Supplementary Information

Organocatalytic Chemoselective Primary Alcohol Oxidation and Subsequent Cleavage of Lignin Model Compounds and Lignin

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1. General Information

1.1. Materials and methods

All reagents were acquired from commercial suppliers and used without further purification, poly[4-(diacetoxyiodo)-styrene] was bought from TCI chemicals (I^{+3} ca. 1.1 mmol/g). 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 tubes.

1.2. Instruments

NMR spectra were recorded on a Varian Inova 400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 101 MHz) or Agilent VNMRS 600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 151 MHz) spectrometer. Chemical shifts (δ) are given in ppm relative to the residual solvent peak (CD_3CN: δ = 1.94 ppm, $CDCl_3$: 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), br.s (broad singlet). Mass spectra were recorded on a Finnigan SSQ 7000 spectrometer (EI) and HRMS on a Finnigan MAT 95 spectrometer (ESI). HPLC measurements were conducted on an Agilent Infinity 1260 HPLC apparatus using an Agilent Eclipse XDB-C18 (4.6 mm ID x 150 mm, 5 mm) column. H_2O/MeOH (70:30) eluent and a flow rate of 1.0 mL/min was used for the measurement of veratraldehyde (**4a**) and guaiacol (**5a**).

The GPC measurements for lignin sample **L1** was performed on an ECO Sec System apparatus (HLC-8320GPC) from TOSOH-Bioscience LLC Company. It was equipped with one pre-column PSS Suprema (50 x 8 mm, 100 Å) and three columns PSS Suprema (300 x 8 mm, 100 Å). Measurements were conducted with a flow rate of 1 mL/min. and an injection volume of 20 µL. A Na_2HPO_4 buffer solution (pH 12) with 0.5 g PEG 6000 was used as solvent, and the signals were detected with an ECO Sec RI and/or UV-detector. The elugrams show the detector response of the RI-detector.

The gas chromatography-mass spectrometry (GC-MS) was performed using an Agilent 7890A series GC system equipped with a Agilent 5975C inert XL EI/CI MSD with triple axis detector and an Agilent DB-5ms column (30 m x 0.25 mm x 0.25 µm) with helium as the carrier gas. The standard method of analysis for which retention times are provided in the text below is a 1 µL injection, a split ration of 50:1, a flow of 1.2 mL/min with a temperature profile starting with 60 °C 5 min isotherm followed by a 10 °C/min ramp for 20 minutes, finishing the ramp at 260 °C, a temperature that was held for 5 minutes. NIST 08 standard reference database was used for characterising the peaks (GC-MS).

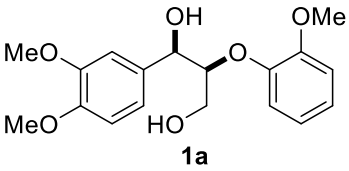
Melting points were measured with a Büchi Melting Point B-540 apparatus.

2. Preparation of starting materials and probable products

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

The lignin model compounds (**1a-f**) used for the cleavage reactions were prepared according to the procedure described in literature.[1,2]

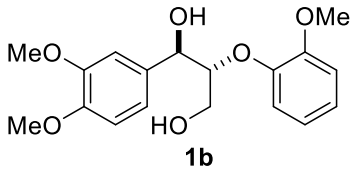
***erythro* 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propandiol (1a)[1]**



1a

White solid, M. P. = 100–101°C. ^{1}H-NMR (400 MHz, ($CDCl_3$)): δ = 7.07 (ddd, *J* = 8.2 Hz, 7.2 Hz and 1.8 Hz, 1H), 6.99–6.89 (m, 5H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.99 (d, *J* = 4.7 Hz, 1H), 4.16 (ddd, *J* = 6.0 Hz, 4.7 Hz and 3.4 Hz, 1H), 3.94–3.90 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.66 (ddd, *J* = 12.1 Hz, 7.2 Hz and 3.4 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, 132.5, 124.4, 121.8, 121.2, 118.5, 112.3, 111.1, 109.3, 87.6, 72.8, 60.9, 56.0 (3C). **MS (EI, 70 eV):** m/z (%): 334 $[M]^+$ (31), 167 (16), 166 (12), 151 (17), 150 (100), 139 (20), 124 (11), 121 (12).

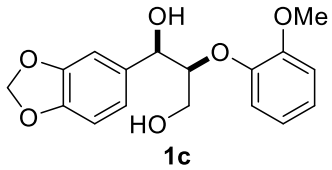
***threo* 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propandiol (1b)[1]**



1b

Colorless liquid. ^{1}H-NMR (400 MHz, ($CDCl_3$)): δ = 7.13 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 7.07 (ddd, *J* = 8.0 Hz, 7.2 Hz and 1.6 Hz, 1H), 7.01–6.96 (m, 2H), 6.95 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 6.93 (ddd, *J* = 8.0 Hz, 8.0 Hz and 1.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 4.7 Hz, 1H), 4.03 (dt, *J* = 7.7 Hz, 3.7 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.69 (br.d, *J* = 1.6 Hz, 1H), 3.63 (dt, *J* = 12.0 Hz, 3.7 Hz, 1H), 3.48 (ddd, *J* = 12.0 Hz, 7.7 Hz and 3.7 Hz, 1H), 2.72 (dd, *J* = 7.7 Hz and 4.7 Hz, 1H). **^{13}C-NMR (101 MHz, ($CDCl_3$)):** δ = 151.5, 149.2, 149.1, 147.7, 132.2, 124.5, 121.9, 121.2, 119.8, 112.3, 111.2, 110.0, 89.7, 74.1, 61.2, 56.0 (3C). **MS (EI, 70 eV):** m/z (%): 334 $[M]^+$ (30), 167 (15), 166 (12), 151 (17), 150 (100), 139 (20), 124 (11), 121 (12).

***erythro*-2-(2-Methoxyphenoxy)-1-[3,4-(methylenedioxy)phenyl]-l,3-propanediol (1c)[1]**

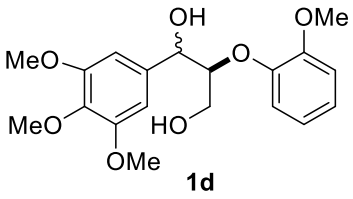


1c

White solid, M. P. = 92–93 °C. ^{1}H-NMR (400 MHz, ($CDCl_3$)): δ = 6.97 (ddd, *J* = 8.0 Hz, 7.2 Hz and 1.6 Hz, 1H), 6.89 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 6.87–6.80 (m, 3H), 6.75 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.86 (q, *J* = 1.2 Hz, 2H), 4.87 (d, *J* = 4.7 Hz, 1H), 4.05 (ddd, *J* = 6.0 Hz, 4.7 Hz and 3.7 Hz, 1H), 3.83 (dt, *J* = 12.0 Hz, 6.0 Hz, 1H), 3.79 (s, 3H), 3.57 (dd, *J* = 12.0 Hz and 3.7 Hz, 1H), 2.92 (br.s, 2H). **^{13}C-NMR (101 MHz, ($CDCl_3$)):** δ = 151.5, 147.7, 147.0, 146.8, 133.9, 124.2, 121.6, 120.9, 119.5,

112.2, 108.1, 106.7, 101.0, 87.2, 72.7, 60.6, 55.9. **MS (EI, 70 eV):** m/z (%): 318 $[M]^+$ (4), 151 (45), 150 (100), 149 (24), 93 (34).

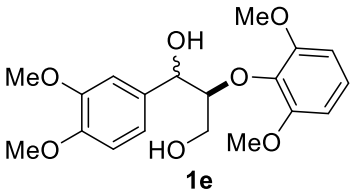
2-(2-Methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)-1,3-propanediol (1d)[2]
erythro : *threo* = 1.89 : 1



1d

Colorless liquid. ^{1}H-NMR (400 MHz, ($CDCl_3$)): δ = 7.09–6.97 (m, 4H), 6.91–6.82 (m, 4H), 6.66 (s, 2H), 6.59 (s, 2H), 4.96–4.90 (m, 2H), 4.14 (ddd, *J* = 6.1Hz, 4.6Hz and 3.2 Hz, 1 H), 4.03 (ddd, *J* = 6.1Hz, 4.6Hz and 3.2 Hz, 1 H), 3.87, 3.84, 3.82, 3.81, 3.78 (all singlets for methoxy groups, 12H for both diastereomers), 3.70–3.60 (m, 1H), 3.53–3.46 (m, 1H,), 2.96 (br.s, 2H). **^{13}C-NMR (101 MHz, ($CDCl_3$)):** δ = major diastereomer: 153.4, 151.6, 147.0, 137.5, 135.9, 124.3, 121.7, 120.8, 112.3, 103.3, 89.1, 87.1, 73.1, 61.0, 56.3, 56.0; minor diastereomer: 153.4, 151.3, 147.7, 137.9, 135.5, 124.3, 121.8, 121.0, 112.3, 104.2, 89.1, 87.1, 74.3, 61.2, 61.0, 56.0. **MS (EI, 70 eV):** m/z (%): 364 $[M]^+$ (5), 197 (27), 196 (80), 169 (39), 150 (100).

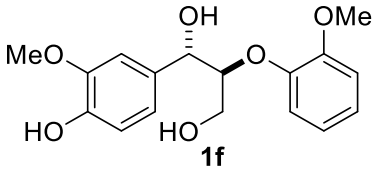
2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propandiol (1e)[2]
erythro : *threo* = 1.6: 1



1e

Yellow liquid. ^{1}H-NMR (400 MHz, ($CDCl_3$)): δ = 7.11–6.94 (m, 5H), 6.86–6.82 (m, 3H), 6.65 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 5.06 (d, *J* = 8.7 Hz, 1H), 5.02 (d, *J* = 3.2 Hz, 1H), 4.36 (br.s, 1H), 4.18–4.13 (m, 2H), 3.94–3.92 (m, 1H), 3.91 (s, 6H), 3.88 (s, 3H), 3.89 (s, 9H), 3.87 (s, 3H), 3.86 (s, 3H), 3.58 (dd, *J* = 10.8 Hz and 2.7 Hz, 1H), 3.50 (d, *J* = 10.8 Hz, 1H), 3.40–3.26 (m, 2H), 3.16 (br.s, 1H). **^{13}C-NMR (101 MHz, ($CDCl_3$)):** δ = 153.5 (2C), 153.2 (2C), 149.0, 148.9, 148.7, 148.2, 135.3, 135.0, 132.6, 132.0, 124.5, 124.4, 119.8, 118.1, 111.0 (2C), 110.3, 109.0, 105.3 (2C), 105.3 (2C), 89.0, 87.0, 74.0, 72.5, 60.6, 60.5, 56.2 (4C), 55.9 (2C), 55.9 (2C). **MS (EI, 70 eV):** m/z (%): 364 $[M]^+$ (4), 181 (16), 180 (100), 154 (32), 139 (25).

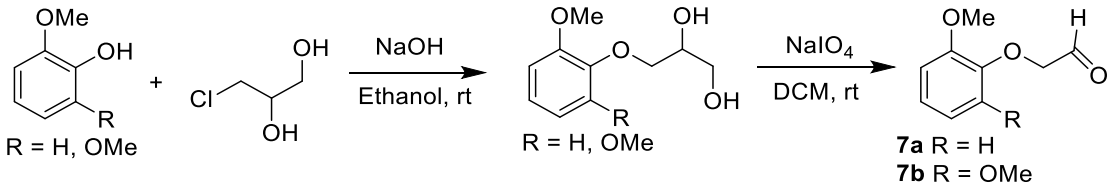
***threo* 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (1f)[1]**



1f

White solid, M. P. = 113–114 °C. ^{1}H-NMR (400 MHz, ($CDCl_3$)): δ = 7.13 (dd, *J* = 8.0 Hz and 1.6 Hz, 1H), 7.09–7.05 (m, 1H), 6.99–6.89 (m, 4H), 6.88 (d, *J* = 8.0 Hz, 1H), 5.75–5.66 (m, 1H), 4.96 (d, *J* = 7.7 Hz, 1H), 4.02 (dt, *J* = 7.7 Hz and 3.7 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.75–3.69 (m, 1H), 3.62 (ddd, *J* = 12.0 Hz, 4.7 Hz and 3.7 Hz, 1H), 3.48 (ddd, *J* = 12.0 Hz, 7.7 Hz and 3.7 Hz, 1H), 2.85–2.74 (m, 1H). **^{13}C-NMR (101 MHz, ($CDCl_3$)):** δ = 151.4, 147.7, 146.8, 145.7, 131.6, 124.4, 121.8, 121.2, 120.3, 114.4, 112.3, 109.5, 89.7, 74.1, 61.1, 56.1, 56.0. **MS (EI, 70 eV):** m/z (%): 320 $[M]^+$ (4), 153 (28), 150 (100), 109 (22), 93 (22), 65 (20).

2.2 Synthesis of 2-aryloxyacetaldehydes 7a and 7b



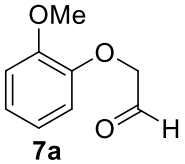
Step 1: Preparation of 3-aryloxypropane-1,2-diols[3]

A solution of the corresponding phenol derivatives (25 mmol, 1 equiv) in ethanol (15 mL) was prepared in a 25 mL round bottom flask. To this was added a solution of NaOH (1.25 equiv) in water (5 mL) and the resulting mixture was refluxed for 15 min under vigorous stirring. A solution of racemic 3-chloropropane-1,2-diol (1.2 equiv) in ethanol (2 mL) was then added dropwise to the above mixture and the resulting reaction was refluxed for 3h. After cooling the solution, the volume of the mixture was reduced to half, followed by extraction with diethyl ether. The resulting crude mixture (2 g) was used for the next step.

Step 2: Preparation of 2-aryloxyacetaldehyde 7a and 7b[4]

The crude mixture from step 1 was dissolved in DCM (100 mL). A solution of $NaIO_4$ (1.3 equiv) prepared in water (27 mL) was added dropwise to the above reaction mixture. The stirring was continued for 1 h at room temperature after which the solution was filtered and extracted with DCM. The resulting crude mixture was then subjected to flash chromatography (EtOAc / *n*-pentane = 30%). The products obtained contained traces of phenol derivative owing to their instability during column chromatography purification. Pure samples of **7a** and **7b** were obtained as a white solid (70%) and liquid (55%) respectively after washing with minimum amount of distilled *n*-pentane.

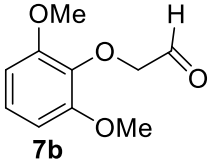
2-(2-methoxyphenoxy)acetaldehyde (7a)[5]



7a

White solid, M. P. = 66–67 °C. ^{1}H-NMR (400 MHz, (CD_3CN)): δ = 9.73 (d, *J* = 1.1 Hz, 1H), 7.01–6.95 (m, 2H), 6.91–6.84 (m, 2H), 4.69 (d, *J* = 1.1 Hz, 2H), 3.82 (s, 3H). **^{13}C-NMR (101 MHz, ($CDCl_3$)):** δ = 199.9, 150.5, 148.3, 123.2, 121.6, 115.3, 113.5, 74.7, 56.3. **MS (EI, 70 eV):** m/z (%): 167 $[M+1]^+$ (15), 166 $[M]^+$ (100), 138 (24), 122 (49), 95 (25), 77 (33).

2-(2,6-dimethoxyphenoxy)acetaldehyde (7b)



7b

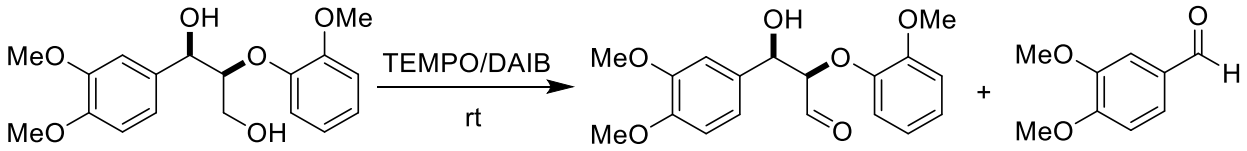
Yellow liquid, ^{1}H-NMR (400 MHz, (CD_3CN)): δ = 9.82 (t, *J* = 1.5 Hz, 1H), 7.03 (t, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.44 (d, *J* = 1.5 Hz, 2H), 3.83 (s, 6H). **^{13}C-NMR (101 MHz, ($CDCl_3$)):** δ = 202.0, 153.9 (2C), 137.5, 125.3, 106.3 (2C), 78.4, 56.6 (2C). **MS (EI, 70 eV):** m/z (%): 197 $[M]^+$ (14), 196 $[M]^+$ (100), 153 (64), 152 (33), 138 (40), 125 (28), 95 (24).

3. Chemoselective γ-alcohol oxidation of lignin model compound 1a.

3.1. General procedure for the TEMPO/DAIB-catalysed γ-alcohol oxidation in 1a.

A 10 mL glass tube with a teflon screw cap and a magnetic stirrer was charged with model compound **1a** (83.6 mg, 0.250 mmol, 1 equiv) and the requisite amounts of TEMPO, DAIB in acetonitrile-d_3 (2.0 mL). The reaction mixture was stirred at room temperature for 7 h. The conversion of **1a** and the yields for **3a** and **4a** were determined by ^{1}H-NMR analysis of the crude reaction mixture with respect to 1,4-dinitrobenzene as internal standard.

3.2. Table S1. Optimisation of the reaction conditions for the TEMPO/DAIB-catalysed γ-alcohol oxidation in 1a.[a]



1a **3a** **4a**

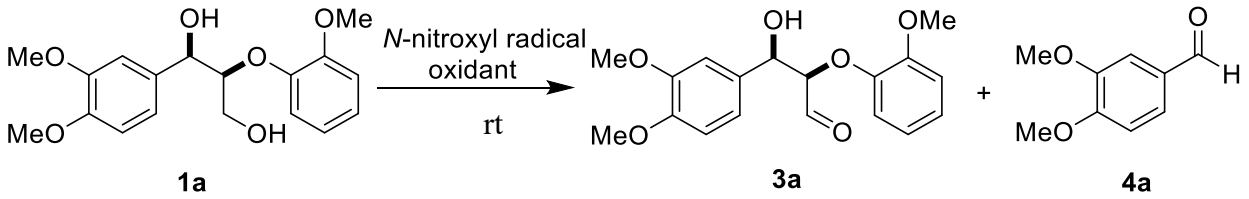
Entry	TEMPO [equiv]	DAIB [equiv]	Solvent (mL)	Time [h]	Conv [%][b]	Yield [%][b] **3a**	**4a**
1	1.00	-	CD_3CN (2)	24	-	-	-
2	-	1.30	CD_3CN (2)	24	10	-	-
3	0.30	1.30	CD_3CN (2)	3	56	43	9
4	0.30	1.30	CD_3CN (2)	7	>99	75	14
5	0.15	1.30	CD_3CN (2)	12	>99	60	16
6	0.15	1.30	CD_3CN (2)	7	>99	75	16
7	0.15	1.30	CD_3CN (1)	7	90	50	15
8	0.15	1.00	CD_3CN (2)	7	84	55	12
9	0.05	1.30	CD_3CN (2)	7	70	45	5
10	0.10	1.30	CD_3CN (2)	7	>99	78	14
11[c]	0.10	1.30	CD_3CN (2)	7	>99	68	24
12	0.15	1.30	$(CD_3)_2CO$ (2)	7	>99	65	8
13	0.15	1.30	$CDCl_3$ (2)	7	>99	44	10
14	0.15	1.30	$(CD_3)_2SO$ (2)	7	50	10	5
15	0.15	1.30	C_7D_8 (2)	7	70	30	10
16	0.15	1.30	C_3H_7NO (2)	7	65	34	4
17	0.15	1.30	DMC (2)	7	20	15	4

[a] Use of 0.250 mmol of **1a** (1 equiv) at rt. [b] Conversion of **1a** as well as the yields of **3a** and **4a** were determined by ^{1}H NMR spectroscopy with 1,4-dinitrobenzene as internal standard. [c] Addition of 2 equiv of AcOH at the beginning of the reaction.

3.3. General procedure for the screening of various nitroxide radical species and terminal oxidants in the γ-alcohol oxidation in 1a.

A 10 mL glass tube with a teflon screw cap and a magnetic stirrer was charged with model compound **1a** (83.6 mg, 0.250 mmol, 1 equiv) and the requisite amounts of the nitroxide radical species and the terminal oxidant in acetonitrile-d_3 (2.0 mL). The reaction mixture was stirred at room temperature for 7 h. The conversion of **1a** and the yields for **3a** and **4a** were determined by ^{1}H NMR analysis of the crude reaction mixture with respect to 1,4-dinitrobenzene as the internal standard.

3.4. Table S2. Screening of various nitroxide radical species and terminal oxidants in the γ-alcohol oxidation in 1a.[a]



1a **3a** **4a**

Entry	*N*-nitroxyl radical (equiv)	Terminal oxidant (equiv)	Conv. [%][b]	Yield [%][b]	
				3a	**4a**
1	TEMPO (0.15)	$PhI(O_2CCH_3)_2$ (1.3)	>99	75	16
2	TEMPO (0.15)	PhI(OH)(OTs) (1.3)	95	-	35
3	TEMPO (0.15)	$PhI(O_2CCF_3)_2$ (1.3)	60	-	15
4	TEMPO (0.15)	PhIO	50	10	-
5	TEMPO (0.15)	$PhIO_2$	30	-	-
6	AcNH-TEMPO (0.15)	$PhI(O_2CCH_3)_2$ (1.3)	>99	60	14
7	OH-TEMPO (0.15)	$PhI(O_2CCH_3)_2$ (1.3)	60	45	8
8	NHPI (0.15)	$PhI(O_2CCH_3)_2$ (1.3)	17	7	-

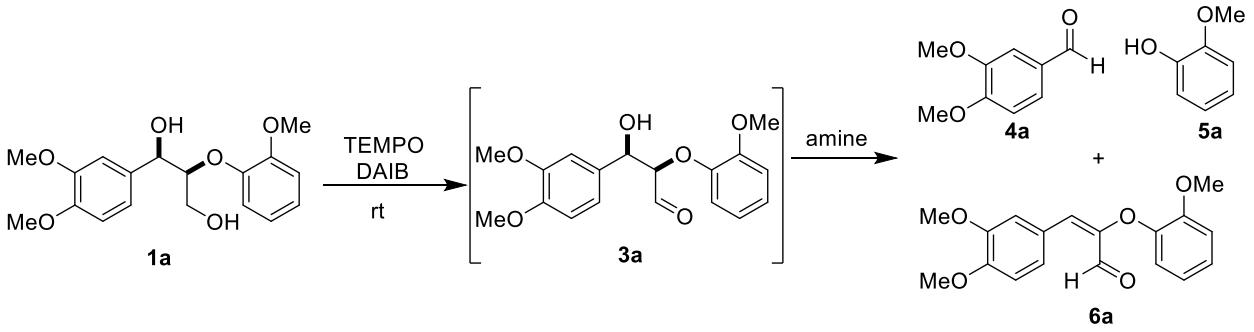
[a] Use of **1a** (0.250 mmol, 1 equiv) and acetonitrile-d_3 (2.0 mL) at rt, 7 h. [b] Conversion of **1a** as well as the yields of **3a** and **4a** were determined by ^{1}H NMR spectroscopy with 1,4-dinitrobenzene as internal standard. AcNH-TEMPO = 4-acetamido-TEMPO, HO-TEMPO = 4-hydroxy-TEMPO, NHPI = *N*- hydroxyphthalimide.

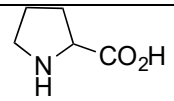
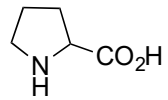
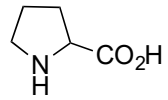
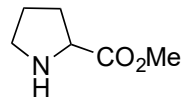
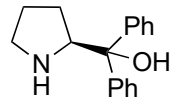
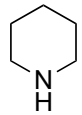
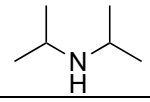
4. One-pot, two-step chemoselective oxidation of lignin β-O-4 model compounds followed by amine-catalysed cleavage reaction.

4.1. General procedure

A 10 mL glass tube with a teflon screw cap and a magnetic stirrer was charged with model compound **1** (0.250 mmol, 1.0 equiv), TEMPO (0.1 equiv), and DAIB (1.3 equiv) in acetonitrile (2.0 mL) and stirred for 7 h at room temperature. To this mixture, a requisite amount of the amine (0.2 equiv) was added and the resulting reaction mixture was further stirred for 5 h at room temperature. Then, the reaction mixture was diluted with water (10 mL). The resulting aqueous phase was then extracted with ethyl acetate (3 x 10 mL). The solvent was removed under reduced pressure, and subsequently, the reaction mixture was subjected to flash chromatography on silica gel using EtOAc : *n*-pentane (1:5) as eluent to give the corresponding products.

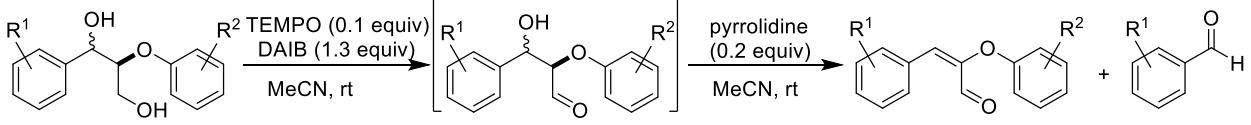
4.2. Table S3. One-pot chemoselective oxidation of 1a followed by amine-catalysed retro-aldol reaction.[a]

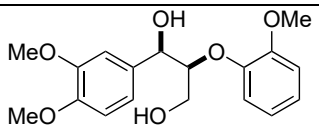
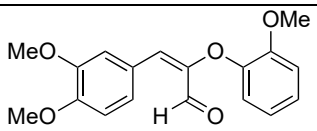
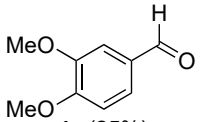
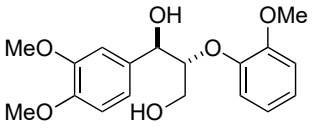
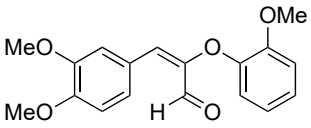
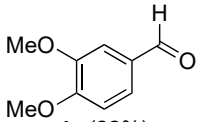
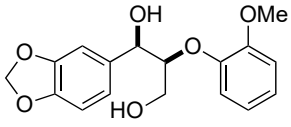
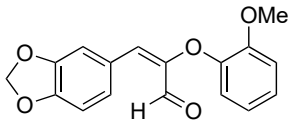
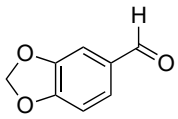
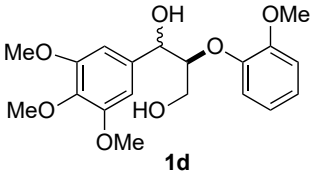
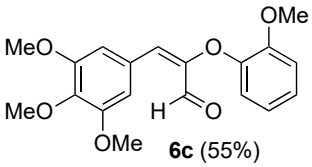
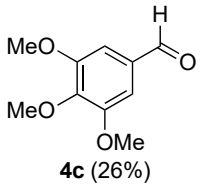
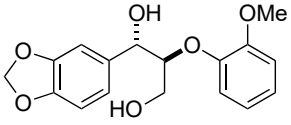
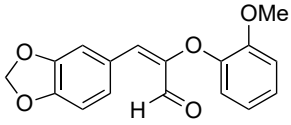
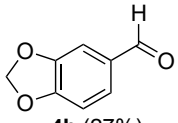


Entry	Catalyst	Equiv	Conv. (%)[b]	Yield (%)[c]			
				3a	**4a**	**5a**	**6a**
1		0.1	>99	-	52	20	-
2[d]		0.1	7	5	2	-	-
3		0.2	>99	-	70	26	5
4		0.2	>99	40	23	5	14
5		0.2	>99	-	25	10	58
6		0.2	>99	50	26	9	4
7		0.2	>99	-	25	12	55
8		1.0	>99	-	25	4	37

[a] Stirring of **1a** (0.250 mmol, 1.0 equiv), TEMPO (0.1 equiv) and DAIB (1.3 equiv) in acetonitrile (2 mL) at rt for 7 h. Then, the required amount of the amine (0.1-1.0 equiv) was added and the stirring was continued for 5 h at rt. [b] Conversions determined by ^{1}H NMR spectroscopy with 1,4-dinitrobenzene as the internal standard. [c] Yields after column chromatography. [d] DL-proline was added at the beginning of the reaction.

4.3. Table S4. One-pot oxidation of 1a-d, 1h followed by pyrrolidine-catalysed formation of the α,β-unsaturated aldehydes 6a-c.[a]

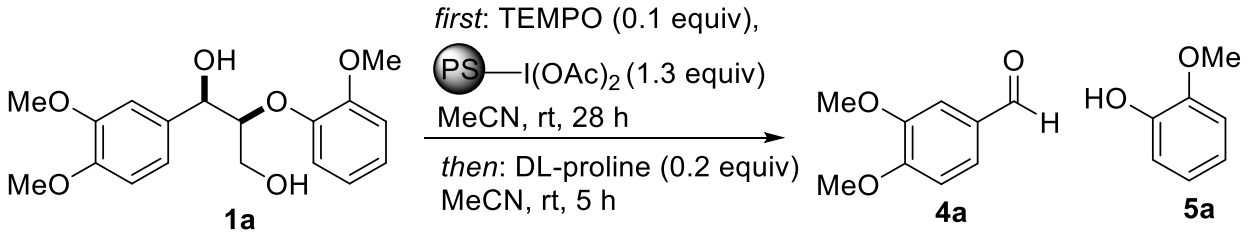


Entry	Substrate	Conv. [%]	Yield [%][b]	
			α,β-Unsaturated aldehyde	Benzaldehyde derivative
1	 **1a**	>99	 **6a** (58%)	 **4a** (25%)
2	 **1b**	>99	 **6a** (60%)	 **4a** (22%)
3	 **1c**	>99	 **6b** (57%)	 **4b** (24%)
4	 **1d**	>99	 **6c** (55%)	 **4c** (26%)
5	 **1h**	>99	 **6b** (56%)	 **4b** (27%)

[a] Stirring of **1** (0.250 mmol, 1 equiv), TEMPO (0.1 equiv), DAIB (1.3 equiv) in acetonitrile (2 mL) for 7 h at rt. Then, pyrrolidine (0.2 equiv) was added and the stirring was continued for 5 h at rt. [b] After column chromatography.

5. Two-step degradation of 1a using the TEMPO/immobilised DAIB catalytic system and DL-proline.

5.1. General procedure



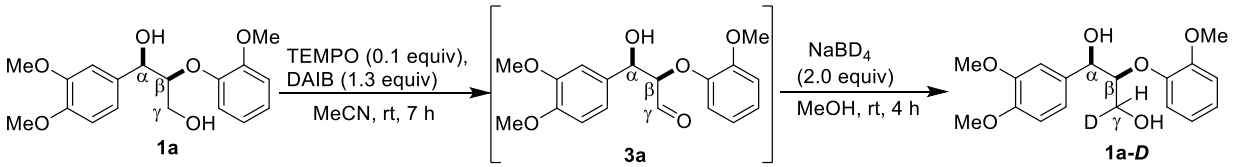
A 10 mL glass tube with a teflon screw cap and a magnetic stirrer was charged with model compound **1a** (0.250 mmol, 1 equiv), TEMPO (0.2 equiv), and poly[4-(diacetoxyiodo)-styrene] (PSDAIB; 1.3 equiv) in acetonitrile (2.0 mL) and stirred for 28 h at room temperature. The resulting reaction mixture was centrifuged and filtered to separate the reduced PSDAIB catalyst. To this filtrate, DL-proline (0.2 equiv) was added and the reaction mixture was further stirred for 5 h at room temperature. Upon completion, propiophenone (0.5 mL, 0.2 M) was added to the reaction mixture as an internal standard. The solution was then diluted with 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.

5.2 Regeneration of poly[4-(diacetoxyiodo)-styrene][6]

A peracetic acid solution was prepared by the dropwise addition of 30% H_2O_2 (2.0 mL) to Ac_2O (6 mL) at 0 °C. The solution was slowly warmed to room temperature and stirred overnight. Then, this solution was added to the recovered poly(4-iodostyrene) (220 mg, 0.325 mmol). The reaction was stirred at 50 °C overnight. The resultant mixture was precipitated with diethyl ether and filtered to give poly[4-(diacetoxyiodo)styrene] (300 mg) as a light yellow powder.

6. Reduction of intermediate 3a to 1a-*D* with $NaBD_4$

6.1. General procedure



A 10 mL tube with a teflon screw cap and a magnetic stirrer was charged with model compound **1a** (0.250 mmol, 1.0 equiv), TEMPO (0.1 equiv), DAIB (1.3 equiv) in CD_3CN (2.0 mL). The mixture was stirred at rt for 7 h. $NaBD_4$ (2 equiv) was added to the above reaction mixture along with 1 mL MeOH and the resulting mixture was stirred at rt for another 4 h. The reaction was then extracted in EtOAc (10 mL), which was evaporated under reduced pressure. The crude reaction mixture was then subjected to 2D-HSQC NMR analysis (Fig. S1).

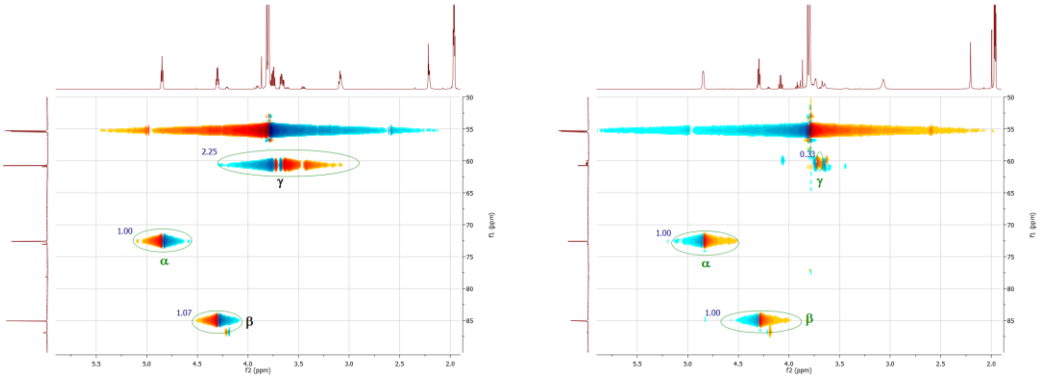
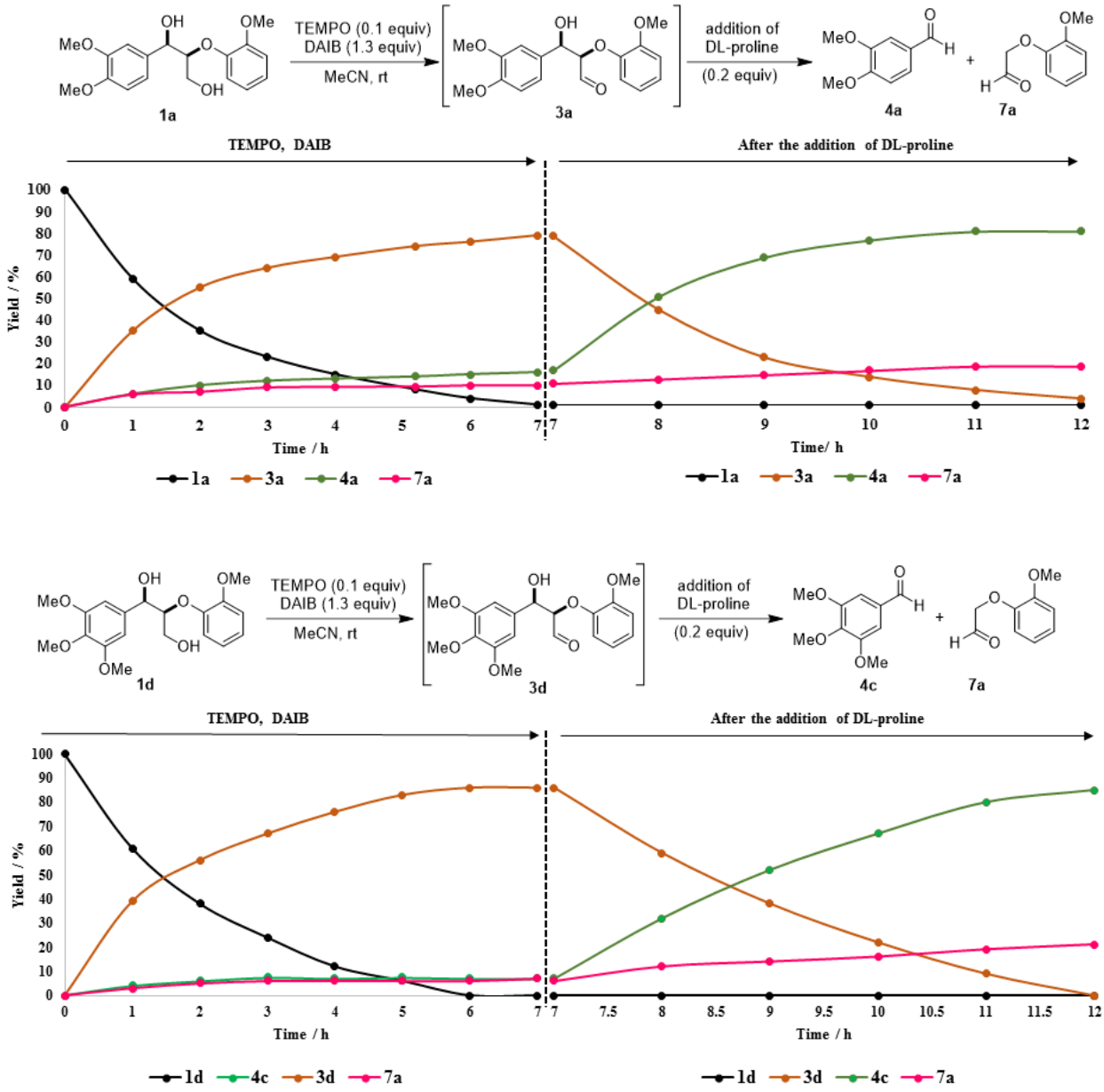


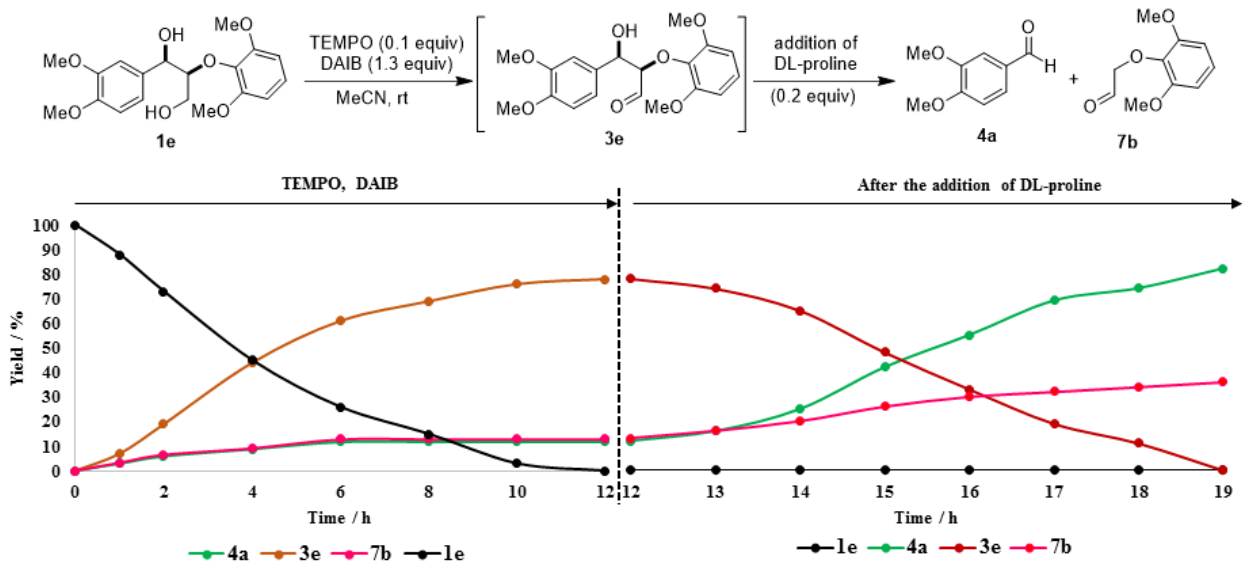
Figure S1. 2D HSQC NMR spectra (zoom of the region 5.4-2.0 ppm recorded in CD_3CN); (a) α,β,γ proton region in **1a** before the reaction (left). (b) α,β,γ proton region in **1a-*D*** after the $NaBD_4$ reduction of the γ alcohol in **3a** (right).

Figure S1b shows the reduction in the integration value for the γ-protons in **1a-*D***, while the integral values corresponding to the α and β protons remained unchanged; similar to **1a**. This confirmed the formation of aldehyde **3a** prior to its reduction with $NaBD_4$.

7. Analysis of the reaction time courses for the one-pot two-step cleavage with model compounds 1a, 1d, and 1e

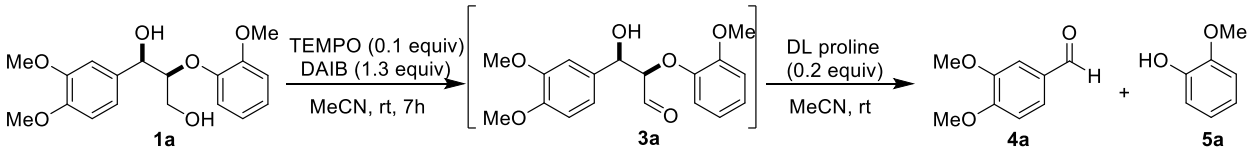
A 10 mL glass tube with a teflon screw cap and a magnetic stirrer was charged with model compound **1** (0.250 mmol, 1.0 equiv), TEMPO (0.1 equiv), DAIB (1.3 equiv) and 1,4-dinitrobenzene (7 mg) as an internal standard in CD_3CN (2.0 mL) and stirred at room temperature while monitoring the progress of the reaction by quantitative ^1H NMR. To this mixture, a requisite amount of the DL-proline (0.2 equiv) was added and the resulting reaction mixture was further monitored overtime. The data from this study are shown below.




TEMPO (0.1 equiv)
DAIB (1.3 equiv)
MeCN, rt
addition of
DL-proline
(0.2 equiv)
1e
3e
4a
7b
TEMPO, DAIB
After the addition of DL-proline
Yield / %
Time / h
Time / h
4a
3e
7b
1e
1e
4a
3e
7b

8. GC-MS analysis of lignin model compounds

8.1. Table S5: Stepwise GC-MS chromatographic analysis of the one-pot two-step oxidative degradation of dilignol (1a).



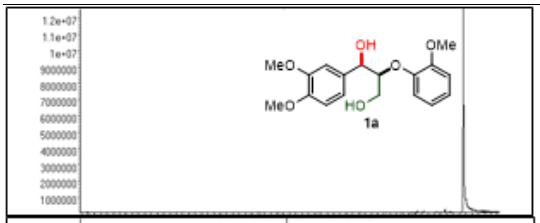
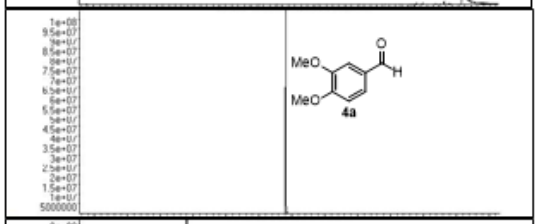
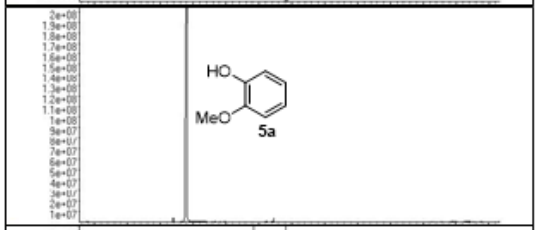
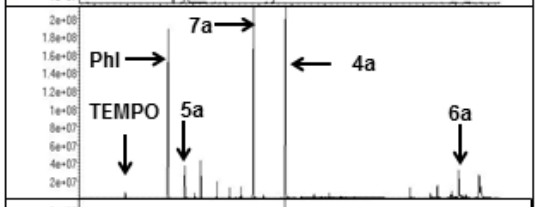
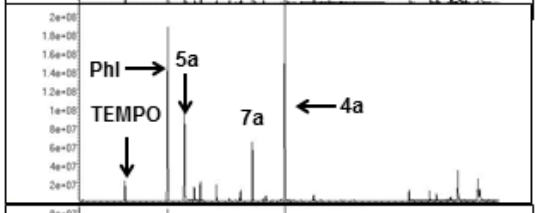
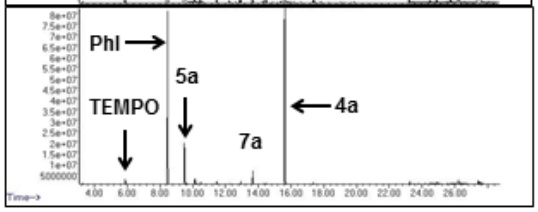
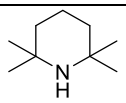
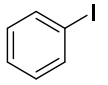
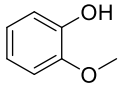
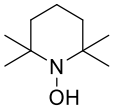
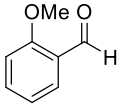
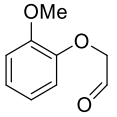
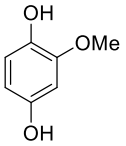
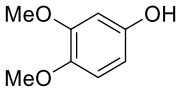
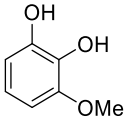
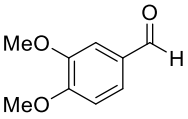
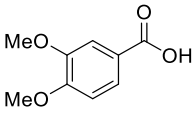
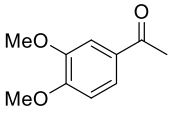
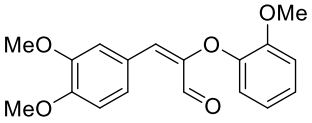
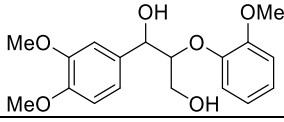
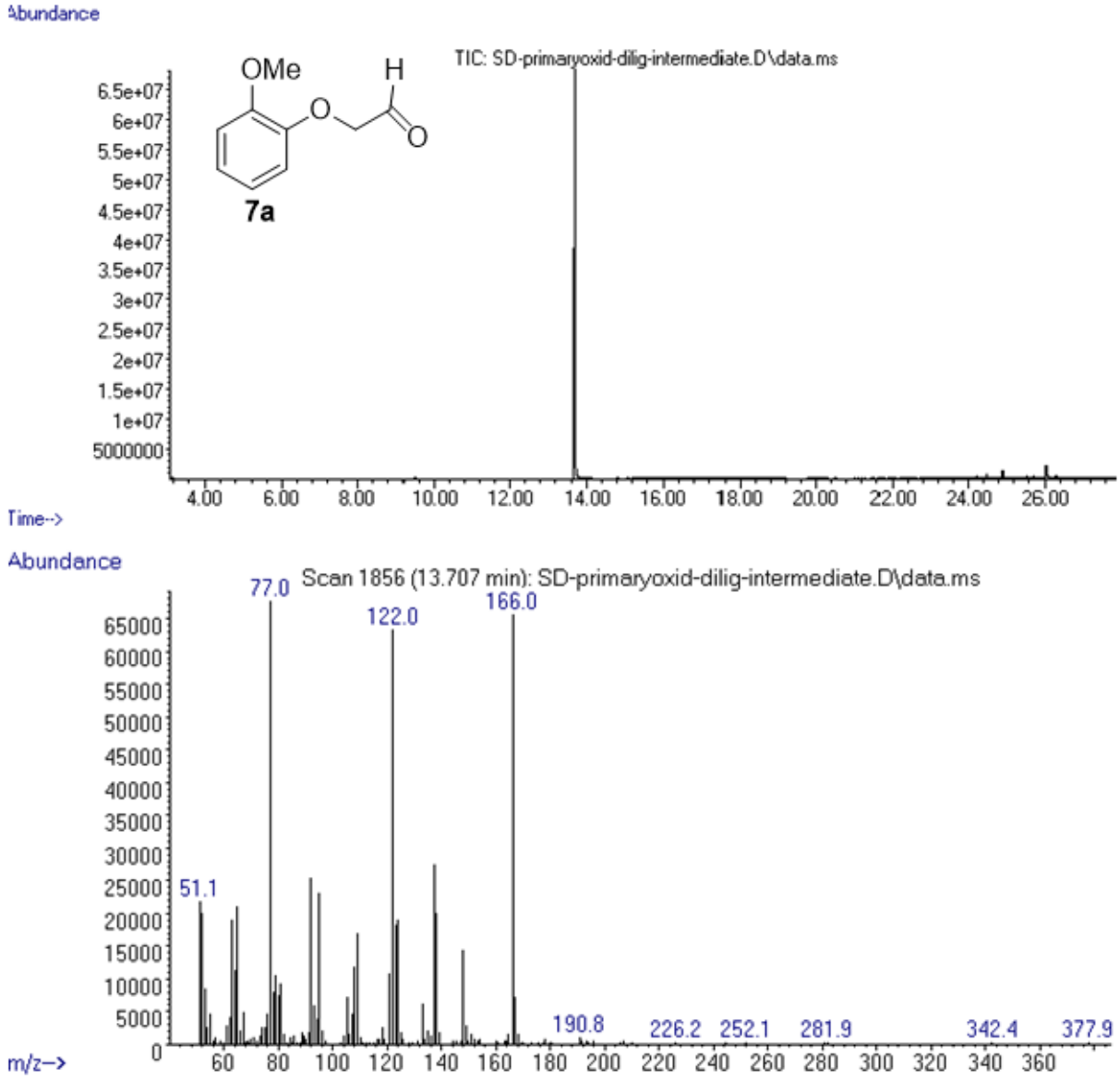
Chromatographic profile	Comments
	**(a)** Dilignol (**1a**); retention time : 27.5 min
	**(b)** Veratraldehyde (**4a**); retention time : 15.6 min
	**(c)** Guaiacol (**5a**); retention time : 9.5 min
	**(d)** Chromatographic profile of the reaction mixture of (**1a**), TEMPO, DAIB after 7 h at rt. (The formation of **3a** was confirmed by ^{1}H NMR and HRMS measurements of the crude reaction mixture. *m/z* calcd. for $C_{18}H_{20}O_6$+Na$^+$: 355.11521 [M+Na$^+$]; found: 355.11520). The intermediate was however unstable under the given GC conditions and cleaved to **7a** and **4a**
	**(e)** Chromatographic profile of the reaction mixture after 3 h of addition of DL-proline to (**d**). Over the course of the reaction, **7a** in the presence of proline gets converted to guaiacol (**5a**).
	**(f)** Chromatographic profile of the reaction mixture after 12 h addition of DL-proline to (**d**)

Table S6: GC-MS peak analysis for the crude reaction mixture after the one-pot two-step oxidative degradation of dilignol (1a).

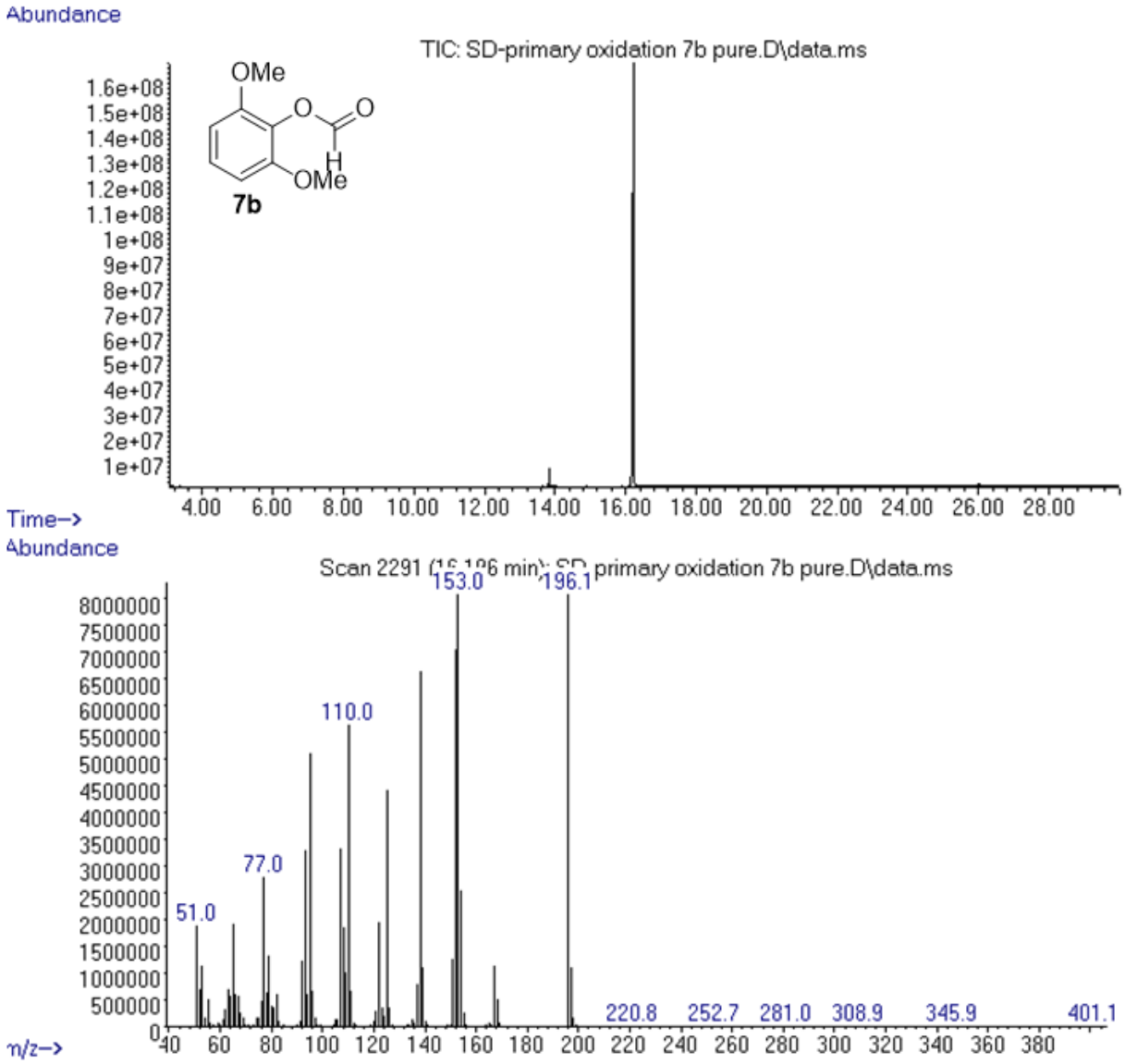
Entry	r.t. (min)	*m*/z	Structure	Database match (%)
1	5.9	141		95
2	8.5	204		96
3	9.5	124		87 sample injected
4	10.5	156		81
5	12.2	136		98
6	13.7	166		sample injected
7	14.5	140		97
8	14.9	154		86
9	15.4	140		83
10	15.6	166		98 sample injected
11	17.4	182		94
12	17.8	180		90
13	26.2	314		sample injected
14	27.5	334		sample injected

8.2. GC quantification of aryloxyacetaldehydes 7a and 7b for model compounds 1a, 1c and 1e after the one-pot, two-step degradation reaction.

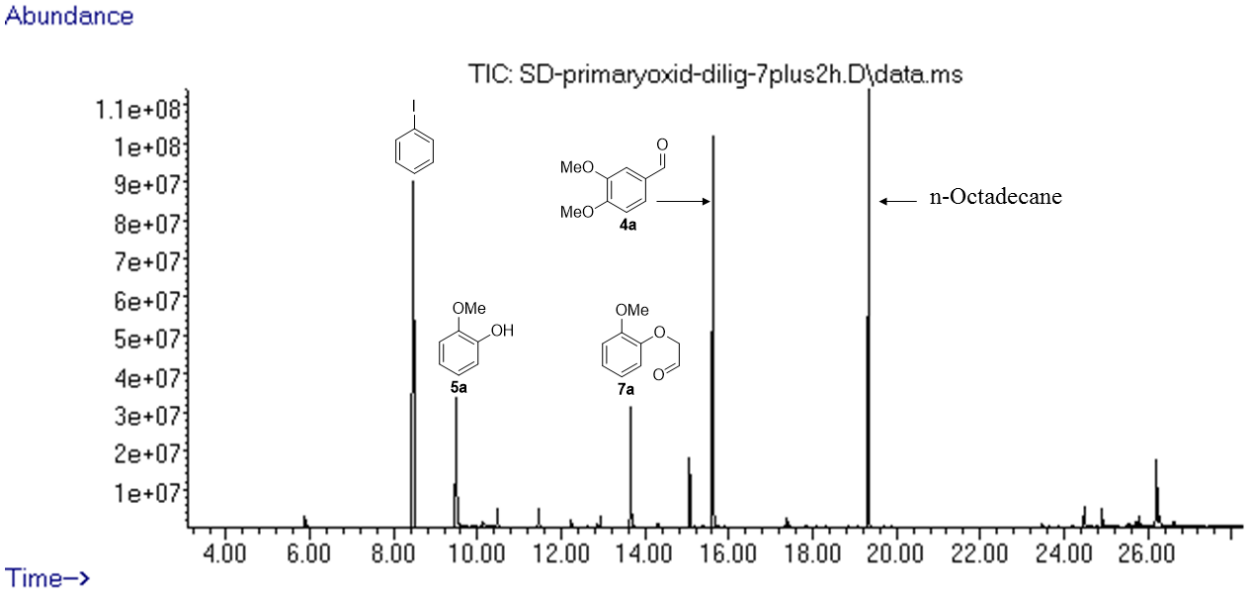
8.2.1 <u>GC-MS for 7a retention time : 13.707 min</u>



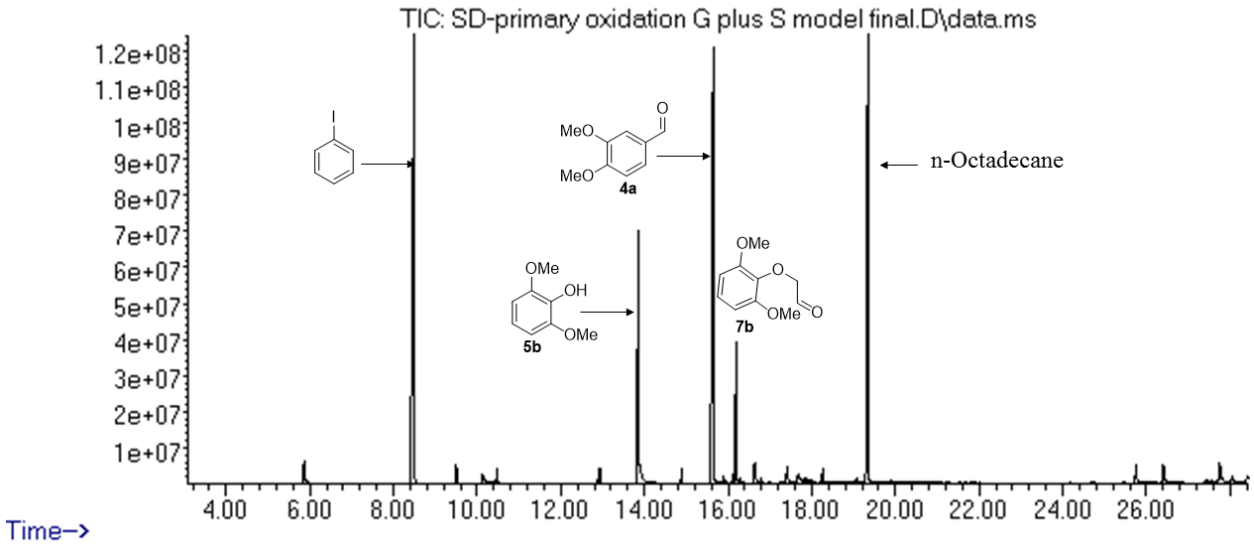
8.2.2 GC-MS for 7b retention time 16.196 min



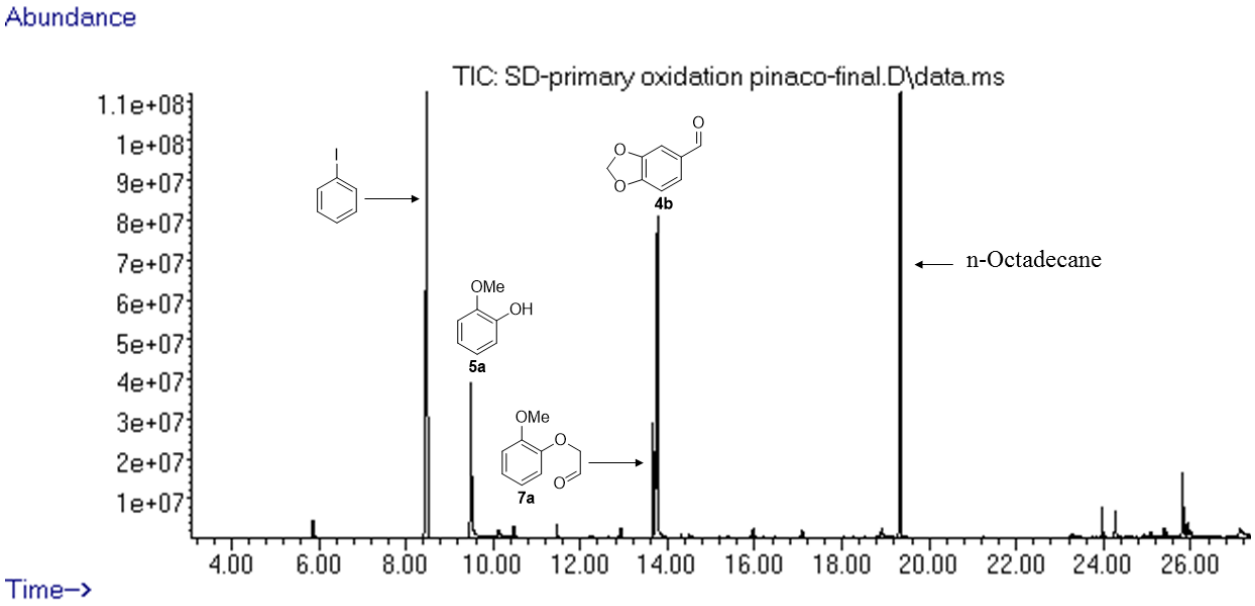
8.2.3 GC-MS chromatogram after the one-pot, two-step degradation of 1a



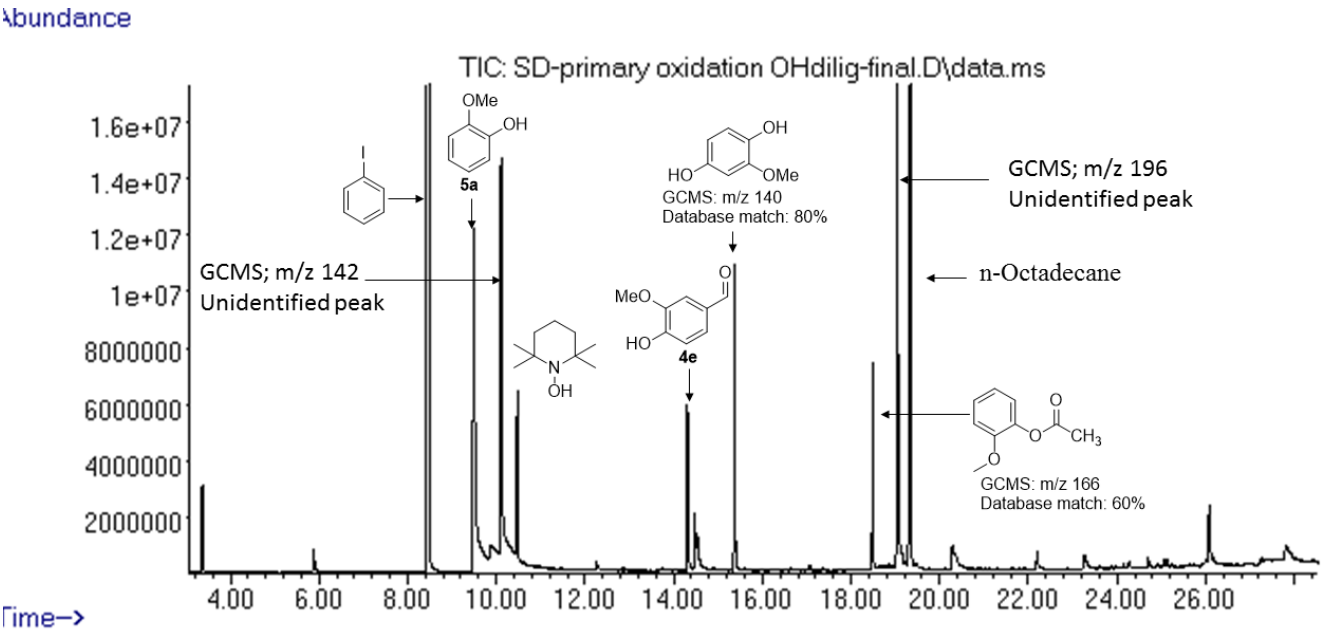
8.2.4 GC-MS chromatogram after the one-pot, two-step degradation of 1e



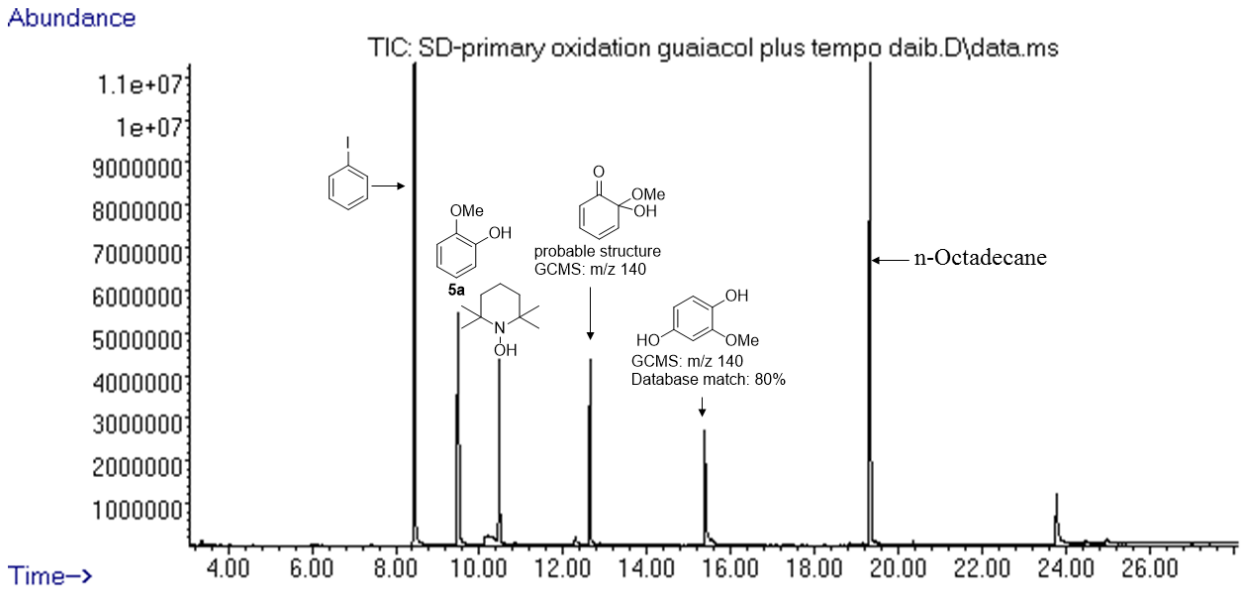
8.2.5 GC-MS chromatogram after the one-pot, two-step degradation of 1c



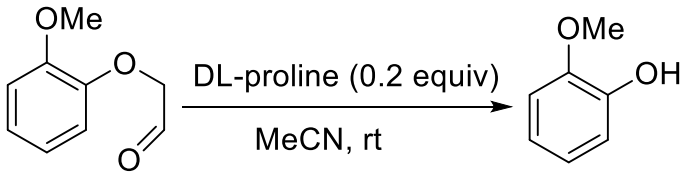
8.2.6 GC-MS chromatogram after the one-pot, two-step degradation of 1f



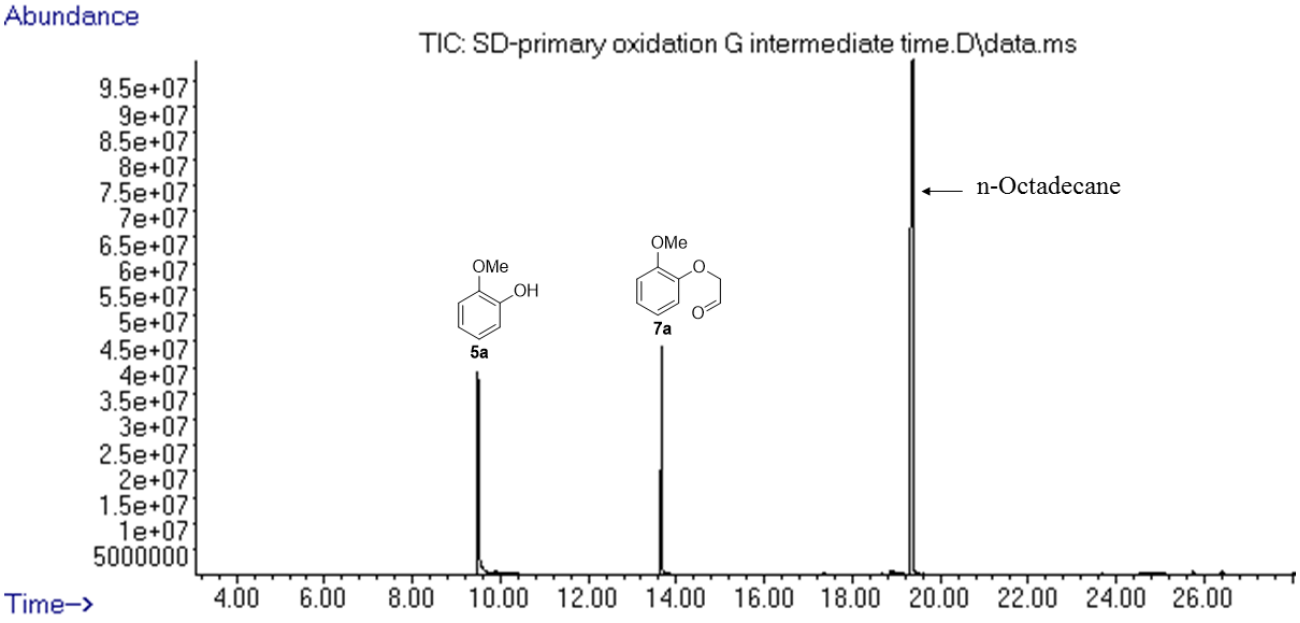
8.2.7 GC-MS chromatogram for the reaction of guaiacol (5a) with TEMPO and DAIB



8.2.8 GC-MS chromatogram for the conversion of aryloxyacetaldehydes (7a) to guaiacol (5a) in the presence of DL-proline

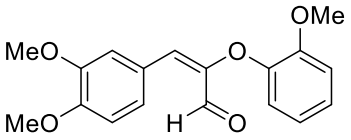


Reaction time / h	Conv. (%) **7a**	Yield (%) **5a**
1	72	69



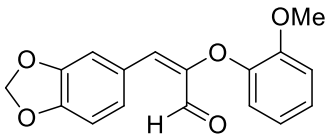
9. Spectroscopic data of the isolated products

(*E*)-3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)acrylaldehyde (6a)



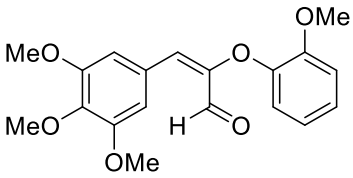
Yellow Solid, M. P. = 101–102 °C. ^{1}H-NMR (600 MHz, CD_3CN): δ = 9.44 (s, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.34 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 7.18 (s, 1H), 7.05 (dd, *J* = 7.8 Hz and 1.2 Hz, 1H), 6.99 (td, *J* =7.8 Hz and 1.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.77 (td, *J* =7.8 Hz and1.2 Hz, 1H), 6.70 (dd, *J* = 7.8 Hz and 1.2 Hz, 1H), 3.88 (s. 3H), 3.82 (s, 3H), 3.67 (s, 3H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 188.7, 152.5, 150.0, 149.8, 148.2, 146.0, 138.4, 126.1, 126.0, 123.8, 121.5, 114.7, 113.7 (2C), 112.4, 56.4, 56.3, 55.9. **IR (ATR):** ν [cm^{-1}] = 2957, 2836, 2322, 2087, 1911, 1590, 1467, 1142, 1022, 933, 750. **MS (EI, 70 eV)**: *m/z* (%) = 316 $[M+2]^+$ (5), 315 $[M+1]^+$ (25), 314 $[M]^+$ (100), 226 (26), 190 (33). **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{18}H_{18}O_5+Na^+$: 337.10464 $[M+Na^+]$; found: 337.10498.

(*E*)-2-(2-Methoxyphenoxy)-3-[3,4-(methylenedioxy)phenyl]acrylaldehyde (6b)



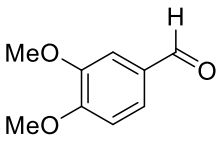
Yellow Solid, M. P. = 105–106 °C. ^{1}H-NMR (600 MHz, CD_3CN): δ = 9.40 (s, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 7.28 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 7.14 (s, 1H), 7.06 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 7.00 (td, *J* = 8.4 Hz and 1.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.78 (td, *J* = 8.4 Hz and 1.8 Hz, 1H), 6.72 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 5.99 (s. 2H), 3.88 (s, 3H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 188.6, 150.8, 150.0, 149.2, 148.5, 145.9, 137.6, 127.6, 124.0, 121.5, 115.3, 113.8, 109.9, 109.5, 103.1 (2C), 56.6. **IR (ATR):** ν [cm^{-1}] = 3466, 2928, 2319, 2088, 1905, 1628, 1458, 1214, 1026, 923, 748. **MS (EI, 70 eV)**: *m/z* (%) = 300 $[M+2]^+$ (2), 299 $[M+1]^+$ (10), 298 $[M]^+$ (38), 211 (85), 135 (75), 77 (100). **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{17}H_{14}O_5+Na^+$: 321.07334 $[M+Na^+]$; found: 321.07370.

(*E*)-2-(2-Methoxyphenoxy)-3-(3,4,5-trimethoxyphenyl)acrylaldehyde (6c)



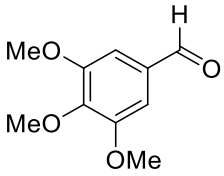
Yellow Solid, M. P. = 118–119 °C. ^{1}H-NMR (600 MHz, CD_3CN): δ = 9.47 (s, 1H), 7.17 (s, 1H), 7.13 (s, 2H), 7.05 (dd, *J* = 8.4 Hz and1.2 Hz, 1H), 6.99 (td, *J* =7.8 Hz and 1.2 Hz, 1H), 6.78 (td, *J* = 7.8 Hz and 1.2 Hz, 1H), 6.69 (dd, *J* =8.4 Hz and 1.2 Hz, 1H), 3.87 (s. 3H), 3.73 (s, 3H), 3.71 (s, 6H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 188.8, 154.2, 149.6, 148.9, 145.8, 141.1, 137.8, 128.7, 123.8 (2C), 121.4, 114.6, 113.5, 108.9 (2C), 60.9, 56.5 (2C), 56.4. **MS (EI, 70 eV)**: *m/z* (%) = 346 $[M+2]^+$ (5), 345 $[M+1]^+$ (25), 344 $[M]^+$ (100), 256 (22), 135 (30). **HRMS (ESI, 70 eV):** *m/z* calcd. for $C_{19}H_{20}O_6+Na^+$: 367.11521 $[M+Na^+]$; found: 367.11557.

3,4-Dimethoxybenzaldehyde (4a)[7]



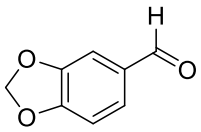
^{1}H-NMR (600 MHz, CD_3CN): δ = 9.82 (s, 1H), 7.49 (dd, *J* = 8.4 Hz and 1.8 Hz, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 3.89, (s, 3H), 3.85(s, 3H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 191.9, 155.5, 150.6, 131.1, 127.1, 111.9, 110.1, 56.6, 56.3. **MS (EI, 70 eV)**: *m/z* (%) = 167 $[M+1]^+$ (15), 166 $[M]^+$ (100), 165 (75), 151 (12), 95 (20), 79 (12), 77 (15), 51 (11).

3,4,5-Trimethoxybenzaldehyde (4c)[8]



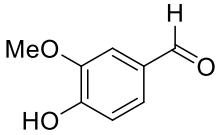
^{1}H-NMR (600 MHz, CD_3CN): δ = 9.84 (s, 1H), 7.18 (s, 2H), 3.88 (s, 6H), 3.81 (s, 3H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 192.3, 154.7 (2C), 144.2, 133.1, 107.5 (2C), 61.0, 56.8 (2C). **MS (EI, 70 eV)**: *m/z* (%) = 197 $[M+1]^+$ (18), 196 $[M]^+$ (100), 181 (35), 125 (90), 110 (53).

Benzo[*d*][1,3]dioxole-5-carbaldehyde (4b)[9]



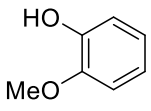
^{1}H-NMR (400 MHz, CD_3CN): δ = 9.77 (s, 1H), 7.45 (dd, *J* = 12 Hz and 2.4 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 12 Hz, 1H) 6.07 (s, 2H). **^{13}C-NMR (101 MHz, CD_3CN):** δ = 191.4, 154.0, 149.7, 132.9, 129.4, 109.2, 107.0, 103.5. **MS (EI, 70 eV)**: *m/z* (%) =151 $[M+1]^+$ (15), 150 $[M]^+$ (100), 149 (90), 121 (34), 64.4 (37).

4-Hydroxy-3-methoxybenzaldehyde (4d)[10]



^{1}H-NMR (600 MHz, CD_3CN): δ = 9.79 (s, 1H), 7.44–7.41 (m, 2H), 7.36 (br.s, 1H), 7.00–6.96 (m, 1H), 3.91, (s, 3H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 191.8, 153.1, 148.8, 130.9, 127.2, 115.7, 110.9, 56.7. **MS (EI, 70 eV)**: *m/z* (%) = 153 $[M+1]^+$ (93), 152 $[M]^+$ (100), 109 (18), 81 (35), 53 (22).

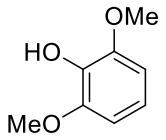
2-Methoxyphenol (5a)[7]



^{1}H-NMR (600 MHz, CD_3CN): δ = 6.95–6.91 (m, 1H), 6.85–6.80 (m, 3H), 6.49 (br.s, 1H), 3.84, (s, 3H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 148.2, 147.0, 122.1, 120.9, 115.7, 112.6, 56.5. **MS (EI, 70 eV)**: *m/z* (%) = 125 $[M+1]^+$ (76), 124 $[M]^+$ (100), 123 (10), 109 (13), 81 (14).

2,6-Dimethoxyphenol (5b)[7]

^{1}H-NMR (600 MHz, CD_3CN): δ = 6.76 (t, 1H), 6.62 (s, 1H), 6.60 (s, 1H), 6.19 (br.s, 1H), 3.81 (s, 6H). **^{13}C-NMR (151 MHz, CD_3CN):** δ = 148.7 (2C), 136.3, 119.8, 106.4 (2C), 56.8 (2C). **MS (EI, 70 eV)**: *m/z* (%) = 155 $[M+1]^+$ (20), 154 $[M^+]$ (100), 139 (27), 111 (22), 96 (15).



10. Selected NMR spectra

Figure S2. *erythro* 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propandiol (**1a**)

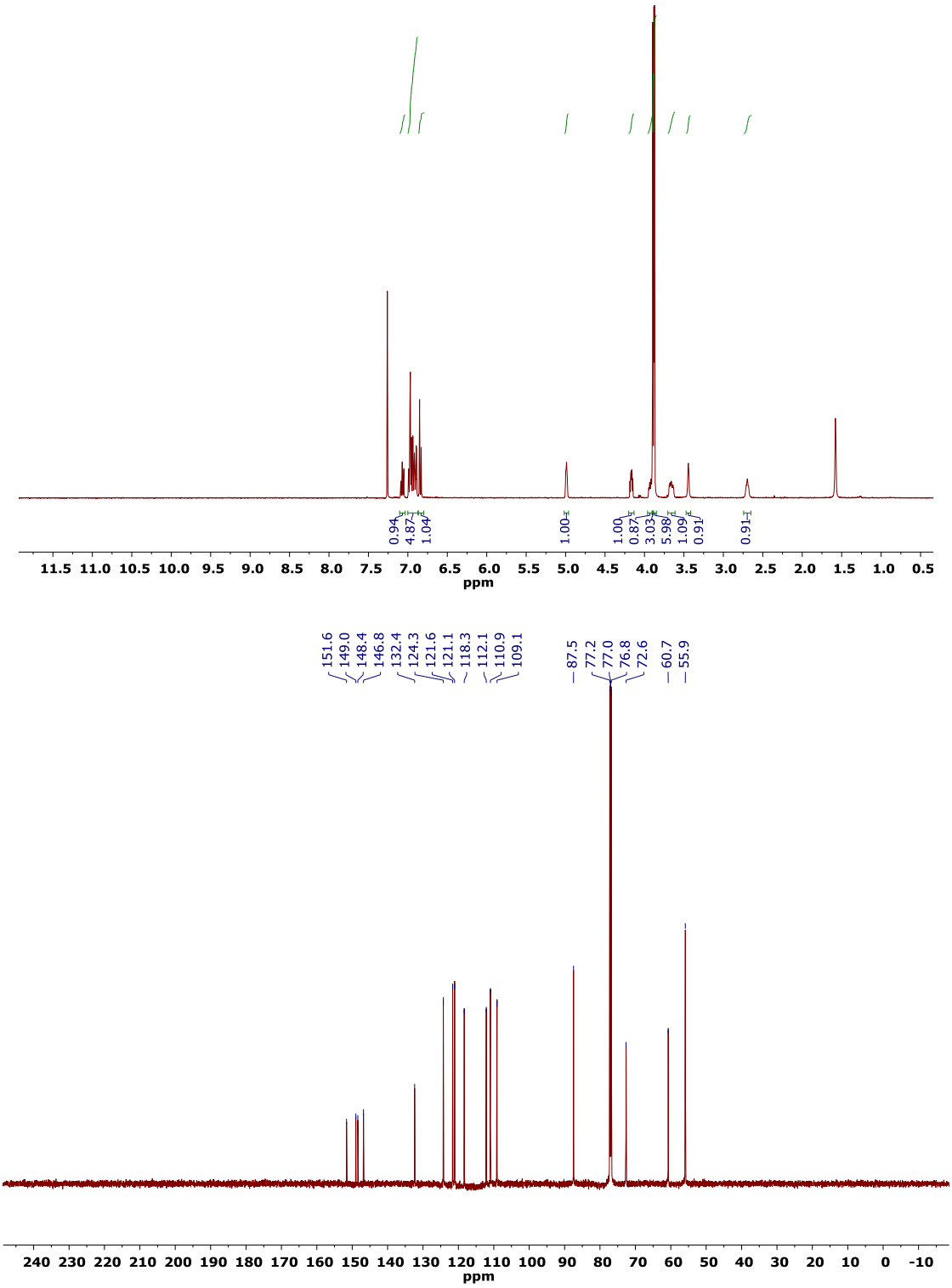
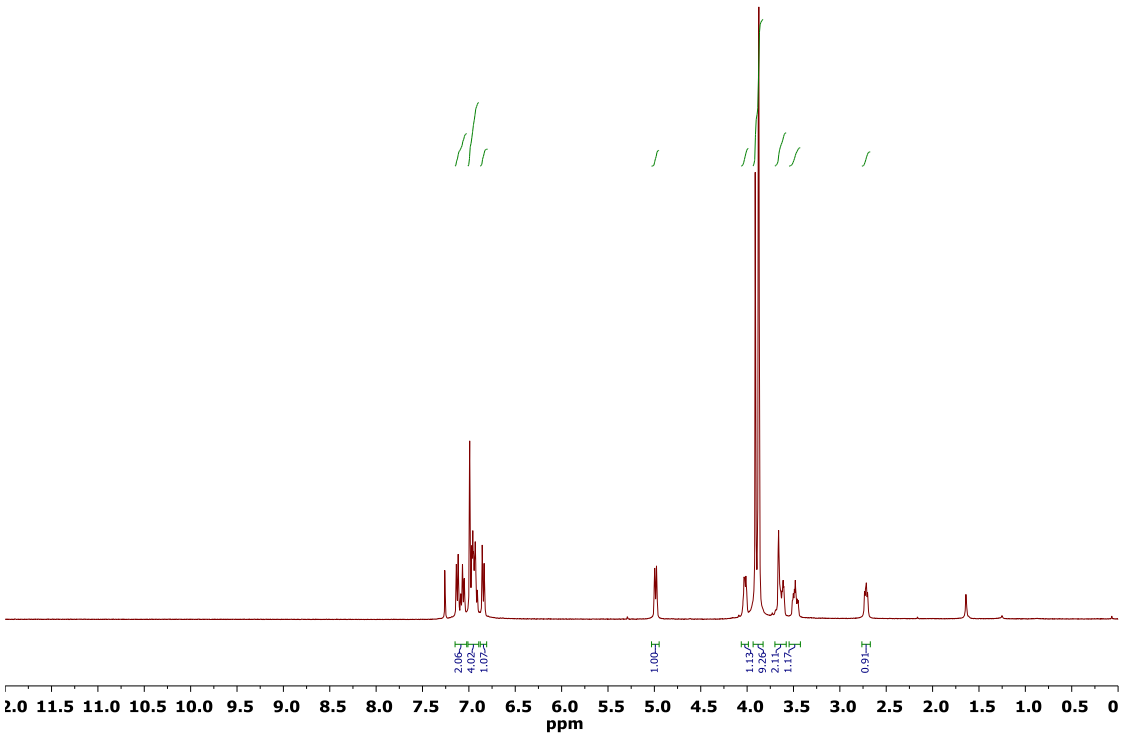


Figure S3. *threo* 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propandiol (**1b**)



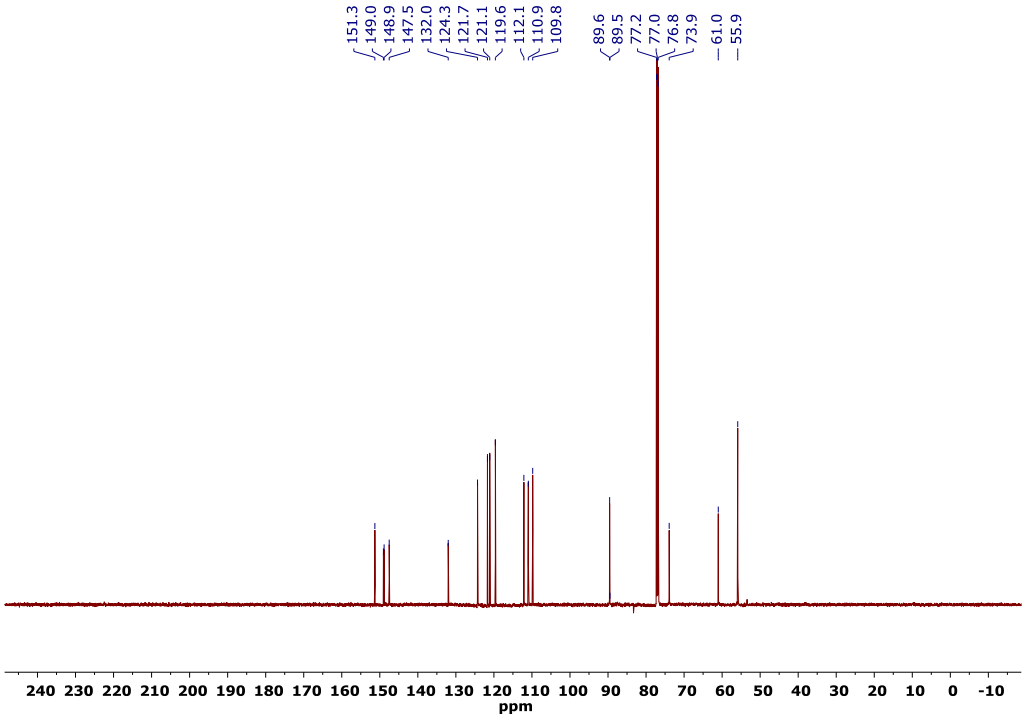


Figure S4. *erythro*-2-(2-Methoxyphenoxy)-1-[3,4-(methylenedioxy)phenyl]-l,3-propanediol **(1c**)

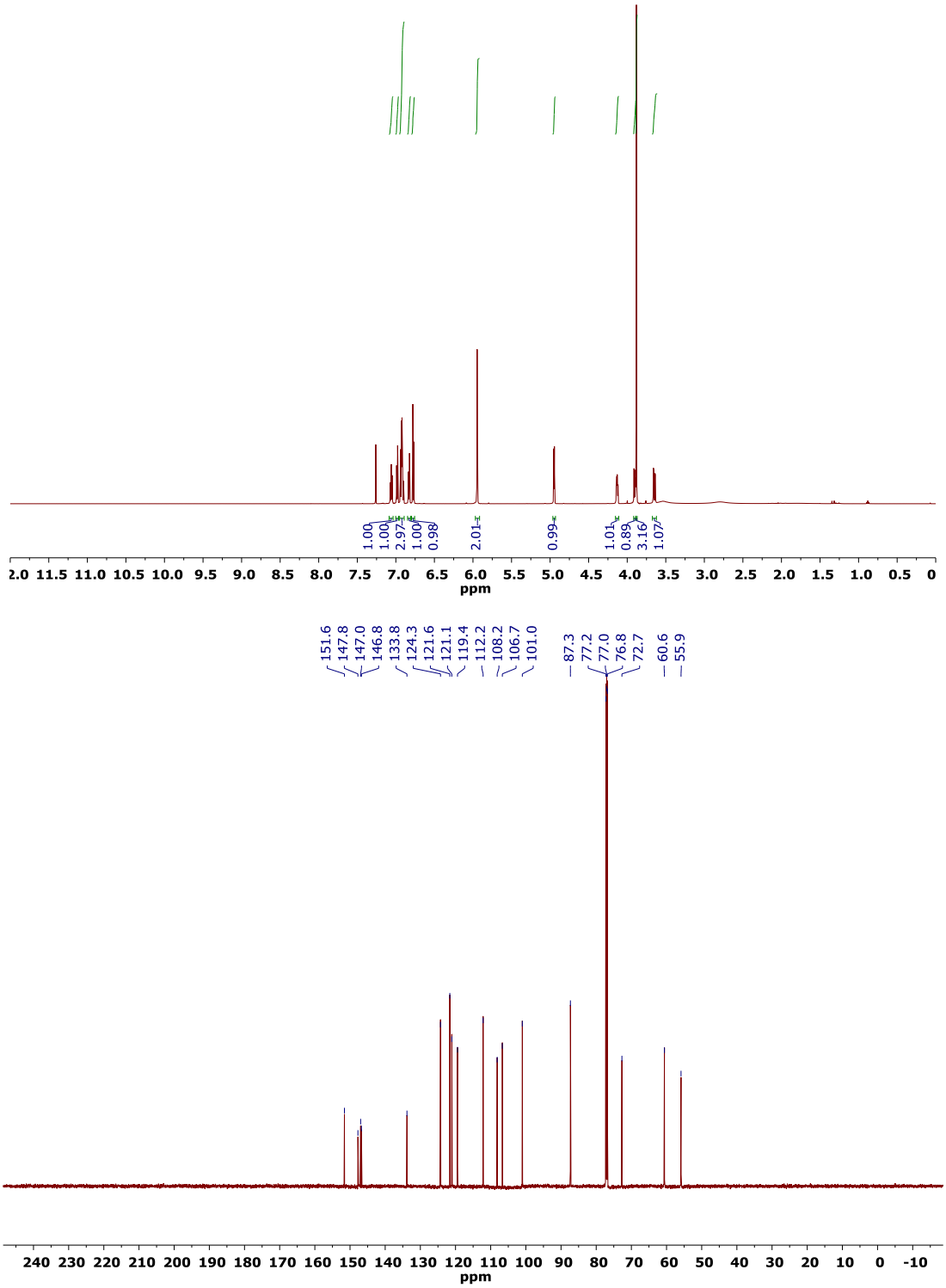


Figure S5. 2-(2-Methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)-1,3-propanediol (**1d)**

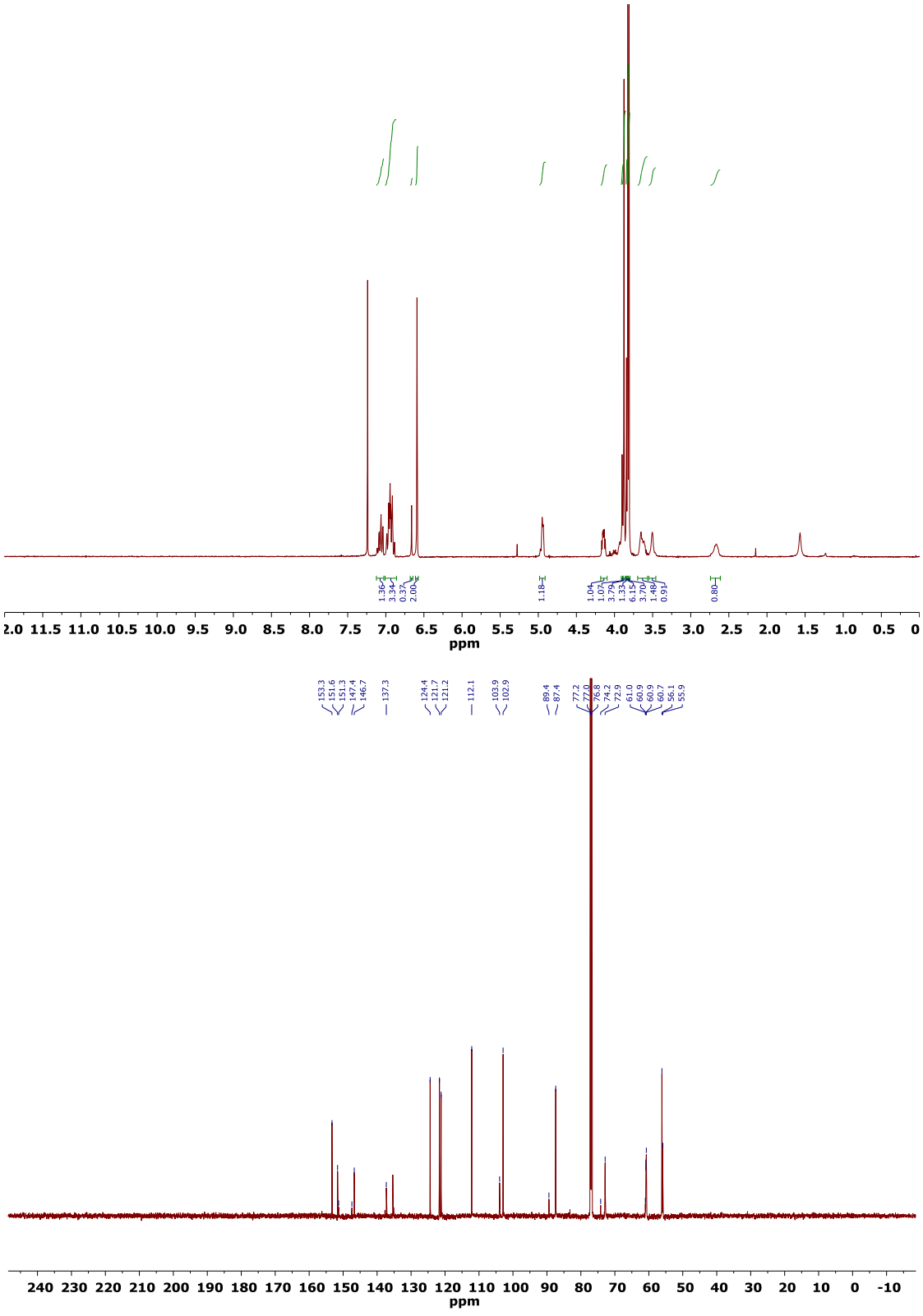


Figure S6. 2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)-1,3-propandiol (**1e**)

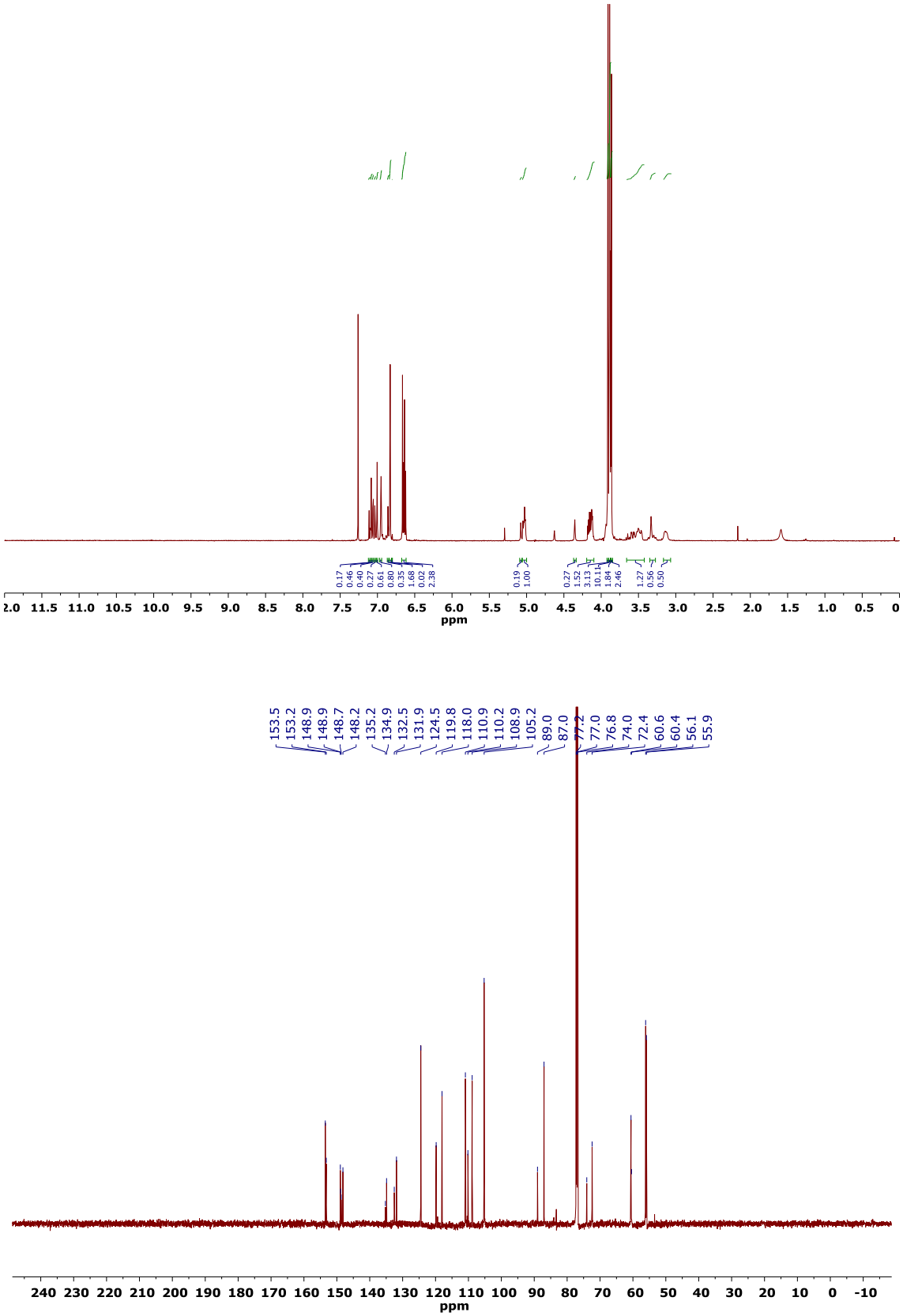


Figure S7. *threo* 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1f**)

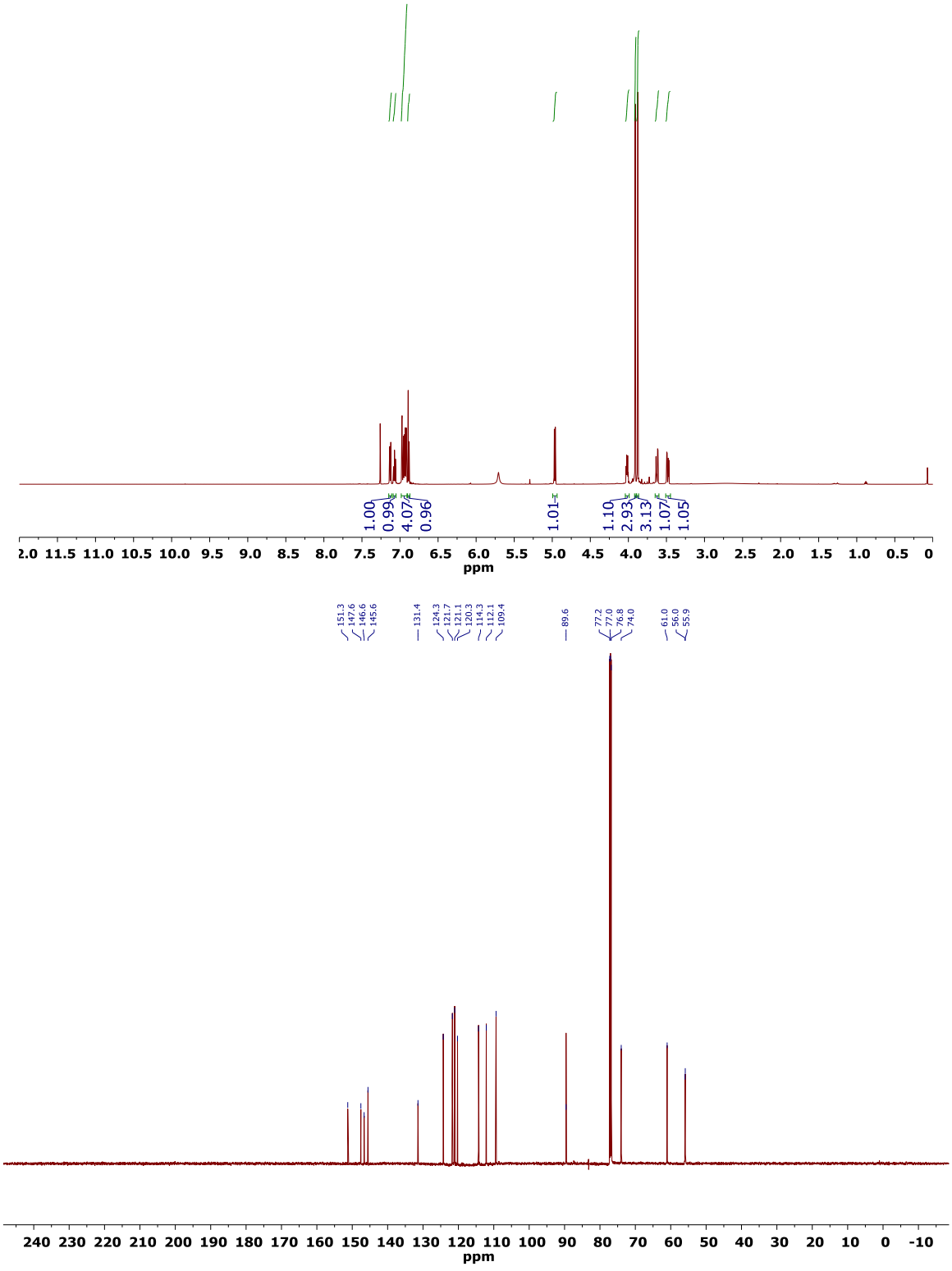
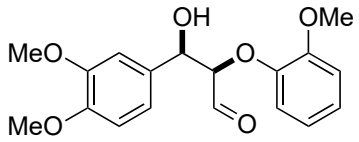
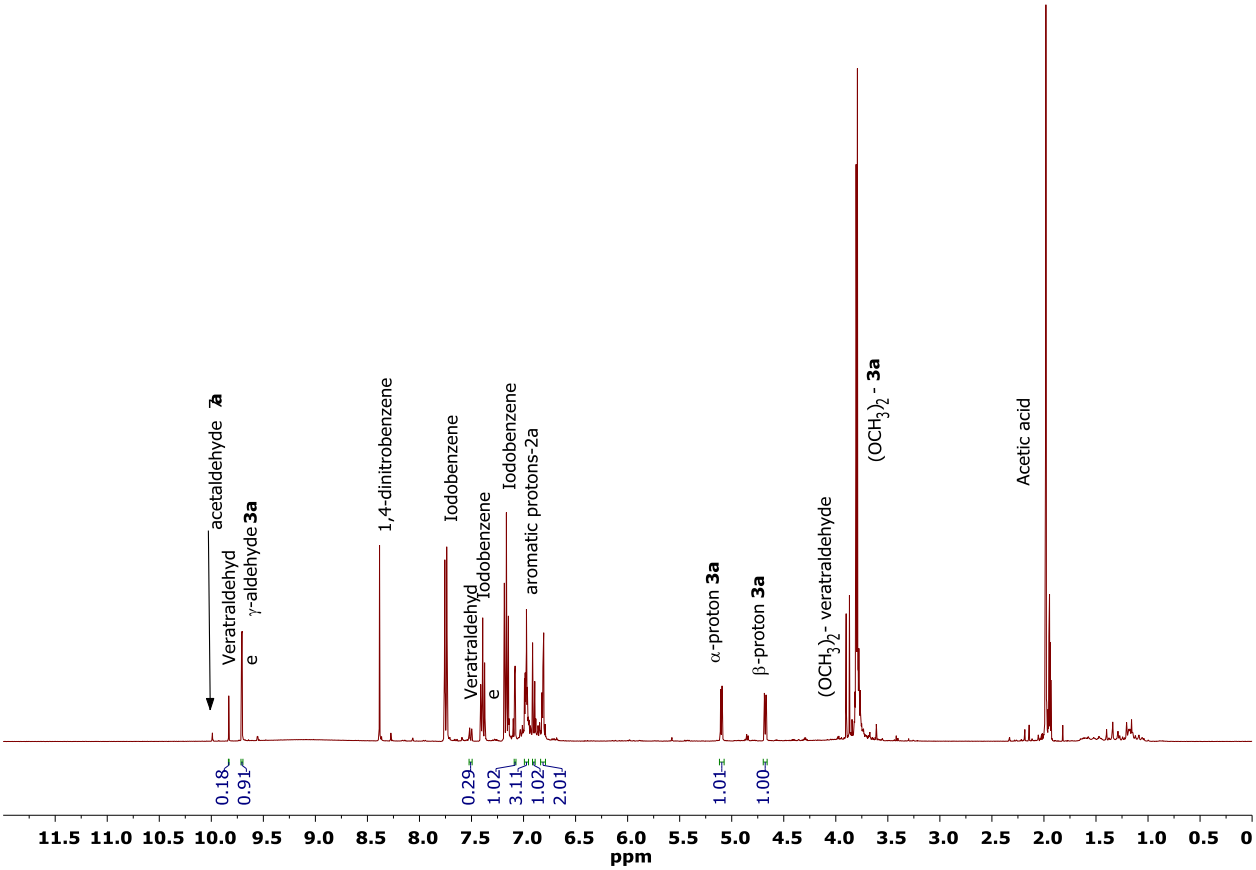


Figure S8. ^{1}H NMR spectrum for the oxidation of **1a** to **3a** with TEMPO/DAIB.



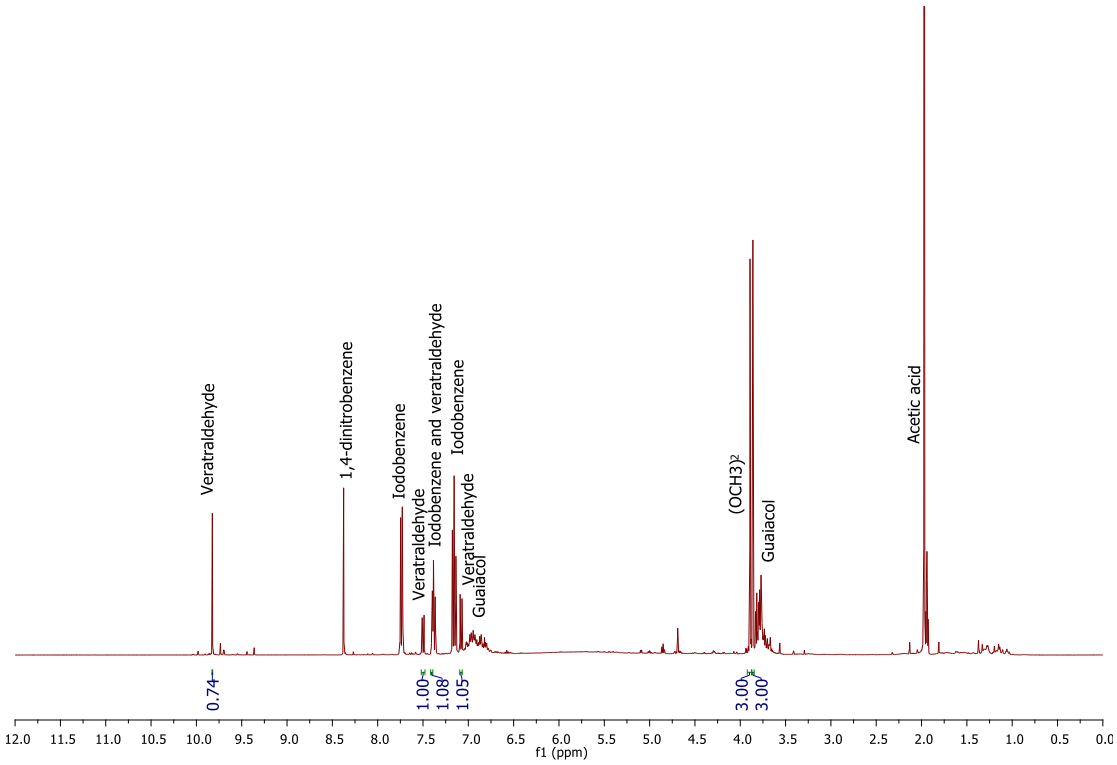
3a



The ^{1}H-NMR spectrum shows the presence of the aldehyde **3a** (major product), veratraldehyde (**4a**), internal standard (1,4-dinitrobenzene) and iodobenzene. The starting **1a** was fully consumed as the peaks corresponding to the α,β protons in **1a** at 4.82 ppm and 4.27 ppm disappeared. A new set of peaks at 5.10 ppm and 4.67 ppm was observed corresponding to the α,β protons for the aldehyde **3a**. Additionally, the formation of **3a** was also confirmed by HRMS measurements of the crude reaction mixture.

HRMS (ESI, 70 eV): *m/z* calcd. for $C_{18}H_{20}O_6$+Na^+ : 355.11521 [M+Na^+]; found: 355.11520.

Figure S9. Top: ^{1}H NMR spectrum of the reaction mixture after the one-pot oxidation, retro-aldol cleavage of **1a**. Bottom: ^{1}H NMR spectrum of veratraldehyde (**4a**).


Veratraldehyde
1,4-dinitrobenzene
Iodobenzene
Veratraldehyde
Iodobenzene and veratraldehyde
Iodobenzene
Veratraldehyde
Guaiacol
(OCH3)2
Guaiacol
Acetic acid
0.74
1.00
1.08
1.05
3.00
3.00
f1 (ppm)

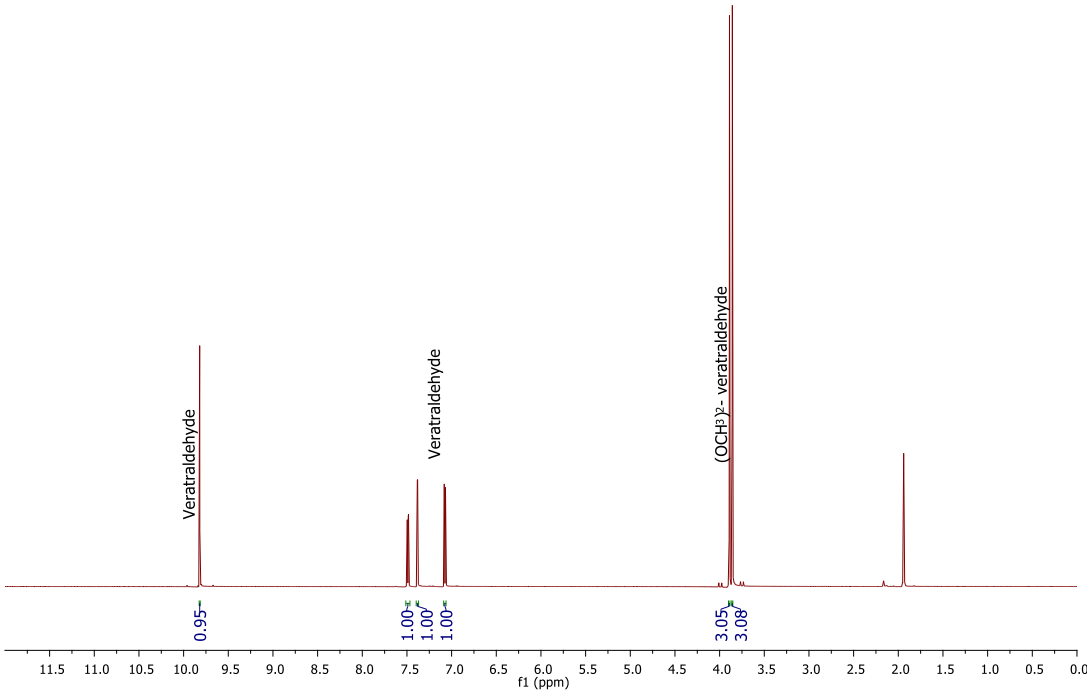
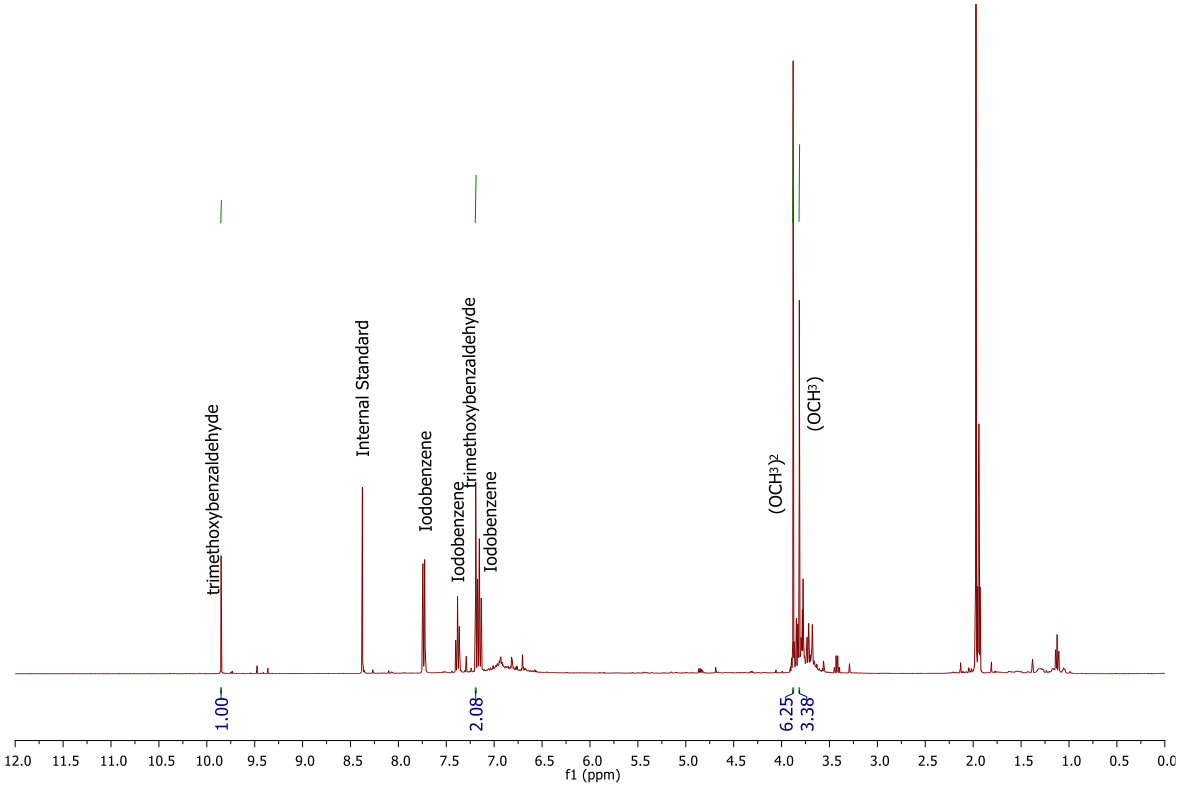

Veratraldehyde
Veratraldehyde
(OCH3)2- veratraldehyde
0.95
1.00
1.00
1.00
3.05
3.08
f1 (ppm)

Figure S10. Top: ^{1}H NMR spectrum of the reaction mixture after the one-pot oxidation, retro-aldol cleavage of **1d**. Bottom: ^{1}H NMR spectrum of 3,4,5-trimethoxybenzaldehyde (**4c**).



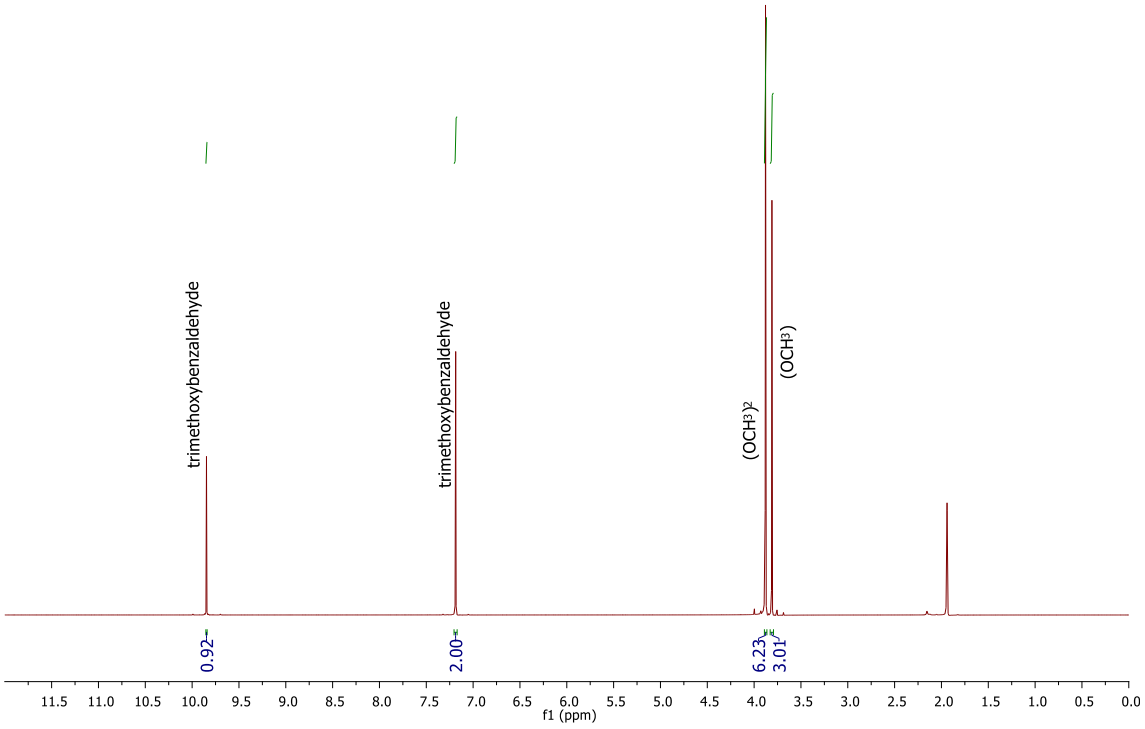


Figure S11. **^{1}H and ^{13}C NMR spectra for (*E*)-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) acryaldehyde (6a)**

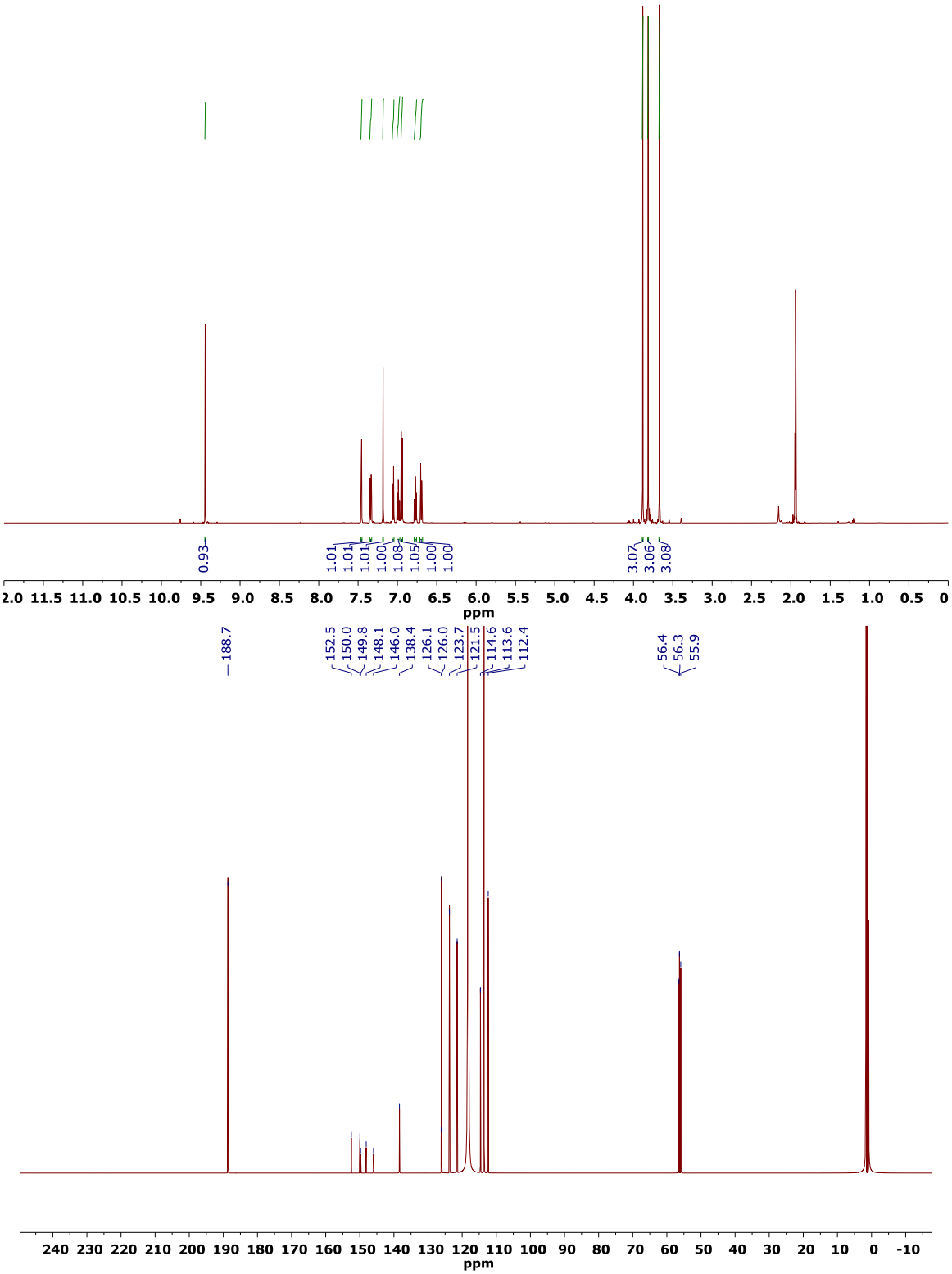


Figure S12. **^{1}H and ^{13}C NMR spectra for (*E*)-2-(2-methoxyphenoxy)-3-[3,4-(methylenedioxy)phenyl] acrylaldehyde (6b)**

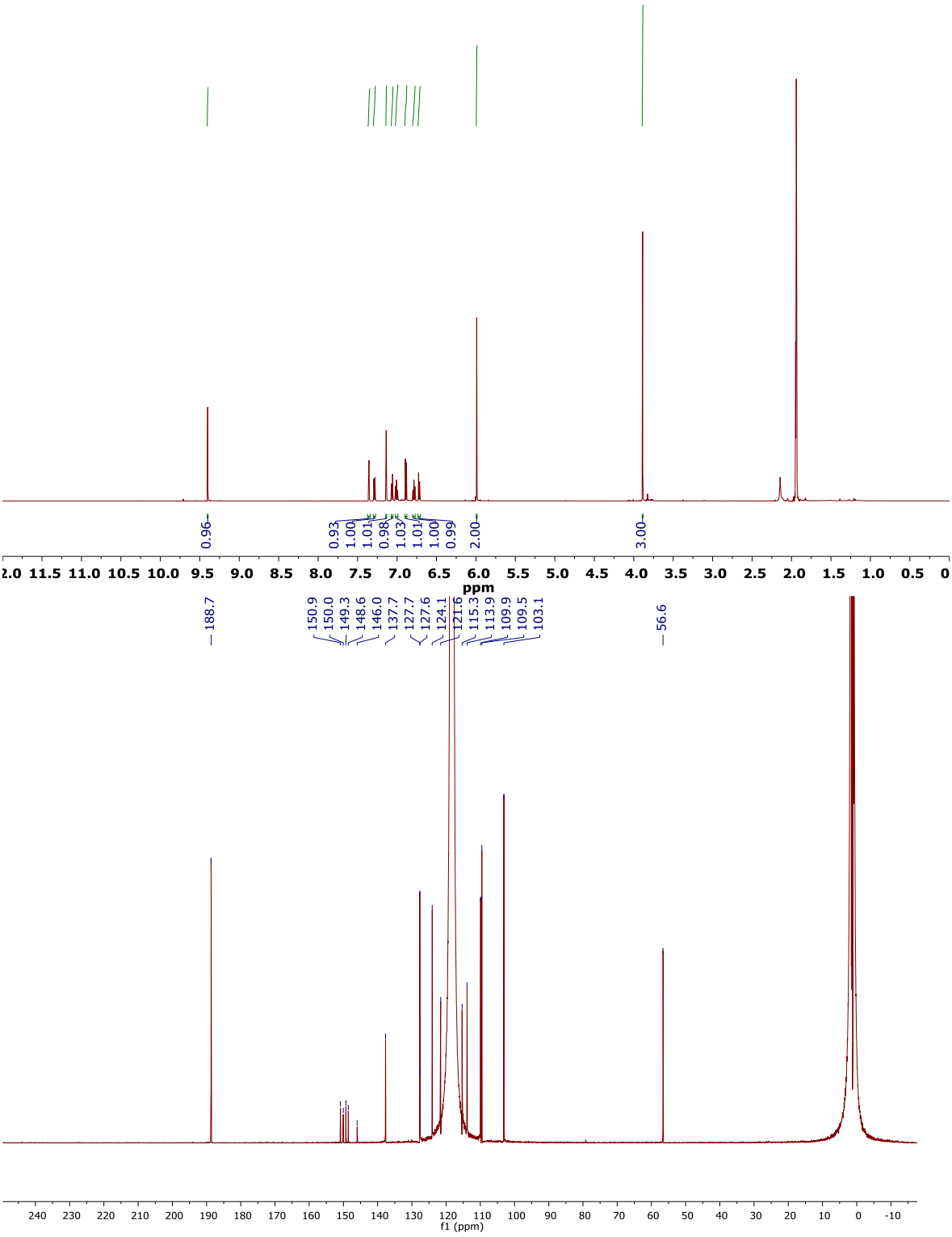
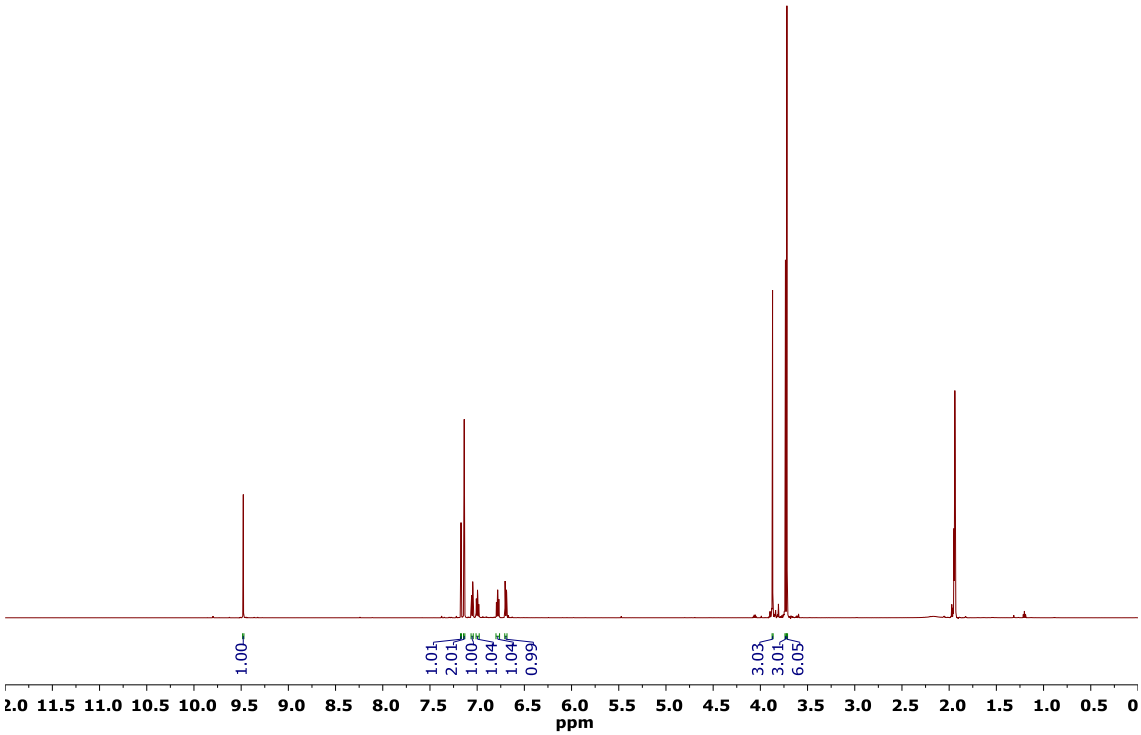


Figure S13. **^{1}H and ^{13}C NMR spectra for (*E*)-2-(2-methoxyphenoxy)-3-(3,4,5-trimethoxyphenyl) acrylaldehyde (6c)**



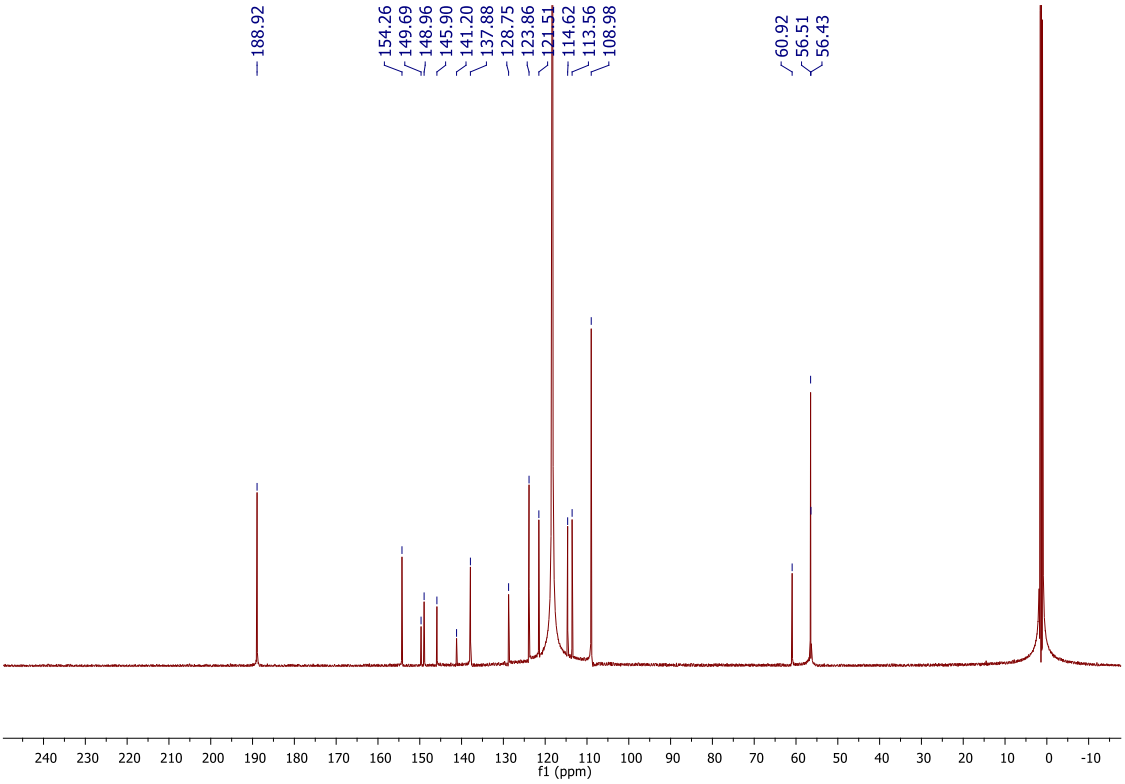


Figure S14. **^{1}H and ^{13}C NMR spectra for 2-(2-methoxyphenoxy)acetaldehyde (7a)**

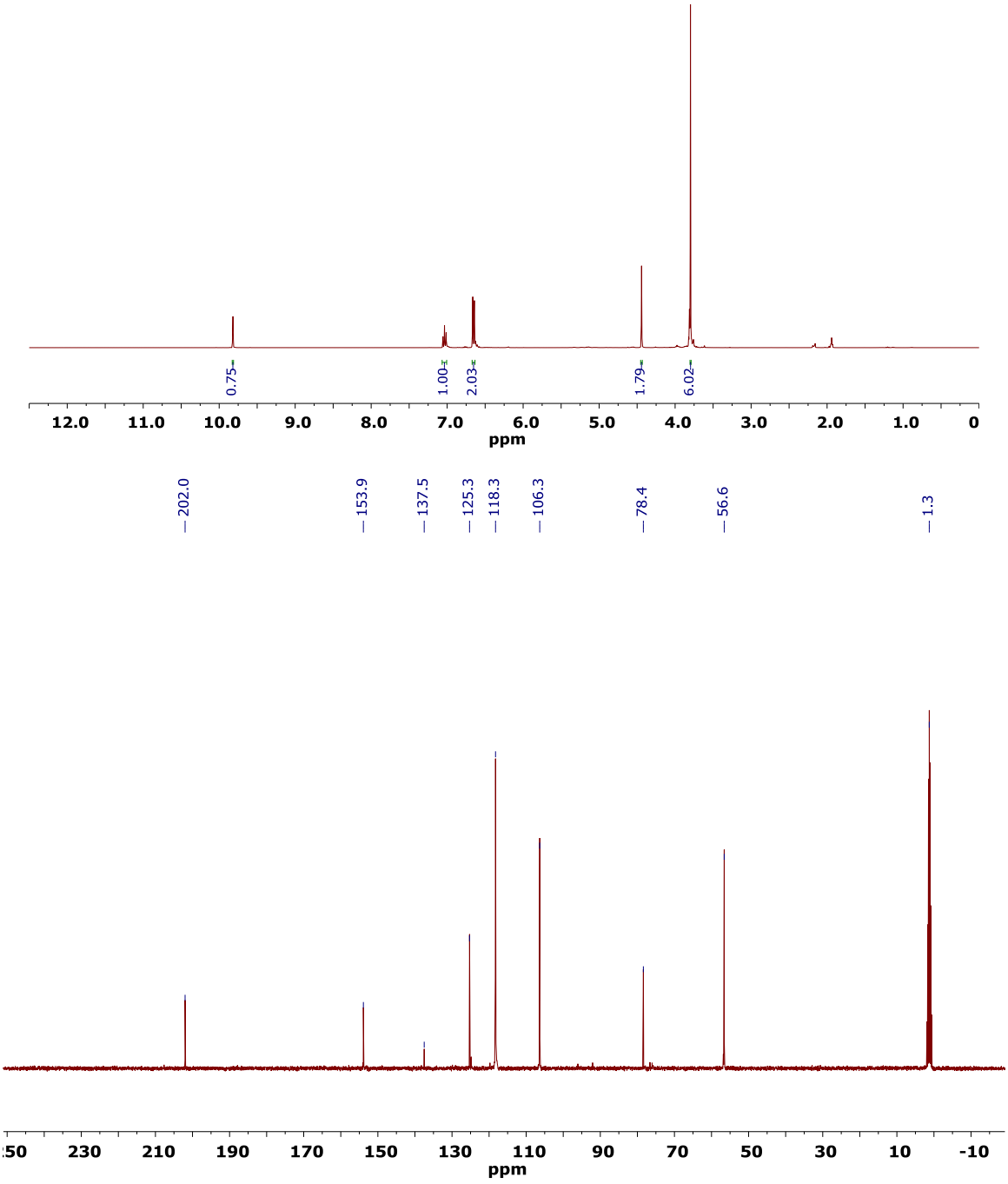
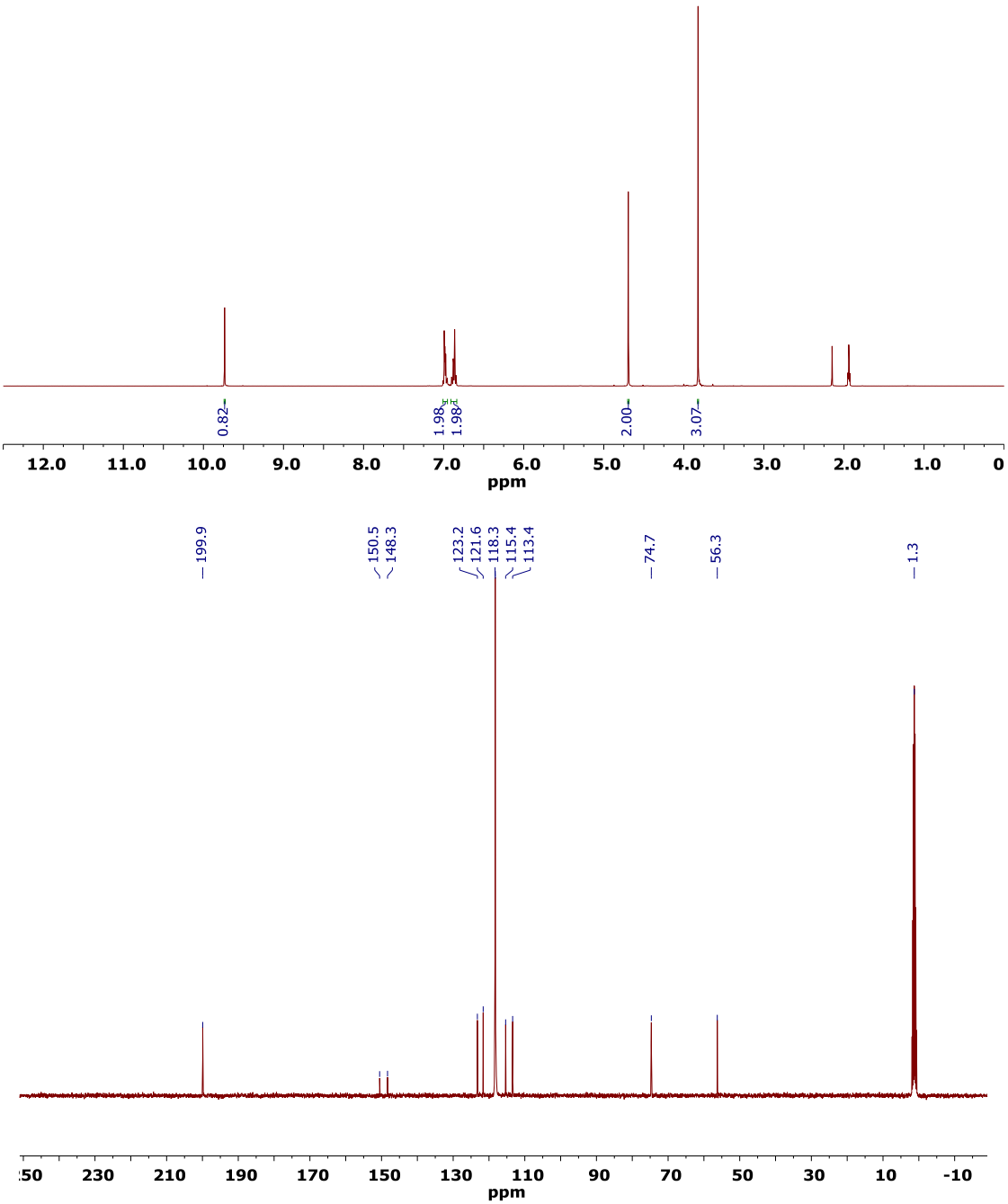


Figure S15. **^{1}H and ^{13}C NMR spectra for 2-(2,6-dimethoxyphenoxy)acetaldehyde (7b)**



11. Pretreatment conditions of the lignin source L1 and its characterization.

Organosolv lignin **L1** was extracted from beechwood chips using an ethanol-based organosolv process: The sample was extracted with aqueous ethanol (50% w/w) without the addition of an acid catalyst. The lignin was precipitated with water and afterwards washed with water to remove the residual carbohydrates. Detailed characterization of **L1** have been described below.

11.1 Lignin Profiling:

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

The organosolv beechwood, lignin was characterized using 2D-HSQC experiments (**Figure S16**) following previously published report.[11] 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 (Table S7).

Table S7. Characterization of lignin L1 by GPC and 2D-HSQC NMR.

Lignin Source	M_n (Da), M_w (Da), Đ [a]	S, G, H (%)[b]	Linkages (per 100 C 9 units)[b]			
			β-O-4-OH[c]	β-O-4-OR[d]	β-5	β–β
OS-BW	3317, 6618, 1.9	73, 27, 0	20	4	3.2	4.1

[a] Determined by GPC using RI detector with respect to polystyrene standards. [b] Determined by 2D-HSQC NMR by comparing the aliphatic and aromatic signal intensities. [c] Amounts of β-O-4 linkages with free α-OH. [d] Amounts of β-O-4 linkages with capped α-OH units.

Quantification Results:

Figure *S*16: These calculations revealed that for ethanosolv beechwood lignin, the β-O-4 content was 24 per 100 aromatic units and an H:G:S ratio of 73:27:0 (Table S7). 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 for comparative studies and not as exact values.

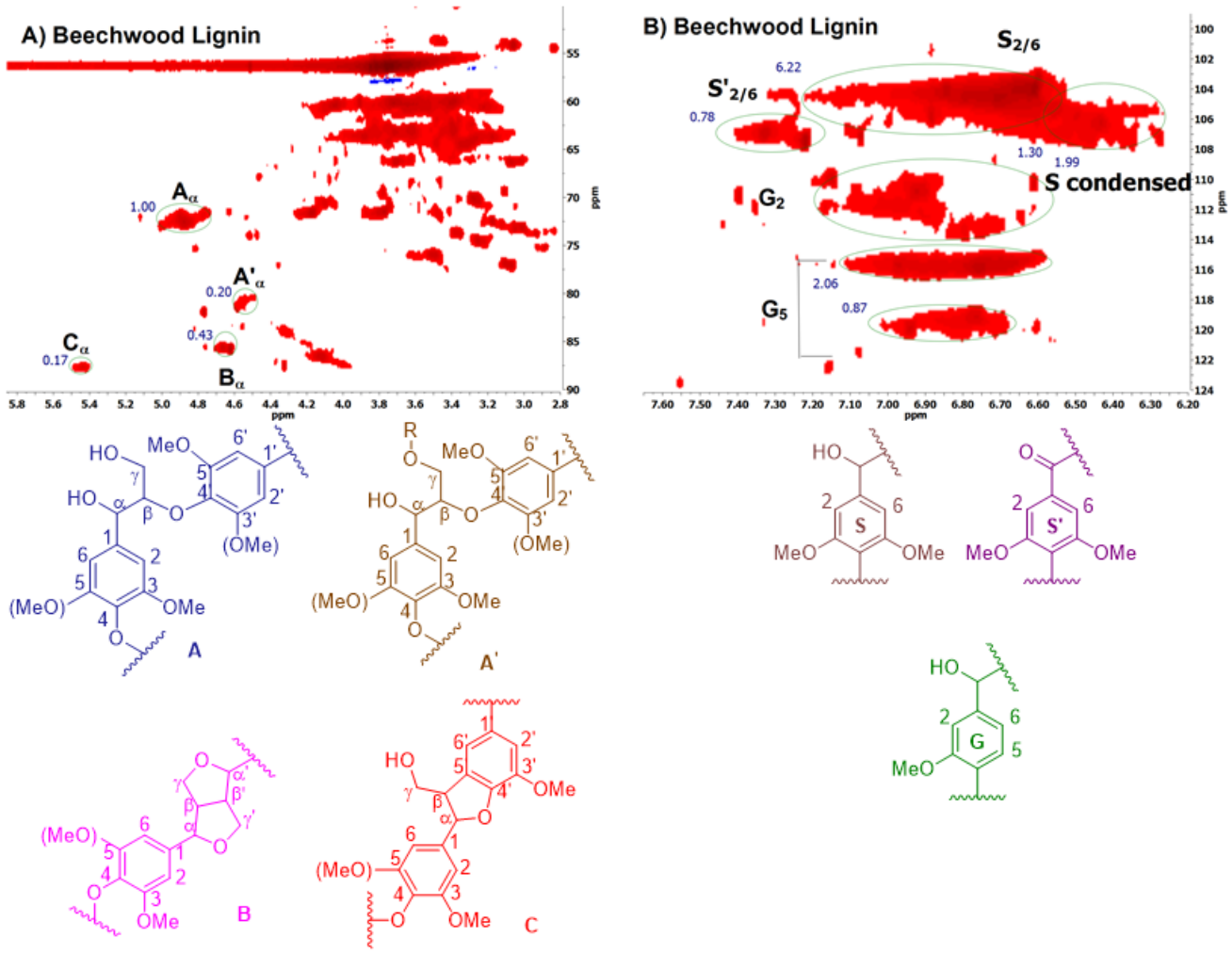


Figure S16: 2 D-HSQC NMR spectra of lignins: A) Region from ppm 2.5-6.0, 90-50; B) Region from ppm 7.2-7.6, 124-100.

12. One-pot two-step chemoselective oxidation followed by DL-proline catalysed degradation of lignin samples L1

12.1. General procedure

A 20 mL glass tube with a teflon screw cap and a magnetic stirrer was charged with organosolv lignin **L1** (200 mg), TEMPO (0.1 equiv), DAIB (1.3 equiv) in acetonitrile (4 mL) and stirred at rt for 12 h. Then, DL-proline (0.2 equiv) was added and the reaction mixture was further stirred at rt for 12 h. Subsequently, the reaction mixture was transferred into a 25 mL round bottom flask, and acetonitrile was removed under reduced pressure. Next, the residue was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) and filtered into an NMR tube or dried overnight under vacuum prior to GPC analysis. In case of GC-MS analysis the residue after removing acetonitrile was extracted with DCM, which was again reduced under pressure. The resulting oil was dissolved in acetone along with the addition of 0.1 mL of 0.05 M *n*-octadecane as an internal standard.

NOTE: The loadings for TEMPO, DAIB and DL-proline were calculated by dividing the mass of the lignin sample **L1** by the molar mass of **1a** to estimate the amount of diol fragments.

***Figure S17*:** A typical lignin reaction in a glass tube reactor showing the solubility of lignin in acetonitrile.

12.2. GC-MS analysis of the lignin oil

***Figure S18*. Complete chromatogram of the DCM soluble fraction of the beechwood lignin post one-pot two-step oxidative degradation.**

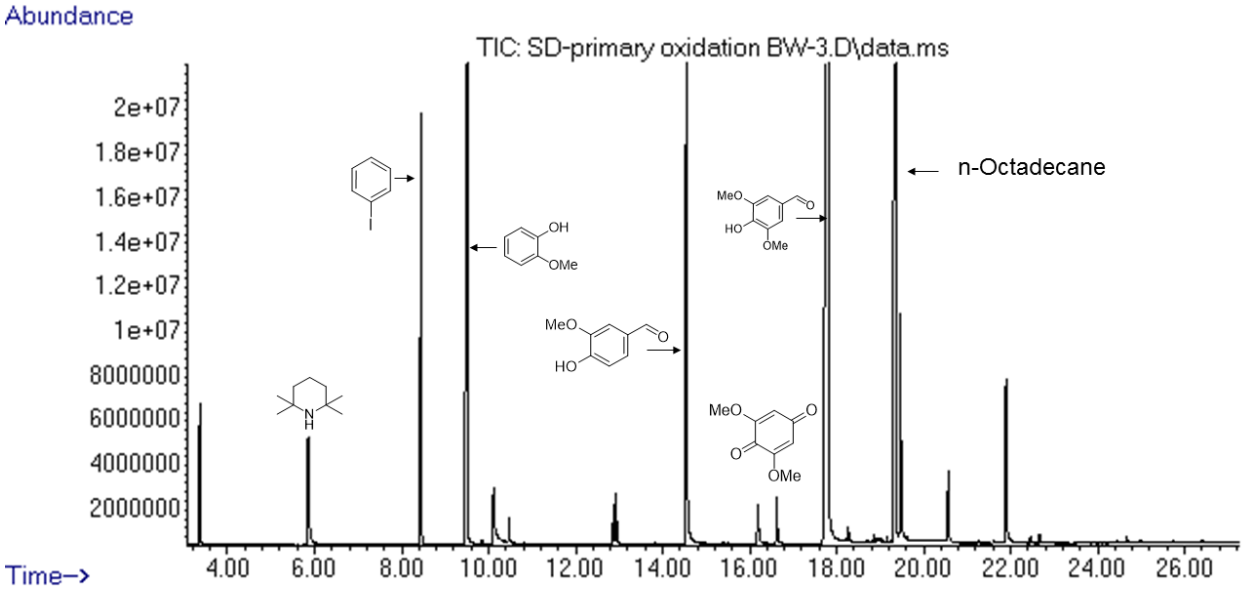
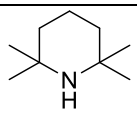
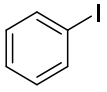
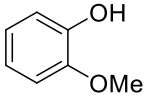
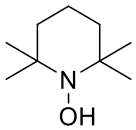
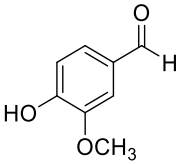
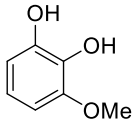
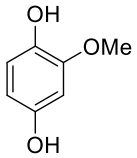
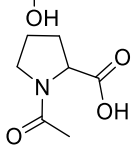
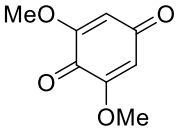
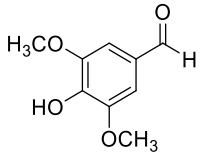
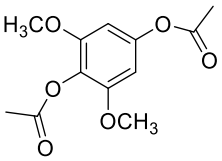


Table S8: Selected GC-MS peaks for the lower molecular weight fractions identified from the depolymerisation of organosolv beechwood lignin with the TEMPO/DAIB followed by DL-proline catalytic system.

Entry	r.t. (min)	*m*/z	Structure	Yield[(a)] (wt%) from starting lignin	Database Match (%)
1	5.9	141		-	95
2	8.5	204			96
3	9.5	124		0.3	Sample injected
4	10.1	142	-		-
5	10.5	156			81
6	12.9	170	-		-

7	14.5	152		1.5	97 sample injected
8	15.4	140		0.1	83 sample injected
9	15.4	140		0.05	72
10	16.1	157		-	64
11	16.6	168		0.1	92 Sample injected
12	17.7	182		2.5	96 Sample injected
13	18.3	254		-	60
14	20.9	256	n-Hexadecanoic acid	-	86
15	23.5	272	-	-	-
16	24.5	536	-	-	-

(a) Yields calculated by GC with respect to *n*-octadecane as an internal standard

13. References

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