Electronic Supplementary Material (ESI) for RSC Sustainability.

Table S1. Yields of monomers obtained from pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar MWL in different solvents (temperature: 350 °C; treatment time: 30 min; Pd/C: 10 mg; H_2: 3 mL/0.1 MPa)

Solvent	H2O	MeOH	Dioxane	Acetone	Anisole	Benzene	Toluene	Hexane
Phenol	-	-	-	-	n*	n*	4.9	n*
Methylphenol	2.3	2.5	-	-	6.0	3.9	1.9	3.8
Ethylphenol	1.7	1.6	0.0	1.8	4.6	3.5	3.6	4.4
Propylphenol	0.7	0.7	-	-	0.8	1.9	1.3	1.1
Guaiacol	7.5	8.2	12.8	8.0	14.2	4.0	5.8	7.9
Methyl guaiacol	5.1	5.4	7.2	5.1	6.3	5.1	3.5	4.8
Ethyl guaiacol	17.5	11.5	16.4	29.8	20.3	21.9	18.9	15.6
Propyl guaiacol	8.5	4.1	4.8	6.6	4.1	6.0	3.3	3.9
Ethyl catechol	3.8	0.0	-	3.4	0.6	-	-	-
Acetovanillone	-	0.1	0.8	0.6	-	-	-	-
Propiovanillone	0.1	0.6	1.0	0.7	-	-	-	-
Guaiacylacetone	0.1	-	-	-	-	-	-	-
Dihydro coniferyl alcohol	2.2	10.5	11.0	-	-	-	-	-
Dihydro-p-coumaryl alcohol	0.0	0.6	-	0.0	-	-	-	-
H-/Alkyl- guaiacols	38.6	29.2	41.2	49.5	45.0	37.0	31.4	32.1
Phenols	4.6	4.8	0.0	1.8	11.4	9.3	6.7	9.3
Catechols	3.8	0.0	0.0	3.4	0.6	0.0	0.0	0.0
DHCA	2.2	10.5	11.0	-	-	-	-	-
Sum	49.6	45.8	54.0	56.0	56.9	46.3	43.1	41.4

- : not detected

n* : Overlapped with other signals

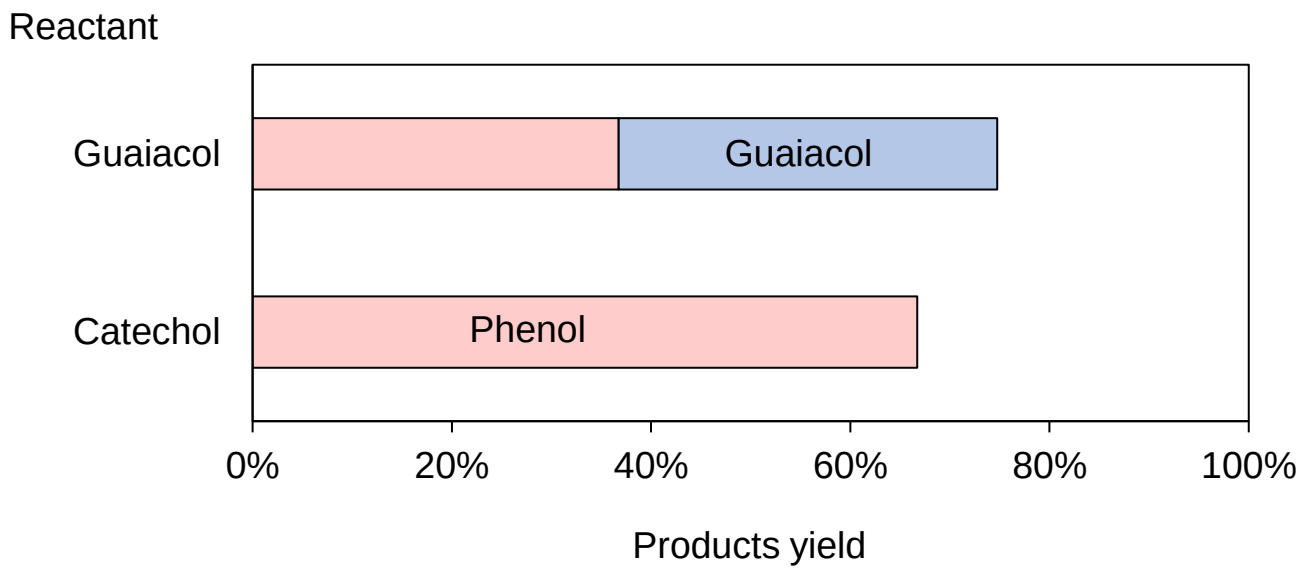


Figure S1. Monomers obtained from pyrolysis-assisted catalytic hydrogenolysis of guaiacol and catechol in water at 350 °C for 60 min (reaction compound: 10 mg; Pd/C: 10 mg; water: 2 mL; H_2: 3 mL/0.1 MPa).

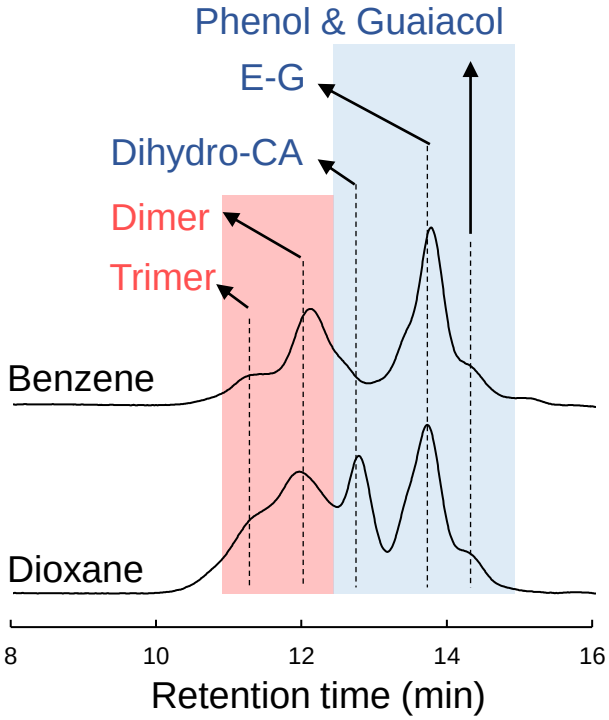


Figure S2. Gel-permeation chromatograms of products obtained from pyrolysis-assisted catalytic hydrogenolysis of MWL after treatment at 350 °C for 30 min in benzene and dioxane.

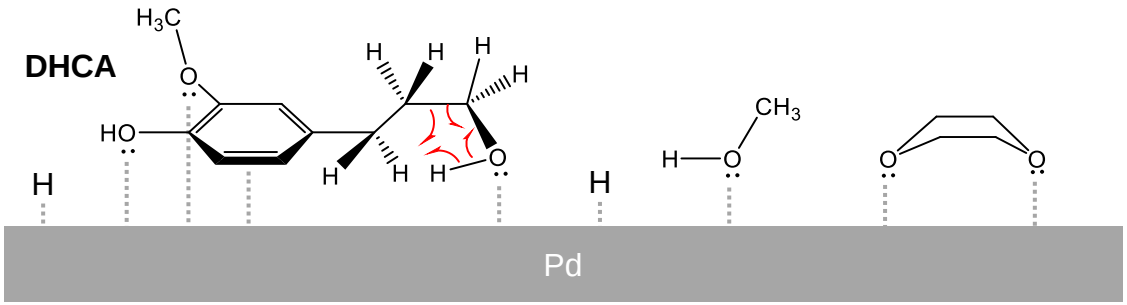
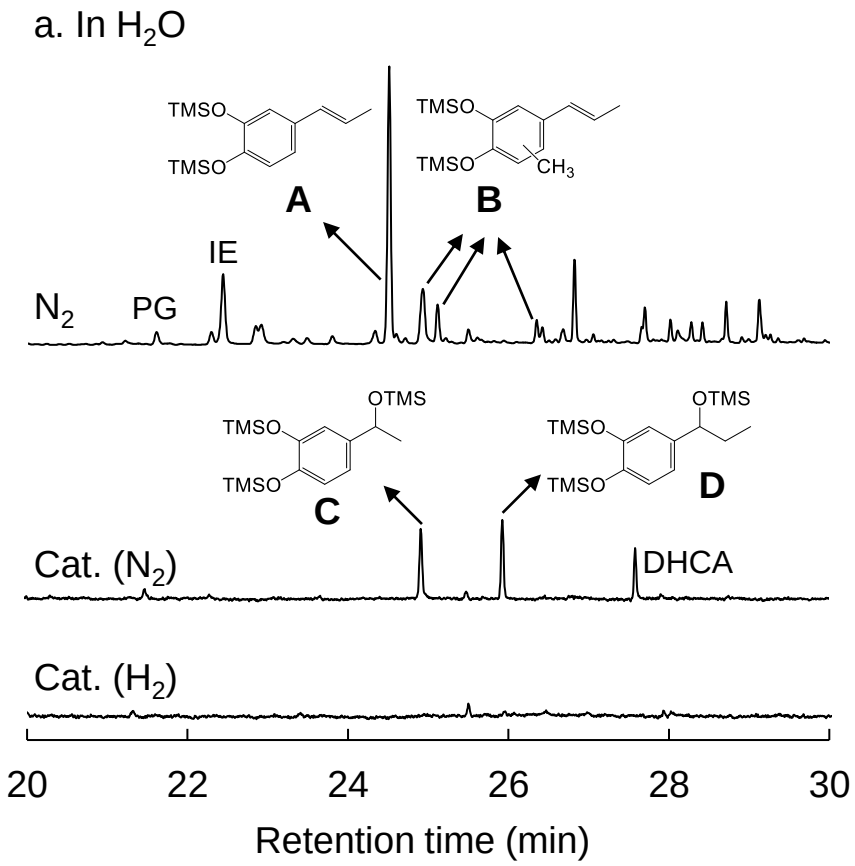
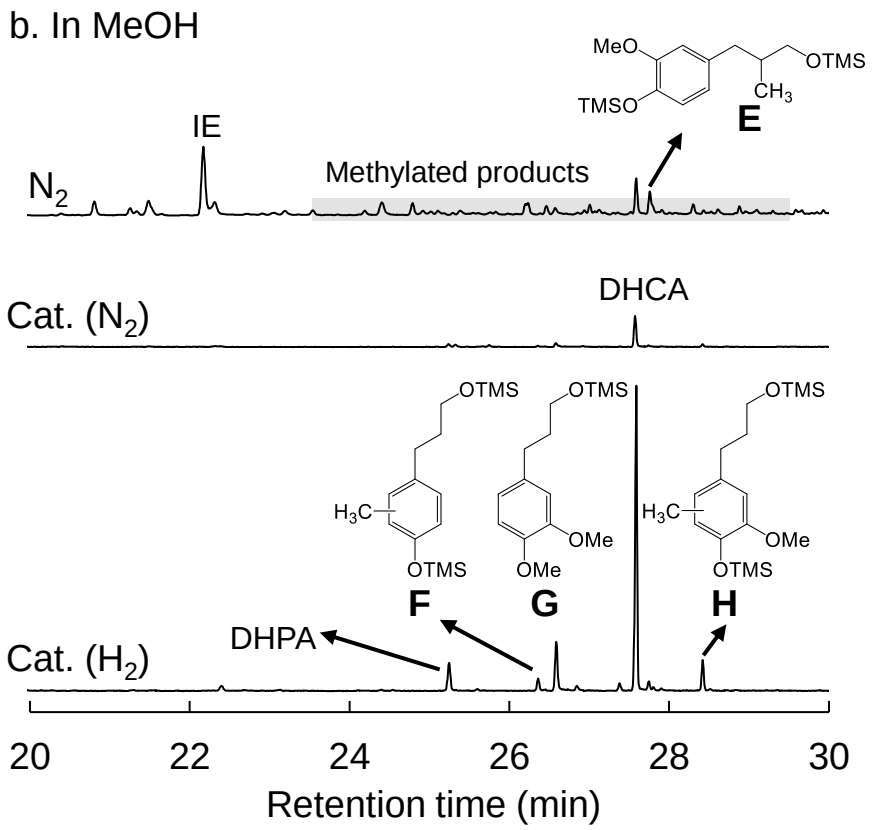
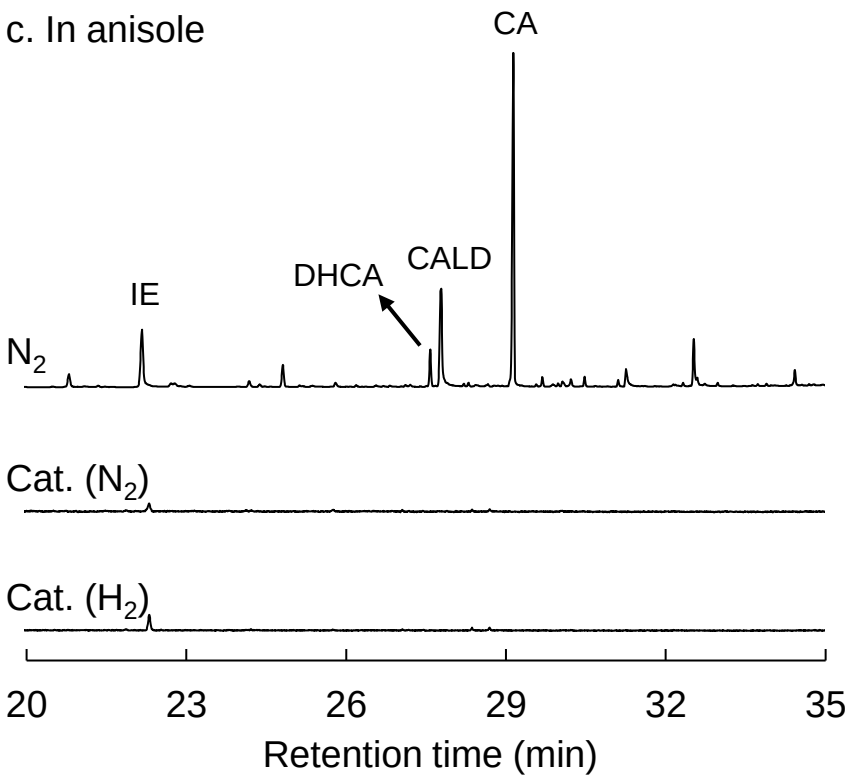
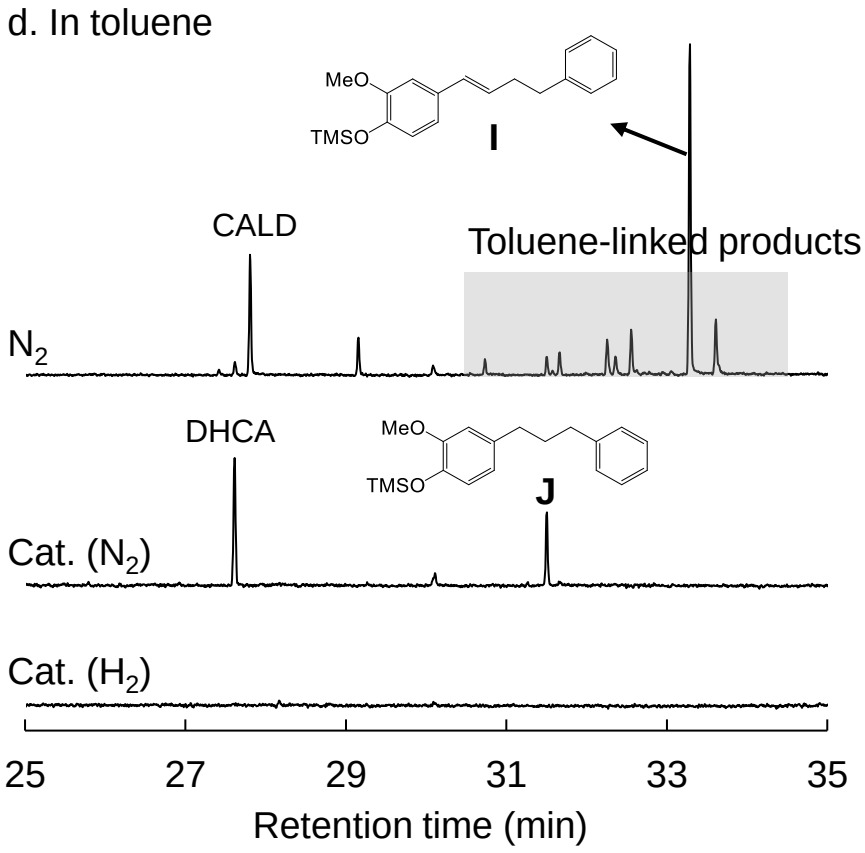


Figure S3. Possible association modes of DHCA, methanol, and dioxane on Pd surface during pyrolysis-assisted hydrogenolysis.


a. In H_2O
TMSO
TMSO
A
TMSO
TMSO
CH_3
B
IE
N_2
PG
OTMS
TMSO
TMSO
C
OTMS
TMSO
TMSO
D
Cat. (N_2)
DHCA
Cat. (H_2)
20
22
24
26
28
30
Retention time (min)


b. In MeOH
MeO
OTMS
TMSO
CH3
E
IE
N2
Methylated products
Cat. (N2)
DHCA
OTMS
OTMS
OTMS
H3C
OMe
OMe
H3C
OMe
OTMS
OTMS
F
G
H
DHPA
Cat. (H2)
20
22
24
26
28
30
Retention time (min)


c. In anisole
CA
CALD
DHCA
IE
N2
Cat. (N2)
Cat. (H2)
20
23
26
29
32
35
Retention time (min)


d. In toluene
MeO
TMSO
I
CALD
Toluene-linked products
N2
DHCA
MeO
TMSO
J
Cat. (N2)
Cat. (H2)
25
27
29
31
33
35
Retention time (min)

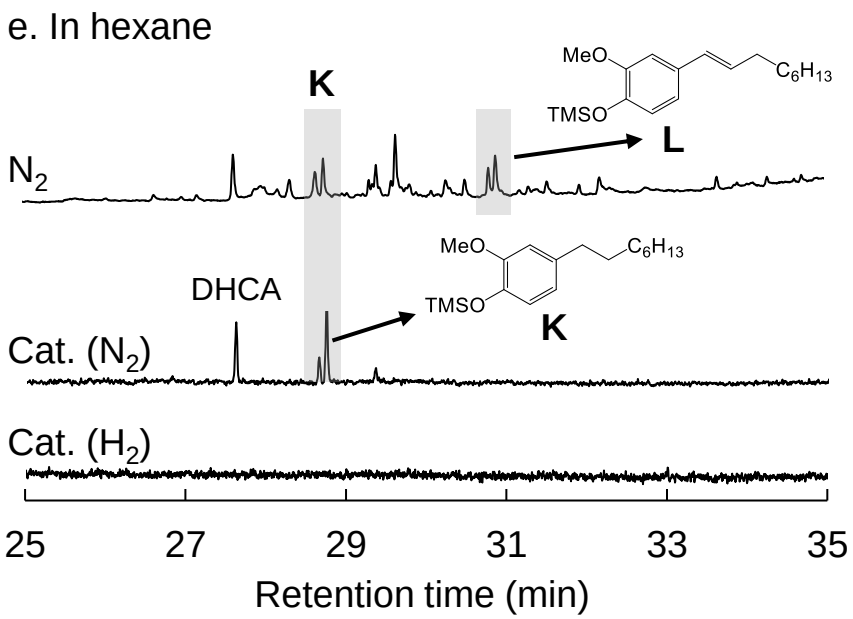
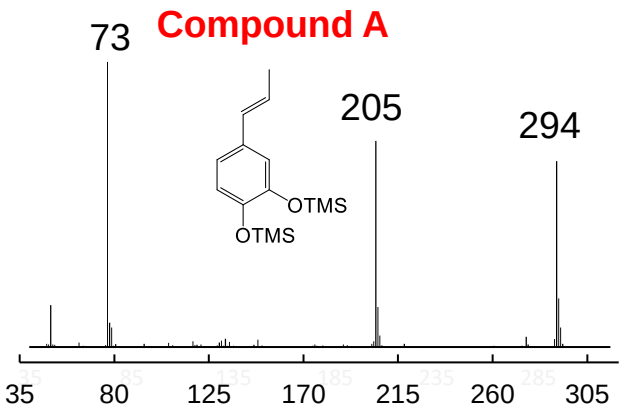
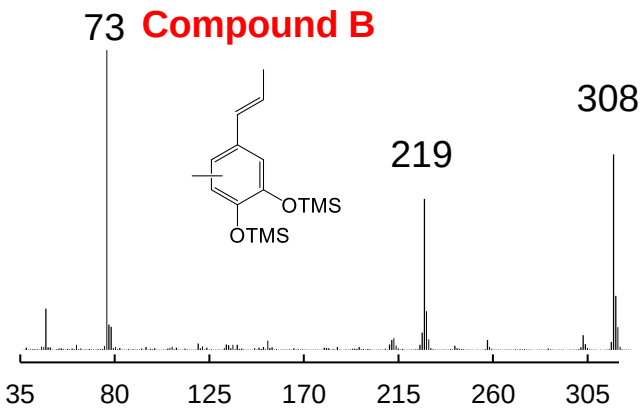
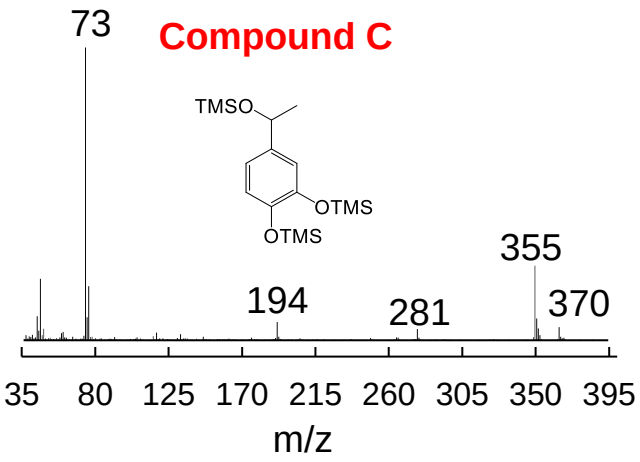
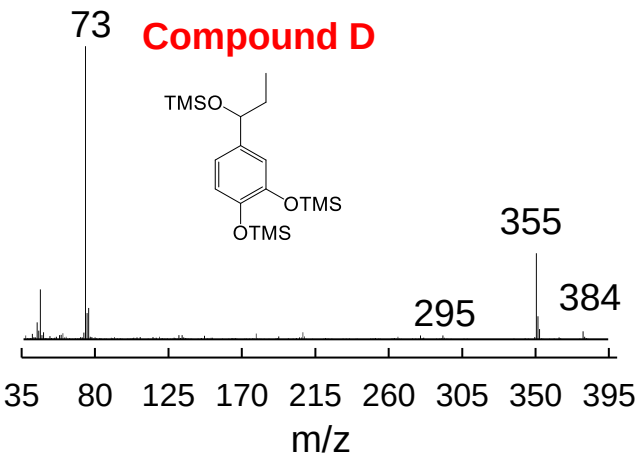


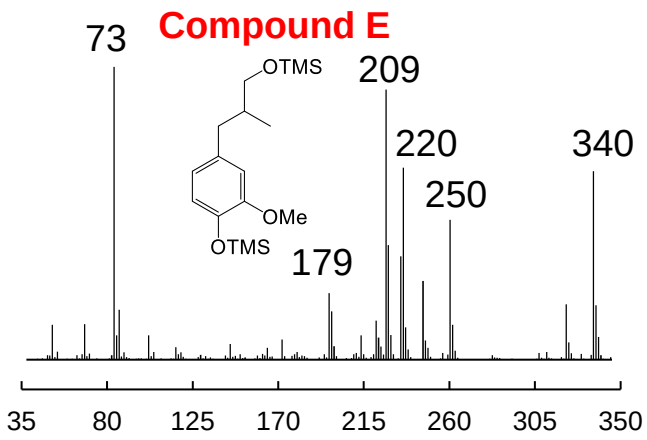
Figure S4. Gas chromatography-mass spectrometry total-ion chromatograms of trimethylsilyl derivatives of reaction mixtures obtained from coniferyl alcohol by thermal treatment in (a) water, (b) methanol, (c) anisole, (d) toluene, and (e) hexane at 350 °C for 60 min.

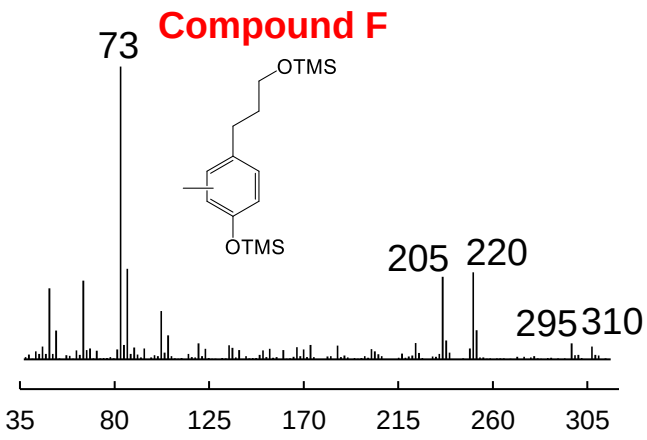

Compound A
73
205
294
OTMS
OTMS
35
80
125
170
215
260
305

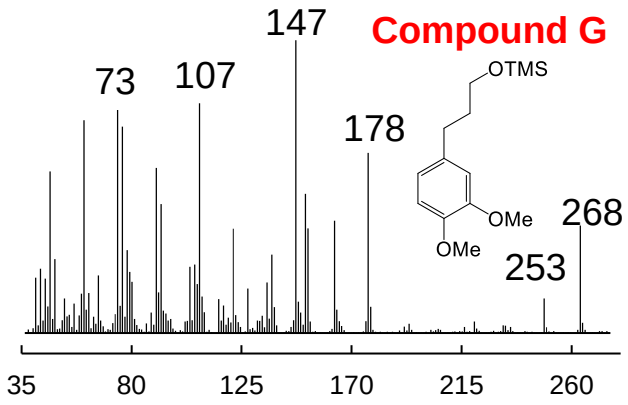

Compound B
73
219
308
OTMS
OTMS
35
80
125
170
215
260
305

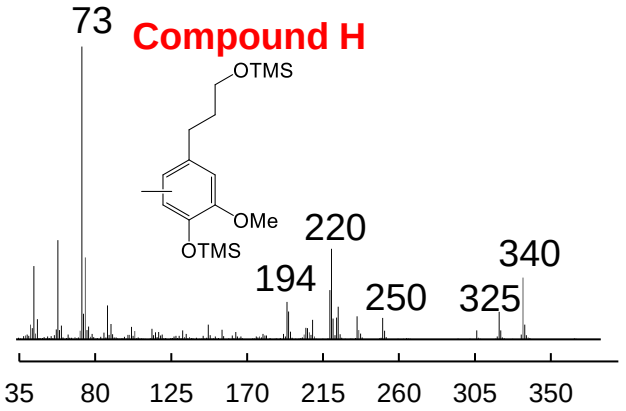

Compound C
73
TMSO
OTMS
OTMS
194
281
355
370
35
80
125
170
215
260
305
350
395
m/z


Compound D
73
TMSO
OTMS
OTMS
295
355
384
35
80
125
170
215
260
305
350
395
m/z


Compound E
73
OTMS
209
220
340
250
OMe
OTMS
179
35 80 125 170 215 260 305 350


Compound F
73
OTMS
OTMS
205
220
295
310
35 80 125 170 215 260 305


Compound G
147
73
107
OTMS
178
OMe
268
OMe
253
35 80 125 170 215 260


Compound H
73
OTMS
OMe
220
OTMS
340
194
250
325
35 80 125 170 215 260 305 350

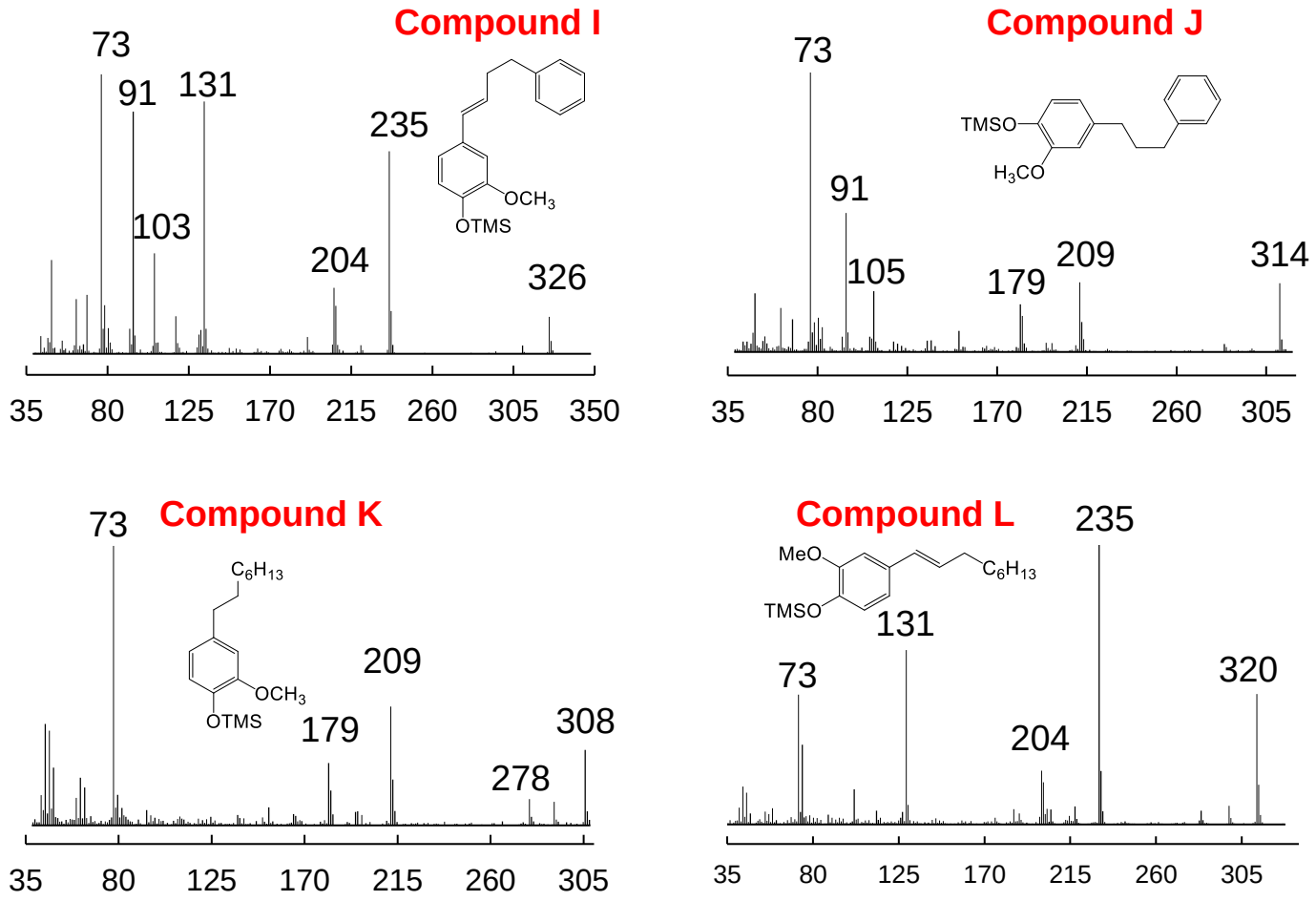


Figure S5. Mass spectra of products corresponding to compounds shown in Figure S3.