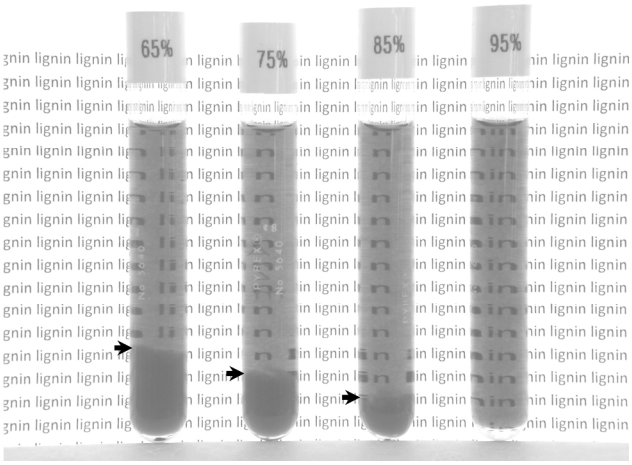

Figure S1: Solubility of 65%, 75%, 85% and 95% EOL (4 h reflux) in THF (50 mg/mL).

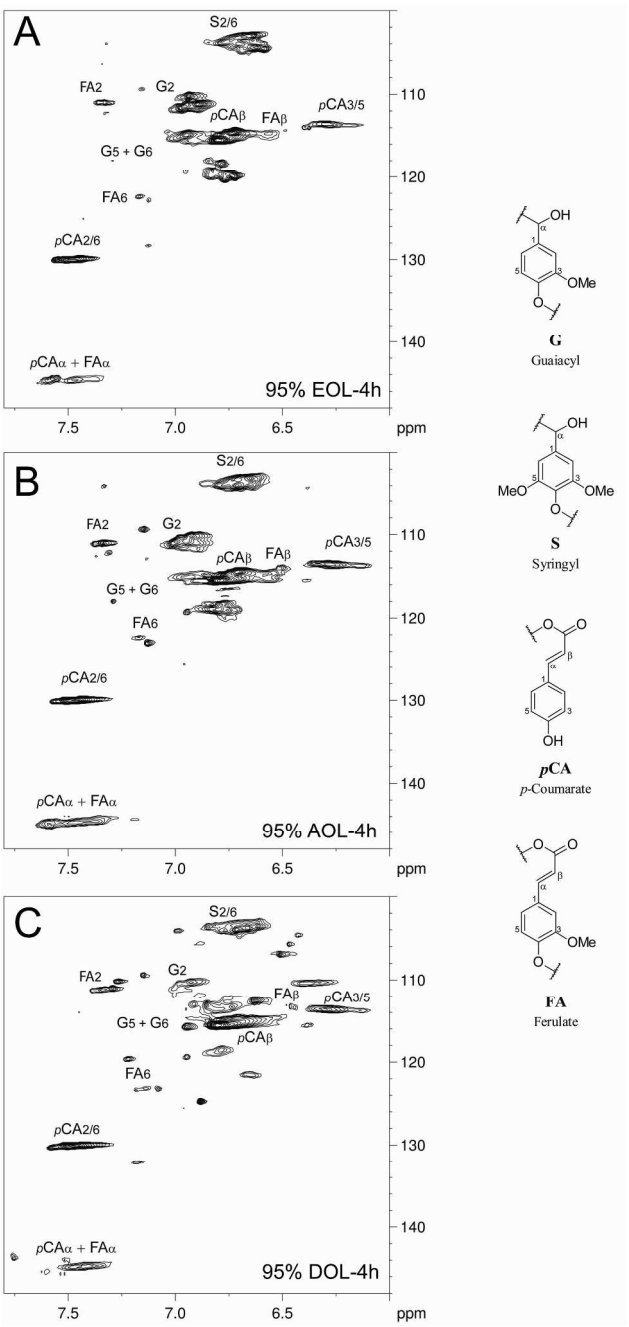

Figure S2: Partial short range ^{13}C-^{1}H (HSQC) correlation spectra (aromatic region only) of organosolv lignins **a** 95% EOL-4 h, **b** 95% AOL-4 h, **c** 95% DOL-4 h isolated from *Miscanthus giganteus*.

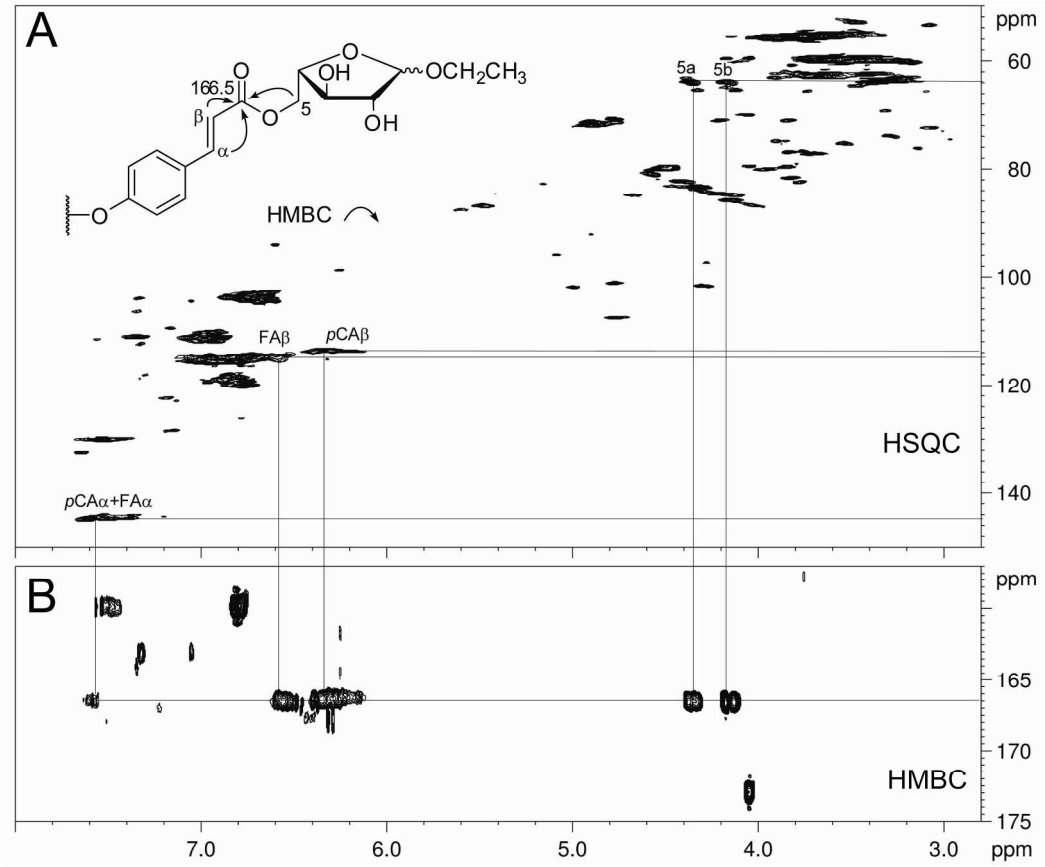

Figure S3: Partial **a** HSQC and **b** HMBC spectra of 95% EOL-4 h, establishing the long range correlations between signals 5 in Ara*f* and alpha and beta positions in *p*CA/FA to the carbonyl in the ester linkage.

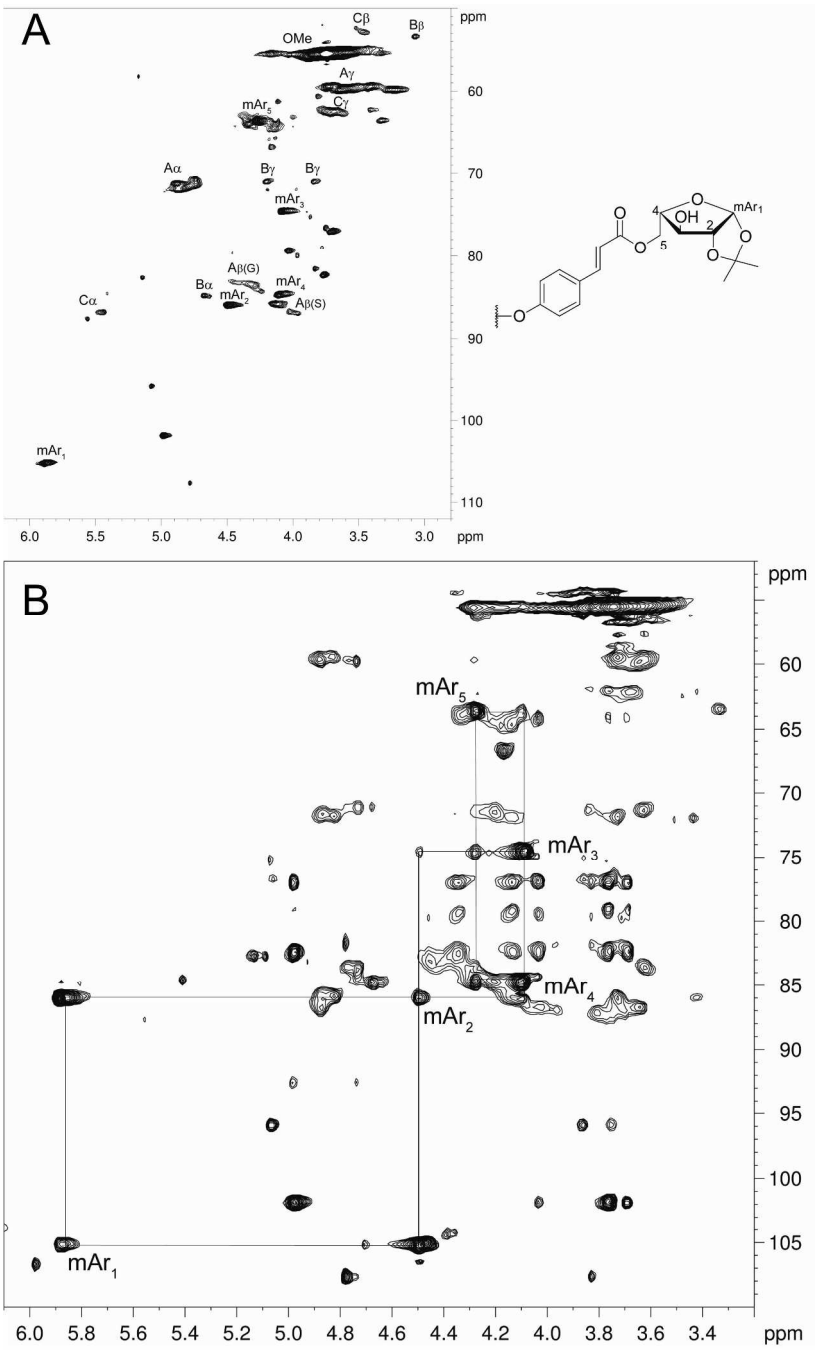

Figure S4: Partial (oxygenated aliphatic region) **a** HSQC and **b** HSQC-TOCSY spectra of 95% AOL-4 h showing *p*-coumaric acid is linked to C5 of arabinofuranose.

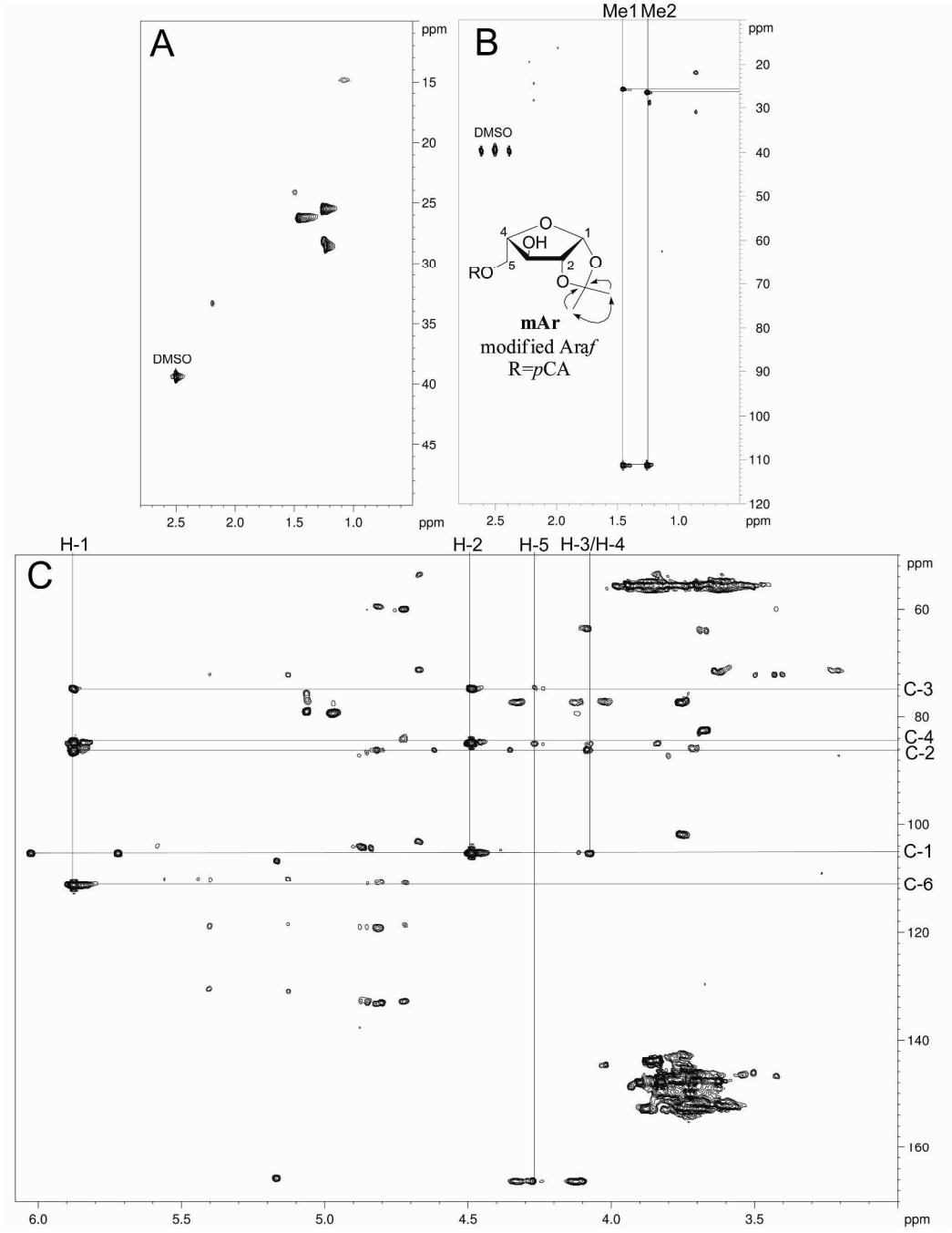

Fig. S5: Partial **a** HSQC (aliphatic region) and **b** HMBC (oxygenated aliphatic region) and **c** HMBC (oxygenated aliphatic region) spectra of 95% AOL-4 h showing modification of hydroxyl groups at C1 and C2 of arabinofuranose by acetone.

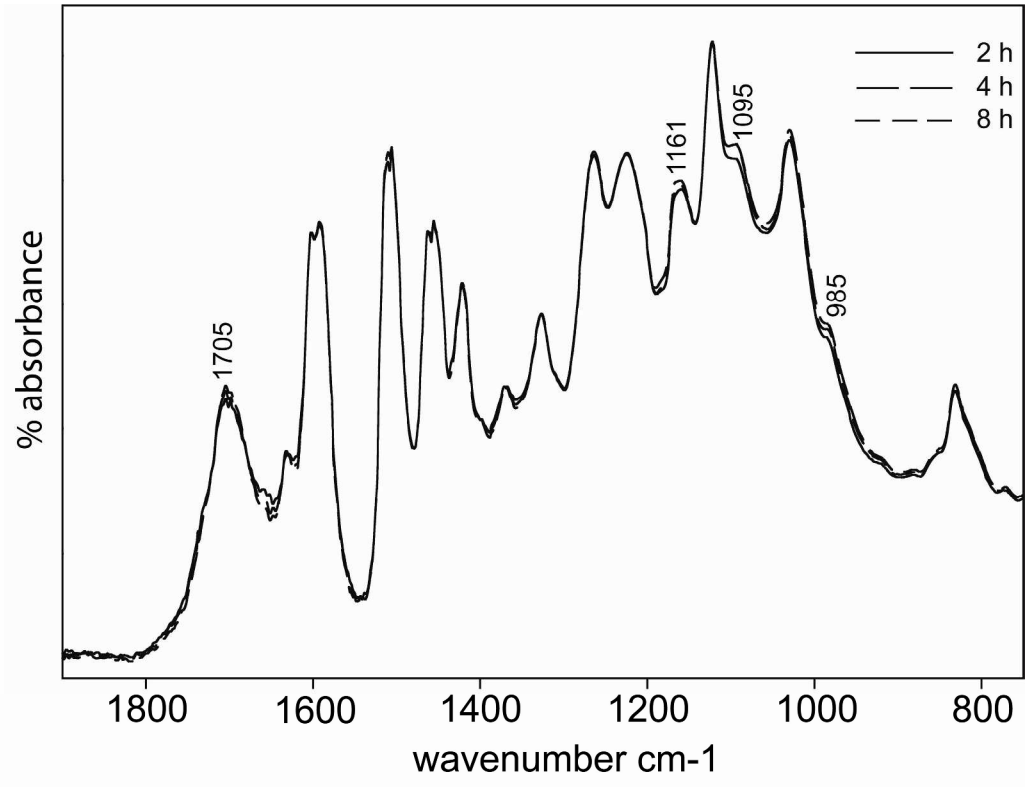

Figure S7: FTIR spectra of 95% EOL with 2, 4 and 8 h reflux time.

Table S1: Assignments of the main ^{13}C-^{1}H correlation signals in the HSQC spectra of organosolv lignins from *Miscanthus giganteus* (aromatic area).

Labels	δ_C/δ_H (ppm)	Assignment
$S_{2,6}$	103.6/6.62	$C_{2,6}$-$H_{2,6}$ in etherified syringyl units (S)
G_2	110.8/6.92	C_2-H_2 in guaiacyl units (G)
FA_2	110.9/7.32	C_2-H_2 in ferulate units (FA)
FA_β	113.7/6.30	C_β-H_β in ferulate units (FA)
pCA$_\beta$	114.4/6.47	C_β-H_β in *p*-coumarates units (pCA)
G_5/G_6	114.8/6.94 and 119.8/6.76	C_5-H_5 and C_6-H_6 in guaiacyl units (G)
pCA$_{3,5}$	115.1/6.75	$C_{3,5}$-$H_{3,5}$ in *p*-coumarates units (pCA)
FA_6	122.9/7.14	C_6-H_6 in ferulate units (FA)
pCA$_{2,6}$	130.0/7.55	$C_{2,6}$-$H_{2,6}$ in *p*-coumarates units (pCA)
pCA$_\alpha$	144.4/7.55	C_α-H_α in *p*-coumarates units (pCA)
FA_α	144.6/7.46	C_α-H_α in ferulate units (FA)