

Supporting Information

**Chiral Benzimidazolium NHC Ligand with Hydroxyamide- or Hydroxyalkyl-
Functionalized Wingtip for Cu-Catalyzed Asymmetric Allylic Alkylation**

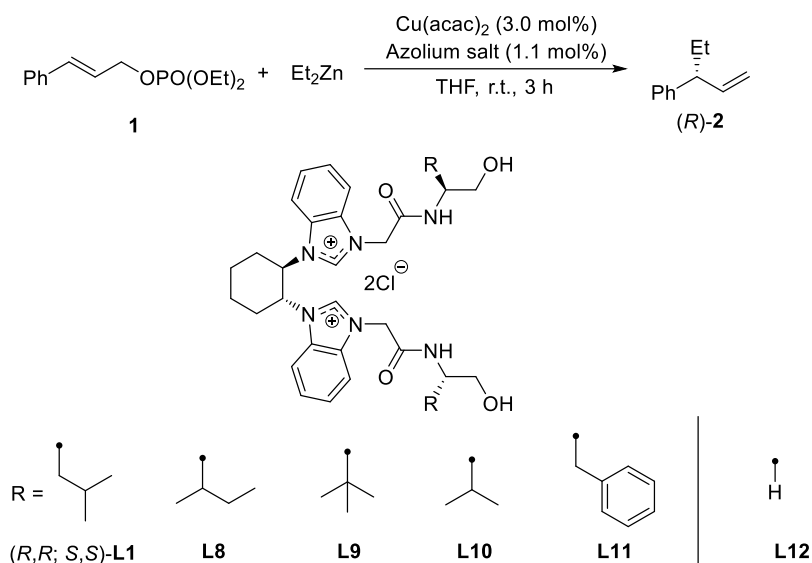
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Contents

1. Table S1. Effect of alkyl group on chiral diazolium salt	p.S2
2. NMR Charts	p.S4
3. Selected Chiral GC and LC Traces	p.S11
4. References	p.S20

Table S1. Effect of alkyl group on chiral diazolinium salt^a

Entry	Azolium salt	R =	Yield [%]	ee [%]
1	(<i>R,R</i> ; <i>S,S</i>)- L1	^t Bu	91	83
2	L8 (^s Bu)	^s Bu	98	79
3	L9 (^t Bu)	^t Bu	75	73
4	L10 (^t Pr)	^t Pr	99	70
5	L11 (Bn)	Bn	97	55
6	L12 (CH ₂)	H	53	39

^a To a solution of Cu(acac)₂ (3 mol%) and azolium salt (1.1 or 2.3 mol%) in THF (6 mL), Et₂Zn (3 mmol) was added first, then **1** (1 mmol). The reaction mixture was stirred at room temperature for 3 h.

L8 (^sBu)

¹H-NMR (DMSO-d₆ at 80 °C): δ 10.60 (br, 2H), 8.52 (d, J = 8.8 Hz, 2H), 7.92 (br, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.40-7.29 (m, 4H), 5.78 (br, 2H), 5.34 (d, J = 16.0 Hz, 2H), 5.25 (d, J = 16.0 Hz, 2H), 4.60 (br, 2H), 3.68-3.61 (m, 2H), 3.50 (br, 4H), 2.60 (br, 2H), 2.45 (br, 1H), 2.42 (br, 1H), 2.04 (br, 2H), 1.84 (br, 2H), 1.64-1.56 (m, 2H), 1.46-1.37 (m, 2H), 1.13-1.06 (m, 2H), 0.85 (d, J = 6.4 Hz, 6H), 0.80 (t, J = 7.4 Hz, 6H); Failure of ¹³C NMR measurement was observed. HRMS (ESI²⁺): m/z calcd for C₃₆H₅₂N₆O₄²⁺: 316.2020; found: 316.2019.

L9 (^tBu)

¹H-NMR (DMSO-d₆ at 80 °C): δ 10.56 (br, 2H), 8.35 (d, J = 9.2 Hz, 2H), 7.90 (br, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.39-7.31 (m, 4H), 5.74 (br, 2H), 5.38 (d, J = 16.0 Hz, 2H), 5.29 (d, J = 16.0 Hz, 2H), 4.52 (br, 2H), 3.66-3.61 (m, 4H), 3.49-3.44 (m, 2H), 2.59 (br, 2H), 2.45 (br, 1H), 2.42 (br, 1H), 2.04 (br, 2H), 1.90-1.78 (m, 2H), 0.88 (s, 18H); Failure of ¹³C NMR measurement was observed. HRMS (ESI²⁺): m/z calcd for C₃₆H₅₂N₆O₄²⁺: 316.2020; found: 316.2025.

L10 (ⁱPr)

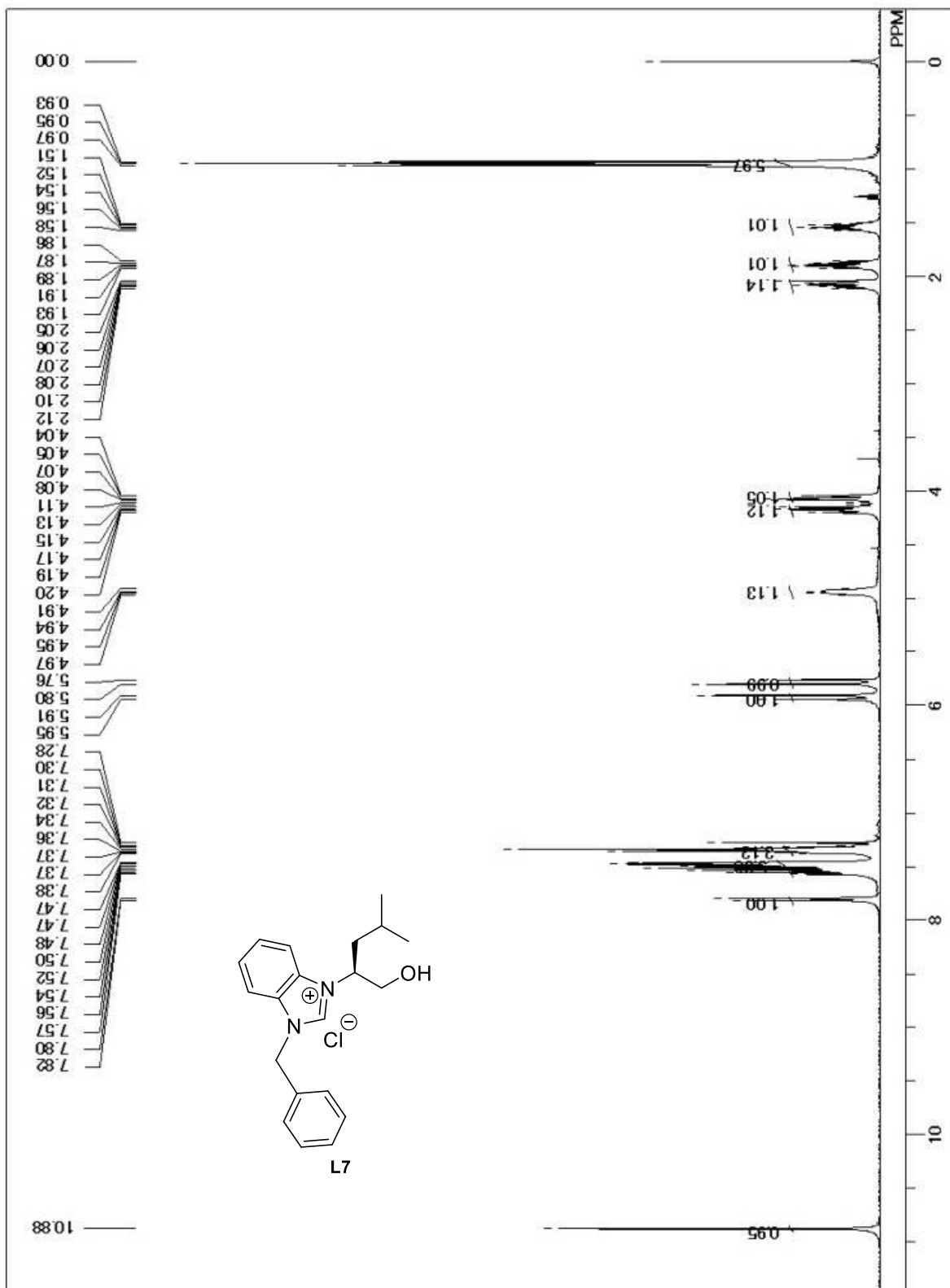
¹H-NMR (DMSO-d₆ at 80 °C): δ 10.42 (br, 2H), 8.35 (d, J = 8.8 Hz, 2H), 7.83 (br, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.42-7.30 (m, 4H), 5.69 (br, 2H), 5.32 (d, J = 16.0 Hz, 2H), 5.22 (d, J = 16.0 Hz, 2H), 4.57 (t, J = 5.6 Hz, 2H), 3.64-3.58 (m, 2H), 3.48 (t, J = 5.0 Hz, 4H), 2.57 (br, 2H), 2.46 (br, 1H), 2.43 (br, 1H), 2.06 (br, 2H), 1.88-1.83 (m, 4H), 0.87 (d, J = 6.4 Hz, 3H), 0.85 (d, J = 6.4 Hz, 3H); Failure of ¹³C NMR measurement was observed. HRMS (ESI²⁺): m/z calcd for C₃₄H₄₈N₆O₄²⁺: 302.1863; found: 302.1863.

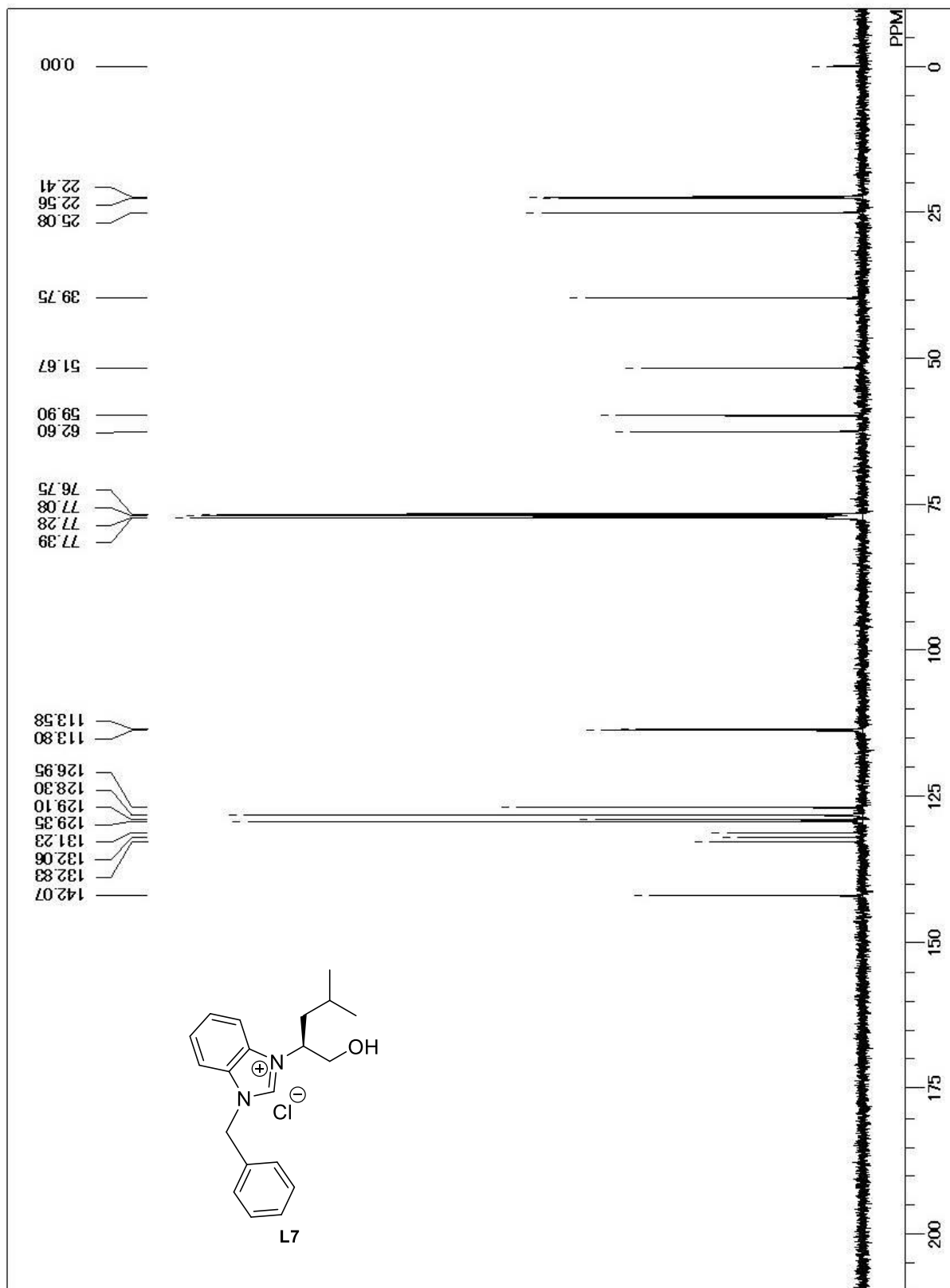
L11 (Bn)

¹H-NMR (DMSO-d₆ at 80 °C): δ 10.50 (br, 2H), 8.76 (d, J = 8.4 Hz, 2H), 7.85 (br, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.31-7.12 (m, 14H), 5.73 (br, 2H), 5.18 (s, 4H), 4.83 (t, J = 5.6 Hz, 2H), 4.01-3.94 (m, 2H), 3.46 (t, J = 5.0 Hz, 4H), 2.88 (dd, J = 6.0 and 13.6 Hz, 2H), 2.71 (dd, J = 8.2 and 13.6 Hz, 2H), 2.57 (br, 2H), 2.42 (br, 1H), 2.39 (br, 1H), 2.03 (br, 2H), 1.82 (br, 2H); Failure of ¹³C NMR measurement was observed. HRMS (ESI²⁺): m/z calcd for C₄₂H₄₈N₆O₄²⁺: 350.1863; found: 350.1865.

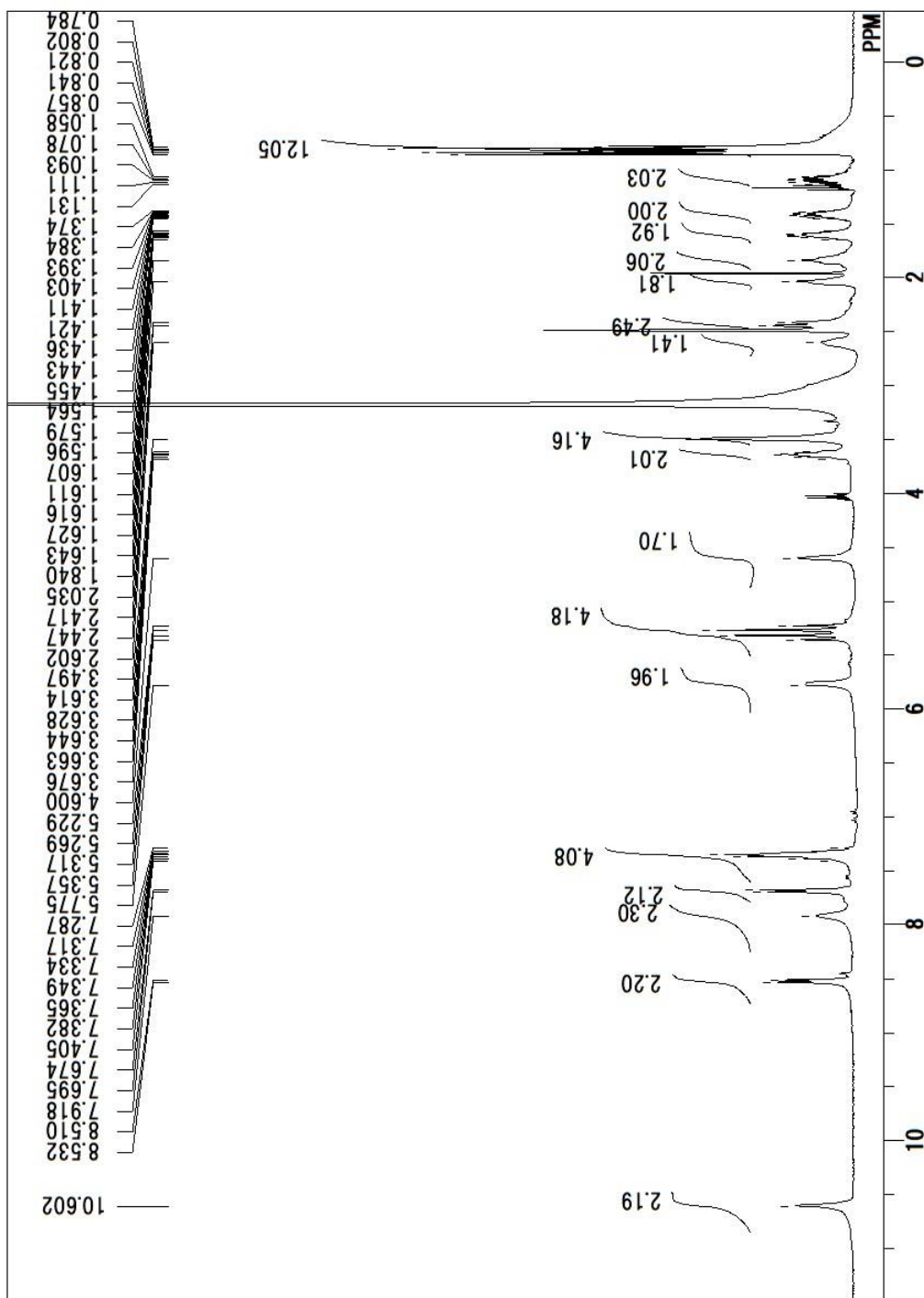
L12 (CH₂)

¹H-NMR (DMSO-d₆ at 80 °C): δ 10.52 (br, 2H), 8.74 (br, 2H), 7.93 (br, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.42-7.35 (m, 4H), 5.77 (br, 2H), 5.26 (d, J = 16.4 Hz, 2H), 5.20 (d, J = 16.4 Hz, 2H), 4.69-4.65 (m, 2H), 3.53-3.48 (m, 4H), 3.25-3.21 (m, 4H), 2.56 (br, 2H), 2.44 (br, 2H), 2.05 (br, 2H), 1.83 (br, 2H); Failure of ¹³C NMR measurement was observed. HRMS (ESI²⁺): m/z calcd for C₂₈H₃₆N₆O₄²⁺: 260.1394; found: 260.1394.

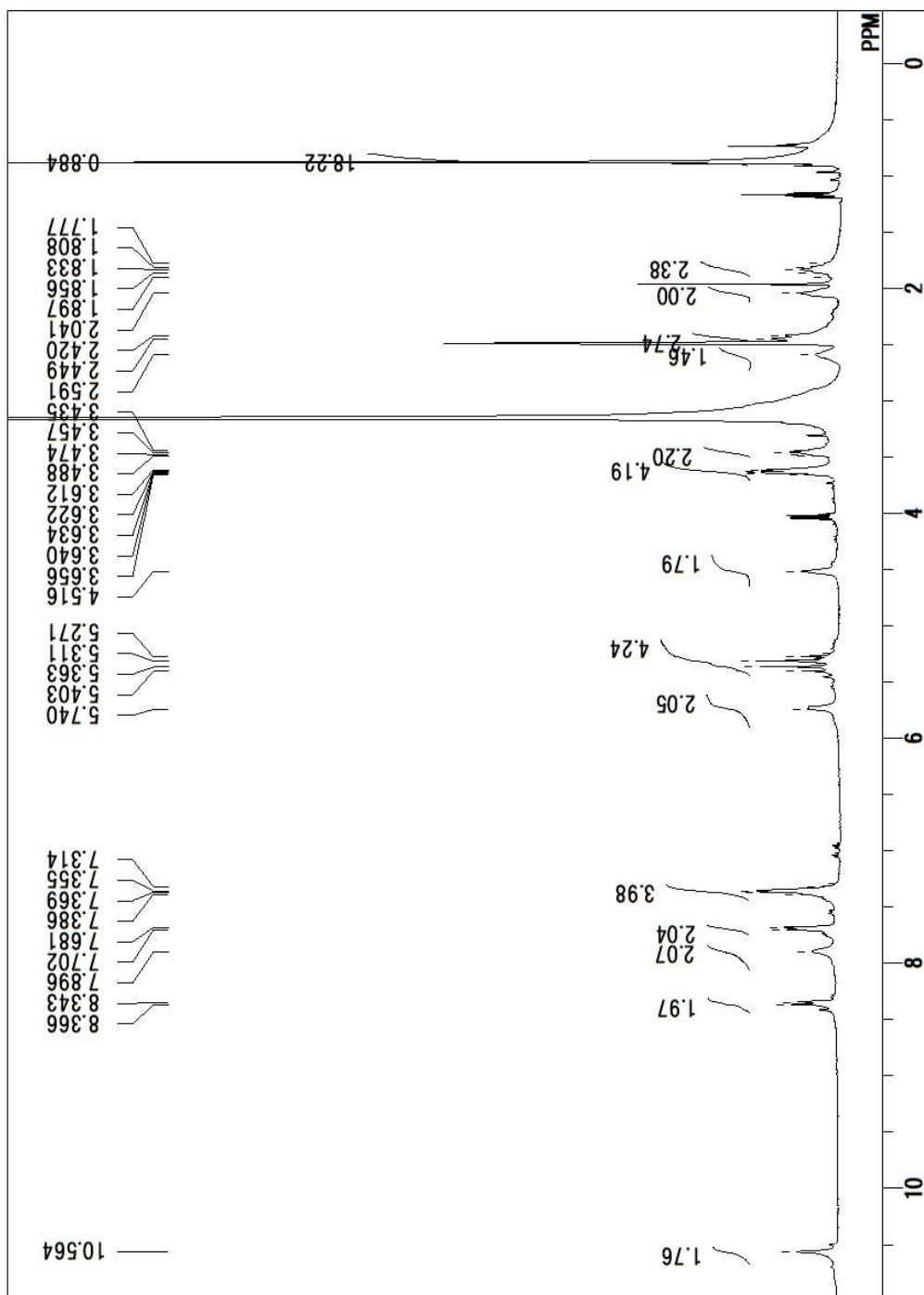




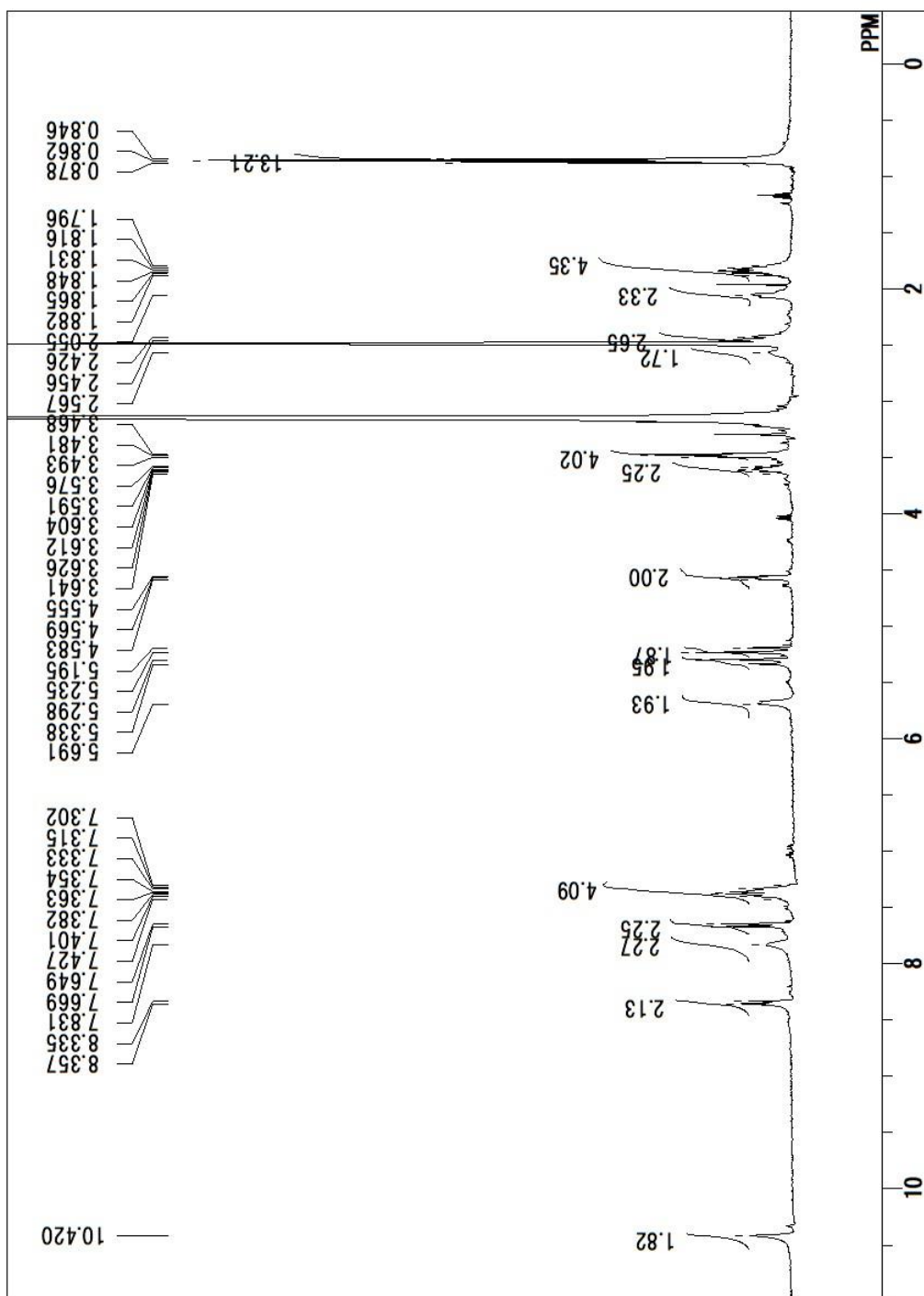
L8 (Bu)



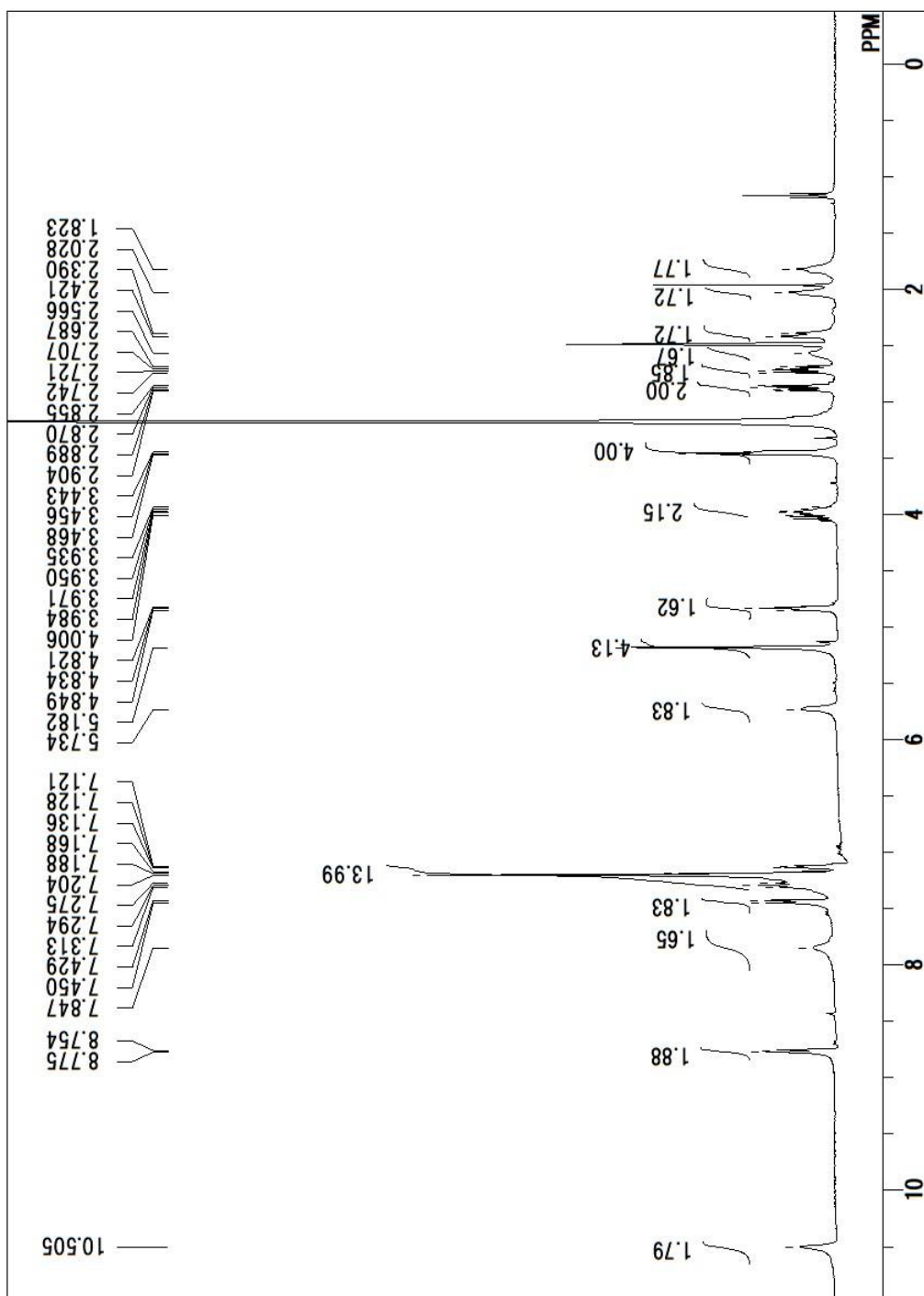
L9 (Bu)



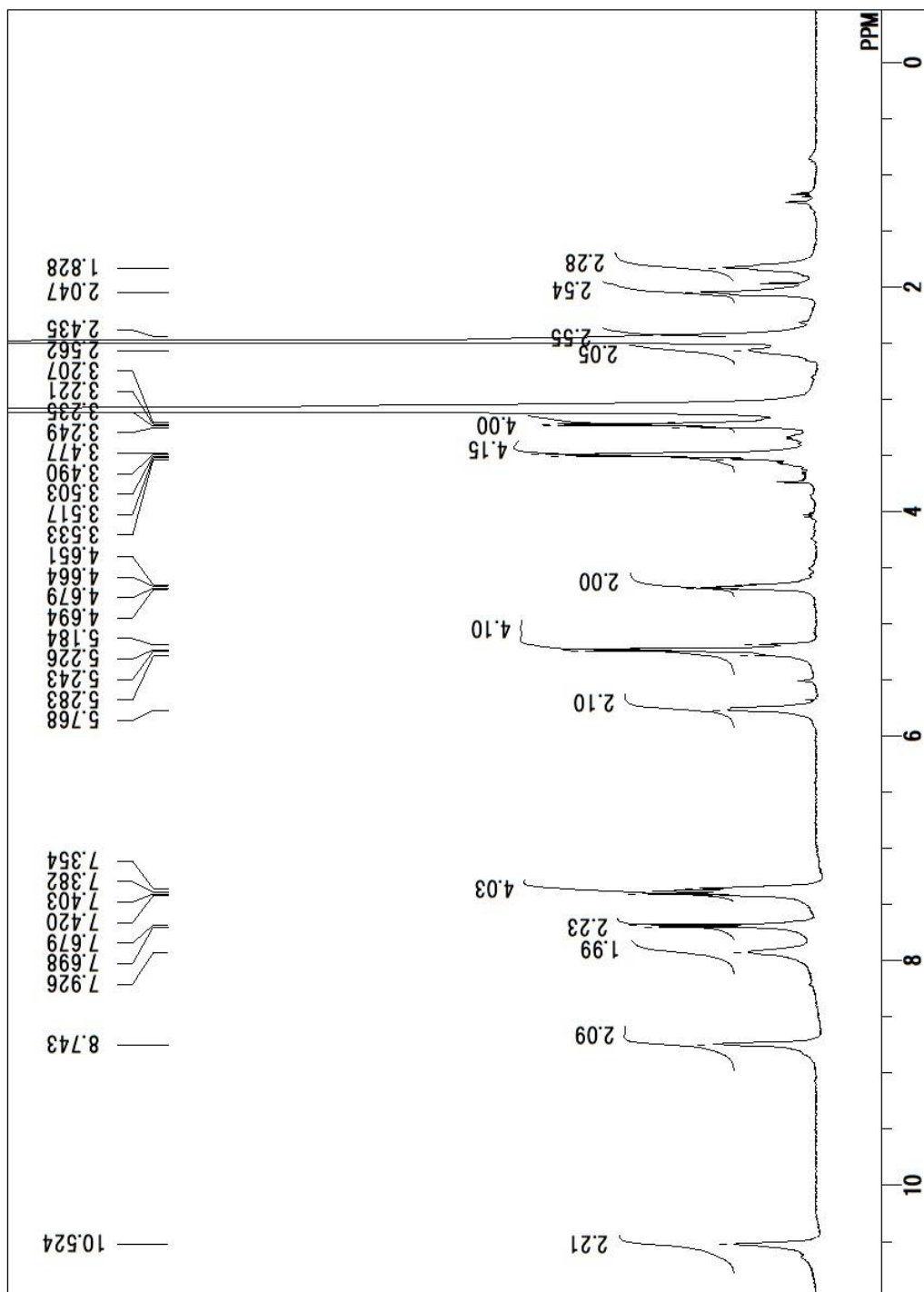
L10 (Pr)



L11 (Bn)



L12 (CH₂)



3-Phenyl-1-pentene (**3**)^[a]

Enantiomeric excess was determined by Chiral GLC (Supelco β -Dex 120, 65 °C, N₂ gas, linear velocity of 27.5 cm/s, Rt = 67 min (*R*), 69 min (*S*))

Racemic compound

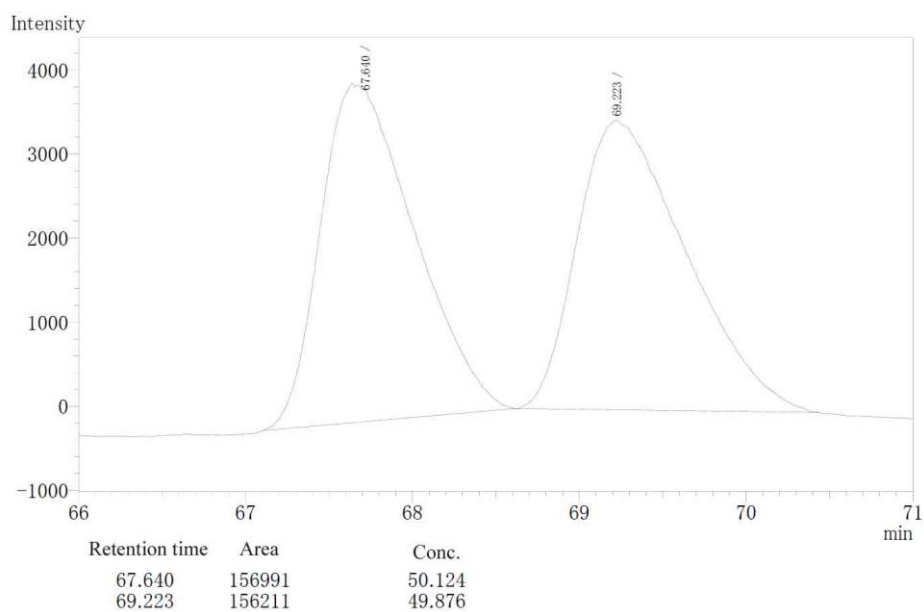


Table 1, entry 6: (*R*)-**2** (74% *ee*)

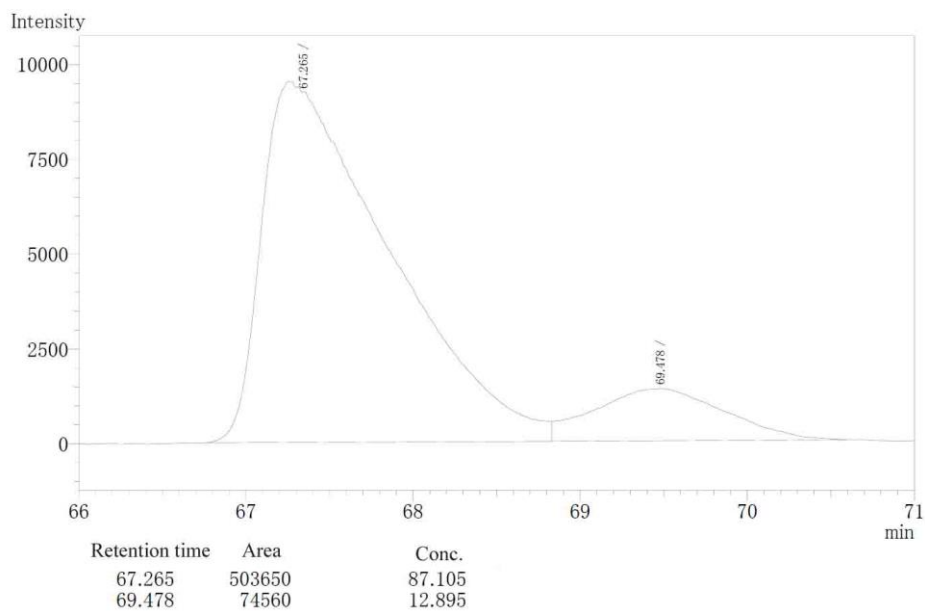


Table 2, entry 2: (*R*)-**2** (77% *ee*)

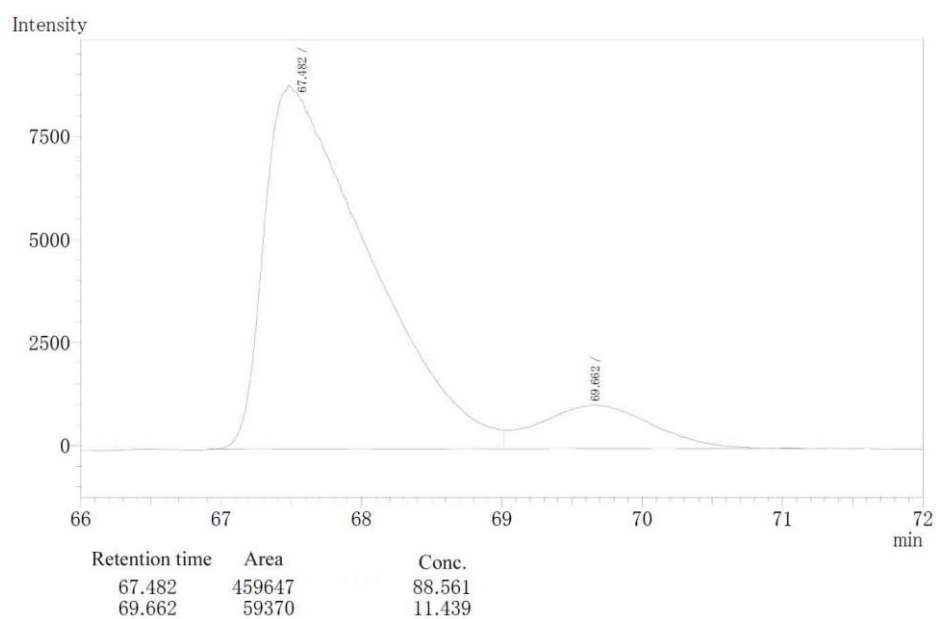


Table 2, entry 4: (*R*)-**2** (75% *ee*)

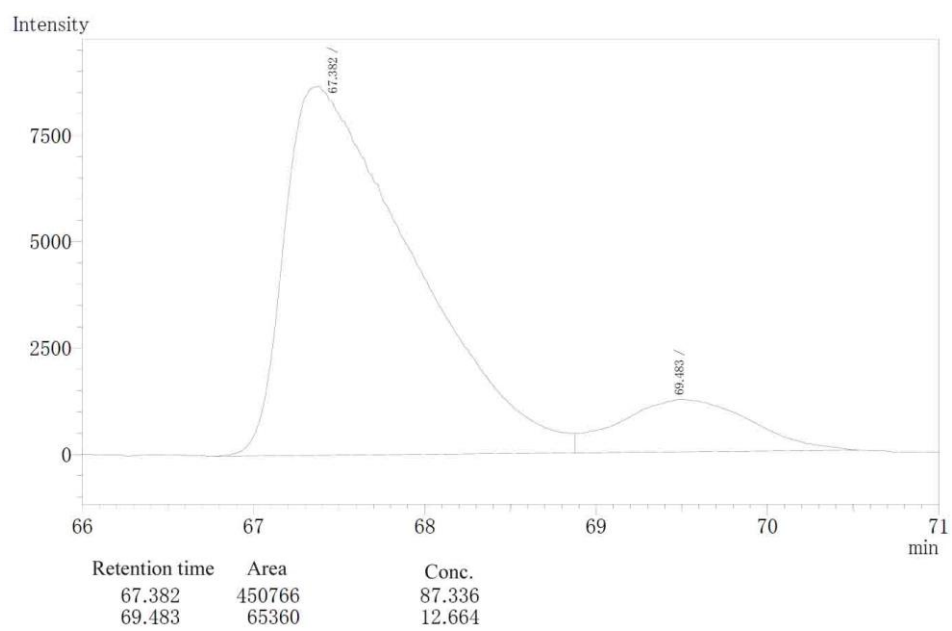


Table 3, entry 2: (*R*)-**2** (83% *ee*)

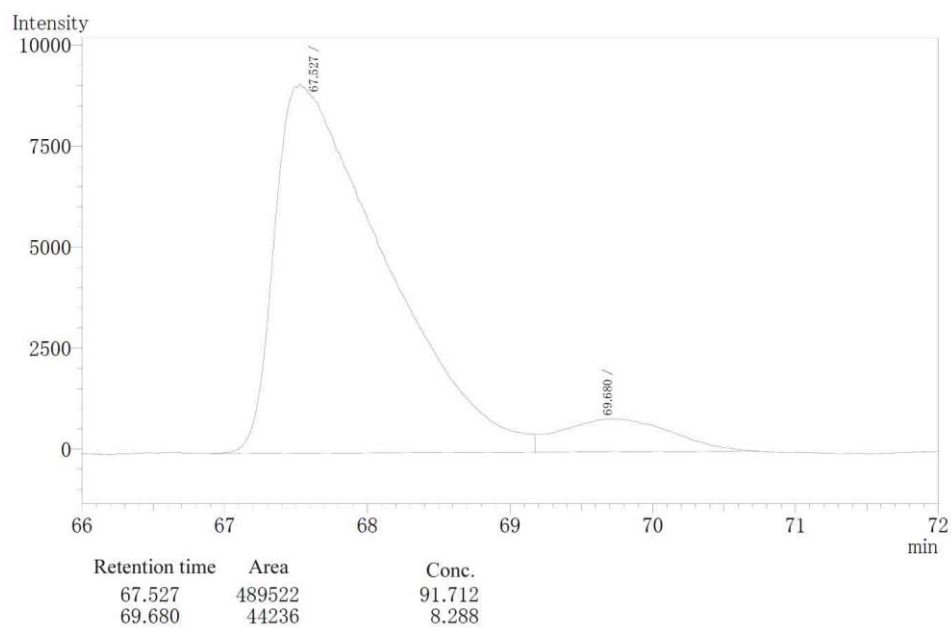


Table 3, entry 3: (*R*)-**2** (81% *ee*)

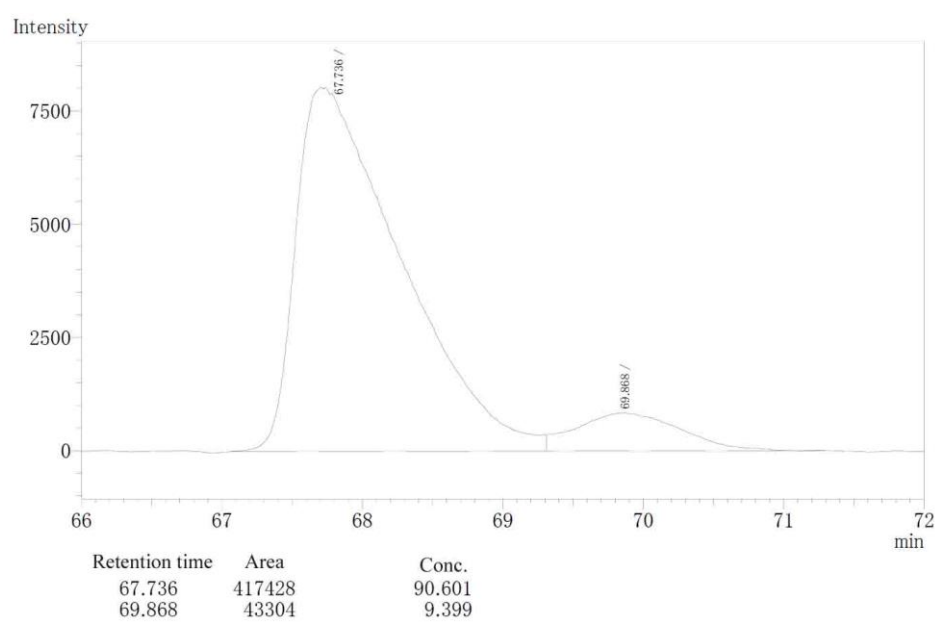


Table 3, entry 4: (*R*)-2 (84% *ee*)

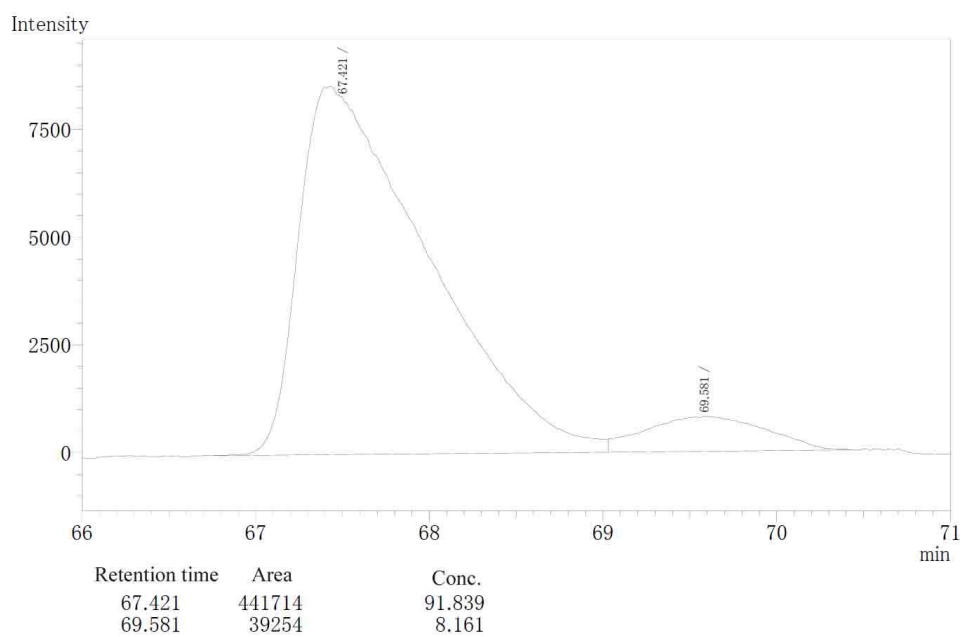


Table 3, entry 11: (*S*)-2 (86% *ee*)

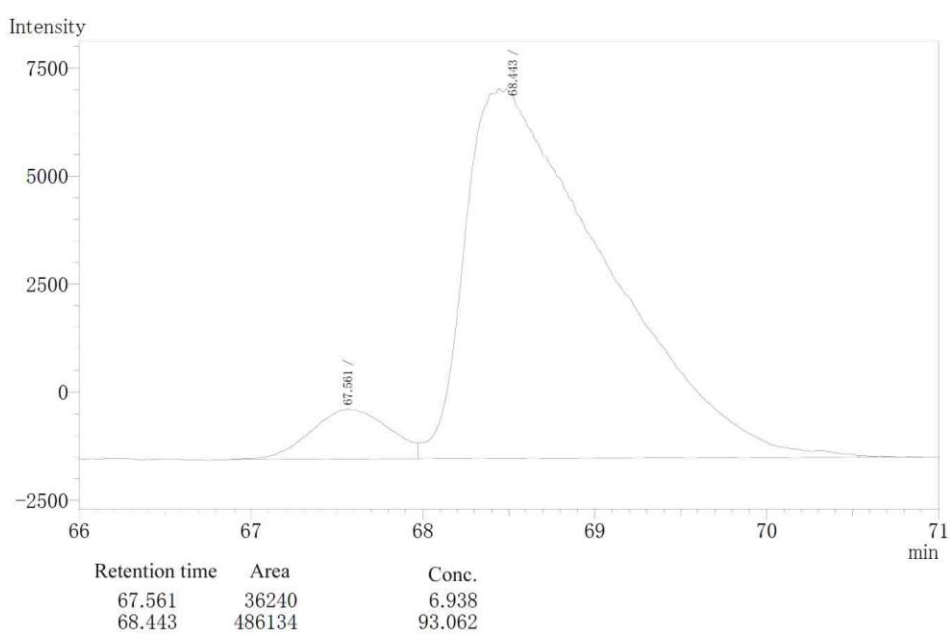
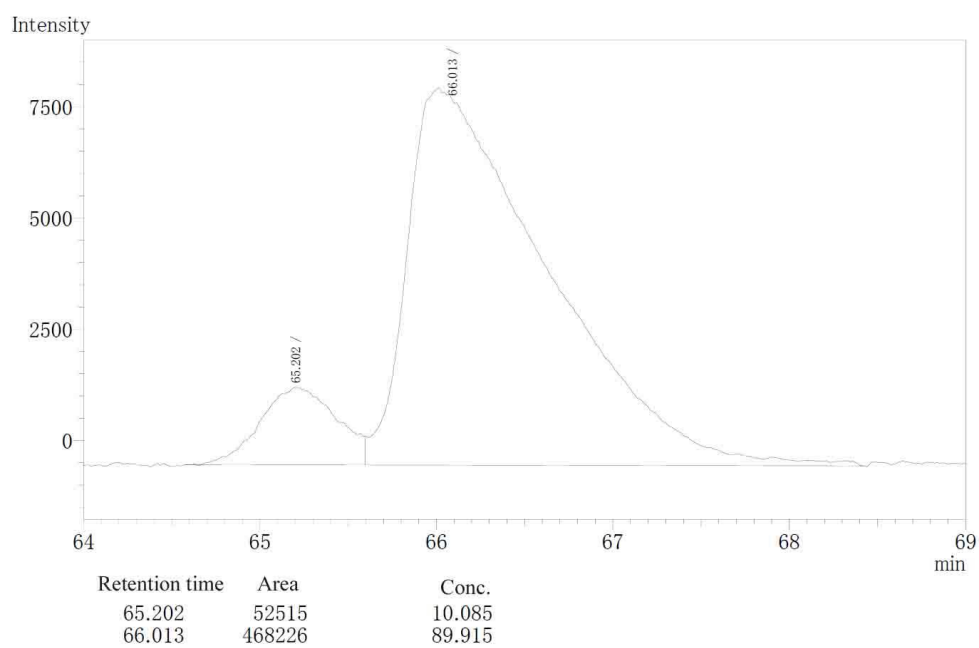
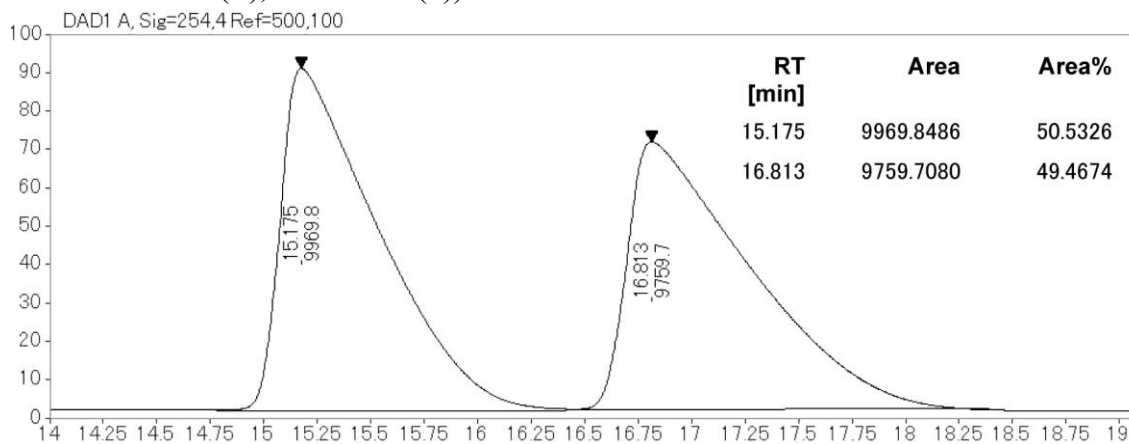


Table 5, entry 8: (*S*)-**2** (80% *ee*)

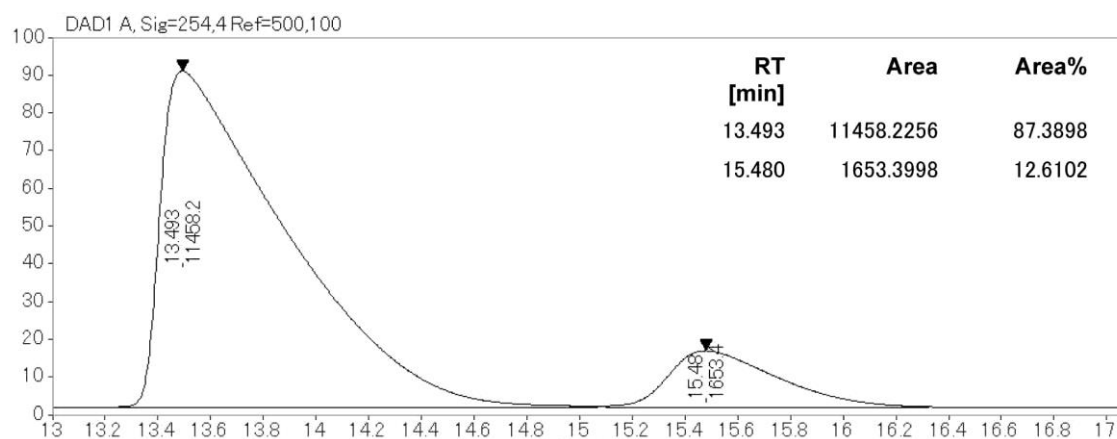


3-(2-Naphthalenyl)-1-pentene^[b]

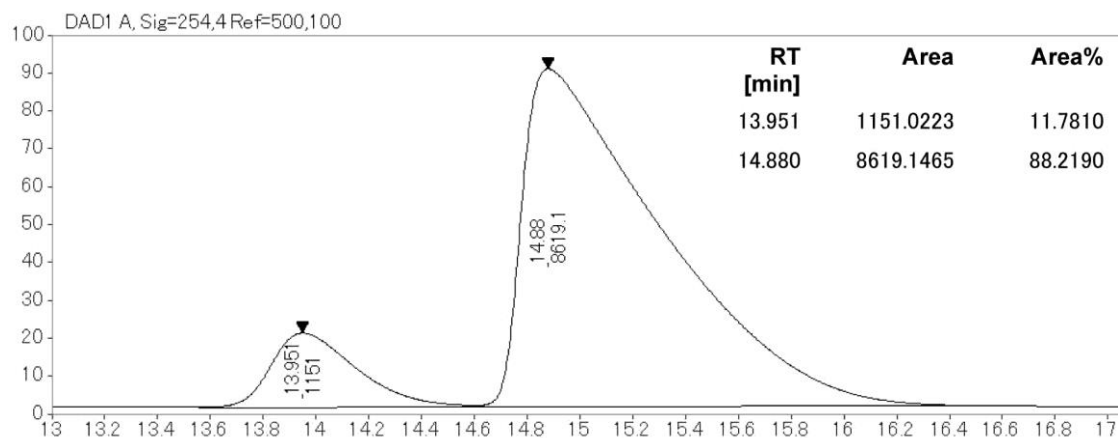
Enantiomeric excess was determined by chiral LC (OJ-H, Hexane, Flow rate: 1.0 mL/min, Rt = 14-15 min (*R*), 15-16 min (*S*)).



Scheme 1: (*R*)-Product (75% ee)

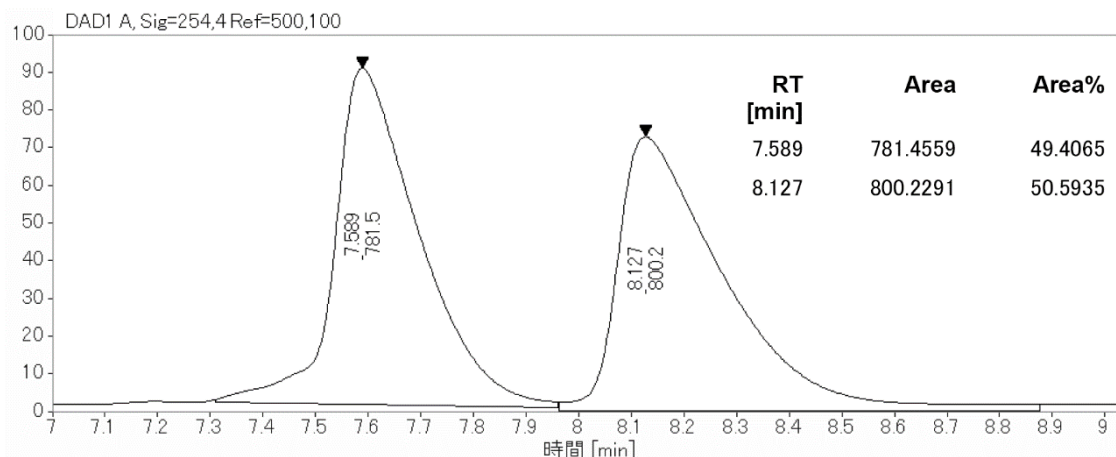


Scheme 1: (*S*)-Product (76% ee)

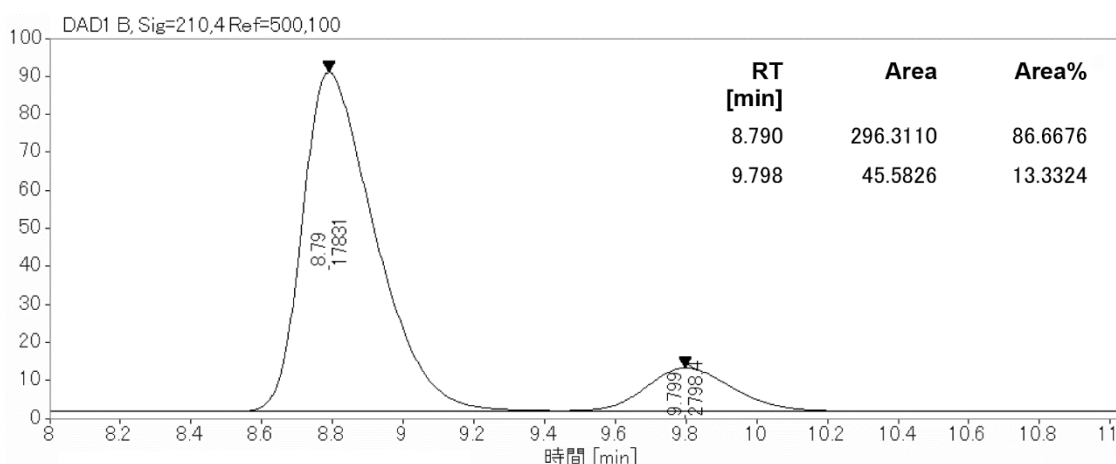


3-(3'-Methylphenyl)-1-pentene^[c]

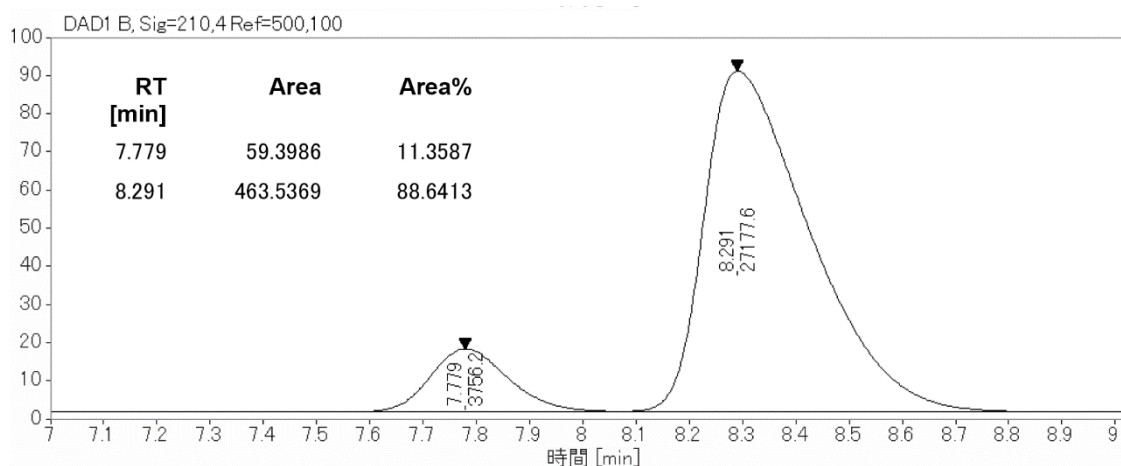
Enantiomeric excess was determined by chiral LC (OJ-H, Hexane, Flow rate: 1.0 mL/min, $R_t = 7.5$ min (*R*), 8.5 min (*S*)).



Scheme 1: (*R*)-Product (73% ee)

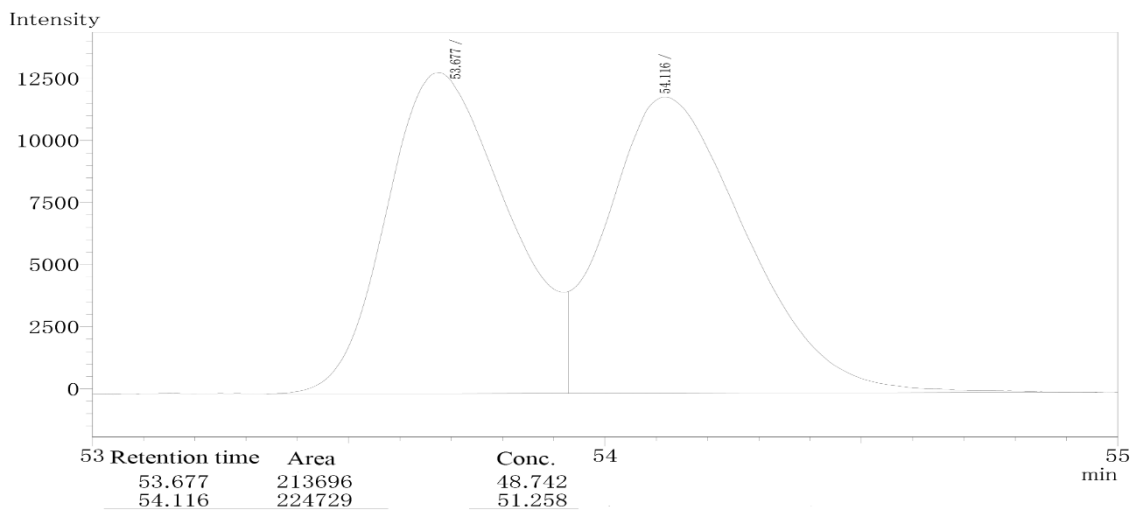


Scheme 1: (*S*)-Product (77% ee)

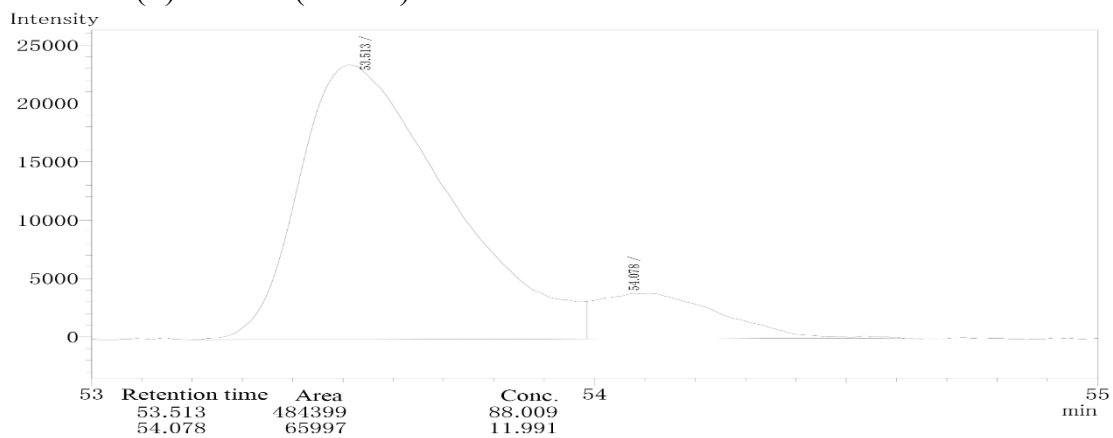


3-(4'-Methylphenyl)-1-pentene^[a]

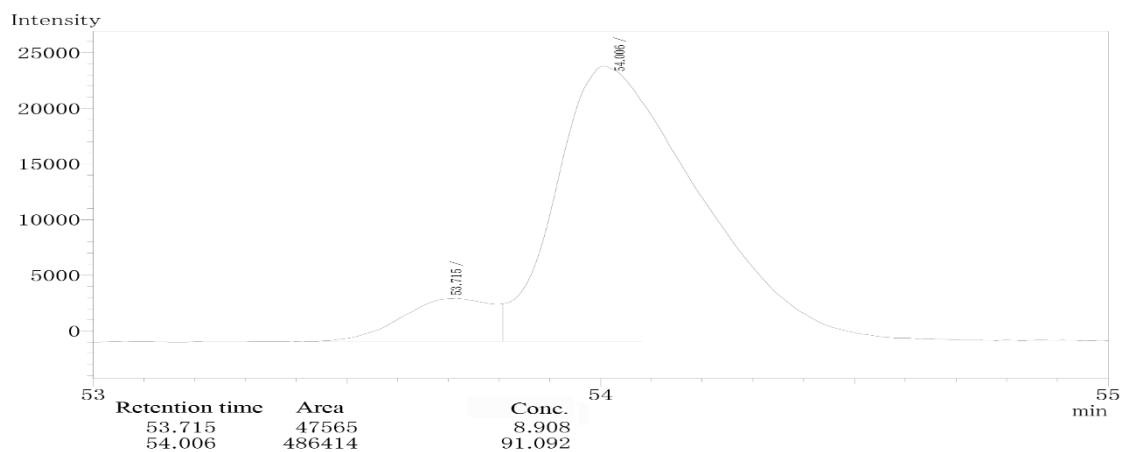
Enantiomeric excess was determined by Chiral GLC (Supelco β -Dex 120, initially at 50 °C, isotherm 15 min, then increase at the rate of 5 °C/min to 90 °C, isotherm 30 min, then increase at the rate of 5 °C/min to 120 °C, N₂ gas, linear velocity of 27.5 cm/s, Rt = 53 min (*R*), 54 min (*S*))



Scheme 1: (*R*)-Product (76% ee)

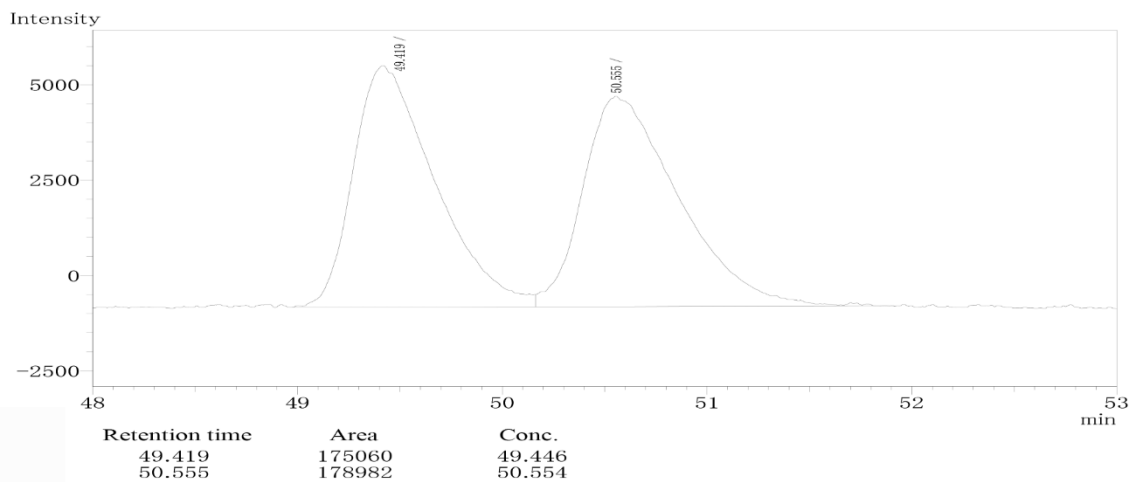


Scheme 1: (*S*)-Product (82% ee)

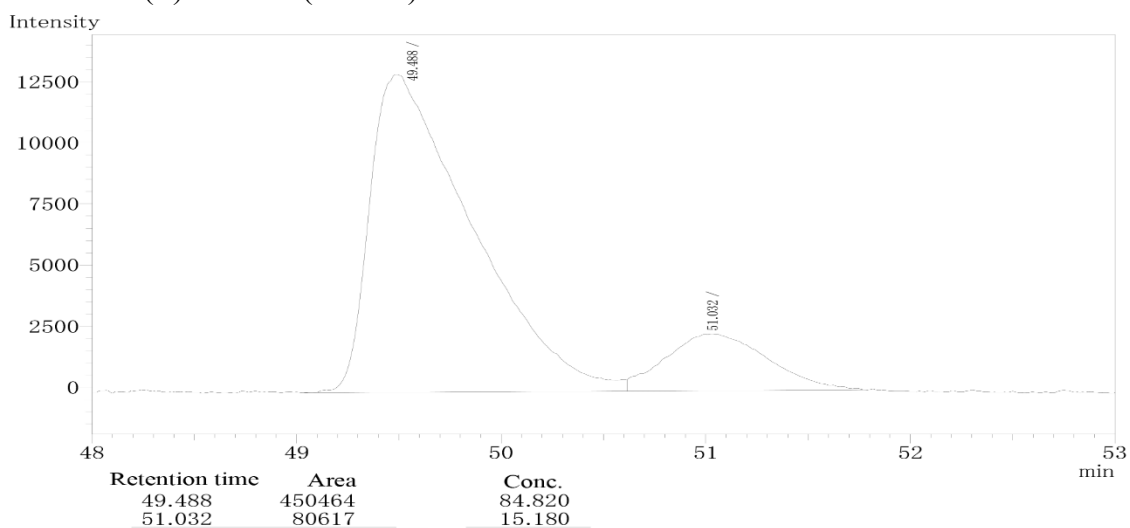


3-(4'-Chlorophenyl)-1-pentene^[d]

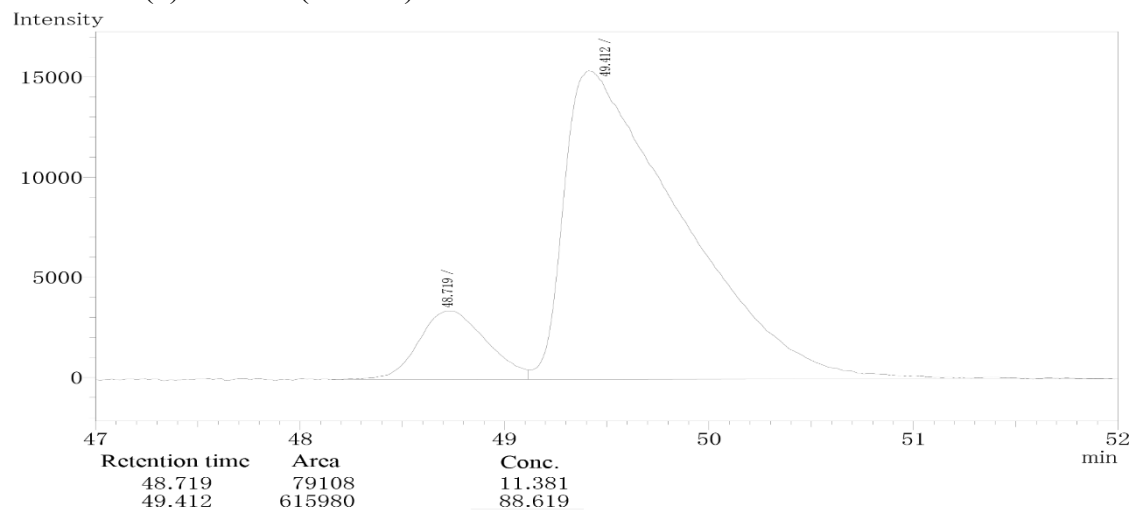
Enantiomeric excess was determined by Chiral GLC (Supelco β -Dex 120, 75 °C, N₂ gas, linear velocity of 27.5 cm/s, Rt = 49 min (*R*), 50 min (*S*))



Scheme 1: (*R*)-Product (70% *ee*)



Scheme 1: (*S*)-Product (77% *ee*)



[a] F. Fang, H. Zhang, F. Xie, G. Yang, W. Zhang, *Tetrahedron* 66 (2010) 3593–3598.

[b] L. Kong, J. Morban, D. Pichon, M. Jean, M. Albalat, T. Vives, S. Colombel-Rouen, M. Giorgi, V. Dorcet, T. Roisnel, C. Crévisy, D. Nuel, P. Nava, S. Humbel, N. Vanthuyne, M. Mauduit, H. Clavier, *J. Am. Chem. Soc.* 142 (2020) 93–98.

[c] W. Xiong, G. Xu, X. Yu, W. Tang, *Organometallics* 38 (2019) 4003–4013.

[d] W.-J. Shi, L.-X. Wang, Y. Fu, S.-F. Zhu, Q.-L. Zhou, *Tetrahedron: Asymmetry* 14 (2003) 3867–3872.