Supplementary material for

Hydrogenolysis of biorefinery corncob lignin into aromatic phenols over activated carbon-supported nickel

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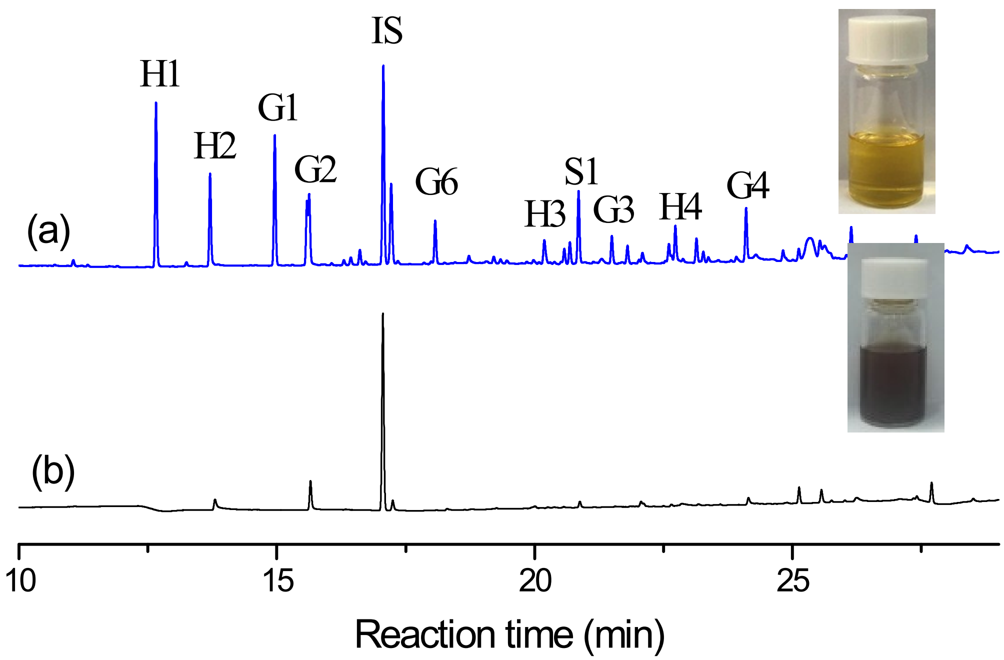


Fig. S1 Gas chromatogram and peak identification of the lignin monomers from the catalytic hydrogenolysis of biorefinery corncob lignin (a) with Ni/AC (reaction condition from Table 1, entry 1), and (b) without catalyst (reaction condition from Table 1, entry 2). IS represents internal standard.

Fig. S2 Images of biorefinery corncob lignin after catalytic hydrogenolysis reaction over the Ni/AC catalyst.

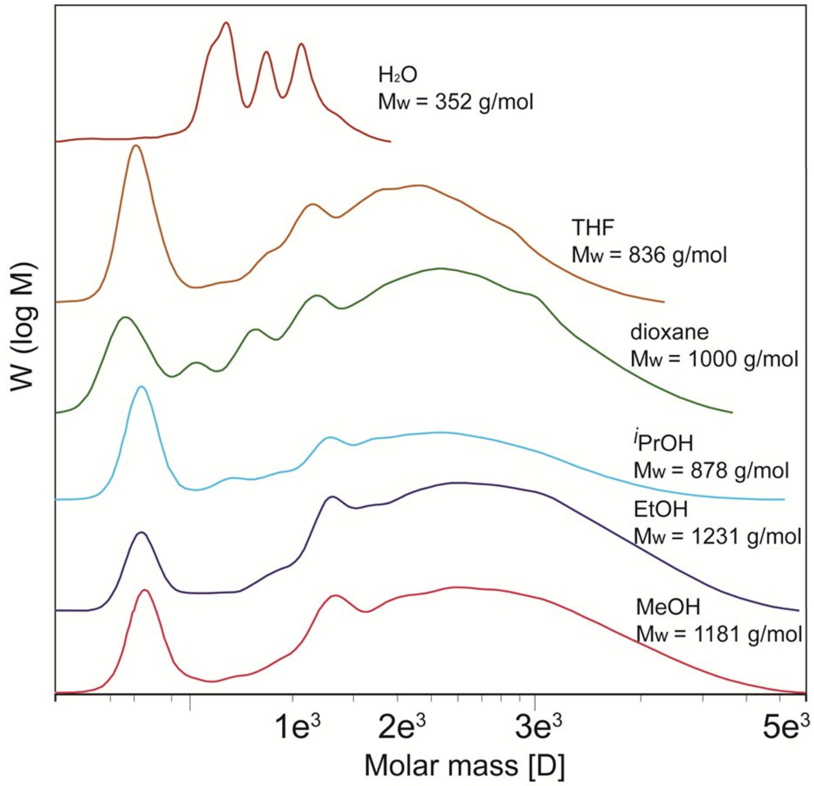


Fig. S3 The molecular weight distribution of lignin oily product from catalytic hydrogenolysis of biorefinery corncob lignin with different solvents. Reaction conditions unless specified otherwise: lignin (50 mg), Ni/AC catalyst (10 mg), solvent (10 mL), 240 ^oC, 4 h, H_2 (3 MPa).

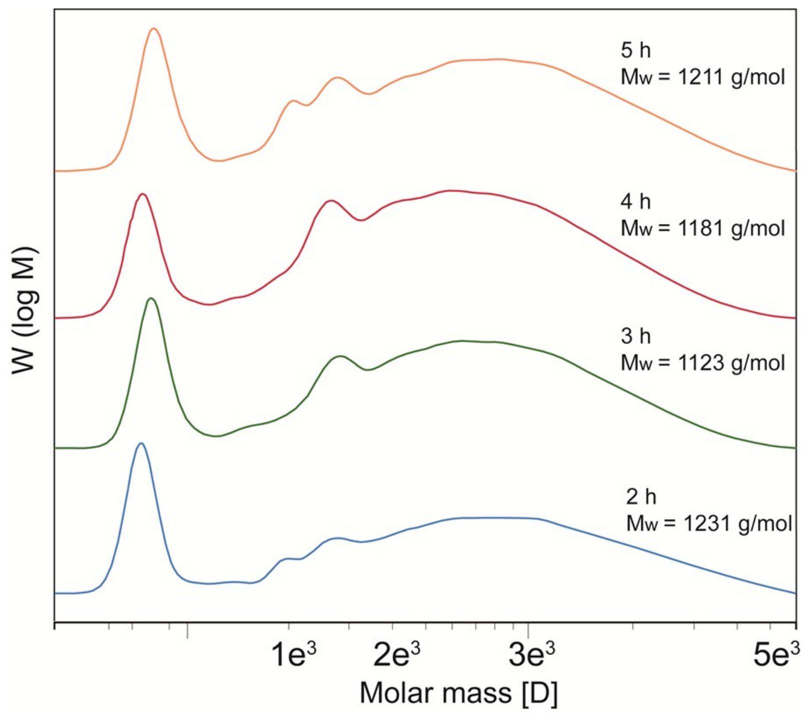


Fig. S4 The molecular weight distribution of lignin oily product from catalytic hydrogenolysis of biorefinery corncob lignin with various reaction times. Reaction condition: lignin (50 mg), Ni/AC catalyst (10 mg), MeOH (10 mL), 240 ^{o}C, H_2 (3 MPa).

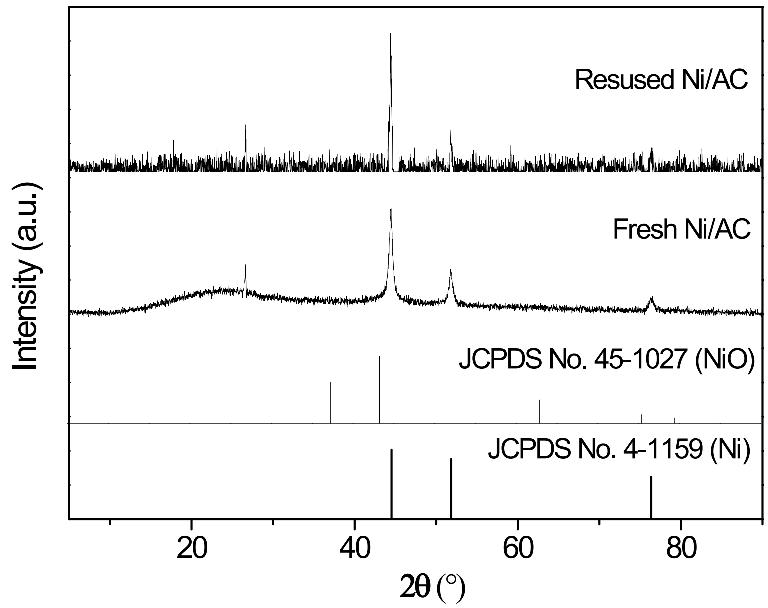


Fig. S5 XRD patterns of the fresh and reused Ni/AC catalyst.

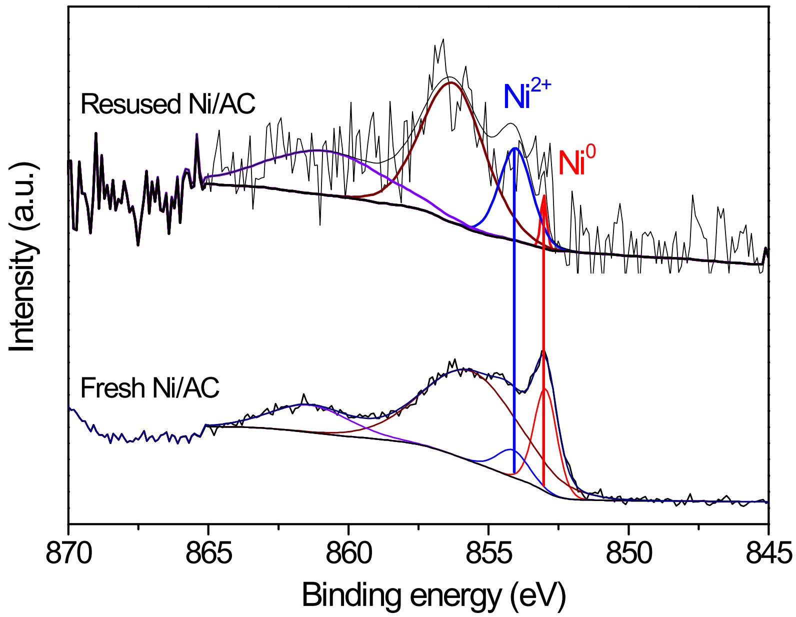
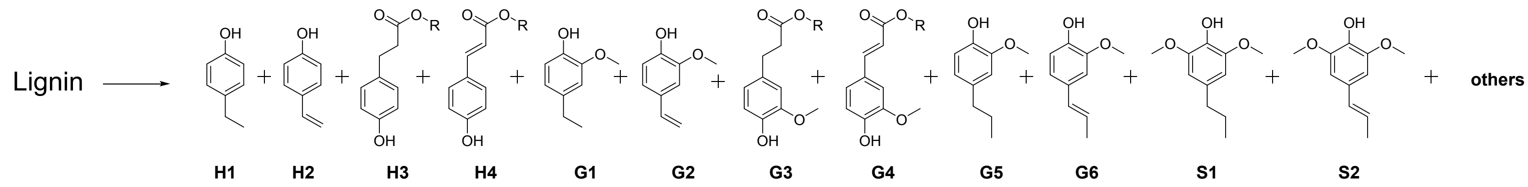


Fig. S6 XPS spectra of the fresh and reused Ni/AC catalyst. The peaks at 852.9 eV and 854.2 eV are assigned to Ni^{o} and Ni^{2+}, respectively. The analysis of the XPS results show that Ni^{o} occupied about 80 wt% based the total content of Ni^{o} and Ni^{2+} for Ni 2p of the fresh Ni/AC catalyst, which is higher than that of the reused Ni/AC catalyst (Ni^{o} occupied about 14 wt% based the total content of Ni^{o} and Ni^{2+}).

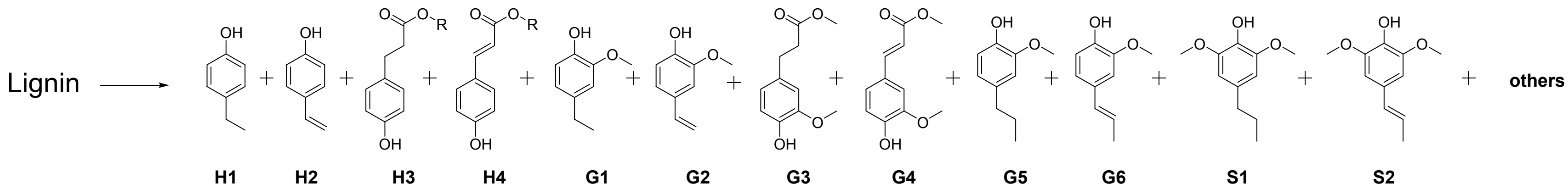
Table S1 Products distribution of catalytic hydrogenolysis of biorefinery corncob lignin with different solvent.[a]



Entry	Catalyst	Solvent	The distribution and yields of phenolic monomers (wt%)[b]															Others	Total monomers yield (wt%)
			Ethyl/vinyl phenol and guaiacol					Methyl coumarate/ferulate and derivatives					Propyl/propenyl guaiacol and syrinol						
			H1	H2	G1	G2	Total yield (wt%)	H3	H4	G3	G4	Total yield (wt%)	G5	G6	S1	S2	Total yield (wt%)		
1	Ni/C	MeOH	0.5	0.8	2.3	0.9	4.5	1.3[c]	0.7[c]	0.7[c]	0.9[c]	3.6	0.4	0.4	1.8	0.1	2.7	1.3	12.1
2	Ni/C	EtOH	0.3	0.4	1.0	0.4	2.1	0.6[e]	0.4[d]	0.5[d]	0.8[d]	2.3	0.4	0.4	0.7	0.2	1.7	2.3	8.4
3	Ni/C	^{i}PrOH	0.5	0.8	1.4	0.6	3.3	0.2[f]	0.1[e]	0.4[e]	0.7[e]	1.4	0.4	0.3	0.9	0.3	1.9	3.7	10.3
4	Ni/C	THF	0.3	0.6	0.8	0.4	2.1	0.2[g]	trace[f]	0.3[f]	trace[f]	0.5	0.4	0.8	0.8	0.3	2.3	0.9	5.8
5	Ni/C	Dioxane	0.1	--	0.5	--	0.6	--	--	--	--	0	0.8	--	0.2	--	1.0	1.5	3.1
6	Ni/C	H_2O	0.8	--	1.9	--	2.7	--	--	--	--	0	0.8	--	0.5	--	1.3	2.5	6.5
7	None	MeOH	--	1.7	--	2.1	3.8	--	0.3	--	0.4	0.7	--	0.3	--	0.2	0.5	1.2	6.2
8	AC	MeOH	--	1.4	--	1.8	3.2	--	0.2	--	0.1	0.3	--	0.2	--	--	0.2	1.6	5.3
9[g]	Ni/C	MeOH	0.1	1.2	0.6	1.3	3.2	--	0.3	--	0.9	1.2	--	0.7	--	0.3	1.0	1.2	6.6

[a] Reaction conditions: lignin (50 mg), catalyst (10 mg), solvent (10 mL), 240 ^{o}C, 4 h. [b] Representing the monomer yield is based on total lignin content. [c] R=CH_3. [d] R=CH_2CH_3. [e] R= CH_3CHCH_3. [f] R=H. [g] Reaction performed under N_2 (0 MPa).

Table S2 Products distribution of catalytic hydrogenolysis of biorefinery corncob lignin with different reaction temperature.[a]

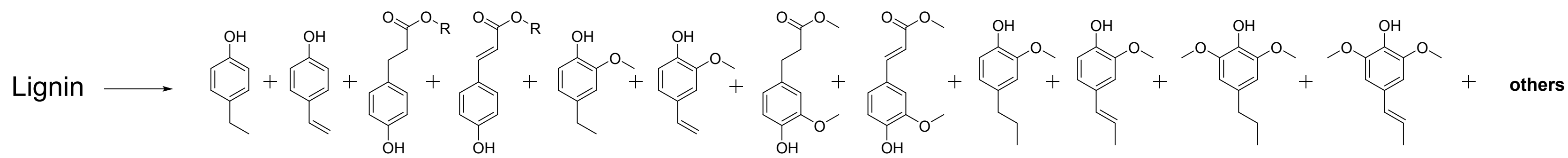


Entry	Tem. (°C)	The distribution and yields of phenolic monomers (wt%)[b]															Others	Total monomers yield (wt%)
		Ethyl/vinyl phenol and guaiacol					Methyl coumarate/ferulate and derivatives					Propyl/propenyl guaiacol and syrinol						
		H1	H2	G1	G2	Total yield (wt%)	H3	H4	G3	G4	Total yield (wt%)	G5	G6	S1	S2	Total yield (wt%)		
1	220	0.3	0.5	1.1	0.5	2.4	1.2	0.4	0.6	0.7	2.9	0.2	1.3	--	0.2	1.7	1.0	8.0
2	230	0.9	1.0	1.0	0.7	3.6	1.2	0.6	0.3	0.8	2.9	0.4	0.8	0.4	0.5	2.1	1.8	10.4
3	240	0.5	0.8	2.3	0.9	4.5	1.3	0.7	0.7	0.9	3.6	0.4	0.4	1.8	0.1	2.7	1.3	12.1
4	260	0.5	0.8	1.2	0.3	2.8	1.0	0.7	0.7	1.1	3.5	0.4	0.4	0.9	1.0	2.7	2.0	11.0
5	280	0.8	--	1.7	0.2	2.7	1.1	0.6	1.3	0.9	3.9	0.4	0.8	0.8	0.6	2.6	1.5	10.7

[a] Reaction conditions: lignin (50 mg), catalyst (10 mg), solvent (10 mL), MeOH, 4 h, 3 MPa (H_2).

[b] Representing the monomer yield is based on total lignin content.

Table S3 Products distribution of catalytic hydrogenolysis of biorefinery corncob lignin with different reaction time.[a]



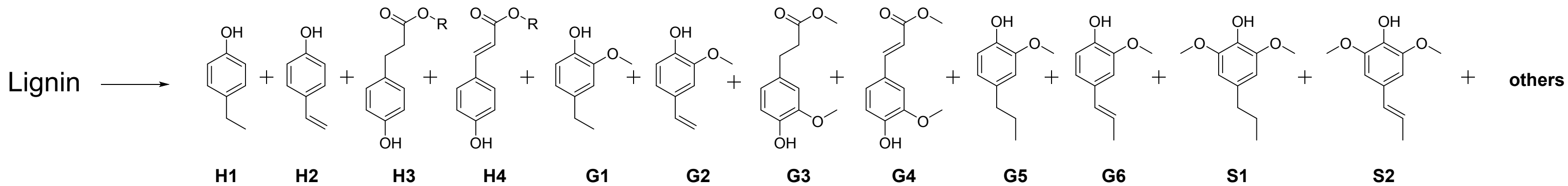
H1 H2 H3 H4 G1 G2 G3 G4 G5 G6 S1 S2

Entry	Time (h)	The distribution and yields of phenolic monomers (wt%)[b]															Others	Total monomers yield (wt%)
		Ethyl/vinyl phenol and guaiacol					Methyl coumarate/ferulate and derivatives					Propyl/propenyl guaiacol and syrinol						
		H1	H2	G1	G2	Total yield (wt%)	H3	H4	G3	G4	Total yield (wt%)	G5	G6	S1	S2	Total yield (wt%)		
1	2	1.2	1.1	0.5	1.2	4.0	1.2	0.5	0.2	0.6	2.5	--	0.7	--	0.3	1.0	1.2	8.7
2	3	1.2	1.1	1.0	0.8	4.1	1.2	0.5	0.6	0.8	3.1	0.3	0.8	0.3	0.4	1.8	1.7	10.7
3	4	0.5	0.8	2.3	0.9	4.5	1.3	0.7	0.7	0.9	3.6	0.4	0.4	1.8	0.1	2.7	1.3	12.1
4	5	1.1	0.9	1.7	0.4	4.1	1.2	0.4	0.6	0.8	3.0	0.4	0.8	0.3	0.5	2.0	2.0	11.1

[a] Reaction conditions: lignin (50 mg), catalyst (10 mg), solvent (10 mL), 240 °C, MeOH, 3 MPa (H_2).

[b] Representing the monomer yield is based on total lignin content.

Table S4 Products distribution of catalytic hydrogenolysis of biorefinery corncob lignin with different run times.[a]



Run time	The distribution and yields of phenolic monomers (wt%)[b]															Others	Total monomers yield (wt%)
	Ethyl/vinyl phenol and guaiacol					Methyl coumarate/ferulate and derivatives					Propyl/ propenyl guaiacol and syrinol						
	H1	H2	G1	G2	Total yield (wt%)	H3	H4	G3	G4	Total yield (wt%)	G5	G6	S1	S2	Total yield (wt%)		
1	0.5	0.8	2.3	0.9	4.5	1.3	0.7	0.7	0.9	3.6	0.4	0.4	1.8	0.1	2.7	1.3	12.1
2	0.1	0.8	2.0	0.7	3.6	1.1	0.6	0.5	0.8	3.0	0.7	0.3	1.4	0.2	2.6	2.4	11.6
3	--	1.3	2.1	0.5	3.9	1.1	0.6	0.6	0.8	3.1	0.5	0.3	1.3	0.1	2.2	1.1	10.3
4	--	1.4	2.3	0.6	4.3	1.2	0.8	0.2	1.2	3.4	--	0.7	0.4	0.1	1.2	3.0	11.9
5	--	1.5	1.8	0.7	4.0	1.1	0.7	0.3	1.0	3.1	--	0.7	0.4	--	1.1	3.2	11.4
6	--	1.5	1.6	0.5	3.6	1.1	0.7	0.2	0.9	2.9	--	0.7	0.4	--	1.1	3.9	11.5

[a] Reaction conditions: lignin (50 mg), catalyst (10 mg), solvent (10 mL), 240 °C, MeOH, 3 MPa (H_2), 4 h.

[b] Representing the monomer yield is based on total lignin content.

Table S5 The assignments of main lignin and lignin monomers ^{13}C-^{1}H correlation signals in the 2D HSQC NMR spectra in Fig. 3.

Lables	δ_C/δ_H (ppm)	Assignment
OMe	55.5/3.69	C-H in methoxyls ($-OCH_3$)
A_α	71.6/4.85	C_α-H_α in *β-O-4* substructures (A)
A_β	86.6/4.09	C_β-H_β in *β-O-4* substructures (A)
A_γ	59.5/3.1-3.79	C_γ-H_γ in *β-O-4* substructures (A)
B_γ	62.4/3.69	C_γ-H_γ in phenylcoumaran substructures (B)
$S_{2,6}$	103.7/6.65	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
$S'_{2,6}$	106.3/7.17	$C_{2,6}$-$H_{2,6}$ in oxidized syringyl units (S')
G_2	110.7/6.92	C_2-H_2 in guaiacyl units (G)
G_5	114.5/6.68	C_5-H_5 in guaiacyl units (G)
G_6	119.0/6.77	C_6-H_6 in guaiacyl units (G)
$G/S_1(7)$	28.3/2.48	C_7-H_7 in compounds **G1** and **H1**
$G/S_1(8)$	16.4/1.14	C_8-H_8 in compounds **G1** and **H1**
$H/G_2(7)$	136.1/6.72	C_7-H_7 in compounds **G2** and **H2** (Chemdraw)
H_3	128.3/6.97	$C_{2,6}$-$H_{2,6}$ in compounds **H3**
	115.9/6.77	$C_{3,5}$-$H_{3,5}$ in compounds **H3**
	29.4/2.73	C_7-H_7 in compounds **H3**
	35.2/2.55	C_8-H_8 in compounds **H3**
G_3	111.9/6.74	C_2-H_2 in compounds **G3**
	114.8/6.58	C_5-H_5 in compounds **G3**
	119.7/6.57	C_6-H_6 in compounds **G3**
	29.4/2.73	C_7-H_7 in compounds **G3**
	35.2/2.55	C_8-H_8 in compounds **G3**
*p*CA/H_4	129.9/7.51	$C_{2,6}$-$H_{2,6}$ in compounds **H4** and ***p*CA**
	115.5/6.78	$C_{3,5}$-$H_{3,5}$ in compounds **H4** and ***p*CA**
	143.9/7.53	C_7-H_7 in compounds **H4** and ***p*CA**
	115.2/6.28	C_8-H_8 in compounds **H4** and ***p*CA**
FA/G_4	111.0/7.28	C_2-H_2 in compounds **G4** and ***p*CA**
	122.2/7.11	C_6-H_6 in compounds **G4** and ***p*CA**
	144.0/7.45	C_7-H_7 in compounds **G4** and ***p*CA**

	116.5/6.40	C_8-H_8 in compounds **G4** and ***p*CA**
	51.1/3.62	C(O)OMe in compounds H/**G4**
G/S_5(7)	37.5/2.43	C_7-H_7 in compounds **G5** and **S5**
G/S_5(8)	24.9/1.55	C_8-H_8 in compounds **G5** and **S5**
G/S_5(9)	13.9/0.87	C_9-H_9 in compounds **G5** and **S5**