Sustainable Allylation of Organosolv Lignin with Diallyl Carbonate and detailed Structural Characterization – Electronic Supplementary Information

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I. Quantitative ^{13}C NMR studies

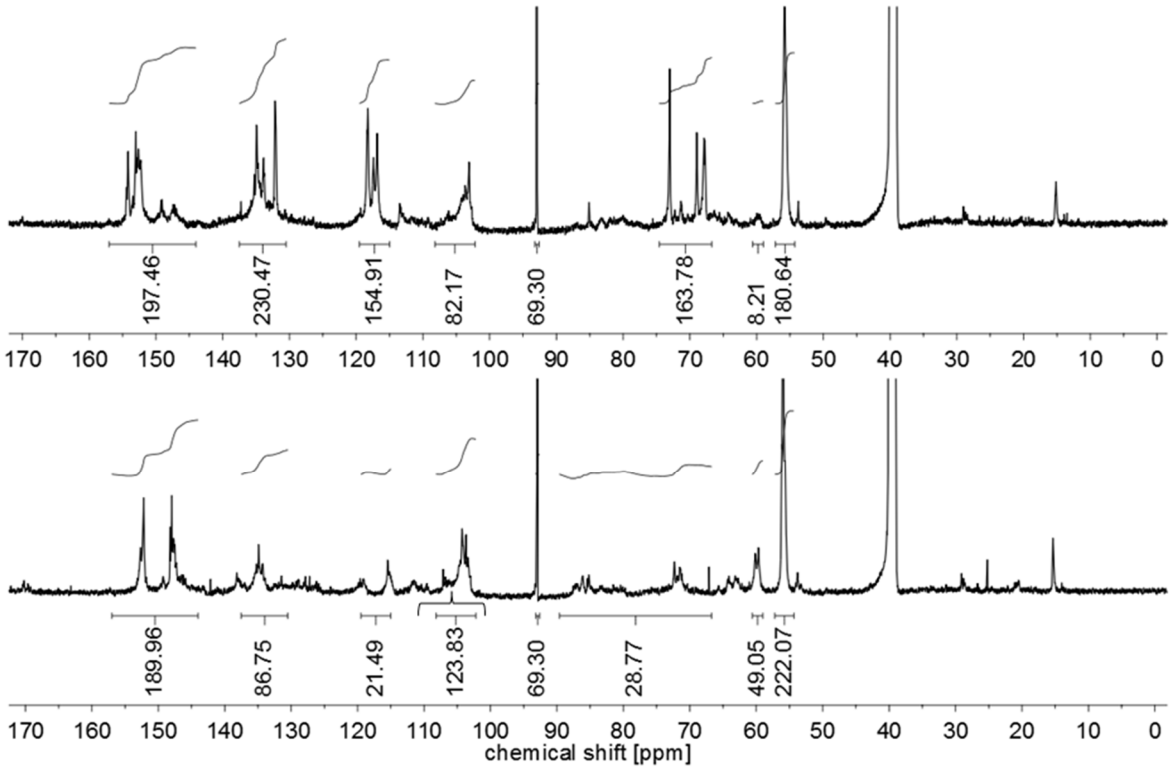

Figure I-1: Quantitative ^{13}C NMR spectra of unmodiefied OL (bottom) and allylated OL (top) in DMSO-*d6* with 1,3,5-trioxane as internal standard.

Table I-1: ^{13}C NMR results for allylated OL

ppm region	157-144	137.5-130.5	119.5-115	108.2-102.2	93.2-92.6 trioxane	74.6-66.7	60.6-59.0	57.2-54.3
allylated OL								
µmol relative to 69.3 µmol trioxane	197.5	230.5	154.9	82.2	69.3 µmol	163.8	8.2	180.6
Carbon content [mmol/g]	**6.2**	**7.3**	**4.9**	**2.6**	2.2	**5.2**	**0.3**	**5.7**
unmodified OL								
µmol relative to 69.3 µmol trioxane	190.0	86.8	21.5	123.8	69.3 µmol	28.8	49.1	222.1
Carbon content [mmol/g]	6.0	2.7	0.7	3.9	2.2	0.9	1.5	7.0

Weighed samples: 94.9 mg allylated OL; 95.4 mg unmodified OL

II. ^{1}H NMR spectra

II.1 Spectrum of the allylated and decarboxylated OL

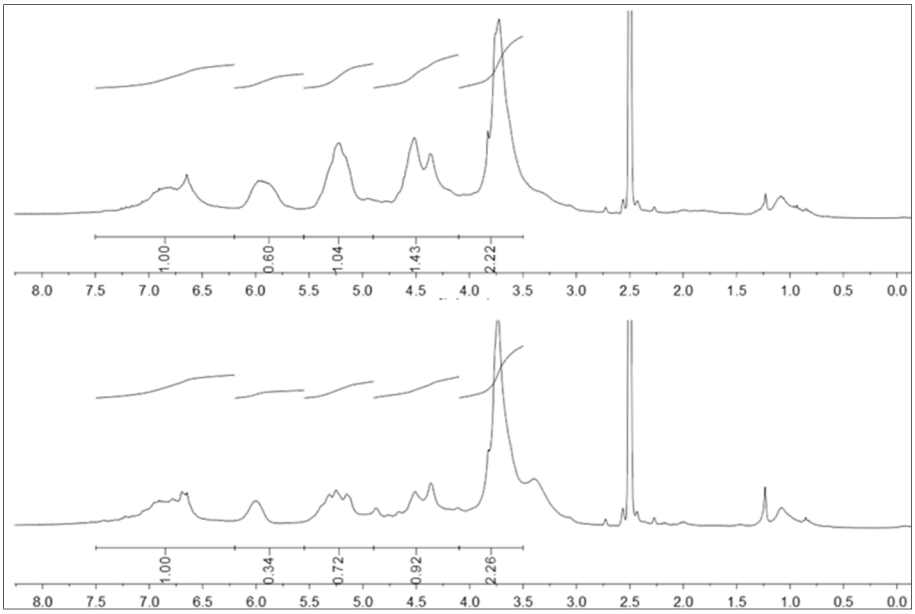

Figure II-1: ^{1}H NMR spectra of allylated OL (top) and partially defunctionalized allylated OL (bottom) in DMSO-d_6.

II.2 ^{1}H NMR spectra of TBAB

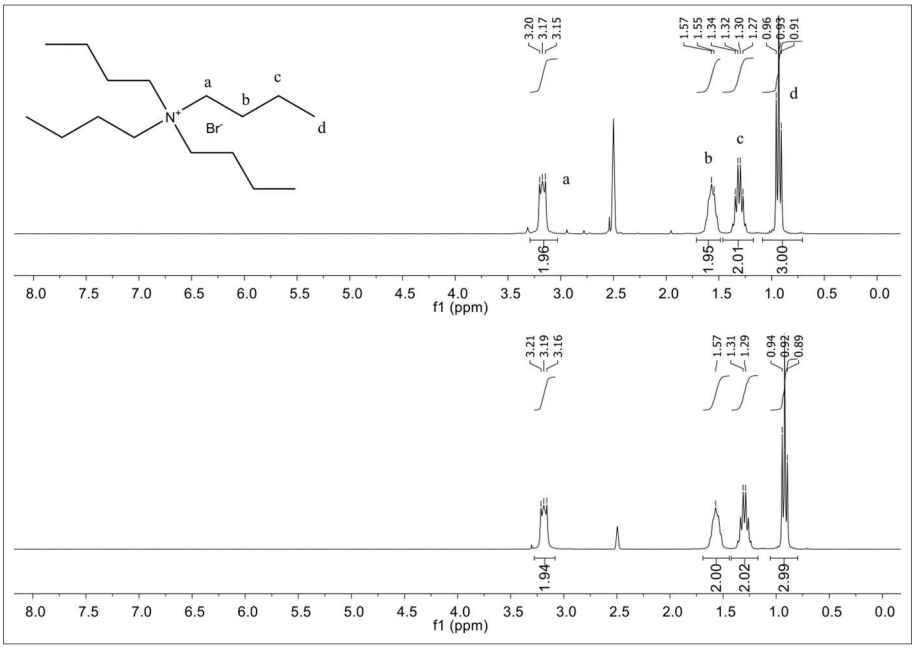

Figure II-2: ^{1}H NMR of commercial TBAB (bottom) and recycled TBAB (top) in DMSO-d_6.

II.3 1H NMR spectrum of DAC

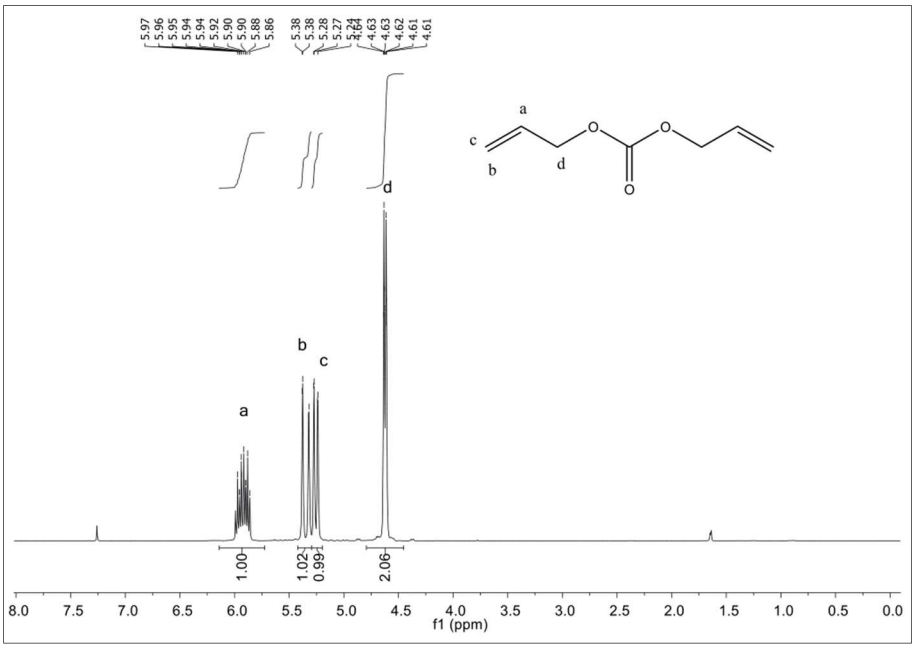

Figure II-3: 1H NMR of recovered diallyl carbonate.

III. IR spectra

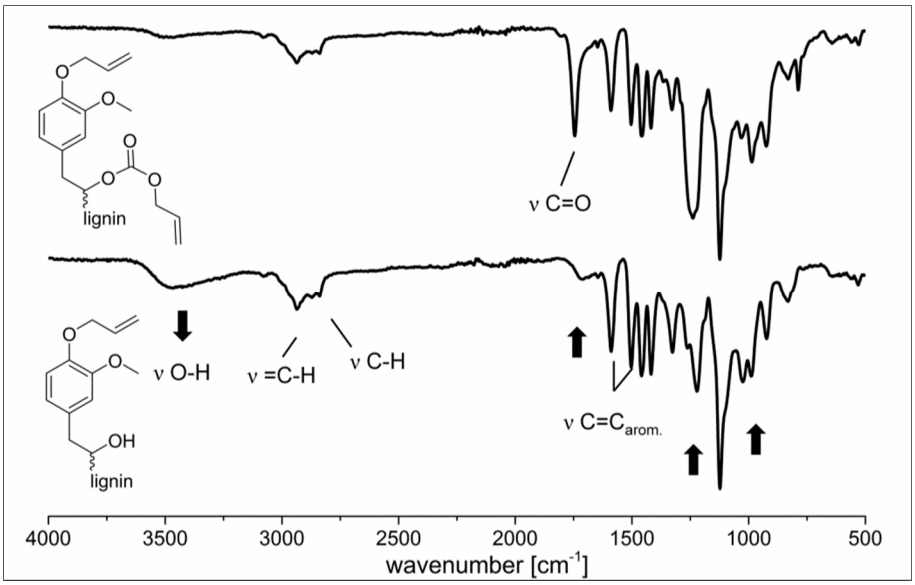

Figure III-1: IR spectra of allylated OL (top) and hydrolyzed allylated OL (bottom). The disappearance of the C=O stretching vibration bond is observed in the decarboxylated product (bottom). Conditions of the hydrolysis: allylated OL was stirred with LiOH (2 eq. per original OH) in THF/H_2O at room temperature for 120 h.

IV. Thermal properties

IV.1 DSC studies

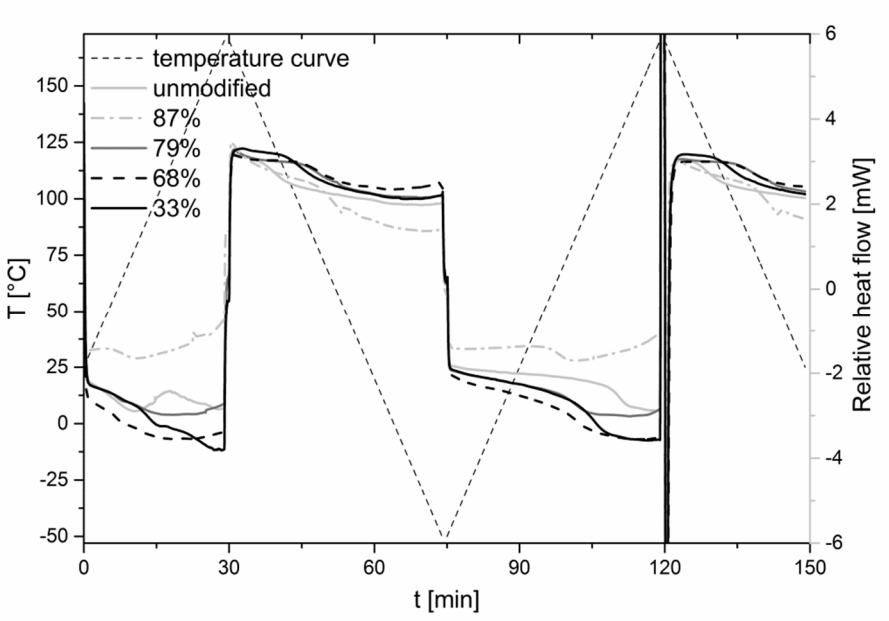

Figure IV-1: DSC analysis of unmodified OL and OL with different hydroxyl groups conversions between 33 and 87% with the following oven temperature program: 25 °C to 170 °C (5 K·min^{-1}) — 170 °C (1 min) — 170 °C to –50 °C (5 K·min^{-1}) — –50 °C (1 min) — –50 °C to 170 °C (5 K·min^{-1}) — 170 °C (1 min) — 170 °C to 25 °C (5 K·min^{-1}).

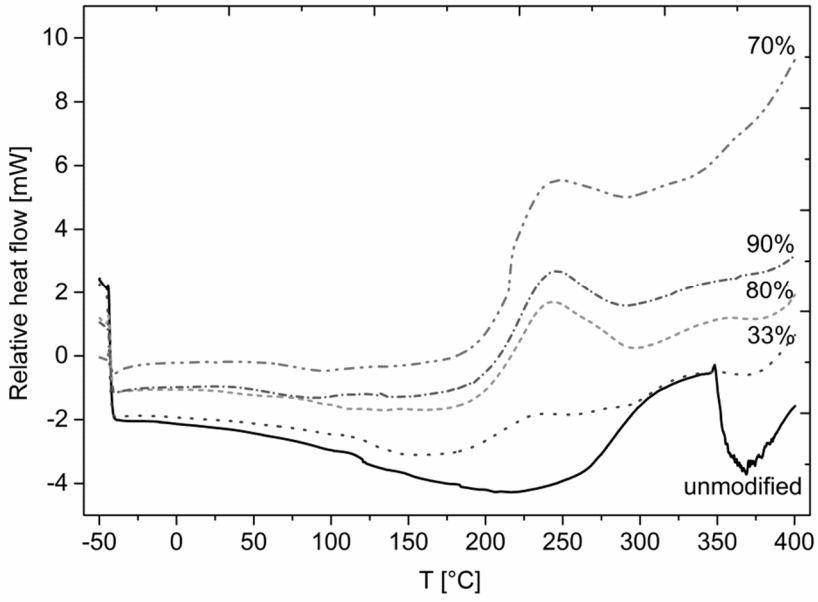

Figure IV-2: DSC analysis of allylated OL having a functionalization grade of 33–90% relatively to the measured baseline from –50 to 400 °C. Oven temperature program: 25 to 80 °C (5 K·min^{-1}); constant at 80 °C for 5 min; 80 to –50 °C (–20 K·min^{-1}); –50 °C to 400 °C (10 K·min^{-1}).

IV.2 SEC analysis after different heating cycles

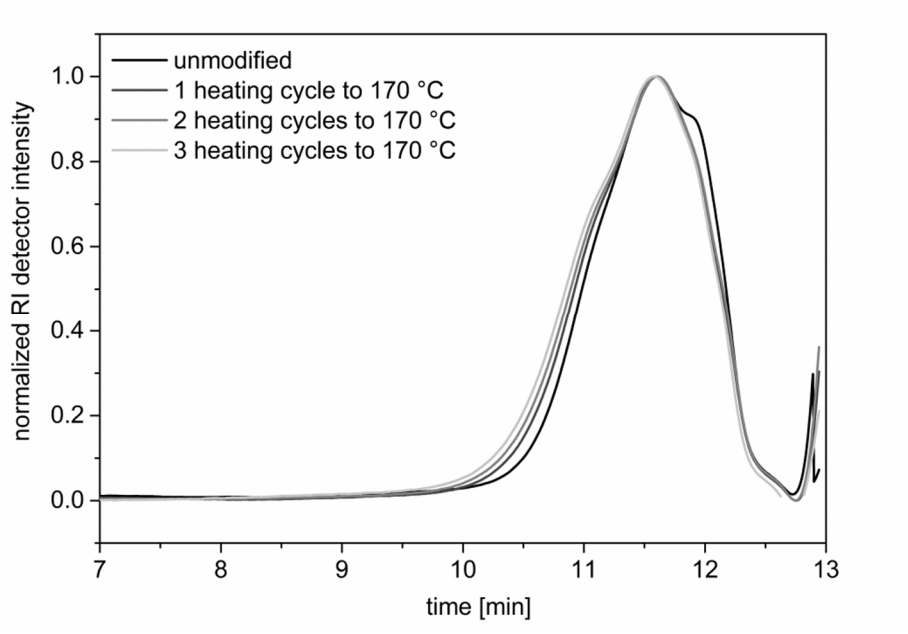

Figure IV-3: SEC traces for the unmodified OL after different heating circles to 170 °C. One cycle: 25 to 170 °C (5 K·min^{-1}); constant at 170 °C for 1 min; 170 to –50 °C (–5 K·min^{-1}); constant at –50 °C for 1 min; –50 °C to 25 °C (5 K·min^{-1}).

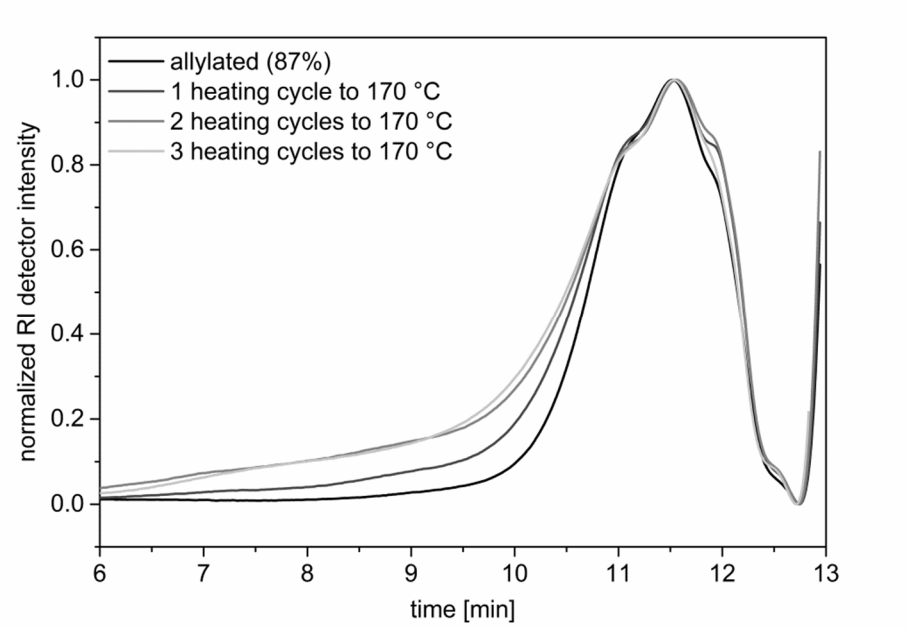

Figure IV-4: SEC traces for an allylated OL sample after different heating circles to 170 °C. One cycle: 25 to 170 °C (5 K·min^{-1}); constant at 170 °C for 1 min; 170 to –50 °C (–5 K·min^{-1}); constant at –50 °C for 1 min; –50 °C to 25 °C (5 K·min^{-1}).

IV.3 TGA traces

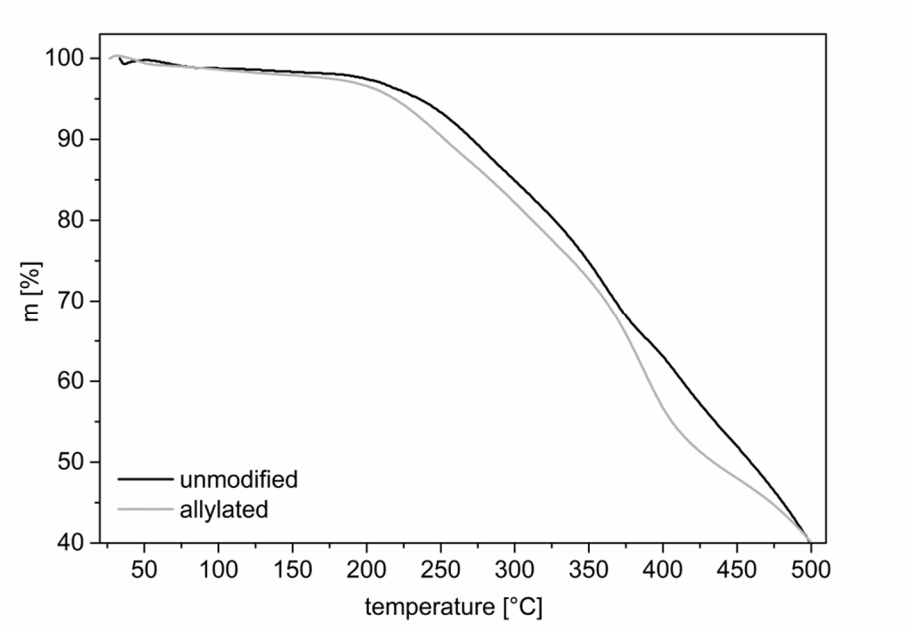

Figure IV-5: TGA traces for unmodified and allylated OL with a heating program from 25 to 500 °C (5 K·min^{-1}).

V. SEC–ESI–MS Analytics

V.1 SEC trace and mass spectra for selected retention times

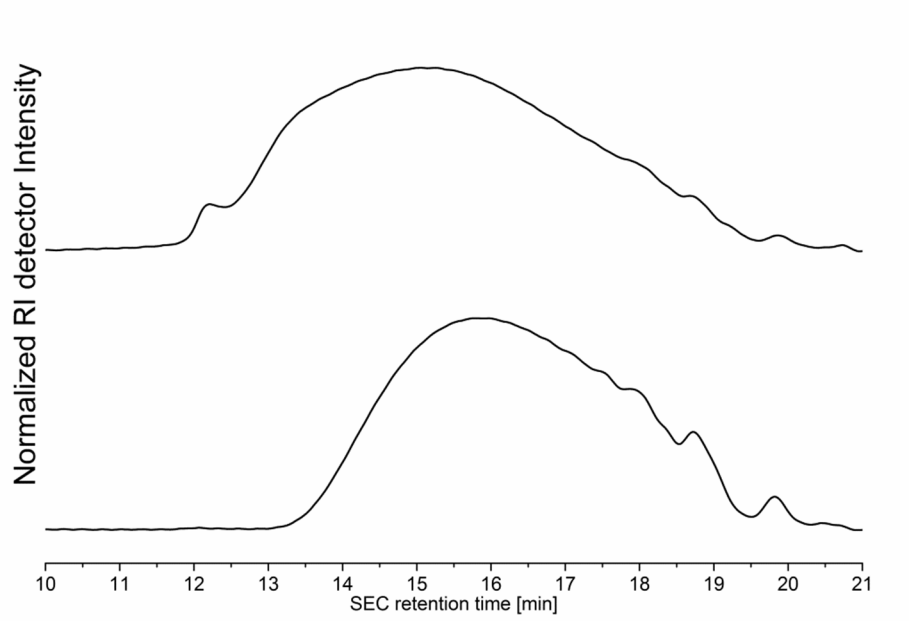

Figure V-1: SEC traces of unmodified OL (bottom) and allylated OL (top). Reaction conditions for the allylation of OL: 3 h at 120 °C with 2 equivalents of TBAB per OH (Fehler! Verweisquelle konnte nicht gefunden werden.**, entry 10).**

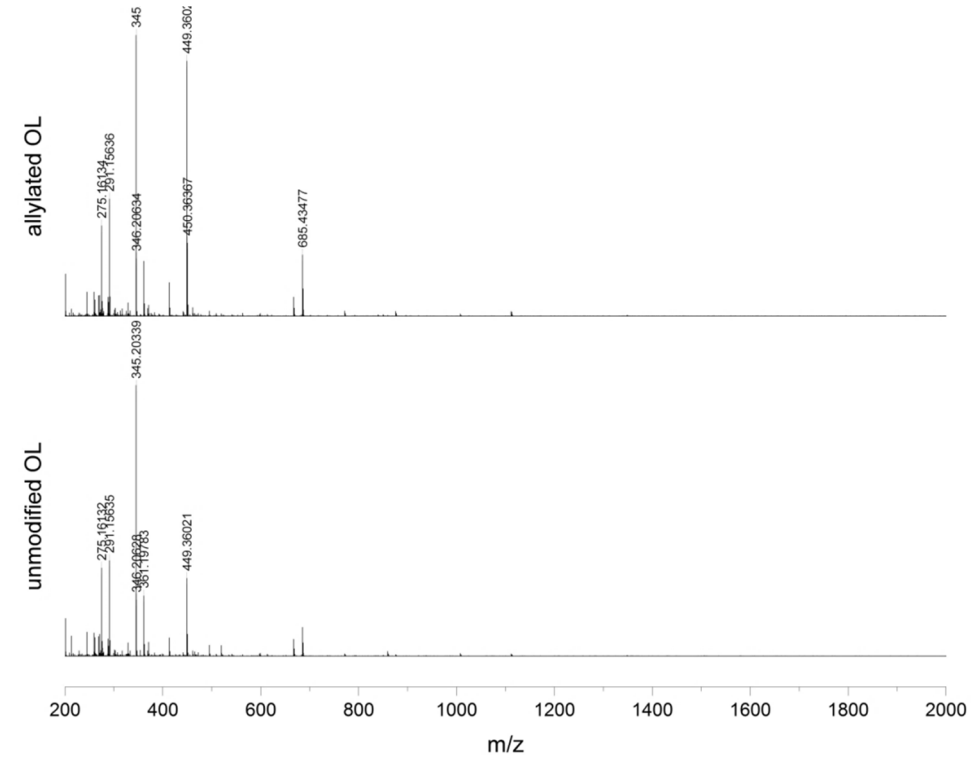

Figure V-1: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 13.0 min.

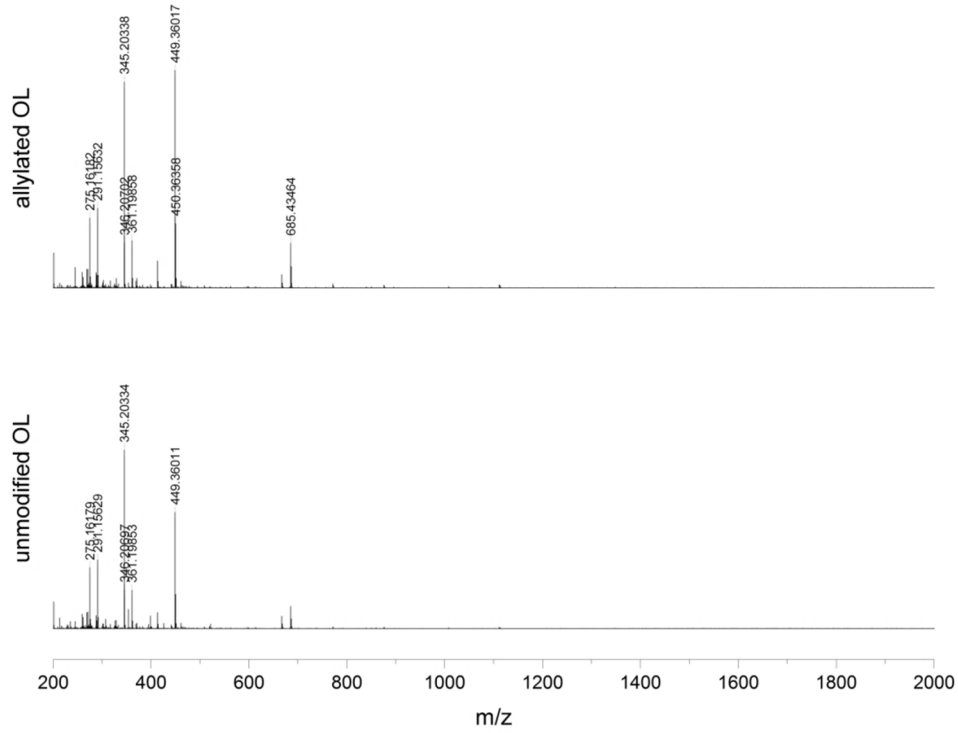

Figure V-2: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 14.0 min.

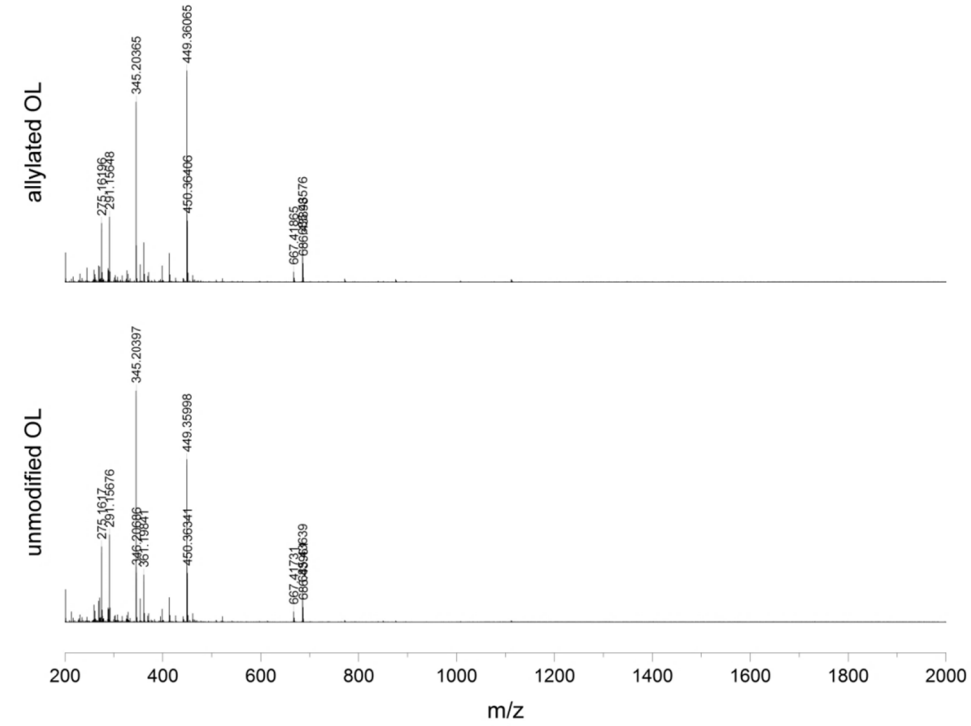

Figure V-3: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 15.0 min.

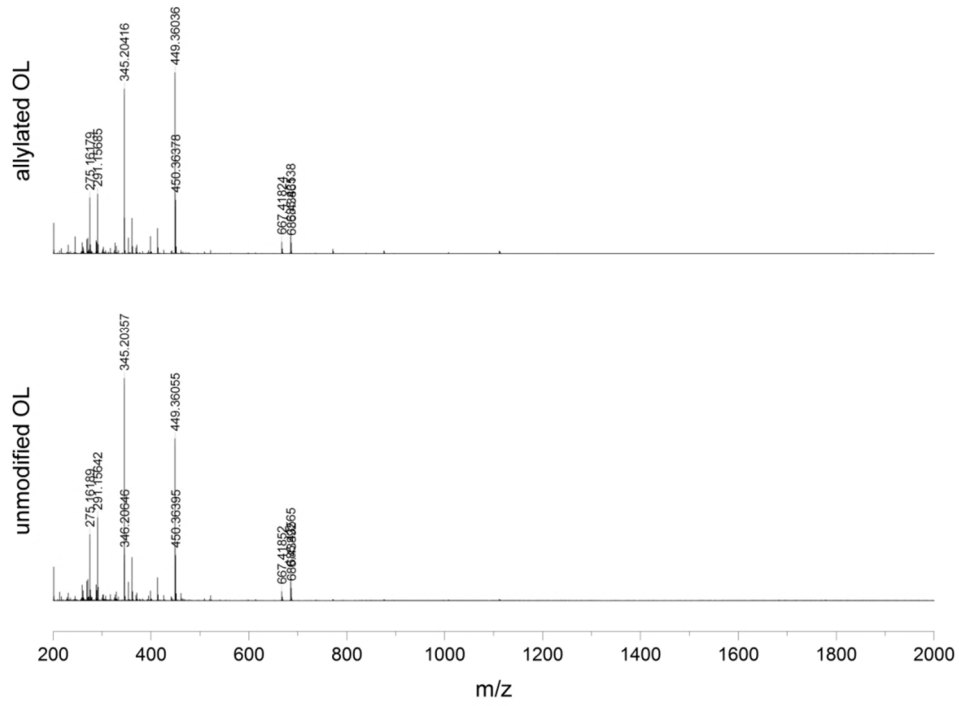

Figure V-4: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 16.0 min.

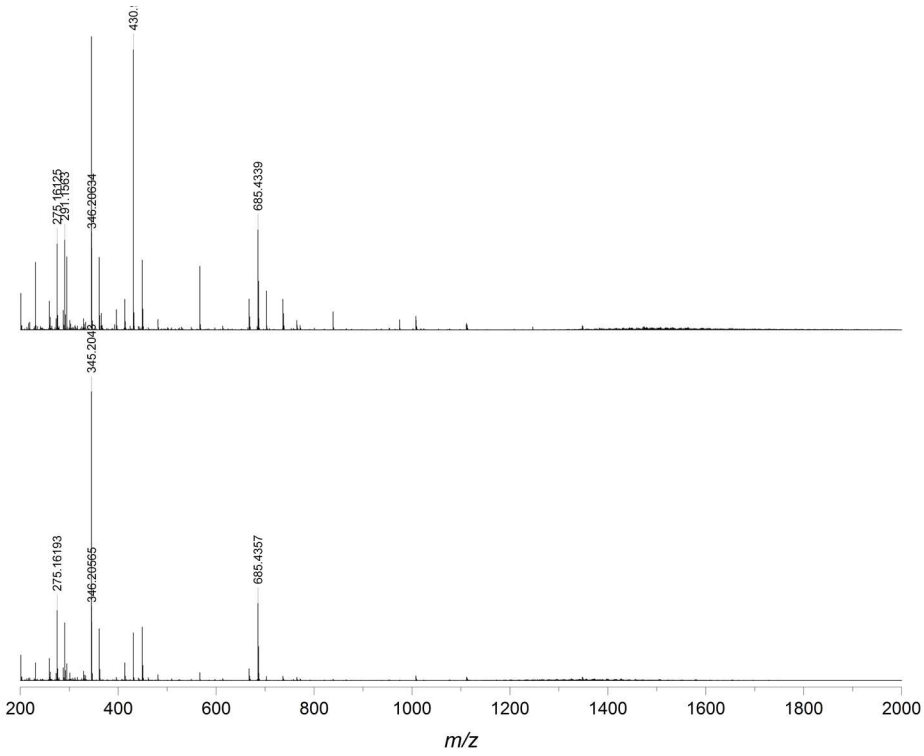

Figure V-5: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 16.5 min.

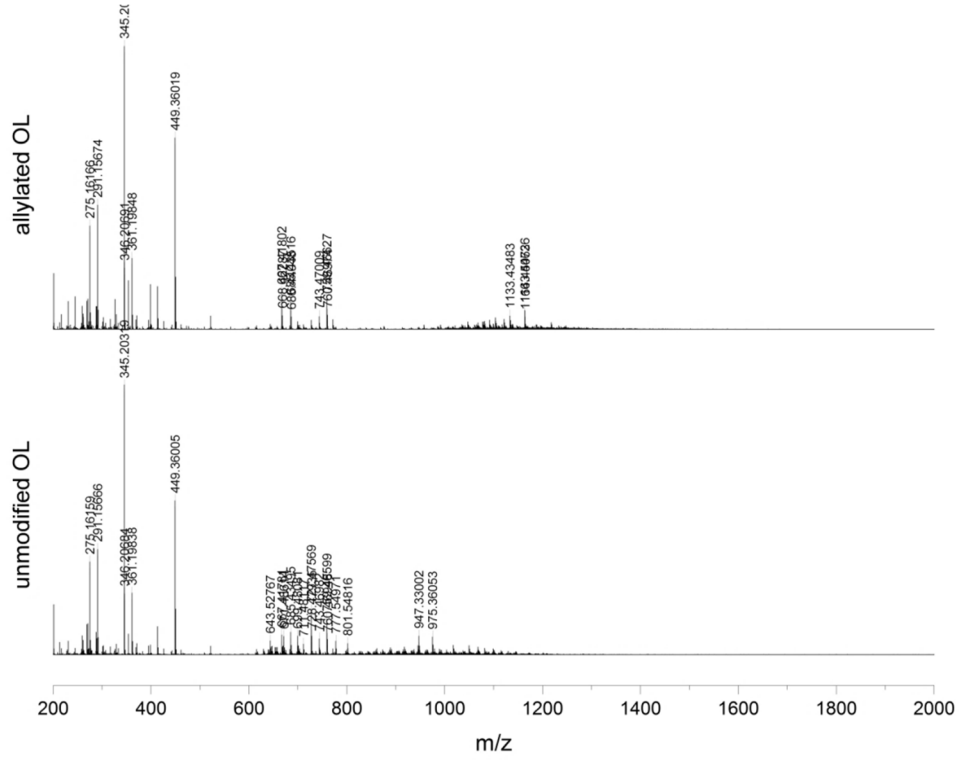

Figure V-6: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 17.0 min.

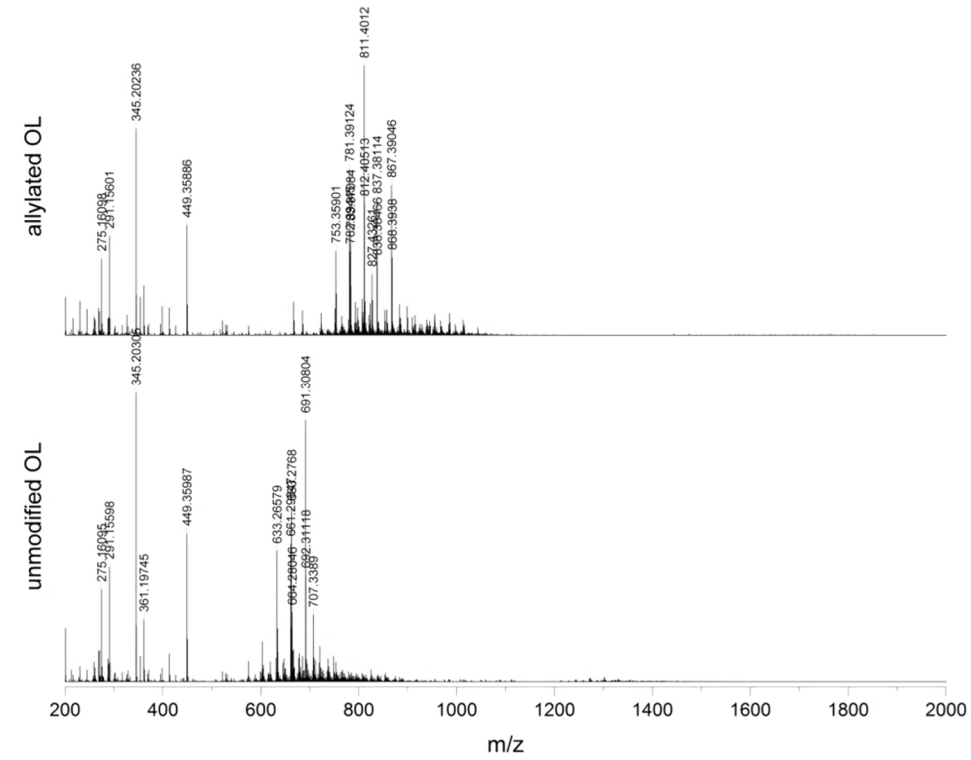

Figure V-7: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 17.5 min.

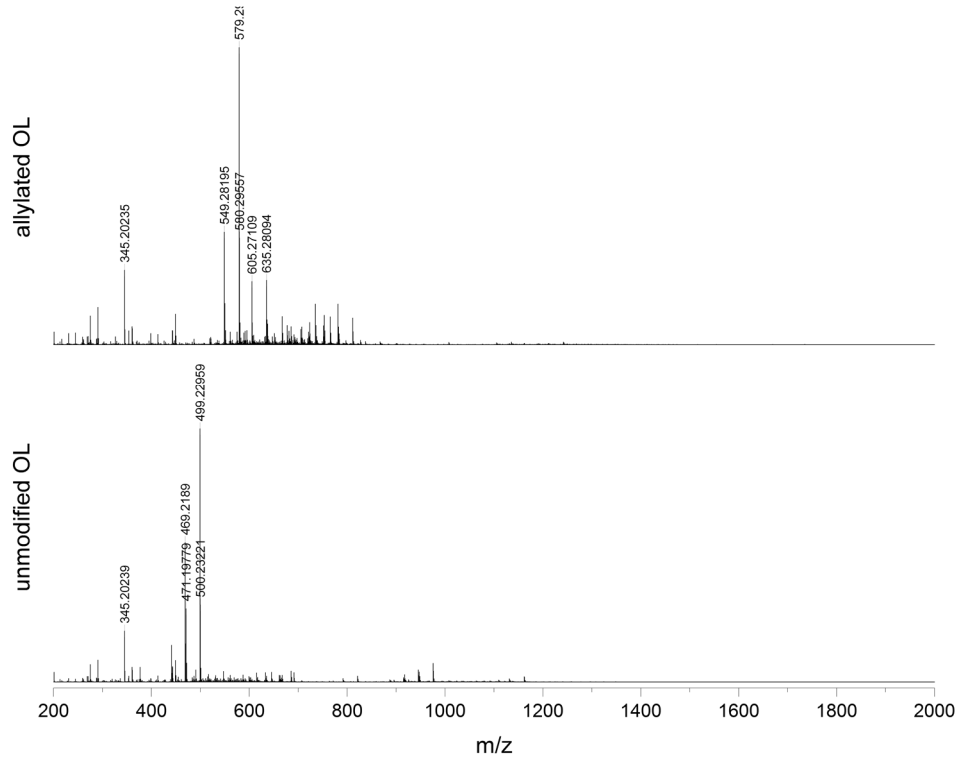

Figure V-8: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of and b) 18.0 min.

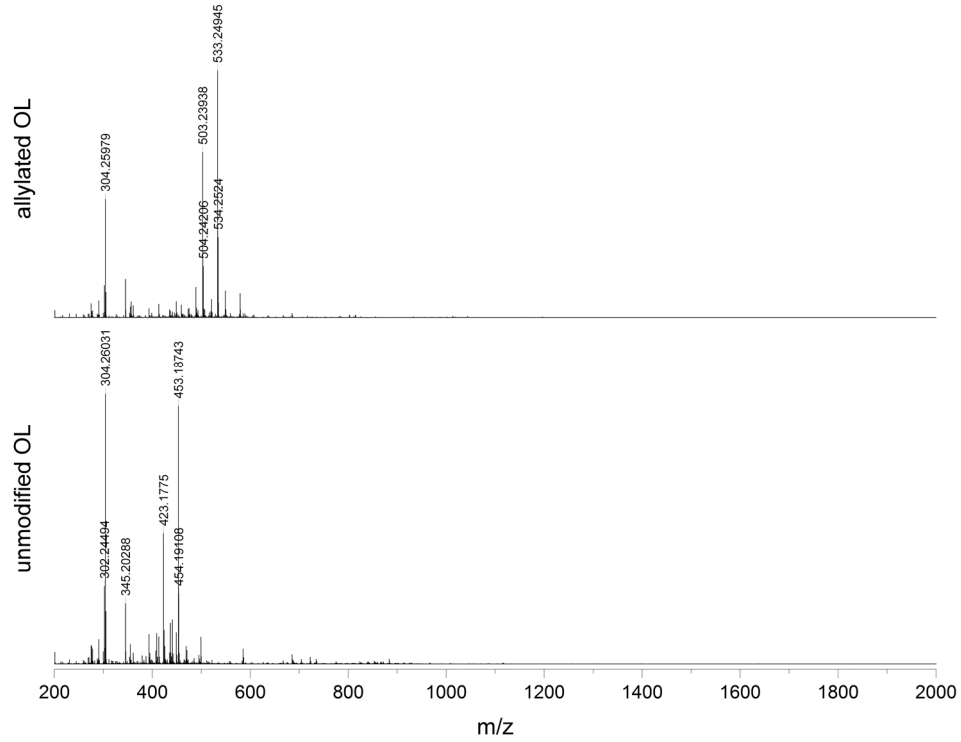

Figure V-9: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 18.5 min.

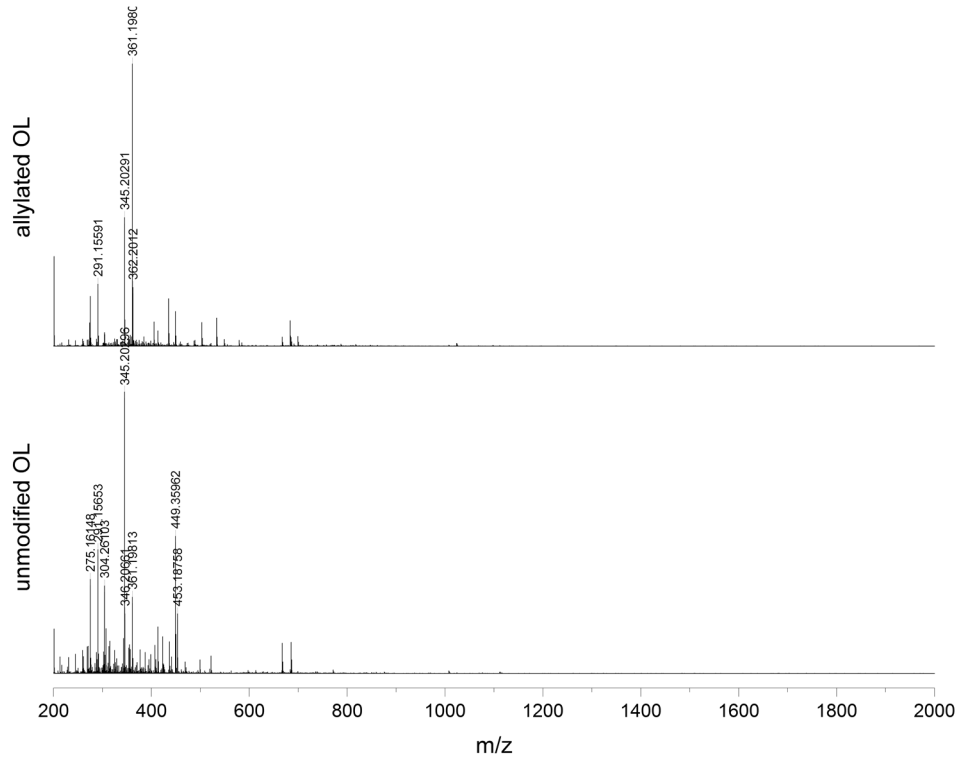

Figure V-10: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 19.0 min.

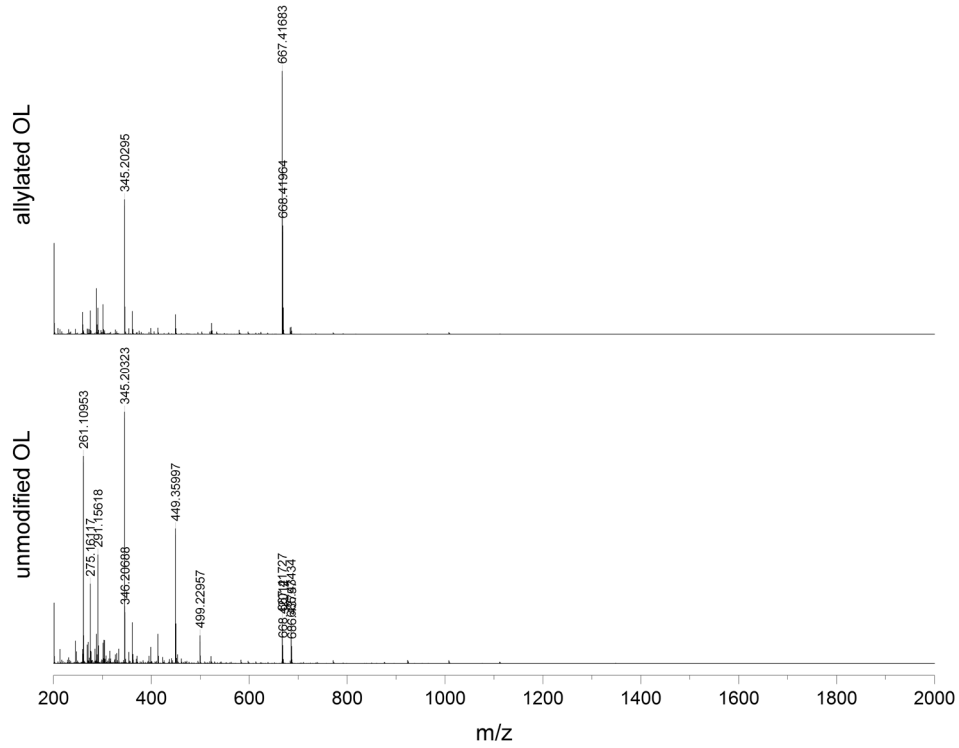

Figure V-11: Mass spectra of OL (bottom) and allylated OL (top) at a retention time of 19.5 min.

Table V-1: Mass analysis for different retention times for the unmodified and allylated OL

retention time	*m/z* (OL)	r	*m* (neutral molecule)	molecular formula	RDB	m/z_{calc} $[M+Na]^+$	*Δ*	*Δm/z*	m/z (allylated OL)	r	*Δm*	proposed structures
17	979.3571	67005	956.3679	$C_{48}H_{60}O_{20}$	19	979.357	-0.0001	0.0146	1103.4252	64905	124.0681	
	947.3306	71407	924.3413	$C_{47}H_{56}O_{19}$	20	947.3308	0.0002	0.0133	1111.4155	64600	164.0850	
	873.3295	75107	850.3402	$C_{45}H_{54}O_{16}$	19	873.3304	0.0009	0.0116	1121.4354	64105	248.1060	
	861.2935	75102	838.3042	$C_{43}H_{50}O_{17}$	19	861.294	0.0005	0.0115	1021.4200	60207	160.1266	
	825.3454	74707	802.3561	$C_{45}H_{54}O_{13}$	19	825.3457	0.0003	0.0110	1077.4096	65904	252.0642	
17.2	855.3561	76907	832.3668	$C_{46}H_{56}O_{14}$	19	855.3562	0.0001	0.0111	1015.4815	70305	160.1254	
	825.3454	76907	802.3561	$C_{45}H_{54}O_{13}$	19	825.3457	0.0003	0.0107	985.4711	71005	160.1257	
	795.3353	78707	772.3460	$C_{44}H_{52}O_{12}$	19	795.3351	-0.0002	0.0101	955.4605	71005	160.1252	Figure V-12
17.5	707.3391	85007	684.3499	$C_{38}H_{52}O_{11}$	13	707.3402	0.0011	0.0083	827.4323	78507	120.0932	
	691.3080	84807	668.3187	$C_{37}H_{48}O_{11}$	14	691.3089	0.0009	0.0082	811.4009	79207	120.0930	Figure V-13
	663.2769	86507	640.2877	$C_{35}H_{44}O_{11}$	14	663.2776	0.0007	0.0077	783.3701	80600	120.0931	Figure V-14
	661.2978	88602	638.3085	$C_{36}H_{46}O_{10}$	14	661.2983	0.0005	0.0075	781.3908	80607	120.0930	
	633.2664	86507	610.2771	$C_{34}H_{42}O_{10}$	14	633.2670	0.0006	0.0073	753.3594	82207	120.0931	Figure V-15
18.0	499.2290	101607	476.2397	$C_{26}H_{36}O_8$	9	499.2302	0.0012	0.0049	579.2918	94607	80.0628	Figure V-16
	471.1974	103602	448.2081	$C_{24}H_{32}O_8$	9	471.1989	0.0015	0.0045	635.2816	88607	164.0842	Figure V-17
	469.2188	104607	446.2295	$C_{25}H_{34}O_7$	9	469.2197	0.0009	0.0045	549.2813	95807	80.0625	Figure V-18
	441.1873	107607	418.1980	$C_{23}H_{30}O_7$	9	441.1884	0.0011	0.0041	521.2500	98107	80.0627	
	441.1873	107607	418.1980	$C_{23}H_{30}O_7$	9	441.1884	0.0011	0.0041	605.2711	91507	164.0838	
18.5	499.2295	102007	476.2403	$C_{26}H_{36}O_8$	9	499.2302	0.0007	0.0049	579.2913	93607	80.0617	Figure V-16
	469.2191	103407	446.2298	$C_{25}H_{34}O_7$	9	469.2197	0.0006	0.0045	549.2808	97007	80.0617	
	453.1877	105707	430.1984	$C_{24}H_{30}O_7$	10	453.1884	0.0007	0.0043	533.2498	98007	80.0621	
	441.1516	107707	418.1624	$C_{22}H_{26}O_8$	10	441.152	0.0004	0.0041	521.2137	98603	80.0621	
	423.1772	109807	400.1879	$C_{23}H_{28}O_6$	10	423.1778	0.0007	0.0039	503.2392	100107	80.0621	
	409.1615	111207	386.1723	$C_{22}H_{26}O_6$	10	409.1622	0.0007	0.0037	489.2238	102407	80.0622	
18.7	453.1877	106107	430.1985	$C_{24}H_{30}O_7$	10	453.1884	0.0007	0.0043	533.2498	96807	80.0621	
	423.1771	110907	400.1879	$C_{23}H_{28}O_6$	10	423.1778	0.0007	0.0038	503.2392	99807	80.0621	
	409.1615	112207	386.1722	$C_{22}H_{26}O_6$	10	409.1622	0.0007	0.0036	489.2237	102607	80.0622	
	355.1146	119307	332.1253	$C_{18}H_{20}O_6$	9	355.1152	0.0006	0.0030	435.1768	106807	80.0623	
	325.1041	124507	302.1149	$C_{17}H_{18}O_5$	9	325.1046	0.0005	0.0026	405.1662	110507	80.0621	

V.2 Likely chemical structures corresponding to the found exact masses

The following structures were determined to the best of our knowledge, but are not necessarily correct.

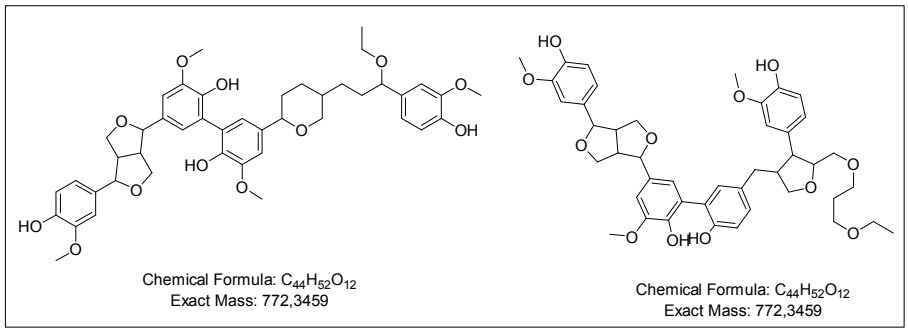

Figure V-12: Proposed chemical structures for m/z = 795.3351 $[M+Na]^+$ (rt = 17.2 min).

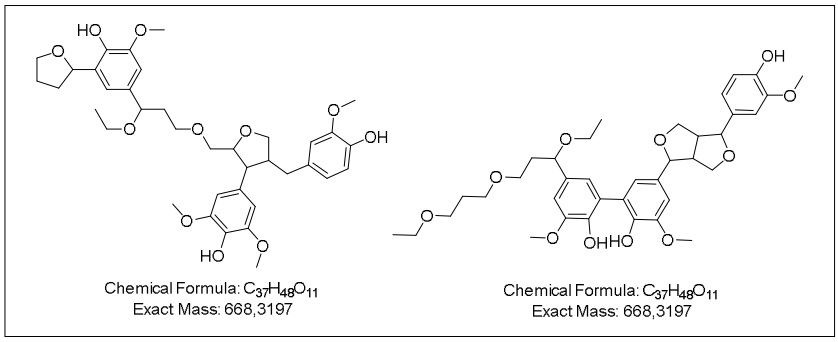

Figure V-13: Proposed chemical structures for m/z = 691.3089 $[M+Na]^+$ (rt = 17.5 min).

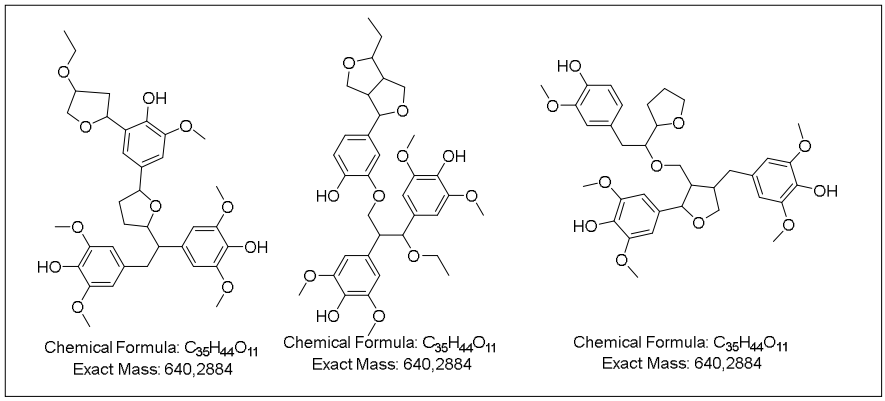

Figure V-14: Proposed chemical structures for m/z = 663.2776 $[M+Na]^+$ (rt = 17.5 min).

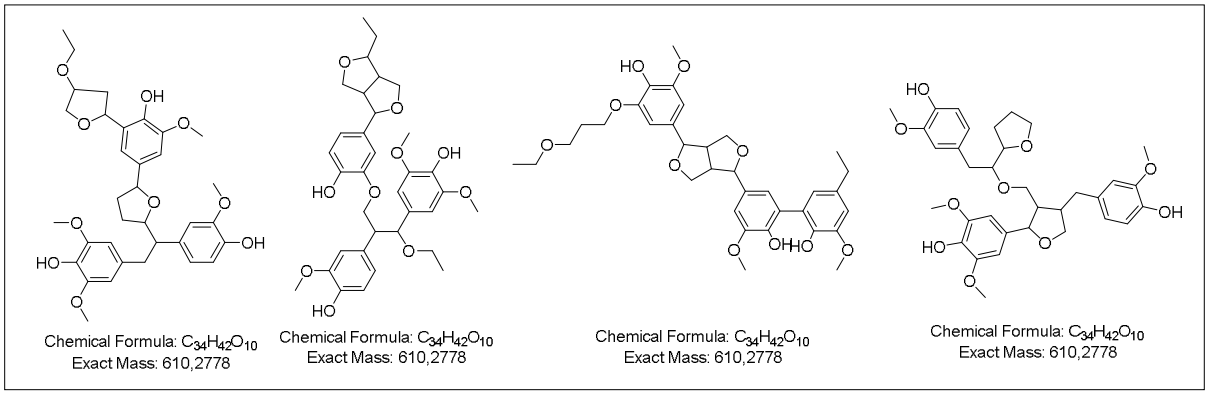

Figure V-15: Proposed chemical structures for m/z = 633.2670 $[M+Na]^+$ (rt = 17.5 min).

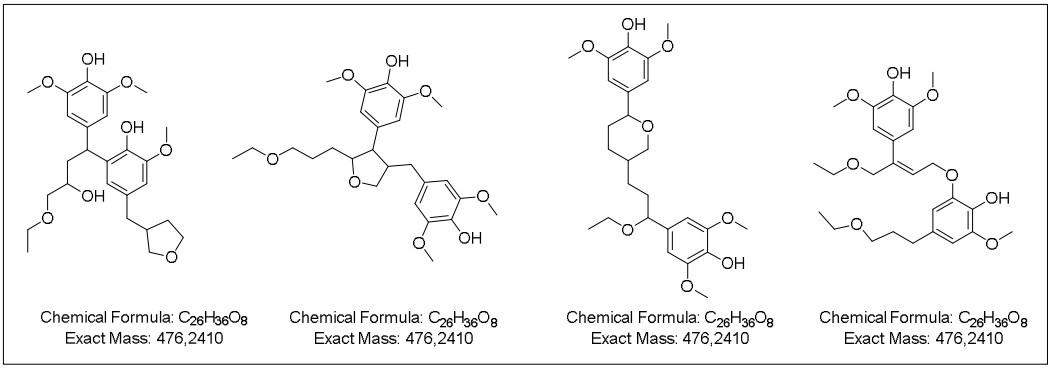

Figure V-16: Proposed chemical structures for m/z = 499.2302 $[M+Na]^+$ (rt = 18 min).

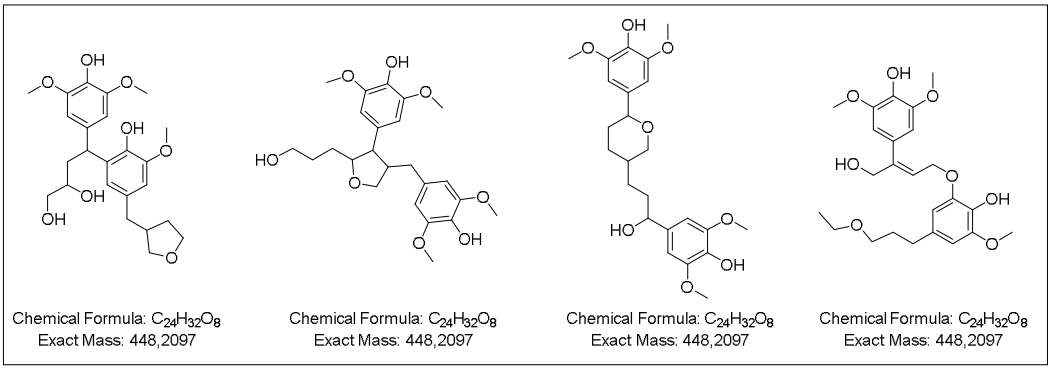

Figure V-17: Proposed chemical structures for m/z = 471.1989 $[M+Na]^+$ (rt = 18 min).

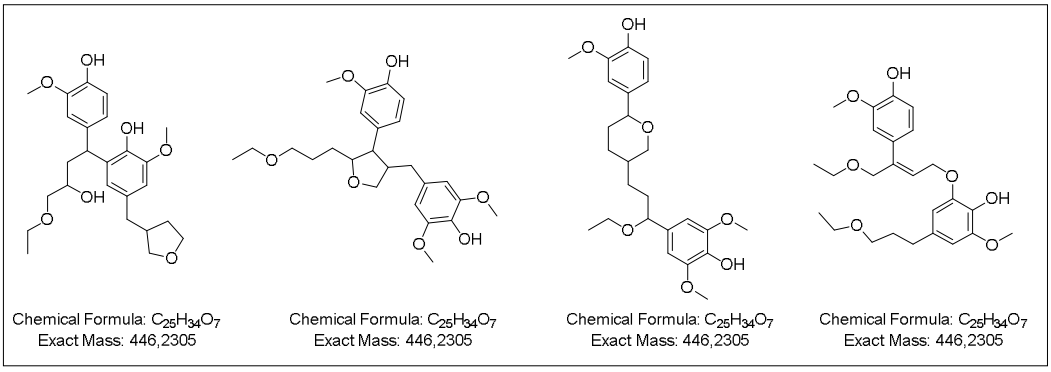

Figure V-18: Proposed chemical structures for m/z = 469.2188 $[M+Na]^+$ (rt = 18 min).