Chem. Res. Chin. Univ., 2016, 32(2), 188—194 doi: 10.1007/s40242-016-5415-0

Synthesis and Herbicidal Activity of Novel *N*-Allyloxy/Propargyloxy Aryloxyphenoxy Propionamide Derivatives

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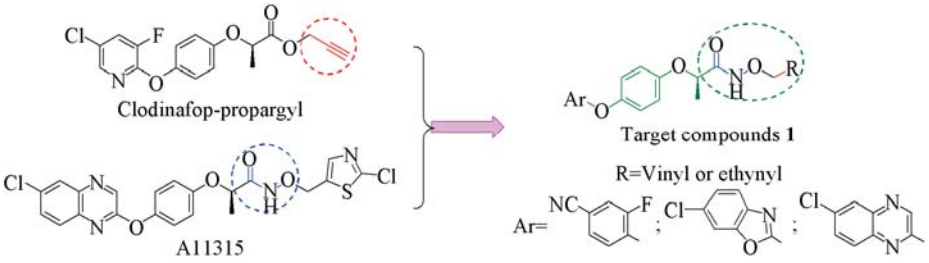
Abstract A series of novel *N*-allyloxy/propargyloxy aryloxyphenoxy propionamide compounds was designed and prepared. The structures of the synthesized compounds were confirmed by means of ^{1}H NMR, ^{13}C NMR, LC-MS, elemental analysis and IR. The bioassay results indicate that when against *Digitaria sanguinalis* and *Echinochloa crus-galli*, (*R*)-*N*-(propargyloxy)-2-{4-[(6-chloroquinoxalin-2-yl)oxy]phenoxy}propanamide(**1**m)(IC_{50}=6.8 and 6.5 g/hm^2, respectively) and (*R*)-*N*-(allyloxy)-2-{4-[(6-chloroquinoxalin-2-yl)oxy]phenoxy}propanamide(**1**r)(IC_{50}=7.4 and 6.0 g/hm^2, respectively) are much more effective than commercial aryloxyphenoxypropionic ester herbicide clodinafop-propargyl(IC_{50}=46.5 and 14.6 g/hm^2, respectively). The results of crop selectivity show that compounds **1**m and **1**r are safe to soybean, rape and cotton and can be used as herbicides for soybean, rape and cotton crop.

Keywords Aryloxyphenoxy propionamide; Allyloxy; Propargyloxy; Herbicidal activity; Crop selectivity

1 Introduction

Aryloxyphenoxypropionic acid(APP) herbicides, which can inhibite acetyl-CoA carboxylase(ACCase) have been identified as one of the most important herbicides. The first APP compound, named as diclofop-methyl[1] by Hoechst AG was developed as an agricultural herbicide to treat monocotyledonnous herbs under the general name. Owing to effective action mode, high efficiency, low toxicity and residue, thousands of analogues of APP bearing diverse structures have been synthesized[2—8] and nearly 20 commercialized products have been developed. Among them, clodinafop-propargyl[9] and metamifop[10] are noteworthy for their remarkable herbicidal activities or safety to specific crop. However, the frequent use of APP herbicides has resulted in the development of resistance to these herbicides in many important grass weed species[11—16]. To solve this problem, new types of herbicides need to be continually developed.

Clodinafop-propargyl(Scheme 1) commercialized by Ciba-Geigy is a novel herbicide with high efficiency and high selectivity. In our previous work[17—20], some *N*-arylmethyl and *N*-hetrocyclo 2-(4-aryloxy phenoxy)propionamides as herbicidal agents were reported, leading to the discovery of a new compound A11315 with more effiency against monocotyledon weeds, such as *Digitaria sanguinalis* and *Echinochloa crus-galli* than clodinafop-propargyl[18]. To search for additional compounds with promising active and higher selectivity in this area, a great effort has been made to modify the structure of A11315 *via* replacing 2-chlorothiazol-5-yl with vinyl or ethynyl groups according to the structures of clodinafop-propargyl. Herein, eighteen *N*-allyloxy/propargyloxy aryloxyphenoxy propionamide compounds were synthesized by a multistep synthetic procedure, and the structures of the



Scheme 1 Design strategy for the target compounds

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Received October 26, 2015; accepted December 30, 2015.

Supported by the National Natural Science Foundation of China(No.21272062), the Startup Foundation of China Three Gorges University(No.KJ2014B084) and the Open Foundation of Hubei Key Laboratory of Tumor Microenvironment and Immunotherapy, China(No.2015KZL09).

copmounds were characterized by means of ^{1}H NMR, ^{13}C NMR, LC-MS, elemental analysis and IR. Their herbicidal activities against *Abutilon theophrasti Medic, Amaranthus ascedense, Chenopodium album, Digitaria sanguinalis, Echinochloa crus-galli* and *Setaria viridis* and the crop selectivity to rice, wheat, maize, soybean, rape and cotton were investigated.

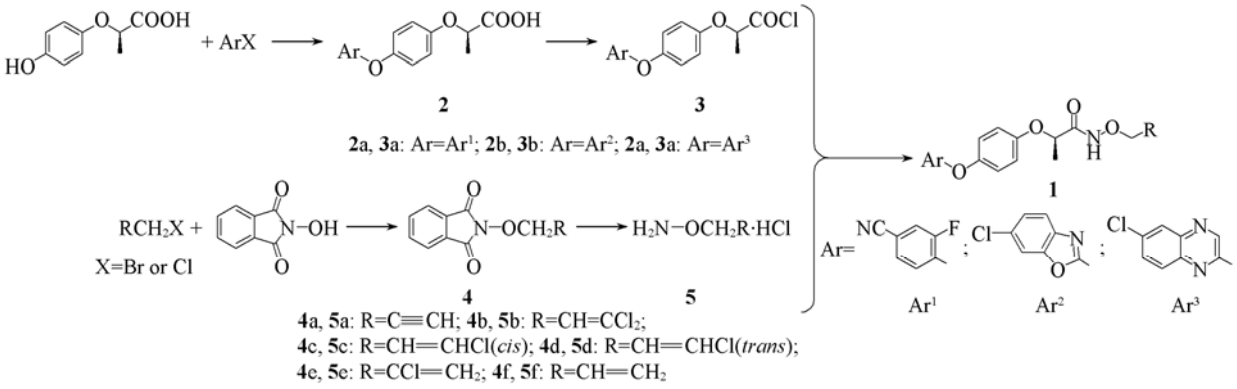
2 Experimental

2.1 Chemicals and Instrumentations

Unless otherwise noted, reagents and solvents were purchased from a business approach. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian INOVA-300 spectrometer using tetramethylsilane(TMS) as internal standard and deuterochloroform($CDCl_3$) as solvent. Mass spectra(MS) were obtained on an Agilent 1100 series LC-MS using positive ion scan mode. Elemental analysis data were obtained on a PE2400 II elemental analyzer. IR spectra were recorded in potassium bromide disks on a PE system 2000 FTIR spectrophotometer. Uncorrected melting points were measured on a WRS-1A digital melting points apparatus.

2.2 Synthesis

The general synthetic route for the designed compounds **1** is shown in Scheme 2. The representative procedure is given below with yields not being optimized.



1a: Ar=Ar^1, R=C≡CH; **1**b: Ar=Ar^1, R=CH=CCl$_2$; **1**c: Ar=Ar^1, R=CH=CHCl(*cis*); **1**d: Ar=Ar^1, R=CH=CHCl(*trans*); **1**e: Ar=Ar^1, R=CCl=CH$_2$; **1**f: Ar=Ar^1, R=CH=CH$_2$; **1**g: Ar=Ar^2, R=C≡CH; **1**h: Ar=Ar^2, R=C=CCL$_2$; **1**i: Ar=Ar^2, R=CH=CHCl(*cis*); **1**j: Ar=Ar^2, R=CH=CHCl(*trans*); **1**k: Ar=Ar^2, R=CCl=CH$_2$; **1**l: Ar=Ar^1, R=CH=CH$_2$; **1**m: Ar=Ar^3, R=C≡CH; **1**n: Ar=Ar^3, R=C=CCL$_2$; **1**o: Ar=Ar^3, R=CH=CHCl(*cis*); **1**p: Ar=Ar^3, R=CH=CHCl(*trans*); **1**q: Ar=Ar^3, R=CCl=CH$_2$; **1**r: Ar=Ar^3, R=CH=CH$_2$

Scheme 2 General synthetic route for the target compounds 1

2.2.1 Synthesis of (R)-2-[4-(4-Cyano-2-fluorophenoxy)phenyl]propanoic Acid(2a)

A mixture of (*R*)-2-(4-hydroxyphenoxy)propanoic acid (98.5%, 3.64 g, 0.02 mol) and K_2CO_3(5.52 g, 0.04 mol) in *N*,*N*-dimethylformamide(DMF)(50 mL) was stirred at 75 °C for 1 h. Then a solution of 3,4-difluorobenzonitrile(2.78 g, 0.02 mol) was added dropwise. After it was stirred at the same temperature for 6 h, the reaction mixture was cooled and poured into 250 mL of ice water and then treated with diluted hydrochloric acid solution to get slightly acidic(pH 4—5). The precipitates formed were filtered, washed with water, and then dried to give 5.20 g of compound **2**a as a gray solid, yield 98.7%, m. p. 50.9—51.8 °C, LC-MS(negative ion), *m/z*: 600.8[2M−H]$^-$.

2.2.2 Synthesis of (R)-2-{4-[(6-Chloro-2-benzoxazolyl)oxy]phenoxy}propanoic Acid(2b)

A mixture of (*R*)-2-(4-hydroxyphenoxy)propanoic acid(98.5%, 3.64 g, 0.02 mol) and sodium hydroxide solution(30 g, 10%) was stirred in an ice water bath for 0.5 h, then was added dropwise to a solution of 2,6-dichlorobenzoxazole (3.76 g, 0.02 mol) in toluene(40 mL). Then tetrabutyl ammonium bromide(0.20 g) was added. The reaction mixture was heated to 50 °C for 3 h and then refluxed for 1 h. After cooled to room temperature, the water phase was separated and treated with diluted hydrochloric acid solution to get slightly acidic(pH 3—4). The precipitates formed were filtered, washed with water, and then dried under vacuum to give 6.02 g of compound **2**b as a gray solid, yield 90.0%, m. p. 162.5—164.8 °C, LC-MS(negative ion), *m/z*: 664.6[2M−H]$^-$.

2.2.3 Synthesis of (R)-2-{4-[(6-Chloroquinoxalin-2-yl)oxy]phenoxy}propanoic Acid(2c)

A mixture of (*R*)-2-(4-hydroxyphenoxy)propanoic acid(98.5%, 3.64 g, 0.02 mol) and K_2CO_3(5.52 g, 0.04 mol) in DMF(40 mL) was stirred at 75 °C for 1 h. Then a solution of 2,6-dichloroquinoxalin(3.98 g, 0.02 mol) was added dropwise and the mixture was stirred at 140 °C for 7 h, then cooled, poured into 300 mL of ice water and treated with diluted hydrochloric acid solution to get slightly acidic(pH 4—5). The precipitates formed were filtered, washed with water and then dried under vacuum to give 6.60 g of compound **2**c as a pale yellow solid, yield 95.9%, m. p. 210.1.0—211.5 °C.

2.2.4 General Synthetic Method of Compounds 3

A mixture of compounds **2**(0.01 mol) and thionyl chloride(3.57 g, 0.03 mol) in toluene(50 mL) was refluxed for 5 h. And the solvent was removed to yield the corresponding compounds **3**.

2.2.5 Synthesis of Propargyloxo Ammonium Chloride(5a)

3-Bromopropyne(11.8 g, 0.10 mol) was added to a solution of *N*-hydroxyphthalimide(16.3 g, 0.10 mol) and DMF(150

mL). After triethylamine(12.2 g, 0.12 mol) was added dropwise, the reaction mixture was stirred at 50 °C for 12 h, then was cooled to room temperature and poured into ice water. The precipitates formed were filtered and washed with water three times to give compound **4**a. Then compound **4**a was added to concentrated hydrochloric acid(37%, 100 mL) without drying. The mixture was stirred at 55 °C for 5 h, cooled to room temperature and filtered. Then the filtrate was concentrated to dryness to give compound **5**a with a yield of 34.6%.

Compounds **5**b—**5**f were synthesized *via* the method similar to that described in the synthesis of compound **5**a.

*2.2.6 General Synthetic Method of Compounds **1***

A mixture of compounds **5**(3.3 mmol), 4-dimethylaminopyridine(DMAP) of catalytic amount and compounds **3**(3.3 mmol) in CH_2Cl_2(50 mL) was stirred in an ice bath for 10 min, then triethylamine(2.22 g, 0.022 mol) was added dropwise. The mixture was stirred for another 2 h, after which the reaction mixture was poured into ice water and then extracted with CH_2Cl_2(50 mL×2). The combined organic layer was dried over anhydrous sodium sulfate, concentrated and purified by column chromatography to yield the corresponding compounds **1**.

Compound **1**a, yield 57.0%, white solid, m. p. 94.0—96.6 °C. ^{1}H NMR, δ: 1.63(d, J=6.9 Hz, 3H, CH_3), 2.51(t, J=2.4 Hz, 1H, C≡CH), 4.58(d, J=2.7 Hz, 2H, CH_2), 4.74(q, J=6.9 Hz, 1H, CH), 6.87—7.06(m, 5H, PhH), 7.34—7.38(m, 1H, PhH), 7.46(dd, J_1=10.5 Hz, J_2=1.8 Hz, 1H, PhH), 9.12(brs, 1H, NH). LC-MS(positive ion), *m/z*: 355.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{15}FN_2O_4$: C 64.40, H 4.27, N 7.91; found C 64.62, H 4.30, N 7.83.

Compound **1**b, yield 68.1%, white solid, m. p. 92.2—92.7 °C. ^{1}H NMR, δ: 1.62(d, J=6.6 Hz, 3H, CH_3), 4.55(d, J=7.2 Hz, 2H, CH_2), 4.73(q, J=6.6 Hz, 1H, CH), 6.14(t, J=7.2 Hz, 1H, CH), 6.87—7.06(m, 5H, PhH), 7.34—7.38(m, 1H, PhH), 7.46(dd, J_1=9.9 Hz, J_2=1.8 Hz, 1H, PhH), 8.93(brs, 1H, NH). ^{13}C NMR, δ: 18.76, 72.64, 75.54, 106.45, 117.13, 117.60, 118.91, 120.75, 121.21, 123.71, 127.07, 129.41, 149.43, 150.12, 151.27, 153.84, 169.58. LC-MS(positive ion), *m/z*: 424.9[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{15}Cl_2FN_2O_4$: C 53.67, H 3.56, N 6.59; found C 53.71, H 3.66, N 6.67.

Compound **1**c, yield 43.8%, white solid, m. p. 95.2—96.3 °C. ^{1}H NMR, δ: 1.61(d, J=6.6 Hz, 3H, CH_3), 4.67(d, J=6.6 Hz, 2H, CH_2), 4.74(q, J=6.6 Hz, 1H, CH), 6.02—6.08(m, 1H, CH), 6.30(d, J=7.5 Hz, 1H, CClH), 6.87—7.09(m, 5H, PhH), 7.34—7.38(m, 1H, PhH), 7.46(dd, J_1=10.2 Hz, J_2=1.8 Hz, 1H, PhH), 8.93(s, 1H, NH). ^{13}C NMR, δ: 18.70, 71.28, 75.39, 106.26, 117.03, 117.60, 118.64, 120.77, 121.16, 123.60, 125.44, 129.37, 149.14, 150.18, 150.66, 154.10, 169.21. LC-MS(positive ion), *m/z*: 391.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{16}ClFN_2O_4$: C 58.40, H 4.13, N 7.17; found: C 58.56, H 4.23, N 7.09. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3223, 3055, 2986, 2231, 1668, 1635, 1614, 1587, 1501, 1450, 1280, 848.

Compound **1**d, yield 41.5%, white solid, m. p. 107.2—110.1 °C. ^{1}H NMR, δ: 1.63(d, J=6.6 Hz, 3H, CH_3), 4.37—4.41(m, 2H, CH_2), 4.72(q, J=6.6 Hz, 1H, CH), 6.05—6.12(m, 1H, CH), 6.24(d, J=13.5 Hz, 1H, CClH), 6.88—7.06(m, 5H, PhH), 7.34—7.38(m, 1H, PhH), 7.46(dd, J_1=10.2 Hz, J_2=1.8 Hz, 1H, PhH), 8.85(s, 1H, NH). LC-MS(positive ion), *m/z*: 391.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{16}ClFN_2O_4$: C 58.40, H 4.13, N 7.17; found: C 58.32, H 4.00, N 7.28.

Compound **1**e, yield 78.9%, white solid, m. p. 109.0—109.6 °C. ^{1}H NMR, δ: 1.63(d, J=6.9 Hz, 3H, CH_3), 4.51(d, J=5.4 Hz, 2H, CH_2), 4.72(q, J=6.9 Hz, 1H, CH), 5.46(d, J=5.4 Hz, 2H, CH═C**H**$_2$), 6.87—7.05(m, 5H, PhH), 7.34—7.38(m, 1H, PhH), 7.46(dd, J_1=10.2 Hz, J_2=1.8 Hz, 1H, PhH), 8.95(s, 1H, NH). ^{13}C NMR, δ: 18.67, 75.02, 78.27, 106.15, 116.92, 117.51, 118.02, 118.61, 120.68, 121.01, 129.27, 135.60, 149.04, 150.08, 150.57, 153.91, 169.02. LC-MS (positive ion), *m/z*: 390.8[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{16}ClFN_2O_4$: C 58.40, H 4.13, N 7.17; found: C 58.55, H 4.21, N 7.00.

Compound **1**f, yield 47.1%, white solid, m. p. 102.4—103.0 °C. ^{1}H NMR, δ: 1.61(d, J=6.6 Hz, 3H, CH_3), 4.35—4.43(m, 2H, CH_2), 4.69(q, J=6.6 Hz, 1H, CH), 5.25—5.33(m, 2H, CH═C**H**$_2$), 5.90—6.03(m, 1H, C**H**═CH_2), 6.86—7.05(m, 5H, PhH), 7.34—7.38(m, 1H, PhH), 7.46(dd, J_1=10.2 Hz, J_2=1.8 Hz, 1H, PhH), 8.85(brs, 1H, NH). ^{13}C NMR, δ: 18.77, 75.19, 77.49, 106.16, 116.90, 117.55, 118.56, 120.70, 121.07, 121.36, 129.33, 131.50, 149.00, 150.01, 150.59, 153.88, 168.73. LC-MS(positive ion), *m/z*: 357.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{17}FN_2O_4$: C 64.04, H 4.81, N 7.86; found: C 63.98, H 4.69, N 7.76.

Compound **1**g, yield 42.7%, white solid, m. p. 154.8—155.2 °C. ^{1}H NMR, δ: 1.64(d, J=6.6 Hz, 3H, CH_3), 2.57(t, J=2.4 Hz, 1H, C≡CH), 4.59(s, 2H, CH_2), 4.77(q, J=6.6 Hz, 1H, CH), 7.02(d, J=9.0 Hz, 2H, PhH), 7.27(dd, J_1=8.4 Hz, J_2=2.4 Hz, 1H, benzoxazole-H), 7.34(d, J=9.0 Hz, 2H, PhH), 7.38(d, J=8.4 Hz, 1H, benzoxazole-H), 7.45(d, J=2.4 Hz, 1H, benzoxazole-H), 9.12(brs, 1H, NH). ^{13}C NMR, δ: 18.71, 63.66, 75.32, 76.70, 77.48, 110.69, 116.68, 119.16, 121.70, 125.11, 128.84, 139.29, 147.22, 148.41, 154.72, 162.81, 168.85. LC-MS(positive ion), *m/z*: 387.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{15}ClN_2O_5$: C 59.00, H 3.91, N 7.24; found: C 59.14, H 3.99, N 7.50.

Compound **1**h, yield 67.6%, white solid, m. p. 142.1—142.6 °C. ^{1}H NMR, δ: 1.62(d, J=6.6 Hz, 3H, CH_3), 4.55(d, J=7.2 Hz, 2H, CH_2), 4.78(q, J=6.6 Hz, 1H, CH), 6.19(t, J=7.2 Hz, 1H, CH), 7.01(d, J=9.0 Hz, 2H, PhH), 7.27(dd, J_1=8.7 Hz, J_2=2.1 Hz, 1H, benzoxazole-H), 7.35(d, J=9.0 Hz, 2H, PhH), 7.39(d, J=8.7 Hz, 1H, benzoxazole-H), 7.46(d, J=2.1 Hz, 1H, benzoxazole-H), 8.95(brs, 1H, NH). ^{13}C NMR, δ: 18.66, 72.54, 75.31, 110.66, 116.58, 119.13, 121.66, 123.60, 125.08, 126.94, 128.81, 139.25, 147.16, 148.36, 154.64, 162.71, 169.40. LC-MS(positive ion), *m/z*: 457.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{15}Cl_3N_2O_5$: C 49.86, H 3.30, N 6.12; found C 50.01, H 3.43, N 6.00. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3196, 3071, 2986, 1663, 1627, 1572, 1505, 1454, 1349, 1242, 863, 828.

Compound **1**i, yield 30.5%, white solid, m. p. 128.2—128.3 °C. ^{1}H NMR, δ: 1.57(d, J=6.6 Hz, 3H, CH_3), 4.66(d, J=6.0 Hz, 2H, CH_2), 4.75(q, J=6.6 Hz, 1H, CH), 6.03—6.05(m, 1H, CH), 6.30(d, J=7.2 Hz, 1H, CClH), 6.97(d, J=9.0 Hz, 2H, PhH), 7.27(dd, J_1=8.4 Hz, J_2=1.8 Hz, 1H, benzoxazole-H), 7.34(d, J=9.0 Hz, 2H, PhH), 7.39(d, J=8.4 Hz,

1H, benzoxazole-H), 7.46(d, *J*=1.8 Hz, 1H, benzoxazole-H), 9.00(brs, 1H, NH). ^{13}C NMR, *δ*: 18.72, 71.39, 75.54, 110.75, 116.79, 119.23, 121.71, 123.77, 125.18, 125.48, 128.94, 139.38, 147.34, 148.49, 154.77, 162.80, 169.26. LC-MS(positive ion), *m/z*: 423.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{16}Cl_2N_2O_5$: C 53.92, H 3.81, N 6.62; found: C 54.01, H 4.03, N 6.50.

Compound **1**j, yield 22.7%, white solid, m. p. 138.9—146.2 °C. ^{1}H NMR, *δ*: 1.62(d, *J*=6.6 Hz, 3H, CH_3), 4.35—4.41(m, 2H, CH_2), 4.73(q, *J*=6.6 Hz, 1H, CH), 6.03—6.12(m, 1H, CH), 6.26(d, *J*=7.5 Hz, 1H, CClH), 6.97(d, *J*=9.3 Hz, 2H, PhH), 7.27(dd, J_1=8.4 Hz, J_2=2.1 Hz, 1H, benzoxazole-H), 7.36(d, *J*=9.3 Hz, 2H, PhH), 7.42(d, *J*=8.4 Hz, 1H, benzoxazole-H), 7.45(d, *J*=2.1 Hz, 1H, benzoxazole-H), 8.84(brs, 1H, NH). ^{13}C NMR, *δ*: 18.85, 74.42, 75.43, 110.74, 116.60, 119.25, 121.75, 125.17, 125.54, 127.00, 128.93, 139.41, 147.34, 148.49, 154.76, 162.78, 169.17. LC-MS(positive ion), *m/z*: 423.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{16}Cl_2N_2O_5$: C 53.92, H 3.81, N 6.62; found: C 53.86, H 3.82, N 6.80.

Compound **1**k, yield 28.3%, white solid, m. p. 134.5—136.5 °C. ^{1}H NMR, *δ*: 1.63(d, *J*=6.9 Hz, 3H, CH_3), 4.51(d, *J*=4.2 Hz, 2H, CH_2), 4.75(q, *J*=6.9 Hz, 1H, CH), 5.43(d, *J*=9.9 Hz, 2H, CCl═CH_2), 7.00(d, *J*=9.0 Hz, 2H, PhH), 7.27(dd, J_1=8.4 Hz, J_2=1.8 Hz, 1H, benzoxazole-H), 7.34(d, *J*=9.0 Hz, 2H, PhH), 7.39(d, *J*=8.4 Hz, 1H, benzoxazole-H), 7.45(d, *J*=1.8 Hz, 1H, benzoxazole-H), 9.01(brs, 1H, NH). ^{13}C NMR, *δ*: 18.71, 75.18, 78.43, 110.86, 116.56, 118.26, 119.13, 121.61, 125.08, 128.81, 135.62, 139.24, 147.17, 148.36, 154.66, 162.70, 169.01. LC-MS(positive ion), *m/z*: 422.8[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{16}Cl_2N_2O_5$: C 53.92, H 3.81, N 6.62; found: C 53.90, H 3.77, N 6.82.

Compound **1**l, yield 30.9%, white solid, m. p. 150.5—160.6 °C. ^{1}H NMR, *δ*: 1.61(d, *J*=6.9 Hz, 3H, CH_3), 4.39—4.43(m, 2H, CH_2), 4.74(q, *J*=6.9 Hz, 1H, CH), 5.26—5.34(m, 2H, CH_2), 5.92—6.01(m, 1H, CH), 6.98(d, *J*=9.0 Hz, 2H, PhH), 7.27(dd, J_1=8.4 Hz, J_2=2.1 Hz, 1H, benzoxazole-H), 7.35(d, *J*=9.0 Hz, 2H, PhH), 7.39(d, *J*=8.4 Hz, 1H, benzoxazole-H), 7.45(d, *J*=2.1 Hz, 1H, benzoxazole-H), 8.83(brs, 1H, NH). ^{13}C NMR, *δ*: 18.82, 75.37, 77.62, 110.67, 116.57, 119.18, 121.58, 121.63, 125.09, 128.81, 131.51, 139.31, 147.14, 148.40, 154.75, 162.74, 168.70. LC-MS(positive ion), *m/z*: 389.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{19}H_{17}ClN_2O_5$: C 58.70, H 4.41, N 7.21; found: C 58.77, H 4.54, N 7.28. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3190, 2996, 1674, 1628, 1572, 1505, 1453, 1348, 1241, 862, 826.

Compound **1**m, yield 30.2%, white solid, m. p. 136.2—139.1 °C. ^{1}H NMR, *δ*: 1.66(d, *J*=6.6 Hz, 3H, CH_3), 2.58(t, *J*=2.1 Hz, 1H, C≡CH), 4.60(d, *J*=6.9 Hz, 2H, CH_2), 4.67(q, *J*=6.6 Hz, 1H, CH), 7.00(d, *J*=9.0 Hz, 2H, PhH), 7.21(d, *J*=9.0 Hz, 2H, PhH), 7.60(dd, J_1=9.0 Hz, J_2=2.1 Hz, 1H, quinoxalin-H), 7.66(d, *J*=9.0 Hz, 1H, quinoxalin-H), 8.07(d, *J*=2.4 Hz, 1H, quinoxalin-H), 8.70(s, 1H, quinoxalin-H), 9.13(brs, 1H, NH). ^{13}C NMR, *δ*: 18.73, 63.48, 75.13, 76.97, 77.01, 116.36, 122.70, 127.83, 128.50, 131.11, 132.80, 138.27, 139.58, 139.97, 146.86, 154.00, 157.00, 169.05. LC-MS(positive ion), *m/z*: 398.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{20}H_{16}ClN_3O_4$: C 60.38, H 4.05, N 10.56; found: C 60.51, H 4.16, N 10.55. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3290, 3197, 3006, 2122, 1675, 1611, 1579, 1508, 1491, 1443, 1401, 1241, 829.

Compound **1**n, yield 41.0%, white solid, m. p. 134.8—135.6 °C. ^{1}H NMR, *δ*: 1.64(d, *J*=6.9 Hz, 3H, CH_3), 4.59(d, *J* =6.9 Hz, 2H, CH_2), 4.80(q, *J*=6.9 Hz, 1H, CH), 6.15(t, *J*=6.9 Hz, 1H, CH), 6.97(d, *J*=9.0 Hz, 2H, PhH), 7.24(d, *J*=9.0 Hz, 2H, PhH), 7.59(dd, J_1=8.7 Hz, J_2=2.4 Hz, 1H, quinoxalin-H), 7.62(d, *J*=8.7 Hz, 1H, quinoxalin-H), 8.06(d, *J*=2.4 Hz, 1H, quinoxalin-H), 8.69(s, 1H, quinoxalin-H), 9.05(brs, 1H, NH). ^{13}C NMR, *δ*: 18.76, 72.54, 75.35, 116.39, 122.82, 123.63, 127.00, 127.88, 128.69, 131.19, 132.92, 138.38, 139.68, 140.02, 147.00, 153.98, 157.02, 169.61. LC-MS(positive ion), *m/z*: 468.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{20}H_{16}Cl_3N_3O_4$: C 51.25, H3.44, N 8.97; found: C 51.32, H 3.57, N 9.01. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3202, 3063, 2994, 1672, 1613, 1579, 1508, 1491, 1446, 1400, 1242, 830.

Compound **1**o, yield 39.8%, white solid, m. p. 132.2—133.4 °C. ^{1}H NMR, *δ*: 1.64(d, *J*=6.9 Hz, 3H, CH_3), 4.67(dd, J_1=6.6 Hz, J_2=1.2 Hz, 2H, CH_2), 4.79(q, *J*=6.9 Hz, 1H, CH), 6.02—6.09(m, 1H, CH), 6.33(d, *J*=7.2 Hz, 1H, CClH), 6.98(d, *J*=9.0 Hz, 2H, PhH), 7.21(d, *J*=9.0 Hz, 2H, PhH), 7.60(dd, J_1=8.7 Hz, J_2=2.4 Hz, 1H, quinoxalin-H), 7.69(d, *J*=8.7 Hz, 1H, quinoxalin-H), 8.07(d, *J*=2.4 Hz, 1H, quinoxalin-H), 8.69(s, 1H, quinoxalin-H), 9.00(brs, 1H, NH). ^{13}C NMR, *δ*: 18.78, 71.27, 75.38, 116.43, 122.79, 123.70, 125.44, 127.89, 128.69, 131.22, 132.94, 138.39, 139.66, 140.02, 146.97, 154.01, 157.04, 169.35. LC-MS(positive ion), *m/z*: 434.0[M+H]$^+$. Elemental anal.(%) calcd. for $C_{20}H_{17}Cl_2N_3O_4$: C 55.32, H 3.95, N 9.68; found: C 55.44, H 3.89, N 9.60. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3187, 3002, 2933, 1672, 1610, 1579, 1509, 1491, 1446, 1400, 1242, 727.

Compound **1**p, yield 33.5%, white solid, m. p. 141.9—143.8 °C. ^{1}H NMR, *δ*: 1.64(d, *J*=6.9 Hz, 3H, CH_3), 4.31—4.46(m, 2H, CH_2), 4.77(q, *J*=6.9 Hz, 1H, CH), 6.03—6.12(m, 1H, CH), 6.19(d, *J*=13.5 Hz, 1H, ClCH), 6.98(d, *J*=9.0 Hz, 2H, PhH), 7.22(d, *J*=9.0 Hz, 2H, PhH), 7.62(dd, J_1=9.0 Hz, J_2=2.4 Hz, 1H, quinoxalin-H), 7.67(d, *J*=9.0 Hz, 1H, quinoxalin-H), 8.06(d, *J*=2.4 Hz, 1H, quinoxalin-H), 8.70(s, 1H, quinoxalin-H), 8.89(brs, 1H, NH). ^{13}C NMR, *δ*: 18.91, 74.36, 75.23, 116.23, 122.90, 125.72, 126.88, 127.91, 128.65, 131.24, 132.96, 138.41, 139.68, 140.03, 146.98, 154.04, 157.06, 169.24. LC-MS(positive ion), *m/z*: 433.8[M+H]$^+$. Elemental anal.(%) calcd. for $C_{20}H_{17}Cl_2N_3O_4$: C 55.32, H 3.95, N 9.68; found: C 55.23, H 4.11, N 9.59. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3194, 3001, 1670, 1611, 1571, 1508, 1491, 1445, 1401, 1240, 828.

Compound **1**q, yield 65.8%, white solid, m. p. 149.9—151.2 °C. ^{1}H NMR, *δ*: 1.66(d, *J*=6.6 Hz, 3H, CH_3), 4.52(d, *J*=3.0 Hz, 2H, CH_2), 4.78(q, *J*=6.6 Hz, 1H, CH), 5.41(d, *J*=1.5 Hz, 1H, CCl═CH_2), 5.47(d, *J*=1.5 Hz, 1H, CCl═CH_2), 6.98(d, *J*=9.3 Hz, 2H, PhH), 7.20(d, *J*=9.3 Hz, 2H, PhH), 7.60(dd, J_1=9.0 Hz, J_2=2.1 Hz, 1H, quinoxalin-H), 7.66(d, *J*=9.0 Hz, 1H, quinoxalin-H), 8.07(d, *J*=2.1 Hz, 1H, quinoxalin-H), 8.70(s, 1H, quinoxalin-H), 9.00(brs, 1H, NH). ^{13}C NMR, *δ*: 18.84, 75.11, 78.43, 116.26, 118.48, 122.76, 127.87, 128.59, 131.16, 132.86, 135.56, 138.33, 139.64, 140.00, 146.93, 154.00, 157.02, 169.16. LC-MS(positive ion), *m/z*:

433.8[M+H]$^+$. Elemental anal.(%) calcd. for $C_{20}H_{17}Cl_2N_3O_4$: C 55.32, H 3.95, N 9.68; found: C 55.54, H 4.09, N 9.66.

Compound **1**r, yield 32.1%, white solid, m. p. 152.0—152.4 °C. ^{1}H NMR, δ: 1.63(d, J=6.9 Hz, 3H, CH_3), 4.40—4.44(m, 2H, CH_2), 4.76(q, J=6.9 Hz, 1H, CH), 5.26—5.34(m, 2H, CH_2), 5.90—6.02(m, 1H, CH), 6.97(d, J=9.0 Hz, 2H, PhH), 7.19(d, J=9.0 Hz, 2H, PhH), 7.60(dd, J_1=8.7 Hz, J_2=2.1 Hz, 1H, quinoxalin-H), 7.69(d, J=8.7 Hz, 1H, quinoxalin-H), 8.07(d, J=2.1 Hz, 1H, quinoxalin-H), 8.69(s, 1H, quinoxalin-H), 8.90(brs, 1H, NH). ^{13}C NMR, δ: 18.89, 75.22, 77.53, 116.26, 121.62, 122.72, 127.84, 128.62, 131.14, 131.47, 132.85, 138.34, 139.62, 140.00, 146.85, 154.06, 157.01, 168.89. LC-MS(negative ion), *m/z*: 397.8[M−H]$^+$. Elemental anal.(%) calcd. for $C_{20}H_{18}ClN_3O_4$: C 60.08, H 4.54, N 10.51; found: C 60.17, H 4.67, N 10.59. IR(KBr), $\tilde{\nu}$/cm^{-1}: 3186, 3008, 1672, 1610, 1580, 1509, 1490, 1445, 1401, 1242, 826.

2.3 Biological Activity

The herbicidal activities of the title compounds against dicotyledon weeds(velvetleaf: *Abutilon theophrasti Medic*; redroot pigweed: *Amaranthus ascedense* L.; fat hen: *Chenopodium album* L.) and monocotyledon weeds(crabgrass: *Digitaria sanguinalis* L.; barnyard grass: *Echinochloa crus-galli* L.; green foxtail: *Setaria viridis* L.) and crop selectivity(rice, wheat, maize, soybean, rape, cotton) were measured with the help of standard operating procedures(SOP) assay described by Huang *et al*.[21]

The IC_{50} values were calculated *via* data processing system(DPS) software.

3 Results and Discussion

3.1 Synthesis and Structure Characterization

The synthetic route shown in Scheme 2 provided an efficient synthetic route for the target compounds. All the reactions were carried out under the protection of dry nitrogen atmosphere or with a calcium chloride tube. The target compounds were synthesized *via* the reaction between allyloxy/propargyloxy ammonium chloride **5** and an appropriate aryloxyphenoxypropanoyl chloride **3**. Their structures were structurally confirmed by means of ^{1}H NMR, ^{13}C NMR, LC-MS, elemental analysis and IR spectroscopy. The observed molecular weight of each target compound was as expected in the MS analysis.

3.2 Herbicidal Activity

Table 1 shows the herbicidal activity of compounds **1** against *Abutilon theophrasti Medic, Amaranthus ascedense* L., *Chenopodium album* L., *Digitaria sanguinalis* L., *Echinochloa crus-galli and Setaria viridis* L. at dosage of 2250 g/hm^2 with clodinafop-propargyl as control group.

Table 1 Herbicidal activity(%) of compounds 1 at dosage of 2250 g/hm^{2*}

Compd.	Preemergence						Postemergence					
	A. T.	*A. A.*	*C. A.*	*D. S.*	*E. C.*	*S. V.*	*A. T.*	*A. A.*	*C. A.*	*D. S.*	*E. C.*	*S. V.*
1a	0	0	0	0	0	0	0	0	0	50	50	50
1b	0	0	0	100	95	100	0	0	0	95	95	95
1c	0	0	0	100	95	100	0	0	0	95	95	95
1d	0	0	0	100	95	100	0	0	0	95	95	95
1e	0	0	0	95	100	100	0	50	70	100	100	100
1f	0	0	0	0	0	0	0	0	0	0	0	0
1g	0	0	0	100	100	100	0	0	0	70	70	70
1h	0	0	0	100	100	100	0	0	0	0	0	0
1i	0	0	0	100	100	100	0	0	0	0	0	0
1j	0	0	0	100	100	100	0	0	0	0	0	0
1k	0	0	0	100	100	100	0	0	0	100	100	100
1l	0	0	0	100	100	100	0	0	0	60	60	60
1m	0	0	0	100	100	100	0	0	0	100	100	100
1n	0	0	0	100	100	100	0	0	0	100	100	100
1o	0	0	0	100	100	100	0	0	0	100	100	100
1p	0	0	0	100	100	100	0	50	50	100	100	100
1q	0	0	0	100	100	100	30	80	80	100	100	100
1r	40	80	60	100	100	100	0	0	0	100	100	100
CK	0	0	0	100	100	100	0	0	0	100	100	100

* The activity was represented in growth inhibition(%); *A. T.*, *Abutilon theophrasti Medic*; *A. A.*, *Amaranthus ascedense* L.; *C. A.*, *Chenopodium album* L.; *D. S.*, *Digitaria sanguinalis* L.; *E. C.*, *Echinochloa crus-galli* L.; *S. V.*, *Setaria viridis* L; CK: clodinafop-propargyl.

As shown in Table 1, compounds **1**(except **1**a, **1**f—**1**j, **1**l) exhibit more than 90% herbicidal efficiency to monocotyledonous herbs(*Digitaria sanguinalis*, *Echinochloa crus-galli and Setaria viridis*) under both pre- and postemergence treatments. Moreover, some of compounds **1** also show excellent inhibitory activity against dicotyledonous weeds. Compounds **1**g—**1**j show 100% herbicidal activity to monocotyledonous herbs under pre-mergence treatments but low or no activity under postemergence treatments. Compounds **1**a and **1**f have no or very low herbicidal activity. Compounds **1** have better activity to monocotyledonous herbs than to dicotyledon weeds, which suggests that the prepared compounds are selectable to monocotyledonous herbs. To evaluate herbicidal activities of compounds **1**, the preliminary herbicidal activities of more effective compounds against monocotyledon weeds(*Digitaria sanguinalis, Echinochloa crus-galli and Setaria viridis*) are

presented in Table 2. It can be seen from Table 2 that compounds **1** exhibit better herbicidal efficacy under postemergence treatments than under preemergence treatments. Compounds **1**m—**1**p and **1**r have more than 90% herbicidal efficiency under both pre- and postemergence treatments, but compounds **1**b—**1**e, **1**g—**1**i and **1**l have no or low herbicidal activity.

Table 2 Preliminary herbicidal activity of compounds 1

Compd.	Activity(%) Postemergence(75 g·hm^{-2})			Preemergence(75 g·hm^{-2})			Compd.	Activity(%) Postemergence(75 g·hm^{-2})			Preemergence(75 g·hm^{-2})		
	D. S.	*E. C.*	*S. V.*	*D. S.*	*E. C.*	*S. V.*		*D. S.*	*E. C.*	*S. V.*	*D. S.*	*E. C.*	*S. V.*
1a	90	NT	NT	NT	NT	NT	**1**k	90	80	90	50	50	50
1b	30	30	30	0	0	0	**1**l	0	0	0	0	0	0
1c	30	30	30	0	0	0	**1**m	100	100	100	100	90	90
1d	30	30	30	0	0	0	**1**n	100	100	100	100	90	90
1e	50	50	50	0	0	0	**1**o	100	100	100	100	90	90
1g	30	0	30	0	0	0	**1**p	100	100	100	90	90	90
1h	0	0	0	0	0	0	**1**q	100	100	100	90	50	90
1i	0	0	0	0	0	0	**1**r	100	100	100	100	90	90
1j	30	0	30	0	0	0	CK*	100	100	100	100	100	100

* CK: clodinafop-propargyl.

Our main interest is to develop a new postemergence APP herbicide. To evaluate their postemergence bioactivity, further herbicidal activity and IC_{50} values of compounds **1**m—**1**r against *Digitaria sanguinalis* and *Echinochloa crus-galli* were determined, and the test results are listed in Table 3. The results show that most of the determined compounds have high growth inhibition activity against *Digitaria sanguinalis*. For example, compounds **1**m—**1**o and **1**r exhibit higher activity(IC_{50} values of $\leqslant$11.6 g/hm^2) comparing to clodinafop-propargyl(46.5 g/hm^2), in particular, compounds **1**m and **1**r have IC_{50} values of 6.8 and 7.4 g/hm^2, which are much more lower than that of clodinafop-propargyl. The results also indicate that some compounds **1** exhibit high growth inhibition activity against *Echinochloa crus-galli.* For example, the IC_{50} values of compounds **1**m—**1**p and **1**r are $\leqslant$6.5 g/hm^2, which are lower than that of clodinafop-propargyl(14.6 g/hm^2).

Table 3 IC_{50} values of compounds 1m—1r against *D. S.* and *E. C.* under postemergence treatments*

Compd.	IC_{50} against *D.S.*/(g·hm^{-2})	IC_{50} against *E.C.*/(g·hm^{-2})
1m	6.8	6.5
1n	11.6	6.2
1o	11.4	5.9
1p	24.6	6.0
1q	46.5	17.9
1r	7.4	6.0
CK	46.5	14.6

* IC_{50}: Inhibitive concentration(g/hm^2) to obtain 50% growth inhibition; CK: clodinafop-propargyl.

Based on comparison of IC_{50} values, it is easy to conclude that the IC_{50} values of compounds **1**m—**1**r to inhibit *Echinochloa crus-galli* are lower than that to inhibit *Digitaria sanguinalis*. Further more, we can conclude that the compounds synthesized are more sensitive to *Echinochloa crus-galli* than to *Digitaria sanguinalis*. Among all the prepared compounds, compounds **1**m—**1**o and **1**r have better herbicidal activity against *Digitaria sanguinalis* and *Echinochloa crus-galli* when compared to clodinafop-propargyl. In particular, compounds **1**m and **1**r are much more effective than clodinafop-propargyl.

3.3 Crop Selectivity

On the basis of the herbicidal activities of compounds **1** and their IC_{50} values against *Digitaria sanguinalis* and *Echinochloa crus-galli*, compounds **1**m and **1**r were chosen for the further evaluation of their crop selectivities in comparison with clodinafop-propargyl. The phytotoxicity data of compounds **1**m and **1**r and clodinafop-propargyl to six crops are listed in Table 4. When applied to rice, wheat and maize, the crop selectivities of compounds **1**m and **1**r are not as good as that of clodinafop-propargyl, but when applied to the broadleaf crop(soybean, rape and cotton), safety of compounds **1**m and **1**r is similar to that of clodinafop-propargyl. In a word, compounds **1**m and **1**r can be used as herbicides for soybean, rape and cotton crop.

Table 4 Phytotoxicity of compounds 1m, 1r and clodinafop-propargyl to crops*

Compd.	Dosage/(g·hm^{-2})	Postemergence RIC	WHE	MAI	SOY	RAP	COT	Preemergence RIC	WHE	MAI	SOY	RAP	COT
1m	30	—	—	—	++	++	++	—	++	++	++	++	++
	60	—	—	—	++	++	++	—	—	++	++	++	++
	120	—	—	—	++	++	++	—	—	—	++	++	++
1r	30	—	—	—	++	++	++	—	++	—	++	++	++
	60	—	—	—	++	++	++	—	—	—	++	++	++
	120	—	—	—	++	++	++	—	—	—	++	++	++
CK	30	—	++	—	++	++	++	—	++	—	++	++	++
	60	—	++	—	++	++	++	—	++	—	++	++	++
	120	—	++	—	++	++	++	—	++	—	++	++	++

* Rating system for phytotoxicity: ++, no growth inhibition; —, >10% growth inhibition; RIC: rice; WHE: wheat; MAI: maize; SOY: soybean; RAP: rape; COT: cotton; CK: clodinafop-propargyl.

3.4 Structure-activity Relationships

In general formula of compounds **1**, the structural change includes two parts, Ar moiety and R moiety. From the results of the test activity data and IC_{50} values, we can see that there are some interesting structure-activity relationships. In general, Ar moiety is the most influential group to the activity, and compounds **1** with the Ar group(6-chloroquinoxalin-2-yl) exhibit higher herbicidal activity than those with phenyl group or benzoxazolyl group, and the following order of the influence of group Ar can be summarized: 6-chloroquinoxalin-2-yl> 6-chloro-2-benzoxazolyl or 4-cyano-2-fluorophenyl. When the Ar moiety is 6-chloroquinoxalin-2-yl, the herbicidal activities are influenced by the substituent group R. As showed in Table 4, when group R is vinyl or ethynyl without substituents, the compounds such as compounds **1**m or **1**r show the highest activity. When R is C═C$(Cl)_2$ or CH═CHCl(*cis*), the activities of compounds are lower than those of compounds **1**m and **1**r with R group but without substituents. The compounds with R═CHCHCl(*trans*) or $CClCH_2$ show the lowest activity.

4 Conclusions

In conclusion, the synthesis and herbicidal activities of a series of *N*-allyloxy/propargyloxy aryloxyphenoxy propionamide derivatives were described. The bioassay data showed that many compounds exhibited excellent herbicidal activities against *Digitaria sanguinalis*, *Echinochloa crus-galli* L. and *Setaria viridis*. In particular, compounds **1**m and **1**r were much more effective against *Digitaria sanguinalis* and *Echinochloa crus-galli* than clodinafop-propargyl. It was imperative that compounds **1**m and **1**r were safe to soybean, rape and cotton crop and could be used as herbicides for soybean, rape and cotton crop.

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