

SUPPORTING INFORMATION

Catalytic synthesis of renewable phenol derivatives from biobased furanic derivatives

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1. Chemicals

Prior to use, furfural and furfuryl alcohol were purified following the guidelines of Armarego and Chai¹. The reagents, catalysts and solvents used in this study are listed below. All of them were used as received from commercial suppliers (unless otherwise indicated).

Table S1. List, CAS number, suppliers and purity of reagents and catalysts used in this work

Name	CAS number	Purity	Supplier
2-Methyl furan	534-22-5	99 %	Sigma-Aldrich
Furfural	98-01-1	97 %	Sigma-Aldrich
Furfuryl alcohol	98-00-0	98%	Sigma-Aldrich
5-Hydroxymethylfurfural	67-47-0	99%	Sigma-Aldrich
2,5-Dimethyl furan	625-86-5	99%	Acros Organics
Phenol	108-95-2	99.5%	Sigma-Aldrich
Amberlyst-15	9037-24-2	-	Acros Organics
Zinc chloride	7646-85-7	> 98%	Alfa Aesar
Zinc Iodide	10139-47-6	≥ 98%	Sigma Aldrich
Copper Chloride	7447-39-4	99%	Sigma Aldrich
Tin(II) Chloride	7772-99-8	98%	Sigma Aldrich
Aluminium chloride	7646-70-0	-	Sigma Aldrich
Copper oxide	1317-38-0	-	Sigma Aldrich
Triflic acid	1493-13-6	98%	Sigma Aldrich
Isobutyric acid	107-92-6	≥ 99%	Sigma Aldrich
Acetic acid	64-19-7	99%	Sigma Aldrich
Hexafluoroisopropanol	920-66-1	≥ 99%	Sigma Aldrich
2-Methyltetrahydrofuran	96-47-6	≥ 99%	Sigma Aldrich
Ethylpropionate	623-47-2	99%	Sigma-Aldrich
Diethylacetylene dicarboxylate	762-21-0	95%	Sigma-Aldrich

¹H NMR and ¹³C NMR were recorded on a Bruker Ultrashield 500 plus (500MHz). All spectra were internally referenced to residual proton solvent signals. Data for ¹H NMR are reported as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad signal), coupling constants (Hz), and integration. Data for ¹³C NMR are reported as chemical shifts.

Gas chromatography (GC) analysis: Samples were prepared by picking up 100 μ L of the reaction medium, which was then diluted to 1 mL with isopropanol. Samples were analyzed on a Scion 436-GC equipped with a HP5MS column (30 m x 0.25 mm x 0.5 Micron, -60 to 325/350 $^{\circ}$ C) and using a flow front of 1 mL/min and a split ratio 60:1. The temperature at the injector was set at 270 $^{\circ}$ C and the injected volume was 5 μ L. Method starts at 40 $^{\circ}$ C for 1 min followed by an increment of 10 $^{\circ}$ C per minute up to 130 $^{\circ}$ C, then 4 min at this temperature followed by an increment of 20 $^{\circ}$ C per minute up to 250 $^{\circ}$ C and it finally stays at this temperature for 4 min.

Gas chromatography-High Resolution Mass Spectrometry (GC-HRMS): GC-HRMS was performed on a Gas Chromatograph (GC) Agilent 7890A coupled to a High-Resolution Mass Spectrometer (quadrupole - Time of flight - QToF HRMS ; Agilent 7200 accurate mass detector) equipped with an Electronic Ionization (EI) source. Products were separated on a HP5MS column (30 m x 0.25 mm x 0.5 Micron, -60 to 325/350 $^{\circ}$ C). Injector temperature was set at 270 $^{\circ}$ C with a split ratio 60:1. Septum purge flow and gas saver flow were 3 mL.min⁻¹ and 20 mL.min⁻¹, respectively. Helium was used as the carrier gas with a flow rate of 1 mL.min⁻¹. The oven temperature was held at 40 $^{\circ}$ C for 1 min, then increased by 10 $^{\circ}$ C.min⁻¹ to 130 $^{\circ}$ C and held for 2 min, and then by 15 $^{\circ}$ C.min⁻¹ to 300 $^{\circ}$ C and held for 10 min. The mass detector was at 250 $^{\circ}$ C and operated in scan mode, with electronic impact ionization (ionization energy 70 eV) and a mass range of 30 to 500 amu. A scan rate of 5 scans.s⁻¹ was used to detect the ions formed.

Ultra High Performance Liquid Chromatography-High Resolution Mass Spectrometry (UHPLC-HRMS): UHPLC-MS was performed on a Thermo scientific Ultimate 3000 coupled with a Bruker impact HD Series Quadrupole-Time of Flight (QTOF) MS equipped with an Electrospray (ESI) ion source. The LC column was a Hypersil GOLD 1.9 μ m, 50 x 2.1 mm, a flow of mobile phase of 0.4 mL min⁻¹ was used, and the temperature of the column was set at 30 $^{\circ}$ C. The mobile phase consisted in ultrapure water (eluent A) and acetonitrile (eluent B), both with 0.1 % of formic acid. After injection of 10 μ L of sample, the gradient started with 95% of B and was constant during 1 min. Then, it reached 99% of B in 11 min and was constant during 1 min. The column was then reconditioned for 2 min with 95 % of A before reuse. For the MS, the ESI source operated in positive polarity and its parameters were fixed as follows: gas temperature 200 $^{\circ}$ C; drying gas 8.0 L min⁻¹; nebulizer 2.1 Bar, capillary 2500 V; the mass range was from 50 to 1000 m/z

2. Calibration curves

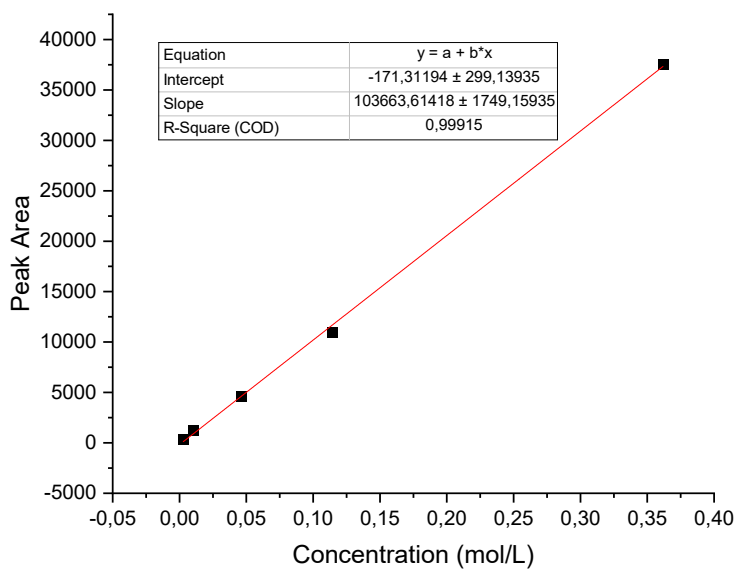


Figure S1 Calibration curve of methylfuran

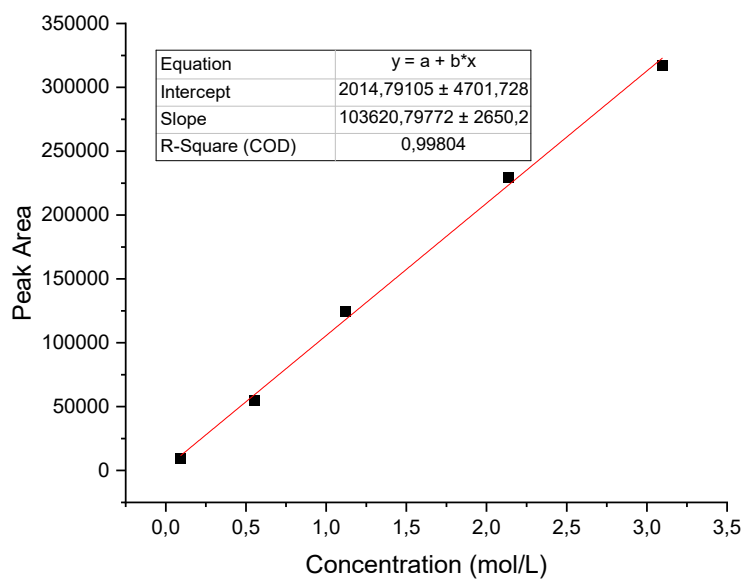


Figure S2 Calibration curve of ethyl propiolate

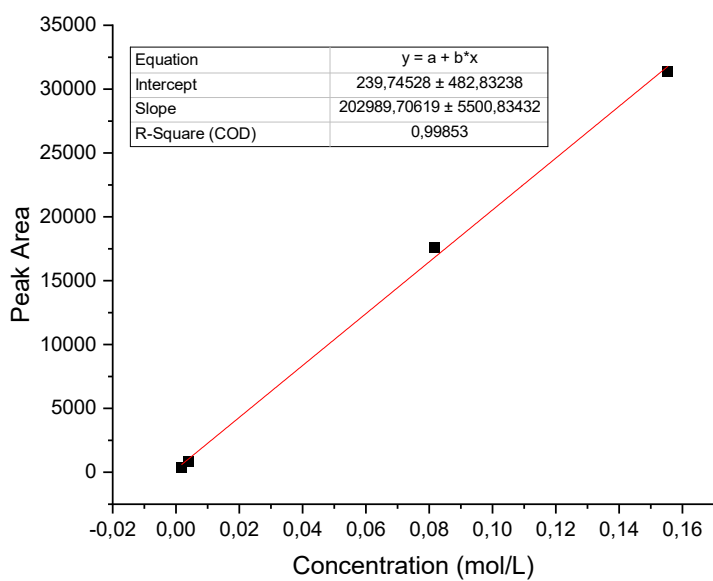


Figure S3 Calibration curve of **1-o**

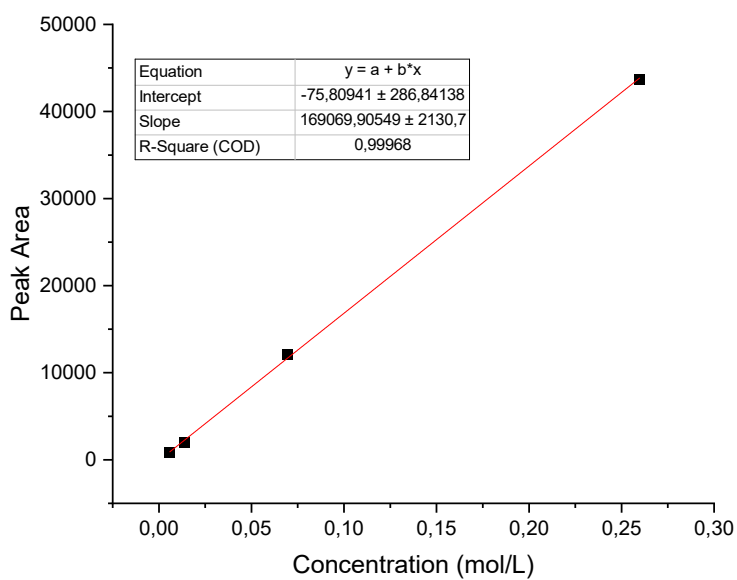


Figure S4 Calibration curve of **1-m**

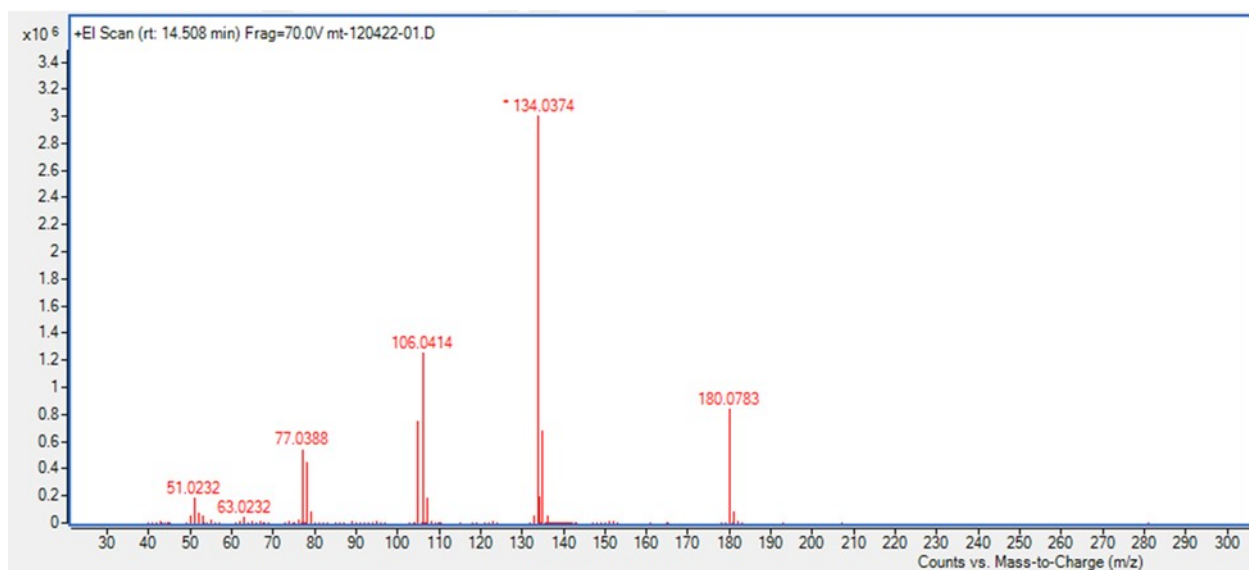


Figure S5 High resolution mass spectra of the four products obtained by reaction of MF (1eq.) with EP (5eq.) in the presence of 15 mol% of ZnCl₂

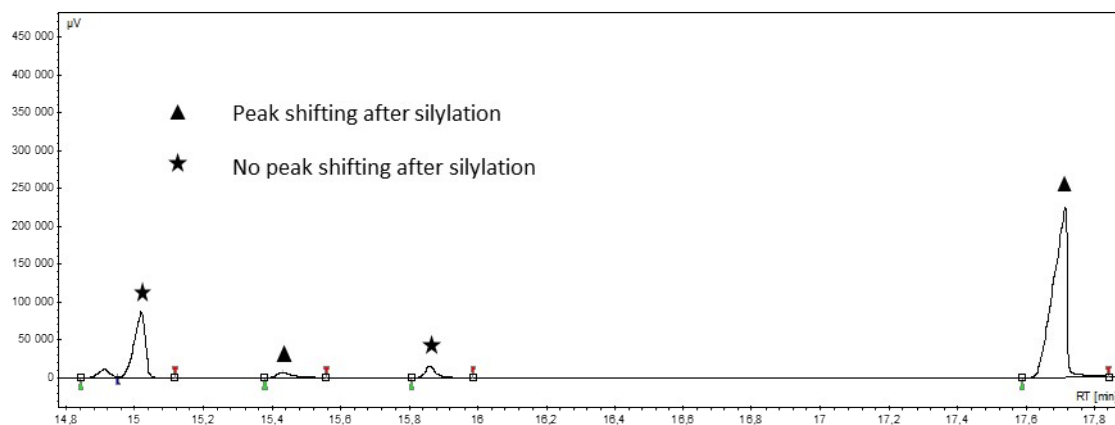


Figure S6 GC profile and peak shifting after silylation of the four reactions products obtained by reaction of MF (1eq.) with EP (5eq.) in the presence of 15 mol% of ZnCl_2

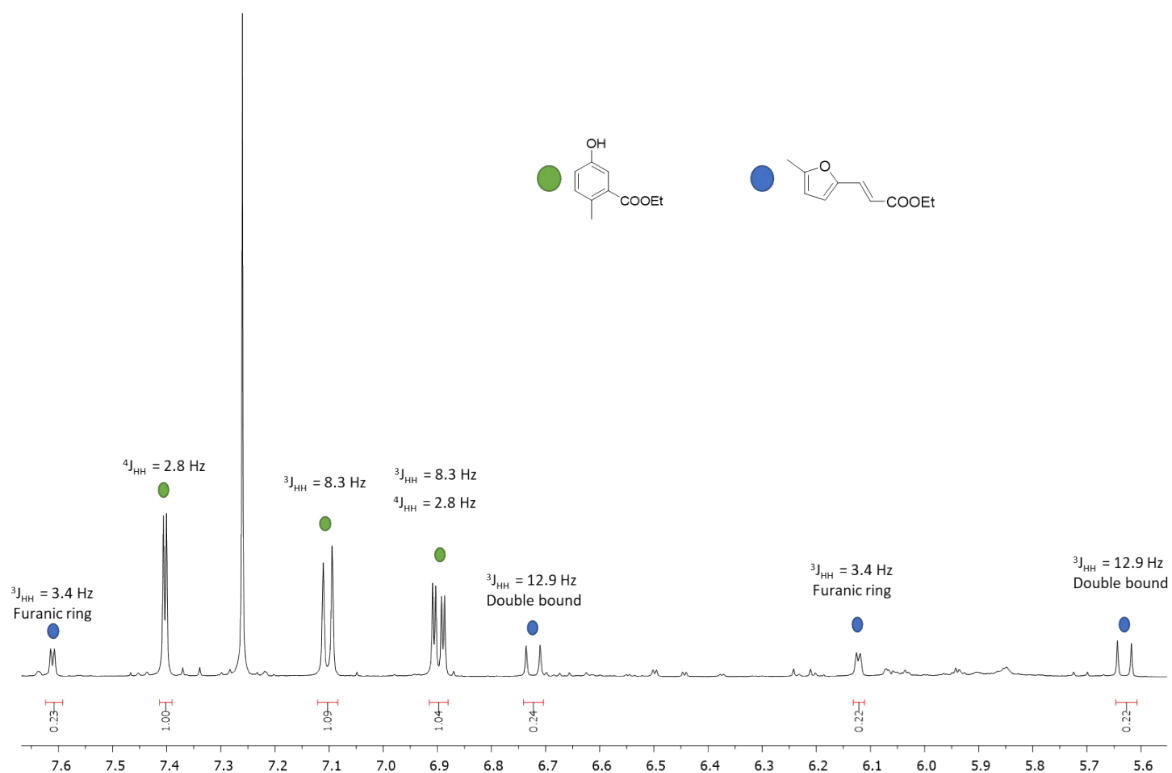


Figure S7 ¹H NMR (in CDCl₃)-zoom on the aromatic region of the crude mixture containing the phenol **1** and the alkylated products **2** (*trans* isomer)

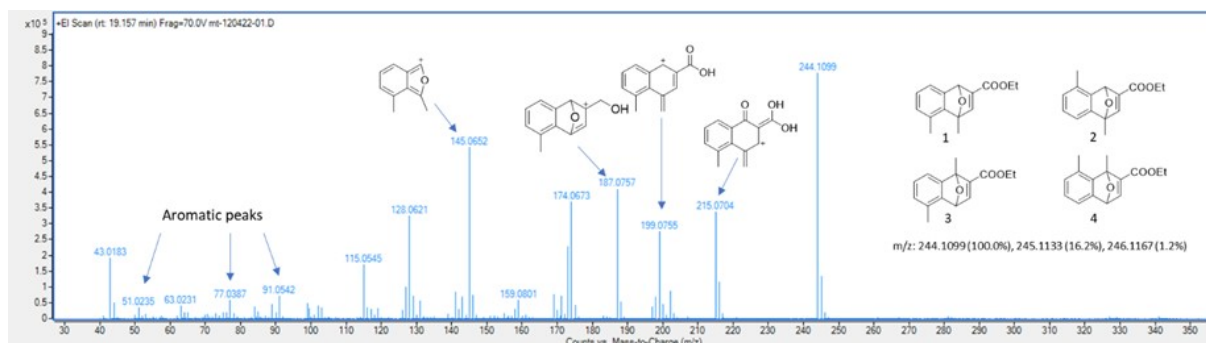


Figure S8 Mass spectrum showing the occurrence of successive Diels Alder reaction between methyl furan and ethyl propiolate and the associated fragments

Note 1: Four structures may correspond to the molecular formula.

Note 2: Fragments were calculated using Mass FrontierTM 8.0 from ethyl 4,5-dimethyl-1,4-dihydro-1,4-epoxynaphthal-ene-2-carboxylate (1).

Note 3: Analysis of mass fragments proved that the ester moiety is grafted on the non-aromatic part.

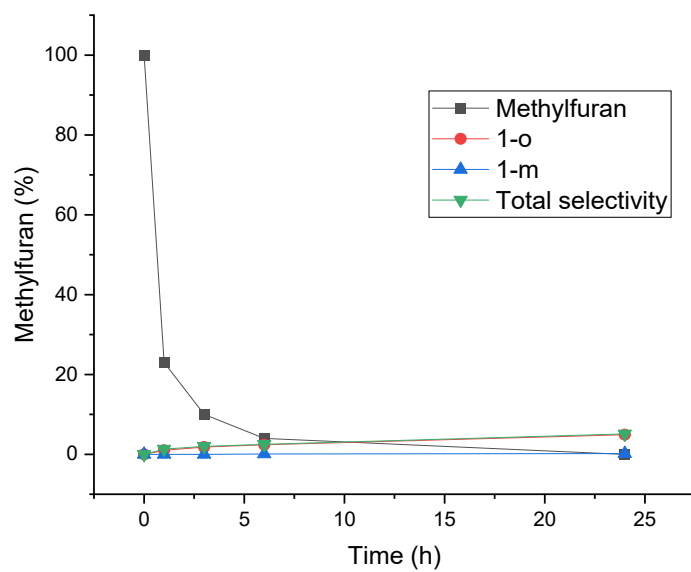


Figure S9 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), Amberlyst-15 (15 mol% of H⁺) and 100°C).

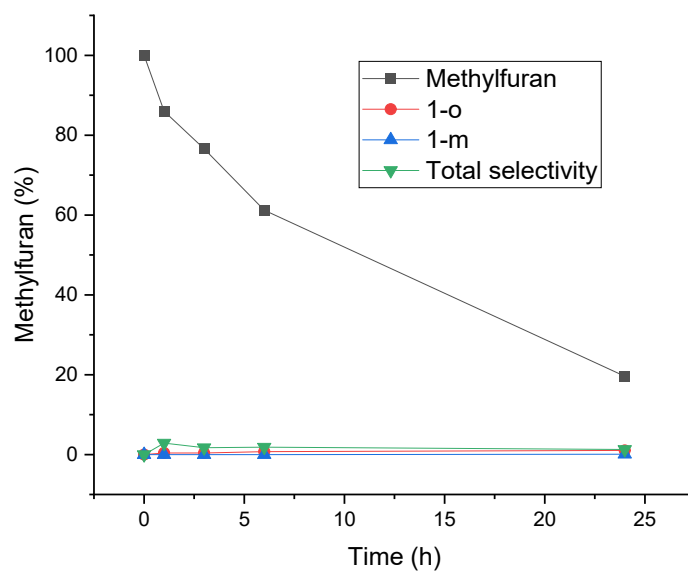


Figure S10 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), acetic acid (15 mol%) and 100°C).

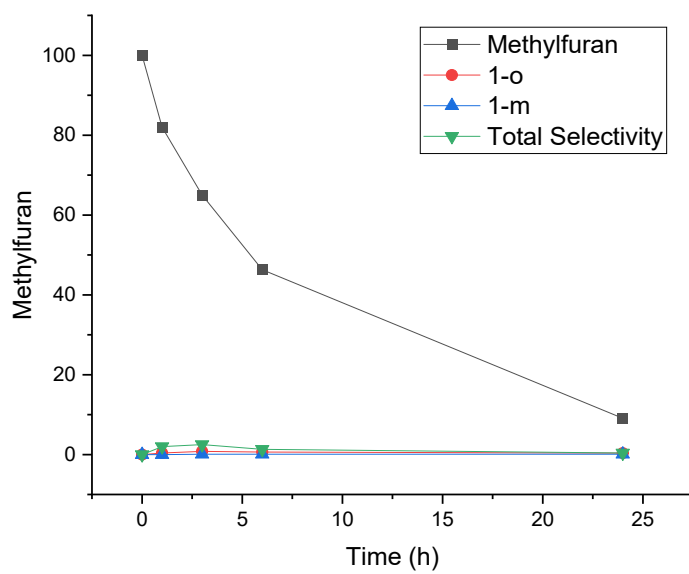


Figure S11 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), isobutyric acid (15 mol%) and 100°C).

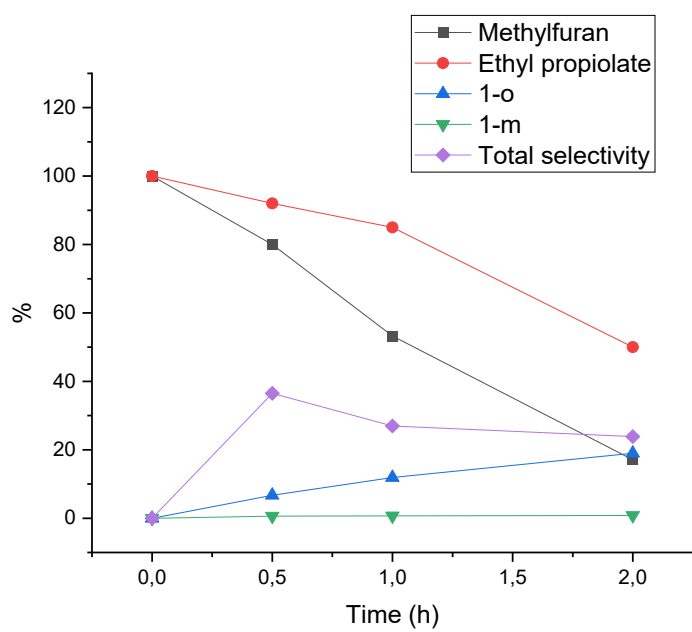


Figure S12 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnI_2 (15 mol%) and 100°C).

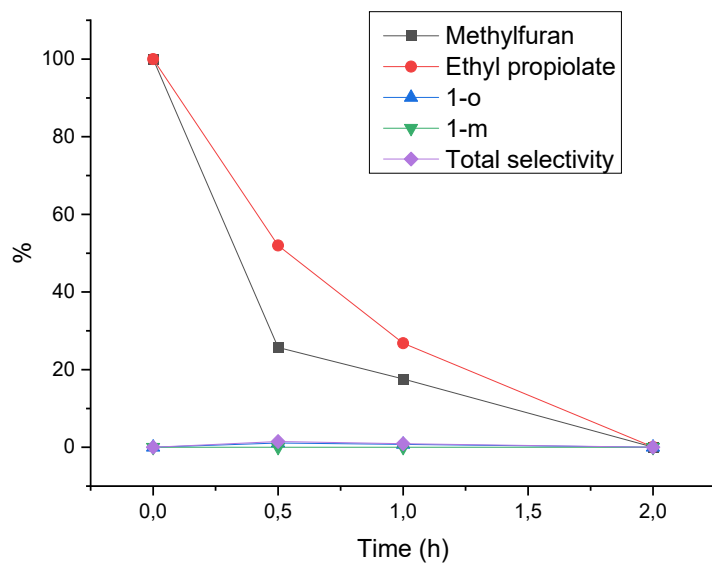


Figure S13 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), CuCl₂ (15 mol%) and 100°C).

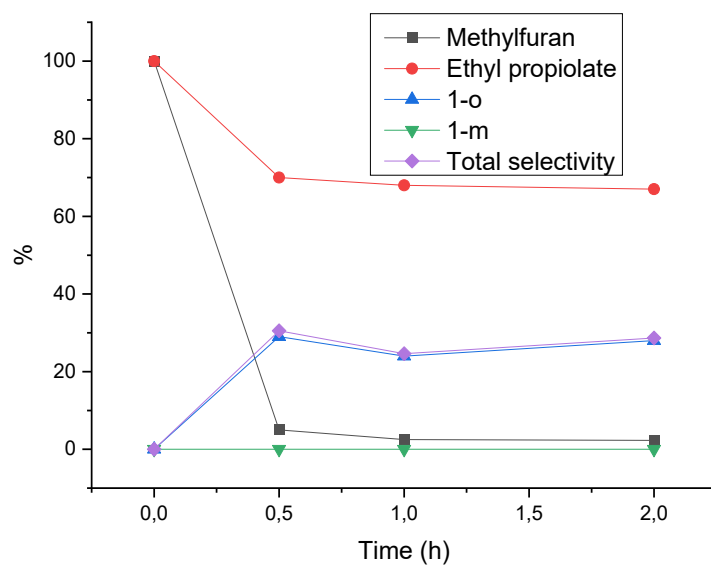


Figure S14 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), AlCl₃ (15 mol%) and 100°C).

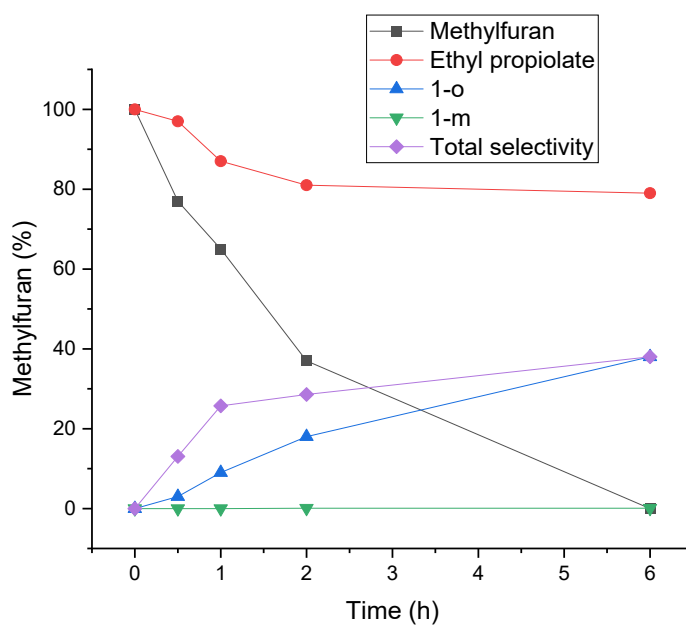


Figure S15 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), SnCl₂ (15 mol%) and 100°C).

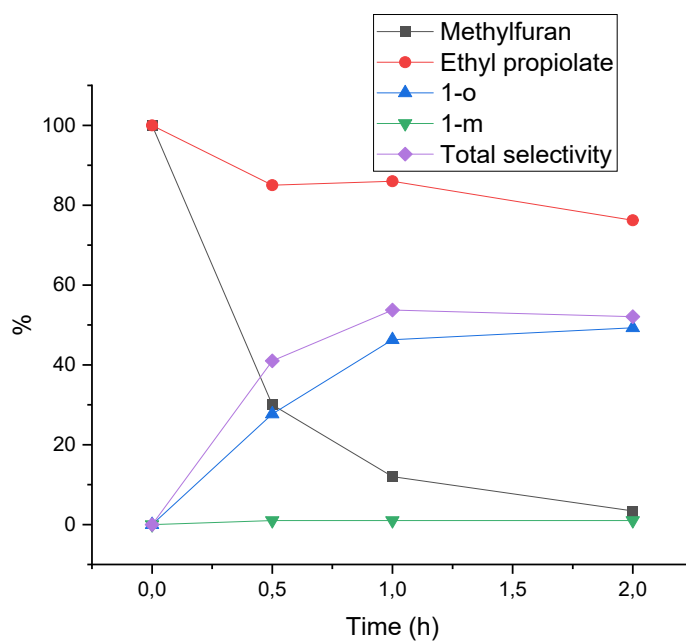


Figure S16 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (15 mol%) and 100°C).

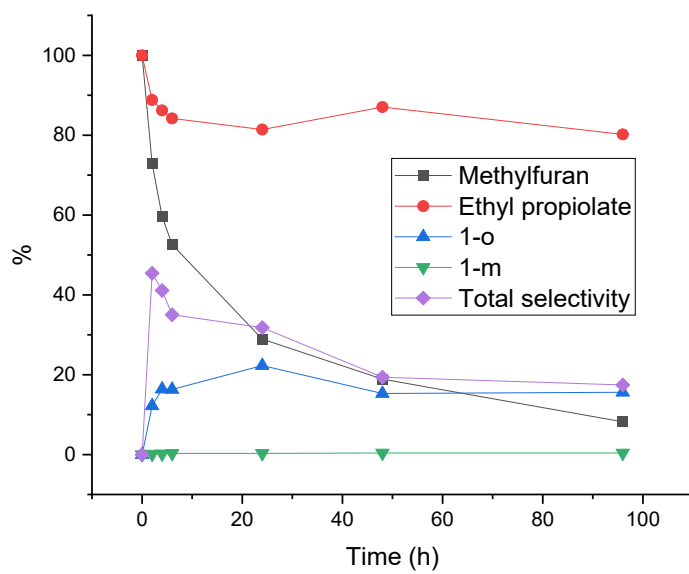


Figure S17 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (15 mol%) and 40°C).

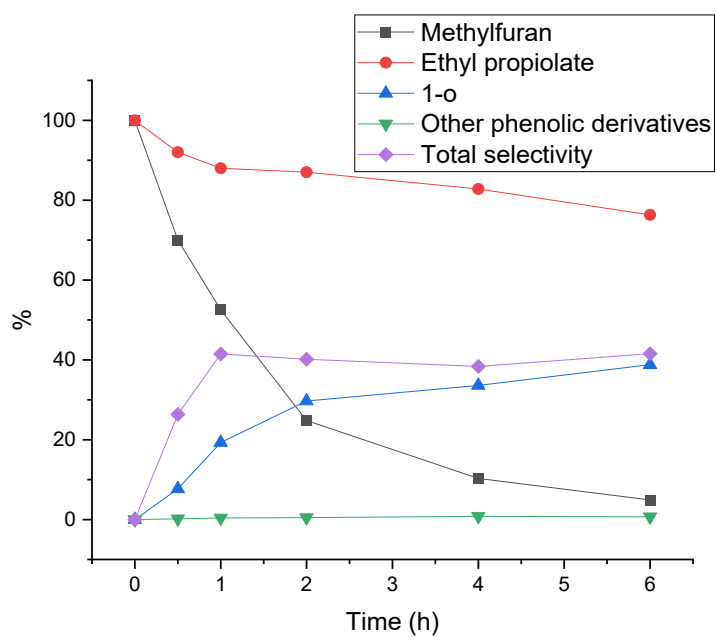


Figure S18 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (15 mol%) and 70°C).

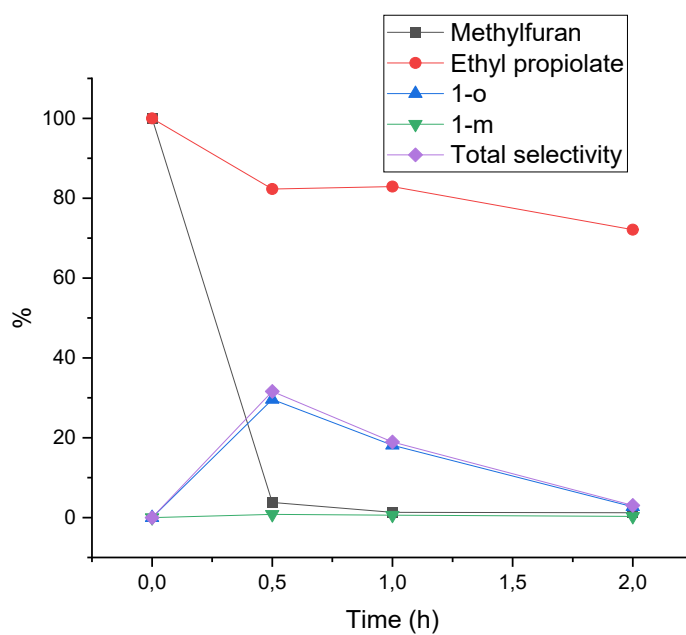


Figure S19 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (15 mol%) and 130°C).

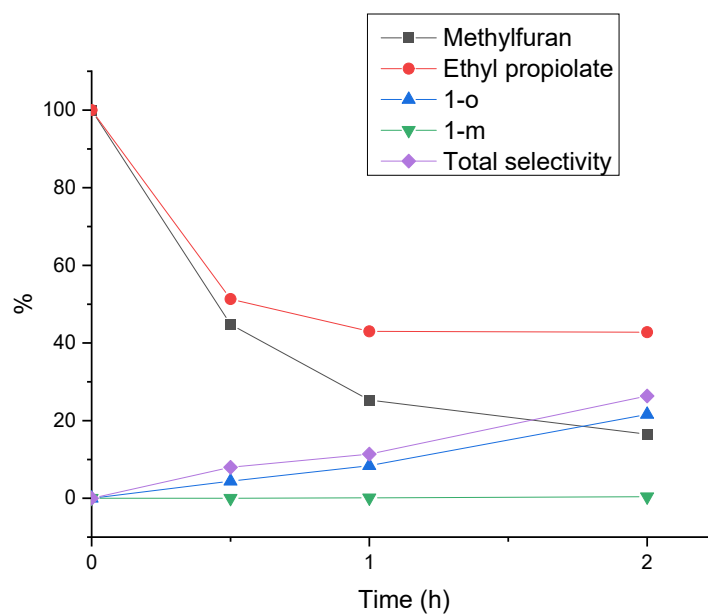


Figure S20 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (15 mol%) and 160°C.

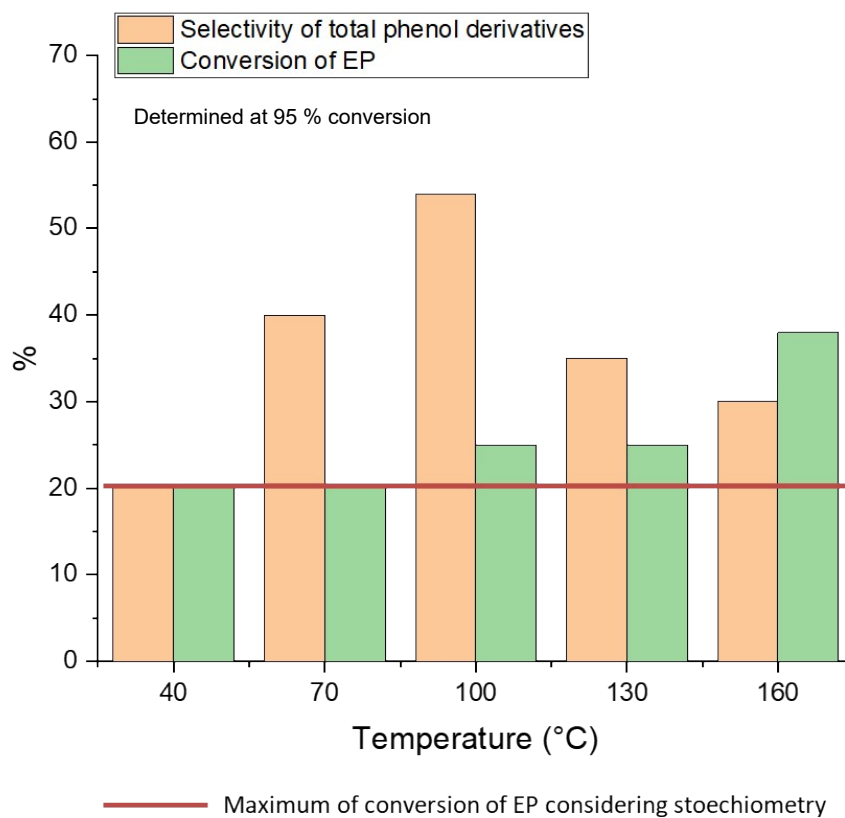


Figure S21 Influence of the temperature on the EP conversion and selectivity to phenol **1o-m** yields (determined at 95% of MF)

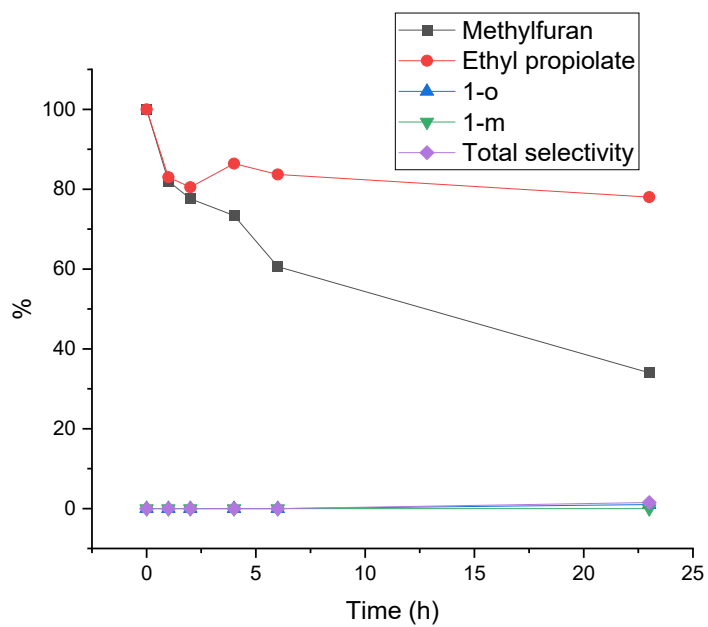


Figure S22 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), at 100°C and without catalyst).

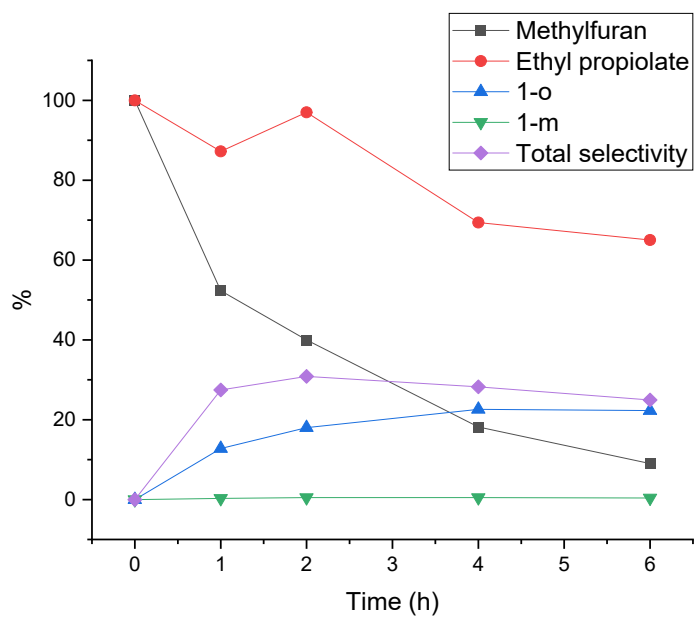


Figure S23 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (5 mol%) and 100°C).

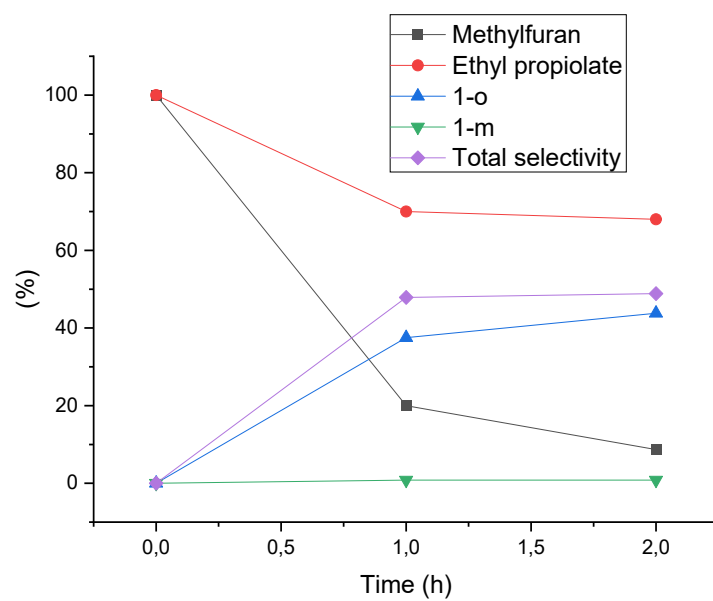


Figure S24 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (10 mol%) and 100°C).

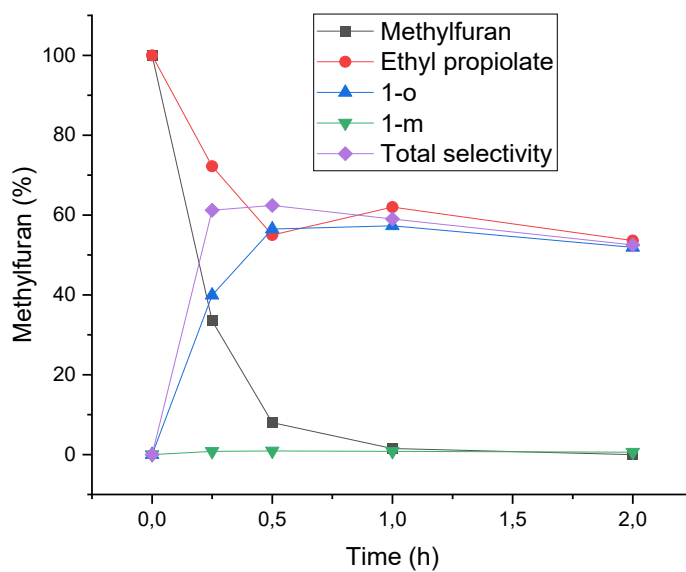


Figure S25 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl_2 (25 mol%) and 100°C).

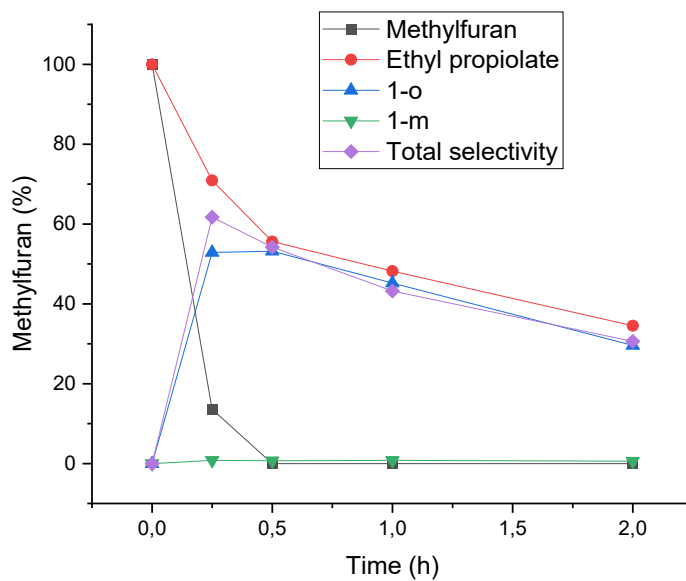


Figure S26 Plot of the MF conversion and phenol yields as a function of the reaction time (MF (1eq.), EP (5eq.), ZnCl₂ (50 mol%) and 100°C).

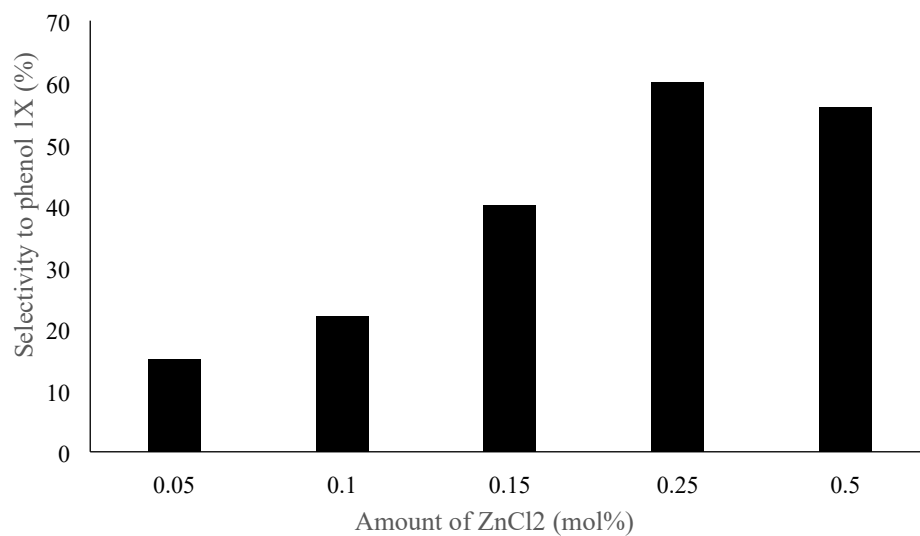


Figure S27 Impact of the amount of ZnCl₂ on the selectivity to phenol **1** (determined at 60% conv. of MF) (MF (1 eq.), EP (5 eq.), 100°C).

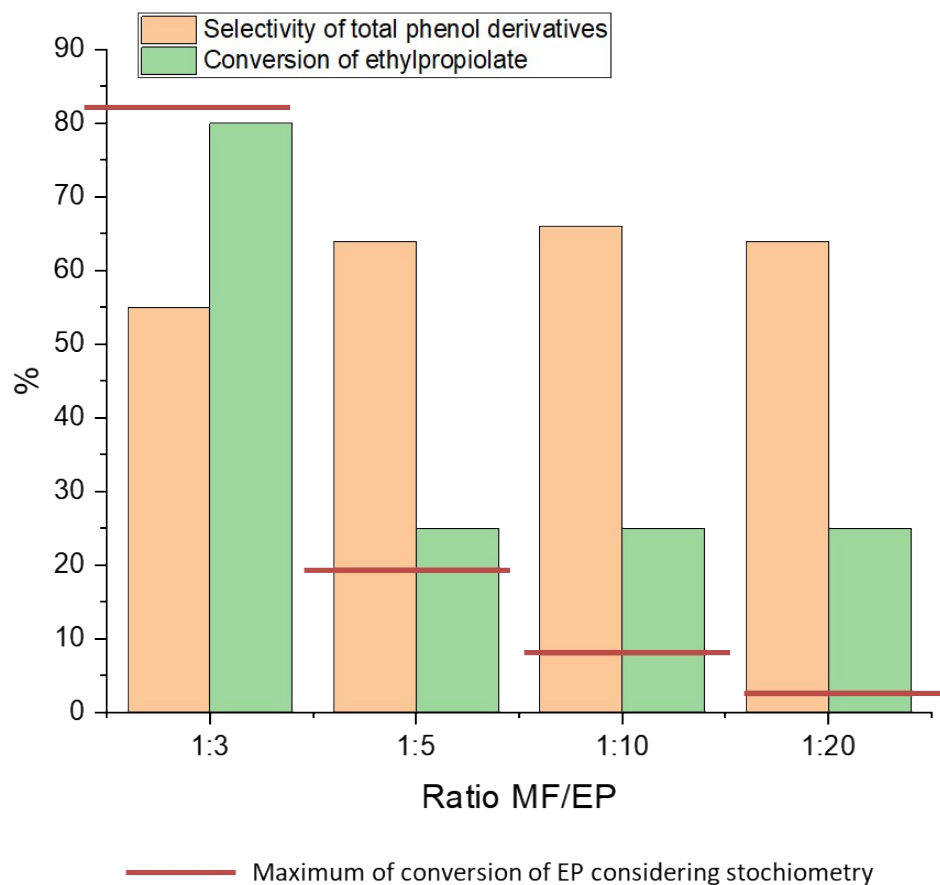


Figure S28 Influence of the MF/EP molar ratio on the stoichiometric conversion of EP and selectivity to phenol **1o-m**

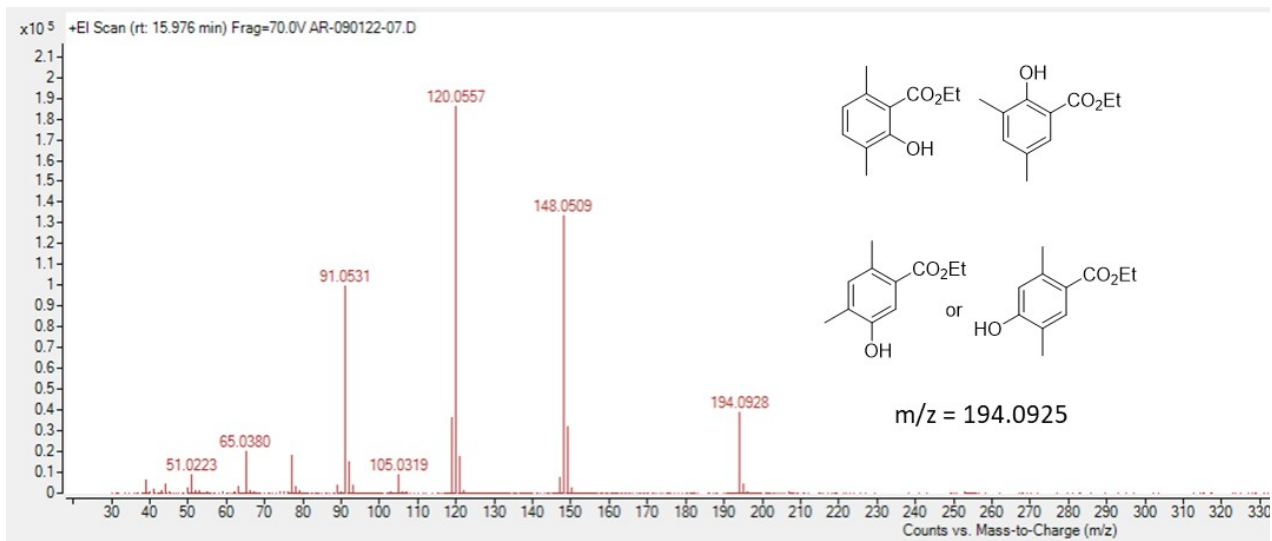


Figure S29 HRMS spectra profile of 10, 11 and 12

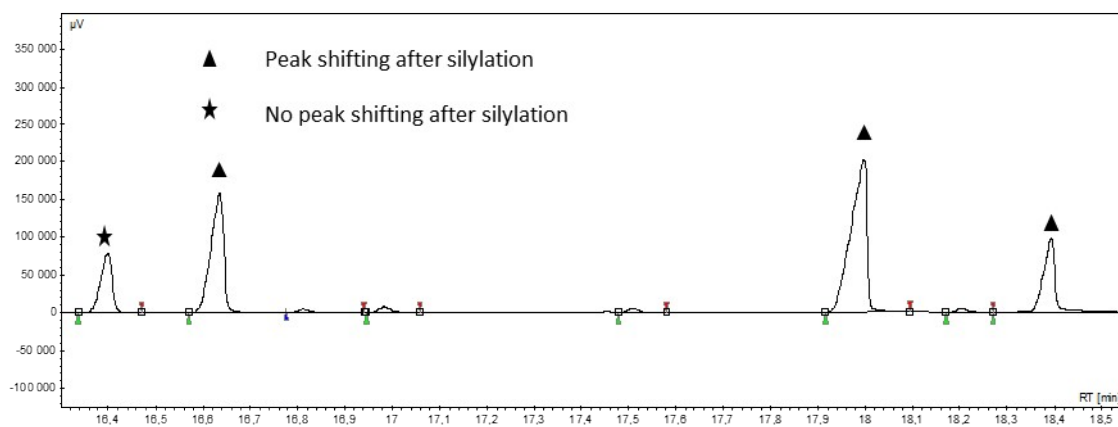


Figure S30 GC profile and peak shifting after silylation (DMF (1eq.), EP (5 eq.), ZnCl₂ (15 mol % and 100°C)

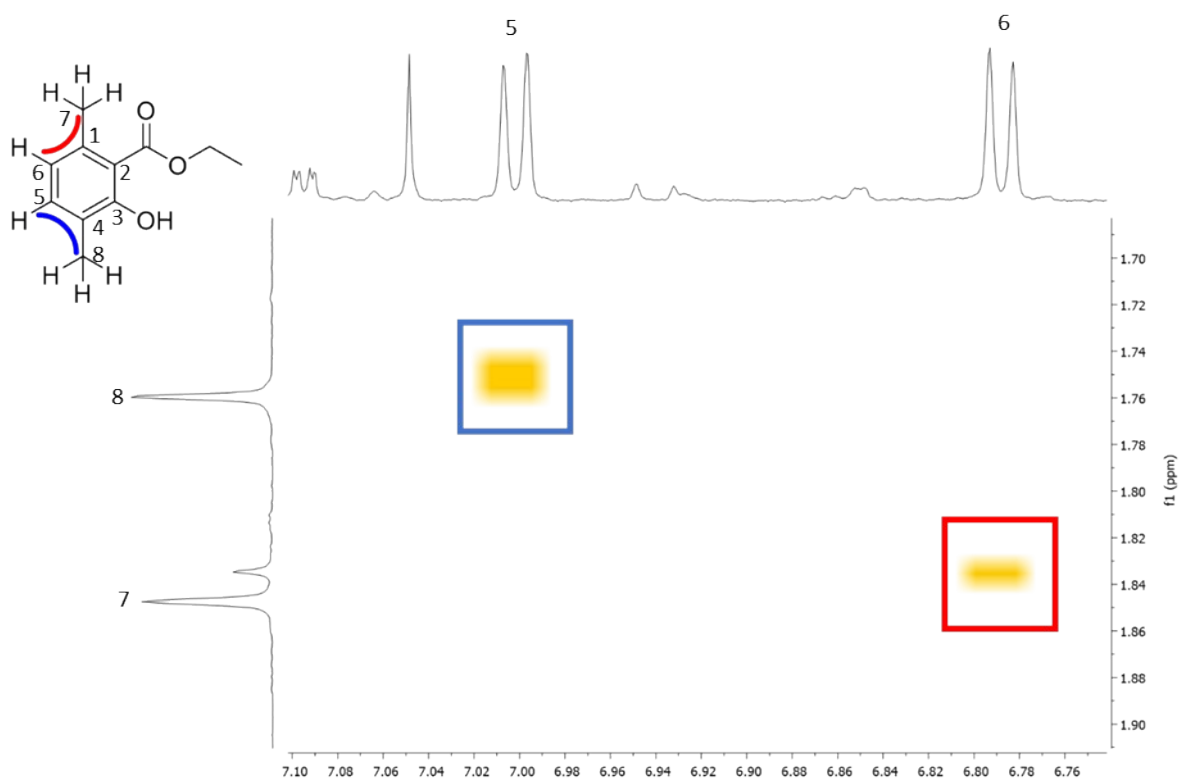


Figure S31 COSY NMR sequence performed on phenol **10**

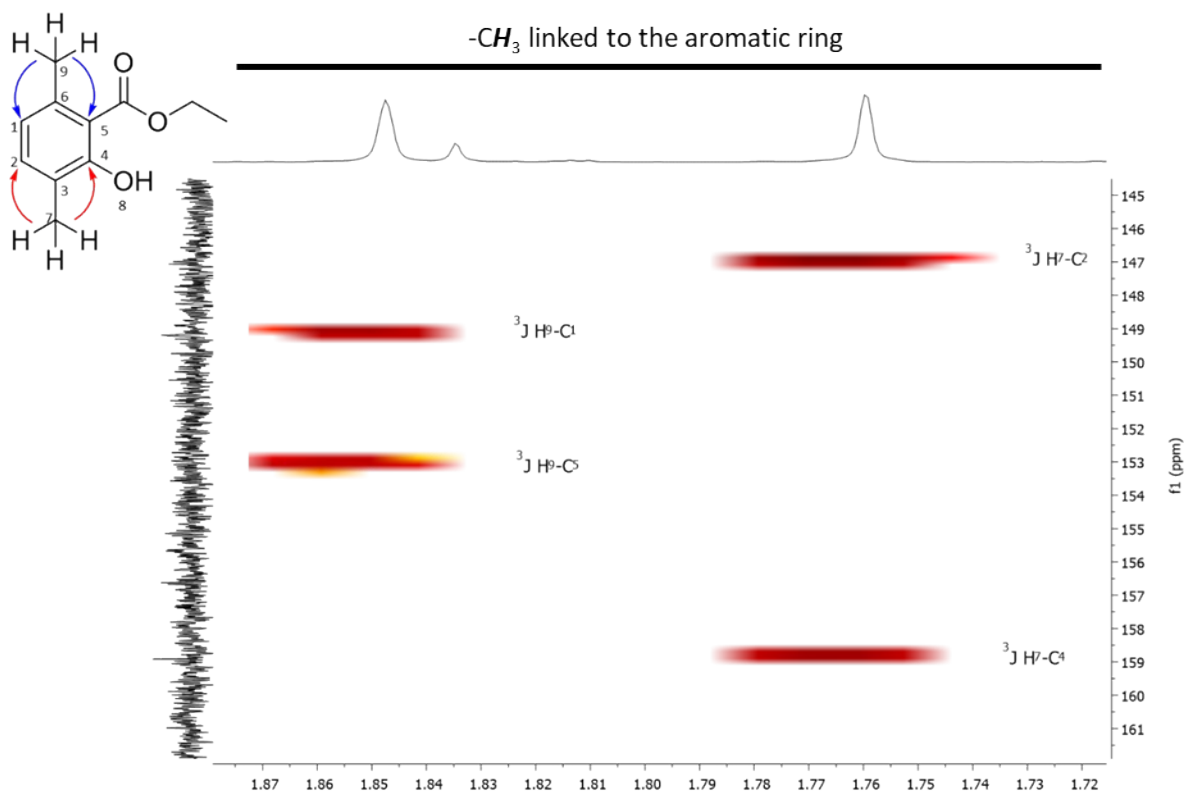


Figure S32 HMBC sequence performed on phenol **10**

Note: H/C correlation was clearly visible in HMBC, although in the ¹³C NMR spectrum the intensity of aromatic carbons in the selected window was very low. Presence of C peaks in this area was further confirmed by other analysis method such as HSQC and COSY sequence

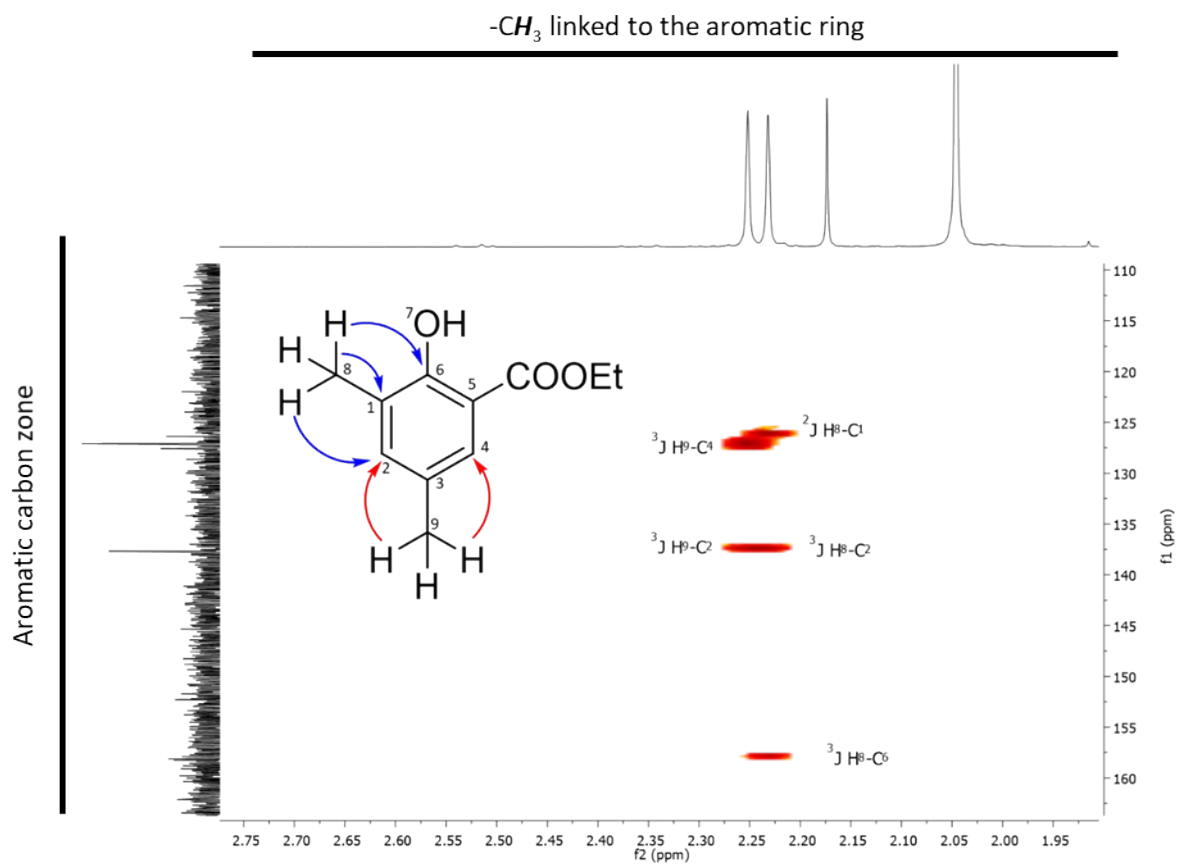


Figure S33 HMBC sequence performed on phenol **11**

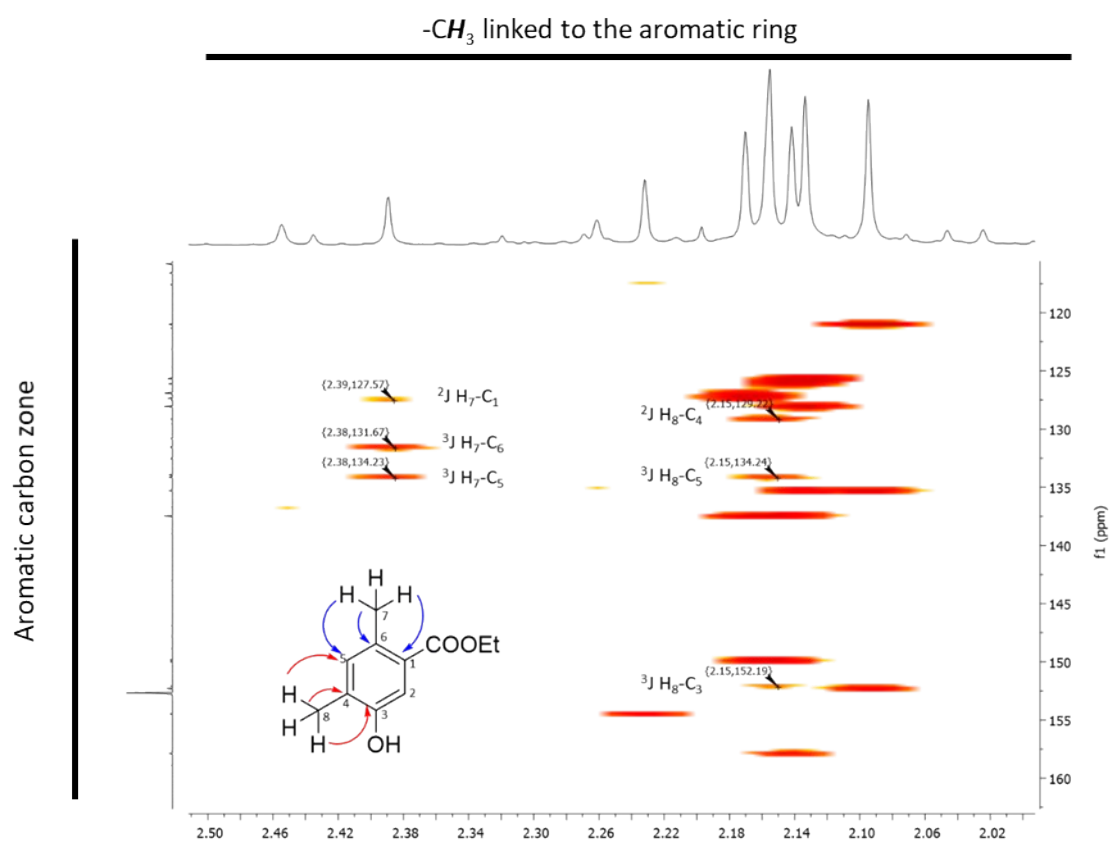


Figure S34. HMBC performed on the crude reaction media for structure analysis of phenol **12a** and **12b** (DMF 1 eq., EP 5 eq., 15 mol% ZnCl₂, 100°C, 2h)

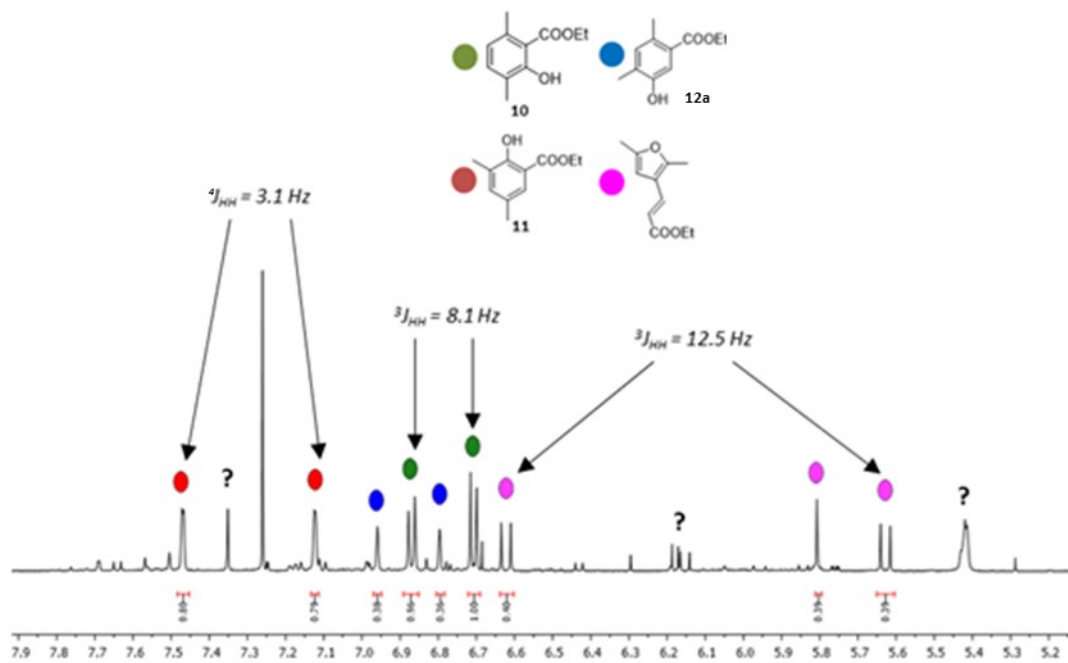


Figure S35 ^1H NMR (in CDCl_3) of crude mixture **10**, **11** and **12** with alkylation products in *trans* position, together with unknown impurities

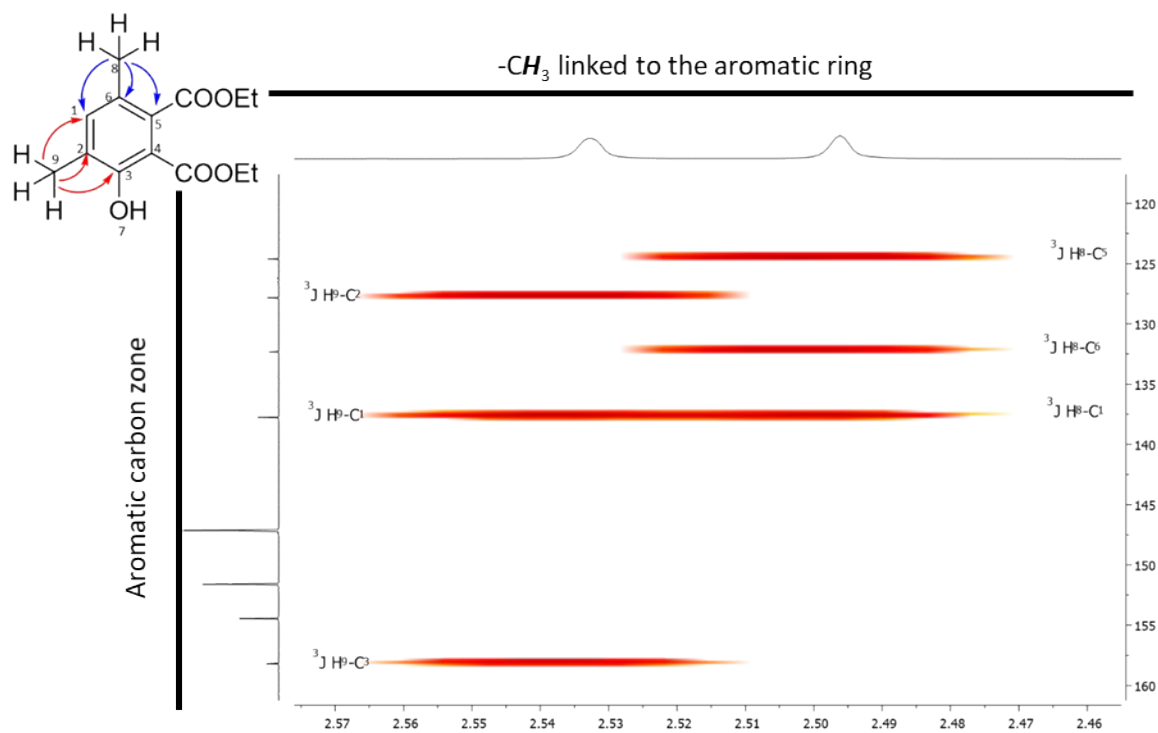
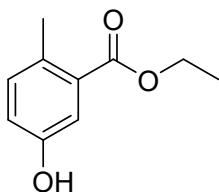


Figure 36 HMBC sequence performed on phenol 16

3. Experimental procedure and chemical characterization

Synthesis of ethoxy-2-hydroxy-3-methylbenzoate (1-o)



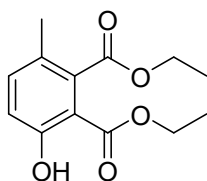
3 mmol of methyl furan (246 mg, 1 eq), 15 mmol of ethylpropiolate (1.471 g, 5 eq) and zinc chloride (60 mg, 15 %mol) were mixed and heated at 100 °C for 1 h. Then, the excess of ethylpropiolate was removed under vacuum (and could be recycled). For analysis, the crude reaction media was purified by flash chromatography (95:5 CH₂Cl₂/MeOH) and the product was recovered as a yellow pale powder.

¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, ⁴J_{H-H} = 2.8 Hz, 1H, =CH), 7.10 (d, ³J_{H-H} = 8.3 Hz, 1H, =CH), 6.91 (dd, ³J_{H-H} = 8.3, ⁴J_{H-H} = 2.8 Hz, 1H, =CH), 5.64 (s, 1H, -OH), 4.35 (q, ³J_{H-H} = 7.1 Hz, 2H, -CH₂-O), 2.50 (s, 3H; Ar-CH₃), 1.38 (t, ³J_{H-H} = 7.1 Hz, 3H, -CH₃).

¹³C NMR (126 MHz, CDCl₃) δ 167.89, 153.65, 133.02, 132.07, 130.62, 119.35, 117.23, 61.15, 21.02, 14.41.

GC-HRMS : m/z calculated for C₁₀H₁₂O₃ [M]⁺ 180.0786, found 180.0789.

Synthesis of diethyl 3-hydroxy-6-methylphthalate (3)



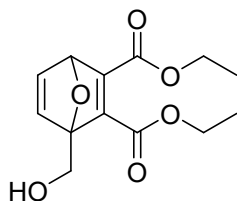
3 mmol of methyl furan (246 mg, 1 eq), 15 mmol of diethylacetylene dicarboxylate (2.552 g, 5 eq) and zinc chloride (60 mg, 15 mol%) were mixed and heated at 100 °C for 2 h. The product was pure enough to directly perform the ¹H NMR without additional purification.

¹H NMR (500 MHz, CDCl₃) δ 10.87 (s, 1H, -OH), 7.23 (d, ³J_{H-H} = 8.6 Hz, 1H, =CH), 6.88 (d, ³J_{H-H} = 8.6 Hz, 1H, =CH), 4.34 – 4.29 (m, 4H, -CH₂-O), 2.16 (s, 3H, Ar-CH₃), 1.34 – 1.30 (m, 6H, -CH₃).

¹³C NMR (126 MHz, CDCl₃) δ 169.09, 169.00, 159.87, 137.19, 134.86, 125.56, 118.67, 108.88, 62.15, 61.30, 18.24, 14.08, 13.84.

GC-HRMS : m/z calculated for C₁₃H₁₆O₅ [M]⁺ 252.0998, found 252.1005.

Synthesis of diethyl 1-(hydroxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (4)



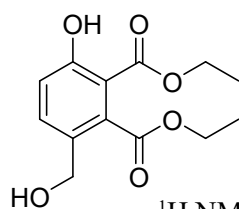
3 mmol of furfuryl alcohol (294 mg, 1 eq), 15 mmol of diethylacetylene dicarboxylate (2.552 g, 5 eq) were mixed and heated at 50 °C for 24 h. The product was pure enough to directly perform the ¹H NMR without additional purification.

¹H NMR (500 MHz, CDCl₃) δ 7.24 (dd, ³J_{H-H} = 5.3, 1.9, 1H, =CH), 7.06 (d, ³J_{H-H} = 5.3 Hz, 1H, =CH), 5.66 (d, ³J_{H-H} = 1.9 Hz, 1H, -CH), 4.34 – 4.22 (m, 6H, -CH₂-O), 1.32 (m, 6H, -CH₃).

¹³C NMR (126 MHz, CDCl₃) δ 164.51, 163.01, 154.09, 152.02, 145.06, 142.67, 98.49, 84.20, 61.97, 61.64, 60.24, 14.26, 14.15.

UHPLC-HRMS: m/z calculated for C₁₃H₁₇O₆ [M+H]⁺ 269.1020, found 269.1025.

Synthesis of diethyl 3-hydroxy-6-(hydroxymethyl)phthalate (5)



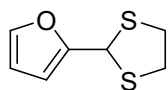
Previous crude reaction media to synthesize diethyl (4) (60 mg, 15 mol%) and heated at 100 °C for 48 h. For analysis, the crude reaction media was purified by preparative thin layer chromatography (95:5 cyclohexane/EtOAc).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.83 (s, 1H, -OH), 7.48 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 1H, =CH), 7.33 (d, $^3J_{\text{H-H}} = 8.5$ Hz, 1H, =CH), 5.17 (s, 2H, Ar- $\text{CH}_2\text{-O}$), 4.39 – 4.17 (m, 4H, - $\text{CH}_2\text{-O}$), 1.46 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, - CH_3), 1.31 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, - CH_3).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 171.35, 169.00, 145.41, 141.93, 140.44, 127.35, 124.99, 124.94, 67.76, 62.72, 60.56, 14.33, 13.99.

UHPLC-HRMS: m/z calculated for $\text{C}_{13}\text{H}_{17}\text{O}_6$ $[\text{M}+\text{H}]^+$ 269.1020, found 269.1030.

Synthesis of 2-(1,3-dithiolan-2-yl)furan (6)



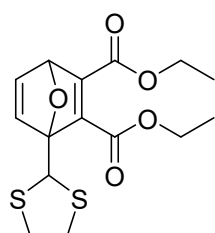
6.0 mL (72 mmol) of freshly distilled furfural, 6.7 mL (80 mmol, 1.1 eq) of ethanedithiol, 155.0 mg (0.7 mmol acid sites, *i.e.* 0.01 eq) of Amberlyst 15 and 60 mL of toluene were charged in a single-neck round bottom flask equipped with a magnetic stirring bar. The mixture was heated at 120°C for 4 hours in a Dean-Stark apparatus to continuously remove water. The reaction mixture was then cooled down to 25°C and Amberlyst 15 was filtered off. The reaction was quantitative by GC analysis. The 2-(1,3-dithiolan-2-yl)furan was isolated as follow: 100 mL of ethyl acetate were added to the crude reaction media and the organic phase was washed with water (20 mL, 3 times). After drying over MgSO_4 , ethyl acetate was evaporated under reduced pressure. Purification by column chromatography over silica gel (cyclohexane:ethyl acetate, 95:5) was finally used to afford 10.92g of a colourless to pale yellow pure product (*i.e.* 87% isolated yield).

$^1\text{H NMR}$ (500MHz, CDCl_3) δ 7.35 (dd, $^3J_{\text{H-H}} = 1.8$, $^4J_{\text{H-H}} = 0.9\text{Hz}$, 1H, =CH), 6.29-6.28 (m, 1H, =CH), 6.27 (dd, $^3J_{\text{H-H}} = 3.2$, $^3J_{\text{H-H}} = 1.8\text{Hz}$, 1H, =CH), 5.62 (s, 1H, -CH(SCH_2) $_2$), 3.41-3.30 (m, 4H, - CH_2).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.30, 142.72, 110.43, 107.18, 47.54, 39.23.

GC-HRMS : m/z calculated for $\text{C}_7\text{H}_8\text{OS}_2$ $[\text{M}]^+$ 172.0017, found 172.0014.

Synthesis of diethyl 1-(1,3-dithiolan-2-yl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7)



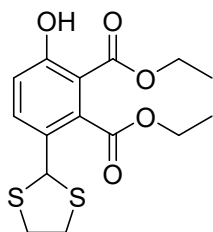
3 mmol of (6) (516 mg, 1 eq), 15 mmol of diethylacetylene dicarboxylate (2.552 g, 5 eq) were mixed and heated at 50 °C for 24 h. The product was pure enough to directly perform the $^1\text{H NMR}$ without additional purification.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18 (dd, $^3J_{\text{H-H}} = 5.2$, 1.9 Hz, 1H, =CH), 6.96 (d, $^3J_{\text{H-H}} = 5.2$ Hz, 1H, =CH), 5.64 (d, $^3J_{\text{H-H}} = 1.9$ Hz, 1H, -CH-O), 5.40 (s, 1H, -CH-(SCH_2) $_2$), 4.15 (q, 4H, - $\text{CH}_2\text{-O}$), 3.40 – 3.08 (m, 4H, - $\text{CH}_2\text{-S}$), 1.31 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, - CH_3), 1.24 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, - CH_3).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.95, 162.26, 153.11, 152.31, 144.79, 143.39, 102.37, 83.59, 61.71, 61.37, 50.38, 39.62, 39.29, 14.22, 13.93.

UHPLC-HRMS: m/z calculated for $\text{C}_{15}\text{H}_{19}\text{O}_5\text{S}_2$ $[\text{M}+\text{H}]^+$ 343.0669, found 343.0661.

Synthesis of diethyl 3-(1,3-dithiolan-2-yl)-6-hydroxyphthalate (8)



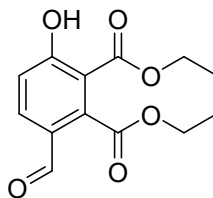
Previous crude reaction media to synthesize (8) was mixed with Amberlyst-15 (60 mg, 15 % eq. H^+) and heated at 100 °C for 6 h. For analysis, the crude reaction media was purified by preparative thin layer chromatography (95:5 cyclohexane/EtOAc).

1H NMR (500 MHz, $CDCl_3$) δ 11.18 (s, 1H, -OH), 8.01 (d, $^3J_{H-H} = 8.9$ Hz, 1H, =CH), 7.06 (d, $^3J_{H-H} = 8.9$ Hz, 1H, =CH), 5.55 (s, 1H, *Ar-CH*-(SCH₂)₂), 4.36 – 4.42 (m, 4H, -CH₂-S), 3.55 – 3.44 (m, 2H, -CH₂-O), 3.38 – 3.29 (m, 2H, -CH₂-O), 1.44 – 1.36 (m, 6H, -CH₃).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.05, 161.77, 143.93, 136.07, 134.33, 128.98, 127.98, 120.10, 62.53, 61.94, 52.03, 40.71, 14.29, 14.24, 14.06.

UHPLC-HRMS: m/z calculated for C₂₅H₁₉O₅S₂ [M+H]⁺ 343.0669, found 343.0667.

Synthesis of diethyl 3-formyl-6-hydroxyphthalate(9)



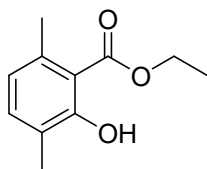
25 mg of diethyl 3-(1,3-dithiolan-2-yl)-6-hydroxyphthalate (0.07 mmol, 1 eq.) were dissolved in 2 mL of a mixture acetone and water (99 :1). 12mg of CuCl₂ (0.08 mmol, 2 eq.) and 15mg of CuO (0.16 mmol, 4 eq.) were then added and the mixture was heated at 30°C for 4 h. Then, it was cooled down to 25°C and 20 mL of diethyl ether was added. The solution was then filtered over silica. After removal of diethyl ether under vacuum, the phenol 9 was recovered as a yellow oil (19 mg, 98% yield).

1H NMR (500 MHz, $CDCl_3$) δ 11.86 (s, 1H, -OH), 9.84 (s, 1H, -CHO), 8.01 (d, $^3J_{H-H} = 8.7$ Hz, 1H, =CH), 7.16 (d, $^3J_{H-H} = 8.7$ Hz, 1H, =CH), 4.42 – 4.48 (m, 4H, -CH₂-O), 1.34 – 1.31 (t, $^3J_{H-H} = 7.1$ Hz, 6H, -CH₃).

^{13}C NMR (126 MHz, $CDCl_3$) δ 207.22, 188.13, 182.66, 158.81, 151.97, 136.33, 126.56, 125.63, 119.60, 63.17, 62.31, 14.19, 14.03.

UHPLC-HRMS: m/z calculated for C₁₃H₁₃O₅S₂ [M-H]⁻ 265.0707, found 265.0658.

Synthesis of ethyl 3-hydroxy-2,6-dimethylbenzoate (10)



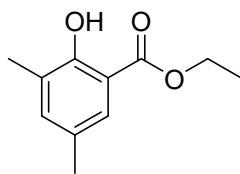
3 mmol of dimethyl furan (288 mg, 1 eq), 15 mmol of ethylpropiolate (1.471 g, 5 eq) and zinc chloride (60 mg, 15 mol%) were mixed and heated at 100 °C for 2 h. For analysis, the crude reaction media was purified by preparative thin layer chromatography (95:5 cyclohexane/EtOAc).

1H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H, =OH), 7.00 (d, $^3J_{H-H} = 8.1$ Hz, 1H, =CH), 6.79 (d, $^3J_{H-H} = 8.1$ Hz, 1H, =CH), 4.09 – 4.15 (m, 4H, -CH₂-O), 1.85 (s, 3H, *Ar-CH*₃), 1.76 (s, 3H, *Ar-CH*₃), 1.33 – 1.28 (m, 6H, -CH₃).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.72, 158.71, 149.22, 147.02, 142.37, 137.96, 134.49, 46.34, 29.84, 21.18, 14.34.

GC-HRMS : m/z calculated for C₁₁H₁₄O₃ [M]⁺ 194.0943, found 194.0925.

Synthesis of 2-hydroxy-3,5-dimethylbenzoate (11)



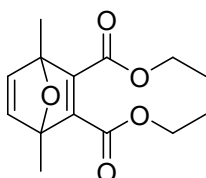
3 mmol of dimethyl furan (288 mg, 1 eq), 15 mmol of ethylpropiolate (1.471 g, 5 eq) and zinc chloride (60 mg, 15 mol%) were mixed and heated at 100 °C for 2 h. For analysis, the crude reaction media was purified by preparative thin layer chromatography (95:5 cyclohexane/EtOAc).

^1H NMR (400 MHz, CDCl_3) δ 10.91 (s, 1H, -OH), 7.49 (d, $^4J_{\text{H-H}} = 3.1$ Hz, 1H, =CH), 7.14 (d, $^4J_{\text{H-H}} = 3.1$ Hz, 1H, =CH), 4.39 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 2H, -CH₂-O), 2.25 (s, 3H, Ar-CH₃), 2.23 (s, 3H, Ar-CH₃), 1.41 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 3H, -CH₃).

^{13}C NMR (101 MHz, CDCl_3) δ 170.59, 158.16, 137.47, 137.43, 128.07, 126.90, 115.80, 61.22, 18.66, 15.49, 12.68.

GC-HRMS : m/z calculated for $\text{C}_{11}\text{H}_{14}\text{O}_3$ [M]⁺ 194.0943, found 194.0923.

Synthesis of diethyl 1,4-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (15)



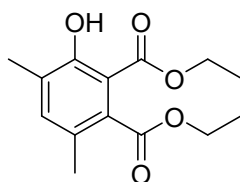
3 mmol of dimethyl furan (288 mg, 1 eq), 15 mmol of diethylacetylene dicarboxylate (2.552 g, 5 eq) were mixed and heated at 50 °C for 24 h. The crude reaction media was pure enough to be directly analyzed by ^1H NMR.

^1H NMR (500 MHz, CDCl_3) δ 6.83 (s, 2H, =CH), 4.14 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 4H, -CH₂-O), 1.67 (s, 6H, -CH₃), 1.19 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 6H, -CH₃).

^{13}C NMR (126 MHz, CDCl_3) δ 169.49, 154.24, 151.38, 147.09, 61.01, 15.19, 13.91.

GC-HRMS : m/z calculated for $\text{C}_{14}\text{H}_{18}\text{O}_5$ [M]⁺ 266.1154, found 266.1154.

Synthesis of diethyl 3-hydroxy-4,6-dimethylphthalate (16)



Previous crude reaction media to synthesize diethyl 3-hydroxy-4,6-dimethylphthalate was mixed with zinc chloride (60 mg, 15 mol%) and heated at 100 °C for 6 h. The crude reaction media was pure enough to be directly analyzed by ^1H NMR.

^1H NMR (500 MHz, CDCl_3) δ 11.47 (s, 1H, -OH), 7.48 (s, 1H, =CH), 4.72 – 4.64 (m, 4H, -CH₂-O), 2.53 (s, 3H, Ar-CH₃), 2.50 (s, 3H, Ar-CH₃), 1.70 – 1.66 (m, 6H, -CH₃).

^{13}C NMR (126 MHz, CDCl_3) δ 169.42, 163.87, 158.15, 154.41, 137.70, 132.20, 127.62, 124.57, 61.91, 61.01, 18.03, 15.52, 13.95, 13.91.

GC-HRMS : m/z calculated for $\text{C}_{14}\text{H}_{18}\text{O}_5$ [M]⁺ 266.1154, found 266.1154.

4. DFT calculations

a. Theoretical methods

All calculations were made using Gaussian 16. Rev B01, at the M062X/6-311++G(d,p) level of theory. It indeed proved reliable in the modelling of organic chemistry reactivity and selectivity, noticeably in related studies on Diels-Alder reactions involving furanic derivatives.²

All geometries were fully optimized, and frequency calculations conducted to confirm the nature of stationary points, in vacuum. In the case of phenol 13, a small imaginary mode (-14 cm^{-1}) proved impossible to remove. Taking the same input file and simply changing the functional by B3LYP, also known to be reliable in organic chemistry, showed no such imaginary mode. Given the modest amplitude of the vibration mode, it was neglected.

Whenever possible, Intrinsic Reaction Coordinates calculations were undertaken to ensure transition states connect to the appropriate reagent and product geometries.

Kinetic and thermodynamic selectivities were then evaluated on the basis of the relative ZPE-corrected electronic energies.

b. Geometries

We list below the geometries, in Cartesian coordinates, of all considered molecules in the manuscript. Please refer to the main text for the labels. ZPE-corrected energy as well as the first vibration frequency (respectively in a.u. and cm^{-1}) are also given.

Adduct A - E+ZPE=-3313.438661 - 1st freq. = 28.5824

C	-2.0461968794	-0.0024945962	1.4897482914
C	-1.8725606803	-0.7589237472	0.1524064924
C	-1.3226302108	1.1021711219	1.3827533356
C	-0.6844600674	1.0709687082	-0.0251174728
C	0.3200063767	-0.1024347282	-0.0356767291
C	-0.4031466272	-1.2105071501	0.0787423336
O	-1.7699067244	0.3913528188	-0.7452663793
C	-2.9235998789	-1.7488993105	-0.2716260957
C	-0.3022695979	2.3785704065	-0.6613194839
H	-0.0623700404	-2.2327429515	0.1640498116
C	1.785131299	0.0507286895	-0.0083150266
O	2.3503815793	1.0998142532	0.1665914003
O	2.414763454	-1.116602769	-0.1763020367
C	3.8437411307	-1.0506286091	-0.1327586162
H	4.1743450054	-0.6776027892	0.8365598613
H	4.2134386221	-0.3898467616	-0.9166332092
H	4.1887053035	-2.0680954659	-0.2927246016
H	-1.1366218202	3.0834916227	-0.6200557772
H	-0.023535506	2.2318487505	-1.7052919571
H	0.5459564709	2.8009827423	-0.1233138269
H	-1.1557111324	1.8925432645	2.1000510435
H	-2.644498903	-0.3624191635	2.3138535146
H	-3.9211354286	-1.3144638072	-0.1999912031
H	-2.8786696001	-2.6189280931	0.3869090224
H	-2.7358729026	-2.0820380881	-1.2941150606
Zn	-3.418523061	1.4697634567	-1.44586445
Cl	-2.7970526356	2.4429953473	-3.2839922731
Cl	-5.0949717651	1.1897125383	-0.0815770277

TSA-1 - E+ZPE=-3313.387071 - 1st freq. = -307.4397

C -0.1686946512 -0.6033923081 2.0688400336
C 0.3767651252 -1.5863748584 1.1416643555
C 0.0484967871 0.6658393145 1.6942224623
C 0.6924865734 0.7839714835 0.3031291086
C 1.9722790179 -0.068978845 0.2825728943
C 1.7339091651 -1.3309001577 0.6464725896
O -0.1756421597 -0.0046628209 -0.5071839896
C -0.2855312964 -2.8739501845 0.9201916466
C 0.8230262343 2.2167797191 -0.1813640809
H 2.4440599838 -2.1447542217 0.5680059778
C 3.3073539391 0.3977070656 -0.1826870136
O 3.6599817443 1.5456101915 -0.1817203364
O 4.0837988969 -0.6221711107 -0.5624188428
C 5.4054647389 -0.259337958 -0.9784511412
H 5.9392054825 0.2198651955 -0.1578376803
H 5.3557442282 0.4260153546 -1.82418656
H 5.888045605 -1.1895331833 -1.2636861098
H -0.167678367 2.6746133061 -0.1716397894
H 1.2094337032 2.2269331002 -1.200311512
H 1.4999957454 2.7941755586 0.4483387838
H -0.3758050595 1.5310276693 2.1916933715
H -0.8026864274 -0.9196333741 2.8872500072
H -1.0217567381 -2.6931984358 0.1130681358
H -0.8681756707 -3.1848582488 1.7889803834
H 0.4004263523 -3.6503307651 0.5854680512
Zn -2.1083095106 0.2241903645 -0.5407556412
Cl -2.8965578216 2.0629097059 0.3974537678
Cl -3.0104506205 -1.7225845571 -1.0895168717

Int.A1 - E+ZPE=-3313.460931 - 1st freq. = 2.3779

C 0.5989553356 1.5970677592 0.9852862106
C -0.1465999632 1.9976887765 -0.0636154381
C 0.3242758438 0.3161717953 1.6525144501
C -0.8860612094 -0.484123787 1.2666201473
C -1.742066261 0.1265441593 0.2147986525
C -1.3427874084 1.2438947377 -0.4220169908
O 0.4424241103 -0.8549598531 0.8091017631
C 0.1651286874 3.2288632264 -0.8635307722
C -1.4355033406 -1.4719415275 2.2605496029
H -1.9505425267 1.6238332713 -1.2347175818
C -2.9958288613 -0.5655446334 -0.2048213726
O -3.3495319405 -1.6425843956 0.1996819173
O -3.6877933096 0.1390575835 -1.1058899777
C -4.8508713974 -0.5110869689 -1.6257932917
H -5.5577881355 -0.7186013834 -0.8226503573
H -4.5705100179 -1.4460874781 -2.1104116248
H -5.2761967758 0.1828152812 -2.3452223689
H -0.6903359303 -1.6533857283 3.0356662886
H -1.6885302153 -2.4085394842 1.7693581743
H -2.342535542 -1.0746408114 2.7182596806
H 0.7533516418 0.1479848579 2.6330336777
H 1.4337460184 2.1899536046 1.3402967443
H 0.3446874333 2.956877212 -1.9077232107
H 1.0499680699 3.7365855465 -0.4815760587

H	-0.6792204523	3.9224923631	-0.8470175014
Zn	1.4118641865	-0.4873048368	-1.0283615077
Cl	3.4118487717	0.0894668878	-0.3844810245
Cl	0.0986841883	-0.8531901742	-2.7237742304

TSA-2 - E+ZPE=-3313.418409 - 1st freq. = -132.0782

C	-0.5189062006	2.2758749138	0.1676630951
C	-1.8036788479	2.4132953819	-0.224307465
C	0.0519762222	0.9734173058	0.6044001766
C	-0.902350521	-0.159562946	0.7370114814
C	-2.202272245	-0.0205465951	0.2141085138
C	-2.6115412814	1.2312553715	-0.2134528533
O	0.7868754752	0.4230097271	-0.4599954316
C	-2.4000550649	3.6996865602	-0.7271827246
C	-0.3640619552	-1.3984362517	1.3385356013
H	-3.6260542894	1.313895378	-0.594273745
C	-3.1368857908	-1.1845277035	0.1233680471
O	-2.8668690505	-2.3041962001	0.4631479372
O	-4.3242938611	-0.8348646775	-0.3848927761
C	-5.2718880367	-1.9028393912	-0.5161335386
H	-5.4859451084	-2.3343346246	0.4611097778
H	-4.8738410767	-2.6754243386	-1.1730089338
H	-6.1624293324	-1.4519143584	-0.9439408542
H	0.6247273296	-1.2264570848	1.7621001828
H	-0.333460785	-2.1978571998	0.5932006362
H	-1.0587546105	-1.7544448771	2.1054135019
H	0.6450329629	1.1028856843	1.524619954
H	0.1775232762	3.107262217	0.108249715
H	-2.753705897	3.5870197895	-1.7544887901
H	-1.6621051344	4.5007806672	-0.7069318483
H	-3.2502671743	4.0017821735	-0.1115299181
Zn	2.6325634642	-0.1826806745	-0.2275549942
Cl	3.638236336	-1.0506282766	-1.9557792144
Cl	3.1126221967	0.1917210297	1.9153334673

Int.A2 - E+ZPE=-3313.475049 - 1st freq. = 26.9998

C	-0.5776690807	2.1900648884	-0.710805613
C	-1.9451080994	2.4128366596	-0.6225971415
C	-0.024263126	0.9199440358	-0.4979926421
C	-0.8648206488	-0.1758765245	-0.1955605082
C	-2.2432774783	0.0727159319	-0.0674263977
C	-2.7745291516	1.3418716518	-0.2888951734
O	1.3008579603	0.776119829	-0.5670520832
C	-2.5241108201	3.7774045602	-0.8912645829
C	-0.2366242836	-1.544424925	-0.0875669943
H	-3.8417876814	1.4912246883	-0.1867010049
C	-3.1592411043	-1.0155997795	0.3904971103
O	-2.8227571068	-1.9731539465	1.0405844244
O	-4.4313045847	-0.8015464102	0.026093878
C	-5.3694658383	-1.7771869458	0.4836435835
H	-5.3679175008	-1.8223838071	1.5728875133
H	-5.1161148744	-2.7602292722	0.0866258459
H	-6.3370498785	-1.4508854345	0.1124184646
H	0.576533281	-1.6338630042	-0.8143027985
H	-0.951235866	-2.3380415938	-0.2874815947

H	0.1484127591	-1.7620136674	0.9204718054
H	-0.2399543983	0.6906430883	1.9062920109
H	0.1060082292	2.999133146	-0.9440738069
H	-2.8075772391	3.869405941	-1.9431896171
H	-1.8008311616	4.5635166373	-0.6714111158
H	-3.4178873741	3.9507574711	-0.2903019302
Zn	2.239043536	-0.2475393989	0.6504260182
Cl	3.830005284	-1.4524870153	1.4135396429
Cl	0.7440002473	0.481092196	2.7324377067

TSA-3 - E+ZPE=-3313.416467 - 1st freq. = -114.2953

C	-1.2528724314	2.662064368	-0.4191800486
C	-2.5090072239	2.1252639693	-0.6743235464
C	-0.3307389131	1.9034258295	0.268947434
C	-0.5314806501	0.4880161907	0.6697278364
C	-1.907517551	-0.0146000037	0.2999626193
C	-2.8190533455	0.7675248916	-0.3128943238
O	0.3445552237	-0.1109637862	-0.2416321557
C	-3.5520690114	2.9080945053	-1.3898283015
C	-0.1775260876	0.2800036809	2.1473013747
H	-3.7798220761	0.3623196182	-0.6073590255
C	-2.2001669561	-1.4724894622	0.5361438329
O	-1.6114740918	-2.1637784726	1.3174368738
O	-3.2022868666	-1.9022342182	-0.234586177
C	-3.5176511601	-3.2942378013	-0.0971982598
H	-3.8346010975	-3.5069259796	0.9235723374
H	-2.6420220265	-3.8966034492	-0.3369609523
H	-4.3225699104	-3.4824566017	-0.8014251401
H	0.7717496719	0.779066073	2.3513795536
H	-0.0808702383	-0.7870930313	2.336221655
H	-0.9473805965	0.6912191464	2.8069953397
H	0.6605115244	2.2908633191	0.4961868088
H	-1.0096058624	3.6613397657	-0.7583644064
H	-3.7810233023	2.4127889807	-2.3396021264
H	-3.2409322042	3.9319526384	-1.5858573177
H	-4.4782875035	2.9073086862	-0.8078288126
Zn	2.2971840858	-0.1468419807	-0.2276243076
Cl	3.2260262695	-1.7633103043	-1.3658000609
Cl	3.0989323309	1.6181914281	0.8860052969

Int.A3 - E+ZPE=-3313.485704 - 1st freq. = 10.8456

C	1.4145904119	-2.5005355791	-0.0826851293
C	2.6309811503	-2.0652788647	-0.4447735946
C	0.3418572171	-1.5926206044	0.4166979125
C	0.5969768734	-0.1308997332	0.1873892121
C	1.9822890717	0.2915652004	-0.009114684
C	2.9040037993	-0.6383692823	-0.3528303489
O	-0.3180438799	0.6929458208	0.1820530317
C	3.7390659581	-2.9686611763	-0.9090496726
C	0.1911968221	-1.7805544298	1.9551701306
H	3.9126059824	-0.2978751081	-0.5711162065
C	2.3387796285	1.7329137275	0.1565336185
O	1.7842718367	2.483370622	0.9068931101
O	3.3912671957	2.0723064043	-0.6023763608
C	3.8260447257	3.4292568343	-0.4578346927

H	4.1338626696	3.618253999	0.570568265
H	3.0168410331	4.1100363444	-0.7205382509
H	4.6638215369	3.5432899968	-1.1397810441
H	-0.0638521482	-2.8197157533	2.1633563496
H	-0.6147535076	-1.1480204801	2.3257615047
H	1.1255944158	-1.5326463447	2.4623120874
H	-0.6252543745	-1.8467568985	-0.0271967817
H	1.1861825541	-3.562556931	-0.0865626848
H	4.0608733741	-2.6982373163	-1.9178082927
H	3.4160402404	-4.0092623639	-0.9197715276
H	4.6090024458	-2.8846031252	-0.252780087
Zn	-2.375301296	0.7501346116	0.1670869149
Cl	-3.0129020583	2.6546163636	-0.6376034281
Cl	-3.1333736784	-1.1880869336	0.8607666495

TSB-1 - E+ZPE=-3313.391257 - 1st freq. = -293.9683

C	-0.3045578548	-1.3564040076	1.3962008138
C	0.0697135647	-1.5622690134	-0.0762819955
C	0.1516408461	-0.1972818867	1.8864187139
C	1.0058150847	0.5445953665	0.9662311893
C	2.0400855139	-0.2434603646	0.274886726
C	1.5780797727	-1.3942117336	-0.2293538354
O	-0.3890891885	-0.3819320799	-0.7221533308
C	-0.4679008665	-2.8482142003	-0.6786459618
C	0.9856553003	2.0090777054	0.9429850485
H	2.1810656883	-2.0573915436	-0.8391819611
C	3.4120735252	0.2908478749	0.0845852634
O	3.7936564161	1.3505417497	0.5095212801
O	4.1780638889	-0.558112197	-0.6004112134
C	5.5286812787	-0.1293787149	-0.8150228865
H	6.0296878631	0.0223516273	0.1406534395
H	5.5397913437	0.8014061543	-1.3812143279
H	6.0018413658	-0.929049087	-1.3770818092
H	0.0368047895	2.4081215252	1.2963657567
H	1.2253287462	2.3877842657	-0.0509770143
H	1.8109783584	2.3300612059	1.5992691779
H	-0.1745259984	0.2726396995	2.8066574562
H	-1.0315619935	-1.9886051522	1.8930873558
H	-1.5535369426	-2.8756673934	-0.5754401412
H	-0.0414060978	-3.7238237339	-0.182086814
H	-0.2143604639	-2.8823092579	-1.7393031142
Zn	-2.1934342576	0.3139079641	-0.4588213512
Cl	-2.1867999905	2.5114289639	-0.6280623308
Cl	-3.6083226922	-1.1677327364	0.3871588664

Int.B1 - E+ZPE=-3313.462791 - 1st freq. = 18.1062

C	-0.5920698875	-1.269104723	1.510775652
C	0.0346543848	-1.9477056481	0.3579819284
C	-0.1301635127	-0.0856521386	1.9507165183
C	1.1018424414	0.5378647826	1.4642748791
C	1.8230861962	-0.1018834801	0.506864958
C	1.2805874871	-1.2991332289	-0.1590875657
O	0.0176625272	-1.1472174753	-0.8515744411
C	-0.2780324115	-3.3956076396	0.1257284221
C	1.5010778821	1.8361060194	2.1050470539

H	1.9678608261	-1.9045406496	-0.7346699792
C	3.1447831067	0.4083638052	0.0607568067
O	3.7383019168	1.3350297159	0.546542808
O	3.6272481671	-0.3018491164	-0.9747790162
C	4.8914021932	0.1385102646	-1.4773974517
H	5.6498628932	0.0771025714	-0.6969886231
H	4.8172054661	1.1688579412	-1.8244449871
H	5.1289715425	-0.5290853108	-2.3009286291
H	0.7042608647	2.1950461963	2.7555451682
H	1.7047673408	2.5873781131	1.3416207824
H	2.4183267394	1.7191529442	2.6846779882
H	-0.6447495166	0.4148820016	2.7634487471
H	-1.443083377	-1.7496727335	1.9803191123
H	-1.3510400795	-3.5072908896	-0.0467210004
H	0.0063207242	-3.984730013	0.9995345603
H	0.2605303368	-3.7661490359	-0.7462621947
Zn	-1.3877807863	0.4245869476	-0.805008286
Cl	-0.4578810708	2.3749714808	-1.0214001202
Cl	-3.2183833946	-0.7544657017	-0.6394970905

TSB-3 - E+ZPE=-3313.425822 - 1st freq. = -202.1995

C	0.1480253683	2.5527409799	0.3445421669
C	0.1978246417	1.889388083	-0.9960172259
C	-0.6965204033	2.1547788874	1.308708193
C	-1.6234378861	1.0667956836	1.1019559341
C	-1.7025578936	0.4493570162	-0.1614000204
C	-0.8805000611	0.8948811072	-1.176807657
O	1.1997744073	0.9006038657	-1.0408425091
C	0.3699459969	2.8885152693	-2.1255845907
C	-2.464481018	0.6563228546	2.254319531
H	-0.9136014384	0.4187627974	-2.149764702
C	-2.6122511081	-0.7114130559	-0.3995057302
O	-3.5558089551	-0.998003327	0.2881168248
O	-2.25721309	-1.3931253247	-1.4913134561
C	-3.0668088575	-2.536284597	-1.7926719237
H	-4.0993918142	-2.2308474556	-1.9601191893
H	-3.0278061398	-3.2457319195	-0.9668448482
H	-2.6379610217	-2.9679227543	-2.6921446366
H	-2.1377361737	1.1487115266	3.167457134
H	-2.4369932136	-0.4266709835	2.3779663524
H	-3.5094996741	0.9065388101	2.0423532693
H	-0.6707626384	2.6048859961	2.2932399113
H	0.8659526097	3.3472397585	0.5270707158
H	1.321520197	3.4060283439	-1.9889944481
H	-0.4408399531	3.6216828905	-2.1440706414
H	0.4033946557	2.3544581144	-3.0757589125
Zn	1.8419178287	-0.481385257	0.1855545426
Cl	3.7385942531	-1.3690313408	-0.4375494042
Cl	0.534970381	-0.9273929692	1.9457363203

Int.B3 - E+ZPE=-3313.437199 - 1st freq. = 21.9370

C	-0.2570429456	1.76440976	0.3301850037
C	-0.1340126585	0.5835936391	1.3073726986
C	1.0434173214	2.290165077	-0.1506665365
C	2.1204527732	1.4987000765	-0.2799593944

C	1.9958959013	0.0685263682	0.09310789
C	0.9494952056	-0.34840748	0.8209092814
O	-1.327546285	-0.091108646	1.5166520785
C	0.3130597703	1.1742715845	2.6612425439
C	3.4279608864	2.0595295684	-0.7633944635
H	0.8577049415	-1.3847396913	1.1264182615
C	3.0151902807	-0.9173166695	-0.3781564668
O	3.8251740966	-0.7067767892	-1.2432951539
O	2.9210461844	-2.0948095996	0.2554101111
C	3.8278582962	-3.1034095531	-0.1951752608
H	4.8577452515	-2.7759403233	-0.0533242956
H	3.663025918	-3.3152396178	-1.2516802821
H	3.6158499334	-3.9798578263	0.4108380359
H	3.3758786564	3.1477233459	-0.7960805591
H	3.6709087933	1.6760254202	-1.7543843241
H	4.2471156419	1.7615653687	-0.1054979581
H	1.0945762148	3.3336864936	-0.4393625701
H	-0.9097547766	2.5293894815	0.7453552048
H	-0.4755568406	1.8316256215	3.0329823854
H	1.2515519507	1.7254179525	2.5841824912
H	0.4301463089	0.349437769	3.3640643078
Zn	-2.4513812509	-0.5363061074	0.1252176566
Cl	-1.2440673027	1.2193447794	-1.1953790109
Cl	-4.0557562665	-1.5712510028	-0.8456186744

TSB-5 - E+ZPE=-3313.429748 - 1st freq. = -280.3961

C	0.0363768836	1.7131083636	1.2415714251
C	-0.086641473	0.2559228281	1.1647411388
C	1.1611184038	2.3523689009	0.8390752517
C	2.2748356542	1.6516282242	0.2752450791
C	2.1989921474	0.2687920109	0.1491629812
C	1.0232759363	-0.4020168443	0.5326583984
O	-1.2822961675	-0.2951566797	1.2034321394
C	0.7517436746	-0.2480506615	2.6436953871
C	3.4580904971	2.4587357451	-0.1623147323
H	0.9294680392	-1.4666323302	0.3620681803
C	3.2965259423	-0.5238628661	-0.4828297779
O	4.2778285328	-0.0536769811	-0.9946444528
O	3.0601224561	-1.8374718281	-0.4136029857
C	4.0272688386	-2.6712758094	-1.0623478355
H	5.0072047161	-2.5337275066	-0.6060320855
H	4.0818487676	-2.4212022537	-2.1213339347
H	3.674280293	-3.6890026266	-0.9245297019
H	3.3234816273	3.5060323556	0.103153334
H	3.5900995958	2.3694771117	-1.2427313333
H	4.3801098716	2.0795827341	0.2801307333
H	1.2247555205	3.4316773177	0.9115203384
H	-0.8197791826	2.2493983862	1.6369643574
H	-0.0672116654	0.0335696009	3.3012465987
H	1.6701805918	0.2936109897	2.8471248537
H	0.8727917281	-1.3275783296	2.6587168658
Zn	-2.1645442314	-0.7832686693	-0.474131654
Cl	-0.5571376913	-0.4150191387	-1.9959166571
Cl	-4.2183373062	-1.498234044	-0.5088309117

TSB-4 - E+ZPE=-3313.427330 - 1st freq. = -310.2134

C	-0.0002328338	-1.6115351446	0.8635607995
C	0.0537937207	-0.1866307111	1.0362179571
C	-1.1536172142	-2.2623255521	0.4045392385
C	-2.2740259118	-1.5583017186	0.0203437984
C	-2.2522295058	-0.1190361577	0.1301434465
C	-1.142324765	0.5234843787	0.5880638569
O	1.1872396424	0.4639180726	1.147297383
C	-0.4359902709	-0.6467315521	2.7034718243
C	-3.4537721021	-2.3085087704	-0.5202027153
H	-1.1046126149	1.6055217334	0.633946336
C	-3.4467591428	0.6965912128	-0.2754810833
O	-4.5395457363	0.2462885325	-0.4950196857
O	-3.1611255858	1.9979006637	-0.3503679463
C	-4.2525360373	2.8478867086	-0.7215651017
H	-5.0585541025	2.7629383551	0.0068520597
H	-4.6250526641	2.5680914173	-1.7064984344
H	-3.8458615784	3.8547414452	-0.7344157522
H	-3.2173262268	-3.3688082955	-0.5954858995
H	-3.7356130417	-1.9274585296	-1.502818943
H	-4.3279436606	-2.1714207841	0.1181117447
H	-1.13484115	-3.3392097513	0.2949952711
H	0.9041314841	-2.1654313282	1.0867209658
H	0.2863711691	-1.3303645757	3.1401243073
H	-1.4635990125	-0.9838618672	2.7918566966
H	-0.2694309536	0.3543936731	3.0928056034
Zn	2.4889297964	0.400767385	-0.31934864
Cl	1.5914981284	-1.121132395	-1.6919196147
Cl	4.2728091699	1.6430415553	-0.2640334729

Int.B5 - E+ZPE=-3313.487927 - 1st freq. = 16.8602

C	0.057882606	-1.6985125763	0.2654153079
C	0.1650977685	-0.2014803852	0.3035333237
C	-1.3145306135	-2.2156640171	-0.0022279937
C	-2.4136528227	-1.4535818113	-0.1126820944
C	-2.2431123846	0.0010995833	0.0061673669
C	-1.0402230488	0.5930207556	0.1833702851
O	1.2564606414	0.3621580021	0.4489505938
C	-3.7650574921	-2.0595182109	-0.3879272708
H	-0.9373413566	1.6682903439	0.247724699
C	-3.461914007	0.8886754027	-0.0059337907
O	-4.5301559874	0.5612960885	0.4329018467
O	-3.2028539582	2.0876013427	-0.5257656339
C	-4.299891136	3.0101146664	-0.5159316229
H	-4.6209219969	3.1976797971	0.508417757
H	-5.1343609469	2.6035330769	-1.0866789641
H	-3.9214882457	3.9176910113	-0.9765713867
H	-3.6511388533	-3.1235733145	-0.5937759145
H	-4.240941551	-1.5896764911	-1.2511518199
H	-4.4389452562	-1.9266240388	0.4578653497
H	-1.4015946015	-3.2942138039	-0.0970448043
H	0.7250922397	-2.0199660338	-0.5497201466
Zn	3.175219843	-0.3710729841	0.4410756383
Cl	3.2916675081	-1.7148822077	-1.2845616861
Cl	4.2354857727	0.326066582	2.1967778732

C	0.6177029251	-2.3055074972	1.5737795034
H	-0.0078478091	-2.0249985944	2.4226608327
H	0.6389092079	-3.392159214	1.4929634832
H	1.6363405651	-1.9640398625	1.7713230983

Int.B4 - E+ZPE=-3313.489742 - 1st freq. = 11.5046

C	0.0998450616	-1.3850854112	-0.1730726893
C	0.1292283302	0.0427731908	0.0690553458
C	1.2629378823	-2.0563535178	-0.2833560597
C	2.5912499126	-1.4528877761	-0.16668939
C	2.6632347396	-0.1127935579	-0.0038196384
C	1.4431480275	0.762829722	-0.0130960726
O	-0.8880361437	0.71447293	0.2761592681
C	3.7693419351	-2.3905226653	-0.2194894262
C	3.9851369595	0.5630275107	0.1503270007
O	5.0561257067	0.0597840321	-0.068367623
O	3.8467679459	1.8261165994	0.5812243372
C	5.0684528695	2.548058221	0.7687375614
H	5.6165921166	2.6094440841	-0.1713236395
H	5.6884885864	2.0482191377	1.5125722822
H	4.775434026	3.5362382009	1.1114673281
H	3.4274810361	-3.4251437413	-0.1970643199
H	4.4511897525	-2.2214154176	0.6132788719
H	4.3510163636	-2.2298533323	-1.1288010676
H	1.228450335	-3.1299037535	-0.4422099686
H	-0.8614293684	-1.8841127818	-0.2085983941
Zn	-2.9160437151	0.4132116352	0.4455528157
Cl	-3.2693846443	-1.6654729392	1.0249874003
Cl	-3.8709664013	2.2913352745	-0.0615555128
H	1.4820555142	1.4750501209	0.8148490728
C	1.3935072873	1.5897774116	-1.3307608113
H	2.2862232765	2.2085826221	-1.4057666982
H	1.3474119663	0.9221743243	-2.1937841744
H	0.5107903617	2.2290393168	-1.3204868985

TSB-2 - E+ZPE=-3313.422028 - 1st freq. = -45.1395

C	-0.8777723205	0.0686267942	2.1318040188
C	-0.5498734434	-1.1532381834	1.5613929016
C	-0.0119628371	1.1377782086	1.9784299833
C	1.2472002529	1.0962551853	1.2801888546
C	1.5496879172	-0.0690964339	0.6526756591
C	0.597839054	-1.2305023794	0.6116601281
O	-0.1059463163	-1.1697568399	-0.6116483733
C	-1.3927856559	-2.3576827416	1.6945593697
C	2.0555097084	2.362932653	1.2243813598
H	1.1341861848	-2.1807031493	0.6970353823
C	2.7559801686	-0.1861496542	-0.2294154508
O	3.4102700105	0.7415539845	-0.6219935803
O	3.0142986702	-1.4600671496	-0.5299724704
C	4.1058497481	-1.6662411999	-1.4322420143
H	5.0296847266	-1.2852984604	-0.9968991154
H	3.9109222185	-1.1513465308	-2.3726090522
H	4.1618638856	-2.740091969	-1.5838624603
H	1.7165911805	3.0578349983	1.9932597606
H	1.9210660051	2.831115205	0.246822766

H	3.1187687993	2.1708585943	1.3529102728
H	-0.3014558652	2.0947913987	2.4033882486
H	-1.8120856005	0.1932183071	2.6655195946
H	-2.3627805649	-2.1418643657	2.137770933
H	-0.8526261855	-3.0909421932	2.3069421142
H	-1.5290585767	-2.7972570674	0.7015037512
Zn	-1.5238344669	0.1592973109	-0.9010683338
Cl	-0.9182252224	2.3030270947	-0.8647496257
Cl	-3.5365124748	-0.7151364168	-0.6478026219

Int.B2 - E+ZPE=-3313.503922 - 1st freq. = 22.9716

C	-2.4445740115	-2.3071708145	1.0418538913
C	-1.0824548138	-2.0060196317	1.5526383252
C	-3.1285237445	-1.4559921375	0.2713311006
C	-2.610847367	-0.137782851	-0.0705091008
C	-1.3969748779	0.2750844816	0.4048443486
C	-0.5519024941	-0.6412014081	1.180243364
O	0.5878951662	-0.3511443197	1.5338836693
C	-0.0730245662	-3.0807667745	1.083788116
C	-3.4885554484	0.686659479	-0.9673614164
H	-1.1037482108	-2.0282913232	2.6512901544
C	-0.8577255469	1.6364013544	0.1519277944
O	0.3194145913	1.9142792911	0.011489946
O	-1.7859247378	2.5788762986	0.1292506944
C	-1.3152900518	3.9183849543	-0.1044978735
H	-0.808430025	3.9719621503	-1.0670843596
H	-0.6247944585	4.2097137799	0.6855401237
H	-2.205385558	4.5400927784	-0.0948673883
H	-4.1281462972	0.0315526041	-1.5582641082
H	-2.9152170886	1.3255051823	-1.6347612975
H	-4.1282872053	1.3331853524	-0.3596656862
H	-4.1031225024	-1.7236925624	-0.1187732201
H	-2.8611487295	-3.2781972184	1.291369283
H	-0.4063564641	-4.0680297184	1.4060755174
H	0.9047660391	-2.8700881639	1.5137968419
H	0.0155819541	-3.0616535168	-0.003169195
Zn	1.9135538198	0.5002041412	0.0586461697
Cl	3.7040265023	1.398587006	0.925155397
Cl	1.2770681266	-0.8411904134	-1.6145470916

Phenol 10 - E+ZPE=-613.701635 - 1st freq. = 28.4332

C	-1.202104525	-0.2951076672	-0.0630534201
C	0.1764695894	-0.3091724355	-0.0142089946
C	0.8448078212	0.9276486168	0.02011124
C	0.131245733	2.1508214224	0.0051361319
C	-1.2888229718	2.1315042381	-0.0454999136
C	-1.9231912021	0.9002333751	-0.0785220834
C	0.9411818367	3.3858162194	0.0442966549
O	2.1616600137	3.4033107886	0.0876871359
O	0.2504300679	4.5248868759	0.0295757348
C	1.0295384989	5.7242476968	0.0673717804
H	1.690736053	5.7723767969	-0.7973963195
H	0.3088072147	6.5372055415	0.0485218703
H	1.6275127783	5.7575018713	0.9776715183

H	-3.0052357721	0.8672080246	-0.1173298886
C	-2.1600870346	3.3650126001	-0.0659807089
H	-2.0082863644	3.9802134789	0.8213129367
H	-1.946763714	3.9946961697	-0.9301507967
H	-3.2061813343	3.0617080816	-0.1052602664
C	0.9847323983	-1.5747012593	0.0037242448
H	1.6030841574	-1.627172559	0.9025616994
H	0.3311234919	-2.4466794502	-0.0274634556
H	1.6660238217	-1.611865047	-0.8492242671
O	2.1823917191	0.8536135426	0.066833678
H	2.5420015321	1.7631986983	0.087300933
H	-1.7362251691	-1.2395181205	-0.0900406939

Phenol 11 - E+ZPE=-613.706275 - 1st freq. = 49.0448

C	-1.1945454355	-0.2882757813	0.0358246985
C	0.2099361631	-0.3214053846	0.0091815503
C	0.8824153202	0.8835293464	-0.0128425002
C	0.1873529599	2.104621223	-0.0087736385
C	-1.2156088133	2.1085889623	0.0180899396
C	-1.9188067344	0.8891971798	0.0407735093
H	-1.7396495134	-1.2286381935	0.0533712647
H	1.9650766815	0.907017658	-0.0337504461
C	0.9036373083	3.3907853189	-0.0322945977
O	0.3578812718	4.480251762	-0.0301117864
O	2.2320252616	3.2718637428	-0.0568894486
C	2.9621967088	4.5008587516	-0.0803191129
H	2.7369458801	5.0905095872	0.8081118434
H	4.0105432073	4.2164251389	-0.0985530154
H	2.7024194641	5.0771686868	-0.9680757016
C	-3.4203988793	0.9209612498	0.0693448537
H	-3.7785219005	1.4601910158	0.9491736864
H	-3.8121080591	1.4480824679	-0.803458895
H	-3.8273777811	-0.0901116099	0.0841819376
C	0.9397011021	-1.6397848482	0.005241232
H	2.0195023658	-1.4889758358	-0.0165492545
H	0.6981622257	-2.2248451245	0.8960513236
H	0.6644635504	-2.2381982495	-0.8667301004
O	-1.9555088931	3.2302363708	0.0237817698
H	-1.353278841	3.9966873654	0.0063160483

Phenol 12a - E+ZPE=-613.695393 - 1st freq. = 35.1247

C	-1.2509311821	-0.3073972983	-0.0566158077
C	0.1459487359	-0.2817926822	-0.1229657982
C	0.82827932	0.9207074781	-0.1090029581
C	0.1350604333	2.1342450064	-0.0283034997
C	-1.2665254722	2.1466366094	0.0397716781
C	-1.916506844	0.9087747096	0.0228577509
H	1.9107194392	0.9330690295	-0.1607171017
C	0.9107713477	3.4056330686	-0.0162320344
O	0.4428075049	4.513534961	0.0494219285
O	2.2403553314	3.1974422925	-0.0884805704
C	3.0403904758	4.3787763721	-0.0810808884
H	2.8768780845	4.9424486505	0.8376736562
H	4.0704759941	4.0377503303	-0.1437738061
H	2.7918183336	5.0111370312	-0.9336709467

C	-1.9702964637	-1.6247503383	-0.0732443153
H	-3.0487186486	-1.4787895861	-0.0157980618
H	-1.7355021986	-2.1795973042	-0.9845687268
H	-1.6514606706	-2.2475697462	0.7657669841
O	0.7795722382	-1.4893462945	-0.2006734921
H	1.73007529	-1.3549575571	-0.2410888226
H	-3.0007689665	0.8953370009	0.074615263
C	-2.0960020033	3.4023739979	0.1286194566
H	-1.8411496219	3.986842687	1.0134626931
H	-1.9250277116	4.054659248	-0.7285836792
H	-3.1537596155	3.1400549639	0.1693380389

Phenol 12b - E+ZPE=-613.695565 - 1st freq. = 25.0315

C	-1.1918864685	-0.3055623203	0.0630536348
C	0.2063958343	-0.2927170176	0.0363172375
C	0.818695683	0.9471184478	0.0120685076
C	0.1030055614	2.1517029368	0.0134538431
C	-1.3028335801	2.1279025729	0.0404226399
C	-1.9211381422	0.8774132374	0.0648890272
C	0.9499187016	3.3769340884	-0.0150818613
O	2.1551801976	3.3647277362	-0.0380871772
O	0.2512736674	4.5252507069	-0.0131607449
C	1.0392857204	5.715706722	-0.0402192551
H	1.6545515218	5.7429567113	-0.9396480532
H	0.3289422509	6.5385455219	-0.0349100862
H	1.688483696	5.7608117393	0.8342957482
H	-3.0062008375	0.8264505983	0.0860284552
C	-2.1916240357	3.3477291008	0.0448991439
H	-1.991857026	3.9802062062	0.9101052161
H	-2.0250230399	3.9624725351	-0.8398869732
H	-3.2378032824	3.0414181073	0.0678263093
C	0.9712071449	-1.5856889716	0.034921337
H	0.7369788798	-2.1764463988	0.9234430435
H	0.7033668408	-2.1944326497	-0.8316893314
H	2.0439779663	-1.3953867919	0.0124379633
O	-1.7913100429	-1.5255069072	0.0868442878
H	-2.7467270724	-1.4218349809	0.103916757
H	1.9008768213	1.0079283993	-0.0091413488

Phenol 13 - E+ZPE=-613.692829 - 1st freq. = -14.3238

C	-2.4230298151	0.424121799	-0.0065398597
C	-1.5604484988	1.5185481119	0.0258276609
C	-0.1962174177	1.2724332902	0.0330684588
C	0.2996064973	-0.0366075651	0.0170625505
C	-0.5558286925	-1.1468708135	-0.022532165
C	-1.9331010392	-0.8746118525	-0.0319197213
H	-3.4985202406	0.5870054301	-0.0127188579
H	0.5023170296	2.0980769801	0.0566851237
C	1.7791915414	-0.2398396914	0.0695276677
O	2.3372220635	-1.2784817169	0.3129714969
O	2.4593851003	0.8944574914	-0.1781600828
C	3.879723758	0.7757804375	-0.114390829
H	4.2335184972	0.0534169034	-0.8503599759
H	4.2681794933	1.767093783	-0.3324323516
H	4.1896427587	0.449924636	0.878867058

C	-2.110498733	2.9205437693	0.0560442747
H	-2.7003378815	3.088671017	0.9604336088
H	-1.3057541671	3.6555775416	0.0353990969
H	-2.7609699462	3.1040629423	-0.802306323
O	-2.7819457552	-1.9441944784	-0.0653731938
H	-3.6898632342	-1.6326014824	-0.0952899534
C	-0.0914107922	-2.579652164	-0.0665018416
H	0.6872821597	-2.7156913115	-0.816151045
H	0.3452589034	-2.8734452271	0.8896364013
H	-0.9292590289	-3.2355219201	-0.2898076581

Phenol 14 - E+ZPE=-613.688077 - 1st freq. = 45.0190

C	-1.2287803239	-0.2660644239	-0.3287363742
C	0.1498156367	-0.3304388313	-0.1746310814
C	0.9011569395	0.8246738472	0.0643480774
C	0.218998788	2.0483964573	0.1186139717
C	-1.172904376	2.137733426	-0.0167602474
C	-1.8755801001	0.9559876168	-0.2460836717
C	0.9803922248	3.3194165834	0.3293567257
O	0.7237402019	4.1525608134	1.1572189277
O	1.9900457528	3.4537777576	-0.5479424257
C	2.7671248349	4.644728754	-0.4052836205
H	3.2245225365	4.683443129	0.5841338644
H	3.527727623	4.5951346957	-1.1797226855
H	2.138414758	5.5251631394	-0.5384158465
O	0.7202812865	-1.5672521552	-0.2602852697
H	1.6775183022	-1.4931047026	-0.2678147304
H	-2.9521517485	0.9970882087	-0.3681230311
C	2.3874291603	0.6961282054	0.2950851233
H	2.9341941517	0.5777890726	-0.6457809173
H	2.7967522404	1.5699098938	0.7964950358
H	2.6033418851	-0.1648970797	0.9349465755
H	-1.772955438	-1.1842876909	-0.5124380677
C	-1.9089577969	3.4521642178	0.0662107858
H	-1.8932906785	3.8466782937	1.0832438248
H	-1.456331416	4.2102440321	-0.5767503347
H	-2.9459051946	3.3188462695	-0.2430589583

Meta Diels-Alder adduct - E+ZPE = -574.324254 - 1st freq. = 56.8673

C	-0.3534167896	-1.5083304314	-0.3165271454
C	-1.8886645906	-1.3105268648	-0.3795552774
C	0.1432395537	-0.2852717307	-0.1608176444
C	-2.3174834752	-0.8750167567	1.0466658122
C	-1.8259022652	0.3458679508	1.2047983232
O	-1.9321329942	-0.0405300492	-1.0424093504
H	0.1685891509	-2.4548563237	-0.3359979167
H	-2.8638516272	-1.497048151	1.7411930186
H	-1.8594052635	1.0004689582	2.062749298
C	1.5194959542	0.1683336033	0.0686460904
O	1.809996761	1.2986427541	0.3706919471
O	2.4206240181	-0.8130331095	-0.0853911036
C	3.7791546879	-0.4296320355	0.1326841205
H	4.0672968631	0.3564558852	-0.5656374533
H	4.3687924287	-1.3267799979	-0.0349748363
H	3.911631486	-0.0660924491	1.1519913362

C -1.0866858082 0.6450427021 -0.1193002854
H -0.9243605787 1.6825260178 -0.3917437185
C -2.7114849623 -2.3568509228 -1.0817411526
H -2.6473215187 -3.3068917197 -0.5471972061
H -3.7557740903 -2.0441986231 -1.1189990324
H -2.3488148099 -2.5001026564 -2.1005119136

Ortho Diels-Alder adduct - E+ZPE = -574.324318 - 1st freq. = 49.5920

C -0.3581307537 -1.4656145707 -0.3243526405
C -1.8858118414 -1.2669557915 -0.3737353259
C 0.131332049 -0.2381358153 -0.1717233294
C -1.1041233324 0.7023164088 -0.1324738714
C -2.3232709 -0.8417064416 1.0499758315
C -1.8336672348 0.3808914414 1.1980103066
O -1.949412053 -0.0130769007 -1.0456968622
H -2.4745925535 -2.0281243228 -0.8763523696
C -0.9378629467 2.1454533281 -0.5230952061
H 0.1735798384 -2.4060008386 -0.3320488184
H -2.862951474 -1.4615575423 1.7502376529
H -1.8646056477 1.0406959517 2.053171065
C 1.5151800717 0.1752862914 0.0948999097
O 1.8318356429 1.2612157758 0.5127447546
O 2.3989903701 -0.8016813712 -0.1608375889
C 3.7628598187 -0.4720811752 0.1057728742
H 4.0724661352 0.3789363564 -0.5012148284
H 4.3358440671 -1.3577003681 -0.1551255402
H 3.8945082774 -0.2243134001 1.159342457
H -0.4684407056 2.2159860932 -1.5053942841
H -0.3052813737 2.6590825562 0.2001633075
H -1.9179164541 2.6231873351 -0.5628134939

Methylpropiolate - E+ZPE = -305.097303 - 1st freq.=135.5147

C -1.9207742127 0.6211931969 -0.000011004
O -0.7345097822 0.4473311638 0.0000034807
O -2.5148713917 1.8158499947 -0.0000191046
C -2.9017883137 -0.4539837693 0.0000646215
C -3.6722041568 -1.3713070619 0.0001246813
H -4.357809392 -2.1860728159 0.0001700104
C -1.621472884 2.9341441226 -0.0000523298
H -2.2575985069 3.814464493 -0.0000629742
H -0.990407134 2.9114097675 0.8885544807
H -0.9904273161 2.9113727887 -0.888672402

Methylfurane- E+ZPE = -269.202049 - 1st freq.=139.3938

C -2.6435640895 -0.1007771687 0.0001469493
C -1.2906207325 -0.1056475885 -0.0001565607
C -0.8933305675 1.2745691197 0.0000900755
C -2.0381168023 2.0037632465 -0.0000942144
O -3.1118766624 1.1723649214 -0.000403253
H -3.3881134115 -0.8783508281 0.0002590659
H -0.6533893751 -0.974668909 -0.0002016877
H 0.1094869461 1.6700794828 0.000223124
C -2.3251730227 3.4612075351 -0.0001784004
H -2.9007193727 3.7452793889 -0.884083035
H -2.9010938101 3.7453036005 0.8834739873

H -1.3895001496 4.0191278794 0.0000138891

Dimethyl acetylene dicarboxylate - E+ZPE = -532.905751 - 1st freq.=24.7113

C	1.779058957596	0.478878688624	0.083319413023
C	2.977967606390	0.515136107315	0.063346397714
C	0.322710146687	0.504354552558	0.117596333032
O	-0.318111159373	1.483378019772	0.373526906897
O	-0.182970198211	-0.692425848945	-0.171298170367
C	4.434303793866	0.532511101141	0.102525909902
O	5.076109572895	0.235934442625	1.069586054900
O	4.938710635787	0.918196379653	-1.067415849855
C	6.369878823872	0.967546110010	-1.122654033732
H	6.785953244494	-0.021307443995	-0.930785976189
H	6.609005143919	1.300477414232	-2.128100084019
H	6.748886253000	1.669413561783	-0.380146912650
C	-1.614209644565	-0.763434954567	-0.160400362572
H	-1.854506226665	-1.792645797704	-0.409584605423
H	-1.994031602868	-0.503598679990	0.827486932985
H	-2.028433046822	-0.077391332513	-0.898990643647

Diels Alder adduct between methylfurane and DEAD - E+ZPE=-802.138685 - 1st freq.=32.0518

C	-0.2940862405	-1.5296174821	-0.4260130466
C	-1.812787603	-1.2807679194	-0.556027797
C	0.2242354453	-0.3304851936	-0.1707466266
C	-0.998693424	0.6380910243	-0.1330790893
C	-2.3188560176	-0.9455739919	0.8645880223
C	-1.7978894143	0.2434829025	1.1333533025
O	-1.7972314237	0.0179638433	-1.1410767591
H	-2.3683459146	-2.0018400498	-1.1461670782
C	-0.7465301537	2.0971574562	-0.3959268531
H	-2.9133182449	-1.5988975115	1.4852521558
H	-1.8402240026	0.8366404752	2.0351323945
C	1.5767691894	0.1097247984	0.2353036814
O	1.7637710498	0.7506606831	1.2380871186
O	2.5278633861	-0.2256658671	-0.6316005579
C	3.8545361029	0.1521250913	-0.2549351633
H	3.9208030334	1.2333613229	-0.1330451171
H	4.4956460737	-0.18466132	-1.0646069701
H	4.1287401935	-0.3315194979	0.6829691472
H	-0.2448260233	2.2251928299	-1.3566098422
H	-0.1187234207	2.5123388463	0.3940081719
H	-1.6957084274	2.6336802012	-0.4194951161
C	0.2813430817	-2.885390227	-0.4124598318
O	-0.3537979307	-3.869922435	-0.6936297735
O	1.5610012052	-2.9094542452	-0.0283005324
C	2.1671357554	-4.203488058	-0.0084150934
H	1.6428220802	-4.8557759629	0.6901528473
H	2.13914978	-4.6483205914	-1.003219473
H	3.1927897045	-4.0423973219	0.3119765392

5. NMR spectra

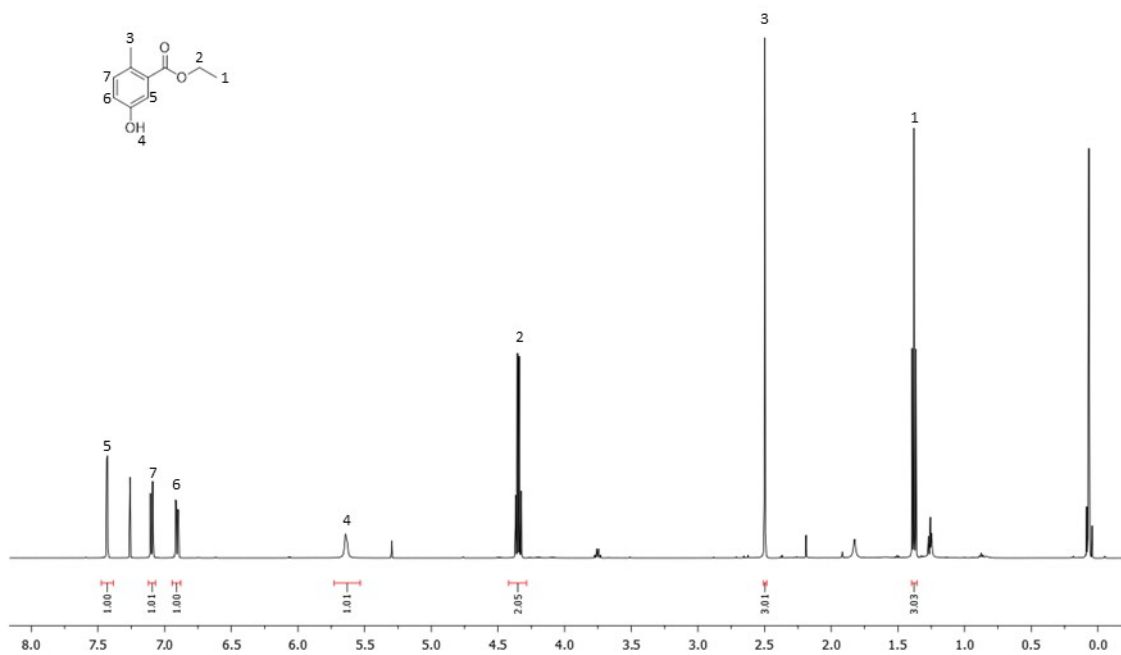


Figure S36 ¹H NMR of 1-o

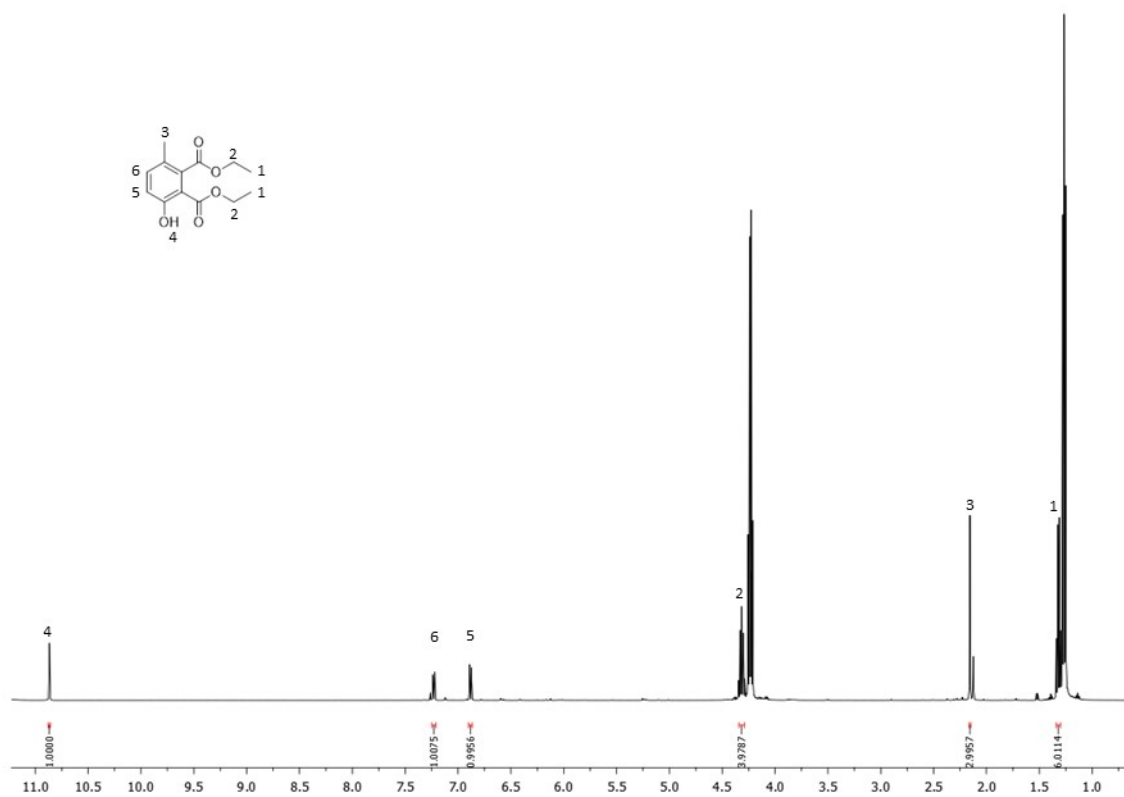


Figure S37 ¹H NMR of 3

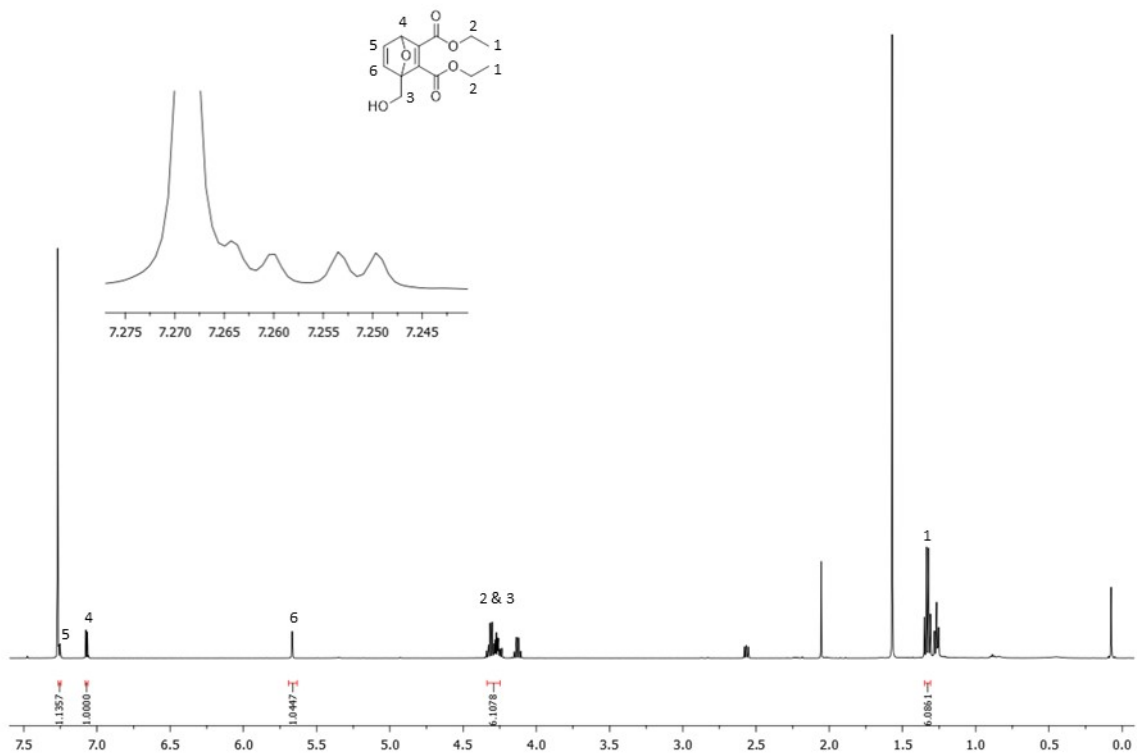


Figure S38 ¹H NMR of 4

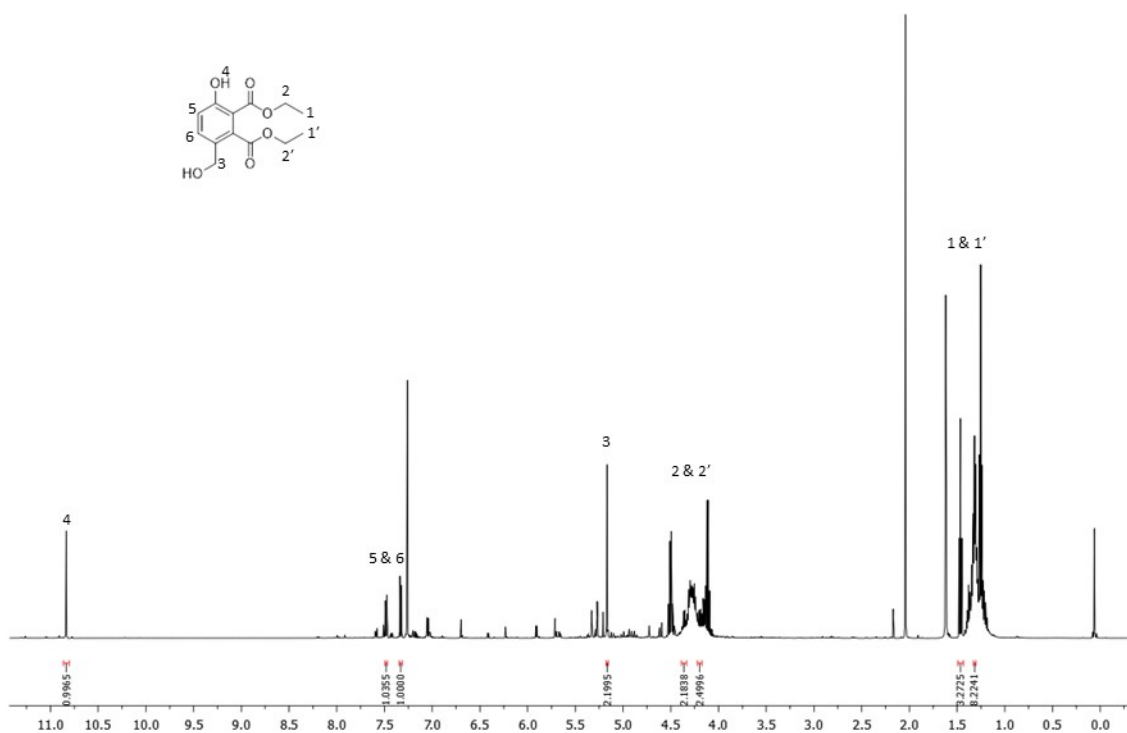


Figure S39 ¹H NMR of 5

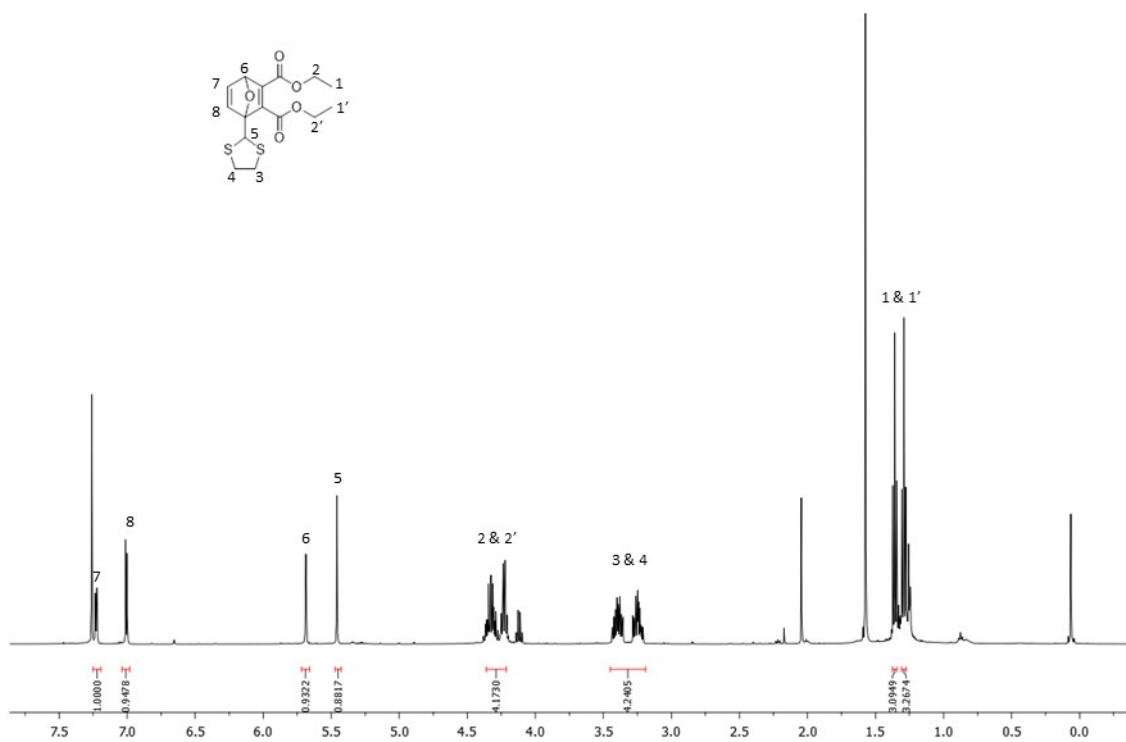


Figure S40 ¹H NMR of 7

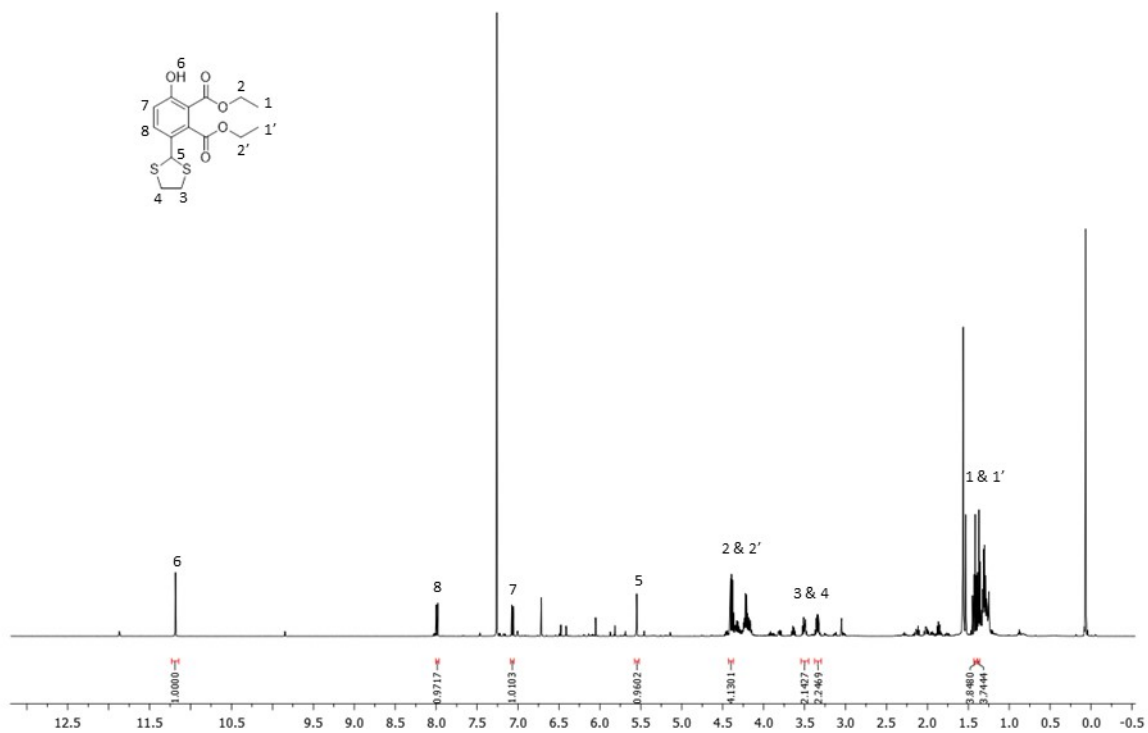


Figure 21 Figure S41 ¹H NMR of **8**

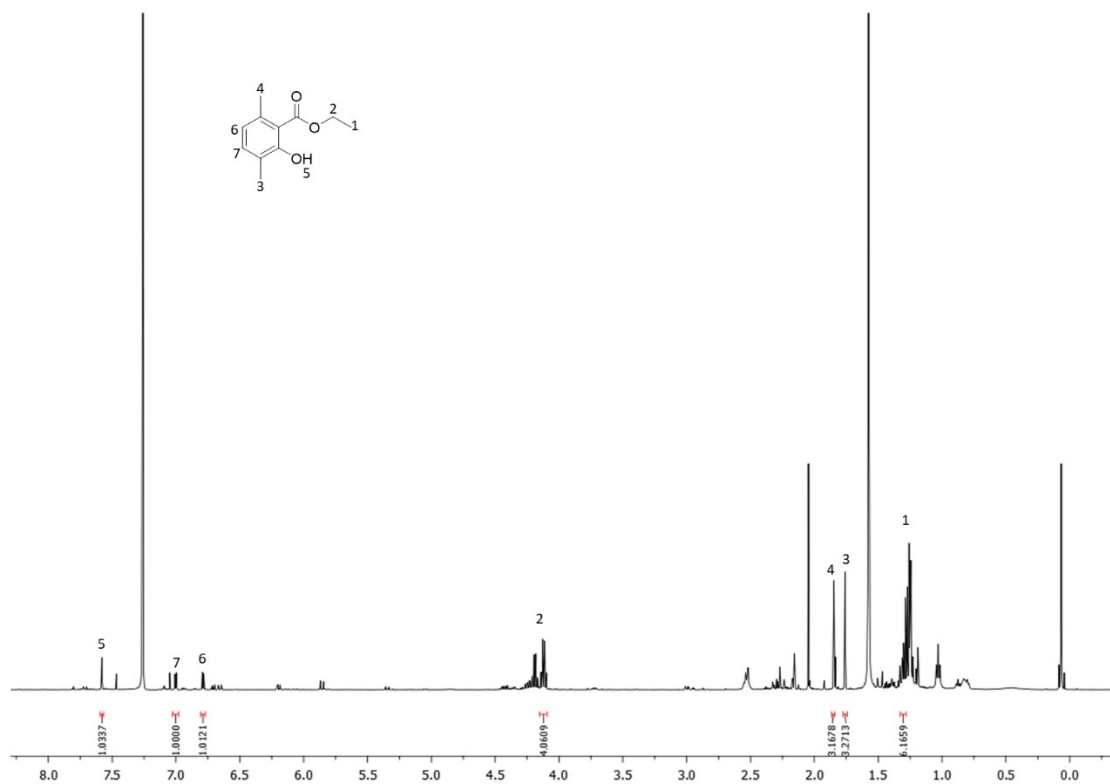


Figure S42 ¹H NMR of 10

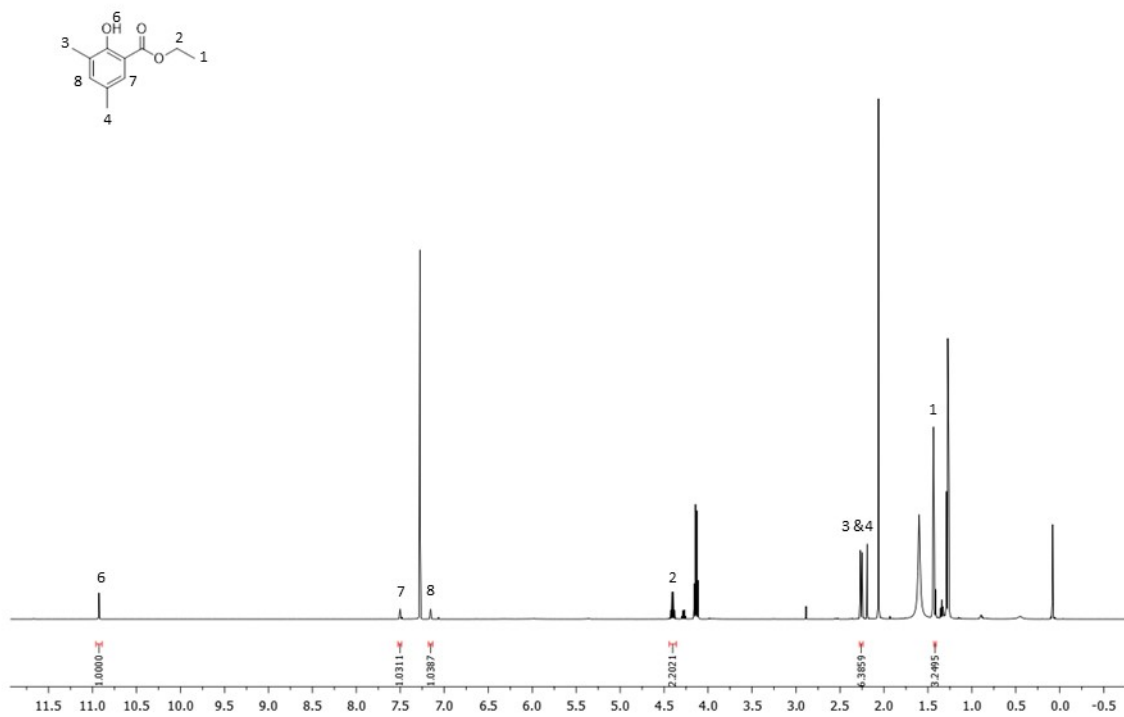


Figure S43 ¹H NMR of 11

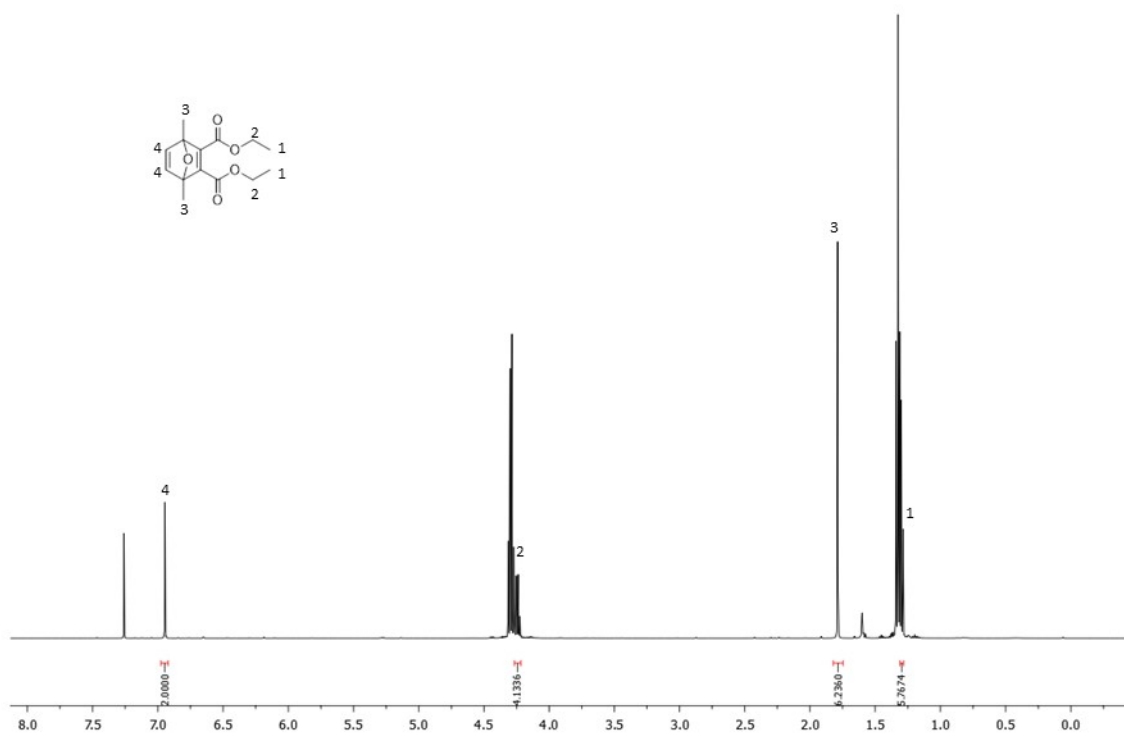


Figure S44 ¹H NMR of 15

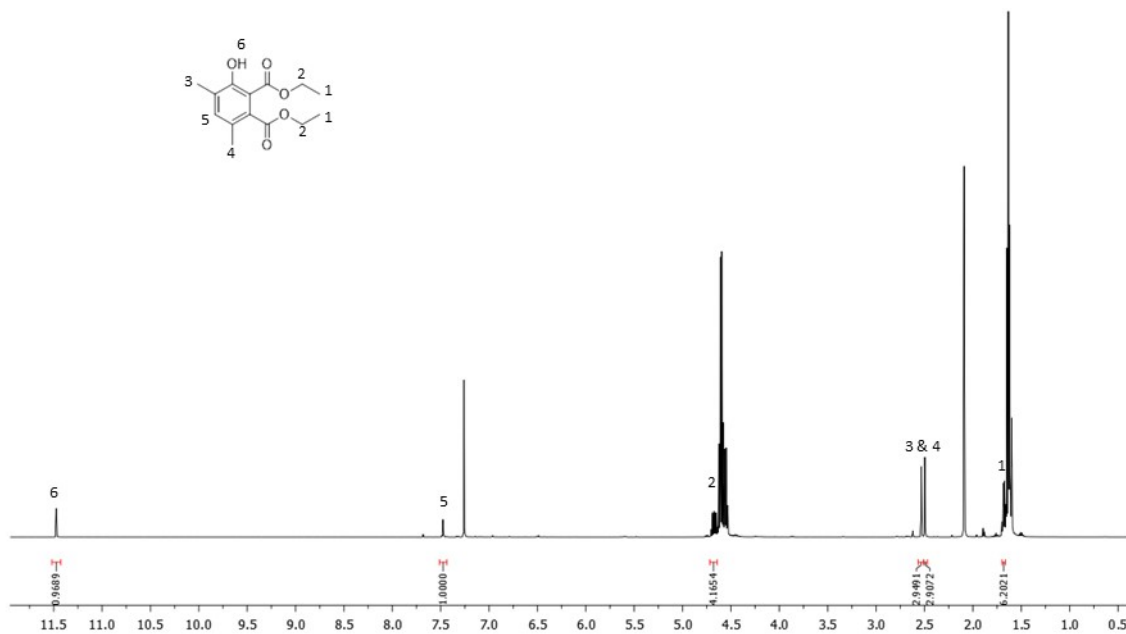


Figure S45 ^1H NMR of 16

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