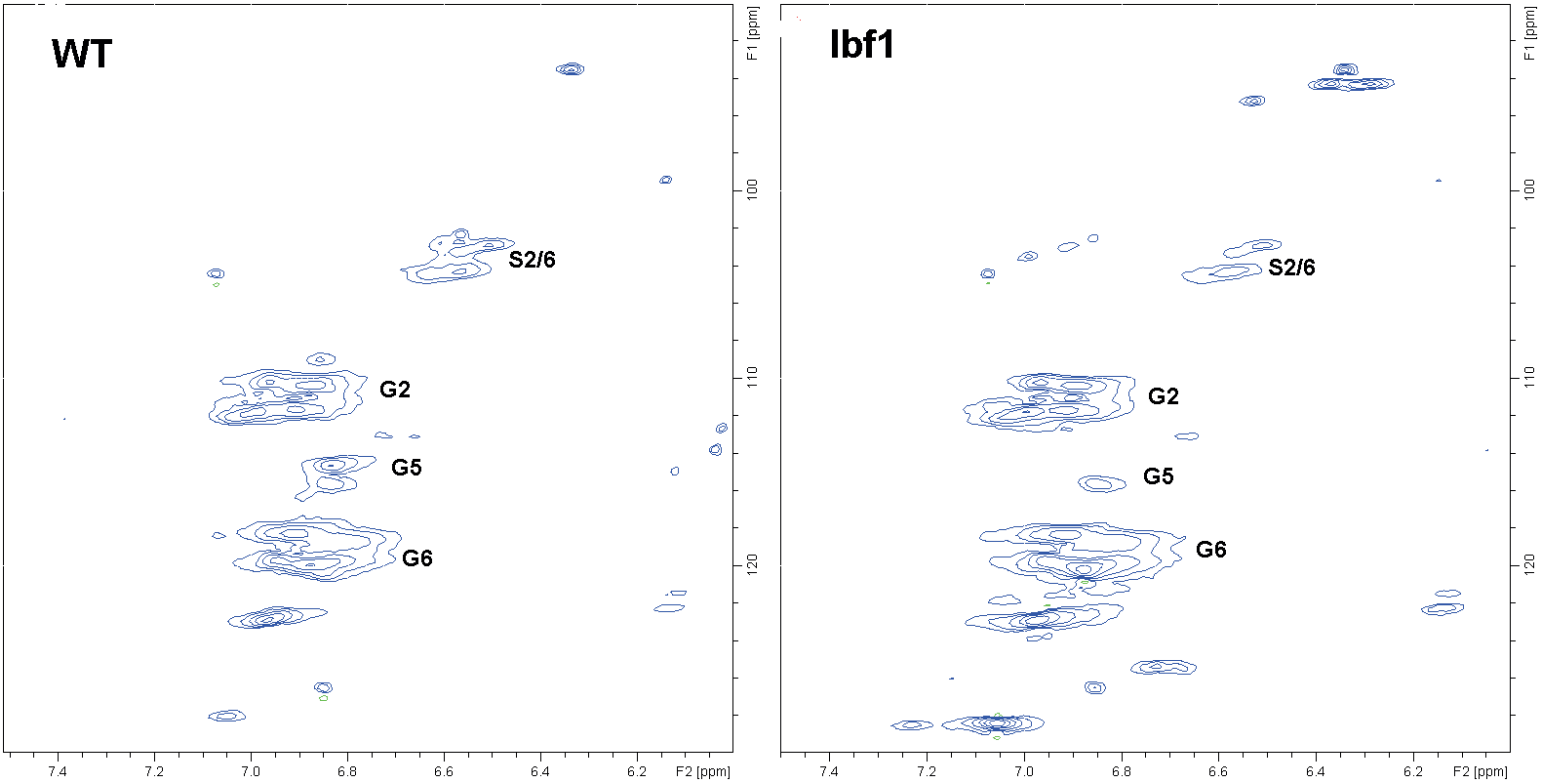
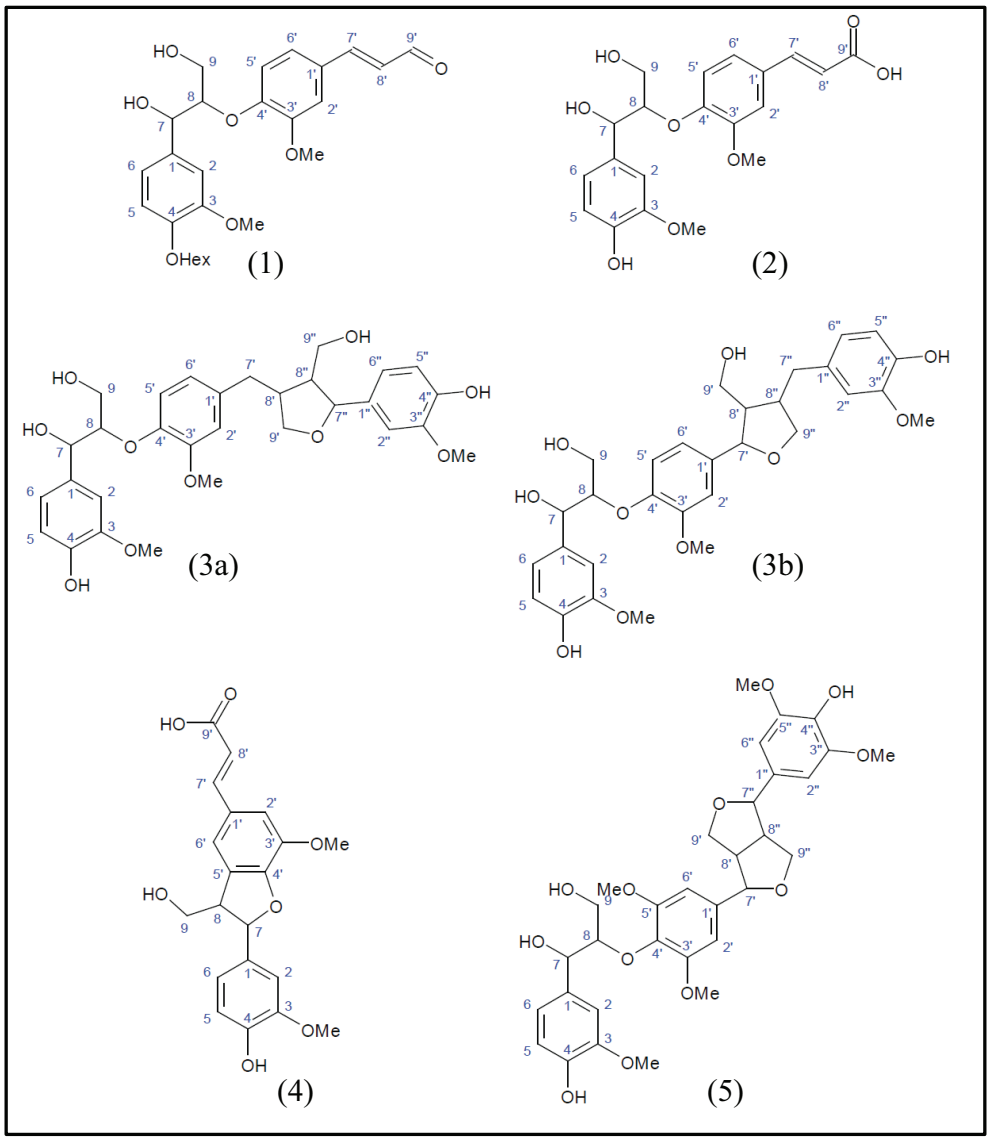


Supplemental Figure 1 : 2D NMR spectra revealing lignin monomer units from WT (left) and *lbf1* (right) inner tissues. Guaiacyl units (G2, G5, G6) and syringyl units (S2/6).



Supplemental Figure 2: Structures of oligolignols previously unidentified in flax

Compound 1. G(8-O-4)G' hex

At 12.88 min, a peak eluted with an m/z value of 595.20111 ($C_{28}H_{35}O_{14}^-$). Its MS^2 spectrum indicated that the compound appeared as acetate adduct (loss of 60 Da). A further loss of a hexose moiety (162 Da) yielded the peak at m/z 373. MS^3 fragmentation of this first product ion lead to second product ions at m/z 355 and 325 due to the loss of water (18 Da) and the combined loss of water and formaldehyde (48 Da), i.e. characteristic pathway I cleavages of a β-aryl ether linkage (AE I ions). The pathway II-typical cleavages yielded ions at m/z 195 (AE II A^-) and m/z 177 (AE II B^-), where the latter fragment dissociated further by methyl radical loss (15 Da), yielding a peak at m/z 162. This pathway II fragmentation pattern indicated that a G unit was connected via an 8–O–4-linkage to a coniferaldehyde unit. As this compound was mainly detected as the acetate adduct, the hexoside likely resides on a phenolic function of the aglycone. Two other isomers of this compound eluted at 13.30 min and 14.90 min.

Compound 2. G(e8-O-4)FA

An m/z 389.12219 ($C_{20}H_{21}O_8^-$) peak appeared at 16.70 min. The MS^2 spectrum showed product ions at m/z 371, 359 and 341 due to the loss of water (18 Da), formaldehyde (30 Da) and the combined loss of water and formaldehyde (48 Da), i.e. characteristic pathway I cleavages of a β-aryl ether linkage (AE I ions). The pathway II-typical cleavages yielded ions at m/z 195 (AE II A^-) and m/z 193 (AE II B^-). Further fragmentation of the AE II B^- yielded ions at m/z 178, 149 and 134. This was confirmed by MS^3 fragmentation of the m/z 193 fragment, indicating that a G unit was connected via an 8–O–4-linkage to a ferulic acid moiety. The MS^2 spectrum of this compound was dominated by the fragment at m/z 193 whereas in another isomer of this compound, eluting at 16.18 min, the MS^2 spectrum was dominated by the fragment at m/z 341. Therefore we conclude that the isomer eluting at 16.70 min is the erythro isomer and the isomer eluting at 16.18 min is the threo isomer.

Compounds 3. G(t8-O-4)lariciresinol : G(t8-O-4)G^{red}(8-8)G (3a) or G(t8-O-4)G(8-8)G^{red} (3b)

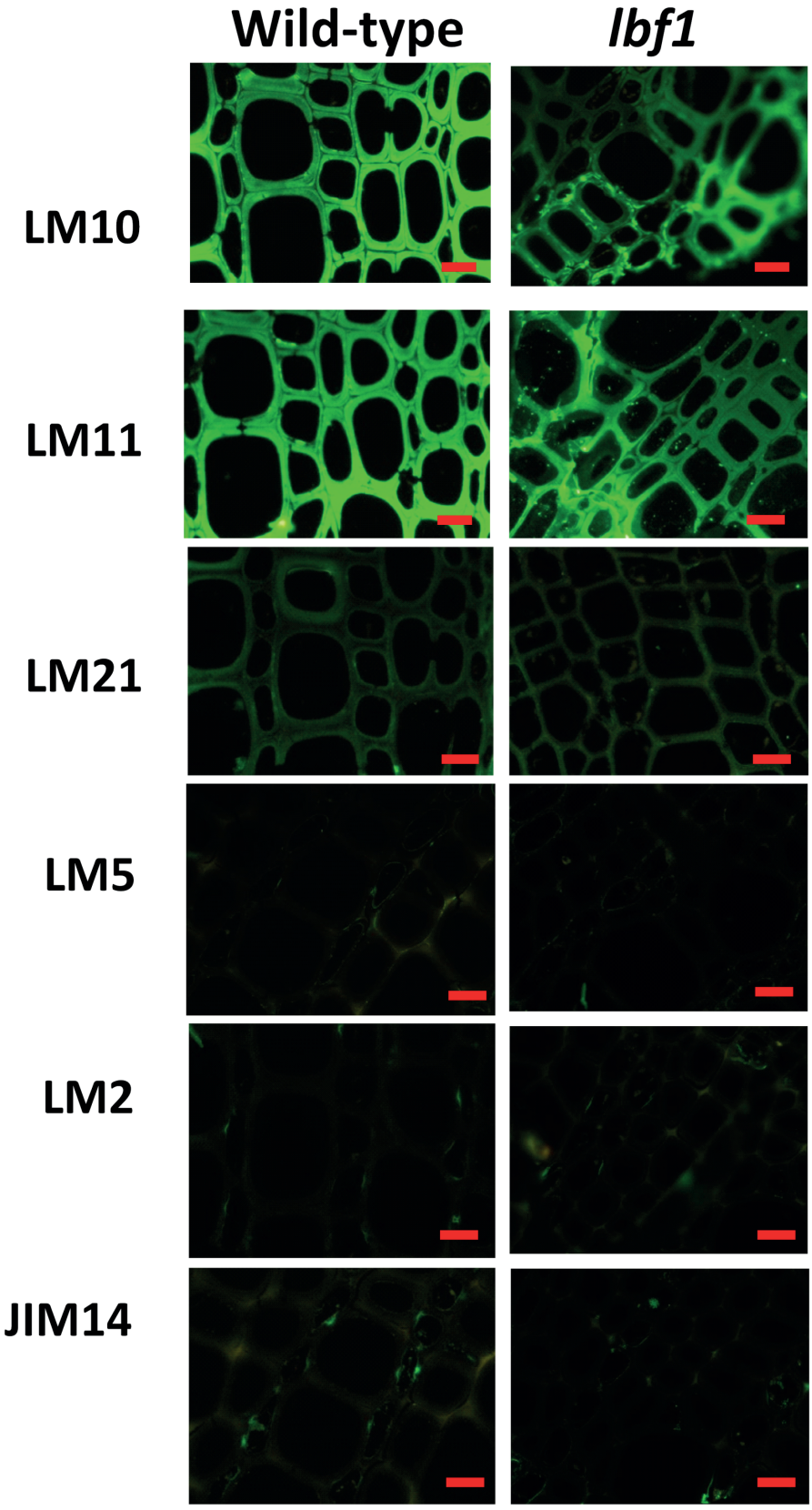
At 22.79 min, a peak eluted with an m/z value of 555.22101 ($C_{30}H_{35}O_{10}^-$). Its mass and MS^2 spectrum correspond to G(e8-O-4)G^{red}(8-8)G which was described previously in flax stem tissues (Huis et al., 2012). However, in the MS2 spectrum of this compound, the peak at m/z 507, resulting from combined loss of water and formaldehyde (48 Da) characteristic for the pathway I cleavage of a β-aryl ether linkage, strongly dominated. We therefore conclude that this compound is the threo isomer : G(t8-O-4)G^{red}(8-8)G or G (t8-O-4)G(8-8)G^{red}.

Compound 4. G(8-5)FA

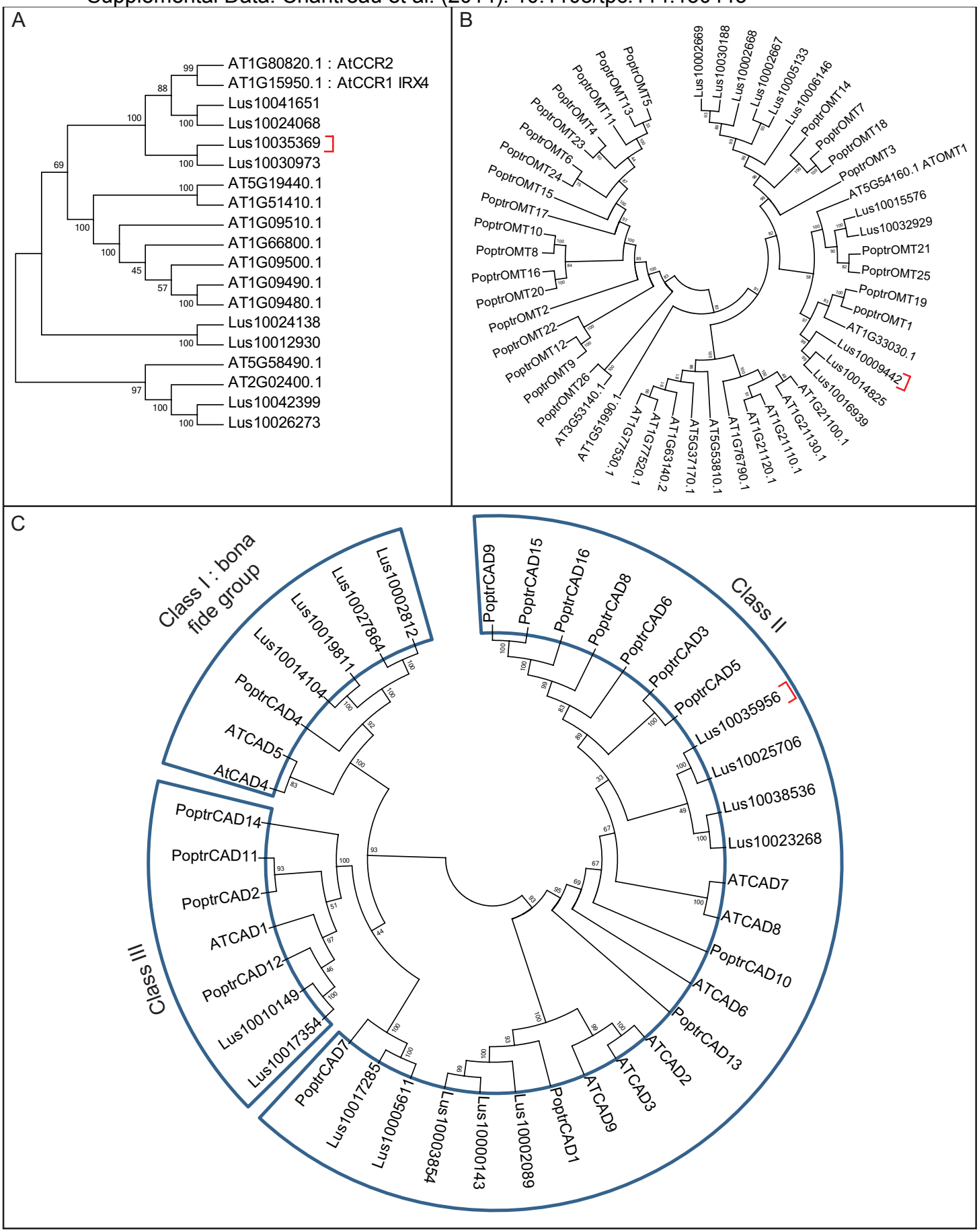
A peak with m/z 371.11249 ($C_{20}H_{19}O_7^-$) eluted at 23.65 min. Water (-18 Da) and formaldehyde (-30 Da) loss in the MS^2 spectrum explains the product ions at m/z 353 and 341 that are typical for a phenylcoumaran (Morreel et al., 2010a). The pathway II fragmentation leads to ions at m/z 191 (PC II, $[M\text{-}H\text{-}CO_2\text{-}A]^-$) and m/z 235 (PC II, B^-), typical for a coniferyl alcohol linked via a phenylcoumaran linkage to a ferulic acid moiety (Morreel et al., 2010a). The hexosylated form of this compound was described previously in flax stem tissues (Huis et al., 2012).

Compounds 5. G(t8-O-4)S(8-8)S and G(e8-O-4)S(8-8)S

At 27.55 min, a compound with m/z 613.22601 ($C_{32}H_{37}O_{12}$) eluted. The MS^2 product ions at m/z 595 and 565 were due to the loss of water (18 Da) and the combined loss of water and formaldehyde (48 Da), i.e. characteristic pathway I cleavages of a β-aryl ether linkage (AE I ions). The dominance of the fragment at m/z 565 in the MS^2 spectrum indicated that the linkage was in the threo form. The pathway II cleavages yielded ions at m/z 417 (AE II B^-) and m/z 387 (AE II $B^- - CH_2O$), corresponding to an S(8-8)S moiety, and an ion at m/z 195 (AE II A^-) indicating that a coniferyl alcohol was linked via the t8-O-4 linkage to the S(8-8)S moiety. This was further confirmed by the ions at m/z 403 and m/z 373, which corresponded to the ions AE II C^- and AE, II, $C^- - CH_2O$ respectively, formed by the characteristic fragmentation pathway of X(8-O-4)X-containing trilignols (Morreel et al., 2010b). Another isomer of this compound, which eluted at 28.86 min and in which the ion at m/z 417 dominated the MS2 spectrum was elucidated as the erythro version of this compound.



Supplemental Figure 3 : Fluorescent microscopy immunolocalisation of cell wall NCPs in inner stem tissues of WT (left) and *lbf1* (right) with LM10, LM11, LM21, LM5, LM2 and JIM14 antibodies. Bar : 10 µm.



Supplemental Figure 4. Phylogenetic trees of flax monolignol biosynthesis proteins.
A : Flax and Arabidopsis CCR proteins
B : Flax, Arabidopsis and poplar COMT proteins
C : Flax, Arabidopsis and poplar CAD proteins
Proteins annotated by a red bracket correspond to transcripts significantly more abundant in lbf1 outer tissues compared to WT.

Supp Table 1: Visual phenotyping classes for flax *lbf* mutants (Chantreau et al., 2013).

Category	**Sub-category**
Cotyledon:	Number
	Shape
Hypocotyl:	Size
Stem:	Size
	Diameter
	Colour
Leaf :	Shape
	Colour
Architecture:	Branching type
	Inter-nodes
Flowering/Fruit:	Inflorescence
	Petal colour
	Reproductive organs