Electronic Supplementary Information

New synthetic routes to optically active α-quaternary α-aryl amino acid derivatives via the diastereoselective Stevens and Sommelet–Hauser rearrangements

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Determination of the absolute configuration of 8b

The absolute configuration of **8b** at α-position was determined as the *R* by a single crystal X-ray diffraction. Recrystallization of **8b** from *n*-heptane gave a single crystal which was suitable for crystallographic analysis.

Crystal data of 8b: $C_{36}H_{51}NO_4$, *MW* = 561.80; *orthorhombic*; space group $P2_12_12_1$ (#19); a = 9.2925(1) Å, b = 12.9908(2) Å, c = 28.1110(4) Å; V = 3393.49(9) Å^3; Z = 4; D_{calcd} = 1.100 g/cm^3; μ = 0.70 cm^{-1}; $2\theta_{max}$ = 51.4°; T = 296 K; R_1 ($I > 2\sigma(I)$) = 0.057; wR_2 (all data) = 0.123; GOF = 1.23 for 6437 reflections and 371 parameters. The absolute structure was determined based on Flack parameter, 0.07(10), refined using 2792 Friedel pairs.

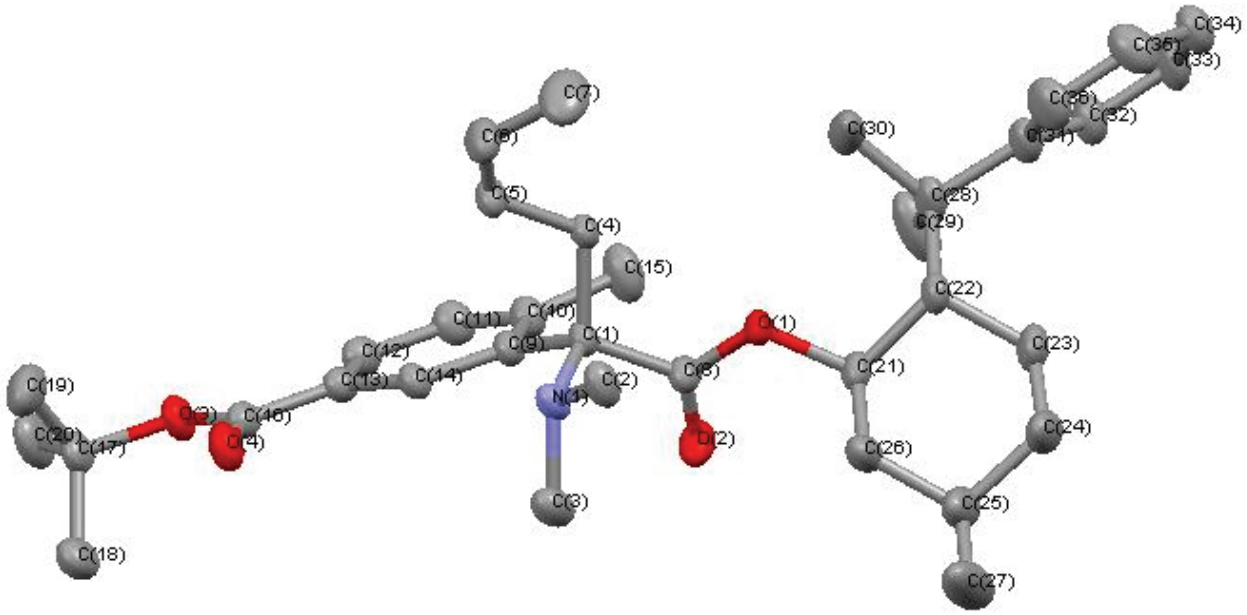
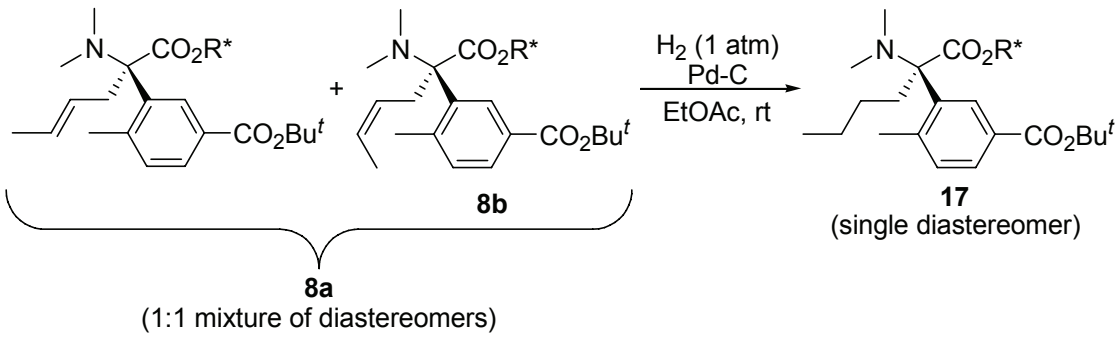


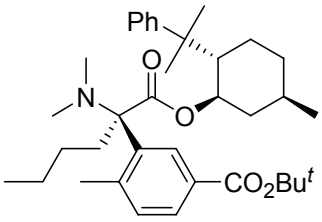
Figure 1. Molecular structure of **8b** (hydrogen atoms are omitted for cleanly)

Determination of the absolute configuration of 8a

Hydrogenation of **8a** afforded the corresponding reduced compound **17** as a single stereoisomer. Thus, **8a** was found to be a 1:1 mixture of *E*- and *Z*-isomer. The absolute configuration of **8a** at α-position was determined as the *R* because the absolute configuration of **8b** was determined as the *R* by a single crystal X-ray diffraction.



A mixture of **8a** (75 mg, 0.13 mmol) and palladium on activated carbon (loading: 10 wt. %, 3 mg) in ethyl acetate (1.3 mL) was stirred for 3 h at room temperature under a hydrogen atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by chromatography on silica gel (hexane/ethyl acetate = 15:1 to 10:1 as eluent) to afford **17** (72.3 mg, 99% yield) as a white solid.

(2*R*)-2-(5'-*tert*-Butoxycarbonyl-2'-methylphenyl)-2-dimethylaminohexanoic acid (–)-8-phenylmenthol ester (17): 

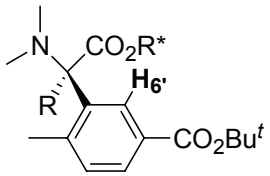
white solid; mp = 53–56 °C; $[\alpha]^{21}_{589}$ = 11.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.26 (1H, s, Ar-H), 7.72 (1H, dd, *J* = 7.8, 1.1 Hz, Ar-H), 7.38-7.22 (4H, m, Ar-H), 7.21-7.09 (2H, m, Ar-H), 4.99 (1H, td, *J* = 10.5, 3.8 Hz, COOCH), 2.34 (6H, s, $(CH_3)_2$N), 2.30 (3H, s, Ar-CH_3), 2.24-1.96 (4H, m, 3-H and 8-Ph-Men-H), 1.69-0.67 (5H, m, 8-Ph-Men-H), 1.59 (9H, s, *t*-Bu), 1.44 (3H, s, 8-Ph-Men-CH_3), 1.27 (3H, s, 8-Ph-Men-CH_3), 0.87 (3H, d, *J* = 5.9 Hz, 8-Ph-Men-CH_3), 0.74 (3H, t, *J* = 7.2 Hz, 6-H), 0.59-0.38 (1H, m, 8-Ph-Men-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 167.8, 166.4, 151.1, 141.0, 139.2, 131.7, 130.6, 128.5, 128.1, 127.3, 125.5 (3C), 80.4, 77.1, 71.8, 50.1, 44.3, 40.3, 39.7, 34.5, 32.1, 31.5, 29.8, 28.2, 27.6, 25.0, 24.2, 22.8, 22.3, 21.9, 13.9; IR (film) 2952, 2868, 2792, 1710, 1606, 1570, 1454, 1390, 1368, 1296, 1256, 1210, 1162, 1142, 1092, 1048, 1030, 990, 956, 904, 848, 756, 700 cm^{-1}; Anal. Calcd for $C_{36}H_{53}NO_4$: C, 76.69; H, 9.47; N, 2.48. Found: C, 76.51; H, 9.68; N, 2.43.

Determination of the absolute configurations of rearrangement products (7a–7d, 8e, 13a–f)

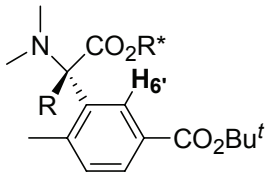
The absolute configurations at α-position of **7a**–**7d**, **8e**, and **13a** were determined by analogy to the ^{1}H NMR chemical shifts with that of such known compounds as (2*R*)-**8a**, (2*R*)-**8b**, (2*R*)-**17**, (2*R*)-**2**, and (2*S*)-**2**.[1] The data were summarized in Table 1. The chemical shifts of $H_{6'}$-proton were observed as > 8.00 ppm for the (2*R*)-isomer and < 8.00 ppm for the (2*S*)-isomer. The absolute configurations of **13b**–**f** were determined by the analogy to **13a**.

(1) E. Tayama, H. Kimura, *Angew. Chem. Int. Ed.,* 2007, **46**, 8869.

Table 1. Summarized data of ^{1}H NMR chemical shifts and coupling constants of the rearrangement products



(2*R*)-isomer



(2*S*)-isomer

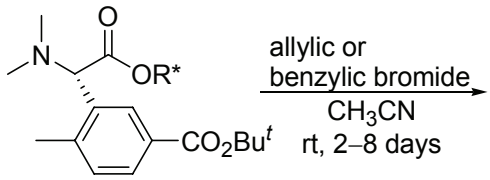
[R* = (–)-8-phenylmenthyl]

R	chemical shift and coupling constant of $H_{6'}$	
	(2*R*)-isomer	(2*S*)-isomer
(*E*)-$CH_2CH=CHCH_3$ (**8a**)[a]	8.18 (d, *J* = 1.4 Hz)	–
(*Z*)-$CH_2CH=CHCH_3$ (**8b**)[a]	8.24 (d, *J* = 1.9 Hz)	–
n-C_4H_9 (**17**)[a]	8.26 (s)	–
H (**2**)[a,b]	8.12 (d, *J* = 1.4 Hz)	7.77-7.72 (multiplet with other peak)
$CH(CH_3)CH=CH_2$ (**7a**)	8.14 (s)	–
$CH(CH_3)CH=CH_2$ (**7b**)	8.16 (s)	–
$CH_2CH=CH_2$ (**7c**)	8.21 (d, *J* = 1.9 Hz)	7.90 (d, *J* = 1.6 Hz)
$CH_2C(CH_3)=CH_2$ (**7d**)	8.17 (d, *J* = 1.9 Hz)	–
(*E*)-$CH_2CH=CHPh$ (**8e**)	8.25 (d, *J* = 1.6 Hz)	–
CH_3 (**13a**)	–	7.94 (d, *J* = 1.6 Hz)

[a] The absolute configurations were determined experimentally.

[b] The spectroscopic data were summarized in ref. 1.

Preparation of quaternary ammonium salts 6a–6e and 9



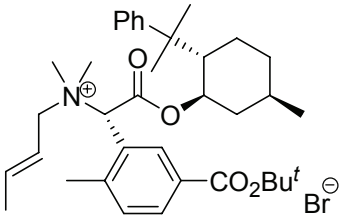
(2*S*)-**2**
[R* = (–)-8-phenylmenthyl]

6a–**6e**, **9**

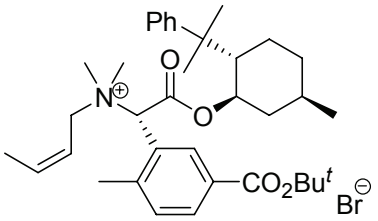
R = (*E*)-CH=$CHCH_3$ (**6a**), quant.
= (*Z*)-CH=$CHCH_3$ (**6b**), quant.
= $CH=CH_2$ (**6c**), 95%
= $C(CH_3)=CH_2$ (**6d**), 85%
= (*E*)-CH=CHPh (**6e**), 96%
= 4-CN-Ph (**9**), 97%

A mixture of (2*S*)-**2**[1] (1.0 equiv) and allylic bromide[2] or 4-cyanobenzyl bromide (3 equiv) in acetonitrile (0.2 M) was stirred for 2–8 days at room temperature. The resulting mixture was concentrated and the residue was purified by chromatography on silica gel (dichloromethane/methanol as eluent) to obtain quaternary ammonium salt **6a**–**6e**, **9** as a white solid.

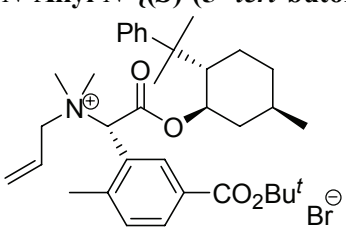
(2) (*E*)-Crotyl bromide was purchased from Aldrich (*E*/*Z* = 85:15). (*Z*)-Crotyl bromide (*E*/*Z* = 15:85) was prepared from 2-butyn-1-ol via hydrogenation and bromination, see: (a) N. A. LeBel, N. Balasubramanian, *J. Am. Chem. Soc.,* 1989, **111**, 3363; (b) P. Fristrup, T. Jensen, J. Hoppe, P.-O. Norrby, *Chem. Eur. J.,* 2006, **12**, 5352.

***N*-[(*E*)-But-2-en-1-yl]-*N*-{(*S*)-(5'-*tert*-butoxycarbonyl-2'-methylphenyl)[(–)-8-phenylmenthyloxycarbonyl] methyl}-*N*,*N*-dimethylammonium bromide (6a):** 

E/*Z* = 85:15 mixture of diastereomers; white solid; mp = 85–88 °C; $[\alpha]^{24}_{589}$ = 13.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.98 (1H, dd, *J* = 8.1, 1.6 Hz, Ar-H), 7.82 (1H, d, *J* = 1.6 Hz, Ar-H), 7.43 (1H, d, *J* = 8.1 Hz, Ar-H), 7.40-7.25 (5H, m, Ar-H), 6.48 (1H, dq, *J* = 15.0, 6.5 Hz, CH_2CH=C<u>H</u>CH_3), 5.76-5.60 (1H, m, CH_2C<u>H</u>=$CHCH_3$), 5.06 (1H, s, NCHCOO), 4.85 (1H, td, *J* = 10.7, 4.1 Hz, COOCH), 4.62-4.45 (2H, m, C<u>H</u>$_2$CH=$CHCH_3$), 3.44 (3H, s, CH_3N), 3.28 (3H, s, CH_3N), 2.52 (3H, s, Ar-CH_3), 1.95-1.77 (2H, m, 8-Ph-Men-H), 1.89 (3H, d, *J* = 6.5 Hz, CH_2CH=CHC<u>H</u>$_3$), 1.70-1.20 (3H, m, 8-Ph-Men-H), 1.56 (9H, s, *t*-Bu), 1.34 (3H, s, 8-Ph-Men-CH_3), 1.26 (3H, s, 8-Ph-Men-CH_3), 1.16-0.97 (1H, m, 8-Ph-Men-H), 0.78-0.60 (1H, m, 8-Ph-Men-H), 0.72 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3), 0.30 (1H, td, *J* = 12.0, 10.7 Hz, 8-Ph-Men-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 165.4, 164.0, 150.6, 145.4, 144.1, 132.7, 131.8, 130.9, 130.5, 128.2, 125.8, 125.7, 125.5, 116.6, 82.0, 78.4, 69.8, 65.3, 49.6, 48.4, 47.6, 39.7, 39.6, 33.9, 30.9, 28.0, 27.7, 26.5, 26.2, 21.4 (2C), 18.5; IR (film) 3416, 2956, 1732, 1714, 1612, 1476, 1454, 1392, 1370, 1304, 1278, 1264, 1216, 1166, 1138, 974, 948, 846, 732, 700 cm^{-1}; Anal. Calcd for $C_{36}H_{52}BrNO_4$: C, 67.28; H, 8.16; N, 2.18. Found: C, 67.25; H, 8.33; N, 2.17.

***N*-[(*Z*)-But-2-en-1-yl]-*N*-{(*S*)-(5'-*tert*-butoxycarbonyl-2'-methylphenyl)[(–)-8-phenylmenthyloxycarbonyl] methyl}-*N*,*N*-dimethylammonium bromide (6b):** 

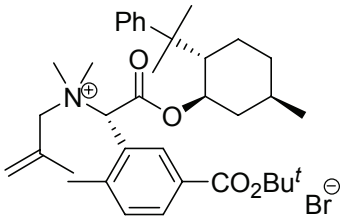
E/*Z* = 15:85 mixture of diastereomers; white solid; mp = 73–76 °C; $[\alpha]^{26}_{589}$ = 3.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.98 (1H, dd, *J* = 8.1, 1.6 Hz, Ar-H), 7.81 (1H, d, *J* = 1.6 Hz, Ar-H), 7.43 (1H, d, *J* = 8.1 Hz, Ar-H), 7.40-7.24 (5H, m, Ar-H), 6.33 (1H, dq, *J* = 10.7, 7.0 Hz, CH_2CH=C<u>H</u>CH_3), 5.77-5.62 (1H, m, CH_2C<u>H</u>=$CHCH_3$), 5.13 (1H, s, NCHCOO), 4.86 (1H, td, *J* = 10.6, 4.3 Hz, COOCH), 4.68 (1H, dd, *J* = 12.7, 7.6 Hz, C<u>H</u>$_2$CH=$CHCH_3$), 4.55 (1H, dd, *J* = 12.7, 8.6 Hz, C<u>H</u>$_2$CH=$CHCH_3$), 3.45 (3H, s, CH_3N), 3.29 (3H, s, CH_3N), 2.51 (3H, s, Ar-CH_3), 1.99-1.77 (2H, m, 8-Ph-Men-H), 1.92 (3H, dd, *J* = 7.0, 1.5 Hz, CH_2CH=CHC<u>H</u>$_3$), 1.75-1.20 (3H, m, 8-Ph-Men-H), 1.56 (9H, s, *t*-Bu), 1.34 (3H, s, 8-Ph-Men-CH_3), 1.24 (3H, s, 8-Ph-Men-CH_3), 1.19-1.10 (1H, m, 8-Ph-Men-H), 0.80-0.61 (1H, m, 8-Ph-Men-H), 0.73 (3H, d, *J* = 6.2 Hz, 8-Ph-Men-CH_3), 0.31 (1H, td, *J* = 11.7, 10.6 Hz, 8-Ph-Men-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 165.5, 163.9, 150.8, 145.4, 140.5, 132.7, 131.8, 131.0, 130.4, 128.2, 125.7, 125.6, 125.5, 115.7, 81.9, 78.5, 70.0, 59.4, 49.4, 48.7, 47.5, 39.6, 39.5, 33.9, 30.9, 28.2, 28.0, 26.4, 25.8, 21.41, 21.38, 14.4; IR (film) 2956, 2924, 1732, 1612, 1478, 1454, 1392, 1368, 1304, 1276, 1264, 1218, 1166, 1138, 1092, 1030, 994, 974, 928, 846, 730, 700 cm^{-1}; Anal. Calcd for $C_{36}H_{52}BrNO_4$: C, 67.28; H, 8.16; N, 2.18. Found: C, 67.06; H, 8.37; N, 2.11.

***N*-Allyl-*N*-{(*S*)-(5'-*tert*-butoxycarbonyl-2'-methylphenyl)[(–)-8-phenylmenthyloxycarbonyl]methyl}-*N*,*N*-dimethylammonium bromide, monohydrate (6c):** 

white solid; mp = 86–89 °C; $[\alpha]^{24}_{589}$ = 13.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.99 (1H, dd, *J* = 7.9, 1.4 Hz, Ar-H), 7.81 (1H, d, *J* = 1.4 Hz, Ar-H), 7.43 (1H, d, *J* = 7.9 Hz, Ar-H), 7.40-7.25 (5H, m, Ar-H), 6.22-5.93 (2H, m, CH_2C<u>H</u>=C<u>H</u>$_2$), 5.83 (1H, dd, *J* = 9.3, 2.0

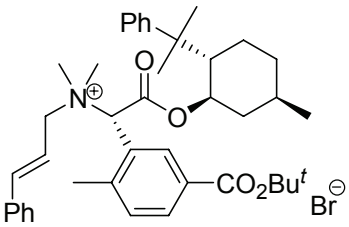
Hz, $CH_2CH=C\underline{H}_2$), 5.05 (1H, s, NCHCOO), 4.85 (1H, td, *J* = 10.6, 4.3 Hz, COOCH), 4.61 (2H, d, *J* = 6.5 Hz, $C\underline{H}_2CH=CH_2$), 3.49 (3H, s, CH_3N), 3.32 (3H, s, CH_3N), 2.52 (3H, s, Ar-CH_3), 1.91-1.77 (2H, m, 8-Ph-Men-H), 1.73-1.19 (3H, m, 8-Ph-Men-H), 1.56 (9H, s, *t*-Bu), 1.33 (3H, s, 8-Ph-Men-CH_3), 1.24 (3H, s, 8-Ph-Men-CH_3), 1.19-0.98 (1H, m, 8-Ph-Men-H), 0.80-0.60 (1H, m, 8-Ph-Men-H), 0.72 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3), 0.31 (1H, td, *J* = 11.6, 10.6 Hz, 8-Ph-Men-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 165.4, 163.9, 150.7, 145.4, 132.8, 131.9, 131.3, 130.9, 130.5, 128.2, 125.8, 125.5 (3C), 123.9, 82.0, 78.6, 70.1, 65.5, 49.5, 48.8, 47.9, 39.7, 39.6, 33.9, 30.9, 28.0 (4C), 26.4, 26.0, 21.4 (2C); IR (film) 3416, 2956, 2924, 1734, 1712, 1612, 1478, 1456, 1392, 1370, 1304, 1278, 1264, 1218, 1168, 1138, 1092, 946, 848, 732, 700 cm^{-1}; Anal. Calcd for $C_{35}H_{52}BrNO_5$: C, 65.00; H, 8.10; N, 2.17. Found: C, 65.05; H, 8.00; N, 2.07.

***N*-{(*S*)-(5'-*tert*-Butoxycarbonyl-2'-methylphenyl)[(–)-8-phenylmenthyloxycarbonyl]methyl}-*N*,*N*-dimethyl-*N*-**



(2-methylprop-2-en-1-yl)ammonium bromide, monohydrate (6d): white solid; mp = 61–64 °C; $[\alpha]^{24}_{589}$ = 9.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.99 (1H, dd, *J* = 8.1, 1.4 Hz, Ar-H), 7.82 (1H, d, *J* = 1.4 Hz, Ar-H), 7.46 (1H, d, *J* = 8.1 Hz, Ar-H), 7.40-7.25 (5H, m, Ar-H), 5.64 (2H, s, $CH_2(CH_3)C=C\underline{H}_2$), 5.50 (1H, s, NCHCOO), 4.84 (1H, td, *J* = 10.7, 4.1 Hz, COOCH), 4.68 (1H, d, *J* = 12.2 Hz, $C\underline{H}_2(CH_3)C=CH_2$), 4.50 (1H, d, *J* = 12.2 Hz, $C\underline{H}_2(CH_3)C=CH_2$), 3.46 (3H, s, CH_3N), 3.34 (3H, s, CH_3N), 2.68 (3H, s, Ar-CH_3), 2.10 (3H, s, $CH_2(C\underline{H}_3)C=CH_2$), 1.90-1.72 (2H, m, 8-Ph-Men-H), 1.65-1.21 (3H, m, 8-Ph-Men-H), 1.57 (9H, s, *t*-Bu), 1.35 (3H, s, 8-Ph-Men-CH_3), 1.29 (3H, s, 8-Ph-Men-CH_3), 1.14-0.95 (1H, m, 8-Ph-Men-H), 0.80-0.58 (1H, m, 8-Ph-Men-H), 0.72 (3H, d, *J* = 6.8 Hz, 8-Ph-Men-CH_3), 0.33 (1H, td, *J* = 11.9, 10.7 Hz, 8-Ph-Men-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 165.8, 164.0, 150.1, 146.1, 132.9, 132.5, 131.8, 131.0, 130.3, 129.8, 128.2, 125.9, 125.8, 125.7, 82.0, 78.7, 71.1, 68.3, 49.7, 49.5, 47.8, 39.9, 39.6, 33.9, 30.9, 28.0, 27.5, 27.2, 26.6, 24.4, 21.9, 21.4; IR (film) 3408, 2960, 1730, 1612, 1476, 1454, 1392, 1368, 1306, 1278, 1214, 1166, 1138, 1092, 1010, 974, 942, 846, 730, 700 cm^{-1}; Anal. Calcd for $C_{36}H_{54}BrNO_5$: C, 65.44; H, 8.24; N, 2.12. Found: C, 65.67; H, 8.36; N, 1.99.

***N*-{(*S*)-(5'-*tert*-Butoxycarbonyl-2'-methylphenyl)[(–)-8-phenylmenthyloxycarbonyl]methyl}-*N*,*N*-dimethyl-*N*-**

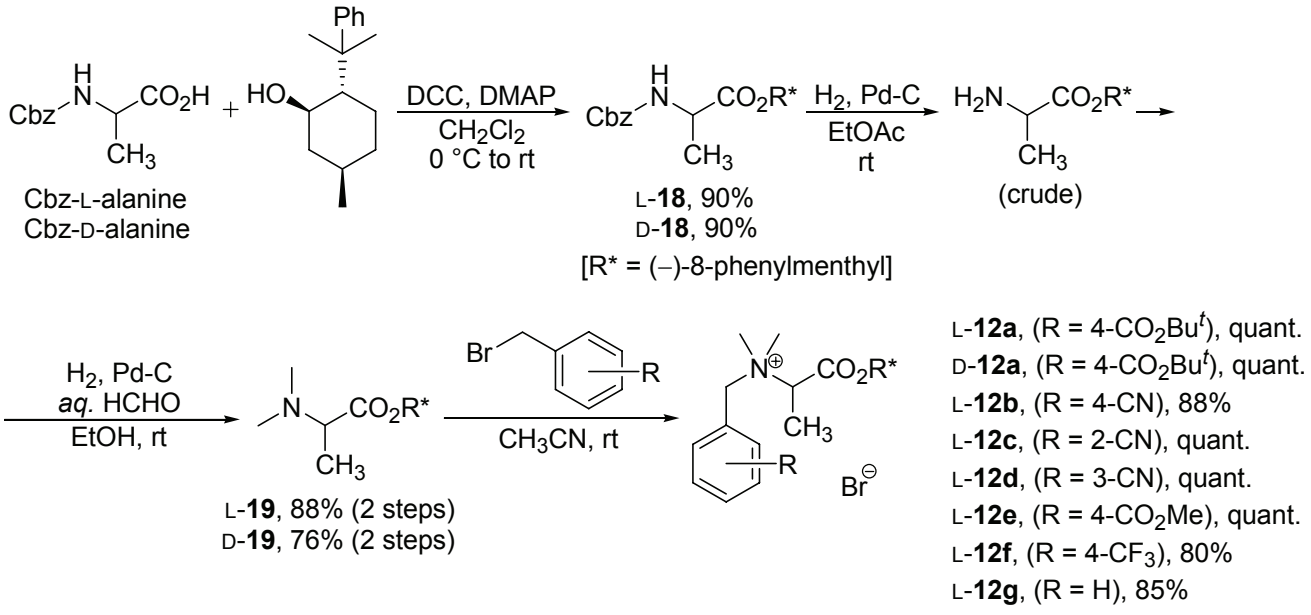


[(*E*)-3-phenylprop-2-en-1-yl]ammonium bromide (6e): white solid; mp = 86–88 °C; $[\alpha]^{26}_{589}$ = 22.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.99 (1H, dd, *J* = 8.1, 1.6 Hz, Ar-H), 7.84 (1H, d, *J* = 1.6 Hz, Ar-H), 7.58-7.50 (2H, m, Ar-H), 7.43 (1H, d, *J* = 8.1 Hz, Ar-H), 7.40-7.17 (9H, m, Ar-H and $CH_2CH=C\underline{H}Ph$), 6.42 (1H, dt, *J* = 15.7, 7.7 Hz, $CH_2C\underline{H}=CHPh$), 5.20 (1H, s, NCHCOO), 4.86 (1H, td, *J* = 10.7, 4.3 Hz, COOCH), 4.80 (2H, d, *J* = 7.7 Hz, $C\underline{H}_2CH=CHPh$), 3.52 (3H, s, CH_3N), 3.37 (3H, s, CH_3N), 2.56 (3H, s, Ar-CH_3), 1.94-1.74 (2H, m, 8-Ph-Men-H), 1.70-1.15 (3H, m, 8-Ph-Men-H), 1.57 (9H, s, *t*-Bu), 1.29 (3H, s, 8-Ph-Men-CH_3), 1.23 (3H, s, 8-Ph-Men-CH_3), 1.15-0.94 (1H, m, 8-Ph-Men-H), 0.81-0.60 (1H, m, 8-Ph-Men-H), 0.73 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3), 0.32 (1H, td, *J* = 12.0, 10.7 Hz, 8-Ph-Men-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 165.5, 164.0, 150.5, 145.5, 145.0, 134.6, 132.8, 131.8, 130.9, 130.4, 129.6, 128.8, 128.2, 127.5, 125.82, 125.81, 125.5, 113.5, 82.0, 78.6, 70.0, 65.8, 49.7, 48.7, 47.7, 39.7, 39.6, 33.9, 30.9, 28.0, 27.6, 26.5, 26.4, 21.6, 21.4; IR (film) 2956, 2928, 1732, 1612, 1476, 1452, 1392, 1370, 1304, 1278, 1264, 1218, 1166, 1138, 1092, 1030, 976, 948,

908, 846, 736, 700 cm^{-1}; Anal. Calcd for $C_{41}H_{54}BrNO_4$: C, 69.87; H, 7.72; N, 1.99. Found: C, 69.76; H, 7.83; N, 2.01.

***N*-{(*S*)-(5'-*tert*-Butoxycarbonyl-2'-methylphenyl)[(–)-8-phenylmenthyloxycarbonyl]methyl}-*N*-(4"-cyano--benzyl)-*N*,*N*-dimethylammonium bromide, monohydrate (9):** white solid; mp = 81–83 °C; $[\alpha]^{22}_{589}$ = 15.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.12 (2H, d, *J* = 8.2 Hz, Ar-H), 8.02 (1H, dd, *J* = 7.9, 1.5 Hz, Ar-H), 7.90 (1H, d, *J* = 1.5 Hz, Ar-H), 7.80 (2H, d, *J* = 8.2 Hz, Ar-H), 7.50 (1H, d, *J* = 7.9 Hz, Ar-H), 7.38-7.23 (5H, m, Ar-H), 6.06 (1H, s, NCHCOO), 5.58 (1H, br, CH_2Ar), 5.37 (1H, d, *J* = 11.9 Hz, CH_2Ar), 4.86 (1H, td, *J* = 10.8, 4.2 Hz, COOCH), 3.38 (3H, s, CH_3N), 3.21 (3H, s, CH_3N), 2.84 (3H, s, Ar-CH_3), 1.85-1.70 (2H, m, 8-Ph-Men-H), 1.66-1.22 (3H, m, 8-Ph-Men-H), 1.58 (9H, s, *t*-Bu), 1.38 (3H, s, 8-Ph-Men-CH_3), 1.36 (3H, s, 8-Ph-Men-CH_3), 1.08-0.94 (1H, m, 8-Ph-Men-H), 0.77-0.57 (1H, m, 8-Ph-Men-H), 0.72 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3), 0.37 (1H, td, *J* = 11.9, 10.8 Hz, 8-Ph-Men-H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.0, 164.1, 149.4, 146.8, 134.9, 133.1, 132.8, 132.0, 131.7, 131.0, 130.4, 128.2, 126.0, 125.9, 125.7, 117.6, 115.1, 82.1, 79.1, 71.5, 64.6, 50.0, 47.8, 46.2, 40.0, 39.7, 33.9, 30.9, 29.0, 28.0, 26.8, 26.6, 22.2, 21.4; IR (film) 3416, 2952, 2924, 2228, 1710, 1612, 1476, 1454, 1368, 1306, 1278, 1214, 1166, 1138, 1014, 974, 944, 846, 736, 700 cm^{-1}; Anal. Calcd for $C_{40}H_{53}BrN_2O_5$: C, 66.56; H, 7.40; N, 3.88. Found: C, 66.53; H, 7.30; N, 4.07.

Preparation of L- or D-alanine-derived quaternary ammonium salts 12a–g



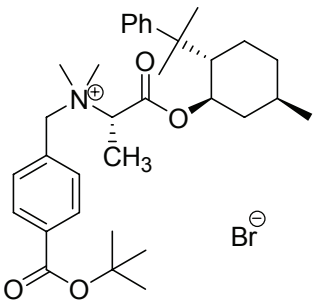
The following procedures are described for L-alanine derivative L-**12a**. Other derivatives (D-**12a**, L-**12b**–**g**) were prepared by the same procedures.

(Step 1) To a mixture of Cbz-L-alanine (0.70 g, 3.1 mmol), (–)-8-phenylmenthol[3] (0.61 g, 2.6 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (64 mg, 0.52 mmol) in dichloromethane (7 mL) was added a solution of *N*,*N*-dicyclohexylcarbodiimide (DCC) (0.59 g, 2.9 mmol) in dichloromethane (7 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and for 16 h at room temperature. The resulting mixture was filtered and the filtrate was concentrated. The residue was purified by chromatography on silica gel (hexane/ethyl acetate = 8:1 to 5:1 as eluent) to afford *N*-Cbz-L-alanine (–)-8-phenylmenthol ester (L-**18**) (1.03 g, 90% yield) as a colorless oil.

(Step 2) A mixture of L-**18** (1.03 g, 2.35 mmol) and palladium on activated carbon (loading: 10 wt. %, 50 mg) in ethyl acetate (8 mL) was stirred for 15 h at room temperature under a hydrogen atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated. The residue was dissolved in ethanol (12 mL) and 37 wt. % aqueous formaldehyde solution (1.9 mL). To the solution was added palladium on activated carbon (loading: 10 wt. %, 0.13 g) and the mixture was stirred for 48 h at room temperature under a hydrogen atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was concentrated to remove ethanol. The residue was diluted with water and extracted with ether. The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was purified by chromatography on silica gel (hexane/ethyl acetate = 4:1 to 2:1 as eluent) to give L-**19** (0.67 g, 86% yield) as a colorless oil.

(Step 3) A mixture of L-**19** (0.12 mg, 0.36 mmol) and (4-*tert*-butoxycarbonyl)benzyl bromide[1] (0.12 g, 0.44 mmol) in acetonitrile (1.8 mL) was stirred for 48 h at room temperature. The resulting mixture was concentrated and the residue was purified by chromatography on silica gel (dichloromethane/methanol = 20:1 to 5:1 as eluent) to obtain quaternary ammonium salt L-**12** (0.22 g, quant.) as a white solid.

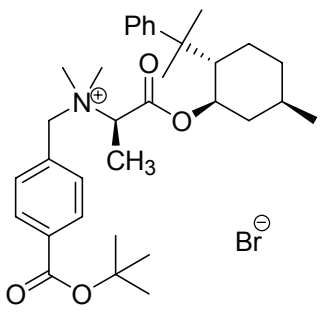
***N*-(4'-*tert*-Butoxycarbonylbenzyl)-*N*,*N*-dimethyl-*N*-{(1*S*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]} ammonium bromide, 0.5 hydrate (L-12a):**



white solid; mp = 97–100 °C; $[\alpha]^{25}_{589}$ = 5.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.07 (2H, d, *J* = 8.4 Hz, Ar-H), 7.72 (2H, d, *J* = 8.4 Hz, Ar-H), 7.16 (2H, d, *J* = 7.6 Hz, Ar-H), 6.98 (2H, t, *J* = 7.6 Hz, Ar-H), 6.76 (1H, t, *J* = 7.6 Hz, Ar-H), 5.39 (1H, d, *J* = 12.7 Hz, CH_2Ar), 5.17 (1H, d, *J* = 12.7 Hz, CH_2Ar), 4.85 (1H, td, *J* = 10.7, 4.3 Hz, COOCH), 3.46 (3H, s, CH_3N), 3.26 (3H, s, CH_3N), 3.18 (1H, q, *J* = 7.3 Hz, NCHCOO), 2.13 (1H, td, *J* = 11.3, 3.5 Hz, 8-Ph-Men-H), 1.96-1.09 (5H, m, 8-Ph-Men-H), 1.62 (9H, s, *t*-Bu), 1.61 (3H, d, *J* = 7.3 Hz, NCH($C\underline{H}_3$)COO), 1.24 (3H, s, 8-Ph-Men-CH_3), 1.14 (3H, s, 8-Ph-Men-CH_3), 1.04-0.83 (2H, m, 8-Ph-Men-H), 0.91 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.9, 164.6, 151.4, 134.3, 133.2, 130.8, 130.1, 127.7, 125.2, 125.0, 81.9, 77.8, 66.2, 65.3, 49.3, 48.7, 48.1, 40.9, 39.3, 34.1, 31.2, 29.9, 28.1, 26.2, 23.0, 21.6, 13.9; IR (film) 3432, 2964, 1718, 1614, 1476, 1454, 1416, 1392, 1368, 1294, 1240, 1206, 1164, 1118, 1020, 974, 954, 908, 842, 770, 730, 702 cm^{-1}; Anal. Calcd for $C_{33}H_{49}BrNO_{4.5}$: C, 64.80; H, 8.07; N, 2.29. Found: C, 64.60; H, 8.28; N, 2.36.

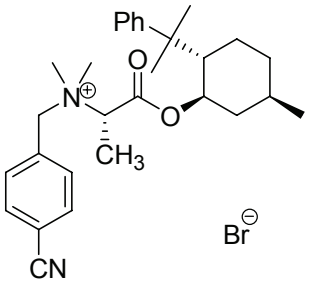
(3) O. Ort, *Org. Syn.,* 1987, **65**, 203.

***N*-(4'-*tert*-Butoxycarbonylbenzyl)-*N*,*N*-dimethyl-*N*-{(1*R*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]}**



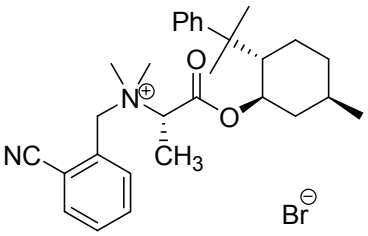
ammonium bromide, 0.5 hydrate (D-12a): white solid; mp = 90–94 °C; $[\alpha]^{25}_{589}$ = 74.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.03 (2H, d, *J* = 8.2 Hz, Ar-H), 7.65 (2H, d, *J* = 8.2 Hz, Ar-H), 7.24-7.09 (5H, m, Ar-H), 5.29 (1H, d, *J* = 12.8 Hz, CH_2Ar), 5.11 (1H, d, *J* = 12.8 Hz, CH_2Ar), 4.87 (1H, td, *J* = 10.8, 4.3 Hz, COOCH), 3.40 (3H, s, CH_3N), 3.18 (3H, s, CH_3N), 3.14 (1H, q, *J* = 6.9 Hz, NCHCOO), 2.16 (1H, td, *J* = 11.3, 3.0 Hz, 8-Ph-Men-H), 1.96-1.07 (5H, m, 8-Ph-Men-H), 1.64 (9H, s, *t*-Bu), 1.49 (3H, d, *J* = 6.9 Hz, NCH($C\underline{H}_3$)COO), 1.24 (3H, s, 8-Ph-Men-CH_3), 1.13 (3H, s, 8-Ph-Men-CH_3), 1.04-0.81 (2H, m, 8-Ph-Men-H), 0.88 (3H, d, *J* = 6.2 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.4, 164.6, 151.5, 134.2, 133.1, 130.6, 130.1, 128.0, 125.4, 125.0, 81.9, 78.4, 66.4, 65.2, 49.1, 49.0, 47.6, 41.0, 39.3, 34.0, 31.2, 29.9, 28.1, 26.1, 22.9, 21.6, 12.6; IR (film) 3416, 2960, 2924, 2868, 1714, 1476, 1458, 1418, 1370, 1296, 1266, 1206, 1166, 1120, 1022, 976, 952, 908, 842, 768, 732, 700 cm^{-1}; Anal. Calcd for $C_{33}H_{49}BrNO_{4.5}$: C, 64.80; H, 8.07; N, 2.29. Found: C, 64.69; H, 8.25; N, 2.36.

***N*-(4'-Cyanobenzyl)-*N*,*N*-dimethyl-*N*-{(1*S*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]}ammonium bromide,**



0.5 hydrate (12b): white solid; mp = 88–91 °C; $[\alpha]^{25}_{589}$ = 11.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.91 (2H, d, *J* = 8.2 Hz, Ar-H), 7.77 (2H, d, *J* = 8.2 Hz, Ar-H), 7.18 (2H, d, *J* = 7.6 Hz, Ar-H), 7.03 (2H, t, *J* = 7.6 Hz, Ar-H), 6.78 (1H, t, *J* = 7.6 Hz, Ar-H), 5.44 (1H, d, *J* = 12.7 Hz, CH_2Ar), 5.30 (1H, d, *J* = 12.7 Hz, CH_2Ar), 4.86 (1H, td, *J* = 10.6, 4.3 Hz, COOCH), 3.43 (3H, s, CH_3N), 3.25 (3H, s, CH_3N), 3.17 (1H, q, *J* = 7.3 Hz, NCHCOO), 2.21-2.03 (2H, m, 8-Ph-Men-H), 1.96-1.37 (3H, m, 8-Ph-Men-H), 1.65 (3H, d, *J* = 7.3 Hz, NCH($C\underline{H}_3$)COO), 1.34-0.82 (3H, m, 8-Ph-Men-H), 1.24 (3H, s, 8-Ph-Men-CH_3), 1.15 (3H, s, 8-Ph-Men-CH_3), 0.91 (3H, d, *J* = 6.8 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.7, 151.4, 134.2, 132.7, 131.8, 127.7, 125.1, 117.5, 114.7, 100.4, 77.9, 66.7, 64.3, 49.2, 48.9, 48.0, 40.8, 39.3, 34.0, 31.1, 29.8, 26.1, 23.1, 21.5, 13.8; IR (film) 3016, 2952, 2920, 2228, 1730, 1600, 1456, 1414, 1388, 1370, 1302, 1266, 1238, 1206, 1162, 1090, 1030, 972, 952, 908, 848, 818, 730, 700 cm^{-1}; Anal. Calcd for $C_{29}H_{40}BrN_2O_{2.5}$: C, 64.92; H, 7.51; N, 5.22. Found: C, 65.17; H, 7.54; N, 5.13.

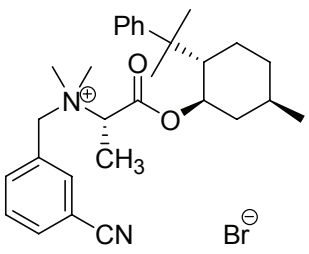
***N*-(2'-Cyanobenzyl)-*N*,*N*-dimethyl-*N*-{(1*S*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]}ammonium bromide,**



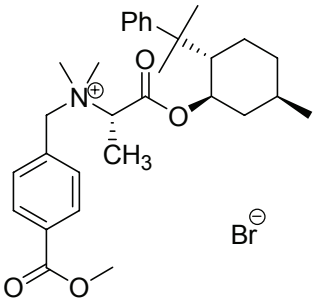
monohydrate (12c): white solid; mp = 76–79 °C; $[\alpha]^{26}_{589}$ = 5.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.60 (1H, d, *J* = 7.6 Hz, Ar-H), 7.89-7.78 (2H, m, Ar-H), 7.70 (1H, t, *J* = 7.6 Hz, Ar-H), 7.39-7.23 (4H, m, Ar-H), 7.15-7.04 (1H, m, Ar-H), 5.44 (1H, d, *J* = 12.7 Hz, CH_2Ar), 4.94 (1H, d, *J* = 12.7 Hz, CH_2Ar), 4.90 (1H, td, *J* = 10.8, 4.3 Hz, COOCH), 3.60 (1H, q, *J* = 7.3 Hz, NCHCOO), 3.36 (3H, s, CH_3N), 3.26 (3H, s, CH_3N), 2.21 (1H, td, *J* = 11.3, 3.4 Hz, 8-Ph-Men-H), 1.97-1.83 (1H, m, 8-Ph-Men-H), 1.81-1.67 (1H, m, 8-Ph-Men-H), 1.76 (3H, d, *J* = 7.3 Hz, NCH($C\underline{H}_3$)COO), 1.60-1.40 (1H, m, 8-Ph-Men-H), 1.38-0.80 (4H, m, 8-Ph-Men-H), 1.31 (3H, s, 8-Ph-Men-CH_3), 1.21 (3H, s, 8-Ph-Men-CH_3), 0.92 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.5, 151.7, 136.8, 134.1, 133.8, 131.6, 129.7, 128.1 (2C), 125.3

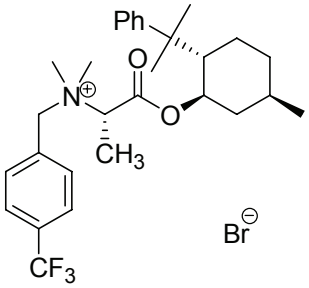
(3C), 117.4, 115.8, 78.0, 69.7, 61.9, 49.3, 48.8, 47.7, 40.6, 39.4, 34.0, 31.1, 29.7, 26.1, 23.3, 21.5, 14.3; IR (film) 3016, 2956, 2924, 2224, 1728, 1598, 1476, 1444, 1414, 1390, 1370, 1266, 1236, 1208, 1166, 1090, 1020, 972, 950, 908, 862, 730, 700 cm^{-1}; Anal. Calcd for $C_{29}H_{41}BrN_2O_3$: C, 63.85; H, 7.58; N, 5.13. Found: C, 63.69; H, 7.29; N, 5.02.

***N*-(3'-Cyanobenzyl)-*N*,*N*-dimethyl-*N*-{(1*S*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]}ammonium bromide, 0.5 hydrate (12d):** white solid; mp = 95–99 °C; $[\alpha]^{26}_{589}$ = 4.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.19 (1H, d, *J* = 7.8 Hz, Ar-H), 7.91 (1H, s, Ar-H), 7.84 (1H, d, *J* = 7.8 Hz, Ar-H), 7.67 (1H, t, *J* = 7.8 Hz, Ar-H), 7.19 (2H, d, *J* = 7.6 Hz, Ar-H), 7.03 (2H, t, *J* = 7.6 Hz, Ar-H), 6.76 (1H, t, *J* = 7.6 Hz, Ar-H), 5.46 (1H, d, *J* = 13.0 Hz, CH_2Ar), 5.33 (1H, d, *J* = 13.0 Hz, CH_2Ar), 4.87 (1H, td, *J* = 10.8, 4.3 Hz, COOCH), 3.47 (3H, s, CH_3N), 3.27 (3H, s, CH_3N), 3.17 (1H, q, *J* = 7.0 Hz, NCHCOO), 2.21-2.07 (1H, m, 8-Ph-Men-H), 1.96-1.09 (5H, m, 8-Ph-Men-H), 1.65 (3H, d, *J* = 7.0 Hz, NCH(C<u>H</u>$_3$)COO), 1.26 (3H, s, 8-Ph-Men-CH_3), 1.15 (3H, s, 8-Ph-Men-CH_3), 1.07-0.82 (2H, m, 8-Ph-Men-H), 0.92 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.6, 151.5, 138.2, 136.1, 134.1, 130.4, 128.7, 127.7, 125.1, 125.0, 117.5, 113.4, 77.8, 66.5, 64.1, 49.2, 48.8, 47.9, 40.8, 39.2, 34.0, 31.1, 29.8, 26.0, 23.0, 21.5, 13.8; IR (film) 3016, 2952, 2920, 2228, 1728, 1598, 1476, 1442, 1412, 1388, 1368, 1304, 1266, 1238, 1206, 1162, 1090, 1030, 972, 950, 908, 846, 806, 730, 700 cm^{-1}; Anal. Calcd for $C_{29}H_{40}BrN_2O_{2.5}$: C, 64.92; H, 7.51; N, 5.22. Found: C, 64.69; H, 7.56; N, 5.02.

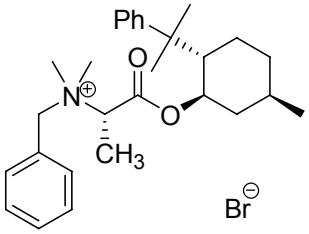


***N*,*N*-Dimethyl-*N*-(4'-methoxycarbonylbenzyl)-*N*-{(1*S*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]}ammonium bromide, monohydrate (12e):** white solid; mp = 88–91 °C; $[\alpha]^{25}_{589}$ = 7.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.06 (2H, d, *J* = 8.2 Hz, Ar-H), 7.71 (2H, d, *J* = 8.2 Hz, Ar-H), 7.14 (2H, d, *J* = 7.6 Hz, Ar-H), 6.94 (2H, t, *J* = 7.6 Hz, Ar-H), 6.66 (1H, t, *J* = 7.6 Hz, Ar-H), 5.41 (1H, d, *J* = 12.8 Hz, CH_2Ar), 5.27 (1H, d, *J* = 12.8 Hz, CH_2Ar), 4.84 (1H, td, *J* = 10.8, 4.3 Hz, COOCH), 3.98 (3H, s, $COOCH_3$), 3.49 (3H, s, CH_3N), 3.25 (3H, s, CH_3N), 3.11 (1H, q, *J* = 7.0 Hz, NCHCOO), 2.18-1.98 (1H, m, 8-Ph-Men-H), 1.95-1.06 (5H, m, 8-Ph-Men-H), 1.64 (3H, d, *J* = 7.0 Hz, NCH(C<u>H</u>$_3$)COO), 1.22 (3H, s, 8-Ph-Men-CH_3), 1.13 (3H, s, 8-Ph-Men-CH_3), 1.04-0.79 (2H, m, 8-Ph-Men-H), 0.91 (3H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.8, 165.9, 151.3, 133.3, 132.2, 131.4, 130.1, 127.6, 125.1, 125.0, 77.7, 66.0, 65.1, 52.5, 49.2, 48.7, 47.9, 40.8, 39.2, 34.1, 31.2, 29.8, 26.1, 22.9, 21.5, 13.9; IR (film) 3020, 2952, 1724, 1612, 1438, 1416, 1388, 1368, 1280, 1236, 1204, 1162, 1110, 1020, 952, 906, 870, 850, 832, 766, 730, 700 cm^{-1}; Anal. Calcd for $C_{30}H_{44}BrNO_5$: C, 62.28; H, 7.67; N, 2.42. Found: C, 62.14; H, 7.45; N, 2.39.



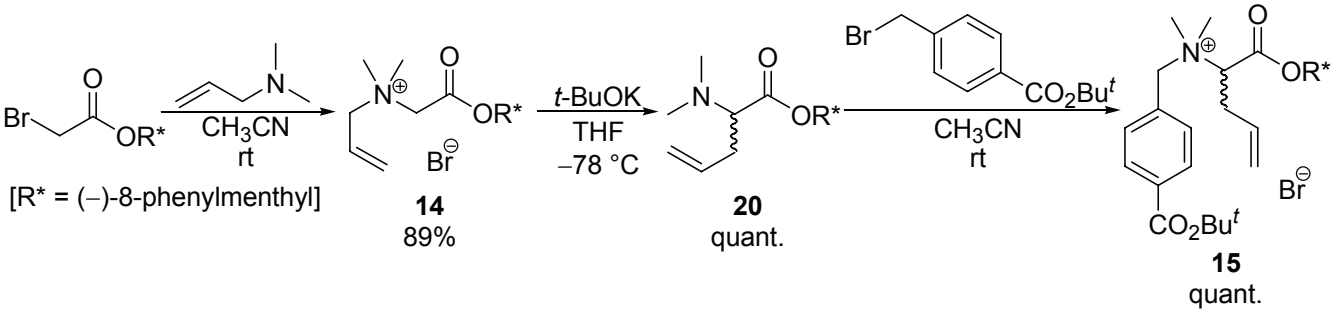
***N*,*N*-Dimethyl-*N*-{(1*S*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]}-*N*-(4'-trifluoromethylbenzyl)ammonium bromide, monohydrate (12f):** 

white solid; mp = 71–76 °C; $[\alpha]^{25}_{589}$ = 4.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.82 (2H, d, *J* = 8.1 Hz, Ar-H), 7.69 (2H, d, *J* = 8.1 Hz, Ar-H), 7.14 (2H, d, *J* = 7.6 Hz, Ar-H), 6.94 (2H, t, *J* = 7.6 Hz, Ar-H), 6.66 (1H, t, *J* = 7.6 Hz, Ar-H), 5.46 (1H, d, *J* = 12.8 Hz, CH_2Ar), 5.32 (1H, d, *J* = 12.8 Hz, CH_2Ar), 4.85 (1H, td, *J* = 10.7, 4.3 Hz, COOCH), 3.49 (3H, s, CH_3N), 3.23 (3H, s, CH_3N), 3.05 (1H, q, *J* = 7.3 Hz, NCHCOO), 2.12 (1H, td, *J* = 11.3, 3.2 Hz, 8-Ph-Men-H), 2.02-1.39 (4H, m, 8-Ph-Men-H), 1.66 (3H, d, *J* = 7.3 Hz, NCH(C<u>H</u>$_3$)COO), 1.37-0.81 (3H, m, 8-Ph-Men-H), 1.23 (3H, s, 8-Ph-Men-CH_3), 1.13 (3H, s, 8-Ph-Men-CH_3), 0.91 (3H, d, *J* = 6.2 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.8, 151.4, 133.8, 132.8 (q, *J* = 33 Hz), 130.8 (q, *J* = 3 Hz), 127.6, 126.0 (q, *J* = 4 Hz), 125.05, 124.99, 123.4 (d, *J* = 271 Hz), 77.8, 66.0, 64.7, 49.1, 48.8, 47.8, 40.9, 39.2, 34.1, 31.2, 30.1, 26.1, 22.6, 21.6, 14.0; IR (film) 3016, 2956, 2920, 1730, 1620, 1598, 1444, 1420, 1388, 1368, 1322, 1264, 1236, 1204, 1166, 1126, 1090, 1066, 1018, 972, 952, 908, 850, 820, 734, 700 cm^{-1}; Anal. Calcd for $C_{29}H_{41}BrF_3NO_3$: C, 59.18; H, 7.02; N, 2.38. Found: C, 59.15; H, 6.87; N, 2.33.

***N*-Benzyl-*N*,*N*-dimethyl-*N*-{(1*S*)-1-[(–)-8-phenylmenthyloxycarbonylethyl]}ammonium bromide, monohydrate (12g):** 

white solid; mp = 61–66 °C; $[\alpha]^{25}_{589}$ = –0.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.66-7.42 (5H, m, Ar-H), 7.17 (2H, d, *J* = 7.6 Hz, Ar-H), 7.00 (2H, t, *J* = 7.6 Hz, Ar-H), 6.77 (1H, t, *J* = 7.6 Hz, Ar-H), 5.25 (1H, d, *J* = 12.8 Hz, CH_2Ph), 5.03 (1H, d, *J* = 12.8 Hz, CH_2Ph), 4.84 (1H, td, *J* = 10.8, 4.3 Hz, COOCH), 3.43 (3H, s, CH_3N), 3.27 (3H, s, CH_3N), 3.19 (1H, q, *J* = 7.3 Hz, NCHCOO), 2.12 (1H, td, *J* = 11.5, 3.5 Hz, 8-Ph-Men-H), 1.95-1.07 (5H, m, 8-Ph-Men-H), 1.58 (3H, d, *J* = 7.3 Hz, NCH(C<u>H</u>$_3$)COO), 1.25 (3H, s, 8-Ph-Men-CH_3), 1.15 (3H, s, 8-Ph-Men-CH_3), 1.04-0.82 (2H, m, 8-Ph-Men-H), 0.91 (3H, d, *J* = 6.2 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.9, 151.4, 133.3, 130.9, 129.4, 127.7, 126.8, 125.3, 125.1, 77.7, 66.2, 66.0, 49.4, 48.4, 48.1, 40.9, 39.3, 34.1, 31.2, 29.7, 26.1, 23.0, 21.6, 13.8; IR (film) 3032, 2956, 1728, 1600, 1450, 1414, 1388, 1368, 1304, 1264, 1234, 1204, 1162, 1088, 1028, 952, 908, 846, 730, 702 cm^{-1}; Anal. Calcd for $C_{28}H_{42}BrNO_3$: C, 64.61; H, 8.13; N, 2.69. Found: C, 64.33; H, 7.90; N, 2.83.

Preparation of α-allyl quaternary ammonium salt 15

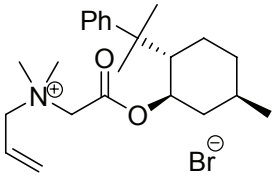


(Step 1) A mixture of bromoacetic acid (–)-8-phenylmenthol ester[1] (358 mg, 1.01 mmol) and *N*,*N*-dimethylallylamine (114 μL, 0.96 mmol) in acetonitrile (5 mL) was stirred for 15 h at room temperature. The resulting mixture was concentrated and the residue was purified by chromatography on silica gel (dichloromethane/methanol = 15:1 to 6:1 as eluent) to obtain **14** (410 mg, 89% yield) as a white solid.

(Step 2) A suspension of **14** (0.21 g, 0.46 mmol) in THF (5 mL) was treated with a 1.0 M THF solution of potassium *tert*-butoxide (0.58 mL, 0.58 mmol) at −78 °C and stirred for 4 h at the same temperature. The resulting mixture was added to stirred ice-cold saturated aqueous ammonium chloride and the mixture was extracted with ether. The combined extracts were washed with saturated aqueous sodium hydrogen carbonate and brine, dried over sodium sulfate, and concentrated. Purification of the residue by chromatography on silica gel (hexane/ethyl acetate = 5:1 to 3:1 as eluent) gave **20** (0.17 g, quant., 3:2 mixture of stereoisomers) as a colorless oil.

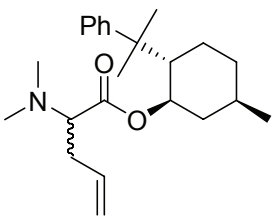
(Step 3) A mixture of **20** (0.17 g, 0.48 mmol) and (4-*tert*-butoxycarbonyl)benzyl bromide (0.38 g, 1.4 mmol) in acetonitrile (2.4 mL) was stirred for 2 days at room temperature. The resulting mixture was concentrated and the residue was purified by chromatography on silica gel (dichloromethane/methanol = 15:1 to 8:1 as eluent) to obtain quaternary ammonium salt **15** (0.32 g, quant., 3:2 mixture of stereoisomers) as a white solid.

***N*-Allyl-*N*,*N*-dimethyl-*N*-[(–)-8-phenylmenthyloxycarbonylmethyl]ammonium bromide, monohydrate (14):**



white solid; mp = 148–151 °C; $[\alpha]^{24}_{589}$ = 12.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.37-7.14 (5H, m, Ph), 5.95-5.71 (3H, m, $CH_2C\underline{H}=C\underline{H}_2$), 4.87 (1H, td, *J* = 10.8, 4.6 Hz, COOCH), 4.55 (1H, dd, *J* = 13.2, 5.9 Hz, $C\underline{H}_2CH=CH_2$), 4.47 (1H, dd, *J* = 13.2, 5.9 Hz, $C\underline{H}_2CH=CH_2$), 4.13 (1H, d, *J* = 16.9 Hz, NCH_2COO), 3.45 (3H, s, CH_3N), 3.35 (3H, s, CH_3N), 2.62 (1H, d, *J* = 16.9 Hz, NCH_2COO), 2.15 (1H, td, *J* = 11.3, 3.5 Hz, 8-Ph-Men-H), 2.03-1.68 (3H, m, 8-Ph-Men-H), 1.56-1.38 (1H, m, 8-Ph-Men-H), 1.33-0.84 (3H, m, 8-Ph-Men-H), 1.28 (3H, s, 8-Ph-Men-CH_3), 1.16 (3H, s, 8-Ph-Men-CH_3), 0.91 (3H, d, *J* = 6.8 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 163.3, 152.0, 130.7, 128.2, 125.4, 125.2, 124.0, 76.8, 67.1, 59.8, 51.0, 50.4, 49.2, 41.2, 39.3, 34.1, 31.2, 30.6, 25.9, 21.9, 21.6; IR (film) 3448, 2956, 2924, 1736, 1598, 1456, 1400, 1242, 1204, 1130, 1090, 1030, 992, 952, 908, 886, 768, 730, 702 cm^{-1}; Anal. Calcd for $C_{23}H_{38}BrNO_3$: C, 60.52; H, 8.39; N, 3.07. Found: C, 60.32; H, 8.21; N, 3.08.

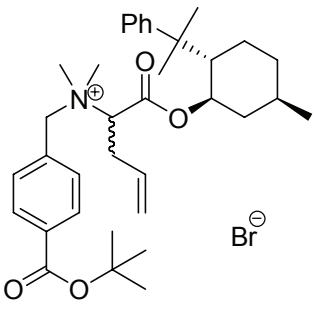
2-Dimethylaminopent-4-enoic acid (–)-8-phenylmenthol ester (20): 3:2 mixture of stereoisomers; colorless oil;



^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.32-7.10 (5H, m, Ph), 5.79-5.59 (1H, m, $CH_2C\underline{H}=CH_2$), 5.15-4.96 (2H, m, $CH_2CH=C\underline{H}_2$), 4.81 (0.6H, td, *J* = 10.8, 4.3 Hz, COOCH), 4.79 (0.4H, td, *J* = 10.5, 4.6 Hz, COOCH), 2.68 (0.6H, t, *J* = 7.2 Hz, NCHCOO), 2.41 (0.4H, t, *J* = 7.4 Hz, NCHCOO), 2.36 (3.6H, s, $(CH_3)_2N$), 2.31-1.87 (4H, m, $C\underline{H}_2CH=CH_2$ and 8-Ph-Men-H), 2.16 (2.4H, s, $(CH_3)_2N$), 1.75-1.39 (3H, m, 8-Ph-Men-H), 1.33 (1.8H, s, 8-Ph-Men-CH_3), 1.29 (1.2H, s, 8-Ph-Men-CH_3), 1.22 (1.8H, s, 8-Ph-Men-CH_3), 1.19 (1.2H, s, 8-Ph-Men-CH_3), 1.15-0.75 (3H, m, 8-Ph-Men-H), 0.88 (1.2H, d, *J* = 5.9 Hz, 8-Ph-Men-CH_3), 0.86 (1.8H, d, *J* = 6.2 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 171.8, 170.4, 151.8, 151.5, 135.1, 134.9, 128.0, 127.9, 125.43, 125.35, 125.1, 125.0, 116.9, 116.8, 75.0, 74.8, 66.4, 66.1, 50.3, 50.1, 42.6, 41.8, 41.5, 41.4, 39.8, 39.6, 34.6, 34.5, 34.1, 33.4, 31.33, 31.26, 28.1,

26.84, 26.76, 26.5, 26.3, 24.7, 21.81, 21.76; IR (film) 3056, 2952, 2864, 2784, 1722, 1640, 1600, 1494, 1454, 1370, 1266, 1224, 1170, 1094, 1048, 1030, 982, 912, 764, 700 cm^{-1}; Anal. Calcd for $C_{23}H_{35}NO_2$: C, 77.27; H, 9.87; N, 3.92. Found: C, 76.98; H, 9.91; N, 3.84.

***N*-(4'-*tert*-Butoxycarbonylbenzyl)-*N*,*N*-dimethyl-*N*-{1-[(–)-8-phenylmenthyloxycarbonylbut-3-en-1-yl]}**



ammonium bromide (15): 3:2 mixture of stereoisomers; white solid; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.04 (0.8H, d, *J* = 8.1 Hz, Ar-H), 8.03 (1.2H, d, *J* = 8.1 Hz, Ar-H), 7.72 (0.8H, d, *J* = 8.1 Hz, Ar-H), 7.71 (1.2H, d, *J* = 8.1 Hz, Ar-H), 7.21-6.96 (4.4H, m, Ar-H), 6.88 (0.6H, t, *J* = 7.3 Hz, Ar-H), 5.57-5.15 (5H, m, $CH_2C\underline{H}=C\underline{H}_2$ and CH_2Ar), 4.84 (0.6H, td, *J* = 10.7, 4.1 Hz, COOCH), 4.77 (0.4H, td, *J* = 10.8, 4.1 Hz, COOCH), 3.50-3.16 (2H, m, NCHCOO and $C\underline{H}_2CH=CH_2$), 3.46 (1.8H, s, CH_3N), 3.45 (1.2H, s, CH_3N), 3.23 (1.2H, s, CH_3N), 3.21 (1.8H, s, CH_3N), 2.89-2.74 (0.4H, m, $C\underline{H}_2CH=CH_2$), 2.70-2.56 (0.6H, m, $C\underline{H}_2CH=CH_2$), 2.21-0.80 (8H, m, 8-Ph-Men-H), 1.64 (3.6H, s, *t*-Bu), 1.62 (5.4H, s, *t*-Bu), 1.20 (3H, s, 8-Ph-Men-CH_3), 1.12 (1.8H, s, 8-Ph-Men-CH_3), 1.10 (1.2H, s, 8-Ph-Men-CH_3), 0.89 (1.2H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3), 0.87 (1.8H, d, *J* = 6.5 Hz, 8-Ph-Men-CH_3); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 166.3 (0.6C), 165.4 (0.4C), 164.59 (0.4C), 164.55 (0.6C), 151.2 (0.6C), 150.8 (0.4C), 134.21 (0.6C), 134.18 (0.4C), 133.3 (1.2C), 133.1 (0.8C), 130.6 (0.8C), 130.1 (1.0C), 130.0 (1.2C), 129.6 (0.6C), 129.3 (0.4C), 127.8 (1.2C), 127.7 (0.8C), 125.4 (0.6C), 125.3 (0.4C), 125.1 (0.8C), 125.0 (1.2C), 122.3 (0.4C), 120.9 (0.6C), 81.84 (0.4C), 81.79 (0.6C), 79.8 (0.4C), 79.0 (0.6C), 70.2 (0.4C), 69.9 (0.6C), 65.8 (0.4C), 65.7 (0.6C), 50.3 (0.4C), 49.6 (0.6C), 49.1 (0.4C), 48.9 (0.6C), 48.4 (0.6C), 48.3 (0.4C), 41.0 (0.6C), 40.7 (0.4C), 39.4 (0.4C), 39.3 (0.6C), 34.09 (0.6C), 34.05 (0.4C), 31.7 (0.6C), 31.3 (0.4C), 31.23 (0.6C), 31.20 (0.4C), 29.3 (0.6C), 28.0 (3.0C), 27.6 (0.4C), 26.5 (0.4C), 26.3 (0.6C), 25.2 (0.4C), 23.9 (0.6C), 21.5 (1.0C); IR (film) 2960, 2868, 1716, 1614, 1476, 1444, 1418, 1392, 1370, 1296, 1196, 1166, 1118, 990, 928, 846, 766, 734, 700 cm^{-1}; Anal. Calcd for $C_{35}H_{50}BrNO_4$: C, 66.87; H, 8.02; N, 2.23. Found: C, 67.15; H, 8.17; N, 2.24.