Catalyst-Free Transesterification Vitrimers: activation via α -difluoroesters

Supporting Information

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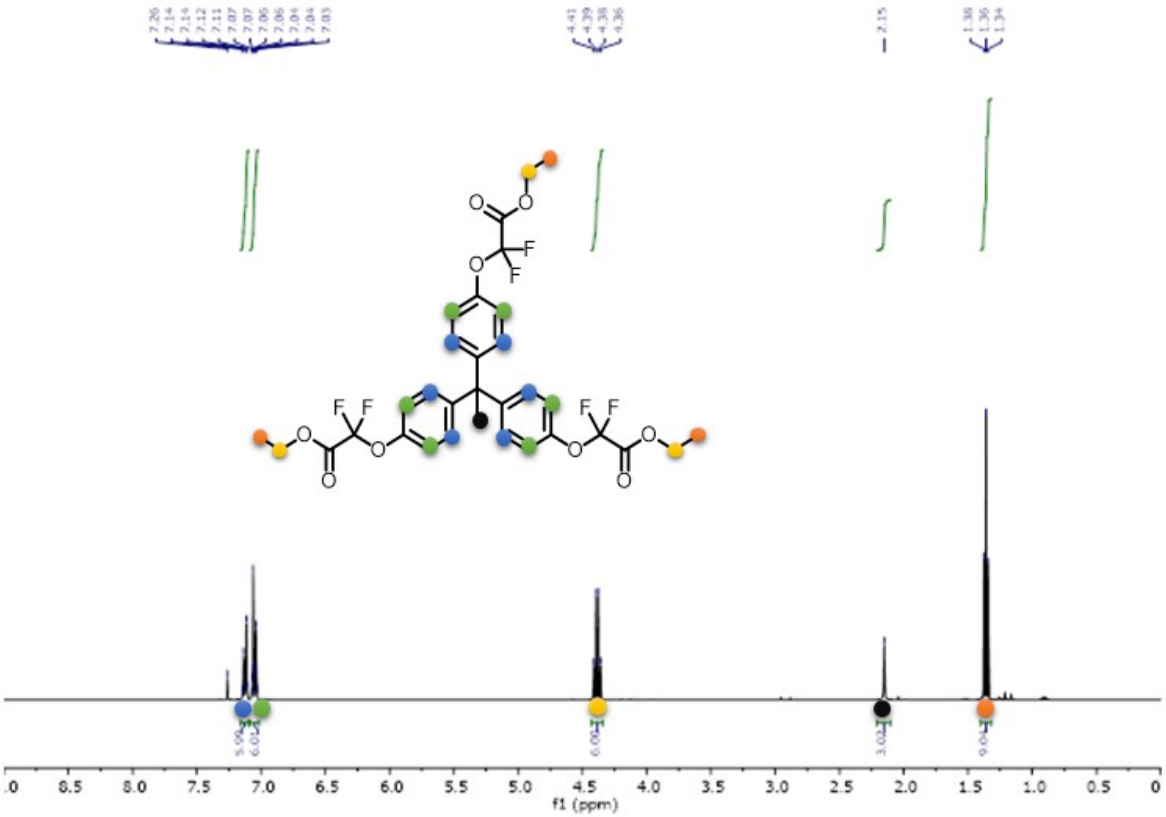


Figure S1. ^{1}H NMR spectrum of the triester TPE-TE in $CDCl_3$

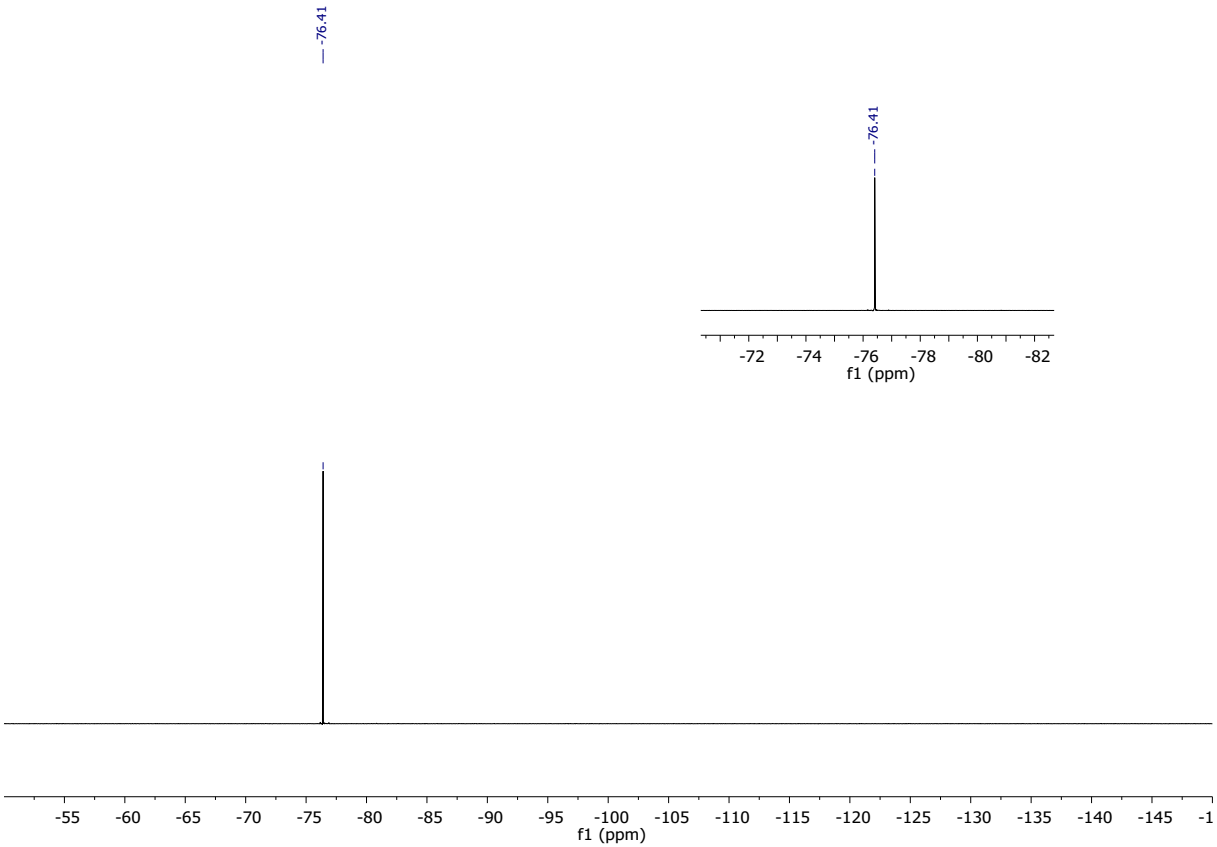


Figure S2. ^{19}F NMR spectrum of the triester TPE-TE in $CDCl_3$

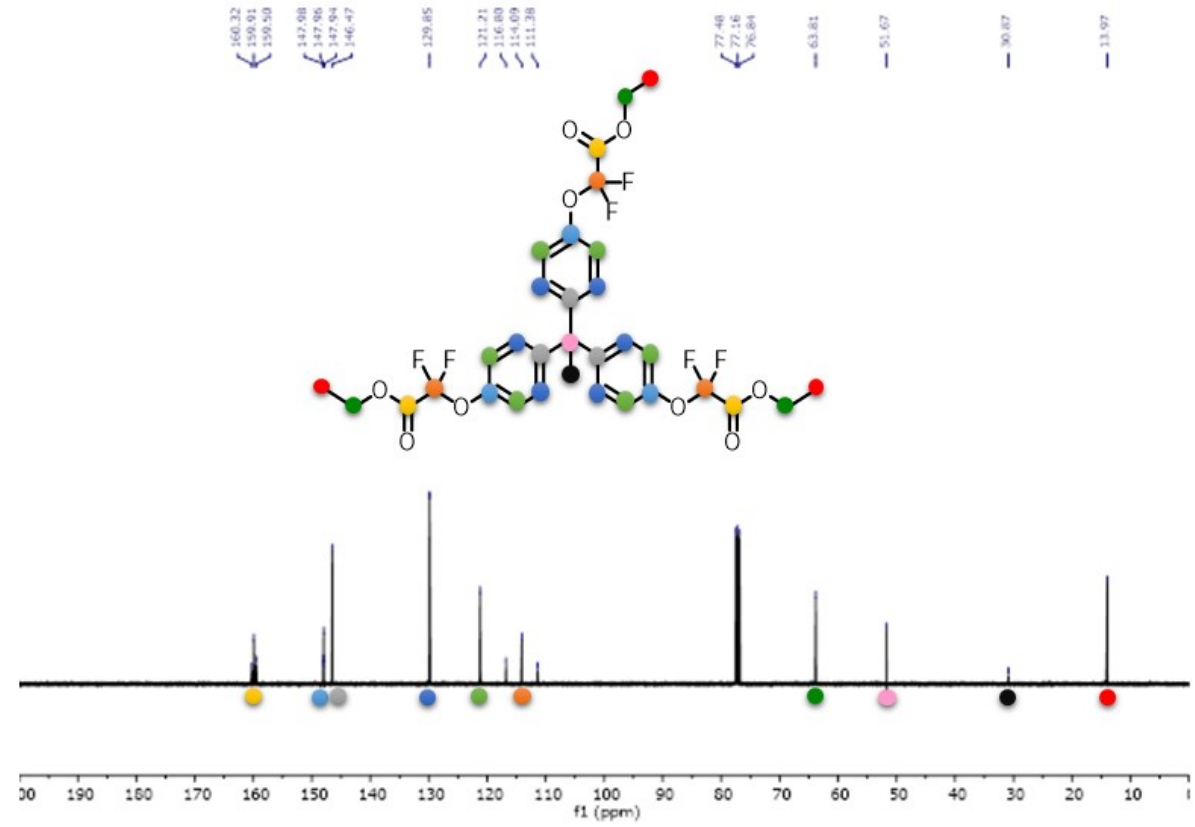


Figure S3. ^{13}C NMR spectrum of the triester TPE-TE in $CDCl_3$

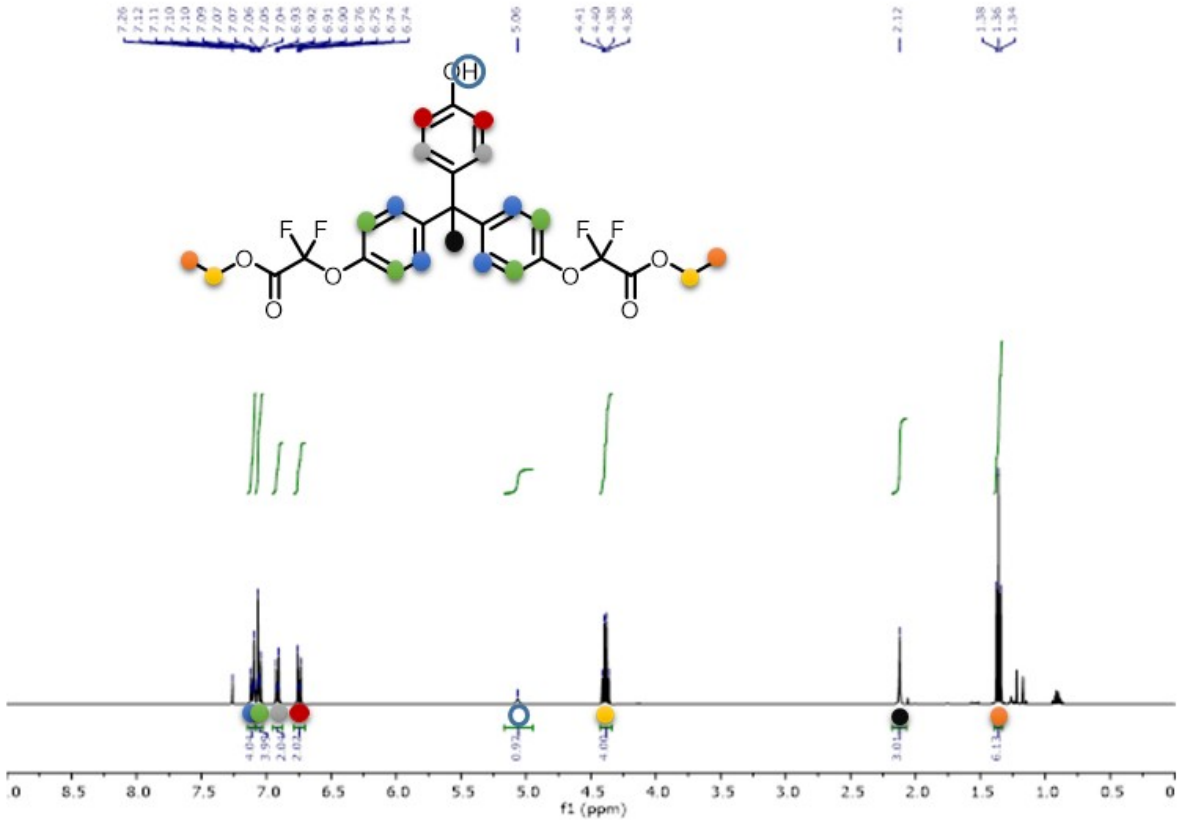


Figure S4. ^{1}H NMR spectrum of the disubstituted byproduct in $CDCl_3$

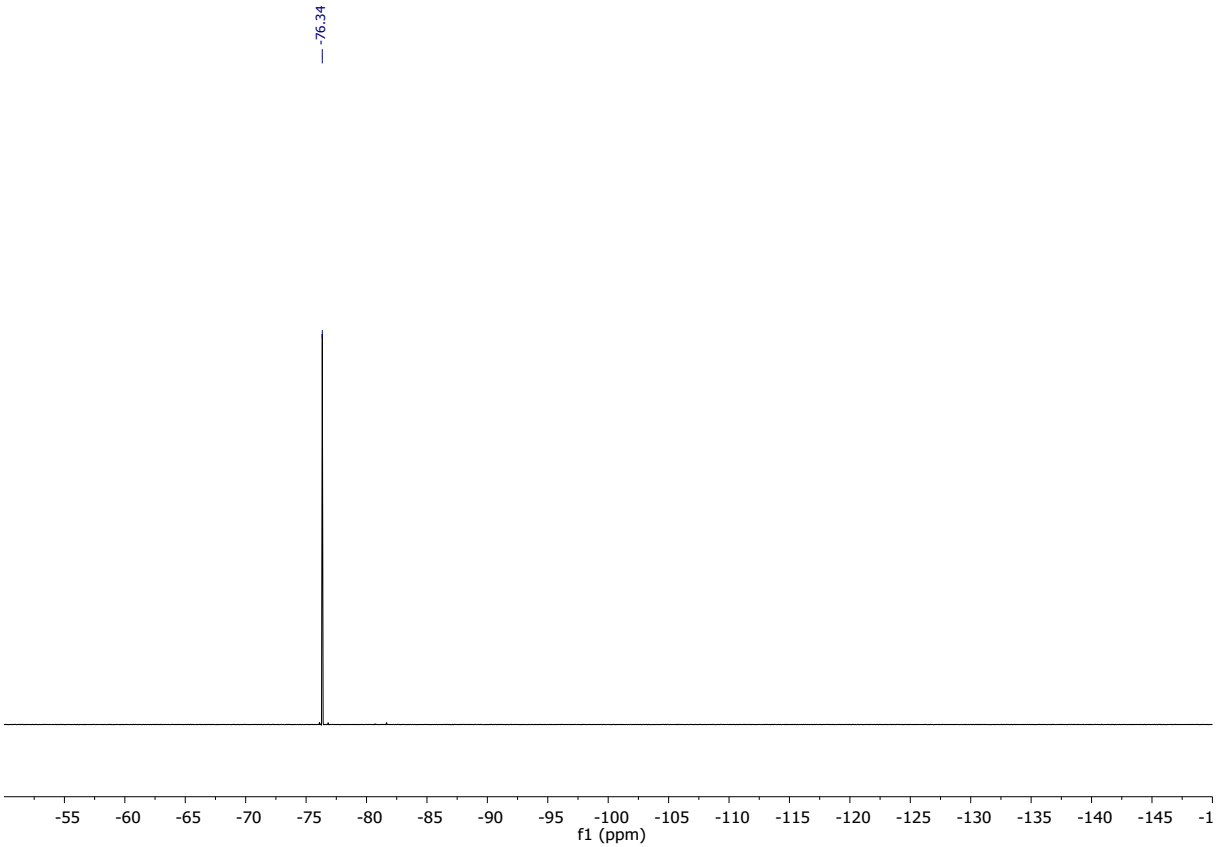


Figure S5. ^{19}F NMR spectrum of the disubstituted byproduct in $CDCl_3$

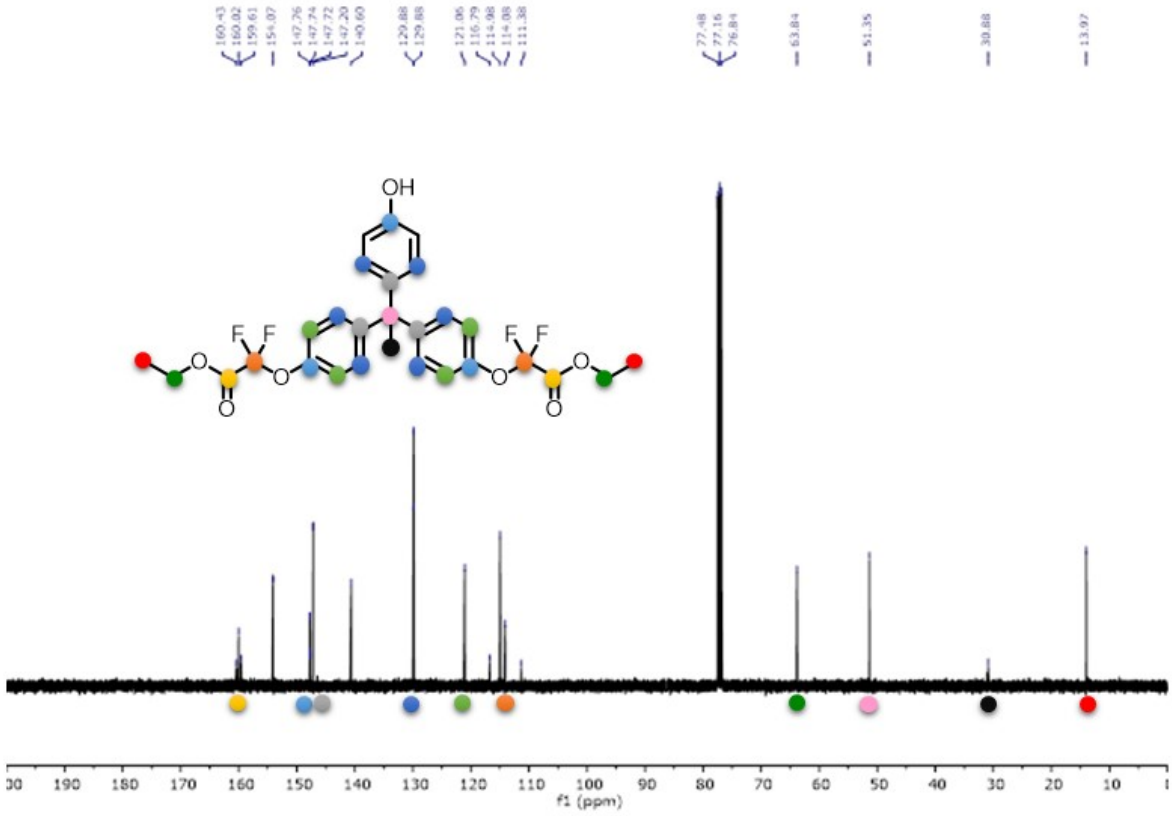


Figure S6. ^{13}C NMR spectrum of the disubstituted byproduct in $CDCl_3$

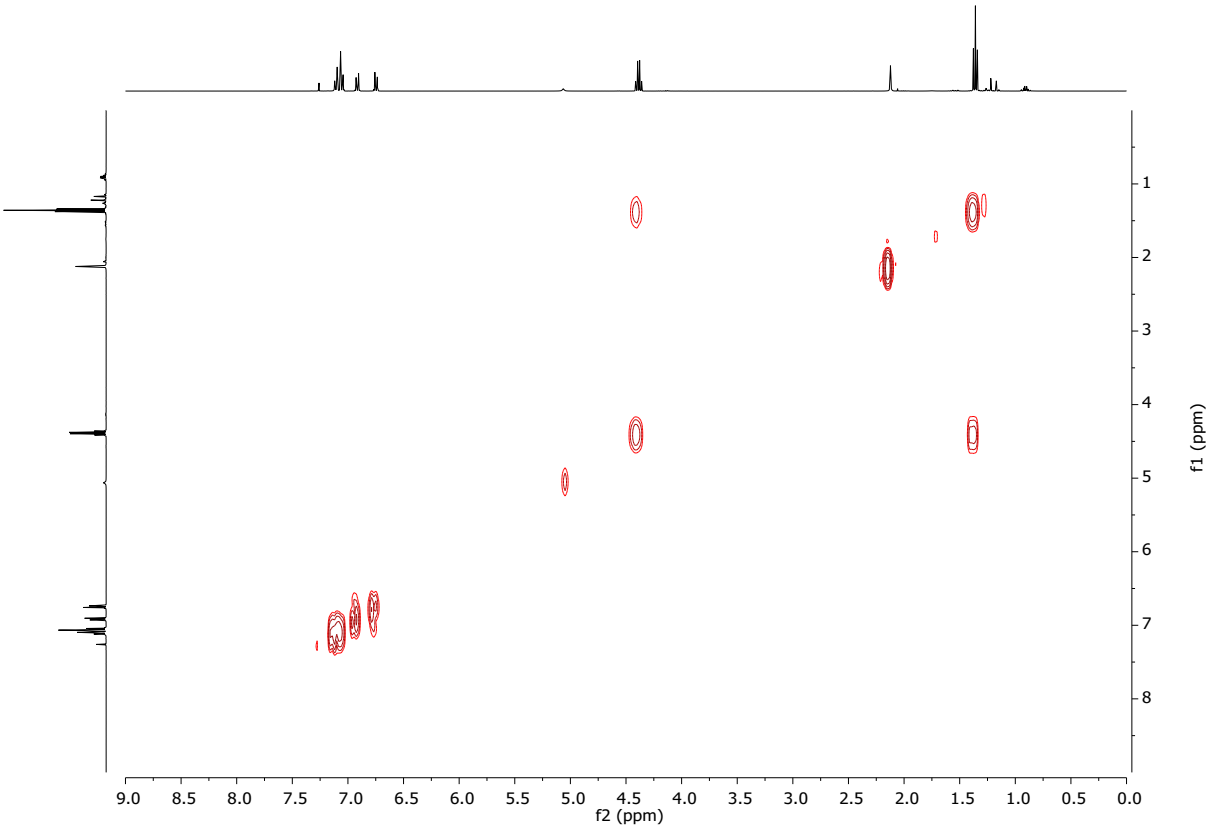
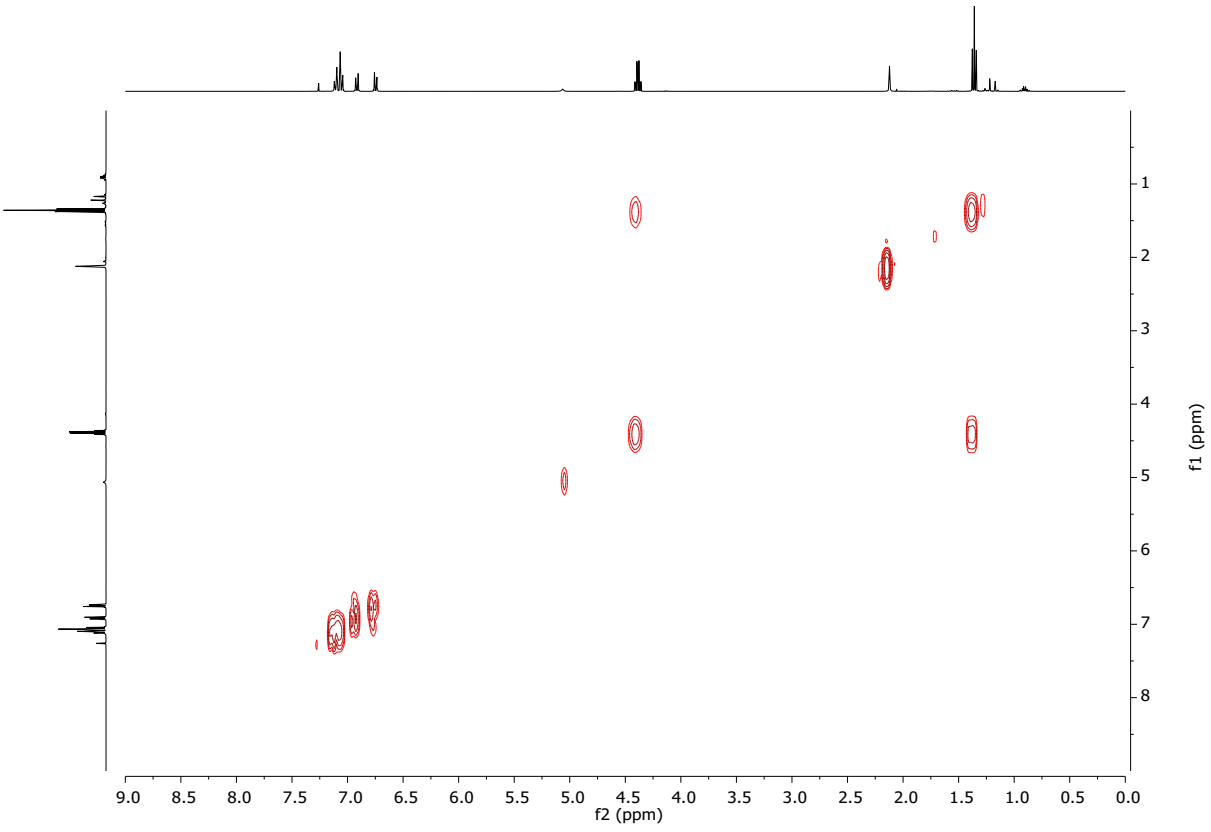


Figure S7. COSY ^{1}H NMR spectrum of the disubstituted byproduct in $CDCl_3$



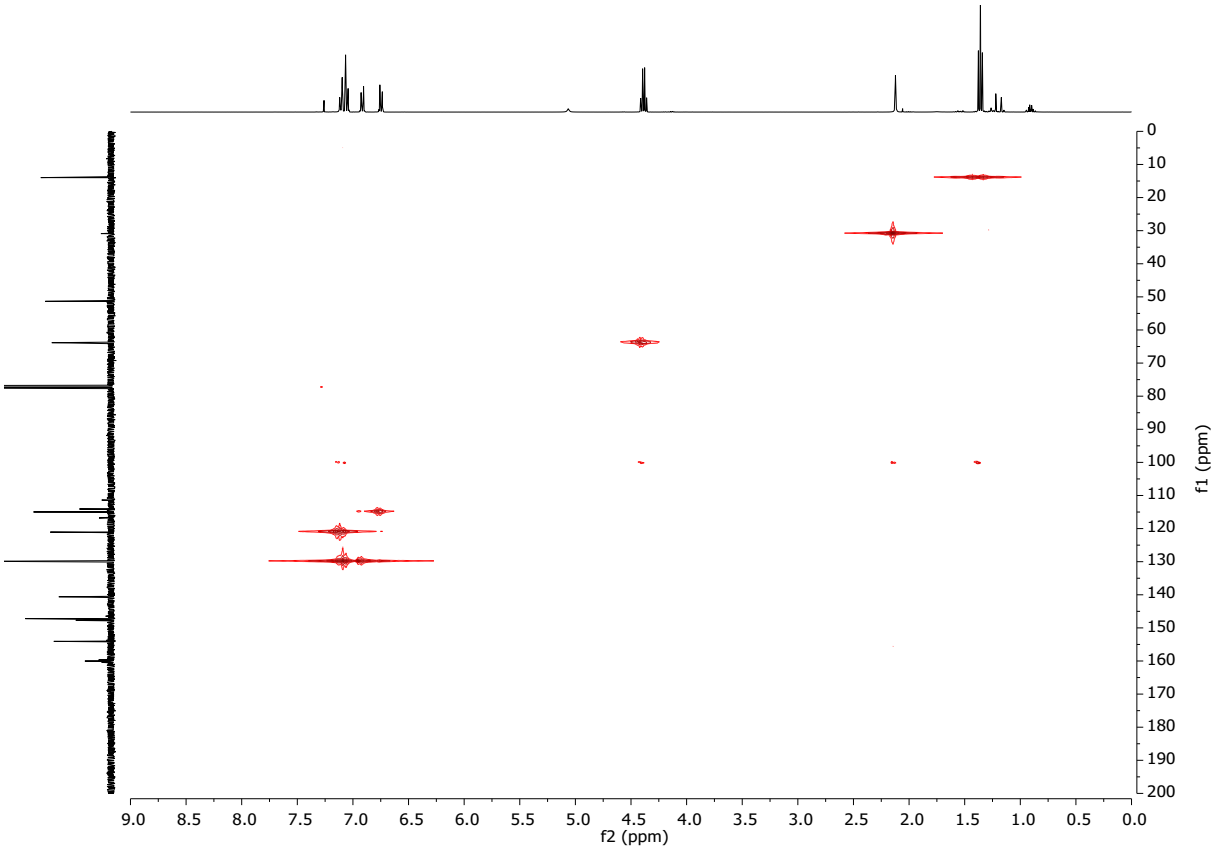


Figure S8. HSQC ^{1}H-^{13}C NMR spectrum of the disubstituted byproduct in $CDCl_3$

II. TPE-TAF characterizations

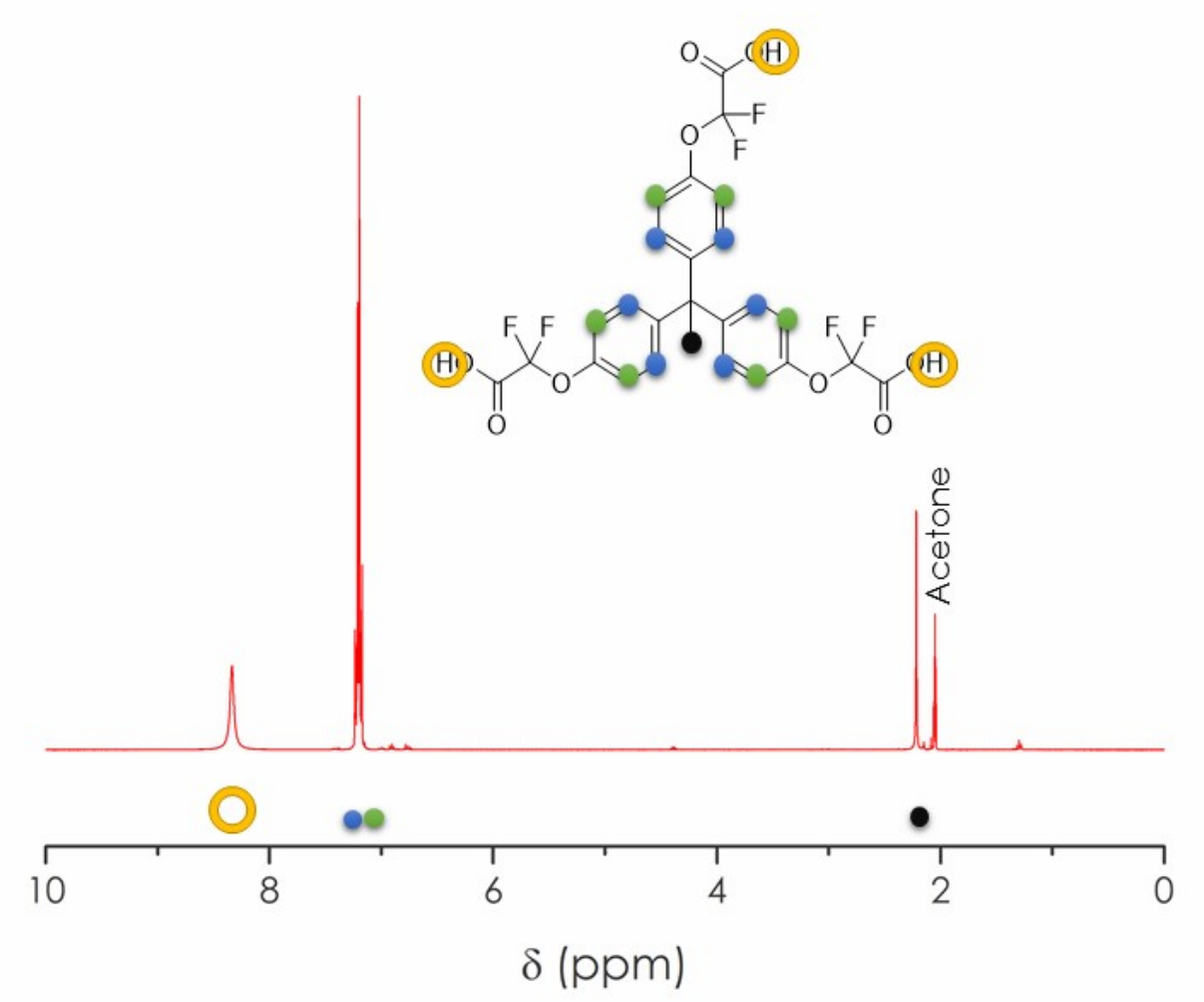


Figure S9. ^{1}H NMR spectrum of the triacid TPE-TAF in acetone-d_6.
Very small signals at 1.30 and 4.39 ppm corresponds to residual ester functions (which amount to less than 2mol% compared to the acid groups).

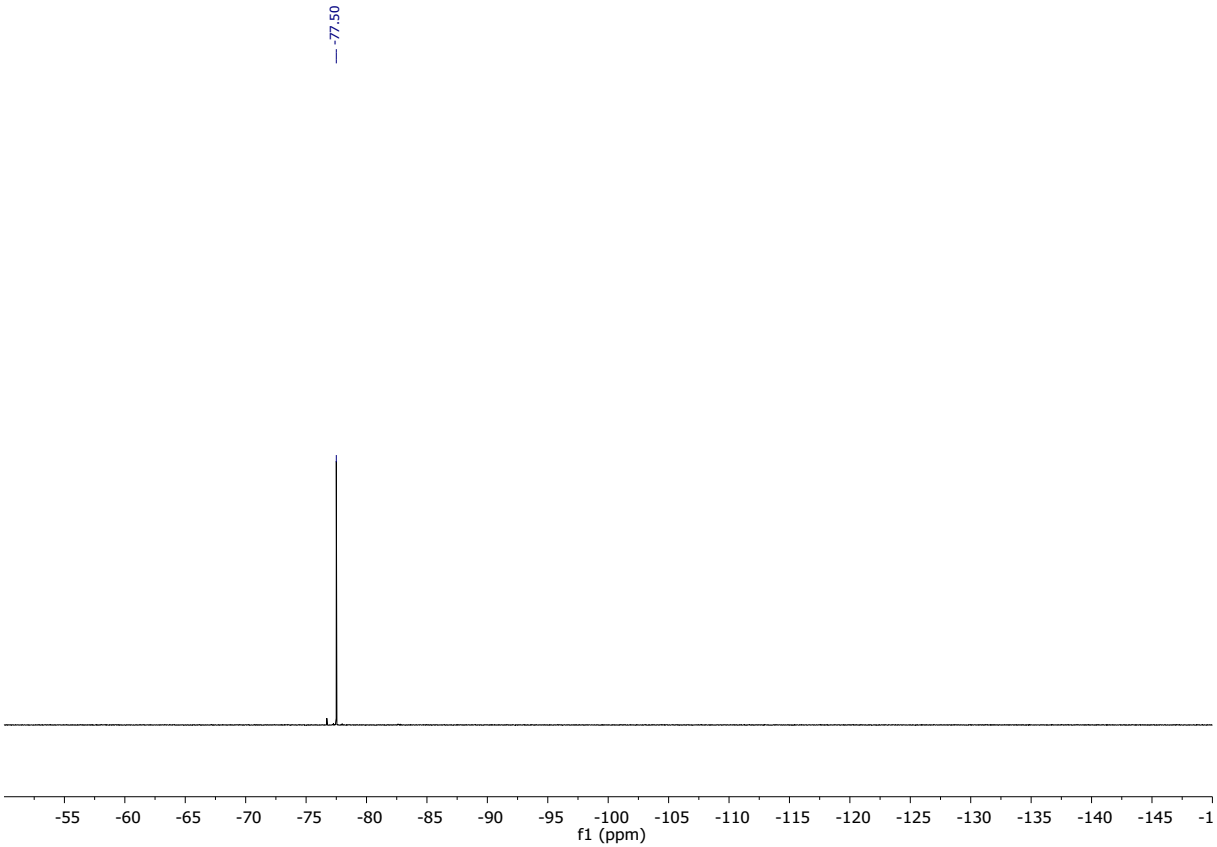


Figure S10. ^{19}F NMR spectrum of the triacid TPE-TAF in acetone-d_6

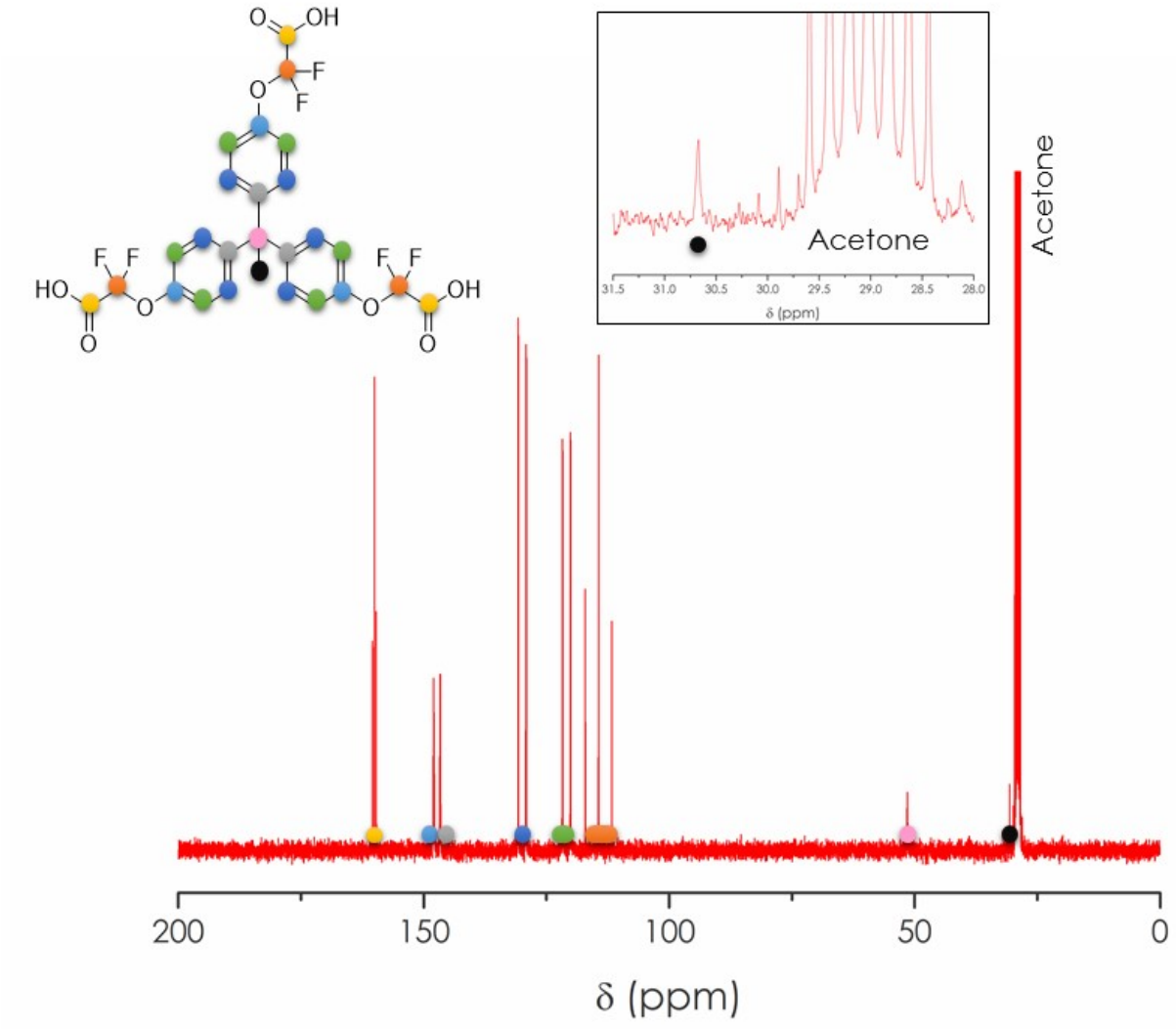


Figure S11. ^{13}C NMR spectrum of the triacid TPE-TAF in acetone-d_6

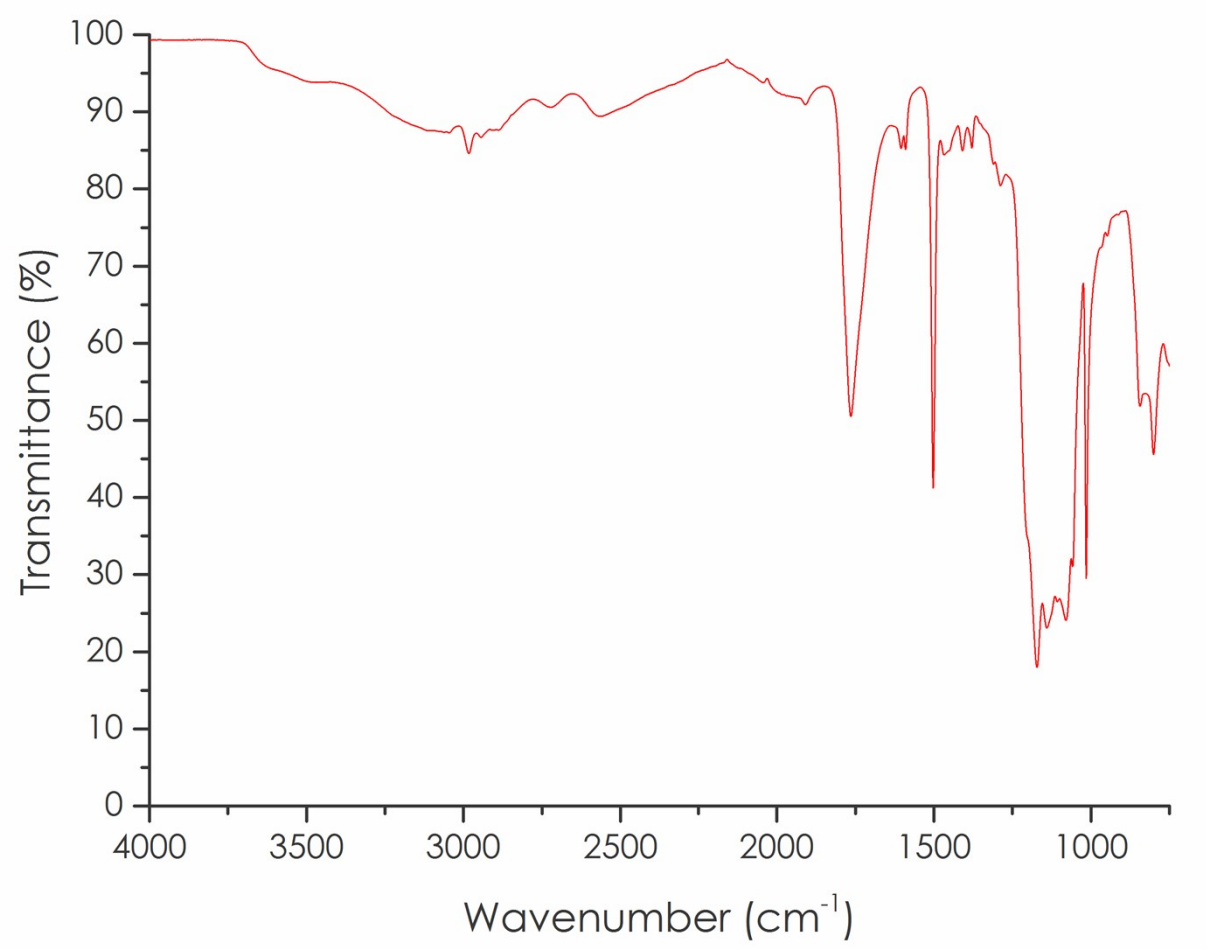


Figure S12. FTIR spectrum of the triacid TPE-TAF

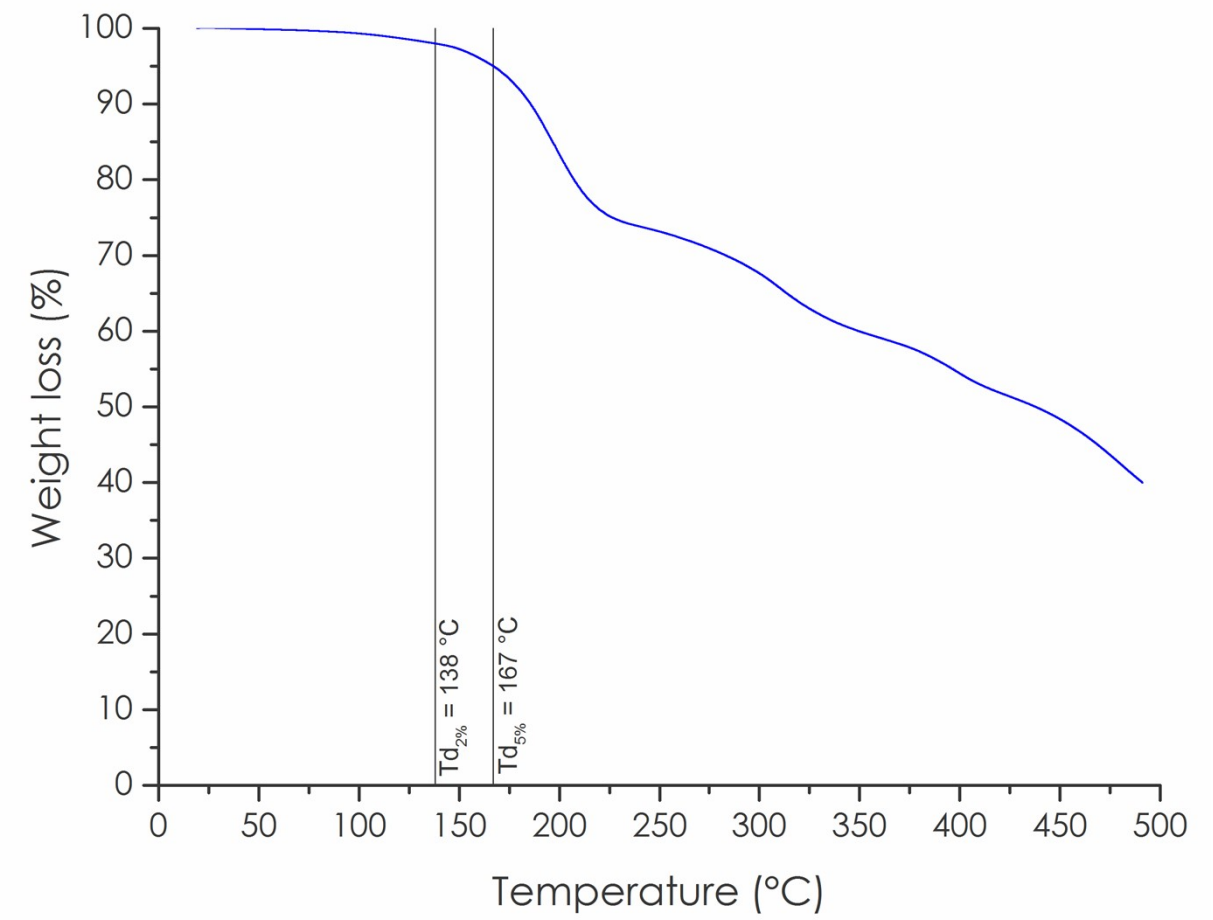


Figure S13. TGA thermogram of the triacid TPE-TAF (air, 20 °C.min^{-1})

III. BDGE characterizations

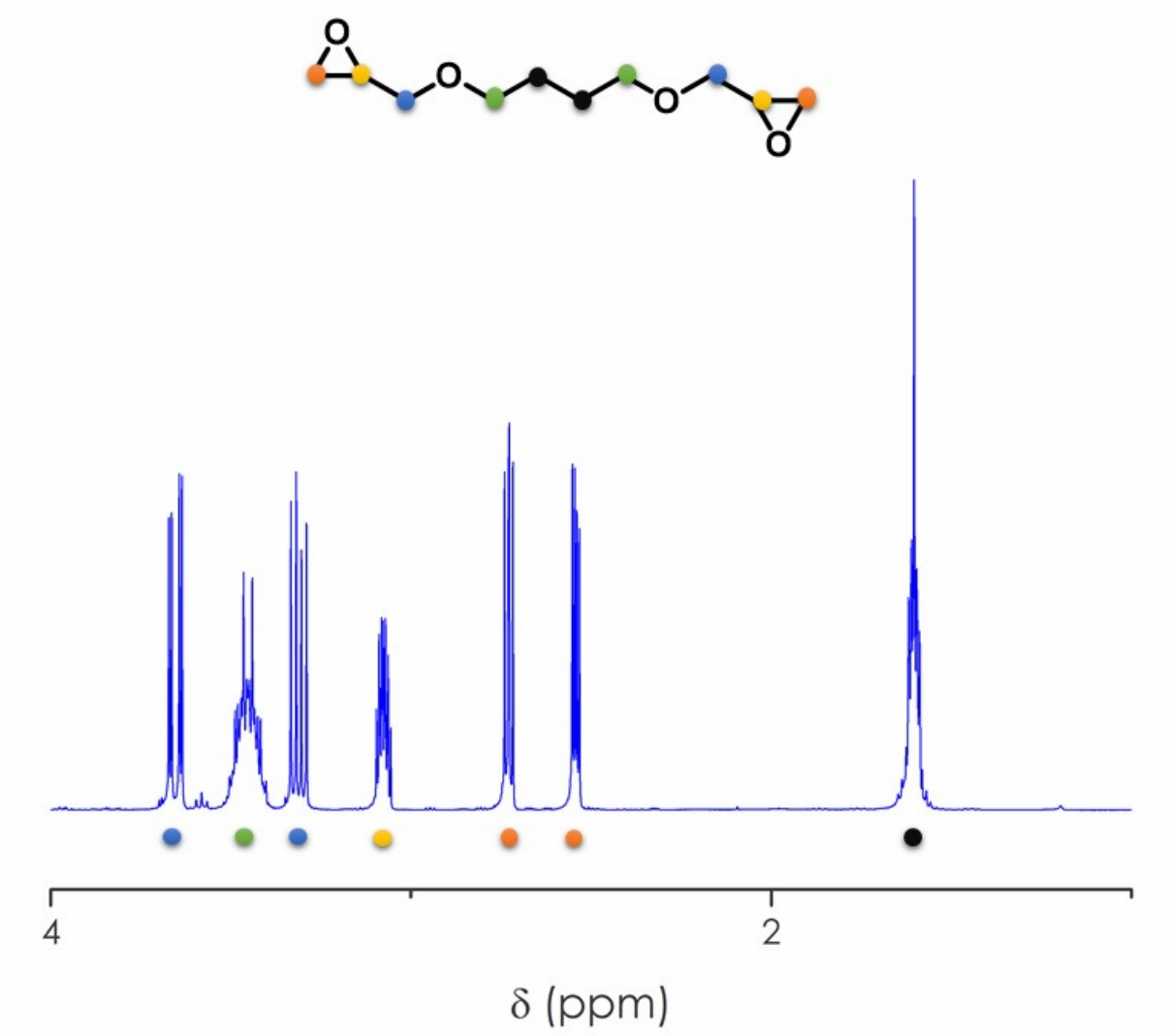


Figure S14. ^{1}H NMR spectrum of the commercial BDGE in $CDCl_3$

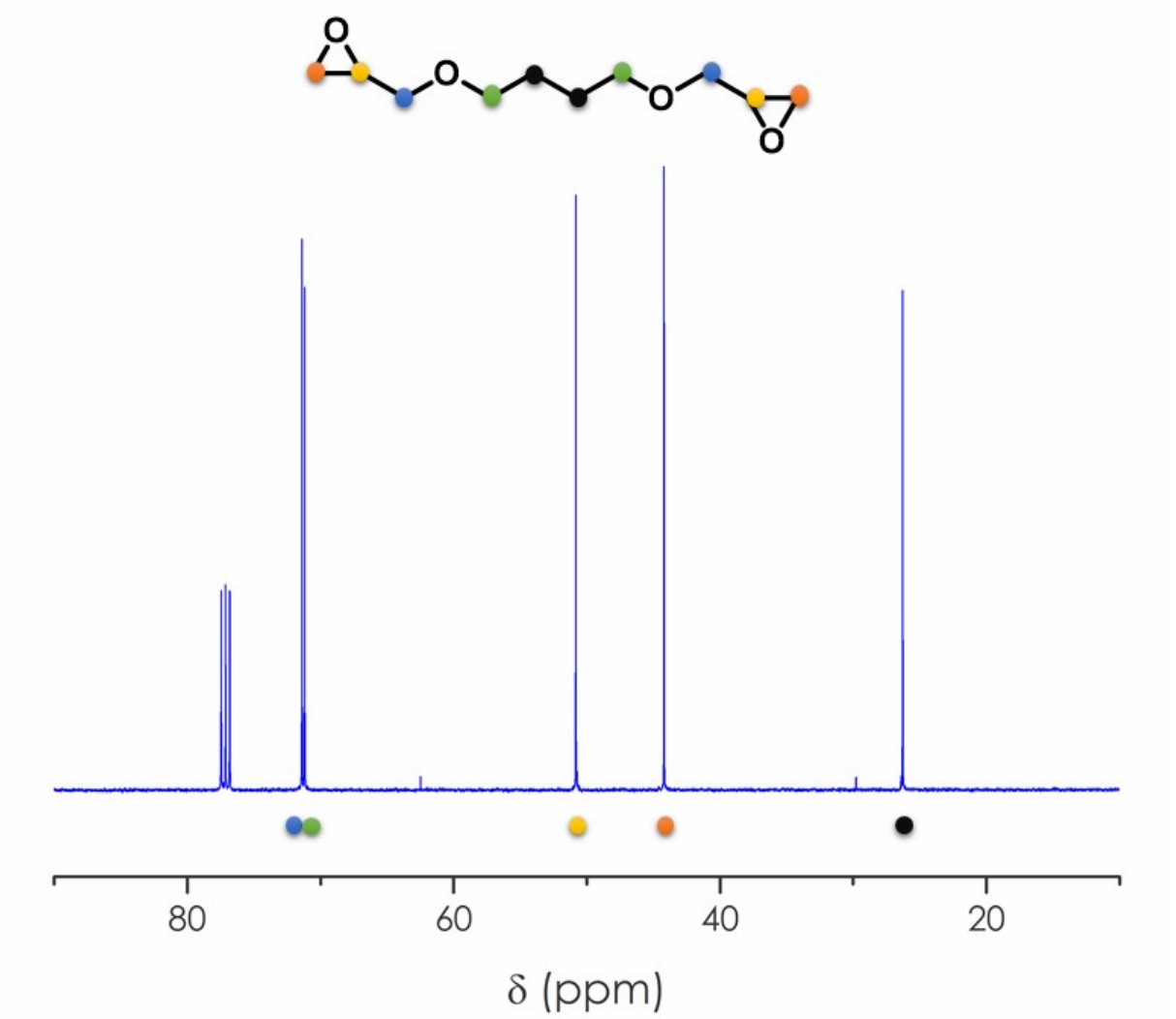


Figure S15. ^{13}C NMR spectrum of the commercial BDGE in $CDCl_3$

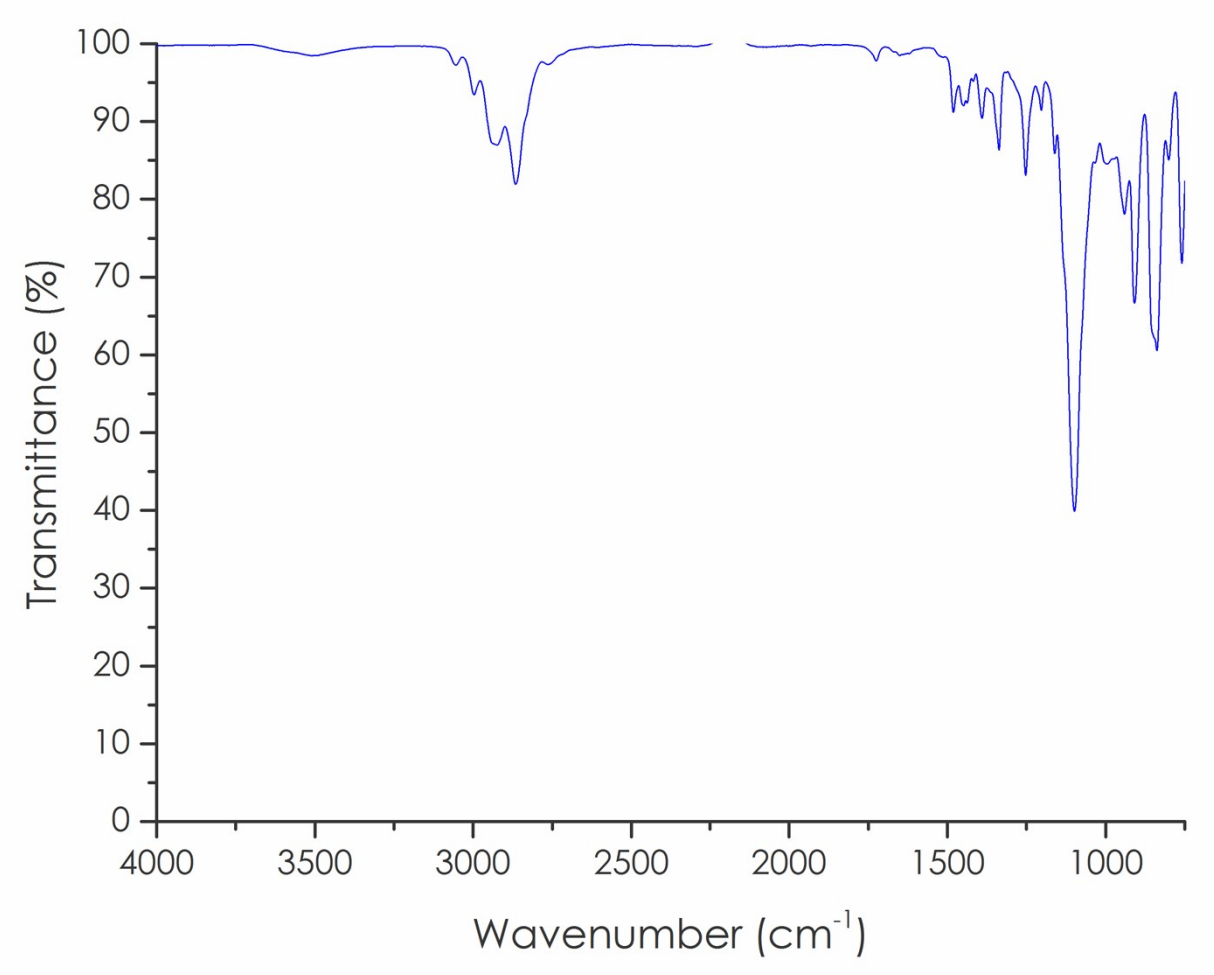
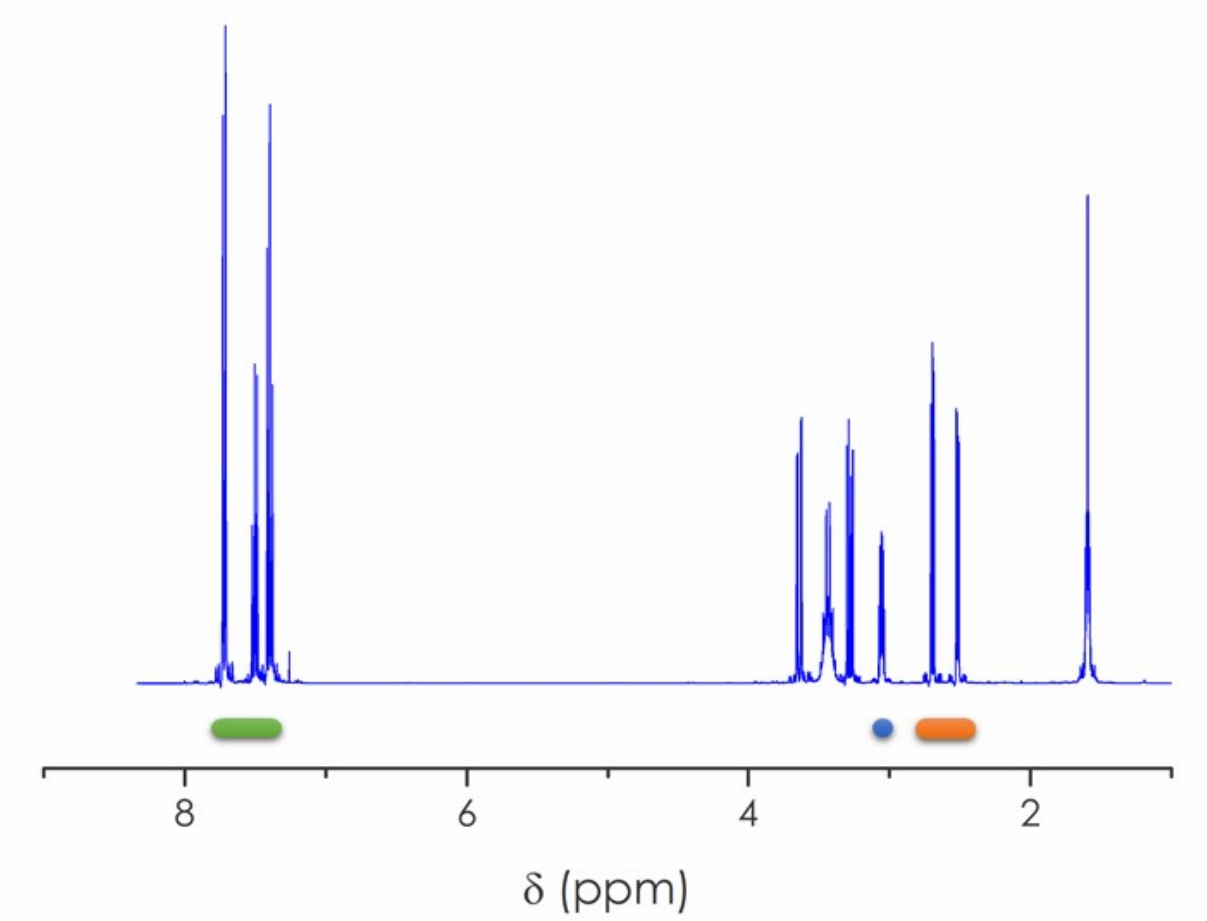


Figure S16. FTIR spectrum of the commercial BDGE

A. Experimental procedure for the determination of BDGE epoxy equivalent weight (EEW) by ^1H NMR in $CDCl_3$



50 to 70 mg of BDGE and 50 to 80 mg of benzophenone were dissolved in deuterated chloroform. ^1H NMR spectra were integrated in the 7.87-7.28 ppm range for benzophenone protons (10 H), in the 3.19-2.97 ppm range for CH oxirane and in the 2.82-2.45 range for CH_2 oxirane. EEW was calculated as follows :

$$EEW_{CH} = \frac{m_{BDGE} \times \int_{7.28}^{7.87} benzophenone \times M_{benzophenone}}{10 \times m_{benzophenone} \times \int_{2.97}^{3.19} CH\ oxirane}$$

$$EEW_{CH_2} = \frac{2 \times m_{BDGE} \times \int_{7.28}^{7.87} benzophenone \times M_{benzophenone}}{10 \times m_{benzophenone} \times \int_{2.45}^{2.82} CH_2\ oxirane}$$

m_{BDGE} (mg)	$m_{benzophenone}$ (mg)	$\frac{\int_{2.97}^{3.19} CH\ oxirane}{\int_{7.28}^{7.87} benzophenone}$	$\frac{\int_{2.45}^{2.82} CH_2\ oxirane}{\int_{7.28}^{7.87} benzophenone}$	EEW_{CH}	EEW_{CH_2}
73.3	80.9	0.157	0.324	117	113
54.6	80.0	0.117	0.241	118	115
57.8	50.7	0.197	0.406	117	114
			Average EEW	**115 ± 4 g/eq**	

B. Experimental procedure for the determination of BDGE epoxy equivalent weight (EEW) by DSC

To confirm the EEW value obtained by NMR, a DSC study was performed. Thermosets of BDGE and succinic acid were made with different stoichiometric ratios. The T_g of the thermosets was measured by DSC, the maximum value corresponding to a acid/epoxy function ratio of 1:1, allowing to calculate the corresponding EEW, knowing the acid HEW (hydrogen equivalent weight). HEW of succinic acid is 59 g/eq.

The coarse acid powder was first crushed in a mortar to obtain a powder as thin as possible. Then it was mixed manually with the right amount of BDGE in a tube. The tube was sealed with a septum and cured overnight at 200 °C in an oven. The thermosets obtained were analysed by DSC (-100 to + 150 °C at 20 °C/min). The Tg was determined upon second heating ramp. The optimal ratio was 1:1, which confirmed the EEW determined by NMR.

$m_{succinic\ acid}$ *(mg)*	m_{BDGE} *(mg)*	*Ratio (based on NMR EEW)*	T_g *(°C)*
66.9	119	0.91	7.9
70.1	134.5	0.99	8
81.6	158.6	1.00	9.4
76.1	156	1.05	7.7
82.8	178.4	1.11	3.7
86.9	206.9	1.22	3.3

IV. TPE-TAF / BDGE vitrimer characterizations

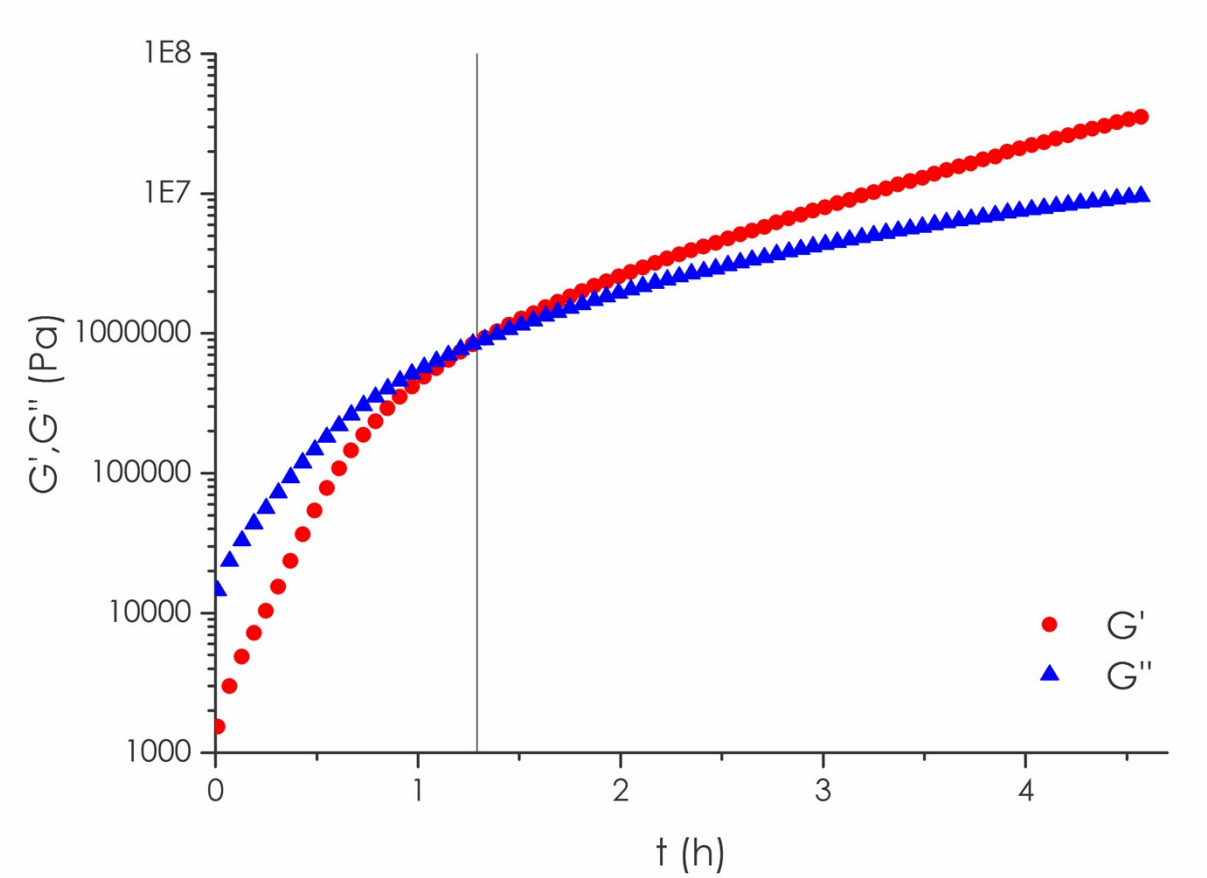


Figure S17. Determination of the gel time of the TPE-TAF/BDGE mixture at 20 °C by rheology

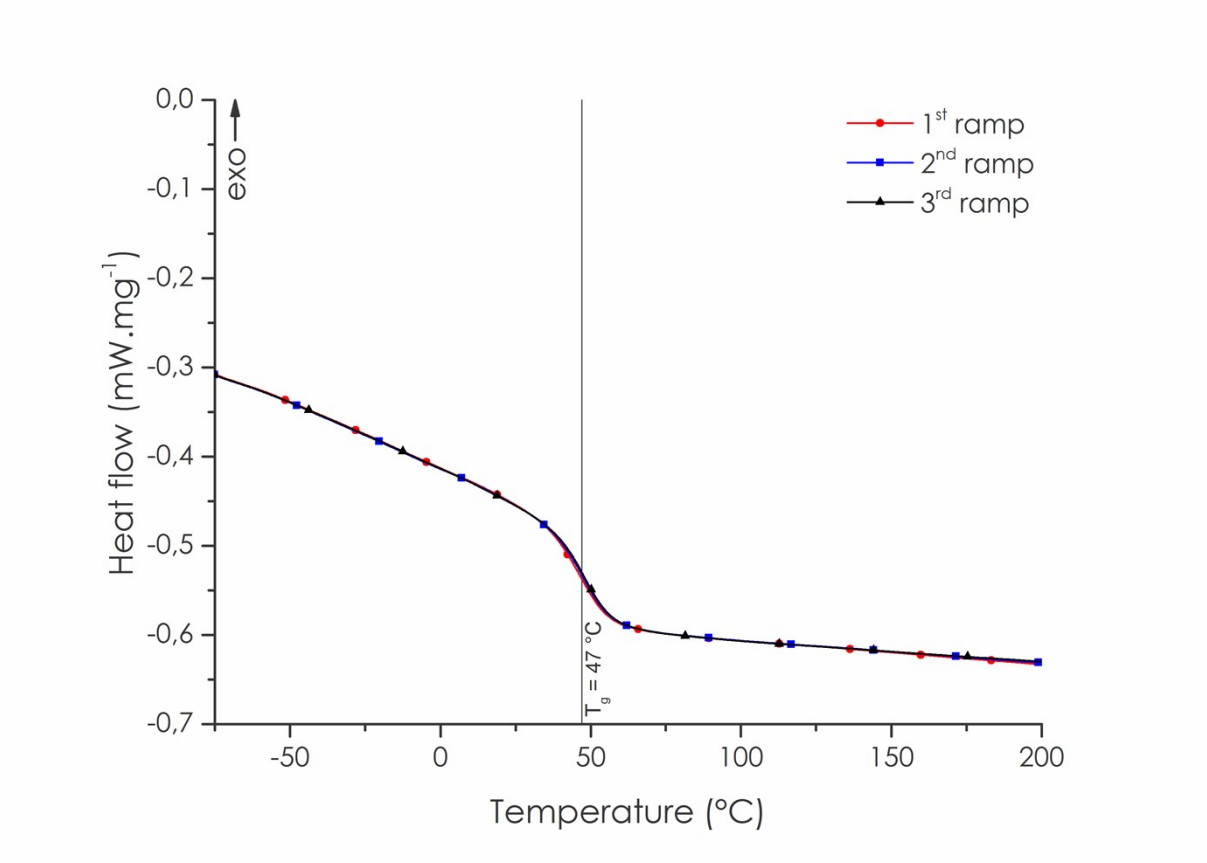


Figure S18. DSC thermogram of the TPE-TAF/BDGE material after curing 3 h at 150 °C (nitrogen, 20 °C.min^{-1})

Table S1. Gel content of the pristine TPE-TAF/BDGE material after curing 3 h at 150 °C in various solvents

Solvent	Acetone	THF	Toluene	Cyclohexane	DMSO	CH_2Cl_2	Acetonitrile
GC (%)	94	94	99	99	96	97	96

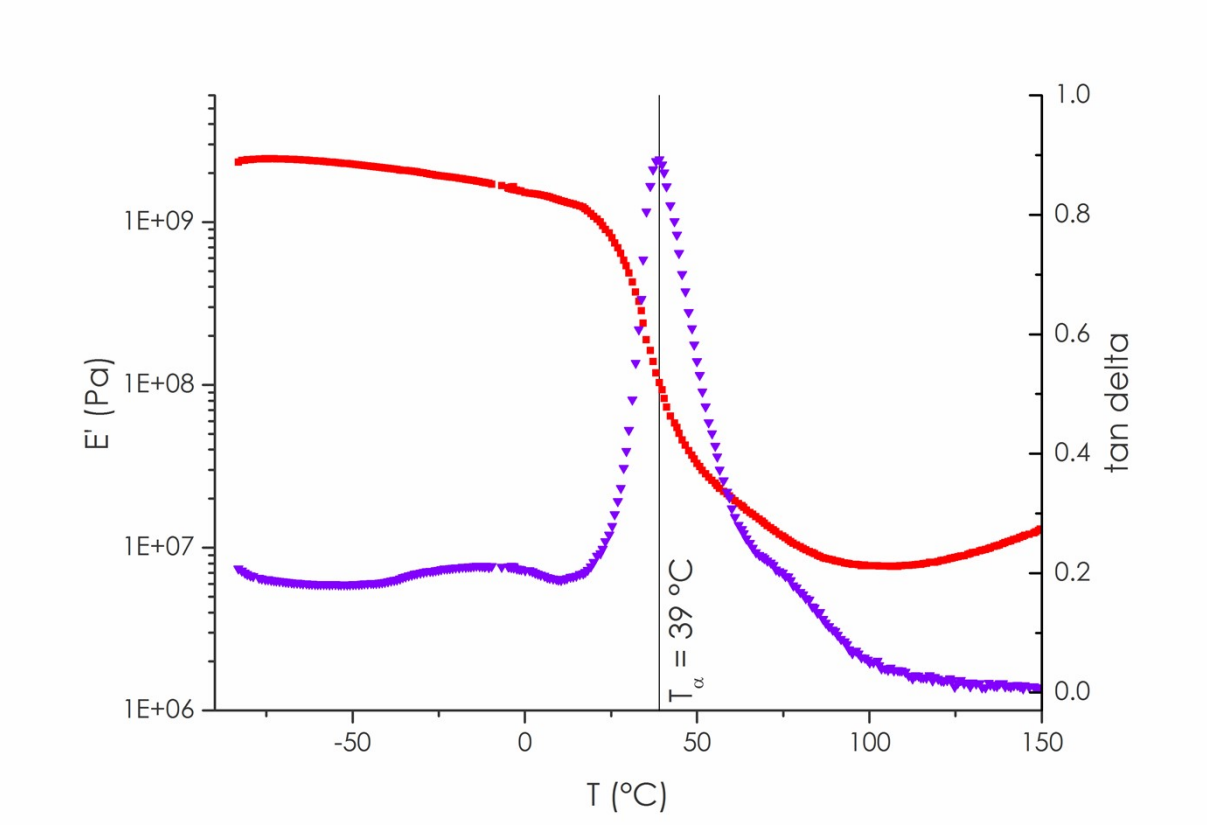


Figure S19. DMA thermogram of the pristine TPE-TAF/BDGE material after curing 3 h at 150 °C

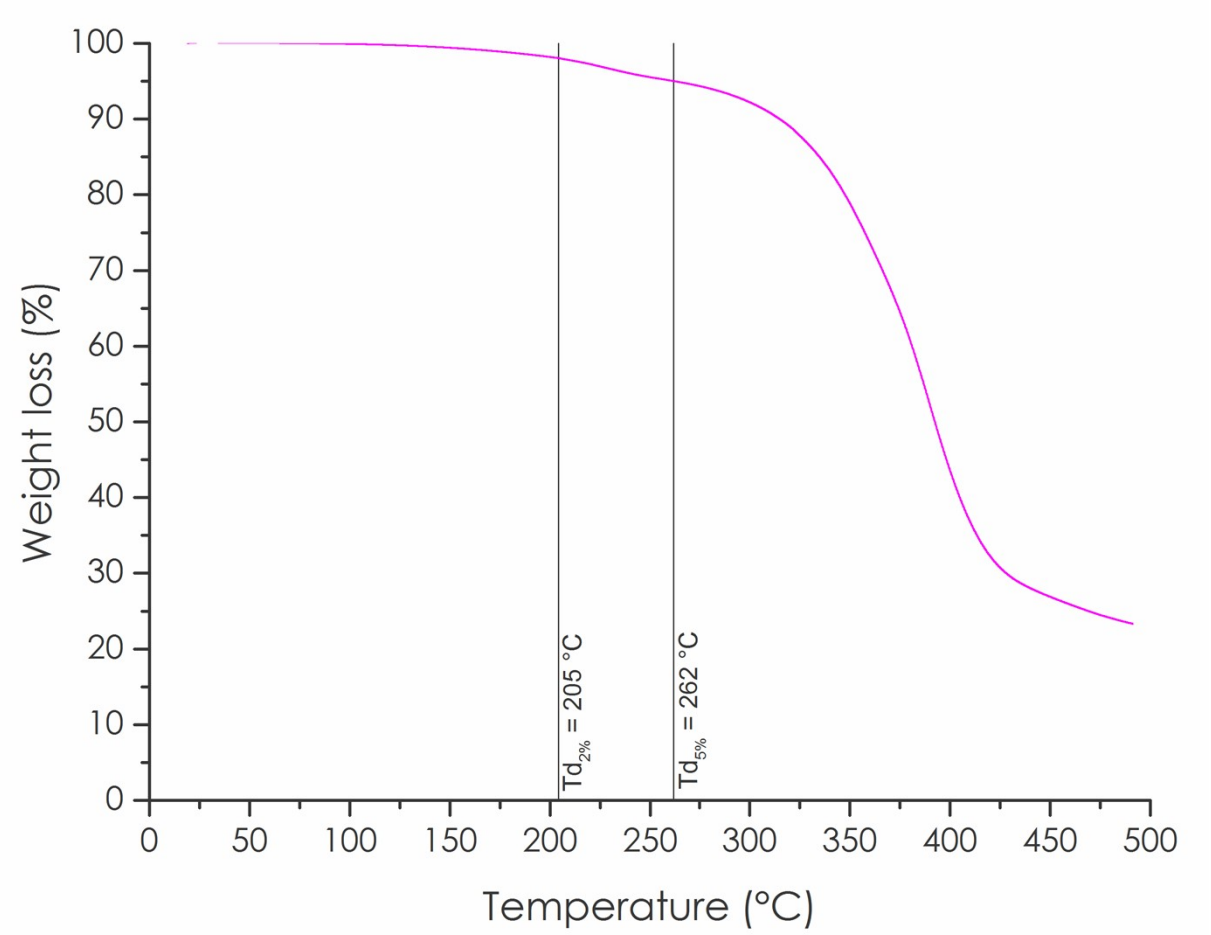


Figure S20. TGA thermogram of the pristine TPE-TAF/BDGE material after curing 3 h at 150 °C (air, 20 °C min^{-1})

Table S2. Equation and fitting parameters of the Kohlrausch-Williams-Watts stretched exponential model for the stress relaxation experiments

$\frac{G}{G_0} = e^{\left(\frac{-t}{\tau}\right)^{\beta}}$	T (°C)	170	180	190	200	210
	τ (s)	79692	43025	30376	20772	13097
	β	0.57	0.58	0.58	0.53	0.56
	R^2	0.99513	0.99975	0.99906	0.99804	0.99923

Note: for β = 1 the KWW expression become the Maxwell equation

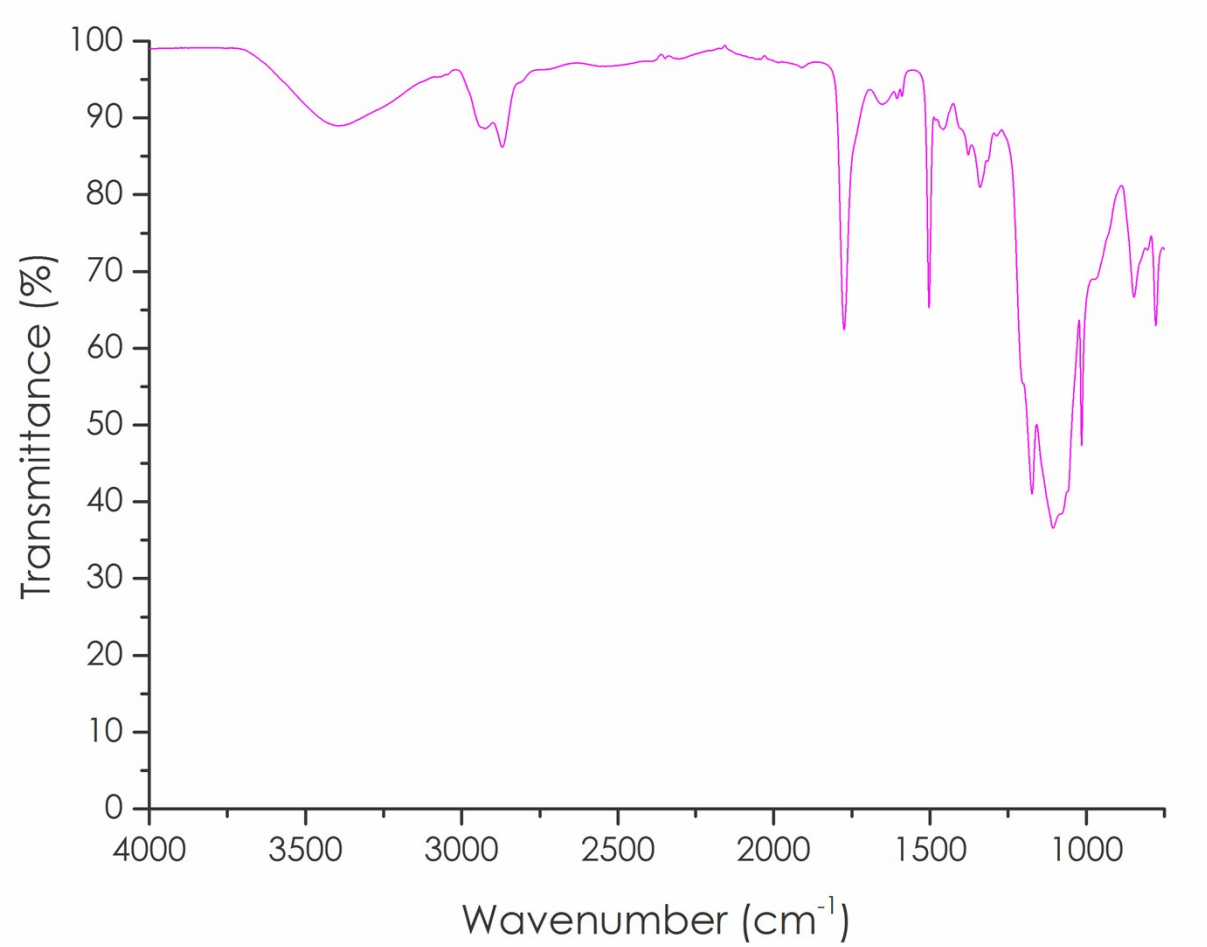


Figure S21. FTIR spectrum of the cured TPE-TAF/BDGE material

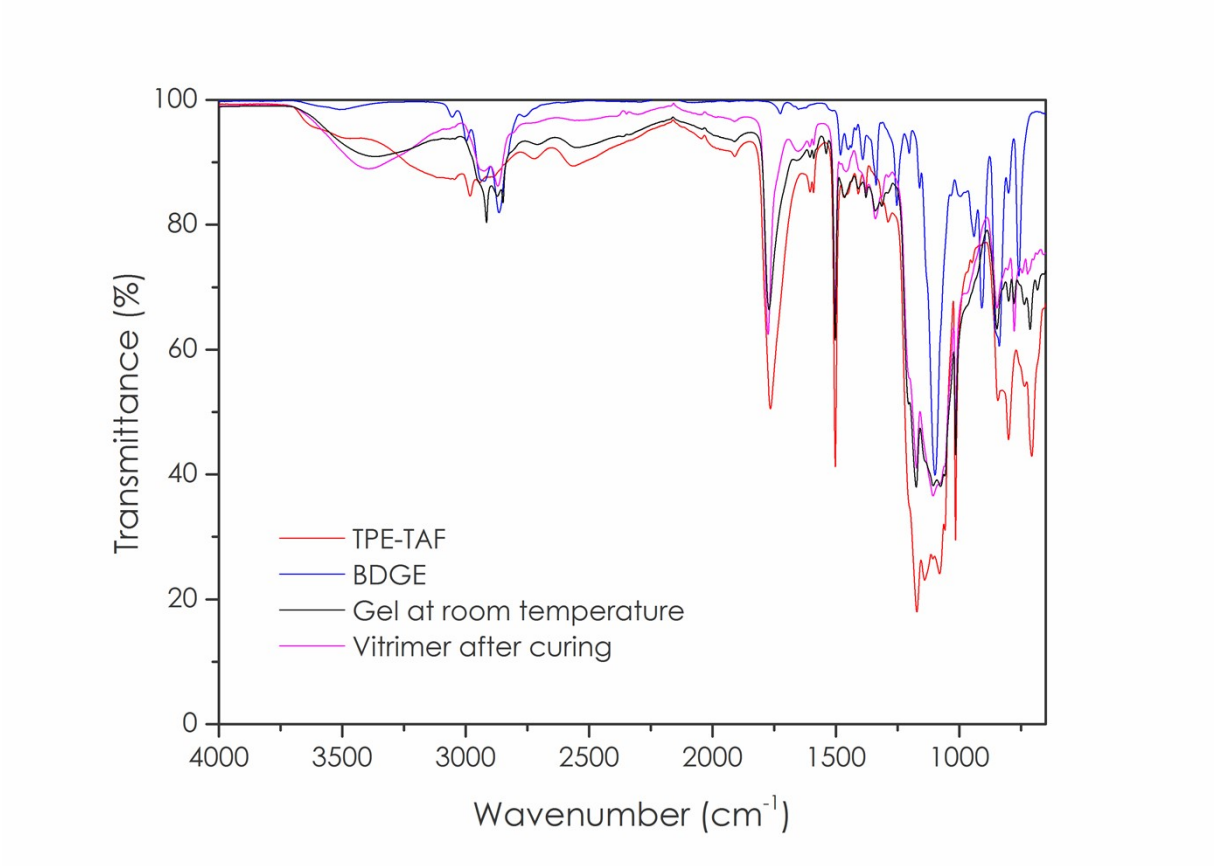


Figure S22. Stacked FTIR spectra of TPE-TAF, BDGE, material after gelation 4 days at room temperature and TPE-TAF/BDGE material after curing 3 h at 150 °C