

Supporting information

Biomass- and calcium carbide-based recyclable polymers

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S1. Spectral data and characterization

Menthyl vinyl ether (1a)

¹H NMR (400 MHz, CDCl₃) δ 6.32 (dd, *J* = 14.1, 6.5 Hz, 1H), 4.28 (dd, *J* = 14.1, 1.3 Hz, 1H), 3.94 (dd, *J* = 6.5, 1.3 Hz, 1H), 3.52 (td, *J* = 10.7, 4.3 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.75 – 1.55 (m, 2H), 1.48 – 1.29 (m, 2H), 1.08 – 0.95 (m, 2H), 0.95 – 0.83 (m, 7H), 0.78 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 151.5, 87.7, 80.0, 47.9, 41.0, 34.6, 31.6, 26.0, 23.7, 22.3, 20.9, 16.5.

Bornyl vinyl ether (2a)

¹H NMR (400 MHz, CDCl₃) δ 6.40 (dd, *J* = 14.3, 6.7 Hz, 1H), 4.12 (dd, *J* = 14.3, 1.3 Hz, 1H), 4.01 (dt, *J* = 9.4, 2.4 Hz, 1H), 3.94 (dd, *J* = 6.7, 1.3 Hz, 1H), 2.22 (m, 1H), 2.00 (m, 1H), 1.78 – 1.70 (m, 1H), 1.70 – 1.64 (m, 1H), 1.33 – 1.16 (m, 2H), 1.07 (dd, *J* = 13.4, 3.3 Hz, 1H), 0.94 – 0.82 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 152.0, 87.1, 84.0, 49.3, 47.9, 45.2, 36.5, 28.1, 26.9, 19.9, 19.0, 13.8.

Fenchyl vinyl ether (3a)

¹H NMR (400 MHz, CDCl₃) δ 6.32 (dd, *J* = 14.1, 6.5 Hz, 1H), 4.26 (dd, *J* = 14.1, 1.3 Hz, 1H), 3.90 (dd, *J* = 6.5, 1.3 Hz, 1H), 3.36 (d, *J* = 1.5 Hz, 1H), 1.84 – 1.64 (m, 3H), 1.54 – 1.47 (m, 1H), 1.47 – 1.36 (m, 1H), 1.14 (dd, *J* = 10.2, 1.2 Hz, 1H), 1.09 (s, 3H), 1.06 (s, 3H), 1.04 – 0.98 (m, 1H), 0.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.5, 92.7, 87.3, 49.2, 48.8, 41.5, 40.1, 31.0, 26.3, 26.1, 20.5, 19.8.

Citronellyl vinyl ether (4a)

¹H NMR (400 MHz, CDCl₃) δ 6.46 (dd, *J* = 14.3, 6.8 Hz, 1H), 5.18 – 5.02 (m, 1H), 4.17 (dd, *J* = 14.3, 1.8 Hz, 1H), 3.97 (dd, *J* = 6.8, 1.8 Hz, 1H), 3.77 – 3.64 (m, 2H), 2.12 – 1.87 (m, 2H), 1.77 – 1.66 (m, 4H), 1.65 – 1.53 (m, 4H), 1.53 – 1.41 (m, 1H), 1.40 – 1.30 (m, 1H), 1.24 – 1.13 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.1, 131.4, 124.8, 86.3, 66.5, 37.3, 36.1, 29.7, 25.9, 25.6, 19.6, 17.8. HRMS (*m/z*): [M]⁺ calcd. for C₁₂H₂₂OAg, 289.0716; found 289.0714.

Javanyl vinyl ether (5a), as a mixture of two isomers

¹H NMR (400 MHz, CDCl₃) δ 6.56 – 6.45 (m, 2H), 4.19 – 4.09 (m, 2H), 3.96 – 3.93 (m, 2H), 3.45 – 3.30 (m, 4H), 1.95 – 1.80 (m, 2H), 1.48 – 1.30 (m, 3H), 1.26 – 1.15 (m, 4H), 1.15 – 1.11 (m, 6H), 1.04 (s, 7H), 1.02 – 0.97 (m, 3H), 0.89 (s, 6H), 0.80 – 0.75 (m, 6H), 0.65 – 0.524 (m, 4H), 0.52 – 0.46 (m, 2H), 0.08 – 0.01 (m, 3H), -0.01 – -0.06 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 86.1, 86.0, 77.7, 77.5, 45.1, 44.8, 41.4, 41.2, 32.5, 32.4, 31.4, 31.3, 29.6, 28.9, 22.9, 22.7, 22.6, 21.7, 21.3, 20.0, 19.8, 19.6, 19.0, 17.4, 17.4, 17.3, 16.8, 16.1, 15.5, 14.0, 13.9. HRMS (*m/z*): [M]⁺ calcd. for C₁₇H₂₈OAg, 355.1186; found 355.1194.

Myrtanyl vinyl ether (6a)

¹H NMR (400 MHz, CDCl₃) δ 6.46 (dd, *J* = 14.3, 6.8 Hz, 1H), 4.15 (dd, *J* = 14.3, 1.7 Hz, 1H), 3.95 (dd, *J* = 6.8, 1.8 Hz, 1H), 3.66 – 3.58 (m, 2H), 2.50 – 2.30 (m, 2H), 2.05 – 1.81 (m, 5H),

1.56 – 1.37 (m, 1H), 1.20 (s, 3H), 0.99 (s, 3H), 0.95 (d, $J = 9.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.3, 86.2, 73.1, 43.4, 41.5, 40.9, 38.7, 33.2, 28.1, 26.1, 23.5, 19.0. HRMS (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{12}\text{H}_{20}\text{OAg}$, 287.0560; found 287.0571.

Vinyl ether of rosaphen (7a)

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 6.48 (dd, $J = 14.3, 6.8$ Hz, 1H), 4.17 (dd, $J = 14.3, 1.7$ Hz, 1H), 3.97 (dd, $J = 6.8, 1.7$ Hz, 1H), 3.55 (dd, $J = 9.5, 6.0$ Hz, 1H), 3.47 (dd, $J = 9.5, 6.6$ Hz, 1H), 2.69 – 2.53 (m, 2H), 1.91 – 1.79 (m, 1H), 1.77 – 1.57 (m, 2H), 1.57 – 1.43 (m, 1H), 1.31 – 1.15 (m, 1H), 0.96 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.3, 142.7, 128.5, 128.4, 125.8, 86.2, 73.4, 36.3, 33.3, 33.1, 29.0, 17.1. HRMS (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{14}\text{H}_{20}\text{OAg}$, 311.0565; found, 311.0556.

S2. NMR spectra of the vinyl ethers

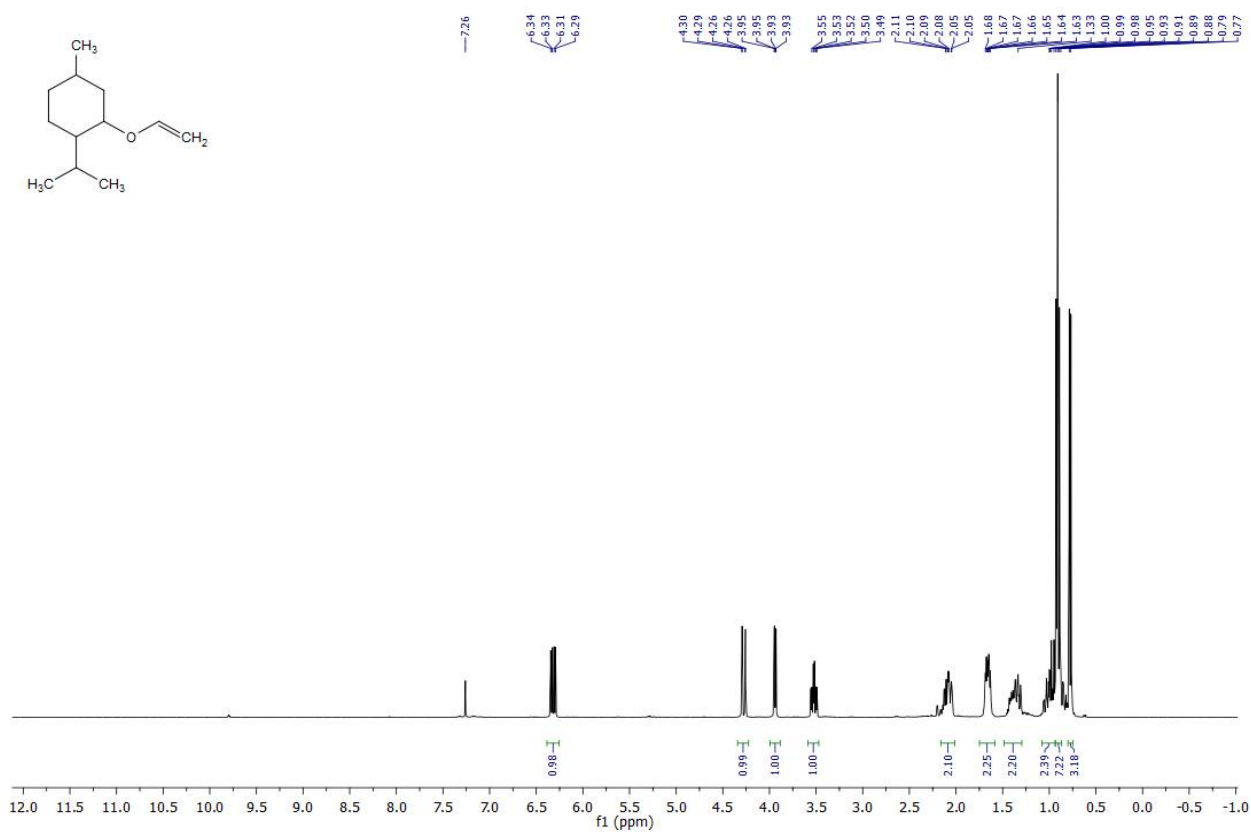


Figure S1. ¹H NMR (400 MHz, CDCl₃) spectrum of menthyl vinyl ether (**1a**)

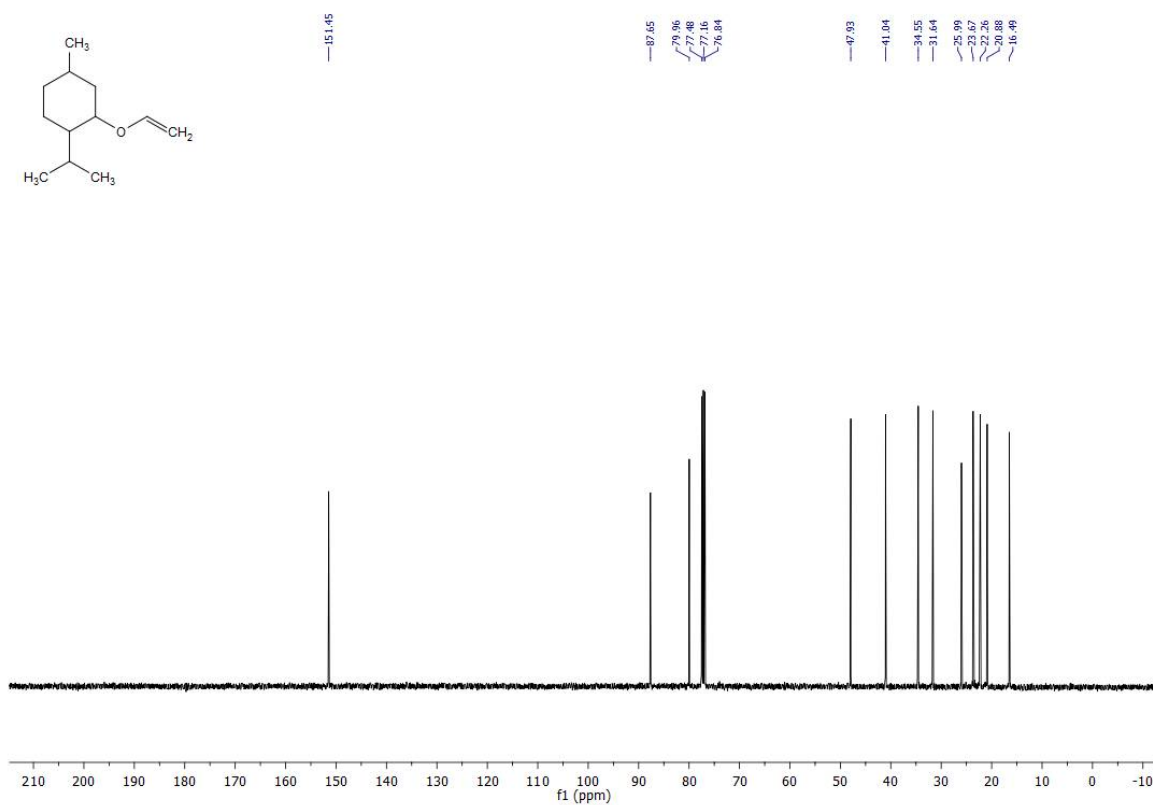
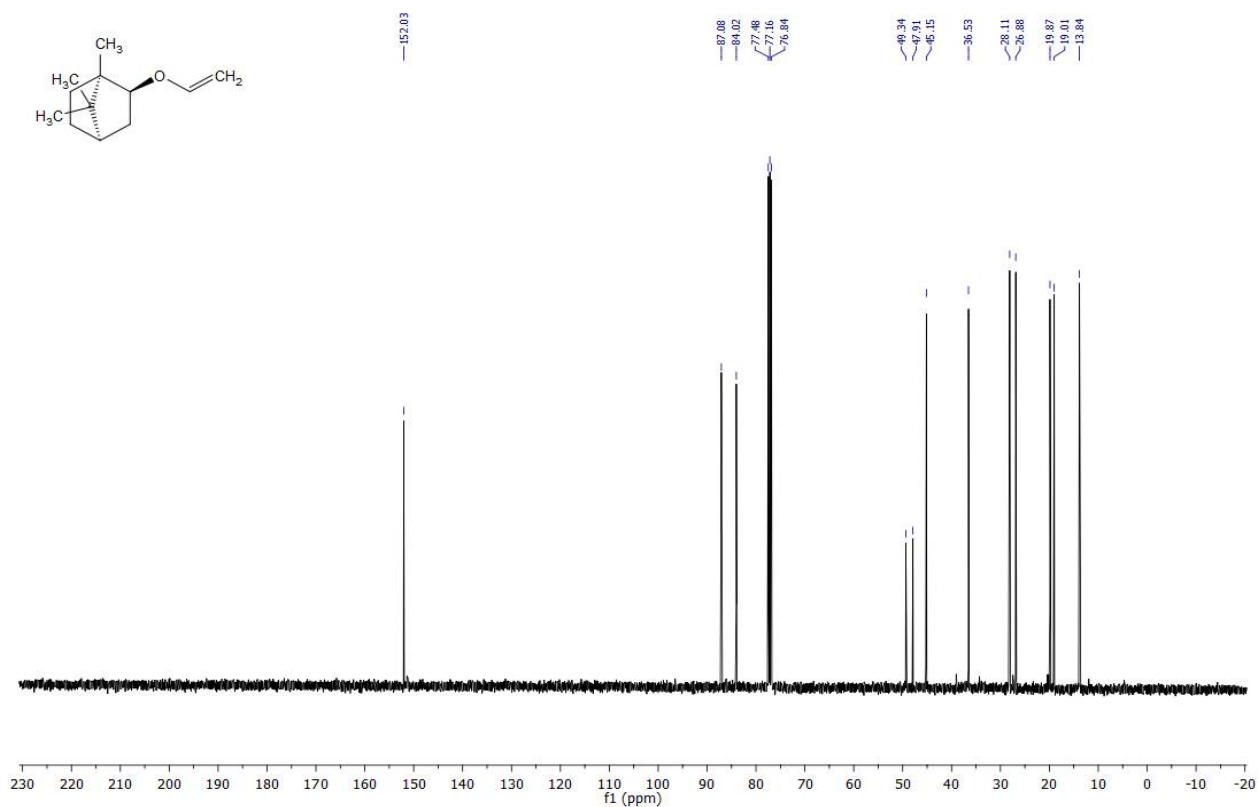
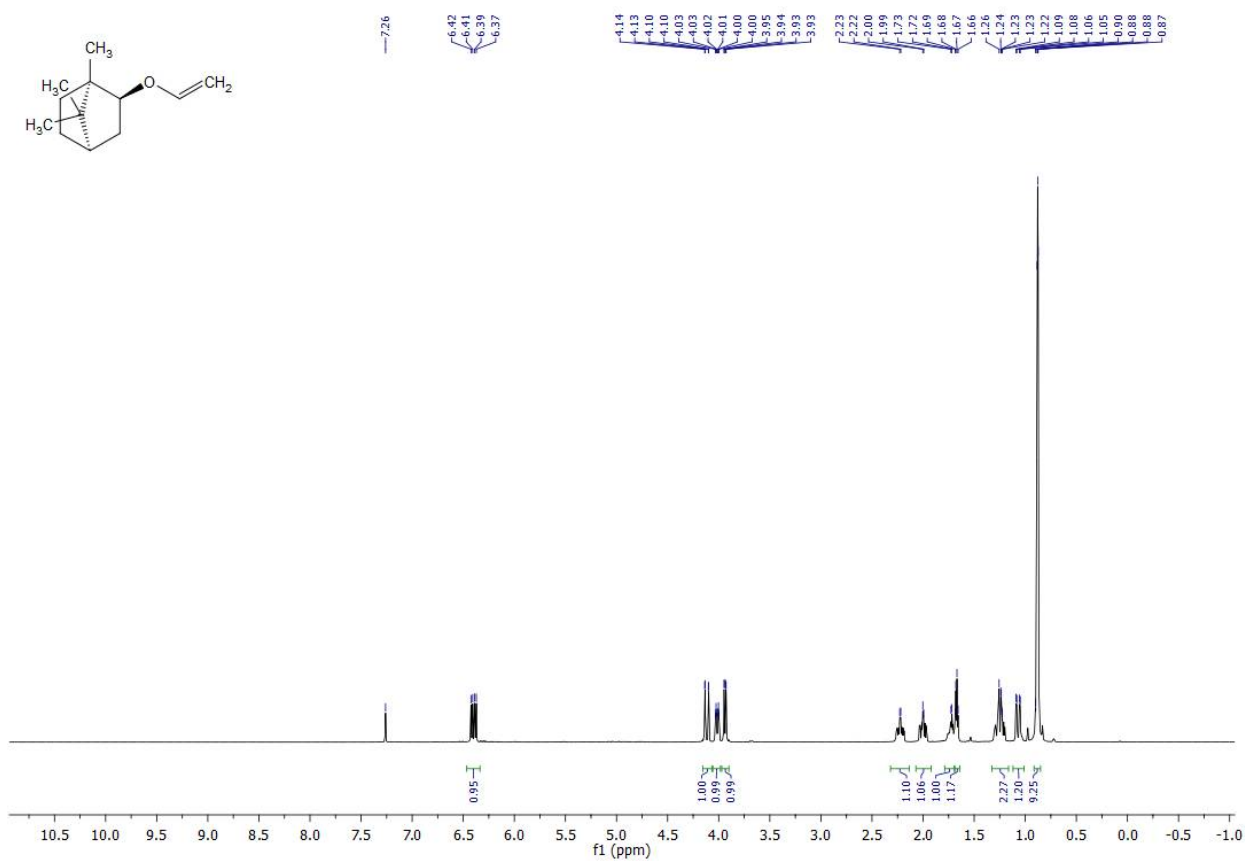


Figure S2. ¹³C NMR (101 MHz, CDCl₃) spectrum of menthyl vinyl ether (**1a**)



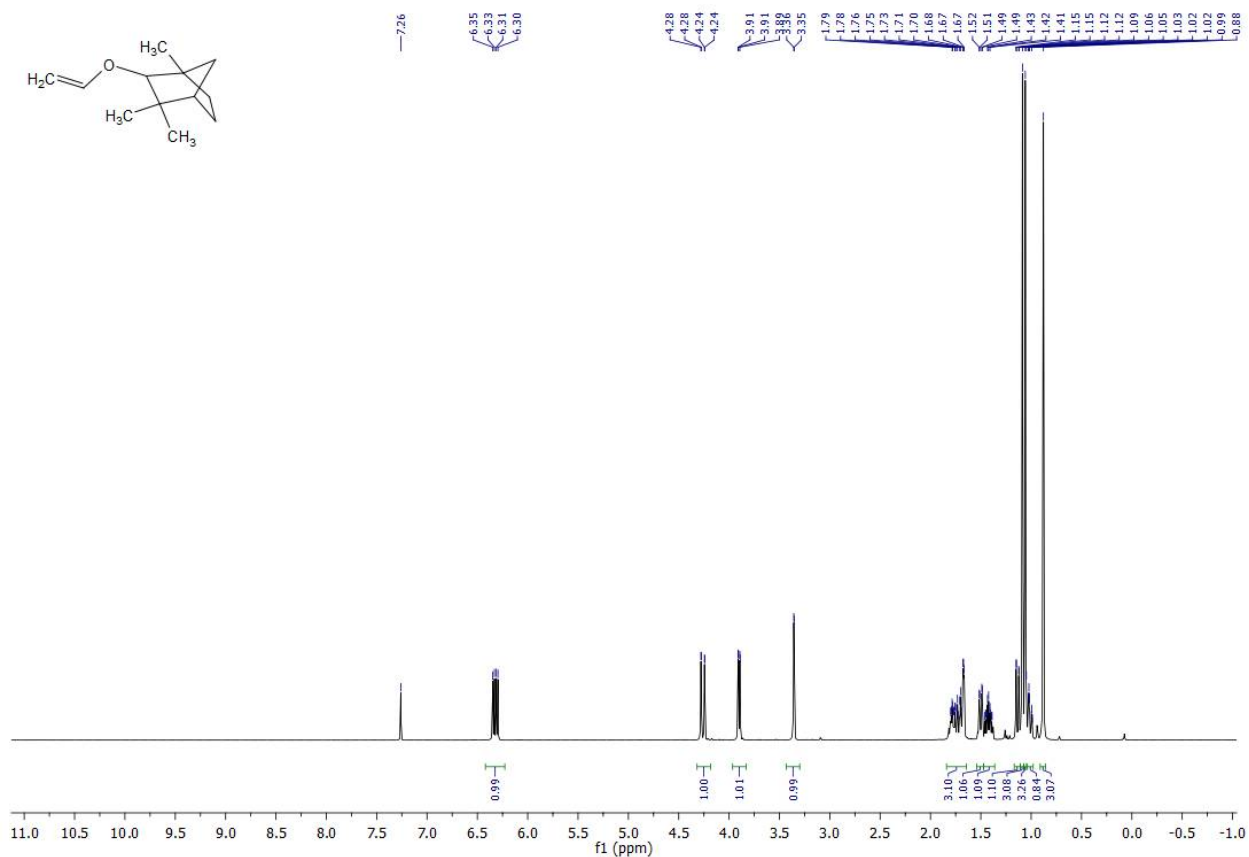


Figure S5. ¹H NMR (400 MHz, CDCl₃) spectrum of fenchyl vinyl ether (**3a**)

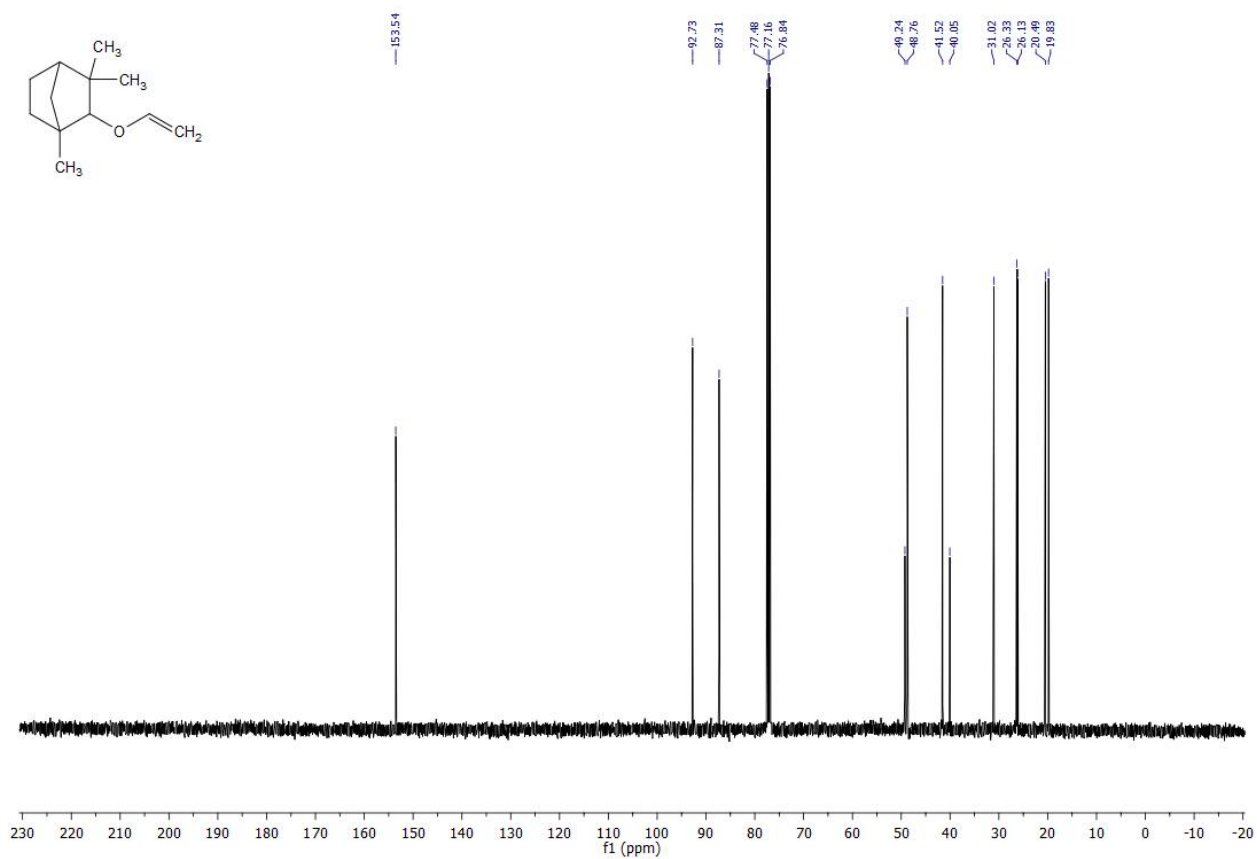


Figure S6. ¹³C NMR (101 MHz, CDCl₃) spectrum of fenchyl vinyl ether (**3a**)

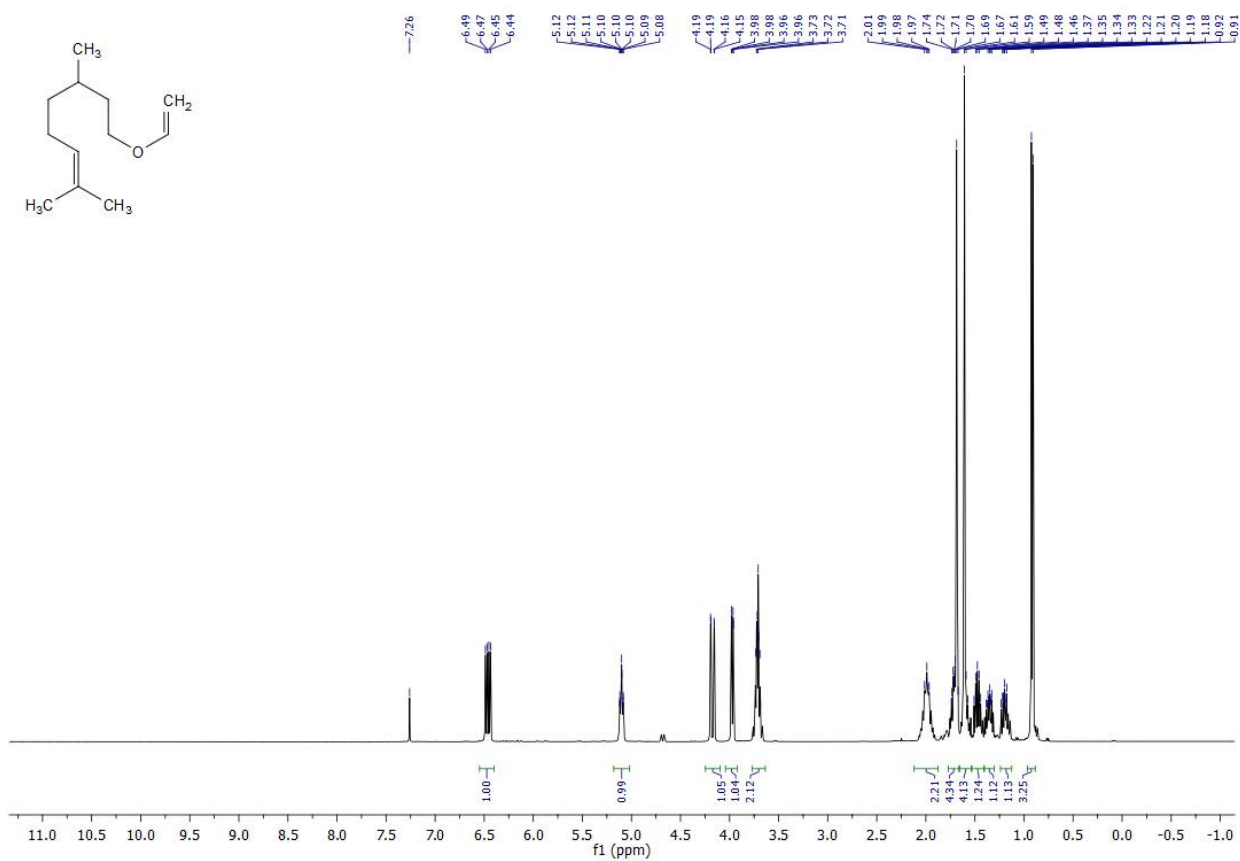


Figure S7. ¹H NMR (400 MHz, CDCl₃) spectrum of citronellyl vinyl ether (4a)

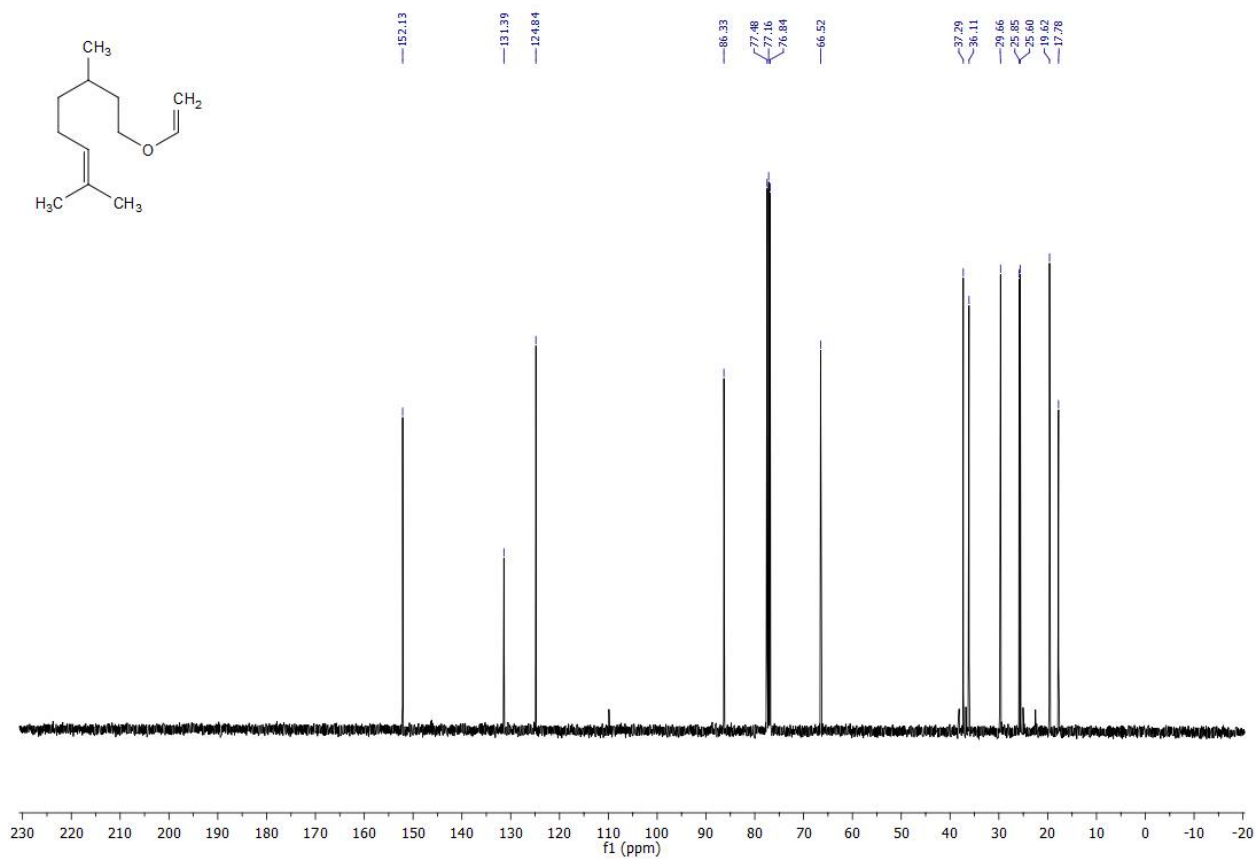


Figure S8. ¹³C NMR (101 MHz, CDCl₃) spectrum of citronellyl vinyl ether (4a)

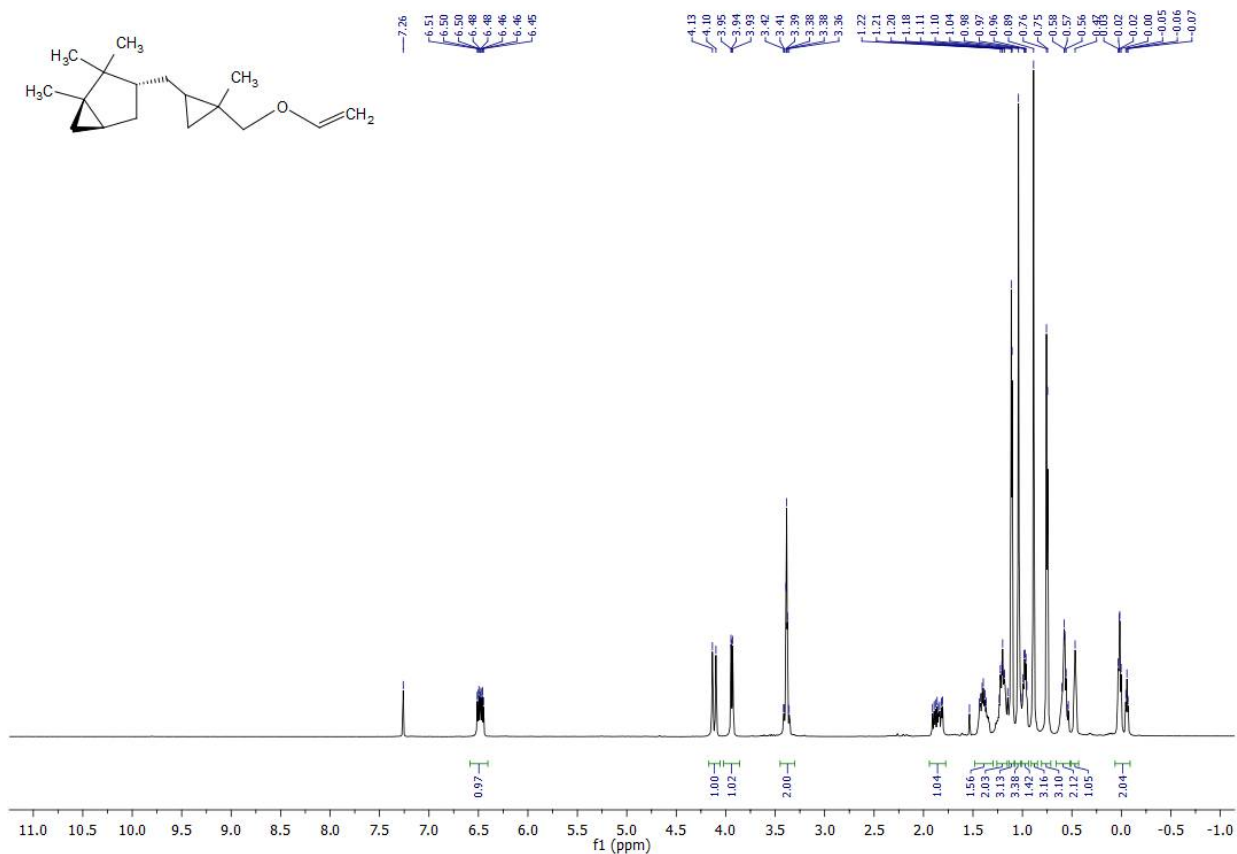


Figure S9. ¹H NMR (400 MHz, CDCl₃) spectrum of javanyl vinyl ether (5a)

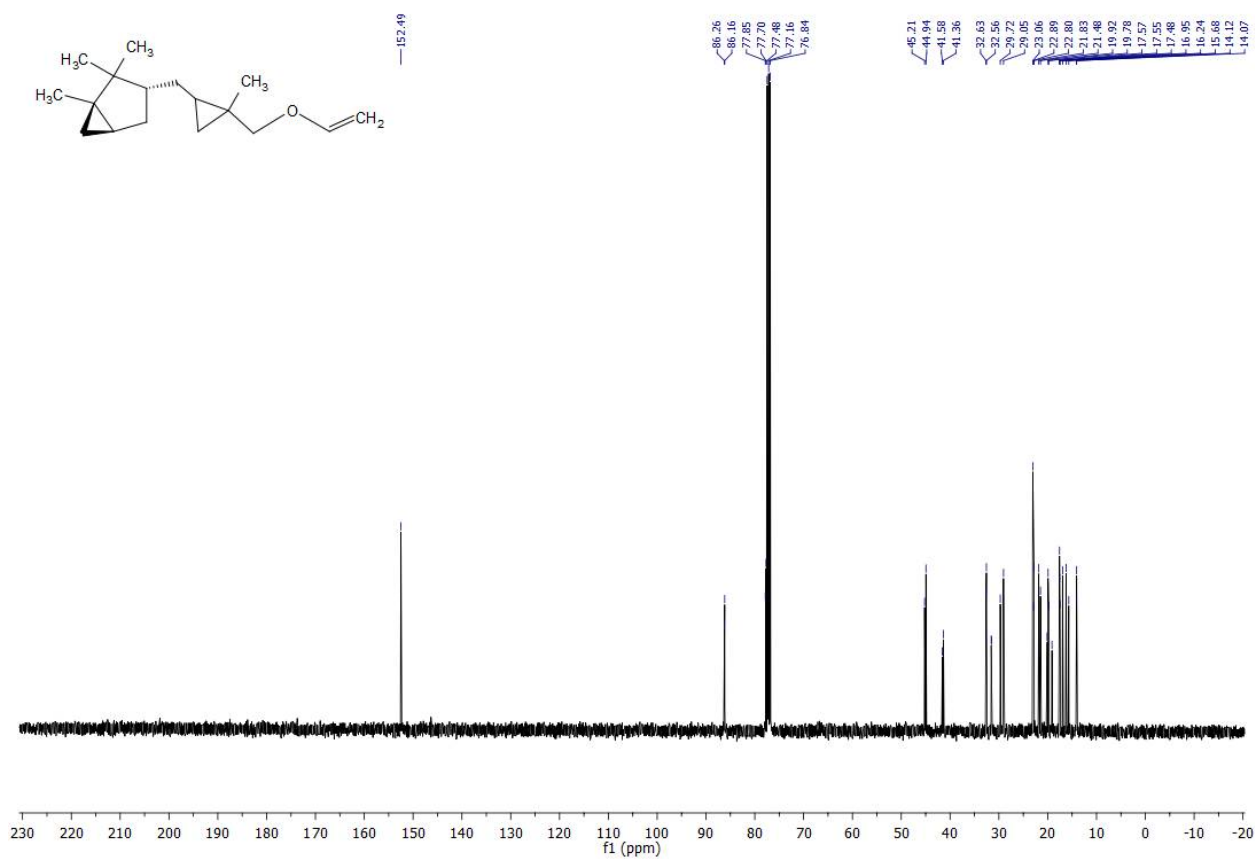


Figure S10. ¹³C NMR (101 MHz, CDCl₃) spectrum of javanyl vinyl ether (5a)

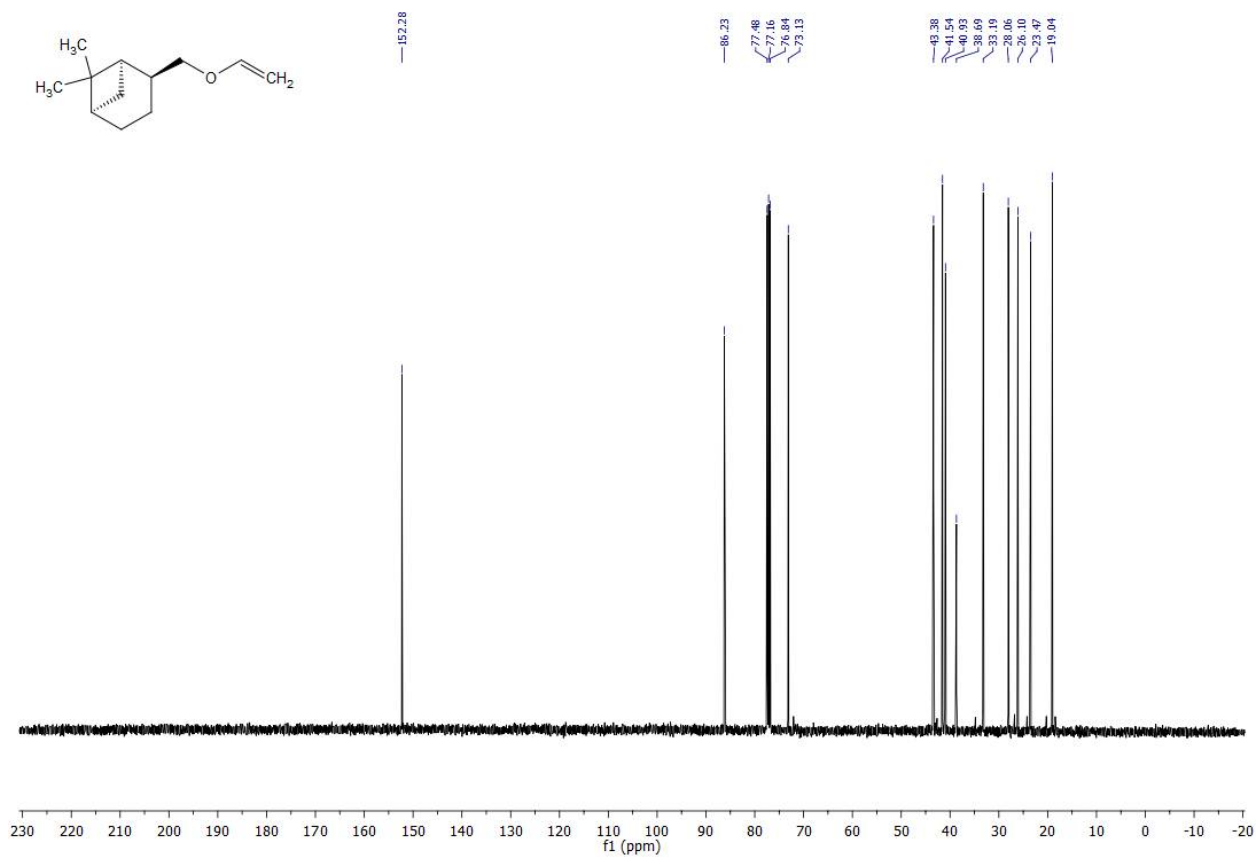
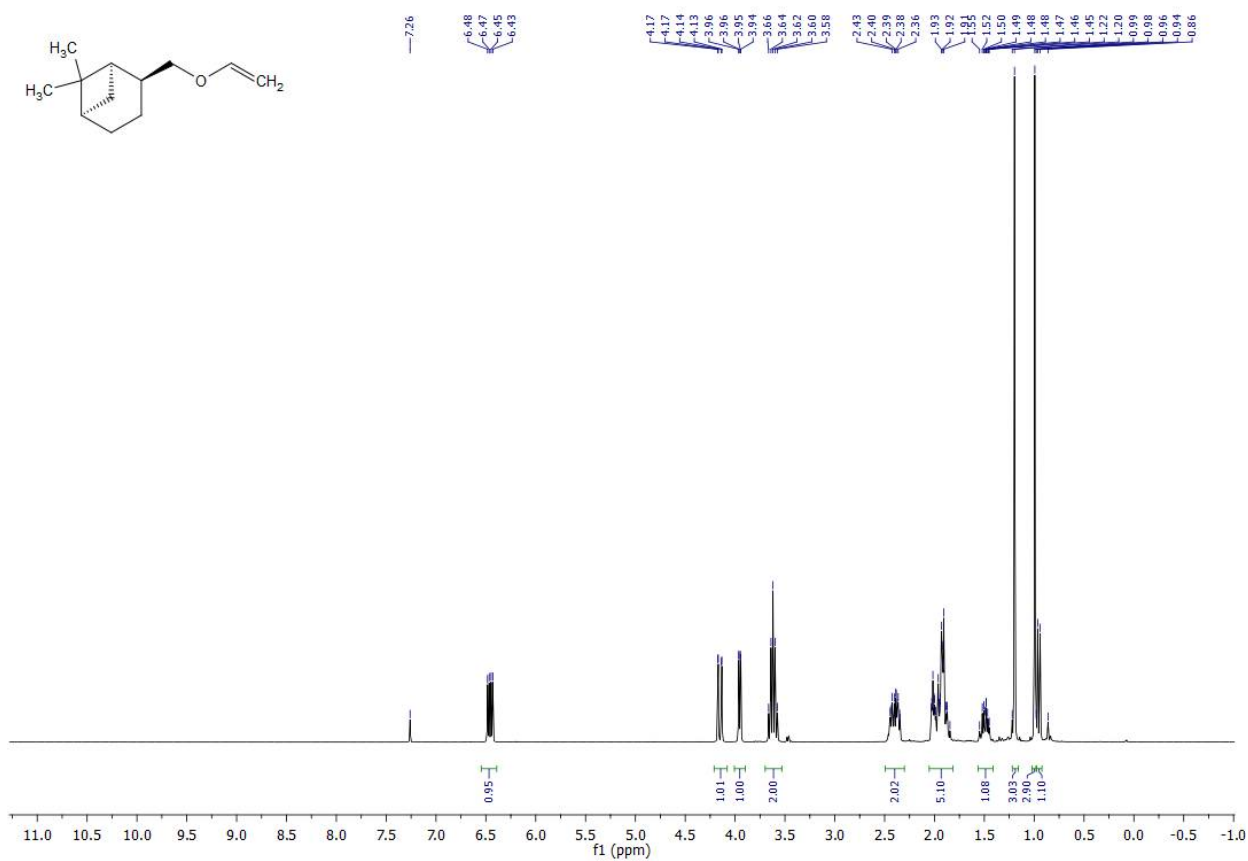


Figure S12. ^{13}C NMR (101 MHz, CDCl_3) spectrum of myrtanyl vinyl ether (**6a**)

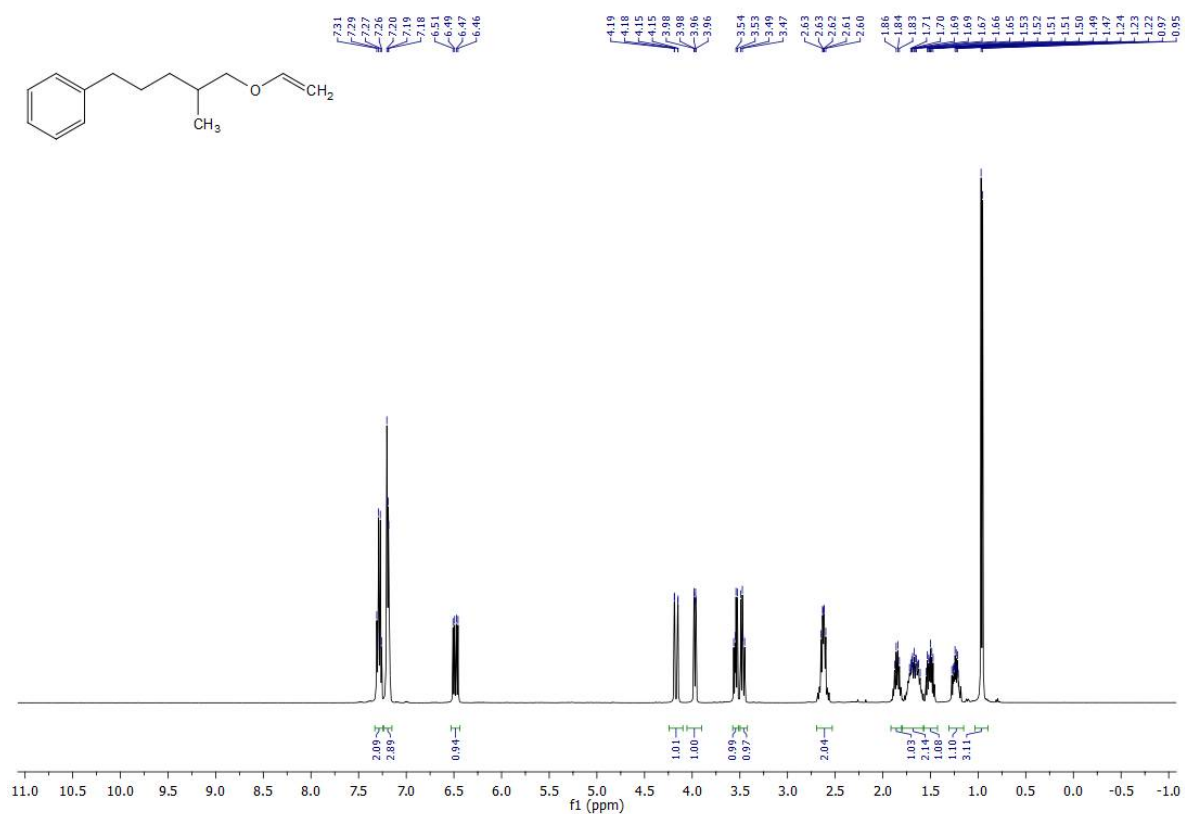


Figure S13. ¹H NMR (400 MHz, CDCl₃) spectrum of vinyl ether of rosaphen (7a)

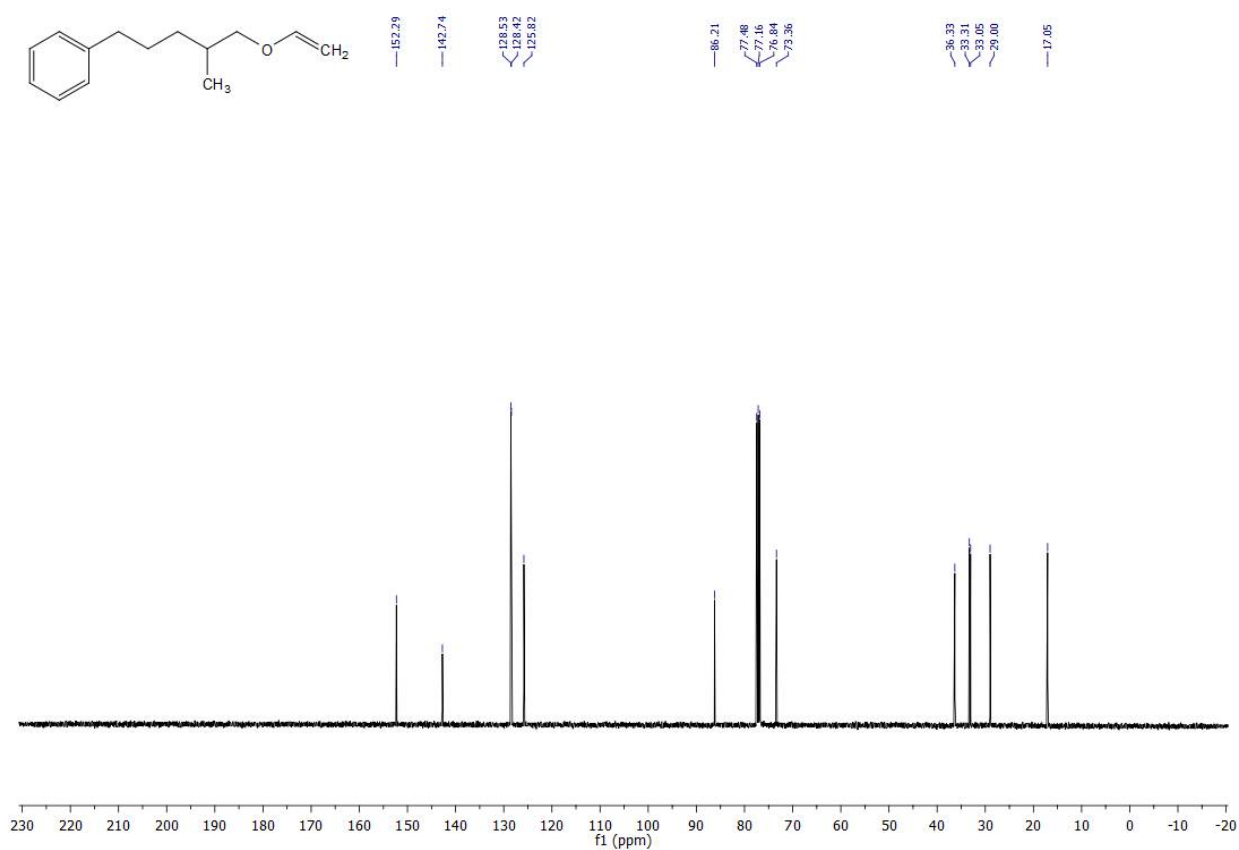


Figure S14. ¹³C NMR (101 MHz, CDCl₃) spectrum of vinyl ether of rosaphen (7a)

S3. NMR spectra of the polymers

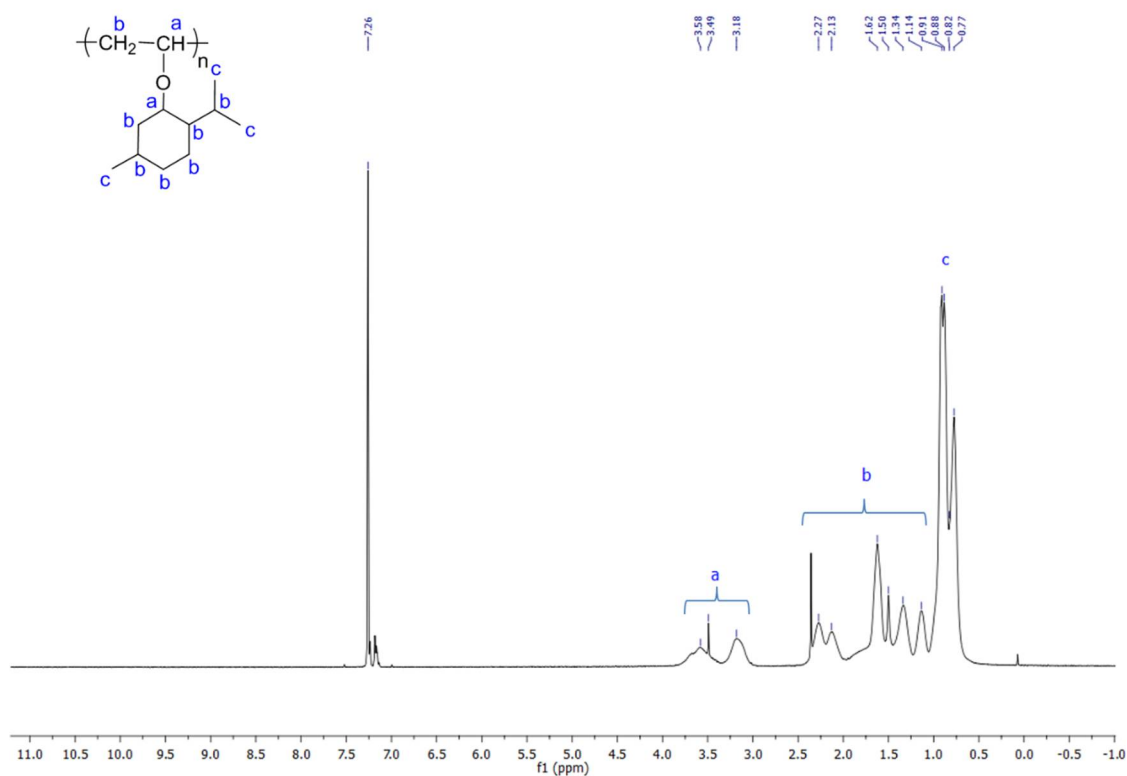


Figure S15. ¹H NMR (400 MHz, CDCl₃) spectrum of polyvinyl menthol (P1)

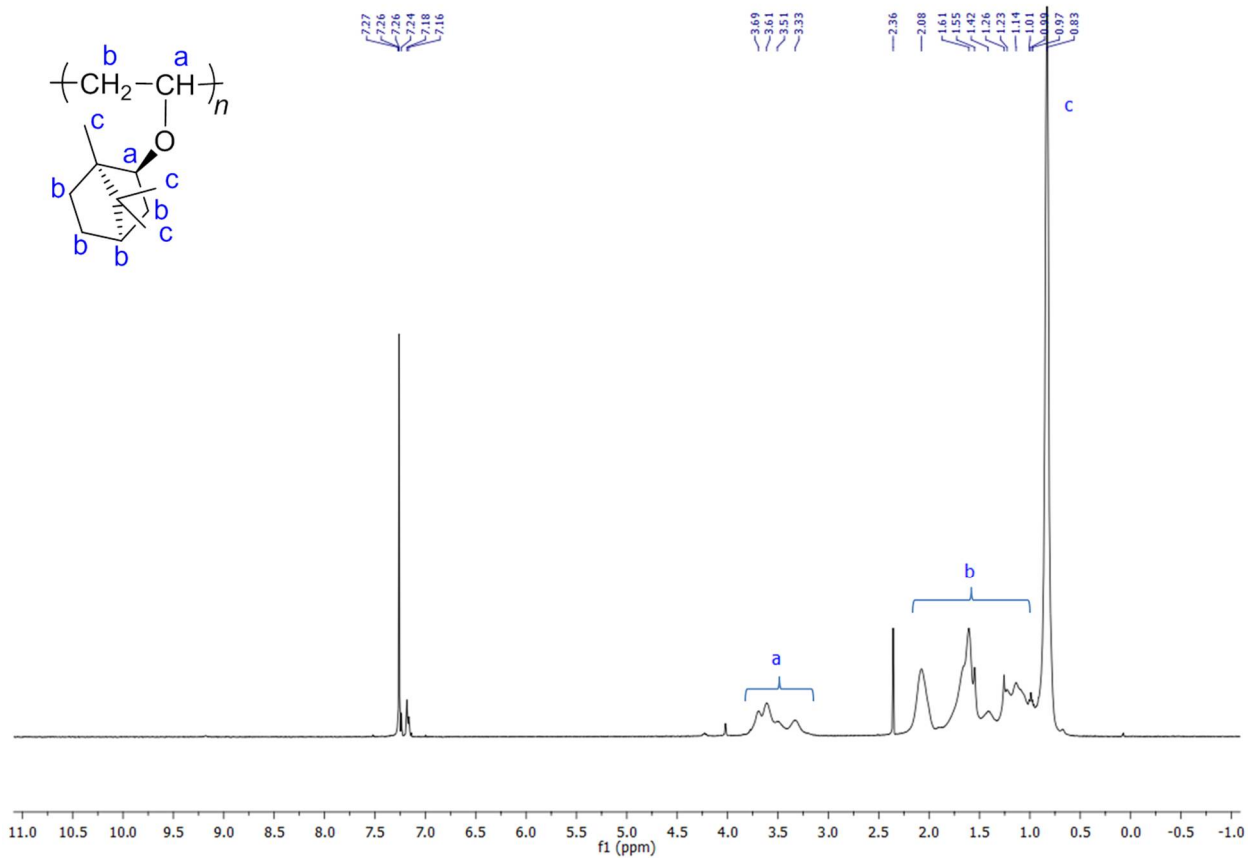


Figure S16. ¹H NMR (400 MHz, CDCl₃) spectrum of polyvinyl borneol (P2)

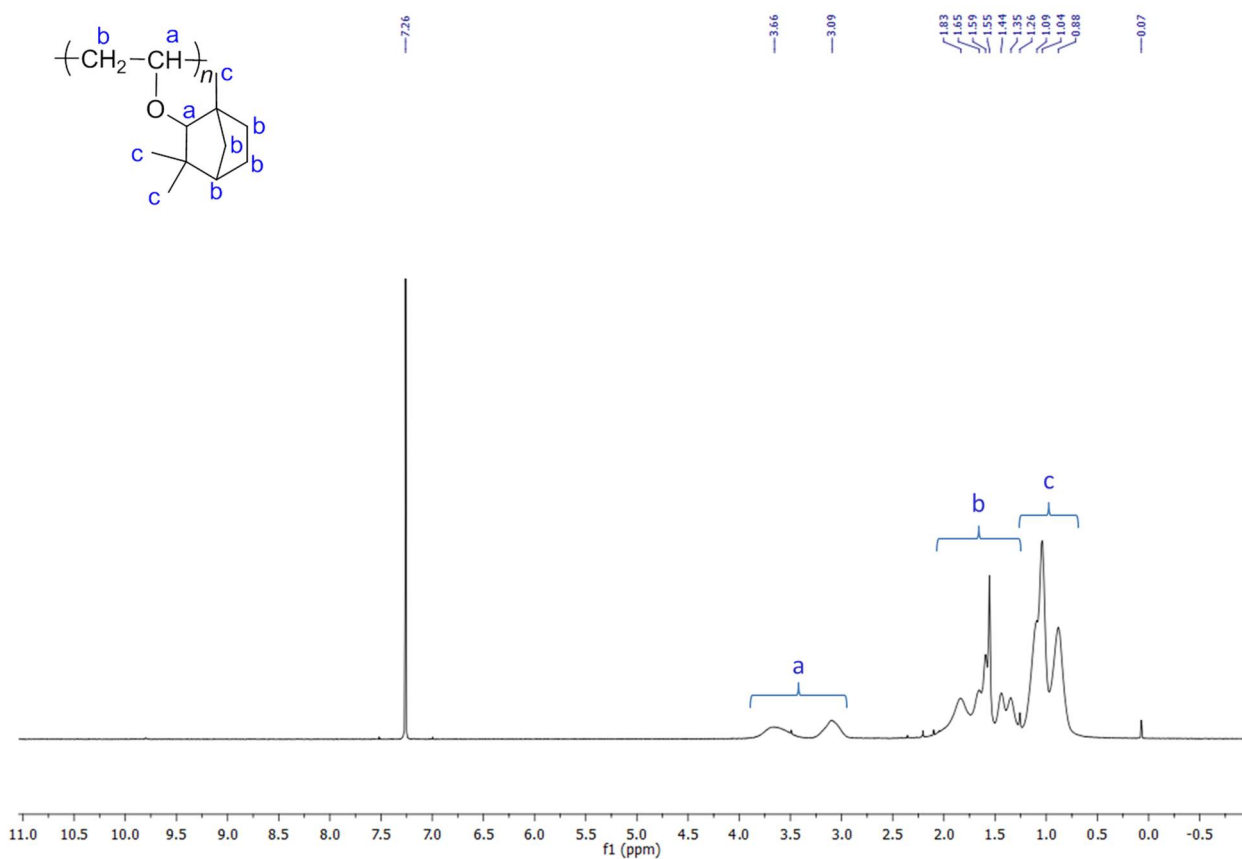


Figure S17. ^1H NMR (400 MHz, CDCl_3) spectrum of polyvinyl fenchol (**P3**)

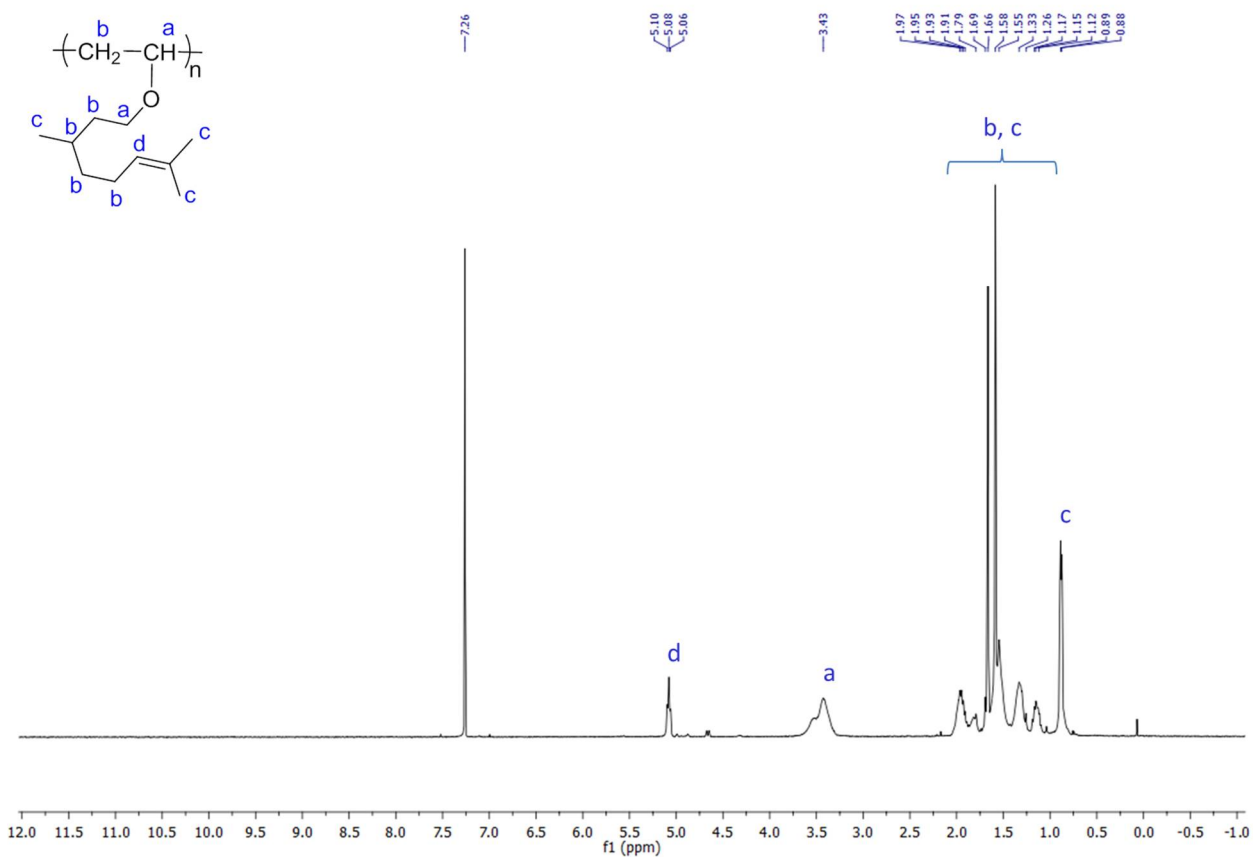


Figure S18. ^1H NMR (400 MHz, CDCl_3) spectrum of polyvinyl citronellol (**P4**)

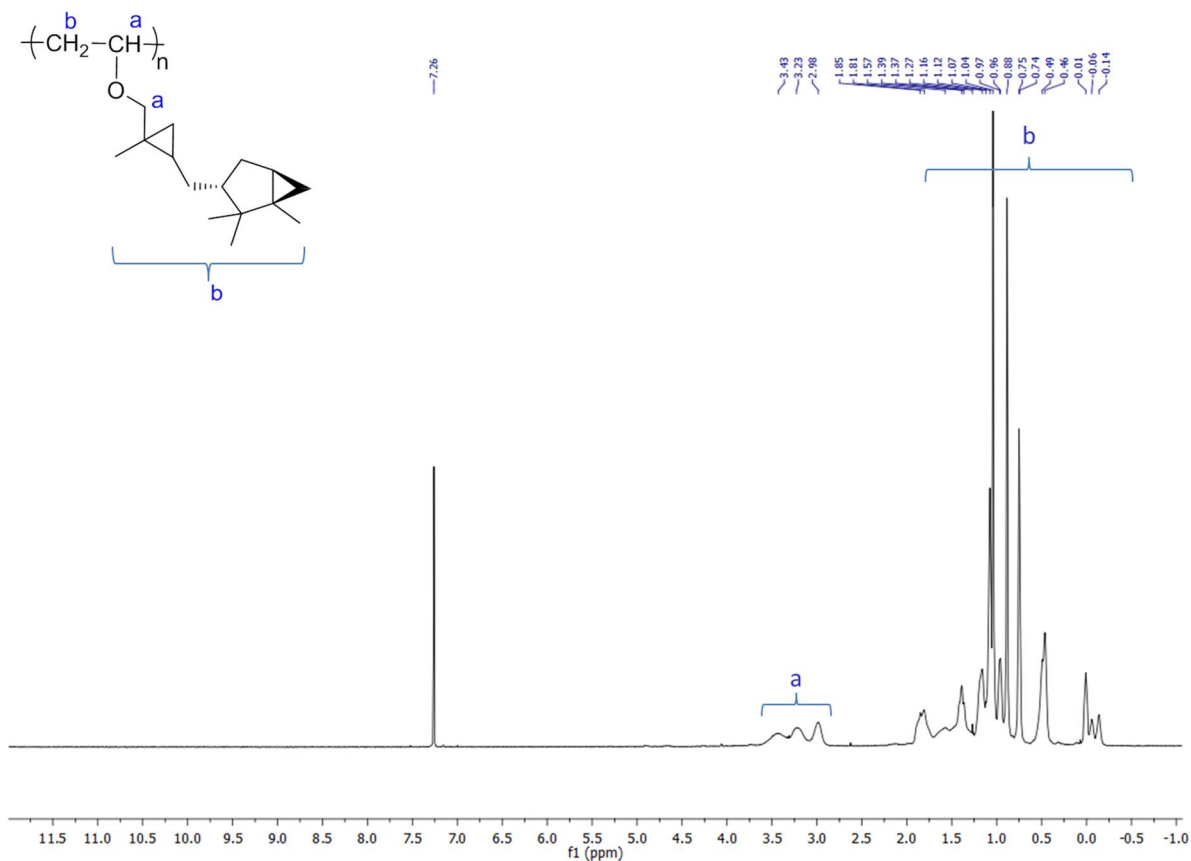


Figure S19. ^1H NMR (400 MHz, CDCl_3) spectrum of polyvinyl javanol (P5)

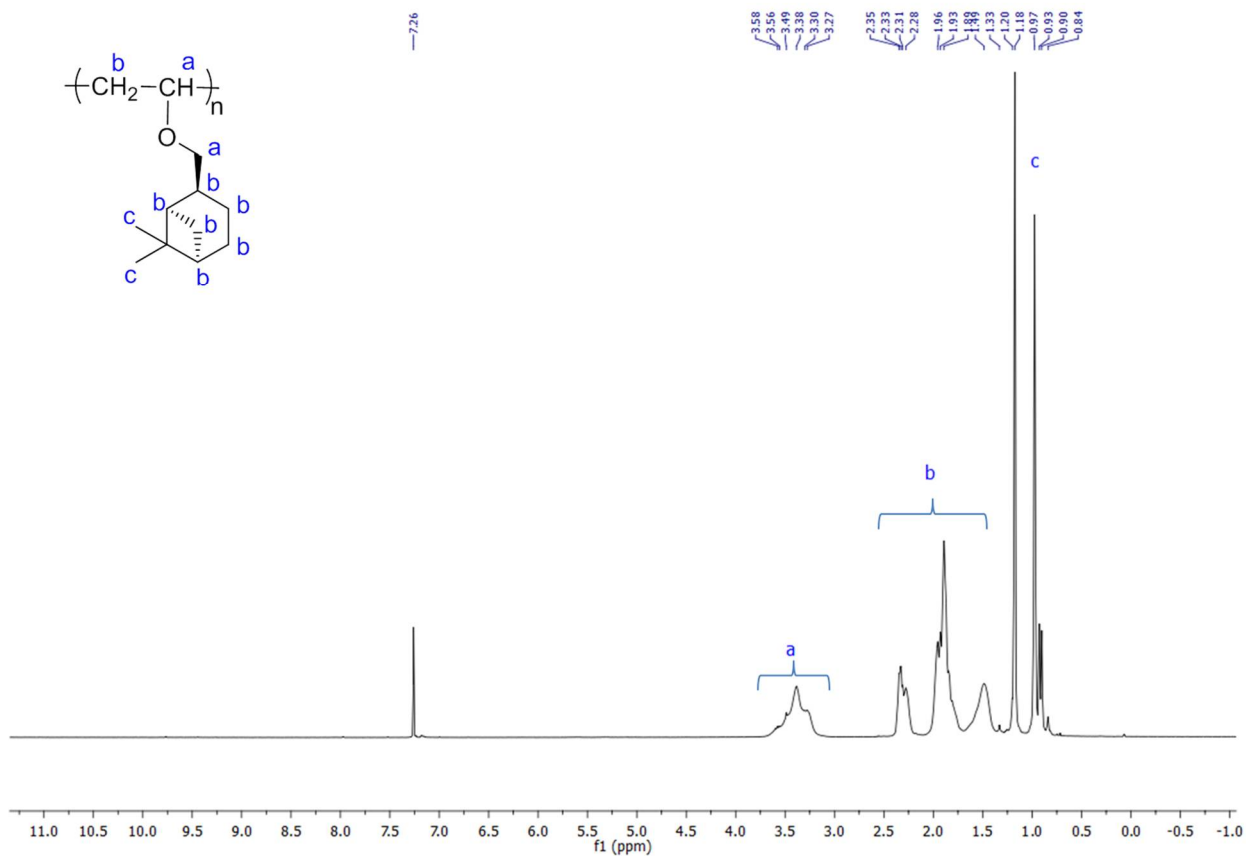


Figure S20. ^1H NMR (400 MHz, CDCl_3) spectrum of polyvinyl myrtanol (P6)

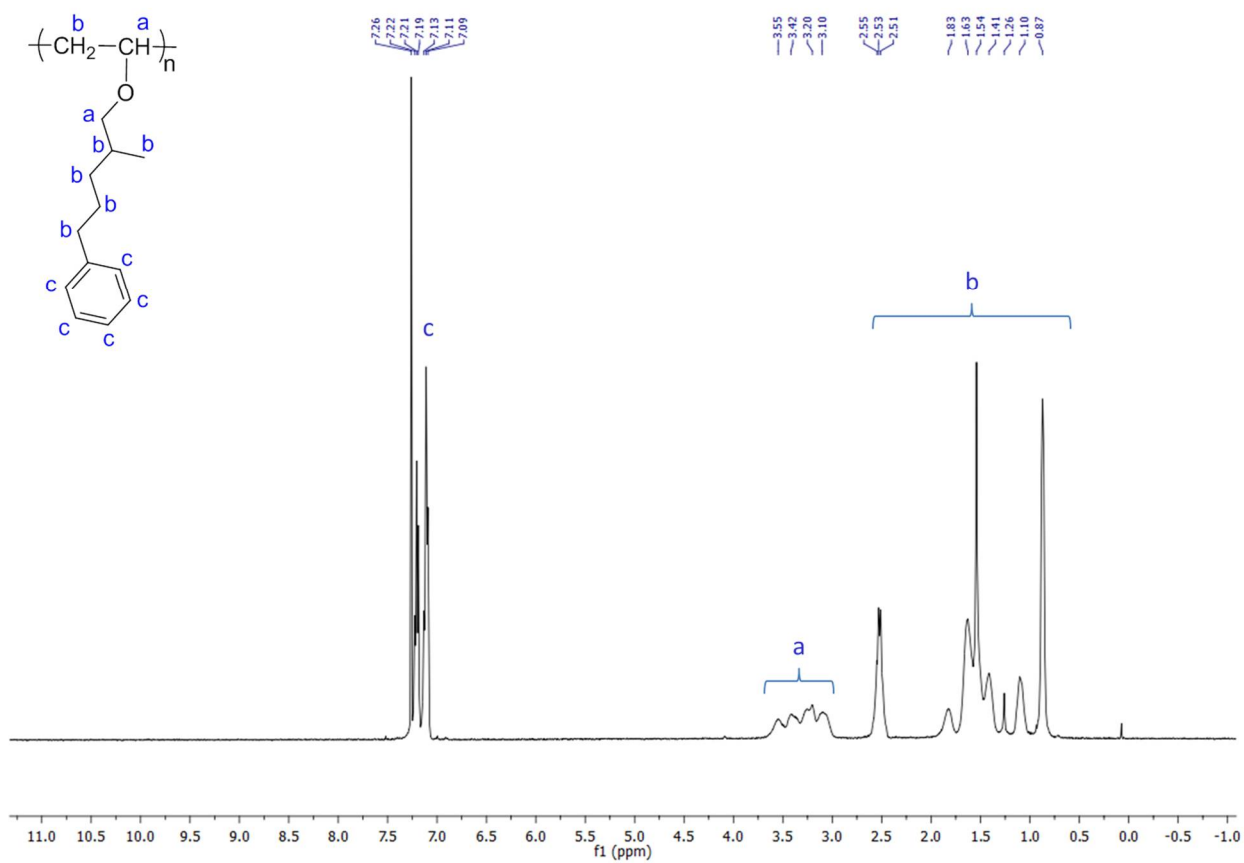


Figure S21. ¹H NMR (400 MHz, CDCl₃) spectrum of polyvinyl rosaphen (**P7**)

S4. Characterization of the polymers

Table S1: Masses and polydispersity indexes of the polymers

Nº	Polymer	Mn (g/mol)	Mw (g/mol)	D
P1	Polyvinyl menthol	5.04×10^4	8.50×10^4	1.69
P2	Polyvinyl borneol	5.54×10^4	7.08×10^4	1.28
P3	Polyvinyl fenchol	1.29×10^4	2.57×10^4	1.98
P4	Polyvinyl citronellol	3.35×10^4	5.38×10^4	1.61
P5	Polyvinyl javanol	6.2×10^3	1.12×10^4	1.82
P6	Polyvinyl myrtanol	2.1×10^4	4.3×10^4	2.02
P7	Polyvinyl rosaphen	5.01×10^4	6.28×10^4	1.25

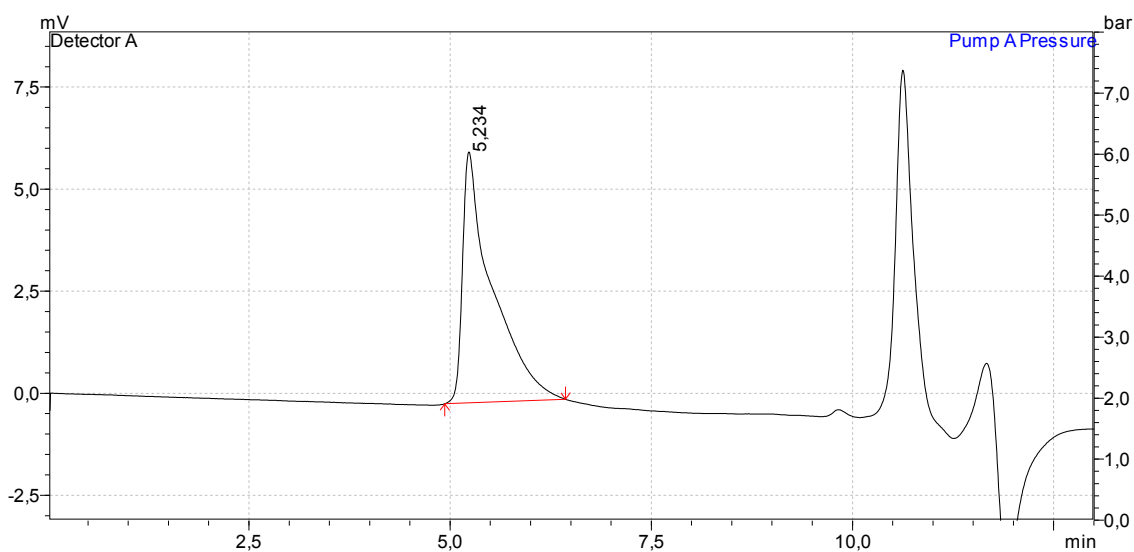


Figure S22. GPC chromatogram of polyvinyl menthol (**P1**)

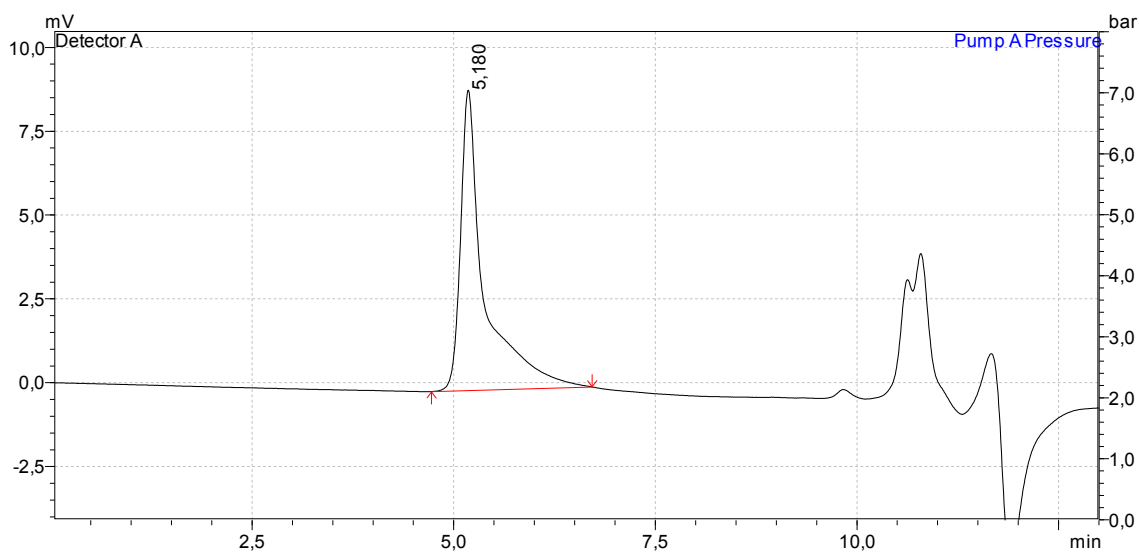


Figure S23. GPC chromatogram of polyvinyl borneol (**P2**)

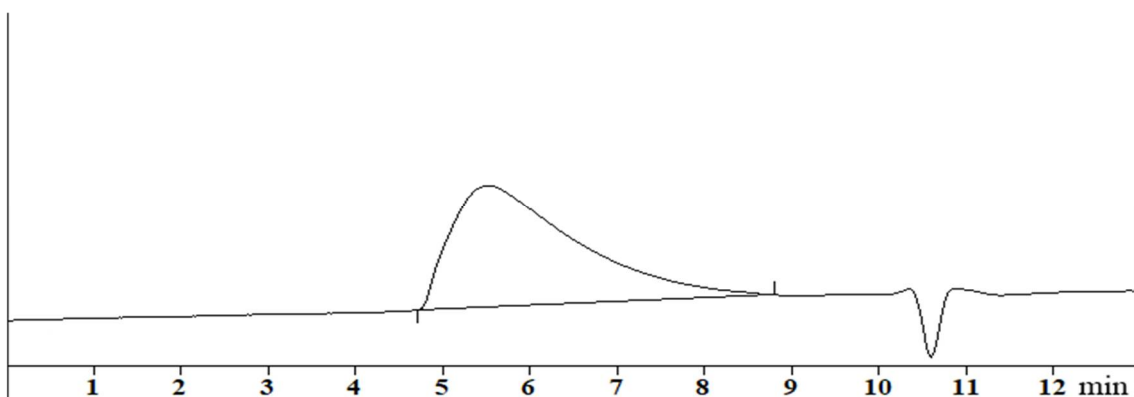


Figure S24. GPC chromatogram of polyvinyl fenchol (**P3**)

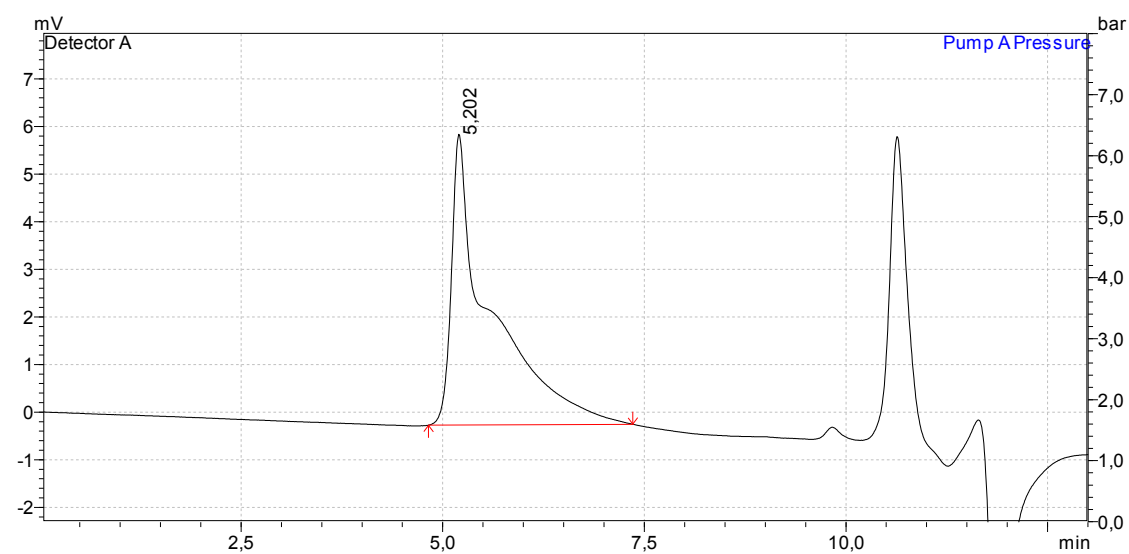


Figure S25. GPC chromatogram of polyvinyl citronellol (**P4**)

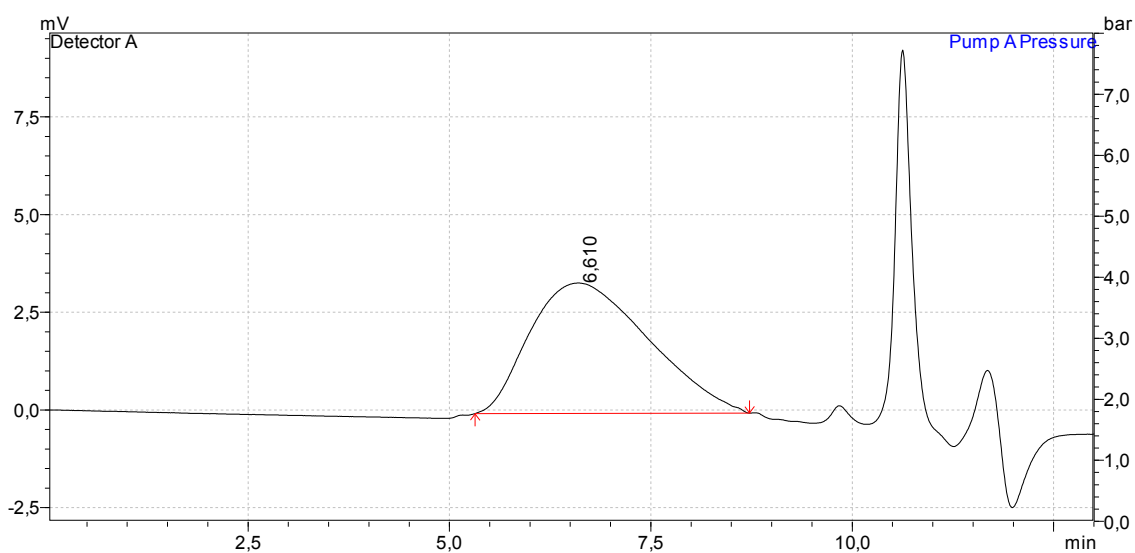


Figure S26. GPC chromatogram of polyvinyl javanol (**P5**)

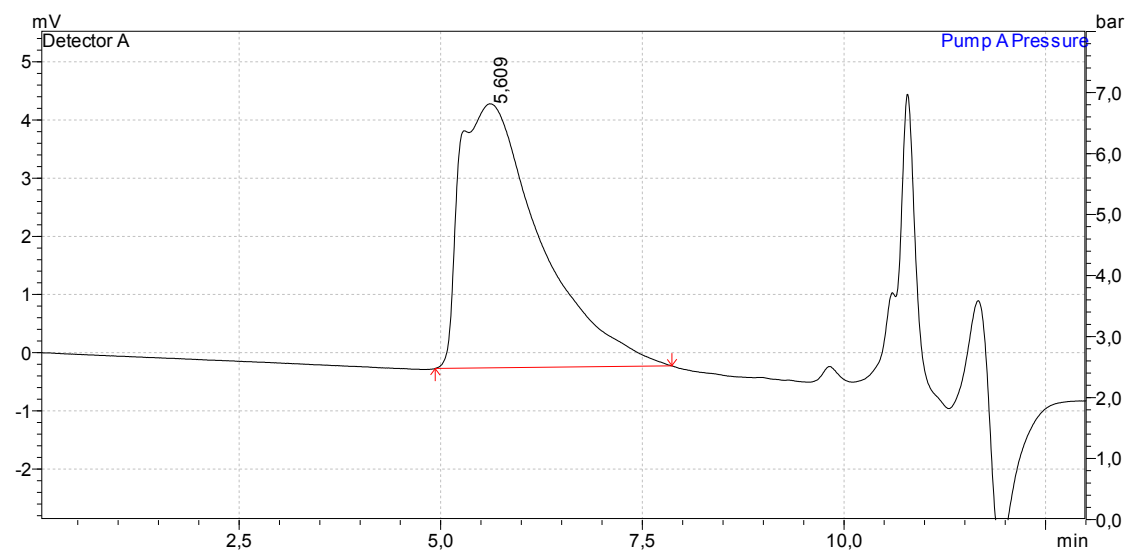


Figure S27. GPC chromatogram of polyvinyl myrtanol (**P6**)

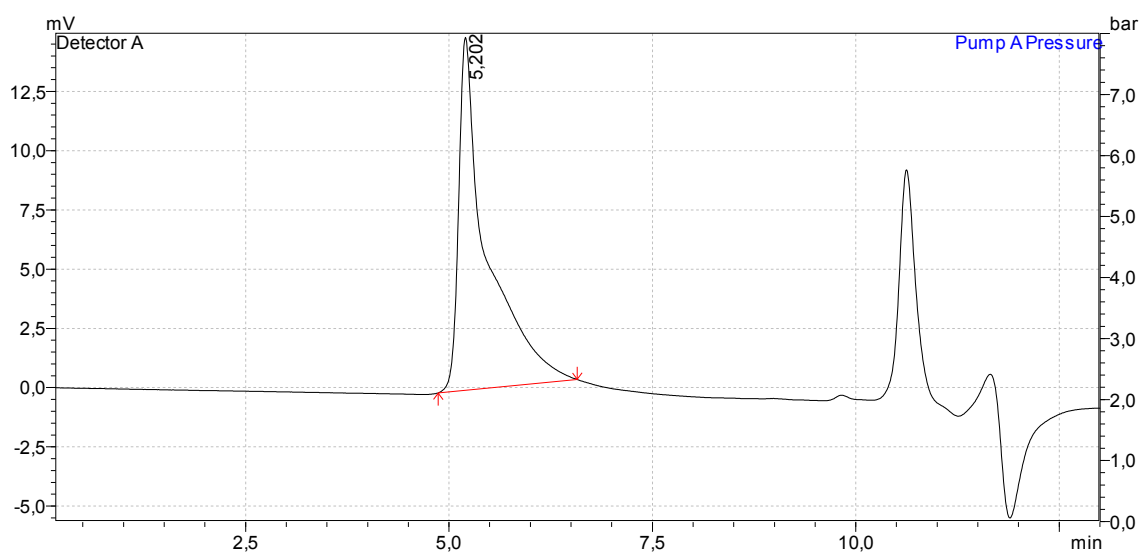


Figure S28. GPC chromatogram of polyvinyl rosaphen (**P7**)

S5. Pyrolysis data

Table S2: The content of an initial alcohol in a mixture after the pyrolysis (mass%)

Polymer	Alcohol	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
P1	menthol (1)	100	34	73	87	73	57
P2	borneol (2)	-	-	4	4	15	37
P3	fenchol (3)	-	-	0	5	25	26
P4	citronellol (4)	-	-	76	66	52	49
P5	javanol (5)	-	-	86	59	62	56
P6	myrtanol (6)	-	-	67	67	45	38
P7	rosaphen (7)	-	-	56	48	48	37

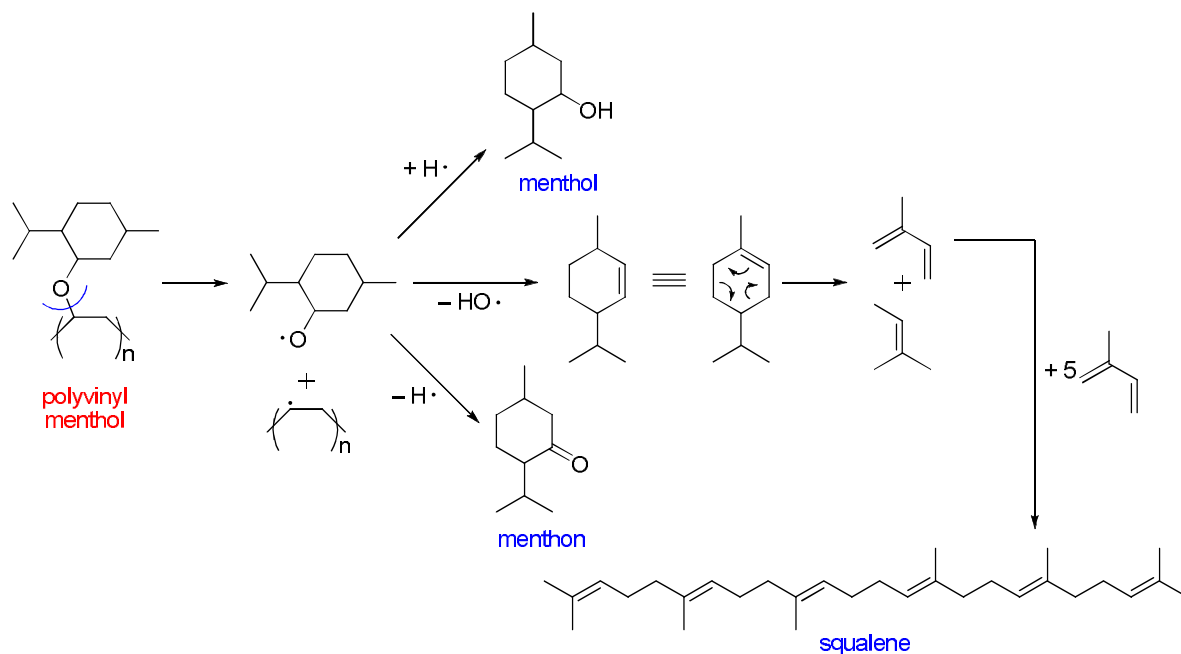
Table S3: The composition of the aldehyde/ketone mixtures after the pyrolysis (mass%)

Polymer	Aldehyde/ketone	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
P1	1c	0	0	1	8	20	21
P2	2c	-	-	5	21	47	59
P3	3c	-	-	11	1	44	52
P4	4b	-	-	10	27	35	32
P5	5b	-	-	3	8	12	13
P6	6b	-	-	2	21	13	9
P7	7b	-	-	44	37	35	39

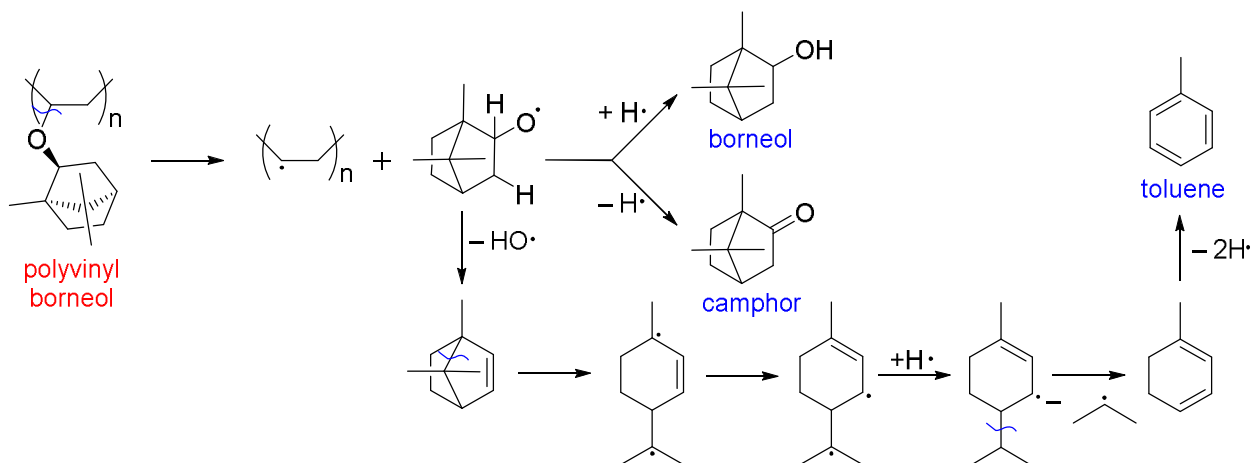
Table S4: The main by-products after polymer pyrolysis (mass%)

By-product	Polymer					
	200 °C	250 °C	300 °C	350 °C	400 °C	450 °C
	P1					
squalene	0	58	26	3	7	2
	P2					
toluene	-	-	84	62	26	1
squalene	-	-	4	11	0	2
	P3					
acetaldehyde	-	-	74	0	3	9
squalene	-	-	0	80	25	0
	P4					
squalene	-	-	7	3	5	0
	P6					
toluene	-	-	21	0	10	10

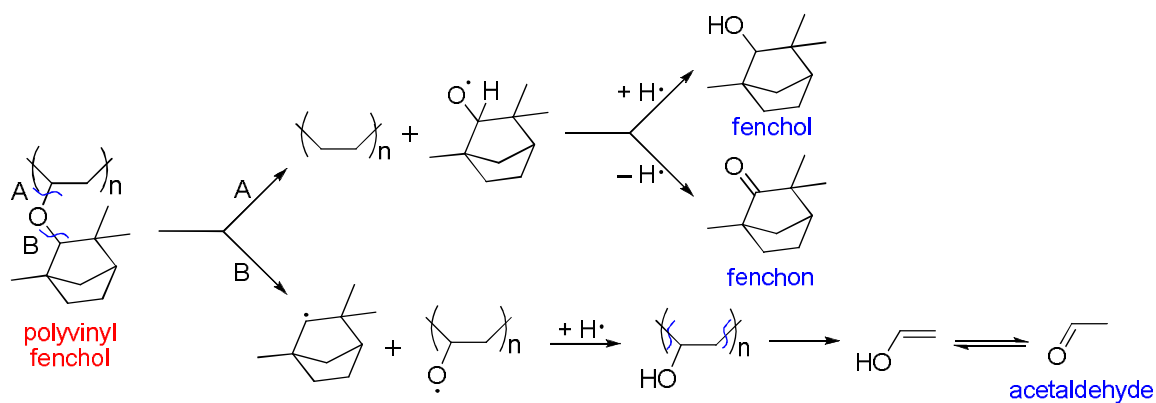
S6. Plausible transformations during the pyrolysis



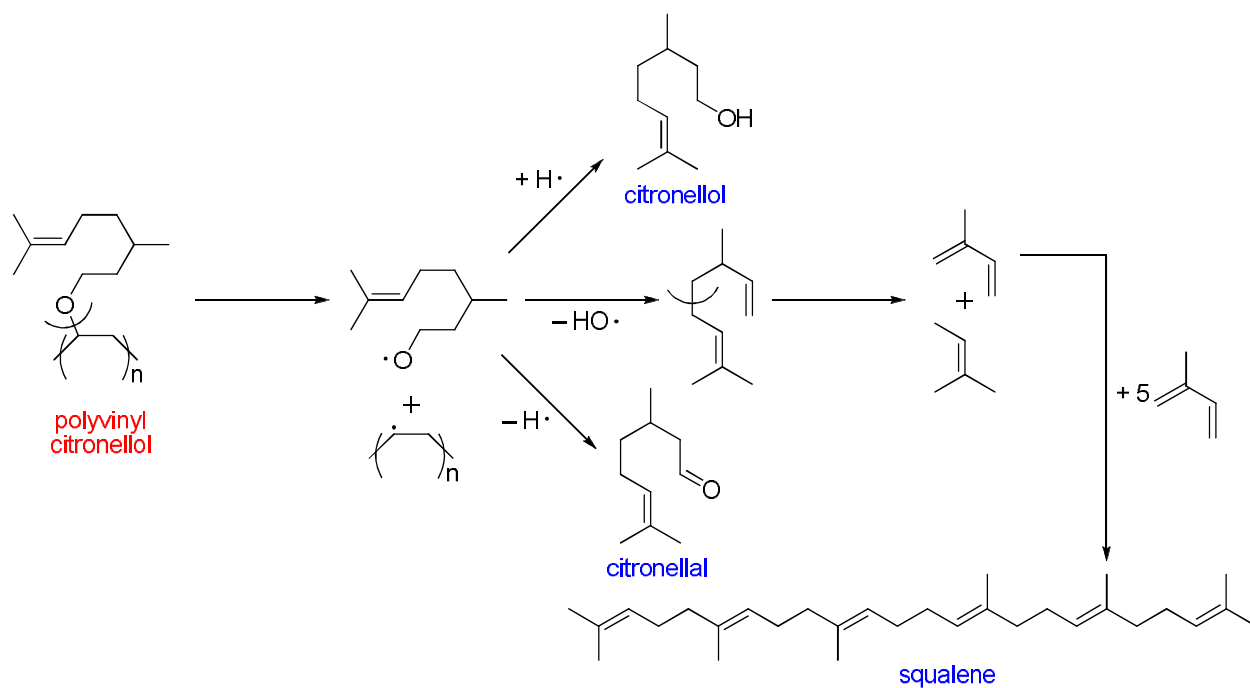
Scheme S1. Plausible routes of polyvinyl menthol (**P1**) decomposition



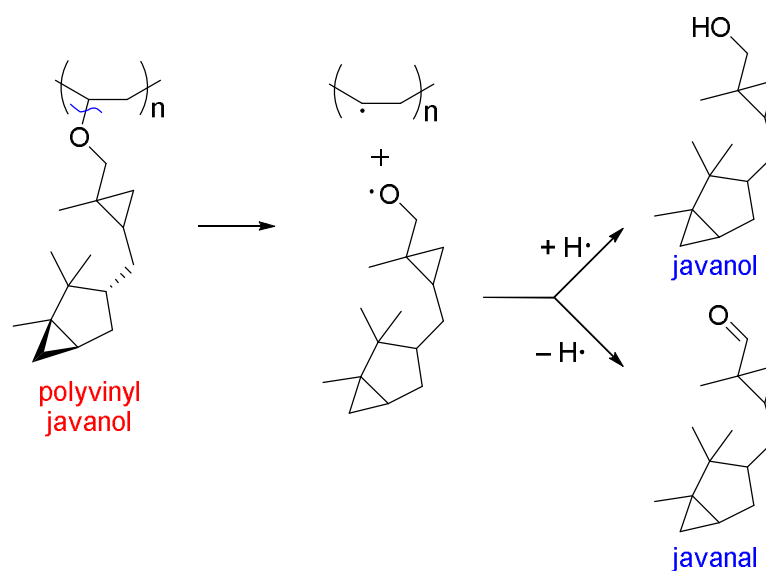
Scheme S2. Plausible routes of polyvinyl borneol (**P2**) decomposition



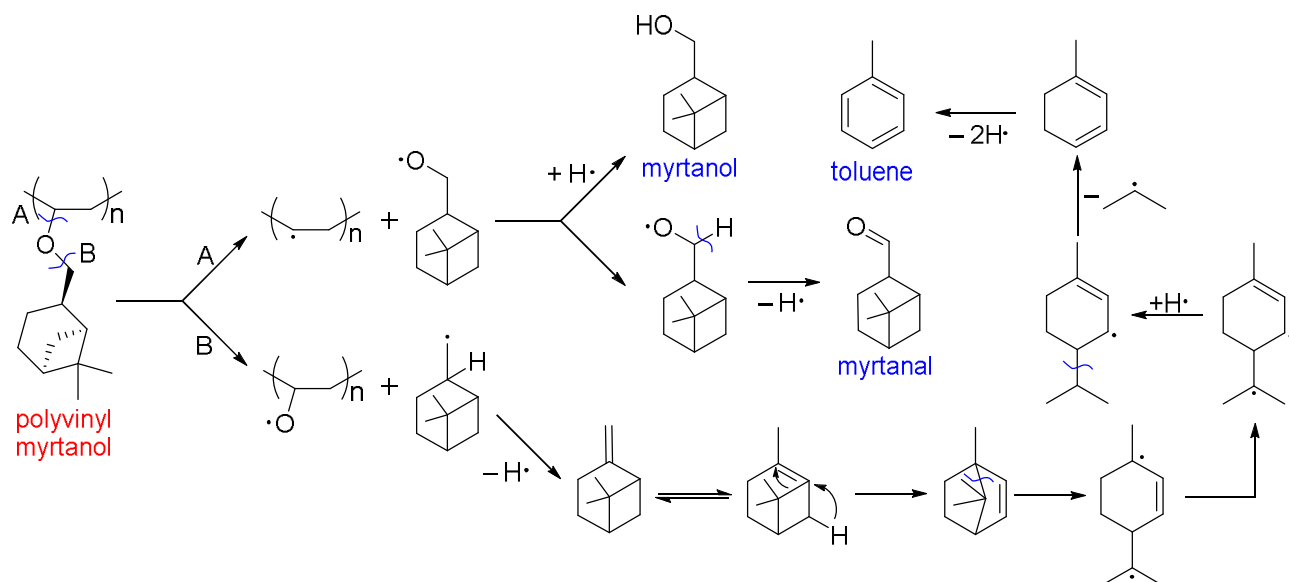
Scheme S3. Plausible routes of polyvinyl fenchol (**P3**) decomposition



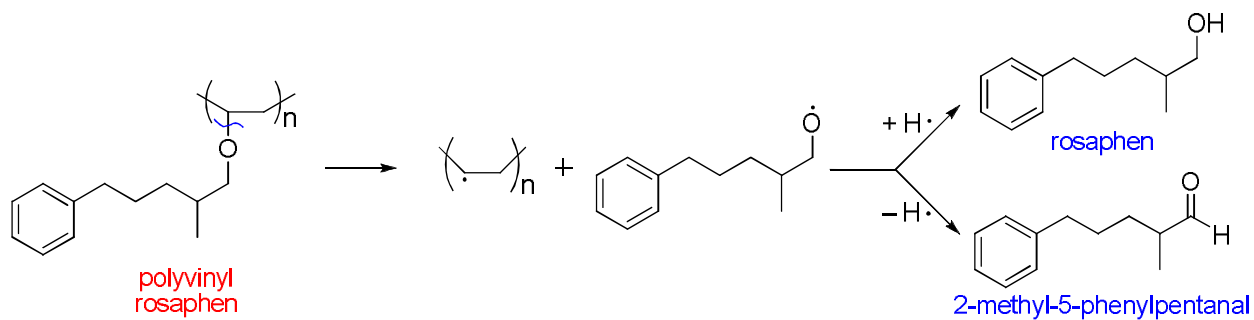
Scheme S4. Plausible routes of polyvinyl citronellol (**P4**) decomposition



Scheme S5. Plausible routes of polyvinyl javanol (**P5**) decomposition



Scheme S6. Plausible routes of polyvinyl myrtanol (**P6**) decomposition



Scheme S7. Plausible routes of polyvinyl rosaphen (**P7**) decomposition

S7. General procedure for the pyrolysis in a quartz tube at 750 °C

All the procedures were performed under argon atmosphere. The furnace was preheated to 750 °C, then, a polymer sample was placed in a part of the tube, and the tube was placed in the furnace (in the case of polyvinyl bornyl and myrtanyl substrates: first, a place of a tube was preheated, which does not contain a sample, and then shifted the tube further and heated the part with a sample).

Polyvinyl menthol (**1b**): loading 25 mg, rapid heating to 415 °C, then heating to 650 °C for 5 minutes, then 5 min to 720 °C, then a very slow increase of temperature. A yellow liquid appeared on the walls of the extended part of the tube. After 30 min of the pyrolysis, the tube was removed and cooled. There was no residue in the part of the tube that originally contained the sample. The liquid part was washed off with methylene chloride, the solvent was evaporated, and samples were taken for NMR and chromatography (in ethyl acetate).

Polyvinyl borneol (**2b**) and polyvinyl myrtanol (**6b**): loading 20 mg, rapid heating to 745 °C, then very slow increase of temperature. A yellow liquid appeared on the walls of the extended part of the tube. After 30 min of pyrolysis, the tube was removed and cooled. There was no residue in the part of the tube that originally contained the sample. The liquid part was washed off with methylene chloride, the solvent was evaporated and samples were taken for NMR and chromatography (in ethyl acetate (polyvinyl borneol) and methylene chloride (polyvinyl myrtanol) due to low solubility in EA. 150 mg of polyvinyl borneol (**2b**) were disassembled in a quartz tube in the same manner at 400 °C bubbling the gas phase through chloroform-d and toluene-d₆.

S8. NMR spectra of the pyrolysis products (from traps and washed from tubes)

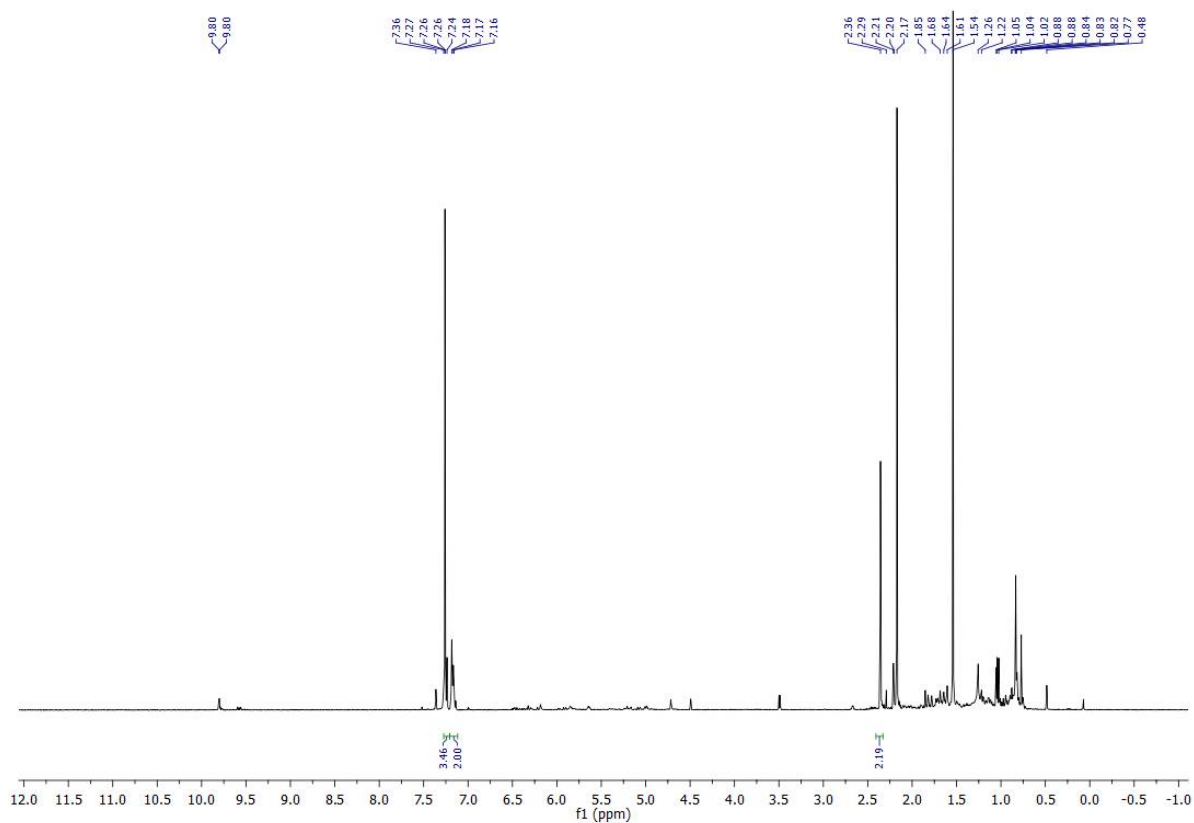


Figure S31. ¹H NMR (400 MHz, CDCl₃) spectrum of the gaseous pyrolysis products of polyvinyl borneol (**P2**) from chloroform trap

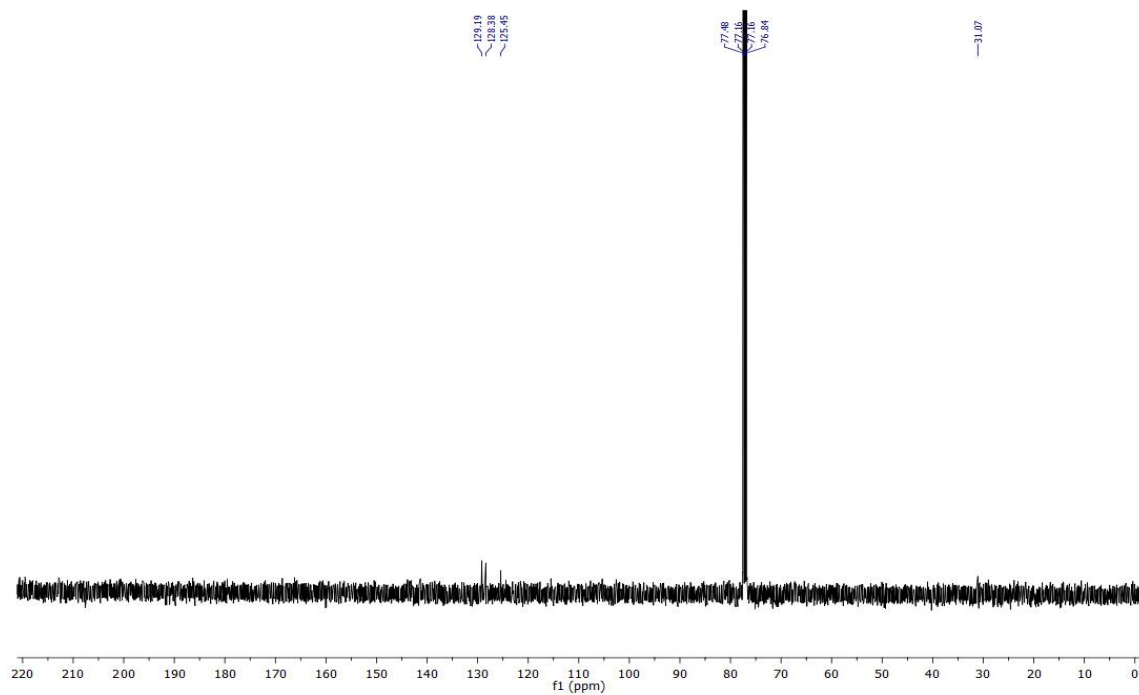


Figure S32. ¹³C NMR (101 MHz, CDCl₃) spectrum of the gaseous products of polyvinyl borneol (**P2**) pyrolysis from chloroform trap

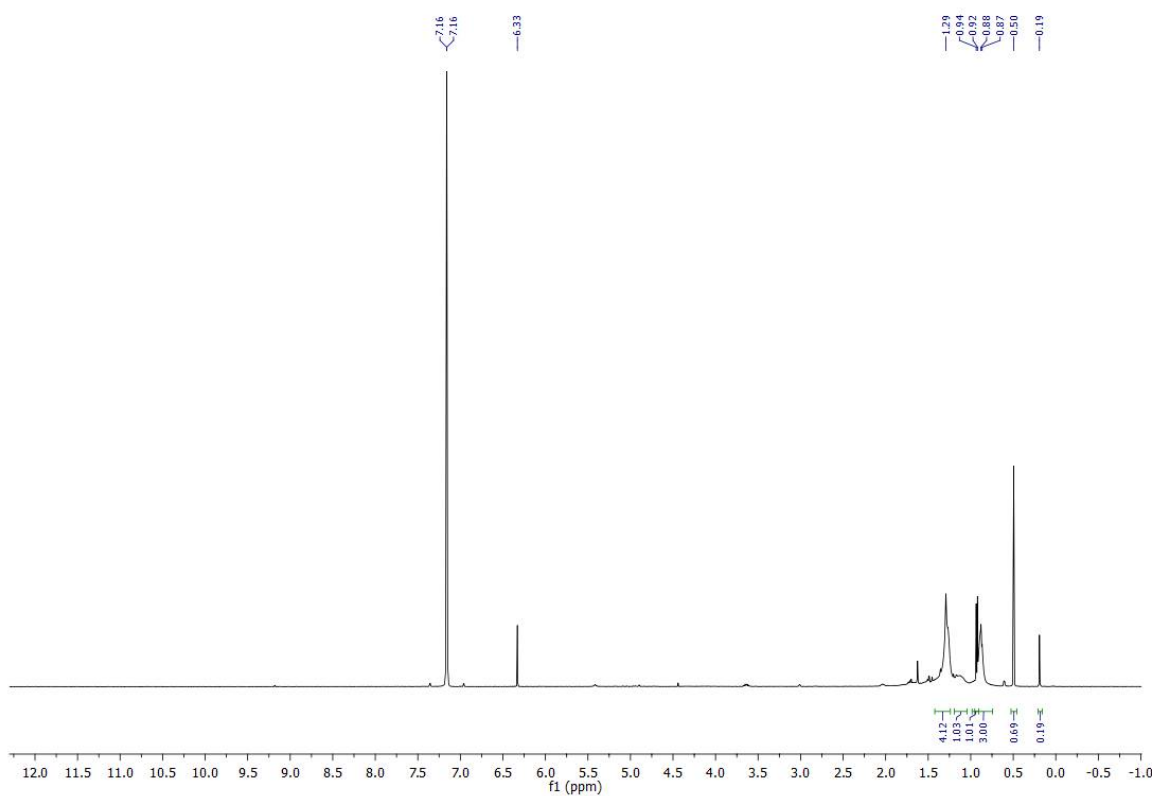


Figure S33. ^1H NMR (400 MHz, C_6D_6) spectrum of the gaseous products of polyvinyl borneol (**P2**) pyrolysis from benzene trap

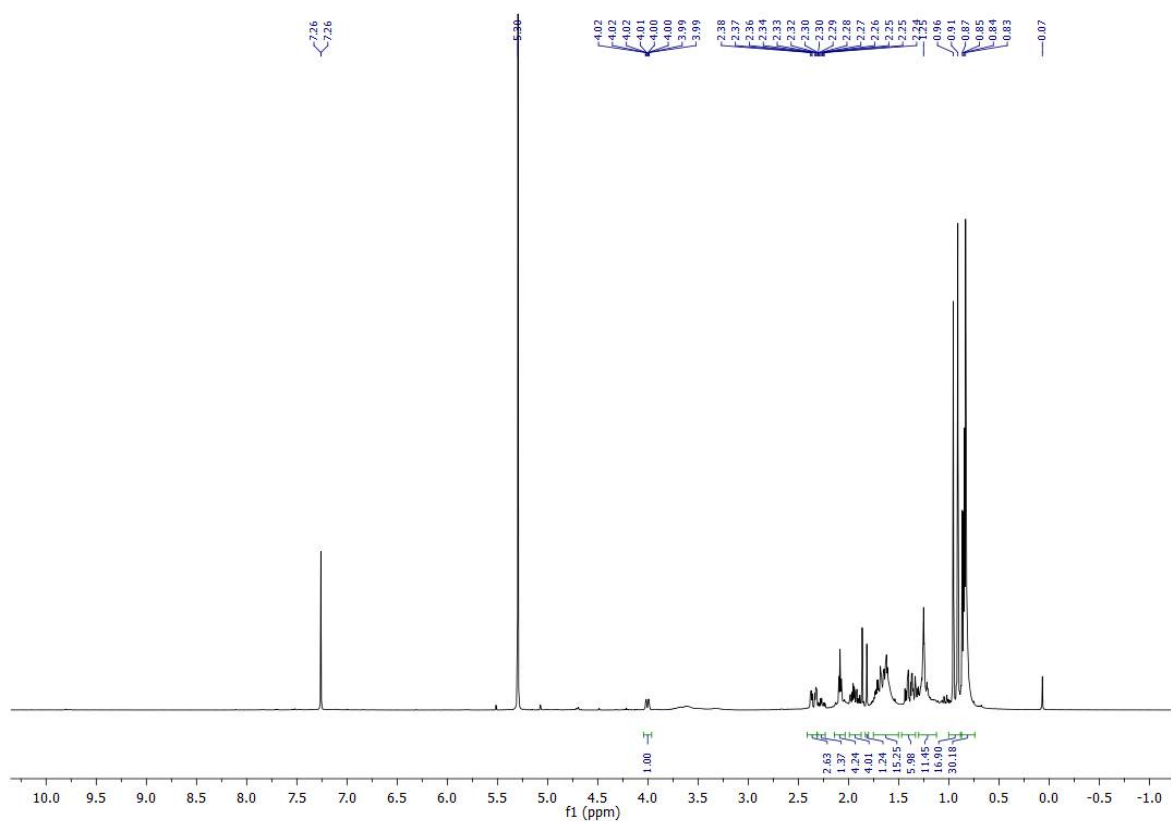


Figure S34. ^1H NMR (400 MHz, CDCl_3) spectrum of the liquid products of polyvinyl borneol (**P2**) pyrolysis washed out from the system with methylene chloride

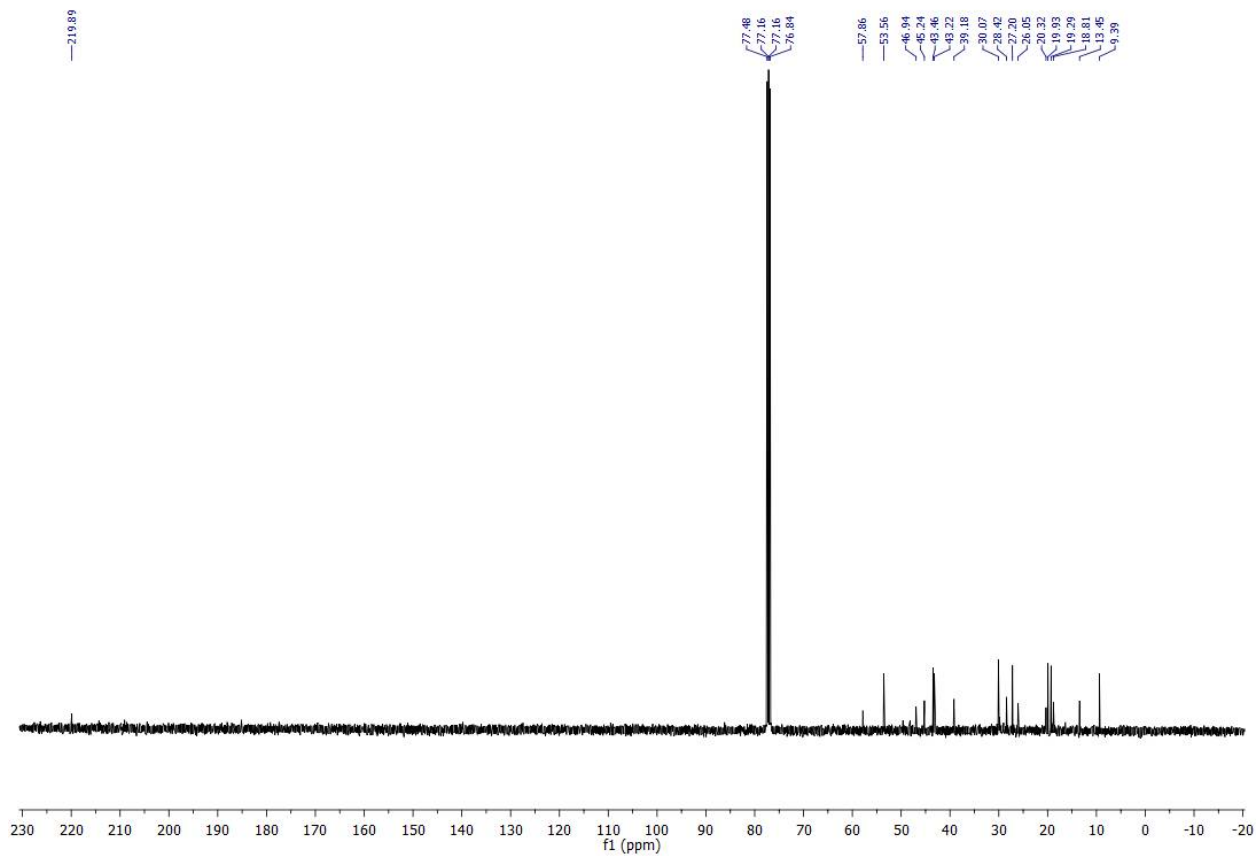


Figure S35. ^{13}C NMR (101 MHz, CDCl_3) spectrum of the liquid products of polyvinyl borneol (**P2**) pyrolysis washed out from the system with methylene chloride

S9. NMR spectra of the mixtures after the reduction

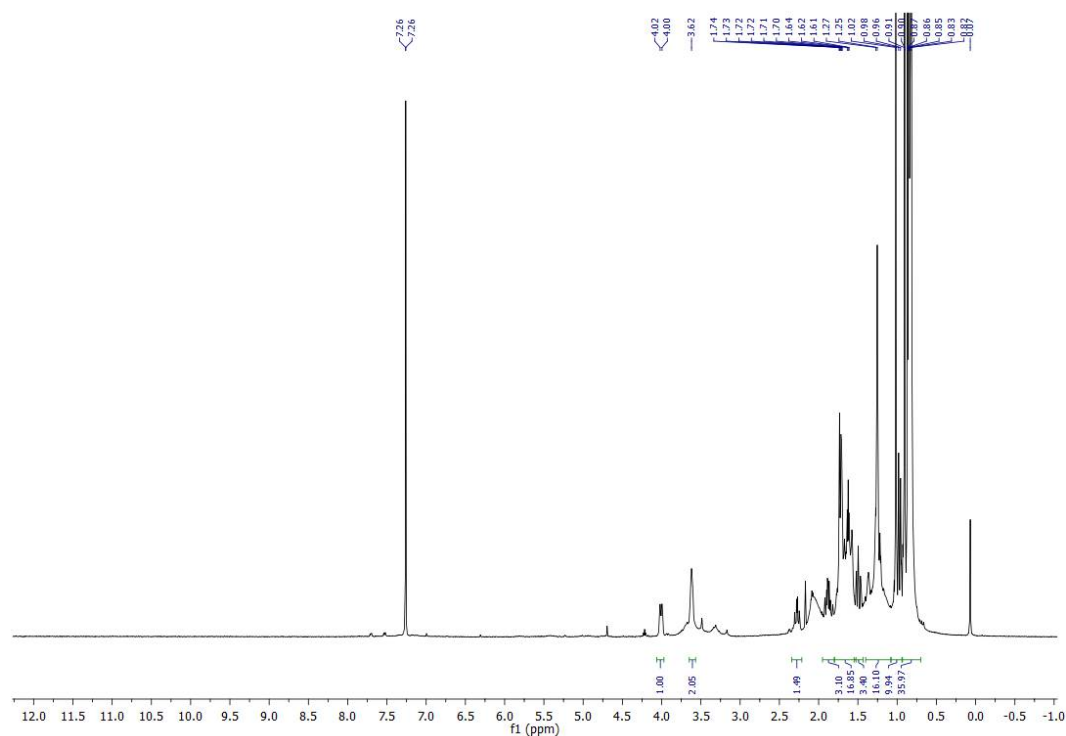


Figure S36. ¹H NMR (400 MHz, CDCl₃) spectrum of the liquid products of polyvinyl borneol (**P2**) pyrolysis after the reduction with NaBH₄

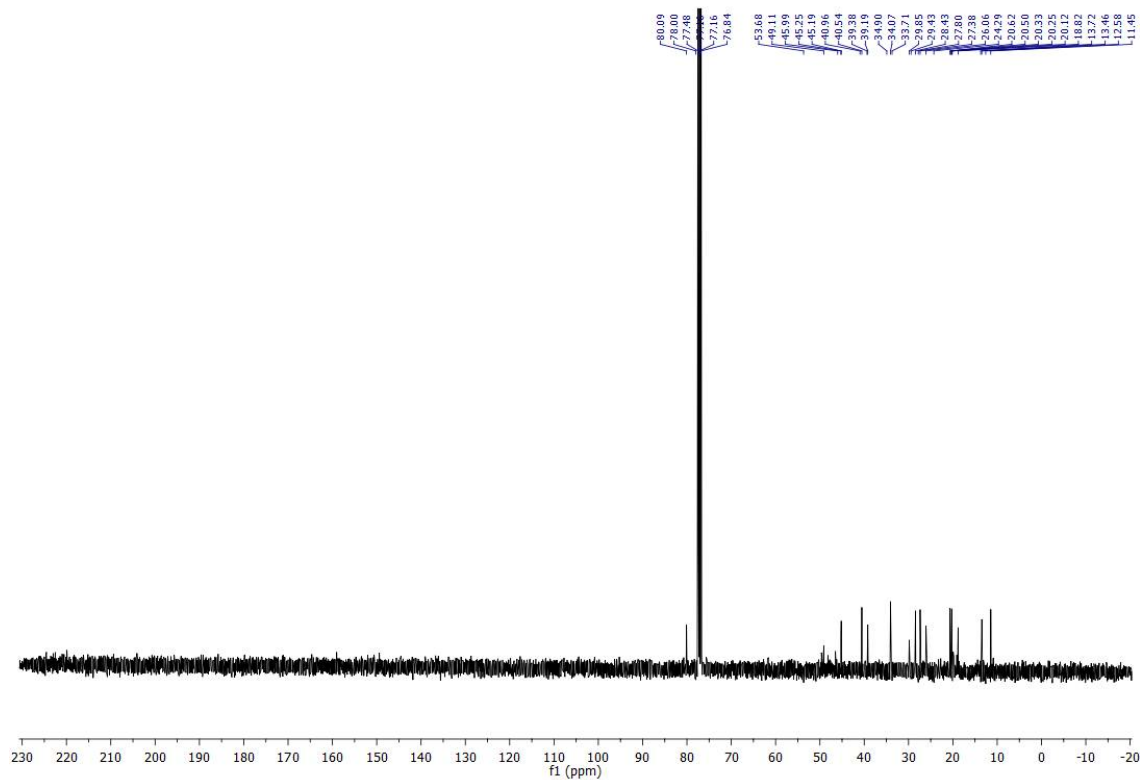
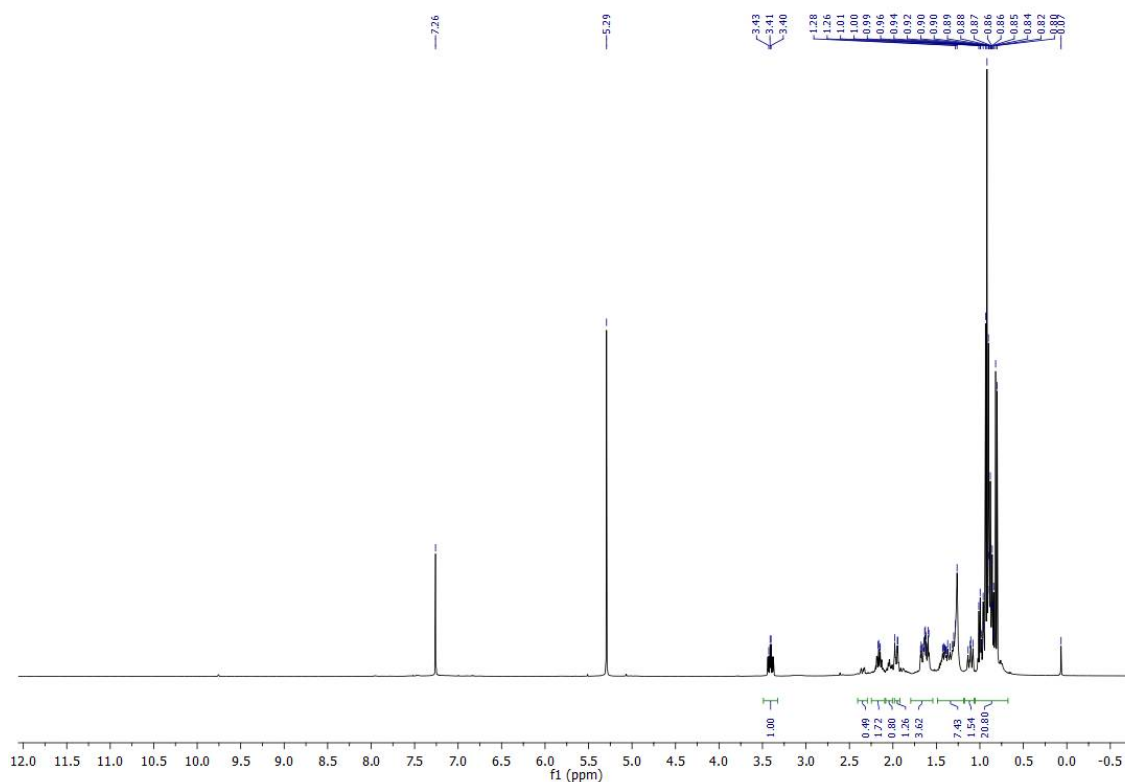


Figure S37. ¹³C NMR (101 MHz, CDCl₃) spectrum of the liquid products of polyvinyl borneol (**P2**) pyrolysis after the reduction with NaBH₄

S10. NMR spectra of the pyrolysis products in a quartz tube



Figure

S38. ^1H NMR (400 MHz, CDCl_3) spectrum of the liquid products of polyvinyl menthol (**P1**) pyrolysis in a quartz tube

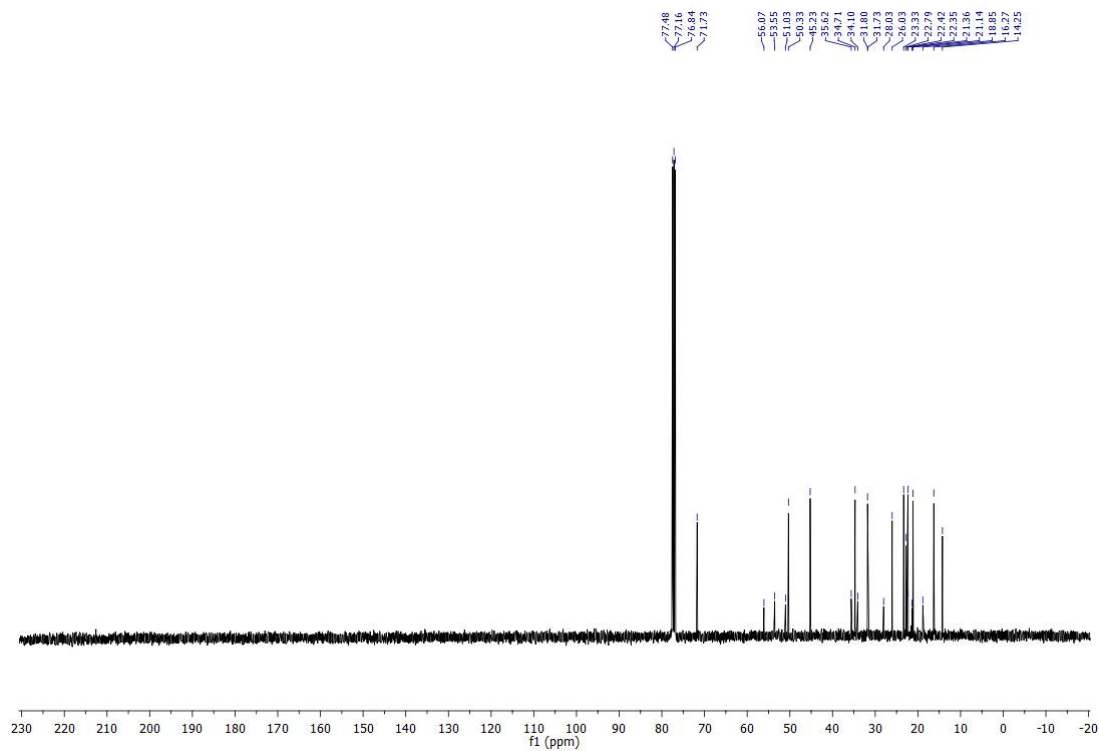


Figure S39. ^{13}C NMR (101 MHz, CDCl_3) spectrum of the liquid products of polyvinyl menthol (**P1**) pyrolysis in a quartz tube

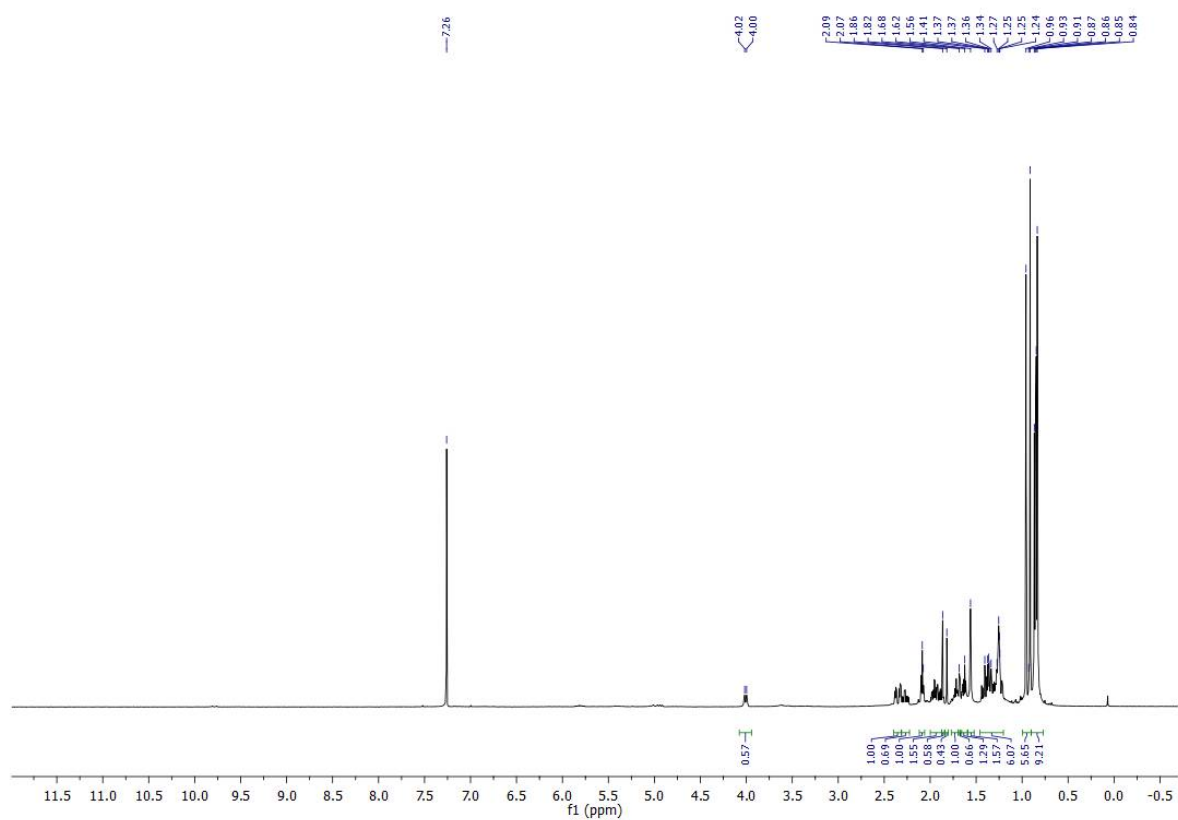


Figure S40. ^1H NMR (400 MHz, CDCl_3) spectrum of the liquid products of polyvinyl borneol (**P2**) pyrolysis in a quartz tube

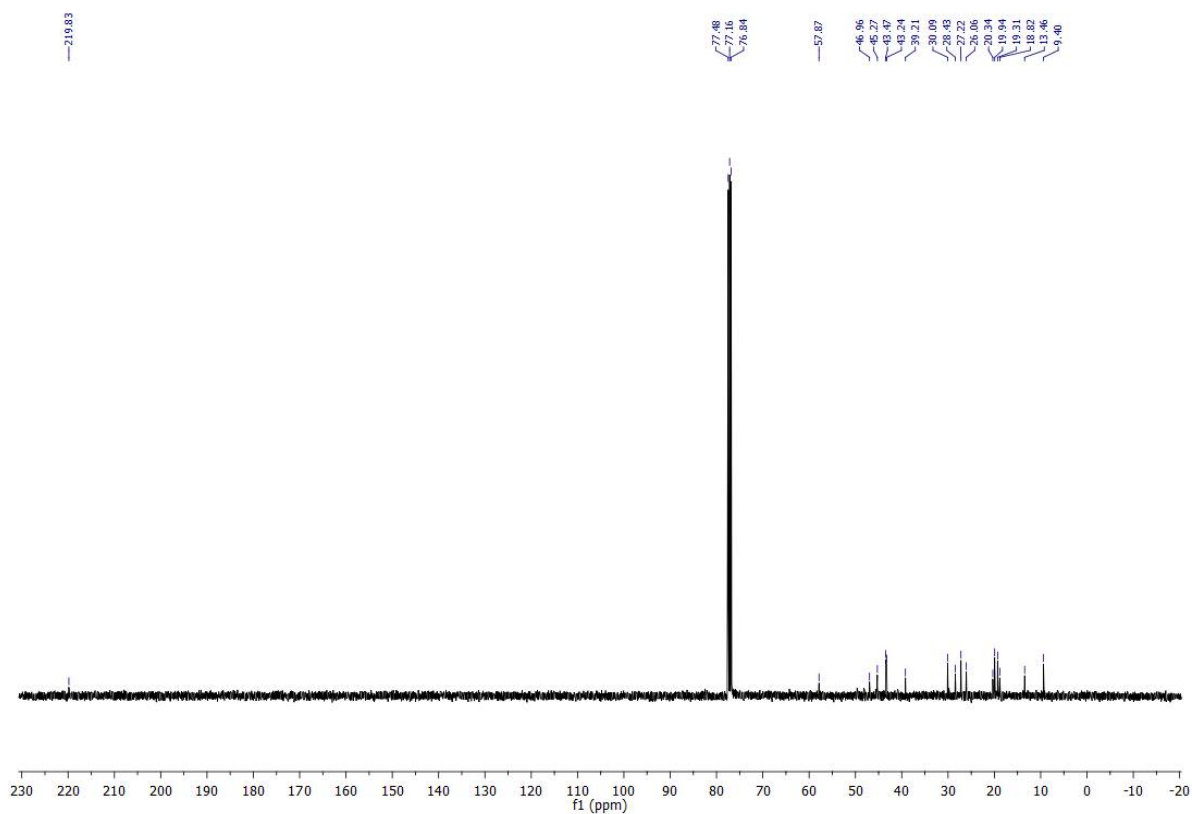


Figure S41. ^{13}C NMR (101 MHz, CDCl_3) spectrum of the liquid products of polyvinyl borneol (**P2**) pyrolysis in a quartz tube

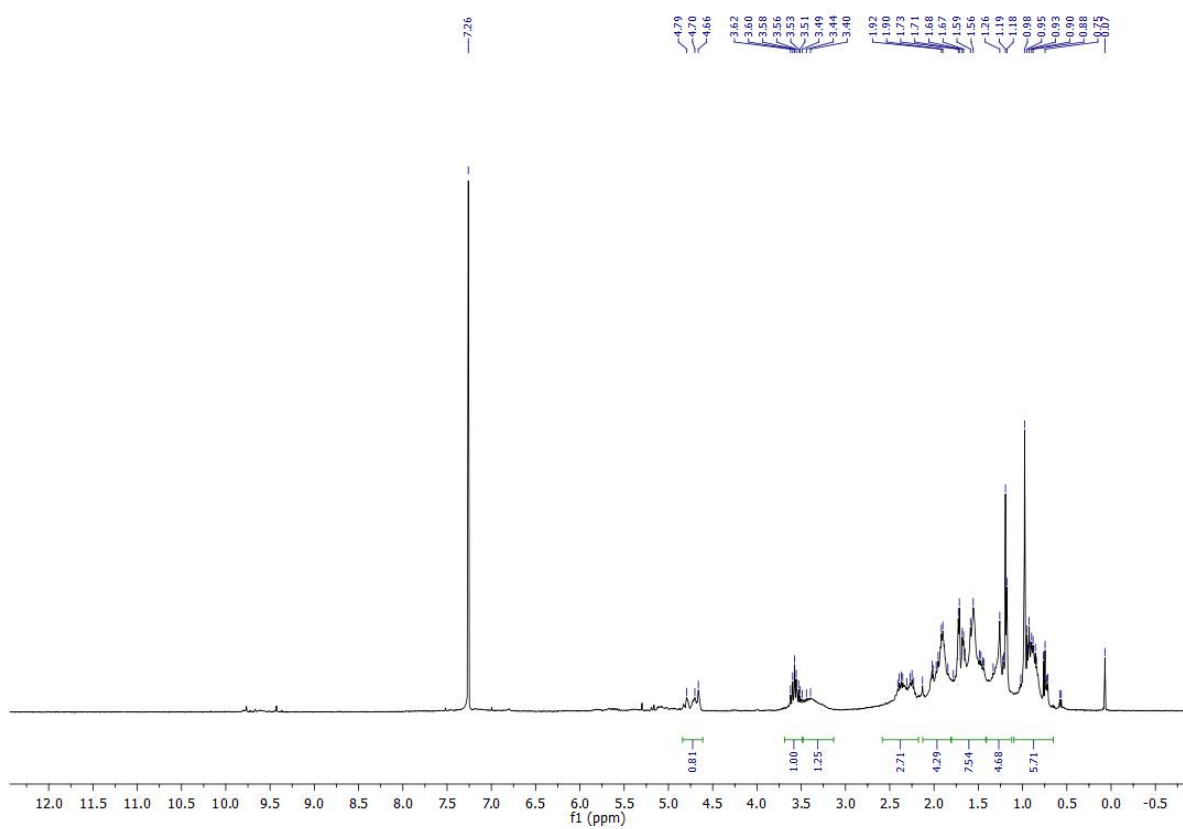


Figure S42. ^1H NMR (400 MHz, CDCl_3) spectrum of the liquid products of polyvinyl myrtanol (**P6**) pyrolysis in a quartz tube