# Organocatalytic Addition of Bis(arylsulfonyl)methane to α,β-Unsaturated Aldehydes and Synthesis of Optically Enriched 3-Methyl-Alkanols

José Luis García Ruano,\* Vanesa Marcos and José Alemán\*

Departamento de Química Orgánica (C-I) Universidad Autónoma de Madrid. Cantoblanco, 28049-Madrid (Spain) Fax: (+) 3491497466 E-mail: joseluis.garcia.ruano@uam.es, jose.aleman@uam.es

## **Supporting Information**

### Contents

General Methods and Materials	S2
Experimental Procedures and Characterizations	S2
Spectra of compounds 7a-7i and 9b, d-g	<b>S</b> 8
HPLC chromatograms of compounds 7a-i	S22

**General Methods.** NMR spectra were acquired on a Bruker 300 spectrometer, running at 300 and 75 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. Chemical shifts ( $\delta$ ) are reported in ppm relative to residual solvent signals (CHCl<sub>3</sub>, 7.26 ppm for <sup>1</sup>H NMR, CDCl<sub>3</sub>, 77.0 ppm. <sup>13</sup>C NMR spectra were acquired on a broad band decoupled mode. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or KMnO<sub>4</sub> dip. Purification of reaction products was carried out by flash chromatography (FC) using silica gel Merck-60 which was previously neutralized with a 10 mol % of Et<sub>3</sub>N in Hexane. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The enantiomeric excess (*ee*) of the products was determined by chiral stationary phase HPLC (Daicel Chiralpak AD or Daicel Chiralcel IC columns).

**Materials.** Commercially available aldehydes **6a-h**, **6j**, bissulfone **5** and catalyst **8c** and solvents were used without further purification. Aldehyde **6i** was synthesized according to the literature.<sup>1</sup>

## **Experimental Procedures and Characterizations.**

General Procedure for the synthesis of the 7a-7i compounds. In an ordinary vial the corresponding aldehyde (0.4 mmol) was added to a stirred solution of catalyst 8c (0.02 mmol), the bis(phenylsulfonyl)methane (0.2 mmol) and LiOAc (0.2 mmol) in THF (0.2 mL) at room temperature. After complete consumption of the bis(phenylsulfonyl)methane (as monitored by <sup>1</sup>H NMR spectroscopy, usually 3-4 days), the crude was reduced with NaBH<sub>4</sub> and directly charged in FC (eluent indicated in each case), affording pure products.

PhO<sub>2</sub>S SO<sub>2</sub>Ph **7a** (*R*)-3-Methyl-4,4-bis(phenylsulfonyl)butan-1-ol (7a). The product was obtained following the standard procedure as colorless oil (95% yield) after FC (eluent 2/1 AcOEt/hexane). The *ee* was determined by HPLC using a Chiralcel IC column [hexane/*i*PrOH (75:25)]; flow rate 1.0 mL/min;  $\tau_{major} = 27.1$  min,  $\tau_{minor} = 35.4$  min, (80% *ee*).  $[\alpha]^{20}_{D} = -1.56$  (*c* = 0.8, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.96-7.89 (m, 4H), 7.66-7.63 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 4H), 5.10 (s, 1H), 3.84-3.77 (m, 1H), 3.61-3.53 (m, 1H), 2.82 (q, *J* = 7.1 Hz, 1H), 2.34-2.22 (m, 1H), 1.90-1.80 (m, 1H), 1.65 (bs, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  140.9, 139.0, 134.4, 134.1, 129.6, 129.0, 128.9, 85.6, 61.4, 36.9, 32.5, 16.8. MS (TOF ES<sup>+</sup>): [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>21</sub>O<sub>5</sub>S<sub>2</sub> 369.0830; found 369.0827.

<sup>&</sup>lt;sup>1</sup> E. Reyes, H. Jiang, A. Milelli, P. Elsner, R. G. Hazell and K. A. Jørgensen, Angew. Chem. Int. Ed., 2007, 46, 9202.



following the standard procedure as colorless oil (92% yield) after FC (1/1 hexane/EtOAc). The ee was determined by HPLC using a Chiralcel IC column 11.7 (c = 0.4, CHCl<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.92-7.89 (m, 4H), 7.63 (t, J = 7.4 Hz, 2H), 7.50 (m, 4H), 5.20 (s, 1H), 3.86-3.79 (m, 1H), 3.57-3.49 (m, 1H), 2.42-2.26 (m, 2H), 1.93-1.71 (m, 3H), 0.75 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 139.9, 139.0, 134.3, 134.1, 129.3 (2C), 129.0 (2C), 83.9, 61.9, 39.9, 33.1, 23.8, 12.6. MS (TOF ES<sup>+</sup>):  $[M+H]^+$  calcd for C<sub>18</sub>H<sub>23</sub>O<sub>5</sub>S<sub>2</sub> 383.0987; found 383.0988.



(S)-3-(Bis(phenylsulfonyl)methyl)pentan-1-ol (ent-7b). The product was obtained following the standard procedure using the enantiomer of the catalyst 8c as a colourless oil (97% yield) after FC (1/1 hexane/EtOAc). Spectral data were identical to compound 7b. The ee was determined by HPLC using a Chiralcel IC

(R)-3-(Bis(phenylsulfonyl)methyl)pentan-1-ol (7b). The product was obtained

column hexane/*i*PrOH (75:25)]; flow rate 1.0 mL/min; ;  $\tau_{major} = 31.1 \text{ min}$ ,  $\tau_{minor} = 27.8 \text{ min}$  (90% *ee*).  $[\alpha]^{20}_{D} = +11.3 \ (c = 0.5, \text{CHCl}_3).$ 



(R)-3-(Bis(phenylsulfonyl)methyl)hexan-1-ol (7c). The product was obtained following the standard procedure as colorless oil (96% yield) after FC (eluent 2/1 AcOEt/hexane). The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (75:25)]; flow rate 1.0 mL/min;  $\tau_{minor} = 8.2 \text{ min}$ ,  $\tau_{maior} = 8.9 \text{ min}$ 

 $(90\% \ ee)$ .  $[\alpha]^{20}_{D} = -13.4 \ (c = 0.7, \ CHCl_3)$ . <sup>1</sup>H NMR (CDCl\_3):  $\delta$  7.86-7.82 (m, 2H), 7.61-7.53 (m, 4H), 7.48-7.41 (m, 3H), 5.10 (s, 1H), 3.78-3.71 (m, 1H), 3.49-3.42 (m, 1H), 2.45-2.41 (m, 1H), 2.31-2.23 (m, 1H), 1.85-1.62 (m, 3H), 1.14-1.03 (m, 3H), 0.68 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ 140.0, 139.1, 134.3, 134.1, 129.3 (2C), 129.0 (2C), 84.1, 61.6, 37.8, 35.5, 32.8, 21.3, 13.6. MS (TOF  $ES^{+}$ ):  $[M+H]^{+}$  calcd for  $C_{19}H_{25}O_5S_2$  397.1143; found 397.1152.



(R)-3-(Bis(phenylsulfonyl)methyl)heptan-1-ol (7d). The product was obtained following the standard procedure as colorless oil (99% yield) after FC (eluent 1/1 AcOEt/hexane). The ee was determined by HPLC using a Chiralcel IC column [hexane/*i*PrOH (75:25)]; flow rate 1.0 mL/min;  $\tau_{major} = 60.8 \text{ min}$ ,  $\tau_{minor} = 67.1$ 

min (90% ee).  $[\alpha]^{20}_{D} = -16.6$  (c = 0.3, CHCl<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.91 (d, J = 7.1 Hz, 4H), 7.63 (q J = 7.5 Hz, 2H), 7.55-7.50 (m, 4H), 5.20 (s, 1H), 3.86-3.79 (m, 1H), 3.57-3.50 (m, 1H), 2.50-2.45 (m, 1H), 2.39-2.29 (m, 1H), 1.94-1.87 (m, 1H), 1.79-1.66 (m, 4H), 1.16-1.06 (m, 3H), 0.78 (t, J = 7.1 Hz,

3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 140.9, 140.0, 135.2, 135.0, 130.2 (2C), 129.9 (2C), 84.8, 62.1, 38.2, 33.8, 30.7, 30.6, 22.4, 14.0. MS (TOF ES<sup>+</sup>): [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>27</sub>O<sub>5</sub>S<sub>2</sub> 411.1300; found 411.1303.



(*R*)-3-(Bis(phenylsulfonyl)methyl)octan-1-ol (7e). The product was obtained following the standard procedure as colorless oil (83% yield) after FC (eluent 1/2 AcOEt/hexane). The *ee* was determined by HPLC using a Chiralcel IC column [hexane/*i*PrOH (90:10)]; flow rate 1.0 mL/min;  $\tau_{major} = 117.7$  min,  $\tau_{minor}$ 

= 126.6 min (96% *ee*). [α]<sup>20</sup><sub>D</sub> = -13.7 (*c* = 0.4, CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.93 (d, *J* = 7.4 Hz, 4H), 7.65 (q, *J* = 7.6 Hz, 2H), 7.57-7.50 (m, 4H), 5.19 (s, 1H), 3.87-3.80 (m, 1H), 3.59-3.52 (m, 1H), 2.48-2.40 (m, 1H), 2.38-2.31 (m, 1H), 1.95-1.88 (m, 1H), 1.81-1.63 (m, 4H), 1.29-1.05 (m, 5H), 0.82 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 140.9, 140.1, 135.2, 134.9, 129.9 (2C), 129.8 (2C), 84.8, 62.1, 38.2, 33.8, 31.6, 31.0, 28.1, 22.6, 14.0. MS (TOF ES<sup>+</sup>): [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>29</sub>O<sub>5</sub>S<sub>2</sub> 425.1456; found 425.1456.

PhO<sub>2</sub>S SO<sub>2</sub>Ph *n*-Hex OH *T*f *R*)-3-(Bis(phenylsulfonyl)methyl)nonan-1-ol (7f). The product was obtained following the standard procedure as colorless oil (83% yield) after FC (eluent 1/2 AcOEt/hexane). The *ee* was determined by HPLC using a Chiralcel IC column [hexane/*i*PrOH (85:15)]; flow rate 1.0 mL/min;  $\tau_{major} = 129.1$  min,  $\tau_{minor} = 137.0$ min (94% *ee*).  $[\alpha]^{20}{}_{D} = -13.4$  (*c* = 0.8, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (dd, *J* = 7.3, 2.2 Hz, 4H), 7.64 (q, *J* = 7.5 Hz, 2H), 7.56-7.4 (m, 4H), 5.20 (s, 1H), 3.81 (dt, *J* = 11.0, 4.7 Hz, 1H), 3.51 (td, *J* = 11.1, 3.3 Hz, 1H), 2.48-2.42 (m, 1H), 2.38-2.26 (m, 1H), 1.92-1.83 (m, 1H), 1.79-1.65 (m, 2H), 1.26-1.04 (m, 9H), 0.84 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  140.0, 139.0, 134.2, 134.0,

129.3 (2C), 128.7 (2C), 84.2, 61.6, 38.0, 33.5, 31.6, 30.7, 28.8, 28.2, 22.4, 13.9. MS (TOF ES<sup>+</sup>):  $[M+H]^+$  calcd for  $C_{22}H_{31}O_5S_2$  439.1613; found 439.1618.



(*R*)-3-(Bis(phenylsulfonyl)methyl)undecan-1-ol (7g). The product was obtained following the standard procedure as colorless oil (73% yield) after FC (eluent 1/2 AcOEt/hexane). The *ee* was determined by HPLC using two Chiralcel IC column in arrow [hexane/*i*PrOH (85:15)]; flow rate 1.0 mL/min;

τ<sub>major</sub> = 108.1 min, τ<sub>minor</sub> = 114.7 min (94%*ee*). [α]<sup>20</sup><sub>D</sub> = -13.0 (*c*= 0.6, CHCl<sub>3</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ
7.92 (d,*J*= 7.4 Hz, 4H), 7.69-7.59 (m, 2H), 7.55-7.48 (m, 4H), 5.18 (s, 1H), 3.82 (dt,*J*= 10.2, 4.5 Hz, 1H), 3.53 (td,*J*= 11.2, 3.3 Hz, 1H), 2.52-2.43 (m, 1H), 2.39-2.27 (m, 1H), 1.94-1.65 (m, 4H), 1.25-1.06 (m, 13H), 0.88 (t,*J*= 6.8 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 140.9, 140.0, 135.1, 134.9,

130.2 (2C), 129.8 (2C), 84.8, 62.0, 38.3, 33.5, 32.0, 31.0, 29.6 (2C), 29.4 (2C), 28.4, 22.8, 14.1. MS (TOF ES<sup>+</sup>):  $[M+H]^+$  calcd for  $C_{22}H_{31}O_5S_2$  439.1613; found 439.1618.



### (R)-3-(Bis(phenylsulfonyl)methyl)-4-methylpentan-1-ol (7h).

The product was obtained following the standard procedure as colorless oil (70% yield) after FC (eluent 1/2 AcOEt/hexane). In this case the time reaction was increased to 10 days. The *ee* was determined by HPLC using a Chiralpak

AD column [hexane/*i*PrOH (75:25)]; flow rate 1.0 mL/min;  $\tau_{major} = 10.4$  min,  $\tau_{minor} = 11.2$  min (90% *ee*).  $[\alpha]^{20}{}_{D} = -29.6$  (*c* = 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.90 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.69-7.62 (m, 2H), 7.56-7.48 (m, 4H), 4.79 (s, 1H), 3.89-3.88 (m, 1H), 3.60-3.50 (m, 1H), 2.62-2.55 (m, 1H), 2.36-2.26 (m, 2H), 2.15-2.04 (m, 1H), 1.81(bs, 1H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.74 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  141.4, 138.2, 134.5, 134.1, 129.3, 129.2, 129.1, 128.7, 84.4, 62.3, 41.8, 31.7, 31.0, 21.5, 20.8. MS (TOF ES<sup>+</sup>): [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>25</sub>O<sub>5</sub>S<sub>2</sub> 397.1143; found 397.1148.



#### (R)-3-(Bis(phenylsulfonyl)methyl)-5-phenylpentan-1-ol (7i).

H The product was obtained following the standard procedure as colorless oil (63% yield) after FC (eluent 1/1 AcOEt/hexane). The *ee* was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (80:20)]; flow rate 1.0

mL/min;  $\tau_{major} = 15.1 \text{ min} (90\% ee)$ ,  $\tau_{minor} = 16.5 \text{ min.} [\alpha]^{20}{}_{D} = -15.4 (c = 0.7, CHCl_3)$ . <sup>1</sup>H NMR (300 MHz, CDCl\_3):  $\delta$  7.93 (d, J = 7.3 Hz, 2H), 7.64-7.58 (m, 4H), 7.52 (t, J = 7.9 Hz, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.31-7.22 (m, 3H), 7.08 (d, J = 7.9, 2H), 5.23 (s, 1H), 3.77 (dt, J = 10.5, 4.6 Hz, 1H), 3.38 (td, J = 8.5, 2.5 Hz, 1H), 2.72-2.62 (m, 1H), 2.51-2.29 (m, 5H), 2.17-2.10 (m, 1H), 1.98-1.90 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl\_3):  $\delta$  140.8, 140.4, 138.7, 134.2, 134.1, 129.3, 129.1, 129.0, 128.9, 128.7, 128.5, 126.1, 83.9, 61.8, 37.5, 34.1, 33.2, 31.9. MS (TOF ES<sup>+</sup>): [M+Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>26</sub>O<sub>5</sub>S<sub>2</sub>Na 481.1123; found 481.1113.

General Procedure for the synthesis of the 9b-9g compounds (Table 3). In a flash a solution of previously activated magnesium<sup>2</sup> (0.8 mmol) in 1.0 ml of MeOH was added a solution of 7b-7g (0.08 mmol) in 4.0 ml of MeOH under argon atmosphere at room temperature. After completed consumption of magnesium (usually 2-4 hours) was added another 0.8 mmol of magnesium. After completed

 $<sup>^{2}</sup>$  Magnesium was previously activated by heating several times under vacuum line and then was placed under argon atmosphere.

consumption of bissulfone (usually 14 hours more, as monitored by TLC), the crude was directly filtered on silice-gel and washed with Et<sub>2</sub>O affording pure products.

(*R*)-3-Methylpentan-1-ol (9b).<sup>3</sup> The product was obtained following the standard procedure as colorless oil (51% yield). Literature:  ${}^{3} [\alpha]^{20}{}_{D}$  ent-9b = +6.70 (c = 1.2, CHCl<sub>3</sub>). Found:  $[\alpha]^{20}{}_{D}$  = -8.96 (c = 0.7, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.68-3.65 (m, 2H), 1.60-1.15 (m, 5H),0.89-0.85 (m, 6H). <sup>13</sup>C

NMR (75 MHz, CDCl<sub>3</sub>): δ 61.3, 36.5, 36.0, 30.0, 26.0, 10.7.

*n*-Pr (R)-3-Methylhexan-1-ol (9c).<sup>4</sup> The product was obtained following the standard procedure as colorless oil (40% yield). Literature:<sup>4</sup>  $[\alpha]^{20}_{D} = +1.54$  (c = 4.0, CHCl<sub>3</sub>),  $[\alpha]^{20}_{D} = +2.00$  (c = 0.5, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.73-

3.62 (m, 2H), 1.64-1.41 (m, 2H), 1.38-1.26 (m, 5H), 0.90-0.86 (m, 6H).

 $\begin{array}{l} \textbf{(R)-3-Methylheptan-1-ol (9d).}^{5} \text{ The product was obtained following the standard} \\ \textbf{gd} & \textbf{(R)-3-Methylheptan-1-ol (9d).}^{5} \text{ The product was obtained following the standard} \\ \textbf{procedure as colorless oil (92% yield). Literature:} {}^{5} [\alpha]^{20}{}_{D} = +2.64 \ (c = 1.45, \\ \text{CH}_2\text{Cl}_2\text{)}. \text{ Found: } [\alpha]^{20}{}_{D} = +3.10 \ (c = 1.0, \text{CH}_2\text{Cl}_2\text{)}. {}^{1}\text{H} \text{ NMR (300 MHz,} \\ \text{CDCl}_3\text{): } \delta 3.70\text{-}3.64 \ (m, 2\text{H}), 1.76\text{-}1.51 \ (m, 2\text{H}), 1.28\text{-}1.25 \ (m, 7\text{H}), 0\text{-}90\text{-}0.88 \ (m, 6\text{H}). {}^{13}\text{C} \text{ NMR (75 MHz, CDCl}_3\text{): } \delta 61.3, 40.1, 36.8, 29.6, 29.2, 22.9, 19.7, 14.1. MS \ (\text{TOF ES}^+\text{): } [\text{M-H}_2\text{O}]^+ \text{ calcd for } \\ \text{C}_8\text{H}_{16;} 112.1252 \ \text{found 112.1254.} \end{array}$ 

 $\begin{array}{l} \textbf{(R)-3-Methyloctan-1-ol (9e).}^{6} \text{ The product was obtained following the standard} \\ \textbf{9e} & \textbf{(R)-3-Methyloctan-1-ol (9e).}^{6} \text{ The product was obtained following the standard} \\ \textbf{procedure as colorless oil (75% yield). Literature:}^{6} [\alpha]^{20}{}_{D} = +4.78 \ (c = 0.62, \\ \textbf{Hexane}). \text{ Found: } [\alpha]^{20}{}_{D} = +17.7 \ (c = 1.3, \text{ Hexane}). \ ^{1}\text{H} \text{ NMR (300 MHz,} \\ \textbf{CDCl}_{3}): \delta 3.71-3.65 \ (m, 2\text{H}), 1.64-1.54 \ (m, 2\text{H}), 1.28-1.26 \ (m, 9\text{H}), 0.90-0.88 \ (m, 6\text{H}). \ ^{13}\text{C} \text{ NMR (75} \\ \textbf{MHz, CDCl}_{3}): \delta 61.3, 40.1, 37.1, 32.1, 29.6, 26.6, 22.6, 19.7, 14.0. \text{ MS (TOF ES}^{+}): [M-H_2O]^{+} \text{ calcd for} \\ \textbf{C}_{9}\text{H}_{18;} 126.1409, \text{ found 126.1411.} \end{array}$ 

<sup>&</sup>lt;sup>3</sup> K. Mori and T. Sugai *Synthesis* 1982, 752.

<sup>&</sup>lt;sup>4</sup> S. Senda and K. Mori. Agric. Biol. Chem. 1983, 47, 795.

<sup>&</sup>lt;sup>5</sup> D. L. Boger, H. Keim, B. Oberhauser, E. P. Schreiner and C. A. Foster J. Am. Chem. Soc., 1999, **121**, 6197.

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 $\begin{array}{c} (R)-3-Methylnonan-1-ol (9f).^{7} \text{ The product was obtained following the standard} \\ \textbf{9f} \\ \textbf{9f} \\ \textbf{9f} \\ \textbf{9f} \\ \textbf{9f} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H), 0.90-0.85 (m, 6H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 11H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m, 2H), 1.26-1.17 (m, 11H).} \\ \textbf{1.76-1.51 (m, 2H), 1.26-1.17 (m,$ 

 $\begin{array}{c} (R)-3-\text{methyldodecan-1-ol} \ (9g). \ ^8 \ \text{The product was obtained following the} \\ & \text{standard procedure as colorless oil (96% yield). } [\alpha]^{20}{}_{\mathrm{D}} = + 1.54 \ (c = 2.4, \mathrm{CHCl_3}). \\ & \mathrm{^{1}H} \ \mathrm{NMR} \ (300 \ \mathrm{MHz}, \mathrm{CDCl_3}): \ \delta \ 3.70-3.64 \ (\mathrm{m}, \ 2\mathrm{H}), \ 1.63-1.56 \ (\mathrm{m}, \ 2\mathrm{H}), \ 1.27-1.25 \\ & (\mathrm{m}, \ 17\mathrm{H}), \ 0.90-0.85 \ (\mathrm{m}, \ 6\mathrm{H}). \ \ ^{13}\mathrm{C} \ \mathrm{NMR} \ (75 \ \mathrm{MHz}, \mathrm{CDCl_3}): \ \delta \ 61.3, \ 40.1, \ 37.2, \ 31.9, \ 29.9, \ 29.7, \ 29.6, \\ & 29.5, \ 29.3, \ 27.0, \ 22.7, \ 19.6, \ 14.0. \end{array}$ 

<sup>&</sup>lt;sup>7</sup> T. Suzuki, J. Ozaki, R Sugawara, Agric. Biol. Chem. 1983, 47, 869.

<sup>&</sup>lt;sup>8</sup> K. Mori and J. Wu, Annal. der Chem., 1991, **5**, 439-43.

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# Spectra of compounds 7a-7i and 9b-9g.













































#### HPLC chromatograms of compounds 7a-7i.



Figure S-1. Racemic and Optically enriched HPLC Chromatogram of compound 7a.



Figure S-2. Racemic and Optically enriched HPLC Chromatogram of compound 7b.



Figure S-3. Racemic and Optically enriched HPLC Chromatogram of compound ent-7b.



Figure S-4. Racemic and Optically enriched HPLC Chromatogram of compound 7c.



Figure S-5. Racemic and Optically enriched HPLC Chromatogram of compound 7d.



Figure S-6. Optically enriched HPLC Chromatogram of compound 7e and 7g.



Figure S-7. Racemic and Optically enriched HPLC Chromatogram of compound 7f.



Figure S-8. Racemic and Optically enriched HPLC Chromatogram of compound 7h.



Figure S-9. Racemic and Optically enriched HPLC Chromatogram of compound 7i.