ol990402f

## SUPPLEMENTARY MATERIAL

***General.*** $^{1}H$, $^{13}C$ and $^{19}F$ NMR were performed on a Varian Unity-300 (299.94 MHz) and Gemini-200 (199.98 MHz) spectrometers using TMS, $CDCl_3$ and $CCl_3F$ as internal standards. High Resolution Mass Spectra (HRMS) were recorded on a JEOL HX110A instrument. Optical rotations were measured on a JASCO P-1010 polarimeter. Melting points (mp) are uncorrected and were obtained in open capillaries. All reagents and solvents, unless otherwise stated, are commercially available and were used as received. Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by $^{1}H$, $^{19}F$ and $^{13}C$ NMR spectrometry. All new compounds were characterized by $^{1}H$, $^{19}F$, $^{13}C$ NMR and HRMS.

**Synthesis of a Ni(II)-complex of the Schiff base of glycine with *o*-[*N*-α-pycolylamino]acetophenone 4b.** Into a suspension of *o*-[*N*-α-pycolylamino]-acetophenone (PAAP) (4.8 g, 20 mmol), glycine (7.5 g, 100 mmol) and $NiCl_2 \cdot 6H_2O$ (9.5 g, 40 mmol) in methanol (100 mL) was added a suspension of NaOH (5.6 g, 40 mmol) in methanol (40 mL) at 60 °C. After being stirred at 60 °C for 4 hours and at room temperature overnight, the reaction mixture was poured into a solution of ice-water (600 mL) and glacial HOAc (10 mL), stirred for a while. The solid was filtered off and dried *in vacuo* to give the desired Ni(II) complex **4b** (6.2 g, 88%).

**General procedure for the reactions of glycine complex 4b with (*S*)- or (*R*)-*N*-(*E*-enoyl)-5-phenyl-3-oxazoline-2-ones (2a-h).** To a suspension of complex **4b** (1.0 mmole) in DMF (3.0 mL), (*S*)- or (*R*)-*N*-(*E*-enoyl)-5-phenyl-3-oxazoline-2-ones (**2a-h**) (1.1 mmol) was added with stirring. The mixture was stirred at rt for 10-15 min to get a homogeneous solution, and then DBU (22 mg, 0.15 mmole) was added. The course of reaction was monitored by TLC ($SiO_2$). Each sample was quenched with 5% aqueous acetic acid and the product was extracted with chloroform before being applied to the plate. Upon disappearance

of the starting **4b**, the reaction mixture was poured into icy 5% aqueous acetic acid (100 mL) and stirred with a glass bar to initiate crystallization of the product. The crystalline product was filtered off, thoroughly washed with water and dried *in vacuo* to give addition products **6**.

**Ni(II) complex of Schiff base of PAAP and (2*R*,3*R*,4'*R*)-3-methyl-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6a).** m.p. 174.0-175.5 °C, $[\alpha]_D^{25}$ -2018, (*c* 0.024, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ 2.07 (3H, d, *J*=6.9 Hz), 2.50 (1H, dqdd, *J*=10.6, 6.9, 4.2, 3.6 Hz), 2.65 (3H, s), 2.94, 3.80 (2H, ABX, *J*=18.8, 10.6, 3.6 Hz), 4.26, 5.42 (2H, ABX, *J*=8.7, 2.7 Hz), 4.57 (1H, d, *J*=4.2 Hz), 4.73 (1H, t, *J*=8.7 Hz), 6.97-7.02 (1H, m), 7.27-7.43 (7H, m), 7.68-7.71 (1H, m), 7.86-7.88 (1H, m), 7.95-8.00 (1H, m), 8.17-8.19 (1H, m), 8.80 (1H, a part of AB, *J*=7.5 Hz). $^{13}$C-NMR ($CDCl_3$) δ 16.8 (s), 19.0 (s), 33.4 (s), 38.6 (s), 57.5 (s), 70.2 (s), 72.6 (s), 121.8 (s), 123.9 (s), 125.7 (s), 126.8 (s), 128.5 (s), 129.1 (s), 130.3 (s), 132.6 (s), 139.3 (s), 140.3 (s), 141.9 (s), 146.8 (s), 153.3 (s), 153.5 (s), 169.6 (s), 170.6 (s), 171.6 (s), 177.7 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{29}H_{27}N_4NiO_6$ 585.1284, found 585.1292.

**Ni(II) complex of Schiff base of PAAP and (2*S*,3*S*,4'*S*)-3-methyl-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6a).** m.p. 175.0-176.0 °C, $[\alpha]_D^{25}$ +1940, (*c* 0.022, $CHCl_3$). HRMS(FAB) $[M+H]^+$ calcd. for $C_{29}H_{27}N_4NiO_6$ 585.1284, found 585.1292.

**Ni(II) complex of Schiff base of PAAP and (2*R*,3*R*,4'*R*)-3-ethyl-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6b).** m.p. 147.0-148.0 °C, $[\alpha]_D^{25}$ -1886, (*c* 0.02, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ 1.09 (3H, d, *J*=7.2 Hz), 1.83-1.94 (1H, m), 2.23-2.30 (1H, m), 2.67 (3H, s), 3.07, 3.72 (2H, ABX, *J*=19.2, 11.1, 2.7 Hz), 3.80-3.88 (1H, m), 4.25, 5.42 (2H, ABX, *J*=8.7, 2.7 Hz), 4.55 (1H, d, *J*=4.5 Hz), 4.71 (1H, t, *J*=8.7 Hz), 6.97-7.02 (1H, m), 7.24-7.43 (7H, m), 7.68-7.71 (1H, m), 7.86-7.88 (1H, m), 7.95-8.00 (1H, m), 8.17-8.19 (1H, m), 8.82 (1H, a part of AB, *J*=7.8 Hz). $^{13}$C-NMR ($CDCl_3$) δ 12.4 (s), 19.2 (s), 22.8 (s), 34.8 (s), 40.2 (s), 57.5 (s), 70.2 (s), 72.3 (s), 121.8 (s), 123.8 (s), 123.9 (s), 125.8 (s), 126.7 (s), 126.8 (s), 128.6 (s), 129.1 (s), 130.4 (s), 132.7 (s), 139.4 (s), 140.4 (s), 141.9 (s), 146.9 (s), 153.3 (s),

153.6 (s), 169.6 (s), 170.7 (s), 172.4 (s), 178.1 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{30}H_{29}N_4NiO_6$ 599.1441, found 599.1432.

**Ni(II) complex of Schiff base of PAAP and (2*R*,3*R*,4'*R*)-3-*n*-propyl-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6c).** m.p. 155.0-156.0 °C, $[\alpha]_D^{25}$ -1852, (*c* 0.019, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ 0.90 (3H, d, *J*=6.9 Hz), 1.26-1.40 (1H, m), 1.56-1.68 (1H, m), 1.79-1.92 (1H, m), 2.33-2.40 (1H, m), 2.66 (3H, s), 3.00, 3.78 (2H, ABX, *J*=19.2, 11.1, 2.7 Hz), 3.54-3.59 (1H, m), 4.25, 5.45 (2H, ABX, *J*=8.7, 2.7 Hz), 4.53 (1H, d, *J*=4.2 Hz), 4.73 (1H, t, *J*=8.7 Hz), 6.92-6.97 (1H, m), 7.28-7.43 (7H, m), 7.65-7.68 (1H, m), 7.83-7.85 (1H, m), 7.93-7.98 (1H, m), 8.11-8.13 (1H, m), 8.79 (1H, a part of AB, *J*=8.4 Hz). $^{13}$C-NMR ($CDCl_3$) δ 14.0 (s), 19.2 (s), 20.6 (s), 31.9 (s), 35.3 (s), 38.1 (s), 57.5 (s), 70.2 (s), 72.1 (s), 121.8 (s), 123.8 (s), 123.9 (s), 125.7 (s), 126.7 (s), 126.8 (s), 128.5 (s), 129.1 (s), 130.3 (s), 132.5 (s), 139.4 (s), 140.3 (s), 141.8 (s), 146.8 (s), 153.2 (s), 153.6 (s), 169.6 (s), 170.9 (s), 172.3 (s), 178.1 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{31}H_{31}N_4NiO_6$ 613.1597, found 613.1612.

**Ni(II) complex of Schiff base of PAAP and (2*R*,3*S*,4'*R*)-3-phenyl-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6e).** m.p. 208.0-209.0 °C, $[\alpha]_D^{25}$ -2363, (*c* 0.02, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ 2.76 (3H, s), 3.44, 4.49 (2H, ABX, *J*=18.9, 11.4, 2.4 Hz), 3.70 (1H, ddd, *J*=11.4, 4.2, 2.4 Hz), 4.28, 5.45 (2H, ABX, *J*=8.4, 2.7 Hz), 4.68 (1H, d, *J*=4.2 Hz), 4.78 (1H, t, *J*=8.4 Hz), 6.71-6.76 (1H, m), 6.97-7.02 (1H, m), 7.09-7.14 (2H, m), 7.24-7.45 (9H, m), 7.54-7.56 (1H, m), 7.66-7.71 (2H, m), 7.84-7.89 (1H, m), 8.54 (1H, a part of AB, *J*=8.7 Hz). $^{13}$C-NMR ($CDCl_3$) δ 18.4 (s), 36.7 (s), 44.8 (s), 57.6 (s), 70.3 (s), 74.1 (s), 121.7 (s), 123.3 (s), 123.9 (s), 125.7 (s), 126.1 (s), 127.2 (s), 127.7 (s), 128.1 (s), 128.7 (s), 129.2 (s), 130.1 (s), 130.5 (s), 132.6 (s), 138.8 (s), 139.2 (s), 139.6 (s), 142.0 (s), 146.6 (s), 153.3 (s), 153.5 (s), 168.6 (s), 169.0 (s), 171.7 (s), 176.8 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{34}H_{29}N_4NiO_6$ 647.1441, found 647.1459.

**Ni(II) complex of Schiff base of PAAP and (2*R*,3*S*,4'*R*)-3-(β-naphthyl)-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6f).** m.p. 217.0-219.0 °C, $[\alpha]_D^{25}$ -2187, (*c* 0.02, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ 2.81 (3H, s), 3.57, 4.59 (2H, ABX, *J*=19.0, 11.1, 2.7 Hz), 3.91 (1H, ddd, *J*=11.1, 4.2, 2.7 Hz), 4.29, 5.45 (2H, ABX, *J*=8.7, 2.7 Hz), 4.71 (1H, d, *J*=4.2 Hz), 4.79 (1H, t, *J*=8.7 Hz), 6.79-6.83 (1H, m), 6.97-7.02 (1H, m), 7.13-7.36 (11H, m), 7.44-7.70 (5H, m), 8.03 (1H, br.s), 8.52 (1H, a part of AB, *J*=8.7 Hz). $^{13}$C-NMR ($CDCl_3$) δ 18.4 (s), 36.9 (s), 45.0 (s), 57.6 (s), 70.3 (s), 74.6 (s), 121.7 (s), 122.8 (s), 123.9 (s), 125.4 (s), 125.6 (s), 125.7 (s), 126.1 (s), 127.3 (s), 127.4 (s), 127.7 (s), 128.2 (s), 128.7 (s), 129.2 (s), 130.1 (s), 132.6 (s), 133.1 (s), 136.5 (s), 139.1 (s), 142.1 (s), 145.6 (s), 152.0 (s), 153.5 (s), 169.0 (s), 171.7 (s), 176.7 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{38}H_{31}N_4NiO_6$ 697.1597, found 697.1606.

**Ni(II) complex of Schiff base of PAAP and (2*S*,3*R*,4'*S*)-3-(*p*-trifluoromethyl-phenyl)-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6g).** m.p. 185.0-186.0 °C, $[\alpha]_D^{25}$ +2045, (*c* 0.031, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ 2.78 (3H, s), 3.43, 4.48 (2H, ABX, *J*=19.2, 11.1, 3.0 Hz), 3.75 (1H, ddd, *J*=11.1, 4.2, 3.0 Hz), 4.30, 5.45 (2H, ABX, *J*=8.7, 2.7 Hz), 4.69 (1H, d, *J*=4.2 Hz), 4.79 (1H, t, *J*=8.7 Hz), 6.97-7.02 (1H, m), 7.23-7.45 (9H, m), 7.52-7.53 (1H, m), 7.58-7.61 (2H, m), 7.67-7.70 (2H, m), 7.84-7.90 (1H, m), 8.59 (1H, a part of AB, *J*=8.1 Hz). $^{19}$F-NMR ($CDCl_3$) δ -63.35 (s). $^{13}$C-NMR ($CDCl_3$) δ 18.5 (s), 36.6 (s), 44.7 (s), 57.6 (s), 70.3 (s), 74.8 (s), 121.8 (s), 123.9 (s), 125.0 (q, *J*=4.0 Hz), 125.7 (s), 126.3 (s), 126.9 (s), 128.8 (s), 129.2 (s), 130.2 (s), 131.0 (s), 132.9 (s), 139.0 (s), 140.3 (s), 142.1 (s), 142.9 (s), 146.0 (s), 152.7 (s), 153.5 (s), 168.7 (s), 169.6 (s), 171.2 (s), 176.5 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{35}H_{28}F_3N_4NiO_6$ 715.1314, found 715.1295.

**Ni(II) complex of Schiff base of PAAP and (2*S*,3*R*,4'*S*)-3-(*p*-methoxyphenyl)-5-[3'-(4'-phenyl-2'-oxazolidinonyl)]glutamic acid (6h).** m.p. 211.0-212.5 °C, $[\alpha]_D^{25}$ +2265, (*c* 0.02, $CHCl_3$). $^1$H-NMR ($CDCl_3$) δ 2.74 (3H, s), 3.39, 4.43 (2H, ABX, *J*=19.2, 11.4, 3.0 Hz), 3.49 (3H, s), 3.67 (1H, ddd, *J*=11.4, 4.2, 3.0 Hz), 4.27, 5.45 (2H, ABX, *J*=8.7, 3.0 Hz), 4.65 (1H, d, *J*=4.2 Hz), 4.77 (1H, t, *J*=8.7 Hz), 6.62 (2H, a part of AB, *J*=9.0 Hz), 6.97-7.02 (1H,

m), 7.27-7.40 (9H, m), 7.57-7.71 (3H, m), 7.86-7.91 (1H, m), 8.51 (1H, a part of AB, *J*=9.0 Hz). $^{13}$C-NMR ($CDCl_3$) δ 18.3 (s), 36.9 (s), 44.1 (s), 54.6 (s), 57.5 (s), 70.3 (s), 74.3 (s), 113.2 (s), 121.7 (s), 123.0 (s), 123.9 (s), 125.7 (s), 126.0 (s), 127.3 (s), 127.6 (s), 128.6 (s), 129.1 (s), 130.1 (s), 130.7 (s), 131.6 (s), 132.5 (s), 139.2 (s), 139.6 (s), 141.8 (s), 146.6 (s), 153.1 (s), 153.5 (s), 159.1 (s), 168.5 (s), 168.8 (s), 171.7 (s), 176.9 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{35}H_{31}N_4NiO_6$ 677.1546, found 677.1539.

**Decomposition of complex 6; Isolation of (2*S*,3*S*)-3-alkyl-, (2*S*,3*R*)-3-arylpyroglutamic acid or (2*R*,3*R*)-3-alkyl-, (2*R*,3*S*)-3-arylpyroglutamic acid 9 and recovery of ligand 8 and starting chiral auxiliary (*S*)-, (*R*)-10.** A solution of diastereomerically pure complex **6** (15 mmol) in MeOH (50 mL) was slowly added with stirring to a mixture of aqueous 3 *N* HCl and MeOH (90 mL, ratio 1/1) at 70 °C. Upon disappearance of the red color of the starting complex, the reaction mixture was evaporated *in vacuo* to dryness. Water (80 mL) was added and the resultant mixture was treated with excess of concd. $NH_4OH$ and extracted with $CHCl_3$. The $CHCl_3$ extracts were dried over $MgSO_4$ and evaporated *in vacuo* to afford 6.0 g of 1:1 mixture (99%) of PAAP **8** and chiral auxiliary (*S*)- or (*R*)-**10**. The aqueous solution was evaporated *in vacuo*, dissolved in a minimum amount of water and loaded on cation exchange resin Dowex 50X2 100. The column was washed with water and the acidic fraction was collected to give, after evaporation *in vacuo*, pyroglutamic acid **9**. Analytically pure sample of the product was obtained by crystallization of the compound from THF/*n*-hexane.

**(2*S*,3*S*)-3-Methylpyroglutamic acid (9a)**. Yield 96%; m.p. 110.0-111.5 °C, $[\alpha]_D^{25}$ +41.0, (*c* 1.16, MeOH). $^1$H-NMR ($CD_3COCD_3$) δ 1.28 (3H, d, *J*=6.6 Hz), 1.93, 2.48 (2H, ABX, *J*=15.9 Hz, *J*=8.5 Hz, *J*=5.7 Hz), 2.53 (1H, dqdd, *J*=8.5 Hz, *J*=6.6 Hz, *J*=5.7 Hz, *J*=5.1 Hz), 3.86 (1H, d, *J*=5.1 Hz), 7.19 (1H, br.s). $^{13}$C-NMR ($CD_3COCD_3$) δ 20.1 (s), 34.8 (s), 38.4 (s), 63.1 (s), 174.0 (s), 178.3 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_6H_{10}NO_3$ 144.0661, found 144.0660.

**(2*S*,3*R*)-3-Phenylpyroglutamic acid (9e)**. Yield 95%; m.p. 139.0-140.0 °C, $[\alpha]_D^{25}$ +82.8, (*c* 1.10, MeOH). $^1$H-NMR ($CD_3COCD_3$) δ 2.34, 2.75 (2H, ABX, *J*=16.8 Hz, *J*=9.3 Hz, *J*=6.3 Hz), 3.72 (1H, ddd, *J*=9.3 Hz, *J*=6.3 Hz, *J*=5.1 Hz), 4.25 (1H, d, *J*=5.1 Hz), 7.25-7.41 (5H, m). $^{13}$C-NMR ($CD_3COCD_3$) δ 38.7 (s), 44.9 (s), 63.1 (s), 127.8 (s), 127.9 (s), 129.6 (s), 143.9 (s), 173.5 (s), 176.4 (s). HRMS(FAB) $[M+H]^+$ calcd. for $C_{11}H_{12}NO_3$ 206.0817, found 206.0809.