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Cathodic reduction of hydroxycarbonyl compound trichloroacetyl esters

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Abstract—New coumarins and new 2-(2′,2′-dichlorovinyl) phenols have been prepared by cathodic reduction under potentiostatic conditions of trichloroacetyl esters of *o*-hydroxyketones and *o*-hydroxyaldehydes in aprotic media. Electroreductions of trichloroacetyl esters of α-hydroxy-1,4-naphthoquinone, 3-hydroxy-2-methyl-4-pyrone, methyl salicylate and benzoin have also been investigated.

1. Introduction

In previous work, we have described an easy methodology to prepare heterocycles such as 3-chloro-4-alkyl(or aryl) coumarins,[1,2] or 1-alkyl-4-alkyl(or aryl)-3-chloro quinolinones[3] in good yield by cathodic reduction of trichloroacetyl esters of *o*-hydroxyphenones or *o*-(*N*-alkyl)aminophenones, respectively. In these cases, the consumption of the charge was corresponding to a $3e^-$/substrate molecule, and after the first electron transfer the electrogenerated radical-anion undergoes C–Cl cleavage to give a chlorine radical and an organic anion. The latter is highly stabilized by the electron withdrawing effect of two halogen atoms and by the resonance effect of the adjacent carbonyl group.[2]

In the present work, we report one pot synthesis of 3-chlorocoumarins and styrenes by cathodic reduction of trichloroacetyl esters of phenones and salicylaldehydes, respectively. An interesting feature of the cathodic reductions of salicylaldehydes is the formation of some styrenes, which have never been described in literature. The electrochemistry has been extensively applied not only to reduce phenones, but also to trichloroacetyl esters of α-hydroxy-1,4-naphthoquinone, 3-hydroxy-2-methyl-4-pyrone, methyl salicylate and *o*-hydroxyphenyl aldehydes.

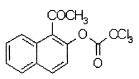
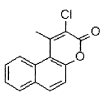
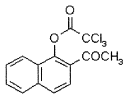
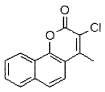
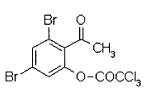
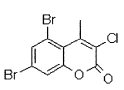
3-Halocoumarins possess hypnotic, insecticidal, and fungicidal properties[4,5] and can be used as potent inhibitors to trigger vasoconstriction.[6] However, in the literature only three methods describe the direct synthesis of 3-chloro-4-alkylcoumarins[4,7] but these syntheses proceed with poor yields and multiple steps.

2. Results and discussion

Electrolysis at a controlled potential of −1 V (vs SCE) of trichloroacetyl esters of 1-acetyl-2-naphthol (**1a**), 2-acetyl-1-naphthol (**1b**) and 1-acetyl-4,6-dibromophenol (**1c**) yielded 3-chloro-4-methyl-benzo[*f*]-coumarin (**2a**), 3-chloro-4-methyl-benzo[*h*]-coumarin (**2b**) and 3-chloro-5,7-dibromo-4-methyl-coumarin (**2c**), respectively, as shown in Table 1.

It is a well known fact that aldehydes are more reactive (vs nucleophiles) as compared to ketones, so we opted to reduce the esters of salicylaldehydes **1**(**d**–**f**) to further improve the yields of the corresponding 3-chloro-coumarins. Surprisingly, the desired coumarins were not

Table 1. Transformation of trichloroacetyl esters **1** into the corresponding coumarins **2**

Substrate	Product	Yield (%)
 (**1a**)	 (**2a**)	63
 (**1b**)	 (**2b**)	45
 (**1c**)	 (**2c**)	62

Keywords: electrosynthesis; cathodic reduction; constant potential; coumarins.

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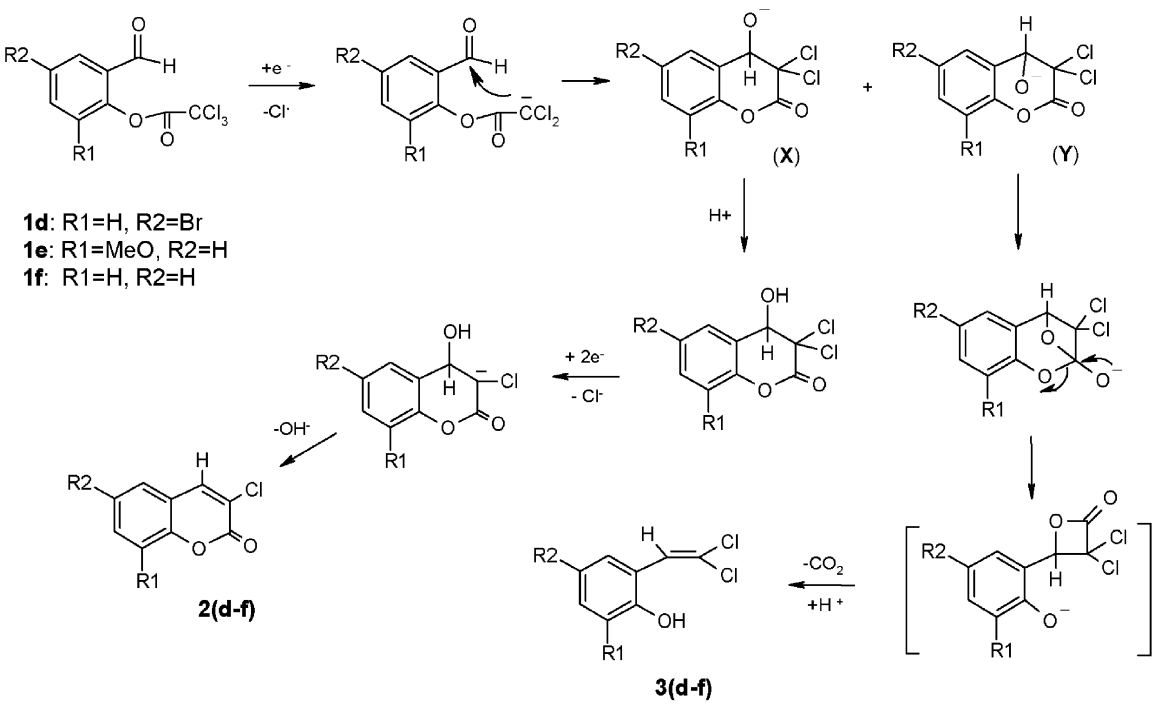


Scheme 1.

obtained in expected yields. When esters of salicylaldehydes were reduced at −1.0 V (vs SCE), 3-chlorocoumarins **2**(**d**–**f**) and a new product **3** were formed in 40–43% and 20–23% yield, respectively. These new products **3**(**d**–**f**) were isolated and identified as 2-(2′,2′-dichlorovinyl)phenols. The formation of **3** can be explained by the mechanism proposed in Scheme 1.

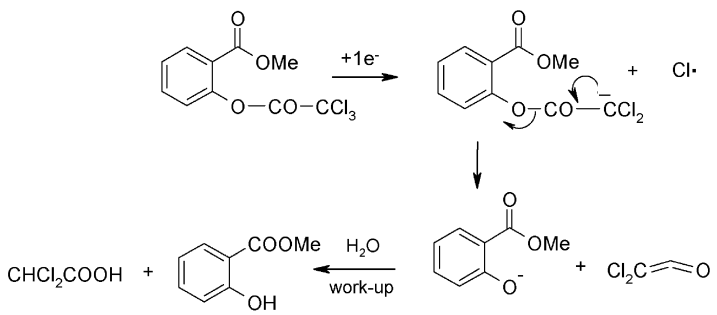
After the first electron transfer, two different conformations *X* and *Y* are obtained for the cyclated anion. The stereochemical environment of conformation *Y* facilitates the formation of phenols **3**. In the *Y* conformation the negatively charged oxygen atom is proximal to the carbonyl group. This approximation is possible only if the aldehydic hydrogen atom is between the two chlorine atoms of the adjacent carbon. In other words, the molecule adopts a *gauche* conformation. However ketones, where the aldehydic hydrogen atom is replaced by an alkyl or aryl group, the molecule in *gauche* conformation is sterically hindered, for this reason, molecules prefer the staggered conformation, and consequently only the expected coumarins **2**(**a**–**c**) are formed. It explains why the corresponding dichlorostyrenes were not obtained when esters of hydroxyketones were reduced.

In the cathodic reduction of salicylaldehyde esters, the presence of substituents on the aromatic ring does not affect, as expected, the yield ratio coumarin/styrene.

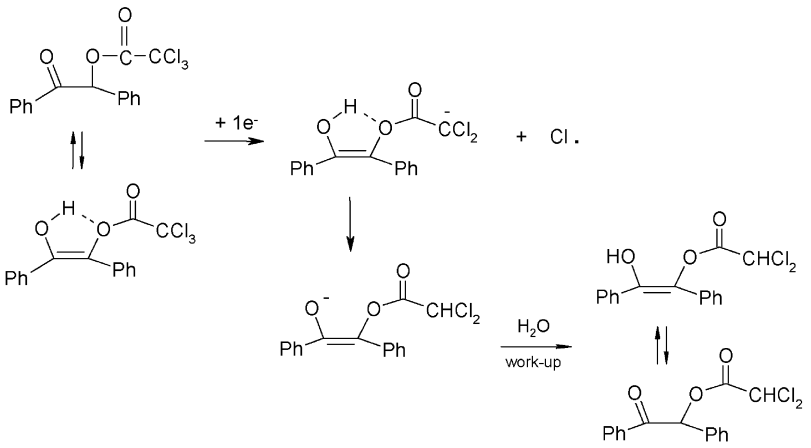
However, the electroreduction of trichloroacetyl esters of hydroxy 1,4-naphthoquinone, 3-hydroxy-2-methyl-4-pyrone and methylsalicylate only afforded the corresponding hydroxy derivatives. In these cases the expected coumarins were not formed due to the lower reactivity of these carbonyl groups. The first electrogenerated anion evolves as indicated in Scheme 2.

It has been reported in the literature that the attempts to obtain coumarin from methylsalicylate by the chemical methods have never been successful.[7a]

In the reduction of **1**(**a**–**c**) and **1**(**d**–**f**), where coumarins were obtained, the experimental charge consumption was always less than theoretically expected for a $3e^-$ process, due to the formation, together with the coumarins, of the corresponding phenols (Scheme 2) or styrenes, respectively, in a $1e^-$ process. In the other cases, where coumarins were not formed, the experimental charge consumption was the corresponding to $1e^-$/substrate molecules.



Scheme 2.



Scheme 3.

Finally, the cathodic reduction of trichloroacetyl ester of benzoin was carried out, leading to the formation of the corresponding dichloroacetyl ester. It can be explained by protonation of the first electrogenerated carbanion by the OH on the highly stabilized enolic form of trichloroacetyl ester of benzoin (Scheme 3).

3. Experimental

The electrolyses were carried out using an Amel potentiostat, Model 552, connected with an electronic coulombimeter-integrator Amel, Model 721.

Mass spectra (EI, ionizing voltage 70 eV) were determined with a Hewlett–Packard Model 5988A mass-selective detector equipped with a Hewlett–Packard MS Chem Station. IR spectra were obtained, as dispersions in KBr, on a Perkin–Elmer Model 583 spectrophotometer. ^{1}H NMR and ^{13}C NMR (300 and 75.4 MHz, respectively) spectra were recorded on a Varian Unity 300 apparatus with deuteriochloroform as an internal standard. The chemical shifts are given in ppm.

Melting points were determined on a Reichert Thermovar microhot stage apparatus, and are uncorrected. Elemental analyses were performed on a Perkin–Elmer Model 240-B analyzer. The products were purified by silica gel 60 (35–70 mesh) in a (24×2.5 cm) column, using mixtures $CHCl_3$/hexane as eluent.

3.1. General procedure

Treatment of α-hydroxy carbonyl compounds with trichloroacetyl chloride gave rise to electroactive esters (**1**) quantitatively. Trichloroacetyl chloride was added dropwise to a stirred solution of α-hydroxy ketones (or aldehydes) in dry THF in the presence of equimolar amount of triethylamine. The crude product was filtered and the esters were obtained from the solution after removal of the solvent.

3.1.1. 1-Acetyl-napthyltrichloroacetate (1a). IR (KBr) ν (cm^{-1}): 3079, 1783, 1695, 1623, 1211, 856, 835, 801, 746, 663. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.57 (s, 3H), 7.17 (d, 1H, J=9 Hz), 7.32–7.43 (m, 2H), 7.62–7.75 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 25.7, 90.0, 119.3, 124.5, 126.9, 128.1, 128.5, 129.4, 130.4, 131.4, 131.9, 143.6, 160.1, 201.3. MS *m/e* (relative intensity) EI: 334 (M^++4, 7), 332 (M^++2, 22), 330 (M^+, 22), 319 (9), 317 (27), 315 (27), 186 (27), 171 (47), 168 (100), 157 (33), 141 (40), 129 (56), 114 (65).

3.1.2. 2-Acetyl-napthyltrichloroacetate (1b). IR (KBr) ν (cm^{-1}): 3070, 1782, 1680, 1627, 1211, 765, 660. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.71 (s, 3H), 7.61–7.66 (m, 2H), 7.87–7.94 (m, 3H), 8.12–8.17 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 29.7, 90.0, 122.2, 125.1, 125.5, 126.7, 127.3, 128.0, 128.2, 129.1, 136.3, 145.0, 160.0, 197.0. MS *m/e* (relative intensity) EI: 334 (M^++4, 2), 332 (M^++2, 7), 330 (M^+, 7), 213 (5), 168 (100), 157 (22), 129 (25), 114 (22).

3.1.3. 2-Acetyl-4,6-dibromo-phenyltrichloroacetate (1c). IR (KBr) ν (cm^{-1}): 2981, 1760, 1694, 1207, 833, 677. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.57 (s, 3H), 7.86 (d, 1H, J=2.3 Hz), 7.94 (d, 1H, J=2.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 29.1, 89.9, 119.2, 121.0, 132.4, 133.0, 139.5, 145.0, 158.8, 194.4. MS *m/e* (relative intensity) EI: 442 (M^++6, 5), 440 (M^++4, 10), 438 (M^++2, 9), 436 (M^+, 3), 323 (8), 321 (16), 319 (8), 278 (30), 276 (54), 274 (25), 199 (18), 158 (14), 156 (15), 143 (23), 119 (93), 117 (100).

3.1.4. 4-Bromo-2-formyl-phenyltrichloroacetate (1d). IR (KBr) ν (cm^{-1}): 3094, 2878, 1784, 1694, 1593, 1209, 1105, 861, 840, 672. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.25 (d, 1H, J=8.4 Hz), 7.80 (dd, 1H, J_1=2.5 Hz, J_2=8.7 Hz), 8.05 (d, 1H, J=2.5 Hz), 10.1 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 90.0, 121.4, 124.2, 129.2, 133.6, 138.5, 150.2, 159.9, 186.2. MS *m/e* (relative intensity) EI: 348 (M^++4, 2), 346 (M^++2, 3), 344 (M^+, 2), 229 (32), 227 (33), 173 (10), 171 (10), 145 (22), 143 (22), 121 (29), 119 (100), 117 (100), 86 (59), 63 (85).

3.1.5. 6-Methoxy-2-formyl-phenyltrichloroacetate (1e). IR (KBr) ν (cm^{-1}): 2950, 2846, 2768, 1785, 1700, 1581, 1445, 1282, 1253, 1207, 1071, 951, 817, 673. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.9 (s, 3H), 7.24–7.29 (m, 1H), 7.37–7.49 (m, 2H), 10.21 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$)

δ: 56.7, 90.0, 118.4, 121.0, 128.2, 128.9, 140.0, 151.2, 160.0, 187.5. MS *m/e* (relative intensity) EI: 300 (M^++4, 1) 298 (M^++2, 2) 296 (M^+, 3), 205 (6), 179 (21), 152 (100), 151 (65), 109 (35), 106 (46), 81 (28).

3.1.6. 2-Formyl-phenyltrichloroacetate (1f). IR (NaCl) ν (cm^{-1}): 2862, 2759, 1791, 1699, 1608, 1211, 822, 754, 674. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32 (d, 1H, *J*=8.2 Hz), 7.49 (t, 1H, *J*=7.4 Hz), 7.7 (dt, 1H, J_1=1.8 Hz, J_2=8 Hz), 7.95 (dd, 1H, J_1=1.8 Hz, J_2=7.7 Hz), 10.12 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 89.4, 122.4, 127.9, 128.0, 131.4, 135.8, 151.0, 160.1, 187.8. MS *m/e* (relative intensity) EI: 268 (M^++2, 1), 266 (M^+, 1), 230 (2), 177 (4), 175 (6), 169 (4), 167 (13), 149 (100), 119 (66), 117 (67).

3.2. General electrochemical procedure

The electrochemical reductions were carried out under the following experimental conditions:

Cathode—mercury pool. Catholyte—$LiClO_4$ (1.7 g, 1.6×10^{-3} mol) in dry CH_3CN (40 mL) and **1** (3×10^{-3} mol). Anode—platinum plate. Anolyte—$LiClO_4$ (0.42 g, 0.4×10^{-3} mol) in dry CH_3CN (10 mL). Electrolysis cell—divided cell equipped with a magnetic stirrer containing a piece of glass tubing with a glass frit of medium porosity at one end (anodic compartment). Solid potassium carbonate (2.1 g, 1.5×10^{-3} mol) was added to the anodic compartment for in situ neutralization of the generated perchloric acid.

A constant cathodic potential of −1.0 V (vs SCE) was applied during electrolysis of salicylaldehydes or ketones. When the initial current value of 200 mA fell to 20 mA the reduction was finished. The reaction time was in all the cases about 1.5 h. At the end, the cathodic solution was filtered and the solvent was evaporated under reduced pressure. Extraction by ether/water followed by concentration in vacuo led to the compounds **2** and **3**, which were purified by chromatography in silica gel, using $CHCl_3$/hexane (1:4, 3:7 or 2:3) as eluent.

3.2.1. 3-Chloro-4-methyl-benzo[*h*]-coumarin (2a). 63% Yield. Mp 229°C. IR (KBr) ν (cm^{-1}): 3077, 1731, 1635, 1090, 980, 808, 768. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.66 (s, 3H), 7.6–7.65 (m, 3H), 7.73 (d, 1H, *J*=8.6 Hz), 7.85–7.87 (m, 1H), 8.53–8.55 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 16.9, 115.1, 120.5, 122.5, 122.9, 124.9, 127.5, 127.7, 128.9, 134.6, 148.3, 148.7, 157.1. MS *m/e* (relative intensity) EI: 246 (M^++2, 34), 244 (M^+, 100), 218 (20), 216 (58), 181 (75), 153 (56), 152 (94), 151 (36), 76 (27), 63 (22). Anal. calcd for $C_{14}H_9ClO_2$: C, 68.71; H, 3.68. Found: C, 68.57; H, 3.71.

3.2.2. 3-Chloro-4-methyl-benzo[*f*]-coumarin (2b). 45% Yield. Mp 136–138°C. IR (KBr) ν (cm^{-1}): 3081, 2924, 1732, 1022, 825, 783, 747. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.05 (s, 3H), 7.47 (d, 1H, *J*=8.9 Hz), 7.58 (t, 1H, *J*=8.0 Hz), 7.66 (t, 1H, *J*=8.6 Hz), 7.94 (d, 1H, *J*=8 Hz), 7.98 (d, 1H, *J*=8.9 Hz), 8.49 (d, 1H, *J*=8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 22.9, 114.5, 117.0, 121.8, 125.0, 125.6, 127.6, 129.3, 129.5, 131.4, 133.4, 149.2, 151.5, 156.4. MS *m/e* (relative intensity) EI: 246 (M^++2, 33) 244 (M^+, 99), 218 (22), 216 (65), 181 (52), 153 (80), 152 (100), 76 (26), 63 (20). Anal. calcd for $C_{14}H_9ClO_2$: C, 68.71; H, 3.68. Found: C, 68.67; H, 3.81.

3.2.3. 3-Chloro-5,7-dibromo-4-methyl-coumarin (2c). 62% Yield. Mp 161–162°C. IR (KBr) ν (cm^{-1}): 3093, 2925, 1743, 1543, 1087, 1001, 866, 750. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.56 (s, 1H), 7.67 (s, 1H), 7.88 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 16.4, 111.7, 117.5, 122.1, 122.9, 126.7, 137.3, 141.5, 146.0, 147.4, 155.3. MS *m/e* (relative intensity) EI: 356 (M^++6, 13), 354 (M^++4, 65), 352 (M^++2, 91), 350 (M^+, 41), 291 (49), 289 (100), 287 (52), 182 (16), 180 (18), 136 (29), 101 (35), 75 (26). Anal. calcd for $C_{10}H_5Br_2ClO_2$: C, 34.04; H, 1.42. Found: C, 34.26; H, 1.52.

3.2.4. 3-Chloro-6-bromo-coumarin (2d). 40% Yield. Mp 161°C. IR (KBr) ν (cm^{-1}): 3039, 1736, 1237, 993, 923, 817, 754. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.27 (m, 1H), 7.60–7.68 (m, 2H), 7.8 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 117.8, 118.6, 120.3, 124.0, 129.5, 134.7, 138.7, 151.5, 157.0. MS *m/e* (relative intensity) EI: 262 (M^++4, 20), 260 (M^++2, 79), 258 (M^+, 60), 234 (11), 232 (45), 230 (36), 169 (14), 167 (14), 125 (32), 123 (100), 97 (19), 87 (35), 62 (68). Anal. calcd for $C_9H_4BrClO_2$: C, 41.62; H, 1.54. Found: C, 41.91; H, 1.67.

3.2.5. 3-Chloro-8-methoxy-coumarin (2e). 42% Yield. Mp 153°C (lit.[7a,b] 153°C). Spectroscopic data (IR, and ^{1}H NMR) are coincident with those described in literature.[7a,b]

^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 56.4, 113.8, 118.6, 119.5, 123.0, 125.1, 140.2, 142.2, 147.0, 156.9. MS *m/e* (relative intensity) EI: 212 (M^++2, 35), 210 (M^+, 100), 184 (5), 182 (15), 169 (8), 167 (22), 141 (12), 139 (36), 113 (6), 111 (18), 89 (10), 75 (19).

3.2.6. 3-Chloro-coumarin (2f). 43% Yield. Mp 121°C (lit.4,7a,b 121°C). Spectroscopic data (IR, and ^{1}H NMR) are coincident with those described in literature.4,7a,b.

^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 116.8, 118.8, 122.3, 125.2, 127.4, 132.0, 140.2, 152.5, 157.3. MS *m/e* (relative intensity) EI: 182 (M^++2, 34), 180 (M^+, 100), 154 (19), 152 (57), 126 (7),124 (23), 89 (87), 63 (29).

3.2.7. 4-Bromo-2-(2′,2′-dichlorovinyl)-phenol (3d). 23% Yield. Mp 57–59°C. IR (KBr) ν (cm^{-1}): 3391, 1615, 1404, 1175, 1110, 926, 807, 621. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.01 (bs, OH), 6.7 (d, 1H, *J*=8.7 Hz), 6.92 (s, 1H), 7.28 (dd, 1H, J_1=2.6 Hz, J_2=8.7 Hz), 7.7 (d, 1H, *J*=2.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 113.0, 117.5, 122.4, 122.9, 132.0, 132.7, 152.1, 164.0. MS *m/e* (relative intensity) EI: 270 (M^++4, 17), 268 (M^++2, 37), 266 (M^+, 23), 235 (13), 233 (55), 231 (42), 207 (14), 205 (59), 203 (46), 154 (34), 152 (100), 123 (48), 89 (60), 63 (58). Anal. calcd for $C_8H_5BrCl_2O$: C, 35.82; H, 1.87. Found: C, 36.03; H, 1.79.

3.2.8. 6-Methoxy-2-(2′,2′-dichlorovinyl)-phenol (3e). 23% Yield. Mp 37–39°C. IR (KBr) ν (cm^{-1}): 3450, 3065, 2940, 1614, 1579, 1360, 1266, 1071, 898, 719, 673. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.88 (s, 3H), 5.9 (bs, OH), 6.75–6.9

(m, 2H), 7.1 (s, 1H), 7.3–7.42 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 56.3, 110.6, 119.4, 119.9, 120.8, 121.0, 123.2, 143.5, 146.3. MS *m/e* (relative intensity) EI: 222 (M^++4, 7), 220 (M^++2, 43), 218 (M^+, 62), 185 (14), 183 (42), 177 (16), 175 (23), 170 (19), 168 (55), 157 (34), 155 (100), 111 (17). Anal. calcd for $C_9H_8Cl_2O_2$: C, 49.31; H, 3.65. Found: C, 48.99; H, 3.67.

3.2.8. 2-(2′,2′-Dichlorovinyl)-phenol (3f). 22% Yield. Mp 40–42°C. IR (KBr) ν (cm^{-1}): 3307, 3037, 1452, 1241, 1098, 912, 745. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.0 (bs, 1H, OH), 6.84 (d, 1H, *J*=7.9 Hz), 7.0 (t, 1H, *J*=7.9 Hz), 7.06 (s, 1H), 7.2–7.3 (m, 1H), 7.64 (d, 1H, *J*=7.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 115.6, 120.9, 121.4, 123.0, 123.9, 129.9, 130.1, 152.7. MS *m/e* (relative intensity) EI: 192 (M^++4, 4), 190 (M^++2, 26), 188 (M^+, 39), 155 (7), 153 (21), 127 (33), 125 (100), 89 (39), 63 (14). Anal. calcd for $C_8H_6Cl_2O$: C, 50.79; H, 3.17. Found: C, 50.83; H, 3.24.

Acknowledgements

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