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# Design, synthesis and insecticidal evaluation of aryloxy dihaloropropene derivatives

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ABSTRACT

*Plutella xylostella* (*P. xylostella*) is a highly migratory, cosmopolitan species and one of the most important pest of cruciferous crops worldwide. Pyridalyl as a novel class of insecticides has good efficacy against *P. xylostella*. On the basis of the commercial insecticide pyridalyl, a series of new aryloxy dihaloropropene derivatives were designed and synthesized by using Intermediate Derivatization Methods. Their chemical structures were confirmed by $^{1}$H NMR, high-resolution mass spectrum (HRMS), and single-crystal X-ray diffraction analysis. The insecticidal activities of the new compounds against *P. xylostella* were evaluated. The results of bioassays indicated that most of the compounds showed moderate to high activities at the tested concentration, especially compounds **10e** and **10g** displayed more than 75% insecticidal activity against *P. xylostella* at 6.25 mg/L, while pyridalyl showed 50% insecticidal activity at the same concentration. The field trials result of the insecticidal activities showed that compound **10e** as a 10% emulsifiable concentrate (EC) was effective in the control of *P. xylostella* at 75–150 g a.i./ha, and the mortality of *P. xylostella* for treatment with compound **10e** at 75 g a.i./ha was equivalent to pyridalyl at 105 g a.i./ha.



## 1. Introduction

*Plutella xylostella* (*P. xylostella*) is one of the most destructive insects of cruciferous plants throughout the word, and it has develop resistance to every class insecticides, even has become resistant to chlorantraniliprole (Chlorantraniliprole is a recently introduced to the market insecticide with a new mode of action targeting the ryanodine receptor and has high potency against sensitive *P. xylostella*).[1] Pyridalyl as a novel class of insecticides has a novel but unknown mode of action with good control efficacy against various *lepidopterous* and *thysanopterous* pests on cotton and vegetables without phytotoxicity. It also appears to be different from other existing insecticides because it controls populations of *Heliothis virescens* (*H. virescens*) and *P. xylostella* which are resistant to various currently used insecticides. Pyridalyl is also less harmful than existing insecticides to various beneficial arthropods.[2,3] Therefore, we are interested in further modifying its chemical structure.

Intermediate Derivatization Methods (IDM) is a useful approach for agrochemical discovery: common intermediate method, terminal group replacement method, and active compound derivatization method.[4–7] Among these three approaches, the terminal group replacement method has been proven as an effective and practical method.[8–19] It is well-known that the aryloxyphenyl derivatives have been widely used in agriculture. For example, pyriproxyfen,[20] fenoxycarb,[20] flufenoxuron,[21] chlorfluazuron[21] and cyhalothrin[22] have been used as commercial insecticides, haloxyfop-methyl[23] and fluazifop-butyl[23] as herbicides, famoxadone[24] as fungicide (Fig. 1). So the terminal group replacement method was applied by introducing aryloxyphenyl to pyridalyl to replace pyridinyl (moiety **B**, Fig. 2). A series of new dihalopropene analog with the substituted aryloxyphenyl were synthesized and bioassayed. The detailed syntheses, bioassays, and structure–activity relationships of these compounds are discussed below.

## 2. Results and discussion

### 2.1. Chemistry

The synthetic routes for all the intermediates and target compounds were illustrated in Schemes 1–4. Starting from *p*-dihydroxybenzene (**1**), the Intermediates **3a**–**3c** were prepared by the chlorination with sulfonyl chloride, which has been reported before (Scheme 1).[15,25–27]

Two routes were used to synthesize the aryloxyphenols **6b**–**6m** and **7a**–**7k** as shown in Scheme 2. Aryloxyphenols **6b**–**6f** were prepared by Baeyer–Villiger oxidation/hydrolysis of aryloxybenzaldehydes **5b**–**5f** with *m*-chloroperoxybenzoic acid (*m*-CPBA) in 50–85% yield. The corresponding aryloxybenzaldehydes **5b**–**5f**

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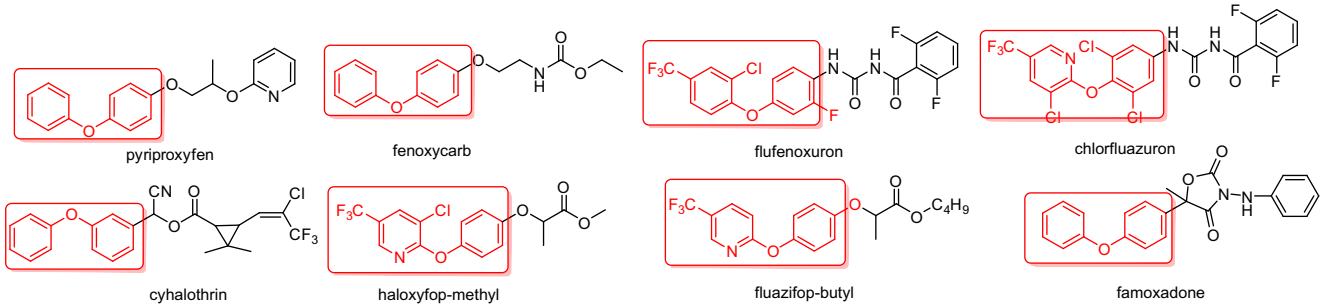



**Figure 1.** Commercial aryloxyphenyl derivatives.

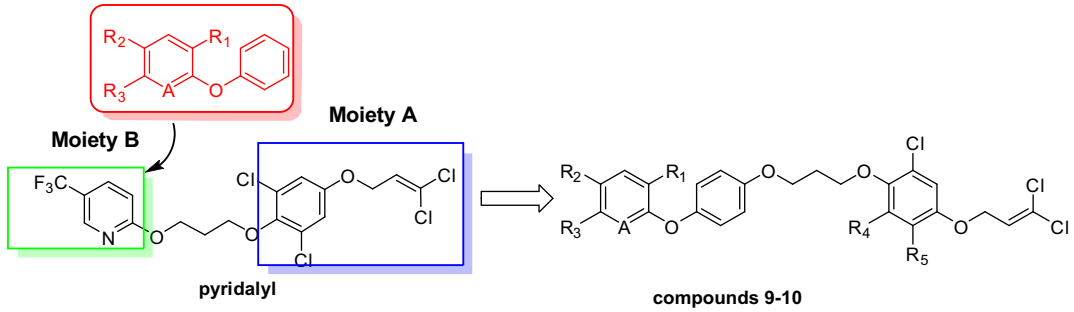
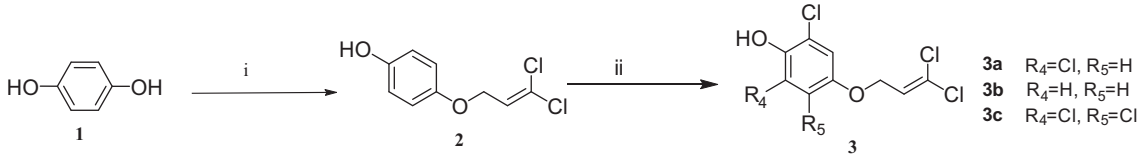
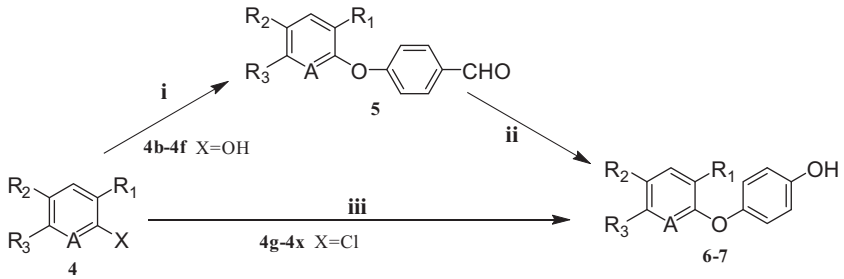



**Figure 2.** Design of aryloxyphenyl compounds.




**Scheme 1.** Synthesis of compounds **3**. Reagents and conditions: (i) 1,1,1,3-tetrachloropropane, $K_2CO_3$, $CH_3OH$, 50 °C, 6 h; (ii) di-*n*-butylamine, $SO_2Cl_2$ (**3a** 1.85–2 equiv, **3b** 0.95–1 equiv, **3c** 3 equiv), toluene, room temperature, 1–2 h, yield 70–90% (**3a** 70%, **3b** 85%, **3c** 90%).

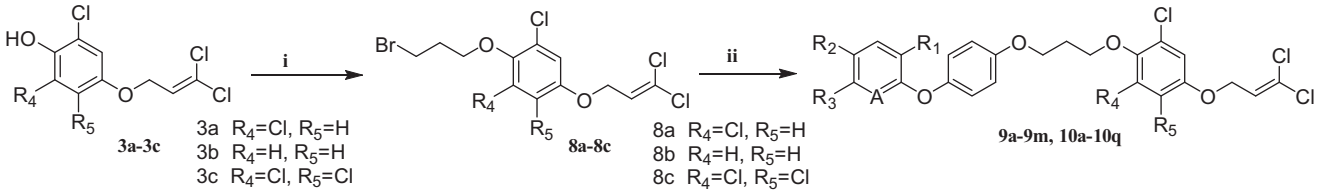



**Scheme 2.** Synthesis of compounds **6–7**. Reagents and conditions: (i) *p*-fluorobenzaldehyde, $K_2CO_3$, dimethylacetamide, reflux, 6–10 h; (ii) *m*-CPBA, $CHCl_3$, room temperature, 1–3 h; (iii) *p*-dihydroxybenzene, $K_2CO_3$, DMF, room temperature, 8–12 h.

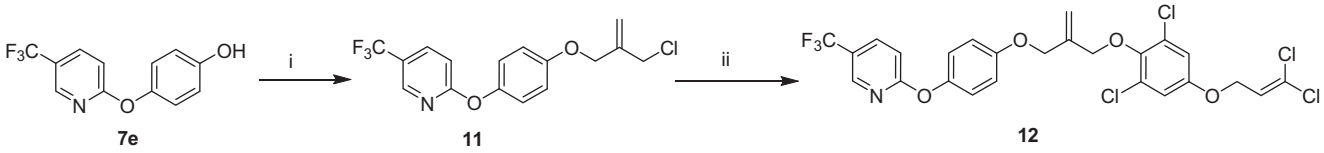
were synthesized from phenols **4** (X = OH) and *p*-fluorobenzaldehyde under basic conditions with yields of 45–80%, while $R_2$ was not strong electron-withdrawing groups and A was carbon atom.[28,29] Aryloxyphenols **6g–6m** and **7a–7k** were synthesized from *p*-dihydroxybenzene and chlorobenzenes or chloropyridines **4** under basic conditions with yields of 50–95%, while $R_2$ was strong electron-withdrawing groups or A=N.[30,31]

The target compounds **9a–9m**, **10a–10q** were synthesized as shown in Scheme 3. Intermediates **3a–3c** were reacted with 1,3-dibromopropane under basic conditions, followed by condensation with aryloxyphenols **6a–6m** or **7a–7k** to afford compounds **9a–9m**, **10a–10q**.

The tether between the two aromatic parts has also been examined with compound **12**. This compound was previously reported in the patent literature as an insecticide.[32] Compound **12** was synthesized by using the same synthetic procedure with pyridinyloxy phenol **7e** and 3-chloro-2-(chloromethyl)prop-1-ene and followed by condensation with **8a** (Scheme 4).

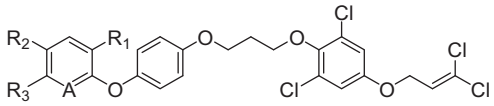



**Scheme 3.** Synthesis of compounds **9a–9m**, **10a–10q**. Reagents and conditions: (i) 1,3-dibromopropane, $K_2CO_3$, DMF, room temperature, 1 h; (ii) **6** or **7**, $K_2CO_3$, $CH_3CN$, reflux, 1 h.




**Scheme 4.** Synthesis of compound **12**. Reagents and conditions: (i) 3-chloro-2-(chloromethyl)prop-1-ene, $K_2CO_3$, $CH_3CN$, reflux, 4 h; (ii) **3a**, $K_2CO_3$, $CH_3CN$, reflux, 1 h.

**Table 1**
Insecticidal activity against *P. xylostella* of compounds **9a–9m**, **10a–10k**



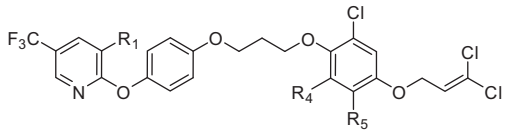
| Compound | A | $R_1$ | $R_2$ | $R_3$ | *P. xylostella* (% mortality at the given concentration in mg/L) | |
|---|---|---|---|---|---|---|
| | | | | | 100 | 10 |
| **9a** | CH | H | H | H | 90 | 10 |
| **9b** | CH | H | $CH_3$ | H | 67 | 48 |
| **9c** | CH | H | Cl | H | 60 | 35 |
| **9d** | CH | H | $OCH_3$ | H | 92 | 33 |
| **9e** | CH | Cl | $CH_3$ | H | 17 | 0 |
| **9f** | CH | Cl | Cl | H | 77 | 5 |
| **9g** | CH | H | $NO_2$ | H | 77 | 65 |
| **9h** | CH | H | $CF_3$ | H | 75 | 0 |
| **9i** | CH | Cl | $NO_2$ | H | 67 | 25 |
| **9j** | CH | Cl | $CF_3$ | H | 12 | 10 |
| **9k** | C-$NO_2$ | H | $CF_3$ | H | 75 | 22 |
| **9l** | C-Cl | Cl | $CF_3$ | H | 54 | 0 |
| **9m** | C-Cl | Cl | $NO_2$ | H | 0 | 0 |
| **10a** | N | H | H | H | 95 | 23 |
| **10b** | N | H | Cl | H | 90 | 53 |
| **10c** | N | H | $NO_2$ | H | 95 | 55 |
| **10d** | N | H | CN | H | 85 | 82 |
| **10e** | N | H | $CF_3$ | H | 100 | 100* |
| **10f** | N | Cl | H | H | 84 | 10 |
| **10g** | N | Cl | $CF_3$ | H | 100 | 75* |
| **10h** | N | Cl | Cl | H | 92 | 70 |
| **10i** | N | F | Cl | H | 90 | 10 |
| **10j** | N | Cl | $CH_3$ | H | 100 | 0 |
| **10k** | N | Cl | Cl | Cl | 80 | 10 |
| | | Pyridalyl | | | 100 | 75 |

* 6.25 mg/L.

## 2.2. Biological activity and the structure–activity relationship

Initially compound **9a** was synthesized by introducing phenoxyphenyl to replace pyridinyl of commercial insecticide pyridalyl by using terminal group replacement method of IDM. Although compound **9a** displayed 90% insecticidal activity against *P. xylostella* at 100 mg $L^{-1}$, it was less potent than pyridalyl (Table 1). Since the Topliss method has often been applied to modification of the substituent of the phenyl ring in optimization strategies.[33] The compounds **9c** (4-chloro), **9b** (4-methyl), **9d** (4-methoxy) were prepared and evaluated according to the Topliss method. However, they provided no significant gain in potency, relative to compound **9a**. More phenoxyphenyl compounds (**9e–9m**) were prepared to investigate structure–activity relationship, which were disubstituted, trisubstituted or substituted by electron-withdrawing group. Although there were a few exceptional patterns, they had better insecticidal activity when $R_2$ was electron-withdrawing group such as $CF_3$ and $NO_2$. Isosteric replacement of benzenes by $CF_3$-substituted pyridines generally led to a number of useful agrochemicals.[34] So compounds **10e**

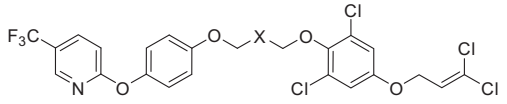
**Table 2**
Insecticidal activity against *P. xylostella* of compounds **10e**, **10g**, **10l**–**10o**



| Compound | $R_1$ | $R_4$ | $R_5$ | *P. xylostella* (% mortality at the given concentration in mg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 600 | 100 | 10 | 6.25 |
| **10e** | H | Cl | H | 100 | 100 | 100 | 100 |
| **10g** | Cl | Cl | H | 100 | 100 | 90 | 75 |
| **10l** | H | H | H | 100 | 80 | 20 | – |
| **10m** | Cl | H | H | 100 | 80 | 20 | – |
| **10n** | H | Cl | Cl | 100 | 50 | 20 | – |
| **10o** | Cl | Cl | Cl | 80 | 30 | 0 | – |
| | Pyridalyl | | | 100 | 100 | 75 | 50 |

and **10g** were prepared by introducing 5-$CF_3$-pyridyloxyphenyl and 2-Cl-5-$CF_3$-pyridyloxyphenyl to replace phenoxyphenyl of compounds **9a**–**9m**, which was important pharmacophore of haloxyfop-methyl and fluazifop-butyl respectively. Compounds **10e** and **10g** showed 100% and 75% control against *P. xylostella*, respectively, at 6.25 mg $L^{-1}$, it was more potent than compounds **9a**–**9m**. More compounds with other substitutional pyridinyloxy were prepared in order to obtain compounds with much higher activity. However, we were disappointed to find that extensive variety of analogs (**10a**, **10b**, **10c**, **10d**, **10f**, **10h**, **10i**, **10j**, **10k**) were significant losses in activity in Table 1. Although it is difficult to construct a clear structure–activity relationship from the data shown in Table 1, it can be concluded that the general trend in insecticidal activity for the substituents of moiety **C** was that A: N > CH; $R_2$: $CF_3$ > $NO_2$ > CN > other.

**Table 3**
Insecticidal activity against *P. xylostella* of compounds **10e** and **12**



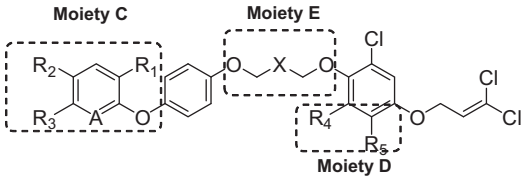
| Compound | X | *P. xylostella* (% mortality at the given concentration in mg/L) | | |
|---|---|---|---|---|
| | | 100 | 10 | 6.25 |
| **10e** | $CH_2$ | 100 | 100 | 100 |
| **12** |  | 80 | 20 | – |
| | Pyridalyl | 100 | 75 | 50 |

**Table 4**
Field trial results for compound **10e** at Shenyang against *P. xylostella* in 2011

| Compound | Rate (g a.i./ha) | Mortality at days after spraying (%) | | |
|---|---|---|---|---|
| | | 1 | 3 | 7 |
| 10% **10e** EC | 75 | 86.0 | 98.7 | 97.6 |
| | 105 | 93.4 | 97.0 | 97.8 |
| | 150 | 90.4 | 97.9 | 97.9 |
| 10% pyridalyl EC | 105 | 95.1 | 97.0 | 94.9 |

**Table 5**
Field trial results for compound **10e** at Wuhan against *P. xylostella* in 2012

| Compound | Rate (g a.i./ha) | Mortality at days after spraying (%) | | | |
|---|---|---|---|---|---|
| | | 1 | 3 | 7 | 10 |
| 10% **10e** EC | 75 | 70.4 | 94.5 | 90.7 | 84.6 |
| | 105 | 78.3 | 98.1 | 93.7 | 86.3 |
| | 150 | 79.5 | 99.3 | 96.3 | 91.6 |
| 10% pyridalyl EC | 105 | 79.4 | 95.3 | 92.5 | 84.3 |




For further studying the structure–activity relationship, A as N, $R_2$ as $CF_3$ were maintained, $R_1$ and moiety **D** were changed (Table 2). Compounds **10e** and **10g** ($R_4$ = Cl, $R_5$ = H) showed better insecticidal activity against *P. xylostella* than other compounds ($R_4$ = $R_5$ = H > $R_4$ = $R_5$ = Cl) and commercial insecticide pyridalyl. The structure–activity relationship could be conjectured, which $R_1$: H > Cl; $R_4$ = Cl, $R_5$ = H > $R_4$ = $R_5$ = H > $R_4$ = $R_5$ = Cl. Following A as N, $R_2$ as $CF_3$, $R_4$ as Cl, $R_5$ as H were maintained, carbon chain of moiety **E** was changed as shown in Table 3. In our biological tests at 10 mg $L^{-1}$, compound **10e** (X = $CH_2$, 100%) was better than compounds **12** (X = 1,1-vinyl, 20%) and it can be hypothesized that the introduction of a carbon $sp^2$ in the tether reducing the liberty degree has a detrimental effect on the insecticidal activity. However, more compounds like the carbonyl equivalent (X = C=O) will be required to elaborate further the hypothesis. Out of our research, compound **10e** was identified as the molecule with the most insecticidal activity. It showed better insecticidal activity in our test system against *P. xylostella* than pyridalyl with 100% and 50% control respectively at 6.25 mg $L^{-1}$. Compound **10e** was therefore tested in field conditions.

The field trial results of insecticidal activities of compound **10e** as a 10% emulsifiable concentrate (EC) carried out at Shenyang (2011) and Wuhan (2012) are summarized in Tables 4 and 5, respectively. The field trial results demonstrate an effective control of *P. xylostella* at 75, 105 and 150 g a.i./ha. The mortality against *P. xylostella* of compound **10e** at 75 g a.i./ha was equivalent to the treatment with pyridalyl at 105 g a.i./ha.

## 3. Conclusion

Using IDM, a series of dichloro-allyloxy-phenol derivatives were synthesized by introducing substituted aryloxy phenyl moiety. Among these compounds, the insecticidal activities of **10e** and **10g** against *P. xylostella* at 6.25 mg $L^{-1}$ are more potent than that of pyridalyl, especially compound **10e** with much more potent insecticidal activity against *P. xylostella* both in greenhouse test and field trials. Compound **10e** is a promising candidate for further development. This study demonstrates the effectiveness of IDM approach to the discovery of high bioactive compounds. More field trials of compound **10e** are in progress.

## 4. Experimental methods

### 4.1. Chemistry

All starting materials and reagents were commercially available and used without further purification except as indicated. Melting

points were determined on a Büchi melting point apparatus M-565 and were uncorrected. $^1$H NMR spectra were recorded with Mercury 300 (Varian, 300 MHz) spectrometer with $CDCl_3$ or DMSO-$d_6$ as the solvent and tetramethylsilane as the internal standard. Liquid chromatography–mass spectra (LC–MS) analysis was performed using the Agilent Technologies 6230 TOF LC/MS. Petroleum ether used for column chromatography had a boiling range of 60–90 °C. Chemical names were generated using ChemDraw Ultra (Cambridge Soft, version 14.0). Intermediates **3a**–**3c** and **8a**–**8c** were prepared in our laboratory according to the methods reported by Li et al.[15,25–27] 4-Phenoxyphenol **6a** was commercially available. Aryloxybenzaldehydes **5b**–**5f**, aryloxyphenols **6b**–**6m** and **7a**–**7k** were prepared according to procedures previously described.[28–31]

#### 4.1.1. General synthetic procedure for compounds 9a–9m, 10a–10q

Aryloxyphenols **6a**–**6m** or **7a**–**7k** (1 equiv), **8a**–**8c** (1 equiv), anhydrous potassium carbonate (1.5 equiv) were added to 100 mL of flask with acetonitrile (50 mL) in sequence, the reaction mixture was then heated to reflux for 1 h. The reaction was monitored by thin-layer chromatography (TLC). After the reaction was completed, the reaction mixture was cooled to room temperature, filtered, concentrated under reduced pressure and the residue was purified via silica gel column chromatography (ethyl acetate/petroleum ether = 1:30) to give the target compounds.

**4.1.1.1. 1,3-Dichloro-5-((3,3-dichloroallyl)oxy)-2-(3-(4-phenoxyphenoxy)-propoxy)benzene (9a).** Pale yellow oil; yield 79%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.27–7.33 (m, 2H), 6.89–7.06 (m, 7H), 6.84 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.25 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.27–2.31 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{21}Cl_4O_4^+$, 513.0194 $[M+H]^+$; found: 513.0199.

**4.1.1.2. 1,3-Dichloro-5-((3,3-dichloroallyl)oxy)-2-(3-(4-(*p*-tolyloxy)phenoxy)-propoxy)benzene (9b).** Viscous oil; yield 81%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.10 (d, $J$ = 3.9 Hz, 2H), 6.84–6.96 (m, 8H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.23 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.34 (s, 3H, $CH_3$), 2.26–2.31 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{25}H_{23}Cl_4O_4^+$, 527.0350 $[M+H]^+$; found: 581.0357.

**4.1.1.3. 1,3-Dichloro-2-(3-(4-(4-chlorophenoxy)phenoxy)propoxy)-5-((3,3-di-chloroallyl)oxy)benzene (9c).** Viscous oil; yield 71%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.24 (d, $J$ = 4.5 Hz, 2H), 6.84–7.03 (m, 8H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.25 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.27–2.31 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{20}Cl_5O_4^+$, 546.9804 $[M+H]^+$; found: 546.9817.

**4.1.1.4. 1,3-Dichloro-5-((3,3-dichloroallyl)oxy)-2-(3-(4-(4-methoxyphenoxy)-phenoxy)propoxy)benzene (9d).** Viscous oil; yield 73%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 6.83–6.94 (m, 10H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.23 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.15 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 3.79 (s, 3H, $OCH_3$), 2.26–2.30 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{25}H_{23}Cl_4O_5^+$, 543.0299 $[M+H]^+$; found: 543.0307.

**4.1.1.5. 5. 1,3-Dichloro-2-(3-(4-(2-chloro-4-methylphenoxy)phenoxy)propoxy)-5-((3,3-dichloroallyl)oxy)benzene (9e).** Viscous oil; yield 66%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 6.78–6.90 (m, 9H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.23 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.15 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 2.26–2.31 (m, 5H, $CH_2$+$CH_3$). HRMS ($ESI^+$) $m/z$ calcd for $C_{25}H_{22}Cl_5O_4^+$, 560.9960[M+H]$^+$; found: 560.9971.

**4.1.1.6. 1,3-Dichloro-5-((3,3-dichloroallyl)oxy)-2-(3-(4-(2,4-dichlorophenoxy)-phenolxy)propoxy)benzene (9f).** Viscous oil; yield 83%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 6.77–6.92 (m, 9H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.24 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.17 (t, $J$ = 5.7 Hz, 2H, $OCH_2$), 2.26–2.31 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{19}Cl_6O_4^+$, 580.9414 $[M+H]^+$; found: 580.9421.

**4.1.1.7. 1,3-Dichloro-5-((3,3-dichloroallyl)oxy)-2-(3-(4-(4-nitrophenoxy)-phenoxy)propoxy)benzene (9g).** Viscous oil; yield 68%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.19 (d, $J$ = 9.3 Hz, 2H), 6.95–7.02 (m, 6H), 6.85 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.29 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 4.17 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.29–2.33 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{20}Cl_4NO_6^+$, 558.0044 $[M+H]^+$; found: 558.0057.

**4.1.1.8. 1,3-Dichloro-5-((3,3-dichloroallyl)oxy)-2-(3-(4-(4-(trifluoromethyl)-phenoxy)phenoxy)propoxy)benzene (9h).** Viscous oil; yield 78%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.54 (d, $J$ = 8.7 Hz, 2H), 6.93–7.02 (m, 6H), 6.84 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.27 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.17 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.28–2.33 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{25}H_{20}Cl_4F_3O_4^+$, 581.0068 $[M+H]^+$; found: 581.0073.

**4.1.1.9. 1,3-Dichloro-2-(3-(4-(2-chloro-4-nitrophenoxy)phenoxy)propoxy)-5-((3,3-dichloroallyl)oxy)benzene (9i).** Viscous oil; yield 63%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.37 (d, $J$ = 3.0 Hz, 1H), 6.98–7.06 (m, 4H), 6.84 (s, 2H), 6.78–6.82 (m, 1H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.29 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.17 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.29–2.33 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{19}Cl_5NO_6^+$, 591.9655 $[M+H]^+$; found: 591.9661.

**4.1.1.10. 1,3-Dichloro-2-(3-(4-(2-chloro-4-(trifluoromethyl)phenoxy)phenoxy)propoxy)-5-((3,3-dichloroallyl)oxy)benzene (9j).** Viscous oil; yield 81%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.75 (d, $J$ = 2.4 Hz, 1H), 7.47 (d, $J$ = 9.0 Hz, 1H), 6.97–7.07 (m, 5H), 6.85 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.09 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 3.71 (t, $J$ = 6.6 Hz, 2H, $OCH_2$), 2.34–2.38 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{25}H_{19}Cl_5F_3O_4^+$, 614.9678[M+H]$^+$; found: 614.9669.

**4.1.1.11. 1,3-Dichloro-5-((3,3-dichloroallyl)oxy)-2-(3-(4-(2-nitro-4-(trifluoro-methyl)phenoxy)phenoxy)propoxy)benzene (9k).** Viscous oil; yield 69%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.21 (s, 1H), 7.66 (d, $J$ = 9.0 Hz, 1H), 6.98–7.07 (m, 5H), 6.84 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.29 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.17 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.29–2.33 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{25}H_{19}Cl_4F_3NO_6^+$, 625.9918 $[M+H]^+$; found: 625.9926.

**4.1.1.12. 1,3-Dichloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)-propoxy)phenoxy)-5-(trifluoromethyl)benzene (9l).** Viscous oil; yield 75%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.66 (s, 2H), 6.78–6.85 (m, 6H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.22 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.27 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{25}H_{18}Cl_6F_3O_4^+$, 648.9288 $[M+H]^+$; found: 648.9279.

**4.1.1.13. 1,3-Dichloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)-propoxy)phenoxy)-5-nitrobenzene (9m).** Viscous oil; yield 67%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.30 (s, 2H), 6.76–6.89 (m, 6H), 6.85 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.22 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.14 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.25–2.29 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{18}Cl_6NO_6^+$ 625.9265 $[M+H]^+$, found: 625.9271.

**4.1.1.14. 2-(4-(3-(2,6-Dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)propoxy)-phenoxy)pyridine (10a).** Viscous oil; yield 81%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.19 (d, $J$ = 7.5 Hz, 1H), 7.66 (t, $J$ = 8.5 Hz, 1H), 6.84–7.09 (m, 8H), 6.84 (s, 2H), 6.12 (t, $J$ = 6.0 Hz, 1H, CH), 4.59 (d, $J$ = 6.0 Hz, 2H, $OCH_2$), 4.26 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 2.28–2.32 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{23}H_{20}Cl_4NO_4^+$, 514.0146 M +H]$^+$; found: 514.0152.

**4.1.1.15. 5-Chloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)-propoxy)phenoxy)pyridine (10b).** Viscous oil; yield 86%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.12 (d, $J$ = 2.7 Hz, 1H), 7.61 (dd, $J$ = 2.7, 8.7 Hz, 1H), 6.82–7.06 (m, 7H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.26 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 2.28–2.32 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{23}H_{19}Cl_5NO_4^+$, 547.9756 [M +H]$^+$; found: 547.9763.

**4.1.1.16. 2-(4-(3-(2,6-Dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)propoxy)-phenoxy)-5-nitropyridine (10c).** Viscous oil; yield 65%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 9.06 (d, $J$ = 2.4 Hz, 1H), 8.46 (dd, $J$ = 2.4, 9 Hz, 1H), 6.98–7.10 (m, 5H), 6.85 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.28 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 4.17 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.29–2.33 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{23}H_{19}Cl_4N_2O_6^+$, 558.9997 [M+H]$^+$; found: 558.0017.

**4.1.1.17. 6-(4-(3-(2,6-Dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)propoxy)-phenoxy)nicotinonitrile (10d).** Viscous oil; yield 81%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.47 (dd, $J$ = 0.6, 2.4 Hz, 1H), 7.89 (dd, $J$ = 2.4, 8.7 Hz, 1H), 6.97–7.08 (m, 5H), 6.84 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.27 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.28–2.32 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{19}Cl_4N_2O_4^+$, 539.0099 [M+H]$^+$; found: 539.0106.

**4.1.1.18. 2-(4-(3-(2,6-Dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)propoxy)-phenoxy)-5-(trifluoromethyl)pyridine (10e).** White solid; yield 87%. Mp 68–70 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.45 (s, 1H), 7.87 (d, $J$ = 8.7 Hz, 1H), 7.07 (d, $J$ = 9.0 Hz, 2H), 6.98 (d, $J$ = 9.0 Hz, 2H), 6.97 (d, $J$ = 8.7 Hz, 1H), 6.84 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H), 4.57 (d, $J$ = 6.3 Hz, 2H), 4.27 (t, $J$ = 6.0 Hz, 2H), 4.17 (t, $J$ = 6.0 Hz, 2H), 2.26–2.32 (m, 2H). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{19}Cl_4F_3NO_4^+$, 582.002 [M+H]$^+$, found: 581.9999.

**4.1.1.19. 3-Chloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)-propoxy)phenoxy)pyridine (10f).** Viscous oil; yield 67%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.02 (dd, $J$ = 1.5, 4.8 Hz, 1H), 7.74 (dd, $J$ = 1.5, 7.5 Hz, 1H), 7.10 (d, $J$ = 2.4 Hz, 2H), 6.91–6.98 (m, 3H), 6.84 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.26 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 2.28–2.32 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{23}H_{19}Cl_5NO_4^+$, 547.9756 [M+H]$^+$; found: 547.9768.

**4.1.1.20. 3-Chloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)-propoxy)phenoxy)-5-(trifluoromethyl)pyridine (10g).** Pale yellow oil; yield 84%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.27 (s, 1H), 7.96 (s, 1H), 7.10 (d, $J$ = 9.0 Hz, 2H), 6.98 (d, $J$ = 9.0 Hz, 2H), 6.84 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H), 4.58 (d, $J$ = 6.3 Hz, 2H), 4.28 (t, $J$ = 6.0 Hz, 2H), 4.17 (t, $J$ = 6.0 Hz, 2H), 2.31 (m, 2H). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{18}Cl_5F_3NO_4^+$, 615.9630 [M +H]$^+$; found: 615.9623.

**4.1.1.21. 3,5-Dichloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy) propoxy)phenoxy)pyridine (10h).** Viscous oil; yield 87%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.97 (d, $J$ = 6.0 Hz, 1H), 7.77 (d, $J$ = 6.0 Hz, 1H), 6.95–7.08 (m, 4H), 6.84 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.26 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.28–2.31 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{23}H_{18}Cl_6NO_4^+$, 581.9367 [M+H]$^+$; found: 581.9377.

**4.1.1.22. 5-Chloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy) propoxy)phenoxy)-3-fluoropyridine (10i).** Pale yellow oil; yield 62%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.90 (d, $J$ = 6.0 Hz, 1H), 7.48–7.54 (m, 1H), 7.08 (d, $J$ = 9.0 Hz, 2H), 6.96 (d, $J$ = 9.0 Hz, 2H), 6.84 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$),), 4.10–4.28 (m, 4H), 2.25–2.32 (m, 2H, $CH_2$). HRMS ($ESI^+$) $m/z$ calcd for $C_{23}H_{17}Cl_5FNO_4^+$, 565.9662 [M+H]$^+$; found: 565.9670.

**4.1.1.23. 3-Chloro-2-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)-propoxy)phenoxy)-5-methylpyridine (10j).** Viscous oil; yield 68%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.83 (s, 1H), 7.57 (s, 1H), 6.92–7.08 (m, 4H), 6.84 (s, 2H), 6.11 (t, $J$ = 6.3 Hz, 1H, CH), 4.58 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.25 (t, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.16 (t, $J$ = 6.0 Hz, 2H, $OCH_2$), 2.27–2.31 (m, 2H, $CH_2$), 2.26 (s, 3H, $CH_3$). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{21}Cl_5NO_4^+$, 561.9913 [M+H]$^+$; found: 561.9925.

**4.1.1.24. 2,3,5-Trichloro-6-(4-(3-(2,6-dichloro-4-((3,3-dichloroallyl)oxy)-phenoxy)propoxy)phenoxy)pyridine (10k).** Oil; yield 68%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 7.89 (s, 1H), 687–7.21 (m, 4H), 6.84 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H, CH), 4.59 (d, $J$ = 6.3 Hz, 2H, $OCH_2$), 4.00–4.28 (m, 4H), 2.25–2.36 (m, 2H). HRMS ($ESI^+$) $m/z$ calcd for $C_{23}H_{17}Cl_7NO_4^+$, 615.8977 [M+H]$^+$; found: 615.8985.

**4.1.1.25. 2-(4-(3-(2-Chloro-4-((3,3-dichloroallyl)oxy)phenoxy) propoxy)-phenoxy)-5-(trifluoromethyl)pyridine (10l).** Viscous oil; yield 82%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.46 (s, 1H), 7.88 (d, $J$ = 8.7 Hz, 1H), 7.07 (d, $J$ = 9.0 Hz, 2H), 6.95–6.98 (m, 3H), 6.90 (d, $J$ = 9.0 Hz, 1H), 6.73–6.77 (m, 1H), 6.13 (t, $J$ = 6.0 Hz, 1H), 4.59 (d, $J$ = 6.0 Hz, 2H), 4.16–4.24 (m, 4H), 2.28–2.34 (m, 2H). HRMS ($ESI^+$) $m/z$ calcd for $C_{24}H_{20}Cl_4F_3NO_4^+$, 548.041 [M+H]$^+$; found: 548.0418.

**4.1.1.26. 3-Chloro-2-(4-(3-(2-chloro-4-((3,3-dichloroallyl)oxy) phenoxy)propoxy)phenoxy)-5-(trifluoromethyl)pyridine (10m).** Viscous oil; yield 79%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.26 (s, 1H), 7.96 (s, 1H), 7.09 (d, $J$ = 9.0 Hz, 2H), 6.95–6.99

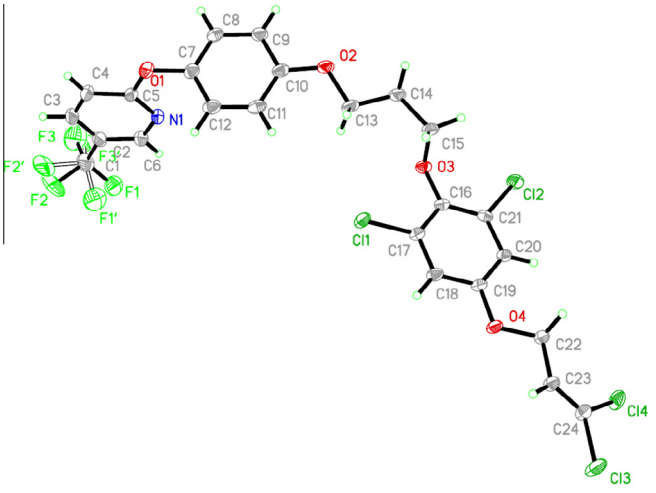



**Figure 3.** Crystal structure of compound **10e**.

**Table 6**
Crystallographic data and structure refinement parameters for **10e**

| | | | |
|---|---|---|---|
| Formula | $C_{24}H_{18}Cl_4F_3NO_4$ | $\gamma$ (deg) | 90.00 |
| Molecular mass | 583.19 | Volume (Å$^3$) | 2504.9(10) |
| $T$ (K) | 113(2) | $Z$ | 4 |
| Crystal system | Monoclinic | Calculated density (g/cm$^3$) | 1.546 |
| Space group | $P2(1)/C$ | Absorption coefficient (mm$^{-1}$) | 0.528 |
| $a$ (Å) | 8.777(2) | F(000) | 1184 |
| $b$ (Å) | 8.0042(18) | Reflections collected | 22,252 |
| $c$ (Å) | 35.670(8) | Independent reflections | 5991 [$R$(int) = 0.0515] |
| $\alpha$ (deg) | 90.00 | Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0458, $wR_2$ = 0.1205 |
| $\beta$ (deg) | 91.759(4) | $R$ indices (all data) | $R_1$ = 0.0578, $wR_2$ = 0.1355 |

(m, 3H), 6.90 (d, $J$ = 9.0 Hz, 1H), 6.73–6.77 (m, 1H), 6.13 (t, $J$ = 6.0 Hz, 1H), 4.59 (d, $J$ = 6.3 Hz, 2H), 4.16–4.24 (m, 4H), 2.28–2.32 (m, 2H). HRMS (ESI$^+$) $m/z$ calcd for $C_{24}H_{19}Cl_4F_3NO_4^+$, 582.002 [M+H]$^+$; found: 582.0018.

#### 4.1.1.27. 2-(4-(3-(2,3,6-Trichloro-4-((3,3-dichloroallyl)oxy)phenoxy)propoxy)-phenoxy)-5-(trifluoromethyl)pyridine (10n).

Viscous oil; yield 76%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.45 (s, 1H), 7.89 (d, $J$ = 9.0 Hz, 1H),7.08 (d, $J$ = 9.0 Hz, 2H), 6.96–6.99 (m, 3H), 6.89 (s, 1H), 6.18 (t, $J$ = 6.3 Hz, 1H), 4.69 (d, $J$ = 6.3 Hz, 2H), 4.27 (t, $J$ = 6.3 Hz, 2H), 4.18 (t, $J$ = 6.0 Hz, 2H), 2.28–2.36 (m, 2H). HRMS (ESI$^+$) $m/z$ calcd for $C_{24}H_{18}Cl_5F_3NO_4^+$, 615.963 [M+H]$^+$; found: 615.9639.

#### 4.1.1.28. 3-Chloro-2-(4-(3-(2,3,6-trichloro-4-((3,3-dichloroallyl)oxy)phenoxy)-propoxy)phenoxy)-5-(trifluoromethyl)pyridine (10o).

Viscous oil; yield 73%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ ppm 8.27 (s, 1H), 7.96 (s, 1H), 7.10 (d, $J$ = 9.0 Hz, 2H), 6.99 (d, $J$ = 9.0 Hz, 2H), 6.89 (s, 1H), 6.18 (t, $J$ = 6.3 Hz, 1H),4.69 (d, $J$ = 6.3 Hz, 2H), 4.28 (t, $J$ = 6.3 Hz, 2H), 4.18 (t, $J$ = 6.3 Hz, 2H), 2.28–2.34 (m, 2H). HRMS (ESI$^+$) $m/z$ calcd for $C_{24}H_{17}Cl_6F_3NO_4^+$, 649.9241 [M+H]$^+$; found: 649.9253.

#### 4.1.2. 2-(4-((2-((2,6-Dichloro-4-((3,3-dichloroallyl)oxy)phenoxy)methyl)allyl)-oxy)phenoxy)-5-(trifluoromethyl)pyridine (12)

Anhydrous potassium *tert*-butoxide 2 g (17.5 mmol) and 3-chloro-2-(chloromethyl)prop-1-ene 0.88 g (7 mmol) were added to 100 mL of three-necked flask with DMF (20 mL) in sequence, a solution of 4-(5-(trifluoromethyl)pyridin-2-yloxy)phenol (**7e**) 2 g (7 mmol) in DMF (10 mL) was added dropwise to the above solution at room temperature, stirred for 2 h at this temperature, a solution of 2,6-dichloro-4-((3,3-dichloroallyl)oxy)phenol (**3a**) 1.70 g (6.7 mmol) in DMF (10 mL) was added dropwise to the reaction solution, and the reaction was monitored by thin-layer chromatography (TLC). After the reaction was completed, the mixture was poured into water (200 mL) and extracted with ethyl acetate (2 × 300 mL). The organic phases were combined, washed with brine (2 × 200 mL), dried over anhydrous magnesium sulfate, concentrated under reduced pressure and the residue was purified via silica gel column chromatography (ethyl acetate/petroleum ether = 1:30) to give compound **12** (1.83 g, 46%) as a viscous oil. $^1$H NMR spectrum (300 MHz, internal standard TMS, solvent $CDCl_3$) is as follows: 8.44 (s, 1H), 7.88 (dd, $J$ = 2.1, 8.7 Hz, 1H), 6.92–7.09 (m, 5H), 6.86 (s, 2H), 6.12 (t, $J$ = 6.3 Hz, 1H), 5.48 (s, 2H), 4.78 (s, 2H), 4.58–4.60 (m, 4H). HRMS (ESI$^+$) $m/z$ calcd for $C_{25}H_{19}Cl_4F_3NO_4^+$, 594.002 [M+H]$^+$; found: 594.0017.

### 4.2. X-ray diffraction

Crystals of compound **10e** were grown by a liquid–liquid diffusion technique from a mixture of methanol and hexane (Fig. 3). Crystallographic data was collected at 113 (2) K using Mo-Ka radiation ($k$ = 0.71073 Å) on a Bruker SMART 1000 CCD diffraction meter. The data was corrected for Lorentz and polarization factors and for absorption by using empirical scan data. The structure was solved with the SHELX program, and refined by full-matrix least-squares methods based on $F^2$, with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located theoretically and not refined. Crystallographic data and structure refinement parameters are listed in Table 6.

### 4.3. Insecticidal assay

#### 4.3.1. Greenhouse test

Each of the test compounds was first dissolved in a mixture of acetone and water, and water containing 0.1% Tween 80 was then added to make the stock solution. Serial test solutions were prepared by using acetone and water (v/v = 9:1). Cabbage leaves were dipped into test solutions prepared above for 5 s. After drying, each leaf was put into a polyethylene cup, then infested with 5–10 3rd-instar larvae and kept at 25 °C in observation room. Mortality was assessed 3 days after treatment. The test results of the insecticidal activities of the title compounds against *P. xylostella* are listed in Tables 1–3. Biological data were presented from the range 0% (indicates no mortality) to 100% (complete mortality).

#### 4.3.2. Field trials against *P. xylostella* on cabbage

The trials were carried out in the test filed of Shenyang Research Institute of Chemical Industry Ltd and Wuhan vegetable research institute. The trial crop was cabbage (Variety: Zhonggan NO 8.). The dosage of the compound **10e** was 75, 105, 150 g a.i./ha and comparative agent pyridalyl is 105 g a.i./ha. The application tool was Shandongweishi WS-16P type backpack manual sprayer. Evenly spraying to whole cabbage which is in rosette stage was conducted. *P. xylostella* was originated at the peak time. The plot area was 10 m$^2$, 3 replicates and randomized block arrangement were set. The amount of spray liquid was 750 L/ha. It was sunny with the highest temperature of 29 °C, and the lowest of 17 °C on the day of the application of the spray. The number of living larvae was counted after 1 day, 3 days, 7 days and 10 days respectively after application and control efficacy was calculated. Calculation method:

Decrease rate of insects (%) = (the number of insects before application − the number of insects after application)/the number of insects before application × 100

Control efficacy (%) = (decrease rate of insects in treated area − decrease rate of insects in blank comparative area)/(100 − decrease rate of insects in blank comparative area) × 100.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bmc.2015.09.030. These data include MOL files and InChiKeys of the most important compounds described in this article.

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