

Supporting Information

Calcium-based catalytic system for the synthesis of bio-derived cyclic carbonates under mild conditions

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1. General considerations

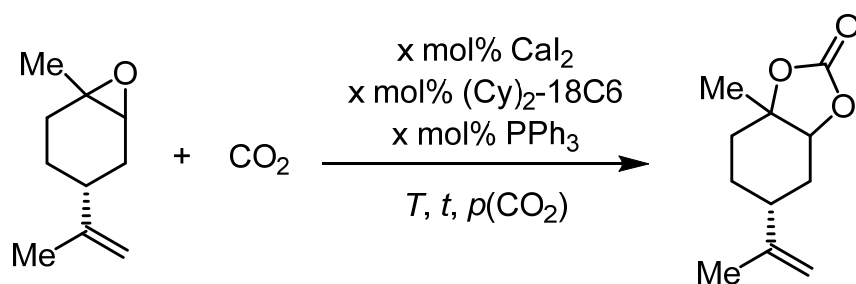
Epoxidized high-oleic sunflower oil (techn. methyl oleate, oxirane number= $4.87 \text{ mmol}\cdot\text{g}^{-1}$), epoxidized iso-octyl oleate (techn. grade, oxirane number= $2.02 \text{ mmol}\cdot\text{g}^{-1}$), epoxidized methyl o-acetyl ricinoleate (techn. grade, oxirane number= $2.48 \text{ mmol}\cdot\text{g}^{-1}$) and epoxidized linseed oil (techn. grade, oxirane number= $8.62 \text{ mmol}\cdot\text{g}^{-1}$) were provided by *HOBUM Oleochemicals*. Epoxidized soybean oil (EPOXOL D65, oxirane number= $4.81 \text{ mmol}\cdot\text{g}^{-1}$) and epoxidized methyl soyate (NEXO E1, oxirane number= $4.36 \text{ mmol}\cdot\text{g}^{-1}$) were provided by *Evonik Industries AG*.

The epoxidation of the respective fatty acid derivatives to obtain compounds **1a–g** were conducted after procedure reported by Behr et al.^[1] Epoxidation of terpene-based alkenes to synthesize compounds **6b–f** was carried out according to Kleij and co-workers.^[2] Compound characterizations of the respective epoxides and copies of NMR spectra can be found in the Supporting Information associated with our previous publications.^[3]

All chemicals were purchased from commercial sources with purities $\geq 95\%$ and used without further purification. (+)-Limonene oxide **6a** was bought from *sigma-aldrich* as a mixture of *cis* and *trans* isomer (40:60). Ligands **3a–f** were dried under vacuum overnight in an oil-bath at a temperature above the melting point of the ligand. Co-catalysts were dried before use with molecular sieves in a suitable solvent. Deuterated solvents were ordered from *Deutero GmbH* and stored over molecular sieves. NMR spectra were received using *Bruker* 300 Fourier, *Bruker* AV 300 and *Bruker* AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s= singlet, d= doublet, t= triplet and m= multiplet. NMR yields were determined by using mesitylene as internal standard. Elementary analysis was performed on a TruSpec CHMS Micro from *Leco*. IR spectra were recorded on a Nicolet iS10 MIR FT-IR-spectrometer from *Thermo Fisher Scientific*. Thin layer chromatography was performed on *Merck* TLC-plates with fluorescence indication (silica type 60, F₂₅₄), spots were visualized using UV-light or potassium permanganate. Flash chromatography was performed using silica with a grain size of 40–63 μm from *Macherey-Nagel*.

2. Optimization of reaction parameters using (+)-limonene oxide as the substrate

Table S1. Optimization of reaction parameters using (+)-limonene oxide as the substrate.



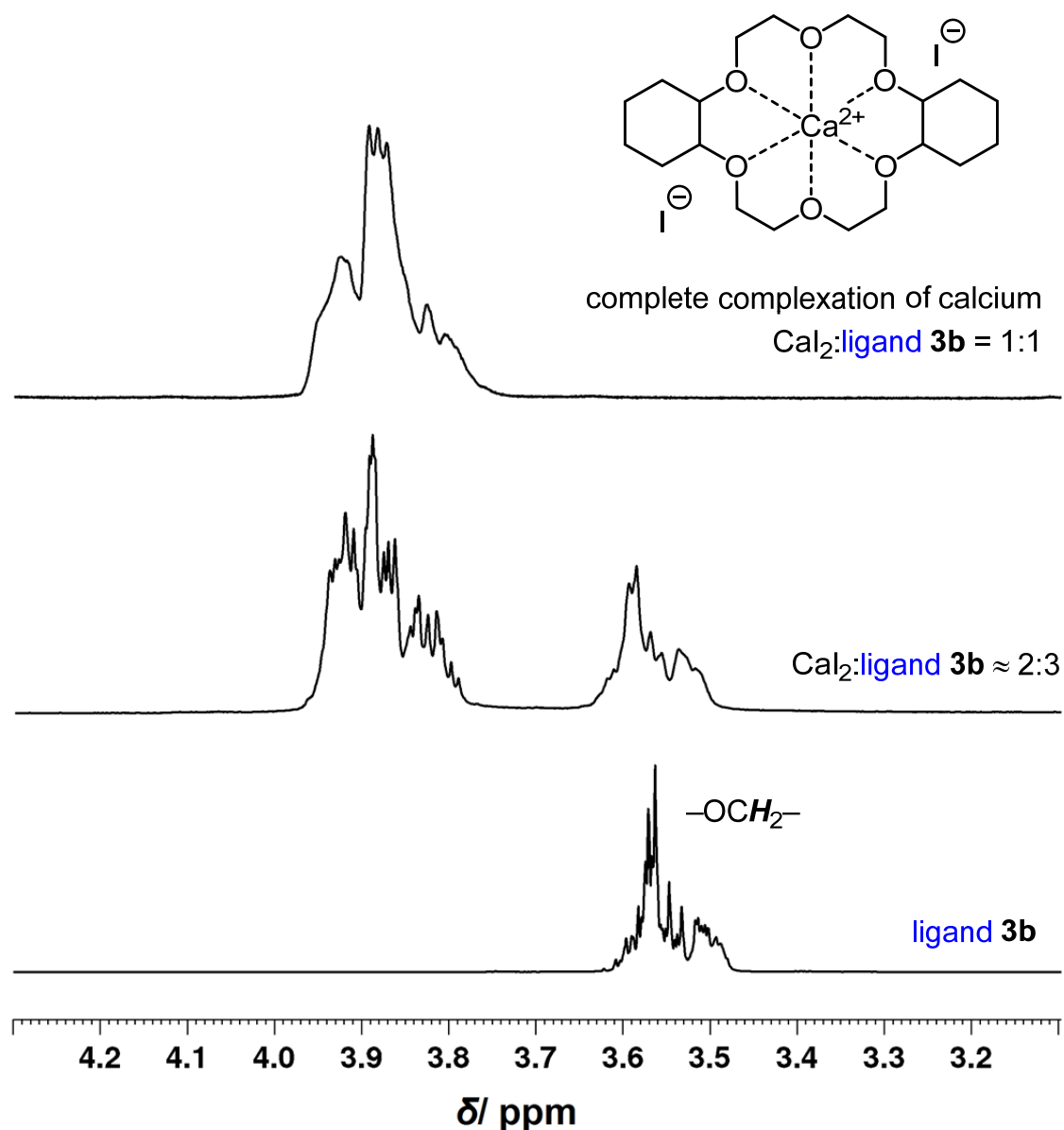
Entry	$x / \text{mol\%}$	$T / ^\circ\text{C}$	$p(\text{CO}_2) / \text{bar}$	t / h	Conversion NMR ^a / %
1	5	45	5	24	36
2	5	60	5	24	35
3 ^b	5	60	5	24	40
4 ^c	5	75	10	24	37
5	10	45	5	48	45
6	10	75	50	48	>99

^a Yields and selectivities determined by ^1H NMR using mesitylene as internal standard. Chemoselectivities were >99%. ^b MeCN as solvent. ^c 2.00 g scale.

3. Mechanistic NMR studies

We confirmed the successful complexation of the calcium with the dicyclohexyl-functionalized 18-crown-6 ether and investigated the interaction of triphenyl phosphane on the catalyst with ^1H and ^{31}P NMR spectroscopy. We first did a series of experiments using different ratios of calcium iodide and the ligand **3b** in acetonitrile. The results are displayed in Figure S1. The ether linked CH_2/CH_1 groups form a multiplett between 3.47–3.63 ppm in the free ligand. When the calcium iodide is added, an equal amount of ligand get down shifted to 3.78–3.99 ppm. When a stoichiometric amount of calcium salt is added, no free ligands can be detected.

Figure S1. ^1H NMR investigation of the complexation of calcium by functionalized crown ether **3b**.



We also wanted to investigate the role of the co-catalyst triphenyl phosphane. We investigated the ^{31}P NMR shift of triphenyl phosphane in combination with calcium iodide and the calcium iodide crown ether complex (Figure S2). Interestingly, no shift of the phosphorus signal could be observed, indicating no impactful interaction between the Lewis acidic calcium and triphenyl phosphane.

Figure S2. ^{31}P NMR investigation into the role of the co-catalyst triphenyl phosphane in combination with calcium iodide and crown ether **3b**.

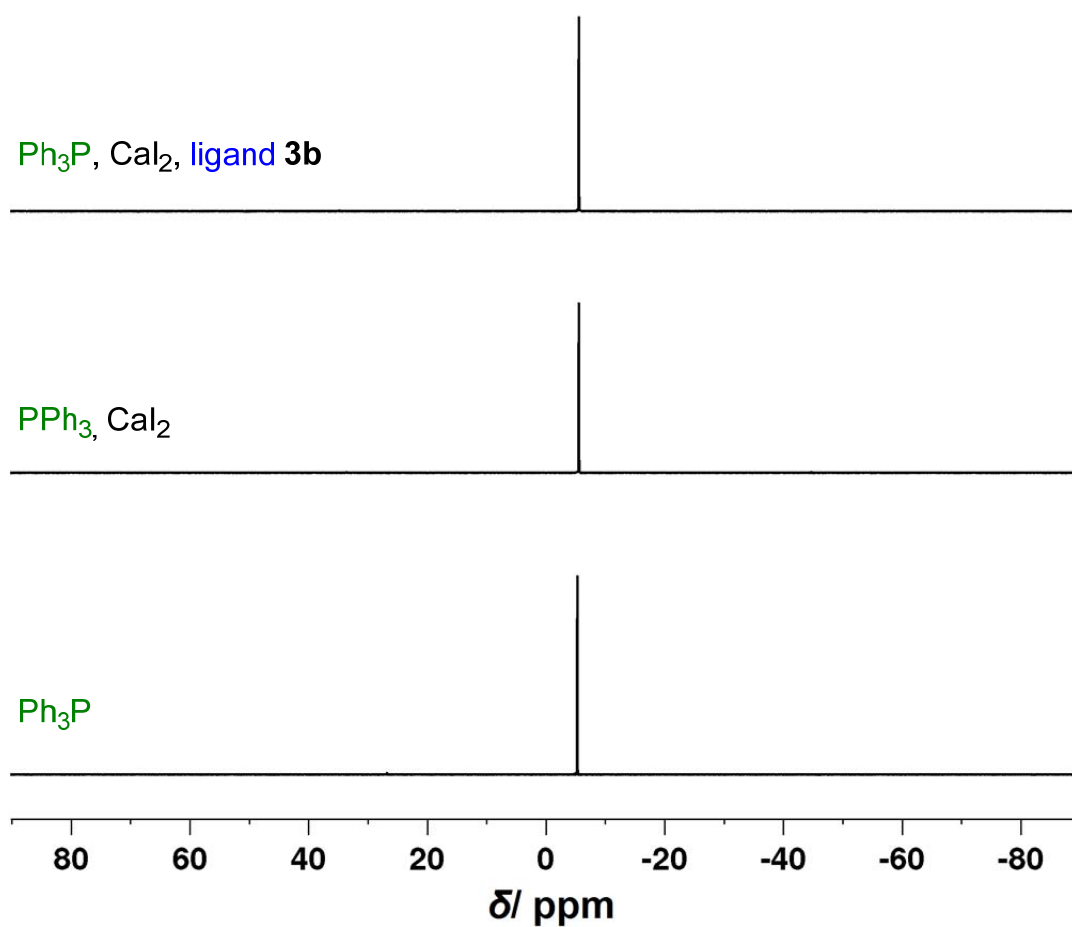
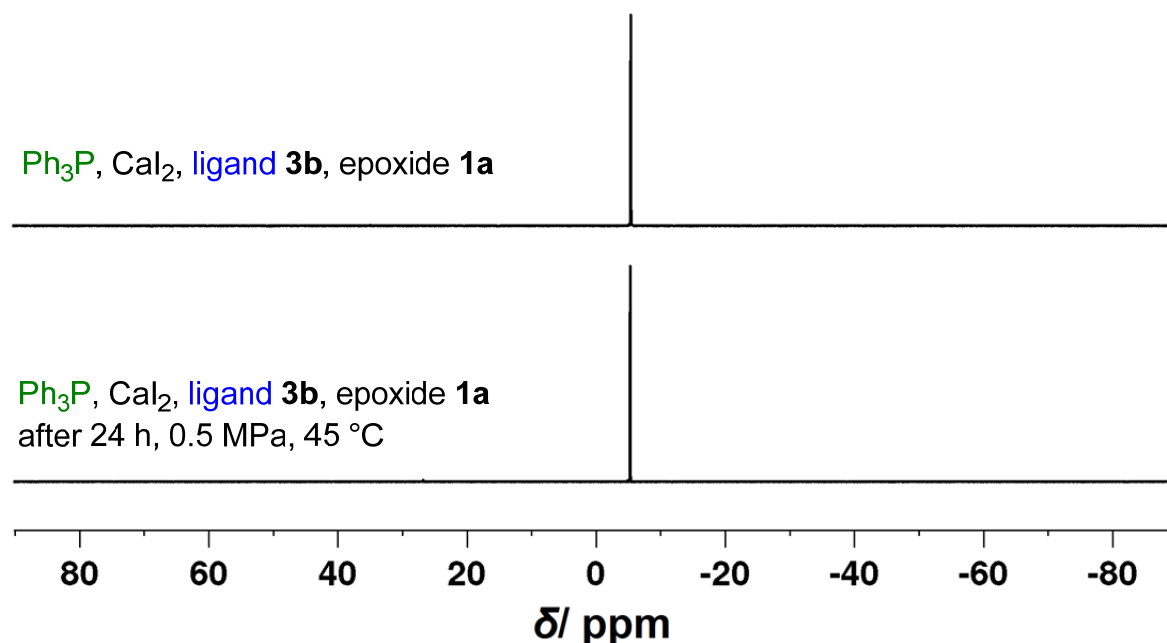


Figure S3. ^{31}P NMR investigation into the possible formation of a phosphonium salt species from triphenyl phosphane in the reaction mixture.



4. Experimental protocols and product characterization

General procedure for the catalyst screening and parameter optimization for epoxidized fatty acid ester derivatives (GP1)

A stainless steel autoclave was charged with CaI₂ (0.025–0.05 equiv), ligand **3** (0.025–0.05 equiv), co-catalyst (0.00–0.05 equiv) and epoxidized methyl oleate **1a** (1.00 g, 3.20 mmol, 1.00 equiv) and immediately purged with CO₂. The reactor was heated to 25–60 °C for 24–48 h, while $p(\text{CO}_2, 25\text{--}60\text{ °C})$ was kept constant at 0.5–1.0 MPa. The reactor was cooled in an ice bath below 20 °C and CO₂ was released slowly. The yields were determined by ^1H NMR using mesitylene as an internal standard directly from the reaction mixture.

General procedure for the substrate scope for epoxidized fatty acid esters or oils (GP2)

A stainless steel autoclave was charged with CaI_2 (0.05 equiv), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv), Ph_3P (0.05 equiv) and epoxidized fatty acid ester **1a–g** (1.0 g, 1.00 equiv) or epoxidized oil **4a–d** (2 g, catalyst amount based on the oxirane number) and immediately purged with CO_2 . The reactor was heated to 45 °C for 24 h while $p(\text{CO}_2, 45\text{ °C})$ was kept constant at 0.5 MPa. The reactor was cooled in an ice bath below 20 °C and CO_2 was released slowly. The crude product was purified by flash chromatography on silica gel (SiO_2) employing *c*Hex/EtOAc as eluent. All volatiles were removed in vacuo to obtain carbonates **2a–g** or **5a–d**.

General procedure for the parameter optimization for terpene-based substrates (GP3)

A stainless steel autoclave was charged with CaI_2 (0.05 equiv, 96 mg, 0.33 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 122 mg, 0.33 mmol), Ph_3P (0.05 equiv, 86 mg, 0.33 mmol), 2 mL of MeCN and (+)-limonene oxide (**6a**, 1.00 g, 6.57 mmol, 1.00 equiv) and immediately purged with CO_2 . The reactor was heated to 45–75 °C for 24–48 h while $p(\text{CO}_2, 45\text{–}75\text{ °C})$ was kept constant at 0.5–5.0 MPa. The reactor was cooled in an ice bath below 20 °C and CO_2 was released slowly. The yields were determined by ^1H NMR using mesitylene as an internal standard directly from the reaction mixture.

General procedure for the substrate scope for terpene-based substrates (GP4)

A stainless steel autoclave was charged with CaI_2 (0.1 equiv), dicyclohexyl-18-crown-6 (**3b**, 0.1 equiv), Ph_3P (0.1 equiv), 1 mL of MeCN and 1.00 equiv of epoxidized terpene **6a–f** (1.00 g, 1.00 equiv) and was immediately purged with CO_2 . The reactor was heated to 75 °C for 48 h while $p(\text{CO}_2, 75\text{ °C})$ was kept constant at 5.0 MPa. The reactor was cooled in an ice bath below 20 °C and CO_2 was released slowly. The crude product was purified by flash chromatography on silica gel (SiO_2) employing *c*Hex/EtOAc or $\text{CH}_2\text{Cl}_2/\text{MeOH}$ as eluent. All volatiles were removed in vacuo to obtain carbonates **7a–f**.

Synthesis of the cyclic carbonates

Methyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate^[3] (2a): According to GP2, epoxidized methyl oleate **1a** (1.00 g, 3.20 mmol) was allowed to react with CO₂ in the presence of CaI₂ (47 mg, 0.70 mmol), dicyclohexyl-18-crown-6 (**3b**, 60 mg, 0.70 mmol), Ph₃P (42 mg, 0.70 mmol). After purification (SiO₂, *c*Hex to *c*Hex/EtOAc 5:1) the product **2a** (981 mg, 2.75 mmol, 86%, *cis:trans*=84:16) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.89 (t, *J*= 7.0 Hz, 3H), 1.21–1.80 (m, 26H), 2.32 (t, *J*= 7.4 Hz, 2H), 3.72 (s, 3H), 4.15–4.28 (m, 2H, *trans*-isomer), 4.57–4.67 (m, 2H, *cis*-isomer) ppm.

Ethyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate^[3] (2b): According to GP2, epoxidized ethyl oleate (**1b**, 1.00 g, 3.06 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 45 mg, 0.70 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 60 mg, 0.70 mmol), Ph₃P (0.05 equiv, 42 mg, 0.70 mmol). After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **2b** (852 mg, 2.30 mmol, 75%, *cis:trans*=84:16) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.89 (t, *J*= 7.0 Hz, 3H), 1.20–1.75 (m, 29H), 2.30 (t, *J*= 7.8 Hz, 2H), 4.13 (q, *J*= 7.1 Hz, 2H), 4.18–4.27 (m, 2H, *trans*-isomer), 4.55–4.68 (m, 2H, *cis*-isomer) ppm.

***iso*-Octyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate^[3] (2c):** According to GP2, epoxidized *iso*-octyl oleate (**1c**, 2.00 g, oxirane number = 2.02 mmol·g⁻¹) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 59 mg, 0.20 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 75 mg, 0.20 mmol), Ph₃P (0.05 equiv, 53 mg, 0.20 mmol) for 48 h. After purifying with column chromatography (*c*Hex/EtOAc 20:1) the product **2c** (2.03 g, 93%, *cis:trans*=83:17) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.85–0.98 (m, 9H), 1.20–1.80 (m, 35H), 2.31 (t, *J*= 7.6 Hz, 2H), 3.93–4.08 (m, 2H), 4.20–4.27 (m, 2H, *trans*-isomer), 4.57–4.74 (m, 2H, *cis*-isomer) ppm.

Methyl 12-(5-octyl-2-oxo-1,3-dioxolan-4-yl)dodecanoate (2d)^[4]: According to GP2, epoxidized erucate (**1d**, 1.00 g, 2.71 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 40 mg, 0.14 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 51 mg, 0.14 mmol), Ph₃P (0.05 equiv, 36 mg, 0.14 mmol). After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **2d** (968 mg, 2.33 mmol, 86%, *cis:trans*=83:17) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.89 (t, *J*= 7.1 Hz, 3H), 1.15–1.79 (m, 34H), 2.31 (t, *J*= 7.6 Hz, 2H), 3.67 (s, 3H), 4.15–4.26 (m, 2H, *trans*-isomer), 4.56–4.78 (m, 2H, *cis*-isomer) ppm.

Methyl 8-(2-oxo-5-((2-oxo-5-pentyl-1,3-dioxolan-4-yl)methyl)-1,3-dioxolan-4-yl)octanoate^[3] (**2e**): According to GP2, epoxidized linoleate (**1e**, 2.00 g, 6.13 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.1 equiv, 180 mg, 0.613 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.1 equiv, 228 mg, 0.613 mmol), Ph₃P (0.1 equiv, 160 mg, 0.613 mmol) for 48 h. After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **2e** (2.29 g, 5.52 mmol, 90%, mixture of four diastereoisomers *dr*= 19:61:12:8) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.87–0.97 (m, 3H), 1.20–2.00 (m, 22H), 2.32 (t, *J*= 7.5 Hz, 2H), 3.66 (s, 3H), , 4.21–4.41 (m, 2H, *trans*-isomer 1), 4.41–4.58 (m, 2H, *trans*-isomer 2), 4.64–4.85 (m, 2H, *cis*-isomer 1), 4.85–4.99 (m, 2H, *cis*-isomer 2) ppm.

Methyl 8-(5-(2-acetoxyoctyl)-2-oxo-1,3-dioxolan-4-yl)octanoate^[3] (**2f**): According to GP2, epoxidized methy O-acetyl ricinoleate (**1f**, 2.00 g, oxirane number = 2.48 mmol·g⁻¹) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 73 mg, 0.25 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 92 mg, 0.25 mmol), Ph₃P (0.05 equiv, 65 mg, 0.25 mmol). After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **2f** (2.17 g, 98%, mixture of four diastereoisomers *dr*= 33:26:27:14) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.87 (t, ³*J*_{H,H} = 6.4 Hz, 3H), 1.15–2.09 (m, 27H), 2.28

(t, J = 7.5 Hz, 2H), 3.65 (s, 3H), 4.05–4.36 (m, 2H, *trans*-isomers), 4.53–4.66 (m, 2H, *cis*-isomer), 4.67–4.80 (m, 2H, *cis*-isomer), 4.89–5.11 (m, 1H) ppm.

Methyl 9-(2-oxo-1,3-dioxolan-4-yl)nonanoate^[3] (2g): According to GP2, epoxidized methyl undecenoate (**1g**, 1.00 g, 4.67 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 69 mg, 0.23 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 87 mg, 0.23 mmol), Ph₃P (0.05 equiv, 61 mg, 0.23 mmol) for 6 h. After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **2g** (1.16 g, 4.49 mmol, 96%) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ = 1.23–1.88 (m, 14H), 2.29 (t, J = 7.4 Hz, 2H), 3.66 (s, 3H), 4.05 (dd, J = 8.3, 7.2 Hz, 1H), 4.52 (t, J = 8.3, 1H), 4.64–4.76 (m, 1H) ppm.

Carbonated high oleic sunflower oil^[3] (5a): According to GP2, epoxidized high oleic sunflower oil (**4a**, 1.00 g, oxirane number = 4.87 mmol·g⁻¹) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 72 mg, 0.24 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 91 mg, 0.24 mmol), Ph₃P (0.05 equiv, 64 mg, 0.24 mmol). After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **5a** (1.19 g, 98%) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ = 0.88 (t, J = 6.9 Hz, 9H), 1.15–1.79 (m, 72H), 2.31 (t, J = 7.4 Hz, 6H), 4.08–4.35 (m, 5H), 4.57–4.68 (m, 3H), 5.21–5.32 (m, 1H) ppm.

Carbonated soybean oil^[3] (5b): According to GP2, epoxidized soybean oil (**4b**, 1.00 g, oxirane number = 4.81 mmol·g⁻¹) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 71 mg, 0.24 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 90 mg, 0.24 mmol), Ph₃P (0.05 equiv, 63 mg, 0.24 mmol). After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **5b** (980 mg, 81%) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ = 0.77–0.97 (m, 9H), 1.14–1.85 (m, 68H), 2.21–2.41 (m, 6H), 4.11–4.19 (m, 2H), 4.24–5.16 (m, 7H), 5.17–5.32 (m, 1H) ppm.

Carbonated linseed oil^[3] (5c): According to GP2, epoxidized linseed oil (**4c**, 1.00 g, oxirane number = 8.62 mmol·g⁻¹) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 127 mg, 0.431 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 161 mg, 0.431 mmol), Ph₃P (0.05 equiv, 113 mg, 0.431 mmol). After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **5c** (1.08 g, 78%) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.73–0.97 (m, 7H), 0.96–1.93 (m, 71H), 2.22–2.40 (m, 6H), 2.24–2.28 (m, 6H), 4.19–5.37 (m, 7H) ppm.

Carbonated methyl soyate^[3] (5d): According to GP2, epoxidized methyl soyate (**4d**, 1.00 g, oxirane number = 4.36 mmol·g⁻¹) was allowed to react with CO₂ in the presence of CaI₂ (0.05 equiv, 64 mg, 0.22 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.05 equiv, 81 mg, 0.22 mmol), Ph₃P (0.05 equiv, 57 mg, 0.22 mmol). After purifying with column chromatography (*c*Hex to *c*Hex/EtOAc 5:1) the product **5d** (661 mg, 55%) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.89–0.99 (m, 3H), 0.99–1.99 (m, 22H), 2.26–2.39 (m, 2H), 3.67 (s, 3H), 4.19–5.11 (m, 3H) ppm.

3a-Methyl-6-(prop-1-en-2-yl)hexahydrobenzo[d][1,3]dioxol-2-one^[2] (7a): According to GP4, (+)-limonene oxide (**6a**, 1.00 g, 6.57 mmol, *cis:trans*=40:60) was allowed to react with CO₂ in the presence of CaI₂ (0.1 equiv, 193 mg, 0.657 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.1 equiv, 245 mg, 0.657 mmol), Ph₃P (0.1 equiv, 172 mg, 0.657 mmol) and 1 mL of MeCN. After purifying twice with column chromatography (*c*Hex/EtOAc 5:1 and CH₂Cl₂:MeOH 100:1) the product **7a** (1.03 g, 5.26 mmol, 80%, *cis:trans*=14:86) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 1.36–2.03 (m, 11H), 2.16–2.40 (m, 2H), 4.29–4.42 (dd, *J*= 9.4, 7.0 Hz, 1H, *trans*-isomer), 4.42–4.47 (m, 1H, *cis*-isomer), 4.68–5.80 (m, 2H) ppm. ¹³C NMR(300 MHz, CDCl₃, *trans*-isomer): δ= 154.8, 147.4, 110.2, 82.2, 80.6, 39.9, 34.0, 33.1, 26.2, 25.7, 20.6 ppm. ¹³C NMR(300 MHz, CDCl₃, *cis*-isomer): δ= 154.6, 147.5, 110.0, 82.7, 81.9, 37.4, 34.2, 30.6, 26.3, 22.3, 20.9 ppm.

3a-Methyl-6-(4-methyl-2-oxo-1,3-dioxolan-4-yl)hexahydrobenzo[d][1,3]dioxol-2-one^[2]

(7b): According to GP4, (+)-limonene dioxide (**6b**, 1.00 g, 5.94 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.1 equiv, 175 mg, 0.594 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.1 equiv, 221 mg, 0.594 mmol), Ph₃P (0.1 equiv, 156 mg, 0.594 mmol) and 1 mL of MeCN. After purifying with column chromatography (*c*Hex/EtOAc 100:1 to *c*Hex/EtOAc 1:2) the product **7b** (1.03 g, 5.26 mmol, 80%) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 1.17–2.44 (m, 13H), 4.02–4.48 (m, 3H) ppm.

(4S,7R)-4-isopropyl-7-methylhexahydrobenzo[d][1,3]dioxol-2-one^[2] (7c): According to GP4, epoxidized menthol derivative (**6c**, 1.00 g, 6.48 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.1 equiv, 191 mg, 0.648 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.1 equiv, 241 mg, 0.648 mmol), Ph₃P (0.1 equiv, 170 mg, 0.648 mmol) and 1 mL of MeCN. After purifying with column chromatography (*c*Hex/EtOAc 100:1 to *c*Hex/EtOAc 5:1) the product **7c** (1.04 g, 5.25 mmol, 81%) was isolated as a light yellow liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.72–1.47 (m, 12H), 1.53–1.93 (m, 4H), 4.04–4.80 (m, 2H) ppm.

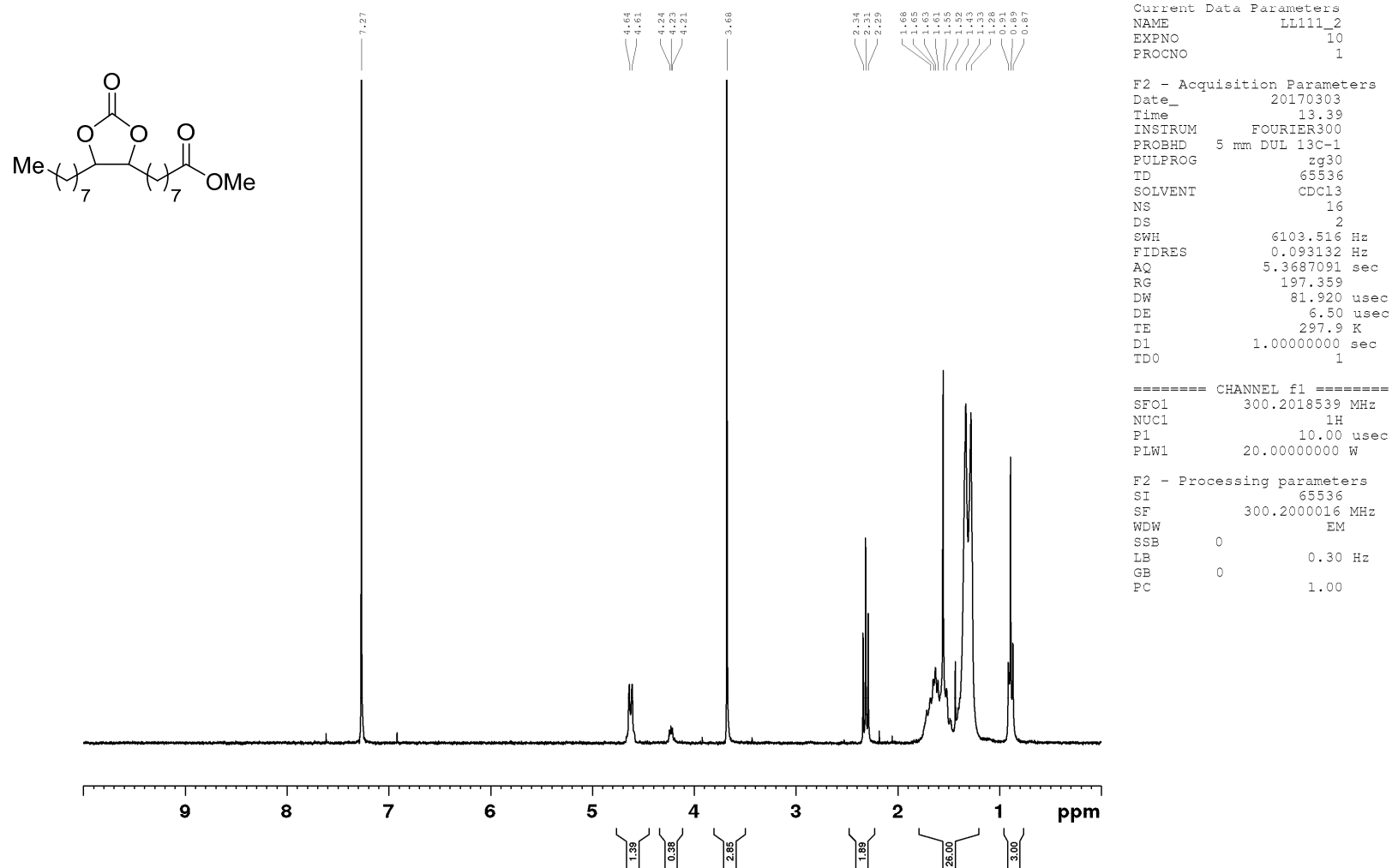
5-(5,5-Dimethyl-2-oxo-1,3-dioxolan-4-yl)-3-methylpentyl propionate (7e): According to GP4, epoxidized citronellyl propionate (**6e**, 2.00 g, 8.76 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.1 equiv, 258 mg, 0.876 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.1 equiv, 326 mg, 0.876 mmol), Ph₃P (0.1 equiv, 230 mg, 0.876 mmol) and 2 mL of MeCN. After purifying with column chromatography (CH₂Cl₂/MeOH 200:1 to 10:1) the product **7e** (450 mg, 5.25 mmol, 19%) was isolated as a colorless liquid. ¹H NMR(300 MHz, CDCl₃): δ= 0.89 (t, *J*= 7.0 Hz, 3H), 1.21–1.80 (m, 26H), 2.32 (t, *J*= 7.4 Hz, 2H), 3.72 (s, 3H), 4.15–4.28 (m, 2H, trans), 4.57–4.67 (m, 2H) ppm. ¹³C NMR(300 MHz, CDCl₃): δ= 9.2, 19.2, 21.2, 26.1, 26.7, 27.6, 29.7, 33.1, 35.3, 62.4, 84.0, 85.7, 154.1, 174.6 ppm. Elemental Analysis: calculated C 61.7%; H 8.88% found C 61.2%; H 8.44%. HRMS (ESI-TOF/MS): *m/z* calculated [M+H]⁺: 273.16965; *m/z* found [M+H]⁺: 273.16963

(E)-5-(5,5-dimethyl-2-oxo-1,3-dioxolan-4-yl)-3-methylpent-2-en-1-yl acetate^[2] (7f):

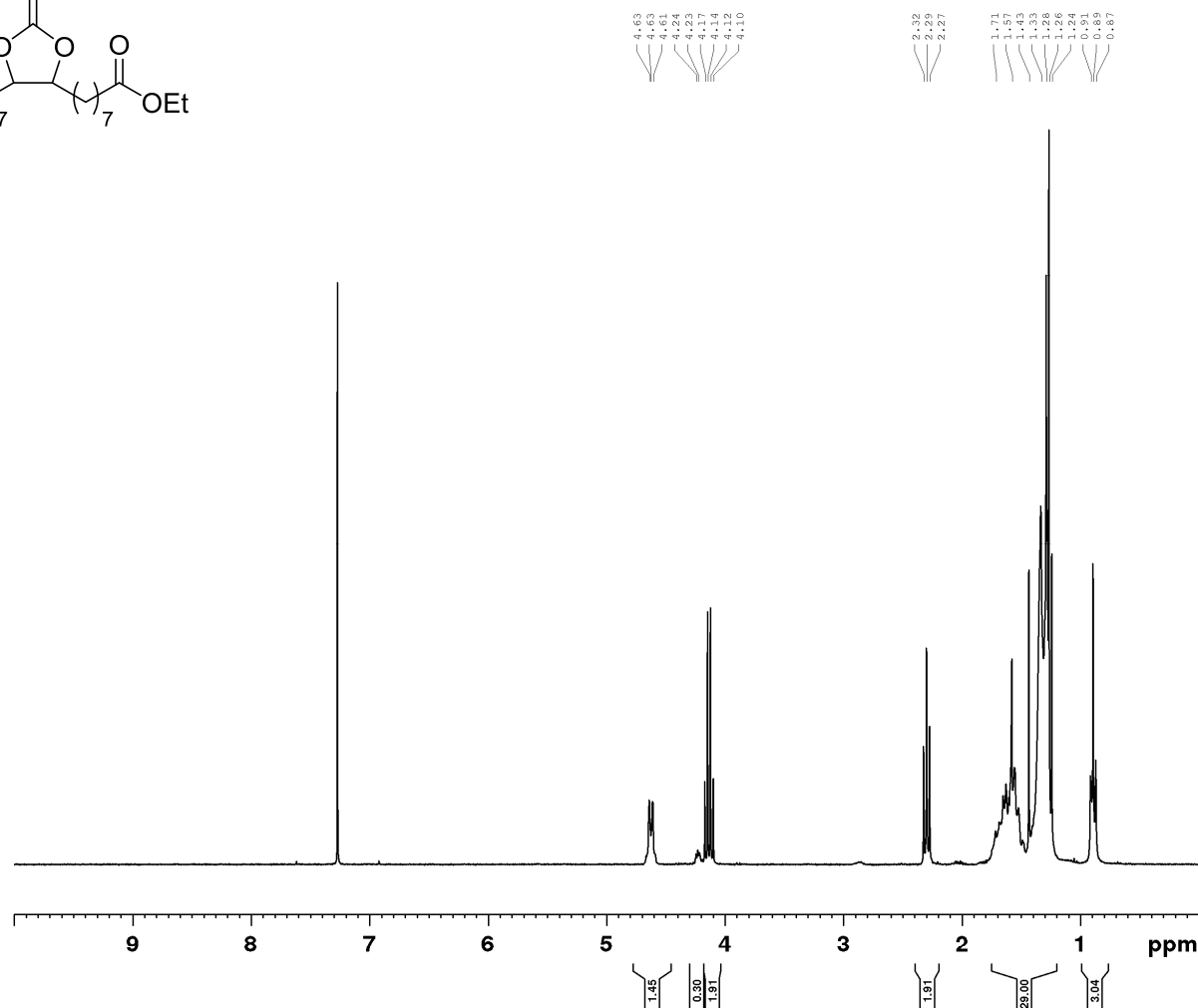
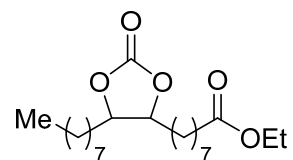
According to GP4, epoxidized geranyl acetate (**6f**, 1.00 g, 4.71 mmol) was allowed to react with CO₂ in the presence of CaI₂ (0.1 equiv, 138 mg, 0.471 mmol), dicyclohexyl-18-crown-6 (**3b**, 0.1 equiv, 176 mg, 0.471 mmol), Ph₃P (0.1 equiv, 124 mg, 0.471 mmol) and 1 mL of MeCN. After purifying twice with column chromatography (*c*Hex/EtOAc 5:1 and CH₂Cl₂/MeOH 100:1 to 10:1) the product **7f** (277 mg, 1.08 mmol, 23%) was isolated as a light yellow liquid. ¹H NMR(300 MHz, CDCl₃): δ= 1.37 (s, 3H), 1.49 (s, 3H), 1.55–1.88 (m, 5H), 1.96–2.38 (m, 5H), 3.72 (s, 3H), 4.17–4.25 (m, 1H), 4.48–4.63 (m, 2H), 5.30–5.51 (m, 1H) ppm.

5. NMR-spectra of the synthesized carbonate

Methyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (2a)



Ethyl 8-(5-octyl-2-oxo-1,3-dioxolan-4-yl)octanoate (2b)



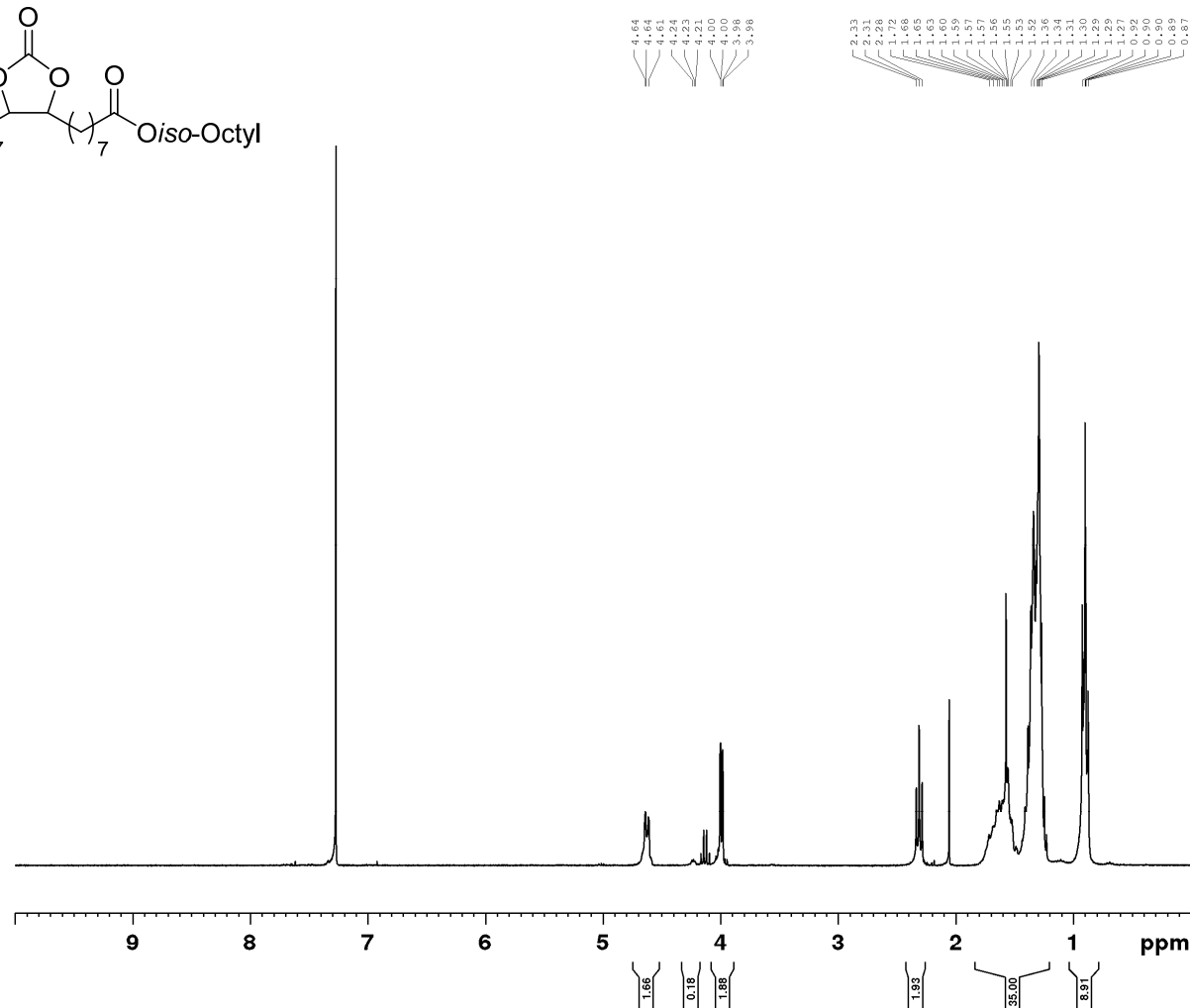
```

Current Data Parameters
NAME          LL120x
EXPNO         10
PROCNO        1

F2 - Acquisition Parameters
Date_         20170309
Time          9.42
INSTRUM       FOURIER300
PROBHD        5 mm DUL 13C-1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6103.516 Hz
FIDRES        0.093132 Hz
AQ            5.3687091 sec
RG            61.44
DW            81.920 usec
DE            6.50 usec
TE            297.7 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
SFO1          300.2018539 MHz
NUC1           1H
P1            10.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI            65536
SF            300.2000016 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

CC(C)(C)OC(=O)C1C(C(C)C)OC(=O)O1

```

Current Data Parameters
NAME                LL105_1
EXPNO                10
PROCNO              1

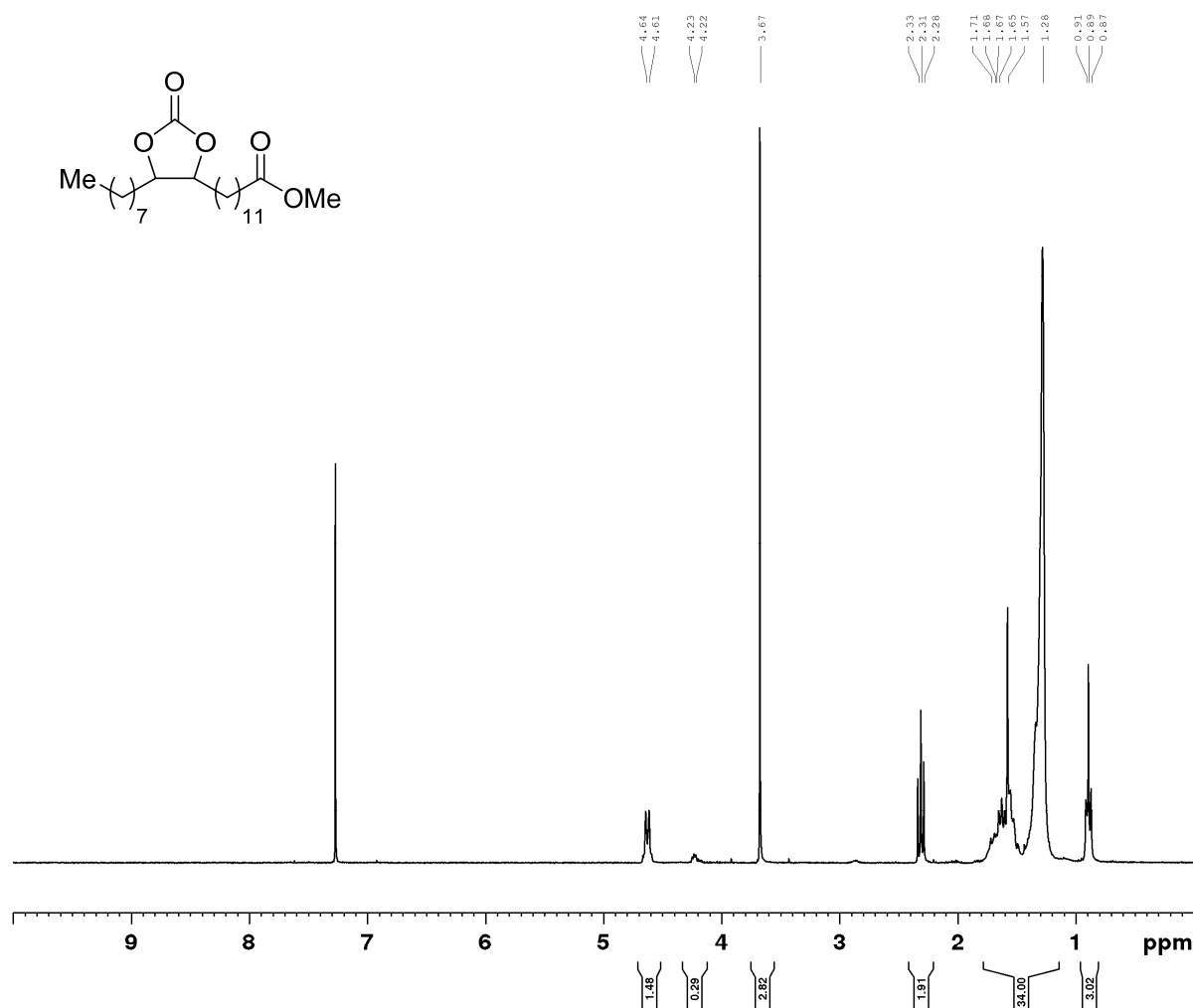
F2 - Acquisition Parameters
Date_                20170228
Time                 8.28
INSTRUM              AV300
PROBHD               5 mm PABBO BB-
PULPROG              zg30
TD                   32768
SOLVENT              CDCl3
NS                    32
DS                    4
SWH                  6172.839 Hz
FIDRES               0.188380 Hz
AQ                   2.6542079 sec
RG                    512
DW                   81.000 usec
DE                   6.00 usec
TE                   294.5 K
D1                   1.00000000 sec
TD0                  1

===== CHANNEL f1 =====
NUC1                  1H
P1                    11.00 usec
PL1                   0 dB
PL1W                  12.28312492 W
SFO1                  300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF                    300.1300120 MHz
WDW                   EM
SSB                   0
LB                    0.10 Hz
GB                   0
PC                    1.00

```


Methyl 12-(5-octyl-2-oxo-1,3-dioxolan-4-yl)dodecanoate (2d)



```

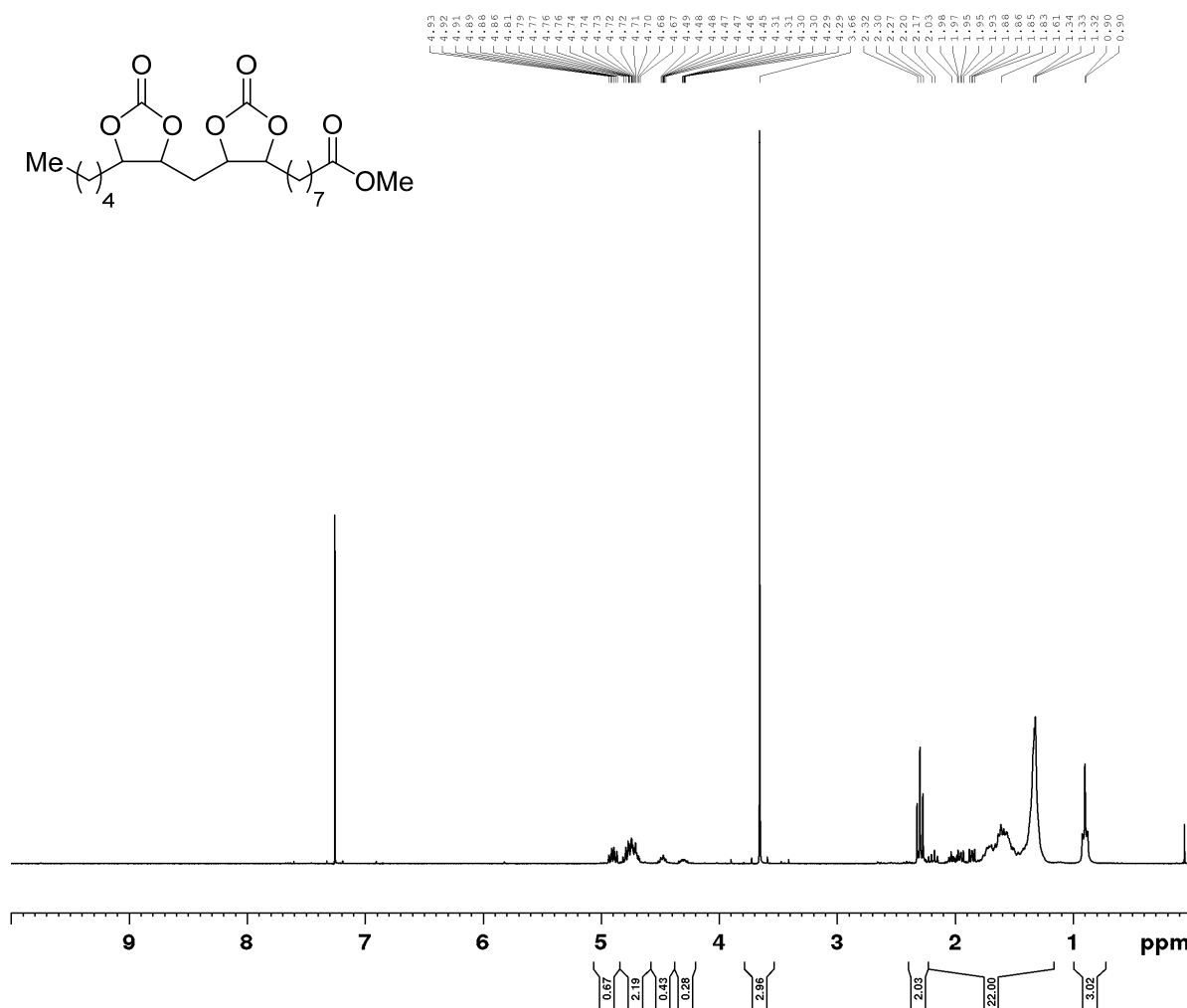
Current Data Parameters
NAME          LL108x
EXPNO         10
PROCNO        1

F2 - Acquisition Parameters
Date_         20170310
Time          10.11
INSTRUM       FOURIER300
PROBHD        5 mm DUL 13C-1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6103.516 Hz
FIDRES        0.093132 Hz
AQ            5.3687091 sec
RG            67.5165
DW            81.920 usec
DE            6.50 usec
TE            297.9 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
SFO1          300.2018539 MHz
NUC1          1H
P1            10.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI            65536
SF            300.2000016 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

Methyl 8-(2-oxo-5-((2-oxo-5-pentyl-1,3-dioxolan-4-yl)methyl)-1,3-dioxolan-4-yl)octanoate (2e)

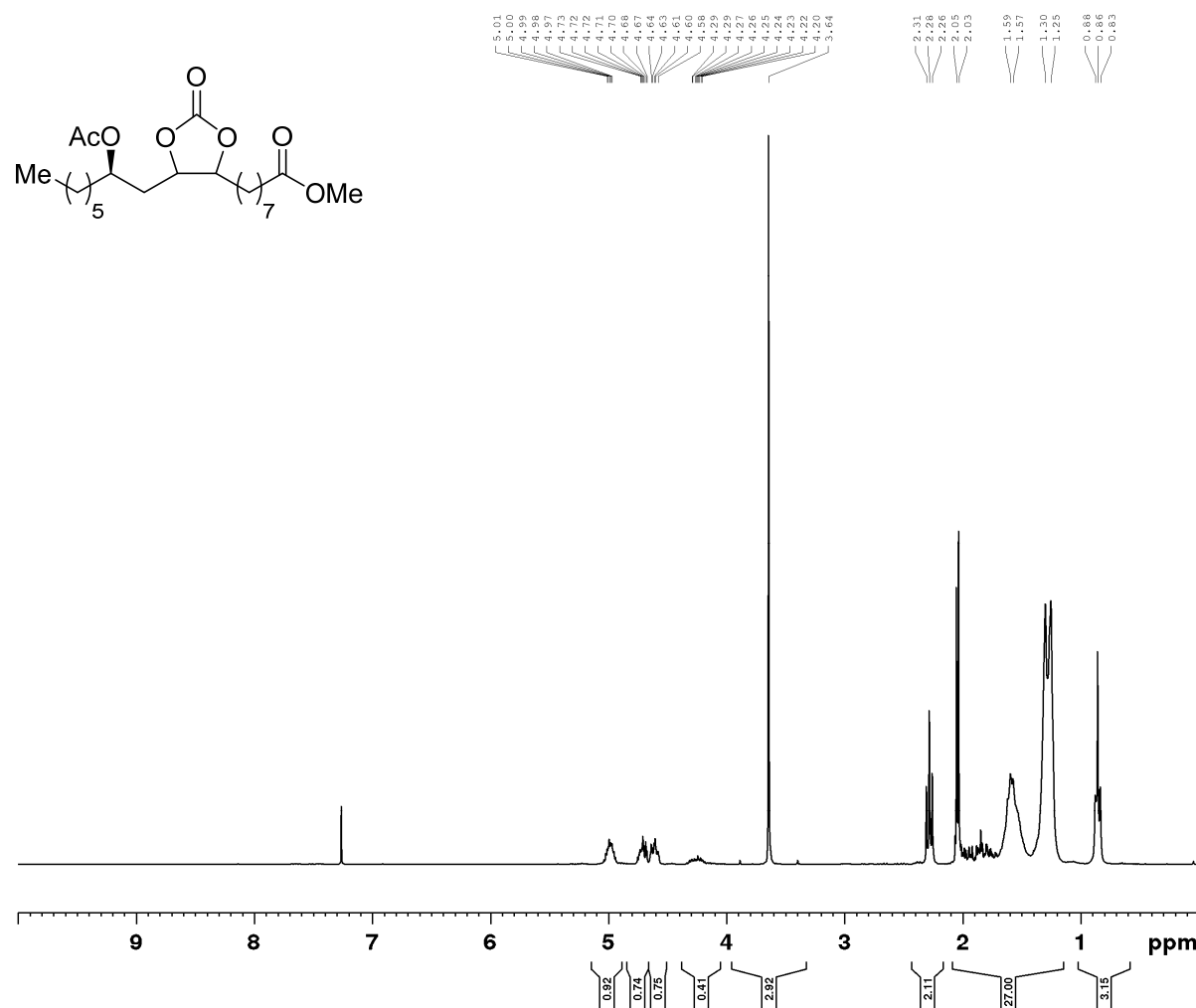


Current Data Parameters
NAME LL148z
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170505
Time 9.48 h
INSTRUM spect
PROBHD Z104275_0387 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 5.4525952 sec
RG 200.94
DW 83.200 usec
DE 6.50 usec
TE 298.6 K
D1 1.00000000 sec
TD0 1
SFO1 300.2018537 MHz
NUC1 1H
P1 13.70 usec
PLW1 9.60000038 W

F2 - Processing parameters
SI 65536
SF 300.2000093 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Methyl 8-(5-(2-acetoxyoctyl)-2-oxo-1,3-dioxolan-4-yl)octanoate (2f)



```

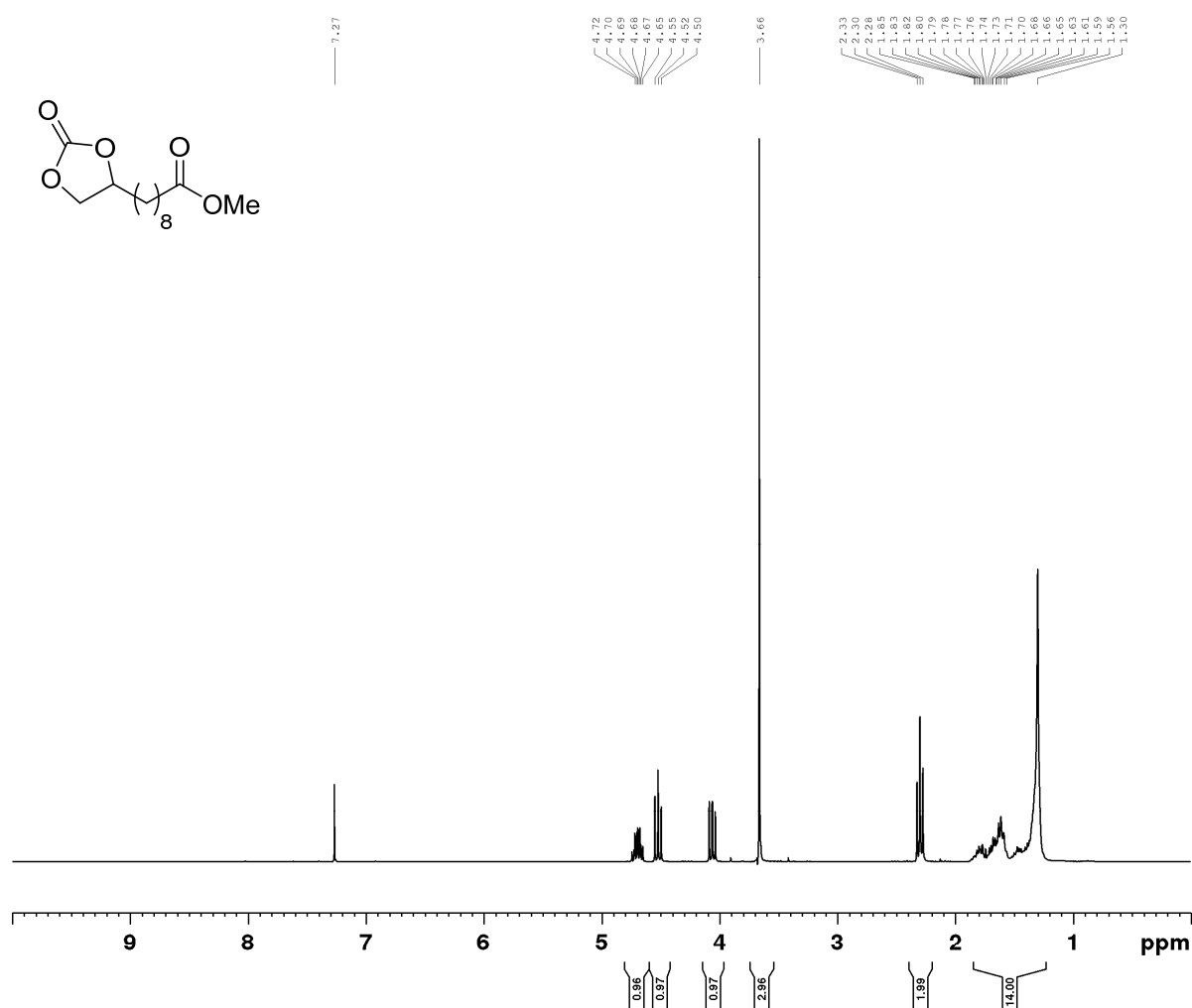
Current Data Parameters
NAME          LL106x
EXPNO         10
PROCNO        1

F2 - Acquisition Parameters
Date_         20170228
Time          8.31
INSTRUM       FOURIER300
PROBHD        5 mm DUL 13C-1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6103.516 Hz
FIDRES        0.093132 Hz
AQ            5.3687091 sec
RG            9.96594
DW            81.920 usec
DE            6.50 usec
TE            297.7 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
SFO1          300.2018539 MHz
NUC1          1H
P1            10.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI            65536
SF            300.2000035 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

Methyl 9-(2-oxo-1,3-dioxolan-4-yl)nonanoate (2g)



```

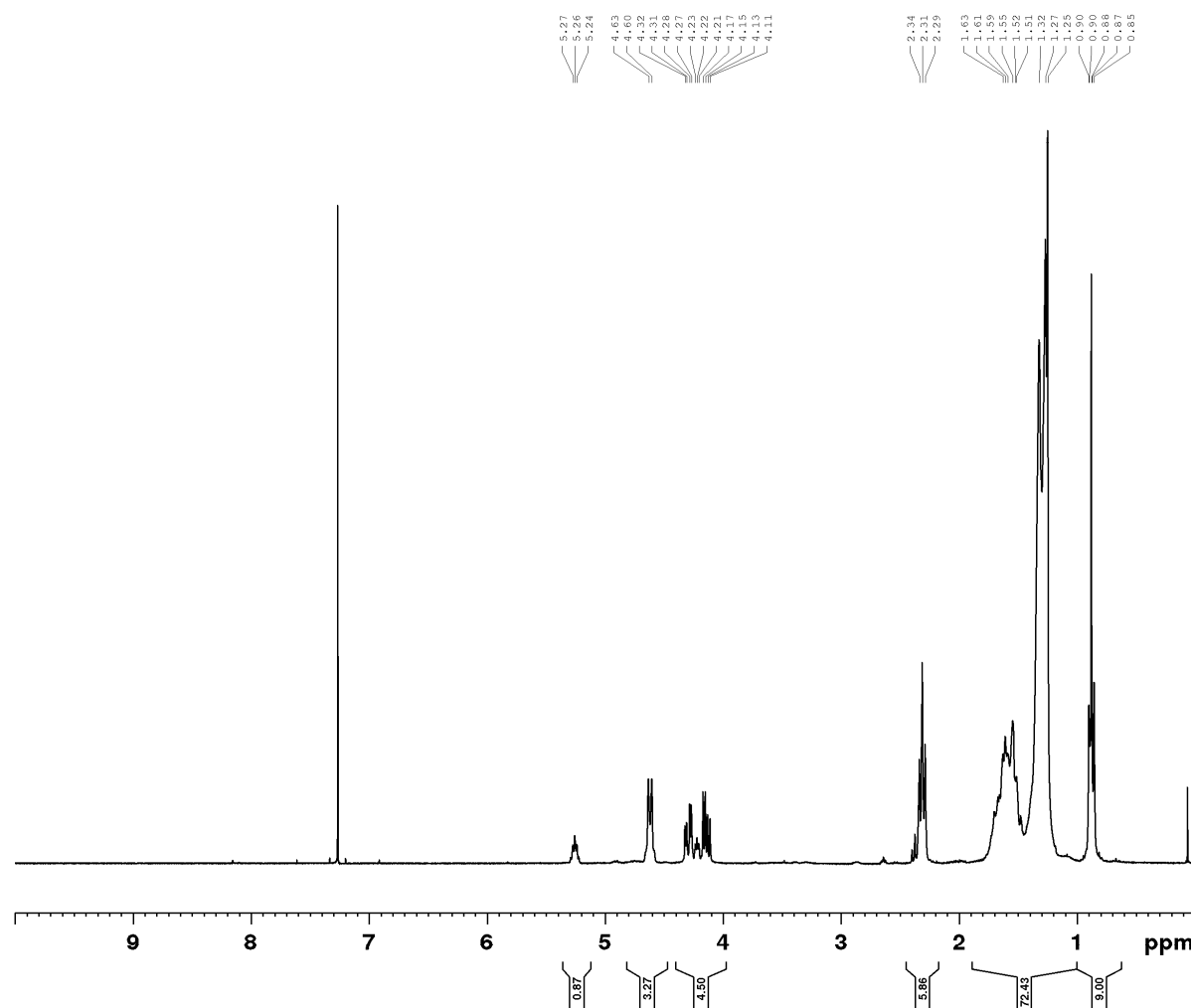
Current Data Parameters
NAME          LL122x
EXPNO         10
PROCNO        1

F2 - Acquisition Parameters
Date_         20170315
Time          9.41
INSTRUM       FOURIER300
PROBHD        5 mm DUL 13C-1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6103.516 Hz
FIDRES        0.093132 Hz
AQ            5.3687091 sec
RG            26.2004
DW            81.920 usec
DE            6.50 usec
TE            297.9 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
SFO1          300.2018539 MHz
NUC1           1H
P1            10.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI            65536
SF            300.2000015 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

Carbonated high oleic sunflower oil (5a)

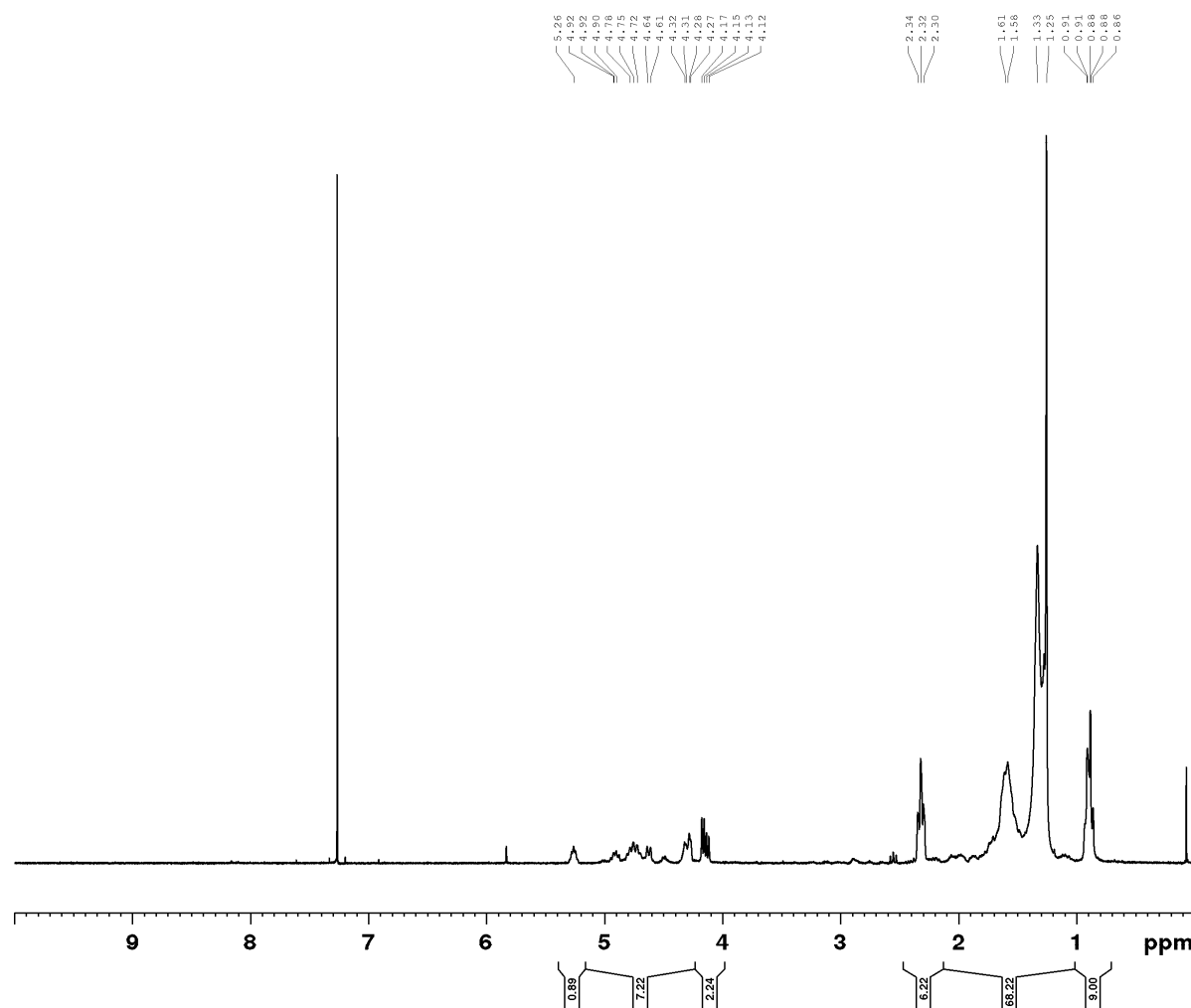


Current Data Parameters
NAME LL124z
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170505
Time 9.33 h
INSTRUM spect
PROBHD Z104275_0387 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 5.4525952 sec
RG 126.51
DW 83.200 usec
DE 6.50 usec
TE 298.5 K
D1 1.00000000 sec
TD0 1
SFO1 300.2018537 MHz
NUC1 1H
P1 13.70 usec
PLW1 9.60000038 W

F2 - Processing parameters
SI 65536
SF 300.2000067 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

Carbonated soybean oil (5b)



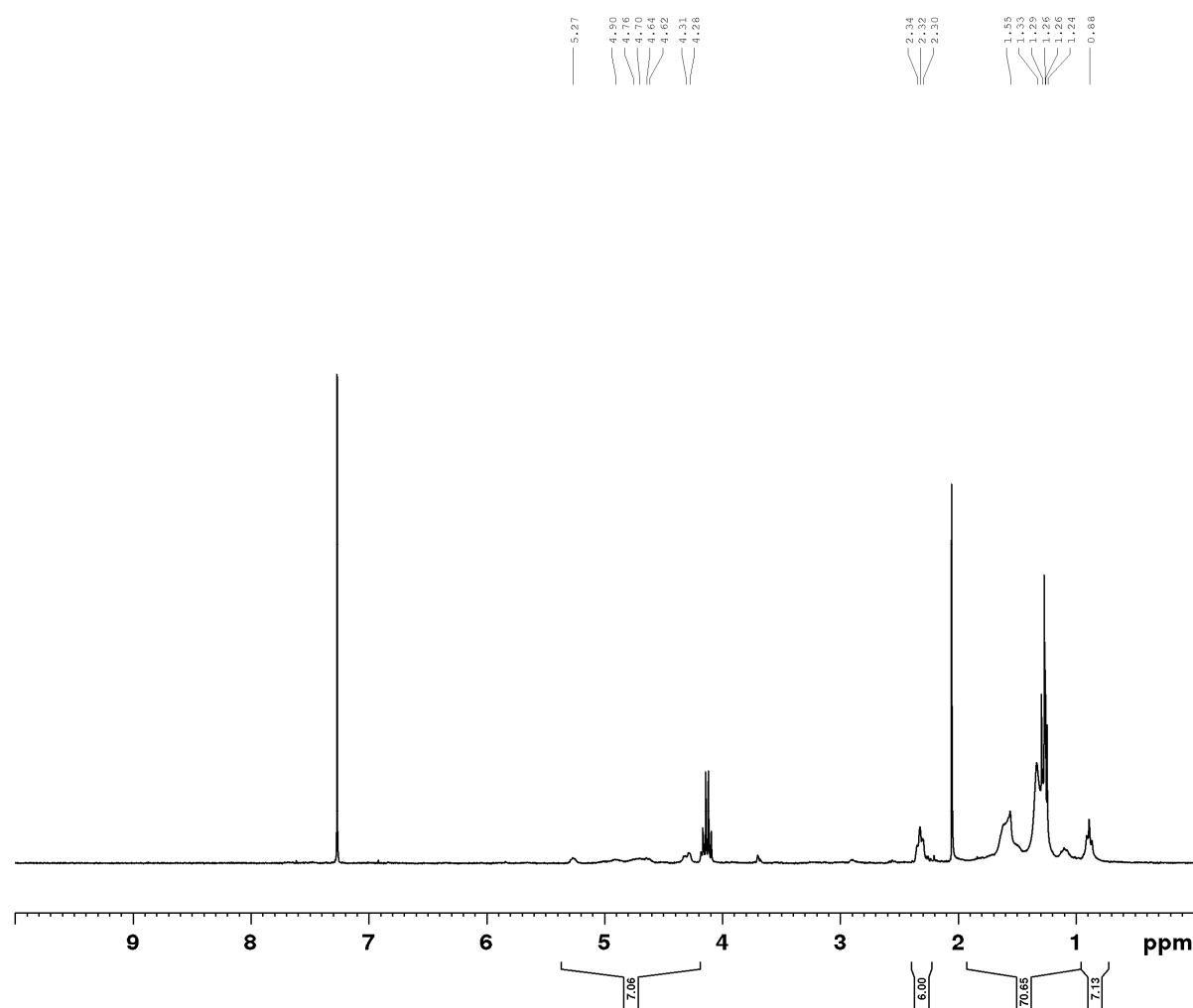
```

Current Data Parameters
NAME          LL125z
EXPNO         10
PROCNO        1

F2 - Acquisition Parameters
Date_         20170505
Time          9.38 h
INSTRUM       spect
PROBHD        Z104275_0387 (
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            5.4525952 sec
RG            200.94
DW            83.200 usec
DE            6.50 usec
TE            298.5 K
D1            1.00000000 sec
TD0           1
SFO1          300.2018537 MHz
NUC1          1H
P1            13.70 usec
PLW1          9.60000038 W

F2 - Processing parameters
SI            65536
SF            300.2000068 MHz
WDW           EM
SSB           0
LB            0 Hz
GB            0
PC            1.00
  
```

Carbonated linseed oil (5c)



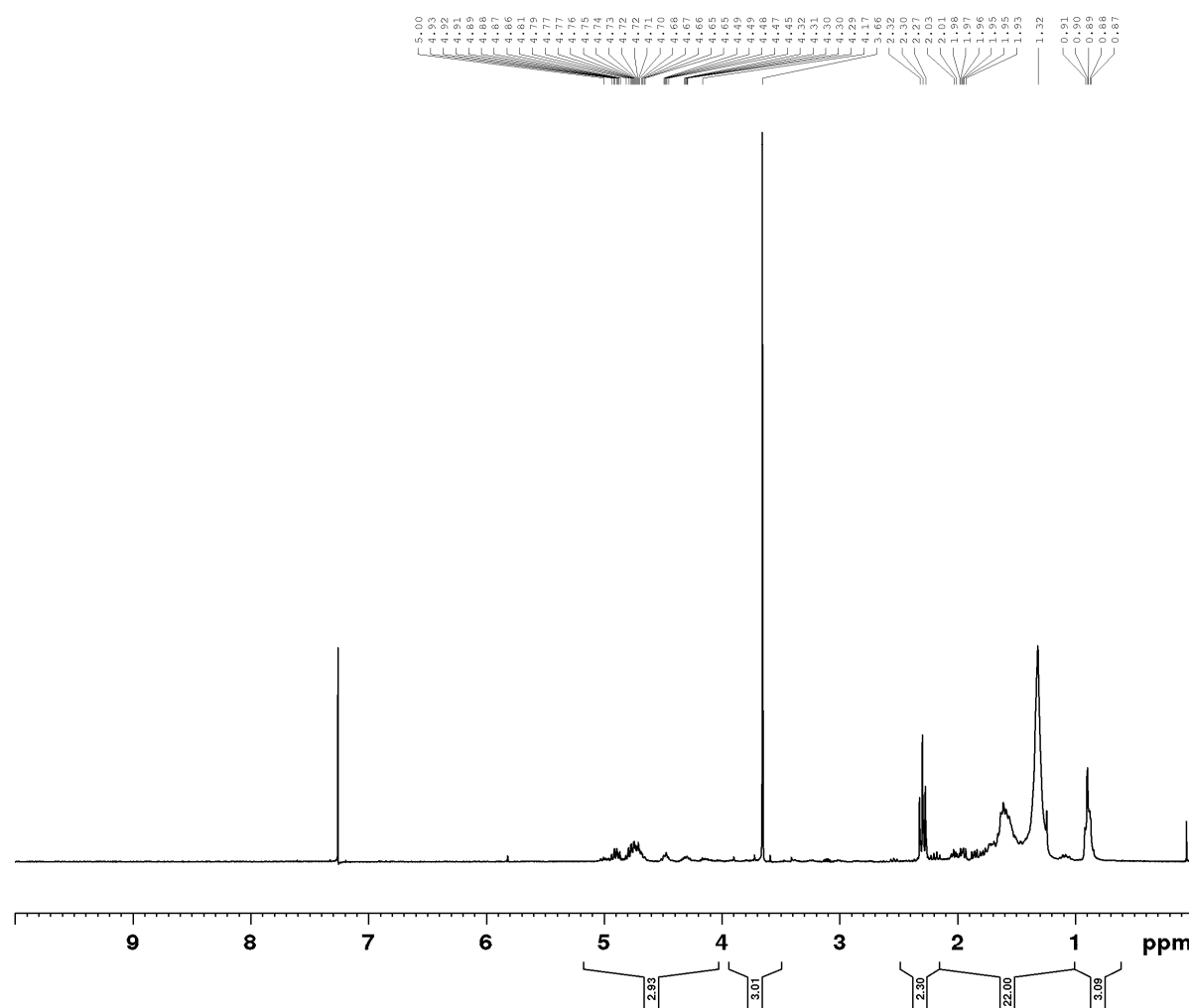
Current Data Parameters
NAME LL126x
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170317
Time 12.36
INSTRUM FOURIER300
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6103.516 Hz
FIDRES 0.093132 Hz
AQ 5.3687091 sec
RG 114.323
DW 81.920 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 300.2018539 MHz
NUC1 1H
P1 10.00 usec
PLW1 20.00000000 W

F2 - Processing parameters
SI 65536
SF 300.2000022 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Carbonated methyl soyate (5d)

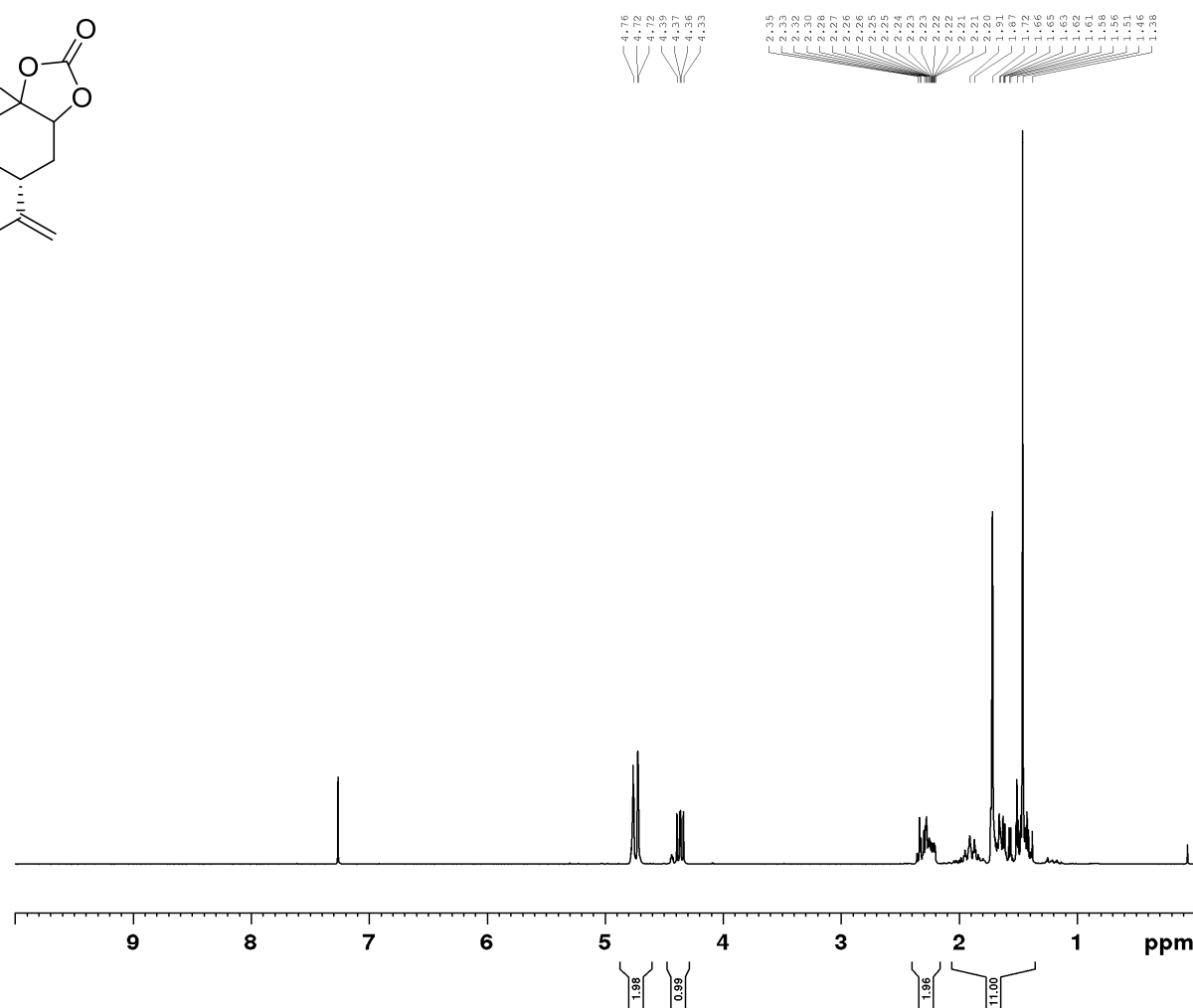
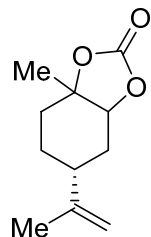


Current Data Parameters
NAME LL136z
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170505
Time 9.43 h
INSTRUM spect
PROBHD Z104275_0387 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 5.4525952 sec
RG 200.94
DW 83.200 usec
DE 6.50 usec
TE 298.6 K
D1 1.00000000 sec
TD0 1
SFO1 300.2018537 MHz
NUC1 1H
P1 13.70 usec
PLW1 9.60000038 W

F2 - Processing parameters
SI 65536
SF 300.2000088 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

3a-Methyl-6-(prop-1-en-2-yl)hexahydrobenzo[d][1,3]dioxol-2-one^[2] (mixture of cis and trans) (7a)



```

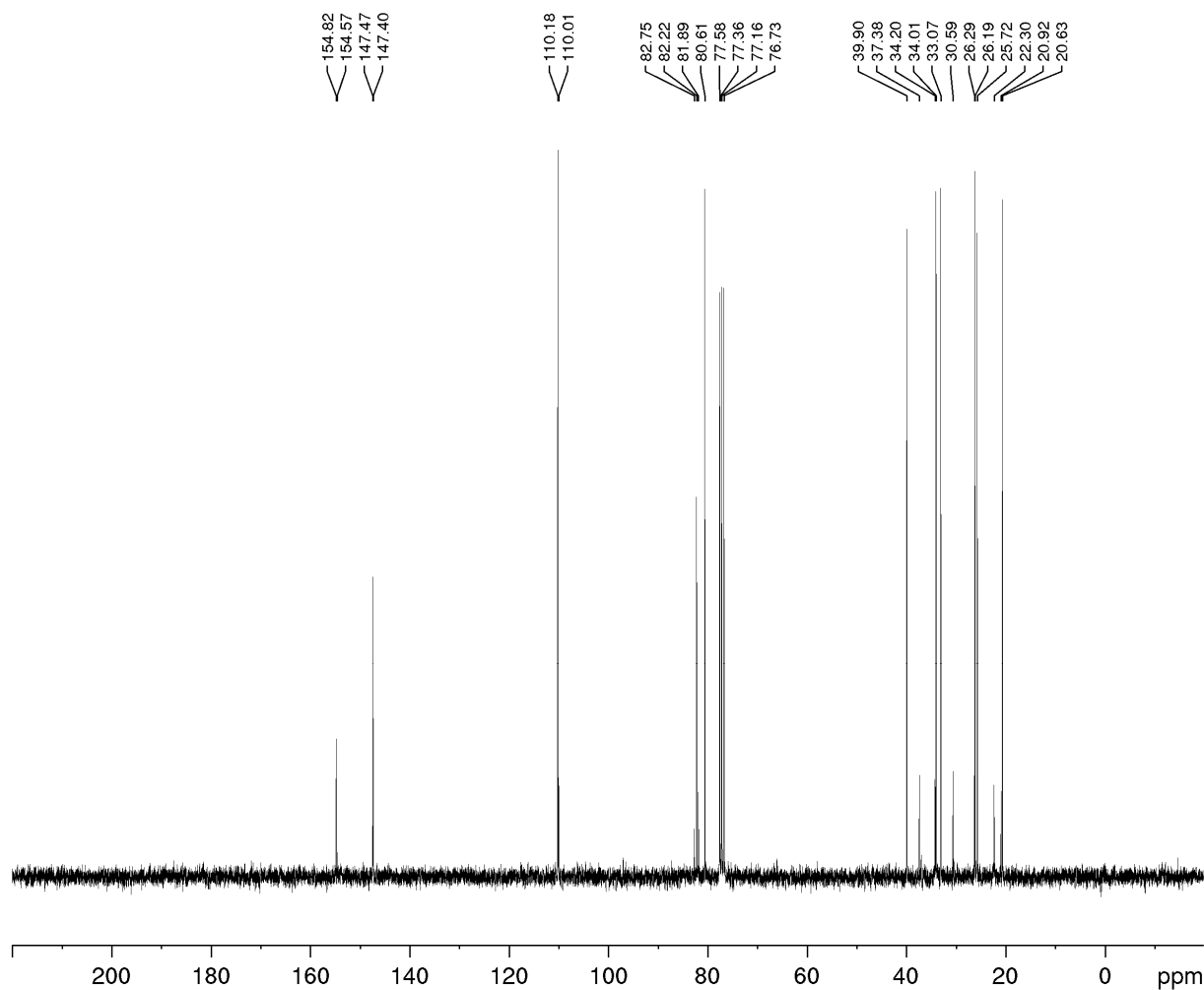
Current Data Parameters
NAME      LL157_x1
EXPNO     10
PROCNO    1

F2 - Acquisition Parameters
Date_     20170407
Time      18.58
INSTRUM   FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        6103.516 Hz
FIDRES     0.093132 Hz
AQ         5.3687091 sec
RG         32.3368
DW         81.920 usec
DE         6.50 usec
TE         297.7 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      300.2018539 MHz
NUC1       1H
P1         10.00 usec
PLW1      20.00000000 W

F2 - Processing parameters
SI         65536
SF         300.2000032 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

^{13}C NMR of 3a-Methyl-6-(prop-1-en-2-yl)hexahydrobenzo[d][1,3]dioxol-2-one^[2] (mixture of cis and trans) (7a)



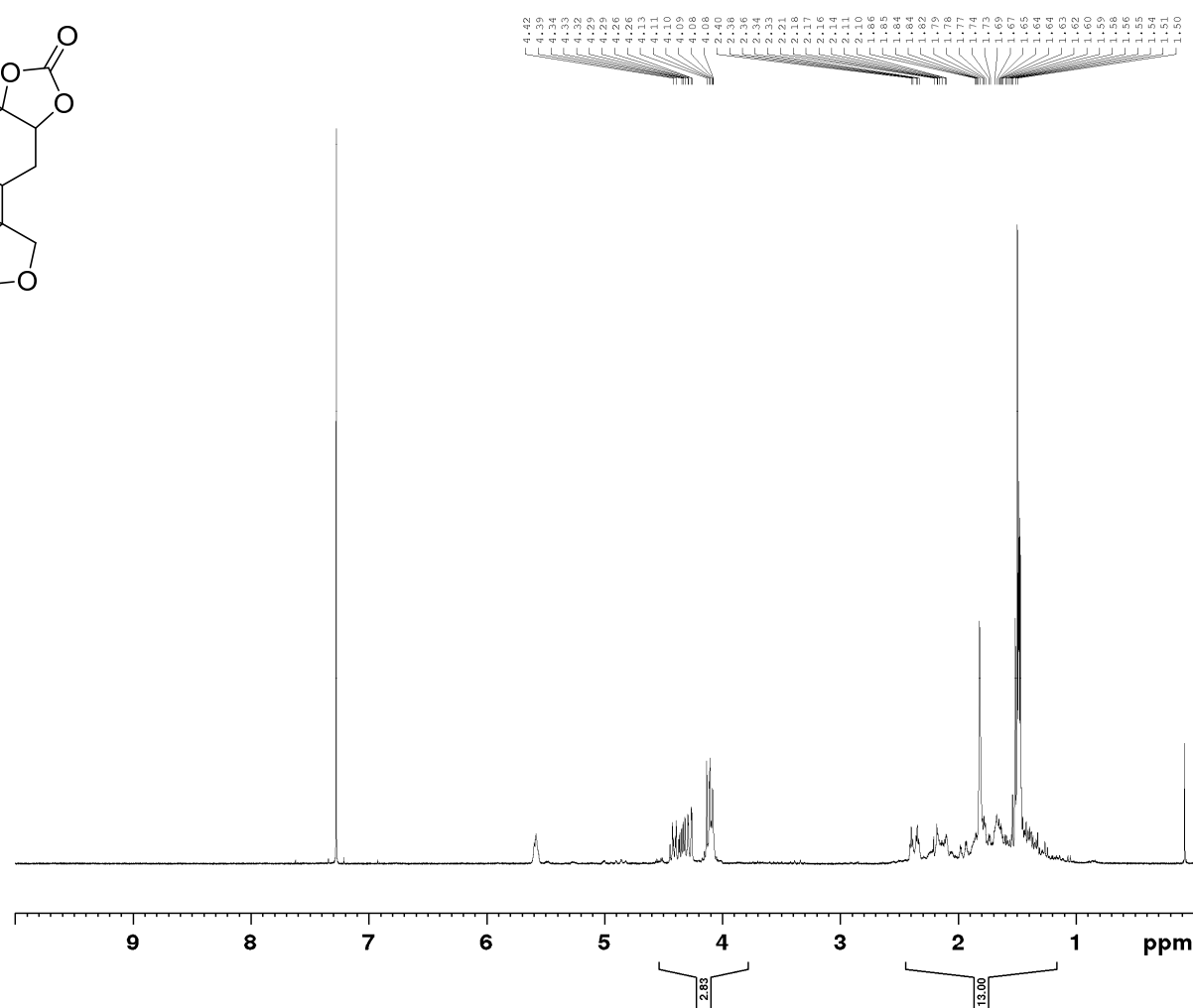
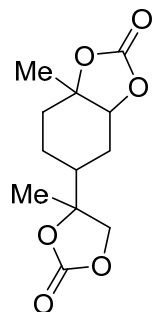
```

Current Data Parameters
NAME      LL157_x11
EXPNO     11
PROCNO    1

F2 - Acquisition Parameters
Date_     20170727
Time      14.57 h
INSTRUM   spect
PROBHD    Z104275_0387 (
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        256
DS        4
SWH       18115.941 Hz
FIDRES    0.552855 Hz
AQ        1.8087935 sec
RG        13.57
DW        27.600 usec
DE        6.50 usec
TE        300.2 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0       1
SFO1      75.4928986 MHz
NUC1      13C
P1        10.00 usec
PLW1      51.53300095 W
SFO2      300.2012008 MHz
NUC2      1H
CPDPRG[2  waltz16
PCPD2     90.00 usec
PLW2      9.60000038 W
PLW12     0.22245000 W
PLW13     0.11189000 W

F2 - Processing parameters
SI        32768
SF        75.4853440 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
    
```

3a-Methyl-6-(4-methyl-2-oxo-1,3-dioxolan-4-yl)hexahydrobenzo[d][1,3]dioxol-2-one^[2] (7b)

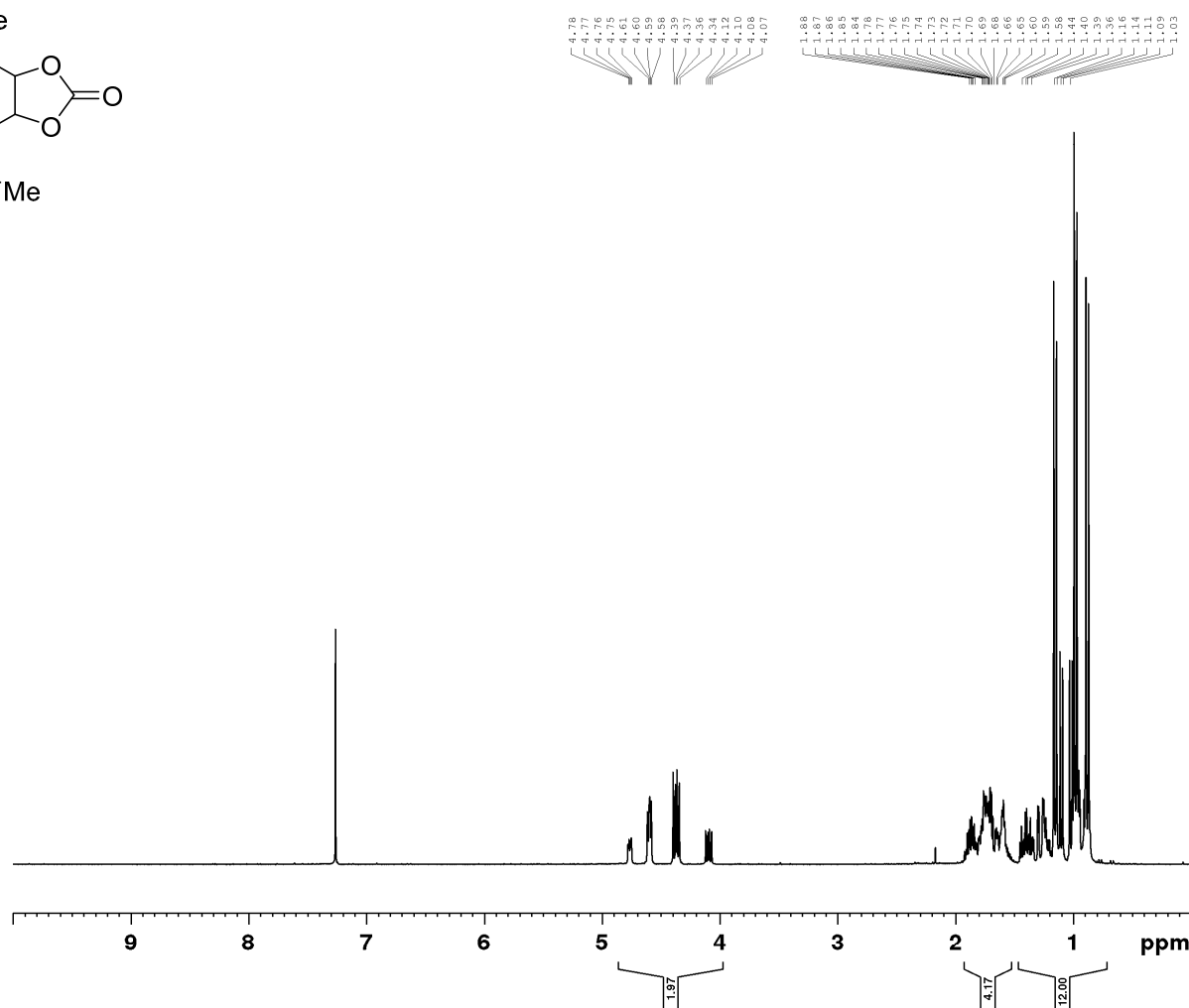
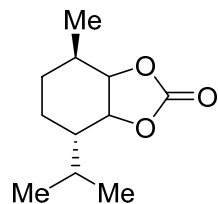


Current Data Parameters
NAME LL154z
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170510
Time 11.43 h
INSTRUM spect
PROBHD Z104275_0387 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 5.4525952 sec
RG 200.94
DW 83.200 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 300.2018537 MHz
NUC1 1H
P1 13.70 usec
PLW1 9.60000038 W

F2 - Processing parameters
SI 65536
SF 300.2000037 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

(4S,7R)-4-isopropyl-7-methylhexahydrobenzo[d][1,3]dioxol-2-one^[2] (7c)



```

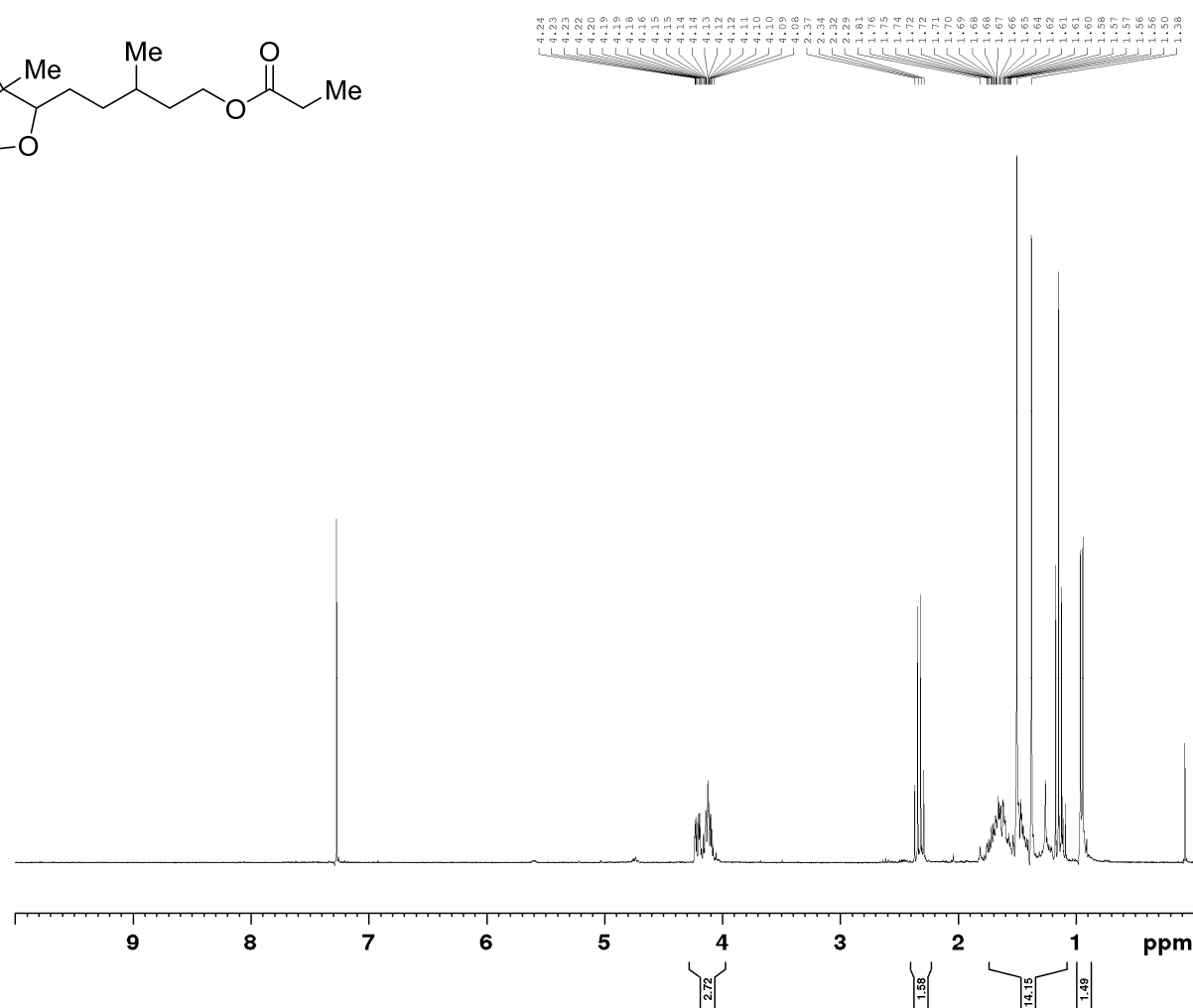
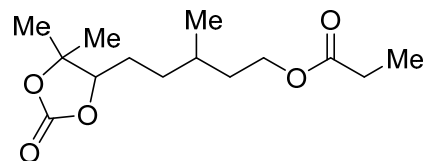
Current Data Parameters
NAME          LL158x
EXPNO         10
PROCNO        1

F2 - Acquisition Parameters
Date_         20170405
Time          11.55
INSTRUM       FOURIER300
PROBHD        5 mm DUL 13C-1
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6103.516 Hz
FIDRES        0.093132 Hz
AQ            5.3687091 sec
RG            45.011
DW            81.920 usec
DE            6.50 usec
TE            298.1 K
D1            1.00000000 sec
TD0           1

===== CHANNEL f1 =====
SFO1          300.2018539 MHz
NUC1          1H
P1            10.00 usec
PLW1          20.00000000 W

F2 - Processing parameters
SI            65536
SF            300.2000039 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

5-(5,5-Dimethyl-2-oxo-1,3-dioxolan-4-yl)-3-methylpentyl propionate (7e)



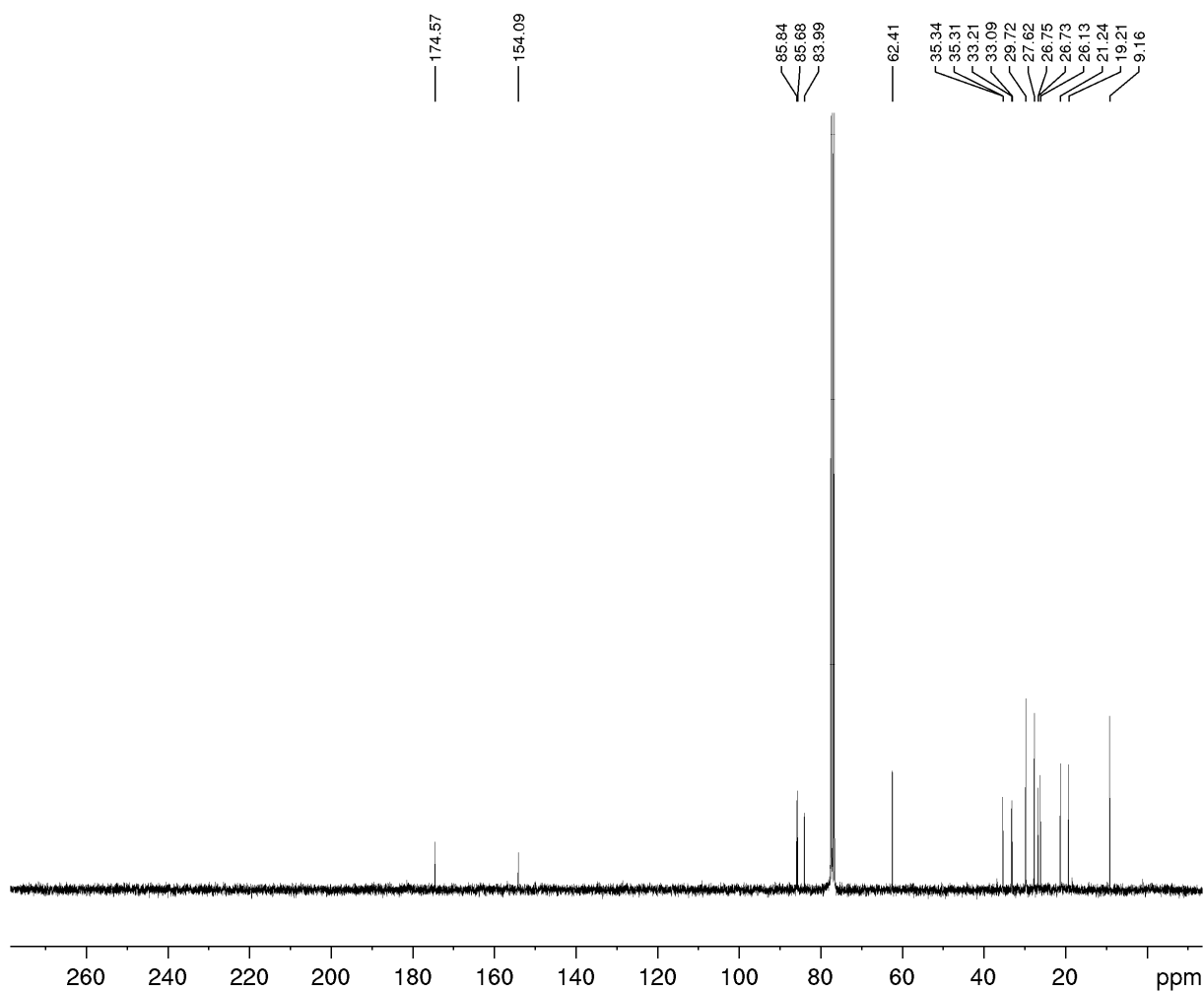
```

Current Data Parameters
NAME          LL152z
EXPNO         10
PROCNO        1

F2 - Acquisition Parameters
Date_         20170505
Time          11.17 h
INSTRUM       spect
PROBHD        Z104275_0387 (
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           6009.615 Hz
FIDRES        0.183399 Hz
AQ            5.4525952 sec
RG            200.94
DW            83.200 usec
DE            6.50 usec
TE            298.3 K
D1            1.00000000 sec
TD0           1
SFO1          300.2018537 MHz
NUC1          1H
P1            13.70 usec
PLW1          9.60000038 W

F2 - Processing parameters
SI            65536
SF            300.2000044 MHz
WDW           EM
SSB           0
LB            0 Hz
GB            0
PC            1.00
    
```

^{13}C NMR 5-(5,5-Dimethyl-2-oxo-1,3-dioxolan-4-yl)-3-methylpentyl propionate (7e)



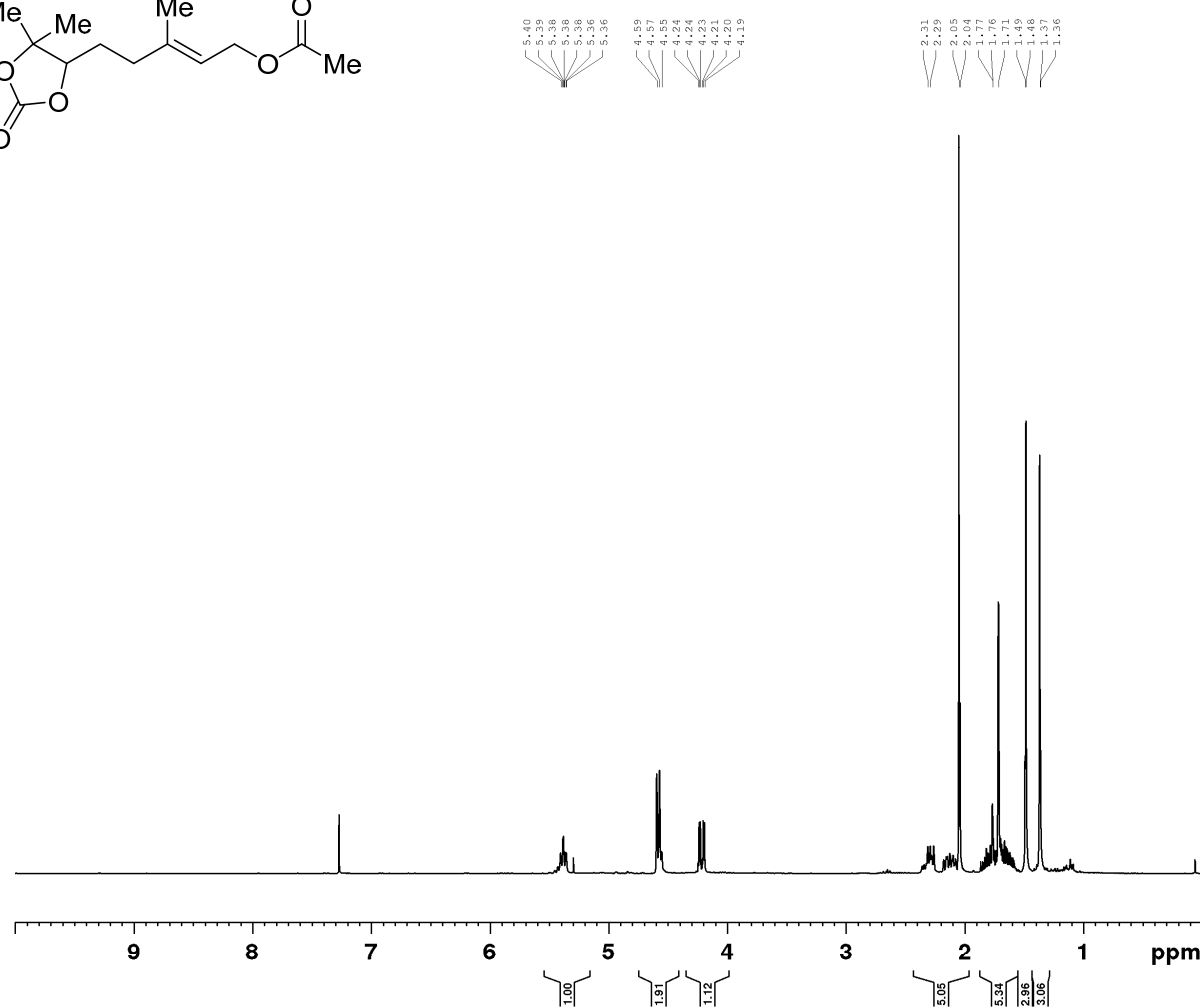
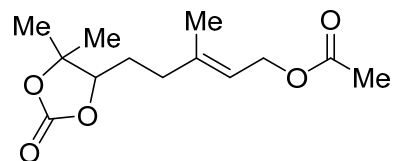
```

Current Data Parameters
NAME          LL152z2
EXPNO         1
PROCNO        1

F2 - Acquisition Parameters
Date_         20170508
Time_         9.44 h
INSTRUM       spect
PROBHD        Z862701_0048 (
PULPROG       zgpg30
TD            32768
SOLVENT       CDCl3
NS            2048
DS            2
SWH           22058.824 Hz
FIDRES        1.346364 Hz
AQ            0.7427413 sec
RG            22.64
DW            22.667 usec
DE            6.50 usec
TE            297.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0           1
SF01          75.4777485 MHz
NUC1          13C
P1            10.00 usec
PLW1          44.40100098 W
SF02          300.1312005 MHz
NUC2          1H
CPDPRG[2]     waltz16
PCPD2         90.00 usec
PLW2          17.52400017 W
PLW12         0.21635000 W
PLW13         0.10882000 W

F2 - Processing parameters
SI            32768
SF            75.4677485 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```

(E)-5-(5,5-dimethyl-2-oxo-1,3-dioxolan-4-yl)-3-methylpent-2-en-1-yl acetate^[2] (7f)



Current Data Parameters
NAME LL153_31
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170407
Time 17.47
INSTRUM FOURIER300
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6103.516 Hz
FIDRES 0.093132 Hz
AQ 5.3687091 sec
RG 17.7572
DW 81.920 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 300.2018539 MHz
NUC1 1H
P1 10.00 usec
PLW1 20.00000000 W

F2 - Processing parameters
SI 65536
SF 300.2000010 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

6. Crystallographic Data

Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structures were solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014: Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3.). Diamond (Klaus Brandenburg, DIAMOND, Version 4.3.1. Crystal Impact GbR, 2017, Bonn, Germany) was used for graphical representations.

Crystal data for CaI_2/Aza crown ether **3c**·2 DMF-complex: $\text{C}_{18}\text{H}_{39}\text{CaI}_2\text{N}_3\text{O}_7$, $M = 703.40$, monoclinic, space group $P2_1/n$, $a = 10.6093(2)$, $b = 7.3183(1)$, $c = 18.0196(3)$ Å, $\alpha = 90^\circ$, $\beta = 96.6981(5)$, $\gamma = 90^\circ$, $V = 1389.53(4)$ Å³, $T = 150(2)$ K, $Z = 2$, 18900 reflections measured, 3338 independent reflections ($R_{\text{int}} = 0.0199$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0196$, $wR_2 = 0.0466$, final R values (all data): $R_1 = 0.0223$, $wR_2 = 0.0480$, 160 parameters.

Crystal data for $\text{CaI}_2 \cdot \mathbf{6}$ DMF·0.8 H₂O-complex: $\text{C}_{18}\text{H}_{43.60}\text{CaI}_2\text{N}_6\text{O}_{6.80}$, $M = 746.87$, monoclinic, space group $P2_1/c$, $a = 12.5906(2)$, $b = 22.4298(4)$, $c = 11.6710(2)$ Å, $\alpha = 90^\circ$, $\beta = 101.8605(7)$, $\gamma = 90^\circ$, $V = 3225.58(10)$ Å³, $T = 150(2)$ K, $Z = 4$, 36482 reflections measured, 7787 independent reflections ($R_{\text{int}} = 0.0221$), final R values ($I > 2\sigma(I)$): $R_1 = 0.0239$, $wR_2 = 0.0554$, final R values (all data): $R_1 = 0.0285$, $wR_2 = 0.0576$, 325 parameters.

CCDC 1565156 and 1565157 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

7. References

- 1 A. Behr, N. Tenhumberg, A. Wintzer, *Eur. J. Lipid Sci. Technol.* **2012**, *114*, 905–910.
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