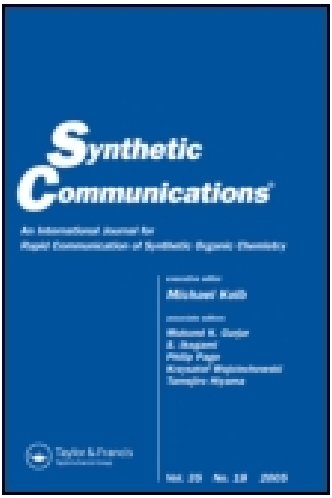

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Direct Formation of 2,3,5-Trichloropyridine and its Nucleophilic Displacement Reactions in Ionic Liquid

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ABSTRACT

Reaction of trichloroacetaldehyde and acrylonitrile in the presence of a catalytic amount of copper (I) chloride in ionic liquid afforded 2,3,5-trichloropyridine, fluorination of which with KF and CsF in ionic liquid afforded 3,5-dichloro-2-fluoropyridine and 5-chloro-2,3-dichloropyridine. Reaction of 2,3,5-trichloropyridine, 3,5-dichloro-2-fluoropyridine, or 5-chloro-2,3-dichloropyride with 2-(4-hydroxyphenoxy)propionates in ionic liquid afforded the corresponding 2-aryloxylpropionates in good yields.

Key Words: Trichloroacetaldehyde; Acrylonitrile; 2,3,5-Trichloropyridine; Ionic liquid; Nucleophilic displacement reactions.

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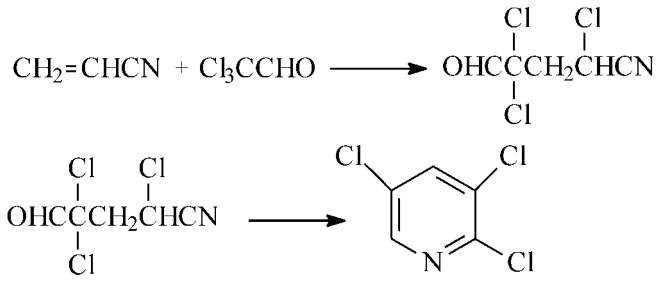
2,3,5-Trichloropyridine can be used as an intermediate for the production of herbicidal active substances.[1,2] Proposed processes for its production have been widely diverse and have included both the selection chlorination of intermediate compounds, the selective dechlorination of higher chlorinated pyridines, and other routes. For example, 2,3,5-trichloropyridine can be prepared by the vapor phase chlorination of 3,5-dichloropyridine.[3] It can also be prepared by reacting 3,5-dichloro-2-pyridone at 75–80°C with phosgene in the presence of a dimethyl formamide (DMF).[4] 2,3,5-Trichloropyridine can also be prepared by reacting 2,3,4,5-tetrachloropyridine using zinc dust in an alkanephosphonic acid dialkyl ester[5] or by the directly reacting pentachloropyridine or 2,3,5,6-tetrachloropyridine with metallic zinc in the presence of a strongly alkaline aqueous solution and a water-immiscible reaction medium[6] and so on.[7,8] But the Lewis acid catalyzed addition of trichloroacetaldehyde to acrylonitrile is the most notable and well-known method for the large-scale production of this compound.[9]

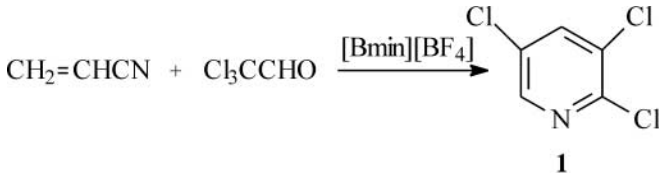
The mechanism of this reaction has been studied, and a two-step reaction has been proposed. 2,4,4-Trichloro-4-formylbutyronitrile is produced by the addition of trichloroacetaldehyde to acrylonitrile under nitrogen atmosphere. The cyclization of 2,4,4-trichloro-4-formylbutyronitrile in the presence of dry HCl or Lewis acid has afforded 2,3,5-trichloropyridine (Scheme 1).

However, those reported methods included some unsatisfied conditions, such as long time, high temperature, and pressure. Recently, we found that the usage of the room temperature ionic liquids as solvent with a catalytic amount of Lewis acid in one step directly synthesized 2,3,5-trichloropyridine **1** and accelerated the formation of **1** remarkably, including being environmentally more benign, and having generality, simplicity of the methodology, ease of product isolation, higher yield, and potential for recycling ionic liquids (Scheme 2).

Room-temperature ionic liquids[10] such as [Bmim][BF_4] are finding growth in applications as alternative reaction media for organic transformations.



Scheme 1.



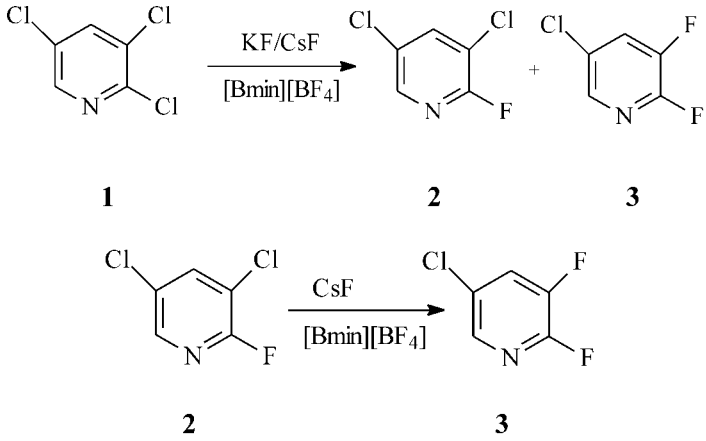
1

Scheme 2.

Recent examples of such organic transformations include Diels–Alder reactions,[11] Friedel–Crafts reactions,[12] Heck reactions,[13] nucleophilic substitution,[14] and so on.

Generally, the fluoropyridines were prepared in dimethyl sulfoxide or dimethyl sulfone by the action of anhydrous potassium fluoride, usually 2 moles of potassium fluoride for each atom of halogen to be replaced, on the appropriate halopyridine.[15] But, the nucleophilic displacement reactions of heterocyclic compounds in ionic liquids have not been reported. It was found that 3,5-dichloro-2-fluoropyridine **2** and 5-chloro-2,3-difluoropyridine **3** can be prepared by 2,3,5-trichloropyridine **1** with an effective amount of KF or CsF in an ionic liquid, such as [Bmim][BF_4], at an elevated temperature under substantially anhydrous conditions with removal of the difluoropyridine product essentially as it is formed. 5-Chloro-2,3-difluoropyridine **3** is also prepared by fluorinating 3,5-dichloro-2-fluoropyridine **2** under favorable conditions (Scheme 3).

Reaction of 2,3,5-trichloropyridine **1**, 3,5-dichloro-2-fluoropyridine **2**, or 5-chloro-2,3-difluoropyridine **3** with 2-(4-hydroxyphenoxy)-propionates **4**



Scheme 3.

and K_2CO_3 in [Bmim][BF_4] afforded 2-[4-(3,5-dichloropyridin-2-yloxy)-phenoxy]-propionates, 2-[4-(5-chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionates **5** (Scheme 4, Table 1).

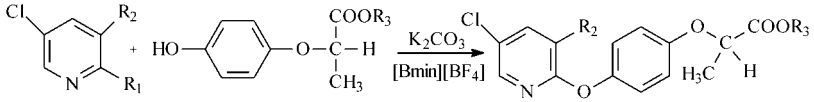
Under basic conditions, hydrolysis of **5** gave their acids. For example, 2-[4-(5-chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionic acid **6** could be given from 2-[4-(5-chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionates **5d** (Scheme 5).

EXPERIMENTAL

Melting points are uncorrected. Thin-layer chromatography (TLC) was performed using precoated silica gel 60 GF_{254} (0.25 mm), column chromatography was performed using silica gel (100–200 mesh), infrared (IR) spectra were recorded on a Bruker VECTOR55 instrument, and ^1H NMR and ^{13}C NMR spectra were recorded on a FT-Bruker AT-300 instrument using tetramethylsilane (TMS) as an internal standard. MS spectra were recorded on a Finnigan DECAX-30000 LCQ DecaXP plus instrument. 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) and 2-(4-hydroxy-phenoxy)-propionates **4** were prepared according to the procedures reported.[16,17]

Synthesis of 1-Butyl-3-Methylimidazoliumtetrafluoroborate ([Bmim]BF_4)

A mixture of *n*-Butyl chloride (0.4 mol), *N*-methylimidazole (0.4 mol) and toluene (100 mL) was stirred at refluxing temperature for 1 or 2 days under nitrogen. The mixture was cooled to ice temperature, and then the mixture appeared in two layers, spilling out the topper, and acetone (50 mL) was added causing precipitation of 1-butyl-3-methyl imidazolium halide salt



4 **5**

Scheme 4. R_1 = Cl, or F; **5a**: R_2 = Cl, $R_3 = C_2H_5$; **5b**: R_2 = F, $R_3 = C_2H_5$; **5c**: R_2 = Cl, $R_3 = CH_3$; **5d**: R_2 = F, $R_3 = CH_3$; **5e**: R_2 = Cl, $R_3 = CH_2C_6H_5$; **5f**: R_2 = Cl, $R_3 = CH_2COC_6H_5$; **5g**: R_2 = Cl, $R_3 = CH_2CO_2C_2H_5$; **5h**: R_2 = Cl, $R_3 = CH_2$ C≡CH.

Table 1. Reaction of 1, 2, or 3 with 2-(4-hydroxyphenolic) propionates.

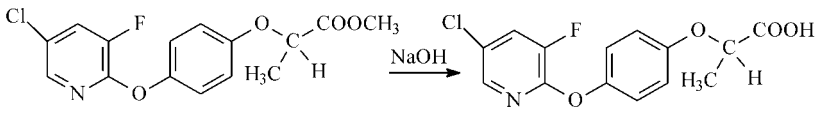
Entry	R_1	R_2	R_3	Product	Yield (%)
1	Cl	Cl	C_2H_5	**5a**	75
2	F	Cl	C_2H_5	**5a**	82
3	F	F	C_2H_5	**5b**	81
4	Cl	Cl	CH_3	**5c**	77
5	F	Cl	CH_3	**5c**	85
6	F	F	CH_3	**5d**	80
7*	F	F	CH_3	**5d**	70
8	Cl	Cl	$CH_2C_6H_5$	**5e**	76
9	Cl	Cl	$CH_2COC_6H_5$	**5f**	75
10	Cl	Cl	$CH_2CO_2C_2H_5$	**5g**	77
11	Cl	Cl	$CH_2C{\equiv}CH_2$	**5h**	75

*Without ionic liquids.

as a white solid. This solid was recovered by filtration and washed with ethyl ether. To prepare the tetrafluoroborate salts, the 1-butyl-3-methyl imidazolium halide salt (0.32 mol) was added to a suspension of $NaBF_4$ (1.2 equiv.) in acetone (150 mL) with a mechanical stirrer. After the mixture was stirred for 48 h at room temperature, the sodium halide precipitate was removed by filtration, and the filtrate was concentrated to oil by rotary evaporation. This oil still contained some 1-butyl-3-methyl imidazolium halide, because it gave a precipitate when mixed with aqueous silver nitrate.

Synthesis of 2,3,5-Trichloropyridine 1

A one-neck reaction flask was charged with $[Bmim]BF_4$ (5 mL), trichloroacetaldehyde (14.7 g, 0.1 mol), acrylonitrile (5.3 g, 0.1 mol), copper(I) chloride (0.5 g, 0.005 mol), and acetonitrile (20 ml). Heated at 120°C with a stirrer, the reaction was monitored by TLC until consumption of the material. After completion of the reaction, the combined reaction mixture was



5d **6**

Scheme 5.

concentrated in vacuo, then distilled with steam, in the process of which the 2,3,5-trichloropyridine was given. The yield is 7.48 g (41% of theory).

2,3,5-Trichloropyridine (1): A white solid. m.p. 49–50°C (lit.[11]: 49–50°C). ^{1}H NMR: $\delta = 8.30$ (*d*, $J = 2.0$ Hz, 1H), 7.82 (*d*, $J = 2.0$ Hz, 1H); ^{13}C NMR: $\delta = 147.3$ (1C), 145.9 (1C), 138.1 (2C), 130.8 (1C). MS $m/z = 182.2$. IR (ν_{max}, KBr): 3040, 1560, 1230, 1120, 1030 cm^{-1}.

Synthesis of 3,5-Dichloro-2-Fluoropyridine 2 and 5-Chloro-2,3-Difluoropyridine 3

In a 100 ml flask was placed 2,3,5-trichloropyridine **1** (10.95 g, 0.06 mmol), KF (6.97 g, 0.12 mol), CsF (3.04 g, 0.02 mol), 0.5 g K_2CO_3, and 40 mL [Bmim]BF_4. The stirred mixture was heated to 200°C for 10 h. The product was extracted with Et_2O (3 × 25 ml) after the reaction was completed. The combined ethereal phases were evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel and elution with 5 : 1 petroleum ether (60–90°C) and ethyl acetate to give 3,5-dichloro-2-fluoropyridine **2** (3.60 g, 36.1% of theory) and 5-chloro-2,3-difluoropyridine **3** (1.89 g, 21.0% of theory).

Synthesis of 5-Chloro-2,3-Difluoropyridine 3 with 3,5-Dichloro-2-Fluoropyridine 2

In a 50 ml flask was placed 2-fluoro-3,5-dichloropyridine **2** (6.65 g, 0.04 mmol), CsF (9.3 g, 0.061 mol), 0.4 g K_2CO_3, and 20 mL [Bmim]BF_4. After the mixture was heated at 100–110°C/200 mmHg for 8 h, the product was extracted with Et_2O (3 × 25 ml). The combined ethereal phases were evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel and elution with 5 : 1 petroleum ether (60–90°C) and ethyl acetate to give 2-fluoro-3,5-dichloropyridine **2** (0.60 g) and 5-chloro-2,3-difluoropyridine **3** (3.75 g, 68.8% of theory).

3,5-Dichloro-2-fluoropyridine 2: A white solid. m.p. 38–39°C (lit.[18]: 38–39°C). ^{1}H NMR: $\delta = 8.01$ (*d*, $J = 2.0$ Hz, 1H), 7.44 (*d*, $J = 2.0$ Hz, 1H); ^{13}C NMR: $\delta = 156.6$ (1C), 146.5 (1C), 138.6 (1C), 131.3 (1C), 119.5 (1C). MS $m/z = 165.7$. IR (ν_{max}, KBr): 3045, 1568, 1235, 1130, 1035 cm^{-1}.

5-Chloro-2,3-difluoropyridine 3: An oil (lit.[19]: boil 135–136°C, or 70–73°C/85 mmHg[20]). ^{1}H NMR: $\delta = 7.94$ (*d*, $J = 2.1$ Hz, 1H), 7.51

(*d*, $J = 2.1$ Hz, 1H); ^{13}C NMR: $\delta = 156.7$ (1C), 151.2 (1C), 141.7 (1C), 129.2 (1C), 123.6 (1C). MS $m/z = 149.3$. IR (ν_{max}, KBr): 3035, 1558, 1225, 1125, 1025 cm^{-1}.

Synthesis of 2-[4-(3,5-Dihalopyridin-2-yloxy)-Phenoxy]-Propionate 5

To a stirred mixture of 2-(4-hydroxyphenoxy)-propionates **4** (0.05 mol), K_2CO_3 (6.91 g, 0.05 mol), and 20 mL [Bmim]BF_4 was added drop-wise a solution of 2,3,5-trichloropyridine **1,** or 3,5-dichloro-2-fluoropyridine **2,** or 5-chloro-2,3-difluoropyridine **3** (0.05 mol) in 15 ml of acetonitrile, and the mixture was heated at a temperature of 50–60°C during 40 h. The mixture was then poured into ice water. The organic material was extracted with ethyl acetate, washed with a saturated salt solution, dried over magnesium sulfate, filtered, and evaporated. The oily residue was purified by column chromatography on silica gel and elution with 3 : 1 petroleum ether (60–90°C) and ethyl acetate to give 2-[4-(3,5-dihalopyridin-2-yloxy)-phenoxy]-propionic acid and its esters **5**.

Ethyl 2-[4-(3,5-dichloropyridin-2-yloxy)-phenoxy]-propionate 5a: An oil. ^{1}H NMR: $\delta = 7.94$ (*d*, $J = 1.3$ Hz, 1H), 7.74 (*d*, $J = 1.3$ Hz, 1H), 7.05 (*d*, $J = 8.9$ Hz, 2H), 6.90 (*d*, $J = 8.9$ Hz, 2H), 4.71 (*q*, $J = 6.7$ Hz, 1H), 4.23 (*q*, $J = 7.1$ Hz, 2H), 1.62 (*d*, $J = 6.7$ Hz, 3H), 1.26 (*t*, $J = 7.1$ Hz, 3H); ^{13}C NMR: $\delta = 171.20$ (1C), 157.79 (1C), 154.80 (1C), 147.51 (1C), 143.37 (1C), 138.65 (1C), 125.35 (1C), 122.40 (1C), 119.32 (2C), 116.23 (2C), 73.08 (1C), 60.53 (1C), 18.78 (1C), 14.20 (1C); MS $m/z = 356.1$; IR (ν_{max}, film): 3030, 1760, 1550, 1210, 1100 cm^{-1}. Anal. Calcd. for $C_{16}H_{15}Cl_2NO_4$: C, 53.95; H, 4.24; N, 3.93. Found: C, 53.61; H, 4.15; N, 3.63.

Ethyl 2-[4-(5-chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionate 5b: An oil. ^{1}H NMR: $\delta = 7.92$ (*m*, 1H), 7.72 (*m*, 1H), 7.04 (*d*, $J = 8.6$ Hz, 2H), 6.90 (*d*, $J = 8.6$ Hz, 2H), 4.71 (*q*, $J = 6.6$ Hz, 1H), 4.22 (*q*, $J = 7.0$, 2H), 1.61 (*d*, $J = 6.6$ Hz, 3H), 1.25 (*t*, $J = 7.0$ Hz, 3H); ^{13}C NMR: $\delta = 169.24$ (1C), 158.13 (1C), 157.02 (1C), 153.51 (1C), 151.26 (1C), 140.03 (1C), 130.22 (1C), 122.71 (1C), 119.68 (2C), 117.51 (2C), 73.13 (1C), 60.85 (1C), 19.49 (1C), 14.46 (1C); MS $m/z = 339.6$; IR (ν_{max}, film): 3035, 1765, 1555, 1220, 1120 cm^{-1}. Anal. Calcd. for $C_{16}H_{15}ClFNO_4$: C, 56.56; H, 4.45; N, 4.12. Found: C, 56.25; H, 4.38; N, 4.08.

Methyl 2-[4-(3,5-dichloropyridin-2-yloxy)-phenoxy]-propionate 5c: An oil. ^{1}H NMR: $\delta = 7.95$ (*d*, $J = 1.5$ Hz, 1H), 7.75 (*d*, $J = 1.5$ Hz, 1H), 7.04 (*d*, $J = 8.8$ Hz, 2H), 6.92 (*d*, $J = 8.8$ Hz, 2H), 4.73 (*q*, $J = 6.8$ Hz, 1H), 3.94 (*s*, 3H), 1.60 (*d*, $J = 6.8$ Hz, 3H); ^{13}C NMR: $\delta = 169.95$ (1C), 157.82 (1C), 157.02 (1C), 153.90 (1C), 140.10 (1C), 130.21 (1C), 130.24 (1C),

122.40 (1C), 119.32 (2C), 116.23 (2C), 73.08 (1C), 51.65 (1C), 18.78 (1C); MS $m/z = 342.3$; IR (ν_{max}, film): 3020, 1755, 1560, 1220, 1120 cm^{-1}. Anal. Calcd. for $C_{15}H_{13}Cl_2NO_4$: C, 52.65; H, 3.83; N, 4.09. Found: C, 52.43; H, 3.64; N, 4.00.

Methyl 2-[4-(5-chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionate 5d: A white solid. m.p. 63–64°C. (lit.[21]: 63–64°C). ^{1}H NMR: $\delta = 7.94$ (*m*, 1H), 7.74 (*m*, 1H), 7.00 (*d*, $J = 8.6$ Hz, 2H), 6.90 (*d*, $J = 8.6$ Hz, 2H), 4.72 (*q*, $J = 6.6$ Hz, 1H), 3.92 (*s*, 3H), 1.62 (*d*, $J = 6.6$ Hz, 3H); ^{13}C NMR: $\delta = 170.02$ (1C), 157.98 (1C), 157.24 (1C), 152.65 (1C), 142.37 (1C), 138.65 (1C), 125.35 (1C), 124.77 (1C), 119.55 (2C), 117.51 (2C), 73.41 (1C), 51.24 (1C), 19.48 (1C); MS $m/z = 325.6$; IR (ν_{max}, film): 3030, 1755, 1550, 1225, 1130 cm^{-1}.

Benzyl 2-[4-(3,5-dichloropyridin-2-yloxy)-phenoxy]-propionate 5e: An oil. ^{1}H NMR: $\delta = 7.96$ (*d*, $J = 2.3$ Hz, 1H), 7.77 (*d*, $J = 2.3$ Hz, 1H), 7.33 (*m*, 5H), 7.04 (*d*, $J = 9.0$ Hz, 2H), 6.92 (*d*, $J = 9.0$ Hz, 2H), 5.22 (*s*, 2H), 4.79 (*q*, $J = 6.8$ Hz, 1H), 1.67 (*d*, $J = 6.8$ Hz, 3H); ^{13}C NMR: $\delta = 170.01$ (1C), 157.81 (1C), 155.79 (1C), 148.53 (1C), 143.37 (1C), 138.63 (1C), 137.01 (1C), 128.86 (1C), 125.33 (2C), 122.41 (2C), 119.32 (1C), 117.28 (2C), 117.05 (2C), 116.22 (1C), 74.12 (1C), 67.23 (1C), 19.49 (1C); MS $m/z = 418.9$; IR (ν_{max}, film): 3035, 1755, 1550, 1200, 1120 cm^{-1}. Anal. Calcd. for $C_{21}H_{17}Cl_2NO_4$: C, 60.30; H, 4.10; N, 3.35. Found: C, 59.92; H, 4.02; N, 3.28.

2-Oxo-2-phenylethyl 2-[4-(3,5-dichloropyridin-2-yloxy)-phenoxy]-propionate 5f: A yellow solid. m.p. 53–55°C. ^{1}H NMR: $\delta = 7.96$ (*d*, $J = 2.4$ Hz, 1H), 7.90 (*m*, 5H), 7.74 (*d*, $J = 2.4$ Hz, 1H), 7.09 (*d*, $J = 9.1$ Hz, 2H), 7.02 (*d*, $J = 9.1$ Hz, 2H), 5.45 (*s*, 2H), 4.93 (*q*, $J = 6.8$ Hz, 1H), 1.78 (*d*, $J = 6.8$ Hz, 3H); ^{13}C NMR: $\delta = 171.46$ (1C), 167.13 (1C), 157.81 (1C), 154.86 (1C), 147.47 (1C), 143.37 (2C), 138.66 (2C), 125.32 (1C), 122.36 (4C), 119.32 (1C), 116.23 (4C), 72.92 (1C), 61.00 (1C), 18.60 (1C); MS $m/z = 446.8$; IR (ν_{max}, KBr): 3035, 1760, 1550, 1210, 1100 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}Cl_2NO_5$: C, 59.21; H, 3.84; N, 3.14. Found: C, 59.02; H, 3.74; N, 3.68.

Oxopropoxymethyl 2-[4-(3,5-dichloropyridin-2-yloxy)-phenoxy]-propionate 5g: An oil. ^{1}H NMR: $\delta = 7.96$ (*d*, $J = 2.4$ Hz, 1H), 7.76 (*d*, $J = 2.4$ Hz, 1H), 7.08 (*d*, $J = 8.8$ Hz, 2H), 6.96 (*d*, $J = 8.8$ Hz, 2H), 4.85 (*q*, $J = 6.8$ Hz, 1H), 4.70 (*s*, 2H), 4.24 (*q*, $J = 7.1$ Hz, 2H), 1.70 (*d*, $J = 6.8$ Hz, 3H), 1.29 (*t*, $J = 7.1$ Hz, 3H); ^{13}C NMR: $\delta = 191.34$ (1C), 171.57 (1C), 154.95 (1C), 147.43 (1C), 143.39 (1C), 138.65 (1C), 128.88 (1C), 128.60 (1C), 127.72 (1C), 122.38 (2C), 116.23 (2C), 73.12 (1C), 66.33 (2C), 18.81 (2C); MS $m/z = 414.0$; IR (ν_{max}, film): 3035, 1751, 1555, 1220, 1120 cm^{-1}. Anal. Calcd. for $C_{18}H_{17}Cl_2NO_6$: C, 52.19; H, 4.14; N, 3.38. Found: C, 51.91; H, 4.05; N, 3.30.

2-propynyl 2-[4-(3,5-dichloropyridin-2-yloxy)-phenoxy]-propionate 5h: A white solid. m.p. 67–69°C. ^{1}H NMR: $\delta = 7.93$ (*d*, $J = 2.3$ Hz, 1H), 7.73 (*d*, $J = 2.3$ Hz, 1H), 7.04 (*d*, $J = 8.8$ Hz, 2H), 6.91 (*d*, $J = 8.8$ Hz, 2H), 4.77 (*q*, $J = 6.8$ Hz, 1H), 4.74 (*s*, 2H), 2.49 (*s*, 1H), 1.63 (*d*, $J = 6.8$ Hz, 3H); ^{13}C NMR: $\delta = 171.20$ (1C), 157.82 (1C), 154.81 (1C), 147.51 (1C), 143.37 (1C), 138.68 (1C), 125.36 (1C), 122.41 (2C), 119.32 (1C), 116.24 (2C), 75.44 (1C), 73.13 (2C), 52.61 (1C), 18.43 (1C); MS $m/z = 366.4$. IR (ν_{max}, KBr): 3035, 1751, 1555, 1220, 1120 cm^{-1}. Anal. Calcd. for $C_{17}H_{13}Cl_2NO_4$: C, 55.76; H, 3.58; N, 3.82. Found: C, 55.63; H, 3.46; N, 3.71.

Synthesis of 2-[4-(5-Chloro-3-Fluoropyridin-2-yloxy)-Phenoxy]-Propionic Acid 6

To a solution of 6.5 g (0.02 mol) of methyl 2-[4-(5-chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionate in 30 ml of dioxane were added 21 ml of 1 N sodium hydroxide, and the mixture was stirred for 3 h at 35°C. Then it was poured onto an ice water mixture and acidified with 11 ml of 2 N hydrochloric acid. The organic material was extracted with ethyl acetate. The organic layers were washed with a saturated salt solution and dried over magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography on silica gel and elution with 3 : 1 petroleum ether (60–90°C) and ethyl acetate to yield 5.1 g (81.8% of the theory) of 2-[4-(5-chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionic acid **6**.

2-[4-(5-Chloro-3-fluoropyridin-2-yloxy)-phenoxy]-propionic acid 6: A white solid. m.p. 95–96°C. (lit.[22]: 95–96°C). ^{1}H NMR: $\delta = 12.2$ (*s*, 1H), 7.90 (*m*, 1H), 7.70 (*m*, 1H), 7.05 (*d*, $J = 8.7$ Hz, 2H), 6.91 (*d*, $J = 8.7$ Hz, 2H), 4.70 (*q*, $J = 6.5$ Hz, 1H), 1.60 (*d*, $J = 6.5$ Hz, 3H); IR (ν_{max}, KBr): 3030, 1735, 1550, 1240 cm^{-1}.

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