**Synthesis of β -Substituted α -Amino Acids Using Iridium-Catalyzed Asymmetric
Allylic Substitution**

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Supporting information

A list of contents:

1. Experimental for compounds **8a-f**, **9a-f**, **15-29**, **31-37**, **41a-b**, **42a-b**, **43** (S2-S18)
2. ^1H NMR spectra for compounds **8a-f**, **9a-f**, **16**, **37**, **41a-b**, **42a-b** (S19-S36)

(2*S*,3*S*)-2-(Benzhydrylidenylamino)-3-phenylpent-4-enoic acid *tert*-Butyl Ester (8a). **(2*R*,3*S*)-2-(Benzhydrylidenylamino)-3-phenylpent-4-enoic acid *tert*-Butyl Ester (9a).** (**Table 1, Entry 1**) To a stirred suspension of 1-phenylpropenyl acetate **2** (60.0 mg, 0.340 mmol), **1** (50.0 mg, 0.170 mmol), **11** (10.6 mg, 0.017 mmol), [Pd₂(dba)₃·CHCl₃] (5.30 mg, 0.005 mmol), and (*R*)-**12** (7.9 mg, 0.015 mmol) in toluene (0.57 ml) was added an aqueous 50% KOH solution (57.3 µl, 0.511 mmol) at 0 °C under an argon atmosphere. After being stirred vigorously at 0 °C for 3.5 h, the mixture was diluted with ether (15 ml). The organic phase was washed with aqueous saturated NaHCO₃ (3 X 5 ml) and brine (5 ml). The extract was dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography [basic silica gel, hexane/AcOEt (300/1)] to give 11.1 mg (16%) of **9a'** and 33.1 mg (48%) of **10** as a colorless oil. (**Table 1, Entry 2**) To a suspension of cinnamyl acetate **3** (30.0 mg, 0.170 mmol), **1** (50.0 mg, 0.170 mmol), **11** (10.6 mg, 0.017 mmol) [Ir(cod)Cl]₂ (11.4 mg, 0.017 mmol), and triphenyl phosphite (17.7 µl, 0.068 mmol) in toluene (0.57 ml) was added an aqueous 50% KOH solution (37.5 µl, 0.511 mmol) under an argon atmosphere, and the resulting mixture was stirred vigorously at room temperature for 20 h. After the usual workup, the crude was purified by column chromatography [basic silica gel, hexane/AcOEt (500/1)] to give 17.0 mg (24%) of **8a** and 4.1 mg (7%) of **9a'**. (**Table 1, Entry 3**) By a procedure similar to that described in Table1-Entry 2, the imine **1** (50 mg, 0.170 mmol) was converted into 21.0 mg (30%) of **8a** and 7.2 mg (7%) of **9a'** using cinnamyl benzoate **4** (30.0 mg, 0.170 mmol). (**Table 1, Entry 4**) By a procedure similar to that described in Table1-Entry 2, the imine **1** (42.2 mg, 0.143 mmol) was converted into 6.0 mg (12%) of **8a** and 1.4 mg (3%) of **9a'** using cinnamyl methyl carbonate **5** (22.9 mg, 0.119 mmol), **11** (9.0 mg, 0.014 mmol), [Ir(cod)Cl]₂ (8.0 mg, 0.012 mmol), triphenyl phosphite (12.4 µl, 0.048 mmol), and aqueous 50% KOH solution (31.7 µl, 0.429 mmol). (**Table 1, Entry 5**) By a procedure similar to that described in Table1-Entry 2, the imine **1** (43.5 mg, 0.147 mmol) was converted into 9.6 mg (19%) of **8a** and 2.0 mg (4%) of **9a'** using cinnamyl phenyl carbonate **6** (31.2 mg, 0.123 mmol), **11** (9.3 mg, 0.015 mmol), [Ir(cod)Cl]₂ (8.3 mg, 0.012 mmol), triphenyl phosphite (12.8 µl, 0.048 mmol), and aqueous 50% KOH solution (31.7 µl, 0.441 mmol). (**Table 1, Entry 6**) By a procedure similar to that described in Table1-Entry 2, the imine **1** (50.0 mg, 0.170 mmol) was converted into 26.8 mg (39%) of **8a** and 5.5 mg (8%) of **9a'** using cinnamyl ethyl phosphate **7** (91.5 mg, 0.340 mmol), [Ir(cod)Cl]₂ (11.4 mg, 0.017 mmol), and triphenyl phosphite (17.7 µl, 0.068 mmol). (**Table 2, Entry 1**) To a stirred suspension of **4** (40.3 mg, 0.170 mmol), **1** (50.0 mg, 0.170mmol), [Ir(cod)Cl]₂ (11.4 mg, 0.017 mmol), and **13** (13.8 mg, 0.034 mmol) in toluene (1.4 ml) was added an aqueous 50% KOH solution (37.5 µl, 0.511 mmol) at 0 °C under an argon atmosphere. After being stirred vigorously at 0 °C for 20 h, the mixture was diluted with ether (15 ml). The organic phase was washed with aqueous saturated NaHCO₃ (2 ml) and brine (2

ml). The extract was dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography [basic silica gel, hexane/AcOEt (500/1)] to give 14.2 mg (20%) of **8a** and 6.3 mg (9%) of **9a**. **(Table 2, Entry 2)** By a procedure similar to that described in Table2-Entry 1, the imine **1** (50.0 mg, 0.170 mmol) was converted into 4.1 mg (6%) of **8a** and 0.6 mg (1%) of **9a** using **14** (26.3 mg, 0.068 mmol) as ligand. **(Table 2, Entry 3)** By a procedure similar to that described in Table2-Entry 1, the imine **1** (50.0 mg, 0.170 mmol) was converted into 3.0 mg (4%) of **8a** and 1.1 mg (2%) of **9a** using **15** (13.6 mg, 0.034 mmol) as ligand. **(Table 2, Entry 4)** By a procedure similar to that described in Table2-Entry 1, the imine **1** (50.0 mg, 0.170 mmol) was converted into 5.2 mg (8%) of **8a** and 1.9 mg (3%) of **9a** using **16** (10.6 mg, 0.0170 mmol) as ligand. **(Table 2, Entry 5) General Procedure for Asymmetric Allylic Alkylation: Method A:** To a stirred suspension of **7** (46.0 mg, 0.170 mmol), **1** (50.0 mg, 0.170mmol), [Ir(cod)Cl]₂ (11.4 mg, 0.017 mmol), and **16** (14.2 mg, 0.034 mmol) in toluene (1.4 ml) was added an aqueous 50% KOH solution (37.5 µl, 0.511 mmol) at 0 °C under an argon atmosphere. After being stirred vigorously at 0 °C for 20 h, the mixture was diluted with ether (15 ml). The organic phase was washed with aqueous saturated NaHCO₃ (2 ml) and brine (2 ml). The extract was dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography [basic silica gel, hexane/AcOEt (500/1)] to give 46.4 mg (67%) of **8a** and 10.6 mg (15%) of **9a** as a colorless oil. **(Table 2, Entry 7)** By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 19.8 mg (28%) of **8a** and 10.2 mg (15%) of **9a** using **17** (14.2 mg, 0.034 mmol). **(Table 2, Entry 8)** By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 1.9 mg (3%) of **8a** and 0.8 mg (1%) of **9a** using **18** (14.7 mg, 0.034 mmol). **(Table 3, Entry 1)** By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 8.4 mg (12%) of **8a** and 3.2 mg (5%) of **9a** using **19** (15.9 mg, 0.034 mmol). **(Table 3, Entry 2)** By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 30.9 mg (44%) of **8a** and 12.7 mg (18%) of **9a** using **20** (16.3 mg, 0.034 mmol). **(Table 3, Entry 3)** By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 34.7 mg (50%) of **8a** and 12.1 mg (17%) of **9a** using **21** (15.2 mg, 0.034 mmol). **(Table 3, Entry 4)** By a procedure similar to that of Method A, the imine **1** (25.0 mg, 0.085 mmol) was converted into 10.4 mg (30%) of **8a** and 2.44 mg (7%) of **9a** using (*R*)-**22** (8.90 mg, 0.017 mmol). **(Table 3, Entry 5)** By a procedure similar to that described in Table 3-Entry 4, the imine **1** (25.0 mg, 0.085 mmol) was converted into 14.4 mg (41%) of **8a** and 3.7 mg (11%) of **9a** using (*S*)-**22** (8.90 mg, 0.017 mmol). **(Table 4, Entry 1)** By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 17.5 mg (25%) of **8a** and 3.3 mg (5%) of **9a** using **11** (10.6 mg, 0.017 mmol) as PTC. **(Table 4, Entry 2)** By a procedure similar to that of Method

A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 14.7 mg (21%) of **8a** and 14.0 mg (20%) of **9a** using hexadecyltrimethylammonium bromide (6.2 mg, 0.017 mmol) as PTC. (**Table 4, Entry 3**) By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 35.0 mg (50%) of **8a** and 14.7 mg (21%) of **9a** using solid KOH (19 mg, 0.340 mmol) as a base. (**Table 4, Entry 4**) By a procedure similar to that of Method B, the imine **1** (50.0 mg, 0.170 mmol) was converted into 15.5 mg (22%) of **8a** and 3.9 mg (6%) of **9a** using $\text{KN}(\text{SiMe}_3)$ (0.5 M in toluene) (0.34 ml, 0.170 mmol) as a base. (**Tables 4, Entry 5**) By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 20.8 mg (30%) of **8a** and 9.3 mg (13%) of **9a** using $\text{CsOH}\cdot\text{H}_2\text{O}$ (43 mg, 0.256 mmol) as a base. (**Tables 4, Entry 6**) To a suspension of 60 % NaH in THF (0.5 ml) was added a solution of **1** (50.0 mg, 0.170 mmol) in THF (0.5 ml) and the mixture was stirred at 0 °C for 0.5 h. A second flask containing $[\text{Ir}(\text{cod})\text{Cl}]_2$ (11.4 mg, 0.017 mmol), **16** (14.2 mg, 0.034 mmol), **7** (46.0 mg, 0.170 mmol), and THF (0.4 ml) was stirred at room temperature for 10 min. To it was added slowly the above solution at 0 °C. After being stirred at 0 °C for 9 h, the mixture was quenched with aqueous NH_4Cl and extracted with ether (3 X 15 ml). The combined extracts were washed with brine (5ml), dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (basic silica gel, hexane /AcOEt=500:1) afforded 12.3 mg (18%) of **8a** and 7.7 mg (11%) of **9a**. (**Table 4, Entry 7**) To a suspension of **7** (46.0 mg, 0.170 mmol), **1** (50.0 mg, 0.170mmol), $[\text{Ir}(\text{cod})\text{Cl}]_2$ (11.4 mg, 0.017 mmol), **16** (14.2 mg, 0.034 mmol), LiBr (22 mg, 0.253 mmol), and THF (1.4 ml) was added DBU (30.0 μl , 0.204 mmol) at room temperature under an argon atmosphere and the mixture was stirred vigorously at room temperature for 7 h. After the usual workup, the crude product was purified by column chromatography [basic silica gel, hexane/AcOEt (500/1)] to give 3.9 mg (6%) of **8a**, 9.9 mg (14%) of **9a** and 16.4 mg (23%) of **10**. (**Table 4, Entry 8**) By a procedure similar to that of Method B, the imine **1** (50.0 mg, 0.170 mmol) was converted into 4.0 mg (6%) of **8a**, 34.9 mg (50%) of **9a** and 2.1 mg (3%) of **10** using freshly prepared LDA (0.170 mmol) as base. (**Table 4, Entry 9**) **General Procedure for Asymmetric Allylic Alkylation (Method B):** To a stirred solution of **1** (75 mg, 0.255 mmol) in THF (0.7 ml) was added a 1.56 M solution of $\text{LiN}(\text{SiMe}_3)_3$ in THF (0.17 ml, 0.255 mmol) at -78 °C. In a second flask, a mixture of $[\text{Ir}(\text{cod})\text{Cl}]_2$ (11.4 mg, 0.017 mmol), **16** (14.2 mg, 0.034 mmol), **7** (46.0 mg, 0.170 mmol), and THF (0.7 ml) was stirred at room temperature for 10 min. To it was added slowly the above solution at 0 °C. After the addition, the mixture was quenched with aqueous NH_4Cl and extracted with ether (3 X 15 ml). The extracts were washed with brine (5ml), dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (basic silica gel, hexane/AcOEt=500:1) afforded the 7.0 mg (10%) of **8a**, 50.3 mg (72%) of **9a** and 0.3 mg (0.4 %) of **10**. **8a**: HPLC [Chiralcel OD-H column, 0.6% 2-

propanol/hexane, 0.3 ml/min, $\lambda = 254$ nm, retention times: (major) 27.3 min, (minor) 24.0 min]. $[\alpha]_D^{24} = -155^\circ$ (*c* 1.47, CHCl_3); ^1H NMR (500 MHz, CHCl_3) δ 1.41 (s, 9H), 4.11 (t, 1H, $J = 8.6$ Hz), 4.22 (d, 1H, $J = 8.6$ Hz), 5.06 (d, 1H, $J = 10.1$ Hz), 5.11 (d, 1H, $J = 17.1$ Hz), 5.98 (ddd, 2H, $J = 8.6, 10.1, 17.1$ Hz), 7.10-7.50 (m, 14H); ^{13}C NMR (126 MHz, CHCl_3) δ 28.0, 53.8, 71.1, 81.2, 116.5, 126.5, 127.8, 127.9, 128.1, 128.2, 128.4, 128.8, 129.1, 130.0, 136.3, 138.1, 139.7, 140.7, 170.1, 170.3; IR (CHCl_3) ν 3007, 1729, 1621 cm^{-1} ; MS (FAB) m/z 416 (MH^+ , 7), 360 (95), 314 (10), 105 (100); Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_2$: C, 81.72; H, 7.10; N, 3.40. Found: C, 81.49; H, 7.12; N, 3.20. **9a**: HPLC [Chiralcel OD-H column, 0.6% 2-propanol/hexane, 0.3 ml/min, $\lambda = 254$ nm, retention times: (**9a**) 24.2 min, (**9a'**) 23.0 min]. $[\alpha]_D^{24} = +169$ (*c* 1.47, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 1.29 (s, 9H), 4.05-4.11 (m, 1H), 4.22 (d, 1H, $J = 6.1$ Hz), 5.12-5.18 (m, 2H), 6.23-6.33 (m, 1H), 6.82-7.64 (m, 15H); ^{13}C NMR (126 MHz, CDCl_3) δ 27.9, 53.7, 70.9, 81.0, 117.0, 126.4, 127.8, 127.9, 128.1, 128.2, 128.3, 128.6, 128.9, 130.1, 136.5, 137.8, 139.6, 141.3, 169.9, 170.6; IR (CHCl_3) ν 3008, 1727, 1623 cm^{-1} ; MS (FAB) m/z 412 (MH^+ , 100), 356 (43), 310 (22), 238 (69); HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{30}\text{NO}_2$ (MH^+) 412.2277, found 412.2285.

(R)-4-Pentyloxy-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (15). By a procedure similar to that of **16**, (*R*)-2,2'-binaphthol (430 mg, 1.5 mmol) was converted into **15** (132 mg, 0.33 mmol) using PCl_3 (0.14 ml, 1.5 mmol), Et_3N (0.63 ml, 4.5 mmol), and 1-pentanol (0.15 ml, 1.4 mmol). $[\alpha]_D^{24} = -1390$ (*c* 1.04, CHCl_3); ^1H NMR (500MHz, C_6D_6) δ 0.74 (t, 3H, $J = 7.0$), 1.03-1.14 (m, 4H), 1.32-1.37 (tt, 2H, $J = 6.7, 6.7$ Hz), 3.60 (ddt, 1H, $J = 6.7, 10.1, 6.7$ Hz), 3.83 (ddt, 1H, $J = 6.7, 10.1, 6.7$ Hz), 6.89-6.92 (m, 2H), 7.10-7.15 (m, 2H), 7.40-7.49 (m, 4H), 7.56-7.62 (m, 4H); ^{13}C NMR (126MHz, C_6D_6) δ 14.1, 22.5, 28.0, 30.88, 30.91, 65.45, 65.47, 122.1, 122.2, 123.3, 124.6, 125.1, 125.2, 126.6, 126.7, 127.3, 127.4, 128.6, 128.7, 130.3, 130.9, 131.4, 132.0, 133.2, 133.4, 148.3, 149.81, 149.85; IR (CHCl_3) ν 2958, 2869, 948, 823 cm^{-1} ; MS m/z : (EI) 402 (M^+ , 16), 382 (100), 268 (44), 239 (31); HRMS: (EI) calcd for $\text{C}_{25}\text{H}_{23}\text{O}_3\text{P}$ (M^+) 402.1385, found 402.1387.

(R)-4-(2-Ethylsulfanyloxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (16) A warm solution (60 °C) of (*R*)-2,2'-binaphthol (0.86 g, 3.0 mmol) in toluene (25 ml) was added in 5 min to a cooled solution (−60 °C) of PCl_3 (0.27 ml, 3.0 mmol) and Et_3N (0.86 ml, 6.0 mmol) in toluene (5ml). The reaction mixture was stirred for 2 h, warmed to room temperature, and filtered. The filtrate was treated with Et_3N (0.41 ml, 2.9 mmol) and ethyl 2-hydroxyethyl sulfide (0.3 ml 2.9 mmol) at −40 °C. After 16 h at room temperature, the reaction mixture was filtered, concentrated, and purified by chromatography [SiO_2 , hexane/AcOEt (10/1)] to give 0.95 g (75 %) of **16**. $[\alpha]_D^{24} = -520$ (*c* 2.10, CHCl_3); ^1H NMR (500 MHz, C_6D_6) δ 0.85 (t, 3H, $J = 7.3$ Hz), 2.03 (q, 2H, $J = 7.3$ Hz), 2.39 (t, 2H, $J = 7.0$ Hz), 3.72 (ddt, 1H, $J = 7.0, 10.4, 7.0$ Hz), 3.88-3.95 (m, 1H), 6.89-6.93 (m, 2H), 7.09-7.16 (m, 2H),

7.38-7.47 (m, 4H), 7.55-7.64 (m, 4H); ^{13}C NMR (126 MHz, C_6D_6) δ 14.8, 26.2, 32.3, 65.0, 122.0, 122.1, 123.2, 124.5, 125.1, 125.3, 126.7, 127.3, 128.6, 128.7, 130.4, 130.9, 131.4, 132.0, 133.2, 133.4, 148.2; IR (CHCl_3) ν 2972, 2929, 945, 826 cm^{-1} ; MS (CI) m/z 421 (MH^+ , 8), 333 (100), 287 (15), 89 (30); HRMS (CI) calcd for $\text{C}_{24}\text{H}_{21}\text{O}_3\text{PS}$ (MH^+) 421.1027, found 421.1034.

(R)-4-(3-Methylsulfanylpropoxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (17).

By a procedure similar to that of **16**, (*R*)-2,2'-binaphthol (430 mg, 1.50 mmol) was converted into **17** (96.7 mg, 0.23 mmol) using PCl_3 (0.14 ml, 1.50 mmol), Et_3N (0.63 ml, 4.50 mmol), and 3-(methylthio)-1-propanol (0.14 ml, 1.40 mmol). $[\alpha]^{24}_{\text{D}} = -423$ (c 0.50, CHCl_3); ^1H NMR (500 MHz, C_6D_6) δ 1.46-1.53 (tt, 2H, $J = 6.7, 6.7\text{ Hz}$), 1.64 (s, 3H), 2.17-2.29 (m, 2H), 3.60-3.68 (m, 1H), 3.81-3.89 (m, 1H), 6.89-6.93 (m, 2H), 7.09-7.16 (m, 2H), 7.38-7.49 (m, 4H), 7.55-7.63 (m, 2H); ^{13}C NMR (126 MHz, C_6D_6) δ : 15.1, 30.3, 30.58, 30.60, 63.8, 122.0, 122.2, 123.27, 123.29, 124.58, 124.62, 125.16, 125.24, 126.66, 126.69, 127.4, 128.6, 128.7, 130.4, 130.9, 131.4, 132.0, 133.2, 133.4, 148.2, 149.68, 149.72; IR (CHCl_3) ν 2961, 2920, 2360, 947, 825 cm^{-1}

(R)-4-(4-Methylsulfanylbutoxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (18).

By a procedure similar to that of **16**, (*R*)-2,2'-binaphthol (860 mg, 3.00 mmol) was converted into **18** (260 mg, 0.60 mmol) using 4-(methylthio)-1-butanol (0.34 ml, 2.80 mmol). $[\alpha]^{24}_{\text{D}} = -490$ (c 2.18, CHCl_3); ^1H NMR (500 MHz, C_6D_6) δ 1.37-1.38 (m, 4H), 1.70 (s, 3H), 2.09 (t, 2H, $J = 6.4\text{ Hz}$), 3.51-3.57 (m, 1H), 3.74-3.80 (m, 1H), 6.90-6.93 (m, 2H), 7.10-7.14 (m, 2H), 7.39-7.49 (m, 4H), 7.56-7.63 (m, 4H); ^{13}C NMR (126 MHz, C_6D_6) δ 15.1, 25.4, 30.07, 30.10, 33.8, 64.9, 122.0, 122.2, 123.29, 123.30, 124.57, 124.61, 125.1, 125.2, 126.6, 126.7, 127.35, 127.39, 128.6, 128.7, 130.3, 130.9, 131.4, 132.0, 133.2, 133.4, 148.3, 149.7, 149.8; IR (CHCl_3) ν 3044, 2919, 943, 826 cm^{-1} ; MS m/z : (CI) 435 (MH^+ , 5.5), 408 (15), 333 (10), 137 (100); HRMS: (CI) calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3\text{PS}$ (MH^+) 435.1184, found 435.1180.

(R)-4-(2-Phenylsulfanylethoxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (19).

By a procedure similar to that of **16**, (*R*)-2,2'-binaphthol (496 mg, 1.73 mmol) was converted into **19** (260 mg, 0.56 mmol) using PCl_3 (0.15 ml, 1.73 mmol), Et_3N (0.72 ml, 4.10 mmol), and 2-(phenylthio)-1-ethanol (267 mg, 1.73 mmol). $[\alpha]^{24}_{\text{D}} = -456$ (c 1.03, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 3.09 (t, 2H), 3.88 (ddt, 1H, $J = 7.3, 10.6, 7.3\text{ Hz}$), 4.07 (ddt, 1H, $J = 7.3, 10.6, 7.3\text{ Hz}$), 7.13-7.50 (m, 11H), 7.84-7.98 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 34.47, 34.50, 63.3, 64.4, 121.4, 121.7, 122.6, 124.01, 124.05, 124.9, 125.1, 126.2, 126.3, 126.5, 127.0X2, 128.33, 128.34, 128.9, 129.9, 130.1, 130.4, 131.0, 131.5, 132.5, 132.8, 134.9, 147.4, 148.4; IR (CHCl_3) ν 3061, 2364, 946, 825 cm^{-1} ; MS m/z : (CI) 469 (MH^+ , 6), 408 (15), 333 (10), 137 (100); HRMS: (CI) calcd for $\text{C}_{28}\text{H}_{22}\text{O}_3\text{PS}$ (MH^+) 469.1027, found 469.1021.

(R)-4-(2-Benzylsulfanylethoxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (20).

By a procedure similar to that of **16**, (*R*)-2,2'-binaphthol (496 mg, 1.73 mmol) was converted into **20** (82 mg, 0.170 mmol) using PCl₃ (0.15 ml, 1.73 mmol), Et₃N (0.72 ml, 4.10 mmol), and 2-(benzylthio)-1-ethanol (291 mg, 1.73 mmol). $[\alpha]_D^{24} = -409$ (*c* 0.76, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.59 (t, 2H), 3.61 (dd, 2H, *J* = 13.4, 24.1 Hz), 4.00 (ddt, 1H, *J* = 7.0, 10.3, 7.0 Hz), 3.82 (ddt, 1H, *J* = 7.0, 10.3, 7.0 Hz), 7.14-7.51 (m, 11H), 7.89-7.99 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 31.6, 36.2, 64.05, 64.09, 121.5, 121.8, 122.66, 122.68, 124.00, 124.04, 124.2, 125.0, 125.1, 126.3, 126.9, 127.0, 127.1, 128.3, 128.4, 128.5, 128.9, 130.1, 130.4, 131.0, 131.4, 131.5, 132.6, 132.8, 137.9, 147.42, 147.44, 148.50, 148.54; IR (CHCl₃) ν 3008, 2361, 947, 825 cm⁻¹; MS *m/z*: (CI) 483 (MH⁺, 8.1), 391 (19), 333 (55), 151 (100); HRMS: (CI) calcd for C₂₉H₂₄O₃PS (MH⁺) 483.1184, found 483.1172.

(R)-4-(2-Isobutylsulfanylethoxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (21).

By a procedure similar to that of **16**, (*R*)-2,2'-binaphthol (496 mg, 1.73 mmol) was converted into **21** (433 mg, 0.97 mmol) using PCl₃ (0.15 ml, 1.73 mmol), Et₃N (0.72 ml, 4.10 mmol), and 2-(isobutylthio)-1-ethanol (233 mg, 1.73 mmol) $[\alpha]_D^{24} = -476$ (*c* 1.15, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 0.88 (m, 6H), 1.66 (m, 1H), 2.28 (d, 2H, *J* = 7.0 Hz), 2.68 (t, 2H, *J* = 7.3 Hz), 3.86 (ddt, 1H, *J* = 7.3, 10.3, 7.3 Hz), 4.04 (ddt, 1H, *J* = 7.3, 10.3, 7.3 Hz), 7.23-7.51 (m, 8H), 7.90-7.98 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 21.8, 28.7, 33.2, 41.6, 64.4, 65.4, 121.5, 121.8, 122.65, 122.67, 124.00, 124.04, 124.9, 125.0, 126.3 X 2, 127.0 X 2, 128.3, 128.4, 130.1, 130.4, 131.0, 131.5, 132.6, 132.8, 147.45, 147.49, 184.5, 184.6; IR (CHCl₃) ν 2961, 2361, 946, 825 cm⁻¹; MS *m/z*: (CI) 449 (MH⁺, 8), 391 (20), 333 (14), 117 (100); HRMS: (CI) calcd for C₂₆H₂₆O₃PS (MH⁺) 449.1340, found 449.1335.

(R)-4-(2-Benzylsulfanyl-3-methylbutoxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (R)-22.

By a procedure similar to that of **16**, (*R*)-2,2'-binaphthol (0.106 g, 0.37 mmol) was converted into (*R*)-**22** (53 mg, 0.10 mmol) using PCl₃ (32 μl, 0.37 mmol), Et₃N (0.15 ml, 1.11 mmol), toluene (4.5 ml), and (*R*)-2-benzylsulfanyl-3-methylbutan-1-ol (70 mg, 0.33 mmol). ¹H NMR (500 MHz, CDCl₃) δ 0.79 (d, 3H, *J* = 6.7 Hz), 0.87 (d, 3H, *J* = 6.7 Hz), 1.99-2.03 (m, 1H), 2.55-2.58 (m, 1H), 3.66 (s, 2H), 3.84-3.88 (m, 1H), 3.98-4.04 (m, 1H), 7.20-7.51 (m, 13H), 7.90-7.99 (m, 4H); IR (CHCl₃) ν 2961, 1260, 1232, 1019 cm⁻¹. MS (CI) *m/z* 525 (MH⁺, 6), 333 (100), 193 (26); HRMS (CI) calcd for C₃₂H₃₀O₃PS (MH⁺) 525.1653, found 525.1664.

(S)-4-(2-Benzylsulfanyl-3-methylbutoxy)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a'*]dinaphthalene (S)-22.

By a procedure similar to that of **16**, (*S*)-2,2'-binaphthol (106 mg, 0.37 mmol) was converted into (*S*)-**22** (60 mg, 0.12 mmol) using PCl₃ (32 μl, 0.370 mmol), Et₃N (0.15 ml, 1.11 mmol), toluene (4.5 ml), and (*R*)-2-benzylsulfanyl-3-methylbutan-1-ol (70 mg, 0.33 mmol). ¹H NMR (500 MHz, CDCl₃) δ 0.80 (d, 3H, *J* = 6.7 Hz), 0.87 (d, 3H, *J* = 6.7 Hz), 2.02-2.06 (m, 1H), 2.55-

2.58 (m, 1H), 3.39-3.48 (m, 2H), 3.78-3.83 (m, 1H), 3.95-4.00 (m, 1H), 7.11-7.51 (m, 13H), 7.91-7.99 (m, 4H); IR (CHCl₃) ν 2962, 1232, 993 cm⁻¹. MS (CI) m/z 525 (MH⁺, 11), 333 (100), 193 (33); HRMS (CI) calcd for C₃₂H₃₀O₃PS (MH⁺) 525.1654, found 525.1641.

(R)-4-(2-Ethylsulfanylethoxy)-2,6-diphenyl-3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-

a']dinaphthalen (23). By a procedure similar to that of **16**, (*R*)-3,3'-diphenyl-2,2'-binaphthol (302 mg, 0.69 mmol) was converted into **23** (145 mg, 0.26 mmol) using PCl₃ (60 μ l, 0.69 mmol), Et₃N (0.29 ml, 2.07 mmol), toluene (10 ml), and 2-(ethylthio)-1-ethanol (72 μ l, 0.69 mmol). $[\alpha]_D^{24} = -562$ (c 0.93, CHCl₃); ¹H NMR (500 MHz, C₆D₆) δ 0.79 (t, 3H, J = 7.3 Hz), 1.91 (q, 2H, J = 7.3 Hz), 2.06-2.10 (m, 2H), 3.31-3.46 (m, 2H), 6.95-7.01 (m, 2H), 7.12-7.25 (m, 8H), 7.52-7.57 (m, 2H), 7.67-7.73 (m, 6H), 7.82-7.90 (m, 2H); ¹³C NMR (126 MHz, C₆D₆) δ 14.8, 26.0, 31.79, 31.82, 64.3, 64.4, 124.7, 125.5, 125.7, 126.0, 126.1, 126.59, 126.64, 127.3, 127.4, 128.46, 128.54, 128.7, 128.8, 130.4, 130.5, 130.7, 131.3, 131.6, 131.9, 132.9, 133.1, 135.0, 135.5, 138.1, 138.5, 145.8, 146.76, 146.80; IR (CHCl₃) ν 3035 2361, 957, 846 cm⁻¹; MS m/z : (CI) 573 (MH⁺, 55), 543 (22), 485 (100); HRMS: (CI) calcd for C₃₆H₃₀O₃PS (MH⁺) 573.1653, found 573.1659.

(R)-4-(2-Ethylsulfanylethoxy)-2,6-dimethyl-3,5-dioxa-4-phosphacyclohepta[2,1-a;3,4-

a']dinaphthalene (24). A warm solution (60 °C) of (*R*)-3,3'-dimethyl-2,2'-binaphthol (216 mg, 0.69 mmol) in toluene (6 ml) was added in 5 min to a cooled mixture (-60 °C) of PCl₃ (60 μ l, 0.69 mmol), Et₃N (0.219 ml, 1.51 mmol), and toluene (2ml). The reaction mixture was stirred for 2 h, warmed to room temperature, and filtered. A second flask was charged with 2-(ethylthio)-1-ethanol (72 μ l, 0.69 mmol) and THF (3 ml). To the cooled solution, a 1.57 M solution of butyllithium in hexane (0.44 ml, 0.69 mmol) was added at 0 °C and then stirring was continued for 0.5 h. The resulting solution was then slowly added (0.5 ml THF rinse) to the cold (-80 °C) solution of the filtrate so as to maintain the internal temperature below -70 °C. The resulting suspension was stirred at -80 °C for 10 min, then allowed to warm to ambient temperature, and maintained under these conditions for 15 h. The solvent was subsequently removed *in vacuo* and the crude was purified by column chromatography [SiO₂, hexane/AcOEt (10/1)] to give **24** (117 mg, 38%). $[\alpha]_D^{24} = -702$ (c 0.77, CHCl₃); ¹H NMR (500 MHz, C₆D₆) δ 0.82 (t, 3H, J = 7.3 Hz), 2.00 (q, 2H, J = 7.3 Hz), 2.35 (t, 2H, J = 7.0 Hz), 3.58 (ddq, 1H, J = 7.0, 10.6, 7.0 Hz), 3.92 (ddq, 1H, J = 7.0, 10.6 7.0 Hz), 6.90-6.93 (m, 2H), 7.14-7.19 (m, 2H), 7.44-7.52 (m, 2H), 7.62-7.63 (m, 2H); ¹³C NMR (126 MHz, C₆D₆) δ 14.8, 17.4, 17.9, 26.1, 32.3, 64.8, 123.37, 123.39, 124.7, 125.2, 125.3, 125.8, 127.3, 127.4, 128.5, 130.06, 130.10, 130.3, 130.5, 131.4, 132.0, 132.1, 132.3, 147.46, 147.49, 149.1, 149.2; IR (CHCl₃) ν 2926, 2361, 906, 791 cm⁻¹; MS m/z : (CI) 449 (MH⁺, 100), 419 (34), 361 (52); HRMS: (CI) calcd for C₂₆H₂₆O₃PS (MH⁺) 449.1340, found 449.1346.

(2*S*,3*S*)-2-(Benzhydrylidénylamino)-3-(4-fluorophenyl)pent-4-enoic Acid *tert*-Butyl Ester (8b). (Table 5, Entry 1) By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 43.6 mg (60%) of **8b** and 12.2 mg (17%) of **9b** using **25** (49.0 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 0.6% 2-propanol/hexane, 0.3 ml/min, λ = 254 nm, retention times: (major) 20.3 min, (minor) 19.5 min]. $[\alpha]_D^{24} = -116$ (*c* 1.13, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.39 (s, 9H), 4.09 (t, 1H, *J* = 8.2 Hz), 4.20 (d, 1H, *J* = 8.2 Hz), 5.06 (d, 1H, *J* = 10.0 Hz), 5.08 (d, 1H, *J* = 18.3 Hz), 6.94 (ddd, 1H, *J* = 8.2, 10.0, 18.3 Hz), 6.84-6.93 (m, 4H), 7.17-7.41 (m, 8H), 7.49-7.50 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 28.0, 52.8, 70.9, 81.3, 114.7, 114.9, 116.6, 127.9, 128.06, 128.11, 128.5, 128.8, 130.5, 130.6, 136.2, 136.42, 136.44, 138.1, 139.6, 160.6, 162.2, 169.9, 170.6; IR (CHCl₃) ν 2981, 1729, 1621 cm⁻¹; MS (FAB) *m/z* 430 (MH⁺, 85), 374 (90), 328 (40), 238 (100); HRMS (FAB) calcd for C₂₈H₂₉FNO₂ (MH⁺) 430.2182, found 430.2189. **(2*R*,3*S*)-2-(Benzhydrylidénylamino)-3-(4-fluorophenyl)pent-4-enoic Acid *tert*-Butyl Ester (9b).** (Table 5, Entry 6) By a procedure similar to that of Method B, the imine **1** (75.5 mg, 0.255 mmol) was converted into 6.1 mg (8%) of **8b** and 52.7 mg (73%) of **9b**, using **25** (49 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 0.3% 2-propanol/hexane, 0.5 ml/min, λ = 254 nm, retention times: (major) 19.7 min, (minor) 21.6 min]. $[\alpha]_D^{24} = +153$ (*c* 0.70, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.31 (s, 9H), 4.07 (dd, 1H, *J* = 6.4, 8.5 Hz), 4.17 (d, 1H, *J* = 6.4 Hz), 5.13 (d, 1H, *J* = 17.5), 5.17 (d, 1H, *J* = 10.3 Hz), 6.26 (ddd, 1H, *J* = 8.5, 10.3, 17.5 Hz), 6.85-6.92 (m, 4H), 7.08-7.11 (m, 2H), 7.30-7.40 (m, 6H), 7.61-7.64 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 27.9, 52.8, 70.9, 81.1, 114.8, 115.0, 117.2, 127.7, 127.9, 128.3, 128.4, 128.8, 130.0, 130.1, 130.2, 136.4, 136.99, 137.01, 137.6, 139.5, 160.6, 162.5, 169.7, 170.8; IR (CHCl₃) ν 2981, 1728, 1622, 1509 cm⁻¹; MS (FAB) *m/z* 430 (MH⁺, 100), 374 (85), 328 (45), 238 (95); HRMS (FAB) calcd for C₂₈H₂₉FNO₂ (MH⁺) 430.2182, found 430.2175. **(2*S*,3*S*)-2-(Benzhydrylidénylamino)-3-(4-trifluoromethylphenyl)pent-4-enoic Acid *tert*-Butyl Ester (8c).** (Table 5, Entry 2) By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 44.8 mg (55%) of **8c** and 18.8 mg (23%) of **9c** using **26** (57.3 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 0.5% 2-propanol/hexane, 0.5 ml/min, λ = 254 nm, retention times: (major) 16.6 min, (minor) 15.1 min]. $[\alpha]_D^{24} = -93.4$ (*c* 0.85, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.39 (s, 9H), 4.16 (t, 1H, *J* = 8.2 Hz), 4.27 (d, 1H, *J* = 8.2 Hz), 5.10 (d, 1H, *J* = 10.7 Hz), 5.11 (d, 1H, *J* = 16.9 Hz), 6.96 (ddd, 1H, *J* = 8.2, 10.7, 16.9 Hz), 6.82-6.83 (m, 2H), 7.26-7.51 (m, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 28.0, 53.4, 70.5, 81.5, 117.2, 124.91, 124.94, 127.9, 128.0, 128.1, 128.6, 128.8, 129.5, 130.3, 136.0, 137.4, 139.4, 145.0, 169.7, 170.7; IR (CHCl₃) ν 2983, 1730, 1618 cm⁻¹; MS (FAB) *m/z* 480 (MH⁺, 82), 424 (85), 378 (45), 238 (100); HRMS (FAB) calcd for C₂₉H₂₉F₃NO₂ (MH⁺) 480.2150, found 480.2158. **(2*R*,3*S*)-2-(Benzhydrylidénylamino)-3-(4-trifluoromethylphenyl)pent-4-enoic Acid *tert*-Butyl**

Ester (9c). (Table 5, Entry 7) By a procedure similar to that of Method B, the imine **1** (75.0 mg, 0.255 mmol) was converted into 6.9 mg (8%) of **8c** and 56.9 mg (70%) of **9c** using **26** (57.3 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 0.1% 2-propanol/hexane, 1.0 ml/min, λ = 254 nm, retention times: (major) 13.2 min, (minor) 15.8 min]. $[\alpha]_D^{24} = +140$ (*c* 1.10, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.31 (s, 9H), 4.14 (dd, 1H, *J* = 6.1, 8.5 Hz), 4.22 (d, 1H, *J* = 6.1 Hz), 5.17 (d, 1H, *J* = 17.4 Hz), 5.21 (d, 1H, *J* = 10.4 Hz), 6.31 (ddd, 1H, *J* = 8.5, 10.4, 17.4 Hz), 6.81-6.82 (m, 2H), 7.24-7.48 (m, 10H), 7.62-7.64 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 27.9, 53.3, 70.5, 81.3, 117.9, 125.02, 125.05, 127.6, 128.0, 128.3, 128.5, 128.9, 129.0, 130.4, 136.2, 136.8, 139.4, 145.6, 169.5, 171.0; IR (CHCl₃) ν 2982, 1728, 1619 cm⁻¹; MS (FAB) *m/z* 480 (MH⁺, 88), 424 (85), 378 (53), 238 (100); HRMS (FAB) calcd for C₂₉H₂₉F₃NO₂ (MH⁺) 480.2150, found 480.2141.

(2S,3S)-2-(Benzhydrylidenylamino)-3-*p*-tolylpent-4-enoic Acid *tert*-Butyl Ester (8d). (Table 5, Entry 3) By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 49.1 mg (68%) of **8d** and 13.3 mg (18%) of **9d** using **27** (48.1 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 0.6% 2-propanol/hexane, 0.15 ml/min, λ = 254 nm, retention times: (major) 42.9 min, (minor) 40.2 min]. $[\alpha]_D^{24} = -128$ (*c* 0.78, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.41 (s, 9H), 2.27 (s, 3H), 4.07 (t, 1H, *J* = 8.5 Hz), 4.20 (d, 1H, *J* = 8.5 Hz), 5.03 (d, 1H, *J* = 10.0 Hz), 5.09 (d, 1H, *J* = 17.3 Hz), 5.96 (ddd, 1H, *J* = 8.5, 10.0, 17.3 Hz), 6.80-6.81 (m, 2H), 7.01-7.05 (m, 4H), 7.25-7.41 (m, 6H), 7.48-7.49 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 21.0, 28.0, 53.5, 71.1, 81.2, 116.3, 127.8, 128.0, 128.2, 128.4, 128.7, 128.9 X 2, 130.0, 135.9, 136.3, 137.6, 138.3, 139.8, 170.17, 170.22; IR (CHCl₃) ν 2982, 1728, 1621 cm⁻¹; MS (FAB) *m/z* 416 (MH⁺, 7), 360 (95), 314 (10), 105 (100); HRMS (FAB) calcd for C₂₉H₃₂NO₂ (MH⁺) 426.2433, found 426.2442.

(2R,3S)-2-(Benzhydrylidenylamino)-3-*p*-tolylpent-4-enoic Acid *tert*-Butyl Ester (9d). (Table 5, Entry 8) By a procedure similar to that of Method B, the imine **1** (75.5 mg, 0.255 mmol) was converted into 7.2 mg (10%) of **8d** and 43.0 mg (60%) of **9d** using **27** (48.1 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 0.1% 2-propanol/hexane, 0.75 ml/min, λ = 254 nm, retention times: (major) 27.1 min, (minor) 32.9 min]. $[\alpha]_D^{24} = +155$ (*c* 1.30, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.30 (s, 9H), 2.27 (s, 3H), 4.04 (dd, 1H, *J* = 6.1, 8.5 Hz), 4.20 (d, 1H, *J* = 6.1 Hz), 5.13 (d, 1H, *J* = 11.3 Hz), 5.14 (d, 1H, *J* = 16.0 Hz), 6.26 (ddd, 1H, *J* = 8.5, 11.3, 16.0 Hz), 6.84-6.85 (m, 2H), 7.01-7.04 (m, 4H), 7.30-7.39 (m, 6H), 7.63-7.64 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 21.0, 27.9, 53.3, 71.0, 80.9, 116.8, 127.85, 128.89, 128.2, 128.3, 128.4, 128.8, 128.9, 130.1, 135.9, 136.5, 138.0, 138.2, 139.7, 170.0, 170.5; IR (CHCl₃) ν 2981, 1726, 1624 cm⁻¹; MS (FAB) *m/z* 416 (MH⁺, 15), 360 (100), 314 (10), 105 (55); HRMS (FAB) calcd for C₂₉H₃₂NO₂ (MH⁺) 426.2433, found 426.2426.

(2S,3S)-2-(Benzhydrylidenylamino)-3-(3-chlorophenyl)pent-4-enoic Acid *tert*-Butyl Ester (8e).

(Table 5, Entry 4) By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 45.6 mg (60%) of **8e** and 14.1 mg (19%) of **9e** using **28** (51.6 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 1% 2-propanol/hexane, 0.5 ml/min, λ = 254 nm, retention times: (major) 18.9 min, (minor) 18.0 min]. $[\alpha]_D^{24} = -60.3$ (*c* 0.49, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.42 (s, 9H), 4.10 (t, 1H, *J* = 8.3 Hz), 4.21 (d, 1H, *J* = 8.3 Hz), 5.08 (d, 1H, *J* = 10.4 Hz), 5.11 (d, 1H, *J* = 17.1 Hz), 5.92 (ddd, 1H, *J* = 8.3, 10.4, 17.1 Hz), 6.84 (s, 2H), 7.10-7.15 (m, 4H), 7.25-7.48 (m, 8H); ¹³C NMR (126 MHz, CDCl₃) δ 28.0, 53.4, 59.6, 70.7, 81.2, 81.5, 117.1, 126.7, 127.6, 127.9, 128.1 X 2, 128.6, 128.8, 129.0, 129.3, 130.2, 133.8, 136.1, 137.4, 139.5, 142.8, 169.7, 170.7; IR (CHCl₃) ν 2982, 1728, 1624 cm⁻¹; MS (FAB) *m/z* 446 (MH⁺, 95), 390 (95), 344 (40), 238 (100); Anal. Calcd for C₂₈H₂₈ClNO₂: C, 75.41; H, 6.33; N, 3.14; O, 7.17. Found: C, 75.26; H, 6.37; N, 3.12; O, 7.25

(2*R*,3*S*)-2-(Benzhydrylidenylamino)-3-(3-chlorophenyl)pent-4-enoic Acid *tert*-Butyl Ester (9e).

(Table 5, Entry 9) By a procedure similar to that of Method B, the imine **1** (75.0 mg, 0.255 mmol) was converted into 6.13 mg (8%) of **8e** and 55.3 mg (73%) of **9e** using **28** (51.6 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 1.5% 2-propanol/hexane, 0.15 ml/min, λ = 254 nm, retention times: (major) 39.3 min, (minor) 37.3 min]. $[\alpha]_D^{24} = +92.8$ (*c* 0.93, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.32 (s, 9H), 4.05 (dd, 1H, *J* = 6.1, 8.6 Hz), 4.19 (d, 1H, *J* = 6.1 Hz), 5.16 (d, 1H, *J* = 17.1 Hz), 5.20 (d, 1H, *J* = 10.4 Hz), 6.27 (ddd, 1H, *J* = 8.6, 10.4, 17.1 Hz), 6.85-6.86 (m, 2H), 7.02-7.03 (m, 1H), 7.11-7.14 (m, 3H), 7.30-7.40 (m, 6H), 7.61-7.63 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 27.9, 53.2, 10.5, 81.2, 117.7, 126.6, 126.7, 127.7, 127.9, 128.3, 128.5, 128.8, 128.9, 129.4, 130.3, 133.9, 136.4, 137.0, 139.5, 143.4, 169.6, 171.0; IR (CHCl₃) ν 2982, 1728, 1624 cm⁻¹; MS (FAB) *m/z* 446 (MH⁺, 80), 390 (85), 344 (45), 238 (100); HRMS (FAB) calcd for C₂₈H₂₉ClNO₂ (MH⁺) 446.1887, found 446.1889.

(2*S*,3*S*)-2-(Benzhydrylidenylamino)-3-(naphthalen-2-yl)pent-4-enoic Acid *tert*-Butyl Ester (8f).

(Table 5, Entry 5) By a procedure similar to that of Method A, the imine **1** (50.0 mg, 0.170 mmol) was converted into 58.5 mg (75%) of **8f** and 17.2 mg (22%) of **9f** using **29** (54 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 1% 2-propanol/hexane, 0.3 ml/min, λ = 254 nm, retention times: (major) 24.5 min, (minor) 21.2 min]. $[\alpha]_D^{24} = -78.5$ (*c* 1.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.42 (s, 9H), 4.29 (t, 1H, *J* = 8.3 Hz), 4.36 (d, 1H, *J* = 8.3 Hz), 5.09 (d, 1H, *J* = 10.1 Hz), 5.14 (d, 1H, *J* = 17.4 Hz), 6.06 (ddd, 1H, *J* = 8.3, 10.1, 17.4 Hz), 6.71 (s, 2H), 7.19-7.44 (m, 12H), 7.69-7.76 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ : 28.1, 53.9, 71.1, 81.3, 116.7, 125.3, 125.7, 127.5 X 2, 127.6, 127.7, 127.8 X 2, 127.9, 128.2, 128.4, 128.8, 130.0, 132.3, 133.4, 136.2, 138.0, 138.3, 139.7, 170.1, 170.4; IR (CHCl₃) ν 2981, 1728, 1619 cm⁻¹; MS (FAB) *m/z* 462 (MH⁺, 100), 406 (95), 360 (25), 238 (100), 167 (50); HRMS (FAB) calcd for C₃₂H₃₂NO₂ (MH⁺) 462.2433, found 462.2438.

(2*R*,3*S*)-2-(Benzhydrylidenylamino)-3-(naphthalen-2-yl)pent-4-enoic Acid *tert*-Butyl Ester (9f).

(Table 5, Entry 10) By a procedure similar to that of Method B, the imine **1** (75.5 mg, 0.255 mmol) was converted into 7.5 mg (10%) of **8f** and 57.6 mg (74%) of **9f** using **29** (54.0 mg, 0.170 mmol). HPLC [Chiralcel OD-H column, 1% 2-propanol/hexane, 0.3 ml/min, λ = 254 nm, retention times: (major) 25.1 min, (minor) 22.8 min]. $[\alpha]_D^{24} = +167$ (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.27 (s, 9H), 4.26 (dd, 1H, *J* = 6.4, 8.2 Hz), 4.35 (d, 1H, *J* = 6.4 Hz), 5.19 (d, 1H, *J* = 10.4 Hz), 5.20 (d, 1H, *J* = 17.0 Hz), 6.41 (ddd, 1H, *J* = 8.2, 10.4, 17.0 Hz), 6.78 (d, 2H, *J* = 6.4 Hz), 7.24-7.41 (m, 9H), 7.63-7.76 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ : 27.9, 53.6, 70.8, 81.0, 117.3, 125.4, 125.8, 127.0, 127.2, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.9, 130.1, 132.2, 133.4, 136.5, 137.7, 138.8, 139.6, 169.6, 170.7; IR (CHCl₃) ν 2981, 1726, 1624 cm⁻¹; MS (FAB) *m/z* 462 (MH⁺, 45), 406 (75), 360 (40), 238 (100), 167 (90); HRMS (FAB) calcd for C₃₂H₃₂NO₂ (MH⁺) 462.2433, found 462.2426.

Phosphoric Acid Diethyl Ester 3-(4-Fluorophenyl)allyl Ester (25). To a mixture of 3-(4-fluorophenyl)prop-2-en-1-ol (2.00 g, 13.1 mmol) and dry THF (100 ml) was added a 1.59 M solution of *n*-butyllithium in hexane (8.30 ml, 13.2 mmol) at 0 °C under an argon atmosphere and the resulting mixture was stirred for 0.5 h. To this, diethyl chlorophosphate (0.49 ml, 13.2 mmol) was added and stirred for 2 h at 0 °C. The mixture was quenched with aqueous saturated NH₄Cl (5 ml) and concentrated *in vacuo*. The residue was extracted with AcOEt (50 ml X 3) and the combined organic layers were washed with brine (10 ml) and dried over MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography (AcOEt/hexane=1/1.5) to give 2.84 g (75%) of **25**. ¹H NMR (500 MHz, CDCl₃) δ 1.34 (dd, 6H, *J* = 7.0, 7.0 Hz), 4.14 (dq, 4H, *J* = 7.0 7.0 Hz), 4.69 (dd, 2H, *J* = 7.0, 7.0 Hz), 6.22 (td, 1H, *J* = 7.0, 15.8 Hz), 6.64 (d, 1H, *J* = 15.8 Hz), 6.98-7.03 (m, 2H), 7.30-7.38 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 16.06, 16.11, 63.77, 63.81, 67.7, 67.8, 115.4, 115.6, 123.29, 123.33, 128.17, 128.24, 132.16, 132.19, 132.7, 132.9, 161.6, 163.6; IR (CHCl₃) ν 3000, 1262, 1235, 1033 cm⁻¹; MS (EI) *m/z* 288 (M⁺, 18), 155 (20), 133 (100), 99 (22); Anal. Calcd for C₁₃H₁₈FO₄P: C, 54.17; H, 6.29; F, 6.59. Found: C, 53.88; H, 6.18; F, 6.50.

Phosphoric Acid Diethyl Ester 3-(4-Trifluoromethylphenyl)allyl Ester (26). By a procedure similar to that of **25**, 3-(4-trifluoromethylphenyl)prop-2-en-1-ol (1.00 g, 4.95 mmol) was converted into 1.39 g (83%) of **26** using *n*-butyllithium (3.20 ml, 4.99 mmol), diethyl chlorophosphate (0.72 ml, 4.98 mmol) and THF (25 ml). ¹H NMR (500 MHz, CDCl₃) δ 1.36 (dt, 6H, *J* = 0.7, 7.3 Hz), 4.15 (dq, 4H, *J* = 7.3, 7.3 Hz), 4.73 (dt, 2H, *J* = 1.2, 6.0 Hz), 6.40 (td, 1H, *J* = 6.0, 15.9 Hz), 6.72 (d, 1H, *J* = 15.9 Hz), 7.49 (d, 2H, *J* = 8.2 Hz), 7.58 (d, 2H, *J* = 8.2 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 16.0, 16.1, 63.8, 63.9, 67.25, 67.29, 122.9, 125.1, 125.5, 125.6, 126.3, 126.4, 126.7, 129.7, 130.0, 131.8, 139.5; IR (CHCl₃) ν 3000, 1326, 1263, 1033, 974 cm⁻¹; MS (EI) *m/z* 338 (M⁺, 11), 318 (9), 183 (100), 164 (95), 115 (46); HRMS (EI) calcd for C₁₄H₁₈F₃O₄P (MH⁺) 338.0895, found 338.0891.

Phosphoric Acid Diethyl Ester 3-*p*-Tolylallyl Ester (27). By a procedure similar to that of **25**, 3-*p*-tolylprop-2-en-1-ol (500 mg, 3.37 mmol) was converted into the crude product **27** using *n*-butyllithium (2.20 ml, 3.43 mmol) and diethyl chlorophosphate (1.90 ml, 3.39 mmol). The product was used for the reaction without purification. ¹H NMR (500 MHz, CDCl₃) δ 1.34 (t, 6H, *J* = 7.0), 2.34 (s, 3H), 4.13 (dq, 4H, *J* = 7.0, 7.0 Hz), 4.69 (dt, 2H, *J* = 1.2, 6.4 Hz), 6.25 (dt, 1H, *J* = 6.4, 15.9 Hz), 6.45 (d, 1H, *J* = 15.9 Hz), 7.13 (d, 2H, *J* = 8.2 Hz), 7.29 (d, 2H, *J* = 8.2 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 16.0, 16.1, 21.2, 63.68, 63.73, 67.99, 68.04, 122.40, 122.45, 126.3, 126.5, 129.3, 133.2, 133.9, 138.0; IR (CHCl₃) ν 3003, 1261, 1034, 1033, 970 cm⁻¹; MS (EI) *m/z* 284 (M⁺, 20), 155 (30), 129 (100), 99 (28); HRMS (EI) calcd for C₁₄H₂₁O₄P (M⁺) 284.1177, found 284.1185.

Phosphoric Acid 3-(3-Chlorophenyl)allyl Ester Diethyl Ester (28). By a procedure similar to that of **25**, 3-(3-chlorophenyl)prop-2-en-1-ol (1.00 g, 5.93 mmol) was converted into **28** (620 mg, 34%) using 60% NaH (237 mg, 5.93 mmol) and diethyl chlorophosphate (0.86 ml, 5.93 mmol). ¹H NMR (500 MHz, CDCl₃) δ 1.35 (dt, 6H, *J* = 0.9, 7.0 Hz), 4.15 (dq, 4H, *J* = 7.0, 7.0 Hz), 4.70 (ddd, 2H, *J* = 1.2, 6.1, 7.6 Hz), 6.31 (td, 1H, *J* = 6.1, 15.8 Hz), 6.62 (d, 1H, *J* = 15.8 Hz), 7.24-7.27 (m, 3H), 7.38 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 16.07, 16.13, 16.2, 63.8, 63.9, 67.4, 67.5, 124.8, 125.1, 125.17, 125.24, 126.5, 126.6, 128.1, 129.8, 132.1, 132.2, 134.6, 137.9; IR (CHCl₃) ν 2999, 1263, 1033, 975 cm⁻¹; MS (EI) *m/z* 304 (M⁺, 26), 151 (49), 115 (100); Anal. Calcd for C₁₃H₁₈ClO₄P: C, 51.24; H, 5.95; Cl, 11.64; P, 10.17. Found: C, 51.46; H, 5.99; Cl, 11.69; P, 10.43.

Phosphoric Acid Diethyl Ester 3-Naphthalen-2-ylallyl Ester (29). By a procedure similar to that of **25**, 3-naphthalen-1-ylprop-2-en-1-ol (3.14 g, 16.4 mmol) was converted into 3.93 g (72%) of **29** using *n*-butyllithium (10.9 ml, 16.4 mmol), diethyl chlorophosphate (2.46 ml, 16.4 mmol) and THF (90 ml). ¹H NMR (500 MHz, CDCl₃) δ 1.35 (t, 6H, *J* = 7.3 Hz), 4.15 (dq, 4H, *J* = 7.3, 7.3 Hz), 4.75 (t, 2H, *J* = 6.7 Hz), 6.43 (dt, 1H, *J* = 6.7, 15.9 Hz), 6.83 (d, 1H, *J* = 15.9 Hz), 7.43-7.47 (m, 2H), 7.58-7.60 (m, 1H), 7.70-7.81 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 16.07, 16.12, 16.13, 63.77, 63.81, 67.89, 67.94, 123.4, 123.8, 123.9, 126.115, 126.123, 126.3, 126.9, 127.6, 128.0, 128.3, 133.2, 133.4, 133.9; IR (CHCl₃) ν 3003, 1263, 1033, 970; MS (EI) *m/z* 320 (M⁺, 12), 165 (100), 127 (8), 99 (7); Anal. Calcd for C₁₇H₂₁O₄P: C, 63.74; H, 6.61; P, 9.67. Found: C, 63.74; H, 6.61; P, 9.87.

(2*S*,3*S*)-2-(Benzhydrylidenylamino)-3-phenylpent-4-enoic Acid Methyl Ester (31). By a procedure similar to that of Method A, **30** (43.0 mg, 0.170 mmol) was converted into 27.6 mg (44%) of **31** and 18.3mg (29%) of **32**. HPLC [Chiralcel OD-H column, 0.7% 2-propanol/hexane, 0.4 ml/min, λ = 254 nm, retention times: (major) 26.8 min, (minor) 24.1 min]. [α]_D²⁴ = -181 (*c* 1.19, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 3.72 (s, 3H), 4.13 (dd, 1H, *J* = 8.9, 8.9 Hz), 4.39 (d, 1H, *J* = 8.9 Hz), 5.07 (d, 1H, *J* = 10.4 Hz), 5.13 (d, 1H, *J* = 17.4 Hz), 5.98 (ddd, 2H, *J* = 8.9, 10.4, 17.4 Hz), 6.70 (s, 2H), 7.09-7.45 (m,

13H); ^{13}C NMR (126 MHz, CDCl_3) δ 52.0, 54.2, 71.2, 116.9, 126.6, 127.9, 128.0, 128.18, 128.20, 128.6 X 2, 128.9, 130.2, 135.9, 137.4, 139.6, 140.2, 171.1, 171.6; IR (CHCl_3) ν 3031, 1737, 1619 cm^{-1} ; MS (FAB) m/z 370 (MH^+ , 100), 310 (13), 252 (60), 193 (19); HRMS (FAB) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_2\text{N}$ (MH^+) 370.1807, found 370.1794

(2R,3S)-2-(Benzhydrylidénylamino)-3-phenylpent-4-enoic Acid Methyl Ester (32) By a procedure similar to that of Method B, **30** (64.5 mg, 0.255 mmol) was converted into 12.0 mg (18%) of **31** and 43.0mg (69%) of **32** as colorless crystals. HPLC [Chiralcel OD-H column, 1.0% 2-propanol/hexane, 0.4 ml/min, λ = 254 nm, retention times: (major) 17.6 min, (minor) 19.9 min]. Mp 100-101 °C (hexane); $[\alpha]_D^{24} = +210$ (c 1.42, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 3.61 (s, 3H), 4.12 (dd, 1H, J = 5.8, 8.9 Hz), 4.37 (d, 1H, J = 5.8 Hz), 5.19 (d, 1H, J = 17.1 Hz), 5.20 (d, 1H, J = 10.0 Hz), 6.32 (ddd, 2H, J = 8.9, 10.0, 17.1 Hz), 6.74 (s, 2H), 7.10-7.41 (m, 11H), 7.62-7.63 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 52.0, 53.7, 70.8, 117.5, 126.6, 127.7, 128.0, 128.3 X 2, 128.5 X 2, 128.9, 130.3, 136.1, 137.3, 139.5, 140.9, 171.3, 171.4; IR (CHCl_3) ν 3031, 1736, 1622 cm^{-1} ; MS (FAB) m/z 370 (MH^+ , 100), 370 (100), 310 (17), 252 (70), 193 (23); Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_2 \cdot 0.15\text{H}_2\text{O}$: C, 80.67; H, 6.31; N, 3.77. Found: C, 80.61; H, 6.31; N, 3.79.

(2S,3S)-2-tert-Butoxycarbonylamino-3-phenylpent-4-enoic Acid tert-Butyl Ester (33). To a solution of **8a** (74.1 mg, 0.180 mmol) in THF (1 ml) was added an aqueous 15% citric acid and the mixture was stirred at room temperature for 4 h. The solution was diluted with Et_2O (15 ml) and then extracted with water (3 X 15 ml). The combined aqueous layers were neutralized with solid K_2CO_3 , then extracted with AcOEt (3 X 30 ml). The combined organic layers were dried over Na_2SO_4 . After evaporation of solvent, to a solution of the residue in dry THF (0.5 ml), triethylamine (38 μl , 0.27 mmol) and di-*t*-butyl dicarbonate (47.2 mg, 0.216 mmol) were added at 0 °C and the mixture was stirred at 0 °C for 1 h. The mixture was quenched with water (2 ml) and extracted with Et_2O (20 ml X 2). The combined organic layers were washed with brine (3 ml) and dried over MgSO_4 . After evaporation of the solvent, the crude product was purified by column chromatography (AcOEt /hexane=1/20) to give 56.8 mg (91%) of **33**. $[\alpha]_D^{24} = +51.2$ (c 1.05, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 1.37 (s, 9H), 1.38 (s, 9H), 3.78 (dd, 1H, J = 7.0, 8.6 Hz), 4.56 (dd, 1H, J = 7.0, 8.6 Hz) 4.88 (d, 1H, J = 8.6 Hz), 5.17 (d, 1H, J = 17.2 Hz), 5.19 (d, 1H, J = 10.1 Hz), 6.09 (ddd, 1H, J = 8.6, 10.1, 17.2 Hz), 7.22-7.32 (m, 5H); ^{13}C NMR (126 MHz, CHCl_3) δ 27.9, 28.2, 52.4, 57.8, 79.7, 82.0, 117.7, 127.0, 128.3, 128.4, 136.5, 139.2, 155.2, 170.3; IR (CHCl_3) ν 3437, 2982, 1711, 1498 cm^{-1} ; MS (FAB) m/z 348 (MH^+ , 9), 292 (15), 236 (100), 192 (32), 57 (30); Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_4$: C, 69.14; H, 8.41; N, 4.03. Found: C, 68.88; H, 8.20; N, 4.03.

(2S,3S)-3-Phenyl-3,6-dihydro-2H-pyridine-1,2-dicarboxylic Acid Di-tert-butyl Ester (34). To a

suspension of 60% NaH (6.1 mg, 0.255 mmol) and dry DMF (1 ml) was added a solution of **33** (17.7 mg, 0.051 mmol) in DMF (1 ml), and the resulting mixture was stirred at 0 °C for 0.5 h under an argon atmosphere. To this, allyl bromide (22 µl, 0.255 mmol) was added and stirring was continued at 0 °C for 2 h. The mixture was quenched with aqueous saturated NaHCO₃ (0.5 ml) and extracted with AcOEt (15 ml X 2). The combined organic layers were washed with brine (5 ml) and dried over MgSO₄. After evaporation of the solvent, the residue was dissolved in dry toluene, and to this, Grubbs catalyst (2nd) (1.9 mg, 0.002 mmol) was added. After the mixture was stirred at room temperature for 6 h, the mixture was evaporated and purified by column chromatography (AcOEt/hexane=1/20) to give 14.7 mg (90%) of **34** as colorless crystals. Mp 113-115 °C (hexane); $[\alpha]_D^{24} = +12.2$ (*c* 1.70, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.05 (s, 4.5H), 1.09 (s, 4.5H), 1.48 (s, 4.5H), 1.49 (s, 4.5H) 3.97-4.21 (m, 3H), 4.85 (d, 0.5H, *J* = 6.4 Hz), 5.12 (d, 0.5H, *J* = 6.4 Hz), 5.90-6.25 (m, 2H), 7.25-7.32 (m, 5H); ¹³C NMR (126 MHz, CHCl₃) δ 27.5, 27.6, 28.4, 41.9, 42.1, 42.5, 56.5, 58.0, 80.35, 80.36, 80.7, 123.9, 124.3, 125.3, 126.9, 127.0, 128.3, 128.8, 139.7, 139.8; IR (CHCl₃) ν 1726, 1689 cm⁻¹; MS (FAB) *m/z* 360 (MH⁺, 32), 304 (18), 248 (71), 204 (100), 202 (96), 158 (32), 57 (59); Anal. Calcd for C₂₁H₂₉NO₄·0.15H₂O: C, 69.64; H, 8.15; N, 3.87. Found: C, 69.66; H, 8.04; N, 3.84.

(2R,3S)-2-Benzoyloxycarbonylamino-3-phenylpent-4-enoic Acid Methyl Ester (35) To a solution of **9a** (91.9 mg, 0.223 mmol) in THF (1 ml) was added aqueous 15% citric acid and the mixture was stirred at room temperature for 4 h. The mixture was diluted with Et₂O (15 ml) and then extracted with water (3 X 15 ml). The combined aqueous layers were neutralized with solid K₂CO₃, then extracted with AcOEt (3 X 30 ml). The combined organic layers were dried over Na₂SO₄. After evaporation of solvent, dry CH₂Cl₂ (0.2 ml) and TFA (0.2 ml) were added to the residue, and stirring was continued at room temperature for 3 h. The mixture was evaporated and the residue was dissolved in 1N NaOH aq (0.3 ml), and to this ZCl (14.4 µl, 0.098 mmol) was added and the solution were stirred at 0 °C for 1 h. The solution was diluted with Et₂O (10 ml) and then extracted with water (3 X 15 ml). The combined aqueous layers were neutralized with conc. HCl, then extracted with AcOEt (3 X 30 ml). The combined organic layers were dried over MgSO₄. After evaporation, dry MeOH (0.5 ml) and thionyl chloride (16 µl, 0.221 mmol) were added at 0 °C to the residue, and the mixture was stirred at room temperature for 1 h. The mixture was concentrated *in vacuo* and the obtained residue was purified by column chromatography (AcOEt/hexane=1/5) to give 7.7 mg (32%) of **35**. $[\alpha]_D^{24} = +6.1$ (*c* 0.77, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 3.55 (s, 3H), 3.73 (dd, 1H, *J* = 7.6, 8.5 Hz), 4.67 (dd, 1H, *J* = 7.6, 7.6 Hz), 5.05-5.27 (m, 5H), 6.07 (ddd, *J* = 8.5, 8.5, 17.4, 1H), 7.19-7.38 (m, 10H); ¹³C NMR (126 MHz, CDCl₃) δ 52.1, 52.8, 58.4, 67.1, 118.6, 127.3, 128.0, 128.1, 128.2, 128.5, 128.6, 135.9, 136.2, 138.8, 155.7, 171.6; IR (CHCl₃) ν 3434, 1722, 1509 cm⁻¹; MS (FAB) *m/z* 340 (MH⁺, 8), 307 (22), 154 (100), 136

(64), 91 (24); HRMS (FAB) calcd for $C_{20}H_{22}NO_4$ (MH^+) 340.1549, found 340.1561.

(2R,3S)-3-Phenyl-3,6-dihydro-2H-pyridine-1,2-dicarboxylic Acid 1-Benzyl Ester 2-Methyl Ester (36). To a suspension of 60% NaH (23.0 mg, 0.578 mmol) and dry DMF (0.5 ml) was added **35** (37.4 mg, 0.116 mmol) in DMF (0.5 ml) and stirred at 0 °C for 1 h under an argon atmosphere. To this allyl bromide (50 μ l, 0.578 mmol) was added and stirred at 0 °C for 2 h. The mixture was quenched with aqueous saturated $NaHCO_3$ (0.5 ml) and extracted with AcOEt (15 ml X 2). The combined organic layers were washed with brine (5 ml) and dried over $MgSO_4$. After evaporation of the solvent, the residue was dissolved to dry toluene, and to this Grubbs catalyst (2^{nd}) (3.5 mg, 0.004 mmol) was added. After the solution was stirred at room temperature for 4 h, the mixture was evaporated and purified by column chromatography (AcOEt/hexane=1/5) to give 26.5 mg (66%) of **36**. $[\alpha]_D^{24} = -118$ (c 0.48, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 1.5H), 3.77 (s, 1.5H), 3.91-4.04 (m, 1H), 4.14 (dd, 1H, $J = 7.0$ Hz), 4.36 (dd, 1H, $J = 18.7, 35.3$ Hz), 4.90-5.13 (m, 3H), 5.89-5.98 (m, 2H), 6.86-6.88 (m, 1H), 7.20-7.36 (m, 9H); IR ($CHCl_3$) ν 3029, 1739, 1699 cm^{-1} ; MS (FAB) m/z 352 (MH^+ , 45), 308 (44), 154 (100), 136 (66), 91 (93); HRMS (FAB) calcd for $C_{21}H_{22}NO_4$ (MH^+) 352.1549, found 352.1555.

(2R,3S)-3-Phenylpiperidine-2-carboxylic Acid Methyl Ester (37) To a solution of **36** (11.5 mg, 0.033 mmol) in dry AcOEt (0.5 ml) was added 10% palladium on charcoal (35.0 mg, 0.033 mmol). After the mixture was stirred at 0 °C for 3 h under a hydrogen atmosphere, the mixture was filtered through a pad of Celite. The filtrate was evaporated, and purified by column chromatography ($CHCl_3/MeOH/Et_3N=50/1/0.25$) to give 3.7 mg (52%) of **37**. $[\alpha]_D^{18} = -31.9$ (c 0.37, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ 1.56-1.65 (m, 1H), 1.73-1.81 (m 3H), 2.01-2.04 (m, 1H), 2.71-2.80 (m, 2H), 3.19-3.23 (m, 1H), 3.40 (s, 3H), 3.49 (d, 1H, $J = 10.4$ Hz), 7.17-7.30 (m, 5H); IR ($CHCl_3$) ν 2934, 1733, 1026 cm^{-1} . MS (FAB) m/z 220 (MH^+ , 100), 160 (52); HRMS (FAB) calcd for $C_{13}H_{18}NO_2$ (MH^+) 220.1338, found 220.1334.

(2S,3S)-2-(Benzoylamino)-2-methyl-3-phenyl-4-pentenoic Acid tert-Butyl Ester (41a). **(2R,3S)-2-(Benzoylamino)-2-methyl-3-phenyl-4-pentenoic Acid tert-Butyl Ester (42a)** (Table 6, Entry 1): To a suspension of **7** (61.8 mg, 0.229 mmol), **38** (61.2 mg, 0.229 mmol), $[Ir(COD)Cl]_2$ (7.7 mg, 0.011 mmol), and **16** (19.2 mg, 0.046 mmol) in toluene (1.9 ml) was added an aqueous 50% KOH solution (50.3 μ l, 0.686 mmol) at 0 °C under an argon atmosphere. After being stirred vigorously at 0 °C for 20 h, the mixture was diluted with ether (20 ml). The organic phase was washed with saturated $NaHCO_3$ solution (2 ml) and brine (2 ml). The extract was dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. To a solution of the crude product in THF (1 ml) was added an aqueous 15% citric acid and the mixture was stirred at room temperature for 4 h. The mixture was diluted with Et_2O (15 ml) and then extracted with water (3 X 15 ml). The combined aqueous layers were neutralized with solid K_2CO_3 , then

extracted with AcOEt (3 X 30 ml). The combined organic layers were dried over Na₂SO₄. After evaporation of solvent, the residue was dissolved in dry THF (0.5 ml), and to this triethylamine (48.0 μ l, 0.343 mmol) and benzoyl chloride (29.0 μ l, 0.252 mmol) were added at 0 °C and the solution were stirred at 0 °C for 2 h. The mixture was quenched with water (2 ml) and extracted with Et₂O (20 ml X 2). The combined organic layers were washed with brine (3 ml) and dried over MgSO₄. After evaporation of the solvent, the crude product was purified by flash chromatography (AcOEt/hexane=1/10) to give 7.6 mg (9%) of **41a** and 7.4 mg (9%) of **42a**. **41a**: HPLC [Chiralcel OD-H column, 1.5% 2-propanol/hexane, 0.5 ml/min, λ = 254 nm, retention times: (major) 12.4 min, (minor) 10.0 min]. $[\alpha]_D^{24}$ = +11.8 (*c* 0.38, CHCl₃); ¹H NMR (500MHz, CDCl₃) δ 1.45 (s, 9H), 1.71 (s 3H), 3.98 (d, 1H, *J* = 9.5 Hz), 5.19 (1H, d, *J* = 16.8 Hz), 5.24 (1H, d, *J* = 10.4 Hz), 6.37 (dt, 1H, *J* = 10.4, 16.8 Hz), 7.26-7.69 (m, 10H); ¹³C NMR (126MHz, CDCl₃) δ 20.1, 27.9, 57.2, 63.0, 82.4, 118.8, 126.8, 127.5, 128.47, 128.54, 129.4, 130.2, 131.2, 133.7, 135.8, 166.4, 171.9; IR (CHCl₃) ν 1712 1669 1276 cm⁻¹; MS (FAB) *m/z* 366 (MH⁺, 22), 310 (100), 105 (70); HRMS (FAB) calcd for C₂₃H₂₈NO₃ (MH⁺) 366.2069, found 366.2061. **42a**: HPLC [Chiralcel OD-H column, 1.0% 2-propanol/hexane, 0.5 ml/min, λ = 254 nm, retention times: (major) 14.7 min, (minor) 20.0 min]. $[\alpha]_D^{24}$ = -9.1 (*c* 1.31, CHCl₃); ¹H NMR (500MHz, CDCl₃) δ 1.49 (s, 9H), 1.81 (s 3H), 4.37 (d, 1H, *J* = 9.8 Hz), 5.27 (1H, d, *J* = 10.1 Hz), 5.34 (1H, d, *J* = 17.1 Hz), 6.46 (1H, dt, *J* = 9.8, 17.1 Hz), 7.19-7.65 (m, 10H); ¹³C NMR (126MHz, CDCl₃) δ 20.9, 28.0, 55.2, 63.6, 83.0, 118.8, 126.7, 127.2, 128.2, 128.47, 128.51, 128.8, 130.2, 133.7, 136.7, 166.5, 172.0; IR (CHCl₃) ν 1712 1655 1281 cm⁻¹; MS (FAB) *m/z* 366 (MH⁺, 26), 310 (100), 105 (68); HRMS (FAB) calcd for C₂₃H₂₈NO₃ (MH⁺) 366.2069, found 366.2075.

(2*S*,3*S*)-2-(Benzoylamino)-2-methyl-3-(naphthalen-1-yl)-4-pentenoic Acid *tert*-Butyl Ester (41b).

(2*R*,3*S*)-2-(Benzoylamino)-2-methyl-3-(naphthalen-1-yl)-4-pentenoic Acid *tert*-Butyl Ester (42b)

(Table 6, Entry 2) By a procedure similar to that described in entry 1 of Table 6, the imine **38** (45.0 mg, 0.170 mmol) was converted into 7.3 mg (11%) of **41b** and 7.4 mg (11%) of **42b** using **29** (54.2 mg, 0.170 mmol), [Ir(cod)Cl]₂ (11.4 mg, 0.017 mmol), **16** (14.2 mg, 0.034 mmol), and 50% KOH solution (37.5 μ l, 0.511 mmol). **(Table 6, Entry 3)** By a procedure similar to that described above, the imine **40** (48.2 mg, 0.170 mmol) was converted into 8.0 mg (11%) of **41b** and 4.3 mg (6%) of **42b** using **11** (10.6 mg, 0.0170 mmol) as PTC. **(Table 6, Entry 4)** By a procedure similar to that described above, the imine **40** (48.2 mg, 0.170 mmol) was converted into 19.0 mg (27%) of **41b** and 15.1 mg (22%) of **42b** using hexadecyltrimethylammonium bromide (6.2 mg, 0.017 mmol) as PTC. **(Table 6, Entry 5)** To a solution of **38** (67.5 mg, 0.255 mmol) in THF (0.7 ml) was added a 1.56 M solution of LiN(SiMe)₃ in THF (0.17 ml, 0.255 mmol) at -78 °C. In another test tube, a mixture of [Ir(cod)Cl]₂ (11.4 mg, 0.017 mmol), **16** (14.2 mg, 0.034 mmol), **29** (54.2 mg, 0.170 mmol), and THF (0.7 ml) was stirred at room

temperature for 10 min. To this mixture, was added slowly the above solution of the enolate at 0 °C. After the addition, the resulting mixture was quenched with saturated NH₄Cl solution, extracted with ether (3 X 15 ml). The combined extracts were washed with brine (5ml), dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The same treatment of the crude products as that described in entry 1 of Table 6 gave 6.9 mg (10%) of **41b** and 33.4 mg (49%) of **42b**. (**Table 6, Entry 6**) By a procedure similar to that described in Entry 5, the imine **39** (66.9 mg, 0.254 mmol) was converted into 6.0 mg (9%) of **41b** and 25.7 mg (38%) of **42b**. (**Table 6, Entry 7**) By a procedure similar to that described in Entry 5, the imine **40** (72.0 mg, 0.254 mmol) was converted into 12.0 mg (16%) of **41b** and 32.3 mg (48%) of **42b**. **41b**: HPLC [Chiralcel OD-H column, 1.5% 2-propanol/hexane, 0.5 ml/min, λ = 254 nm, retention times: (major) 38.5 min, (minor) 23.4 min]. $[\alpha]_D^{24} = +52.7$ (*c* 0.53, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.45 (s, 9H), 1.76 (s, 3H), 4.19 (d, 1H, *J* = 9.5 Hz), 5.22 (d, 1H, *J* = 16.8 Hz), 5.27 (d, 1H, *J* = 9.5 Hz), 6.49 (ddd, 2H, *J* = 9.5, 9.5, 16.8 Hz), 6.95 (s, 1H), 7.38-7.50 (m, 6H), 7.68-7.83 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 20.4, 27.9, 57.1, 63.2, 82.5, 118.9, 126.0, 126.3, 126.8, 127.3, 127.6, 127.7, 127.9, 128.4, 128.6, 131.4, 132.5, 133.2, 135.1, 135.9, 136.6, 166.4, 172.0; IR (CHCl₃) ν 3412, 2931, 1727, 1664, 1513, 1483 cm⁻¹; MS (CI) *m/z* 416 (MH⁺, 100), 360 (59), 248 (20), 194 (38), 169 (49); HRMS (CI) calcd for C₂₇H₃₀NO₃ (MH⁺) 416.2226, found 416.2234. **42b**: HPLC [Chiralcel OD-H column, 1.0% 2-propanol/hexane, 0.5 ml/min, λ = 254 nm, retention times: (major) 26.3 min, (minor) 34.5 min]. $[\alpha]_D^{24} = -1.7$ (*c* 0.96, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.50 (s, 9H), 1.86 (s, 3H), 4.59 (d, 1H, *J* = 9.8 Hz), 5.31 (d, 1H, *J* = 9.8 Hz), 5.38 (d, 1H, *J* = 16.8 Hz), 6.60 (ddd, 2H, *J* = 9.8, 9.8, 16.8 Hz), 7.03 (s, 1H), 7.32-7.46 (m, 6H), 7.62-7.78 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 21.2, 28.0, 55.0, 63.8, 83.1, 119.0, 125.7, 126.0, 126.7, 126.8, 127.5, 127.65 X 2, 127.70, 128.5, 131.3, 132.5, 133.2, 135.3, 136.7, 137.0, 166.5, 172.1; IR (CHCl₃) ν 3400, 3007, 1719, 1658, 1514, 1484 cm⁻¹; MS (CI) *m/z* 416 (MH⁺, 100), 360 (46), 248 (11), 194 (15), 169 (18); HRMS (CI) calcd for C₂₇H₃₀NO₃ (MH⁺) 416.2226, found 416.2219.

(2R,3S)-2-(Benzoylamino)-2-methyl-3-phenyl-4-pentenoic Acid Methyl Ester (43) To a solution of **42a** (9.7 mg, 0.027 mmol) in CH₂Cl₂ (0.2 ml) was added TFA (0.2 ml) and the mixture was stirred at room temperature for 30 min. After evaporation of the mixture, dry MeOH (0.5 ml) and thionyl chloride (4 μ l, 0.054 mmol) were added at 0 °C to the residue. The resulting mixture was heated at 60°C for 12 h. The mixture was concentrated *in vacuo* and the obtained residue was purified by column chromatography (AcOEt/hexane=1/5) to give 6.4 mg (74%) of **43**. HPLC [Chiralcel OD-H column, 2.0% 2-propanol/hexane, 0.75 ml/min, λ = 254 nm, retention times: (major) 22.4 min, (minor) 21.4 min].

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