Electronic Supplementary Materials (ESI)

Methylation-triggered fractionation of lignocellulosic biomass to afford three functional polymers via click chemistry

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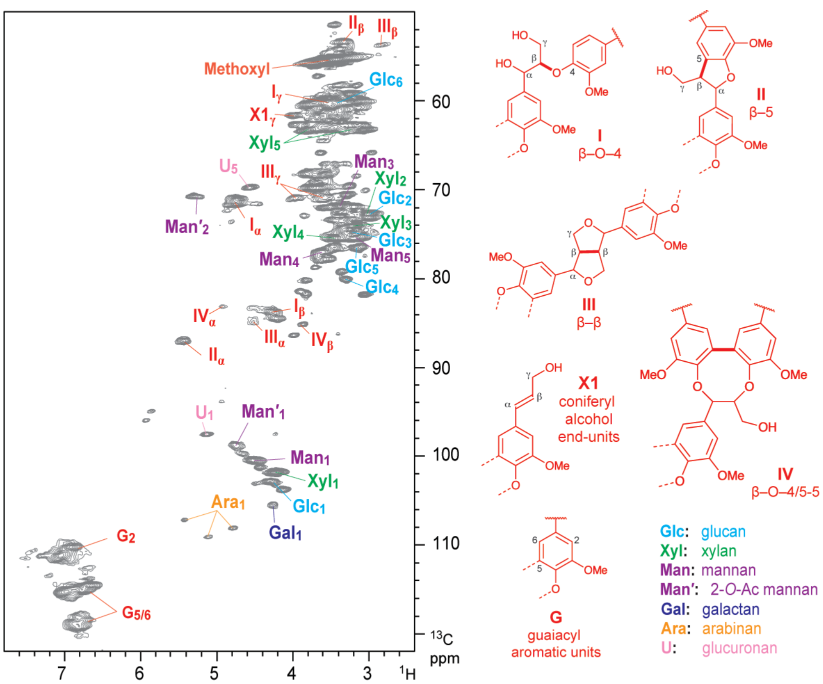

Fig. S1 Whole cell wall NMR analysis of Japanese larch wood meals. HSQC spectrum was collected by the gel-state cell-wall NMR method developed by Kim and Ralph (2010)[1] and signal assignment was based on comparison with literature data[1-4].

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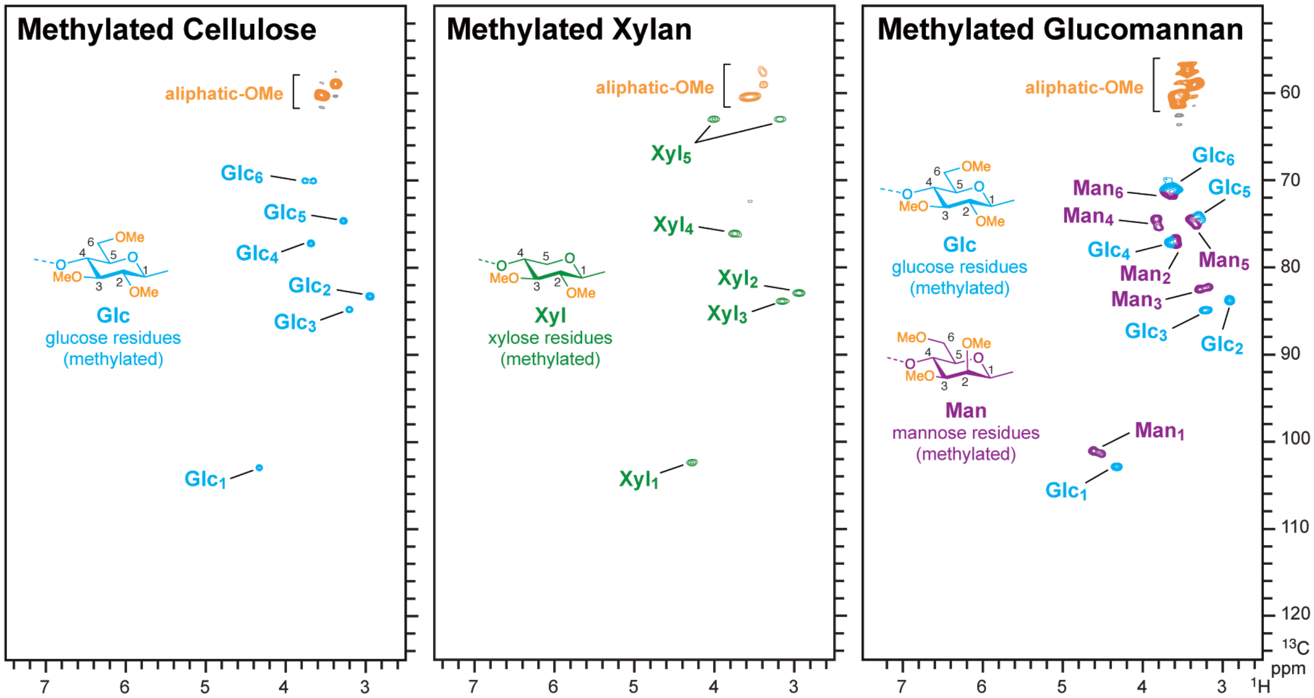

Fig. S2 HSQC NMR spectra of permethylated polysaccharides and dehydrogenation polymer (DHP) lignin.

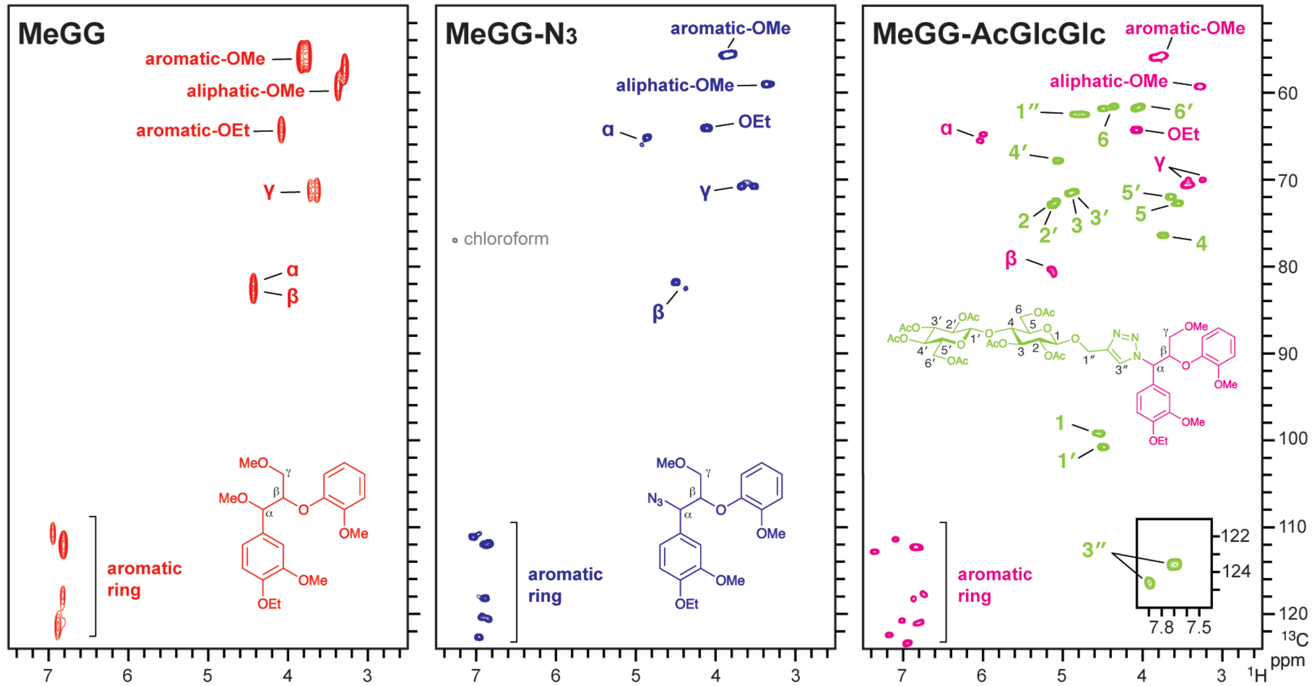

Fig. S3 Azido-functionalization of lignin model compounds followed by the grafting of acetylated cellobiose derivatives *via* CuAAC reaction.

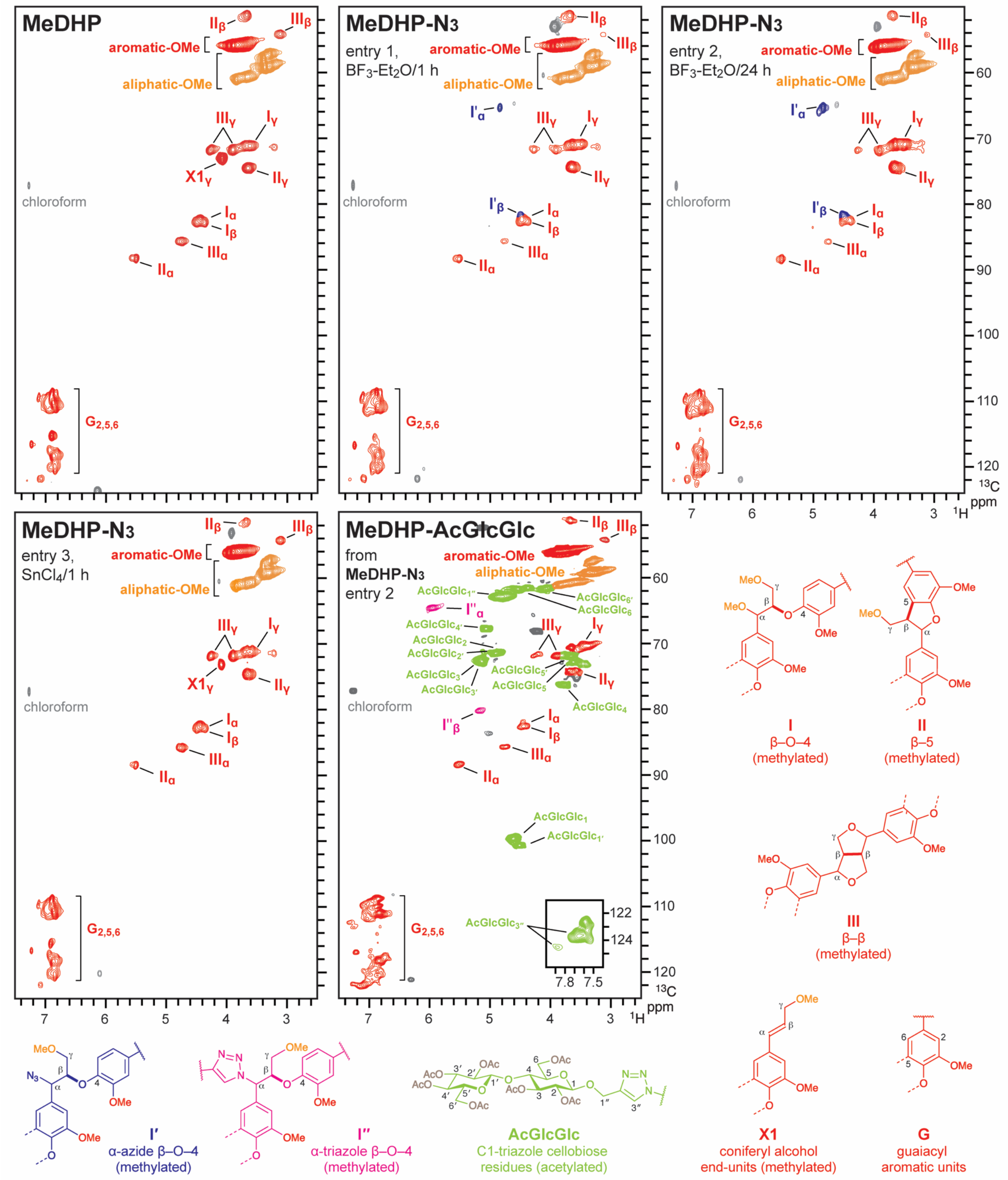

Fig. S4 HSQC spectra of methylated lignin model (dehydrogenative polymerization (DHP)) and its azido-functionalization.

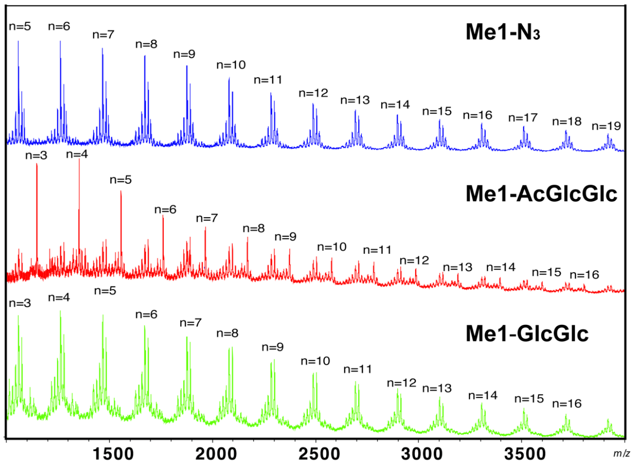

Fig. S5 MALDI-TOF MS spectra of **Me1-N₃**, **Me1-AcGlcGlc**, and **Me1-GlcGlc**.

(A) (B)

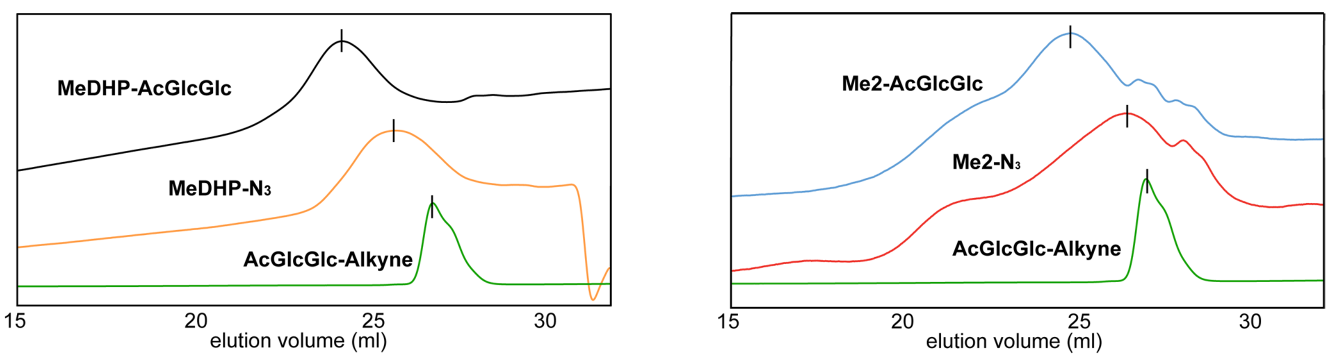

Fig. S6 Size exclusion chromatograms of functionalized **MeDHP** (A) and functionalized **Me2** (B).

Table S1 Neutral sugar analysis and alkaline nitrobenzene oxidation of *Larix kaempferi* (Lamb.) Carrière

Neutral sugar analysis (%) [a]							Lignin analysis (%)				
Extractives	Rha	Ara	Xyl	Man	Gal	Glc	Klason lignin	P[b]	V[b]	S[b]	P+V+S[b]
2.2	0.1	1.0	4.3	9.6	4.7	38.7	29.1	0.054	4.21	0.00	14.6

[a]Yield (%) was calculated based on dry weight.

[b]Yield (%) of nitrobenzene oxidation, based on Klason lignin.; P, p-coumaryl alcohol; S, syringaldehyde; V, vanillin;
Rha, rhamnose; Ara, arabinose; Xyl, xylose; Man, mannose; Gal, galactose; Glc, glucose.

Table S2 Chemical shift assignments of HSQC spectra of methylated lignin derivatives

Labels	δ_C/δ_H (ppm)	Assignment
I_α	82.3/4.43	Cα/Hα in β-O-4/α-O-Me linkage (Cα-OMe)
I_β	82.3/4.43	Cβ/Hβ in β-O-4/α-O-Me linkage (Cα-OMe)
I_γ	71.1/3.20	Cγ/Hγ in β-O-4/α-O-Me linkage (Cα-OMe)
I'_α	65.2/4.84	Cα/Hα in β-O-4/α-N_3 linkage (Cα-N_3)
I'_β	81.6/4.49	Cβ/Hβ in β-O-4/α-N_3 linkage (Cα-N_3)
I'_γ	70.7/3.49-3.6	Cγ/Hγ in β-O-4/α-N_3 linkage (Cα-N_3)
I''_α	65.1/6.01	Cα/Hα in β-O-4/α-triazole-AcGlcGLc linkage (1-Cα-4-(AcGlcGlc)-1*H*-1,2,3-triazole)
I''_β	80.3/5.13	Cβ/Hβ in β-O-4/α-triazole-AcGlcGLc linkage (1-Cα-4-(AcGlcGlc)-1*H*-1,2,3-triazole)
I''_γ	70.0/3.24-3.42	Cγ/Hγ in β-O-4/α-triazole-AcGlcGLc linkage (1-Cα-4-(AcGlcGlc)-1*H*-1,2,3-triazole)
II_α	88.0/5.50	Cα/Hα in β-5/α-O-4 linkage (phenylcoumaran)
II_β	51.1/3.65	Cβ/Hβ in β-5/α-O-4 linkage (phenylcoumaran)
II_γ	74.4/3.62	Cγ/Hγ in β-5/α-O-4 linkage (phenylcoumaran)
III_α	85.5/4.73	Cα/Hα in β-β/α-O-γ linkage (resinol)
III_β	53.9/3.09	Cβ/Hβ in β-β/α-O-γ linkage (resinol)
III_γ	71.7/3.88-4.25	Cγ/Hγ in β-β/α-O-γ linkage (resinol)
IV_α	83.5/5.00	Cα/Hα in β-β/β-O-4/α-O-4 linkage (dibenzodioxocin)
IV_β	84.5/3.95	Cβ/Hβ in β-β/β-O-4/α-O-4 linkage (dibenzodioxocin)
$X1_\gamma$	73.0/3.64	Cγ/Hγ of coniferyl alcohol
G2	110/6.65-7.05	C2/H2 in guaiacyl units
G5, 6	125/6.65-7.05	C5/H5, C6/H6 in guaiacyl units
triazole	123.6/7.70	C5/H5 in triazole ring
triazole-CH_2	62.47/4.70-4.86	C/H methylene beside C4 of triazole ring

Table S3 Azido-functionalization of **MeDHP** and **Me2**

entry	SM	Lewis acid	time	yield	$M_n \times 10^3$	M_w/M_n	relative signal intensity of lignin substructures[a]				
							I^0	I	I'	II	III
1	MeDHP	—	—	—	4.1	1.6	0	49.4	0.0	29.9	20.7
2	MeDHP	BF_3-Et_2O	1	86.9	3.2	3.6	0	40.4	19.4	32.4	7.8
3	MeDHP	BF_3-Et_2O	24	84.1	2.3	2.1	0	17.1	52.0	25.5	5.4
4	MeDHP	$SnCl_4$	1	68.3	2.9	1.8	0	48.8	trace	26.9	24.3
5	Larch sawdust	—	—	—	—	—	77.5	0.0	0.0	19.3	3.3
6	Me2	—	—	—	2.5	6.0	0	91.9	0.0	1.4	6.7
7	Me 2	BF_3-Et_2O	3	64.8	0.8	4.7	0	52.2	41.8	4.4	1.7
8	Me 2	BF_3-Et_2O	6	61.9	1.7	1.3	0	44.7	51.2	4.1	trace

I^0: β-O-4/α-OH; I: β-O-4/α-OMe; I': β-O-4/α-N_3; II: β-5/α-O-4 (phenylcoumaran); III: β-β/α-O-γ (resinol)

References

1. H. Kim and J. Ralph, *Organic & Biomolecular Chemistry*, 2010, **8**, 576-591.
2. M. Brennan, J. P. McLean, C. Altaner, J. Ralph and P. J. Harris, *Cellulose*, 2012, **19**, 1385-1404.
3. D. Tarmadi, Y. Tobimatsu, M. Yamamura, T. Miyamoto, Y. Miyagawa, T. Umezawa and T. Yoshimura, *Sci Rep-Uk*, 2018, **8**.
4. Y. Tobimatsu, F. Chen, J. Nakashima, L. L. Escamilla-Treviño, L. Jackson, R. A. Dixon and J. Ralph, *The Plant Cell*, 2013, **25**, 2587-2600.