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Investigation of the Synthesis of Phenoxypropionic Acid Derivatives Based on 1,3,5-Triazine System

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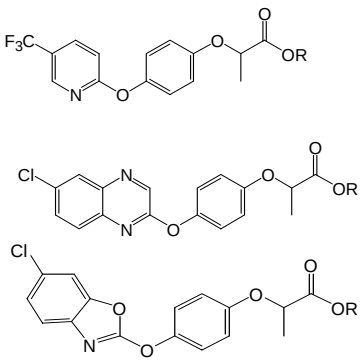
Abstract: A new series of phenoxyalkanecarboxylic acid derivatives based on 1,3,5-triazine were successfully prepared from 2,4,6-trichloro-1,3,5-triazine and various phenoxypropionic acid derivatives involving the aromatic nucleophilic substitution followed by other specific reactions.

Keywords: phenoxyalkanoic acids; triazine; nucleophilic substitution.

1. Introduction

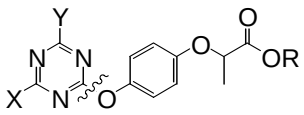
The use of 2,4-dichlorophenoxyacetic acid as a herbicide has been for more than 50 years [1]. Subsequently, the related products based on pyridine, pyrazine, etc moieties were developed and marketed for other specific applications by some major companies such as Zeneca, Novartis, Nissan, DuPont and AgrEvo [2-4]. Their chemical structures are illustrated in Figure 1.



R= H or alkyl

Figure 1.

Their preparations involved the aromatic nucleophilic substitution of proper halogen substituted aromatic compounds with phenoxypropionic acids and were detailed in the literature [2-4]. This type of compounds exhibits certain biological activity in agricultural applications such as a herbicide and/or growth regulator. In this paper, we wish to report the synthesis of phenoxypropionic acid derivatives based on the 1,3,5-triazine as a core. Our target compounds are depicted in Figure 2.



X ,Y =Cl , triazole, EtNH, CN, PhO,etc.

R= H, CH_3

Figure 2.

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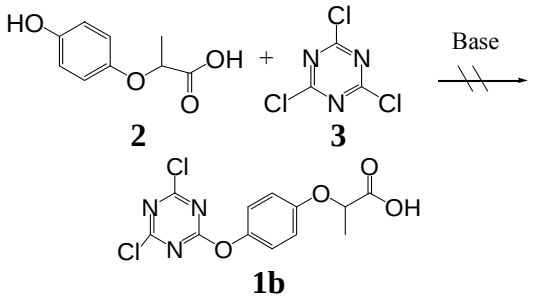
2. Results and discussion

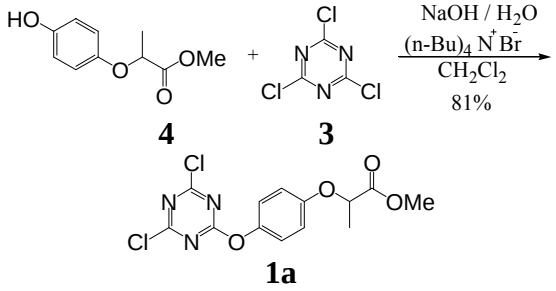
Initially, the synthesis of target compound **1b** was attempted by coupling of **2** and trichlorotriazine **3** in Scheme 1 but failed in recovering starting materials of **2** mainly.

Scheme 1



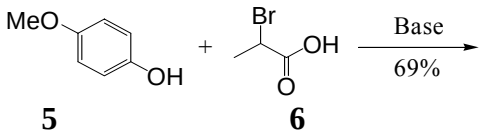
Alternatively, **2** first was esterified to form methyl ester **4** with methanol in the presence of sulfuric acid as catalyst. Then, **4** and **3** were further coupled to form **1a** as shown in Scheme 2.

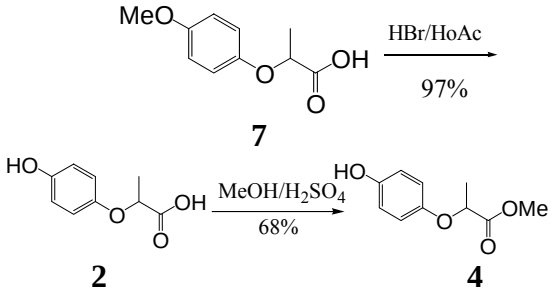
Scheme 2



In turn, **4** conceivably was prepared by nucleophilic substitution of 2-bromo- propionic acid and hydroquinone under different conditions and followed by methylation but all failed in the former step. Therefore, **4** was synthesized from 4-methoxyphenol **5** and 2-bromo- propinoic acid **6** by the literature method [5] followed by removal of methyl group from phenyl ring and methylation. as shown in Scheme 3.

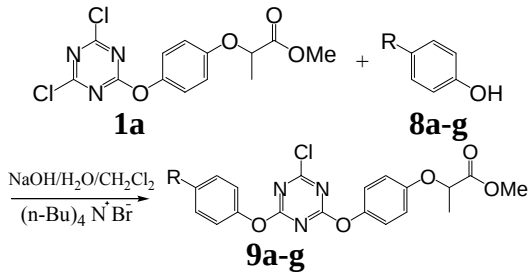
Scheme 3





With **1a** in our hand, several substituted phenol were selected for further nucleophilic substitution to form products **9a-g** depicted in Scheme 4.

Scheme 4



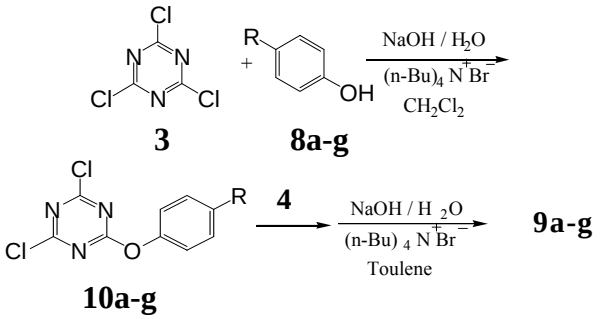
Their test results of Scheme 4 were summarized in Table 1.

Table 1.

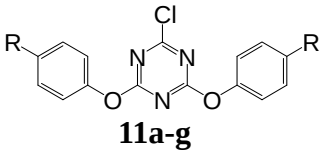
Compound	R	Yield
9a	Cl	67%
9b	Br	73%
9c	F	72%
9d	$C(O)CH_3$	51%
9e	NO_2	62%
9f	o-CH_3	64%
9g	H	42%

The general reactions of Scheme 4 did not afford any trisubstituted products of 1,3,5-trichlortriazine. On the other hand, the target compound **9a-g** in principle could also be prepared from a two-step reaction involving (a) trichlortriazine **3** and **8** to intermediate **10a-g** and then (b) **10a-g** and **4** under proper conditions depicted in Scheme 5.

Scheme 5



In fact, the first step reaction of Scheme 5 afforded not only 10a-g but also another disubstituted products 11a-g as shown in Figure 3 as a minor component despite that molar ratio of 1:1 for 1,3,5-trichlortriazine and 8a-g was utilized. Then, 11a-g needed to be removed prior to the subsequent reaction.



11a-g

Figure 3.

The experimental results of the first step of Scheme 5 were summarized in Table 2.

Table 2.

Compound	R	Weight ratio of **10**:**11**	Total yield
10a, 11a	Cl	3 : 1	98%
10b, 11b	Br	3 : 1	84%
10c, 11c	F	4 : 1	86%
10d, 11d	$C(O)CH_3$	4 : 1	78%
10e, 11e	NO_2	4 : 1	96%
10f, 11f	o-CH_3	3 : 1	82%
10g, 11g	H	3 : 1	93%

In order to prepare 9a-g, each 10a-g was chromatographically separated from the corresponding 11a-g and further reacted with 4 under phase transfer condition as shown in Scheme 5. Their test results were summarized in Table 3.

Table 3.

Compound	R	Total yield
9a	Cl	40%
9b	Br	48%
9c	F	56%
9d	$C(O)CH_3$	52%
9e	NO_2	48%
9f	o-CH_3	48%
9g	H	37%

In comparison of the two synthetic routes for **9a-g** depicted in Schemes 4 and 5, the overall results indicated Scheme 4 being superior in saving a step of tedious chromatographic purification and reaction yields. An offshoot interest to investigate the effectiveness of nucleophilic substitution of 1,3,5-trichlortriazine by phenols as shown in the first step in Scheme 5, the 1:2 molar ratio of 1,3,5-trichlortriazine to phenols was attempted instead of 1:1 to see any tri-substituted product would form. Both 4-methoxyphenol and 4-chlorophenol afforded only disubstituted products in 62% and 80%, respectively. However, when 4-aceto- phenol was used, the molar ratio of disubstituted and trisubstituted products was obtained in 2:1.

Finally, the hydrolysis of propionate **1a** was conducted in aqueous, methanolic alkaline solution under various conditions but all attempts failed to afford the target propionic acid as shown in Scheme 6. Instead, the cleavage products, **12** and **2** were recovered. The reaction conditions were summarized in Table 4.

Scheme 6

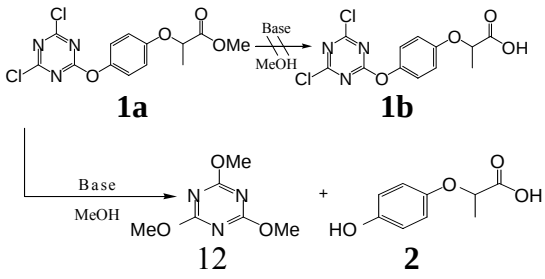


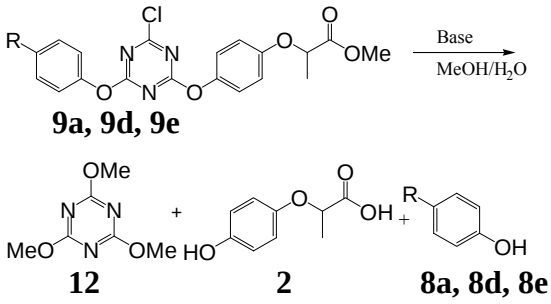
Table 4. Hydrolysis conditions of 1a

Base	Reaction time	Yield of 12	Yield of 2
3N NaOH	3-hr	40%	57
52N NaOH	3.5-hr	43%	54%
1N NaOH	3.5-hr	46%	53%
0.5N NaOH	3-hr	59%	26%
LiOH	3.5-hr	62%	8%

Furthermore, the hydrolysis was examined in hydrochloric acid and failed similarly to those in alkaline conditions.

In addition, **9a**, **9d**, and **9e** were also examined for hydrolysis in alkaline condition and afforded the cleavage products as shown in Scheme 7.

Scheme 7



3. Conclusion

The nucleophilic substitution of tri- chlorotriazine **3** with hydroquinone appeared straightforward but it did not undergo favorably unless one of the hydroxy group of hydroquinoe was protected as a methoxy group.

The nucleophilic substitutions of **3** with various phenols could be conducted in a two-phase transfer reaction in dichlormethane or toluene.

We have demonstrated successfully the syntheses of various phenoxypropionate based on 1,3,5-triazine system such as 1a and 9a-g. However, the hydrolysis of these compounds failed under various conditions at the moment of reporting.

For future work, the direct coupling of 2 and 3 and the hydrolysis of 1a will be investigated further. And other nucleophiles than phenolic compounds will be pursued.

4. Experimental section

NMR spectra were obtained at 200MHz in $CDCl_3$ solvent (unless otherwise noted), and chemical shifts were reported in δ ppm.

Melting points are uncorrected. IR spectra were obtained by Perkin Elmer Paragon 500 and reported in wave number. All the raw materials were used as received (unless otherwise noted). Mass spectra and HRMS data were obtained at Instruments Center, National Chung Hsing University.

2-(4-Methoxyphenoxy) propionic acid (7).

A solution of 2-bromopropionic acid (5.05 g; 33 mmol) dissolved in 2 N NaOH (16.5 mL) was added to another solution of 4-methoxyphenol (4.09 g; 33 mmol) dissolved in 2 N NaOH (16.5 mL). The mixture was refluxed for 24-hr and cooled to room temperature. The resulting solution was acidified with 5 N HCl and extracted with ethyl acetate (25 mLx4).

The combined organic extracts were washed with a brine solution (25 mL), dried with anhydrous sodium sulfate, filtered and evaporated to give brown solid product. Recrystallization from ethyl acetate/ hexane afforded 4.5 g (69%) white needle crystal: IR 3406, 3033, 2995, 2947, 2354, 1738, 1504, 1452, 1214 cm^{-1};^{1}H NMRδ6.83 (4H, m), 4.70 (1H, q, *J*=6.8Hz), 3.77 (3H, s), 1.63 (3H, d, *J*=6.8Hz); ^{13}CNMRδ18.4, 55.6, 73.2, 114.7, 116.7, 151.1, 154.7, 177.3; mp 91-93℃.

2-(4-Hydroxyphenoxy) propionic acid (2).

To a solution of 7 (0.73 g; 3.7 mmol) and tetra-n-butylammonium bromide (0.12 g; 0.37 mol) dissolved in acetic acid (7 mL) was added

48% HBr (5 mL) and refluxed for 3-hour, cooled, diluted with water (150 mL), extracted with ethyl actate (25 mLx3). The organic extracts were washed with brine, dried, and rotary evaporated to give a solide product.

Recrystallization from ethyl acetate/hexane afforded crystal of 0.45 g (97%): IR 3450, 3074, 2975, 2925, 2350, 1740, 1524, 1448, 1224 cm^{-1};^{1}HNMRδ7.02 (4H, m), 4.62 (1H, q, *J*=6.8Hz), 4.05 (br,OH),1.59 (3H, d, *J*=6.8Hz); ^{13}CNMRδ18.4, 73.3, 115.8, 116.5, 150.8, 151.1, 175.0; mp146-148℃.

2-(4-Hydroxyphenoxy)propionic acid methyl ester (4).

To a solution of 2 (2 g; 11 mmol) in methanol (150mL) was added a few drops of 98% Sulfuric acid and refluxed for 4-hour, cooled, rotarily evaporated, extracted with ethyl acetate (20x3 mL). The extracts were washed, dried, filtered and evaporated to give brow oil (2.1 g; 68%): ^{1}HNMRδ 6.73 (4H, m), 4.67 (1H, q, *J*=6.8Hz), 3.75 (3H, s),1.60 (3H, d, *J*=7Hz); ^{13}CNMR δ 18.6, 52.4, 73.5, 116.1, 116.6, 150.4, 151.4, 173.3; MS-EI 196.2 (59, M^{+}), 137 (63), 110 (100), 81 (88), 59 (54), 53 (53); Exact Mass： Calculated for $C_{10}H_{12}O_4$: 196.0736; Found: 196.0729.

2-[4-(4,6-Dichloro[1,3,5]-triazin-2-yloxy)phenoxy]propionic acid methyl ester (1a).

To a solution of 4 (2.51 g; 12.8 mmol) and tetra-n-butylammonium bromide (0.41 g; 1.28 mol) in dichloro- methane (45 mL) was added 3 (2.60 g, 14 mmol) and a solution of NaOH (0.56 g; 14.1 mmol) in water (10 mL), refluexed for 24-hour, cooled, and separated.

The aqueous layer was extracted with ethyl aetate (25 mLx3). The combined extracts were washed with brine, dried, filtered and evaporated to amber oil solid.

Recrystallization from ethyl acetate/hexane afforded white soild (3.58 g; 81%): IR 3205, 2993, 2852, 2359, 1752, 1736, 1598, 1537, 1500, 1415, 1376, 1297, 1261 cm^{-1}; ^{1}HNMRδ7.07 (2H, d, *J*=12.6Hz), 6.91 (2H, d, *J*=9.2Hz), 4.75 (3H, q, *J*=6.8Hz), 3.77 (3H, s), 1.63 (1H, d, *J*=6.8Hz); ^{13}CNMRδ18.5, 52.4, 72.9, 116.0, 121.9, 145.1, 155.9, 171.2, 172.2, 172.9; MS-EI 347 (7, M+4), 345 (41, M+1), 343 (62,M^{+}), 286 (59), 284 (100), 222 (82); Exact Mass: Calculated for $C_{13}H_{11}Cl_2N_3O_4$: 343.0127; Found: 343.0135; mp 89-91℃.

General procedure for preparation of compounds 9a-g.

Method A:

To a solution of 1a (0.9 mmol) and tetra-n-butylammonium bromide (0.09 mol) dissolved in dichloromethane (10 mL) was added 8a-g (0.9 mmol) and a solution of sodium hydroxide (1.0 mmol) in water (2 mL), refluxed for 24-hour, cooled, extracted with ethyl acetate (20mLx3). The combined extracts were washed with brine, dried, filtered, and evaporated to give the crude products.

Recrystallization or column chromatography with ethyl acetate and hexane afforded the target products.

Method B:

To a solution of 4 (2.7 mmol), 10a-g (2.7 mmol), and tetra-n-butylammonium bromide (0.27 mmol) dissolved in toluene (15 mL) was added a solution of sodium hydroxide (2.96 mmol) in water (3 mL), refluxed for 24-hour, cooled, extracted with ethyl acetate (25mLx3). The combined extracts were washed with brine, dried, filtered, and evaporated to the crude products.

Recrystallization or column chromatography with ethyl acetate and hexane afforded the target products.

2-{4-[4-Chloro-6-(4-chlorophenoxy)-[1,3,5]triazin-2-yloxy]phenoxy}propionic acid methyl ester (9a)

IR 2993, 2852, 2514, 2311, 2047, 1880, 1754, 1632, 1597, 1555, 1502, 1485, 1446, 1404, 1363 cm^{-1}; ^{1}HNMRδ 7.35 (2H, d, *J*=12Hz), 7.06 (4H, m), 6.88 (2H, d, *J*=12.6Hz), 4.74 (1H, q, *J*=6.8Hz), 3.77 (3H, s), 1.63 (3H, d, *J*=6.8Hz);^{13}CNMRδ18.5, 52.4, 73.1, 115.9, 122.1, 122.6, 122.8, 129.7, 131.9, 145.4, 149.7,

155.7, 172.1, 172.3, 172.5, 173.8; MS-EI 438 (12, M+4), 437 (57, M+2), 435(81, M^+), 376 (66), 308 (100), 111 (46), 75 (33); Exact Mass: Calculated for $C_{19}H_{15}Cl_2N_3O_5$ 435.0389; Found 435.0384; mp 67.6-69.4℃.
Yield: Method A (67%); Method B (40%).

2-{4-[4-(4-Bromophenoxy)-6-chloro[1,3,5]triazin-2-yloxy]-phenoxy}propionic acid methyl ester (9b)

IR 2987, 2847, 2525, 2326, 2056, 1878, 1750, 1635, 1592, 1558, 1505, 1494, 1443, 1407, 1365, 1250 cm^{-1}; ^{1}HNMRδ7.46~7.54 (2H, m), 7.04 (4H, m),6.82~6.99 (2H, m), 4.74 (1H, q, *J*=7Hz), 3.78 (3H, s), 1.63 (3H, d, *J*=6.8Hz);
^{13}CNMRδ18.6, 52.4, 73.0, 115.9, 119.7, 122.1, 123.0, 123.2, 132.5, 145.4, 150.2, 155.7, 172.0, 172.4, 172.5, 173.7;MS-EI 483 (24,M+4), 481 (96, M+2), 479 (M^+), 444 (40), 422 (59), 308 (100), 222 (32); Exact Mass: Calculated for $C_{19}H_{15}ClBrN_3O_5$：478.9884;
Found：478.9874; mp 73.5-74.6℃.
Yield: Method A (73%); Method B (48%).

2-{4-[4-Chloro-6-(4-fluorophenoxy)-[1,3,5]triazin-2-yloxy]-phenoxy}propionic acid methyl ester (9c)

IR（film）cm^{-1}3057, 2994, 2955, 2923, 2852, 2512, 2312, 2053, 1878, 1755, 1660, 1631, 1600, 1557, 1453, 1418, 1365 cm^{-1}; ^{1}HNMRδ6.85~7.20 (8H, m), 4.74 (1H, q, *J*=6.8Hz), 3.78 (3H, s), 1.63 (3H, d, *J*=6.8Hz); ^{13}CNMRδ 18.6, 52.4, 73.1, 115.9, 116.3, 116.6, 122.1, 122.6, 122.8, 145.5, 147.1, 155.7, 162.9, 172.3, 173.8; MS-EI 421 (36, M+2), 419 (100, M^+), 360 (77), 308(88), 298 (36), 222 (30), 95 (56), 75 (28);
Exact Mass: Calculated for $C_{19}H_{15}ClN_3O_5F$: 419.0784; Found: 419.0687; mp 58.5-59.7℃.
Yield: Method A (72%); Method B (56%).

2-{4-[4-(4-Acetylphenoxy)-6-chloro-[1,3,5]triazin-2-yloxy]phenoxy}-propionic acid methyl ester (9d)

IR 3059, 2992, 2948, 2915, 2848, 2514, 2325, 2059, 1871, 1752, 1668, 1636, 1604, 1551, 1456, 1418, 1369 cm^{-1};
^{1}HNMRδ7.97~8.01 (2H, d, *J*=8.6Hz), 7.20~7.26 (2H, d, *J*=17.4Hz), 6.99~7.05 (2H, d, *J*=12.6Hz), 6.81~6.87 (2H, d, *J*=12.6Hz), 4.70 (1H, q, *J*=6.8Hz), 3.76 (3H, s), 2.60 (3H,s), 1.61 (3H, d, *J*=7Hz);
^{13}CNMRδ18.6, 26.6, 52.4, 115.8, 121.6, 122.2, 130.0, 135.0, 145.6, 154.9, 155.5, 172.4, 173.2, 173.9, 196.7;
MS-EI 445 (32, M+2), 443 (100, M^+), 408 (87), 341 (67),308 (77), 249 (52), 222 (42), 95 (38);
Exact Mass: Calculated for $C_{21}H_{18}ClN_3O_6$: 443.0875;
Found: 443.0884; mp 140-142℃.
Yield: Method A (51%); Method B (52%).

2-{4-[4-Chloro-6-(4-nitrophenoxy)-[1,3,5]triazin-2-yloxy]-phenoxy}propionic acid methyl ester (9e)

IR 3057, 2998, 2285, 2511, 2319, 2052, 1875, 1754, 1669,1633, 1600, 1556, 1525, 1458, 1410, 1350, 1262 cm^{-1};
^{1}HNMRδ8.33~8.27 (2H, d, *J*=12Hz), 7.32~7.38 (2H, d, *J*=12.2Hz), 7.01~7.07 (2H, d, *J*=12.6Hz), 6.86~6.92 (2H, d, *J*=12.8Hz), 4.73 (1H, q, *J*=6.8Hz),3.78 (3H, s), 1.64 (3H, d, *J*=6.8Hz); ^{13}C NMRδ18.5, 52.4, 72.9, 115.8, 122.0, 122.4, 125.4, 145.3, 145.6, 155.7, 172.3, 172.9, 173.9; MS-EI 448 (32, M+2), 446 (M^+, 100), 418 (64), 376 (65), 312 (51), 288 (54), 272 (44), 159 (32);
Exact Mass: Calculated for $C_{19}H_{15}ClN_4O_7$: 446.0635;
Found：446.0629; mp 128-130℃.
Yield: Method A (62%); Method B (48%).

2-[4-(4-Chloro-6-o-*tolyloxy*-[1,3,5]triazin-2-yloxy)-phenoxy]propionic acid methyl ester (9f)

IR 3052, 2994, 2920, 2842, 2520, 2325, 2059, 1874, 1755, 1670, 1631, 1608, 1552, 1419, 1364, 1265 cm^{-1}; ^{1}HNMRδ 7.18~7.26 (5H, m), 6.83~7.09 (4H, m), 4.73 (1H, q,*J*=6.6Hz), 3.78 (3H, s), 2.17 (3H, s),1.64 (3H, d, *J*=7Hz); ^{13}CNMRδ 16.2, 17.8, 52.5, 116.0, 121.2, 122.8, 127.1, 128.1, 129.9, 131.6, 145.4, 149.9, 155.5, 171.5, 172.4; MS-EI: 417 (32, M+2), 415 (100, M^+), 328 (38), 297 (40), 269 (51), 253 (51), 165 (32), 78(35); Exact Mass: Calculated for $C_{20}H_{18}ClN_3O_5$: 415.0935; Found: 415.0941; mp135-136℃. Yield: Method A (64%); Method B (48%).

2-[4-(4-Chloro-6-phenoxy-[1,3,5]triazin-2-yloxy)-phenoxy]propionic acid methyl ester (9g)

IR 3058, 2993, 2851, 2660, 2514, 2360, 2314, 2054, 1944, 1870, 1755, 1596, 1555, 1502, 1448, 1365, 1296, 1220, 1190, 1163 cm^{-1}; ^{1}HNMRδ6.84~7.44 (9H, m), 4.73 (1H, q, *J*=6.8Hz), 3.77 (3H, s), 1.62 (3H, d, *J*=6.8Hz); ^{13}CNMR δ 18.5, 52.4, 73.0, 115.8, 121.1, 122.1, 126.4, 129.6, 145.4, 151.2, 155.6, 173.3, 172.5, 173.6; MS-EI: 403 (36, M+2), 401 (100, M^+), 342 (61), 308 (87), 153 (33),77 (98), Exact Mass: Calculated for $C_{19}H_{16}ClN_3O_5$: 401.0778; Found：401.0787; mp 82-83℃. Yield: Method A (42%); Method B (37%).

General procedure for preparation of compounds 10a-g.

To a solution of 3 (5.4 mmol), 8a-g (5.4 mmol), and tetra-n-butylammonium bromide (0.54 mmol) dissolved in dichloromethane (15 mL) was a solution of sodium hydroxide (11.0 mmol) in water (4 mL), refluexed for 24-hour, cooled, extracted with ethyl acetate (15mLx3).

The combined extracts were washed with brine, dried, filtered, and evaporated to give the crude products. Column chromatography of crude product with ethy acetate/hexane afforded 10a-g and other minor product, respectively.

2, 4-Dichloro-6-(4-chlorophenoxy)-[1,3,5]triazine (10a)

IR 3096, 2918, 2355, 1664, 1590, 1514, 1483, 1441, 1419, 1296, 1261 cm^{-1}; ^{1}HNMRδ7.41~7.45 (2H, m),7.11~7.15 (2H, m); ^{13}CNMRδ122.7, 130.4, 132.7,149.7, 171.2, 173.4; MS-EI: 279 (4, M+4), 277 (13, M+2), 275 (14, M^+), 242 (62), 240 (100), 111 (25), 75 (27), 63 (23); Exact Mass: Calculated for $C_9H_4Cl_3$: 274.9420; Found 274.9427; mp 100-102℃. Yield: 74%.

2-(4-Bromophenoxy)-4,6-dichloro-[1,3,5]triazine (10b)

IR（film）cm^{-1}： 3092, 2920, 2359, 1668, 1595, 1512, 1486, 1447, 1415, 1293 cm^{-1}; ^{1}HNMRδ7.59~7.6 (2H, m), 7.05~7.09 (2H, m); ^{13}CNMRδ120.3, 122.8, 133.0, 149.9, 170.8, 173.2; MS-EI 324 (10, M+6), 322 (64, M+4), 320 (97, M+2), 318 (100, M^+), 283 (47), 248 (52), 239 (60), 163 (42), 147 (35); ExactMass: Calculated for $C_9H_4BrCl_2N_3O$：318.8915; Found：318.8925; mp 98-99 ℃ Yield: 63%.

2, 4-Dichloro-6-(4-fluorophenoxy)-[1,3,5]triazine (10c)

IR 3091, 2920, 2350, 1668, 1591, 1512, 1485, 1447, 1403 cm^{-1}; ^{1}HNMRδ 7.12~7.17 (4H, m); ^{13}CNMRδ 116.5, 116.9, 122.5, 122.7, 146.9, 158.4, 163.3, 171.2, 173.2; MS-EI 263 (1, M+4), 261 (8, M+2), 259 (14, M^+), 226 (43), 224 (100), 95 (33), 83 (21), 75 (22), 63 (18); Exact Mass: Calculated for $C_9H_4FCl_2N_3O$：258.9715; Found：258.9707; mp 110-112℃. Yield: 69%.

1-[4-(4,6-Dichloro-[1,3,5]triazin-2-yloxy)-phenyl]ethanone (10d)

IR 3054, 2997, 2941, 2911, 2844, 2512, 2327, 2051, 1872, 1757, 1668, 1636, 1604, 1552, 1457, 1415 cm^{-1}; ^{1}HNMR δ 7.26~7.31 (2H, d, *J*=8.4Hz), 8.06~8.10 (2H, d, *J*=9.6Hz), 2.64 (3H, s); ^{13}CNMR δ29.7, 121.4, 130.4, 135.7, 154.3, 170.7, 173.3, 196.5; MS-EI 287 (3, M+4), 285 (15, M+2), 283 (23, M^+), 270 (64),268 (100), 87 (15), 75 (24), 63 (15); Exact Mass: Calculated for $C_{11}H_7Cl_2N_3O_2$: 282.9915; Found：282.9919; mp147-148℃; Yield: 55%.

2, 4-Dichloro-6-(4-nitrophenoxy)-[1,3,5]triazine (10e)

IR 3087, 2935, 2342, 1667, 1595, 1508, 1488, 1443, 1407 cm^{-1}; ^{1}HNMRδ 8.24~8.29 (2H, d, *J*=14.6Hz), 7.28~7.33 (2H, d, *J*=12.6Hz); ^{13}CNMR δ122.3, 125.7, 146.2, 155.1, 170.4, 173.4; MS-EI 289 (10, M+4), 287 (64, M+2), 285 (100, M^+), 250 (42),235 (42), 215 (45), 159 (35), 143 (28); Exact Mass: Calculated for $C_9H_4Cl_2N_4O_3$: 285.9660; Found：285.9652; mp 135-137℃; Yield: 64%.

2, 4-Dichloro-6-o-*t*olyloxy-[1,3,5]triazine (10f)

IR 3010, 2957, 2912, 2833, 2358, 1872, 1651, 1633, 1557, 1491, 1410 cm^{-1}; ^{1}H NMRδ7.04~7.34 (5H, m), 2.19 (3H, s); ^{13}CNMR δ 16.2, 121.0, 127.1, 127.4, 129.7, 131.7, 149.7, 170.9, 173.1; MS-EI: 258 (11, M+4), 256 (64, M+2), 254 (100, M^+), 239 (58), 184 (42), 163 (50), 147 (38); Exact Mass: Calculated for $C_{10}H_7Cl_2N_3O$: 254.9966; Found: 254.9954; mp118-120℃; Yield: 50%.

2, 4-Dichloro-6-phenoxy-[1,3,5]triazine (10g)

IR 3094, 2933, 2354, 1661, 1590, 1511, 1484, 1442, 1413 cm^{-1}; ^{1}HNMR δ 7.11~7.51 (5H, m); ^{13}CNMR δ120.8, 126.9, 129.6, 150.8, 170.9, 172.9; MS-EI 244 (10, M+4), 242 (64, M+2), 240 (100, M^+), 205 (32), 170 (38), 163 (47), 147 (40); Exact Mass: Calculated for $C_9H_5ClN_3O$：240.9810; Found 240.9821; mp 89-91℃; Yield: 77%.

Hydrolysis of 2-[4-(4,6-Dichloro-[1,3,5]-triazin-2-yloxy)phenoxy]pro- pionic acid methyl ester (1a).

To a solution of 1a (0.2 g, 0.58 mmol) in methanol (10 mL) was added various concentrations of equalivant sodium hydroxide and stirred for about 3.5-hour at room temperature. The resulting mixture was evaporated, diluted with water (10-15 mL), extracted with ehtyl acetate (15 mLx3). The combined organic extracts were dried, filtered, and evaporated to give 12 which was confirmed by NMR spectra, exact mass and melting point. The aqueous solution was acidified, extracted and worked up as usual to give 2.

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