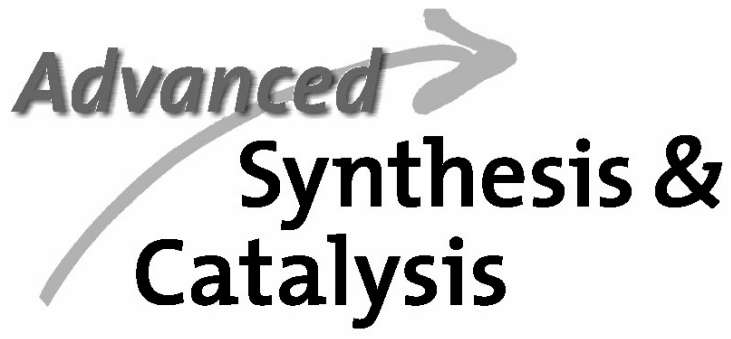


Supporting Information

Supporting Information for the communication

Pd-catalysed telomerisation of isoprene with glycerol and polyethyleneglycol: A facile route to new terpene derivatives

Alvaro Gordillo, Laura Durán Pachón, Ernesto de Jesús and Gadi Rothenberg*

Van't Hoff Institute of Molecular Science, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

E-mail: G.Rothenberg@uva.nl

Materials and instrumentation. All reagents were obtained from commercial sources (>98% pure) and used as received. ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury vx300 NMR spectrometer at 25 °C. Chemical shifts (δ ppm, $SiMe_4$) were measured by internal referencing to the deuterated solvent (^{13}C and residual ^{1}H). Coupling constants (*J*) are given in hertz. Where needed, two-dimensional ^{1}H-^{13}C HSQC experiments were carried out for assigning of ^{1}H and ^{13}C resonances. GC analysis was performed on an InterScience GC-8000 gas chromatograph with a DB-1 capillary column (30 m × 0.21 mm). All products were identified by their GC retention times and their NMR spectra. Samples for GC were diluted with 1 mL methanol (MeOH) and filtered through an alumina plug prior to injection. GC conditions: ramp at 10 ºC/min to 255 ºC; isotherm at 255 ºC (13 min). EI-MS analysis was performed on an Agilent Technologies 6890/5973-GC/MS with a cross-linked phase 5% PhMe siloxane column (30 m × 0.25 mm).

Data of kinetic experiments

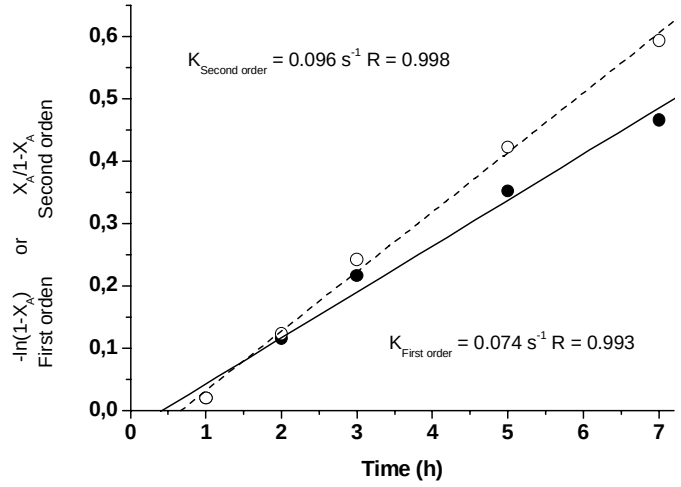
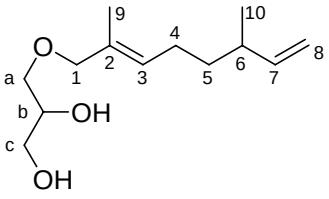
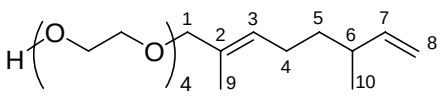


Figure S1. Reaction profile for glycerol telomerisation with isoprene in the presence of 0.05 mol% $Pd(acac)_2$ and 0.075 mol% carbene ligand at 90 °C. We only analyze the T2H isomer **(3)**.

Products Characterization



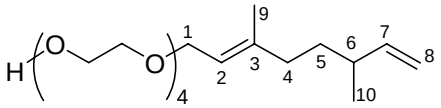
Glycerol Product (tail-to-head isomer) (3): Purification by flash chromatography with hexane/ethyl acetate 1:3 (R_f = 0.33). Colorless oil. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 0.94 (d, $^3J_{10,6}$ = 6.5, 3 H, CH_3; H^{10}), 1.31 (m, 2 H; H^5), 1.54 (s, 3 H, CH_3; H^9), 1.97 (m, 2 H; H^4), 2.09 (m, 1 H; H^6), 3.18-3.53 (m, 5 H; H^a, H^b, H^c), 3.77 (s, 2 H; H^1), 4.46 (bs, 1 H; OH), 4.60 (bs, 1 H; OH), 4.90-4.98 (m, 2 H; H^8), 5.34 (t, $^3J_{3,4}$ = 6.6, 1 H; H^3), 5.69 (m, 1 H; H^7). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 14.5 (C^9), 20.7 (C^{10}), 25.6 (C^4), 36.7 (C^5), 37.6 (C^6), 64.0 (C^b), 71.4, 71.9 (C^a, C^c), 77.0 (C^8), 113.9 (C^8), 127.7 (C^3), 133.0 (C^2), 145.1 (C^7). EI/MS (70 eV): *m/z* (%) 228 [M^+] (1), 213 (1), 199 (1), 171 (5), 158 (7), 145 (5), 137 (16), 136 (23), 121 (34), 107 (41), 95 (55), 81 (100), 67 (48), 55 (48), 41 (40).



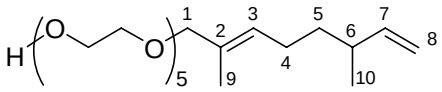
Tail-to-head isomer of PEG (6b): Purification by flash chromatography with hexane/ethyl acetate 1:3 (R_f = 0.30). Colorless oil. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 0.94 (d, $^3J_{10,6}$ = 6.5, 3 H,

CH_3; H^{10}), 1.29 (m, 2 H; H^5), 1.54 (s, 3 H, CH_3; H^9), 1.98 (m, 2 H; H^4), 2.08 (m, 1 H; H^6), 3.32-3.49 (m, 16 H; PEG), 3.78 (s, 2 H; H^1), 4.46 (bs, 1 H; OH), 4.90-4.98 (m, 2 H; H^8), 5.35 (t, $^3J_{3,4}$ = 6.6, 1 H; H^3), 5.69 (m, 1 H; H^7). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 14.5 (C^9), 20.7 (C^{10}), 25.6 (C^4), 36.7 (C^5), 37.5 (C^6), 61.0 (CH_2OH), 69.1 (C-PEG), 70.6 (C-PEG), 73.1 (C-PEG), 76.8 (C^1), 113.9 (C^8), 127.9 (C^3), 132.9 (C^2), 145.1 (C^7). EI/MS (70 eV): *m/z* (%) 281 (1), 216 (2), 167 (1), 136 (27), 121 (21), 107 (32), 89 (46), 81 (49), 67 (22), 55 (22), 45 (100).

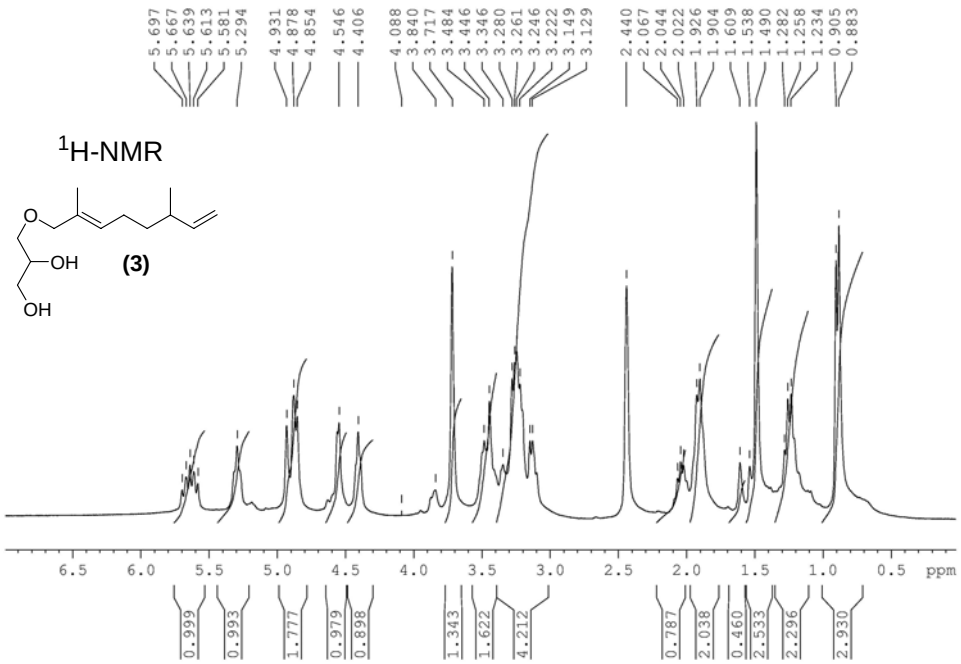
Head-to-head isomer of PEG (7b): Purification by flash chromatography with hexane/ethyl acetate 1:3 (R_f = 0.30). Detected in a mixture 1:1 with tail-to-head isomer. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 0.95 (d, $^3J_{10,6}$ = 6.5, 3 H, CH_3; H^{10}), 1.29 (m, 2 H; H^5), 1.59 (s, 3 H, CH_3; H^9), 1.95 (m, 2 H; H^4), 2.08 (m, 1 H; H^6), 3.24-3.49 (m, 16 H; PEG), 3.92 (d, $^3J_{10,6}$ =6.6, 2 H; H^1), 4.57 (bs, 1 H; OH), 4.90-4.98 (m, 2 H; H^8), 5.23 (t, $^3J_{3,4}$ = 6.6, 1 H; H^3), 5.69 (m, 1 H; H^7). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 17.0 (C^9), 20.7 (C^{10}), 34.9 (C^5), 37.4, 37.5 (C^4, C^6), 67.5 (C^1), 61.0 (CH_2OH; PEG), 69.4 (C-PEG), 70.6 (C-PEG), 73.1 (C-PEG), 113.9 (C^8), 122.9 (C^3), 139.7 (C^2), 145.1 (C^7). EI/MS (70 eV): *m/z* (%) 281 (1), 195 (4), 177 (5), 163 (2), 151 (1), 136 (31), 121 (20), 107 (31), 89 (56), 81 (42), 67 (15), 55 (19), 45 (100).

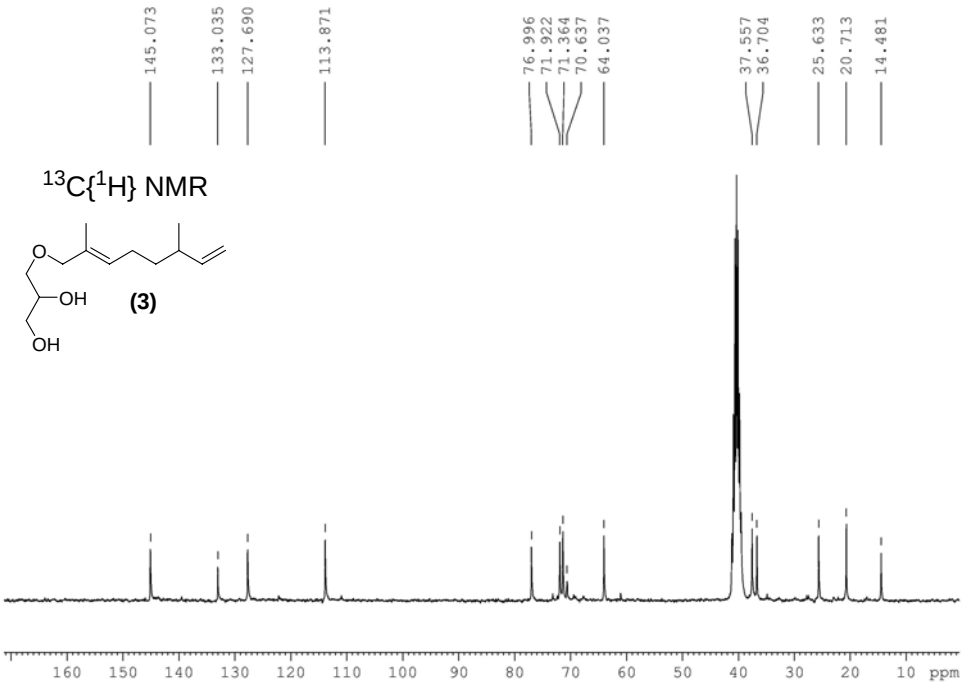


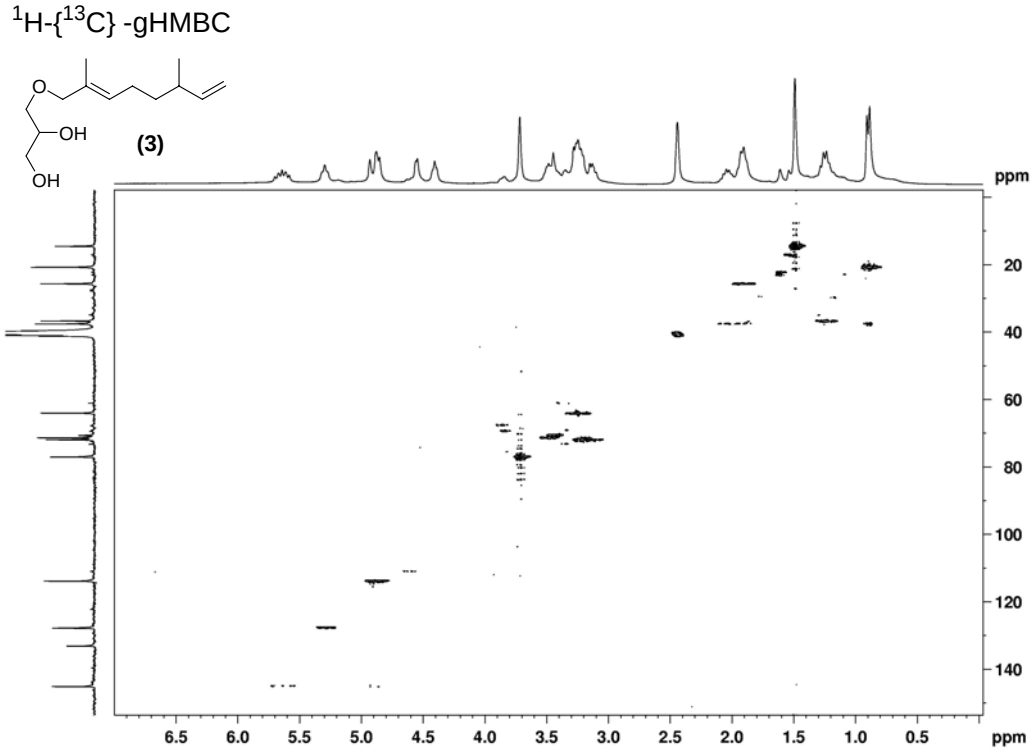
Tail-to-head isomer of PEG (6c): Purification by flash chromatography with hexane/ethyl acetate 1:6 (R_f = 0.19). Colorless oil. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 0.94 (d, $^3J_{10,6}$ = 6.6, 3 H, CH_3; H^{10}), 1.29 (m, 2 H; H^5), 1.54 (s, 3 H, CH_3; H^9), 1.96 (m, 2 H; H^4), 2.09 (m, 1 H; H^6), 3.33-3.56 (m, 20 H; PEG), 4.58 (bs, 1 H; OH), 4.90-4.98 (m, 2 H; H^8), 5.35 (t, $^3J_{3,4}$ = 7.1, 1 H; H^3), 5.69 (m, 1 H; H^7). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 14.5(C^9), 20.7 (C^{10}), 25.6 (C^4), 36.7 (C^5), 37.6 (C^6), 61.0 (CH_2OH), 69.1 (C-PEG), 70.6 (C-PEG), 73.2 (C-PEG), 76.8 (C^1), 113.9 (C^8), 127.9 (C^3), 132.9 (C^2), 145.1 (C^7). EI/MS (70 eV): *m/z* (%) 446 (1), 330 (1) 195 (5), 177 (6), 136 (41), 121 (22), 107 (33), 89 (57), 81 (46), 67 (19), 55 (21), 45 (100).

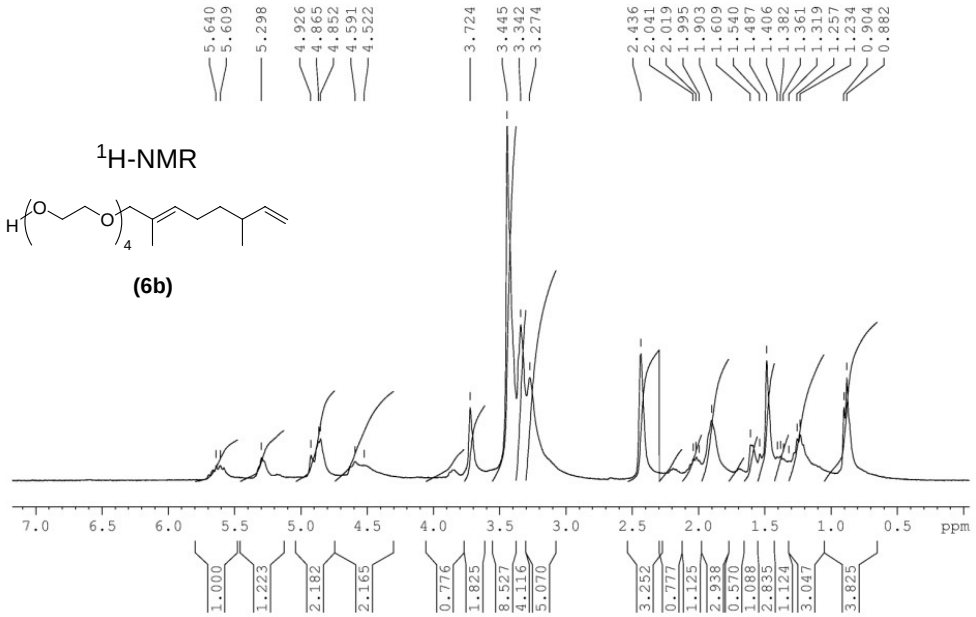


^{1}H, ^{13}C{^{1}H} AND 2D NMR SPECTRA



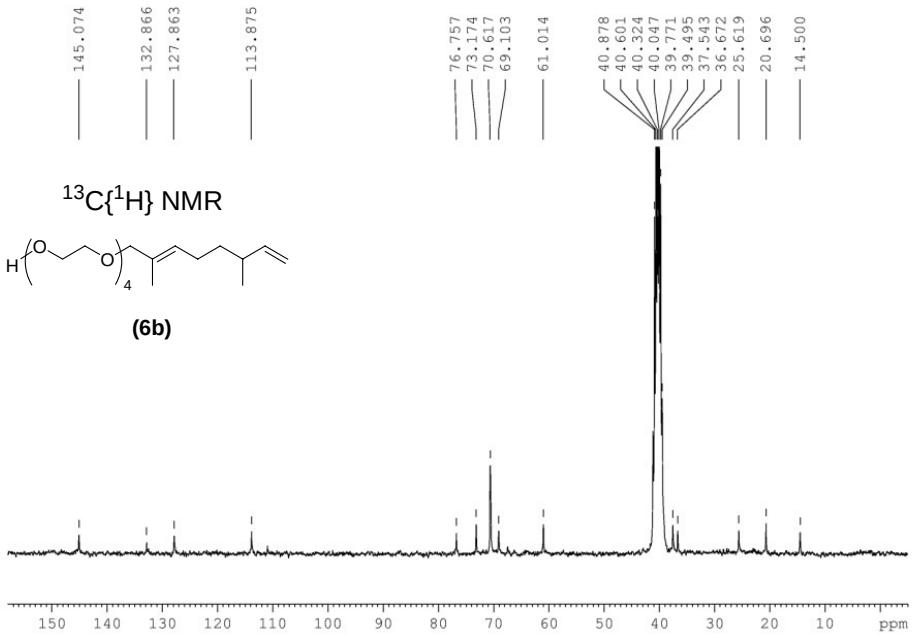

145.073
133.035
127.690
113.871
76.996
71.922
71.364
70.637
64.037
37.557
36.704
25.633
20.713
14.481
$^{13}C\{^{1}H\}$ NMR
O
OH
OH
(3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{1}H-{^{13}C} -gHMBC
O
OH
OH
(3)
ppm
20
40
60
80
100
120
140
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



^{1}H-NMR

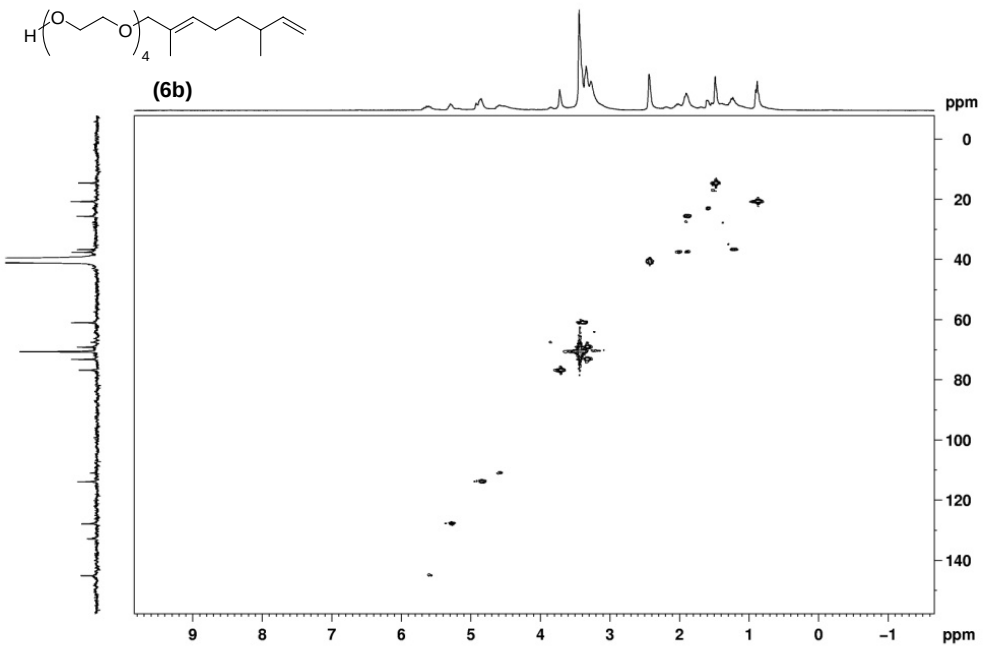
(6b)

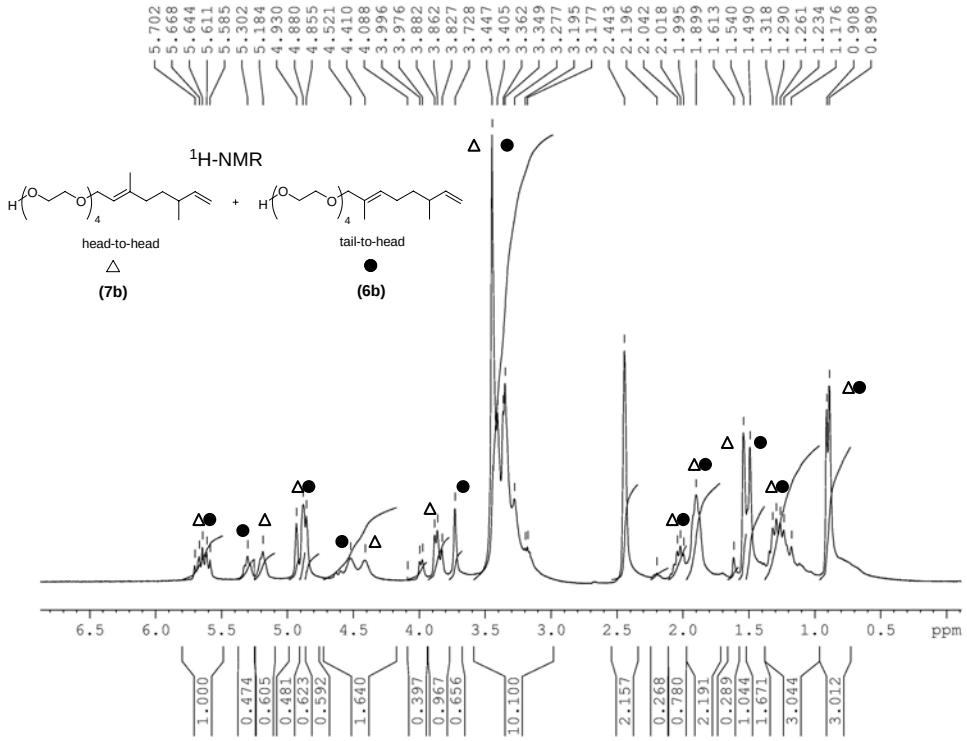


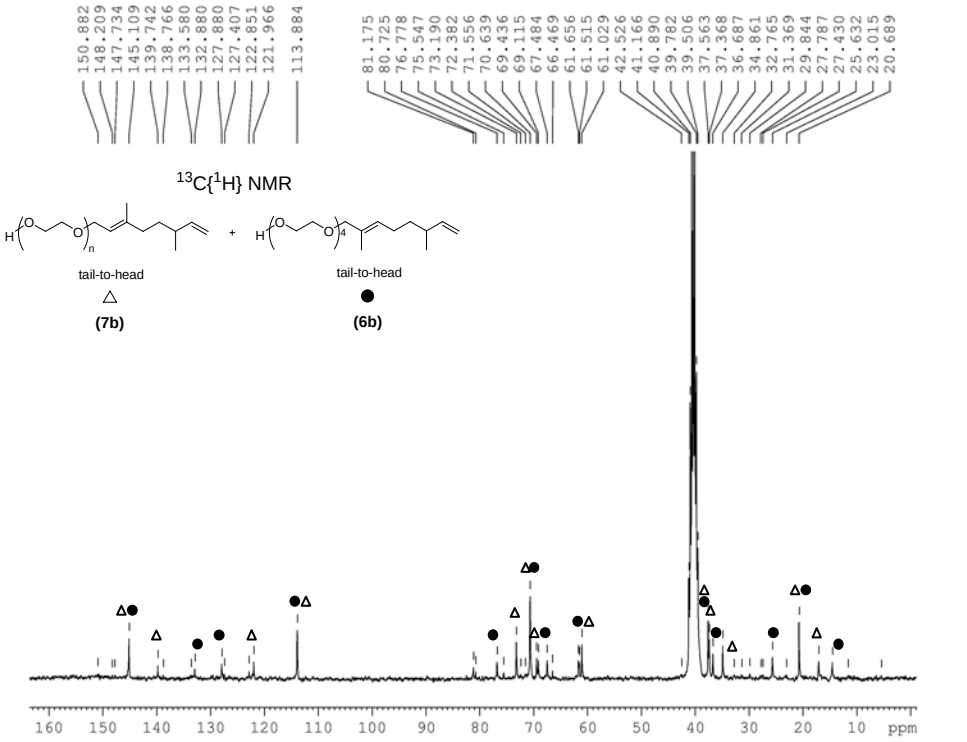
^{13}C{^{1}H} NMR

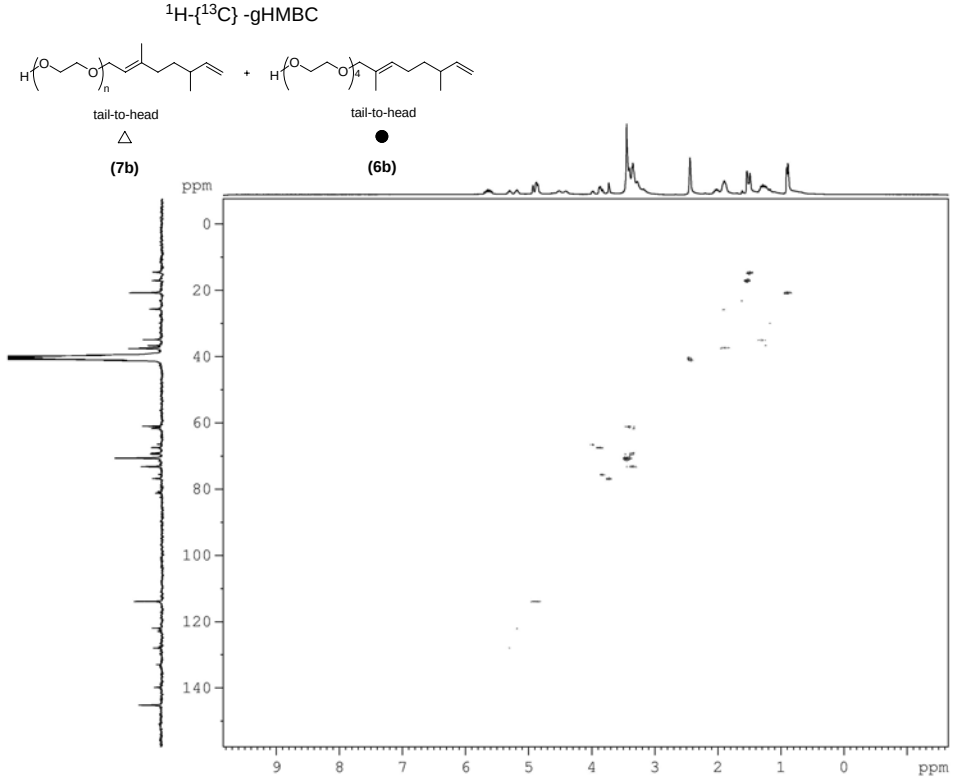
(6b)

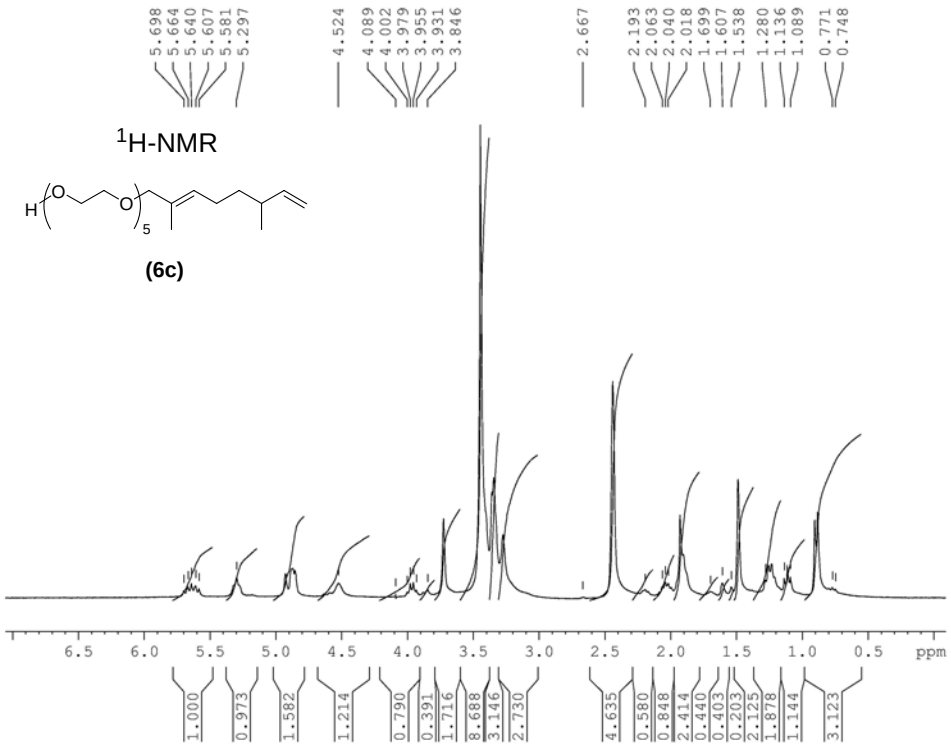
^{1}H-{^{13}C} -gHMBC

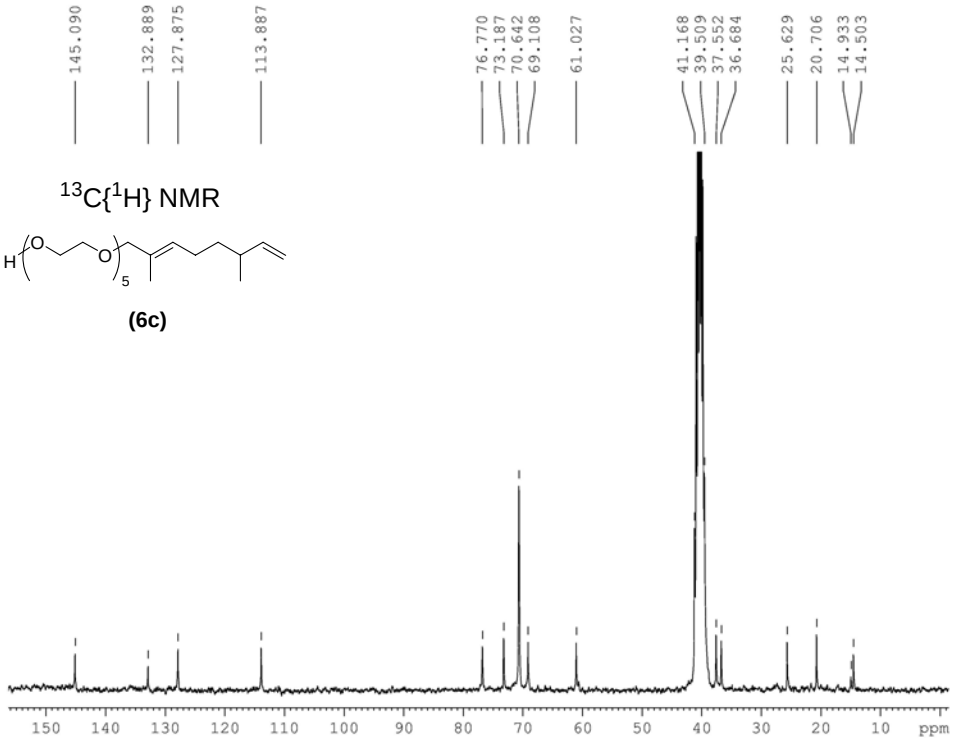

(6b)
ppm
0
20
40
60
80
100
120
140
9
8
7
6
5
4
3
2
1
0
−1
ppm

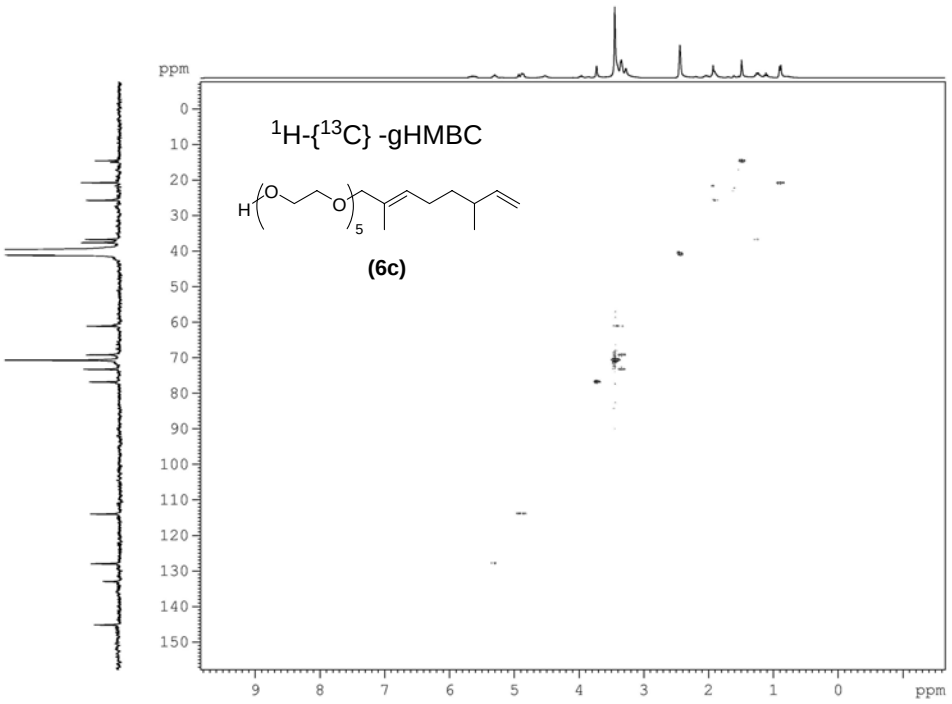

5.702
5.668
5.644
5.611
5.585
5.302
5.184
4.930
4.880
4.855
4.521
4.410
4.088
3.996
3.976
3.882
3.862
3.827
3.728
3.447
3.405
3.362
3.349
3.277
3.195
3.177
2.443
2.196
2.042
2.018
1.995
1.899
1.613
1.540
1.490
1.318
1.290
1.261
1.234
1.176
0.908
0.890
^{1}H-NMR
head-to-head
(7b)
tail-to-head
(6b)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
0.474
0.605
0.481
0.623
0.592
1.640
0.397
0.967
0.656
10.100
2.157
0.268
0.780
2.191
0.289
1.044
1.671
3.044
3.012


150.882
148.209
147.734
145.109
139.742
138.766
133.580
132.880
127.880
127.407
122.851
121.966
113.884
81.175
80.725
76.778
75.547
73.190
72.382
71.556
70.639
69.436
69.115
67.484
66.469
61.656
61.515
61.029
42.526
41.166
40.890
39.782
39.506
37.563
37.368
36.687
34.861
32.765
31.369
29.844
27.787
27.430
25.632
23.015
20.689
13C{1H} NMR
tail-to-head
(7b)
tail-to-head
(6b)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


1H-{13C} -gHMBC
tail-to-head
(7b)
tail-to-head
(6b)
ppm
0
20
40
60
80
100
120
140
9 8 7 6 5 4 3 2 1 0 ppm


5.698
5.664
5.640
5.607
5.581
5.297
4.524
4.089
4.002
3.979
3.955
3.931
3.846
2.667
2.193
2.063
2.040
2.018
1.699
1.607
1.538
1.280
1.136
1.089
0.771
0.748
1H-NMR
H
O
O
5
(6c)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
0.973
1.582
1.214
0.790
0.391
1.716
8.688
3.146
2.730
4.635
0.580
0.848
2.414
0.440
0.403
0.203
2.125
1.878
1.144
3.123


145.090
132.889
127.875
113.887
76.770
73.187
70.642
69.108
61.027
41.168
39.509
37.552
36.684
25.629
20.706
14.933
14.503
13C{1H} NMR
H
O
O
5
(6c)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
^{1}H-{^{13}C} -gHMBC
H
O
O
5
(6c)
9
8
7
6
5
4
3
2
1
0
ppm