Supporting information for

Continuous Flow Processing as a Tool for the Generation of Terpene-Derived Monomer Libraries

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Sumário

1. General Methods

Commercially available reagents and solvents were used without further purification, unless otherwise stated. Progress of the reactions was monitored by GC-MS. ^{1}H, ^{13}C and DEPT 135 NMR spectra were recorded on a Bruker DPX-250, Bruker Avance III 400 MHz, and Avance III 500 MHz spectrometers. Chemical shifts (δ) are given in parts per million, referenced to the residual peak of $CDCl_3$, δ = 7.26 (^{1}H NMR) and δ = 77.0 (^{13}C NMR) as internal references. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets and m = multiplet. NMR spectra were processed using MestReNova version 6.0.2-5475 software. GC-MS analysis was performed on a 9870A Agilent GC system. FTIR spectra were obtained on an Agilent Cary 630 FTIR spectrometer (neat, ATR sampling) with the intensities of the characteristic signals being reported as weak (w, <30% of tallest signal), medium (m, 31–70% of tallest signal) or strong (s, >71% of tallest signal). High-resolution mass spectrometry data was acquired using an Agilent ifunnel Q-TOF 6550 LC-MS instrument equipped with an electrospray ionization source (Dual Agilent Jet Stream ESI) operating in the positive mode. Melting points were recorded on a Mettler Toledo MP50 benchtop melting point system with a heating rate of 5 °C min^{-1} and are uncorrected. Continuous flow experiments were carried out using a Vapourtec R2+R4 RS100 and an AZURA P4.1S pump.

2. Continuous Flow Data.

2.1 General Diels-Alder Procedure in Continuous Flow Process.

For all terpenes, the flow equipment was set up according to the entry 8 of Table 1. Terpene (3 mmol) was taken up in 1.5 mL of AcOEt (2 M) and filled into loop of 1 mL. Maleic anhydride (**7**, 3.3 mmol) was taken up in 1.5 mL of AcOEt (2.2 M) and filled into another loop of 1 mL. The two loops were simultaneously injected into streams of AcOEt at 0.25 mL min^{-1} (each pump at 0.125 mL min^{-1}), and the plugs met at a T-piece before passing through a coil reactor (10 mL, 40 min) at 140 °C, pressurized by a 10 bar back-pressure regulator. The reaction evolution was monitored by GC-MS and the yield were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard as well as isolated.

2.1.1 Scale up Diels-Alder Experiment in Flow for Monomer 2.

The flow equipment was set up according to the Scheme on Table 2. A solution of α-terpinene **1** (100 mmol, 18.3 mL) in 31.7 mL of AcOEt and a solution of maleic anhydride **7** (110 mmol, 15.3 g) in AcOEt (50 mL solution) were pumped at 0.125 mL min^{-1} through streams 1 and 2, and mixed via a T-piece. The resulting stream passed through a coil reactor at 140 °C (10 mL, 40 min residence time). The system was pressurized by a 10 bar back-pressure regulator, and the combined streams gave us a total flow rate of 0.25 mL min^{-1}. After steady-state operation (two residence times, i.e. 80 min), the reactor output was collected for 3 hours in a flask of 50 mL (45 mmol of monomer **2**). The reaction evolution and conversion was monitored by GC-MS. After 3 hours, product **2** was obtained in 95% yield (45 mmol, 10.6 g).

2.2 Sequential Diels-Alder and Heterogeneous Hydrogenation in Flow.

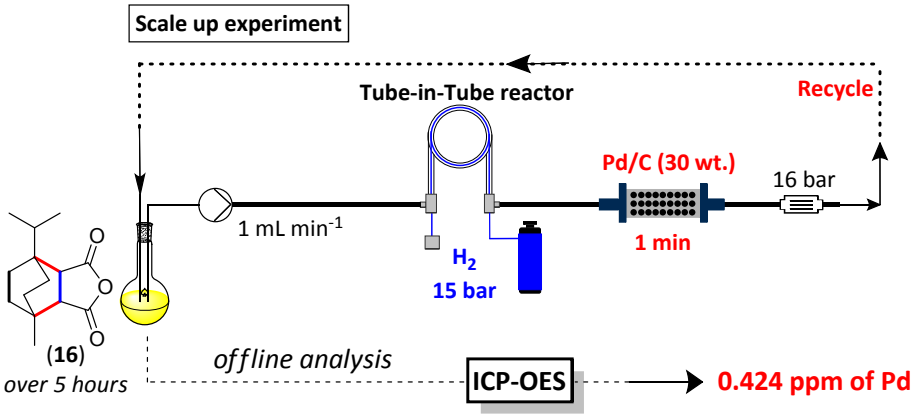
The flow equipment was set up according to the scheme on the Table 4. Terpene (3 mmol) was taken up in 1.5 mL of AcOEt (2 M) and filled into loop of 1 mL. Maleic anhydride **7** (3.3 mmol) was taken up in 1.5 mL of AcOEt (2.2 M) and filled into another loop of 1 mL. The two loops were simultaneously injected into streams of AcOEt at 0.25 mL min^{-1} (each pump at 0.125 mL min^{-1}), and the plugs met at a T-piece before passing through a coil reactor (10 mL, 40 min) at 140 °C, pressurized by a 10 bar back-pressure regulator. Then, the cycloaddition product was collected in a flask of 20 mL and directly pumped by an AZURA P4.1S pump using a flow rate of 1 mL min^{-1} through the tube-in-tube reactor, pressurized at 15 bar of hydrogen, in order to saturate the liquid stream with H_2. The reaction mixture containing the monomer and solubilized H_2 was subsequently passed through the cartridge (6.6 mm i.d. × 50.0 mm length) containing Pd-C catalyst (30 % Pd-C, 750 mg, void volume ca. 1 mL). The hydrogenation system was pressurized by a 16 bar back-pressure regulator. The pump inlets were placed in the same round bottomed flask so that the same reaction mixture was recycled through the system until complete hydrogenation of substrate, which varied from 80 to 510 min. The reaction evolution was monitored by GC-MS.

2.2.1 Scale up Heterogeneous Hydrogenation in Flow for Monomer 16.

In a flask of 250 mL was added 10 g of monomer **2** (43 mmol, 1 M in AcOEt) and directly pumped by an AZURA P4.1S pump using a flow rate of 1 mL min^{-1} through the tube-in-tube reactor, pressurized at 15 bar of hydrogen, in order to saturate the liquid stream with H_2. The reaction mixture containing the monomer **2** and solubilized H_2 was subsequently passed through the cartridge (6.6 mm i.d. × 50.0 mm length) of Pd-C catalyst (30 % Pd-C, 750 mg, void volume ca. 1 mL) and the hydrogenation reaction take place. The system was pressurized by a 16 bar back-pressure regulator. The pump inlets were placed in the same 250 mL flask so that the same reaction mixture was recycled through the system by 16 hours to complete hydrogenation of monomer **2**. The reaction evolution and conversion was monitored by GC-MS. The crude product presented just succinic anhydride in small quantity as impurity and the monomer **16** was afforded in 95% yield (43 mmol, 10.15 g).

2.2.2 Flow Experiment to evaluate Pd-leaching.

To confirm the non-significant leaching, the product **16** was recirculated by additional five hours through the system and the crude reaction mixture was analyzed by quantitative inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the amount of palladium leached. The analysis revealed that 0.00942% of palladium was leached in the liquid stream after five hours of flow experiment by recycling. Note that this amount is non-significant and explains the similar results. This result also shows the importance of activated carbon as support for palladium, preventing the easy leaching of the metal during a flow experiment using a fixed-bed flow reactor.



50 mL of crude reaction containing **16** in 1M was recirculated by 5 hours and 0.424 ppm of Pd of a column packed with 750 mg of Pd/C in 30% wt was leached, which corresponds to 0.00942% of Pd.

3. Picture of the Optimized Diels-Alder/hydrogenation Setup

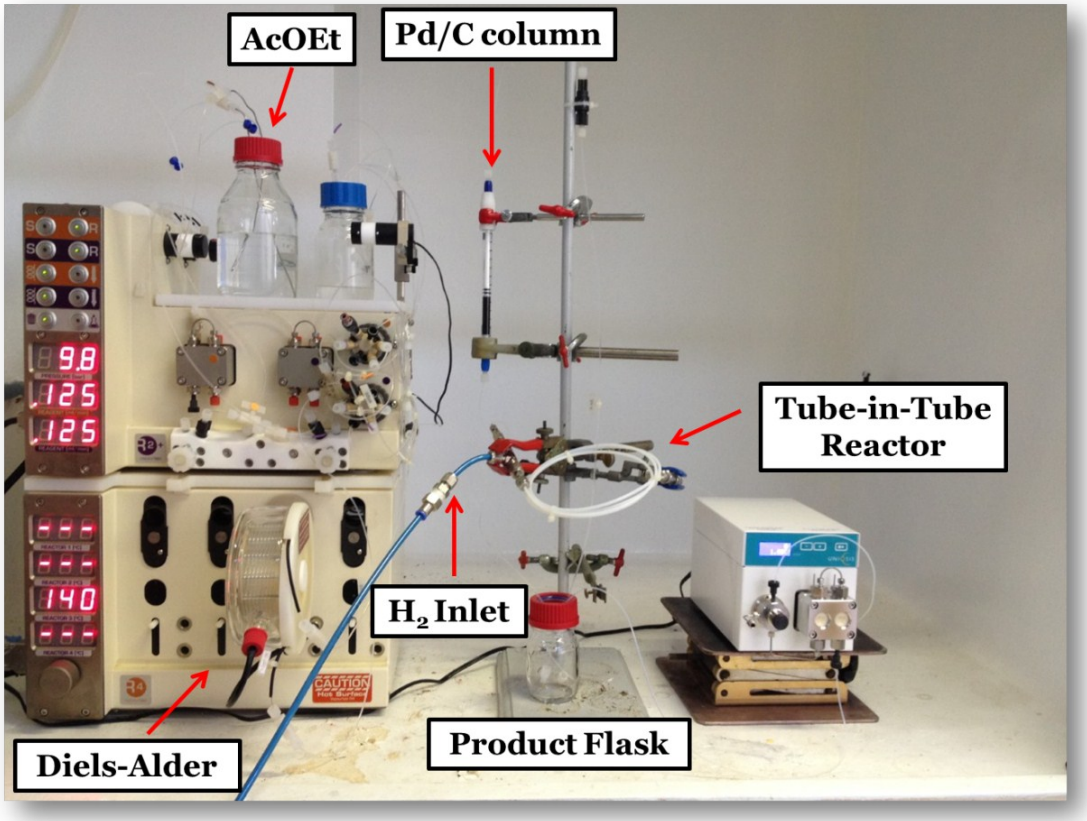
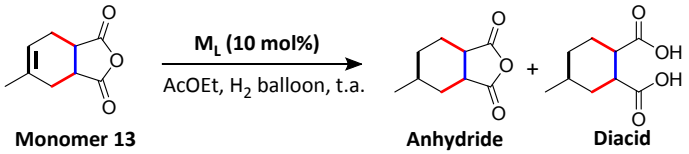


Figure S1. Setup of flow equipment for Diels-Alder/Hydrogenation reactions.

4. Heterogeneous Optimization using different catalysts.

Table S1. Heterogeneous hydrogenation in batch using different metal as catalysts.



Monomer 13 **Anhydride** **Diacid**

Entry	Catalyst	Reaction Time (hr)	Ratio[a] anhydride/diacid
1	$Pd(OAc)_2$	6	1:1
2[b]	$Pd(OH)_2$	6	1:9 (90%)
3[b]	$PdBaSO_4$	3	1:9 (90%)
4	Pd/alumina dry	3	9:1
5[c]	Pd/C	3	1:0 (99%)
6[d]	$Ru(Cl)_3$	48	-
7[d]	Ni-Raney	6	-
8	Rh/C	3	1:9

[a] The ratio was determined by ^1H or ^{13}C NMR data. [b] Diacid was isolated in 90% yield. [c] Anhydride product was isolated in 99% yield. [d] Anhydride or diacid was not observed by ^1H or ^{13}C NMR data.

5. NMR Data

5.1 ^{1}H NMR spectra from the crude heterogeneous scale up process.

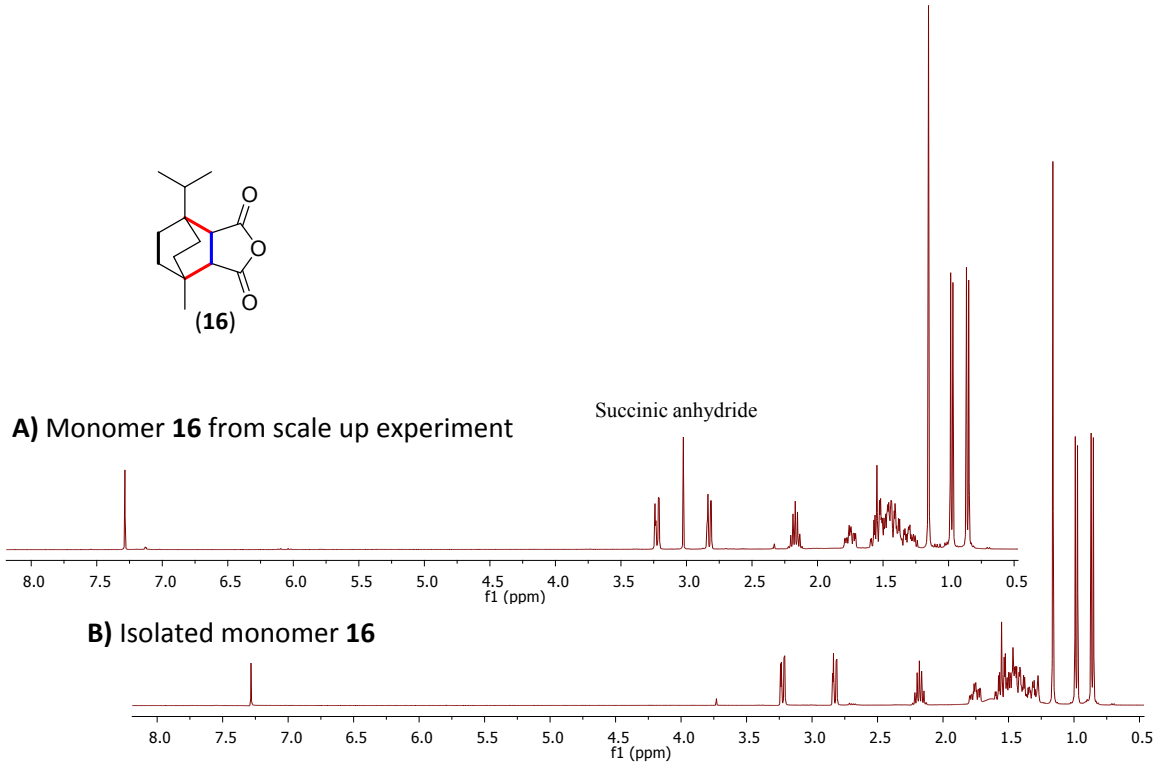
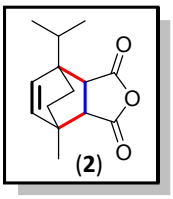
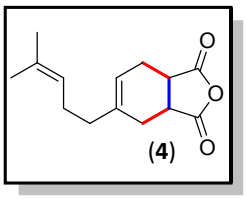


Figure S2. Comparison between isolated and crude reaction mixture for monomer **16**; **A)** ^{1}H NMR spectrum for monomer **16** from scale up experiment in flow regime after simple removal of the solvent by evaporation; **B)** ^{1}H NMR spectrum from isolated monomer **16**.

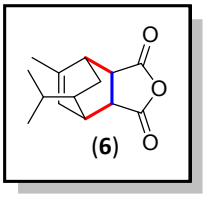
5.2 Unsaturated monomers data



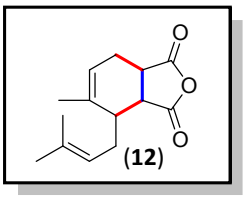
1-Isopropyl-7-methyl-4-oxatricyclo[5.2.2.0]undec-8-ene-3,5-dione (2). Obtained in 95% yield (444 mg) as a white solid. **M.p.** = 64-66 °C. **IR** (ATR, cm^{-1}): 2990 (w), 2359 (w), 1834 (w), 1780 (s), 1216 (m), 1082 (m), 935 (s), 778 (m), and 701 cm^{-1} (m). **^{1}H NMR** (500 MHz, $CDCl_3$); δ = 6.09 (d, *J* = 8.5 Hz, 1H), 6.01 (d, *J* = 8.5 Hz, 1H), 3.24 (d, *J* = 8.7 Hz, 1H), 2.87 (d, *J* = 8.7 Hz, 1H), 2.55 (hept, *J* = 6.8 Hz, 1H), 1.56-1.23 (m, 7H), 1.07 (d, *J* = 7.5 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$); δ = 171.56, 170.94, 136.98, 136.27, 50.91, 47.20, 43.49, 36.67, 33.56, 29.34, 22.64, 22.15, 18.26, 16.63. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{18}O_3H^+$ $[M+H]^+$ 235.1328; found: 235.1330.



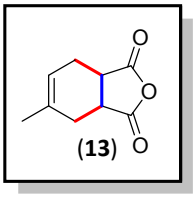
5-(4-Methyl-3-penten-1-yl)-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione (4). Obtained in 93% yield (435 mg) as a white solid. **M.p.** =119-122 °C. **IR** (ATR, cm^{-1}): 2919 (w), 1700 (s), 1417 (w), 1260 (m), 946 (m), and 777 (w) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$); δ = 5.69-5.61 (m, 1H), 5.03 (m, 1H), 3.45-3.39 (td, *J* = 7.5, 2.5 Hz, 1H) 3.39-3.33 (td, *J* = 7.5, 2.5 Hz, 1H), 2.61 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.53 (d, *J* = 15.4 Hz, 1H), 2.28 (m, 2H), 2.12-2.00 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$); δ = 174.55, 174.38, 140.61, 132.21, 123.28, 120.02, 40.20, 39.76, 37.23, 27.47, 25.84, 25.64, 24.03, 17.70. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{18}O_3H^+$ $[M+H]^+$ 235.1328; found: 235.1331.



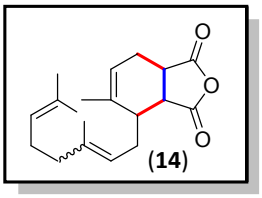
10-Isopropyl-8-methyl-4-oxatricyclo[5.2.2.0]undec-8-ene-3,5-dione (6). Obtained in 91% yield (425 mg) as a white solid. **M.p.** = 108-112 °C. **IR** (ATR, cm^{-1}): 2945 (w), 2364 (w), 1769 (s), 1558 (m), 1457 (m), 1242 (m), 1079 (m), 955 (s), and 906 (s) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$); δ = 5.79 (d, *J* = 6.2 Hz, 1H), 3.25-3.19 (m, 1H), 3.12 (dd, *J* = 8.8, 3.3 Hz, 1H), 3.07 (dd, *J* = 8.8, 3.1 Hz, 1H), 2.99 (s, 1H), 1.84-1.75 (m, 4H), 1.32 (dd, *J* = 14.2, 8.9 Hz, 1H), 1.14 (m, 1H), 1.10-1.04 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$); δ = 173.09, 172.77, 142.50, 122.53, 46.31, 44.60, 44.28, 37.92, 35.26, 33.12, 29.99, 20.99, 20.73, 20.38. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{18}O_3H^+$ $[M+H]^+$ 235.1328; found: 235.1329.



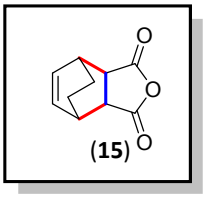
5-Methyl-4-(3-methyl-2-buten-1-yl)-3a,4,7,7a-tetrahydro-2-benzofuran-1,3-dione (12). Obtained in 86% yield (402 mg) as a white solid. **M.p.** = 149-156 °C. **IR** (ATR, cm^{-1}): 2922 (w), 1715 (s), 1422 (w), 1268 (w), and 1234 cm^{-1} (w). **^{1}H NMR** (250 MHz, $CDCl_3$); δ = 5.63 (m, 1H), 5.10 (m, 1H), 3.33 (m, 2H), 2.66-2.48 (m, 2H), 2.47-2.16 (m, 3H), 1.76 (s, 3H), 1.69 (s, 3H), 1.65 (s, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$); δ = 174.69, 172.31, 140.85, 134.81, 121.40, 120.80, 43.58, 40.28, 39.43, 26.53, 25.83, 24.02, 20.65, 17.90. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{18}O_3H^+$ $[M+H]^+$ 235.1328; found: 235.1328.



4-Methyl-1,2,3,6-tetrahydrophthalic Anhydride (13). Obtained in quantitative yield (332 mg) as a white solid. **M.p.** = 147-152 °C. **IR** (ATR, cm^{-1}): 1694 (s), 1418 (w), 1261 (m), 1216 (w) 938 (w), and 639 (w) cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$); δ = 5.68-5.60 (m, 1H), 3.38-3.44 (m, 1H), 3.38-3.32 (m, 1H), 2.59 (ddd, *J* = 15.7, 6.4, 2.7 Hz, 1H), 2.52 (dd, *J* = 15.6, 2.8 Hz, 1H), 2.33-2.23 (m, 2H), 1.78 (d, *J* = 0.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$); δ = 174.42, 174.27, 136.59, 120.16, 40.09, 39.45, 28.40, 24.08, 23.48. **HRMS** (ESI +) *m/z*: Calcd. for $C_9H_{10}O_3H^+$ $[M+H]^+$ 167.0702; found: 167.0704.

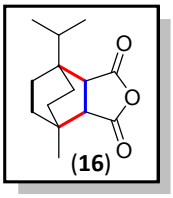


4-(3,7-dimethylocta-2,6-dien-1-yl)-5-methyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (14). Obtained in 99% yield (598 mg) as a viscous clear liquid. **IR** (ATR, cm^{-1}): 2925 (w), 2970 (w), 1708 (s), 1442 (w), 1377 (w), 1219 (m), 1080 (w), 930 (m), and 778 (w) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$); δ = 5.72-5.60 (m, 1H), 5.19-4.98 (m, 2H), 3.32-3.43 (m, Hz, 2H), 2.63 (ddd, *J* = 15.6, 6.6, 2.6 Hz, 1H), 2.55 (ddd, *J* = 15.4, 6.5, 2.8 Hz, 1H), 2.34-2.20 (m, 2H), 2.16-1.93 (m, 8H), 1.80-1.57 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$); δ = 174.45, 174.30, 140.66, 135.89, 131.37, 124.27, 123.12, 120.01, 40.19, 39.75, 37.26, 31.98, 27.50, 26.65, 25.70, 24.05, 23.36, 17.69, 16.05. **HRMS** (ESI +) *m/z*: Calcd. for $C_{19}H_{26}O_3H^+$ $[M+H]^+$ 303.1954; found: 303.1950.

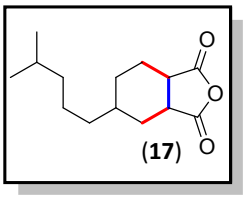


4-Oxatricyclo[5.2.2.02,6]undec-8-ene-3,5-dione (15). Obtained in quantitative yield (356 mg) as a white solid. **M.p.** = 130-136 °C. **IR** (ATR, cm^{-1}): 2963 (w), 2359 (w), 1778 (s), 1220 (s), 1077 (s), 940 (s) 900 (s), 866 (m) 781 (m), 728 (s), and 684 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$); δ = 6.37-6.29 (m, 2H), 3.24 (m, 2H), 3.17-3.11 (m, 2H), 1.67-1.57 (m, 2H), 1.47-1.37 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$); δ = 172.81, 133.04, 44.77, 31.63, 22.96. **HRMS** (ESI +) *m/z*: Calcd. for $C_{10}H_{10}O_3H^+$ $[M+H]^+$ 179.0702; found: 179.0707.

5.3 Saturated monomers data

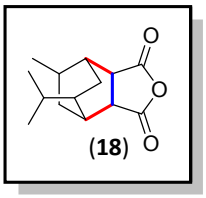


1-Isopropyl-7-methyl-4-oxatricyclo[5.2.2.0]undecane-3,5-dione (16). Obtained in 95% yield (448 mg) as a white solid. **M.p.** = 50-54 °C. **IR** (ATR, cm^{-1}): 2962 (w), 2870 (w) 1779 (s), 1693 (w), 1249 (w), 1214 (m), 1077 (m) and 927 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.22 (dd, *J* = 10.3, 2.4 Hz, 1H), 2.83 (dd, *J* = 10.3, 2.1 Hz, 1H), 2.18 (hept, *J* = 6.9 Hz, 1H), 1.82-1.71 (m, 1H), 1.60-1.23 (m, 7H), 1.16 (s, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.38, 172.08, 49.55, 45.70, 36.66, 33.32, 30.86, 29.13, 26.53, 24.76, 22.77, 17.15, 16.87. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{20}O_3H^+$ $[M+H]^+$ 237.1485; found: 237.1480.



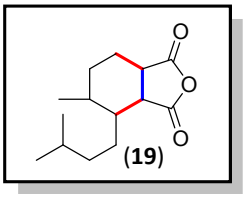
(**17**)

5-(4-Methylpentyl)hexahydro-2-benzofuran-1,3-dione (17). Obtained in 96% yield (457 mg) as a viscous clear liquid. **IR** (ATR, cm^{-1}): 2946 (w), 2875 (w), 1774 (s), 1214 (m), 1075 (m), 900 (s) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.32 (s, 1H), 2.51 (dt, *J* = 12.2, 3.9 Hz, 1H), 2.30 (d, *J* = 12.0 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.72 – 1.46 (m, 4H), 1.39 – 1.11 (m, 8H), 0.88 (d, *J* = 6.6 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.97, 172.77, 40.89, 40.73, 38.98, 36.66, 34.22, 32.76, 28.54, 28.37, 27.88, 24.22, 22.56, 21.36. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{22}O_3H^+$ $[M+H]^+$ 239.1641; found: 239.1644.



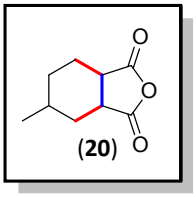
(**18**)

5-isopropyl-8-methylhexahydro-4,7-ethanoisobenzofuran-1,3-dione (18). Obtained in 94% yield (429 mg) as a viscous clear liquid. **IR** (ATR, cm^{-1}): 2957 (w), 2927 (w), 2872 (w), 1774 (s), 1228 (w), 1094 (w), 925 (m), 906 (m) 892 (m) cm^{-1}. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 3.05-2.94 (m, 2H), 2.32 (m, 1H), 2.11 (m, 1H), 2.04-1.89 (m, 1H), 1.87-1.69 (m, 2H), 1.51-1.08 (m, 4H), 0.94 (m, 9H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 174.43, 174.01, 46.16, 41.93, 41.71, 35.13, 33.94, 32.79, 30.08, 29.16, 26.67, 21.61, 21.12, 21.01. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{20}O_3H^+$ $[M+H]^+$ 237.1485; found: 237.1487.



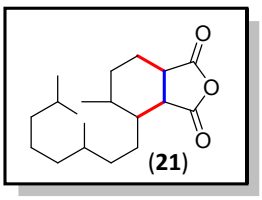
(**19**)

4-isopentyl-5-methylhexahydroisobenzofuran-1,3-dione (19). Obtained in 86% yield (402 mg) as a viscous clear liquid. **IR** (ATR, cm^{-1}): 2954 (w), 2924 (w), 2867 (w), 1701 (s), 1471 (w), 1305 (w), 1244 (w) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.16 (dd, *J* = 8.4, 5.7 Hz, 1H), 3.09-2.98 (m, 1H), 2.06-1.92 (m, 1H), 1.90-1.51 (m, 1H), 1.30-1.19 (m, 1H), 0.93 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.35, 172.23, 41.81, 41.40, 38.27, 36.97, 29.76, 29.72, 28.15, 27.51, 22.63, 22.56, 21.13, 13.87. **HRMS** (ESI +) *m/z*: Calcd. for $C_{14}H_{22}O_3H^+$ $[M+H]^+$ 239.1641; found: 239.1641.



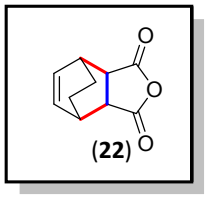
(**20**)

Methylhexahydrophthalic Anhydride (20). Obtained in 96% yield (322 mg) clear liquid. **IR** (ATR, cm^{-1}): 2359 (w), 2340 (w), 1694 (s), 1452 (w), 1413 (w), 1336 (w), 1293 (w), 1251(w) cm^{-1}. **^{1}H NMR** (250 MHz, $CDCl_3$) δ 3.25-2.96 (m, 2H), 2.38-2.08 (m, 2H), 1.76-1.58 (m, 2H), 1.51-1.21 (m, 2H), 0.99-0.87 (m, 4H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ 172.88, 172.61, 40.86, 40.32, 34.45, 30.34, 29.22, 21.96, 21.29. **HRMS** (ESI +) *m/z*: Calcd. for $C_9H_{12}O_3H^+$ $[M+H]^+$ 169.0859; found: 169.0855.



(**21**)

4-(3,7-dimethyloctyl)-5-methylhexahydroisobenzofuran-1,3-dione (21). Obtained in 96% yield (591 mg) as a viscous clear liquid. **IR** (ATR, cm^{-1}): 2951 (w) 2925 (m) 2853 (w), 1704 (s), 1455 (w), 1417 (w), 1253 (m), 1225 (m) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.31 (s, 1H), 2.54-2.44 (m, 1H), 2.37-2.24 (m, 1H), 2.10-1.98 (m, 1H), 1.76–1.46 (m, 5H), 1.25 (m, 6H), 1.15 (m, 3H), 1.11-1.05 (m, 2H), 0.92-0.82 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 180.91, 180.58, 43.07, 41.67, 39.35, 37.30, 37.27, 36.93, 34.83, 32.74, 30.16, 28.69, 28.10, 27.98, 24.80, 24.16, 22.73, 22.63, 19.69. **HRMS** (ESI +) *m/z*: Calcd. for $C_{19}H_{32}O_3H^+$ $[M+H]^+$ 309.2424; found: 309.2422.



(**22**)

4-Oxatricyclo[5.2.2.0]undecane-3,5-dione (22). Obtained in 94% yield (338 mg) as a white solid. **M.p.** = 185-187 °C **IR** (ATR, cm^{-1}): 2946 (w), 2875 (w), 1774 (s), (1214 (m), 1075 (m), 936 (m), 900 (s) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.16-3.07 (m, 2H), 2.24 (s, 2H), 1.78-1.71 (m, 2H), 1.65-1.57 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.94, 44.26, 25.98, 24.12, 21.37. **HRMS** (ESI +) *m/z*: Calcd. for $C_{10}H_{12}O_3H^+$ $[M+H]^+$ 181.0859; found: 181.0860.

5.3 ^{1}H and ^{13}C NMR spectra for Diels-Alder monomers.

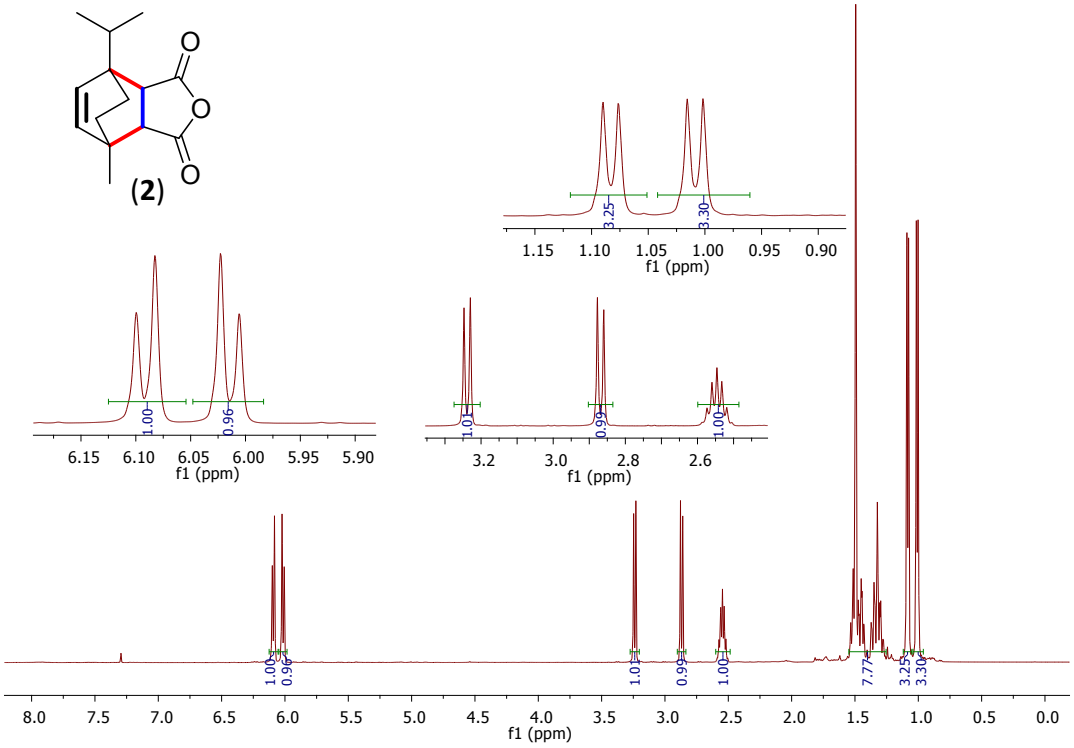


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **2** synthetized from *α*-terpinene.

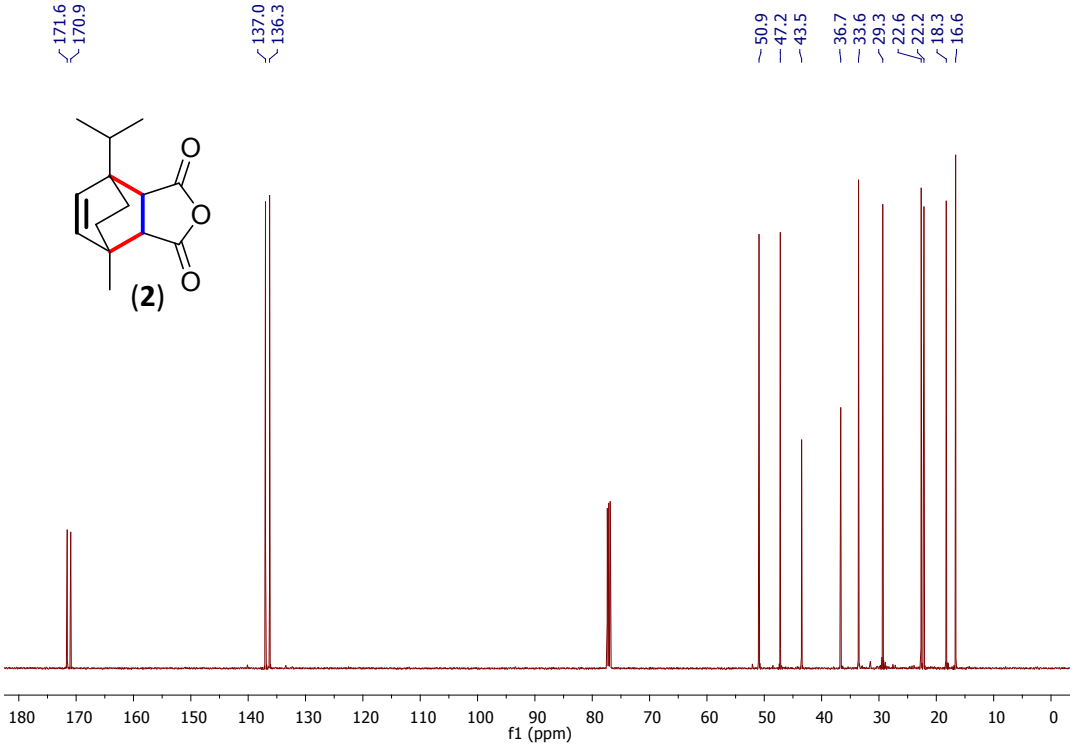


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **2** synthetized from α-terpinene.

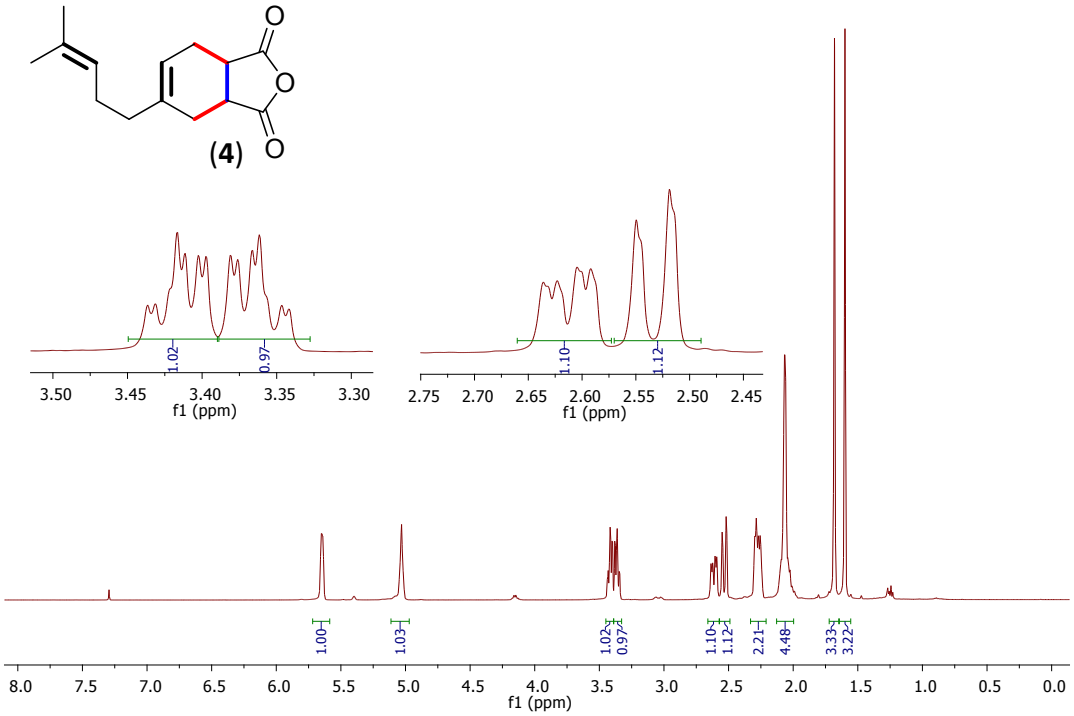


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **4** synthetized from myrcene.

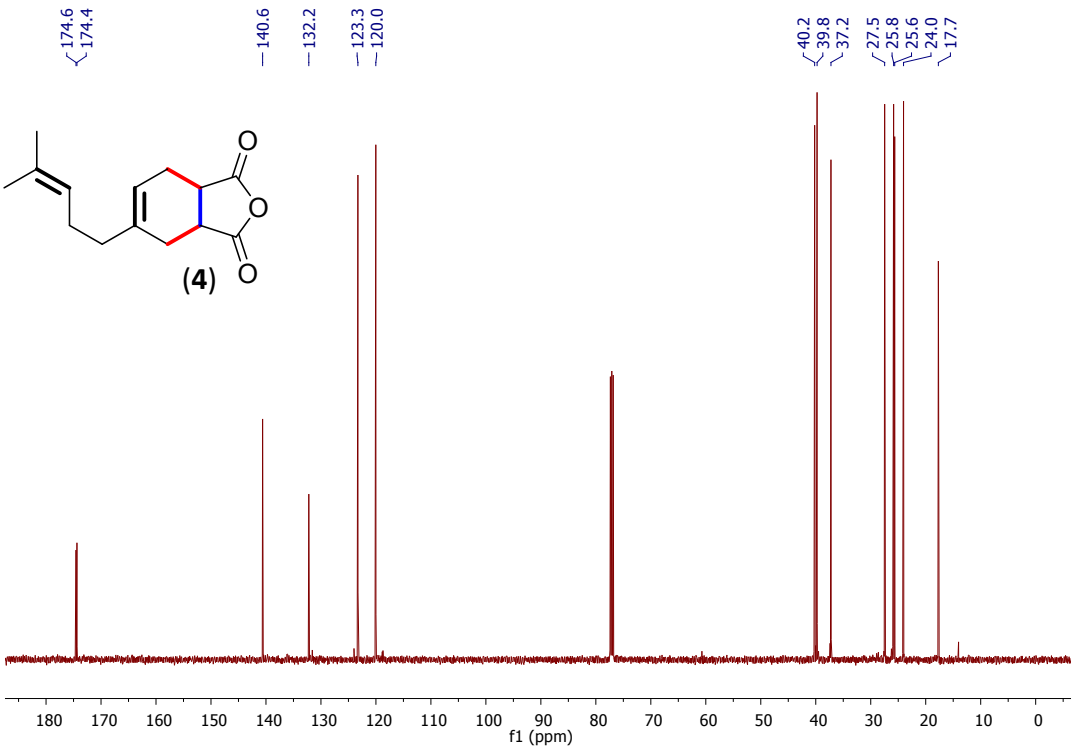


Figure S4. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **4** synthetized from myrcene.

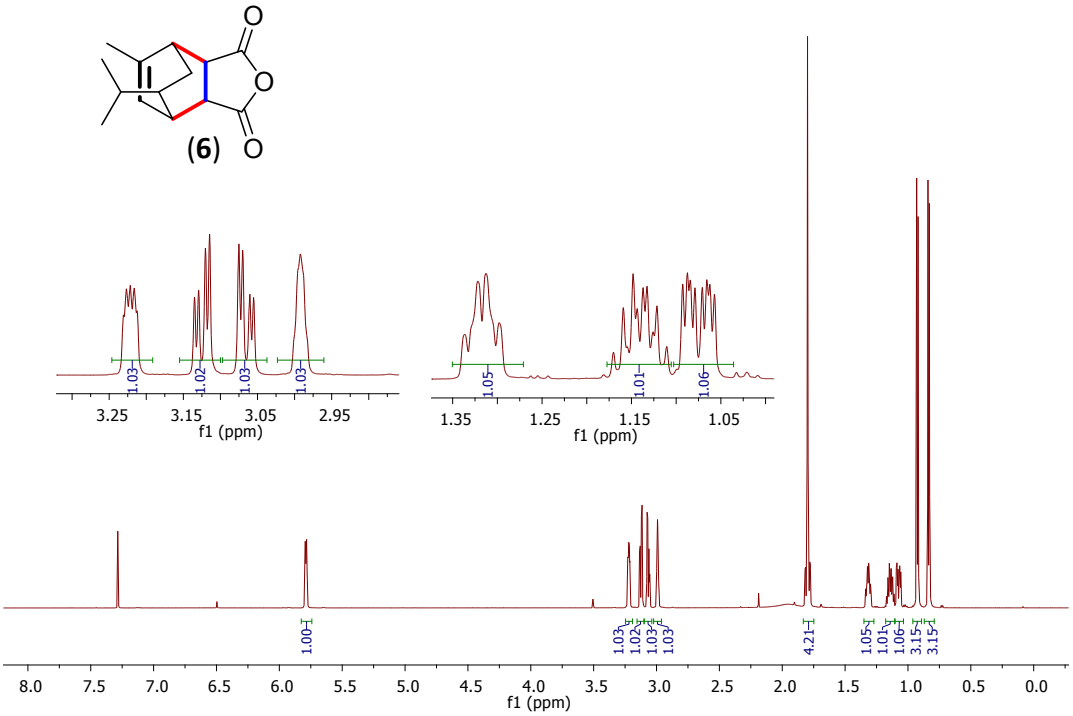


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of monomer **6** synthetized from phellandrene.

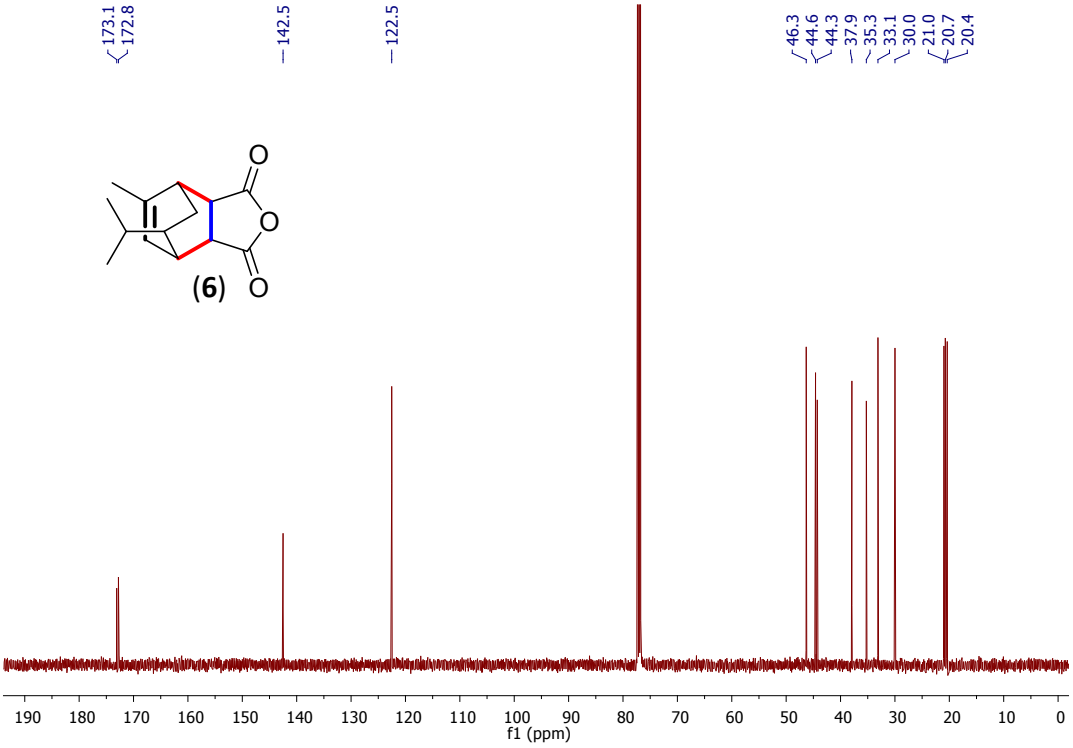


Figure S6. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **6** synthetized from phellandrene.

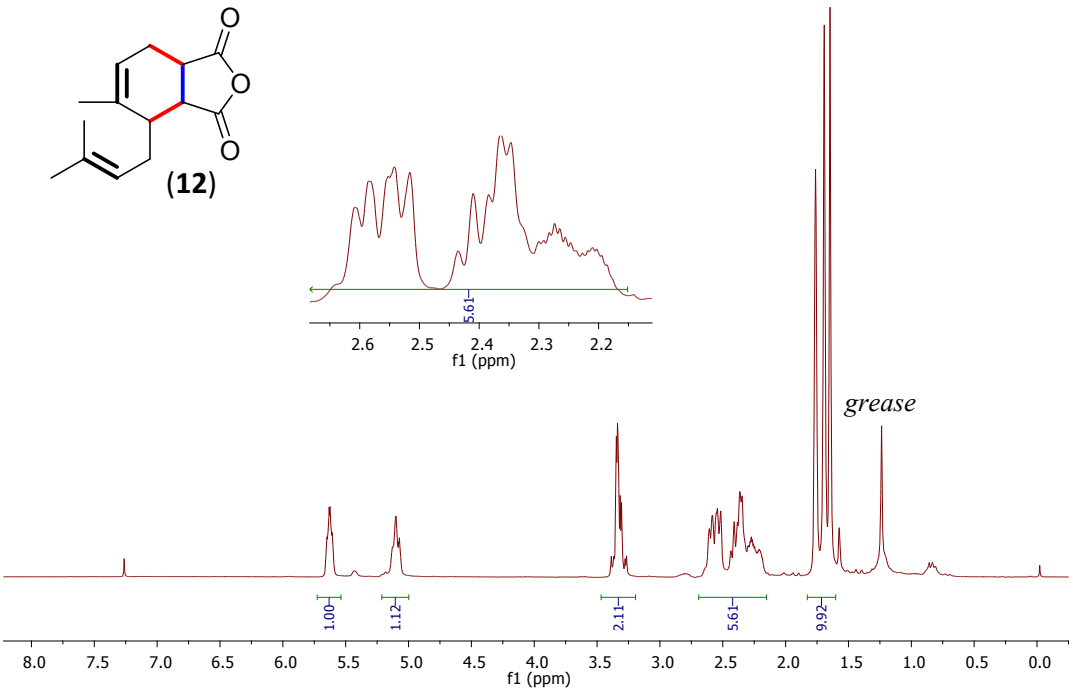


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of monomer **12** synthetized from ocimene.

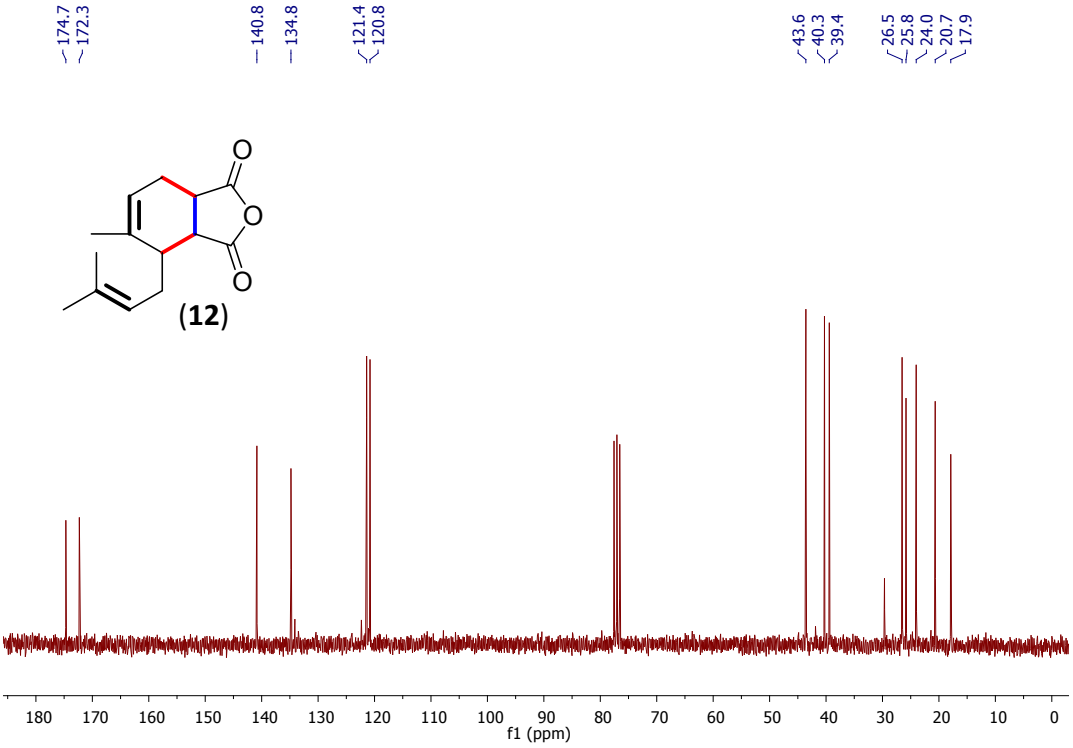


Figure S8. ^{13}C NMR spectrum ($CDCl_3$, 63 MHz) of monomer **12** synthetized from ocimene.

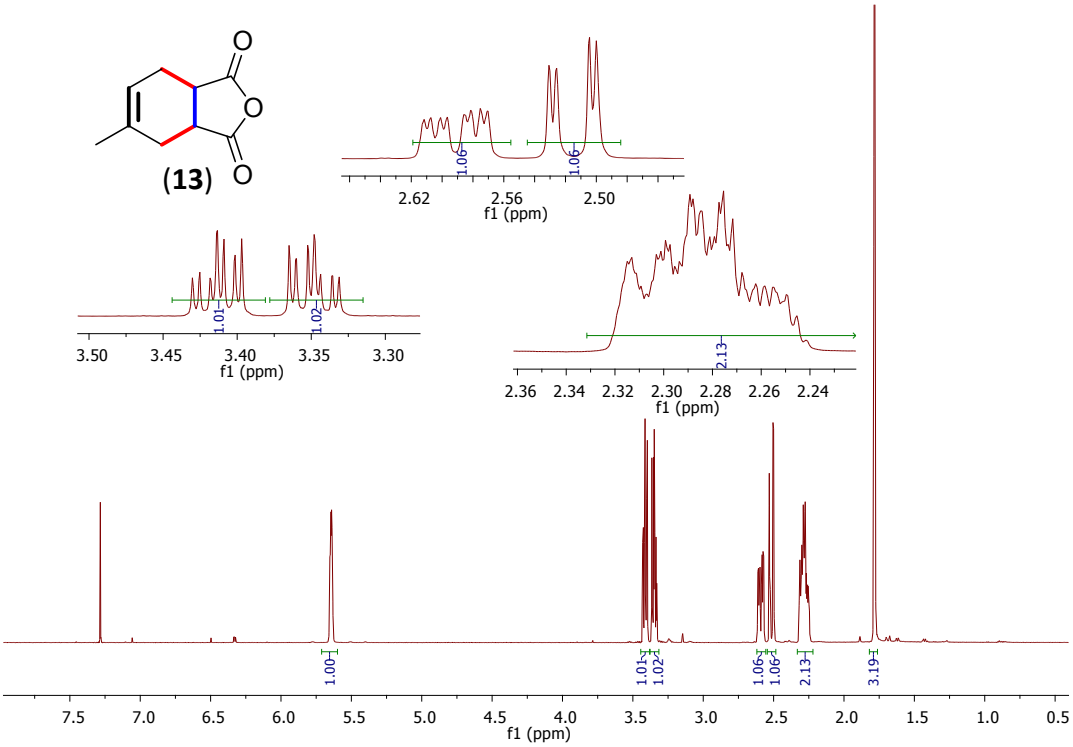


Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of monomer **13** synthetized from isoprene.

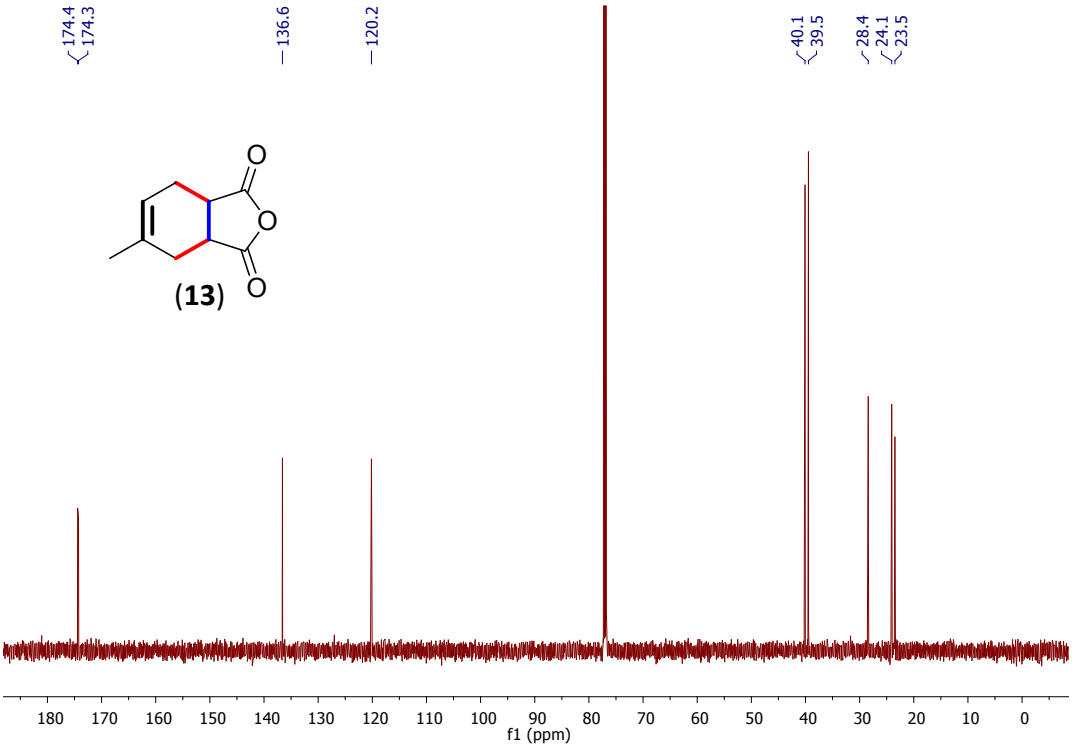


Figure S10. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of monomer **13** synthetized from isoprene.

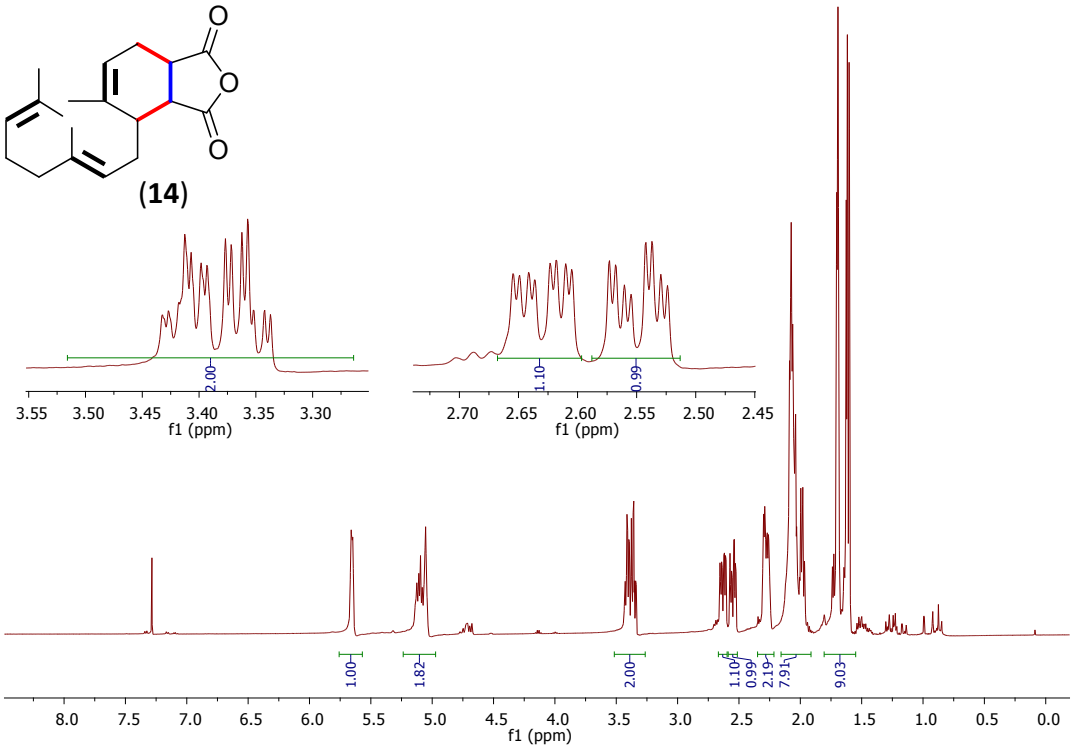


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **14** synthetized from farnesene.

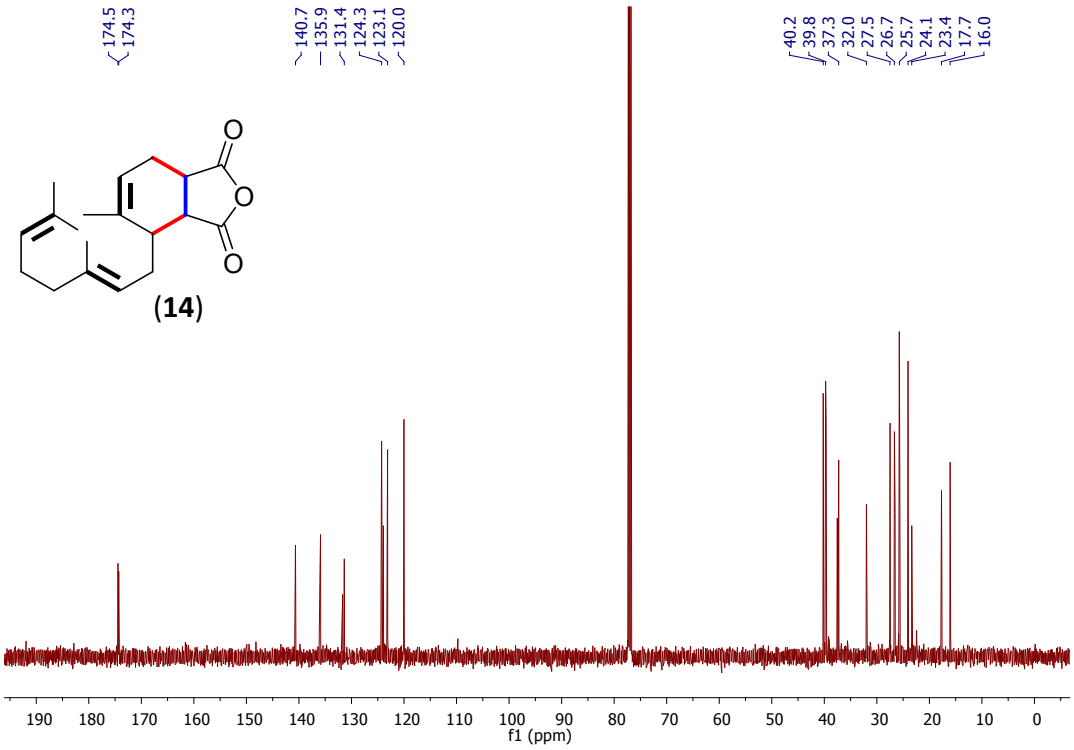


Figure S12. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **14** synthetized from isoprene.

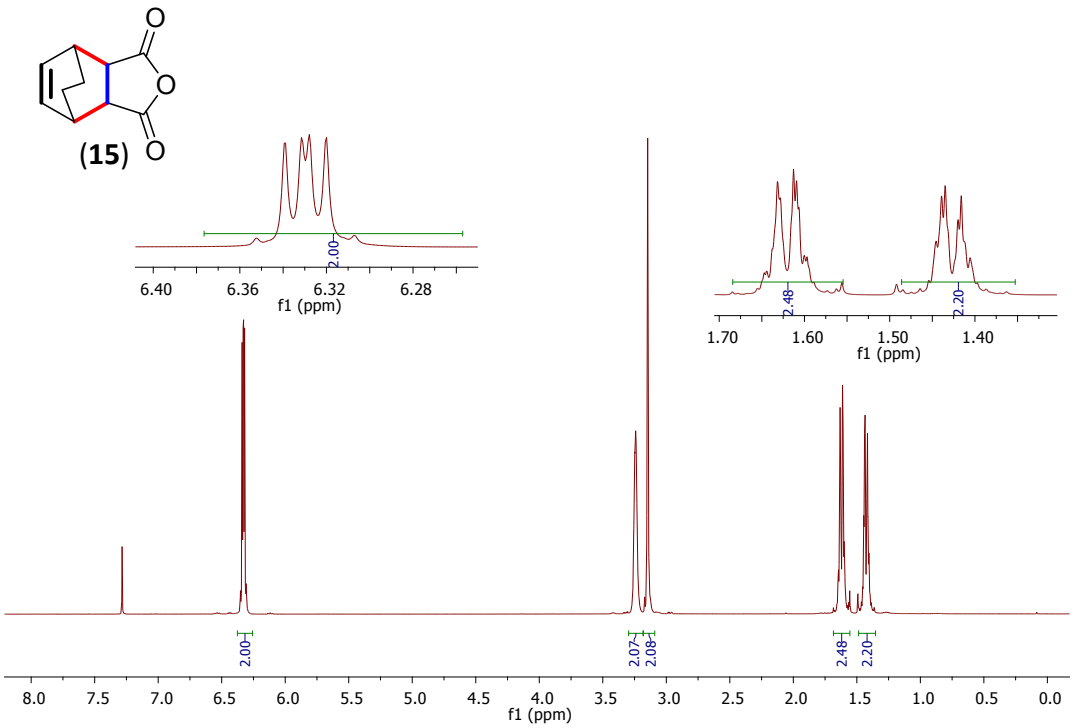


Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of monomer **15** synthetized from 1,3-cyclohexadiene.

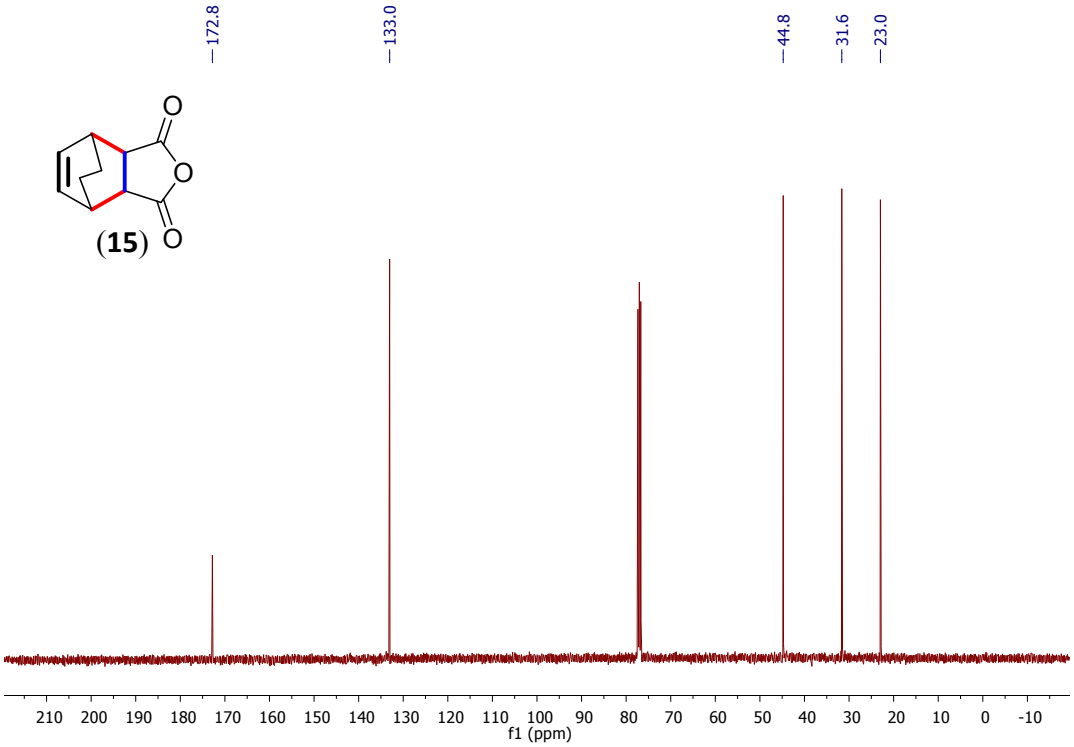


Figure S14. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of monomer **15** synthetized from 1,3-cyclohexadiene.

5.4. ^{1}H and ^{13}C NMR spectra for Hydrogenated monomers.

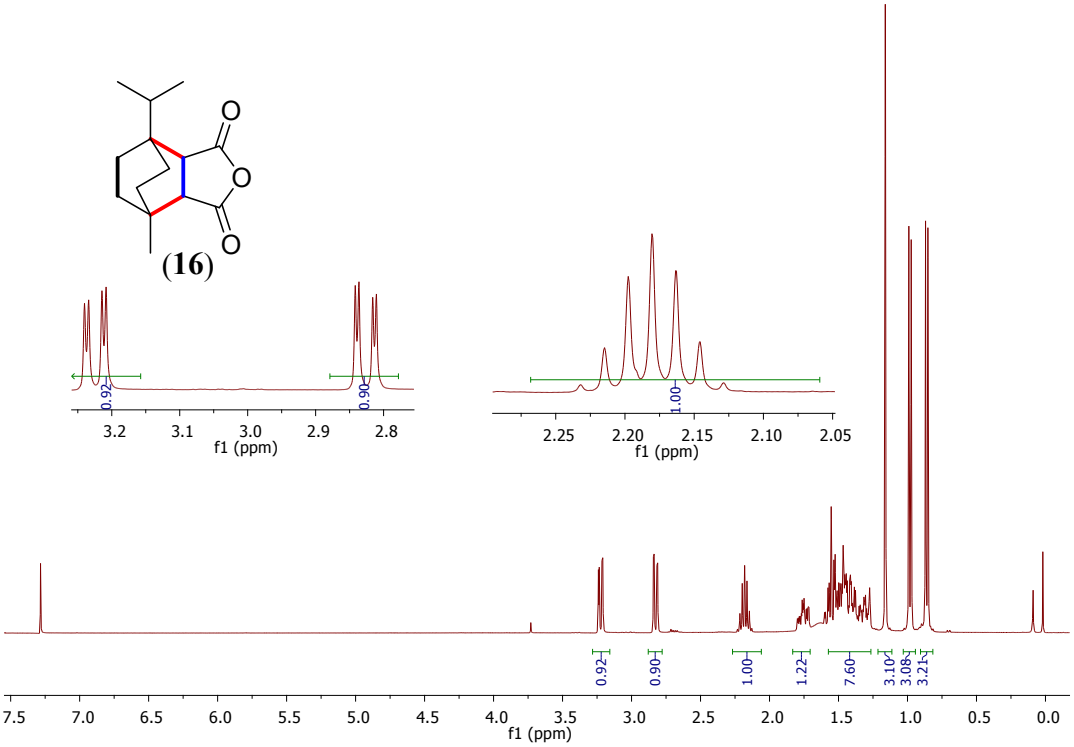


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of monomer **16** synthetized from α-terpinene.

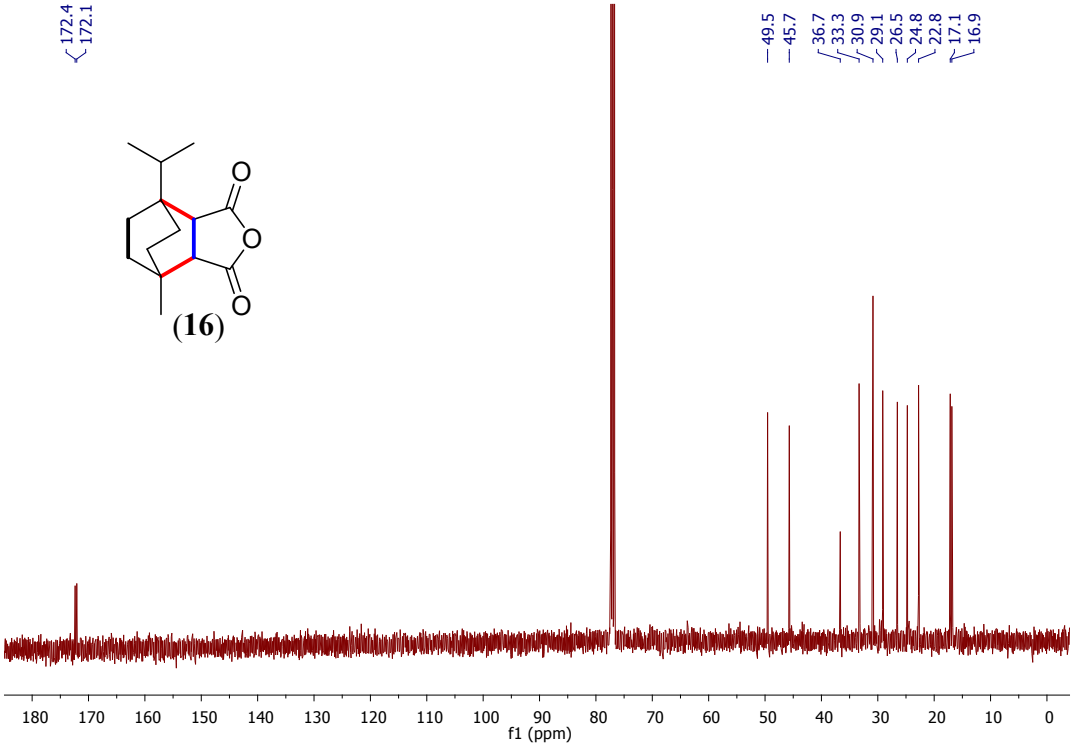


Figure S16. ^{13}C NMR spectrum ($CDCl_3$, 101 MHz) of monomer **16** synthetized from α-terpinene.

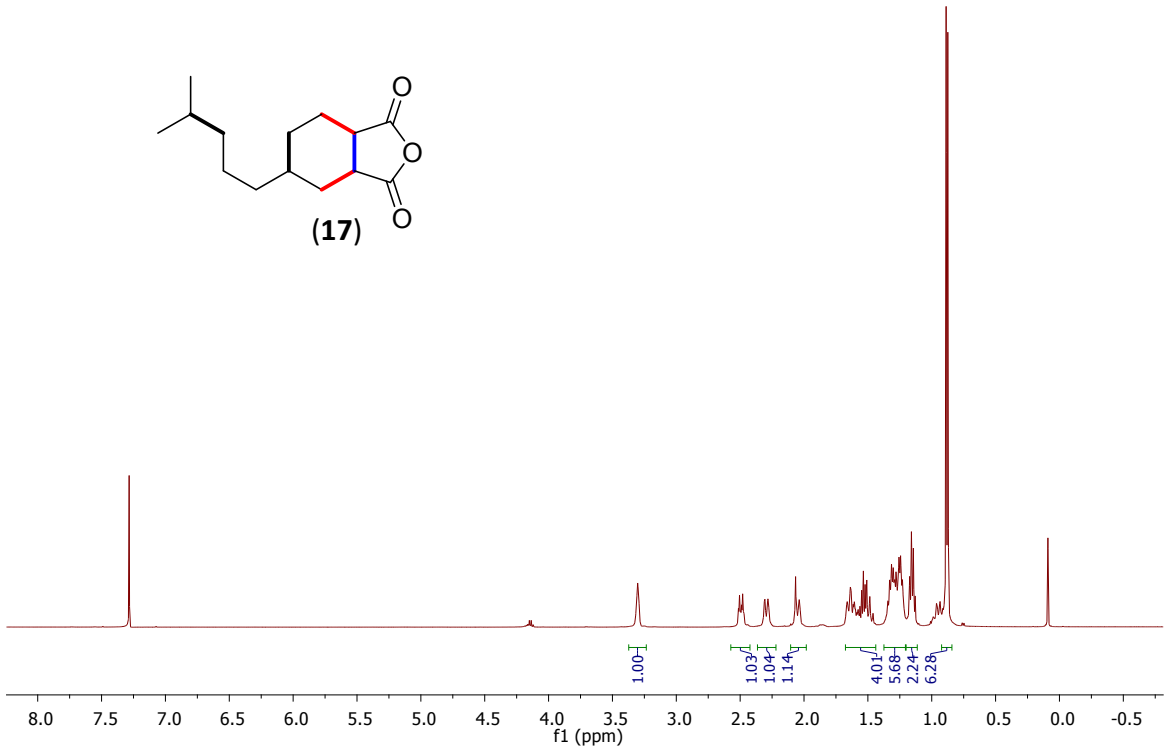


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **17** synthetized from mircene.

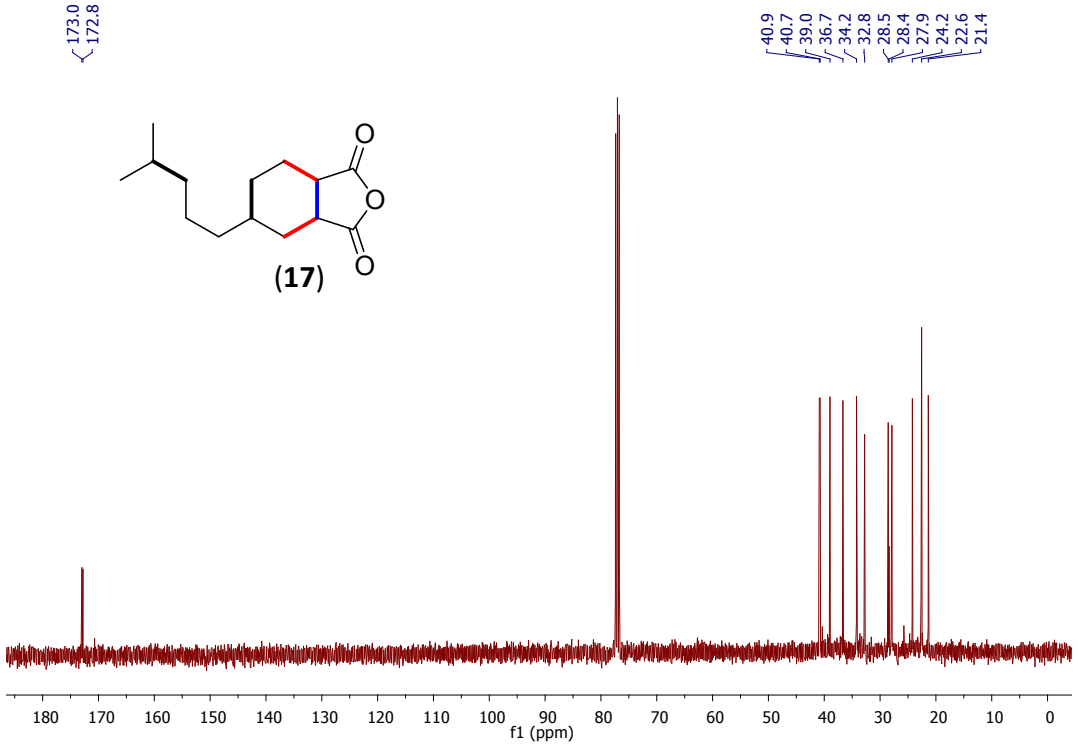


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **17** synthetized from mircene.

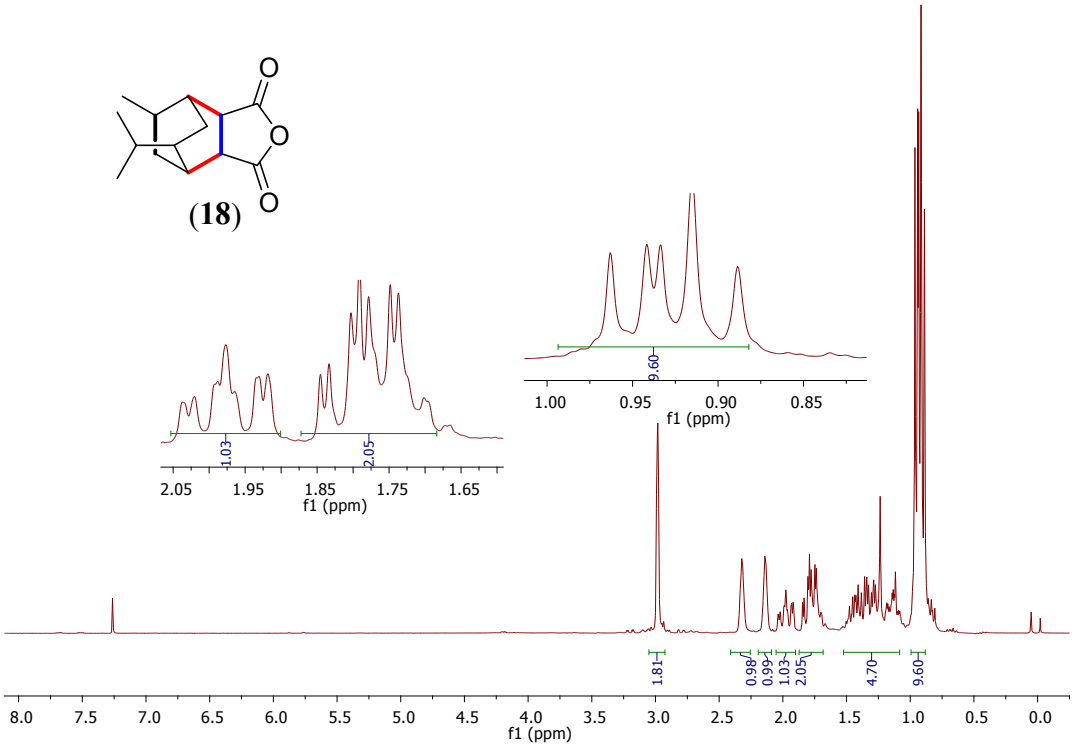


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of monomer **18** synthetized from phellandrene.

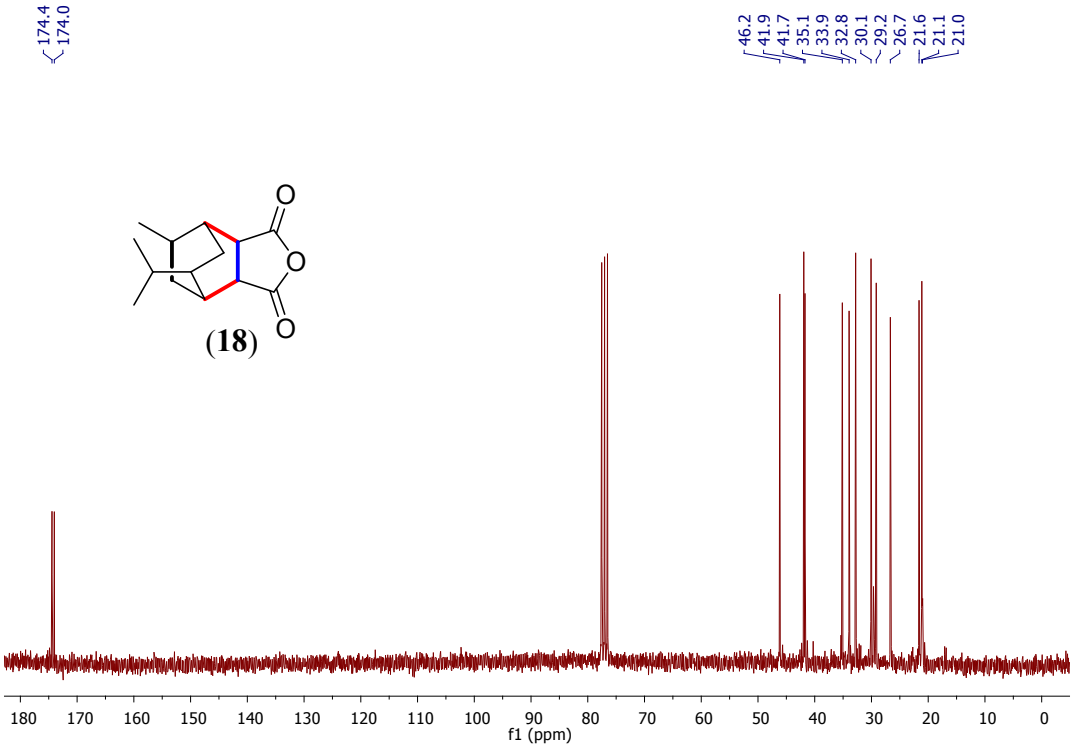


Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 63 MHz) of monomer **18** synthetized from *α*-phellandrene.

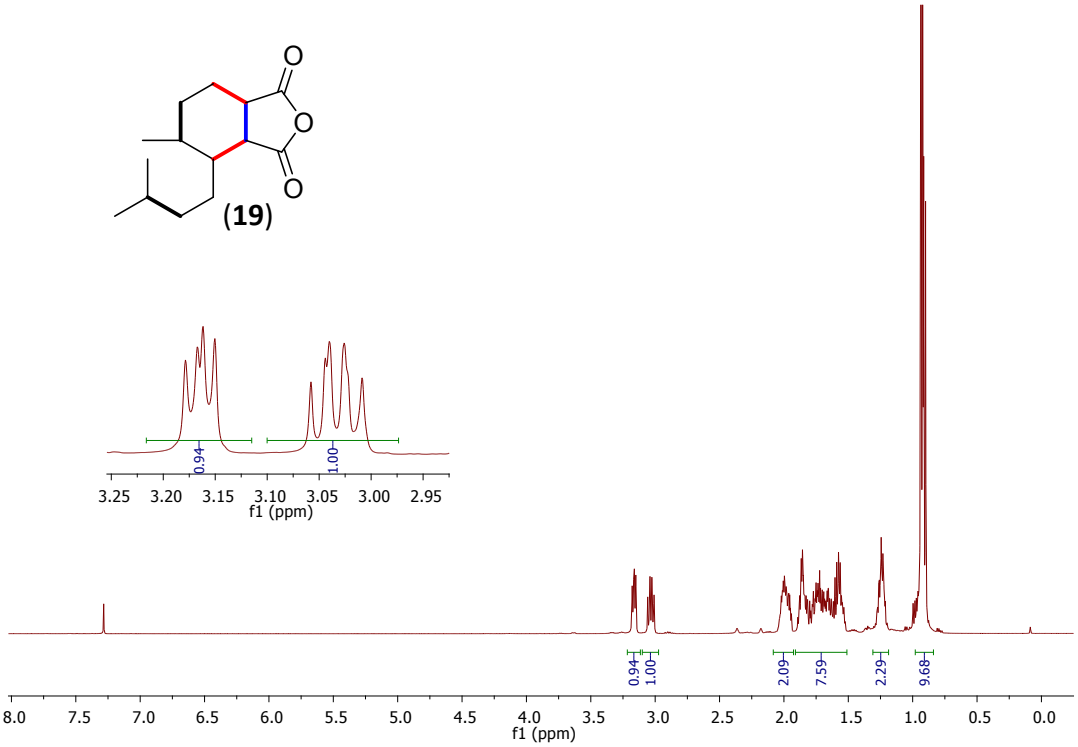


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **19** synthetized from ocimene.

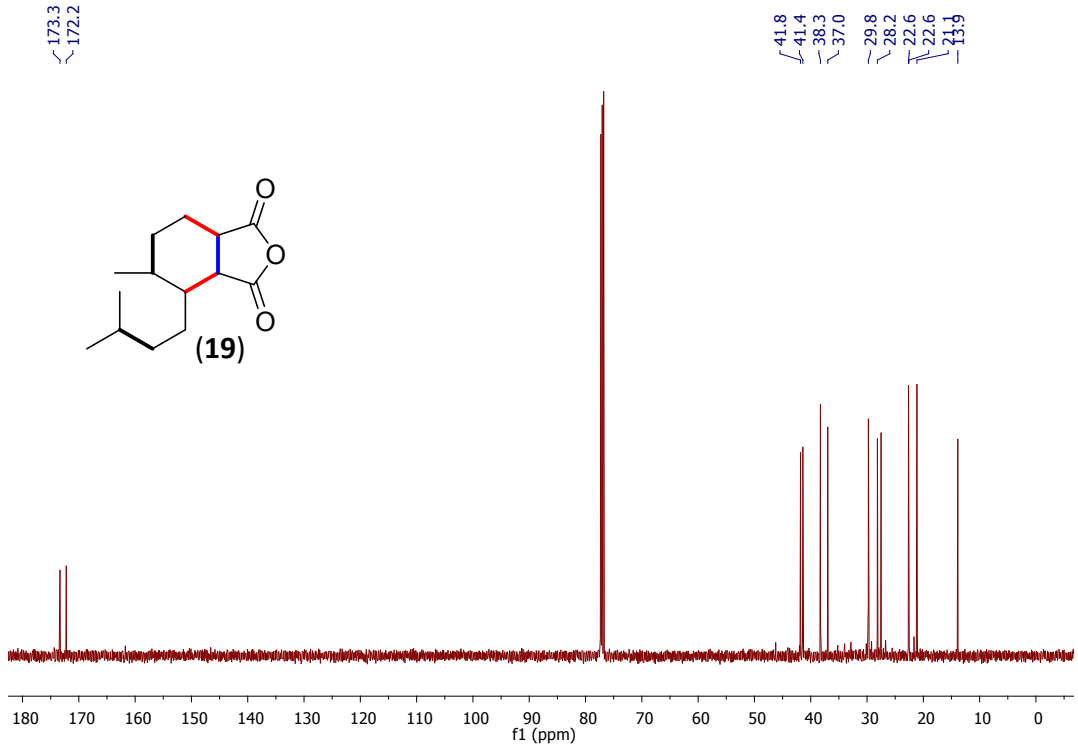


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **19** synthetized from ocimene.

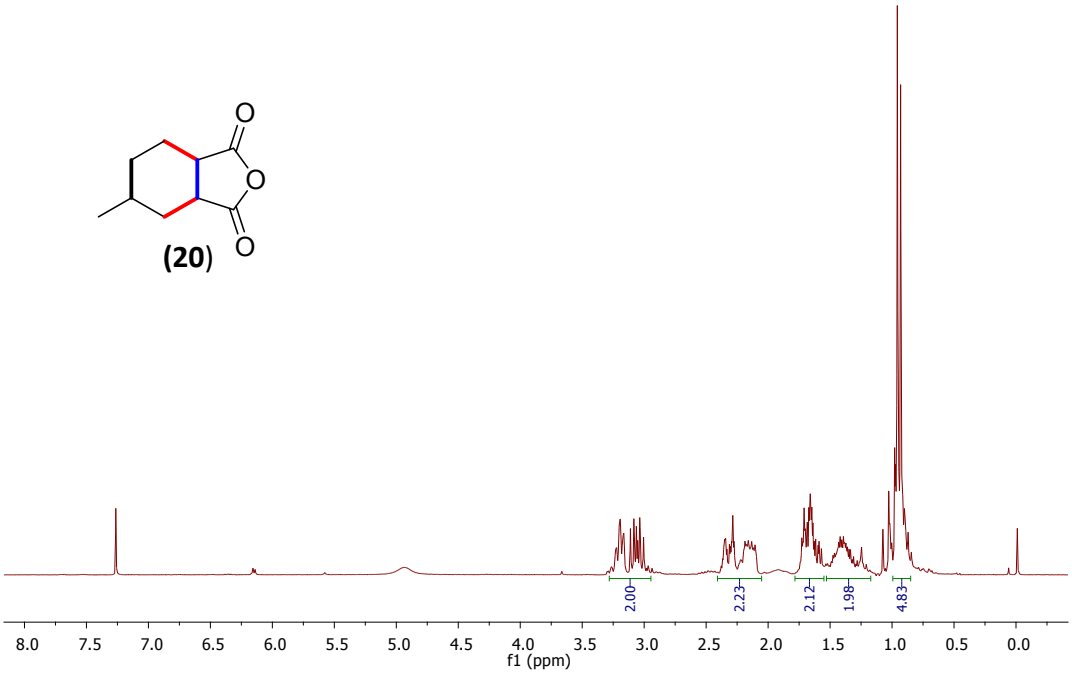


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 250 MHz) of monomer **19** synthetized from isoprene

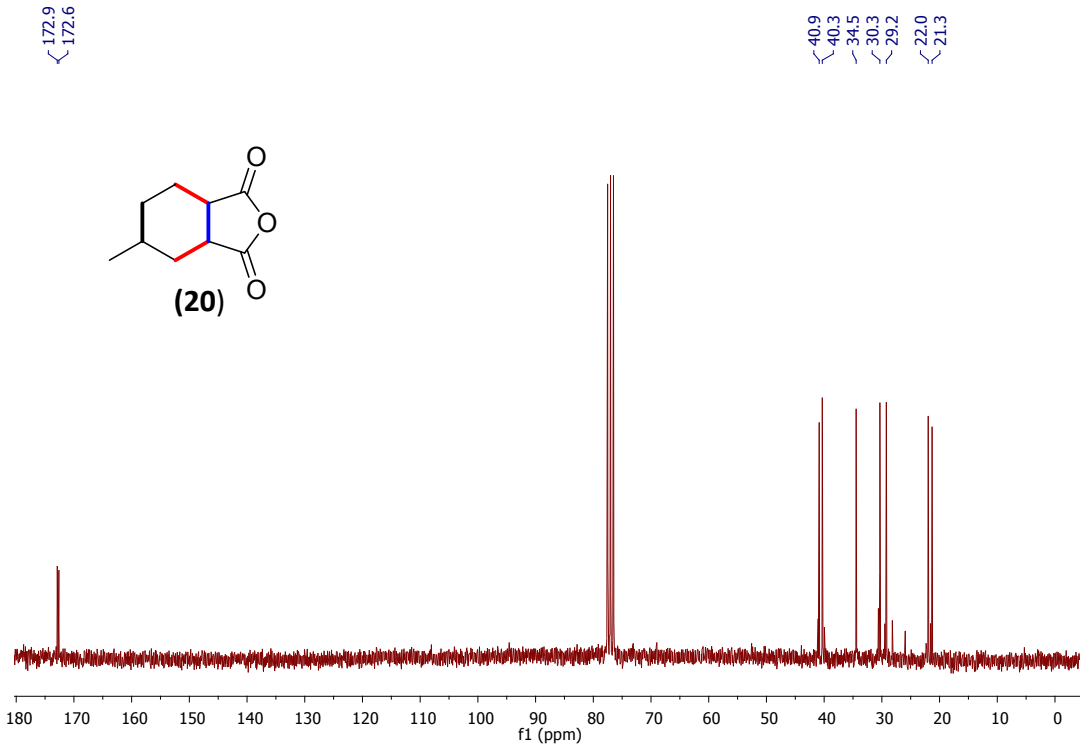


Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 63 MHz) of monomer **19** synthetized from isoprene.

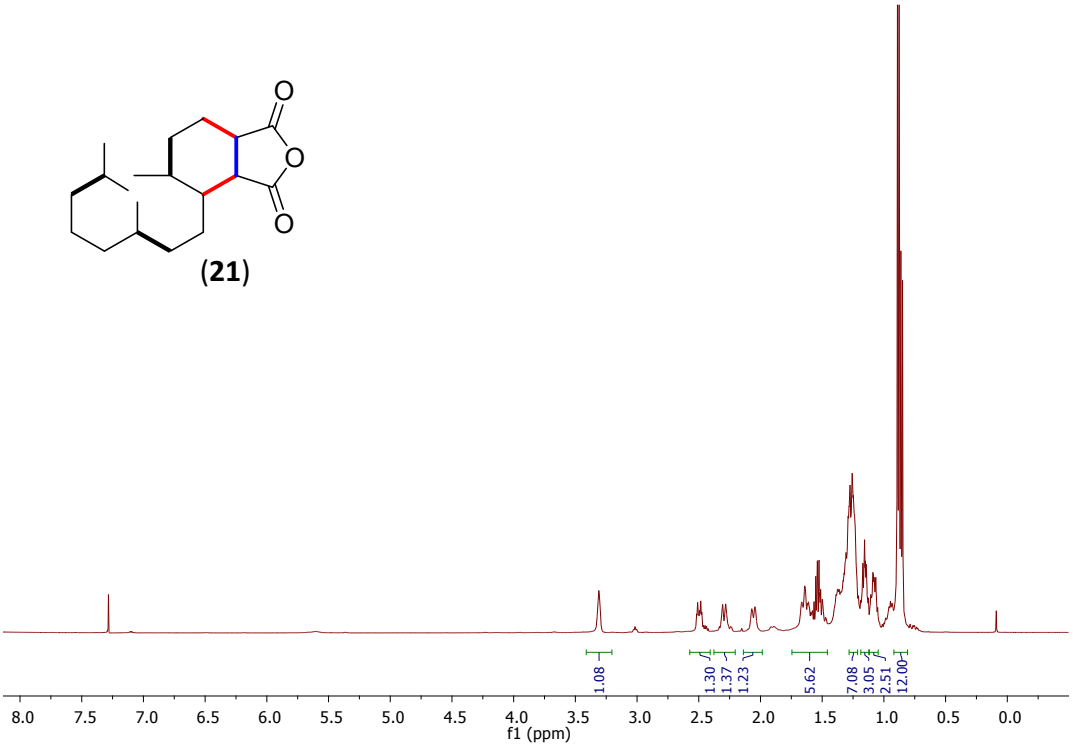


Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **21** synthetized from farnesene.

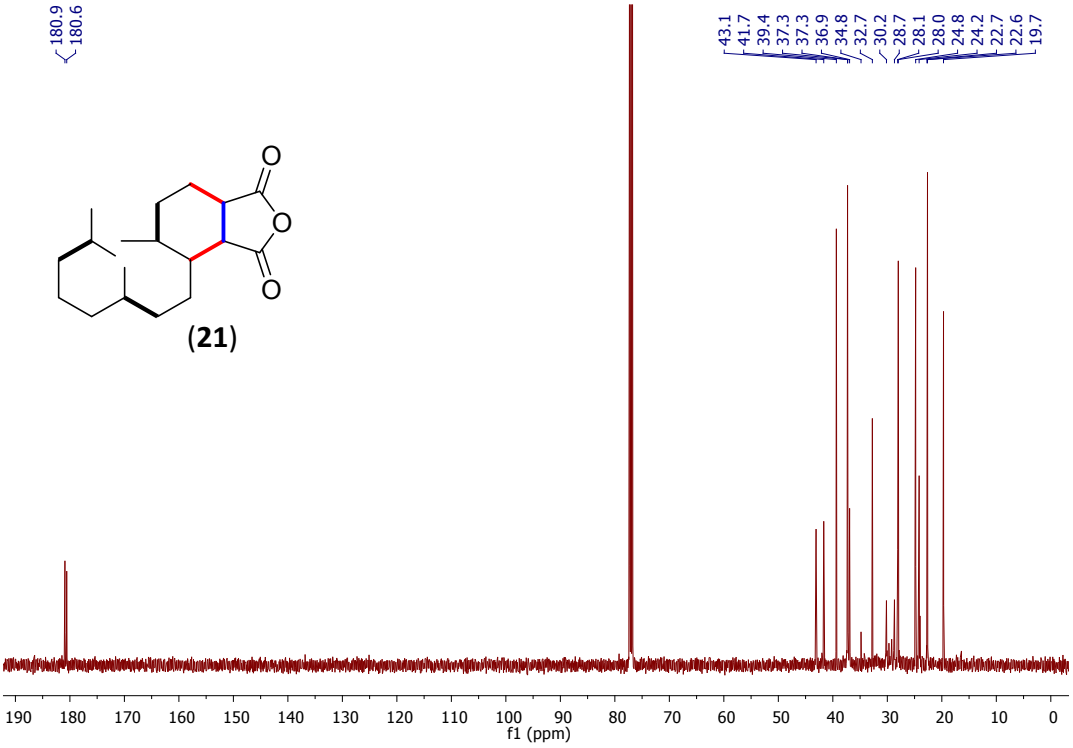


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **21** synthetized from farnesene.

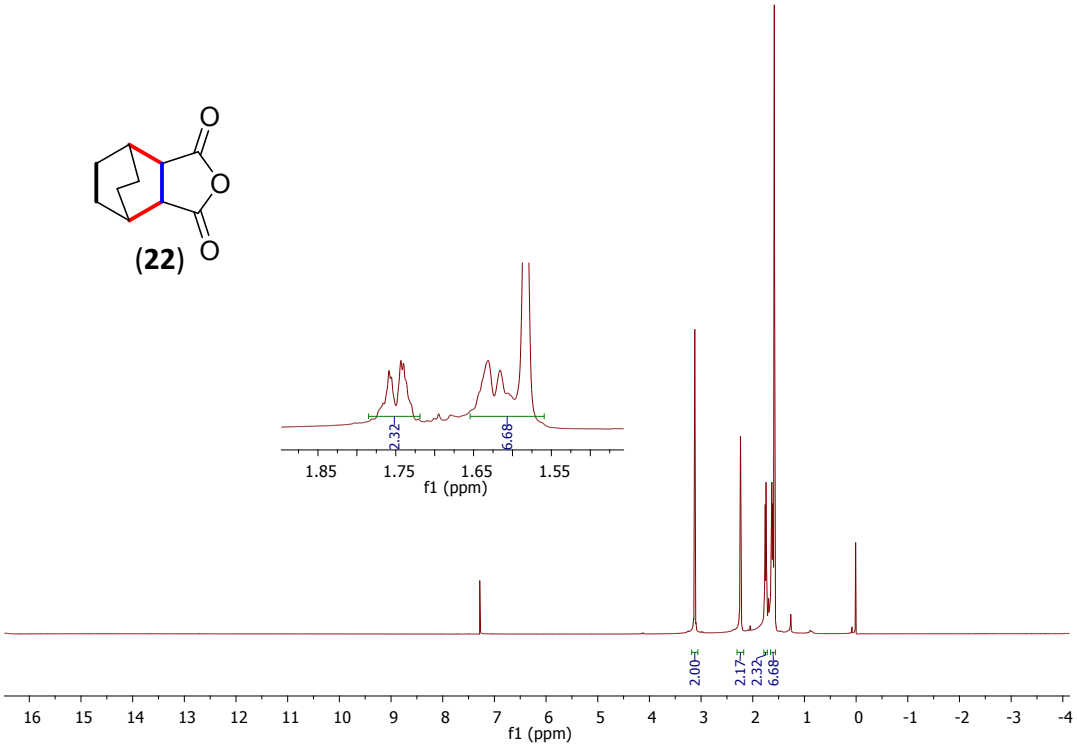


Figure S23. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of monomer **22** synthetized from 1,3-cyclohexadiene.

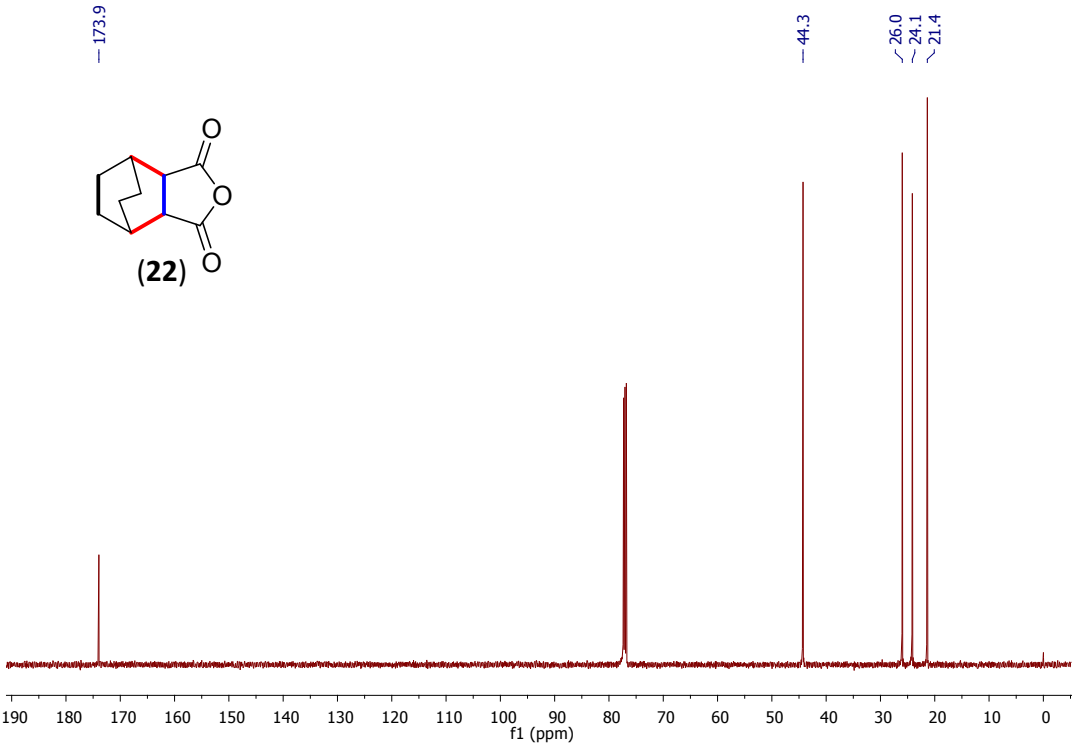


Figure S24. ^{13}C NMR spectrum ($CDCl_3$, 126 MHz) of monomer **22** synthetized from 1,3-cyclohexadiene.