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Naphthyl Groups in Chiral Recognition: Structures of Salts and Esters of 2-Methoxy-2-naphthylpropanoic Acids

Akio Ichikawa,*[a] Hiroshi Ono,[b] and Yuji Mikata[c]

Abstract: The crystal structures of salt **8**, which was prepared from (*R*)-2-methoxy-2-(2-naphthyl)propanoic acid ((*R*)-MβNP acid, (*R*)-**2**) and (*R*)-1-phenylethylamine ((*R*)-PEA, (*R*)-**6**), and salt **9**, which was prepared from (*R*)-2-methoxy-2-(1-naphthyl)propanoic acid ((*R*)-MαNP acid, (*R*)-**1**) and (*R*)-1-(*p*-tolyl)ethylamine ((*R*)-TEA, (*R*)-**7**), were determined by X-ray crystallography. The MβNP and MαNP anions formed ion-pairs with the PEA and TEA cations, respectively, through a methoxy-group-assisted salt bridge and aromatic CH···π interactions. The networks of salt bridges formed 2_1 columns in both salts. Finally, (*S*)-(2*E*,6*E*)-(1-$^2H_1$)farnesol ((*S*)-**13**) was prepared from the reaction of (2*E*,6*E*)-farnesal (**11**) with deuterated (*R*)-BINAL-H (i.e., (*R*)-BINAL-D. The enantiomeric excess of compound (*S*)-**13** was determined by NMR analysis of (*S*)-MαNP ester **14**. The solution-state structures of MαNP esters that were prepared from primary alcohols were also elucidated.

Keywords: chirality · conformational analysis · crystal engineering · molecular recognition · pi interactions

Introduction

2-Aryl-2-methoxypropanoic acids **1**–**3** possess unracemizable chiral centers and polycyclic aromatic groups (Figure 1).[1,2] Therefore, these acids are attractive for the development of new methods for the preparation and structural elucidation of single-enantiomers.[1–13] We have previously reported the synthesis of acids **1**–**3**[10,12,13] and applied them as agents for the enantioresolution of biofunctional molecules.[6–8] Acids **1**–**3** exhibited powerful chiral-resolving ability in the HPLC separation of their diastereomeric esters and amides. Acids **1** and **3** exhibited large shielding effects during the acquisition of NMR spectra. Acids **1** and **3** showed similar chiral-resolving ability,[8] which was superior to that of 3,3,3-trifluoro-2-methoxy-2-phenylpropanoic acid (MTPA, **4**).[7] However, many properties of acid **2** have not yet been fully clarified.

Recent studies have shown a high degree of crystallinity in acids **1**–**3** and their derivatives.[3,4,10,14–16] Therefore, these compounds are expected to be useful in the preparation of crystalline diastereomeric salts.

In 2003, it was estimated that more than half of the chiral pharmaceuticals on the market were produced by the crys-

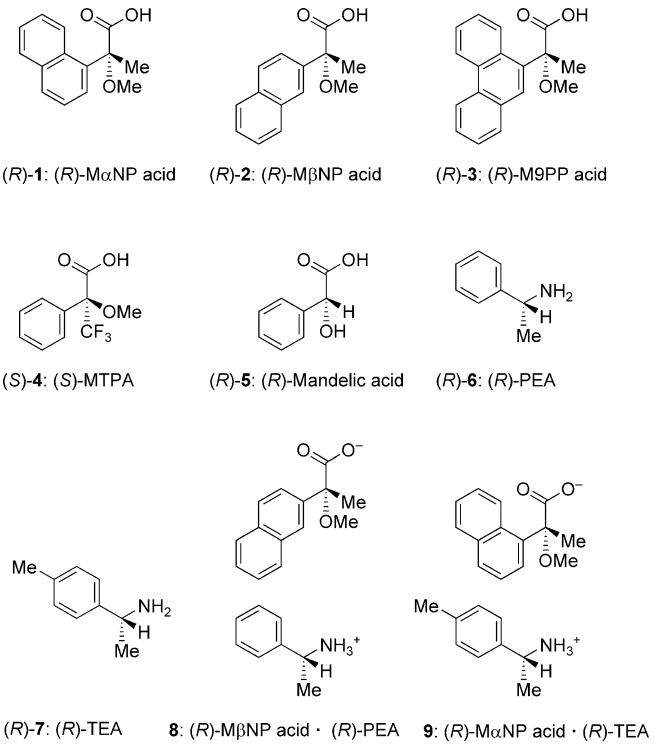

Figure 1. Structures of chiral resolving agents and their derivatives.

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tallization of diastereomeric salts.[17] The use of diastereomeric-salt formation to separate enantiomers[18–21] does not require heavy metals and removes impurities. This method has been used with mandelic acid (**5**) as a chiral resolving agent for the preparation of single enantiomers that contain amino group.[22,23] Crystal engineering[24–27] of these salts is also important for elucidating stereochemistry because X-ray crystallography is the most reliable method aside from synthesis.

In 1978, Goto et al. prepared acids (*R*)-(−)-**1** and (*R*)-(−)-**2** by the formation of diastereomeric salts with (*R*)-**6**.[28] Recently, we determined the crystal structures of diastereomeric MαNP salts (*R*)-**1**·(*R*)-**6** and (*S*)-**1**·(*R*)-**6** (Figure 2a,b).[14] The mechanism for chiral recognition in these

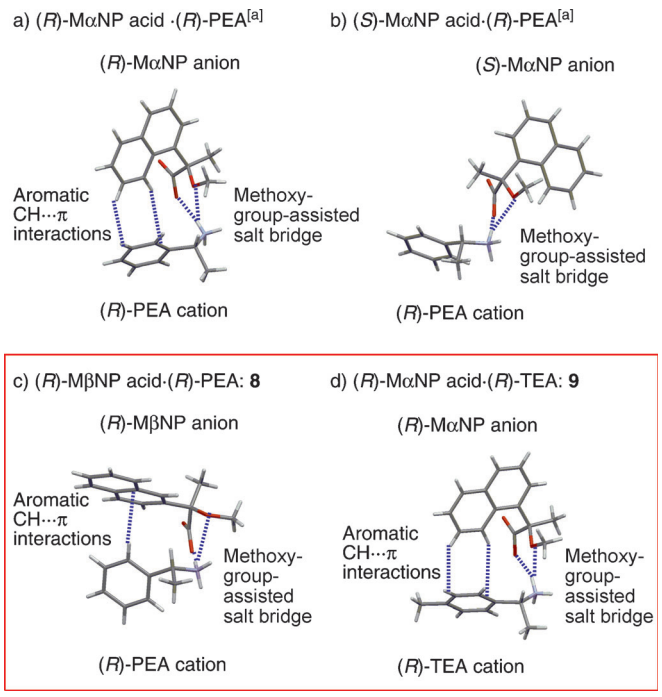

Figure 2. Crystal structures of MαNP and MβNP salts. [a] See reference [14].

MαNP salts was as follows: 1) The MαNP anion and the PEA cation formed a closest ion-pair through bifurcated hydrogen bonds,[4] that is, a methoxy-group-assisted salt bridge (Figure 3). 2) The aromatic CH···π interactions[29–31] between the 1-naphthyl group of the (*R*)-MαNP anion and the phenyl group of the (*R*)-PEA cation stabilized the ion-pair to form the less-soluble salt (*R*)-**1**·(*R*)-**6** (Figure 2a). The aromatic groups of the more-soluble salt, (*S*)-**1**·(*R*)-**6**, did not overlap (Figure 2b).

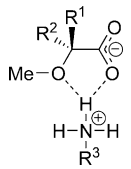

Figure 3. Structure of the methoxy-group-assisted salt bridge.

The methoxy-group-assisted salt bridge was also evident in the X-ray crystallographic analysis of the less-soluble MβNP salt (**8**), which consisted of (*R*)-**2** and (*R*)-**6** (Figure 2c). However, the conformational features of the MβNP anion differed significantly from those of the MαNP anion. In addition, the crystal structure of salt **9**, which was prepared from (*R*)-**1** and (*R*)-**7**, was elucidated by X-ray crystallography (Figure 2d). The distance between the 1-naphthyl- and *p*-tolyl groups in salt **9** was shorter than the distance between the 1-naphthyl- and phenyl groups in salt (*R*)-**1**·(*R*)-**6**. This result suggests that crystalline MαNP salts are useful for identifying substituent effects on aromatic CH···π interactions. The crystal packing of salts **8** and **9** were also elucidated.

Many molecules contain multiple CH groups and π orbitals; moreover, interactions between these groups are important in supramolecular chemistry, in determining the stereoselectivity of reactions, and in the specificity of biomacromolecules.[29–31] Individual CH···π interactions are weak but become significant when multiple interactions act cooperatively. Furthermore, it has been reported that CH···π interactions function even in relatively remote positions.[32] The T-shaped interactions of aromatic groups are known as aromatic CH···π interactions.[21,29–31]

Recently, Suzuki et al. reported that CH···π interactions, a hydrogen bond, and van der Waals interactions are important for the binding of juvenile hormones to their carrier protein.[33] Therefore, understanding the properties of weak interactions in crystalline salts is valuable for the rational design of agrochemicals.

In 2009, Mayoral et al. characterized an insect farnesol dehydrogenase (*Aa*SDR-1), which oxidizes (2*E*,6*E*)-farnesol (**10**) into (2*E*,6*E*)-farnesal (**11**, Scheme 1), a biosynthetic intermediate of juvenile hormone in the corpora allata of mosquito *Aedes aegypti*.[34] They noted that *Aa*SDR-1 is a rate-limiting enzyme in juvenile hormone biosynthesis. Yeast alcohol dehydrogenase converts (*S*)-(1-$^2H_1$)ethanol into (1-^{2}H)acetoaldehyde in the presence of nicotinamide adenine dinucleotide (NAD^+), a coenzyme.[35] However, to the best of our knowledge, the stereoselectivity of *Aa*SDR-1 and its orthologues have not yet been identified.

In 1984, Noyori et al. reported the preparation of (*R*)-**13** from (2*E*,6*E*)-(1-^{2}H)farnesal (**12**) by using binaphthol-modified lithium aluminum hydride agent (*R*)-BINAL-H (see the Supporting Information, Scheme 2).[36,37]

Recently, the development of deuterium-containing pharmaceuticals has become important.[38–40] Because the C–D bond is stronger than the C–H bond, the pharmacological or metabolic profiles of deuterated pharmaceuticals differ from those of their protonated analogues.[40]

A single enantiomer of compound **13** would allow the clarification and determination of the stereoselectivity and rate-limiting step of farnesol dehydrogenase. This fact prompted us to prepare compound (*S*)-**13** from compound **11** by using deuterated (*R*)-BINAL-H (i.e., (*R*)-BINAL-D), which was prepared from lithium aluminum deuteride ($LiAlD_4$, Scheme 1). The enantiomeric excess of compound (*S*)-**13** was determined by analysis of the ^{1}H NMR spectrum of (*S*)-MαNP ester **14**. The assignment of prochiral methyl-

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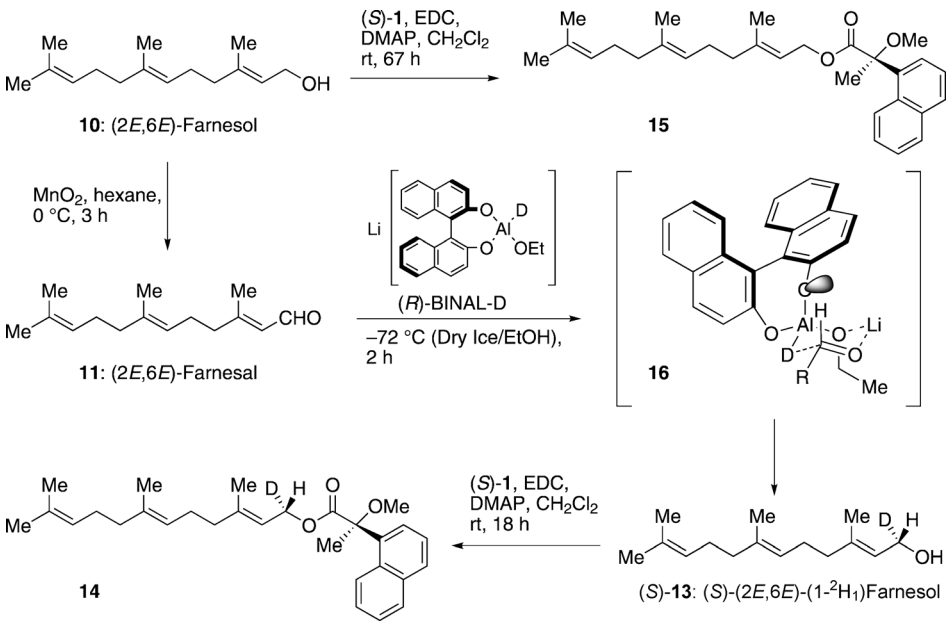


Scheme 1. Preparation of (*S*)-(2*E*,6*E*)-(1-$^2H_1$)farnesol and related compounds.

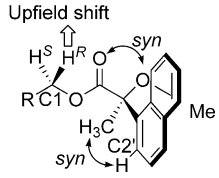


Figure 4. Conformation of (*S*)-MαNP ester that was prepared from a primary alcohol.

ene signals at the 1-position in ester **15**, which was prepared from compounds **10** and (*S*)-**1**, was made by comparison with the ^{1}H NMR spectrum of ester **14**. The conformation of the MαNP ester that was prepared from the primary alcohol was the first to be elucidated (Figure 4).

In addition to conventional chiral resolving agents, 2-aryl-2-methoxypropanoic acids **1**–**3** are suitable for stereochemical studies of biofunctional molecules, agrochemicals, and pharmaceuticals. Herein, we demonstrate the versatility of acids **1** and **2** and provide new methods for the preparation of single enantiomers through the crystal engineering of salts, reductive deuteration, and the structural elucidation of α-deuterated primary terpene alcohols. These methods are applicable to studies in insect endocrinology and to research and development in the agrochemical and pharmaceutical industries.

Results and Discussion

Crystal Conformation of MβNP Salt 8

Salt **8**[28] was prepared from compounds *rac*-**2** and (*R*)-**6** in MeOH and $CHCl_3$ as less-soluble needle-like crystals. Recrystallization from a "greener" solution of EtOH and water yielded thicker crystals of salt **8**, which were analyzed by X-ray crystallography (Table 1 and Figure 5 show the crystallographic data and ORTEP, respectively). Salt **8** crystallized in the monoclinic space group $P2_1$ with two ion-pairs per unit cell. This result is the first structural elucidation of a crystalline MβNP salt.

A methoxy-group-assisted salt bridge (Figure 3), a structural motif that has previously been observed in crystalline MαNP salts,[14] was also observed in salt **8**. The interatomic distances between ammonium hydrogen atom H1A and carboxylate oxygen atom O1 (d^1) or methoxy oxygen atom O3 (d^2) were 1.85 Å and 2.58 Å, respectively (Table 2). The interatomic angles N1-H1A···O1 and N1-H1A···O3 were 171° and 116°, respectively; that is, the H1A atom was inclined toward the O1 atom. This result suggested that the salt bridge and the NH$^+$···O hydrogen bond were the major and minor components, respectively.[41] Notably, the 2-naphthyl group in salt **8** acted as a C–H acceptor, whereas the 1-naphthyl group of the MαNP anion acted as a C–H donor (Figure 2). Aromatic hydrogen atom H18 of the phenyl group was on the naphthyl plane (d^5 = 2.7 Å). Furthermore, hydrogen atom H15, which was on the chiral center of the PEA cation, was almost on the naphthyl plane so that the bulky methyl group of the PEA cation was orientated in the opposite direction. These results suggest that chiral recognition

Table 1. X-ray crystallographic data for salts **8** and **9**.

Compound	**8**	**9**
chemical formula	$C_{22}H_{25}NO_3$	$C_{23}H_{27}NO_3$
M_w	351.44	365.47
crystal system	monoclinic	monoclinic
space group	$P2_1$	$C2$
Z	2	4
a [Å]	12.042(5)	23.437(3)
b [Å]	6.570(3)	6.7299(4)
c [Å]	12.267(5)	21.582(3)
β [°]	96.696(6)	141.392(3)
V [Å^3]	963.9(7)	2124.1(4)
$D_{calculated}$	1.211	1.143
μ [cm^{-1}]	0.799	0.749
$2\theta_{max}$ [°]	54.9	55.0
T [K]	123	123
total reflns	7545	8391
unique reflns	4225	4818
R_{int}	0.0252	0.0208
parameters	235	244
final $R1$ ($I>2\theta(I)$)[a]	0.0519	0.0554
$wR2$ (all data)[b]	0.1356	0.1597
GOF	1.103	1.173
Flack parameter	−1.1(14)	0.9(13)

[a] $R1 = (\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)$. [b] $wR2 = \{[\Sigma w(F_o^2-F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

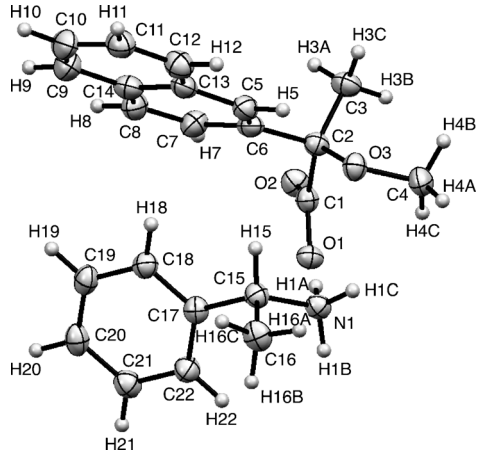
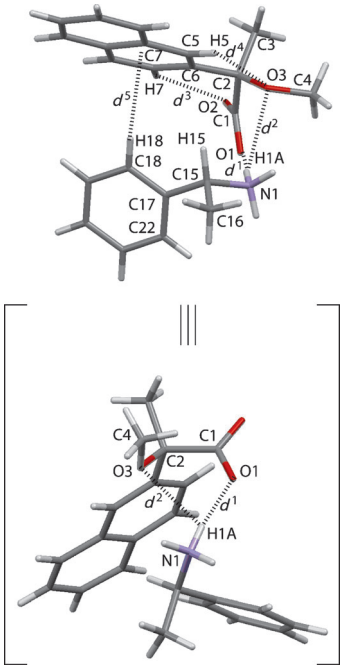


Figure 5. ORTEP of salt **8**. Ellipsoids set at 50% probability.

Table 2. Dihedral angles, interatomic distances, and interatomic angles in crystalline salt **8**.[a]



Dihedral angle [°]	
O1-C1-C2-O3	+26.4(3)
C4-O3-C2-C1	+67.2(3)
C3-C2-C6-C5	−94.6(3)
N1-C15-C17-C22	+53.1(3)
Interatomic distance [Å]	
H1A···O1 (d^1)	1.85
H1A···O3 (d^2)	2.58
H7···O2 (d^3)	2.48
H5···O3 (d^4)	2.33
H18···π (d^5)	2.7
Interatomic angle [°]	
N1-H1A···O1	171
N1-H1A···O3	116
C7-H7···O2	125
C5-H5···O3	101

[a] **8**: (*R*)-MβNP acid·(*R*)-PEA salt. Van der Waals radii [Å]: C 1.70, H 1.20, O 1.52; half-thickness of the aromatic ring: 1.77.

by using methoxy-group-assisted salt bridges and CH···π interactions are common in crystalline salts that are prepared from 2-aryl-2-methoxypropanoic acids.

The conformational properties of the MβNP anion differed significantly from those of the MαNP anions. The methyl group that was attached to the chiral center was almost perpendicular to the naphthyl plane, with a C3-C2-C6-C5 dihedral angle of −94.6(3)° (Figure 6, Table 2). Short distances were observed between aromatic hydrogen atom H7 and carboxylate oxygen atom O2 (d^3 = 2.48 Å) and between atom H5 and methoxy oxygen atom O3 (d^4 = 2.33 Å), thus suggesting the presence of CH···O hydrogen bonds.[4,25,29,30] The interatomic C7-H7···O2 and C5-H5···O3 angles were 125° and 101°, respectively. As in the case of the MαNP anions, the three oxygen atoms of the MβNP anion were almost in the same plane, with a O1-C1-C2-O3 dihedral angle of +26.4(3)°. In contrast, the methyl group of the methoxy moiety was not in the MβNP plane, with a C4-O3-C2-C1 dihedral angle of +67.2(3)°.

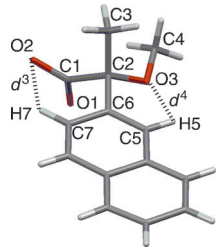


Figure 6. Conformation of the MβNP anion in the single crystal.

Crystallization is a kinetically controlled process.[24] Therefore, it is not clear whether this MβNP anion is the major conformer in solution. However, it is probable that the 2-naphthyl group affords the MβNP moiety with altered conformational properties.[12] Sekiguchi et al. reported the crystal structure of an MβNP amide, in which the methyl group was in the naphthyl plane.[3] Also, note that aromatic hydrogen atoms H5 and H7 of the MβNP anion were almost equivalent about the bond between *ipso*-carbon atom C6 and chiral center C2 (Figure 6). Ohba et al. reported a flipped conformation of the 2-hydroxymethyl-2-(2-naphthyl)-propanoate derivative.[42]

The crystalline salts that were prepared from acids **1** or **2** suggested moderate flexibility of the PEA cations. The N1-C15-C17-C22 dihedral angle in salt **8** was +53.1(3)°. The equivalent dihedral angle in the other PEA cations varied somewhat: (*R*)-**1**·(*R*)-**6** +55.8(2)°,[14] (*S*)-**1**·(*R*)-**6** +28.9(2)°.[14] A statistical study suggested that the majority of PEA cations were in a narrow angular region, with an average value of +59.75°.[43]

The conformational difference between the MαNP and MβNP anions is important for the preparation of crystalline diastereomeric salts from a wide variety of amines.

Crystal Packing of MβNP Salt 8

Figure 7a shows the crystal packing of salt **8**, as viewed along the *a* axis. The closest ion-pairs, which consisted of the MβNP anion and the PEA cation, formed 2_1 columns with strong interactions between the carboxylate and ammonium groups (i.e., salt bridges[14,25,41], Figure 7b). In addition to

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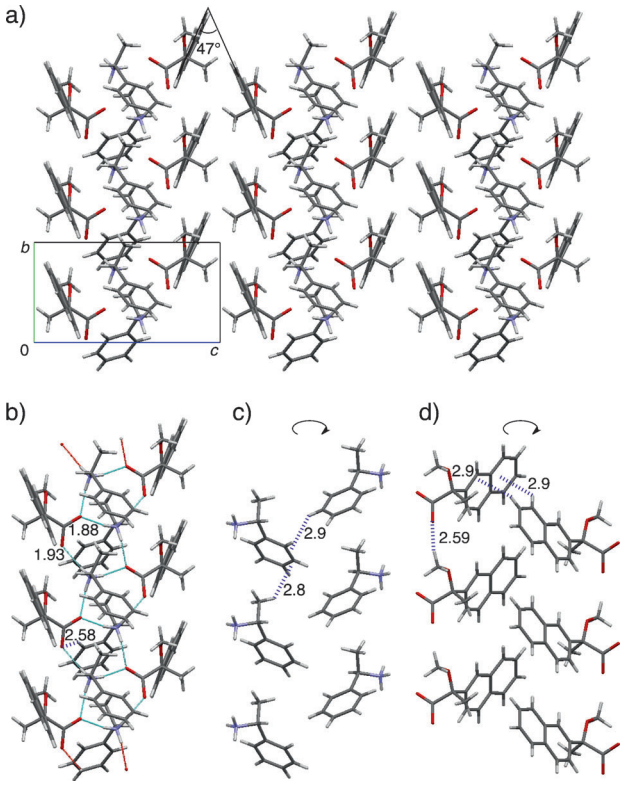


Figure 7. Crystal packing of salt **8** as viewed along the *a* axis. The packing in c) and d) was rotated for clarity of the intermolecular interactions.

the methoxy-group-assisted salt bridge, other salt bridges were observed between the MβNP anion and their neighboring PEA cations. The interatomic distance between ammonium hydrogen atom H1B and its neighboring carboxylate oxygen atom (O1) was 1.88 Å, whilst the interatomic distance between ammonium hydrogen atom H1C and its neighboring carboxylate oxygen atom (O2) was 1.93 Å. It is certain that these salt bridges were the strongest intermolecular interactions in the crystal. Furthermore, the interatomic distance between aromatic hydrogen atom H22 of the phenyl group and its neighboring carboxylate oxygen atom (O2) was 2.58 Å, thus suggesting the presence of a CH···O hydrogen bond.

Aromatic CH···π and CH···π interactions were also observed between the PEA cations (Figure 7c). The distance between aromatic hydrogen atom H19 and its neighboring phenyl group was 2.9 Å. The distance between hydrogen atom H16C of the methyl group and its neighboring phenyl group was 2.8 Å.

As shown in Figure 7d, the CH···O hydrogen bond bound the MβNP anions. The interatomic distance between hydrogen atom H4A of the methoxy group and its neighboring carboxylate oxygen atom (O2) was 2.59 Å.

The core moiety of the column that was formed by the network of salt bridges was covered with 2-naphthyl- and phenyl groups. The columns were bound together by interactions between these aromatic groups.[19,44] The homo-aromatic CH···π interactions were observed between the 2-naphthyl groups. The distances between aromatic hydrogen atoms H11 and H12 and the neighboring 2-naphthyl group were both 2.9 Å (Figure 7d); the interplanar angle between the 2-naphthyl groups was 47° (Figure 7a).

Figure 8 shows the crystal packing of salt **8**, as viewed along the *c* axis. In addition to the interactions noted above, two other heteroaromatic CH···π interactions were observed: 1) The intermolecular distance between atom H9 and its neighboring phenyl group was 2.9 Å; and 2) the intermolecular distance between atom H20 and its neighboring 2-naphthyl group was 3.0 Å.

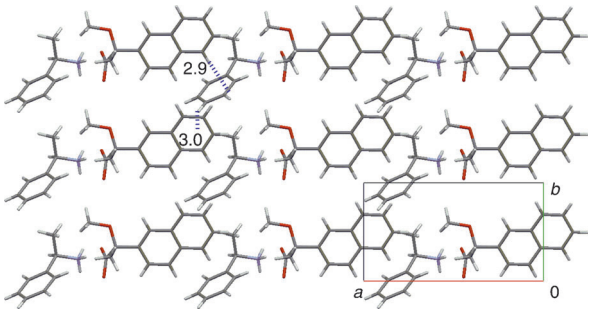


Figure 8. Crystal packing of salt **8** as viewed along the *c* axis.

Saigo and Sakai developed the "space-filler" concept,[19,20,22] which states that, if the molecular length of the resolving agent is identical to—or slightly longer than—that of the racemic substance, then enantioresolution is likely to be successful. If a gap exists between the lengths of the resolving agent and the substrate, it can be compensated for by a protic solvent, such as water or MeOH.[19,20] In this case, the 2-naphthyl- and phenyl groups of salt **8** assembled to fill the gap (see the Supporting Information, Figure 14).

These results suggested that the aromatic CH···π interactions are important for chiral recognition and for the formation of the crystal structure.

Crystal Conformation of MαNP Salt 9

Salt **9** was prepared from compounds (*R*)-**1** and (*R*)-**7** and was recrystallized in a solution of MeOH and $CHCl_3$ (Table 1 and Figure 9 show the crystallographic data and ORTEP, respectively). Salt **9** crystallized in the monoclinic space group *C*2 with four ion-pairs per unit cell.

The crystal conformation of salt **9** was similar to that of MαNP salt (*R*)-**1**•(*R*)-**6** (Figure 2a,d). The closest ion-pair of the MαNP anion and the TEA cation was formed through a methoxy-group-assisted salt bridge. The interatomic distances between ammonium hydrogen atom H1A and carboxylate oxygen atom O1 (d^1) or methoxy oxygen atom O3 (d^2) were 2.03 Å and 2.16 Å, respectively (Table 3). Aromatic CH···π interactions were observed between aromatic hydrogen atoms H11 and H12 and the *p*-tolyl group (d^5 = 2.6 Å, d^6 = 3.1 Å), that is, the 1-naphthyl group of the MαNP anion acted as a C–H donor. The methyl group at the chiral

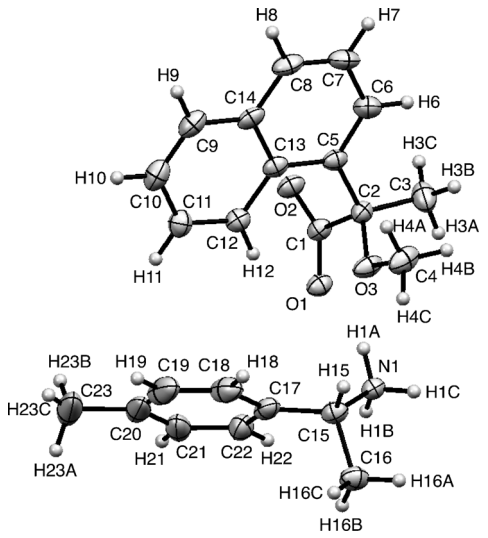


Figure 9. ORTEP of salt **9**. Ellipsoids set at 50% probability.

center of the TEA cation was orientated in the opposite direction to that of the MαNP anion.

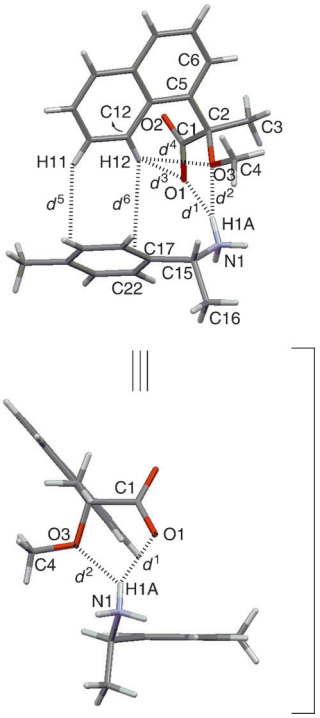
The carboxylate and methoxy groups formed the MαNP plane with O1-C1-C2-O3 and C4-O3-C2-C1 dihedral angles of −27.4(4)° and −177.7(2)°, respectively. The methyl group of the MαNP moiety was in the 1-naphthyl plane, with a C3-C2-C5-C6 dihedral angle of −6.3(3)°. The distances between aromatic hydrogen atom H12 and oxygen atoms O1 (d^3) or O3 (d^4) were 2.79 and 2.51 Å, respectively. These conformational properties are typical of the MαNP moiety.[4,5,13] However, this conformational analysis of crystalline salt **9** contributed to the NMR analysis of MαNP esters that were prepared from farnesols. The N1-C15-C17-C22 dihedral angle was +45.9(5)° in the TEA cation.

The crystalline MαNP salt represented a new molecular balance[45] and provided an opportunity to observe substituent effects on the intermolecular aromatic CH···π interactions by using X-ray crystallography. However, the influence of other intermolecular interactions could not be ignored. Substitution of the face component by a methyl group reportedly stabilizes the aromatic CH···π interactions.[46] In fact, the intermolecular distances between the 1-naphthyl- and *p*-tolyl groups were shorter than those between the 1-naphthyl- and phenyl groups in salt (*R*)-**1**•(*R*)-**6**[14] (Table 4): In salt **9**, the interatomic distance between the C11 and C19 atoms (d^L) = 3.68 Å and the interatomic distance between the C12 and C18 atoms (d^M) = 3.72 Å; in salt (*R*)-**1**•(*R*)-**6**,[14] d^L = 3.71 Å and d^M = 3.79 Å. These results suggest that crystalline MαNP salts can be used to clarify and evaluate the effect of the substituent on aromatic CH···π interactions.

Crystal Packing of MαNP Salt 9

The crystal packing of salt **9**, as viewed along the *a* axis, was similar to that of MαNP salt (*R*)-**1**•(*R*)-**6** (Figure 10a).[14] The closest ion-pairs, which consisted of the MαNP anion and the TEA cation, formed 2_1 columns through strong salt bridges (Figure 10b). In addition to the methoxy-group-assisted salt bridge, two other salt bridges were observed in the column. The interatomic distance between ammonium hydrogen atom H1B and its neighboring carboxylate oxygen atom (O1) was 1.95 Å, whilst the interatomic distance between ammonium hydrogen atom H1C and its neighboring carboxylate oxygen atom (O2) was 1.99 Å. It is certain that these salt bridges were the strongest intermolecular interactions in the crystal of salt **9**, as in the crystal of salt **8**. Furthermore, intermolecular CH···O interactions were also observed in the columns. The interatomic distance between hydrogen atom H16A of the *p*-tolyl group and its neighboring

Table 3. Dihedral angles, interatomic distances, and interatomic angles of crystalline salt **9**.[a]



Dihedral angle [°]	
O1-C1-C2-O3	−27.4(4)
C4-O3-C2-C1	−177.7(2)
C3-C2-C5-C6	−6.3(3)
N1-C15-C17-C22	+45.9(5)
Interatomic distance [Å]	
H1A···O1 (d^1)	2.03
H1A···O3 (d^2)	2.16
H12···O1 (d^3)	2.79
H12···O3 (d^4)	2.51
H11···π (d^5)	2.6
H12···π (d^6)	3.1
Interatomic angle [°]	
N1-H1A···O1	149
N1-H1A···O3	133
C12-H12···O1	144
C12-H12···O3	115

[a] **9**: (*R*)-MαNP acid•(*R*)-TEA salt. Van der Waals radii [Å]: C 1.70, H 1.20, O 1.52; half-thickness of aromatic ring: 1.77.

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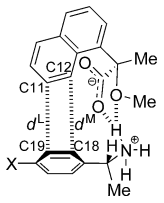
Table 4. Interatomic distances between the 1-naphthyl- and phenyl groups in crystalline MαNP salts.



Compound	X	$d^{L[a]}$ [Å]	$d^{M[b]}$ [Å]
9	H_3C	3.68	3.72
(*R*)-**1**·(*R*)-**6**[c]	H	3.71	3.79

Carbon atoms C11 and C12 were slightly offset from the phenyl planes; [a] d^{L} is the interatomic distance between the C11 and C19 atoms; [b] d^{M} is the interatomic distance between the C12 and C18 atoms; [c] for the crystalline structure of salt (*R*)-**1**·(*R*)-**6**, see reference [14].

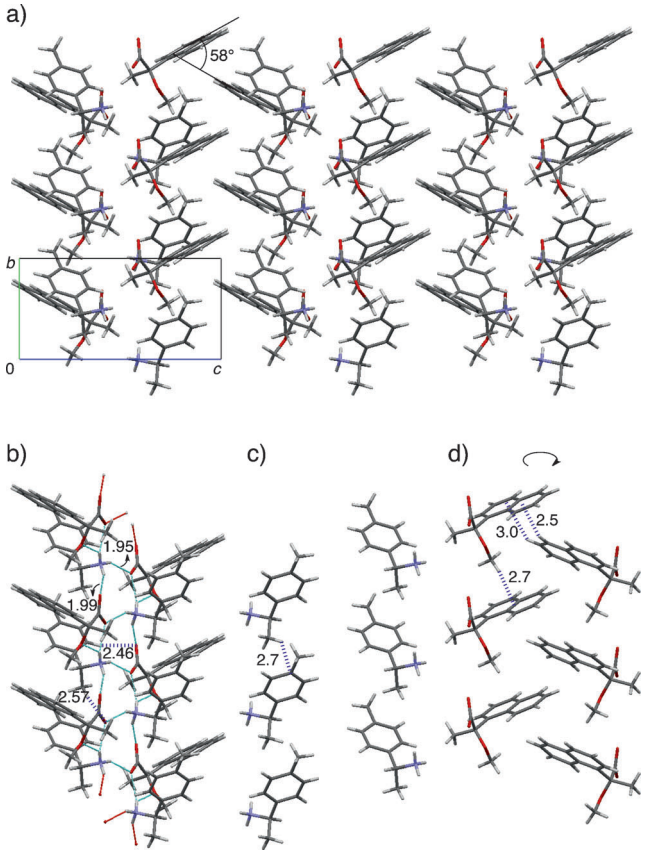


Figure 10. Crystal packing of salt **9** as viewed along the *a* axis. The packing in d) was rotated for clarity of the intermolecular interactions.

oxygen atom (O1) was 2.57 Å, whilst the interatomic distance between hydrogen atom H22 of the *p*-tolyl group and its neighboring oxygen atom (O2) was 2.46 Å (Figure 10b).

As described previously,[14] the MαNP anions formed stacks that were stabilized by CH···π interactions between the methoxy- and 1-naphthyl groups, where the distance between methoxy hydrogen atom H4C and its neighboring 1-naphthyl group was 2.7 Å (Figure 10d). The TEA cations formed similar stacks through CH···π interactions between the methyl- and 1-naphthyl groups, where the distance between methyl hydrogen atom H16C and its neighboring *p*-tolyl group was 2.7 Å (Figure 10c).

Homoaromatic CH···π interactions were observed between the 1-naphthyl groups. The distances between aromatic hydrogen atoms H9 and H10 and their neighboring 1-naphthyl group were 2.5 Å and 3.0 Å, respectively (Figure 10d), whilst the interplanar angle between the 1-naphthyl groups of the MαNP moieties was 58° (Figure 10a). This angle was larger than that between the 2-naphthyl groups of the MβNP moieties in salt **8**. A perpendicular geometry (i.e., 90°) has been reported to maximize the efficiency of aromatic CH···π interactions.[47]

As shown in Figure 11, the crystal packing of salt **9**, as viewed along the *c* axis, was significantly different to that of salt (*R*)-**1**·(*R*)-**6**.[14] To avoid overlap between the bulky *p*-

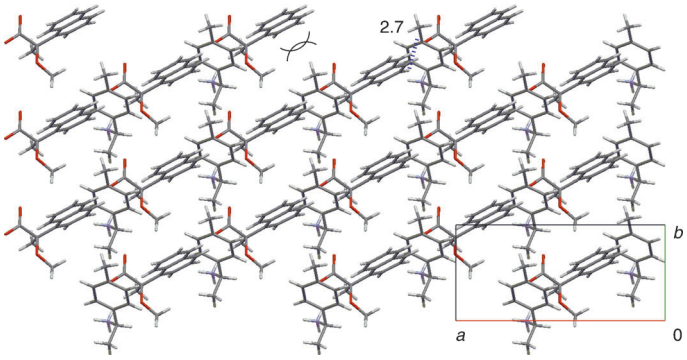


Figure 11. Crystal packing of salt **9** as viewed along the *c* axis.

tolyl- and 1-naphthyl groups, each of the stacking sheets was offset by half a unit. A heteroaromatic CH···π interaction was observed between the 1-naphthyl- and *p*-tolyl groups, with a distance between aromatic hydrogen atom H7 and its neighboring *p*-tolyl group of 2.7 Å.

As viewed along the *b* axis, the six aromatic groups formed an oval motif[25] so as to bind the 2_1 columns together (see the Supporting Information, Figure 15).

Crystal engineering by using acids **1**–**3** may be important in the development of agrochemicals and pharmaceuticals as a means of assessing the benefits and potential risks of each enantiomer.

MαNP Esters of Farnesol and (1-$^2H_1$)Farnesol

(2*E*,6*E*)-Farnesal (**11**) was prepared from (2*E*,6*E*)-farnesol (**10**) by using activated manganese(IV) oxide (MnO_2) in *n*-hexane (Scheme 1). The reductive deuteration of compound **11** was performed with deuterated (*R*)-BINAL-H[36,37] (i.e., (*R*)-BINAL-D), which was prepared from the reaction of $LiAlD_4$, EtOH, and (*R*)-1,1′-binaphthol, to yield compound (*S*)-**13** in 56% yield and 83% *ee* (*ee* value determined by ^{1}H NMR analysis of the (*S*)-MαNP esters, $[\alpha]_D^{29} = +0.54$, $c = 3.0$, cyclopentane; cf. compound (*R*)-**13**,[37] 88% *ee*, $[\alpha]_D^{24} = -0.80$, $c = 4.0$, cyclopentane). Noyori et al. explained this

stereoselectivity by using chair-like transition state **16**, in which the n/π-type electronic repulsion between the axial oxygen atom and the unsaturated moiety is smaller.[36]

Acylation of compounds (*S*)-**13** and **10** with compound (*S*)-**1** by using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) and 4-dimethylaminopyridine (DMAP) afforded esters **14** and **15**, respectively. The NMR signals of ester **14** and **15** were assigned based on analysis of their COSY, NOESY, HSQC, and HMBC spectra (800 MHz, $CDCl_3$). Figure 12 shows the ^{1}H NMR signals

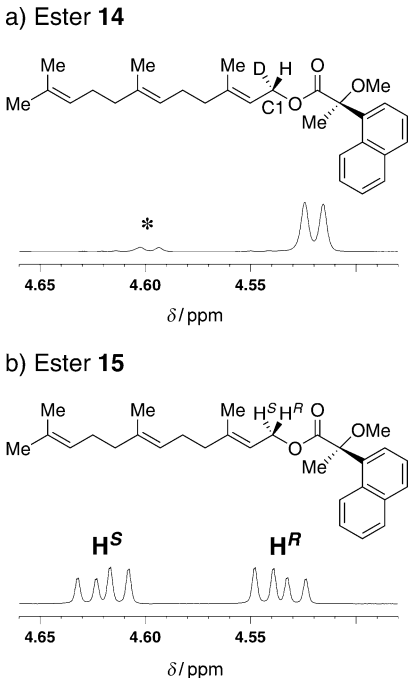
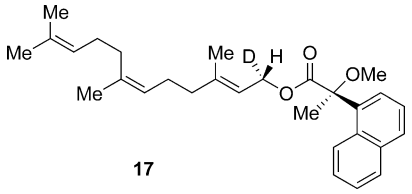


Figure 12. Region of the ^{1}H NMR spectra of esters **14** and **15** (800 MHz, $CDCl_3$); expansion of the signals at the 1-positions of the farnesol moieties. * The minor doublet at 4.60 ppm (8.3%) is due to the ($R_{alcohol}$,S_{acid})-diastereomer.

of the methylene protons at the 1-positions of esters **14** and **15**. The proton at the 1-position of ester **14** ($\delta = 4.52$ ppm, 91.7%) was shifted upfield compared to that of the minor ($R_{alcohol}$,S_{acid})-diastereomer ($\delta = 4.60$ ppm, 8.3%; Figure 12a). It has been reported that the α-D atom of the CHD group perturbs the chemical shift of the remaining H atom by about $\delta = 0.02$ ppm upfield of the signal of the parent CH_2 hydrogen atoms.[48] Therefore, the chemical shifts of the pro-*S* and pro-*R* hydrogen atoms (H^S and H^R) at the 1-position of ester **15** were assigned to the peaks at $\delta = 4.62$ ppm and $\delta = 4.54$ ppm, respectively (Figure 12b), that is, the 1-naphthyl group of the MαNP moiety shielded the H^R atom of ester **15**. The conformation of the MαNP moiety has already been clarified (Figure 2 and Table 3).[4,5,13] These results suggested that the carbonyl group of ester **15** was located between the hydrogen atoms of the methylene group at the 1-position (Figure 4). Nicolaou et al. observed similar conformations in the crystal structures of esters that were prepared from halogen-containing primary alcohols.[49]

Previously, the enantiomeric excess and absolute configuration of the α-deuterated primary alcohols were determined by ^{1}H NMR analysis of their (−)-camphanic acid esters with $Eu(dpm)_3$.[50] The prochiral methylene signals of MαNP ester **15** were well-separated without the need for an NMR shift reagent (Figure 12b). Therefore, acid **1** can be used to investigate the stereochemistry of α-deuterated primary alcohols.

Mixtures of the *cis*/*trans* isomers of compound **11** underwent reductive deuteration with (*R*)-BINAL-D. After acylation of the α-deuterated primary alcohols with compound (*S*)-**1**, ester **17** (Figure 13) was isolated by using preparative



17

Figure 13. Structure of ester **17**.

HPLC in two steps, along with ester **14**. ^{1}H NMR analysis of esters **14** and **17** elucidated that they were formed in 28% and 31% *de*, respectively (see the Supporting Information, Figure 16). The *E*/*Z* configuration at the 6-position of farnesol had little influence on the stereoselectivity of the reductive-deuteration reaction.

Yamakawa et al. reported that CH···π interactions are important for asymmetric hydrogen transfer in solution.[51] A better understanding of CH···π and, therefore, aromatic CH···π interactions is crucial for understanding the stereoselectivity of reactions.

Conclusions

MβNP salt **8** and MαNP salt **9** formed methoxy-group-assisted salt bridges in crystals. The conformation of the MβNP anion was significantly different from that of the MαNP anion. The methyl group was perpendicular to the naphthyl plane in the MβNP anion and the 2-naphthy group acted as a C−H acceptor. Conversely, the methyl group was in the naphthyl plane in the MαNP anion and the 1-naphthyl group acted as a C−H donor. In both salts, the methyl groups at the chiral centers of the ammonium cations were in the opposite direction of the carboxylate anions. The networks of strong salt bridges bound the carboxylate and ammonium groups to form the 2_1 columns. Acids **1** and **2** can be used to effectively extend the range of crystallizable amines in the preparation of salts. The distance between 1-naphthyl- and *p*-tolyl groups was shorter than the corresponding distance between 1-naphthyl- and phenyl groups. This suggested that the crystalline MαNP salts can be used to clarify the properties of the aromatic CH···π interactions. (*S*)-**13** was prepared by reductive deuteration with the

BINOL-modified agent, originally developed by Noyori.[36,37] The prochiral methylene protons at the 1-position of MαNP ester **15** were unambiguously assigned by comparing with that of deuterated ester **14**. In addition, the conformational model of the MαNP ester prepared from primary alcohol was elucidated. This demonstrates the utility of the MαNP method in determining the stereochemistry of primary terpene alcohols containing a deuterium atom at the 1-position. 2-Aryl-2 methoxypropanoic acids showed potential for use in the development of single-enantiomer biofunctional molecules, agrochemicals, and pharmaceuticals.

Experimental Section

General

NMR spectroscopy was performed on Bruker Avance 800 and Avance 500 spectrometers (Bruker BioSpin, Rheinstetten, Germany) that were equipped with cryoprobes. ^{13}C NMR spectra were obtained with ^{1}H composite pulse decoupling. IR spectra were recorded on an FTIR-8200 spectrophotometer (Shimadzu, Kyoto, Japan) with a KBr cell. MS data were obtained on an Apex 70e ESI-FTICR MS instrument (Bruker Daltonics, Bremen, Germany) in positive-ion mode. HPLC was performed on LC10AT VP systems (Shimadzu) that were equipped with a UV or a photodiode array detector. A Kusano C.I.G. pre-packed Si-5 column (100 mm × 22 mm I.D., Kusano, Tokyo, Japan) and a capcell pak C18 AG120 column (250 mm × 20 mm I.D., Shiseido, Tokyo, Japan) were used for preparative HPLC.

X-ray crystallography

Single crystals of salts **8** (0.400 mm × 0.100 mm × 0.100 mm) and **9** (0.200 mm × 0.100 mm × 0.050 mm) were covered by paraffin oil and mounted onto a glass fiber. All data were collected at 123 K on a Rigaku Mercury CCD detector with monochromatic $Mo_{K\alpha}$ radiation, operating at 50 kV/40 mA. Data were processed on a PC by using CrystalClear Software (Rigaku, Tokyo, Japan). Structures were solved by using direct methods and refined by full-matrix least-squares methods on F^2 (SHELXL-97).

CCDC 871215 (salt **8**) and CCDC 871216 (salt **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

*Preparation of salt **8***

A mixture of compounds *rac*-**2** (77.5 mg, 337 μmol) and (*R*)-**6** (41.3 mg, 341 μmol) was dissolved in MeOH/$CHCl_3$ (1:1, v/v, 6 mL). The solution was partially concentrated under vacuum in a water bath at 45 °C. The solution was allowed to stand in a refrigerator. After removal of the mother liquor from the mixture, the crystals were washed with cold EtOH (about 0.5 mL) to afford crude salt **8**[28] (52.8 mg, 150 μmol) in 45% yield. The same recrystallization procedure was then repeated twice at RT to give needle-like crystals. Finally, salt **8** was recrystallized from EtOH/water (19:1, v/v) to give colorless crystals that were used for X-ray crystallography.

*(R)-1-Phenylethylammonium (R)-2-methoxy-2-(2-naphthyl)propanoate (**8**)*

M.p. 134 °C; elemental analysis calcd (%) for $C_{22}H_{25}NO_3$: C 75.19, H 7.17, N 3.99; found: C 75.06, H 7.15, N 3.87.

*Preparation of salt **9***

A mixture of compounds (*R*)-**1** (30.0 mg, 130 μmol) and (*R*)-**7** (24.4 mg, 180 μmol) was dissolved in MeOH/$CHCl_3$ (2:1, v/v, 3 mL). The solution was partially concentrated under vacuum in a water bath at 45 °C. The solution was allowed to stand at RT to give colorless crystals of salt **9** (28.9 mg, 79 μmol) in 61% yield.

*(R)-1-(p-Tolyl)ethylammonium (R)-2-methoxy-2-(1-naphthyl)propanoate (**9**)*

M.p. 157 °C; elemental analysis calcd (%) for $C_{23}H_{27}NO_3$: C 75.59, H 7.45, N 3.83; found: C 75.15, H 7.65, N 3.80.

*Preparation of (2E,6E)-farnesal (**11**)*

A mixture of (2*E*,6*E*)-farnesol **10** (24.9 mg, 112 μmol, Sigma–Aldrich, St. Louis, Missouri, USA) and activated MnO_2 (519.0 mg, 5.97 mmol, Sigma–Aldrich) was stirred in dry *n*-hexane for 3 h at 0 °C. The mixture was directly purified by column chromatography on silica gel (Supelco, Discovery DSC-Si SPE tube, 2 g, Sigma–Aldrich). The column was eluted with *n*-hexane/CH_2Cl_2. The eluent was concentrated in vacuo to give aldehyde **11** (20.0 mg, 90.8 μmol) in 81% yield. Aldehyde **11** was kept in *n*-hexane under an argon atmosphere at −30 °C and used in the next reaction without characterization.

*Preparation of (S)-(2E,6E)-(1-$^2H_1$)farnesol ((S)-**13**)*

Noyori et al. originally reported the preparation of compound (*R*)-**13** (88% *ee*) from (2*E*,6*E*)-(1-^{2}H)farnesal (**12**) with (*R*)-BINAL-H at −100 °C in 91% yield.[36,37] This reaction was modified as follows: A solution of (*R*)-BINAL-D was prepared from the reaction of $LiAlD_4$ (2.2 mL, 1.0 mol L^{-1} in THF, uncorrected value, Sigma–Aldrich), a solution of EtOH (140 μL, 2.4 mmol) in THF (2 mL), and a solution of (*R*)-binaphthol (626.7 mg, 2.19 mmol, Tokyo Kasei, Tokyo, Japan) in THF (4 mL). Subsequently, the solution of (*R*)-BINAL-D was used directly in the reductive deuteration of a solution of aldehyde **11** (155.6 mg, 706 μmol) in THF (1 mL) to afford compound (*S*)-**13**[52] (88.5 mg, 396 μmol, 83% *ee* (see below)) in 56% yield. The reaction time was 2 h and the reaction temperature was −72 °C (dry-ice/EtOH bath). Compound (*S*)-**13** was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2, 2:1 to 1:1).

*(S)-(2E,6E)-(1-$^2H_1$)Farnesol ((S)-**13**)*

$[\alpha]_D^{29} = +0.54$ ($c = 3.0$, cyclopentane); ^{1}H NMR (800 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 5.42$ (br d, $J = 7$ Hz, 1H), 5.11 (tsext, $J = 7$, 1 Hz, 1H), 5.09 (tsept, $J = 7$, 1 Hz, 1H), 4.13 (m, 1H), 2.12 (br q, $J = 7$ Hz, 2H), 2.06 (br q, $J = 7$ Hz, 2H), 2.04 (br t, $J = 7$ Hz, 2H), 1.98 (br t, $J = 7$ Hz, 2H), 1.69 (br d, $J = 1$ Hz, 3H), 1.68 (br d, $J = 1$ Hz, 3H), 1.60 (br s, 3H), 1.60 (br s, 3H), 1.12 ppm (br d, $J = 5$ Hz, 1H; this coupling constant suggested free rotation of the primary hydroxy group[53]); ^{13}C NMR (201 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 139.94$, 135.38, 131.36, 124.32, 123.78, 123.27, 59.09 (t, $J = 22$ Hz), 39.70, 39.55, 26.72, 26.30, 25.70, 17.70, 16.29, 16.01 ppm; IR (KBr, $CHCl_3$): $\tilde{\nu} = 3612$, 3448, 3009, 2968, 2918, 2856, 1665, 1448, 1383, 1107, 986, 934, 891, 837 cm^{-1}; HRMS (ESI-FTICR): *m*/*z* calcd for $C_{15}H_{25}ODNa^+$: 246.1939 $[M+Na]^+$; found: 246.1939.

*Preparation of ester **14***

Ester **14** (9.5 mg, 22 μmol) was prepared from compounds (*S*)-**13** (4.9 mg, 22 μmol) and (*S*)-**1** (34.7 mg, 151 μmol) with EDC·HCl (119.8 mg, 625 μmol), DMAP (99.2 mg, 812 μmol), and CH_2Cl_2 (0.4 mL) in 99% yield. The reaction time was 18 h. The crude product was purified by HPLC on a pre-packed Si-5 column (*n*-hexane/EtOAc). For details, see references [6,8].

*(S)-(2E,6E)-3,7,11-Trimethyl(1-$^2H_1$)-2,6,10-dodecatrienyl (S)-2-methoxy-2-(1-naphthyl)propanoate (**14**)*

^{1}H NMR (800 MHz, $CDCl_3$, 25 °C, $CHCl_3$; see the Supporting Information): $\delta = 8.37$ (m, 1H), 7.84 (m, 1H), 7.83 (br d, $J = 8$ Hz, 1H), 7.60 (dd, $J = 7$ and 1 Hz, 1H), 7.47 (m, 1H), 7.46 (m, 1H), 7.45 (dd, $J = 8$ and 7 Hz, 1H), 5.13 (br d, $J = 7$ Hz, 1H), 5.07 (tsept, $J = 7$ and 1 Hz, 1H), 5.02 (tsext, $J = 7$ and 1 Hz, 1H), 4.60 (br d, $J = 7$ Hz, 0.083H; ($R_{alcohol}$,S_{acid})-diastereomer), 4.52 (br d, $J = 7$ Hz, 0.917H), 3.09 (s, 3H), 2.04 (br q, $J = 7$ Hz, 2H), 1.98 (s, 3H), 1.96 (m, 2H), 1.95 (br t, $J = 7$ Hz, 2H), 1.89 (br t, $J = 7$ Hz, 2H), 1.67 (br d, $J = 1$ Hz, 3H), 1.59 (br s, 3H), 1.55 (br s, 3H), 1.47 ppm (br s, 3H); ^{13}C NMR (201 MHz, $CDCl_3$, 25 °C, TMS; see the

Supporting Information): δ=174.06, 142.91, 135.34, 135.27, 134.11, 131.33, 131.32, 129.42, 128.66, 126.34, 125.63, 125.63, 125.28, 124.67, 124.31, 123.65, 117.63, 81.64, 61.96 (t, J=22 Hz), 50.97, 39.67, 39.36, 26.71, 26.12, 25.70, 21.89, 17.70, 16.34, 15.98 ppm; IR (KBr, $CHCl_3$): $\tilde{\nu}$= 3011, 2934, 2855, 1732, 1508, 1456, 1339, 1258, 1136 cm^{-1}; HRMS (ESI-FTICR): m/z calcd for $C_{29}H_{37}O_3DNa^+$: 458.2776 $[M+Na]^+$; found: 458.2776.

*Preparation of ester **15***

Ester **15** (33.9 mg, 78 μmol) was prepared from the reaction of compounds (2*E*,6*E*)-farnesol **10** (42.3 mg, 190 μmol) and (*S*)-**1** (24.3 mg, 106 μmol) with EDC·HCl (92.7 mg, 484 μmol), DMAP (96.4 mg, 789 μmol), and CH_2Cl_2 (0.5 mL) in 74% yield. The reaction time was 67 h. See above for details.

*(2E,6E)-3,7,11-Trimethyl-2,6,10-dodecatrienyl (S)-2-methoxy-2-(1-naphthyl)propanoate (**15**)*

$[\alpha]_D^{27}$=+11.2 (c=0.339, EtOH); ^{1}H NMR (800 MHz, $CDCl_3$, 25°C, TMS; see the Supporting Information): δ=8.37 (m, 1H), 7.84 (m, 1H), 7.83 (brd, J=8 Hz, 1H), 7.61 (dd, J=7 and 1 Hz, 1H), 7.46 (m, 1H), 7.46 (m, 1H), 7.45 (dd, J=8 and 7 Hz, 1H), 5.14 (tsext, J=7 and 1 Hz, 1H), 5.08 (tsept, J=7 and 1 Hz, 1H), 5.02 (tsext, J=7 and 1 Hz, 1H), 4.62 (brdd, J=12 and 7 Hz, 1H), 4.54 (brdd, J=12 and 7 Hz, 1H), 3.09 (s, 3H), 2.04 (brq, J=7 Hz, 2H), 1.99 (s, 3H), 1.96 (m, 2H), 1.95 (brt, J=7 Hz, 2H), 1.89 (brt, J=7 Hz, 2H), 1.68 (brd, J=1 Hz, 3H), 1.60 (brs, 3H), 1.56 (brs, 3H), 1.47 ppm (brs, 3H); ^{13}C NMR (201 MHz, $CDCl_3$, 25°C, TMS; see the Supporting Information): δ=174.10, 142.85, 135.32, 135.16, 134.06, 131.34, 131.29, 129.44, 128.65, 126.35, 125.66, 125.64, 125.24, 124.67, 124.28, 123.62, 117.64, 81.57, 62.26, 50.94, 39.66, 39.34, 26.67, 26.08, 25.72, 21.83, 17.70, 16.33, 15.97 ppm; IR (KBr, $CHCl_3$): $\tilde{\nu}$=3011, 2934, 2856, 1732, 1452, 1377, 1259, 1134, 937 cm^{-1}; HRMS (ESI-FTICR): m/z calcd for $C_{29}H_{38}O_3Na^+$: 457.2713 $[M+Na]^+$; found: 457.2715.

*Preparation of ester **17***

(*R*)-BINAL-D was prepared from $LiAlD_4$ (2.2 mL, 1.0 mol L^{-1} in THF), EtOH (2.2 mL, 1 mol L^{-1} in THF), and (*R*)-binaphthol (621 mg, 2.17 mmol). (1-$^2H_1$)Farnesol (mixture of *E*/*Z* isomers, 38.2 mg, 171 μmol) was obtained from the reaction of farnesal (mixture of *E*/*Z* isomers, 168.7 mg, 766 μmol, Sigma–Aldrich) in THF (1 mL) with the solution of (*R*)-BINAL-D in 22% yield. The reaction time was 2 h and the reaction temperature was −72°C. For details, see references [36,37].

Then, (1-$^2H_1$)farnesol (mixture of *E*/*Z* isomers, 19 mg, 85 μmol) was acylated with compound (*S*)-**1** (49.6 mg, 215 μmol) by using EDC·HCl (85.1 mg, 444 μmol), DMAP (88.6 mg, 725 μmol), and CH_2Cl_2 (0.5 mL) to give a crude mixture of MαNP esters (44.9 mg). The reaction time was 19 h. Considering the retention time of ester **15**, the crude products were purified by preparative HPLC (pre-packed Si-5 column, *n*-hexane/EtOAc 91:9, flow rate: 3 mL min^{-1}, UV detection: 315 nm) to give a mixture of esters **14** and **17** (61:39, 27.2 mg, 62 μmol). Finally, esters **14** and **17** (1 mg of each) were obtained by reversed-phase preparative HPLC (capcell pak C18 AG120 column, MeCN/water 94:6, flow rate: 4 mL min^{-1}, UV detection: 280 nm). The retention times of esters **14** and **17** were 38.89 min and 37.58 min, respectively. ^{1}H NMR analysis elucidated that esters **14** and **17** were formed in 28% and 31% *de*, respectively. The stereochemistry of ester **17** and the ($R_{alcohol}$,S_{acid})-diastereomer were determined from the ^{1}H NMR chemical shifts in the 1-positions (δ=4.52 ppm and 4.60 ppm, respectively).

*(S)-(2E,6Z)-3,7,11-Trimethyl(1-$^2H_1$)-2,6,10-dodecatrienyl (S)-2-methoxy-2-(1-naphthyl)propanoate (**17**)*

^{1}H NMR (800 MHz, $CDCl_3$, 25°C, $CHCl_3$, see the Supporting Information): δ=8.36 (m, 1H), 7.84 (m, 1H), 7.83 (brd, J=8 Hz, 1H), 7.61 (dd, J=7 and 1 Hz, 1H), 7.47 (m, 1H), 7.46 (m, 1H), 7.45 (m, 1H), 5.13 (brd, J=7 Hz, 1H), 5.09 (tsept, J=7 and 1 Hz, 1H), 5.02 (brt, J=7 Hz, 1H), 4.60 (brd, J=7 Hz, 0.344H; ($R_{alcohol}$,S_{acid})-diastereomer), 4.52 (brd, J= 7 Hz, 0.656H), 3.09 (s, 3H), 2.02 (brq, J=7 Hz, 2H), 1.99 (m, 2H), 1.98 (s, 3H), 1.96 (m, 2H), 1.88 (brt, J=7 Hz, 2H), 1.68 (brd, J=1 Hz, 3H), 1.66 (brq, J=1 Hz, 3H), 1.59 (brs, 3H), 1.47 ppm (brs, 3H); ^{13}C NMR (201 MHz, $CDCl_3$, 25°C, $CDCl_3$, see the Supporting Information): δ= 174.09, 142.83, 135.45, 135.14, 134.04, 131.60, 131.27, 129.43, 128.63, 126.34, 125.65, 125.63, 125.21, 124.65, 124.39, 124.22, 117.60, 81.55, 61.95 (t, J=22 Hz), 50.92, 39.62, 31.90, 26.53, 25.89, 25.74, 23.35, 21.82, 17.64, 16.28 ppm; IR (KBr, $CHCl_3$): $\tilde{\nu}$=2932, 2855, 1734, 1456, 1375, 1259, 1136 cm^{-1}; HRMS (ESI-FTICR): m/z calcd for $C_{29}H_{37}O_3DNa^+$: 458.2776 $[M+Na]^+$; found: 458.2778.

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FULL PAPER

Crystal Engineering

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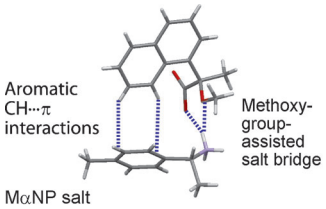
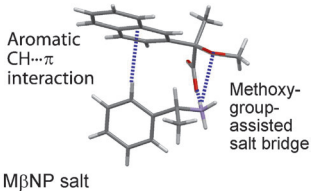
Naphthyl Groups in Chiral Recognition: Structures of Salts and Esters of 2-Methoxy-2-naphthylpropanoic Acids





Princess and the PEA: The crystal structures of the MαNP and MβNP salts were determined by X-ray crystallography. The 1-naphthyl group of the MαNP anion and the 2-naphthyl group of the MβNP anion acted as a C–H donor and -acceptor, respectively.