Supplementary Information of

Base-catalysed cleavage of lignin β-O-4 model compounds in dimethyl carbonate

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TABLE OF CONTENT

1. General

1.1. Materials and methods

Dimethyl carbonate (DMC) was purchased from Alfa Aesar and used without further purification. Cesium carbonate and lithium *tert*-butoxide were purchased from Sigma Aldrich and Acros Organics, respectively. The calcined hydrotalcite was provided by Prof. Avelino Corma, Instituto de Tecnología Química (UPV-CSIC), Valencia, Spain and was synthesized in accordance to the procedure by Cavani *et al.*.[1] All other bases were acquired from commercial suppliers and used without further purification. The organosolv beech wood lignin was provided by Hybrid Catalysis. THF was dried by distillation over Solvona® (sodium on molecular sieves) in the presence of benzophenone and then stored under a nitrogen atmosphere. Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, visualised by UV light irradiation (254 nm). Catalytic reactions were carried out in screw cap pressure tubes or in a 51.10201.0000 Büchi "tiny clave steel" type 1/25 mL autoclave.

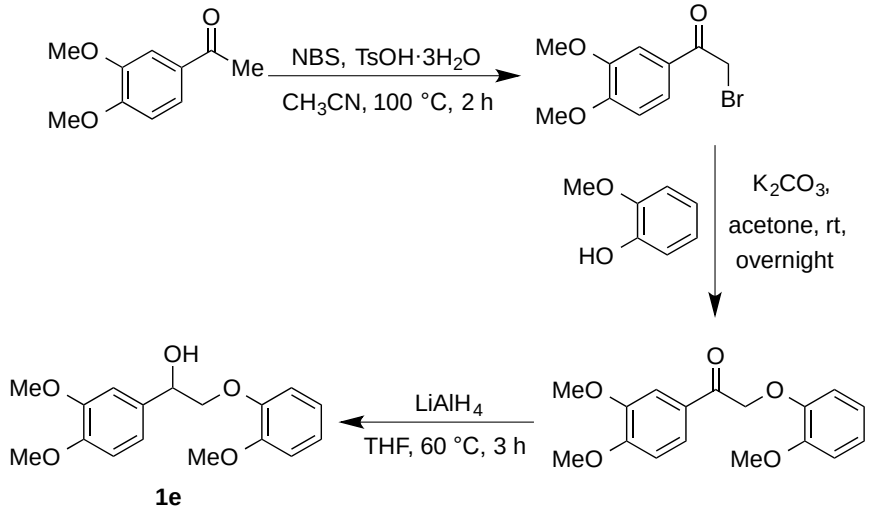
1.2. Instruments

NMR spectra were recorded on a Varian Inova 400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 101 MHz) or Agilent VNMRS 600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 151 MHz) spectrometer. Chemical shifts (δ) are given in ppm relative to the residual solvent peak ($CDCl_3$: δ = 7.26 ppm, DMSO-d_6: δ = 2.50 ppm). Spin-spin coupling constants (*J*) are given in Hz. Mass spectra were recorded on a Finnigan SSQ 7000 spectrometer (EI) and HRMS on a Finnigan MAT 95 spectrometer (ESI). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), bs (broad singlet). HPLC measurements were conducted on an Agilent Infinity 1260 HPLC apparatus using an Agilent Eclipse XDB-C18 (4.6 mm ID x 150 mm, 5 mm) column. H_2O/MeOH (60:40) eluent and a flow rate of 1.0 mL/min was used for the measurement of veratrol and methyl 3,4-dimethoxybenzoate. Alkene **2a** along with dicarbonate **6** was measured using a H_2O/MeOH (40:60) eluent and a flow rate of 1.0 mL/min.

2. Preparation of starting materials and product

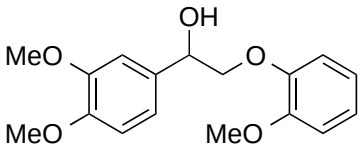
2.1. Synthesis of lignin β-O-4 model compounds

The lignin model compounds (**1a-d** and **1f-h**) used for the cleavage reactions were prepared according to the procedure described in literature.[2] Monolignol **1e** was prepared in three step procedure. The first two reaction steps were prepared in accordance to the procedure by Picart *et al.*.[3] In the final step we used a modified procedure by Bolm and co-workers.[2]



1e

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol (1e)[4]



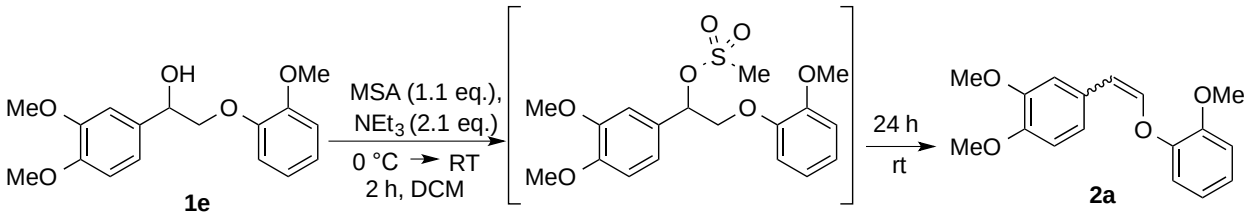
A dry 250 mL three-necked flask equipped with a reflux condenser, an argon inlet, a dropping funnel and a magnetic stirrer was charged with $LiAlH_4$ (12.4 mmol, 0.469 g, 1 eq.) in dry THF (31 mL) and cooled to 0 °C. 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (12.4 mmol, 3.74 g, 1 eq.) was dissolved in dry THF (43 mL) and added dropwise over 15 min at 0 °C. The resulting solution was heated to 60 °C and stirred for 3 h. Then, the reaction mixture was cooled to 0 °C and quenched by the sequential and dropwise addition of water (0.470 mL), aqueous NaOH solution (15 % w/w, 0.470 mL) and additional water (1.410 mL). Upon completion it was stirred for 1 h at room temperature. The reaction mixture was filtered over celite, washed with DCM (150 mL), dried over $MgSO_4$, and the solvent removed under reduced pressure. The product was purified by column chromatography (pentane/EtOAc, 1/1) and **1e** was obtained as a colorless solid (3.06 g, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03-6.88 (m, 6H), 6.86 (d, *J* = 8.2 Hz, 1H), 5.05 (dd, *J* = 9.4 Hz, 2.9 Hz, 1H), 4.17 (dd, *J* = 10.0 Hz, 3.0 Hz, 1H), 3.97 (t, *J* = 9.4 Hz 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.44 (bs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.1, 149.0, 148.7, 147.9, 132.2, 122.5, 121.0, 118.6, 116.9, 111.9, 110.9, 109.3, 76.3, 72.0, 55.9, 55.8, 55.7.

MS (EI, 70 eV): *m/z* (%): 305 $[M+1]^+$ (48), 304 $[M^+]$ (90), 288 (14), 287 (55), 181 (10), 180 (56), 168 (18), 167 (100), 164 (10), 151 (73), 149 (28), 139 (90), 138 (80), 137 (10), 124 (43), 122 (16), 121 (15), 109 (19), 108 (11), 95 (11), 77 (30), 65 (10).

2.2. Synthesis of (*Z*)-1,2-dimethoxy-4-[2-(2-methoxyphenoxy)vinyl]benzene (2a)[5]



To a solution of **1e** (0.2 g, 0.657 mmol) in dichloromethane (5 mL), cooled to 0 °C, was added methanesulfonic anhydride (MSA = 0.13g, 0.722 mmol, 1.1 eq.) and triethylamine (0.2 mL, 2.1 eq.). The reaction was stirred at 0 °C for 30 minutes and then allowed to warm up to room temperature. After stirring overnight, the reaction mixture was diluted with water (10 mL) and extracted with dichloromethane. The organic phase was successively washed with 20 mL of a 1 M HCl solution, brine (30 mL) and water and dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography (pentane/acetone 97:3) to obtain the *Z* isomer of **2a** in 52% yield.

3. Base-catalysed cleavage of lignin β-O-4 model compounds

3.1. General procedure for the base-catalysed cleavage of lignin β-O-4 model compounds in dimethyl carbonate

A 10 mL pressure tube with a teflon screw cap and a magnetic stirrer was charged with model compound **1a-h** (0.250 mmol) and base (0.012 mmol) in dimethyl carbonate (1.2 mL). The mixture was stirred at 180 °C for 8 h or 12 h (depending on the reaction conditions) followed by cooling down to room temperature. A standard solution (1.000 mL of 3,4-dimethoxy benzylalcohol in methanol, c = 0.2 mol/L, for veratrol and methyl 3,4-dimethoxybenzoate and diphenylether in methanol, c = 0.2 mol/L, for alkene **2a**) was added with an Eppendorf pipette to the reaction mixture. The solution was then diluted with water (10 mL) and extracted with dichloromethane. The organic phase was successively washed with 20 mL of a 1 M HCl solution, brine (30 mL) and water and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting residue was dissolved in acetonitrile (15 mL) and three samples were prepared for HPLC measurements by diluting 0.2 mL of the above solution with acetonitrile (1.0 mL) for each sample, followed by filtration into a HPLC vial.

3.2. General procedure for the scaled-up conversion of dilignol 1a

A 25 mL glass-autoclave was charged with dilignol **1a** (0.668 g, 2.00 mmol, 1.0 eq.), cesium carbonate (0.0325g, 0.1 mmol, 0.05 eq.), dimethyl carbonate (9.6 mL) and a magnetic stirrer. The mixture was stirred in a preheated oil bath at 180 °C with 500 rpm for 8 h. The increase in pressure was monitored along the course of the reaction and reached 6 bar at the end of the reaction. After the expiration of the reaction time the autoclave was taken out of the oil bath and

cooled down to room temperature. The remaining pressure (1 bar of extra pressure) was released and the autoclave opened. The mixture was transferred to a 100 mL extraction funnel and the autoclave rinsed with dichloromethane (40 mL).The organic phase was then washed with 40 mL of a 1 M HCl-solution. The aqueous phase was extracted with dichloromethane (5x 20 mL). Next, the combined organic phases were washed with brine (3x 50 mL), dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The products were purified by column chromatography (pentane/acetone 97:3).

4. Pretreatment conditions of the lignin source

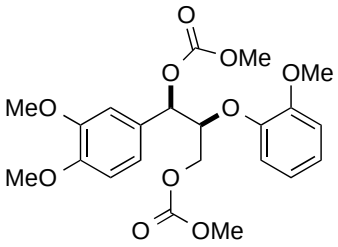
The lignin was extracted from beech wood chips using an organosolv process with aqueous ethanol (60-40% w/w). The lignin was precipitated from both the organosolv liquor and the pulp washing liquor by adding these liquors to an excess of water. The lignin precipitate was sedimented by centrifugation and the liquor above decanted. Finally, the lignin was dried and pulverized.

4.1 General procedure for the base-catalysed cleavage of lignin in dimethyl carbonate followed by NMR measurements.

A 20 mL pressure tube with a teflon screw cap and a magnetic stirrer was charged with organosolv lignin (100 mg) and either Cs_2CO_3 (5 mg, 0.0153 mmol) or LiO*t*-Bu (1.23 mg, 0.0153 mmol) in dimethyl carbonate (5 mL). The mixture was stirred at 180 °C for 8 h or 12 h (depending on the base) followed by cooling down to room temperature. The reaction mixture was then transferred into a 25 mL round bottom flask, followed by removal of dimethyl carbonate under reduced pressure. Next, the product was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) solution and filtered into a NMR tube.

5. Spectroscopic data of the isolated products

Erythro-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diyl dimethyl biscarbonate



clear, viscous liquid

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.00-6.95 (m, 3H), 6.86-6.79 (m, 4H), 5.87 (d, *J* = 6 Hz, 1H), 4.68 (m, 1H), 4.50 (dd, *J* = 12 Hz, 5.4 Hz, 1H), 4.33 (dd, *J* = 12 Hz, 4.3 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H).

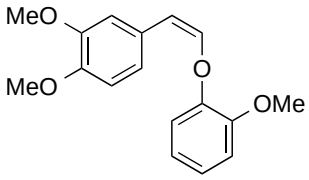
^{13}C NMR (151 MHz, $CDCl_3$): δ = 155.5, 154.7, 151.0, 149.2, 148.8, 146.9, 128.2, 123.6, 120.9, 120.0, 119.4, 112.5, 110.7, 110.5, 79.9, 77.8, 65.8, 55.8 (2C), 55.7, 54.9 (2C).

MS (EI, 70 eV): *m/z* (%): 451 $[M+1]^+$ (10), 450 $[M^+]$ (37), 251 (54), 225 (100), 181 (70).

HRMS (ESI, 70 eV): *m/z* calcd. for $C_{22}H_{26}O_{10}+Na^+$: 473.14182 $[M+Na^+]$; found: 473.14166.

HPLC (MeOH/H_2O, 60/40): t_R = 8.2 min.

(*Z*)-1,2-Dimethoxy-4-[2-(2-methoxyphenoxy)vinyl]benzene[6]



pale yellow solid, mp 77 – 78 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 1.8 Hz, 1H), 7.13 (dd, *J* = 8.2 Hz, 1.8 Hz, 1H), 7.09 (dd, *J* = 8.1 Hz, 1.6 Hz, 1H), 7.09-7.06 (m, 1H), 6.97 (dd, *J* = 9.9 Hz, 1.5 Hz, 1H), 6.94 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 6.9 Hz, 1H), 5.56 (d, *J* = 6.9 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.9, 148.5, 147.7, 146.5, 140.7, 128.1, 123.7, 121.4, 120.9, 116.6, 112.5, 111.9, 110.8, 109.9, 55.9, 55.8, 55.6.

MS (EI, 70 eV): *m/z* (%): 287 $[M+1]^+$ (20), 286 $[M^+]$ (100), 271 (13), 226 (25), 151 (22), 77(34).

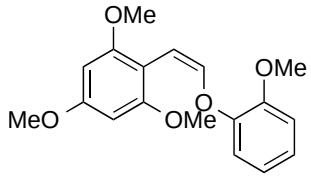
HRMS (ESI, 70 eV): *m/z* calcd. for $C_{17}H_{18}O_4+Na^+$: 309.10973 $[M+Na^+]$; found: 309.11053.

HPLC (MeOH/H_2O, 60/40): t_R = 21.3 min.

Note: (*E*)-1,2-dimethoxy-4-[2-(2-methoxyphenoxy)vinyl]benzene: This alkene was obtained as a minor product and the yields were determined by ^{1}H-NMR.

HPLC (MeOH/H_2O, 60/40): t_R = 15.3 min.

(*Z*)-1,3,5-Trimethoxy-2-[2-(2-methoxyphenoxy)vinyl]benzene



pale white solid, mp 90 – 91 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 12.3 Hz, 1H), 7.09 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.04-7.01 (m, 1H), 6.95-6.93 (m, 1H), 6.92 (dd, *J* = 7.6 Hz, 1.7 Hz, 1H), 6.70 (d, *J* = 12.3 Hz, 1H), 6.15 (s, 2H) 3.90 (s, 3H), 3.83 (s, 6H), 3.81 (s, 3H).

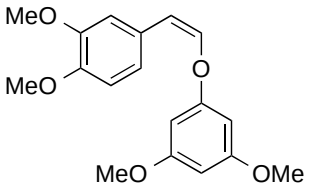
^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.3, 158.3 (2C), 149.6, 147.1, 145.1, 122.8, 120.8, 116.7, 112.2, 105.5, 105.0, 90.8 (2C), 56.0, 55.7 (2C), 55.3.

MS (EI, 70 eV): *m/z* (%): 317 $[M+1]^+$ (10), 316 $[M^+]$ (39), 194 (18), 181 (40), 122 (66), 92 (80), 77 (100).

HRMS (ESI, 70 eV): *m/z* calcd. for $C_{18}H_{20}O_5$+Na^+: 339.12029 $[M+Na^+]$; found: 339.12076.

The stereochemistry of the alkene was determined by NOESY experiments.

(*Z*)-4-[2-(3,5-Dimethoxyphenoxy)vinyl]-1,2-dimethoxybenzene



pale white solid, mp 61– 63 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 1.8 Hz, 1H), 7.17 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.52 (d, *J* = 8.3 Hz, 1H), 6.29 (d, *J* = 2.1 Hz, 2H), 6.22 (t, *J* = 2.1 Hz, 1H), 5.57 (d, *J* = 6.9 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.78 (s, 6H).

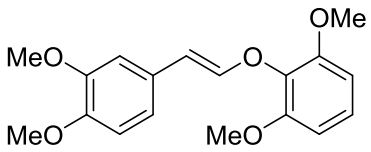
^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.5 (2C), 158.9, 148.5, 147.9, 139.8, 127.8, 121.5, 111.8, 110.9, 110.6, 95.4 (2C), 95.3, 55.8, 55.7, 55.4 (2C).

MS (EI, 70 eV): *m/z* (%): 317 $[M+1]^+$ (20), 316 $[M^+]$ (100), 162 (30).

HRMS (ESI, 70 eV): *m/z* calcd. for $C_{18}H_{20}O_5$+Na^+: 339.12029 $[M+Na^+]$; found: 339.12030.

The stereochemistry of the alkene was determined by NOESY experiments.

(*E*)-2-[(3,4-Dimethoxystyryl)oxy]-1,3-dimethoxybenzene



^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.11 (t, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 12.6 Hz, 1H), 6.77-6.75 (m, 3H), 6.65 (d, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 12.6 Hz, 1H), 3.86 (s, 6H), 3.85 (s, 3H), 3.84 (s, 3H).

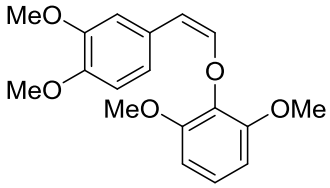
^{13}C NMR (151 MHz, $CDCl_3$): δ = 152.9 (2C), 148.9, 147.4, 146.5, 134, 128.6, 125.1, 118, 111.3, 108.4, 108.2, 105.3 (2C), 56.3 (2C), 55.9, 55.7.

MS (EI, 70 eV): *m/z* (%): 317 $[M+1]^+$ (25), 316 $[M^+]$ (100), 287 (15), 256 (13), 150.9 (10).

HRMS (ESI, 70 eV): *m/z* calcd. for $C_{18}H_{20}O_5+K^+$: 355.09423 $[M+K^+]$; found: 355.09421.

The stereochemistry of the alkene was determined by NOESY experiments.

(*Z*)-2-[(3,4-Dimethoxystyryl)oxy]-1,3-dimethoxybenzene



^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 1.8 Hz, 1H), 7.18-7.16 (m, 1H), 7.07 (t, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 6.6 Hz, 1H), 5.36 (d, *J* = 6.6 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.84 (s, 6H).

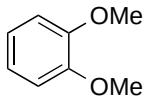
^{13}C NMR (151 MHz, $CDCl_3$): δ = 152.8 (2C), 148.4, 147.2, 145.5, 135.9, 128.7, 124.7, 121.3, 112.2, 110.7, 106.5, 105.5 (2C), 56.3 (2C), 55.8, 55.6.

MS (EI, 70 eV): *m/z* (%): 317 $[M+1]^+$ (20), 316 $[M^+]$ (100), 287 (19), 256 (18), 150.9 (12).

HRMS (ESI, 70 eV): *m/z* calcd. for $C_{18}H_{20}O_5+Na^+$: 339.12029 $[M+Na^+]$; found: 339.12036.

The stereochemistry of the alkene was determined by NOESY experiments.

1,2-Dimethoxybenzene[7]



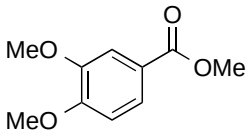
^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.94-6.88 (m, 4H), 3.88 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.9 (2C), 120.8 (2C), 111.2 (2C), 55.7 (2C).

MS (EI, 70 eV): *m/z* (%): 138 $[M^+]$ (100), 94.9 (14).

HPLC ($MeOH/H_2O$, 40/60): t_R = 10.0 min.

Methyl 3,4-dimethoxybenzoate[8]



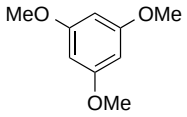
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.8, 152.9, 148.5, 123.5, 122.6, 111.9, 110.2, 56.0, 55.9, 52.0.

MS (EI, 70 eV): *m/z* (%): 196 [M^+] (100), 165 (83), 124.9 (18), 79(25).

HPLC (MeOH/H_2O, 40/60): t_R = 14.3 min.

1,3,5-Trimethoxybenzene[9]

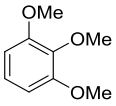


^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.09 (s, 3H), 3.77 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.4 (3C), 92.8 (3C), 55.2 (3C).

MS (EI, 70 eV): *m/z* (%): 169 [M+1]$^+$ (14), 168 [M^+] (100), 139 (52), 124.9 (14).

1,2,3-Trimethoxybenzene[10]

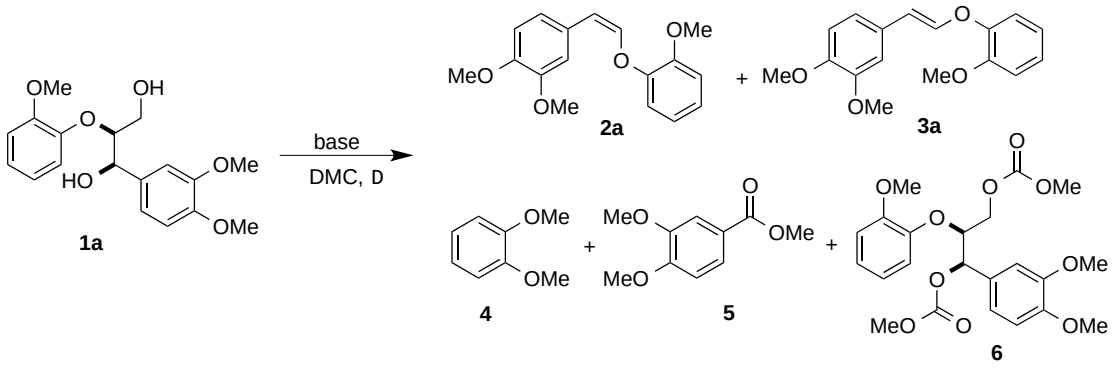


^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (t, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 6H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.4 (2C), 138, 123.6, 105.1 (2C), 60.8, 56 (2C).

MS (EI, 70 eV): *m/z* (%): 169 [M+1]$^+$ (10), 168 [M^+] (100), 153 (49), 124.8 (24), 109.8 (23).

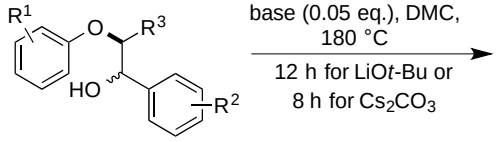
6. Screening of various bases for the bond cleavage reactions of dilignol 1a

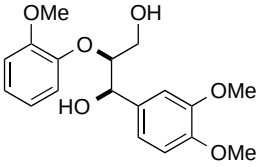
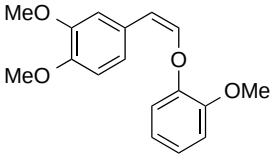
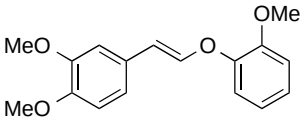
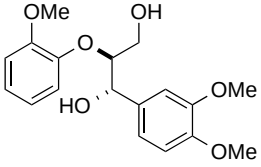
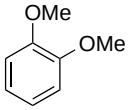
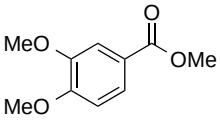
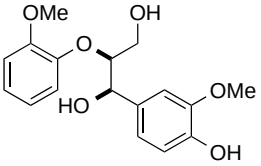
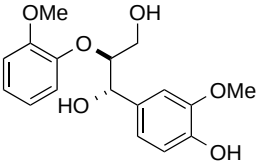
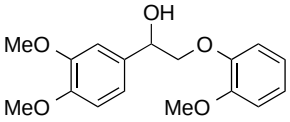
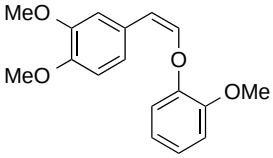
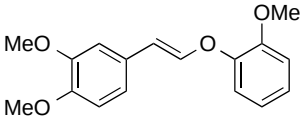
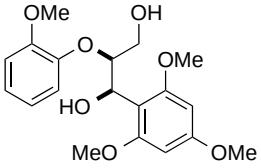
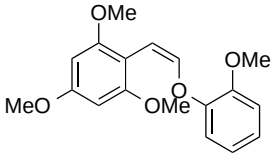
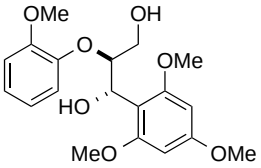
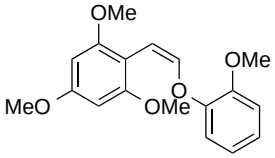
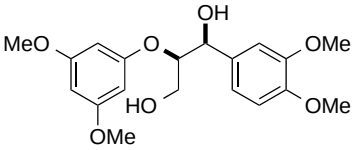
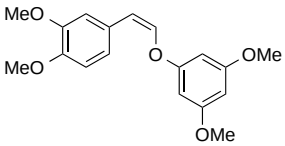


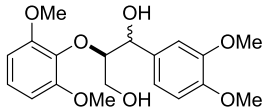
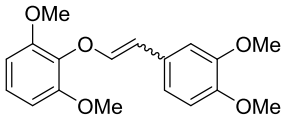
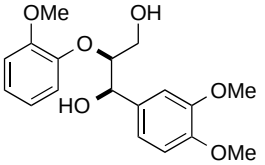
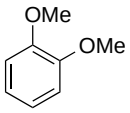
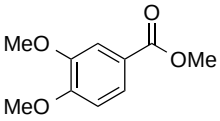
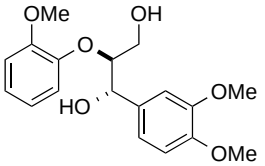
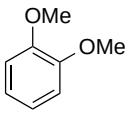
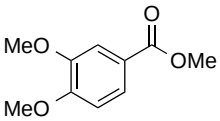
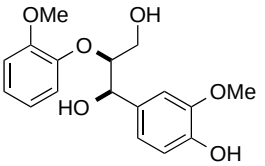
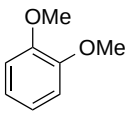
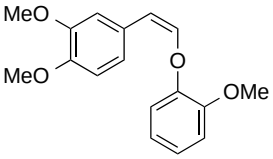
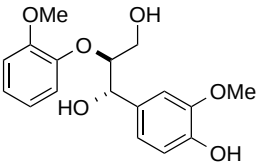
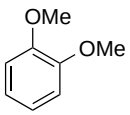
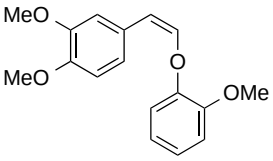
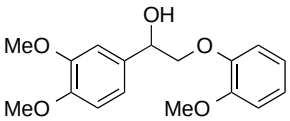
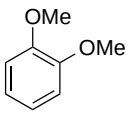
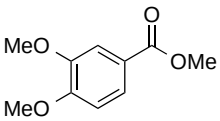
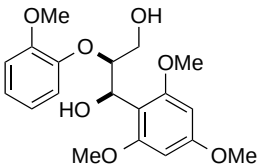
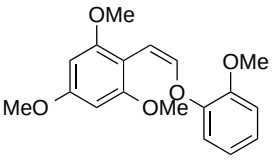
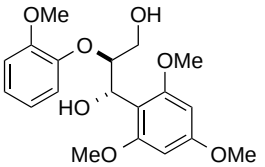
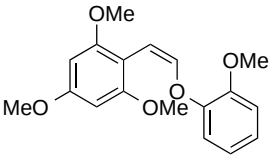
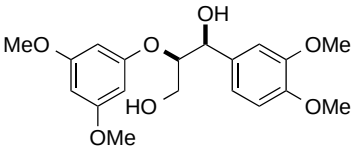
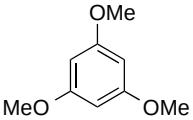
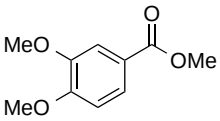
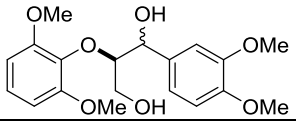
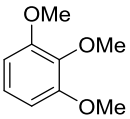
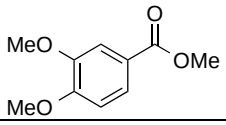
Entry	Base	Conv. [%]	Product [%] 2a[e]	3a[f]	4[e]	5[e]	6[e]
1	LiO*t*-Bu	100	56	8	-	-	20
2[a]	LiO*t*-Bu	100	75	9	-	-	-
3[b]	LiO*t*-Bu	100	73	11	-	-	-
4[d]	LiO*t*-Bu	100	23	1	-	-	-
5[a]	LiOH	100	34	2	-	-	25
6[a]	Li_2CO_3	100	2	-	-	-	60
7	NaOH	100	9	trace	14	1.0	5
8	Na_2CO_3	100	4	trace	6	0.5	22
9	$NaHCO_3$	100	17	1	5	0.5	10
10	$NaOCH_3$	100	8	1	12	1.5	15
11	NaOAc	100	3	trace	7	1.0	50
12	NaI	100	7	trace	10	1.0	43
13	NaO*t*-Bu	100	2	-	8	trace	10
14	KO*t*-Bu	100	-	-	36	6	3
15	KOH	100	-	-	36	7	2
16[b]	KOH	100	-	-	55	15	trace
17	K_2CO_3	100	-	-	32	5	2
18[b]	K_2CO_3	100	-	-	54	16	trace
19	K_3PO_4	100	-	-	26	4	trace
20	KBr	100	-	-	9	1	15
21[b]	KBr	100	-	-	55	15	trace
22	Cs_2CO_3	100	-	-	60	14	-
23[c]	Cs_2CO_3	100	-	-	23	2	-
24[d]	Cs_2CO_3	100	-	-	24	3	-
25[b]	HT-Sigma	100	30	2	-	-	15
26	HT-Sigma	100	4	trace	-	-	40
27	HT-Calcined	100	43	2	-	-	trace
28	Et_3N	100	-	-	22	3	26

Reaction conditions: dilignol **1a** (0.25 mmol), base (0.0125 mmol, 0.05 eq.), DMC (1.2 mL), 8 h, 180 °C, 500 rpm; [a] 12 h; [b] 24 h; [c] 150 °C; [d] reflux; [e] yields determined by HPLC with 3,4-dimethoxybenzyl alcohol and diphenyl ether as internal standards; [f] yields determined by ^{1}H-NMR

7. Expanding the scope of the reaction to other model compounds



Entry	Substrate	Base	Product 1	Yield [%]	Product 2	Yield [%]
1[a]		LiO*t*-Bu		75		9
2[a]		LiO*t*-Bu		20		6
3		LiO*t*-Bu	-	-	-	-
4		LiO*t*Bu	-	-	-	-
5[a]		LiO*t*-Bu		13		1
6[b]		LiO*t*-Bu		85	-	-
7[b]		LiO*t*-Bu		81	-	-
8[b]		LiO*t*-Bu		82	-	-

9[b]		LiO*t*-Bu		64	-	-
10[a]		Cs_2CO_3		60		14
11[a]		Cs_2CO_3		61		15
12[a]		Cs_2CO_3		45		15
13[a]		Cs_2CO_3		42		13
14[a]		Cs_2CO_3		18		16
15[b]		Cs_2CO_3		80	-	-
16[b]		Cs_2CO_3		82	-	-
17[b]		Cs_2CO_3		57		12
18[b]		Cs_2CO_3		62		16

Reaction conditions: **1** (0.25 mmol), LiO*t*-Bu / Cs_2CO_3 (0.05 eq.), dimethyl carbonate (1.25 mL), 180 °C, 12 h / 8h. [a] yields determined by HPLC with 3,4-dimethoxybenzyl alcohol and diphenyl ether as internal standards; [b] yields after column chromatography.

8.References

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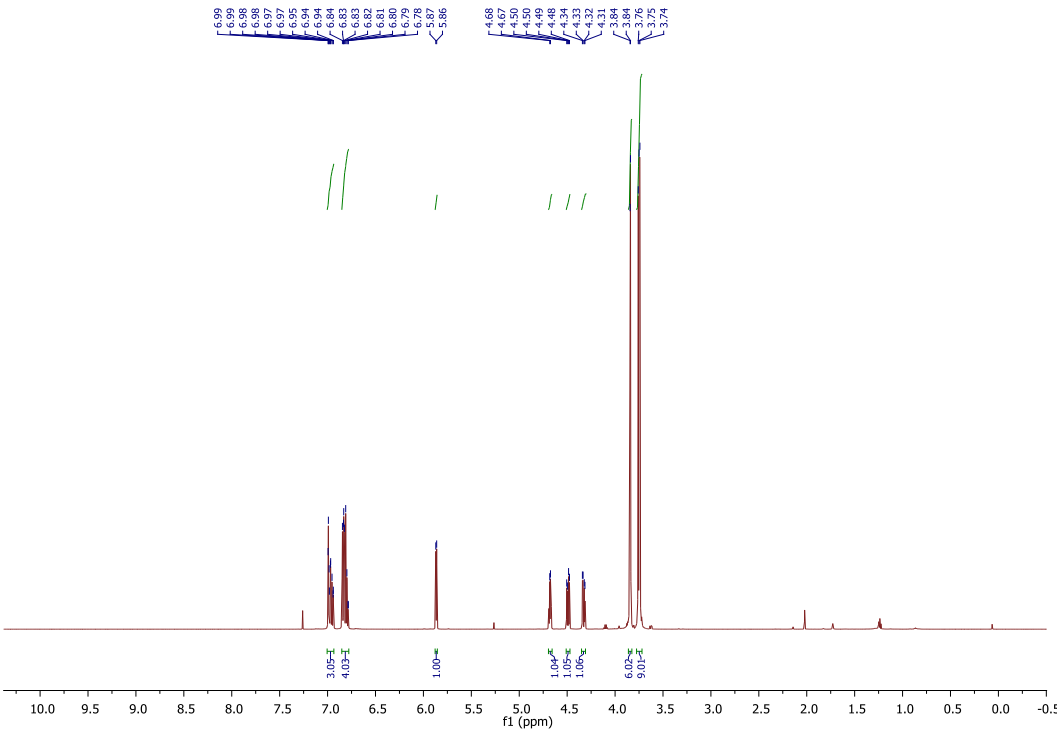
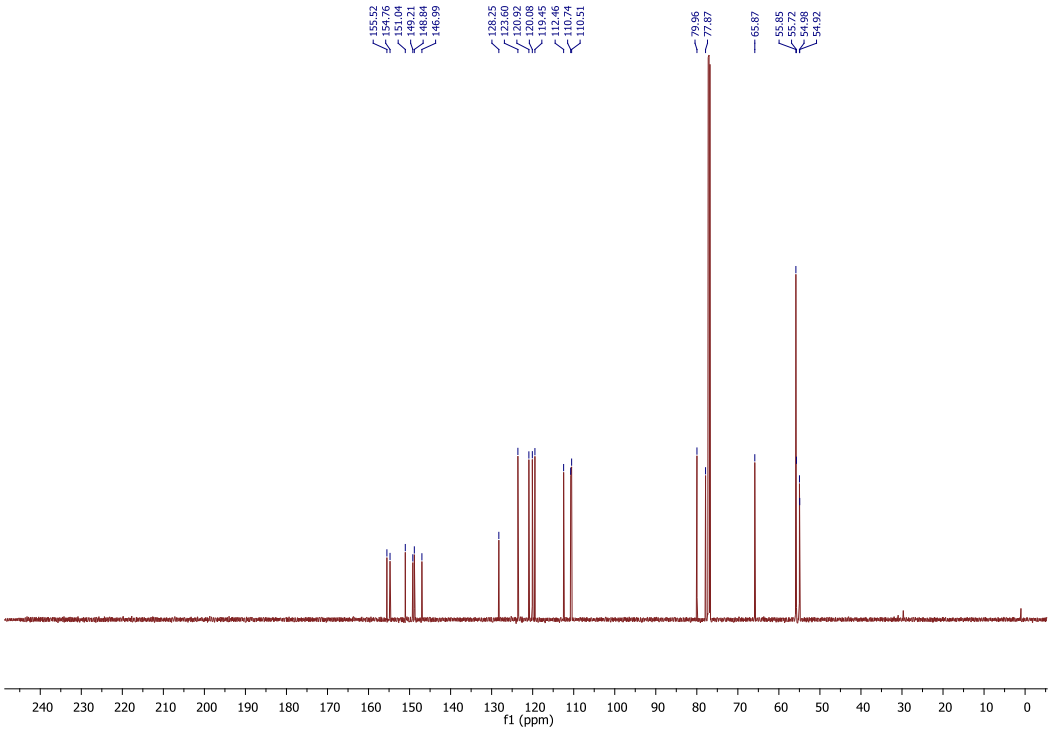
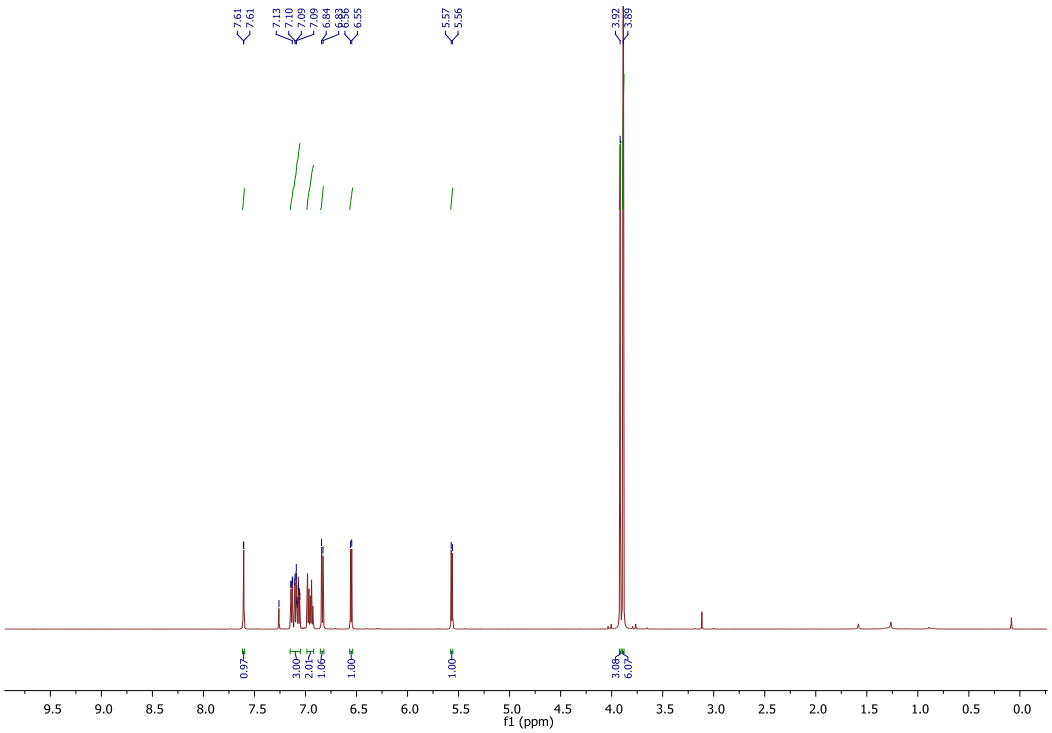
9.NMR spectra:

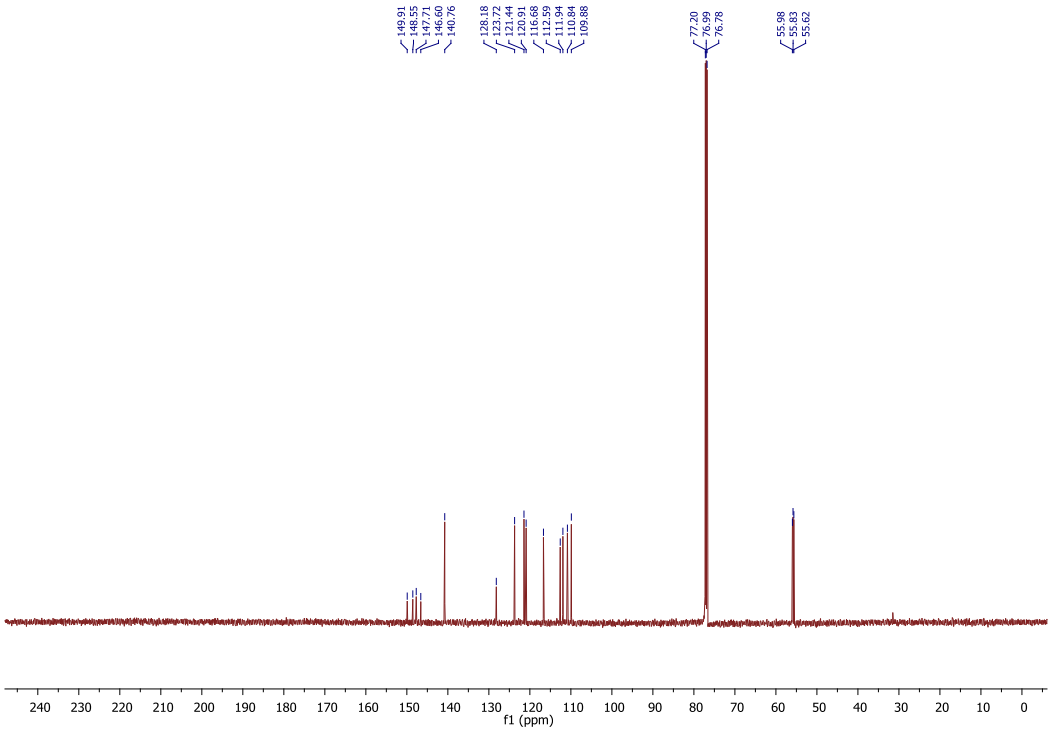
9.1 *Erythro*-1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diyl dimethyl biscarbonate



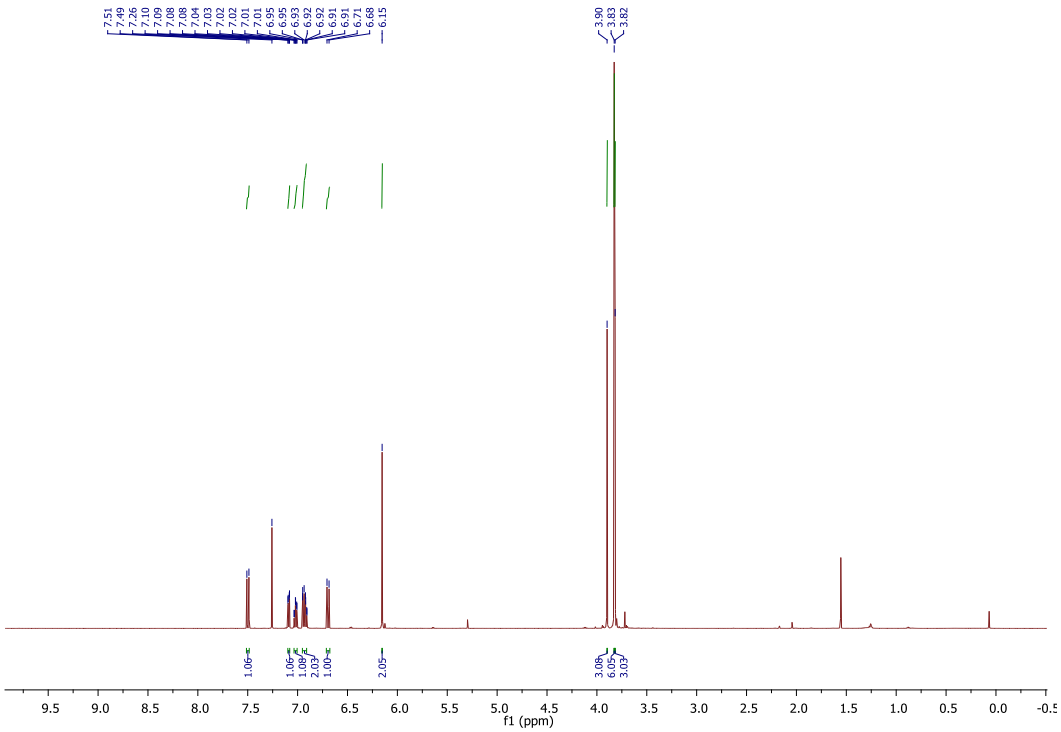


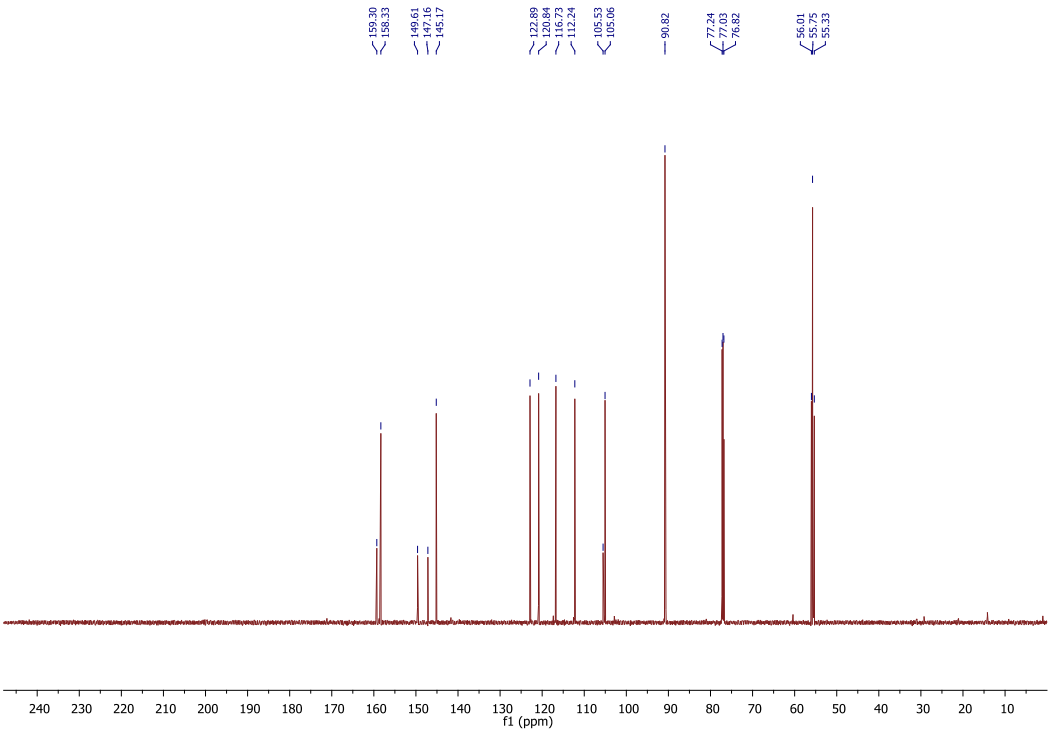
9.2 (*Z*)-1,2-Dimethoxy-4-[2-(2-methoxyphenoxy)vinyl]benzene



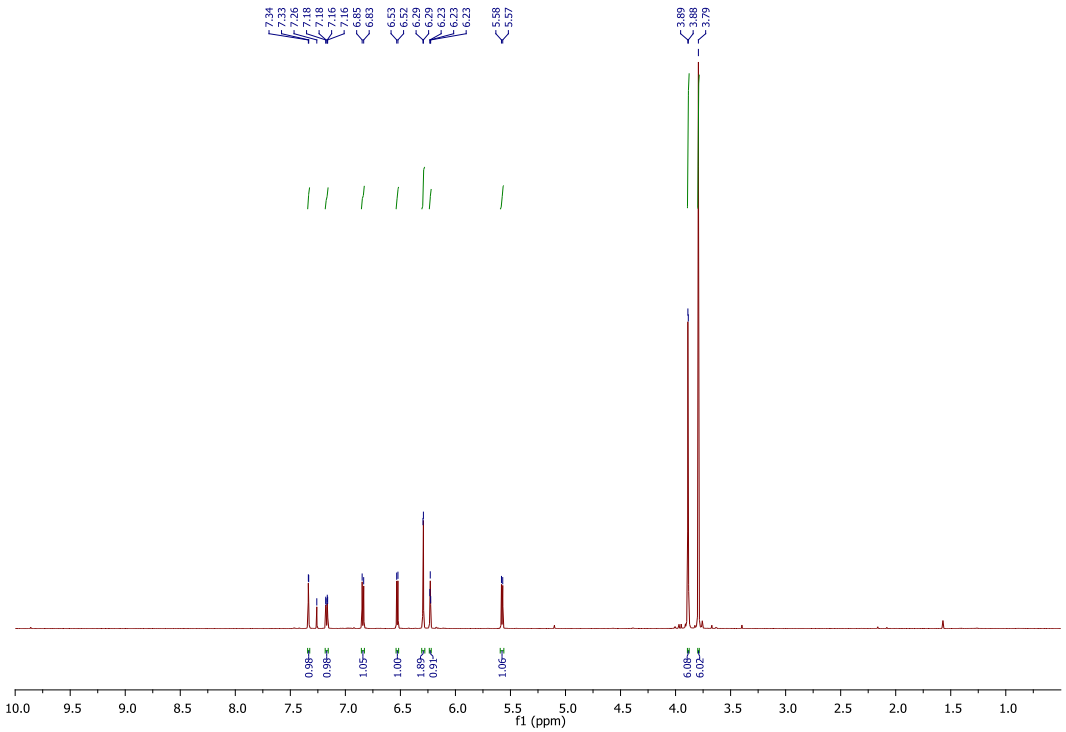


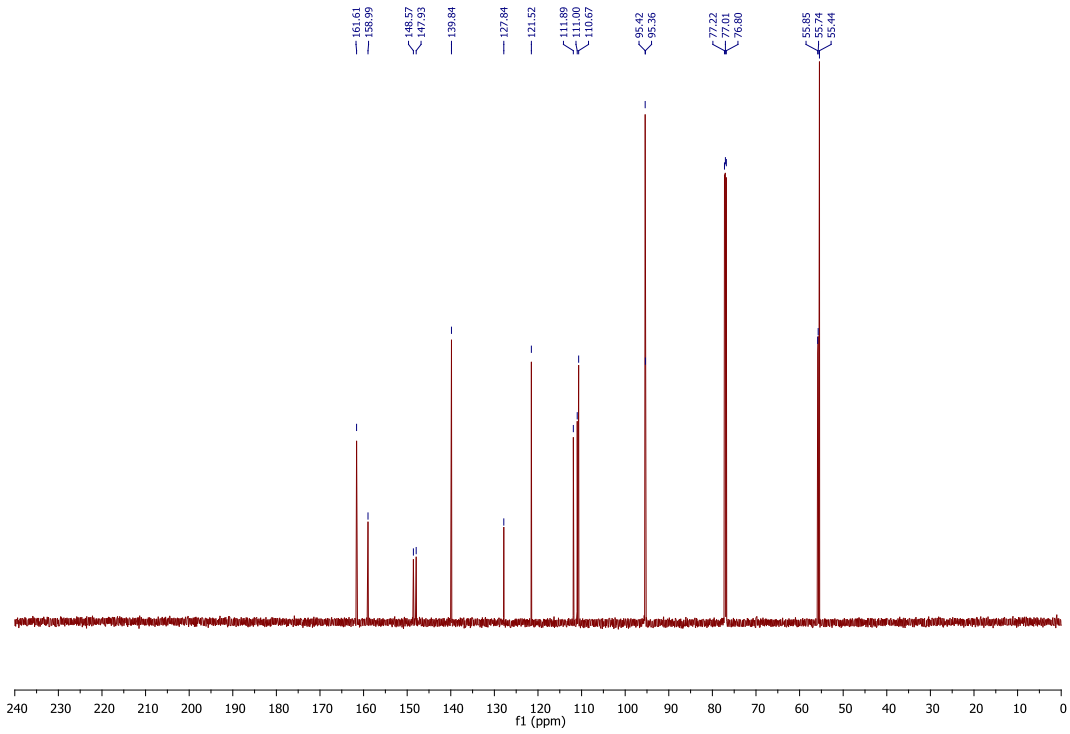
9.3 (*Z*)-1,3,5-Trimethoxy-2-[2-(2-methoxyphenoxy)vinyl]benzene



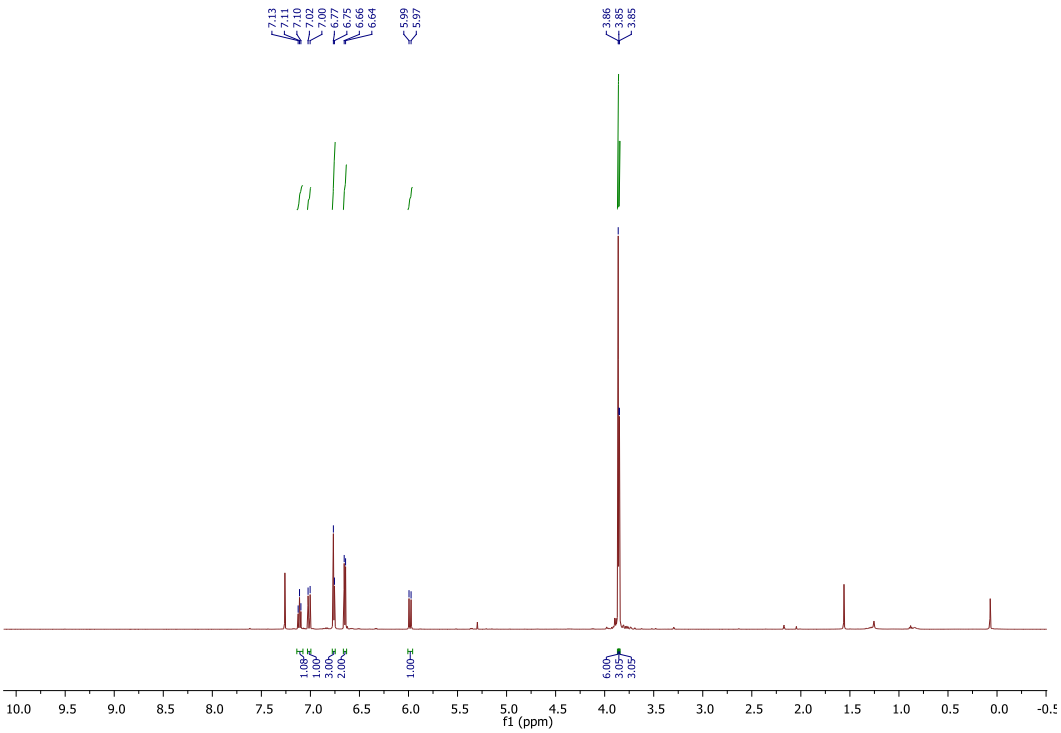


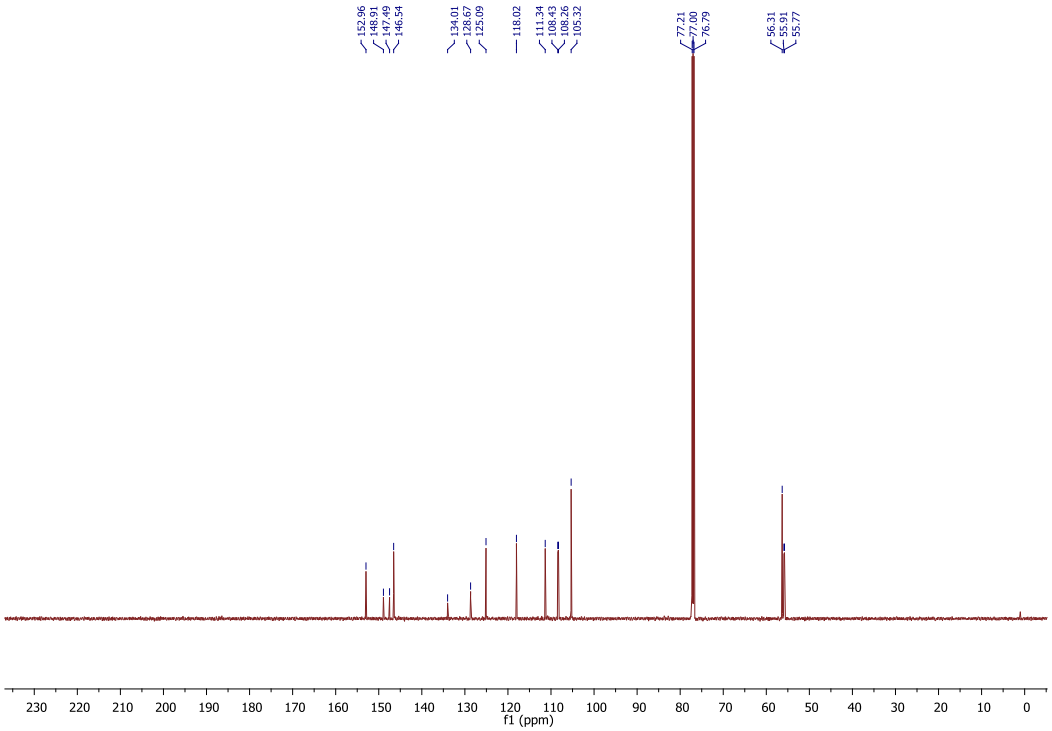
9.4 (*Z*)-4-[2-(3,5-Dimethoxyphenoxy)vinyl]-1,2-dimethoxybenzene



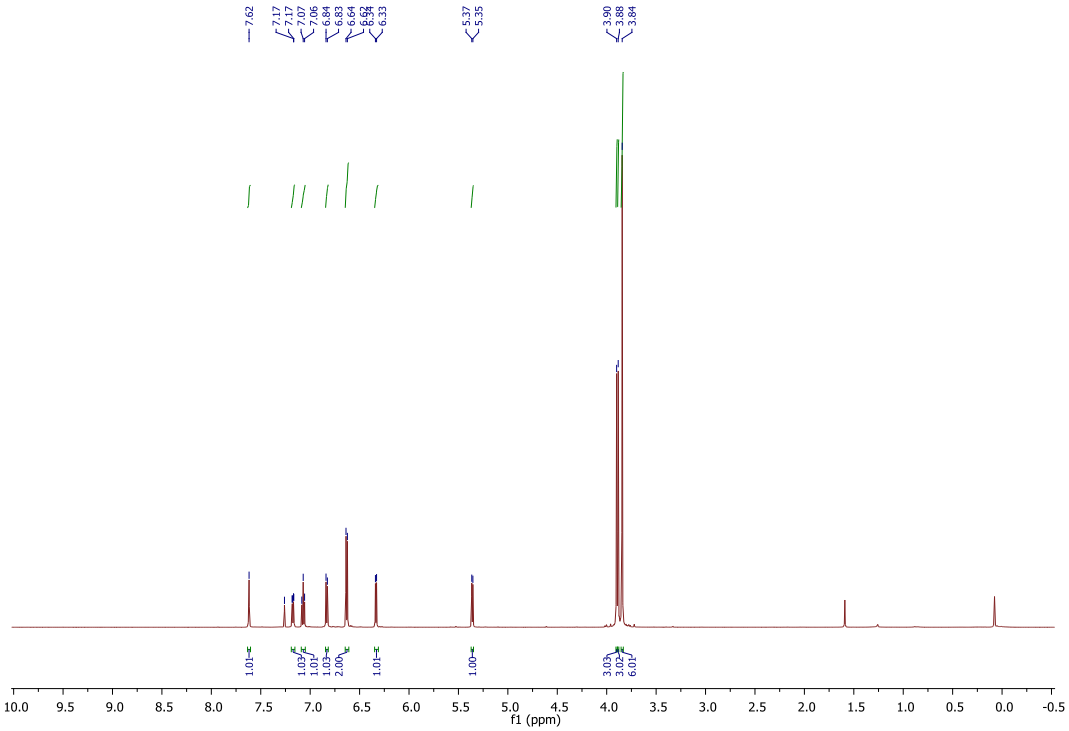


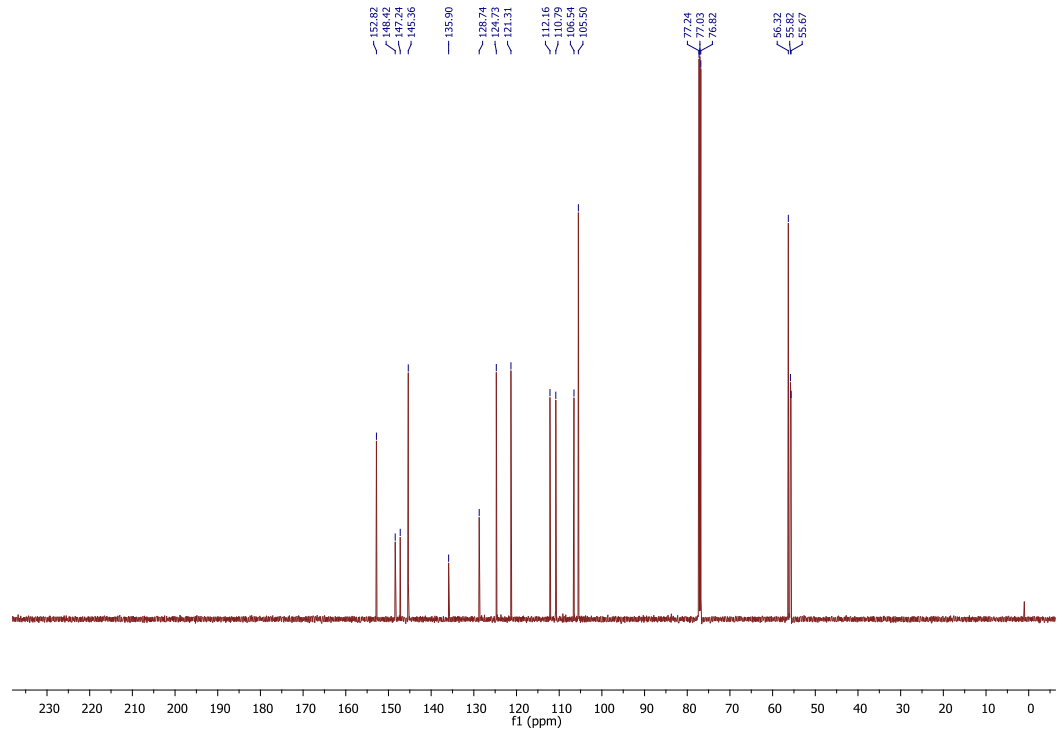
9.5 (*E*)-2-[(3,4-Dimethoxystyryl)oxy]-1,3-dimethoxybenzene





9.6 (*Z*)-2-[(3,4-Dimethoxystyryl)oxy]-1,3-dimethoxybenzene





9.7 NMR measurements for lignin

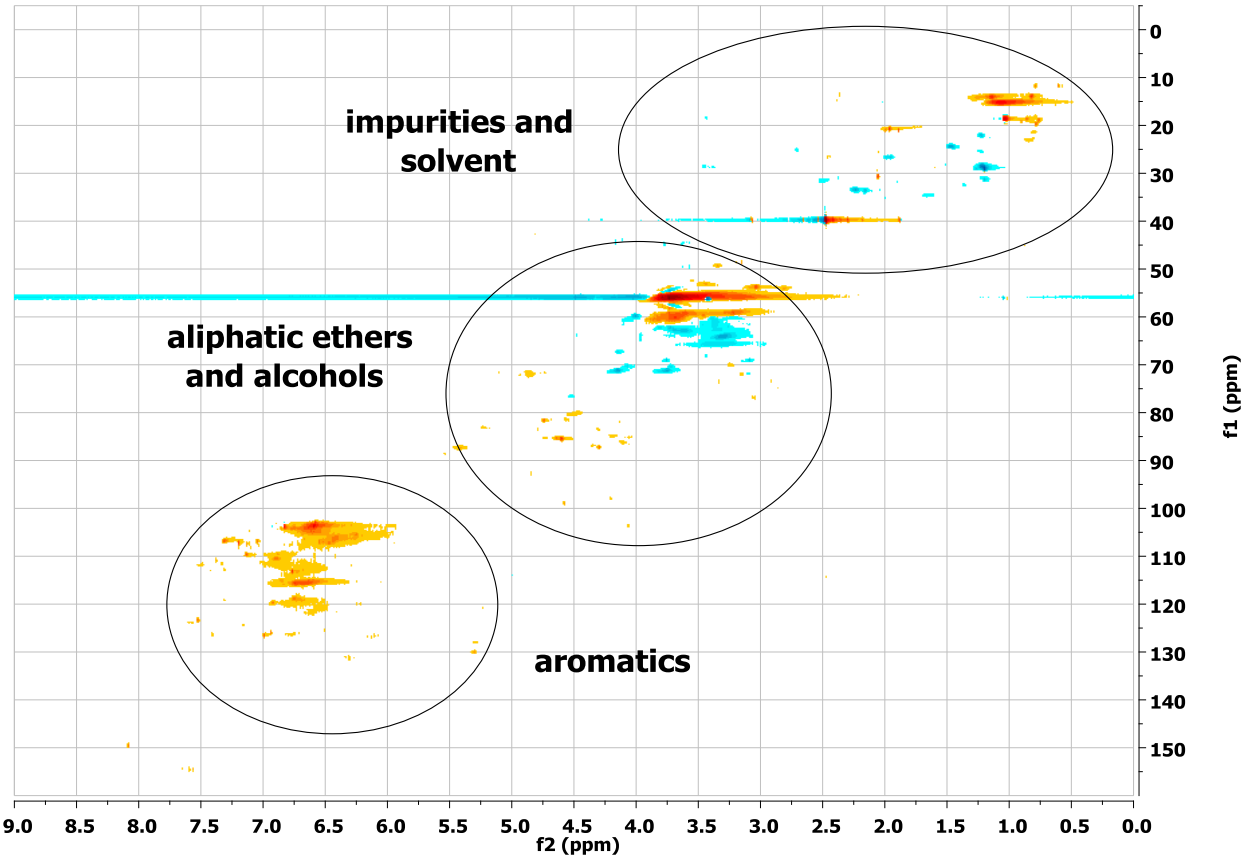


Figure S1: HSQC NMR spectrum of organosolv beech lignin in DMSO-d_6 before the reaction.

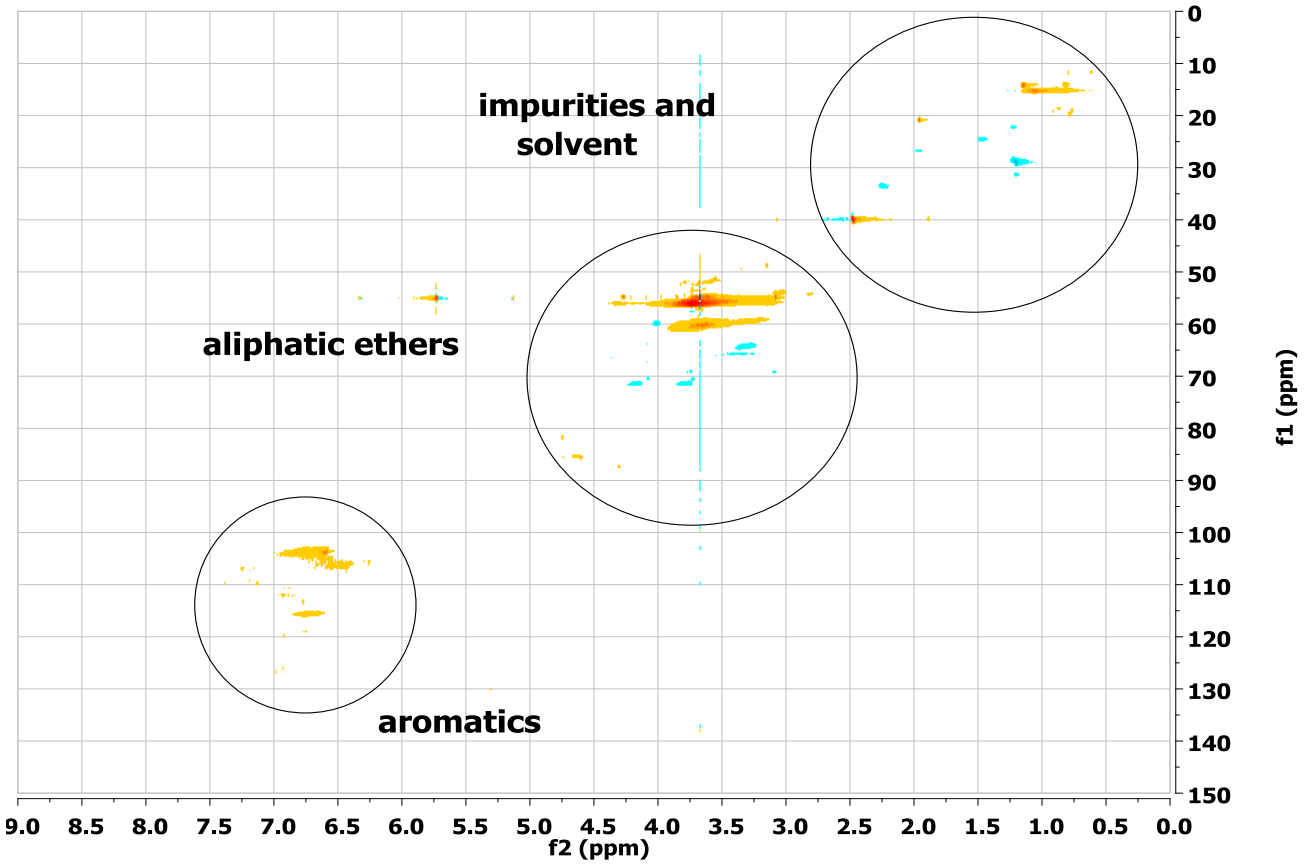


Figure S2: HSQC NMR spectrum of organosolv beech lignin in DMSO-d_6 after the reaction with Cs_2CO_3.

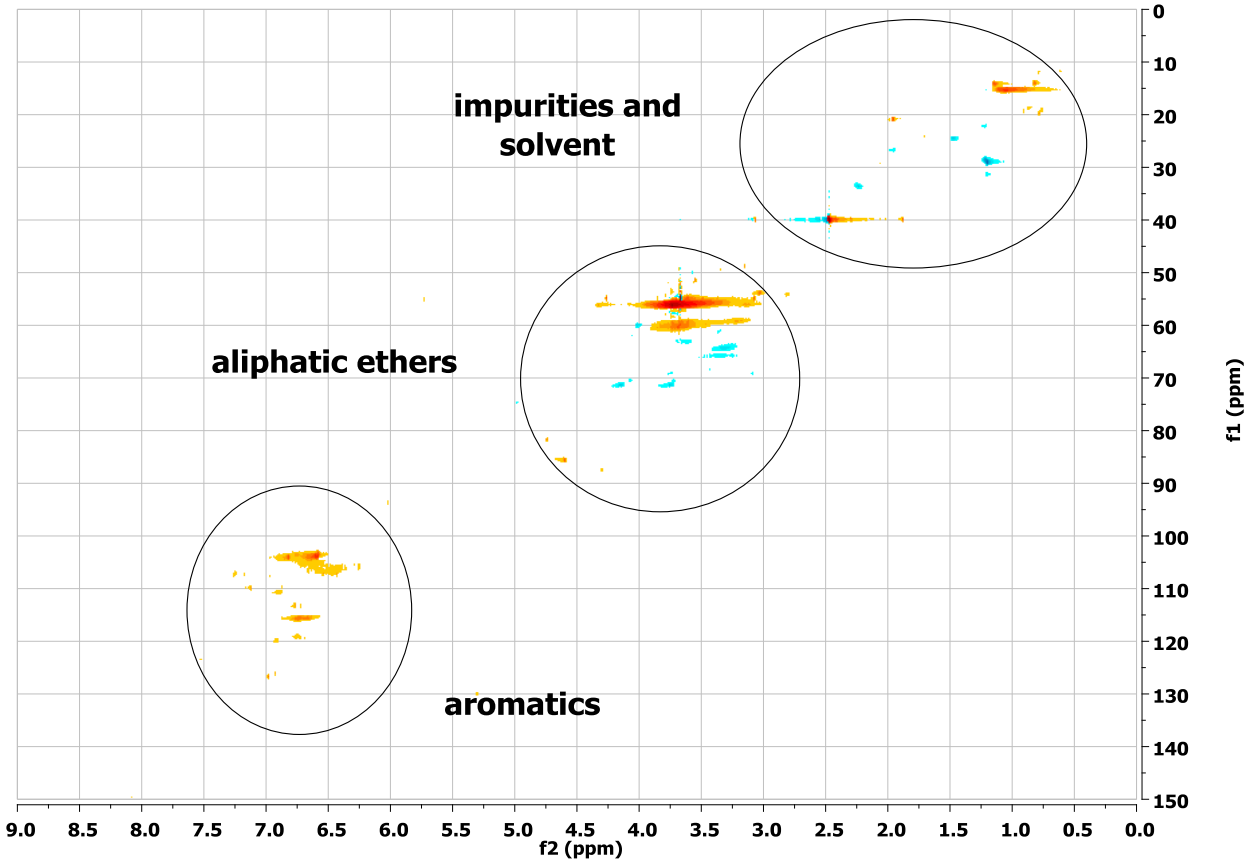


Figure S3: HSQC NMR spectrum of organosolv beech lignin in DMSO-d_6 after the reaction with LiO*t*-Bu.