Supporting Information

for

Relative Reactivity of *anti*- and *syn*-Oximino-Carbonates and Carbamates of 2-Pyridyl Acetic Acid Esters

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Experimental

General Procedure

All reagents purchased were used as received. Methylene chloride (CH_2Cl_2) and dimethylsulfoxide (DMSO) were distilled from calcium hydride. Sodium sulfate was anhydrous.. All recrystallization, chromatographic, and work-up solvents were distilled. Glassware was oven dried and/or flamed dried. Reactions were carried out under a positive pressure of argon in anhydrous solvents, and the reaction flasks were fitted with rubber septa for the introduction of substrates and reagents via syringe. Progress of reactions was monitored by thin layer chromatography (TLC). TLC was performed on glass-backed silica gel 60 F 254 plates (EM reagents, 0.25 mm) and eluted with (v/v) EtOAc in hexane. TLC plates were visualized with UV (254 nm) and/or with TLC staining solution activated with heat. The commonly employed TLC visualizing solution was p-anisaldehyde solution (360 mL absolute ethanol, 20 mL concentrated H_2SO_4, 4mL glacial acetic acid, 20 mL p-anisaldehyde).

Analytical samples were obtained from flash silica gel chromatography (sgc), using silica gel of 230-400 mesh, or from recrystallization of the crude products. Melting points were obtained on a MEL-TEMP capillary melting point apparatus and are uncorrected. ^{1}H-NMR and ^{13}NMR spectra were recorded on a Varian 300 (300 MHz) spectrometer. NMR spectra were determined in chloroform-d_1 ($CDCl_3$) or dimethylsulfoxide-d_6 (DMSO-d_6) solution and reported in parts million (ppm) from the residual chloroform (7.27 ppm and 77.23 ppm) or DMSO (2.50 ppm and 39.51 ppm) standard, respectively. Peak multiplicities in ^{1}H-NMR spectra, when reported, are abbreviated as s (singlet), d (doublet), t (triplet), m multiplet, and/or br (broad). Mass spectra were run by the Purdue University campus wide mass spectrometry facility. The low resolution EI and CI (isobutane) spectra were obtained in a Finnigan 4000 mass spectrometer with a Nova 4 data system with the molecular ion designated as "M^{+}". The high resolution mass spectra were obtained on a Kratos MS-50 instrument. Compounds characterized by exact mass were homogeneous by TLC and NMR. NMR shift assignment were performed by analogy to known compounds and should be regarded as tentative.

*General procedure for the preparation of 2- or 4-Pyridylacetate **6, 23, 24.***

To a suspended solution of 2- or 4-pyridylacetic acid hydrochloride (3.0 mmol) and alcohol (allyl or t-butyl alcohol, 4.5 mmol) in 15 mL of dichloromethane was added triethylamine (6.0 mmol), 1,3-dicyclohexylcarbodiimide (3.0 mmol) and a catalytic amount of 4-(dimethylamino)pyridine (0.15 mmol) at 25˚C. After stirring 12 h at 45˚C, the reaction mixture was filtered through a Büchner funnel to remove 1,3-dicyclohexylurea. The filterate was washed with water (15 mL x 3) and dried over anhydrous sodium sulfate. Purification by column chromatography (25% EtOAc/hexane) afforded the desired ester of 2- or 4-pyridylacetic acid **6**, **23**, **24**.

Allyl 2-pyridylacetate **6**, yield: 81%, yellow liquid; TLC (EA:hex = 1:2), R_f 0.37; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (1H, d, J=4.9 Hz), 7.69 (1H, dd, J=7.6, 7.6 Hz), 7.29 (1H, d, J=7.6 Hz), 7.32 (1H, m), 5.89 (1H, m), 5.30 (1H, d, J=17.2 Hz), 5.24 (1H, d, J=10.4 Hz), 4.66 (2H, d, J=5.6 Hz), 3.91 (2H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 170.34, 154.53, 149.63, 136.74, 132.14, 124.00, 122.25, 118.36, 65.64, 43.99; MS (EI) m/z (relative intensity): 178 (M^{+}+H), 162 (M-CH_3), 134 (M-C_3H_7, 32), 92 (M-$C_4H_5O_2$, 100); MS (CI) m/z: 178 (M+H, base peak).

t-Butyl 2-pyridylacetate **23**, yield: 74%, light yellow oil; TLC (EA:hex = 2:1), R_f 0.60; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (1H, d, J=4.9 Hz), 7.62 (1H, dd, J=7.7, 7.7 Hz), 7.27 (1H, d, J=7.7 Hz), 7.14 (1H, m), 3.75 (2H, s), 1.44 (9H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 169.82, 155.05, 149.33, 136.41, 123.80, 121.86, 80.87, 45.10, 28.03; MS (EI) m/z (relative intensity): 193 (M^{+}), 120 (M-$C_4H_9O_1$, 9), 92 (M-$C_5H_9O_2$, 18), 57(C_4H_9, 100); MS (CI) m/z: 194 (M+H, base peak).

Allyl 4-pyridylacetate **24**, yield: 75%, light yellow liquid; TLC (EA:hex = 2:1), R_f 0.47; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (2H, d, J=6.0 Hz), 7.12 (2H, d, J=6.0 Hz), 5.78 (1H, m), 5.17 (1H, d, J=18.8 Hz), 5.13 (1H, d, J=10.3 Hz), 4.51 (2H, d, J=5.6 Hz), 3.55 (2H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 169.79, 150.12, 142.85, 131.88, 124.68, 118.74, 65.90, 40.62; MS (EI) m/z (relative intensity): 177 (M^+, 8), 120 ($M-C_3H_5O_1$, 35), 92 ($M-C_4H_5O_2$, 100); MS (CI) m/z: 178 (M+H, base peak).

*General procedure[1] for the preparation of anti- or syn-Oxime ester **7a, 7s, 12a, 12s, 25a/25s**.*

To a solution of 2- or 4-pyridylacetate (allyl ester or t-butyl ester **6**, **23**, **24**, 4.0 mmol) and excess acetic acid (1.5 mL) was added dropwise a solution of sodium nitrite (4.0 mmol) in water (3.0 mL) at 0°C. An additional 3.0 mL of water was added to facilitate stirring and the reaction mixture was allowed to slowly warm to room temperature over 3 h. The aqueous solution was extracted with dichloromethane (10 mL x 2) and the organic layer was washed twice with water (10 mL x 2). The dichloromethane layer was dried over anhydrous sodium sulfate and concentrated by evaporation. *Anti*- and *syn*-oximes were separated by flash column chromatography (20% EtOAc/hexane) affording **7a/7s** (1/3 ratio, quantitative yield), **12a/12s** (1.0/1.4 ratio, quantitative yield), **25a/25s** (93% yield).

Allyl α-*anti*-oximino-α-(2-pyridyl)acetate **7a**, light yellow solid; mp 95-96°C; TLC (EA:hex = 1:2), R_f 0.29; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (1H, d, J=5.0 Hz), 8.17 (1H, d, J=8.1 Hz), 8.01 (1H, dd, J=7.8, 8.1 Hz), 7.55 (1H, m), 6.15-6.01 (1H, m), 5.48 (1H, d, J=16.9 Hz), 5.35 (1H, d, J=10.3 Hz), 4.90 (2H, d, J=5.8 Hz); ^{13}H NMR (75 MHz, $CDCl_3$) δ 163.63, 149.93, 145.53, 143.10, 138.84, 131.68, 125.83, 124.06, 119.57, 66.78; MS (CI) m/z: 207 (M+H, base peak).

Allyl α-*syn*-oximino-α-(2-pyridyl)acetate **7s**, light yellow solid; mp 84.5-86°C; TLC (EA:hex = 1:2), R_f 0.39; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.88 (1H, brs) 8.66 (1H, d, J=4.9 Hz), 7.88 (1H, d, J=8.1 Hz), 7.77 (1H, dd, J=7.7, 8.1 Hz), 7.36 (1H, m), 6.11-5.98 (1H, m), 5.50 (1H, d, J=17.1 Hz), 5.32 (1H, d, J=10.3 Hz), 4.96 (2H, d, J=5.9 Hz); ^{13}H NMR (75 MHz, $CDCl_3$) δ 163.35, 151.71, 150.50, 149.61, 137.21, 131.66, 124.75, 121.19, 119.31, 66.71; MS (EI) m/z (relative intensity): 207 (M^++H, 7), 176 (M-NO), 121 ($M-C_4H_5O_2$, 62), 105 ($M-C_4H_5O_3$, 100), 78 ($C_5H_4N_1$, 86); MS (CI) m/z: 207 (M+H, base peak).

t-Butyl α-*anti*-oximino-α-(2-pyridyl)acetate **12a**, white solid; mp 131-132.5°C; TLC (EA:hex = 1:2), R_f 0.31; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (1H, d, J=4.9 Hz), 7.97 (2H, m), 7.51 (1H, m), 1.63 (9H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 162.90, 149.73, 145.72, 144.85, 138.26, 125.30, 123.85, 83.22, 28.05; MS (CI) m/z: 223 (M+H, base peak).

t-Butyl α-*syn*-oximino-α-(2-pyridyl)acetate **12s**, white solid; mp 133.5-134°C; TLC (EA:hex = 1:2), R_f 0.43; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.45 (1H, brs), 8.66 (1H, d, J=4.9 Hz), 7.77 (2H, m), 7.32 (1H, m), 1.65 (9H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 162.84, 151.69, 150.67, 149.45, 136.76, 124.16, 121.06, 84.12, 28.28; MS (EI) m/z (relative intensity): 207 ($M-CH_3$), 166 ($M-C_4H_8$, 59), 105 ($C_6H_5N_{21}$, 100), 78 ($C_5H_4N_1$, 20), 57 (C_4H_9, 78); MS (CI) m/z: 223 (M+H, base peak).

Allyl α-oximino-α-(4-pyridyl)acetate **25a/25s mixture**, pale yellow solid; TLC (EA:hex = 2:1), R_f 0.49 (anti), R_f 0.57 (syn); ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.92 (anti, 1H, brs), 12.67 (syn, 1H, brs), 8.67 (anti, 2H + syn 2H, m), 7.48 (syn, 2H, d, J=4.6 Hz), 7.42 (anti, 2H, d, J=4.5 Hz), 6.05-5.92 (anti, 1H + syn, 1H, m), 5.48-5.24 (anti, 2H + syn, 2H, m), 4.89 (syn, 2H, d, J=5.6 Hz), 4.75 (syn, 2H, d, J=5.5 Hz); MS (EI) m/z: 206 (M^+); MS (CI) m/z: 207 (M+H, base peak).

*General procedure[2] for the preparation of Methyl anti- or syn-carbonate **8a, 8s, 13a, 13s**.*

To a solution of pure α-*anti*- or α-*syn*-oximino-α-(2-pyridyl)acetate (**7a**, **7s**, **12a**, **12s**, 1.0 mmol) in 5.0 mL of dichloromethane was added triethylamine (2.0 mmol) and methyl chloroformate (1.05 mmol) at 25°C. After stirring 30 min, the resulting solution was added 5.0 mL of water and extracted with dichloromethane (5.0 mL x 3). The organic layer was dried over anhydrous sodium sulfate and concentrated to give methyl *anti*- or *syn*-oximino carbonate **8a**, **8s**, **13a**, **13s**.

Allyl α-*anti*-(methoxycarbonyl)oximino-α-(2-pyridyl)acetate **8a**, yield: 99%, colorless oil; TLC (EA:hex = 1:2), R_f 0.31; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (1H, d, J=4.6 Hz), 7.87 (2H, m), 7.44 (1H, m), 6.09-5.96 (1H, m), 5.45 (1H, d, J=17.2 Hz), 5.33 (1H, d, J=10.2 Hz), 4.89 (2H, d, J=5.7 Hz) 3.97 (3H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 162.34, 155.31, 153.47, 150.04, 147.25, 136.85, 131.24, 126.74, 125.59, 119.80, 67.57, 56.23; MS (CI) m/z: 265 (M+H, base peak).

Allyl α-*syn*-(methoxycarbonyl)oximino-α-(2-pyridyl)acetate **8s**, yield: quantitative, colorless oil; TLC (EA:hex = 1:2), R_f 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (1H, d, J=4.7 Hz), 8.14 (1H, d, J=7.9 Hz), 7.81 (1H, dd, J=6.0, 7.9 Hz), 7.42 (1H, m), 6.10-6.00 (1H, m), 5.50 (1H, d, J=17.2 Hz), 5.34 (1H, d, J=10.4 Hz), 4.97 (2H, d, J=5.3 Hz) 3.96 (3H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 161.08, 157.13, 153.32, 149.81, 148.53, 136.95, 131.03, 125.96, 122.17, 119.28, 66.81, 55.81; MS (EI) m/z (relative intensity): 264 (M^+, 1), 220 (M-CO_2, 3), 105 ($C_6H_5N_2$, 42), 78 ($C_5H_4N_1$, 100); MS (CI) m/z: 265 (M+H, base peak).

t-Butyl α-*anti*-(methoxycarbonyl)oximino-α-(2-pyridyl)acetate **13a**, yield: 93%, light green oil; TLC (EA:hex = 1:2), R_f 0.37; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (1H, d, J=4.7 Hz), 7.82 (2H, m), 7.40 (1H, m), 3.93 (3H, s), 1.59 (9H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 161.19, 156.10, 153.38, 149.64, 147.56, 136.44, 126.25, 125.02, 84.52, 55.74, 27.95; MS (CI) m/z: 281 (M+H, base peak).

t-Butyl α-*syn*-(methoxycarbonyl)oximino-α-(2-pyridyl)acetate **13s**, yield: quantitative, light green oil; TLC (EA:hex = 1:2), R_f 0.51; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (1H, d, J=4.6 Hz), 8.12 (1H, d, J=7.9 Hz), 7.79 (1H, m), 7.40 (1H, m), 3.97 (3H, s), 1.66 (9H, s); ^{13}H NMR (75 MHz, $CDCl_3$) δ 160.40, 157.62, 153.53, 149.81, 148.83, 136.72, 125.64, 122.19, 85.12, 55.60, 28.21; MS (EI) m/z (relative intensity): 265 (M-CH_8), 224 (M-C_4H_8, 27), 57 (C_4H_9, 100); MS (CI) m/z: 281 (M+H, base peak).

*General procedure for the preparation of trans-2-Methylcyclohexyl anti- or syn-carbonate **9a, 9s, 14a, 14s, 10a/10s**.*

A solution of *trans*-2-methylcyclohexanol (1.00 mmol), pyridine (1.33 mmol) and triphosgene (0.33 mmol) in 4.0 mL of dichloromethane was heated on an oil bath for 1.5 h at 50°C and cooled to 25°C. To this solution was added a solution of *anti*- or *syn*-oxime (**7a**, **7s**, **12a**, **12s**, **25a/25s**, 1.00 mmol) and trethylamine (2.00 mmol) in 3.0 mL of dichloromethane through cannula. This reaction mixture was stirred for 1.5 h at 25°C, quenched with 5.0 mL of water and extracted with dichloromethane (5.0 mL x 3). The combined organic layer was washed with water (5.0 mL x 2), dried over anhydrous sodium sulfate and concentrated to yield *trans*-2-methylcyclohexyl *anti*- or *syn*-carbonate **9a**, **9s**, **14a**, **14s**, **10a/10s**.

Allyl α-*anti*-[(*trans*-2-methylcyclohexyloxy)carbonyl]oximino-α-(2-pyridyl)acetate **9a**, yield: 97%, light purple oil; TLC (EA:hex = 1:2), R_f 0.50; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (1H, d, J=4.7 Hz), 7.90 (2H, m), 7.43 (1H, m), 6.09-5.99 (1H, m), 5.45 (1H, d, J=17.3 Hz), 5.32 (1H, d, J=10.4 Hz), 4.89 (2H, d, J=5.8 Hz), 4.45 (1H, m), 2.14 (1H, m), 1.84-1.04 (8H, m), 0.98 (3H, d, J=6.4 Hz); ^{13}H NMR (75 MHz, $CDCl_3$) δ 162.23, 154.67, 152.52, 149.67, 147.12, 136.61, 131.06, 126.53, 125.25, 119.30, 84.81, 67.11, 37.16, 33.37, 31.40, 25.06, 24.60, 18.28; MS (EI) m/z: 347 (M^++H); MS (CI) m/z: 347 (M+H, base peak).

Allyl α-*syn*-[(*trans*-2-methylcyclohexyloxy)carbonyl]oximino-α-(2-pyridyl)acetate **9s**, yield: quantitative, light purple oil; TLC (EA:hex = 1:2), R_f 0.53; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (1H, d, J=4.9 Hz), 8.15 (1H, d, J=7.9 Hz), 7.80 (1H, dd, J=7.8, 7.9 Hz), 7.41 (1H, m), 6.10-5.97 (1H, m), 5.50 (1H, d, J=17.2 Hz), 5.32 (1H, d, J=10.5 Hz), 4.98 (2H, d, J=5.2 Hz), 4.43 (1H, m), 2.16 (1H, m), 2.06-1.10 (8H, m), 1.00 (3H, d, J=6.7 Hz); ^{13}H NMR (75 MHz, CDCl$_3$) δ 161.25, 156.77, 152.64, 149.75, 149.18, 136.89, 131.13, 125.81, 122.14, 119.04, 84.64, 66.66, 37.24, 33.40, 31.43, 25.11, 24.64, 18.32; MS (EI) m/z: 347 (M$^+$+H); MS (CI) m/z: 347 (M+H, base peak).

t-Butyl α-*anti*-[(*trans*-2-methylcyclohexyloxy)carbonyl]oximino-α-(2-pyridyl)acetate **14a**, yield: 98%, light purple oil; TLC (EA:hex = 1:2), R$_f$ 0.57; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.72 (1H, d, J=4.7 Hz), 7.83 (2H, m), 7.39 (1H, m), 4.41 (1H, m), 2.15 (1H, m), 1.80-0.96 (8H, m), 1.59 (9H, s), 0.98 (3H, d, J=6.4 Hz); ^{13}H NMR (75 MHz, CDCl$_3$) δ 163.37, 155.70, 152.69, 149.57, 147.66, 136.45, 126.33, 124.94, 84.52, 84.28, 37.14, 33.36, 31.40, 27.94, 25.06, 24.59, 18.28; MS (ESI, positive): 363 [M+H]$^+$, 385 ([M+Na]$^+$, base peak); HRMS (ESI, positive): calcd. for $C_{19}H_{26}N_2O_5$ 363.1920, found 363.1917.

t-Butyl α-*syn*-[(*trans*-2-methylcyclohexyloxy)carbonyl]oximino-α-(2-pyridyl)acetate **14s**, yield: 98%, light purple oil; TLC (EA:hex = 1:2), R$_f$ 0.63; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.69 (1H, d, J=4.8 Hz), 8.13 (1H, d, J=8.0 Hz), 7.79 (1H, dd, J=7.7, 8.0 Hz), 7.40 (1H, m), 4.43 (1H, m), 2.17 (1H, m), 1.85-0.97 (8H, m), 1.67 (9H, s), 1.03 (3H, d, J=6.5 Hz); ^{13}H NMR (75 MHz, CDCl$_3$) δ 160.59, 157.50, 152.78, 149.77, 148.99, 136.66, 125.54, 122.11, 84.89, 84.22, 37.21, 33.34, 31.39, 28.21, 25.06, 24.59, 18.26; MS (ESI, positive): 363 [M+H]$^+$, 385 ([M+Na]$^+$, base peak); HRMS (ESI, positive): calcd. for $C_{19}H_{26}N_2O_5$ 363.1920, found 363.1913.

Allyl α-[(*trans*-2-methylcyclohexyloxy)carbonyl]oximino-α-(4-pyridyl)acetate **10a/10s mixture**, yield: 91%, pale yellow oil; TLC (EA:hex = 1:2), R$_f$ 0.40 (a/s); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.79-8.74 (anti, 2H + syn, 2H, m), 7.60 (2H, d, J=6.2 Hz), 7.38 (2H, d, J=6.1 Hz), 6.08-5.94 (anti, 1H + syn, 1H, m), 5.52-5.32 (anti, 2H, + syn, 2H, m), 4.95 (2H, d, J=5.8 Hz), 4,85 (2H, d, J=5.8 Hz), 4.48-4.37 (anti, 1H + syn, 1H, m), 2.17-0.93 (anti, 9H + syn, 9H, m), 1.00 (3H, d, J=6.4 Hz), 0.94 (3H, d, J=6.4 Hz); MS (EI) m/z: 347 (M$^+$+H); MS (CI) m/z: 347 (M+H, base peak).

General procedure[3] *for the preparation of (S)*-α-*Methylbenzyl anti- or syn-carbamate* ***15a, 15s****.*

A mixture solution of *anti*- or *syn*-oxime (**7a** or **7s**, 1.00 mmol), (S)-(-)-α-methylbenzyl isocyanate (1.10 mmol) and triethylamine (2.05 mmol) in 5.0 mL of dichloromethane was heated on an oil bath for 10 h at 50°C. The resulting solution was combined with 10 mL of water and extracted dichloromethane (15 mL x 2). The organic layer was dried over anhydrous sodium sulfate and concentrated through a rotary evaporator. Purification by flash column chromatography (25% EtOAc/hexane) provided carbamate **15a**, **15s**.

t-Butyl α-*anti*-{[(S)-α-methylbenzyl]carbamoyl}oximino-α-(2-pyridyl)acetate **15a**, yield: quantitative, white solid; mp 152-154°C; TLC (EA:hex = 1:2), R$_f$ 0.31; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.73 (1H, d, J=4.2 Hz), 7.97 (1H, d, J=8.1 Hz), 7.86 (1H, dd, J=7.8, 7.9 Hz), 7.41-7.30 (6H, m), 6.72 (1H, br-d, J=7.2 Hz), 5.04 (1H, m), 1.65 (3H, d, J=6.7 Hz), 1.59 (9H, s); ^{13}H NMR (75 MHz, CDCl$_3$) δ 161.43, 153.29, 149.69, 147.53, 145.76, 136.85, 129.00, 127.86, 127.02, 126.33, 125.30, 124.08, 84.59, 51.36, 28.20, 22.31; MS (EI) m/z: 369 (M$^+$); MS (CI) m/z: 370 (M+H); MS (ESI, positive): 392 ([M+Na]$^+$, base peak).

t-Butyl α-*syn*-{[(S)-α-methylbenzyl]carbamoyl}oximino-α-(2-pyridyl)acetate **15s**, yield: 99%, light yellow oil; TLC (EA:hex = 1:2), R$_f$ 0.43; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.70 (1H, d, J=4.7 Hz), 7.97 (1H, d, J=7.7 Hz), 7.81 (1H, dd, J=7.7, 7.9 Hz), 7.44-7.30 (6H, m), 6.19 (1H, br-d, J=6.7 Hz), 5.06 (1H, m), 1.67 (9H, s), 1.64 (3H, d, J=7.0 Hz); ^{13}H NMR (75 MHz, CDCl$_3$) δ 161.25, 153.11, 149.93, 147.23, 145.55, 142.87, 137.27, 129.00, 127.85, 126.41, 125.82, 122.16, 85.47, 51.32, 28.49, 22.18; MS (EI) m/z (relative intensity): 369 (M$^+$), 105 ($C_6H_5N_2$, 51), 57 (C_4H_9, 100); MS (CI) m/z: 370 (M+H); MS (ESI, positive): 370 [M+H]$^+$, 392 ([M+Na]$^+$, base peak).

α-*Oximino*-α-*(2-pyridyl)acetic acid* ***19a/19s****.*

A solution of t-butyl α-oximino-α-(2-pyridyl)acetate **12a/12s** (0.10 g, 0.45 mmol) and trifluoroacetic acid (0.35 mL, 4.50 mmol) in 5.0 mL of dichloromethane was stirred 16 h at 25°C. The resulting solution was concentrated to one-third volume and treated with hexane. The triturated solid was collected by decantation, washing with hexane, to give the desired oximino-acids **19a/19s**, yield: quantitative, light yellow solid; TLC (EA:hex = 2:1), origin spot; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.69 (1H, d, J=4.1 Hz), 8.59 (1H, d, J=4.4 Hz), 8.01-7.73 (anti, 2H + syn, 2H, m), 7.53-7.43 (anti, 1H + syn, 1H, m); MS (ESI, positive): 167 $[M+H]^+$; HRMS (ESI, positive): calcd. for $C_7H_6N_2O_3$ 167.0457, found 167.0455.

General procedure for the preparation of acid-catalyzed deprotected acid ***16s, 17s, 18s****.*

A solution of the t-butyl ester of α-*syn*-oxime derivative (**13s**, **14s**, **15s**, 0.2 mmol) and trifluoroacetic acid (2.0 mmol) in 2.0 mL of dichloromethane was stirred for 6 ~ 48 h at 25°C. The resulting solution was concentrated to half volume and triturated with diethyl ether/hexane to give **16s**, **17s**, and with MeOH/ether/hexane to give **18s**.

α-*syn*-(Methoxycarbonyl)oximino-α-(2-pyridyl)acetic acid **16s**, yield: 99%, white solid; mp 42°C (softens), 88-90°C (dec.); TLC (EA:hex = 1:2), origin spot; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.73 (1H, d, J=4.6 Hz), 8.03-8.01 (2H, m), 7.65 (1H, dd, J=4.4, 4.8 Hz), 3.91 (3H, s); MS (ESI, positive): 225 $[M+H]^+$.

α-*syn*-[(*trans*-2-Methylcyclohexyloxy)carbonyl]oximino-α-(2-pyridyl)acetic acid **17s**, yield: 88%, white solid; mp 87°C (dec.); TLC (EA:hex = 1:2), origin spot; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.71 (1H, d, J=3.5 Hz), 8.00 (2H, m), 7.61 (1H, m), 4.36 (1H, m), 2.02 (1H, m), 1.76-1.09 (8H, m), 0.93 (3H, d, J=5.9 Hz); MS (ESI, positive): 307 ($[M+H]^+$, base peak), 329 $[M+Na]^+$.

α-*syn*-{[(S)-α-Methylbenzyl]carbamoyl}oximino-α-(2-pyridyl)acetic acid **18s**, yield: 80%, white solid; mp 88°C (dec.); TLC (EA:hex = 1:2), origin spot; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.70 (1H, d, J=4.4 Hz), 8.32 (1H, d, J=7.9 Hz), 8.14 (1H, d, J=7.8 Hz), 7.99 (1H, m), 7.60-7.25 (5H, m), 4.82 (1H, m), 1.48 (3H, d, J=7.0 Hz); MS (ESI, positive): 337 $[M+H+Na]^+$.

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