Electronic Supporting Information

Mechanistic studies of base-catalysed lignin depolymerisation in dimethyl carbonate

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1. General

1.1 Materials and methods

Dimethyl carbonate (DMC) was purchased from Alfa Aesar and was used without further purification. Cesium carbonate and lithium *tert*-butoxide were purchased from Sigma Aldrich and Acros Organics, respectively. Kraft Lignin **370959** was purchased from Sigma Aldrich. THF used for the model compound synthesis 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.

1.2 Instruments

Nuclear Magnetic Resonance (NMR): The 2D-HSQC NMR spectra for lignin samples were recorded on a Bruker Avance III 500 MHz or Bruker Ascend 700 MHz spectrometer using previously described methods in DMSO-d_6 solvent.[1] The ^{31}P NMR analysis for the lignin samples were recorded on a Varian Mercury 300 MHz spectrometer. The ^{1}H and ^{13}C spectra for the analysis of reactions with model compounds 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. Abbreviations are as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), dt (doublet of triplet) br.s (broad singlet), br.d (broad doublet), br.t (broad triplet).

Mass spectrometry: The mass data were recorded on a Finnigan SSQ 7000 spectrometer (EI) and HRMS on a Finnigan MAT 95 spectrometer (ESI).

High performance liquid chromatography (HPLC): The measurements were conducted on a Shimadzu UFLC system equipped with a photodiode detector (Shimadzu SPD-M20A Prominence) and an Agilent Eclipse XDB-C18 Column (5 μm 4.6 x 150 mm). Analysis was performed using Shimadzu Lab solutions Version 5.51 software. MeCN (0.1% formic acid) (A)/H_2O (0.1% formic acid) (B) were used as eluents with a flow rate of 1.0 mL/min.

HPLC Method: 5% A/95% B for 10 minutes followed by a gradient to 95% A/5% B over 30 minutes followed by 10 minutes at 95% A/5% B followed by a gradient to 5% A/95% B over 5 minutes followed by 5 minutes at 5% A/95% B at a flow rate of 1.0 mL/min.

Gel Permeation Chromatography (GPC): The GPC measurements were performed on an Agilent technologies 1200 series system equipped with an Isocratic pump G1310 A. Three PL-gel 3lm MIXED-E columns were operated in series at 42 °C. A mixture of DMF with 0.2 M LiCl was used as solvent with a flow-rate of 1 mL/min and an injection volume of 100 μL. The signals were detected with an ECO Sec RI detector. The molecular weight was determined using polystyrene sulfonate standards of known molecular weight distribution.

Melting Point: Melting points were measured with a Büchi Melting Point B-540 apparatus.

Reaction profile: Modelled rate analysis lines were obtained using DYNAFIT software**.**

Computational Details: All quantum chemical calculations were performed with a Gaussian 09 Revision D.0[2] on the facilities of the IT Centre of RWTH Aachen University. For geometry optimisations Head-Gordon's long-range corrected density functional ζB97X-D[3] was used with the SDD pseudopotential[4] for cesium and Dunning's double-ζ cc-pVDZ basis set[5] for all other atoms. Single-point calculations were performed with the SDD pseudopotential for cesium Pople's triple-ζ basis set 6-311++G(d,p).[6] Solvation effects were simulated with a polarisable continuum model (PCM) for dimethyl carbonate.[7] The static dielectric constant was defined as 3.13[8] and the dynamic dielectric constant as 1.87 based on the refractive index of dimethyl carbonate.[9] The nature of the obtained structure was evaluated with normal mode analysis. Gibbs free energies were calculated for a temperature of 298.15 K. A standard state correction for a 1 M solution was applied.

2. Experimental Information for BCD of lignin

2.1 Lignin organosolv extraction processes:

a) Dioxasolv cherry and oak lignin: The lignins were extracted following a previously established literature procedure[1]

A 2 L flask was charged with either cherry or oak sawdust (200 g) and 1,4-dioxane (1.5 L) was added followed by the addition of 2N HCl (0.16 L) solution. The mixture was heated to a gentle reflux under a N_2 atmosphere for 1 hour. It was then cooled to room temperature and the lignin containing liquor was collected by filtration. This liquor was concentrated under vacuum, resulting in a gummy residue, which was then taken up in acetone/water (9:1, ~250 mL) and precipitated by addition to rapidly stirring water (2.5 L). The crude lignin was collected by filtration and dried under vacuum. The dried crude lignin was taken up in acetone/methanol (9:1) and precipitated by dropwise addition to rapidly stirring Et_2O (2.0 L). The precipitated lignin was collected by filtration and dried under vacuum to give purified samples of cherry/ oak lignin (ca. 20 g). These lignins were used in subsequent experiments without further processing.

b) Ethanosolv beechwood Lignin:

The beechwood lignin was extracted from the corresponding wood chips using the following ethanol-based organosolv process. The lignin was extracted with aqueous ethanol (50% w/w) without the addition of an acid catalyst. Lignin was then precipitated with water and afterwards washed with water to remove the residual carbohydrates. The precipitate was sedimented by centrifugation and the liquor above decanted. Finally, the lignin was dried and pulverised.

2.2 Lignin Profiling:

a) Identification and quantification of major structures in the lignin polymers by 2D-HSQC NMR methodology:

The organosolv beechwood, oak and cherry lignins along with Aldrich-Kraft lignin were characterised using 2D-HSQC experiments (**Fig. S1**) following a previously published report.[10] The signals corresponding to the major structural linkages in the 2D-HSQC NMR spectra were identified and their respective areas were used to determine relative quantities of the major linkages. This was done by taking integrals corresponding to the α-proton in various linkages (**A**: β-O-4, **B**: β-β, **C**: β-5) relative to the aromatic signals while maintaining the same contour level.

Quantification Results:

Figure S1: These calculations revealed a low β-O-4 content of 5 per 100 aromatic units for Aldrich-kraft lignin having an S:G:H ratio of trace:100:0. Oak and cherry lignins on the contrary resulted in a β-O-4 content of 33 per 100 aromatic units and 49 per 100 aromatic units respectively, with an S:G:H ratio of 84:14:0 corresponding to both lignin samples. The ethanosolv beechwood lignin afforded a β-O-4 content of 24 per 100 aromatic units and an S:G:H ratio of 73:27:0. It is important to note that the above values are bound to have a certain degree of error owing to differences in relaxation time, therefore they should mainly be referred to for comparative studies of different lignins and not as exact values.

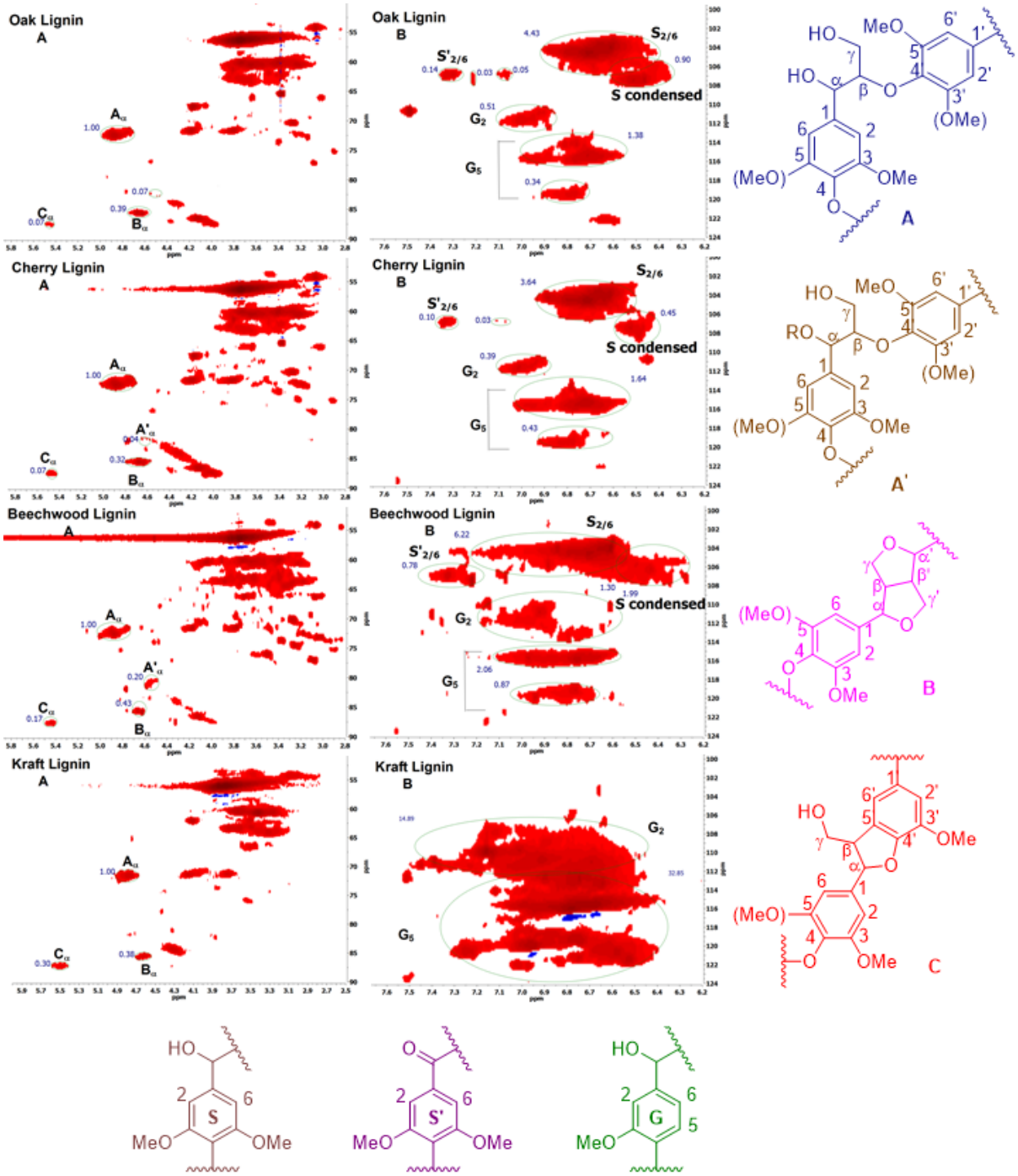

Fig. S1 2D-HSQC NMR spectra of lignins: A) Region from ppm 2.5–6.0 in the ^{1}H, 50–90 in the ^{13}C; B) Region from ppm 7.2–7.6 in the ^{1}H, 100–124 in the ^{13}C. **A:** β-O-4′ aryl ether linkages with a free-OH at the α-carbon; **A′:** β-O-4′ aryl ether linkages with α-methoxylated/ethoxylated units; **B:** resinol substructures formed by β–β′-, α-O-γ′-, and γ-O-α′-linkages; **C:** phenyl coumaran substructures formed by β-5′- and α-O-4′-linkages; e) **S:** syringyl units; **S′:** syringyl unit with oxidised benzylic position; **G:** guaiacyl units.

b) Quantitative ^{31}P NMR spectroscopy:

The quantitative ^{31}P NMR analysis for the phenolic and the aliphatic hydroxyl groups in the lignins, both before and after the base-catalysed depolymerisation (BCD) (**Fig. 3**), were conducted on a Brukner 300 MHz spectrometer following previous literature reports.[11] 30 mg vacuum dried lignin sample was dissolved in 700 µL of an anhydrous solvent mixture (pyridine:$CDCl_3$, 1.6:1, v/v). 100 µL of a cyclohexanol solution (10.85 mg/mL) was added as an internal standard along with 100 µL of chromium (III) acetylacetonate solution (5.2 mg/mL) as the relaxation reagent. Finally, 100 µL of the phosphitylating agent (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxa phospholane) was added and the mixture was transferred into a 5 mm NMR tube for NMR acquisition using 512 scans, 250 ppm sweep width and a relaxation delay of 10 sec.

Table S1: Comparative study based on quantitative ^{31}P NMR calculating the decrease in the amount of hydroxyl groups (mmol/g) following the BCD approach.

Lignins	OH (mmol/g)[(a)]				
	Aliphatic OH	5-Substituted OH	Guaiacyl OH (G)	*p*-Hydroxyphenyl OH (H)	COOH
OS-Oak (before rxn.)	**2.37**	**1.06**	**0.56**	**0.05**	**0.12**
OS-Oak (rxn. with Cs_2CO_3)	0.05	0.02	0.01	-	-
OS-Oak (rxn.with LiO*t*-Bu)	0.37	0.55	0.15	-	-
OS-BW (before rxn.)	**2.38**	**1.24**	**0.69**	**0.01**	**0.01**
OS-BW (rxn. with Cs_2CO_3)	0.03	0.03	0.01	-	-
OS-BW (rxn. with LiO*t*-Bu)	0.25	0.40	0.18	-	-
OS-C (before rxn.)	**1.90**	**1.70**	**0.88**	**0.03**	**0.07**
OS-C (rxn. with Cs_2CO_3)	0.04	0.03	0.03	-	-
OS-C (rxn. with LiO*t*-Bu)	0.15	0.61	0.23	-	-
Kraft (before rxn.)	**1.79**	**0.90**	**1.77**	**0.17**	**0.20**
Kraft (rxn. with Cs_2CO_3)	0.01	0.01	0.02	-	-
Kraft (rxn. with LiO*t*-Bu)	0.07	0.06	0.12	-	-

(a) Quantifications are relative to a known amount of cyclohexanol as an internal standard.

C) GPC analysis of lignin samples:

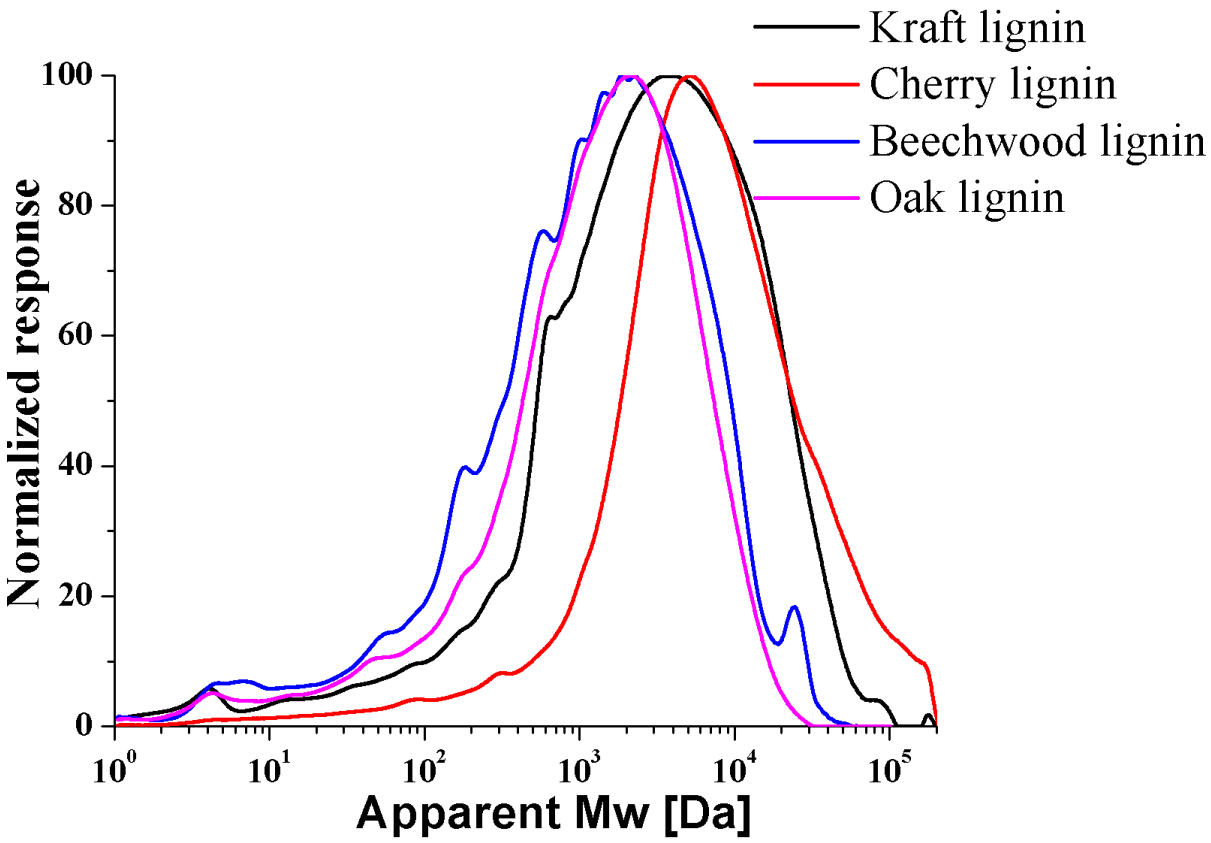

Fig. S2 GPC (DMF/LiCl) graphs of organosolv and kraft lignin measured using RI detector with respect to polystyrene sulfonate standards.

Table S2 The average molar mass (M_n) and weight average molar mass (M_w) determined by GPC (DMF/LiCl) using polystyrene sulfonate standards.

Entry	Lignin	M_n (g/mol)	M_w (g/mol)
1	Aldrich-Kraft	137	7106
2	Beechwood	113	3103
3	Cherry	441	15220
4	Oak	117	2610

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2.3 General procedure for the BCD of lignin in DMC

A 20 mL pressure tube with a Teflon screw cap and a magnetic stirrer was charged with lignin (100 mg) and either Cs_2CO_3 (10 wt%, 0.03 mmol) or LiO*t*-Bu (10 wt%, 0.125 mmol) in dimethyl carbonate (5.0 mL). The mixture was stirred at 180 °C for 8 h or 12 h (depending on the base) followed by cooling to room temperature.

Workup for 2D-HSQC NMR: The reaction mixture was transferred into a 25 mL round bottom flask, followed by the removal of dimethyl carbonate under reduced pressure. Next, the residue was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) solution and filtered into an NMR tube.

Workup for GPC analysis and ^{31}P NMR: The reaction mixture was transferred into a 25 mL round bottom flask, followed by removal of dimethyl carbonate under reduced pressure. The resulting residue was further analysed by GPC or died overnight under reduced pressure and used for ^{31}P NMR analysis.

Workup for GC-MS analysis: After the completion of the reaction, the solvent (DMC) was removed under reduced pressure. The resulting residue was then transferred into a centrifuge tube with EtOAc (5 mL) and spun at 5000 rpm for 10 min. The EtOAc soluble products were separated from the insoluble residue by multiple centrifugations using fresh EtOAc for each run (3·5 mL). The soluble fractions were combined and the solvents evaporated under reduced pressure resulting in an oil. The insoluble residue was then washed with water (3·5 mL) and pentane (3·5 mL). The oil and residue fractions were further dried overnight at 40 °C under vacuum and the weights corresponding to each fraction are given in **Table S2**. The oil containing the low molecular weight components was re-dissolved in EtOAc and a known amount of external standard (*n*-octadecane) was added to it. This mixture was analysed by GC-MS for the identification and quantification of methoxy-capped compounds.

2.4. Analysis of depolymerised lignin reaction mixtures

Table S3: Dry weights of the oil and residue fractions for lignin samples after BCD.

Base	Lignin Type	Weight of oil (mg)	Weight of residue (mg)
Cs_2CO_3	OS- Oak	**58**	**48**
	OS-Cherry	**52**	**42**
	OS-Beechwood	**67**	**37**
	Aldrich-Kraft	**60**	**36**
LiO*t*-Bu	OS-Oak	**29**	**80**
	OS-Cherry	**10**	**94**
	OS-Beechwood	**35**	**66**
	Aldrich-Kraft	**20**	**86**

2.4.1 GC-MS measurements for lignin (oil fractions) obtained after BCD with Cs_2CO_3

(a) Beechwood lignin

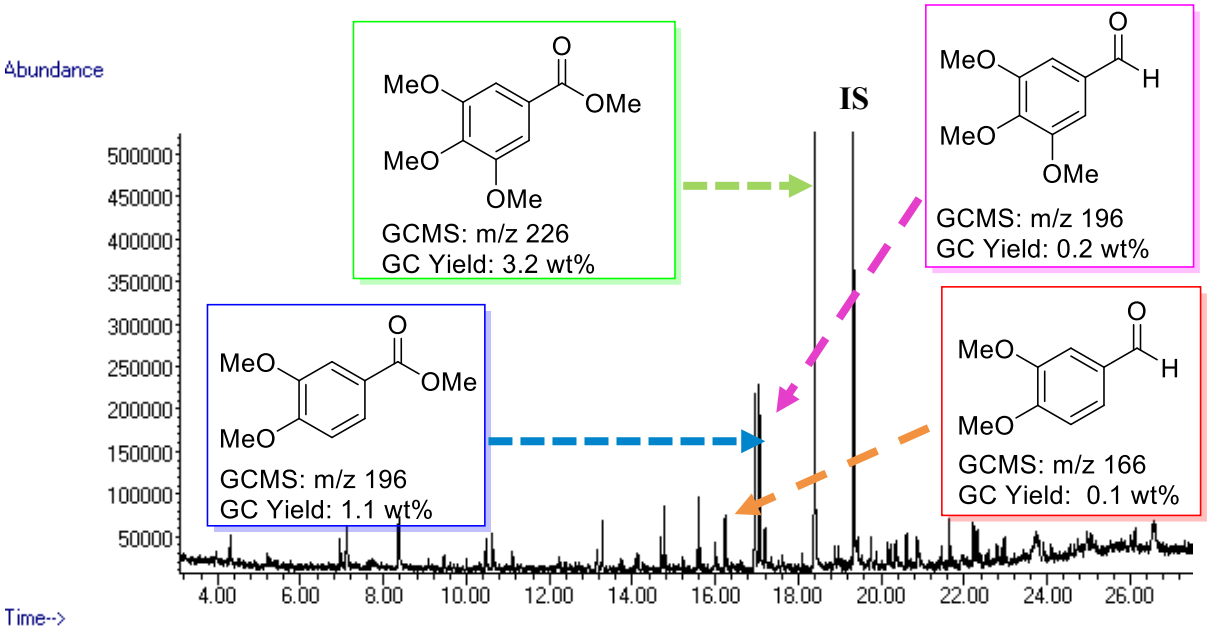
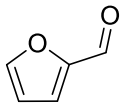
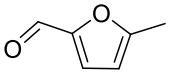
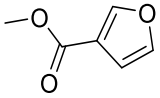
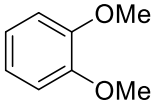
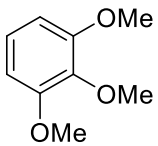
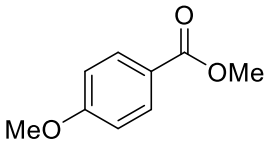
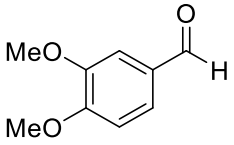
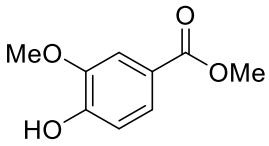
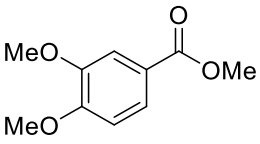
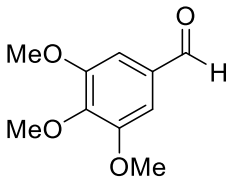
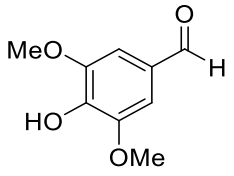
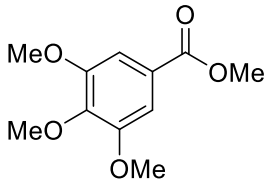
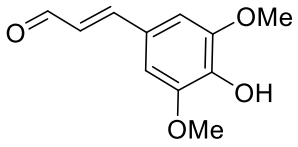


Fig. S3 GC spectrum for beechwood (OS-BW) lignin with Cs_2CO_3.

Table S4 Complete overview of the GC-FID signals, identification, quantification and designation obtained from the depolymerisation of beechwood (OS-BW) lignin.

Entry	Ret. (min.)	Quant (mg)	Found mass (m/z)	Structure	Match (%)
1	3.26	-	96	 furan-2-carbaldehyde	80
2	6.59	-	110	 5-methylfuran-2-carbaldehyde	90
3	6.94	-	126	 methyl furan-3-carboxylate	80
5	10.62	0.05	138	 Veratrole	87 Sample injected
6	13.27	0.1	168	 1,2,3-trimethoxybenzene	85 Sample injected

7	13.74	0.03	166	 methyl 4-methoxybenzoate	90 Sample injected
9	15.60	0.1	166	 3,4-dimethoxybenzaldehyde	91 Sample injected
10	16.06	0.2	182	 methyl 4-hydroxy-3-methoxybenzoate	89 Sample injected
11	16.96	1.1	196	 methyl 3,4-dimethoxybenzoate	94 Sample injected
12	17.06	0.2	196	 3,4,5-trimethoxybenzaldehyde	96 Sample injected
13	17.73	0.05	182	 4-hydroxy-3,5-dimethoxybenzaldehyde	96 Sample injected
14	18.40	3.2	226	 methyl 3,4,5-trimethoxybenzoate	99 Sample injected
15	21.14	-	208	 3-(4-hydroxy-3,5-dimethoxyphenyl) acrylaldehyde	83

(b) Oak lignin

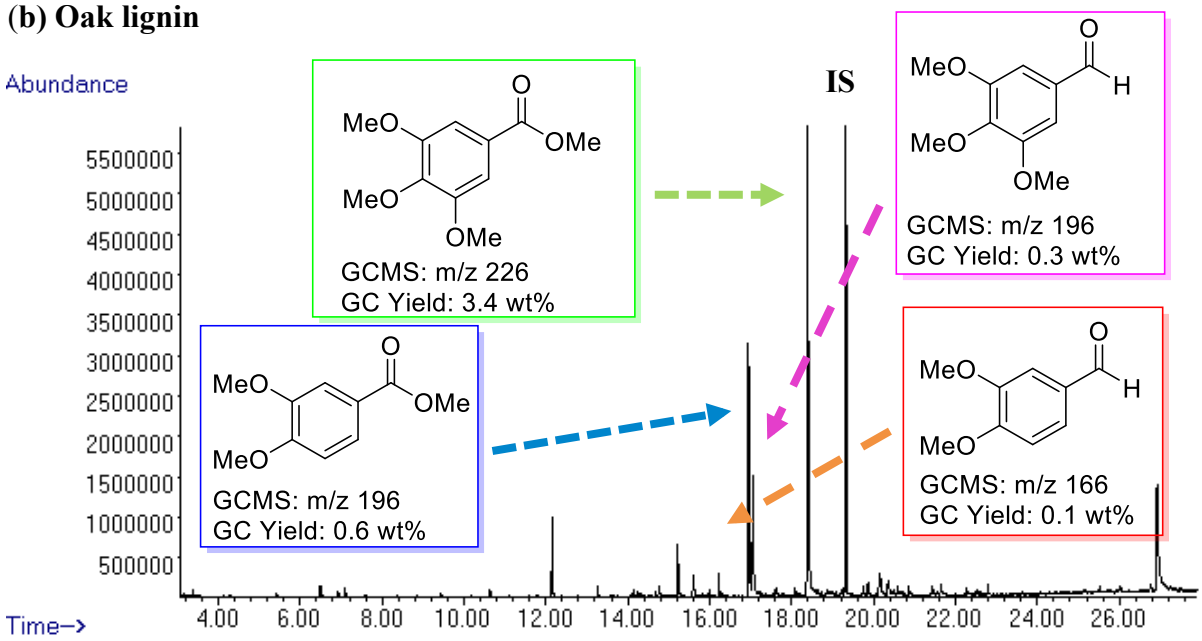
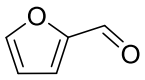
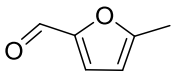
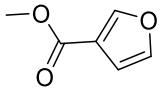
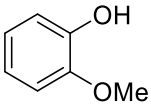
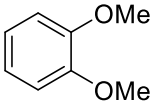
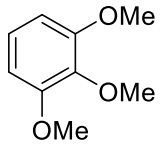
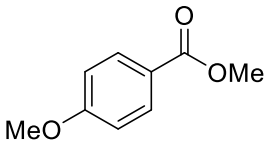
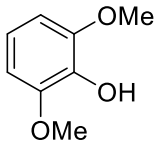
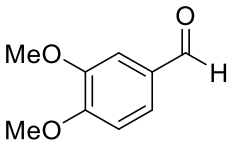
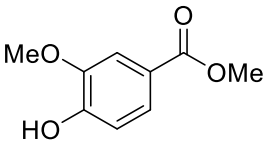
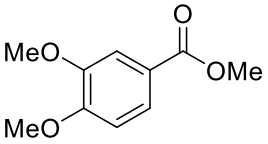
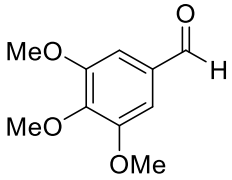
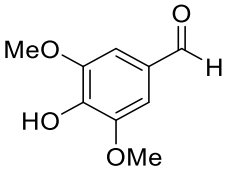
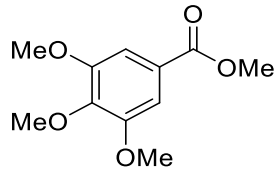
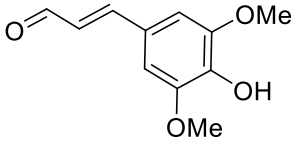


Fig. S4 GC spectrum for Oak (OS-O) lignin with Cs_2CO_3.

Table S5 Complete overview of the GC-FID signals, identification, quantification and designation obtained from the depolymerisation of Oak (OS-O) lignin.

Entry	Ret. (min.)	Quant (mg)	Found mass (m/z)	Structure	Match (%)
1	3.26	-	96	 furan-2-carbaldehyde	80
2	6.59	-	110	 5-methylfuran-2-carbaldehyde	90
3	6.94	-	126	 methyl furan-3-carboxylate	80
4	9.49	0.01	124	 2-methoxyphenol	79 Sample injected
5	10.62	0.03	138	 Veratrole	90 Sample injected

6	13.27	0.2	168	 1,2,3-trimethoxybenzene	96 Sample injected
7	13.74	0.01	166	 methyl 4-methoxybenzoate	90 Sample injected
8	13.85	0.02	154	 2,6-dimethoxyphenol	67 Sample injected
9	15.60	0.1	166	 3,4-dimethoxybenzaldehyde	91 Sample injected
10	16.06	0.1	182	 methyl 4-hydroxy-3-methoxybenzoate	89 Sample injected
11	16.96	0.6	196	 methyl 3,4-dimethoxybenzoate	94 Sample injected
12	17.06	0.3	196	 3,4,5-trimethoxybenzaldehyde	96 Sample injected
13	17.73	0.02	182	 4-hydroxy-3,5-dimethoxybenzaldehyde	96 Sample injected

14	18.40	3.4	226	 methyl 3,4,5-trimethoxybenzoate	99 Sample injected
15	21.14	-	208	 3-(4-hydroxy-3,5-dimethoxyphenyl) acrylaldehyde	83

(c) Cherry lignin

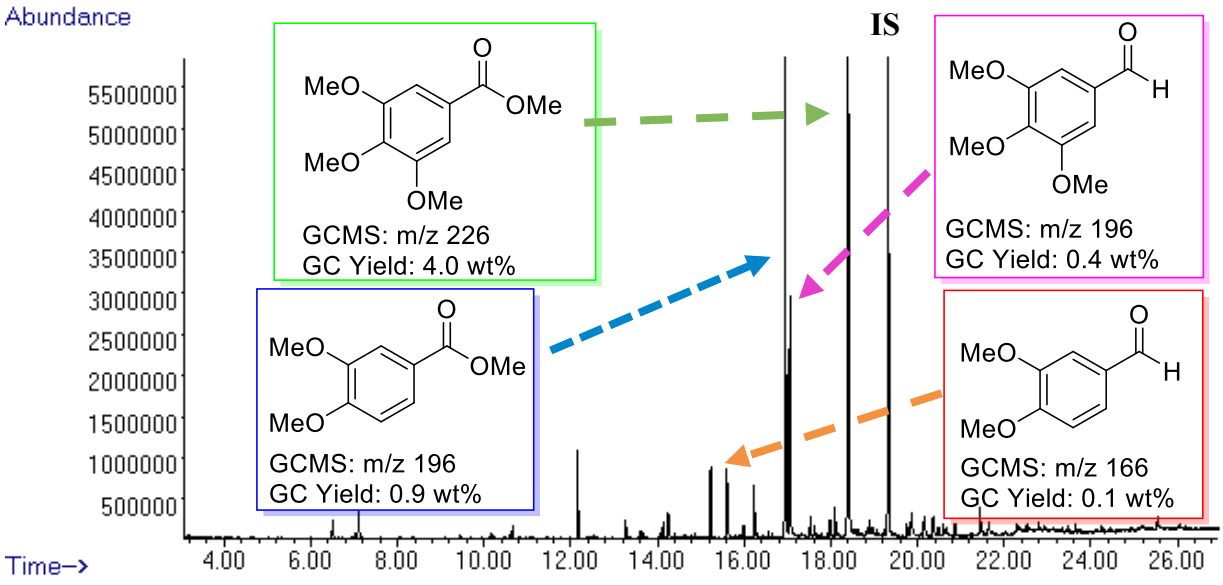
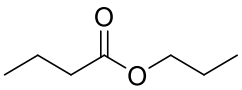
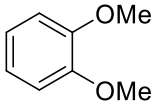
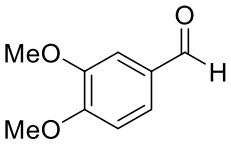
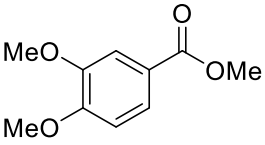
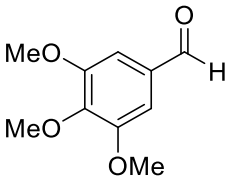
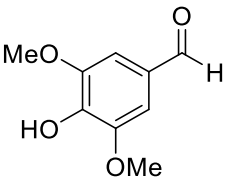
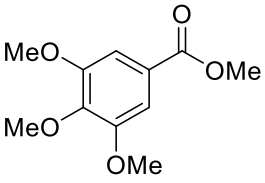


Fig. S5 GC spectrum for Cherry (OS-C) lignin with Cs_2CO_3.

Table S6 Complete overview of the GC-FID signals, identification, quantification and designation obtained from the depolymerisation of cherry (OS-C) lignin.

Entry	Ret. (min.)	Quant (mg)	Found mass (m/z)	Structure	Match (%)
1	3.55	-	130	 propyl butyrate	76
2	10.62	0.02	138	 Veratrole	87 Sample injected

3	15.60	0.1	166	 3,4-dimethoxybenzaldehyde	91 Sample injected
4	16.96	0.9	196	 methyl 3,4-dimethoxybenzoate	95 Sample injected
5	17.06	0.4	196	 3,4,5-trimethoxybenzaldehyde	96 Sample injected
6	17.73	0.05	182	 4-hydroxy-3,5-dimethoxybenzaldehyde	96 Sample injected
7	18.40	4.0	226	 methyl 3,4,5-trimethoxybenzoate	99 Sample injected
8	18.65		180	-	-
9	19.51		210	-	-
10	20.92		226	Dimer	-
11	21.14		208	Dimer	

(d) Kraft Lignin

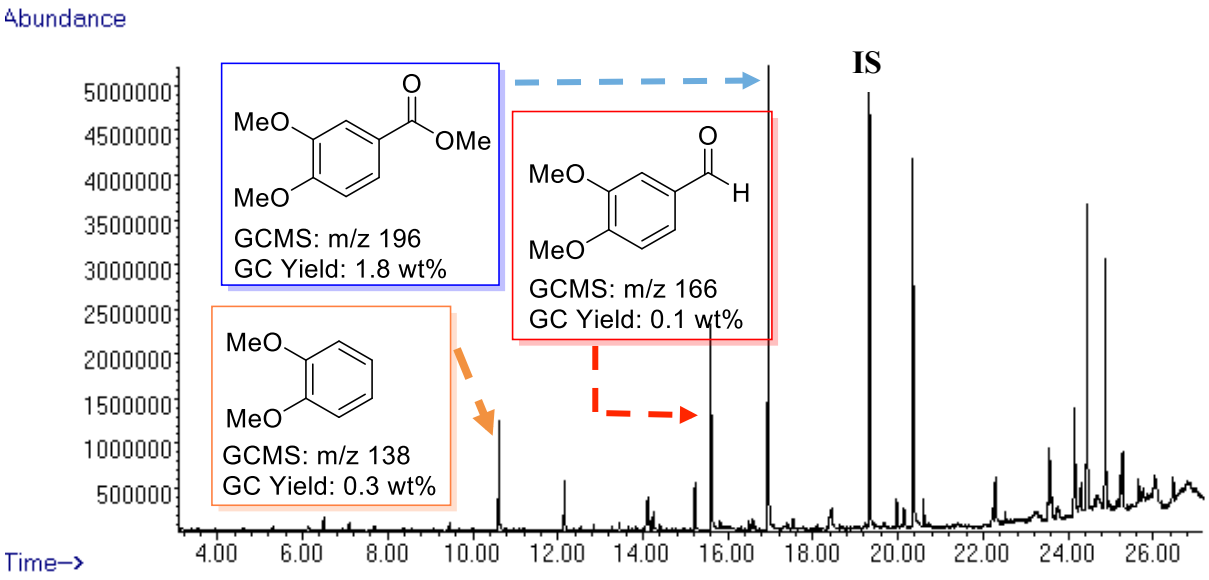
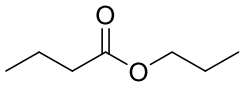
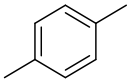
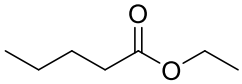
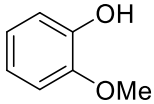
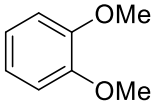
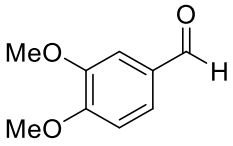
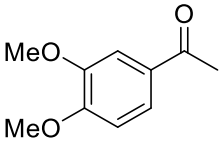
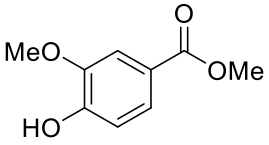
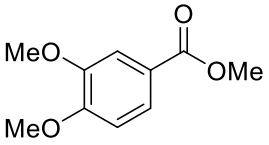
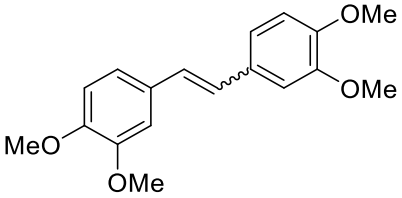


Fig. S6 GC spectrum for Kraft lignin with Cs_2CO_3.

Table S7 Complete overview of the GC-FID signals, identification, quantification and designation obtained from the depolymerisation of Aldrich Kraft (KL) lignin.

Entry	Ret. (min.)	Quant (mg)	Found mass (m/z)	Structure	Match (%)
1	3.55	-	130	 propyl butyrate	76
2	4.04	-	106	 p-xylene	50
3	4.82	-	130	 ethyl pentanoate	72
4	8.36	-	104	-	-
5	9.50	0.03	124	 2-methoxyphenol	80 Sample injected
6	10.62	0.3	138	 Veratrole	84 Sample injected

7	14.58	-	198	Tetradecane	76
8	15.60	0.1	166	 3,4-dimethoxybenzaldehyde	96 Sample injected
9	16.64	0.08	180	 1-(3,4-dimethoxyphenyl)ethan-1-one	90 Sample injected
10	16.06	0.01	182	 methyl 4-hydroxy-3-methoxybenzoate	89 Sample injected
11	16.96	1.8	196	 methyl 3,4-dimethoxybenzoate	94 Sample injected
12	17.10	-	184	-	-
13	20.35	-	254	-	-
14	24.55	-	281	Dimer	76
15	24.44	-	314	Dimer	90
16	24.88	-	316	Dimer	95
17	**27.96**	-	300	 1,2-bis(3,4-dimethoxyphenyl)ethene	**70**

2.4.2 GC-MS Measurements for lignin (oil) obtained after BCD with KOH

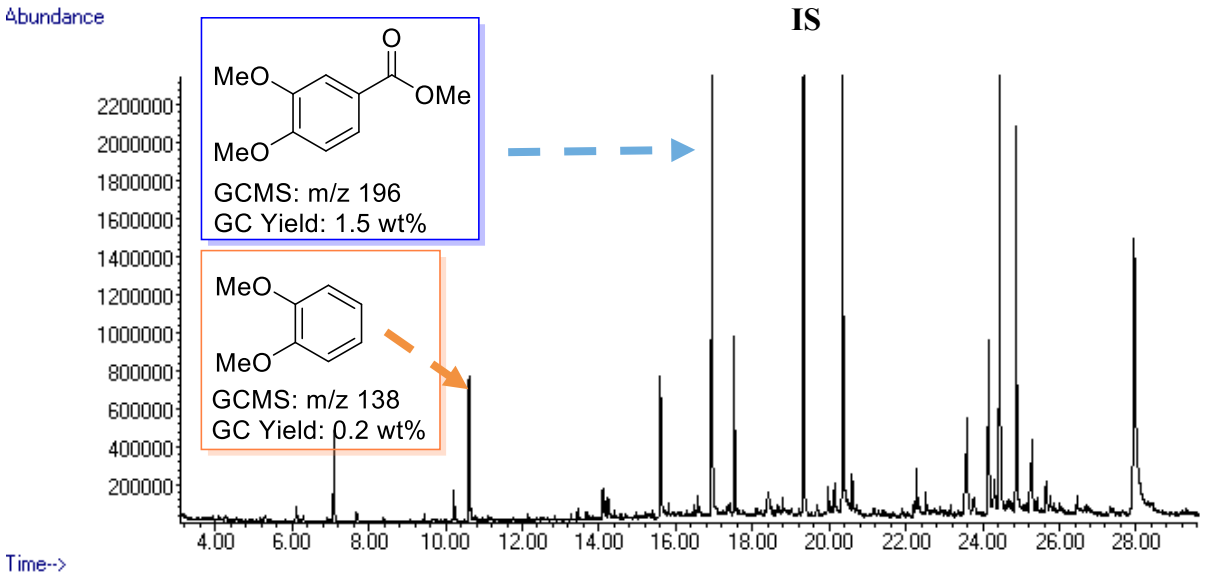
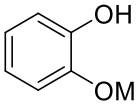
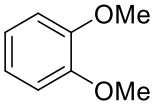
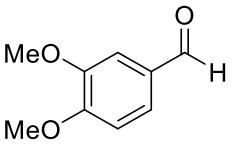
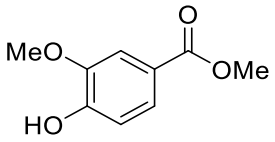
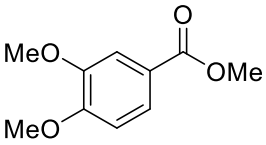
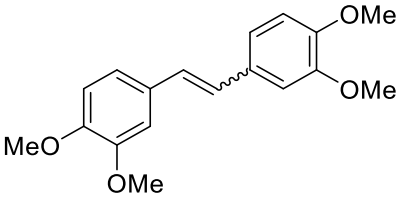


Fig. S7 GC spectrum for Kraft lignin with KOH (10 wt%).

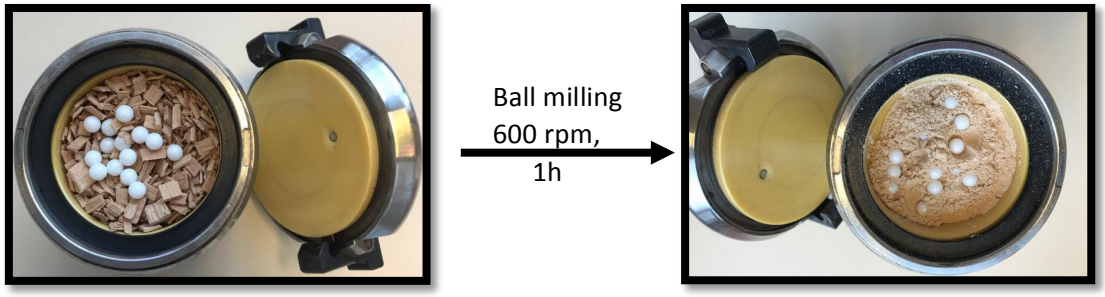
Table S8 Complete overview of the GC-FID signals, identification, quantification and designation obtained from the depolymerisation of Aldrich Kraft (KL) lignin.

Entry	Ret. (min.)	Quant (mg)	Found mass (m/z)	Structure	Match (%)
1	7.01	-		-	
2	9.50	0.02	124	 2-methoxyphenol	80 Sample injected
3	10.62	0.2	138	 Veratrole	94 Sample injected
4	14.58	-	198	Tetradecane	76
5	15.60	0.3	166	 3,4-dimethoxybenzaldehyde	96 Sample injected

6	16.06	0.01	182	 methyl 4-hydroxy-3-methoxybenzoate	89 Sample injected
7	16.95	1.5	196	 methyl 3,4-dimethoxybenzoate	94 Sample injected
8	17.10	-	184	-	-
9	20.35	-	254	-	-
10	24.55	-	281	Dimer	76
11	24.44	-	314	Dimer	90
12	24.88	-	316	Dimer	95
13	27.96	-	300	 1,2-bis(3,4-dimethoxyphenyl)ethene	70

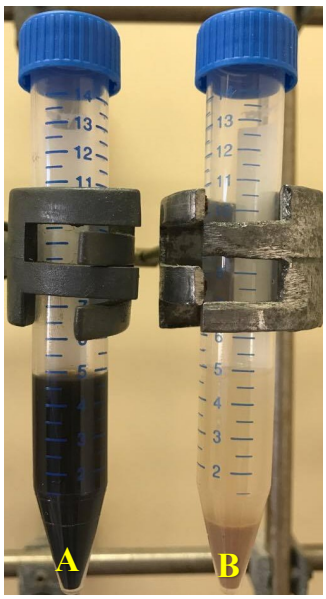
2.5. General procedure for the BCD of beechwood chips in DMC

a) Pre-grinding the woodchips in a planetary ball mill



Beechwood chips (2 g) were taken in a FRITSCH Planetary micro mill model "Pulverisette 7 premium line" in a milling jar containing 20 balls of diameter (5 mm) and milled for 1h at 1600 rpm to get a fine powder. The jars (20 ml in volume) and balls (5 mm diameter) are made of ZrO_2.

b) BCD of beechwood powder in DMC



Reaction tube A: A 20 mL pressure tube with a Teflon screw cap and a magnetic stirrer was charged with beechwood powder (100 mg) and Cs_2CO_3 (10 mg) in DMC (5 mL). The mixture was stirred at 180 °C for 8 h followed by its cooling to room temperature. To the above mixture was added 200 µl of internal standard (*n*-octadecane, 0.062 M solution) and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in EtOAc (5 mL) and centrifuged to separate the soluble products from the residual powder which sedimented at the bottom of the tube. This process was repeated 3 times. The combined fractions were then dried under reduced pressure to get an oil residue. A sample of this residue was dissolved in EtOAc and was injected in the GC-MS for further quantitative product analysis.

Control reaction tube B: To rule out any cleavage reaction induced during the pre-milling of wood chips, and to highlight the role of Cs_2CO_3 in the current system, a control experiment was performed with beechwood powder (100 mg) in DMC (5 mL) but in the absence of Cs_2CO_3 (10 mg). A similar workup procedure and product analysis was performed as above.

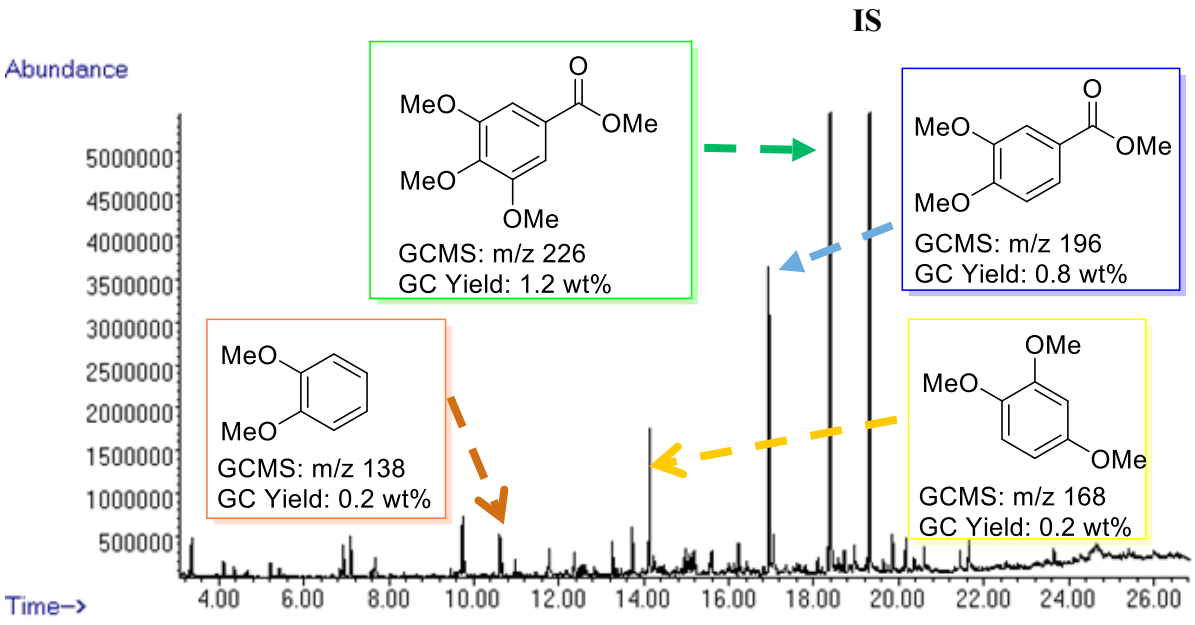
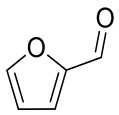
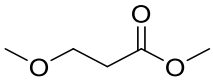
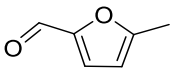
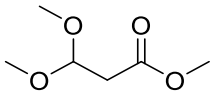
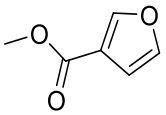
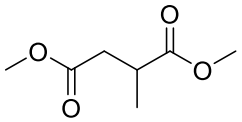
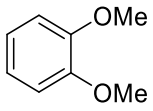
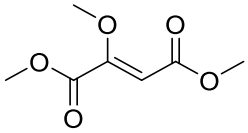
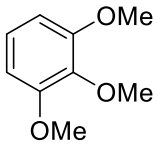
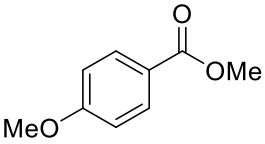
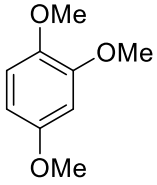
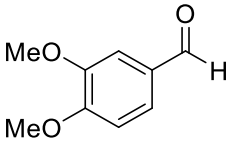
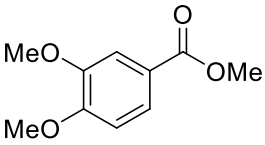
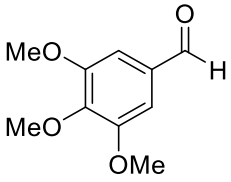
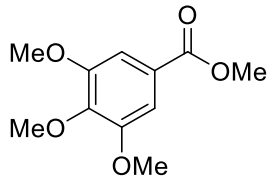
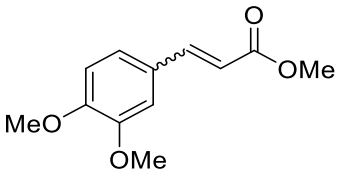
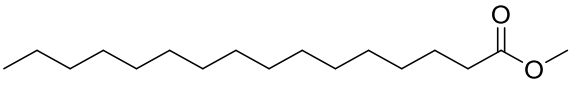
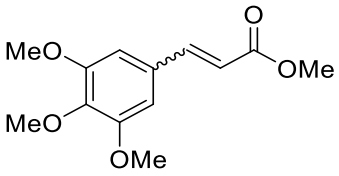


Fig. S8 GC spectrum for beechwood powder (oil fraction) after BCD by method **A**.

Table S9 Complete overview of the GC-FID signals, identification, quantification and designation obtained from the depolymerisation of beechwood powder.

Entry	Ret. (min.)	Quant (mg)	Found mass (m/z)	Structure	Match (%)
1	3.26	-	96	 furan-2-carbaldehyde	80
2	3.38	-	118	 methyl 3-methoxypropanoate	72
3	6.59	-	110	 5-methylfuran-2-carbaldehyde	90
4	6.85	-	148	 methyl 3,3 dimethoxy propionate	78
5	6.94	-	126	 methyl furan-3-carboxylate	80

6	9.06	-	160	 Butanedioic acid, methyl, dimethyl ester	72
7	10.62	0.2	138	 Veratrole	84 Sample injected
8	12.36	-	174	 2-Methoxy-2-butenedioic acid dimethyl ester	93
9	13.26	0.05	168	 1,2,3-trimethoxybenzene	94 Sample injected
10	13.73	0.02	166	 methyl 4-methoxybenzoate	95 Sample injected
11	14.13	0.2	168	 1,2,4-trimethoxybenzene	98 Sample injected
12	15.23	-	194	-	-
13	15.60	0.1	166	 3,4-dimethoxybenzaldehyde	91 Sample injected
14	16.95	0.8	196	 methyl 3,4-dimethoxybenzoate	99 Sample injected
15	17.05	0.2	196	 3,4,5-trimethoxybenzaldehyde	96 Sample injected

16	18.40	1.2	226	 methyl 3,4,5-trimethoxybenzoate	99 Sample injected
17	20.133	-	222	 methyl 3-(3,4-dimethoxyphenyl)acrylate	93
18	20.60	-	270	 hexadecanoic acid methylester	93
19	21.43	-	252	 methyl 3-(3,4,5-trimethoxyphenyl)acrylate	93

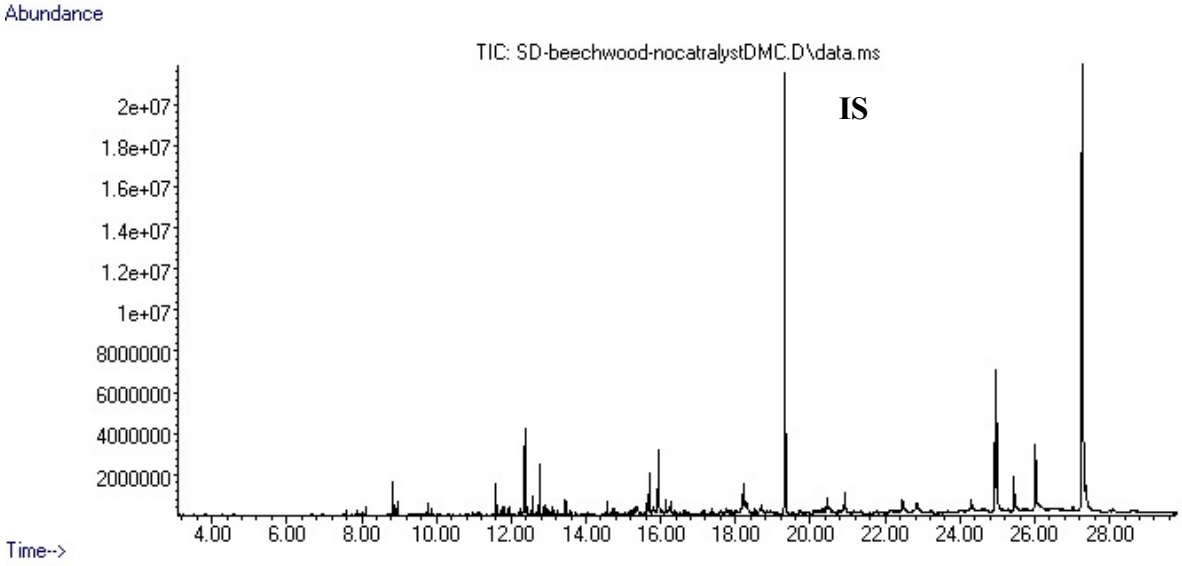
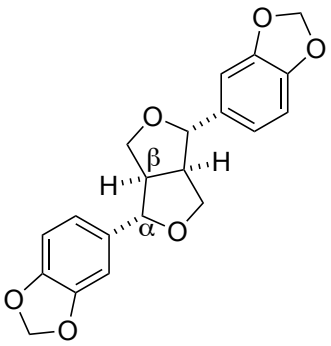


Fig. S9 GC spectrum for beechwood chips (oil fraction) after method **B**.

3. Experimental Information for BCD of lignin model compounds

3.1 Isolating lignin *β*-*β* model compound from sesame oil:

(1*S*,3a*R*,4*S*,6a*R*)-1,4-Bis(benzo[d][1,3]dioxol-5-yl)tetrahydro-1H,3H-furo[3,4-c]furan, Sesamin (1a)

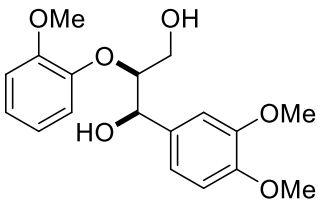


A solution of Kunella Feinkost sesame oil (200 mL) in pentane (500 mL) was loaded onto a column pre-packed with 50 g of silica in pentane. Next the column was eluted with pentane (700 mL) until a colorless eluent was obtained. Elution was then continued using a mixture of pentane/EtOAc (750 mL of a 9/1 mix followed by 750 mL of a 1/9 mix). The column was then flushed with EtOAc to afford the remaining sesamin. The combined fractions were concentrated *in vacuo* to give a light yellow semi-solid which was triturated with hexanes to afford sesamin **1a** as a white solid in 98% purity. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 6.85 (s, 2H), 6.83–6.74 (m, 4H), 5.94 (s, 4H), 4.71 (d, *J* = 4.24 Hz, 2H), 4.23 (ddd, *J* = 9.2 Hz, 4.4 Hz and 2.1 Hz, 2H), 3.86 (dd, *J* = 9.2 Hz and 3.6 Hz, 2H), 3.08–2.99 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 148.1 (2C), 147.2 (2C), 135.2 (2C), 119.5 (2C), 108.3 (2C), 106.6 (2C), 101.2 (2C), 85.9 (2C), 71.8 (2C), 54.5 (2C). **mp:** 121–122 °C (lit. 122–122.5 °C). ^{1}H NMR data are in accordance with those previously reported.[12]

3.2 Synthesis of lignin *β*-O-4 model compounds

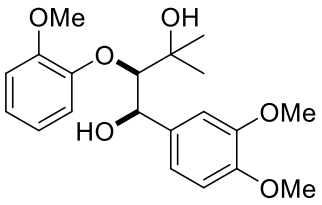
The lignin model compounds (**1b-g**) used for the cleavage reactions were prepared according to the procedure described in literature.[13]

***erythro*-1- (3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-l,3-propanediol (1b)**



White solid, mp: 100–101 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.06 (ddd, *J* = 8.0 Hz, 7.2 Hz and 1.6 Hz, 1H), 6.99–6.88 (m, 5H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.98 (br.t, *J* = 4.7 Hz, 1H), 4.16 (ddd, *J* = 6.0 Hz, 4.7 Hz and 3.7 Hz, 1H), 3.95–3.89 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.87 (s, 3H), 3.66 (ddd, *J* = 12.0 Hz, 7.2 Hz and 3.7 Hz, 1H), 3.55 (br.s, 1H), 2.79 (br.s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 151.7, 149.1, 148.6, 147.0, 132.6, 124.3, 121.7, 121.1, 118.5, 112.3, 111.1, 109.3, 87.5, 72.8, 60.9, 56.0 (3C). **MS (EI, 70 eV):** *m/z* (%): 334 $[M]^+$ (6), 167 (15), 166 (12), 151 (14), 150 (100), 139 (20), 124 (10), 121 (12), 109 (10). **HPLC MeCN (0.1% formic acid):** t_R = 22.1 min.

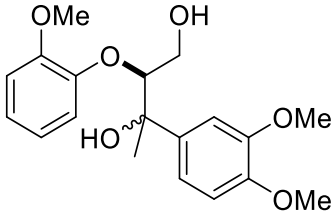
***erythro*-1-(3,4-Dimethoxyphenyl)-3,3-dimethyl-2-(2-methoxyphenoxy)-l,3-propanediol (1c)**



White solid, mp: 102–103 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.01 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 8.0 Hz and 2.0 Hz, 1H), 6.85–6.80 (m, 1H), 6.77 (dd, *J* = 8.0 Hz and 2.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.67 (ddd, *J* = 8.0 Hz, 6.9 Hz and 2.0 Hz, 1H), 6.44 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 4.96 (d, *J* = 7.2 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.75 (s, 3H), 3.55 (br.s, 2H), 1.41 (s, 3H), 1.21 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 150.0, 148.8, 148.6, 148.5, 134.0, 122.2, 121.0, 119.4, 117.0, 111.9, 110.8, 110.1, 89.1, 74.5, 74.2, 55.9 (2C), 55.8, 27.1, 25.1. **MS (EI, 70 eV):** *m/z* (%): 362 (2) [M^+], 180 (18), 179 (100), 167 (12), 139 (19), 124 (18), 123 (13), 77 (12).

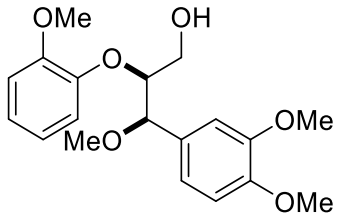
3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)butane-1,3-diol (1d)

Mixture of *erythro*+*threo* diol = 1.3:0.6



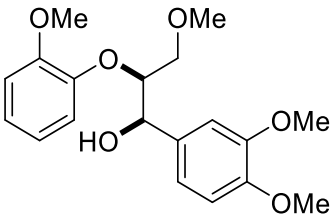
Colorless liquid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.14 (d, *J* = 2.1 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 7.10 (dd, *J* = 8.3 Hz and 1.5 Hz, 1H), 7.07–6.92 (m, 7H), 6.89–6.84 (m, 3H), 6.83 (d, *J* = 8.3 Hz, 1H), 4.19 (dd, *J* = 5.7 Hz and 3.8 Hz, 1H), 4.15 (t, *J* = 3.9 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.80 (dd, *J* = 12.3 Hz and 5.7 Hz, 1H), 3.68 (dd, *J* = 12.3 Hz and 3.8 Hz, 1H), 3.56 (qd, *J* = 12.6 Hz and 3.9 Hz, 2H), 1.70 (s, 3H), 1.69 (s, 3H). **^{13}C NMR (101 Hz, $CDCl_3$):** δ = 151.1, 150.8, 148.8, 148.6, 148.3, 148.0, 147.9 (2C), 137.6, 137.3, 123.7, 123.6, 121.6, 121.5, 120.0, 119.7, 117.8, 117.1, 112.2, 112.0, 110.9, 110.6, 109.3, 108.6, 89.9, 87.9, 76.6, 75.8, 61.5, 61.0, 55.8, 55.9 (2C), 55.9 (3C), 27.7, 25.1. **MS (EI, 70 eV):** *m/z* (%): 348 (3) [M^+],182 (34), 181 (53), 165 (17), 151 (15), 150 (100), 139 (18), 124 (19), 121 (15), 109 (13), 77 (16).

***erythro*-3-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)-1-propanol (1e)**



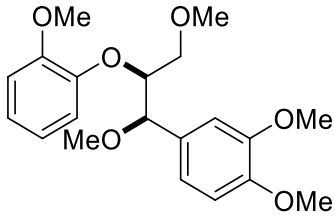
White solid, mp: 76–77 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 6.97–6.92 (m, 3H), 6.87–6.82 (m, 2H), 6.76 (td, *J* = 7.8 Hz and 1.5 Hz, 1H), 6.53 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 4.43 (d, *J* = 7.2 Hz, 1H), 4.07 (ddd, *J* = 7.2 Hz, 4.6 Hz and 3.8 Hz, 1H), 3.92 (dd, *J* = 12.0 Hz and 4.7 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.84–3.80 (m, 1H), 3.82 (s, 3H), 3.31 (s, 3H), 3.17 (m, 1H). **^{13}C NMR (101 Hz, $CDCl_3$):** δ = 151.2, 149.0, 148.7, 147.5, 131.4, 123.6, 121.3, 120.4, 120.3, 112.0, 110.8, 110.2, 86.7, 82.8, 61.6, 57.1, 55.9, 55.9, 55.8. **MS (EI, 70 eV):** *m/z* (%): 348 (3) [M^+], 182 (17), 181 (100), 151 (11).

***erythro*-1-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)-1-propanol (1f)**



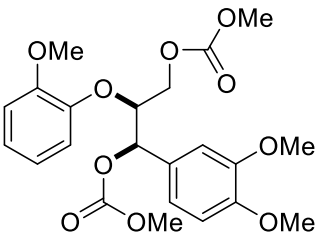
White solid, mp: 68–69 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.08–7.05 (m, 1H), 7.03–6.99 (m, 2H), 6.92–6.87 (m, 3H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.87 (d, *J* = 3.6 Hz, 1H), 4.34 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.85 (s, 3H), 3.63 (dd, *J* = 10.2 Hz and 6.0 Hz, 1H), 3.43 (dd, *J* = 10.2 Hz and 3.6 Hz, 1H), 3.33 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 151.4, 148.8, 148.3, 147.3, 132.5, 123.7, 121.4, 120.6, 118.6, 112.1, 110.8, 109.6, 85.1, 72.9, 71.4, 59.3, 55.9, 55.8, 55.8. **MS (EI, 70 eV):** *m/z* (%)**:** 348 (2) [M^+], 181 (11), 167 (12), 166 (12), 165 (10), 151 (20), 150 (100), 139 (24), 124 (15), 121 (18), 109 (15), 95 (14), 77 (18).

***erythro*-1,3-dimethoxy-1- (3,4-Dimethoxyphenyl)-2- (2-methoxyphenoxy) propane (1g)**



White solid, mp: 50–51 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 6.96 (d, *J* = 1.8 Hz, 1H), 6.93–6.87 (m, 2H), 6.85–6.76 (m, 4H), 4.47–4.42 (m, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 3.75 (s, 3H), 3.74–3.70 (m, 1H) 3.64–3.60 (m, 1H), 3.37 (s, 3H), 3.29 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$):** δ = 150.8, 148.8, 148.5, 147.9, 130.9, 122.3, 120.8, 120.4, 118.1, 112.2, 110.7, 110.5, 82.6, 82.3, 71.3, 59.3, 57.2, 55.8, 55.8, 55.7. **MS (EI, 70 eV):** *m/z* (%)**:** 362 (6) [M^+], 182 (20), 181 (100), 151 (14), 45 (11).

***erythro*-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diyldimethyl biscarbonate (1h)[14]**



Colorless oil. ^{1}H NMR (400 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 and 5.4 Hz, 1H), 4.33 (dd, *J* = 12 Hz and 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 (101 MHz, $CDCl_3$):** δ = 155.5, 154.7, 151.0, 149.2, 148.8, 146.9, 128.2, 123.6, 120.9, 120.1, 119.4, 112.5, 110.7, 110.5, 79.9, 77.8, 65.9, 55.8 (2C), 55.7, 55.0, 54.9. **IR (ATR):** ν [cm^{-1}] = 2956, 2077, 1747, 1597, 1466, 1242, 952, 759. **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{22}H_{26}O_{10}$+Na^+: 473.14182 [M+Na^+]; found: 473.14166**. HPLC MeCN (0.1% formic acid):** t_R = 29.6 min.

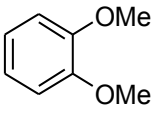
3.3 General procedure for the BCD of lignin β-O-4 model compounds in DMC

A 10 mL pressure tube with a Teflon screw cap and a magnetic stirrer was charged with model compound **1a-h** (0.25 mmol, 1.00 equiv) and base (0.01 mmol, 0.05 equiv) 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 to room temperature. A standard solution (1.00 mL of naphthalene in DMC, c = 0.2 mol/L) was added with an Eppendorf pipette to the reaction mixture. The solution was then diluted with MeCN (10.0 mL) and passed through microfilter. Three samples were then 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.

Note: In the case of model **1a**, the crude reaction mixture was vacuum dried to remove DMC and analysed by quantitative ^{1}H NMR with respect to 1,4-dinitrobenzene which was added as the internal standard to monitor the progress of the reaction.

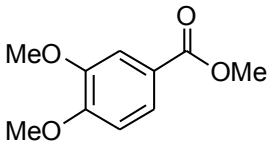
3.4 Spectroscopic data of the isolated products

1,2-Dimethoxybenzene (2a)[15]



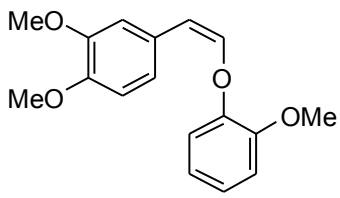
Colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$):** δ = 6.94–6.88 (m, 4H), 3.88 (s, 6H).**^{13}C NMR (151 MHz, $CDCl_3$):** δ= 148.9 (2C), 120.8 (2C), 111.2 (2C), 55.7 (2C).**MS (EI, 70 eV)**: *m/z* (%) = 138 [M^+] (100), 94.9 (14). **HPLC MeCN (0.1% formic acid):** t_R = 22.8 min.

Methyl 3,4-dimethoxybenzoate (3a)[16]



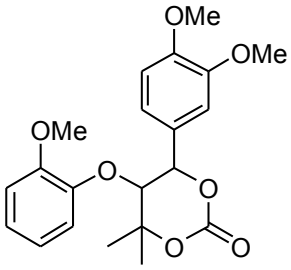
Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.89 (s, 3H).**^{13}C NMR (151 MHz, $CDCl_3$):** δ= 166.8, 152.9, 148.5, 123.5, 122.6, 111.9, 110.2, 56.0, 55.9, 52.0. **MS (EI, 70 eV)**: *m/z* (%) = 196 [M^+] (100), 165 (83), 124.9 (18), 79(25). **HPLC MeCN (0.1% formic acid):** t_R = 23.6 min.

(*Z*)-1,2-Dimethoxy-4-[2-(2-methoxyphenoxy)vinyl]benzene (4a)[14]



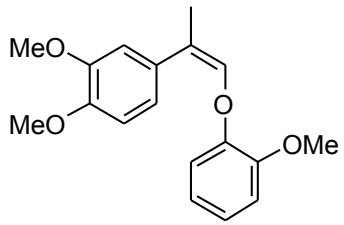
Yellow Solid. mp: 77–78 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ = 7.60 (d, *J* = 1.8 Hz, 1H), 7.13 (dd, *J* = 8.2 Hz and 1.8 Hz, 1H), 7.09 (dd, *J* = 8.1 Hz and 1.6 Hz, 1H), 7.09–7.06 (m, 1H), 6.97 (dd, *J* = 9.9 Hz and 1.5 Hz, 1H), 6.94 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 6.9 Hz, 1H), 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.

6-(3,4-Dimethoxyphenyl)-5-(2-methoxyphenoxy)-4,4-dimethyl-1,3-dioxan-2-one (5)



White solid, mp: 133–134 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ = 6.96 (dd, *J* = 8.4 Hz and 2.4 Hz, 1H), 6.90 (m, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 6.64 (m, 1H), 6.24 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 5.43 (d, *J* = 9.0 Hz, 1H), 4.38 (d, *J* = 9.0 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 1.74 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$):** δ = 150.3, 149.7, 149.3, 148.5, 147.3, 128.7, 123.9, 121.1, 119.9, 118.3, 112.4, 111.1, 109.7, 82.7, 81.8, 80.0, 56.1, 56.0, 55.8, 26.7, 21.8. **IR (ATR):** ν [cm^{-1}] = 3457, 2954, 2590, 2300, 2085, 1738, 1591, 1497, 1351, 1226, 1121, 645. **MS (EI, 70 eV):** *m/z* (%) = 389 $[M+1]^+$ (23), 388 $[M^+]$ (94), 189 (32), 178 (100), 165 (32), 124 (42). **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{21}H_{24}O_7$: 388.15165 $[M^+]$; found: 388.15187.

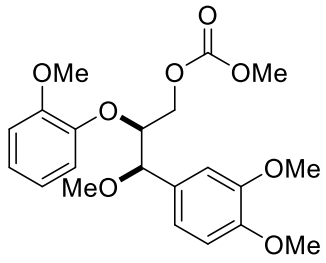
(*Z*)-1,2-Dimethoxy-4-(1-(2-methoxyphenoxy)prop-1-en-2-yl)benzene (6a)



Yellow solid, mp: 82–83 °C. **^{1}H NMR (600 MHz, $CDCl_3$):** δ = 7.06–7.01 (m, 2H), 6.98–6.90 (m, 4H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.68 (q, *J* = 2.4 Hz and 1.2 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 2.15 (d, *J* = 1.2 Hz, 3H).**^{13}C NMR (151 MHz, $CDCl_3$):** δ = 149.6, 148.8, 148.1, 147.1, 138.9, 132.8, 123,2, 120.9, 120.8, 117.9, 116.8, 112.4, 111.1, 108.9, 56.1, 55.9, 55.8, 13.4. **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{18}H_{20}O_4$+ Na^+: 323.12538 [M+ Na^+]; found: 323.12497.

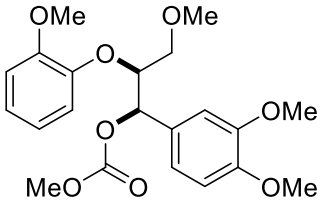
Note: (*E*)-1,2-Dimethoxy-4-(1-(2-methoxyphenoxy)prop-1-en-2-yl)benzene (6b): This alkene was obtained as a minor product and the yields were determined by ^{1}H NMR.

***erythro*-3-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)propyl methyl carbonate (7)**



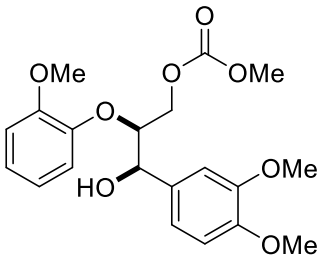
Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.92–6.87 (m, 3H), 6.82–6.80 (m, 2H), 6.78–6.74 (m, 1H), 6.69 (dd, *J* = 1.8 Hz and 7.8 Hz, 1H), 4.54–4.50 (m, 1H), 4.47–4.43 (m, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 3.73(s, 3H), 3.72 (s, 3H), 3.27 (s, 3H).**^{13}C NMR (151 MHz, $CDCl_3$):** δ = 155.6, 150.9, 148.9, 148.7, 147.5, 130.4, 122.9, 120.8, 120.2, 118.9, 112.3, 110.6, 110.3, 82.1, 81.6, 66.6, 57.1, 55.8 (2C), 55.6, 54.7. **IR (ATR):** ν [cm^{-1}] = 2942, 2316, 2086, 1747, 1596, 1470, 1248, 1119, 1025, 755. **MS (EI, 70 eV):** *m/z* (%) = 407 $[M+1]^+$ (8),406 $[M^+]$ (24), 182 (19), 181 (100). **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{21}H_{26}O_8$+Na^+: 429.15199 [M+Na^+]; found: 429.15155.

***erythro*-1-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)propyl methyl carbonate (8)**



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 2 Hz, 1H), 7.00 (dd, *J* = 2 Hz and 8.4 Hz, 1H), 6.97–6.80 (m, 5H), 5.86 (d, *J* = 5.6 Hz, 1H), 4.67–4.63 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.69–3.64 (m, 1H), 3.56–3.51 (m, 1H), 3.35 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$):** δ = 154.8, 150.8, 149.0, 148.6, 147.5, 128.6, 122.8, 120.8, 120.3, 118.4, 112.4, 110.9, 110.5, 80.7, 78.3, 70.8, 59.2, 55.8, 55.7 (2C), 54.8. **IR (ATR):** ν [cm^{-1}] = 2935, 2087, 1745, 1596, 1475, 1243, 1130, 1024, 757. **MS (EI, 70 eV):***m/z* (%) =407 $[M+1]^+$ (25),406 $[M^+]$ (100), 251 (29), 225 (31), 181 (36). **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{21}H_{26}O_8$+Na^+: 429.15199 [M+Na^+]; found: 429.15195

***erythro*-3-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propyl methyl carbonate. (MC)**



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.04 (m, 2H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.96–6.90 (m, 2H), 6.89–6.81 (m, 2H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.51–4.43 (m, 2H), 4.17–4.12 (m, 1H), 3.88 (s, 6H), 3.86 (s, 3H), 3.74 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 155.7, 151.6, 148.9, 148.5, 146.8, 131.3, 124.3, 121.6, 121.0, 118.4, 112.2, 110.9, 109.1, 84.6, 71.7, 66.2, 55.9 (2C), 55.8 54.9. **IR (ATR):** ν [cm^{-1}] = 3501, 2951, 2840, 2587, 2284, 2083, 2001,1919, 1749, 1595, 1504, 1455, 1251, 1171, 1126, 1023, 917, 855, 747. **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{20}H_{24}O_8$+ Na^+: 415.13634 [M+ Na^+]; found: 415.13535. **HPLC MeCN (0.1% formic acid):** t_R = 26.3 min.

4. Reaction Profile and rate calculations for model compound 1b

4.1 General procedure for monitoring the reaction progress for model compound 1b:

Individual reactions were set up to monitor the progress at different time intervals. Dilignol **1b** (1 equiv) was placed in a 20 mL microwave vial with a magnetic stirring bar. A known amount of either Cs_2CO_3 or LiO*t*-Bu (0.05 equiv) was then added to the reactor along with DMC (1.5 mL) and heated at 180 °C. An internal standard (naphthalene, 1 mL from a 0.2 M stock solution in DMC) was added each time towards the end of the reaction. After this, samples (50 μL) from the mixture were taken out and diluted with MeCN (ca. 1 mL). The samples were then analysed by HPLC. In case of measurements corresponding to the initial time (0 h), point sample (50 μL) was taken out at room temperature. The modelled reaction rates were obtained using DynaFit software.[17] First, feasible reaction pathways for each model compound were proposed to assemble the reaction parameters. These reaction pathways are shown in Schemes S1 and S2. The dashed boxes indicate compounds for which

yields have been experimentally determined while those between brackets were not detected but rationalised based on experimental data. To account for any possible decomposition of the formed reaction products, several reaction sinks were incorporated into the model. The obtained reaction rate values for each individual pathway are shown between brackets. An overview of the data points with an overlay of the modelling data are given in Figures S13-S14.

4.2 HPLC chromatograms

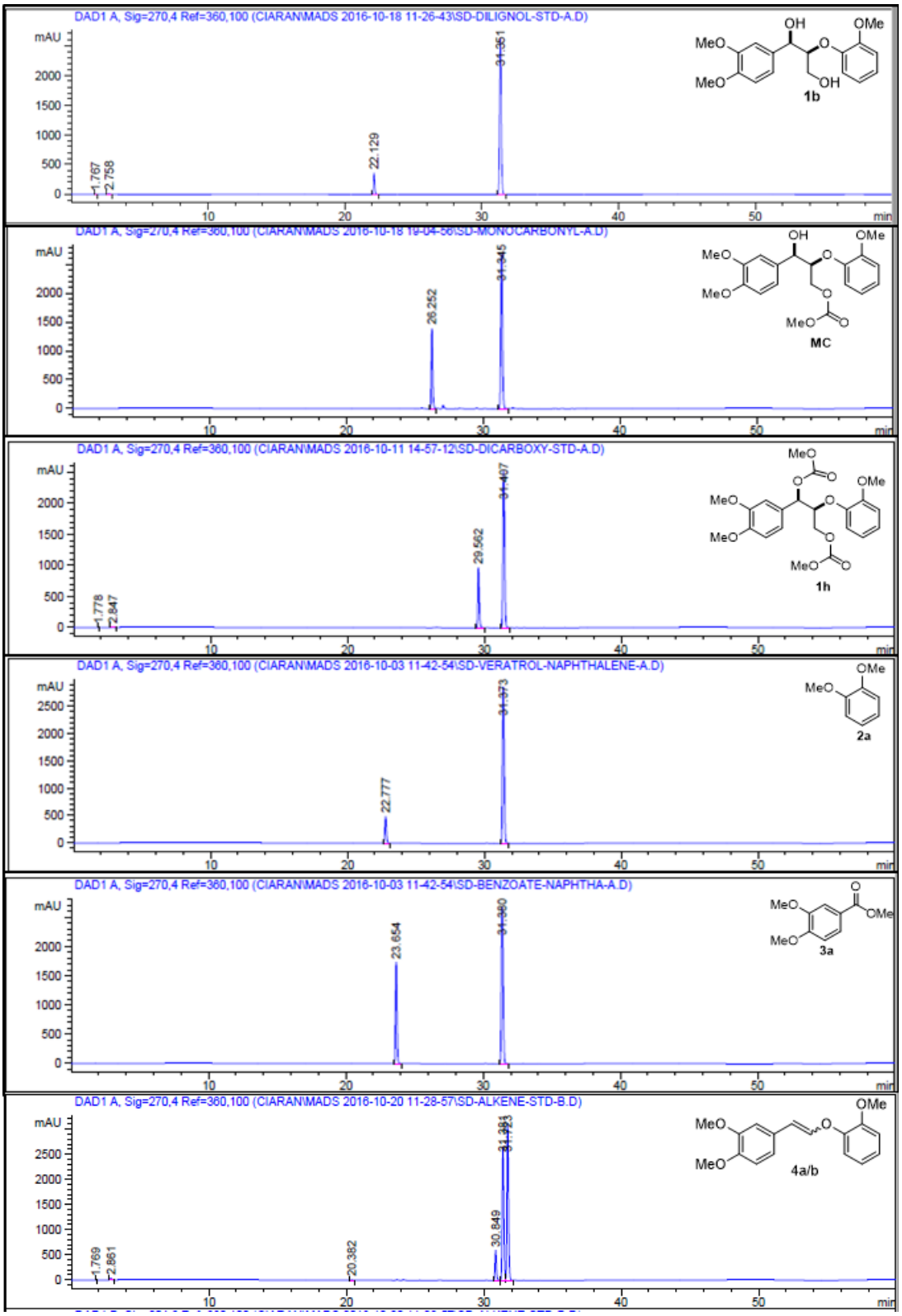


Fig. S10 Representative HPLC chromatograms showcasing individual retention times for the starting material (**1b**), intermediates (**MC**, **1h**) and products (**2a**, **3a**, **4a/b**).

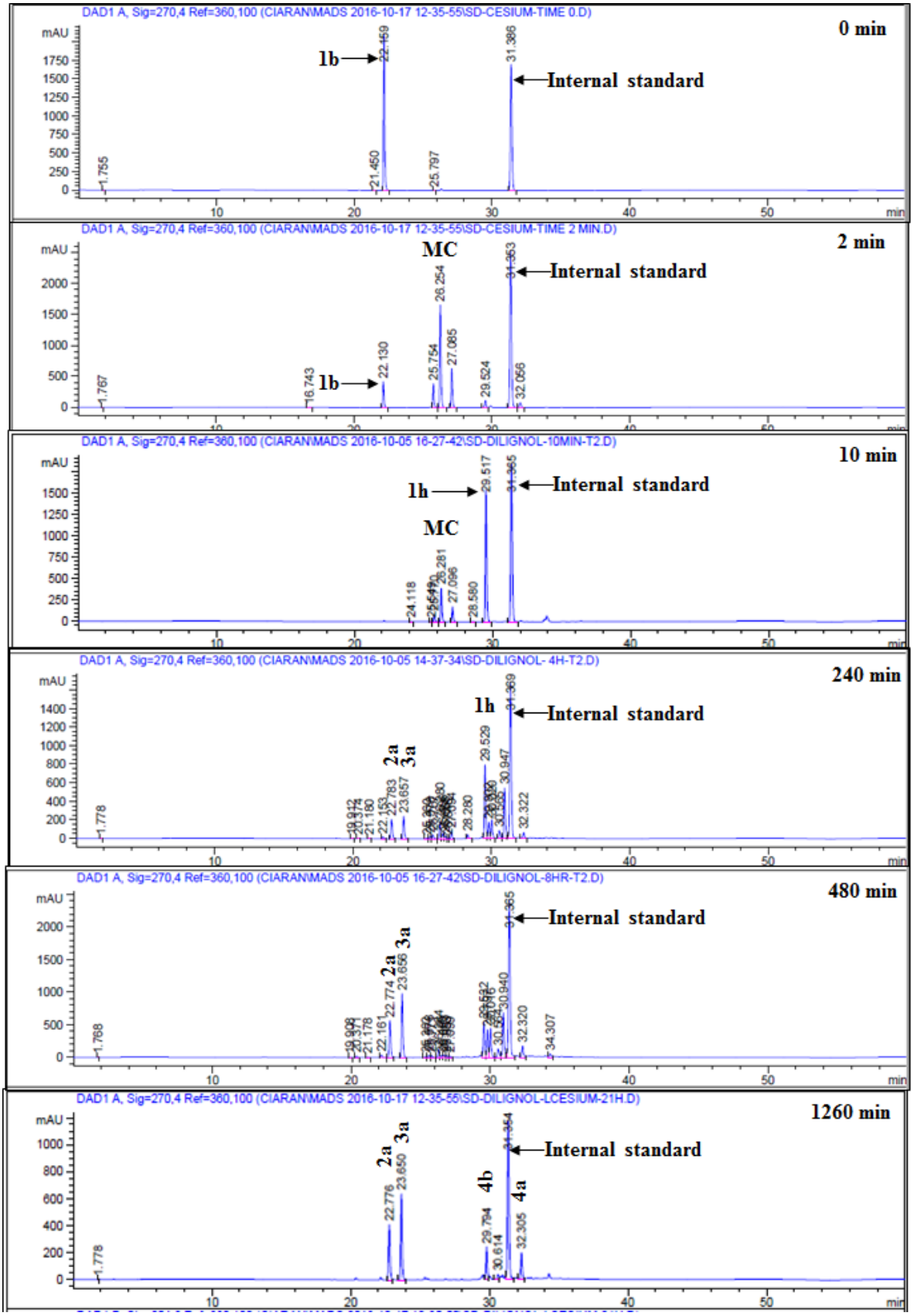


Fig. S11 Representative HPLC chromatograms for the reaction progress of **1b** with Cs_2CO_3.

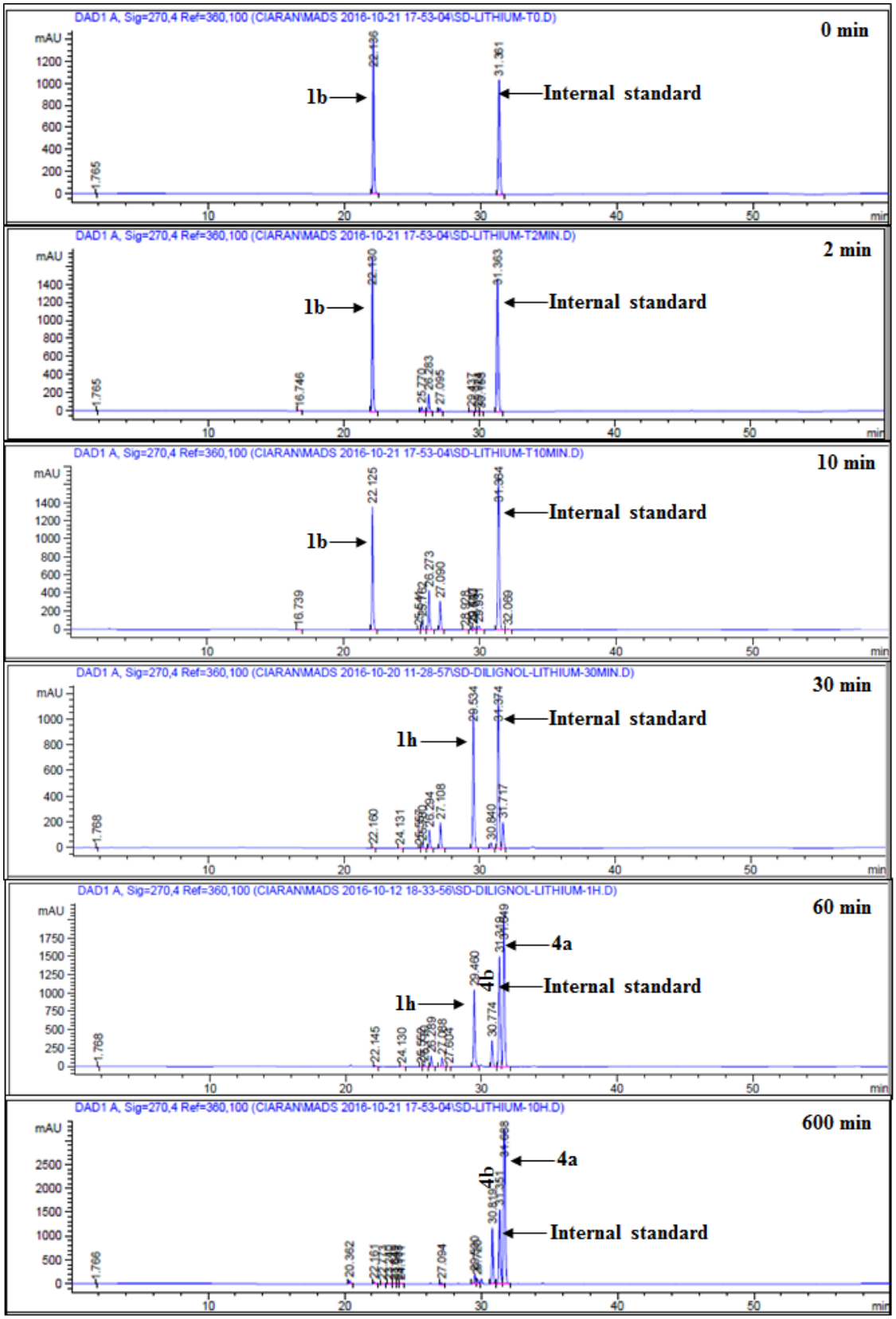
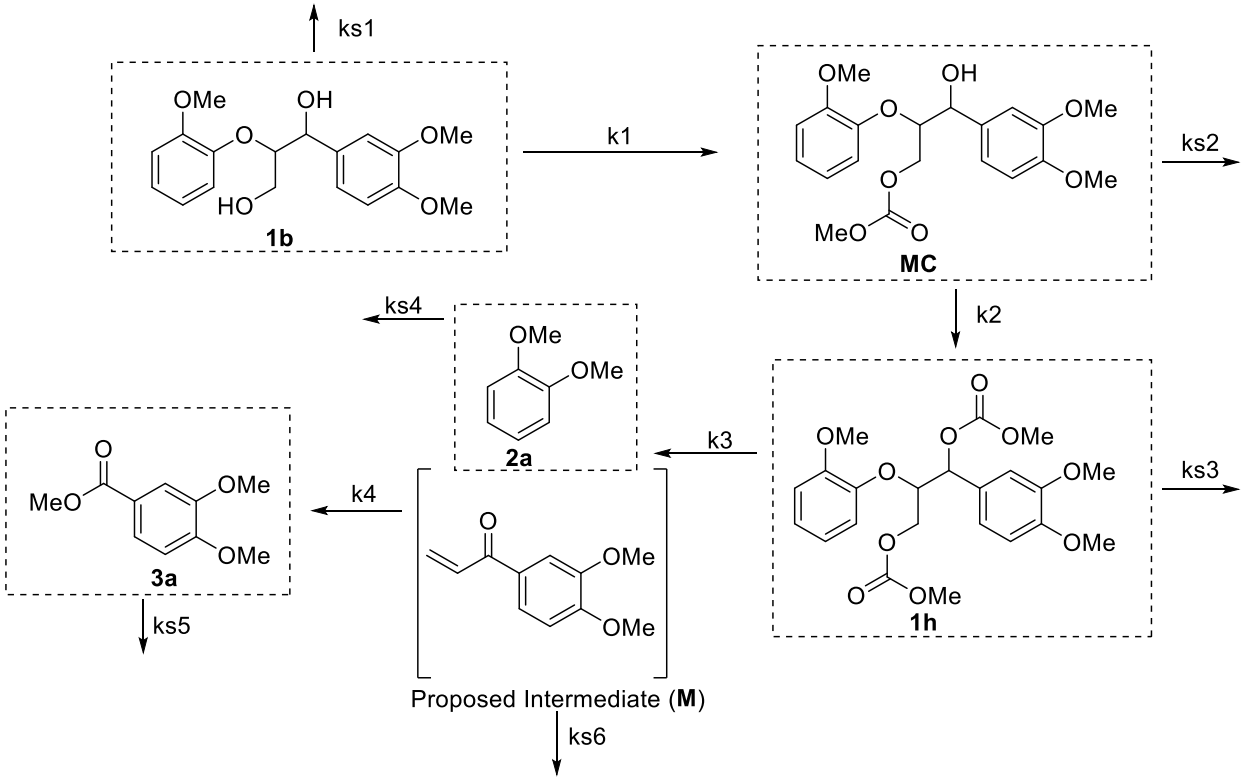


Fig. S12 Representative HPLC chromatograms for the reaction progress of **1b** with LiO*t*-Bu.

4.3 Reaction profile for cleavage of 1b with Cs_2CO_3 in DMC



Scheme S1 Reaction pathways considered in the modelling of reaction parameters for the stepwise catalytic deconstruction of *β*-O-4 model compound **1b** using Cs_2CO_3. End products are veratrole **(2a)** and dimethoxy benzoate **(3a)**.

Reaction Pathways:

dilignol(**1b**)	-->	monocarboxylated (**MC**)	:	k1 (0.69 $mins^{-1}$ ±0.07)
monocarboxylated (**MC**)	-->	dicarboxylated (**1h**)	:	k2 (0.15 $mins^{-1}$ ±0.01)
dicarboxylated (**1h**)	-->	veratole (**2a**) + **M**	:	k3 (0.0032 $mins^{-1}$ ±0.0003)
M	-->	benzoate (**3a**)	:	k4 (0.0014 $mins^{-1}$ ±0.002)

Sinks:

dilignol (**1b**)	-->	sink	:	ks1 (0.15 $mins^{-1}$ ±0.07)
monocarboxylated (**MC**)	-->	sink	:	ks2 ($1 \cdot 10^{-10}$ $mins^{-1}$ ±0.02)
dicarboxylated (**1h**)	-->	sink	:	ks3 (0.00051 $mins^{-1}$ ±0.0006)
veratrole (**2a**)	-->	sink	:	ks4 ($9.9 \cdot 10^{-5}$ $mins^{-1}$ ±0.0002)
benzoate (**3a**)	-->	sink	:	ks5 (0.00038 $mins^{-1}$ ±0.005)
M	-->	sink	:	ks6 (0.002 $mins^{-1}$ ±0.01)

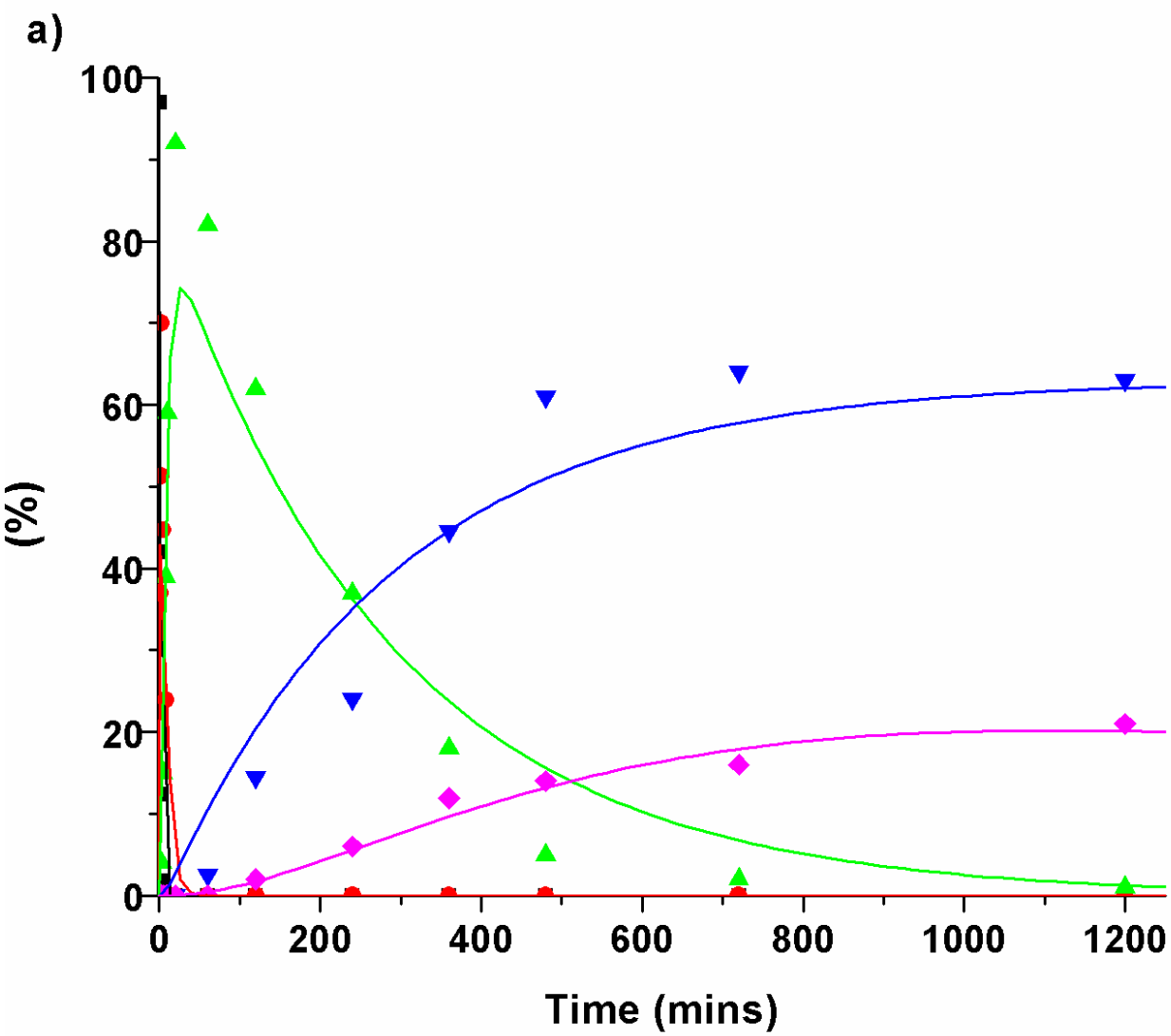
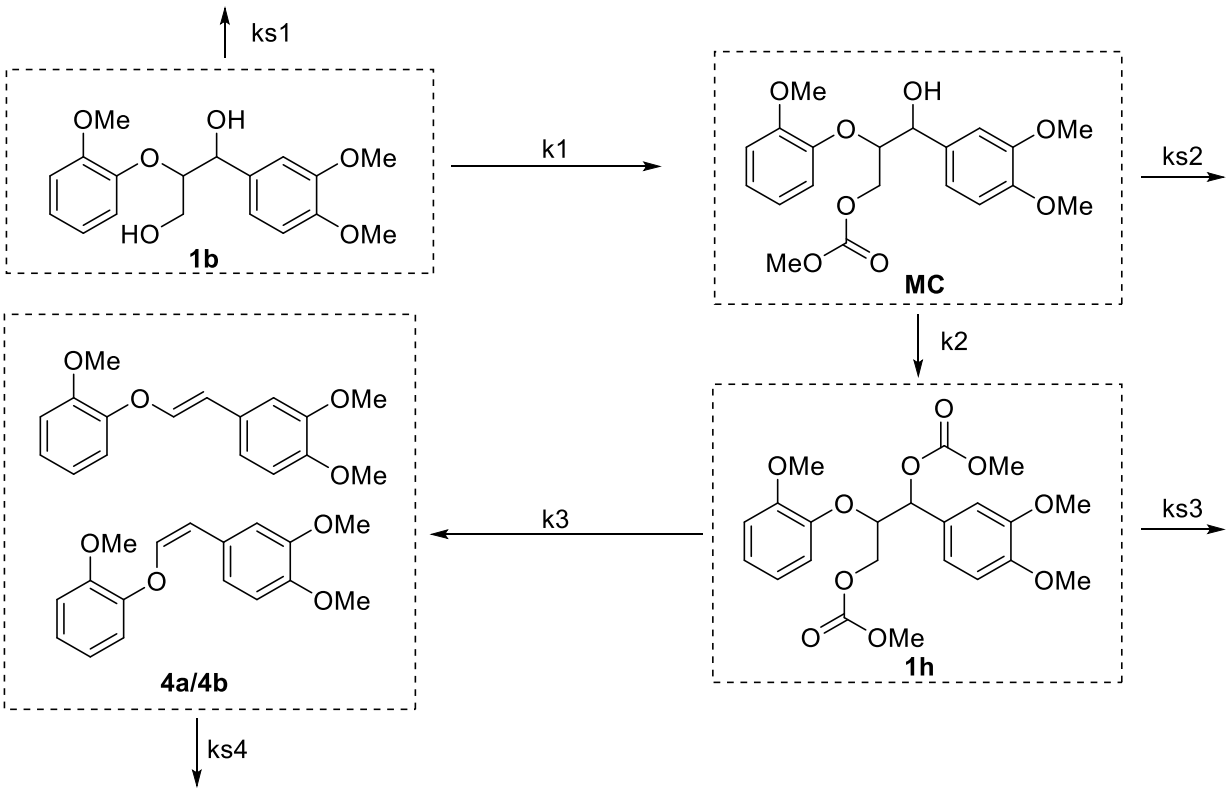


Fig. S13 Reaction profile for the formation of veratrole **(2a)** and dimethoxy benzoate **(3a)** upon cleavage of *β*-O-4 model compound dilignol **(1b)**. Reaction conditions:**1b** (0.250 mmol, 1 equiv), Cs_2CO_3 (0.05 equiv), DMC (1.2 mL), 180 ^{o}C. Dots show experimental data points, whereas the line is a modeled reaction. Black: **1b**; Red: **MC**; Green: **1h**; Blue: **2a**; Pink: **3a**.

4.4. Reaction profile for cleavage of 1b with LiO*t*-Bu in DMC



Scheme S2 Reaction pathways considered in the modelling of reaction parameters for the stepwise catalytic deconstruction of *β*-O-4 model compound **Ib** using LiO*t*-Bu. End products are *cis*/*trans* alkenes **(4a/4b)**

Reaction Pathways

dilignol (**Ib**)	-->	monocarboxylated (**MC**)	:	k1 (0.2 $mins^{-1}$ ±0.04)
monocarboxylated (**MC**)	-->	dicarboxylated (**1h**)	:	k2 (0.025 $mins^{-1}$ ±0.003)
dicarboxylated (**1h**)	-->	alkenes (**4a/4b**)	:	k3 (0.005 $mins^{-1}$ ±0.0007)

Sinks

dilignol (**1b**)	-->	sink	:	ks1 ($1{\cdot}10^{-1}$ $mins^{-1}$ ±0.02)
monocarboxylated (**MC**)	-->	sink	:	ks2 ($1{\cdot}10^{-11}$ $mins^{-1}$ ±0.005)
dicarboxylated (**1h**)	-->	sink	:	ks3 (0.0011 $mins^{-1}$ ±0.001)
alkenes (**4a/4b**)	-->	sink	:	ks4 ($1{\cdot}10^{-11}$ $mins^{-1}$ ±0.0002)

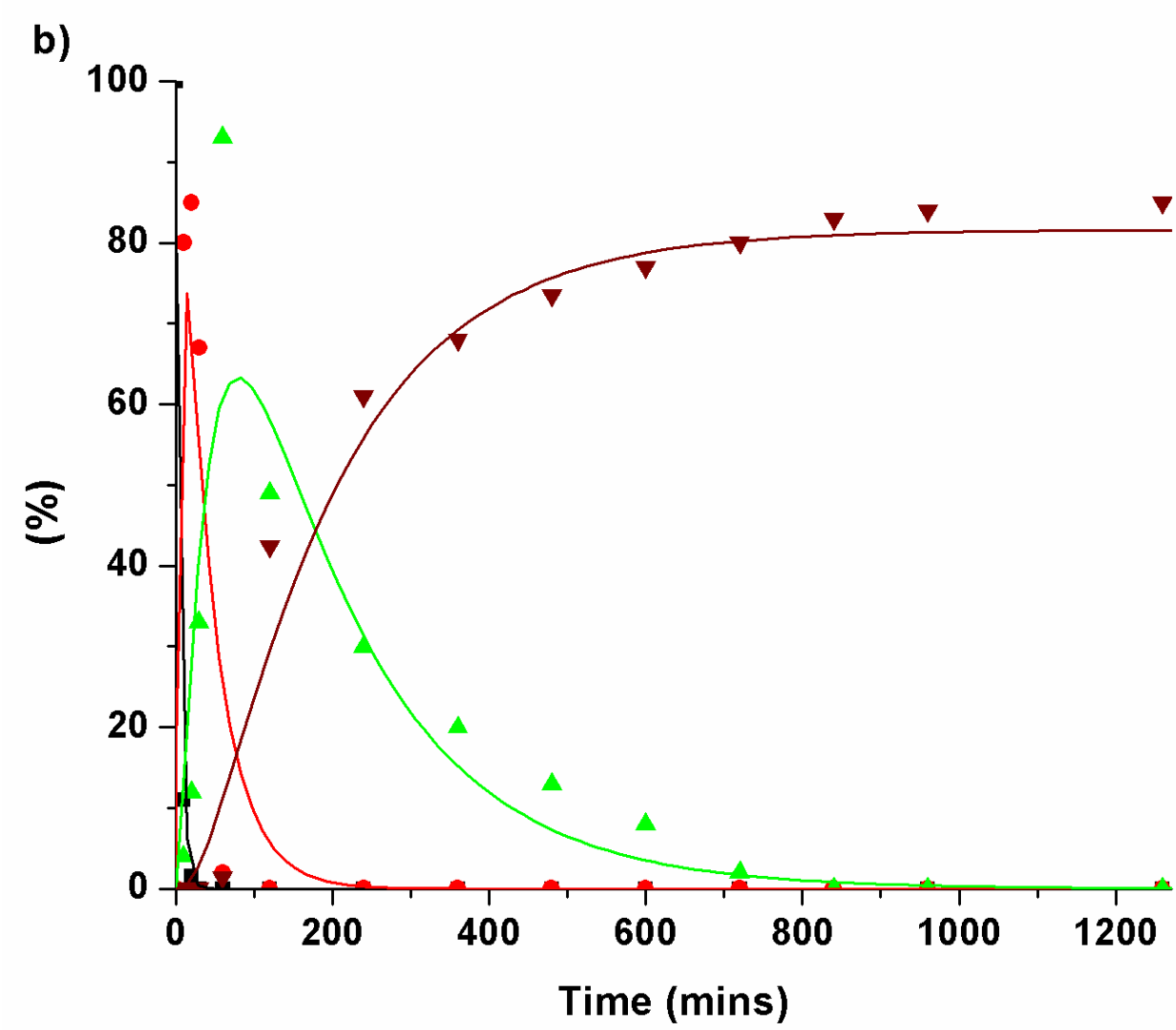


Fig. S14 Reaction profile for the formation of *cis/trans* alkenes **(4a/4b)** upon modification of *β*-O-4 model compound dilignol **(1b).** Reaction conditions: **1b** (0.250 mmol, 1 equiv), LiO*t*-Bu (0.05 equiv), DMC (1.2 mL), 180 °C. Dots show experimental data points, whereas the line is a modeled reaction. Black: **Ib**; Red: **MC**; Green: **1h**; Brown: *cis/trans* alkenes (**4a/4b**).

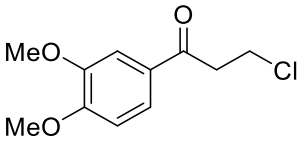
5. Synthesis and reactivity of vinyl ketone M4

5.1 Synthesis of vinyl ketone M4

The vinyl ketone was synthesised following literature procedures. Starting from veratrole and 3-chloropropionylchlorid, a Friedel-Craft acylation reaction led to 3-chloro-1-(3,4-dimethoxy phenyl)propan-1-one in 93% yield. Subsequent elimination of HCl afforded **M4** in good yield.

Synthesis of 3-chloro-1-(3,4-dimethoxyphenyl)propan-1-one[18]

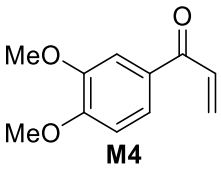
A flame-dried and argon flushed 250 mL three-neck flask equipped with a magnetic stirrer and an argon inlet was charged with $AlCl_3$ (2.7 g, 20.4 mmol, 1.03 equiv) and dry CH_2Cl_2 (76 mL). The solution was cooled to 0 °C and 3-chloropropionylchlorid (1.7 mL, 17.3 mmol, 1.1 equiv) was added dropwise. A solution of veratrole (2.0 mL, 16.0 mmol, 1.0 equiv) in dry CH_2Cl_2 was then added dropwise. The reaction mixture was allowed to warm to room temperature and heated at 40 °C for 3 h. The mixture was again cooled to room temperature and aq. HCl (6 M, 10 mL) was added. The phases were separated and the organic phase was washed with water (100 mL), aq. NaOH (10%, 100 mL) and brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The title compound was obtained without further purification as a pink solid (4.0 g, 14.6 mmol, 93%) with spectroscopic data in accordance with the literature.[19]



mp: 110–112 °C. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 7.57 (dt, *J* = 8.4 Hz and 1.9 Hz, 1H), 7.53 (t, *J* = 1.7, 1H), 6.90 (dd, *J* = 8.4 Hz and 1.4 Hz, 1H), 3.94 (s, 3H), 3.95 (s, 3H), 3.74 (td, *J* = 6.8 Hz and 1.2 Hz 2H), 3.48–3.60 (td, *J* = 6.8 Hz and 1.2 Hz, 2H).

Synthesis of 1-(3,4-dimethoxyphenyl)prop-2-en-1-one (10)[18]

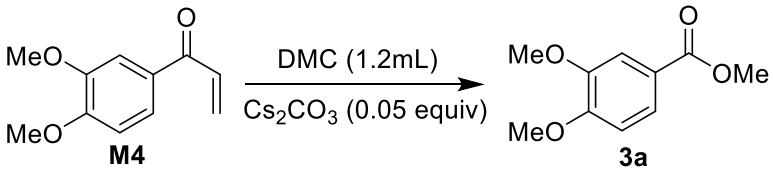
A flame-dried and argon flushed 100 mL two-neck flask equipped with a reflux condenser, a magnetic stirrer and an argon inlet was charged with 3-chloro-1-(3,4-dimethoxyphenyl)propan-1-one (4.02 g, 14.7 mmol, 1.0 equiv) and dry toluene (52 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene (2.4 mL, 16.2 mmol, 1.1 equiv) was added dropwise and the reaction mixture was heated at 80 °C for 3.5 h. The solution was then allowed to cool to room temperature and water (100 mL) was added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (Hexane to Hexane/Et_2O 1/1) yielding compound **M4** (2.00 g, 10.4 mmol, 71%) as a yellow viscous oil with spectroscopic data in accordance with the literature.[19]



M4

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.56 (m, 2H). 7.19 (dd, *J* = 17.0 Hz and 10.5 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.44 (dd, *J* = 17.0 Hz and 1.8 Hz, 1H), 5.88 (dd, *J* = 10.5 Hz and 1.9 Hz, 1H), 3.95 (s, 3H), 3.96 (s, 3H).

5.2 Reaction of the vinyl ketone in DMC in the presence of Cs_2CO_3

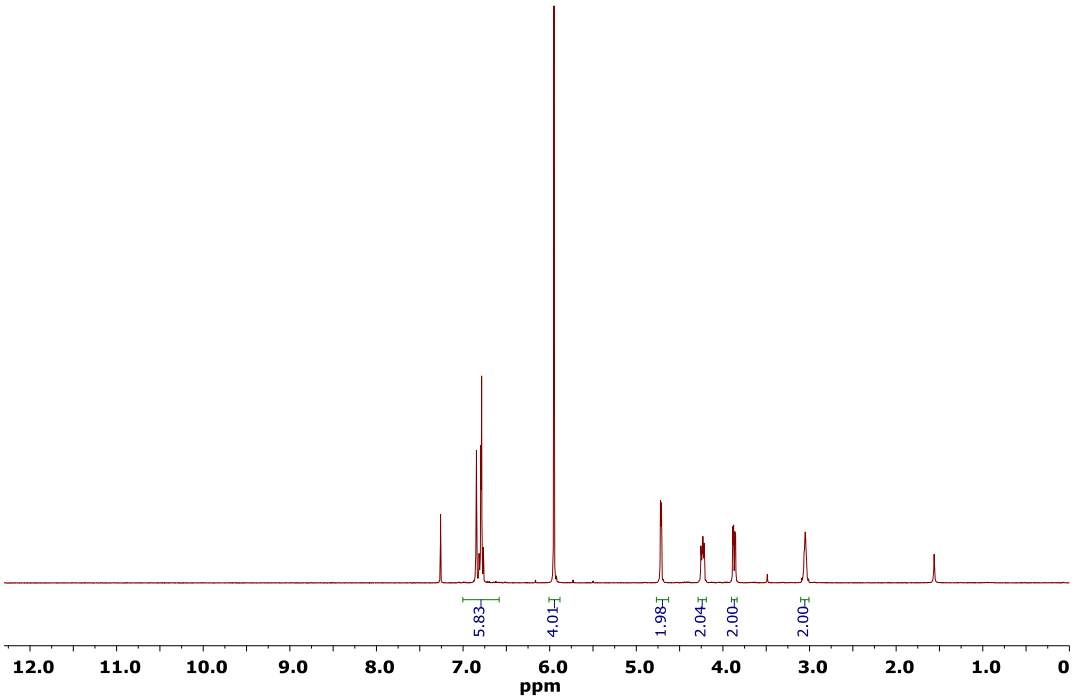


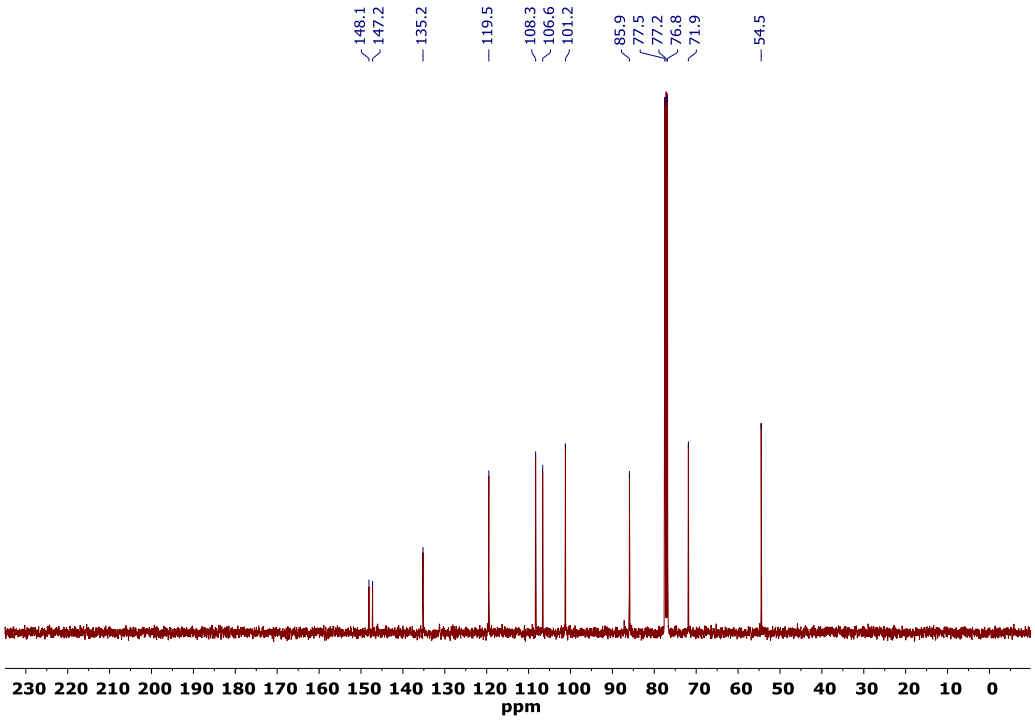
M4 **3a**

A 20 mL pressure tube with a Teflon screw cap and a magnetic stirrer was charged with vinyl ketone (0.25 mmol, 1.00 equiv) and Cs_2CO_3 (0.05 equiv) in dimethyl carbonate (1.2 mL). The mixture was stirred at 180 °C for 8 h followed by cooling to room temperature. A standard solution (1.00 mL of 3,4-dimethoxy benzylalcohol in methanol, c = 0.2 mol/L) 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. The average yield for the dimethoxy benzoate (**3a**) was hence calculated to be 40 %.

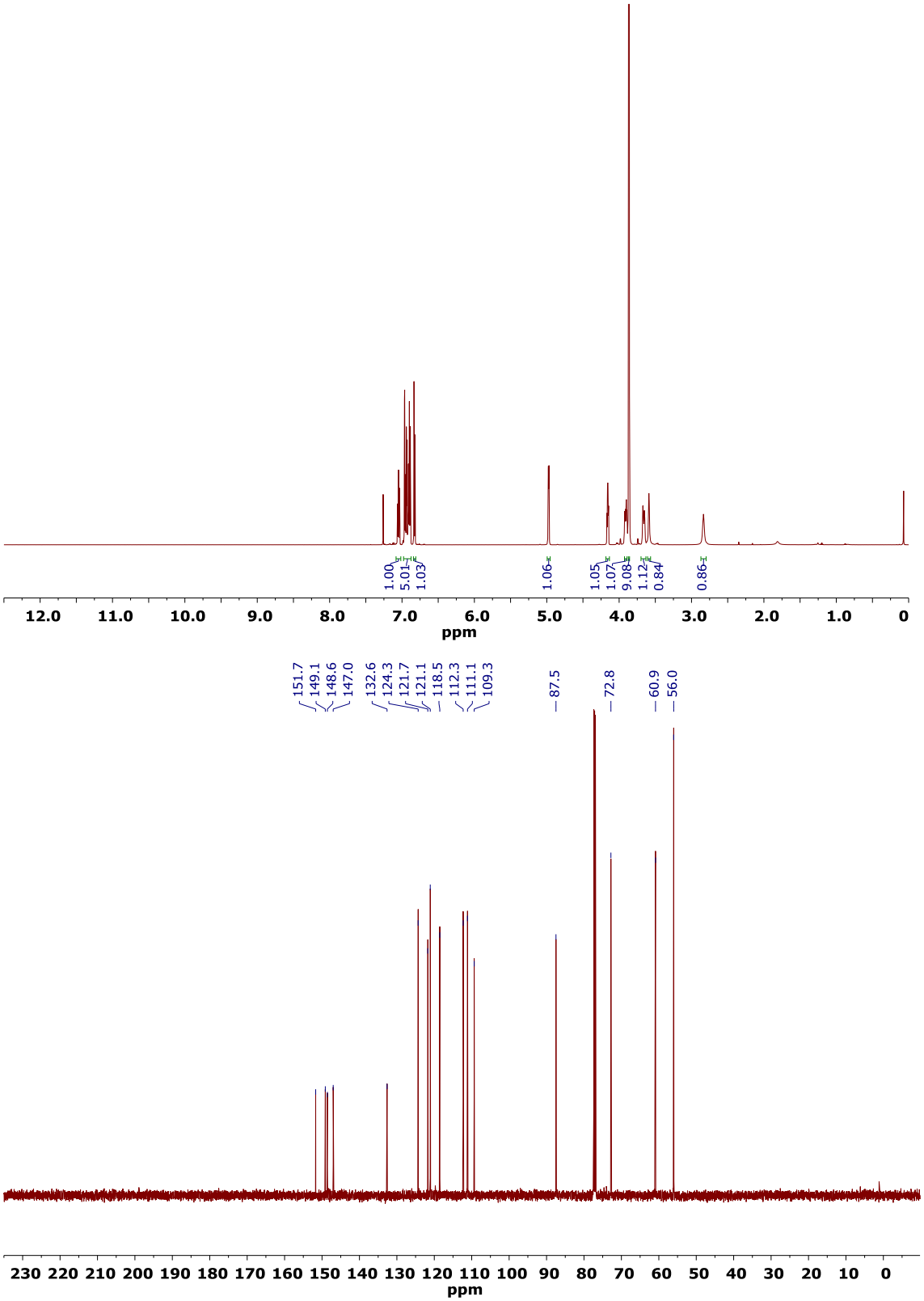
6. NMR spectra:

(1*S*,3a*R*,4*S*,6a*R*)-1,4-Bis(benzo[d][1,3]dioxol-5-yl)tetrahydro-1H,3H-furo[3,4-c]furan, Sesamin (1a)

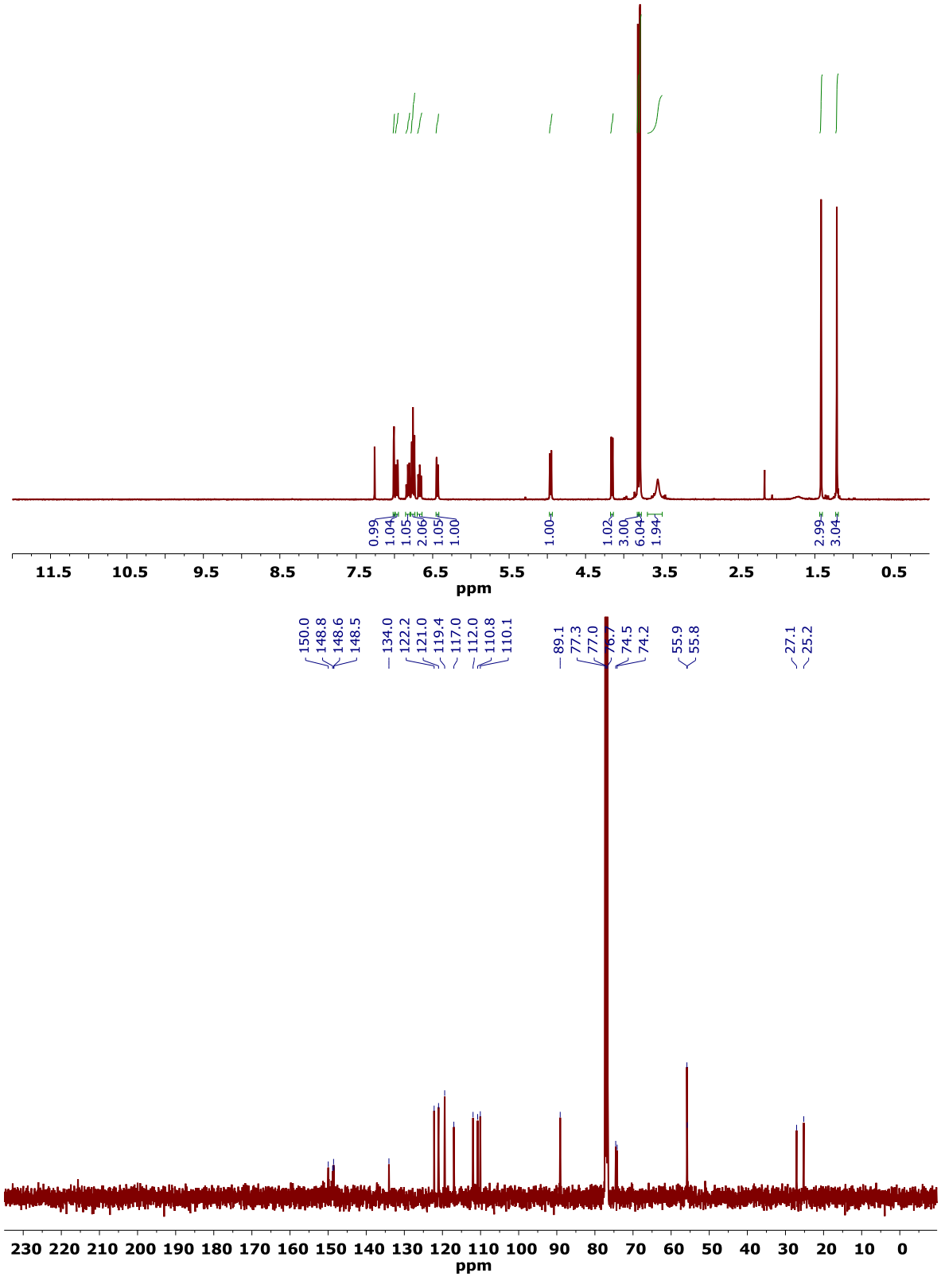




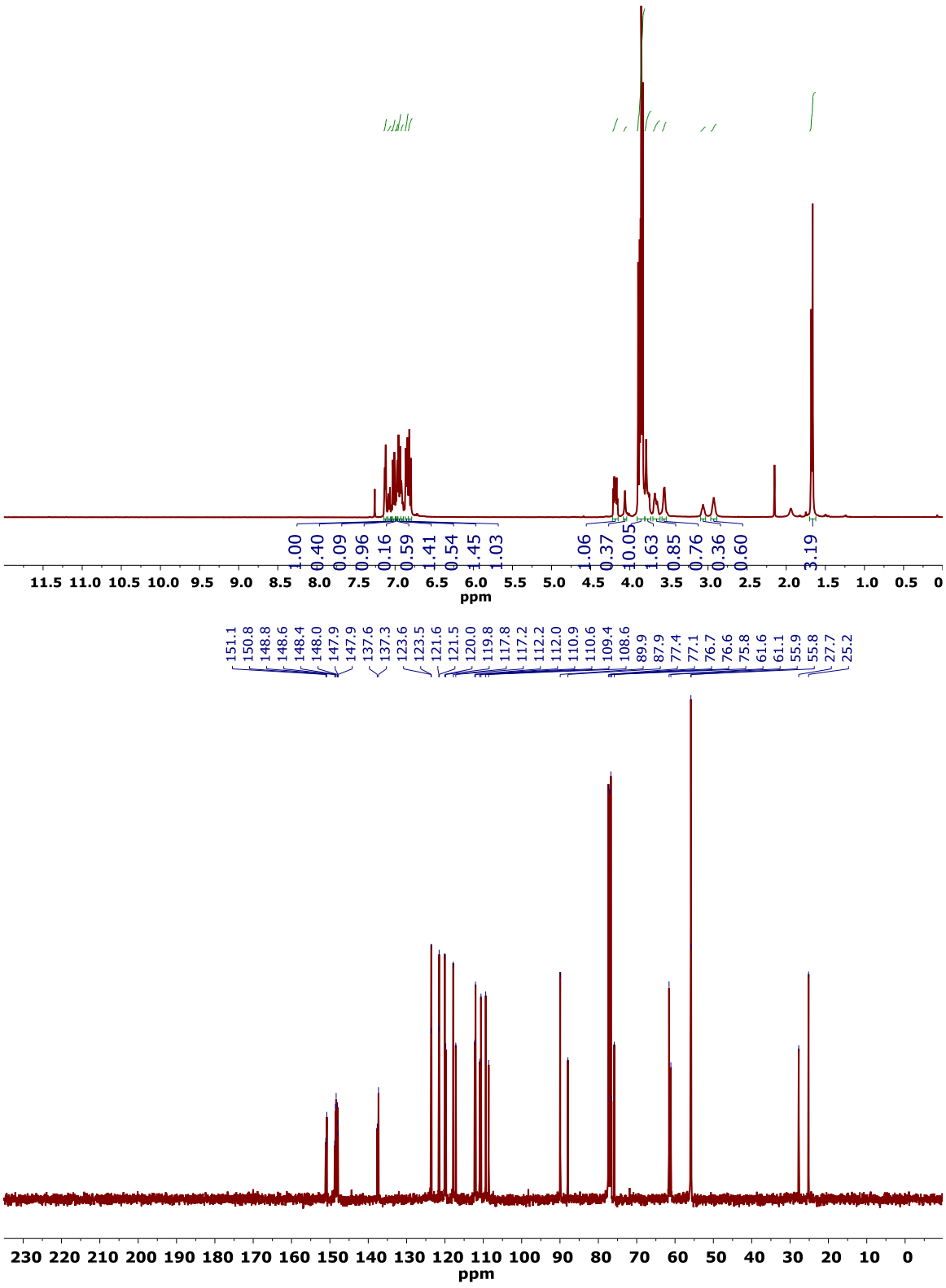
erythro-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-l,3-propanediol (1b)



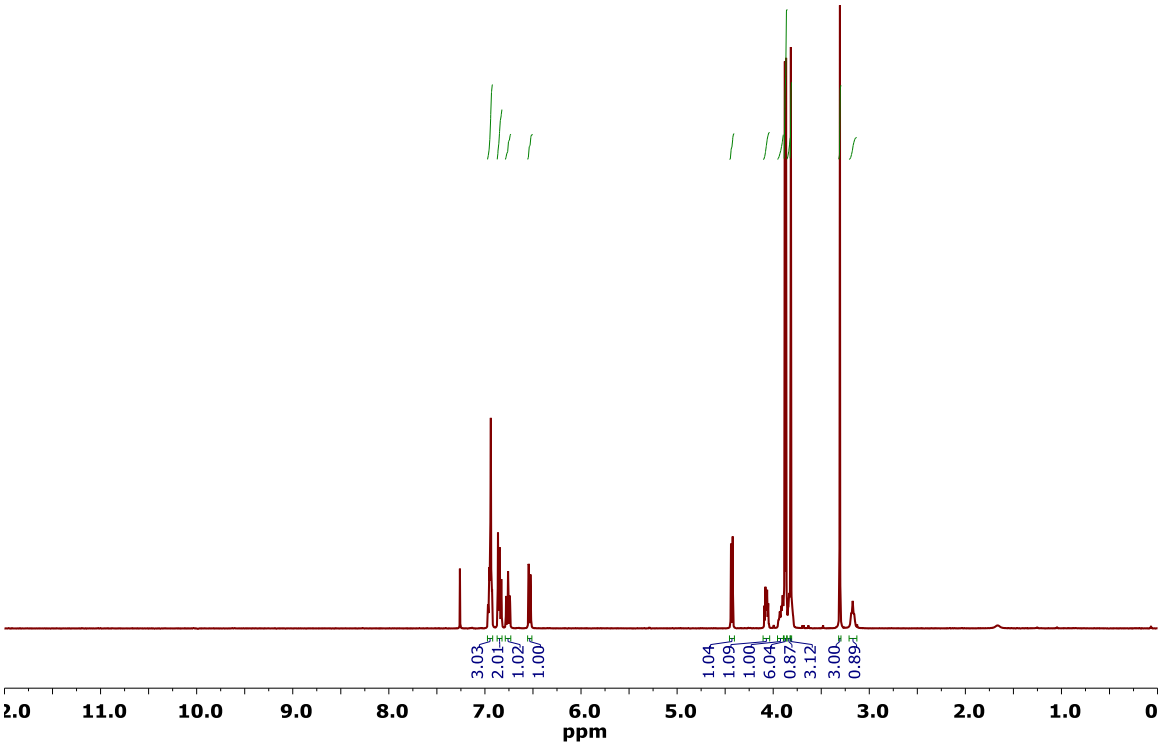
erythro-1–(3,4–Dimethoxyphenyl)–3,3–dimethyl–2–(2–methoxyphenoxy)–l,3–propanediol (1c)

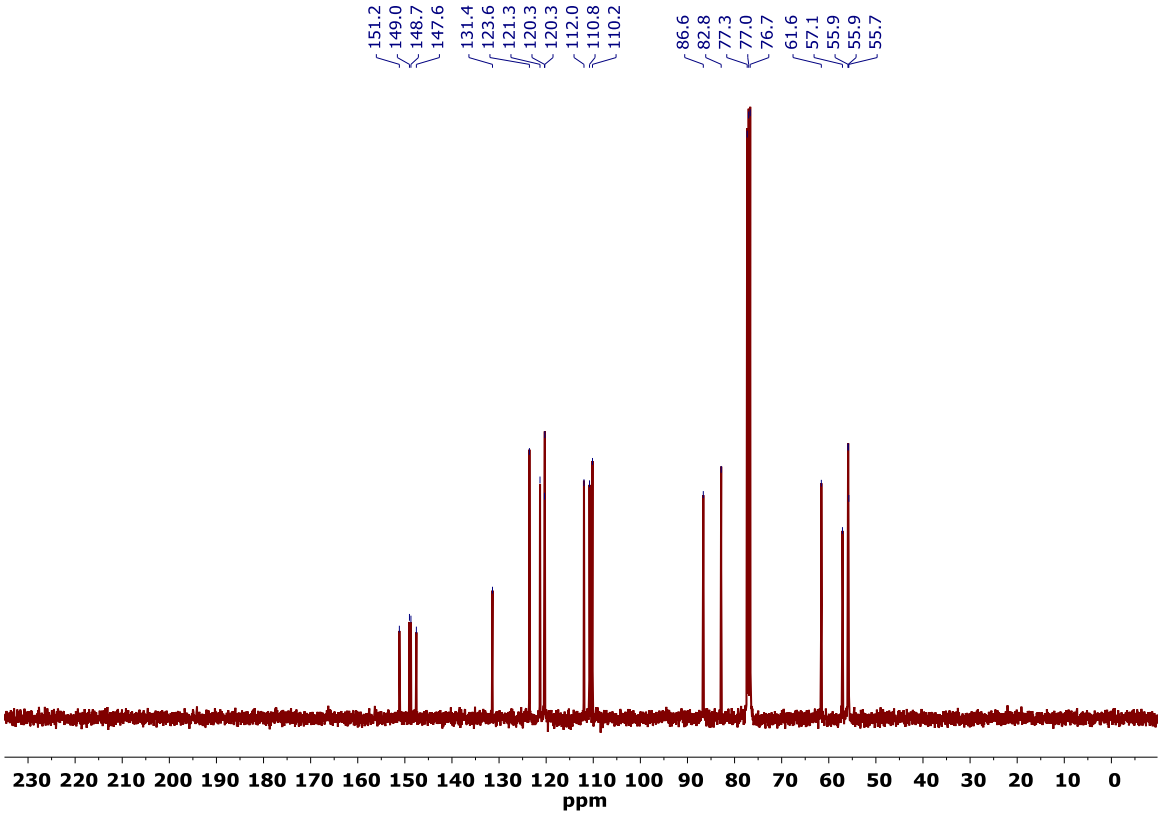


3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy) butane-1,3-diol (1d)

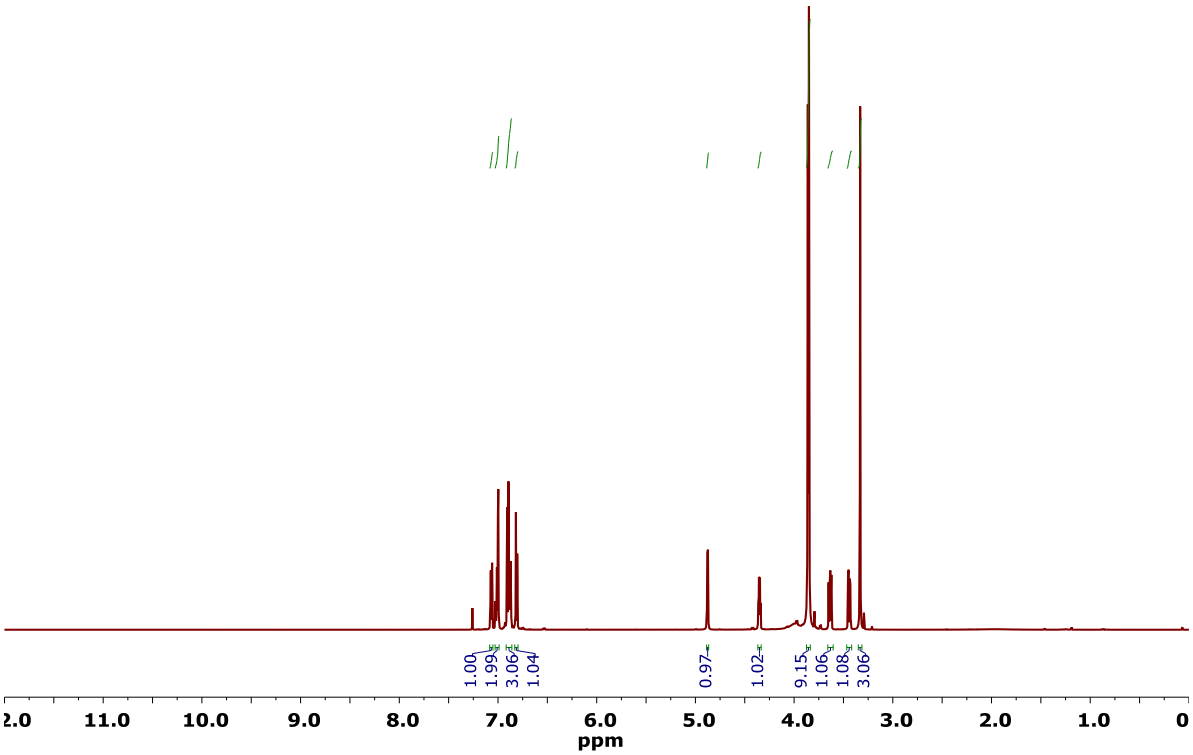


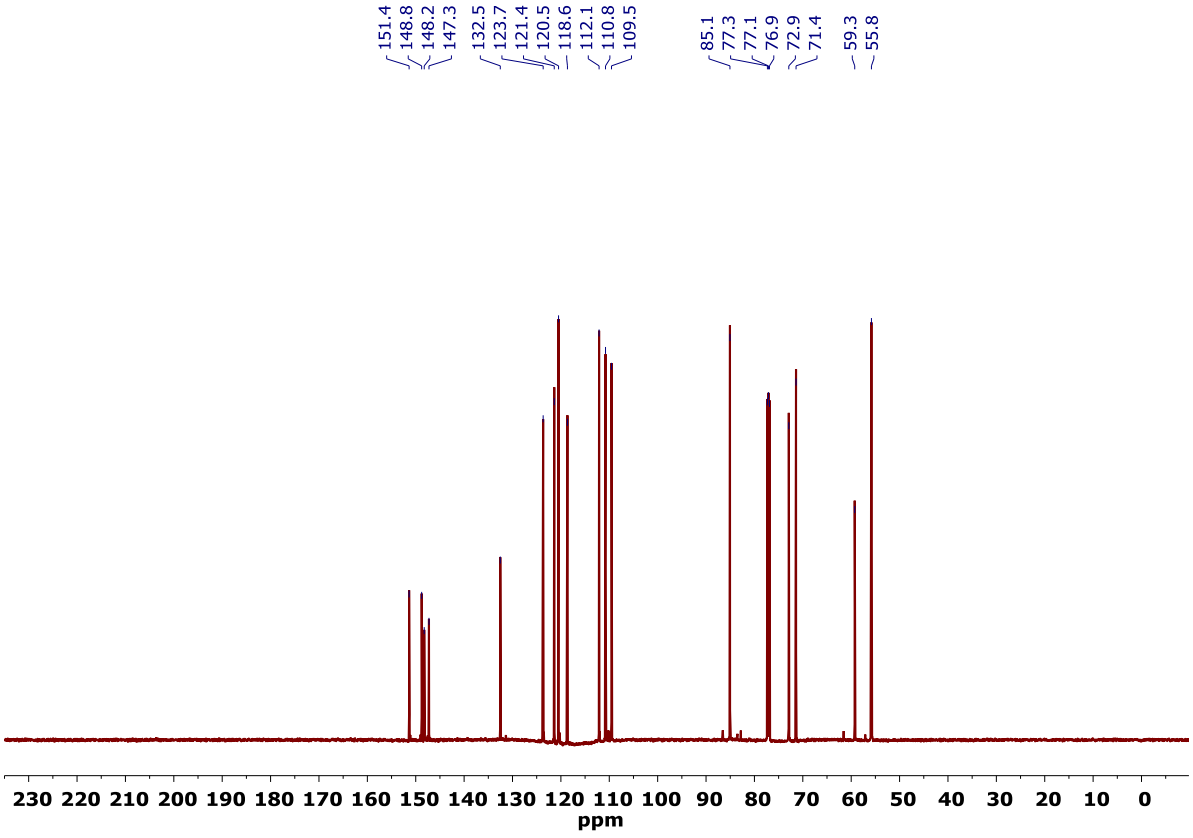
erythro-3-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)-1-propanol (1e)



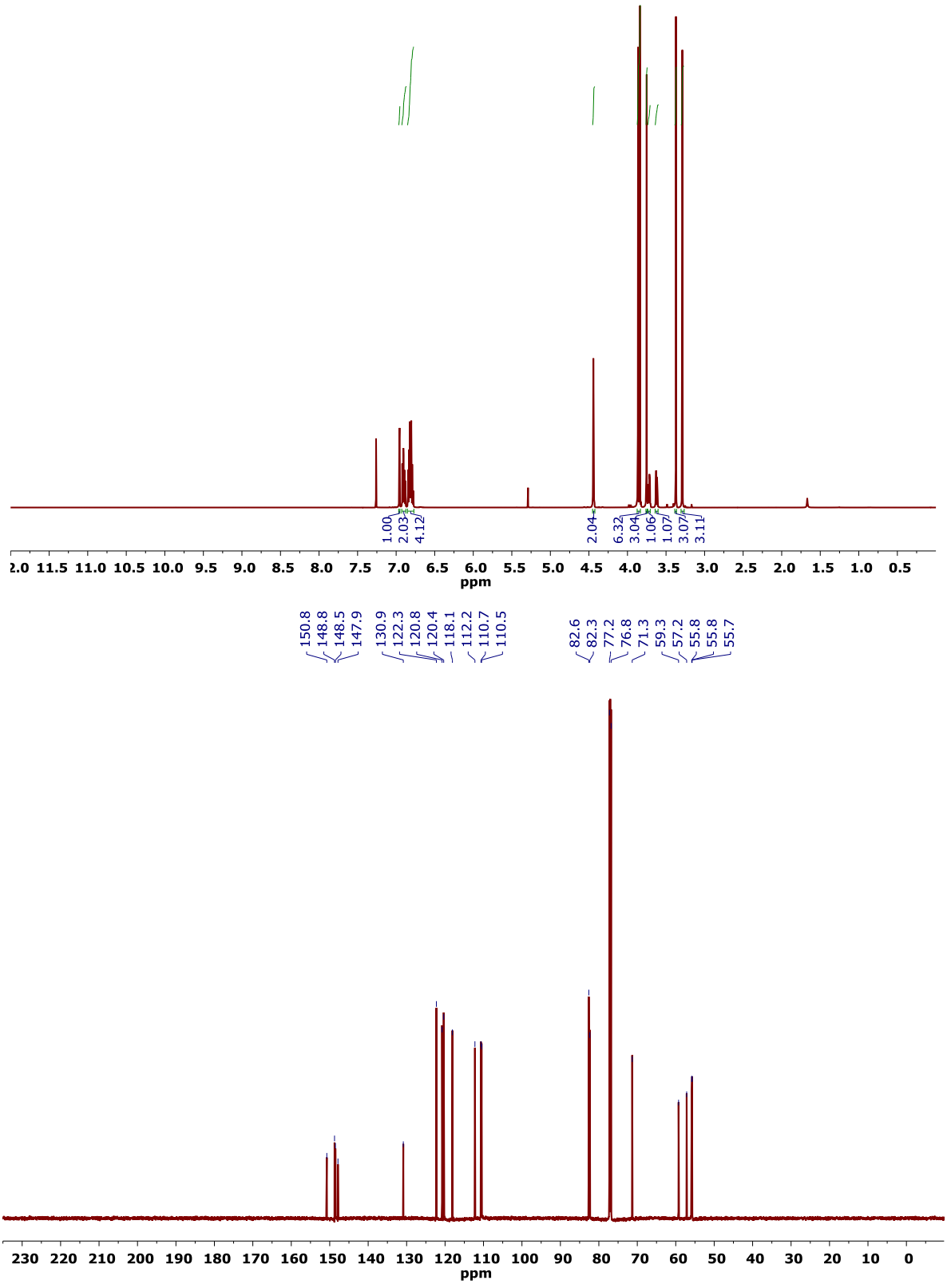


erythro-1-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)-1-propanol (1f)

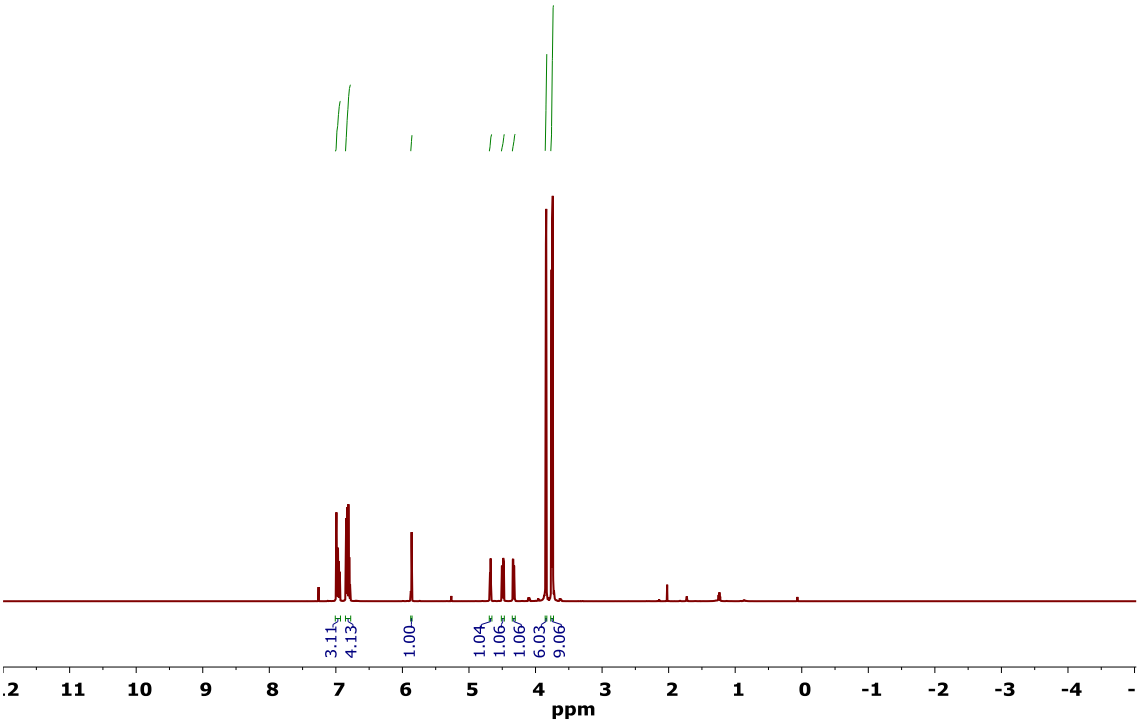


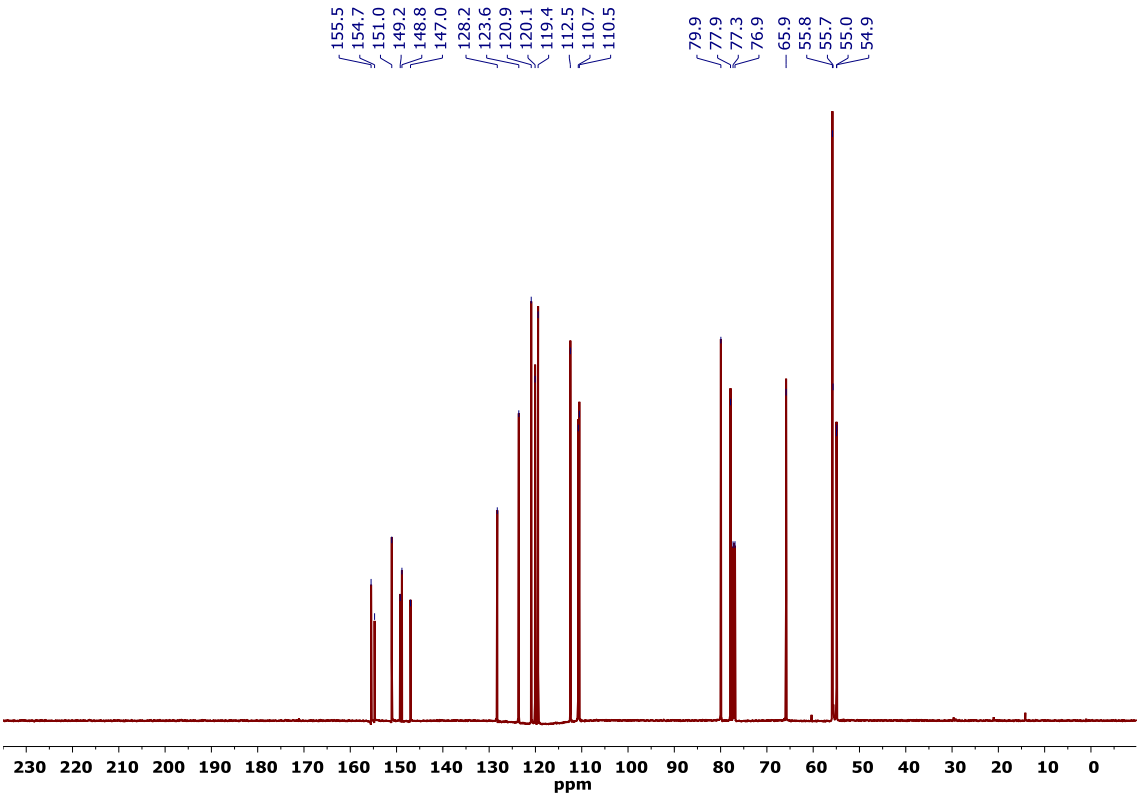


erythro-1,3–Dimethoxy–1–(3,4–dimethoxyphenyl)–2–(2–methoxyphenoxy) propane (1g)

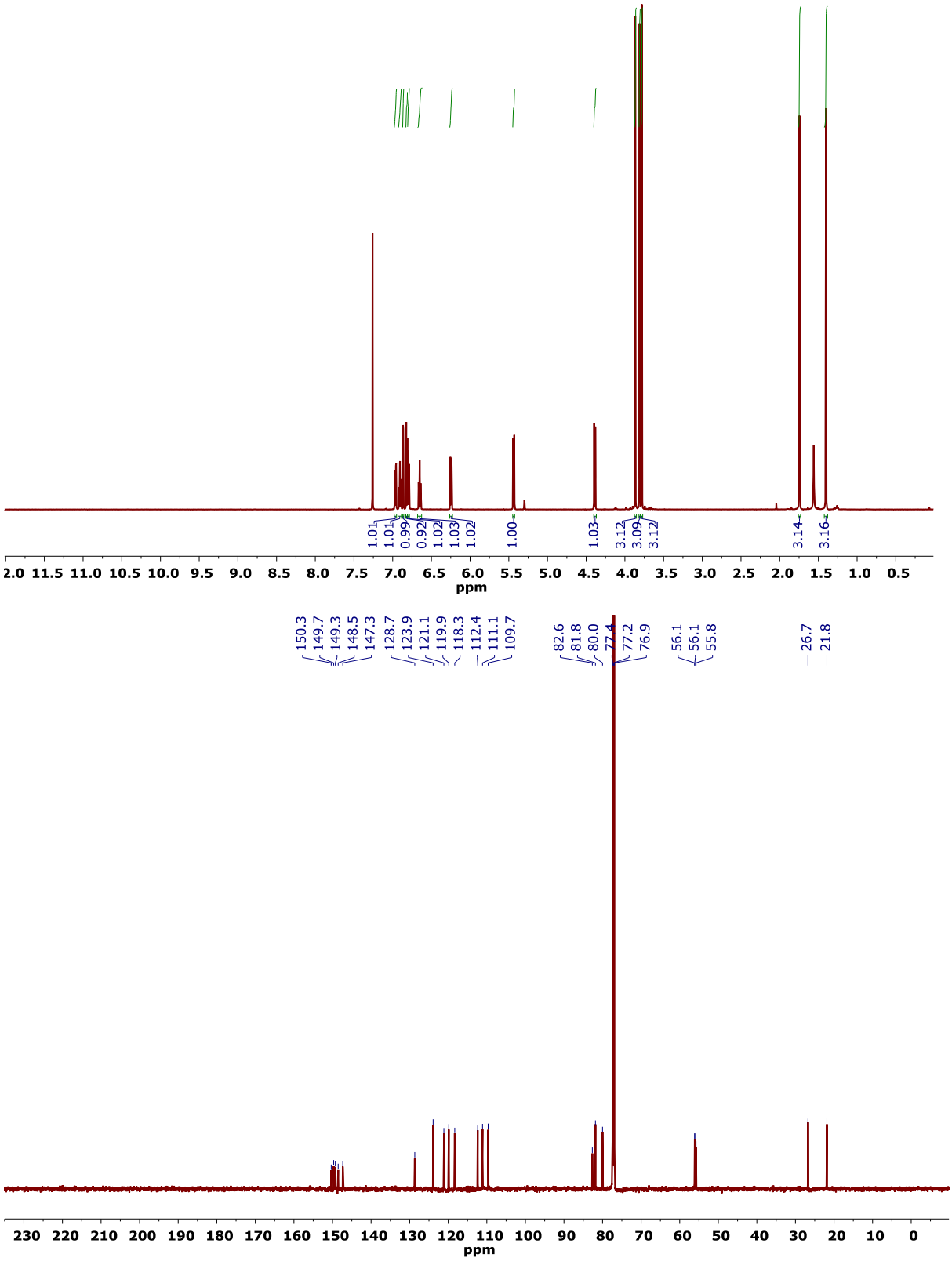


erythro-1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-propane-1,3-diyldimethyl biscarbonate (1h)

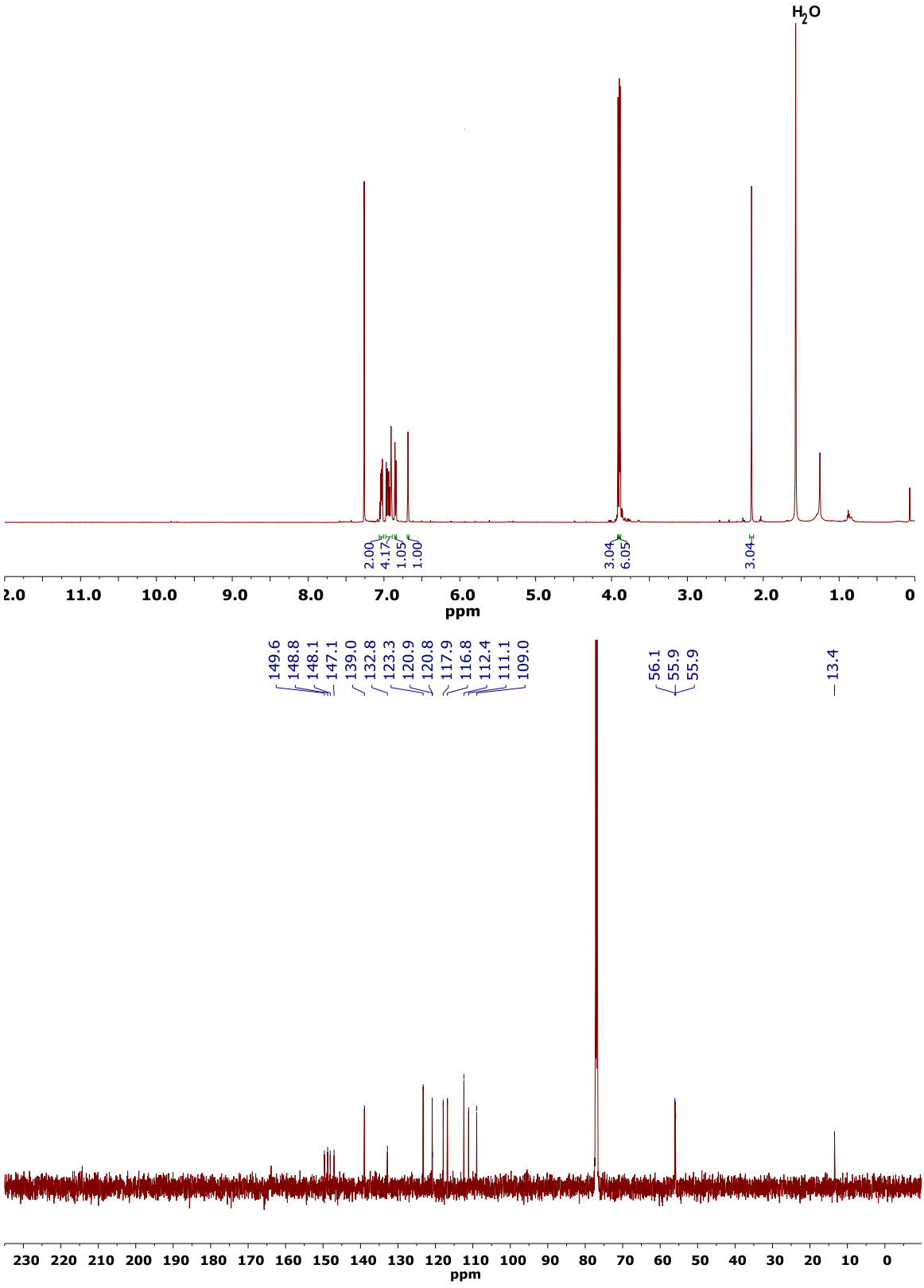




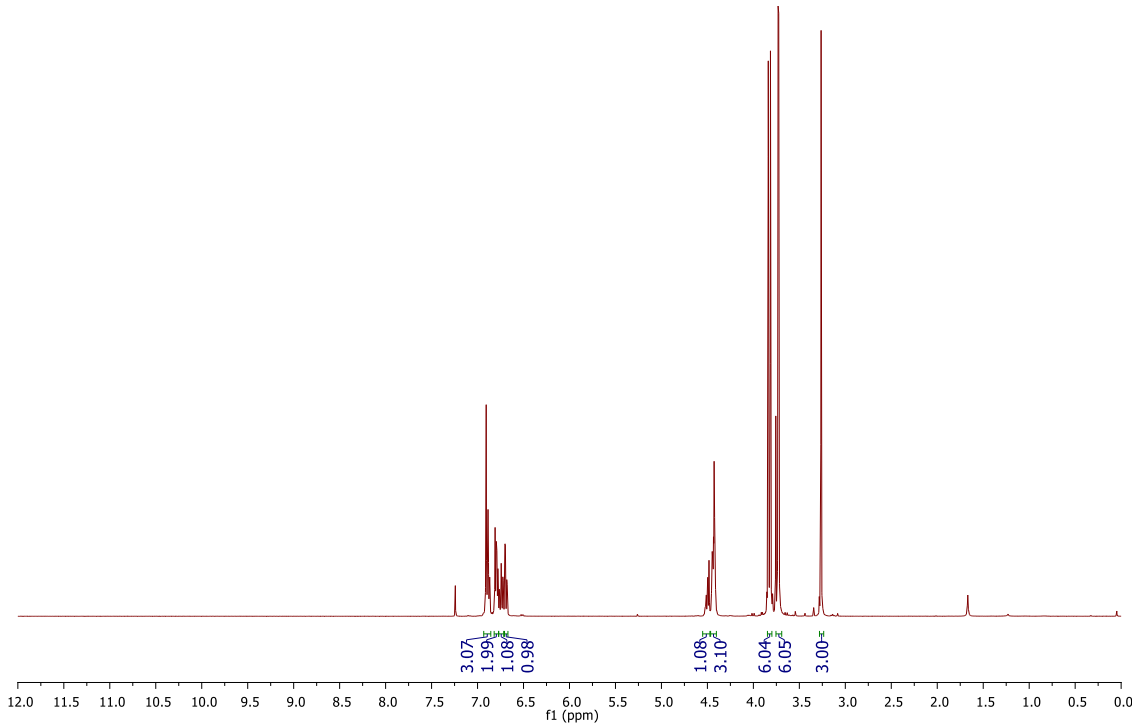
6-(3,4-Dimethoxyphenyl)-5-(2-methoxyphenoxy)-4,4-dimethyl-1,3-dioxan-2-one (5)

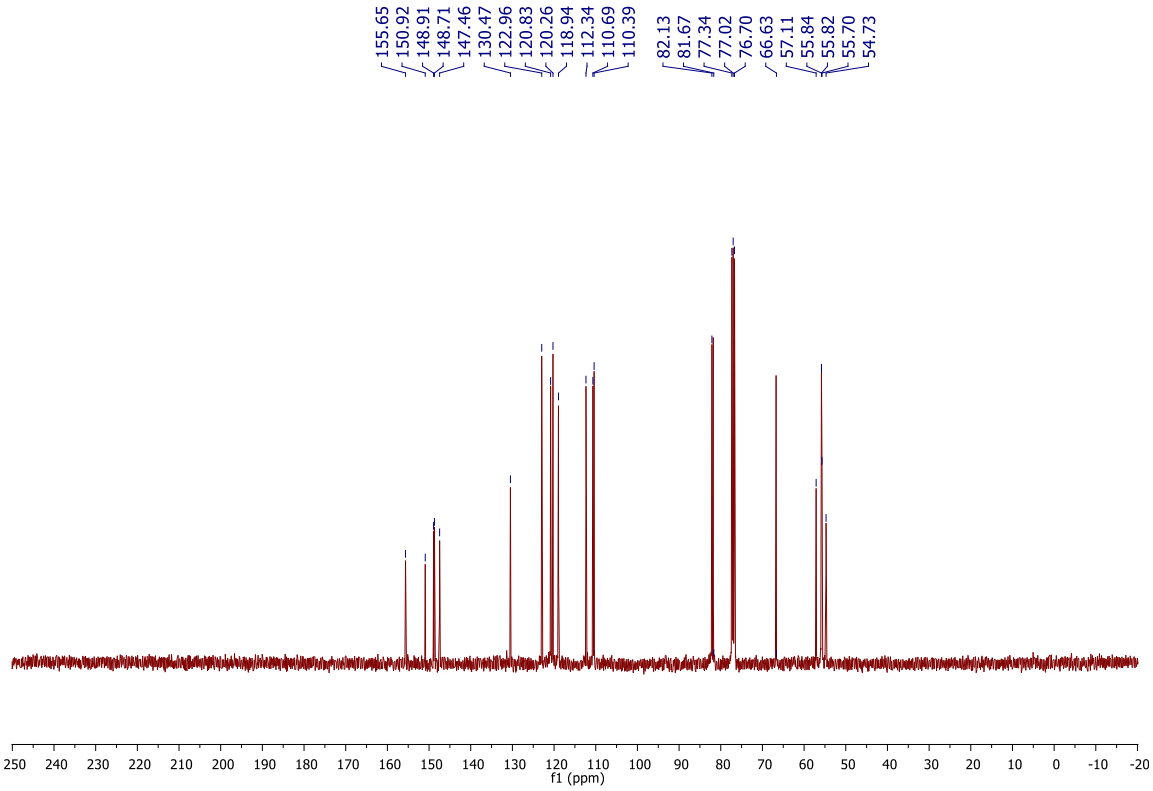


(*Z*)-1,2-Dimethoxy-4-(1-(2-methoxyphenoxy)prop-1-en-2-yl)benzene (6a)

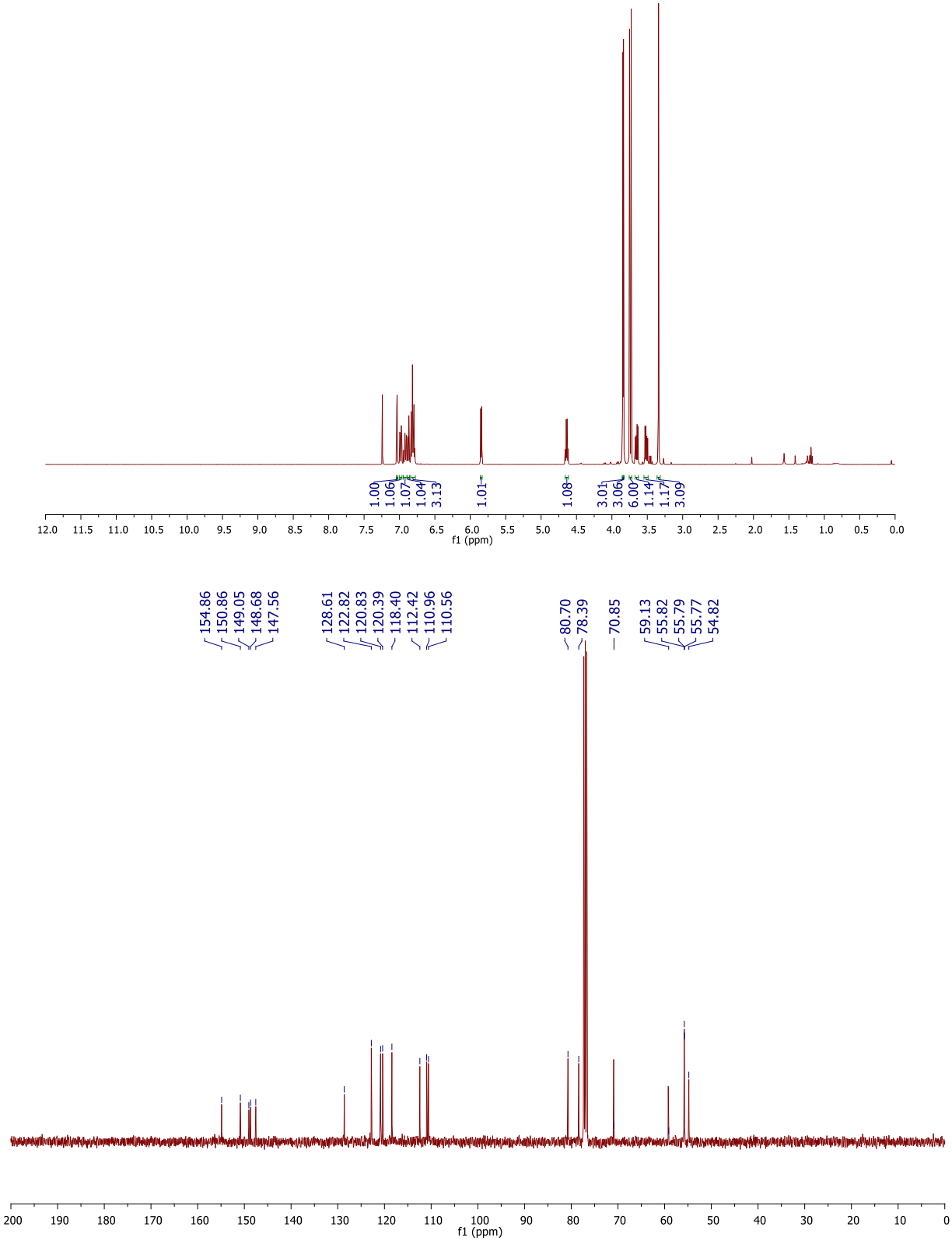


erythro-3-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)propyl methyl carbonate (7)

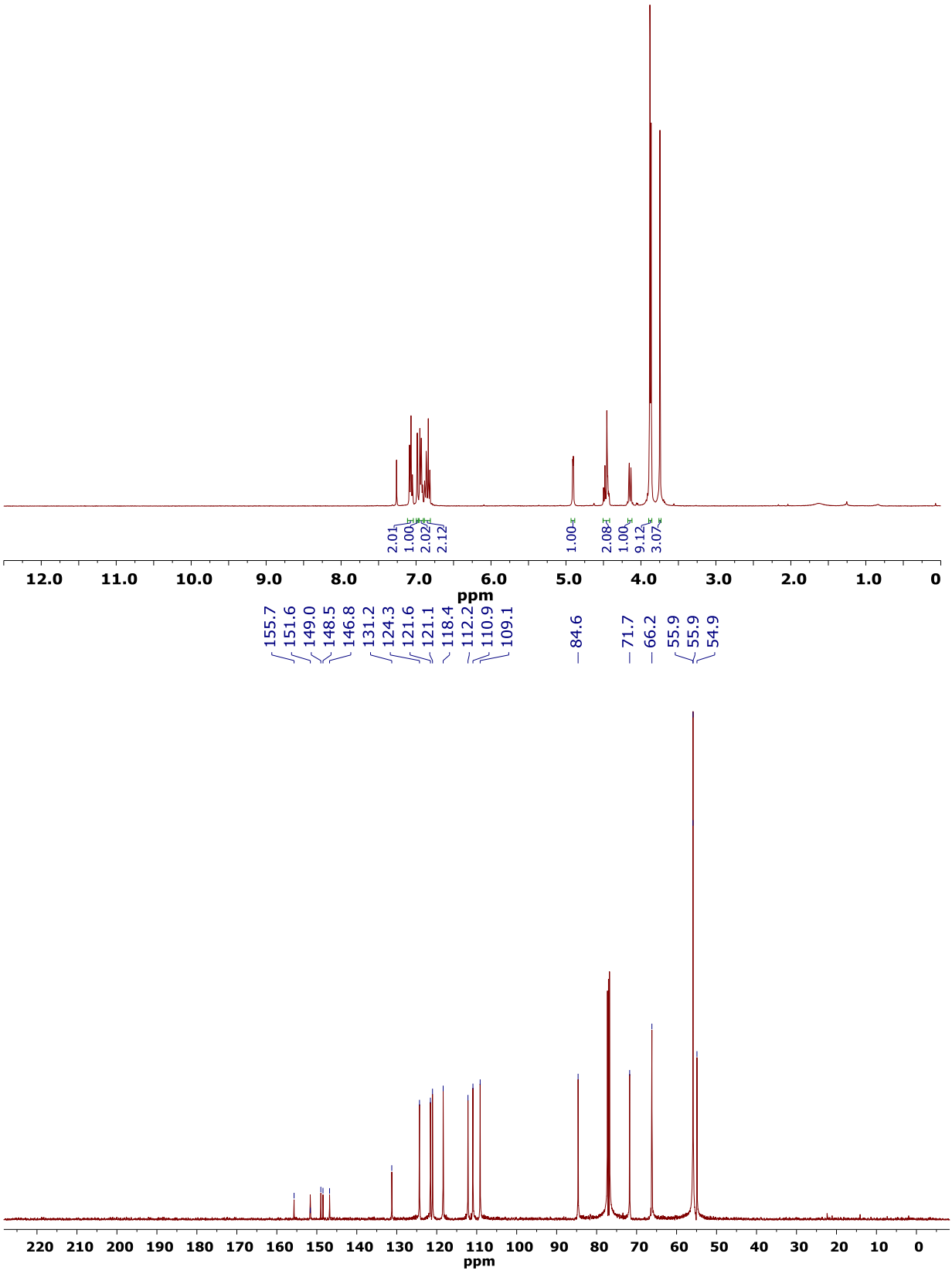




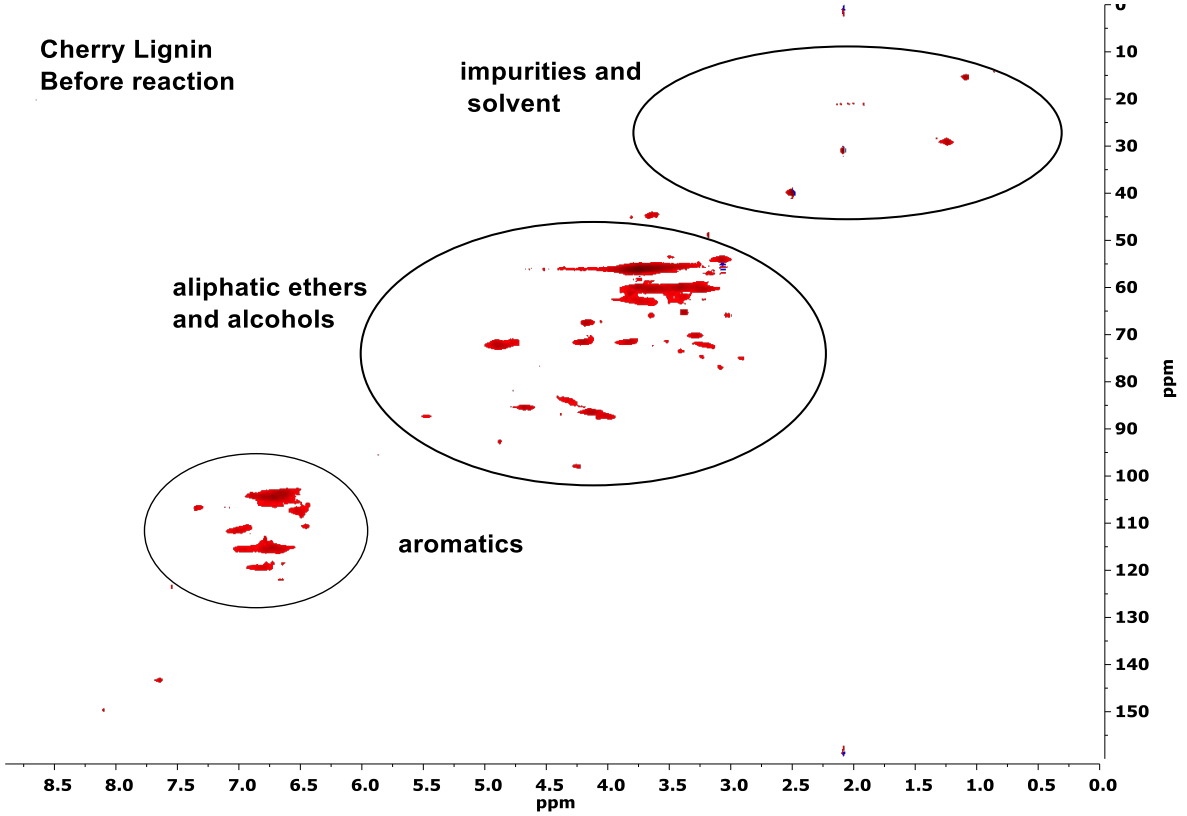
erythro-1-(3,4-Dimethoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)propyl methyl carbonate (8)

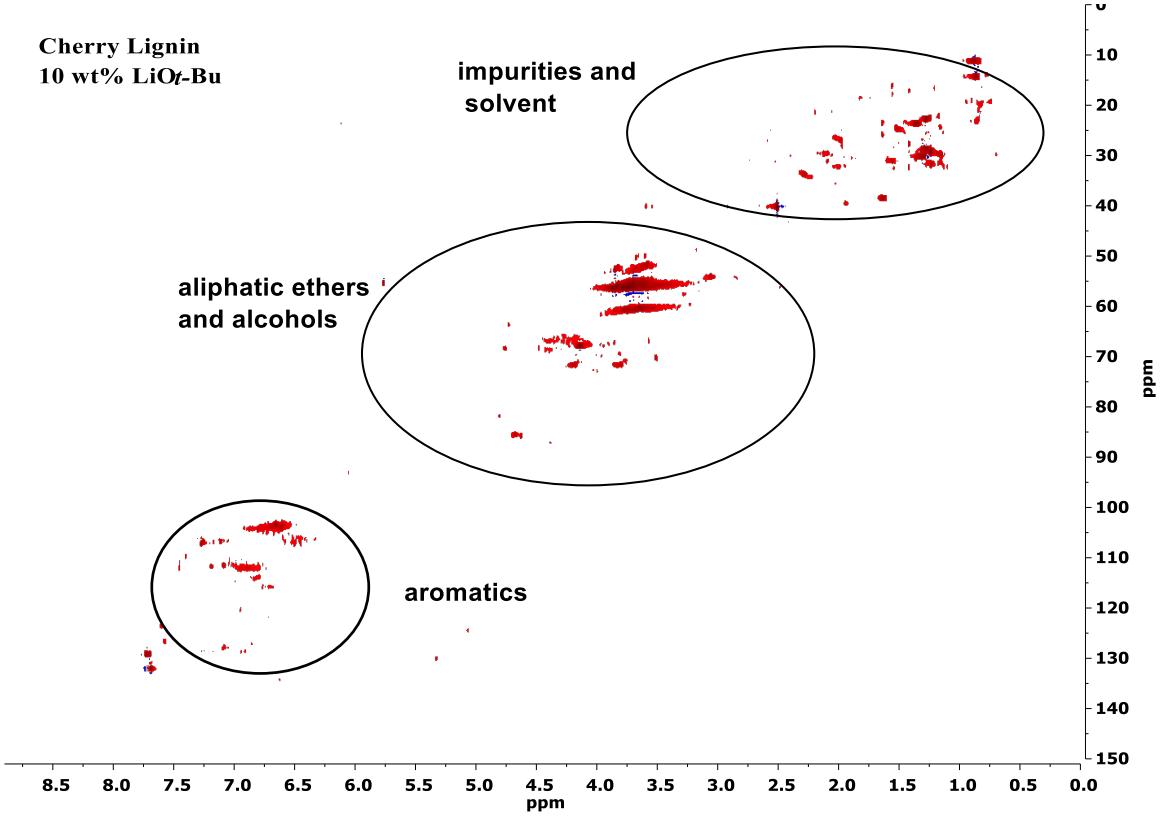


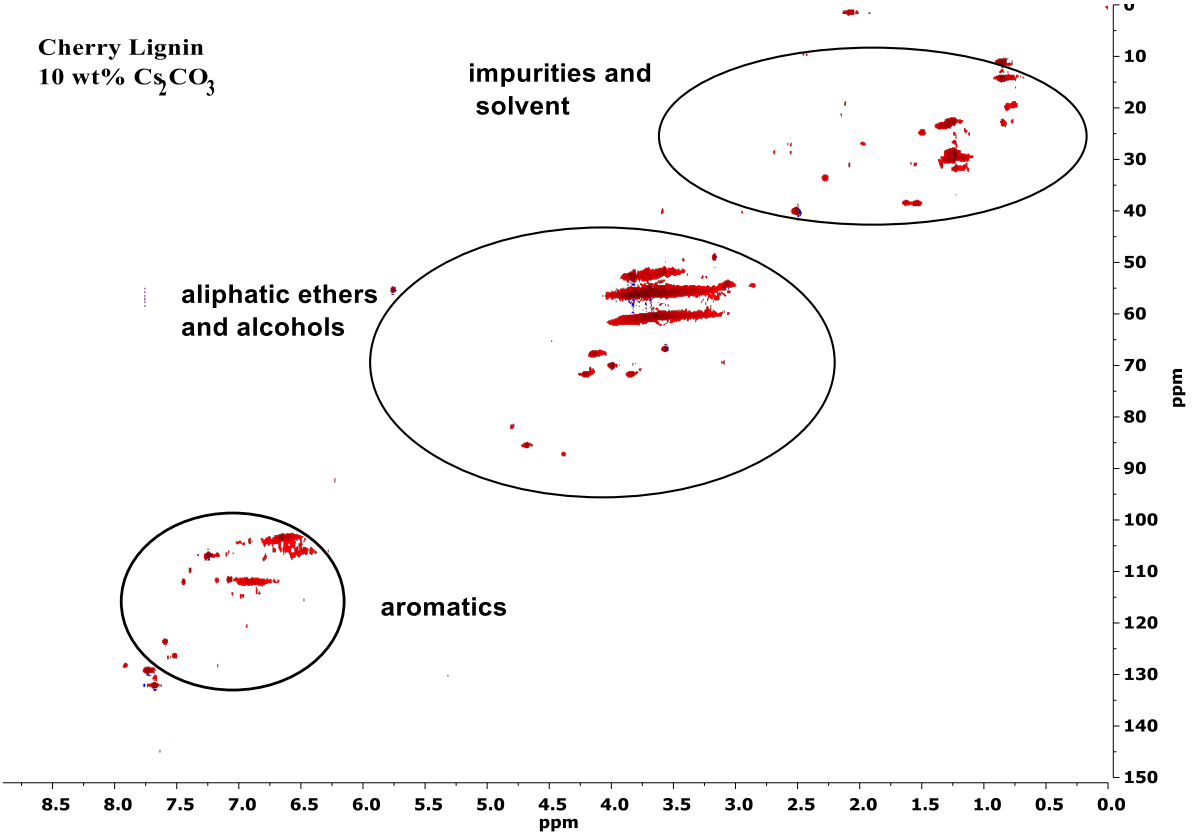
erythro-3-(3,4-Dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propyl methyl carbonate. (MC)

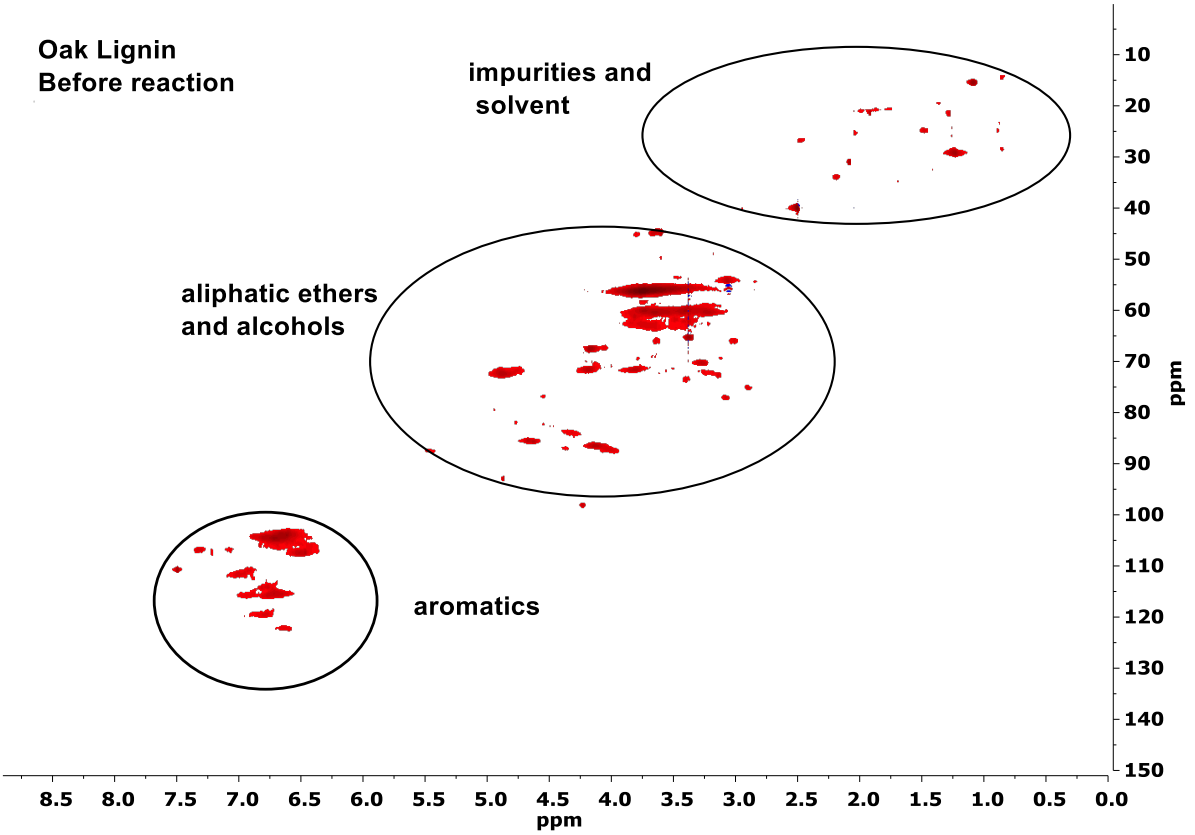


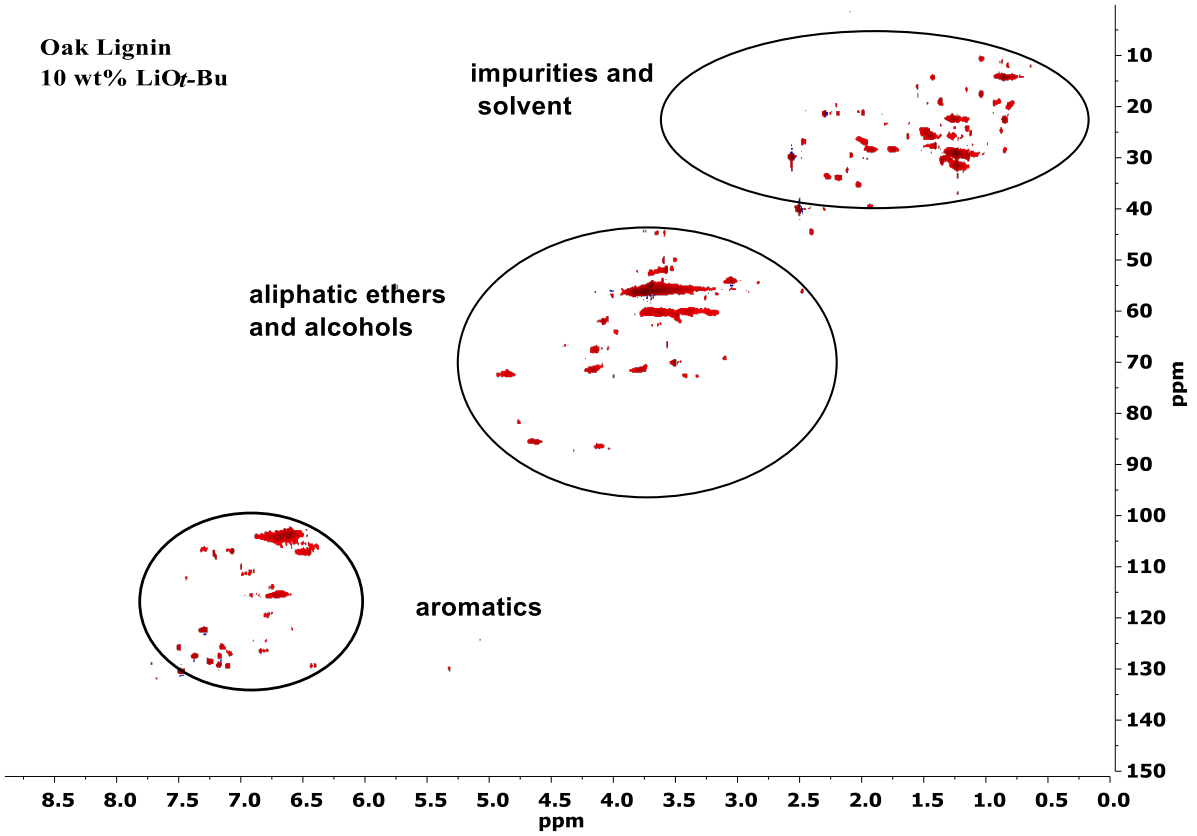
NMR measurements for lignin

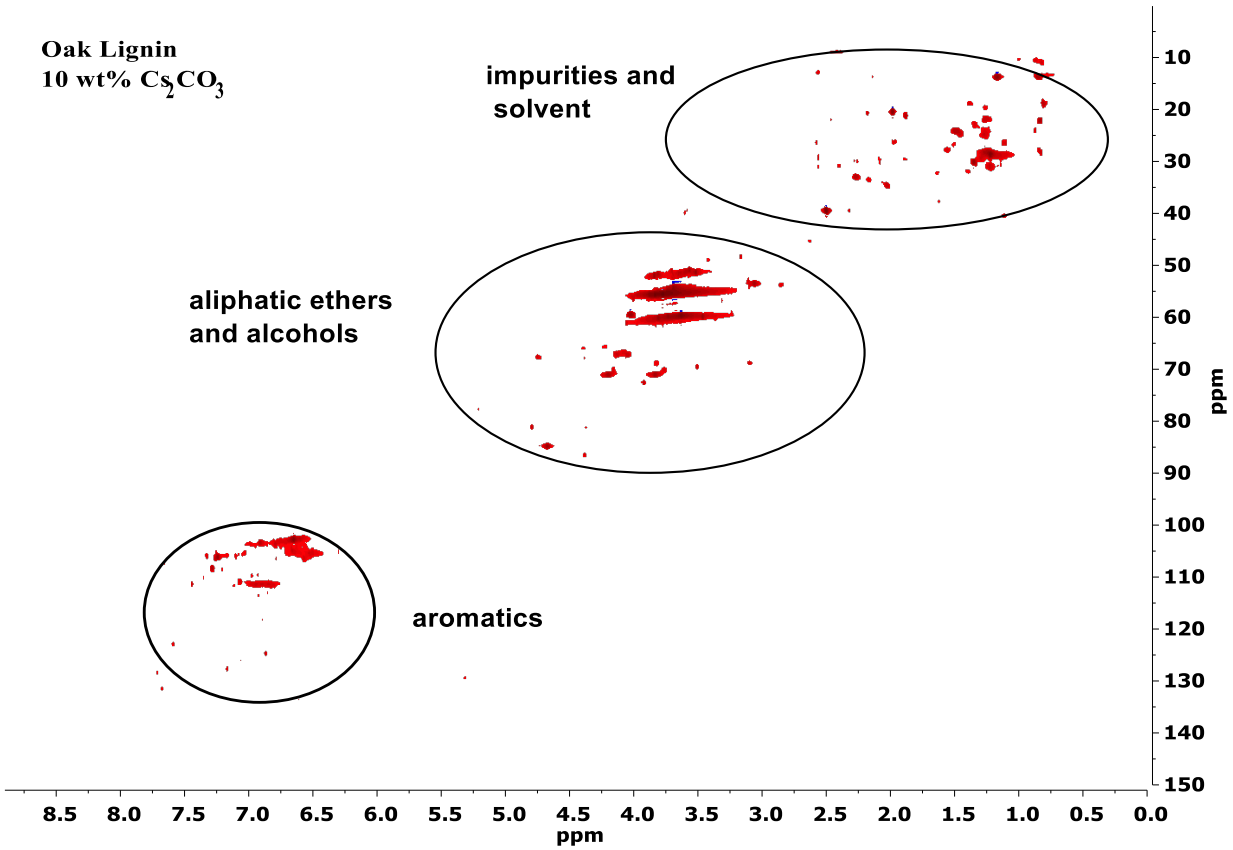


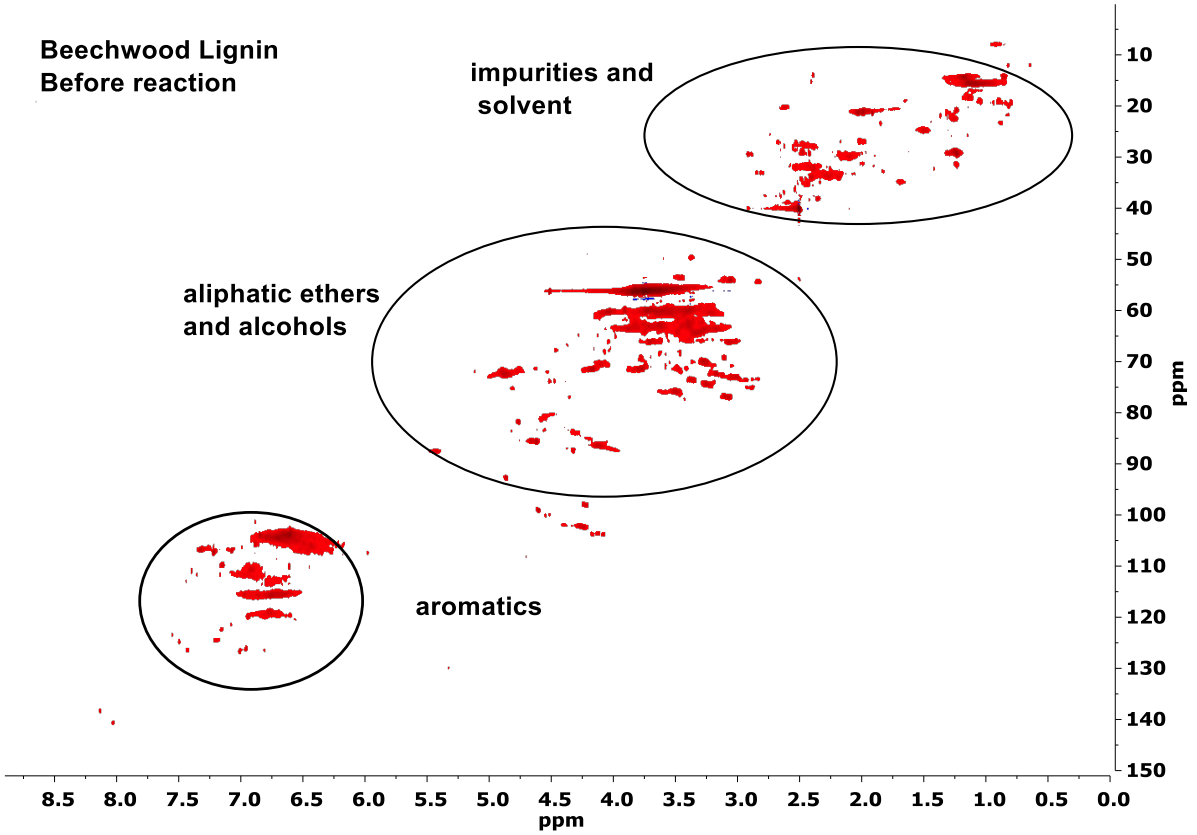


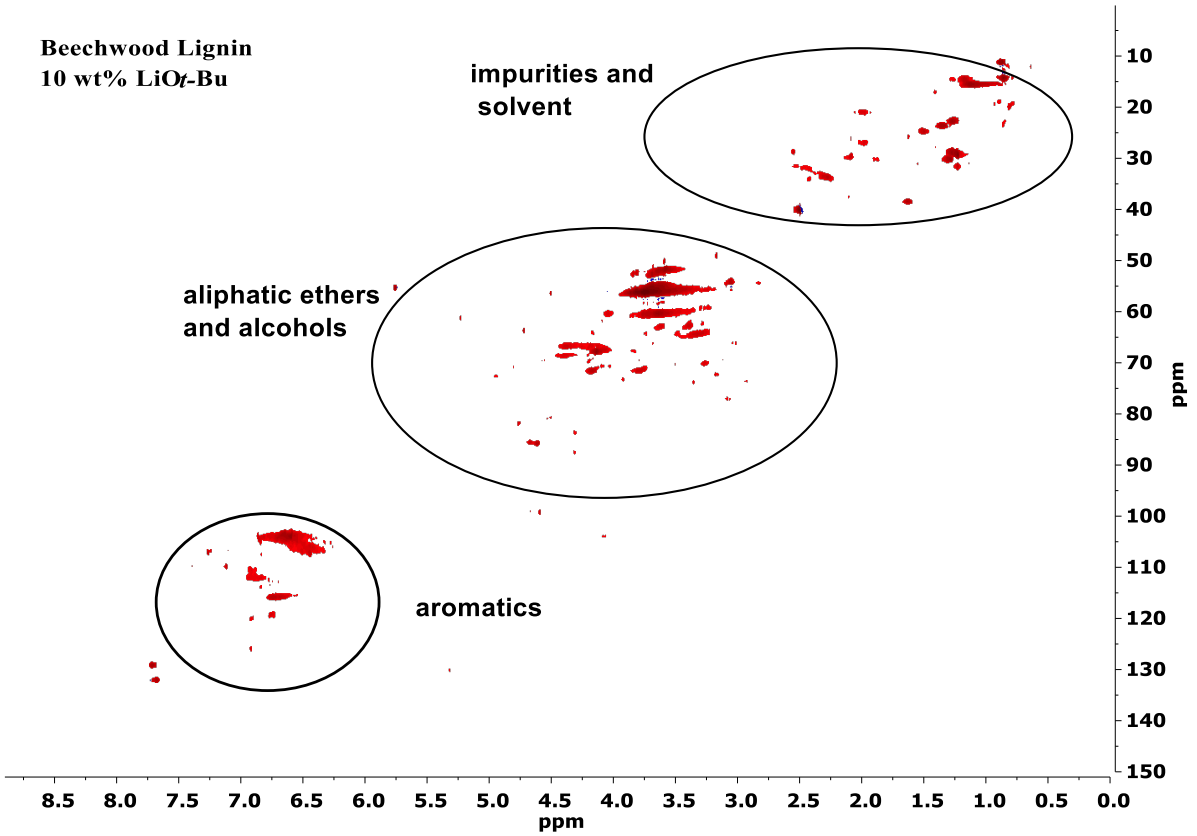

Cherry Lignin
10 wt% Cs_2CO_3
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm

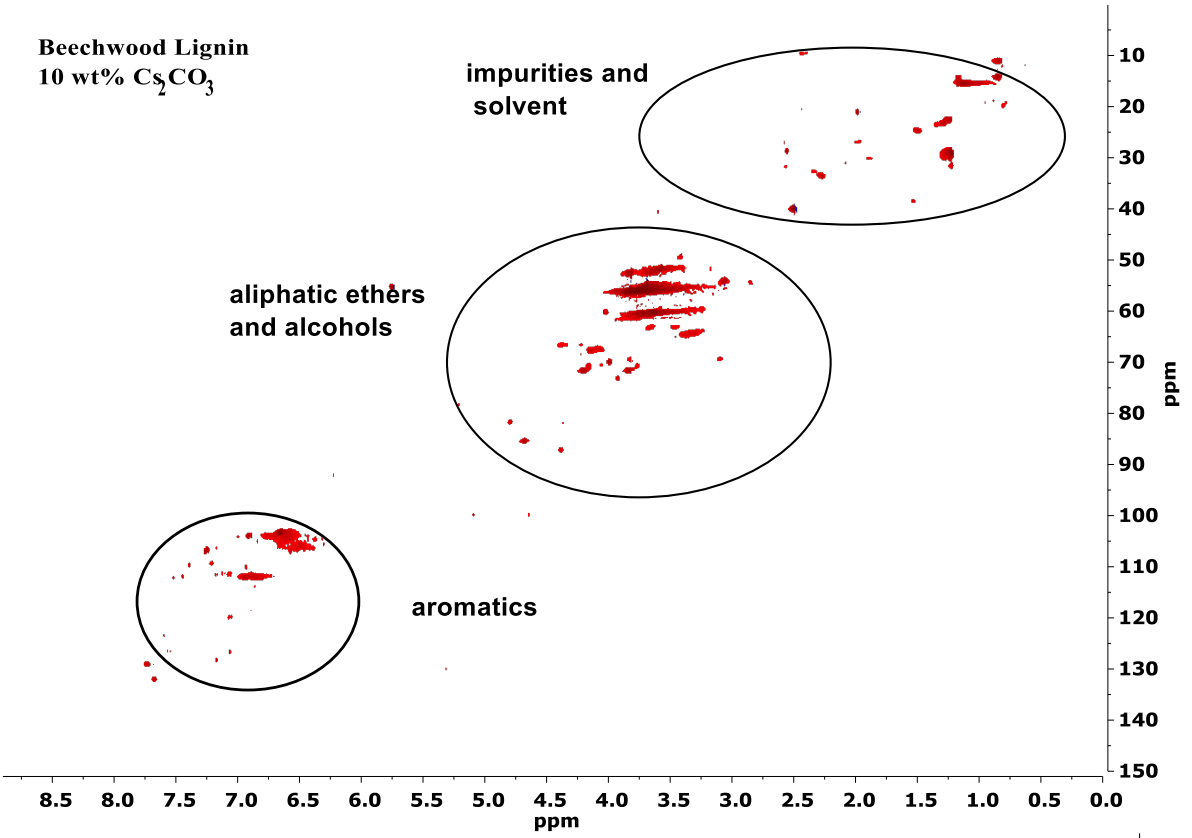

Oak Lignin
Before reaction
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm

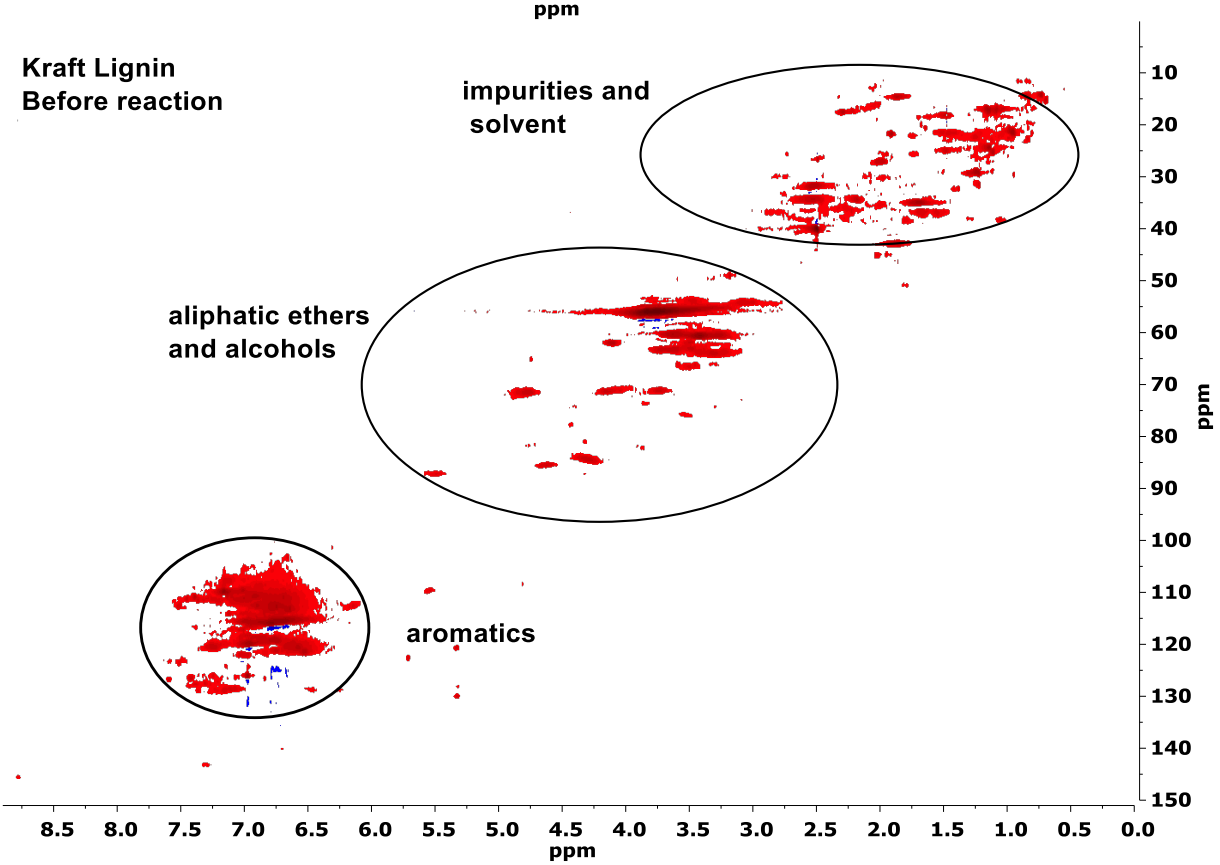

Oak Lignin
10 wt% LiO*t*-Bu
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm

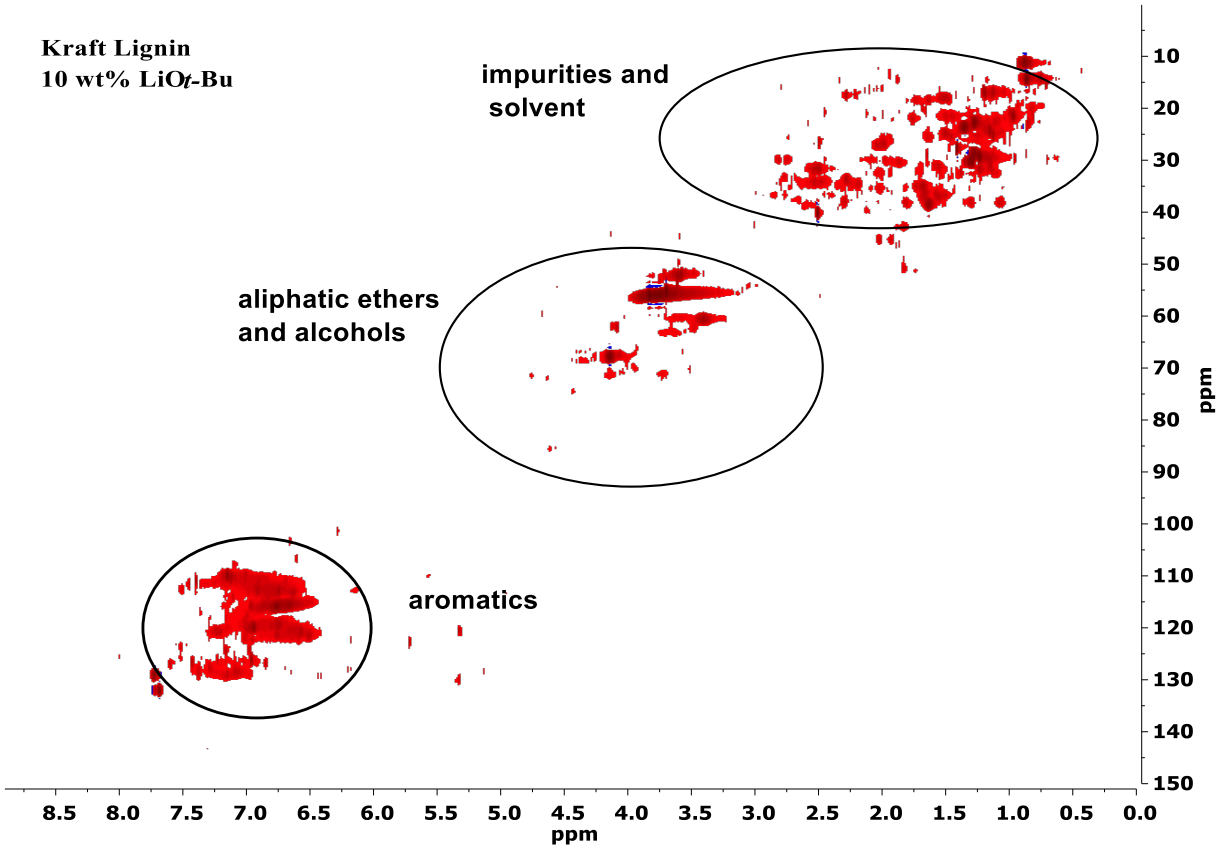

Oak Lignin
10 wt% Cs_2CO_3
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm

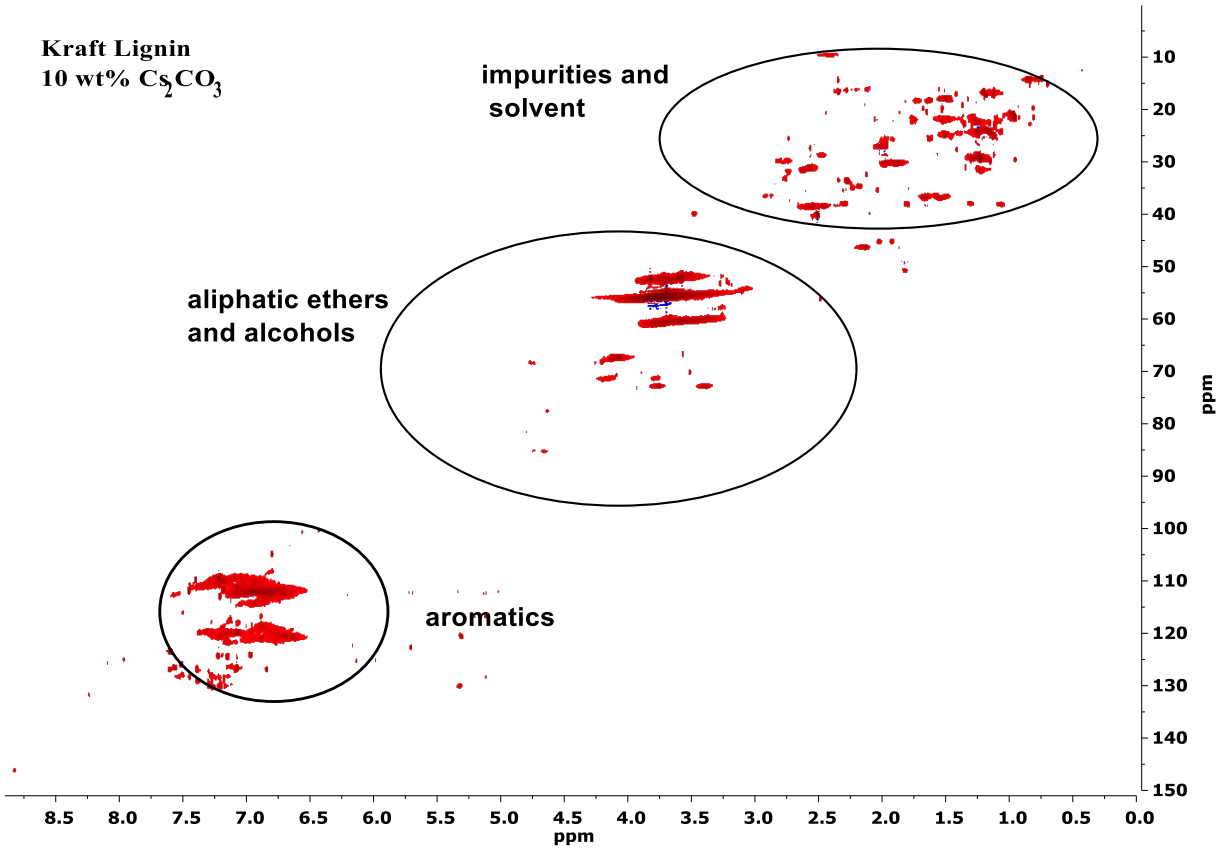

Beechwood Lignin
Before reaction
impurities and
solvent
aliphatic ethers
and alcohols
aromatics
ppm
ppm


Beechwood Lignin
10 wt% LiO*t*-Bu
impurities and
solvent
aliphatic ethers
and alcohols
aromatics
ppm
ppm


Beechwood Lignin
10 wt% Cs_2CO_3
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm


Kraft Lignin
Before reaction
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm


Kraft Lignin
10 wt% LiO*t*-Bu
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm


Kraft Lignin
10 wt% Cs_2CO_3
impurities and solvent
aliphatic ethers and alcohols
aromatics
ppm
ppm

7. Computational Details

Table S10: Calculation of the relative Gibbs energies.

Molecules	**GSP+SSC [a.u.]**	**ΔG [kcal mol^{-1}]**
1b + 2 **DMC** − 2 **MeOH** + **CsOMe**	−1741.067161	0.0
1h + **CsOMe**	−1741.06478	1.5
TS-1 + **Cs(DMC)** − **DMC**	−1741.00793	37.2
M1 + **Cs(DMC)** − **DMC** + **MeOH**	−1741.0084	36.9
TS-2 + **Cs(DMC)** − **DMC** + **MeOH**	−1741.00788	37.2
M2 + **MeOH** + **11-Cs**	−1741.09926	−20.1
TS-3 + **MeOH** − **CsOMe** + **Cs(DMC)** − **DMC** + **11-Cs**	−1741.04537	13.7
M3 + **MeOH** − **CsOMe** + **Cs(DMC)** − **DMC** + **11-Cs**	−1741.0679	−0.5
TS-4 + **MeOH** − **CsOMe** + **Cs(DMC)** − **DMC** + **11-Cs**	−1741.06479	1.5
M4 + **MeOH** − **CsOMe** + **DMC** + **11-Cs** + **CsMMC**	−1741.18683	−75.1
TS-5 − 2 **CsOMe** + **Cs(DMC)** + **MeOH** + **11-Cs** + **CsMMC**	−1741.186828	−38.3
M5 − 2 **CsOMe**+ **Cs(DMC)** + **MeOH** + **11-Cs** + **CsMMC**	−1741.128167	−61.6
TS-6 − 2 **CsOMe** + **Cs(DMC)** − **DMC** + **MeOH** + **11-Cs** + **CsMMC**	−1741.165268	−40.6
M6 − 2 **CsOMe** + **Cs(DMC)** − **DMC** + **MeOH** + **11-Cs** + **CsMMC**	−1741.131792	−48.3
TS-7 − 2 **CsOMe** + **Cs(DMC)** − **DMC** + **MeOH** + **11-Cs** + **CsMMC**	−1741.144158	−41.3
M7 − 2 **CsOMe** + **Cs(DMC)** − **DMC** + **MeOH** + **11-Cs** + **CsMMC**	−1741.133031	−51.0
TS-8 − 2 **CsOMe** + **Cs(DMC)** − **DMC** + **MeOH** + **11-Cs** + **CsMMC**	−1741.148394	−48.0
3a − 2 **CsOMe** + **M8** + **MeOH** + **11-Cs** + **CsMMC**	−1741.167347	−92.8
TS-9 + **Cs(DMC)**	−1740.95655	69.4
M11 + **DMC** + **Cs(DMC)**	−1741.027114	25.1
TS-10a + **DMC** + **Cs(DMC)**	−1740.993539	46.2
TS10b + **DMC** + **Cs(DMC)**	−1740.985107	51.5
2a + **DMC** + **CsMMC** + **FA**	−1741.112372	−28.4
3a + **DMC** + **CsMMC** + **FA**	−1741.113758	−29.2

1b

E [a.u.] = −1150.149700
G [a.u.] = −1149.824298
E_{SP} [a.u.] = −1150.392543

Charge = 0; Multiplicity = 1

C	4.6847	0.385571	−1.891936
C	3.336093	0.109354	−1.655256
C	2.805934	0.24542	−0.379097
C	3.625599	0.653207	0.69184
C	4.969832	0.939392	0.447554
C	5.492907	0.803367	−0.84195
H	5.095677	0.275848	−2.896546
H	2.6604 −	0.220018	−2.446381
H	5.624584	1.258987	1.257794
H	6.547456	1.02612	−1.013429
O	1.480631	0.021641	−0.130202
C	1.043642	−1.331837	−0.173837
H	1.864546	−1.979255	−0.525015
C	0.651278	−1.713898	1.247309
H	1.552852	−1.647368	1.881707
H	−0.076165	−0.967584	1.614506
C	−0.105535	−1.481041	−1.176538
H	−0.414625	−2.539698	−1.122402
O	0.107771	−3.021397	1.224661
H	−0.213846	−3.223385	2.108601
O	3.020765	0.724383	1.9052
C	3.797506	1.147162	3.000253
H	3.123584	1.156265	3.86533
H	4.634	0.454782	3.201553
H	4.201439	2.163058	2.847316
O	0.442647	−1.185007	−2.449768
H	−0.282024	−1.196368	−3.084497
C	−1.296678	−0.610097	−0.838003
C	−2.341835	−1.118378	−0.057275
C	−1.362683	0.713921	−1.259607
C	−3.419991	−0.32615	0.308342
H	−2.309044	−2.146513	0.309484
C	−2.447524	1.521699	−0.911385
H	−0.549646	1.12437	−1.858421
C	−3.480141	1.016171	−0.121198
H	−2.467369	2.556332	−1.25273
O	−4.388286	−0.846745	1.123437
O	−4.567034	1.72206	0.286709
C	−4.633816	3.085303	−0.06211
H	−5.554814	3.471147	0.390809
H	−3.771929	3.647882	0.335783
H	−4.682989	3.226902	−1.155874
C	−5.630824	−1.086389	0.483617
H	−6.301485	−1.499796	1.247975
H	−6.065492	−0.157085	0.083421
H	−5.517848	−1.820762	−0.333601

1h

E [a.u.] = −1605.815694
G [a.u.] = −1605.415125
E_{SP} [a.u.] = −1606.149998

Charge = 0; Multiplicity = 1

C	4.4789701344	2.5378402576	1.2940877758
C	3.2193968961	1.9398830653	1.2197928546
C	3.1023447409	0.5643870512	1.0869255394
C	4.2566514654	−0.2397482406	1.0070691798
C	5.513903108	0.3616044115	1.0718461839
C	5.6188308591	1.7476143677	1.2191138489
H	4.5607869263	3.6203804055	1.3987303234
H	2.304823487	2.5316774413	1.2437602565
H	6.4201318594	−0.2403923487	1.0151667729
H	6.609634304	2.2018280954	1.2728948951
O	1.8618811848	−0.0205929704	1.0958792285
C	1.4016483374	−0.5740717686	−0.1335090121
H	2.2317437632	−0.6020336642	−0.8572050461
C	0.9264180745	−1.983194028	0.1996601134
H	1.7929279147	−2.6234570261	0.405740454
H	0.2761304145	−1.9572736443	1.0833772429
C	0.2849405398	0.2886887395	−0.7402010083
H	0.1110966573	−0.0599324691	−1.7666254934
O	0.2029363335	−2.4971492284	−0.9209566699
O	4.0368663458	−1.5734505209	0.8632800612
C	5.1585044561	−2.4204635419	0.7574335261
H	4.7637016806	−3.4372449981	0.645403208
H	5.7734419305	−2.1719800755	−0.1247251493
H	5.7881153199	−2.3759086852	1.6623549878
O	0.8260332121	1.6207995679	−0.7910977755
C	−1.0242196464	0.2585475548	0.0101617245
C	−2.16288397	−0.252604151	−0.6203078655
C	−1.128047038	0.6931519332	1.3294095067
C	−3.3650978194	−0.3759387539	0.0572545626
H	−2.120769174	−0.5945074598	−1.6558079934
C	−2.339583343	0.5994469865	2.0156351517
H	−0.2494492647	1.0886608687	1.8381239953
C	−3.4651788275	0.0550448307	1.3945791867
H	−2.3876410225	0.9373618713	3.0501133047
O	−4.4288432286	−0.9701679862	−0.5691628695
O	−4.6785473438	−0.1014756139	1.9793021337
C	−4.8096200294	0.2671249775	3.3337750561
H	−5.8462627812	0.0419857527	3.6105870379
H	−4.1284886351	−0.3136772356	3.9786661955
H	−4.6202339379	1.3441676248	3.4834835358
C	−5.4700294507	−0.0811516731	−0.9430182756
H	−6.2365957649	−0.6900000155	−1.4389313938
H	−5.9096062461	0.4117742294	−0.0620922385
H	−5.0988833838	0.682826901	−1.6477840679
C	0.2909559576	2.4245887775	−1.7121926629
O	−0.515106046	2.1170965665	−2.5536106141
O	0.8183325636	3.6384676056	−1.5416734968
C	−0.9521356034	−3.1177187367	−0.637990879
O	−1.347001926	−3.4272237407	0.4561188031
O	−1.5817114561	−3.3321984001	−1.7915781434
C	−2.8934555678	−3.8872748917	−1.6558473907
H	−3.2107230576	−4.1350484846	−2.6749048532
H	−2.8712519857	−4.7897435355	−1.0301557122
H	−3.5735598658	−3.1436732786	−1.215294272
C	0.3591145902	4.6172537021	−2.4705504851
H	0.8707550018	5.5457652482	−2.1950487113
H	0.6170967614	4.3307922587	−3.5000121686
H	−0.7303674043	4.7431470749	−2.3977343985

TS-1

E [a.u.] = −1720.915311
G [a.u.] = −1720.483169
E_{SP} [a.u.] = −1721.32861

Charge = −1; Multiplicity = 1

C	4.9976149269	−0.1994748472	1.1316523442
C	3.6151386256	−0.1841798156	0.9253254152
C	3.0821471	−0.4831522635	−0.3268340998
C	3.9572028817	−0.7925496635	−1.394174847
C	5.3343506615	−0.8223581581	−1.1779243051
C	5.8534574025	−0.5222072515	0.0871284541
H	5.3969120865	0.033462604	2.1207002457
H	2.9158869312	0.0434633201	1.7320584546
H	6.0181567243	−1.0655326907	−1.9915995959
H	6.9343796883	−0.5450566287	0.2409568939
O	1.7558506097	−0.5290966314	−0.5691631228
C	0.9638043823	0.6804051586	−0.2961480384
H	1.6562406939	1.4524969513	0.0764361105
C	0.4682892633	1.102413974	−1.6793049457
H	1.3002354592	1.0011637233	−2.3890242604
H	−0.373054645	0.4818555836	−2.013974791
C	−0.1162540149	0.4670271476	0.7289194718
H	−1.0036302163	1.6033623867	0.7709276813
O	0.0927626604	2.4811786314	−1.6669253896
O	3.3545178603	−1.0368019826	−2.5906614195
C	4.1733857169	−1.3759259966	−3.6757398945
H	3.5008732676	−1.5369137383	−4.527758142
H	4.8860216907	−0.569156534	−3.9286319216
H	4.7434316685	−2.3045037396	−3.4883138006
O	0.663757132	0.2605103246	1.97225629
C	−0.9495033205	−0.7567207288	0.4623888266
C	−2.1683917463	−0.585872948	−0.2143345082
C	−0.5804775192	−2.0450941386	0.8401314613
C	−2.9787974218	−1.6667742085	−0.5385429666
H	−2.4651910719	0.4283170103	−0.4772561463
C	−1.4009384003	−3.1393623818	0.5449793562
H	0.3616350662	−2.2038403368	1.3657989254
C	−2.5944467015	−2.9670924447	−0.1496569655
H	−1.0846927241	−4.135920287	0.8559411082
O	−4.1613270646	−1.5674169935	−1.2086398127
O	−3.4597604987	−3.9738385845	−0.4932046913
C	−3.0888401515	−5.2764655358	−0.1463529718
H	−3.8894519085	−5.9353824122	−0.5092810147
H	−2.1353750506	−5.5788567519	−0.619326642

H	−2.988427671	−5.4069893165	0.9478811635
C	−4.5754461925	−0.2647037574	−1.5606335548
H	−5.52076681	−0.3876438944	−2.1061862342
H	−4.7496567491	0.3599717987	−0.6666275587
H	−3.8382087381	0.2516852343	−2.1967252776
C	0.0416842081	0.4137194754	3.1195824792
O	−1.1252862152	0.6158668681	3.3376396847
O	0.9784506948	0.2866909058	4.1006379211
C	−1.1973742646	2.7577826332	−1.8542955602
O	−2.051604225	1.9917613337	−2.2371063326
O	−1.3652631938	4.0723078841	−1.6863564243
C	−2.7261156193	4.4364140055	−1.4828119394
H	−2.7221263866	5.5220873666	−1.3241810249
H	−3.3397388437	4.1806845048	−2.3603289878
H	−3.091513076	3.9062267936	−0.5902588923
C	0.4551821643	0.4226179581	5.4076679533
H	1.3069564163	0.2971300972	6.0888519981
H	−0.0029433022	1.4130149477	5.5550773876
H	−0.3096697687	−0.3418614709	5.6153199407
O	−1.6987770861	2.5549417028	0.7270618688
C	−1.0147709763	3.5122866417	1.4444154018
H	−0.9702821673	4.4896060087	0.9109963539
H	−1.4562826719	3.7105007282	2.4495074923
H	0.0498604301	3.2252814288	1.6294463955

M1

E [a.u.] = −1605.202416
G [a.u.] = −1604.817187
E_{SP} [a.u.] = −1605.587331

Charge = −1; Multiplicity = 1

C	−4.021826342	1.4472463029	0.6490549007
C	−3.1437436525	0.3918968006	0.3792416738
C	−2.6853789273	0.1637423423	−0.9187955713
C	−3.1149332209	1.0335775604	−1.9530941782
C	−3.9979926575	2.0718221538	−1.677514207
C	−4.4538351295	2.2820117828	−0.3689769818
H	−4.3552542744	1.6100354929	1.6760676939
H	−2.7897671893	−0.2371254996	1.1943828707
H	−4.3303855002	2.740893946	−2.4713839169
H	−5.1373424762	3.1084111998	−0.1640442509
O	−1.8686948001	−0.8317741902	−1.284219115
C	−0.9516219945	−1.4637129494	−0.2499796638
H	−1.5741708519	−2.1487153164	0.35031645
C	−0.0887506202	−2.3301602391	−1.1748639258
H	−0.7073479457	−2.8363230937	−1.9279575494
H	0.7015397992	−1.7431772659	−1.6588295115
C	−0.2316560195	−0.5818476888	0.6550387923
O	0.4964819329	−3.366304323	−0.3786863246
O	−2.603936159	0.7622029642	−3.1925712914
C	−2.9679786151	1.6195953494	−4.238647079
H	−2.4494729496	1.2517358836	−5.1341257877
H	−4.0582214317	1.6047061244	−4.4262169327
H	−2.6552523672	2.6626736266	−4.0483267528
O	−0.6981191674	−0.6665976561	2.0217774783
C	0.4176232322	0.6314495145	0.3120273836
C	0.5822943993	1.0154171786	−1.0536731854
C	0.9179300437	1.5447955957	1.2702208102
C	1.2220097197	2.1870641204	−1.4220158697
H	0.1351912871	0.3939306561	−1.8253834535
C	1.5561393855	2.7264730582	0.8895352126
H	0.7980094132	1.3337130436	2.3331818978
C	1.7325561272	3.0681511242	−0.4469143213
H	1.9222975505	3.3900430503	1.6755414434
O	1.3823759245	2.5887480153	−2.7224220526
O	2.3555355548	4.2111137395	−0.9156326783
C	2.829454009	5.0976351444	0.04815424
H	3.2804614201	5.9418033808	−0.4934968788
H	2.0217071873	5.4857594018	0.7003466619
H	3.6009725156	4.6421912952	0.7007835447
C	0.9066490731	1.7204389107	−3.7160054153
H	1.1024289081	2.2176339928	−4.6765839903
H	1.4326199009	0.7476088928	−3.6991231656
H	−0.1751333123	1.5227984297	−3.6166738051
C	0.0465369726	−1.339621164	2.8771993656
O	1.1084590399	−1.8888388363	2.7143161615
O	−0.5999727755	−1.3196821989	4.0704641298
C	1.7639272407	−3.184208482	−0.0067518129
O	2.5578328044	−2.4054388731	−0.4676454262
O	2.038566425	−4.1011240131	0.9334421073
C	3.2912587316	−3.9025690022	1.571292422
H	3.3982593774	−4.7328193159	2.2809530293
H	4.1164797695	−3.9140311513	0.8433001927
H	3.2854692954	−2.9435133512	2.1071670411
C	0.0838505637	−1.9968336618	5.1067266215
H	−0.5538569203	−1.90700247	5.9957438883
H	0.2396079484	−3.0584269018	4.859643466
H	1.0673857471	−1.5423474306	5.3031756158

M1b

E [a.u.] = −1605.175406
G [a.u.] = −1604.792309
E_{SP} [a.u.] = −1605.560929

Charge = −1; Multiplicity = 1

C	4.8535315671	1.5641093724	0.0570525401
C	3.5270952045	1.1472169661	−0.0504682316
C	2.961331351	0.2938535183	0.9037579616
C	3.757175883	−0.1345637859	1.9890394232
C	5.078988018	0.2966167515	2.0882775211
C	5.6357502611	1.1444705163	1.130000578
H	5.2674659165	2.2355763462	−0.6988124684
H	2.8918502948	1.5091812446	−0.8593638081
H	5.659964065	−0.0564058702	2.94292113
H	6.6743323228	1.4696496602	1.2225913299
O	1.6692309718	−0.0889291291	0.8742278035
C	1.1316465334	−0.6412907029	−0.3692822109
H	1.8752040406	−0.5071236306	−1.1725885809
C	0.8893494427	−2.1192506368	−0.2094984802
H	−0.1573204523	−2.3071031736	0.0887735362
C	−0.0695273473	0.24408678	−0.7328728083
H	−0.5054912609	−0.1397937111	−1.6632543721
O	1.0113628166	−2.6948208141	−1.5996682668
O	3.249713708	−0.9202377772	2.980672302
C	2.94387788	−2.2608951198	2.5828960286
H	2.3946508249	−2.7063068568	3.4246769277
H	2.3233202919	−2.3074583023	1.6640305971
H	3.8835870289	−2.8262863427	2.4298845763
O	0.4462021566	1.5885719105	−1.0024553947
C	−1.1407353887	0.325812923	0.3262139025
C	−2.2461012158	−0.5301863968	0.2638087205
C	−1.0431760943	1.2220264048	1.385908312
C	−3.2321235346	−0.4847091821	1.2384355096
H	−2.3251140447	−1.2587007409	−0.5462465249
C	−2.0362362028	1.2840147695	2.3656474816
H	−0.1761365382	1.8784563195	1.4530305114
C	−3.1392611387	0.4332192522	2.2997767163
H	−1.9269912757	1.9953895568	3.1841456929
O	−4.2958853872	−1.355448625	1.1793415894
O	−4.1701533584	0.4157962892	3.198626946
C	−4.0802778557	1.2838675076	4.2967604634
H	−4.9759631914	1.1052308467	4.9060163891
H	−3.1830026846	1.0817932281	4.9087765228
H	−4.061993607	2.3446703508	3.9859425463
C	−5.4705431265	−0.7722984216	0.6583024218
H	−6.233081989	−1.5634377619	0.6300277123
H	−5.8312294703	0.0531569488	1.296538717
H	−5.3074041464	−0.3918234335	−0.366204553
C	−0.2228587363	2.3193684951	−1.8749864271
O	−1.2011244164	2.010770169	−2.5110918539
O	0.3925004603	3.5164315236	−1.9621606999
C	−0.0395490568	−2.8280492357	−2.3489760329
O	−1.1932057479	−2.4833822283	−2.1525093785
O	0.3235165518	−3.476535015	−3.4934655154
C	−0.738749562	−3.6899262005	−4.3995261582
H	−0.2946277045	−4.1862826575	−5.2731048897
H	−1.5203249187	−4.3320040142	−3.9628989431
H	−1.2102841487	−2.7422581071	−4.7040250481
C	−0.203927868	4.4098166015	−2.8872276088
H	0.3801223924	5.3361090576	−2.8247899213
H	−0.1649542405	4.0080012501	−3.911262803
H	−1.2557542733	4.606036313	−2.6312134303

TS-2

E [a.u.] = −1605.201871
G [a.u.] = −1604.816219
E_{SP} [a.u.] = −1605.587231

Charge = −1; Multiplicity = 1

C	−2.0999711254	−2.762471807	2.3273100914
C	−1.1869159807	−2.5974981858	1.280592962
C	−1.6178842349	−2.2631945127	−0.0090572098
C	−3.0143941419	−2.0830184913	−0.2130513078
C	−3.9175177768	−2.2659459018	0.8272530763
C	−3.4595221476	−2.6039539861	2.1090006597
H	−1.7274337608	−3.0143348439	3.3229247081

H	−0.1209365751	−2.7141734243	1.4706280123
H	−4.9869255911	−2.1303172364	0.6624106251
H	−4.1779887149	−2.7319006921	2.9213562918
O	−0.8204035556	−2.1065904234	−1.056369777
C	0.697526675	−1.4926441051	−0.8150315063
H	1.2994250944	−2.393609719	−0.6349395501
C	0.9241576526	−1.0324423334	−2.250476317
H	0.5300183331	−1.7651020472	−2.9641252944
H	0.4974802843	−0.0403812001	−2.4400498212
C	0.883333333	−0.5551118247	0.2336415803
O	2.3439869577	−0.9976150289	−2.4705157379
O	−3.3706844367	−1.7288661824	−1.4890398895
C	−4.7378327286	−1.6099980975	−1.7624641448
H	−4.8202299265	−1.3601120727	−2.8290533245
H	−5.2808770322	−2.5552641005	−1.5732360724
H	−5.2155238015	−0.8057243915	−1.1717663646
O	1.583758166	−1.073682941	1.3839631224
C	0.1663885894	0.660328913	0.4595797578
C	−0.910615346	1.0367686844	−0.3908743137
C	0.4436184006	1.5264260328	1.5352372942
C	−1.6160772387	2.2154145571	−0.207795967
H	−1.2246205628	0.3422858993	−1.1671627434
C	−0.2785469913	2.7066428166	1.7243988666
H	1.2338496728	1.2783550161	2.2438806037
C	−1.3017042231	3.0801324484	0.8608040154
H	−0.0183249706	3.34439684	2.5711192755
O	−2.6604494008	2.6098635812	−0.9983387789
O	−2.0630433613	4.226162362	0.9638254458
C	−1.7677178356	5.0756658681	2.0293999693
H	−2.4680836937	5.9202357924	1.9612931001
H	−1.9017225127	4.5817505594	3.0119073104
H	−0.7323899652	5.466921023	1.9822020298
C	−2.965965893	1.7911708415	−2.0975696488
H	−3.8292898305	2.2560315081	−2.5938296651
H	−2.1244421169	1.7351443578	−2.8127074648
H	−3.2233900945	0.7615677008	−1.7957646152
C	2.8758228012	−0.8154271822	1.4631134831
O	3.5817447733	−0.1809768621	0.7174388815
O	3.3336642198	−1.4046096201	2.5948011458
C	2.9364831971	0.1833042645	−2.29663634
O	2.4147899238	1.2681177028	−2.272998524
O	4.2589120444	−0.0370633745	−2.2310531747
C	5.0073990709	1.1119253297	−1.8643615895
H	4.7188209878	1.4371805775	−0.8553485872
H	6.0588523499	0.7973453583	−1.8757243665
H	4.8482751755	1.9353822468	−2.5769465048
C	4.7118589711	−1.1946250397	2.8362759806
H	4.9403719383	−1.7390806854	3.761519548
H	5.3283387466	−1.5781771843	2.0089294261
H	4.9365922084	−0.1244447848	2.9655963379

M3

E [a.u.] = −1183.903514
G [a.u.] = −1183.632778
E_{SP} [a.u.] = −1184.158208

Charge = 0; Multiplicity = 1

C	1.9246728001	−0.7229104665	−1.6489165134
H	2.4217708641	−1.6938561192	−1.7159783085
C	2.0232833659	0.1494882048	−2.8595044194
H	1.5233749475	−0.3326800302	−3.7111048197
H	1.592225724	1.1452581168	−2.7044868
C	1.2257825588	−0.47501621	−0.5385289196
O	3.3909857822	0.2593852303	−3.2956398117
O	1.0962065502	−1.5476848175	0.3545490605
C	0.4404383774	0.7210332303	−0.1617469771
C	−0.8505898998	0.5330847597	0.370392938
C	0.9486734207	2.0063475082	−0.2868680205
C	−1.6277469438	1.6174314723	0.7474343591
H	−1.2295478082	−0.4822145291	0.4805175507
C	0.1672800216	3.105122891	0.08736816
H	1.9598794903	2.1626486646	−0.6624011522
C	−1.1126024906	2.9303080422	0.6005912879
H	0.5870351497	4.1049445681	−0.0158529389
O	−2.8789133812	1.5398276268	1.2611475164
O	−1.941625655	3.9232338342	0.9949901134
C	−1.4856402396	5.2492749481	0.8619705616
H	−2.2986487844	5.8863759106	1.2294554113
H	−0.5804107354	5.4339910852	1.4660271253
H	−1.2734264531	5.5029432966	−0.1912637057
C	−3.4336046752	0.258002044	1.4361955506
H	−4.4338346405	0.4150419688	1.856701175
H	−3.525676465	−0.2829975191	0.477976849
H	−2.8381428612	−0.3544559968	2.1358964349
C	1.6366096122	−1.3617478788	1.5761493718
O	2.3708735424	−0.4698771752	1.9002535967
O	1.2190977885	−2.3657500027	2.3467882647
C	4.1112415531	1.2349847836	−2.7448486921
O	3.7144053582	2.0916551917	−1.9920163145
O	5.362564075	1.1166392529	−3.1858579733
C	6.2621797993	2.1045025972	−2.6872120727
H	6.320687122	2.0603887651	−1.5904312359
H	7.2347734292	1.866174534	−3.1309311159
H	5.9422127643	3.1123983657	−2.9872531732
C	1.741187181	−2.3401891673	3.6742885492
H	1.3315281158	−3.2277366086	4.1683119753
H	2.8394227325	−2.3812617571	3.6612161595
H	1.4241739071	−1.4278036144	4.1990059534

TS-3

E [a.u.] = −1299.003439
G [a.u.] = −1298.697738
E_{SP} [a.u.] = −1299.343161

Charge = −1; Multiplicity = 1

C	1.808619114	1.0318982114	1.4194194719
H	2.1707676331	2.0370944116	1.6491772841
C	2.708265082	−0.0923594493	1.8045787737
H	2.8935345933	−0.0900553676	2.8891796643
H	2.3261891504	−1.0741508723	1.5037906718
C	0.5597158349	0.9427821472	0.9324018806
O	4.0400751707	0.1067529548	1.2522731195
O	−0.1639202734	2.1151740457	0.9269751289
C	−0.1997891362	−0.2768310665	0.5724770791
C	−1.5450292506	−0.3220931055	0.9603315851
C	0.343072973	−1.3339428915	−0.1503359167
C	−2.3530153139	−1.3957578836	0.6202525819
H	−1.9711889173	0.5502791218	1.4428379626
C	−0.4508921574	−2.4434929285	−0.4565608793
H	1.3716841298	−1.2964086354	−0.507600077
C	−1.7915497998	−2.4855392481	−0.0791006554
H	−0.0114094785	−3.2606750647	−1.0281394096
O	−3.6789165652	−1.4616695037	0.8911982986
O	−2.647143514	−3.5128643514	−0.3582855112
C	−2.1545735626	−4.560327661	−1.1452624008
H	−2.9876402769	−5.2624803643	−1.2835644028
H	−1.8119037631	−4.2085501623	−2.1357244165
H	−1.3174292046	−5.0928877739	−0.6554537132
C	−4.293823392	−0.2424341178	1.3015200754
H	−5.3722183614	−0.3922135722	1.1532702878
H	−4.1088539315	−0.0635784438	2.3784490888
H	−3.9183508023	0.6247144978	0.7141240292
C	−0.5540483716	2.6055849619	−0.3066679607
O	−0.1183516008	2.1897287402	−1.3516575152
O	−1.0367460017	3.835464279	−0.0555819738
C	4.3228012405	−0.5160734461	0.119887185
O	3.6661116555	−1.3538252802	−0.4503103758
O	5.5193979642	−0.0763170997	−0.302248572
C	5.9552002345	−0.6605243177	−1.52239395
H	5.232515377	−0.4716607333	−2.3291772524
H	6.9153698389	−0.1833606468	−1.7512983141
H	6.0870327369	−1.7476675999	−1.4153703783
C	−1.7998463512	4.3709669108	−1.1256666502
H	−1.9776747581	5.4264406226	−0.8753761438
H	−1.2483606601	4.2942033303	−2.076015137
H	−2.7302363794	3.7847913512	−1.175625256
O	−2.7033460992	1.8065962536	−0.3999476305
C	−2.8667410012	1.1247733738	−1.5657510514
H	−3.5253952614	0.2138035266	−1.4739182603
H	−3.3400986787	1.7276087541	−2.3982123183
H	−1.9073918649	0.7449600927	−2.004517046

M3

E [a.u.] = −1299.022607
G [a.u.] = −1298.715763
E_{SP} [a.u.] = −1299.366834

Charge = −1; Multiplicity = 1

C	−1.6635489544	1.062150764	−1.379616871
H	−2.1769941138	1.9836223004	−1.6664018381
C	−2.271039545	−0.2107880893	−1.8472666168
H	−2.3493437707	−0.2536725134	−2.944973978
H	−1.7402825623	−1.1005543976	−1.4868571909
C	−0.4743344	1.2155534552	−0.7532025579
O	−3.6785014559	−0.2965795729	−1.4452331035
O	0.0407676179	2.4404690447	−0.6421991927

C	0.3987102258	0.0800202098	−0.3246292684
C	1.7352048951	0.1096389731	−0.749886975
C	−0.0242631351	−0.9531332587	0.4980465123
C	2.6371075458	−0.8649607342	−0.357459173
H	2.0553445864	0.9704743115	−1.3318424878
C	0.870700653	−1.9625596748	0.8743691575
H	−1.0498224565	−0.9756082665	0.8625424398
C	2.1969647299	−1.9314399693	0.4560705629
H	0.5141128885	−2.7624833154	1.5232692713
O	3.9648495126	−0.8603885721	−0.6775984533
O	3.1484363418	−2.8559710425	0.787073408
C	2.7620211287	−3.8860302325	1.6539306971
H	3.6527084727	−4.5093059518	1.8101789369
H	2.4180075758	−3.4982775469	2.6303393035
H	1.9585162917	−4.5129839371	1.2245678603
C	4.4486308952	0.3059614839	−1.3009594264
H	5.5402329937	0.1971339965	−1.3505269991
H	4.05302466	0.4174344864	−2.3272202888
H	4.1891691146	1.2136757455	−0.7291692914
C	0.5120222065	2.8524495172	0.7750939815
O	−0.1350078048	2.3480600169	1.7070401951
O	0.4231919436	4.2665085325	0.543882529
C	−3.9534893866	−0.9514031238	−0.3350933278
O	−3.2165128815	−1.6408685403	0.3303221615
O	−5.2564891622	−0.7575892507	−0.053717246
C	−5.6949295238	−1.4016082174	1.1323923699
H	−5.1129150528	−1.0651856882	2.0026818178
H	−6.7488041891	−1.1209972845	1.249443593
H	−5.6009665343	−2.4953061292	1.0499697502
C	0.7298913745	4.9805435955	1.7021685772
H	0.4717955059	6.0370945746	1.5223155001
H	0.1547675563	4.6060114216	2.5686450691
H	1.8096746678	4.9220475283	1.9532912049
O	1.9506548076	2.5798209706	0.7437583638
C	2.3999033997	1.8242903451	1.835301661
H	3.4153642167	1.4688089084	1.5867743346
H	2.4560964916	2.422894386	2.7669159773
H	1.7521655595	0.9566182114	2.0399683705

TS-4

E [a.u.] = −1299.021223
G [a.u.] = −1298.715297
E_{SP} [a.u.] = −1299.36281

Charge = −1; Multiplicity = 1

C	1.736252	0.995813	1.515065
H	2.093992	1.99478	1.779751
C	2.6143	−0.132876	1.898597
H	2.863031	−0.123484	2.972233
H	2.211987	−1.118184	1.633703
C	0.453274	0.952407	1.045913
O	3.963637	0.003847	1.305561
O	−0.28073	2.033726	1.018775
C	−0.256741	−0.317079	0.657794
C	−1.614815	−0.395298	1.006077
C	0.297645	−1.347514	−0.092168
C	−2.407381	−1.457577	0.607119
H	−2.033408	0.462418	1.52766
C	−0.485277	−2.447531	−0.469678
H	1.337283	−1.301094	−0.41493
C	−1.832183	−2.515656	−0.130188
H	−0.022855	−3.237932	−1.061287
O	−3.749968	−1.54796	0.841512
O	−2.682294	−3.529717	−0.477182
C	−2.153944	−4.562349	−1.261577
H	−2.977208	−5.266039	−1.443955
H	−1.774003	−4.193072	−2.232237
H	−1.333005	−5.097273	−0.748417
C	−4.372643	−0.37997	1.32618
H	−5.453729	−0.567948	1.27804
H	−4.092734	−0.169302	2.374392
H	−4.116614	0.502557	0.714763
C	−0.901586	2.665407	−0.547502
O	−0.034966	2.607664	−1.407564
O	−1.264851	3.876784	0.062959
C	4.204837	−0.617619	0.174841
O	3.526539	−1.445293	−0.392068
O	5.407058	−0.206845	−0.279973
C	5.795075	−0.797862	−1.50915
H	5.058695	−0.589579	−2.29916
H	6.761489	−0.345433	−1.763647
H	5.902533	−1.889208	−1.411163
C	−1.568423	4.845657	−0.90165
H	−1.753496	5.790028	−0.367047
H	−0.736842	4.984675	−1.614618
H	−2.479562	4.584048	−1.477839
O	−2.100879	1.945958	−0.70956
C	−2.081742	1.053009	−1.79989
H	−3.048103	0.525463	−1.781509
H	−1.967243	1.58904	−2.758264
H	−1.268463	0.314444	−1.724858

M4

E [a.u.] = −651.8439394
G [a.u.] = −651.675224
E_{SP} [a.u.] = −651.9780577

Charge = 0; Multiplicity = 1

C	3.2538628417	−1.9050174816	−0.5061586971
H	2.4431905159	−2.559379548	−0.8286629661
C	4.5009259355	−2.3720992589	−0.4228800003
H	4.7436797052	−3.4058573656	−0.6747982076
H	5.3057988936	−1.7097323463	−0.094814169
C	2.9576763358	−0.4823717248	−0.1461832699
O	3.8451563901	0.241399359	0.2749434991
C	1.5666747228	0.0395915466	−0.3019432352
C	1.3321052172	1.3607720416	0.1283454945
C	0.5153701366	−0.6891569239	−0.8476585088
C	0.0800600325	1.9371730943	0.0223338684
H	2.1792267836	1.9030334974	0.5452262877
C	−0.7557592265	−0.1173628919	−0.9661648923
H	0.6541793661	−1.7099341053	−1.2012289666
C	−0.9883122103	1.1849062175	−0.5369325055
H	−1.5642498698	−0.7043080002	−1.3996919384
O	−0.2416344918	3.1915493744	0.4108055647
O	−2.1716694263	1.8265075275	−0.6028726544
C	−3.2698999521	1.1325182364	−1.1506599951
H	−4.1169300475	1.8268447288	−1.1087885025
H	−3.0869146491	0.8465014974	−2.2007751637
H	−3.5124384762	0.2287806075	−0.5653717471
C	0.7835878231	3.9790870576	0.9742345055
H	0.3233150761	4.943351492	1.2196365048
H	1.1872406421	3.5230431118	1.8945967905
H	1.6105924614	4.1408554366	0.2616080744

TS-5

E [a.u.] = −766.9163463
G [a.u.] = −766.716208
E_{SP} [a.u.] = −767.154704

Charge = 0 Multiplicity = 1

C	2.71482	−0.36656	−1.38371
H	2.18394	−1.13351	−1.96477
C	3.39988	0.59923	−2.00469
H	3.53649	0.63416	−3.08982
H	3.82399	1.42004	−1.41371
C	2.0255	0.25221	0.30047
O	2.49802	1.30864	0.62829
C	0.58181	−0.10865	0.22782
C	−0.31088	0.94959	−0.01418
C	0.10727	−1.4018	0.37618
C	−1.67244	0.71133	−0.11135
H	0.09823	1.95363	−0.1134
C	−1.26692	−1.64871	0.28733
H	0.80254	−2.21372	0.57992
C	−2.16161	−0.61251	0.04137
H	−1.63031	−2.66732	0.4164
O	−2.61589	1.65328	−0.34145
O	−3.50108	−0.74767	−0.0682
C	−4.04559	−2.03874	0.07898
H	−5.12844	−1.92687	−0.0496
H	−3.65963	−2.73359	−0.68711
H	−3.84017	−2.45616	1.07994
C	−2.18191	2.98491	−0.4971
H	−3.08595	3.57828	−0.6772
H	−1.67745	3.35804	0.41094
H	−1.49912	3.09331	−1.35764
O	2.83566	−1.11271	0.98481
H	3.08337	−0.89342	−0.22187
C	3.78872	−0.77188	1.9699
H	3.96543	0.31684	1.9699
H	3.41976	−1.0804	2.96039
H	4.73505	−1.29308	1.75929

M5

E [a.u.] = −766.9666954
G [a.u.] = −766.762786
E_{SP} [a.u.] = −767.1955756

Charge = −1 Multiplicity = 1

C	3.41784	−0.86374	0.06313
H	3.10289	−1.90737	0.00676
C	4.86566	−0.58	0.08809
H	5.42292	−1.10232	−0.72656
H	5.01073	0.51008	−0.03956
C	2.49309	0.17148	0.09359
O	2.7405	1.41279	0.12073
C	1.00563	−0.2006	0.06115
C	0.11042	0.87771	−0.01437
C	0.46974	−1.48488	0.1128
C	−1.26388	0.693	−0.04723
H	0.59383	1.85676	−0.0371
C	−0.91538	−1.69022	0.08039
H	1.12607	−2.3522	0.18903
C	−1.79335	−0.6132	−0.00143
H	−1.29908	−2.71068	0.1242
O	−2.18676	1.7029	−0.12037
O	−3.16235	−0.70894	−0.0379
C	−3.71111	−1.99324	0.0198
H	−4.80207	−1.86651	−0.01427
H	−3.3976	−2.62194	−0.83523
H	−3.44237	−2.52175	0.95404
C	−1.68027	3.01122	−0.15766
H	−2.55369	3.6759	−0.2106
H	−1.09133	3.2545	0.74472
H	−1.03873	3.18263	−1.04053
O	5.49966	−0.98935	1.32675
C	6.85817	−0.71872	1.31517
H	7.2874	−1.04185	2.27818
H	7.39709	−1.25555	0.49932
H	7.07983	0.36395	1.18172

TS-6

E [a.u.] = −1110.490152
G [a.u.] = −1110.195236
E_{SP} [a.u.] = −1110.790278

Charge = −1 Multiplicity = 1

C	−1.82876	0.31227	−0.29935
C	−3.06303	1.1475	−0.21111
H	−3.9653	0.51014	−0.28589
H	−3.08784	1.66576	0.76687
C	−0.68835	0.78269	0.44492
O	−0.74391	1.56148	1.41257
C	0.68922	0.27771	0.05654
C	1.79106	0.99573	0.54698
C	0.91792	−0.84576	−0.72824
C	3.09118	0.62866	0.23501
H	1.56162	1.84258	1.19351
C	2.22644	−1.23451	−1.03918
H	0.07871	−1.45815	−1.05827
C	3.31689	−0.50439	−0.57678
H	2.3791	−2.12817	−1.64482
O	4.21446	1.28406	0.66012
O	4.62774	−0.7965	−0.8364
C	4.88514	−1.92727	−1.62184
H	5.97684	−1.99224	−1.72321
H	4.5131	−2.85487	−1.14893
H	4.43603	−1.84548	−2.62906
C	4.01603	2.39105	1.49949
H	5.01511	2.78219	1.73473
H	3.42358	3.18359	1.00786
H	3.50556	2.11138	2.4386
O	−3.09826	2.12629	−1.26252
C	−4.2681	2.87314	−1.22447
H	−4.24577	3.59303	−2.05867
H	−5.17883	2.24255	−1.32993
H	−4.37796	3.4427	−0.27558
H	−1.5933	0.02454	−1.33015
C	−2.40762	−1.59599	0.41207
O	−3.6183	−1.51665	0.62584
O	−1.49371	−1.8186	1.42493
O	−1.91725	−2.37238	−0.64947
C	−2.81602	−2.45946	−1.72365
H	−2.93569	−1.48616	−2.23578
H	−2.38915	−3.18574	−2.43093
H	−3.81007	−2.79299	−1.38674
C	−1.90487	−1.26935	2.65741
H	−1.10522	−1.50154	3.37498
H	−2.01861	−0.17584	2.58887
H	−2.85666	−1.71226	2.99456

M6

E [a.u.] = −1110.503019
G [a.u.] = −1110.206575
E_{SP} [a.u.] = −1110.804172

Charge = −1 Multiplicity = 1

C	3.43705	−1.29618	−0.34375
C	4.83331	−0.85284	0.03422
H	5.52486	−1.69882	−0.11653
H	5.15612	−0.02426	−0.6216
C	2.50657	−0.10375	−0.44836
O	2.92467	1.03221	−0.60467
C	1.02368	−0.30942	−0.26462
C	0.24412	0.83301	−0.0228
C	0.41038	−1.55443	−0.32198
C	−1.12314	0.73824	0.18142
H	0.76653	1.78912	−0.01031
C	−0.97141	−1.65791	−0.12726
H	1.00274	−2.44126	−0.5647
C	−1.74466	−0.52991	0.13039
H	−1.43624	−2.64203	−0.18808
O	−1.95454	1.79338	0.435
O	−3.09272	−0.53351	0.34279
C	−3.74932	−1.77046	0.27088
H	−4.811	−1.56774	0.46433
H	−3.64787	−2.2353	−0.72662
H	−3.37652	−2.48383	1.02847
C	−1.3632	3.0658	0.47225
H	−2.17263	3.77527	0.68992
H	−0.59403	3.14134	1.26191
H	−0.89681	3.33296	−0.49306
O	4.83538	−0.42638	1.39226
C	6.06847	0.09602	1.76435
H	6.01135	0.38794	2.82461
H	6.89077	−0.64247	1.6458
H	6.34127	0.9911	1.16666
H	3.0652	−1.94794	0.4619
C	3.50459	−2.18042	−1.68469
O	4.65864	−2.47108	−2.10004
O	2.63191	−1.46588	−2.59349
O	2.63239	−3.40568	−1.39537
C	3.35662	−4.44838	−0.82788
H	3.60024	−4.26902	0.24594
H	2.74593	−5.36714	−0.8816
H	4.30984	−4.60172	−1.36306
C	2.67052	−1.97908	−3.89393
H	2.11075	−1.28249	−4.53852
H	3.71058	−2.06889	−4.25123
H	2.20061	−2.97998	−3.94948

TS-7

E [a.u.] = −1110.498703
G [a.u.] = −1110.200417
E_{SP} [a.u.] = −1110.794888

Charge = −1 Multiplicity = 1

C	−2.19689	0.21314	−0.69374
C	−3.22389	1.31006	−0.96222
H	−4.18021	0.84668	−1.23331
H	−3.36627	1.89921	−0.03893
C	−1.10335	0.64774	0.31044
O	−1.27775	1.63753	1.03241
C	0.32119	0.21026	0.02505
C	1.34515	1.06461	0.45293
C	0.65403	−0.95711	−0.6504
C	2.67954	0.77186	0.20494
H	1.03191	1.95907	0.9912
C	1.99472	−1.26416	−0.90334
H	−0.13614	−1.64683	−0.95006
C	3.01376	−0.41098	−0.487
H	2.23296	−2.19094	−1.42607
O	3.73524	1.55622	0.58017
O	4.35014	−0.62129	−0.69272
C	4.71374	−1.78154	−1.38734
H	5.80951	−1.76828	−1.4608
H	4.40198	−2.70042	−0.85726
H	4.2865	−1.8065	−2.40702
C	3.42817	2.73664	1.27464

H	4.38743	3.23053	1.47975
H	2.79326	3.41526	0.67701
H	2.91325	2.53324	2.23055
O	−2.88691	2.16117	−2.0497
C	−1.74894	2.94705	−1.82372
H	−1.68082	3.66683	−2.65493
H	−1.80604	3.49453	−0.86449
H	−0.81591	2.34992	−1.80233
H	−1.74333	−0.07405	−1.65454
C	−2.86143	−1.02769	−0.07879
O	−4.00224	−1.02986	0.37905
O	−1.61696	−1.01039	1.32081
O	−2.35847	−2.1705	−0.7237
C	−2.73493	−3.36676	−0.08758
H	−3.82789	−3.42201	0.04171
H	−2.38738	−4.1936	−0.72506
H	−2.25575	−3.43163	0.90472
C	−2.17189	−0.67236	2.53685
H	−1.95906	0.39172	2.78801
H	−3.27657	−0.78926	2.50973
H	−1.77052	−1.30973	3.3536

M7

E [a.u.] = −1110.509036
G [a.u.] = −1110.21304
E_{SP} [a.u.] = −1110.807961

Charge = −1 Multiplicity = 1

C	2.25914	−0.2369	−0.85813
H	2.08255	−0.94846	−1.67684
C	3.74463	0.19077	−0.92864
H	4.30935	−0.57827	−1.47894
H	3.79148	1.1366	−1.49547
C	1.2822 0.99019	−1.06794	
O	1.54553	2.05964	−0.39442
C	−0.18049	0.48346	−0.90136
C	−0.89028	0.95447	0.20759
C	−0.80192	−0.41029	−1.76233
C	−2.18246	0.52505	0.4745
H	−0.35003	1.67909	0.8191
C	−2.11007	−0.84755	−1.51363
H	−0.26756	−0.75863	−2.64751
C	−2.80553	−0.39425	−0.39675
H	−2.57826	−1.54851	−2.20606
O	−2.93324	0.92878	1.54623
O	−4.0811	−0.7669	−0.0569
C	−4.711 −1.70357	−0.88266	
H	−5.69631	−1.89662	−0.43674
H	−4.85361	−1.32518	−1.91267
H	−4.14957	−2.6551	−0.93821
C	−2.31571	1.82146	2.43624
H	−3.04511	2.01191	3.23555
H	−1.39531	1.39613	2.87521
H	−2.05175	2.77681	1.94851
O	4.40004	0.30024	0.31901
C	4.20939	1.5546	0.94438
H	3.16136	1.88963	0.85313
H	4.50802	1.43631	1.99846
H	4.86267	2.32306	0.47888
C	1.99676	−1.0345	0.39435
O	1.98733	−2.24533	0.4632
O	1.75951	−0.26512	1.47545
C	1.46242	−0.97286	2.66138
H	1.31774	−0.20966	3.43686
H	0.54514	−1.57089	2.54459
H	2.28583	−1.64867	2.93999
O	1.46889	1.14308	−2.57141
C	0.95548	2.35473	−3.03073
H	1.41129	2.57585	−4.01195
H	−0.14943	2.32349	−3.1636
H	1.18855	3.16447	−2.31648

TS-8

E [a.u.] = −1110.49772
G [a.u.] = −1110.202863
E_{SP} [a.u.] = −1110.802058

Charge = −1 Multiplicity = 1

C	2.18193	0.22725	−0.48183
H	3.10278	0.81544	−0.41412
C	2.34355	−1.21214	−0.16024
H	2.70284	−1.30814	0.88422
H	1.36835	−1.73344	−0.23281
C	1.2774	0.9823	1.35876
O	1.7878	0.30304	2.26134
C	−0.15479	0.78438	0.93985
C	−0.75808	−0.42995	1.2883
C	−0.88445	1.7286	0.231
C	−2.05489	−0.7228	0.89572
H	−0.15091	−1.12508	1.86684
C	−2.20139	1.45016	−0.15159
H	−0.41284	2.6665	−0.05465
C	−2.79254	0.23096	0.16159
H	−2.75435	2.19908	−0.71936
O	−2.70598	−1.8934	1.16794
O	−4.06401	−0.1406	−0.18728
C	−4.77465	0.73285	−1.01862
H	−5.73766	0.24727	−1.22675
H	−4.96596	1.70925	−0.53489
H	−4.24825	0.91542	−1.97388
C	−1.95118	−2.90292	1.78623
H	−2.61264	−3.77645	1.86299
H	−1.05878	−3.1713	1.19294
H	−1.6194	−2.61238	2.79956
O	3.27774	−1.88014	−1.02975
C	3.42444	−3.21643	−0.68467
H	2.46761	−3.78043	−0.75526
H	4.14776	−3.67618	−1.37763
H	3.80133	−3.35049	0.35388
C	1.37497	0.63609	−1.59619
O	1.38428	1.71711	−2.17471
O	0.43283	−0.31533	−1.95181
C	−0.46782	0.08768	−2.95292
H	−1.21118	−0.71836	−3.03917
H	−0.97273	1.03054	−2.69085
H	0.03685	0.2339	−3.92421
O	1.61416	2.3267	1.21187
C	2.87768	2.65669	1.7215
H	2.99023	3.74356	1.59928
H	2.97372	2.37916	2.78377
H	3.68405	2.14683	1.16377

3a

E [a.u.] = −688.991895
G [a.u.] = −688.823222
E_{SP} [a.u.] = −689.1384311

Charge = 0; Multiplicity = 1

C	0.7144255579	2.2912523201	−0.0009690461
C	1.4126417875	1.0702196577	−0.0007234795
C	0.7229020236	−0.1317143271	−0.0002765126
C	−0.6968317092	−0.1238343175	−0.0000716669
C	−1.3779783468	1.0902582491	−0.0002808124
C	−0.6731846346	2.2959647777	−0.0007422152
H	2.5001269361	1.0914875938	−0.0009201921
H	−2.4669235919	1.1101575644	−0.0000529367
H	−1.2002041913	3.2497388949	−0.0009074633
O	1.2919772033	−1.360220256	−0.000013287
O	−1.2778480293	−1.3413307761	0.0004099713
C	−2.6866081128	−1.3985554921	−0.0008241304
H	−2.9455887511	−2.4636670936	−0.0013720515
H	−3.113118719	−0.9217625163	0.8984024625
H	−3.1115188104	−0.9211870668	−0.9004991979
C	2.6990018243	−1.4250192997	−0.0003704077
H	2.9531542822	−2.4912721731	−0.0001293052
H	3.1288928073	−0.9498852753	−0.899361363
H	3.1293860798	−0.9493653399	0.8981081287
C	1.4219631381	3.5974013739	−0.0014305836
O	0.8773166157	4.6774890849	−0.0017720216
O	2.7619448424	3.4554878413	−0.0011729572
C	3.5022784845	4.6720412928	−0.001245359
H	4.5578817097	4.3782172467	0.0001240488
H	3.2724602331	5.2698329806	−0.8947575253
H	3.270445351	5.2711651957	0.8908417829

TS-9

E [a.u.] = −1377.311456
G [a.u.] = −1376.96636
E_{SP} [a.u.] = −1377.653012

Charge = −1; Multiplicity = 1

C	−5.52237	0.0679	−1.9271
C	−4.24408	−0.35341	−1.554
C	−3.83225	−0.36442	−0.20299
C	−4.77942	0.12087	0.75757

C	−6.05708	0.52116	0.38039
C	−6.43717	0.49543	−0.97121
H	−5.80396	0.05562	−2.9844
H	−3.49628	−0.68343	−2.27856
H	−6.77346	0.87256	1.12549
H	−7.44251	0.8152	−1.25565
O	−2.65522	−0.76102	0.18441
C	−1.20555	0.37143	−0.61046
H	−1.95569	1.11751	−0.88036
C	−0.72443	0.38203	0.81667
H	−1.49589	0.75072	1.49789
H	−0.40946	−0.61828	1.13241
C	−0.3293	−0.02595	−1.74139
H	−0.19967	0.799	−2.49271
O	0.41017	1.29172	0.89906
O	−4.3124	0.14758	2.05026
C	−5.18721	0.59763	3.03878
H	−4.63824	0.55041	3.98959
H	−5.51618	1.64182	2.86928
H	−6.09184	−0.03638	3.11896
O	−1.23253	−0.99913	−2.05068
C	1.05909	−0.53418	−1.37916
C	2.19872	0.27223	−1.44295
C	1.19383	−1.84118	−0.92498
C	3.42932	−0.19283	−1.00312
H	2.13555	1.30577	−1.79131
C	2.42209	−2.32063	−0.46678
H	0.29274	−2.45742	−0.92084
C	3.54238	−1.49145	−0.47605
H	2.48636	−3.33572	−0.07425
O	4.51694	0.65555	−1.00955
O	4.77757	−1.8324	0.01403
C	4.86182	−3.02676	0.7487
H	5.8839	−3.07279	1.14757
H	4.14254	−3.03688	1.58601
H	4.68564	−3.91609	0.11651
C	5.50882	0.30862	−1.95274
H	6.29865	1.06985	−1.87873
H	5.94007	−0.68371	−1.7412
H	5.09902	0.31434	−2.97928
C	1.47741	0.86004	1.55527
O	1.60492	−0.17722	2.16117
O	2.42498	1.80795	1.46104
C	3.66808	1.45586	2.05384
H	4.28061	2.36463	2.01109
H	3.53006	1.1326	3.09605
H	4.16055	0.65578	1.48301

MMC

E [a.u.] = −303.65836996
G [a.u.] = −303.633228
E_{SP} [a.u.] = −303.81911238

Charge = −1; Multiplicity = 1

C	0.0003165909	0.0986938132	0.0354847962
O	−0.0008579944	−0.0820267186	1.2646073542
O	0.0002664247	1.1094370659	−0.6707195809
O	0.0000080758	−1.120199363	−0.7640480139
C	−0.0007734554	−2.2999226757	−0.0233283766
H	−0.885871603	−2.3965711604	0.6361792809
H	−0.0008990276	−3.140621755	−0.743480886
H	0.883789989	−2.3973322062	0.6367794261

DMC

E [a.u.] = −343.521334
G [a.u.] = −343.455881
E_{SP} [a.u.] = −343.6056438

Charge = 0; Multiplicity = 1

C	−0.0466694862	1.7610133752	0.2249446763
O	1.1431915721	1.6363233391	0.0730722627
O	−0.6966460067	2.9102774696	0.4117353513
C	0.1404317403	4.0644532801	0.4232753851
H	−0.5320299726	4.9138193357	0.584287979
H	0.8796904711	4.0028379465	1.2345076405
H	0.6704610473	4.1719551055	−0.5337039202
O	−0.9430271465	0.7737954823	0.2355262093
C	−0.3887433513	−0.5261863614	0.046394486
H	0.3290187458	−0.7644489628	0.844107219
H	−1.2388002719	−1.2160019367	0.0797143127
H	0.1222414128	−0.5955887676	−0.9244173236

Formaldehyde (FA)

E [a.u.] = −114.4687442
G [a.u.] = −114.463678
E_{SP} [a.u.] = −114.5018821

Charge = 0; Multiplicity = 1

O	0.0994633333	1.0827003942	−0.6494304743
C	1.0995797342	1.4650995789	−1.1918942641
H	1.7971926997	0.7676545438	−1.7167906177
H	1.3955861752	2.5424986467	−1.2060732734

Methanol (MeOH)

E [a.u.] = −115.6872615
G [a.u.] = −115.658462
E_{SP} [a.u.] = −115.7266544

Charge = 0; Multiplicity = 1

O	−0.0013579627	1.1494312637	−0.6170425745
C	1.330145292	1.451316151	−0.9596080745
H	2.0200003071	1.4036186882	−0.0953329807
H	1.729982506	0.7951481068	−1.7561928906
H	1.3425203644	2.4825847617	−1.3397438706
H	−0.0196175467	0.2460795787	−0.2854507291

Methanolate

E [a.u.] = −115.0400258
G [a.u.] = −115.027059
E_{SP} [a.u.] = −115.1724325

Charge = −1; Multiplicity = 1

O	−0.0119416269	1.0755238896	−0.7120948882
C	1.2126659765	1.4258391436	−0.9665300804
H	1.9995857154	1.3550897726	−0.1018606678
H	1.7918707418	0.8456227037	−1.8030538786
H	1.4119538291	2.5246119303	−1.3199194652

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E [a.u.] = −421.29245611
G [a.u.] = −421.200784
E_{SP} [a.u.] = −421.45239422

Charge = −1; Multiplicity = 1

C	−3.971061819	−3.522317575	−1.0818866767
C	−2.935857669	−2.9070182505	−0.3787440579
C	−2.9984696916	−1.5553437681	0.1112188571
C	−4.265875991	−0.8955455654	−0.2074637265
C	−5.2867227639	−1.5170293081	−0.9065394734
C	−5.1579360708	−2.8488363835	−1.3591158917
H	−3.8434971558	−4.5578163802	−1.4213949312
H	−2.0076538401	−3.4482926929	−0.1674515275
H	−6.2156417158	−0.9802820482	−1.1198932163
H	−5.9734559129	−3.32436514	−1.9096730033
O	−2.0804198335	−0.9812396712	0.745411042
O	−4.3362198425	0.4059683945	0.2601308966
C	−5.5038310086	1.108977692	0.0026165696
H	−5.3793946957	2.1104155561	0.4429521028
H	−5.7055178173	1.2250582574	−1.083219395
H	−6.4002221724	0.6349598831	0.4553374314

2a

E [a.u.] = −461.16415614
G [a.u.] = −461.031057
E_{SP} [a.u.] = −461.2606828

Charge = 0; Multiplicity = 1

C	−4.0102853057	−3.5297434208	−1.1613541191
C	−2.9064248088	−2.8490227592	−0.6287842431
C	−3.0262912696	−1.528543408	−0.2116019133
C	−4.2763993145	−0.87051498	−0.3283009605
C	−5.3636723232	−1.5557006682	−0.8577936169
C	−5.2304800474	−2.8875481374	−1.2749311444
H	−3.8962963671	−4.5657856554	−1.4832877137
H	−1.9505845644	−3.3653012492	−0.5444840275
H	−6.32968517	−1.0605960878	−0.9525465079
H	−6.0954037548	−3.4083670884	−1.6880665284
O	−2.0270187893	−0.779740504	0.3154100314
O	−4.2948032419	0.41392727	0.1037377146
C	−5.5111207482	1.1155384065	0.0159599791

H	−5.3122430897	2.1179873484	0.4135454079
H	−5.8591020286	1.2041205517	−1.0283754795
H	−6.3040955554	0.638990671	0.6189427895
C	−0.7631149337	−1.3817771642	0.4547981048
H	−0.1100212654	−0.6176346609	0.8929506268
H	−0.7971678819	−2.2562826036	1.1281095694
H	−0.3484341505	−1.6953383606	−0.5194614193

11−Cs

E [a.u.] = −441.4865854
G [a.u.] = −441.396953
E_{SP} [a.u.] = −441.6126241

Charge = 0; Multiplicity = 1

C	−1.73999	−0.74641	−0.00002
C	−1.38807	0.60054	−0.00009
C	−0.03784	1.05075	−0.00007
C	0.93565	−0.01664	0.00007
C	0.58345	−1.35802	0.00016
C	−0.76593	−1.74102	0.0001
H	−2.79827	−1.02367	−0.00005
H	−2.15574	1.3789	−0.00019
H	1.34874	−2.13683	0.00026
H	−1.03326	−2.79862	0.00016
O	0.29541	2.28741	−0.00007
O	2.26866	0.41836	0.00012
C	3.26062	−0.56821	0.
H	4.23226	−0.0476	−0.00008
H	3.21097	−1.21377	0.8961
H	3.21077	−1.21373	−0.89611
Cs	2.80989	3.33337	0.00042

Cs(DMC)

E [a.u.] = −363.5757014
G [a.u.] = −363.51729
E_{SP} [a.u.] = −363.7130839

Charge = 1; Multiplicity = 1

O	−0.59122	−1.33189	0.04279
C	−0.44704	−0.02768	−0.07324
O	0.49461	0.54376	−0.584
O	−1.46106	0.66881	0.43999
Cs	0.45199	3.52415	−0.48462
C	−2.56256	−0.03454	1.04494
H	−3.26382	0.74437	1.36085
H	−3.03893	−0.70345	0.3172
H	−2.21821	−0.6115	1.9128
C	0.47743	−2.13387	−0.49123
H	0.56342	−1.97385	−1.57348
H	1.42352	−1.87581	0.00105
H	0.19604	−3.16815	−0.27358

M8−Cs

E [a.u.] = −441.6927223
G [a.u.] = −441.594039
E_{SP} [a.u.] = −441.8250543

Charge = 0 Multiplicity = 1

C	0.28593	−0.86071	0.66621
H	0.60031	−1.80704	1.1099
C	1.22358	0.27976	0.61471
H	0.697	1.24207	0.63313
H	1.95571	0.2607	1.44477
O	2.04489	0.38455	−0.61981
C	3.03706	−0.60011	−0.65698
H	2.6102	−1.62551	−0.62507
H	3.61248	−0.47966	−1.58968
H	3.74185	−0.51205	0.19414
C	−1.0845	−0.75709	0.40697
O	−1.98278	−1.59919	0.47131
O	−1.44319	0.53308	−0.1217
C	−2.83111	0.73556	−0.24838
H	−2.97223	1.80047	−0.48547
H	−3.2741	0.11944	−1.05504
H	−3.37209	0.48305	0.6758
Cs	−0.07524	−0.56093	−2.59088

CsOMe

E [a.u.] = −135.2455828
G [a.u.] = −135.238188
E_{SP} [a.u.] = −135.3287795

Charge = 0 Multiplicity = 1

O	1.17909	−0.71294	0.00013
Cs	2.49739	1.58673	0.00549
C	2.03154	−1.74523	−0.0002
H	1.5715	−2.77481	−0.00241
H	2.75637	−1.80258	−0.89161
H	2.75379	−1.80526	0.89312

CsMMC

E [a.u.] = −323.85830037
G [a.u.] = −323.836347
E_{SP} [a.u.] = −323.9718611

Charge = 0 Multiplicity = 1

C	−0.85521	−0.14508	−0.18332
O	−0.01017	−0.51729	0.66955
O	−2.08356	0.02096	−0.02812
O	−0.40198	0.12172	−1.46053
C	0.98061	−0.05815	−1.66241
H	1.29362	−1.09753	−1.46864
H	1.1739	0.19422	−2.7153
H	1.58107	0.59683	−1.00955
Cs	−2.0166	−0.73036	2.73038

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