ANGEWANDTE
CHEMIE
A Journal of the
Gesellschaft
Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z19929

69451 Weinheim, Germany

Cobalt-Catalyzed Coupling Reaction of Alkyl Halides with Allylic Grignard Reagents

Takashi Tsuji, Hideki Yorimitsu, and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous $CoCl_2$ was purchased from Wako Pure Chemicals and was used after removal of water (vide infra). The ligand dppp was purchased from Tokyo Kasei Kogyo.

Experimental Section

The reaction was quite sensitive to water. Commercially available anhydrous $CoCl_2$ may contain some water. Completely anhydrous salt is clear blue, whereas purchased $CoCl_2$ is somewhat reddish-blue. Handling $CoCl_2$ under air as usual also caused a low yield. Hence, in each experiment, $CoCl_2$ was dried in a reaction flask carefully under reduced pressure (0.5 torr) by heating with a hair dryer for 2 min immediately before use.

Tertiary bromides **1a–1d** were prepared from the corresponding alcohols by the action of PBr_3 in ether at –10 ˚C. Secondary bromides **1e** and **1f** were prepared in a similar fashion at –14 ˚C. Chloride **1a-Cl** was obtained from the corresponding alcohol by treatment with concd. HCl at room temperature. Halo acetals **1h**, **1h-I**, and **7** were prepared according to the literature.[1] Iodide **1i-I** was prepared according to the literature.[2]

---

[1] a) R. Inoue, J. Nakao, H. Shinokubo, K. Oshima, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2039–2049; b) J. Nakao, R. Inoue, H. Shinokubo, K. Oshima, *J. Org. Chem.* **1997**, *62*, 1910–1911.

[2] A. Inoue, K. Maeda, H. Shinokubo, K. Oshima, *Tetrahedron* **1999**, *53*, 665–674.

A Typical Procedure for Cobalt-catalyzed Allylation of Alkyl Halide.

Anhydrous cobalt(II) chloride (7.0 mg, 0.050 mmol) was placed in a 25-mL flask and was heated with a hair dryer in vacuo for 2 min. After the color of cobalt salt became blue, dppp (25 mg, 0.060 mmol) and anhydrous THF (1.0 mL) were sequentially added under argon. The mixture was stirred for about 10 min at room temperature. 2-Bromo-2-methyldecane (**1a**, 0.12 g, 0.50 mmol) and allylmagnesium chloride (1.0 M THF solution, 1.5 mL, 1.5 mmol) were successively added dropwise to the reaction mixture at –20 ˚C. While the Grignard reagent was being added, the mixture turned reddish-brown. After being stirred for 2 h at –20 ˚C, the reaction mixture was poured into saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL × 2). The combined organic layer was dried over Na_2SO_4 and concentrated. Silica gel column purification (hexane) of the crude product provided 4,4-dimethyl-1-dodecene (**2a**) and 2-methyl-1-decene (**3a**) (94 mg, 90% and 8% yields, respectively, judged by ^{1}H NMR.).

Characterization Data

Spectral data for **1c** was found in the literature[3]

2-Bromo-2-methyldecane (1a): IR (neat) 1101, 1138, 1369, 1387, 1466, 2341, 2361, 2856, 2928 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.24–1.36 (m, 12H), 1.44–1.56 (m, 2H), 1.75 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.55, 26.19, 29.17, 29.40, 29.52, 31.78, 34.15, 47.56, 68.75. Found: C, 56.35; H, 10.09%. Calcd for $C_{11}H_{23}Br$: C, 56.17; H, 9.86%.

2-Chloro-2-methyldecane (1a-Cl): IR (neat) 1107, 1138, 1369, 1386, 1468, 2341, 2856, 2928 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 9.6 Hz, 3H), 1.22–1.39 (m, 10H), 1.40–1.54 (m, 2H), 1.57 (s, 6H), 1.68–1.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.55, 25.04, 29.17, 29.43, 29.66, 31.79, 32.33, 46.08, 71.29. Found: C, 69.40; H, 12.37%. Calcd for $C_{11}H_{23}Cl$: C, 69.26; H, 12.15%.

2-Bromo-2-cyclohexyl-4-phenylbutane (1b): IR (neat) 698, 746, 895, 1049, 1379, 1450, 1497,

---

[3] W. Damm, B. Giese, J. Hartung, T. Hasskerl, K. N. Houk, O. Hüter, H. Zipse, *J. Am. Chem. Soc.* **1992**, *114*, 4067–4079.

1603, 2853, 2928, 3026 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.10–1.32 (m, 6H), 1.60–1.74 (m, 4H), 1.76 (s, 3H), 2.04–2.26 (m, 3H), 2.78–2.90 (m, 2H), 7.17–7.23 (m, 3H), 7.26–7.33 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 26.27, 26.52, 26.80, 28.53, 28.59, 29.08, 30.09, 32.09, 45.53, 79.05, 126.02, 128.51, 128.54, 141.99.

2-Bromo-3,3-dimethyl-2-(4-methoxyphenyl)butane (1d): IR (nujol) 696, 741, 831, 1040, 1051, 1186, 1256, 1298, 1512, 1611, 2343, 2360 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.07 (s, 9H), 2.77 (s, 3H), 3.81 (s, 3H), 6.80 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 27.08, 29.52, 41.17, 55.23, 82.99, 112.01, 130.67, 135.99, 158.34. Found: C, 57.29; H, 6.88%. Calcd for $C_{13}H_{19}BrO$: C,57.57; H, 7.06%.

2-Bromo-1-(4-methoxyphenyl)octane (1f): IR (neat) 818, 1038, 1178, 1250, 1302, 1441, 1466, 1512, 1012, 2856, 2930 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.88 (t, *J* = 6.9 Hz, 3H), 1.18–1.40 (bs, 8H), 1.70–1.85 (m, 2H), 3.11 (dd, *J* = 7.2, 3.6 Hz, 2H), 3.71 (s, 3H), 4.12–4.21 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 13.92, 22.45, 27.44, 28.53, 31.56, 37.97, 44.77, 55.16, 58.40, 113.81, 130.28, 130.84, 158.53. HRMS Found 298.0932. Calcd for $C_{15}H_{23}BrO$ (M^+) 298.0938.

4,4-Dimethyl-1-dodecene (2a): IR (neat) 912, 995, 1366, 1468, 1639, 2855, 2928, 3076 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.84 (s, 6H), 0.88 (t, *J* = 6.6 Hz, 3H), 1.10–1.40 (bs, 14H), 1.94 (d, *J* = 7.2 Hz, 2H), 4.94–5.04 (m, 2H), 5.81 (ddt, *J* = 16.8, 10.5, 7.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.98, 22.59, 23.87, 26.91, 29.28, 29.60, 30.52, 31.51, 31.85, 41.95, 46.44, 116.45, 136.12. Found: C, 85.61; H, 14.63%. Calcd for $C_{14}H_{28}$: C, 85.63; H, 14.37%.

4-Cyclohexyl-4-methyl-6-phenyl-1-hexene (2b): IR (neat) 698, 741, 910, 995, 1377, 1450, 1497, 1600, 1638, 2341, 2361, 2853, 2928, 3026, 3063 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.86 (s, 3H), 0.90–1.32 (m, 5H), 1.47–1.58 (m, 2H), 1.58–1.84 (m, 6H), 2.03–2.18 (m, 2H), 2.15 (t, *J* = 9.0 Hz, 2H), 5.03–5.10 (m, 2H), 5.85 (ddt, *J* = 16.5, 11.1, 7.2 Hz, 1H), 7.12–7.21 (m, 3H), 7.21–7.30 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 21.78, 26.76, 26.92, 27.20, 29.92, 37.74, 39.48, 41.45, 44.59, 116.71, 125.61, 128.39, 128.40, 135.90, 143.80. Found: C, 88.98; H, 11.10%. Calcd for $C_{19}H_{28}$: C, 88.99; H, 11.01%.

***cis*-4-*tert*-Butyl-1-methyl-1-(2-propenyl)cyclohexane (2c)**: IR (neat) 910, 997, 1366, 1452, 1639, 2844, 2868, 2941, 3074 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (s, 3H), 0.85 (s, 9H), 1.03–1.22 (m, 5H), 1.49–1.57 (m, 4H), 2.02 (s, 1H), 2.04 (s, 1H), 4.95 (m, 2H), 5.79 (ddt, *J* = 15.9, 10.8, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.48, 27.25, 27.60, 29.46, 32.48, 38.30, 40.03, 47.99, 116.39, 135.78. Found: C, 86.46; H, 13.51%. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48%. The stereochemistry of **1c** and **2c** was determined by ^{13}C NMR experiments according to the literature.[4]

4-(4-Methoxyphenyl)-4,5,5-trimethyl-1-hexene (2d): IR (neat) 831, 910, 1038, 1188, 1252, 1294, 1375, 1464, 1514, 1611, 2361, 2955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (s, 9H), 1.27 (s, 3H), 2.24 (dd, *J* = 14.1, 8.4 Hz, 1H), 3.00 (dd, *J* = 14.1, 3.6 Hz, 1H), 3.80 (s, 3H), 4.88 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 5.42–5.55 (m, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 7.20(d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.26, 26.26, 36.51, 39.47, 45.22, 55.08, 112.15, 116.43, 130.12, 136.33, 136.85, 157.11. HRMS Found 232.1828. Calcd for $C_{16}H_{24}O$ (M^+) 232.1831.

4-(4-Methoxybenzyl)-1-decene (2f): IR (neat) 804, 910, 1040, 1177, 1246, 1300, 1466, 1512, 1612, 2854, 2926 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.16–1.38 (bs, 10H), 1.60–1.70 (m, 1H), 2.01 (dd, *J* = 7.8, 7.2 Hz, 2H), 2.48 (d, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 4.97–5.03 (m, 2H), 5.72–5.85 (m, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.55, 26.54, 29.49, 31.78, 32.81, 37.39, 39.14, 39.68, 55.18, 113.62, 116.03, 129.31, 130.16, 137.35, 147.81. Found: C, 83.02; H, 11.03%. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84%.

4-Pentenal Dibutyl Acetal (2h): IR (neat) 912, 1049, 1074, 1128, 1261, 1350, 1379, 1458, 1641, 2933, 2959 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 6H), 1.38 (m, 4H), 1.56 (m, 4H), 1.70 (m, 2H), 2.11 (m, 2H), 3.41 (dt, *J* = 6.6, 9.3 Hz, 2H), 3.58 (dt, *J* = 6.6, 9.6 Hz, 2H), 4.48 (t, *J* = 5.7

---

[4] P. Crews, S. Naylor, F. J. Hanke, E. R. Hogue, E. Kho, R. Braslau, *J. Org. Chem.* **1984**, *49*, 1371. Also see ref. 3.

Hz, 1H), 4.94–5.06 (m, 2H), 5.82 (ddt, *J* = 17.1, 10.5, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.77, 19.34, 28.94, 31.93, 32.59, 65.32, 102.62, 114.69, 138.27. Found: C, 72.72; H, 12.11%. Calcd for $C_{13}H_{26}O_2$: C, 72.84; H, 12.23%.

***cis*-2-(1-Octynyl)-3-(2-propenyl)-1-oxacyclohexane (*cis*-2i)**: IR (neat) 1078, 1350, 1439, 1641, 2239, 2341, 2858, 2932, 3076 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.22–1.36 (m, 4H), 1.36–1.48 (m, 2H), 1.48–1.66 (m, 6H), 1.72–1.86 (m, 1H), 1.93–2.03 (m, 1H), 2.07–2.16 (m, 1H), 2.26 (dt, *J* = 1.8, 7.2 Hz, 2H), 3.59–3.70 (m, 1H), 3.85–3.95 (m, 1H), 4.54 (bs, 1H), 4.99–5.09 (m, 2H), 5.75 (ddt, *J* = 16.8, 10.2, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.90, 18.64, 22.47, 25.28, 25.37, 28.46, 28.70, 31.23, 36.71, 39.19, 62.71, 69.60, 75.84, 89.00, 116.30, 136.28. HRMS Found 234.1984. Calcd for $C_{16}H_{26}O$ (M^+) 234.1979.

***trans*-2-(1-Octynyl)-3-(2-propenyl)-1-oxacyclohexane (*trans*-2i)**: IR (neat) 1084, 1333, 1439, 1641, 2858, 2932, 3076 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.08–1.45 (m, 7H), 1.45–1.70 (m, 5H), 1.84–1.98 (m, 2H), 2.24 (m, 2H), 2.40–2.49 (m, 1H), 3.39 (m, 1H), 3.80 (dt, *J* = 9.0, 2.7 Hz, 1H), 3.98 (dt, *J* = 11.1, 2.7 Hz, 1H), 5.03 (d, *J* = 8.7 Hz, 1H), 5.05 (d, *J* = 17.4 Hz, 1H), 5.79 (ddt, *J* = 17.4, 8.7, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.89, 18.62, 22.41, 25.29, 27.93, 28.46, 28.49, 31.21, 36.71, 41.07, 67.64, 72.65, 78.42, 86.61, 116.57, 135.97. HRMS Found 234.1984. Calcd for $C_{16}H_{26}O$ (M^+) 234.1976.

2-Methyl-6-phenyl-1-hexene (4): IR (neat) 698, 746, 885, 1030, 1373, 1454, 1497, 1605, 1649, 2345, 2858, 2934, 3026, 3072 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44–1.55 (m, 2H), 1.58–1.69 (m, 2H), 1.71 (s, 3H), 2.05 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 4.68 (s, 1H), 4.71 (s, 1H), 7.16–7.21 (m, 3H), 7.26–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.22, 27.13, 30.98, 35.75, 37.55, 109.87, 125.69, 128.32, 128.48, 142.84, 146.03. Found: C, 89.30; H, 10.27%. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41%.

3-Methyl-6-phenyl-1-hexene (5b): IR (neat) 698, 746, 910, 995, 1373, 1419, 1454, 1497, 1605, 1639, 2858, 2932, 3028, 3065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (d, *J* = 6.6 Hz, 3H), 1.30–1.37 (m, 2H), 1.55–1.67 (m, 2H), 2.09–2.19 (m, 1H), 2.59 (t, *J* = 7.8 Hz, 2H), 4.88–4.98 (m, 2H), 5.68 (ddd, *J* = 17.6, 9.9, 7.5 Hz, 1H), 7.15–7.22 (m, 3H), 7.24–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.09, 29.06, 35.97, 36.20, 37.62, 112.54, 125.68, 128.32, 128.48, 142.88, 144.81. Found: C, 89.66; H, 10.57%. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41%.

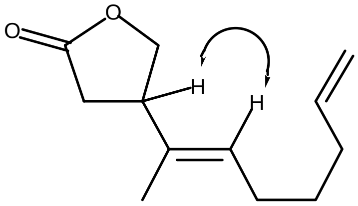
4-(3-Butenyl)-4,5-dihydro-2(3*H*)-furanone (9a): IR (neat) 839, 814, 1001, 1173, 1379, 1420, 1641, 1778, 2856, 2924, 3078 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56–1.63 (m, 2H), 2.06–2.25 (m, 3H), 2.53–2.68 (m, 2H), 3.94 (dd, *J* = 9.0, 7.5 Hz, 1H), 4.43 (dd, *J* = 9.0, 7.8 Hz, 1H), 5.00–5.09 (m, 2H), 5.78 (ddt, *J* = 19.8, 7.2, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 31.31, 32.02, 34.24, 34.96, 73.12, 115.65, 137.18, 177.14. Found: C, 68.45; H, 8.45%. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

4-(3-Butenyl)-4,5-dihydro-5,5-dimethyl-2(3*H*)-furanone (9b): IR (neat) 918, 959, 1096, 1128, 1217, 1258, 1375, 1389, 1641, 1771, 2934, 2978 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.43 (s, 3H), 1.38–1.46 (m, 1H), 1.51–1.65 (m, 1H), 1.95–2.32 (m, 4H), 2.59–2.69 (m, 1H), 4.98–5.10 (m, 2H), 5.77 (ddt, *J* = 16.8, 10.5, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.79, 27.35, 28.77, 32.26, 34.49, 45.08, 86.64, 115.70, 137.39, 175.67. Found: C, 71.36; H, 9.78%. Calcd for $C_{10}H_{16}O_2$: C,71.39; H, 9.59%.

4,5-Dihydro-4-(1,1-dimethyl-3-butenyl)-2(3*H*)-furanone (9c): IR (neat) 918, 1003, 1026, 1175, 1470, 1639, 1780, 2964, 3076 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 3H), 0.91 (s, 3H), 1.98 (d, *J* = 7.5 Hz, 2H), 2.31–2.58 (m, 3H), 4.11 (dd, *J* = 9.0, 8.1 Hz, 1H), 4.32 (dd, *J* = 9.6, 8.1 Hz, 1H), 5.03–5.12 (m, 1H), 5.72–5.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 23.38, 23.67, 29.63, 34.22, 44.00, 45.29, 69.37, 118.32, 133.87, 177.37. Found: C, 71.11; H, 9.74%. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%.

4,5-Dihydro-4-(1-methyl-1,6-heptadienyl)-2(3*H*)-furanone (9e, (*E*)-isomer): IR (neat) 847, 910, 1013, 1171, 1439, 1639, 1782, 2341, 2361, 2858, 2926 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.63 (s, 3H), 2.00–2.09 (m, 4H), 2.46 (dd, *J* = 17.7, 8.7 Hz, 1H), 2.60 (dd, *J* = 17.7, 8.7 Hz, 1H), 3.18 (tt, *J* = 8.1, 8.1 Hz, 1H), 4.08 (dd, *J* = 8.7, 7.5 Hz, 1H), 4.41 (dd, *J* = 8.7, 7.5

Hz, 1H), 4.94–5.05 (m, 2H), 5.28 (t, *J* = 7.2 Hz, 1H), 5.80 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.50, 27.09, 28.52, 32.80, 33.19, 43.81, 71.77, 114.74, 127.20, 132.02, 138.61, 177.04. Found: C, 73.93; H, 9.57%. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%. The stereochemistry was assigned on the basis of NOE difference.



4-(4-Methoxyphenyl)-4,5,5-trimethyl-1-hexanol (12): IR (neat) 829, 1040, 1188, 1252, 1292, 1375, 1466, 1514, 1611, 2876, 2955, 3342 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9H), 1.10–1.50 (m, 3H), 1.29 (s, 3H), 1.59 (dt, *J* = 5.1, 12.6 Hz, 1H), 2.17 (dt, *J* = 3.0, 12.6 Hz, 1H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 6.81 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.00, 26.12, 28.37, 30.51, 36.67, 45.29, 55.06, 63.89, 112.35, 129.93, 136.66, 157.32. HRMS Found 250.1934. Calcd for $C_{16}H_{26}O_2$ (M^+) 250.1939. The enantiomeric excess was determined by HPLC (Daicel Chiralcel-OD (0.46 cm × 25 cm), hexane/*i*-PrOH = 90/10, 1.0 mL/min, oven temp. = 20 ˚C). The retention time of the faster moving compound was 6.2 min, and that of the slower one was 8.6 min. The later peak represented the major enantiomer.