Supporting Information

Facile and Efficient Chemical Functionalization of Aliphatic Polyesters by Cross Metathesis

Lucie Fournier, Carine Robert, Sylvie Pourchet, Alice Gonzalez, Lewis Williams, Joëlle Prunet & Christophe M. Thomas

1. **General Considerations**

All manipulations requiring a dry atmosphere were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Toluene and THF were freshly distilled from sodium under argon and all solvents were degassed thoroughly by freeze–thaw–vacuum cycles prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance300 or a Bruker Avance400 spectrometers at 297 K at 300 MHz and 75 MHz or 400 MHz and 100 MHz, respectively and referenced to the residual solvent peaks. Size exclusion chromatography (SEC) was performed in THF at 35 °C using an Agilent 1260 Infinity Series GPC (ResiPore 3 µm, 300 ×7.5 mm, 1.0 mL min-1, UV (250 nm) and RI (PLGPC 220) detectors. The number of average molecular masses (M_n) and polydispersity index (M_w/M_n) of the polymers were calculated with reference to a universal calibration *vs*. polystyrene standards (limits M_w = 200 to 400 000 g mol^{-1}). Glass transition temperatures (T_g) were determined by differential scanning calorimetry (Perkin Elmer Pyris DSC 6). Experiments were performed under nitrogen with a sample mass of 15 ±5 mg. Samples were heated from -60°C to 220°C at a heating rate of 10°C/min.

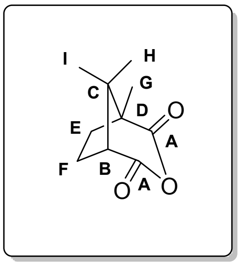
2. **Materials**

Limonene oxide (mixture of *cis* and *trans*), allyl glycidyl ether, isoprene monoxide, 1,2-epoxy-5-hexene (all purchased from Aldrich) were stirred over calcium hydride, put through three freeze-pump-thaw cycles, then vacuum transferred under argon (twice) and stored in a glove box. (1*R*,3*S*)-(+)-camphoric acid was purchased from Sigma-Aldrich, then recrystallized three times from THF/pentane or methylene chloride/diethyl ether and dried overnight under vacuum. Dimethyldicarbonate (purchased from Aldrich) was carefully stored in the freezer and used as received. (1*R*,2*R*)-(-)-[1,2,-Cyclohexanediamino-*N*,*N*'-bis(3,5-di-*t*-butylsalicylidene)] aluminium(III) chloride was purchased from Strem Chemicals and used as received in the glovebox. Bis(triphenylphosphoranylidene)ammonium chloride (purchased from Fluka) was recrystallized twice from acetone/pentane or methylene chloride/pentane, dried overnight under vacuum and then stored in the freezer of the glovebox.

3. Representative Tandem Synthesis Procedure

In the glovebox, 10 µmol of salen Al(III) chloride, 10 µmol of PPNCl (bis(triphenylphosphoranylidene)ammonium chloride), 1 mmol of camphoric acid, 110 µL of dimethyl dicarbonate (1.00 mmol, 134 mg) and 1 mL of tetrahydrofuran were placed in a Schlenk tube with a small stirring bar. The tube was closed, removed from the glovebox and heated to 40 °C in a preheated oil bath. After 1.5h, the tube was removed from the heat bath, placed under argon flux with the Schlenk line and a small aliquot was taken for crude ^{1}H NMR analysis to determine dicarboxylic acid conversion. When the conversion was complete, the solution was evaporated and dried under vacuum overnight. Then, the Schlenk tube is placed in the glovebox. Epoxide (limonene oxide, allyl glycidyl ether, isoprene monoxide, 1,2-epoxy-5-hexene) was added to the vial. For such cases, 0.8 mL of toluene is added in the Schlenk tube before the epoxide addition. The Schlenk tube was removed from the glovebox and heated to the desired temperature. After the allocated reaction time, the Schlenk tube was removed from the heat bath and a small aliquot was taken for crude ^{1}H NMR analysis to determine monomer conversion. Acidic methanol was added. The mixture was then concentrated under vacuum the resulting product solubilized with methylene chloride and precipitated in pentane/diethyl ether solution three times. The operation was repeated again with some drops of hydrochloric acid to remove [PPN]Cl salts.

A. Camphoric anhydride



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	172.0; 170.0
B	2.84	54.3
C	-	53.8
D	-	43.7
E	2.24; 2.13; 1.98	33.4
F	2.24; 2.13; 1.98	24.4
G, H, I	1.27; 1.10; 1.00	20.7; 20.2; 14.1

Figure S1: ^{1}H NMR Spectrum of Camphoric Anhydride (300 MHz, $CDCl_3$)

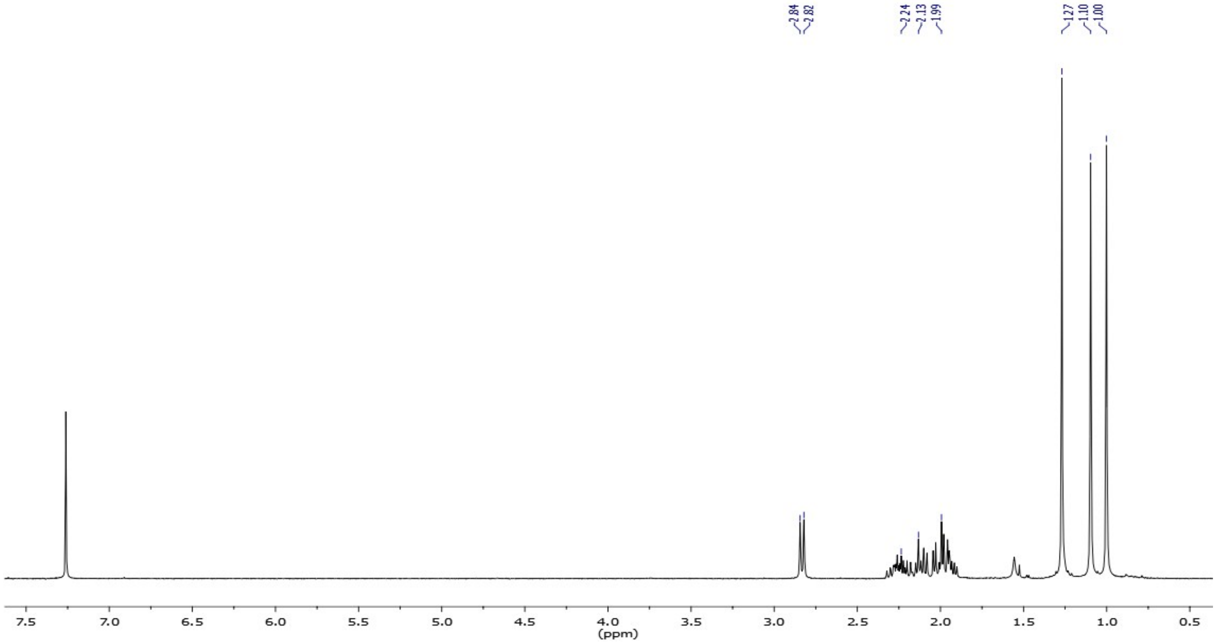
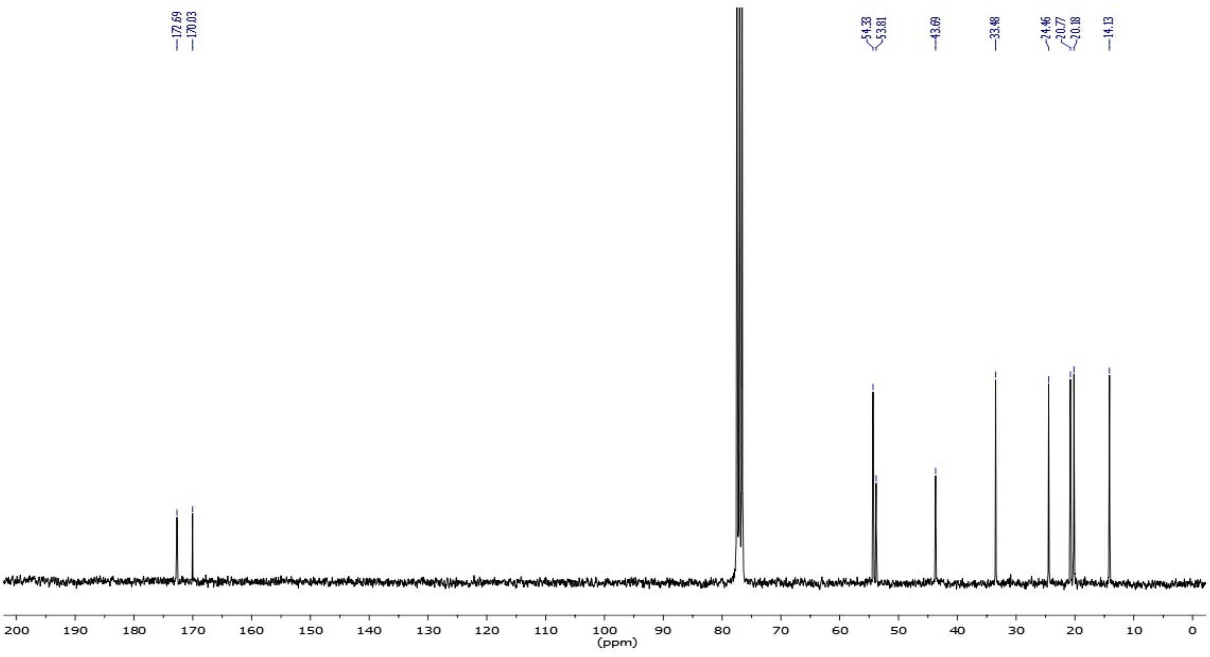
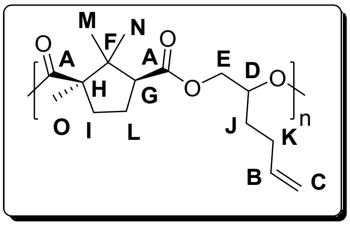


Figure S2: ^{13}C{^{1}H} NMR Spectrum of Camphoric Anhydride (75 MHz, $CDCl_3$)



B. Poly(5-epoxyhexene camphorate)



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	175.2; 174.8; 173.5; 173.1
B	5.78	136.9
C	5.10-4.98	115.7
D	5.10-4.98	111.0
E	4.05-4.25	64.8
F	-	56.3
G	2.93	54.0
H	-	46.8
I	2.77; 1.5	32.4
J	1.72	30.0-29.3
K	2.10	30.0-29.3
L, M, N, O	1.3-0.5	23.0-19.1

Figure S3: ^{1}H NMR spectrum of poly(5-epoxyhexene camphorate) (300 MHz, $CDCl_3$)

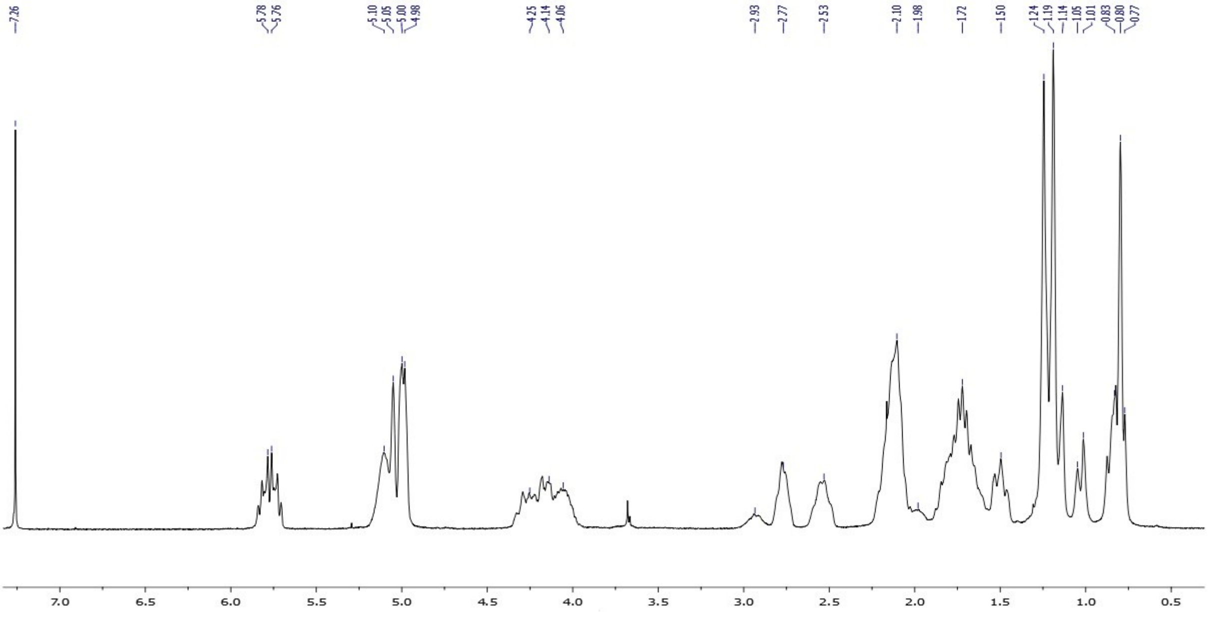
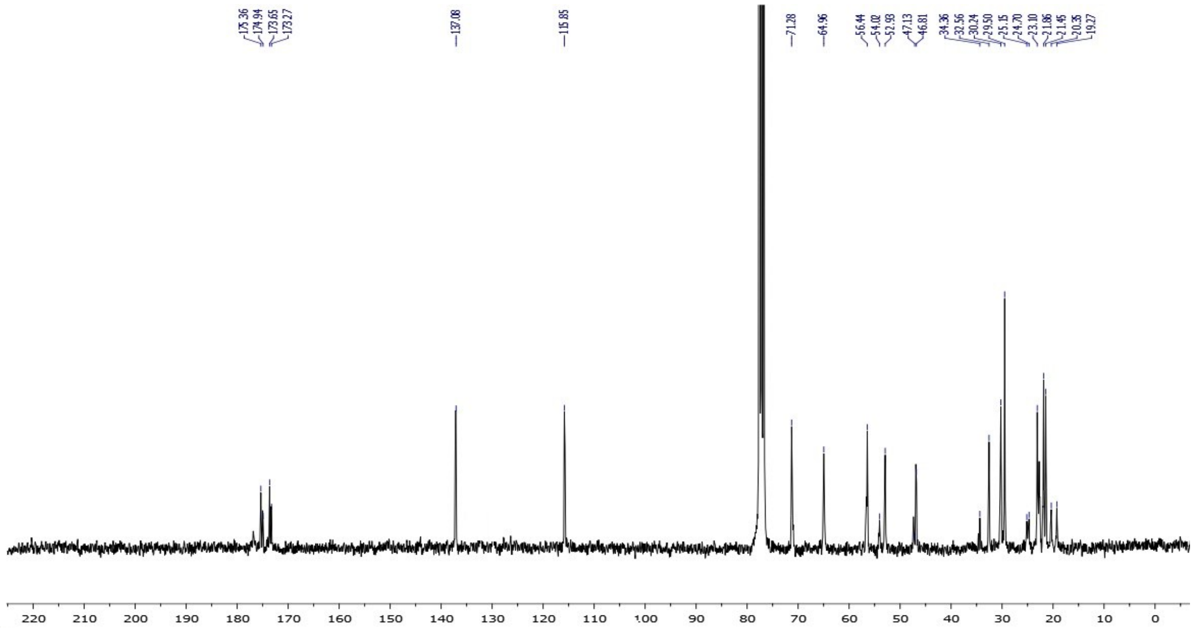
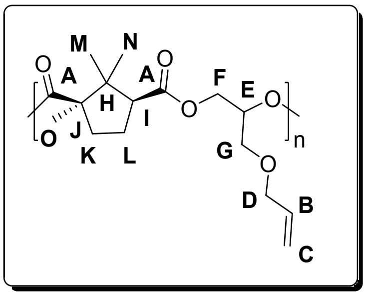


Figure S4: $^{13}C\{^1H\}$ NMR spectrum of poly(5-epoxyhexene camphorate) (75 MHz, $CDCl_3$)



C. Poly(allyl glycidyl ether camphorate)



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	175.1; 174.72; 173.4; 173.0
B	5.83	134.1
C	5.27-5.15	117.4
D	3.98	72.1
E	5.27-5.15	70.0
F	4.3-4.16	68.3
G	3.57	62.8
H	-	56.2
I	2.8	52.7
J	-	46.8
K, L, M, N, O	1.9-0.5	32.4; 24.5-19.0

Figure S5: ^{1}H NMR spectrum of poly(allyl glycidyl ether camphorate) (300 MHz, $CDCl_3$)

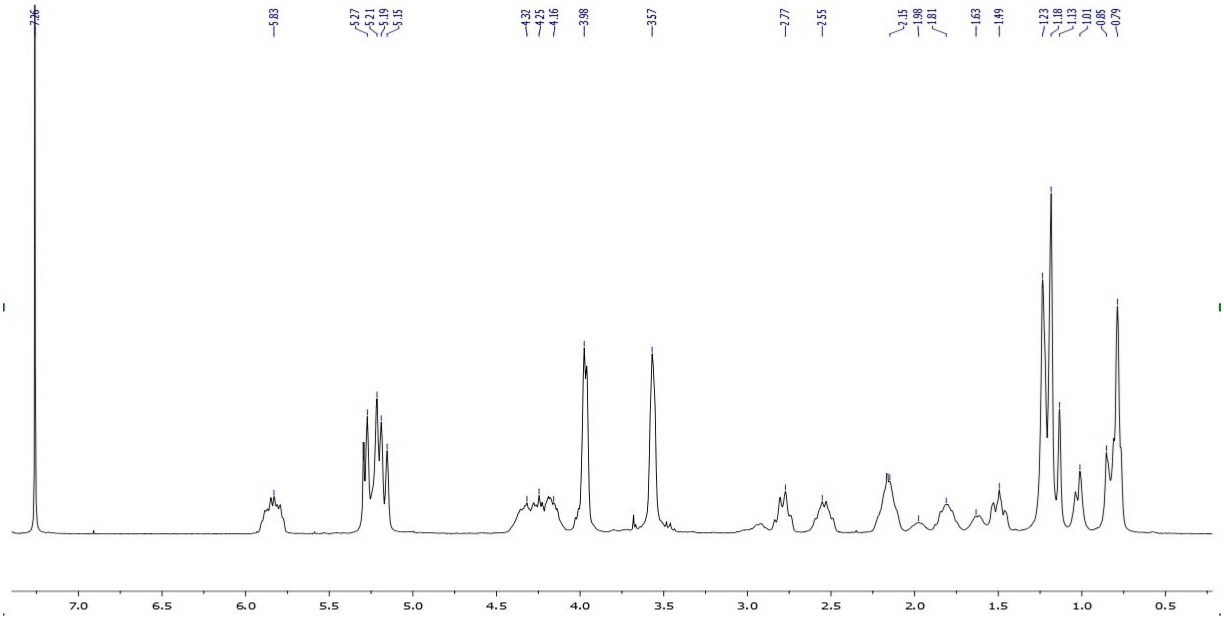
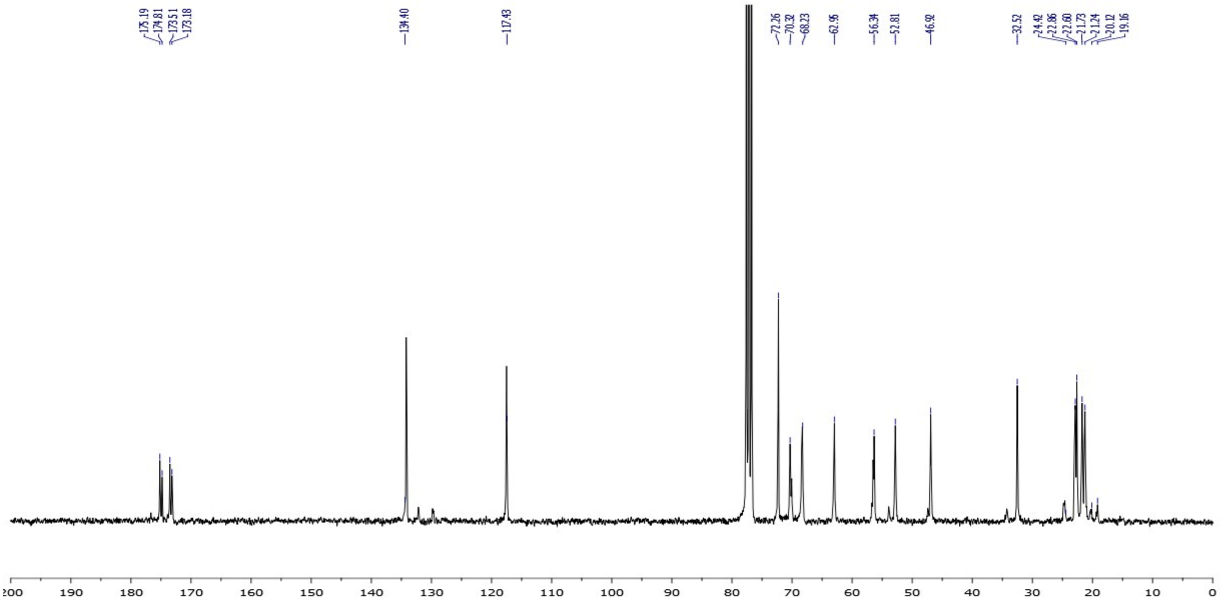
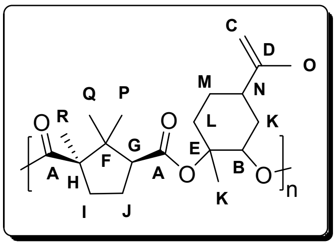


Figure S6: $^{13}C\{^1H\}$ NMR spectrum of poly(allyl glycidyl ether camphorate) (75 MHz, $CDCl_3$)



Poly(limonene camphorate)



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	174.6; 174.3; 173.1; 172.8
B	5.42-5.21	72.7
C	4.71-4.67	148.5
D	-	109.2
E	-	81.2
F	-	57.4; 56.9
G	2.79	53.5
H	-	47.0; 46.7
I	2.56; 1.42	32.6
J	2.20; 1.81	22.5
K, L, M	2.0-1.2	31.1; 25.9; 22.5
N	2.0-1.2	38.3; 38.2
O	1.48	24.0-20.0
P, Q, R	1.32; 1.22; 0.89	24.0-20.0

Figure S7: ^{1}H NMR spectrum of poly(limonene camphorate) (300 MHz, $CDCl_3$)

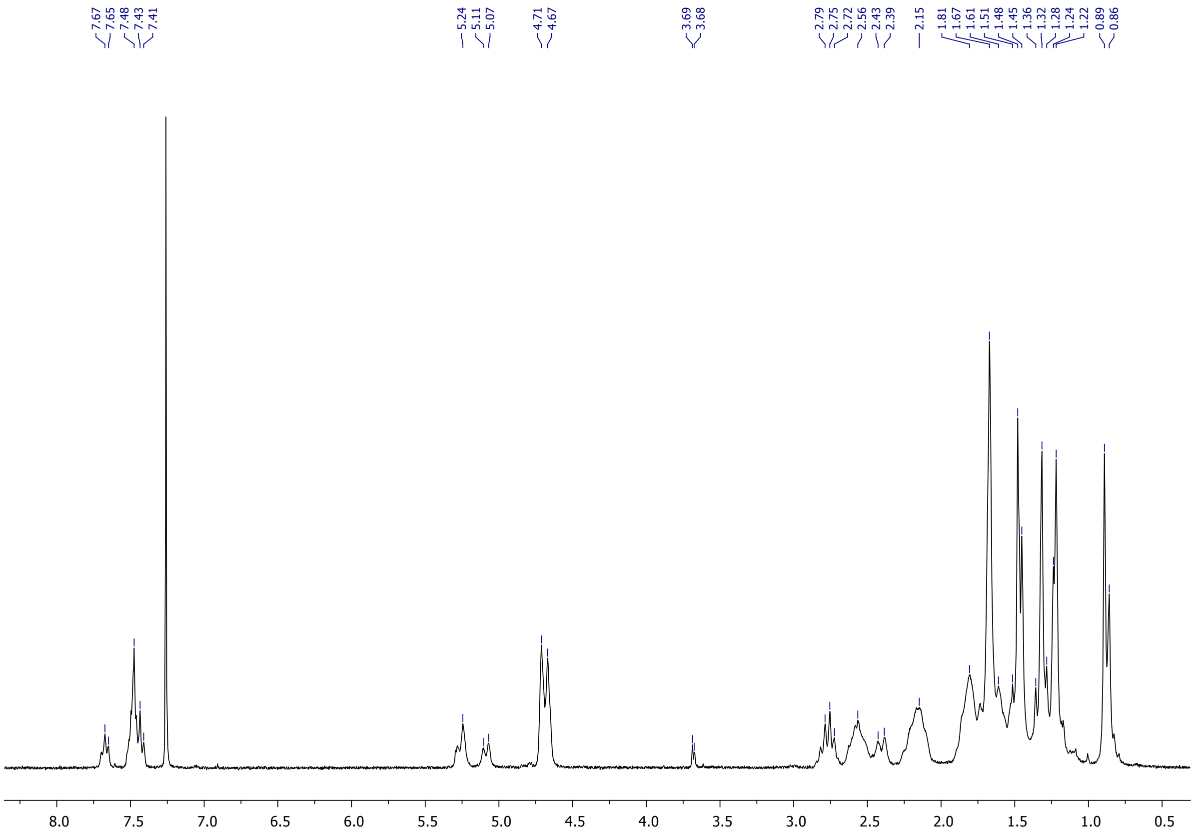
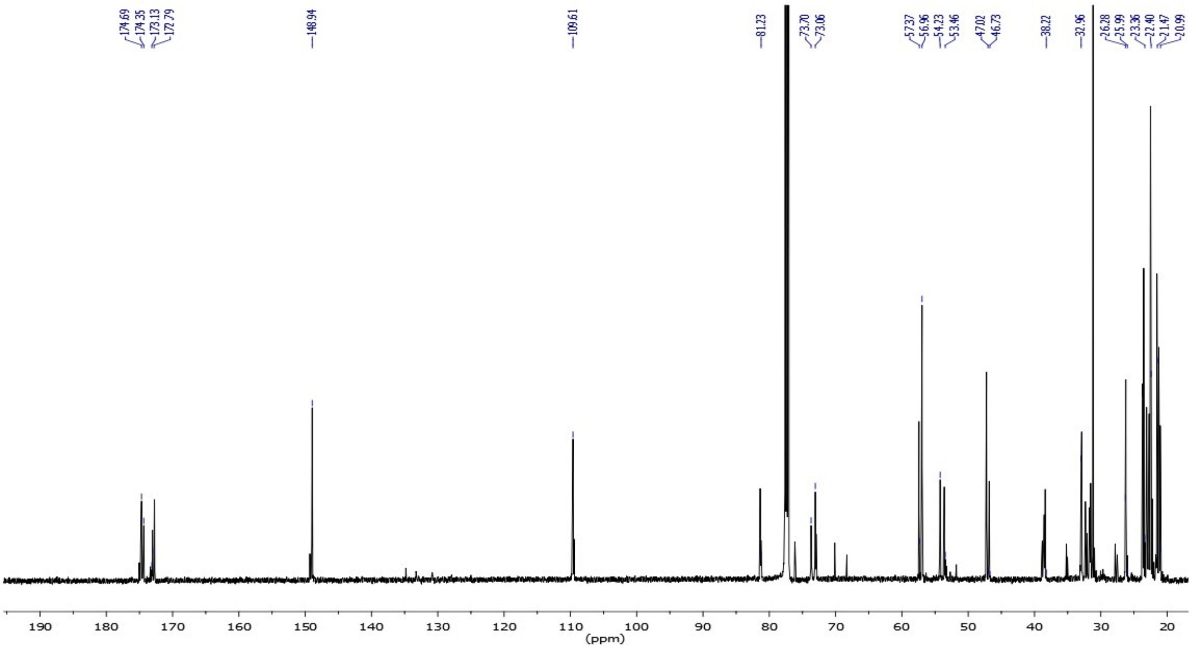
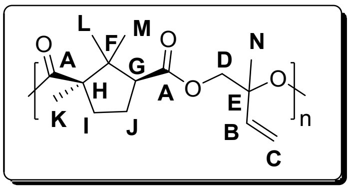


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of poly(limonene camphorate) (75 MHz, $CDCl_3$)



D. Poly(isoprene camphorate)



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	175.0; 174.1; 173.3; 172.4
B	6.01	138.5
C	5.21-5.31	115.7
D	4.3-4.27	80.6
E	-	68.4
F	-	56.4
G	2.74	53.2
H	-	46.8
I	2.5; 1.7	32.4
J	2.1; 1.5	23.5-20.0
K, L, M	1.2; 0.7	
N	1.6	23.5-20.0

Figure S9: ^{1}H NMR spectrum of poly(isoprene camphorate) (300 MHz, $CDCl_3$)

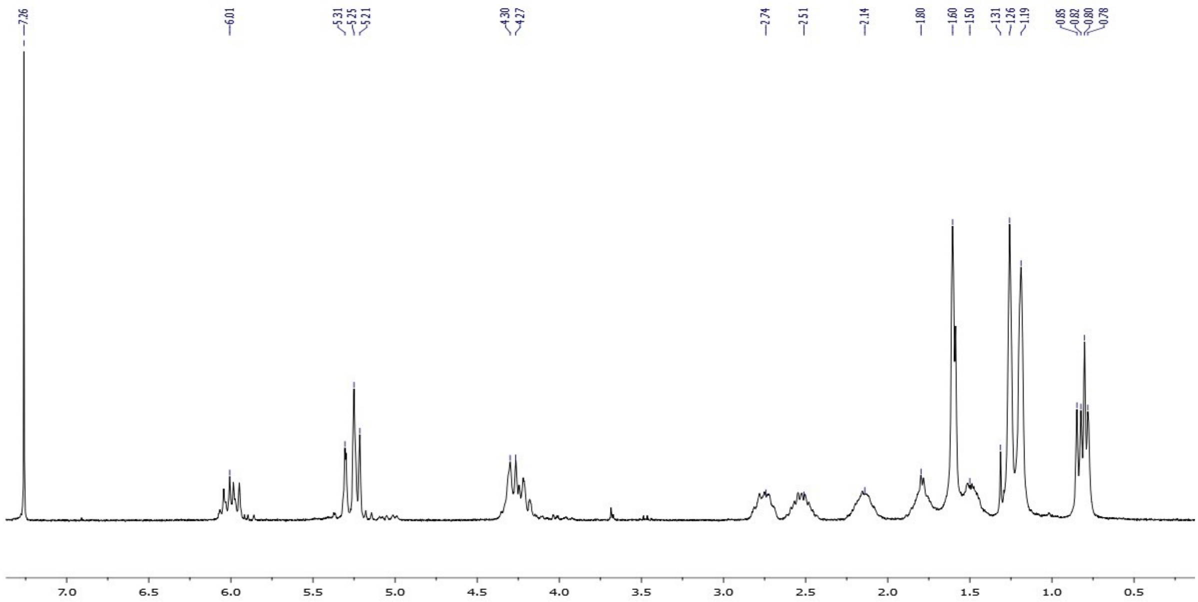
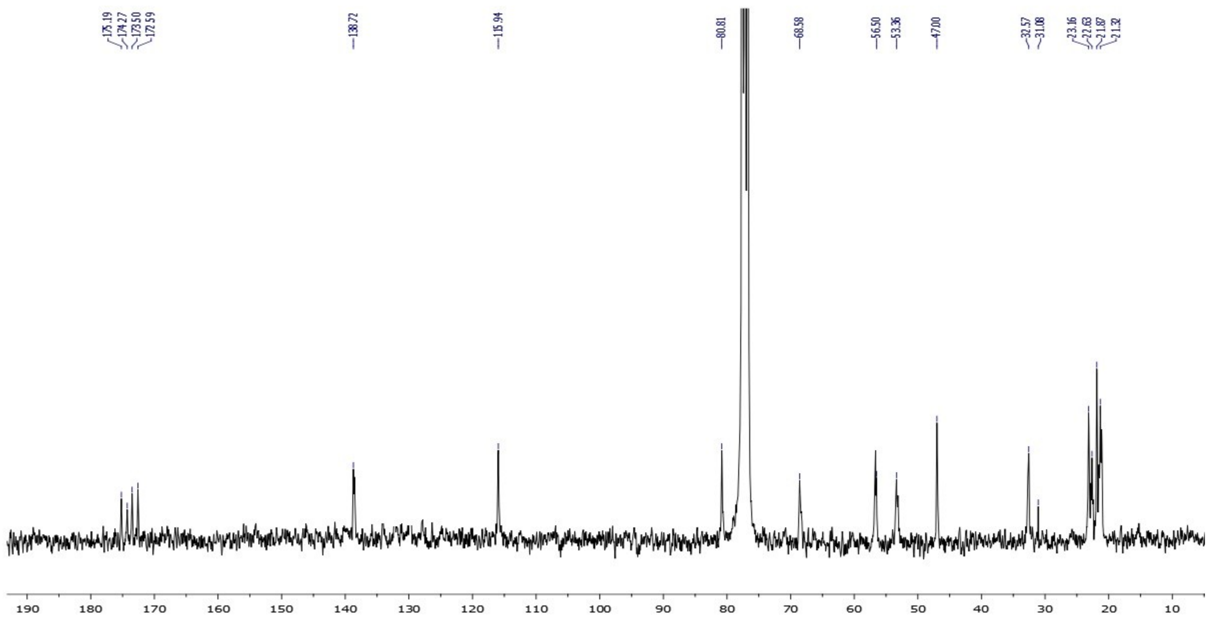


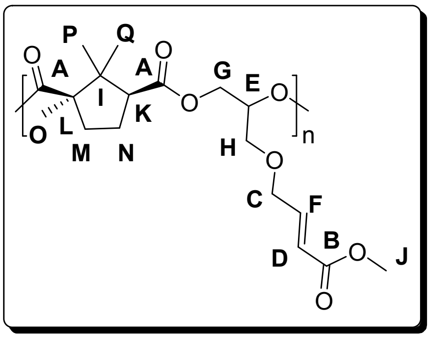
Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of poly(isoprene camphorate) (75 MHz, $CDCl_3$)



4. Representative Cross Metathesis Procedure

A dry-bottomed flask, equipped with a magnetic stirring bar, was flame-dried and charged with Hoveyda-Grubbs II catalyst (40 mg, 62 µmol), poly(allyl glycidyl ether camphorate) (100 mg, 12.5 µmol, M_n = 10000 g.mol^{-1}, 6.6 eq. of olefin moieties), 10 ml of dry methylene chloride and allyltrimethylsilane (0.40 ml, 2.5 mmol, 40 eq.). The mixture is heated at reflux and the conversion is monitored by ^{1}H NMR. The mixture was concentrated under vacuum and purified following the polymer purification procedure then analyzed by SEC and NMR.

E. Poly(allyl glycidyl ether camphorate) functionalized by MA



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	176.6-173.0
B	-	166.6
C	6.91-6.87	70.1
D	6.05-6.01	121.1
E	5.24-5.21	69.9
F	4.14	143.7
G	4.38-4.29	69.2
H	3.62	62.7
I	-	56.5
J	3.73	51.7
K	2.79-2.77	52.8
L	-	47.2
M, N	2.54-1.50	24.3; 22.4
O, P, Q	1.22-1.19; 0.78	21.1-20.7

Figure S11: ^{1}H NMR spectrum of poly(allyl glycidyl ether camphorate) functionalized by MA (300 MHz, $CDCl_3$)

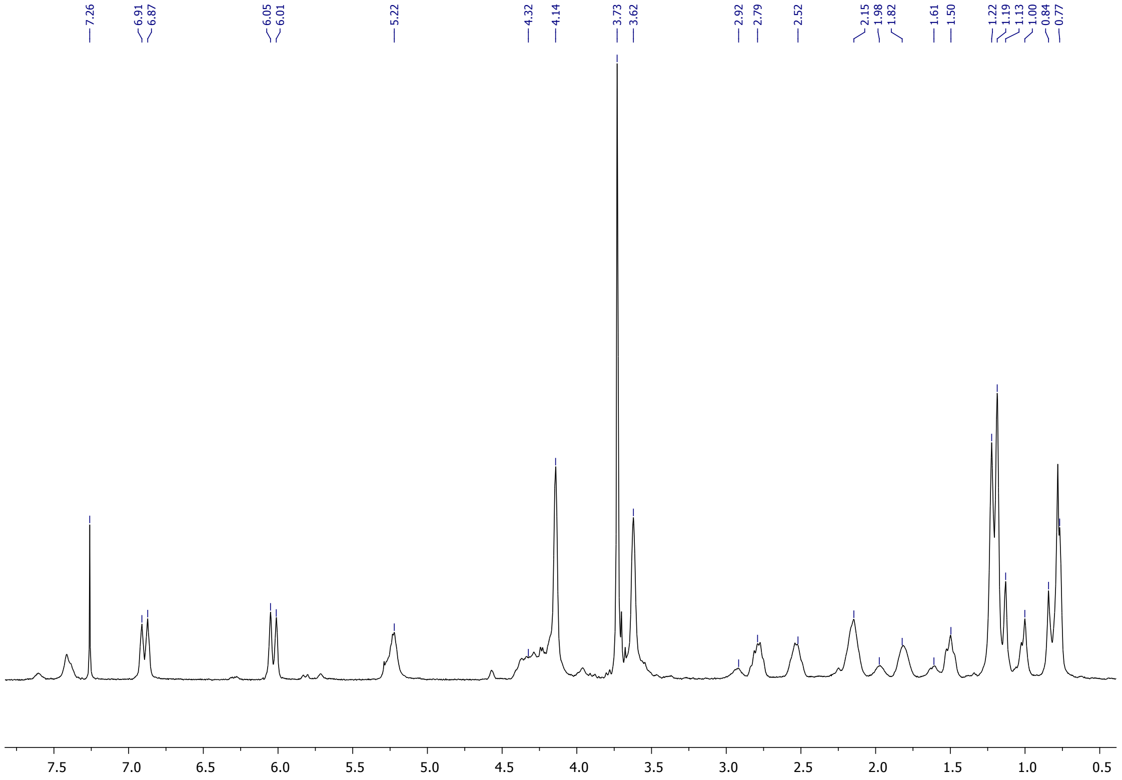
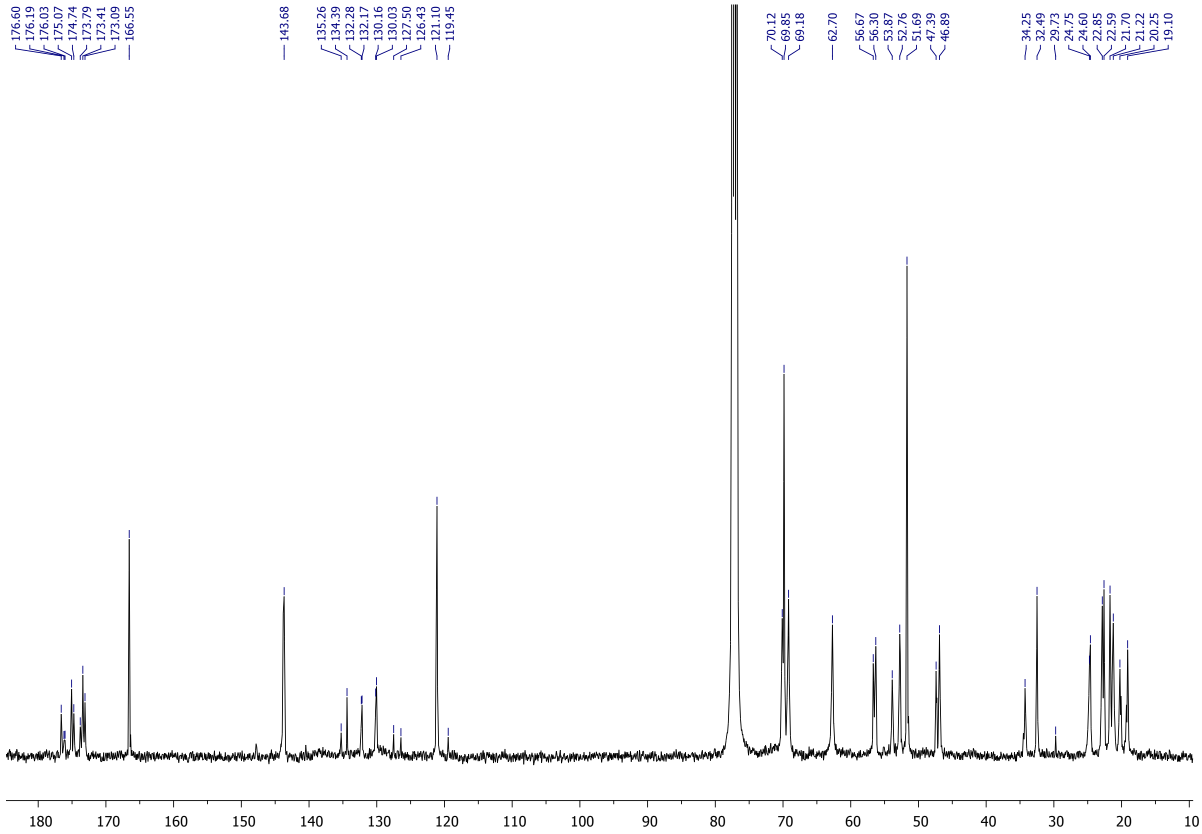
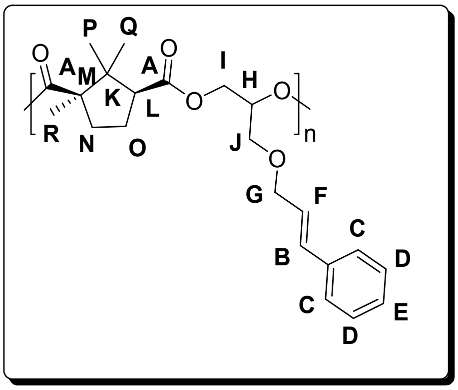


Figure S12: $^{13}C\{^1H\}$ NMR spectrum of poly(allyl glycidyl ether camphorate) functionalized by MA (75 MHz, $CDCl_3$)



Poly(allyl glycidyl ether camphorate) functionalized by SY



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	175.1-173.5
B	6.55-6.59	133
C, D, E	7.18-7.65	128.7-126.6
F	6.20	125.5
G	4.19-4.15	87.3
H	5.27-5.25	69.7
I	4.36-4.27	66.1
J	3.83	63.0
K	-	56.6
L	2.79-2.77	52.9
M	-	47.2
N, O	2.55-1.50	34.6-22.7
P, Q, R	1.23-0.79	21.8-19.2

Figure S13: ^{1}H NMR spectrum of poly(allyl glycidyl ether camphorate) functionalized by SY 1:1 *E*/*Z* mixture (300 MHz, $CDCl_3$)

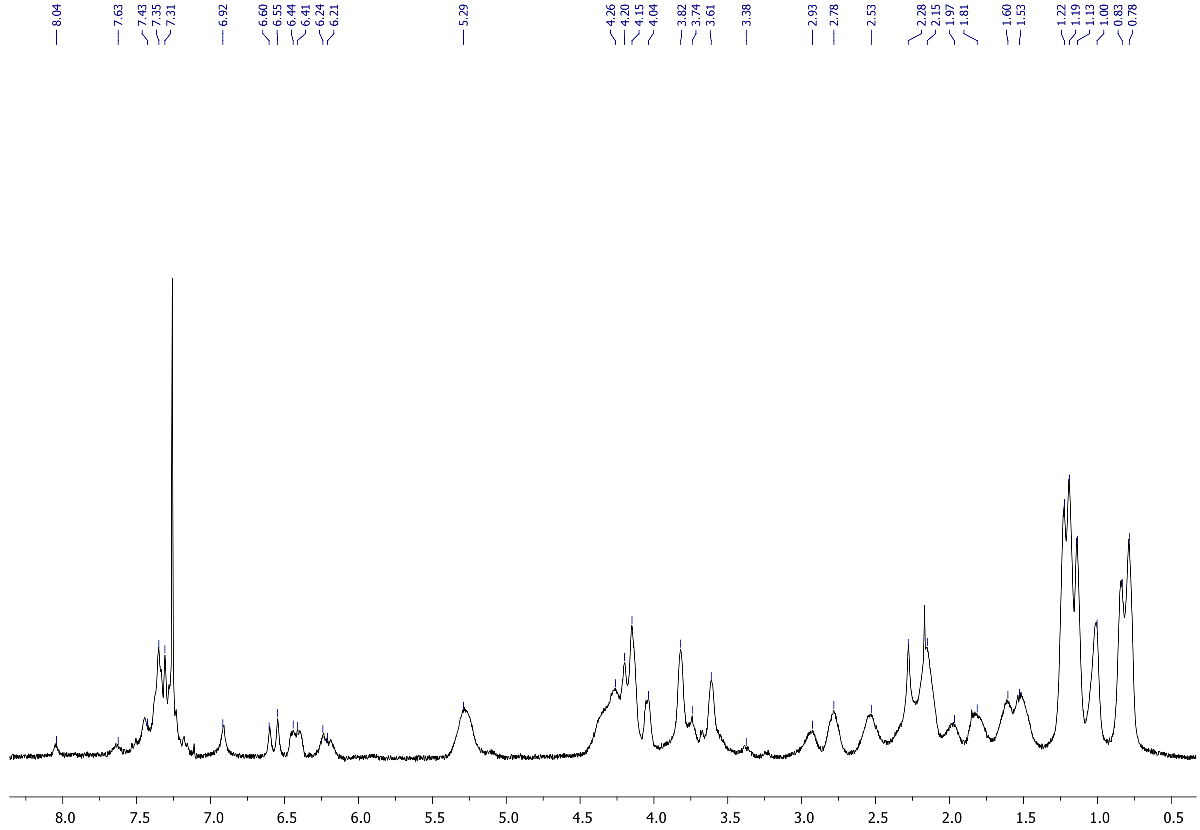


Figure S14: $^{13}C\{^1H\}$ NMR spectrum of poly(allyl glycidyl ether camphorate) functionalized by SY 1:1 *E*/*Z* mixture (75 MHz, $CDCl_3$)

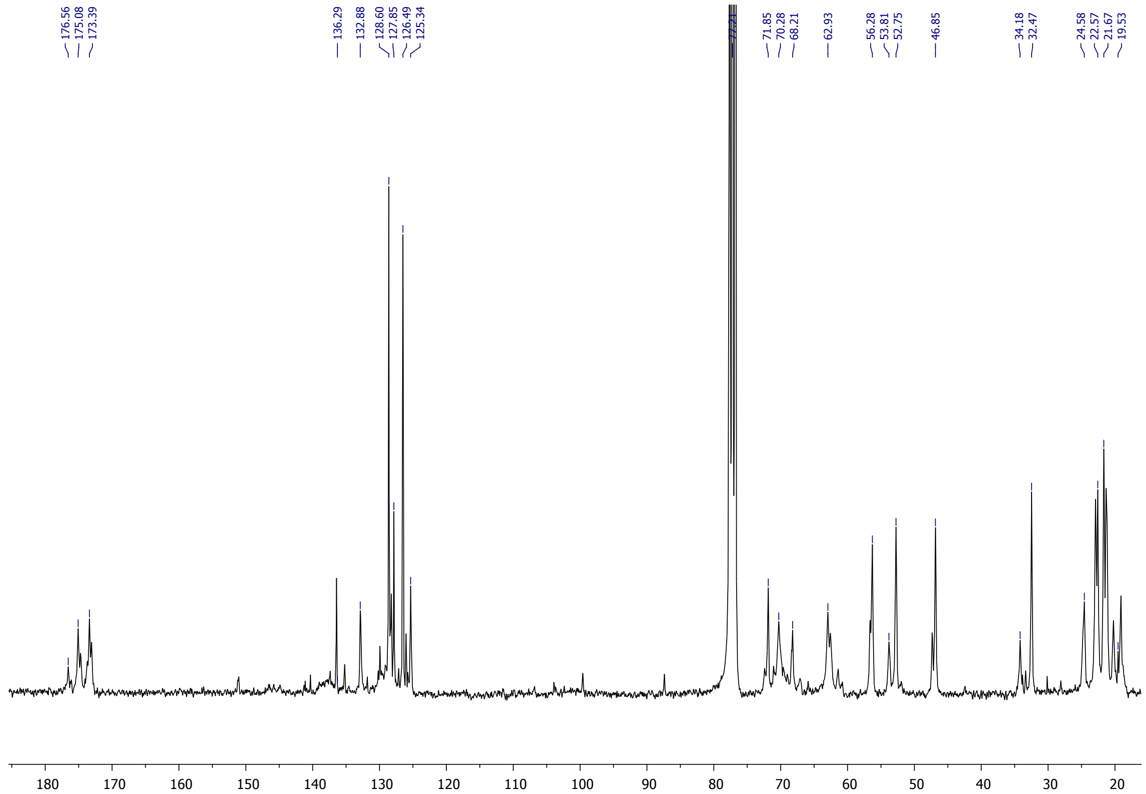
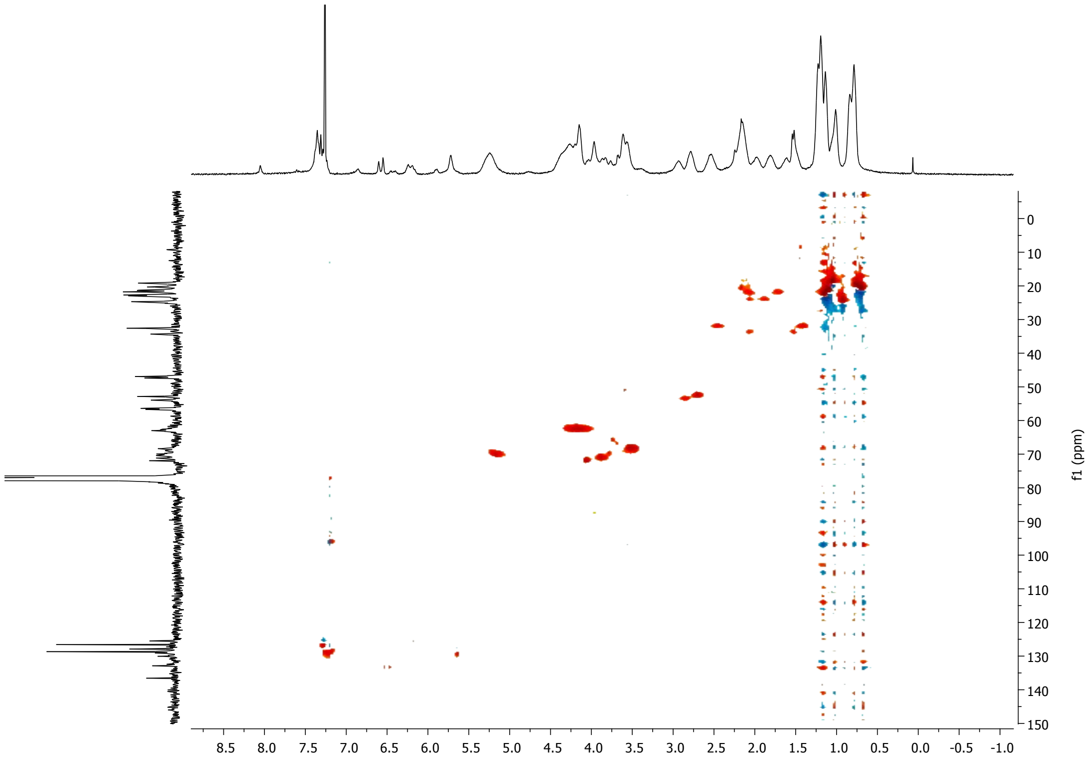
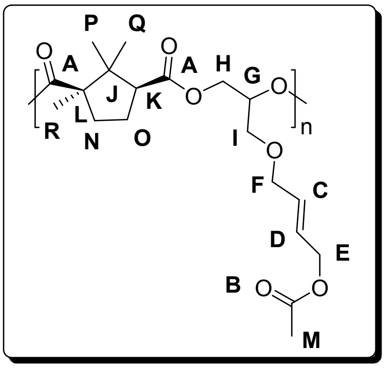


Figure S15: 2D ^{13}C-^{1}H NMR spectrum of poly(allyl glycidyl ether camphorate) functionalized by SY 1:1 *E*/*Z* mixture (75 MHz, CDCl$_3$)



Poly(allyl glycidyl ether camphorate) functionalized by AA



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	176.7-173.6
B	-	170.8
C	5.8	134.2
D	5.7	127
E	4.5	64.2
F	3.9	71.1
G	5.2	70.5
H	3.6	68.7
I	4.2	63.0
J	-	56.6
K	2.8	52.9
L	-	47.5
M	2.1	21.1
N, O, P,Q, R	1.9-0.5	32.6; 24.7-19.0

Figure S16: ^{1}H NMR spectrum of poly(allyl glycidyl ether) functionalized by AA (300 MHz, $CDCl_3$)

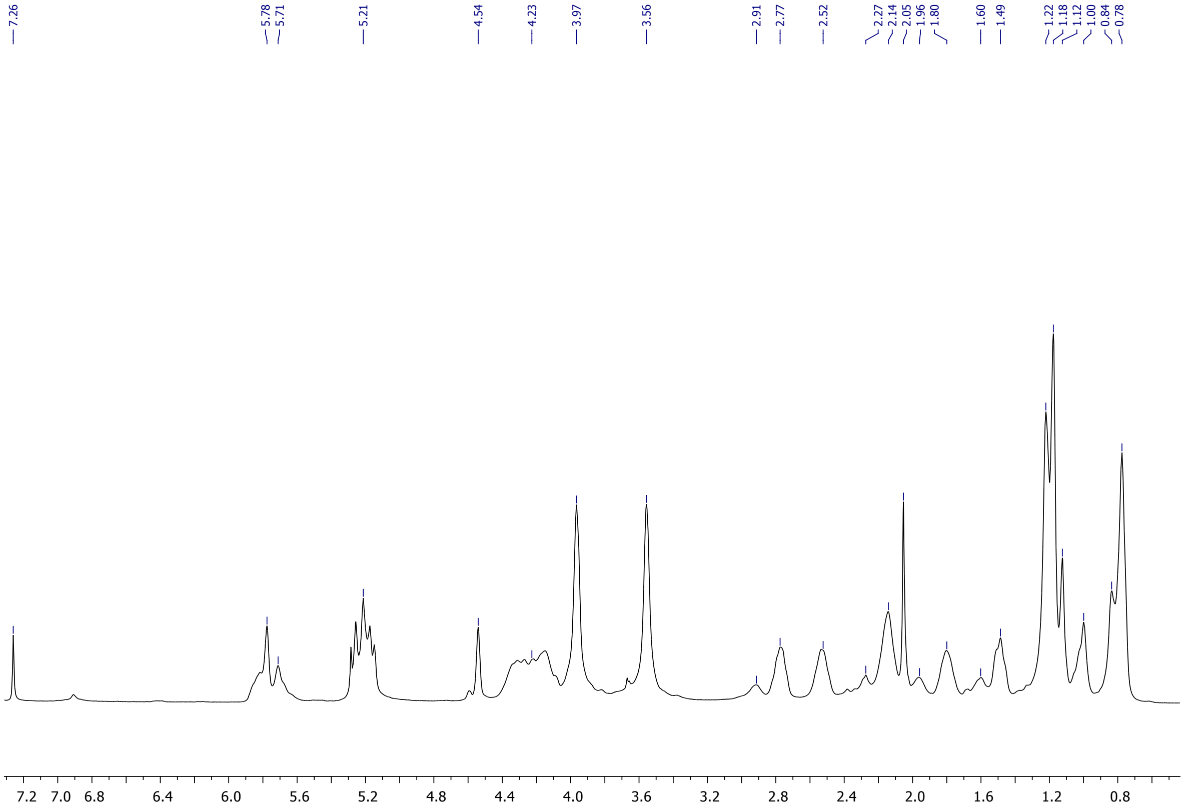


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of poly(allyl glycidyl ether) functionalized by AA (75 MHz, $CDCl_3$)

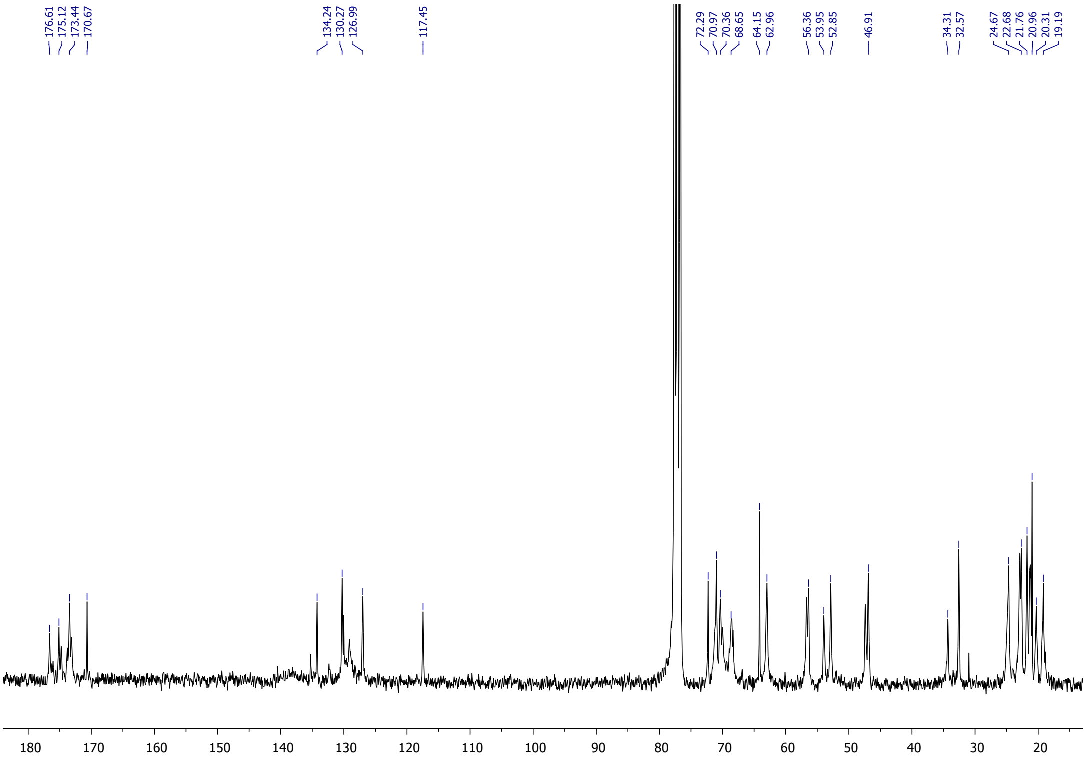
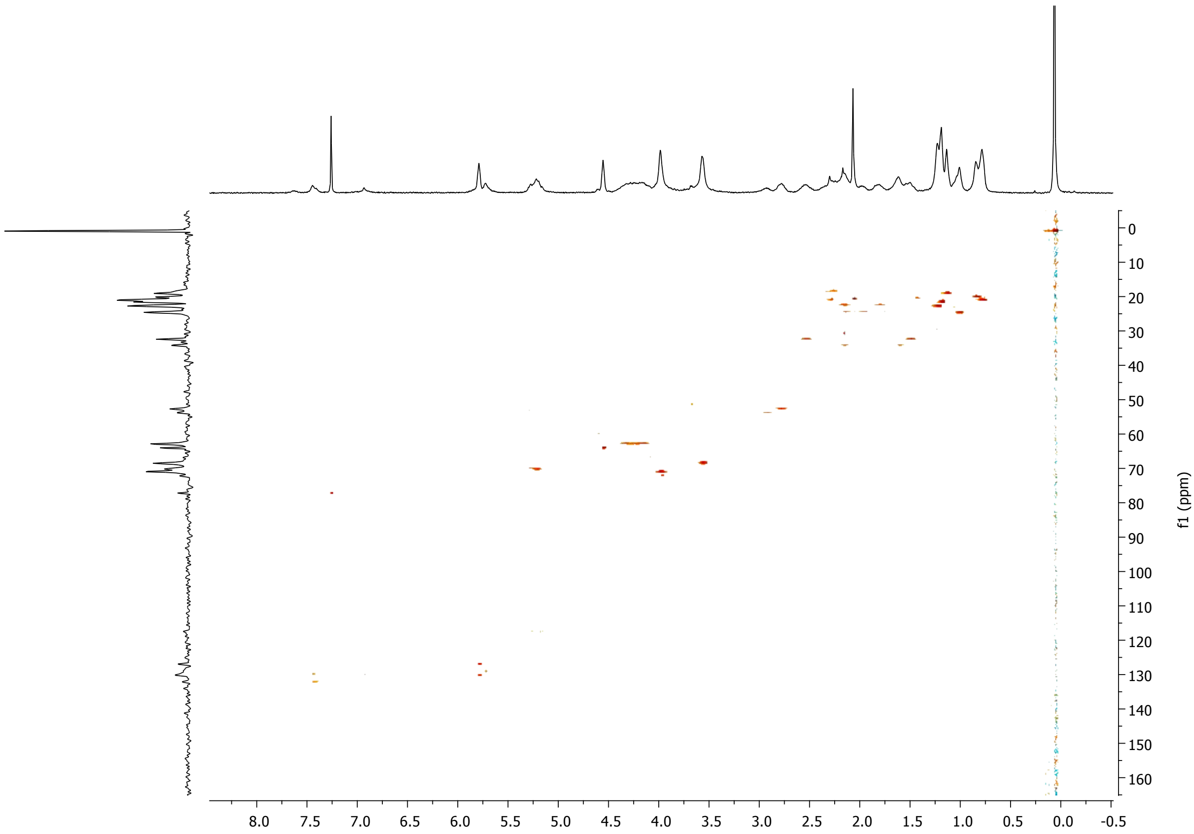
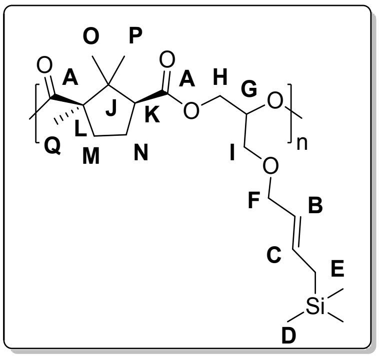


Figure S18: 2D ^{13}C-^{1}H NMR spectrum of poly(allyl glycidyl ether) functionalized by AA (75 MHz, $CDCl_3$)



Poly(allyl glycidyl ether camphorate) functionalized by ATMS



Group	^{1}H NMR (δ ppm)	^{13}C{^{1}H} NMR (δ ppm)
A	-	176.7-173.1
B	5.9	143
C	5.3	124.2
D	-0.08-0.05	-2-1.15
E	1.4	23.0
F	3.9	72.5
G	5.2	70.0
H	3.8	65.7
I	4.3	63.0
J	-	56.5
K	2.8	52.9
L	-	47.0
M, N	2.5-1.5	34.3-14.4
O, P, Q	2.2-0.7	

Figure S19: ^{1}H NMR spectrum of poly(allyl glycidyl ether) functionalized by ATMS (300 MHz, CDCl$_3$)

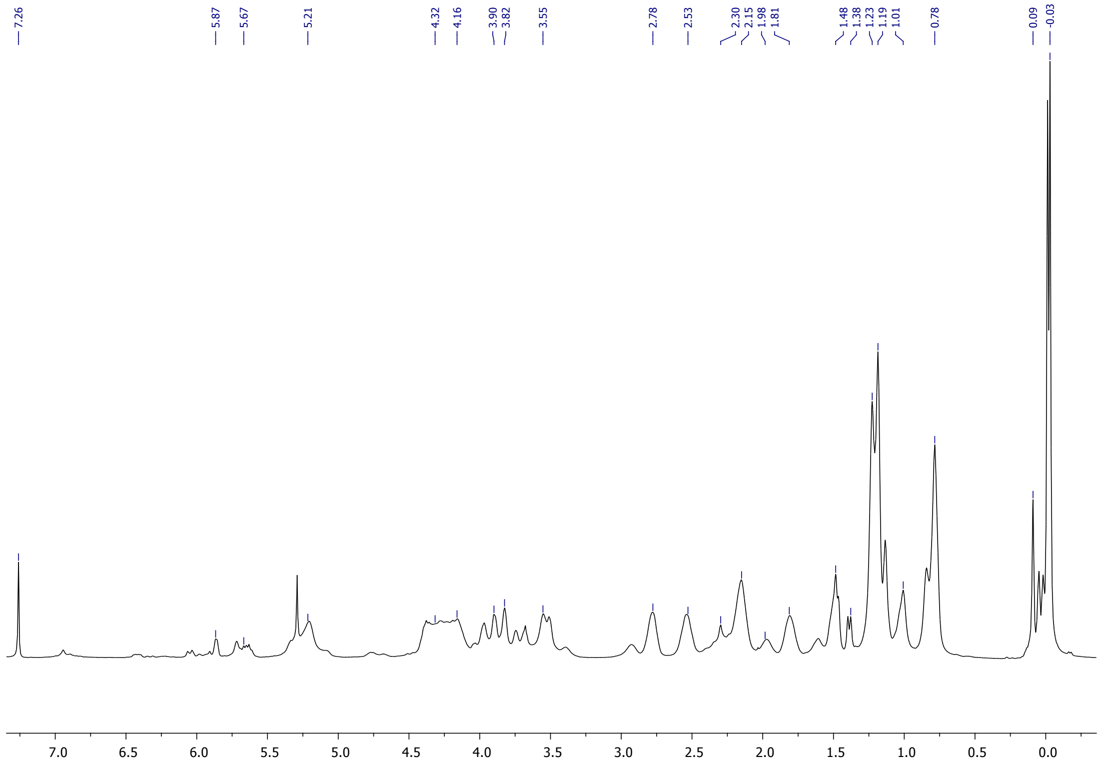


Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum of poly(allyl glycidyl ether) functionalized by ATMS (75 MHz, $CDCl_3$)

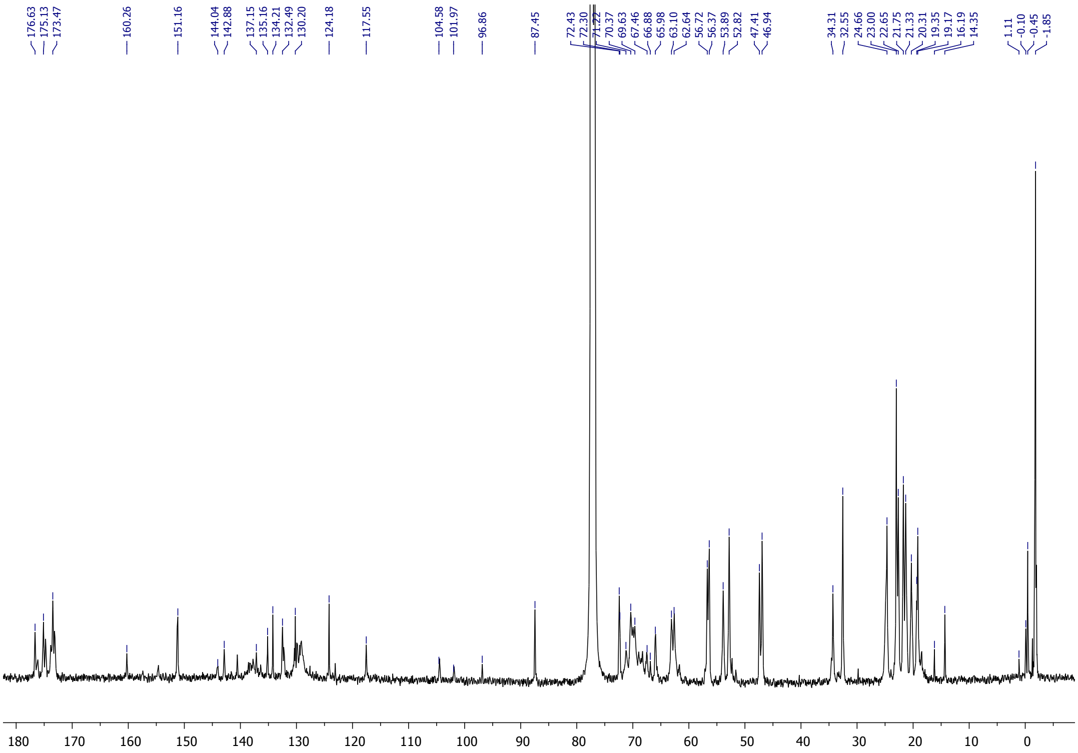
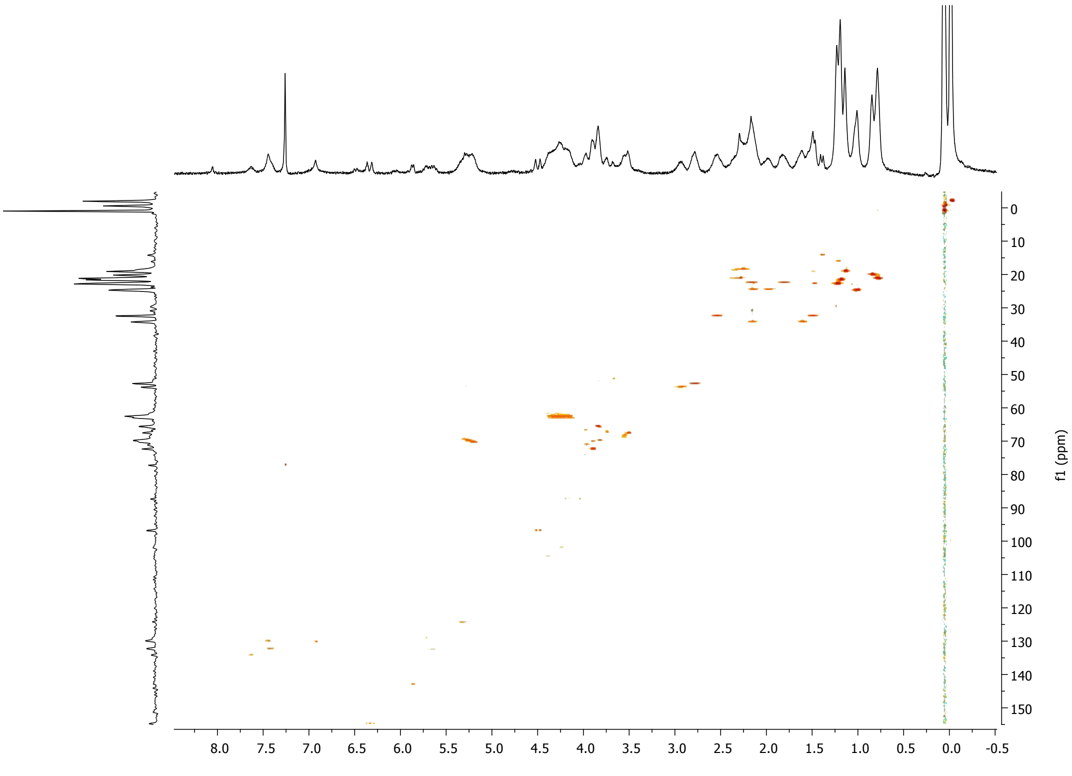
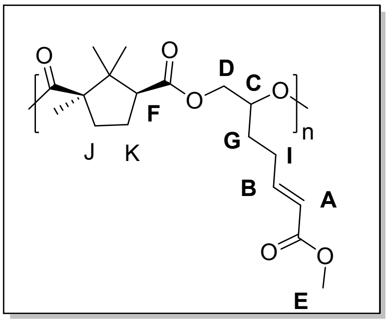


Figure S21: 2D ^{13}C-^{1}H NMR spectrum of poly(allyl glycidyl ether) functionalized by ATMS (75 MHz, $CDCl_3$)



Poly(epoxy hexene camphorate) functionalized by MA



Group	^{1}H NMR (δ ppm)
A, B	6.90; 5.80
C	5.09
D	4.15
E	3.71
F	2.76
G, I	2.0-1.6
J, K	2.5-1.5
L, M, N	1.2-0.8

Figure S22: ^{1}H NMR spectrum of poly(epoxy hexene camphorate) functionalized by MA (300 MHz, CDCl$_3$)

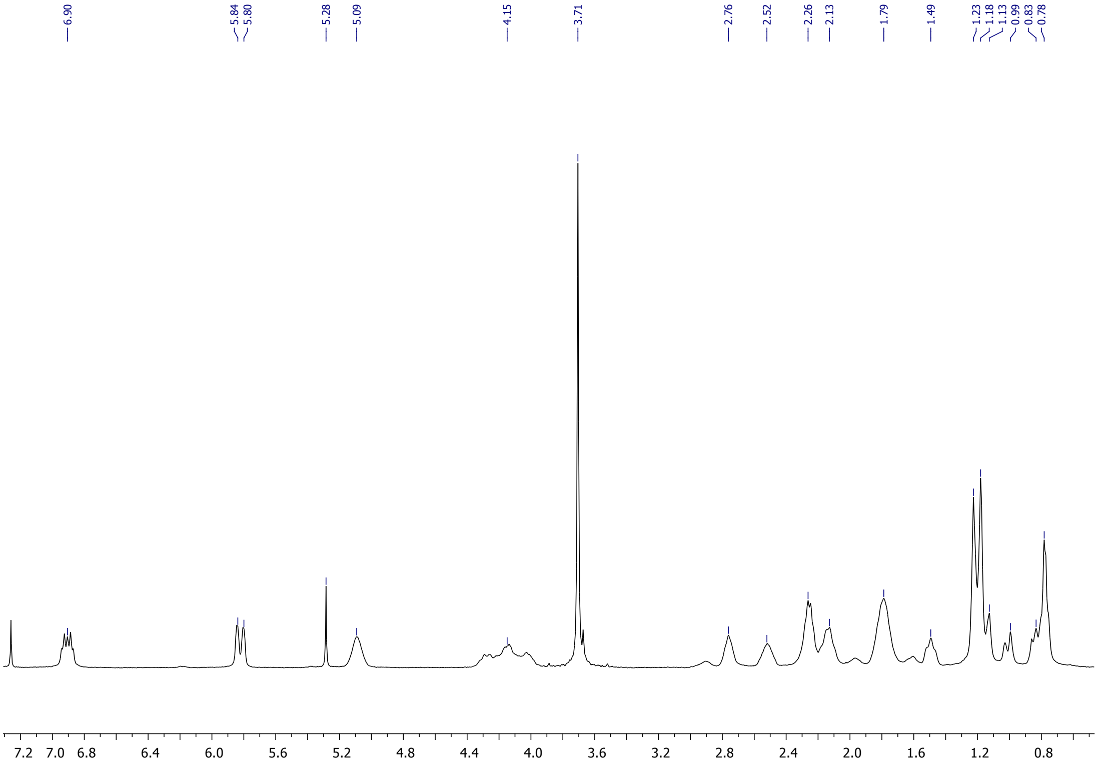
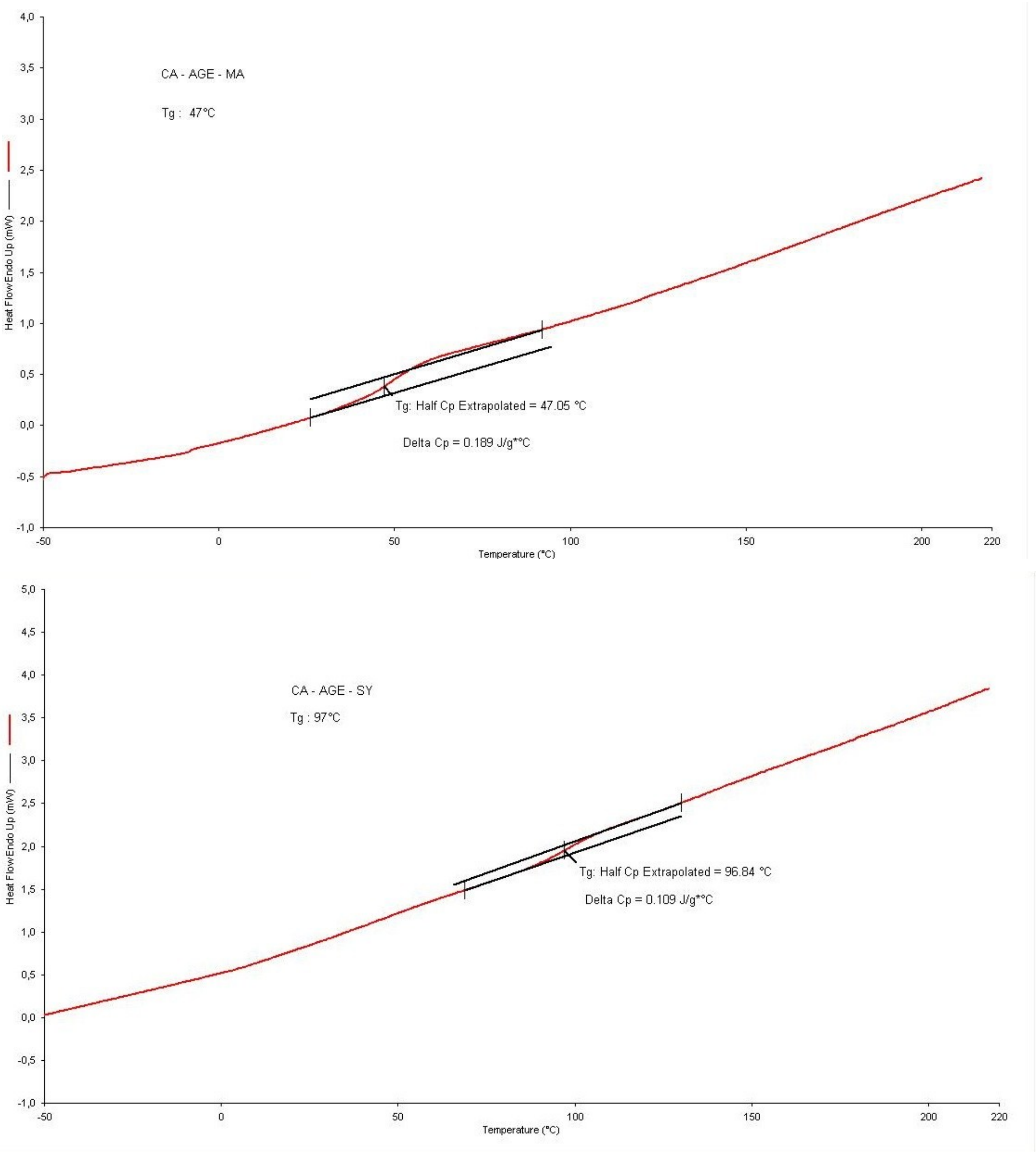
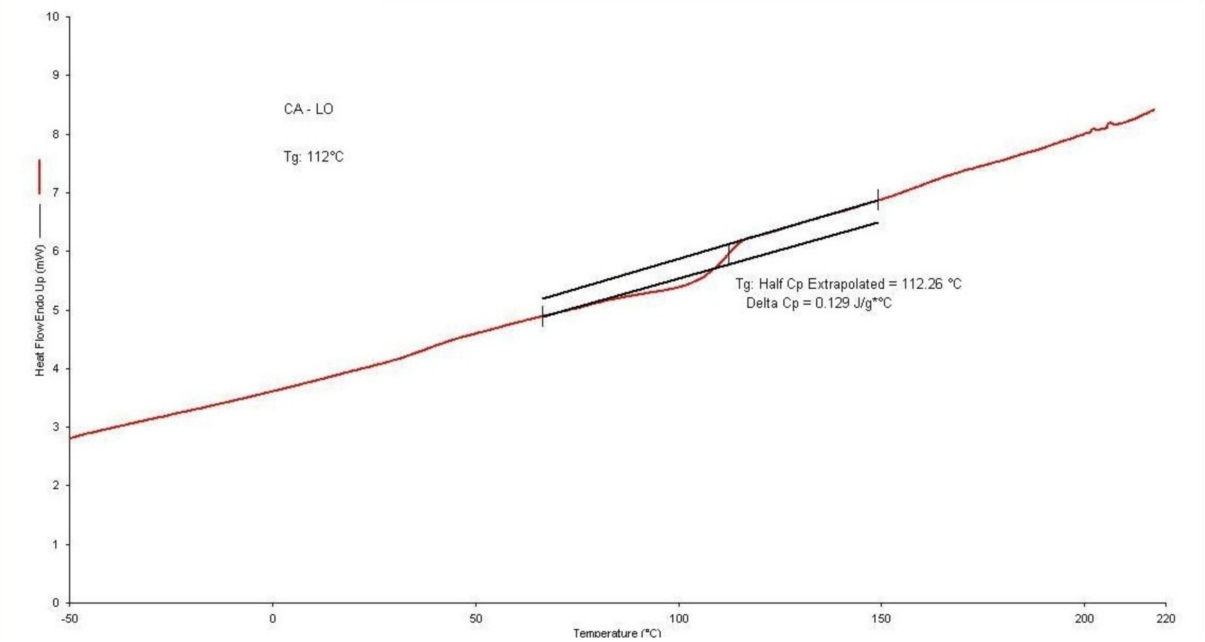
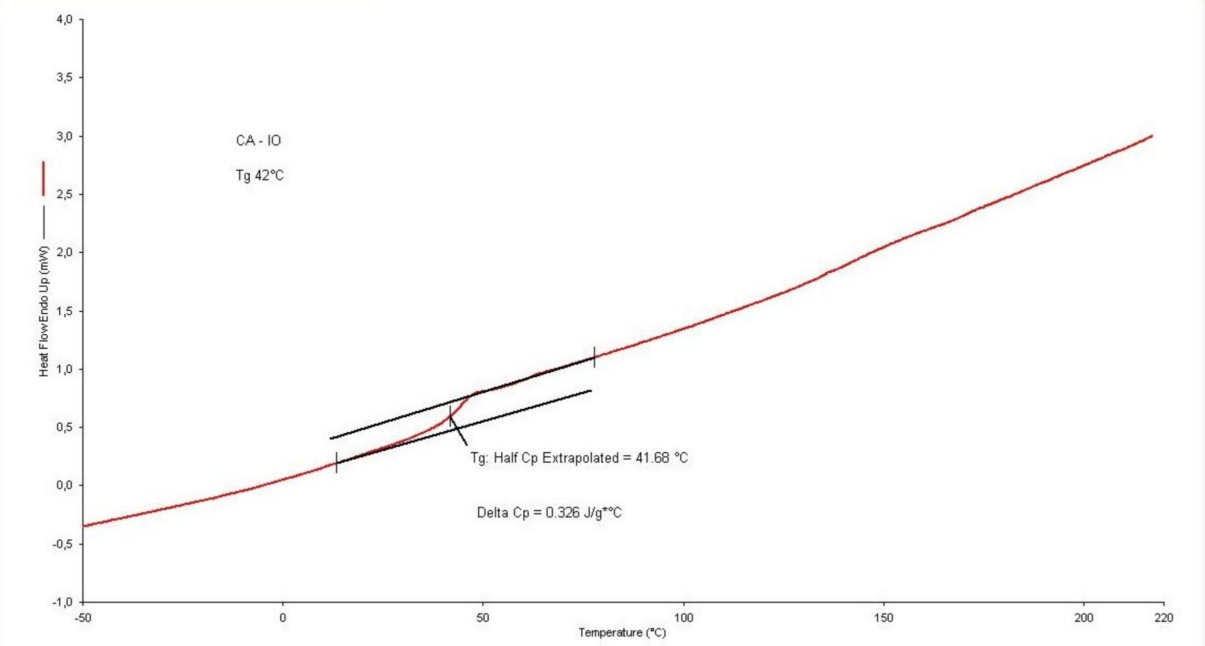


Figure S23: T_g determination by DSC analysis: typical curves obtained for different polymers.





CA - LO
Tg: 112°C
Tg: Half Cp Extrapolated = 112.26 °C
Delta Cp = 0.129 J/g*°C
Heat FlowEndo Up (mW)
Temperature (°C)
10
9
8
7
6
5
4
3
2
1
0
-50
0
50
100
150
200
220



CA - IO
Tg 42°C
Tg: Half Cp Extrapolated = 41.68 °C
Delta Cp = 0.326 J/g*°C
Heat FlowEndo Up (mW)
Temperature (°C)
4,0
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
-0,5
-1,0
-50
0
50
100
150
200
220