

## **Supplementary Materials**

# **Synthesis of Enantiostructured Triacylglycerols Possessing a Saturated Fatty Acid, a Polyunsaturated Fatty Acid and an Active Drug Intended as Novel Prodrugs**

**Lena Rós Jónsdóttir<sup>1</sup> and Guðmundur G. Haraldsson<sup>1\*</sup>**

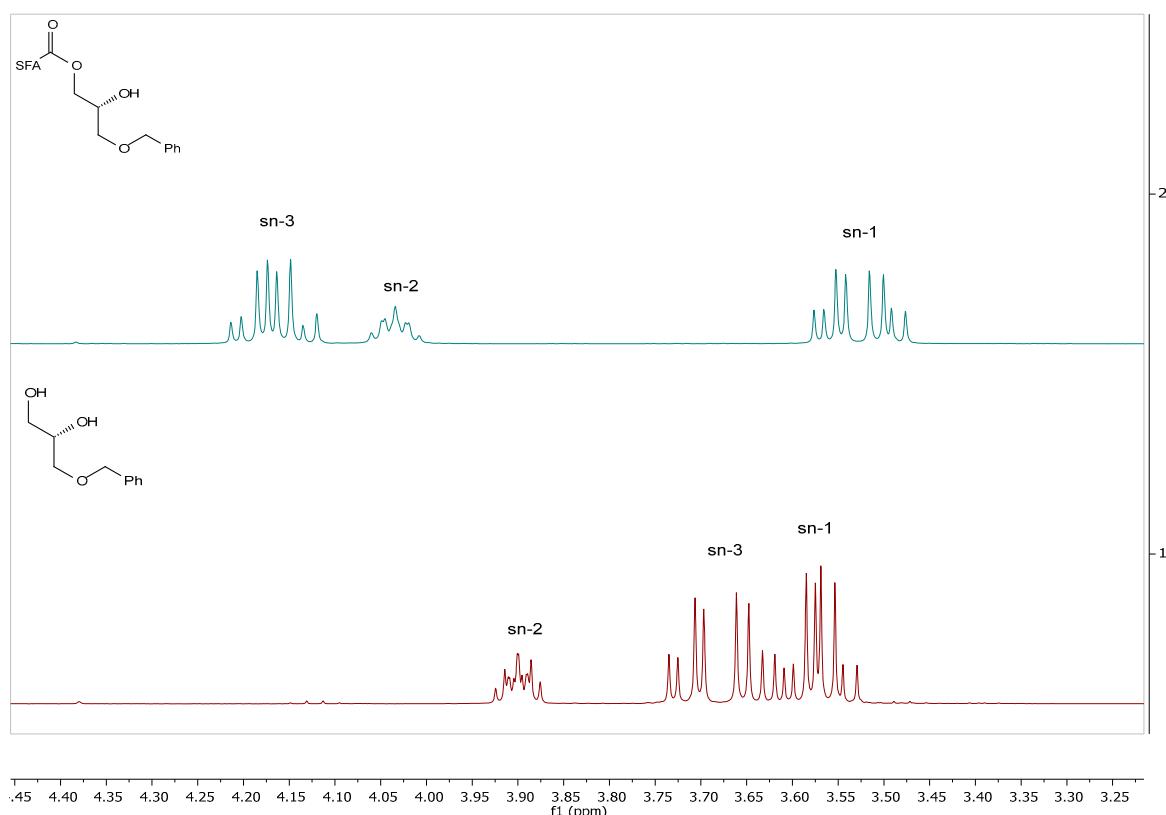
1) Science Institute, Chemistry Department, University of Iceland, Dunhaga 3, 107 Reykjavik, Iceland

## **Table of Contents**

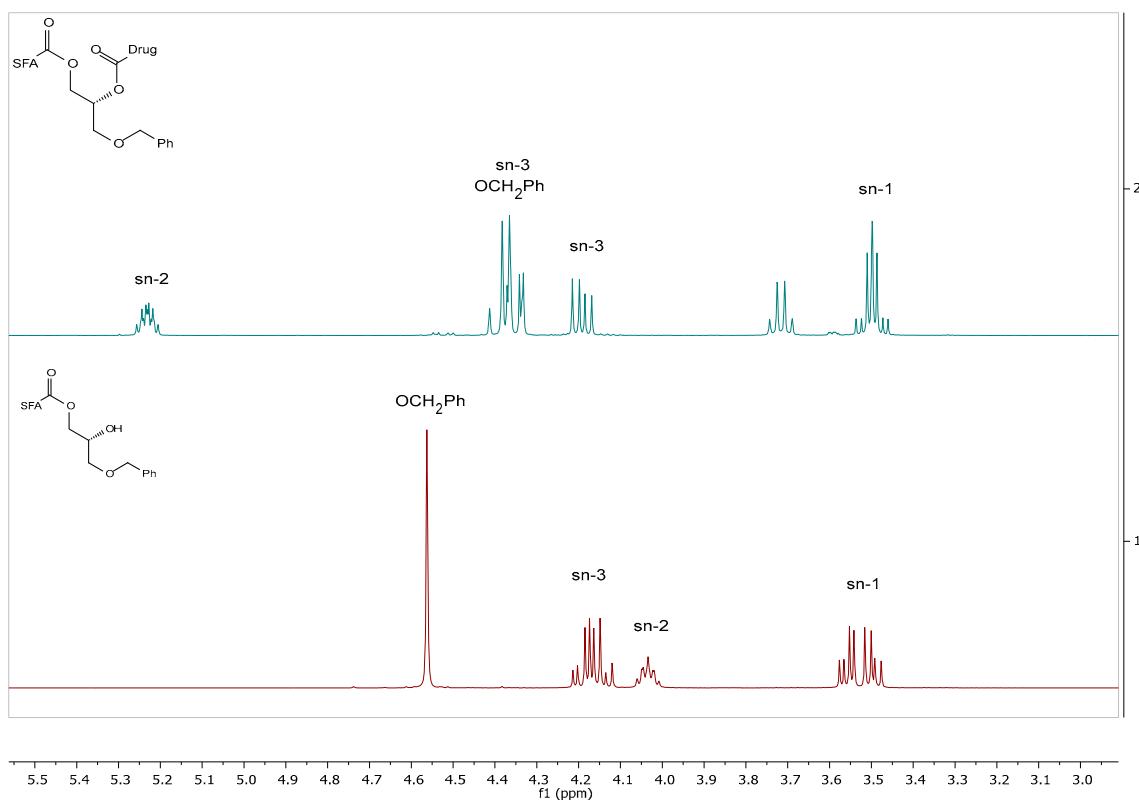
<b>Figures S1 – S4</b>	<b>S1-S4</b>
<b>Experimental Information</b>	<b>S5-S37</b>
<b>NMR Spectra</b>	<b>S38-S73</b>
Compound ( <i>R</i> )- <b>5a</b>	<b>S38</b>
Compound ( <i>S</i> )- <b>5a</b>	<b>S40</b>
Compound ( <i>R,S'</i> )- <b>6a</b>	<b>S42</b>
Compound ( <i>S,S'</i> )- <b>6a</b>	<b>S44</b>
Compound ( <i>R,S'</i> )- <b>7a</b>	<b>S46</b>
Compound ( <i>S,S'</i> )- <b>7a</b>	<b>S48</b>
Compound ( <i>R,S'</i> )- <b>8a</b>	<b>S50</b>
Compound ( <i>S,S'</i> )- <b>8a</b>	<b>S52</b>

Compound ( <i>R,S'</i> )- <b>9a</b>	S54
Compound ( <i>S,S'</i> )- <b>9a</b>	S56
Compound ( <i>S,S'</i> )- <b>10a</b>	S58
Compound ( <i>R,S'</i> )- <b>10a</b>	S60
Compound ( <i>S,S'</i> )- <b>11a</b>	S62
Compound ( <i>R,S'</i> )- <b>11a</b>	S64
Compound ( <i>S,S'</i> )- <b>12a</b>	S66
Compound ( <i>R,S'</i> )- <b>12a</b>	S68
Compound ( <i>S,S'</i> )- <b>13a</b>	S70
Compound ( <i>R,S'</i> )- <b>13a</b>	S72

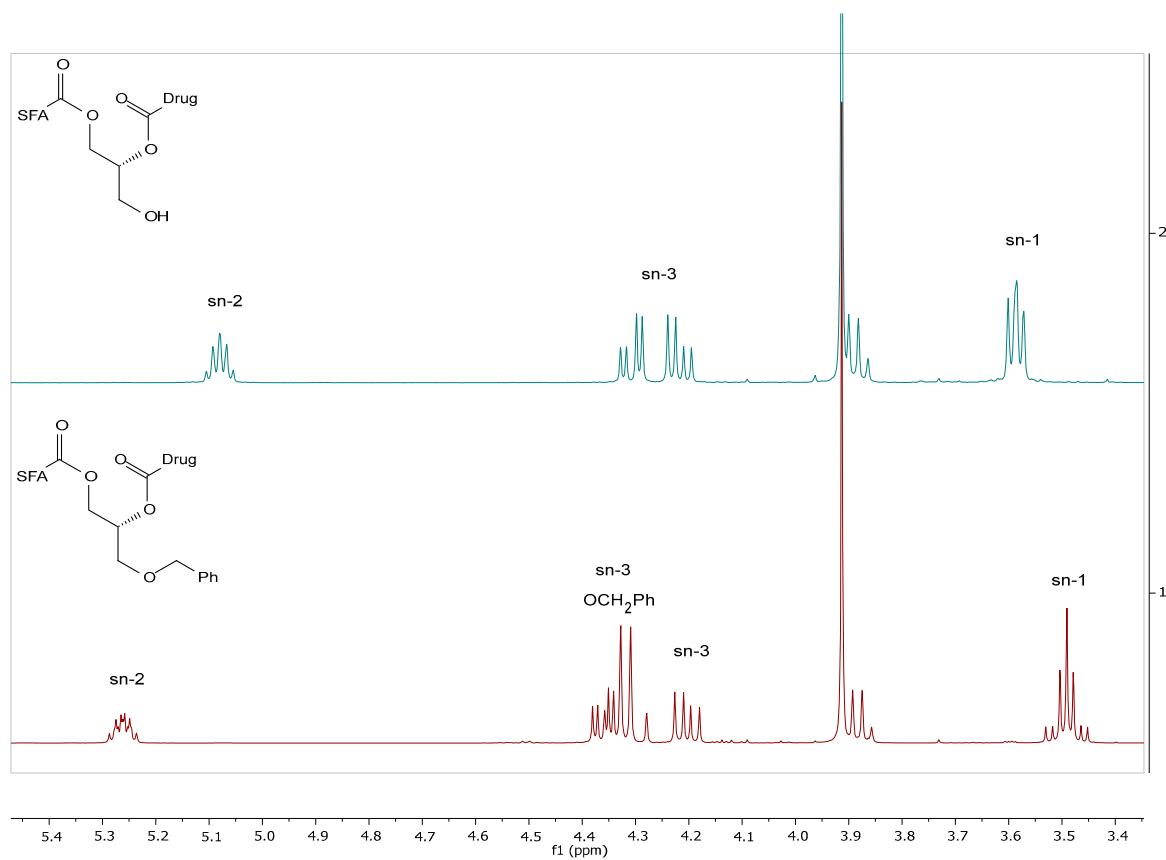
**Figures S1 – S4**



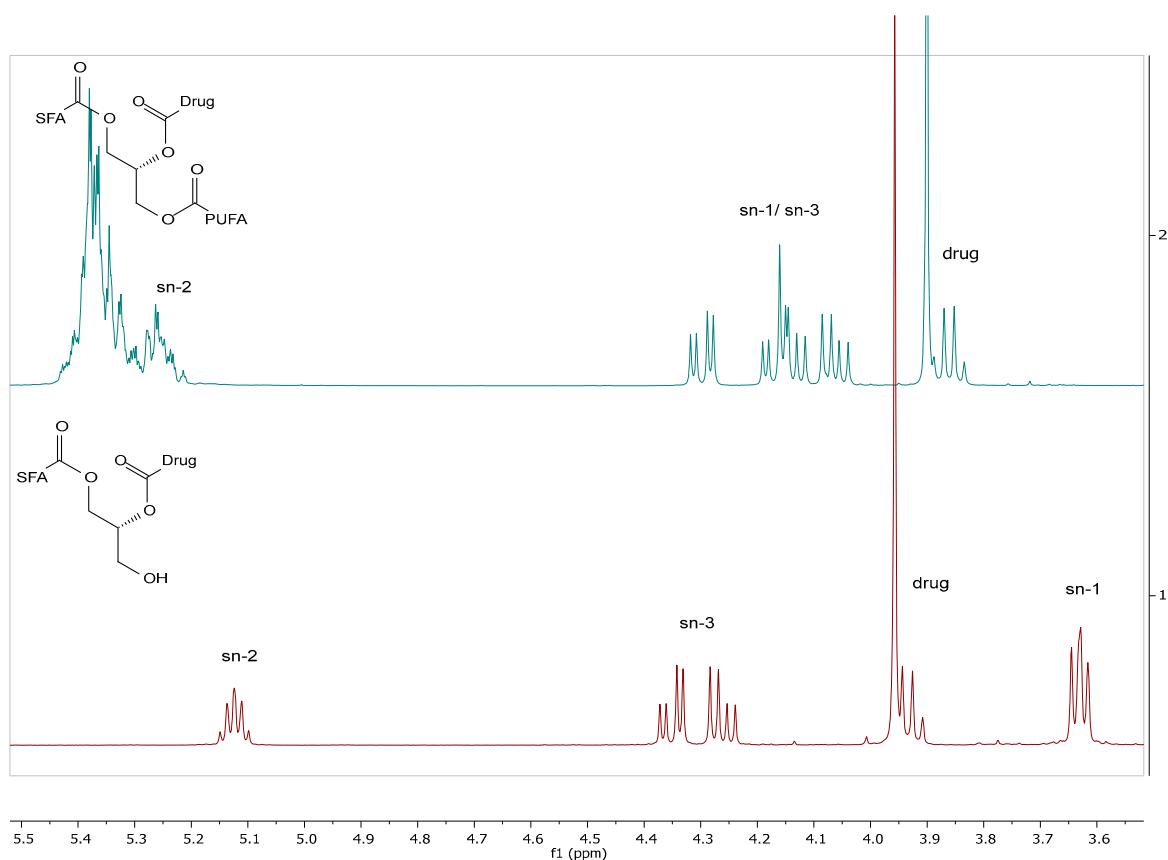
**Figure S1.** Comparison of the glyceryl proton region of the <sup>1</sup>H NMR spectra for the 1-*O*-benzyl-*sn*-glycerol starting material (bottom) and the benzyl-protected monoacylglycerol (*R*-**5a**) (top).



**Figure S2.** Comparison of the glyceryl proton region of the <sup>1</sup>H NMR spectra for (R)-5a (bottom) and (R,S')-6a possessing (S)-ibuprofen (bottom).



**Figure S3.** Comparison of the glyceryl proton region of the <sup>1</sup>H NMR spectra for (*R,S'*)-6a (bottom) and its deprotected product (*R,S'*)-8a (bottom).



**Figure S4.** Comparison of the glyceryl proton region of the <sup>1</sup>H NMR spectra for (R,S')-9c (bottom) and its product (R,S')-11c acylated with EPA (top).

## Experimental Information

### 3.2. The enzymatic coupling of the SFAs: Synthesis of (*R*)-5*b-f* and (*S*)-5*b-f*

#### 3.2.1. Synthesis of 1-O-benzyl-3-octanoyl-*sn*-glycerol, (*R*)-5*b*

The same procedure was followed as described for (*R*)-5*a* using immobilized CAL-B (18 mg), 1-O-benzyl-*sn*-glycerol (150 mg, 0.823 mmol), vinyl octanoate (160 mg, 0.940 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R*)-5*b* as a colorless liquid in 94% yield (239 mg, 0.775 mmol). [α]<sup>20</sup><sub>D</sub> = -2.22 (c. 10.1, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3459 (br), 3031 (s), 2955 (vs), 2928 (vs), 2857 (vs), 1739 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.38-7.27 (m, 5H, Ph-H), 4.56 (s, 2H, PhCH<sub>2</sub>), 4.19 (dd, J=11.5, 4.5 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.14 (dd, J=11.5, 6.0 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.06-4.01 (m, 1H, CH *sn*-2), 3.56 (dd, J=9.6, 4.4 Hz, 1H, CH<sub>2</sub> *sn*-1), 3.49 (dd, J=9.6, 6.1 Hz, 1H, CH<sub>2</sub> *sn*-1), 2.56 (bs, 1H, OH), 2.32 (t, J=7.6 Hz, 2H, CH<sub>2</sub>COO), 1.65-1.58 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.32-1.22 (m, 8H, CH<sub>2</sub>), 0.88 (t, J=6.9 Hz, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1, 137.8, 128.6 (2), 128.0, 127.9 (2), 73.6, 71.0, 69.1, 65.48, 34.3, 31.6, 29.2, 29.0, 25.0, 22.7, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>28</sub>O<sub>4</sub>Na 331.1880; found, 331.1871.

#### 3.2.2. Synthesis of 1-O-benzyl-3-decanoyl-*sn*-glycerol, (*R*)-5*c*

The same procedure was followed as described for (*R*)-5*a* using immobilized CAL-B (18 mg), 1-O-benzyl-*sn*-glycerol (150 mg, 0.823 mmol), vinyl decanoate (186 mg, 0.940 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R*)-5*c* as a colorless liquid in 97% yield (268 mg, 0.797 mmol). [α]<sup>20</sup><sub>D</sub> = -1.59 (c. 10.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3459 (br), 3031 (s), 2926 (vs), 2857 (vs), 1739 (vs), 1173 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.38-7.27 (m, 5H, Ph-H), 4.56 (s, 2H, PhCH<sub>2</sub>), 4.19 (dd, J=11.5, 4.5 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.14 (dd, J=11.5, 6.0 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.06-4.01 (m, 1H, CH *sn*-2), 3.56 (dd, J=9.6, 4.4 Hz, 1H, CH<sub>2</sub> *sn*-1), 3.55 (dd, J=9.6, 6.1 Hz, 1H, CH<sub>2</sub> *sn*-1), 2.57 (bs, 1H, OH), 2.32 (t, J=7.6 Hz, 2H, CH<sub>2</sub>COO), 1.66-1.57 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.35-1.26 (m, 12H, CH<sub>2</sub>), 0.87 (t, J=6.9 Hz, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1, 137.8, 128.6 (2), 128.0, 127.9 (2), 73.6, 71.0, 69.1, 65.5, 34.3, 32.0, 29.5 (2), 29.4, 29.3, 24.0, 22.8, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>32</sub>O<sub>4</sub>Na 359.2193; found, 359.2193.

#### 3.2.3. Synthesis of 1-O-benzyl-3-dodecanoyl-*sn*-glycerol, (*R*)-5*d*

The same procedure was followed as described for (*R*)-5*a* using immobilized CAL-B (18 mg), 1-O-benzyl-*sn*-glycerol (150 mg, 0.823 mmol), vinyl dodecanoate (213 mg, 0.940 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R*)-5*d* as a colorless liquid in 97% yield (277 mg, 0.799 mmol). [α]<sup>20</sup><sub>D</sub> = -1.91 (c. 10.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3459 (br), 3031 (s), 2925 (vs), 2854 (vs), 1739 (v), 1174 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.38-7.27 (m, 5H, Ph-H), 4.56 (s, 2H, PhCH<sub>2</sub>), 4.19 (dd, J=11.5, 4.5 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.14 (dd, J=11.5, 6.0 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.06-4.00 (m, 1H, CH *sn*-2), 3.56 (dd, J=9.6, 4.3 Hz, 1H, CH<sub>2</sub> *sn*-1), 3.50 (dd, J=9.6, 6.1 Hz, 1H, CH<sub>2</sub> *sn*-1), 2.48 (bs, 1H, OH), 2.32 (t, J=7.5 Hz, 2H, CH<sub>2</sub>COO), 1.65-1.57 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.32-1.26 (m, 16H, CH<sub>2</sub>), 0.88 (t, J=6.9 Hz, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1, 137.8, 128.6 (2), 128.0, 127.9, 73.6, 71.0, 69.1, 65.5, 34.3, 32.0, 29.7 (2), 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>36</sub>O<sub>4</sub>Na 387.2506; found, 387.2498.

#### 3.2.4. Synthesis of 1-O-benzyl-3-tetradecanoyl-*sn*-glycerol, (*R*)-5*e*

The same procedure was followed as described for (*R*)-5*a* using immobilized CAL-B (18 mg), 1-O-benzyl-*sn*-glycerol (150 mg, 0.823 mmol), vinyl tetradecanoate (239 mg, 0.940 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate

(7:3) as eluent afforded the product (*R*)-**5e** as a colorless liquid in 94% yield (304 mg, 0.774 mmol).  $[\alpha]^{20}_D = -1.31$  (c. 10.2,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3458 (br), 3064 (s), 3031 (s), 2925 (vs), 2854 (vs), 1739 (vs), 1174 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.38-7.27 (m, 5H, Ph-H), 4.56 (s, 2H, PhCH<sub>2</sub>), 4.19 (dd,  $J=11.5, 4.5$  Hz, 1H, CH<sub>2</sub> *sn*-3), 4.14 (dd,  $J=11.5, 6.0$  Hz, 1H, CH<sub>2</sub> *sn*-3), 4.06-4.00 (m, 1H, CH *sn*-2), 3.56 (dd,  $J=9.6, 4.3$  Hz, 1H, CH<sub>2</sub> *sn*-1), 3.50 (dd,  $J=9.6, 6.1$  Hz, 1H, CH<sub>2</sub> *sn*-1), 2.48 (bs, 1H, OH), 2.32 (t,  $J=7.6$  Hz, 2H, CH<sub>2</sub>COO), 1.66-1.58 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.38-1.24 (m, 20H, CH<sub>2</sub>), 0.88 (t,  $J=6.9$  Hz, 3H, CH<sub>3</sub>) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1, 137.8, 128.6 (2), 128.0, 127.9 (2), 73.7, 71.0, 69.1, 65.5, 34.3, 32.1, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{24}\text{H}_{40}\text{O}_4\text{Na}$  415.2819; found, 415.2806.

### 3.2.5. Synthesis of 1-*O*-benzyl-3-hexadecanoyl-*sn*-glycerol, (*R*)-**5f**

The same procedure was followed as described for (*R*)-**5a** using immobilized CAL-B (18 mg), 1-*O*-benzyl-*sn*-glycerol (150 mg, 0.823 mmol), vinyl hexadecanoate (266 mg, 0.940 mmol) and  $\text{CH}_2\text{Cl}_2$  (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R*)-**5f** as a colorless liquid in 94% yield (326 mg, 0.775 mmol).  $[\alpha]^{20}_D = -2.37$  (c. 10.5,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3459 (br), 3064 (s), 3031 (s), 2924 (vs), 2853 (vs), 1739 (vs), 1174 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.39-7.27 (m, 5H, Ph-H), 4.56 (s, 2H, PhCH<sub>2</sub>), 4.19 (dd,  $J=11.5, 4.5$  Hz, 1H, CH<sub>2</sub> *sn*-3), 4.14 (dd,  $J=11.5, 6.0$  Hz, 1H, CH<sub>2</sub> *sn*-3), 4.07-4.00 (m, 1H, CH *sn*-2), 3.56 (dd,  $J=9.6, 4.4$  Hz, 1H, CH<sub>2</sub> *sn*-1), 3.50 (dd,  $J=9.6, 6.1$  Hz, 1H, CH<sub>2</sub> *sn*-1), 2.51 (bs, 1H, OH), 2.32 (t,  $J=7.6$  Hz, 2H, CH<sub>2</sub>COO), 1.67-1.56 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.38-1.24 (m, 24H, CH<sub>2</sub>), 0.88 (t,  $J=6.8$  Hz, 3H, CH<sub>3</sub>) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1, 137.8, 128.6 (2), 128.0, 127.9 (2), 73.7, 71.0, 69.1, 65.5, 34.3, 32.1, 29.8 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{44}\text{O}_4\text{Na}$  443.3132; found, 443.3127.

### 3.2.6. Synthesis of 3-*O*-benzyl-1-octanoyl-*sn*-glycerol, (*S*)-**5b**

The same procedure was followed as described for (*R*)-**5a** using immobilized CAL-B (35 mg), 3-*O*-benzyl-*sn*-glycerol (284 mg, 1.54 mmol), vinyl octanoate (300 mg, 1.76 mmol) and  $\text{CH}_2\text{Cl}_2$  (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*S*)-**5b** as a colorless liquid in 95% yield (450 mg, 1.46 mmol). Spectroscopic data identical to those for (*R*)-**5b** were obtained.  $[\alpha]^{20}_D = +2.10$  (c. 1.6,  $\text{CH}_2\text{Cl}_2$ ). HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Na}$  331.1880; found, 331.1882.

### 3.2.7. Synthesis of 3-*O*-benzyl-1-decanoyl-*sn*-glycerol, (*S*)-**5c**

The same procedure was followed as described for (*R*)-**5a** using immobilized CAL-B (24 mg), 3-*O*-benzyl-*sn*-glycerol (250 mg, 1.37 mmol), vinyl decanoate (350 mg, 1.76 mmol) and  $\text{CH}_2\text{Cl}_2$  (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*S*)-**5c** as a colorless liquid in 97% yield (447 mg, 1.33 mmol). Spectroscopic data identical to those for (*R*)-**5c** were obtained.  $[\alpha]^{20}_D = +1.48$  (c. 10.0,  $\text{CH}_2\text{Cl}_2$ ). HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{32}\text{O}_4\text{Na}$  359.2193; found, 359.2193.

### 3.2.8. Synthesis of 3-*O*-benzyl-1-dodecanoyl-*sn*-glycerol, (*S*)-**5d**

The same procedure was followed as described for (*R*)-**5a** using immobilized CAL-B (20 mg), 3-*O*-benzyl-*sn*-glycerol (103 mg, 0.57 mmol), vinyl dodecanoate (163 mg, 0.72 mmol) and  $\text{CH}_2\text{Cl}_2$  (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*S*)-**5d** as a colorless liquid in 96% yield (199 mg, 0.55 mmol). Spectroscopic data identical to those for (*R*)-**5d** were obtained.  $[\alpha]^{20}_D = +1.31$  (c. 4.7,  $\text{CH}_2\text{Cl}_2$ ). HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{22}\text{H}_{36}\text{O}_4\text{Na}$  387.2506; found, 387.2499.

### 3.2.9. Synthesis of 3-O-benzyl-1-tetradecanoyl-*sn*-glycerol, (*S*)-**5e**

The same procedure was followed as described for (*R*)-**5a** using immobilized CAL-B (6 mg), 3-O-benzyl-*sn*-glycerol (50 mg, 0.27 mmol), vinyl tetradecanoate (79 mg, 0.31 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*S*)-**5e** as a colorless liquid in 94% yield (100 mg, 0.25 mmol). Spectroscopic data identical to those for (*R*)-**5e** were obtained. [α]<sup>20D</sup> = +3.64 (c. 5.0, CH<sub>2</sub>Cl<sub>2</sub>). HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>40</sub>O<sub>4</sub>Na 415.2819; found, 415.2825.

### 3.2.10. Synthesis of 3-O-benzyl-1-hexadecanoyl-*sn*-glycerol, (*S*)-**5f**

The same procedure was followed as described for (*R*)-**5a** using immobilized CAL-B (18 mg), 3-O-benzyl-*sn*-glycerol (100 mg, 0.55 mmol), vinyl hexaadecanoate (117 mg, 0.63 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL). Purification on a 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*S*)-**5f** as a colorless liquid in 87% yield (90 mg, 0.48 mmol). Spectroscopic data identical to those for (*R*)-**5f** were obtained. [α]<sup>20D</sup> = +1.11 (c. 9.0, CH<sub>2</sub>Cl<sub>2</sub>). HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>44</sub>O<sub>4</sub>Na 443.3132; found, 443.3133.

## 3.3. The coupling of the active drugs: Synthesis of (*R,S'*)-**6b-f**, (*S,S'*)-**6b-f**, (*R,S'*)-**7b-f** and (*S,S'*)-**7b-f**

### 3.3.1. Synthesis of 1-O-benzyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-3-octanoyl-*sn*-glycerol, (*R,S'*)-**6b**

The same procedure was followed as described for (*R,S'*)-**6a** using 1-O-benzyl-3-octanoyl-*sn*-glycerol (*R*)-**5b** (100 mg, 0.324 mmol), (*S*)-ibuprofen (81 mg, 0.391 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (35 mg, 0.285 mmol) and EDCI (66 mg, 0.344 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R,S'*)-**6b** as a pale-yellow oil, in 91% yield (146 mg, 0.294 mmol). [α]<sup>20D</sup> = -0.99 (c. 10.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3028 (s), 2955 (vs), 2927 (vs), 2868 (vs), 1740 (vs), 1161 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.34-7.25 (m, 3H, Ph-H), 7.21 (m, 2H, Ibu-2,6 and 2H, Ph-H), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.27-5.21 (m, 1H, CH *sn*-2), 4.42-4.34 (m, 1H, CH<sub>2</sub> *sn*-3 and 2H, PhCH<sub>2</sub>), 4.20 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.72 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 3.55-3.46 (m, 2H, CH<sub>2</sub> *sn*-1), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.26 (t, *J*=7.5 Hz, 2H, CH<sub>2</sub>COO), 1.83 (nonet, *J*=6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.64-1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.50 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.36-1.25 (m, 8H, CH<sub>2</sub>), 0.90 (t, *J*=6.8 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Ibu), 173.5 (SFA), 140.7, 137.9, 137.6, 129.4 (2), 128.5 (2), 127.8 (2), 127.6 (2), 127.3, 73.4, 70.8, 68.4, 62.8, 45.3, 45.2, 34.2, 31.8, 30.3, 29.2, 29.1, 25.0, 22.8, 22.5 (2), 18.7, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>31</sub>H<sub>44</sub>O<sub>5</sub>Na 519.3081; found, 519.3072.

### 3.3.2. Synthesis of 1-O-benzyl-3-decanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**6c**

The same procedure was followed as described for (*R,S'*)-**6a** using 1-O-benzyl-3-decanoyl-*sn*-glycerol (*R*)-**5c** (100 mg, 0.324 mmol), (*S*)-ibuprofen (74 mg, 0.358 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (32 mg, 0.261 mmol) and EDCI (60 mg, 0.315 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R,S'*)-**6c** as a pale-yellow oil, in 98% yield (154 mg, 0.293 mmol). [α]<sup>20D</sup> = -0.58 (c. 3.8, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3029 (s), 2955 (vs), 2927 (vs), 2856 (vs), 1740 (vs), 1159 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.35-7.25 (m, 3H, Ph-H), 7.23-7.17 (m, 2H, Ibu-2,6 and 2H, Ph-H), 7.06 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.27-5.19 (m, 1H, CH *sn*-2), 4.42-4.32 (m, 1H, CH<sub>2</sub> *sn*-3 and 2H, PhCH<sub>2</sub>), 4.19 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.72 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 3.54-3.45 (m, 2H, CH<sub>2</sub> *sn*-1), 2.42 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.26 (t, *J*=7.6 Hz, 2H, CH<sub>2</sub>COO), 1.82 (nonet, *J*=6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.63-1.52 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.50 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.35-1.21 (m, 12H, CH<sub>2</sub>), 0.89 (t, *J*=7.2 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Ibu), 173.5 (SFA),

140.7, 137.9, 137.6, 129.4 (2), 128.5 (2), 127.8 (2), 127.6 (2), 127.3, 73.5, 70.8, 68.4, 62.8, 45.3, 45.2, 34.25, 32.0, 30.3, 29.6, 29.4, 29.3, 25.01, 22.8 (2), 22.5, 18.7, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>33</sub>H<sub>48</sub>O<sub>5</sub>Na 547.3394; found, 547.3388.

### 3.3.3. Synthesis of 1-*O*-benzyl-3-dodecanoyl-2-[*(S)*-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**6d**

The same procedure was followed as described for (*R,S'*)-**6a** using 1-*O*-benzyl-3-dodecanoyl-*sn*-glycerol (*R*)-**5d** (100 mg, 0.289 mmol), (*S*)-ibuprofen (72 mg, 0.348 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (31 mg, 0.254 mmol) and EDCI (59 mg, 0.301 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*R,S'*)-**6d** as a pale-yellow oil, in 91% yield (141 mg, 0.262 mmol). [α]<sub>20D</sub> = -0.86 (c. 2.9, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3029 (s), 2954 (vs), 2926 (vs), 2854 (vs), 1741 (vs), 1161 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.34-7.25 (m, 3H, Ph-H), 7.23-7.17 (m, 2H, Ibu-2,6 and 2H, Ph-H), 7.07 (d, *J*=8.2 Hz, 2H, Ibu-3,5), 5.27-5.21 (m, 1H, CH *sn*-2), 4.42-4.33 (m, 1H, CH<sub>2</sub> *sn*-3 and 2H, PhCH<sub>2</sub>), 4.20 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.72 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 3.55-3.46 (m, 2H, CH<sub>2</sub> *sn*-1), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.26 (t, *J*=7.2 Hz, 2H, CH<sub>2</sub>COO), 1.83 (nonet, *J*=6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.63-1.52 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.50 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.34-1.23 (m, 16H, CH<sub>2</sub>), 0.90 (t, *J*=7.8 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Ibu), 173.5 (SFA), 140.7, 137.9, 137.6, 129.4 (2), 128.5 (2), 127.8 (2), 127.6 (2), 127.3, 73.5, 70.8, 68.4, 62.8, 45.3, 45.2, 34.3, 32.1, 30.3, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8 (2), 22.5, 18.7, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>35</sub>H<sub>52</sub>O<sub>5</sub>Na 575.3707; found, 575.3711.

### 3.3.4. Synthesis of 1-*O*-benzyl-2-[*(S)*-2-(4-isobutylphenyl)propanoyl]-3-tetradecanoyl-*sn*-glycerol, (*R,S'*)-**6e**

The same procedure was followed as described for (*R,S'*)-**6a** using 1-*O*-benzyl-3-teradecanoyl-*sn*-glycerol (*R*)-**5e** (100 mg, 0.255 mmol), (*S*)-ibuprofen (63 mg, 0.307 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (27 mg, 0.224 mmol) and EDCI (52 mg, 0.271 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R,S'*)-**6e** as a pale-yellow oil, in 95% yield (141 mg, 0.243 mmol). [α]<sub>20D</sub> = -0.93 (c. 3.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3029 (s), 2923 (vs), 2854 (vs), 1739 (vs), 1647 (vs), 1159 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.34-7.25 (m, 3H, Ph-H), 7.21 (m, 2H, Ibu-2,6 and 2H, Ph-H), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.27-5.21 (m, 1H, CH *sn*-2), 4.42-4.34 (m, 1H, CH<sub>2</sub> *sn*-3 and 2H, PhCH<sub>2</sub>), 4.20 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.72 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 3.55-3.46 (m, 2H, CH<sub>2</sub> *sn*-1), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.26 (t, *J*=7.5 Hz, 2H, CH<sub>2</sub>COO), 1.83 (nonet, *J*=6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.63-1.52 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.50 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.36-1.25 (m, 20H, CH<sub>2</sub>), 0.90 (t, *J*=6.8 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Ibu), 173.5 (SFA), 140.7, 137.9, 137.6, 129.4 (2), 128.5 (2), 127.8 (2), 127.6 (2), 127.3, 73.5, 70.8, 68.4, 62.8, 45.3, 45.2, 34.3, 32.1, 30.3, 29.83 (2), 29.81, 29.8, 29.6, 29.5, 29.4, 29.3, 25.0, 22.8 (2), 22.5, 18.7, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>37</sub>H<sub>56</sub>O<sub>5</sub>Na 603.4020; found, 603.4006.

### 3.3.5. Synthesis of 1-*O*-benzyl-3-hexadecanoyl-2-[*(S)*-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**6f**

The same procedure was followed as described for (*R,S'*)-**6a** using 1-*O*-benzyl-3-hexadecanoyl-*sn*-glycerol (*R*)-**5f** (115 mg, 0.273 mmol), (*S*)-ibuprofen (59 mg, 0.287 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (26 mg, 0.210 mmol) and EDCI (49 mg, 0.253 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*R,S'*)-**6f** as a pale-yellow oil, in 98% yield (164 mg, 0.268 mmol). [α]<sub>20D</sub> = -0.57 (c. 3.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3029 (s), 2925 (vs), 2854 (vs), 1742 (vs), 1513 (s), 1162 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.34-7.25 (m, 3H, Ph-H), 7.22-7.20 (m, 2H, Ibu-2,6 and 2H, Ph-H), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.27-5.21 (m, 1H, CH *sn*-2), 4.42-4.34 (m, 1H, CH<sub>2</sub> *sn*-3 and 2H, PhCH<sub>2</sub>), 4.20 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.72 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 3.55-3.46 (m, 2H, CH<sub>2</sub> *sn*-1), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.26 (t, *J*=7.5 Hz, 2H, CH<sub>2</sub>COO), 1.83 (nonet, *J*=6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.64-1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.50 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.36-1.25 (m, 24H, CH<sub>2</sub>), 0.90 (t, *J*=6.8 Hz, 3H,

$\text{CH}_2\text{CH}_3$ ), 0.89 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1 (Ibu), 173.5 (SFA), 140.7, 137.9, 137.6, 129.4 (2), 128.5 (2), 127.8 (2), 127.6 (2), 127.3, 73.5, 70.8, 68.4, 62.8, 45.3, 45.2, 34.3, 32.1, 30.3, 29.84, 29.81 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8 (2), 22.5, 18.7, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{39}\text{H}_{60}\text{O}_5\text{Na}$  631.4333; found, 631.4336.

### 3.3.6. Synthesis of 3-O-benzyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-1-octanoyl-sn-glycerol, (S,S')-6b

The same procedure was followed as described for (R,S')-6a using 3-O-benzyl-1-octanoyl-sn-glycerol (S)-5b (102 mg, 0.331 mmol), (S)-ibuprofen (75 mg, 0.364 mmol),  $\text{CH}_2\text{Cl}_2$  (3 mL), DMAP (35 mg, 0.286 mmol) and EDCI (67 mg, 0.350 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (S,S')-6b as a pale-yellow oil, in 95% yield (154 mg, 0.314 mmol).  $[\alpha]^{20}_{\text{D}} = +21.0$  (c. 10.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3028 (s), 2955 (vs), 2929 (vs), 2869 (vs), 1740 (vs), 1162 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.37-7.26 (m, 5H, Ph-H), 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.06 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.26-5.20 (m, 1H, CH sn-2), 4.51 (AB q,  $J=12.1$  Hz, 2H, PhCH<sub>2</sub>), 4.24 (dd,  $J=11.9$ , 3.9 Hz, 1H, CH<sub>2</sub> sn-1), 4.12 (dd,  $J=11.9$ , 6.8 Hz, 1H, CH<sub>2</sub> sn-1), 3.72 (q,  $J=7.1$  Hz, 1H, CHCH<sub>3</sub>), 3.63-3.55 (m, 2H, CH<sub>2</sub> sn-3), 2.43 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.11 (t,  $J=7.6$  Hz, 2H, CH<sub>2</sub>COO), 1.83 (nonet,  $J=6.7$  Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  and 3H, CHCH<sub>3</sub>), 1.33-1.20 (m, 8H, CH<sub>2</sub>), 0.90 (t,  $J=6.8$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.89 (d,  $J=6.6$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.0 (Ibu), 173.3 (SFA), 140.5, 137.7, 137.4, 129.2 (2), 128.4 (2), 127.7 (2), 127.6 (2), 127.1, 73.3, 70.4, 68.3, 62.5, 45.1, 45.0, 33.9, 31.7, 30.2, 29.1, 28.9, 24.7, 22.6 (2), 22.4, 18.4, 14.1 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{31}\text{H}_{44}\text{O}_5\text{Na}$  519.3081; found, 519.3072.

### 3.3.7. Synthesis of 3-O-benzyl-1-decanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol, (S,S')-6c

The same procedure was followed as described for (R,S')-6a using 3-O-benzyl-1-decanoyl-sn-glycerol (S)-5c (200 mg, 0.590 mmol), (S)-ibuprofen (132 mg, 0.640 mmol),  $\text{CH}_2\text{Cl}_2$  (5.5 mL), DMAP (64 mg, 0.520 mmol) and EDCI (121 mg, 0.630 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (S,S')-6c as a pale-yellow oil, in 81% yield (254 mg, 0.480 mmol).  $[\alpha]^{20}_{\text{D}} = +22.0$  (c. 9.5,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3028 (s), 2951 (vs), 2926 (vs), 2855 (vs), 1740 (vs), 1162 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.40-7.22 (m, 5H, Ph-H), 7.22-7.16 (m, 2H, Ibu-2,6), 7.10-7.02 (m, 2H, Ibu-3,5), 5.24 (dt,  $J=6.8$ , 5.2, 3.9 Hz, 1H, CH sn-2), 4.51 (AB q,  $J=12.1$  Hz, 2H, PhCH<sub>2</sub>), 4.26 (dd,  $J=11.8$ , 3.9 Hz, 1H, CH<sub>2</sub> sn-1), 4.12 (dd,  $J=11.8$ , 6.8 Hz, 1H, CH<sub>2</sub> sn-1), 3.73 (q,  $J=7.2$  Hz, 1H, CHCH<sub>3</sub>), 3.63-3.50 (m, 2H, CH<sub>2</sub> sn-3), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.12 (t,  $J=7.6$  Hz, 2H, CH<sub>2</sub>COO), 1.84 (nonet,  $J=6.8$  Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.55-1.39 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  and 3H, CHCH<sub>3</sub>), 1.30-1.22 (m, 12H, CH<sub>2</sub>), 0.89 (t,  $J=7.2$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.88 (d,  $J=6.6$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1 (Ibu), 173.4 (SFA), 140.6, 137.9, 137.6, 129.4 (2), 128.5 (2), 127.9 (2), 127.7 (2), 127.3, 73.4, 70.6, 68.4, 62.7, 45.2, 34.3, 32.0, 30.3 (2), 29.6, 29.4, 29.3, 25.0, 22.8 (2), 22.5, 18.5, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{33}\text{H}_{48}\text{O}_5\text{Na}$  547.3394; found, 547.3390.

### 3.3.8. Synthesis of 3-O-benzyl-1-dodecanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol, (S,S')-6d

The same procedure was followed as described for (R,S')-6a using 3-O-benzyl-1-dodecanoyl-sn-glycerol (S)-5d (150 mg, 0.411 mmol), (S)-ibuprofen (95 mg, 0.460 mmol),  $\text{CH}_2\text{Cl}_2$  (4 mL), DMAP (45 mg, 0.368 mmol) and EDCI (90 mg, 0.469 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (S,S')-6d as a pale-yellow oil, in 84% yield (191 mg, 0.346 mmol).  $[\alpha]^{20}_{\text{D}} = +19.3$  (c. 3.9,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3028 (s), 2954 (vs), 2925 (vs), 2854 (vs), 1740 (vs), 1162 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.38-7.26 (m, 5H, Ph-H), 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.06 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.26-5.20 (m, 1H, CH sn-2), 4.51 (AB q,  $J=12.1$  Hz, 2H, PhCH<sub>2</sub>), 4.24 (dd,  $J=11.8$ , 3.9 Hz, 1H, CH<sub>2</sub> sn-1), 4.12 (dd,  $J=11.8$ , 6.8 Hz, 1H, CH<sub>2</sub> sn-1), 3.72 (q,  $J=7.1$  Hz, 1H, CHCH<sub>3</sub>), 3.64-3.55 (m, 2H, CH<sub>2</sub> sn-3), 2.43 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.11 (t,  $J=7.6$  Hz, 2H, CH<sub>2</sub>COO), 1.83 (nonet,  $J=6.7$  Hz, 1H,

$CH(CH_3)_2$ , 1.48 (m, 2H,  $CH_2CH_2COO$  and 3H,  $CHCH_3$ ), 1.33-1.20 (m, 16H,  $CH_2$ ), 0.90 (t,  $J=6.9$  Hz, 3H,  $CH_2CH_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $CH(CH_3)_2$ ) ppm.  $^{13}C\{H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta_c$ : 174.0 (Ibu), 173.2 (SFA), 140.4, 137.7, 137.4, 129.5 (2), 128.4 (2), 127.9 (2), 127.6 (2), 127.1, 73.3, 70.4, 68.3, 62.5, 45.3, 45.2, 33.9, 31.8, 30.1, 29.4 (2), 29.3 (2), 29.1 (2), 24.7, 22.6 (2), 22.4, 18.4, 14.1 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $C_{35}H_{52}O_5Na$  575.3707; found, 575.3708.

### 3.3.9. Synthesis of 3-O-benzyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-1-tetradecanoyl-*sn*-glycerol, (*S,S'*)-**6e**

The same procedure was followed as described for (*R,S'*)-**6a** using 3-O-benzyl-1-tetradecanoyl-*sn*-glycerol (*S*)-**5e** (50 mg, 0.127 mmol), (*S*)-ibuprofen (30 mg, 0.145 mmol),  $CH_2Cl_2$  (2 mL), DMAP (16 mg, 0.131 mmol) and EDCI (30 mg, 0.156 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent afforded the product (*S,S'*)-**6e** as a pale-yellow oil, in 91% yield (69 mg, 0.119 mmol).  $[\alpha]^{20}_D = +17.9$  (c. 7.2,  $CH_2Cl_2$ ). IR (NaCl,  $\nu_{max}$  / cm<sup>-1</sup>): 2955 (vs), 2929 (vs), 2854 (vs), 1740 (vs), 1159 (br s).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$ : 7.34-7.25 (m, 5H, Ph-H), 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.06 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.27-5.21 (m, 1H, CH *sn*-2), 4.51 (AB q,  $J=12.1$  Hz, 2H, PhCH<sub>2</sub>), 4.24 (dd,  $J=11.8, 3.9$  Hz, 1H,  $CH_2$  *sn*-1), 4.12 (dd,  $J=11.8, 6.8$  Hz, 1H,  $CH_2$  *sn*-1), 3.72 (q,  $J=7.2$  Hz, 1H,  $CHCH_3$ ), 3.55-3.46 (m, 2H,  $CH_2$  *sn*-3), 2.43 (d,  $J=7.2$  Hz, 2H,  $CH_2CH(CH_3)_2$ ), 2.26 (t,  $J=7.5$  Hz, 2H,  $CH_2COO$ ), 1.83 (nonet,  $J=6.7$  Hz, 1H,  $CH(CH_3)_2$ ), 1.64-1.54 (m, 2H,  $CH_2CH_2COO$  and 3H,  $CHCH_3$ ), 1.36-1.25 (m, 20H,  $CH_2$ ), 0.90 (t,  $J=6.8$  Hz, 3H,  $CH_2CH_3$ ), 0.89 (d,  $J=6.6$  Hz, 6H,  $CH(CH_3)_2$ ) ppm.  $^{13}C\{H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta_c$ : 174.12 (Ibu), 173.4 (SFA), 140.6, 137.9, 137.6, 129.4 (2), 128.6 (2), 127.9 (2), 127.7 (2), 127.3, 73.5, 70.6, 68.5, 62.7, 45.2, 45.2, 34.1, 32.1, 30.3, 29.83 (2), 29.80, 29.7, 29.5, 29.4, 29.3, 24.9, 22.8 (2), 22.5, 18.5, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $C_{37}H_{56}O_5Na$  603.4020; found, 603.4009.

### 3.3.10. Synthesis of 3-O-benzyl-1-hexadecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**6f**

The same procedure was followed as described for (*R,S'*)-**6a** using 3-O-benzyl-1-hexadecanoyl-*sn*-glycerol (*S*)-**5f** (45 mg, 0.107 mmol), (*S*)-ibuprofen (24 mg, 0.118 mmol),  $CH_2Cl_2$  (1 mL), DMAP (12 mg, 0.094 mmol) and EDCI (22 mg, 0.113 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*S,S'*)-**6f** as a pale-yellow oil, in 84% yield (55 mg, 0.090 mmol).  $[\alpha]^{20}_D = +11.6$  (c. 5.0,  $CH_2Cl_2$ ). IR (NaCl,  $\nu_{max}$  / cm<sup>-1</sup>): 3028 (s), 2955 (vs), 2924 (vs), 2854 (vs), 1740 (vs), 1686 (s, 1163 (br s).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$ : 7.37-7.25 (m, 5H, Ph-H), 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.06 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.27-5.19 (m, 1H, CH *sn*-2), 4.51 (AB q,  $J=12.1$  Hz, 2H, PhCH<sub>2</sub>), 4.25 (dd,  $J=11.8, 3.9$  Hz, 1H,  $CH_2$  *sn*-1), 4.13 (dd,  $J=11.8, 6.8$  Hz, 1H,  $CH_2$  *sn*-1), 3.72 (q,  $J=7.2$  Hz, 1H,  $CHCH_3$ ), 3.64-3.55 (m, 2H,  $CH_2$  *sn*-3), 2.43 (d,  $J=7.2$  Hz, 2H,  $CH_2CH(CH_3)_2$ ), 2.11 (t,  $J=7.5$  Hz, 2H,  $CH_2COO$ ), 1.83 (nonet,  $J=6.7$  Hz, 1H,  $CH(CH_3)_2$ ), 1.55-1.46 (m, 2H,  $CH_2CH_2COO$  and 3H,  $CHCH_3$ ), 1.36-1.25 (m, 24H,  $CH_2$ ), 0.90 (t,  $J=6.8$  Hz, 3H,  $CH_2CH_3$ ), 0.89 (d,  $J=6.6$  Hz, 6H,  $CH(CH_3)_2$ ) ppm.  $^{13}C\{H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta_c$ : 174.2 (Ibu), 173.4 (SFA), 140.6, 137.9, 137.6, 129.4 (2), 128.6 (2), 127.9 (2), 127.7 (2), 127.3, 73.5, 70.6, 68.5, 62.7, 45.5, 45.2, 34.1, 32.1, 30.3, 29.84 (2), 29.81 (2), 29.78, 29.7, 29.5, 29.4, 29.3, 24.9, 22.8 (2), 22.5, 18.5, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $C_{39}H_{60}O_5Na$  631.4333; found, 631.4332.

### 3.3.11. Synthesis of 1-O-benzyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-octanoyl-*sn*-glycerol, (*R,S'*)-**7b**

The same procedure was followed as described for (*R,S'*)-**7a** using 1-O-benzyl-3-octanoyl-*sn*-glycerol (*R*)-**5b** (109 mg, 0.353 mmol), (*S*)-naproxen (90 mg, 0.391 mmol),  $CH_2Cl_2$  (3 mL), DMAP (35 mg, 0.285 mmol) and EDCI (66 mg, 0.344 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent afforded the product (*R,S'*)-**7b** as a pale-yellow oil, in 95% yield (175 mg, 0.336 mmol).  $[\alpha]^{20}_D = -3.02$  (c. 17.5,  $CH_2Cl_2$ ). IR (NaCl,  $\nu_{max}$  / cm<sup>-1</sup>): 3031 (vs), 2955 (vs), 2931 (vs), 2857 (vs), 1739 (vs), 1634 (vs), 1607 (vs), 1175 (br s).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$ : 7.68-7.66 (m, 3H, H-1,4,8 Nap), 7.41 (dd,  $J=8.5, 1.7$  Hz, 1H, H-3 Nap), 7.25-7.19 (m, 3H, Ph-H), 7.14 (dd,  $J=8.9, 2.6$  Hz, 1H, H-7 Nap), 7.12-

7.09 (m, 2H, Ph-H and 1H, Nap-5), 5.30-5.23 (m, 1H, CH *sn*-2), 4.36-4.28 (m, 1H, CH<sub>2</sub> *sn*-3 and 2H, PhCH<sub>2</sub>), 4.21 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.89 (q, *J*=7.2, 1H, CHCH<sub>3</sub>), 3.54-3.44 (m, 2H, CH<sub>2</sub> *sn*-1), 2.22 (t, *J*=7.2 Hz, 2H, CH<sub>2</sub>COO), 1.60-1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO and 3H, CHCH<sub>3</sub>), 1.33-1.21 (m, 8H, CH<sub>2</sub>), 0.90 (t, *J*=6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.0 (Nap), 173.5 (SFA), 157.8, 137.8, 135.6, 133.8, 129.4, 129.1, 128.4 (2), 127.7, 127.5 (2), 127.2, 126.3, 126.1, 119.1, 105.7, 73.4, 70.9, 68.4, 62.7, 55.4, 45.6, 34.2, 31.8, 29.2, 29.0, 25.0, 22.7, 18.6, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>40</sub>O<sub>6</sub>Na 543.2717; found, 543.2720.

### 3.3.12. Synthesis of 1-O-benzyl-3-decanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-7c

The same procedure was followed as described for (*R,S'*)-7a using 1-O-benzyl-3-decanoyl-*sn*-glycerol (*R*)-5c (100 mg, 0.297 mmol), (*S*)-naproxen (82 mg, 0.358 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (32 mg, 0.261 mmol) and EDCI (60 mg, 0.315 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent followed by recrystallization from n-hexane afforded the product (*R,S'*)-7c as very fine white needles, in 96% yield (157 mg, 0.286 mmol). Mp. 37.4-37.8°C. [α]<sup>20</sup><sub>D</sub> = -3.23 (c. 3.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3061 (s), 3031 (s), 2923 (vs), 2854 (vs), 1732 (vs), 1634 (vs), 1607 (vs), 1184 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.68-7.66 (m, 3H, H-1,4,8 Nap), 7.41 (dd, *J*=8.5, 1.7 Hz, 1H, H-3 Nap), 7.25-7.19 (m, 3H, Ph-H), 7.14 (dd, *J*=8.9, 2.6 Hz, 1H, H-7 Nap), 7.11-7.09 (m, 2H, Ph-H and 1H, Nap-5), 5.30-5.23 (m, 1H, CH *sn*-2), 4.36 (dd, *J*=11.9, 3.8 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.36-4.28 (m, 2H, PhCH<sub>2</sub>), 4.21 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.89 (q, *J*=7.2, 1H, CHCH<sub>3</sub>), 3.54-3.44 (m, 2H, CH<sub>2</sub> *sn*-1), 2.22 (t, *J*=7.7 Hz, 2H, CH<sub>2</sub>COO), 1.60-1.53 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.59 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.33-1.21 (m, 12H, CH<sub>2</sub>), 0.90 (t, *J*=6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Nap), 173.5 (SFA), 157.8, 137.8, 135.6, 133.9, 129.4, 129.1, 128.4 (2), 127.7, 127.5 (2), 127.2, 126.4, 126.1, 119.1, 105.7, 73.4, 70.9, 68.4, 62.7, 55.4, 45.6, 34.2, 32.0, 29.6 (2), 29.4, 29.3, 25.0, 22.8, 18.6, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>34</sub>H<sub>44</sub>O<sub>6</sub>Na 571.3030; found, 571.3026.

### 3.3.13. Synthesis of 1-O-benzyl-3-dodecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-7d

The same procedure was followed as described for (*R,S'*)-7a using 1-O-benzyl-3-dodecanoyl-*sn*-glycerol (*R*)-5d (100 mg, 0.289 mmol), (*S*)-naproxen (80 mg, 0.348 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (31 mg, 0.254 mmol) and EDCI (59 mg, 0.307 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent followed by recrystallization from n-hexane afforded the product (*R,S'*)-7d as very fine white needles, in 92% yield (148 mg, 0.265 mmol). Mp. 36.5-37.1°C. [α]<sup>20</sup><sub>D</sub> = -2.00 (c. 4.3, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 2917 (vs), 2851 (vs), 1742 (vs), 1720 (vs), 1606 (vs), 1184 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.68-7.66 (m, 3H, H-1,4,8 Nap), 7.41 (dd, *J*=8.5, 1.7 Hz, 1H, H-3 Nap), 7.25-7.19 (m, 3H, Ph-H), 7.14 (dd, *J*=8.9, 2.6 Hz, 1H, H-7 Nap), 7.11-7.09 (m, 2H, Ph-H and 1H, Nap-5), 5.30-5.23 (m, 1H, CH *sn*-2), 4.36 (dd, *J*=11.9, 3.8 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.36-4.28 (m, 2H, PhCH<sub>2</sub>), 4.21 (dd, *J*=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.89 (q, *J*=7.1, 1H, CHCH<sub>3</sub>), 3.54-3.44 (m, 2H, CH<sub>2</sub> *sn*-1), 2.22 (t, *J*=7.5 Hz, 2H, CH<sub>2</sub>COO), 1.60-1.53 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.59 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.33-1.21 (m, 16H, CH<sub>2</sub>), 0.90 (t, *J*=6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Nap), 173.5 (SFA), 157.8, 137.8, 135.6, 133.9, 129.4, 129.1, 128.4 (2), 127.7, 127.5 (2), 127.2, 126.4, 126.1, 119.1, 105.7, 73.4, 70.9, 68.4, 62.7, 55.4, 45.6, 34.2, 32.1, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8, 18.6, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>36</sub>H<sub>48</sub>O<sub>6</sub>Na 599.3343; found, 599.3349.

### 3.3.14. Synthesis of 1-O-benzyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-tetradecanoyl-*sn*-glycerol, (*R,S'*)-7e

The same procedure was followed as described for (*R,S'*)-**7a** using 1-*O*-benzyl-3-tetradecanoyl-*sn*-glycerol (*R*)-**5e** (100 mg, 0.255 mmol), (*S*)-naproxen (71 mg, 0.307 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.6 mL), DMAP (27 mg, 0.224 mmol) and EDCI (52 mg, 0.271 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent followed by recrystallization from n-hexane afforded the product (*R,S'*)-**7e** as very fine white powder, in 98% yield (151 mg, 0.250 mmol). Mp. 45.8-46.5°C. [α]<sub>D</sub><sup>20</sup> = -1.33 (c. 4.5, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 2917 (vs), 2850 (vs), 1742 (vs), 1723 (vs), 1605 (s), 1157 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.68-7.66 (m, 3H, H-1,4,8 Nap), 7.41 (dd, J=8.5, 1.6 Hz, 1H, H-3 Nap), 7.25-7.19 (m, 3H, Ph-H), 7.14 (dd, J=8.9, 2.6 Hz, 1H, H-7 Nap), 7.11-7.08 (m, 2H, Ph-H and 1H, Nap-5), 5.32-5.24 (m, 1H, CH *sn*-2), 4.36 (dd, J=11.9, 3.8 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.36-4.28 (m, 2H, PhCH<sub>2</sub>), 4.21 (dd, J=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.89 (q, J=7.1, 1H, CHCH<sub>3</sub>), 3.54-3.44 (m, 2H, CH<sub>2</sub> *sn*-1), 2.22 (t, J=7.5 Hz, 2H, CH<sub>2</sub>COO), 1.60-1.53 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.59 (d, J=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.33-1.21 (m, 20H, CH<sub>2</sub>), 0.90 (t, J=6.8 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Nap), 173.5 (SFA), 157.8, 137.8, 135.6, 133.9, 129.4, 129.1, 128.4 (2), 127.7, 127.5 (2), 127.3, 126.4, 126.1, 119.1, 105.7, 73.4, 70.9, 68.4, 62.7, 55.4, 45.6, 34.2, 32.1, 29.8 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8, 18.6, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>38</sub>H<sub>52</sub>O<sub>6</sub>Na 627.3656; found, 627.3647.

### 3.3.15. Synthesis of 1-*O*-benzyl-3-hexadecanoyl-2-[*(S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**7f**

The same procedure was followed as described for (*R,S'*)-**7a** using 1-*O*-benzyl-3-hexadecanoyl-*sn*-glycerol (*R*)-**5e** (100 mg, 0.238 mmol), (*S*)-naproxen (66 mg, 0.287 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL), DMAP (26 mg, 0.210 mmol) and EDCI (49 mg, 0.253 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent followed by recrystallization from n-hexane afforded the product (*R,S'*)-**7f** as very fine white powder, in 96% yield (145 mg, 0.229 mmol). Mp. 50.6-51.6°C. [α]<sub>D</sub><sup>20</sup> = -2.00 (c. 3.3, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 2917 (vs), 2849 (vs), 1743 (vs), 1727 (vs, 1634, 1605 (vs), 1156 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.68-7.66 (m, 3H, H-1,4,8 Nap), 7.41 (dd, J=8.5, 1.7 Hz, 1H, H-3 Nap), 7.25-7.19 (m, 3H, Ph-H), 7.14 (dd, J=8.9, 2.6 Hz, 1H, H-7 Nap), 7.11-7.08 (m, 2H, Ph-H and 1H, Nap-5), 5.30-5.23 (m, 1H, CH *sn*-2), 4.36 (dd, J=11.9, 3.8 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.36-4.28 (m, 2H, PhCH<sub>2</sub>), 4.21 (dd, J=11.9, 6.6 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.89 (q, J=7.1, 1H, CHCH<sub>3</sub>), 3.54-3.44 (m, 2H, CH<sub>2</sub> *sn*-1), 2.22 (t, J=7.8 Hz, 2H, CH<sub>2</sub>COO), 1.60-1.53 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.59 (d, J=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.33-1.21 (m, 24H, CH<sub>2</sub>), 0.90 (t, J=6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.1 (Nap), 173.5 (SFA), 157.8, 137.8, 135.6, 133.85, 129.4, 129.1, 128.4 (2), 127.7, 127.5 (2), 127.2, 126.4, 126.1, 119.1, 105.7, 73.4, 70.9, 68.4, 62.7, 55.4, 45.6, 34.2, 32.1, 29.9 (2), 29.8 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8, 18.6, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>40</sub>H<sub>56</sub>O<sub>6</sub>Na 655.3969; found, 655.3960.

### 3.3.16. Synthesis of 3-*O*-benzyl-2-[*(S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-octanoyl-*sn*-glycerol, (*S,S'*)-**7b**

To a solution of 3-*O*-benzyl-1-octanoyl-*sn*-glycerol (*S*)-**5b** (100 mg, 0.324 mmol) and (*S*)-naproxen (82 mg, 0.357 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) were added DMAP (35 mg, 0.285 mmol) and EDCI (66 mg, 0.344 mmol). The solution was stirred on a magnetic stirrer at room temperature for 31 h. The reaction was disconnected by passing the reaction mixture through a short column packed with silica gel by use of Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> (1:9). The solvent was removed in vacuo on a rotary evaporator. The concentrate was applied to a silica gel chromatography using petroleum ether/ethyl acetate (8.5:1.5) as eluent, which afforded the product (*S,S'*)-**7b** as a clear oil, in 97% yield (164 mg, 0.314 mmol). [α]<sub>D</sub><sup>20</sup> = +4.82 (c. 3.2, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3030 (s), 2931 (vs), 2857 (vs), 1739 (vs), 1634 (vs), 1162 (br s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.73-7.63 (m, 3H, H-1,4,8 Nap), 7.41 (dd, J=8.6, 1.8 Hz, 1H, H-3 Nap), 7.37-7.26 (m, 5H, Ph-H), 7.14 (dd, J=8.9, 2.5 Hz, 1H, H-7 Nap), 7.10 (d, J=2.5 Hz, 1H, Nap-5), 5.26-5.20 (m, 1H, CH *sn*-2), 4.51 (AB q, J=12.1 Hz, 2H, PhCH<sub>2</sub>), 4.24 (dd, J=11.9, 3.7 Hz, 1H, CH<sub>2</sub> *sn*-1), 4.12 (dd, J=11.9, 6.9 Hz, 1H, CH<sub>2</sub> *sn*-1), 3.91 (s, 3H, OCH<sub>3</sub>), 3.72 (q, J=7.1, 1H, CHCH<sub>3</sub>), 3.61-3.59 (m, 2H, CH<sub>2</sub> *sn*-3), 1.94-1.87 (m, 2H, CH<sub>2</sub>COO), 1.58 (d, J=7.2 Hz, 3H,

$\text{CHCH}_3$ ), 1.40-1.31 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.23-1.05 (m, 8H,  $\text{CH}_2$ ), 0.85 (t,  $J=7.2$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.0 (Nap), 173.3 (SFA), 157.8, 137.8, 135.6, 133.8, 129.4, 129.1, 128.5 (2), 127.9, 127.7 (2), 127.2, 126.4, 126.1, 119.1, 105.7, 73.4, 70.7, 68.5, 62.6, 55.4, 45.6, 33.8, 31.3, 29.5, 29.4, 24.4, 22.4, 18.5, 14.1 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{32}\text{H}_{40}\text{O}_6\text{Na}$  543.2717; found, 543.2720.

### 3.3.17. Synthesis of 3-O-benzyl-1-decanoyl-2-[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (S,S')-7c

The same procedure was followed as described for (S,S')-7b using 3-O-benzyl-1-decanoyl-*sn*-glycerol (S)-5c (102 mg, 0.297 mmol), (S)-naproxen (75 mg, 0.327 mmol),  $\text{CH}_2\text{Cl}_2$  (10.0 mL), DMAP (32 mg, 0.261 mmol) and EDCI (65 mg, 0.356 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (R,S')-7c as a clear oil, in 92% yield (151 mg, 0.273 mmol).  $[\alpha]^{20}_{\text{D}} = +6.69$  (c. 3.0,  $\text{CH}_2\text{Cl}_2$ ). IR ( $\text{NaCl}$ ,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 2945 (vs), 2927 (vs), 2855 (vs), 1739 (vs), 1634 (s), 1607 (s), 1177 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.73-7.63 (m, 3H, H-1,4,8 Nap), 7.41 (dd,  $J=8.6$ , 1.8 Hz, 1H, H-3 Nap), 7.37-7.26 (m, 5H, Ph-H), 7.14 (dd,  $J=8.9$ , 2.5 Hz, 1H, H-7 Nap), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.26-5.20 (m, 1H, CH *sn*-2), 4.51 (AB q,  $J=12.1$  Hz, 2H,  $\text{PhCH}_2$ ), 4.23 (dd,  $J=11.9$ , 3.7 Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.12 (dd,  $J=11.9$ , 6.9 Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.88 (q,  $J=7.1$ , 1H,  $\text{CHCH}_3$ ), 3.61-3.59 (m, 2H,  $\text{CH}_2$  *sn*-3), 1.94-1.87 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.58 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.40-1.31 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.28-1.12 (m, 12H,  $\text{CH}_2$ ), 0.85 (t,  $J=7.2$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1 (Nap), 173.4 (SFA), 157.8, 137.8, 135.6, 133.8, 129.4, 129.1, 128.5 (2), 127.9, 127.7 (2), 127.2, 126.4, 126.1, 119.1, 105.7, 73.5, 70.7, 68.5, 62.6, 55.4, 45.6, 33.9, 32.0, 29.6, 29.4, 29.2, 24.8, 22.8, 18.5, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{34}\text{H}_{44}\text{O}_6\text{Na}$  571.3030; found, 571.3032.

### 3.3.18. Synthesis of 3-O-benzyl-1-dodecanoyl-2-[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (S,S')-7d

The same procedure was followed as described for (S,S')-7b using 3-O-benzyl-1-dodecanoyl-*sn*-glycerol (S)-5d (41 mg, 0.112 mmol), (S)-naproxen (30 mg, 0.130 mmol),  $\text{CH}_2\text{Cl}_2$  (2 mL), DMAP (13 mg, 0.106 mmol) and EDCI (25 mg, 0.130 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent followed by recrystallization from n-hexane afforded the product (S,S')-7d as very fine white needles, in 92% yield (148 mg, 0.265 mmol). Mp. 34.1-34.6°C.  $[\alpha]^{20}_{\text{D}} = +17.1$  (c. 5.8,  $\text{CH}_2\text{Cl}_2$ ). IR ( $\text{NaCl}$ ,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3009 (vs), 2982 (vs), 2948 (vs), 2917 (vs), 2848 (vs), 2804 (vs), 1734 (vs), 1631 (s), 1605 (s), 1083 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.70-7.63 (m, 3H, H-1,4,8 Nap), 7.41 (dd,  $J=8.6$ , 1.8 Hz, 1H, H-3 Nap), 7.37-7.27 (m, 5H, Ph-H), 7.14 (dd,  $J=8.9$ , 2.5 Hz, 1H, H-7 Nap), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.26-5.20 (m, 1H, CH *sn*-2), 4.51 (AB q,  $J=12.1$  Hz, 2H,  $\text{PhCH}_2$ ), 4.24 (dd,  $J=11.9$ , 3.7 Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.13 (dd,  $J=11.9$ , 6.9 Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.88 (q,  $J=7.1$ , 1H,  $\text{CHCH}_3$ ), 3.61-3.59 (m, 2H,  $\text{CH}_2$  *sn*-3), 2.02-1.87 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.58 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.40-1.31 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.28-1.05 (m, 16H,  $\text{CH}_2$ ), 0.85 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1 (Nap), 173.4 (SFA), 157.8, 137.8, 135.5, 133.8, 129.4, 129.0, 128.5 (2), 127.9, 127.7 (2), 127.5, 127.2, 126.0, 119.1, 105.7, 73.4, 70.7, 68.5, 62.6, 55.4, 45.5, 33.9, 32.0, 29.8 (2), 29.6, 29.5, 29.4, 29.2, 24.7, 22.8, 18.5, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{36}\text{H}_{48}\text{O}_6\text{Na}$  599.3343; found, 599.3334.

### 3.3.19. Synthesis of 3-O-benzyl-2-[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-tetradecanoyl-*sn*-glycerol, (S,S')-7e

The same procedure was followed as described for (S,S')-7b using 1-O-benzyl-3-tetradecanoyl-*sn*-glycerol (S)-5e (50 mg, 0.127 mmol), (S)-naproxen (34 mg, 0.147 mmol),  $\text{CH}_2\text{Cl}_2$  (2.3 mL), DMAP (15 mg, 0.121 mmol) and EDCI (28 mg, 0.145 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent followed by recrystallization from n-hexane afforded the product (S,S')-7e as very fine white needles, in 75% yield (57 mg, 0.095 mmol). Mp. 45.2-45.9°C.  $[\alpha]^{20}_{\text{D}} = +15.3$  (c. 5.2,

$\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  /  $\text{cm}^{-1}$ ): 2952 (vs), 2913 (vs), 2869 (vs), 2848 (vs), 1732 (vs), 1631, 1604 (s), 1115 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.70-7.63 (m, 3H, H-1,4,8 Nap), 7.41 (dd,  $J=8.6$ , 1.8 Hz, 1H, H-3 Nap), 7.37-7.27 (m, 5H, Ph-H), 7.14 (dd,  $J=8.9$ , 2.5 Hz, 1H, H-7 Nap), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.26-5.20 (m, 1H, CH *sn*-2), 4.51 (AB q,  $J=12.1$  Hz, 2H, PhCH<sub>2</sub>), 4.24 (dd,  $J=11.9$ , 3.7 Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.13 (dd,  $J=11.9$ , 6.9 Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.91 (s, 3H, OCH<sub>3</sub>), 3.88 (q,  $J=7.1$ , 1H, CHCH<sub>3</sub>), 3.61-3.59 (m, 2H,  $\text{CH}_2$  *sn*-3), 2.02-1.87 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.58 (d,  $J=7.2$  Hz, 3H, CHCH<sub>3</sub>), 1.42-1.31 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.28-1.05 (m, 20H,  $\text{CH}_2$ ), 0.85 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1 (Nap), 173.4 (SFA), 157.6, 137.7, 135.4, 133.7, 129.2, 129.0, 128.5 (2), 127.9, 127.7 (2), 127.5, 127.2, 126.0, 119.1, 105.7, 73.4, 70.7, 68.45, 62.6, 55.4, 45.5, 33.9, 32.0, 29.8 (2), 29.6, 29.5, 29.4, 29.2, 24.7, 22.8, 18.5, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{38}\text{H}_{52}\text{O}_6\text{Na}$  627.3656; found, 627.3635.

### 3.3.20. Synthesis of 3-*O*-benzyl-1-hexadecanoyl-2-[*(S)*-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-7f

The same procedure was followed as described for (*S,S'*)-7b using 3-*O*-benzyl-1-hexadecanoyl-*sn*-glycerol (*R*)-5f (45 mg, 0.107 mmol), (*S*)-naproxen (27 mg, 0.118 mmol),  $\text{CH}_2\text{Cl}_2$  (1 mL), DMAP (12 mg, 0.094 mmol) and EDCI (22 mg, 0.113 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent followed by recrystallization from n-hexane afforded the product (*S,S'*)-7f as a very fine white powder, in 77% yield (52 mg, 0.082 mmol).  $[\alpha]^{20\text{D}} = +15.3$  (c. 5.2,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  /  $\text{cm}^{-1}$ ): 2916 (vs), 2850 (vs), 1732 (vs), 1631 (s), 1605 (s), 1161 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.70-7.62 (m, 3H, H-1,4,8 Nap), 7.40 (dd,  $J=8.6$ , 1.8 Hz, 1H, H-3 Nap), 7.35-7.27 (m, 5H, Ph-H), 7.13 (dd,  $J=8.9$ , 2.5 Hz, 1H, H-7 Nap), 7.11 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.30-5.16 (m, 1H, CH *sn*-2), 4.51 (AB q,  $J=12.1$  Hz, 2H, PhCH<sub>2</sub>), 4.22 (dd,  $J=11.9$ , 3.8 Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.12 (dd,  $J=11.9$ , 6.8 Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.90 (s, 3H, OCH<sub>3</sub>), 3.89 (q,  $J=7.1$ , 1H, CHCH<sub>3</sub>), 3.50 (m, 2H,  $\text{CH}_2$  *sn*-3), 2.22 (t,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.57 (d,  $J=6.9$  Hz, 3H, CHCH<sub>3</sub>), 1.53-1.51 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.38-1.30 (m, 24H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1 (Nap), 173.4 (SFA), 157.8, 137.6, 135.6, 133.8, 129.4, 129.1, 128.5 (2), 127.9, 127.7 (2), 127.2, 126.4, 126.1, 119.1, 105.7, 73.5, 70.7, 68.5, 62.6, 55.4, 45.6, 33.9, 32.1, 29.8 (2), 29.6 (2), 29.4, 29.2, 24.8, 22.8, 18.5, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{40}\text{H}_{56}\text{O}_6\text{Na}$  655.3969; found, 655.3962.

### 3.4. The removal of the benzyl protective group: Synthesis of (*R,S'*)-8b-f, (*S,S'*)-8b-f, (*R,S'*)-9b-f and (*S,S'*)-9b-f

#### 3.4.1. Synthesis of 2-[*(S)*-2-(4-isobutylphenyl)propanoyl]-3-octanoyl-*sn*-glycerol, (*R,S'*)-8b

The same procedure was followed as described for (*R,S'*)-8a using Pd/C catalyst (26 mg), 1-*O*-benzyl-3-octanoyl-2-[*(S)*-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-6b (116 mg, 0.236 mmol), THF (7 mL) and n-hexane (11.2 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, afforded the product (*R,S'*)-8b as a pale-yellow oil, in 86% yield (77 mg, 0.203 mmol).  $[\alpha]^{20\text{D}} = +18.3$  (c. 2.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.07-5.03 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9$ , 4.5 Hz, 1H,  $\text{CH}_2$  *sn*-3), 4.20 (dd,  $J=11.9$ , 5.9 Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.73 (q,  $J=7.1$  Hz, 1H, CHCH<sub>3</sub>), 3.60-3.57 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.29 (t,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.84 (nonet,  $J=6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.64-1.54 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.2$  Hz, 3H, CHCH<sub>3</sub>), 1.32-1.24 (m, 8H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Ibu), 173.8 (SFA), 141.0, 137.8, 129.6 (2), 127.2 (2), 72.7, 62.1, 61.6, 45.3, 45.1, 34.2, 31.8, 30.3, 29.2, 29.1, 25.0, 22.7 (2), 22.5, 18.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{24}\text{H}_{38}\text{O}_5\text{Na}$  429.2611; found, 429.2608.

#### 3.4.2. Synthesis of 3-decanoyl-2-[*(S)*-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-8c

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (25 mg), 1-*O*-benzyl-3-decanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**6c** (116 mg, 0.224 mmol), THF (6.4 mL) and n-hexane (10.5 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent, afforded the product (*R,S'*)-**8c** as a pale-yellow oil, in 98% yield (94 mg, 0.216 mmol).  $[\alpha]^{20}_{\text{D}} = +7.50$  (c. 0.9,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.07-5.03 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9, 4.5$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 4.21 (dd,  $J=11.9, 5.9$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.73 (q,  $J=7.2$  Hz, 1H,  $\text{CHCH}_3$ ), 3.61-3.57 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.44 (d,  $J=7.1$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.29 (t,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.62-1.55 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.33-1.23 (m, 12H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.5$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Ibu), 173.8 (SFA), 141.0, 137.8, 129.6 (2), 127.2 (2), 72.7, 62.1, 61.6, 45.3, 45.2, 34.2, 32.0, 30.3, 29.6 (2), 29.4, 29.3, 25.0, 22.8 (2), 22.5, 18.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{42}\text{O}_5\text{Na}$  457.2924; found, 457.2922.

#### 3.4.3. Synthesis of 3-dodecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**8d**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (23 mg), 1-*O*-benzyl-3-dodecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**6d** (111 mg, 0.208 mmol), THF (6 mL) and n-hexane (10 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent, afforded the product (*R,S'*)-**8d** as a pale-yellow oil, in 92% yield (85 mg, 0.191 mmol).  $[\alpha]^{20}_{\text{D}} = +2.43$  (c. 3.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.10-5.00 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9, 4.5$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 4.21 (dd,  $J=11.9, 5.9$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.73 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 3.61-3.57 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.44 (d,  $J=7.1$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.37-2.25 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.59-1.51 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.33-1.23 (m, 16H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.7$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Ibu), 173.8 (SFA), 141.0, 137.8, 129.6 (2), 127.2 (2), 72.7, 62.1, 61.6, 45.3, 45.2, 34.2, 32.1, 30.3, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8 (2), 22.5, 18.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{28}\text{H}_{46}\text{O}_5\text{Na}$  485.3237; found, 485.3237.

#### 3.4.4. Synthesis of 2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-3-tetradecanoyl-*sn*-glycerol, (*R,S'*)-**8e**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (21 mg), 1-*O*-benzyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-3-tetradecanoyl-*sn*-glycerol (*R,S'*)-**6e** (111 mg, 0.191 mmol), THF (5.5 mL) and n-hexane (9 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent, afforded the product (*R,S'*)-**8e** as a pale-yellow oil, in 84% yield (78 mg, 0.160 mmol).  $[\alpha]^{20}_{\text{D}} = +8.00$  (c. 1.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.08-5.02 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9, 4.5$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 4.21 (dd,  $J=11.9, 5.9$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.73 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 3.62-3.56 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.29 (t,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.84 (nonet,  $J=6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.63-1.57 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.1$  Hz, 3H,  $\text{CHCH}_3$ ), 1.29-1.23 (m, 20H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.7$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Ibu), 173.8 (SFA), 141.0, 137.8, 129.6 (2), 127.2 (2), 72.7, 62.1, 61.6, 45.3, 45.2, 34.3, 32.1, 30.3, 29.8 (2), 29.8, 29.6, 29.5, 29.4, 29.3, 25.0, 22.9 (2), 22.5, 18.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{30}\text{H}_{50}\text{O}_5\text{Na}$  513.3550; found, 513.3550.

#### 3.4.5. Synthesis of 3-hexadecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**8f**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (25 mg), 1-*O*-benzyl-3-hexadecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**6f** (135 mg, 0.222 mmol), THF (6.4 mL) and n-hexane (10.5 mL). Purification on 4% boric acid impregnated flash silica gel

chromatography using pet. ether/ethyl acetate (7:3) as eluent, afforded the product (*R,S'*)-**8f** as a pale-yellow oil, in 90% yield (104 mg, 0.200 mmol).  $[\alpha]^{20}_{\text{D}} = +0.75$  (c. 2.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.07-5.03 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9, 4.5$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 4.21 (dd,  $J=11.9, 5.9$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.73 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 3.61-3.57 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.29 (t,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.62-1.56 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.29-1.23 (m, 24H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Ibu), 173.8 (SFA), 141.0, 137.8, 129.6 (2), 127.2 (2), 72.7, 62.1, 61.6, 45.3, 45.2, 34.2, 32.1, 30.3, 29.8 (2), 29.8 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8 (2), 22.5, 18.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{32}\text{H}_{54}\text{O}_5\text{Na}$  541.3863; found, 541.3857.

#### 3.4.6. Synthesis of 2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-1-octanoyl-*sn*-glycerol, (*S,S'*)-**8b**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (10 mg), 3-*O*-benzyl-1-octanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**6b** (48 mg, 0.097 mmol), THF (3 mL) and n-hexane (4.6 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent, afforded the product (*S,S'*)-**8b** as a pale-yellow oil, in 86% yield (77 mg, 0.203 mmol).  $[\alpha]^{20}_{\text{D}} = +18.8$  (c. 1.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3478 (br), 2928 (vs), 2870 (vs), 1739 (vs).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.09 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.07-5.02 (m, 1H, CH *sn*-2), 4.21 (dd,  $J=11.9, 4.6$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.20 (dd,  $J=11.9, 6.0$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.77-3.68 (m, 2H,  $\text{CH}_2$  *sn*-3 and 1H,  $\text{CHCH}_3$ ), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.18 (t,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.98-1.92 (bs, 1H, OH), 1.84 (nonet,  $J=6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.58-1.49 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.33-1.23 (m, 8H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.3 (Ibu), 173.6 (SFA), 140.7, 137.3, 129.3 (2), 127.0 (C-1,3 Ibu), 72.5, 61.8, 61.6, 45.1, 45.0, 33.9, 31.77, 30.2, 29.1, 28.9, 24.8, 22.6 (2), 22.4, 18.3, 14.0 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{24}\text{H}_{38}\text{O}_5\text{Na}$  429.2611; found, 429.2604.

#### 3.4.7. Synthesis of 1-decanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**8c**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (27 mg), 3-*O*-benzyl-1-decanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**6c** (150 mg, 0.285 mmol), THF (9 mL) and n-hexane (12 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent, afforded the product (*S,S'*)-**8c** as a pale-yellow oil, in 89% yield (110 mg, 0.253 mmol).  $[\alpha]^{20}_{\text{D}} = +20.2$  (c. 1.5,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3486 (br), 2955 (vs), 2926 (vs), 2855 (vs), 1739 (vs), 1162 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.09-5.03 (m, 1H, CH *sn*-2), 4.21 (dd,  $J=11.9, 4.6$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.14 (dd,  $J=11.9, 6.0$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.77-3.68 (m, 2H,  $\text{CH}_2$  *sn*-3 and 1H,  $\text{CHCH}_3$ ), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.20-2.15 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.84 (nonet,  $J=6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.63 (bs, 1H, OH), 1.58-1.49 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  and 3H,  $\text{CHCH}_3$ ), 1.34-1.27 (m, 12H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.5 (Ibu), 173.8 (SFA), 140.8, 137.5, 129.6 (2), 129.5 (2), 72.7, 62.0, 61.7, 45.3, 45.2, 34.1, 32.0, 30.3, 29.8, 29.6, 29.4, 293, 24.9, 22.5 (2), 22.5, 18.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{42}\text{O}_5\text{Na}$  457.2924; found, 457.2923.

#### 3.4.8. Synthesis of 1-dodecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**8d**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (8 mg), 3-*O*-benzyl-1-dodecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**6d** (50 mg, 0.090 mmol), THF (3.5 mL) and n-hexane (4.5 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (7:3) as eluent, afforded the product (*S,S'*)-**8d** as a pale-yellow oil, in 93% yield (40 mg, 0.082 mmol).  $[\alpha]^{20}_{\text{D}} = +13.8$  (c. 2.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3469 (br), 2956 (vs), 2926 (vs), 2855

(vs), 1736 (vs), 1513 (s), 1165 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.07-5.02 (m, 1H, CH *sn*-2), 4.21 (dd,  $J=11.9, 4.6$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.21 (dd,  $J=11.9, 6.0$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.78-3.68 (m, 2H,  $\text{CH}_2$  *sn*-3 and 1H,  $\text{CHCH}_3$ ), 2.44 (d,  $J=7.1$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.18 (t,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.91 (s, 1H, OH), 1.84 (nonet,  $J=6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.59-1.50 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.34-1.27 (m, 16H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.5 (Ibu), 173.8 (SFA), 140.8, 137.4, 129.5 (2), 127.2 (2), 72.7, 62.0, 61.7, 45.3, 45.2, 34.1, 32.32, 30.3, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 24.9, 22.8 (2), 22.5, 18.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{28}\text{H}_{46}\text{O}_5\text{Na}$  485.3237; found, 485.3226.

### 3.4.9. Synthesis of 2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-1-tetradecanoyl-*sn*-glycerol, (*S,S'*)-**8e**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (14 mg), 3-O-benzyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-3-tetradecanoyl-*sn*-glycerol (*S,S'*)-**6e** (69 mg, 0.119 mmol), THF (4.5 mL) and n-hexane (6 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (3:2) as eluent, afforded the product (*S,S'*)-**8e** as a pale-yellow oil, in 94% yield (55 mg, 0.112 mmol).  $[\alpha]^{20\text{D}} = +4.20$  (c. 4.9,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3461 (br), 2955 (vs), 2925 (vs), 2854 (vs), 1740 (vs), 1512 (s), 1164 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.11-5.01 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9, 4.6$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.21 (dd,  $J=11.9, 6.0$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.79-3.66 (m, 2H,  $\text{CH}_2$  *sn*-3 and 1H,  $\text{CHCH}_3$ ), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.17 (t,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.92 (s, 1H, OH), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.59-1.50 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.50 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.34-1.27 (m, 20H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.5 (Ibu), 173.8 (SFA), 140.8, 137.4, 129.5 (2), 127.2 (2), 72.7, 62.0, 61.7, 45.3, 45.2, 34.1, 32.32, 30.3, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 24.9, 22.8 (2), 22.5, 18.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{30}\text{H}_{50}\text{O}_5\text{Na}$  513.3550; found, 513.3546.

### 3.4.10. Synthesis of 1-hexadecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**8f**

The same procedure was followed as described for (*R,S'*)-**8a** using Pd/C catalyst (4.6 mg), 3-O-benzyl-1-hexadecanoyl-2-[*(S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**6f** (25 mg, 0.041 mmol), THF (1.6 mL) and n-hexane (2.3 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (3:2) as eluent, afforded the product (*S,S'*)-**8f** as a pale-yellow oil, in 90% yield (19 mg, 0.037 mmol).  $[\alpha]^{20\text{D}} = +15.0$  (c. 1.9,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3378 (br), 2925 (vs), 2855 (vs), 1740 (vs), 1512 (s), 1162 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.19 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.10 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.06-5.02 (m, 1H, CH *sn*-2), 4.21 (dd,  $J=11.9, 4.5$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.13 (dd,  $J=11.9, 6.0$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.75-3.70 (m, 2H,  $\text{CH}_2$  *sn*-3 and 1H,  $\text{CHCH}_3$ ), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.20-2.14 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.67-1.55 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.61 (s, 1H, OH), 1.50 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.34-1.27 (m, 24H,  $\text{CH}_2$ ), 0.90 (t,  $J=6.1$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.5 (Ibu), 173.8 (SFA), 140.8, 137.4, 129.5 (2), 127.2 (2), 72.7, 62.0, 61.7, 45.2, 45.2, 34.1, 32.1, 30.3, 29.8 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.27, 24.9, 22.8 (2), 22.5, 18.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{32}\text{H}_{54}\text{O}_5\text{Na}$  541.3863; found, 541.3860.

### 3.4.11. Synthesis of 2-[*(S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-octanoyl-*sn*-glycerol, (*R,S'*)-**9b**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (31 mg), 1-O-benzyl-2-[*(S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-octanoyl-*sn*-glycerol (*S,S'*)-**7b** (145 mg, 0.278 mmol), THF (8 mL) and n-hexane (13 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, afforded the product (*R,S'*)-**9b** as a pale-yellow oil, in 94% yield (112 mg, 0.260 mmol).  $[\alpha]^{20\text{D}} = +7.17$  (c. 3.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ :

7.75-7.63 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J$ =8.5, 1.9 Hz, 1H, Nap-3), 7.14 (dd,  $J$ =8.9, 2.5 Hz, 1H, Nap-7), 7.11 (d,  $J$ =2.5 Hz, 1H, Nap-5), 5.13-5.01 (m, 1H, CH *sn*-2), 4.31 (dd,  $J$ =11.9, 4.4 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.21 (dd,  $J$ =11.9, 5.9 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.91-3.80 (m, 1H, CHCH<sub>3</sub>), 3.60-3.56 (m, 2H, CH<sub>2</sub> *sn*-1), 2.25 (t,  $J$ =7.2 Hz, 2H, CH<sub>2</sub>COO), 1.68 (t,  $J$ =6.6 Hz, 1H, OH), 1.58 (d,  $J$ =7.2 Hz, 3H, CHCH<sub>3</sub>), 1.56 (quint,  $J$ =7.2 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.38-1.23 (m, 8H, CH<sub>2</sub>), 0.89 (t,  $J$ =7.0 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.3 (Nap), 173.8 (SFA), 157.9, 135.6, 133.9, 129.4, 129.1, 127.4, 126.1, 126.0, 119.3, 105.8, 72.8, 62.1, 61.5, 55.5, 45.6, 34.2, 31.8, 29.2, 29.0, 25.0, 22.7, 18.5, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>25</sub>H<sub>34</sub>O<sub>6</sub>Na 453.2248; found, 453.2248.

#### 3.4.12. Synthesis of 3-decanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**9c**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (22 mg), 1-O-benzyl-3-decanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**7c** (107 mg, 0.195 mmol), THF (5.6 mL) and n-hexane (9.2 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, followed by recrystallization from n-hexane afforded the product (*R,S'*)-**9c** as very fine white needles, in 84% yield (75 mg, 0.164 mmol). Mp. 64.7-65.3°C. [α]<sup>20</sup><sub>D</sub> = +5.70 (c. 2.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.74-7.64 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J$ =8.5, 1.9 Hz, 1H, Nap-3), 7.15 (dd,  $J$ =8.9, 2.5 Hz, 1H, Nap-7), 7.11 (d,  $J$ =2.5 Hz, 1H, Nap-5), 5.13-5.03 (m, 1H, CH *sn*-2), 4.31 (dd,  $J$ =11.9, 4.4 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.22 (dd,  $J$ =11.9, 5.9 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.89 ((q,  $J$ =7.2 Hz, CHCH<sub>3</sub>), 3.62-3.56 (m, 2H, CH<sub>2</sub> *sn*-1), 2.26 (m, 2H, CH<sub>2</sub>COO and 3H, CHCH<sub>3</sub>), 1.66-1.52 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.30-1.22 (m, 12H, CH<sub>2</sub>), 0.89 (t,  $J$ =7.0 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.3 (Nap), 173.8 (SFA), 157.9, 135.6, 133.9, 129.4, 129.1, 127.5, 126.1, 126.0, 119.3, 105.8, 72.8, 62.1, 61.6, 55.5, 45.6, 34.2, 32.0, 29.6, 29.4, 29.3, 25.0, 22.8, 18.5, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>27</sub>H<sub>38</sub>O<sub>6</sub>Na 481.2561; found, 481.2565.

#### 3.4.13. Synthesis of 3-dodecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**9d**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (21 mg), 1-O-benzyl-3-dodecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**7d** (103 mg, 0.184 mmol), THF (5.3 mL) and n-hexane (8.7 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, followed by recrystallization from n-hexane afforded the product (*R,S'*)-**9d** as very fine white needles, in 94% yield (81 mg, 0.173 mmol). Mp. 68.4-68.7°C. [α]<sup>20</sup><sub>D</sub> = +3.08 (c. 2.6, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.75-7.65 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J$ =8.5, 1.9 Hz, 1H, Nap-3), 7.15 (dd,  $J$ =8.9, 2.5 Hz, 1H, Nap-7), 7.11 (d,  $J$ =2.5 Hz, 1H, Nap-5), 5.13-5.03 (m, 1H, CH *sn*-2), 4.31 (dd,  $J$ =11.9, 4.4 Hz, 1H, CH<sub>2</sub> *sn*-3), 4.22 (dd,  $J$ =11.9, 5.9 Hz, 1H, CH<sub>2</sub> *sn*-3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.89 ((q,  $J$ =7.2 Hz, CHCH<sub>3</sub>), 3.62-3.56 (m, 2H, CH<sub>2</sub> *sn*-1), 2.26 (m, 2H, CH<sub>2</sub>COO and 3H, CHCH<sub>3</sub>), 1.65-1.51 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO), 1.30-1.22 (m, 16H, CH<sub>2</sub>), 0.89 (t,  $J$ =7.0 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 174.3 (Nap), 173.8 (SFA), 157.9, 135.6, 133.9, 129.4, 129.1, 127.5, 126.1, 126.0, 119.3, 105.8, 72.8, 62.1, 61.6, 55.5, 45.6, 34.2, 32.1, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.8, 18.5, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>29</sub>H<sub>42</sub>O<sub>6</sub>Na 509.2874; found, 509.2867.

#### 3.4.14. Synthesis of 2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-tetradecanoyl-*sn*-glycerol, (*R,S'*)-**9e**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (20 mg), 1-O-benzyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-tetradecanoyl-*sn*-glycerol, (*R,S'*)-**7e** (106 mg, 0.175 mmol), THF (5 mL) and n-hexane (8.3 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, followed by recrystallization from n-hexane afforded the product (*R,S'*)-**9e** as very fine white needles, in 89% yield (80 mg, 0.155 mmol). Mp. 64.9-65.2°C. [α]<sup>20</sup><sub>D</sub> = +2.04 (c. 2.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.72-7.65 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J$ =8.5, 1.9 Hz, 1H, Nap-3), 7.15 (dd,  $J$ =8.9, 2.5 Hz, 1H, Nap-7), 7.11 (d,  $J$ =2.5 Hz, 1H, Nap-5), 5.13-5.03 (m, 1H, CH *sn*-

2), 4.31 (dd,  $J=12.0, 4.4$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 4.22 (dd,  $J=12.0, 5.9$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.89 ((q,  $J=7.2$  Hz,  $\text{CHCH}_3$ ), 3.63-3.55 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.26 (m, 2H,  $\text{CH}_2\text{COO}$  and 3H,  $\text{CHCH}_3$ ), 1.62-1.52 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.30-1.22 (m, 20H,  $\text{CH}_2$ ), 0.88 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.3 (Nap), 173.8 (SFA), 157.9, 135.6, 133.9, 129.4, 129.1, 127.5, 126.1, 126.0, 119.3, 105.8, 72.9, 62.1, 61.6, 55.5, 45.6, 34.2, 32.1, 29.9 (2), 29.8, 29.6, 29.5, 29.4, 29.3, 25.0, 22.8, 18.5, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{31}\text{H}_{46}\text{O}_6\text{Na}$  537.3187; found, 537.3181.

### 3.4.15. Synthesis of 3-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**9f**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (20 mg), 1-*O*-benzyl-3-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**7f** (110 mg, 0.174 mmol), THF (5 mL) and n-hexane (8.3 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, followed by recrystallization from n-hexane afforded the product (*R,S'*)-**9f** as very fine white needles, in 91% yield (86 mg, 0.158 mmol). Mp. 73.6-74.9°C.  $[\alpha]^{20}_{\text{D}} = +4.95$  (c. 2.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.79-7.58 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.15 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.11 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.13-5.03 (m, 1H,  $\text{CH}$  *sn*-2), 4.31 (dd,  $J=12.0, 4.4$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 4.22 (dd,  $J=12.0, 5.9$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.89 ((q,  $J=7.2$  Hz,  $\text{CHCH}_3$ ), 3.63-3.55 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.26 (m, 2H,  $\text{CH}_2\text{COO}$  and 3H,  $\text{CHCH}_3$ ), 1.62-1.52 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.30-1.22 (m, 24H,  $\text{CH}_2$ ), 0.88 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.3 (Nap), 173.8 (SFA), 157.9, 135.6, 133.9, 129.4, 129.1, 127.5, 126.0, 126.0, 119.3, 105.8, 72.8, 62.1, 61.6, 55.5, 45.6, 34.2, 32.1, 29.9 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.0, 22.9, 18.5, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{33}\text{H}_{50}\text{O}_6\text{Na}$  565.3500; found, 565.3500.

### 3.4.16. Synthesis of 2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-octanoyl-*sn*-glycerol, (*S,S'*)-**9b**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (10 mg), 3-*O*-benzyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-octanoyl-*sn*-glycerol (*S,S'*)-**7b** (50 mg, 0.096 mmol), THF (3 mL) and n-hexane (4.6 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, afforded the product (*S,S'*)-**9b** as a pale-yellow oil, in 97% yield (40 mg, 0.093 mmol).  $[\alpha]^{20}_{\text{D}} = +18.0$  (c. 3.4,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3497 (br), 2930 (vs), 2856 (vs), 1736 (vs), 1634 (cs), 1607 (vs).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.77-7.62 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.14-5.01 (m, 1H,  $\text{CH}$  *sn*-2), 4.19 (dd,  $J=11.9, 4.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.13 (dd,  $J=11.9, 6.1$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.72 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 3.60-3.56 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.05-1.90 (t,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 1.59 (d,  $J=7.1$  Hz, 3H,  $\text{CHCH}_3$ ), 1.39 (quint,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.34-1.08 (m, 8H,  $\text{CH}_2$ ), 0.86 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Nap), 173.7 (SFA), 157.9, 135.4, 133.9, 129.4, 129.1, 127.3, 126.2, 126.1, 119.2, 105.7, 72.8, 61.9, 61.7, 55.5, 45.6, 34.0, 32.0, 29.4, 29.2, 24.8, 22.8, 18.5, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for  $\text{C}_{25}\text{H}_{34}\text{O}_6\text{Na}$  453.2248; found, 453.2253.

### 3.4.17. Synthesis of 1-decanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**9c**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (21 mg), 3-*O*-benzyl-1-decanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**7c** (100 mg, 0.181 mmol), THF (7 mL) and n-hexane (9.2 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, afforded the product (*S,S'*)-**9c** as a pale-yellow oil in 92% yield (75 mg, 0.164 mmol).  $[\alpha]^{20}_{\text{D}} = +8.56$  (c. 0.9,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3363 (br), 2973 (vs), 2927 (vs), 1739 (vs), 1634 (s), 1607 (s), 1177 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.77-7.62 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.14-5.01 (m, 1H,  $\text{CH}$  *sn*-2), 4.19 (dd,  $J=11.9, 4.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.13 (dd,  $J=11.9, 6.1$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.72 ((q,  $J=7.0$  Hz,  $\text{CHCH}_3$ ), 3.62-3.56 (m, 2H,  $\text{CH}_2$  *sn*-3), 2.05-1.90 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.59

(d,  $J=7.1$  Hz, 3H,  $\text{CHCH}_3$ ), 1.39 (quint,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.34-1.08 (m, 12H,  $\text{CH}_2$ ), 0.86 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Nap), 173.7 (SFA), 157.9, 135.4, 133.9, 129.4, 129.1, 127.3, 126.2, 126.1, 119.2, 105.7, 72.8, 61.9, 61.7, 55.5, 45.6, 34.0, 32.0, 29.6, 29.4, 29.2, 24.8, 22.8, 18.5, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{27}\text{H}_{38}\text{O}_6\text{Na}$  481.2561; found, 481.2561.

### 3.4.18. Synthesis of 1-dodecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**9d**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (10 mg), 3-*O*-benzyl-1-dodecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**7d** (50 mg, 0.087 mmol), THF (3.5 mL) and n-hexane (5 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent. A second chromatography was needed to obtain pure product (*S,S'*)-**9d** as a colourless oil in 87% yield (38 mg, 0.076 mmol).  $[\alpha]^{20}_{\text{D}} = +17.2$  (c. 1.6,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3501 (br), 2926 (vs), 2854 (vs), 1736 (vs), 1634 (s), 1607 (vs), 1177 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.71-7.65 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.12-5.03 (m, 1H, CH *sn*-2), 4.19 (dd,  $J=11.9, 4.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.12 (dd,  $J=11.9, 6.1$  Hz, 1H,  $\text{CH}_2$  *sn*-3), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.72 ((q,  $J=7.1$  Hz,  $\text{CHCH}_3$ ), 3.63-3.56 (m, 2H,  $\text{CH}_2$  *sn*-1), 2.05-1.90 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.59 (d,  $J=7.1$  Hz, 3H,  $\text{CHCH}_3$ ), 1.43-1.34 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.32-1.09 (m, 16H,  $\text{CH}_2$ ), 0.86 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Nap), 173.7 (SFA), 157.9, 135.4, 133.9, 129.4, 129.1, 127.3, 126.2, 126.1, 119.2, 105.7, 72.8, 61.9, 61.7, 55.4, 45.6, 33.9, 32.1, 29.8 (2), 29.8 (2), 29.6, 29.5, 29.4, 29.2, 24.8, 22.8, 18.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{29}\text{H}_{42}\text{O}_6\text{Na}$  509.2874; found, 509.2874.

### 3.4.19. Synthesis of 2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-tetradecanoyl-*sn*-glycerol, (*S,S'*)-**9e**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (5 mg), 3-*O*-benzyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-tetradecanoyl-*sn*-glycerol, (*S,S'*)-**7e** (30 mg, 0.050 mmol), THF (1.5 mL) and n-hexane (2.5 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, afforded the product (*S,S'*)-**9e** as a pale-yellow oil in 90% yield (23 mg, 0.045 mmol).  $[\alpha]^{20}_{\text{D}} = +17.9$  (c. 3.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3366 (br), 3061 (s), 2924 (vs), 854 (vs), 1739 (vs), 1634 (s), 1607 (vs), 1162 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.72-7.63 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.12-5.03 (m, 1H, CH *sn*-2), 4.19 (dd,  $J=11.9, 4.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.12 (dd,  $J=11.9, 6.1$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.71 ((q,  $J=7.1$  Hz,  $\text{CHCH}_3$ ), 3.64-3.56 (m, 2H,  $\text{CH}_2$  *sn*-3), 2.07-1.90 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.59 (d,  $J=7.1$  Hz, 3H,  $\text{CHCH}_3$ ), 1.44-1.34 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.32-1.09 (m, 20H,  $\text{CH}_2$ ), 0.86 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Nap), 173.7 (SFA), 157.9, 135.4, 133.9, 129.4, 129.0, 127.3, 126.3, 126.1, 119.2, 105.7, 72.7, 62.0, 61.7, 55.4, 45.5, 33.9, 32.1, 29.8 (2), 29.8, 29.8, 29.6, 29.5, 29.4, 29.2, 24.8, 22.83, 18.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{31}\text{H}_{46}\text{O}_6\text{Na}$  537.3187; found, 537.3189.

### 3.4.20. Synthesis of 1-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**9f**

The same procedure was followed as described for (*R,S'*)-**9a** using Pd/C catalyst (8 mg), 3-*O*-benzyl-1-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**7f** (46 mg, 0.073 mmol), THF (2.8 mL) and n-hexane (4.1 mL). Purification on 4% boric acid impregnated flash silica gel chromatography using pet. ether/ethyl acetate (1:1) as eluent, afforded the product (*S,S'*)-**9f** as a pale-yellow oil in 90% yield (36 mg, 0.066 mmol).  $[\alpha]^{20}_{\text{D}} = +17.0$  (c. 3.5,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3409 (br), 3060 (s), 2924 (vs), 2853 (vs), 1738 (vs), 1635 (s), 1607 (vs), 1175 (br s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.78-7.53 (m, 3H, Nap-1,4,8), 7.39 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.12-5.03 (m, 1H, CH *sn*-2), 4.19 (dd,  $J=11.9, 4.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 4.12 (dd,  $J=11.9, 6.1$  Hz, 1H,  $\text{CH}_2$  *sn*-1), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.72 ((q,  $J=7.2$  Hz,  $\text{CHCH}_3$ ), 3.64-3.55 (m, 2H,  $\text{CH}_2$  *sn*-3), 2.06-1.91 (m, 2H,  $\text{CH}_2\text{COO}$ ), 1.59 (d,  $J=7.1$  Hz, 3H,  $\text{CHCH}_3$ ), 1.43-1.33 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$ ), 1.30-1.22 (m, 24H,  $\text{CH}_2$ ), 0.86 (t,  $J=6.8$  Hz,

3H,  $\text{CH}_2\text{CH}_3$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.4 (Nap), 173.7 (SFA), 157.9, 135.4, 133.9, 129.4, 129.1, 127.3, 126.2, 126.1, 119.2, 105.7, 72.8, 61.9, 61.7, 55.4, 45.6, 33.9, 32.1, 29.9 (2), 29.8 (2), 29.8, 29.6, 29.5, 29.4, 29.2, 24.8, 22.8, 18.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{33}\text{H}_{50}\text{O}_6\text{Na}$  565.3500; found, 565.3496.

### 3.5. Coupling of EPA: Synthesis of (*S,S'*)-**10b-f**, (*R,S'*)-**10b-f**, (*S,S'*)-**11b-f** and (*R,S'*)-**11b-f**

#### 3.5.1. Synthesis of 1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)-propanoyl]-3-octanoyl-*sn*-glycerol, (*S,S'*)-**10b**

The same procedure was followed as described for (*S,S'*)-**10a** using 2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-3-octanoyl-*sn*-glycerol (*R,S'*)-**8b** (37 mg, 0.096 mmol), EPA (32 mg, 0.095 mmol),  $\text{CH}_2\text{Cl}_2$  (3 mL), DMAP (10 mg, 0.078 mmol) and EDCI (18 mg, 0.094 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*S,S'*)-**10b** as a pale-yellow oil, in 91% yield (60 mg, 0.087 mmol).  $[\alpha]^{20}_{\text{D}} = +9.60$  (c. 4.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.41-5.33 (m, 10H, =CH), 5.32-5.24 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.19 (dd,  $J=11.9$ , 4.5 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.13 (dd,  $J=11.9$ , 6.0 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.07 (dd,  $J=11.9$ , 6.4 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.70 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 2.86-2.80 (m, 8H, = $\text{CHCH}_2\text{CH}=$ ), 2.43 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.28 (t,  $J=7.5$  Hz, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.18 (t,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 2.09-2.00 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and = $\text{CHCH}_2\text{CH}_3$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.63-1.50 (m, 4H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA and  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.49 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.32-1.26 (m, 8H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.90 (t,  $J=7.2$  Hz, 3H,  $\text{CH}_3$  SFA), 0.89 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Ibu), 173.4 (SFA), 173.0 (EPA), 140.7, 137.4, 132.2, 129.4 (2), 129.0, 129.0, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 127.3 (2), 127.1, 69.3, 62.2, 62.1, 45.2, 45.1, 34.1, 33.4, 31.8, 30.3, 29.2, 29.0, 26.6, 25.8 (2), 25.7 (2), 25.0, 24.7, 22.7 (2), 22.5, 20.7, 18.5, 14.4, 14.0 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{44}\text{H}_{66}\text{O}_6\text{Na}$  713.4752; found, 713.4747.

#### 3.5.2. Synthesis of 3-decanoyl-1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**10c**

The same procedure was followed as described for (*S,S'*)-**10a** using 3-decanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**8c** (45 mg, 0.103 mmol), EPA (33 mg, 0.109 mmol),  $\text{CH}_2\text{Cl}_2$  (4 mL), DMAP (13 mg, 0.106 mmol) and EDCI (28 mg, 0.146 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*S,S'*)-**10c** as a pale-yellow oil, in 88% yield (66 mg, 0.091 mmol).  $[\alpha]^{20}_{\text{D}} = +8.40$  (c. 6.5,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.41-5.33 (m, 10H, =CH), 5.32-5.24 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.19 (dd,  $J=11.9$ , 4.5 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.13 (dd,  $J=11.9$ , 6.0 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.07 (dd,  $J=11.9$ , 6.4 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.70 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 2.86-2.80 (m, 8H, = $\text{CHCH}_2\text{CH}=$ ), 2.43 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.28 (t,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.18 (t,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{COO}$ ), 2.09-2.00 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and = $\text{CHCH}_2\text{CH}_3$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.62-1.51 (m, 4H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA and  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.49 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.32-1.26 (m, 12H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.90 (t,  $J=7.2$  Hz, 3H,  $\text{CH}_3$  SFA), 0.89 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Ibu), 173.4 (SFA), 173.0 (EPA), 140.7, 137.4, 132.1, 129.4 (2), 129.1, 128.9, 128.7, 128.4, 128.3, 128.3, 128.2, 129.0, 128.2 (2), 127.1, 69.3, 62.2, 62.1, 45.2, 45.2, 34.1, 33.4, 32.0, 30.3, 29.6, 29.5, 29.4, 29.2, 26.6, 25.8 (2), 25.7 (2), 25.0, 24.7, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{46}\text{H}_{70}\text{O}_6\text{Na}$  741.5065; found, 741.5067.

#### 3.5.3. Synthesis of 3-dodecanoyl-1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**10d**

The same procedure was followed as described for (*S,S'*)-**10a** using 3-dodecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**8d** (40 mg, 0.090 mmol), EPA (26 mg, 0.087 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (9 mg, 0.071 mmol) and EDCI (17 mg, 0.086 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*S,S'*)-**10d** as a pale-yellow oil, in 87% yield (57 mg, 0.078 mmol). [α]<sup>20D</sup> = +7.98 (c. 5.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.41-5.33 (m, 10H, =CH), 5.32-5.24 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.19 (dd, *J*=11.9, 4.5 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.13 (dd, *J*=11.9, 6.0 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.07 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.86-2.80 (m, 8H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.27 (t, *J*=7.6 Hz, 2H, CH<sub>2</sub>COO EPA), 2.18 (t, *J*=7.2 Hz, 2H, CH<sub>2</sub>COO), 2.09-2.00 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH= and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.84 (nonet, *J*=6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.66-1.53 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>COO SFA and CH<sub>2</sub>CH<sub>2</sub>COO EPA), 1.48 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.32-1.26 (m, 16H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> EPA), 0.90 (t, *J*=7.2 Hz, 3H, CH<sub>3</sub> SFA), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 173.9 (Ibu), 173.4 (SFA), 173.0 (EPA), 140.7, 137.4, 132.1, 129.4 (2), 129.0, 128.9, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 128.2 (2), 127.1, 69.3, 62.2, 62.1, 45.2, 45.15, 34.1, 33.4, 32.0, 30.3, 29.7 (2), 29.6, 29.5, 29.4, 29.2, 26.6, 25.6 (2), 25.7 (2), 25.0, 24.7, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>48</sub>H<sub>74</sub>O<sub>6</sub>Na 769.5378; found, 769.5366.

### 3.5.4. Synthesis of 1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)-propanoyl]-3-tetradecanoyl-*sn*-glycerol, (*S,S'*)-**10e**

The same procedure was followed as described for (*S,S'*)-**10a** using 2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-3-tetradecanoyl-*sn*-glycerol (*R,S'*)-**8e** (49 mg, 0.100 mmol), EPA (33 mg, 0.110 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3.8 mL), DMAP (11 mg, 0.090 mmol) and EDCI (21 mg, 0.109 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*S,S'*)-**10e** as a pale-yellow oil, in 89% yield (67 mg, 0.089 mmol). [α]<sup>20D</sup> = +6.58 (c. 6.4, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.40-5.35 (m, 10H, =CH), 5.34-5.25 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.19 (dd, *J*=11.9, 4.5 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.13 (dd, *J*=11.9, 6.0 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.07 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.86-2.80 (m, 8H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.27 (t, *J*=7.6 Hz, 2H, CH<sub>2</sub>COO EPA), 2.18 (t, *J*=7.2 Hz, 2H, CH<sub>2</sub>COO), 2.10-2.01 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH= and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.84 (nonet, *J*=6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.65-1.54 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>COO SFA and CH<sub>2</sub>CH<sub>2</sub>COO EPA), 1.48 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.32-1.26 (m, 20H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> EPA), 0.88 (t, *J*=7.2 Hz, 3H, CH<sub>3</sub> SFA), 0.87 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 173.9 (Ibu), 173.4 (SFA), 173.0 (EPA), 140.7, 137.4, 132.2, 129.4 (2), 129.0, 129.0, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 128.2, 127.1 (2), 69.3, 62.2, 62.1, 45.2, 45.1, 34.2, 33.4, 32.1, 30.3, 30.1, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 26.6, 25.8 (2), 25.7 (2), 25.0, 24.7, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>50</sub>H<sub>78</sub>O<sub>6</sub>Na 797.5691; found, 797.5685.

### 3.5.5. Synthesis of 3-hexadecanoyl-1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**10f**

The same procedure was followed as described for (*S,S'*)-**10a** using 3-hexadecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**8f** (42 mg, 0.081 mmol), EPA (27 mg, 0.089 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (9 mg, 0.073 mmol) and EDCI (17 mg, 0.088 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*S,S'*)-**10f** as a pale-yellow oil, in 86% yield (56 mg, 0.070 mmol). [α]<sup>20D</sup> = +6.68 (c. 6.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.40-5.35 (m, 10H, =CH), 5.34-5.25 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.19 (dd, *J*=11.9, 4.5 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.13 (dd, *J*=11.9, 6.0 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.07 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.86-2.80 (m, 8H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.27 (t, *J*=7.6 Hz, 2H, CH<sub>2</sub>COO EPA), 2.18 (t, *J*=7.2 Hz, 2H, CH<sub>2</sub>COO), 2.10-2.01 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH= and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.84 (nonet, *J*=6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.65-1.54 (m, 4H,

$\text{CH}_2\text{CH}_2\text{COO}$  SFA and  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.48 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.32-1.26 (m, 24H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.88 (t,  $J=7.2$  Hz, 3H,  $\text{CH}_3$  SFA), 0.87 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 174.1 (Ibu), 173.8 (SFA), 173.3 (EPA), 140.7, 137.4, 132.2, 129.4 (2), 129.0, 129.0, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 128.2 (2), 127.1, 69.3, 62.2, 62.1, 45.2, 45.1, 34.2, 33.4, 32.1, 30.3, 30.1 (2), 29.8 (2), 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 26.6, 25.8 (2), 25.7 (2), 25.0, 24.7, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{52}\text{H}_{82}\text{O}_6\text{Na}$  825.6004; found, 825.5950.

### 3.5.6. Synthesis of 3-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2-[(S)-2-(4-isobutylphenyl)-propanoyl]-1-octanoyl-sn-glycerol, (R,S')-10b

The same procedure was followed as described for (S,S')-10a using 2-[(S)-2-(4-isobutylphenyl)propanoyl]-1-octanoyl-sn-glycerol (S,S')-8b (29 mg, 0.071 mmol), EPA (23 mg, 0.076 mmol),  $\text{CH}_2\text{Cl}_2$  (3 mL), DMAP (10 mg, 0.077 mmol) and EDCI (21 mg, 0.110 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (R,S')-10b as a pale-yellow oil, in 84% yield (41 mg, 0.059 mmol).  $[\alpha]^{20}_{\text{D}} = +9.11$  (c. 4.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3013 (vs), 2957 (vs), 2929 (vs, 2859 (vs), 1743 (vs).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.18 (dd,  $J=8.1, 1.7$  Hz, 2H, Ibu-2,6), 7.07 (dd,  $J=8.1, 3.8$  Hz, 2H, Ibu-3,5), 5.45-5.29 (m, 10H, =CH), 5.28-5.22 (m, 1H, CH sn-2), 4.30 (dd,  $J=11.9, 4.3$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 4.19 (dd,  $J=11.9, 4.3$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 4.13 (dd,  $J=11.9, 6.4$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 4.06 (dd,  $J=11.9, 6.3$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 3.70 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 2.87-2.77 (m, 8H, =CH $\text{CH}_2\text{CH}=$ ), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.33-2.22 (m, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.18-2.04 (m, 6H,  $\text{CH}_2\text{COO}$  SFA,  $\text{CH}_2\text{CH}_2\text{CH}=$  and =CH $\text{CH}_2\text{CH}_3$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.61-1.59 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.58-1.50 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.49 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.33-1.20 (m, 8H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.89 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.88 (t,  $J=6.5$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.8 (bu), 173.1 (SFA), 172.9 (EPA), 140.6, 137.2, 132.0, 129.3 (2), 129.2, 128.9, 128.7, 128.9, 128.8, 128.6, 128.2, 128.1, 127.8 (2), 127.1, 69.2, 62.1, 61.9, 45.2, 34.0, 33.5, 31.6, 30.2, 29.7 (2), 29.0, 28.9, 26.5, 25.6 (2), 25.5 (2), 24.8, 24.7, 22.6 (2), 22.4, 20.5, 18.3, 14.2, 14.0 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{44}\text{H}_{66}\text{O}_6\text{Na}$  713.4752; found, 713.4755.

### 3.5.7. Synthesis of 1-decanoyl-3-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2-[(S)-2-(4-isobutyl-phenyl)propanoyl]-sn-glycerol, (R,S')-10c

The same procedure was followed as described for (S,S')-10a using 1-decanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol (S,S')-8c (55 mg, 0.127 mmol), EPA (43 mg, 0.142 mmol),  $\text{CH}_2\text{Cl}_2$  (4 mL), DMAP (18 mg, 0.147 mmol) and EDCI (42 mg, 0.219 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent afforded the product (R,S')-10c as a pale-yellow oil, in 76% yield (70 mg, 0.097 mmol).  $[\alpha]^{20}_{\text{D}} = +7.44$  (c. 5.9,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3013 (s), 2956 (vs), 2927 (vs), 2855 (vs), 1743 (vs).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.21-7.13 (m, 2H, Ibu-2,6), 7.10-7.05 (m, 2H, Ibu-3,5), 5.45-5.29 (m, 10H, =CH), 5.25 (tt,  $J=6.3, 4.3$  Hz, 1H, CH sn-2), 4.30 (dd,  $J=11.9, 4.3$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 4.19 (dd,  $J=11.9, 4.3$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 4.14 (dd,  $J=11.9, 6.3$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 4.06 (dd,  $J=11.9, 6.3$  Hz, 1H,  $\text{CH}_2$  sn-1/3), 3.70 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 2.88-2.78 (m, 8H, =CH $\text{CH}_2\text{CH}=$ ), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.30 (t,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.17-2.05 (m, 6H,  $\text{CH}_2\text{COO}$  SFA,  $\text{CH}_2\text{CH}_2\text{CH}=$  and =CH $\text{CH}_2\text{CH}_3$ ), 1.84 (nonet,  $J=6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.75-1.63 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.52-1.48 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.49 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.34-1.22 (m, 12H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.89 (d,  $J=6.7$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.88 (t,  $J=7.1$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Ibu), 173.3 (SFA), 173.1 (EPA), 140.7, 137.4, 132.2, 129.5 (2), 129.4, 129.08, 129.1, 128.9, 128.7, 128.4, 128.4, 128.3, 128.3 (2), 127.1, 69.3, 62.3, 62.1, 45.2, 34.0, 33.5, 32.0, 30.3, 29.4, 29.2, 26.6, 26.6, 25.8, 25.7 (2), 25.0 (2), 24.9, 24.8, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{46}\text{H}_{70}\text{O}_6\text{Na}$  741.5065; found, 741.5064.

3.5.8. Synthesis of 1-dodecanoyl-3-[5Z,8Z,11Z,14Z,17Z)-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**10d**

The same procedure was followed as described for (*S,S'*)-**10a** using 1-dodecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**8d** (30 mg, 0.065 mmol), EPA (31 mg, 0.099 mmol), CH<sub>2</sub>Cl<sub>2</sub> (4 mL), DMAP (14 mg, 0.112 mmol) and EDCI (32 mg, 0.166 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent afforded the product (*R,S'*)-**10d** as a yellow oil, in 75% yield (37 mg, 0.049 mmol).  $[\alpha]^{20}_{\text{D}} = +7.57$  (c. 3.5, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3013 (s), 2950 (vs), 2926 (vs), 2854 (vs), 1743 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ <sub>H</sub>: 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.44-5.30 (m, 10H, =CH), 5.25 (tt, *J*=6.3, 4.3 Hz, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.19 (dd, *J*=11.9, 4.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.14 (dd, *J*=11.9, 6.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.06 (dd, *J*=11.9, 6.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.89-2.77 (m, 8H, =CHCH<sub>2</sub>CH=), 2.44 (d, *J*=7.1 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.30 (t, *J*=7.6 Hz, 2H, CH<sub>2</sub>COO EPA), 2.15 (t, *J*=7.1, 2H, CH<sub>2</sub>COO SFA), 2.12-2.03 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH= and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.84 (nonet, *J*=6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (quint, *J*=7.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>COO EPA), 1.54-1.47 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.30-1.22 (m, 16H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> EPA), 0.88 (t, *J*=7.1 Hz, 3H, CH<sub>3</sub> SFA), 0.87 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ <sub>C</sub>: 173.9 (Ibu), 173.3 (SFA), 173.1 (EPA), 140.7, 137.4, 132.2, 129.4 (2), 129.1, 129.0, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 127.3 (2), 127.2, 69.4, 62.3, 62.1, 45.2, 45.1, 34.01, 33.5, 32.1, 30.3, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 26.7, 25.8 (2), 25.7 (2), 24.9, 24.8, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>48</sub>H<sub>74</sub>O<sub>6</sub>Na 769.5378; found, 769.5409.

3.5.9. Synthesis of 3-[5Z,8Z,11Z,14Z,17Z)-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)-propanoyl]-1-tetradecanoyl-*sn*-glycerol, (*R,S'*)-**10e**

The same procedure was followed as described for (*S,S'*)-**10a** using 2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-1-tetradecanoyl-*sn*-glycerol (*S,S'*)-**8e** (30 mg, 0.061 mmol), EPA (21 mg, 0.069 mmol), CH<sub>2</sub>Cl<sub>2</sub> (4 mL), DMAP (10 mg, 0.082 mmol) and EDCI (17 mg, 0.089 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*R,S'*)-**10e** as a pale-yellow oil, in 75% yield (35 mg, 0.046 mmol).  $[\alpha]^{20}_{\text{D}} = +7.12$  (c. 2.5, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3013 (s), 2956 (vs), 2926 (vs), 2854 (vs), 1743 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ <sub>H</sub>: 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.44-5.30 (m, 10H, =CH), 5.25 (tt, *J*=6.3, 4.3 Hz, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.18 (dd, *J*=11.9, 4.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.14 (dd, *J*=11.9, 6.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.06 (dd, *J*=11.9, 6.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.89-2.77 (m, 8H, =CHCH<sub>2</sub>CH=), 2.44 (d, *J*=7.1 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.30 (t, *J*=7.6 Hz, 2H, CH<sub>2</sub>COO EPA), 2.15 (t, *J*=7.1, 2H, CH<sub>2</sub>COO SFA), 2.12-2.03 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH= and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.84 (nonet, *J*=6.8 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (quint, *J*=7.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>COO EPA), 1.54-1.47 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.30-1.22 (m, 20H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> EPA), 0.88 (t, *J*=7.1 Hz, 3H, CH<sub>3</sub> SFA), 0.87 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ <sub>C</sub>: 173.9 (Ibu), 173.3 (SFA), 173.1 (EPA), 140.7, 137.4, 132.2, 129.4 (2), 129.1, 129.0, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 127.3 (2), 127.2, 69.4, 62.3, 62.1, 45.2, 45.1, 34.0, 33.5, 32.1, 30.3, 30.1, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 26.7, 25.8 (2), 25.7 (2), 24.9, 24.8, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>50</sub>H<sub>78</sub>O<sub>6</sub>Na 797.5691; found, 797.5692.

3.5.10. Synthesis of 3-hexadecanoyl-1-[5Z,8Z,11Z,14Z,17Z)-eicosa-5,8,11,14,17-pentaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**10f**

The same procedure was followed as described for (*S,S'*)-**10a** using 1-hexadecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**8f** (12 mg, 0.023 mmol), EPA (8 mg, 0.023 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL), DMAP (3 mg, 0.021 mmol) and EDCI (5 mg, 0.025 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent afforded the product (*R,S'*)-**10f** as a pale-yellow oil, in 78% yield (14 mg, 0.017 mmol).  $[\alpha]^{20}_{\text{D}} = +7.43$  (c. 1.4, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3012 (s), 2965 (vs), 2925 (vs), 2855

(vs), 1744 (vs).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.46-5.30 (m, 10H, =CH), 5.29-5.19 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9, 4.3$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.18 (dd,  $J=11.9, 4.3$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.14 (dd,  $J=11.9, 6.3$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9, 6.3$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.70 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 2.88-2.77 (m, 8H, = $\text{CHCH}_2\text{CH}=$ ), 2.43 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.30 (t,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.18 (t,  $J=7.6$ , 2H,  $\text{CH}_2\text{COO}$  SFA), 2.19-2.01 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and = $\text{CHCH}_2\text{CH}_3$ ), 1.84 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.69-1.61 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.60-1.50 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.48 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.32-1.23 (m, 24H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.89 (t,  $J=7.1$  Hz, 3H,  $\text{CH}_3$  SFA), 0.88 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}$ {H} NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Ibu), 173.3 (SFA), 173.1 (EPA), 140.7, 137.4, 132.2 (2), 129.4 (2), 129.1, 129.0, 128.7, 128.4, 128.3, 128.3, 128.0, 127.3, 127.2 (2), 69.3, 62.3, 62.1, 45.2, 45.2, 34.0, 33.5, 32.1, 30.3, 29.9 (2), 29.8 (2), 29.8 (2), 29.7, 29.5, 29.4, 29.3, 26.7, 25.8 (2), 25.7 (2), 24.9, 24.8, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{52}\text{H}_{82}\text{O}_6\text{Na}$  825.6004; found, 825.6004.

### 3.5.11. Synthesis of 1-[5Z,8Z,11Z,14Z,17Z)-eicosa-5,8,11,14,17-pentaenoyl]-2[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-octanoyl-*sn*-glycerol, (S,S')-11b

The same procedure was followed as described for (S,S')-11a using 2-[(S)-2-(4-isobutylphenyl)propanoyl]-3-octanoyl-*sn*-glycerol (*R,S'*)-9b (35 mg, 0.081 mmol), EPA (27 mg, 0.089 mmol),  $\text{CH}_2\text{Cl}_2$  (4 mL), DMAP (9 mg, 0.074 mmol) and EDCI (17 mg, 0.089 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (S,S')-11b as a yellow oil, in 94% yield (54 mg, 0.076 mmol).  $[\alpha]^{20}_{\text{D}} = +6.00$  (c. 5.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.73-7.62 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.45-5.28 (m, 10H, =CH), 5.30-5.19 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.22-4.09 (m, 2H,  $\text{CH}_2$  *sn*-1/3), 4.07 (dd,  $J=11.9, 6.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.86 (q,  $J=7.2$  Hz, 1H,  $\text{CHCH}_3$ ), 2.89-2.72 (m, 8H, = $\text{CHCH}_2\text{CH}=$ ), 2.29-2.20 (m, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.14-2.01 (m, 2H,  $\text{CH}_2\text{COO}$  SFA), 2.00 (td,  $J=7.6, 5.5$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{CH}=$ ), 1.98-1.88 (m, 2H, = $\text{CHCH}_2\text{CH}_3$ ), 1.63-1.51 (m, 5H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA and  $\text{CHCH}_3$ ), 1.46 (quint,  $J=7.4$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.35-1.21 (m, 8H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}$ {H} NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.8 (Nap), 173.4 (SFA), 172.9 (EPA), 157.8, 135.3, 133.8, 132.1, 129.4, 129.0, 128.9, 128.9, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 127.2, 127.1, 126.2, 126.1, 119.2, 105.7, 69.5, 62.1, 62.1, 55.4, 45.5, 34.1, 33.2, 31.8, 29.2, 29.0, 26.5, 25.8, 25.7 (2), 25.7, 24.9, 24.6, 22.7, 20.7, 18.4, 14.39, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{45}\text{H}_{62}\text{O}_7\text{Na}$  737.4388; found, 737.4385.

### 3.5.12. Synthesis of 3-decanoyl-1-[5Z,8Z,11Z,14Z,17Z)-eicosa-5,8,11,14,17-pentaenoyl]-2[(S)-2-(6-methoxy-naphthalen-2-yl)propanoyl]-*sn*-glycerol, (S,S')-11c

The same procedure was followed as described for (S,S')-11a using 3-decanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-9c (35 mg, 0.076 mmol), EPA (25 mg, 0.084 mmol),  $\text{CH}_2\text{Cl}_2$  (2.5 mL), DMAP (8 mg, 0.067 mmol) and EDCI (16 mg, 0.081 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (S,S')-11c as a yellow oil, in 84% yield (48 mg, 0.064 mmol).  $[\alpha]^{20}_{\text{D}} = +6.58$  (c. 4.5,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.73-7.62 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.6$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.6$  Hz, 1H, Nap-5), 5.45-5.27 (m, 10H, =CH), 5.29-5.21 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.22-4.09 (m, 2H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9, 6.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.86 (q,  $J=7.2$  Hz, 1H,  $\text{CHCH}_3$ ), 2.89-2.71 (m, 8H, = $\text{CHCH}_2\text{CH}=$ ), 2.24 (t,  $J=7.4$  Hz, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.14-2.02 (m, 2H,  $\text{CH}_2\text{COO}$  SFA), 2.06-1.95 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}=$ ), 1.98-1.88 (m, 2H, = $\text{CHCH}_2\text{CH}_3$ ), 1.62-1.51 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.58 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.52-1.39 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.31-1.26 (m, 12H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}$ {H} NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.4 (SFA), 173.0 (EPA), 157.8, 135.3, 133.9, 132.2, 129.4, 129.0, 128.92, 128.90, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 127.2, 127.2, 126.3, 126.1, 119.2, 105.7, 69.5, 62.2, 62.1, 55.4, 45.5, 34.1, 33.2, 32.0, 29.6, 29.4, 29.2, 26.5, 25.8, 25.7

(2), 25.7, 25.0, 24.6, 22.8, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for C<sub>47</sub>H<sub>66</sub>O<sub>7</sub>Na 765.4701; found, 765.4708.

### 3.5.13. Synthesis of 3-dodecanoyl-1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-sn-glycerol, (S,S')-11d

The same procedure was followed as described for (S,S')-11a using 3-dodecanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol (R,S')-9d (25 mg, 0.054 mmol), EPA (18 mg, 0.058 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2 mL), DMAP (6 mg, 0.050 mmol) and EDCI (11 mg, 0.058 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (S,S')-11d as a pale-yellow oil, in 96% yield (39 mg, 0.052 mmol).  $[\alpha]^{20D} = +4.89$  (c. 3.8, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 7.71-7.64 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.10 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.44-5.29 (m, 10H, =CH), 5.29-5.21 (m, 1H, CH sn-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.20-4.15 (m, 2H, CH<sub>2</sub> sn-1/3), 4.06 (dd,  $J=11.9, 6.4$  Hz, 1H, CH<sub>2</sub> sn-1/3), 3.90 (s, 3H, OCH<sub>3</sub>), 3.86 (q,  $J=7.2$  Hz, 1H, CHCH<sub>3</sub>), 2.88-2.72 (m, 8H, =CHCH<sub>2</sub>CH=), 2.28-2.20 (m, 2H, CH<sub>2</sub>COO EPA), 2.14-2.04 (m, 2H, CH<sub>2</sub>COO SFA), 2.00 (td,  $J=7.7, 5.6$  Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH=), 1.98-1.88 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.62-1.51 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.58 (d,  $J=7.2$  Hz, 3H, CHCH<sub>3</sub>), 1.50-1.41 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO EPA), 1.31-1.26 (m, 16H, CH<sub>2</sub>), 0.97 (t,  $J=7.5$  Hz, 3H, CH<sub>3</sub> EPA), 0.89 (t,  $J=6.8$  Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_C$ : 173.9 (Nap), 173.4 (SFA), 173.0 (EPA), 157.8, 135.3, 133.9, 132.2, 129.43, 129.4, 129.0, 129.0, 128.7, 128.4, 128.3, 128.3, 128.2, 128.0, 127.2, 127.2, 126.3, 126.1, 119.2, 105.7, 69.5, 62.2, 62.1, 55.4, 45.5, 34.1, 33.2, 32.1, 29.8, 29.8, 29.6, 29.5, 29.4, 29.2, 26.5, 25.8, 25.7 (2), 25.7, 25.0, 24.6, 22.8, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for C<sub>49</sub>H<sub>70</sub>O<sub>7</sub>Na 793.5013; found, 793.5013.

### 3.5.14. Synthesis of 1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-tetracanoyl-sn-glycerol, (S,S')-11e

The same procedure was followed as described for (S,S')-11a using 2-[(S)-2-(4-isobutylphenyl)propanoyl]-3-tetracanoyl-sn-glycerol (R,S')-9e (32 mg, 0.062 mmol), EPA (21 mg, 0.068 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.3 mL), DMAP (7 mg, 0.056 mmol) and EDCI (23 mg, 0.068 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (S,S')-11e as a pale-yellow oil, in 90% yield (45 mg, 0.056 mmol).  $[\alpha]^{20D} = +5.29$  (c. 4.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 7.74-7.62 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5, 1.9$  Hz, 1H, Nap-3), 7.14 (dd,  $J=8.9, 2.5$  Hz, 1H, Nap-7), 7.09 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.46-5.31 (m, 10H, =CH), 5.30-5.19 (m, 1H, CH sn-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.20-4.11 (m, 2H, CH<sub>2</sub> sn-1/3), 4.06 (dd,  $J=11.9, 6.4$  Hz, 1H, CH<sub>2</sub> sn-1/3), 3.90 (s, 3H, OCH<sub>3</sub>), 3.86 (q,  $J=7.2$  Hz, 1H, CHCH<sub>3</sub>), 2.89-2.70 (m, 8H, =CHCH<sub>2</sub>CH=), 2.28-2.20 (m, 2H, CH<sub>2</sub>COO EPA), 2.14-2.04 (m, 2H, CH<sub>2</sub>COO SFA), 2.00 (td,  $J=7.7, 5.6$  Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>CH=), 1.97-1.89 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.63-1.52 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.58 (d,  $J=7.2$  Hz, 3H, CHCH<sub>3</sub>), 1.54 (quint,  $J=7.3$  Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>COO EPA), 1.31-1.26 (m, 20H, CH<sub>2</sub>), 0.97 (t,  $J=7.5$  Hz, 3H, CH<sub>3</sub> EPA), 0.89 (t,  $J=6.8$  Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_C$ : 173.9 (Nap), 173.4 (SFA), 173.0 (EPA), 157.8, 135.3, 133.9, 132.2, 129.4, 129.4, 129.0, 128.9, 128.7, 128.4, 128.32, 128.30, 128.2, 128.0, 127.22, 127.15, 126.3, 126.1, 119.2, 105.7, 69.5, 62.2, 62.1, 55.4, 45.5, 34.1, 33.2, 32.1, 30.1, 29.8, 29.8, 29.6, 29.5, 29.4, 29.3, 26.5, 25.8, 25.72 (2), 25.68, 25.0, 24.6, 22.8, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for C<sub>51</sub>H<sub>74</sub>O<sub>7</sub>Na 821.5327; found, 821.5327.

### 3.5.15. Synthesis of 1-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-3-hexadecanoyl-2[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-sn-glycerol, (S,S')-11f

The same procedure was followed as described for (S,S')-11a using 3-hexadecanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol (R,S')-9f (40 mg, 0.074 mmol), EPA (25 mg, 0.081 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (8 mg, 0.067 mmol) and EDCI (16 mg, 0.081 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (S,S')-11f as a pale-yellow oil, in 91%

yield (51 mg, 0.067 mmol).  $[\alpha]^{20}_{\text{D}} = +5.44$  (c. 5.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.71-7.64 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5$ , 1.9 Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9$ , 2.5 Hz, 1H, Nap-7), 7.09 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.44-5.23 (m, 10H, =CH), 5.23-5.12 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.18 (dd,  $J=11.9$ , 4.3 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.14 (dd,  $J=11.9$ , 6.1 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.07 (dd,  $J=11.9$ , 6.5 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.90 (s, 3H, OCH<sub>3</sub>), 3.86 (q,  $J=7.2$  Hz, 1H, CHCH<sub>3</sub>), 2.90-2.73 (m, 8H, =CHCH<sub>2</sub>CH= and =CHCH<sub>2</sub>CH<sub>3</sub>), 2.24 (t,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.20-2.13 (m, 2H,  $\text{CH}_2\text{COO}$  SFA), 2.14-1.97 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.58 (d,  $J=7.2$  Hz, 3H, CHCH<sub>3</sub>), 1.56-1.49 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.46 (quint,  $J=7.3$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.37-1.20 (m, 24H, CH<sub>2</sub>), 0.97 (t,  $J=7.5$  Hz, 3H, CH<sub>3</sub> EPA), 0.89 (t,  $J=6.8$  Hz, 3H, CH<sub>3</sub> SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.4 (SFA), 173.0 (EPA), 157.8, 135.3, 133.9, 132.12, 129.4, 129.03, 128.95, 128.9, 128.7, 128.4, 128.32, 128.29, 128.2, 128.0, 127.2, 127.1, 126.3, 126.1, 119.2, 105.7, 69.5, 62.2 (2), 62.1, 55.4, 45.5, 34.1, 33.2, 32.1, 29.83 (2), 29.80 (2), 29.76 (2), 29.6 (2), 29.5, 29.4, 29.3, 25.8 (2), 25.7 (2), 25.0, 23.0, 22.6, 20.8, 18.7, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>53</sub>H<sub>78</sub>O<sub>7</sub>Na 849.5640; found, 849.5600.

### 3.5.16. Synthesis of 3-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-octanoyl-*sn*-glycerol, (*R,S'*)-**11b**

The same procedure was followed as described for (*R,S'*)-**11a** using 2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-1-octanoyl-*sn*-glycerol (*R,S'*)-**9b** (35 mg, 0.081 mmol), EPA (27 mg, 0.089 mmol),  $\text{CH}_2\text{Cl}_2$  (4 mL), DMAP (9 mg, 0.074 mmol) and EDCI (17 mg, 0.089 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*R,S'*)-**11b** as a yellow oil, in 94% yield (54 mg, 0.076 mmol).  $[\alpha]^{20}_{\text{D}} = +4.97$  (c. 3.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3012 (s), 2958 (vs), 2931 (vs), 2856 (vs), 1743 (vs), 1634 (s), 1607 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.76-7.54 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5$ , 1.9 Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9$ , 2.6 Hz, 1H, Nap-7), 7.09 (d,  $J=2.6$  Hz, 1H, Nap-5), 5.47-5.30 (m, 10H, =CH), 5.30-5.19 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.22-4.11 (m, 2H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9$ , 6.4 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.86 (q,  $J=7.1$  Hz, 1H, CHCH<sub>3</sub>), 2.96-2.73 (m, 8H, =CHCH<sub>2</sub>CH=), 2.31-2.23 (m, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.13-2.01 (m, 2H,  $\text{CH}_2\text{COO}$  SFA), 2.01-1.86 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.60-1.55 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.57 (d,  $J=7.1$  Hz, CHCH<sub>3</sub>), 1.37 (quint,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.31-1.08 (m, 8H, CH<sub>2</sub>), 0.97 (t,  $J=7.5$  Hz, 3H, CH<sub>3</sub> EPA), 0.89 (t,  $J=6.8$  Hz, 3H, CH<sub>3</sub> SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.3 (SFA), 173.1 (EPA), 157.9, 135.3, 133.9, 132.2, 129.4, 129.08, 129.05, 129.0, 128.7, 128.4, 128.34, 128.31, 128.2, 128.0, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.29, 62.0, 55.4, 45.5, 33.9, 33.5, 32.1, 29.4, 29.2, 26.7, 25.8 (2), 25.7 (2), 24.8, 24.8, 22.8, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>45</sub>H<sub>62</sub>O<sub>7</sub>Na 737.4388; found, 737.4379.

### 3.5.17. Synthesis of 1-decanoyl-3-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2[(*S*)-2-(6-methoxy-naphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**11c**

The same procedure was followed as described for (*R,S'*)-**11a** using 1-decanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**9c** (23 mg, 0.052 mmol), EPA (24 mg, 0.079 mmol),  $\text{CH}_2\text{Cl}_2$  (5 mL), DMAP (11 mg, 0.087 mmol) and EDCI (20 mg, 0.105 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*R,S'*)-**11c** as a yellow oil, in 86% yield (34 mg, 0.045 mmol).  $[\alpha]^{20}_{\text{D}} = +8.76$  (c. 2.1,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3012 (vs), 2958 (vs), 2928 (vs), 2855 (vs), 1743 (vs), 1634 (s), 1607 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.76-7.54 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5$ , 1.9 Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9$ , 2.6 Hz, 1H, Nap-7), 7.09 (d,  $J=2.6$  Hz, 1H, Nap-5), 5.47-5.30 (m, 10H, =CH), 5.30-5.19 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.22-4.11 (m, 2H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9$ , 6.4 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.86 (q,  $J=7.1$  Hz, 1H, CHCH<sub>3</sub>), 2.96-2.73 (m, 8H, =CHCH<sub>2</sub>CH=), 2.31-2.23 (m, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.13-2.02 (m, 2H,  $\text{CH}_2\text{COO}$  SFA), 2.02-1.86 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.60-1.55 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.57 (d,  $J=7.1$  Hz, CHCH<sub>3</sub>), 1.39 (quint,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.31-1.08 (m, 12H, CH<sub>2</sub>), 0.97 (t,  $J=7.5$  Hz, 3H, CH<sub>3</sub>

EPA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.3 (SFA), 173.1 (EPA), 157.9, 135.3, 133.9, 132.2, 129.4, 129.08, 129.05, 129.0, 128.7, 128.4, 128.4, 128.3, 128.2, 128.0, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.3, 62.0, 55.4, 45.5, 33.9, 33.5, 32.1, 29.6, 29.5, 29.4, 29.2, 26.7, 25.8 (2), 25.7 (2), 24.80, 24.76, 22.8, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{47}\text{H}_{66}\text{O}_7\text{Na}$  765.4701; found, 765.4620.

### 3.5.18. Synthesis of 1-dodecanoyl-3-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (R,S')-**11d**

The same procedure was followed as described for (R,S')-**11a** using 1-dodecanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (S,S')-**9d** (19 mg, 0.038 mmol), EPA (13 mg, 0.041 mmol),  $\text{CH}_2\text{Cl}_2$  (1.6 mL), DMAP (5 mg, 0.041 mmol) and EDCI (11 mg, 0.056 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (R,S')-**11d** as a pale-yellow oil, in 74% yield (22 mg, 0.028 mmol).  $[\alpha]^{20}_{\text{D}} = +5.20$  (c. 1.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3012 (vs), 2926 (vs), 2854 (vs), 1743 (vs), 1634 (s), 1607 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.77-7.54 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5$ , 1.9 Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9$ , 2.6 Hz, 1H, Nap-7), 7.09 (d,  $J=2.6$  Hz, 1H, Nap-5), 5.47-5.30 (m, 10H, =CH), 5.30-5.19 (m, 1H, CH *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.22-4.11 (m, 2H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9$ , 6.4 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.86 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 2.96-2.73 (m, 8H, =CH $\text{CH}_2\text{CH}=$ ), 2.30-2.23 (m, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.13-2.01 (m, 2H,  $\text{CH}_2\text{COO}$  SFA), 2.01-1.86 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and =CH $\text{CH}_2\text{CH}_3$ ), 1.60-1.55 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.57 (d,  $J=7.1$  Hz,  $\text{CHCH}_3$ ), 1.37 (quint,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.31-1.08 (m, 16H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.3 (SFA), 173.1 (EPA), 157.9, 135.3, 133.9, 132.2, 129.39, 129.08, 129.05, 129.0, 128.7, 128.44, 128.35, 128.3, 128.2, 128.0, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.3, 62.0, 55.4, 45.5, 33.9, 33.5, 32.1, 29.8 (2), 29.6, 29.5, 29.4, 29.2, 26.7, 25.8 (2), 25.7 (2), 24.80, 24.76, 22.8, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{49}\text{H}_{70}\text{O}_7\text{Na}$  793.5013; found, 793.5013.

### 3.5.19. Synthesis of 3-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-2[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-tetracanoyl-*sn*-glycerol, (R,S')-**11e**

The same procedure was followed as described for (R,S')-**11a** using 2-[(S)-2-(4-isobutylphenyl)propanoyl]-1-tetracanoyl-*sn*-glycerol (S,S')-**9e** (13 mg, 0.025 mmol), EPA (8 mg, 0.027 mmol),  $\text{CH}_2\text{Cl}_2$  (1 mL), DMAP (3 mg, 0.024 mmol) and EDCI (7 mg, 0.037 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (R,S')-**11e** as a pale-yellow oil, in 90% yield (15 mg, 0.019 mmol).  $[\alpha]^{20}_{\text{D}} = +6.30$  (c. 1.5,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3012 (s), 2951 (vs), 2926 (vs), 2854 (vs), 1743 (vs), 1633 (s), 1607 (s).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.71-7.62 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5$ , 1.9 Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9$ , 2.6 Hz, 1H, Nap-7), 7.09 (d,  $J=2.6$  Hz, 1H, Nap-5), 5.44-5.29 (m, 10H, =CH), 5.30-5.12 (m, 1H, CH *sn*-2), 4.29 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.19-4.11 (m, 2H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9$ , 6.4 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.86 (q,  $J=7.1$  Hz, 1H,  $\text{CHCH}_3$ ), 2.88-2.74 (m, 8H, =CH $\text{CH}_2\text{CH}=$ ), 2.30-2.23 (m, 2H,  $\text{CH}_2\text{COO}$  EPA), 2.13-2.02 (m, 2H,  $\text{CH}_2\text{COO}$  SFA), 2.02-1.89 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}=$  and =CH $\text{CH}_2\text{CH}_3$ ), 1.60-1.55 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA), 1.57 (d,  $J=7.1$  Hz,  $\text{CHCH}_3$ ), 1.37 (quint,  $J=7.6$  Hz, 2H,  $\text{CH}_2\text{CH}_2\text{COO}$  EPA), 1.32-1.06 (m, 20H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  EPA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.3 (SFA), 173.1 (EPA), 157.9, 135.4, 133.9, 132.2, 129.40, 129.09, 129.05, 129.0, 128.7, 128.44, 128.35, 128.3, 128.2, 128.0, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.30, 62.0, 55.4, 45.5, 33.9, 33.5, 32.1, 30.1 (2), 29.9, 29.82, 29.78, 29.6, 29.5, 29.4, 29.2, 26.7 (2), 25.7 (2), 24.80, 24.77, 22.9, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{51}\text{H}_{74}\text{O}_7\text{Na}$  821.5327; found, 821.5302.

### 3.5.20. Synthesis of 3-[5Z,8Z,11Z,14Z,17Z]-eicosa-5,8,11,14,17-pentaenoyl]-1-hexadecanoyl-2[(S)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (R,S')-**11f**

The same procedure was followed as described for (*R,S'*)-**11f** using 1-hexadecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**9f** (10 mg, 0.018 mmol), EPA (6 mg, 0.020 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL), DMAP (2 mg, 0.016 mmol) and EDCI (4 mg, 0.020 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent afforded the product (*R,S'*)-**11f** as a pale-yellow oil, in 89% yield (13 mg, 0.016 mmol).  $[\alpha]^{20}_{\text{D}} = +6.23$  (c. 1.3, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3012 (s), 2962 (vs), 2925 (vs), 1741 (vs), 1635 (s), 1607 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.72-7.60 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.6 Hz, 1H, Nap-7), 7.09 (d, *J*=2.6 Hz, 1H, Nap-5), 5.46-5.28 (m, 10H, =CH), 5.30-5.12 (m, 1H, CH *sn*-2), 4.29 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.17-4.09 (m, 2H, CH<sub>2</sub> *sn*-1/3), 4.05 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.90 (s, 3H, OCH<sub>3</sub>), 3.86 (q, *J*=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.90-2.73 (m, 8H, =CHCH<sub>2</sub>CH=), 2.31-2.22 (m, 2H, CH<sub>2</sub>COO EPA), 2.14-2.08 (m, 2H, CH<sub>2</sub>COO SFA), 2.04-1.86 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH= and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.60-1.56 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.57 (d, *J*=7.1 Hz, CHCH<sub>3</sub>), 1.35 (quint, *J*= 7.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>COO EPA), 1.18-1.06 (m, 24H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> EPA), 0.89 (t, *J*=6.8 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 173.9 (Nap), 173.3 (SFA), 173.1 (EPA), 157.8, 135.3, 133.9, 132.2, 129.3, 129.1, 129.04, 129.0, 128.7, 128.4, 128.34, 128.31, 128.2, 128.0, 127.23, 127.15, 126.3, 126.1, 119.2, 105.7, 69.5, 62.3, 62.0, 55.4, 45.5, 33.9, 33.5, 32.1, 30.1 (2), 29.9 (2), 29.81, 29.77, 29.6, 29.5, 29.4, 29.2, 26.6, 25.8 (2), 25.7 (2), 24.78, 24.75, 22.8, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>53</sub>H<sub>78</sub>O<sub>7</sub>Na 849.5640; found, 849.5638.

### 3.6. Coupling of DHA: Synthesis of (*S,S'*)-**12b-f**, (*R,S'*)-**12b-f**, (*S,S'*)-**13b-f** and (*R,S'*)-**13b-f**

#### 3.6.1. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-3-octanoyl-*sn*-glycerol, (*S,S'*)-**12b**

The same procedure was followed as described for (*S,S'*)-**12a** using 2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-3-octanoyl-*sn*-glycerol (*R,S'*)-**8b** (25 mg, 0.061 mmol), DHA (22 mg, 0.067 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (7 mg, 0.059 mmol) and EDCI (14 mg, 0.071 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*S,S'*)-**12b** as a pale-yellow oil, in 86% yield (38 mg, 0.052 mmol).  $[\alpha]^{20}_{\text{D}} = +4.44$  (c. 2.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.45-5.22 (m, 13H, =CH and CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.18 (dd, *J*=11.9, 4.5 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.14 (dd, *J*=11.9, 6.0 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.06 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.89-2.77 (m, 10H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.30-2.24 (m 6H, CH<sub>2</sub>CH<sub>2</sub>COO DHA and CH<sub>2</sub>COO SFA), 2.12-2.08 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.83 (nonet, *J*=6.9 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.64-1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.33-1.20 (m, 8H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.90 (t, *J*=6.4 Hz, 3H, CH<sub>3</sub> SFA), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 173.8 (Ibu), 173.2 (SFA), 172.4 (DHA), 140.6, 137.3, 132.0, 129.4 (2), 129.3, 128.6, 128.30, 128.27, 128.25, 128.09, 128.07, 128.0, 127.9, 127.7 (2), 127.1, 127.0, 69.2, 62.1, 62.0, 45.04, 45.02, 34.0, 33.7, 31.7, 30.2, 29.1, 28.9, 25.7 (2), 25.6, 25.5 (2), 24.8, 22.6, 22.5 (2), 22.4, 20.6, 18.4, 14.3, 14.1 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>46</sub>H<sub>68</sub>O<sub>6</sub>Na 739.4908; found, 739.4896.

#### 3.6.2. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-3-decanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*S,S'*)-**12c**

The same procedure was followed as described for (*S,S'*)-**12a** using 3-decanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**8c** (40 mg, 0.092 mmol), DHA (33 mg, 0.101 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3.5 mL), DMAP (10 mg, 0.083 mmol) and EDCI (19 mg, 0.100 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*S,S'*)-**12c** as a yellow oil, in 95% yield (65 mg, 0.087 mmol).  $[\alpha]^{20}_{\text{D}} = +4.05$  (c. 6.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.41-5.32 (m, 12H, =CH), 5.28-5.22 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.19 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.13 (dd, *J*=11.9, 6.0 Hz,

1H, CH<sub>2</sub> *sn*-1/3), 4.08 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.86-2.80 (m, 10H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.30-2.24 (m 6H, CH<sub>2</sub>CH<sub>2</sub>COO DHA and CH<sub>2</sub>COO SFA), 2.08-2.06 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.83 (nonet, *J*=6.9 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.62-1.56 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.33-1.20 (m, 12H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.90 (t, *J*=6.4 Hz, 3H, CH<sub>3</sub> SFA), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>c</sub>: 173.8 (Ibu), 173.2 (SFA), 172.4 (DHA), 140.6, 137.3, 132.0, 129.4 (2), 129.3, 128.6, 128.30, 128.29, 128.26, 128.08, 128.06, 127.91, 127.85, 127.7 (2), 127.1, 127.0, 69.2, 62.1, 62.0, 45.0, 45.0, 34.0, 33.7, 31.9, 30.2 (2), 29.4, 29.3, 29.1, 25.62 (2), 25.57, 25.5 (2), 24.8, 22.7, 22.5 (2), 22.4, 20.5, 18.4, 14.3, 14.1 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>48</sub>H<sub>72</sub>O<sub>6</sub>Na 767.5221; found, 767.5224.

### 3.6.3. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-3-dodecanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (S,S')-12d

The same procedure was followed as described for (S,S')-12a using 3-dodecanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-8d (15 mg, 0.034 mmol), DHA (29 mg, 0.057 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (9 mg, 0.071 mmol) and EDCI (12 mg, 0.088 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (S,S')-12d as a yellow oil, in 89% yield (23 mg, 0.030 mmol). [α]<sup>20</sup><sub>D</sub> = +5.30 (c. 2.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.41-5.25 (m, 13H, =CH and CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.19 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.13 (dd, *J*=11.9, 5.8 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.08 (dd, *J*=11.9, 6.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.86-2.80 (m, 10H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.30-2.24 (m 6H, CH<sub>2</sub>CH<sub>2</sub>COO DHA and CH<sub>2</sub>COO SFA), 2.08-2.06 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.83 (nonet, *J*=6.9 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.59-1.48 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.32-1.26 (m, 16H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.88 (t, *J*=6.4 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>c</sub>: 173.8 (Ibu), 173.4 (SFA), 172.6 (DHA), 140.8, 137.4, 132.2, 129.5 (2), 129.4, 128.7, 128.5, 128.43, 128.40, 128.3, 128.23, 128.16, 128.0, 127.8 (2), 127.3, 127.2, 69.3, 62.24, 62.17, 45.19, 45.18, 34.2, 33.8, 32.1, 30.3, 29.9, 29.8, 29.6, 29.5, 29.4, 29.2, 25.8 (2), 25.74, 25.70 (2), 25.0, 22.8, 22.7 (2), 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>50</sub>H<sub>76</sub>O<sub>6</sub>Na 795.5534; found, 795.5539.

### 3.6.4. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(S)-2-(4-isobutylphenyl)propanoyl]-3-tetradecanoyl-*sn*-glycerol, (S,S')-12e

The same procedure was followed as described for (S,S')-12a using 2-[(S)-2-(4-isobutylphenyl)propanoyl]-3-tetradecanoyl-*sn*-glycerol (*R,S'*)-8e (19 mg, 0.039 mmol), DHA (25 mg, 0.076 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.6 mL), DMAP (8 mg, 0.062 mmol) and EDCI (16 mg, 0.075 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (S,S')-12e as a yellow oil, in 82% yield (26 mg, 0.032 mmol). [α]<sup>20</sup><sub>D</sub> = +7.54 (c. 2.6, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.41-5.32 (m, 12H, =CH), 5.32-5.22 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.19 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.13 (dd, *J*=11.9, 5.8 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.08 (dd, *J*=11.9, 6.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.86-2.80 (m, 10H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.31-2.22 (m 6H, CH<sub>2</sub>CH<sub>2</sub>COO DHA and CH<sub>2</sub>COO SFA), 2.08-2.06 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.83 (nonet, *J*=6.9 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.59-1.48 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.32-1.26 (m, 20H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (d, *J*=6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.88 (t, *J*=6.4 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>c</sub>: 173.9 (Ibu), 173.4 (SFA), 172.6 (DHA), 140.8, 137.4, 132.2, 129.5 (2), 129.4, 128.7, 128.5, 128.42, 128.40, 128.3, 128.22, 128.16, 128.0, 127.8 (2), 127.3, 127.2, 69.3, 62.24, 62.17, 45.19, 45.18, 34.2, 33.8, 32.1, 30.3, 30.1 (2), 29.84, 29.81, 29.78, 29.6, 29.5, 29.4, 29.3 (2), 25.8, 25.7 (2), 25.0, 22.8, 22.7 (2), 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>52</sub>H<sub>80</sub>O<sub>6</sub>Na 823.5847; found, 823.5840.

### 3.6.5. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(S)-3-hexadecanoyl-2-(4-isobutylphenyl)propanoyl]-sn-glycerol, (S,S')-**12f**

The same procedure was followed as described for (S,S')-**12a** using 3-hexadecanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol (R,S')-**8f** (42 mg, 0.081 mmol), DHA (30 mg, 0.089 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (9 mg, 0.073 mmol) and EDCI (17 mg, 0.088 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (S,S')-**12f** as a yellow oil, in 85% yield (57 mg, 0.069 mmol).  $[\alpha]^{20}_D = +3.16$  (c. 5.7, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.45-5.28 (m, 12H, =CH), 5.28-5.22 (m, 1H, CH sn-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.19 (dd,  $J=11.9, 4.2$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.13 (dd,  $J=11.9, 5.8$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.08 (dd,  $J=11.9, 6.3$  Hz, 1H, CH<sub>2</sub> sn-1/3), 3.70 (q,  $J=7.2$  Hz, 1H, CHCH<sub>3</sub>), 2.89-2.78 (m, 10H, =CHCH<sub>2</sub>CH=), 2.43 (d,  $J=7.2$  Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.34-2.19 (m 6H, CH<sub>2</sub>CH<sub>2</sub>COO DHA and CH<sub>2</sub>COO SFA), 2.09-2.07 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.83 (nonet,  $J=6.9$  Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.64-1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d,  $J=7.2$  Hz, 3H, CHCH<sub>3</sub>), 1.34-1.20 (m, 24H, CH<sub>2</sub>), 0.97 (t,  $J=7.5$  Hz, 3H, CH<sub>3</sub> DHA), 0.89 (d,  $J=6.8$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.88 (t,  $J=7.1$  Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_C$ : 173.9 (Ibu), 173.4 (SFA), 172.6 (DHA), 140.8, 137.4, 132.2, 129.5 (2), 129.4, 128.7, 128.5 (2), 128.4, 128.3, 128.22, 128.16, 128.0, 127.8 (2), 127.3, 127.2, 69.3, 62.23, 62.17, 45.19, 45.18, 34.2, 33.9, 32.1, 30.3, 30.1 (2), 29.9 (2), 29.81, 29.78, 29.6, 29.5, 29.4, 29.3, 25.8 (2), 25.73, 25.69 (2), 25.0, 22.8, 22.7 (2), 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>54</sub>H<sub>84</sub>O<sub>6</sub>Na 851.6160; found, 851.6158.

### 3.6.6. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(S)-2-(4-isobutylphenyl)propanoyl]-1-octanoyl-sn-glycerol, (R,S')-**12b**

The same procedure was followed as described for (R,S')-**12a** using 2-[(S)-2-(4-isobutylphenyl)propanoyl]-1-octanoyl-sn-glycerol (S,S')-**8b** (29 mg, 0.071 mmol), DHA (25 mg, 0.076 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (10 mg, 0.077 mmol) and EDCI (20 mg, 0.101 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (R,S')-**12b** as a yellow oil, in 83% yield (43 mg, 0.059 mmol).  $[\alpha]^{20}_D = +7.86$  (c. 3.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{max}$  / cm<sup>-1</sup>): 3013 (s), 2958 (vs), 2931 (vs), 2870 (vs), 1741 (vs), 1657 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.45-5.22 (m, 13H, =CH and CH sn-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.18 (dd,  $J=11.9, 4.2$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.14 (dd,  $J=11.9, 6.0$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.06 (dd,  $J=11.9, 6.3$  Hz, 1H, CH<sub>2</sub> sn-1/3), 3.70 (q,  $J=7.2$  Hz, 1H, CHCH<sub>3</sub>), 2.89-2.77 (m, 10H, =CHCH<sub>2</sub>CH=), 2.43 (d,  $J=7.2$  Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.40-2.27 (m 4H, CH<sub>2</sub>CH<sub>2</sub>COO DHA), 2.17-2.13 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 2.08 (t,  $J=7.4$  Hz, 2H, CH<sub>2</sub>COO SFA), 1.83 (nonet,  $J=6.8$  Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.64-1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.49 (d,  $J=7.2$  Hz, 3H, CHCH<sub>3</sub>), 1.37-1.24 (m, 8H, CH<sub>2</sub>), 0.97 (t,  $J=7.5$  Hz, 3H, CH<sub>3</sub> DHA), 0.90 (d,  $J=6.6$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.89 (t,  $J=6.4$  Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_C$ : 173.8 (Ibu), 173.1 (SFA), 172.5 (DHA), 140.6, 137.2, 132.0, 129.5 (2), 129.3, 128.6, 128.31, 128.26, 128.2, 128.08, 128.06, 128.0, 127.9, 127.7, 127.1 (2), 127.0, 69.2, 62.2, 61.9, 45.1, 45.0, 33.9, 33.8, 31.7, 30.2, 29.0, 28.9, 25.63 (2), 25.58, 25.5 (2), 24.7, 22.9, 22.6 (2), 22.4, 20.54, 18.3, 14.3, 14.0 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>46</sub>H<sub>68</sub>O<sub>6</sub>Na 739.4908; found, 739.4897.

### 3.6.7. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-1-decanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol, (R,S')-**12c**

The same procedure was followed as described for (R,S')-**12a** using 1-decanoyl-2-[(S)-2-(4-isobutylphenyl)propanoyl]-sn-glycerol (S,S')-**8c** (55 mg, 0.127 mmol), DHA (45 mg, 0.140 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (19 mg, 0.197 mmol) and EDCI (38 mg, 0.197 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (R,S')-**12c** as a yellow oil, in 80% yield (75 mg, 0.101 mmol).  $[\alpha]^{20}_D = +4.57$  (c. 6.5, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{max}$  / cm<sup>-1</sup>): 3013 (s), 2957 (vs), 2927 (vs), 2855 (vs), 1744 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.45-5.22 (m, 13H, =CH and CH sn-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H, CH<sub>2</sub> sn-1/3), 4.18 (dd,

$J=11.9, 4.2$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.14 (dd,  $J=11.9, 6.0$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9, 6.4$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.70 (q,  $J=7.2$  Hz, 1H,  $\text{CHCH}_3$ ), 2.89-2.77 (m, 10H,  $=\text{CHCH}_2\text{CH}=$ ), 2.43 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.40-2.27 (m 4H,  $\text{CH}_2\text{CH}_2\text{COO DHA}$ ), 2.17-2.13 (m, 2H,  $=\text{CHCH}_2\text{CH}_3$ ), 2.08 (t,  $J=7.4$  Hz, 2H,  $\text{CH}_2\text{COO SFA}$ ), 1.83 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.61-1.56 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO SFA}$ ), 1.49 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.37-1.24 (m, 12H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  DHA), 0.90 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.89 (t,  $J=6.4$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 173.9 (Ibu), 173.3 (SFA), 172.6 (DHA), 140.7, 137.4, 132.1, 129.6 (2), 129.4, 128.7, 128.5, 128.40, 128.38, 128.22, 128.20, 128.12, 128.08, 128.00 (2), 127.8, 127.2, 69.3, 62.34, 62.0, 45.16, 45.15, 34.0, 32.0, 30.3, 30.2, 29.6 (2), 29.4, 29.2, 25.8 (2), 25.72, 25.67 (2), 24.9, 22.8, 22.7 (2), 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{48}\text{H}_{72}\text{O}_6\text{Na}$  767.5221; found, 767.5218.

### 3.6.8. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-1-dodecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**12d**

The same procedure was followed as described for (*R,S'*)-**12a** using 3-dodecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*S,S'*)-**8d** (40 mg, 0.082 mmol), DHA (32 mg, 0.097 mmol),  $\text{CH}_2\text{Cl}_2$  (4 mL), DMAP (13 mg, 0.106 mmol) and EDCI (30 mg, 0.156 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent afforded the product (*R,S'*)-**12d** as a yellow oil, in 78% yield (50 mg, 0.064 mmol).  $[\alpha]^{20}\text{D} = +6.57$  (c. 4.2,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3418 (br), 3012 (vs), 2925 (vs), 2854 (vs), 1743 (vs).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.52-5.30 (m, 12H,  $=\text{CH}$ ), 5.30-5.17 (m, 1H,  $\text{CH}$  *sn*-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.23-4.09 (m, 2H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9, 6.3$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.70 (q,  $J=7.2$  Hz, 1H,  $\text{CHCH}_3$ ), 2.89-2.74 (m, 10H,  $=\text{CHCH}_2\text{CH}=$ ), 2.44 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.40-2.32 (m 4H,  $\text{CH}_2\text{CH}_2\text{COO DHA}$ ), 2.18-2.11 (m, 2H,  $=\text{CHCH}_2\text{CH}_3$ ), 2.08 (t,  $J=7.4$  Hz, 2H,  $\text{CH}_2\text{COO SFA}$ ), 1.83 (nonet,  $J=6.7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.59-1.48 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO SFA}$ ), 1.49 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.37-1.24 (m, 16H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  DHA), 0.90 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.89 (t,  $J=7.2$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 173.9 (Ibu), 173.3 (SFA), 172.6 (DHA), 140.7, 137.4, 132.2, 129.6 (2), 129.4, 128.7, 128.5, 128.41, 128.39, 128.23, 128.21, 128.1, 127.8, 127.2 (2), 127.1, 127.0, 69.3, 62.4, 62.1, 45.17, 45.15, 34.0, 32.0, 30.3, 30.2, 29.8 (2), 29.6, 29.5, 29.4, 29.3, 25.8, 25.74 (2), 25.68, 25.0 (2), 24.9, 22.82, 22.75 (2), 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{50}\text{H}_{76}\text{O}_6\text{Na}$  795.5534; found, 795.5535.

### 3.6.9. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-1-tetradecanoyl-*sn*-glycerol, (*R,S'*)-**12e**

The same procedure was followed as described for (*R,S'*)-**12a** using 2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-1-tetradecanoyl-*sn*-glycerol (*S,S'*)-**8e** (30 mg, 0.061 mmol), DHA (23 mg, 0.070 mmol),  $\text{CH}_2\text{Cl}_2$  (4 mL), DMAP (9 mg, 0.074 mmol) and EDCI (18 mg, 0.099 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*R,S'*)-**12e** as a yellow oil, in 82% yield (40 mg, 0.050 mmol).  $[\alpha]^{20}\text{D} = +7.01$  (c. 4.0,  $\text{CH}_2\text{Cl}_2$ ). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3013 (s), 2956 (vs), 2925 (vs), 2853 (vs), 1743 (vs).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.18 (d,  $J=8.1$  Hz, 2H, Ibu-2,6), 7.07 (d,  $J=8.1$  Hz, 2H, Ibu-3,5), 5.47-5.27 (m, 12H,  $=\text{CH}$ ), 5.31-5.20 (m, 1H,  $\text{CH}$  *sn*-2), 4.30 (dd,  $J=11.9, 4.2$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.19 (dd,  $J=11.9, 4.2$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.13 (dd,  $J=11.9, 5.9$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.06 (dd,  $J=11.9, 6.3$  Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.70 (q,  $J=7.2$  Hz, 1H,  $\text{CHCH}_3$ ), 2.90-2.77 (m, 10H,  $=\text{CHCH}_2\text{CH}=$ ), 2.43 (d,  $J=7.2$  Hz, 2H,  $\text{CH}_2\text{CH}(\text{CH}_3)_2$ ), 2.41-2.32 (m 4H,  $\text{CH}_2\text{CH}_2\text{COO DHA}$ ), 2.20-2.11 (m, 2H,  $=\text{CHCH}_2\text{CH}_3$ ), 2.14-2.01 (m, 2H,  $\text{CH}_2\text{COO SFA}$ ), 1.83 (nonet,  $J=6.8$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 1.60-1.48 (m, 2H,  $\text{CH}_2\text{CH}_2\text{COO SFA}$ ), 1.49 (d,  $J=7.2$  Hz, 3H,  $\text{CHCH}_3$ ), 1.36-1.18 (m, 20H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  DHA), 0.90 (d,  $J=6.6$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 0.89 (t,  $J=6.4$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 174.0 (Ibu), 173.3 (SFA), 172.7 (DHA), 140.7, 137.4, 132.2, 129.6 (2), 129.4, 128.7, 128.5, 128.43, 128.41, 128.3, 128.23, 128.15, 128.0, 127.8 (2), 127.3, 127.2, 69.3, 62.4, 62.1, 45.18, 45.15, 34.02, 33.97, 31.4, 30.3, 29.8 (2), 29.6 (2), 29.5 (2), 29.4, 29.3, 25.79, 25.75 (2), 25.7, 24.56 (2), 22.8, 22.4 (2), 22.8, 20.7, 18.5, 14.4, 14.1 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{52}\text{H}_{80}\text{O}_6\text{Na}$  823.5847; found, 823.5843.

3.6.10. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-1-hexadecanoyl-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol, (*R,S'*)-**12f**

The same procedure was followed as described for (*R,S'*)-**12a** using 1-hexadecanoyl-2-[(*S*)-2-(4-isobutylphenyl)propanoyl]-*sn*-glycerol (*R,S'*)-**8f** (12 mg, 0.023 mmol), DHA (8 mg, 0.025 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL), DMAP (3 mg, 0.021 mmol) and EDCI (5 mg, 0.025 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*R,S'*)-**12f** as a yellow oil, in 79% yield (18 mg, 0.018 mmol).  $[\alpha]^{20}_{\text{D}} = +3.93$  (c. 1.5, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{\text{max}}$  / cm<sup>-1</sup>): 3030 (s), 2963 (vs), 2925 (vs), 2855 (vs), 1743 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.18 (d, *J*=8.1 Hz, 2H, Ibu-2,6), 7.07 (d, *J*=8.1 Hz, 2H, Ibu-3,5), 5.47-5.27 (m, 12H, =CH), 5.28-5.22 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.23-4.09 (m, 2H, CH<sub>2</sub> *sn*-1/3), 4.06 (dd, *J*=11.9, 6.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.70 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.91-2.77 (m, 10H, =CHCH<sub>2</sub>CH=), 2.43 (d, *J*=7.2 Hz, 2H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.42-2.31 (m 4H, CH<sub>2</sub>CH<sub>2</sub>COO DHA), 2.20-2.10 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 2.14-2.01 (m, 2H, CH<sub>2</sub>COO SFA), 1.83 (nonet, *J*=6.7 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.63-1.54 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.48 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.30-1.22 (m, 24H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (d, *J*=6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.88 (t, *J*=7.1 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 174.0 (Ibu), 173.3 (SFA), 172.7 (DHA), 140.7, 137.4, 132.2, 129.6 (2), 129.4, 128.7, 128.5, 128.43, 128.41, 128.25, 128.23, 128.15, 128.0, 127.8 (2), 127.3, 127.2, 69.3, 62.4, 62.1, 45.19 (2), 34.0, 33.9, 32.1, 30.3, 30.1 (2), 29.9 (2), 29.82, 29.79, 29.7, 29.5, 29.4, 29.3, 25.80 (2), 25.75, 25.7 (2), 24.9, 22.9, 22.8 (2), 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>54</sub>H<sub>84</sub>O<sub>6</sub>Na 851.6160; found, 851.6155.

3.6.11. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxy-naphthalen-2-yl)propanoyl]-3-octanoyl-*sn*-glycerol, (*S,S'*)-**13b**

The same procedure was followed as described for (*S,S'*)-**13a** using 2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-octanoyl-*sn*-glycerol (*R,S'*)-**9b** (35 mg, 0.081 mmol), DHA (29 mg, 0.089 mmol), CH<sub>2</sub>Cl<sub>2</sub> (4 mL), DMAP (9 mg, 0.074 mmol) and EDCI (17 mg, 0.089 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*S,S'*)-**13b** as a yellow oil, in 85% yield (51 mg, 0.069 mmol).  $[\alpha]^{20}_{\text{D}} = +2.78$  (c. 4.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.72-7.62 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.5 Hz, 1H, Nap-7), 7.09 (d, *J*=2.5 Hz, 1H, Nap-5), 5.49-5.22 (m, 12H, =CH), 5.20-5.14 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.18 (dd, *J*=11.9, 4.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.14 (dd, *J*=11.9, 6.1 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.07 (dd, *J*=11.9, 6.5 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.90 (s, 3H, OCH<sub>3</sub>), 3.86 (q, *J*=7.5 Hz, 1H, CHCH<sub>3</sub>), 2.91-2.72 (m, 10H, =CHCH<sub>2</sub>CH=), 2.28-2.20 (m, 2H, CH<sub>2</sub>COO DHA), 2.19-2.11 (m, 2H, CH<sub>2</sub>COO DHA), 2.14-1.96 (m, 4H, CH<sub>2</sub>COO SFA and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.61-1.51 (m, 5H, CH<sub>2</sub>CH<sub>2</sub>COO SFA and CHCH<sub>3</sub>), 1.36-1.19 (m, 8H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (t, *J*=6.8 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 173.9 (Nap), 173.4 (SFA), 172.5 (DHA), 157.9, 135.4, 133.9, 132.2, 129.4 (2), 129.0, 128.7, 128.42, 128.40, 128.38, 128.3, 128.23, 128.18, 128.0, 127.8, 127.24, 127.16, 126.3, 126.1, 119.2, 105.7, 69.5, 62.20, 62.17, 55.4, 45.5, 34.1, 33.7, 31.8, 29.2, 29.1, 25.8 (2), 25.7, 25.6 (2), 25.0, 22.8, 22.5, 20.7, 18.5, 14.4, 14.2 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>47</sub>H<sub>64</sub>O<sub>7</sub>Na 763.4544; found, 763.4543.

3.6.12. Synthesis of 3-decanoyl-1-[4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**13c**

The same procedure was followed as described for (*S,S'*)-**13a** using 3-decanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol (*R,S'*)-**9c** (20 mg, 0.044 mmol), DHA (16 mg, 0.048 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL), DMAP (5 mg, 0.040 mmol) and EDCI (9 mg, 0.048 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*S,S'*)-**13c** as a yellow oil, in 89% yield (30 mg, 0.039 mmol).  $[\alpha]^{20}_{\text{D}} = +6.60$  (c. 3.0, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.73-7.62 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.5 Hz, 1H, Nap-7), 7.09 (d, *J*=2.5 Hz, 1H, Nap-5), 5.44-5.23 (m, 12H, =CH), 5.23-5.09 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3),

4.18 (dd,  $J=11.9$ , 4.3 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.14 (dd,  $J=11.9$ , 6.1 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.07 (dd,  $J=11.9$ , 6.5 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.86 (q,  $J=7.5$  Hz, 1H,  $\text{CHCH}_3$ ), 2.89-2.64 (m, 10H,  $=\text{CHCH}_2\text{CH}=$ ), 2.28-2.20 (m, 2H,  $\text{CH}_2\text{COO}$  DHA), 2.20-2.13 (m, 2H,  $\text{CH}_2\text{COO}$  DHA), 2.13-1.98 (m, 4H,  $\text{CH}_2\text{COO}$  SFA and  $=\text{CHCH}_2\text{CH}_3$ ), 1.61-1.51 (m, 5H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA and  $\text{CHCH}_3$ ), 1.36-1.19 (m, 12H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  DHA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.4 (SFA), 172.5 (DHA), 157.9, 135.3, 133.9, 132.2, 129.4 (2), 129.0, 128.7, 128.42, 128.42, 128.39, 128.3, 128.22, 128.17, 128.0, 127.8, 127.24, 127.16, 126.3, 126.1, 119.20, 105.7, 69.5, 62.19, 62.16, 55.4, 45.5, 34.1, 33.7, 32.0, 29.6 (2), 29.41, 29.39, 25.8 (2), 25.7, 25.6 (2), 25.0, 22.8, 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{49}\text{H}_{68}\text{O}_7\text{Na}$  791.4857; found, 791.4853.

### 3.6.13. Synthesis of 3-dodecanoyl-1-[4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**13d**

The same procedure was followed as described for (*S,S'*)-**13a** using 3-dodecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol (*R,S'*)-**9d** (43 mg, 0.085 mmol), DHA (31 mg, 0.094 mmol),  $\text{CH}_2\text{Cl}_2$  (3 mL), DMAP (10 mg, 0.077 mmol) and EDCI (18 mg, 0.093 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*S,S'*)-**13d** as a yellow oil, in 92% yield (61 mg, 0.078 mmol).  $[\alpha]^{20}_{\text{D}} = +3.67$  (c. 6.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.71-7.64 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5$ , 1.9 Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9$ , 2.5 Hz, 1H, Nap-7), 7.09 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.43-5.23 (m, 12H,  $=\text{CH}$ ), 5.23-5.09 (m, 1H,  $\text{CH}$  *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.18 (dd,  $J=11.9$ , 4.3 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.14 (dd,  $J=11.9$ , 6.1 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.07 (dd,  $J=11.9$ , 6.5 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.86 (q,  $J=7.5$  Hz, 1H,  $\text{CHCH}_3$ ), 2.88-2.74 (m, 10H,  $=\text{CHCH}_2\text{CH}=$ ), 2.27-2.21 (m, 2H,  $\text{CH}_2\text{COO}$  DHA), 2.21-2.13 (m, 2H,  $\text{CH}_2\text{COO}$  DHA), 2.13-1.98 (m, 4H,  $\text{CH}_2\text{COO}$  SFA and  $=\text{CHCH}_2\text{CH}_3$ ), 1.61-1.51 (m, 5H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA and  $\text{CHCH}_3$ ), 1.36-1.19 (m, 12H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  DHA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.4 (SFA), 172.5 (DHA), 157.8, 135.3, 133.9, 132.2, 129.4 (2), 129.0, 128.7, 128.5, 128.42, 128.39, 128.3, 128.22, 128.17, 128.0, 127.8, 127.23, 127.16, 126.3, 126.1, 119.2, 105.7, 69.5, 62.19, 62.16, 55.4, 45.5, 34.1, 33.7, 32.1, 29.84 (2), 29.76, 29.6, 29.5, 29.4, 29.3 (2), 25.8, 25.7 (2), 25.0, 22.8, 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{51}\text{H}_{72}\text{O}_7\text{Na}$  819.5170; found, 819.5162.

### 3.6.14. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxy-naphthalen-2-yl)propanoyl]-3-tetradecanoyl-*sn*-glycerol, (*S,S'*)-**13e**

The same procedure was followed as described for (*S,S'*)-**13a** using 2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-3-tetradecanoyl-*sn*-glycerol (*R,S'*)-**9e** (25 mg, 0.049 mmol), DHA (18 mg, 0.054 mmol),  $\text{CH}_2\text{Cl}_2$  (2 mL), DMAP (5 mg, 0.044 mmol) and EDCI (10 mg, 0.053 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*S,S'*)-**13e** as a yellow oil, in 93% yield (43 mg, 0.046 mmol).  $[\alpha]^{20}_{\text{D}} = +7.37$  (c. 3.0,  $\text{CH}_2\text{Cl}_2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 7.72-7.64 (m, 3H, Nap-1,4,8), 7.38 (dd,  $J=8.5$ , 1.9 Hz, 1H, Nap-3), 7.13 (dd,  $J=8.9$ , 2.5 Hz, 1H, Nap-7), 7.09 (d,  $J=2.5$  Hz, 1H, Nap-5), 5.45-5.23 (m, 12H,  $=\text{CH}$ ), 5.23-5.09 (m, 1H,  $\text{CH}$  *sn*-2), 4.30 (dd,  $J=11.9$ , 4.2 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.18 (dd,  $J=11.9$ , 4.3 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.14 (dd,  $J=11.9$ , 6.1 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 4.07 (dd,  $J=11.9$ , 6.5 Hz, 1H,  $\text{CH}_2$  *sn*-1/3), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.86 (q,  $J=7.5$  Hz, 1H,  $\text{CHCH}_3$ ), 2.89-2.73 (m, 10H,  $=\text{CHCH}_2\text{CH}=$ ), 2.27-2.21 (m, 2H,  $\text{CH}_2\text{COO}$  DHA), 2.21-2.13 (m, 2H,  $\text{CH}_2\text{COO}$  DHA), 2.14-1.99 (m, 4H,  $\text{CH}_2\text{COO}$  SFA and  $=\text{CHCH}_2\text{CH}_3$ ), 1.60-1.50 (m, 5H,  $\text{CH}_2\text{CH}_2\text{COO}$  SFA and  $\text{CHCH}_3$ ), 1.37-1.20 (m, 12H,  $\text{CH}_2$ ), 0.97 (t,  $J=7.5$  Hz, 3H,  $\text{CH}_3$  DHA), 0.89 (t,  $J=6.8$  Hz, 3H,  $\text{CH}_3$  SFA) ppm.  $^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 173.9 (Nap), 173.4 (SFA), 172.5 (DHA), 157.9, 135.3, 133.9, 132.2, 129.4 (2), 129.0, 128.7, 128.5, 128.42, 128.39, 128.3, 128.22, 128.17, 128.0, 127.8, 127.24, 127.16, 126.3, 126.1, 119.2, 105.7, 69.5, 62.19, 62.16, 55.4, 45.5, 34.1, 33.7, 32.1, 29.83 (2), 29.80 (2), 29.77, 29.6, 29.5, 29.4, 29.3 (2), 25.8, 25.7 (2), 25.0, 22.8, 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI)  $m/z$ : [M + Na]<sup>+</sup> calcd for  $\text{C}_{53}\text{H}_{76}\text{O}_7\text{Na}$  847.5483; found, 847.5483.

3.6.15. Synthesis of 1-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-3-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*S,S'*)-**13f**

The same procedure was followed as described for (*S,S'*)-**13a** using 3-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol (*R,S'*)-**9f** (40 mg, 0.074 mmol), DHA (27 mg, 0.081 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL), DMAP (8 mg, 0.067 mmol) and EDCI (16 mg, 0.081 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*S,S'*)-**13f** as a yellow oil, in 92% yield (58 mg, 0.068 mmol).  $[\alpha]^{20}_{\text{D}} = +3.60$  (c. 5.5, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.71-7.64 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.5 Hz, 1H, Nap-7), 7.09 (d, *J*=2.5 Hz, 1H, Nap-5), 5.44-5.23 (m, 12H, =CH), 5.23-5.09 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.18 (dd, *J*=11.9, 4.3 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.14 (dd, *J*=11.9, 6.1 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.07 (dd, *J*=11.9, 6.5 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.90 (s, 3H, OCH<sub>3</sub>), 3.86 (q, *J*=7.5 Hz, 1H, CHCH<sub>3</sub>), 2.90-2.73 (m, 10H, =CHCH<sub>2</sub>CH=), 2.27-2.21 (m, 2H, CH<sub>2</sub>COO DHA), 2.20-2.13 (m, 2H, CH<sub>2</sub>COO DHA), 2.14-1.97 (m, 4H, CH<sub>2</sub>COO SFA and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.60-1.52 (m, 5H, CH<sub>2</sub>CH<sub>2</sub>COO SFA and CHCH<sub>3</sub>), 1.37-1.20 (m, 12H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (t, *J*=6.8 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 173.9 (Nap), 173.4 (SFA), 172.5 (DHA), 157.9, 135.3, 133.9, 132.2, 129.4 (2), 129.0, 128.7, 128.5, 128.42, 128.40, 128.3, 128.22, 128.17, 128.0, 127.8, 127.24, 127.16, 126.3, 126.1, 119.2, 105.7, 69.5, 62.19, 62.16, 55.4, 45.5, 34.1, 33.7, 32.1, 29.9 (2), 29.81 (2), 29.78 (2), 29.6 (2), 29.5, 29.4, 29.3 (2), 25.8, 25.7 (2), 25.0, 22.8, 22.5, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>55</sub>H<sub>80</sub>O<sub>7</sub>Na 875.5796; found, 875.5796.

3.6.16. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-octanoyl-*sn*-glycerol, (*R,S'*)-**13b**

The same procedure was followed as described for (*R,S'*)-**13a** using 2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-octanoyl-*sn*-glycerol (*S,S'*)-**9b** (44 mg, 0.061 mmol), DHA (23 mg, 0.070 mmol), CH<sub>2</sub>Cl<sub>2</sub> (4 mL), DMAP (9 mg, 0.074 mmol) and EDCI (18 mg, 0.099 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*R,S'*)-**13b** as a yellow oil, in 72% yield (47 mg, 0.063 mmol).  $[\alpha]^{20}_{\text{D}} = +2.01$  (c. 5.7, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3013 (s), 2959 (vs), 2856 (vs), 1743 (vs), 1634 (vs), 1607 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.70-7.64 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.5 Hz, 1H, Nap-7), 7.10 (d, *J*=2.5 Hz, 1H, Nap-5), 5.42-5.31 (m, 12H, =CH), 5.28-5.24 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.21-4.10 (m, 2H, CH<sub>2</sub> *sn*-1/3), 4.05 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.86 (q, *J*=7.2 Hz, 1H, CHCH<sub>3</sub>), 2.87-2.70 (m, 10H, =CHCH<sub>2</sub>CH=), 2.37-2.29 (m, 4H, CH<sub>2</sub>COO DHA), 2.14-2.01 (m, 2H, CH<sub>2</sub>COO SFA), 2.01-1.88 (m, 2H, =CHCH<sub>2</sub>CH<sub>3</sub>), 1.58 (d, *J*=7.2 Hz, 3H, CHCH<sub>3</sub>), 1.37 (quint, *J*=7.5 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.29-1.19 (m, 8H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.84 (t, *J*=7.0 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$ : 174.2 (Nap), 173.5 (SFA), 172.7 (DHA), 157.9, 137.9, 135.6, 133.9, 129.5, 129.1, 129.1, 128.7, 128.5, 128.44, 128.41, 128.3, 128.23, 128.16, 128.0, 127.8, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.4, 62.0, 55.4, 45.5, 34.0, 33.8, 31.3, 29.4, 29.2, 25.8 (2), 25.74, 25.70 (2), 24.8, 22.8, 22.4, 20.7, 18.5, 14.4, 14.0 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>47</sub>H<sub>64</sub>O<sub>7</sub>Na 763.4544; found, 763.4546.

3.6.17. Synthesis of 1-decanoyl-3-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**13c**

The same procedure was followed as described for (*R,S'*)-**13a** using 1-decanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol (*S,S'*)-**9c** (23 mg, 0.052 mmol), DHA (28 mg, 0.085 mmol), CH<sub>2</sub>Cl<sub>2</sub> (5 mL), DMAP (11 mg, 0.087 mmol) and EDCI (20 mg, 0.105 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*R,S'*)-**13c** as a yellow oil, in 80% yield (33 mg, 0.042 mmol).  $[\alpha]^{20}_{\text{D}} = +3.93$  (c. 2.9, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl,  $\nu_{\text{max}} / \text{cm}^{-1}$ ): 3013 (s), 2956 (vs), 2925 (vs), 2854 (vs), 1742 (vs), 1634 (s), 1607 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\text{H}}$ : 7.74-7.59 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.5 Hz, 1H, Nap-7), 7.09 (d, *J*=2.5 Hz, 1H, Nap-5), 5.46-

5.27 (m, 12H, =CH), 5.32-5.21 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.21-4.10 (m, 2H, CH<sub>2</sub> *sn*-1/3), 4.05 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.86 (q, *J*=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.94-2.75 (m, 10H, =CHCH<sub>2</sub>CH=), 2.41-2.07 (m, 4H, CH<sub>2</sub>COO DHA), 2.04-1.86 (m, 4H, CH<sub>2</sub>COO SFA) and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.58 (d, *J*=7.1 Hz, 3H, CHCH<sub>3</sub>), 1.44-1.06 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.29-1.22 (m, 12H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (t, *J*=7.0 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 173.9 (Nap), 173.3 (SFA), 172.7 (DHA), 157.9, 135.3, 133.9, 132.2, 129.6, 129.4, 129.1, 128.7, 128.5, 128.43, 128.41, 128.3, 128.23, 128.16, 128.0, 127.8, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.4, 62.0, 55.4, 45.5, 34.0, 33.9, 32.1, 29.6, 29.5, 29.4, 29.2, 25.8 (2), 25.74, 25.70 (2), 24.8, 22.8, 22.7, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>49</sub>H<sub>68</sub>O<sub>7</sub>Na 791.4857; found, 791.4812.

### 3.6.18. Synthesis of 1-dodecanoyl-3-[4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**13d**

The same procedure was followed as described for (*R,S'*)-**13a** using 1-dodecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol (*S,S'*)-**9d** (19 mg, 0.038 mmol), DHA (14 mg, 0.041 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1.6 mL), DMAP (5 mg, 0.041 mmol) and EDCI (11 mg, 0.056 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (8.5:1.5) as eluent afforded the product (*R,S'*)-**13d** as a yellow oil, in 92% yield (20 mg, 0.025 mmol). [α]<sub>20D</sub> = +3.50 (c. 2.0, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3013 (s), 2925 (vs), 2926 (vs), 2854 (vs), 1743 (vs), 1634 (s), 1607 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.74-7.59 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.5 Hz, 1H, Nap-7), 7.09 (d, *J*=2.5 Hz, 1H, Nap-5), 5.46-5.27 (m, 12H, =CH), 5.32-5.21 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.21-4.10 (m, 2H, CH<sub>2</sub> *sn*-1/3), 4.05 (dd, *J*=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.86 (q, *J*=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.94-2.75 (m, 10H, =CHCH<sub>2</sub>CH=), 2.41-2.27 (m, 4H, CH<sub>2</sub>COO DHA), 2.04-1.86 (m, 4H, CH<sub>2</sub>COO SFA) and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.58 (d, *J*=7.1 Hz, 3H, CHCH<sub>3</sub>), 1.44-1.06 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.29-1.22 (m, 16H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (t, *J*=7.0 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 173.9 (Nap), 173.3 (SFA), 172.7 (DHA), 157.9, 135.3, 133.9, 132.2, 129.6, 129.4, 129.1, 128.7, 128.5, 128.43, 128.41, 128.3, 128.23, 128.16, 128.0, 127.8, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.4, 62.0, 55.4, 45.5, 34.0, 33.9, 32.1, 29.8 (2), 29.6, 29.5, 29.4, 29.2, 25.8 (2), 25.7, 25.7 (2), 24.8, 22.8, 22.7, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>51</sub>H<sub>72</sub>O<sub>7</sub>Na 819.5170; found, 819.5169.

### 3.6.19. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z)-docosa-4,7,10,13,16,19-hexaenoyl]-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-tetradecanoyl-*sn*-glycerol, (*R,S'*)-**13e**

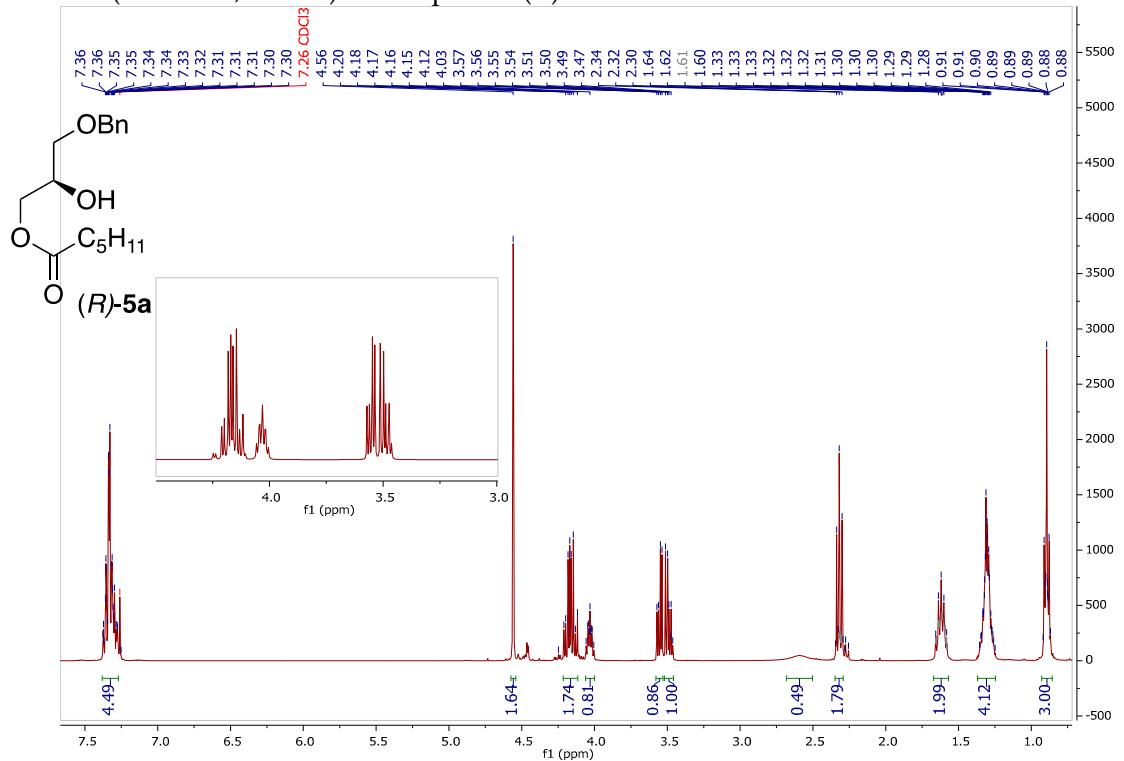
The same procedure was followed as described for (*R,S'*)-**13a** using 2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-1-tetradecanoyl-*sn*-glycerol (*S,S'*)-**9e** (13 mg, 0.025 mmol), DHA (9 mg, 0.027 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL), DMAP (3 mg, 0.024 mmol) and EDCI (7 mg, 0.037 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (4:1) as eluent afforded the product (*R,S'*)-**13e** as a yellow oil, in 88% yield (18 mg, 0.022 mmol). [α]<sub>20D</sub> = +4.58 (c. 1.8, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3013 (s), 2924 (vs), 2953 (vs), 2853 (vs), 1743 (vs), 1632 (s), 1607 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.72-7.60 (m, 3H, Nap-1,4,8), 7.38 (dd, *J*=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, *J*=8.9, 2.5 Hz, 1H, Nap-7), 7.09 (d, *J*=2.5 Hz, 1H, Nap-5), 5.46-5.28 (m, 12H, =CH), 5.28-5.21 (m, 1H, CH *sn*-2), 4.30 (dd, *J*=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.21-4.10 (m, 2H, CH<sub>2</sub> *sn*-1/3), 4.05 (dd, *J*=11.9, 6.5 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.89 (s, 3H, OCH<sub>3</sub>), 3.85 (q, *J*=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.89-2.77 (m, 10H, =CHCH<sub>2</sub>CH=), 2.40-2.07 (m, 4H, CH<sub>2</sub>COO DHA), 2.04-1.86 (m, 4H, CH<sub>2</sub>COO SFA and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.58 (d, *J*=7.1 Hz, 3H, CHCH<sub>3</sub>), 1.44-1.06 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.29-1.22 (m, 20H, CH<sub>2</sub>), 0.97 (t, *J*=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (t, *J*=7.0 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 173.9 (Nap), 173.3 (SFA), 172.7 (DHA), 157.9, 135.3, 133.89, 132.2, 129.6, 129.4, 129.1, 128.7, 128.5, 128.44, 128.41, 128.3, 128.23, 128.16, 128.0, 127.2, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 62.4, 62.0, 55.3, 45.5, 34.0, 33.9, 32.1, 29.9 (2), 29.82, 29.78, 29.7, 29.5, 29.4, 29.2, 25.8 (2), 25.8, 25.7 (2), 24.8, 22.9, 22.7, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>53</sub>H<sub>76</sub>O<sub>7</sub>Na 847.5483; found, 847.5418.

3.6.20. Synthesis of 3-[4Z,7Z,10Z,13Z,16Z,19Z]-docosa-4,7,10,13,16,19-hexaenoyl]-1-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol, (*R,S'*)-**13f**

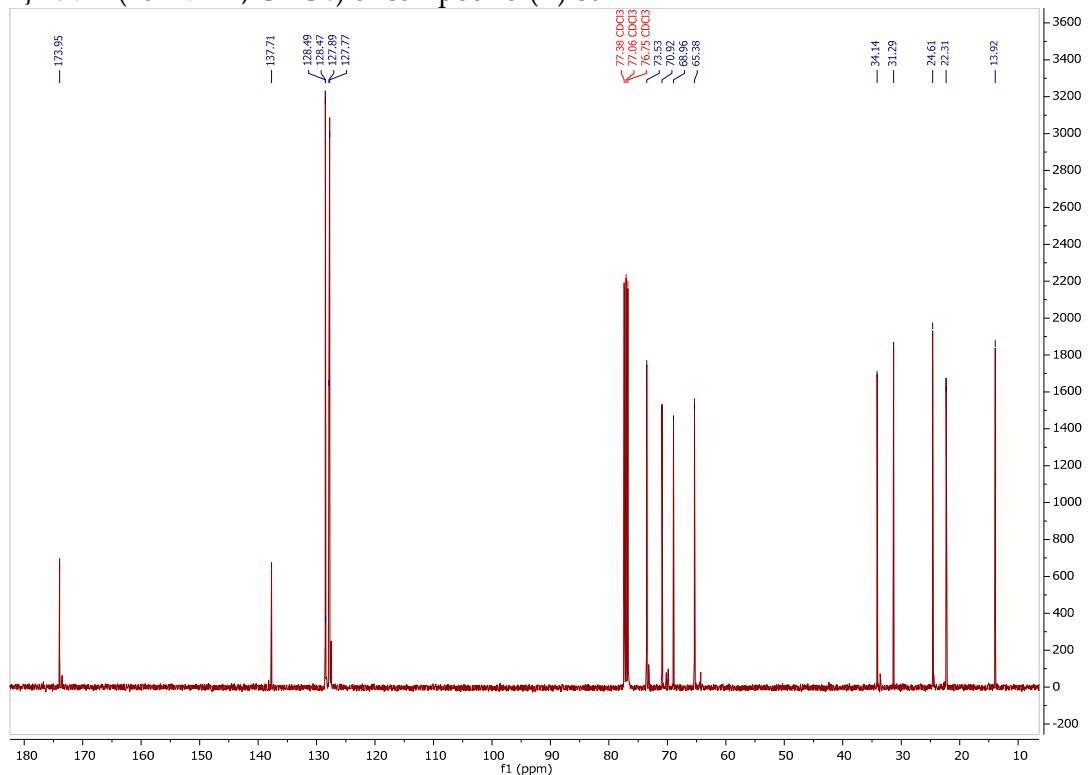
The same procedure was followed as described for (*R,S'*)-**13a** using 1-hexadecanoyl-2-[(*S*)-2-(6-methoxynaphthalen-2-yl)propanoyl]-*sn*-glycerol (*S,S'*)-**9f** (10 mg, 0.018 mmol), DHA (7 mg, 0.020 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL), DMAP (2 mg, 0.016 mmol) and EDCI (4 mg, 0.020 mmol). Purification on a silica gel chromatography using pet. ether/ethyl acetate (9:1) as eluent afforded the product (*R,S'*)-**13f** as a yellow oil, in 89% yield (14 mg, 0.016 mmol). [α]<sup>20D</sup> = +2.14 (c. 1.4, CH<sub>2</sub>Cl<sub>2</sub>). IR (NaCl, ν<sub>max</sub> / cm<sup>-1</sup>): 3013 (s), 2967 (vs), 2925 (vs), 2854 (vs), 1741 (vs), 1634 (s), 1607 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 7.72-7.62 (m, 3H, Nap-1,4,8), 7.38 (dd, J=8.5, 1.9 Hz, 1H, Nap-3), 7.13 (dd, J=8.9, 2.5 Hz, 1H, Nap-7), 7.09 (d, J=2.5 Hz, 1H, Nap-5), 5.46-5.27 (m, 12H, =CH), 5.31-5.21 (m, 1H, CH *sn*-2), 4.30 (dd, J=11.9, 4.2 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 4.21-4.10 (m, 2H, CH<sub>2</sub> *sn*-1/3), 4.05 (dd, J=11.9, 6.4 Hz, 1H, CH<sub>2</sub> *sn*-1/3), 3.91 (s, 3H, OCH<sub>3</sub>), 3.86 (q, J=7.1 Hz, 1H, CHCH<sub>3</sub>), 2.89-2.77 (m, 10H, =CHCH<sub>2</sub>CH=), 2.40-2.07 (m, 4H, CH<sub>2</sub>COO DHA), 2.04-1.86 (m, 4H, CH<sub>2</sub>COO SFA) and =CHCH<sub>2</sub>CH<sub>3</sub>), 1.57 (d, J=7.1 Hz, 3H, CHCH<sub>3</sub>), 1.42-1.31 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>COO SFA), 1.29-1.22 (m, 24H, CH<sub>2</sub>), 0.97 (t, J=7.5 Hz, 3H, CH<sub>3</sub> DHA), 0.89 (t, J=7.3 Hz, 3H, CH<sub>3</sub> SFA) ppm. <sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 173.9 (Nap), 173.3 (SFA), 172.7 (DHA), 157.9, 135.3, 133.9, 132.2, 129.6 (2), 129.4, 129.0, 128.73, 128.5, 128.44, 128.41, 128.23, 128.16, 128.0, 127.8, 127.24, 127.17, 126.3, 126.1, 119.2, 105.7, 69.5, 64.5, 62.4, 55.4, 45.5, 37.9, 34.0, 32.1, 30.1 (2), 29.9 (2), 29.82 (2), 29.78, 29.6, 29.5, 29.4, 29.2 (2), 25.8, 25.7 (2), 24.8, 22.9, 22.8, 20.7, 18.5, 14.4, 14.3 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup> calcd for C<sub>55</sub>H<sub>80</sub>O<sub>7</sub>Na 875.5796; found, 875.5787.

## NMR Spectra

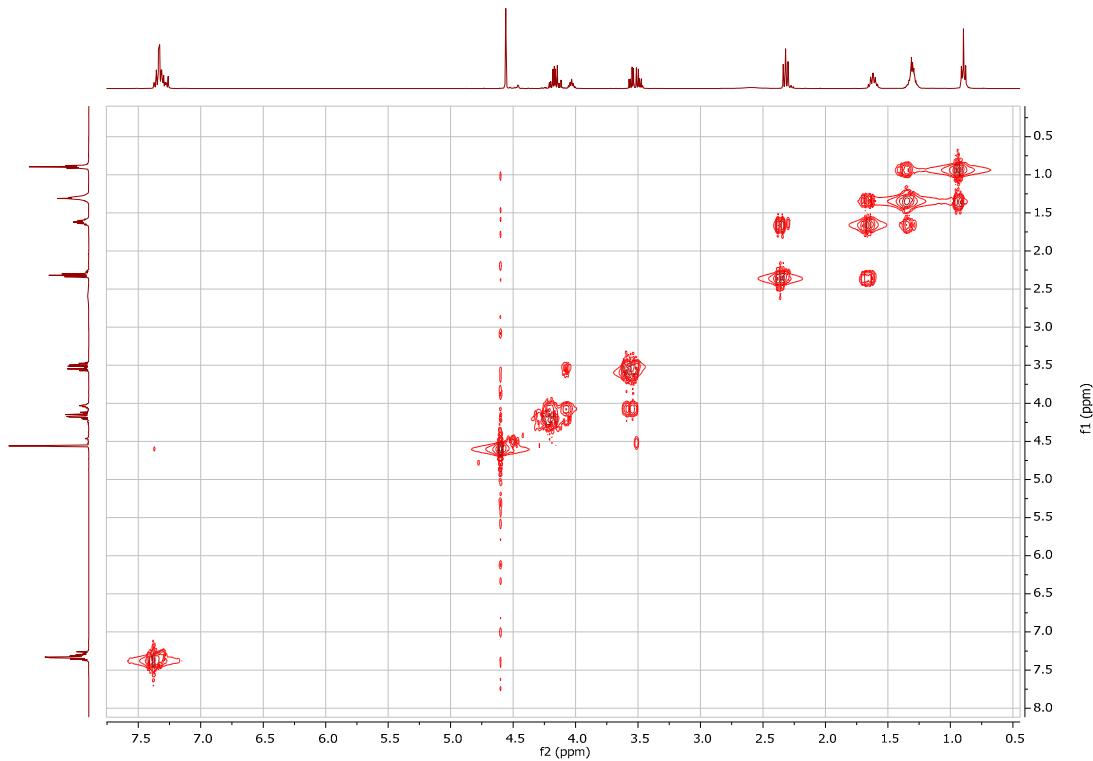
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound (*R*)-5a



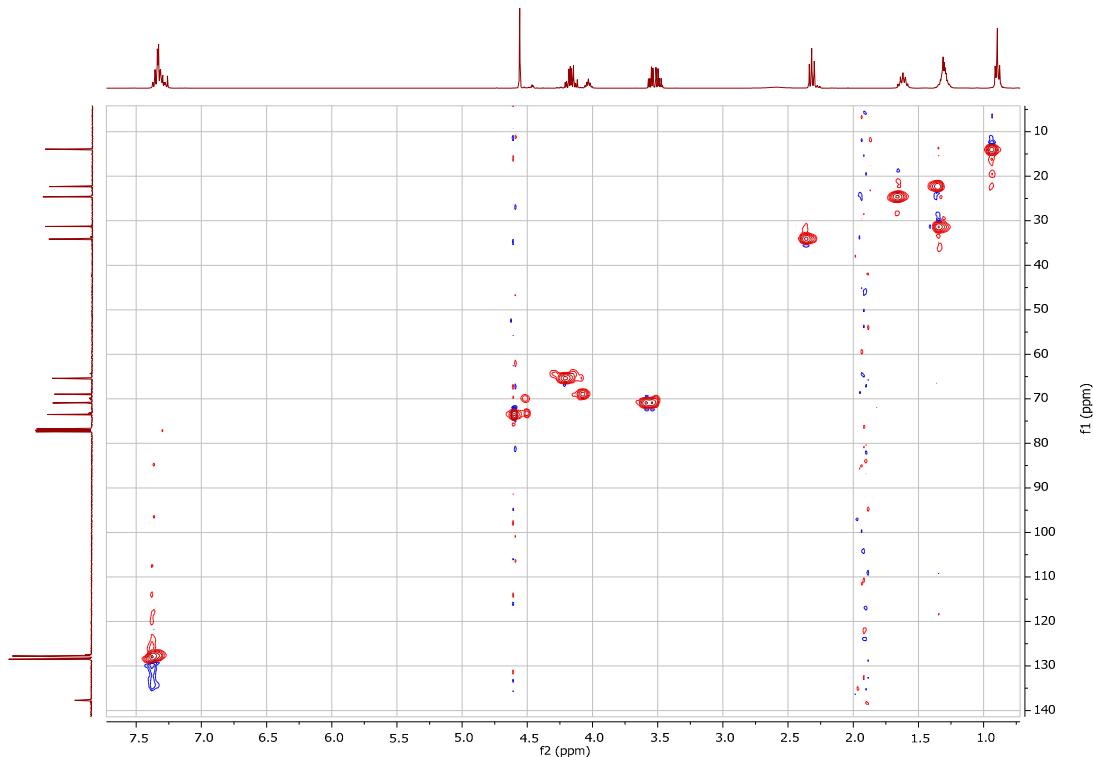
$^{13}\text{C}\{\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of compound (*R*)-5a



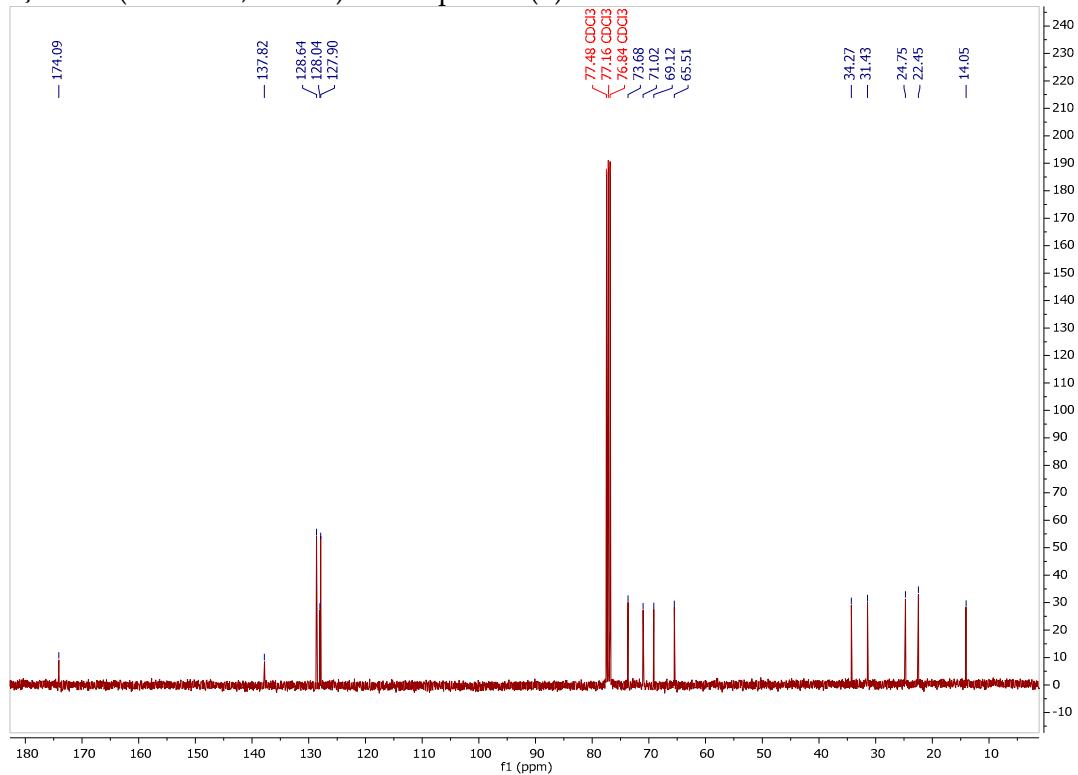
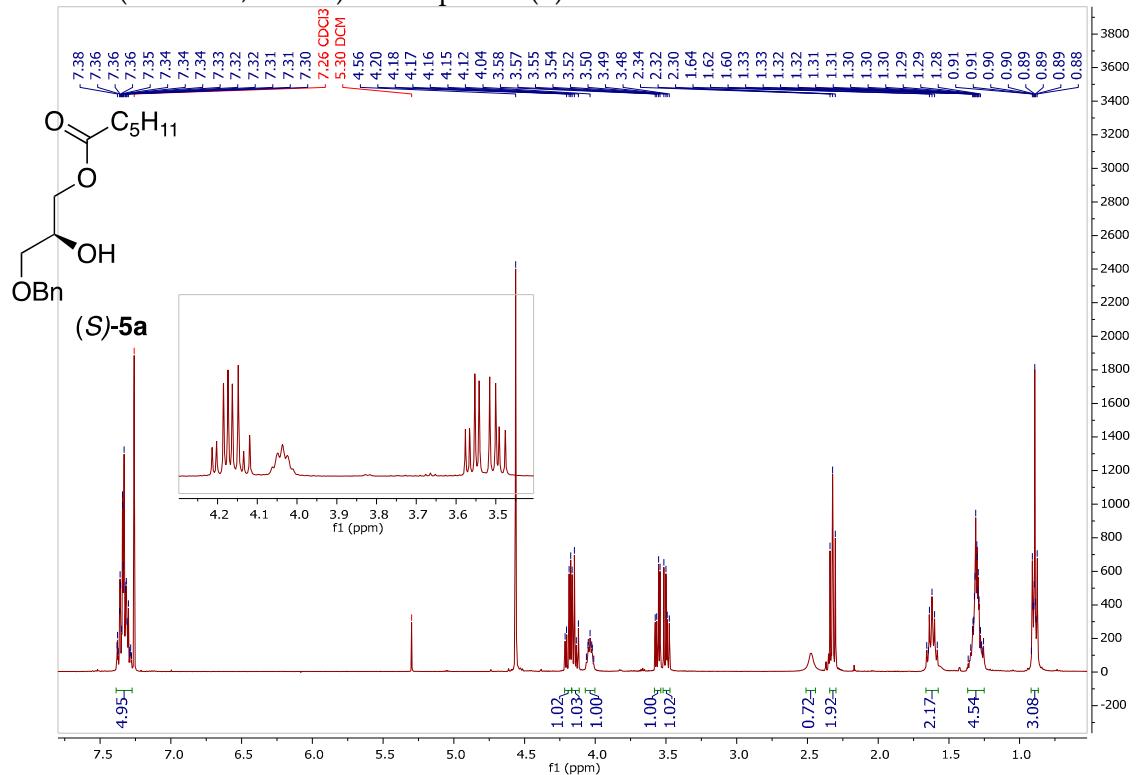
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*R*)-5a



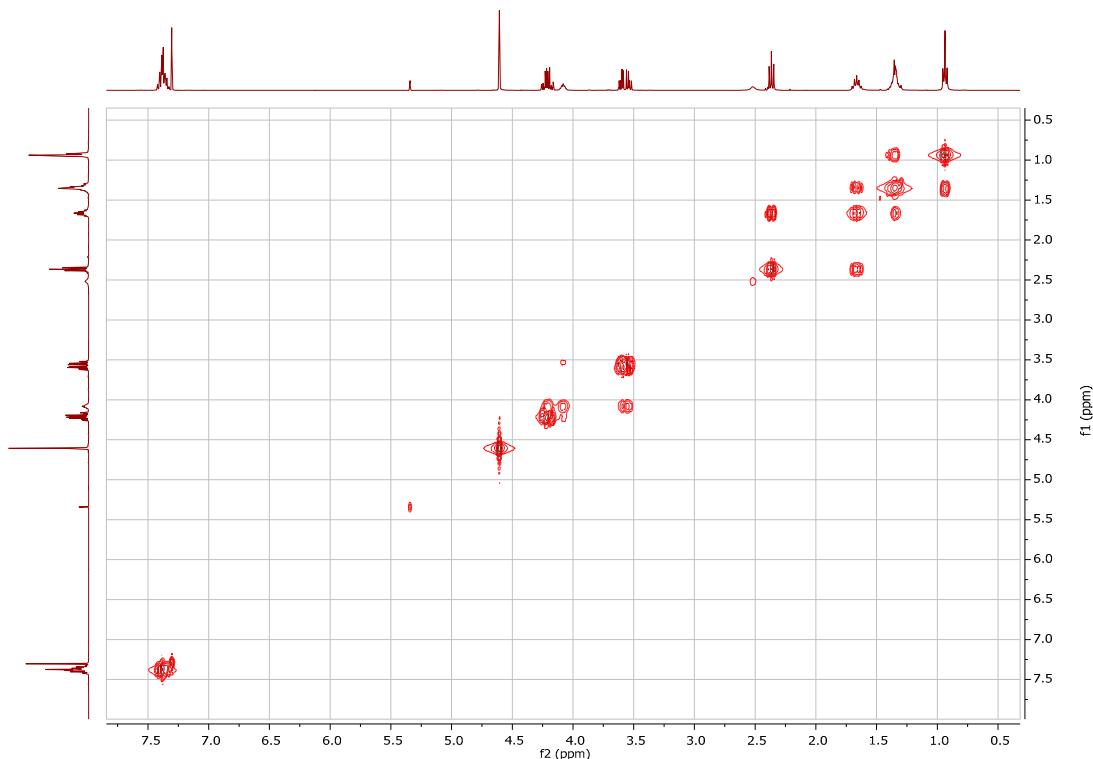
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*R*)-5a



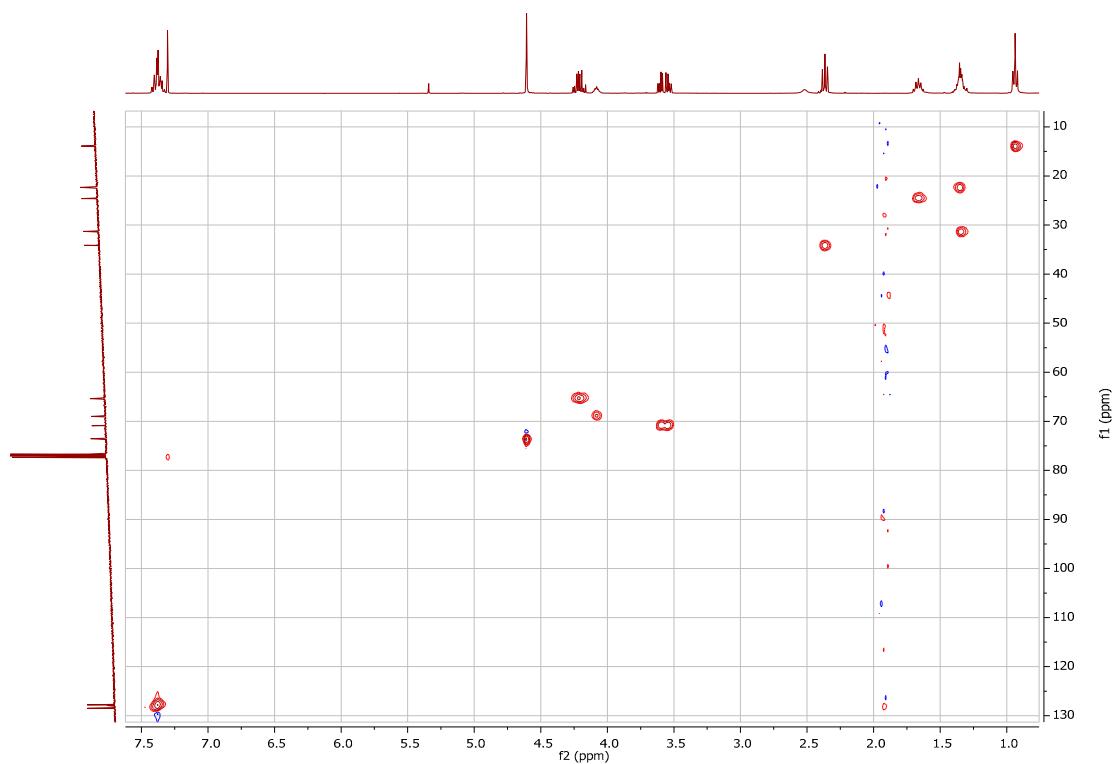
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S)-5a



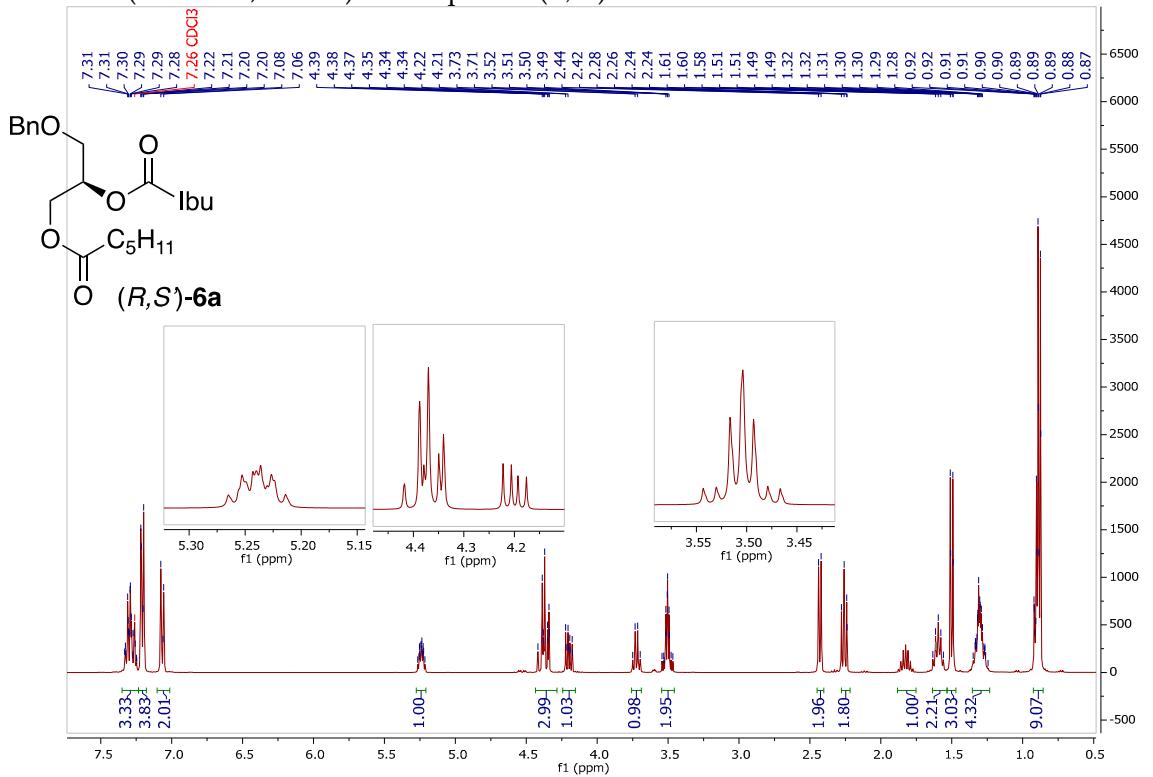
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S*)-5a



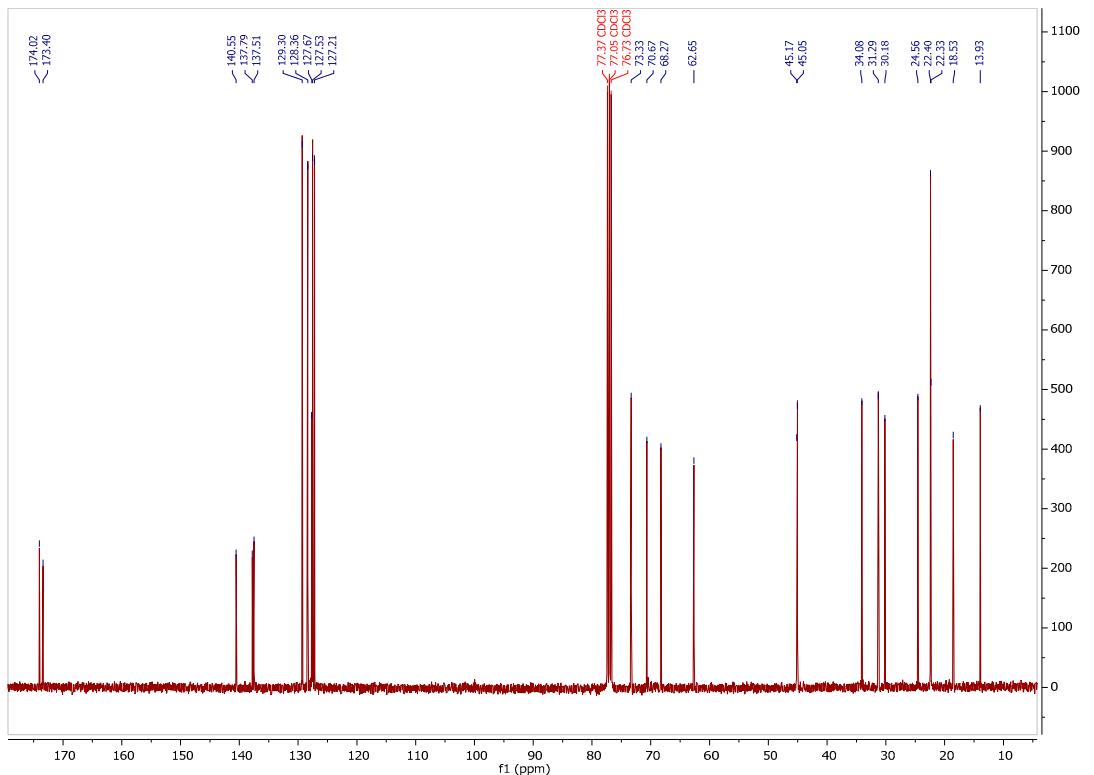
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S*)-5a



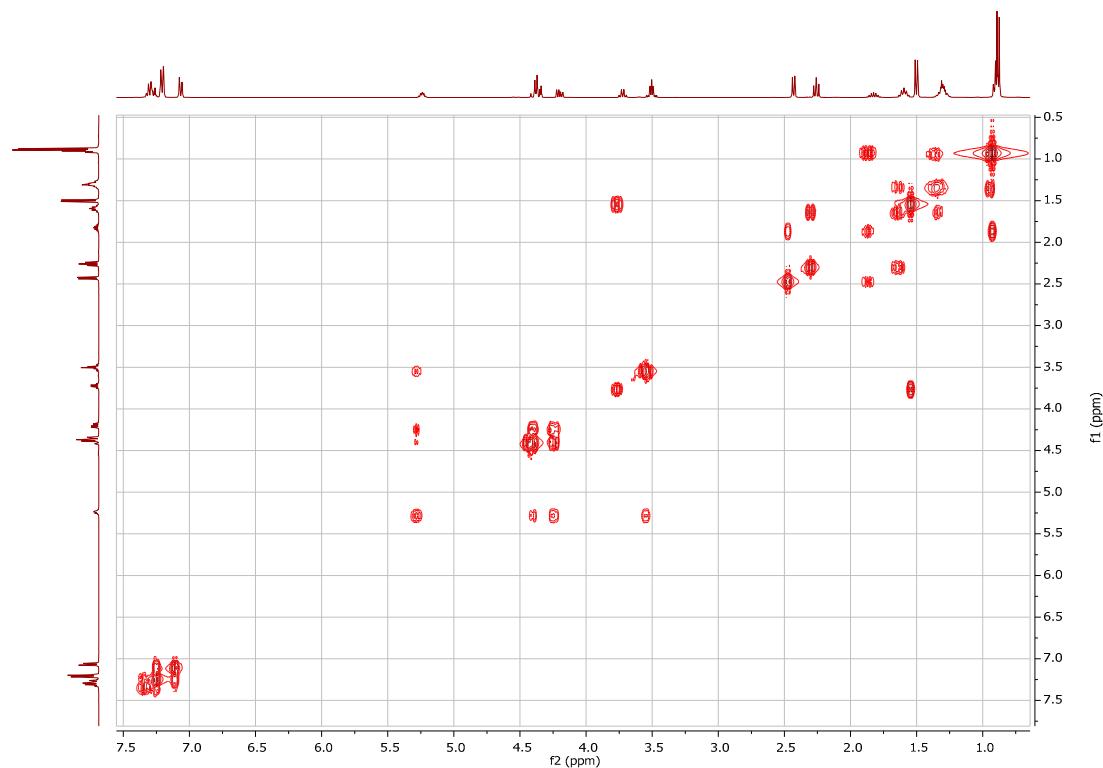
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (R,S')-6a



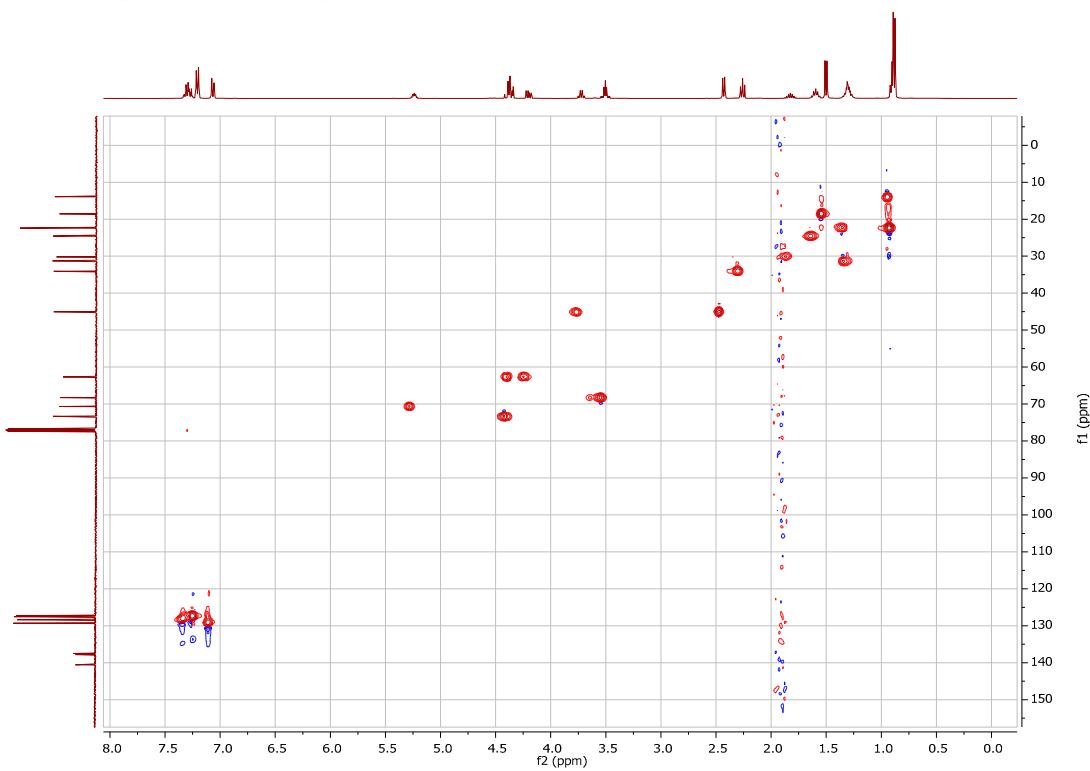
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (R,S')-6a



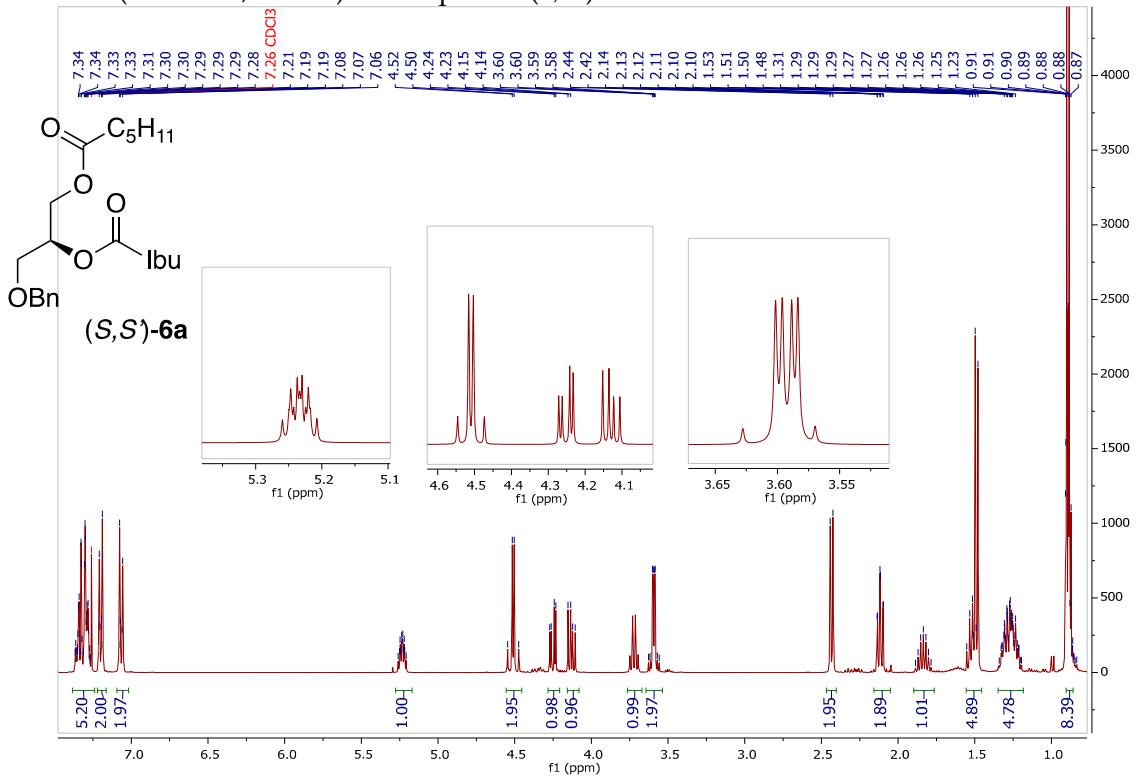
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*R,S'*)-6a



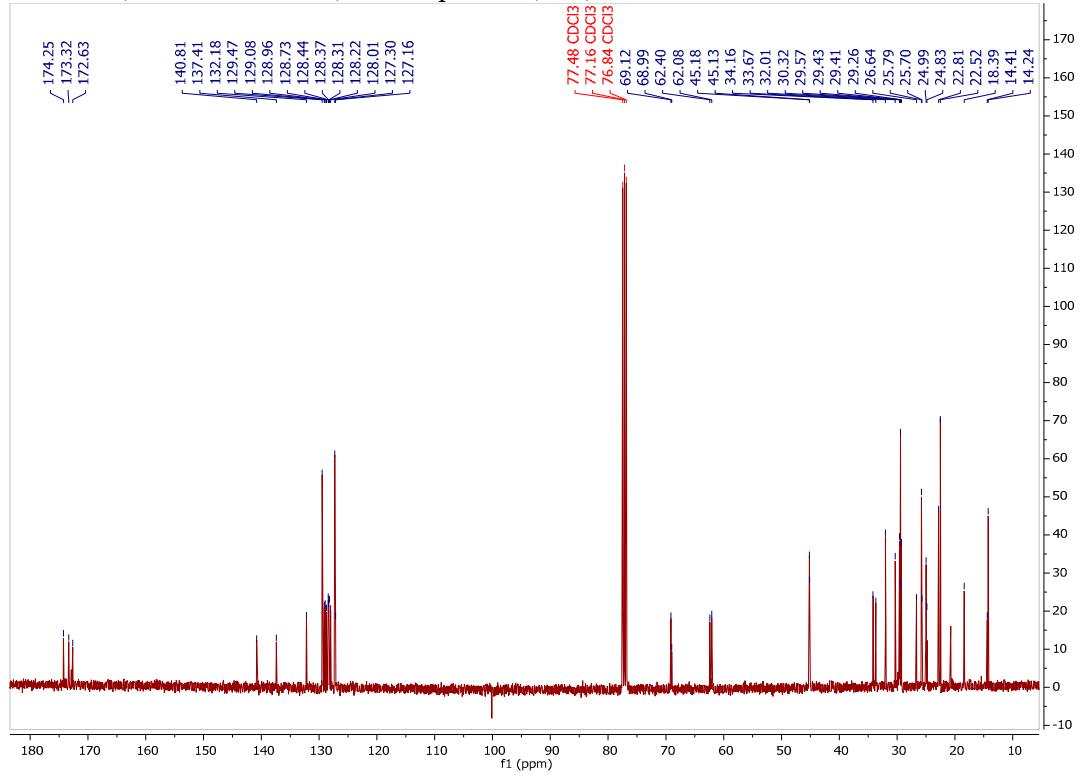
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*R,S'*)-6a



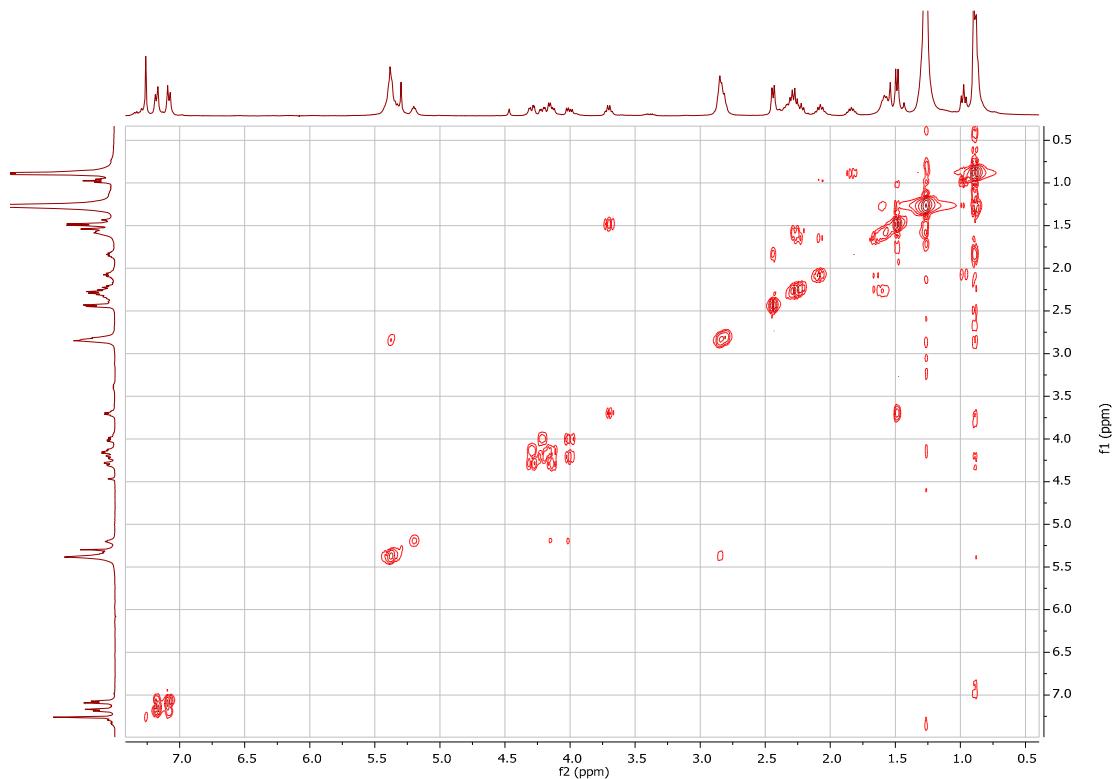
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S,S')-6a



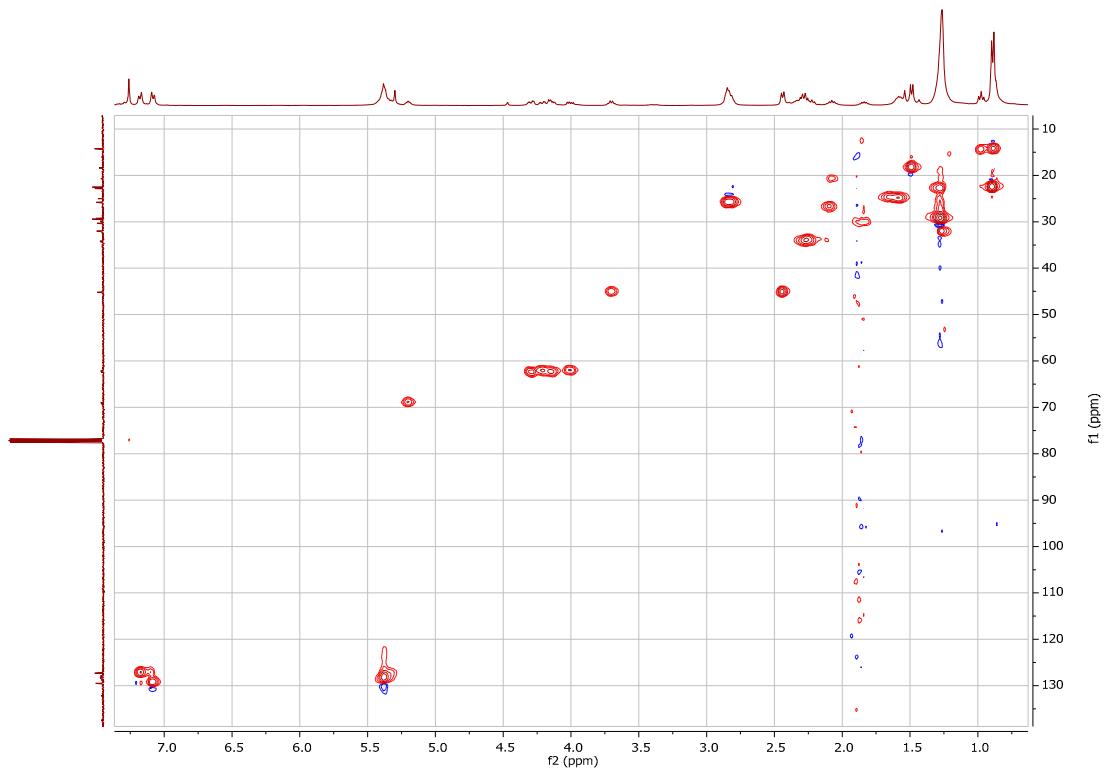
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (S,S')-6a



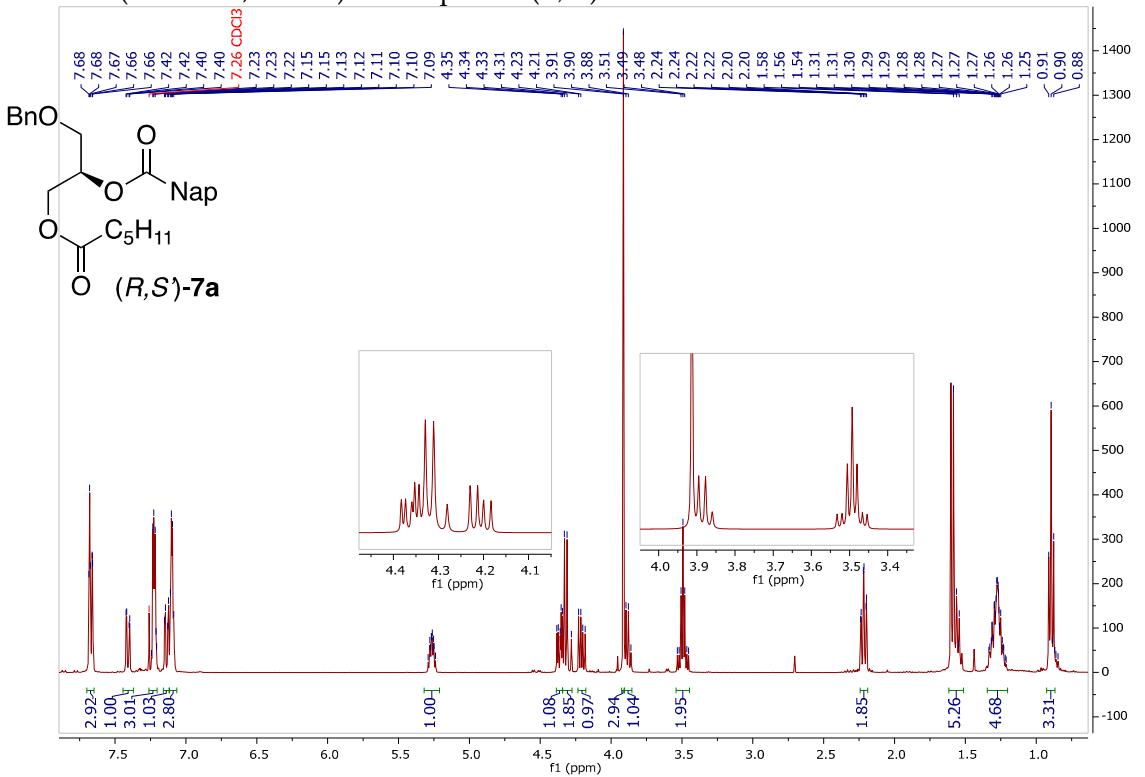
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-6a



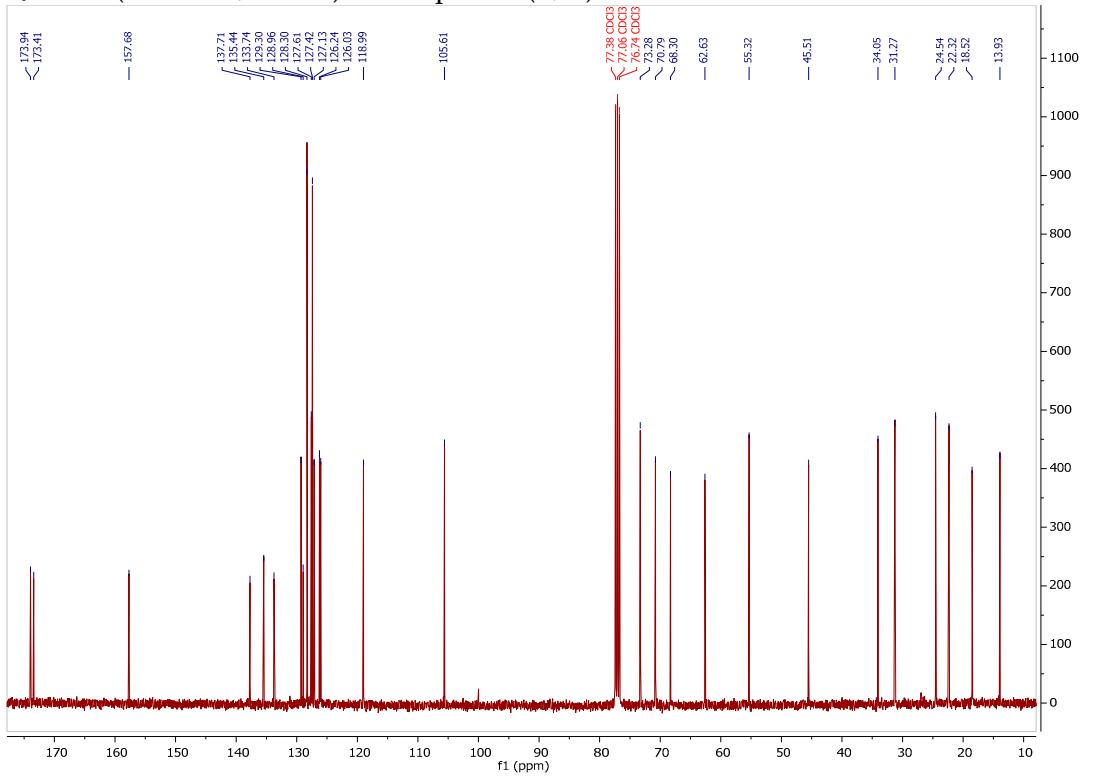
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-6a



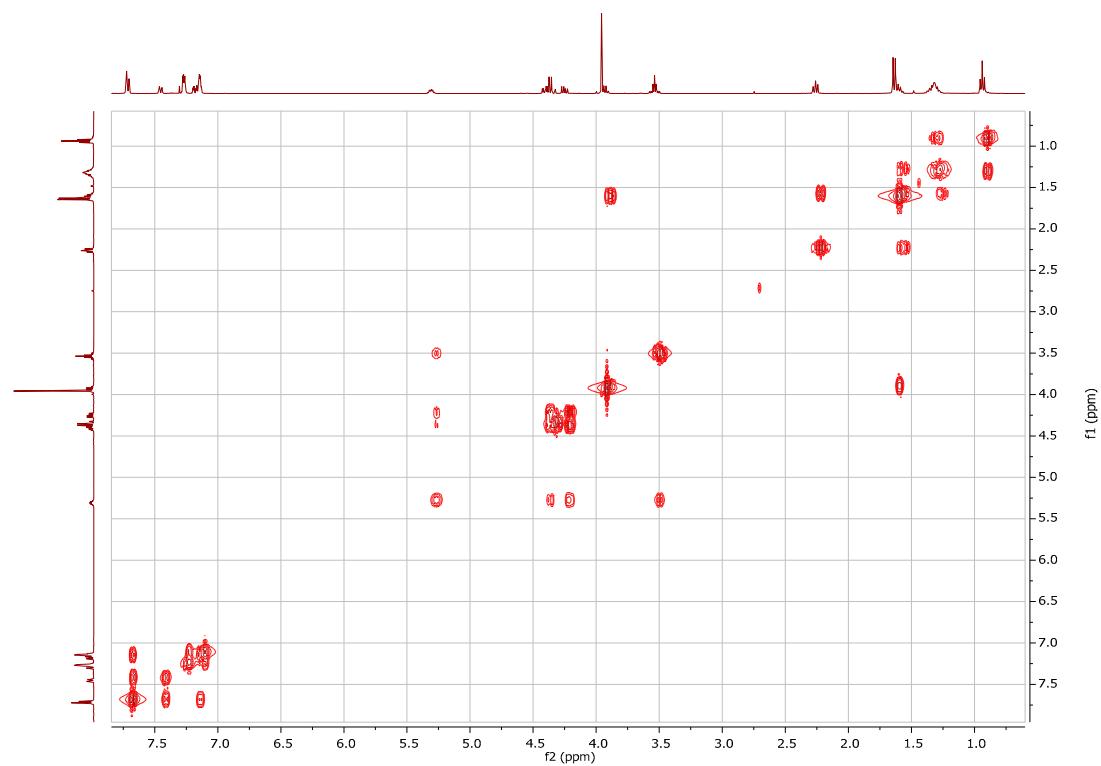
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (*R,S'*)-7a



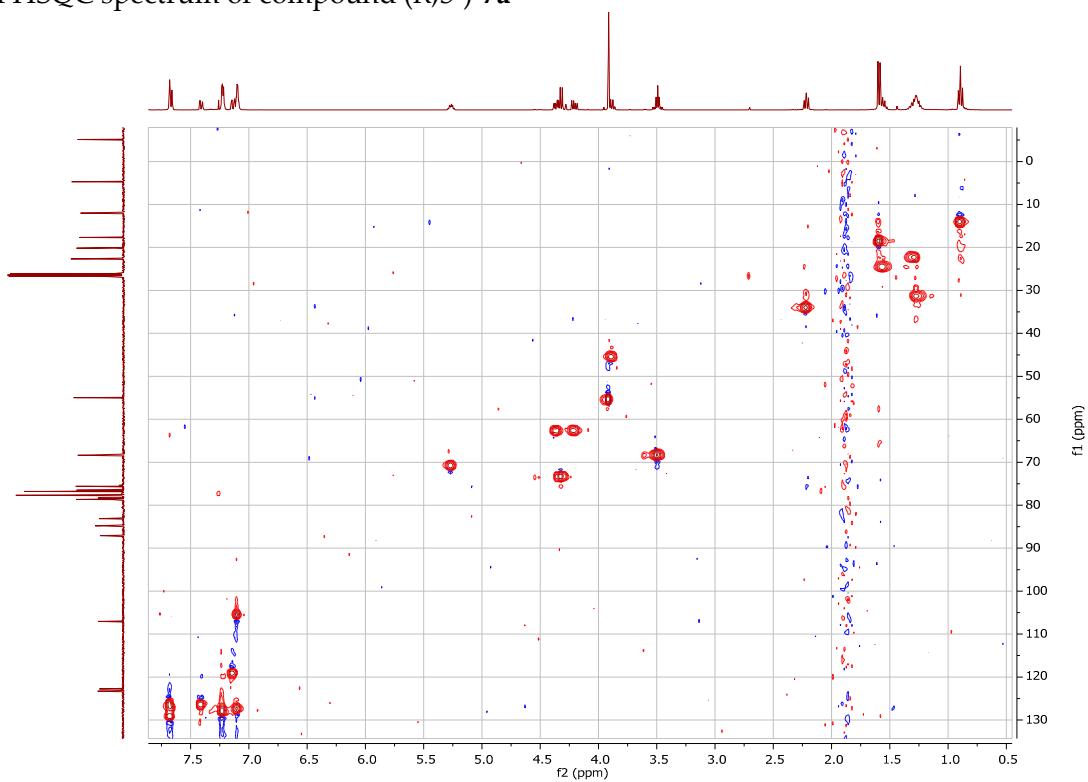
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (R,S')-7a

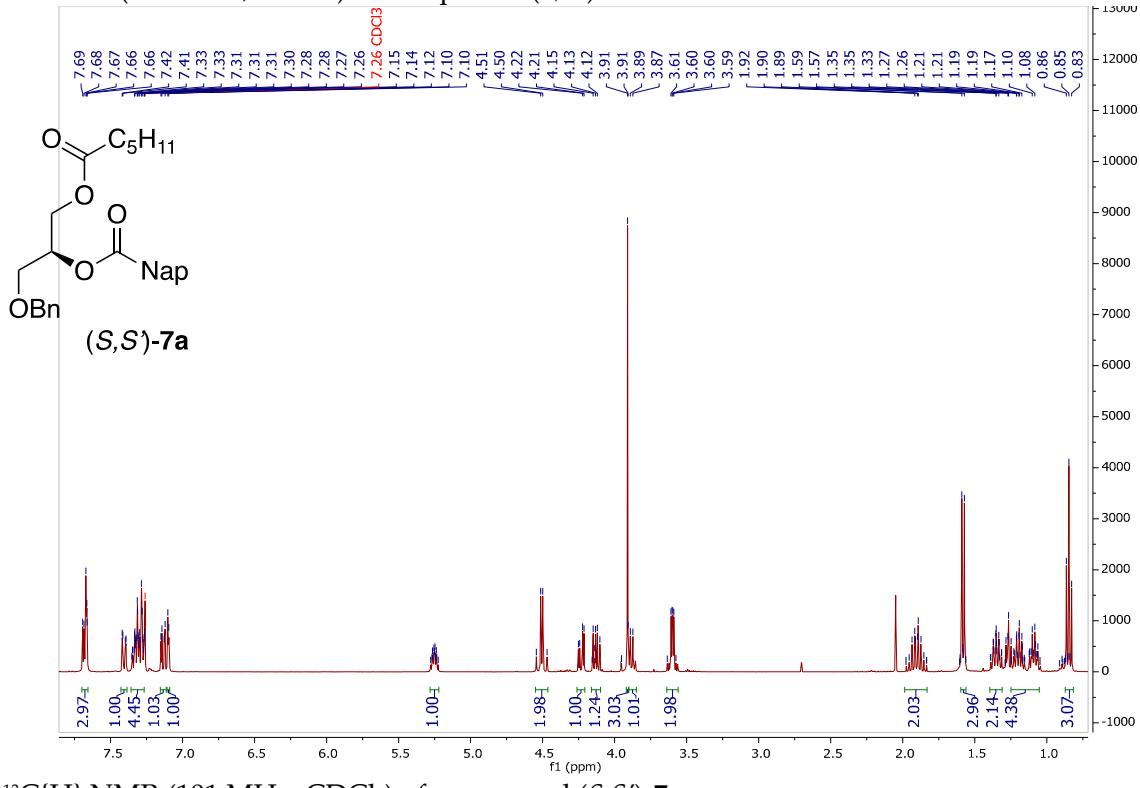


$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*R,S'*)-7a

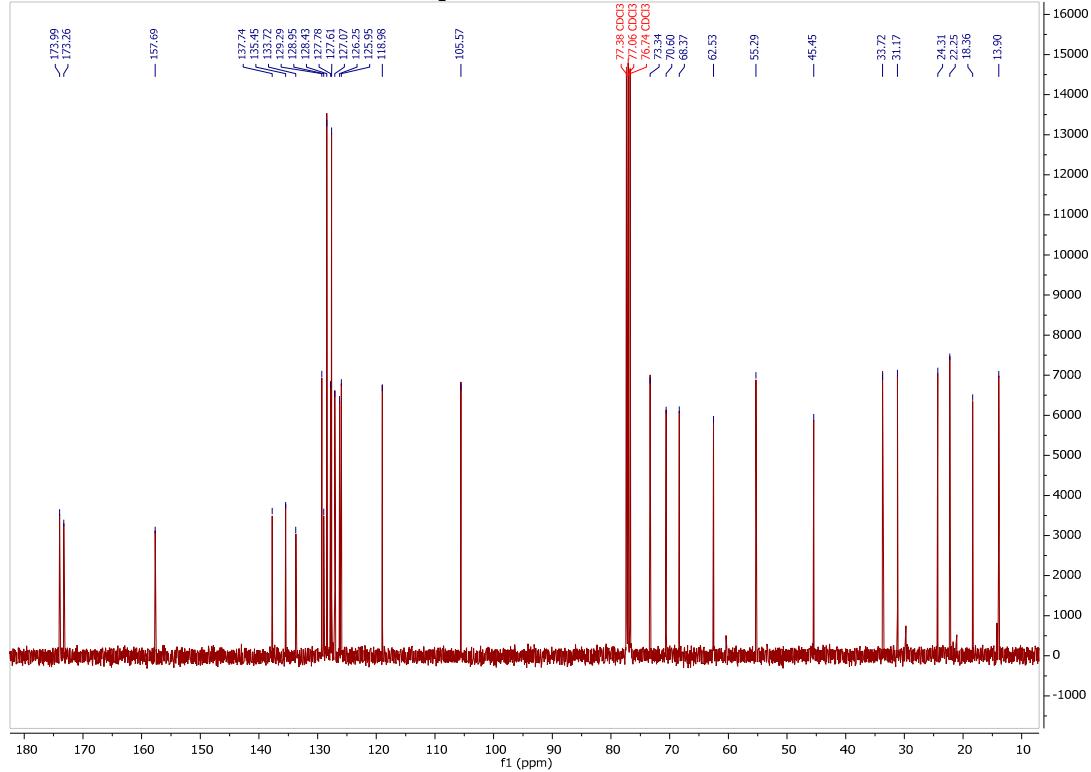


$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*R,S'*)-7a

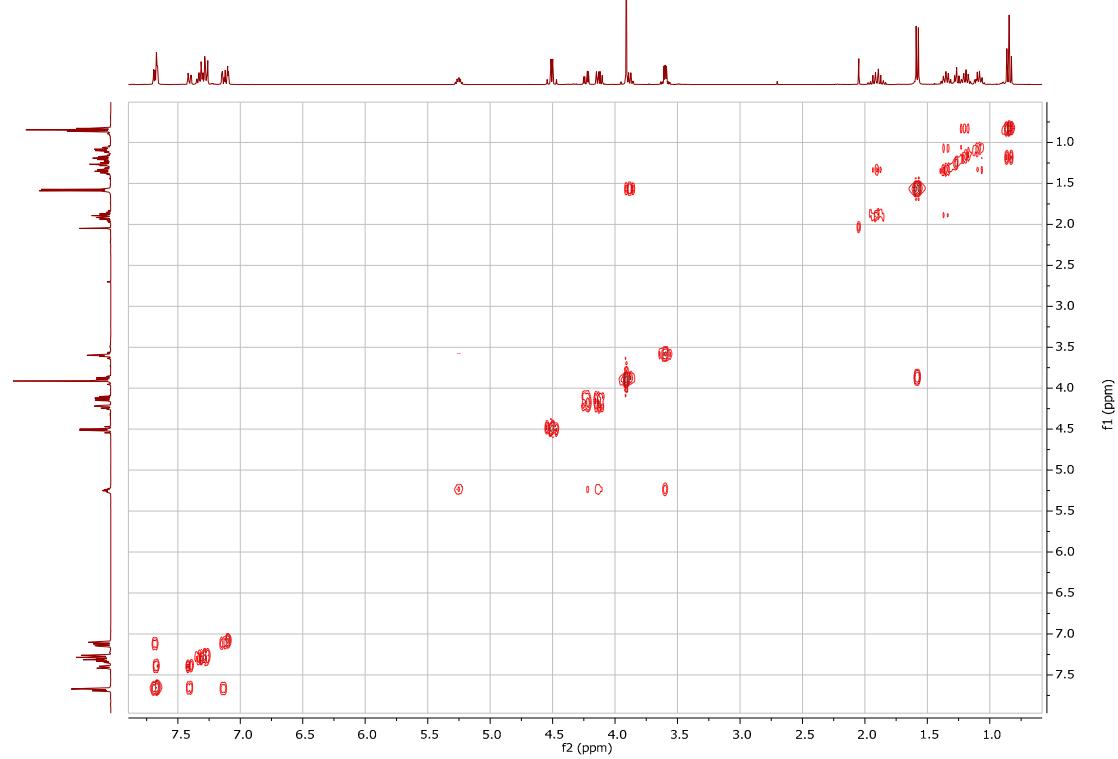




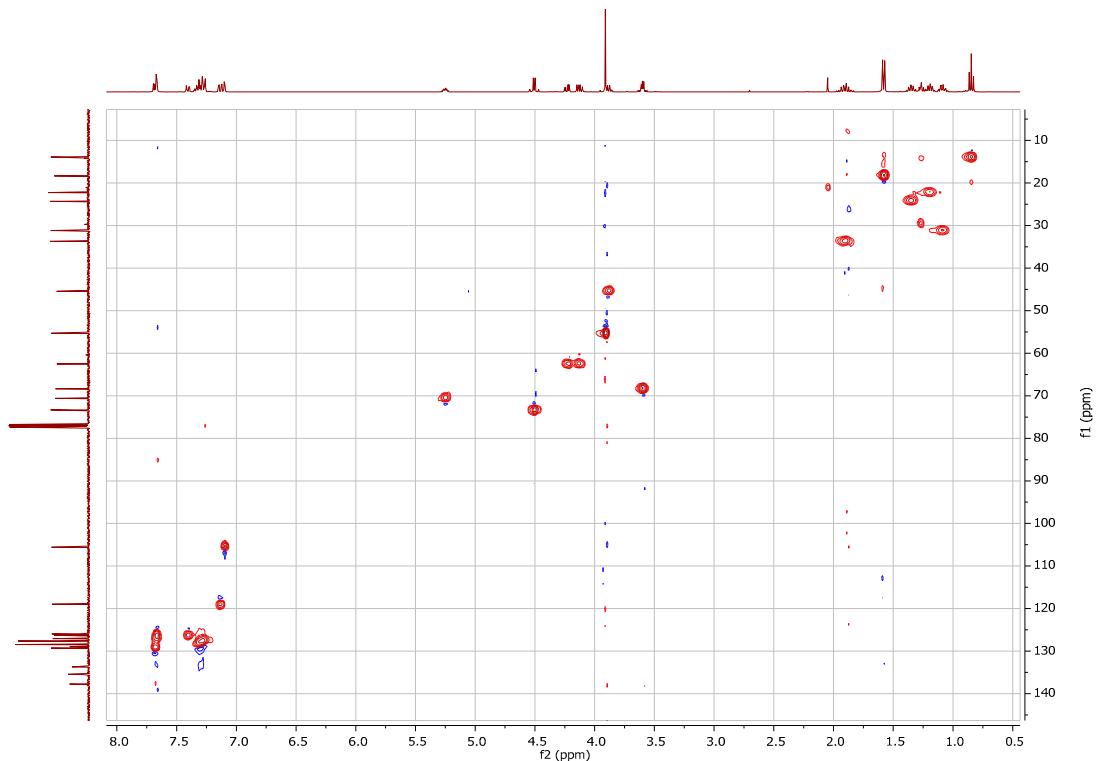
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (S,S')-7a



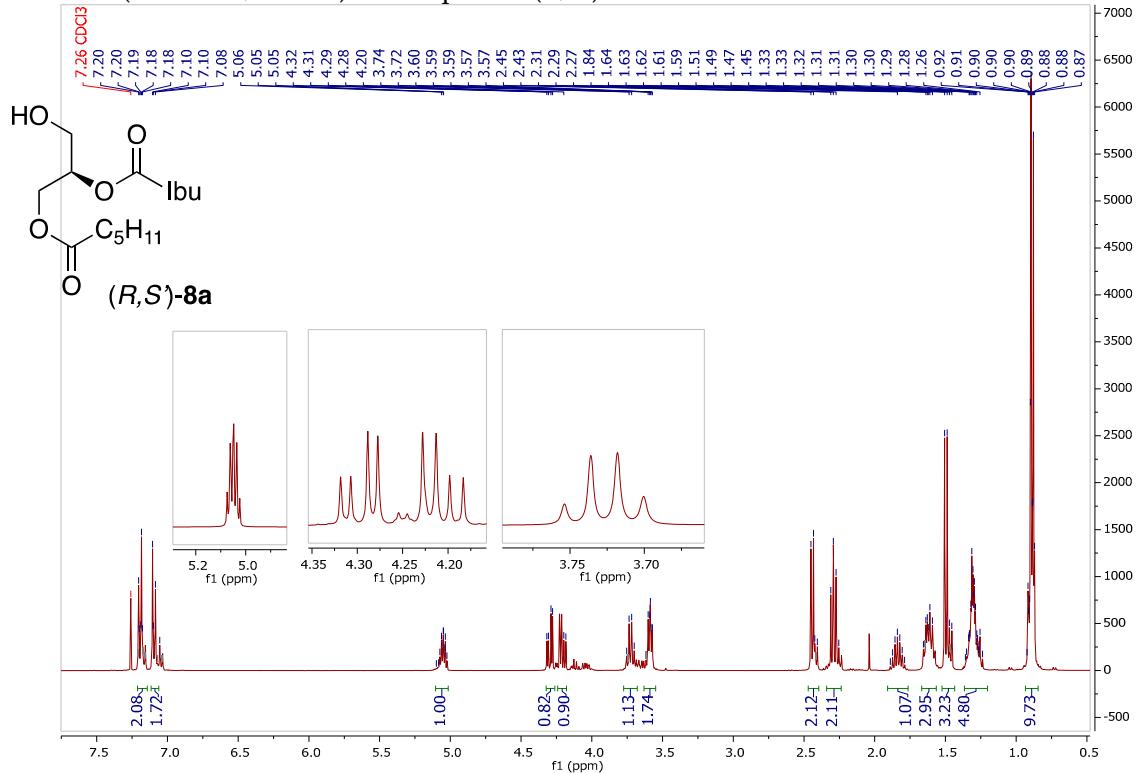
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-7a



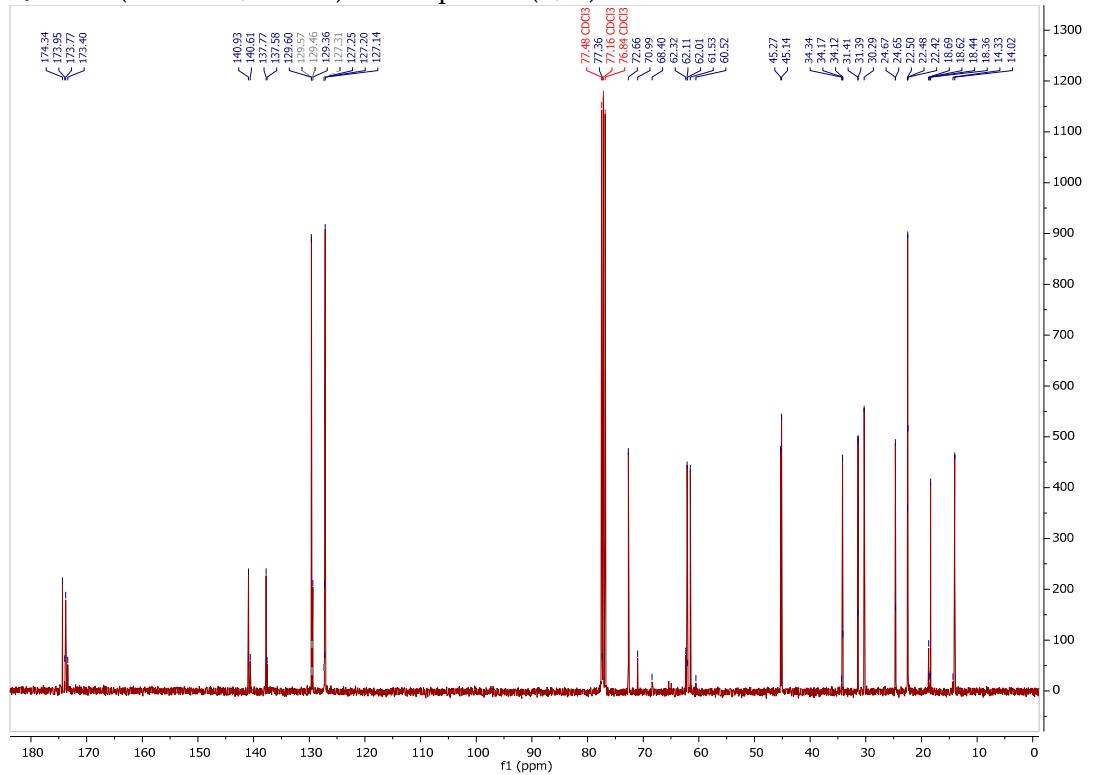
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-7a



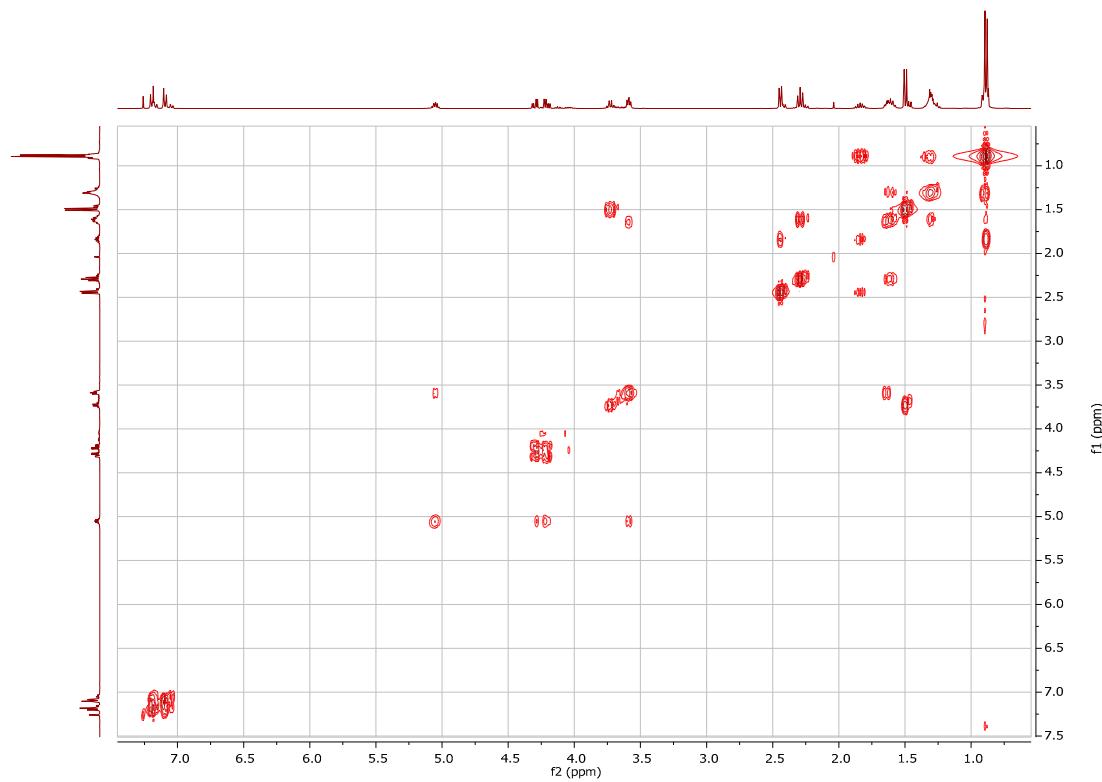
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (R,S')-8a



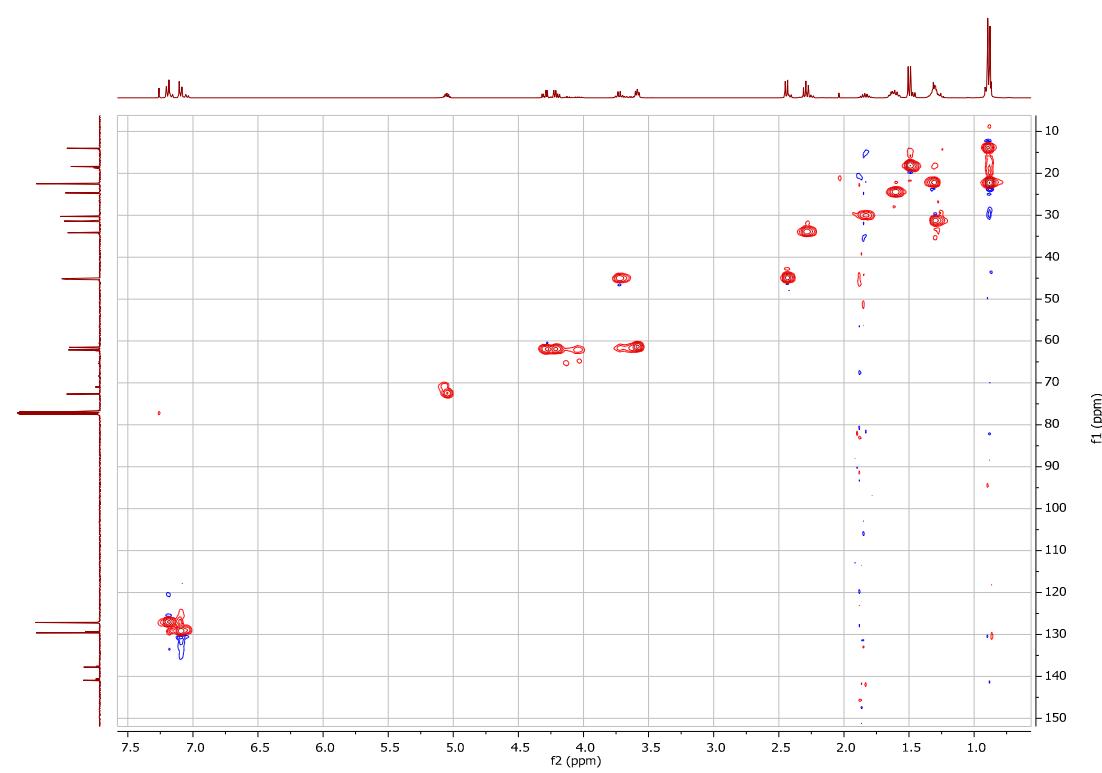
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (R,S')-8a



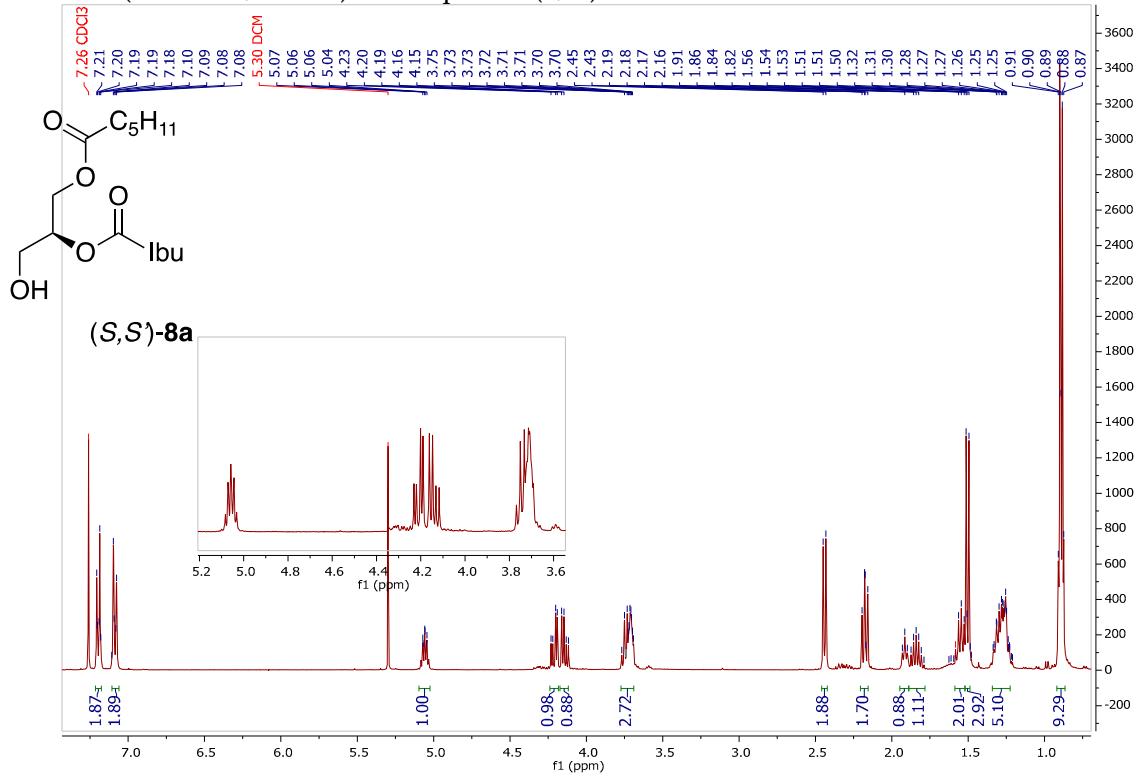
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound  $(R,S')$



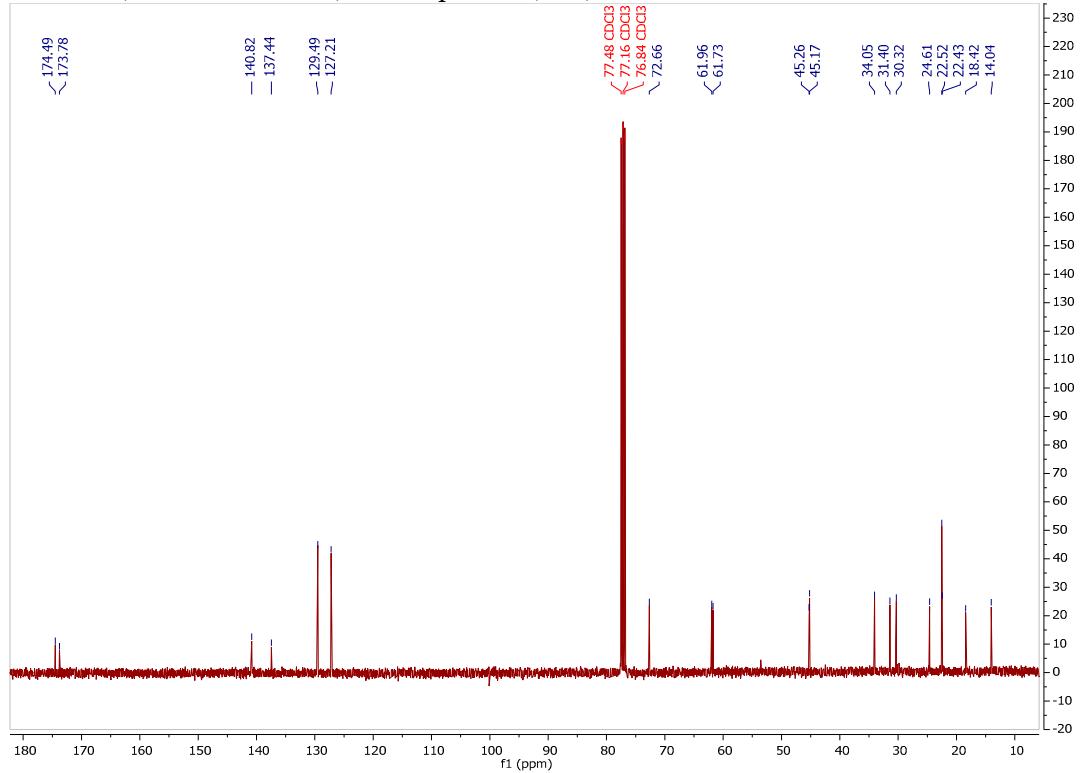
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound  $(R,S')$



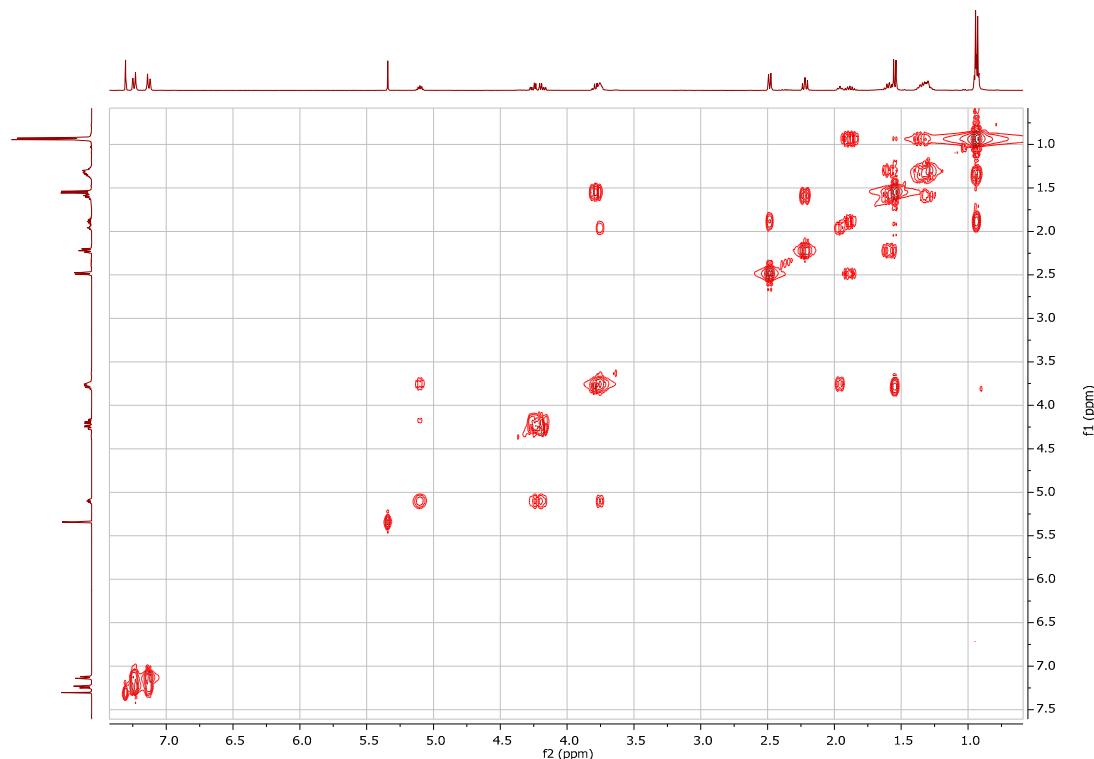
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S,S')-8a



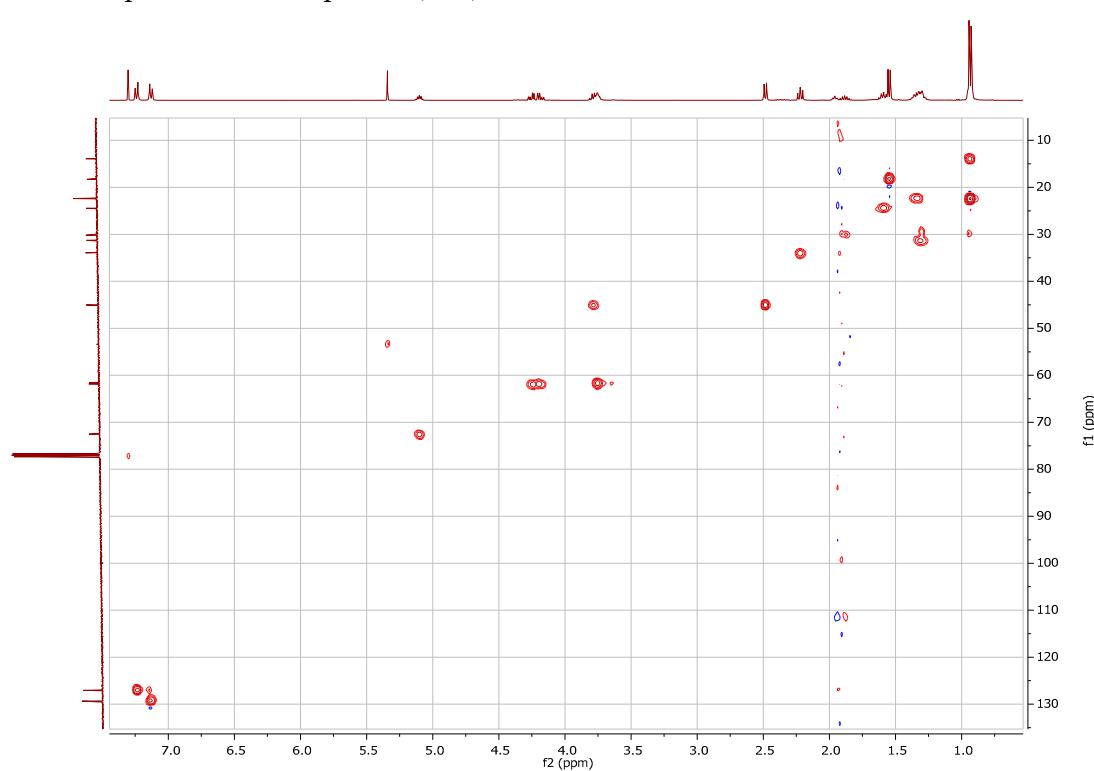
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (S,S')-8a



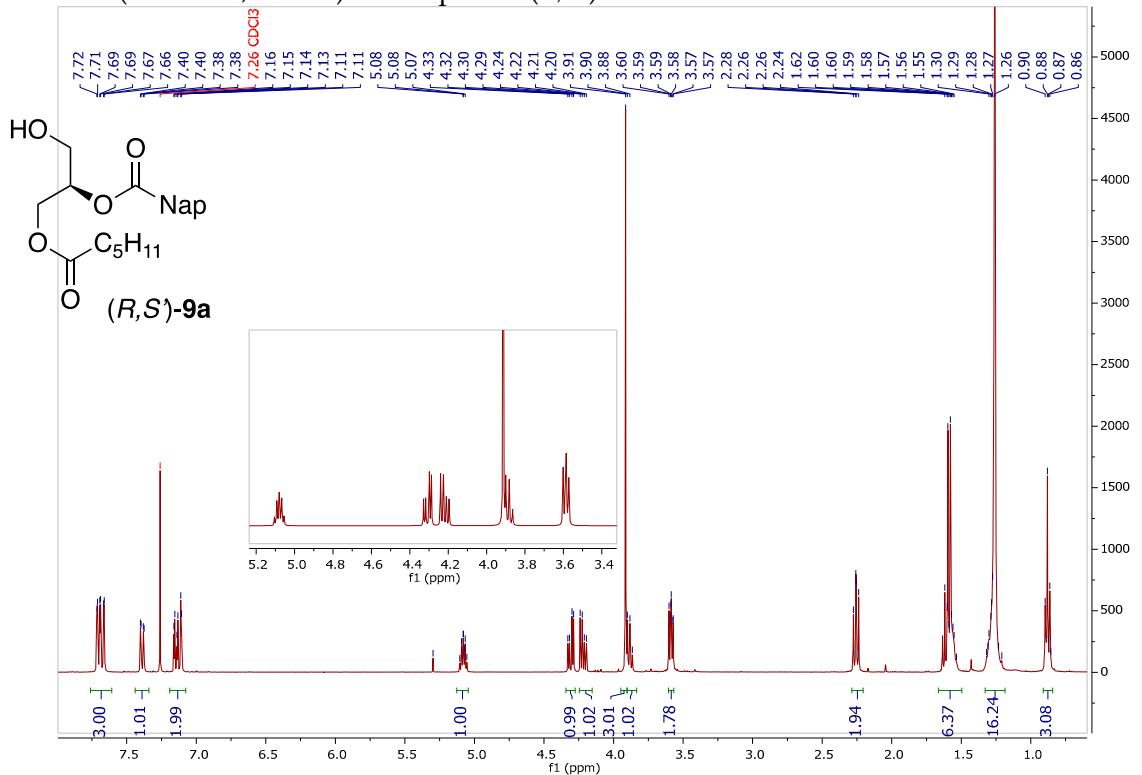
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-8a



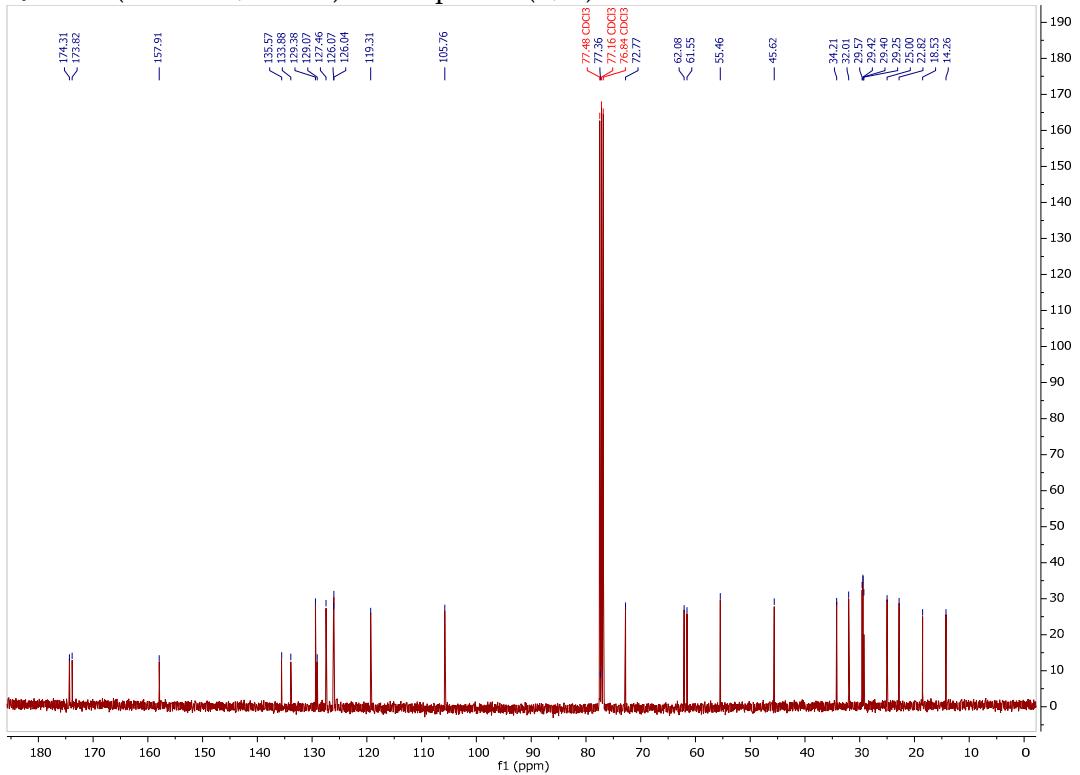
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-8a



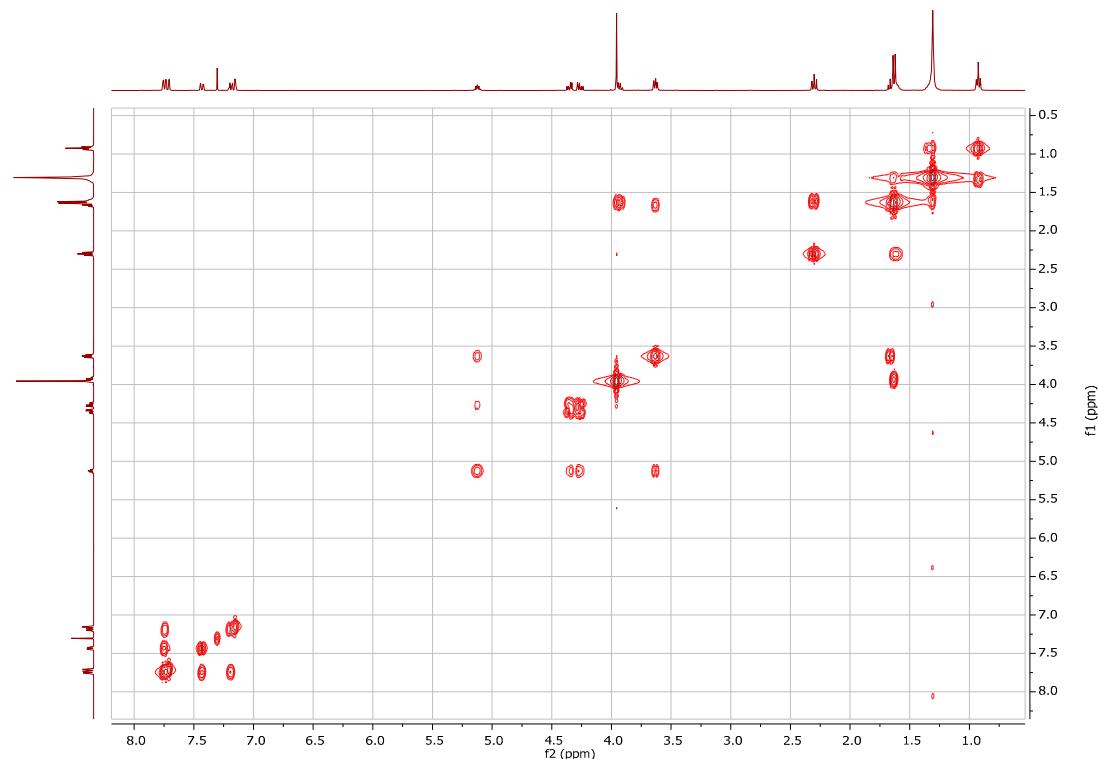
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (R,S')-9a



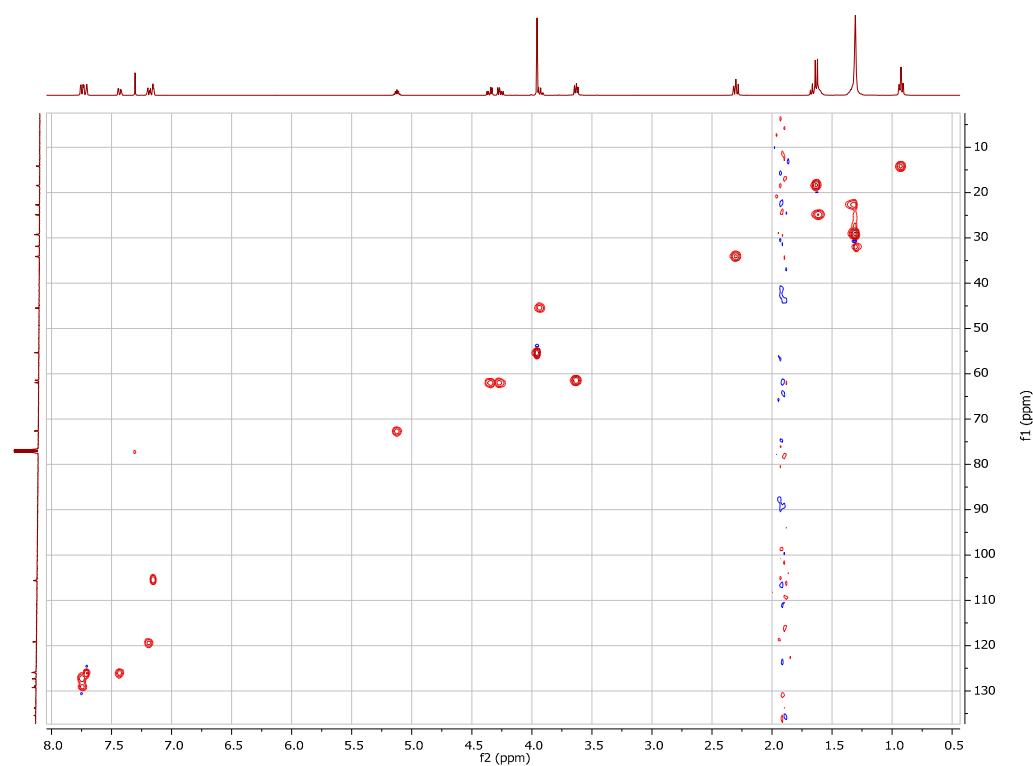
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (R,S')-9a



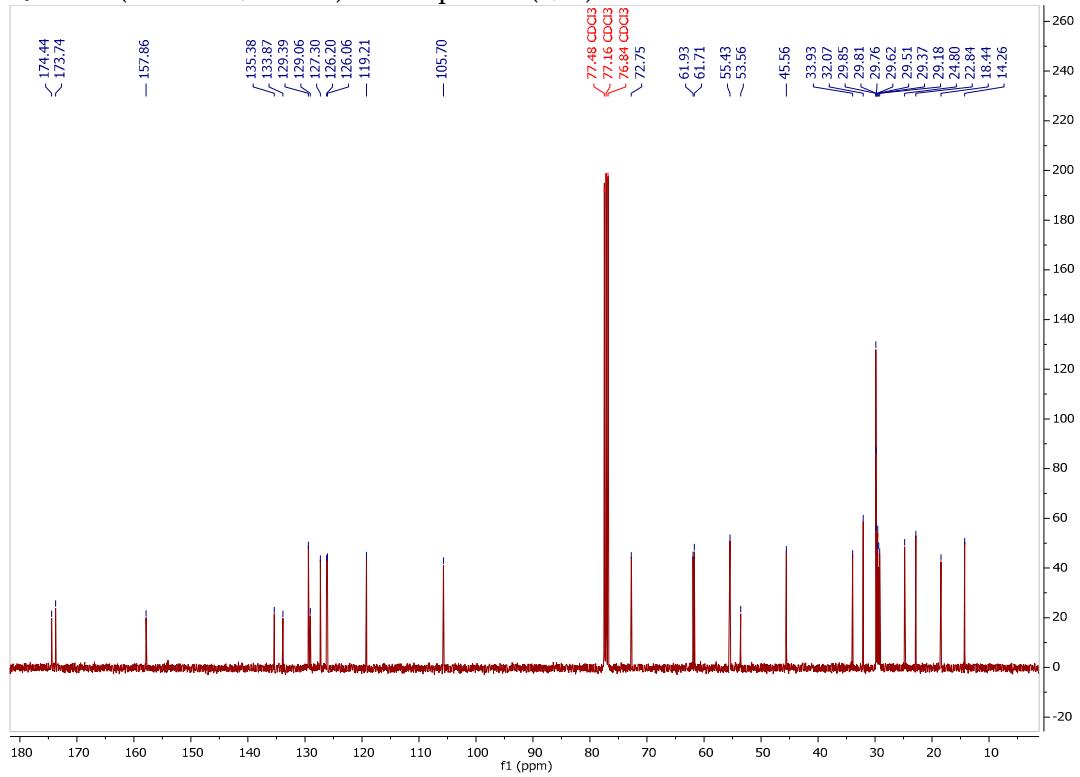
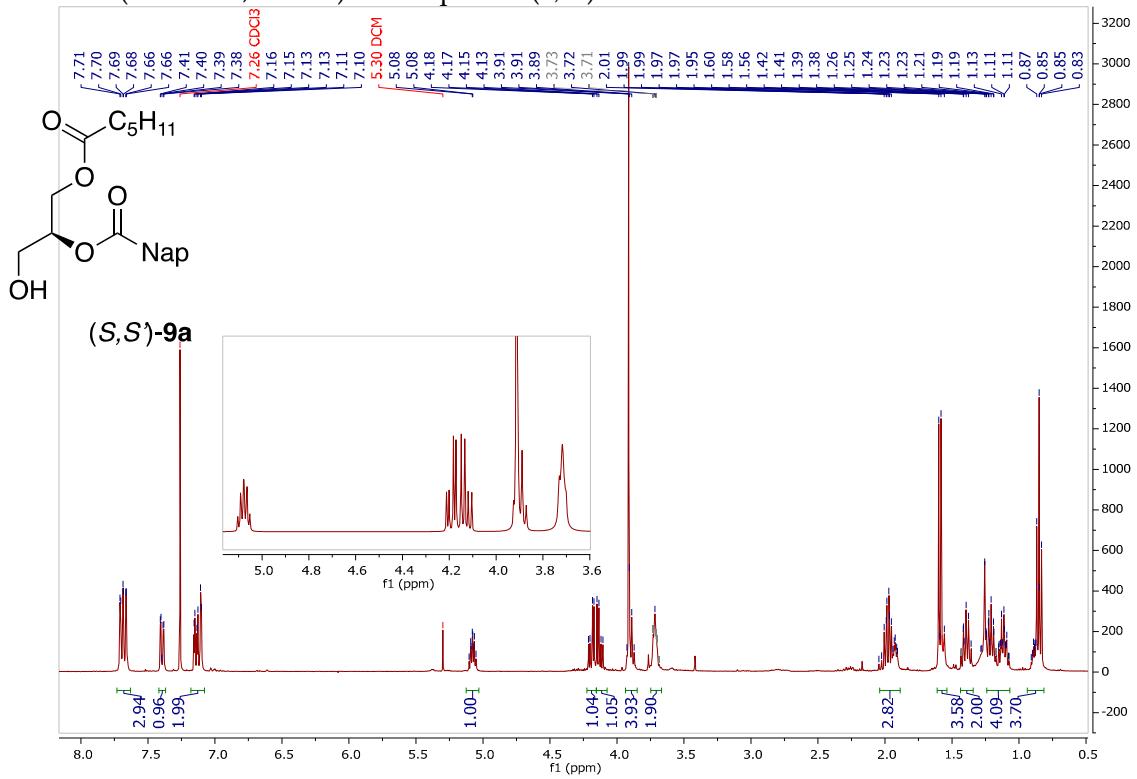
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*R,S'*)-9a



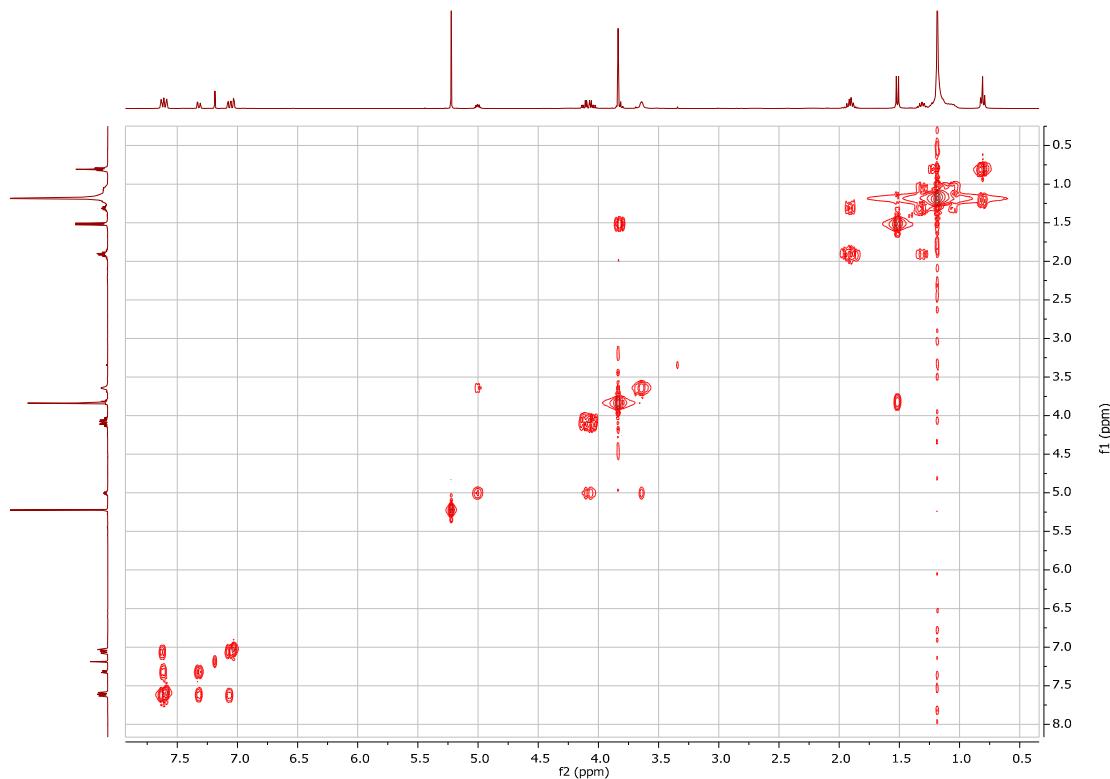
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*R,S'*)-9a



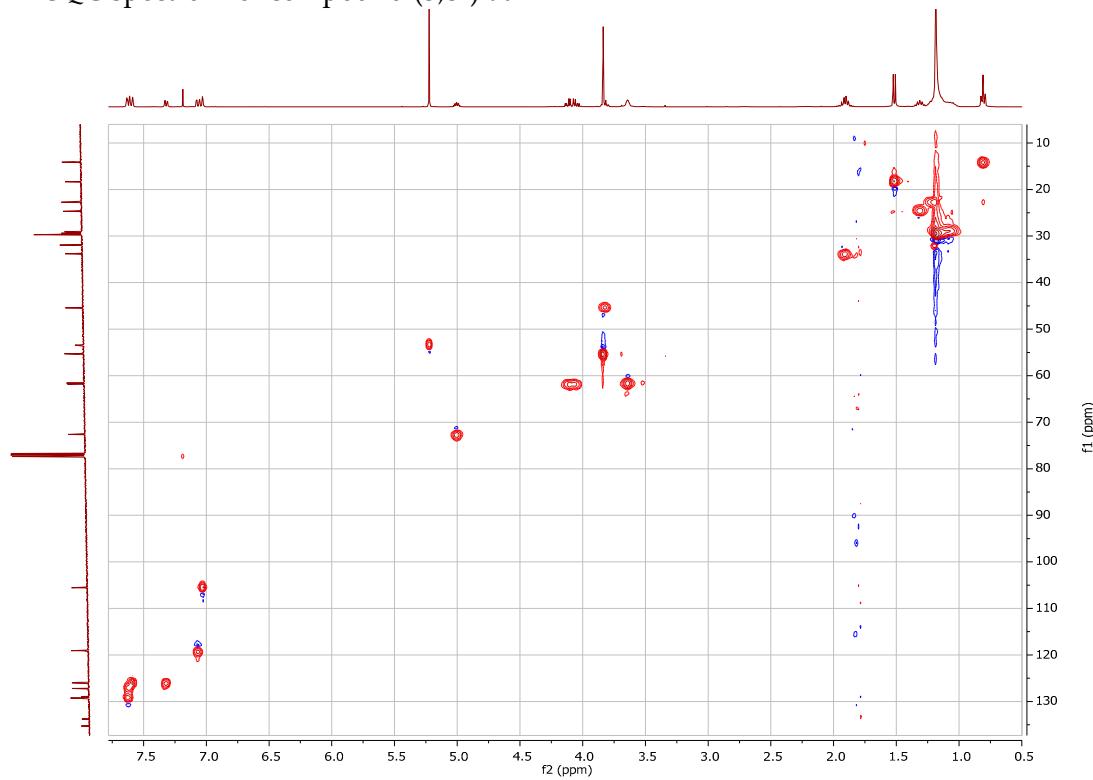
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S,S')-9a



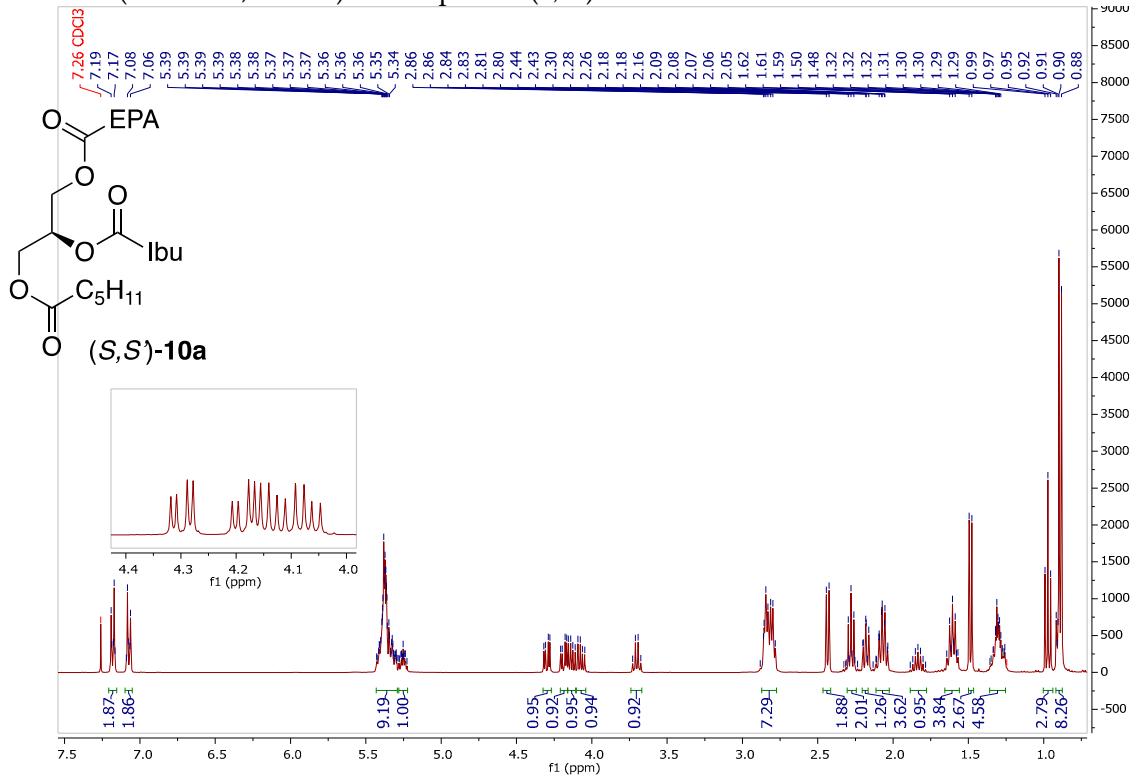
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-9a



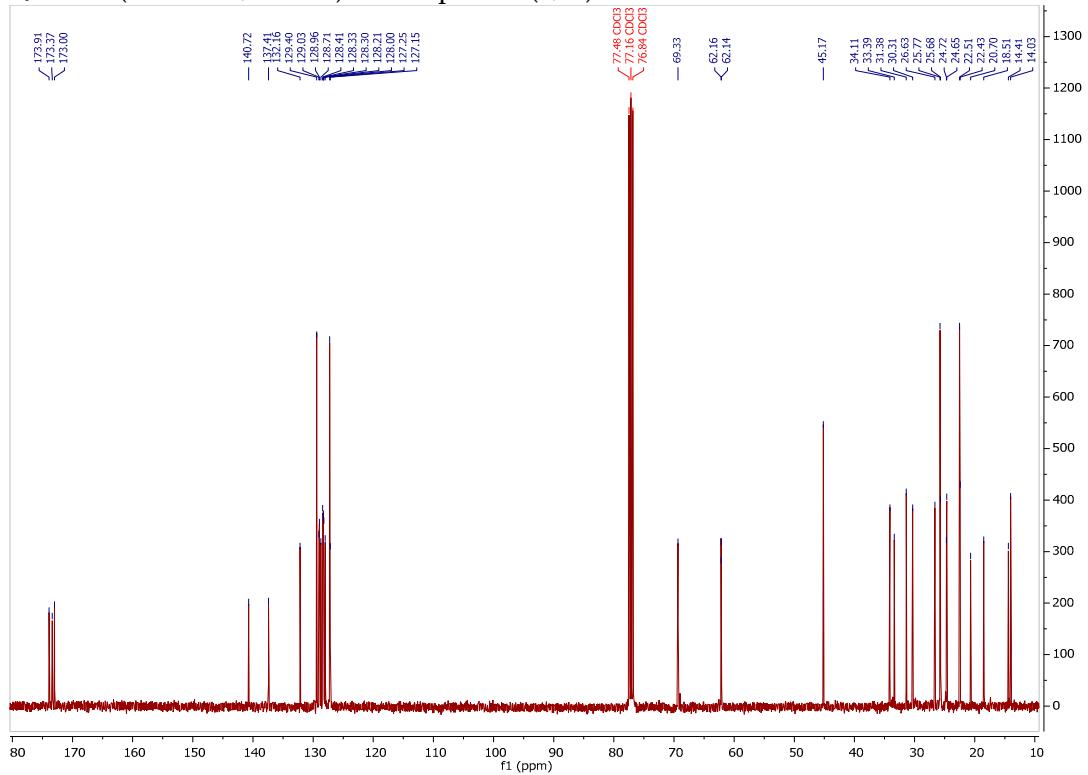
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-9a



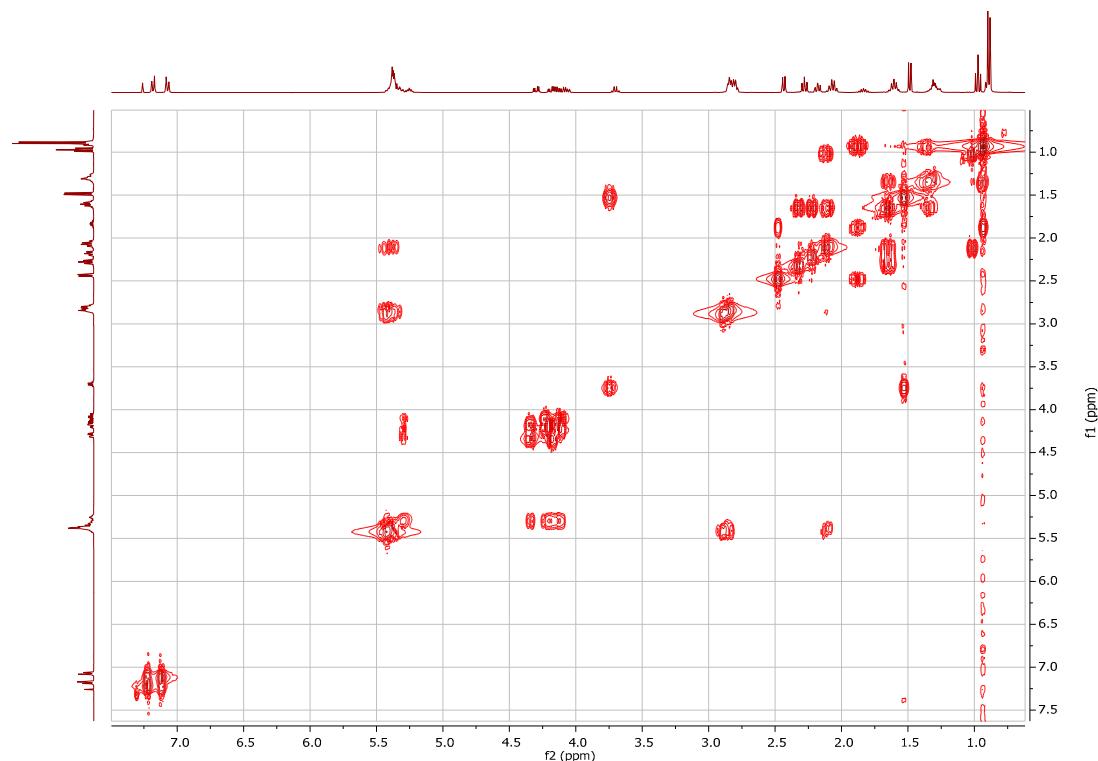
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S,S')-10a



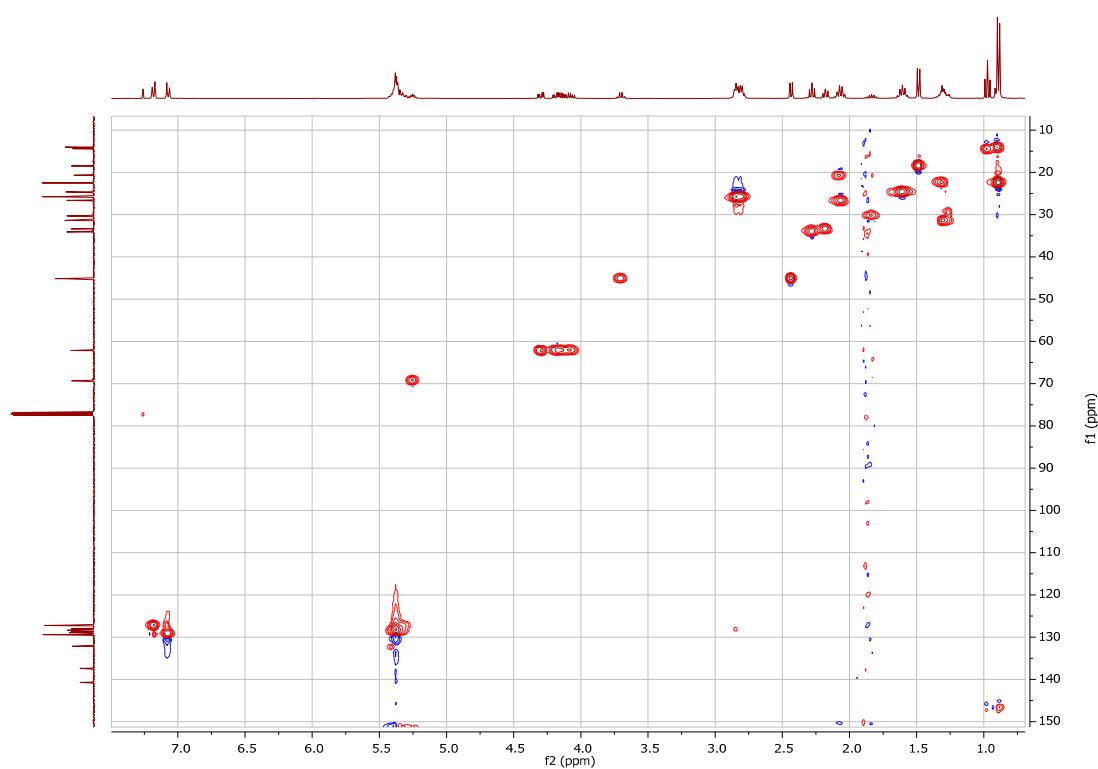
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (S,S')-10a



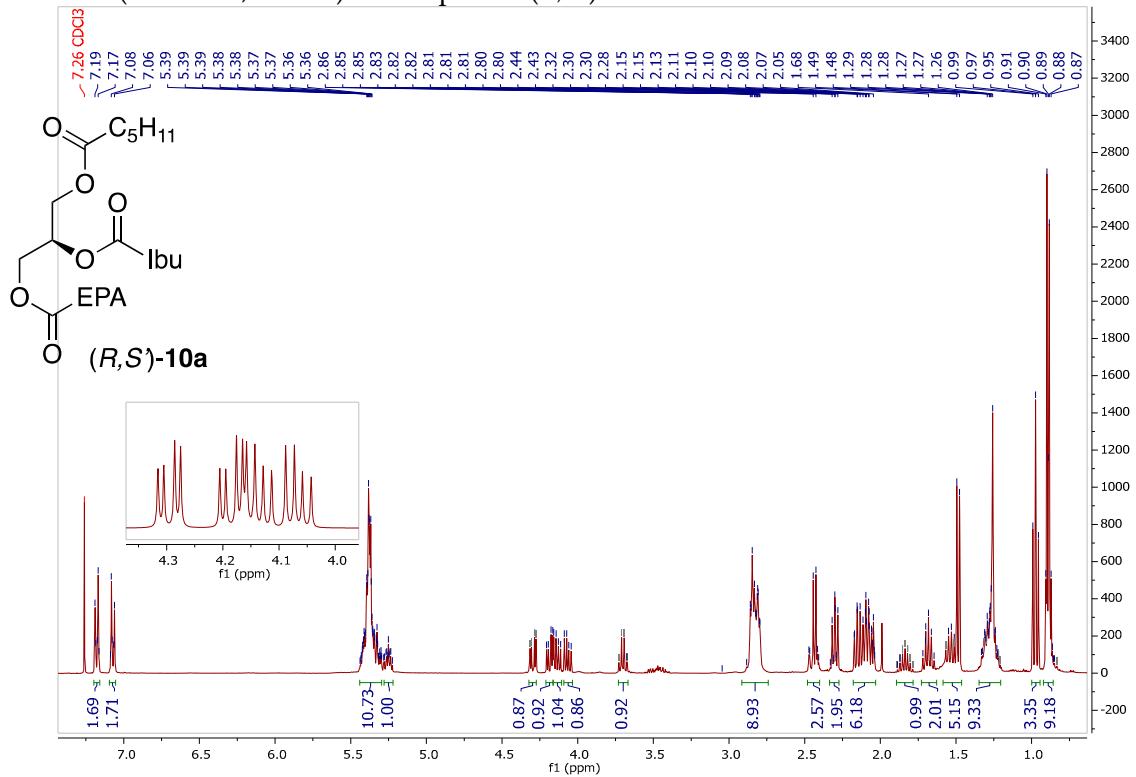
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-**10a**



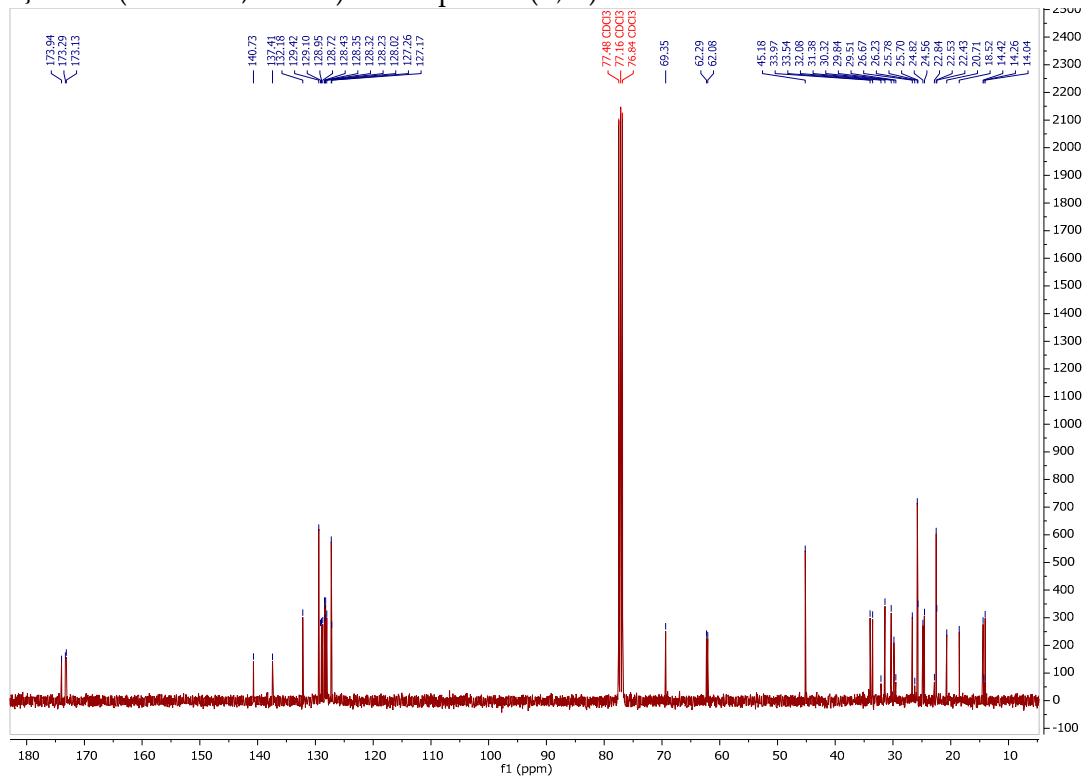
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-**10a**



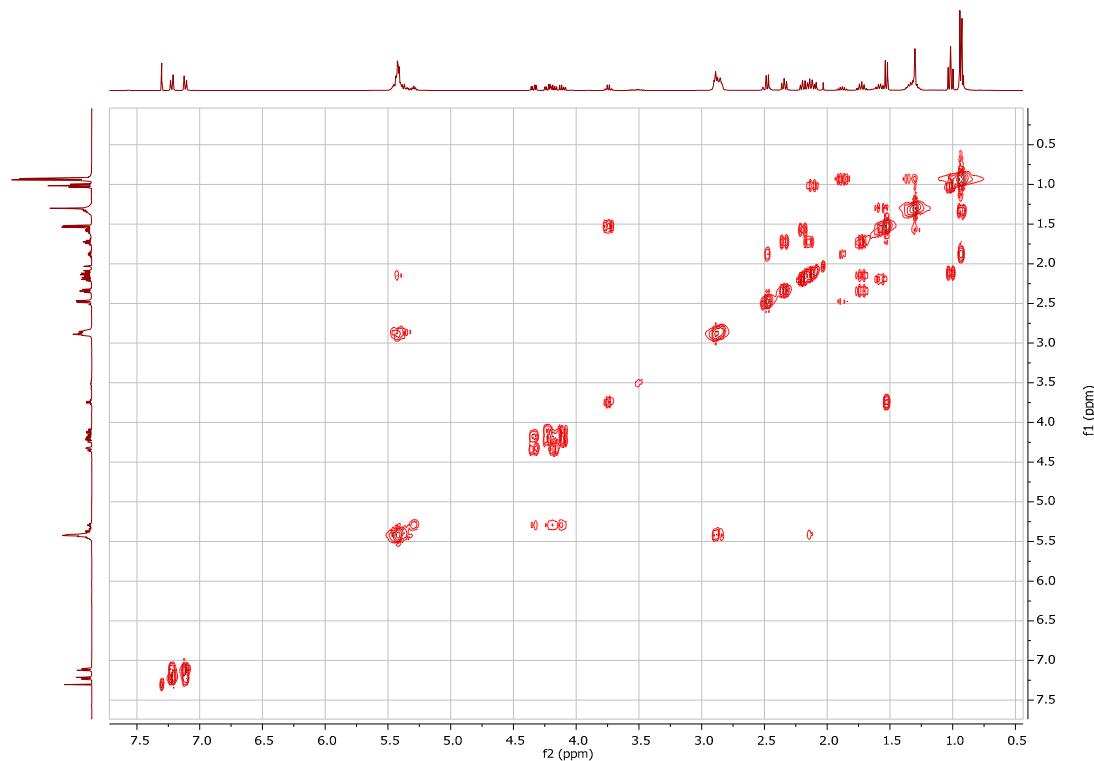
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (R,S')-10a



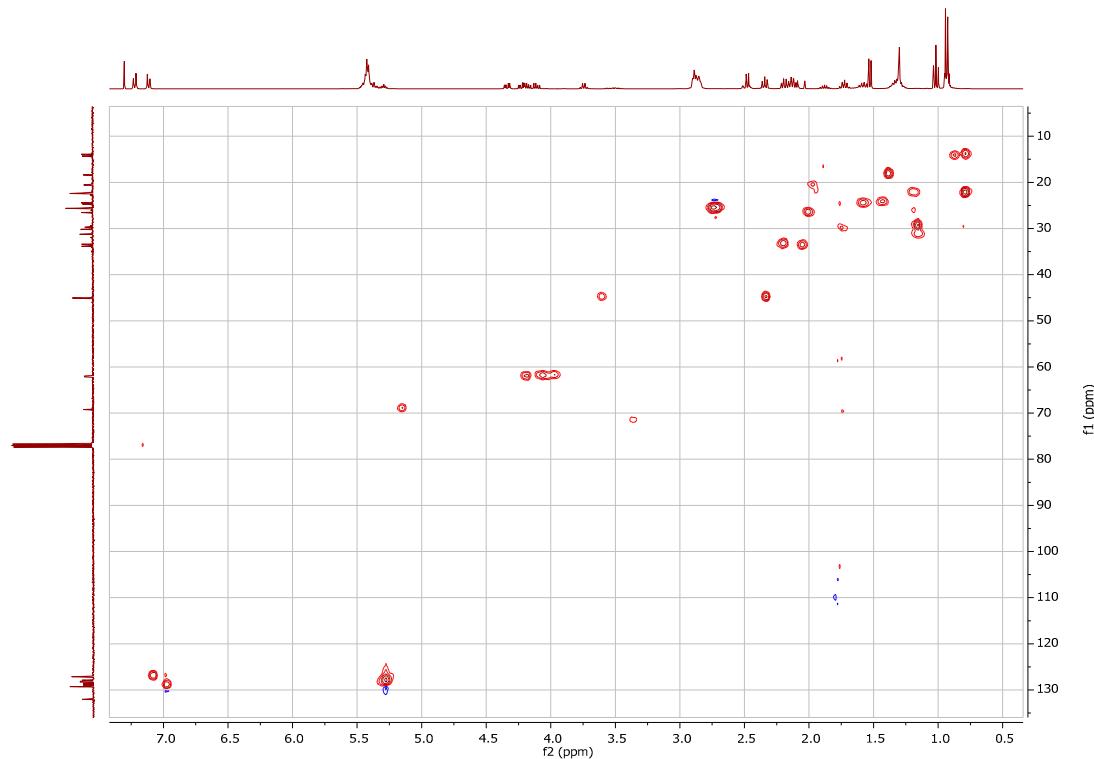
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (R,S')-10a



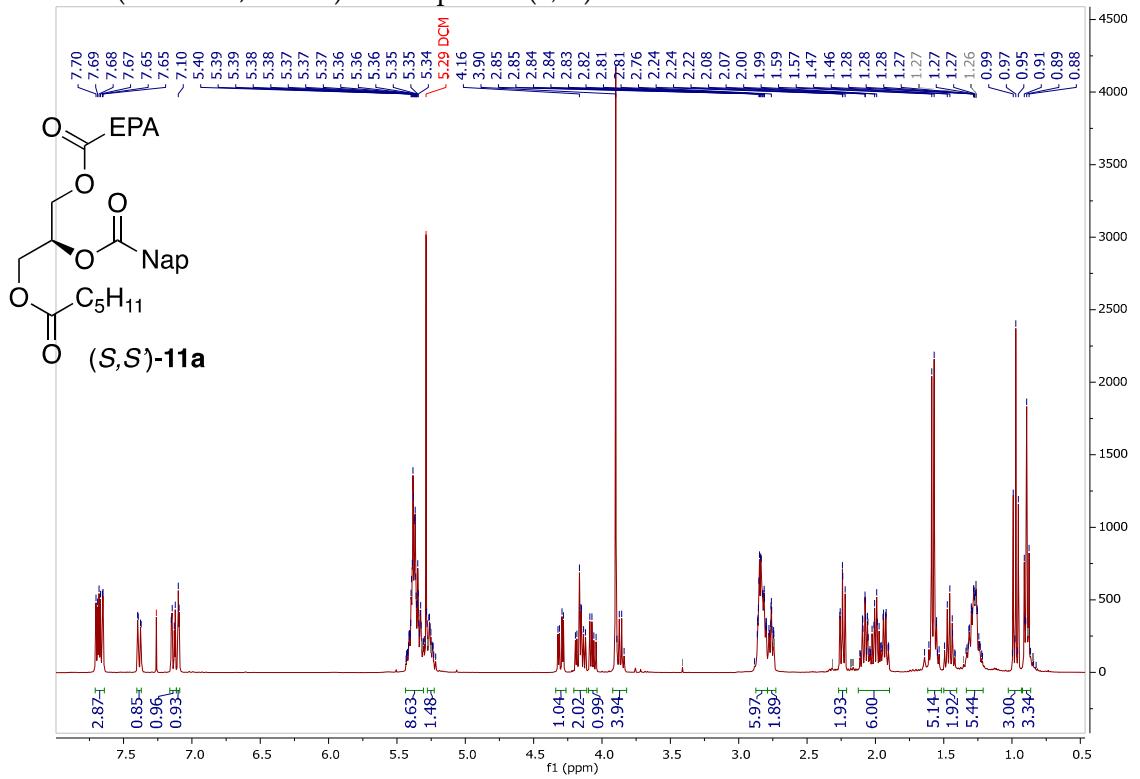
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound  $(R,S')$



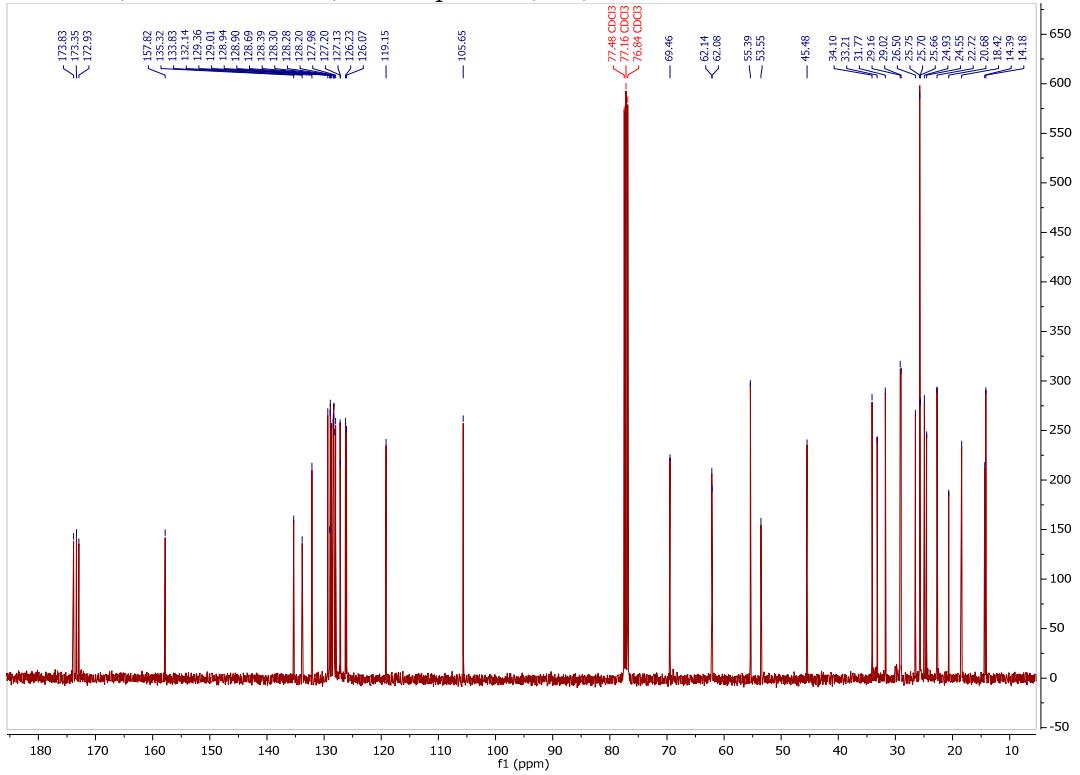
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound  $(R,S')$



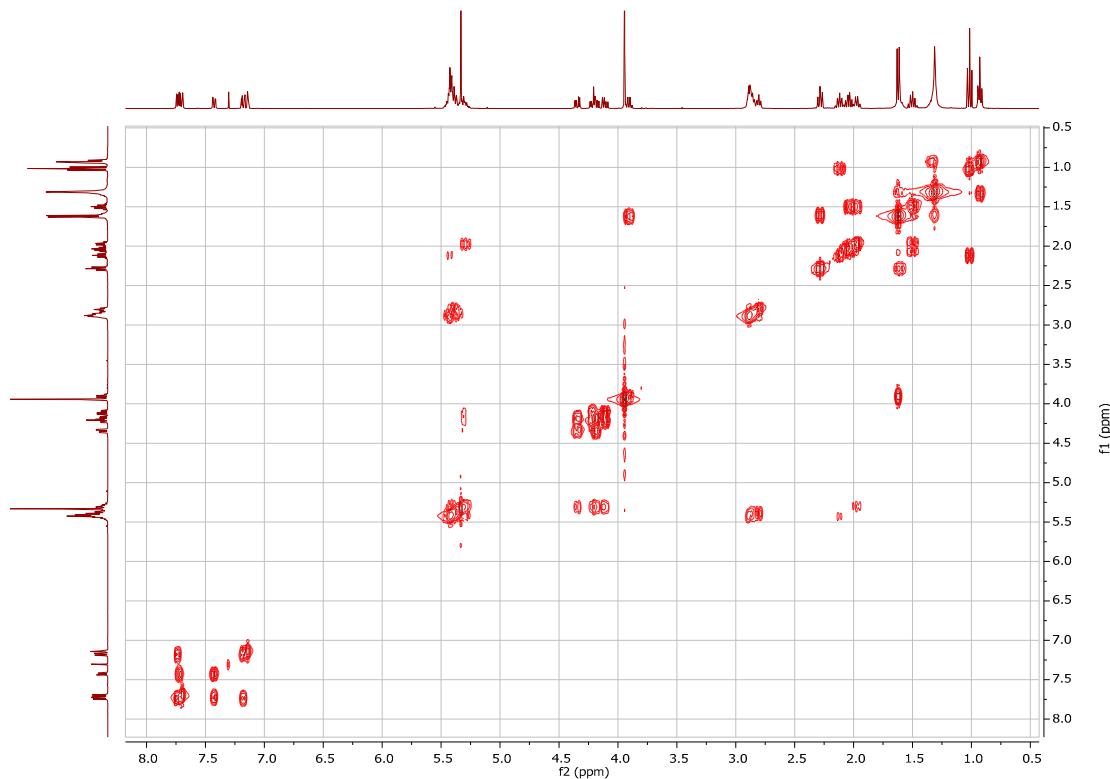
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S,S')-11a



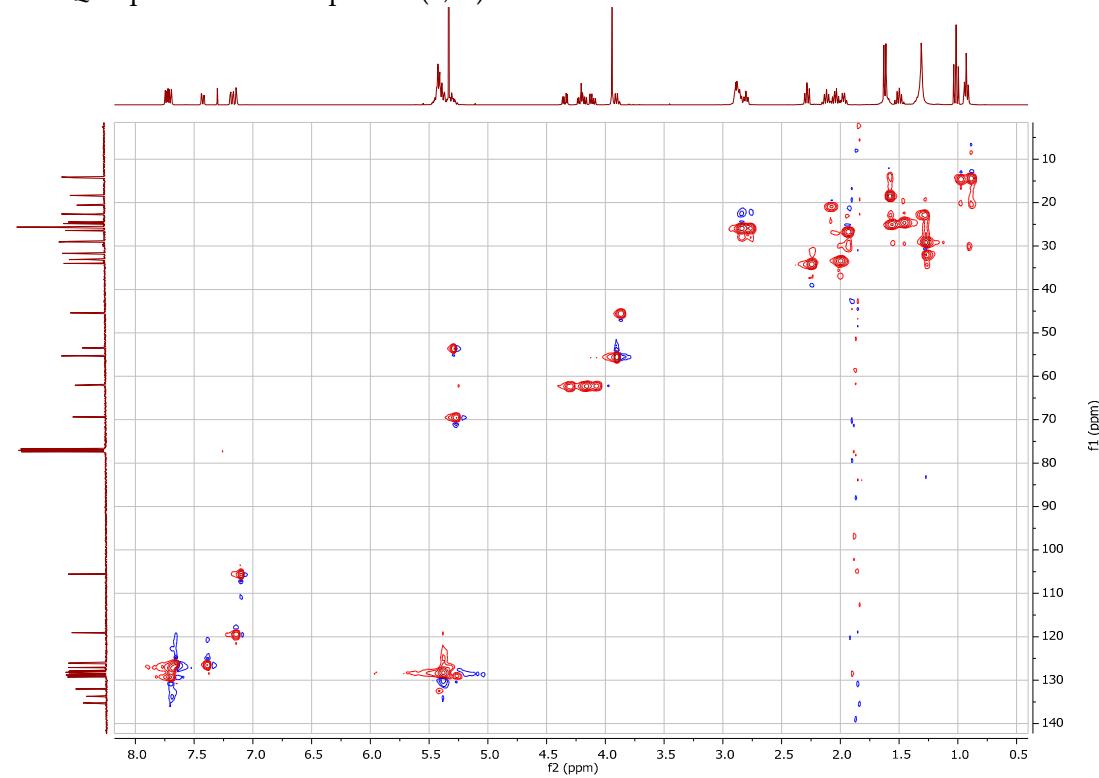
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (S,S')-11a

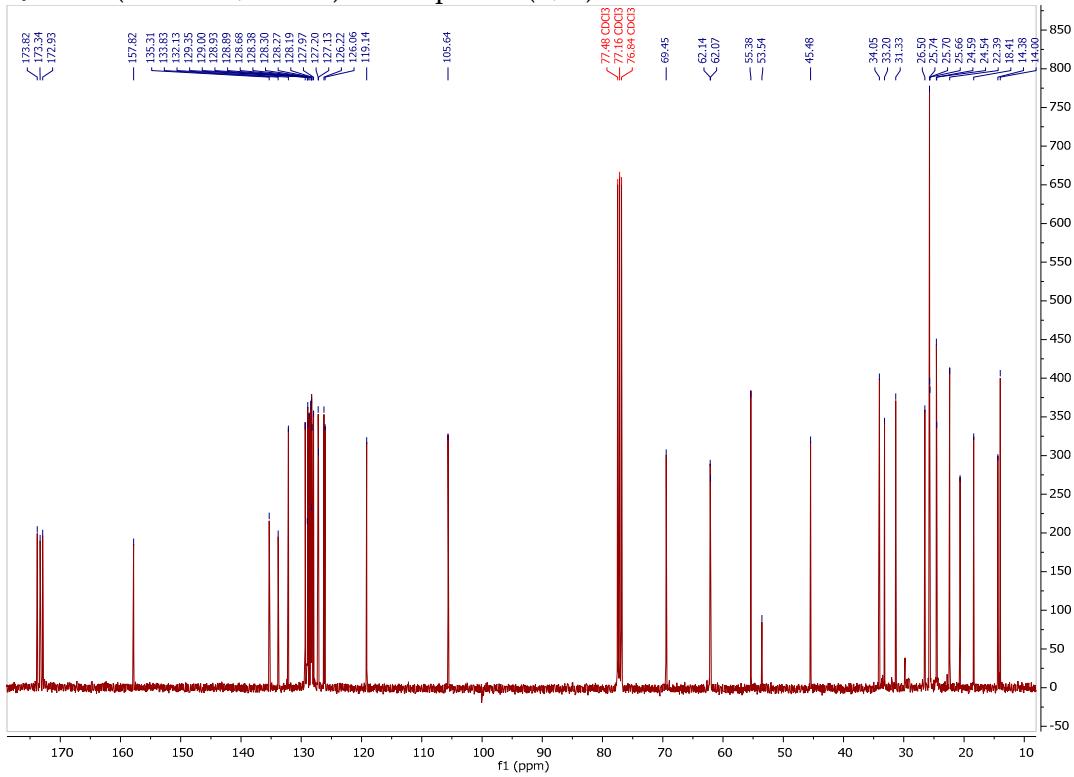
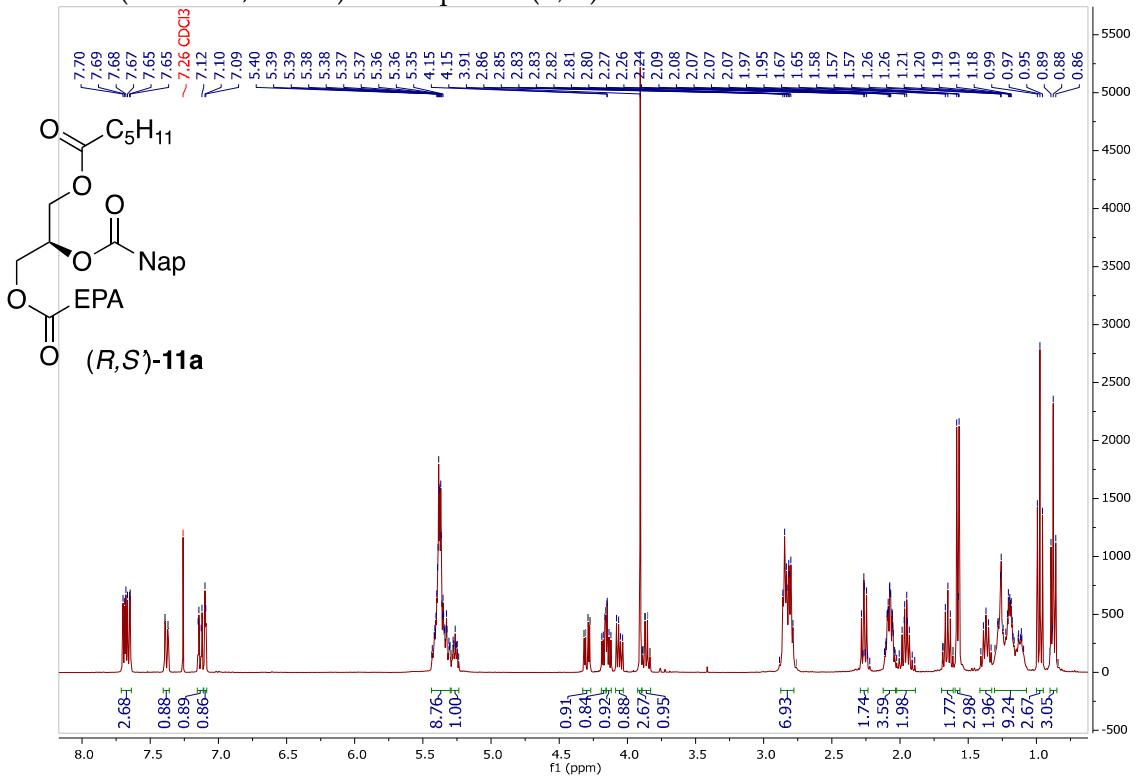
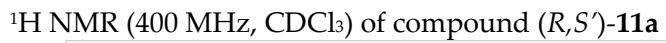


$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-**11a**

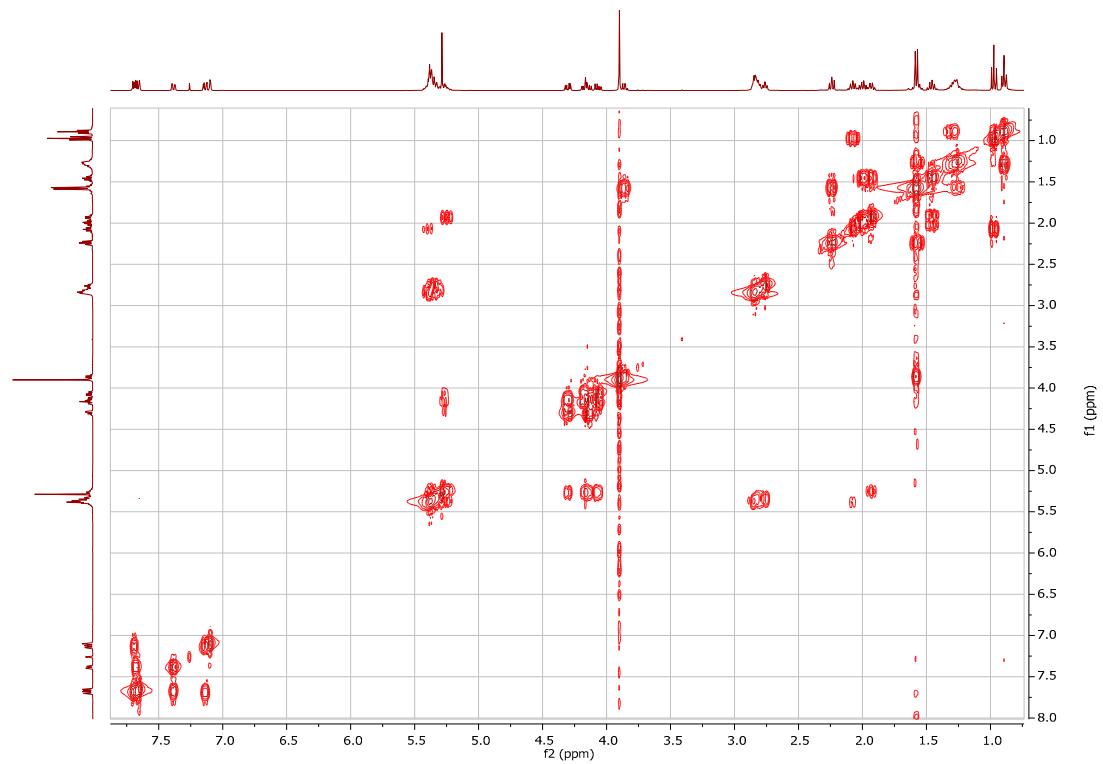


$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-**11a**

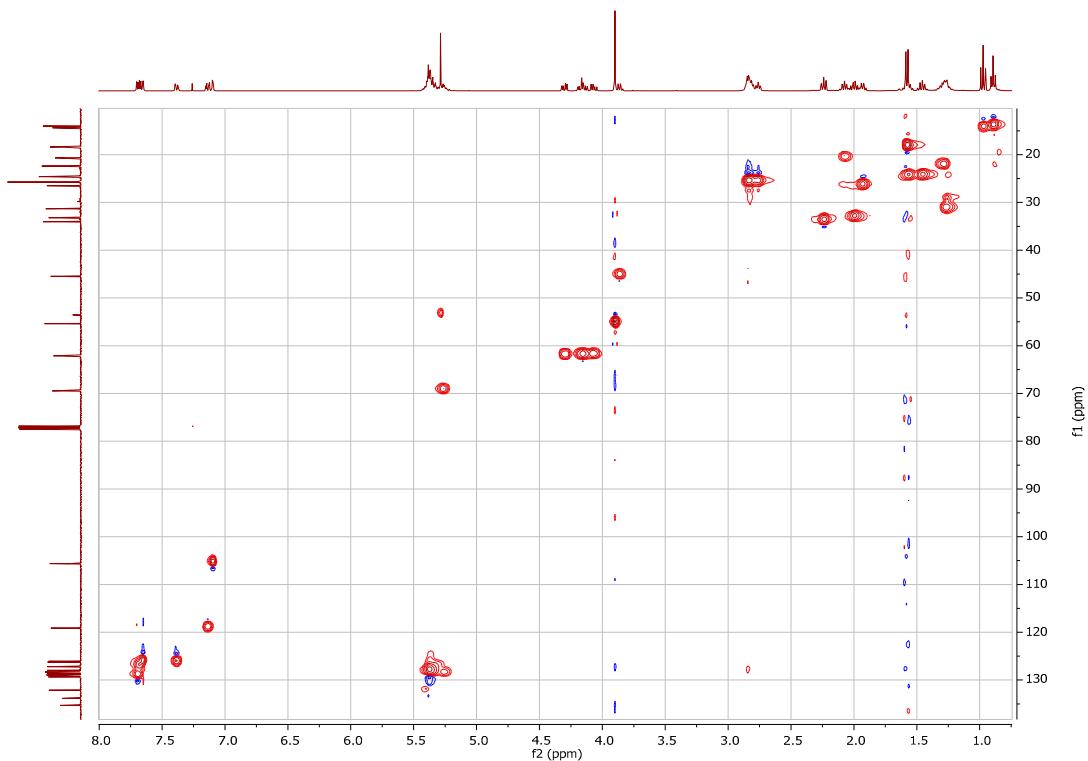




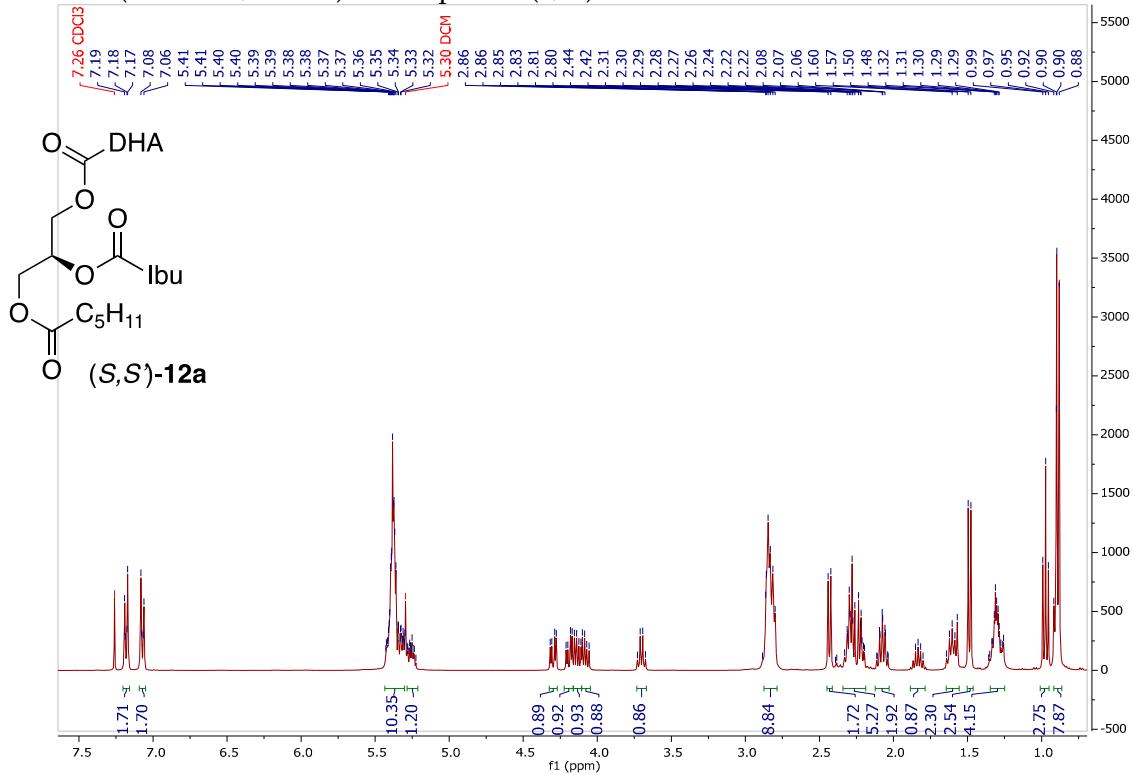
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*R,S'*)-**11a**



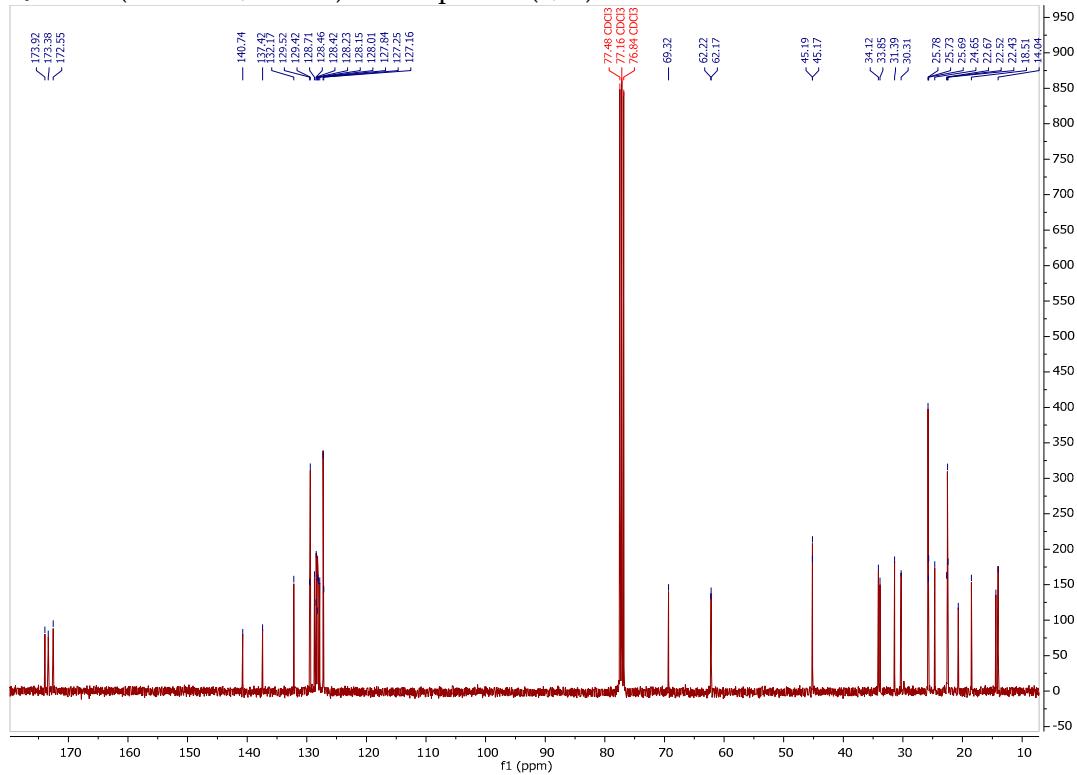
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*R,S'*)-**11a**



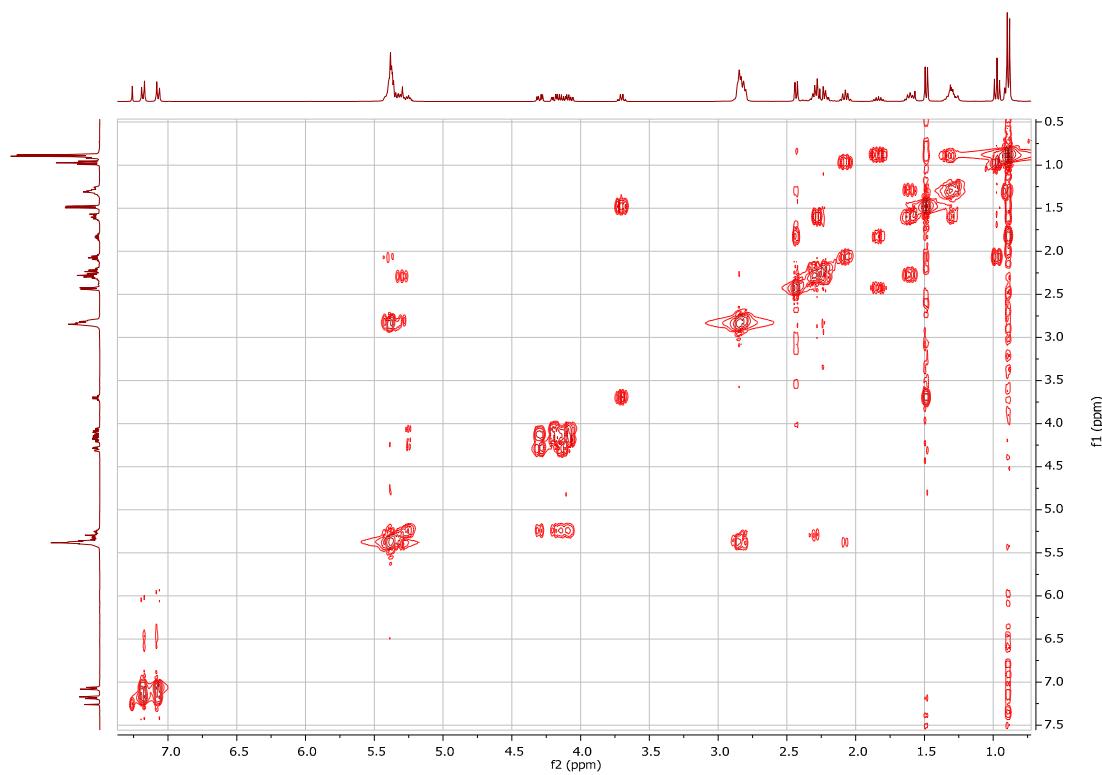
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S,S')-12a



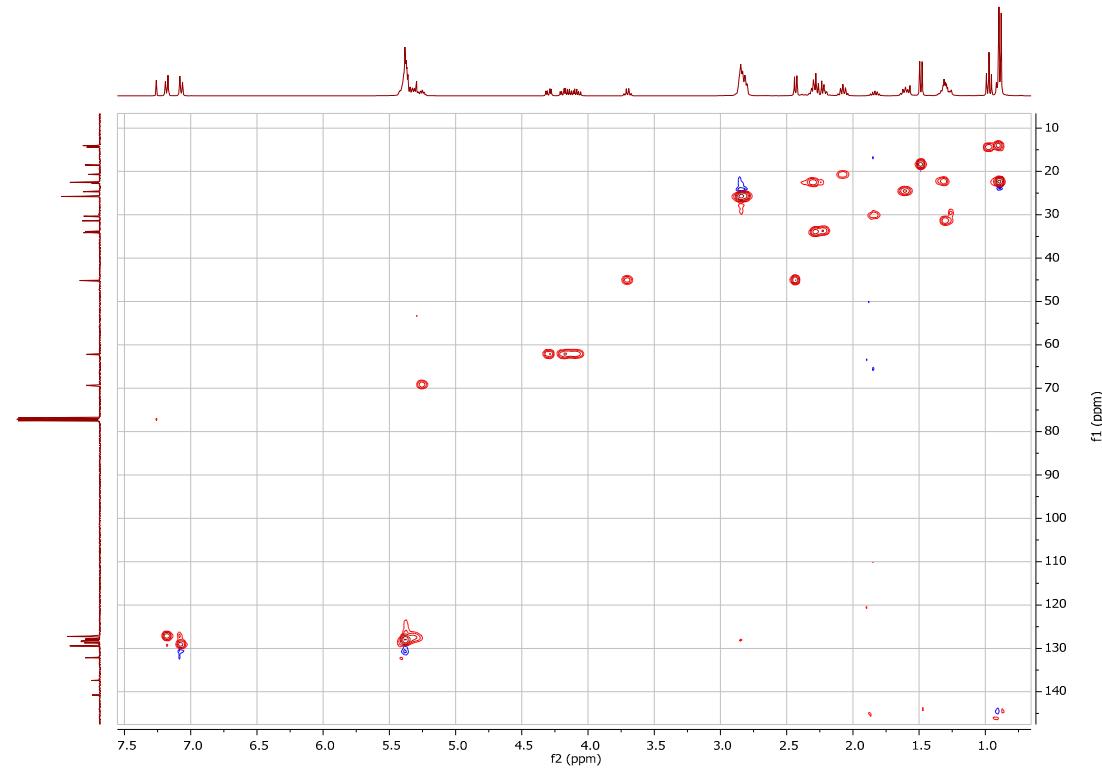
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (S,S')-12a



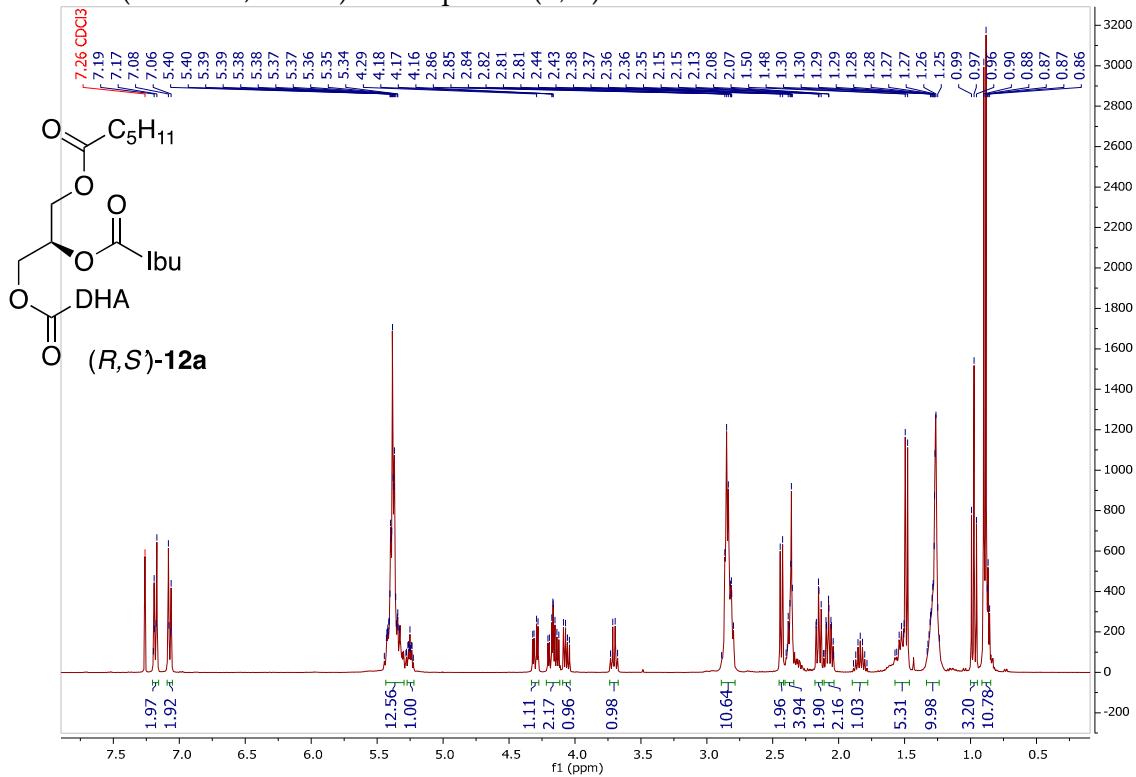
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-**12a**



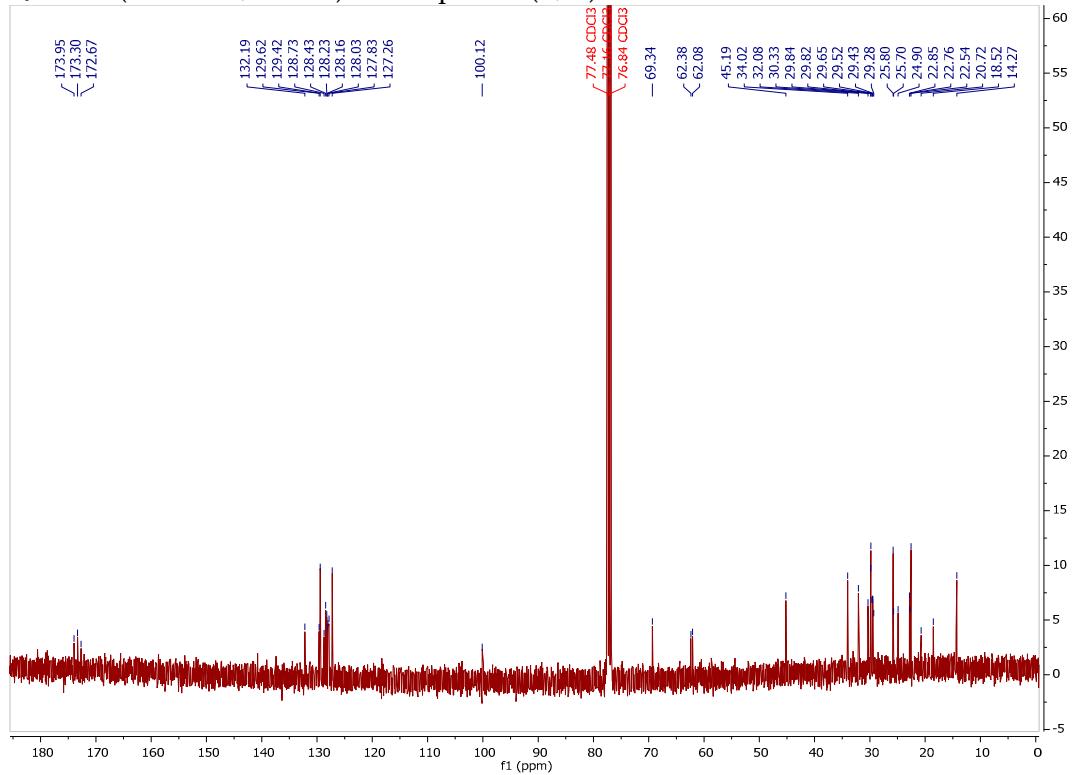
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-**12a**



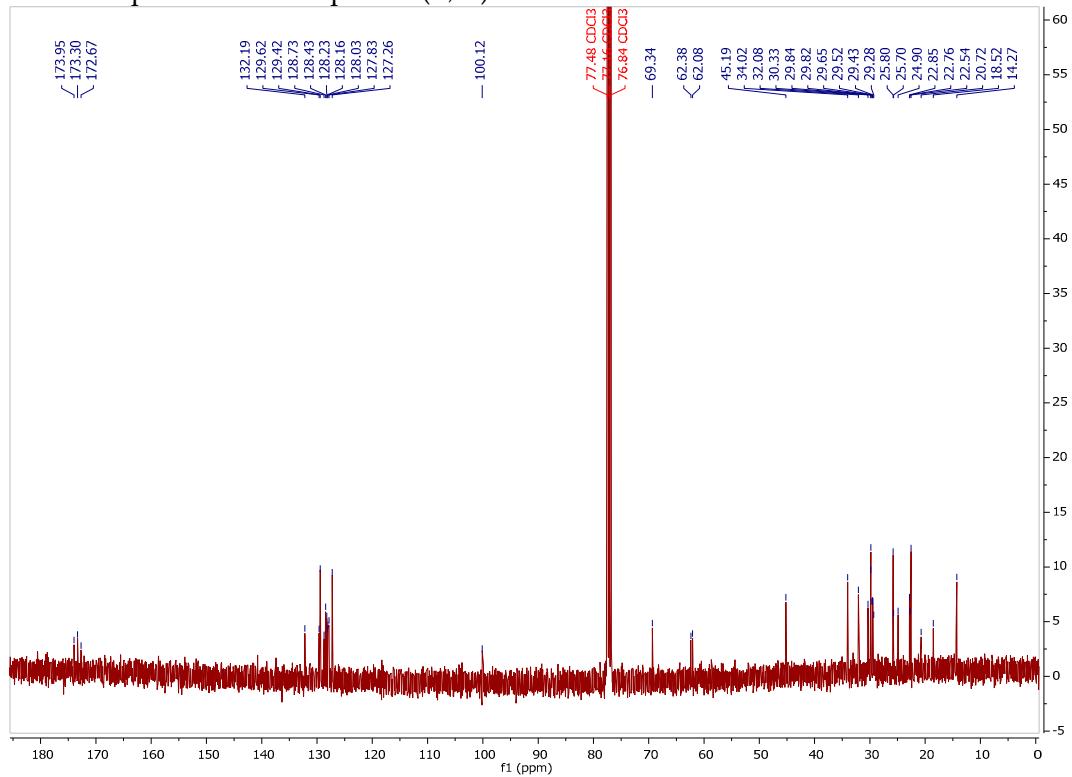
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (R,S')-12a



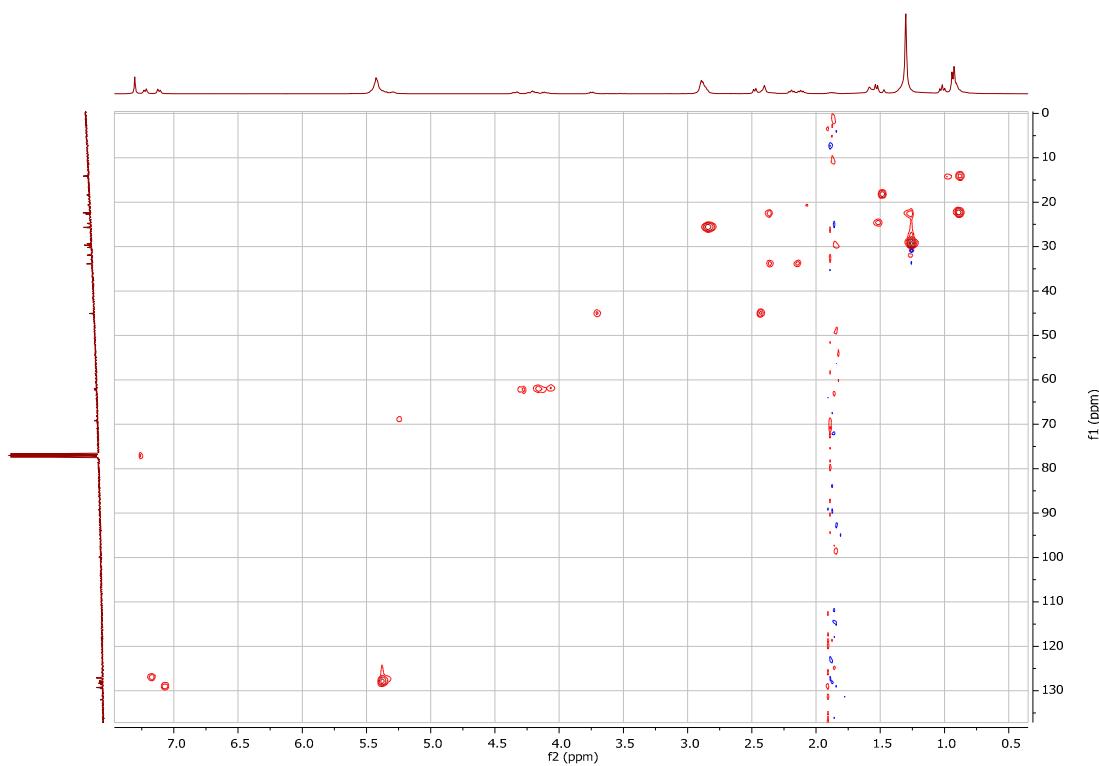
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (R,S')-12a



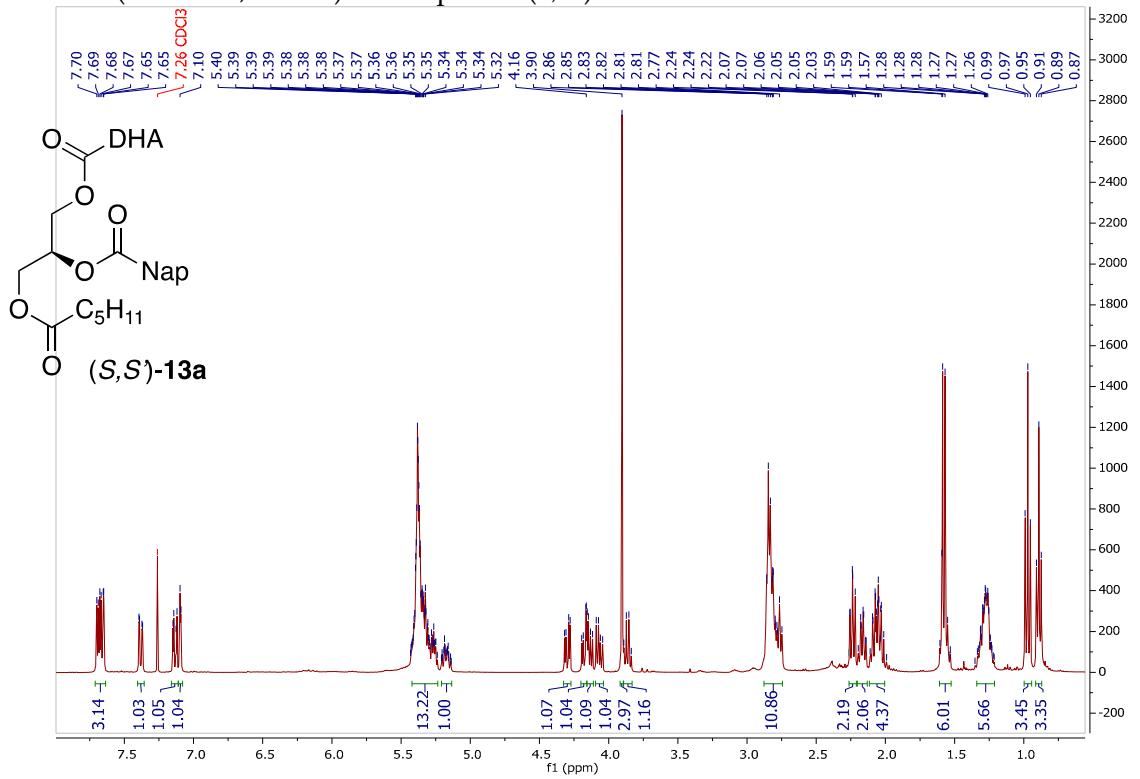
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*R,S'*)-12a



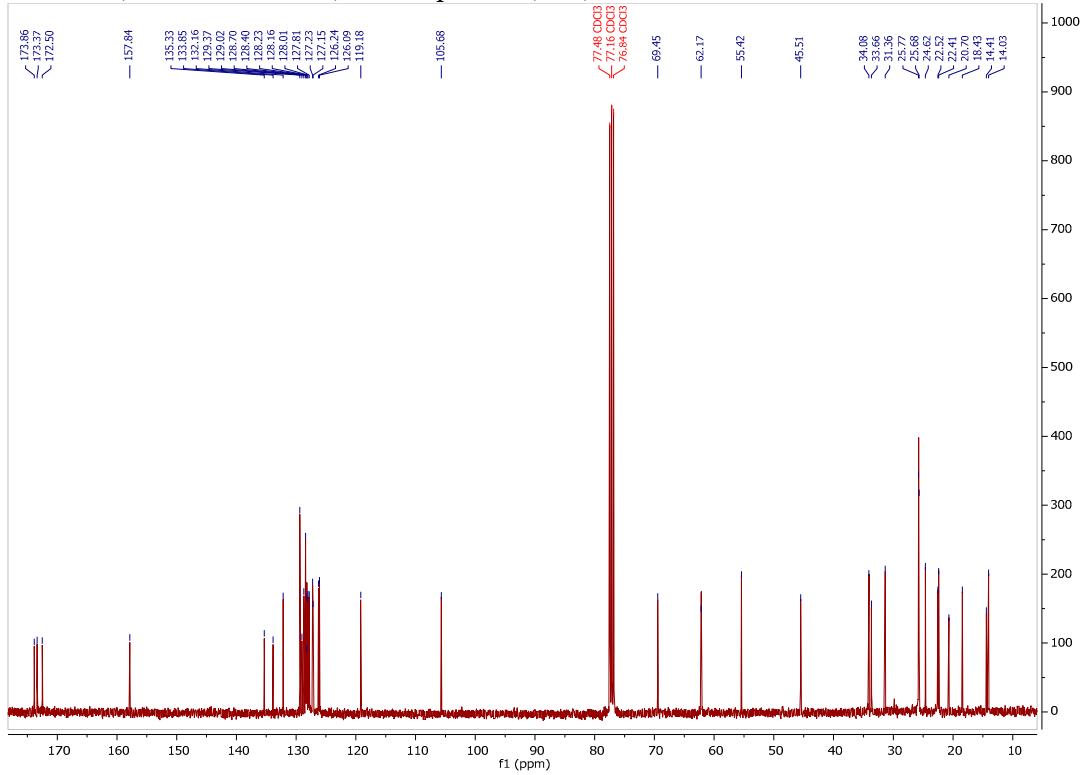
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*R,S'*)-12a



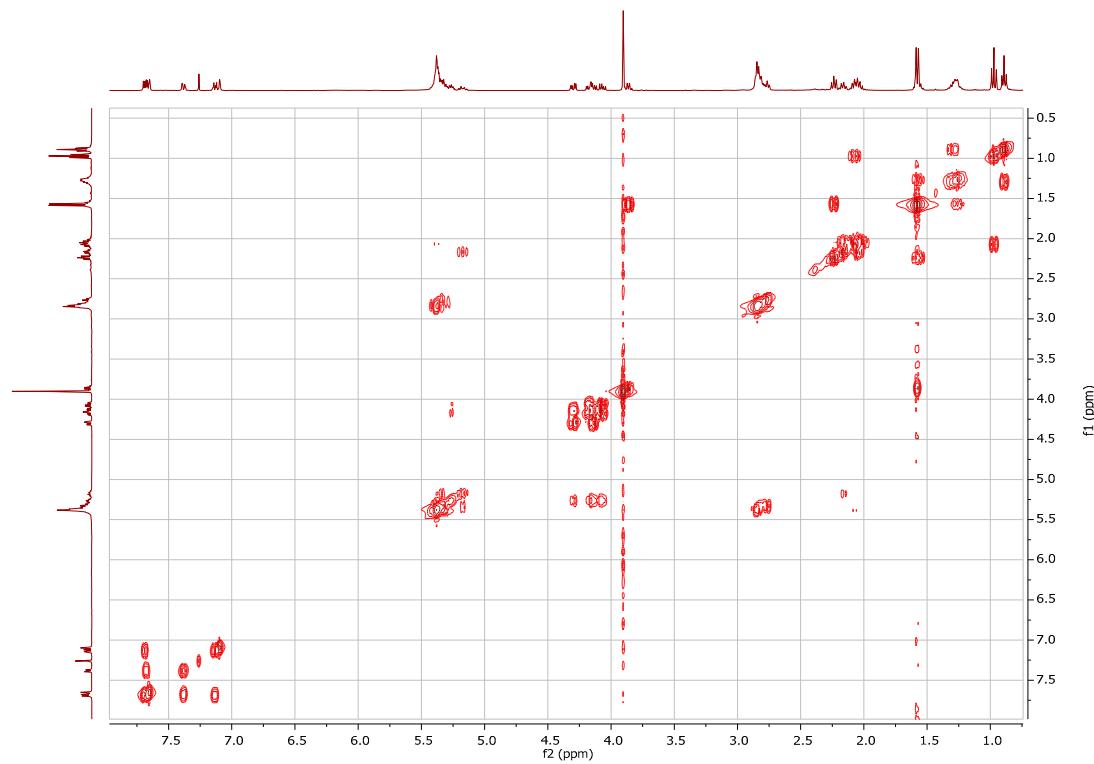
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (S,S')-13a



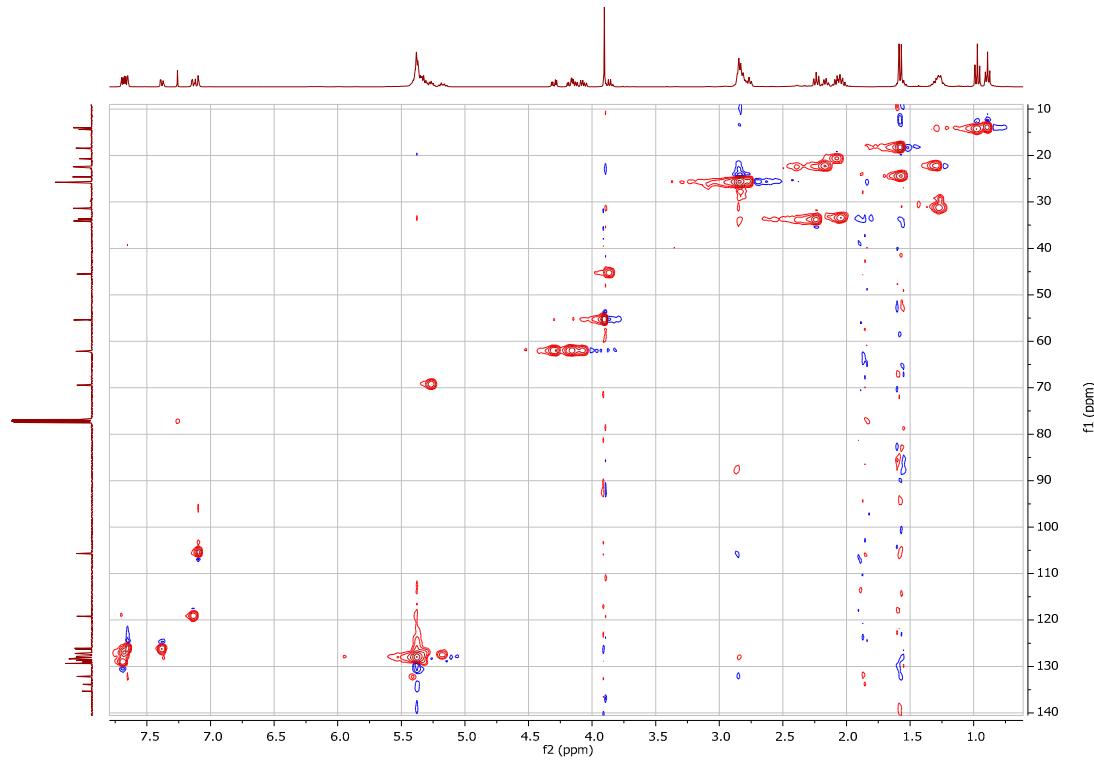
<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (S,S')-13a



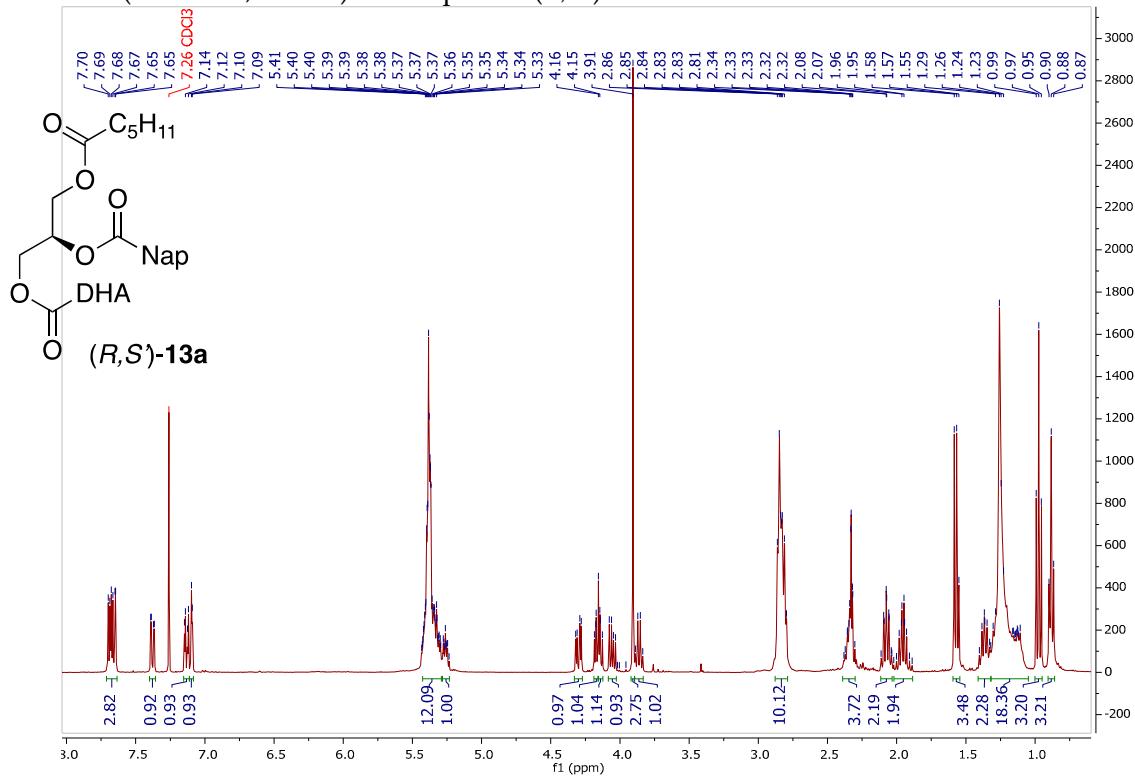
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*S,S'*)-**13a**



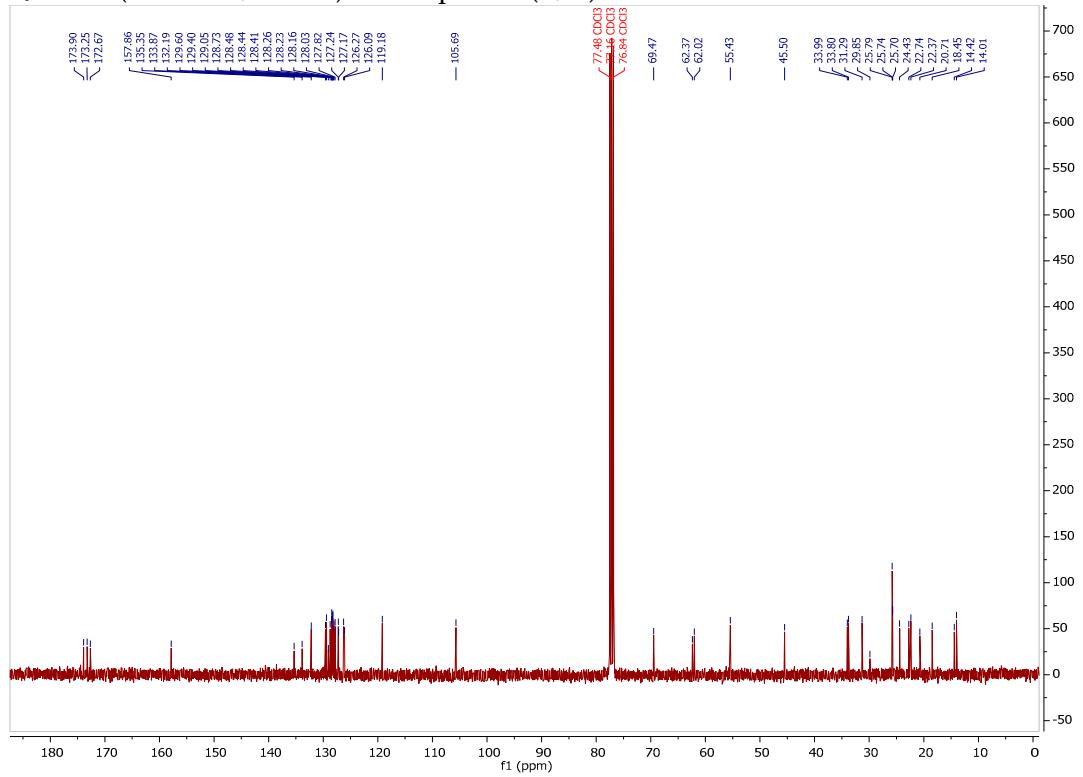
$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*S,S'*)-**13a**



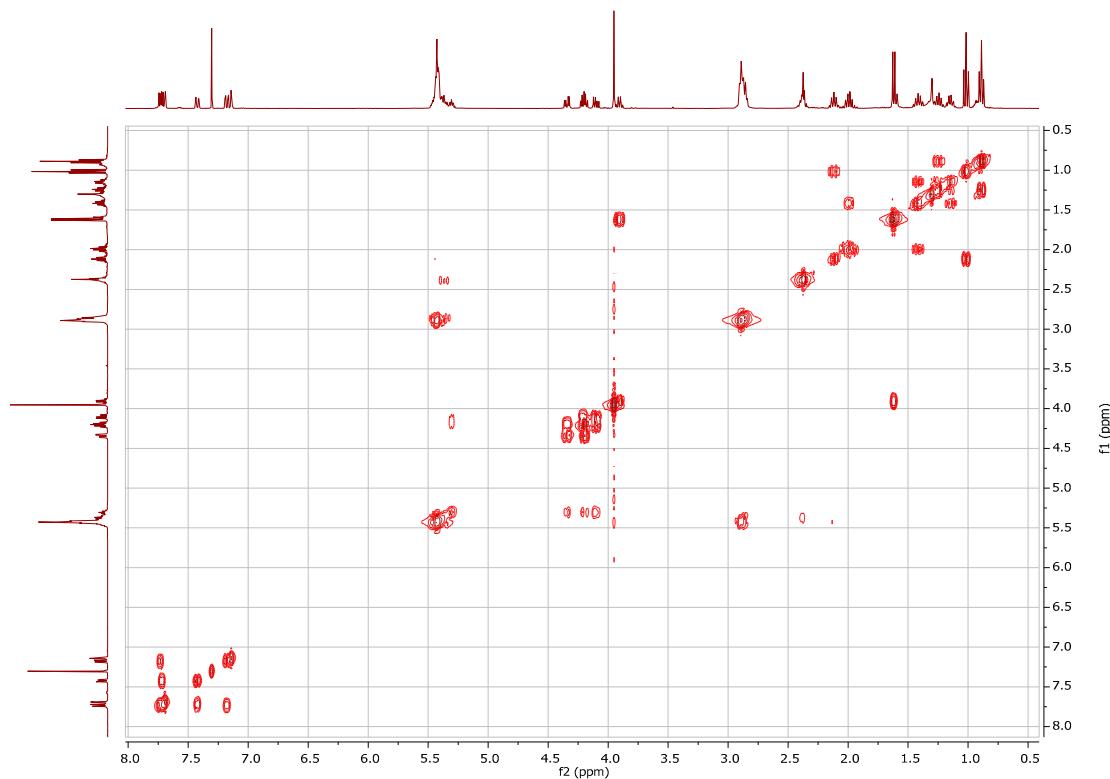
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound (R,S')-13a



<sup>13</sup>C{H} NMR (101 MHz, CDCl<sub>3</sub>) of compound (R,S')-13a



$^1\text{H}$ - $^1\text{H}$  COSY spectrum of compound (*R,S'*)-13a



$^{13}\text{C}$ - $^1\text{H}$  HSQC spectrum of compound (*R,S'*)-13a

