Vinylphosphonium Salt Mediated Reaction between Alkyl Propiolates and Aminophenols or Hydroxyphenols

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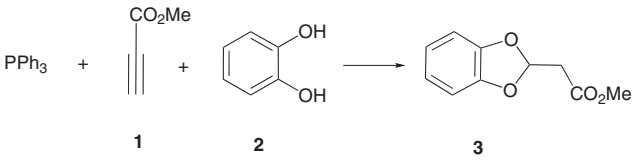
Abstract: Addition of catechol to methyl propiolate or ethyl phenylpropiolate in the presence of Ph_3P leads to methyl 2-(1,3-benzodioxol-2-yl)acetate or 3-(1-phenylmethylidene)-1,4-benzodioxin-2-one. 2-Aminophenols react with alkyl propiolates in the presence of Ph_3P to produce a nearly 1:1 mixture of 3-methyl-2*H*-1,4-benzoxazin-2-one derivatives and methyl (*E*)-3-(2-aminophenoxy)-2-propenoates.

Key words: alkyl propiolates, triphenylphosphine, hydroxylphenol, aminophenol, benzodioxol, 2*H*-1,4-benzoxazin-2-one, *O*-vinylation

Vinyl ethers of alcohols and phenols are well established monomers, building blocks and auxiliaries in organic synthesis, steadily expanding their scope of application.[1–3] The O-alkylated phenols have numerous industrial applications, particularly in the production of dyes and agrochemicals.[3–6] Recently, we described[6] a convenient method for preparation of alkyl 2-arylacrylates and alkyl 3-aryloxypropenoates by nucleophilic conjugate addition of phenols to alkyl propiolates in the presence of triphenylphosphine (Ph_3P). In this paper, we wish to extend that methodology using bifunctional reagents such as aminophenols and hydroxyphenols.

The reaction of catechol (**2**) with methyl propiolate (**1**) in the presence of Ph_3P was carried out in dichloromethane. The colorless oil separated from the reaction mixture was identified as methyl 2-(1,3-benzodioxol-2-yl)acetate (**3**; Scheme 1).



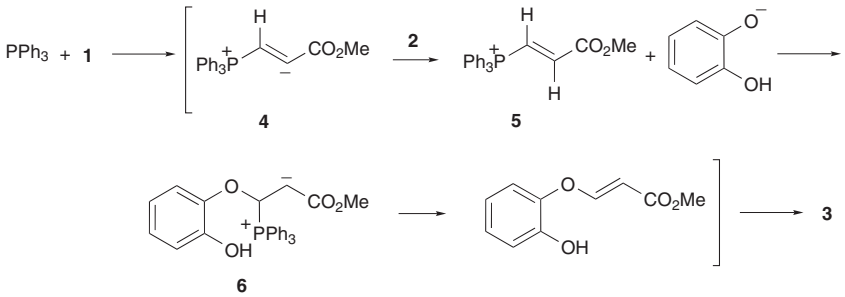
Scheme 1

A possible mechanism for this transformation is proposed in Scheme 2. It is conceivable that the initial event is the formation of 1,3-dipolar intermediate **4** from Ph_3P and the acetylenic compound, which is subsequently protonated by **2**.[7–10] Nucleophilic attack of the oxygen atom of the conjugate base of **2** on the vinylphosphonium cation **5** then produces the 1,3-dipolar intermediate **6**, which is converted to **3**, by elimination of Ph_3P and cyclization (see Scheme 2).

When the same reaction was carried out with ethyl phenylpropiolate (**7**), 3-(1-phenylmethylidene)-1,4-benzodioxin-2-one **8** was obtained (Scheme 3).

The plausible mechanism proposed for formation of product **8** is similar to that shown in Scheme 2, except for the addition of the conjugate base of **2** to the vinylphosphonium cation, which leads to ylide **9**. The intermediate **9** is converted to the 1,3-dipolar species **10** by [1,3]-H^+ shift. Next, intermediate **10** is converted to **8** via the vinyl ether **11** by elimination of Ph_3P and ethanol (see Scheme 4).

The reaction of 2-aminophenol (**12**) with **1** in the presence of Ph_3P was carried out in dichloromethane. Two products were isolated from the reaction mixture and identified as



Scheme 2

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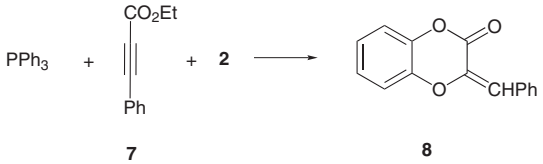
DOI: 10.1055/s-2006-950230; Art ID: P04306SS



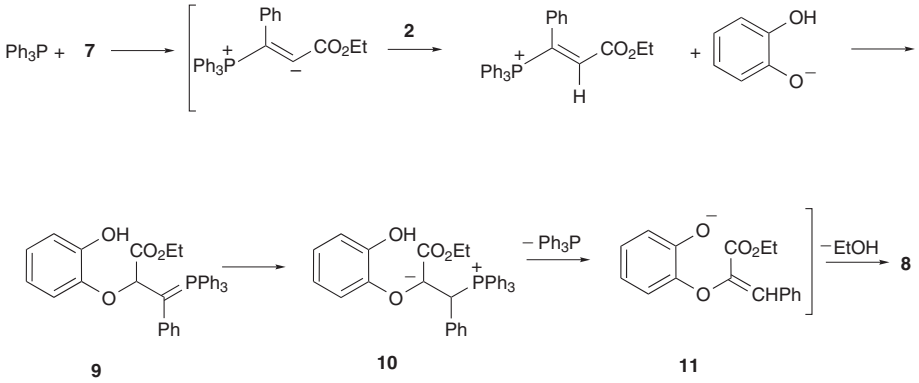
Scheme 3

3-methyl-2*H*-1,4-benzoxazin-2-one (**13a**) and methyl (*E*)-3-(2-aminophenoxy)-2-propenoate (**14a**; see Table 1).

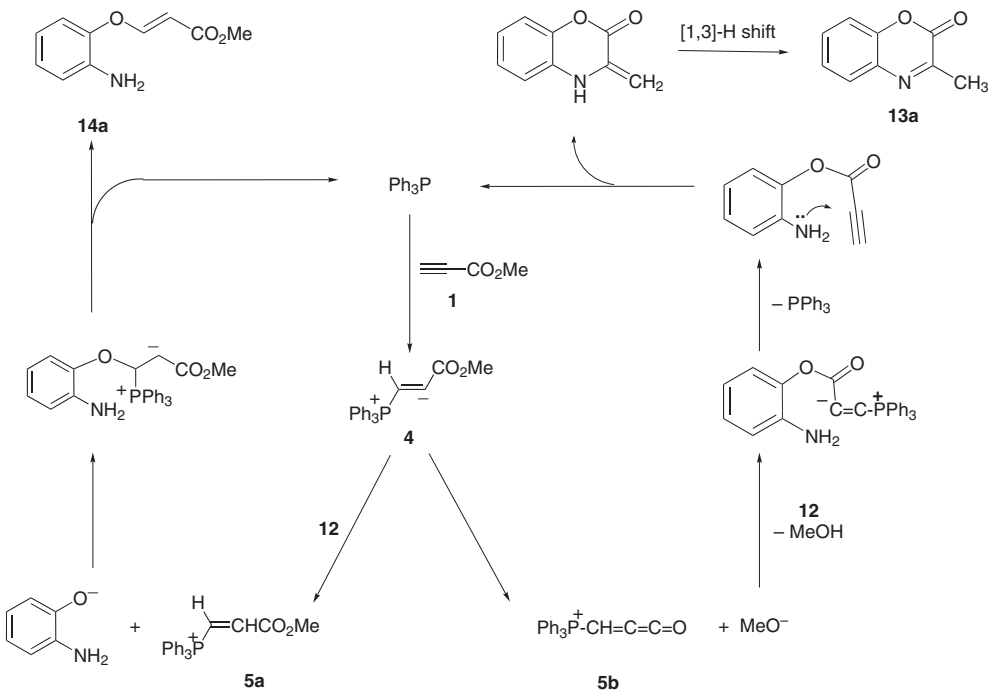
A plausible mechanism for the formation of products **13a** and **14a** is shown in Scheme 5. The reaction starts from addition of Ph_3P to the electron-deficient acetylenic ester to form the zwitterionic intermediate **4**,[7–10] which is either subsequently protonated by the OH-acid **12** to produce vinylphosphonium cation **5a**, or loses a methoxy group to give **5b**. Then, addition of conjugate base of the OH-acidic **12** to **5a** or **5b** produces **13a** or **14a** in nearly 1:1 ratio. Similar pathways can be proposed for formation of **13b–f** and **14b–f**.

The structures of compounds **13a–f** and **14a–f** were determined on the basis of their elemental analyses, mass spectra, ^1H and ^{13}C NMR and IR spectroscopic data. Observation of two characteristic doublets with $^3J_{HH}$ of about 12 Hz in the ^1H NMR spectra of **14a–f** is consistent with O-vinylation of the aromatic ring and formation of alkyl (*E*)-aryloxy propenoates (**14a–f**). The ^{13}C NMR spectra of **13a–f** and **14a–f** show distinct resonances in agreement with the proposed structures.

Under the same reaction conditions given for catechol, two products were isolated from the reaction mixture of resorcinol or hydroquinone with alkyl propiolates in the presence of Ph_3P (see Table 2). When 3- or 4-aminophe-

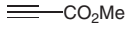
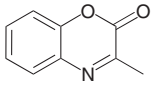
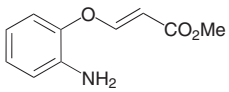
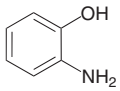
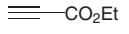
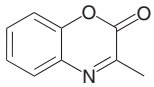
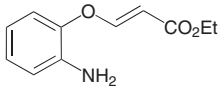
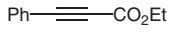
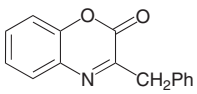
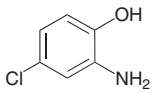
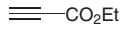
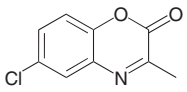
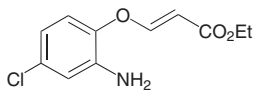
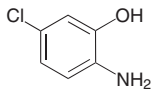
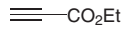
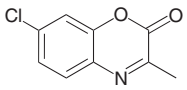
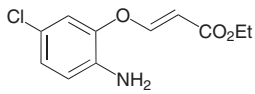
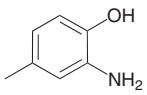
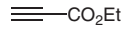
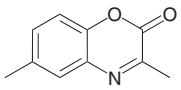
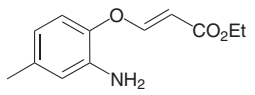
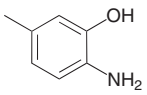
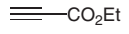
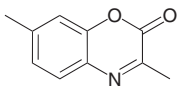
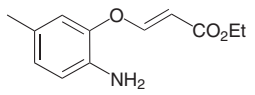


Scheme 4



Scheme 5

Table 1 Reaction of Alkyl Propiolates with 2-Aminophenols in the Presence of Triphenylphosphine

Entry	Aminophenol	Alkyl propiolate	Products	
1		 **1**	 **13a** (50%)	 **14a** (40%)
2	 **12**	 **4b**	 **13a** (50%)	 **14b** (40%)
3		 **7**	 **13b** (75%)	–
4	 **15**	 **4b**	 **13c** (40%)	 **14c** (45%)
5	 **16**	 **4b**	 **13d** (70%)	 **14d** (30%)
6	 **17**	 **4b**	 **13e** (55%)	 **14e** (40%)
7	 **18**	 **4b**	 **13f** (65%)	 **14f** (30%)

nol was treated with ethyl propiolate in the presence of Ph_3P only the O-vinylation products were obtained (Table 2).

The presented reactions provide simple entries to the synthesis of methyl 2-(1,3-benzodioxol-2-yl)acetate (**3**), 3-alkyl-2*H*-1,4-benzoxazin-2-one derivatives **13a–f**, and alkyl (*E*)-3-(aminophenoxy)-2-propenoates **14a–f**, **27**, and **28** of potential synthetic interest.

Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance instrument with $CDCl_3$ as solvent at 500.1 MHz and 125.7 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Alkyl propiolates, hydroxyphenols, aminophenols, and Ph_3P were obtained from Fluka and were used without further purification.

Preparation of Compounds 3, 8, 13, and 14; General Procedure

To a stirred solution of the phenol derivative (2 mmol) and the alkyl propiolate (2 mmol) in CH_2Cl_2 (10 mL) was added dropwise at –10 °C over 10 min Ph_3P (2 mmol). The reaction mixture was then allowed to warm to r.t. and stand for 24 h. The solvent was removed under reduced pressure and the residue was separated by silica gel column chromatography (Merck 230–400 mesh) using *n*-hexane–EtOAc (4:1) as eluent to give the product.

Methyl 2-(1,3-Benzodioxol-2-yl)acetate (3)

Yield: 0.06 g (20%); colorless oil.

IR (KBr): 1732 (C=O), 1224 (CO) cm^{-1}.

^{1}H NMR: δ = 3.0 (d, $^3J_{HH}$ = 5.2 Hz, 2 H, CH_2), 3.77 (s, 3 H, OCH_3), 6.5 (t, $^3J_{HH}$ = 5.2 Hz, 1 H, CH), 6.83 (m, 2 H, 2 × CH), 7.3 (m, 2 H, 2 × CH).

^{13}C NMR: δ = 40.1 (CH_2), 52.1 (OCH_3), 107.5 (OCHO), 121.7 (CH), 128.7 (CH), 133.8 (C), 168.7 (C=O).

MS: *m*/*z* (%) = 195 (5) [M$^+$ + 1], 194 (10) [M$^+$], 163 (15), 110 (100), 57 (20).

Anal. Calcd for $C_{10}H_{10}O_4$ (194.1): C, 61.85; H, 5.19. Found: C, 61.80; H, 5.20.

3-(1-Phenylmethylidene)-1,4-benzodioxin-2-one (8)

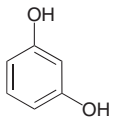
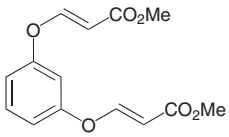
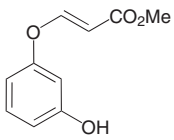
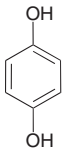
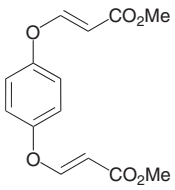
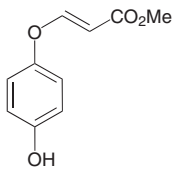
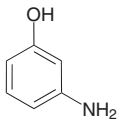
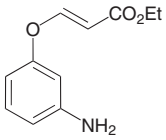
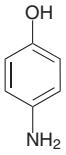
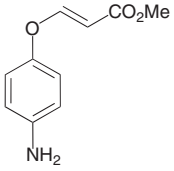
Yield: 0.26 g (55%); white solid; mp 109–110 °C.

IR (KBr): 1731 (C=O), 1632, 1487, 1358, 1286, 1180 (CO) cm^{-1}.

^{1}H NMR: δ = 7.01 (m, 1 H, CH), 7.10 (m, 2 H, 2 × CH), 7.12 (s, 1 H, CH), 7.17 (m, 1 H, CH), 7.36 (m, 2 H, CH), 7.41 (m, 1 H, 2 × CH), 7.82 (m, 2 H, 2 × CH).

^{13}C NMR: δ = 116.2 (CH), 117.4 (CH), 119.1 (CH), 123.8 (CH), 125.4 (CH), 128.7 (CH), 129.6 (CH), 130.7 (CH), 132.6 (C), 136.0 (C), 139.3 (C), 139.5 (C), 162.0 (C).

Table 2 O-Vinylation of Resorcinol, Hydroquinone, 1,3-Diaminobenzene, and 1,4-Diaminobenzene with Alkyl Propiolates in the Presence of Triphenylphosphine

Entry	Hydroxyphenol	Products	
1	 **19**	 **23** (50%)	 **24** (40%)
2	 **20**	 **25** (60%)	 **26** (30%)
3	 **21**	 **27** (60%)	–
4	 **22**	 **28** (80%)	–

MS: *m/z* (%) = 239 (3) [M$^+$ + 1], 238 (8) [M$^+$], 210 (9), 147 (21), 132 (37), 130 (40), 91 (100), 44 (52).

Anal. Calcd for $C_{15}H_{10}O_3$ (238.2): C, 75.62; H, 4.23. Found: C, 75.60; H, 4.26.

3-Methyl-2*H*-1,4-benzoxazine-2-one (13a)
Yield: 0.16 g (50%); white solid; mp 97–98 °C.

IR (KBr): 1718 (C=O), 1087 (CO) cm^{-1}.

^{1}H NMR: δ = 2.60 (s, 3 H, CH_3), 7.31 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH), 7.37 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, CH), 7.50 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, CH), 7.70 (d, $^3J_{HH}$ = 7.4 Hz, 1 H, CH).

^{13}C NMR: δ = 21.3 (CH_3), 116.4 (CH), 125.4 (CH), 128.6 (CH), 131.1 (CH), 132.0 (CN), 146.6 (CO), 153.2 (N=C), 155.1 (C=O).

MS: *m/z* (%) = 162 (3) [M$^+$ + 1], 161 (6) [M$^+$], 146 (50), 120 (5), 118 (20), 76 (15).

Anal. Calcd for $C_9H_7NO_2$ (161.2): C, 67.08; H, 4.38; N, 8.69. Found: C, 67.18; H, 4.30; N, 8.73.

3-Benzyl-2*H*-1,4-benzoxazin-2-one (13b)
Yield: 0.34 g (75%); pale yellow solid; mp 116–118 °C.

IR (KBr): 1732 (C=O), 1052 (CO) cm^{-1}.

^{1}H NMR: δ = 4.20 (s, 2 H, CH_2), 7.25 (d, $^3J_{HH}$ = 7.1 Hz, 2 H, 2 × CH), 7.31 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, CH), 7.34 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, CH), 7.40–7.47 (m, 4 H, 4 × CH), 7.74 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, CH).

^{13}C NMR: δ = 40.6 (CH_2), 125.4 (CH), 127.1 (CH), 128.6 (CH), 129.1 (CH), 129.6 (CH), 130.8 (CH), 131.3 (CH), 132.3 (C), 135.5 (C), 146.6 (C), 152.8 (C), 156.3 (C=O).

MS: *m/z* (%) = 238 (6) [M$^+$ + 1], 237 (8) [M$^+$], 146 (51), 91 (100), 44 (12).

Anal. Calcd for $C_{15}H_{11}NO_2$ (237.2): C, 75.94; H, 4.67; N, 5.90. Found: C, 76.00; H, 4.50; N, 5.75.

6-Chloro-3-methyl-2*H*-1,4-benzoxazin-2-one (13c)
Yield: 0.14 g (40%); yellow oil.

IR (KBr): 1732 (C=O), 1218, 1115 cm^{-1}.

^{1}H NMR: δ = 2.44 (s, 3 H, CH_3), 7.05 (s, 1 H, CH), 7.13 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, CH), 7.55 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, CH).

^{13}C NMR: δ = 21.5 (CH_3), 116.4 (CH), 126.4 (CH), 128.1 (CH), 128.5 (CCl), 129.1 (CN), 146.4 (CO), 153.4 (C), 153.7 (C=O).

MS: *m/z* (%) = 196 (7) [M$^+$], 181 (23), 168 (34), 141 (63), 55 (100).

Anal. Calcd for $C_9H_6ClNO_2$ (195.6): C, 55.26; H, 3.09; N, 7.16. Found: C, 55.21; H, 3.00; N, 7.25.

7-Chloro-3-methyl-2*H*-1,4-benzoxazin-2-one (13d)
Yield: 0.26 g (70%); yellow solid; mp 55 °C.

IR (KBr): 1728 (C=O), 1187, 1113 cm^{-1}.

^{1}H NMR: δ = 2.56 (s, 3 H, CH_3), 7.30 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, CH), 7.33 (s, 1 H, CH), 7.71 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, CH).

^{13}C NMR: δ = 29.7 (CH_3), 116.7 (CH), 125.9 (CH), 129.5 (CH), 132.2 (C), 132.3 (C), 133.6 (C), 133.8 (C), 155.1 (C=O).

MS: *m/z* (%) = 196 (9) [M$^+$], 181 (27), 168 (41), 141 (53), 55 (100).

Anal. Calcd for $C_9H_6ClNO_2$ (195.6): C, 55.26; H, 3.09; N, 7.16. Found: C, 55.21; H, 3.10; N, 7.34.

3,6-Dimethyl-2*H*-1,4-benzoxazine-2-one (13e)
Yield: 0.18 g (55%); yellow crystal; mp 139–143 °C.

IR (KBr): 1725 (C=O), 1095 (CO) cm^{-1}.

^1H NMR: δ = 2.42 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 7.16 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH), 7.26 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH), 7.32 (s, 1 H, CH).

^{13}C NMR: δ = 20.8 (CH_3), 21.3 (CH_3), 115.9 (CH), 131.4 (CH), 135.3 (CH), 137.1 (C), 137.2 (C), 144.5 (C), 153.5 (C), 154.9 (CO).

MS: *m*/*z* (%) = 176 (3) [M^+ + 1], 175 (8) [M^+], 160 (31), 120 (70), 91 (100), 55 (72).

Anal. Calcd for $C_{10}H_9NO_2$ (175.2): C, 68.56; H, 5.18; N, 8.00. Found: C, 68.50; H, 5.23; N, 8.08.

3,7-Dimethyl-2*H*-1,4-benzoxazin-2-one (13f)
Yield: 0.22 g (65%); pale yellow oil.

IR (KBr): 1719 (C=O), 1099 (CO) cm^{-1}.

^1H NMR: δ = 2.44 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 7.0 (s, 1 H, CH), 7.13 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, CH), 7.55 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, CH).

^{13}C NMR: δ = 21.2 (CH_3), 21.5 (CH_3), 116.4 (CH), 126.4 (CH), 128.1 (C), 129.1 (CH), 141.6 (C), 146.4 (C), 153.4 (C), 153.7 (CO).

MS: *m*/*z* (%) = 176 (4) [M^+ + 1], 175 (9) [M^+], 160 (43), 120 (65), 91 (100), 55 (59).

Anal. Calcd for $C_{10}H_9NO_2$ (175.2): C, 68.56; H, 5.18; N, 8.00. Found: C, 68.50; H, 5.20; N, 8.34.

Methyl (*E*)-3-(2-Aminophenoxy)-2-propenoate (14a)
Yield: 0.14 g (40%); yellow oil.

IR (KBr): 3270 (NH_2), 1697 (C=O), 1192 (CO) cm^{-1}.

^1H NMR: δ = 3.73 (s, 3 H, Me), 3.90 (br s, 2 H, NH_2), 5.60 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH), 6.73 (t, $^3J_{HH}$ = 6.6 Hz, 1 H, CH), 6.78 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH), 6.93 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH), 7.02 (t, $^3J_{HH}$ = 6.6 Hz, 1 H, CH), 7.78 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH).

^{13}C NMR: δ = 51.3 (CH_3), 101.2 (CH), 116.6 (CH), 118.6 (CH), 120.7 (CH), 126.0 (CH), 141.5 (C), 143.2 (C), 159.9 (CH), 170.6 (C=O).

MS: *m*/*z* (%) = 194 (4) [M^+ + 1], 193 (8) [M^+], 178 (19), 162 (42), 134 (60), 107 (100), 92 (51), 86 (39), 60 (42).

Anal. Calcd for $C_{10}H_{11}NO_3$ (193.2): C, 62.17; H, 5.74; N, 7.25. Found: C, 62.25; H, 5.38; N, 7.40.

Ethyl (*E*)-3-(2-Aminophenoxy)-2-propenoate (14b)
Yield: 0.16 g (40%); yellow oil.

IR (KBr): 3265 (NH_2), 1696 (C=O), 1117 (CO) cm^{-1}.

^1H NMR: δ = 1.31 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3), 3.9 (br s, 2 H, NH_2), 4.20 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2), 5.53 (d, $^3J_{HH}$ = 12.1 Hz, 1 H, CH), 6.70 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, CH), 6.81 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH), 6.90 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH), 7.01 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, CH), 7.78 (d, $^3J_{HH}$ = 12.1 Hz, 1 H, CH).

^{13}C NMR: δ = 14.3 (CH_3), 60.1 (CH_2), 101.6 (CH), 116.6 (CH), 118.7 (CH), 118.8 (CH), 125.9 (CH), 137.5 (C), 143.7 (C), 159.7 (CH), 169.8 (C=O).

MS: *m*/*z* (%) = 208 (4) [M^+ + 1], 207 (9) [M^+], 178 (21), 162 (37), 134 (82), 107 (100), 100 (37), 92 (44), 74 (29), 45 (31).

Anal. Calcd for $C_{11}H_{13}NO_3$ (207.2): C, 63.76; H, 6.32; N, 6.76. Found: C, 63.71; H, 6.37; N, 6.64.

Ethyl (*E*)-3-(2-Amino-4-chlorophenoxy)-2-propenoate (14c)
Yield: 0.20 g (45%); yellow oil.

IR (KBr): 3270 (NH_2), 1698 (C=O), 1633, 1490, 1192 (CO), 1115 cm^{-1}.

^1H NMR: δ = 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3), 4.16 (br s, 2 H, NH_2), 4.17 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2), 5.51 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH), 6.71 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.4 Hz, 1 H, CH), 6.79 (d, $^4J_{HH}$ = 2.4 Hz, 1 H, CH), 6.86 (d, $^3J_{HH}$ = 8.5 Hz, 1 H), 7.68 (d, $^3J_{HH}$ = 12.2 Hz, 1 H).

^{13}C NMR: δ = 14.3 (CH_3), 60.2 (CH_2), 102.2 (CH), 116.4 (CH), 118.6 (CH), 119.6 (CH), 131.1 (CN), 138.2 (CCl), 141.3 (CO), 159.1 (CH), 166.9 (C=O).

MS: *m*/*z* (%) = 242 (9) [M^+], 227 (16), 213 (31), 197 (70), 169 (64), 142 (100), 100 (52), 73 (21), 29 (15).

Anal. Calcd for $C_{11}H_{12}ClNO_3$ (241.7): C, 54.6; H, 5.0; N, 5.8. Found: C, 54.2; H, 5.5; N, 5.16.

Ethyl (*E*)-3-Amino-5-chlorophenoxy-2-propenoate (14d)
Yield: 0.14 g (30%); yellow oil.

IR (KBr): 3275 (NH_2), 1685 (C=O), 1490, 1281, 1198 cm^{-1}.

^1H NMR: δ = 1.28 (t, $^3J_{HH}$ = 7.4 Hz, 3 H, CH_3), 4.31 (q, $^3J_{HH}$ = 7.4 Hz, 2 H, CH_2), 5.53 (q, $^3J_{HH}$ = 12.1 Hz, 1 H, CH), 6.66 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH), 6.87 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH), 6.94 (s, 1 H, CH), 7.69 (d, $^3J_{HH}$ = 12.1 Hz, 1 H, CH).

^{13}C NMR: δ = 14.3 (CH_3), 60.5 (CH_2), 102.5 (CH), 117.1 (CH), 122.8 (CH), 128.7 (CH), 136.1 (CCl), 142.7 (CN), 152.0 (CO), 158.8 (CH), 167.9 (C=O).

MS: *m*/*z* (%) = 242 (7) [M^+], 227 (31), 213 (22), 197 (65), 169 (69), 142 (100), 100 (64), 73 (27), 29 (18).

Anal. Calcd for $C_{11}H_{12}ClNO_3$ (241.7): C, 54.67; H, 5.00; N, 5.80. Found: C, 54.61; H, 5.08; N, 5.47.

Ethyl (*E*)-3-(2-Amino-4-methylphenoxy)-2-propenoate (14e)
Yield: 0.16 g (40%); yellow oil.

IR (KBr): 3267 (NH_2), 1119 (CO), 1699 (C=O) cm^{-1}.

^1H NMR: δ = 1.28 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 4.16 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 3.86 (br s, 2 H, NH_2), 5.46 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH), 6.53 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, CH), 6.59 (s, 1 H, CH), 6.81 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, CH), 7.72 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH).

^{13}C NMR: δ = 14.3 (CH_3), 29.7 (CH_3), 60.0 (CH_2), 101.2 (CH), 117.2 (CH), 118.7 (CH), 119.4 (CH), 135.9 (C), 137.1 (C), 140.1 (C), 160.1 (CH), 167.2 (CO).

MS: *m*/*z* (%) = 221 (7) [M^+], 192 (41), 148 (29), 130 (12), 121 (72), 100 (39), 91 (100).

Anal. Calcd for $C_{12}H_{15}NO_3$ (221.2): C, 65.14; H, 6.83; N, 6.33. Found: C, 65.20; H, 6.54; N, 6.19.

Ethyl (*E*)-3-(2-Amino-5-methylphenoxy)-2-propenoate (14f)
Yield: 0.12 g (30%); yellow oil.

IR (KBr): 3260 (NH_2), 1697 (C=O), 1633, 1587, 1169 (CO) cm^{-1}.

^1H NMR: δ = 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 4.16 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH_2), 5.49 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH), 6.68 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH), 6.75 (s, 1 H, CH), 6.8 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH), 7.74 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH).

^{13}C NMR: δ = 14.0 (CH_3), 20.4 (CH_3), 60.0 (CH_2), 101.4 (CH), 116.6 (CH), 119.2 (CH), 126.4 (CH), 128.5 (C), 134.7 (C), 142.7 (C), 159.8 (CH), 167.2 (CO).

MS: *m*/*z* (%) = 221 (6) [M^+], 192 (34), 148 (42), 130 (21), 121 (70), 100 (46), 91 (100).

Anal. Calcd for $C_{12}H_{15}NO_3$ (221.3): C, 65.14; H, 6.83; N, 6.33. Found: C, 65.24; H, 6.73; N, 6.25.

Preparation of Compounds 23–28; General Procedure
To a solution of the hydroxyphenol (2 mmol) and the alkyl propiolate (4 mmol) in CH_2Cl_2 (10 mL) was added dropwise at –10 °C over 10 min a solution of Ph_3P (4 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was allowed to warm to r.t. and stand for 24 h. The solvent was removed under reduced pressure and the residue was separated by silica gel column chromatography (Merck 230–400 mesh) using *n*-hexane–EtOAc (4:1) as eluent to give the product.

Methyl (*E*)-3-(3-{[(*E*)-3-Methoxy-3-oxo-1-propenyl]oxy}phenoxy)-2-propenoate (23)
Yield: 0.26 g (50%); colorless oil.

IR (KBr): 1697 (C=O), 1148 (CO) cm^{-1}.

^1H NMR: δ = 3.75 (s, 6 H, 2 × CH_3), 5.63 (d, $^3J_{HH}$ = 12.1 Hz, 2 H, CH), 6.80 (t, $^4J_{HH}$ = 2.2 Hz, 1 H, CH), 6.91 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.2 Hz, 2 H, 2 × CH), 7.38 (t, $^3J_{HH}$ = 8.2 Hz, 1 H, CH), 7.70 (d, $^3J_{HH}$ = 12.1 Hz, 2 H, CH).

^{13}C NMR: δ = 51.4 (2 × CH_3), 102.9 (2 × CH), 108.2 (CH), 114.1 (2 × CH), 131.1 (CH), 156.9 (2 × CH), 158.0 (2 × C), 167.3 (2 × C=O).

MS: *m*/*z* (%) = 279 (6) [M^+ + 1], 278 (12) [M^+], 150 (18), 108 (73), 57 (100).

Anal. Calcd for $C_{14}H_{14}O_6$ (278.3): C, 60.43; H, 5.07. Found: C, 60.54; H, 5.17.

Methyl (*E*)-3-(3-Hydroxyphenoxy)-2-propenoate (24)
Yield: 0.14 g (40%); yellow oil.

IR (KBr): 3365 (OH), 1676 (C=O), 1141 (CO) cm^{-1}.

^1H NMR: δ = 3.75 (s, 3 H, CH_3), 5.59 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH), 6.59 (s, 1 H, CH), 6.62 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, CH), 6.67 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, CH), 7.2 (t, $^3J_{HH}$ = 8.1 Hz, 1 H, CH), 7.80 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH).

^{13}C NMR: δ = 51.5 (CH_3), 101.8 (CH), 105.5 (CH), 109.8 (CH), 112.1 (CH), 130.6 (CH), 156.9 (CH), 157.3 (C), 159.1 (C), 168.1 (C=O).

MS: *m*/*z* (%) = 194 (8) [M^+], 179 (23), 135 (51), 108 (100), 86 (72), 59 (21), 31 (18).

Anal. Calcd for $C_{10}H_{10}O_4$ (194.2): C, 61.85; H, 5.19. Found: C, 61.80; H, 5.20.

Methyl (*E*)-3-(4-{[(*E*)-3-Methoxy-3-oxo-1-propenyl]oxy}phenoxy)-2-propenoate (25)
Yield: 0.32 g (60%); white solid; mp 120–122 °C.

IR (KBr): 1705 (C=O), 1114 (CO) cm^{-1}.

^1H NMR: δ = 3.71 (s, 6 H, 2 × OMe), 5.53 (d, $^3J_{HH}$ = 12.6 Hz, 2 H, 2 × CH), 7.06 (s, 4 H, CH), 7.73 (d, $^3J_{HH}$ = 12.6 Hz, 2 H, 2 × CH).

^{13}C NMR: δ = 51.3 (2 × CH_3), 102.1 (2 × CH), 119.6 (4 × CH), 152.7 (2 × C), 159.0 (2 × CH), 167.4 (2 × C=O).

MS: *m*/*z* (%) = 279 (4) [M^+ + 1], 278 (11) [M^+], 150 (10), 108 (70), 57 (100).

Anal. Calcd for $C_{14}H_{14}O_6$ (278.3): C, 60.43; H, 5.07. Found: C, 60.37; H, 5.27.

Methyl (*E*)-3-(4-Hydroxyphenoxy)-2-propenoate (26)
Yield: 0.1 g (30%); yellow oil.

IR (KBr): 3365 (OH), 1688 (C=O) cm^{-1}.

^1H NMR: δ = 3.74 (s, 3 H, CH_3), 5.47 (d, $^3J_{HH}$ = 12.3 Hz, 1 H, CH), 6.83 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, CH), 6.90 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, CH), 7.71 (d, $^3J_{HH}$ = 12.3 Hz, 1 H, CH).

^{13}C NMR: δ = 51.5 (CH_3), 100.5 (CH), 116.4 (2 × CH), 119.5 (2 × CH), 149.2 (C), 153.6 (C), 161.1 (CH), 168.7 (C=O).

MS: *m*/*z* (%) = 194 (5) [M^+], 179 (20), 135 (43), 108 (100), 86 (64), 59 (32), 31 (12).

Anal. Calcd for $C_{10}H_{10}O_4$ (194.2): C, 61.85; H, 5.19. Found: C, 61.75; H, 5.30.

Ethyl (*E*)-3-(3-Aminophenoxy)-2-propenoate (27)
Yield: 0.24 g (60%); yellow oil.

IR (KBr): 3260 (NH_2), 1698 (C=O), 1112 (CO) cm^{-1}.

^1H NMR: δ = 1.28 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, CH_3), 3.78 (br s, 2 H, NH_2), 4.18 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, CH), 5.54 (d, $^3J_{HH}$ = 12.1 Hz, 1 H, CH), 6.33 (s, 1 H, CH), 6.44 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, CH), 6.48 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, CH), 7.1 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, CH), 7.76 (d, $^3J_{HH}$ = 12.1 Hz, 1 H, CH).

^{13}C NMR: δ = 14.3 (CH_3), 60.0 (CH_2), 101.9 (CH), 104.6 (CH), 107.6 (CH), 111.6 (CH), 130.5 (CH), 148.7 (CN), 157.0 (CO), 159.0 (CH), 167.3 (CO).

MS: *m*/*z* (%) = 208 (4) [M^+ + 1], 207 (11) [M^+], 178 (29), 134 (45), 107 (100), 100 (65), 73 (24), 29 (12).

Anal. Calcd for $C_{11}H_{13}NO_3$ (207.2): C, 63.76; H, 6.32; N, 6.76. Found: C, 63.70; H, 6.36; N, 6.81.

Methyl (*E*)-3-(4-Aminophenoxy)-2-propenoate (28)
Yield: 0.3 g (80%); pale yellow solid; mp 55 °C.

IR (KBr): 3385 (NH_2), 1728 (CO), 1162 (CO) cm^{-1}.

^1H NMR: δ = 3.68 (s, 3 H, CH_3), 3.77 (s, 2 H, NH_2), 5.42 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH), 6.61 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, 2 × CH), 6.8 (d, $^3J_{HH}$ = 8.7 Hz, 2 H, 2 × CH), 7.71 (d, $^3J_{HH}$ = 12.2 Hz, 1 H, CH).

^{13}C NMR: δ = 51.2 (CH_3), 100.3 (CH), 115.9 (2 × CH), 119.3 (2 × CH), 143.9 (C), 148.2 (C), 160.9 (CH), 167.9 (C=O).

MS: *m*/*z* (%) = 194 (2) [M^+ + 1], 193 (6) [M^+], 178 (22), 162 (64), 134 (40), 107 (100), 86 (56), 59 (13), 31 (14).

Anal. Calcd for $C_{10}H_{11}NO_3$ (193.2): C, 62.17; H, 5.74; N, 7.25. Found: C, 62.27; H, 5.63; N, 7.31.

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