Supplementary Information

for

β-Phenylproline: the high β-turn forming propensity of proline combined with an aromatic side chain

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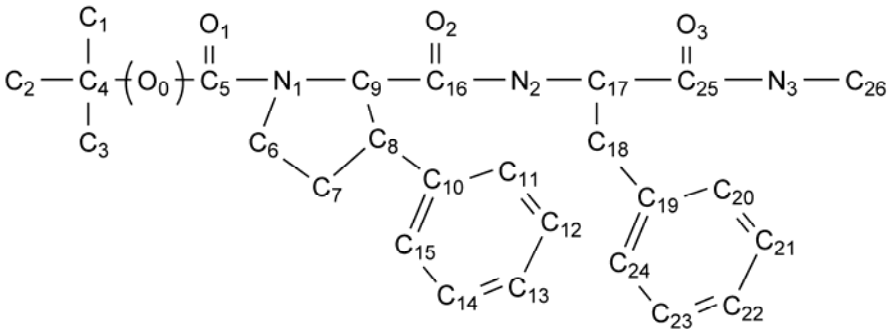
Contents

Geometrical parameters for the X-ray diffraction structures of 1-4, 4a

Atom numbering for all structures:



Geometrical parameters for the X-ray diffraction structure of Piv-L-*cis*(βPh)Pro-L-Phe-NHMe (1)

Bond lengths [Å] with standard deviations for 1.

O(1)-C(5)	1.2419(19)
O(2)-C(16)	1.236(2)
O(3)-C(25)	1.238(2)
N(1)-C(5)	1.347(2)
N(1)-C(9)	1.474(2)
N(1)-C(6)	1.476(2)
N(2)-C(16)	1.344(2)
N(2)-C(17)	1.453(2)
N(3)-C(25)	1.335(2)
N(3)-C(26)	1.446(2)
C(1)-C(4)	1.536(2)
C(2)-C(4)	1.540(2)
C(3)-C(4)	1.535(2)
C(4)-C(5)	1.538(2)
C(6)-C(7)	1.523(2)
C(7)-C(8)	1.524(2)
C(8)-C(10)	1.515(2)
C(8)-C(9)	1.555(2)
C(9)-C(16)	1.518(2)
C(10)-C(11)	1.375(3)
C(10)-C(15)	1.377(3)
C(11)-C(12)	1.386(3)
C(12)-C(13)	1.377(3)
C(13)-C(14)	1.373(3)
C(14)-C(15)	1.381(3)
C(17)-C(18)	1.518(2)
C(17)-C(25)	1.529(2)
C(18)-C(19)	1.516(2)
C(19)-C(20)	1.385(2)
C(19)-C(24)	1.388(2)
C(20)-C(21)	1.384(2)
C(21)-C(22)	1.379(2)
C(22)-C(23)	1.375(3)
C(23)-C(24)	1.387(2)

Bond angles [deg] with standard deviations for 1.

C(5)-N(1)-C(9)	118.75(13)
C(5)-N(1)-C(6)	128.87(13)
C(9)-N(1)-C(6)	111.48(13)
C(16)-N(2)-C(17)	120.76(14)
C(25)-N(3)-C(26)	120.96(15)
C(3)-C(4)-C(1)	108.02(15)
C(3)-C(4)-C(5)	115.02(15)
C(1)-C(4)-C(5)	107.29(14)
C(3)-C(4)-C(2)	110.33(15)
C(1)-C(4)-C(2)	108.10(17)
C(5)-C(4)-C(2)	107.85(14)
O(1)-C(5)-N(1)	118.67(15)
O(1)-C(5)-C(4)	119.19(16)
N(1)-C(5)-C(4)	122.08(14)
N(1)-C(6)-C(7)	103.30(13)
C(6)-C(7)-C(8)	103.38(15)
C(10)-C(8)-C(7)	116.79(15)
C(10)-C(8)-C(9)	114.64(14)
C(7)-C(8)-C(9)	102.53(13)
N(1)-C(9)-C(16)	109.30(13)
N(1)-C(9)-C(8)	103.46(13)
C(16)-C(9)-C(8)	111.47(14)
C(11)-C(10)-C(15)	117.87(17)
C(11)-C(10)-C(8)	122.85(16)
C(15)-C(10)-C(8)	119.27(17)
C(10)-C(11)-C(12)	121.92(18)
C(13)-C(12)-C(11)	119.5(2)
C(14)-C(13)-C(12)	119.12(18)
C(13)-C(14)-C(15)	120.84(18)
C(10)-C(15)-C(14)	120.77(19)
O(2)-C(16)-N(2)	122.11(16)
O(2)-C(16)-C(9)	121.32(15)
N(2)-C(16)-C(9)	116.57(15)
N(2)-C(17)-C(18)	112.68(14)
N(2)-C(17)-C(25)	111.43(13)
C(18)-C(17)-C(25)	112.13(14)
C(19)-C(18)-C(17)	116.64(14)
C(20)-C(19)-C(24)	117.83(16)
C(20)-C(19)-C(18)	123.66(15)
C(24)-C(19)-C(18)	118.52(16)
C(21)-C(20)-C(19)	120.44(16)
C(22)-C(21)-C(20)	120.80(18)
C(23)-C(22)-C(21)	119.79(18)
C(22)-C(23)-C(24)	119.09(17)
C(23)-C(24)-C(19)	122.03(17)
O(3)-C(25)-N(3)	121.90(16)
O(3)-C(25)-C(17)	121.47(15)
N(3)-C(25)-C(17)	116.37(15)

Torsion angles [deg] with standard deviations for 1.

C(9)-N(1)-C(5)-O(1)	-3.7(2)
C(6)-N(1)-C(5)-O(1)	-171.75(17)
C(9)-N(1)-C(5)-C(4)	173.70(15)
C(6)-N(1)-C(5)-C(4)	5.6(3)
C(3)-C(4)-C(5)-O(1)	-138.80(16)
C(1)-C(4)-C(5)-O(1)	-18.6(2)
C(2)-C(4)-C(5)-O(1)	97.62(18)
C(3)-C(4)-C(5)-N(1)	43.9(2)
C(1)-C(4)-C(5)-N(1)	164.04(17)
C(2)-C(4)-C(5)-N(1)	-79.7(2)
C(5)-N(1)-C(6)-C(7)	152.87(17)
C(9)-N(1)-C(6)-C(7)	-15.9(2)
N(1)-C(6)-C(7)-C(8)	34.48(19)
C(6)-C(7)-C(8)-C(10)	-166.06(15)
C(6)-C(7)-C(8)-C(9)	-39.84(18)
C(5)-N(1)-C(9)-C(16)	-59.93(19)
C(6)-N(1)-C(9)-C(16)	110.13(16)
C(5)-N(1)-C(9)-C(8)	-178.79(15)
C(6)-N(1)-C(9)-C(8)	-8.73(19)
C(10)-C(8)-C(9)-N(1)	157.37(15)
C(7)-C(8)-C(9)-N(1)	29.78(17)
C(10)-C(8)-C(9)-C(16)	40.0(2)
C(7)-C(8)-C(9)-C(16)	-87.57(16)
C(7)-C(8)-C(10)-C(11)	8.6(3)
C(9)-C(8)-C(10)-C(11)	-111.3(2)
C(7)-C(8)-C(10)-C(15)	-170.42(17)
C(9)-C(8)-C(10)-C(15)	69.6(2)
C(15)-C(10)-C(11)-C(12)	0.3(3)
C(8)-C(10)-C(11)-C(12)	-178.77(18)
C(10)-C(11)-C(12)-C(13)	-0.6(3)
C(11)-C(12)-C(13)-C(14)	0.5(3)
C(12)-C(13)-C(14)-C(15)	0.0(3)
C(11)-C(10)-C(15)-C(14)	0.2(3)
C(8)-C(10)-C(15)-C(14)	179.28(17)
C(13)-C(14)-C(15)-C(10)	-0.3(3)
C(17)-N(2)-C(16)-O(2)	0.9(2)
C(17)-N(2)-C(16)-C(9)	-178.92(14)
N(1)-C(9)-C(16)-O(2)	-49.7(2)
C(8)-C(9)-C(16)-O(2)	64.01(19)
N(1)-C(9)-C(16)-N(2)	130.07(15)
C(8)-C(9)-C(16)-N(2)	-116.17(16)
C(16)-N(2)-C(17)-C(18)	-74.78(18)

C(16)-N(2)-C(17)-C(25)	52.3(2)
N(2)-C(17)-C(18)-C(19)	-76.54(18)
C(25)-C(17)-C(18)-C(19)	156.77(15)
C(17)-C(18)-C(19)-C(20)	-6.4(2)
C(17)-C(18)-C(19)-C(24)	173.60(15)
C(24)-C(19)-C(20)-C(21)	1.5(2)
C(18)-C(19)-C(20)-C(21)	-178.48(18)
C(19)-C(20)-C(21)-C(22)	-0.8(3)
C(20)-C(21)-C(22)-C(23)	-0.2(3)
C(21)-C(22)-C(23)-C(24)	0.5(3)
C(22)-C(23)-C(24)-C(19)	0.2(3)
C(20)-C(19)-C(24)-C(23)	-1.2(3)
C(18)-C(19)-C(24)-C(23)	178.77(17)
C(26)-N(3)-C(25)-O(3)	5.1(2)
C(26)-N(3)-C(25)-C(17)	179.29(15)
N(2)-C(17)-C(25)-O(3)	-151.15(15)
C(18)-C(17)-C(25)-O(3)	-23.8(2)
N(2)-C(17)-C(25)-N(3)	34.68(19)
C(18)-C(17)-C(25)-N(3)	162.03(15)

Dimensions [Å, deg.] of the D-H...A hydrogen bonds for 1.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(1)	0.96	2.05	2.9547(18)	156.4
N(2)-H(2)...O(3)#1	0.94	2.03	2.9320(17)	159.5

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z

Geometrical parameters for the X-ray diffraction structure of Piv-L-*cis*(βPh)Pro-D-Phe-NHMe (2)

Bond lengths [Å] with standard deviations for 2.

O(1)-C(5)	1.253(4)
O(2)-C(16)	1.233(4)
O(3)-C(25)	1.231(4)
N(1)-C(5)	1.341(4)
N(1)-C(6)	1.465(4)
N(1)-C(9)	1.473(4)
N(2)-C(16)	1.334(4)
N(2)-C(17)	1.449(4)
N(3)-C(25)	1.336(4)
N(3)-C(26)	1.450(4)
C(1)-C(4)	1.534(4)
C(2)-C(4)	1.528(5)
C(3)-C(4)	1.521(4)
C(4)-C(5)	1.520(4)
C(6)-C(7)	1.505(5)
C(7)-C(8)	1.524(4)
C(8)-C(10)	1.508(4)
C(8)-C(9)	1.538(5)
C(9)-C(16)	1.519(4)
C(10)-C(11)	1.386(4)
C(10)-C(15)	1.387(4)
C(11)-C(12)	1.377(5)
C(12)-C(13)	1.389(5)
C(13)-C(14)	1.361(5)
C(14)-C(15)	1.371(5)
C(17)-C(18)	1.521(4)
C(17)-C(25)	1.526(4)
C(18)-C(19)	1.520(4)
C(19)-C(20)	1.371(4)
C(19)-C(24)	1.381(4)
C(20)-C(21)	1.385(5)
C(21)-C(22)	1.369(4)
C(22)-C(23)	1.372(5)
C(23)-C(24)	1.371(4)

Bond angles [deg] with standard deviations for 2.

C(5)-N(1)-C(6)	129.7(3)
C(5)-N(1)-C(9)	117.6(3)
C(6)-N(1)-C(9)	111.6(3)
C(16)-N(2)-C(17)	119.4(3)
C(25)-N(3)-C(26)	120.9(3)
C(5)-C(4)-C(3)	116.3(3)
C(5)-C(4)-C(2)	108.2(3)
C(3)-C(4)-C(2)	107.2(3)
C(5)-C(4)-C(1)	107.9(3)
C(3)-C(4)-C(1)	108.7(3)
C(2)-C(4)-C(1)	108.4(3)
O(1)-C(5)-N(1)	118.7(3)
O(1)-C(5)-C(4)	118.7(3)
N(1)-C(5)-C(4)	122.5(3)
N(1)-C(6)-C(7)	103.9(3)
C(6)-C(7)-C(8)	104.2(3)
C(10)-C(8)-C(7)	118.4(3)
C(10)-C(8)-C(9)	114.3(3)
C(7)-C(8)-C(9)	102.4(3)
N(1)-C(9)-C(16)	109.3(2)
N(1)-C(9)-C(8)	103.4(2)
C(16)-C(9)-C(8)	111.7(3)
C(11)-C(10)-C(15)	117.3(3)
C(11)-C(10)-C(8)	119.4(3)
C(15)-C(10)-C(8)	123.3(3)
C(12)-C(11)-C(10)	121.9(4)
C(11)-C(12)-C(13)	119.4(3)
C(14)-C(13)-C(12)	119.2(4)
C(13)-C(14)-C(15)	121.2(4)
C(14)-C(15)-C(10)	121.0(3)
O(2)-C(16)-N(2)	122.5(3)
O(2)-C(16)-C(9)	120.4(3)
N(2)-C(16)-C(9)	117.1(3)
N(2)-C(17)-C(18)	111.0(3)
N(2)-C(17)-C(25)	113.1(3)
C(18)-C(17)-C(25)	106.8(3)
C(19)-C(18)-C(17)	116.6(3)
C(20)-C(19)-C(24)	117.8(3)
C(20)-C(19)-C(18)	122.4(3)
C(24)-C(19)-C(18)	119.7(3)
C(19)-C(20)-C(21)	121.3(3)
C(22)-C(21)-C(20)	120.5(3)
C(21)-C(22)-C(23)	118.1(3)
C(24)-C(23)-C(22)	121.5(3)
C(23)-C(24)-C(19)	120.7(3)
O(3)-C(25)-N(3)	122.5(3)
O(3)-C(25)-C(17)	120.5(3)
N(3)-C(25)-C(17)	116.9(3)

Torsion angles [deg] with standard deviations for 2.

C(6)-N(1)-C(5)-O(1)	-171.4(3)
C(9)-N(1)-C(5)-O(1)	-5.0(4)
C(6)-N(1)-C(5)-C(4)	4.6(5)
C(9)-N(1)-C(5)-C(4)	170.9(3)
C(3)-C(4)-C(5)-O(1)	-141.6(3)
C(2)-C(4)-C(5)-O(1)	-20.9(4)
C(1)-C(4)-C(5)-O(1)	96.2(3)
C(3)-C(4)-C(5)-N(1)	42.4(4)
C(2)-C(4)-C(5)-N(1)	163.1(3)
C(1)-C(4)-C(5)-N(1)	-79.8(4)
C(5)-N(1)-C(6)-C(7)	155.2(3)
C(9)-N(1)-C(6)-C(7)	-11.8(3)
N(1)-C(6)-C(7)-C(8)	31.2(3)
C(6)-C(7)-C(8)-C(10)	-165.3(3)
C(6)-C(7)-C(8)-C(9)	-38.6(3)
C(5)-N(1)-C(9)-C(16)	-61.8(4)
C(6)-N(1)-C(9)-C(16)	106.9(3)
C(5)-N(1)-C(9)-C(8)	179.1(3)
C(6)-N(1)-C(9)-C(8)	-12.1(3)
C(10)-C(8)-C(9)-N(1)	160.1(3)
C(7)-C(8)-C(9)-N(1)	30.7(3)
C(10)-C(8)-C(9)-C(16)	42.7(4)
C(7)-C(8)-C(9)-C(16)	-86.7(3)
C(7)-C(8)-C(10)-C(11)	-160.8(3)
C(9)-C(8)-C(10)-C(11)	78.4(4)
C(7)-C(8)-C(10)-C(15)	20.2(5)
C(9)-C(8)-C(10)-C(15)	-100.6(4)
C(15)-C(10)-C(11)-C(12)	1.9(5)
C(8)-C(10)-C(11)-C(12)	-177.2(3)
C(10)-C(11)-C(12)-C(13)	-1.5(6)
C(11)-C(12)-C(13)-C(14)	0.0(6)
C(12)-C(13)-C(14)-C(15)	1.0(6)
C(13)-C(14)-C(15)-C(10)	-0.6(6)
C(11)-C(10)-C(15)-C(14)	-0.9(5)
C(8)-C(10)-C(15)-C(14)	178.2(4)
C(17)-N(2)-C(16)-O(2)	3.5(5)
C(17)-N(2)-C(16)-C(9)	-176.8(3)
N(1)-C(9)-C(16)-O(2)	-46.5(4)
C(8)-C(9)-C(16)-O(2)	67.2(4)
N(1)-C(9)-C(16)-N(2)	133.8(3)
C(8)-C(9)-C(16)-N(2)	-112.4(3)
C(16)-N(2)-C(17)-C(18)	-178.1(3)

C(16)-N(2)-C(17)-C(25)	61.9(4)
N(2)-C(17)-C(18)-C(19)	60.5(4)
C(25)-C(17)-C(18)-C(19)	-175.8(3)
C(17)-C(18)-C(19)-C(20)	55.7(4)
C(17)-C(18)-C(19)-C(24)	-126.2(3)
C(24)-C(19)-C(20)-C(21)	-1.4(5)
C(18)-C(19)-C(20)-C(21)	176.7(3)
C(19)-C(20)-C(21)-C(22)	1.4(5)
C(20)-C(21)-C(22)-C(23)	-0.7(5)
C(21)-C(22)-C(23)-C(24)	0.2(5)
C(22)-C(23)-C(24)-C(19)	-0.2(5)
C(20)-C(19)-C(24)-C(23)	0.8(5)
C(18)-C(19)-C(24)-C(23)	-177.3(3)
C(26)-N(3)-C(25)-O(3)	3.4(5)
C(26)-N(3)-C(25)-C(17)	179.2(3)
N(2)-C(17)-C(25)-O(3)	-158.3(3)
C(18)-C(17)-C(25)-O(3)	79.3(4)
N(2)-C(17)-C(25)-N(3)	25.8(4)
C(18)-C(17)-C(25)-N(3)	-96.6(3)

Dimensions [Å, deg] of the D-H...A hydrogen bonds for 2.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(1)	1.05	1.94	2.904(3)	150.6
N(2)-H(2)...O(3)#1	1.03	1.92	2.915(3)	162.0

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z

Geometrical parameters for the X-ray diffraction structure of Piv-L-*trans*(βPh)Pro-L-Phe-NHMe (3)

Bond lengths [Å] with standard deviations for 3.

Molecule A	
O(1)-C(5)	1.2321(16)
O(2)-C(16)	1.2273(15)
O(3)-C(25)	1.2230(16)
N(1)-C(5)	1.3548(17)
N(1)-C(6)	1.4699(17)
N(1)-C(9)	1.4736(16)
N(2)-C(16)	1.3431(16)
N(2)-C(17)	1.4563(16)
N(3)-C(25)	1.3353(18)
N(3)-C(26)	1.4508(18)
C(1)-C(4)	1.525(2)
C(2)-C(4)	1.538(2)
C(3)-C(4)	1.532(2)
C(4)-C(5)	1.544(2)
C(6)-C(7)	1.5098(19)
C(7)-C(8)	1.5261(18)
C(8)-C(10)	1.5012(19)
C(8)-C(9)	1.5499(18)
C(9)-C(16)	1.5239(18)
C(10)-C(15)	1.3857(18)
C(10)-C(11)	1.3919(19)
C(11)-C(12)	1.374(2)
C(12)-C(13)	1.380(2)
C(13)-C(14)	1.371(2)
C(14)-C(15)	1.3819(19)
C(17)-C(25)	1.5340(19)
C(17)-C(18)	1.5438(19)
C(18)-C(19)	1.4989(19)
C(19)-C(24)	1.383(2)
C(19)-C(20)	1.3846(19)
C(20)-C(21)	1.377(2)
C(21)-C(22)	1.376(2)
C(22)-C(23)	1.368(2)
C(23)-C(24)	1.377(2)

Molecule B

O(1')-C(5')	1.2323(15)
O(2')-C(16')	1.2305(15)
O(3')-C(25')	1.2244(16)
N(1')-C(5')	1.3532(17)
N(1')-C(9')	1.4687(16)
N(1')-C(6')	1.4711(16)
N(2')-C(16')	1.3448(16)
N(2')-C(17')	1.4557(15)
N(3')-C(25')	1.3331(17)
N(3')-C(26')	1.4467(18)
C(1')-C(4')	1.530(2)
C(2')-C(4')	1.534(2)
C(3')-C(4')	1.528(2)
C(4')-C(5')	1.5362(19)
C(6')-C(7')	1.503(2)
C(7')-C(8')	1.5335(18)
C(8')-C(10')	1.5030(19)
C(8')-C(9')	1.5365(18)
C(9')-C(16')	1.5192(17)
C(10')-C(15')	1.374(2)
C(10')-C(11')	1.376(2)
C(11')-C(12')	1.391(2)
C(12')-C(13')	1.362(2)
C(13')-C(14')	1.362(2)
C(14')-C(15')	1.381(2)
C(17')-C(18')	1.5316(19)
C(17')-C(25')	1.540(2)
C(18')-C(19')	1.507(2)
C(19')-C(24')	1.3799(19)
C(19')-C(20')	1.3850(19)
C(20')-C(21')	1.382(2)
C(21')-C(22')	1.378(2)
C(22')-C(23')	1.371(2)
C(23')-C(24')	1.388(2)

Bond angles [deg] with standard deviations for 3.

Molecule A

C(5)-N(1)-C(6)	130.53(11)
C(5)-N(1)-C(9)	118.02(11)
C(6)-N(1)-C(9)	111.42(10)
C(16)-N(2)-C(17)	122.40(11)
C(25)-N(3)-C(26)	120.22(12)
C(1)-C(4)-C(3)	108.91(13)
C(1)-C(4)-C(2)	107.93(13)
C(3)-C(4)-C(2)	110.34(13)
C(1)-C(4)-C(5)	107.19(13)
C(3)-C(4)-C(5)	110.95(12)
C(2)-C(4)-C(5)	111.39(12)
O(1)-C(5)-N(1)	118.45(12)
O(1)-C(5)-C(4)	120.59(12)
N(1)-C(5)-C(4)	120.94(13)
N(1)-C(6)-C(7)	102.83(11)
C(6)-C(7)-C(8)	102.61(11)
C(10)-C(8)-C(7)	116.01(11)
C(10)-C(8)-C(9)	115.80(11)
C(7)-C(8)-C(9)	101.86(10)
N(1)-C(9)-C(16)	110.54(10)
N(1)-C(9)-C(8)	102.88(10)
C(16)-C(9)-C(8)	110.08(10)
C(15)-C(10)-C(11)	117.95(13)
C(15)-C(10)-C(8)	119.38(12)
C(11)-C(10)-C(8)	122.64(12)
C(12)-C(11)-C(10)	120.88(13)
C(11)-C(12)-C(13)	120.51(14)
C(14)-C(13)-C(12)	119.23(14)
C(13)-C(14)-C(15)	120.54(13)
C(14)-C(15)-C(10)	120.85(13)
O(2)-C(16)-N(2)	123.28(12)
O(2)-C(16)-C(9)	120.70(12)
N(2)-C(16)-C(9)	115.97(12)
N(2)-C(17)-C(25)	114.38(11)
N(2)-C(17)-C(18)	113.45(11)
C(25)-C(17)-C(18)	111.88(11)
C(19)-C(18)-C(17)	113.58(11)
C(24)-C(19)-C(20)	117.46(13)
C(24)-C(19)-C(18)	121.54(13)
C(20)-C(19)-C(18)	120.98(13)
C(21)-C(20)-C(19)	121.64(14)
C(22)-C(21)-C(20)	119.66(15)

C(23)-C(22)-C(21)	119.70(16)
C(22)-C(23)-C(24)	120.31(15)
C(23)-C(24)-C(19)	121.22(14)
O(3)-C(25)-N(3)	122.52(13)
O(3)-C(25)-C(17)	119.88(13)
N(3)-C(25)-C(17)	117.35(12)

Molecule B

C(5')-N(1')-C(9')	117.88(10)
C(5')-N(1')-C(6')	130.70(11)
C(9')-N(1')-C(6')	111.26(10)
C(16')-N(2')-C(17')	122.29(11)
C(25')-N(3')-C(26')	121.65(12)
C(3')-C(4')-C(1')	108.83(13)
C(3')-C(4')-C(2')	110.22(13)
C(1')-C(4')-C(2')	107.66(13)
C(3')-C(4')-C(5')	110.96(12)
C(1')-C(4')-C(5')	107.73(12)
C(2')-C(4')-C(5')	111.33(11)
O(1')-C(5')-N(1')	118.46(12)
O(1')-C(5')-C(4')	120.55(12)
N(1')-C(5')-C(4')	120.97(11)
N(1')-C(6')-C(7')	102.55(10)
C(6')-C(7')-C(8')	102.90(10)
C(10')-C(8')-C(7')	114.17(10)
C(10')-C(8')-C(9')	118.20(11)
C(7')-C(8')-C(9')	101.28(10)
N(1')-C(9')-C(16')	110.11(10)
N(1')-C(9')-C(8')	103.51(10)
C(16')-C(9')-C(8')	111.33(11)
C(15')-C(10')-C(11')	117.55(14)
C(15')-C(10')-C(8')	118.05(13)
C(11')-C(10')-C(8')	124.33(13)
C(10')-C(11')-C(12')	120.57(14)
C(13')-C(12')-C(11')	121.02(15)
C(14')-C(13')-C(12')	118.73(15)
C(13')-C(14')-C(15')	120.56(17)
C(10')-C(15')-C(14')	121.54(16)
O(2')-C(16')-N(2')	122.98(11)
O(2')-C(16')-C(9')	121.64(11)
N(2')-C(16')-C(9')	115.35(12)
N(2')-C(17')-C(18')	112.48(10)
N(2')-C(17')-C(25')	112.74(11)
C(18')-C(17')-C(25')	111.66(11)
C(19')-C(18')-C(17')	114.42(11)

C(24')-C(19')-C(20')	118.49(13)
C(24')-C(19')-C(18')	121.28(13)
C(20')-C(19')-C(18')	120.14(12)
C(21')-C(20')-C(19')	120.94(14)
C(22')-C(21')-C(20')	119.94(14)
C(23')-C(22')-C(21')	119.73(15)
C(22')-C(23')-C(24')	120.24(14)
C(19')-C(24')-C(23')	120.64(14)
O(3')-C(25')-N(3')	123.46(13)
O(3')-C(25')-C(17')	119.87(12)
N(3')-C(25')-C(17')	116.47(12)

Torsion angles [deg] with standard deviations for 3.

Molecule A

C(6)-N(1)-C(5)-O(1)	178.11(13)
C(9)-N(1)-C(5)-O(1)	-3.92(17)
C(6)-N(1)-C(5)-C(4)	-3.2(2)
C(9)-N(1)-C(5)-C(4)	174.72(12)
C(1)-C(4)-C(5)-O(1)	5.88(18)
C(3)-C(4)-C(5)-O(1)	124.68(14)
C(2)-C(4)-C(5)-O(1)	-111.98(15)
C(1)-C(4)-C(5)-N(1)	-172.73(12)
C(3)-C(4)-C(5)-N(1)	-53.94(17)
C(2)-C(4)-C(5)-N(1)	69.41(17)
C(5)-N(1)-C(6)-C(7)	-163.72(13)
C(9)-N(1)-C(6)-C(7)	18.21(15)
N(1)-C(6)-C(7)-C(8)	-37.52(15)
C(6)-C(7)-C(8)-C(10)	169.38(12)
C(6)-C(7)-C(8)-C(9)	42.70(14)
C(5)-N(1)-C(9)-C(16)	-52.52(15)
C(6)-N(1)-C(9)-C(16)	125.82(12)
C(5)-N(1)-C(9)-C(8)	-170.03(11)
C(6)-N(1)-C(9)-C(8)	8.31(14)
C(10)-C(8)-C(9)-N(1)	-157.92(10)
C(7)-C(8)-C(9)-N(1)	-31.11(13)
C(10)-C(8)-C(9)-C(16)	84.24(14)
C(7)-C(8)-C(9)-C(16)	-148.94(11)
C(7)-C(8)-C(10)-C(15)	131.26(13)
C(9)-C(8)-C(10)-C(15)	-109.41(14)
C(7)-C(8)-C(10)-C(11)	-46.70(19)
C(9)-C(8)-C(10)-C(11)	72.64(17)
C(15)-C(10)-C(11)-C(12)	-2.1(2)
C(8)-C(10)-C(11)-C(12)	175.91(13)
C(10)-C(11)-C(12)-C(13)	1.3(2)
C(11)-C(12)-C(13)-C(14)	0.7(2)
C(12)-C(13)-C(14)-C(15)	-1.8(2)
C(13)-C(14)-C(15)-C(10)	1.0(2)
C(11)-C(10)-C(15)-C(14)	0.91(19)
C(8)-C(10)-C(15)-C(14)	-177.14(12)
C(17)-N(2)-C(16)-O(2)	1.62(19)
C(17)-N(2)-C(16)-C(9)	179.07(11)
N(1)-C(9)-C(16)-O(2)	-50.27(16)
C(8)-C(9)-C(16)-O(2)	62.72(15)
N(1)-C(9)-C(16)-N(2)	132.21(11)
C(8)-C(9)-C(16)-N(2)	-114.80(12)
C(16)-N(2)-C(17)-C(25)	63.56(16)
C(16)-N(2)-C(17)-C(18)	-66.42(16)
N(2)-C(17)-C(18)-C(19)	-90.17(14)
C(25)-C(17)-C(18)-C(19)	138.60(12)
C(17)-C(18)-C(19)-C(24)	94.09(16)

C(17)-C(18)-C(19)-C(20)	-87.63(16)
C(24)-C(19)-C(20)-C(21)	0.4(2)
C(18)-C(19)-C(20)-C(21)	-178.00(14)
C(19)-C(20)-C(21)-C(22)	0.6(2)
C(20)-C(21)-C(22)-C(23)	-1.1(2)
C(21)-C(22)-C(23)-C(24)	0.7(3)
C(22)-C(23)-C(24)-C(19)	0.3(3)
C(20)-C(19)-C(24)-C(23)	-0.8(2)
C(18)-C(19)-C(24)-C(23)	177.56(14)
C(26)-N(3)-C(25)-O(3)	3.9(2)
C(26)-N(3)-C(25)-C(17)	178.02(12)
N(2)-C(17)-C(25)-O(3)	-166.23(12)
C(18)-C(17)-C(25)-O(3)	-35.48(18)
N(2)-C(17)-C(25)-N(3)	19.44(17)
C(18)-C(17)-C(25)-N(3)	150.20(12)

Molecule B

C(9')-N(1')-C(5')-O(1')	-3.50(17)
C(6')-N(1')-C(5')-O(1')	171.54(12)
C(9')-N(1')-C(5')-C(4')	174.82(11)
C(6')-N(1')-C(5')-C(4')	-10.1(2)
C(3')-C(4')-C(5')-O(1')	127.23(14)
C(1')-C(4')-C(5')-O(1')	8.20(18)
C(2')-C(4')-C(5')-O(1')	-109.62(14)
C(3')-C(4')-C(5')-N(1')	-51.05(17)
C(1')-C(4')-C(5')-N(1')	-170.08(12)
C(2')-C(4')-C(5')-N(1')	72.10(16)
C(5')-N(1')-C(6')-C(7')	-157.45(13)
C(9')-N(1')-C(6')-C(7')	17.84(14)
N(1')-C(6')-C(7')-C(8')	-37.35(13)
C(6')-C(7')-C(8')-C(10')	171.01(11)
C(6')-C(7')-C(8')-C(9')	42.87(13)
C(5')-N(1')-C(9')-C(16')	-55.99(14)
C(6')-N(1')-C(9')-C(16')	128.05(11)
C(5')-N(1')-C(9')-C(8')	-175.09(11)
C(6')-N(1')-C(9')-C(8')	8.95(14)
C(10')-C(8')-C(9')-N(1')	-156.88(11)
C(7')-C(8')-C(9')-N(1')	-31.39(12)
C(10')-C(8')-C(9')-C(16')	84.86(14)
C(7')-C(8')-C(9')-C(16')	-149.65(11)
C(7')-C(8')-C(10')-C(15')	88.85(16)
C(9')-C(8')-C(10')-C(15')	-152.21(14)
C(7')-C(8')-C(10')-C(11')	-88.26(16)
C(9')-C(8')-C(10')-C(11')	30.68(19)
C(15')-C(10')-C(11')-C(12')	0.1(2)
C(8')-C(10')-C(11')-C(12')	177.19(13)
C(10')-C(11')-C(12')-C(13')	-1.2(2)
C(11')-C(12')-C(13')-C(14')	1.0(2)
C(12')-C(13')-C(14')-C(15')	0.2(3)
C(11')-C(10')-C(15')-C(14')	1.2(2)
C(8')-C(10')-C(15')-C(14')	-176.14(16)

C(13')-C(14')-C(15')-C(10')	-1.3(3)
C(17')-N(2')-C(16')-O(2')	2.24(18)
C(17')-N(2')-C(16')-C(9')	-179.70(11)
N(1')-C(9')-C(16')-O(2')	-46.92(16)
C(8')-C(9')-C(16')-O(2')	67.30(15)
N(1')-C(9')-C(16')-N(2')	134.99(11)
C(8')-C(9')-C(16')-N(2')	-110.79(12)
C(16')-N(2')-C(17')-C(18')	-67.40(15)
C(16')-N(2')-C(17')-C(25')	59.95(15)
N(2')-C(17')-C(18')-C(19')	-73.77(15)
C(25')-C(17')-C(18')-C(19')	158.31(11)
C(17')-C(18')-C(19')-C(24')	89.82(16)
C(17')-C(18')-C(19')-C(20')	-93.65(15)
C(24')-C(19')-C(20')-C(21')	1.3(2)
C(18')-C(19')-C(20')-C(21')	-175.33(14)
C(19')-C(20')-C(21')-C(22')	-0.8(2)
C(20')-C(21')-C(22')-C(23')	-0.1(2)
C(21')-C(22')-C(23')-C(24')	0.6(2)
C(20')-C(19')-C(24')-C(23')	-0.8(2)
C(18')-C(19')-C(24')-C(23')	175.79(13)
C(22')-C(23')-C(24')-C(19')	-0.2(2)
C(26')-N(3')-C(25')-O(3')	6.7(2)
C(26')-N(3')-C(25')-C(17')	-178.56(12)
N(2')-C(17')-C(25')-O(3')	-160.39(12)
C(18')-C(17')-C(25')-O(3')	-32.61(18)
N(2')-C(17')-C(25')-N(3')	24.62(17)
C(18')-C(17')-C(25')-N(3')	152.40(12)

Dimensions [Å, deg] of the D-H...A hydrogen bonds for 3.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(1)	0.88	2.03	2.8848(15)	161.3
N(3')-H(3')...O(1')	0.88	2.05	2.8773(14)	156.5
N(2')-H(2')...O(2)	0.84	2.31	3.1352(14)	169.3
N(2)-H(2)...O(2')#1	0.87	2.17	3.0319(13)	167.4

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z

Geometrical parameters for the X-ray diffraction structure of Piv-L-*trans*(βPh)Pro-D-Phe-NHMe (4)

Bond lengths [Å] with standard deviations for 4.

Molecule A

O(1)-C(5)	1.234(3)
O(2)-C(16)	1.233(3)
O(3)-C(25)	1.223(3)
N(1)-C(5)	1.351(3)
N(1)-C(9)	1.471(3)
N(1)-C(6)	1.485(3)
N(2)-C(16)	1.335(3)
N(2)-C(17)	1.461(3)
N(3)-C(25)	1.327(4)
N(3)-C(26)	1.451(3)
C(1)-C(4)	1.522(4)
C(2)-C(4)	1.522(4)
C(3)-C(4)	1.534(4)
C(4)-C(5)	1.533(4)
C(6)-C(7)	1.520(4)
C(7)-C(8)	1.520(4)
C(8)-C(10)	1.511(4)
C(8)-C(9)	1.534(3)
C(9)-C(16)	1.521(4)
C(10)-C(11)	1.383(4)
C(10)-C(15)	1.385(4)
C(11)-C(12)	1.387(5)
C(12)-C(13)	1.375(5)
C(13)-C(14)	1.369(4)
C(14)-C(15)	1.385(4)
C(17)-C(18)	1.531(4)
C(17)-C(25)	1.541(3)
C(18)-C(19)	1.509(4)
C(19)-C(24)	1.384(4)
C(19)-C(20)	1.385(4)
C(20)-C(21)	1.379(4)
C(21)-C(22)	1.380(5)
C(22)-C(23)	1.374(4)
C(23)-C(24)	1.390(4)

Molecule B

O(1')-C(5')	1.232(3)
O(2')-C(16')	1.233(3)
O(3')-C(25')	1.227(3)
N(1')-C(5')	1.350(3)
N(1')-C(6')	1.467(3)
N(1')-C(9')	1.469(3)
N(2')-C(16')	1.339(3)
N(2')-C(17')	1.455(3)
N(3')-C(25')	1.333(4)
N(3')-C(26')	1.462(4)
C(1')-C(4')	1.529(4)
C(2')-C(4')	1.531(4)
C(3')-C(4')	1.529(4)
C(4')-C(5')	1.542(4)
C(6')-C(7')	1.513(4)
C(7')-C(8')	1.523(4)
C(8')-C(10')	1.515(4)
C(8')-C(9')	1.550(3)
C(9')-C(16')	1.525(3)
C(10')-C(15')	1.356(5)
C(10')-C(11')	1.387(4)
C(11')-C(12')	1.385(5)
C(12')-C(13')	1.348(6)
C(13')-C(14')	1.342(6)
C(14')-C(15')	1.400(5)
C(17')-C(18')	1.536(4)
C(17')-C(25')	1.537(4)
C(18')-C(19')	1.511(4)
C(19')-C(24')	1.380(4)
C(19')-C(20')	1.386(4)
C(20')-C(21')	1.380(5)
C(21')-C(22')	1.387(4)
C(22')-C(23')	1.386(4)
C(23')-C(24')	1.378(4)

Bond angles [deg] with standard deviations for 4.

Molecule A

C(5)-N(1)-C(9)	118.3(2)
C(5)-N(1)-C(6)	130.3(2)
C(9)-N(1)-C(6)	110.6(2)
C(16)-N(2)-C(17)	122.92(19)
C(25)-N(3)-C(26)	121.7(2)
C(2)-C(4)-C(1)	108.2(3)
C(2)-C(4)-C(5)	107.8(3)
C(1)-C(4)-C(5)	112.1(2)
C(2)-C(4)-C(3)	108.5(3)
C(1)-C(4)-C(3)	109.7(3)
C(5)-C(4)-C(3)	110.4(2)
O(1)-C(5)-N(1)	118.3(3)
O(1)-C(5)-C(4)	120.2(2)
N(1)-C(5)-C(4)	121.5(3)
N(1)-C(6)-C(7)	102.8(2)
C(8)-C(7)-C(6)	102.1(2)
C(10)-C(8)-C(7)	120.1(2)
C(10)-C(8)-C(9)	112.2(2)
C(7)-C(8)-C(9)	102.1(2)
N(1)-C(9)-C(16)	112.7(2)
N(1)-C(9)-C(8)	103.3(2)
C(16)-C(9)-C(8)	111.1(2)
C(11)-C(10)-C(15)	117.9(3)
C(11)-C(10)-C(8)	122.6(3)
C(15)-C(10)-C(8)	119.3(2)
C(10)-C(11)-C(12)	121.0(3)
C(13)-C(12)-C(11)	119.7(3)
C(14)-C(13)-C(12)	120.4(3)
C(13)-C(14)-C(15)	119.6(3)
C(14)-C(15)-C(10)	121.4(3)
O(2)-C(16)-N(2)	123.6(2)
O(2)-C(16)-C(9)	120.7(2)
N(2)-C(16)-C(9)	115.7(2)
N(2)-C(17)-C(18)	109.76(19)
N(2)-C(17)-C(25)	113.4(2)
C(18)-C(17)-C(25)	109.8(2)
C(19)-C(18)-C(17)	116.0(2)
C(24)-C(19)-C(20)	117.6(3)
C(24)-C(19)-C(18)	120.6(2)
C(20)-C(19)-C(18)	121.8(3)
C(21)-C(20)-C(19)	121.2(3)

C(20)-C(21)-C(22)	120.6(3)
C(23)-C(22)-C(21)	118.9(3)
C(22)-C(23)-C(24)	120.3(3)
C(19)-C(24)-C(23)	121.3(3)
O(3)-C(25)-N(3)	123.8(3)
O(3)-C(25)-C(17)	118.8(3)
N(3)-C(25)-C(17)	117.4(2)

Molecule B

C(5')-N(1')-C(6')	129.9(2)
C(5')-N(1')-C(9')	118.11(19)
C(6')-N(1')-C(9')	112.0(2)
C(16')-N(2')-C(17')	123.5(2)
C(25')-N(3')-C(26')	120.6(2)
C(3')-C(4')-C(1')	111.3(2)
C(3')-C(4')-C(2')	107.5(2)
C(1')-C(4')-C(2')	108.1(2)
C(3')-C(4')-C(5')	113.6(2)
C(1')-C(4')-C(5')	109.2(2)
C(2')-C(4')-C(5')	106.9(2)
O(1')-C(5')-N(1')	119.0(2)
O(1')-C(5')-C(4')	119.7(2)
N(1')-C(5')-C(4')	121.2(2)
N(1')-C(6')-C(7')	103.2(2)
C(6')-C(7')-C(8')	105.9(2)
C(10')-C(8')-C(7')	115.8(2)
C(10')-C(8')-C(9')	113.12(19)
C(7')-C(8')-C(9')	103.4(2)
N(1')-C(9')-C(16')	111.2(2)
N(1')-C(9')-C(8')	105.0(2)
C(16')-C(9')-C(8')	110.1(2)
C(15')-C(10')-C(11')	116.7(3)
C(15')-C(10')-C(8')	120.6(3)
C(11')-C(10')-C(8')	122.8(3)
C(12')-C(11')-C(10')	121.6(4)
C(13')-C(12')-C(11')	120.1(4)
C(14')-C(13')-C(12')	119.7(4)
C(13')-C(14')-C(15')	120.6(4)
C(10')-C(15')-C(14')	121.3(4)
O(2')-C(16')-N(2')	123.4(2)
O(2')-C(16')-C(9')	121.6(2)
N(2')-C(16')-C(9')	114.9(2)
N(2')-C(17')-C(18')	110.6(2)
N(2')-C(17')-C(25')	113.7(2)
C(18')-C(17')-C(25')	109.0(2)

C(19')-C(18')-C(17')	115.2(2)
C(24')-C(19')-C(20')	118.2(3)
C(24')-C(19')-C(18')	120.6(3)
C(20')-C(19')-C(18')	121.2(3)
C(21')-C(20')-C(19')	120.5(3)
C(20')-C(21')-C(22')	120.9(3)
C(23')-C(22')-C(21')	118.6(3)
C(24')-C(23')-C(22')	120.0(3)
C(23')-C(24')-C(19')	121.8(3)
O(3')-C(25')-N(3')	123.7(3)
O(3')-C(25')-C(17')	119.9(3)
N(3')-C(25')-C(17')	116.4(2)

Torsion angles [deg] with standard deviations for 4.

Molecule A

C(9)-N(1)-C(5)-O(1)	1.0(3)
C(6)-N(1)-C(5)-O(1)	169.5(2)
C(9)-N(1)-C(5)-C(4)	-179.3(2)
C(6)-N(1)-C(5)-C(4)	-10.8(4)
C(2)-C(4)-C(5)-O(1)	11.9(3)
C(1)-C(4)-C(5)-O(1)	130.9(3)
C(3)-C(4)-C(5)-O(1)	-106.5(3)
C(2)-C(4)-C(5)-N(1)	-167.8(2)
C(1)-C(4)-C(5)-N(1)	-48.8(3)
C(3)-C(4)-C(5)-N(1)	73.8(3)
C(5)-N(1)-C(6)-C(7)	-153.3(2)
C(9)-N(1)-C(6)-C(7)	16.0(3)
N(1)-C(6)-C(7)-C(8)	-36.6(3)
C(6)-C(7)-C(8)-C(10)	168.5(2)
C(6)-C(7)-C(8)-C(9)	43.6(2)
C(5)-N(1)-C(9)-C(16)	-58.3(3)
C(6)-N(1)-C(9)-C(16)	131.0(2)
C(5)-N(1)-C(9)-C(8)	-178.3(2)
C(6)-N(1)-C(9)-C(8)	11.0(2)
C(10)-C(8)-C(9)-N(1)	-163.6(2)
C(7)-C(8)-C(9)-N(1)	-33.6(2)
C(10)-C(8)-C(9)-C(16)	75.4(3)
C(7)-C(8)-C(9)-C(16)	-154.6(2)
C(7)-C(8)-C(10)-C(11)	-25.3(4)
C(9)-C(8)-C(10)-C(11)	94.6(3)
C(7)-C(8)-C(10)-C(15)	159.0(3)
C(9)-C(8)-C(10)-C(15)	-81.0(3)
C(15)-C(10)-C(11)-C(12)	-0.2(4)
C(8)-C(10)-C(11)-C(12)	-175.9(3)
C(10)-C(11)-C(12)-C(13)	1.0(5)
C(11)-C(12)-C(13)-C(14)	-0.7(5)
C(12)-C(13)-C(14)-C(15)	-0.4(5)
C(13)-C(14)-C(15)-C(10)	1.2(5)
C(11)-C(10)-C(15)-C(14)	-0.9(4)
C(8)-C(10)-C(15)-C(14)	174.9(3)
C(17)-N(2)-C(16)-O(2)	2.7(4)
C(17)-N(2)-C(16)-C(9)	-179.6(2)
N(1)-C(9)-C(16)-O(2)	-54.5(3)
C(8)-C(9)-C(16)-O(2)	60.9(3)
N(1)-C(9)-C(16)-N(2)	127.7(2)
C(8)-C(9)-C(16)-N(2)	-116.9(2)
C(16)-N(2)-C(17)-C(18)	-165.4(2)
C(16)-N(2)-C(17)-C(25)	71.5(3)
N(2)-C(17)-C(18)-C(19)	71.6(3)
C(25)-C(17)-C(18)-C(19)	-163.2(2)
C(17)-C(18)-C(19)-C(24)	73.1(3)

C(17)-C(18)-C(19)-C(20)	-109.2(3)
C(24)-C(19)-C(20)-C(21)	1.0(5)
C(18)-C(19)-C(20)-C(21)	-176.8(3)
C(19)-C(20)-C(21)-C(22)	0.5(5)
C(20)-C(21)-C(22)-C(23)	-1.6(5)
C(21)-C(22)-C(23)-C(24)	1.2(5)
C(20)-C(19)-C(24)-C(23)	-1.3(4)
C(18)-C(19)-C(24)-C(23)	176.5(3)
C(22)-C(23)-C(24)-C(19)	0.3(5)
C(26)-N(3)-C(25)-O(3)	5.8(4)
C(26)-N(3)-C(25)-C(17)	-175.5(2)
N(2)-C(17)-C(25)-O(3)	-176.2(2)
C(18)-C(17)-C(25)-O(3)	60.7(3)
N(2)-C(17)-C(25)-N(3)	5.0(3)
C(18)-C(17)-C(25)-N(3)	-118.1(3)

Molecule B

C(6')-N(1')-C(5')-O(1')	-172.5(2)
C(9')-N(1')-C(5')-O(1')	5.6(3)
C(6')-N(1')-C(5')-C(4')	5.1(4)
C(9')-N(1')-C(5')-C(4')	-176.8(2)
C(3')-C(4')-C(5')-O(1')	-134.8(2)
C(1')-C(4')-C(5')-O(1')	100.3(3)
C(2')-C(4')-C(5')-O(1')	-16.4(3)
C(3')-C(4')-C(5')-N(1')	47.6(3)
C(1')-C(4')-C(5')-N(1')	-77.3(3)
C(2')-C(4')-C(5')-N(1')	166.0(2)
C(5')-N(1')-C(6')-C(7')	159.0(3)
C(9')-N(1')-C(6')-C(7')	-19.3(3)
N(1')-C(6')-C(7')-C(8')	31.3(3)
C(6')-C(7')-C(8')-C(10')	92.8(3)
C(6')-C(7')-C(8')-C(9')	-31.5(3)
C(5')-N(1')-C(9')-C(16')	-59.6(3)
C(6')-N(1')-C(9')-C(16')	118.8(2)
C(5')-N(1')-C(9')-C(8')	-178.6(2)
C(6')-N(1')-C(9')-C(8')	-0.1(3)
C(10')-C(8')-C(9')-N(1')	-106.6(3)
C(7')-C(8')-C(9')-N(1')	19.4(3)
C(10')-C(8')-C(9')-C(16')	133.7(2)
C(7')-C(8')-C(9')-C(16')	-100.3(3)
C(7')-C(8')-C(10')-C(15')	141.8(3)
C(9')-C(8')-C(10')-C(15')	-99.1(4)
C(7')-C(8')-C(10')-C(11')	-37.5(4)
C(9')-C(8')-C(10')-C(11')	81.5(3)
C(15')-C(10')-C(11')-C(12')	2.4(5)
C(8')-C(10')-C(11')-C(12')	-178.2(3)
C(10')-C(11')-C(12')-C(13')	-0.8(5)
C(11')-C(12')-C(13')-C(14')	-1.3(6)
C(12')-C(13')-C(14')-C(15')	1.8(7)
C(11')-C(10')-C(15')-C(14')	-2.0(6)
C(8')-C(10')-C(15')-C(14')	178.7(4)

C(13')-C(14')-C(15')-C(10')	-0.1(7)
C(17')-N(2')-C(16')-O(2')	3.5(4)
C(17')-N(2')-C(16')-C(9')	179.8(2)
N(1')-C(9')-C(16')-O(2')	-55.9(3)
C(8')-C(9')-C(16')-O(2')	60.0(3)
N(1')-C(9')-C(16')-N(2')	127.7(2)
C(8')-C(9')-C(16')-N(2')	-116.4(2)
C(16')-N(2')-C(17')-C(18')	-146.3(2)
C(16')-N(2')-C(17')-C(25')	90.6(3)
N(2')-C(17')-C(18')-C(19')	61.1(3)
C(25')-C(17')-C(18')-C(19')	-173.2(2)
C(17')-C(18')-C(19')-C(24')	99.6(3)
C(17')-C(18')-C(19')-C(20')	-81.9(3)
C(24')-C(19')-C(20')-C(21')	-0.4(4)
C(18')-C(19')-C(20')-C(21')	-178.9(3)
C(19')-C(20')-C(21')-C(22')	-0.4(5)
C(20')-C(21')-C(22')-C(23')	0.7(5)
C(21')-C(22')-C(23')-C(24')	-0.3(4)
C(22')-C(23')-C(24')-C(19')	-0.5(4)
C(20')-C(19')-C(24')-C(23')	0.8(4)
C(18')-C(19')-C(24')-C(23')	179.3(2)
C(26')-N(3')-C(25')-O(3')	2.3(4)
C(26')-N(3')-C(25')-C(17')	-177.7(2)
N(2')-C(17')-C(25')-O(3')	169.0(2)
C(18')-C(17')-C(25')-O(3')	45.1(3)
N(2')-C(17')-C(25')-N(3')	-11.0(3)
C(18')-C(17')-C(25')-N(3')	-134.9(2)

Dimensions [Å, deg] of the D-H...A hydrogen bonds for 4.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(1)	0.99	1.93	2.880(3)	158.7
N(3')-H(3')...O(1')	0.95	1.95	2.856(3)	158.4
N(2)-H(2)...O(2')	0.93	2.05	2.965(2)	168.6
N(2')-H(2')...O(2)#1	0.91	2.03	2.934(2)	171.5

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z

Geometrical parameters for the X-ray diffraction structure of Boc-L-*trans*(βPh)Pro-D-Phe-NHMe (4a)

Bond lengths [Å] with standard deviations for 4a.

Molecule A

O(0)-C(5)	1.347(5)
O(0)-C(4)	1.471(5)
O(1)-C(5)	1.229(5)
O(2)-C(16)	1.225(5)
O(3)-C(25)	1.240(5)
N(1)-C(5)	1.341(5)
N(1)-C(9)	1.454(5)
N(1)-C(6)	1.470(5)
N(2)-C(16)	1.344(5)
N(2)-C(17)	1.446(5)
N(3)-C(25)	1.318(5)
N(3)-C(26)	1.452(5)
C(1)-C(4)	1.520(6)
C(2)-C(4)	1.513(6)
C(3)-C(4)	1.522(6)
C(6)-C(7)	1.503(5)
C(7)-C(8)	1.519(6)
C(8)-C(10)	1.515(5)
C(8)-C(9)	1.543(5)
C(9)-C(16)	1.520(6)
C(10)-C(11)	1.380(6)
C(10)-C(15)	1.384(6)
C(11)-C(12)	1.393(6)
C(12)-C(13)	1.370(6)
C(13)-C(14)	1.371(6)
C(14)-C(15)	1.365(5)
C(17)-C(18)	1.520(5)
C(17)-C(25)	1.537(5)
C(18)-C(19)	1.495(5)
C(19)-C(20)	1.380(6)
C(19)-C(24)	1.390(6)
C(20)-C(21)	1.391(6)
C(21)-C(22)	1.373(6)
C(22)-C(23)	1.374(6)
C(23)-C(24)	1.389(6)

Molecule B

O(0')-C(5')	1.328(5)
O(0')-C(4')	1.446(5)
O(1')-C(5')	1.233(5)
O(2')-C(16')	1.223(5)
O(3')-C(25')	1.243(5)
N(1')-C(5')	1.346(5)
N(1')-C(9')	1.447(5)
N(1')-C(6')	1.466(5)
N(2')-C(16')	1.357(5)
N(2')-C(17')	1.455(5)
N(3')-C(25')	1.314(5)
N(3')-C(26')	1.452(5)
C(1')-C(4')	1.520(7)
C(2')-C(4')	1.497(6)
C(3')-C(4')	1.517(6)
C(6')-C(7')	1.502(6)
C(7')-C(8')	1.531(6)
C(8')-C(10')	1.496(6)
C(8')-C(9')	1.553(6)
C(9')-C(16')	1.534(6)
C(10')-C(11')	1.383(6)
C(10')-C(15')	1.390(6)
C(11')-C(12')	1.373(6)
C(12')-C(13')	1.386(7)
C(13')-C(14')	1.357(7)
C(14')-C(15')	1.375(7)
C(17')-C(18')	1.517(5)
C(17')-C(25')	1.524(6)
C(18')-C(19')	1.523(6)
C(19')-C(24')	1.375(6)
C(19')-C(20')	1.378(6)
C(20')-C(21')	1.387(6)
C(21')-C(22')	1.380(7)
C(22')-C(23')	1.378(7)
C(23')-C(24')	1.369(7)

Bond angles [deg] with standard deviations for 4a.

Molecule A

C(5)-O(0)-C(4)	120.0(4)
C(5)-N(1)-C(9)	119.3(4)
C(5)-N(1)-C(6)	127.2(4)
C(9)-N(1)-C(6)	113.4(3)
C(16)-N(2)-C(17)	122.3(4)
C(25)-N(3)-C(26)	121.3(4)
O(0)-C(4)-C(2)	102.7(4)
O(0)-C(4)-C(1)	108.0(4)
C(2)-C(4)-C(1)	110.8(4)
O(0)-C(4)-C(3)	111.7(4)
C(2)-C(4)-C(3)	110.1(4)
C(1)-C(4)-C(3)	113.0(4)
O(1)-C(5)-N(1)	123.2(4)
O(1)-C(5)-O(0)	124.5(4)
N(1)-C(5)-O(0)	112.2(5)
N(1)-C(6)-C(7)	102.1(3)
C(6)-C(7)-C(8)	104.3(3)
C(10)-C(8)-C(7)	116.1(3)
C(10)-C(8)-C(9)	116.2(4)
C(7)-C(8)-C(9)	103.0(3)
N(1)-C(9)-C(16)	111.9(3)
N(1)-C(9)-C(8)	102.6(3)
C(16)-C(9)-C(8)	111.8(3)
C(11)-C(10)-C(15)	118.4(4)
C(11)-C(10)-C(8)	117.8(4)
C(15)-C(10)-C(8)	123.8(4)
C(10)-C(11)-C(12)	120.6(5)
C(13)-C(12)-C(11)	119.9(5)
C(12)-C(13)-C(14)	119.4(5)
C(15)-C(14)-C(13)	121.0(5)
C(14)-C(15)-C(10)	120.7(5)
O(2)-C(16)-N(2)	122.5(4)
O(2)-C(16)-C(9)	122.5(4)
N(2)-C(16)-C(9)	114.9(4)
N(2)-C(17)-C(18)	110.7(3)
N(2)-C(17)-C(25)	113.1(3)
C(18)-C(17)-C(25)	110.0(4)
C(19)-C(18)-C(17)	114.7(4)
C(20)-C(19)-C(24)	116.7(4)
C(20)-C(19)-C(18)	123.0(4)

C(24)-C(19)-C(18)	120.3(4)
C(19)-C(20)-C(21)	121.9(5)
C(22)-C(21)-C(20)	119.9(5)
C(21)-C(22)-C(23)	119.8(5)
C(22)-C(23)-C(24)	119.4(5)
C(23)-C(24)-C(19)	122.2(5)
O(3)-C(25)-N(3)	123.7(4)
O(3)-C(25)-C(17)	119.0(4)
N(3)-C(25)-C(17)	117.3(4)

Molecule B

C(5')-O(0')-C(4')	122.0(4)
C(5')-N(1')-C(9')	120.0(4)
C(5')-N(1')-C(6')	126.1(4)
C(9')-N(1')-C(6')	113.9(4)
C(16')-N(2')-C(17')	121.2(4)
C(25')-N(3')-C(26')	120.5(4)
O(0')-C(4')-C(2')	103.7(4)
O(0')-C(4')-C(3')	110.4(4)
C(2')-C(4')-C(3')	109.6(4)
O(0')-C(4')-C(1')	109.7(4)
C(2')-C(4')-C(1')	111.6(4)
C(3')-C(4')-C(1')	111.6(5)
O(1')-C(5')-O(0')	125.0(4)
O(1')-C(5')-N(1')	122.8(4)
O(0')-C(5')-N(1')	112.2(4)
N(1')-C(6')-C(7')	102.4(4)
C(6')-C(7')-C(8')	104.5(4)
C(10')-C(8')-C(7')	117.6(4)
C(10')-C(8')-C(9')	112.5(4)
C(7')-C(8')-C(9')	103.6(3)
N(1')-C(9')-C(16')	110.4(3)
N(1')-C(9')-C(8')	103.0(3)
C(16')-C(9')-C(8')	112.3(3)
C(11')-C(10')-C(15')	116.8(5)
C(11')-C(10')-C(8')	120.4(5)
C(15')-C(10')-C(8')	122.7(5)
C(12')-C(11')-C(10')	122.0(5)
C(11')-C(12')-C(13')	120.5(5)
C(14')-C(13')-C(12')	117.6(5)
C(13')-C(14')-C(15')	122.5(6)
C(14')-C(15')-C(10')	120.5(5)
O(2')-C(16')-N(2')	123.7(4)
O(2')-C(16')-C(9')	121.8(4)
N(2')-C(16')-C(9')	114.5(4)

N(2')-C(17')-C(18')	111.4(4)
N(2')-C(17')-C(25')	114.1(4)
C(18')-C(17')-C(25')	109.7(4)
C(17')-C(18')-C(19')	116.1(4)
C(24')-C(19')-C(20')	117.4(5)
C(24')-C(19')-C(18')	119.6(5)
C(20')-C(19')-C(18')	122.6(4)
C(19')-C(20')-C(21')	122.1(5)
C(22')-C(21')-C(20')	118.5(6)
C(23')-C(22')-C(21')	120.5(5)
C(24')-C(23')-C(22')	119.3(5)
C(23')-C(24')-C(19')	122.2(6)
O(3')-C(25')-N(3')	123.2(4)
O(3')-C(25')-C(17')	117.2(4)
N(3')-C(25')-C(17')	119.6(4)

Torsion angles [deg] with standard deviations for 4a.

Molecule A

C(5)-O(0)-C(4)-C(2)	-178.9(4)
C(5)-O(0)-C(4)-C(1)	64.0(5)
C(5)-O(0)-C(4)-C(3)	-61.0(5)
C(9)-N(1)-C(5)-O(1)	5.1(7)
C(6)-N(1)-C(5)-O(1)	-179.2(4)
C(9)-N(1)-C(5)-O(0)	-173.9(3)
C(6)-N(1)-C(5)-O(0)	1.8(6)
C(4)-O(0)-C(5)-O(1)	14.2(7)
C(4)-O(0)-C(5)-N(1)	-166.8(4)
C(5)-N(1)-C(6)-C(7)	-160.0(4)
C(9)-N(1)-C(6)-C(7)	15.8(5)
N(1)-C(6)-C(7)-C(8)	-33.1(4)
C(6)-C(7)-C(8)-C(10)	166.7(4)
C(6)-C(7)-C(8)-C(9)	38.5(5)
C(5)-N(1)-C(9)-C(16)	-56.0(5)
C(6)-N(1)-C(9)-C(16)	127.7(4)
C(5)-N(1)-C(9)-C(8)	-176.0(4)
C(6)-N(1)-C(9)-C(8)	7.8(5)
C(10)-C(8)-C(9)-N(1)	-156.1(4)
C(7)-C(8)-C(9)-N(1)	-28.0(4)
C(10)-C(8)-C(9)-C(16)	83.9(5)
C(7)-C(8)-C(9)-C(16)	-148.0(4)
C(7)-C(8)-C(10)-C(11)	80.6(5)
C(9)-C(8)-C(10)-C(11)	-158.0(4)
C(7)-C(8)-C(10)-C(15)	-97.7(5)
C(9)-C(8)-C(10)-C(15)	23.7(6)
C(15)-C(10)-C(11)-C(12)	0.1(7)
C(8)-C(10)-C(11)-C(12)	-178.3(4)
C(10)-C(11)-C(12)-C(13)	-1.9(8)
C(11)-C(12)-C(13)-C(14)	2.9(8)
C(12)-C(13)-C(14)-C(15)	-2.1(8)
C(13)-C(14)-C(15)-C(10)	0.3(7)
C(11)-C(10)-C(15)-C(14)	0.7(7)
C(8)-C(10)-C(15)-C(14)	179.0(4)
C(17)-N(2)-C(16)-O(2)	0.2(6)
C(17)-N(2)-C(16)-C(9)	177.8(3)
N(1)-C(9)-C(16)-O(2)	-55.1(6)
C(8)-C(9)-C(16)-O(2)	59.3(5)
N(1)-C(9)-C(16)-N(2)	127.2(4)
C(8)-C(9)-C(16)-N(2)	-118.4(4)
C(16)-N(2)-C(17)-C(18)	-149.6(4)
C(16)-N(2)-C(17)-C(25)	86.4(5)
N(2)-C(17)-C(18)-C(19)	56.8(5)
C(25)-C(17)-C(18)-C(19)	-177.5(4)
C(17)-C(18)-C(19)-C(20)	26.1(6)
C(17)-C(18)-C(19)-C(24)	-155.8(4)

C(24)-C(19)-C(20)-C(21)	-0.6(7)
C(18)-C(19)-C(20)-C(21)	177.6(4)
C(19)-C(20)-C(21)-C(22)	-1.0(7)
C(20)-C(21)-C(22)-C(23)	3.1(7)
C(21)-C(22)-C(23)-C(24)	-3.5(7)
C(22)-C(23)-C(24)-C(19)	1.9(7)
C(20)-C(19)-C(24)-C(23)	0.2(7)
C(18)-C(19)-C(24)-C(23)	-178.0(4)
C(26)-N(3)-C(25)-O(3)	2.3(7)
C(26)-N(3)-C(25)-C(17)	-178.3(4)
N(2)-C(17)-C(25)-O(3)	-176.2(4)
C(18)-C(17)-C(25)-O(3)	59.4(5)
N(2)-C(17)-C(25)-N(3)	4.3(6)
C(18)-C(17)-C(25)-N(3)	-120.1(4)

Molecule B

C(5')-O(0')-C(4')-C(2')	-174.9(4)
C(5')-O(0')-C(4')-C(3')	-57.6(6)
C(5')-O(0')-C(4')-C(1')	65.9(6)
C(4')-O(0')-C(5')-O(1')	-2.4(7)
C(4')-O(0')-C(5')-N(1')	177.3(4)
C(9')-N(1')-C(5')-O(1')	-1.8(7)
C(6')-N(1')-C(5')-O(1')	-179.2(5)
C(9')-N(1')-C(5')-O(0')	178.5(4)
C(6')-N(1')-C(5')-O(0')	1.1(6)
C(5')-N(1')-C(6')-C(7')	-163.3(4)
C(9')-N(1')-C(6')-C(7')	19.2(5)
N(1')-C(6')-C(7')-C(8')	-32.8(5)
C(6')-C(7')-C(8')-C(10')	159.8(4)
C(6')-C(7')-C(8')-C(9')	35.0(5)
C(5')-N(1')-C(9')-C(16')	-55.1(5)
C(6')-N(1')-C(9')-C(16')	122.5(4)
C(5')-N(1')-C(9')-C(8')	-175.2(4)
C(6')-N(1')-C(9')-C(8')	2.4(5)
C(10')-C(8')-C(9')-N(1')	-150.8(4)
C(7')-C(8')-C(9')-N(1')	-22.8(4)
C(10')-C(8')-C(9')-C(16')	90.3(5)
C(7')-C(8')-C(9')-C(16')	-141.6(4)
C(7')-C(8')-C(10')-C(11')	175.0(4)
C(9')-C(8')-C(10')-C(11')	-64.7(5)
C(7')-C(8')-C(10')-C(15')	-7.1(6)
C(9')-C(8')-C(10')-C(15')	113.1(5)
C(15')-C(10')-C(11')-C(12')	0.2(7)
C(8')-C(10')-C(11')-C(12')	178.2(4)
C(10')-C(11')-C(12')-C(13')	-0.2(8)
C(11')-C(12')-C(13')-C(14')	0.2(9)
C(12')-C(13')-C(14')-C(15')	-0.2(9)
C(13')-C(14')-C(15')-C(10')	0.2(9)
C(11')-C(10')-C(15')-C(14')	-0.1(8)
C(8')-C(10')-C(15')-C(14')	-178.1(5)
C(17')-N(2')-C(16')-O(2')	0.9(6)

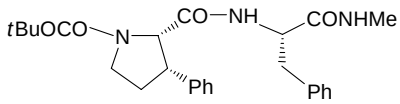
C(17')-N(2')-C(16')-C(9')	-179.6(3)
N(1')-C(9')-C(16')-O(2')	-49.9(5)
C(8')-C(9')-C(16')-O(2')	64.5(5)
N(1')-C(9')-C(16')-N(2')	130.6(4)
C(8')-C(9')-C(16')-N(2')	-115.0(4)
C(16')-N(2')-C(17')-C(18')	-153.9(4)
C(16')-N(2')-C(17')-C(25')	81.2(5)
N(2')-C(17')-C(18')-C(19')	70.6(5)
C(25')-C(17')-C(18')-C(19')	-162.1(4)
C(17')-C(18')-C(19')-C(24')	-153.8(4)
C(17')-C(18')-C(19')-C(20')	32.9(7)
C(24')-C(19')-C(20')-C(21')	0.0(8)
C(18')-C(19')-C(20')-C(21')	173.5(5)
C(19')-C(20')-C(21')-C(22')	-1.1(8)
C(20')-C(21')-C(22')-C(23')	1.5(9)
C(21')-C(22')-C(23')-C(24')	-0.8(9)
C(22')-C(23')-C(24')-C(19')	-0.3(9)
C(20')-C(19')-C(24')-C(23')	0.7(8)
C(18')-C(19')-C(24')-C(23')	-172.9(5)
C(26')-N(3')-C(25')-O(3')	-0.9(7)
C(26')-N(3')-C(25')-C(17')	-179.6(4)
N(2')-C(17')-C(25')-O(3')	-178.4(4)
C(18')-C(17')-C(25')-O(3')	55.8(5)
N(2')-C(17')-C(25')-N(3')	0.4(6)
C(18')-C(17')-C(25')-N(3')	-125.4(4)

Dimensions [Å, deg] of the D-H...A hydrogen bonds for 4a.

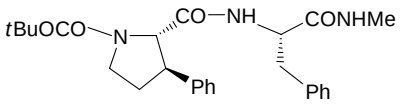
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(1)	1.04	1.91	2.900(5)	157.2
N(3')-H(3')...O(1')	1.05	1.94	2.905(5)	151.2
N(2')-H(2')...O(3)	1.05	1.86	2.906(4)	173.5
N(2)-H(2)...O(3')#1	1.02	1.85	2.842(5)	162.8

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1

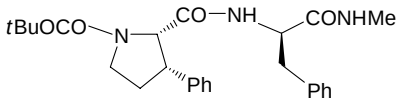
Characterization of compounds **1a**–**4a**



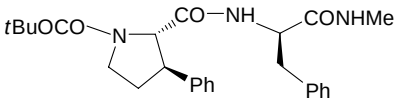
Boc-L-*cis*(βPh)Pro-L-Phe-NHMe (**1a**)



Boc-L-*trans*(βPh)Pro-L-Phe-NHMe (**3a**)



Boc-L-*cis*(βPh)Pro-D-Phe-NHMe (**2a**)



Boc-L-*trans*(βPh)Pro-D-Phe-NHMe (**4a**)

General:

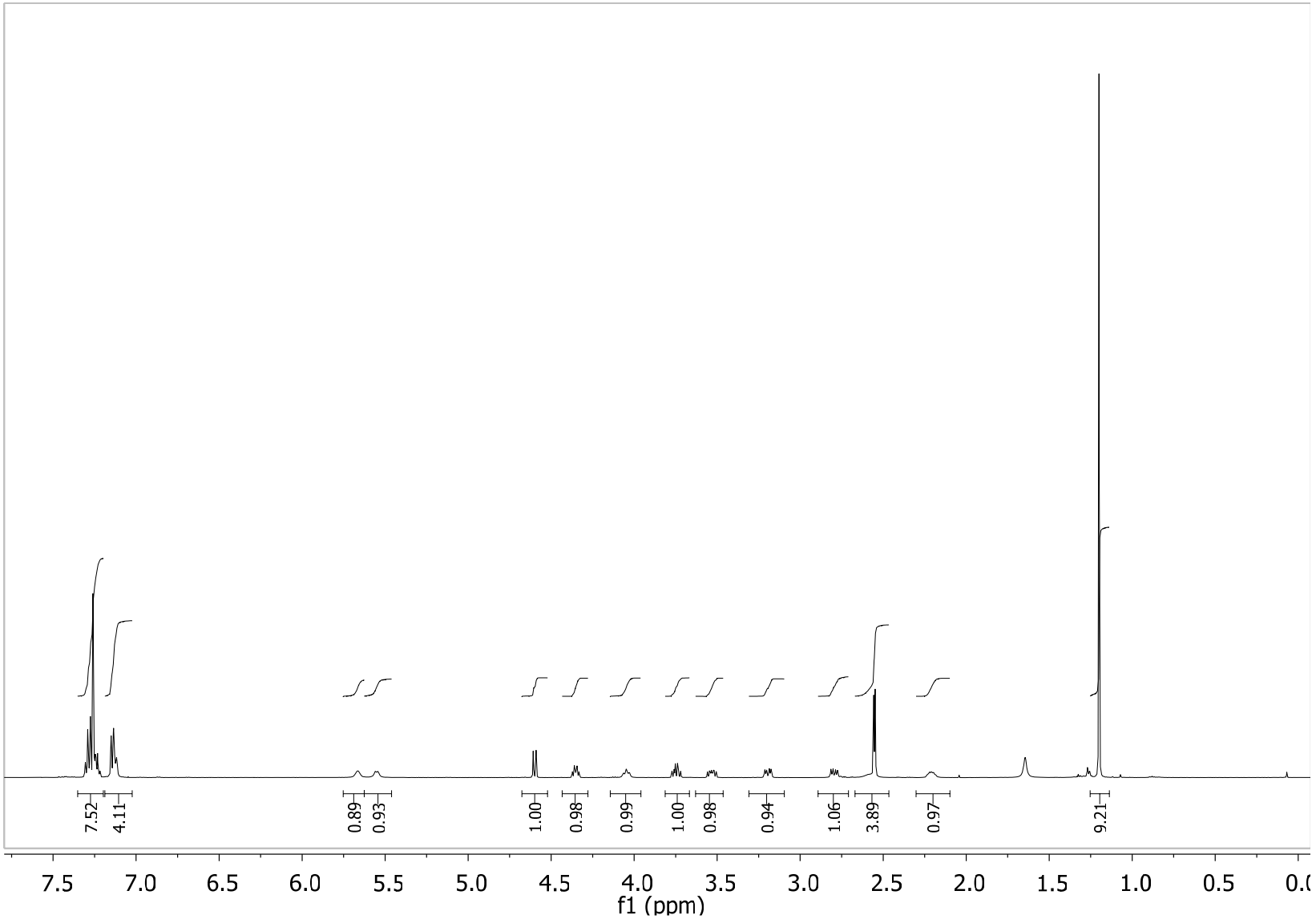
Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were registered on a Nicolet Avatar 360 FTIR spectrophotometer; ν_{max} is given for the main absorption bands. Optical rotations were measured at room temperature using a JASCO P-1020 polarimeter. ^{1}H- and ^{13}C-NMR spectra were registered on Bruker AV-300 or AV-500 instruments at room temperature or 333K using the residual solvent signal as the internal standard; chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hertz. Peptide solutions at 10 mM concentration were used for the ^{1}H-NMR spectra. For **4a** only a very small percentage of species with a *cis* Boc group was observed (signals non reported). High-resolution mass spectra were obtained on a Bruker Microtof-Q spectrometer.

Boc-L-*cis*(βPh)Pro-L-Phe-NHMe (1a): mp 116 ºC; $[\alpha]_D^{20}$ = +72.1 (c = 0.44, MeOH); IR (nujol) ν_{max}/cm^{-1} 3387, 3332, 1711, 1698, 1653; ^{1}H-NMR (300 MHz, $CDCl_3$, 333K) δ_H 1.43 (9H, s), 2.11 (1H, m), 2.37 (1H, m), 2.56 (3H, d, J = 4.7 Hz), 2.85 (1H, m), 3.08 (1H, m), 3.49 (1H, m), 3.62 (1H, m), 3.75 (1H, m), 4.27 (1H, m), 4.35 (1H, d, J = 8.9 Hz), 5.30–6.00 (2H, m), 7.10–7.47 (10H, m); ^{13}C-NMR (125 MHz, $CDCl_3$, 298K) (when observed, the signals corresponding to the minor rotamer are in italics) δ_C 26.10, *27.24*/28.87, 28.28, 37.10/*37.75*, *46.02*/46.56, 46.73/*47.97*, 53.36/*54.66*, 65.43, 80.66, 127.01, 127.29, 127.87, 128.36, 128.69, 129.33, 136.77, 137.13, *154.00*/155.03, 169.38, *170.28*/170.68; HRMS (ESI) $C_{26}H_{33}N_3NaO_4$ $[M+Na]^+$: calcd. 474.2363, found 474.2382.

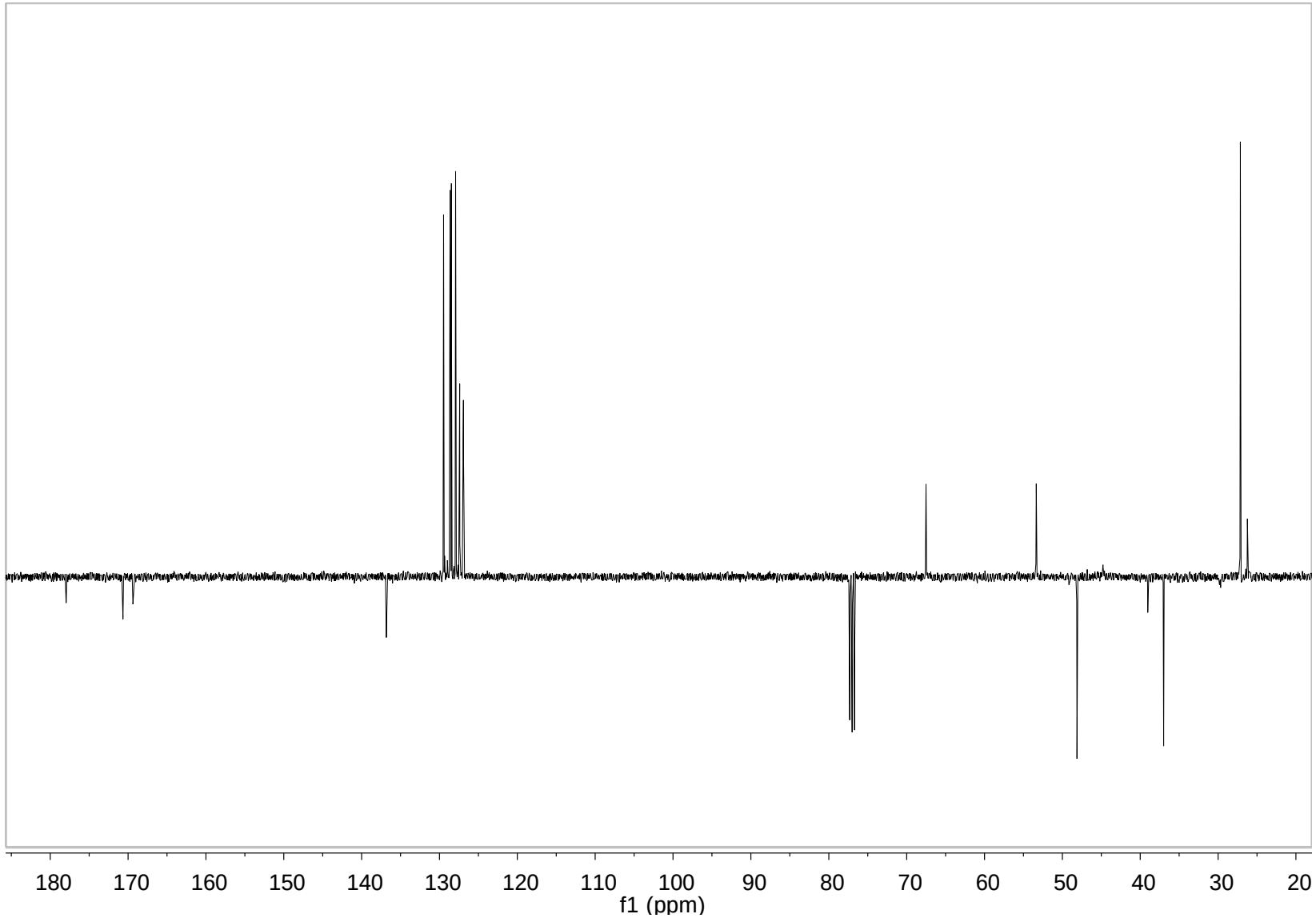
Boc-L-*cis*(βPh)Pro-D-Phe-NHMe (2a): mp 218 ºC; $[\alpha]_D^{20}$ = +127.6 (c = 0.53, MeOH); IR (nujol) ν_{max}/cm^{-1} 3338, 3269, 1676, 1646, 1637; ^{1}H-NMR (500 MHz, $CDCl_3$, 333K) δ_H 1.45 (9H, s), 2.11 (1H, m), 2.25 (1H, m), 2.65 (3H, m), 2.81 (1H, m), 3.24 (1H, m), 3.46 (1H, m), 3.57 (1H, m), 3.86 (1H, m), 4.09 (1H, m), 4.41 (1H, m), 5.32 (1H, m), 6.58–7.00 (3H, m), 7.08–7.48 (8H, m); ^{13}C-NMR (125 MHz, $CDCl_3$, 298K) (when observed, the signals corresponding to the minor rotamer are in italics) δ_C 26.28, *27.31*/28.52, 28.37, 35.78/*37.87*, *46.00*/46.61, 47.33/*48.22*, 52.60/*54.17*, *65.43*/65.91, *80.15*/80.59, 126.92, 127.67, 128.13, 128.55, 128.57, *129.20*/129.47, 135.96, 136.57, *153.79*/155.30, 170.19, 170.69. HRMS (ESI) $C_{26}H_{33}N_3NaO_4$ $[M+Na]^+$: calcd. 474.2363, found 474.2385.

Boc-L-*trans*(βPh)Pro-L-Phe-NHMe (3a): mp 172 ºC; $[\alpha]_D^{25}$ = +30.5 (c = 0.22; MeOH); IR (nujol) ν_{max}/cm^{-1} 3347, 3219, 1698, 1687, 1656; ^{1}H-NMR (300 MHz, $CDCl_3$, 333K) 1.44 (9H, s), 1.94 (1H, m), 2.10 (1H, m), 2.73 (3H, d, *J* = 4.6 Hz), 3.17 (2H, m), 3.27–3.52 (2H, m), 3.62 (1H, m), 4.27 (1H, m), 4.65 (1H, m), 6.15–6.55 (2H, m), 7.12–7.61 (10H, m); ^{13}C-NMR (125 MHz, $CDCl_3$, 298K) (when observed, the signals corresponding to the minor rotamer are in italics) δ_C 26.20, 28.25, *31.73*/32.57, 37.12/*37.69*, 46.15, 47.54/*49.37*, 53.48/*54.14*, 66.82/*67.38*, 81.11, 126.84, 126.99, 127.05, 128.67, 128.74, 129.23, 136.87, 141.04, *154.13*/155.39, 170.94, 170.95; HRMS (ESI) $C_{26}H_{33}N_3NaO_4$ $[M+Na]^+$: calcd. 474.2363, found 474.2355.

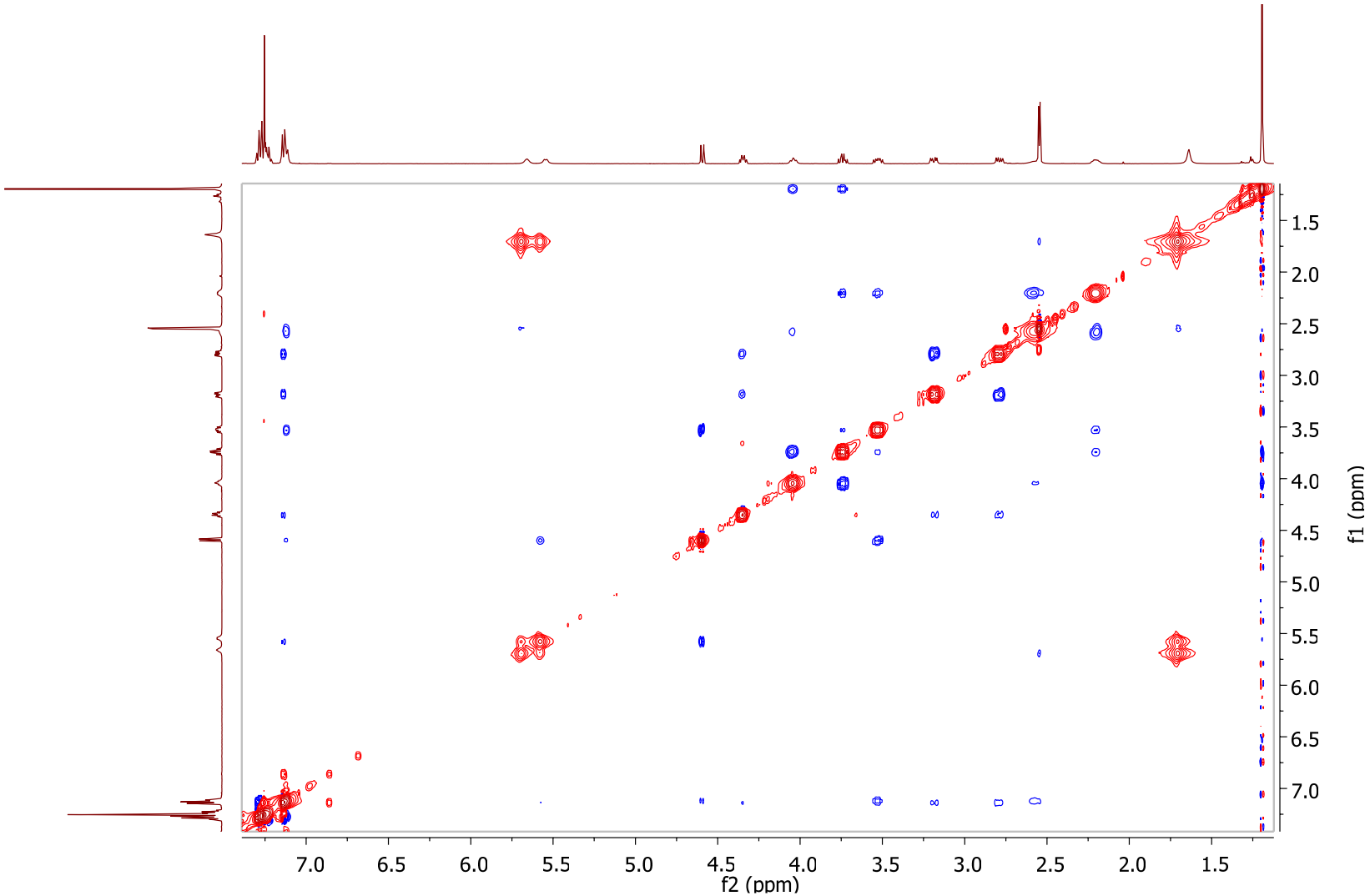
Boc-L-*trans*(βPh)Pro-D-Phe-NHMe (4a): mp 176 ºC; $[\alpha]_D^{25}$ = +70.3 (c = 0.40, MeOH); IR (nujol) ν_{max}/cm^{-1} 3331, 3310, 3280, 1680, 1673, 1649; ^{1}H-NMR (500 MHz, $CDCl_3$, 298K) δ_H 1.45 (9H, s), 2.08 (1H, m), 2.27 (1H, m), 2.73 (3H, d, *J* = 4.6 Hz), 2.76 (1H, dd, *J* = 13.8, 5.6 Hz), 3.33 (1H, dd, *J* = 13.8, 5.4 Hz), 3.55 (2H, m), 3.67–3.81 (1H, m) overlapped with 3.75 (1H, d, *J* = 8.6 Hz), 4.80 (1H, ddd, *J* = 9.4, 5.6, 5.4 Hz), 5.55 (1H, br d, *J* = 9.4 Hz), 6.75 (2H, m), 7.04–7.21 (5H, m), 7.30–7.43 (4H, m); ^{13}C-NMR (125 MHz, $CDCl_3$, 298K) δ_C 26.31, 28.41, 32.73, 36.25, 47.26, 48.65, 53.09, 68.67, 80.77, 126.79, 127.20, 127.45, 128.58, 128.89, 129.35, 136.19, 139.50, 154.95, 170.80, 171.11; HRMS (ESI) $C_{26}H_{33}N_3NaO_4$ $[M+Na]^+$: calcd. 474.2363, found 474.2346.



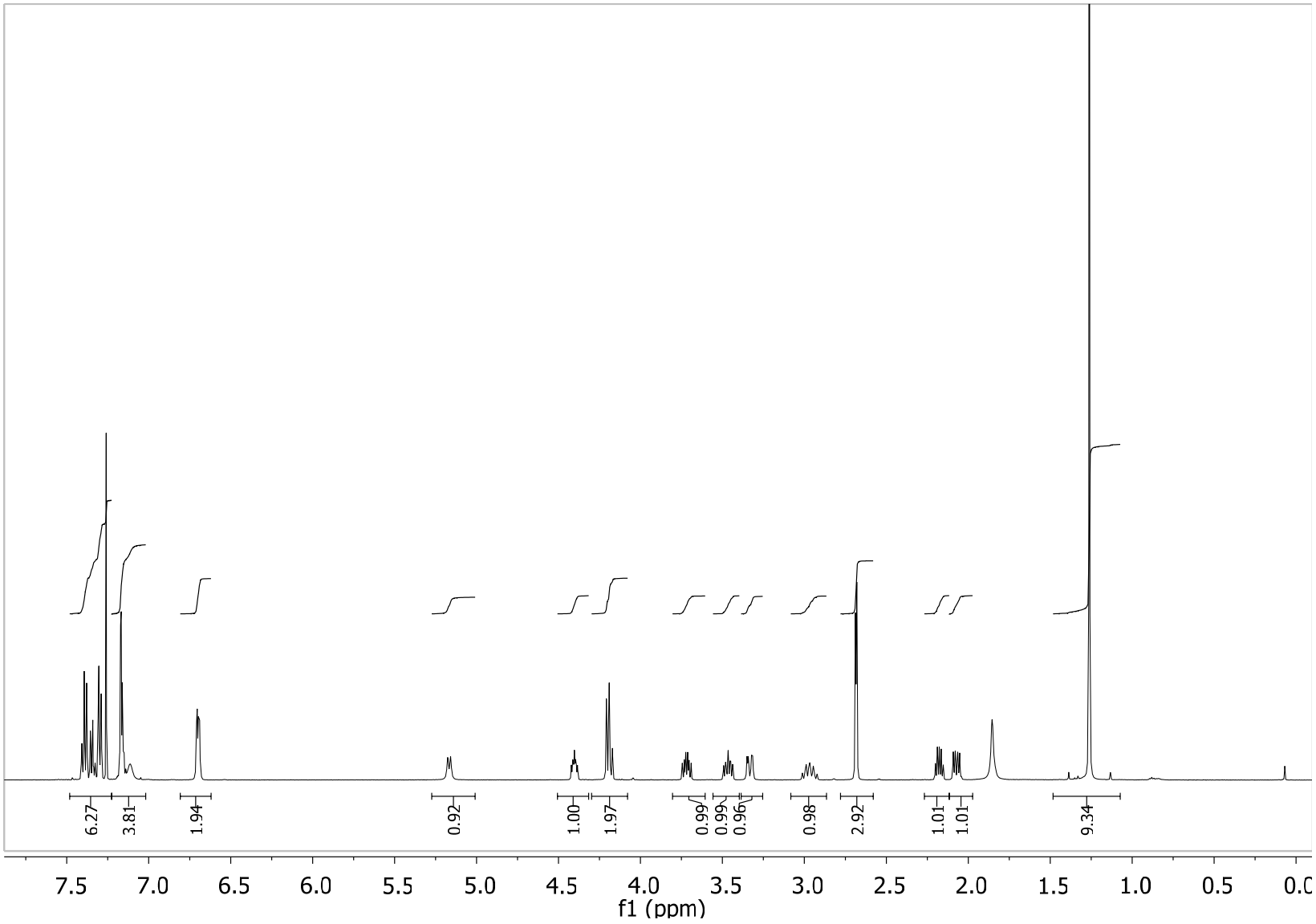
^{1}H-NMR spectrum of Piv-L-*cis*(βPh)Pro-L-Phe-NHMe (**1**) in $CDCl_3$ (10 mM, 500 MHz, 298K)



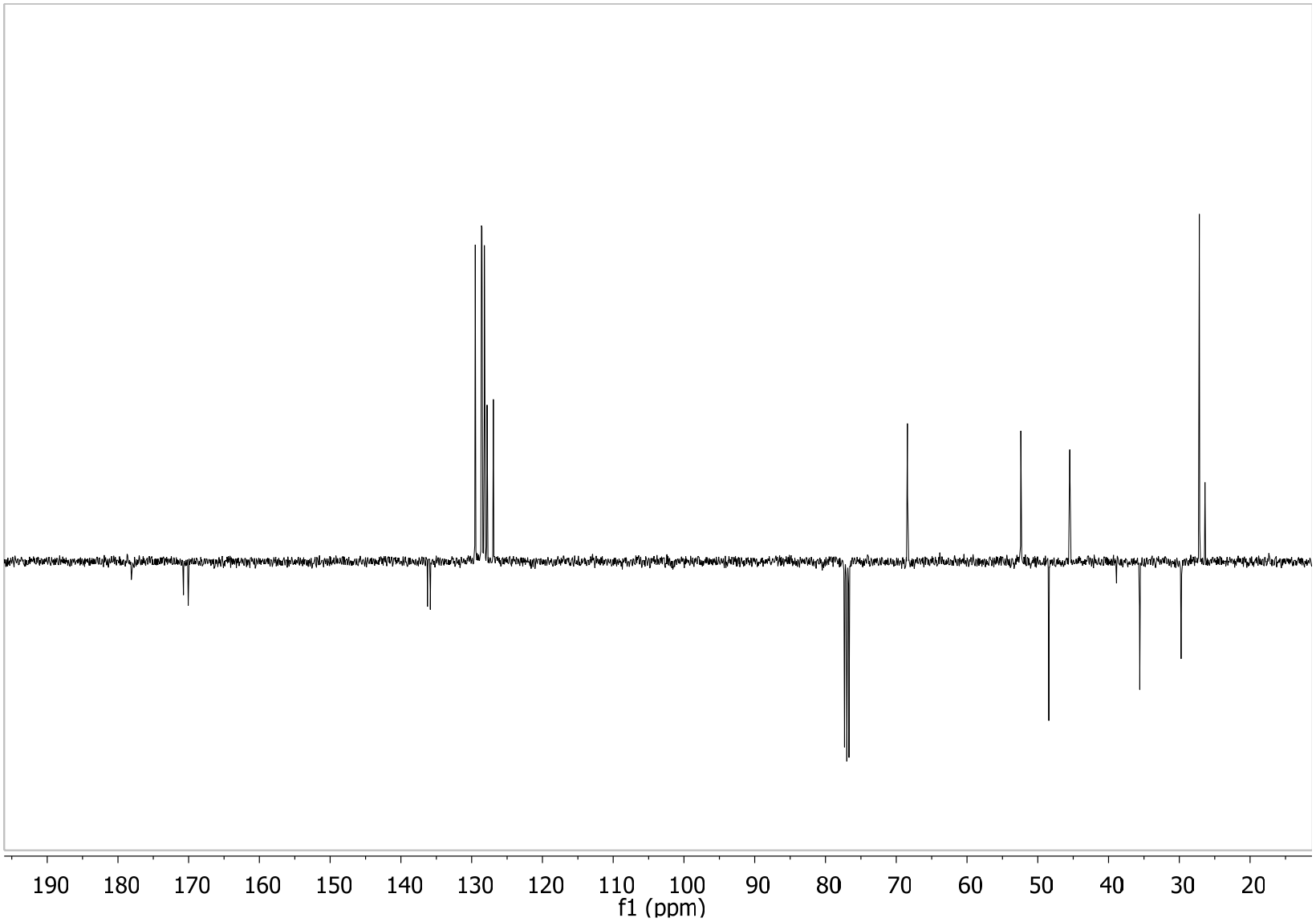
^{13}C-NMR spectrum of Piv-L-*cis*(βPh)Pro-L-Phe-NHMe (**1**) in $CDCl_3$ (100 MHz, 298K)



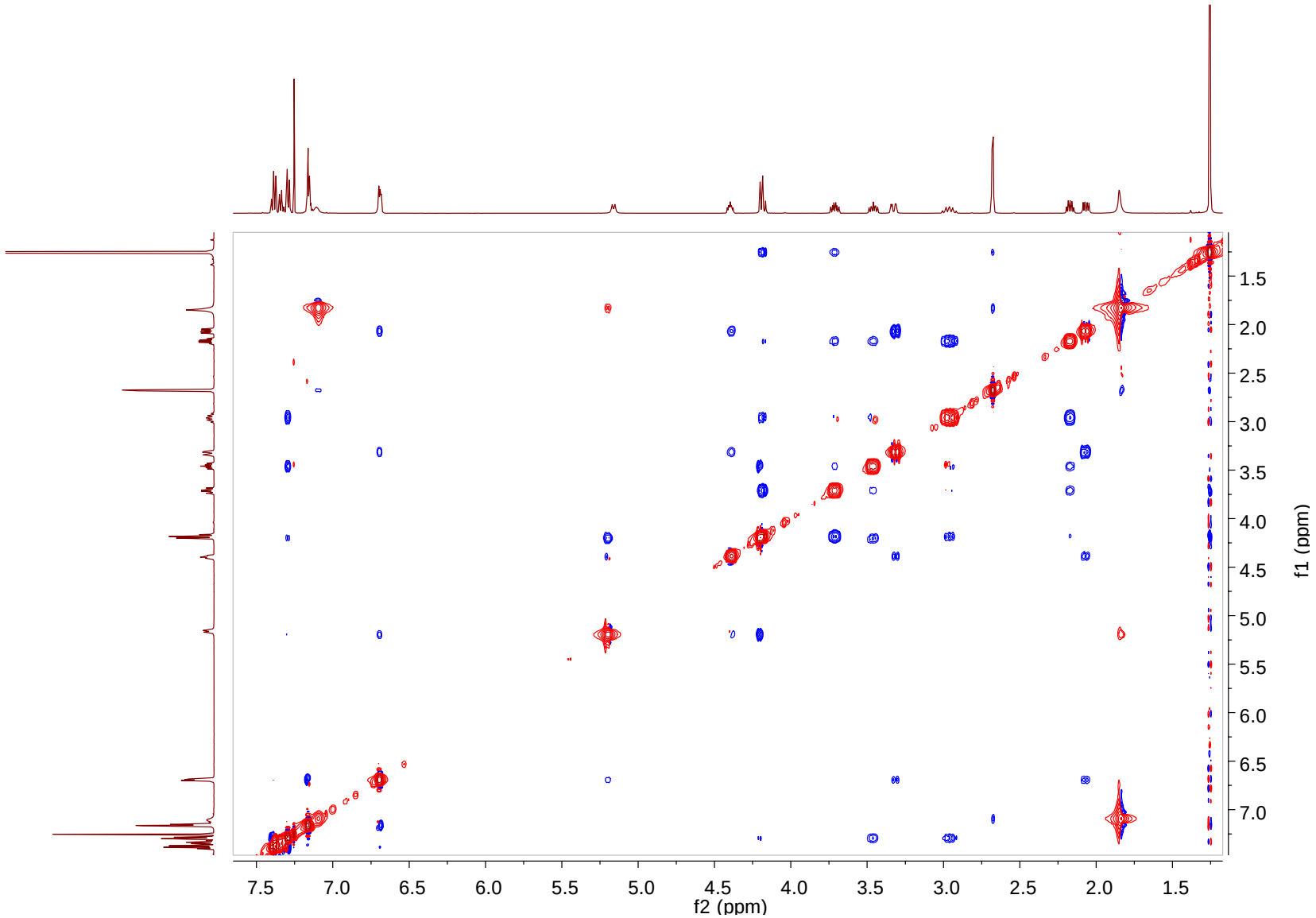
2D-NOESY spectrum of Piv-L-*cis*(βPh)Pro-L-Phe-NHMe (**1**) in $CDCl_3$ (10 mM, 500 MHz, 298K, 500 ms mixing time)



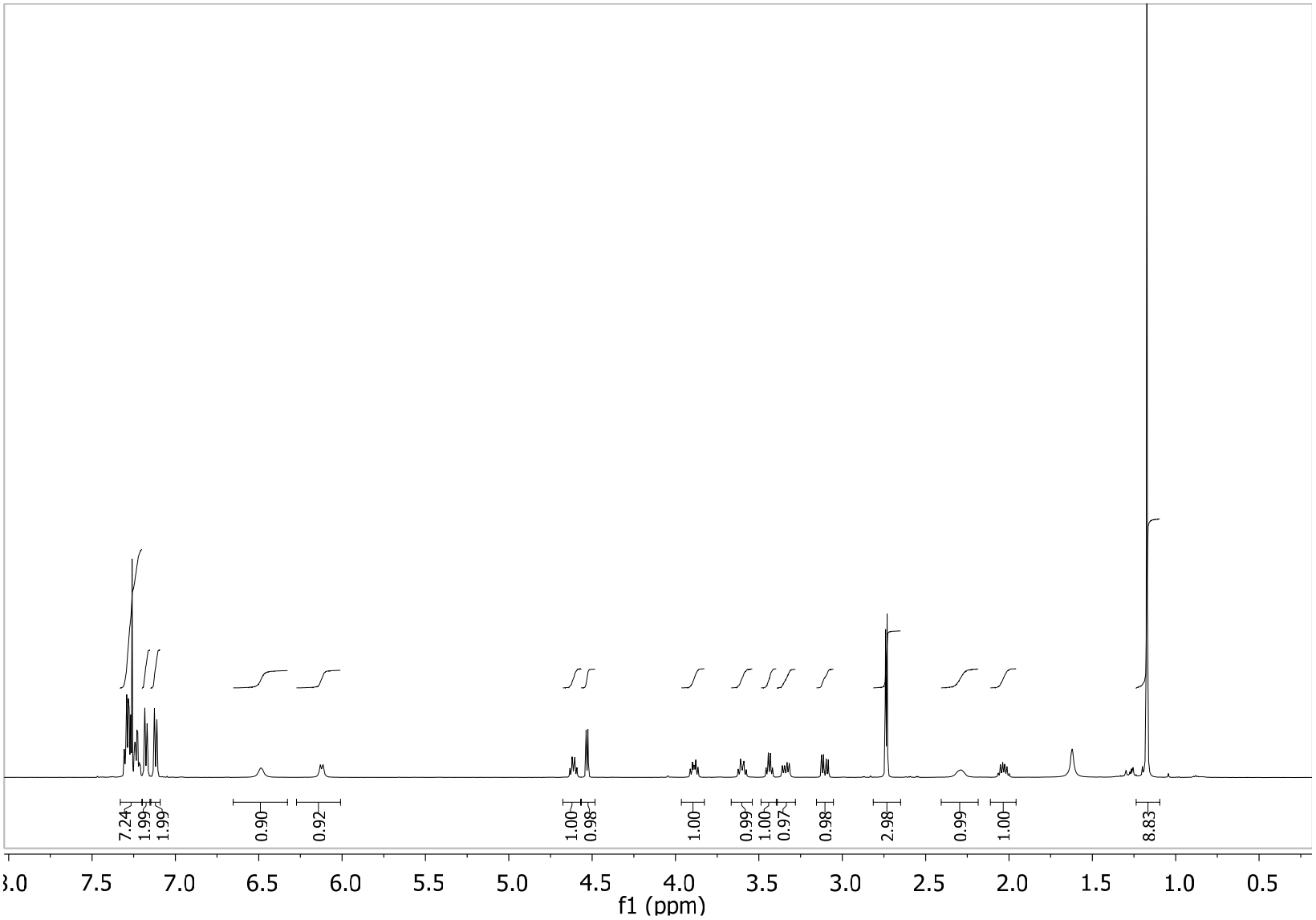
^{1}H-NMR spectrum of Piv-L-cis(βPh)Pro-D-Phe-NHMe (**2**) in $CDCl_3$ (10 mM, 500 MHz, 298K)



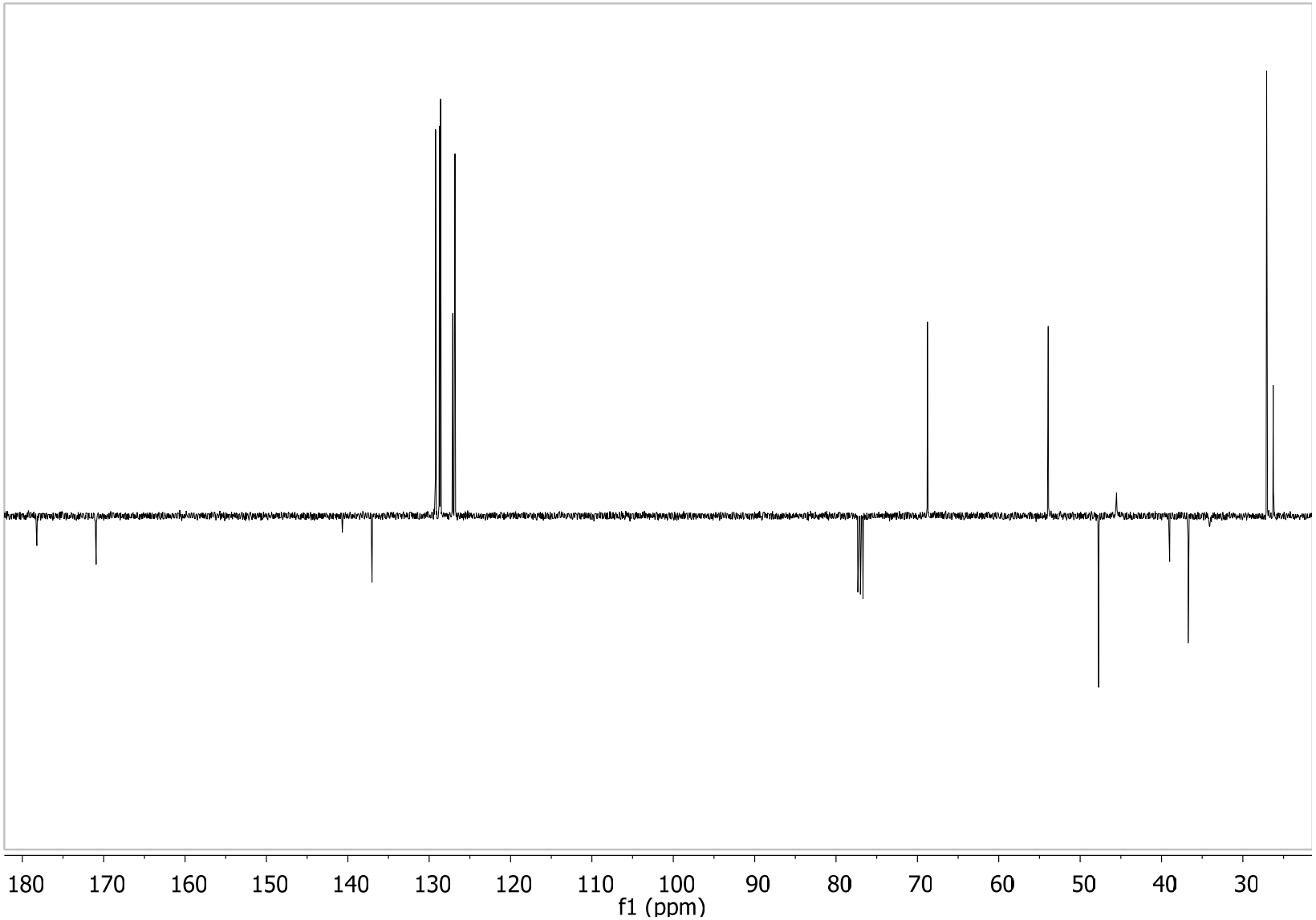
^{13}C-NMR spectrum of Piv-L-cis(βPh)Pro-D-Phe-NHMe (**2**) in $CDCl_3$ (100 MHz, 298K)



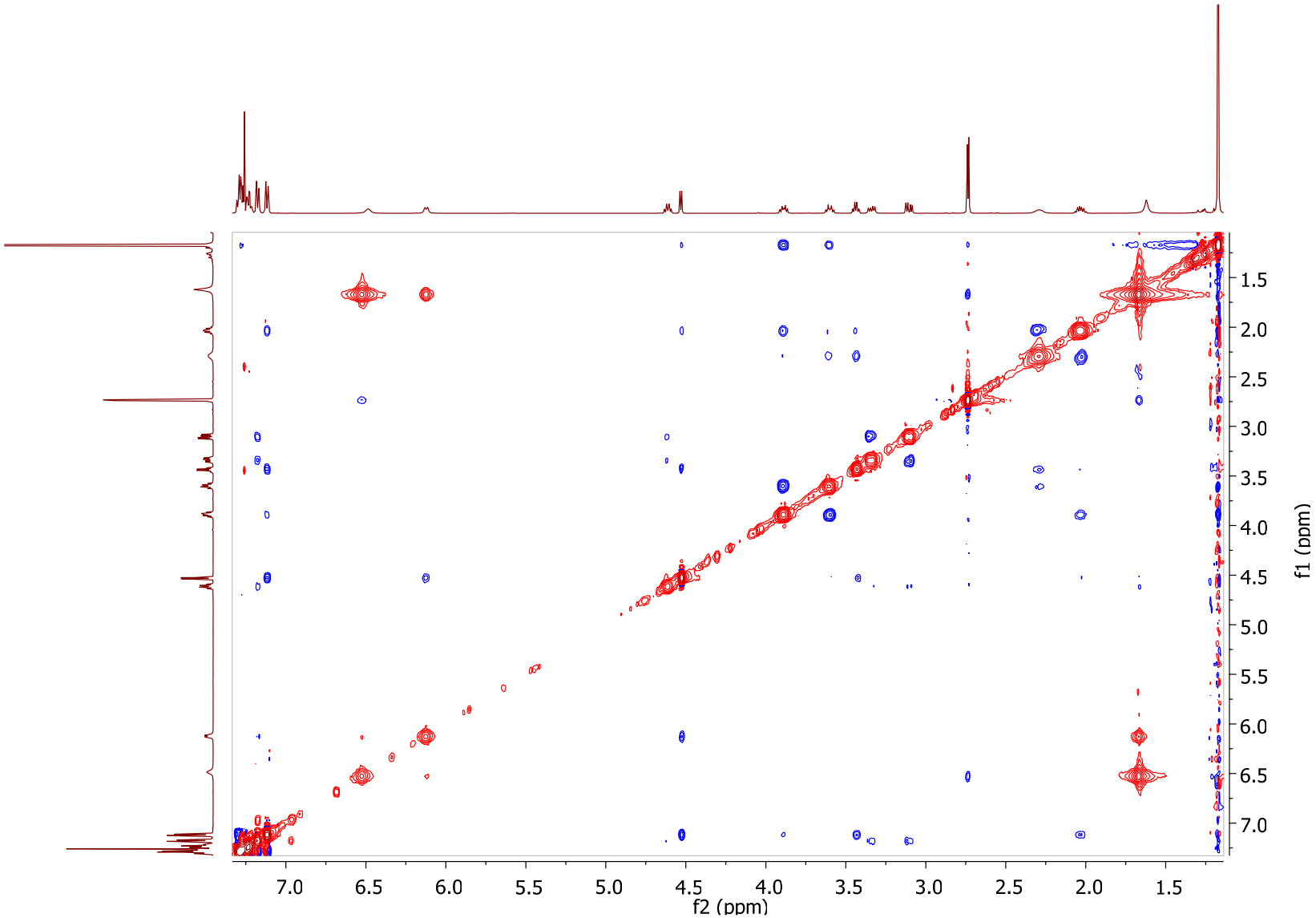
2D-NOESY spectrum of Piv-L-cis(βPh)Pro-D-Phe-NHMe (**2**) in $CDCl_3$ (10 mM, 500 MHz, 298K, 500 ms mixing time)



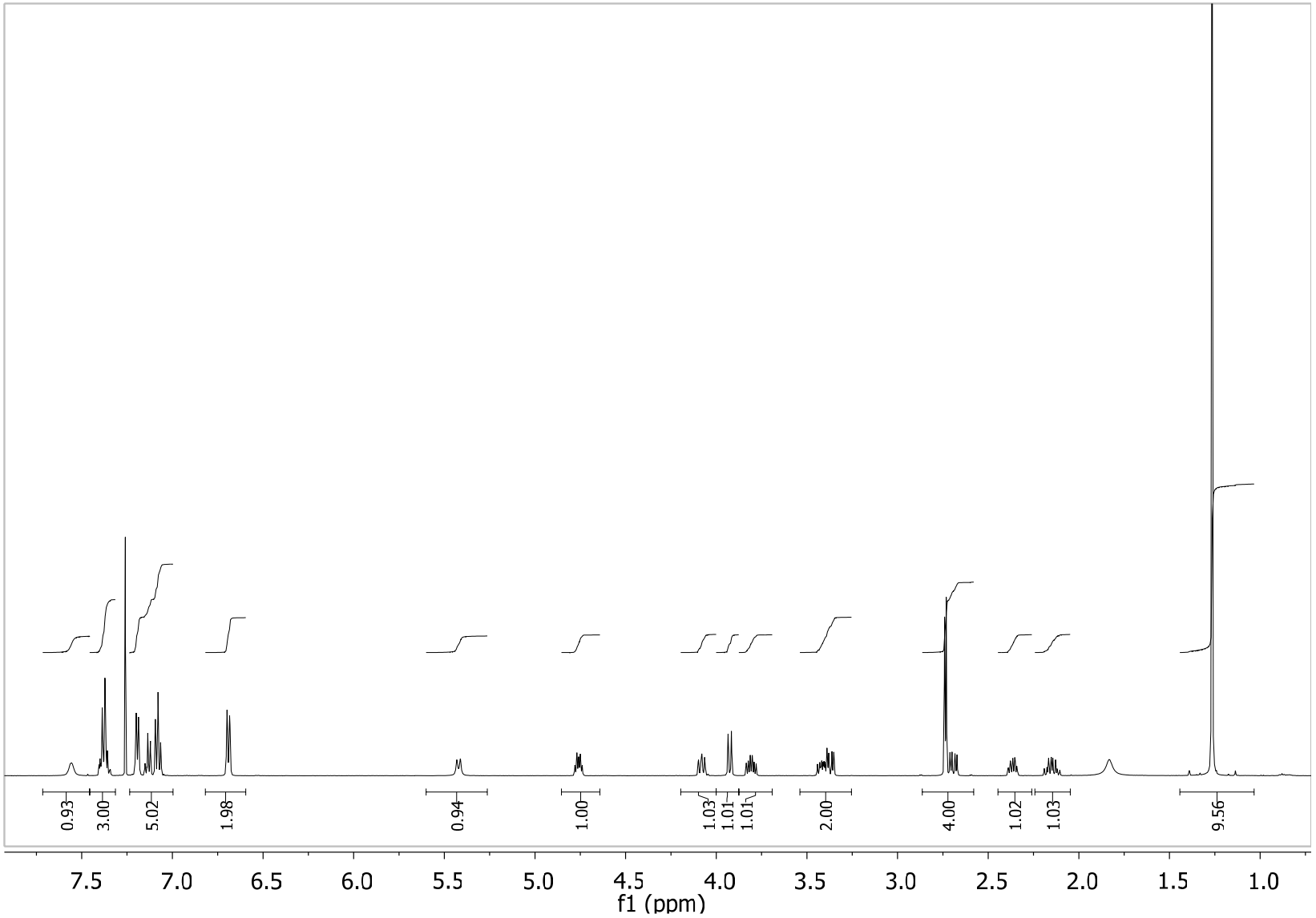
^{1}H-NMR spectrum of Piv-L-*trans*(βPh)Pro-L-Phe-NHMe (**3**) in $CDCl_3$ (10 mM, 500 MHz, 298K)



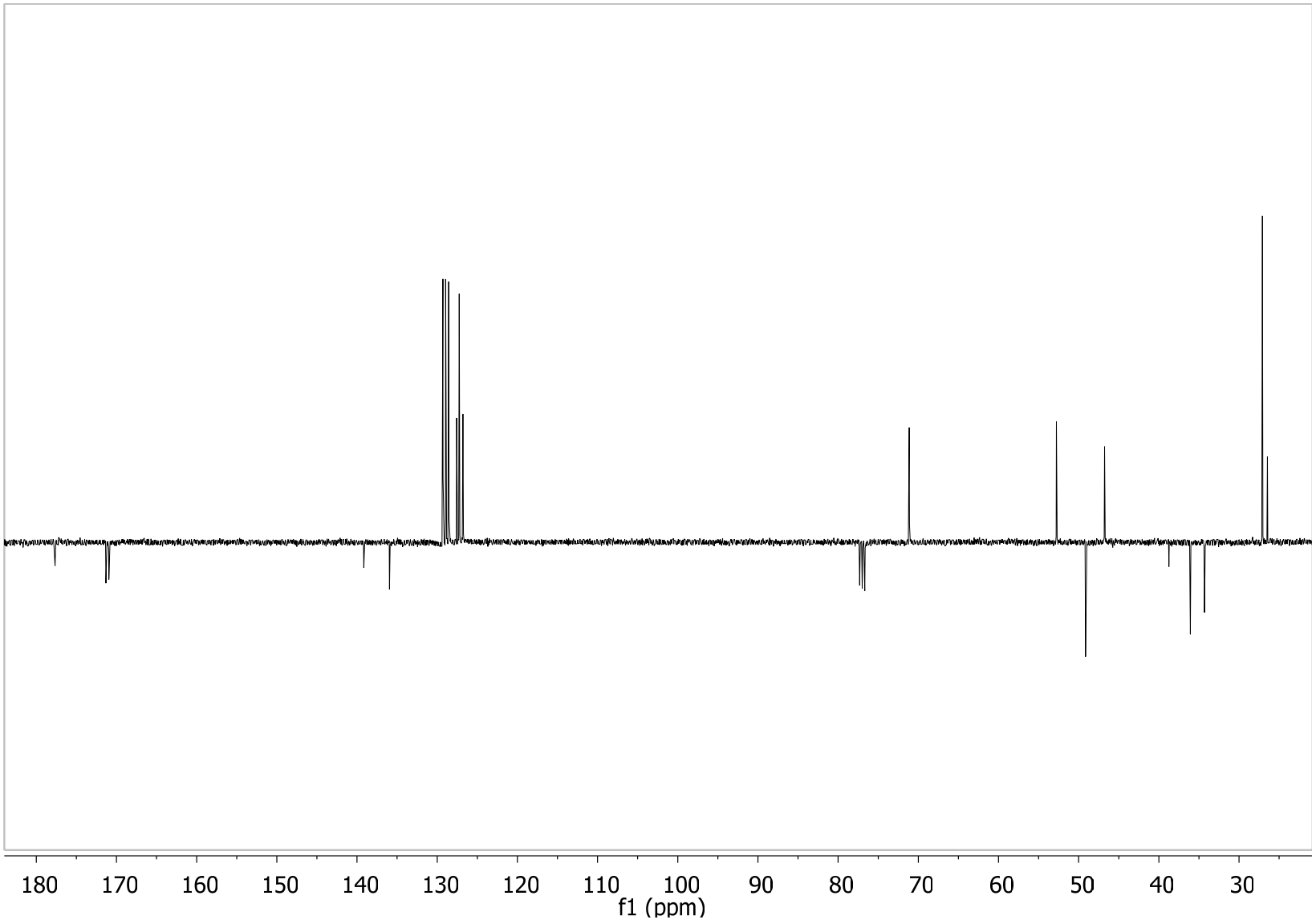
^{13}C-NMR spectrum of Piv-L-*trans*(βPh)Pro-L-Phe-NHMe (**3**) in $CDCl_3$ (100 MHz, 298K)



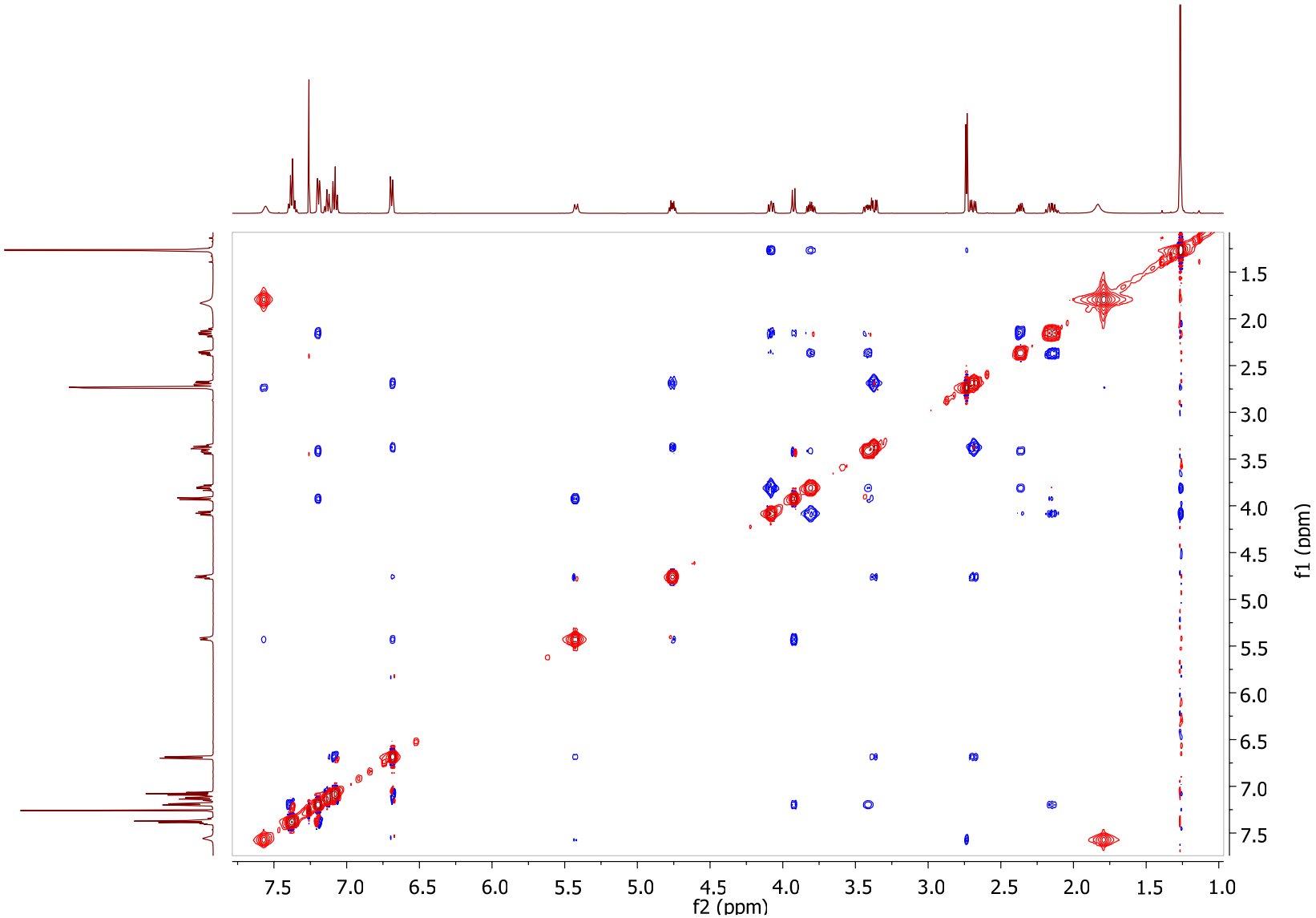
2D-NOESY spectrum of Piv-L-*trans*(βPh)Pro-L-Phe-NHMe (**3**) in $CDCl_3$ (10 mM, 500 MHz, 298K, 500 ms mixing time)



^{1}H-NMR spectrum of Piv-L-*trans*(βPh)Pro-D-Phe-NHMe (**4**) in $CDCl_3$ (10 mM, 500 MHz, 298K)



^{13}C-NMR spectrum of Piv-L-*trans*(βPh)Pro-D-Phe-NHMe (**4**) in $CDCl_3$ (100 MHz, 298K)



2D-NOESY spectrum of Piv-L-*trans*(βPh)Pro-D-Phe-NHMe (**4**) in $CDCl_3$ (10 mM, 500 MHz, 298K, 500 ms mixing time)