Supporting Information
No.1

Synthesis of (*Z*)-Alkene and (*E*)-Fluoroalkene Containing Diketopiperazine Mimetics Utilizing Organocopper-mediated Reduction-alkylation and Diastereoselectivity Examination Using DFT Calculations

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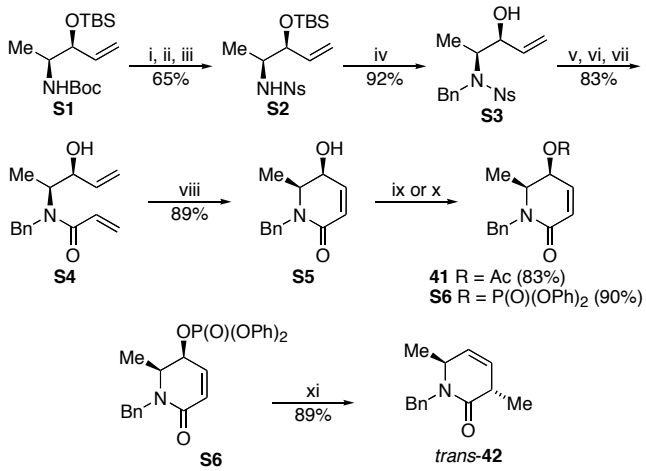
Synthesis of alanine-derived substrates 41 and structure determination of compound 42.

Scheme S1.



Reagents: (i) 4 M HCl in dioxane; (ii) Ns-Cl, 2,4,6-collidine, $CHCl_3$; (iii) TBS-OTf, 2,6-lutidine, CH_2Cl_2; (iv) Bn-Br, K_2CO_3, DMF; (v) $HSCH_2CO_2H$, $LiOH{\cdot}H_2O$, DMF; (vi) CH_2=CHCOCl, Et_3N, CH_2Cl_2; (vii) TBAF, THF; (viii) Grubbs' catalyst second generation, CH_2Cl_2; (ix) Ac_2O, pyridine, DMAP, CH_2Cl_2; (x) $ClP(O)(OPh)_2$, pyridine, CH_2Cl_2; (xi) MeCu·LiI·LiBr, THF.

The acetate **41** was synthesized from the known allylic alcohol derivative **S1**[1] by use of a procedure identical with that described for the preparation of acetate **2** from the allylic alcohol derivative **7** (Scheme S1). The phosphate derivative **S6** was also synthesized by treatment of lactam **S5** with $(PhO)_2P(O)Cl$ in the presence of pyridine. Treatment of the phosphate **S6** with MeCu·LiI·LiBr in THF gave a S_N2' derivative **42** as a single diastereomer, *which was identical to the minor product of organocopper-mediated reduction/alkylation of acetate **41***. In our previous study[2], it was confirmed that the S_N2' reactions of phenylalanine-derived γ-phosphoryloxy-α,β-unsaturated-δ-lactam with organocopper reagent prepared from equimolar amount of copper salt and organometallic reagent proceed in an *anti*-S_N2' manner without exception.[2] Organocopper-mediated *anti*-S_N2' reactions of allylic phosphate derivatives have been well documented by other groups.[3] Therefore, the relative configuration of **42** obtained from phosphate **S6** was presumed to be 3,6-*trans*.

References: (1) Ibuka, T.; Habashita, H.; Otaka, A.; Fujii, N.; Oguchi, Y.; Uyehara, T.; Yamamoto, Y. *J. Org. Chem.* **1991**, *56*, 4370. (2) Niida, A.; Oishi, S.; Sasaki, Y.; Mizumoto, M.; Tamamura, H.; Fujii, N.; Otaka, A. *Tetrahedron Lett.* **2005**, *46*, 4183. (3) (a) Torneiro, M.; Fall, Y.; Castedo, L.; Mouriño, A. *J. Org. Chem.* **1997**, *62*, 6344. (b) Belelie, J. L.; Chong, J. M. *J. Org. Chem.* **2001**, *66*, 5552. (c) Calaza, M. I.; Hupe, E.; Knochel, P. *Org. Lett.* **2003**, *5*, 1059. (d) Soorukram, D.; Knochel, P. *Org. Lett.* **2004**, *6*, 2409.

(3*S*,4*S*)-3-[(*tert*-Butyl)dimethylsiloxy]-4-[*N*-(2-nitrobenzenesulfonyl)amino]pent-1-en (S2). By use of a procedure identical with that described for the preparation of the

sulfonamide **8** from **7**, the the allylic alcohol derivative **S1** (4.0 g, 12.7 mmol) was converted into the title compound **S2** (3.28 g, 64.5% yield) as colorless crystals: mp 98–99 °C; $[\alpha]^{23}_{D}$ –40.5 (c 0.87, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.05 (s, 3H), 1.16 (d, J = 6.6 Hz, 3H), 3.50–3.63 (m, 1H), 4.00–4.08 (m, 1H), 4.86 (dt, J = 10.5, 1.5 Hz, 1H), 5.09 (dt, J = 17.3, 1.5 Hz, 1H), 5.58 (ddd, J = 17.1, 10.5, 5.9 Hz, 1H), 5.67 (d, J = 8.3 Hz, 1H), 7.69–7.75 (m, 2H), 7.81–7.88 (m, 1H), 8.07–8.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –5.0, –4.4, 18.0, 18.9, 25.7, 55.3, 75.8, 116.4, 125.2, 130.3, 132.7, 133.1, 135.4, 137.5, 147.8. Anal. Calcd for $C_{17}H_{28}N_2O_5SSi$: C, 50.97; H, 7.05; N, 6.99. Found: C, 50.69; H, 6.81; N, 6.97.

(3*S*,4*S*)-4-[*N*-Benzyl-*N*-(2-nitrobenzenesulfonyl)]amino-3-[(*tert*-Butyl)dimethylsiloxy]pent-1-en (S3). By use of a procedure identical with that described for the preparation of the *N*-methyl sulfonamide **9a** from **8**, the sulfonamide **S2** (2.54 g, 6.34 mmol) was converted into the title compound **S3** (2.86 g, 91.9% yield) as colorless oil: $[\alpha]^{25}_{D}$ –134.2 (c 1.18, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.03 (s, 3H), 0.85 (s, 9H), 1.25 (d, J = 6.6 Hz, 3H), 4.10–4.22 (m, 2H), 4.62 (d, J = 16.0 Hz, 1H), 4.67 (d, J = 16.3 Hz, 1H), 5.04 (dd, J = 10.5, 0.7 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 5.80 (ddd, J = 17.1, 10.2, 6.3 Hz, 1H), 7.04–7.13 (m, 3H), 7.16–7.27 (m, 3H), 7.41–7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.8, –4.3, 16.4, 18.0, 25.8, 48.9, 58.7, 77.3, 116.9, 123.5, 127.1, 128.0, 128.2, 131.0, 131.2, 125.5, 135.0, 137.2, 138.3, 147.3; HRMS (FAB), *m*/*z* calcd for $C_{24}H_{35}N_2O_5SSi$ (MH^+) 491.2036, found 491.2037.

(3*S*,4*S*)-4-(*N*-Acryloyl-*N*-benzyl)aminopent-1-en-3-ol (S4) By use of a procedure identical with that described for the preparation of the acrylamide **10a** from **9a**, the sulfonamide **S3** (2.76 g, 5.62 mmol) was converted into the title compound **S4** (1.14 g, 82.6% yield) as colorless oil (rotamer mixture: ca. 1:0.1): $[\alpha]^{25}_{D}$ –21.3 (c 0.69, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, main rotamer) δ 1.24 (*d*, J = 6.8 Hz, 3H), 4.00–4.16 (m, 2H), 4.52 (d, J = 17.6 Hz, 1H), 4.68 (d, J = 17.6 Hz, 1H), 5.15 (d, J = 10.5 Hz, 1H), 5.32 (d, J = 17.1 Hz, 1H), 5.67 (dd, J = 9.5, 2.7 Hz, 1H), 5.81 (ddd, J = 17.1, 10.3, 5.9 Hz, 1H), 6.36–6.52 (m, 2H), 7.16–7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 51.2, 58.7, 75.3, 115.9, 126.4, 127.4, 128.3, 128.6, 129.1, 137.0, 138.5, 168.6; HRMS (FAB), *m*/*z* calcd for $C_{15}H_{20}NO_2$ (MH^+) 246.1494, found 246.1486.

(5*S*,6*S*)-1-Benzyl-5,6-dihydro-5-hydroxy-6-methylpyridin-2-one (S5). By use of a procedure identical with that described for the preparation of the lactam **11a** from **10a**, the acrylamide **S4** (1.05 g, 4.28 mmol) was converted into the title compound **S5** (832 mg, 89.5% yield) as colorless crystals: mp 141–142 °C; $[\alpha]^{21}_{D}$ +21.8 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (d, J = 6.8 Hz, 3H), 3.30–3.42 (m, 1H), 3.44–3.56 (m, 1H), 3.84 (d, J = 15.1 Hz, 1H), 4.59–4.68 (m, 1H), 5.24 (d, J = 15.1 Hz, 1H), 5.83 (dd, J = 10.0, 2.2 Hz, 1H), 6.35 (dt, J = 11.7, 1.7 Hz, 1H), 7.19–7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.8, 47.2, 55.0, 67.1, 123.5, 127.4, 127.6, 128.6, 137.6, 142.6, 163.4. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.84; H, 6.91; N,

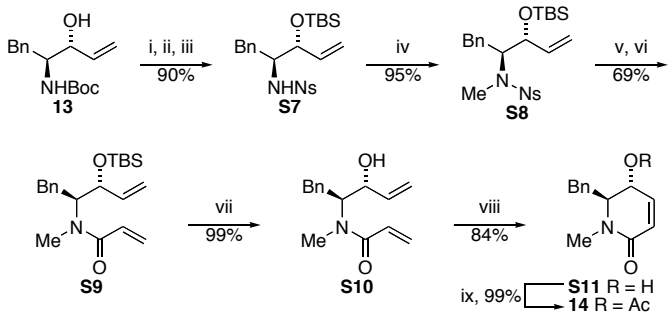
6.45.

(5*S*,6*S*)-5-Acetoxy-1-Benzyl-5,6-dihydro-6-methylpyridin-2-one (41). By use of a procedure identical with that described for the preparation of the acetate **2** from **11a**, the the lactam **S5** (100 mg, 0.460 mmol) was converted into the title compound **41** (99.0 mg, 82.9% yield) as colorless oil: $[\alpha]^{25}_{D}$ +46.4 (c 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, J = 6.6 Hz, 3H), 2.08 (s, 3H), 3.66–3.79 (m, 1H), 4.02 (d, J = 15.1 Hz, 1H), 5.23 (d, J = 15.1 Hz, 1H), 5.59 (dt, J = 6.1, 2.4 Hz, 1H), 6.03 (dd, J = 10.0, 2.2 Hz, 1H), 6.32 (dt, J = 11.7, 1.7 Hz, 1H), 7.24–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 20.8, 47.3, 52.5, 69.1, 125.5, 127.5, 127.7, 128.7, 137.4, 137.6, 162.8, 169.9; HRMS (FAB), m/z calcd for $C_{15}H_{18}NO_3$ (MH^+) 260.1287, found 260.1292.

(5*S*,6*S*)-1-Benzyl-5,6-dihydro-6-methyl-5-(diphenylphosphoryloxy)pyridin-2-one (S6). To a solution of the alcohol **S5** (30.2 mg, 0.139 mmol) and pyridine (89.8 μL, 1.11 mmol) in CH_2Cl_2 (1 mL), was added dropwise diphenylphosphoryl chloride (116 μL, 0.556 mmol) at 0 °C, and the mixture was stirred at 0 °C for 2 h. H_2O (1 mL) was added to the above mixture, and the whole was extracted with EtOAc. The extract was washed successively with saturated citric acid, brine, saturated $NaHCO_3$, and brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (1:1) gave the title compound **S6** (56.1 mg, 89.8% yield) as colorless oil: $[\alpha]^{20}_{D}$ +27.8 (c 0.84, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, J = 6.6 Hz, 3H), 3.61–3.72 (m, 1H), 3.96 (d, J = 15.1 Hz, 1H), 5.21 (d, J = 15.1 Hz, 1H), 5.38–5.45 (ddt, J = 8.3, 6.1, 2.2 Hz, 1H), 6.00 (dd, J = 10.0, 1.5 Hz, 1H), 6.35 (dt, J = 10.0, 2.0 Hz, 1H), 7.06–7.37 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.6, 47.3, 53.6, 73.9, 119.8, 119.9, 125.6, 125.7, 127.6, 127.8, 128.8, 129.9, 130.0, 137.1, 137.4, 150.2, 162.5; HRMS (FAB), m/z calcd for $C_{25}H_{25}NO_5P$ (MH^+) 450.1470, found 450.1467.

Organocopper-mediated *anti*-S_N2' reaction of phosphate S6. Synthesis of (3*S*,6*S*)-1-Benzyl-3,6-dihydro-3,6-dimethylpyridine-2-one (*trans*-42). To a suspension of CuI (33.5 mg, 0.176 mmol) in THF (0.75 mL), was added dropwise a solition of MeLi·LiBr in Et_2O (1.5 M, 117 μL, 0.176 mmol) at – 78 °C under argon, and the mixture was stirred for 10 min at 0 °C. To the above mixture, was added dropwise a solution of the phosphate **S6** (26.3 mg, 0.0585 mmol) in THF (0.75 mL) at – 78 °C, and the mixture was stirred for 20 min at – 78 °C. The reaction was quenched at – 78 °C by addition of a 1:1 saturated NH_4Cl-28%NH_4OH solution (2 mL) with additional stirring at room temperature for 30 min. The mixture was extracted with Et_2O and the extract was washed with H_2O and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (1:1) gave the title compound *trans*-**42** (11.2 mg, 88.9% yield) as colorless oil.

Synthesis of acetate 14



Reagents: (i) 4 M HCl in dioxane; (ii) Ns-Cl, 2,4,6-collidine, $CHCl_3$; (iii) TBSOTf, 2,6-lutidine, CH_2Cl_2; (iv) MeI, K_2CO_3, DMF; (v) $HSCH_2CH_2CO_2H$, LiOH, DMF; (vi) CH_2=CHCOCl, Et_3N, CH_2Cl_2; (vii) TBAF, THF; (viii) Grubbs' catalyst second generation; (ix) Ac_2O, pyridine, DMAP, $CHCl_3$.

By use of a procedure identical with that described for the preparation of the acetate **2** from the allilic alcohol **7**, the acetate **14** was synthesized from the allylic alcohol **13** as shown in the above scheme.

(3*R*,4*S*)-3-[(*tert*-Butyl)dimethylsiloxy]-4-[*N*-(2-nitrobenzenesulfonyl)amino]-5-phenylpent-1-en (S7). By use of a procedure identical with that described for the preparation of **8** from **7**, the allylic alcohol **13** (1.70 g, 6.13 mmol) was converted into the title compound **S7** (2.64 g, 90.4% yield) as colorless oil: $[\alpha]^{28}_D$ +110.0 (c 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.08 (s, 3H), 0.89 (s, 9H), 2.67 (dd, J = 14.4, 10.0 Hz, 1H), 2.89 (dd, J = 14.4, 4.8 Hz, 1H), 3.66–3.80 (m, 1H), 4.40–4.48 (m, 1H), 5.28 (dt, J = 10.4, 1.6 Hz, 1H), 5.37 (dt, J = 16.8, 1.6 Hz, 1H), 5.50 (d, J = 8.0 Hz, 1H), 5.91 (ddd, J = 17.2, 10.8, 5.2 Hz, 1H), 6.88–7.00 (m, 5H), 7.44–7.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.9, –4.5, 18.2, 25.8, 35.6, 62.3, 76.0, 117.2, 125.4, 126.4, 128.0, 128.1, 129.0, 129.8, 132.4, 132.9, 135.0, 137.2, 137.6, 146.9; HRMS (FAB), m/z calcd for $C_{23}H_{33}N_2O_5SSi$ (MH^+) 477.1879, found 477.1885.

(3*R*,4*S*)-3-[(*tert*-Butyl)dimethylsiloxy]-4-[*N*-methyl-*N*-(2-nitrobenzenesulfonyl)amino]-5-phenylpent-1-en (S8). By use of a procedure identical with that described for the preparation of **9a** from **8**, the sulfonamide **S7** (600 mg, 1.25 mmol) was converted into the title compound **S8** (585 mg, 95.4% yield) as colorless crystals: mp 95–97 °C; $[\alpha]^{29}_D$ +22.1 (c 1.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.10 (s, 3H), 0.94 (s, 9H), 2.80 (dd, J = 14.6, 10.7 Hz, 1H), 3.05 (s, 3H), 3.08 (dd, J = 14.8, 3.6 Hz, 1H), 4.13 (dt, J = 10.9, 4.0 Hz, 1H), 4.44 (m, 1H), 5.19 (dd, J = 10.5, 0.9 Hz, 1H), 5.29 (dd, J = 17.1, 1.2 Hz, 1H), 5.88 (ddd, J = 17.1, 10.2, 6.8 Hz, 1H), 6.97-7.12 (m, 5H), 7.20-7.35 (m, 2H), 7.37-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.9, –3.8, 18.0, 25.9, 30.8, 32.3, 64.8, 77.8, 116.8, 123.6, 128.2, 129.0, 130.1, 131.3, 132.5, 133.4, 138.2, 138.9, 147.8. Anal. Calcd for $C_{24}H_{34}N_2O_5SSi$: C, 58.75; H, 6.98; N, 5.71. Found: C, 58.57; H, 7.13; N, 5.66.

(3*R*,4*S*)-4-(*N*-Acryloyl-*N*-methylamino)-3-[(*tert*-butyl)dimethylsiloxy]-5-phenylpent-1-en (S9). By use of a procedure identical with that described for the

preparation of *O*-TBS-**10a** from **9a**, the sulfonamide **S8** (510 mg, 1.03 mmol) was converted into the title compound **S9** (256 mg, 90.4% yield) as colorless oil (rotamer mixture): $[\alpha]^{21}_{D}$ –59.7 (c 1.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ –0.13–-0.02 (m, 6H), 0.75–0.89 (m, 9H), 2.52–3,15 (m, 5H), 3,70–4.50 (m, 2H), 4.96–6.26 (m, 6H), 6.90–7.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.8, –4.0, –3.9, –3.6, 18.0, 18.1, 25.6, 25.8, 28.5, 32.7, 34.5, 64.8, 75.4, 115.9, 117.2, 126.0, 126.5, 127.1, 128.2, 128.4, 128.5, 128.6, 128.8, 129.0, 138.1, 138.9, 139.3, 167.1, 168.2; HRMS (FAB), *m*/*z* calcd for $C_{21}H_{34}NO_2Si$ (MH^+) 360.2359, found 360.2365.

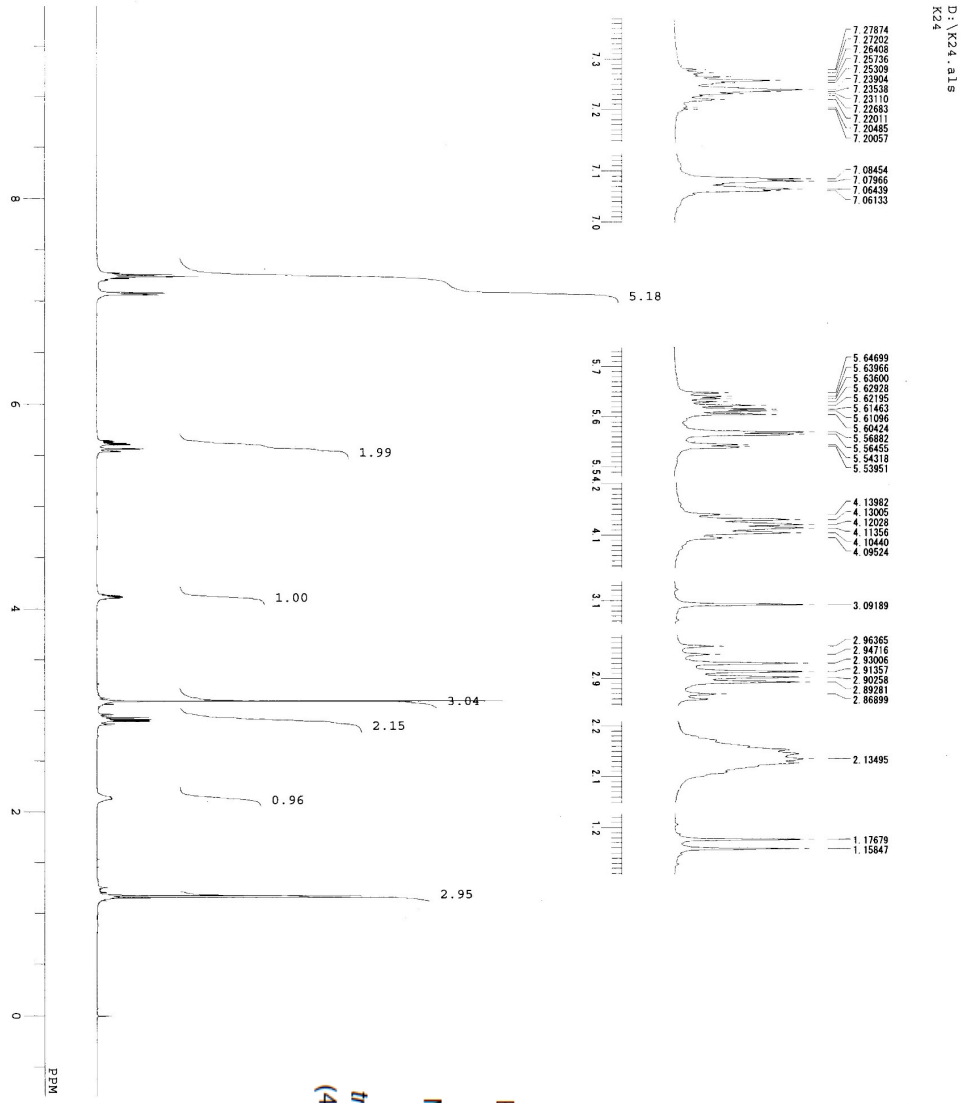
(3*R*,4*S*)-4-(*N*-Acryloyl-*N*-methylamino)-5-phenylpent-1-en-3-ol (S10). By use of a procedure identical with that described for the preparation of **10a** from *O*-TBS-**10a**, the acrylamide **S9** (103 mg, 0.286 mmol) was converted into the title compound **S10** (69.9 mg, 99.6% yield) as colorless oil (rotamer mixture): $[\alpha]^{29}_{D}$ –100.8 (c 1.92, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.73 (s, 3H), 2.81 (dd, *J* = 14.1, 10.9 Hz, 0.6H), 2.90 (s, 1.8H), 3.02 (dd, *J* = 14.5, 4.3 Hz, 1H), 3.18 (dd, *J* = 14.5, 11.5 Hz, 1H), 3.24 (dd, *J* = 14.1, 3.2 Hz, 0.6H), 3.81–3.86 (m, 0.2H), 3.98 (ddd, *J* = 10.8, 8.0, 3.0 Hz, 0.4H), 4.15 (m, 1H), 4.24 (t, *J* = 7.4 Hz, 0.5H), 4.48 (m, 1H), 5.21 (d, *J* = 10.4 Hz, 0.3H), 5.23 (dt, *J* = 11.8, 1.1 Hz, 1H), 5.34 (m, 1H), 5.40 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.66 (dd, *J* = 10.4, 1.9 Hz, 1H), 5.79–5.88 (m, 0.75H), 5.96 (ddd, *J* = 16.5, 10.4, 5.8 Hz, 1H), 6.04 (dd, *J* = 16.9, 10.7 Hz, 0.4H), 6.26 (dd, *J* = 16.7, 1.9 Hz, 1H), 6.35 (dd, *J* = 16.7, 10.4 Hz, 0.4H), 6.36 (dd, *J* = 16.8, 10.4 Hz, 1H), 7.10–7.30 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 28.5, 29.6, 31.7, 34.4, 36.1, 63.7, 65.8, 74.0, 74.2, 75.0, 116.3, 117.4, 126.2, 126.3, 126.5, 128.0, 128.2, 128.4, 128.5, 128.7, 128.8, 128.9, 137.6, 137.9, 138.2, 138.5, 168.2, 168.3; HRMS (FAB), *m*/*z* calcd for $C_{15}H_{20}NO_2$ (MH^+) 246.1494, found 246.1495.

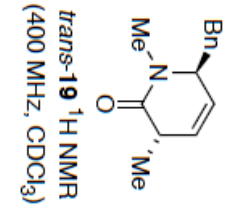
(5*R*,6*S*)-6-Benzyl-5,6-dihydro-1-methyl-5-hydroxypyridin-2-one (S11). By use of a procedure identical with that described for the preparation of **11a** from **10a**, the acrylamide **S10** (31 mg, 0.126 mmol) was converted into the title compound **S11** (23.1 mg, 84.3% yield) as colorless crystals: mp 129–131 °C; $[\alpha]^{24}_{D}$ –301.5 (c 0.47, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.63 (dd, *J* = 13.5, 8.6 Hz, 1H), 2.88 (s, 3H), 2.91 (dd, *J* = 13.5, 8.7 Hz, 1H), 3.65–3.78 (m, 1H), 3.92–4.00 (m, 1H), 5.99 (d, *J* = 9.5 Hz, 1H), 6.57 (ddd, *J* = 9.5, 5.6, 1.4 Hz, 1H), 7.06–7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.4, 37.6, 63.6, 67.4, 126.8, 126.9, 128.8, 129.1, 136.9, 137.0, 162.5. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.71; H, 6.97; N, 6.26.

(5*R*,6*S*)-5-Acetoxy-6-benzyl-5,6-dihydro-1-methylpyridin-2-one (14). By use of a procedure identical with that described for the preparation of **2** from **11a**, the lactam **S11** (366 mg, 1.68 mmol) was converted into the title compound **14** (435 mg, 99.9% yield) as colorless crystals: mp 71–73 °C; $[\alpha]^{26}_{D}$ –353.8 (c 0.96, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.76 (dd, *J* = 13.8, 8.3 Hz, 1H), 2.90 (s, 3H), 2.97 (dd, *J* = 13.8, 6.3 Hz, 1H), 3.69–3.74 (m, 1H), 5.04 (dd, *J* = 5.7, 0.9 Hz, 1H), 6.14 (d, *J* = 9.6 Hz, 1H), 6.51 (ddd, *J* = 9.6, 5.7, 1.2 Hz, 1H), 7.13–7.17 (m, 2H), 7.24–7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 34.2, 37.5, 64.1, 65.7, 127.2, 128.9, 129.1, 129.7, 132.3,

136.4, 161.9, 170.1. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.42; H, 6.68; N, 5.28.

NMR charts of representative compounds





trans-**19** ^{1}H NMR
(400 MHz, $CDCl_3$)

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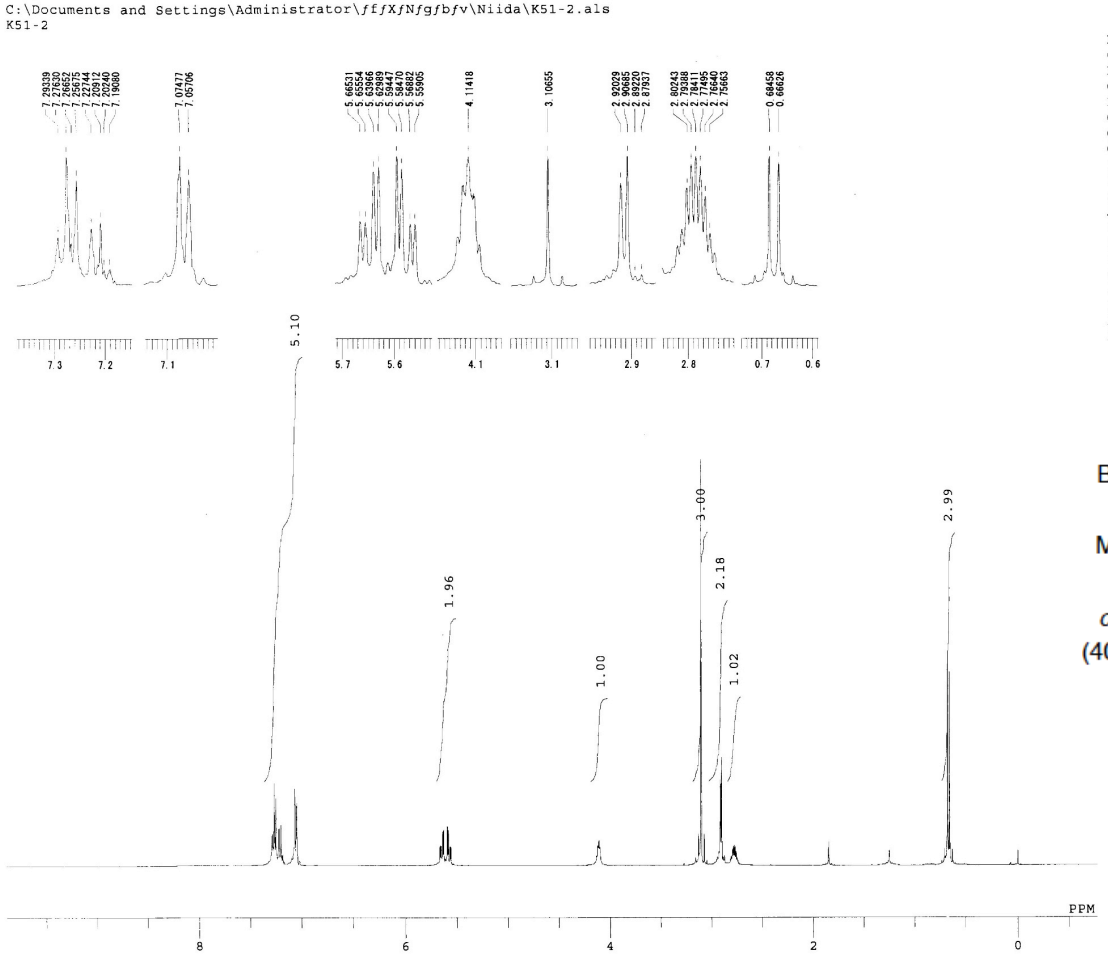
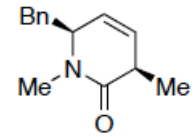
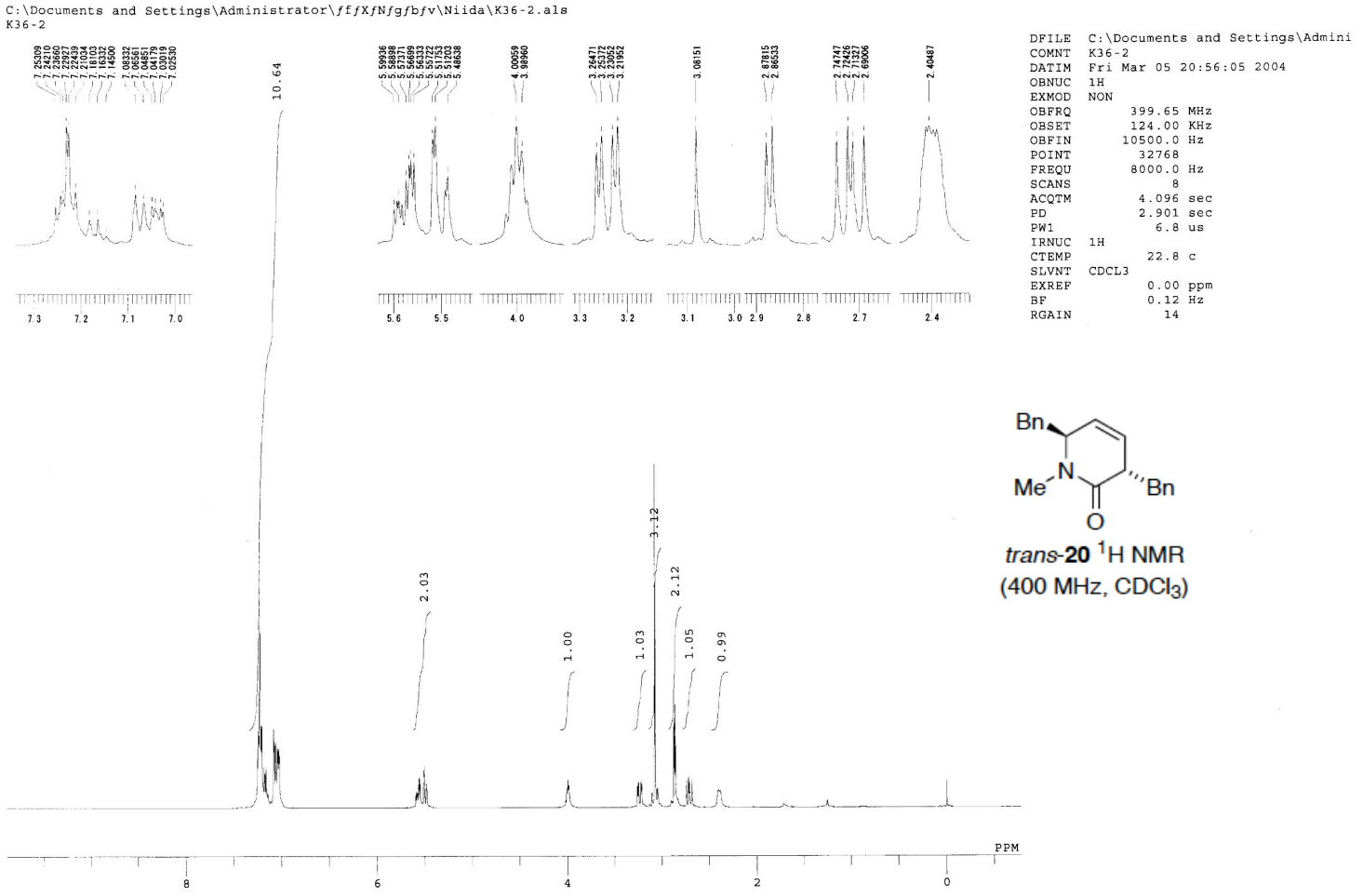
BF 0.12 Hz
RGAIN 13

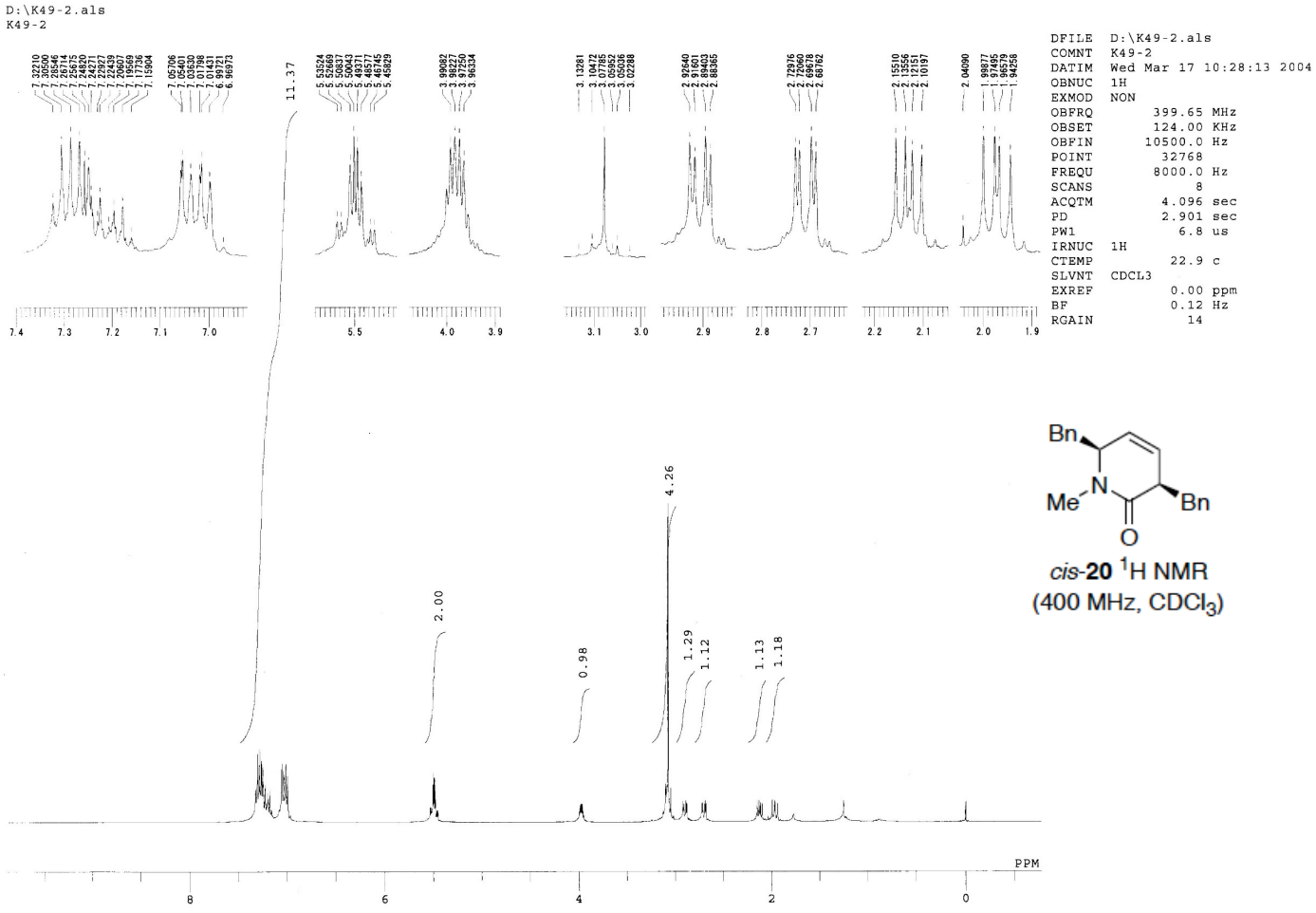



```
DFILE   C:\Documents and Settings\Admini
COMNT   K51-2
DATIM   Thu Mar 18 11:30:57 2004
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU         8000.0 Hz
SCANS             8
ACQTM          4.096 sec
PD             2.901 sec
PW1              6.8 us
IRNUC   1H
CTEMP           22.3 c
SLVNT   CDCL3
EXREF             0.00 ppm
BF                0.12 Hz
RGAIN               14
```

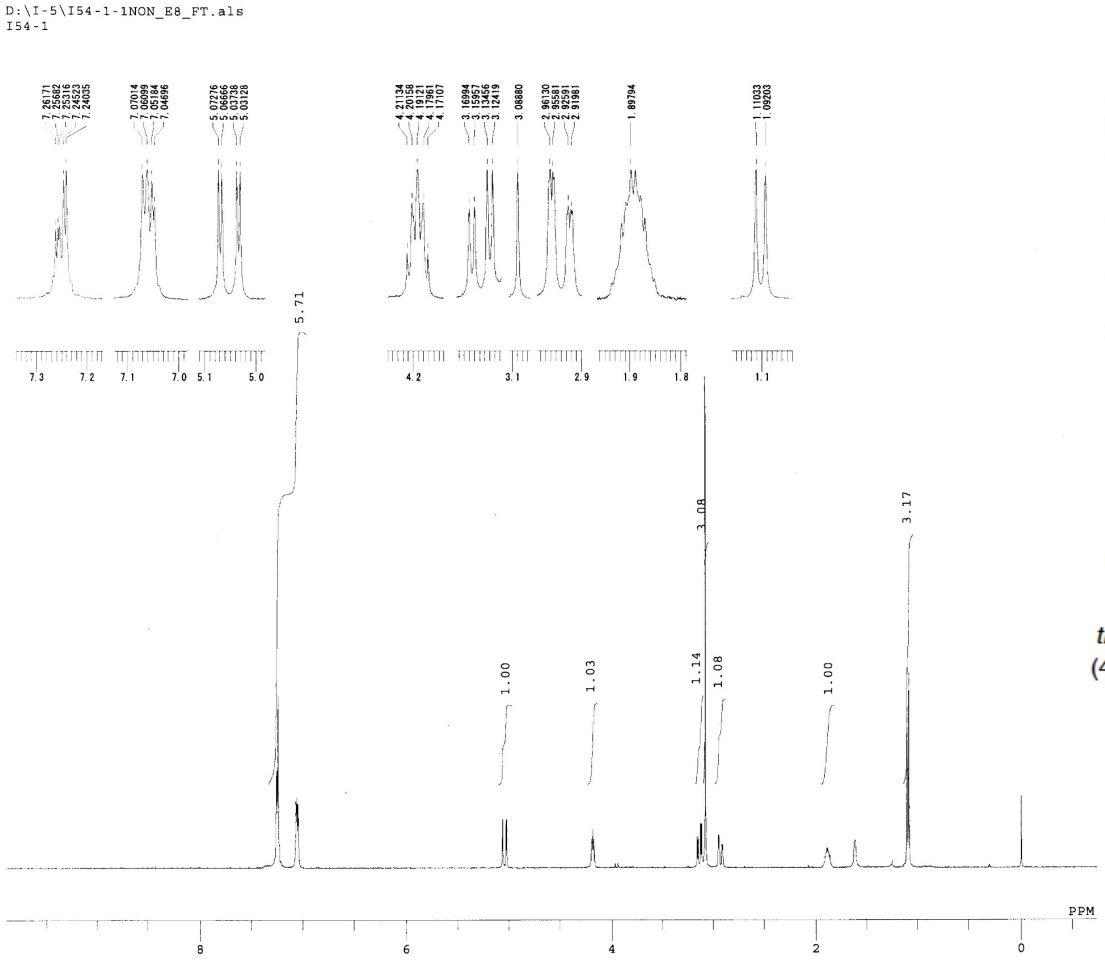


cis-**19** ^{1}H NMR
(400 MHz, $CDCl_3$)

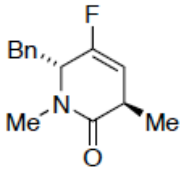

C:\Documents and Settings\Administrator\ffXfNfgfbfv\Niida\K36-2.als
K36-2
DFILE C:\Documents and Settings\Admini
COMNT K36-2
DATIM Fri Mar 05 20:56:05 2004
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 2.901 sec
PW1 6.8 us
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14
10.64
2.03
1.00
1.03
3.12
2.12
1.05
0.99
PPM
Bn
N
Me
Bn
O
trans-20 1H NMR
(400 MHz, CDCl3)



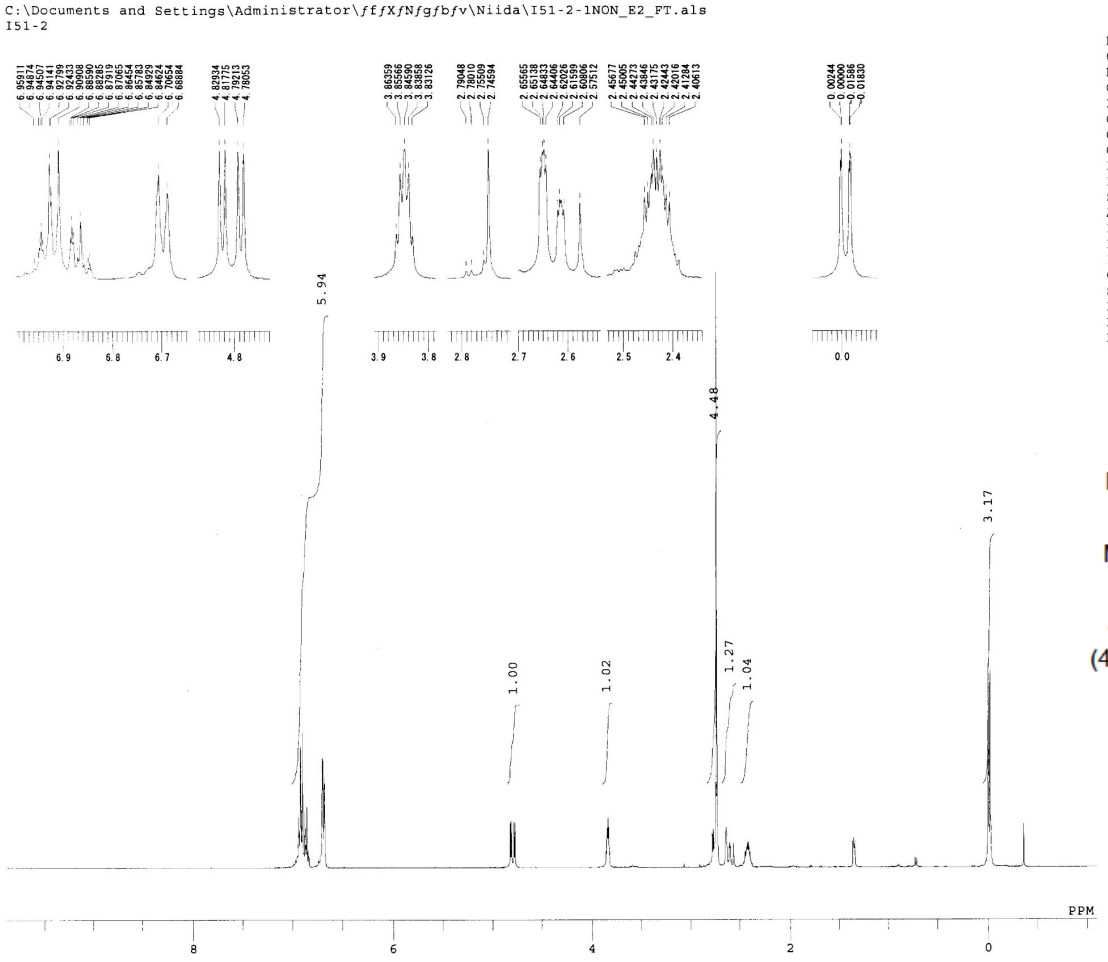
cis-**20** ^{1}H NMR
(400 MHz, $CDCl_3$)



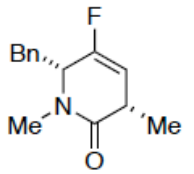

```
DFILE   D:\I-5\I54-1-1NON_E8_FT.als
COMNT   I54-1
DATIM   Tue Dec 14 22:09:58 2004
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN        10500.0 Hz
POINT          32768
FREQU         7992.0 Hz
SCANS             8
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.0 us
IRNUC   1H
CTEMP           22.5 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            20
```



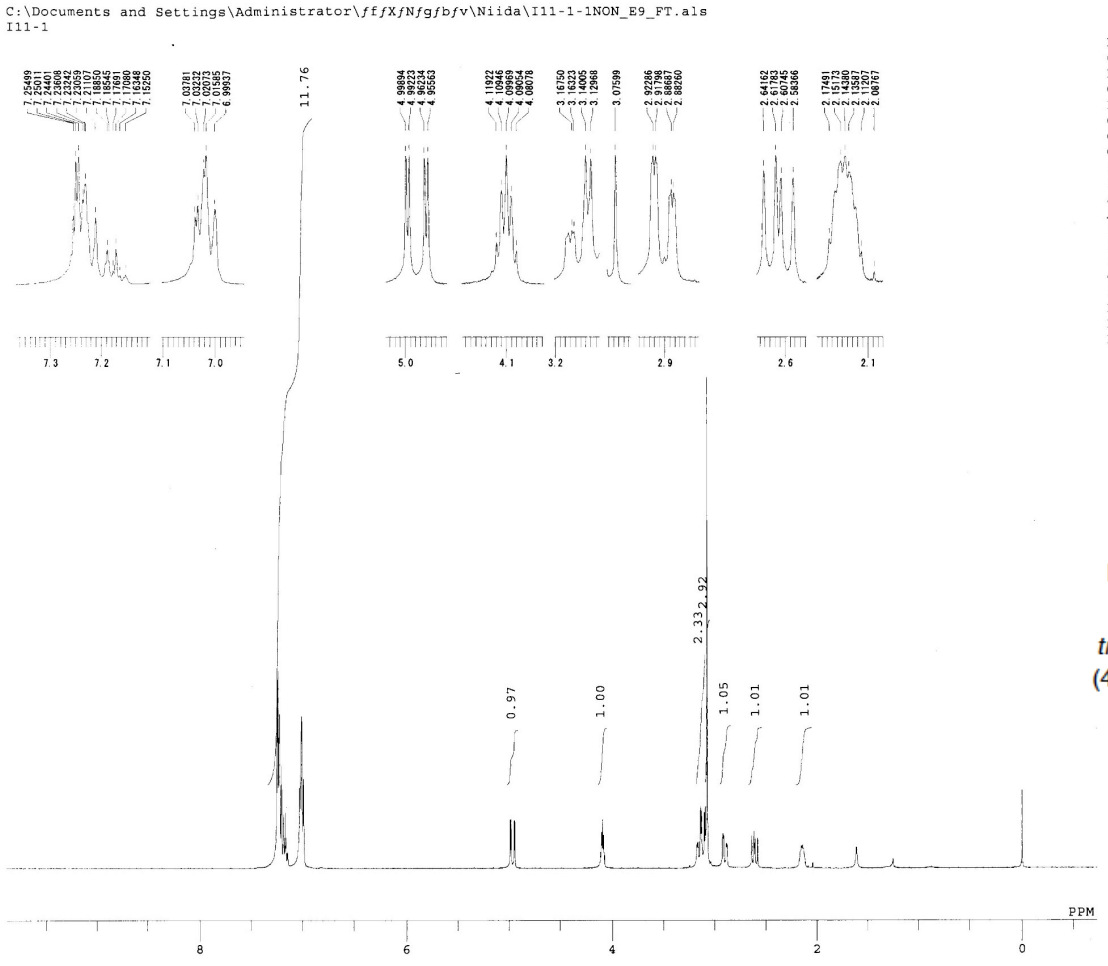
trans-**27** ^{1}H NMR
(400 MHz, $CDCl_3$)



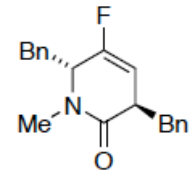

```
DFILE   C:\Documents and Settings\Admini
COMNT   I51-2
DATIM   Mon Dec 13 09:22:28 2004
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU        7992.0 Hz
SCANS             8
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.0 us
IRNUC   1H
CTEMP           23.3 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             18
```



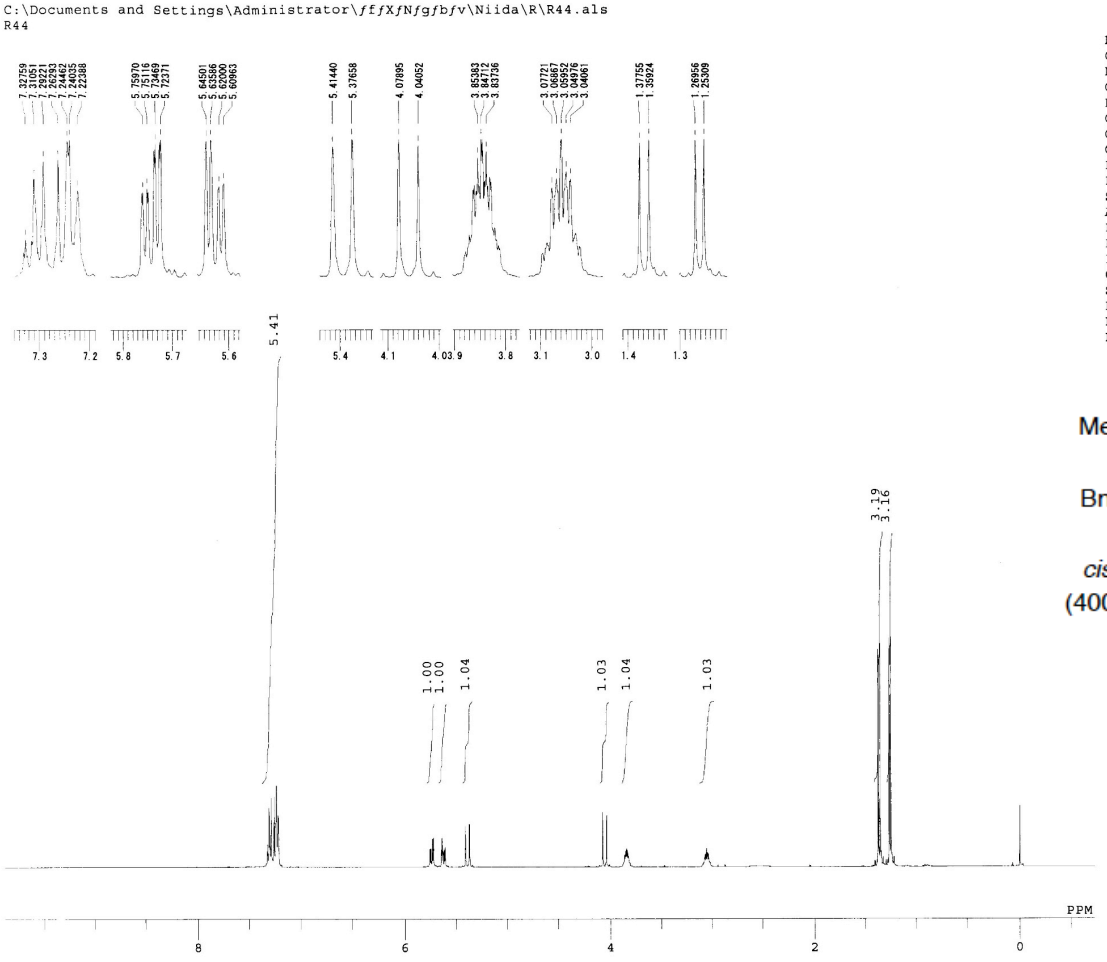
cis-**27** ^{1}H NMR
(400 MHz, $CDCl_3$)



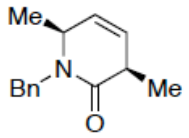

```
DFILE   C:\Documents and Settings\Admini
COMNT   I11-1
DATIM   Fri Nov 05 13:42:25 2004
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU         7992.0 Hz
SCANS             8
ACQTM           4.100 sec
PD              2.900 sec
PW1               6.0 us
IRNUC   1H
CTEMP            22.8 c
SLVNT   CDCL3
EXREF             0.00 ppm
BF                0.12 Hz
RGAIN               18
```



trans-**28** ^{1}H NMR (400 MHz, $CDCl_3$)

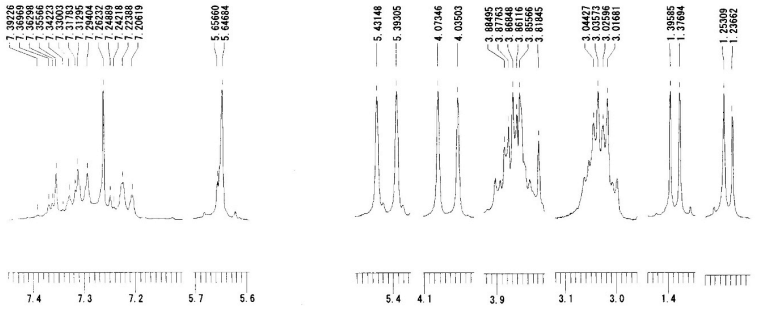



```
DFILE   C:\Documents and Settings\Admini
COMNT   R44
DATIM   Sat Nov 19 13:41:29 2005
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU         7992.0 Hz
SCANS            16
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.0 us
IRNUC   1H
CTEMP           23.0 c
SLVNT   CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              16
```

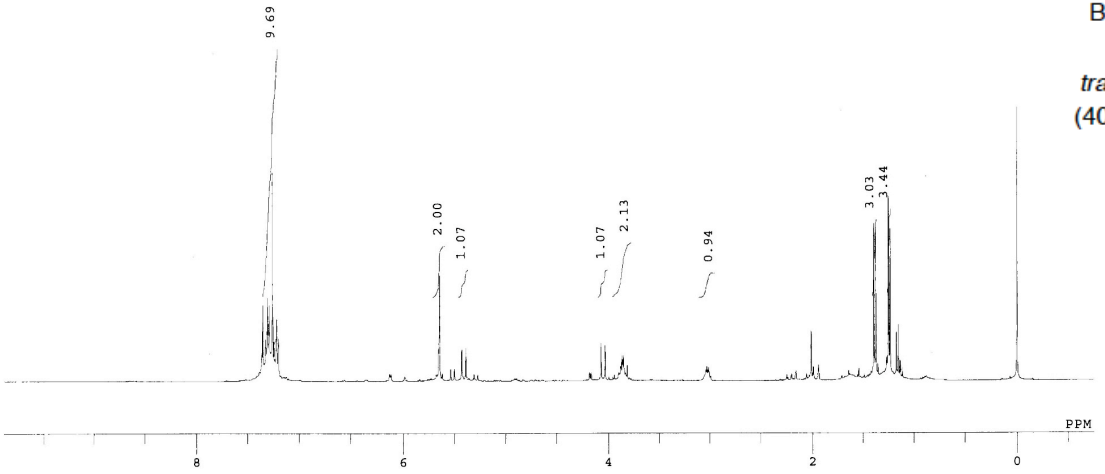


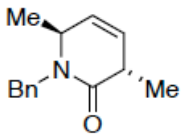
cis-**42** ^{1}H NMR
(400 MHz, $CDCl_3$)

C:\Documents and Settings\Administrator\ƒƒƒXƒNƒgƒbƒv\Niida\R\R54-1-2.als
R54-1

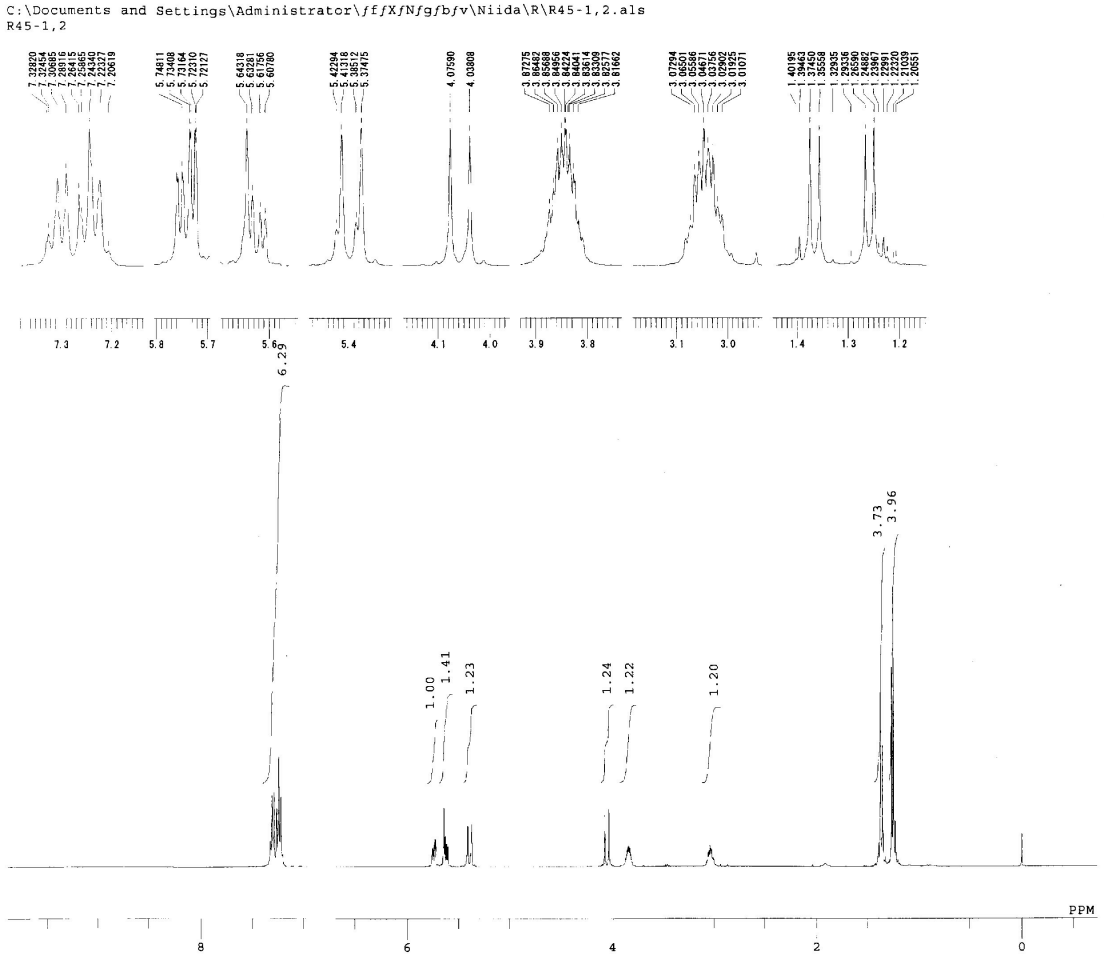



```
DFILE   C:\Documents and Settings\Admini
COMNT   R54-1
DATIM   Wed Jan 18 11:20:58 2006
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN        10500.0 Hz
POINT          32768
FREQU         7992.0 Hz
SCANS            128
ACQTM          4.100 sec
PD             2.900 sec
PW1              5.5 us
IRNUC   1H
CTEMP           17.8 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             19
```

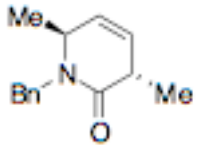




trans-**42** ^{1}H NMR
(400 MHz, $CDCl_3$)




```
DFILE   C:\Documents and Settings\Admini
COMNT   R45-1,2
DATIM   Tue Nov 22 13:50:46 2005
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.0 Hz
POINT         32768
FREQU         7992.0 Hz
SCANS            32
ACQTM          4.100 sec
PD             2.900 sec
PW1              6.0 us
IRNUC   1H
CTEMP           22.5 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             13
```



42 ^{1}H NMR

trans : *cis* = 17 : 83

(400 MHz, $CDCl_3$)