

Supporting Information

Substituted Phthalic Anhydrides from Biobased Furanics: A New Approach to Renewable Aromatics

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1. Experimental Section

1.1. Materials

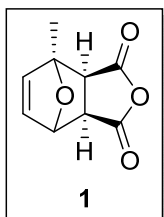
Furan ($\geq 99\%$, Aldrich), 2-methylfuran (99%, Aldrich), 2,5-dimethylfuran (99%, Aldrich), maleic anhydride ($\geq 99.0\%$, Fluka), amberlyst 70 (Hydrogen ion form), nafion-NR 50 (Hydrogen ion form, Aldrich), Pd/C (10 wt% Pd basis, Aldrich), Pd/C (5 wt% Pd basis, Aldrich), Pt/C (5 wt% Pt basis, Aldrich), Ru/C (5 wt% Ru basis, Aldrich), Rh/C (5 wt% Rh basis, Aldrich), 1,4-dinitrobenzene (analytical standard, Aldrich), zeolite Y (CBV600 with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio: 5.2, Zeolyst), zeolite Beta (CP814E with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio: 25, Zeolyst), H-VUSY zeolite (CBV712 with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio: 12, Zeolyst). All zeolite materials were converted to the H-form by calcination at 550 °C for 12 h prior to use. Tetrahydrofuran (THF, anhydrous, $\geq 99.9\%$, Sigma-Aldrich), toluene (anhydrous, 99.8%, Sigma-Aldrich), methanol (Merck, p.a.), petroleum ether (PE, Acros Organics, 40–60 °C), ethyl acetate (Acros Organics, 99+ %), silicagel (Alfa Aesar, 230-400 mesh), chloroform-D (99.8 atom % D, Aldrich), toluene- d_8 (anhydrous, 99.6 atom % D, Aldrich), tetrahydrofuran- d_8 (anhydrous, 99.5 atom % D, Aldrich), methanol- d_4 (anhydrous, 99.8 atom % D, Aldrich), activated carbon (Norit, CN1), magnesium sulfate (Acros Organics, 99 % extra pure, dried, contains 3 to 4 moles of water), celite® 545 coarse (Fluka). Hydrogen and nitrogen gases (volume % purity 99.99%) were purchased from Linde Netherlands. All chemicals were used as received, unless denoted otherwise.

1.2. Methods

Fourier transform infrared (FT-IR) spectra were collected on a Varian Scimitar 1000 FT-IR spectrometer equipped with a Pike MIRacle ATR Diamond/ZnSe single reflection plate and a DTSG-detector. Nuclear magnetic resonance (NMR) spectra were recorded on Varian 400-MR and Bruker Avance III spectrometers operating at 400.17 MHz (^1H) and 100.62 MHz (^{13}C). Gas chromatograms (GC) were collected using an Interscience Focus gas chromatograph equipped with an AS 3000 series autosampler. The GC parameters used were as follows: Injection volume 1 μL . Injector temperature 275 °C. Split ratio 1:33. Column flow (at 275 °C) 50 mL/min helium. GC column: Restek Rxi-5ms, 30 m x 0.25 mm x 0.25 μm . GC program (2,5-FDA.mth); hold 2 min at 70 °C, ramp 10 °C/min, final temperature 300 °C, hold 2 min. Total run time 27 min. Detector; FID at 300 °C. GC-MS analysis was performed on an Interscience Trace GC Ultra GC with AS3000 II auto sampler (He carrier gas, flow 1 mL/min, split flow 20 mL/min; Restek GC column Rxi-5ms 30 m x 0.25 mm x 0.25 μm ; GC program: hold 3 min at 50 °C, ramp 7.5 °C/min, final temperature 330 °C) connected to an Interscience Trace DSQ II XL quadrupole mass selective detector (EI, mass range 35-500 Dalton, 150 ms sample speed). Electrospray Ionisation (ESI) mass spectrometric measurements were carried out using a Waters LCT Premier XE Micromass system. Thermogravimetric analysis (TGA) was performed on an STA 6000 (Simultaneous Thermal Analyser) TG analyzer (Perkin Elmer Instruments). The samples were heated from 30 °C to 600 °C at a heating rate of 10 °C/min under a nitrogen flow of 40 mL/min. Melting point determinations were carried out using Differential Scanning Calorimetry (DSC) (Perkin Elmer Diamond series DSC). The temperature range used was 20 °C up to 200 °C at a heating rate of 10 °C/min.

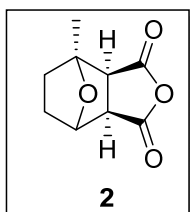
Short path distillation and sublimation experiments were carried out using a Kugel-rohr oven (Buchi Glass Oven B-585). For the stability measurements of DA adduct **1** and hydrogenated DA adduct **2**, the samples were dissolved in d-toluene and allowed to stand for 10 min at selected temperatures before the NMR analyses are performed.

1.3. Diels-Alder Reaction: Synthesis of (3a*S*,4*R*,7*S*,7a*R*)-4-methyl-3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione: **1**



A round-bottom flask equipped with a water-cooled condenser and mechanical over-head stirrer was charged with 2-methylfuran (59.9 g, 0.73 mol) and maleic anhydride (59.7 g, 0.60 mol). The suspension was stirred at 10-15 °C in an ice bath. During the course of the reaction, the suspension turned into a clear homogeneous solution, from which a crystalline solid precipitated over the course of 2-3 h. The pale-yellow adduct **1** obtained was further subjected to high vacuum treatment (0.02 mbar, for 3 h) to remove the residual 2-methylfuran. Yield (crude): 105.0 g, 96%; m.p. 83–85 °C (lit.^[1] m.p. 79–80 °C); ¹H NMR (400 MHz, CDCl₃): mainly *exo* isomer: δ = 6.56 (dd, J = 5.7, 1.8 Hz, 1H), 6.36 (d, J = 5.6 Hz, 1H), 5.35 (d, J = 1.8 Hz, 1H), 3.30 (d, J = 6.7 Hz, 1H), 3.04 (d, J = 6.7 Hz, 1H), 1.80 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 170.21, 168.71, 140.59, 137.41, 89.48, 81.83, 51.84, 50.96, 15.33 ppm; FT-IR (neat): ν = 661, 673, 736, 794, 830, 845, 877, 895, 922, 957, 983, 992, 1144, 1201, 1230, 1274, 1322, 1390, 1447, 1772, 1838 cm⁻¹.

1.4. Hydrogenation of DA Adduct **1**: Synthesis of (3a*S*,4*R*,7*S*,7a*R*)-4-methylhexahydro-4,7-epoxyisobenzofuran-1,3-dione: **2**



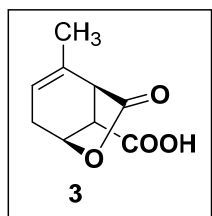
A stainless steel pressure reactor (Parr Series 5000 Multiple Reactor System) was charged with the crude adduct **1** (75.0 g, 0.41 mol), 10 wt% Pd/C catalyst (2.0 wt%) (1.5 g), and THF (450 mL). The reactor was then purged with 10 bar of N₂ (3 times), and then pressurized with 80 bar of hydrogen (For practical reasons the reaction was performed using 80 bar of hydrogen, however, in principle, 20-25 bar of hydrogen is also sufficient to perform the hydrogenation resulting in longer reaction time for completion; a reaction on a 5 g scale was run with 5 bar to full conversion overnight). The reactor was then stirred at room temperature at 300 rpm. A drop in the hydrogen pressure during the reaction was observed. Subsequently the reactor was re-pressurized to 80 bar. After 5.0 h conversion was

complete, as indicated by lack of further hydrogen consumption. Excess hydrogen gas was cautiously vented off and the reactor was flushed with 5 bar of nitrogen gas (3 times). The reaction mixture was filtered over a glass filter containing Celite. The clear pale-yellow filtrate obtained was concentrated to dryness under reduced pressure using a rotary evaporator. The crude product **2** was further purified by recrystallization from ethyl acetate, which afforded **2** as a colorless crystalline solid. Yield: 73.0 g, 96%; m.p. 98–100 °C (lit.^[2] m.p. 105–106 °C); ¹H NMR (400 MHz, CDCl₃): predominantly *exo* isomer: δ = 4.92 (d, J = 5.4 Hz, 1H), 3.27 (d, J = 7.4 Hz, 1H), 3.05 (d, J = 7.3 Hz, 1H), 2.07 – 1.97 (m, 1H), 1.71 – 1.65 (m, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 169.36, 167.76, 84.74, 77.56, 50.59, 50.12, 33.52, 27.81, 15.37 ppm; IR (neat): ν = 2990, 1768, 1226, 1976, 1194, 1085, 909 cm⁻¹; ESI-MS (TOF): (MH⁺) found 183.0316. C₉H₁₁O₄ requires 183.0657.

1.5. Aromatization of Hydrogenated DA adduct (**2**)

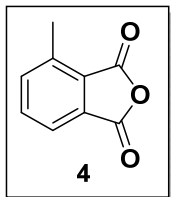
All aromatization reactions were performed using 75-ml stainless steel autoclaves (Parr Series 5000 Multiple Reactor System). In a typical experiment, the reactor was charged with hydrogenated DA adduct **2** (0.50 g, 2.7 mmol), the zeolite (see Table 1, main text) and dehydrogenation catalysts (see Table 1, main text), and toluene (30 mL). The reactor was then purged and with 10 bar of nitrogen(3 times) and then magnetically stirred (750 rpm) at the temperature and for the time specified in Table 1 (in main text). After completion, the reactor was cooled to room temperature and excess pressure (up to 3 bar) vented off carefully. Molecular hydrogen formed in the reaction was detected using a hydrogen detector (Hydrogen leak controller, Benelux LC 10). The crude reaction mixture was filtered over a G-3 glass filter funnel containing Celite and washed with toluene (3 x 10 mL) giving a pale yellow clear solution, which was then concentrated to dryness under reduced pressure using a rotary evaporator yielding pale yellow crystalline material. The analysis of the crude product by ¹H NMR spectroscopy confirmed the formation of desired aromatic compound 3-methylphthalic anhydride **4** in addition to four different products. The product distribution in the crude mixture was calculated by quantitative NMR (q-NMR) analysis using 1,4-dinitrobenzene as internal standard. For analytical means, the products **3**, **4**, **5a**, **5b** and **6** were isolated and purified by techniques including sublimation, distillation, and column chromatography, as described below.

(1S,5S)-2-Methyl-7-oxo-6-oxabicyclo[3.2.1]oct-2-ene-8-carboxylic acid: **3**



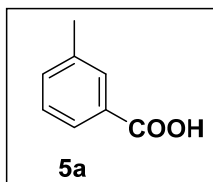
Kugel-rohr oven short path distillation condition: 130 °C at 0.02 mbar for 2-3 h to afford a colorless transparent oil. ¹H NMR (400 MHz, CDCl₃): δ = 9.51 (br, COOH), 5.44 (s, 1H), 5.04 (s, 1H), 3.12 (s, 1H), 2.96 (s, 1H), 2.65 – 2.44 (m, 2H), 1.89 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 176.57, 174.28, 133.56, 119.93, 119.85, 49.05, 44.69, 32.63, 22.40 ppm; IR (neat): ν = 2903, 1770, 1727, 1428, 1228, 1190, 906 cm⁻¹; ESI-MS (TOF): (MH⁻) found 181.0501. C₉H₉O₄ requires 181.0501.

4-Methylisobenzofuran-1,3-dione: 4



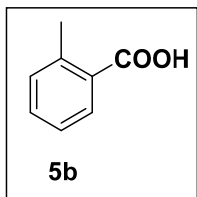
Sublimation conditions: 110-120 °C at 0.02 mbar for 2.0 h giving a colorless needle-shaped product. M.p. 119-121 °C (lit.^[1] m.p. 115-116 °C); ¹H NMR (400 MHz, CDCl₃): δ = 7.83 (d, J = 15.2 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 7.6, 0.9 Hz, 1H), 2.74 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 161.73, 161.62, 139.10, 136.55, 134.32, 130.25, 127.15, 121.91, 16.33 ppm; FT-IR (neat): ν = 667, 693, 730, 770, 817, 875, 1042, 1061, 1139, 1216, 1240, 1256, 1272, 1352, 1480, 1694, 1755, 1838 cm⁻¹; ESI-MS (TOF): found 162.0302. C₉H₆O₃ requires 162.0310.

meta-Toluic acid: 5a



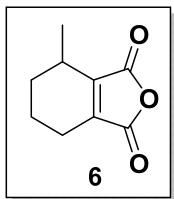
Column chromatography conditions: Eluent: ethyl acetate/petr. ether, (1:9) giving a pale yellow crystalline material. M.p. 111-113 °C (lit.^[3] m.p. 112-114 °C); ¹H NMR (400 MHz, CDCl₃): δ = 12.56 (COOH), 7.91 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 2.41 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 172.82, 138.31, 134.63, 130.72, 129.24, 128.40, 127.39, 21.38 ppm; IR (neat): ν = 2829, 2667, 1676, 1423, 1287, 922, cm⁻¹.

ortho-Toluic acid: 5b



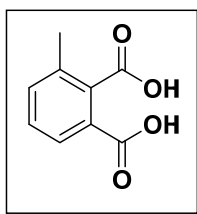
Column chromatography conditions: Eluent: ethyl acetate/petr. ether, (1:9) giving pale yellow crystalline material. M.p. 104-106 °C (lit.^[3] m.p. 101-102 °C); ¹H NMR (400 MHz, CDCl₃): δ 12.42 (s, 1H), 8.08 (d, 1H), 7.44 (t, J = 8.2 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 2.66 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 173.73, 141.42, 133.02, 131.95, 131.63, 128.32, 125.91, 22.23 ppm; IR (neat): ν = 2882, 2645, 1671, 1403, 1267, 907 cm⁻¹.

4-Methyl-4,5,6,7-tetrahydroisobenzofuran-1,3-dione: 6



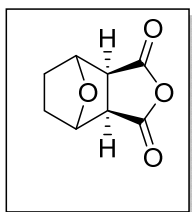
Column chromatography conditions: Eluent: ethyl acetate/petr. ether, (1:19) giving colourless transparent oil. ^1H NMR (400 MHz, CDCl_3): δ = 2.82 – 2.67 (m, 1H), 2.45 – 2.34 (m, 2H), 1.98 – 1.69 (m, 3H), 1.60 – 1.47 (m, 1H), 1.28 (d, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 163.20 , 162.81 , 146.97 , 143.26 , 28.10 , 25.58 , 19.39 , 19.37 , 17.20 , 16.59 ppm; IR (neat): ν = 2960, 1728, 1440, 1172, 992 cm^{-1} ; GCMS (EI): found 166.069. $\text{C}_9\text{H}_{10}\text{O}_3$ requires 166.063.

1.6. Synthesis of 3-methylphthalic acid



A round-bottom flask equipped with a water-cooled condenser and an addition funnel was charged with **4** (2.00 g, 12.3 mmol) in ethanol (20 mL). Then, potassium hydroxide (2.76 g, 49.3 mmol) in ethanol was added drop-wise at room temperature with vigorous stirring. The resulting suspension was further refluxed at 80 °C for 15 h. After cooling down to room temperature, the dipotassium salt of 3-methylphthalate was filtered off and dried in a vacuum oven at 50 °C for 5 h. Next, the dipotassium salt was dissolved in water (20 mL) and cooled down to 5 °C. Subsequently, the solution was acidified with conc. HCl to a pH of 1. After stirring for 15-30 min at 5 °C, the precipitate formed was filtered off and dried in a vacuum oven at 50 °C for 5 h. The crude product was further purified by recrystallization from diethyl ether to afford colourless crystals. Yield: 2.1 g, 95 %; m.p. 146–148 °C (lit.^[4] m.p. 155 °C); ^1H NMR (400 MHz, CDCl_3): δ = 7.82 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 174.58, 168.97, 135.19, 134.83, 134.68, 129.46, 127.60, 126.26, 17.88 ppm; IR (neat): ν = 3220, 2870, 2669, 1669, 1426, 1282, 900 cm^{-1} ; ESI-MS (TOF): (MH-) found 179.0344. $\text{C}_9\text{H}_7\text{O}_4$ requires 179.0344.

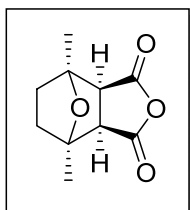
Synthesis of (3aR, 4S, 7R, 7aS)-hexahydro-4,7-epoxyisobenzofuran-1,3-dione



A round-bottom flask equipped with a water-cooled condenser and mechanical over-head stirrer was charged with furan (4.2 g, 61.2 mmol) and maleic anhydride (5.0 g, 50.9 mmol). The suspension was stirred at 10-15 °C using an ice/water bath. During the course of the reaction, the suspension turned into a clear homogeneous solution, and finally to a crystalline solid after 2-3 h. The reaction mixture was further subjected to high vacuum (0.02 mbar) for 3.0 h at room temperature to remove residual furan. The colorless adduct was obtained in quantitative yield.

Subsequently, a pressure reactor was charged with the crude adduct (8.0 g, 48.1 mmol), 10 wt% Pd/C catalyst (2.0 wt%) (0.16 g), and THF (50 mL). Next, the reactor was purged with 10 bar of nitrogen (3 times), and then pressurized with 80 bar of H₂. The reactor was then stirred at room temperature at 300 rpm. A drop in the hydrogen pressure during the progress of reaction was noted and the vessel was subsequently re-pressurized to 80 bar. No further consumption of hydrogen gas indicated completion of reaction and the starting material had been completely converted within 5 h. Excess hydrogen gas was cautiously vented off and the reactor was flushed with 5 bar of nitrogen gas (3 times). The reaction mixture was filtered over a G-3 glass filter containing Celite, giving a colorless clear solution, which was then concentrated to dryness under reduced pressure using a rotary evaporator. The crude product was further purified by recrystallization from ethyl acetate which afforded hydrogenated DA adduct as colorless crystalline material. Yield: 7.8 g, 96 %; m.p. 109-111 °C (lit.^[5] m.p. 115.8-117.7 °C); ¹H NMR (400 MHz, CDCl₃): δ = 5.09 – 4.91 (m, 1H), 3.18 (s, 1H), 1.96 – 1.77 (m, 1H), 1.69 – 1.48 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 171.49, 80.39, 50.79, 28.58 ppm; IR (neat): ν = 2990, 1770, 1418, 1213, 1079, 894 cm⁻¹; ESI-MS (TOF): found 168.0636. C₈H₈O₄ requires 168.042.

Synthesis of (3aR,4R,7R,7aS)-4,7-dimethylhexahydro-4,7-epoxyisobenzofuran-1,3-dione



A round-bottom flask equipped with a water-cooled condenser and mechanical over-head stirrer was charged with 2,5-dimethylfuran (5.8 g, 61.2 mmol) and maleic anhydride (5.0 g, 50.9 mmol). The suspension was stirred at 10-15 °C using an ice/water bath. During the course of the reaction, the suspension turned in to a clear homogeneous solution, from which a crystalline solid formed in 2-3 h. The reaction flask was further subjected to high vacuum, 0.02 mbar, for 3.0 h at room temperature to remove residual 2,5-dimethylfuran. The colorless adduct was obtained in quantitative yield and used as such directly in the hydrogenation reaction.

Subsequently, a pressure reactor was charged with the crude adduct (8.5 g, 43.7 mmol), 10 wt% Pd/C catalyst (2.0 wt%) (0.17 g), and THF (50 mL). Next, the reactor was purged with 10 bar of nitrogen(3 times), and then pressurized with 80 bar of hydrogen. The reactor was then stirred at room temperature at 300 rpm. A drop in the hydrogen pressure during the progress of reaction was noted

and the vessel was subsequently re-pressurized to 80 bar. No further consumption of hydrogen gas indicated completion of reaction and the starting material had been completely converted within 5 h. Excess hydrogen gas was cautiously vented off and the reactor was flushed with 5 bar of nitrogen gas (3 times). The reaction mixture was filtered over a G-3 glass filter containing Celite, giving a colourless clear solution, which was then evaporated to dryness under reduced pressure using a rotary evaporator. The crude product was further purified by recrystallization from ethyl acetate which afforded the hydrogenated DA adduct as colorless crystalline solid. Yield: 8.1 g, 94 %; m.p. 136–138 °C (lit.^[6] m.p. 140-143 °C); ¹H NMR (400 MHz, CDCl₃): δ = 3.14 (s, 1H), 1.78 (s, 2H), 1.61 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 170.74, 170.07, 86.02, 54.37, 37.62, 28.39, 17.81 ppm; IR (neat): ν = 2970, 1769, 1418, 1204, 1069, 910 cm⁻¹; GCMS (EI): found 196.096. C₁₀H₁₂O₄ requires 196.073.

2. Stability of DA adduct (1) and hydrogenated DA adduct (2)

2.1. Variable temperature ^1H NMR analyses of adduct 1 (MA: maleic anhydride, MF: 2-methylfuran)

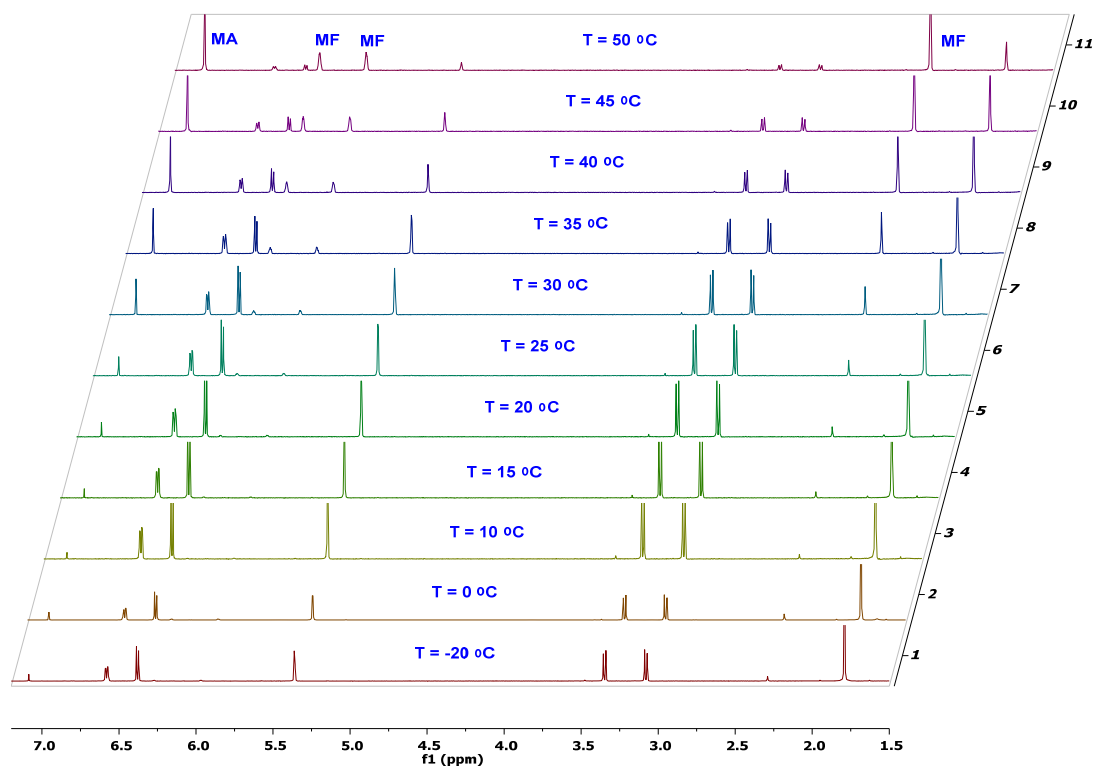


Figure S1. Retro Diels-Alder reaction of DA adduct 1 in CDCl_3 monitored by variable temperature ^1H NMR spectroscopy.

2.2. Stability of DA adduct 1 in different solvents as a function of time

The stability of DA adduct 1 at $20\text{ }^\circ\text{C}$ was assessed using different solvents (d-chloroform, d-toluene, d-methanol, and d-THF) as a function of time. Among the solvents used, d-chloroform and d-methanol showed significant retro-DA of DA adduct 1. Conversely, DA adduct 1 was found to be reasonably stable in both d-toluene and d-THF. In d-toluene, for example, only $<7\%$ and 55% r-DA reactions were observed after 1 h and 19 h, respectively; hence, toluene was chosen as solvent for the initial aromatization reactions with the non-hydrogenated DA adduct

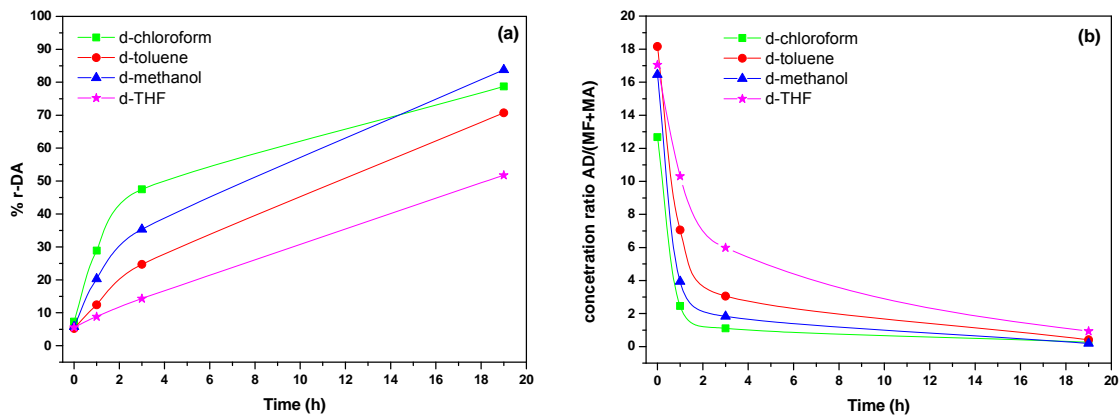


Figure S2. The graphs depict (a) time versus % retro-Diels-Alder reaction and (b) time versus concentration ratio of DA adduct / MF+MA (MF+MA = 2-methylfuran and maleic anhydride DA adduct)

2.3. Stability of DA adduct 1 and hydrogenated DA adduct 2 in d-toluene as a function of time

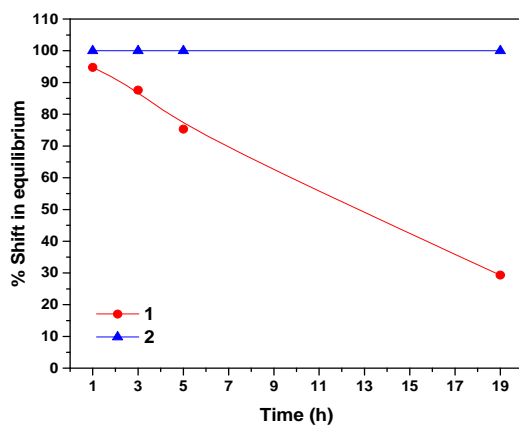


Figure S3. The stability of adducts 1 and 2 were compared in d-toluene at 20 °C as a function of time.

3. Calculations

Conversion of the starting material, molar yields and selectivities of the products were calculated using the following equations:

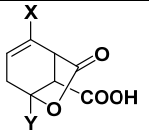
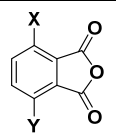
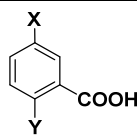
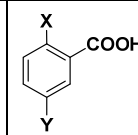
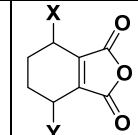
$$\text{Molar yield \%} = \frac{\text{moles of analyte}}{\text{moles of substrate}} \times 100\%$$

$$\text{Selectivity\%} = \frac{\text{moles of analyte}}{\text{moles of substrate converted}} \times 100\%$$

$$\text{Conversion\%} = \frac{(\text{moles of substrate before reaction}) - (\text{moles of substrate after reaction})}{\text{moles of substrate before reaction}} \times 100\%$$

Mole balance = sum of the molar yields of all the products (including the starting adduct) calculated from the crude mixture after the reaction.

4. Table S1. Optimization of aromatization conditions of hydrogenated DA-adduct 2.

Entry	zeolite Y (wt%) ^a	Metal on carbon (3wt%)	Time (h)	Temp (°C)	Conversion (mol%)	Molar yield (%) [Selectivity (%)] ^b					Mole balance (%) ^c
											
1	H-Y (10%)	- ^d	24	150	50	23 [45]	4 [8]	2 [5]	- ^f	3 [6]	84
2	H-Y (50%)	- ^d	24	150	91	52 [57]	6 [7]	2 [3]	- ^f	3 [3]	72
3	H-Y (10%)	Pd/C ^e	24	150	44	14 [33]	14 [33]	2 [4]	- ^f	8 [18]	94
5	- ^d	Pd/C ^e	24	200	0	- ^f	- ^f	- ^f	- ^f	- ^f	- ^f
6	H-Y (10%)	Pd/C ^e	01	200	54	15 [28]	17 [31]	4 [7]	- ^f	2 [3]	84
7	H-Y (10%)	Pd/C ^e	03	200	87	11 [13]	37 [42]	9 [10]	1 [1]	4 [5]	75
8	H-Y (10%)	Pd/C ^e	05	200	90	6 [7]	46 [51]	15 [17]	2 [2]	3 [4]	82
9	H-Y (10%)	Pd/C ^e	08	200	90	6 [6]	47 [52]	16 [18]	1 [1]	2 [3]	82

a. wt% based on adduct; b. calculated from q-NMR analyses using 1,4-dinitro benzene as internal standard; c. mole balance is determined from the total number of moles calculated from the crude mixture after the reaction by NMR analysis; d. no catalyst was added; e. 10wt% metal on carbon; f. not observed.

5. ^1H and ^{13}C NMR spectra of all compounds

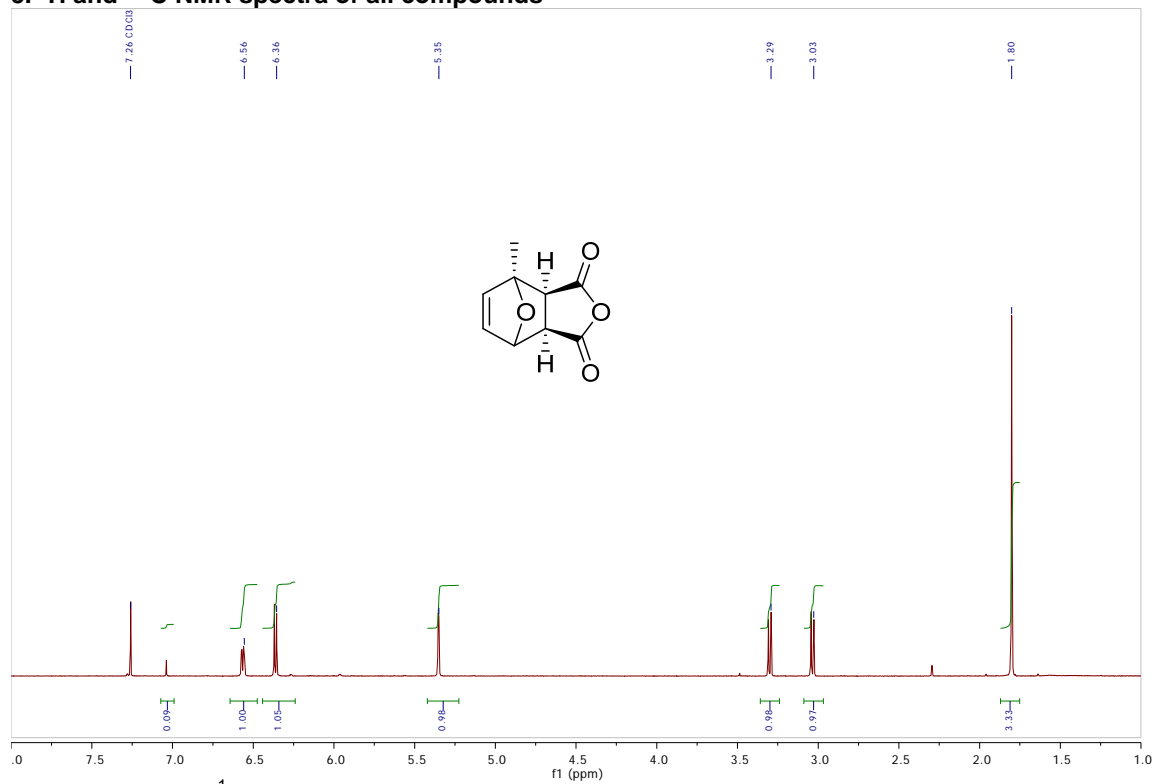


Figure S5.1. ^1H NMR spectrum of (3aS,4R,7S,7aR)-4-methyl-3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione **1** in CDCl_3 .

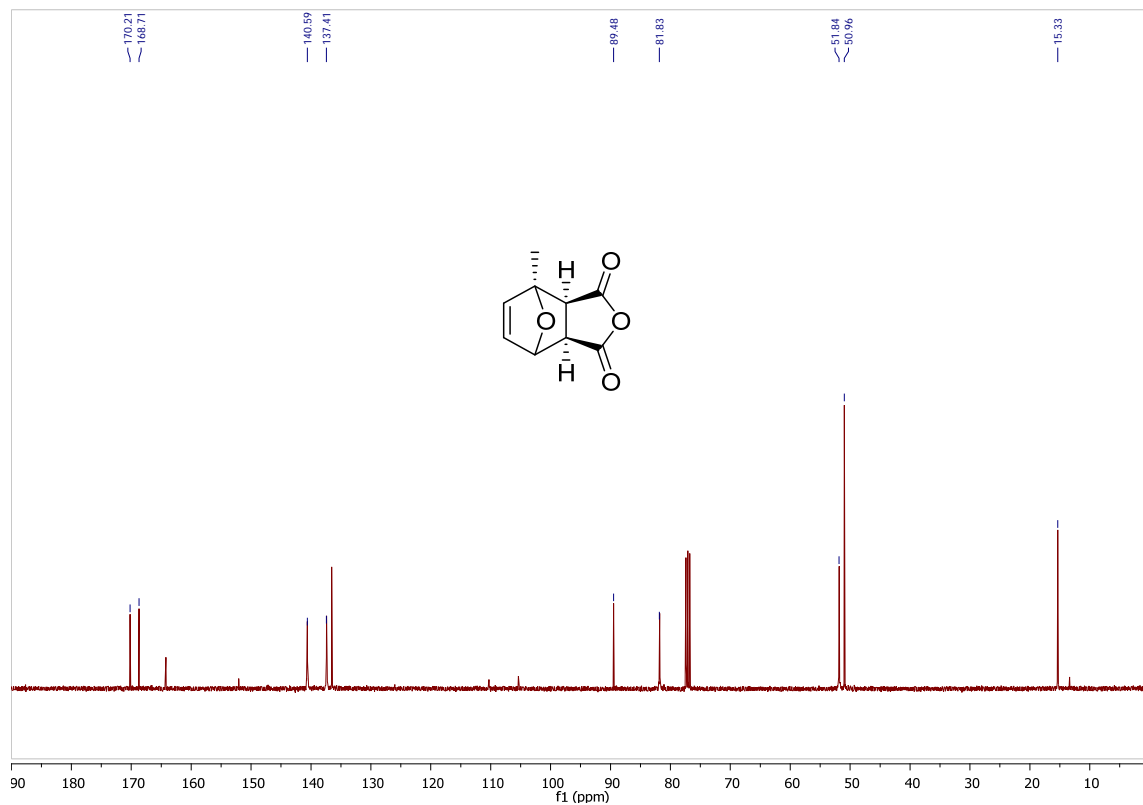


Figure S5.2. ^{13}C NMR spectrum of (3aS,4R,7S,7aR)-4-methyl-3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione **1** in CDCl_3 .

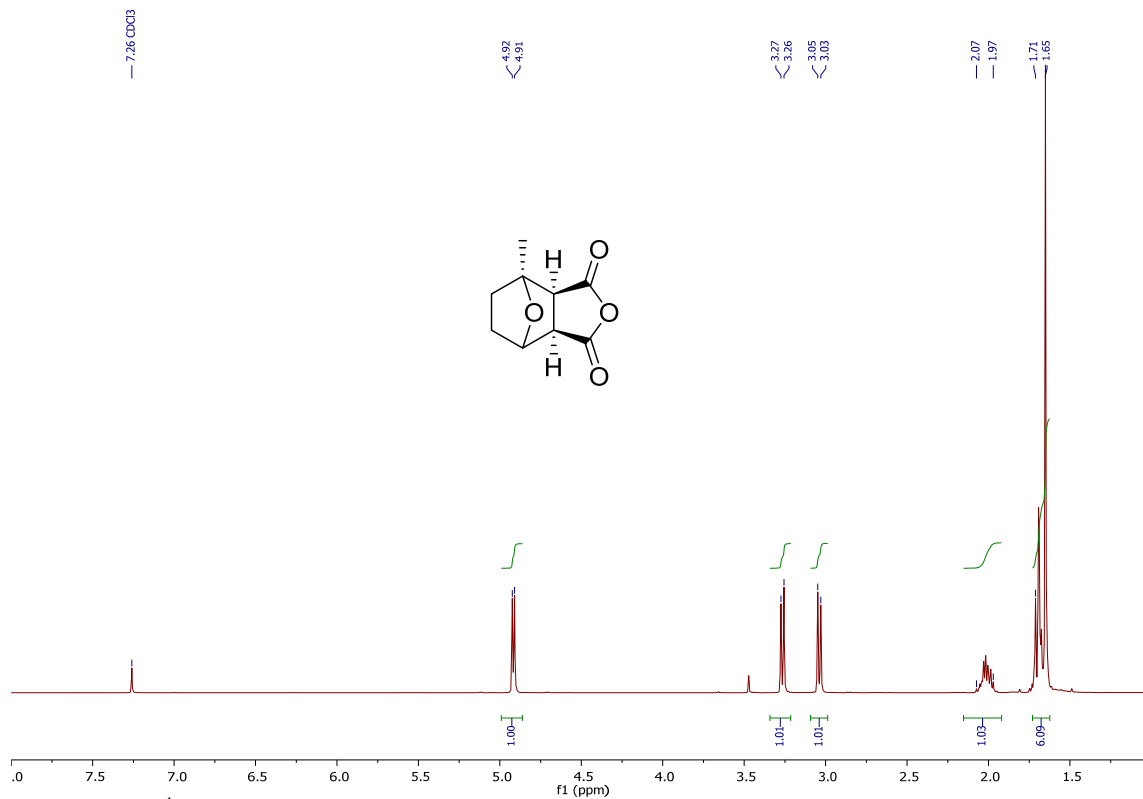


Figure S5.3. ¹H NMR spectrum of (3aS,4R,7S,7aR)-4-methylhexahydro-4,7-epoxyisobenzofuran-1,3-dione **2** in CDCl₃.

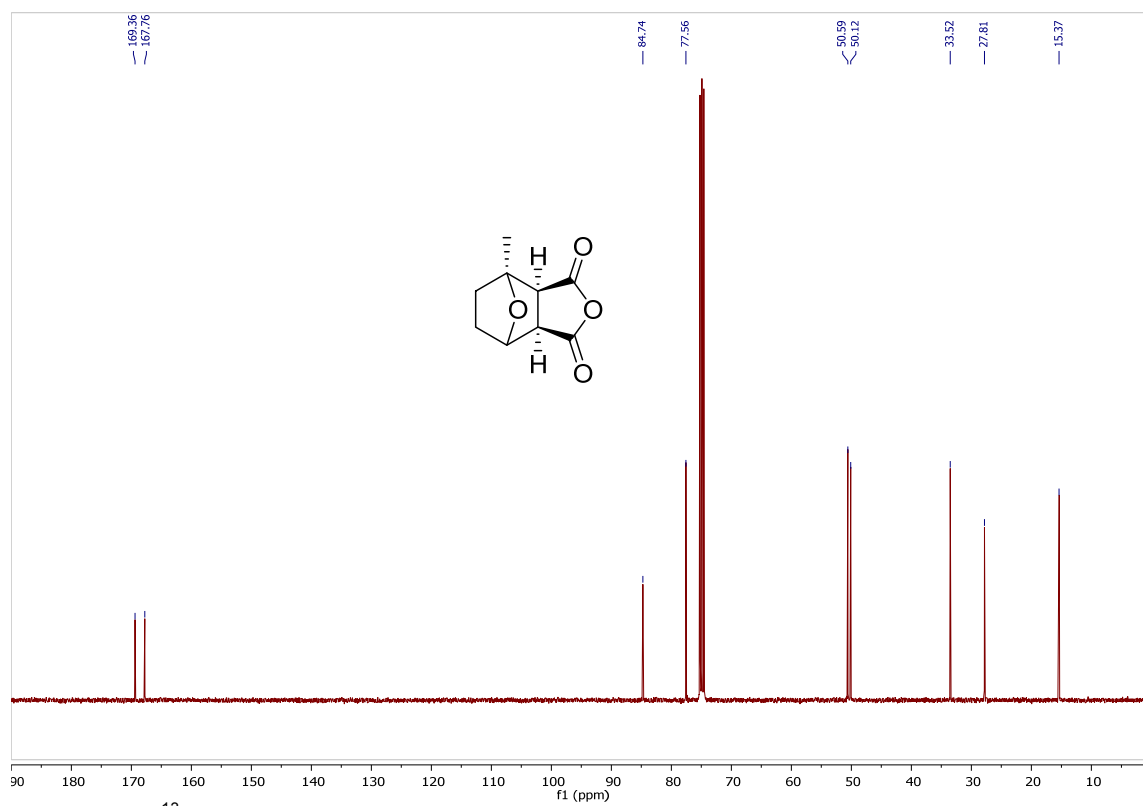


Figure S5.4. ¹³C NMR spectrum of (3aS,4R,7S,7aR)-4-methylhexahydro-4,7-epoxyisobenzofuran-1,3-dione **2** in CDCl₃.

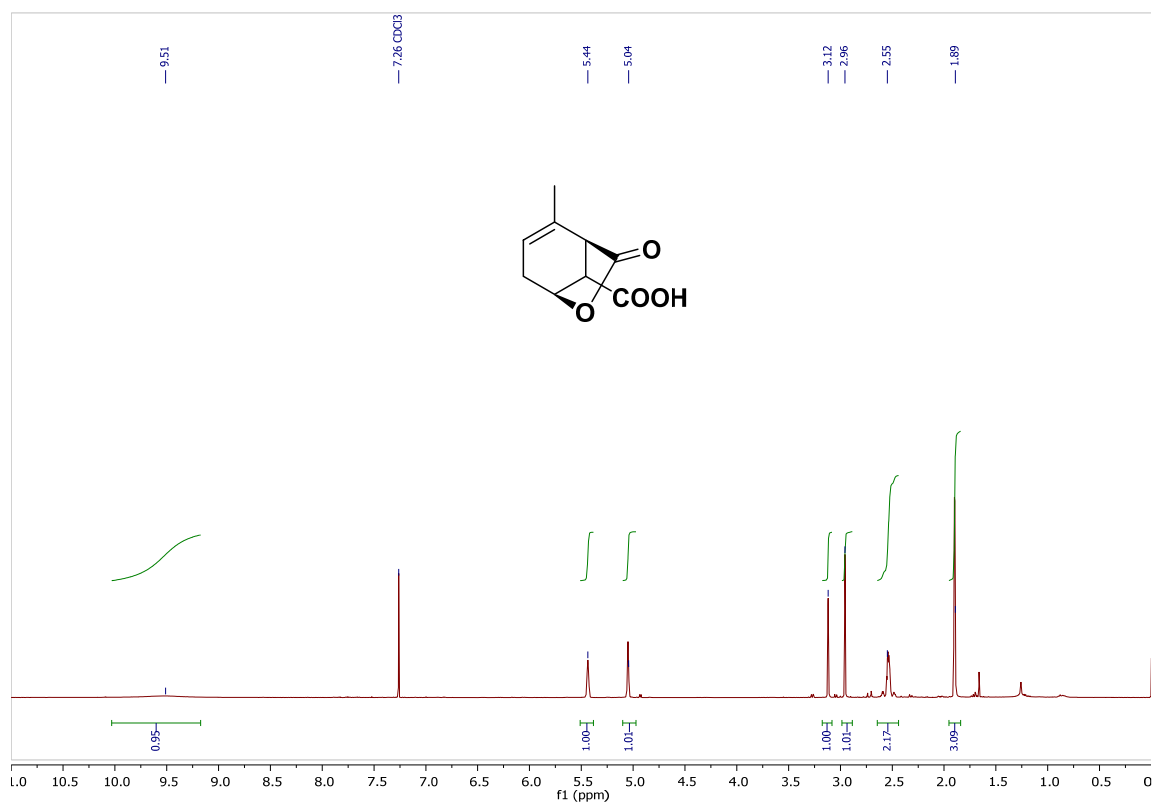


Figure S5.5. ¹H NMR spectrum of (1S,5S)-2-methyl-7-oxo-6-oxabicyclo[3.2.1]oct-2-ene-8-carboxylic acid **3** in CDCl₃.

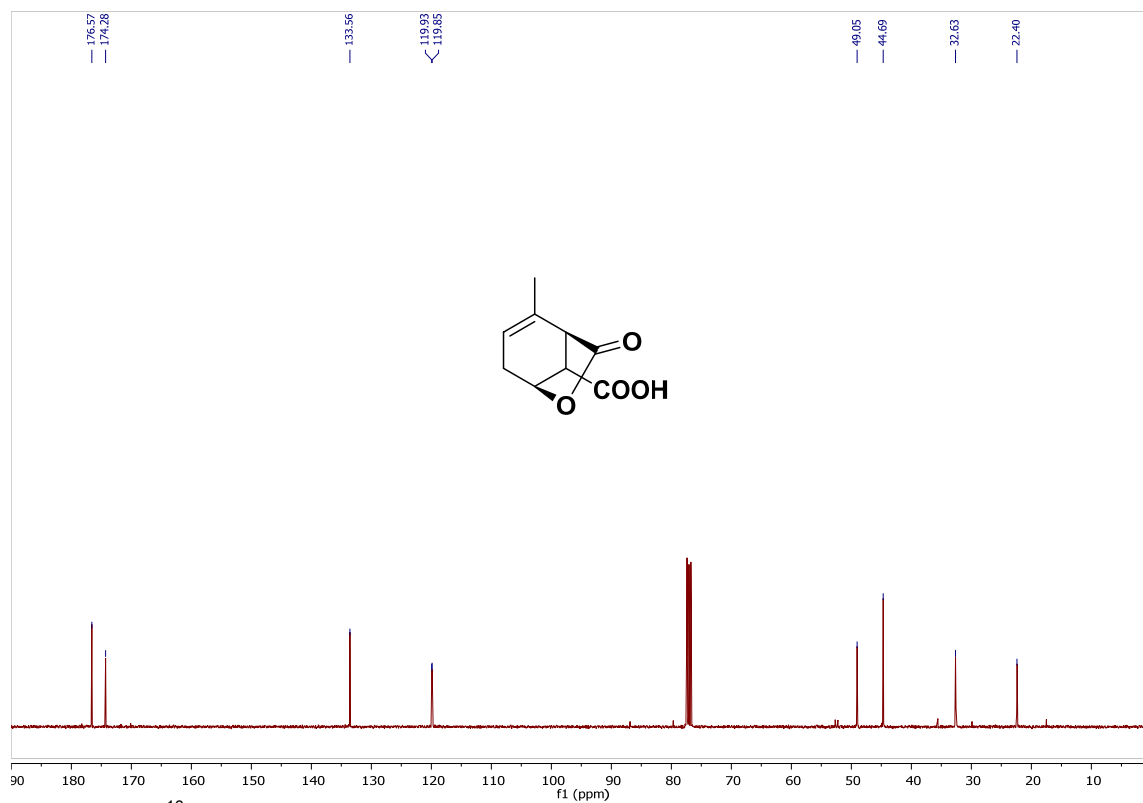


Figure S5.6. ¹³C NMR spectrum of (1S,5S)-2-methyl-7-oxo-6-oxabicyclo[3.2.1]oct-2-ene-8-carboxylic acid **3** in CDCl₃.

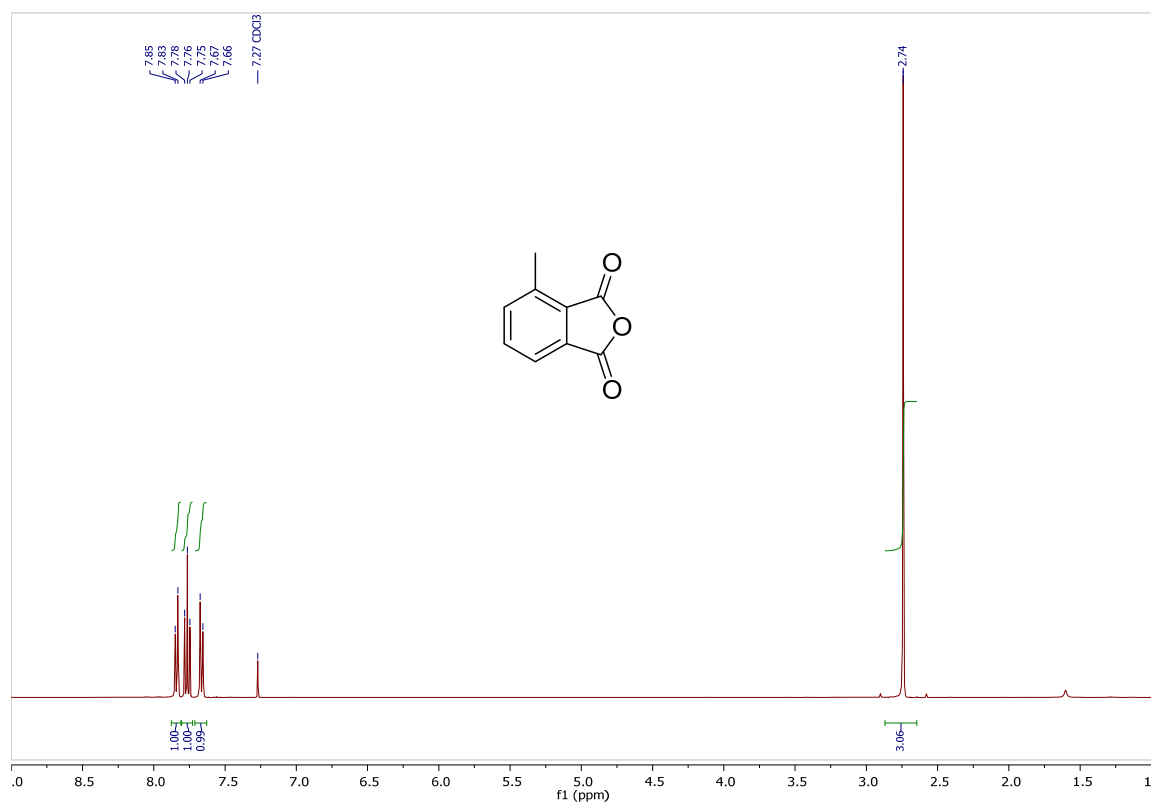


Figure S5.7. ¹H NMR spectrum of 4-methylisobenzofuran-1,3-dione **4** in CDCl₃.

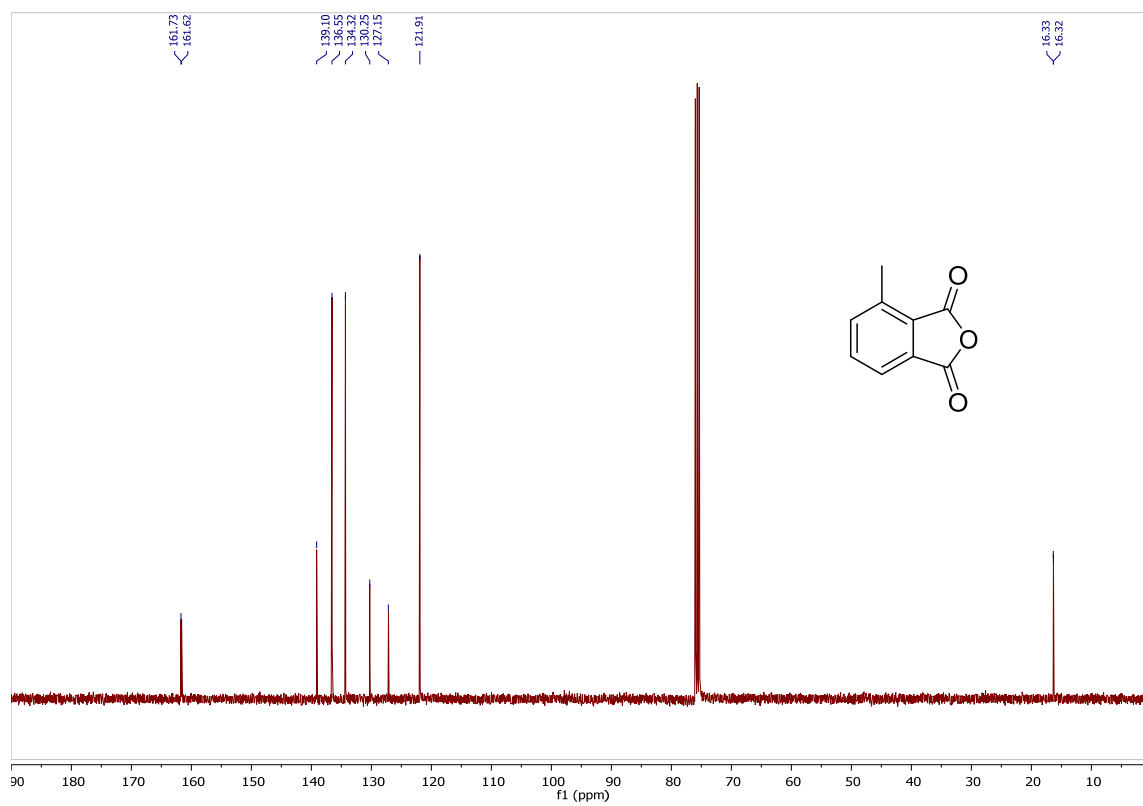


Figure S5.8. ¹³C NMR spectrum of 4-methylisobenzofuran-1,3-dione **4** in CDCl₃.

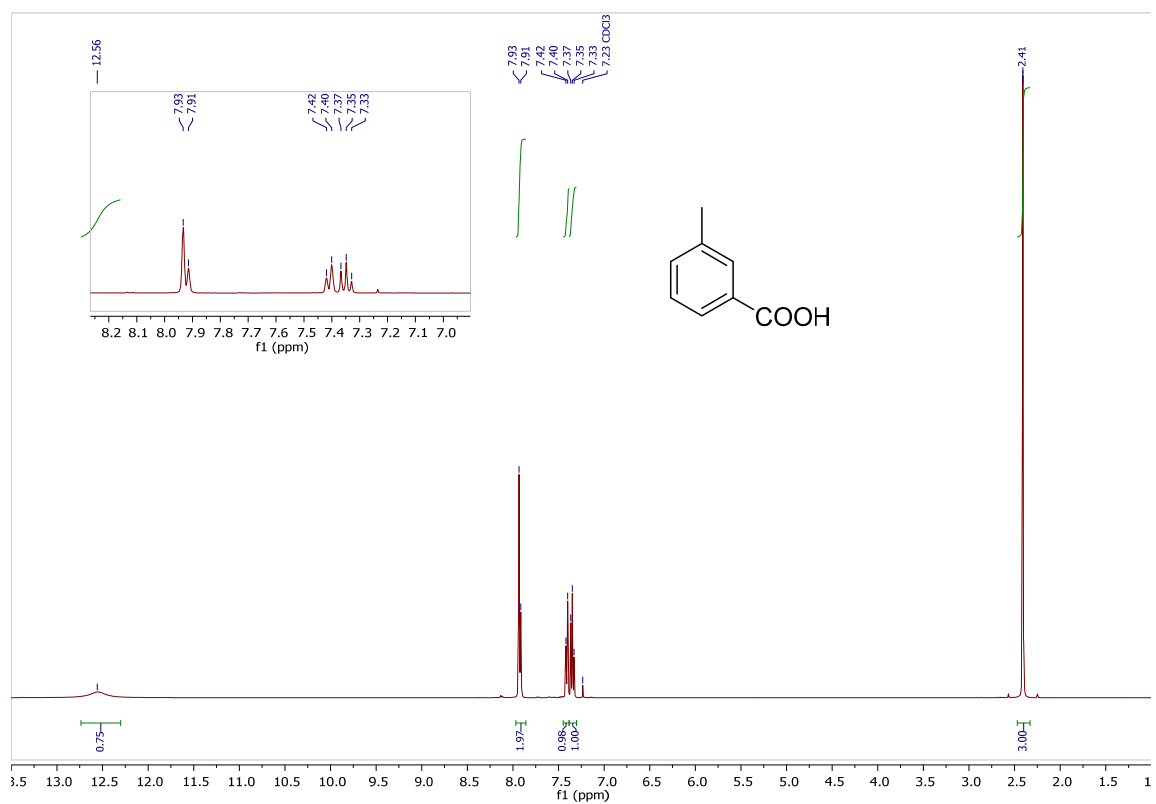


Figure S5.9. ¹H NMR spectrum of meta-toluic acid **5a** in CDCl₃.

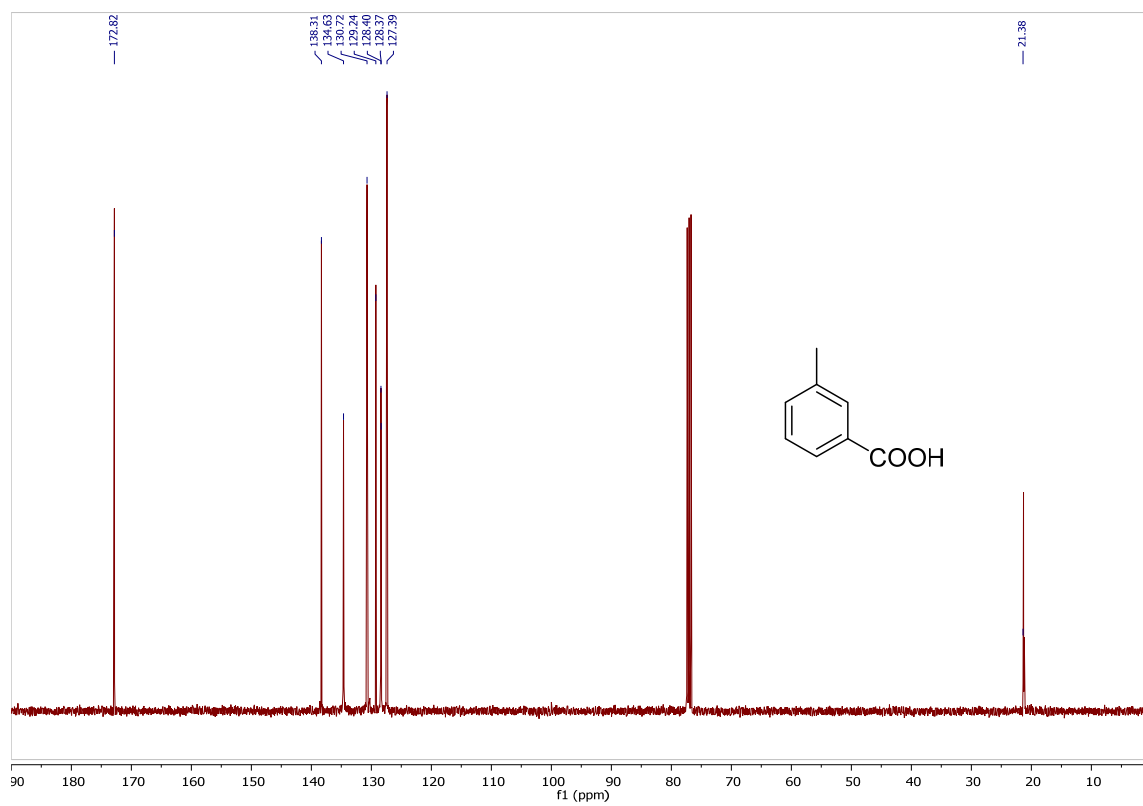


Figure S5.10. ¹³C NMR spectrum of meta-toluic acid **5a** in CDCl₃.

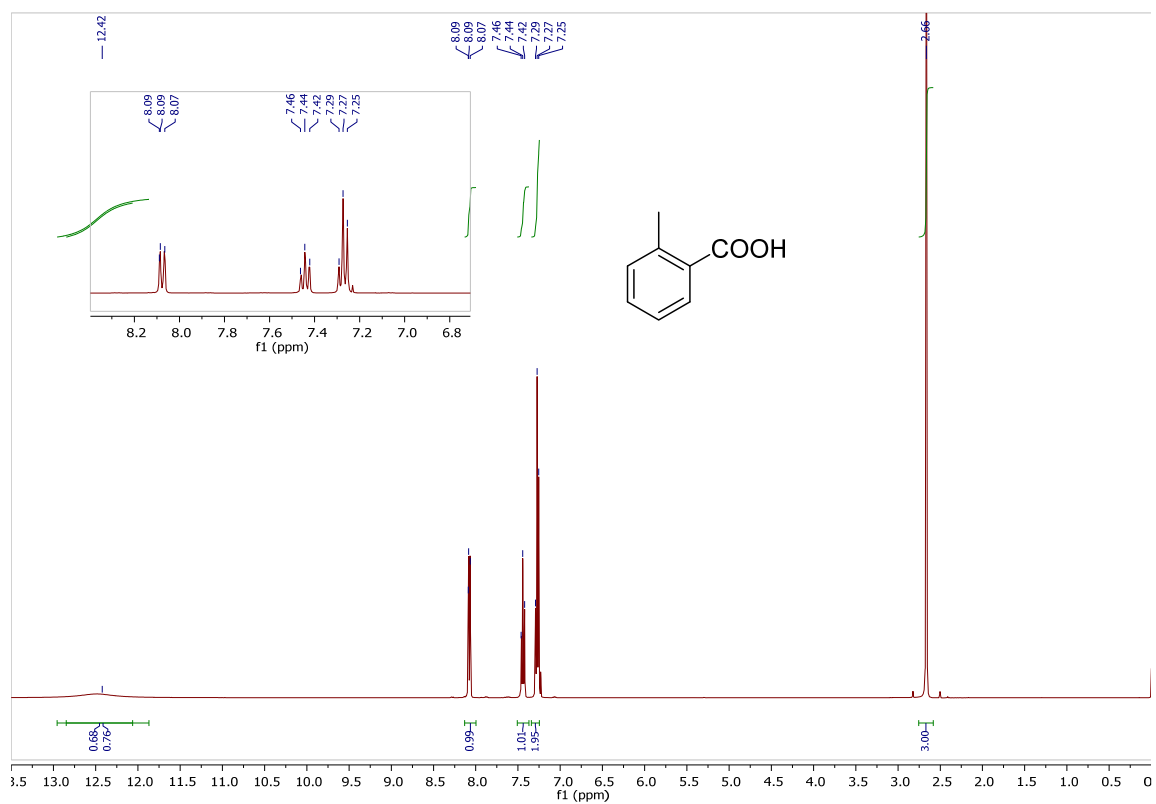


Figure S5.11. ^1H NMR spectrum of ortho-toluic acid **5b** in CDCl_3 .

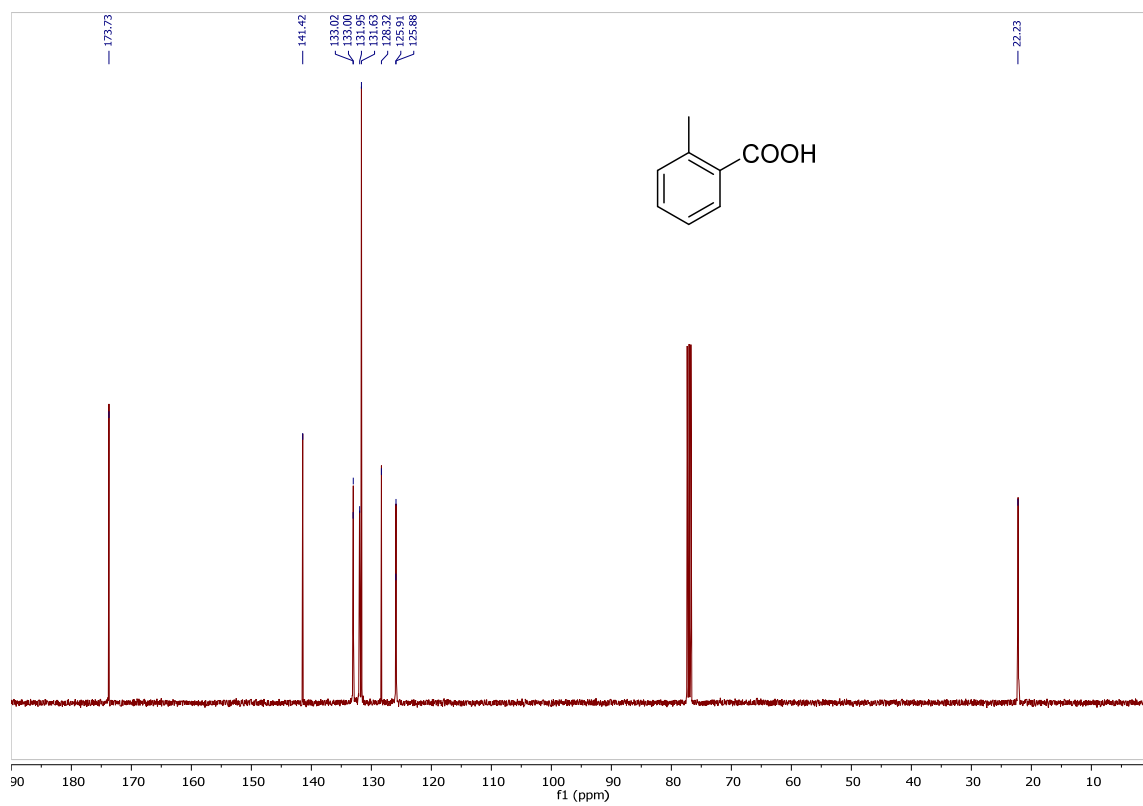


Figure S5.12. ^{13}C NMR spectrum of ortho-toluic acid **5b** in CDCl_3 .

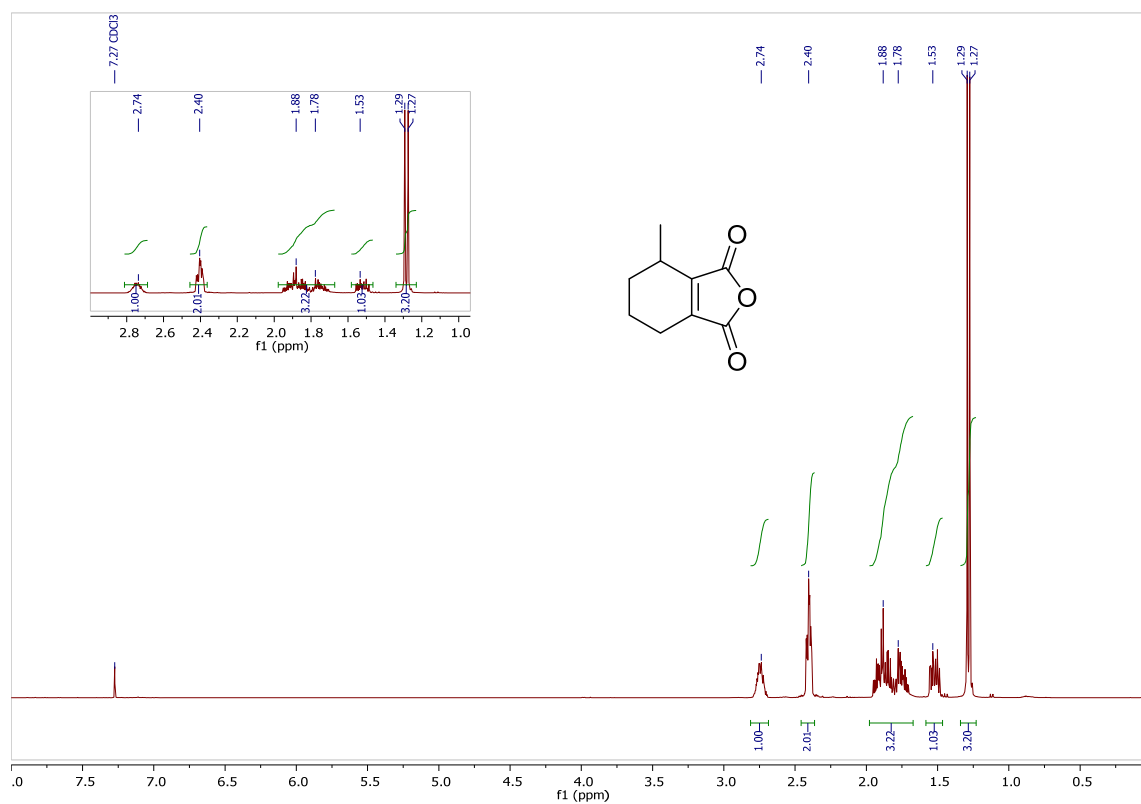


Figure S5.13. ^1H NMR spectrum of 4-methyl-4,5,6,7-tetrahydroisobenzofuran-1,3-dione **6** in CDCl_3 .

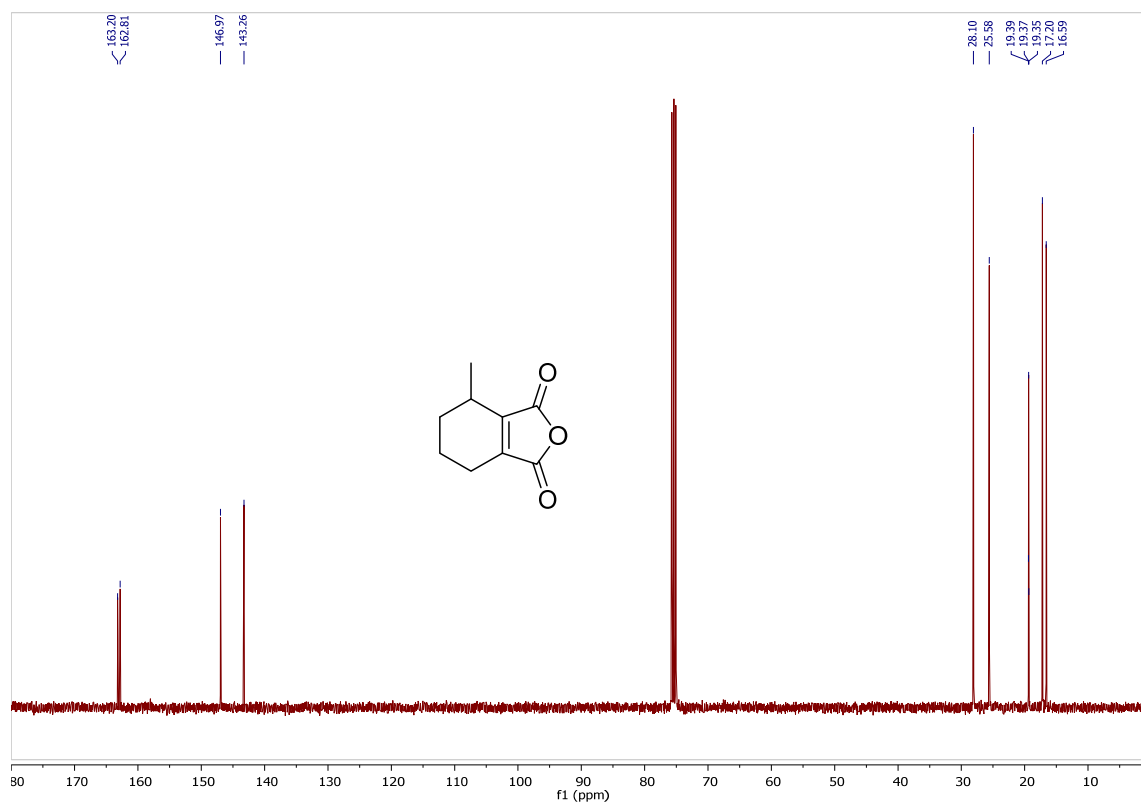


Figure S5.14. ^{13}C NMR spectrum of 4-methyl-4,5,6,7-tetrahydroisobenzofuran-1,3-dione **6** in CDCl_3 .

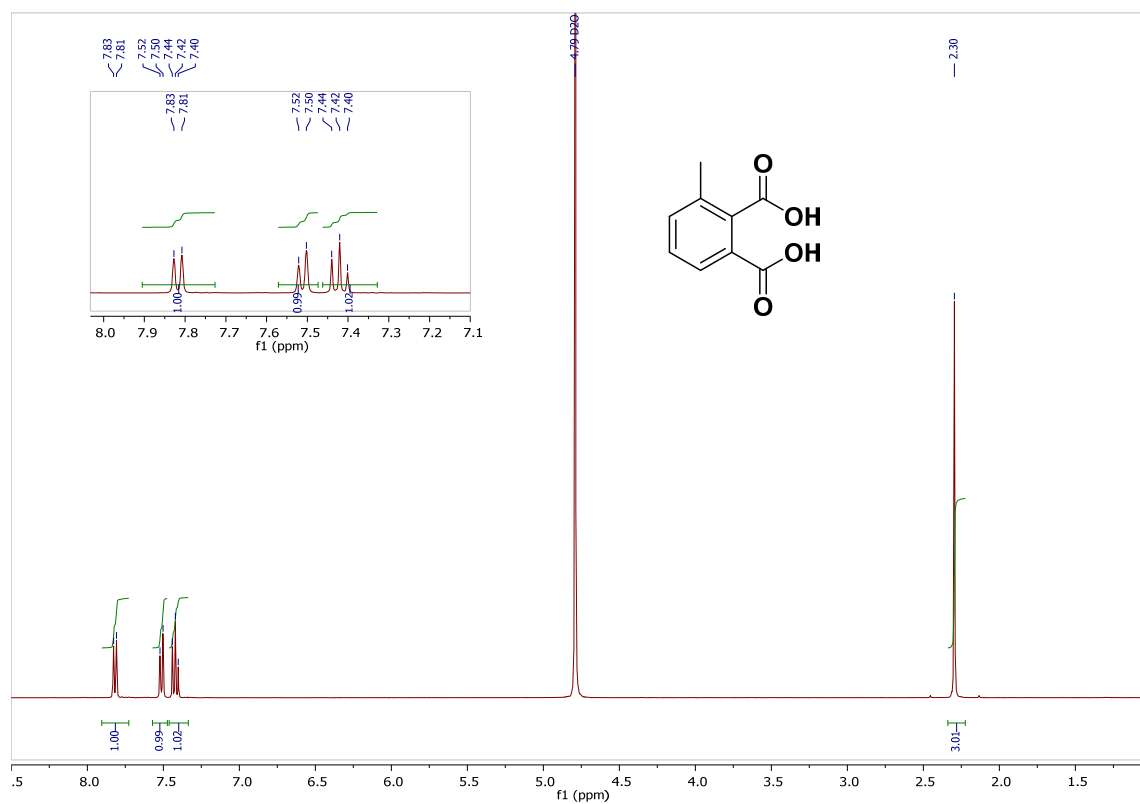


Figure S5.15. ^1H NMR spectrum of 3-methylphthalic acid in D_2O .

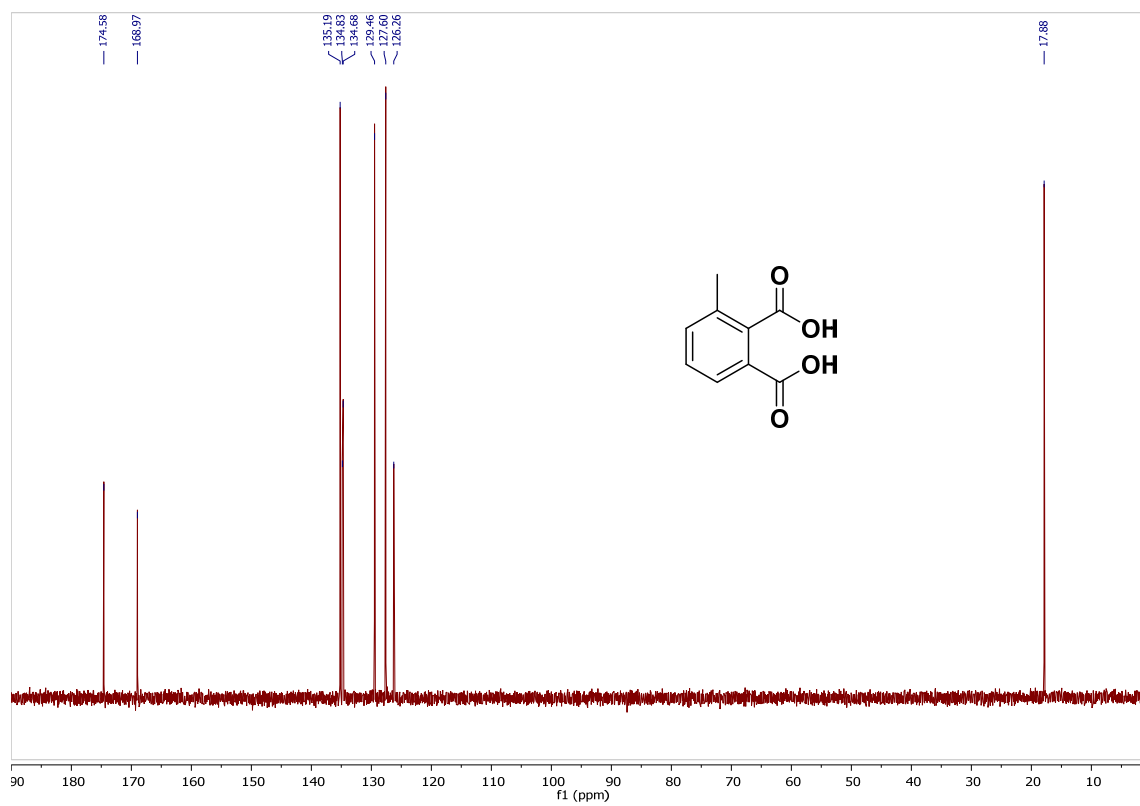


Figure S5.16. ^{13}C NMR spectrum of 3-methylphthalic acid in D_2O .

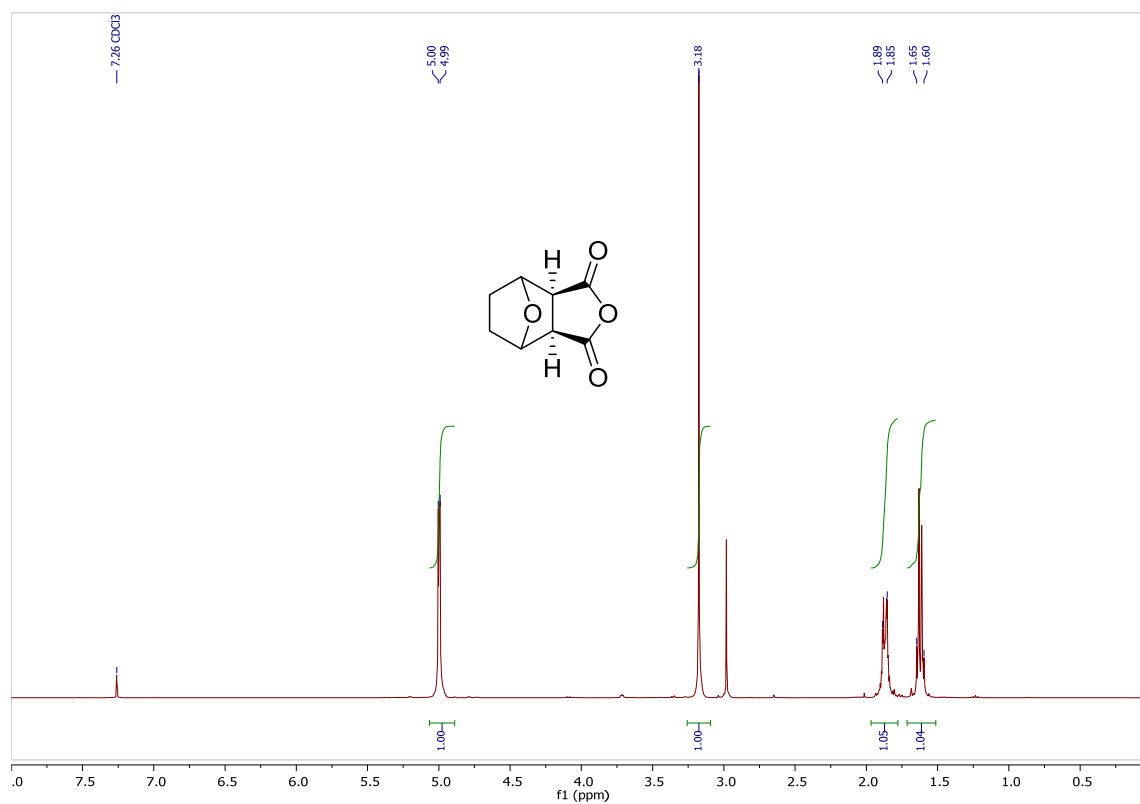


Figure S5.17. ¹H NMR spectrum of hexahydro-4,7-epoxyisobenzofuran-1,3-dione in CDCl₃.

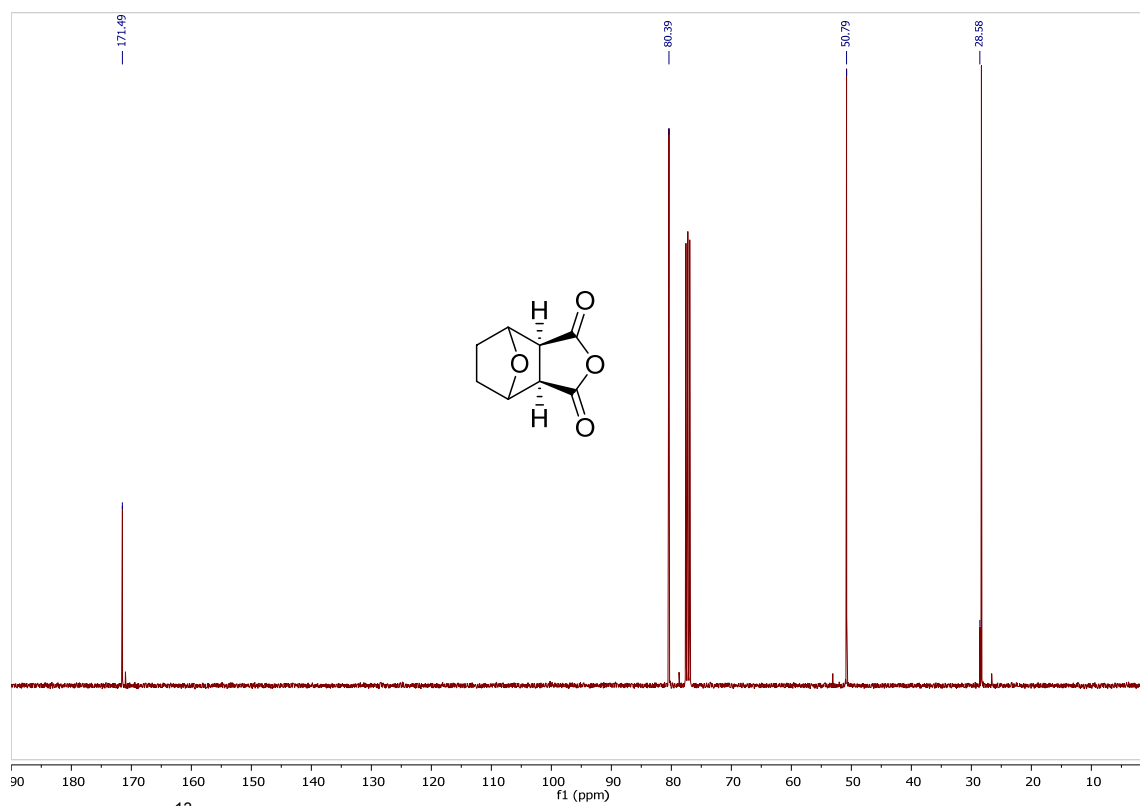


Figure S5.18. ¹³C NMR spectrum of hexahydro-4,7-epoxyisobenzofuran-1,3-dione in CDCl₃.

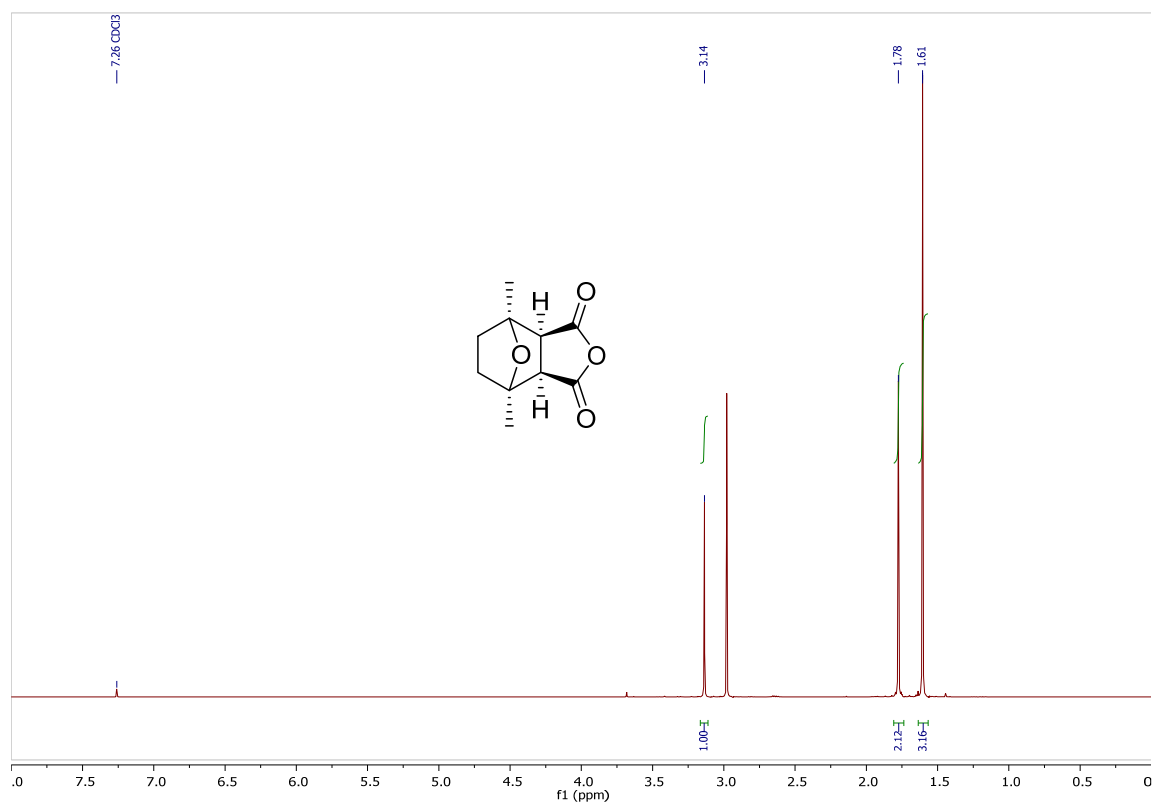


Figure S5.19. ^1H NMR spectrum of 4,7-dimethylhexahydro-4,7-epoxyisobenzofuran-1,3-dione in CDCl_3 .

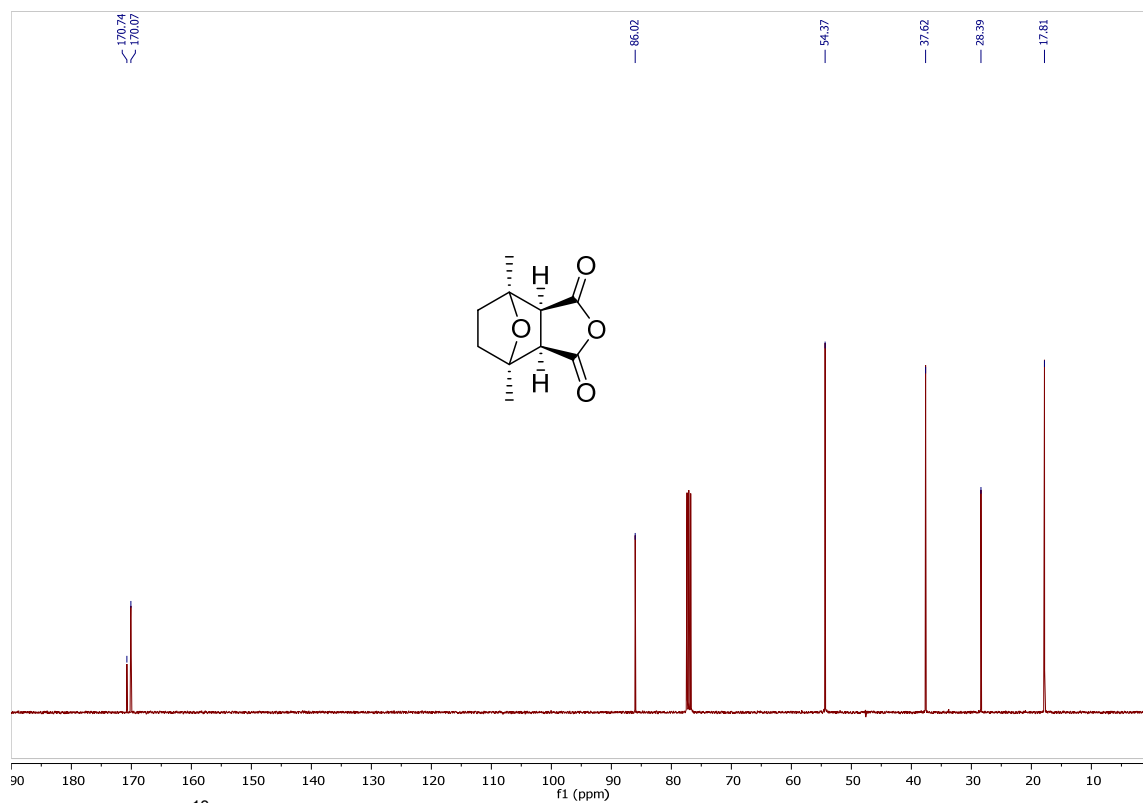


Figure S5.20. ^{13}C NMR spectrum of 4,7-dimethylhexahydro-4,7-epoxyisobenzofuran-1,3-dione in CDCl_3 .

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