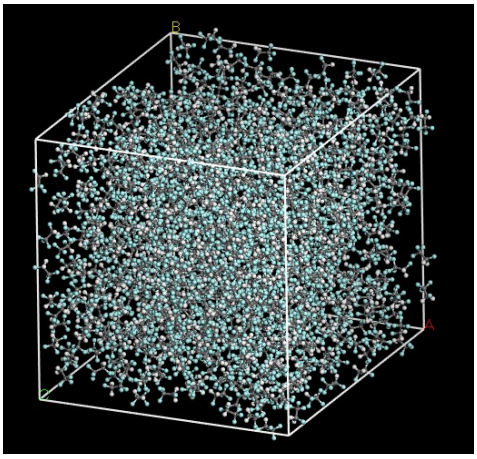
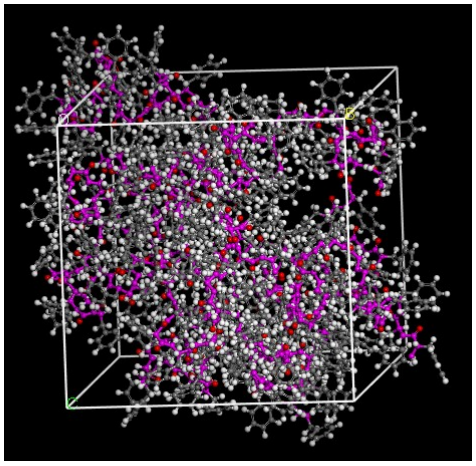
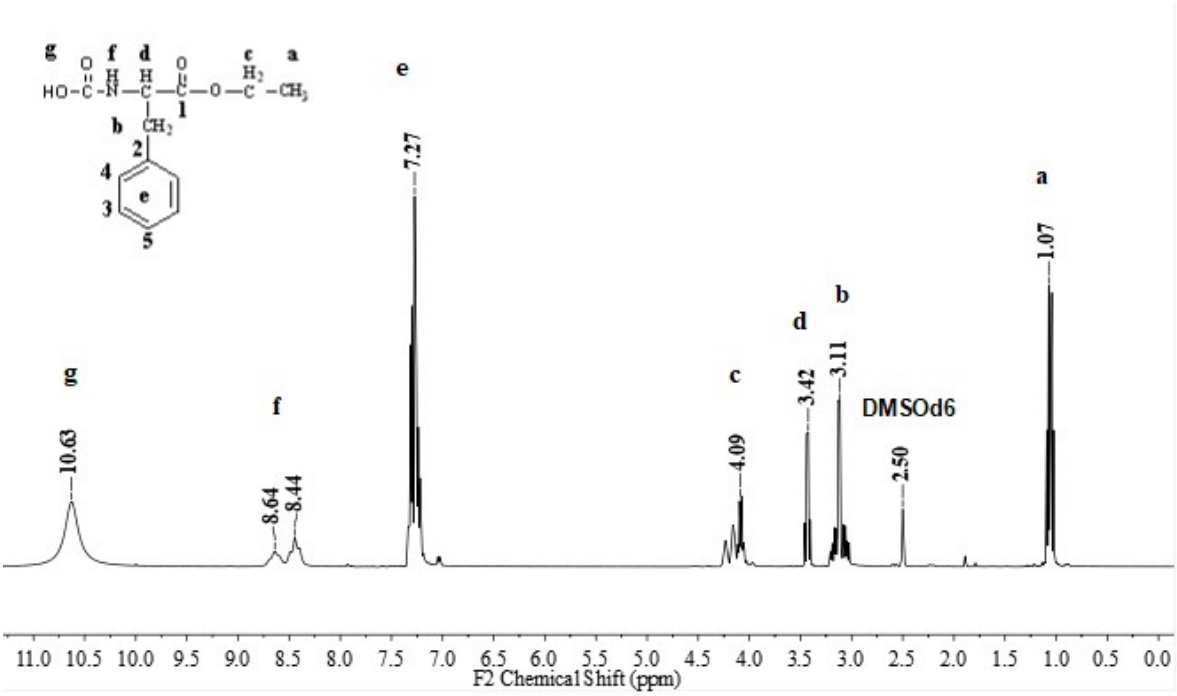
Supplemental information 1: Molecular Modelling Typical box for a) liquid 1,1,1,2-tetrafluoroethane and b) poly(L-PheOEt).



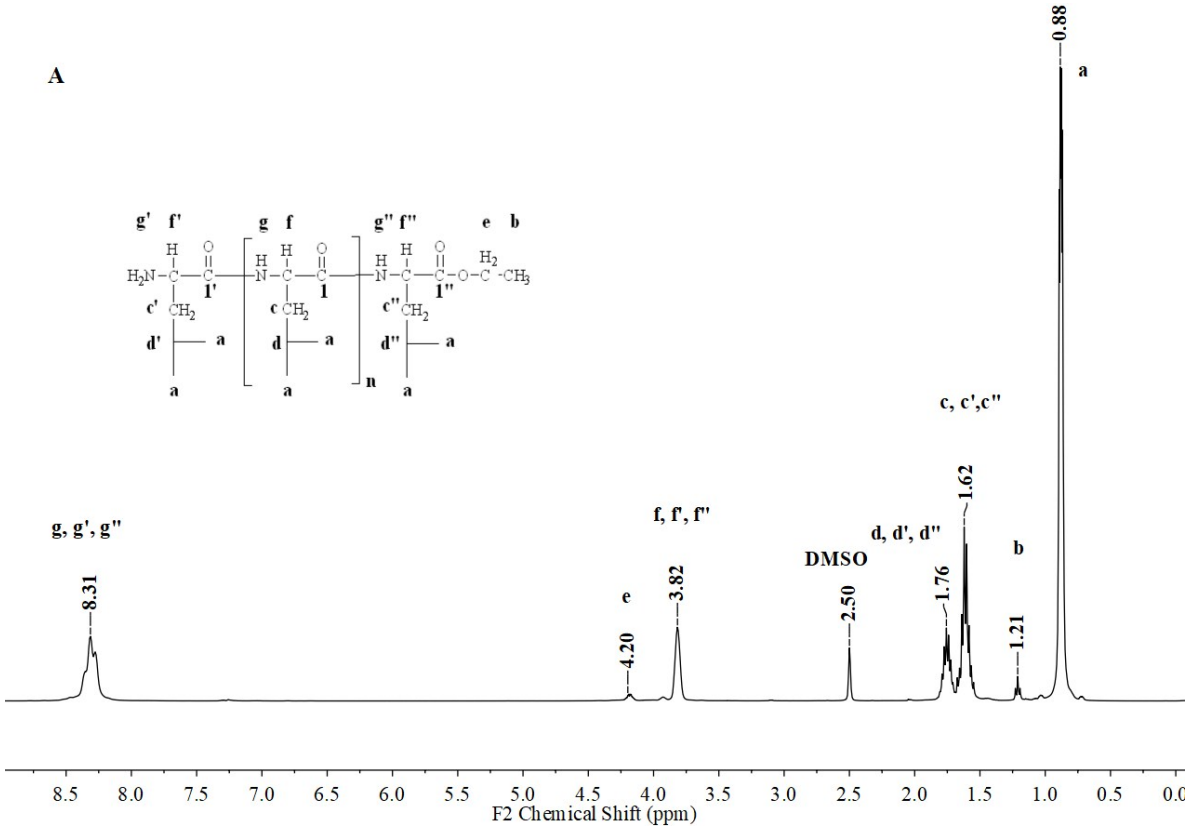


Supplemental information 2: representative 1H NMR spectrum of the carbamate product formed when attempted polymerization reaction in $scCO_2$

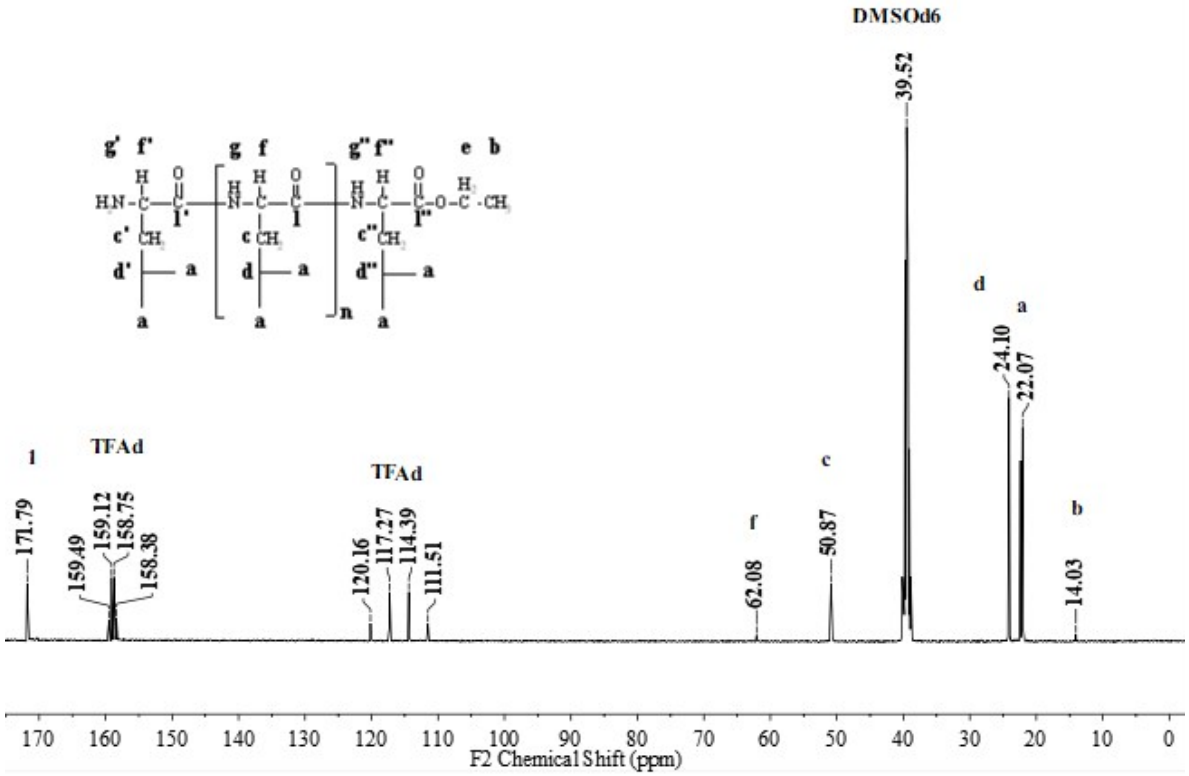


Supplemental information 3: NMR analyses of the products

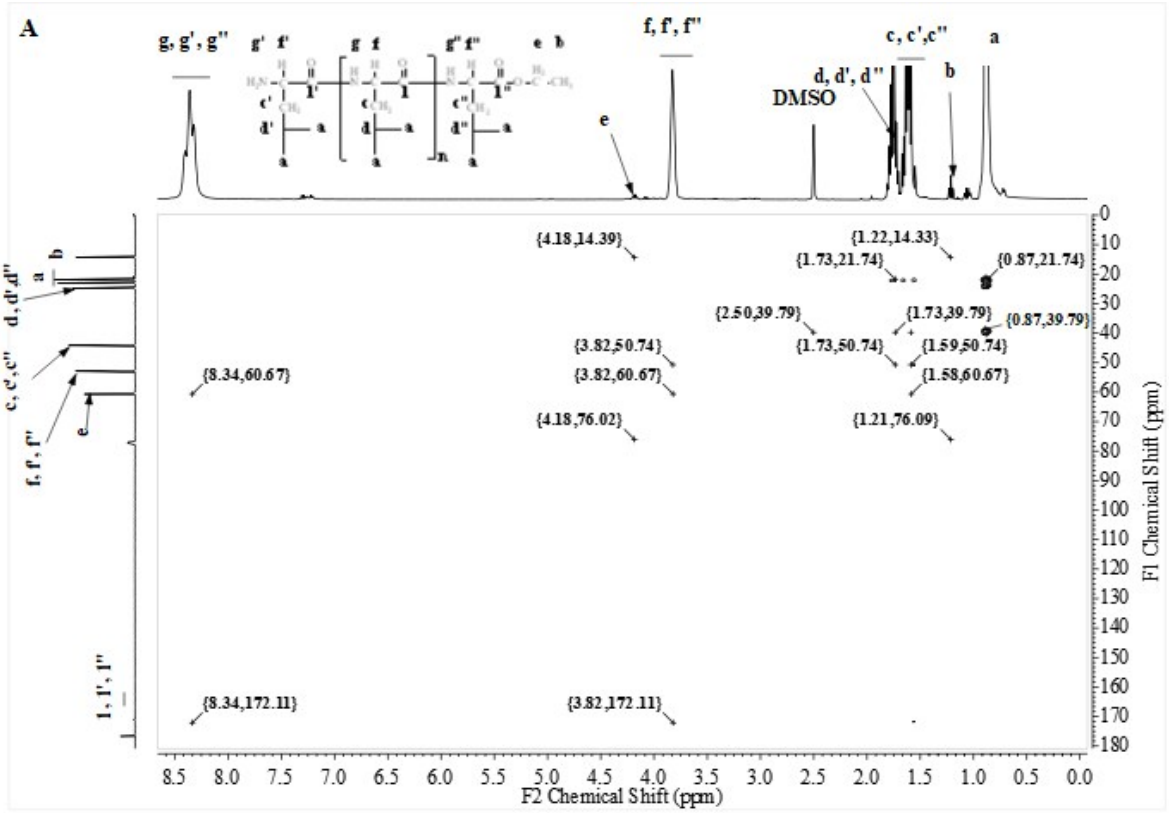
Representative 1H NMR (A) and 13C NMR (B) spectra protease Subtilisin Carlsberg-mediated poly(L-LeuOEt) in liquid 1,1,1,2-tetrafluoroethane (40 °C, 25 bar)



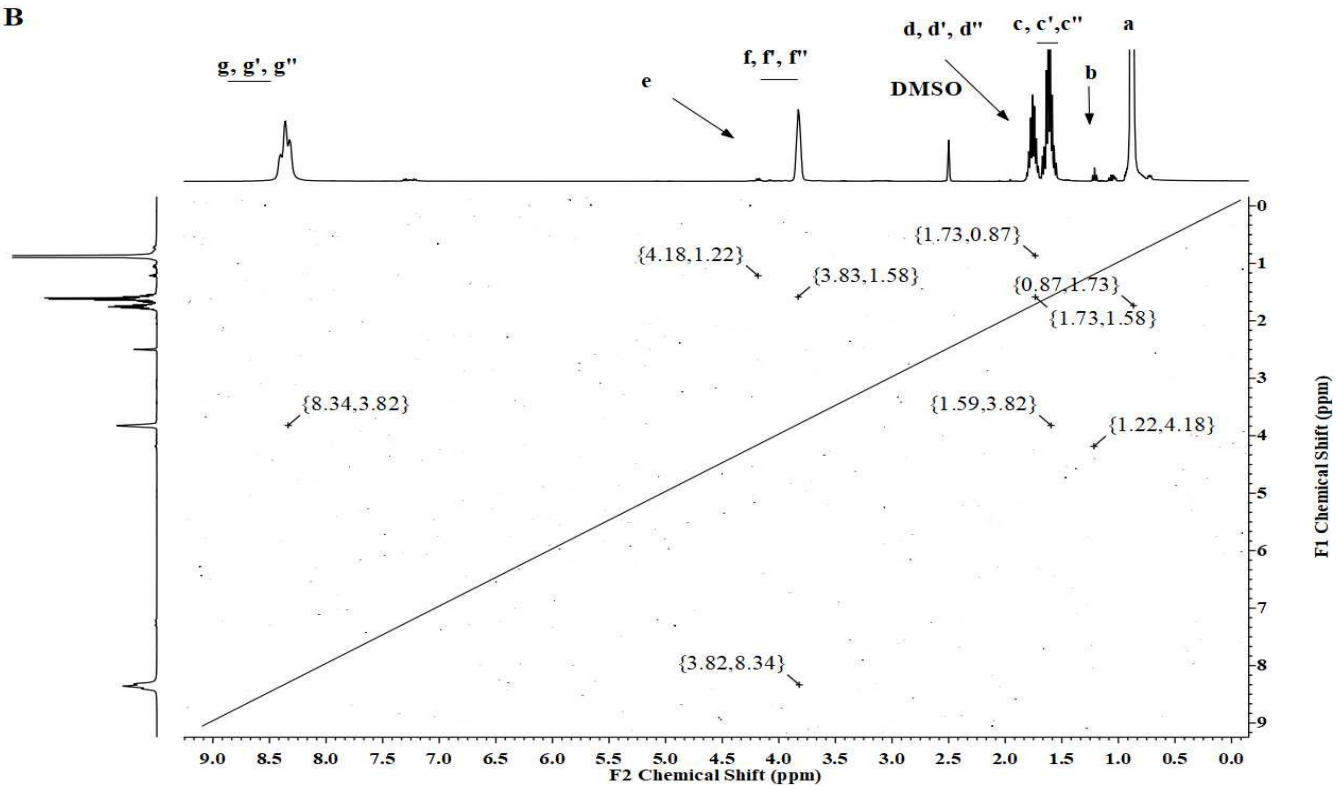
B


DMSOd6
39.52
g' f' g f g" f" e b
c' c c"
d' d d"
a a a a a a
n
d
a
24.10
22.07
1
TFAd
TFAd
c
b
171.79
159.49
159.12
158.75
158.38
120.16
117.27
114.39
111.51
f
62.08
50.87
14.03
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
F2 Chemical Shift (ppm)

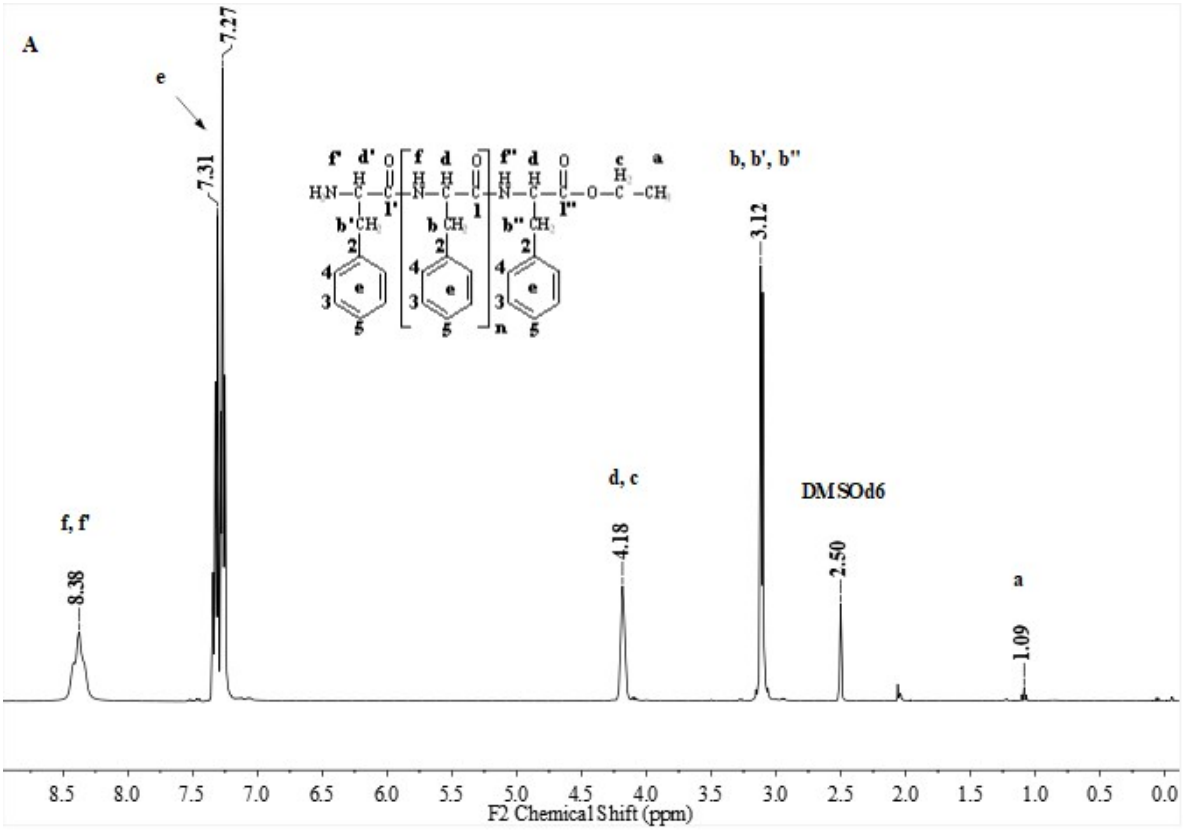
Representative HMBCAD (A) and COSY (B) spectra for protease Subtilisin Carlsberg-mediated Poly(L-LeuOEt) in liquid 1,1,1,2-tetrafluoroethane (40 °C, 25 bar)



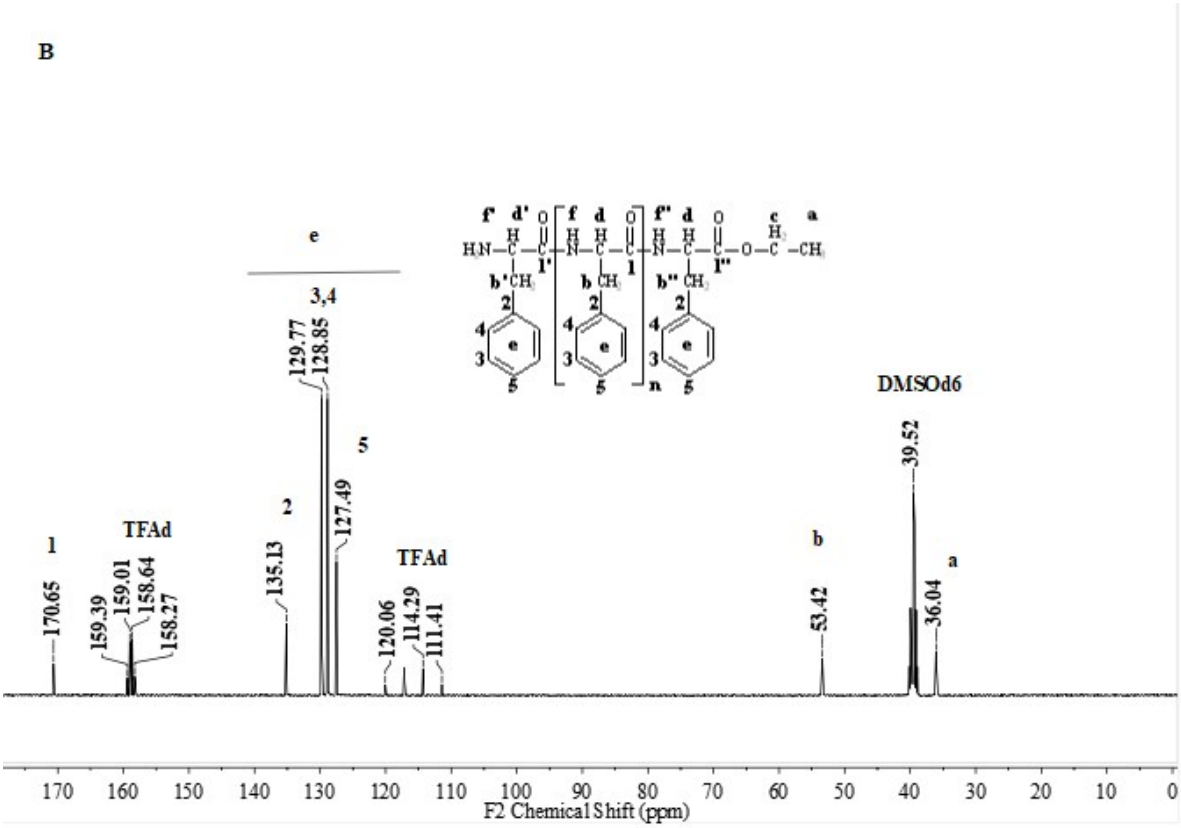
B


g, g', g''
e
f, f', f''
d, d', d''
DMSO
c, c',c''
b
a
{1.73,0.87}
{4.18,1.22}
{3.83,1.58}
{0.87,1.73}
{1.73,1.58}
{8.34,3.82}
{1.59,3.82}
{1.22,4.18}
{3.82,8.34}
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

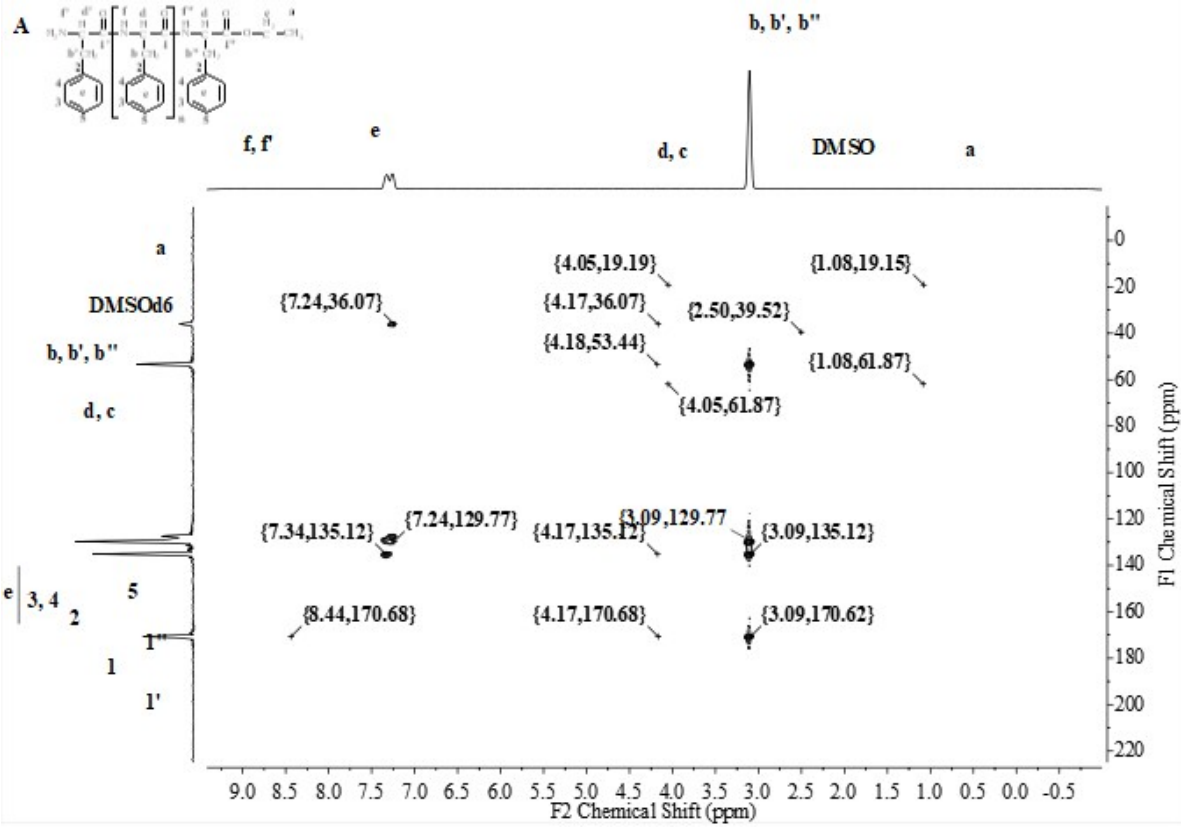
Representative 1H NMR and 13C NMR spectra for protease Subtilisin Carlsberg-mediated Poly(L-PheOEt) in liquid 1,1,1,2-tetrafluoroethane (40 °C, 25 bar)

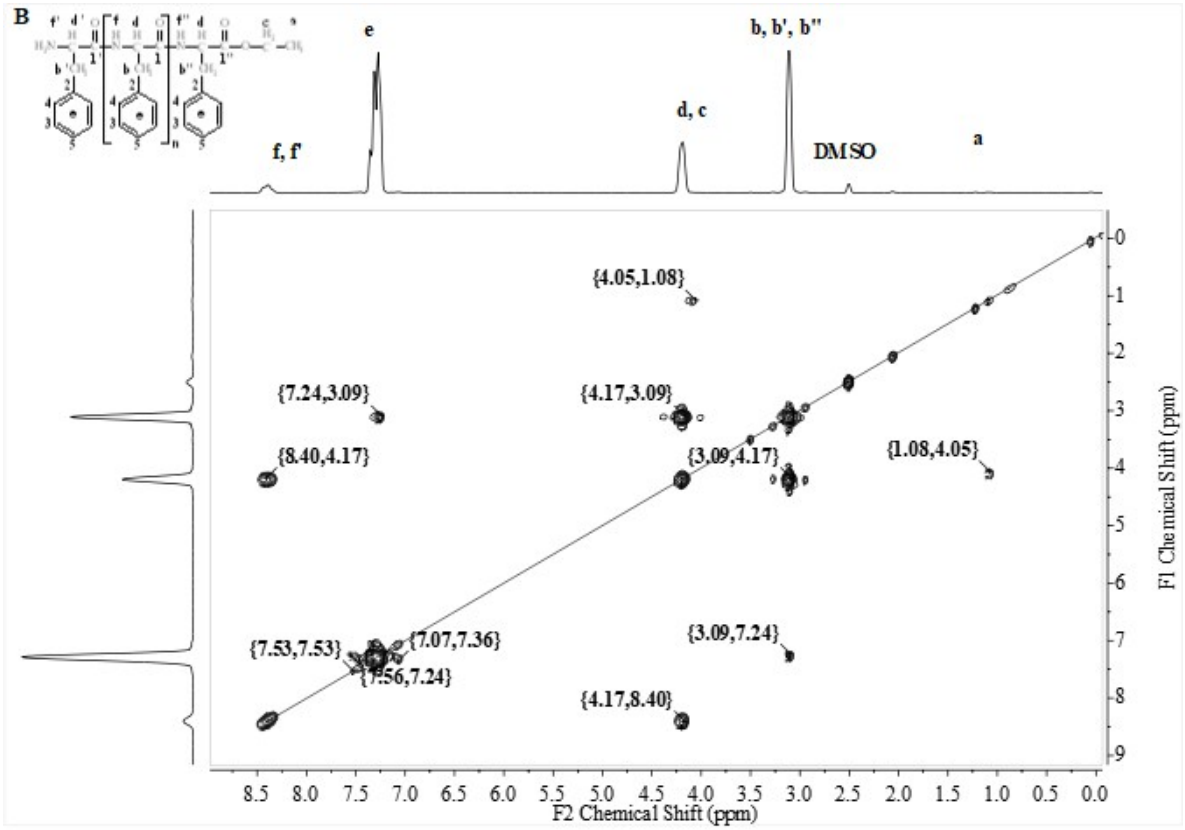


B

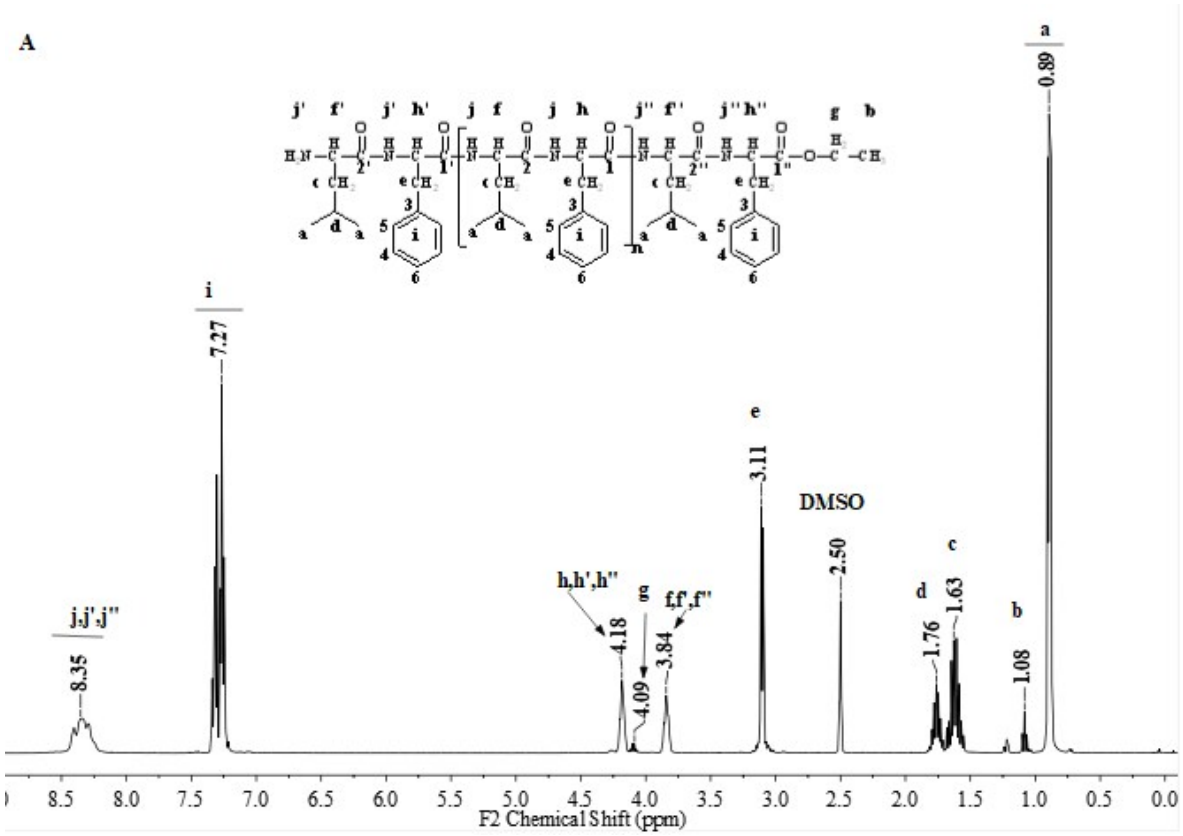

e
3,4
129.77
128.85
5
127.49
2
135.13
TFAd
1
170.65
159.39
159.01
158.64
158.27
TFAd
120.06
114.29
111.41
b
53.42
DMSOd6
39.52
a
36.04
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
F2 Chemical Shift (ppm)

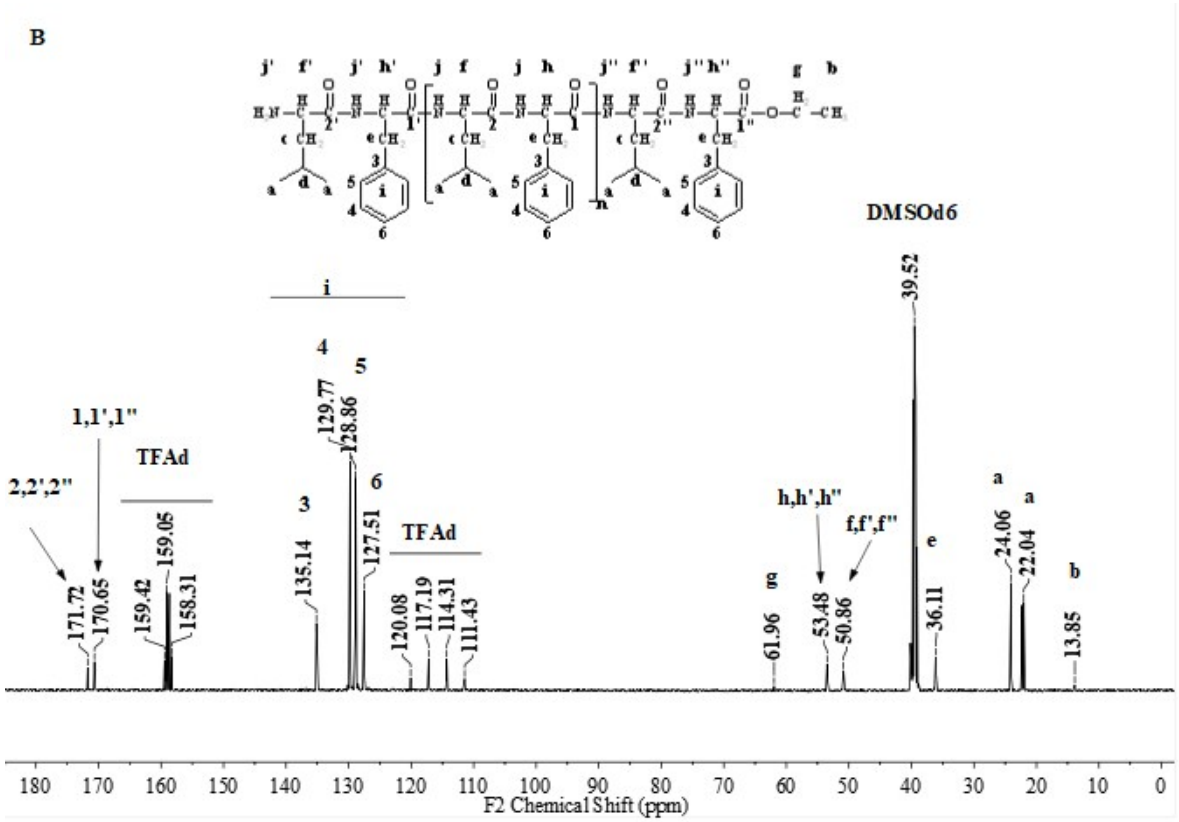
Representative HMBCAD (A) and COSY (B) spectra for protease Subtilisin Carlsberg-mediated Poly(L-PheOEt) in liquid 1,1,1,2-tetrafluoroethane (40 °C, 25 bar)



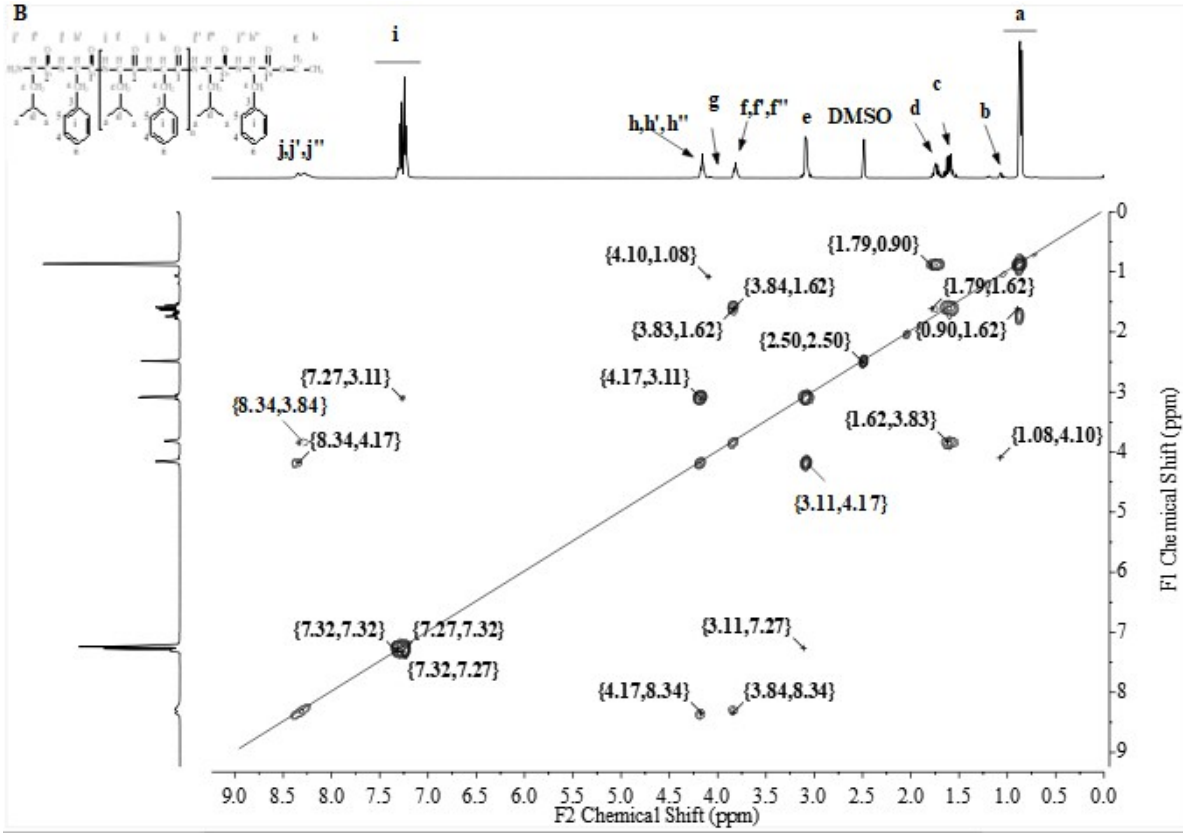

B
e
b, b', b''
d, c
f, f'
DMSO
a
{4.05,1.08}
{7.24,3.09}
{4.17,3.09}
{8.40,4.17}
{3.09,4.17}
{1.08,4.05}
{7.53,7.53}
{7.07,7.36}
{7.56,7.24}
{3.09,7.24}
{4.17,8.40}
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

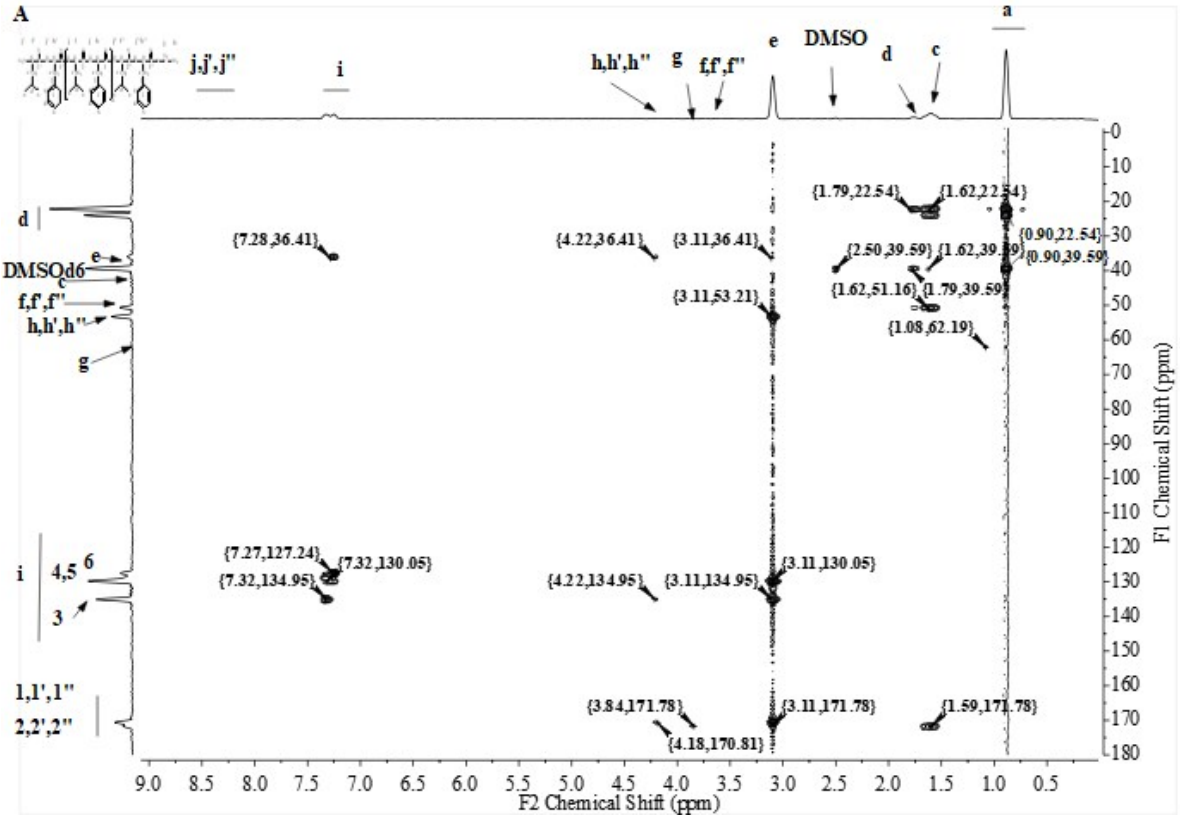
Representative NMR spectra for protease of Subtilisin Carlsberg-mediated Poly(L-LeuOEt-co-L-PheOEt) in liquid 1,1,1,2-tetrafluoroethane (40 °C, 25 bar)



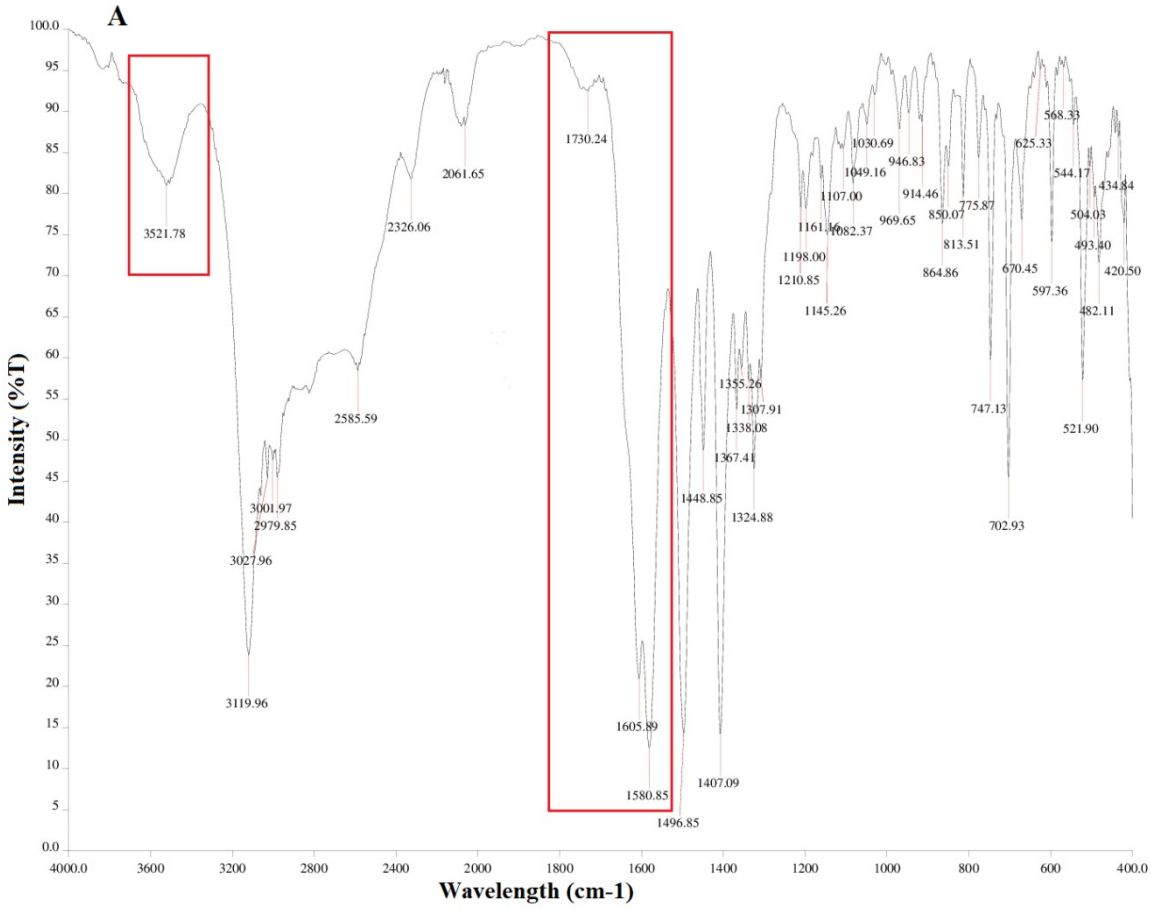

B
DMSOd6
i
4
5
129.77
128.86
1,1',1"
TFAd
2,2',2"
3
6
159.05
127.51
TFAd
159.42
158.31
135.14
171.72
170.65
120.08
117.19
114.31
111.43
h,h',h"
f,f',f"
g
a
a
e
39.52
24.06
22.04
b
61.96
53.48
50.86
36.11
13.85
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
F2 Chemical Shift (ppm)

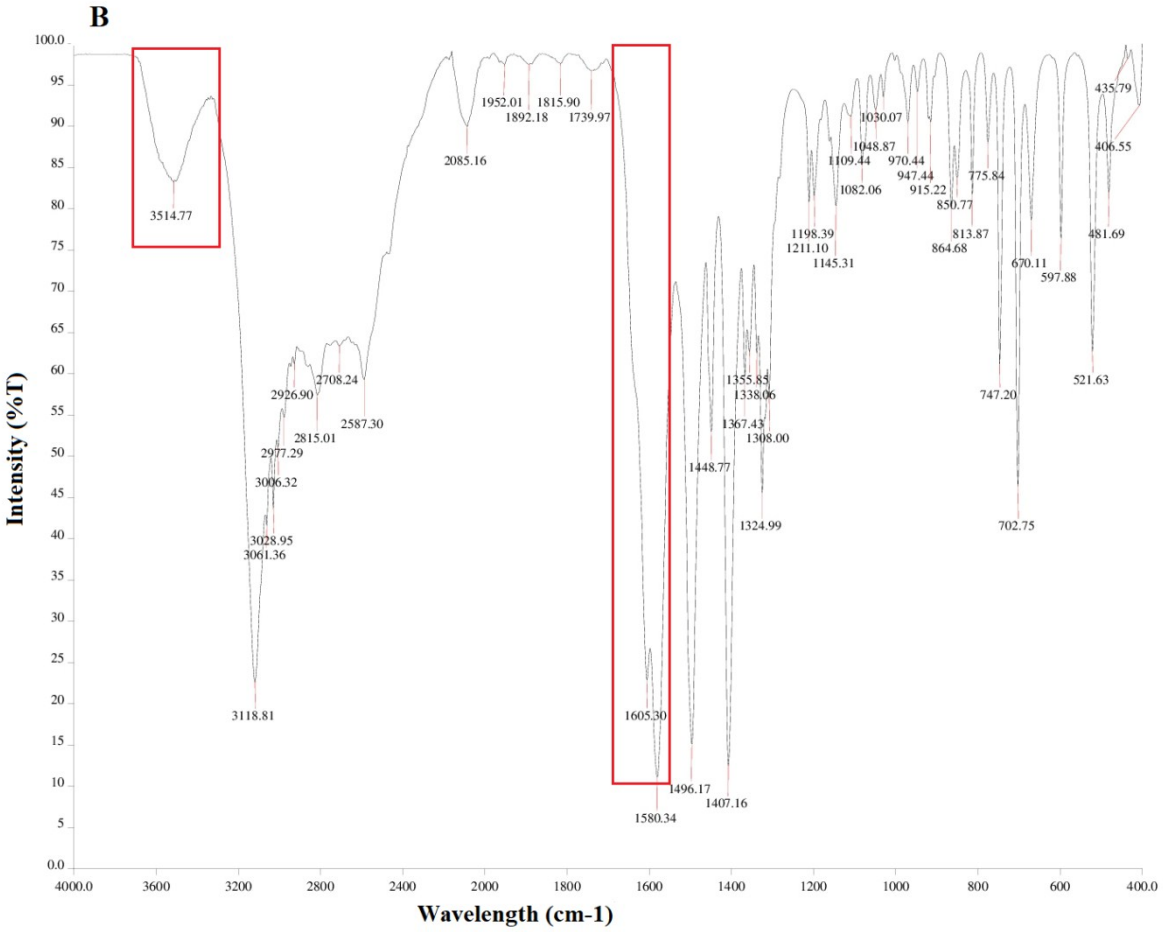
Representative HMBCAD (A) and COSY (B) spectra for protease Subtilisin Carlsberg-mediated Poly(L-PheOEt-co-L-LeuOEt) in liquid 1,1,1,2-tetrafluoroethane (40 °C, 25 bar)

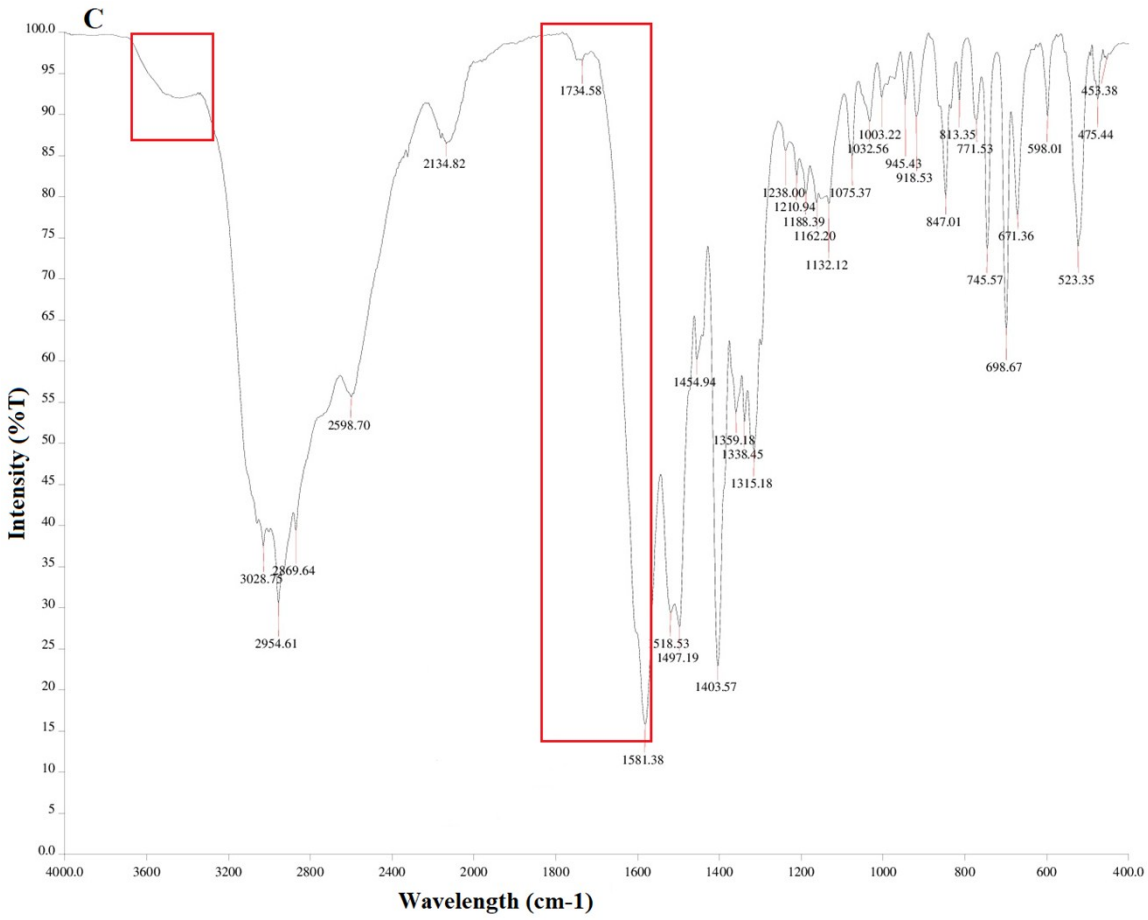



A
a
DMSO
d
c
e
h,h',h''
g
f,f',f''
i
j,j',j''
DMSOd6
{7.28,36.41}
{4.22,36.41}
{3.11,36.41}
{1.79,22.54}
{1.62,22.54}
{0.90,22.54}
{2.50,39.59}
{1.62,39.59}
{0.90,39.59}
{1.62,51.16}
{1.79,39.59}
{3.11,53.21}
{1.08,62.19}
{7.27,127.24}
{7.32,130.05}
{7.32,134.95}
{4.22,134.95}
{3.11,134.95}
{3.11,130.05}
{3.84,171.78}
{3.11,171.78}
{1.59,171.78}
{4.18,170.81}
4,5
6
3
1,1',1''
2,2',2''
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

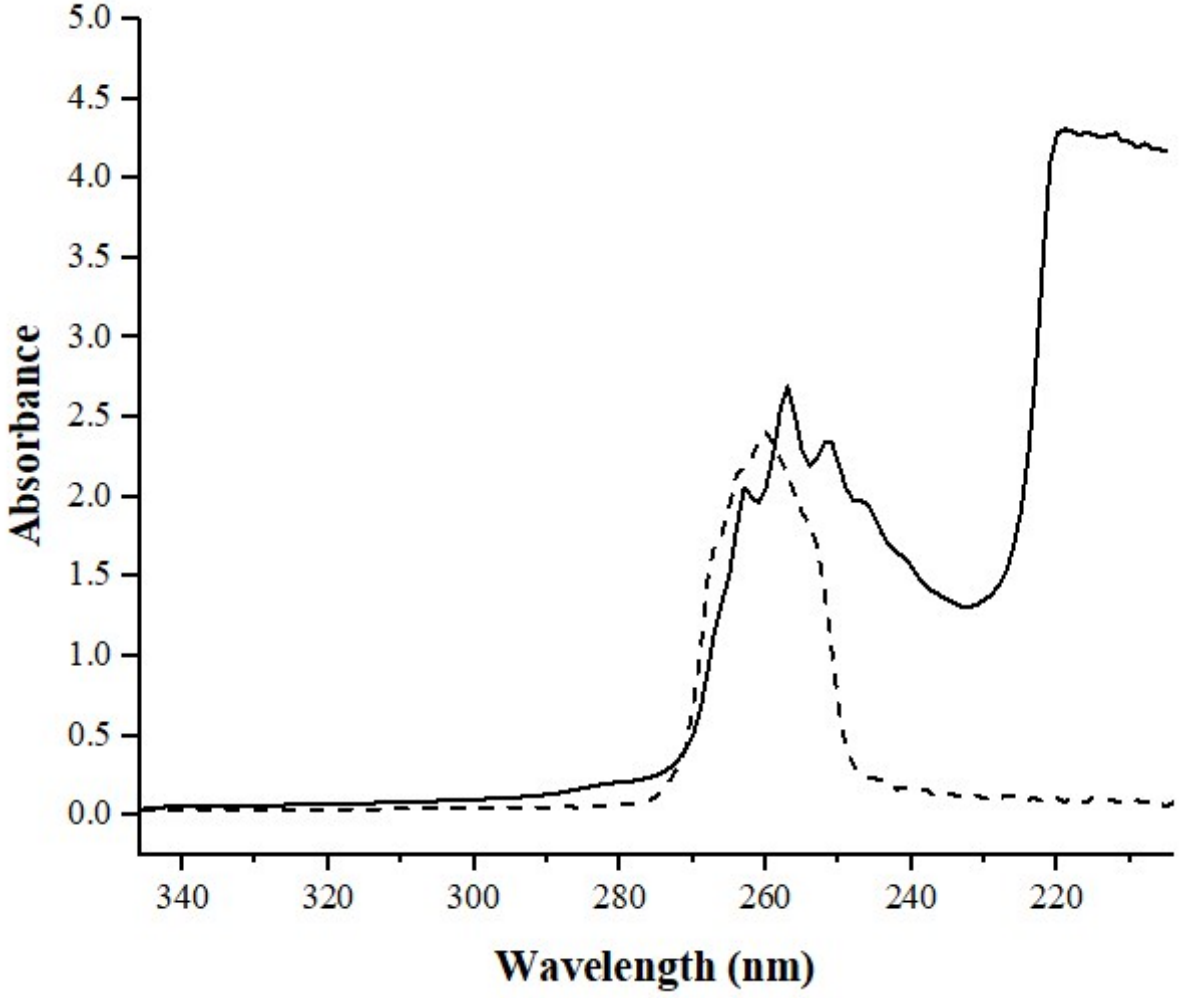
Supplemental information 4. Representative ATR-FTIR spectra of each synthesized compounds. Poly(L-LueOEt) (A); Poly(L-PheOEt) (B) and Poly(L-LeuOEt-co-PheOEt) (C)




B
Intensity (%T)
Wavelength (cm-1)
100.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
3514.77
3118.81
3061.36
3028.95
3006.32
2977.29
2926.90
2815.01
2708.24
2587.30
2085.16
1952.01
1892.18
1815.90
1739.97
1605.30
1580.34
1496.17
1448.77
1407.16
1367.43
1355.85
1338.06
1324.99
1308.00
1211.10
1198.39
1145.31
1109.44
1082.06
1048.87
1030.07
970.44
947.44
915.22
864.68
850.77
813.87
775.84
747.20
702.75
670.11
597.88
521.63
481.69
435.79
406.55

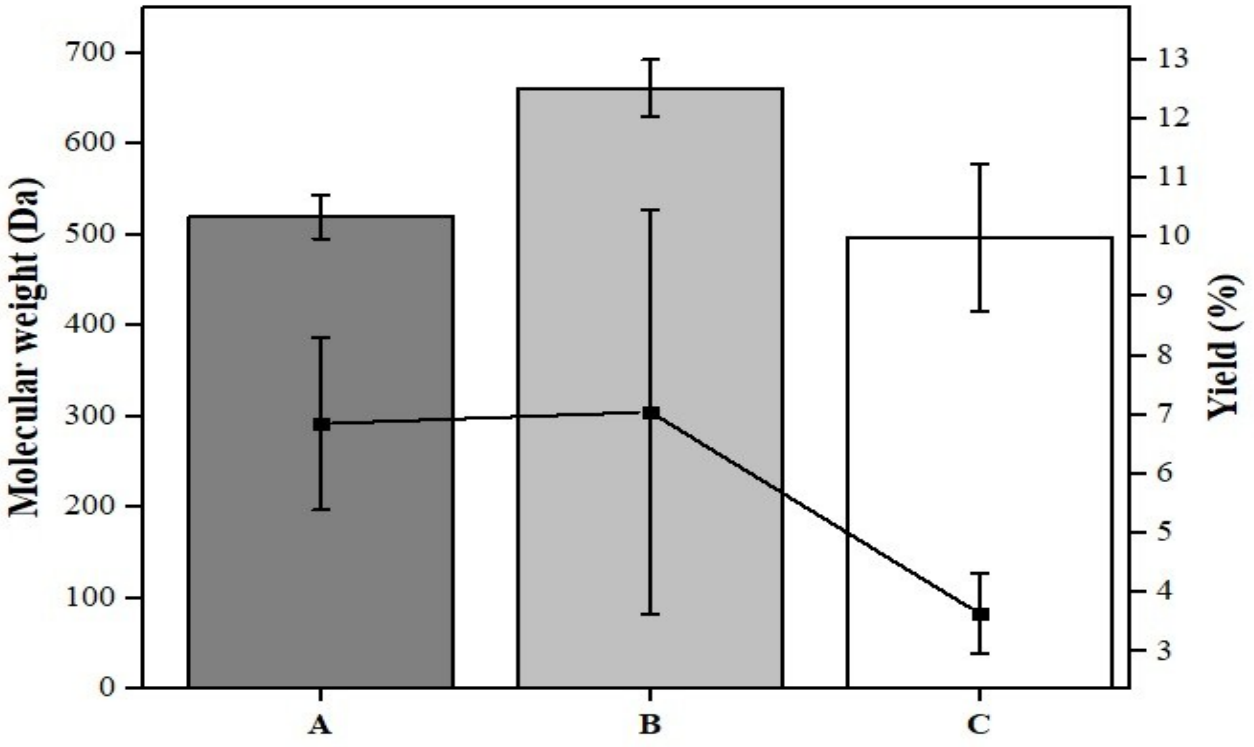

C
Intensity (%T)
Wavelength (cm-1)
100.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.0
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
3028.75
2954.61
2869.64
2598.70
2134.82
1734.58
1581.38
1497.19
1454.94
1403.57
1359.18
1338.45
1315.18
1238.00
1210.94
1188.39
1162.20
1132.12
1075.37
1032.56
1003.22
945.43
918.53
847.01
813.35
771.53
745.57
698.67
671.36
598.01
523.35
518.53
475.44
453.38

Supplemental information 5. UV spectra for poly(L-PheOEt) in solid line and L-PheOEt in dash line.

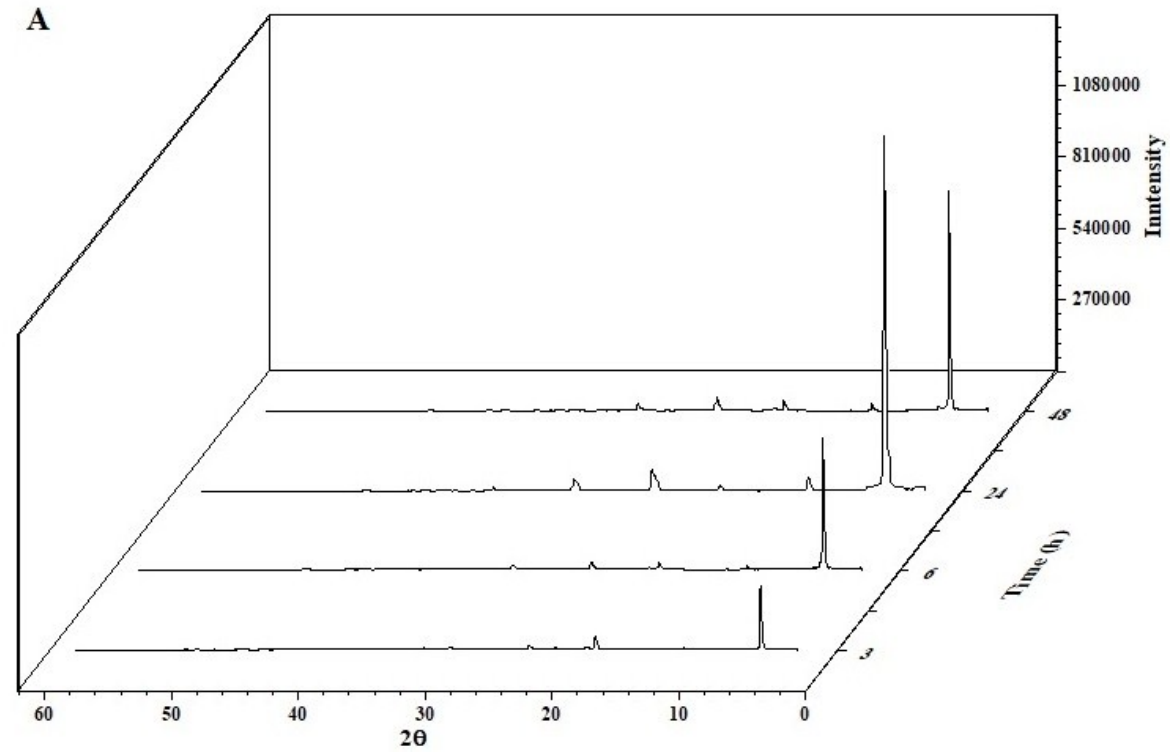


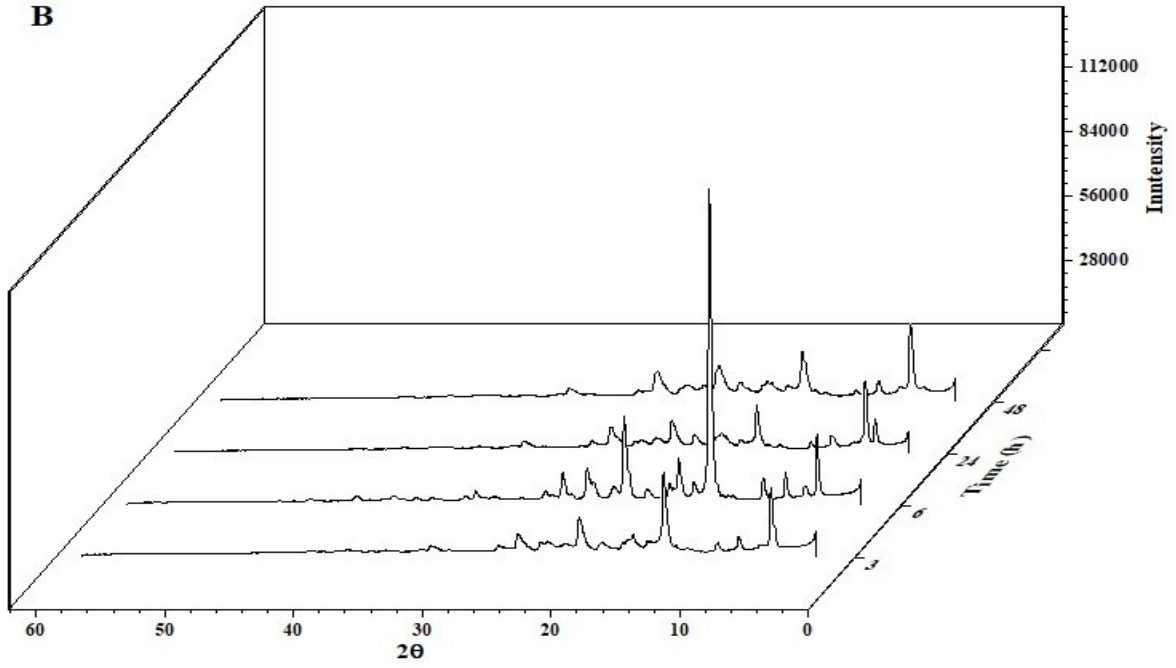
Supplemental information 6. Graphical representation of the results of control polymerization reactions without enzyme

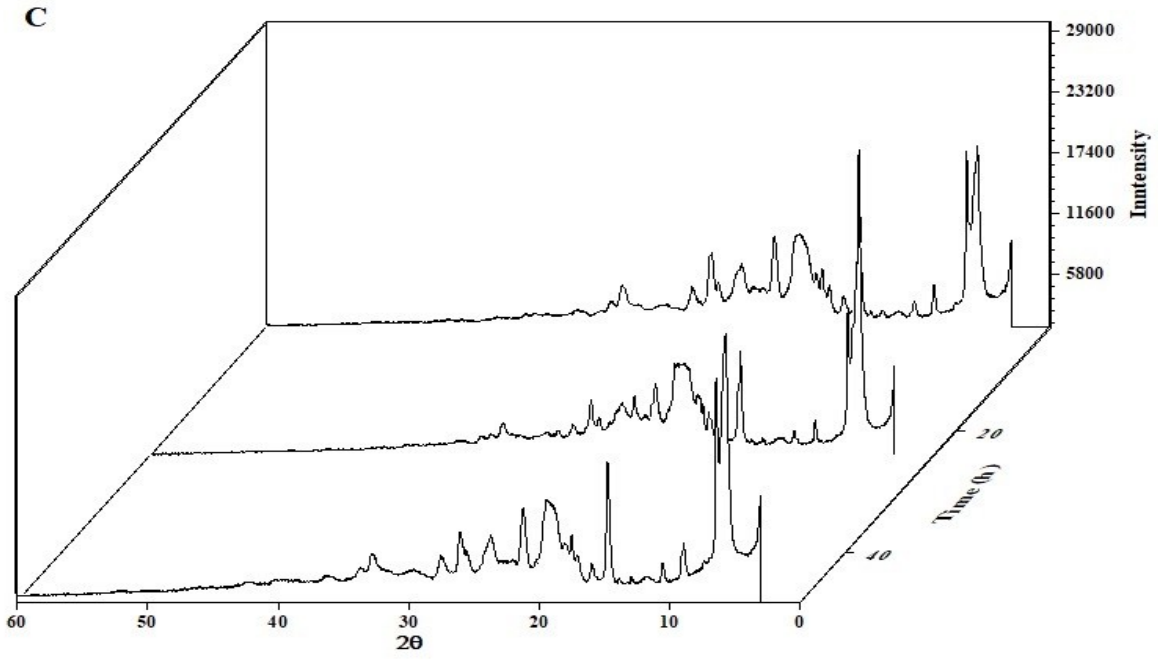
Bars: average molar mass by 1H NMR (Da) of poly(L-LeuOEt) (A); poly(L-PheOEt) (B), poly(L-LeuOEt-co-L-PheOEt) (C) products in reactions carried out in liquid 1,1,1,2-tetrafluoroethane (40 °C and 25 bar) Line: average yield of weight of the polymers (%). Error bars represents the standard deviation of 3 replicates.



Supplemental information 7. PXRD diffractograms for the poly(L-PheOEt) (A), poly(L-LeuOEt) (B), and poly(L-LeuOEt-co-L-PheOEt) (C) at different reaction times (h).






C
29000
23200
17400
11600
5800
Intensity
20
Time (h)
10
60
50
40
30
20
10
0
2θ