Supporting Information for

Polymer precursors from catalytic reactions of natural oils

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NMR and other spectra for the compounds formed during the study are shown below, together with GC analysis of the minor products obtained from the carbonylation of sunflower and olive oils.

Dimethyl nonadecanedioate

1H-NMR from dimethyl nonadecanedioate obtained from olive oil

13C NMR spectrum from dimethyl nonadecanedioate obtained from olive oil
$^1$H-NMR from dimethyl nonadecanedioate obtained from rapeseed oil

$^1$H-NMR from dimethyl nonadecanedioate obtained from sunflower oil
GCMS of crude product obtained from the methoxycarbonylation of sunflower oil
GCMS of crude product obtained from the methoxycarbonylation of olive oil
Table 1 Tentative assignment of GCMS peaks based on observed highest mass peaks and comparisons with library spectra where possible.

<table>
<thead>
<tr>
<th></th>
<th>Highest mass peak</th>
<th>Assignment</th>
<th>% Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>methyl hexadecanoate</td>
<td>270 [M]^+</td>
<td>97</td>
</tr>
<tr>
<td>b</td>
<td>methyl octadecanoate</td>
<td>298 [M]^+</td>
<td>98</td>
</tr>
<tr>
<td>c, c', c''</td>
<td></td>
<td>294</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>281</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td></td>
<td>326</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td></td>
<td>324*</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>322</td>
<td></td>
</tr>
<tr>
<td>g'</td>
<td></td>
<td>324*</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td></td>
<td>324*</td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>1,2-bis((di-tert-butylphosphino)methyl)benzene</td>
<td>337 [M - Bu]^+</td>
<td></td>
</tr>
<tr>
<td>j</td>
<td>isomer of dimethyl nonadecenedioate</td>
<td>354 [M]^+</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>dimethyl nonadecenidioate</td>
<td>356 [M]^+</td>
<td>91</td>
</tr>
<tr>
<td>l</td>
<td></td>
<td>323</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td></td>
<td>371</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td></td>
<td>382</td>
<td></td>
</tr>
<tr>
<td>n'</td>
<td></td>
<td>354</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td></td>
<td>386</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>1,2-bis((di-tert-butylphosphoryl)methyl)benzene</td>
<td>426 [M]^+</td>
<td></td>
</tr>
</tbody>
</table>

Peaks with mass 324 are probably from branched isomers of C19 dimethyl esters, but the spectra for different isomers are so we have not provided assignments.
Scan 2688 (16.026 min): FM317#.D

#115417: Hexadecanoic acid, methyl ester
Scan 2848 (16.974 min): FM317#.D

#115469: Octadecanoic acid, methyl ester
Scan 2859 (17.039 min): FM317#.D

Abundance
Scan 2998 (17.864 min): FM317#.D
Scan 3058 (18.219 min): FM317#.D

m/z -->

Abundance
$g'$ (from olive oil)
Scan 3120 (18.587 min): FM317#.D
1,2-bis(di-tert-butylphosphino)methylbenzene (337) is from [M-tBu]+.
Scan 3184 (18.966 min): FM317#.D

#42697: Nonadecanedioic acid, dimethyl ester
Scan 3318 (19.761 min): FM317#.D

m/z ->

Abundance
1,2-bis((di-tert-butylphosphoryl)methyl)benzene
FID of crude product from the methoxycarbonylation of olive oil

Response_
Zoom FID for crude product from methoxycarbonylation of olive oil

Response

Glycerol

Time
Characterisation of reduction products

1,19-nonadecanediol:

First method:

$^1$H NMR spectrum

$^{13}$C NMR spectrum
Second method:

$^1$H NMR spectrum

$^{13}$C NMR spectrum
1, 19-Nonadecanedioic acid:

\(^1\)H NMR spectrum

\(^{13}\)C NMR spectrum
Oligoesters prepared from the hydrogenation of 1,19-nonadecadanoic acid

\(^1\)H NMR spectrum of purified product (the crude product also contained diol)

Integration of the resonances between 2 and 4.5 ppm gives an average chain length of 3 monomer units terminated mainly by \(-\text{CH}_2\text{OH}\) groups. The small resonance at 0.8 ppm is from methyl endgroups which can arise from decarboxylation as shown in Scheme 2 of the main paper and/or from dehydration of an alcohol end group followed by hydrogenation of the terminal alkene.

\(^{13}\)C NMR Spectrum
**Oligoesters used for hydrogenation in the presence of water**

A sample of oligoester was prepared by the first method described for the hydrogenation of dimethyl 1,19-nonadecanedioate in the presence of 10 % water, but using an impure sample of triphos. This preparation led to oligoesters, but was not reproducible when using other batches of triphos.

**\(^1\)H NMR spectrum**

The average chain length is calculated as 3 units and the main end groups are –CH\(_2\)OH (signal...
at 3.64 ppm. Some -CO$_2$Me end groups are also observed (small signals 3.5 (MeO) and 2.3 (CH$_3$CO$_2$Me) ppm next to the in chain CH$_2$C(O)- signal at 2.28 ppm. The signal at 4.05 ppm is from the in chain CH$_2$O.

$^{13}$C NMR spectrum

IR spectrum
MALDI-TOF MS

n=

4700 Reflector Spec #1: MC[BP = 692.9, 880]