2)	-158.11(11)
C(2)-C(1)-N(3)-N(2)	-40.17(15)
C(3)-C(1)-N(3)-N(2)	83.71(14)
O(1)-C(4)-N(4)-C(5)	-10.97(17)
C(1)-C(4)-N(4)-C(5)	168.06(9)
C(7)-C(5)-N(4)-C(4)	-69.00(13)
C(6)-C(5)-N(4)-C(4)	170.87(10)
C(8)-C(5)-N(4)-C(4)	52.04(13)
O(2)-C(8)-N(5)-C(9)	-6.41(16)
C(5)-C(8)-N(5)-C(9)	171.43(9)
C(11)-C(9)-N(5)-C(8)	-63.55(12)
C(10)-C(9)-N(5)-C(8)	175.88(9)
C(12)-C(9)-N(5)-C(8)	59.54(12)
O(3)-C(12)-N(6)-C(13)	10.63(16)
C(9)-C(12)-N(6)-C(13)	-175.84(9)
C(14)-C(13)-N(6)-C(12)	71.03(13)
C(16)-C(13)-N(6)-C(12)	-54.21(13)
C(15)-C(13)-N(6)-C(12)	-168.21(10)
O(4)-C(16)-O(5)-C(17)	3.12(17)
C(13)-C(16)-O(5)-C(17)	177.37(10)

Table 13.Hydrogen bonds for N_3Aib_4OMe[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4)...O(4)#1	0.842(17)	2.451(17)	3.2555(13)	160.1(14)
N(5)-H(5)...O(3)#2	0.841(17)	2.187(16)	2.9758(12)	156.1(14)
N(6)-H(6)...O(1)	0.827(17)	2.240(17)	3.0077(13)	154.6(14)

N_3Aib_4OMe

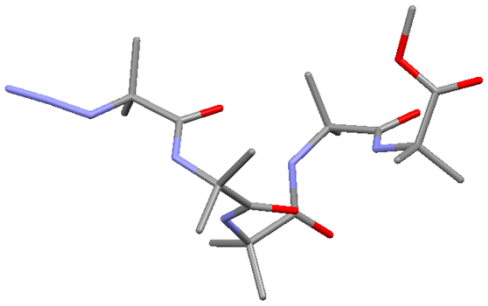


Table 14. Crystal data and structure refinement for N_3Aib_5OMe

Identification code	N_3Aib_5OMe	
Empirical formula	C21 H39 N7 O7	
Formula weight	501.59	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3347(4) Å	a= 62.527(2)°.
	b = 16.1397(5) Å	b= 85.251(2)°.
	c = 16.8748(6) Å	g = 81.446(2)°.
Volume	2708.10(16) $Å^3$	
Z	4	
Density (calculated)	1.230 Mg/m^3	
Absorption coefficient	0.776 mm^{-1}	
F(000)	1080	
Crystal size	0.33 x 0.22 x 0.15 mm^3	
Theta range for data collection	2.95 to 70.27°.	
Index ranges	-13<=h<=13, -19<=k<=19, -20<=l<=13	
Reflections collected	16634	
Independent reflections	9674 [R(int) = 0.0269]	
Completeness to theta = 66.60°	95.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8925 and 0.747956	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9674 / 0 / 697	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.1158	
R indices (all data)	R1 = 0.0533, wR2 = 0.1245	
Largest diff. peak and hole	1.287 and -0.271 $e.Å^{-3}$	

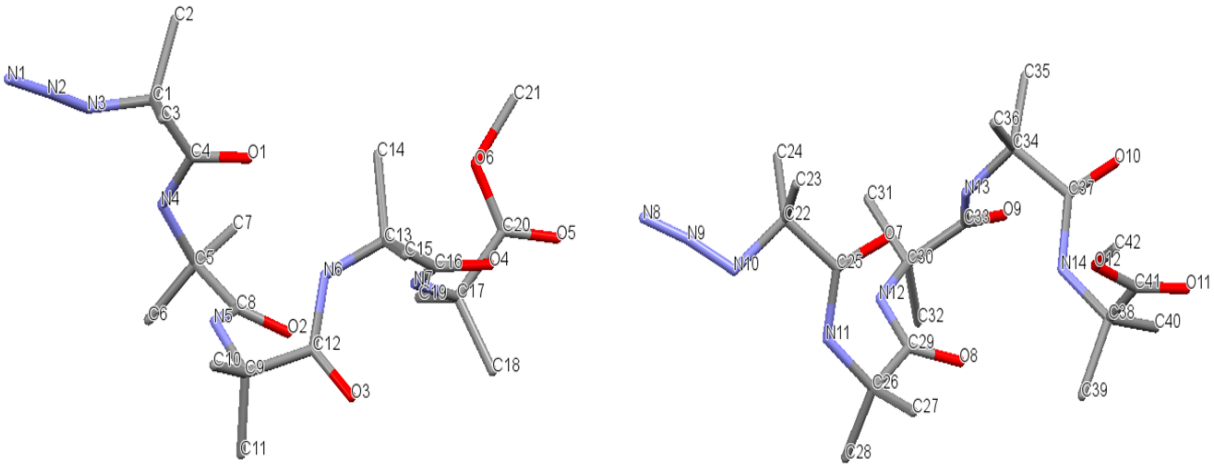


Table 15. Torsion angles [°] for N_3Aib_5OMe

N(3)-C(1)-C(4)-O(1)	177.71(15)
C(2)-C(1)-C(4)-O(1)	59.3(2)
C(3)-C(1)-C(4)-O(1)	-61.7(2)
N(3)-C(1)-C(4)-N(4)	-5.2(2)
C(2)-C(1)-C(4)-N(4)	-123.63(18)
C(3)-C(1)-C(4)-N(4)	115.44(17)
N(4)-C(5)-C(8)-O(2)	-145.14(15)
C(7)-C(5)-C(8)-O(2)	-23.0(2)
C(6)-C(5)-C(8)-O(2)	97.27(18)
N(4)-C(5)-C(8)-N(5)	37.29(19)
C(7)-C(5)-C(8)-N(5)	159.43(15)
C(6)-C(5)-C(8)-N(5)	-80.30(17)
N(5)-C(9)-C(12)-O(3)	-154.54(15)
C(10)-C(9)-C(12)-O(3)	88.32(19)
C(11)-C(9)-C(12)-O(3)	-32.4(2)
N(5)-C(9)-C(12)-N(6)	31.2(2)
C(10)-C(9)-C(12)-N(6)	-85.99(17)
C(11)-C(9)-C(12)-N(6)	153.25(15)
N(6)-C(13)-C(16)-O(4)	-156.88(15)
C(15)-C(13)-C(16)-O(4)	-31.7(2)
C(14)-C(13)-C(16)-O(4)	87.24(18)
N(6)-C(13)-C(16)-N(7)	30.71(19)
C(15)-C(13)-C(16)-N(7)	155.85(14)
C(14)-C(13)-C(16)-N(7)	-85.17(16)

N(7)-C(17)-C(20)-O(5)	141.18(18)
C(18)-C(17)-C(20)-O(5)	17.7(2)
C(19)-C(17)-C(20)-O(5)	-102.6(2)
N(7)-C(17)-C(20)-O(6)	-43.5(2)
C(18)-C(17)-C(20)-O(6)	-166.98(15)
C(19)-C(17)-C(20)-O(6)	72.73(19)
N(10)-C(22)-C(25)-O(7)	-173.94(16)
C(24)-C(22)-C(25)-O(7)	67.3(2)
C(23)-C(22)-C(25)-O(7)	-53.8(2)
N(10)-C(22)-C(25)-N(11)	9.0(2)
C(24)-C(22)-C(25)-N(11)	-109.78(19)
C(23)-C(22)-C(25)-N(11)	129.11(19)
N(11)-C(26)-C(29)-O(8)	149.13(14)
C(27)-C(26)-C(29)-O(8)	26.6(2)
C(28)-C(26)-C(29)-O(8)	-93.67(17)
N(11)-C(26)-C(29)-N(12)	-32.53(19)
C(27)-C(26)-C(29)-N(12)	-155.06(14)
C(28)-C(26)-C(29)-N(12)	84.68(16)
N(12)-C(30)-C(33)-O(9)	152.46(16)
C(32)-C(30)-C(33)-O(9)	29.9(2)
C(31)-C(30)-C(33)-O(9)	-90.56(19)
N(12)-C(30)-C(33)-N(13)	-33.1(2)
C(32)-C(30)-C(33)-N(13)	-155.62(15)
C(31)-C(30)-C(33)-N(13)	83.90(17)
N(13)-C(34)-C(37)-O(10)	161.90(15)
C(35)-C(34)-C(37)-O(10)	35.9(2)
C(36)-C(34)-C(37)-O(10)	-82.71(19)
N(13)-C(34)-C(37)-N(14)	-25.2(2)
C(35)-C(34)-C(37)-N(14)	-151.23(15)
C(36)-C(34)-C(37)-N(14)	90.15(17)
N(14)-C(38)-C(41)-O(11)	-141.42(18)
C(40)-C(38)-C(41)-O(11)	-17.5(2)
C(39)-C(38)-C(41)-O(11)	102.2(2)
N(14)-C(38)-C(41)-O(12)	44.9(2)
C(40)-C(38)-C(41)-O(12)	168.84(16)
C(39)-C(38)-C(41)-O(12)	-71.45(19)
N(1)-N(2)-N(3)-C(1)	172.5(15)
C(2)-C(1)-N(3)-N(2)	-90.1(2)

C(4)-C(1)-N(3)-N(2)	150.94(17)
C(3)-C(1)-N(3)-N(2)	33.7(2)
O(1)-C(4)-N(4)-C(5)	0.1(2)
C(1)-C(4)-N(4)-C(5)	-176.84(15)
C(7)-C(5)-N(4)-C(4)	-70.91(19)
C(6)-C(5)-N(4)-C(4)	167.46(15)
C(8)-C(5)-N(4)-C(4)	51.0(2)
O(2)-C(8)-N(5)-C(9)	-6.8(2)
C(5)-C(8)-N(5)-C(9)	170.68(14)
C(10)-C(9)-N(5)-C(8)	170.86(14)
C(11)-C(9)-N(5)-C(8)	-67.68(19)
C(12)-C(9)-N(5)-C(8)	55.6(2)
O(3)-C(12)-N(6)-C(13)	1.3(3)
C(9)-C(12)-N(6)-C(13)	175.34(14)
C(15)-C(13)-N(6)-C(12)	-60.8(2)
C(14)-C(13)-N(6)-C(12)	179.61(15)
C(16)-C(13)-N(6)-C(12)	64.1(2)
O(4)-C(16)-N(7)-C(17)	-2.9(3)
C(13)-C(16)-N(7)-C(17)	169.35(14)
C(18)-C(17)-N(7)-C(16)	70.0(2)
C(19)-C(17)-N(7)-C(16)	-168.11(16)
C(20)-C(17)-N(7)-C(16)	-52.5(2)
N(8)-N(9)-N(10)-C(22)	-167(2)
C(24)-C(22)-N(10)-N(9)	-60.2(3)
C(23)-C(22)-N(10)-N(9)	63.5(3)
C(25)-C(22)-N(10)-N(9)	-177.28(18)
O(7)-C(25)-N(11)-C(26)	-0.4(2)
C(22)-C(25)-N(11)-C(26)	176.49(14)
C(27)-C(26)-N(11)-C(25)	69.50(19)
C(28)-C(26)-N(11)-C(25)	-168.44(15)
C(29)-C(26)-N(11)-C(25)	-51.9(2)
O(8)-C(29)-N(12)-C(30)	4.3(2)
C(26)-C(29)-N(12)-C(30)	-173.97(13)
C(32)-C(30)-N(12)-C(29)	70.73(19)
C(31)-C(30)-N(12)-C(29)	-168.44(14)
C(33)-C(30)-N(12)-C(29)	-52.97(19)
O(9)-C(33)-N(13)-C(34)	-0.3(3)
C(30)-C(33)-N(13)-C(34)	-174.54(14)

C(35)-C(34)-N(13)-C(33)	58.3(2)
C(36)-C(34)-N(13)-C(33)	177.83(16)
C(37)-C(34)-N(13)-C(33)	-67.4(2)
O(10)-C(37)-N(14)-C(38)	4.5(3)
C(34)-C(37)-N(14)-C(38)	-168.17(15)
C(40)-C(38)-N(14)-C(37)	-70.1(2)
C(39)-C(38)-N(14)-C(37)	168.46(15)
C(41)-C(38)-N(14)-C(37)	52.4(2)
O(5)-C(20)-O(6)-C(21)	3.5(3)
C(17)-C(20)-O(6)-C(21)	-171.9(2)
O(11)-C(41)-O(12)-C(42)	-4.1(3)
C(38)-C(41)-O(12)-C(42)	169.66(18)

Table 16. Hydrogen bonds for N_3Aib_5OMe [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(12)-H(12)...O(14)#1	0.82(2)	2.15(2)	2.953(2)	167(2)
N(11)-H(11)...O(11)#1	0.85(2)	2.57(2)	3.3439(19)	152(2)
N(14)-H(14)...O(8)	0.84(3)	2.14(3)	2.9634(18)	167(2)
N(13)-H(13)...O(7)	0.84(2)	2.25(2)	3.0653(18)	165.0(18)
N(5)-H(5)...O(13)	0.79(2)	2.25(2)	3.026(2)	165(2)
N(4)-H(4)...O(5)#1	0.84(2)	2.50(2)	3.2346(19)	146(2)
N(4)-H(4)...N(3)	0.84(2)	2.20(2)	2.615(2)	110.1(18)
N(7)-H(7)...O(2)	0.89(2)	2.12(2)	2.9811(18)	165(2)
N(6)-H(6)...O(1)	0.80(2)	2.30(2)	3.0763(18)	163(2)
O(14)-H(14E)...O(3)	0.85(3)	2.28(3)	3.113(2)	165(3)
O(14)-H(14D)...O(10)	0.82(3)	2.12(3)	2.940(2)	177(3)
O(13)-H(13B)...O(9)	0.90(3)	2.12(3)	2.9959(19)	164(3)
O(13)-H(13A)...O(4)#1	0.86(3)	2.13(3)	2.9908(18)	173(3)

Unit Cell Packing in $N_3Aib_2O^tBu$

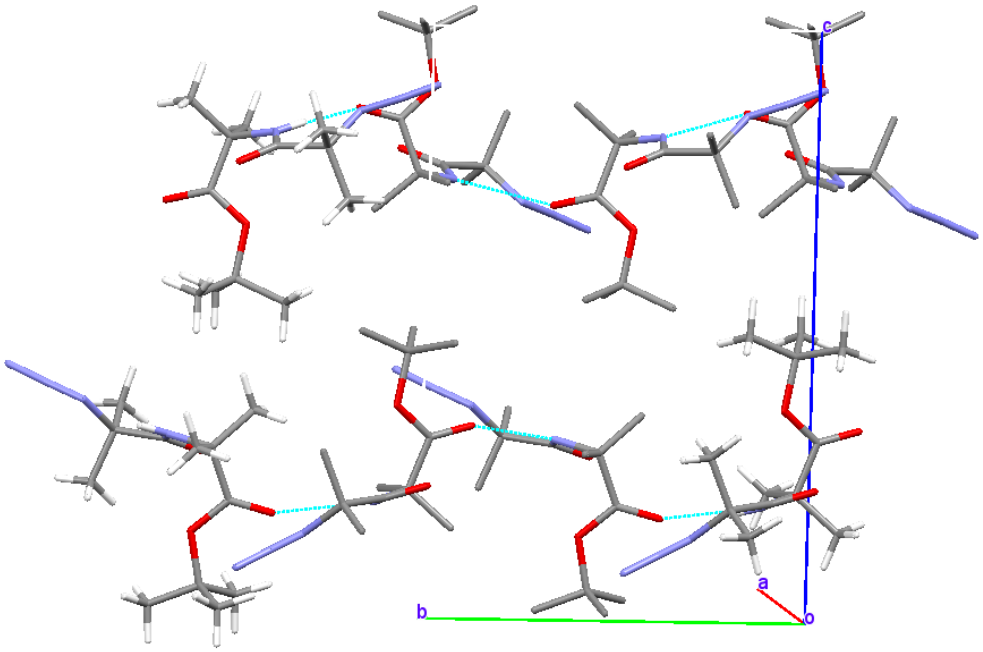


Figure 6. Unit cell packing in $N_3Aib_2O^tBu$ as viewed along the *b* axis highlighting the anti-parallel packing arrangement of molecules. C atoms are shown in grey, N in light blue and O in red.

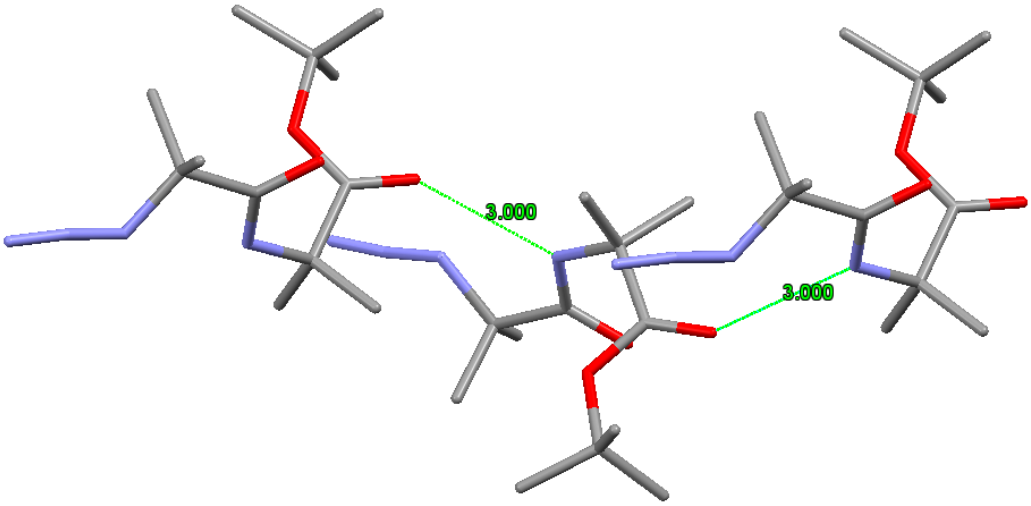


Figure 7. Intermolecular hydrogen-bonding interaction between adjacent molecules in $N_3Aib_2O^tBu$ (3.00 Å) C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

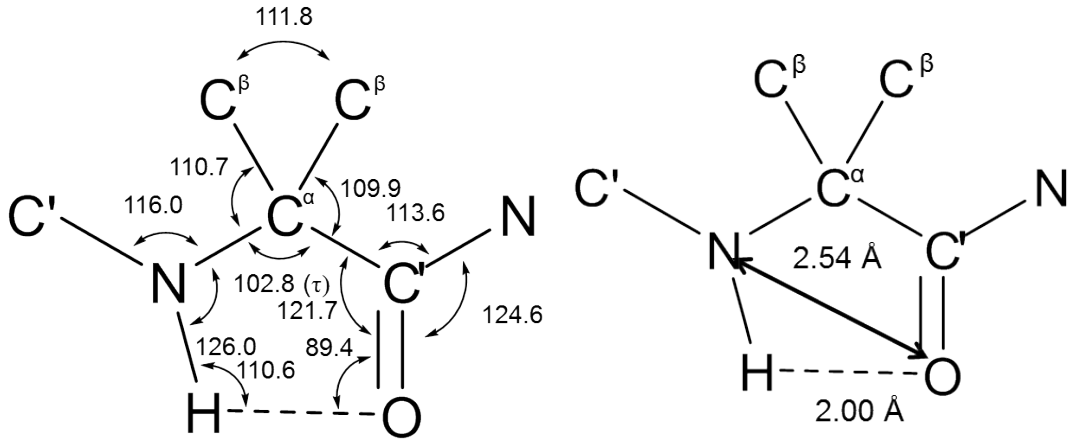


Figure 8. Average values for the parameters characterising the fully-extended C_5 conformation.[3]

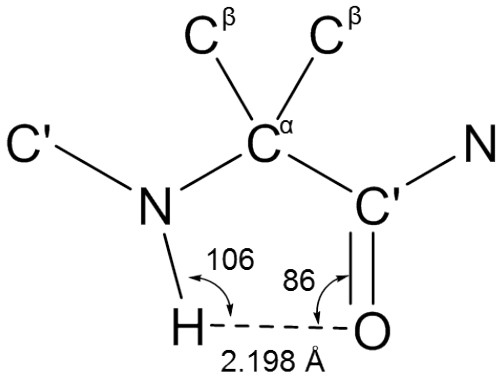


Figure 9. Average values for the parameters characterising the fully-extended C_5 conformation.[4]

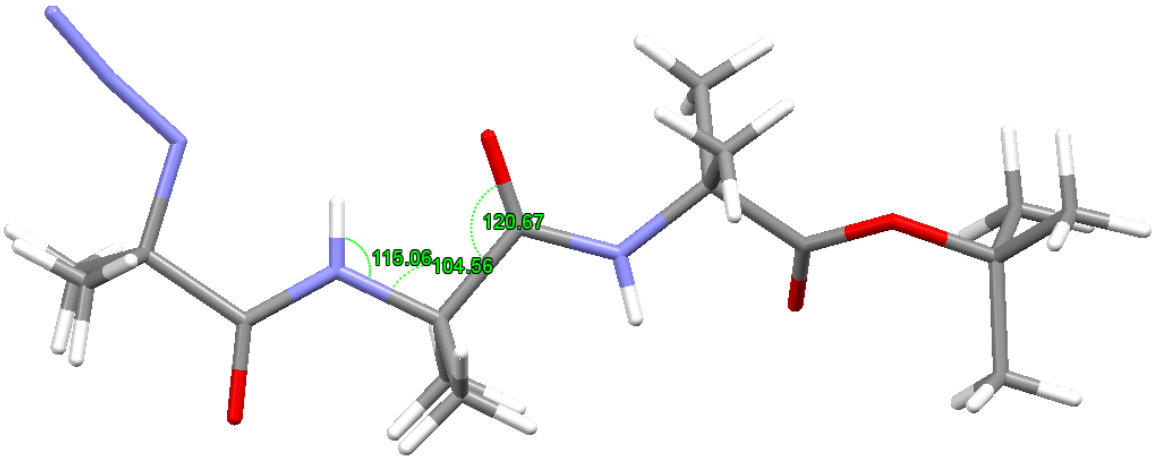


Figure 10. C_5 conformation in $N_3Aib_3O^tBu$ confirmed by angles between N(4)-C(5)-C(8), O(2)-C(8)-C(5) and N(H4A)-N(4)-C(5). C atoms are shown in grey, N in light blue and O in red and H atoms are shown in white.

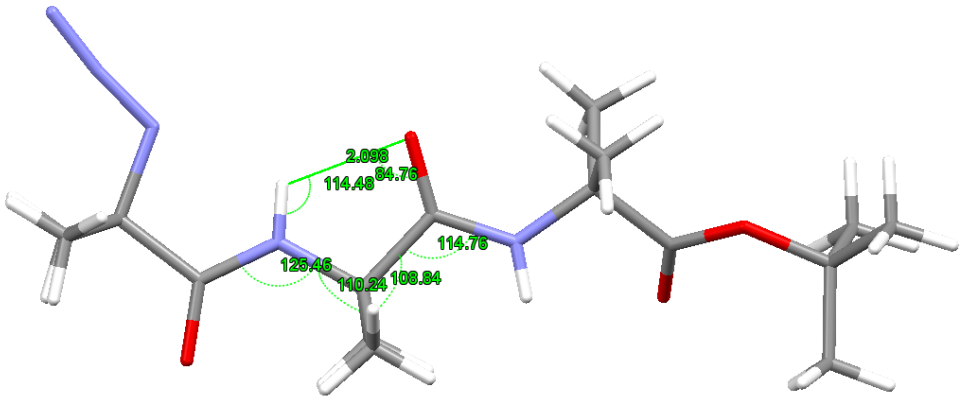


Figure 11. C_5 conformation in $N_3Aib_3O^tBu$ confirmed by angles between C(4)-N(4)-C(5), O(2)-N(H4A)-N(4), N(4)-C(5)-C(7), C(6)-C(5)-C(8), C(5)-C(8)-N(5), distance between N(4)H…O(2). C atoms are shown in grey, N in light blue and O in red and H atoms are shown in white.

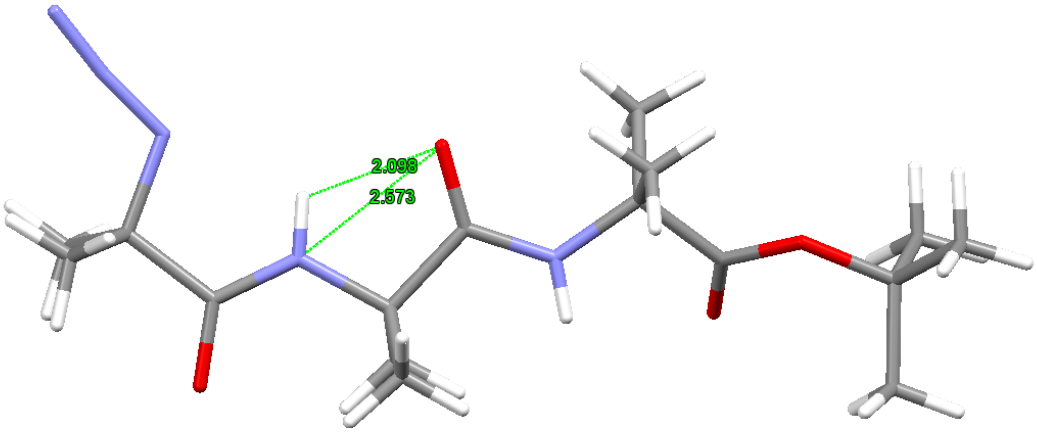


Figure 12. C_5 conformation in $N_3Aib_3O^tBu$ confirmed by distances between N(4)-H…O(2) and N(4)…O(2). C atoms are shown in grey, N in light blue and O in red and H atoms are shown in white.

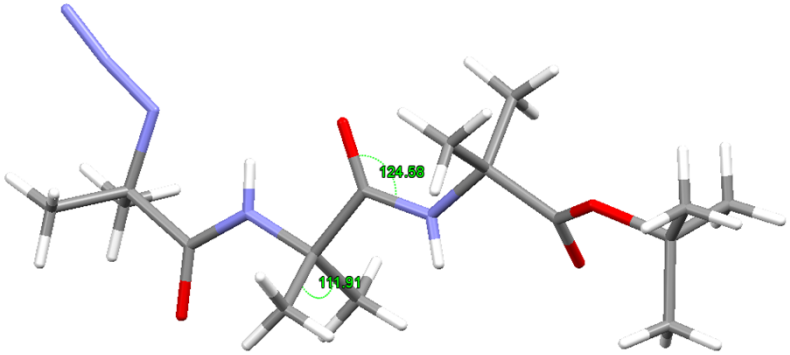


Figure 13. C_5 conformation in $N_3Aib_3O^tBu$ confirmed by angles between C(6)-C(5)-C(7) and O(2)-C(8)-N(5). C atoms are shown in grey, N in light blue and O in red and H atoms are shown in white.

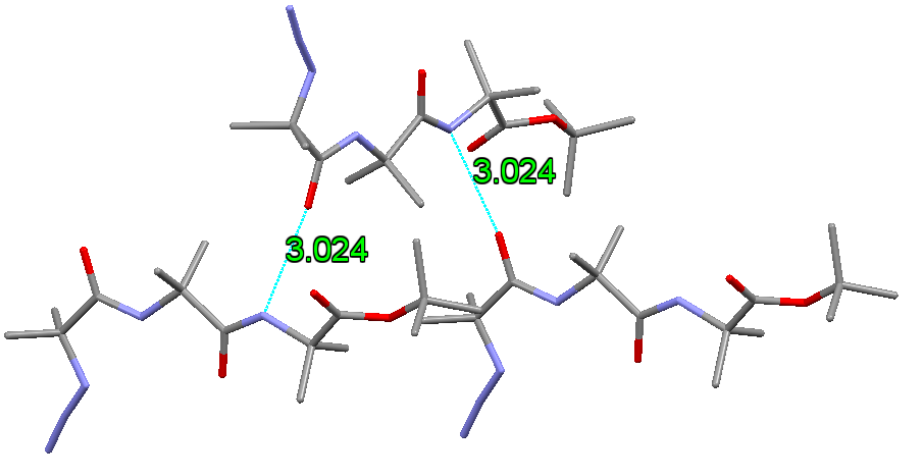


Figure 14. Intermolecular hydrogen-bonding interaction between adjacent molecules in $N_3Aib_3O^tBu$ (3.02 Å) C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

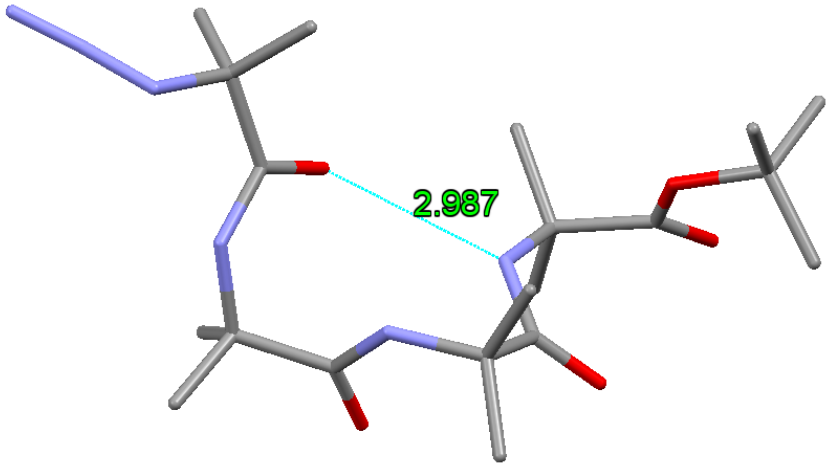


Figure 15. Intramolecular hydrogen-bonding interaction (2.987 Å), between first carbonyl of the chain and the third NH, forming the basis of the 3_{10} helix in **3**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

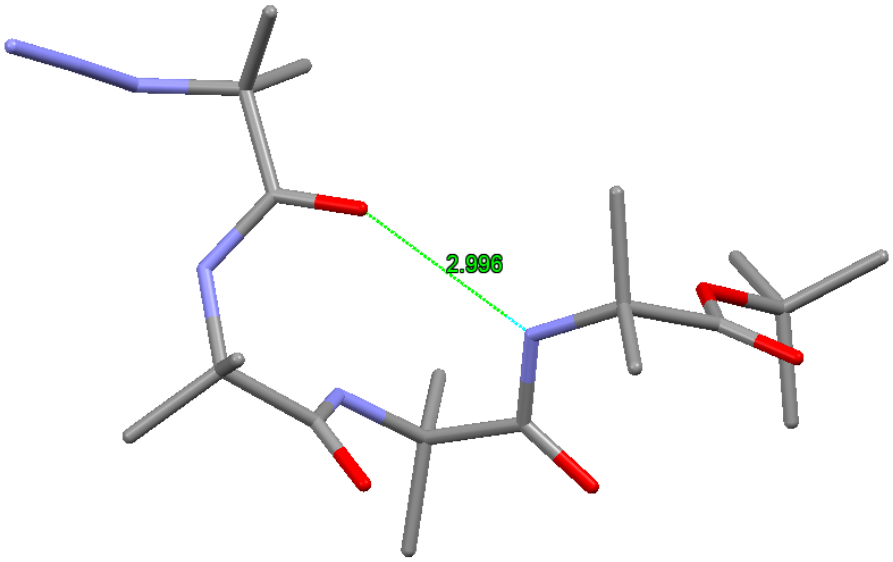


Figure 16. Intramolecular hydrogen-bonding interaction (2.996 Å), between first carbonyl of the chain and the third NH, forming the basis of the 3_{10} helix in **3**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

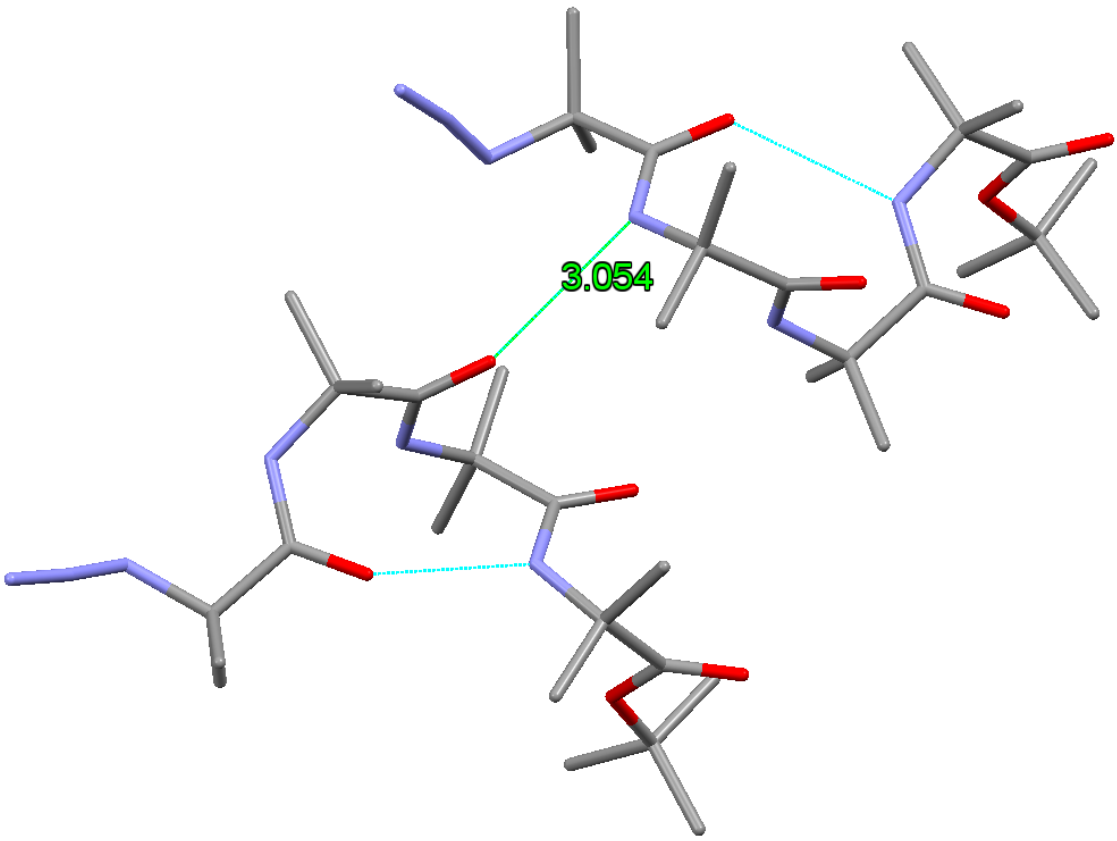


Figure 17. Intermolecular hydrogen-bonding interaction (3.054 Å), between first NH of one oligomer and the second carbonyl on an adjacent oligomer in **3**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

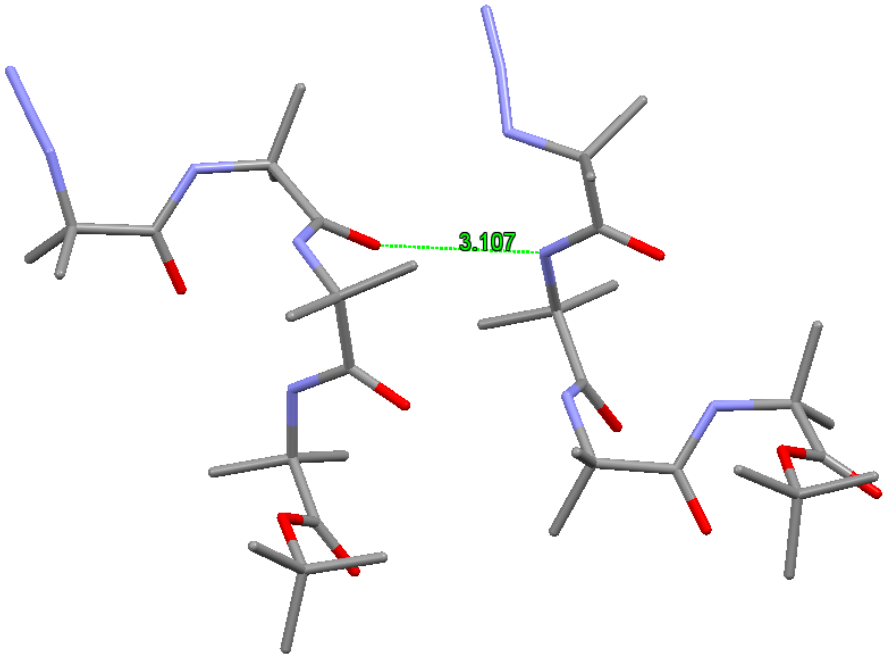


Figure 18. Intermolecular hydrogen-bonding interaction (3.107 Å), between first NH of one oligomer and the second carbonyl on an adjacent oligomer in **3**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

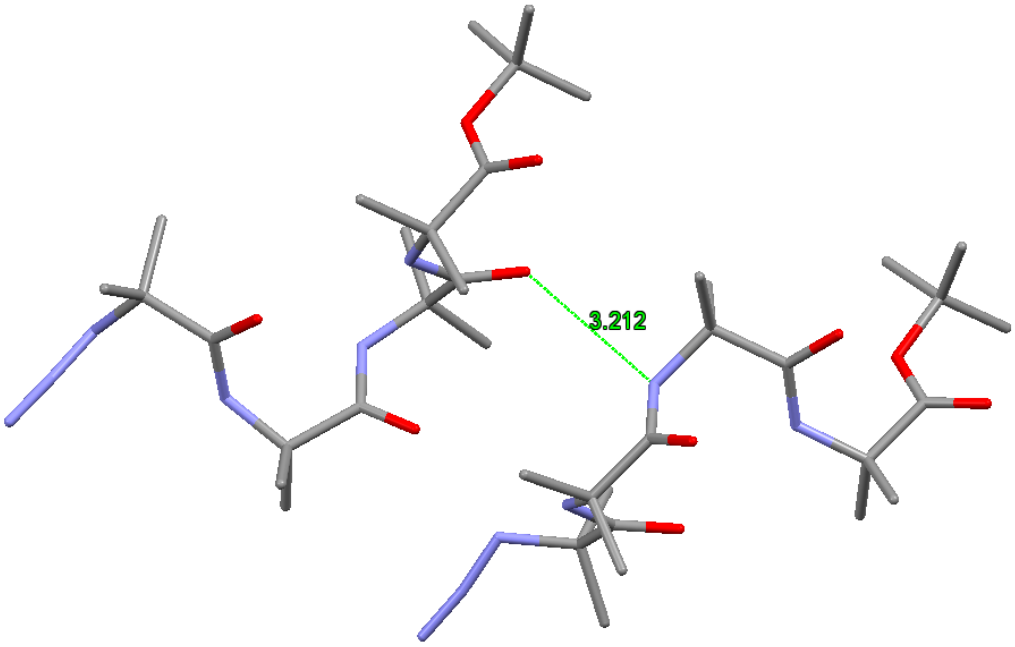


Figure 19. Intermolecular hydrogen-bonding interaction (3.212 Å), between second NH of one oligomer and the third carbonyl on an adjacent oligomer in **3**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

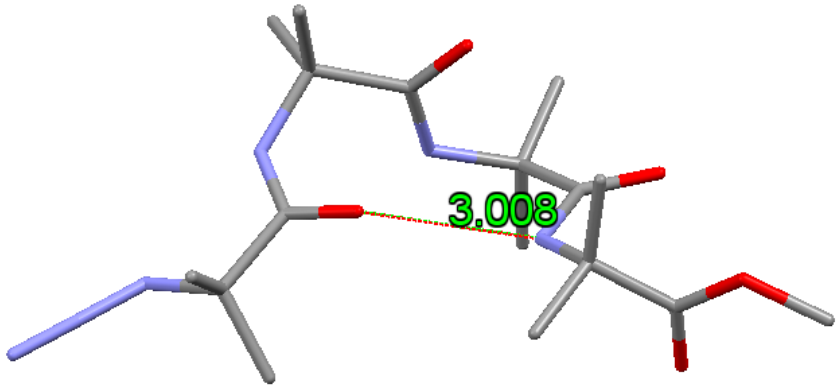


Figure 20. Intramolecular hydrogen-bonding interaction (3.008 Å), between first carbonyl of the chain and the third NH, forming the basis of the 3_{10} helix in **4**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

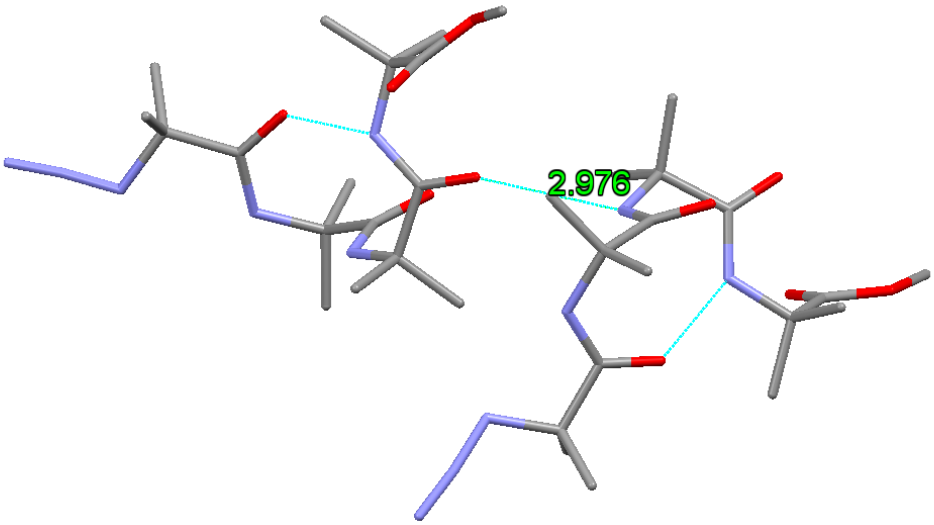


Figure 21. Intermolecular hydrogen-bonding interaction (2.976 Å), between second NH of one oligomer and the third carbonyl on an adjacent oligomer in **4**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

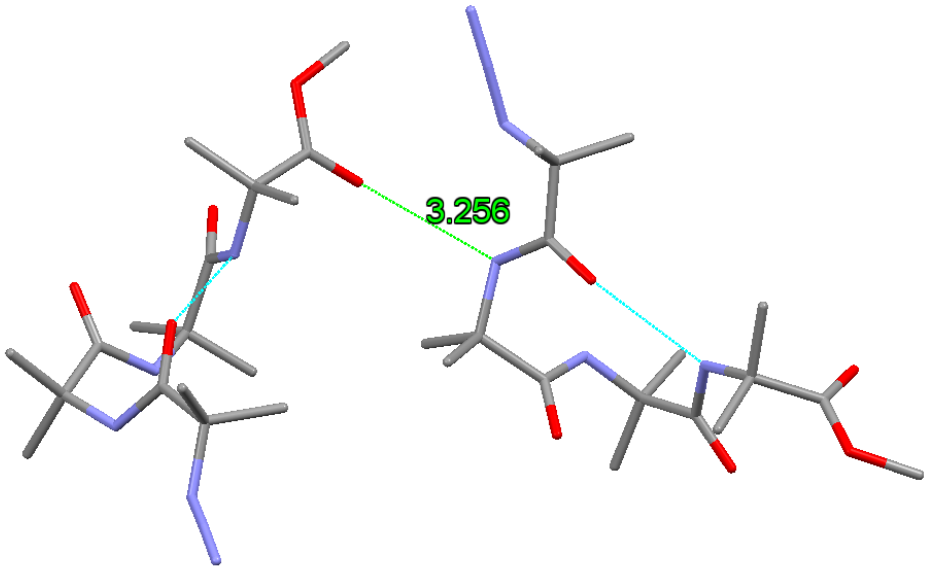


Figure 22. Intermolecular "head-to-tail" hydrogen-bonding interaction (3.256 Å), between first NH of one oligomer and the carbonyl of the ester group an adjacent oligomer in **4**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

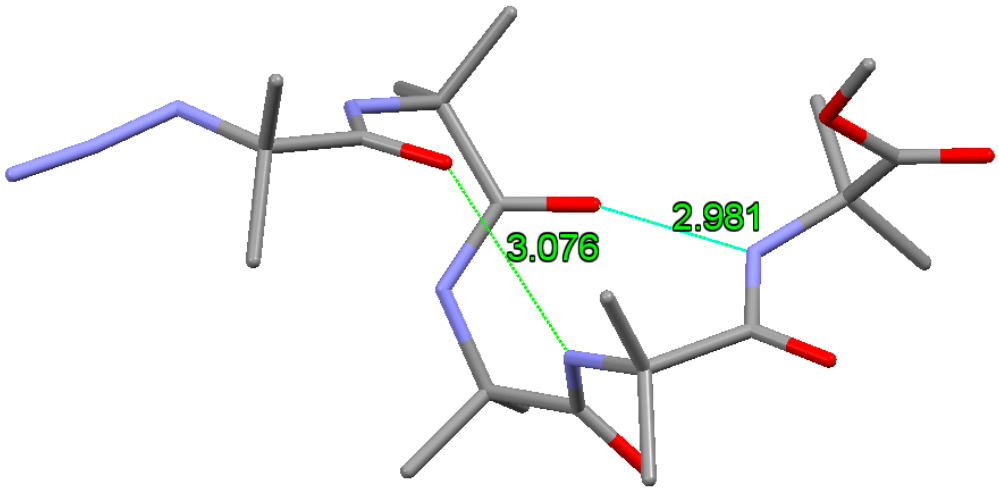


Figure 23. Intramolecular hydrogen-bonding interactions between first carbonyl of the chain and the third NH (3.076 Å) and second carbonyl of the chain and the fourth NH (2.981 Å) forming the basis of the 3_{10} helix in **5**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

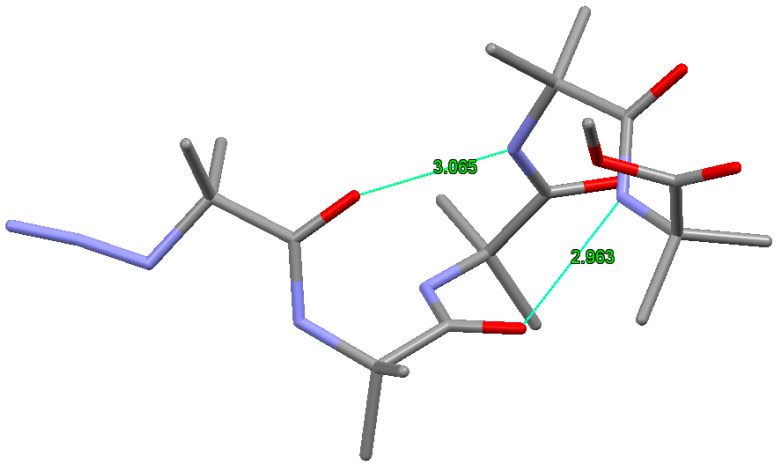


Figure 24. Intramolecular hydrogen-bonding interactions between first carbonyl of the chain and the third NH (3.065 Å) and second carbonyl of the chain and the fourth NH (2.963 Å) forming the basis of the 3_{10} helix in **5**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

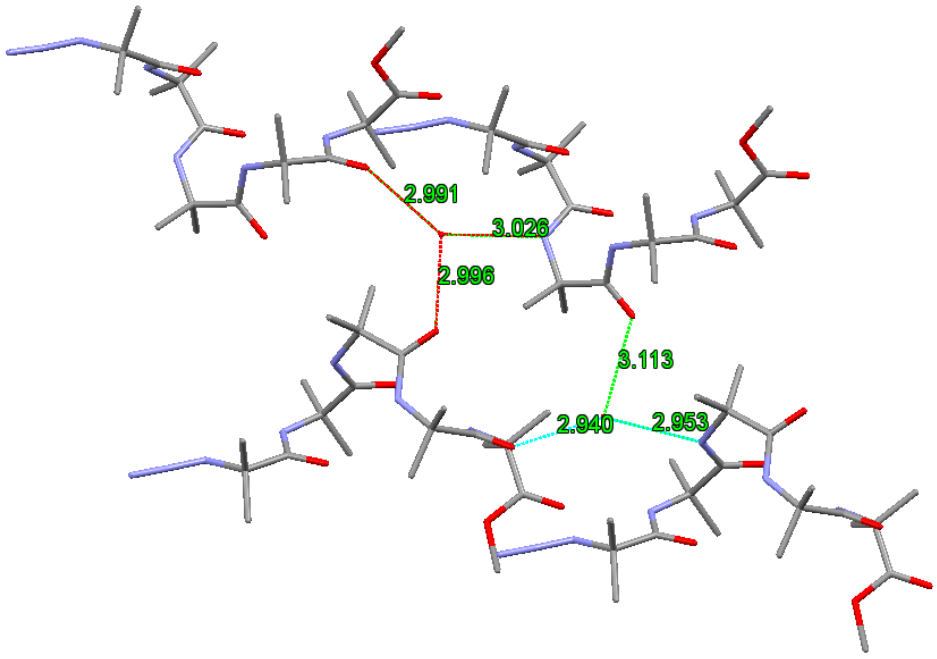


Figure 25. Intermolecular hydrogen-bonding interactions involving a bridging water molecule and three oligomers in **5**. Intermolecular interaction between third carbonyl of one oligomer and water molecule (2.996 Å), another intermolecular hydrogen-bonding interaction between fourth carbonyl of one oligomer and the water molecule (2.991 Å), another intermolecular hydrogen-bonding interaction between the second NH of one oligomer and a water molecule (3.026 Å), a foruth intermolecular hydrogen-bonding interaction between the second NH of one oligomer and a water molecule (2.953 Å), an intermolecular interaction

between fourth carbonyl of one oligomer and water molecule (2.940 Å) and an intermolecular interaction between third carbonyl of one oligomer and water molecule (3.113 Å),

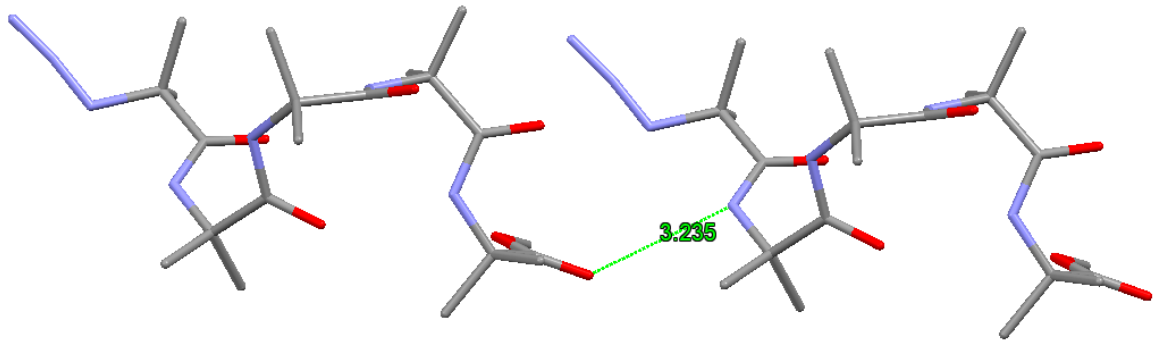


Figure 27. Intermolecular "head-to-tail" hydrogen-bonding interaction (3.235 Å), between first NH of one oligomer and the carbonyl of the ester group an adjacent oligomer in **5**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

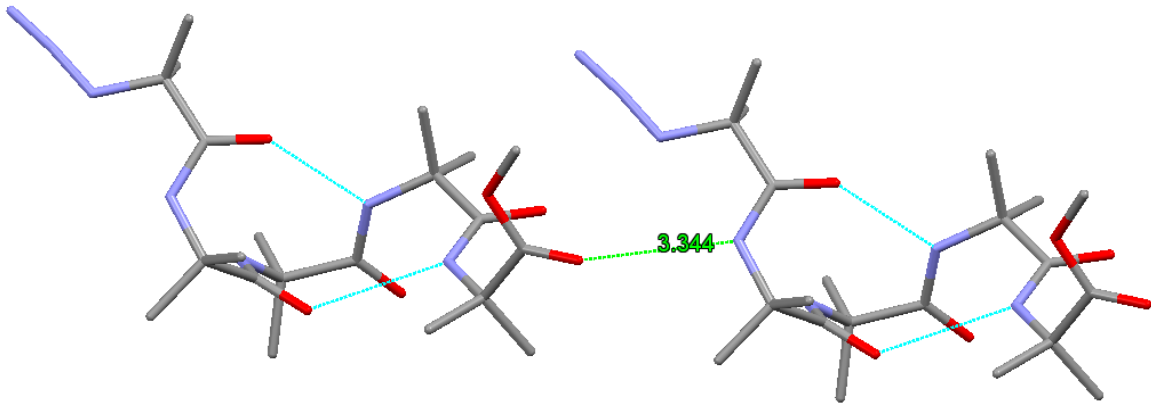


Figure 28. Intermolecular "head-to-tail" hydrogen-bonding interaction (3.344 Å), between first NH of one oligomer and the carbonyl of the ester group an adjacent oligomer in **5**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

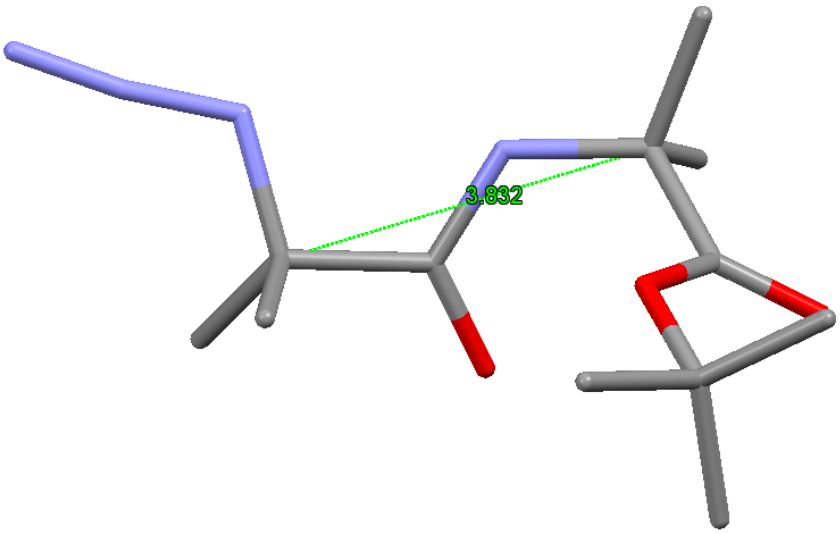


Figure 29. Distance of 3.832Å between first αC (of Aib residue) and last αC (of Aib residue) in **1**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

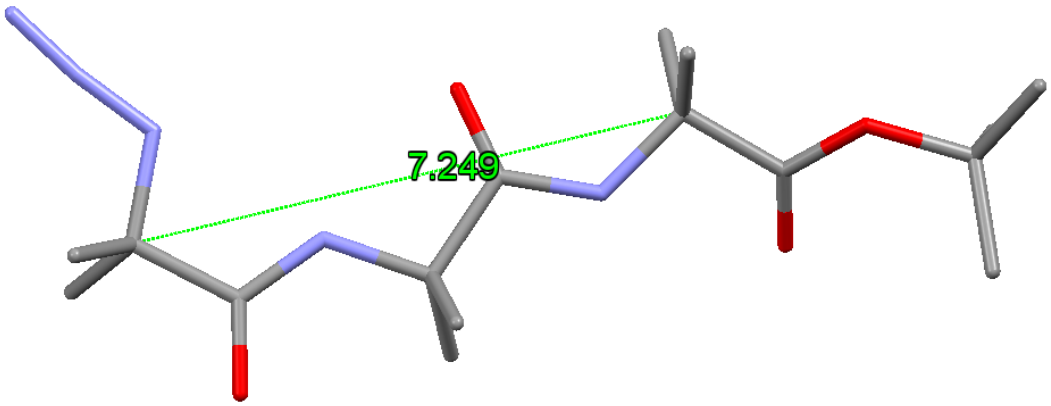


Figure 30. Distance of 7.249 Å between first αC (of Aib residue) and last αC (of Aib residue) in **2**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

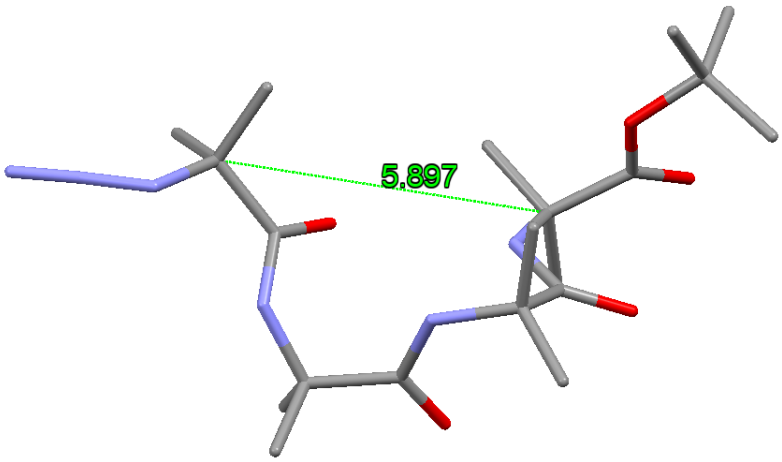


Figure 31 Distance of 5.897 Å between first αC (of Aib residue) and last αC (of Aib residue) in **3**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

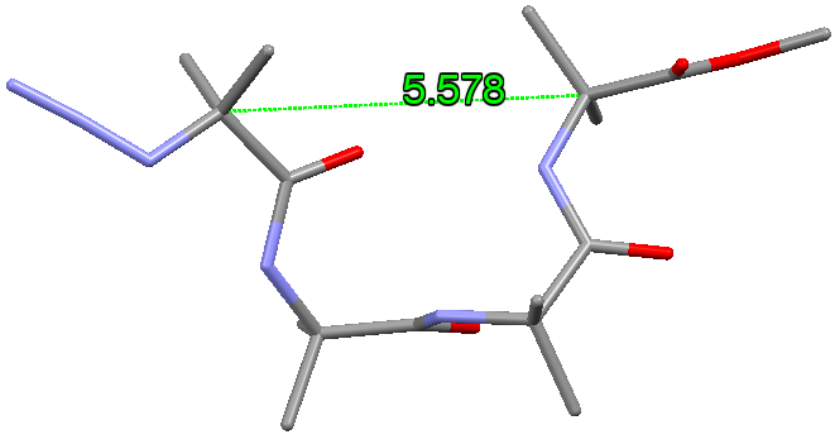


Figure 32. Distance of 5.578 Å between first αC (of Aib residue) and last αC (of Aib residue) in **4**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

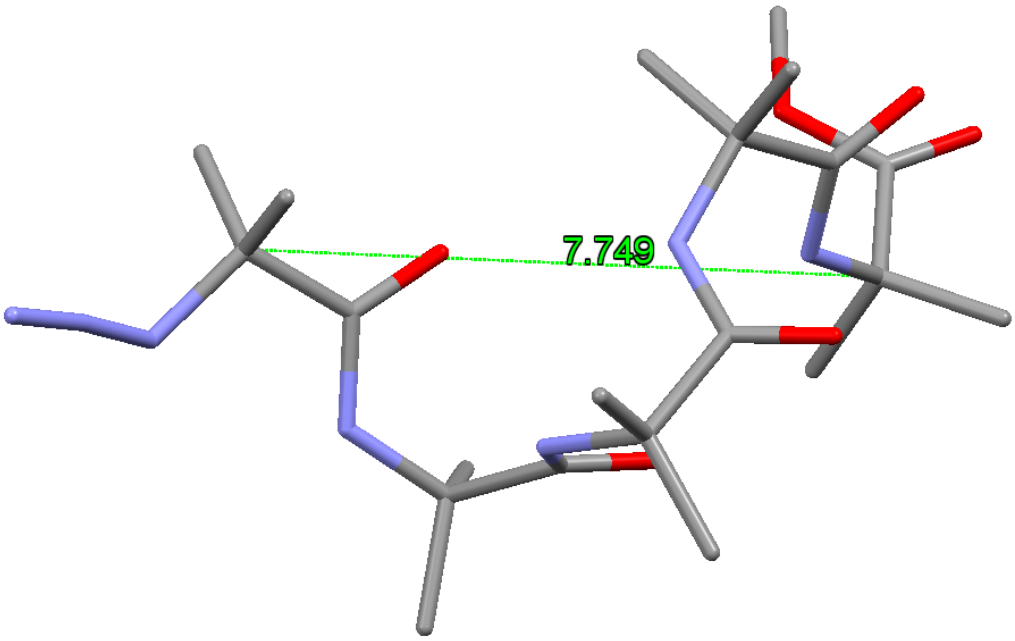
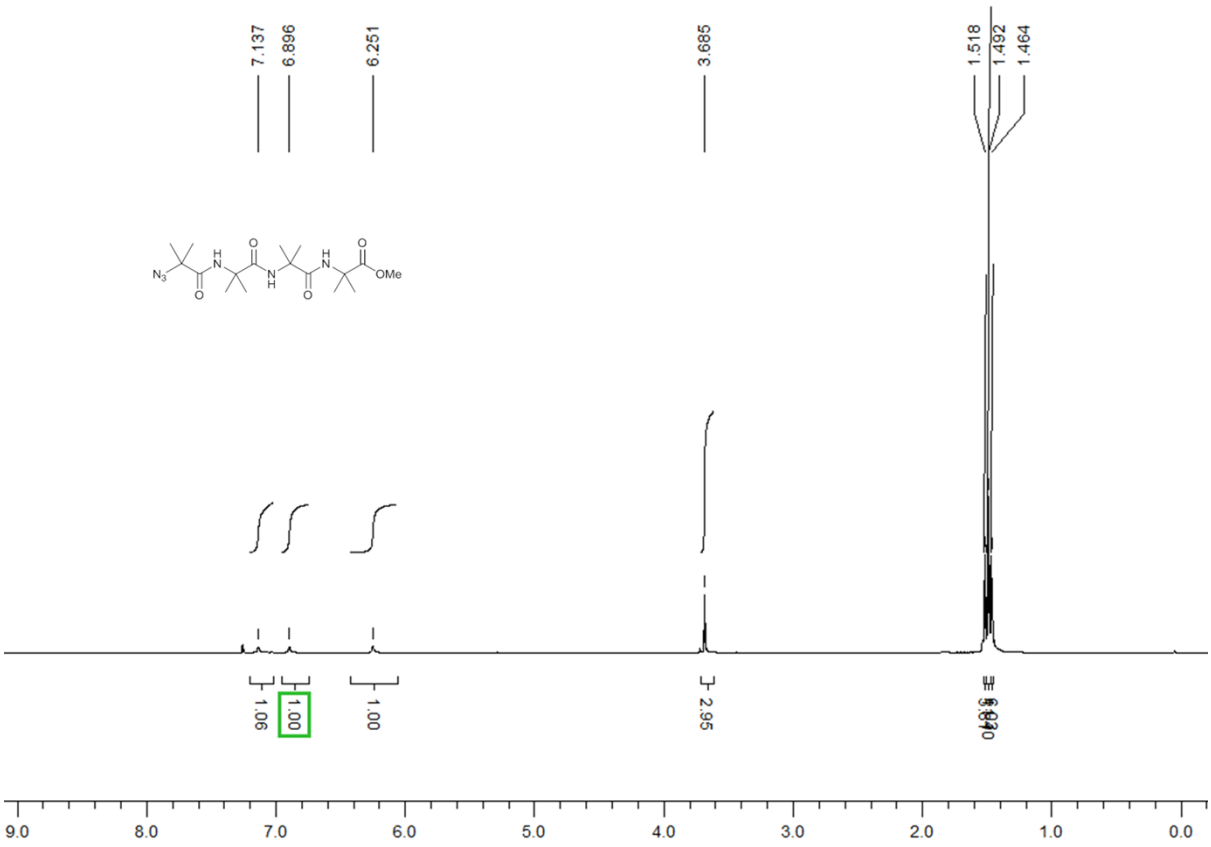
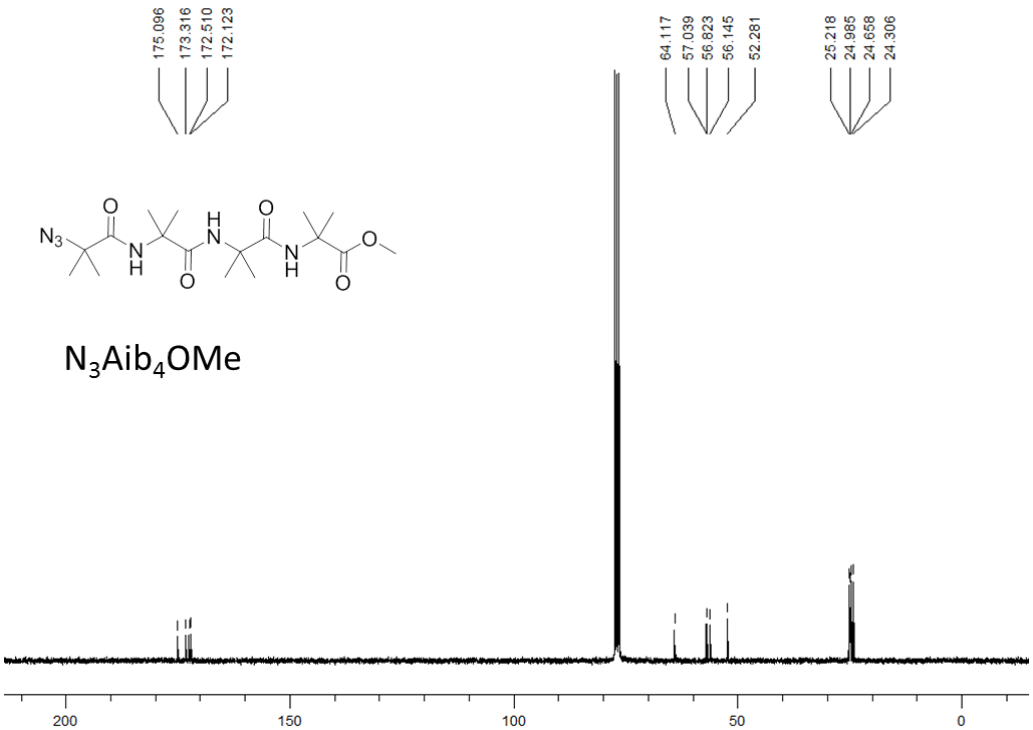


Figure 33. Distance of 7.749 Å between first αC (of Aib residue) and last αC (of Aib residue) in **5**. C atoms are shown in grey, N in light blue and O in red; H atoms have been removed for clarity.

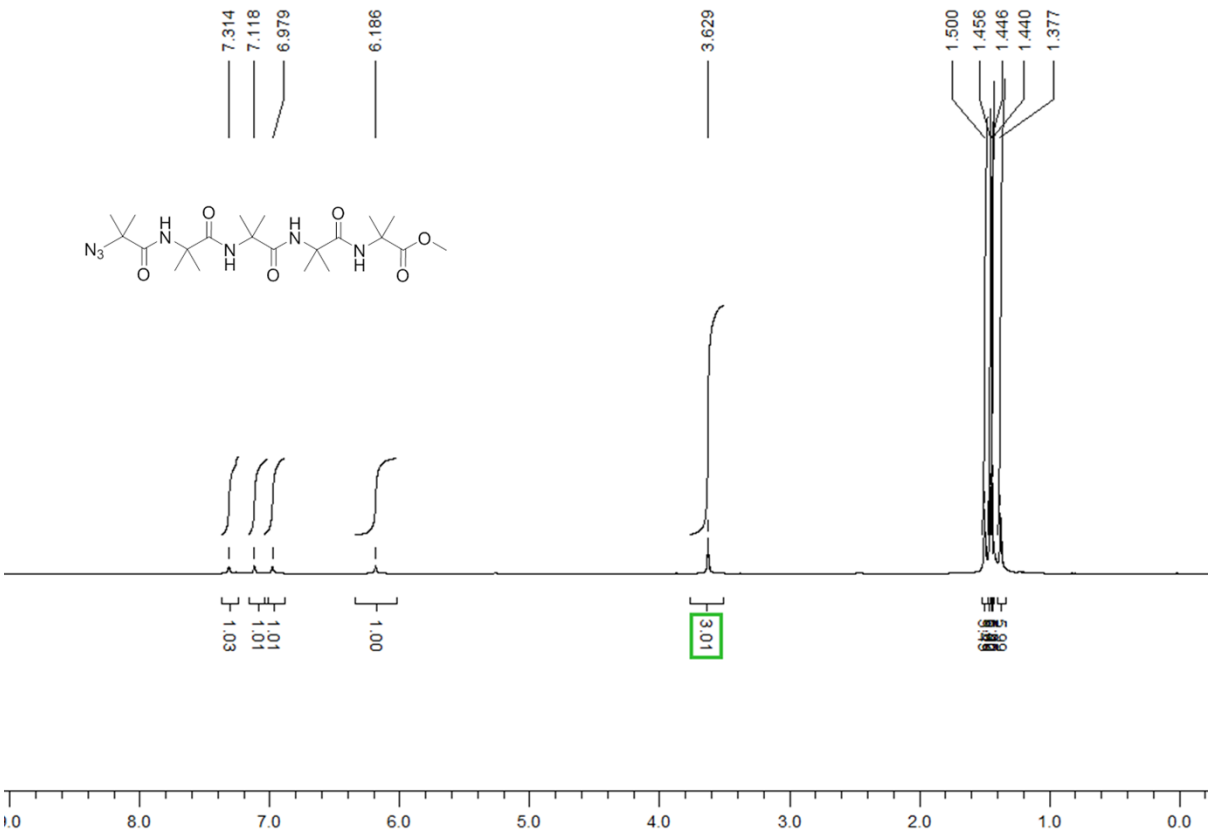
^{1}H and ^{13}C NMR Spectra



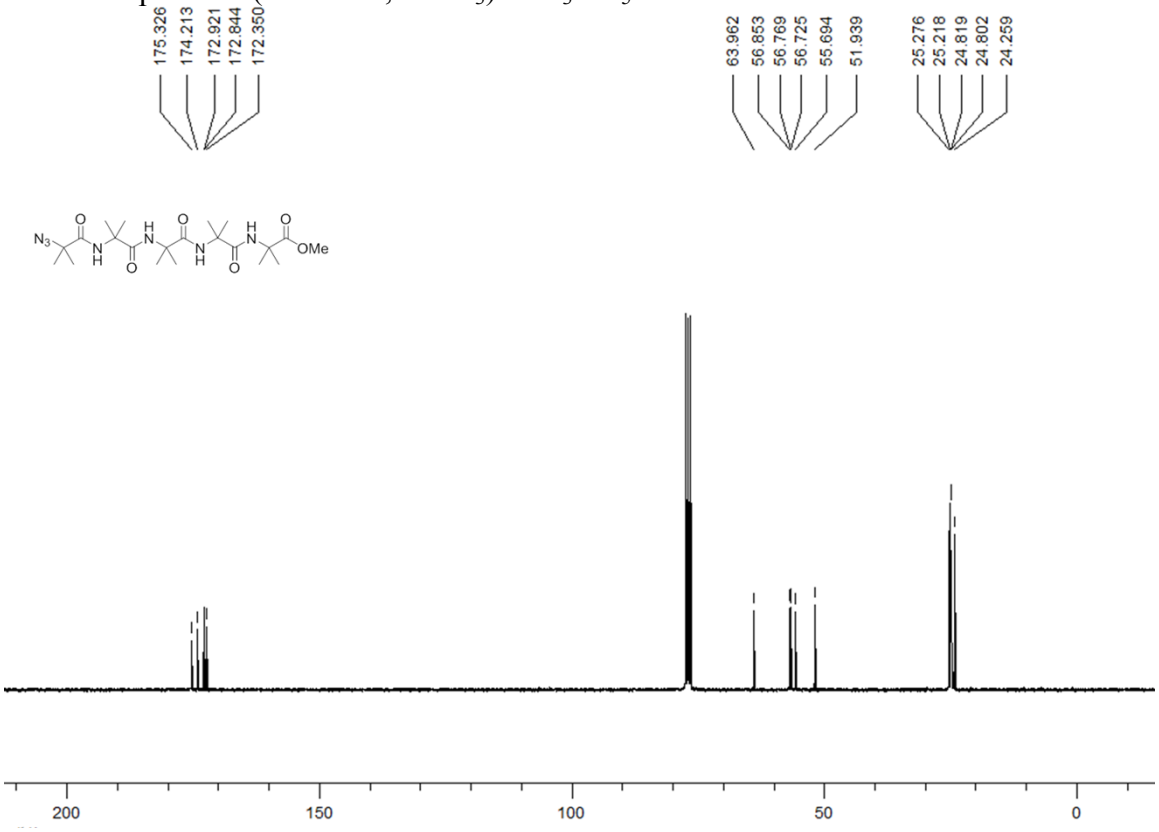
^{1}H NMR spectrum (300MHz, $CDCl_3$) of N_3Aib_4OMe.



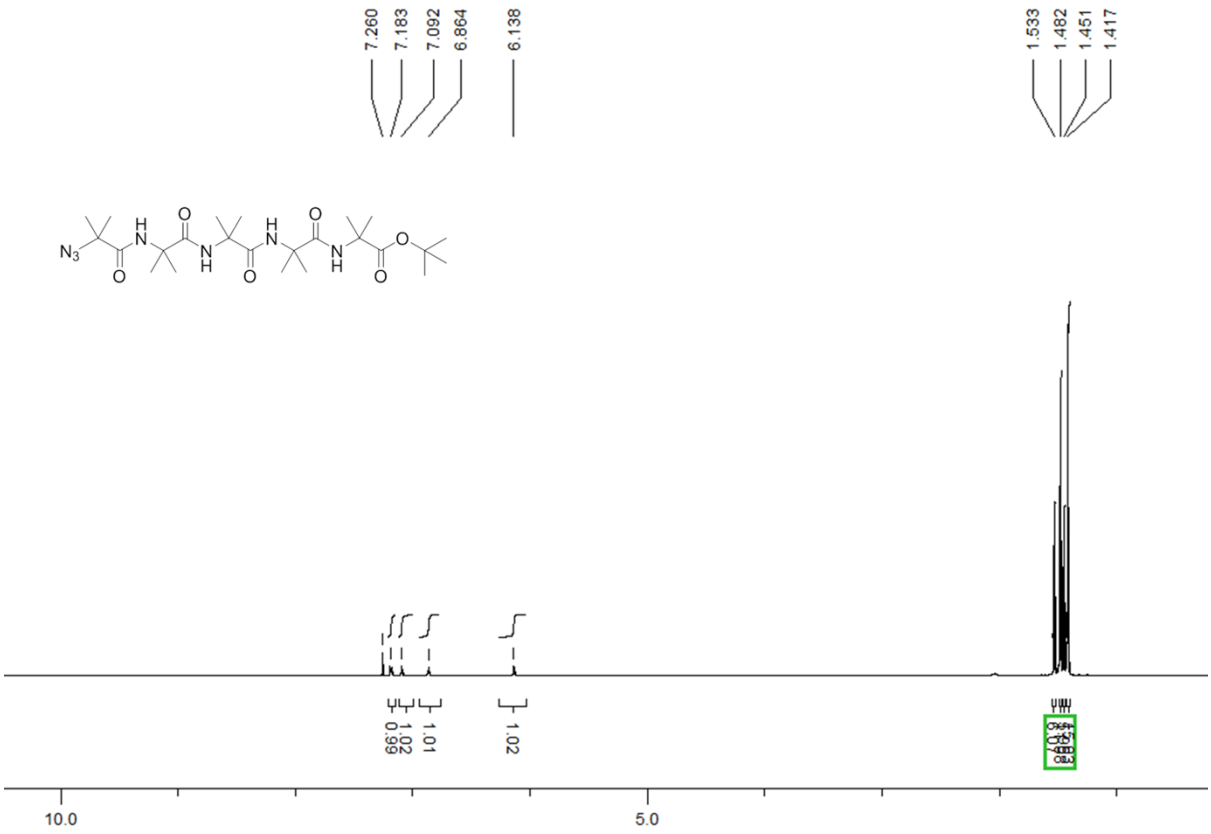
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of N_3Aib_4OMe.



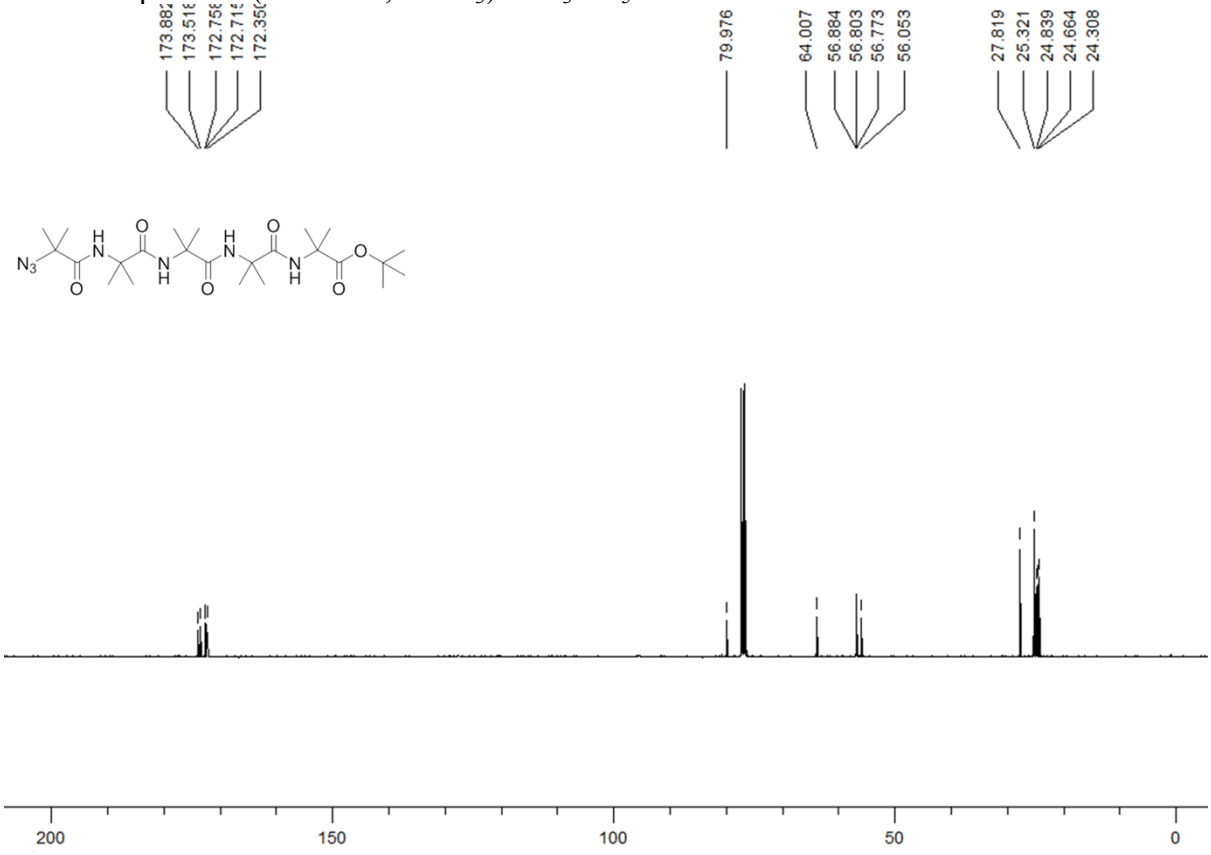
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of N_3Aib_5OMe.



^{13}C NMR spectrum (75 MHz, $CDCl_3$) of N_3Aib_5OMe.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of $N_3Aib_5O^tBu$.



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of $N_3Aib_5O^tBu$

References

1. R. A. Brown, T. Marcelli, M. De Poli, J. Solà, J. Clayden, *Angew. Chem. Int. Ed.,* 2012, **51**, 1395.

2. For a recent example of an azide involved in a hydrogen-bonding interaction see: J. W. Shin, K. S. Min, *Acta Cryst.,* 2008, E**64**, m941.

3. C. Peggion, A. Moretto, F. Formaggio, M. Crisma, C. Toniolo, *Biopolymers (Peptide Science)*, 2013, **100**, 621;

4. S. Scheiner, *J. Phys. Chem. B.,* 2005, **109**, 16132.