Supplementary Materials

1) For ^{13}C spectra, $CDCl_3$ was set as a reference with chemical shift 77.000 ppm.

2) For ^{1}H spectra, the reference is TMS with shift 0.

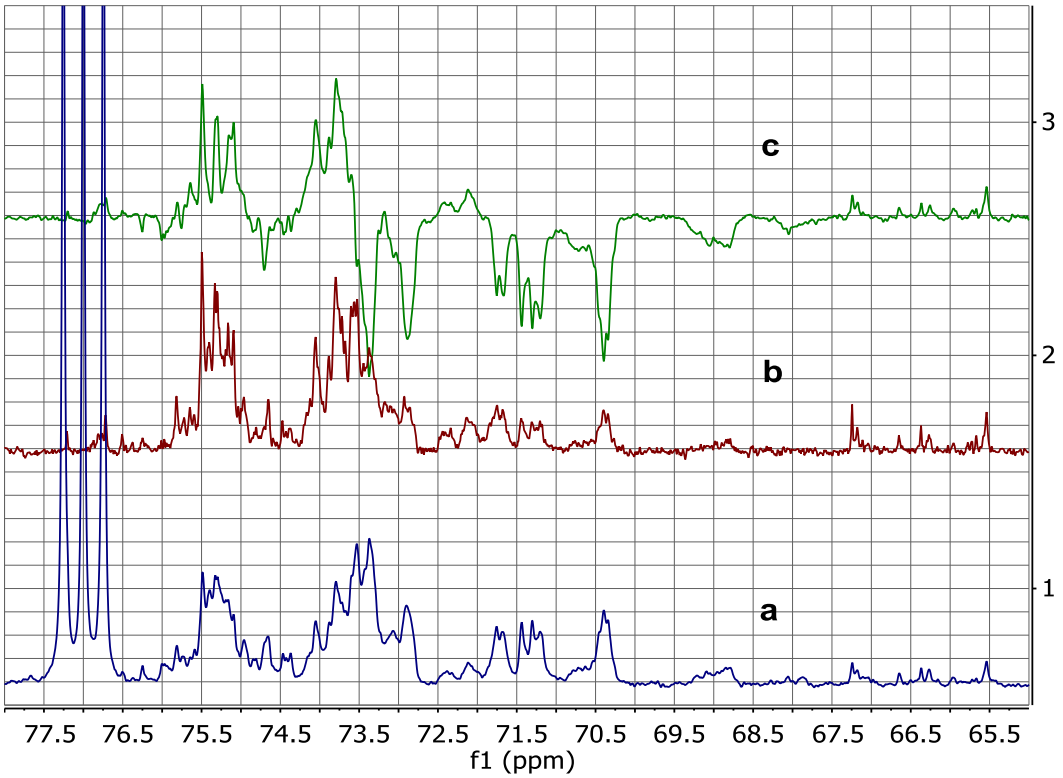


Figure S1. ^{13}C NMR spectra of **OECHD** in the region from 65 to 78 ppm: ordinary ^{13}C NMR (a), DEPT 90 (b), DEPT 135 (c).

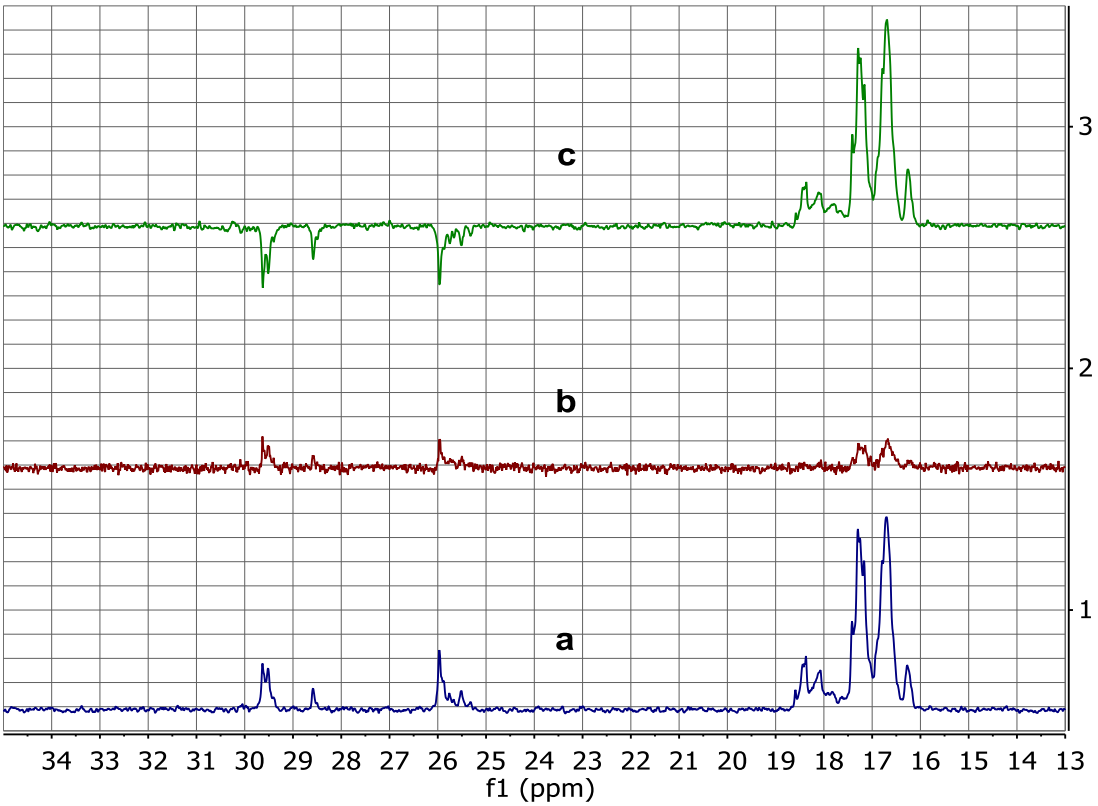


Figure S2. ^{13}C NMR spectra of **OECHD** in the region from 13 to 45 ppm: ordinary ^{13}C NMR (a), DEPT 90 (b), DEPT 135 (c).

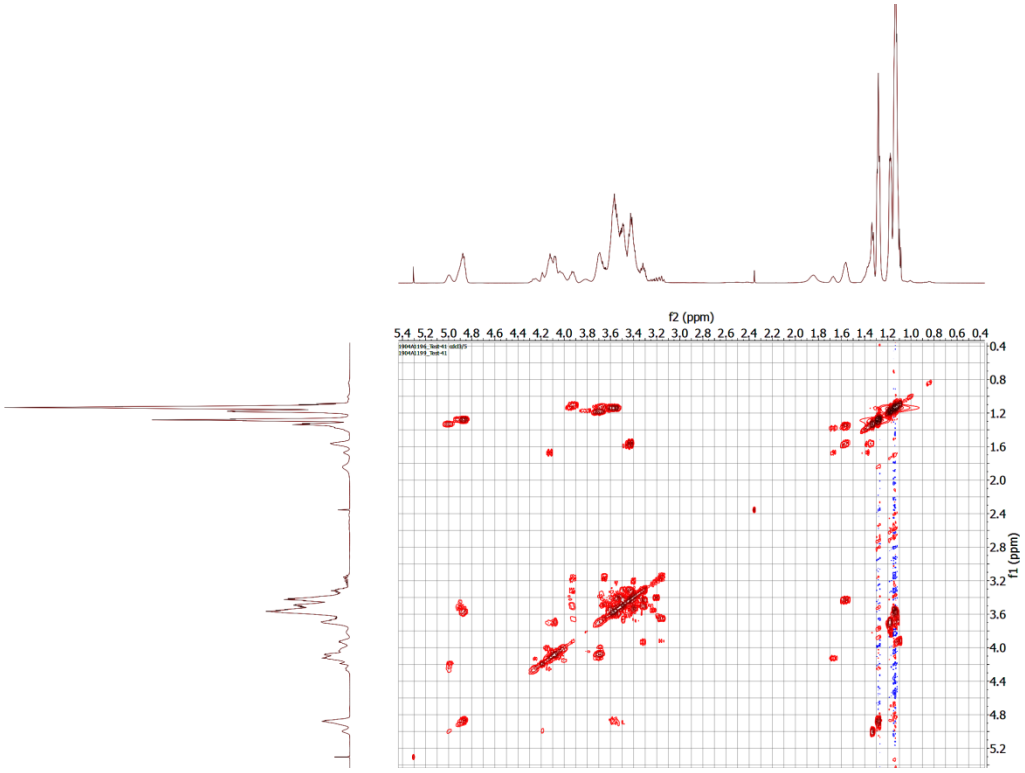


Figure S3. COSY spectrum of **OECHD** (the sample had CH_2Cl_2 and toluene as impurities).

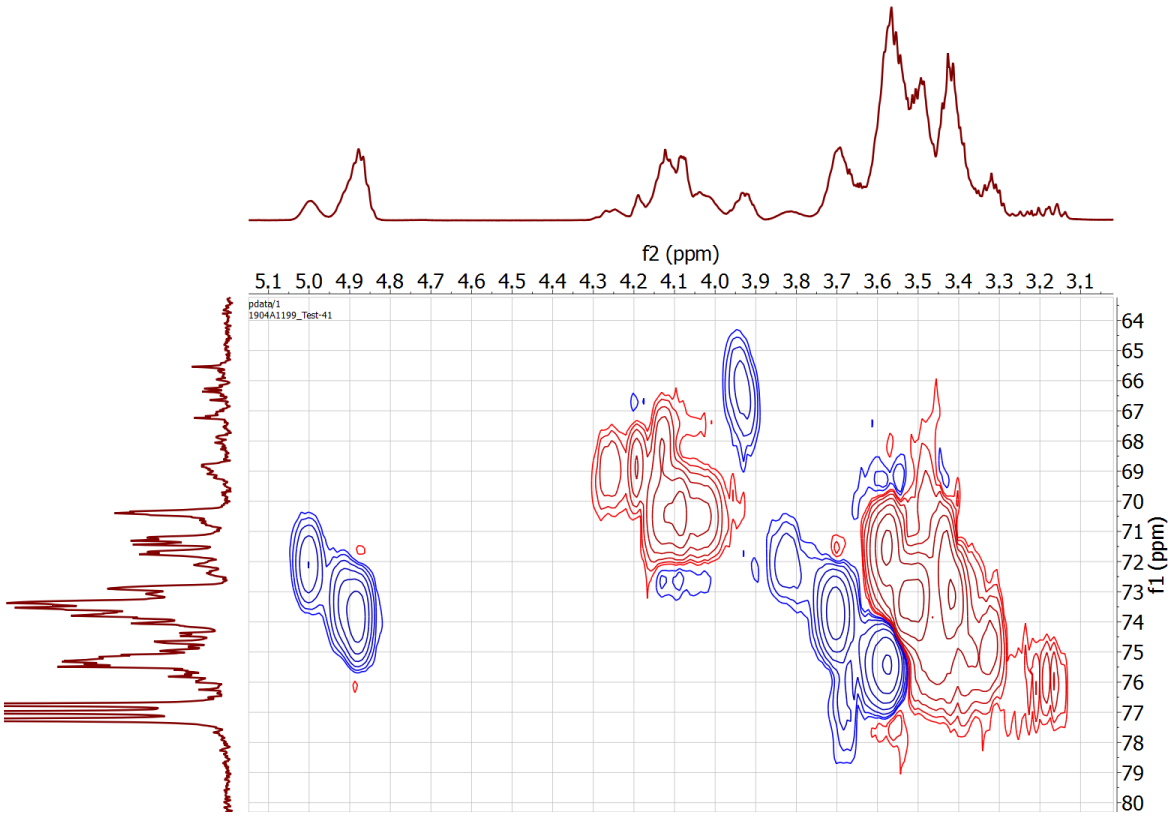


Figure S4. A fragment of an HSQC spectrum of **OECHD**.

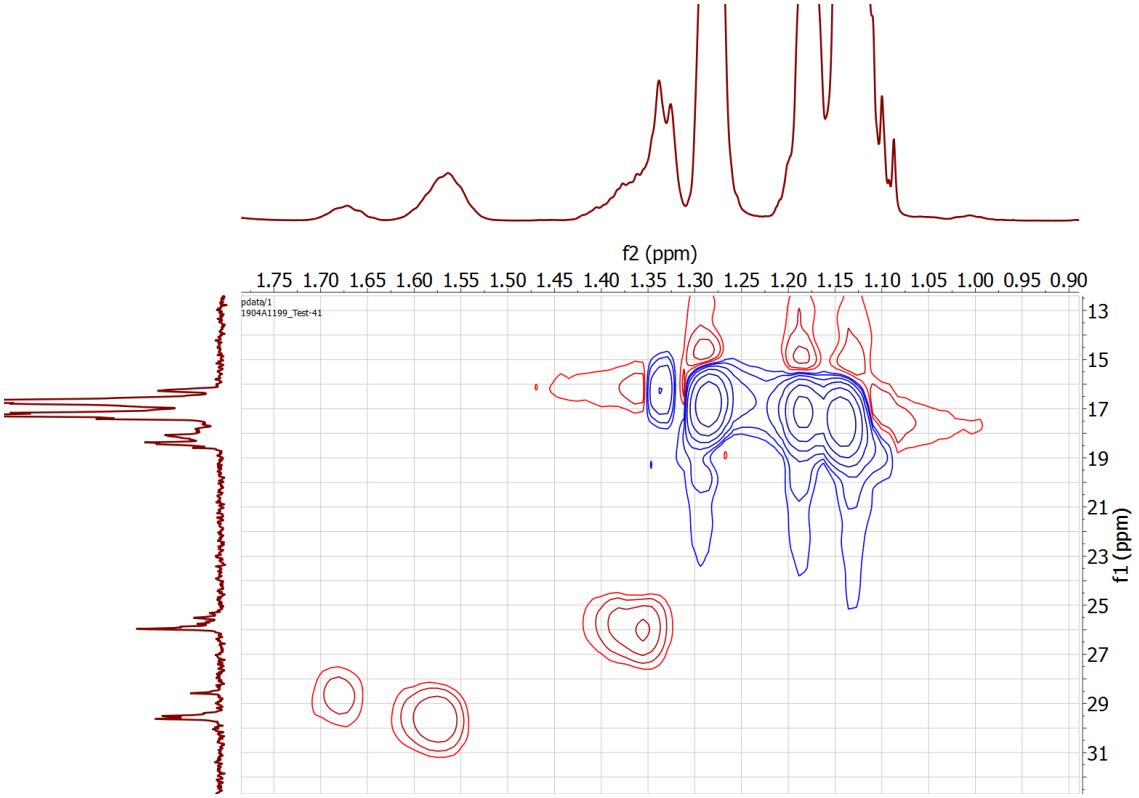


Figure S5. A fragment of an HSQC spectrum of **OECHD**.

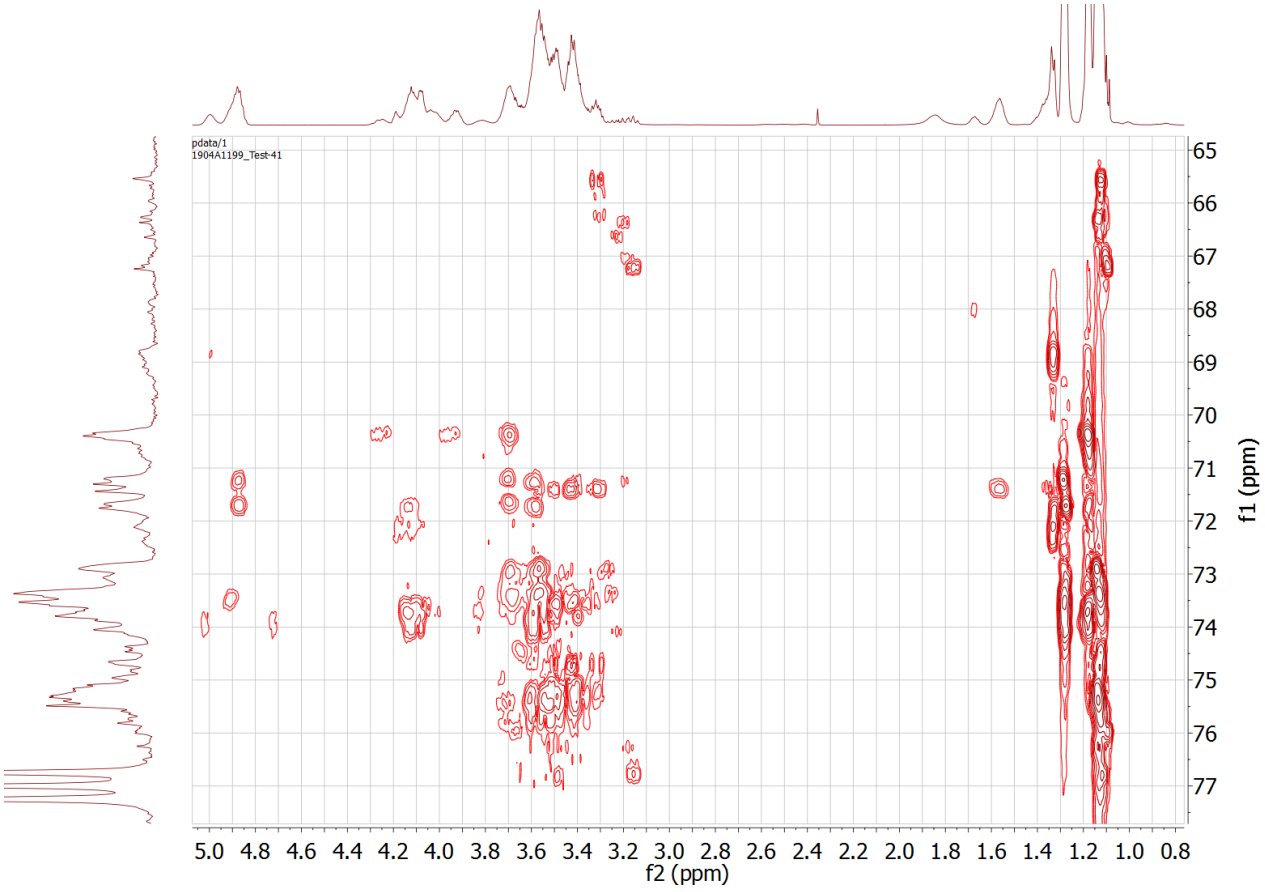


Figure S6. Selective HMBC spectrum of **OECHD**.

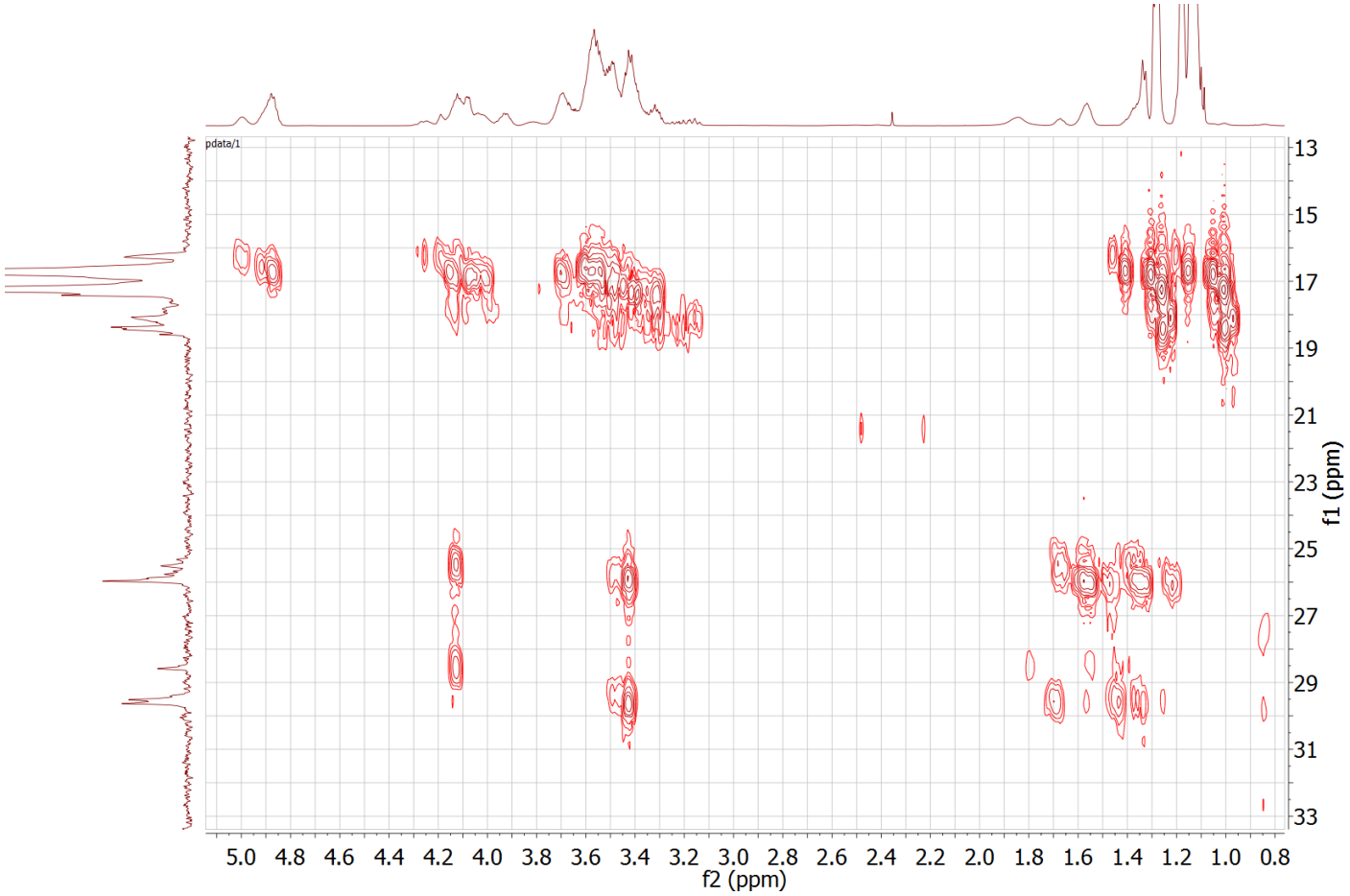


Figure S7. A fragment of an HMBC spectrum of **OECHD**.

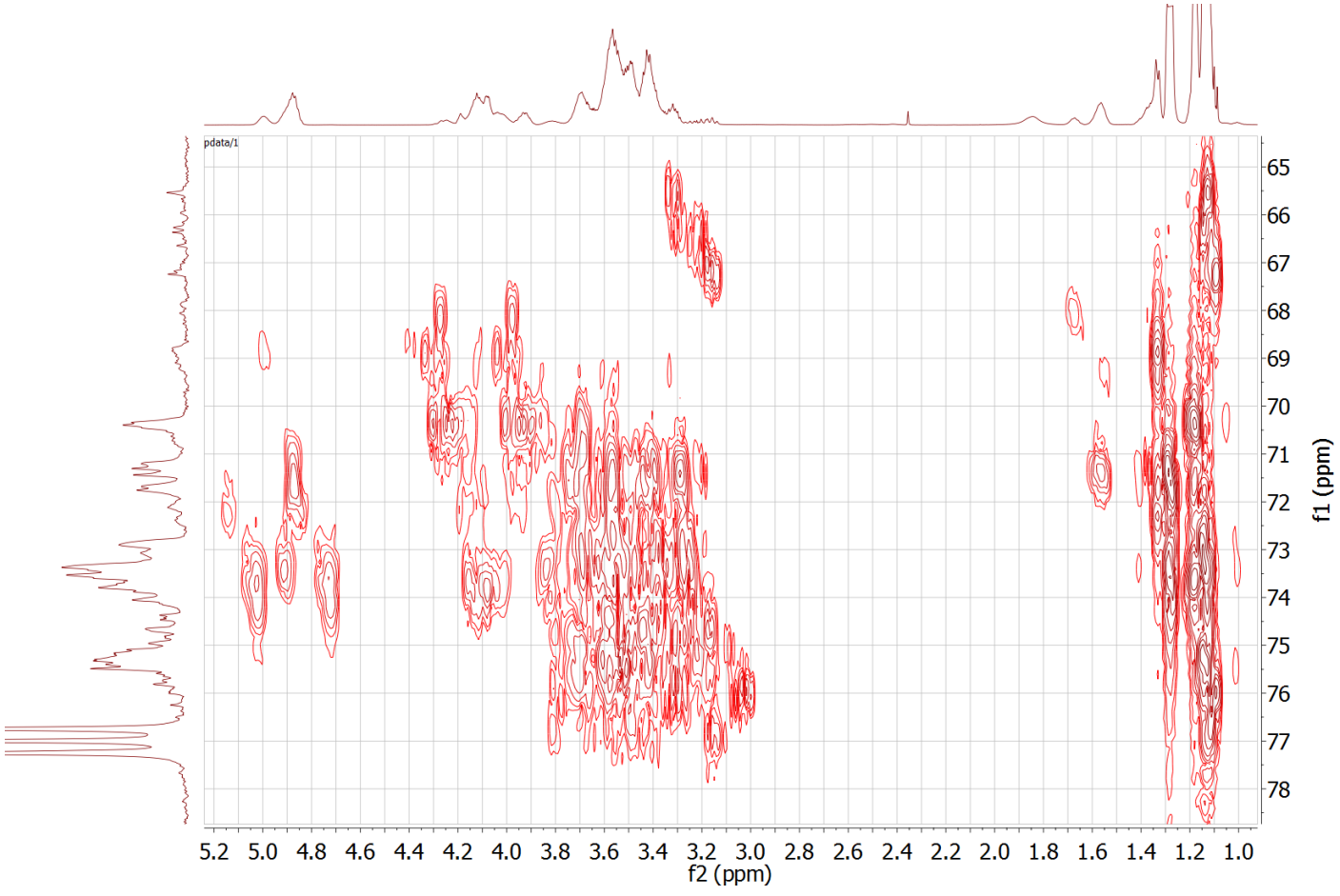
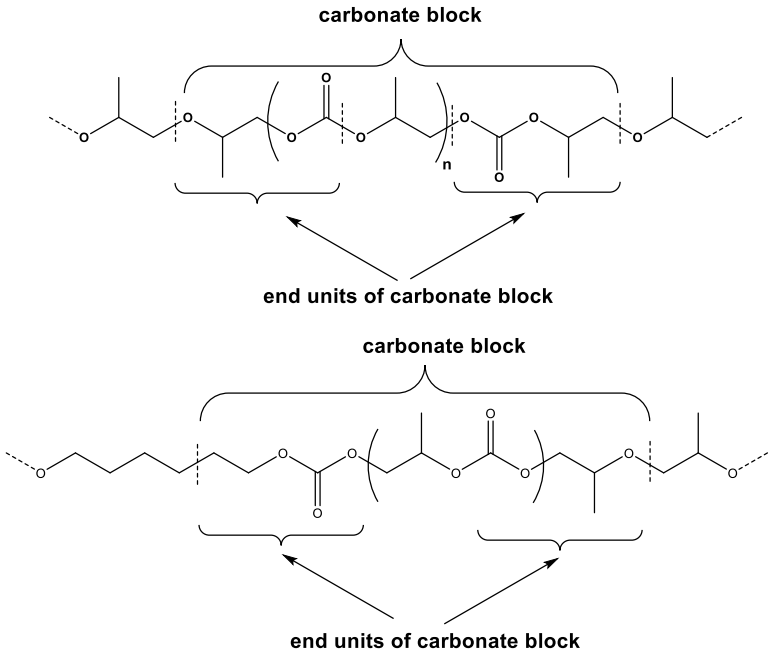


Figure S8. A fragment of an HMBC spectrum of **OECHD**.

Calculations of polymer composition



Number of $POCO_2$ units

$$n(POCO2) = H_a + \frac{H_b + \frac{H_{d,d'} + H_o}{2}}{2}$$

We divide (H_b+$H_{dd'}$/2+H_o/2) by 2 not to count the same carbonate group twice. In this way, one PO unit at one end of the carbonate block will be counted as a $POCO_2$ unit, and a PO unit at another end of the carbonate block will be counted as a polyether unit.

$$H_{d,d',o} = H_{c,c',o,d,d'} - H_{c,c'} = H_{c,c',o,d,d'} - 2H_a$$

$$n(POCO2) = H_a + \frac{H_b + \frac{H_{c,c',o,d,d'} - 2H_a}{2}}{2}$$

To calculate the fraction of POCO2 units, it is necessary to divide *n*(*POCO2*) by the total number of polymer chain units (PO and HD units):

$$n(total) = \frac{1}{3} \cdot \left(H_a + H_b + H_{c,c',o,d,d'} + H_s + H_{e,f,f',g,g',m} - H_q - H_p\right) + \frac{(H_q + H_p)/2}{2}$$

$$\nu(POCO2) = \frac{n(POCO2)}{n(total)}$$

Here we treat HD units as PO units. The expression (H_q+H_p)/2 gives us the number of HD units calculated using CH_2 integrals, as H_q+H_p is the total number of HD "ends" and every HD unit has two ends, therefore dividing by two gives us the total number of HD units. In our counting, one H corresponds to one polymer chain unit, therefore we divide (H_q+H_p)/2 by two to use only one H to count one HD unit.

It should be noted that even for the polymer obtained at CTA/cat = 0.94, nearly the same result is obtained if to treat the spectra in the described way but as having no HD units.

To calculate the mass fraction of PC in the product mixture (polymer plus PC), we used the integral for PC (H_{PC}):

$$w(PC) = \frac{H_{PC} \cdot 102.09}{\left(\begin{array}{c} \frac{1}{3} \cdot \left(H_a + H_b + H_{c,c',o,d,d'} + H_s + H_{e,f,f',g,g',m} - H_q - H_p\right) \cdot 58.08 + \\ H(POCO2) \cdot 44.01 + \frac{(H_q + H_p)/2}{2} \cdot 118.18 + H_{PC} \cdot 102.09 \end{array}\right)}$$