Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Nucleophilic thiol-Michael chemistry and hyperbranched (co)polymers: synthesis and ring-opening metathesis (co)polymerization of novel difunctional *exo*-7-oxanorbornenes with *in situ* inimer formation

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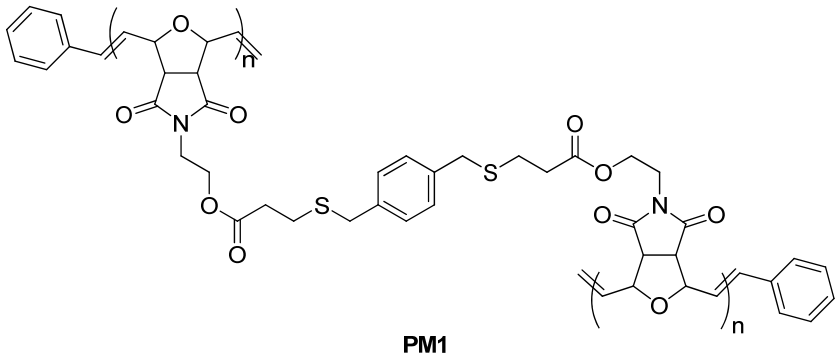
1. Experimental Procedure and Characterization of Compounds and polymers

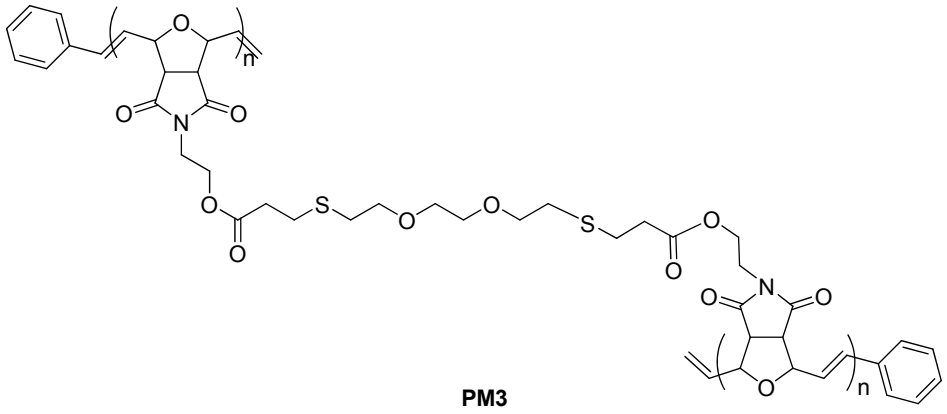
Real-time ^{1}H NMR monitoring of thiol-Michael adduct ROMP kinetics



PM1

Homopolymerization of M1

Using **M1** (32.9 mg, 0.047 mmol) and $RuCl_2(PCy_3)_2CHPh$ (2.9 mg, 0.0035 mmol for a targeted molecular weight of 10,000). **PM1**: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.69-1.75 (m, 4H), 2.43-2.68 (m, 4H), 3.33-3.76 (m, 12H), 4.31-5.05 (m, 8H), 5.84-6.12 (m, 4H), 7.28-7.33 (m, 4H). M_n (NMR) =10,956; M_n (DMAC GPC) = 23,634; M_w = 33,166, PDI = 1.40; c/t ratio =26.5/73.5.

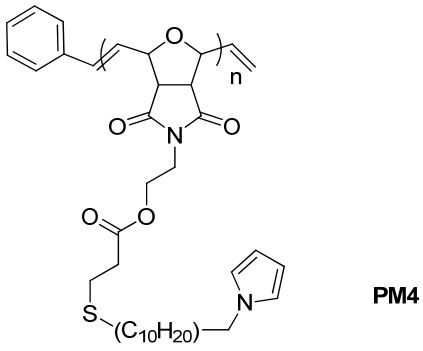


PM3

Homopolymerization of M3

Using **M3** (28.8 mg, 0.041 mmol) and $RuCl_2(PCy_3)_2CHPh$ (2.7 mg, 0.0032 mmol for a targeted molecular weight of 10,000). **PM3**: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.63-1.93 (m, 4H), 2.60-2.83 (m, 12H), 3.39-3.80 (m, 12H), 4.26-5.04 (m, 8H), 5.81-6.13 (m, 4H). M_n (NMR) = 6329; M_n (DMAC GPC) = 17,316;

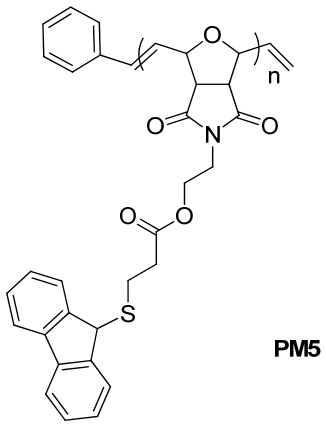
M_w = 26,126, PDI = 1.50; c/t ratio = 30.0/70.0.



PM4

Homopolymerization of M4

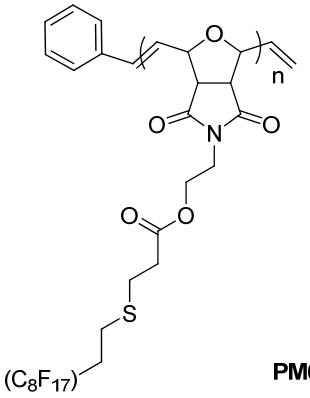
Using **M4** (12.9 mg, 0.025 mmol) and $RuCl_2(PCy_3)_2CHPh$ (1.1 mg, 0.0013 mmol for a targeted molecular weight of 10,000). **PM4**: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.28-2.06 (m, 20H), 2.51-2.74 (m, 5H), 3.01-3.37 (m, 5H), 3.79-3.90 (m, 3H), 4.21-5.23 (m, 3H), 5.85-6.12 (m, 2H), 6.35-6.82 (m, 1H), 7.19-7.51 (m, 1H). M_n (NMR) = 17,106; M_n (DMAC GPC) = 10,045; M_w = 13,705, PDI = 1.36; c/t ratio = 33.9/66.1.



PM5

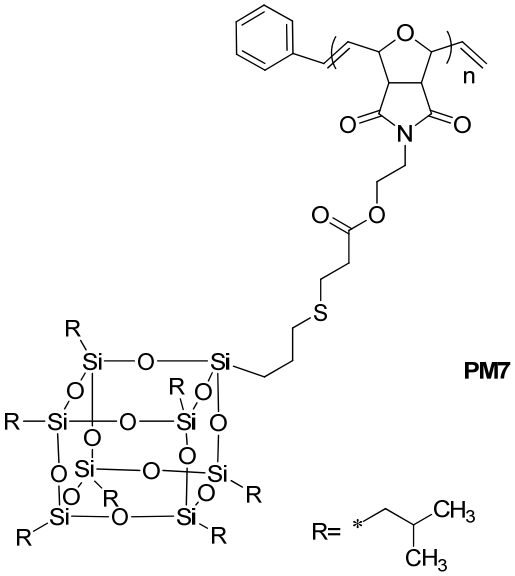
Homopolymerization of M5

Using **M5** (11.5 mg, 0.025 mmol) and $RuCl_2(PCy_3)_2CHPh$ (1.0 mg, 0.0012 mmol for a targeted molecular weight of 10,000). **PM5**: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.68-2.27 (m, 6H), 3.23-3.40 (m, 2H), 4.08-5.08 (m, 5H), 5.77-6.12 (m, 2H), 7.34-7.78 (m, 8H). M_n (NMR) = 9555; M_n (DMAC GPC) = 16,128; M_w = 25,844, PDI = 1.60; c/t ratio = 27.8/72.2.



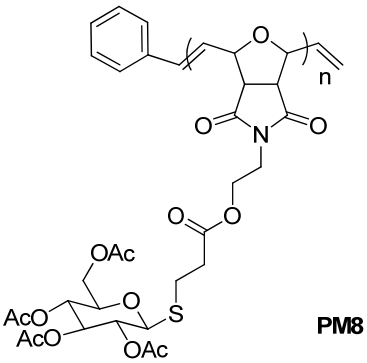
PM6

See our previous report[1].



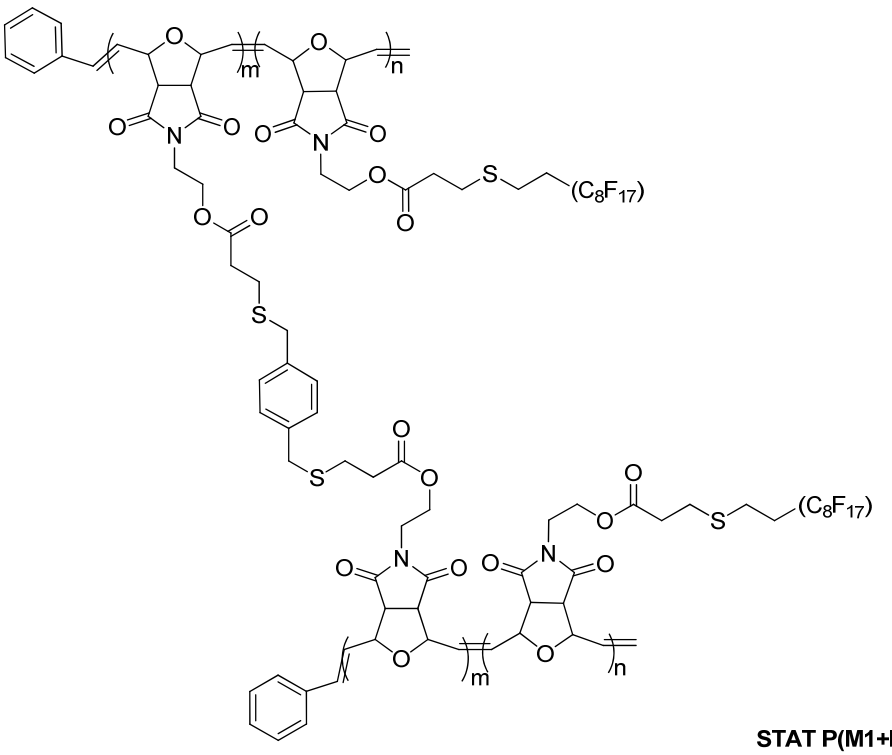
PM7

See our previous report[1].



PM8

See our previous report[1].



STAT P(M1+M6)

Copolymerization of M1/M6 (25:75)

Using **M1** (8.7 mg, 0.0125 mmol), **M6** (27.9 mg, 0.0375 mmol) and $RuCl_2(PCy_3)_2CHPh$ (3.1 mg, 0.0037 mmol for a targeted molecular weight of 10,000).

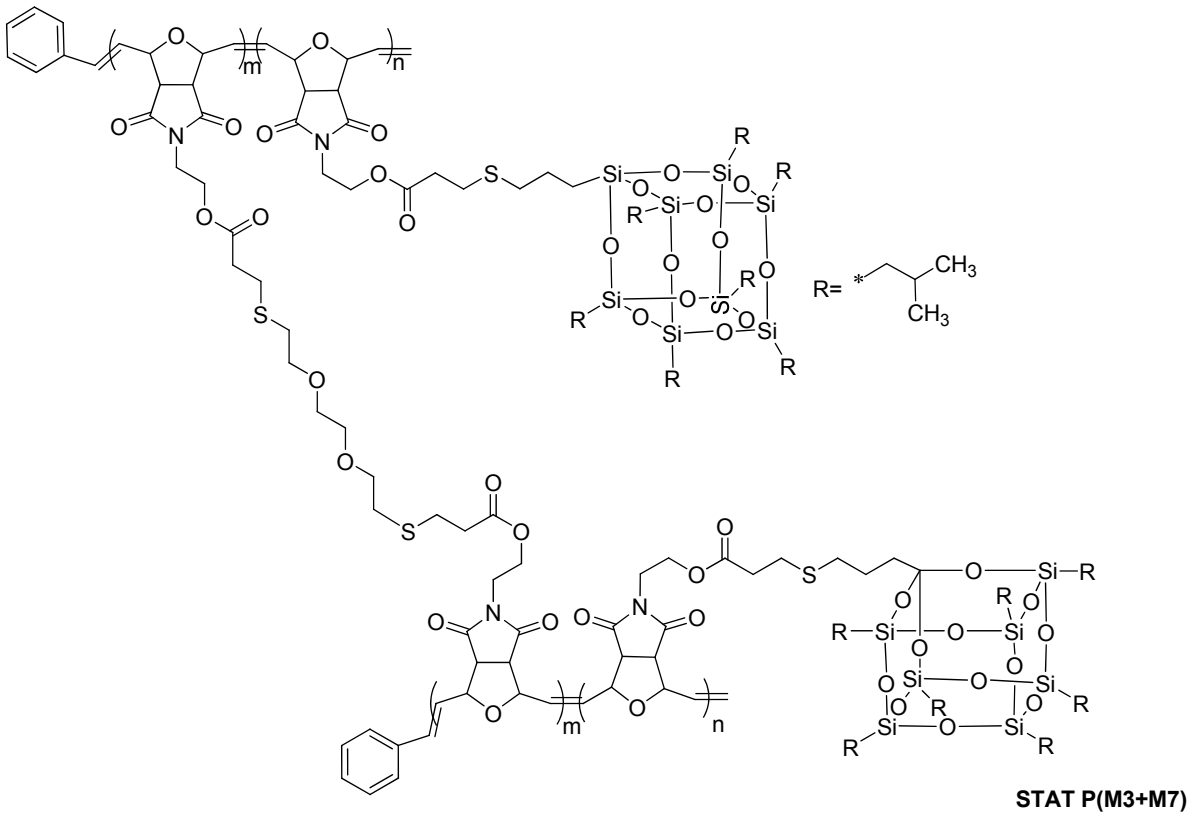
Copolymerization of M1/M6 (50:50)

Using **M1** (17.4 mg, 0.025 mmol), **M6** (18.6 mg, 0.025 mmol) and $RuCl_2(PCy_3)_2CHPh$ (3.0 mg, 0.0036 mmol for a targeted molecular weight of 10,000).

Copolymerization of M1/M6 (75:25)

Using **M1** (26.1 mg, 0.0375 mmol), **M6** (9.3 mg, 0.0125 mmol) and $RuCl_2(PCy_3)_2CHPh$ (2.96 mg, 0.0035 mmol for a targeted molecular weight of 10,000).

STAT P(M1+M6): ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.58-1.91 (m, 12H), 2.44-2.81 (m, 22H), 3.42-3.45 (m, 7H), 4.28-5.11 (m, 13H), 5.83-6.75 (m, 6H), 7.26-7.51 (m, 4H). M_n (NMR) = 9162; c/t ratio = 28.0/72.0.



STAT P(M3+M7)

Copolymerization of M3/M7 (25:75)

Using **M3** (8.85 mg, 0.0125 mmol), **M7** (43.3 mg, 0.0375 mmol) and $RuCl_2(PCy_3)_2CHPh$ (4.36 mg, 0.0052 mmol for a targeted molecular weight of 10,000).

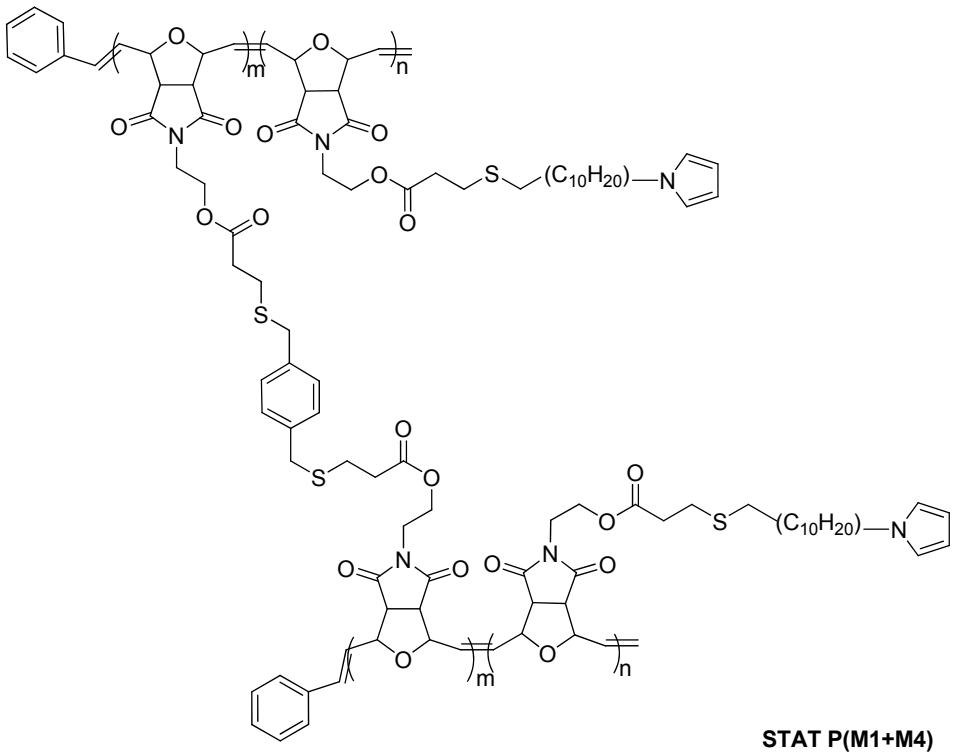
Copolymerization of M3/M7 (50:50)

Using **M3** (17.7 mg, 0.025 mmol), **M7** (28.8 mg, 0.025 mmol) and $RuCl_2(PCy_3)_2CHPh$ (3.9 mg, 0.0047 mmol for a targeted molecular weight of 10,000).

Copolymerization of M3/M7 (75:25)

Using **M3** (26.6 mg, 0.0375 mmol), **M7** (14.42 mg, 0.0125 mmol) and $RuCl_2(PCy_3)_2CHPh$ (3.43 mg, 0.0041 mmol for a targeted molecular weight of 10,000).

STAT P(M3+M7): ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.62-2.01 (m, 50H), 2.61-2.86 (m, 18H), 3.40-3.80 (m, 22H), 4.11-5.15 (m, 12 H), 5.89-6.48 (m, 6H), 7.31-7.50 (m, 1H). M_n (NMR) = 11,673; c/t ratio = 30.6/69.4.

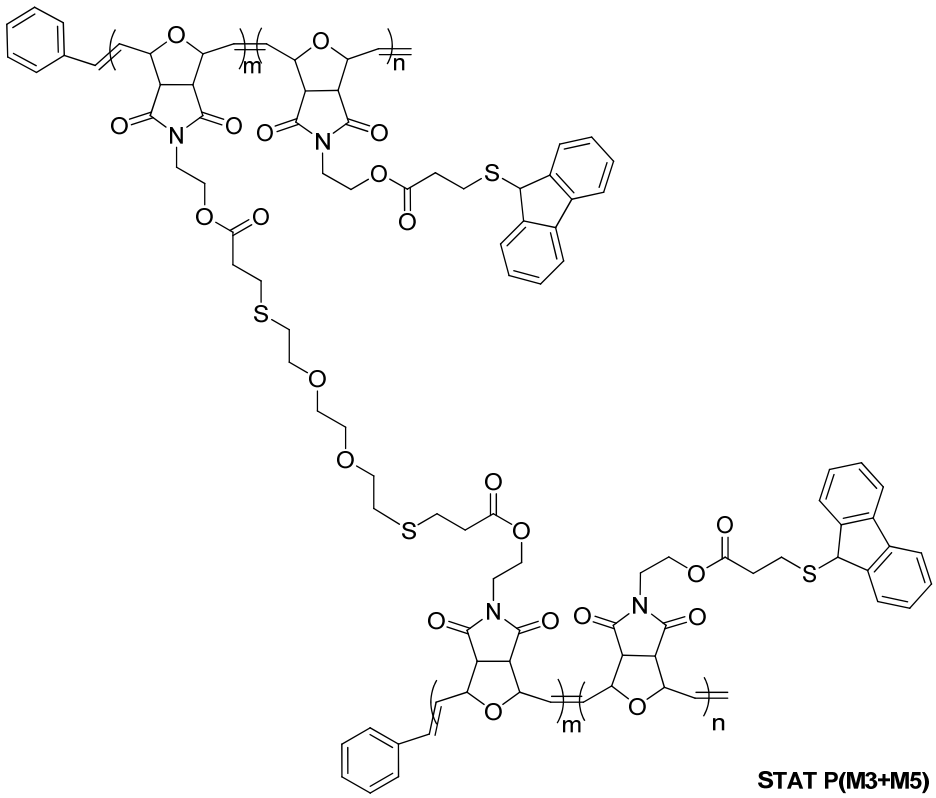


STAT P(M1+M4)

Copolymerization of M1/M4 (50:50)

Using **M1** (17.4 mg, 0.025 mmol), **M4** (12.9 mg, 0.025 mmol) and $RuCl_2(PCy_3)_2CHPh$ (2.5 mg, 0.0030 mmol for a targeted molecular weight of 10,000).

STAT P(M1+M4): ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.28-1.85 (m, 32H), 2.46-2.72 (m, 12H), 3.30-3.77 (m, 12H), 4.20-5.06 (m, 12H), 5.82-6.12 (m, 6H), 7.28-7.51 (m, 4H). M_n (NMR) = 12,381; M_n (DMAC GPC) = 26,200; M_w = 63,500, PDI = 2.42; c/t ratio = 24.6/75.4.



STAT P(M3+M5)

Copolymerization of M3/M5 (50:50)

Using **M3** (17.7 mg, 0.025 mmol), **M5** (11.5 mg, 0.025 mmol) and $RuCl_2(PCy_3)_2CHPh$ (2.4 mg, 0.0029 mmol for a targeted molecular weight of 10,000).

STAT P(M3+M5): ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.28-2.82 (m, 22H), 3.78-3.79 (m, 16H), 4.29-5.07 (m, 11H), 5.84-6.14 (m, 6H), 7.38-7.76 (m, 8H). M_n (NMR) = 29,379; M_n (DMAC GPC) = 28,100, M_w = 73,950, PDI = 2.63; c/t ratio = 28.8/71.2.

Determination of ROMP kinetics via an aliquot approach

ROMP kinetics via an aliquot approach of M1/M6 (25:75)

Using **M1** (0.087 g, 0.125 mmol), **M6** (0.279 g, 0.375 mmol) and $RuCl_2(PCy_3)_2CHPh$ (30.6 mg, 0.037 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 15, 20, 25, 30, 35, 40, 50, 65 and 90 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M1/M6 (50:50)

Using **M1** (0.17 g, 0.25 mmol), **M6** (0.185 g, 0.25 mmol) and $RuCl_2(PCy_3)_2CHPh$ (29.7 mg, 0.035 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180 and 200 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M1/M6 (75:25)

Using **M1** (0.26 g, 0.375 mmol), **M6** (0.093 g, 0.125 mmol) and $RuCl_2(PCy_3)_2CHPh$ (29.5 mg, 0.035 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180 and 200 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M3/M7 (25:75)

Using **M3** (0.089 g, 0.125 mmol), **M7** (0.433 g, 0.375 mmol) and $RuCl_2(PCy_3)_2CHPh$ (43 mg, 0.051 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 15, 20, 25, 30, 35, 40, 50, 67 and 90 min, with intervals based on prior kinetic experiments).

ROMP kinetics via an aliquot approach of M3/M7 (50:50)

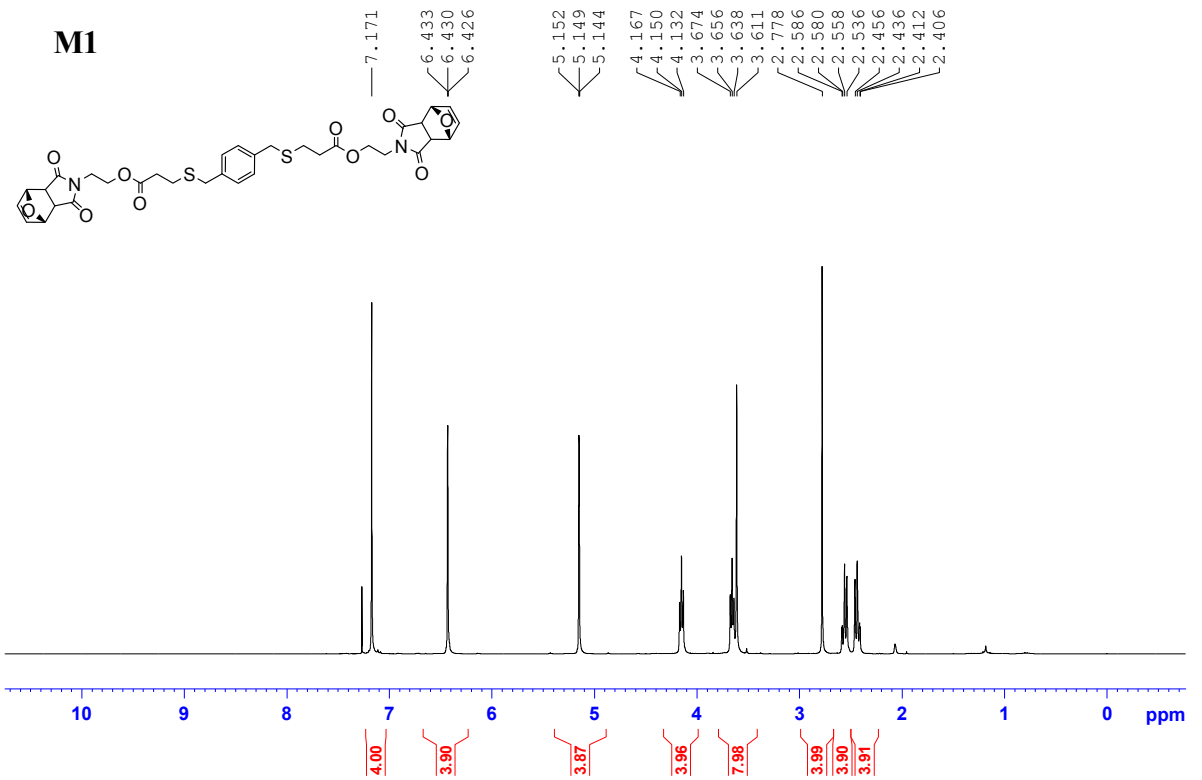
Using **M3** (0.177 g, 0.25 mmol), **M7** (0.288 g, 0.25 mmol) and $RuCl_2(PCy_3)_2CHPh$ (38.9 mg, 0.046 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30, 40, 60, 80, 100, 130, 150, 180 and 200 min, with intervals based on prior kinetic experiments).

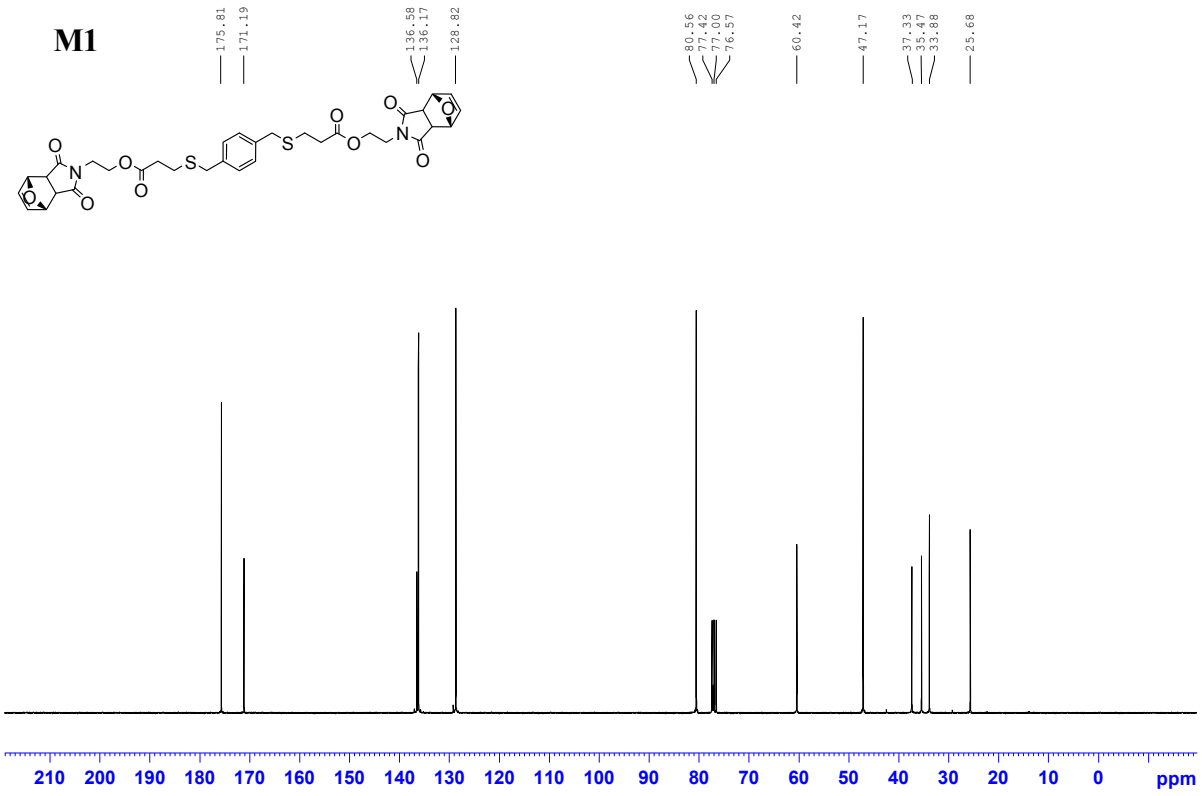
ROMP kinetics via an aliquot approach of M3/M7 (75:25)

Using **M3** (0.266 g, 0.375 mmol), **M7** (0.144 g, 0.125 mmol) and $RuCl_2(PCy_3)_2CHPh$ (34.3 mg, 0.041 mmol for a targeted molecular weight of 10,000). Aliquots were withdrawn periodically (at 2, 5, 10, 20, 30,

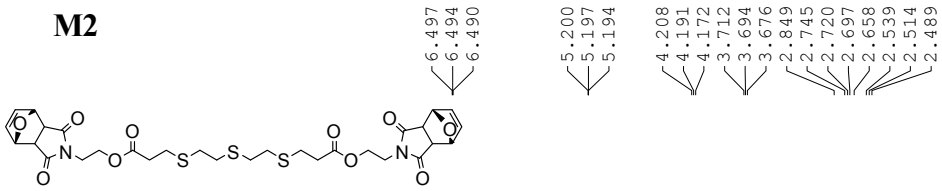
40, 60, 80, 100, 120, 150, 180 and 200 min, with intervals based on prior kinetic experiments).

2. Copies of ^{1}H- and ^{13}C spectra





M2



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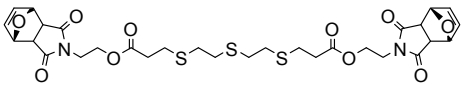
4.06

M2



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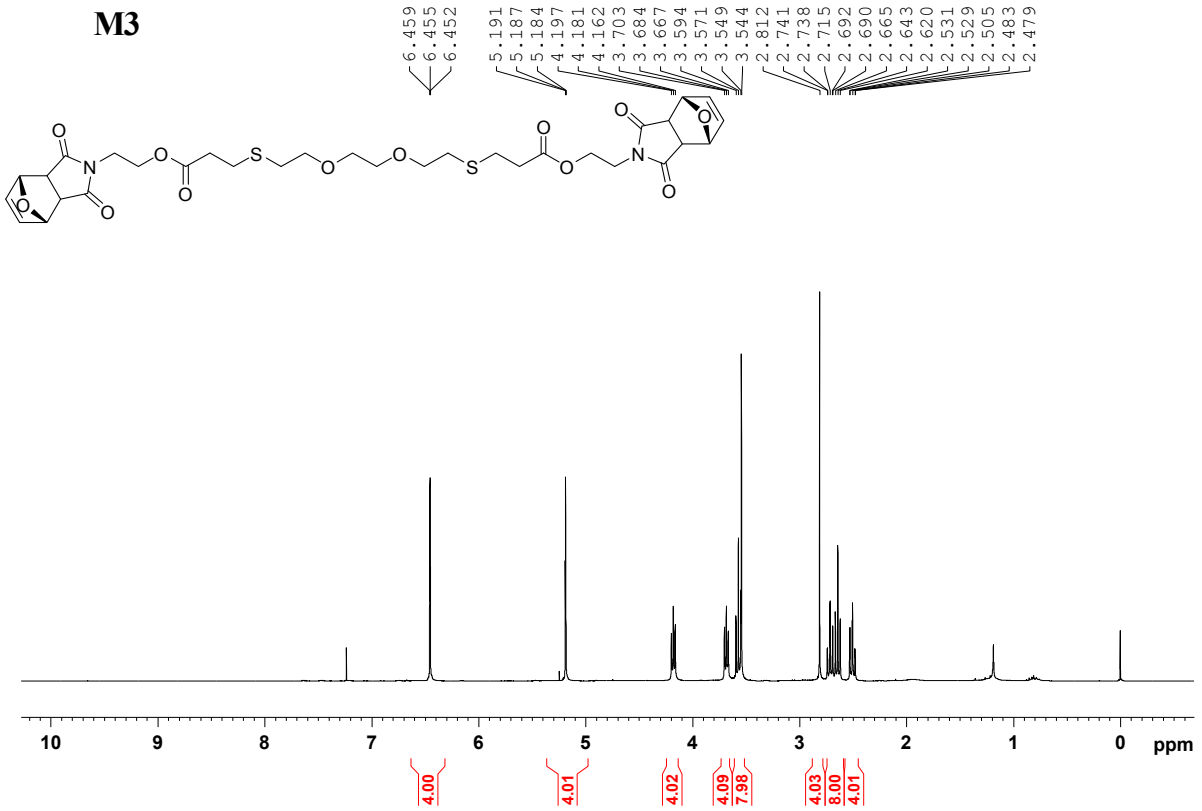
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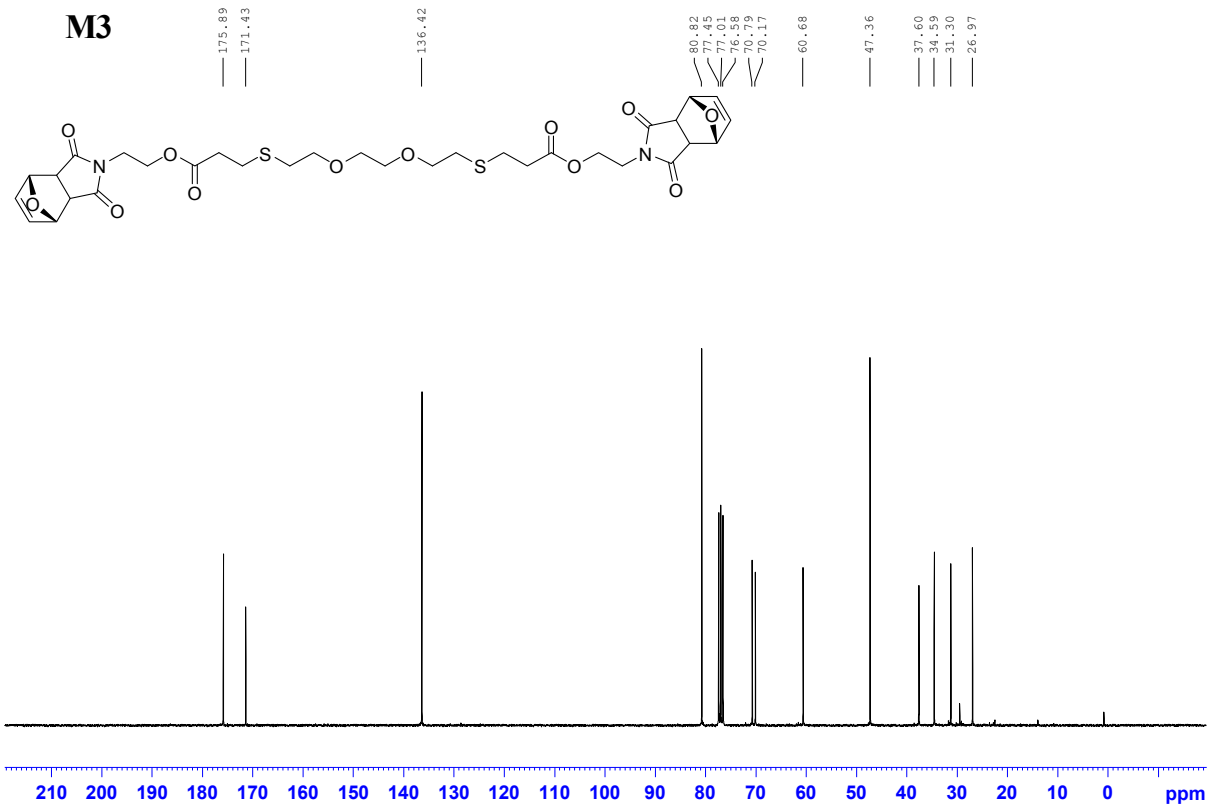
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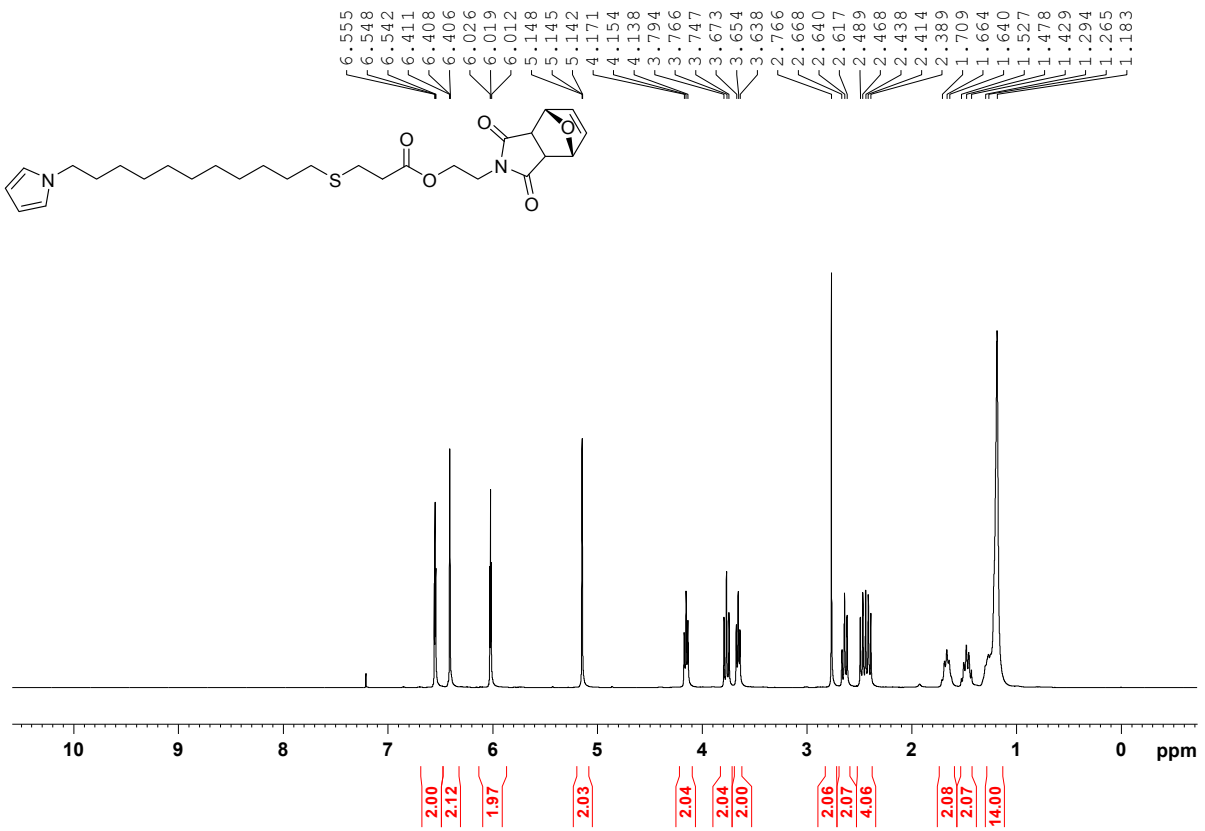

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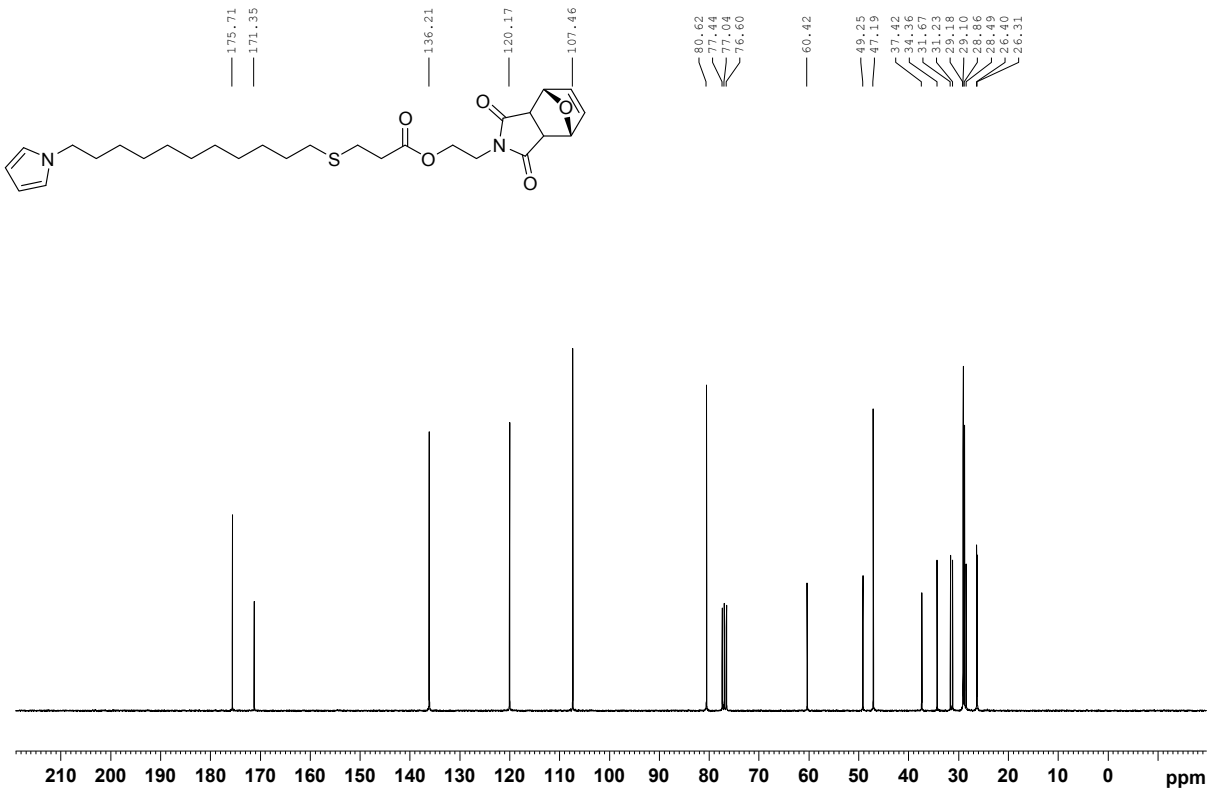

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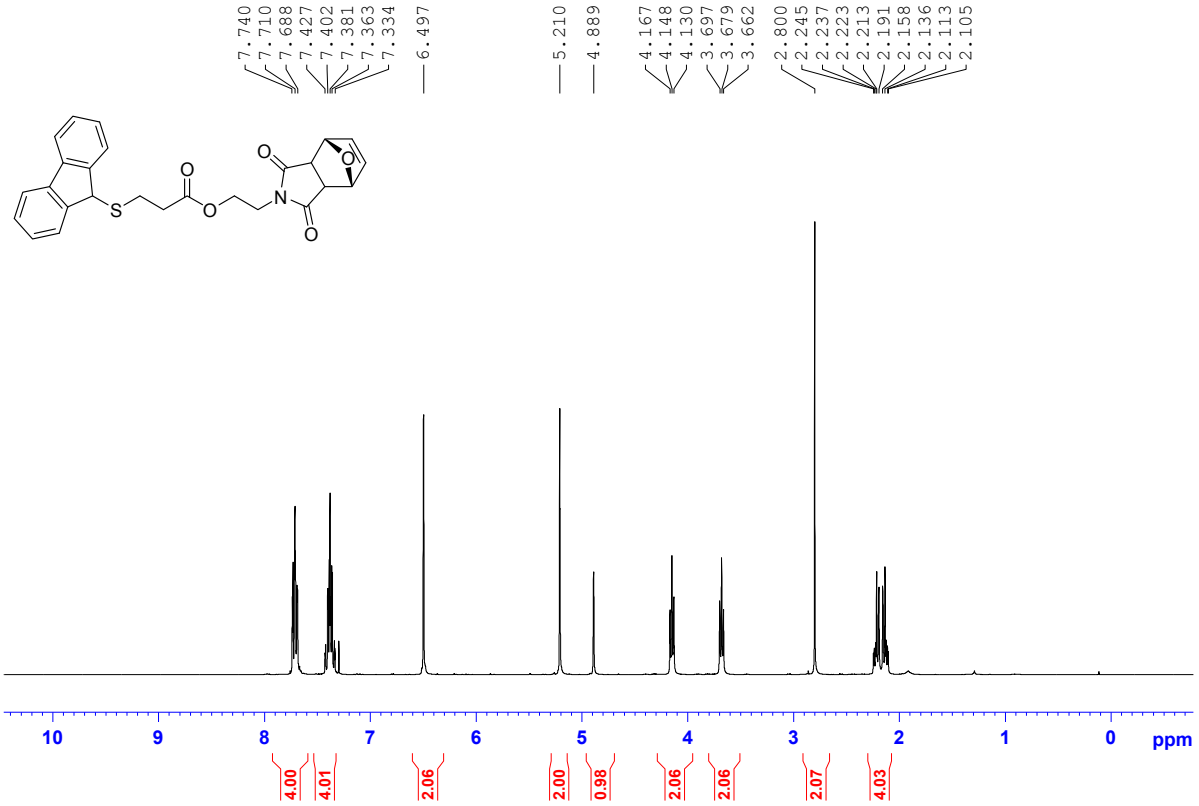

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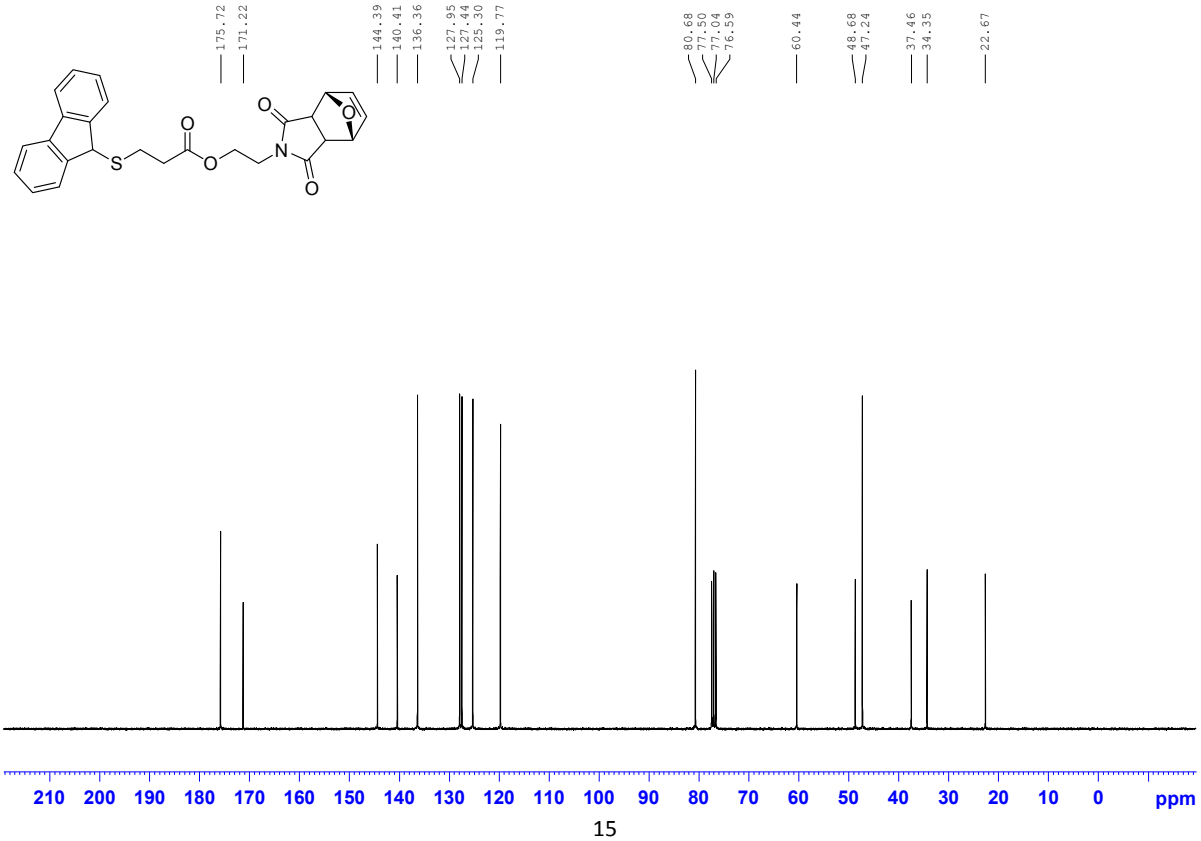

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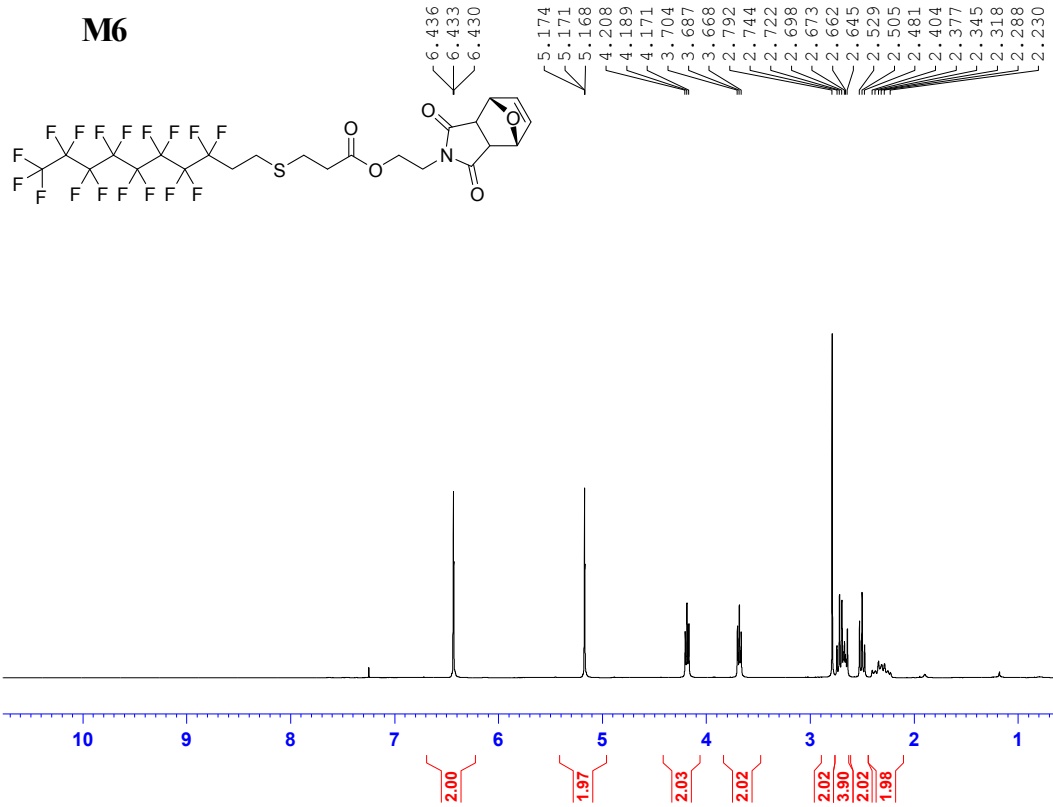
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2.744
2.722
2.698
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2.645
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6
5
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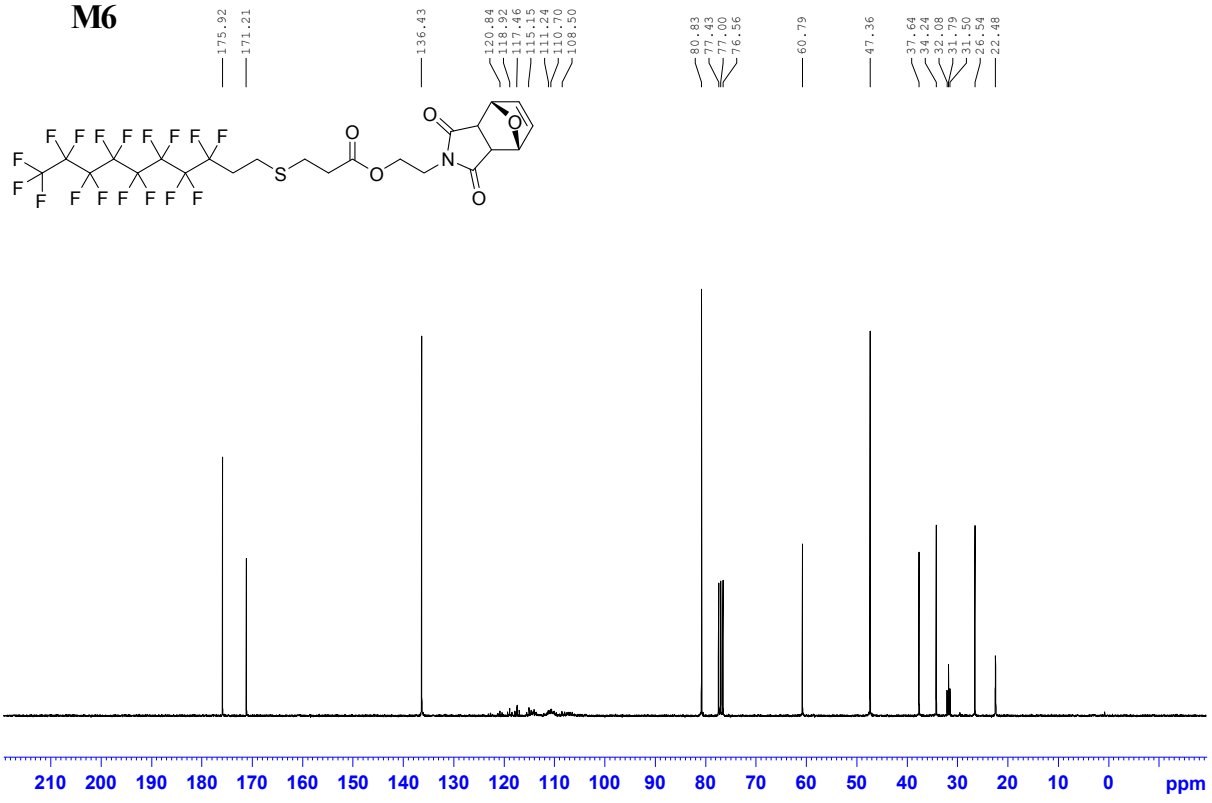
M6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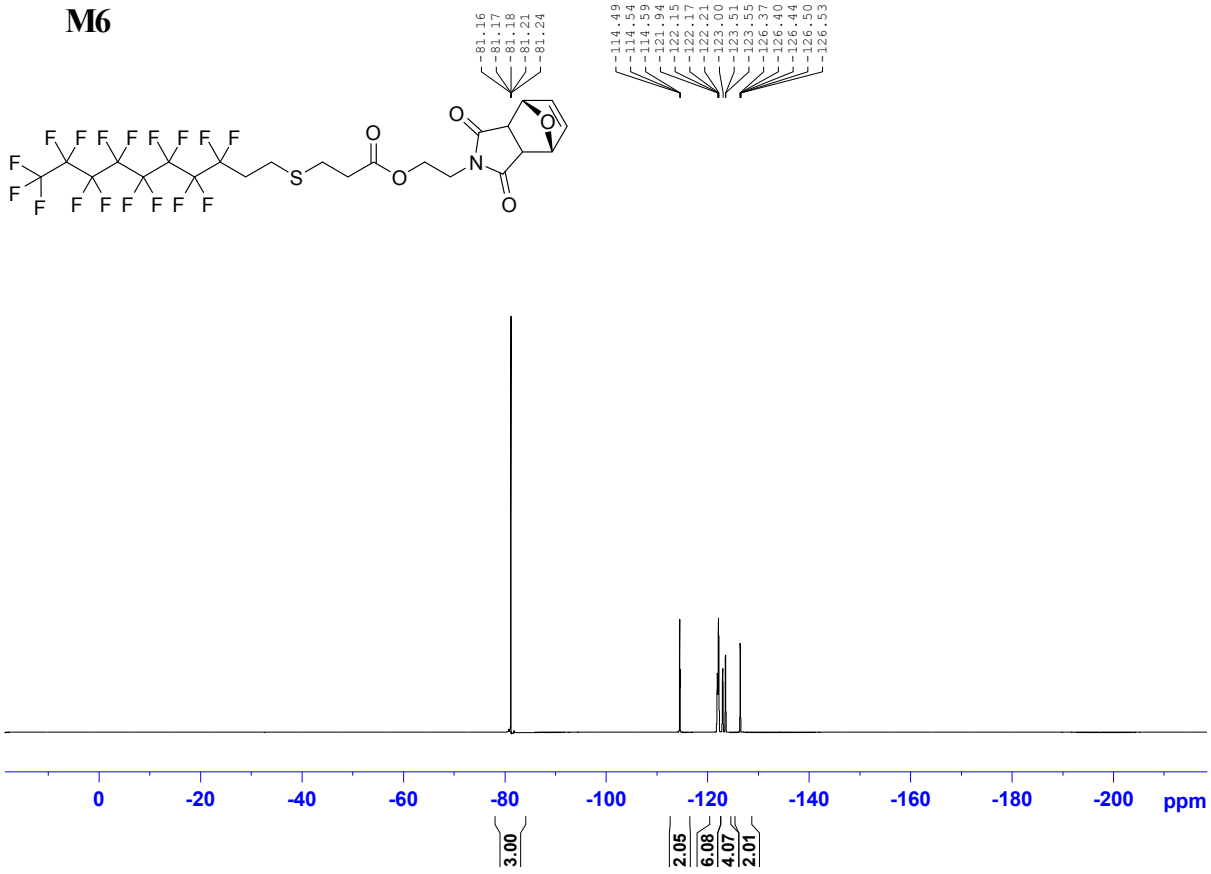
M6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-126.53
F F F F F F F F F F F F F F F F F
S
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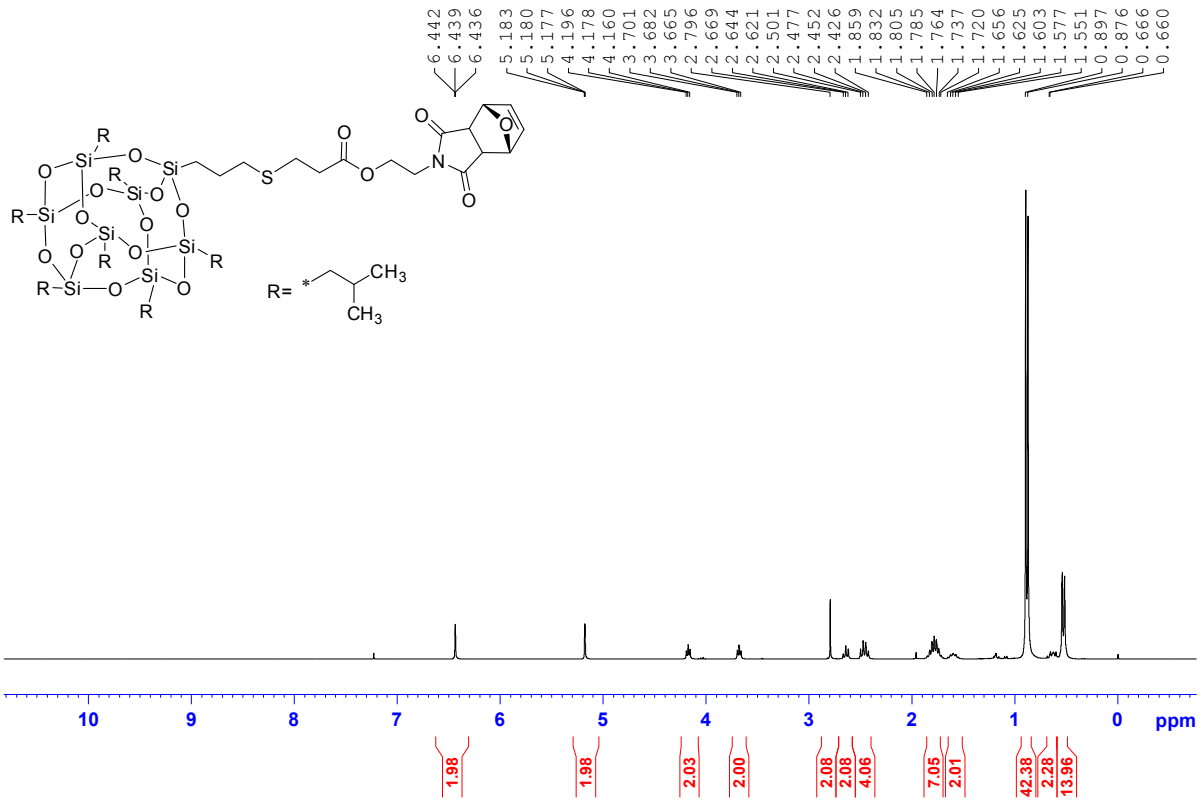
M7



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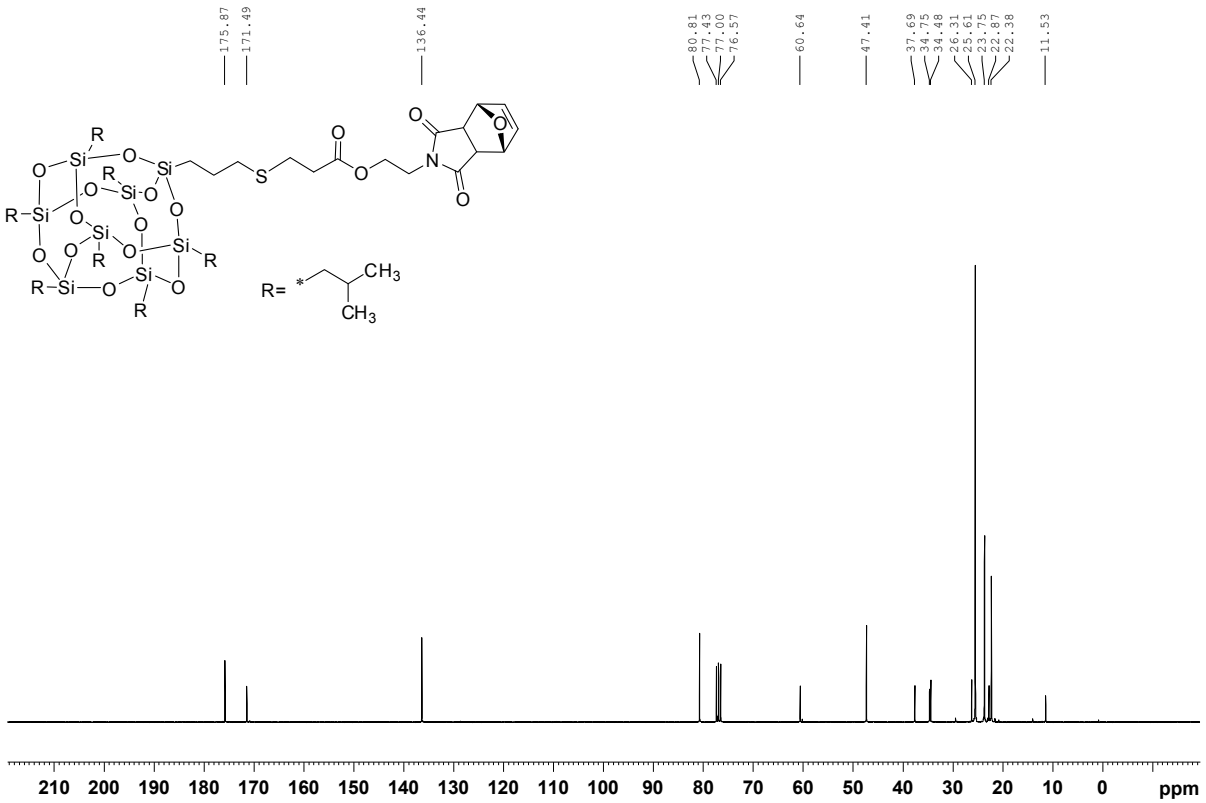

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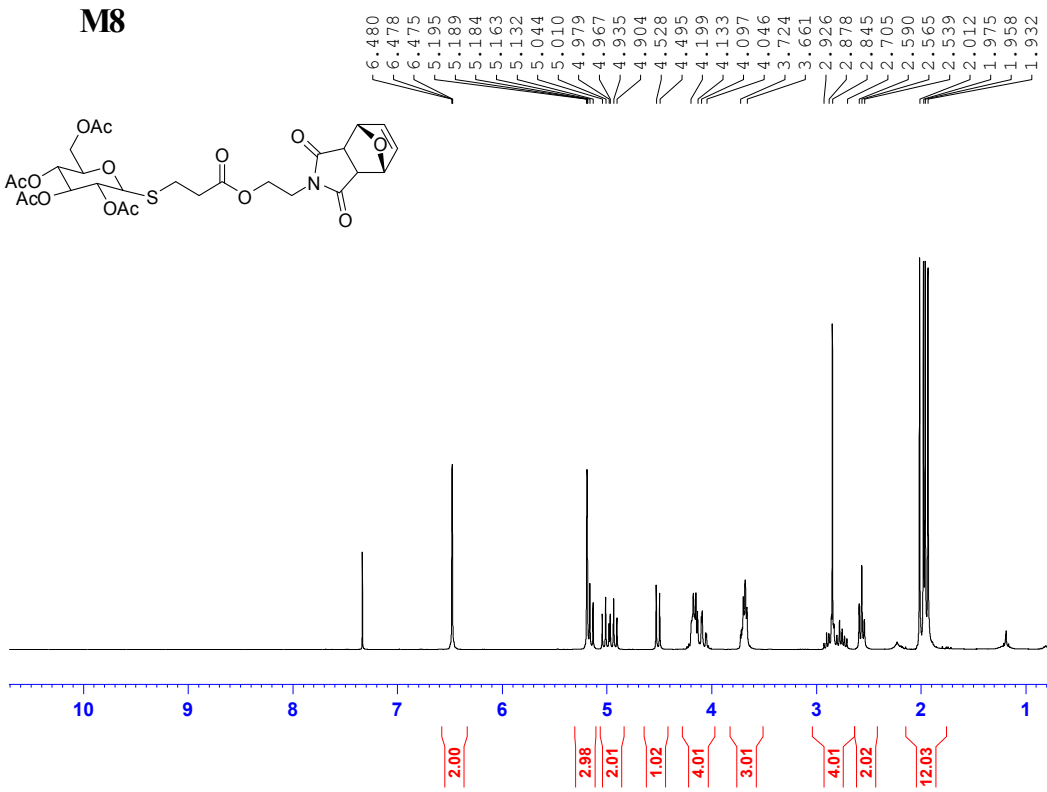
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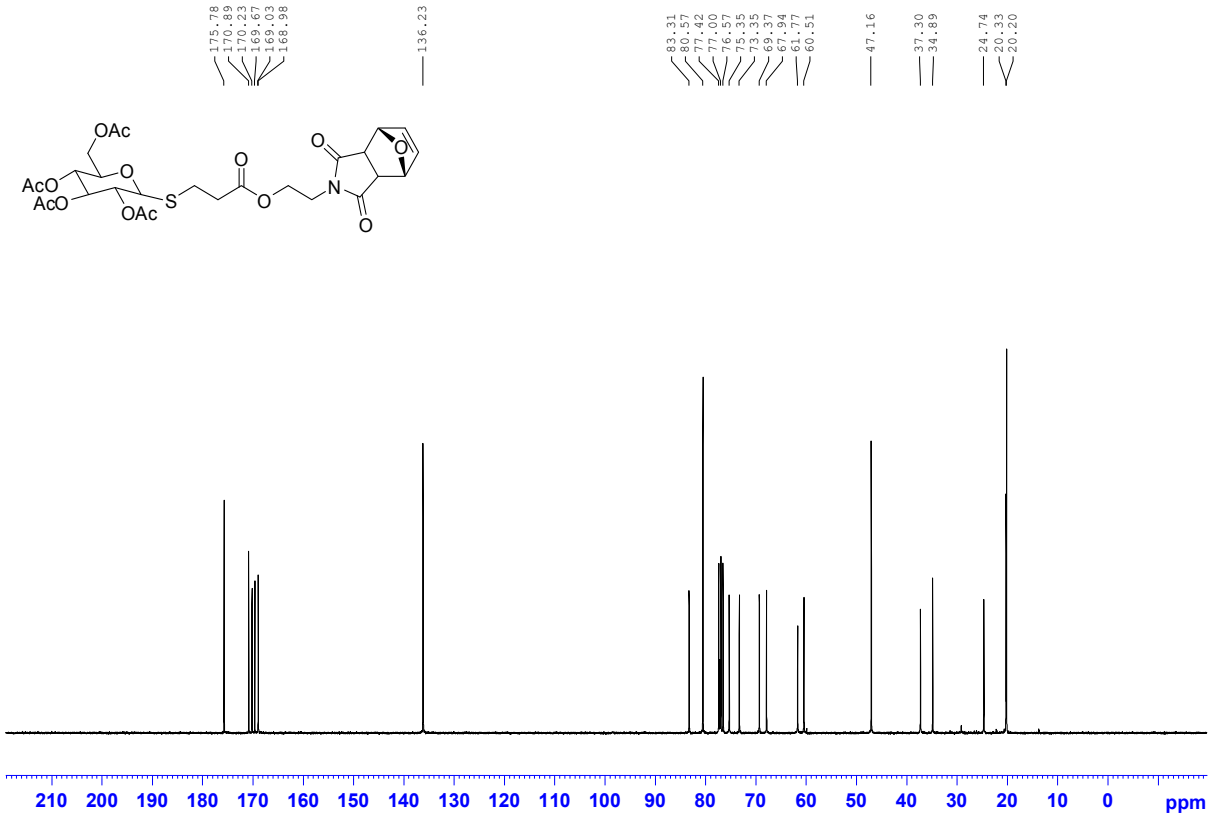
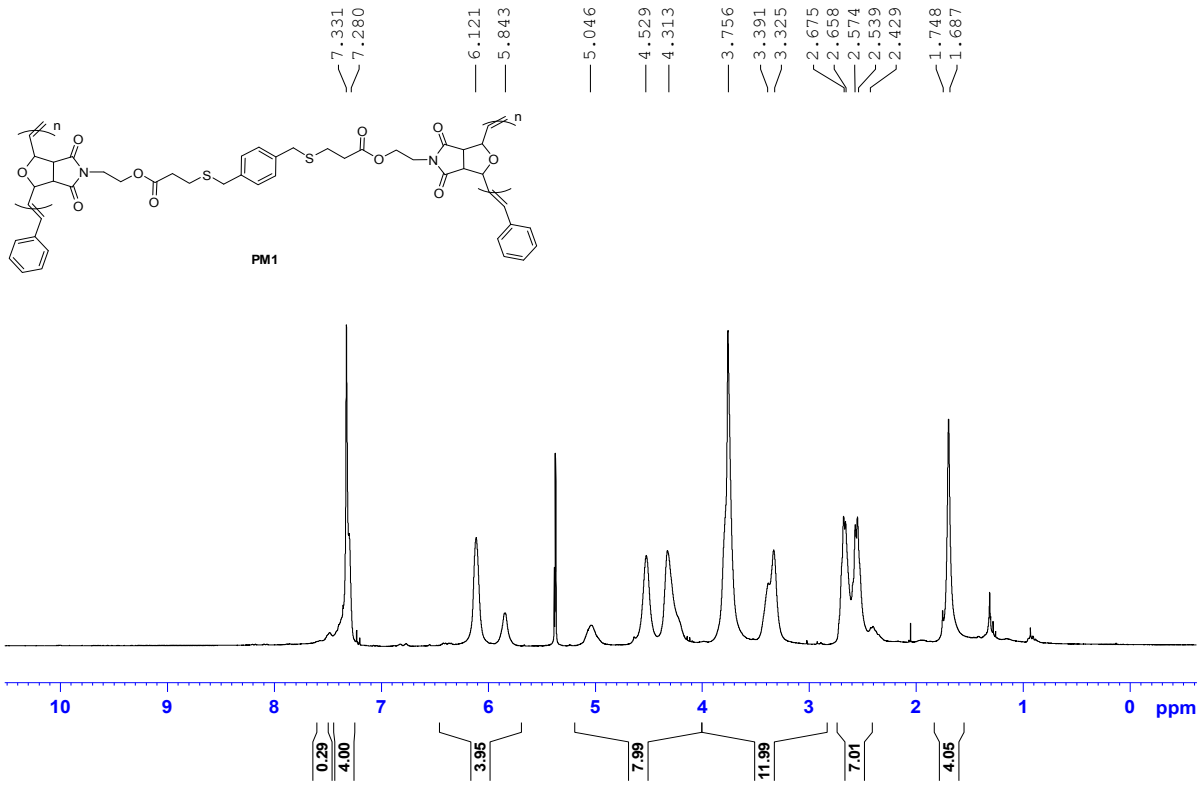
5.044
5.010
4.979
4.967
4.935
4.904
4.528
4.495
4.199
4.133
4.097
4.046
3.724
3.661
2.926
2.878
2.845
2.705
2.590
2.565
2.539
2.012
1.975
1.958
1.932
OAc
AcO
AcO
OAc
S
O
N
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.98
2.01
1.02
4.01
3.01
4.01
2.02
12.03

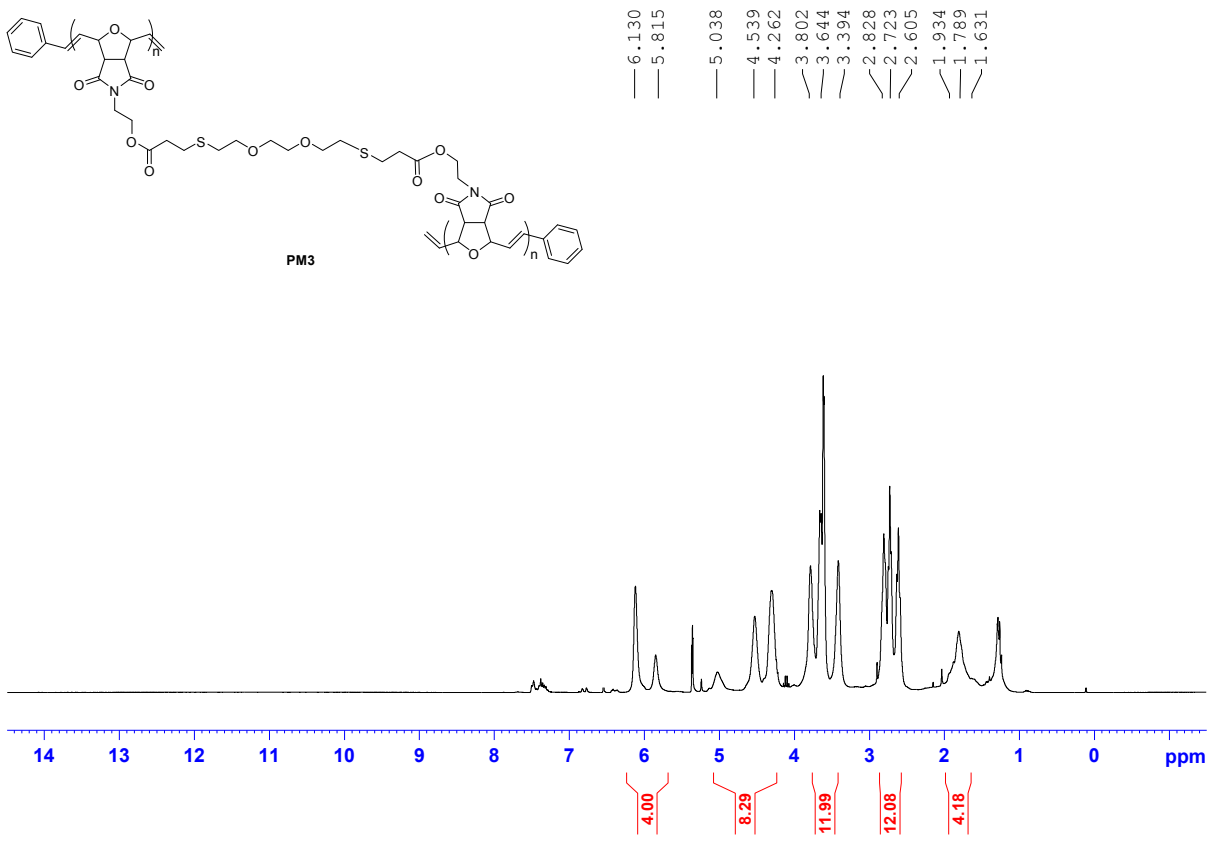
M8


175.78
170.89
170.23
169.67
169.03
168.98
136.23
83.31
80.57
77.42
77.00
76.57
75.35
73.35
69.37
67.94
61.77
60.51
47.16
37.30
34.89
24.74
20.33
20.20
OAc
AcO
AcO
OAc
S
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

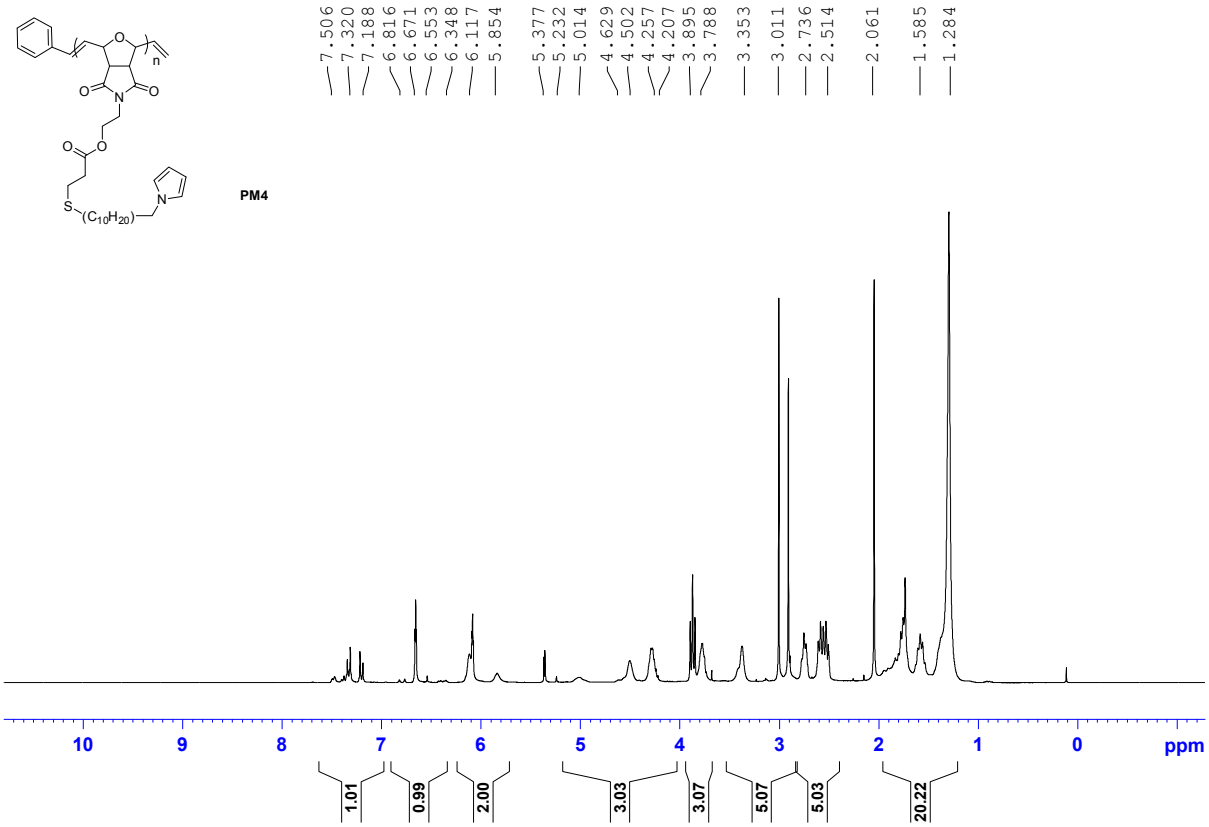
PM1


7.331
7.280
6.121
5.843
5.046
4.529
4.313
3.756
3.391
3.325
2.675
2.658
2.574
2.539
2.429
1.748
1.687
PM1
10
9
8
7
6
5
4
3
2
1
0
ppm
0.29
4.00
3.95
7.99
11.99
7.01
4.05

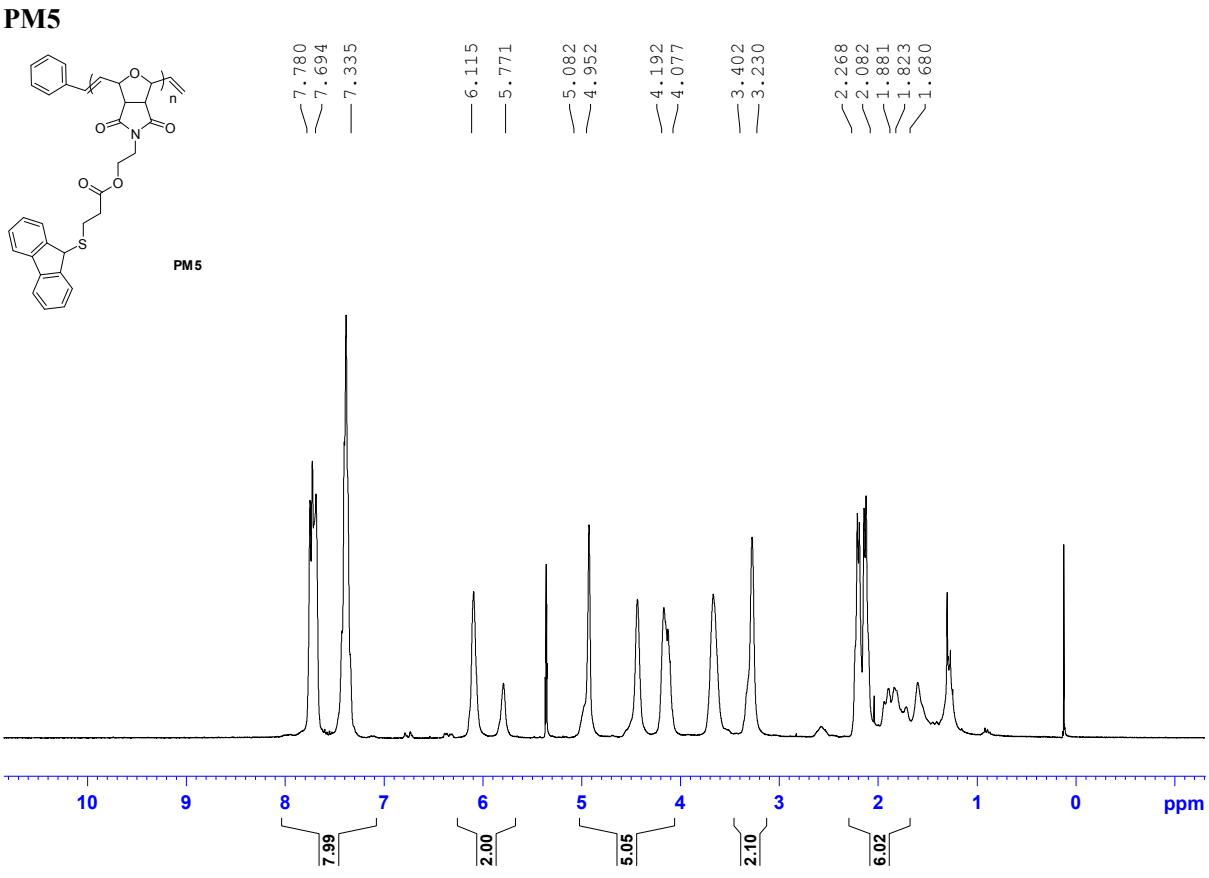
PM3


6.130
5.815
5.038
4.539
4.262
3.802
3.644
3.394
2.828
2.723
2.605
1.934
1.789
1.631
PM3
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
8.29
11.99
12.08
4.18

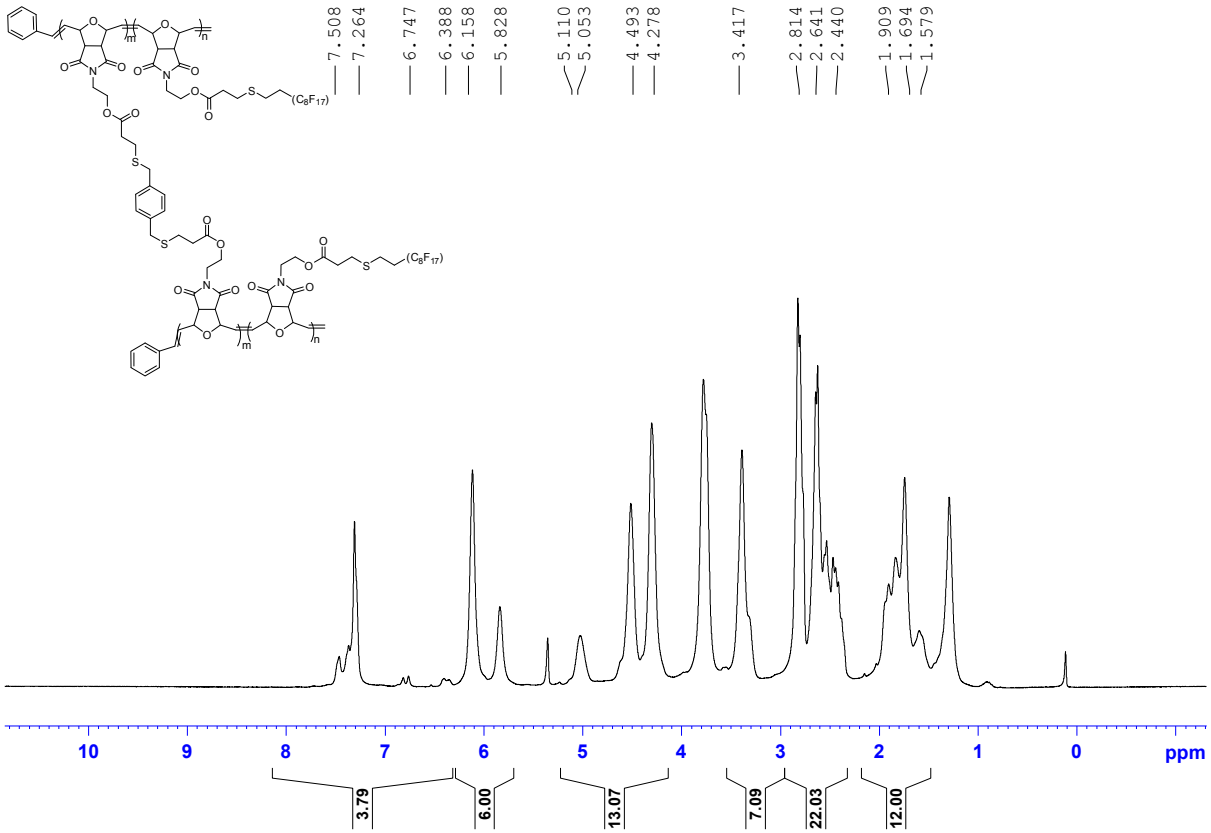
PM4


7.506
7.320
7.188
6.816
6.671
6.553
6.348
6.117
5.854
5.377
5.232
5.014
4.629
4.502
4.257
4.207
3.895
3.788
3.353
3.011
2.736
2.514
2.061
1.585
1.284
PM4
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.99
2.00
3.03
3.07
5.07
5.03
20.22

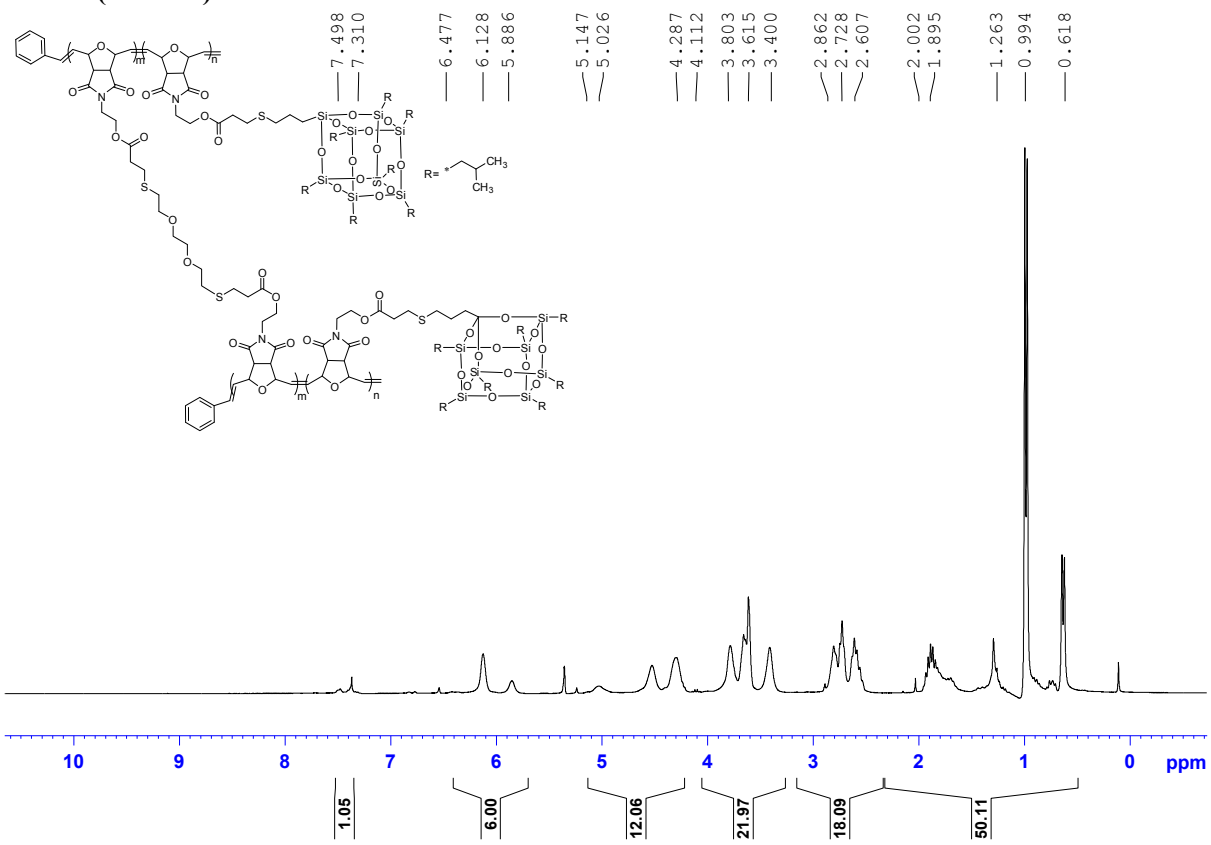
PM5


7.780
7.694
7.335
6.115
5.771
5.082
4.952
4.192
4.077
3.402
3.230
2.268
2.082
1.881
1.823
1.680
PM5
10
9
8
7
6
5
4
3
2
1
0
ppm
7.99
2.00
5.05
2.10
6.02

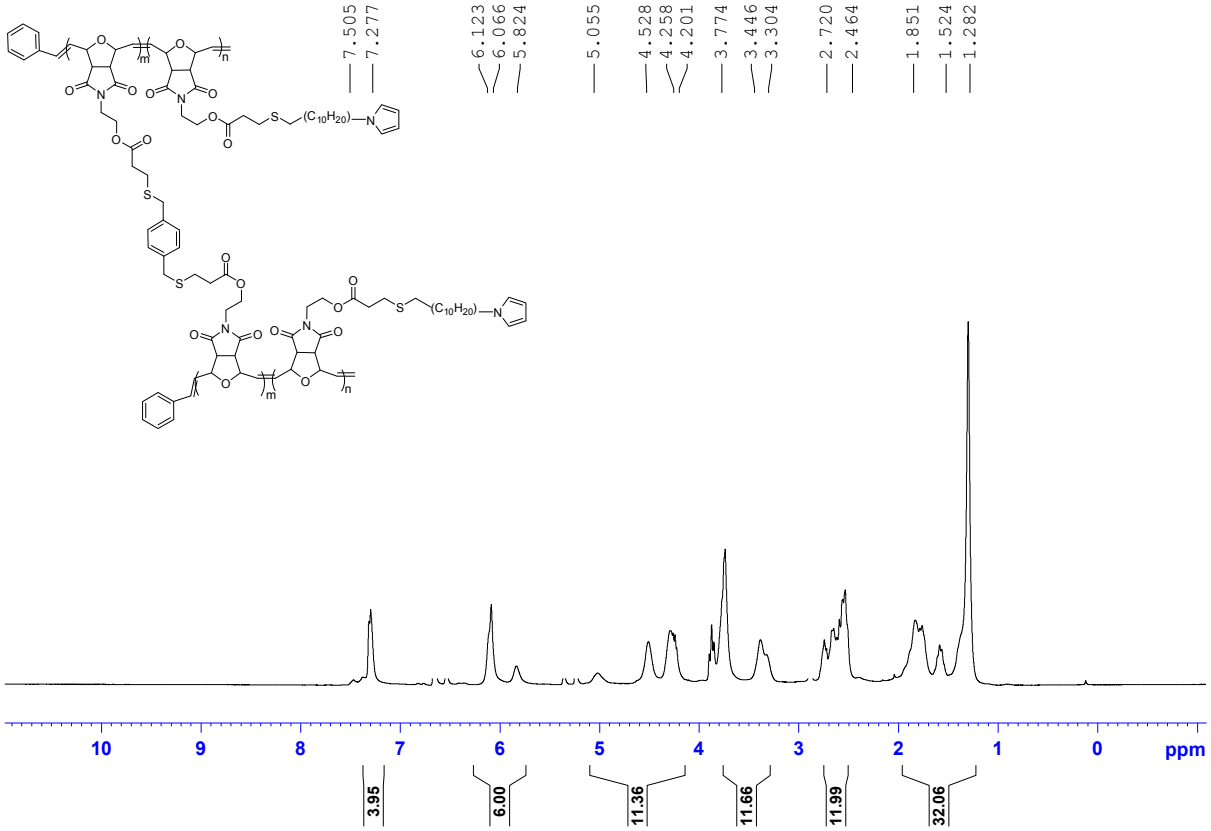
STAT P(M1+M6)



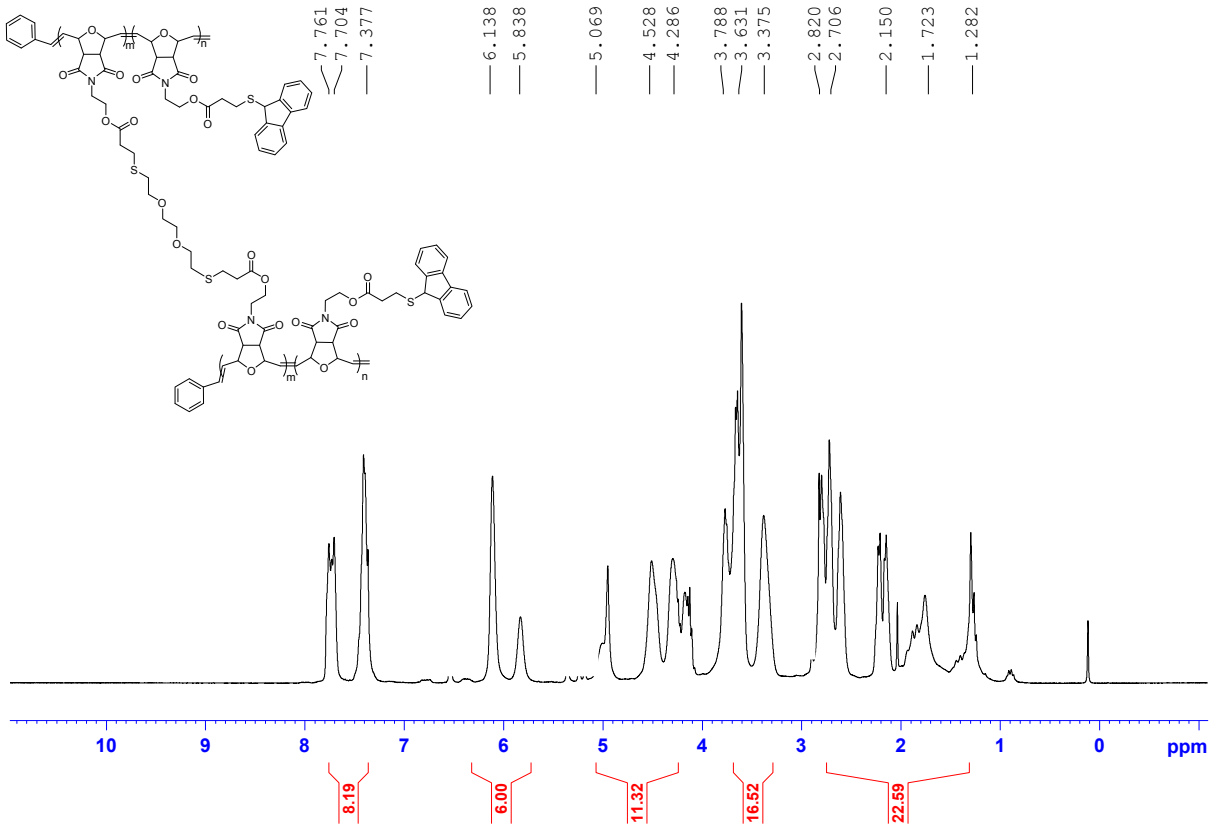
STAT P(M3+M7)



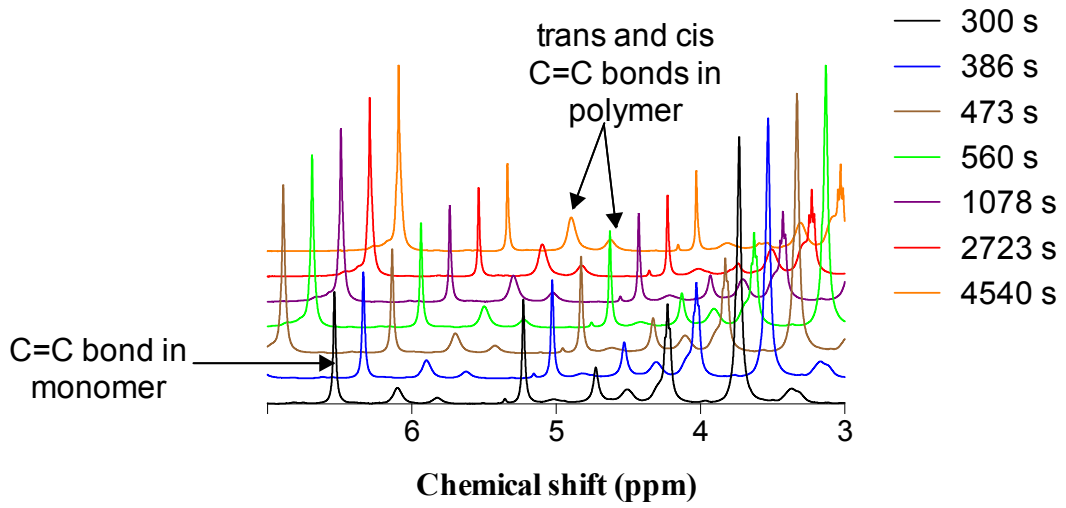
STAT P(M1+M4)



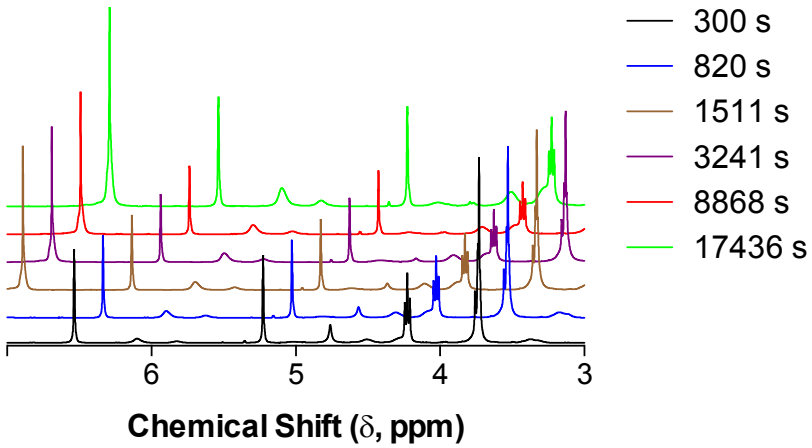
STAT P(M3+M5)



PM1, [Ru]:M1, 1:20



PM1, [Ru]:M1, 1:40



3. References

[1] Liu, M.; van Hensbergen, J.; Burford, R. P.; Lowe, A. B. *Polym. Chem.* **2012**, *3*, 1647.