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ONE-POT PREPARATION OF ETHYL 2(*Z*)-4-(ANILINOXY)-PENTENOATE BY α-AMINOXYLATION OF PROPANAL FOLLOWED BY *Z*-SELECTIVE HWE REACTION AND THE STUDY ON ITS CYCLIZATION REACTION

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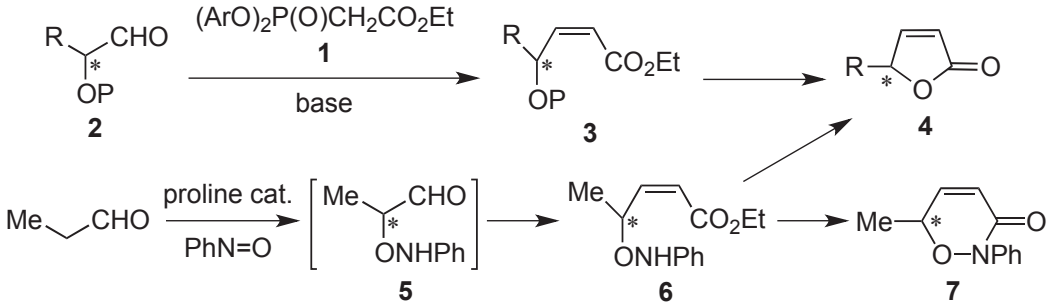
† Dedicated to Professor Kiyoshi Tomioka on the occasion of his 70th birthday

Abstract – A one-pot sequence of α-aminoxylation of *n*-propanal catalyzed by L-proline followed by the *Z*-selective Horner-Wadsworth-Emmons reaction was developed. The highly functionalized chiral γ-anilinoxy-*Z*-α,β-unsaturated ester **6** was obtained in 57-58% yield with 98:2 *Z*-selectivity from *n*-propanal in one-pot procedure. The transformation of the anilinoxy group of **6** into a hydroxyl group can be carried out by treatment with catalytic amount of $CuSO_4$ in methanol to give either the corresponding alcohol **8** or chiral γ-valerolactone **4a** in moderate yield. Chiral 6-methyl-2-phenyl-2*H*-1,2-oxazin-3(6*H*)-one **7** was obtained in 75% yield from **6** by treatment with CSA.

The Horner-Wadsworth-Emmons (HWE) reaction is a widely used method for the preparation of α,β-unsaturated esters.[1] Generally, it gives more stable *E*-olefins selectively. In order to prepare *Z*-olefins, Still and Gennari invented bis(trifluoroethyl)phosphonate reagents[2] and we invented diarylphosphonate reagents **1**.[3] These reagents were successfully applied for the syntheses of many bioactive compounds.[4] As an application of our *Z*-selective HWE reagents, we planned the concise synthesis of the chiral α,β-unsaturated γ-lactones **4**[5] using *Z*-selective HWE reaction of α-oxyaldehydes **2** and the following cyclization (Scheme 1).[6] The chiral γ-lactone moieties are not only found in many bioactive compounds such as acaterin and incrustoporine, but also used as useful chiral building blocks.



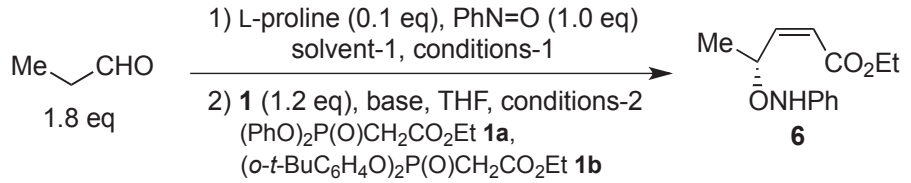
Scheme 1

Chiral α-hydroxy carbonyl compounds are useful intermediates in organic synthesis. Highly enantioselective α-aminoxylation of aldehydes catalyzed by proline has been reported by MacMillan,[7a] Hayashi,[7b] and Zhong[7c] almost simultaneously. Since proline is commercially available in both enantiopure forms, the proline-catalyzed α-aminoxylation with nitrosobenzene will give α-anilinoxy aldehyde **5** in either *R* or *S* form with high optical purity. Although the α-anilinoxy aldehydes could not be isolated in good yields, they were converted to the corresponding α-anilinoxy alcohols by one-pot reduction with $NaBH_4$ in good yields. In addition, the product aldehydes have been utilized in the subsequent HWE reaction to afford γ-anilinoxy-*E*-α,β-unsaturated carbonyl compounds by one-pot procedure without loss of enantiopurity.[8] In these studies, the transformation of the anilinoxy moiety into a hydroxyl group can be carried out by either treatment with $CuSO_4$[9] or hydrogenolysis (H_2, Pd/C). Therefore, we planned the enantioselective synthesis of the angelica lactone **4a** (R = Me)[5a] via **6** prepared by α-aminoxylation of *n*-propanal and the following *Z*-selective HWE reaction using one-pot procedure. Although the N-O bond cleavage of **6** by copper salts was not efficient and **4a** was obtained in moderate yield, chiral 6-methyl-2-phenyl-2*H*-1,2-oxazin-3(6*H*)-one **7** was obtained in good yield (75%). Here we would like to describe our results.

For the α-aminoxylation reaction of *n*-propanal, MacMillan performed the reaction in $CHCl_3$ at 4 °C for 4 h (88% yield, 97% ee), Hayashi performed the reaction in MeCN at -20 °C for 24 h (quant., 98% ee), and Zhong performed the reaction in DMSO at room temperature for 10-20 min (60% yield, 97% ee). When 1.2 equiv of *n*-propanal was treated with nitrosobenzene (1.0 equiv) and L-proline (0.3 equiv) in DMSO at room temperature[7c] for 30 min, the color of the solution changed from emerald green to yellow. At this point, premixed MeCN solution of **1a** (1.0 equiv) with NaI (1.6 equiv) and DBU (1.6 equiv)[3e] was added to the above solution at 0 °C and stirring was continued for 1 h at this temperature. After work up, the α,β-unsaturated ester **6** was obtained in only 14% isolated yield with *Z*:*E* = 78:22 selectivity (entry 1 in Table 1). The α-anilinoxy aldehyde **5** seemed to be unstable at room temperature under the reaction conditions to give **6** in low yield. When the α-aminoxylation reaction was performed in MeCN at 4 °C

followed by the *Z*-selective HWE reaction in the same solvent at -40 to 0 °C, **6** was obtained in 45% yield with disappointing *Z*-selectivity (*Z*:*E* = 66:34) (entry 2). Changing the solvent for the HWE reaction to THF provided 75:25 *Z*-selectivity and 50% yield (entry 3). The selectivity did not much improved even when the HWE reaction was performed at -78 to 0 °C (entry 4). Use of $CHCl_3$ as solvent for the α-aminoxylation decreased the selectivity of the HWE reaction to 68:32 (entry 5). Since the HWE reaction of **1a** with **2** (R = Me, P = *t*-$BuMe_2Si$) in THF gave 97:3 *Z*-selectivity,[3b] this low selectivity for the HWE reactions in entries 1-5 could be derived from some interaction between the sodium enolate derived from **1a** and the anilinoxyl group of **5**. In our former study, we found that ortho-substituted phenyl reagents **1** (Ar = *o*-RC_6H_4, R = Me, *i*-Pr) showed higher *Z*-selectivity.[3b] After that, Touchard et al. developed **1b** (Ar = *o*-*t*-BuC_6H_4) as the *Z*-selective HWE reagent at room temperature.[10] The *Z*-selectivity of the HWE reaction was dramatically improved to 99:1 by using the reagent **1b** and the yield was 57% (entry 6). Even when the HWE reaction was performed at 0 °C, 97:3 selectivity was obtained in lower 45% yield (entry 7). When the α-aminoxylation reaction was performed at 0 °C and the

Table 1. One-pot α-aminoxylation reaction followed by HWE reaction with **1**



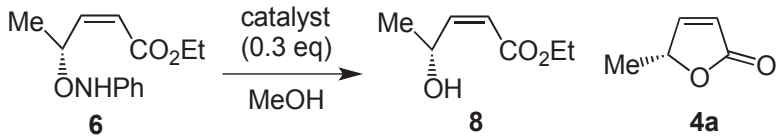
entry	**1**	solvent-1	conditions-1	base[a]	conditions-2	yield[b]	*Z*:*E*
1	**1a**	DMSO	rt, 30 min[c]	NaI, DBU	0 °C, 1 h[d]	14	78:22
2	**1a**	MeCN	4 °C, 1 h	NaI, DBU	-40 to 0 °C[d,e]	45	66:34
3	**1a**	MeCN	4 °C, 1 h	NaI, DBU	-40 to 0 °C[e]	50	76:24
4	**1a**	MeCN	4 °C, 1 h	NaI, DBU	-78 to 0 °C[e]	18	76:24
5	**1a**	$CHCl_3$	4 °C, 1 h	NaI, DBU	-78 to 0 °C[e]	41	68:32
6	**1b**	MeCN	4 °C, 40 min	NaI, DBU	-40 to 0 °C[e]	57	99:1
7	**1b**	MeCN	4 °C, 50 min	NaI, DBU	0 °C, 1 h	45	97:3
8	**1b**	MeCN	0 °C, 30 min	NaI, DBU	-20 to 0 °C[f]	58	99:1
9	**1b**	MeCN	0 °C, 30 min	NaI, DBU	-20 to 0 °C[e]	45	>99:1
10	**1b**	MeCN	0 °C, 40 min	NaH	-20 to 0 °C[f]	57	98:2
11	**1b**	MeCN	0 °C, 40 min	NaH	-20 to 0 °C[f,g]	58	98:2

a: Either 1.6 eq of NaI-DBU or 1.3 eq of NaH was used. b: Isolated yield. c: 0.4 eq of L-proline and 1.2 eq of propanal were used. d: MeCN was used instead of THF. e: Warmed over 1 h. f: After the mixture was kept at -20 °C for 1 h, it was warmed to 0 °C over 0.5 h. g: Reverse addition.

following HWE reaction was performed at -20 °C for 1 h and then warmed to 0 °C, 58% yield of **6** was obtained with 99:1 *Z*-selectivity (entry 8). When the HWE mixture was immediately warmed to 0 °C after the addition of **1b** and NaI-DBU at -20 °C, the yield of **6** decreased to 45% with higher *Z*-selectivity (>99:1) (entry 9). Unfortunately, the HWE reaction mixture sometimes set to gel under the reaction conditions of entries 6-9 and the reaction did not go to completion when gelation took place. When NaH was used as base instead of NaI-DBU, 57% yield of **6** was obtained with 98:2 selectivity reproducibly (entry 10). The inverse addition, that is, the addition of the aminoxylation reaction mixture to the solution of **1b** and NaH in THF provided almost the same result (58% yield of **6** with 98:2 *Z*-selectivity) (entry 11). Thus, the reaction can be best performed under the reaction conditions of either entry 10 or 11.

We next tried to transform the obtained HWE product **6** to **4a**[5a] (R = Me). When **6** was treated with 0.3 equiv of $CuSO_4$ in MeOH for 3 h, the corresponding alcohol **8** was obtained in 53% yield along with **4a** (3%), *Z*-γ-methoxy-α,β-unsaturated ethyl ester **9** (24%), and *E*-**6** (1%) (entry 1 in Table 2). During the silica gel column chromatography, the alcohol **8** gradually cyclized to **4a**. Therefore, we could not isolate **8** as pure form. The same reaction at 0 °C gave **8**, **4a**, **9**, and *E*-**6** in 51%, 10%, 27%, and 2% yields, respectively (entry 2). Since Momiyama and Yamamoto reported that the cleavage of the N-O bond in α-anilinoxy ketone with $CuSO_4$ afforded α-hydroxy ketone without loss of enantioselectivity,[9] we were surprised to know the formation of **9**, which seemed to form by S_N2 reaction with MeOH as the nucleophile and anilinoxy group as the leaving group. In order to test the effect of water, the reaction was conducted in the presence of 1.5 equiv of H_2O for 24 h. The alcohol **8** was obtained in 39% yield along with **4a** (30%), **9** (17%), and *E*-**6** (4%) (entry 3). The reaction was at least not much accelerated by water and the alcohol **8** was gradually transformed to the lactone **4a**. When the reaction was conducted in THF, **8** was obtained in 56% yield along with **4a** (3%), **6** (3%), and *E*-**6** (22%) (entry 4). Large quantity of isomerization of *Z*-α,β-unsaturated ester **6** to *E*-**6** occurred in the presence of $CuSO_4$ in THF. Use of $Cu(OAc)_2$ as catalyst instead of $CuSO_4$ not only increased the yield of **4a** to 25% after 8 h and 41% after 26 h, but also caused the formation of the enoate **10**[11] (entries 5 and 6). We further attempted the synthesis of **4a** by one-pot deamination and cyclization reaction of **6** by treating with $CuSO_4$ (0.3 equiv) and 10-camphorsulfonic acid (CSA) (0.3 equiv). Although **4a** was obtained in highest 46% yield, the yield of **9** also increased to 32% and a new compound, 6-methyl-2-phenyl-2*H*-1,2-oxazin-3(6*H*)-one **7** was obtained in 17% yield from direct cyclization of **6** (entry 7). When **6** was treated with CSA in methanol at room temperature, the yield of **7** increased to 75% along with small quantity of **4a** (entry 8). The same reaction in THF gave **7** in 64% yield along with **4a** (9%) (entry 9).

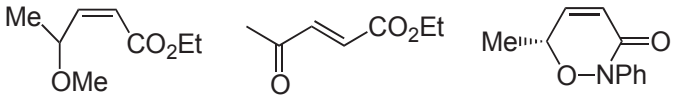
Table 2. The deamination and cyclization reactions of **6**[a]



6 **8** **4a**

entry	catalyst	solvent	conditions	**8**	**4a**	**9**	*E*-**6**	**10**	**7**
1	$CuSO_4$	MeOH	rt, 3 h	53	3	24	2	trace	-
2	$CuSO_4$	MeOH	0 °C, 21 h	51	10	27	2	5	-
3	$CuSO_4$, H_2O[b]	MeOH	rt, 24 h	39	30	17	4	trace	-
4	$CuSO_4$	THF	rt, 18 h	56	3	-	22	-	-
5	$Cu(OAc)_2$	MeOH	rt, 8 h	36	25	-	13	25	-
6	$Cu(OAc)_2$	MeOH	rt, 26 h	-	41	2	7	19	-
7	$CuSO_4$, CSA	MeOH	rt, 15 h	-	46	32	1	-	17
8	CSA	MeOH	rt, 15 h	-	3	-	1	-	75
9	CSA	THF	rt, 1.5 h	-	9	-	1	-	64

a: The yield was calculated by ^{1}H NMR using methyl benzoate as a standard material.
b: 1.5 eq of H_2O was added.



9 **10** **7**

In summary, we have developed a one-pot sequence of α-aminoxylation of propanal followed by *Z*-selective HWE reaction. The highly functionalized chiral γ-anilinoxy-*Z*-α,β-unsaturated ester **6** was obtained in 57-58% yield with 98:2 *Z*-selectivity from a simple aldehyde in one-pot procedure. The transformation of the anilinoxy group of **6** into a hydroxyl group can be carried out by treatment with catalytic amount of $CuSO_4$ in MeOH to give the alcohol **8** in 52% yield. Chiral γ-valerolactone **4a** was also obtained by the treatment with $CuSO_4$ and CSA in 46% yield. Chiral 6-methyl-2-phenyl-2*H*-1,2-oxazin-3(6*H*)-one **7** was obtained in 75% yield from **6** by treatment with CSA. The [1,2]-oxazinones are useful synthetic intermediates and can be transformed to the core structure of FR900482, which is a promising cancer chemotherapeutic reagent.[12] Thus, the one-pot sequence of α-aminoxylation of aldehydes catalyzed by L-proline followed by the *Z*-selective Horner-Wadsworth-Emmons reaction offers a quick access to both chiral γ-lactones such as **4a** and the chiral [1,2]-oxazinones such as **7**.

EXPERIMENTAL

Commercially available reagents were used without purification. THF (tetrahydrofuran) and MeOH were dried using Molecular Sieves 4A and 3A, respectively. All reactions in dry solvents were carried out under argon atmosphere. Silica gel column chromatography was carried out using Kanto silica gel 60N (spherical, neutral, 63–210 μm). The ^{1}H NMR and ^{13}C spectra (400 and 100 MHz) were recorded on a JEOL α-400 in $CDCl_3$ using tetramethylsilane as an internal standard. High-resolution mass spectra were recorded on a Waters Xevo Q-Tof mass spectrometer (ESI) or a JEOL AccuTof DART mass spectrometer (DART).

Typical procedure for the one-pot α-aminoxylation reaction followed by the HWE reaction with 1 (entry 10 in Table 1): To a MeCN solution (2 mL) of nitrosobenzene (0.321 g, 3.0 mmol) and L-proline (34.5 mg, 0.30 mmol) was added *n*-propanal (0.388 mL, 5.4 mmol) at 0 °C. The color of the solution changed from emerald green to yellow after 40 min and the solution was immediately cooled to -20 °C (solution A). A THF solution (8 mL) of **1b** (1.557 g, 3.3 mmol) was treated with 60% NaH (0.156 g, 3.9 mmol) at 0 °C for 10 min and the resulting mixture was added to solution A and the resulting mixture was stirred for 1 h at -20 °C. After the reaction mixture was allowed to warm to 0 °C over 0.5 h, the reaction was quenched with aqueous NH_4Cl, and the mixture was extracted with AcOEt (10 mL x 2). The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. Column chromatography (silica gel; hexane:AcOEt = 15:1) provided **6** (0.401 g, 57%) as a yellow oil (*Z*:*E* = 98:2). $[\alpha]^{25}_D$ +6.8° (c 1.13, $CHCl_3$), *Z*-isomer: ^{1}H NMR δ 1.27 (3H, t, *J* = 7.4 Hz), 1.40 (3H, d, *J* = 6.8 Hz), 4.15 (2H, q, *J* = 7.4 Hz), 5.47-5.56 (1H, m), 5.85 (1H, dd, *J* = 11.7, 1.4 Hz), 6.36 (1H, dd, *J* = 11.7, 7.8 Hz), 6.90-6.98 (4H, m), 7.22-7.29 (2H, m). ^{13}C NMR δ 14.2, 18.5, 60.2, 76.6, 114.2, 120.4, 121.9, 129.1, 148.7, 150.9, 165.7. HRMS (EI): *m/z* calcd for $C_{13}H_{17}NO_3^+$ (M^+) 235.1208, found 235.1190. *E*-isomer: ^{1}H NMR δ 1.31 (3H, t, *J* = 7.2 Hz), 1.42 (3H, d, *J* = 6.6 Hz), 4.22 (2H, q, *J* = 7.2 Hz), 5.49-5.57 (1H, m), 6.04 (1H, dd, *J* = 15.9, 1.2 Hz), 6.99 (1H, dd, *J* = 15.9, 6.4 Hz), 6.90-7.00 (4H, m), 7.24-7.30 (2H, m).

Treatment of 6 with $CuSO_4$ (entry 1 in Table 2): To a MeOH solution (3.0 mL) of **6** (0.072 g, 0.30 mmol) was added $CuSO_4$ (0.015 g, 0.09 mmol) and the resulting mixture was stirred for 3 h. The reaction was quenched with brine and the mixture was extracted with AcOEt (8 mL x 2). The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. From the ^{1}H NMR of the crude mixture, the yields of **8** (53%), **4a** (3%), **9** (24%), and *E*-**6** (2%) were calculated by using methyl benzoate as a standard material. Column chromatography (silica gel; hexane:AcOEt = 3:1) provided **8** (0.015 g, 35%) along with **4a** (0.006 g, 21%) as a pale yellow oil. **8**: ^{1}H NMR δ 1.30 (3H, t, *J* = 7.1 Hz), 1.34 (3H, d, *J* = 6.4 Hz), 3.38 (1H, brs), 4.20 (2H, q, *J* = 7.1 Hz), 5.05 (1H, quin, *J* = 6.4 Hz), 5.81 (1H, dd, *J* = 11.9, 1.4 Hz), 6.29 (1H, dd, *J* = 11.9, 6.7 Hz). **4a**[5a]: ^{1}H NMR δ 1.46 (3H, d, *J* = 6.9 Hz), 5.15 (1H, qdd, *J* = 6.9, 1.8, 1.4 Hz), 6.10 (1H, dd, *J* = 5.7, 1.8 Hz), 7.46 (1H, dd, *J* = 5.7, 1.4 Hz). ^{13}C NMR δ 18.8, 79.6,

121.3, 157.3, 173.1.

Cyclization reaction of 6 (entry 7 in Table 2): To a THF solution (1.0 mL) of **6** (0.120 g, 0.50 mmol) was added 10-camphorsulfonic acid (0.012 g, 0.05 mmol) and the resulting mixture was stirred for 30 h. The reaction was quenched with aqueous $NaHCO_3$, and the mixture was extracted with AcOEt (8 mL x 2). The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. Column chromatography (silica gel; hexane:AcOEt = 3:1) provided **7** (0.061 g, 64%) as a pale brown oil. $[\alpha]^{25}_D$ +6.0° (c 1.00, $CHCl_3$), ^{1}H NMR δ 1.49 (3H, d, *J* = 6.8 Hz), 4.89-4.96 (1H, m), 6.10 (1H, dd, *J* = 10.0, 2.0, Hz), 6.67 (1H, dd, *J* = 10.0, 2.7 Hz), 7.18 (1H, t, *J* = 7.6 Hz), 7.38 (2H, dd, *J* = 8.6, 7.6 Hz), 7.68 (2H, d, *J* = 8.6 Hz). ^{13}C NMR δ 17.2, 74.1, 120.1, 123.1, 125.4, 128.6, 139.4, 143.7, 161.7. HRMS (EI): *m/z* calcd for $C_{11}H_{11}NO_2^+$ (M^+) 189.0790, found 189.0786.

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