Supporting Information

for

Systematic synthetic study of four diastereomERICally distinct limonene-1,2-diols and their corresponding cyclic carbonates

Hiroshi Morikawa, Jun-ichi Yamaguchi, Shun-ichi Sugimura, Masato Minamoto, Yuuta Gorou, Hisatoyo Morinaga and Suguru Motokucho


Experimental, synthesis, and NMR and FTIR spectra of all the compounds
# Table of contents

1. General .......................................................................................................................... S3

2. Synthesis .......................................................................................................................... S4–S10

3. Characteristic data (Tables S1 and S2) ........................................................................... S11

4. NMR Spectra

   For 1a
   - $^1$H NMR spectrum ........................................................................................................ S12
   - $^{13}$C and DEPT135 spectra .......................................................................................... S13
   - HETCOR spectra ........................................................................................................... S14
   - $^1$H-$^1$H COSY spectra ............................................................................................... S15–S16

   For 1b
   - $^1$H NMR spectrum ........................................................................................................ S17
   - $^{13}$C and DEPT135 spectra .......................................................................................... S18
   - HETCOR spectra ........................................................................................................... S19
   - $^1$H-$^1$H COSY spectra ............................................................................................... S20–S21

   For 1c
   - $^1$H NMR spectrum ........................................................................................................ S22
   - $^{13}$C and DEPT135 spectra .......................................................................................... S23
   - HETCOR spectra ........................................................................................................... S24
   - $^1$H-$^1$H COSY spectra ............................................................................................... S25–S26

   For 1d
   - $^1$H NMR spectrum ........................................................................................................ S27
   - $^{13}$C and DEPT135 spectra .......................................................................................... S28
   - HETCOR spectra ........................................................................................................... S29
   - $^1$H-$^1$H COSY spectra ............................................................................................... S30–S31

   For comparison among 1a–1d
   - $^1$H NMR spectra ........................................................................................................... S32
   - $^{13}$C NMR spectra ........................................................................................................ S33

   For 2a
   - $^1$H NMR spectrum ........................................................................................................ S34
   - $^{13}$C and DEPT135 spectra .......................................................................................... S35
   - HETCOR spectra ........................................................................................................... S36
   - $^1$H-$^1$H COSY spectra ............................................................................................... S37–S38
   - HMBC spectra .............................................................................................................. S39
   - 1,1-ADEQUATE spectrum .............................................................................................. S40

   For 2b
   - $^1$H NMR spectrum ........................................................................................................ S41
   - $^1$H NMR spectra (in benzene-$d_6$ and in CD$_3$OD) .................................................... S42
   - $^{13}$C and DEPT135 spectra .......................................................................................... S43
   - HETCOR spectra ........................................................................................................... S44
   - $^1$H-$^1$H COSY spectra ............................................................................................... S45–S46
   - HMBC spectra .............................................................................................................. S47
   - 1,1-ADEQUATE spectrum .............................................................................................. S48

   For 2c
   - $^1$H NMR spectrum ........................................................................................................ S49
   - $^{13}$C and DEPT135 spectra .......................................................................................... S50
   - HETCOR spectra ........................................................................................................... S51
   - $^1$H-$^1$H COSY spectra ............................................................................................... S52–S53
   - HMBC spectra .............................................................................................................. S54

   For 2d
   - $^1$H NMR spectrum ........................................................................................................ S55
   - $^{13}$C and DEPT135 spectra .......................................................................................... S56
   - HETCOR spectra ........................................................................................................... S57
5. FTIR spectra ................................................................. S63–S65

6. GC chart (typical example) ................................................... S66–S68

7. References ........................................................................ S69
1. General

(R)-Limonene oxide (LO) comprising a mixture of cis- and trans-isomers (43:57) was purchased from Wako (Osaka, Japan) and was used as received. Pure trans-LO (>99% de) and cis-LO (96% de) were individually prepared from the LO mixture [1]. Triphosgene (TCI, Japan), tetrabutylammonium chloride (TBAC, TCI, Japan) and lithium aluminium hydride (LAH, Wako, Japan) were used as received. Carbon dioxide was used as dry-ice. Pyridine, diethyl ether and CH₂Cl₂ were dried by distillation over CaH₂, CaH₂ and P₂O₅, respectively. All other reagents and solvents were reagent grade and used as received. Syntheses of 1a, 1d and 2d were performed in a similar manner to the previous study [2].

¹H and ¹³C NMR spectra (400 MHz ¹H; 100 MHz ¹³C), DEPT 135 and two-dimensional NMR spectra (¹H-¹H COSY, HETCOR, HMBC) were recorded on a JEOL JNM-ECA 400 spectrometer at room temperature. The solvents were CDCl₃ except for 2b in CD₃OD or in benzene-d₆ in Supporting Information page S42. The concentration was adjusted to 5–15 mg mL⁻¹ dependent on the measurements. Chemical shifts were determined using tetramethylsilane as an internal standard. All the chemical shift values (ppm) in ¹³C NMR analyses of the LM5CCs and LMDiols are listed in Tables 1 and 2. 1,1-ADEQUATE spectra were measured at the Office for Research Initiative and Development / Common Facilities Division in Nagasaki University by a Varian NMR System 500 at 24 °C in CDCl₃, and operated using VnmrJ 4.2 Rev. A software. The concentration was adjusted to approximately 100 mg mL⁻¹.

FTIR spectra were recorded on a JASCO FTIR 460 spectrometer, and the transmission spectra were measured from KBr discs. High-resolution mass spectra (HRMS) were recorded using a JEOL JMS-700N instrument using electron ionisation
(EI) mass spectrometry, and measured at the Office for Research Initiative and Development / Common Facilities Division in Nagasaki University. Melting point (mp) was measured on a YANAKO MP-500D hot-stage apparatus. Optical rotations were measured in a 100 mm length cell on a JASCO Model P-2200 digital polarimeter at 25 °C, and an average value from ten measurements was calculated. Gas chromatography (GC) analysis was performed on a SHIMADZU GC2014. The injector and detector temperatures were set at 230 and 350 °C, respectively. The temperature of column (Rxi-5Sil MS column, GL Sciences Inc., Japan) was initially at 100 °C for 1 min, then raised to 330 °C at 20 °C /min, and finally hold at 330 °C. Kovats retention index of each compound was estimated according to the literature [3] as references to mixed hydrocarbon standards (C9–C40) in n-hexane (GL Sciences Inc., Japan).

Thin-layer chromatography (TLC) was performed using GF254 silica gel plates (Merck). Acidic p-anisaldehyde was used for TLC visualisation.

2. Synthesis

Synthesis of carbonate 1a from trans-LO

Conditions (a) in Scheme 3

LM5CC 1a was synthesised by a modification of the procedure from our previous report [2]. Briefly, a mixture of pure trans-LO (762 mg, 5.01 mmol), TBAC (140 mg, 0.504 mmol), and dry-ice was heated in a autoclave (Type TVS-N2, Taiatsu Glass Kogyo Co., Japan) with stirring at 100 °C for 72 h under 5 MPa CO₂. After carbonation, the reaction mixture was purified using SiO₂ column chromatography (n-hexane/ethyl acetate (10:1, v/v) as an eluent) to afford 1a (829 mg, 4.23 mmol) as a white solid in an 84% yield. Though the mp and 1H and 13C NMR were measured
previously [2], their measurements were re-performed in this study for more detail characterization.

**1a [2,4,5]:** mp 35–37 °C (lit [2]; 37–38 °C); $^1$H NMR (CDCl$_3$) δ 4.76 (q, $J = 1.4$ Hz, 1H), 4.72 (s, 1H), 4.37 (dd, $J = 9.6$ and 6.9 Hz, 1H), 2.31 (ddd, $J = 15.5$, 3.7 and 3.7 Hz, 1H), 2.28–2.22 (m, 1H), 1.92 (dddd, $J = 11.9$, 11.9, 3.2 and 3.2 Hz, 1H), 1.72 (s, 3H), 1.71–1.59 (m, 2H), 1.51–1.40 (m, 2H), 1.47 (s, 3H). The IR, HRMS data and the optical rotation value were reported previously [2].

**Synthesis of carbonate 1d from cis-LO**

**Conditions (a) in Scheme 3**

In a similar manner to that used for 1a, 1d [2] was synthesised from a mixture of pure cis-LO (766 mg, 5.03 mmol), TBAC (136 mg, 4.89 mmol) and dry-ice, which was reacted under 5 MPa CO$_2$ at 100 °C for 72 h. The carbonate 1d (301 mg, 1.53 mmol) was obtained as a white solid in a 30% yield following SiO$_2$ column chromatography (n-hexane/ethyl acetate (10:1, v/v) as an eluent). Though the mp and $^1$H and $^{13}$C NMR were measured previously [2], their measurements were re-performed in this study for more detail characterization.

**1d[2]:** mp 40–41 °C(lit [2]; 40–41 °C); $^1$H NMR (CDCl$_3$) δ 4.78 (q, $J = 1.4$ Hz, 1H), 4.72 (m, 1H), 4.44 (dd, $J = 3.2$ and 2.3 Hz, 1H), 2.31–2.22 (m, 2H), 2.01 (ddd, $J = 13.3$, 4.6 and 4.1 Hz, 1H), 1.88–1.79 (m, 2H), 1.74 (s, 3H), 1.56 (ddd, $J = 14.3$, 13.3 and 3.6 Hz, 1H), 1.51 (s, 3H), 1.25–1.15 (m, 1H). The IR, HRMS data and the optical rotation value were reported previously [2].

**Synthesis of carbonate 1a from diol 2a**

**Conditions (c) in Scheme 3**
In a 100 mL round-bottomed flask, 2a (341.7 mg, 2.007 mmol) and dry pyridine (652.9 mg, 8.254 mmol) were dissolved in dry CH₂Cl₂ (18 mL). Triphosgene (289.7 mg, 0.9763 mmol) in dry CH₂Cl₂ (2 mL) was added to the solution under cooling in an ice bath. After stirring at room temperature for 2 h under N₂ atmosphere, the consumption of 2a was confirmed by TLC. Then, water (20 mL) was added to the solution. The organic layer was separated and washed with saturated aqueous NH₄Cl solution. The organic layer was collected, dried over anhydrous MgSO₄ and filtered. After evaporation, the crude product was purified by SiO₂ column chromatography eluted with n-hexane/ethyl acetate (10:1, v/v) to obtain 1a (370.5 mg, 1.888 mmol) in a 94% yield. The spectroscopic data were identical to those of an authentic sample prepared from trans-LO and CO₂.

Synthesis of carbonate 1d from diol 2d

Conditions (c) in Scheme 3

LM5CC 1d was synthesised in a similar manner to that used to prepare 1a from 2a and triphosgene. From 2d (346.8 mg, 2.037 mmol) and triphosgene (286.0 mg, 0.9638 mmol), 1d (374.5 mg, 1.908 mmol) was obtained as a white solid in a 94% yield. The spectroscopic data were identical to those of the authentic sample prepared from cis-LO and CO₂.

Synthesis of carbonate 1b from diol 2b

Conditions (c) in Scheme 3

LM5CC 1b was synthesised in a similar manner to 1a. From 2b (340.5 mg, 2.000 mmol) and triphosgene (623.6 mg, 2.102 mmol), 1b (96.1 mg, 0.489 mmol) was obtained as a white solid in a 24% yield.
**1b**: mp 35–36 °C; IR (KBr) ν_{C=O} 1805 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) δ 4.98 (bs, 1H), 4.89 (s, 1H), 4.37 (dd, J = 13.7 and 3.7 Hz, 1H), 2.61 (t, J = 5.0 Hz, 1H), 2.30 (ddd, J = 12.4, 1.8 and 1.8 Hz, 1H), 2.17–2.12 (m, 1H) 2.13–2.03 (m, 1H), 1.98–1.95 (m, 1H), 1.89 (ddd, J = 12.8, 12.8 and 6.0 Hz, 1H), 1.79 (s, 3H), 1.77–1.71 (m, 1H), 1.41 (s, 3H); HRMS (EI, m/z) [M]+ Calcd. for C\(_{11}H_{16}O_3\), 196.1099; found, 196.1099; \([\alpha]^{25}_D = -25.4\) (c 1.00, CHCl\(_3\)).

**Synthesis of carbonate 1c from diol 2c**

Conditions (c) in Scheme 3

LM5CC 1c was synthesised in a similar manner to 1a. From 2c (341.3 mg, 2.004 mmol) and triphosgene (609.0 mg, 2.053 mmol), 1c (227.3 mg, 1.158 mmol) was obtained as a white solid in a 58% yield.

**1c**: mp 34–36 °C; IR (KBr) ν_{C=O} 1806 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) δ 4.80 (q, J = 1.4 Hz, 1H), 4.78 (s, 1H), 4.17 (dd, J = 12.8 and 3.7 Hz, 1H), 2.28 (ddddd, J = 12.4, 11.9, 4.6 and 4.1 Hz, 1H), 2.20 (dd, J = 11.9, 3.7 and 3.2 Hz, 1H), 2.11–2.06 (m, 1H), 1.96–1.85 (m, 2H), 1.76 (s, 3H), 1.75 (ddd, J = 12.8, 11.9 and 11.9 Hz, 1H), 1.55–1.45(m, 1H), 1.38 (s, 3H); HRMS (EI, m/z) [M]+ Calcd. for C\(_{11}H_{16}O_3\), 196.1099; found, 196.1092; \([\alpha]^{25}_D = +3.3\) (c 1.00, CHCl\(_3\)).

**Synthesis of diol 2a from carbonate 1a**

Conditions (b) in Scheme 3

In a 200-mL round-bottomed flask, 1a (2.0177 g, 10.28 mmol) was dissolved in dry diethyl ether (40 mL) under N\(_2\) atmosphere. The flask was immersed into an ice bath and LAH (726.7 mg, 19.14 mmol) was added portionwise with cooling. After stirring for 2 h at room temperature, the consumption of 1a was confirmed by TLC. Then, ethyl acetate (100 mL) and brine (100 mL) were carefully added to the mixture. The
organic layer was separated, dried over anhydrous MgSO₄, and filtered. After evaporation and purification using SiO₂ column chromatography (n-hexane/ethyl acetate, 1:5, v/v), 2a (1.6135 g, 9.4773 mmol) was obtained as a white solid in a 92% yield.

2a: mp 75 °C; IR (KBr) νOH 3348, νC-H 2933, 2860 cm⁻¹; ¹H NMR (CDCl₃) δ 4.71–4.69 (m, 2H), 3.41(dd, J = 11.4 and 4.6 Hz, 1H), 1.96 (dddd, J = 12.4, 11.9, 3.2 and 3.2Hz, 1H), 1.84 (ddd, J = 13.7, 3.2 and 3.2 Hz, 1H), 1.79 (dd, J = 12.4, 3.3 and 3.2 Hz, 1H), 1.73 (s, 3H), 1.54–1.48 (m, 3H), 1.42–1.34 (m, 1H), 1.27 (s, 3H); HRMS (EI, m/z) [M]⁺ Calcd. for C₁₀H₁₈O₂, 170.1307; found, 170.1307; [α]²⁵_D = +4.8 (c 1.00, CHCl₃).

Synthesis of diol 2b from carbonate 1b

Conditions (b) in Scheme 3

Diol 2b was synthesised in a similar manner to 2a. Carbonate 1b (103.3 mg, 0.5264 mmol) and LAH (41.2 mg, 1.09 mmol) were reacted to obtain 2b (75.5 mg, 0.443 mmol) as a white solid in an 84% yield. The spectroscopic data were identical to those of a sample prepared from cis-LO and water.

2b: mp 72–73 °C (lit [6]; 69–71 °C, lit [7]; 68–70 °C); IR (KBr) νOH 3330, νC-H 2938, 2869 cm⁻¹; ¹H NMR (CDCl₃) δ 4.73 (s, 2H), 3.63 (t, J = 3.2 Hz, 1H), 2.26 (ddd, J = 11.8, 4.2 and 3.2Hz, 1H), 1.93 (ddd J = 13.7, 4.2 and 4.2 Hz, 1H), 1.78–1.72 (m, 1H), 1.73 (s, 3H), 1.66 (ddd, J = 13.7, 4.2 and 3.2 Hz, 1H), 1.60–1.50 (m, 3H), 1.26 (s, 3H); HRMS (EI, m/z) [M]⁺ Calcd. for C₁₀H₁₈O₂, 170.1307; found, 170.1302; [α]²⁵_D = +25.8 (c 1.00, CHCl₃), (lit [6]; [α]¹₈_D = +27.2 (c 0.49, CHCl₃), lit [7]; [α]²₀_D = +18.1 (c 0.01, CHCl₃)).
Synthesis of diol 2c from carbonate 1c

Conditions (b) in Scheme 3

Diol 2c was synthesised in a similar manner to 2a. From 1c (149.3 mg, 0.7608 mmol) and LAH (58.6 mg, 1.54 mmol), 2c (122.4 mg, 0.7189 mmol) was obtained as a white solid in a 94% yield. The spectroscopic data were identical to those of a sample prepared from trans-LO and water.

2c: mp 73–74 °C (lit [7]; 74–76 °C, lit [8]; 71–73 °C); IR (KBr) \( \nu_{OH} \ 3363, \nu_{C-H} \ 2936, 2864 \ \text{cm}^{-1} \); \(^1H\) NMR (CDCl\(_3\)) \( \delta \ 4.71 \ (s, 2H), 3.58 \ (dd, J = 11.4 \text{ and } 4.1 \text{ Hz}, 1H), 2.07 \ (ddddd, J = 12.4, 12.4, 3.7 \text{ and } 3.7 \text{ Hz}, 1H), 1.95–1.89 \ (m, 1H), 1.80 \ (ddd, J = 12.8, 3.2 \text{ and } 3.2 \text{ Hz}, 1H), 1.73(s, 3H), 1.73–1.69 \ (m, 1H), 1.49 \ (ddd, J = 13.7, 12.8 \text{ and } 4.6 \  \text{Hz}, 1H), 1.36–1.24 \ (m, 2H), 1.21 \ (s, 3H); \) HRMS (El, \( m/z \)) \([M]^+\) Calcd. for \( \text{C}_{10}\text{H}_{18}\text{O}_2, 170.1307; \) found, 170.1317; \([\alpha]^{25}_D = -5.0 \ (c \ 1.00, \text{CHCl}_3), \) (lit[7]; \([\alpha]^{20}_D = -5.5 \ (c \ 0.01, \text{CHCl}_3), \) lit [8]; \([\alpha]^{20}_D = -6.6 \ (c \ 1.099, \text{CHCl}_3)).

Synthesis of diol 2d from carbonate 1d

Conditions (b) in Scheme 3

The synthesis was reported previously in ref.[2]. Though the mp and \(^1H\) and \(^{13}C\) NMR were measured previously [2], their measurements were re-performed in this study for more detail characterization.

2d[2]: mp 46–47 °C (lit [2]; 48–49 °C); \(^1H\) NMR (CDCl\(_3\)) \( \delta \ 4.72 \ (m, 1H), 4.71 \ (m, 1H), 3.66 \ (t, J = 3.5\text{Hz}, 1H), 2.35 \ (dddd, J = 11.9, 11.9, 3.7 \text{ and } 3.7 \text{ Hz}, 1H), 1.93–1.88 \ (m, 1H), 1.87–1.80 \ (m, 1H), 1.72 \ (s, 3H), 1.74–1.68 \ (m, 1H), 1.58–1.51 \ (m, 2H), 1.30 \ (dddd, J = 13.3, 13.3, 11.9 \text{ and } 3.7 \text{ Hz}, 1H), 1.25 \ (s, 3H). \) The IR, HRMS data and the optical rotation value were reported previously [2].
**Synthesis of diol 2b from cis-LO**

Conditions (e) in Scheme 3

A mixture of pure cis-LO (465.4 mg, 3.057 mmol) and water (2.66 g, 148 mmol) in a 15 mL test tube was stirred at 90 °C for 12 h. After cooling to ambient temperature, a white precipitate appeared and was collected by filtration (203.9 mg). The filtrate was extracted with diethyl ether (10 mL) twice. The organic layer was isolated and dried over anhydrous MgSO₄. After evaporation, the residue was purified using SiO₂ column chromatography (n-hexane/ethyl acetate, 2:1, v/v) to obtain a white solid (161.5 mg). This solid was combined with the filtered solid to obtain 2b (365.4 mg, 2.146 mmol) as a white solid in a 70% yield overall.

**Synthesis of diol 2c from trans-LO**

Conditions (d) in Scheme 3

A mixture of pure trans-LO (468.2 mg, 3.076 mmol), water (1.34 g, 74.4 mmol) and 1,4-dioxane (1.34 mL) was sealed in a 10 mL pressure-resistant glass tube. This mixture was stirred at 120 °C for 72 h. After cooling, the pressure was released. Brine (10 mL) was added to the mixture, and it was extracted twice with ethyl acetate (15 mL). The organic layer was isolated and dried over anhydrous MgSO₄. The filtrate was evaporated and the residue was purified using SiO₂ column chromatography (n-hexane/ethyl acetate, 1:1, v/v). The diol 2c (97.4 mg, 0.572 mmol) was isolated as a white solid in a 19% yield along with 2b (305.0 mg, 58%).
3. Characteristic data

Some data have been already shown in the aforementioned experimental section of this Supporting Information and cited from ref.[2].

Table S1: Characteristic data of LM5CCs, 1a–d

<table>
<thead>
<tr>
<th>compounds</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melting point (°C)</strong></td>
<td>35–37</td>
<td>35–36</td>
<td>34–36</td>
<td>40–41</td>
</tr>
<tr>
<td><strong>IR absorption band (KBr)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_{\text{C=O}}$ (cm$^{-1}$)</td>
<td>1794$^c$</td>
<td>1805</td>
<td>1806</td>
<td>1807$^c$</td>
</tr>
<tr>
<td><strong>specific rotation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[^{25}\alpha]_D$ (c 1.00, CHCl$_3$)</td>
<td>+53.7$^c$</td>
<td>-25.4</td>
<td>+3.3</td>
<td>-15.8$^c$</td>
</tr>
<tr>
<td><strong>$R_f$ on TLC$^a$</strong></td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>Kovats retention index$^b$</strong></td>
<td>1618</td>
<td>1699</td>
<td>1665</td>
<td>1620</td>
</tr>
</tbody>
</table>

$^a$developing with n-hexane/ethyl acetate = 5/1 (v/v). $^b$determined by GC using hydrocarbon standards as reference samples. $^c$cited from ref.[2]

Table S2: Characteristic data of LMdiols, 2a–d

<table>
<thead>
<tr>
<th>compounds</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
<th>2d</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melting point (°C)</strong></td>
<td>75</td>
<td>72–73</td>
<td>73–74</td>
<td>46–47</td>
</tr>
<tr>
<td><strong>IR absorption band (KBr)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_{\text{OH}}$ (cm$^{-1}$)</td>
<td>3348</td>
<td>3330</td>
<td>3363</td>
<td>3322$^c$</td>
</tr>
<tr>
<td><strong>specific rotation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[^{25}\alpha]_D$ (c 1.00, CHCl$_3$)</td>
<td>+4.8</td>
<td>+25.8</td>
<td>-5.0</td>
<td>+28.3$^c$</td>
</tr>
<tr>
<td><strong>$R_f$ on TLC$^a$</strong></td>
<td>0.40</td>
<td>0.40</td>
<td>0.20</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>Kovats retention index$^b$</strong></td>
<td>1348</td>
<td>1363</td>
<td>1373</td>
<td>1359</td>
</tr>
</tbody>
</table>

$^a$developing with n-hexane/ethyl acetate = 1/1 (v/v). $^b$determined by GC using hydrocarbon standards as reference samples. $^c$cited from ref.[2]
$^1$H NMR spectrum of 1a in CDCl$_3$. 
(top) DEPT135 and (bottom) $^13$C NMR spectra of 1\text{a} in CDCl$_3$. 
HETCOR spectra of 1a in CDCl₃; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 1a in CDCl$_3$; (top) full range and (bottom) selected range.
$^1\text{H}^\text{H}$ COSY spectra of 1a in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
$^1$H NMR spectrum of 1b in CDCl$_3$. 
(top) DEPT135 and (bottom) $^{13}$C NMR spectra of 1b in CDCl$_3$. 
HETCOR spectra of 1b in CDCl₃; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 1b in CDCl$_3$: (top) full range and (bottom) selected range.
$^1$H-1H COSY spectra of 1b in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
$^1$H NMR spectrum of $1c$ in CDCl$_3$. 
DEPT135 and $^{13}$C NMR spectra of 1c in CDCl$_3$. 
HETCOR spectra of 1c in CDCl₃: (top) full range and (bottom) selected range.
$^1$H–$^1$H COSY spectra of **1c** in CDCl$_3$; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 1c in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
$^1$H NMR spectrum of 1d in CDCl$_3$. 
(top) DEPT135 and (bottom) $^{13}$C NMR spectra of 1d in CDCl$_3$. 
HETCOR spectra of 1d in CDCl₃; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 1d in CDCl$_3$; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 1d in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
$^1$H NMR spectra of four LM5CCs (1a–1d) in full scales in CDCl$_3$. 
$^{13}$C NMR spectra of four LM5CCs (1a–1d) in full scales in CDCl$_3$. 

\[ \text{Chemical Structures} \]
$^1H$ NMR spectrum of 2a in CDCl$_3$. 
(top) DEPT135 and (bottom) $^{13}$C NMR spectra of 2a in CDCl$_3$
HETCOR spectra of 2a in CDCl₃; (top) full range and (bottom) selected range.
\(^1\)H-\(^1\)H COSY spectra of \(2a\) in CDCl\(_3\); (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 2a in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
HMBC spectra of 2a in CDCl₃; (top) full range and (bottom) selected range. The marks (g* and h*) represent side-band peaks.
1,1-ADEQUATE spectrum of 2a in CDCl₃.
\(^1H\) NMR spectrum of 2b in CDCl\(_3\).
$^1$H NMR spectra of 2b (top) in CD$_3$OD and (bottom) in benzene-d$_6$
(top) DEPT135 and (bottom) $^{13}$C NMR spectra of 2b in CDCl$_3$. 
HETCOR spectra of 2b in CDCl₃; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 2b in CDCl$_3$; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 2b in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
HMBC spectra of 2b in CDCl$_3$; (top) full range and (bottom) selected range. The marks ($g^*$ and $h^*$) represent for side-band peaks.
1,1-ADEQUATE spectrum of 2b in CDCl₃.
$^1$H NMR spectrum of 2c in CDCl$_3$. 
(top) DEPT135 and (bottom) $^{13}$C NMR spectra of 2c in CDCl$_3$. 
HETCOR spectra of 2c in CDCl₃: (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 2c in CDCl$_3$; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 2c in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
HMBC spectra of 2c in CDCl₃; (top) full range and (bottom) selected range. The marks (g* and h*) represent for side-band peaks.
$^1$H NMR spectrum of 2d in CDCl$_3$. 
(top) DEPT135 and (bottom) $^{13}$C NMR spectra of 2d in CDCl$_3$. 
HETCOR spectra of 2d in CDCl₃; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 2d in CDCl$_3$; (top) full range and (bottom) selected range.
$^1$H-$^1$H COSY spectra of 2d in CDCl$_3$; selected range with (top) high sensitivity and (bottom) low sensitivity.
HMBC spectra of 2d in CDCl₃; (top) full range and (bottom) selected range.

The marks (g* and h*) represent for side-band peak.
$^1$H NMR spectra of four LMdiols (2a–2d) in full scales in CDCl$_3$. 
$^{13}$C NMR spectra of four LMdiols (2a–2d) in full scales in CDCl$_3$. 
IR spectrum of 1b

IR spectrum of 1c.
IR spectrum of 2a.

IR spectrum of 2b.
IR spectra for 1a, 1d, and 2d were reported in Supporting Information of ref.[2].
** GC chart of compound 1a as a typical sample. **

<table>
<thead>
<tr>
<th>CH PNO</th>
<th>TIME</th>
<th>AREA</th>
<th>HEIGHT</th>
<th>MK</th>
<th>IDNO</th>
<th>CONC</th>
<th>NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.851</td>
<td>35674816</td>
<td>10172392</td>
<td>E</td>
<td>99.8037</td>
<td>0.0026</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.11</td>
<td>15805</td>
<td>4193</td>
<td>V</td>
<td>0.0045</td>
<td>0.0026</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.227</td>
<td>85809</td>
<td>38222</td>
<td>SV</td>
<td>0.0020</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.827</td>
<td>3244</td>
<td>1394</td>
<td>T</td>
<td>0.0001</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.283</td>
<td>374</td>
<td>150</td>
<td></td>
<td>0.0001</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4.643</td>
<td>109</td>
<td>36</td>
<td></td>
<td>0.0001</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5.177</td>
<td>11519</td>
<td>4638</td>
<td></td>
<td>0.0032</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5.794</td>
<td>538</td>
<td>252</td>
<td></td>
<td>0.0002</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>5.901</td>
<td>434</td>
<td>181</td>
<td></td>
<td>0.0001</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6.784</td>
<td>306</td>
<td>115</td>
<td></td>
<td>0.0001</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6.951</td>
<td>588</td>
<td>236</td>
<td>V</td>
<td>0.0002</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>7.542</td>
<td>491</td>
<td>86</td>
<td></td>
<td>0.0001</td>
<td>0.0089</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>8.661</td>
<td>551748</td>
<td>197526</td>
<td>V</td>
<td>0.1544</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>9.208</td>
<td>471</td>
<td>84</td>
<td></td>
<td>0.0001</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>10.846</td>
<td>121</td>
<td>44</td>
<td></td>
<td>0</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>11.508</td>
<td>189</td>
<td>28</td>
<td></td>
<td>0.0001</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>11.667</td>
<td>176</td>
<td>29</td>
<td></td>
<td>0</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>11.953</td>
<td>291</td>
<td>92</td>
<td></td>
<td>0.0001</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>12.036</td>
<td>598</td>
<td>239</td>
<td>V</td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>12.592</td>
<td>783</td>
<td>46</td>
<td>V</td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>13.013</td>
<td>2756</td>
<td>782</td>
<td></td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>13.118</td>
<td>1497</td>
<td>481</td>
<td>V</td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>13.886</td>
<td>10784</td>
<td>2914</td>
<td>V</td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>14.542</td>
<td>3583</td>
<td>60</td>
<td>V</td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>14.733</td>
<td>659</td>
<td>46</td>
<td>V</td>
<td>0.0002</td>
<td>0.0001</td>
<td></td>
</tr>
</tbody>
</table>
GC chart of mixed hydrocarbon standards (C9 - C40).
GC chart of a mixed solution of hydrocarbon standards (C9 - C40) and four carbonates, 1a-1d.
References

doi.org/10.1016/S0957-4166(02)00646-8

2. Morikawa, H.; Minamoto, M.; Gorou, Y.; Yamaguchi, J.; Morinaga, H.; Motokucho,  
doi.org/10.1007/s00289-015-1546-6

doi.org/10.1002/hlca.19580410703

doi.org/10.1002/cssc.201700898

5. Fiorani, G.; Stuck, M.; Martín, C.; Belmonte, M. M.; Martin, E.; Escudero-Adán, E.  
doi.org/10.1002/cssc.201600238

doi.org/10.1002/ajoc.201500233
