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Preparation of single-enantiomer semiochemicals using 2-methoxy-2-(1-naphthyl)propionic acid and 2-methoxy-2-(9-phenanthryl)propionic acid

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Abstract—Enantioresolution of 3-octanol, 6-methyl-5-hepten-2-ol (sulcatol), and 1-octen-3-ol was conducted using (*S*)-(+)-2-methoxy-2-(1-naphthyl)propionic acid (MαNP acid) and (*S*)-(+)-2-methoxy-2-(9-phenanthryl)propionic acid (M9PP acid). In each case, the diastereomeric esters obtained were readily separated by HPLC. The stereochemistry of the esters could be assigned from their respective ^{1}H NMR analyses. Solvolyses of the esters gave enantiopure alcohols and acids. MαNP and M9PP acids displayed almost equivalent properties in ^{1}H NMR anisotropy. The chiral resolving ability of M9PP acid was slightly superior to that of MαNP acid in HPLC.

1. Introduction

Semiochemicals are compounds involved in the chemical interactions between organisms. A semiochemical that conveys information between the same species is known as a pheromone. Various relationships have been reported between the chirality of insect pheromones and their biological activity.[1,2] Therefore, enantiopure compounds are necessary for evaluating the biological activity of each enantiomer. Enantiopurity is particularly important in pharmaceuticals, because the presence of a minor enantiomer impurity could cause undesirable effects.

Dale and Mosher reported various ^{1}H NMR shift reagents.[3] Of these, MTPA **1** and MPA **2** have been used most widely to determine the absolute configurations of secondary alcohols and primary amines (Fig. 1).[4–6] In the case of MPA **2**, Trost et al. reported a slight loss of enantiopurity during the base hydrolysis of its ester derivative.[4] To increase the ^{1}H NMR anisotropy of MPA **2**, Kusumi and Riguera added large aryl groups; that is, 2-methoxy-2-(2-naphthyl)acetic acid **3** (2NMA).[7–9]

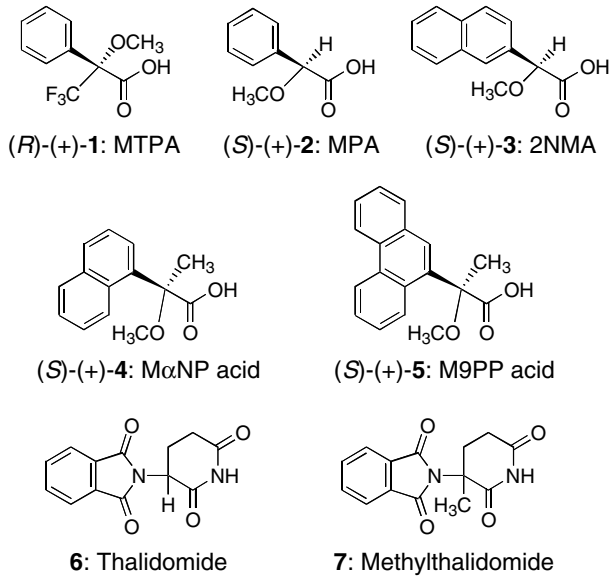

Figure 1. The structures of chiral resolving agents **1**–**5**, thalidomide **6**, and methylthalidomide **7**.[10,11]

Hashimoto et al. determined the rate of racemization of single-enantiomer thalidomide **6** under physiological conditions.[10,11] They also prepared both enantiomers of methylthalidomide **7**, a nonracemizable thalidomide

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analogue, and found that only (*S*)-**7** caused an increase in tumor necrosis factor (TNF)-α production. This prompted us to develop 2-methoxy-2-(aryl)propionic acids as nonracemizable chiral resolving agents.

MαNP acid **4** and M9PP acid **5** are useful for preparing enantiopure alcohols, because of their susceptibility to chiral separation and the advantage of not racemizing during condensation reactions and HPLC separation.[12–22] Acids **4** and **5** are also useful for determining the absolute configuration of secondary alcohols using the ^{1}H NMR anisotropy method.

Considering the crystalline structure of (1*R*,2*S*,5*R*)-menthol M9PP ester,[21] we proposed the conformational model[22] shown in Figure 2: (1) the methoxyl and carbonyl oxygen atoms are *syn*-periplanar to each other; (2) the alcohol methine proton is also *syn*-periplanar to the ester carbonyl oxygen atom; (3) the methyl group is *syn*-periplanar to H-2 in the MαNP ester or H-10 in the M9PP ester.

Recently, Seco et al. proposed a new conformational model for MTPA esters;[9] three conformations of similar populations are present for both (*R*)- and (*S*)-MTPA esters, resulting in smaller $\Delta\delta$ values. By contrast, the MαNP and M9PP esters show large $\Delta\delta$ values in ^{1}H NMR and large separation factors in HPLC.

M9PP acid (*S*)-(+)-**5** has been used for the enantioresolution of 3-octanol (±)-**8** and sulcatol (±)-**9** (Fig. 3).[21,22] Application examples are still necessary in order to develop 2-methoxy-2-(aryl)propionic acids as chiral resolving agents. Here, we report the enantioresolution of three semiochemicals (3-octanol **8**, sulcatol **9**, and 1-octen-3-ol **10**) (Fig. 3) using MαNP acid (*S*)-(+)-**4**. The results were compared to those obtained with M9PP acid (*S*)-(+)-**5** in terms of their HPLC separation and ^{1}H NMR anisotropy. We also investigated the stability of the MαNP and M9PP moieties toward catalytic hydrogenation.

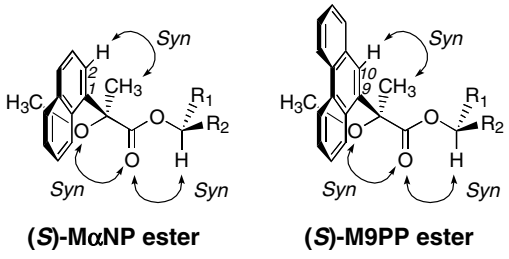


Figure 2. The preferred conformations of (*S*)-MαNP and (*S*)-M9PP esters.

2. Results and discussion

Compounds **8**–**10** are mono-alcohols possessing C8-carbon skeletons (Fig. 3); the simple structures of alcohols **8**–**10** are useful for developing the novel chiral resolving agents.

The enantioresolution of 3-octanol (±)-**8** was conducted using MαNP acid (*S*)-(+)-**4**. Both enantiomers of **8** are ant pheromones. Fujiwhara and Mori synthesized (*R*)-(−)- and (*S*)-(+)-3-octanol from methyl (*R*)-3-hydroxypentanoate and its (*S*)-isomer, respectively.[24] 3-Octanol (±)-**8** was esterified with MαNP acid (*S*)-(+)-**4** using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and 4-dimethylaminopyridine (DMAP) in CH_2Cl_2. The crude products were purified using normal phase HPLC to afford the two diastereomeric esters (−)-**11a** and (+)-**11b** in 41% and 43% yields, respectively. As shown in Figure 4, the separation factor (α value) for esters (−)-**11a** and (+)-**11b** was 1.45 with the Silica SG80 column.

Figure 5 shows the ^{1}H NMR chemical shifts of esters (−)-**11a** and (+)-**11b**, and the $\Delta\delta$ {= δ[(+)-**11b**] − δ[(−)-**11a**]} values in $CDCl_3$. The ^{1}H NMR signals of esters (−)-**11a** and (+)-**11b** were assigned from DQF COSY, PS NOESY, and HMBC spectra (600 or 800 MHz, $CDCl_3$). The positive $\Delta\delta$ values were observed for the protons at the 1- and 2-positions of the alcohol moiety (+0.56 and +0.2, respectively). Conversely, negative $\Delta\delta$ values were observed for the protons at the 4- to 8-positions. Based on the conformational hypotheses shown in Figure 2, the stereochemistry was represented as (*S*,*R*)-(−)-**11a** and (*S*,*S*)-(+)-**11b**. (See lit.[17] for the definition of $\Delta\delta$ and the assignment of stereochemistry.) The zigzag conformation of the alcohol moiety explained the largest $\Delta\delta$ values at the γ-position.[7]

As shown in Scheme 1, the solvolysis of the first-eluted ester (*S*,*R*)-(−)-**11a** gave 3-octanol (*R*)-(−)-**8** {63%, $[\alpha]_D^{30} = -8$ (*c* 0.16, $CHCl_3$), lit.[24]: $[\alpha]_D^{22} = -9.7$ (*c* 0.93,

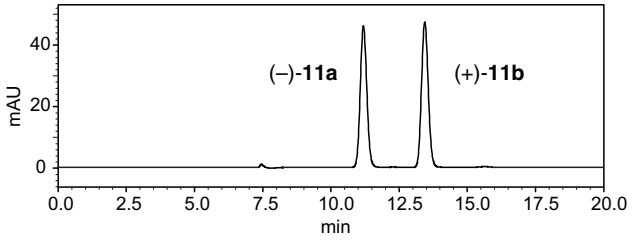


Figure 4. The HPLC separation of diastereomeric esters formed from 3-octanol (±)-**8** and MαNP acid (*S*)-(+)-**4** (Silica SG80, hexane–EtOAc 9:1, UV 300 nm, $\alpha = 1.45$, T_0: 1,3,5-tri-*tert*-butylbenzene).

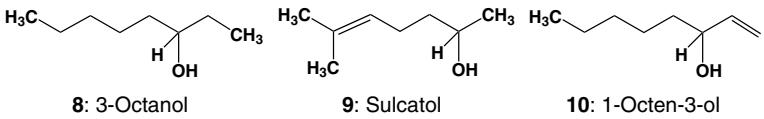


Figure 3. The structures of 3-octanol **8**, sulcatol **9**, and 1-octen-3-ol **10**.

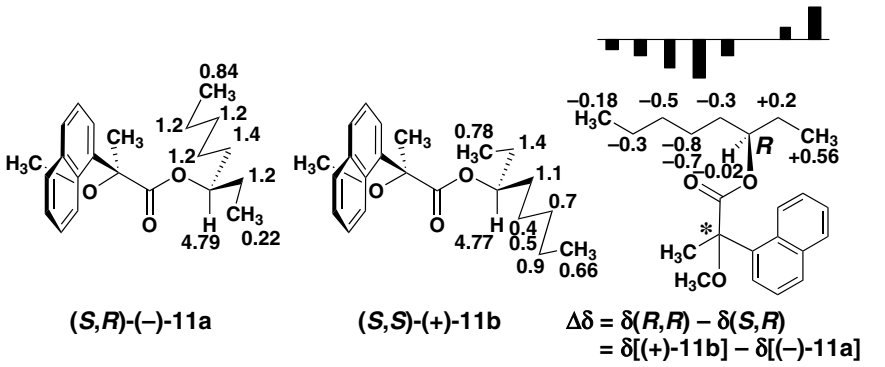
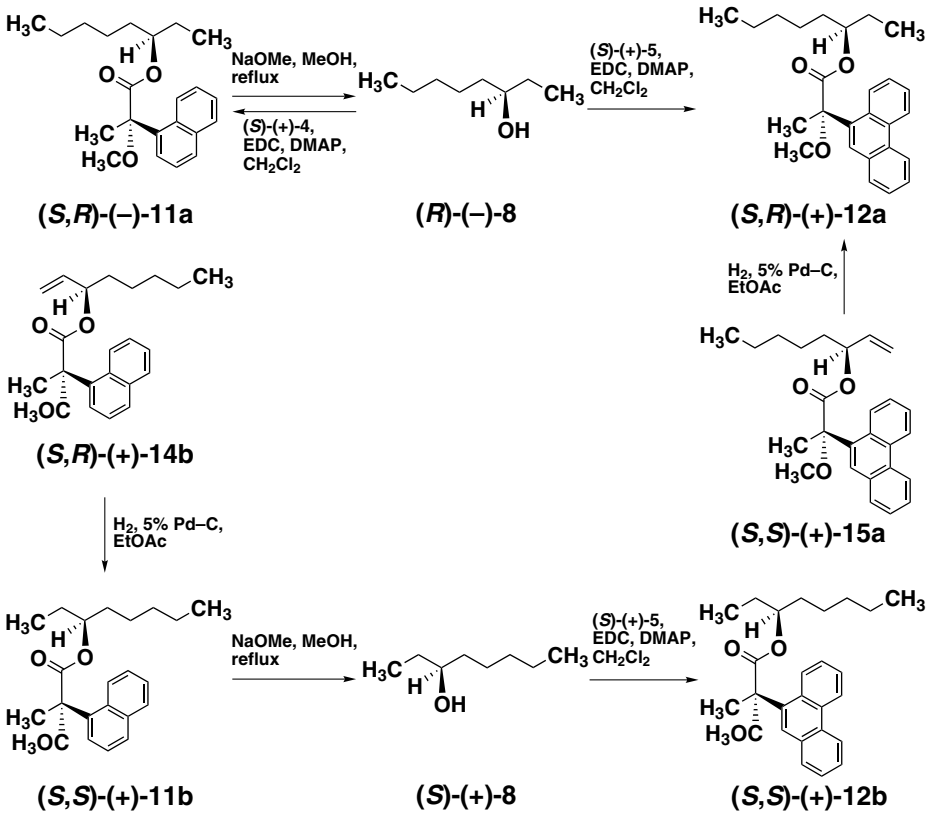


Figure 5. The ^{1}H NMR chemical shift data and $\Delta\delta$ values for esters (−)-**11a** and (+)-**11b** (600 MHz, $CDCl_3$). The black bars show the relative intensity of the $\Delta\delta$ values.



Scheme 1. Preparation of single enantiomer 3-octanol, M9PP esters (+)-**12a**, and (+)-**12b**.

$CHCl_3$)}. 3-Octanol (*R*)-(−)-**8** was esterified with acids (*S*)-(+)-**4** and (*S*)-(+)-**5** to give enantiopure (*S*,*R*)-(−)-**11a** and (*S*,*R*)-(+)-**12a**,[21] respectively. Notably, the retention of the stereochemistry after the solvolysis was confirmed. The solvolysis of the second-eluted ester (*S*,*S*)-(+)-**11b** gave 3-octanol (*S*)-(+)-**8** {54%, $[\alpha]_D^{37} = +10$ (*c* 0.14, $CHCl_3$), lit.[24]: $[\alpha]_D^{22} = +10.1$ (*c* 0.82, $CHCl_3$)}. 3-Octanol (*S*)-(+)-**8** was esterified with M9PP acid (*S*)-(+)-**5** giving ester (*S*,*S*)-(+)-**12b**.[21]

We have already reported the enantioresolution of 3-octanol (±)-**8** using M9PP acid (*S*)-(+)-**5**.[21] In the case of 3-octanol (±)-**8**, acids (*S*)-(+)-**4** and (*S*)-(+)-**5** revealed nearly equivalent chiral resolving abilities in HPLC (Table 1, $\alpha = 1.45$ and 1.47, respectively) and ^{1}H NMR anisotropy. [See lit.[21] for the $\Delta\delta$ values of M9PP esters (*S*,*R*)-(+)-**12a** and (*S*,*S*)-(+)-**12b**.]

6-Methyl-5-hepten-2-ol **9** (sulcatol) is known as the aggregation pheromone of the ambrosia beetle, *Gnathotrichus sulcatus*.[25,26] Sulcatol (±)-**9** was esterified with MαNP acid (*S*)-(+)-**4** using EDC and DMAP in CH_2Cl_2. The crude products were purified by preparative HPLC using the prepacked glass column, affording esters (−)-**13a** and (+)-**13b** in 43% and 37% yields, respectively. The separation factor (α value) for esters (−)-**13a** and (+)-**13b** was 1.31 with the Silica SG80 column (Fig. 6).

Table 1. Separation factors for MαNP and M9PP esters

	3-Octanol (±)-**8**	Sulcatol (±)-**9**	1-Octen-3-ol (±)-**10**
MαNP acid (*S*)-(+)-**4**	$\alpha = 1.45$	1.31	1.47
M9PP acid (*S*)-(+)-**5**	$\alpha = 1.47$	1.37	1.52

Silica SG80, hexane/EtOAc, UV 300 nm, $\alpha = (T_2 - T_0)/(T_1 - T_0)$, T_0: 1,3,5-tri-*tert*-butylbenzene.

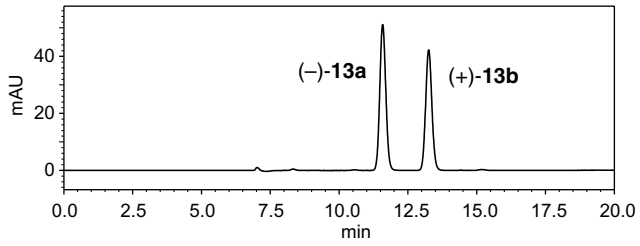


Figure 6. The HPLC separation of diastereomeric esters formed from sulcatol (±)-**9** and MαNP acid (*S*)-(+)-**4** (Silica SG80, hexane–EtOAc 9:1, UV 300 nm, $\alpha = 1.31$, T_0: 1,3,5-tri-*tert*-butylbenzene).

The ^{1}H NMR signals of esters (−)-**13a** and (+)-**13b** were assigned from DQF COSY and PS NOESY spectra (800 MHz, $CDCl_3$). The chemical shift and the $\Delta\delta$ {$= \delta$[(+)−**13b**] − δ[(−)-**13a**]} values are shown in Figure 7. A positive $\Delta\delta$ value was observed for the terminal methyl protons (+0.27), and the negative $\Delta\delta$ values were observed for the protons of the rest of alcohol moiety (Fig. 7). Therefore, the stereochemistry was assigned as (*S*,*R*)-(−)-**13a** and (*S*,*S*)-(+)-**13b**.[17]

The solvolysis of first-eluted ester (*S*,*R*)-(−)-**13a** gave sulcatol (*R*)-(−)-**9** {69%, $[\alpha]_D^{26} = -13$ (*c* 0.19, EtOH), lit.[26]: $[\alpha]_D^{23} = -14.5$ (*c* 0.74, EtOH)}, together with enantiopure MαNP acid (*S*)-(+)-**4** (87%). Sulcatol (*R*)-(−)-**9** was esterified with the recovered MαNP acid (*S*)-(+)-**4** using EDC and DMAP in CH_2Cl_2 yielding ester (*S*,*R*)-(−)-**13a** only, in 79% yield (Scheme 2). The solvolysis of the second-eluted ester (*S*,*S*)-(+)-**13b** gave sulcatol (*S*)-(+)-**9** {93%, $[\alpha]_D^{27} = +15$ (*c* 0.21, EtOH), lit.[26]: $[\alpha]_D^{23} = +14.4$ (*c* 0.998, EtOH)} and MαNP acid (*S*)-(+)-**4** (91%). Sulcatol (*S*)-(+)-**9** was esterified with the recovered MαNP acid (*S*)-(+)-**4** using EDC and DMAP in CH_2Cl_2 yielding ester (*S*,*S*)-(+)-**13b** only (85%).

The separation factor for sulcatol MαNP esters (*S*,*R*)-(−)-**13a** and (*S*,*S*)-(+)-**13b** was 1.31, while that of M9PP esters[22] was 1.37 (Table 1). In the case of sulcatol (±)-**9**, the observed $\Delta\delta$ values of MαNP esters were nearly equal to those of M9PP esters. (See lit.[22] for the NMR data of sulcatol M9PP esters.)

1-Octen-3-ol **10** has been isolated from many natural sources:[27–30] 1-Octen-3-ol **10** was isolated from cattle odors as a potent olfactory stimulant and attractant for tsetse flies.[27] 1-Octen-3-ol **10** was also reported as an attractive semiochemical for the foreign grain beetle, *Ahasverus advena*[29] and the African malaria mosquito, *Anopheles gambiae*.[30] The absolute configuration of 1-octen-3-ol (−)-**10** was determined as *R* by empirical NMR studies.[28] 1-Octen-3-ol (±)-**10** was condensed with MαNP acid (*S*)-(+)-**4** using EDC and DMAP in CH_2Cl_2 to give esters (−)-**14a** and (+)-**14b** in 40% and 43% yields, respectively. The separation factor for esters (−)-**14a** and (+)-**14b** was 1.47 with the Silica SG80 column (Fig. 8).

The ^{1}H NMR signals of esters (−)-**14a** and (+)-**14b** were assigned from DQF COSY spectra (500 MHz, $CDCl_3$). The $\Delta\delta$ {$=\delta$[(+)−**14b**] − δ[(−)-**14a**]} values were presented in Figure 9, from which the stereochemistry was assigned as (*S*,*S*)-(−)-**14a** and (*S*,*R*)-(+)-**14b**.[17]

The solvolysis of the first-eluted ester (*S*,*S*)-(−)-**14a** yielded enantiopure 1-octen-3-ol (*S*)-(+)-**10** {77%, $[\alpha]_D^{26} = +19$ (*c* 0.18, EtOH), lit.[28]: $[\alpha]_D^{20} = +20.6$ (*c* 5.3, EtOH)}, together with MαNP acid (*S*)-(+)-**4** (95%). 1-Octen-3-ol (*S*)-(+)-**10** was condensed with recovered (*S*)-(+)-**4** using EDC and DMAP in CH_2Cl_2 giving (*S*,*S*)-(−)-**14a** only (Scheme 3). The catalytic hydrogenation of (*S*,*R*)-(+)-**14b** gave (*S*,*S*)-(+)-**11b** only, in 89% yield (Scheme 1); therefore, the empirical NMR study of 1-octen-3-ol **10** was linked to the asymmetric synthesis of 3-octanol **8**.[24,28]

Finally, the enantioresolution of 1-octen-3-ol (±)-**10** was attempted using M9PP acid (*S*)-(+)-**5**. 1-Octen-3-ol (±)-**10** was esterified with (*S*)-(+)-**5** using 1,3-dicyclohexyl-

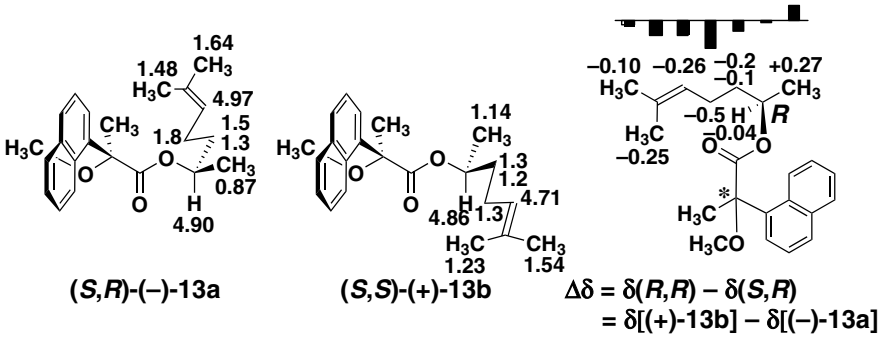
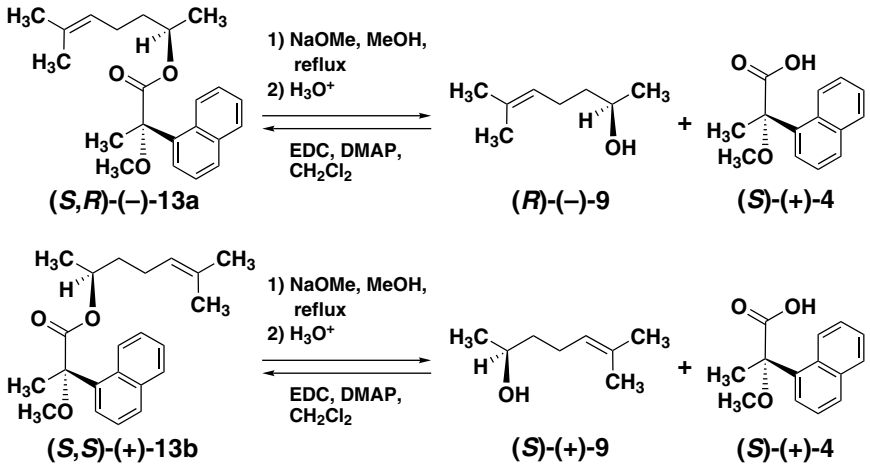


Figure 7. The ^{1}H NMR chemical shift data and $\Delta\delta$ values for esters (−)-**13a** and (+)-**13b** (800 MHz, $CDCl_3$). The black bars show the relative intensity of the $\Delta\delta$ values.



Scheme 2. Preparation of the single-enantiomer sulcatol and the reformations of MαNP esters (−)-**13a** and (+)-**13b**.

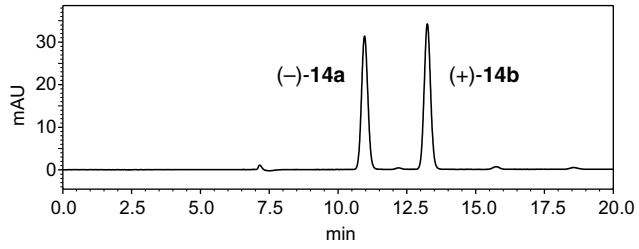


Figure 8. The HPLC separation of diastereomeric esters formed from 1-octen-3-ol (±)-**10** and MαNP acid (*S*)-(+)-**4** (Silica SG80, hexane–EtOAc 92:8, UV 300 nm, $\alpha = 1.47$, T_0: 1,3,5-tri-*tert*-butylbenzene).

carbodiimide (DCC), DMAP, and (+)-10-camphorsulfonic acid (CSA) in CH_2Cl_2 affording esters (+)-**15a** and (+)-**15b** in 37% and 43% yields, respectively. The separation factor for esters (+)-**15a** and (+)-**15b** was 1.52 with the Silica SG80 column (Fig. 10).

The ^{1}H NMR signals of esters (+)-**15a** and (+)-**15b** were assigned from DQF COSY and HSQC spectra (800 MHz, $CDCl_3$). The stereochemistry was assigned as (*S*,*S*)-(+)-**15a** and (*S*,*R*)-(+)-**15b** from the $\Delta\delta$ {$= \delta$[(+)-**15b**] − δ[(+)-**15a**]} values (Fig. 11).[17]

The solvolysis of the first fraction (*S*,*S*)-(+)-**15a** yielded 1-octen-3-ol (*S*)-(+)-**10** {80%, $[\alpha]_D^{26} = +19$ (*c* 0.21, EtOH)} and M9PP acid (*S*)-(+)-**5** (82%). 1-Octen-3-ol (*S*)-(+)-**10** was condensed with (*S*)-(+)-**5** using DCC, DMAP, and CSA in CH_2Cl_2 giving ester (*S*,*S*)-(+)-**15a** (Scheme 4). The catalytic hydrogenation of (*S*,*S*)-(+)-**15a** gave ester (*S*,*R*)-(+)-**12a**[21] in 70% yield (Scheme 1).

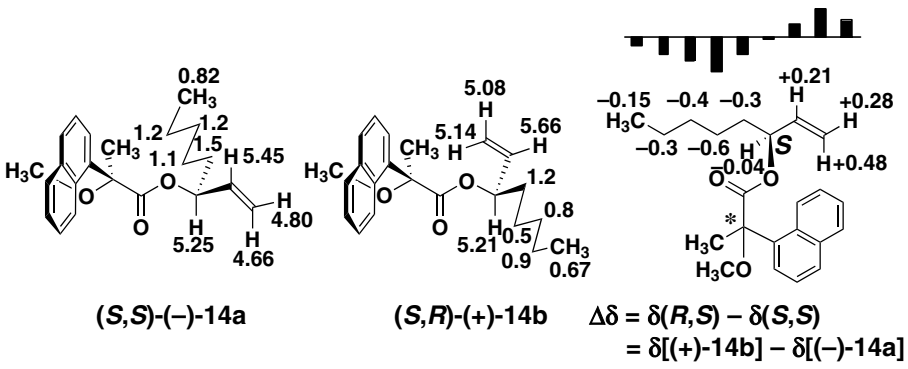
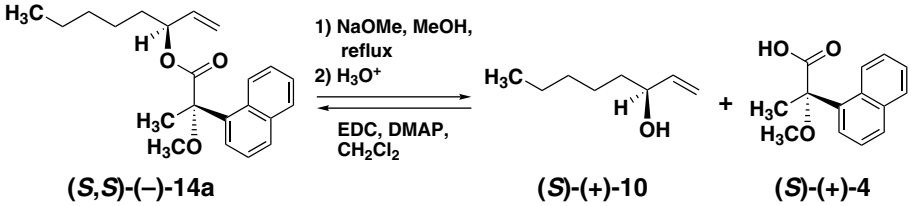


Figure 9. The ^{1}H NMR chemical shift data and $\Delta\delta$ values for esters (−)-**14a** and (+)-**14b** (500 MHz, $CDCl_3$). The black bars show the relative intensity of the $\Delta\delta$ values.



Scheme 3. Preparation of the single-enantiomer 1-octen-3-ol and reformation of MαNP ester (−)-**14a**.

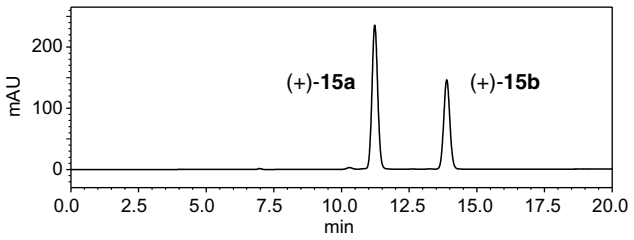


Figure 10. The HPLC separation of diastereomeric esters formed from 1-octen-3-ol (±)-**10** and M9PP acid (*S*)-(+)-**5** (Silica SG80, hexane–EtOAc 9:1, UV 300 nm, $\alpha = 1.52$, T_0: 1,3,5-tri-*tert*-butylbenzene). Only in the case of 1-octen-3-ol M9PP esters, were the separated diastereomers mixed again, and analyzed by HPLC.

The solvolysis of the second fraction (*S*,*R*)-(+)-**15b** yielded 1-octen-3-ol (*R*)-(−)-**10** {82%, $[\alpha]_D^{27} = -19$ (*c* 0.23, EtOH), lit.[28]: $[\alpha]_D^{20} = -20.2$ (*c* 7.3, EtOH)}, and M9PP acid (*S*)-(+)-**5** (49%). 1-Octen-3-ol (*R*)-(−)-**10** was esterified with M9PP acid (*S*)-(+)-**5** yielding ester (*S*,*R*)-(+)-**15b** (76%).

The separation factor for 1-octen-3-ol MαNP esters (*S*,*S*)-(−)-**14a** and (*S*,*R*)-(+)-**14b** was 1.47, while that of M9PP esters (*S*,*S*)-(+)-**15a** and (*S*,*R*)-(+)-**15b** was 1.52 (Table 1). In the case of 1-octen-3-ol (±)-**10**, MαNP esters and M9PP esters had similar $\Delta\delta$ values on ^{1}H NMR (Figs. 9 and 11).

The MαNP and M9PP moieties caused similar ^{1}H NMR anisotropy in the alcohol part of the esters. The conformational models shown in Figures 2 and 5 could explain these results: The two benzene rings that exist in both acids are important for the recognition of the alcohol chirality. A similar conformational model has been proposed for the 2NMA ester.[9] The chiral resolving ability of M9PP acid (*S*)-(+)-**5** was slightly superior to that of MαNP acid (*S*)-(+)-**4** in HPLC (Table 1).

3. Conclusion

MαNP and M9PP acids are recyclable and effective for HPLC separation and ^{1}H NMR anisotropy: (1) both the acids could resolve the alcohol enantiomers via esterification; (2) successive NMR analyses assigned the stereochemistry of MαNP and M9PP esters; and (3) solvolysis of the esters yielded enantiopure alcohols and acids. The method using the MαNP and M9PP acids was applicable to 1-octen-3-ol, an allylic alcohol. The MαNP and M9PP moieties were stable against catalytic hydrogenation. Clearly, enantioresolution using

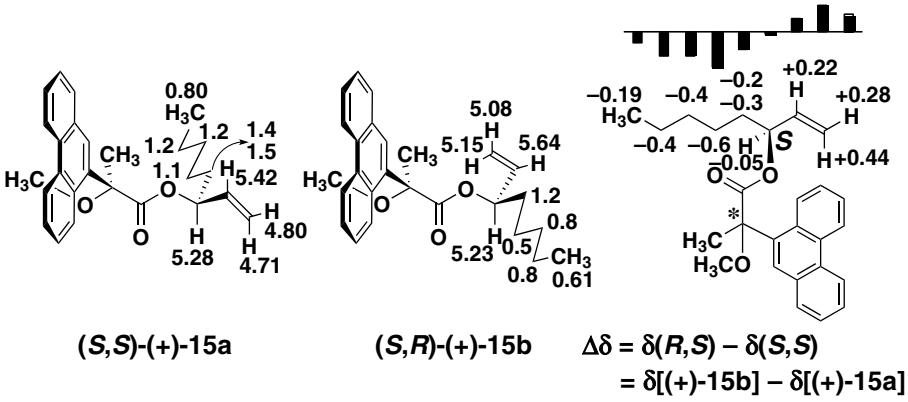
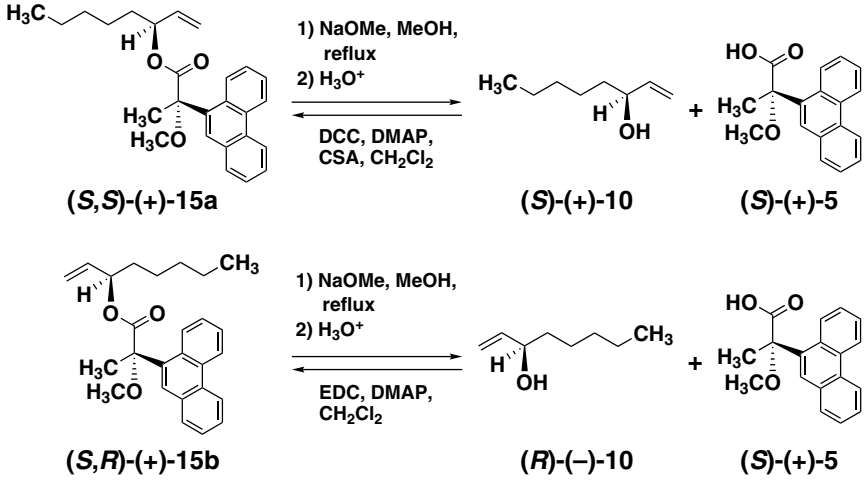


Figure 11. The ^{1}H NMR chemical shift data and $\Delta\delta$ values for esters (+)-**15a** and (+)-**15b** (800 MHz, $CDCl_3$). The black bars show the relative intensity of the $\Delta\delta$ values.



Scheme 4. Preparation of single-enantiomer 1-octen-3-ol and re-formation of M9PP esters (+)-**15a** and (+)-**15b**.

MαNP and M9PP acids is useful for the small-scale synthesis of natural products and the preparation of single enantiomer agrochemicals and pharmaceuticals.

4. Experimental

4.1. General

The NMR spectra were obtained using a Bruker (Rheinstetten, Germany) Avance800, a Bruker DRX600, or a Bruker Avance500 in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. The IR spectra were recorded as thin films (neat) mounted on KBr plates with a Perkin–Elmer (Norwalk, CT) 1760X or a Shimadzu (Kyoto, Japan) FTIR-8200. The MS data were obtained with an Agilent (Palo Alto, CA) 1100 LC/MSD system. The optical rotations were determined on a JASCO (Tokyo, Japan) DIP1000 spectropolarimeter. Wakogel C-200 (Wako Pure Chemical Industries, Osaka, Japan) was used for the open column chromatography. HPLC was performed using the Shimadzu LC10AT VP systems equipped with: (1) diode array detector–refractive index detector, (2) UV–vis detector. The CIG prepacked silica gel and ODS columns (Kusano Scientific Instrument, Tokyo, Japan) were used for preparative HPLC. A Silica SG80 column (4.6 mm∅ × 250 mm, Shiseido, Tokyo, Japan) was used for analytical HPLC.

4.2. Enantioresolution of (±)-3-octanol using MαNP acid

A mixture of MαNP acid (*S*)-(+)-**4** (49 mg), EDC (81 mg), DMAP (109 mg), and 3-octanol (±)-**8** (120 μL) in CH_2Cl_2 (0.75 mL) was allowed to stand for 16 h. The mixture was chromatographed over silica gel with CH_2Cl_2. The diastereomeric esters obtained were separated by HPLC on silica gel (hexane–EtOAc 47:3), giving the first eluted ester (*S*,*R*)-(−)-**11a** (30 mg, 41%) and the second eluted ester (*S*,*S*)-(+)-**11b** (31 mg, 43%).

4.2.1. 3-Octanol MαNP ester (*S*,*R*)-(−)-11a. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 (1H, m), 7.83 (1H, m), 7.82 (1H, m), 7.61 (1H, dd, J = 7, 1 Hz), 7.48–7.43 (3H, m), 4.79 (1H, m), 3.11 (3H, s), 2.00 (3H, s), 1.4 (2H, m), 1.2 (8H, m), 0.84 (3H, t, J = 7 Hz), 0.22 (3H, t, J = 7.5 Hz); ^{13}C NMR (151 MHz): δ 173.89, 135.37, 134.02, 131.45, 129.29, 128.56, 126.32, 125.64, 125.62, 125.42, 124.62, 81.57, 76.57, 50.87, 33.10, 31.60, 26.32, 24.81, 22.49, 21.74, 13.97, 8.52; IR (KBr, neat): ν_{max} 2934, 2860, 1746, 1727, 1254, 1139, 1114, 806, 780 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 24:1): *m*/*z* 365 ([M+Na]$^+$, 100), 311 (2), 199 (11); $[\alpha]_D^{31} = -12$ (*c* 0.68, EtOH).

4.2.2. 3-Octanol MαNP ester (*S*,*S*)-(+)-11b. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.48 (1H, m), 7.83 (1H, m), 7.81 (1H, br d, J = 8 Hz), 7.60 (1H, dd, J = 7, 1 Hz), 7.48–7.43 (3H, m), 4.77 (1H, sept, J = 6 Hz), 3.09 (3H, s), 2.00 (3H, s), 1.4 (2H, m), 1.1 (2H, m), 0.9 (2H, m), 0.78 (3H, t, J = 7.5 Hz), 0.7 (2H, m), 0.66 (3H, t, J = 7 Hz), 0.5 (1H, m), 0.4 (1H, m); ^{13}C NMR (151 MHz): δ 173.88, 135.20, 134.04, 131.53, 129.33, 128.55, 126.38, 125.72, 125.68, 125.48, 124.59, 81.50, 76.46, 50.80, 32.91, 31.33, 26.58, 23.83, 22.22, 21.68, 13.89, 9.54; IR (KBr, neat): ν_{max} 2934, 2860, 1746, 1252, 1139, 1114, 806, 780 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 24:1): *m*/*z* 365 ([M+Na]$^+$, 100), 311 (2), 199 (10); $[\alpha]_D^{33} = +15$ (*c* 0.72, EtOH).

4.2.3. 3-Octanol (*R*)-(−)-8. A mixture of ester (*S*,*R*)-(−)-**11a** (67 mg) and 28% NaOMe/MeOH (1.5 mL) was refluxed for 7 h under argon. The solution was diluted with ice water, and extracted with CH_2Cl_2 twice. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed over silica gel with CH_2Cl_2 to give 3-octanol (*R*)-(−)-**8** (16 mg, 63%): $[\alpha]_D^{30} = -8$ (*c* 0.16, $CHCl_3$).

4.2.4. 3-Octanol (*S*)-(+)-8. Ester (*S*,*S*)-(+)-**11b** (68 mg) was similarly hydrolyzed with 28% NaOMe/MeOH (1.5 mL) yielding 3-octanol (*S*)-(+)-**8** (14 mg, 54%): $[\alpha]_D^{37} = +10$ (*c* 0.14, $CHCl_3$).

4.2.5. Preparation of MαNP ester (*S*,*R*)-(−)-11a from (*R*)-(−)-3-octanol. 3-Octanol (*R*)-(−)-**8** (8 mg) prepared above was esterified with MαNP acid (*S*)-(+)-**4** (21 mg) using EDC (40 mg) and DMAP (55 mg) in CH_2Cl_2 (0.5 mg). The crude product was chromatographed over silica gel giving ester (*S*,*R*)-(−)-**11a** (10 mg, 48%), which was identical with the authentic sample.

4.2.6. Preparation of M9PP ester (*S*,*R*)-(+)-12a from (*R*)-(−)-3-octanol. 3-Octanol (*R*)-(−)-**8** (8 mg) prepared above was similarly esterified with M9PP acid (*S*)-(+)-**5** (11 mg) yielding ester (*S*,*R*)-(+)-**12a** (13 mg, 84%), which was identical with the authentic sample.[21]

4.2.7. Preparation of M9PP ester (*S*,*S*)-(+)-12b from (*S*)-(+)-3-octanol. 3-Octanol (*S*)-(+)-**8** (7 mg) prepared above was similarly esterified with M9PP acid (*S*)-(+)-**5** (10 mg) yielding ester (*S*,*S*)-(+)-**12b** (12 mg, 86%), which was identical with the authentic sample.[21]

4.3. Enantioresolution of (±)-sulcatol using MαNP acid

A mixture of MαNP acid (*S*)-(+)-**4** (50 mg), EDC (77 mg), DMAP (103 mg), and sulcatol (±)-**9** (95 μL) in CH_2Cl_2 (0.5 mL) was allowed to stand for 16 h. The crude products were chromatographed over silica gel with CH_2Cl_2. The diastereomeric esters obtained were separated by HPLC on silica gel (hexane–EtOAc 9:1) giving the first eluted ester (*S*,*R*)-(−)-**13a** (32 mg, 43%) and the second eluted ester (*S*,*S*)-(+)-**13b** (27 mg, 37%).

4.3.1. Sulcatol MαNP ester (*S*,*R*)-(−)-13a. ^{1}H NMR (800 MHz, $CDCl_3$): δ 8.40 (1H, m), 7.84 (1H, m), 7.82 (1H, dt, J = 8, 1 Hz), 7.61 (1H, dd, J = 7, 1 Hz), 7.46 (2H, m), 7.45 (1H, m), 4.97 (1H, m), 4.90 (1H, m), 3.11 (3H, s), 1.99 (3H, s), 1.8 (2H, m), 1.64 (3H, br d, J = 1 Hz), 1.48 (3H, br s), 1.5 (1H, m), 1.3 (1H, m), 0.87 (3H, d, J = 6 Hz); ^{13}C NMR (126 MHz): δ 173.77, 135.39, 134.03, 132.06, 131.26, 129.30, 128.63, 126.27, 125.62, 125.51, 125.23, 124.65, 123.34, 81.55,

71.94, 50.96, 35.67, 25.65, 23.85, 21.79, 19.36, 17.56; IR (KBr, neat): ν_{max} 2974, 2932, 1744, 1727, 1251, 1132, 1123, 1065, 806, 780 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 19:1): *m/z* 363 ($[M+Na]^+$, 100), 309 (4), 199 (31); $[\alpha]_D^{25} = -37$ (*c* 0.54, EtOH).

4.3.2. Sulcatol MαNP ester (*S*,*S*)-(+)-13b. ^1H NMR (800 MHz, $CDCl_3$): δ 8.44 (1H, br d, $J = 8$ Hz), 7.82 (1H, m), 7.81 (1H, br d, $J = 8$ Hz), 7.59 (1H, dd, $J = 7$, 1 Hz), 7.47 (1H, m), 7.45 (1H, m), 7.44 (1H, m), 4.86 (1H, m), 4.71 (1H, br t, $J = 7$ Hz), 3.09 (3H, m), 1.98 (3H, br s), 1.54 (3H, br d, $J = 1$ Hz), 1.3 (3H, m), 1.23 (3H, br s), 1.2 (1H, m), 1.14 (3H d, $J = 6$ Hz); ^{13}C NMR (126 MHz): δ 173.79, 135.14, 134.05, 131.71, 131.44, 129.40, 128.62, 126.39, 125.70, 125.68, 125.35, 124.58, 123.22, 81.45, 71.92, 50.86, 35.61, 25.54, 23.22, 21.68, 19.71, 17.35; IR (KBr, neat): ν_{max} 2973, 2932, 1743, 1734, 1250, 1133, 1122, 1066, 806, 780 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 19:1): *m/z* 363 ($[M+Na]^+$, 100), 309 (2), 199 (8); $[\alpha]_D^{27} = +52$ (*c* 0.46, EtOH).

4.3.3. Sulcatol (*R*)-(−)-9. A mixture of ester (*S*,*R*)-(−)-**13a** (73 mg) and 28% NaOMe/MeOH (1.5 mL) was refluxed for 6 h under argon. The solution was diluted with ice water, and extracted with CH_2Cl_2 three times. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was chromatographed over silica gel with CH_2Cl_2 to give sulcatol (*R*)-(−)-**9** (19 mg, 69%): $[\alpha]_D^{26} = -13$ (*c* 0.19, EtOH). The aqueous layer was acidified with 2 M HCl and extracted with CH_2Cl_2 three times. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo giving MαNP acid (*S*)-(+)-**4** (43 mg, 87%). The chiral HPLC analysis (Chiralcel OD-RH, CH_3CN–H_2O 13:7) of the (*S*)-MαNP acid methyl ester (prepared using 2 M trimethylsilyldiazomethane[23] ether solution) revealed that (*S*)-(+)-**4** recovered was enantiopure.

4.3.4. Sulcatol (*S*)-(+)-9. Ester (*S*,*S*)-(+)-**13b** (60 mg) was similarly hydrolyzed with 28% NaOMe/MeOH (1.5 mL) yielding sulcatol (*S*)-(+)-**9** (21 mg, 93%): $[\alpha]_D^{27} = +15$ (*c* 0.21, EtOH), and enantiopure MαNP acid (*S*)-(+)-**4** (37 mg, 91%).

4.3.5. Preparation of MαNP ester (*S*,*R*)-(−)-13a from (*R*)-(−)-sulcatol. Sulcatol (*R*)-(−)-**9** (10 mg) was similarly converted to MαNP ester (*S*,*R*)-(−)-**13a** (21 mg, 79%), which was identical with the authentic sample described above.

4.3.6. Preparation of MαNP ester (*S*,*S*)-(+)-13b from (*S*)-(+)-sulcatol. Sulcatol (*S*)-(+)-**9** (8 mg) was similarly converted to MαNP ester (*S*,*S*)-(+)-**13b** (18 mg, 85%), which was identical with the authentic sample described above.

4.4. Enantioresolution of (±)-1-octen-3-ol using MαNP acid

A mixture of MαNP acid (*S*)-(+)-**4** (39 mg), EDC (103 mg), DMAP (130 mg), and 1-octen-3-ol (±)-**10** (120 μL) in CH_2Cl_2 (0.5 mL) was allowed to stand for 20 h. The crude products were chromatographed over silica gel with CH_2Cl_2. The diastereomeric esters obtained were separated by HPLC on silica gel (hexane–EtOAc 9:1), giving the first eluted ester (*S*,*S*)-(−)-**14a** (23 mg, 40%) and the second eluted ester (*S*,*R*)-(+)-**14b** (25 mg, 43%).

4.4.1. 1-Octen-3-ol MαNP ester (*S*,*S*)-(−)-14a. ^1H NMR (500 MHz, $CDCl_3$): δ 8.38 (1H, m), 7.84 (1H, m), 7.82 (1H, br d, $J = 8$ Hz), 7.63 (1H, dd, $J = 7$, 1 Hz), 7.48–7.42 (3H, m), 5.45 (1H, ddd, $J = 17$, 11, 6 Hz), 5.25 (1H, m), 4.80 (1H, dt, $J = 11$, 1 Hz), 4.66 (1H, dt, $J = 17$, 1 Hz), 3.13 (3H, s), 2.00 (3H, s), 1.55–1.40 (2H, m), 1.25–1.05 (6H, m), 0.82 (3H, t, $J = 7$ Hz); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.39, 135.78, 135.40, 134.03, 131.25, 129.34, 128.63, 126.33, 125.63, 125.52, 125.32, 124.68, 116.25, 81.67, 75.53, 51.02, 33.96, 31.39, 24.54, 22.43, 21.91, 13.94; IR (KBr, neat): ν_{max} 2934, 2860, 1747, 1730, 1250, 1134, 1121, 806, 779 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 24:1): 363 ($[M+Na]^+$, 100), 144 (6); $[\alpha]_D^{28} = -5$ (*c* 0.58, EtOH).

4.4.2. 1-Octen-3-ol MαNP ester (*S*,*R*)-(+)-14b. ^1H NMR (500 MHz, $CDCl_3$): δ 8.45 (1H, m), 7.86–7.80 (2H, m), 7.59 (1H, dd, $J = 7$, 1 Hz), 7.49–7.43 (3H, m), 5.66 (1H, ddd, $J = 17$, 11, 6 Hz), 5.21 (1H, m), 5.14 (1H, dt, $J = 17$, 1 Hz), 5.08 (1H, dt, $J = 11$, 1 Hz), 3.10 (3H, s), 2.00 (3H, s), 1.30–1.15 (2H, m), 0.95–0.72 (4H, m), 0.67 (3H, t, $J = 7$ Hz), 0.60–0.40 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.39, 136.16, 135.04, 134.04, 131.50, 129.41, 128.58, 126.43, 125.74, 125.69, 125.40, 124.58, 116.57, 81.44, 75.36, 50.84, 33.64, 31.12, 23.70, 22.19, 21.60, 13.87; IR (KBr, neat): ν_{max} 2932, 2860, 1747, 1730, 1250, 1136, 1123, 806, 779 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 24:1): 363 ($[M+Na]^+$, 100); $[\alpha]_D^{28} = +9$ (*c* 0.63, EtOH).

4.4.3. 1-Octen-3-ol (*S*)-(+)-10. (*S*,*S*)-(−)-**14a** (104 mg) was similarly hydrolyzed with 28% NaOMe/MeOH (1.5 mL) yielding 1-octen-3-ol (*S*)-(+)-**10** (30 mg, 77%): $[\alpha]_D^{26} = +19$ (*c* 0.18, EtOH), and MαNP acid (*S*)-(+)-**4** (67 mg, 95%). The chiral HPLC analysis of (*S*)-MαNP acid methyl ester revealed that acid (*S*)-(+)-**4** recovered was enantiopure.

4.4.4. Preparation of MαNP ester (*S*,*S*)-(−)-14a from (*S*)-(+)-1-octen-3-ol. 1-Octen-3-ol (*S*)-(+)-**10** (2 mg) prepared above was esterified with MαNP acid (*S*)-(+)-**4** (60 mg) using EDC (121 mg) and DMAP (121 mg) in CH_2Cl_2 (0.5 mL). The crude product was chromatographed over silica gel (1st CH_2Cl_2; 2nd hexane/EtOAc) giving ester (*S*,*S*)-(−)-**14a** (5 mg, 94%).

4.4.5. Hydrogenation of MαNP ester (*S*,*R*)-(+)-14b. Ester (*S*,*R*)-(+)-**14b** (30 mg) and 5% palladium–carbon (11 mg) were stirred in EtOAc (2 mL) under H_2 for 3 h. The suspension was filtered through Celite, and concentrated in vacuo. The crude product was chromatographed on silica gel (Kieselgel 60, EtOAc) giving ester (*S*,*S*)-(+)-**11b** (27 mg, 89%).

4.5. Enantioresolution of (±)-1-octen-3-ol using M9PP acid

1-Octen-3-ol (±)-**10** (120 μL) was similarly esterified with M9PP acid (*S*)-(+)-**5** (53 mg) using DCC (112 mg), DMAP (123 mg), and CSA (26 mg) in CH_2Cl_2 (0.5 mL) yielding the first eluted ester (*S*,*S*)-(+)-**15a** (27 mg, 37%) and the second eluted ester (*S*,*R*)-(+)-**15b** (32 mg, 43%).

4.5.1. 1-Octen-3-ol M9PP ester (*S*,*S*)-(+)-15a. ^{1}H NMR (800 MHz, $CDCl_3$): δ 8.72 (1H, br d, J = 8 Hz), 8.66 (1H, br d, J = 8 Hz), 8.44 (1H, dd, J = 8, 1 Hz), 7.91 (1H, br d, J = 8 Hz), 7.90 (1H, br s), 7.67 (1H, ddd, J = 8, 7, 1 Hz), 7.63 (1H, ddd, J = 8, 7, 1 Hz), 7.61 (1H, ddd, J = 8, 7, 1 Hz), 7.55 (1H, ddd, J = 8, 7, 1 Hz), 5.42 (1H, ddd, J = 17, 11, 6 Hz), 5.28 (1H, m), 4.80 (1H, dt, J = 11, 1 Hz), 4.71 (1H, dt, J = 17, 1 Hz), 3.16 (3H, s), 2.07 (3H, s), 1.52–1.40 (2H, m), 1.21–1.10 (6H, m), 0.80 (3H, t, J = 7 Hz); ^{13}C NMR (201 MHz, $CDCl_3$): δ 173.45, 135.74, 133.76, 130.91, 130.82, 130.69, 130.08, 129.09, 127.22, 127.12, 126.85, 126.71, 126.41, 126.02, 122.94, 122.45, 116.50, 81.57, 75.72, 51.03, 33.92, 31.37, 24.59, 22.41, 21.93, 13.91; IR (KBr, neat): ν_{max} 2932, 2859, 1746, 1730, 1250, 1127, 750, 731 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 9:1): 413 ([M+Na]$^+$, 100), 359 (24), 249 (11); $[\alpha]_D^{28} = +32$ (*c* 0.49, EtOH).

4.5.2. 1-Octen-3-ol M9PP ester (*S*,*R*)-(+)-15b. ^{1}H NMR (800 MHz, $CDCl_3$): δ 8.71 (1H, br d, J = 8 Hz), 8.66 (1H, br d, J = 8 Hz), 8.50 (1H, dd, J = 8, 1 Hz), 7.91 (1H, br d, J = 8 Hz), 7.86 (1H, br s), 7.67 (1H, ddd, J = 8, 7, 1 Hz), 7.63 (1H, ddd, J = 8, 7, 1 Hz), 7.61 (1H, ddd, J = 8, 7, 1 Hz), 7.57 (1H, ddd, J = 8, 7, 1 Hz), 5.64 (1H, ddd, J = 17, 11, 6 Hz), 5.23 (1H, m), 5.15 (1H, dt, J = 17, 1 Hz), 5.08 (1H, dt, J = 11, 1 Hz), 3.13 (3H, s), 2.07 (3H, s), 1.25–1.15 (2H, m), 0.88–0.73 (4H, m), 0.61 (3H, t, J = 7 Hz), 0.58–0.46 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.49, 136.13, 133.39, 130.83, 130.77, 130.72, 130.27, 129.04, 127.37, 127.25, 126.93, 126.70, 126.48, 126.06, 122.89, 122.44, 116.71, 81.35, 75.55, 50.85, 33.60, 31.11, 23.77, 22.13, 21.61, 13.79; IR (KBr, neat): ν_{max} 2933, 2860, 1748, 1250, 1132, 750, 732 cm^{-1}; LC–MS (API-ESI, CH_3CN–H_2O 9:1): 413 ([M+Na]$^+$, 100), 359 (20), 249 (20); $[\alpha]_D^{28} = +34$ (*c* 0.55, EtOH).

4.5.3. 1-Octen-3-ol (*S*)-(+)-10. Ester (*S*,*S*)-(+)-**15a** (80 mg) was hydrolyzed with 28% NaOMe/MeOH (1.5 mL) yielding 1-octen-3-ol (*S*)-(+)-**10** (21 mg, 80%): $[\alpha]_D^{26} = +19$ (*c* 0.21, EtOH), and M9PP acid (*S*)-(+)-**5** (47 mg, 82%). The chiral HPLC analysis (Chiralcel OD-RH, CH_3CN–H_2O 13:7) of (*S*)-M9PP acid methyl ester (prepared using 2 M trimethylsilyldiazomethane[23] hexane solution) revealed that the (*S*)-(+)-**5** recovered was enantiopure.

4.5.4. Preparation of M9PP ester (*S*,*S*)-(+)-15a from (*S*)-(+)-1-octen-3-ol. 1-Octen-3-ol (*S*)-(+)-**10** (14 mg) was esterified with M9PP acid (*S*)-(+)-**5** (40 mg) using DCC (104 mg), DMAP (128 mg), and CSA (38 mg) in CH_2Cl_2 (0.6 mL). The crude product was purified using a silica gel cartridge (Wako Presep-C Silica Gel) and a column chromatography (silica gel, hexane/EtOAc) giving ester (*S*,*S*)-(+)-**15a** (20 mg, 47%).

4.5.5. 1-Octen-3-ol (*R*)-(−)-10. Ester (*S*,*R*)-(+)-**15b** (85 mg) was hydrolyzed with 28% NaOMe/MeOH (1.5 mL) giving 1-octen-3-ol (*R*)-(−)-**10** (23 mg, 82%): $[\alpha]_D^{27} = -19$ (*c* 0.23, EtOH), and M9PP acid (*S*)-(+)-**5** (30 mg, 49%).

4.5.6. Preparation of M9PP ester (*S*,*R*)-(+)-15b from (*R*)-(−)-1-octen-3-ol. 1-Octen-3-ol (*R*)-(−)-**10** (10 mg) was esterified with M9PP acid (*S*)-(+)-**5** (25 mg) using EDC (103 mg) and DMAP (127 mg) in CH_2Cl_2 (0.6 mL). The crude product was chromatographed over silica gel (1st CH_2Cl_2; 2nd hexane/EtOAc) giving ester (*S*,*R*)-(+)-**15b** (23 mg, 76%).

4.5.7. Hydrogenation of M9PP ester (*S*,*S*)-(+)-15a. Ester (*S*,*S*)-(+)-**15a** (20 mg) and 5% palladium–carbon (13 mg) were stirred in EtOAc (2 mL) under H_2 for 6 h. The suspension was filtrated, and purified using HPLC (silica gel, hexane/EtOAc) giving ester (*S*,*R*)-(+)-**12a** (14 mg, 70%).

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