

Supporting Information

A sustainable polymer and coating system based on renewable raw materials

*Johannes G.H. Hermens, Thomas Freese, Georgios Alachouzos, Mathieu L. Lepage, Keimpe J. van den Berg, Niels Elders, Ben L. Feringa**

Paints and coatings are widely used in modern society and their current production is mainly dependent on the petrochemical industry. The establishment of processes using sustainable alternative monomers based on biorenewable resources, using exclusively biobased reagents and using green synthetic transformations are highly warranted for a more sustainable future. Herein, we report on a sustainable polymer and coating system based on the monomer methoxybutenolide, a biobased acrylate alternative. Methoxybutenolide and the comonomer dodecyl vinyl ether are synthesized from biobased platform chemicals using the environmentally benign synthetic transformations photooxygenation and vinylation. For the photooxygenation, a biobased photosensitizer was developed exerting high quantum yields. The monomers were copolymerized using biomass derived (photo)initiators to yield fully biobased polymers and coatings with properties comparable to acrylate based coatings.

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General Considerations

Commercial reagents and solvents: Unless stated otherwise, all reagents and solvents were obtained from the commercial sources: Sigma–Aldrich, TCI, Boom and Linde-gas and were used as received. Anhydrous solvents were purified by passage through solvent purification columns (MBraun SPS-800).¹ For aqueous solutions, demineralized water was used.

Reagents: Furfural (99%), methylene blue, α -angelica lactone (98%), MnO_2 (>99%) 1-dodecanol (98%), 1,4-butanediol (99%), calcium carbide (granulated, >75%), α -terpinene (95%), vanillin (99%), allyl bromide (97%), anhydrous triethylamine (>99.5%), diphenylphosphite, phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO, 97%) were purchased from *Sigma–Aldrich* (Zwijndrecht, The Netherlands).

Tert-butyl peroxy-3,5,5-trimethylhexanoate (Trigonox 42S) was obtained from *AkzoNobel Car Refinishes BV* (Sassenheim, The Netherlands).

Diformylfuran (>98%) was purchased from *TCI* (Zwijndrecht, Belgium).

Oxygen compressed (technical grade) was purchased from *Linde-gas* (Schiedam, The Netherlands).

Solvents: Methanol (MeOH, 99%, AR grade), diethyl ether (Et_2O , stabilized with BHT, AR grade), and pentane (*n*-pentane, HPLC grade), ethyl acetate (technical grade), DMSO, THF (HPLC grade), DCM were purchased from *Boom* (Meppel, The Netherlands).

1,4-dioxane (99.8%), GVL (99%) and butyl acetate (>99.5%) were purchased from *Sigma–Aldrich* (Zwijndrecht, The Netherlands).

Equipment: white light LED lamps (575 lm, 8 W each; 5750 lm, 80 W total) as light source for the rotary photoreactor.

LEDs (OSRAM Oslon SSL 80 royal blue, LDCQ7P-2U3U, 500 mW, $\lambda = 445$ nm, 180 mW/cm²) as light source for batch photooxygenations.

UV Flood 36 (12 x 3 W, $\lambda = 395$ nm, 21 mW/cm²)

Byk applicator (50-200 μm , 10 cm) to apply coatings.

General Analytical Information: Nuclear Magnetic Resonance spectra were measured with an Agilent Technologies 400-MR (400/54 Premium Shielded) spectrometer (400 MHz). All spectra were measured at room temperature (22–24 °C). Chemical shifts for the specific NMR spectra were reported relative to the residual solvent peak [in ppm; CDCl_3 : $\delta\text{H} = 7.26$; CDCl_3 : $\delta\text{C} = 77.16$].² The multiplicities of the signals are denoted by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br s (broad signal), app (apparent). All ¹³C-NMR spectra are ¹H-broadband decoupled.

High-resolution mass spectrometric measurements were performed using a Thermo scientific LTQ OrbitrapXL spectrometer with ESI ionization. The molecule-ion M^+ , $[\text{M} + \text{H}]^+$ and $[\text{M} - \text{X}]^+$, respectively, are given in m/z-units.

UV-vis spectra were recorded with an Agilent 8543 spectrophotometer.

GPC spectra were measured with an Agilent 1100 series, PLgel Mixed E 3 μm column, 2-methylTHF as solvent, 1 mL/min flow, GBC LC 1240 RI detector, 40°C, toluene as internal standard and 20 μL injection.

Knoop hardness's (Related to ASTM D1474, method A) are measured using the Fischerscope HM 2000 Xyp equipment calibrated using poly(methyl methacrylate) (PMMA).

The indentation hardness is determined by measuring the indentation depth after applying a 98 mN (10 gram) load for 18 seconds using a diamond pyramidal shaped indenter (longitudinal angles: 172°30' and transverse angles: 130°) to the dried coating. Five consecutive measurements on different

predefined spots are performed making sure the indentation depth does not exceed 75% of the coating thickness. The Knoop hardness is calculated by:

Equation S1 Knoop hardness.

$$H_K = \frac{P}{C \times d^2}$$

Where:

H_K = Knoop hardness in kg/mm².

P = load applied on the indenter in kg.

C = indenter correction constant: 65.438.

d = indentation depth in mm.

Glass temperatures (T_g) were measured with a Differential Scanning Calorimeter (DSC) Q2000 (TA Instruments) in a modulated way from -80°C/110°C at 5°C/min in two consecutive runs using helium (50 mL/min) as purge gas. Fourier transformation enables the separation of the modulated heat flow into a heat capacity component (Reversing Heat Flow) and a kinetic component (Non-reversing Heat Flow) allowing to separate different thermal events occurring at the same time.

At the materials T_g (observed in the reversing heat flow curve) the heat capacity of the material changes rapidly resulting in a strong decrease of the reversing heat flow curve over a certain transfer area. The T_g is calculated at the point of inflection ($T_g(I)$) for both runs.

MEK double rub resistances are measured by rubbing the coating back and forth (5 cm) with a cloth soaked in 2-butanone (MEK) applying 10 N downward pressure. The number of double rubs (= 1x back and 1x forth) until the coating failure (dissolution) are counted with a maximum for 200 double rubs. At >200 double rub resistance the film appearance is described (e.g. dulling, staining, or any other change in appearance).

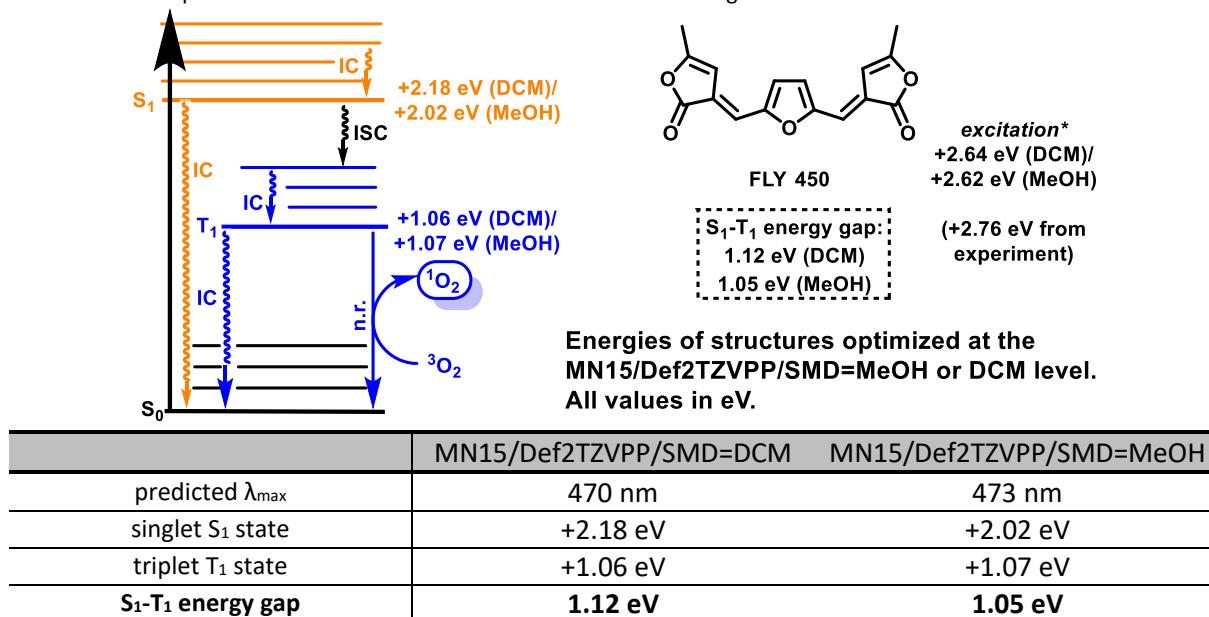
DFT calculations

Overview of Methods and Results

All computational input files were prepared in GaussView 6.0 on a local Windows 10 terminal. Input files were then transferred to the Rijksuniversiteit Groningen Peregrine HPC cluster where DFT or TD-DFT calculations were carried out using the Gaussian 16 (g16) suite of programs.

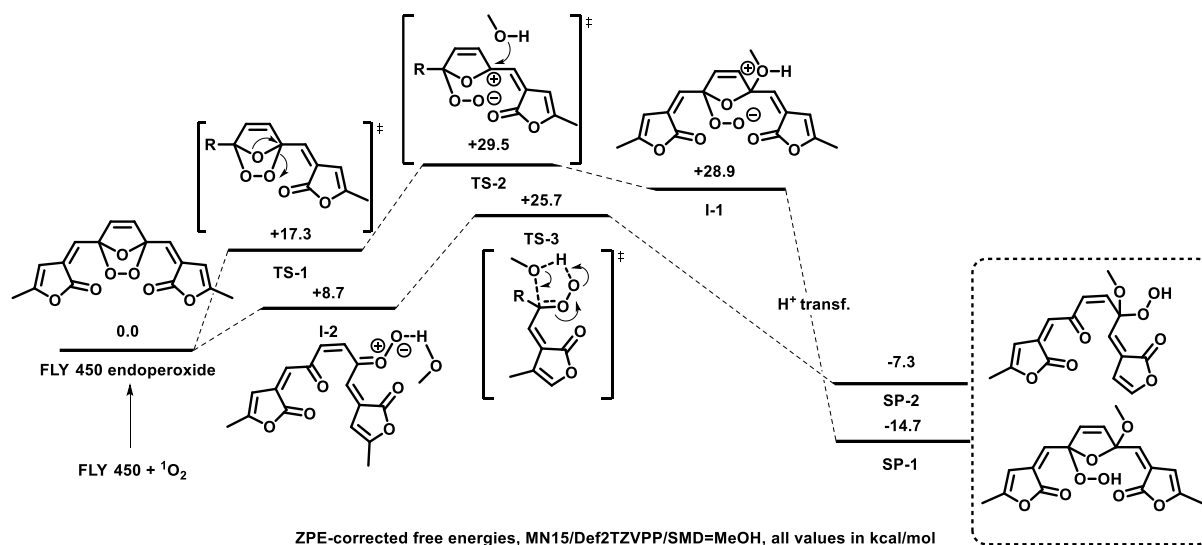
The DFT or TD-DFT energies for the S_0 ground state and both S_1 and T_1 excited states of **FLY 450**, were obtained at the MN15/Def2TZVPP/SMD=MeOH and the MN15/Def2TZVPP/SMD=DCM level. Geometry optimization to the most stable double bond isomer of either ground state S_0 or excited state S_1 or T_1 minima was carried out using the *g16 opt* command at the MN15 functional and Def2TZVPP basis set level of theory with implicit solvation using the Solvation Model based on Density (SMD = MeOH or DCM),³⁻⁵ and the energies reported were read from the *g16* output file. Vertical excitations are obtained from a TD-DFT calculation at the MN15/Def2TZVPP/SMD=MeOH and the MN15/Def2TZVPP/SMD=DCM level, using the S_0 geometry optimized at the same level of theory as the input geometry.

Table S1 The computed excited state S_1 or T_1 and vertical excitation energies of FLY 450.



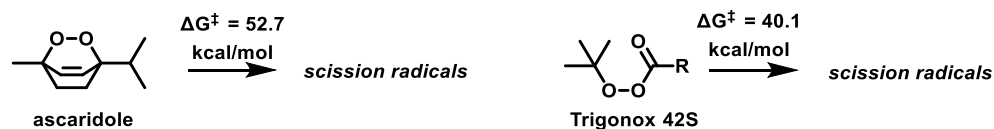
The DFT thermochemistry of decomposition pathways for **FLY 450** - endoperoxide in MeOH was also calculated. Stationary points, in addition to transition states leading to two proposed decomposition products were examined at the MN15/Def2TZVPP/SMD=MeOH level. Geometry optimization to either stationary point structures or transition state (TS) structures were carried out using the *g16 opt* command at the MN15 functional and Def2SVP basis set level of theory with implicit solvation using the Solvation Model based on Density (SMD = MeOH).³⁻⁵ Transition state geometry inputs were the result of rational guess based on bond length during bond breaking or forming events, or were the result of potential energy surface relaxed coordinate scans using the *g16 scan* command at the MN15/Def2SVP/SMD=MeOH level. Intrinsic reaction coordinate (IRC)iv calculations were carried out on the transition state structures to verify that they connected to the associated reactant and product minima structures. After optimization, frequency DFT calculations of all obtained optimized structures were carried out using the *g16 freq* command at the MN15/Def2TZVPP/SMD=MeOH level, to confirm that minima structures had zero imaginary frequencies and that transition states had a single imaginary

frequency. All shown free energies (**Scheme S1**) are ZPE and thermally corrected and were obtained from the frequency calculations. All shown free energies are reported in kcal/mol, at 298.15 K / 1 atm.



Scheme S1 The computed free energies for the decomposition pathway of the FLY 450 endoperoxide.

The DFT thermochemistry of the homolytic *O-O bond* scission for both ascaridole and Trigonox 42s (acetate used instead of 3,5,5-trimethylhexanoate) was calculated. A reactant stationary point, in addition to the homolytic *O-O bond* scission transition state was examined at the MN15/Def2TZVPP/SMD=THF level, as THF from the g16 package has the closest polarity to the employed gamma-valerolactone (GVL). Geometry optimization to either stationary point structures or transition state (TS) structures were carried out using the g16 *opt* command at the MN15 functional and Def2TZVPP basis set level of theory with implicit solvation using the Solvation Model based on Density (SMD = THF).³⁻⁵ Transition state geometry inputs were the result of potential energy surface relaxed coordinate scans using the g16 *scan* command at the MN15/Def2TZVPP/SMD=THF level. Intrinsic reaction coordinate (IRC)iv calculations were carried out on the transition state structures to verify that they connected to the associated reactant and product minima structures. After optimization, frequency DFT calculations of all obtained optimized structures were carried out using the g16 *freq* command at the MN15/Def2TZVPP/SMD=THF level, to confirm that minima structures had zero imaginary frequencies and that transition states had a single imaginary frequency. All shown free energies (**Scheme S2**) are ZPE and thermally corrected and were obtained from the frequency calculations. All shown free energies are reported in kcal/mol, at 298.15 K / 1 atm.



Scheme S2 The computed barrier of activation for the homolytic decomposition of biobased radical initiator ascaridole and reference radical initiator Trigonox 42S.

Experimental Procedures

Regarding optimization and justification of sustainability of our experimental procedures, we report our attempts below.

Fly 450 was synthesized according to an adapted procedure.⁶ Although it was reported that high yields were only achieved using Mn₂O₃ in 1,4-dioxane, we opted for the more sustainable condensation of diformylfuran with α -angelica lactone using CaCO₃ in water. To our delight, **FLY 450** could be isolated via a filtration in similar high yields.

The photooxidation and subsequent condensation of furfural towards **hydroxybutenolide** and **methoxybutenolide** have been previously extensively optimized towards the highest productivity.⁷ It is important to note that the photooxidation can be performed in the more environmentally benign solvents ethanol or isopropanol.⁸ However, since we were exclusively interested in **methoxybutenolide**, we performed the photooxidation in methanol in which the crude reaction mixture of the photooxidation can be used directly in the condensation, preventing an extra purification step.

From a safety perspective, the larger scale synthesis of **ascaridole** was performed at a lower concentration than the previously optimized reaction conditions for the photooxidation of furfural.⁷ Besides, we opted for the more sustainable solvent isopropanol⁸ in combination with methylene blue as photosensitizer which resulted in shorter irradiation times due to the higher absolute rate of singlet oxygen production (Table 1).

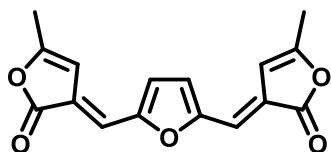
The vinylation of 1-dodecanol and 1,4-butanediol using calcium carbide was carried out according to the reported procedure.⁹ Attempts were made to isolate both **dodecyl vinyl ether** and **1,4-butanedivinyl ether** with distillation under reduced pressure, however high purities could only be achieved using column chromatography.

4-(allyloxy)-3-methoxybenzaldehyde (1) was synthesized according to the reported literature procedure.¹⁰ Rather than using distillation under reduced pressure, the product (**1**) was obtained with high purity after the extraction, allowing us to continue without further purification. The compounds **((4-(allyloxy)-3-methoxyphenyl)(hydroxy)methyl)diphenylphosphine oxide (2)** and **(4-(allyloxy)-3-methoxyphenyl)(diphenylphosphoryl)methanone (VAPO)** were synthesized according to the literature procedure. An attempt was made to isolate **VAPO** by precipitation from ethyl acetate using pentane, but proved unsuccessful to increase the purity.

The free radical copolymerization of **methoxybutenolide** with **dodecyl vinyl ether** was carried out according to the previously reported optimized reaction conditions.⁷ The solvent butyl acetate was replaced by the biobased and more sustainable solvent GVL. Although we aim to obtain full conversion of both our monomers, the copolymerization is occasionally inhibited, leading to incomplete conversion. Previously we rationalized the inhibition of the copolymerization can be attributed to the H-abstraction from the acetal position of the butenolide by the propagating radical, generating a captodative stabilized radical.⁷ This secondary radical process is more prominent with lower observed polymerization rates, hence lower conversions are obtained when using ascaridole as thermal initiator (Table 2). For determination of the polymer molecular weight, the solvent and remaining monomers are removed under reduced pressure. In theory, these monomers can be recovered and reused, however as we performed the polymerization reactions on a considerable small scale, this process was impractical.

The UV-curing of **methoxybutenolide** and **1,4-butanedivinyl ether** is performed in the absence of any solvent. Although the conversion of the monomers in the dry film was not measured, we propose there is only a minimal amount Volatile Organic Compounds (VOC) released as the curing speeds are generally very high.

FLY 450



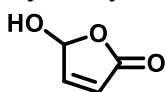
A solution of diformylfuran (100 mg, 0.81 mmol, 1 eq.), α -angelica lactone (237 mg, 2.42 mmol, 3 eq.) and CaCO_3 (242 mg, 2.42 mmol, 3 eq.) in demineralized H_2O (5.5 mL, 0.15 M) was prepared and stirred at reflux for 3 h. The reaction mixture was allowed to cool down, subsequently filtered and the volatiles were removed under reduced pressure. The residue was dissolved in EtOAc (10 mL), activated charcoal (500 mg) was added and the suspension was stirred at room temperature for 1 h. The mixture was filtered and concentrated under reduced pressure to obtain **FLY 450** as a bright red solid (160 mg, 0.56 mmol, 70%).

^1H NMR (400 MHz, CDCl_3) δ 6.97 (t, J = 0.9 Hz, 2H), 6.83 (s, 2H), 6.42 (t, J = 1.3 Hz, 2H), 2.25 (t, J = 1.1 Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.11, 154.79, 124.72, 120.13, 117.63, 103.96, 15.51.

HRMS calculated 286.07910, found 286.07896.

Hydroxybutenolide (rotary photoreactor, methylene blue as photosensitizer)



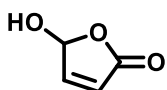
A solution of freshly distilled (50°C, 1×10^{-2} mbar) furfural (1.0 g, 10 mmol, 1 eq.) and methylene blue (17 mg, 52 μmol , 0.5 mol%) in 10 mL O_2 enriched methanol (1 M) was prepared in a round bottom flask (1 L). The mixture was put under an O_2 atmosphere in a standard lab rotary evaporator (175 rpm), as described *vide infra*, and irradiated by 10 LED lamps (8 W per LED, 80 W total) at room temperature for 20 min. The light sources were placed at a distance of approximately 5 cm from the flask. After the reaction, methanol was evaporated under reduced pressure. The obtained oil solidified upon standing. The product 5-hydroxy-2(5H)-furanone could be used without further purification (1.0 g, 10 mmol, >99% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 5.7 Hz, 1H), 6.25 (s, 1H), 6.23 (d, J = 5.7 Hz, 1H), 5.04 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.80, 152.31, 124.70, 99.05.

HRMS calculated 99.0088, found 99.0090.

Hydroxybutenolide (batch photooxygenation, FLY 450 as photosensitizer)



A solution of freshly distilled (50°C, 1×10^{-2} mbar) furfural (35 mg, 362 μmol , 1 eq.) and **FLY 450** (1 mg, 3.5 μmol , 1 mol%) in 5 mL O_2 enriched methanol (0.1 M) was prepared in a 5 mL vial with septum. The mixture was irradiated at room temperature with blue light (LED, 500 mW, λ = 445 nm, 180 mW/cm²), as described *vide infra* for 20 h. After the reaction, methanol was evaporated under reduced pressure. The obtained oil solidified upon standing. The product 5-hydroxy-2(5H)-furanone could be used without further purification (36 mg, 362 μmol , >99% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 5.7 Hz, 1H), 6.25 (s, 1H), 6.23 (d, J = 5.7 Hz, 1H), 5.04 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.80, 152.31, 124.70, 99.05.

HRMS calculated 99.0088, found 99.0090.

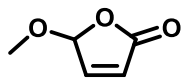
Ascaridole (rotary photoreactor, methylene blue as photosensitizer)



A solution of α -terpinene (250 mg, 1.84 mmol, 1 eq.) and methylene blue (12 mg, 37 μmol , 2 mol%) in 10 mL O_2 enriched *i*-PrOH (0.18 M) was prepared in a round bottom flask (1 L). The mixture was put under an O_2 atmosphere in a standard lab rotary evaporator (175 rpm), as described *vide infra*, and irradiated by 10 LED lamps (8 W per LED, 80 W total) at room temperature for 20 min. The light sources were placed at a distance of approximately 5 cm from the flask. After the reaction, *i*-PrOH was carefully evaporated under reduced pressure and an oil was obtained. The oil was further purified by column chromatography (silica gel, *n*-pentane/ethyl acetate : 90/10, R_f = 0.5), yielding ascaridole (260 mg, 1.55 mmol, 84%) as a slightly yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 6.49 (d, $J = 8.5$ Hz, 1H), 6.40 (d, $J = 8.5$ Hz, 1H), 2.10 – 1.95 (m, 2H), 1.91 (dq, $J = 13.9, 6.8$ Hz, 1H), 1.64 – 1.46 (m, 2H), 1.37 (s, 3H), 0.99 (d, $J = 7.0$ Hz, 6H).
 ^{13}C NMR (101 MHz, CDCl_3) δ 136.52, 133.17, 79.91, 74.48, 32.25, 29.63, 25.72, 21.52, 17.36, 17.28.
HRMS calculated 170.12566, found 170.12560.

Methoxybutenolide



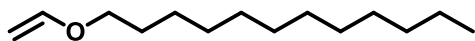
Hydroxybutenolide (10 g, 100 mmol) was dissolved in 100 ml methanol and heated at reflux for 20 hours. The conversion was followed by ^1H NMR until all hydroxybutenolide was consumed. The solvent was evaporated under reduced pressure, and the crude was distilled under reduced pressure (70°C, 1.0×10^{-2} mbar), yielding methoxybutenolide (8.7 g, 76 mmol, 76%) as a slightly yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.20 (dd, $J = 5.7, 1.2$ Hz, 1H), 6.24 (dd, $J = 5.7, 1.2$ Hz, 1H), 5.86 (t, $J = 1.2$ Hz, 1H), 3.58 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 193.87, 150.20, 125.41, 104.17, 57.23.

HRMS calculated 115.03897, found 115.038892.

Dodecyl vinyl ether

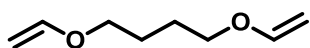


A solution of dodecanol (500 mg, 2.68 mmol 1 eq.), KOH (166 mg, 2.95 mmol, 1.1 eq.), KF (624 mg, 10.73 mmol, 4 eq.) and calcium carbide (1.03 g, 16.10 mmol, 6 eq.) in 13 mL DMSO (0.2 M) was prepared and added to a pressure flask. H_2O (1.2 mL, 24 eq., 4:1 calcium carbide) was added and the pressure flask was sealed tight. The reaction mixture was heated to 130°C and stirred for 3 h. After completion, the reaction mixture was extracted with hexane (3 x 20 mL) and the crude solution was filtered over celite. The solvent was evaporated under reduced pressure and the resulting oil was further purified by column chromatography (silica gel, n-pentane, $R_f = 0.7$) to obtain dodecyl vinyl ether (416 mg, 1.96 mmol, 73%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 6.47 (ddd, $J = 14.4, 6.8, 1.6$ Hz, 1H), 4.17 (dt, $J = 14.3, 1.8$ Hz, 1H), 3.97 (dt, $J = 6.8, 1.8$ Hz, 1H), 1.71 – 1.59 (m, 2H), 1.45 – 1.15 (m, 21H), 0.88 (td, $J = 6.9, 1.7$ Hz, 7H).

^{13}C NMR (101 MHz, CDCl_3) δ 152.15, 86.31, 68.31, 32.08, 29.81, 29.79, 29.74, 29.72, 29.54, 29.50, 29.24, 26.17, 22.84, 14.26.

1,4-butanedivinyl ether



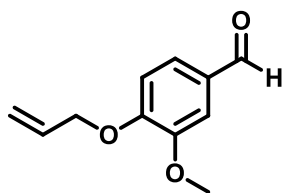
A solution of 1,4-butanediol (500 mg, 5.55 mmol 1 eq.), KOH (685 mg, 12.21 mmol, 2.2 eq.), KF (2.58 g, 44.38 mmol, 8 eq.) and calcium carbide (4.27 g, 66.58 mmol, 12 eq.) in 28 mL DMSO (0.2 M) was prepared and added to a pressure flask. H_2O (4.8 mL, 48 eq., 4:1 calcium carbide) was added and the pressure flask was sealed tight. The reaction mixture was heated to 130°C and stirred for 3 h. After completion, the reaction mixture was extracted with hexane (3 x 40 mL) and the crude solution was filtered over celite. The solvent was evaporated under reduced pressure and the resulting oil was further purified by column chromatography (silica gel, n-pentane, $R_f = 0.7$) to obtain 1,4-butanedivinyl ether as a colorless oil (550 mg, 3.87 mmol, 70%).

^1H NMR (400 MHz, CDCl_3) δ 6.46 (dd, $J = 14.3, 6.8$ Hz, 1H), 4.17 (dd, $J = 14.3, 2.0$ Hz, 1H), 3.98 (ddd, $J = 6.8, 2.0, 0.7$ Hz, 1H), 3.71 (h, $J = 3.1$ Hz, 2H), 1.76 (tt, $J = 3.5, 1.8$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.99, 86.53, 67.65, 25.85.

HRMS calculated 143.10666, found 143.10664.

4-(allyloxy)-3-methoxybenzaldehyde (1)



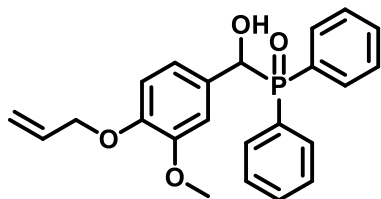
A solution of vanillin (5.0 g, 32.86, 1 eq.) in DMF (66 mL, 0.5 M) was prepared and cooled to 0°C. K₂CO₃ (18.17 g, 131.45 mmol, 4 eq.), was added and the solution was stirred for 10 min. Allyl bromide (15.9 g, 131.45 mmol, 4 eq.) was added over 30 min and the reaction mixture was allowed to warm up to room temperature. The mixture was stirred for 24 h at room temperature in which full conversion was achieved. Demineralized water (150 mL) was added and the reaction mixture was extracted with ethyl acetate (3 x 150 mL). The organic phase was washed 7 times with demineralized water (150 mL) to remove residual DMF. The organic phase was dried with MgSO₄, filtered and the solvent, unreacted allyl bromide and allyl alcohol were evaporated under reduced pressure (60°C, 1 mbar) to obtain 4-(allyloxy)-3-methoxybenzaldehyde as a yellow viscous oil (6.0 g, 31.22 mmol, 95%).

¹H NMR (400 MHz, CDCl₃) δ 9.84 (d, *J* = 1.9 Hz, 1H), 7.42 (dd, *J* = 7.0, 1.9 Hz, 2H), 6.97 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.07 (dddd, *J* = 17.8, 10.7, 5.4, 2.8 Hz, 1H), 5.43 (dp, *J* = 17.3, 1.6 Hz, 1H), 5.33 (dt, *J* = 10.5, 1.7 Hz, 1H), 4.70 (dq, *J* = 5.3, 1.7 Hz, 2H), 3.93 (d, *J* = 1.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.71, 153.29, 149.69, 132.02, 129.99, 126.39, 118.58, 111.72, 109.09, 69.60, 55.82.

HRMS calculated 193.08592, found 193.08580.

((4-(allyloxy)-3-methoxyphenyl)(hydroxy)methyl)diphenylphosphine oxide (2)



A solution of 4-(allyloxy)-3-methoxybenzaldehyde (2.0 g, 10.41 mmol, 1 eq.) and diphenylphosphine oxide (2.10 g, 10.41 mmol, 1 eq.) in anhydrous THF (40 mL, 0.26 M) was prepared and stirred at room temperature. Anhydrous triethylamine (1.05 g, 1.4 mL, 10.41 mmol, 1 eq.) was added dropwise and reaction mixture was stirred for 24 h, in which a white precipitate was formed. The precipitated product was filtered, washed with cold THF and dried in air to obtain ((4-(allyloxy)-3-methoxyphenyl)(hydroxy)methyl)diphenylphosphine oxide as a white solid (3.45 g, 8.75 mmol, 84%).

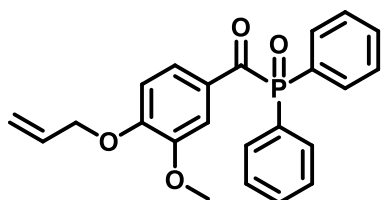
¹H NMR (400 MHz, CDCl₃) δ 7.75 (ddt, *J* = 10.9, 8.2, 1.3 Hz, 1H), 7.58 – 7.31 (m, 3H), 6.72 – 6.63 (m, 1H), 6.59 (s, 1H), 6.04 (ddtd, *J* = 17.1, 10.7, 5.4, 1.2 Hz, 0H), 5.43 – 5.30 (m, 1H), 5.26 (dq, *J* = 10.5, 1.4 Hz, 0H), 4.63 (s, 0H), 4.57 – 4.49 (m, 1H), 3.53 (d, *J* = 1.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 148.69, 147.57, 132.98, 132.27, 132.19, 131.97, 131.88, 131.73, 128.15, 128.09, 128.03, 127.98, 119.99, 117.84, 112.45, 110.70, 74.15, 73.34, 55.36.

³¹P NMR (162 MHz, CDCl₃) δ 30.59.

HRMS calculated 395.14067, found 395.14042.

(4-(allyloxy)-3-methoxyphenyl)(diphenylphosphoryl)methanone (VAPO)



A solution of ((4-(allyloxy)-3-methoxyphenyl)(hydroxy)methyl)diphenylphosphine oxide (1.0 g, 2.54 mmol, 1 eq.) in anhydrous DCM (25 mL, 0.1 M) was prepared and stirred at room temperature. Activated MnO₂ (4.41 g, 50.71 mmol, 20 eq.) was added and the reaction mixture was purged with N₂ for 30 min. Thereafter, the reaction mixture was stirred at room temperature for 24 hours. The solution was filtered over celite and protected from light. The solvent was evaporated under reduced pressure and the resulting crude solid was further purified by column chromatography (silica gel, n-pentane/ethyl acetate : 90/10, R_f = 0.5) to obtain (4-(allyloxy)-3-methoxyphenyl)(diphenylphosphoryl)methanone (VAPO) as a white solid (0.64 g, 1.63 mmol, 64%).

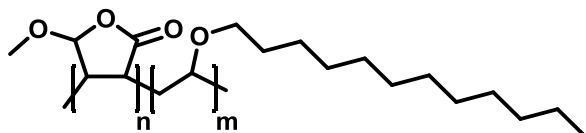
¹H NMR (400 MHz, CDCl₃) δ 8.56 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.92 – 7.81 (m, 5H), 7.59 – 7.44 (m, 6H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.05 (ddt, *J* = 16.5, 10.7, 5.4 Hz, 1H), 5.42 (dd, *J* = 17.4, 6.7 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 4.69 (d, *J* = 5.5 Hz, 2H), 3.91 (d, *J* = 11.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 132.61, 132.49, 132.46, 132.19, 132.06, 131.97, 128.82, 128.70, 127.34, 124.37, 119.09, 118.76, 112.83, 112.08, 112.00, 111.04, 111.01, 69.95, 56.12.

^{31}P NMR (162 MHz, CDCl_3) δ 22.28.

HRMS calculated 393.12502, found 393.12474.

Copolymerization methoxybutenolide and dodecyl vinyl ether (BVE1, BVE2) (Trigonox 42S)

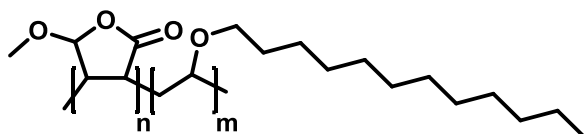


To a 4-ml vial with screwcap with septum, a solution of methoxybutenolide (100 mg, 0.88 mmol, 1 eq.) and dodecyl vinyl ether (186 mg, 0.88 mmol, 1 eq.) in butyl acetate or GVL (0.44 ml) were

added. The mixture was heated to 120°C, and Trigonox 42S (12 mg, 0.013 μl , 0.05 mmol, 0.06 eq.) was added to initiate polymerization. The mixture was refluxed for 2 h. The reaction mixture was concentrated under reduced pressure to obtain the methoxybutenolide-dodecyl vinyl ether copolymers, **BVE1** (butyl acetate), **BVE2** (GVL) with 95% and >99% conversion, respectively.

1,3,5-Trimethoxybenzene (49 mg, 0.29 mmol, 0.33 eq.) was added as an internal standard before the initiation for ^1H NMR kinetic measurements. At regular intervals, a sample of 50 μL was taken from the mixture and put in a small vial, which was flash frozen (-18°C) to stop polymerization.

Copolymerization methoxybutenolide and dodecyl vinyl ether (BVE3) (ascaridole)

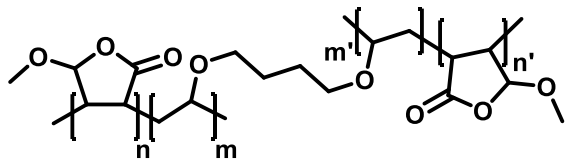


To a 4-ml vial with screwcap with septum, a solution of methoxybutenolide (100 mg, 0.88 mmol, 1 eq.) and dodecyl vinyl ether (186 mg, 0.88 mmol, 1 eq.) in GVL (0.44 ml) were added. The

mixture was heated to 140°C, and ascaridole (9 mg, 0.05 mmol, 0.06 eq.) was added to initiate polymerization. The mixture was refluxed for 5 h. The reaction mixture was concentrated under reduced pressure to obtain the methoxybutenolide-dodecyl vinyl ether copolymer, **BVE3** with 76% conversion.

1,3,5-Trimethoxybenzene (49 mg, 0.29 mmol, 0.33 eq.) was added as an internal standard before the initiation for ^1H NMR kinetic measurements. At regular intervals, a sample of 50 μL was taken from the mixture and put in a small vial, which was flash frozen (-18°C) to stop polymerization.

UV curing of butenolide based coatings



To a 4 ml vial, methoxybutenolide (200 mg, 1.75 mmol, 1 eq.), 1,4-butanedivinyl ether (125 mg, 0.88 mmol, 0.5 eq.), and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (**BAPO**) (22 mg, 53 μmol , 3 mol%) or (4-(allyloxy)-3-

methoxyphenyl)(diphenylphosphoryl)methanone (**VAPO**) (41 mg, 105 μmol , 6 mol%) were added and stirred until the reaction mixture became homogeneous. The mixture was applied on a glass surface, and the surface (10 \times 20 cm) was coated with a Byk applicator (50 μm thickness). The glass surface was irradiated with $\lambda = 395$ nm (UV Flood 36, 12 \times 3 W) at 5-cm distance for 20 min.

Photooxygenation setups

Rotary photoreactor

The previously described rotary evaporator allows for efficient larger scale photooxygenation due to the fast rotation creating a thin film, optimal for light penetration, and creating a high mass transfer of oxygen into the solution. To allow for an oxygen atmosphere in the rotary photoreactor, the photoreactor was purged with O₂ through vacuum/oxygen cycles using an O₂ filled balloon that was attached to the rotary evaporator. A home-built white light setup (575 lm, 8 W each; 5750 lm, 80 W total) consisting of standard white light LED bulbs was placed at a distance of approximately 5 cm around the 1 L flask, containing the reaction mixture (**Figure S1**). The photooxygenations were carried out according to the **Experimental procedures**.

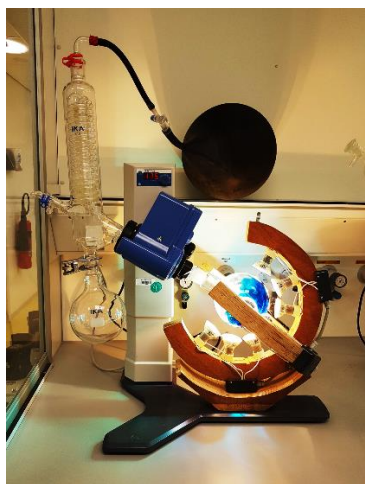


Figure S1 Rotary photoreactor in operation. Reaction conditions: 1 L flask, 1 M furfural in MeOH (10 mL), 10 x 8W LED, 0.5 mol% methylene blue.

Batch photooxygenation

The previously described rotary evaporator was used for the preliminary experiment utilizing **FLY-450** (0.5 mol%) as photosensitizer. Photooxidation of furfural (1.0 g, 10 mmol, 1 eq.) led to 85% conversion towards hydroxybutenolide in 1h (**Figure S2**, left).

The smaller scale photooxygenation using **FLY 450** as photosensitizer was carried out in 5 mL vial, in a block of 6 slots, with irradiation of 500 mW LED from the bottom (**Figure S2**, right). To allow for an oxygen atmosphere and saturation of the solution, oxygen was bubbled using a needle. The temperature of the LEDs was controlled at 20°C by a liquid circulator. The photooxygenation was carried out according to the **Experimental procedure**.

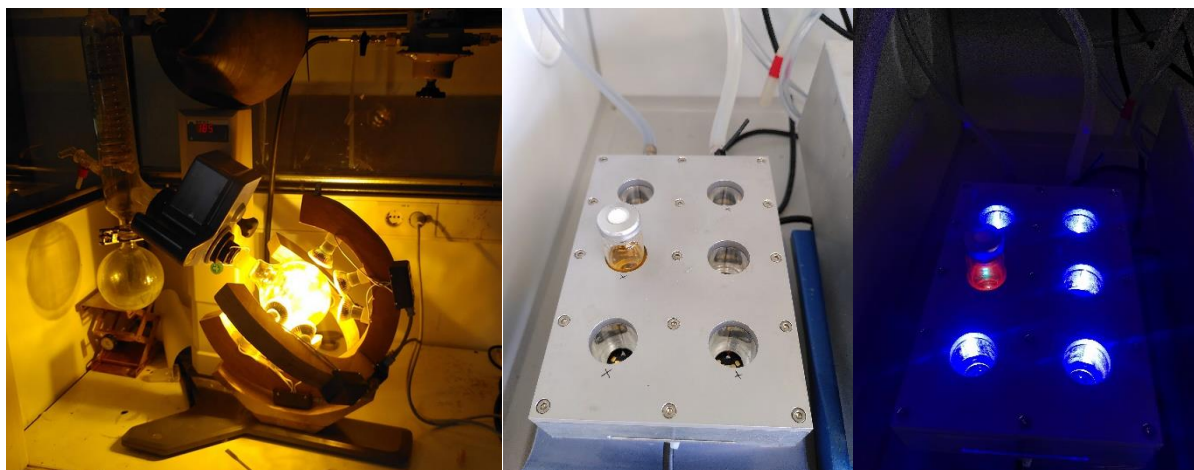


Figure S2 Rotary photoreactor in operation (left). Reaction conditions: 1 L flask, 1 M furfural in MeOH (10 mL), 10 x 8W LED, 0.5 mol% **FLY 450**. Batch photooxygenation in operation (middle/right). Reaction conditions: 5 mL vial with septum, 0.07 M furfural in MeOH (5 mL), 1 x 500 mW LED ($\lambda_{\text{irr}} = 445 \text{ nm}$), 1 mol% **FLY 450**.

Normalized UV VIS absorption spectrum

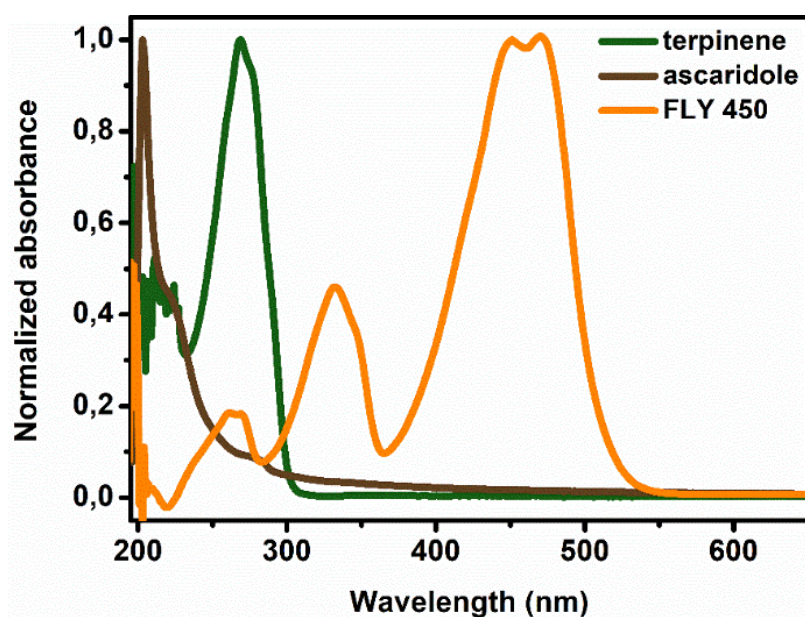


Figure S3 Normalized UV VIS absorption spectra of α -terpinene, ascaridole and FLY 450.

Normalized emission spectrum OSRAM Oslon SSL 80 royal blue

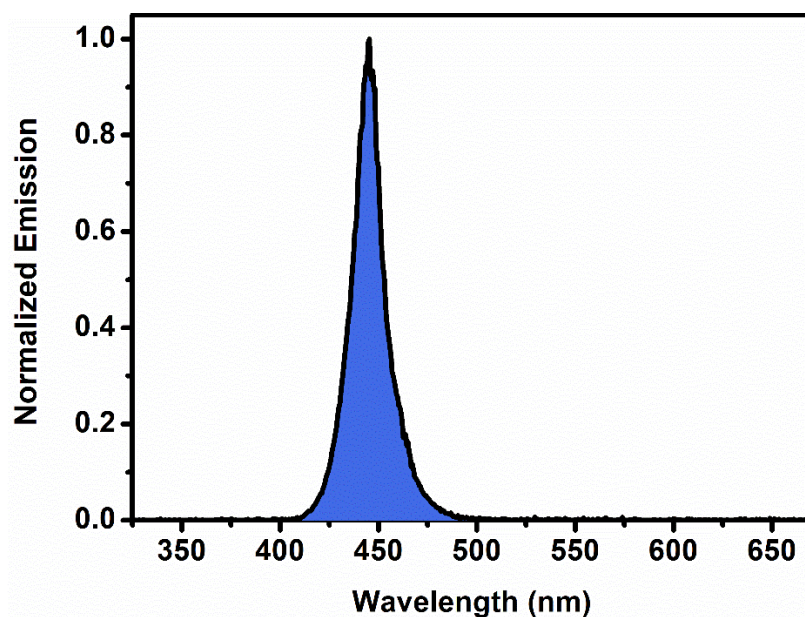


Figure S4 Normalized emission spectrum LED OSRAM Oslon SSL 80 royal blue (500 mW, $\lambda = 445$ nm, 180 mW/cm²) as light source for batch photooxygenations.

Normalized emission spectrum UV Flood 36

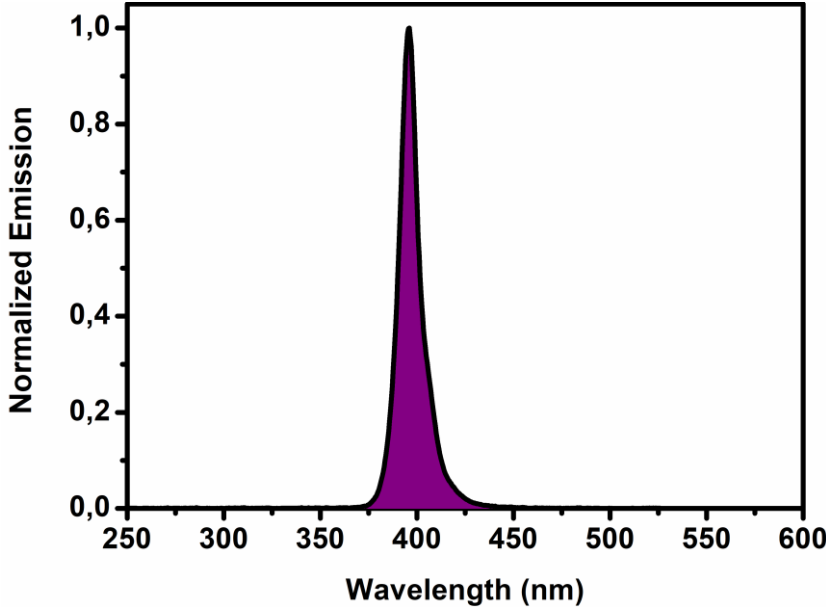


Figure S5 Normalized emission spectrum LED Beacon UV FLOOD 395 nm (12 x 3 W, $\lambda = 395$ nm, 21 mW/cm²) for coating formation.

Singlet oxygen quantum yield

In order to determine the quantum yield of **FLY 450** in methanol and dichloromethane (DCM) the scavenger decay rate was determined. Originally, 1,3-Diphenylisobenzofuran (DPiBF) was used ($\lambda_{\text{max}} = 450 \text{ nm}$). However using blue light irradiation DPiBF showed undesired self-photosensitization towards singlet oxygen at 445 nm.¹¹ Therefore it was decided to utilize the bio-based singlet oxygen scavenger α -terpinene. (**Figure S6**).

As **FLY 450** contains a similar furan moiety as DPiBF and furfural, slight photobleaching was observed in MeOH, which was also confirmed by DFT studies (**Scheme S1**).

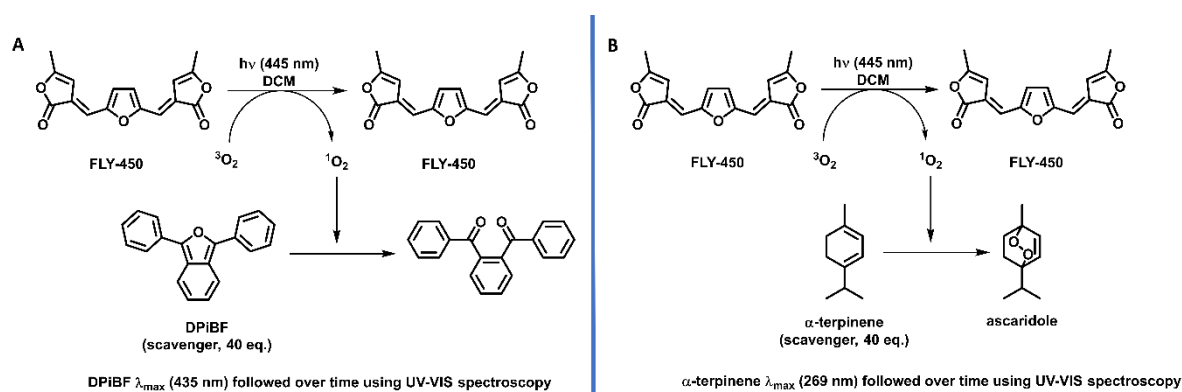


Figure S6 General strategy for following the production of singlet oxygen via decay of DPiBF (A) or α -terpinene (B) over time (s) monitored at the respective main absorption band in MeOH at 293 K.

A 2.0 ml solution containing **FLY 450** (1 μM) along with α -terpinene as a singlet oxygen scavenger (40 μM) in pre-oxygenated DCM or methanol was placed in a 2 mL cuvette. Thereafter, the **FLY 450** + α -terpinene solution was irradiated ($\lambda_{\text{irr}} = 445 \text{ nm}$) with a UV/VIS-mounted Sahlmann Photochemical Solutions 445 nm LED system (peak wavelength 445 nm, FWHM 18 nm). During 445 nm irradiation, the solutions' UV/VIS spectrum was monitored for the disappearance of the main absorption band of α -terpinene at 269 nm, signifying consumption of the singlet oxygen acceptor by the generated singlet oxygen, to produce the graphs shown below (measured as triplicates, single measurements shown in **Figure S7** **Figure s10**). The rate of singlet oxygen formation was determined at the initial decay of absorbance of α -terpinene at 5% to 20% conversion assuming every molecule of singlet oxygen is captured by the excess of scavenger present. The quantum yield (average of triplicate measurement) was calculated, using methylene blue as the reference compound of which its rate was also determined, following the equations accordingly:

$$A = \log_{10} \frac{I_0}{I} \quad \text{where} \quad I_0 = 1$$

Gives

$$I = \frac{1}{10^A}$$

where A = absorbance of the photosensitizer at λ_{irr} , I_0 = intensity incident light and I = transmitted intensity. Following from the aforementioned equations the quantum yield (Φ_{Δ}) is defined as:¹²

$$\Phi_{\Delta \text{ FLY 450}} = \frac{I_{\text{Methylene blue}}}{I_{\text{FLY 450}}} \times \frac{k_{\text{FLY 450}}}{k_{\text{Methylene blue}}} \times \Phi_{\Delta \text{ Methylene blue}}$$

where k = rate of scavenger consumption at λ_{irr} .

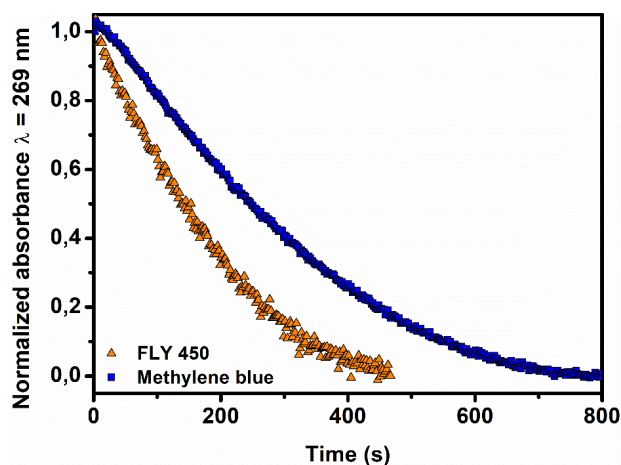


Figure S7 Decay of α -terpinene ($40 \mu\text{M}$) over time (s) monitored at the main absorption band ($\lambda_{\text{irr}} = 269 \text{ nm}$) in MeOH at 293 K.

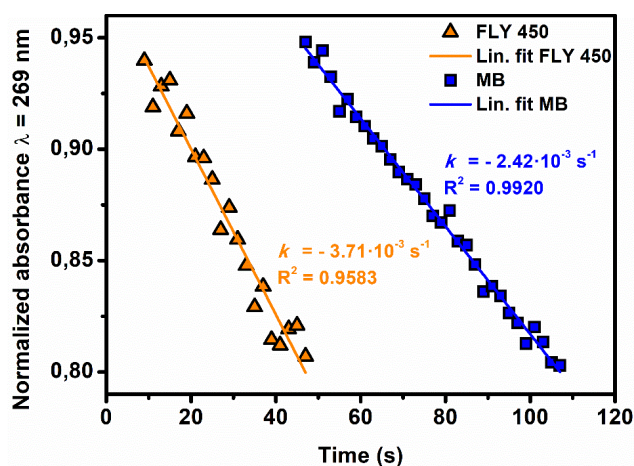


Figure S8 Rate of decay of α -terpinene ($40 \mu\text{M}$) over time (s) monitored at the main absorption band ($\lambda_{\text{irr}} = 269 \text{ nm}$) in MeOH at 293 K, measured from the initial decay at 5% to 20% conversion.

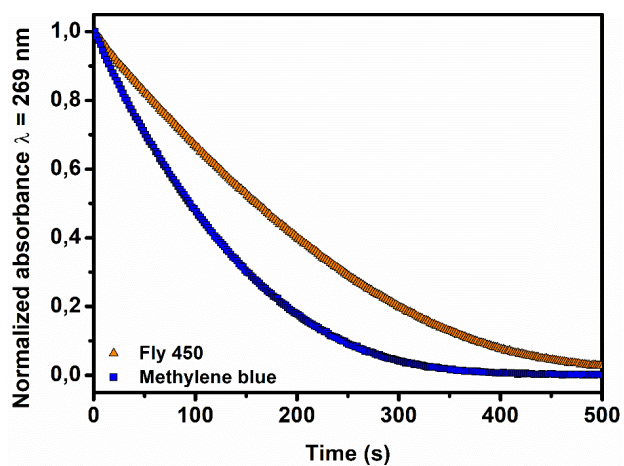


Figure S9 Decay of α -terpinene ($40 \mu\text{M}$) over time (s) monitored at the main absorption band ($\lambda_{\text{irr}} = 269 \text{ nm}$) in DCM at 293 K.

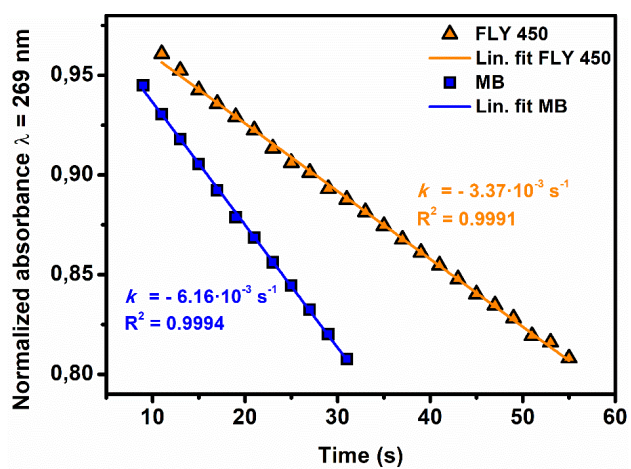


Figure S10 Rate of decay of α -terpinene ($40 \mu\text{M}$) over time (s) monitored at the main absorption band ($\lambda_{\text{irr}} = 269 \text{ nm}$) in DCM at 293 K, measured from the initial decay at 5% to 20% conversion.

Free radical polymerization kinetics

The rate of polymerization R_p for the copolymers of methoxybutenolide and dodecyl vinyl ether has been determined following the equations accordingly:

Equation S2 Rate of polymerization.

$$R_p = -\frac{dc_M}{dt} = k_p \cdot \left(f \frac{k_d}{k_t}\right)^{0.5} \cdot c_M \cdot (c_{ini})^{0.5}$$

In copolymerization, the monomer concentration C_M , is substituted for:¹³

Equation S3 Substitution of C_M in copolymerization.

$$c_M = ([M_1] + [M_2])$$

Equation S2 is integrated from 0 to t giving:

Equation S4 Integration of rate of polymerization from 0 to t.

$$\ln\left(\frac{c_M^0}{c_M}\right) = k_p \left(f \frac{k_d}{k_t} c_{ini}\right)^{0.5} \cdot t$$

The conversion of (co)polymerization is determined by:

Equation S5 Conversion of polymer.

$$U = \frac{c_M^0 - c_M}{c_M^0}$$

Substituting U in **Equation S4** and combining the constants and variables we obtain:

Equation S6 Rate of polymerization as a function of t.

$$\ln\left(\frac{1}{1-U}\right) = k_{obs} \cdot t$$

By plotting $\ln\left(\frac{1}{1-U}\right)$ against t (**Equation S6**) it is possible to obtain the rate constant k_{obs} in s^{-1} . This rate constant is a combination of different parameters, which are specific to reaction and reaction conditions. It includes:

$$f \cdot k_p \left[\frac{L}{mol \cdot s}\right] = \text{rate constant for propagation}$$

$$k_d [s^{-1}] = \text{rate constant for dissociation}$$

$$k_t \left[\frac{L}{mol \cdot s}\right] = \text{rate constant for termination}$$

Additionally, it is assumed that the radical concentration c_{ini} is constant and does not change over time. A substance specific correction value f is included as well. Without specific determination of the different rate constants (k_p, k_d, k_t), the relative reactivity between the copolymers can be compared through the comparison of the value for k_{obs} .

¹H NMR spectroscopy

The reaction kinetics of the copolymerization of methoxybutenolide and dodecyl vinyl ether were determined using ¹H NMR spectroscopy. The concentrations of the monomers were followed by integrating the proton NMR signals. To determine the absolute concentration at a certain point, 1,3,5-trimethoxybenzene, an internal standard, was added to the reaction mixture (0.5 eq.). The equations (**Equation S2–Equation S6**, *vide supra*) were used to determine the values for $\ln(1/(1-U))$. Plotting these values against t resulted in a linear relation in which the slope of the function is the value for k_{obs} .

For the copolymerization using ascaridole as radical initiator an initial fast rate (k^1_{obs}) followed by a slower secondary rate (k^2_{obs}) is observed (**Figure S22**). Previously we have described these findings in butenolide polymerization reactions as a result of increased inhibition.⁷

¹H-NMR shifts that have been followed are ¹H NMR (400 MHz, CDCl₃): methoxybutenolide δ 6.21 (1H), dodecyl vinyl ether δ 6.43 (1H).

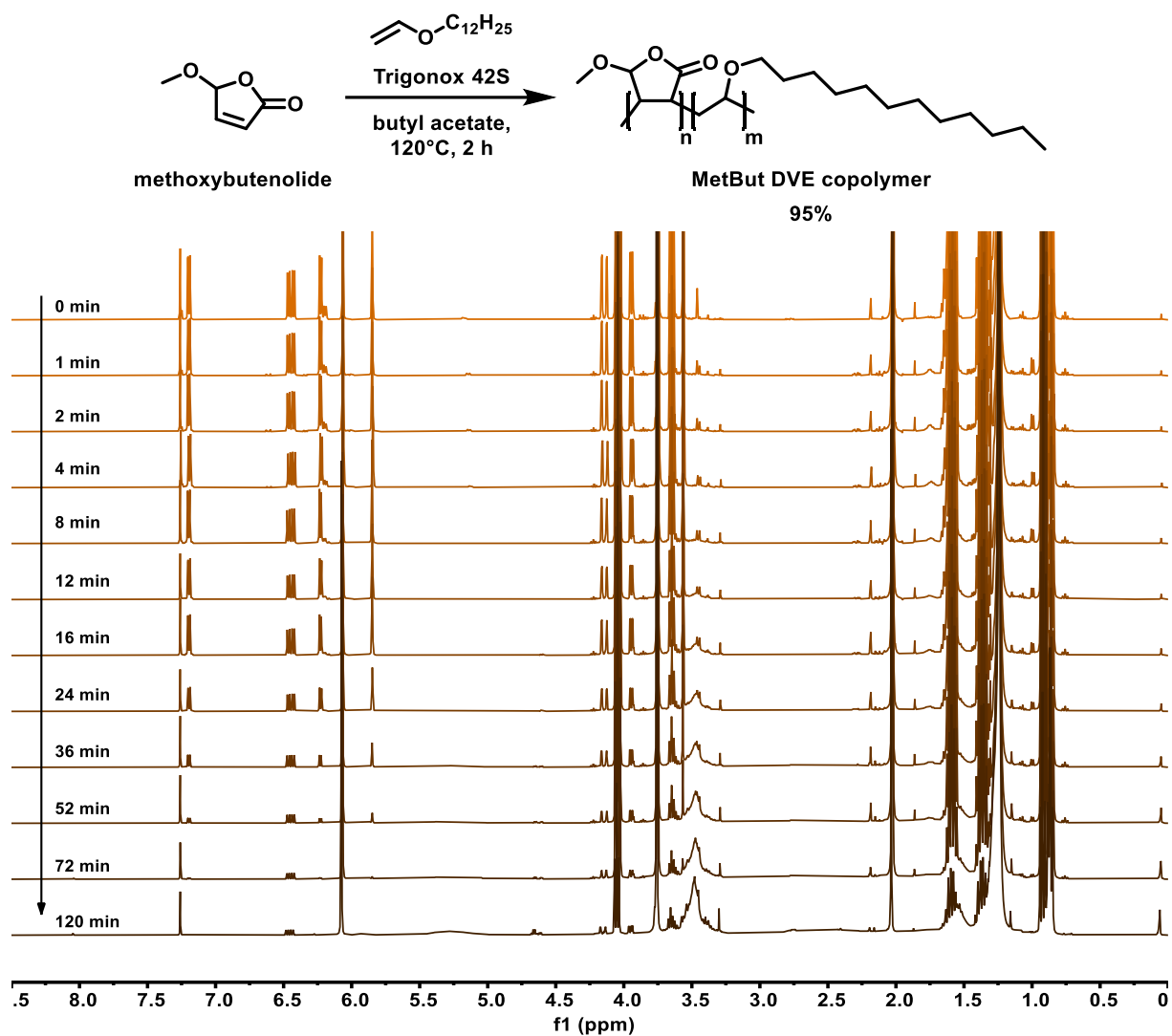


Figure S11 Reaction scheme copolymerization methoxybutenolide with dodecyl vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2 M in butyl acetate, 120°C, 2 h (top). ¹H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

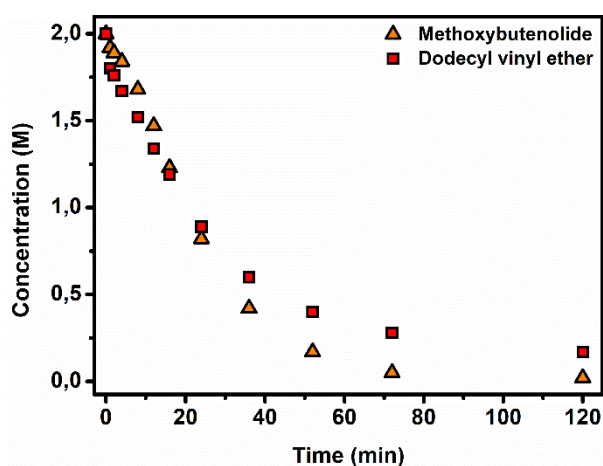


Figure S12 Concentration of monomers over time of the copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) followed by ¹H NMR signals over time by taking samples and flash freezing (−18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2 M in butyl acetate 120°C, 2 h.

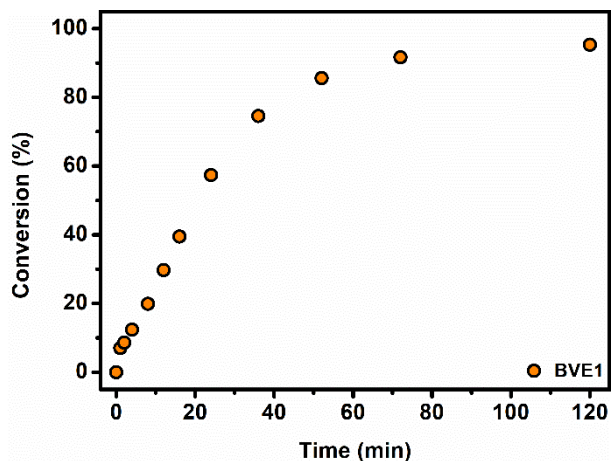


Figure S13 Conversion of MetBut DVE copolymer over time; copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2 M in butyl acetate 120°C , 2 h.

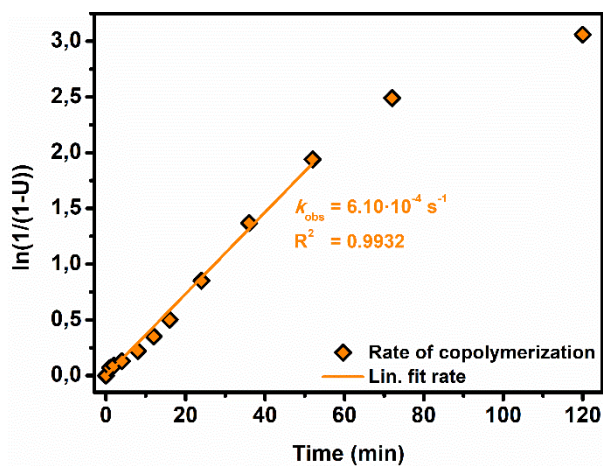


Figure S14 Rate of copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) over time, followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2 M in butyl acetate 120°C , 2 h.

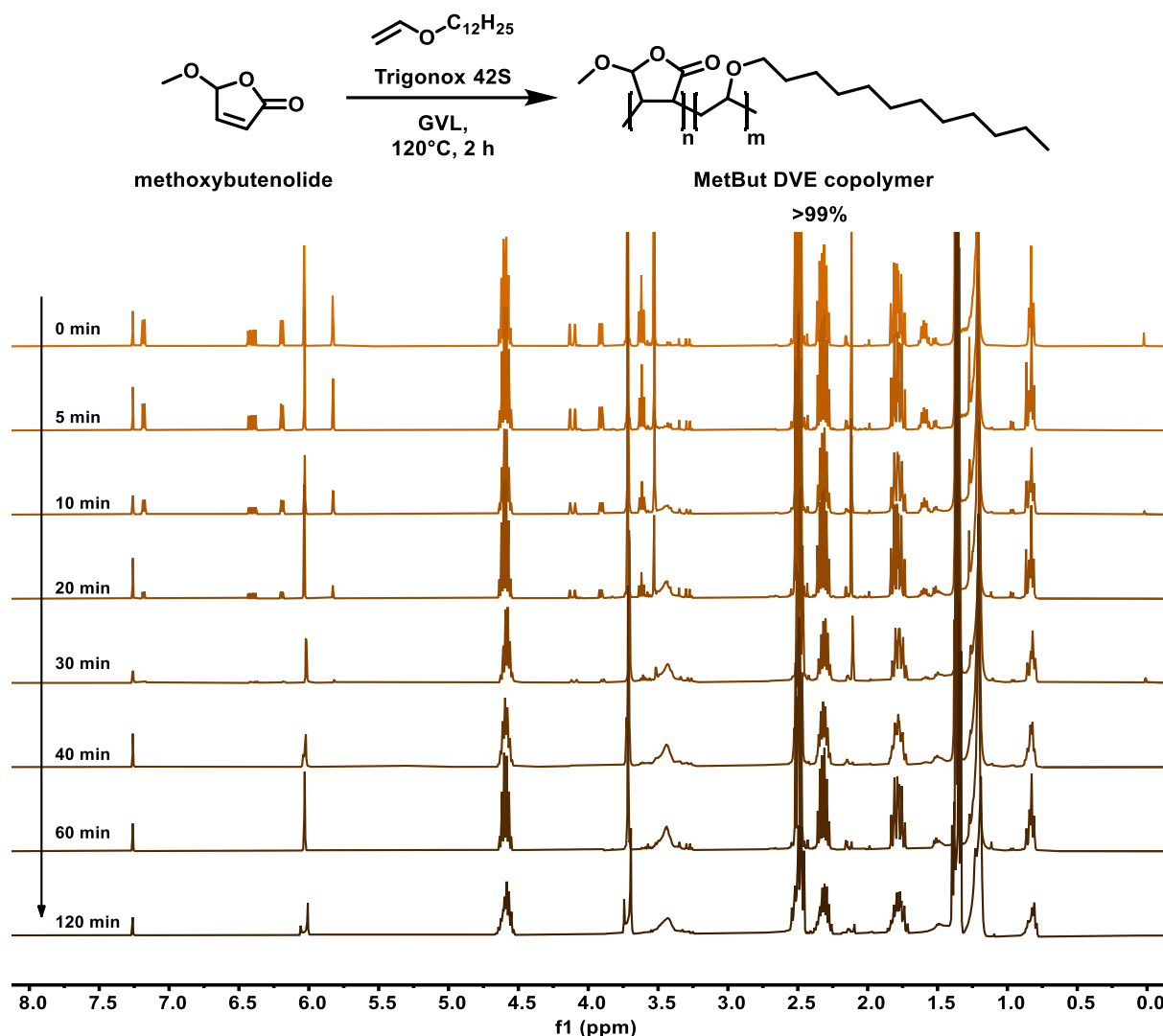


Figure S15 Reaction scheme copolymerization methoxybutenolide with dodecyl vinyl ether (1:1 ratio), reaction conditions: Trigonox 42S (6 mol%), 2 M in GVL, 120°C, 2 h (top). ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

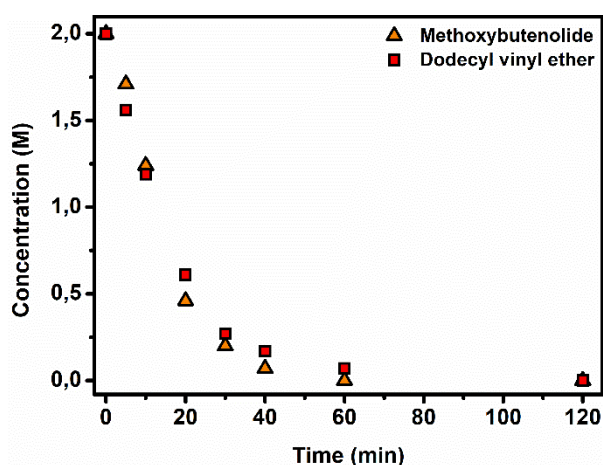


Figure S16 Concentration of monomers over time of the copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2 M in GVL, 120°C, 2 h.

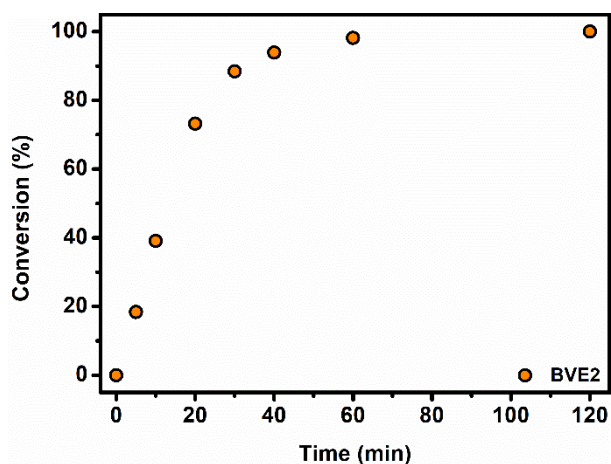


Figure S17 Conversion of MetBut DVE copolymer over time; copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2 M in GVL, 120°C , 2 h.

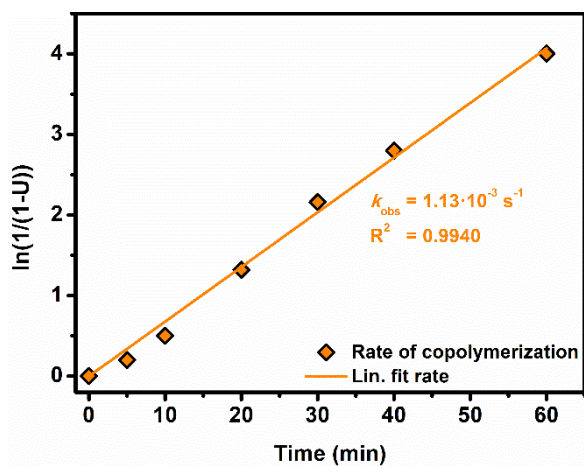


Figure S18 Rate of copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) over time, followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: Trigonox 42S (6 mol%), 2 M in GVL 120°C , 2 h.

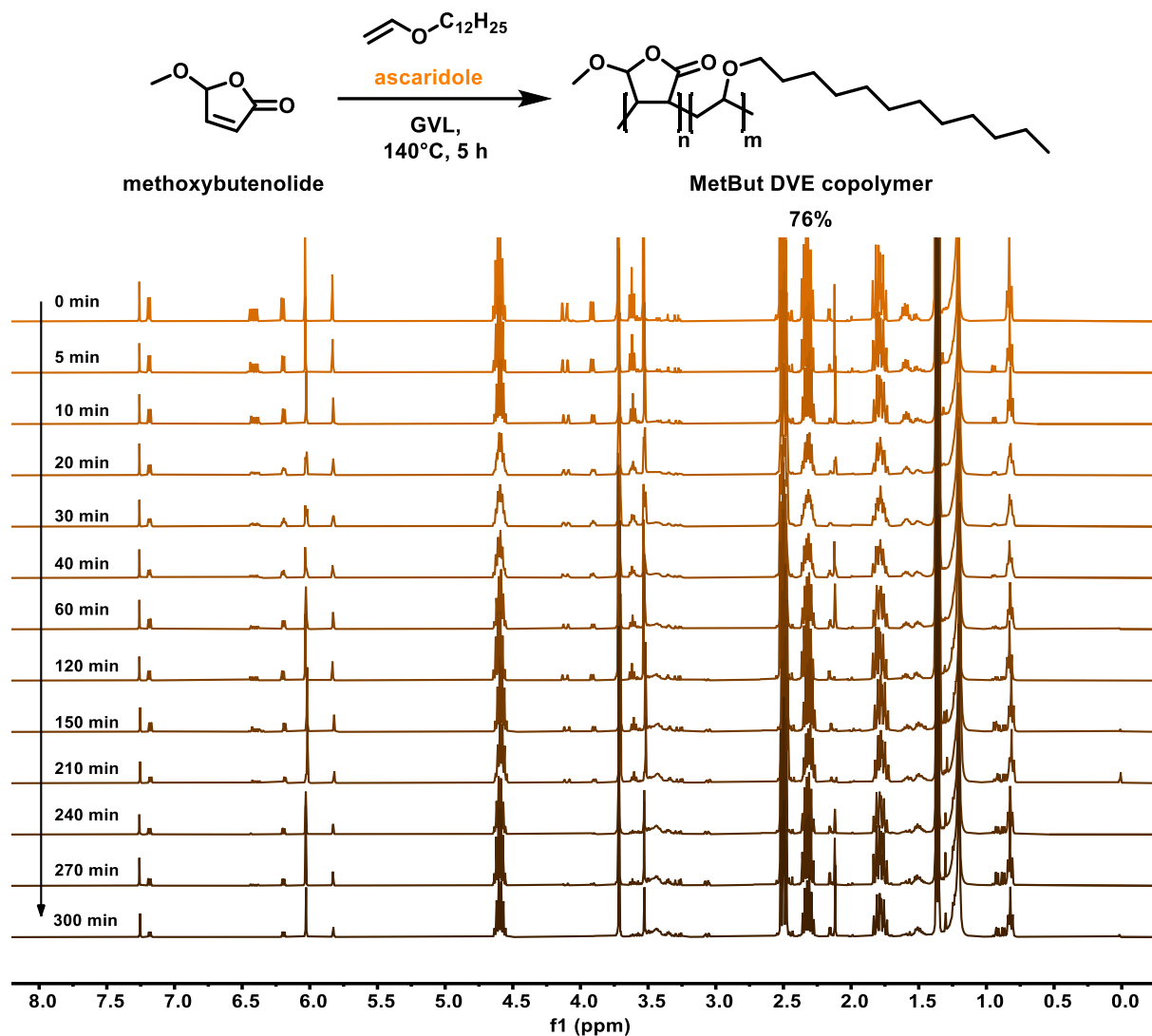


Figure S19 Reaction scheme copolymerization methoxybutenolide with dodecyl vinyl ether (1:1 ratio), reaction conditions: ascaridole (6 mol%), 2 M in butyl acetate, 140°C, 2 h (top). ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard (bottom).

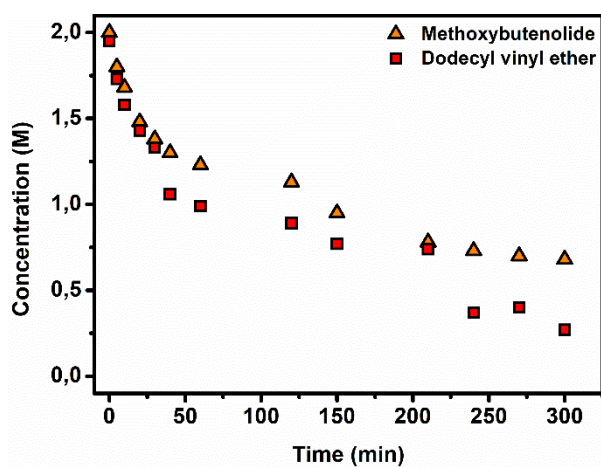


Figure S20 Concentration of monomers over time of the copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: ascaridole (6 mol%), 2 M in GVL, 140°C, 2 h.

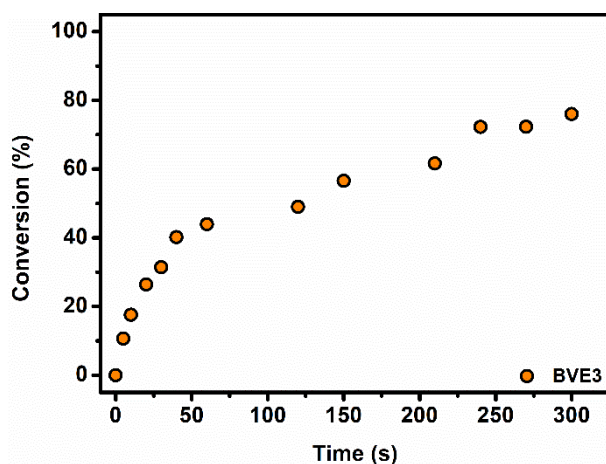


Figure S21 Conversion of MetBut DVE copolymer over time; copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: ascaridole (6 mol%), 2 M in GVL, 140°C , 2 h.

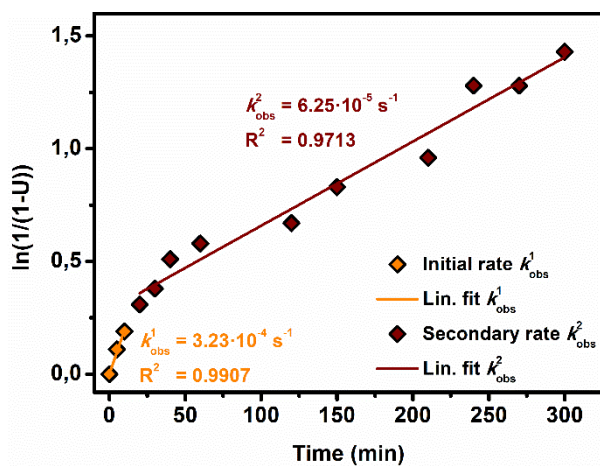


Figure S22 Rate of copolymerization of methoxybutenolide with dodecyl vinyl ether (1:1 ratio) over time, followed by ^1H NMR signals over time by taking samples and flash freezing (-18°C) them at certain timestamps and using 1,3,5-trimethoxybenzene (0.5 eq.) as internal standard, reaction conditions: ascaridole (6 mol%), 2 M in GVL 140°C , 2 h.

Methoxybutenolide–1,4-butanediviny ether coatings

Following the **UV curing procedure** coatings were prepared using 3 mol% and 6 mol% **VAPO** and 3 mol% **BAPO**. Applying 3 mol% of **VAPO** as photoinitiator resulted in a tacky non-uniform coating (**Figure S23**, left). A higher loading of 6 mol% **VAPO** resulted in a clear hard coating (**Figure S23**, middle). Applying 3 mol% **BAPO** resulted in a hard but opaque coating, presumably caused by unreacted monomers (**Figure S23**, right).



Figure S23 UV cured methoxybutenolide–1,4-butanediviny ether coatings using as photoinitiator 3 mol% **VAPO** (left), 6 mol% **VAPO** (middle) and 3 mol% **BAPO** (right). Coating formation conditions: methoxybutenolide–1,4-butanediviny ether (1:0.5 ratio), **VAPO/BAPO** (3–6 mol%), UV irradiation ($\lambda_{irr} = 395 \text{ nm}$), 20 min.

The properly formed methoxybutenolide–1,4-butanediviny ether coatings **BVEC1** (6 mol% **VAPO**) and **BVEC2** (3 mol% **BAPO**) were subjected to DSC, Knoop hardness measurement and MEK solvent resistance test (**Figure S24**).

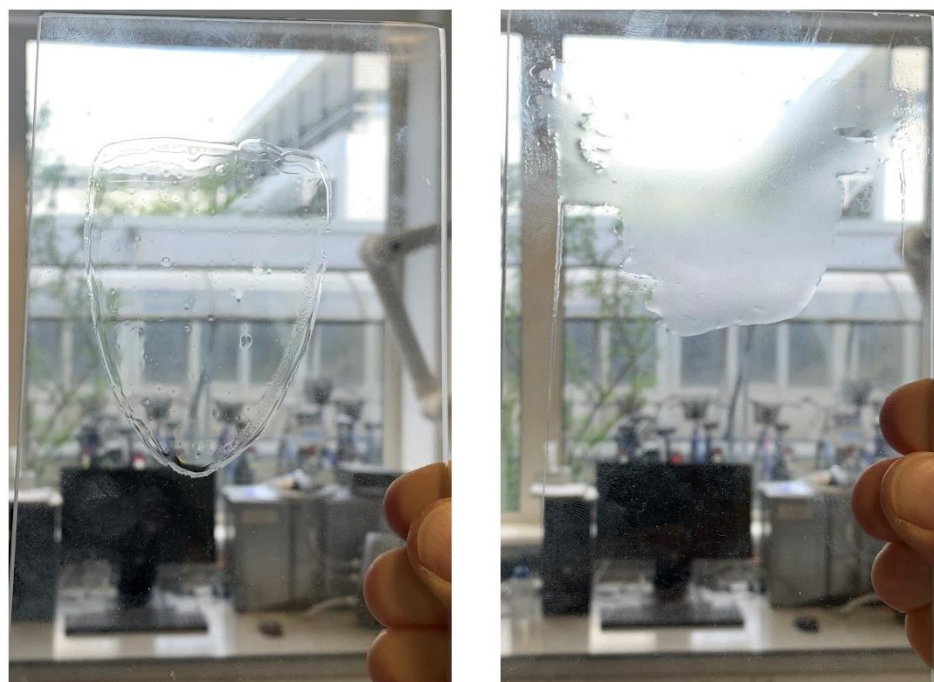


Figure S24 Clear hard methoxybutenolide–1,4-butanediviny ether coating (**BVEC1**) made using **VAPO** (6 mol%) as photoinitiator (left). Hard methoxybutenolide–1,4-butanediviny ether coating (**BVEC2**) made using **BAPO** (3 mol%) as photoinitiator (right).

After subjection of the coatings **BVEC1** and **BVEC2** to the MEK double rub test, where the coatings are rubbed with a soaked cloth in 2-butanone (MEK) back and forth (5 cm) while applying 10 N downward pressure, no apparent damage was present to the surface of the coatings, except for slight whitening (**Figure S25**). The cracking of the coating **BVEC2** was caused by the Knoop hardness experiment performed before the MEK double rub test (**Figure S25**, right). The part of the coating that was subjected to the MEK double rub test is encircled in black.



Figure S25 UV cured methoxybutenolide–1,4-butanedivinyl ether coatings **BVEC1** (left) and **BVEC2** (right) subjected to DSC, Knoop hardness measurement and MEK solvent resistance test. Only slight whitening and no other damage or deterioration of the surfaces was apparent after 200 MEK double rubs.

DSC Spectra

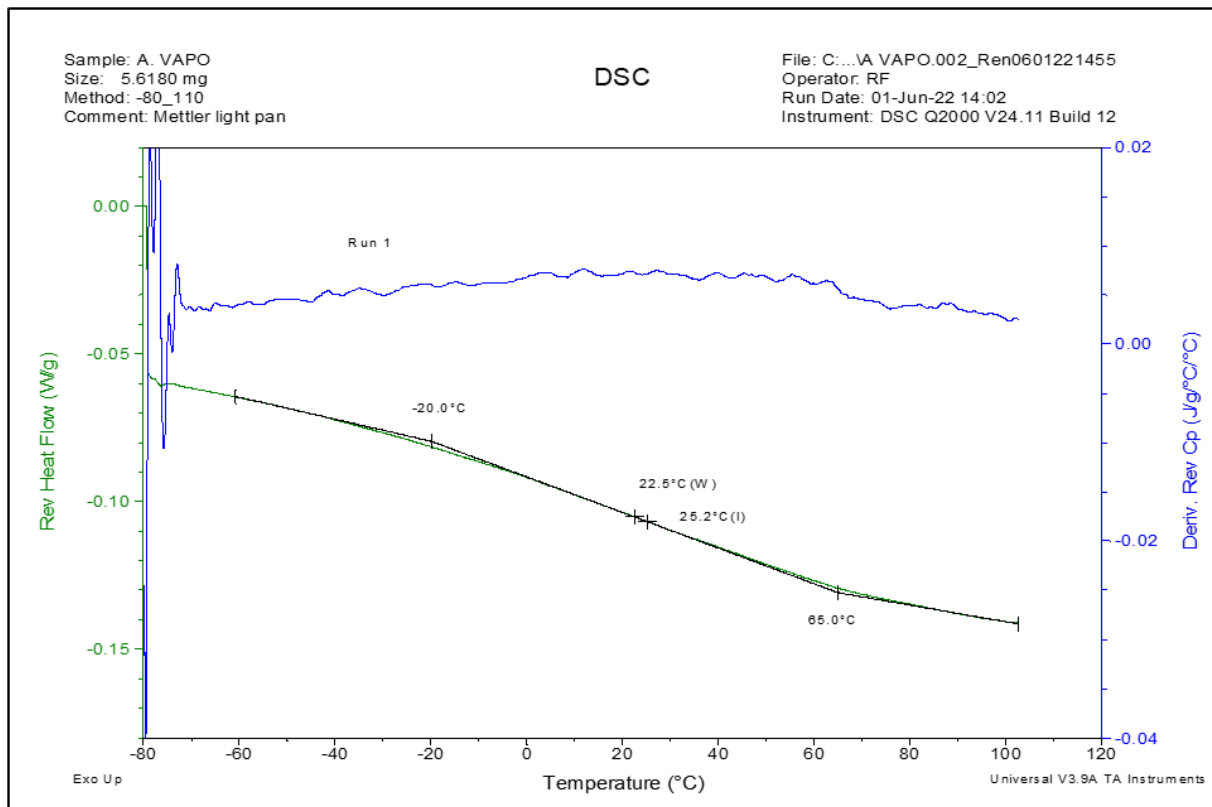


Figure S26 DSC spectrum of methoxybutenolide/1,4-butane divinyl ether coating **BVEC1** cured with **VAPO** as photoinitiator.

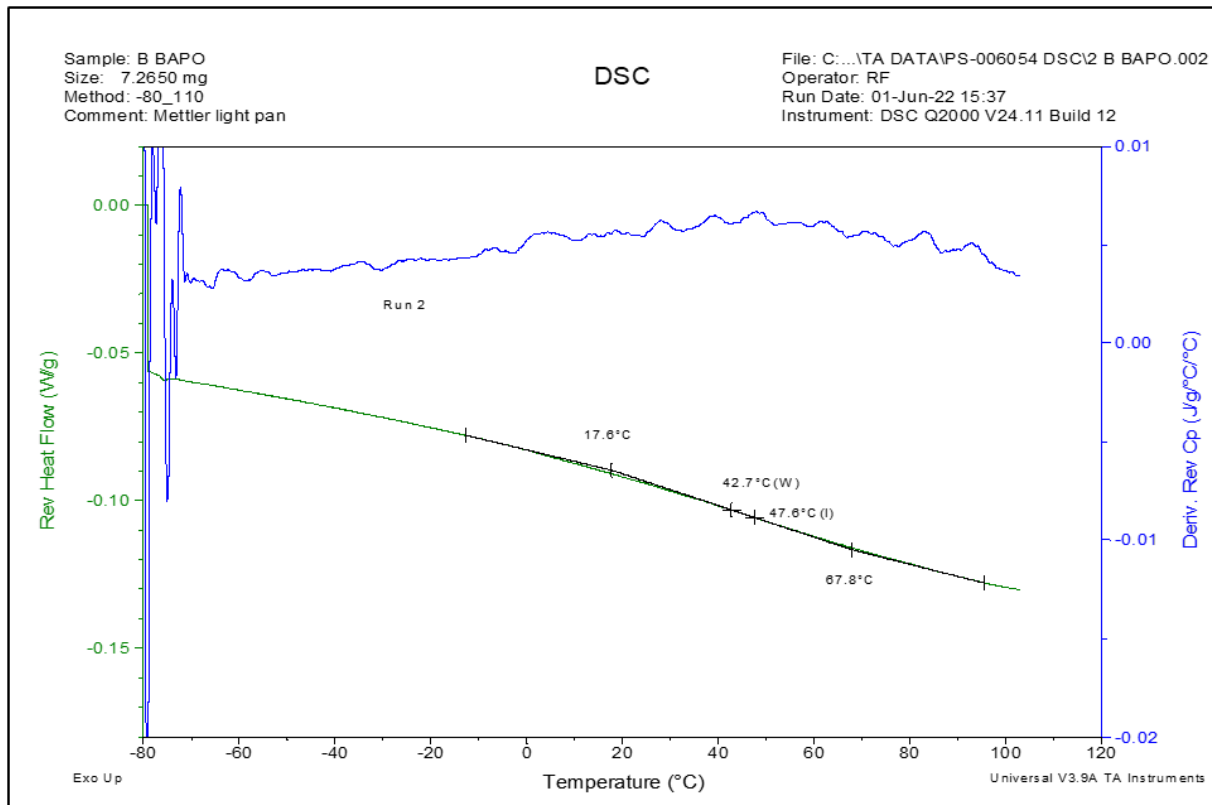


Figure S27 DSC spectrum of methoxybutenolide/1,4-butane divinyl ether coating **BVEC2** cured with **BAPO** as photoinitiator.

GPC Spectra

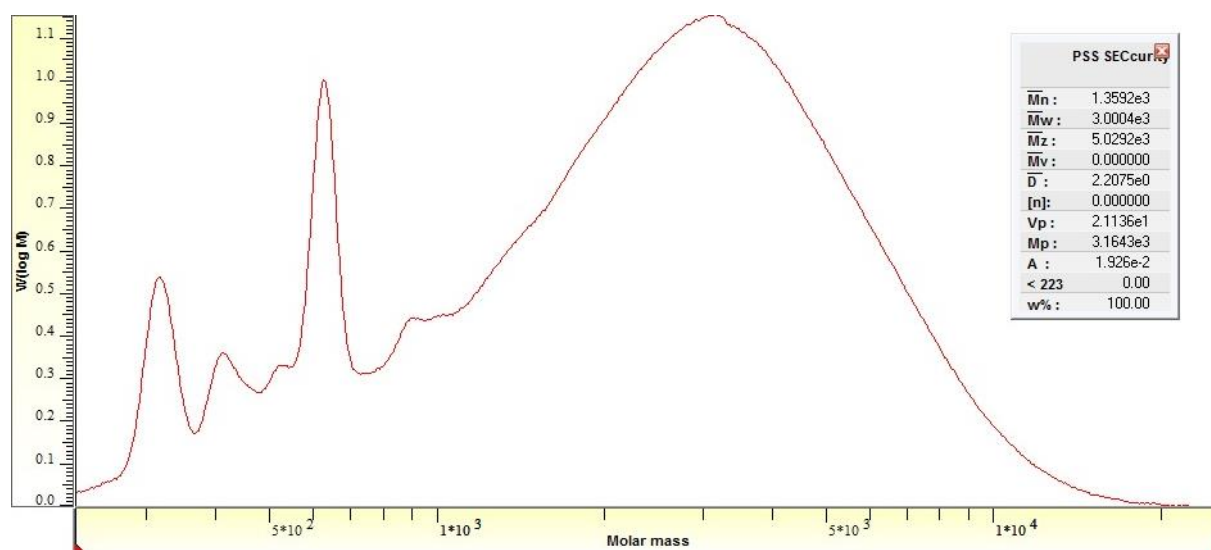


Figure S28 GPC chromatogram of methoxybutenolide/dodecyl vinyl ether copolymer **BVE1** polymerized using Trigonox 42S as radical initiator in butyl acetate.

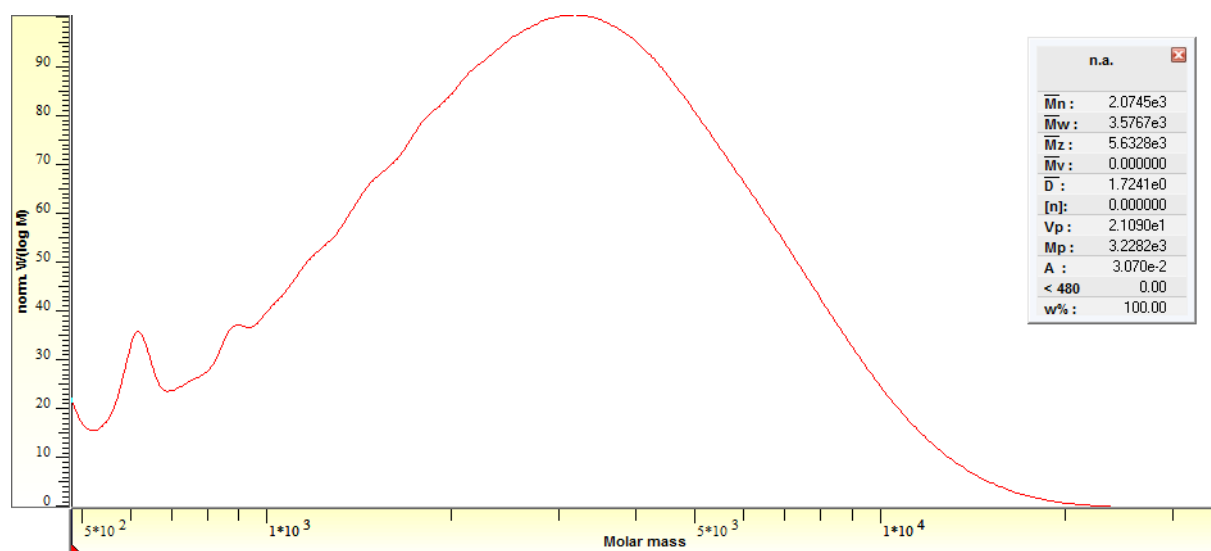


Figure S29 GPC chromatogram of methoxybutenolide/dodecyl vinyl ether copolymer **BVE2** polymerized using Trigonox 42S as radical initiator in GVL.

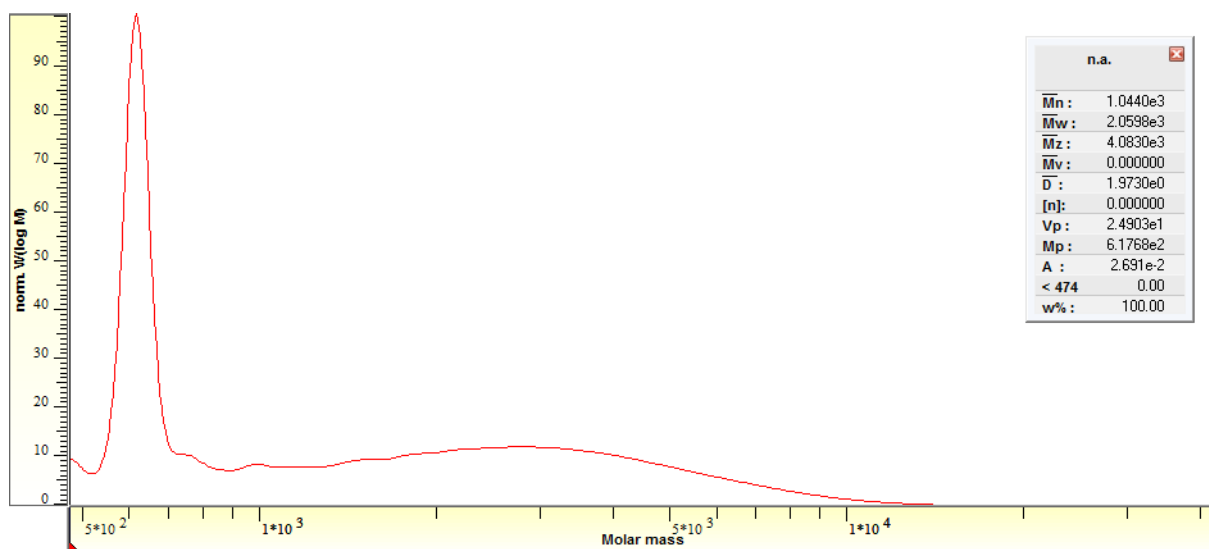


Figure S30 GPC chromatogram of methoxybutenolide/dodecyl vinyl ether copolymer **BVE3** polymerized using ascaridole as radical initiator in GVL.

NMR Spectra

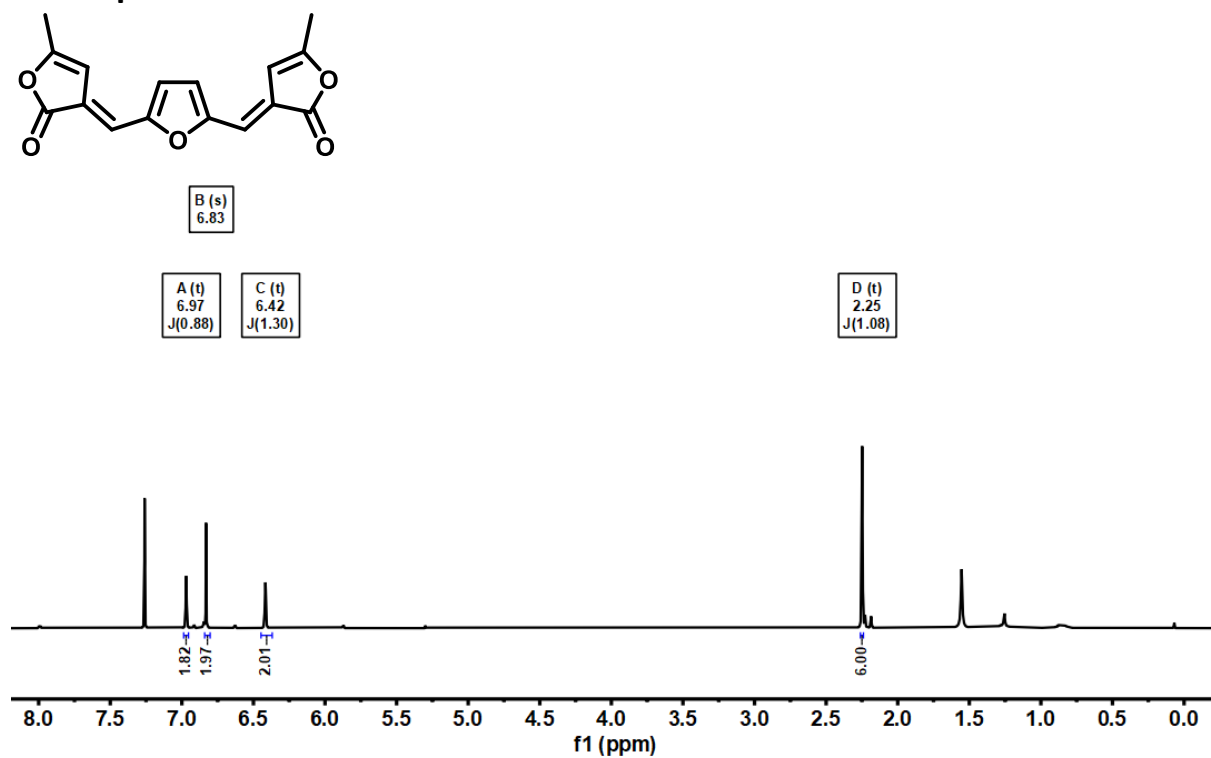


Figure S31 ^1H NMR spectrum of **FLY450** measured at 293 K in CDCl_3 .

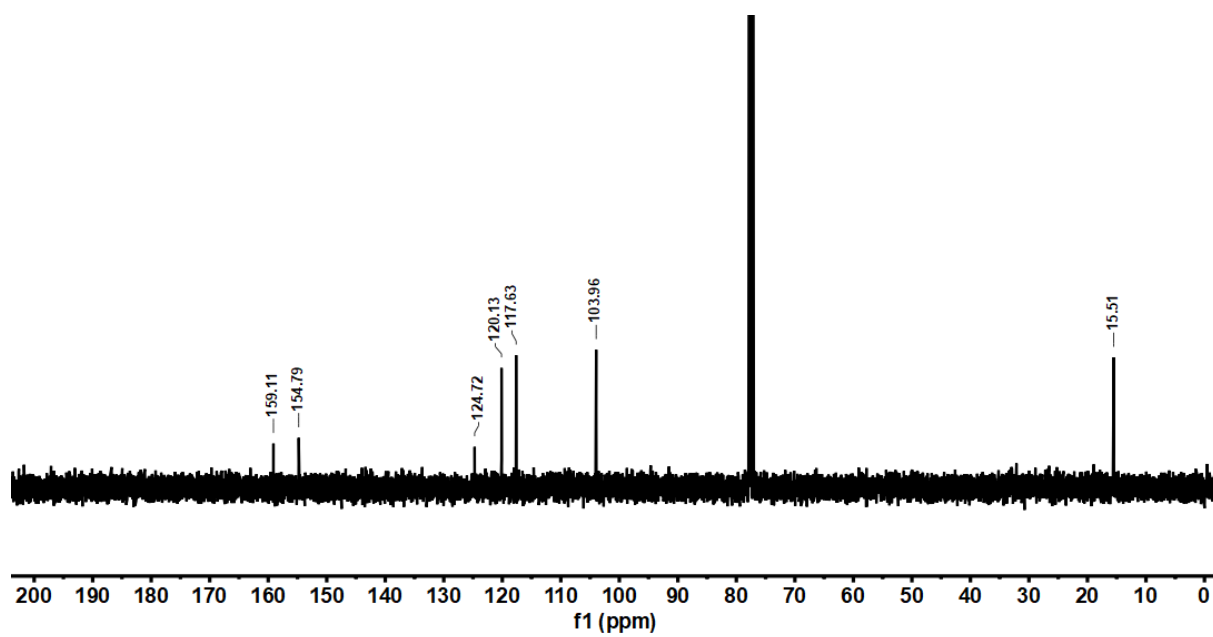
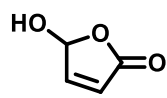


Figure S32 ^{13}C NMR spectrum of FLY450 measured at 293 K in CDCl_3 .



A (m)
7.30

B (m)
6.23

C (s)
4.60

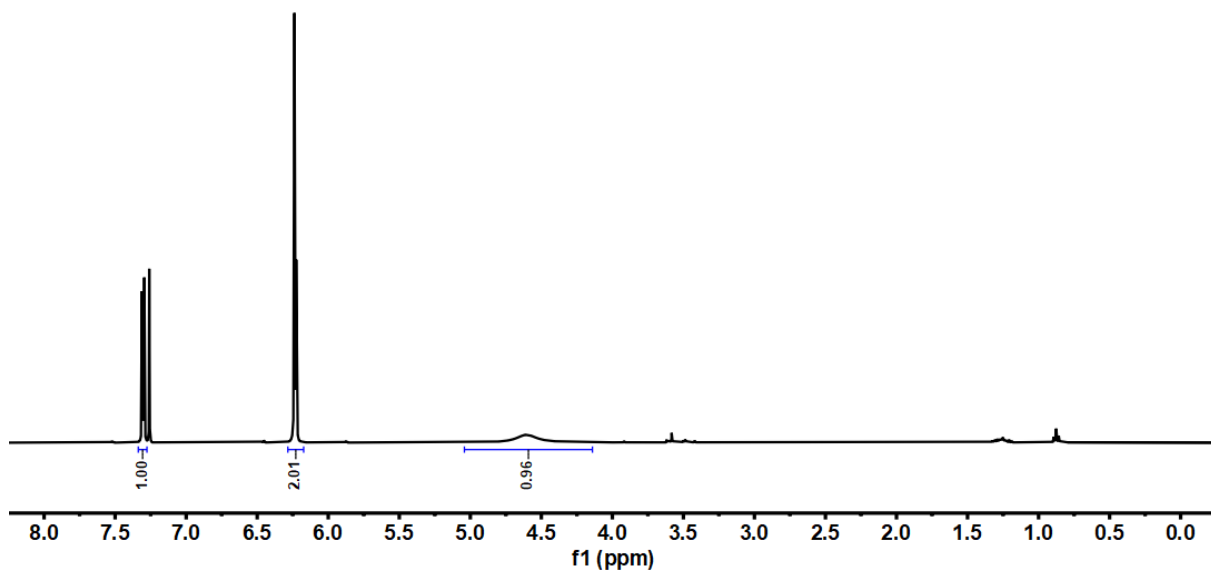


Figure S33 ¹H NMR spectrum of hydroxybutenolide measured at 293 K in CDCl₃.

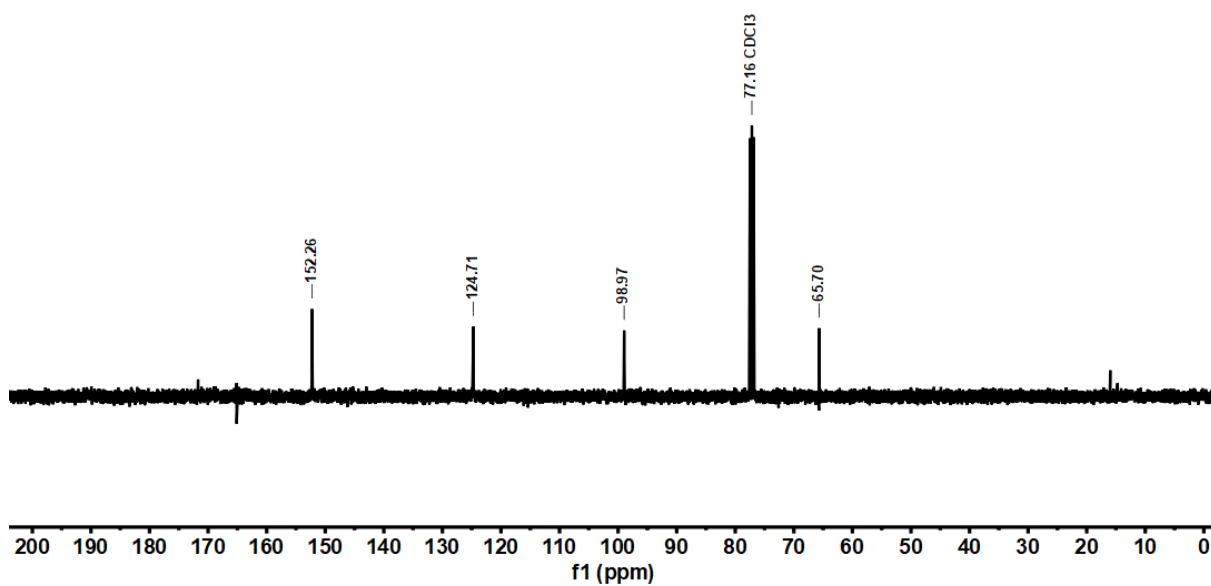


Figure S34 ¹³C NMR spectrum of hydroxybutenolide measured at 293 K in CDCl₃.

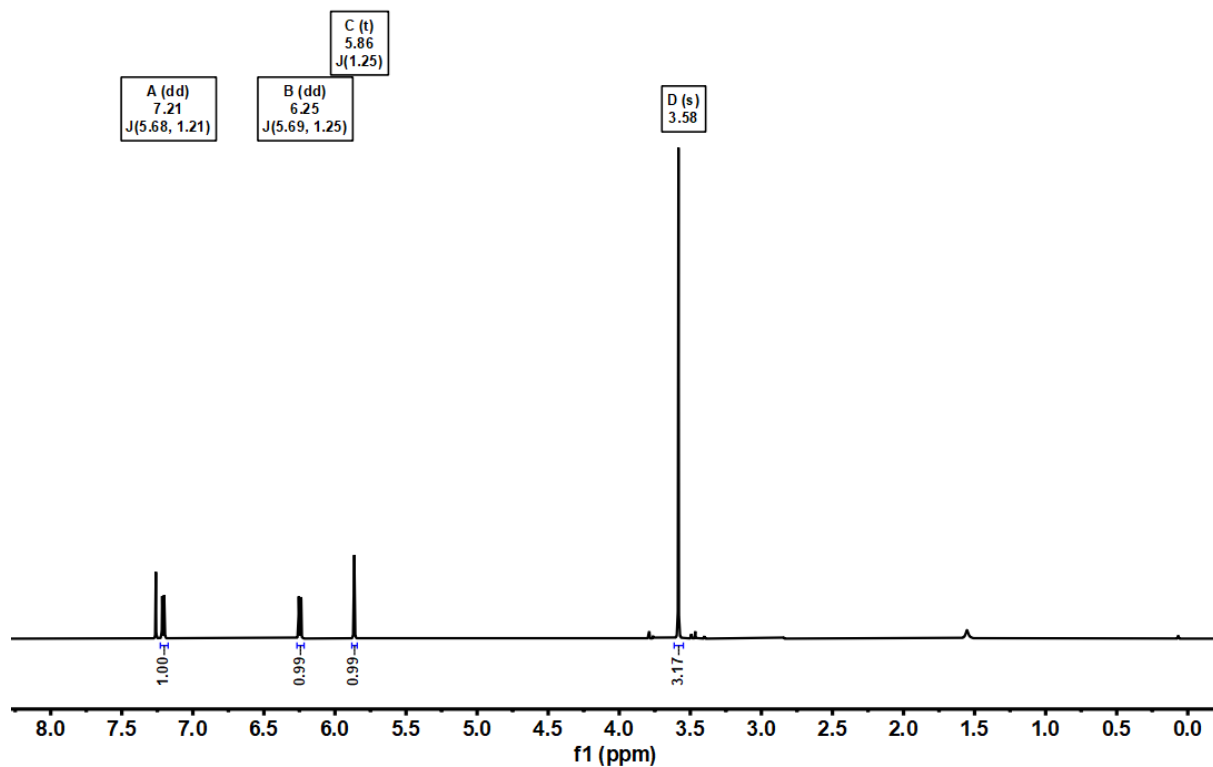
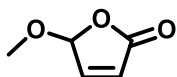


Figure S35 ^1H NMR spectrum of methoxybutenolide measured at 293 K in CDCl_3 .

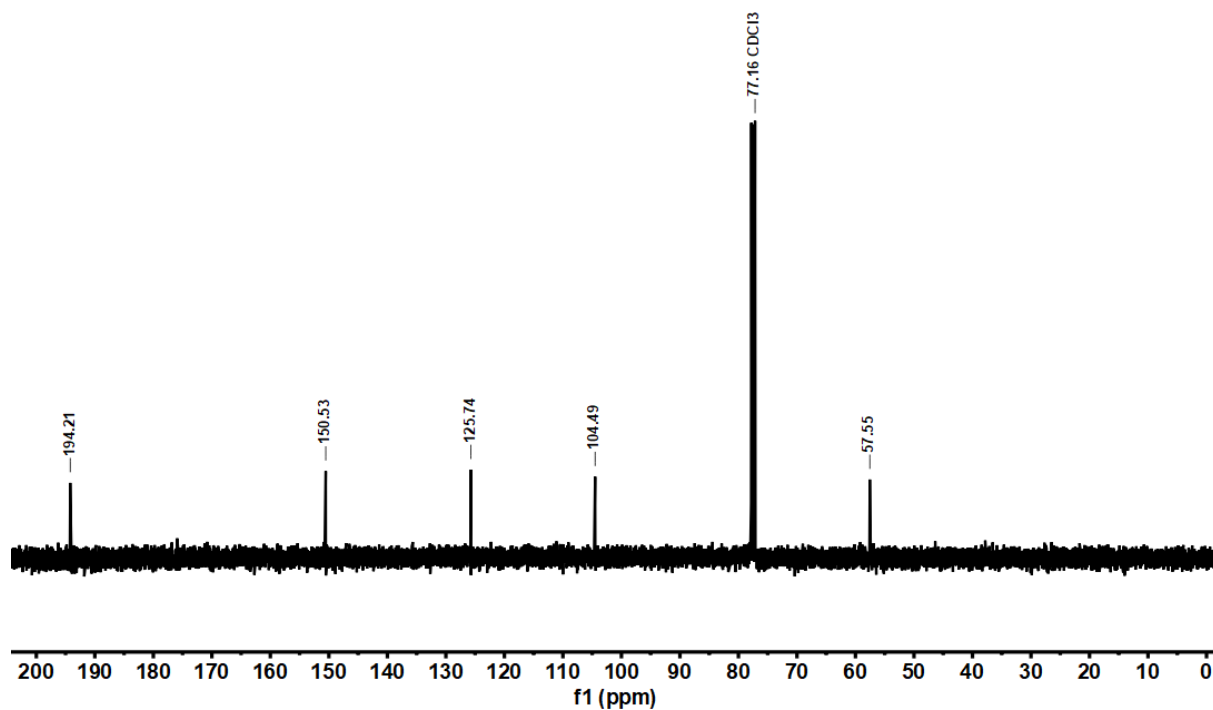


Figure S36 ^{13}C NMR spectrum of methoxybutenolide measured at 293 K in CDCl_3 .

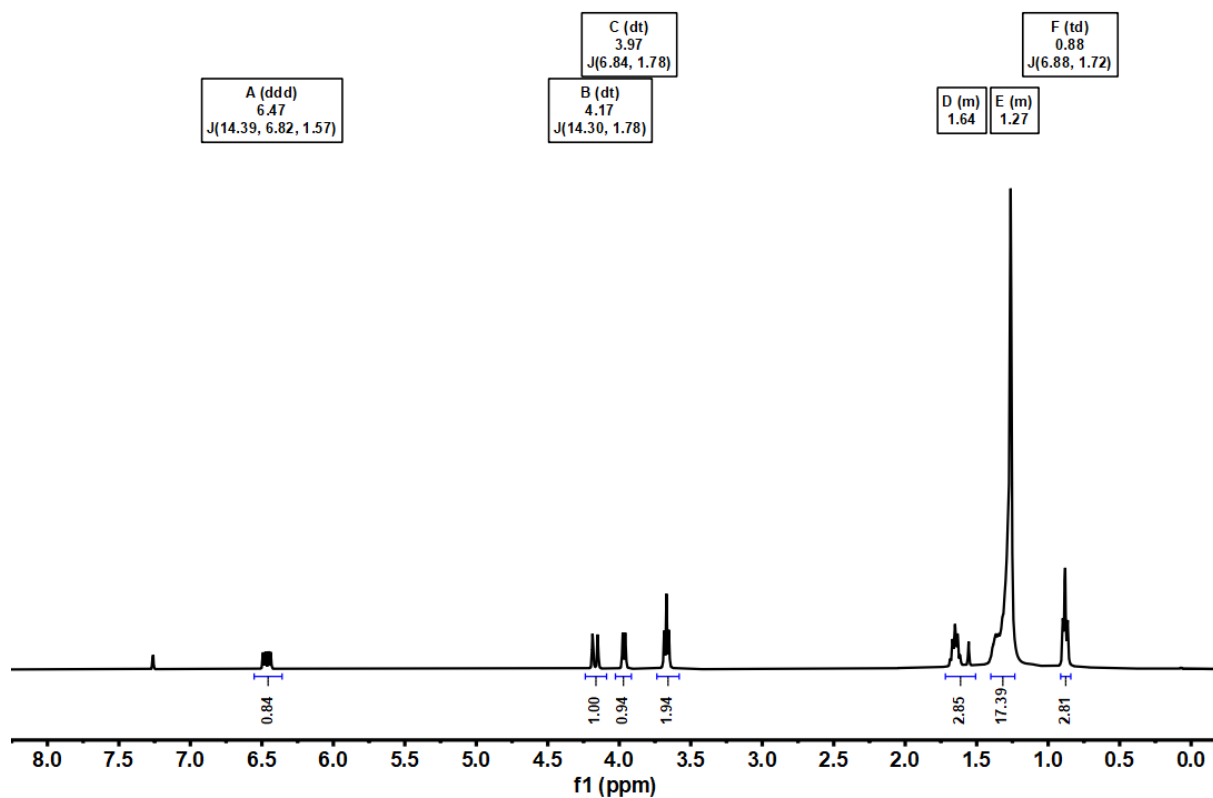
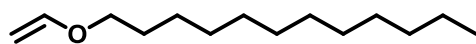


Figure S37 ^1H NMR spectrum of dodecyl vinyl ether measured at 293 K in CDCl_3 .

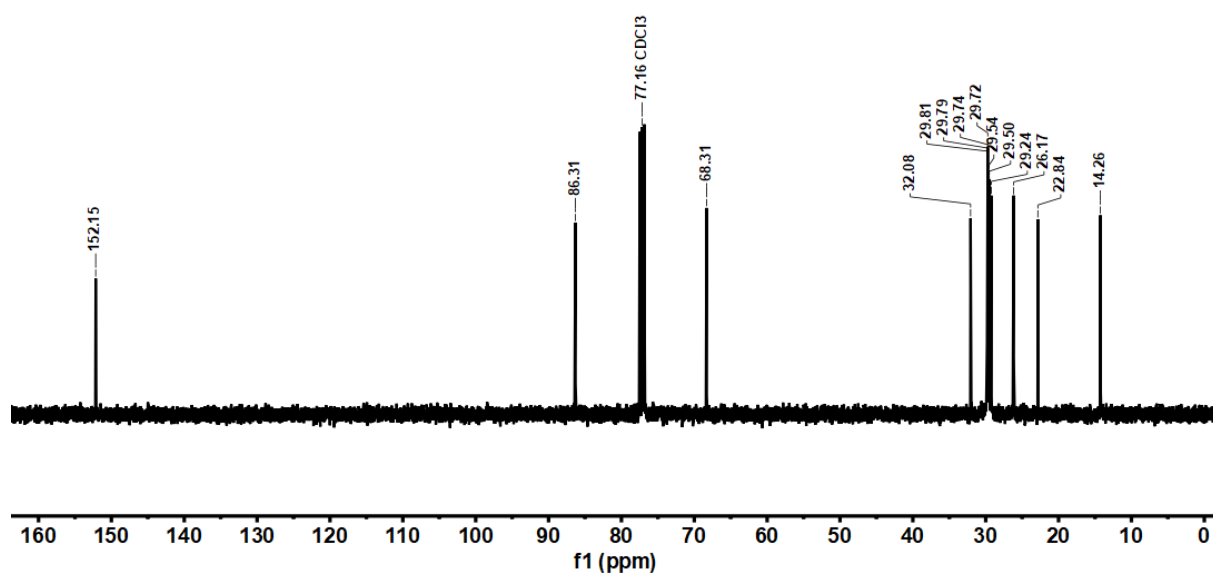


Figure S38 ^{13}C NMR spectrum of dodecyl vinyl ether measured at 293 K in CDCl_3 .

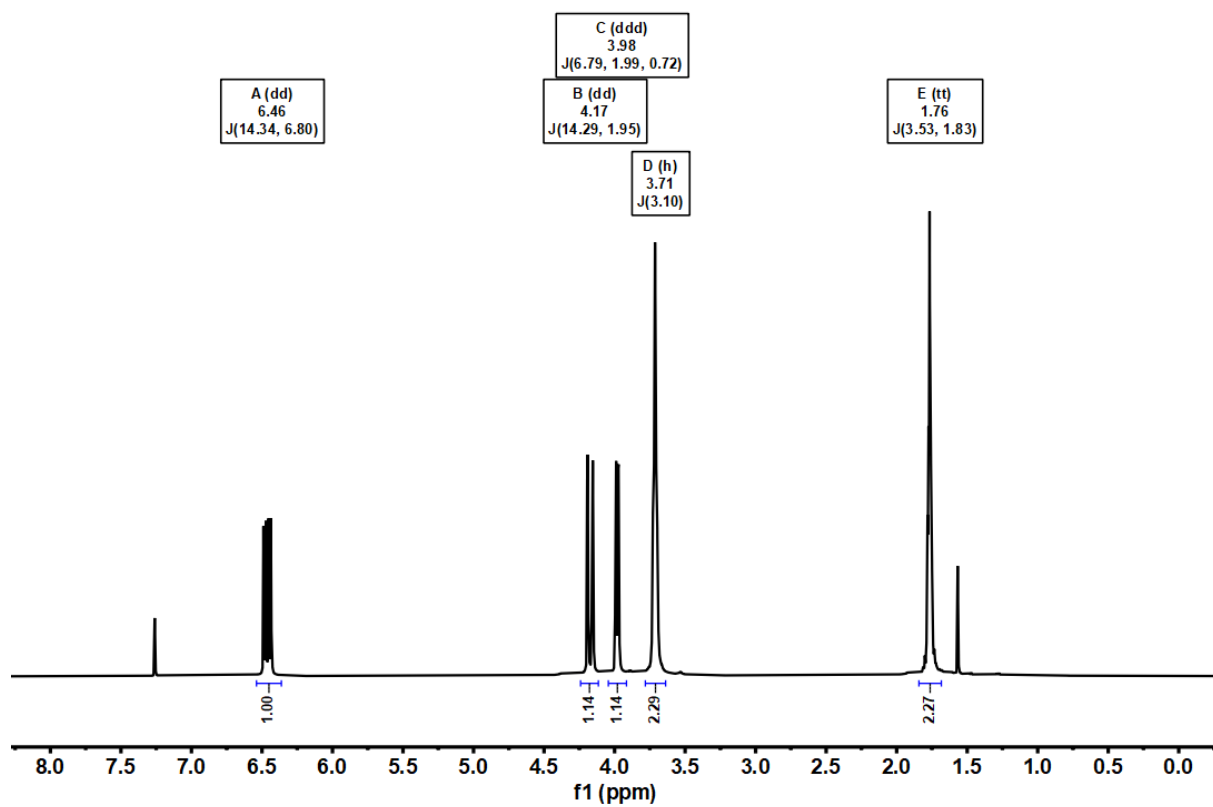
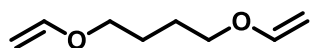


Figure S39 ^1H NMR spectrum of 1,4-butane divinyl ether measured at 293 K in CDCl_3 .

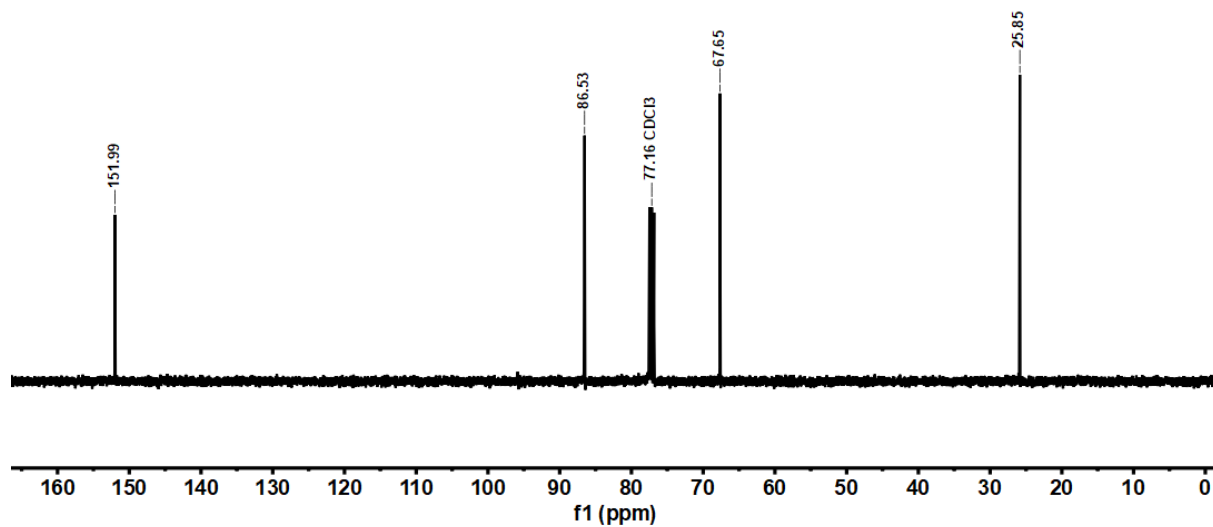


Figure S40 ^{13}C NMR spectrum of 1,4-butane divinyl ether measured at 293 K in CDCl_3 .

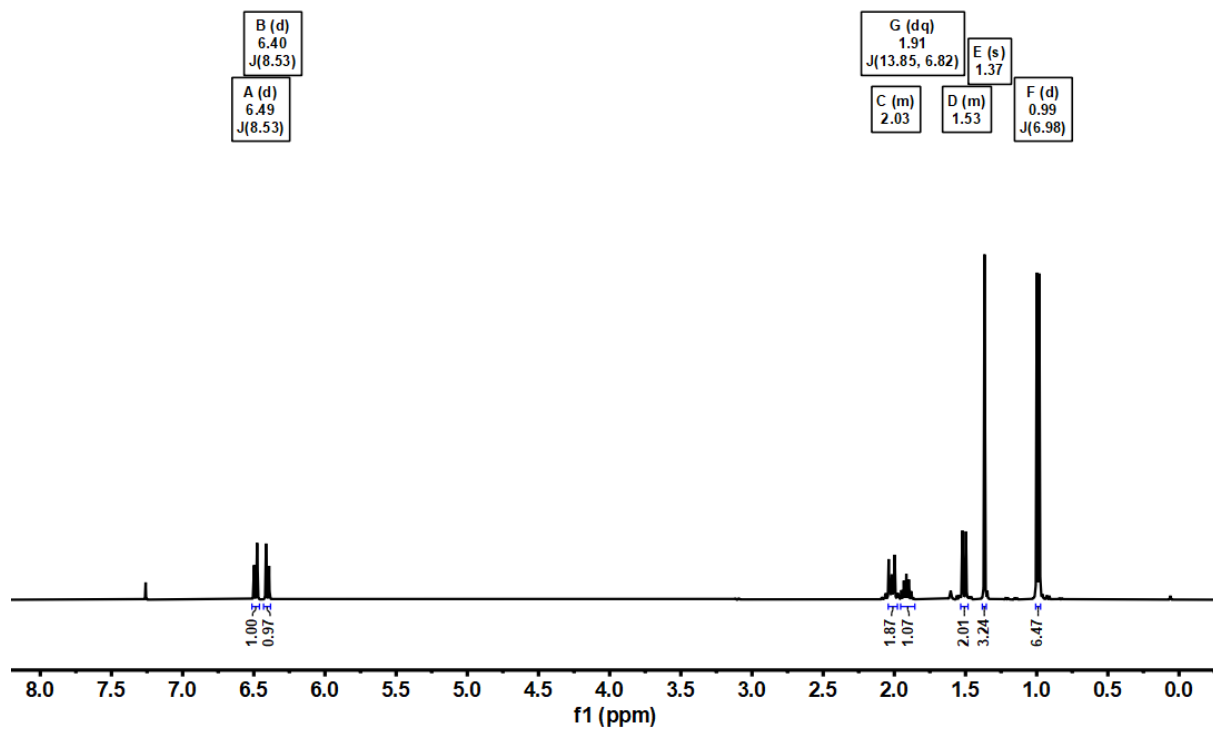
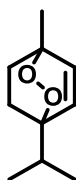


Figure S41 ^1H NMR spectrum of ascaridole measured at 293 K in CDCl_3 .

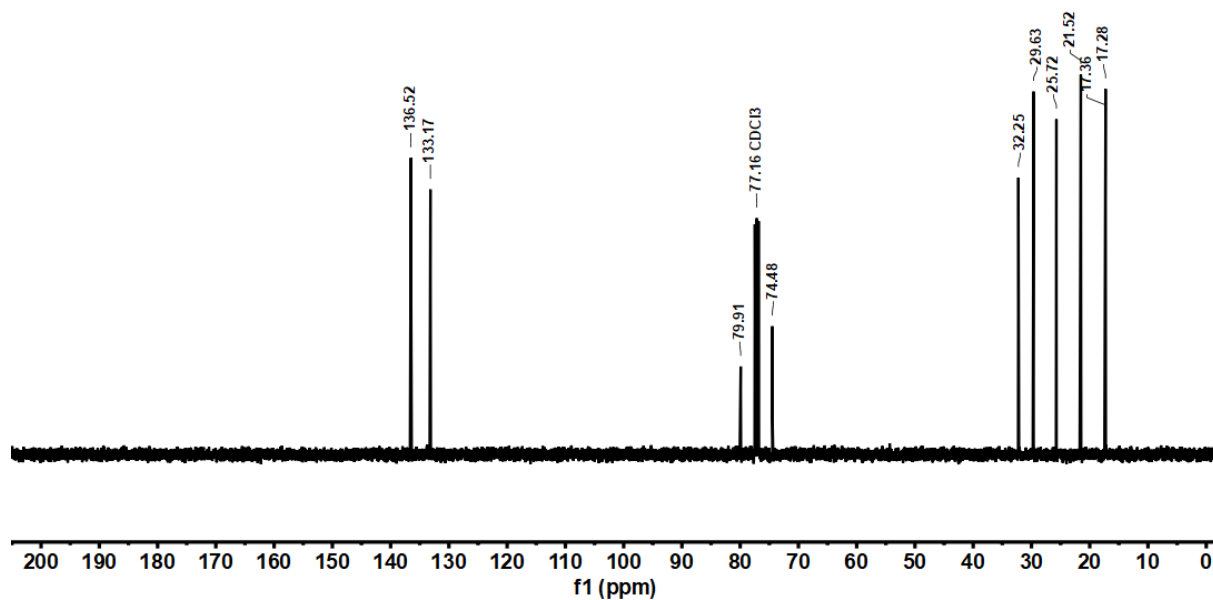


Figure S42 ^{13}C NMR spectrum of ascaridole measured at 293 K in CDCl_3 .

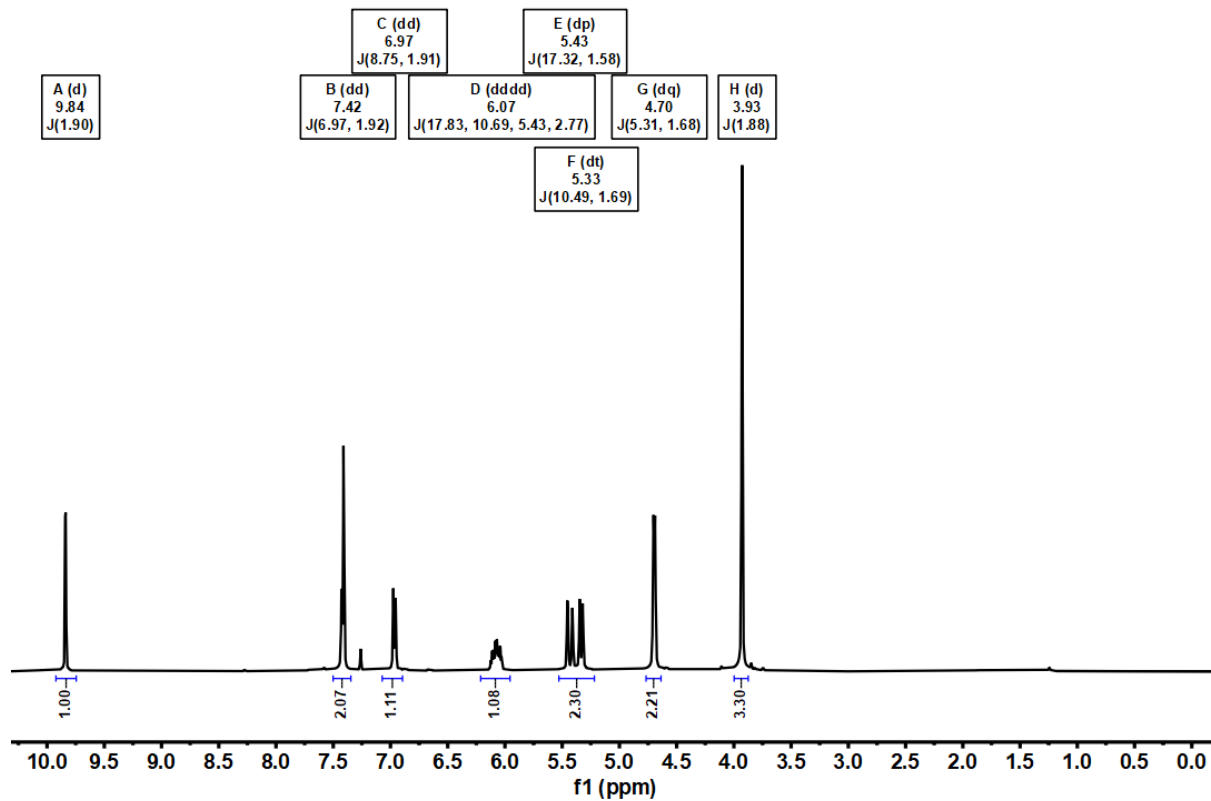
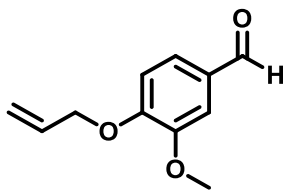


Figure S43 ^1H NMR spectrum of 4-(allyloxy)-3-methoxybenzaldehyde measured at 293 K in CDCl_3 .

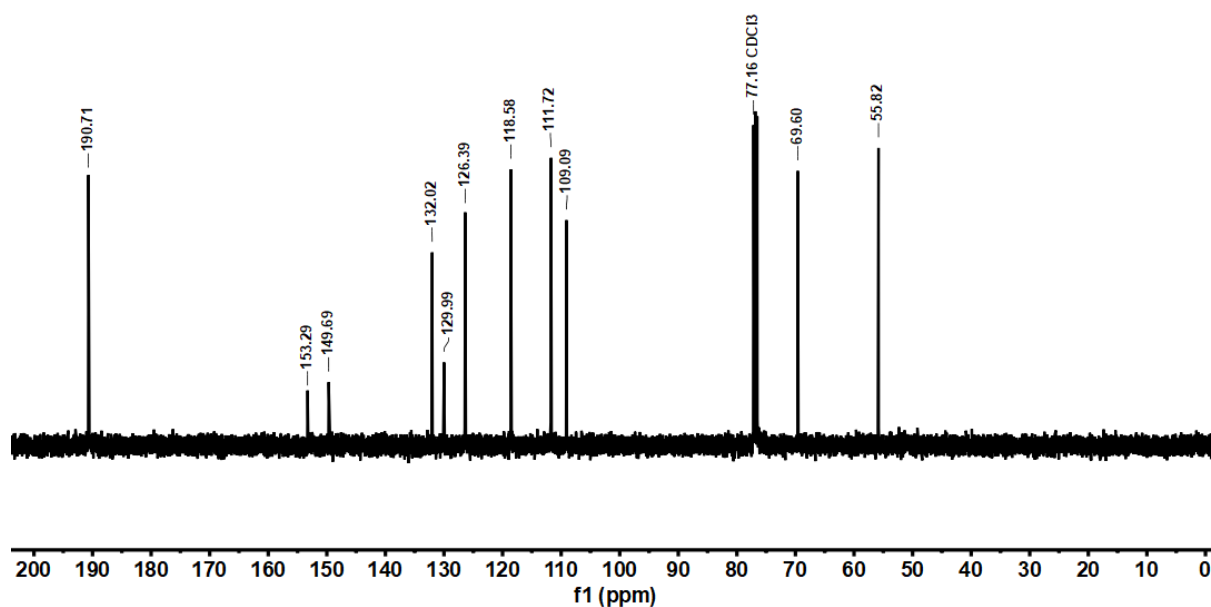


Figure S44 ^{13}C NMR spectrum of 4-(allyloxy)-3-methoxybenzaldehyde measured at 293 K in CDCl_3 .

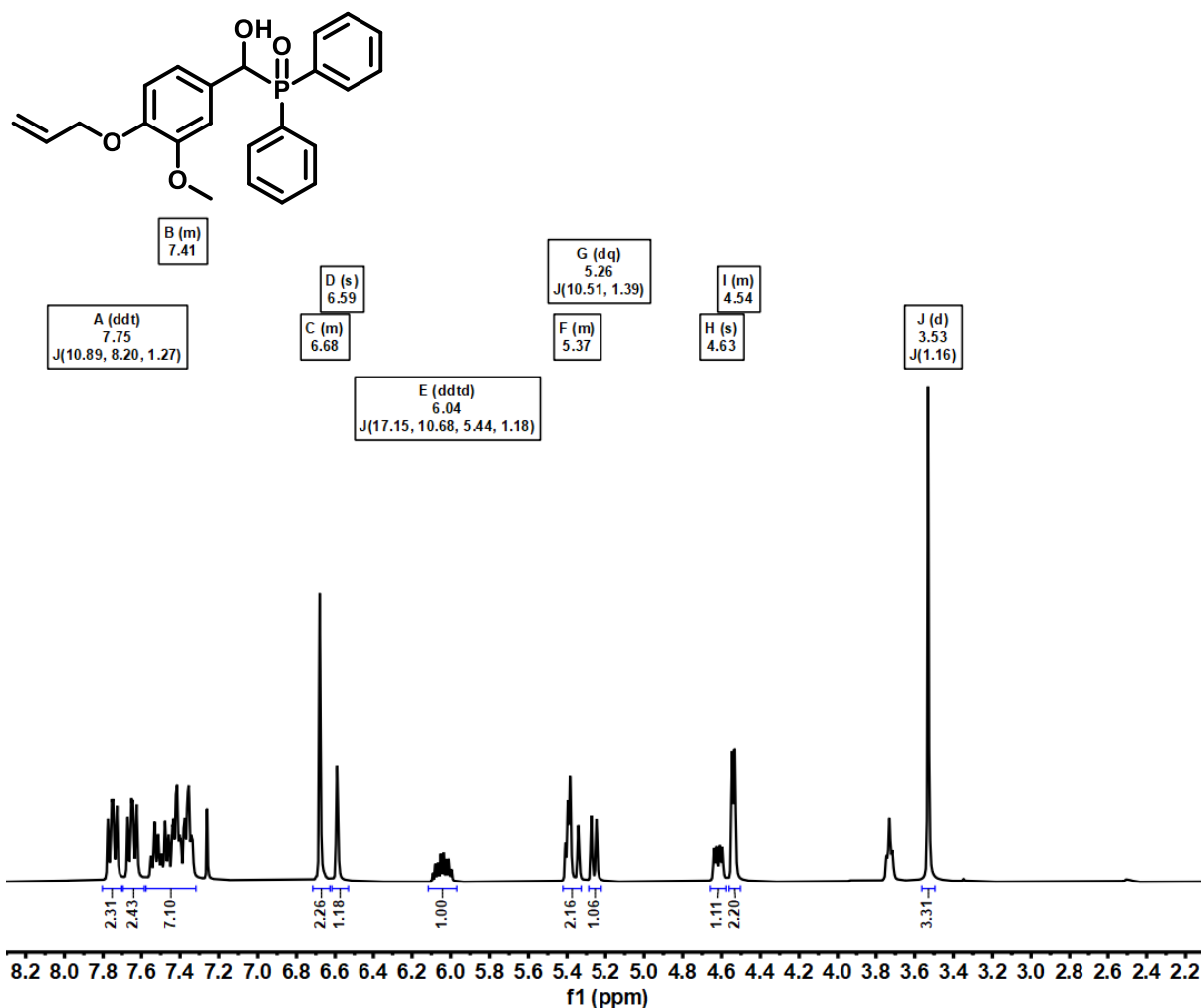


Figure S45 ¹H NMR spectrum of ((4-(allyloxy)-3-methoxyphenyl)(hydroxy)methyl)diphenylphosphine oxide measured at 293 K in CDCl₃.

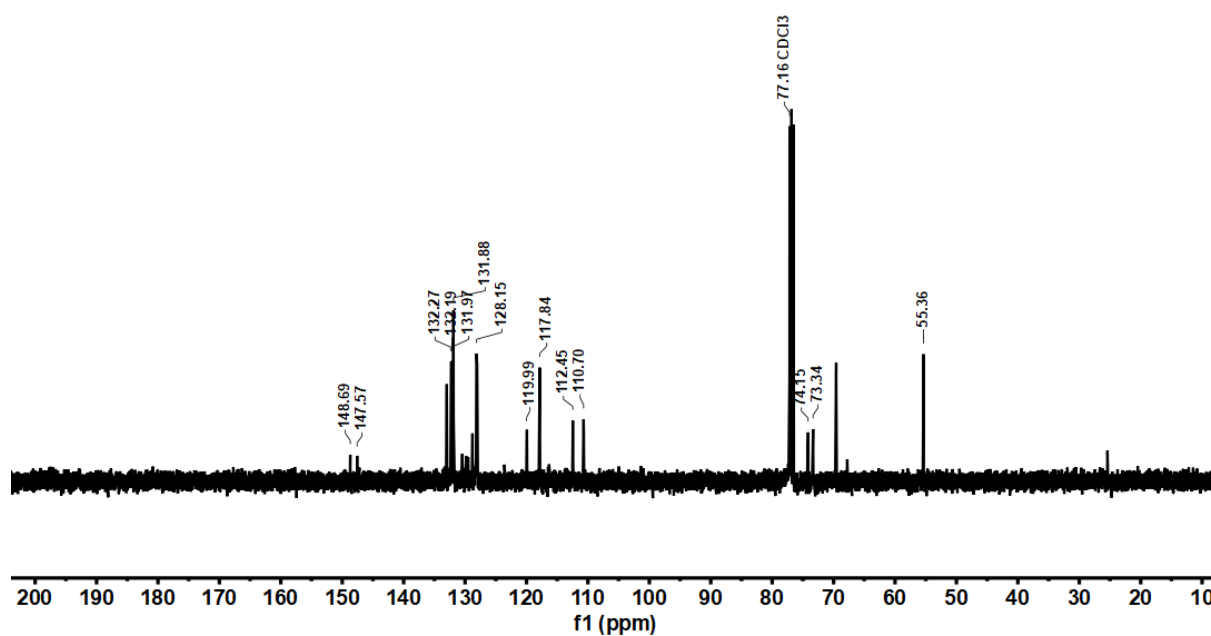


Figure S46 ¹³C NMR spectrum of ((4-(allyloxy)-3-methoxyphenyl)(hydroxy)methyl)diphenylphosphine oxide measured at 293 K in CDCl₃.

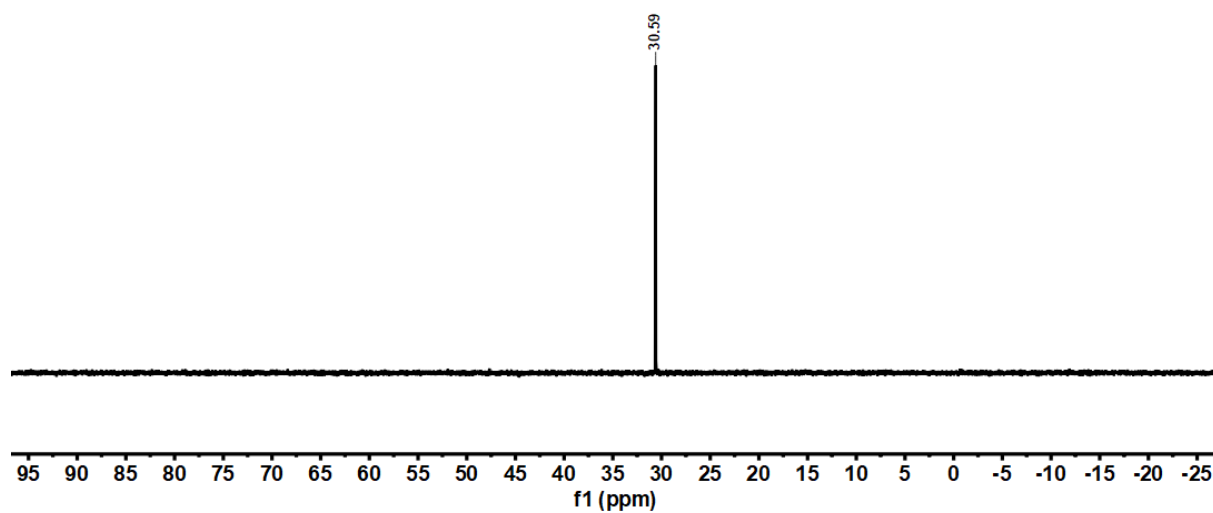


Figure S47 ^{31}P NMR spectrum of ((4-(allyloxy)-3-methoxyphenyl)(hydroxy)methyl)diphenylphosphine oxide measured at 293 K in CDCl_3 .

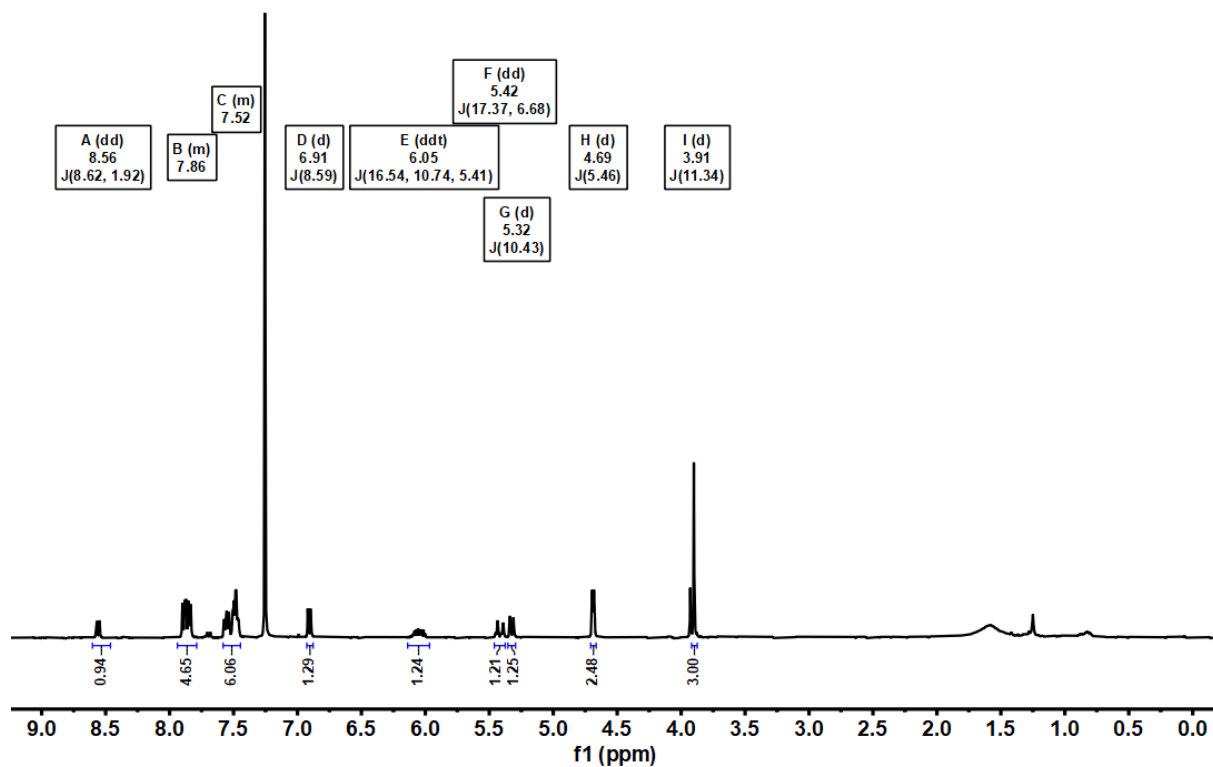
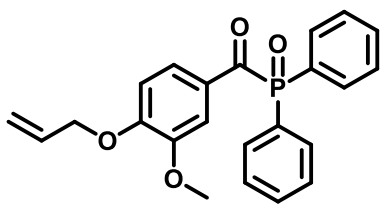


Figure S48 ^1H NMR spectrum of VAPO measured at 293 K in CDCl_3 .

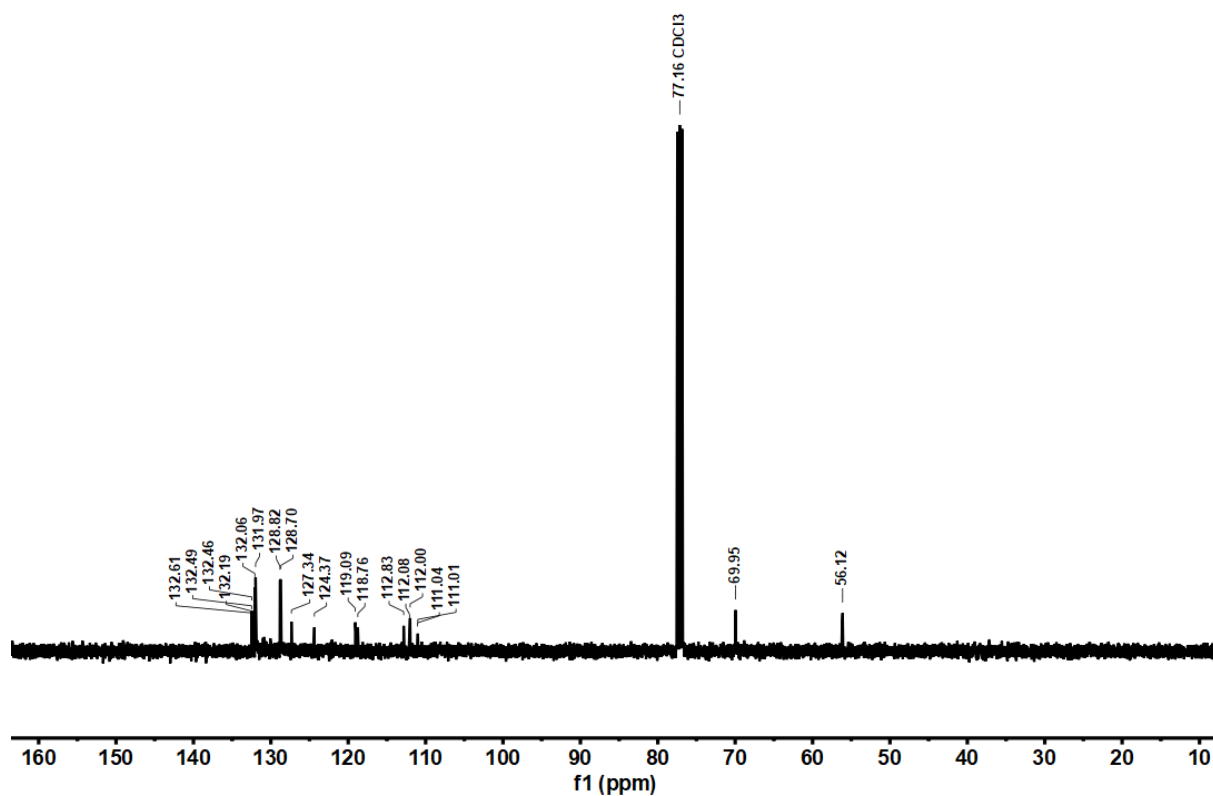


Figure S49 ^{13}C NMR spectrum of VAPO measured at 293 K in CDCl_3 .

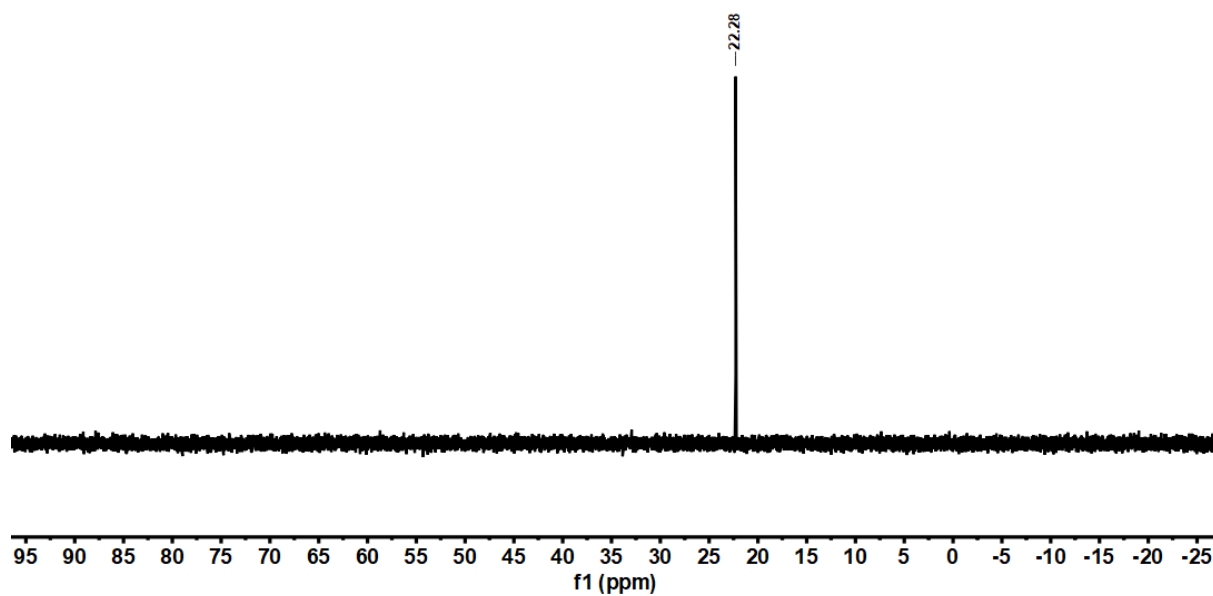
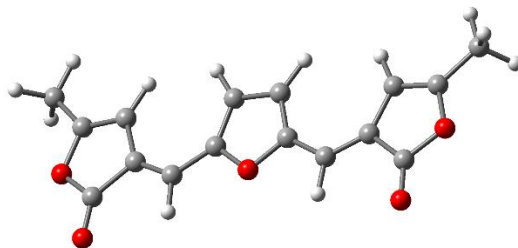


Figure S50 ^{31}P NMR spectrum of VAPO measured at 293 K in CDCl_3 .

Optimized Geometries and XYZ Coordinates

FLY 450 (S0) optimized geometry (# opt scrf=(smd,solvent=dichloromethane) def2tzvpp mn15)

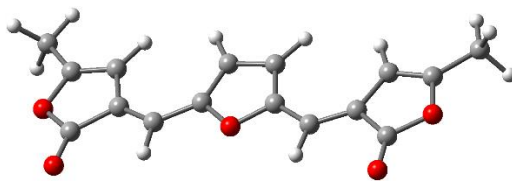


E(RMN15): -992.313007 Ha

0 1

C	-5.45068900	0.96899100	-0.05162800
C	-4.11161100	1.06326400	-0.00845900
C	-3.59017500	-0.28285000	0.00805600
C	-4.78351400	-1.16004900	-0.02938600
O	-5.88234600	-0.34475700	-0.06293500
H	-3.56365700	1.98977200	0.00175900
O	-4.88335300	-2.35812500	-0.03265100
C	-6.51994700	1.98257800	-0.09141900
H	-7.18557300	1.86544900	0.76583000
H	-6.09176100	2.98194400	-0.07850300
H	-7.12286900	1.86141000	-0.99339900
C	-2.35497700	-0.82914600	0.03878600
C	-1.10083300	-0.14859800	0.08196000
C	-0.70346900	1.16751600	0.16265900
O	-0.00000700	-0.94023300	0.03873300
C	0.70344000	1.16751300	0.16283000
H	-1.34708800	2.02808500	0.22260900
C	1.10080700	-0.14860500	0.08216100
H	1.34702700	2.02809800	0.22291200
H	-2.29769700	-1.91296300	0.02517000
C	5.45070400	0.96898500	-0.05189300
C	4.11163300	1.06328700	-0.00875300
C	3.59018400	-0.28281900	0.00824700
C	4.78351600	-1.16003900	-0.02896700
O	5.88235100	-0.34477400	-0.06280200
H	3.56370300	1.98982200	0.00110900
O	4.88333700	-2.35811700	-0.03189600
C	6.51996500	1.98254800	-0.09211100
H	6.09180100	2.98192800	-0.07943800
H	7.18567000	1.86562900	0.76509900
H	7.12279100	1.86113400	-0.99412800
C	2.35497700	-0.82912400	0.03916000
H	2.29772800	-1.91295300	0.02592000

FLY 450 (S₀) optimized geometry (# opt scrf=(smd,solvent=methanol) def2tzvpp mn15)

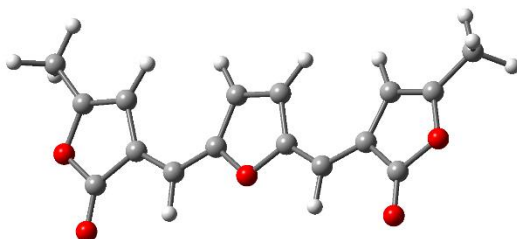


E(RMN15): -992.307214 Ha

0 1

C	-5.44733600	-0.97544800	0.04674700
C	-4.10927000	-1.06436800	0.00946300
C	-3.58980400	0.28318500	-0.00587400
C	-4.78077400	1.15510400	0.02602600
O	-5.87812500	0.34713600	0.05538300
H	-3.55836000	-1.98924200	0.00182900
O	-4.88535700	2.35893900	0.02791500
C	-6.52054500	-1.98289000	0.08246800
H	-7.18005800	-1.86445200	-0.77947400
H	-6.09539700	-2.98365300	0.07405000
H	-7.12755700	-1.85681600	0.98116700
C	-2.35403600	0.83029300	-0.03328800
C	-1.10125600	0.15026100	-0.07315000
C	-0.70295600	-1.16596500	-0.15004600
O	-0.00000100	0.94464400	-0.03196000
C	0.70295500	-1.16595300	-0.15016900
H	-1.34509500	-2.02799800	-0.20722000
C	1.10125200	0.15026800	-0.07322100
H	1.34510800	-2.02797700	-0.20735100
H	-2.29289600	1.91398600	-0.02041100
C	5.44733100	-0.97545400	0.04702900
C	4.10926900	-1.06437700	0.00966300
C	3.58980500	0.28316800	-0.00616000
C	4.78078200	1.15509600	0.02548900
O	5.87812000	0.34713800	0.05526800
H	3.55833600	-1.98923900	0.00214800
O	4.88536500	2.35892700	0.02703200
C	6.52053600	-1.98287900	0.08329900
H	6.09540300	-2.98364800	0.07489300
H	7.18037600	-1.86455900	-0.77840600
H	7.12720500	-1.85666100	0.98221400
C	2.35404500	0.83029300	-0.03355300
H	2.29291300	1.91398900	-0.02086600

FLY 450 (S₁) optimized geometry # opt td=(root=1) scrf=(smd,solvent=dichloromethane) def2tzvpp
mn15)

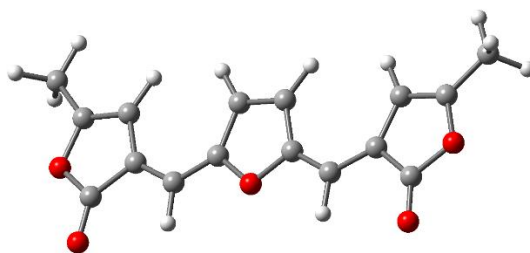


E(RMN15): -992.233011 Ha

0 1

C	-5.44293500	1.00353200	0.06057200
C	-4.07888100	1.05008300	0.08703700
C	-3.60547000	-0.28386900	-0.00813000
C	-4.80171600	-1.12161200	-0.08893900
O	-5.89723500	-0.27515400	-0.04658900
H	-3.51098000	1.96082900	0.17776600
O	-4.94296500	-2.31828200	-0.17926300
C	-6.46328900	2.06043300	0.12871500
H	-7.12685300	1.89551700	0.98142400
H	-5.99158800	3.03539400	0.22417000
H	-7.08588600	2.04823100	-0.76973100
C	-2.34375100	-0.87989400	-0.02794800
C	-1.11055300	-0.25586200	-0.00755600
C	-0.68430200	1.09652900	-0.00451600
O	0.00000100	-1.05048200	0.00054800
C	0.68436200	1.09650200	0.00553100
H	-1.33091700	1.95716100	-0.01569000
C	1.11056900	-0.25589800	0.00855100
H	1.33102400	1.95709300	0.01669100
H	-2.32947700	-1.96401300	-0.06685000
C	5.44286300	1.00357900	-0.06103900
C	4.07879800	1.05009700	-0.08673900
C	3.60547300	-0.28388800	0.00848100
C	4.80178100	-1.12160900	0.08848900
O	5.89725400	-0.27512400	0.04561000
H	3.51079400	1.96083800	-0.17682600
O	4.94310800	-2.31829100	0.17853800
C	6.46315200	2.06052000	-0.12955700
H	5.99136100	3.03547000	-0.22468700
H	7.08614500	2.04827500	0.76862300
H	7.12634300	1.89570100	-0.98256300
C	2.34376900	-0.87994000	0.02862900
H	2.32951100	-1.96405900	0.06743700

FLY 450 (S₁) optimized geometry (# opt td=(root=1) scrf=(smd,solvent=methanol) def2tzvpp mn15)

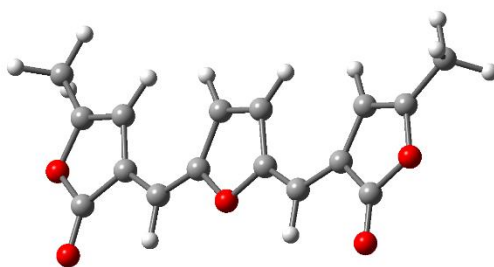


E(RMN15): -992.232904 Ha

0 1

C	-5.43804600	1.01186200	0.03223300
C	-4.07506300	1.05461500	0.01207600
C	-3.60512600	-0.28394900	-0.00026900
C	-4.79876500	-1.11767400	0.01482000
O	-5.89338700	-0.27732100	0.03233000
H	-3.50404400	1.96774600	0.01596600
O	-4.94704900	-2.32480500	0.01352200
C	-6.45948700	2.06747300	0.05744600
H	-7.08557000	1.96911300	0.94802500
H	-5.98872100	3.04745500	0.05517000
H	-7.11797600	1.98065500	-0.81065600
C	-2.34128000	-0.88222300	-0.01047000
C	-1.11170800	-0.26023400	-0.04674200
C	-0.68258600	1.09192000	-0.12173300
O	0.00000300	-1.05600400	-0.01009500
C	0.68264600	1.09189900	-0.12167300
H	-1.32732400	1.95220700	-0.17799800
C	1.11172700	-0.26026900	-0.04671400
H	1.32741800	1.95215700	-0.17793800
H	-2.32307100	-1.96670600	0.01815800
C	5.43801500	1.01187700	0.03203400
C	4.07503100	1.05458800	0.01179000
C	3.60512300	-0.28398800	-0.00024400
C	4.79877900	-1.11767900	0.01510100
O	5.89338300	-0.27729200	0.03237900
H	3.50398300	1.96769500	0.01539200
O	4.94709300	-2.32480300	0.01423900
C	6.45942600	2.06752500	0.05703900
H	5.98863400	3.04749200	0.05450100
H	7.08545300	1.96939200	0.94768800
H	7.11797500	1.98052200	-0.81099300
C	2.34128300	-0.88227300	-0.01042900
H	2.32307500	-1.96675600	0.01809900

FLY 450 (T₁) optimized geometry (# opt scrf=(smd,solvent=dichloromethane) def2tzvpp mn15)

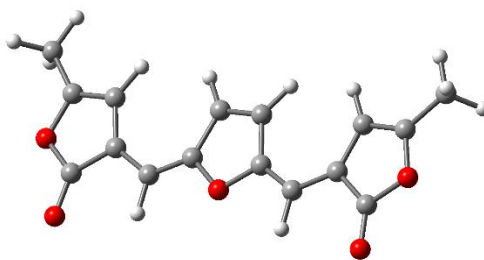


E(RMN15): -992.272445 Ha

0 3

C	-5.41557400	1.03880000	-0.02030300
C	-4.04608600	1.05289600	-0.01755500
C	-3.60774300	-0.28572900	-0.00660300
C	-4.81717300	-1.09904600	-0.00484600
O	-5.89549000	-0.23396800	-0.01150300
H	-3.45794600	1.95471900	-0.02993900
O	-4.97726500	-2.29842100	0.00172700
C	-6.41010700	2.12432600	-0.03356500
H	-7.05407600	2.06294900	0.84635000
H	-5.91166500	3.09056200	-0.04361100
H	-7.05193200	2.04316500	-0.91338600
C	-2.33904300	-0.92085800	-0.00715100
C	-1.11670400	-0.33104300	0.02377700
C	-0.67417200	1.03936700	0.09062700
O	0.00000800	-1.12461900	-0.00732400
C	0.67428000	1.03934300	0.09069800
H	-1.32048800	1.89884600	0.14004700
C	1.11674900	-0.33108300	0.02364500
H	1.32064000	1.89878300	0.14028900
H	-2.35556800	-2.00483400	-0.03790400
C	5.41552100	1.03882500	-0.02004000
C	4.04601900	1.05287700	-0.01721200
C	3.60773900	-0.28576700	-0.00654100
C	4.81718900	-1.09904500	-0.00510400
O	5.89547800	-0.23393000	-0.01161200
H	3.45782700	1.95467500	-0.02942800
O	4.97732200	-2.29842100	0.00108100
C	6.41001600	2.12438100	-0.03322900
H	5.91154800	3.09061100	-0.04269000
H	7.05432700	2.06263400	0.84640400
H	7.05149500	2.04361700	-0.91334400
C	2.33905900	-0.92090600	-0.00721900
H	2.35559200	-2.00488200	-0.03801000

FLY 450 (T₁) optimized geometry (# opt scrf=(smd,solvent=methanol) def2tzvpp mn15)

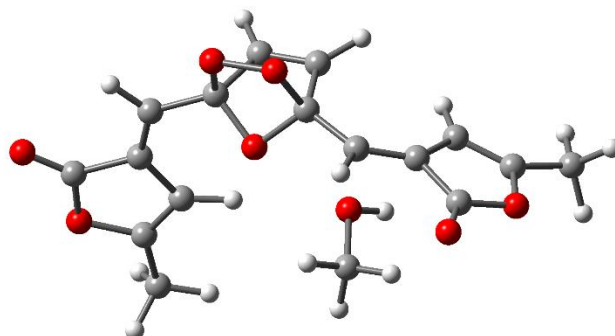


E(RMN15): -992.267854 Ha

0 3

C	-5.41470600	1.04025700	0.01697000
C	-4.04613800	1.05242200	0.01602500
C	-3.60746700	-0.28627000	0.00648400
C	-4.81412900	-1.09613200	0.00323000
O	-5.89313400	-0.23949800	0.00823300
H	-3.45735600	1.95379100	0.02810400
O	-4.97790000	-2.30141700	-0.00343900
C	-6.41385300	2.11892700	0.02799400
H	-7.05538200	2.03341600	0.90777100
H	-5.92012600	3.08752100	0.03735100
H	-7.05608100	2.05103700	-0.85283300
C	-2.33765700	-0.91892900	0.00813800
C	-1.11787100	-0.32473100	-0.01865700
C	-0.67413700	1.04500900	-0.07876200
O	0.00001800	-1.12121800	0.00979400
C	0.67416800	1.04502100	-0.07865500
H	-1.31898800	1.90601400	-0.12318800
C	1.11793800	-0.32471700	-0.01865000
H	1.31897800	1.90606000	-0.12293100
H	-2.34659500	-2.00324600	0.03583100
C	5.41465700	1.04028400	0.01710100
C	4.04607000	1.05236700	0.01634500
C	3.60749300	-0.28632800	0.00663400
C	4.81417400	-1.09613700	0.00308100
O	5.89314000	-0.23943600	0.00810000
H	3.45718900	1.95367400	0.02866300
O	4.97801300	-2.30140900	-0.00386400
C	6.41373700	2.11901100	0.02812800
H	5.91994300	3.08756400	0.03817600
H	7.05572600	2.03311200	0.90752500
H	7.05551300	2.05159600	-0.85307100
C	2.33765100	-0.91895900	0.00829200
H	2.34649800	-2.00328100	0.03582300

FLY 450-endoperoxide optimized geometry, paired with a single molecule of methanol
 (# opt freq scrf=(smd,solvent=methanol) def2tzvpp mn15)



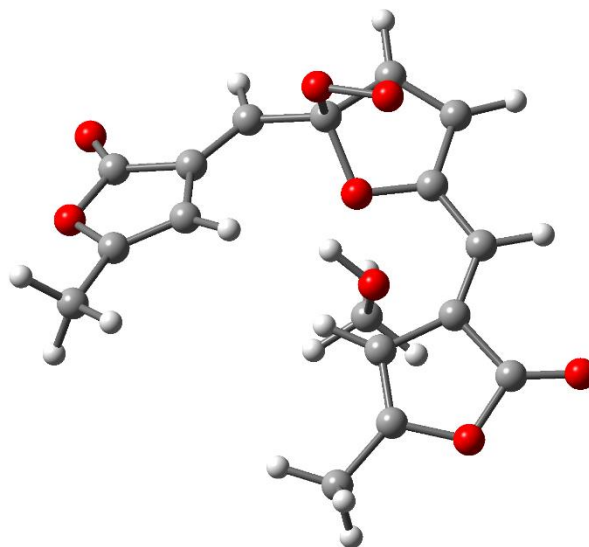
EE + Thermal Free Energy Correction: -1257.947960 Ha

0 1

C	-3.74695600	1.94559100	-0.07575000
C	-2.74232800	1.08173000	0.11586800
C	-3.30161800	-0.24968600	0.01939300
C	-4.75194000	-0.04231500	-0.24801500
O	-4.96374200	1.29830000	-0.30045200
H	-1.71635400	1.34506300	0.31733500
O	-5.64100100	-0.83763300	-0.40451900
C	-3.81277300	3.41566400	-0.09552700
H	-4.50119000	3.77394300	0.67213700
H	-2.82467000	3.83450000	0.08131900
H	-4.18508600	3.76281100	-1.06120700
C	-2.77712700	-1.47314200	0.12203200
C	-1.33511200	-1.68987900	0.38000600
C	-0.74211700	-1.50167000	1.76339000
O	-0.46951600	-0.94316700	-0.44336300
C	0.56571900	-1.40094100	1.55345900
H	-1.29343500	-1.60423400	2.68474200
C	0.71524600	-1.52830700	0.05437100
H	1.37459100	-1.41915900	2.26615100
H	-3.40682500	-2.35014900	0.03050400
C	4.51306300	0.85183500	0.70179600
C	3.35755600	0.21639400	0.93913900
C	2.95225400	-0.41675300	-0.29755300
C	4.03197100	-0.06296400	-1.27188800
O	4.94243900	0.69960200	-0.61524800
H	2.84419400	0.21933300	1.88472900
O	4.15560400	-0.34817400	-2.43283800
C	5.39627500	1.66795600	1.54923400
H	4.99281600	1.73579500	2.55638300
H	6.39325300	1.22488200	1.58661000
H	5.49711600	2.67069000	1.12971100

C	1.90993700	-1.13659100	-0.72478800
H	1.89244300	-1.45088900	-1.76326600
O	-0.97208600	-3.04065500	-0.00545600
O	0.43795700	-2.93880000	-0.21917000
O	0.61750600	1.95845700	0.60479200
C	0.82479000	2.29086100	-0.75765200
H	0.44611000	3.29012400	-0.98768300
H	1.88450800	2.24527200	-1.02780600
H	0.28239200	1.56550900	-1.36343000
H	1.12180200	2.56638000	1.15870400

FLY 450-endoperoxide TS-1 optimized geometry, paired with a single molecule of methanol
 (# opt=(ts,noeigentest) freq scrf=(smd,solvent=methanol) def2tzvpp mn15)



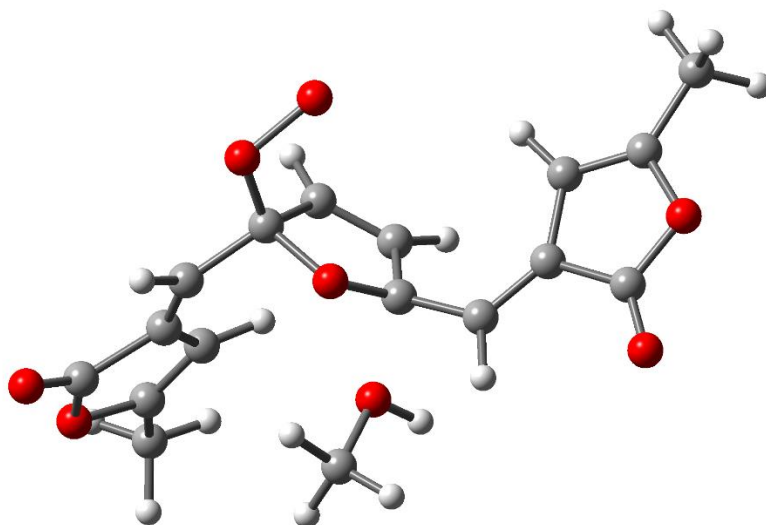
EE + Thermal Free Energy Correction: -1257.920362 Ha

0 1

C	-2.89099300	2.14433900	-0.58538200
C	-2.08994100	1.09165600	-0.79853700
C	-2.69494600	-0.04569900	-0.14166400
C	-3.94227100	0.48680200	0.47883300
O	-4.00719900	1.81074400	0.18257500
H	-1.18156600	1.10081800	-1.37761500
O	-4.78555800	-0.06480800	1.13487900
C	-2.82552800	3.55428400	-1.00013500
H	-2.81634400	4.20378700	-0.12275400
H	-1.92931500	3.73055400	-1.58986400
H	-3.70570600	3.81254900	-1.59199500
C	-2.34737800	-1.33123000	-0.01807700
C	-1.09413000	-1.86456800	-0.61517900
C	-0.64715400	-3.23718600	-0.22687700
O	0.04788300	-1.04219100	-0.26029200
C	0.68587900	-3.22518500	-0.16235800
H	-1.32303300	-4.07684500	-0.17570500
C	1.08387600	-1.83826200	-0.31173200
H	1.38004200	-4.04023600	-0.03646500
H	-2.98482400	-2.01702800	0.52566700
C	2.81014700	2.22391700	-0.04828000
C	1.93003200	1.19382600	-0.12427500
C	2.69135500	0.00074200	-0.22599500
C	4.12462400	0.44965300	-0.20150000
O	4.12184300	1.81148900	-0.09435800
H	0.85949800	1.30127700	-0.10295500
O	5.13334400	-0.18742700	-0.26052400

C	2.60773800	3.66987900	0.07246500
H	1.54753600	3.90478900	0.10373400
H	3.09704200	4.03322100	0.97882300
H	3.07658200	4.17636900	-0.77401100
C	2.40126500	-1.32483000	-0.30822400
H	3.21055700	-2.04222900	-0.34376100
O	-1.15924900	-1.74409000	-2.02413200
O	0.11204800	-2.02235800	-2.58131400
O	0.46977200	-0.81866100	2.64508900
C	0.32824200	-0.77035200	4.05634400
H	-0.19334500	0.13422800	4.37720000
H	-0.20868300	-1.64241400	4.43636700
H	1.32848100	-0.76476100	4.48579500
H	-0.40488700	-0.82238600	2.23558800

FLY 450-endoperoxide TS-2 optimized geometry (# opt=(ts,noeigentest) freq
 scrf=(smd,solvent=methanol) def2tzvpp mn15)



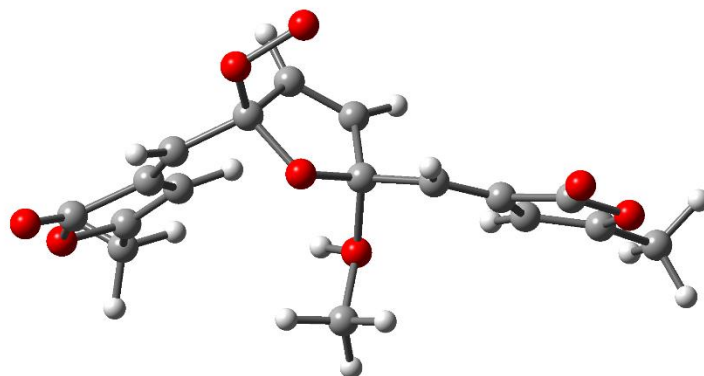
EE + Thermal Free Energy Correction: -1257.900967 Ha

0 1

C	-4.38467300	-0.78288100	-1.24575600
C	-3.15845100	-0.25456100	-1.14334500
C	-3.10672900	0.47855800	0.10687900
C	-4.46242800	0.29697200	0.70450900
O	-5.18800900	-0.46859500	-0.15092000
H	-2.37677200	-0.37345600	-1.87356100
O	-4.92247100	0.70572700	1.73868100
C	-5.03401800	-1.61531600	-2.27136700
H	-5.91892700	-1.10851300	-2.66095600
H	-4.34298100	-1.81205700	-3.08729800
H	-5.36087000	-2.56194200	-1.83698900
C	-2.19606600	1.20032300	0.76892100
C	-0.77945900	1.49072500	0.37321200
C	-0.39838900	1.26517700	-1.06438500
O	0.07786000	0.47837100	1.06402700
C	0.42187800	0.23277800	-1.18376100
H	-0.79884200	1.88742100	-1.85100800
C	0.64970300	-0.30824900	0.17316700
H	0.85387700	-0.19945700	-2.07260400
H	-2.47922700	1.62942000	1.72537400
C	4.90827100	0.30874500	-0.84696400
C	3.57072100	0.39196000	-0.81908800
C	3.10204000	-0.58926700	0.13303300
C	4.34243700	-1.25089400	0.64224300
O	5.39647700	-0.67530300	0.01100700
H	2.98464000	1.10244900	-1.37773000
O	4.47705800	-2.13551200	1.44365800

C	5.93991400	1.05237600	-1.58531800
H	5.47846300	1.80145800	-2.22360100
H	6.62086400	1.54029500	-0.88541300
H	6.53044300	0.36705400	-2.19632500
C	1.90582100	-0.94745900	0.61216300
H	1.84675200	-1.68264200	1.40704500
O	-0.48000400	2.71593600	0.86581300
O	0.82858600	3.11285600	0.40984600
O	-0.45507900	-1.69005100	0.12118600
C	-0.92504600	-2.22276800	1.37361100
H	-1.17266100	-1.37596900	2.00630900
H	-1.82030300	-2.80493500	1.16768500
H	-0.16030600	-2.84215800	1.83726700
H	-0.13264600	-2.39170100	-0.47110100

FLY 450-endoperoxide I-1 optimized geometry (# opt freq scrf=(smd,solvent=methanol) def2tzvpp mn15)



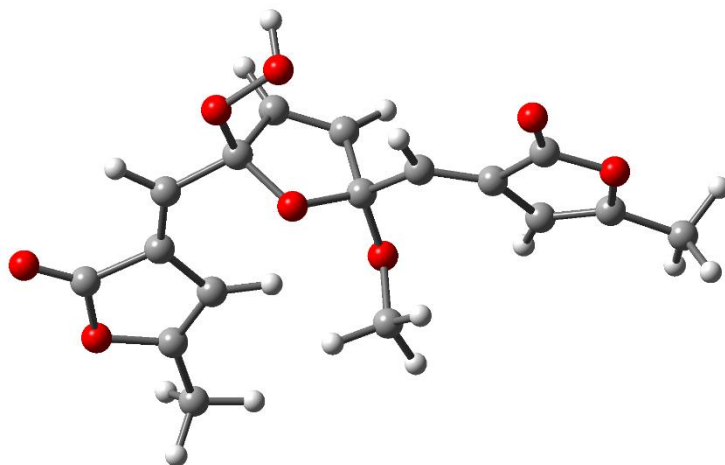
EE + Thermal Free Energy Correction: -1257.901855 Ha

0 1

C	-4.02204100	1.90846800	0.41262000
C	-2.97859000	1.10733800	0.66412400
C	-3.23553800	-0.15940300	0.00384500
C	-4.56044000	0.02394700	-0.65510600
O	-4.98534900	1.28470500	-0.37643600
H	-2.12532800	1.38234100	1.26063700
O	-5.21355800	-0.73144900	-1.32706000
C	-4.34167500	3.29055200	0.80554500
H	-5.27445300	3.31333700	1.37213600
H	-3.54071300	3.70206900	1.41480600
H	-4.47911900	3.91243100	-0.08093600
C	-2.59313100	-1.32535300	-0.12538300
C	-1.24808600	-1.69762000	0.42707600
C	-0.77216100	-0.94532400	1.64358100
O	-0.22471400	-1.35365000	-0.56628400
C	0.31896400	-0.24821600	1.37707300
H	-1.29868100	-1.01161800	2.58443600
C	0.67556300	-0.47738200	-0.05801400
H	0.91351600	0.37566100	2.02767700
H	-3.06611900	-2.10661900	-0.71267200
C	4.62816800	1.53719500	0.31705400
C	3.31261300	1.27804500	0.32102200
C	3.14285700	-0.07459000	-0.15781800
C	4.52452900	-0.55753200	-0.44545200
O	5.37751200	0.45576100	-0.14001000
H	2.54276300	1.96292000	0.63514300
O	4.91066500	-1.61412100	-0.86752300
C	5.41660200	2.71950400	0.69616100

H	4.76011500	3.51582700	1.03753600
H	6.11851900	2.46135300	1.49135100
H	6.00024800	3.06982300	-0.15726500
C	2.08366100	-0.86423600	-0.36241900
H	2.21806800	-1.87672300	-0.72428300
O	-1.27747200	-3.05477800	0.57781500
O	-0.05528300	-3.50116100	1.19200600
O	0.45415100	0.88822300	-0.75360200
C	0.39435400	0.87315600	-2.21303800
H	-0.51475200	0.37089900	-2.52814600
H	0.41567100	1.91057800	-2.52697000
H	1.28088100	0.34574200	-2.55102100
H	-0.31212400	1.35245300	-0.35892400

FLY 450-endoperoxide SP-1 optimized geometry (# opt freq scrf=(smd,solvent=methanol) def2tzvpp mn15)



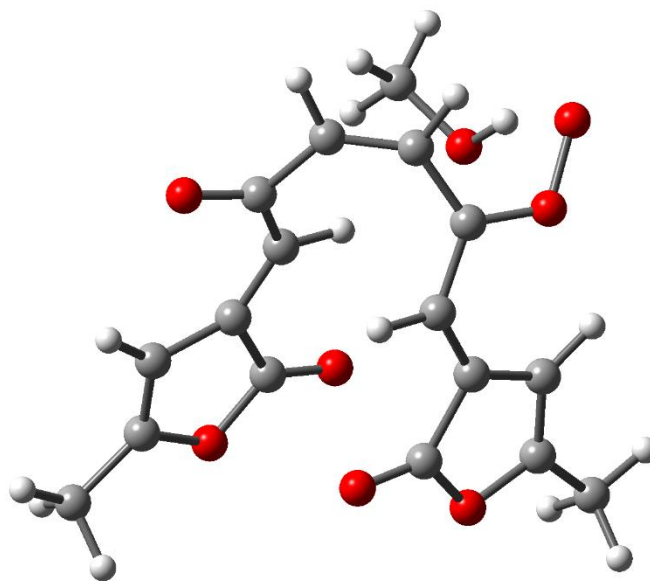
EE + Thermal Free Energy Correction: -1257.971319 Ha

0 1

C	-3.86976900	1.98077200	0.05573900
C	-2.81800300	1.16090400	0.17611400
C	-3.30010200	-0.18729800	-0.03922700
C	-4.75843300	-0.03691600	-0.29997500
O	-5.04701800	1.28882700	-0.23402700
H	-1.80941600	1.46193600	0.40465700
O	-5.60333100	-0.86171400	-0.53548600
C	-4.02432700	3.44016700	0.16984000
H	-4.73534800	3.68301900	0.96176600
H	-3.06552800	3.90197800	0.39262800
H	-4.41585100	3.85150600	-0.76244500
C	-2.73094300	-1.39531700	-0.03537500
C	-1.27212100	-1.65092400	0.22170600
C	-0.81876400	-1.39635600	1.63447400
O	-0.43559500	-0.83379400	-0.56334900
C	0.23001200	-0.59212000	1.63158300
H	-1.31416500	-1.84742800	2.48154400
C	0.57190200	-0.20043500	0.21748000
H	0.80193000	-0.22508800	2.47128200
H	-3.35195000	-2.26745700	-0.20889500
C	4.77605500	1.39408400	0.19854100
C	3.44748600	1.29127600	0.32758500
C	3.07663300	-0.04769200	-0.08974900
C	4.36014300	-0.69494900	-0.47341600
O	5.34980100	0.21681200	-0.28279200
H	2.79498500	2.06980200	0.68364300
O	4.59041500	-1.80368500	-0.88507400
C	5.73008500	2.48431900	0.46104000

H	5.20408700	3.36126400	0.83050100
H	6.46943700	2.16855300	1.19951300
H	6.26723000	2.74376700	-0.45325300
C	1.92499600	-0.72137200	-0.19079000
H	1.95074300	-1.74706500	-0.53938700
O	-1.13247500	-3.00870100	-0.17004300
O	0.19850500	-3.42299900	0.03659700
H	0.15067000	-3.92045600	0.87024400
O	0.47480500	1.18463700	0.11075300
C	0.52306000	1.69764300	-1.21437400
H	-0.40373800	1.47744100	-1.74795800
H	0.64362300	2.77516200	-1.12998100
H	1.36496000	1.28328500	-1.77367900

FLY 450-endoperoxide I-2 optimized geometry, with hydrogen bonding to a single molecule of methanol (# opt freq scrf=(smd,solvent=methanol) def2tzvpp mn15)



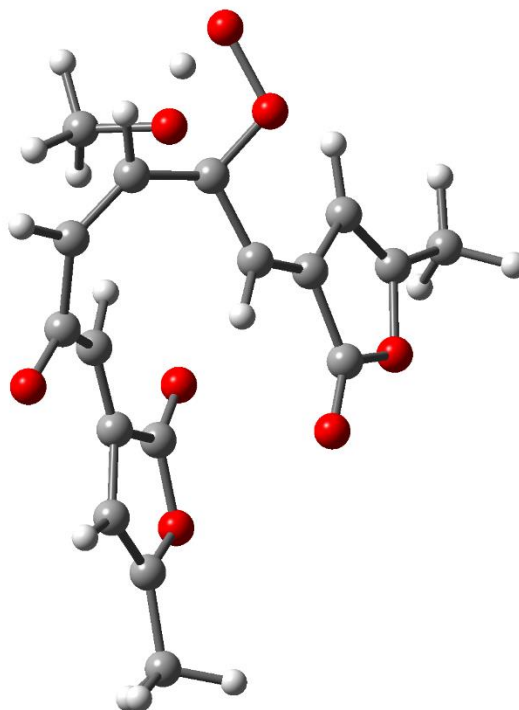
EE + Thermal Free Energy Correction: -1257.934094 Ha

0 1

C	0.36568800	3.40528200	0.00055200
C	1.30443800	2.45141200	-0.19414800
C	0.70903000	1.43609400	-0.99844300
C	-0.69441500	1.90112200	-1.23429300
O	-0.83392200	3.10567400	-0.61619300
H	2.30728400	2.48799800	0.19340900
O	-1.60156200	1.35641200	-1.79801700
C	0.38967800	4.67070800	0.74138800
H	-0.37212600	4.64997000	1.52400400
H	1.36774900	4.83132700	1.18611900
H	0.14630400	5.49762100	0.07109800
C	1.08021300	0.20804100	-1.43929000
C	2.30335200	-0.42530800	-1.05202600
C	2.52880500	-1.86032100	-1.06221500
O	-0.55152000	-3.62944900	-0.88963000
C	1.63545100	-2.83784900	-0.85870400
H	3.55477500	-2.12979300	-1.28622300
C	0.19638800	-2.74554400	-0.48764900
H	1.96224800	-3.86042800	-1.01292300
H	0.37620600	-0.37366200	-2.02024900
C	-3.76830100	-0.88260500	0.20530600
C	-2.80141900	-1.74675500	-0.15655200
C	-1.56938100	-1.25720600	0.39445400
C	-1.93937400	0.00497200	1.10294400
O	-3.27969500	0.17598600	0.96098000

H	-2.95325700	-2.63782000	-0.73956800
O	-1.24525200	0.80296800	1.67418300
C	-5.21551100	-0.84932000	-0.04497500
H	-5.51573500	-1.71077900	-0.63558000
H	-5.75733400	-0.84790900	0.90292800
H	-5.47959100	0.06794900	-0.57521700
C	-0.27529900	-1.62589200	0.33110900
H	0.45735600	-1.02740400	0.85920300
O	3.26767600	0.34586300	-0.71530500
O	4.34553700	-0.25811700	-0.08953800
O	2.47556700	-0.40613100	1.96644300
C	2.29822500	-1.61733800	2.67540000
H	1.36589000	-1.54670700	3.23542900
H	2.23053600	-2.47825600	2.00122500
H	3.11365900	-1.79345200	3.38176100
H	3.29598400	-0.45126500	1.43405600

FLY 450-endoperoxide TS-3 optimized geometry (# opt=(ts,noeigentest) freq
 scrf=(smd,solvent=methanol) def2tzvpp mn15)



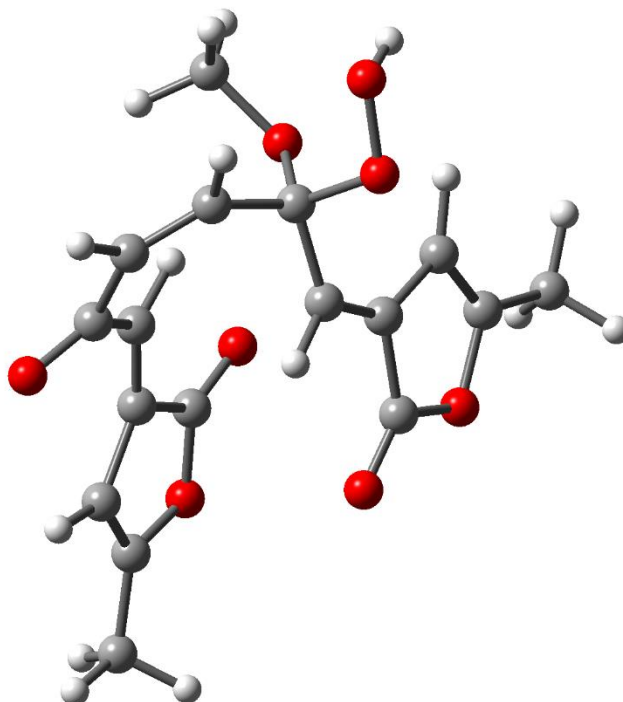
EE + Thermal Free Energy Correction: -1257.907061 Ha

0 1

C	0.76212100	3.36161900	-0.03236400
C	1.56353300	2.28378400	-0.05436700
C	0.84900900	1.24006500	-0.73985900
C	-0.47062700	1.84240400	-1.09265300
O	-0.46558400	3.12241900	-0.64503000
H	2.55919800	2.23688800	0.35154600
O	-1.42777600	1.34759900	-1.62753600
C	0.92979600	4.71908900	0.50564400
H	0.15658000	4.92268200	1.24900700
H	1.90998700	4.82392200	0.96335500
H	0.81950300	5.45419700	-0.29393000
C	1.08165400	-0.05146000	-1.02041000
C	2.29913600	-0.76955300	-0.61790400
C	2.31125400	-2.24424500	-0.56344000
O	-0.94934800	-3.68327500	-0.53317000
C	1.29359400	-3.09117800	-0.37056100
H	3.29359300	-2.65923600	-0.75176400
C	-0.15392500	-2.84579900	-0.12208100
H	1.50872600	-4.14928900	-0.47790300
H	0.34304300	-0.60702600	-1.58418900
C	-3.94586500	-0.53323400	0.01379700
C	-3.05079900	-1.51706400	-0.19359100

C	-1.84320900	-1.13745900	0.48318700
C	-2.14260500	0.19355000	1.08977400
O	-3.42896900	0.50224800	0.78284000
H	-3.23492900	-2.41471900	-0.75709100
O	-1.42939100	0.93918900	1.70779300
C	-5.33826400	-0.34990800	-0.41765500
H	-5.42476500	0.56196000	-1.01203600
H	-5.66475200	-1.20153500	-1.00866100
H	-5.98753900	-0.23732800	0.45279600
C	-0.59931700	-1.64251700	0.58780000
H	0.11708100	-1.08906000	1.17893700
O	3.39076200	-0.17342700	-1.08320800
O	4.52766700	-0.67441500	-0.37870400
O	2.68762700	-0.33033500	1.11116100
C	2.40068200	-1.08474600	2.28585800
H	1.58120800	-0.60235600	2.81497100
H	2.12955200	-2.11469900	2.04307100
H	3.28955900	-1.09463500	2.91586400
H	3.68705200	-0.46988600	0.79581300

FLY 450-endoperoxide SP-2 optimized geometry (# opt freq scrf=(smd,solvent=methanol) def2tzvpp mn15)



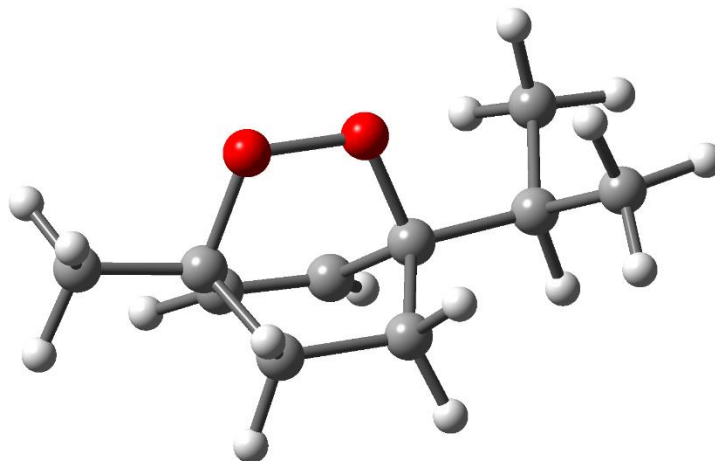
EE + Thermal Free Energy Correction: -1257.959586 Ha

0 1

C	0.30813600	3.41817800	0.06746000
C	1.20182100	2.42287900	0.13781200
C	0.68345100	1.32579600	-0.65084200
C	-0.63365900	1.80288500	-1.14889300
O	-0.80741800	3.06975700	-0.69595000
H	2.14021400	2.46160100	0.66363300
O	-1.48104000	1.22809700	-1.78632000
C	0.27203200	4.77899600	0.62693500
H	-0.59615900	4.89422600	1.27873400
H	1.17746100	4.97415200	1.19634100
H	0.18288400	5.51395500	-0.17530200
C	1.09802300	0.08438100	-0.93046700
C	2.33905300	-0.52794800	-0.32326200
C	2.44279900	-2.02531000	-0.52451200
O	-0.65900000	-3.81010100	-0.31472000
C	1.51223300	-2.97443600	-0.40331000
H	3.43321200	-2.34115700	-0.83141400
C	0.08263400	-2.87339400	-0.03252300
H	1.79532400	-3.99045000	-0.65764000
H	0.52675700	-0.51553900	-1.62839500
C	-3.84960100	-0.85106200	-0.00663700

C	-2.87305600	-1.75969000	-0.17398800
C	-1.71059300	-1.26530200	0.51469900
C	-2.13233500	0.04737000	1.08408700
O	-3.43344400	0.24138100	0.74715000
H	-2.96992200	-2.68238500	-0.71859900
O	-1.49915200	0.86496600	1.69898000
C	-5.24548800	-0.79145900	-0.46320700
H	-5.49036200	-1.67757900	-1.04299000
H	-5.91718100	-0.71931000	0.39447100
H	-5.39814100	0.09913300	-1.07617800
C	-0.43454200	-1.67410300	0.64423600
H	0.24519000	-1.06426700	1.22716500
O	3.37912200	0.10495200	-1.07361100
O	4.63115900	-0.30951800	-0.56105100
O	2.44189700	-0.13708400	1.01267600
C	2.96970200	-1.05360500	1.96857400
H	3.17079000	-0.46902500	2.86313600
H	2.24352400	-1.83368300	2.20625600
H	3.89606700	-1.51295800	1.62245500
H	4.79968700	0.33863100	0.14412500

Ascaridole optimized geometry (# opt freq scrf=(smd,solvent=tetrahydrofuran) def2tzvpp mn15)

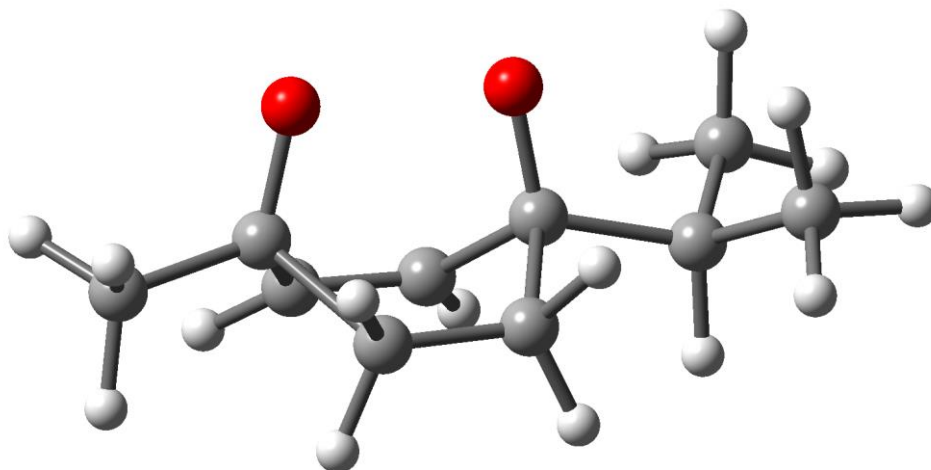


EE + Thermal Free Energy Correction: -540.399136 Ha

0 1

O	-1.13125500	-0.19287500	-1.30917700
C	-1.84215600	-0.05712400	-0.05872100
C	-1.34426300	-1.10614400	0.89236200
C	-1.48701100	1.31461500	0.51308100
H	-1.85670100	2.07926100	-0.17263800
H	-1.99497400	1.44489100	1.46948200
C	-3.29889500	-0.19094800	-0.42862300
H	-3.50215900	-1.17542600	-0.85061600
H	-3.90824000	-0.06217400	0.46670600
H	-3.58024100	0.57274000	-1.15399600
C	-0.03108200	-1.04760300	1.08148800
C	0.04180900	1.38833400	0.65457600
H	0.44841500	2.13851000	-0.02307500
H	0.35279700	1.64575700	1.66838500
C	0.63362000	0.03023000	0.26929600
O	0.29309600	-0.19872700	-1.11342700
C	2.16166700	-0.03325800	0.34254200
H	2.38602300	-0.01518400	1.41494400
C	2.84819400	1.15350800	-0.32295800
H	3.92867900	0.99907400	-0.32714700
H	2.52031800	1.25399500	-1.35984000
H	2.64964600	2.09302600	0.19281600
C	2.69154600	-1.33755100	-0.24560000
H	3.75323800	-1.44617400	-0.01898300
H	2.16915400	-2.21086000	0.14838300
H	2.57582700	-1.33990400	-1.33039300
H	-2.01736300	-1.82152400	1.34919000
H	0.54028100	-1.70754900	1.72295600

Ascaridole--scission-TS optimized geometry (# opt=(TS,noeigentest) freq
 scrf=(smd,solvent=tetrahydrofuran) def2tzvpp mn15)

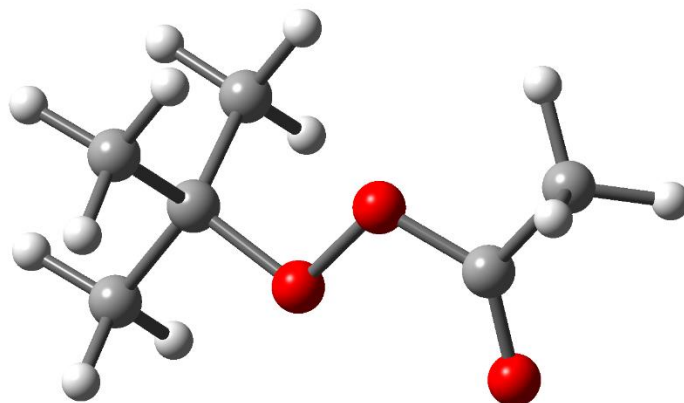


EE + Thermal Free Energy Correction: -540.315197 Ha

0 1

O	1.65830700	-0.16569400	1.40740900
C	1.99296600	-0.18288500	0.15881900
C	1.33495200	-1.25201300	-0.67939900
C	1.39041300	1.33174100	-0.52800800
H	1.87165100	2.02849900	0.14955300
H	1.86115500	1.28289800	-1.50577900
C	3.49421300	0.01434800	-0.07581800
H	4.01598500	-0.86996900	0.29266900
H	3.70414500	0.13468100	-1.13871400
H	3.84799900	0.88550600	0.47222100
C	0.00901500	-1.23089900	-0.76176200
C	-0.04529600	1.35877900	-0.55530900
H	-0.50813900	2.05080500	0.13769300
H	-0.47468900	1.39560200	-1.55463600
C	-0.72424400	-0.14646600	0.00246300
O	-0.53689500	-0.16450100	1.28255500
C	-2.22271400	0.00305500	-0.41224500
H	-2.22617800	0.00963900	-1.50725300
C	-2.89246500	1.25783900	0.11917300
H	-3.97401900	1.17167600	0.00027300
H	-2.67824900	1.37310200	1.18383800
H	-2.57723300	2.16126200	-0.40165800
C	-2.96355800	-1.22959300	0.09899900
H	-3.97925300	-1.24848200	-0.29949700
H	-2.47072800	-2.16057600	-0.18443900
H	-3.02225100	-1.19635200	1.18873500
H	1.95300700	-1.97813200	-1.19769900
H	-0.55419300	-1.94204600	-1.35649500

Trigonox 42S optimized geometry (# opt freq scrf=(smd,solvent=tetrahydrofuran) def2tzvpp mn15)

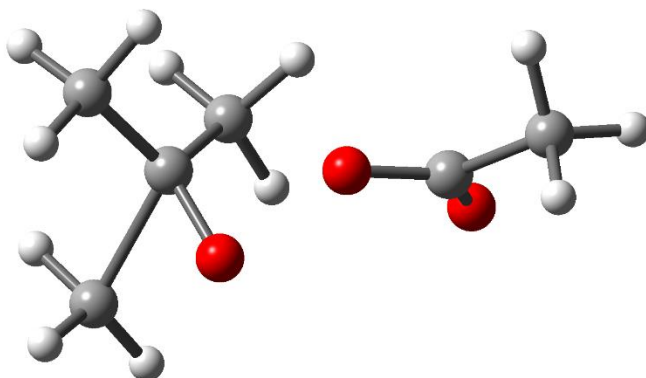


EE + Thermal Free Energy Correction: -460.998352 Ha

0 1

O	0.77820000	0.35065900	0.05105600
C	2.00144700	-0.22228200	0.00517000
C	3.05154300	0.84546200	-0.02035000
H	3.45701400	0.94876600	0.98674100
H	3.85479900	0.53188300	-0.68272000
H	2.65130000	1.80452100	-0.33835800
C	-1.50387700	0.04540700	-0.00768600
O	-0.23932300	-0.63575600	0.13312200
O	2.19144800	-1.40745700	0.00903500
C	-2.48890500	-1.10470800	0.10252600
H	-2.32187300	-1.83249800	-0.69219600
H	-2.39289100	-1.60329200	1.06761000
H	-3.50286100	-0.71511700	0.01083500
C	-1.69982700	1.03968800	1.12307600
H	-1.57220600	0.54664600	2.08790900
H	-0.99330400	1.86601100	1.04996600
H	-2.70972300	1.44900500	1.07308300
C	-1.59732500	0.71360800	-1.36772700
H	-1.40129100	-0.00984000	-2.16049300
H	-2.60224100	1.11514700	-1.50469800
H	-0.88767100	1.53614700	-1.45344000

Trigonox 42S-scission-TS optimized geometry (# opt=(TS,noeigentest) freq
 scrf=(smd,solvent=tetrahydrofuran) def2tzvpp mn15)



EE + Thermal Free Energy Correction: -460.934406 Ha

0 1

O	0.77820000	0.35065900	0.05105600
C	2.00144700	-0.22228200	0.00517000
C	3.05154300	0.84546200	-0.02035000
H	3.45701400	0.94876600	0.98674100
H	3.85479900	0.53188300	-0.68272000
H	2.65130000	1.80452100	-0.33835800
C	-1.50387700	0.04540700	-0.00768600
O	-0.23932300	-0.63575600	0.13312200
O	2.19144800	-1.40745700	0.00903500
C	-2.48890500	-1.10470800	0.10252600
H	-2.32187300	-1.83249800	-0.69219600
H	-2.39289100	-1.60329200	1.06761000
H	-3.50286100	-0.71511700	0.01083500
C	-1.69982700	1.03968800	1.12307600
H	-1.57220600	0.54664600	2.08790900
H	-0.99330400	1.86601100	1.04996600
H	-2.70972300	1.44900500	1.07308300
C	-1.59732500	0.71360800	-1.36772700
H	-1.40129100	-0.00984000	-2.16049300
H	-2.60224100	1.11514700	-1.50469800
H	-0.88767100	1.53614700	-1.45344000

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