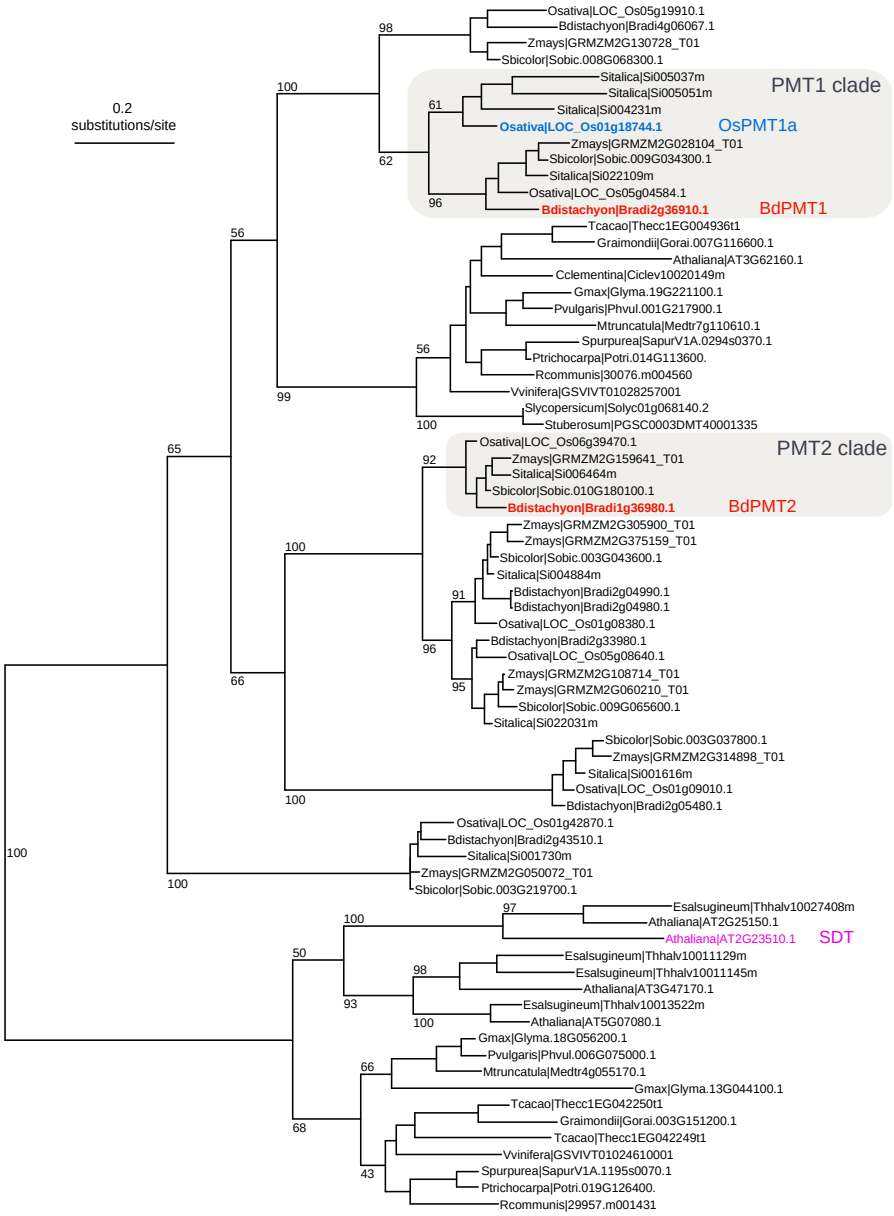
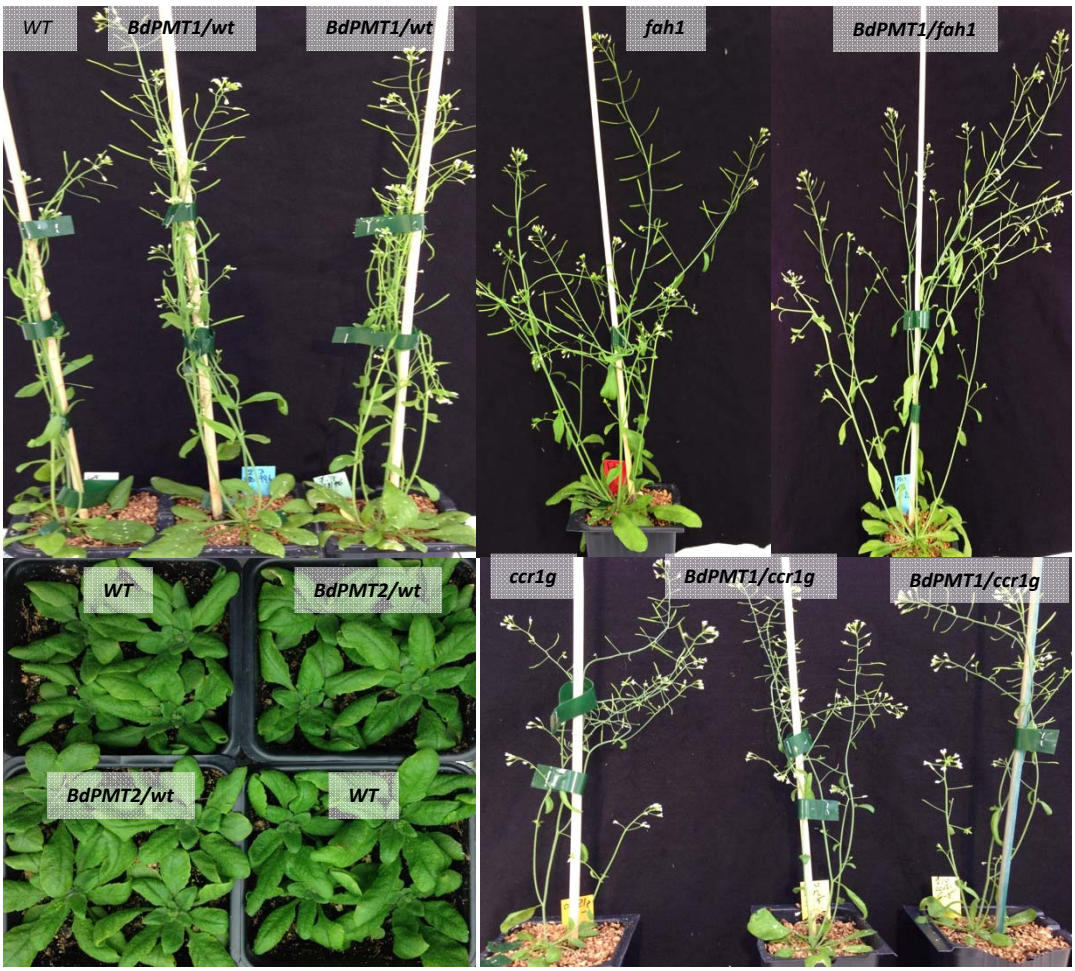
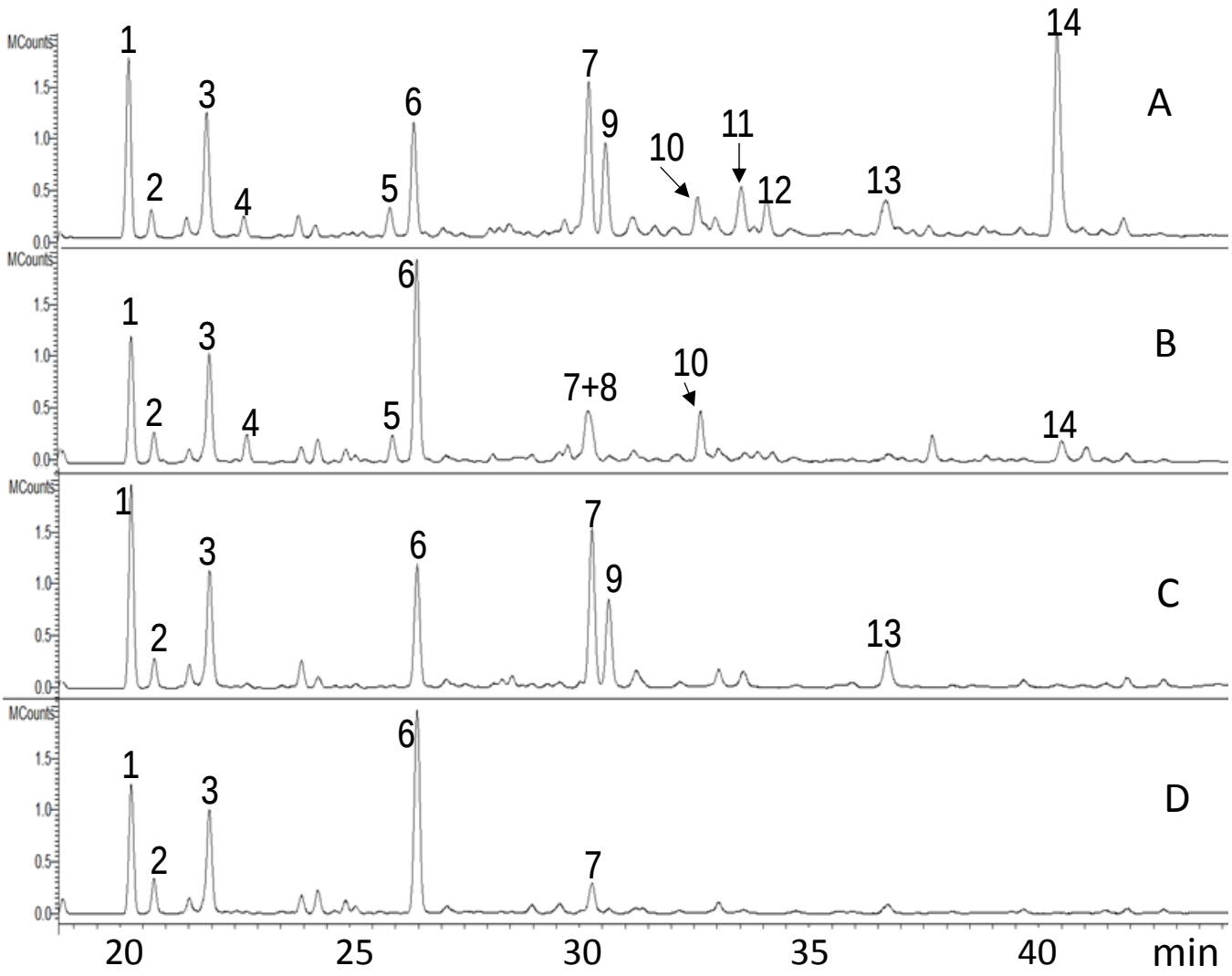


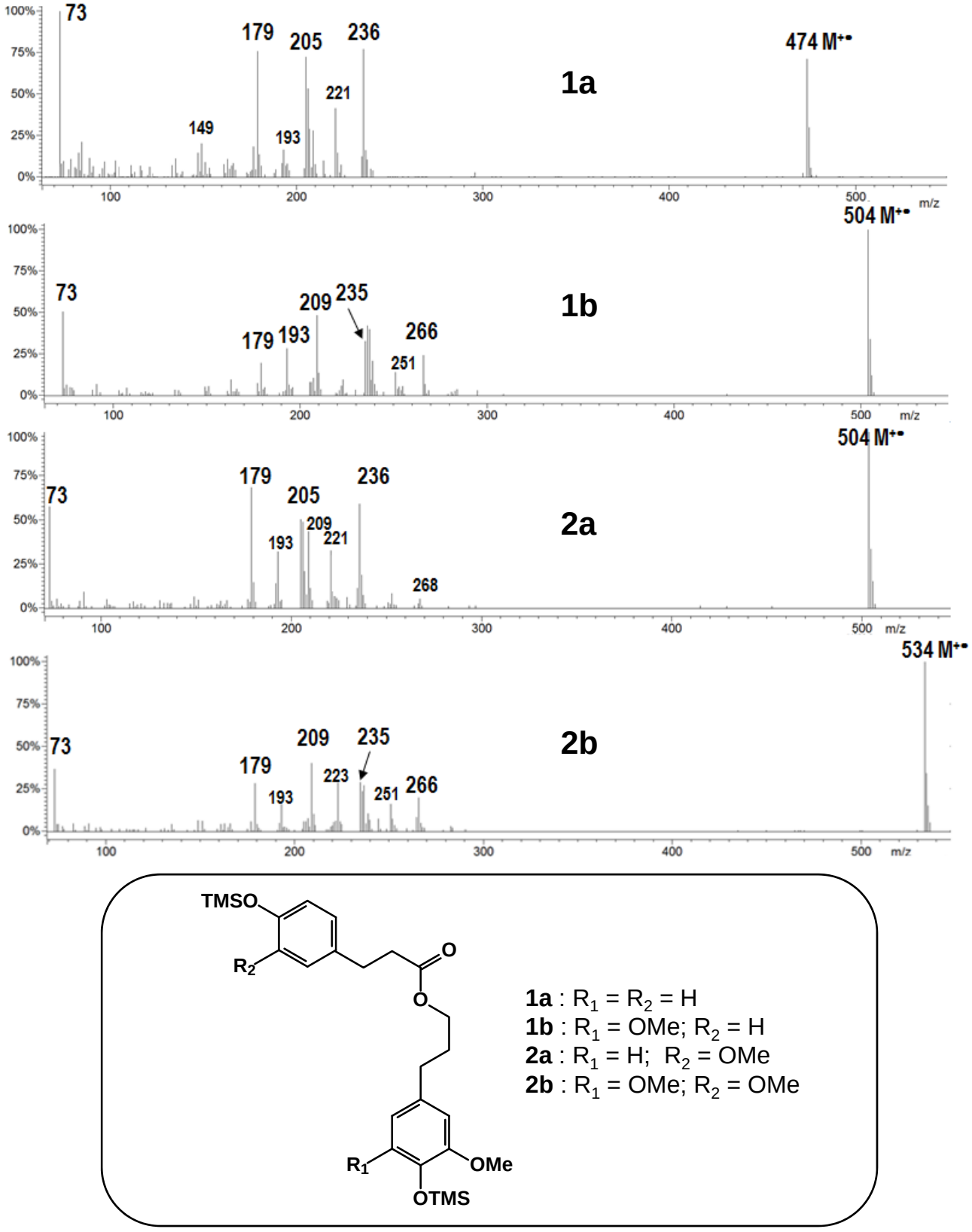
Supp. Fig. 1. Phylogeny of the PMT-related subset of the BAHD superfamily in Angiosperms. Protein maximum likelihood tree was built using 73 sequences derived from 18 species. Two distinct PMT clades containing proteins characterized either previously or in this study can be defined. Bootstraps values (%) are indicated on main branches. Proteins alignment, ambiguous sites masking and subsequent phylogeny reconstruction were performed with the MUSCLE v3.8, Gblocks and PhyML3.0 softwares, respectively.



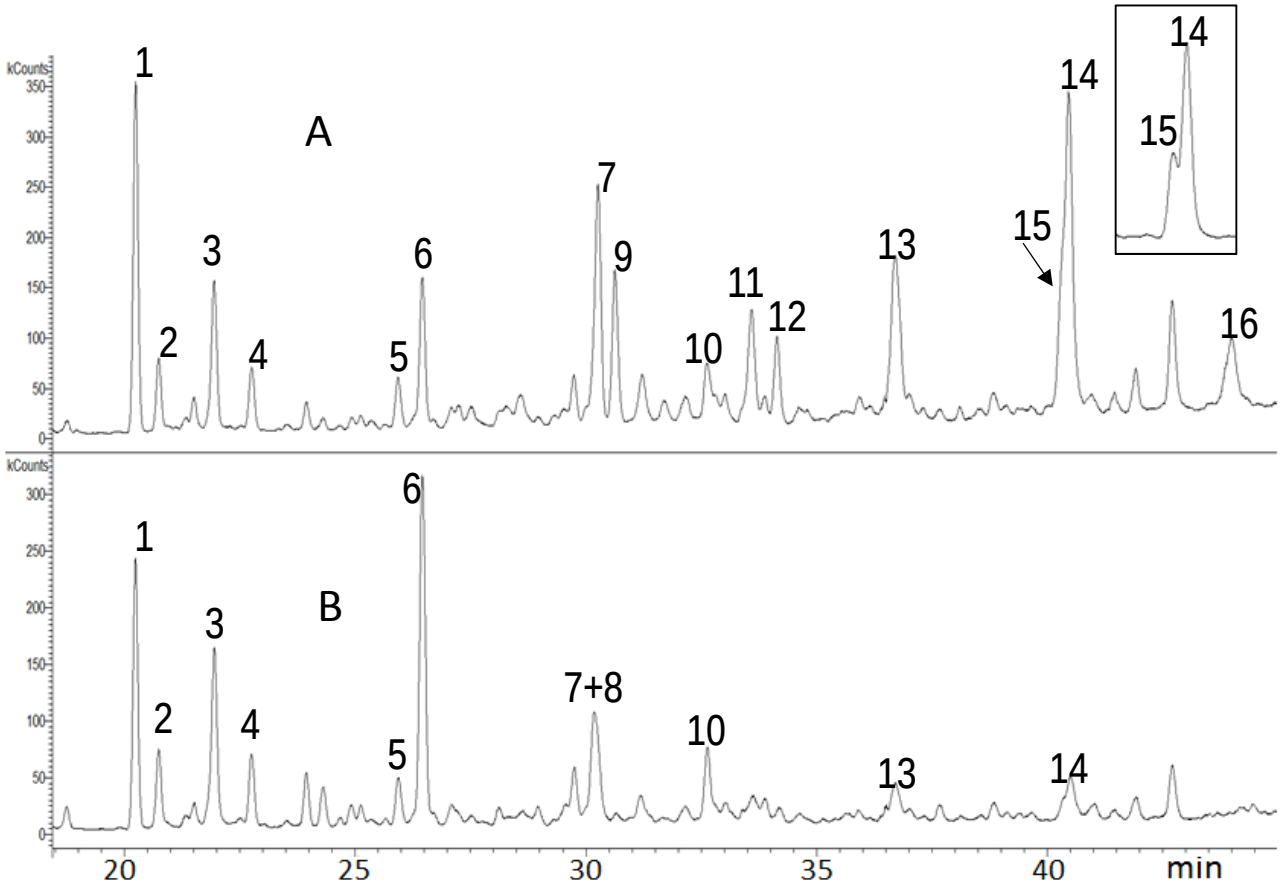
Supp. Fig. 2. Representative pictures of Arabidopsis plants expressing the *BdPMT1* or *BdPMT2* gene under the control of the *AtC4H* promoter and in the WT, *fah1* or *ccr1g* background. Relative to the corresponding control, there is no visible impact of the PMT expression.



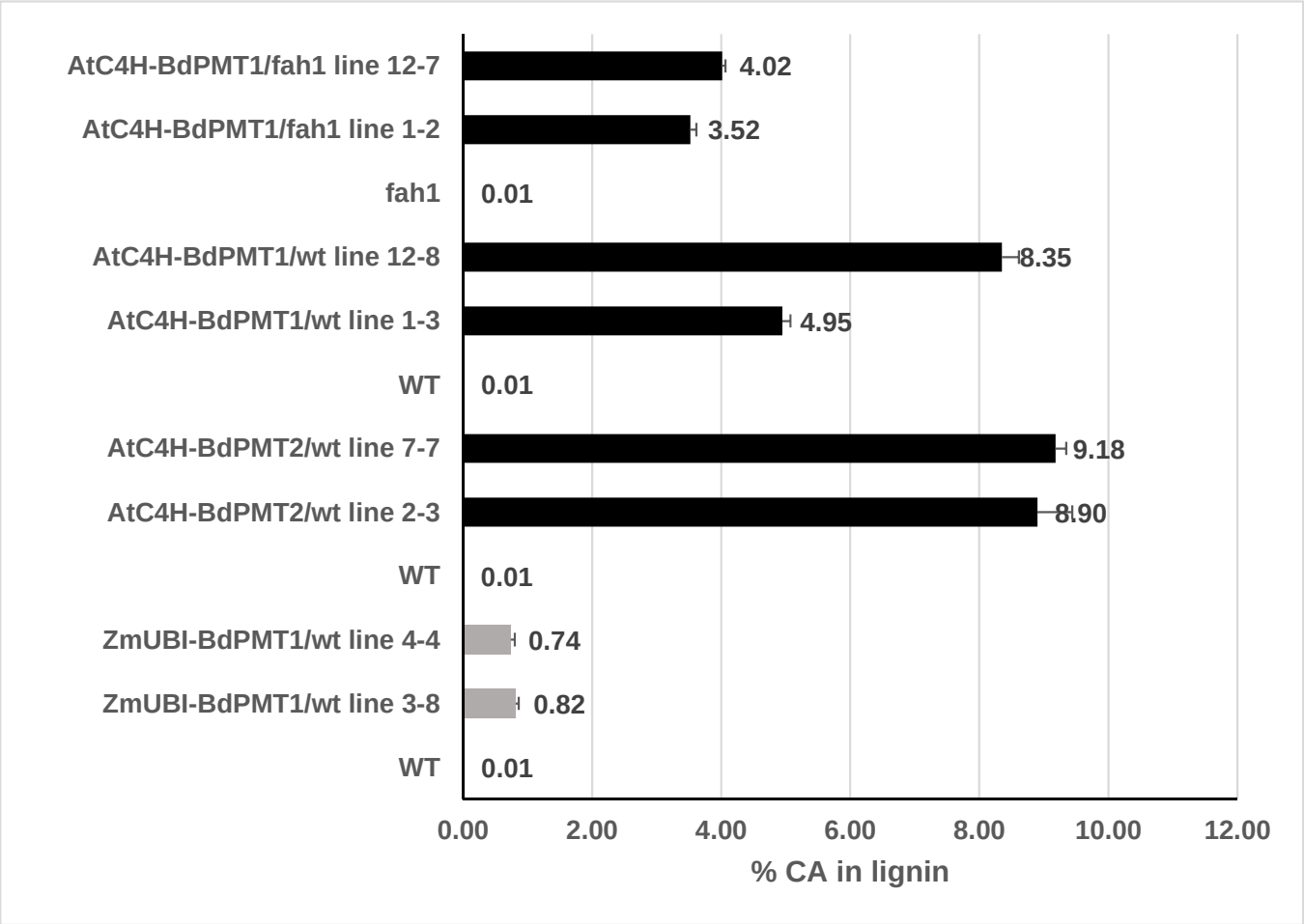
Supp Fig. 3. Partial GC-MS traces showing the separation of the main dimers (analyzed as their TMS derivatives) obtained by thioacidolysis and Raney nickel desulphuration of dioxane lignin fractions purified from Arabidopsis mature stems of *BdPMT1/wt* (A and B) and of *Bd910/fah1* (C and D) lines. Peak identification is given in Supplemental Table 2. Traces A and C are obtained from 1-hour long thioacidolysis. Traces B and D are obtained with the standard 4 hour-long thioacidolysis. Peaks 13 and 14, which respectively correspond to dihydroconiferyl and sinapyl alcohol acylated by *p*-dihydrocoumaric acid (compounds **1a** and **1b** Fig. 1), are reduced to trace components after 4-hour long thioacidolysis.



Supp Fig. 4. Mass spectra (electronic impact , 70 eV) of the 4 compounds diagnostic for the incorporation of *p*-coumaric acid (**1a** and **1b**) or ferulic acid (**2a** and **2b**) into Arabidopsis lignins. The compounds display very similar mass spectra with prominent molecular ions together with allylsyringol (at 266 m/z) or allylguaiacol (at 236 m/z) ions respectively diagnostic for S or G units. Compounds **2a** and **2b** are observed only in *BdPMT1/ccr1g* lines.



Supp Fig. 5. Partial GC-MS traces showing the separation of the main dimers (analyzed as their TMS derivatives) obtained by thioacidolysis and Raney nickel desulphuration of a dioxane lignin fraction purified from Arabidopsis mature stems of *BdPMT1/ccr1g* line with A] 1 hour-long thioacidolysis and B] 4 hour-long thioacidolysis. Peak identification is given in Supplemental Table 2. Peaks 13 and 14 correspond to dihydroconiferyl and sinapyl alcohol acylated by *p*-dihydrocoumaric acid, respectively. Peaks 15 and 16 correspond to dihydroconiferyl and sinapyl alcohol acylated by dihydroferulic acid, respectively. The inset in part A shows a better separation of peaks 14 and 15 obtained with different chromatographic conditions. These acylated compounds disappear almost entirely after 4-hour long thioacidolysis.



Supp Fig. 6. Weight percentage of *p*-coumaric acid CA ester-linked to Arabidopsis lignins in the mature stems of control lines (WT or *fah1*) or transgenic lines expressing the *BdPMT1* or *BdPMT2* gene under the control of the *AtC4H* promoter (black bars) or of the *ZmUbi* promoter (grey bars). These percentages are calculated values (% of Klason lignin) obtained with the assumption that all CA units are ester-linked to lignins.

Supplemental Table S1. Amount of *p*-coumaric acid (CA) released by mild alkaline hydrolysis of extractive-free mature stems from Col0-derived Arabidopsis WT and transgenic lines expressing *BdPMT1* under the *ZmUbi* promoter control.

Genotype	CA mg/g
WT	0.02 (0.004)
ZmUbi-BdPMT1 line 3-2	0.77 (0.01)
ZmUbi-BdPMT1 line 4-1	0.89 (0.02)
ZmUbi-BdPMT1 line 1-6	1.05 (0.01)
ZmUbi-BdPMT1 line 4-4	1.31 (0.12)
ZmUbi-BdPMT1 line 1-12	1.42 (0.09)
ZmUbi-BdPMT1 line 3-8	1.61 (0.09)

The data represent mean values (and SD) from 3 different plant pools (about 20 plants per pool) per genotype.

Supplemental Table S2. Abbreviated mass spectra (electronic impact, 70 eV) of the main compounds corresponding to peaks quoted in Supp. Fig. 3 and in Supp. Fig. 5. These lignin-derived dimers are analysed as TMS derivatives.

Peak number	Dimer type[a]	m/z (relative intensity)
1	GG Biphenyl 5-5’	474 (100), 459 (50), 445 (40), 415 (15), 385 (10), 357 (8), 343 (10), 147 (5), 73 (100)
2	GG Biphenyl ether 4-O-5’	402 (100), 387 (40), 373 (40), 372 (50), 357 (25), 343 (25), 221 (15), 209 (10), 179 (5), 157 (5), 73 (70)
3	GG Diarylpropane β-1’	418 (10), 403 (3), 209 (100), 193 (5), 179 (25), 149 (5), 73 (25)
4	SG Biphenyl ether 4-O-5’	432 (100), 417 (40), 403 (25), 387 (8), 373 (8), 239 (5), 172 (8), 73 (50)
5	SG Diarylpropane β-1’	448 (25), 433 (5), 239 (100), 223 (10), 209 (50), 193 (5), 179 (15), 149 (5), 73 (30)
6	GG β-5’ without CH_2OH at Cγ	460 (25), 445 (5), 251 (20), 236 (7), 221 (5), 209 (100), 207 (20), 193 (7), 179 (5), 73 (40)
7	GG β-5’ with CH_2OH at Cγ	562 (25), 472 (15), 457 (5), 352 (10), 322 (5), 263 (15), 209 (40), 191 (50), 179 (15), 103 (5), 73 (100)
8	SG β-5’ without CH_2OH at Cγ	490 (30), 251 (10), 239 (100), 236 (5), 209 (25), 207 (5), 73 (30)
9	GG β-O-4’[b]	490 (1), 324 (5), 294 (4), 235 (15), 223 (5), 209 (100), 193 (5), 179 (20), 149 (8),73 (40)
10	SS β- β’ from syringaresinol	532 (70), 517 (5), 501 (15), 445 (10), 384 (8), 306 (60), 291 (8), 275 (15), 239 (8), 187 (20), 73 (100)
11	SG β-5’ with CH_2OH at Cγ	592 (30), 502 (5), 471 (5), 352 (5), 263 (10), 239 (50), 209 (10), 191 (60), 179 (5), 103 (5), 73 (100)
12	SG β-O-4’ [b]	520 (8), 354 (10), 324 (4), 265 (20), 239 (100), 223 (7), 209 (15), 179 (12),73 (45)
13	Compound **1a**	474 (75), 236 (75), 221 (45), 209 (25), 207 (25), 206 (55), 205 (70), 193 (22), 179 (80), 149 (20), 73 (100)
14	Compound **1b**	504 (100), 266 (25), 251 (15), 239 (25), 237 (43), 236 (45), 235 (35), 223 (10), 209 (45), 193 (25), 179 (20), 73 (50)
15	Compound **2a**	504 (100), 268 (5), 253 (7), 236 (55), 221 (30), 209 (45), 206 (50), 205 (55), 193 (31), 179 (70), 73 (60)
16	Compound **2b**	534 (100), 266 (25), 251 (20), 239 (10), 237 (23), 236 (20), 235 (25), 223 (25), 209 (40), 193 (20), 179 (30), 73 (40)

[a] G : guaiacyl unit; S : syringyl uit; Compounds **1a** and **1b** are dihydroconiferyl and dihydrosinapyl alcohols acylated by *p*-dihydrocoumaric acid (Fig. 1); Compounds **2a** and **2b** are dihydroconiferyl and dihydrosinapyl alcohols acylated by dihydroferulic acid (Fig. 1).

[b] Peaks 9 and 12 diagnostic for residual β-O-4’ dimers are observed with1 hour-long thioacidolysis.

Supplemental Table S3. Analysis of Arabidopsis extract-free mature stems from Col0-derived WT or transgenic lines expressing the *Brachypodium BPMT1* gene under the control of the constitutive *ZmUbi* promoter : weight percentage of Klason lignin (KL) and total yield of (H+G+S) thioacidolysis monomers expressed on a KL basis.

Genotype	KL %	ABL %	(H+G+S) µmol/g KL
WT	19.00 (0.68)	14.65 (0.69)	1125 (18)
BdPMT1/wt line3-8	19.66 (0.31)	16.29 (0.26)	1025 (47)
BdPMT1/wt line4-4	19.16 (0.31)	15.03 (0.35)	994 (23)

The data represent mean values (and SD) from 3 different plant pools per genotype.