Supplementary Material (ESI) for Organic & Biomolecular Chemistry

ELECTRONIC SUPPORTING INFORMATION

A New Tool for Photoaffinity Labeling Studies: a Conformationally Rigidified, Benzophenone Based, α-Amino Acid

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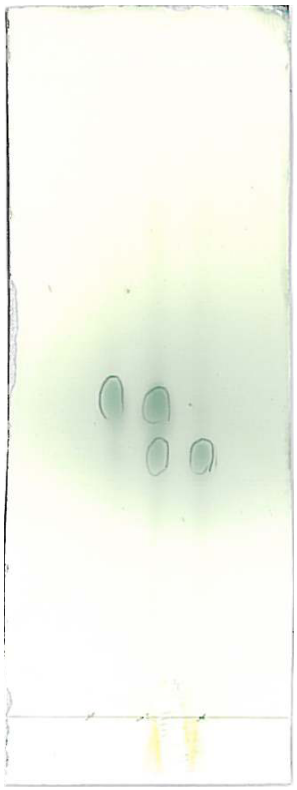
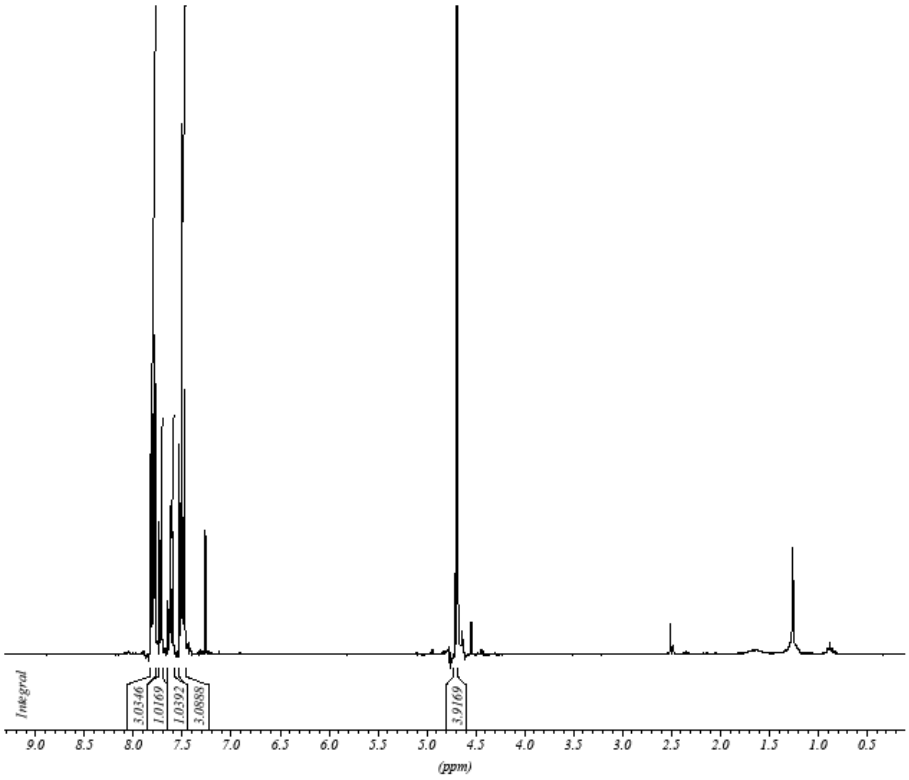
TLC



TLC of Z-(*RS*)-BpAib-(*S*)-Phe-NHChx separation. (Kieselgel F 254, Merck).
Eluent : Cyclohexane : Ethyl acetate 1 : 1.
Left lane : Z-(*S*)-BpAib-(*S*)-Phe-NHChx **7a** Rf 0.45
Middle lane : Z-(*RS*)-BpAib-(*S*)-Phe-NHChx (artificial mixture)
Right lane : Z-(*R*)-BpAib-(*S*)-Phe-NHChx **8a** Rf 0.37

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

3,4-*bis*-(bromomethy)lbenzophenone **3**



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PROCNO	:	1
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O1	:	2851.24 Hz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
NC_proc	:	-3
*** 1D NMR Plot Parameters ***		
Height	:	16.28 cm
Width	:	22.10 cm
XOffset	:	1.00 cm
YOffset	:	1.00 cm
Start	:	9.31 ppm
Stop	:	0.11 ppm
Offset	:	2.11 %
SR	:	14.93 Hz
wx	:	204463136.00
wy	:	-4402037.50
wx_p	:	10000.00
wy_p	:	0.00
ppm_cm	:	0.42
Hz_cm	:	124.95
YVal_cm	:	12829556.00
xstart	:	16599
xstop	:	30932
xstart_p	:	0
xstop_p	:	0
NC_proc	:	-3
BaseInt	:	5019225330
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DecoFct	:	10000
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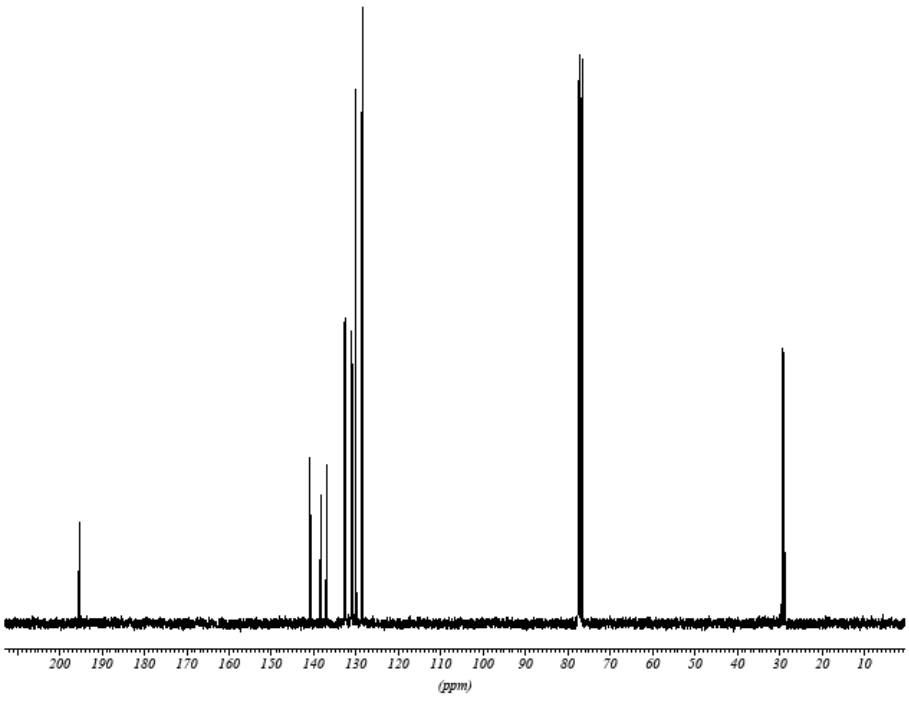
MPSF	:	1.0000000
AQ_time	:	2.5952260 sec



*** Current Data Parameters ***		
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EXPNO	:	11
PROCNO	:	1
*** Acquisition Parameters ***		
NUCLEUS	:	off
O1	:	7546.30 Hz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
NC_proc	:	-6
*** 1D NMR Plot Parameters ***		
Height	:	17.78 cm
Width	:	22.10 cm
XOffset	:	1.00 cm
YOffset	:	1.00 cm
Start	:	212.91 ppm
Stop	:	0.43 ppm
Offset	:	3.43 %
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wy	:	-10435611.00
wx_p	:	10000.00
wy_p	:	0.00
ppm_cm	:	9.61
Hz_cm	:	725.59
YVal_cm	:	17107560.00
xstart	:	858
xstop	:	30073
xstart_p	:	0
xstop_p	:	0
NC_proc	:	-6
BaseInt	:	5019225330
NormInt	:	1.000
DecoFct	:	10000
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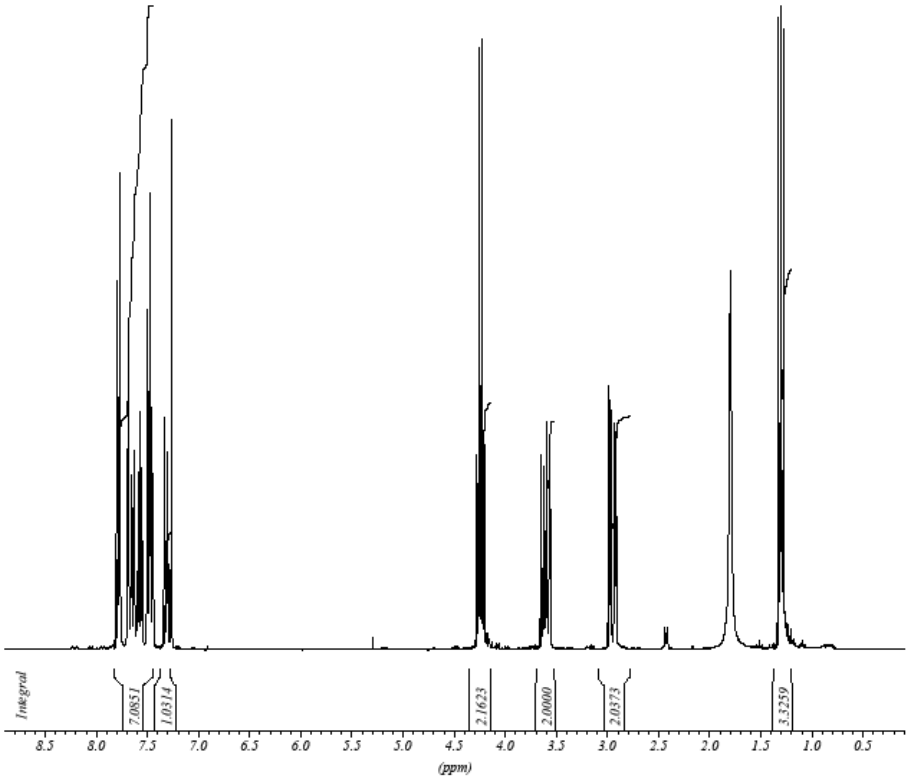
AQ_time	:	1.8219010 sec

H-(*RS*)-BpAib-OEt **4**

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PROCNO    :  1
*** Acquisition Parameters ***
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O1        :  2851.24 Hz
SOLVENT   :  CDCl3
*** Processing Parameters ***
NC_proc   :  -4
*** 1D NMR Plot Parameters ***
Height    :  16.28 cm
Width     :  22.10 cm
XOffset   :  1.00 cm
YOffset   :  1.00 cm
Start     :  8.89 ppm
Stop      :  0.09 ppm
Offset    :  3.01 %
SR        :  14.93 Hz
wx        :  181499312.00
wy        :  -5632341.00
wx_p      :  10000.00
wy_p      :  0.00
ppm_cm    :  0.40
Hz_cm     :  119.51
YVal_cm   :  11494573.00
xstart    :  17256
xstop     :  30965
xstart_p  :  0
xstop_p   :  0
NC_proc   :  -4
BaseInt   :  3986980602
NormInt   :  2.000
DecoFct   :  10000
Rec       :  F1
MPSF      :  1.0000000
AQ_time   :  2.5952260 sec
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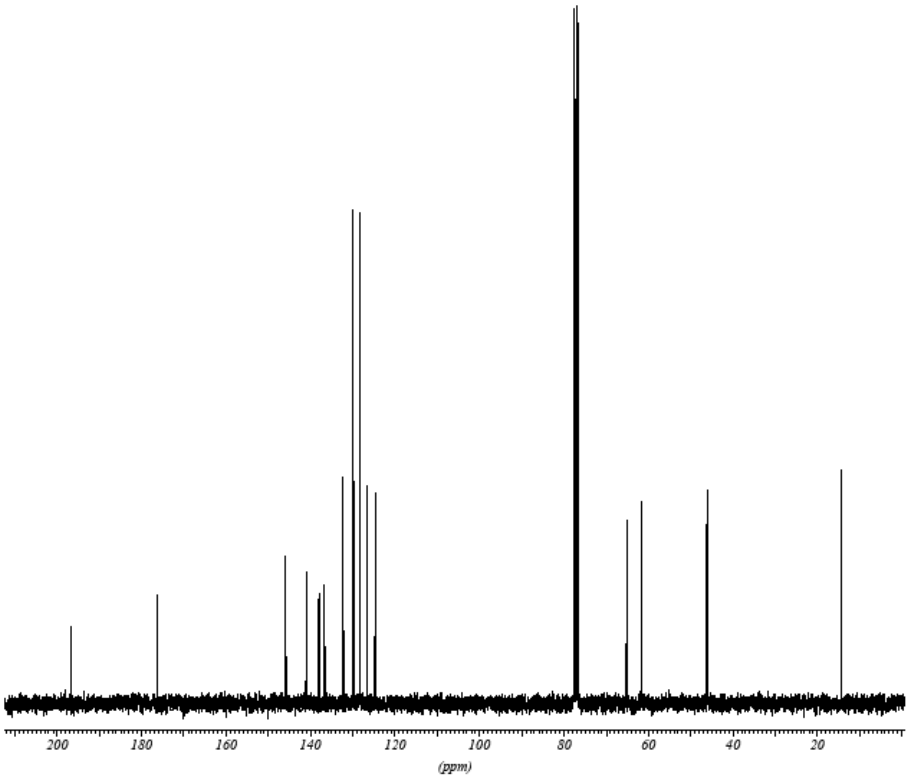


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EXPNO     :  11
PROCNO    :  1
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O1        :  7546.30 Hz
SOLVENT   :  CDCl3
*** Processing Parameters ***
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*** 1D NMR Plot Parameters ***
Height    :  17.78 cm
Width     :  22.10 cm
XOffset   :  1.00 cm
YOffset   :  1.00 cm
Start     :  212.34 ppm
Stop      :  -0.70 ppm
Offset    :  3.58 %
SR        :  0.00 Hz
wx        :  243885232.00
wy        :  -9048644.00
wx_p      :  10000.00
wy_p      :  0.00
ppm_cm    :  9.64
Hz_cm     :  727.50
YVal_cm   :  14225752.00
xstart    :  937
xstop     :  30229
xstart_p  :  0
xstop_p   :  0
NC_proc   :  -7
BaseInt   :  3986980602
NormInt   :  1.000
DecoFct   :  10000
Rec       :  F1
MPSF      :  1.0000000
AQ_time   :  1.8219010 sec
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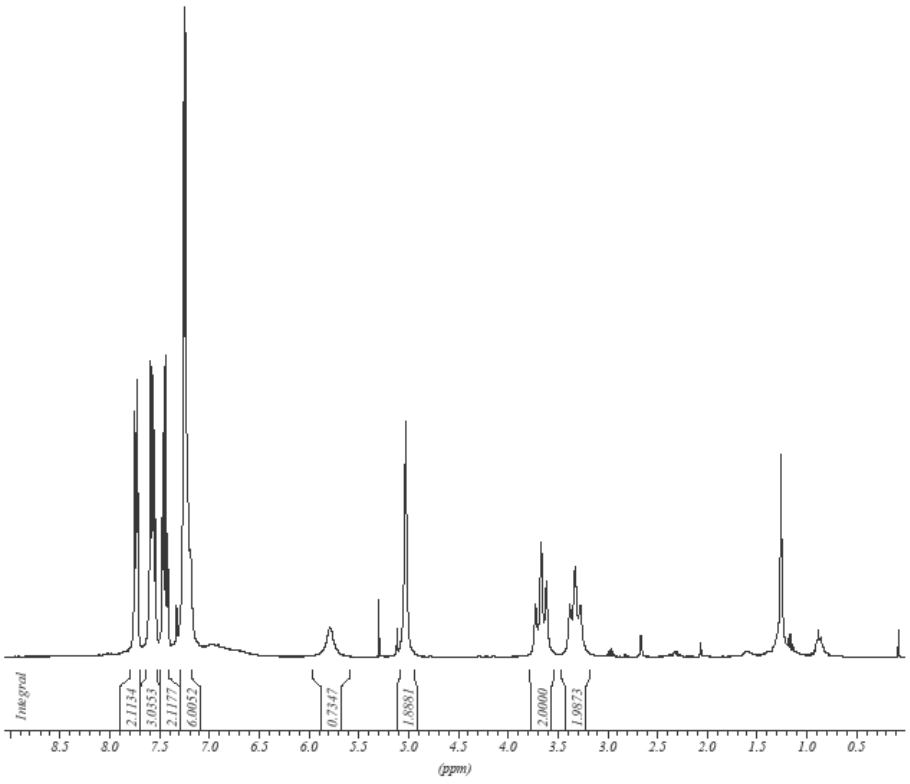
Z-(*RS*)-BpAib-OH **5**

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EXPNO     :            10
PROCNO    :             1
*** Acquisition Parameters ***
NUCLEUS   :           off
O1        :       2851.24 Hz
SOLVENT   :          CDCl3
*** Processing Parameters ***
NC_proc   :            -2
*** 1D NMR Plot Parameters ***
Height    :       16.28 cm
Width     :       22.10 cm
XOffset   :        1.00 cm
YOffset   :        1.00 cm
Start     :        9.06 ppm
Stop      :        0.02 ppm
Offset    :        1.95 %
SR        :       14.93 Hz
wx        :  275114528.00
wy        :   -5481538.00
wx_p      :       10000.00
wy_p      :           0.00
ppm_cm    :           0.41
Hz_cm     :         122.75
YVal_cm   :   17235630.00
xstart    :          16999
xstop     :          31079
xstart_p  :              0
xstop_p   :              0
NC_proc   :             -2
BaseInt   :     5567615474
NormInt   :          2.000
DecoFct   :          10000
Rec       :             F1
MPSF      :     1.0000000
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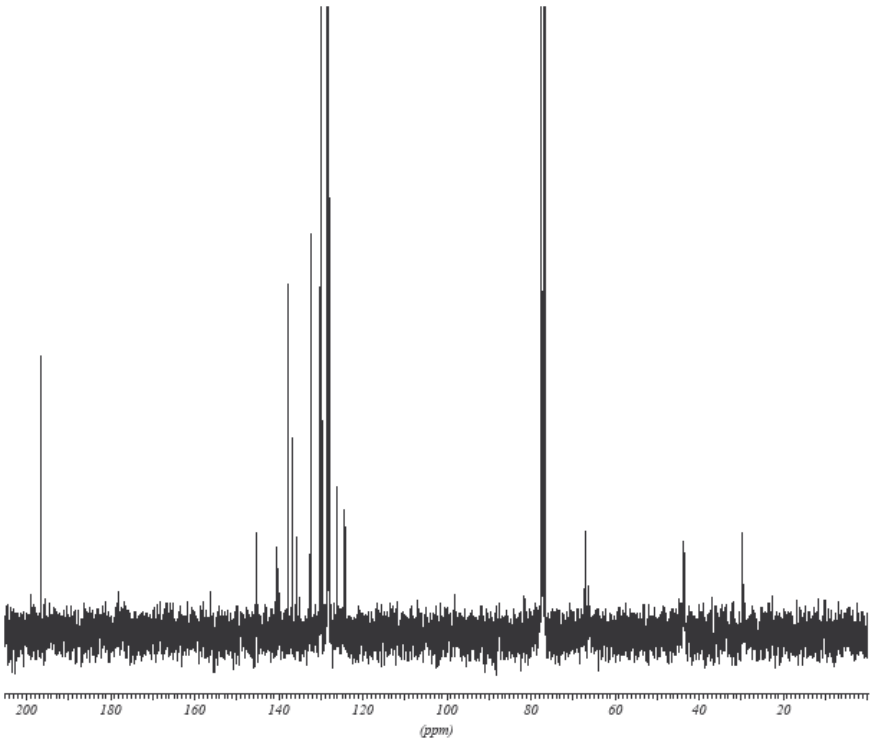


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*** Current Data Parameters ***
NAME      :      fc37k638
EXPNO     :            11
PROCNO    :             1
*** Acquisition Parameters ***
NUCLEUS   :           off
O1        :       7546.30 Hz
SOLVENT   :          CDCl3
*** Processing Parameters ***
NC_proc   :            -5
*** 1D NMR Plot Parameters ***
Height    :       16.88 cm
Width     :       21.20 cm
XOffset   :        1.00 cm
YOffset   :        1.00 cm
Start     :      205.16 ppm
Stop      :       -0.20 ppm
Offset    :        8.83 %
SR        :        5.77 Hz
wx        :   29139450.00
wy        :   -2823002.50
wx_p      :       10000.00
wy_p      :           0.00
ppm_cm    :           9.69
Hz_cm     :         731.07
YVal_cm   :    1893510.25
xstart    :          1913
xstop     :         30150
xstart_p  :              0
xstop_p   :              0
NC_proc   :             -5
BaseInt   :     5567615474
NormInt   :          1.000
DecoFct   :          10000
Rec       :             F1
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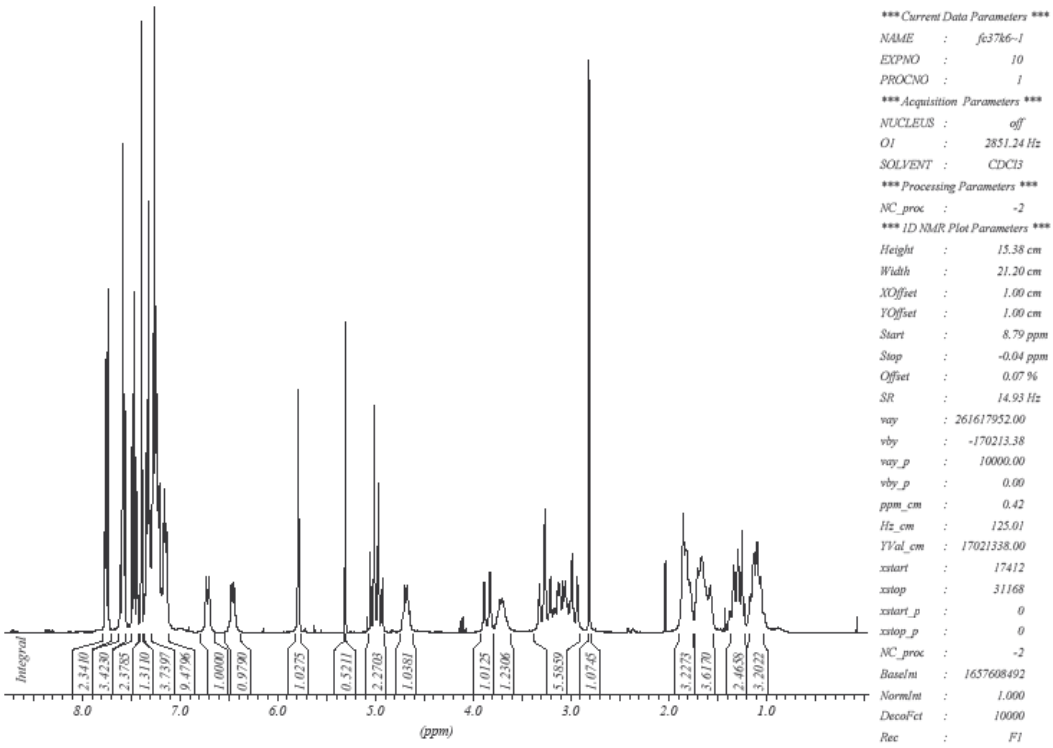
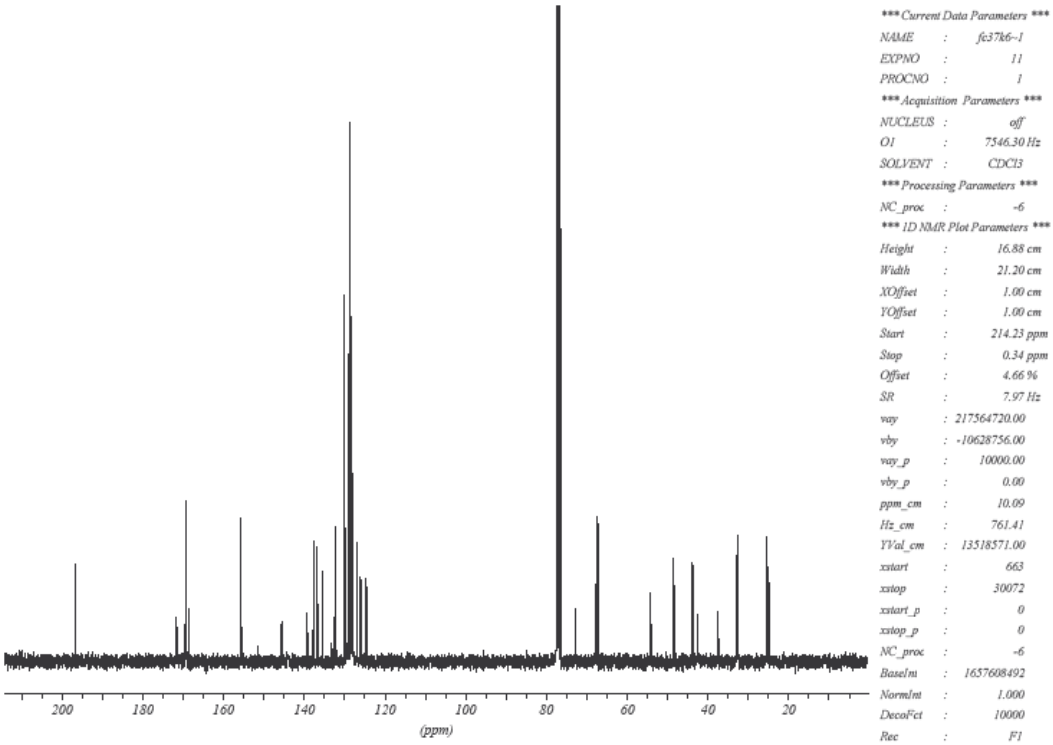
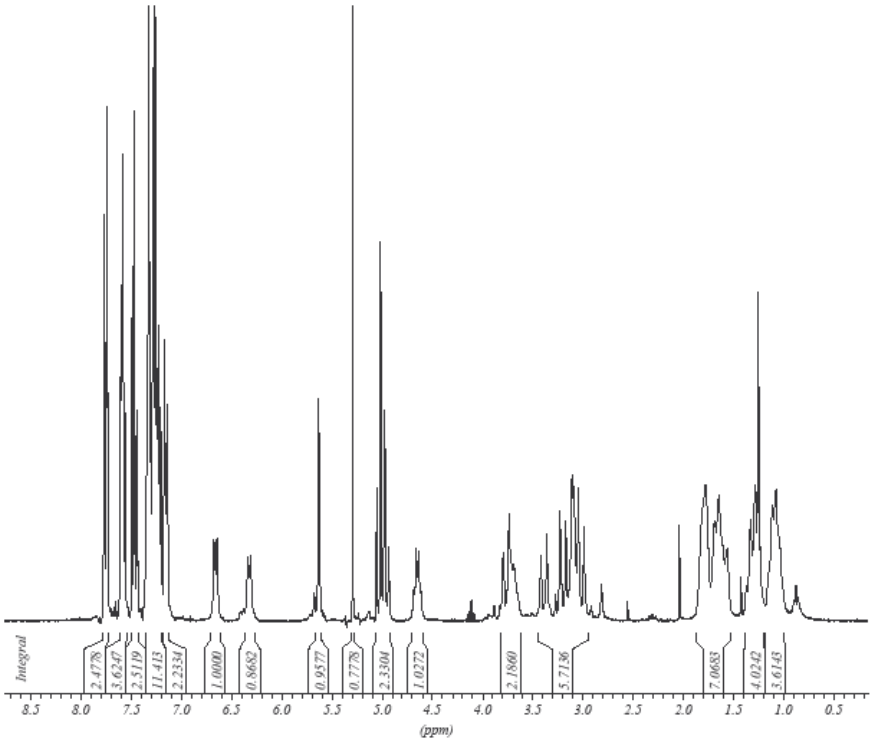
Z-(*S*)-BpAib-(*S*)-Phe-NHChx **7a**





Z-(*R*)-BpAib-(*S*)-Phe-NHChx **8a**




```
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EXPNO     :   10
PROCNO    :   1
*** Acquisition Parameters ***
NUCLEUS   :   off
O1        :   2851.24 Hz
SOLVENT   :   CDCl3
*** Processing Parameters ***
NC_proc   :   -5
*** 1D NMR Plot Parameters ***
Height    :   15.38 cm
Width     :   21.20 cm
XOffset   :   1.00 cm
YOffset   :   1.00 cm
Start     :   8.76 ppm
Stop      :   0.16 ppm
Offset    :   1.89 %
SR        :   15.12 Hz
vay       :   287711776.00
vby       :   -5529252.00
vay_p     :   10000.00
vby_p     :   0.00
ppm_cm    :   0.41
Hz_cm     :   121.75
YVal_cm   :   19066386.00
xstart    :   17458
xstop     :   30855
xstart_p  :   0
xstop_p   :   0
NC_proc   :   -5
BaseInt   :   2704222900
NormInt   :   1.000
DecoFct   :   10000
Rec       :   F1
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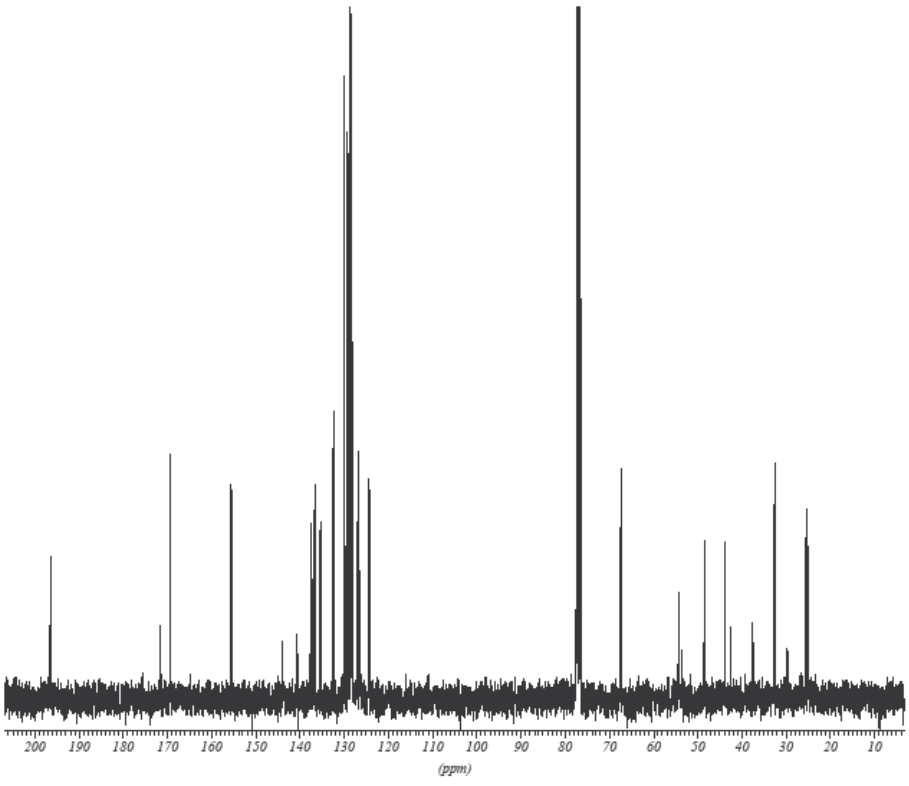


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*** Current Data Parameters ***
NAME      :   fc37k6~2
EXPNO     :   11
PROCNO    :   1
*** Acquisition Parameters ***
NUCLEUS   :   off
O1        :   7546.30 Hz
SOLVENT   :   CDCl3
*** Processing Parameters ***
NC_proc   :   -6
*** 1D NMR Plot Parameters ***
Height    :   17.78 cm
Width     :   22.10 cm
XOffset   :   1.00 cm
YOffset   :   1.00 cm
Start     :   206.85 ppm
Stop      :   3.18 ppm
Offset    :   4.55 %
SR        :   6.87 Hz
vay       :   92406576.00
vby       :   -4406553.00
vay_p     :   10000.00
vby_p     :   0.00
ppm_cm    :   9.22
Hz_cm     :   695.51
YVal_cm   :   5445058.00
xstart    :   1679
xstop     :   29683
xstart_p  :   0
xstop_p   :   0
NC_proc   :   -6
BaseInt   :   2704222900
NormInt   :   1.000
DecoFct   :   10000
Rec       :   F1
MPSF      :   1.0000000
AQ_time   :   1.8219031 sec
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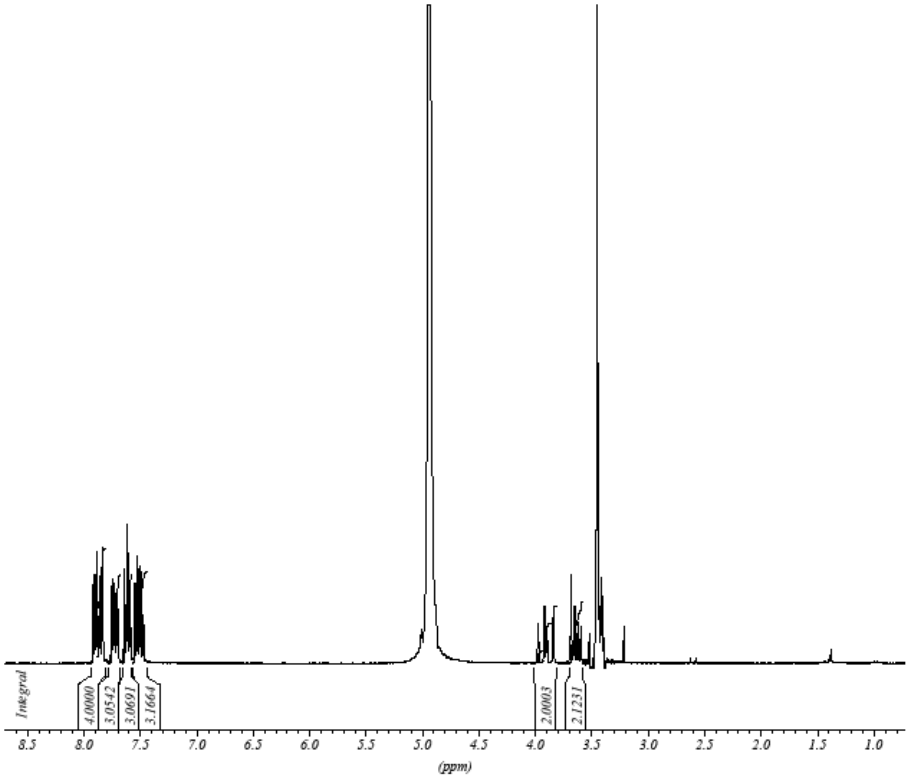
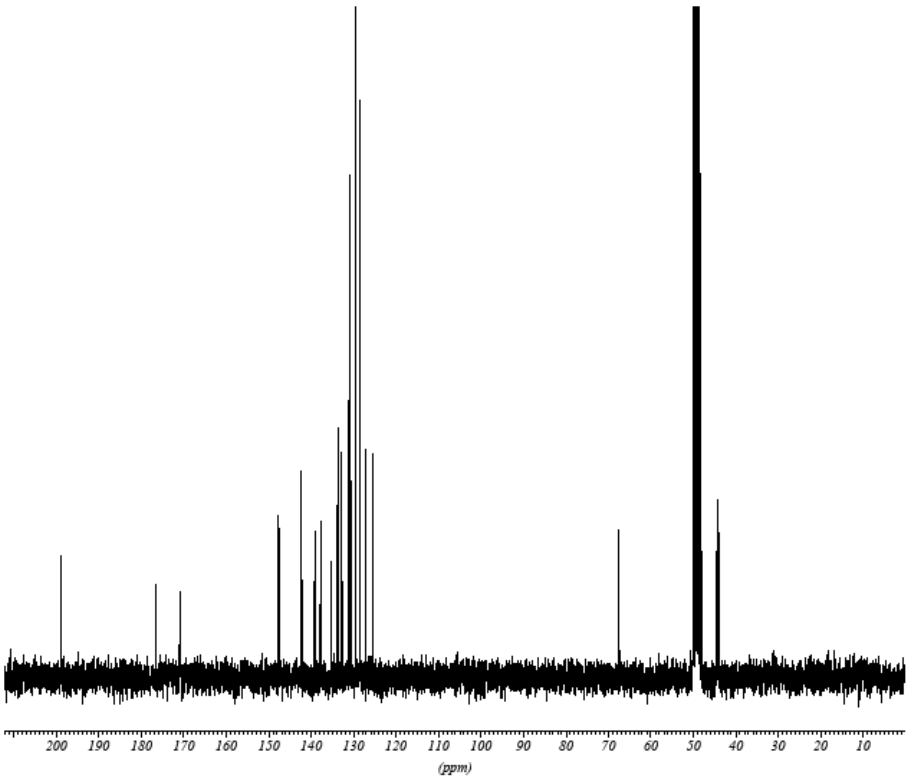
Bz-(*RS*)-BpAib-OH **6**



*** Current Data Parameters ***		
NAME	:	mw29k459
EXPNO	:	10
PROCNO	:	1
*** Acquisition Parameters ***		
NUCLEUS	:	off
O1	:	2851.24 Hz
SOLVENT	:	MeOD
*** Processing Parameters ***		
NC_proc	:	-2
*** 1D NMR Plot Parameters ***		
Height	:	16.28 cm
Width	:	22.10 cm
XOffset	:	1.00 cm
YOffset	:	1.00 cm
Start	:	8.70 ppm
Stop	:	0.73 ppm
Offset	:	0.73 %
SR	:	-478.04 Hz
wx	:	43778816.00
wy	:	-323873.16
wx_p	:	10000.00
wy_p	:	0.00
ppm_cm	:	0.36
Hz_cm	:	108.27
YVal_cm	:	2709010.50
xstart	:	20114
xstop	:	32534
xstart_p	:	0
xstop_p	:	0
NC_proc	:	-2
BaseInt	:	418816358
NormInt	:	4.000
DecoFct	:	10000
Rec	:	F1
MPSF	:	1.0000000
AQ_time	:	2.5952260 sec



*** Current Data Parameters ***		
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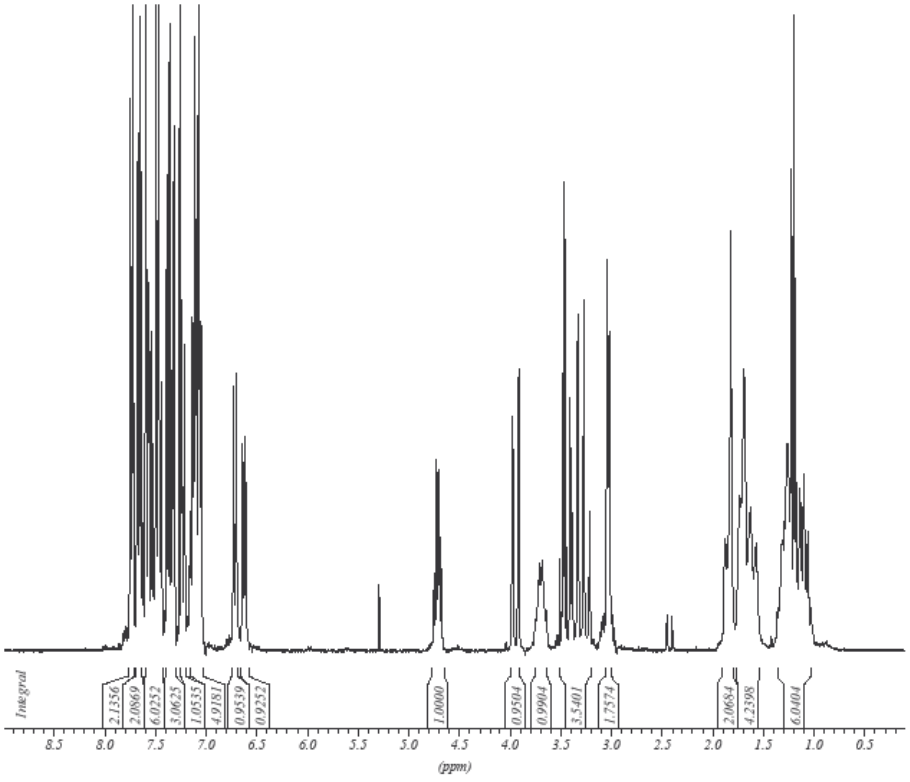
EXPNO	:	11
PROCNO	:	1
*** Acquisition Parameters ***		
NUCLEUS	:	off
O1	:	7546.30 Hz
SOLVENT	:	MeOD
*** Processing Parameters ***		
NC_proc	:	-6
*** 1D NMR Plot Parameters ***		
Height	:	17.78 cm
Width	:	22.10 cm
XOffset	:	1.00 cm
YOffset	:	1.00 cm
Start	:	212.09 ppm
Stop	:	0.18 ppm
Offset	:	7.31 %
SR	:	-217.14 Hz
wx	:	74831904.00
wy	:	-5898938.00
wx_p	:	10000.00
wy_p	:	0.00
ppm_cm	:	9.59
Hz_cm	:	723.62
YVal_cm	:	4540542.50
xstart	:	1367
xstop	:	30503
xstart_p	:	0
xstop_p	:	0
NC_proc	:	-6
BaseInt	:	418816358
NormInt	:	1.000
DecoFct	:	10000
Rec	:	F1
MPSF	:	1.0000000
AQ_time	:	1.8219010 sec

Bz-(*S*)-BpAib-(*S*)-Phe-NHChx **7b**

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*** Current Data Parameters ***
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EXPNO     :            10
PROCNO    :             1
*** Acquisition Parameters ***
NUCLEUS   :           off
O1        :       2851.24 Hz
SOLVENT   :          CDCl3
*** Processing Parameters ***
NC_proc   :            -6
*** 1D NMR Plot Parameters ***
Height    :         16.28 cm
Width     :         22.10 cm
XOffset   :          1.00 cm
YOffset   :          1.00 cm
Start     :         8.99 ppm
Stop      :         0.11 ppm
Offset    :         2.63 %
SR        :        14.93 Hz
wx        :  262853360.00
wy        :   -7100849.50
wx_p      :      10000.00
wy_p      :          0.00
ppm_cm    :          0.40
Hz_cm     :        120.61
YVal_cm   :   16581954.00
xstart    :         17104
xstop     :         30939
xstart_p  :             0
xstop_p   :             0
NC_proc   :            -6
BaseInt   :    4215022188
NormInt   :         1.000
DecoFct   :         10000
Rec       :            F1
MPSF      :    1.0000000
AQ_time   :    2.5952260 sec
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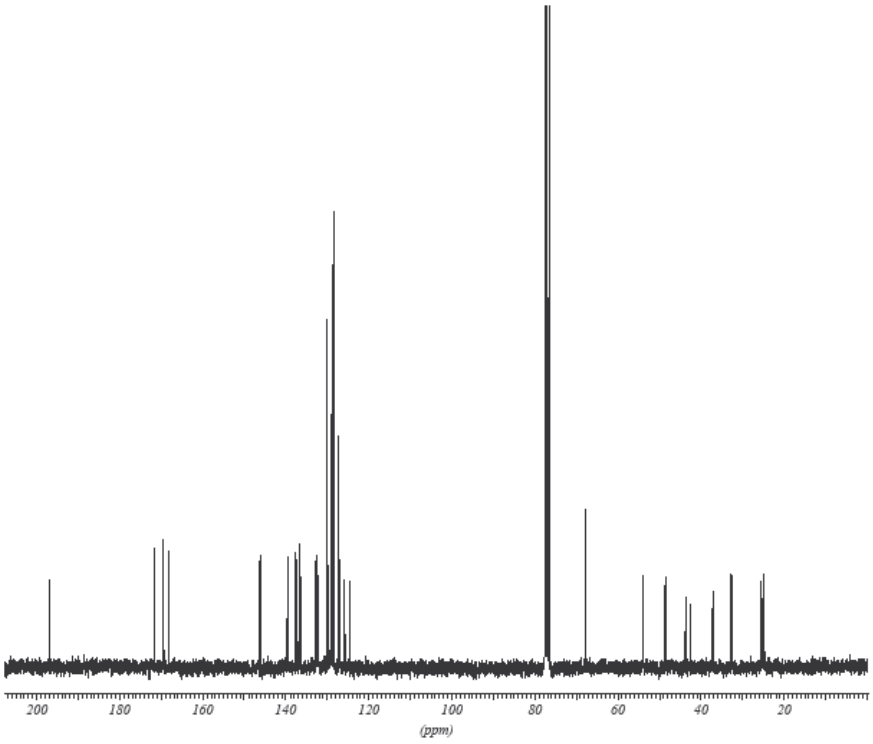


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*** Current Data Parameters ***
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EXPNO     :            11
PROCNO    :             1
*** Acquisition Parameters ***
NUCLEUS   :           off
O1        :       7546.30 Hz
SOLVENT   :          CDCl3
*** Processing Parameters ***
NC_proc   :            -6
*** 1D NMR Plot Parameters ***
Height    :         16.88 cm
Width     :         21.20 cm
XOffset   :          1.00 cm
YOffset   :          1.00 cm
Start     :        207.70 ppm
Stop      :         -0.22 ppm
Offset    :         3.85 %
SR        :         6.87 Hz
wx        :  185008720.00
wy        :   -7414036.00
wx_p      :      10000.00
wy_p      :          0.00
ppm_cm    :          9.81
Hz_cm     :        740.16
YVal_cm   :   11399452.00
xstart    :          1562
xstop     :         30150
xstart_p  :             0
xstop_p   :             0
NC_proc   :            -6
BaseInt   :    3728877495
NormInt   :         1.000
DecoFct   :         10000
Rec       :            F1
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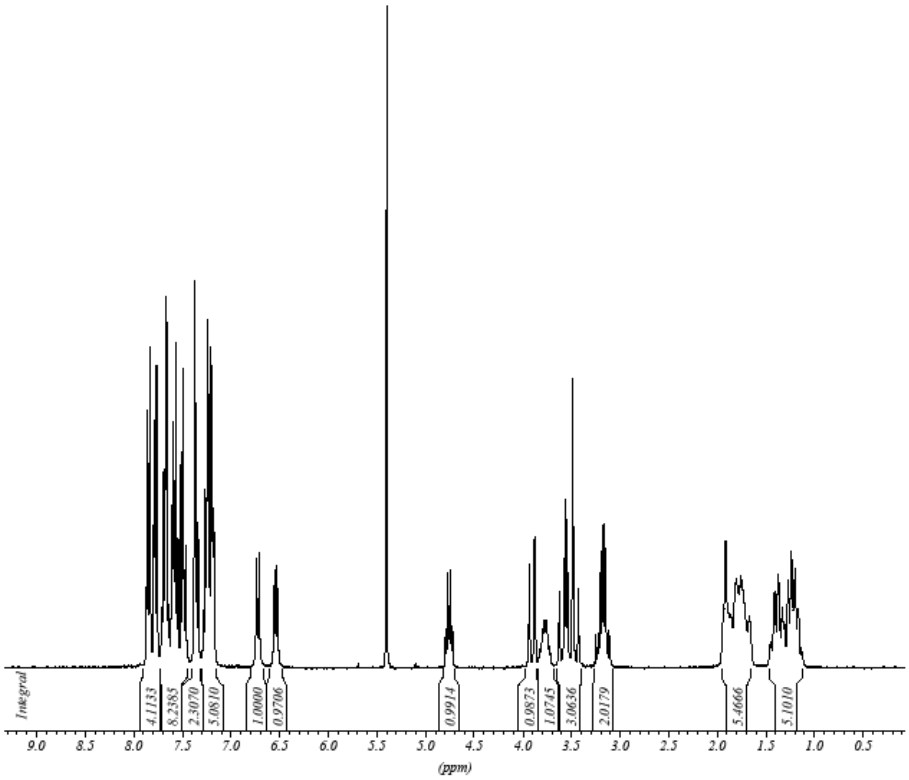
Bz-(*R*)-BpAib-(*S*)-Phe-NHChx **8b**



*** Current Data Parameters ***
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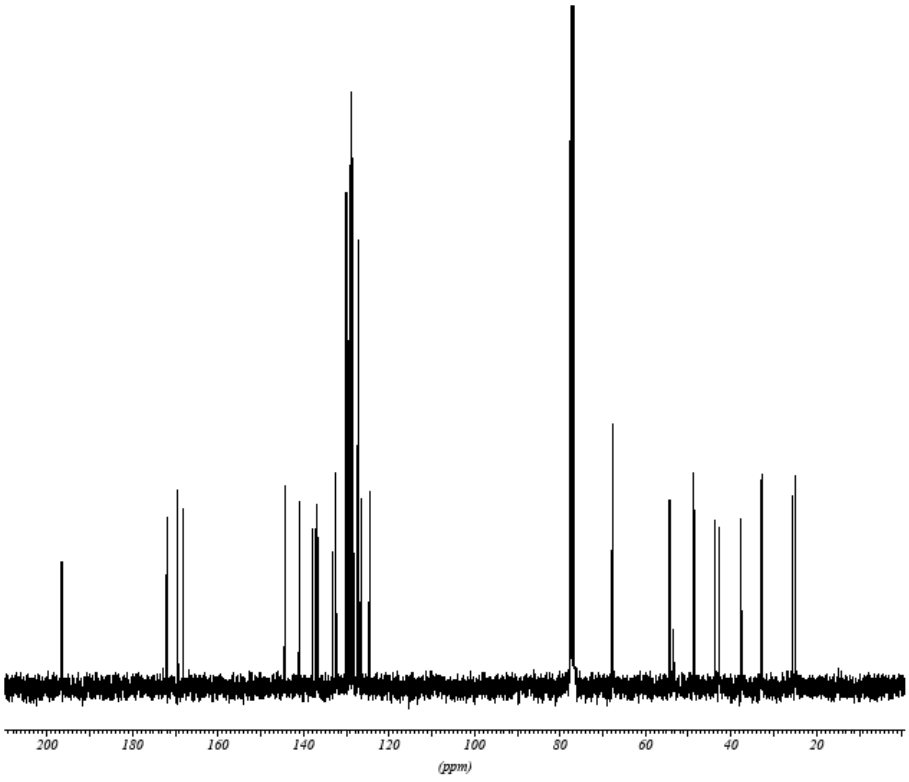
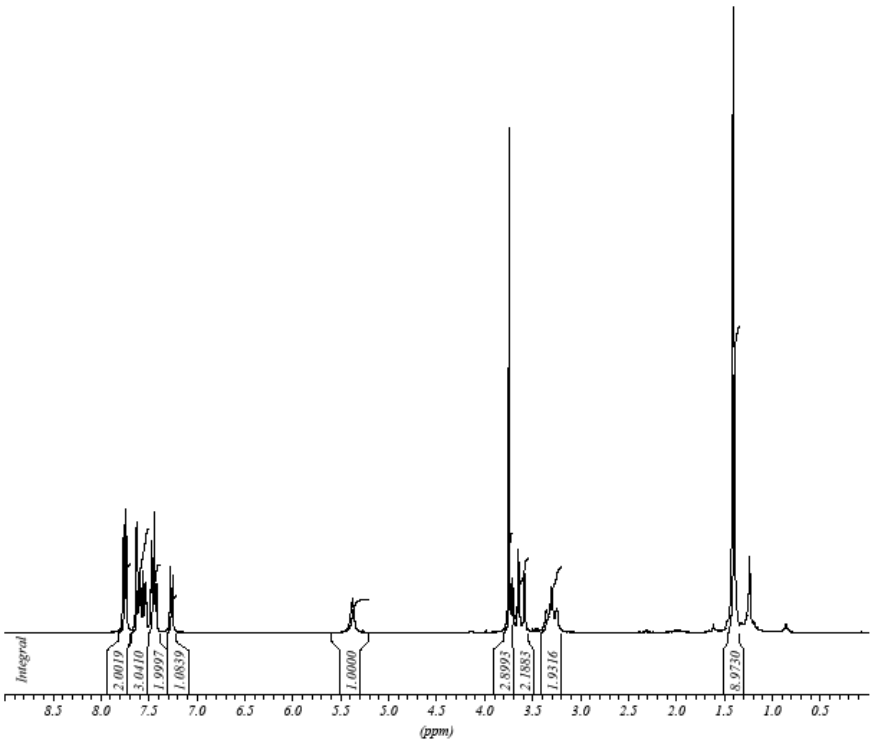
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
NUCLEUS : off
O1 : 2851.23 Hz
SOLVENT : CDCl3
*** Processing Parameters ***
NC_proc : -6
*** 1D NMR Plot Parameters ***
Height : 16.28 cm
Width : 22.10 cm
XOffset : 1.00 cm
YOffset : 1.00 cm
Start : 9.32 ppm
Stop : 0.07 ppm
Offset : 0.22 %
SR : -18.40 Hz
wx : 489872256.00
wy : -1063237.13
wx_p : 10000.00
wy_p : 0.00
ppm_cm : 0.42
Hz_cm : 125.64
YVal_cm : 30155742.00
xstart : 16755
xstop : 31167
xstart_p : 0
xstop_p : 0
NC_proc : -6
BaseInt : 4001854895
NormInt : 1.000
DecoFct : 10000
Rec : F1
MPSF : 1.0000000
AQ_time : 2.5952260 sec



*** Current Data Parameters ***
NAME : fc25k6--1
EXPNO : 11
PROCNO : 1
*** Acquisition Parameters ***
NUCLEUS : off
O1 : 7546.30 Hz
SOLVENT : CDCl3
*** Processing Parameters ***
NC_proc : 0
*** 1D NMR Plot Parameters ***
Height : 17.78 cm
Width : 22.10 cm
XOffset : 1.00 cm
YOffset : 1.00 cm
Start : 209.78 ppm
Stop : -0.70 ppm
Offset : 5.85 %
SR : 0.00 Hz
wx : 225360288.00
wy : -14010299.00
wx_p : 10000.00
wy_p : 0.00
ppm_cm : 9.52
Hz_cm : 718.76
YVal_cm : 13459538.00
xstart : 1289
xstop : 30229
xstart_p : 0
xstop_p : 0
NC_proc : 0
BaseInt : 4001854895
NormInt : 1.000
DecoFct : 10000
Rec : F1
MPSF : 1.0000000
AQ_time : 1.8219010 sec

Boc-(*S*)-BpAib-OMe **9**



*** Current Data Parameters ***
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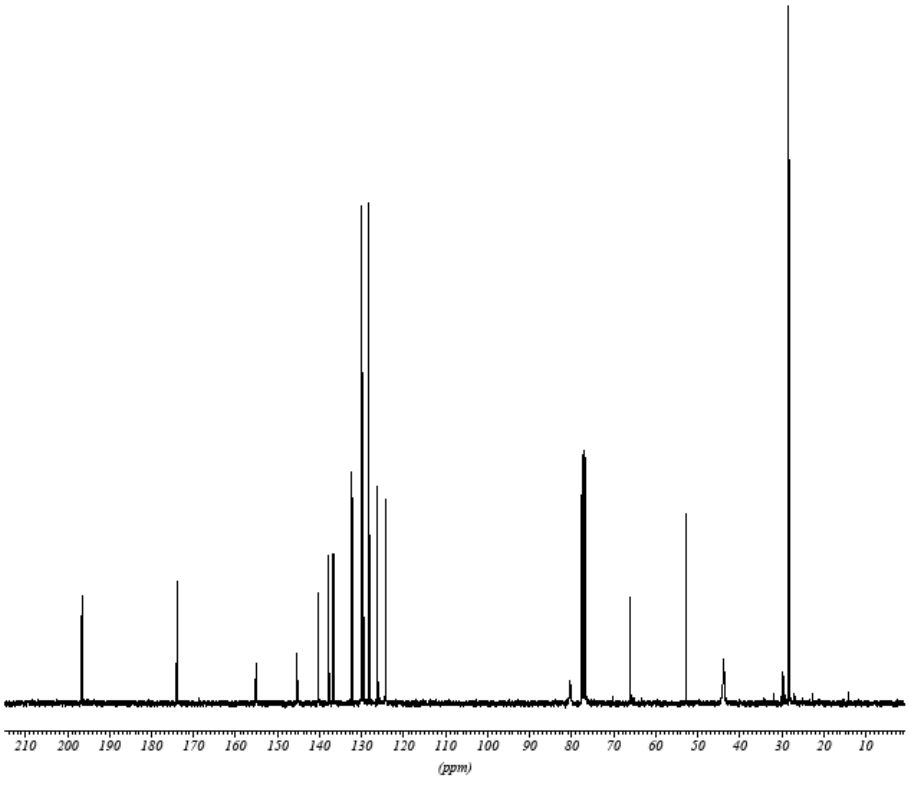
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
NUCLEUS : off
O1 : 2851.24 Hz
SOLVENT : CDCl3
*** Processing Parameters ***
NC_proc : -4
*** 1D NMR Plot Parameters ***
Height : 15.38 cm
Width : 21.20 cm
XOffset : 1.00 cm
YOffset : 1.00 cm
Start : 9.00 ppm
Stop : 0.00 ppm
Offset : 0.07 %
SR : 14.93 Hz
vay : 228746784.00
vby : -148826.78
vay_p : 10000.00
vby_p : 0.00
ppm_cm : 0.42
Hz_cm : 127.41
YVal_cm : 14882680.00
xstart : 17085
xstop : 31105
xstart_p : 0
xstop_p : 0
NC_proc : -4
BaseInt : 1055053782
NormInt : 1.000
DecoFct : 10000
Rec : F1



*** Current Data Parameters ***
NAME : fc36k539
EXPNO : 11
PROCNO : 1
*** Acquisition Parameters ***
NUCLEUS : off
O1 : 7546.30 Hz
SOLVENT : CDCl3
*** Processing Parameters ***
NC_proc : -5
*** 1D NMR Plot Parameters ***
Height : 17.78 cm
Width : 22.10 cm
XOffset : 1.00 cm
YOffset : 1.00 cm
Start : 214.89 ppm
Stop : 0.72 ppm
Offset : 3.72 %
SR : 0.00 Hz
vay : 409177344.00
vby : -15811870.00
vay_p : 10000.00
vby_p : 0.00
ppm_cm : 9.69
Hz_cm : 731.37
YVal_cm : 23902656.00
xstart : 586
xstop : 30034
xstart_p : 0
xstop_p : 0
NC_proc : -5
BaseInt : 1055053782
NormInt : 1.000
DecoFct : 10000
Rec : F1
MPSF : 1.0000000
AQ_time : 1.8219010 sec

*X-Ray diffraction data of **8a***

Single crystals of Z-(*R*)-BpAib-(*S*)-Phe-NHChx were grown by slow evaporation from a dichloromethane – methanol solution. Diffraction data were collected at T = 293(2) K with CuKα radiation (λ = 1.54178 Å) using a Philips PW 1100 diffractometer in the θ – 2θ scan mode up to θ = 55°. The crystal did not significantly diffract at higher resolution. Cell parameters were obtained by least-squares refinement of the angular settings of 48 carefully centered reflections in the 12 – 18° θ range. Three standard reflections, periodically monitored, showed an intensity decay that reached 15% at the end of data collection. Intensities were re-scaled accordingly. Intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods with the SIR 2002 program [S1]. The asymmetric unit is composed of one peptide molecule and one co-crystallized dichloromethane molecule. Refinement was carried out by full-matrix block least-squares procedures on F^2, using all data, by application of the SHELXL 97 program [S2], and allowing the positional parameters and the anisotropic displacement parameters of the non-hydrogen atoms to refine at alternate cycles. All non-hydrogen atoms were refined anisotropically. A common population parameter for the atoms of the co-crystallized dichloromethane molecule refined to the value of 0.712(7). Hydrogen atoms were calculated at idealized positions and refined using a riding model.

Formula: $C_{40}H_{41}N_3O_5 \times 0.71\ CH_2Cl_2$; formula weight: 703.2; orthorhombic, space group $P2_12_12_1$; unit cell parameters: a = 10.949(3), b = 14.354(3), c = 24.633(5) Å; V = 3871.4(15) Å^3; Z = 4; D_{calcd} = 1.207 Mg m^{-3}; crystal size: 0.50 × 0.20 × 0.10 mm^3; 3104 reflections collected, of which 3061 independent (R_{int} = 0.045); index ranges: $-1 \le h \le 11$, $0 \le k \le 15$, $0 \le l \le 26$; data / parameters: 3061/ 414; R_1 = 0.0678 [on $F \ge 4\sigma(F)$]; wR_2 = 0.2070 (on F^2, all data); goodness of fit on F^2: 1.019; Flack parameter 0.95(7); largest peak and hole in the final difference Fourier map: 0.413 and –0.222 e Å^{-3}.

Crystallographic data (including atomic coordinates, bond distances, bond angles, torsion angles, intra- and intermolecular H-bonds parameters) have been deposited at The Cambridge Crystallographic Data Centre with deposition number CCDC-746110, and may be found in the Supporting Information as a CIF file.

Supporting references

[S1] Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2003**, *36*, 1103.

[S2] Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122.

Mass spectrum of the mixture of the two diastereomeric products (**11A** and **11B**) isolated after the photoreaction.