Electronic Supplementary Material (ESI) for Green Chemistry.

Dihydrolevoglucosenone (Cyrene™) as a versatile biobased solvent for lignin fractionation, processing, and chemistry

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ELECTRONIC SUPPLEMENTARY INFORMATION

Calculation of the Hansen solubility parameters (HSP) of Cyrene – water mixtures

Table S1. Hansen solubility parameters (HSP) of the solvents and lignins

Compound	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)	R_0	Reference
Cyrene	18.8	10.6	6.9	-	Sherwood et al.[1]
Geminal diol	19.4	11.2	15.9	-	Milescu et al.[2]
Water	15.5	16	42.3	-	Hansen[3]
DMSO	18.4	16.4	10.2	-	Hansen[3]
DMF	17.4	13.7	11.3	-	Hansen[3]
Lignin	21.9	14.1	16.9	13.7	Hansen & Björkman[4]
	21.71	14.18	16.93	13.45	Cañete Vebber et al.[5]
	21.42	8.57	21.80	13.56	Novo & Curvelo[6]

The HSP of Cyrene, geminal diol and water are given in Table S1. De bruyn et al.[7] determined the concentrations of the different constituents in the mixture, depending on the Cyrene content (in %wt). The values are reported in Table S2. They were used to calculate the molar fractions of the different components in the mixture, which are plotted in Figure 1 in the main text as a function of the Cyrene content. The HSP of solvent mixtures are usually calculated based on the volumetric fractions of each solvents. However, since the density of the geminal diol is unknown, the molar fractions were used instead, as previously reported by Milescu et al.[2] The HSP of the mixtures were calculated according to Equation S1:

$$\delta_X = \delta_X^{Cyrene} \times x_{Cyrene} + \delta_X^{Gem.\ diol} \times x_{Gem.\ diol} + \delta_X^{water} \times x_{water} \qquad \text{(S1)}$$

where δ_X stands for either δ_D, δ_P or δ_H, and x is the molar fraction (Table S2).

The calculated values are given in Table S2. They are also plotted in Figure S1. They were used to calculate the RED with lignin, as described in the main text (Figure 2).

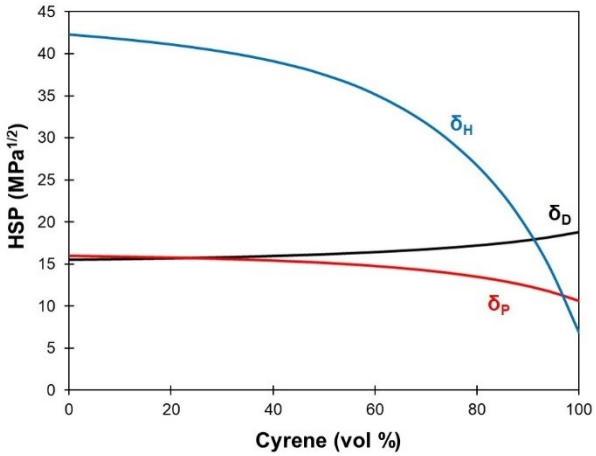

Figure S1. HSP of the Cyrene – water mixtures depending on the amount of Cyrene

Table S2. HSP of Cyrene - geminal diol - water ternary mixture depending on the percentage of Cyrene in the mixture

		Data from De Bruyn et al.[7]			Molar fractions			Hansen solubility parameters ($MPa^{1/2}$)		
Cyrene (%wt)	Cyrene (%vol)	[Cyrene] (mol L^{-1})	[Gem. diol] (mol L^{-1})	[Water] (mol L^{-1})	x_{Cyrene}	$x_{Gem.\ diol}$	x_{water}	δ_D	δ_P	δ_H
0	0	-	-	-	0	0	1	15.5	16.0	42.3
5.2	4.2	0.02	0.39	53.01	0.000	0.007	0.992	15.5	16.0	42.1
10.1	8.2	0.03	0.78	50.73	0.001	0.015	0.984	15.6	15.9	41.9
15.0	12.4	0.06	1.17	48.44	0.001	0.024	0.975	15.6	15.9	41.6
20.0	16.7	0.09	1.58	46.01	0.002	0.033	0.965	15.6	15.8	41.4
25.0	21.1	0.12	2.01	43.50	0.003	0.044	0.953	15.7	15.8	41.0
30.2	25.7	0.18	2.45	40.79	0.004	0.056	0.939	15.7	15.7	40.7
35.1	30.2	0.23	2.89	38.05	0.006	0.070	0.924	15.8	15.6	40.2
39.5	34.3	0.30	3.26	35.57	0.008	0.083	0.909	15.9	15.6	39.8
45.0	39.6	0.42	3.72	32.27	0.012	0.102	0.886	15.9	15.4	39.2
50.3	44.7	0.61	4.10	28.99	0.018	0.122	0.860	16.0	15.3	38.4
53.8	48.2	0.80	4.28	26.79	0.025	0.134	0.841	16.1	15.2	37.9
60.1	54.6	1.26	4.51	22.79	0.044	0.158	0.798	16.3	15.0	36.6
65.0	59.8	1.87	4.45	19.77	0.072	0.171	0.758	16.4	14.8	35.3
70.3	65.4	2.64	4.26	16.47	0.113	0.182	0.705	16.6	14.5	33.5
75.5	71.1	3.62	3.84	13.40	0.174	0.184	0.642	16.8	14.2	31.3
80.1	76.3	4.59	3.35	10.65	0.247	0.180	0.573	17.0	13.8	28.8
84.9	81.8	5.69	2.73	7.96	0.347	0.167	0.486	17.3	13.3	25.6
89.9	87.7	7.00	1.89	5.21	0.496	0.134	0.370	17.7	12.7	21.2
95.1	93.9	8.35	1.00	2.44	0.708	0.085	0.207	18.2	11.8	15.0
100	100	-	-	-	1	0	0	18.8	10.6	6.9

Stability tests of Cyrene in the presence of various catalysts

50 µL of catalyst (1-methylimidazole, 1-MIM, dibutyltin dilaurate, DBTL, or N,N'-dimethylcyclohexylamine, DMCHA) were added to 1 mL Cyrene in a glass vial, which was then placed in an oil bath regulated at 50 °C for 20 h. After 20 h, the mixture was analyzed by ^{1}H NMR and compared to the spectrum of fresh Cyrene to detect any change in chemical structure.

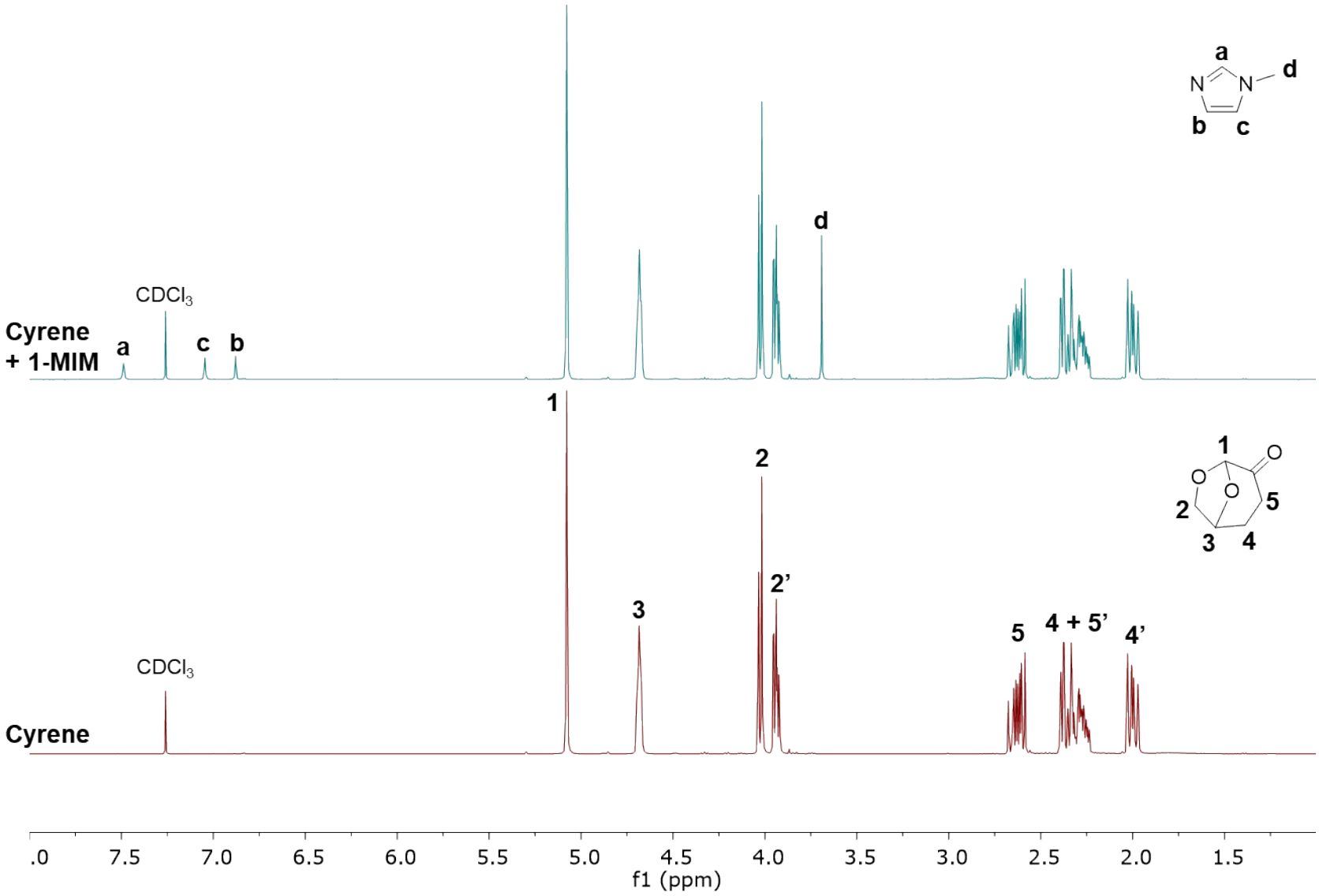

Figure S2. ^{1}H NMR of fresh Cyrene and Cyrene containing 1-methylimidazole (1-MIM) after overnight stirring at 50 °C.

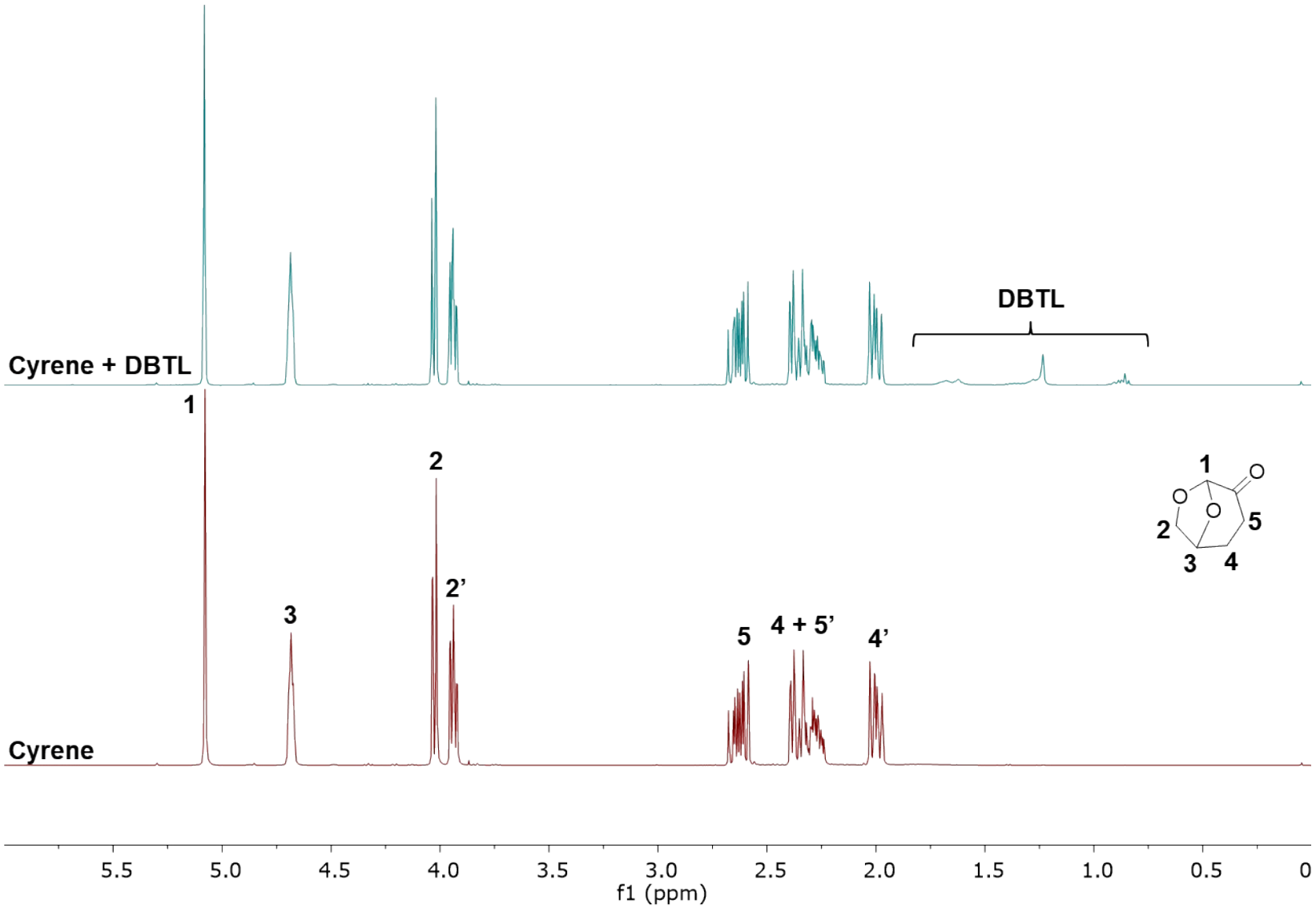

Figure S3. ^{1}H NMR of fresh Cyrene and Cyrene containing dibutyltin dilaurate (DBTL) after overnight stirring at 50 °C.

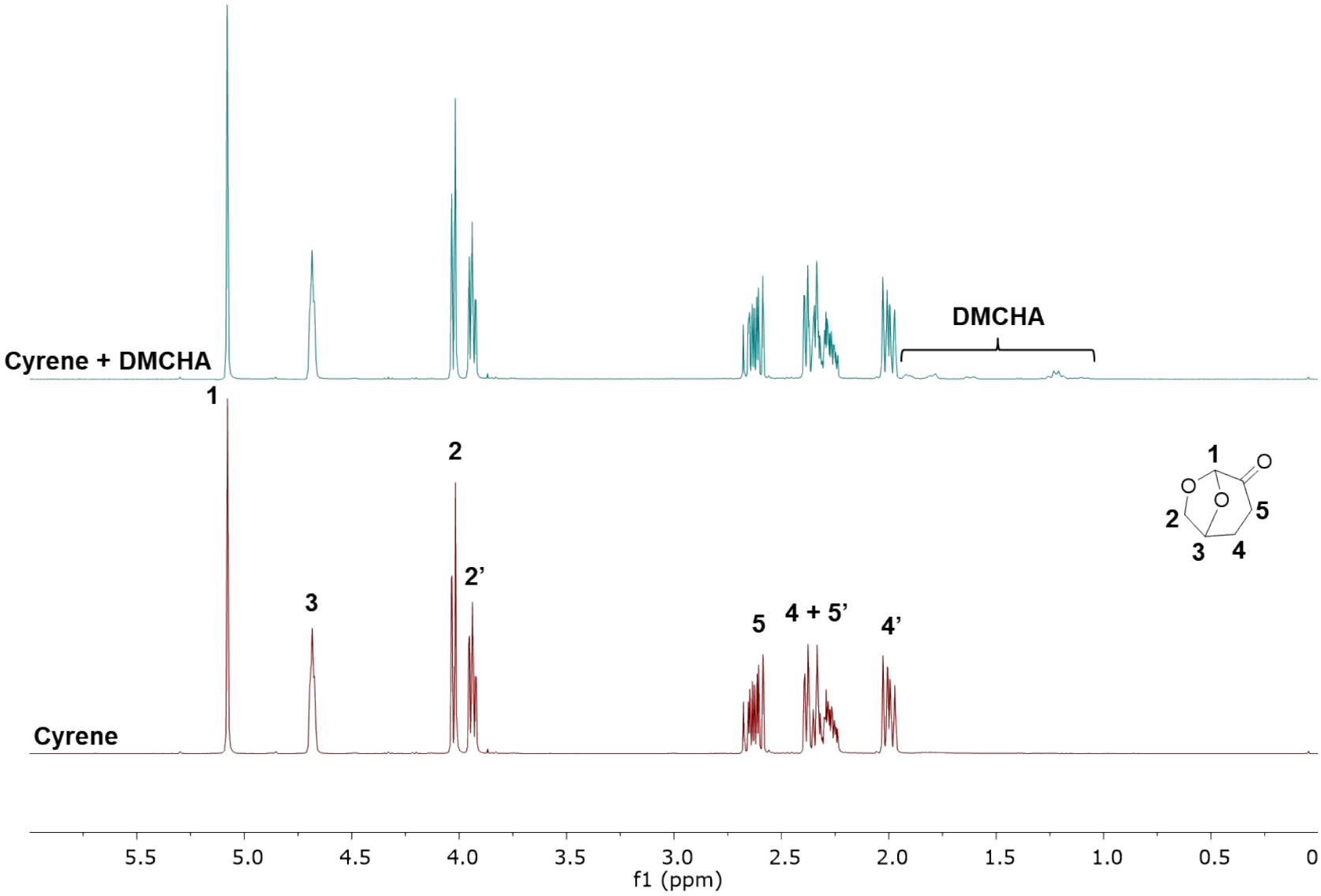

Figure S4. ^{1}H NMR of fresh Cyrene and Cyrene containing N,N'-dimethylcyclohexylamine (DMCHA) after overnight stirring at 50 °C.

^{31}P NMR spectra

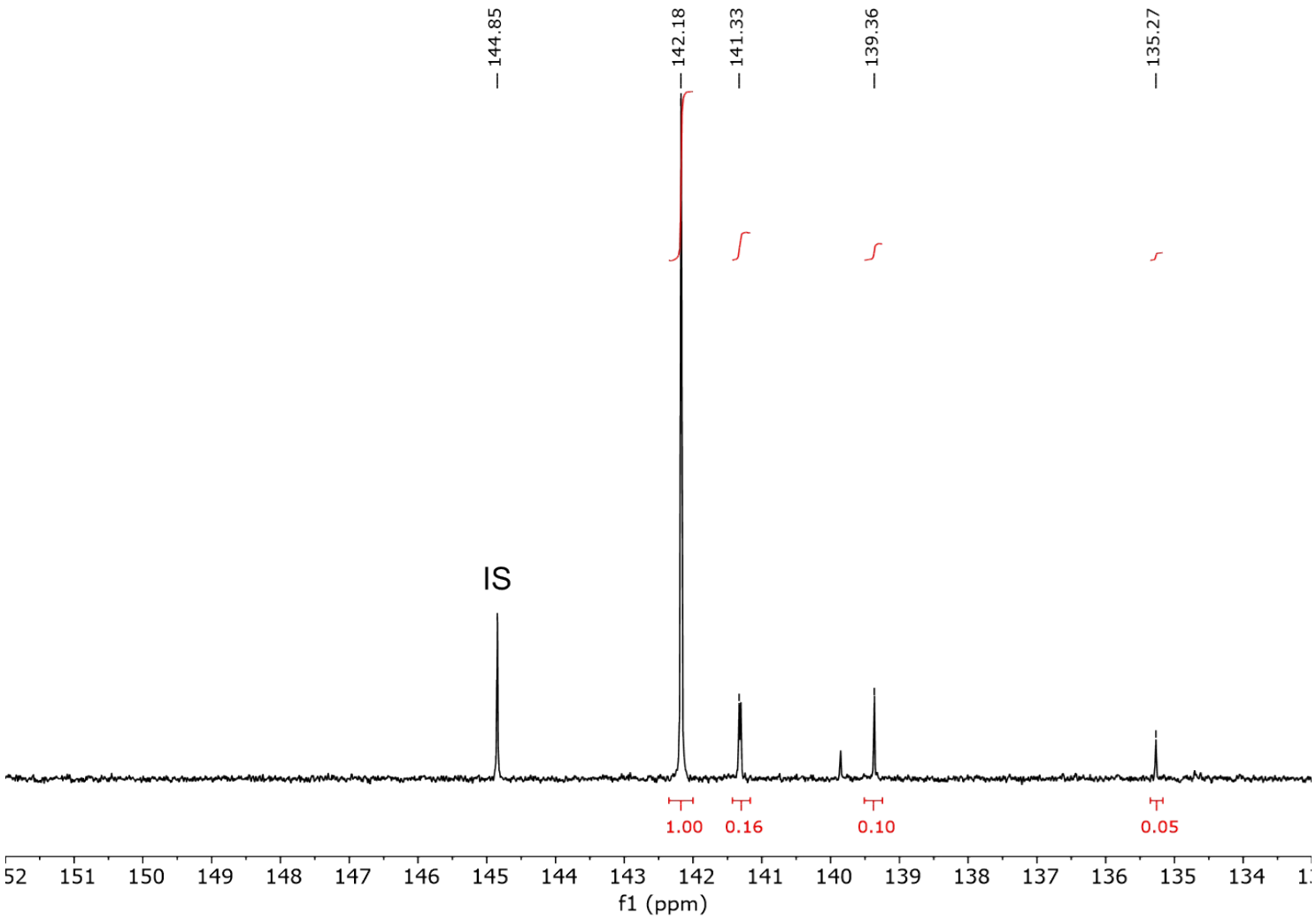

Figure S5. ^{31}P NMR spectrum of Cyrene. 4 peaks can be seen, showing that Cyrene reacts with the phosphorous reagent to form various reaction products, which were not identified. IS = internal standard (cholesterol).

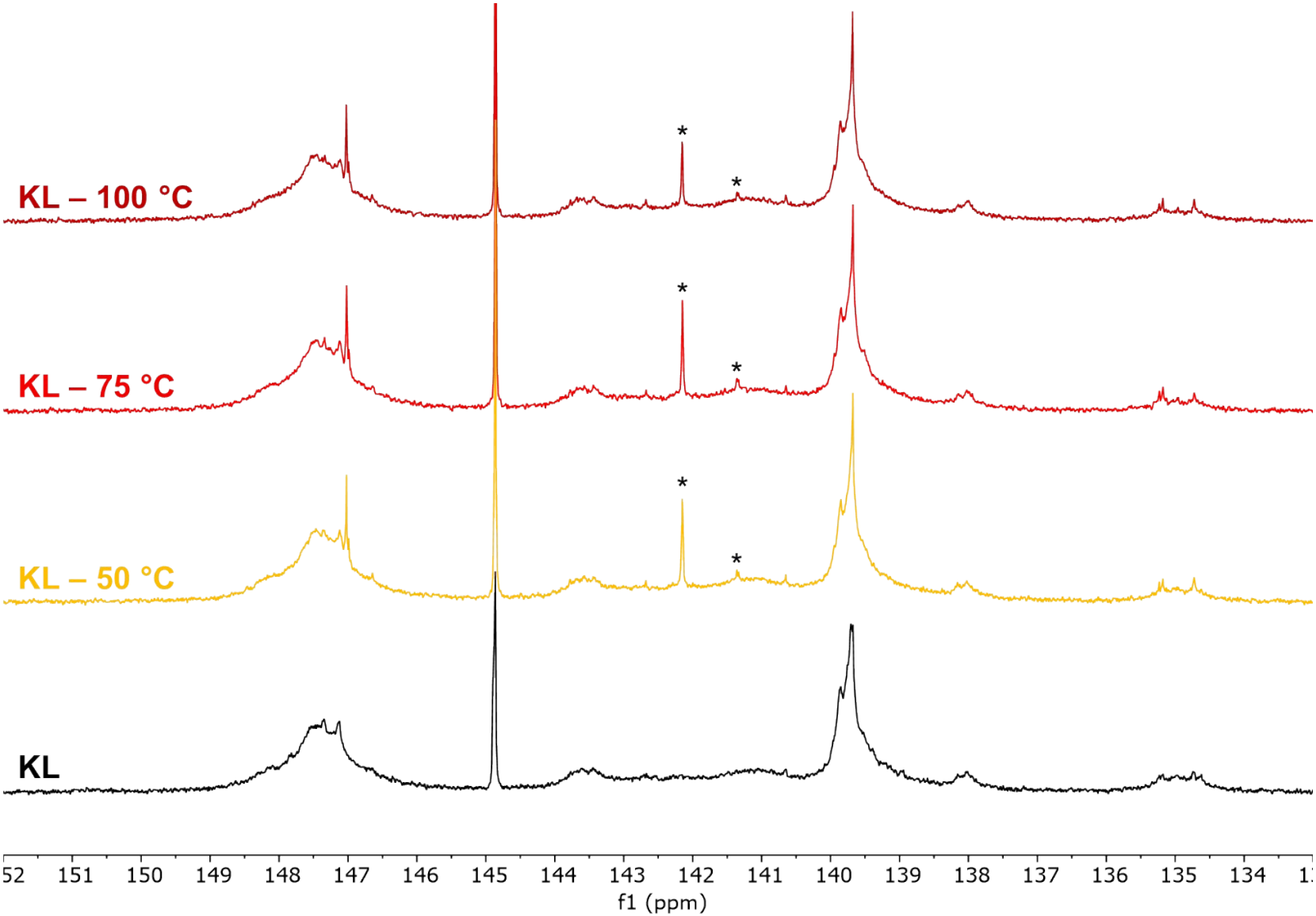

Figure S6. ^{31}P NMR spectra of KL before and after overnight treatment in Cyrene at different temperatures. * = peaks of residual Cyrene.

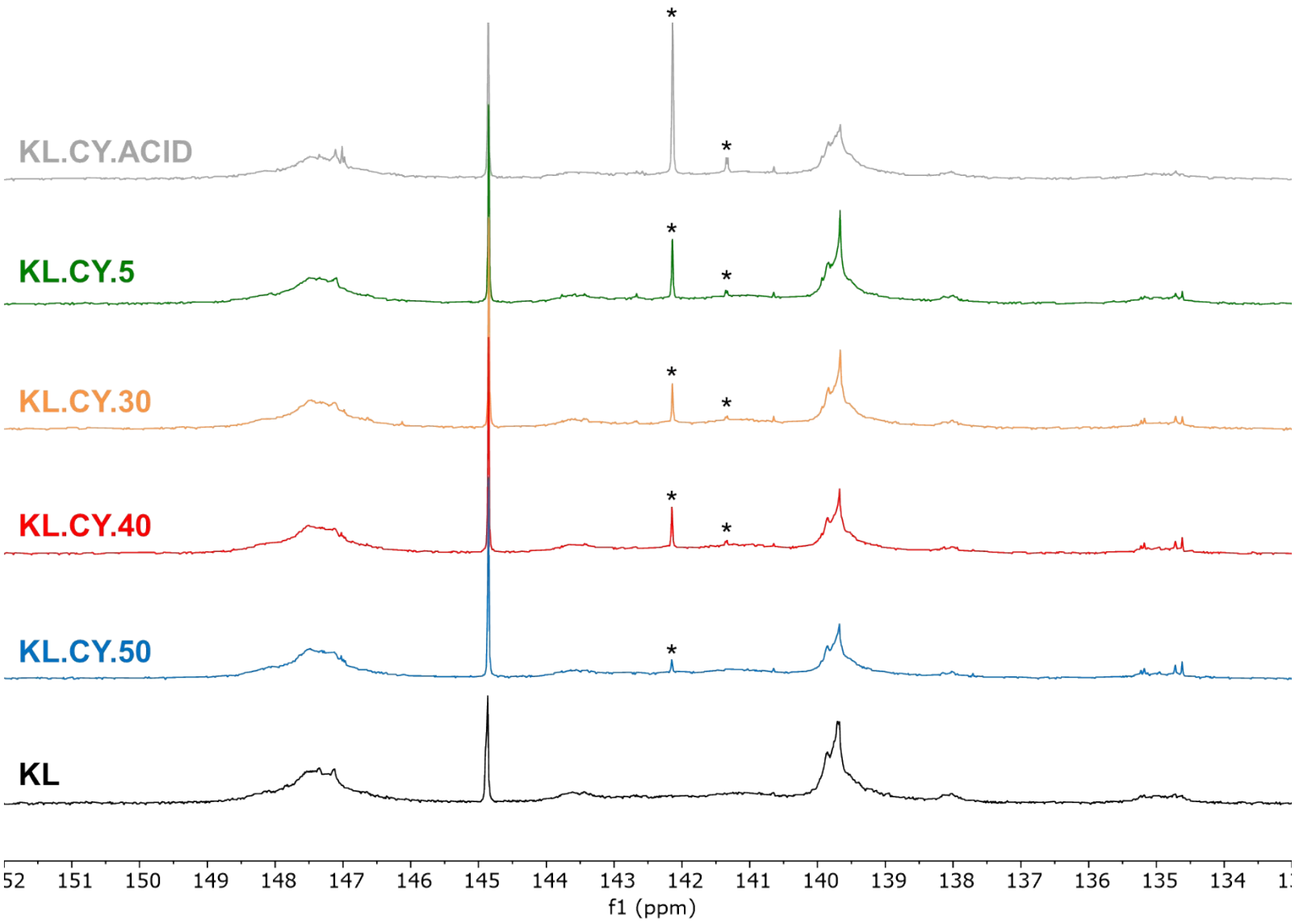

Figure S7. ^{31}P NMR spectra of KL and KL fractions obtained from fractional precipitation with Cyrene – water mixtures. * = peaks of residual Cyrene.

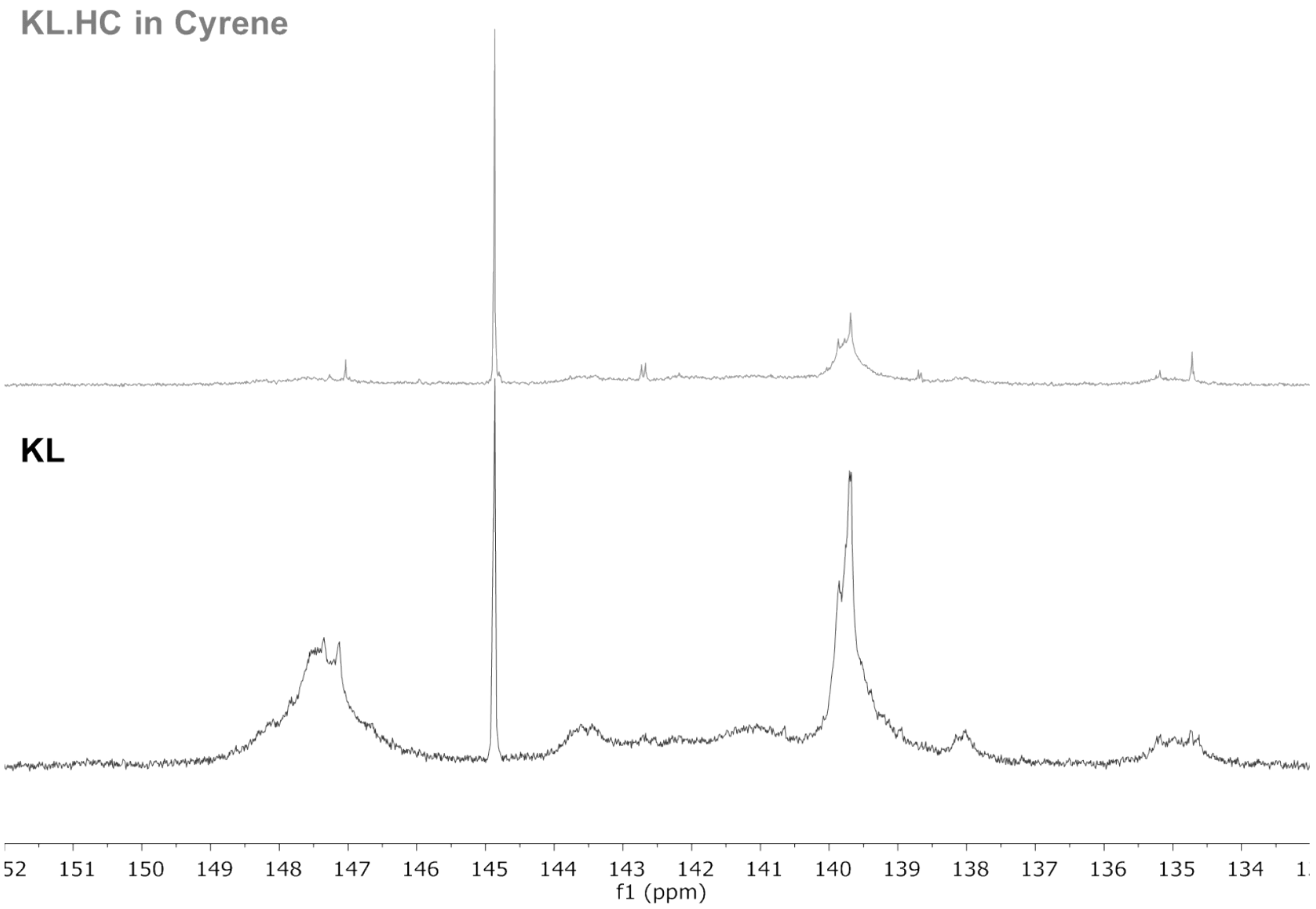

Figure S8. ^{31}P NMR spectra of KL modified with heptanoyl chloride (HC) in Cyrene.

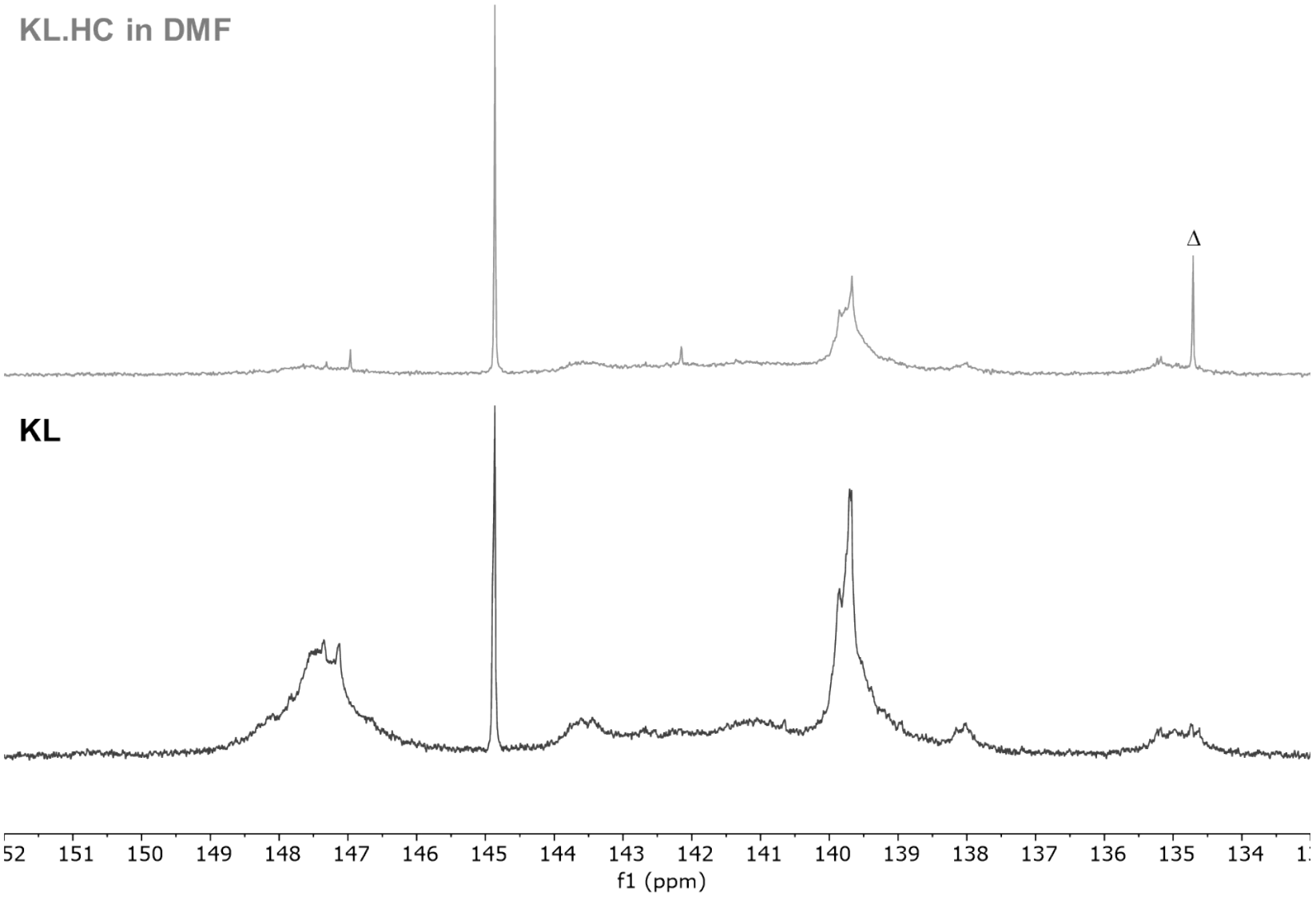

Figure S9. ^{31}P NMR spectra of KL modified with heptanoyl chloride (HC) in DMF. Δ = peak of residual heptanoic acid (impurity).

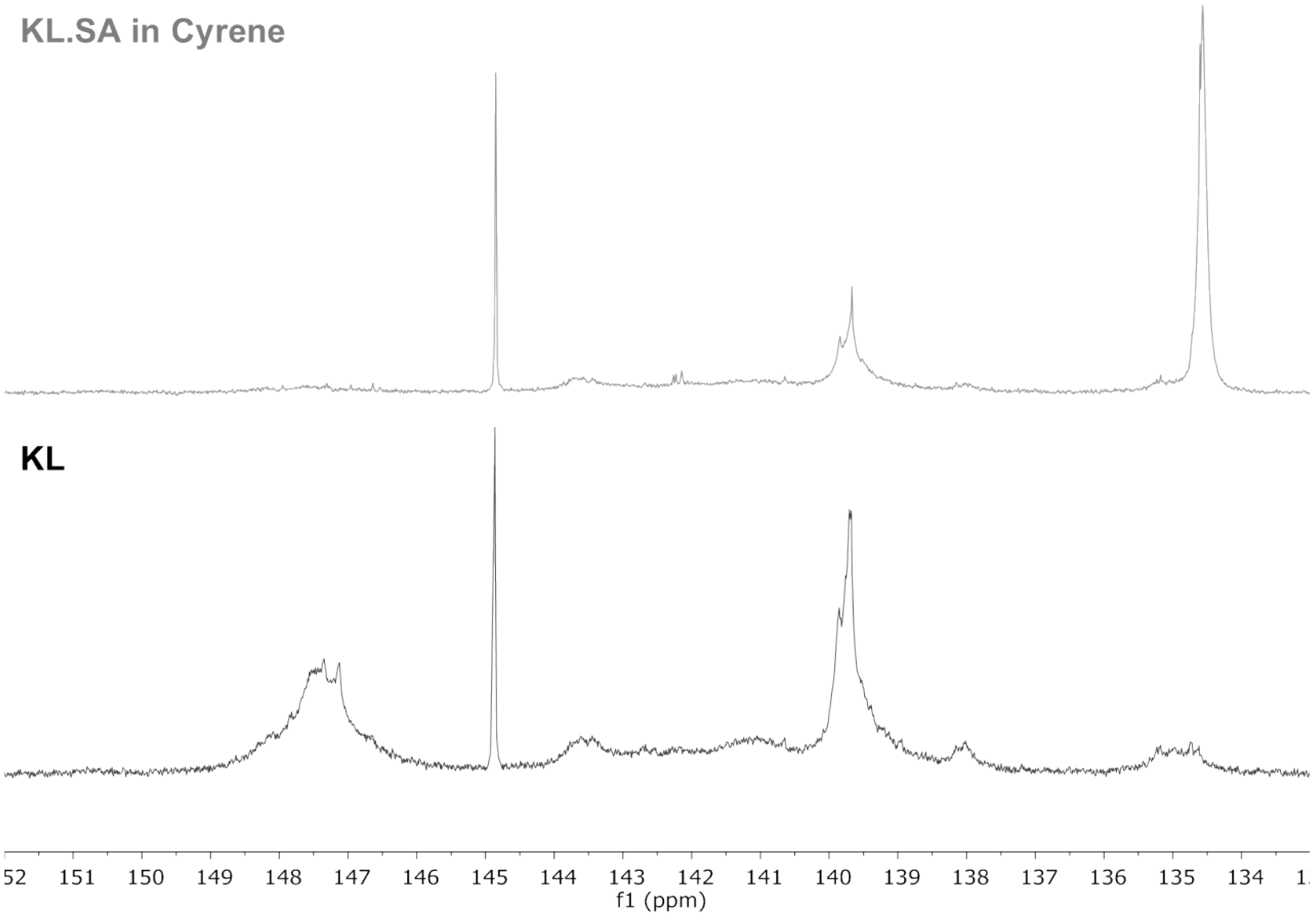

Figure S10. ^{31}P NMR spectra of KL modified with succinic anhydride (SA) in Cyrene.

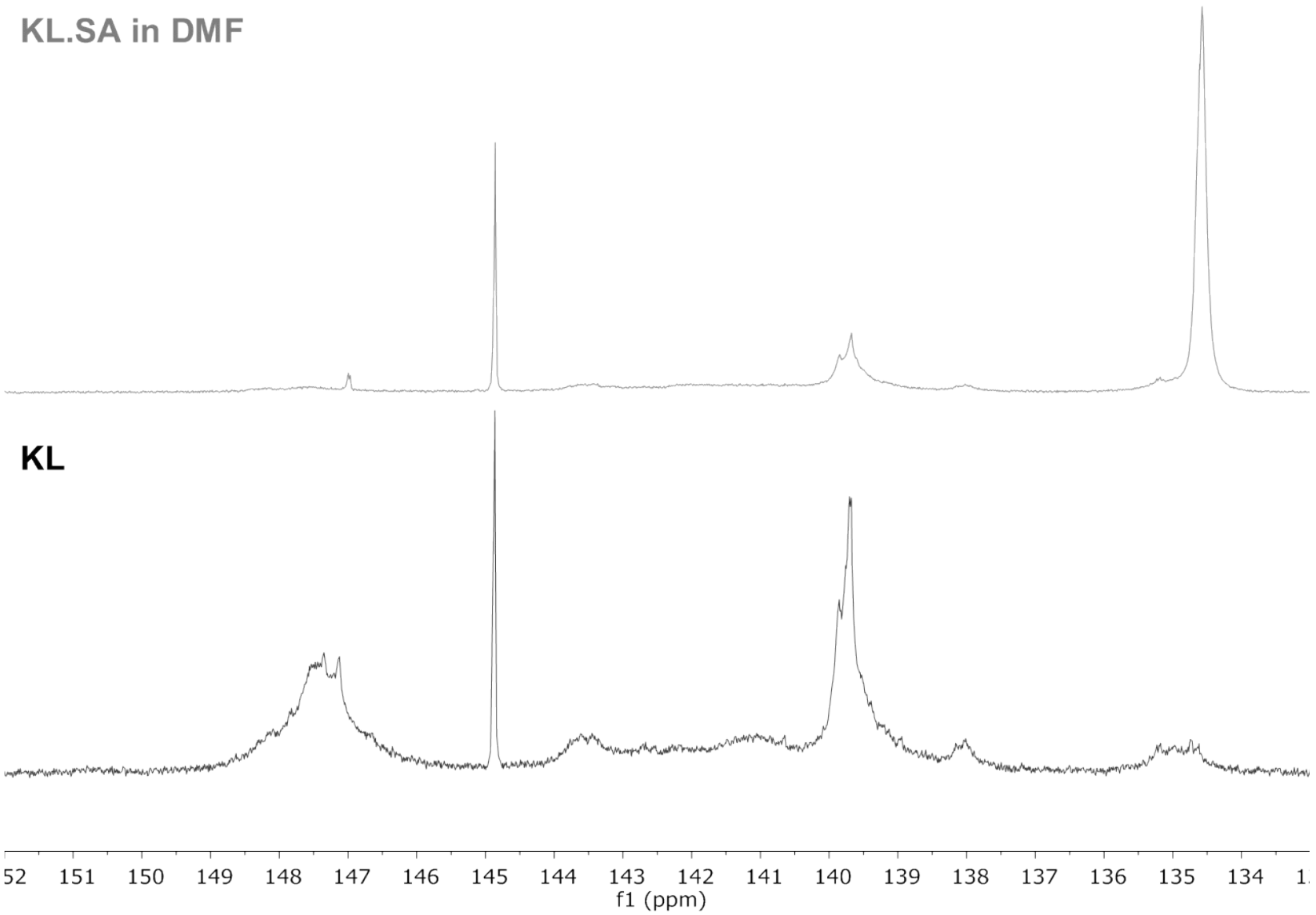

Figure S11. ^{31}P NMR spectra of KL modified with succinic anhydride (SA) in DMF.

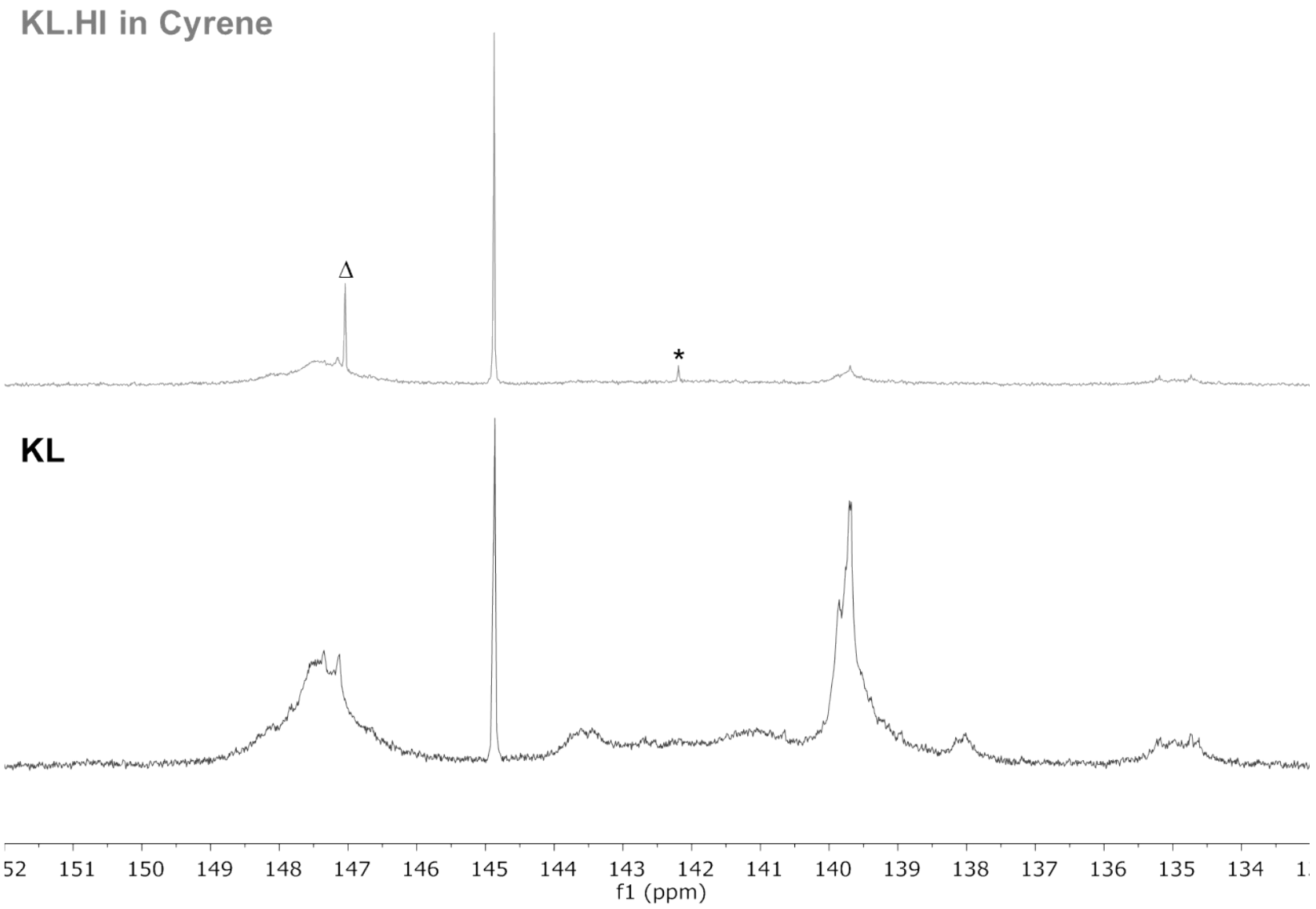

Figure S12. ^{31}P NMR spectra of KL modified with hexyl isocyanate (HI) in Cyrene. * = peak of residual Cyrene. Δ = impurity (unknown).

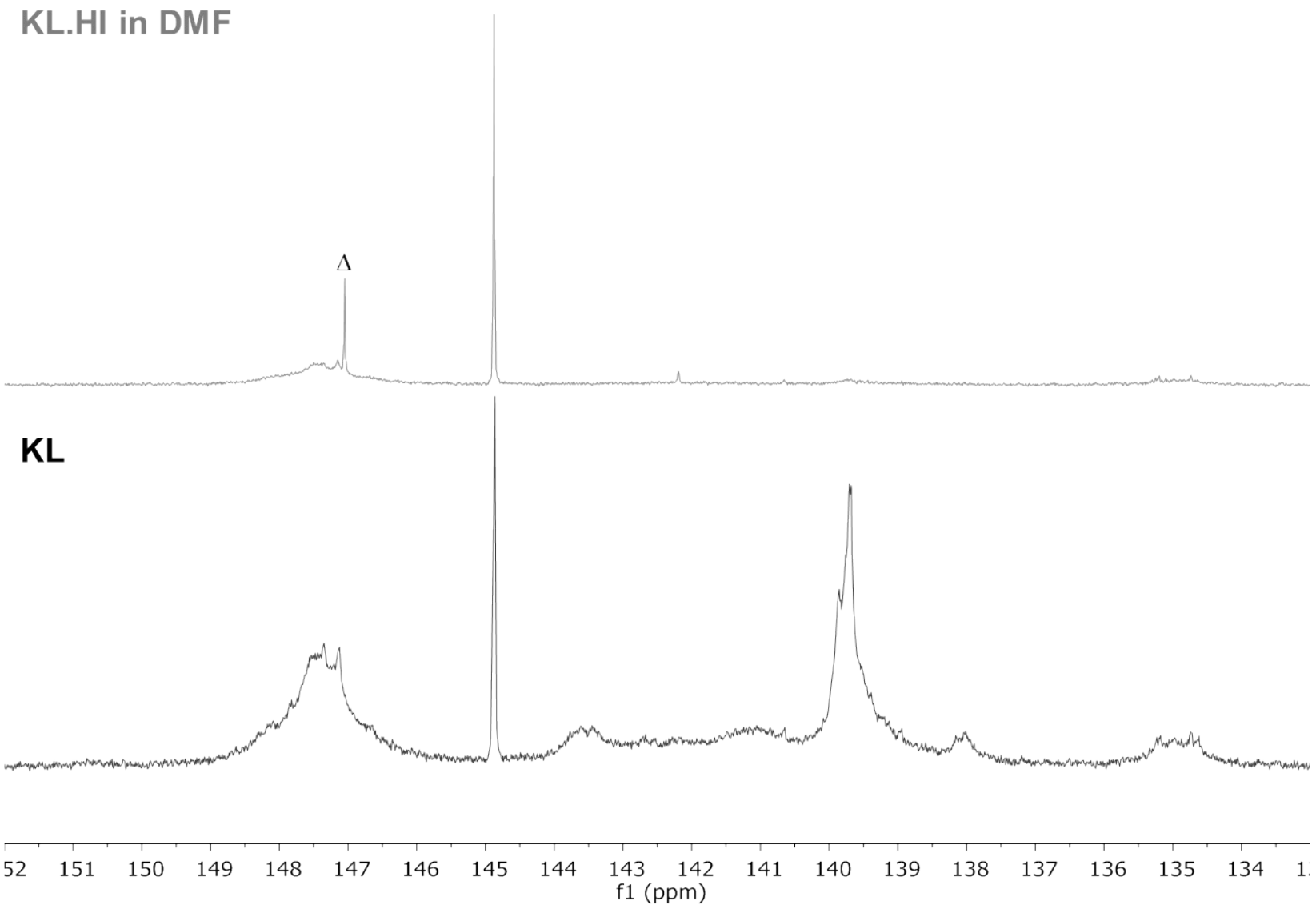

Figure S13. ^{31}P NMR spectra of KL modified with hexyl isocyanate (HI) in DMF. Δ = impurity (unknown).

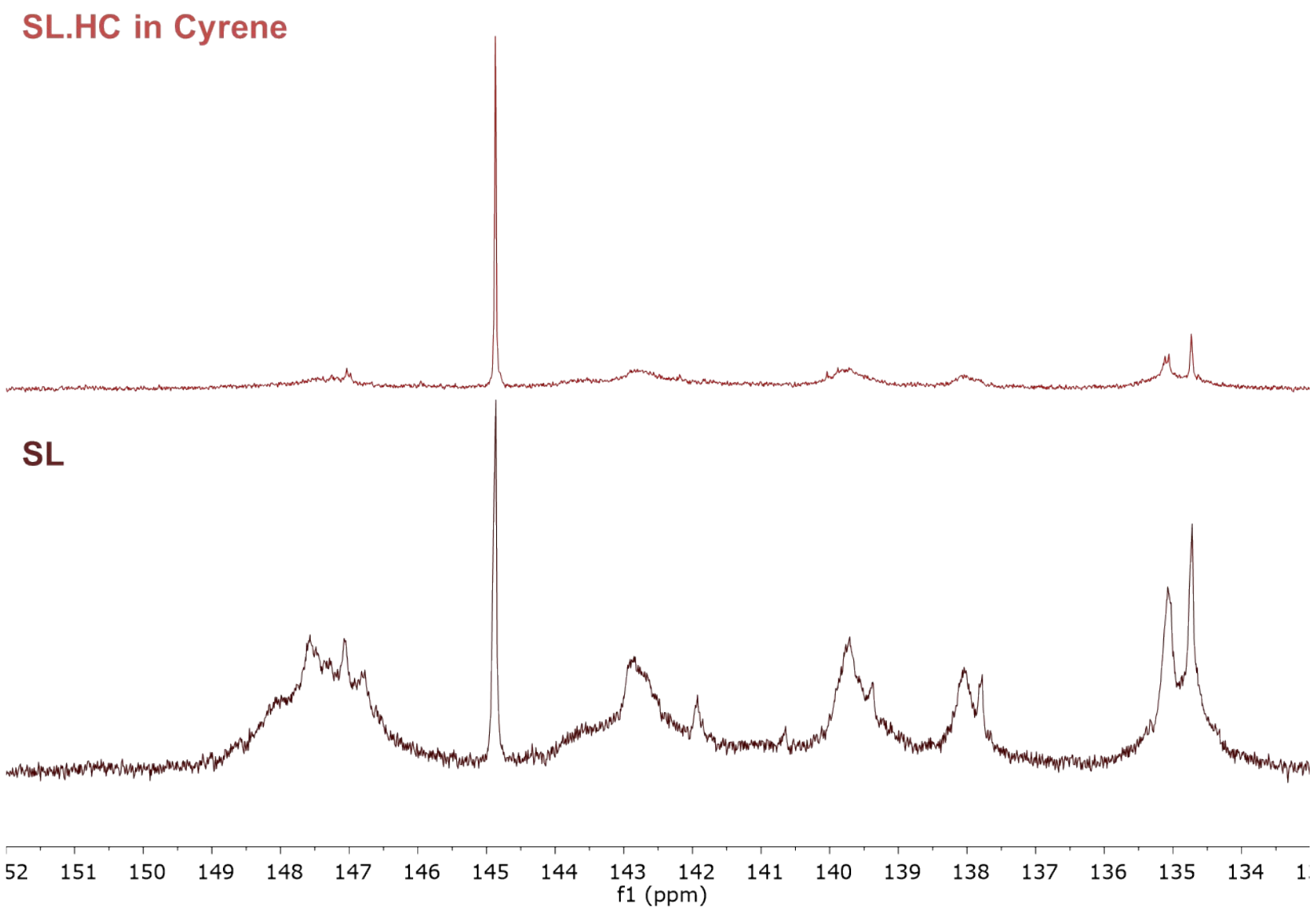

Figure S14. ^{31}P NMR spectra of SL modified with heptanoyl chloride (HC) in Cyrene.

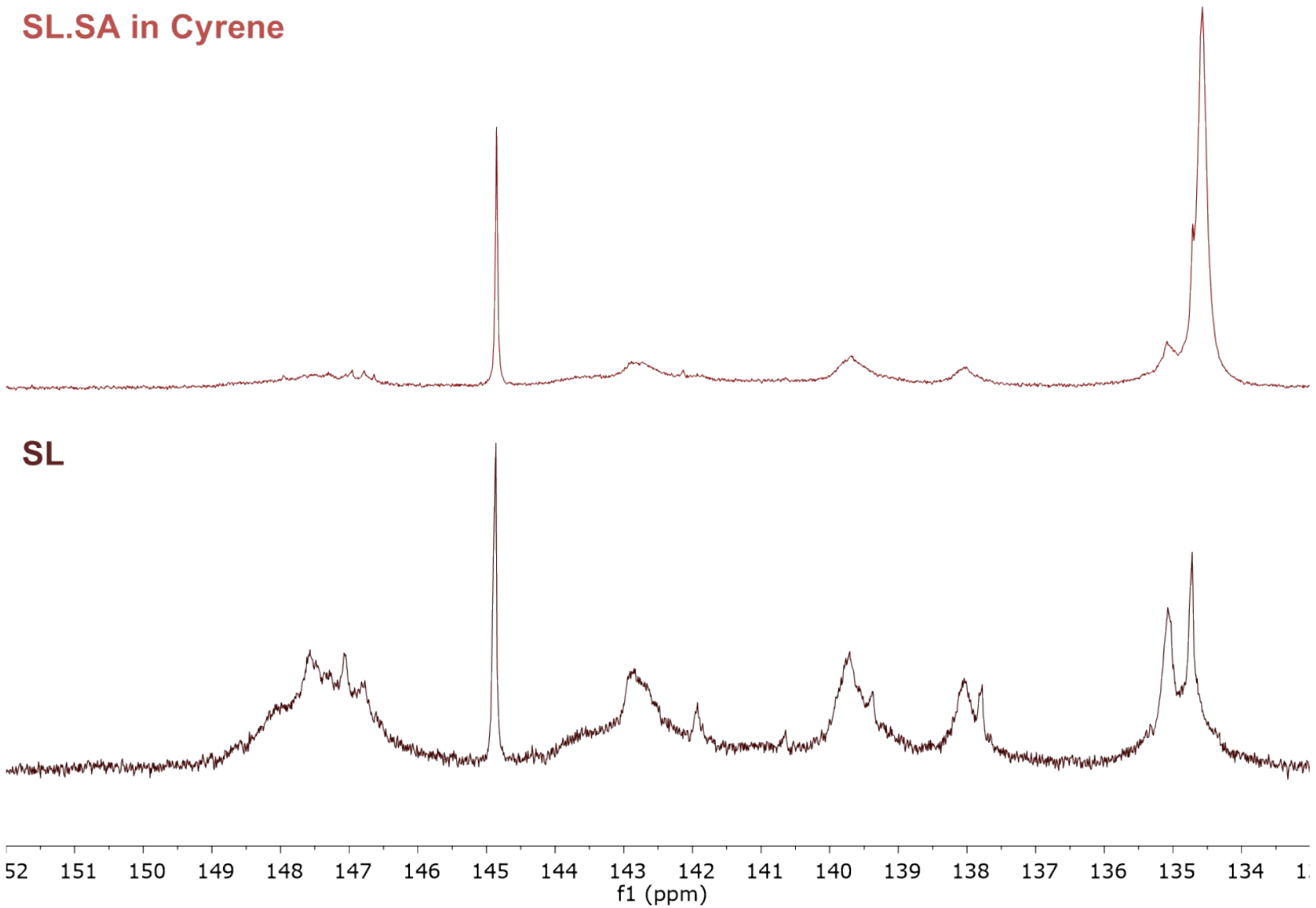

Figure S15. ^{31}P NMR spectra of SL modified with succinic anhydride (SA) in Cyrene.

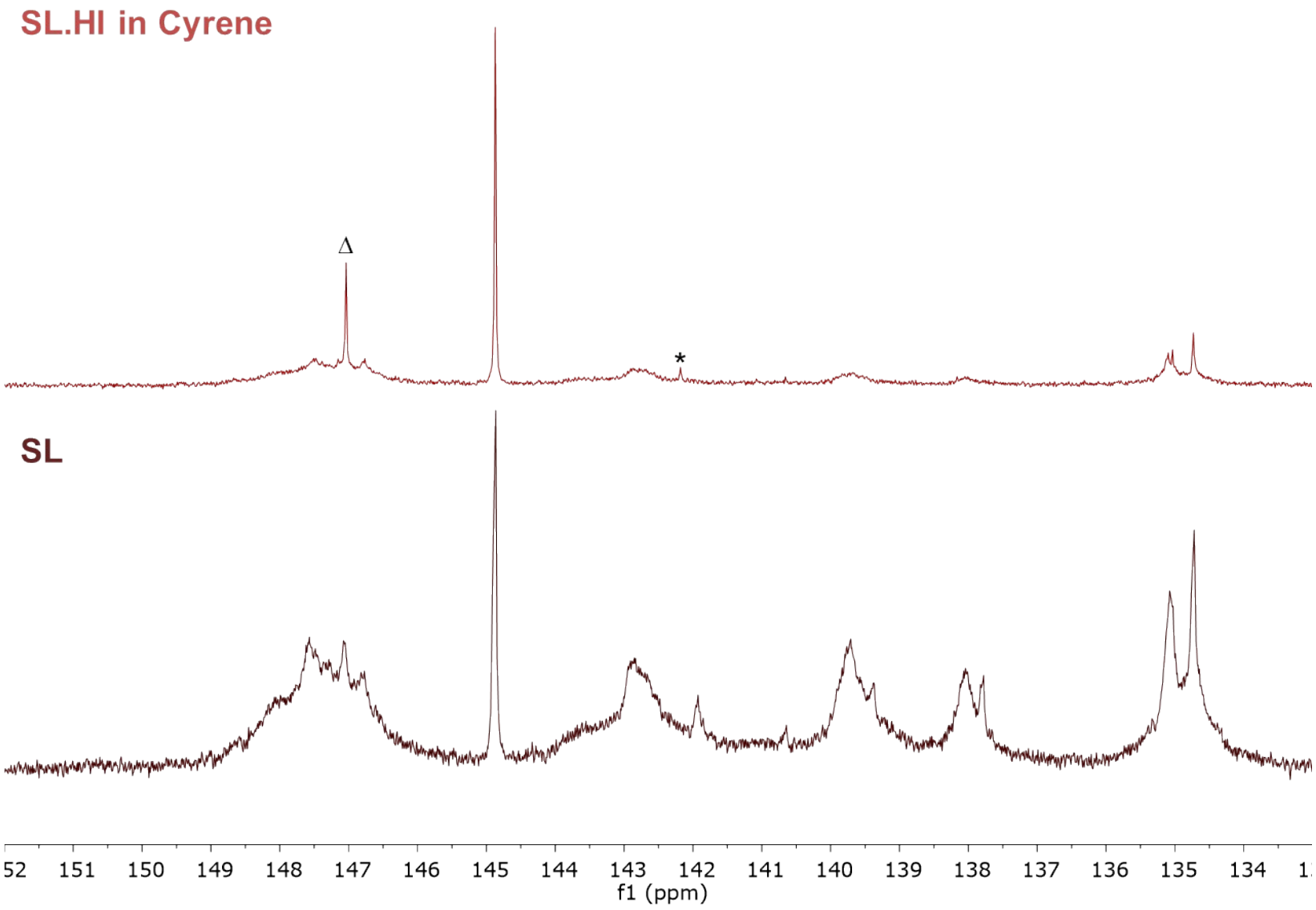

Figure S16. ^{31}P NMR spectra of SL modified with hexyl isocyanate (HI) in Cyrene. * = peak of residual Cyrene. Δ = impurity (unknown).

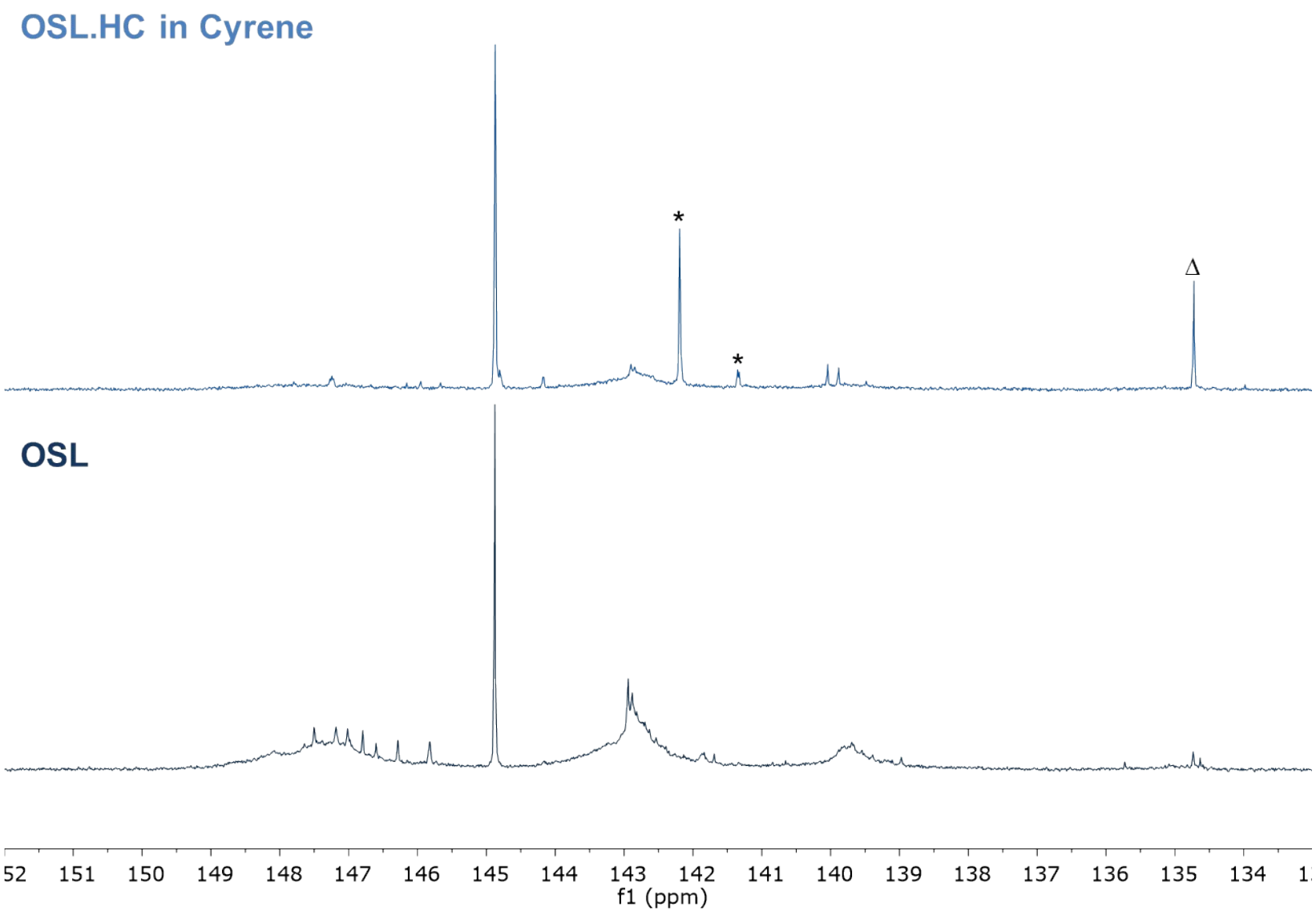

Figure S17. ^{31}P NMR spectra of OSL modified with heptanoyl chloride (HC) in Cyrene. * = peaks of residual Cyrene. Δ = peak of residual heptanoic acid (impurity).

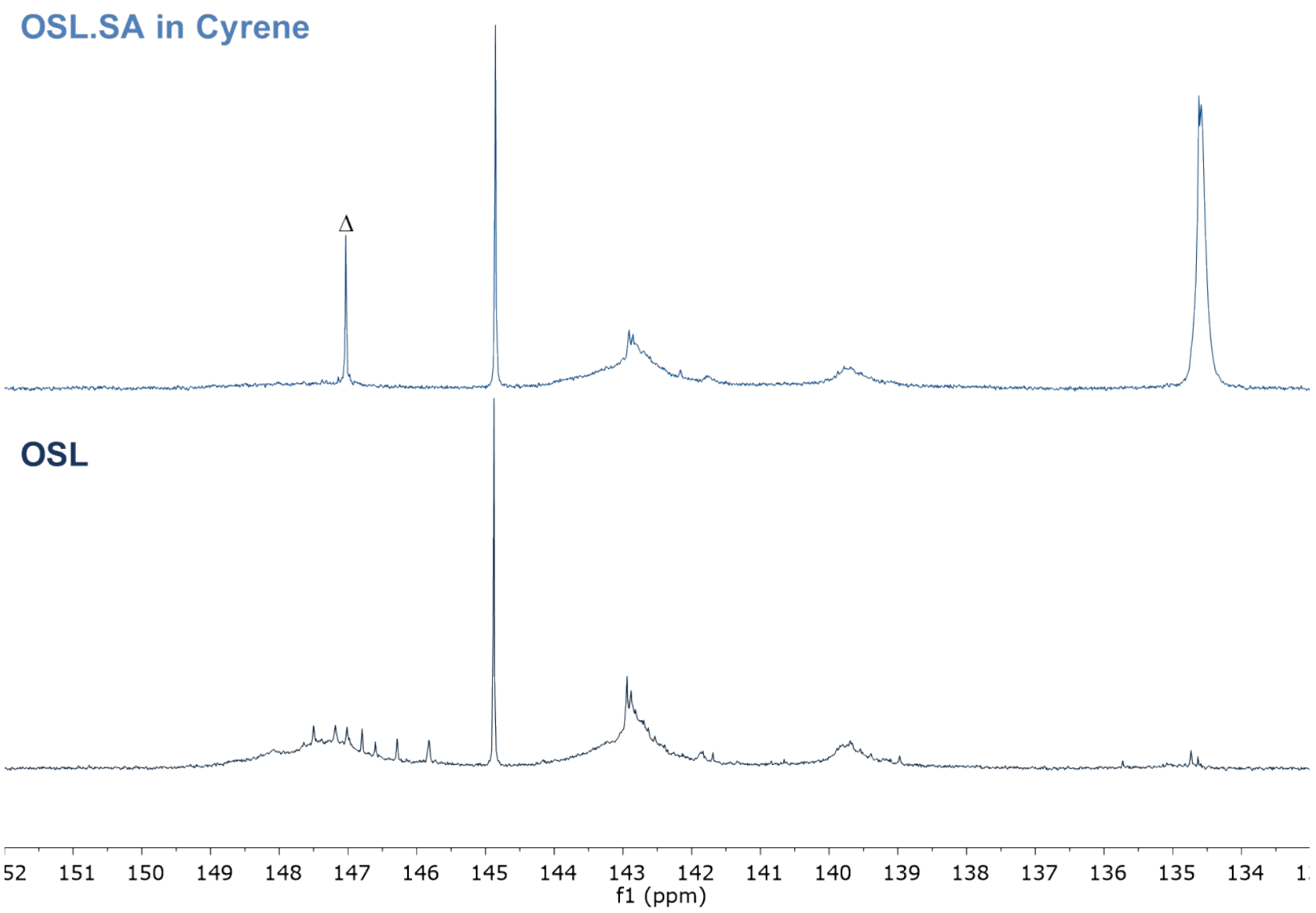

Figure S18. ^{31}P NMR spectra of OSL modified with succinic anhydride (SA) in Cyrene. Δ = impurity (unknown).

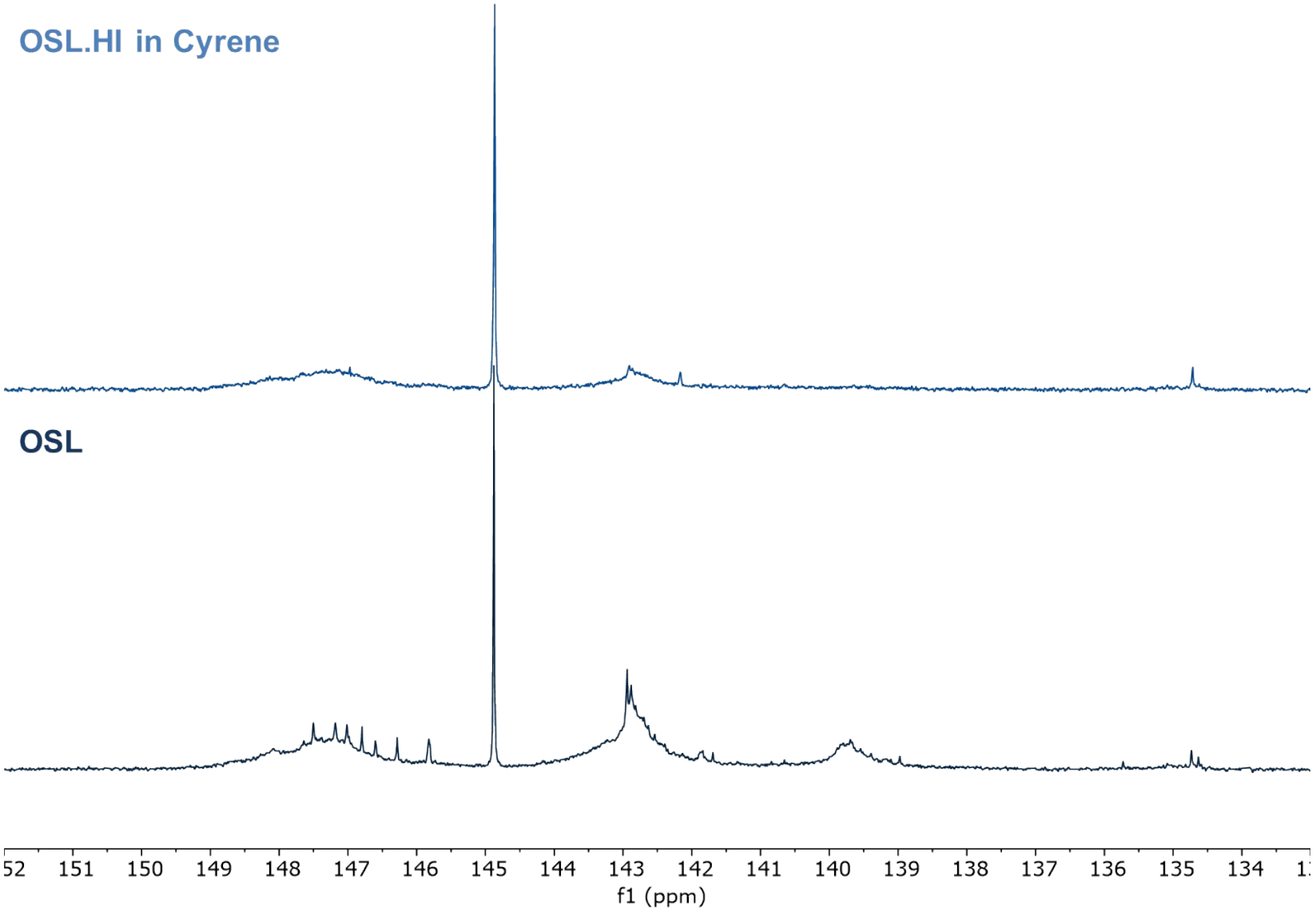

Figure S19. ^{31}P NMR spectra of OSL modified with hexyl isocyanate (HI) in Cyrene.

^{1}H NMR spectra

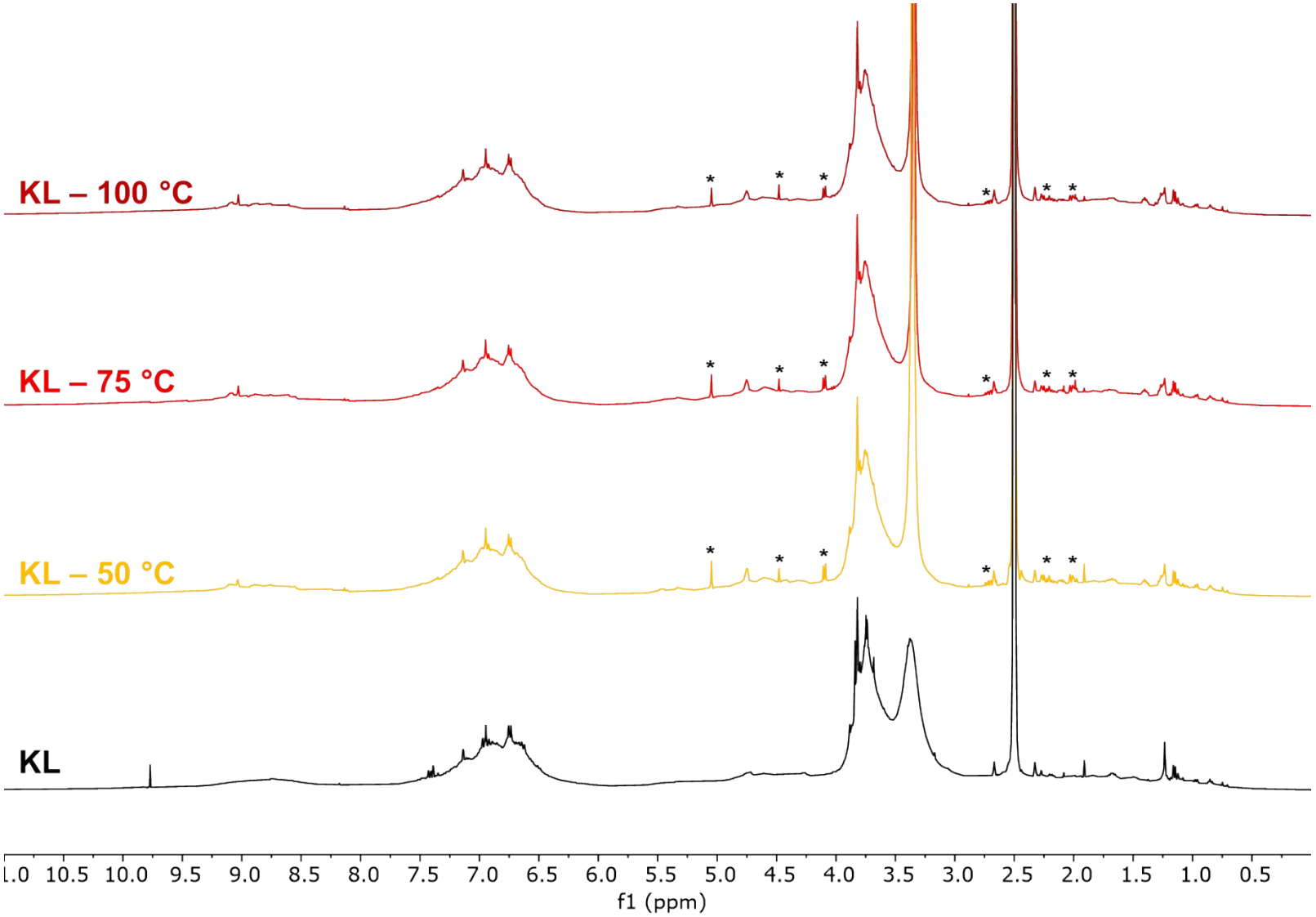

Figure S 20. ^{1}H NMR spectra of KL before and after overnight treatment in Cyrene at different temperatures. * = peaks of residual Cyrene.

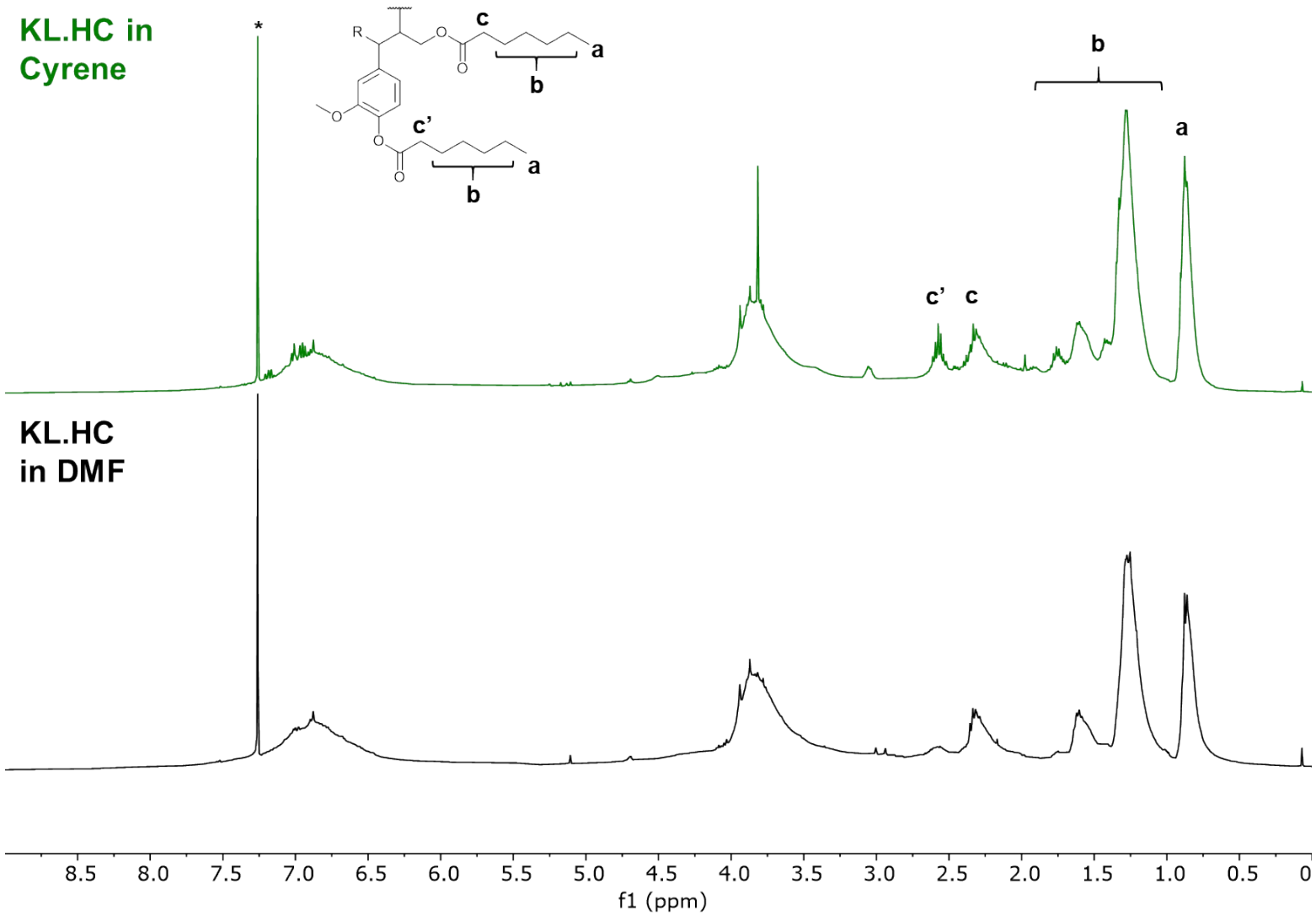

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of KL modified with heptanoyl chloride (HC) in DMF and Cyrene, with assignation of the signals from the grafted groups. * = solvent ($CDCl_3$)

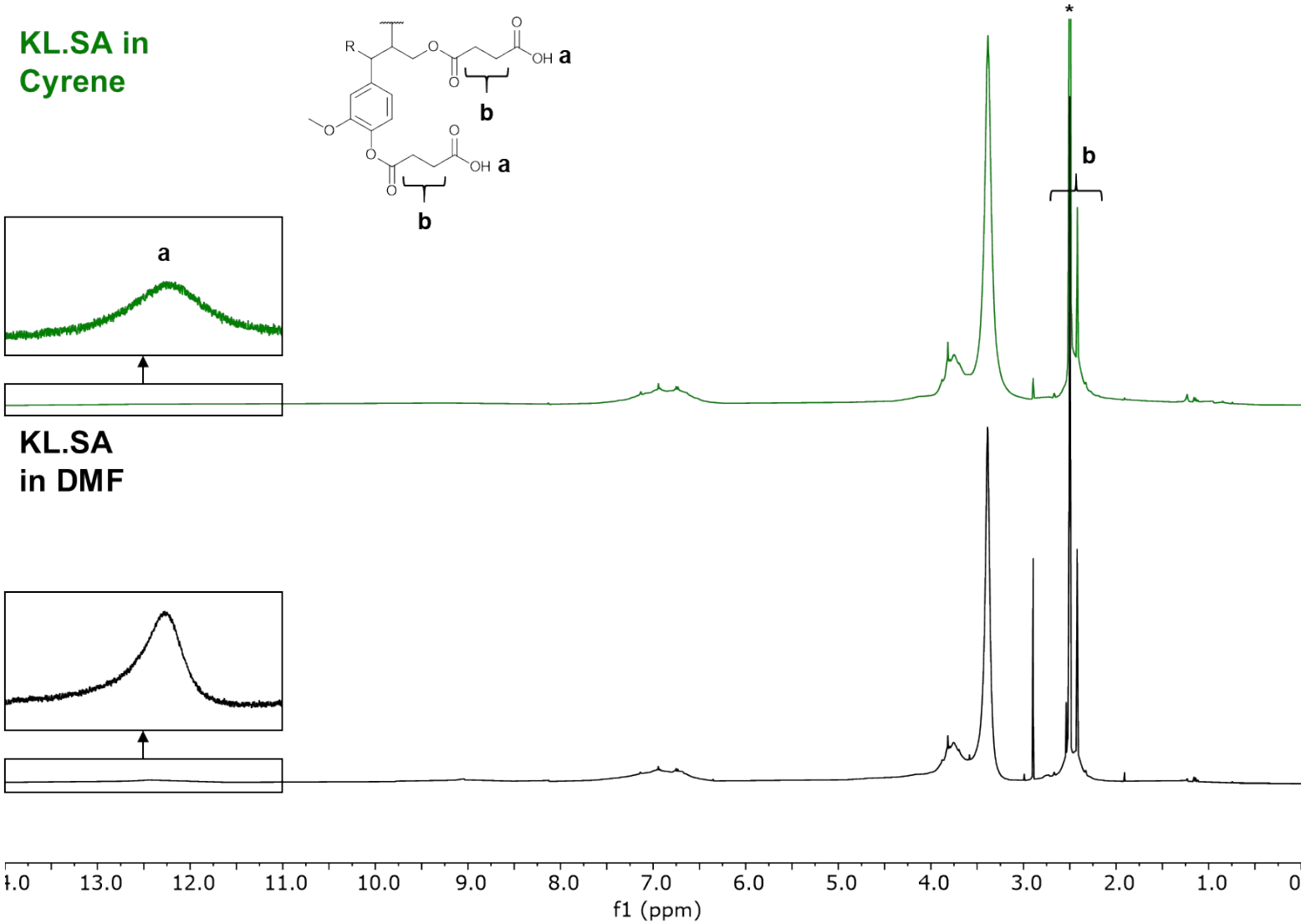

Figure S22. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of KL modified with succinic anhydride (SA) in DMF and Cyrene, with assignation of the signals from the grafted groups. * = solvent (DMSO)

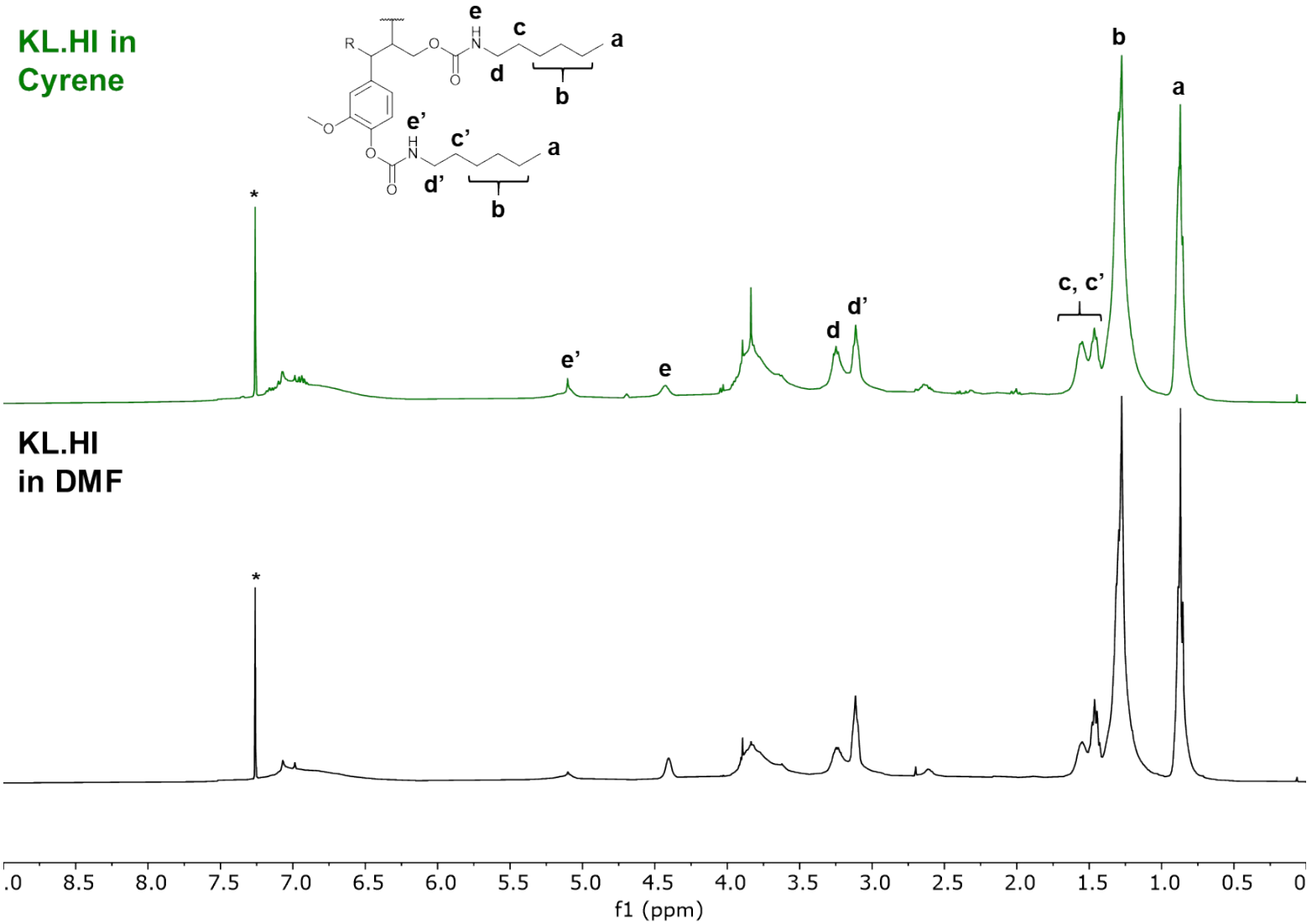

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of KL modified with hexyl isocyanate (HC) in DMF and Cyrene, with assignation of the signals from the grafted groups. * = solvent ($CDCl_3$)

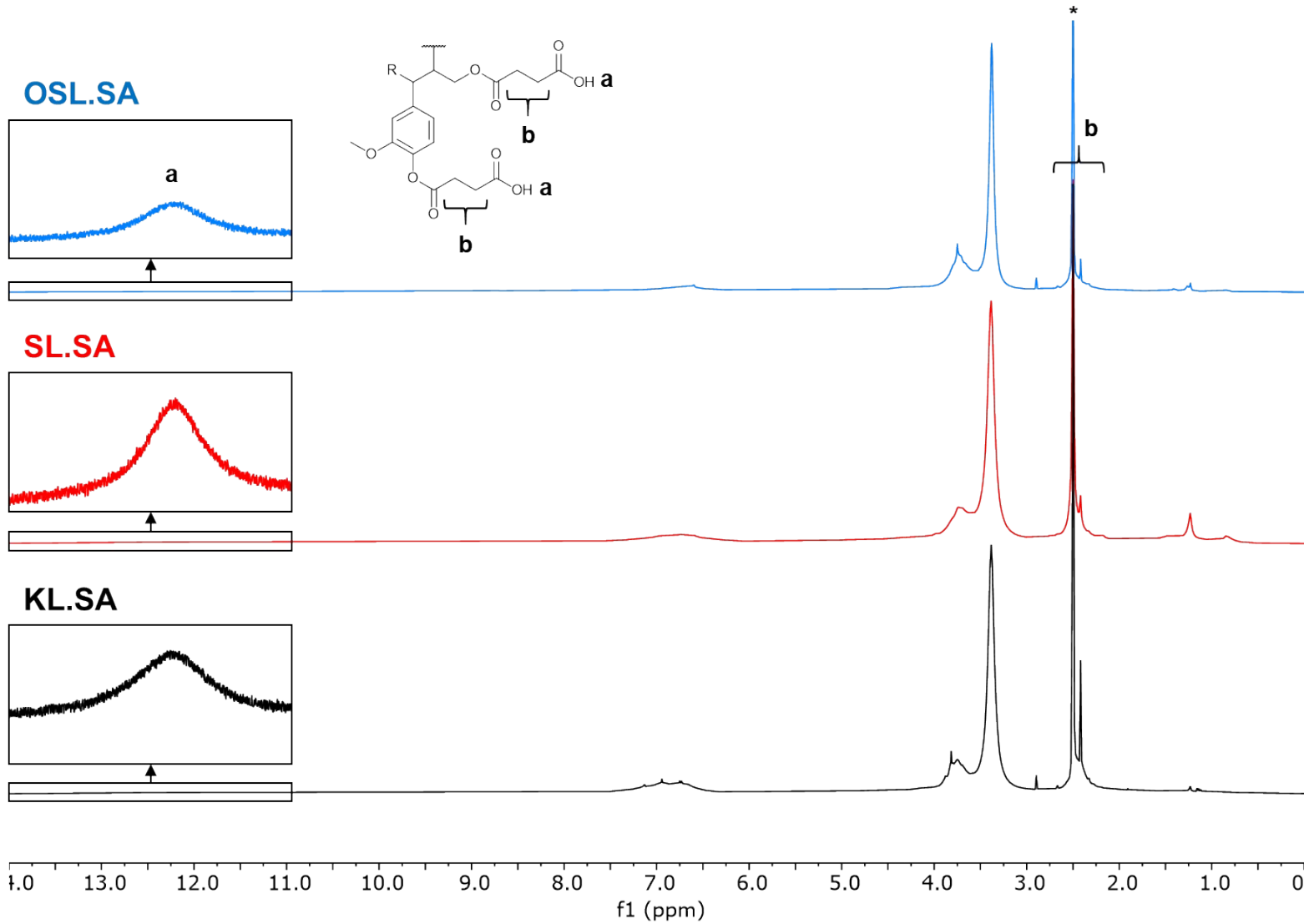

Figure S24. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of KL, SL and OSL modified with succinic anhydride (SA) in Cyrene, with assignation of the signals from the grafted groups. * = solvent (DMSO)

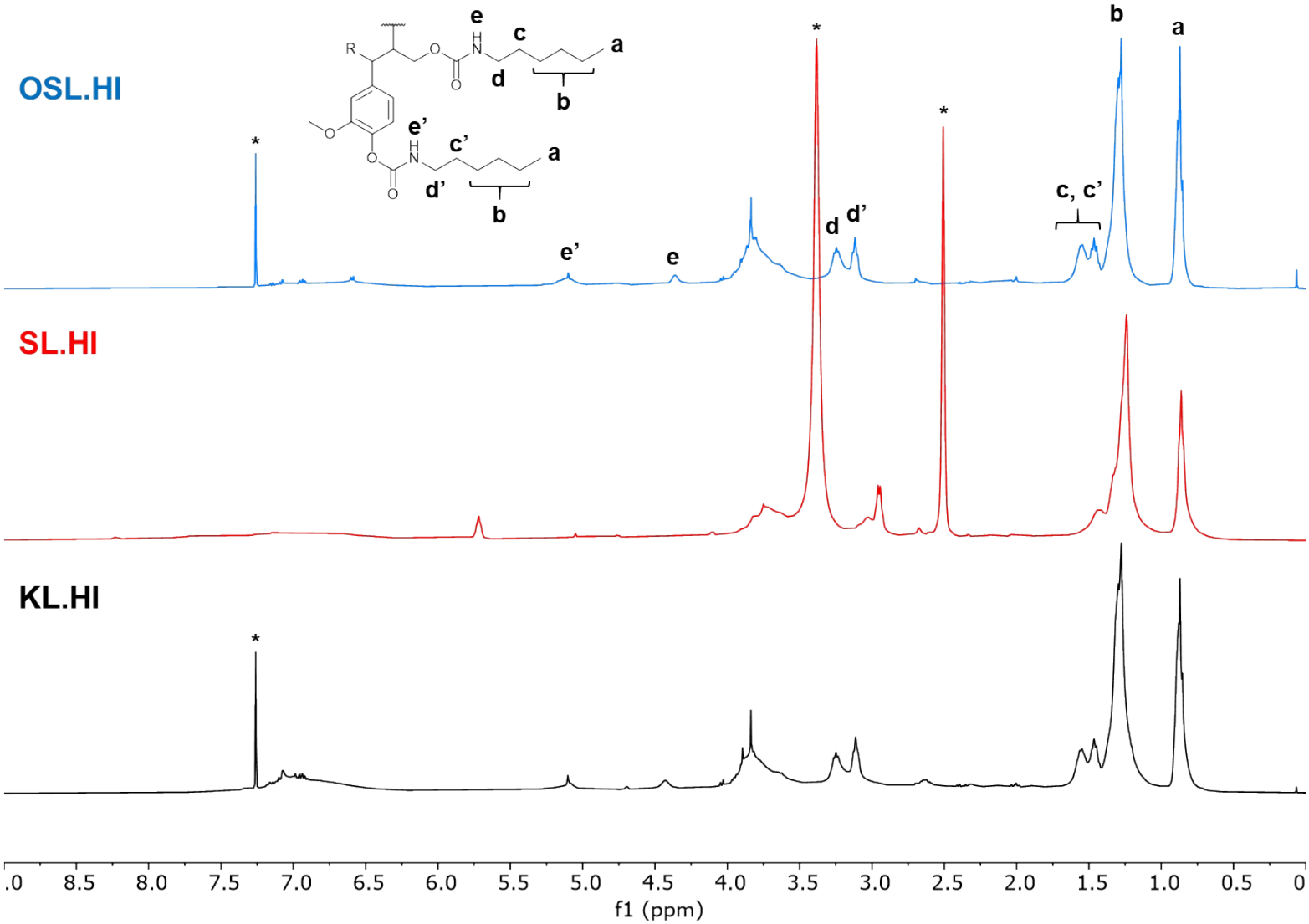

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$ or DMSO-d_6) spectra of KL, SL and OSL modified with hexyl isocyanate (HC) in Cyrene, with assignation of the signals from the grafted groups. For solubility reasons, SL.HI was analyzed in DMSO-d_6, whereas KL.HI and OSL.HI were analyzed in $CDCl_3$, leading to slightly different chemical shifts. * = solvent ($CDCl_3$ or DMSO and H_2O).

HSQC NMR

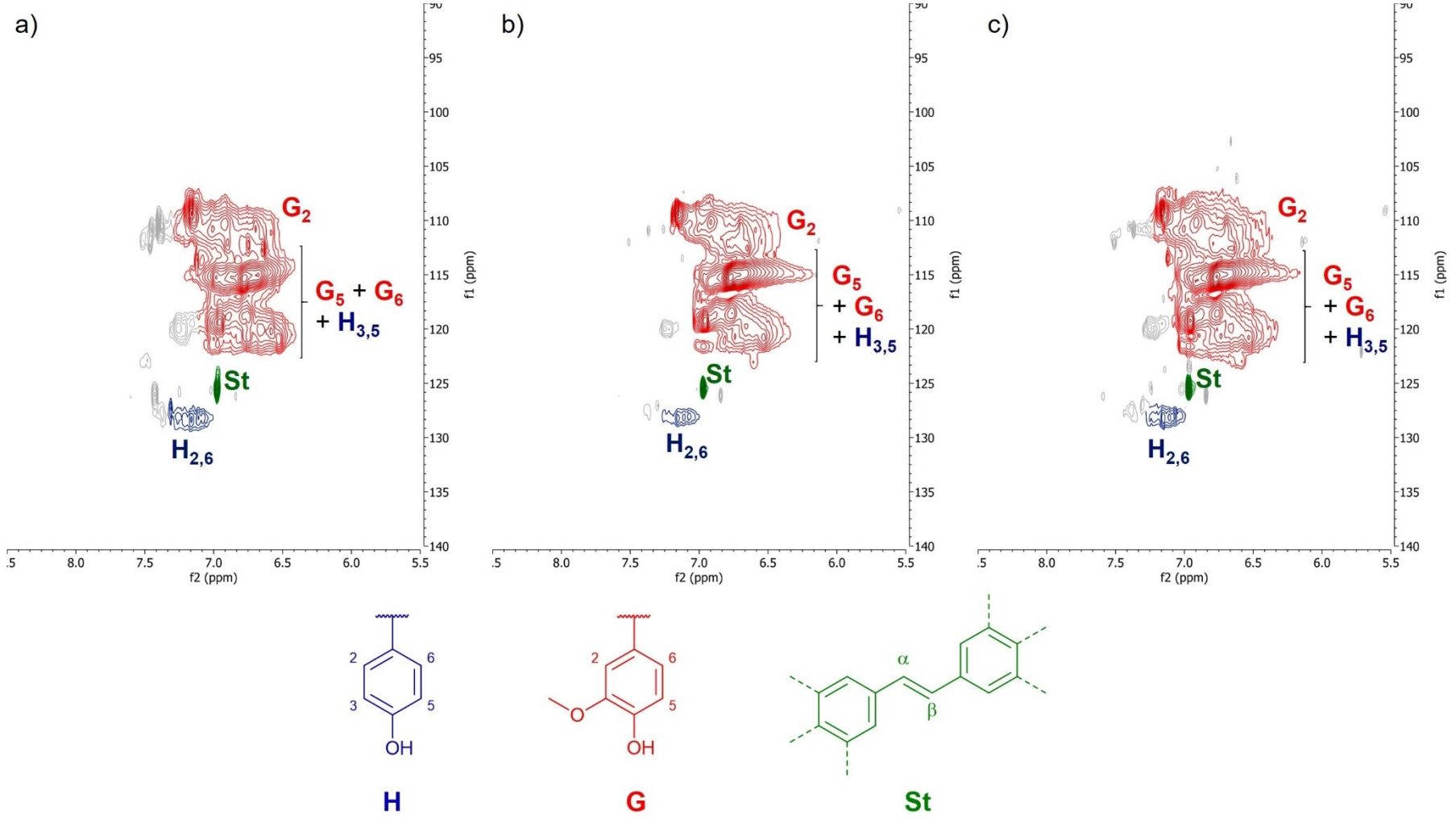

Figure S 26. Aromatic regions of the HSQC NMR spectra of KL (a) and KL treated in Cyrene at 50 °C (b) or 100 °C (c). Assignation of the main lignin structural motifs was performed according to recent literature.[8,9]

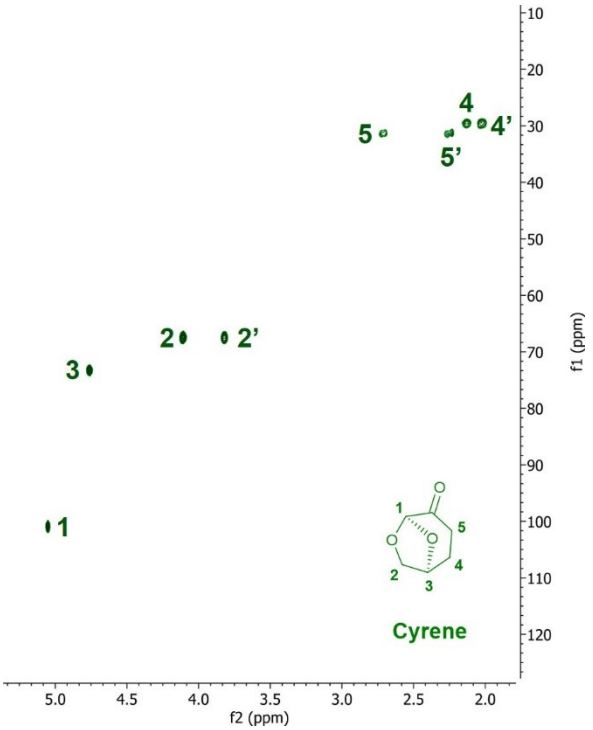

Figure S 27. HSQC NMR spectrum of Cyrene.

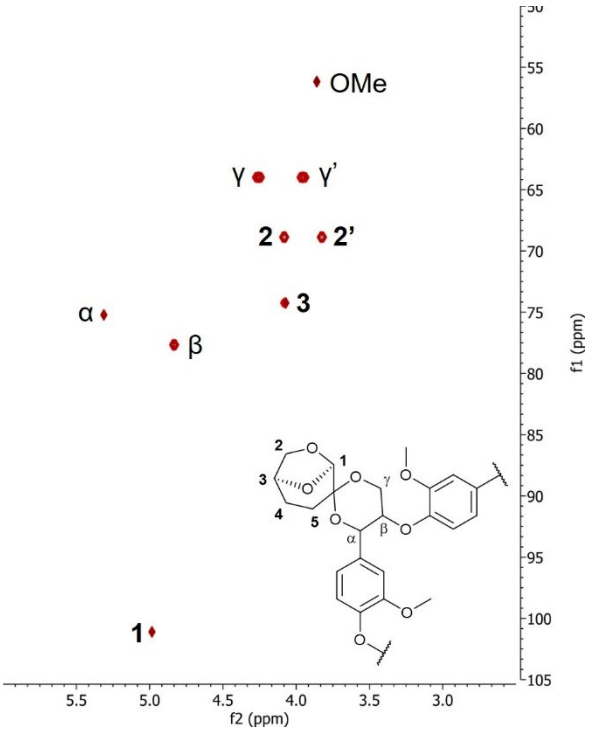

Figure S 28. Simulated HSQC NMR spectrum of the hypothetical structure formed by reaction between Cyrene and the β-O-4 motif of KL. Simulation was performed with MestReNova software (version 14.2.0, Mestrelab Research).

SEC data

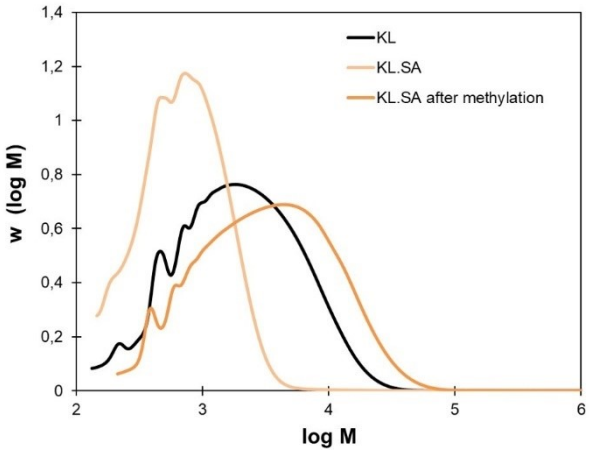

Figure S29. SEC distributions of KL, KL modified by succinic anhydride (KL.SA) and KL.SA after methylation

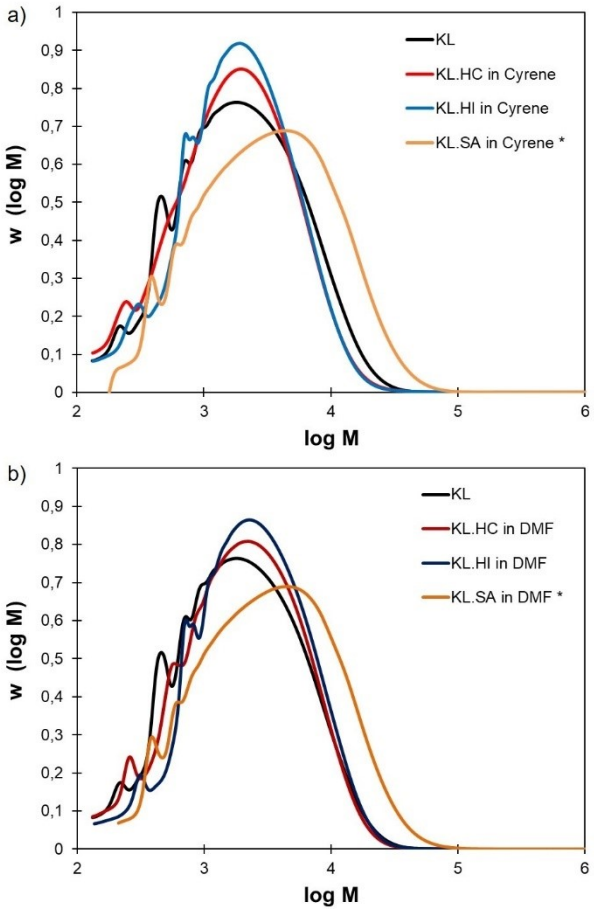

Figure S30. SEC distributions of KL modified with the different reagents in Cyrene (a) or DMF (b). * = methylated prior to SEC analysis.

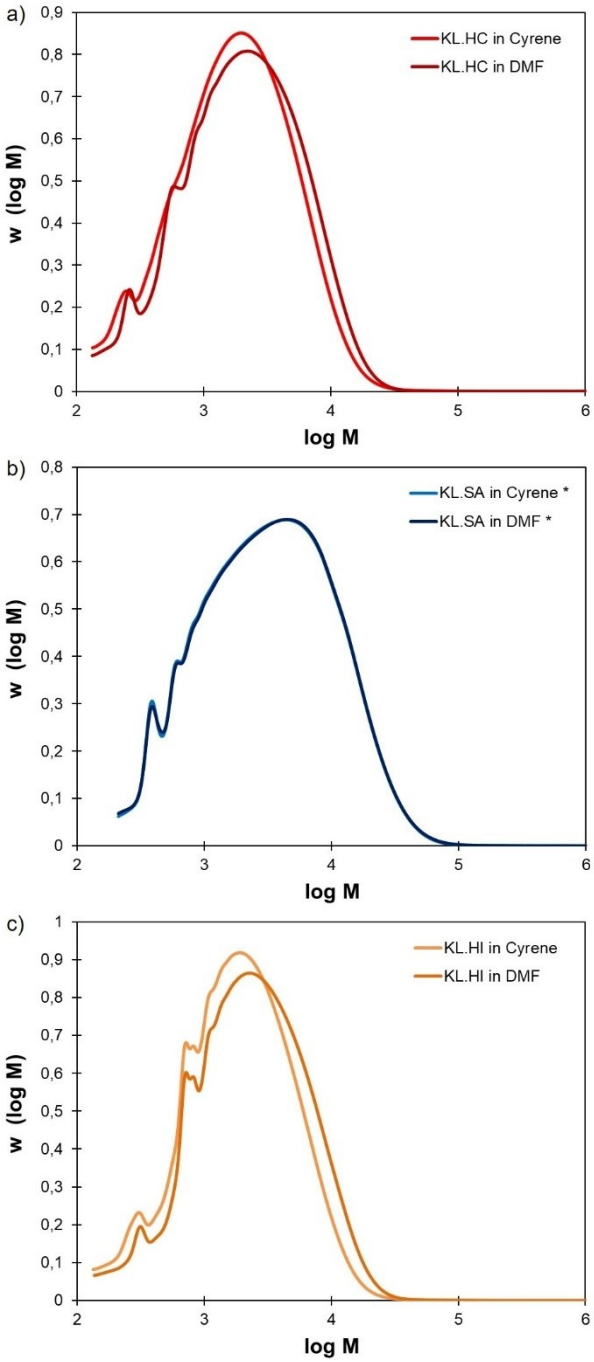

Figure S31. Comparison of SEC distributions of KL modified in Cyrene and DMF with hexanoyl chloride (a), succinic anhydride (b) or hexyl isocyanate (c). * = methylated prior to SEC analysis.

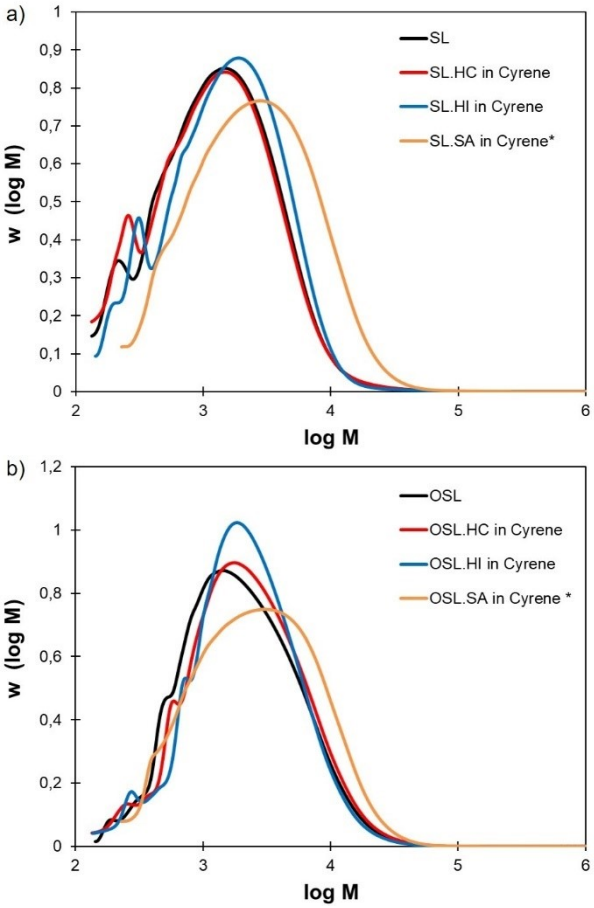

Figure S32. SEC distributions of SL (a) and OSL (b) modified with the different reagents in Cyrene. * = methylated prior to SEC analysis.

References

1 J. Sherwood, M. D. Bruyn, A. Constantinou, L. Moity, C. R. McElroy, T. J. Farmer, T. Duncan, W. Raverty, A. J. Hunt and J. H. Clark, *Chem. Commun.*, 2014, **50**, 9650–9652.

2 R. A. Milescu, M. L. Segatto, A. Stahl, C. R. McElroy, T. J. Farmer, J. H. Clark and V. G. Zuin, *ACS Sustainable Chem. Eng.*, 2020, **8**, 18245–18257.

3 C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, CRC Press, Boca Raton, FL, 2007.

4 C. M. Hansen and A. Björkman, *Holzforschung*, 1998, **52**, 335–344.

5 G. Cañete Vebber, P. Pranke and C. Nunes Pereira, *Journal of Applied Polymer Science*, 2014, **131**, 39696.

6 L. P. Novo and A. A. S. Curvelo, *Ind. Eng. Chem. Res.*, 2019, **58**, 14520–14527.

7 M. De bruyn, V. L. Budarin, A. Misefari, S. Shimizu, H. Fish, M. Cockett, A. J. Hunt, H. Hofstetter, B. M. Weckhuysen, J. H. Clark and D. J. Macquarrie, *ACS Sustainable Chem. Eng.*, 2019, **7**, 7878–7883.

8 S. Constant, H. L. J. Wienk, A. E. Frissen, P. de Peinder, R. Boelens, D. S. van Es, R. J. H. Grisel, B. M. Weckhuysen, W. J. J. Huijgen, R. J. A. Gosselink and P. C. A. Bruijnincx, *Green Chem.*, 2016, **18**, 2651–2665.

9 C. Crestini, H. Lange, M. Sette and D. S. Argyropoulos, *Green Chem.*, 2017, **19**, 4104–4121.