Synthesis of Novel 3-Aryl-5-dichloromethyl-Δ^2-1,2,4-oxadiazolines

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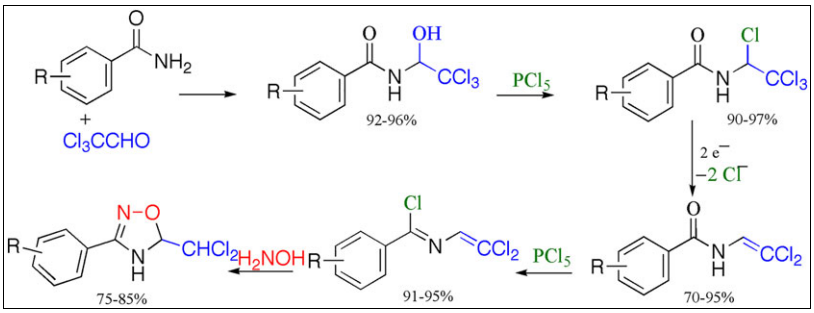

The first synthetic approach to hitherto unknown 3-aryl-5-dichloromethyl-Δ^2-1,2,4-oxadiazolines, of synthetic and biological interest, has been developed involving high-yield reactions between *N*-(2,2-dichlorovinyl)benzimidoyl chlorides and hydroxylamine. The molecular structure of one member of this new family of compounds—5-dichloromethyl-3-(4-fluorophenyl)-1,2,4-oxadiazoline—has been determined by X-ray crystallography. Density functional theory calculations supporting the proposed reaction pathway for the formation of these products have been carried out.

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INTRODUCTION

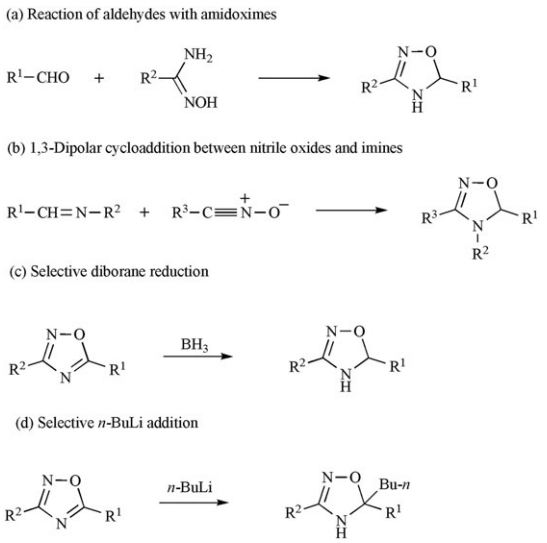
The chemistry, properties, and applications of heterocyclic compounds comprising a 1,2,4-oxadiazole ring have been thoroughly reviewed [1–15], showing that this nucleus confers a wide variety of biological and pharmacological activities. Regarding oxadiazolines, 4,5-dihydro-1,2,4-oxadiazoles (Δ^2-1,2,4-oxadiazolines) are distinguished as substances of significant synthetic [5,16–19] and biological [20–26] interest. For example, they have been reported to possess antifungal [20,22,23,25], antitumor [24], anti-HIV [26], antidiabetic [21], and anti-inflammatory [27] properties. Therefore, the synthesis of these substances has received considerable attention. The oldest preparative method is by Tiemann [28], who discovered that aldehydes react with amidoximes to give Δ^2-1,2,4-oxadiazolines (Scheme 1a). Over the years, the earlier preparative method and some procedures developed from it have been exploited to prepare many of these compounds [5,16,21,27,29–32]. 1,3-Dipolar cycloadditions between nitrile oxides and imines [16,17,19,21,33,34] (Scheme 1b) have proved to be highly useful. Conversions of 1,2,4-oxadiazoles to Δ^2-1,2,4-oxadiazolines have also been reported (Scheme 1c [31]; Scheme 1d [35]).

It should also be pointed out that a dichloromethyl group is an important structural framework present in different types of bioactive compounds such as cytochrome P-450 inhibitors [36], antibiotics [37], diuretics [38], analgesics [39], anticancer [40] agents, and herbicidal [41] agents. Therefore, the research of effective methods to incorporate dichloromethyl groups into organic molecules is a subject that has attracted attention and is still receiving successful effort [39,42–44].

Given the high interest in expanding the range of oxadiazolines available, and to complete a main issue of our research project on the synthesis of heterocyclic compounds through chloral derivatives, we report here the first synthesis of 3-aryl-5-dichloromethyl-Δ^2-1,2,4-oxadiazolines **6** (Scheme 4). The preparation of these hitherto unknown compounds is in itself highly significant in order to encourage the development of future plausible biological studies, but so too is the presence in these products of a dichloromethyl functional group. It should be noted that it shows a versatile reactivity [45,46], which is able to undergo a variety of transformations *via* nucleophilic attack [47], as well as elimination [48], coupling [49], and exchange [50] processes. Therefore, compounds **6** could have a significant synthetic impact, making access to a variety of oxadiazoline and oxadiazole derivatives feasible.

In a recent work, we significantly improved the synthesis of *N*-(1,2,2,2-tetrachloroethyl)benzimidoyl chlorides **3** by treatment of chloralamides **2** with a

Scheme 1. Preparative methods of Δ^2-1,2,4-oxadiazolines.

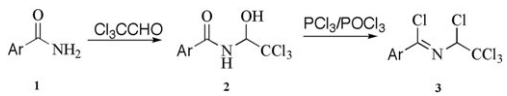


phosphorus pentachloride/phosphorus oxychloride mixture (Scheme 2). Compounds **3** were then successfully used as dielectrophilic agents to react with hydrazine, resulting in a highly convenient new approach to 3-aryl-1,2,4-triazoles [51]. These results suggested a straightforward preparation of the still unavailable products **6** through compounds **3** to react with hydroxylamine, but this strategy was unsuccessful. Fortunately, an alternative route involving *N*-(2,2-dichlorovinyl)benzamides **9** gave satisfactory results (Scheme 4).

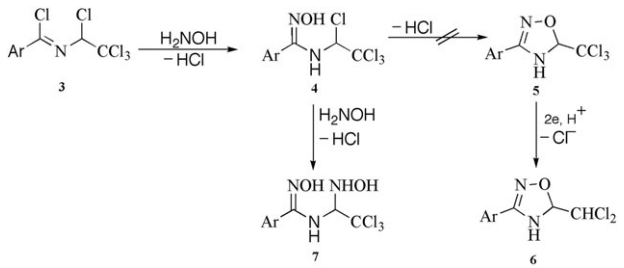
RESULTS AND DISCUSSION

In the search for an effective synthetic method of compounds **6**, we first attempted an approach involving intermediates **3**. On this basis, and taking into consideration that an imidoyl halide function is capable of reacting with hydroxylamine, providing hydroxamic acid derivatives [52], one might reasonably expect that reactions of compounds **3** with hydroxylamine could lead to *N′*-hydroxy-*N*-(1,2,2,2-tetrachloroethyl)benzamidines **4**, whose two active centers of opposite polarity could internally react to give 5-trichloromethyl-1,2,4-oxadiazolines **5** (Scheme 3). Finally, electroreduction of products **5** in the presence of a proton donor [53] would provide the targeted oxadiazolines **6**.

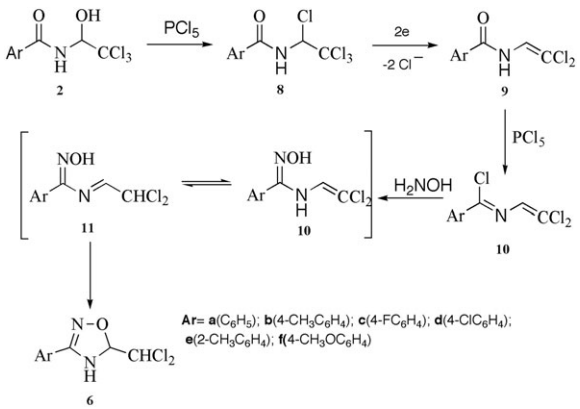
Scheme 2. Synthesis of *N*-(1,2,2,2-tetrachloroethyl)benzimidoyl chlorides **3** through chloralamides **2**.



Scheme 3. Reaction of *N*-(1,2,2,2-tetrachloroethyl)benzimidoyl chlorides **3** with hydroxylamine.



Scheme 4. Synthesis of 3-Aryl-5-dichloromethyl-Δ^2-1,2,4-oxadiazolines **6**.



In order to check this strategy, *N*-(1,2,2,2-tetrachloroethyl)-4-chlorobenzimidoyl chloride **3d** (Ar = 4-Cl-C_6H_4) was taken as a model compound. However, when it was subjected to hydroxylamine treatment, and formation of the expected products, **4d** or **5d**, did not take place. Instead, a previously undescribed substance—4-chloro-*N′*-hydroxy-*N*-(2,2,2-trichloro-1-(hydroxyamino)ethyl)benzamidine **7d**—was obtained, whose formation clearly corresponds to a indiscriminate double attack on the part of hydroxylamine at both electrophilic sites of **3d**. When an experiment between equimolar amounts of reactants, but with the slow addition of a solution of hydroxylamine to a solution of **3d**, was carried out, the exclusive formation of **7d** (accompanied by unaltered **3d**) instead product **4d** or **5d** was observed, even though the reaction occurred at a high concentration of **3d** versus hydroxylamine. This result clearly showed that preparation of the targeted products **6** was unfeasible.

Though unfavorable, the aforementioned results were helpful in overcoming the synthetic adversity found. Hence, we considered that *N*-(2,2-dichlorovinyl) benzimidoyl chlorides **10** exhibit only one potentially active electrophilic center able to react directly with

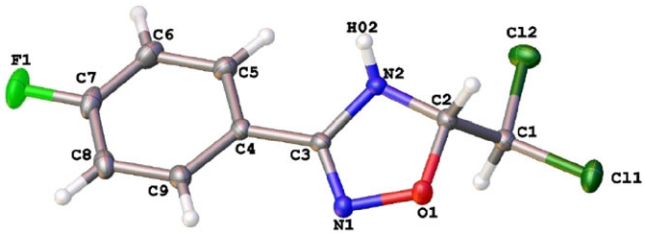


Figure 1. X-ray crystal structure of compound **6c** (thermal ellipsoids drawn at the 50% probability level). [Color figure can be viewed at wileyonlinelibrary.com]

hydroxylamine. However, they also contain another masked electrophilic function, which could be liberated after the total consumption of hydroxylamine during the generation of the corresponding intermediates **11**. Therefore, we focused our attention on exploiting the reaction sequence displayed in Scheme 4. This synthetic approach involves effective conversions of chloralamides **2** to *N*-(1,2,2,2-tetrachloroethyl)benzamides **8** followed by electrochemical reduction to give *N*-(2,2-dichlorovinyl) benzamides **9** [54]. Efficient and easy chlorination of compounds **9** would provide intermediates **10**.

As expected, compounds **10** were found to be crucial to circumvent the double nucleophilic attack on the part of hydroxylamine, given that these reactions directly led to the compounds **6** being sought out. The formation of these products can be explained by a first reaction with hydroxylamine to produce *N*-(2,2-dichlorovinyl)-*N*′-hydroxybenzamidines **11**, whose isomerization could provide *N*-(2,2-dichloroethylidene)-*N*′-hydroxybenzamidine intermediates **12** able to undergo intramolecular additions to give the final products **6**.

Complementary support for this plausible reaction pathway was obtained with computational theoretical calculations [55] of the relative stabilities of isomers **11a**, **12a**, and **6a** (as regards compound **12a**), which were determined at the B3LYP/6-316(d) level of theory, with the result that **11a** and **12a** are very close in energy (ΔE = +1.4 kcal mol^{-1}), whereas **6a** is considerably more stable than **12a** (ΔE = −14.4 kcal mol^{-1}).

Key intermediates in this new synthetic approach are *N*-(2,2-dichlorovinyl)benzamides **9**, which were easily available in near quantitative yields through our improved preparative method involving the electrochemical reduction [54] of *N*-(1,2,2,2-tetrachloroethyl)benzamides **8**. Intermediates **9** were efficiently converted to *N*-(2,2-dichlorovinyl)benzimidoyl chlorides [56,57] **10** (91–95%), which reacted with hydroxylamine directly to provide 3-aryl-5-dichloromethyl-Δ^2-1,2,4-oxadiazolines **6** in good to high yields of 75% to 85%.

Structural features of this class of compounds were obtained by single-crystal X-ray diffraction analysis of **6c**. Figure 1 shows a view of the structure determined.

CONCLUSIONS

Novel 3-aryl-5-dichloromethyl-Δ^2-1,2,4-oxadiazolines of biological and preparative interest have been synthesized using a proficient and general new method involving *N*-(2,2-dichlorovinyl)benzimidoyl chlorides to react with hydroxylamine. Versatility, good yields, easy availability of starting materials, mildness, and a simple experimental procedure are noteworthy advantages of this approach, which allows a privileged access to previously unattainable products. A plausible reaction pathway has been proposed, supported by density functional theory computational calculations. The development of syntheses for some other classes of heterocycles by applying a similar strategy also appears feasible.

EXPERIMENTAL

General. NMR spectra were determined at 25°C on Bruker AV-200, Bruker AV-300, or Bruker AV-400 (Bruker Corp., Billerica, MA) with tetramethylsilane as internal reference. High-resolution mass spectra (HRMS) were obtained using an Agilent TOF 6220 time-of-flight instrument (Agilent Technologies, Santa Clara, CA) equipped with electrospray ionization (ESI). Microanalyses were performed on a Carlo Erba (Milan, Italy) EA 1108 analyzer. IR spectra were recorded on a Nicolet Impact 400 Spectrometer (Thermo Fisher, Madison, MI). Melting points were determined on a Büchi (Essen, Germany) Melting point B-540 and are uncorrected. Compounds **2**, **8**, and **9** were prepared in high yields as previously reported in detail [54]. Chloral hydrate, benzamides, and hydroxylamine were purchased from Sigma-Aldrich Corp. (St. Louis, MO) and were used directly without purification.

General procedure for the synthesis of compounds 6. To hydroxylamine hydrochloride (0.09 mol) in triethylamine (15 mL), a solution of the corresponding *N*-(2,2-dichlorovinyl)benzimidoyl chloride **10** (0.015 mol) in dry tetrahydrofuran (30 mL) was added dropwise. The reaction mixture was stirred at r.t. under nitrogen

atmosphere for 5 h. The solvent was then removed under reduced pressure, leaving a residue, which was washed with water (50 mL). The solid precipitate was collected by filtration, dried, and crystallized from petroleum ether or hexane.

5-Dichloromethyl-3-phenyl-1,2,4-oxadiazoline (6a). Pale yellow powder (pet ether), yield 82%, mp 102–105°C; ir (potassium bromide): 3151, 1604, 1510, 1468, 1400, 1339, 1303, 1205, 1126, 1093, 846, 777, 766, 692 cm^{-1}; ^1H NMR δ ($CDCl_3$, 200 MHz): 5.63 (d, 1H, J = 4.2 Hz), 5.66 (br s, 1H), 5.92 (t, 1H, J = 3.2 Hz), 7.41–7.49 (m, 3H), 7.70 (d, 2H, J = 7.0 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 72.11, 93.94, 123.95, 126.67, 128.82, 131.42, 155.30; HRMS (ESI) m/z: $(M + H)^+$: calcd for $C_9H_9Cl_2N_2O$ 231.0086, found 231.0093. *Anal*. Calcd for $C_9H_8Cl_2N_2O$: C, 46.78; H, 3.49; N, 12.12. Found: C, 46.84; H, 3.53; N, 12.17.

5-Dichloromethyl-3-(4-methylphenyl)-1,2,4-oxadiazoline (6b). Beige powder (hexane), yield 80%, mp 115–118°C; ir (potassium bromide): 3363, 1644, 1609, 1524, 1456, 1368, 1298, 1105, 848, 823, 759, 714, 697, 657 cm^{-1}; ^1H NMR δ ($CDCl_3$, 400 MHz): 2.39 (s, 3H), 5.55 (br s, 1H), 5.62 (d, 1H, J = 4.8 Hz), 5.89 (t, 1H, J = 4.0 Hz), 7.23 (d, 2H, J = 8.0 Hz), 7.58 (d, 2H, J = 8.0 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 21.48, 72.16, 93.87, 121.09, 126.60, 129.52, 141.89, 155.24; HRMS (ESI) m/z: $(M + H)^+$: calcd for $C_{10}H_{11}Cl_2N_2O$ 245.0243, found 245.0245. *Anal*. Calcd for $C_{10}H_{10}Cl_2N_2O$: C, 49.00; H, 4.11; N, 11.43. Found: C, 49.18; H, 4.06; N, 11.49.

5-Dichloromethyl-3-(4-fluorophenyl)-1,2,4-oxadiazoline (6c). Orange powder (pet ether), yield 84%, mp 82–85°C; ir (potassium bromide): 3139, 1654, 1608, 1573, 1523, 1461, 1400, 1242, 1162, 1117, 926, 848, 790, 608, 518 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz); 5.63 (d, 1H, J = 4.5 Hz), 5.76 (br s, 1H), 5.92 (t, 1H, J = 3.6 Hz), 7.10 (t, 2H, J = 8.4 Hz), 7.69 (dd, 2H, J = 5.1 Hz, J = 3.3 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 72.09, 94.03, 116.07 (d, J = 22.16 Hz), 120.23 (d, J = 3.24 Hz), 128.90 (d, J = 8.75 Hz), 154.61, 162.78 HRMS (ESI) m/z: $(M + H)^+$: calcd for $C_9H_8Cl_2FN_2O$ 248.9992, found 248.9989. *Anal*. Calcd for $C_9H_7Cl_2FN_2O$: C, 43.40; H, 2.83; N, 11.25. Found: C, 43.56; H, 2.78; N, 11.33.

Crystal data: $C_9H_7Cl_2FN_2O$, M_r = 249.07, triclinic, space group $P2_1/n$, a = 12.6252(7), b = 4.9144(3), c = 16.3239(9) Å, b = 94.334(2), V = 1009.92(10) $Å^3$ at 100(2) K; Z = 4, D_x = 1.638 g cm^{-3}, F(000) = 504, m = 0.629 mm^{-1}. Data collection: A colorless lath measuring 0.03 × 0.12 × 0.35 mm was mounted in inert oil on a glass fiber and transferred to the cold gas stream of the diffractometer (Bruker D8 QUEST). Measurements were performed to $2q_{max}$ 61.22° with monochromated Mo-Kα radiation. Of 33,059 measured reflections, 3114 were unique (R_{int} = 0.0434) and were used for all calculations. Structure refinement: The structures were refined anisotropically against F2 (program SHELXTL) [58]. The hydrogen atoms were refined using a riding model and the NH as free. The final wR2 value was 0.0940 for all reflections and 140 parameters, with R1 0.0344 for reflections with $I > 2$ s(I); max. Dr 0.815 e $Å^{-3}$, S 1.055. Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 1573712. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

5-Dichloromethyl-3-(4-chlorophenyl)-1,2,4-oxadiazoline (6d). Brown powder (pet ether), yield 75%, mp 117–120°C; ir (potassium bromide): 3138, 1597, 1440, 1400, 1354, 1283, 1208, 1109, 1091, 1015, 920, 846, 828, 786, 762, 716, 470 cm^{-1}; ^1H NMR δ ($CDCl_3$, 400 MHz): 5.59 (br s, 1H), 5.66 (d, 1H, J = 4.4 Hz), 5.93 (t, 1H, J = 4.0 Hz), 7.26 (d, 2H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.0 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 72.09, 94.14, 122.49, 128.01, 129.16, 137.52, 154.61; HRMS (ESI) m/z: $(M + H)^+$: calcd for $C_9H_8Cl_3N_2O$ 264.9697, found 264.9689. *Anal*. Calcd for $C_9H_7Cl_3N_2O$: C, 40.71; H, 2.66; N, 10.55. Found: C, 40.57; H, 2.68; N, 10.63.

5-Dichloromethyl-3-(2-methylphenyl)-1,2,4-oxadiazoline (6e). Brown powder (pet ether), yield 80%, mp 89–91°C; ir (potassium bromide): 3151, 1663, 1607, 1592, 1502, 1445, 1400, 1345, 1302, 1230, 1199, 1141, 1113, 965, 874, 864, 843, 764, 604, 569, 545, 508, 479, 446 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz): 2.49 (s, 3H), 5.40 (br s, 1H), 5.62 (br s, 1H), 5.87 (br s, 1H), 7.22–7.49 (m, 4H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.22, 72.21, 93.18, 123.35, 125.97, 128.64, 130.80, 131.37, 138.11, 155.32; HRMS (ESI) m/z: $(M + H)^+$: calcd for $C_{10}H_{11}Cl_2N_2O$ 245.0243, found 245.0248. *Anal*. Calcd for $C_{10}H_{10}Cl_2N_2O$: C, 49.00; H, 4.11; N, 11.43. Found: C, 48.88; H, 4.16; N, 11.38.

5-Dichloromethyl-3-(4-methoxyphenyl)-1,2,4-oxadiazoline (6f). Pale orange powder (hexane), yield 85%; mp 108–111°C; ir (potassium bromide): 3357, 3137, 1609, 1524, 1461, 1440, 1400, 1296, 1259, 1182,1027, 837, 762, 696, 656, 618, 592, 520, 463 cm^{-1}; ^1H NMR δ ($CDCl_3$, 400 MHz): 3.82 (s, 3H), 5.60 (d, 1H, J = 4 Hz), 5.61 (br s, 1H), 5.86 (d, 1H, J = 3.6 Hz), 6.89 (d, 1H, J = 8.4 Hz), 7.61 (d, 2H, J = 8.4 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 55.38, 72.22, 93.81, 114.25, 116.18, 128.37, 155.06, 162.02; HRMS (ESI) m/z: $(M + H)^+$: calcd for $C_{10}H_{11}Cl_2N_2O_2$ 261.0192, found 261.0199. *Anal*. Calcd for $C_{10}H_{10}Cl_2N_2O_2$: C, 46.00; H, 3.86; N, 10.73. Found: C, 46.22; H, 3.91; N, 10.75.

General procedure for the synthesis of compounds 10. To a suspension of *N*-(2,2-dichlorovinyl)benzamide **9** (0.05 mol) in dry toluene (55 mL), phosphorus pentachloride (0.053 mol) was added in small portions.

The mixture was stirred at 45°C for 2 h. The suspension turned to total dissolution while gaseous hydrogen chloride was expelled. The solvent was then removed under reduced pressure, leaving a solid residue (oil for **10c**), which was crystallized from petroleum ether.

N-(2,2-Dichlorovinyl)benzimidoyl chloride (10a). White needless (peth ether), yield 92%, mp 42–43°C (lit. [56], mp 41–43°C); ir (potassium bromide): 1620, 1446, 1288, 1233, 1127, 943, 890, 852, 763, 682, 665, 610, 559 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz): 7.41–7.53 (m, 4H), 8.13 (d, 2H, J = 7.2 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 126.60, 128.53, 129.47, 132.37, 132.58, 135.01, 144.74; MS (EI) *m/z* (%): 233 (M^+, 24), 235 (M^++2, 24), 198 (M^+-Cl, 100), 200 (71), 104 (33), 77 (14). *Anal*. Calcd for $C_9H_6Cl_3N$: C, 46.09; H, 2.58; N, 5.97. Found: C, 45.98; H, 2.60; N, 6.01.

N-(2,2-Dichlorovinyl)-4-methylbenzimidoyl chloride (10b). Pale yellow needless (peth ether), yield 92%, mp 72–73°C; ir (potassium bromide): 1618, 1568, 1287, 1247, 1232, 1182, 1133, 1120, 945, 902, 855, 820, 786, 617, 609, 457 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz): 2.40 (s, 3H), 7.22 (d, 2H, J = 8.0 Hz), 7.51 (s, 1H), 8.01 (d, 2H, J = 8.3 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.55, 125.88, 129.27, 129.49, 132.36, 132.65, 143.22, 144.83; MS (EI) *m/z* (%): 247 (M^+, 22), 249 (M^++2, 22), 212 (M^+-Cl, 100), 214 (69), 118 (21), 91 (11). *Anal*. Calcd for $C_{10}H_8Cl_3N$: C, 48.33; H, 3.24; N, 5.64. Found: C, 48.24; H, 3.06; N, 5.77.

N-(2,2-Dichlorovinyl)-4-fluorobenzimidoyl chloride (10c). White needless (peth ether), yield 95%, mp 40–42°C; ir (potassium bromide): 1621, 1598, 1570, 1503, 1401, 1294, 1237, 1158, 1132, 1098, 945, 905, 853, 836, 615, 604, 539, 466 cm^{-1}; ^1H NMR δ ($CDCl_3$, 400 MHz): 7.12 (t, 2H, J = 8.6 Hz), 7.50 (s, 1H), 8.14 (dd, 2H, J = 9.0 Hz, J = 5.3 Hz); ^{13}C NMR δ ($CDCl_3$, 100.8 MHz): 115.72 (d, J = 22.1 Hz), 126.71, 131.23 (d, J = 3.2 Hz), 131.74 (d, J = 9.1 Hz), 132.45, 143.36, 165.45 (d, J = 254.7); MS (EI) *m/z* (%): 251 (M^+, 17), 253 (M^++2, 17), 216 (M^+-Cl, 100), 218 (66), 122 (63), 95 (37). *Anal*. Calcd for $C_9H_5Cl_3FN$: C, 42.81; H, 2.00; N, 5.55. Found: C, 42.98; H, 2.03; N, 5.68.

N-(2,2-Dichlorovinyl)-4-chlorobenzimidoyl chloride (10d). Pale yellow needless (peth ether), yield 91%, mp 91–93°C; ir (potassium bromide): 1687, 1614, 1592, 1561, 1484, 1458, 1400, 1297, 1236, 1131, 1089, 1013, 938, 899, 854, 833, 724, 604, 584, 461, 442 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz): 7.41 (d, 2H, J = 8.8 Hz), 7.50 (s, 1H), 8.06 (d, 2H, J = 8.8 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 127.19, 128.82, 130.61, 132.43, 133.44, 138.82, 143.40; MS (EI) *m/z* (%): 267 (M^+, 24), 269 (M^++2, 31), 271 (M^++4, 14), 232 (M^+-Cl, 98), 234 (100), 236 (38), 138 (33). *Anal*. Calcd for $C_9H_5Cl_4N$: C, 40.19; H, 1.87; N, 5.21. Found: C, 40.28; H, 1.81; N, 5.32.

N-(2,2-Dichlorovinyl)-2-methylbenzimidoyl chloride (10e). Pale yellow oil, yield 95%; ir (neat): 1626, 1456, 1282, 1228, 1128, 1113, 943, 890, 780, 762, 716, 657, 620, 582 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz): 2.59 (s, 3H), 7.24–7.35 (m, 3H), 7.52 (s, 1H), 7.83 (d, 1H, J = 8.0 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 22.25, 125.88, 126.74, 130.81, 130.93, 131.57, 132.64, 135.16, 138.52, 144.06; MS (EI) *m/z* (%): 247 (M^+, 17), 249 (M^++2, 17), 212 (M^+-Cl, 100), 214 (71), 177 (21), 116 (24), 89 (16). *Anal*. Calcd for $C_{10}H_8Cl_3N$: C, 48.33; H, 3.24; N, 5.64. Found: C, 48.01; H, 3.18; N, 5.64.

N-(2,2-Dichlorovinyl)-4-methoxylbenzimidoyl chloride (10f). Pale yellow needless (peth ether), yield 94%, mp 71–72°C; ir (potassium bromide): 1624, 1603, 1569, 1502, 1419, 1325, 1307, 1291, 1258, 1244, 1176, 1131, 1108, 1028, 941, 893, 853, 832, 647, 612, 606, 541, 466 cm^{-1}; ^1H NMR δ ($CDCl_3$, 300 MHz): 3.86 (s, 3H), 6.92 (d, 2H, J = 8.9 Hz), 7.49 (s, 1H), 8.09 (d, 2H, J = 8.9 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 55.49, 113.87, 125.07, 127.52, 131.43, 132.68, 144.30, 163.11; MS (EI) *m/z* (%): 263 (M^+, 16), 265 (M^++2, 16), 228 (M^+-Cl, 100), 230 (69), 134 (10). *Anal*. Calcd for $C_{10}H_8Cl_3NO$: C, 45.40; H, 3.05; N, 5.29. Found: C, 45.31; H, 3.01; N, 5.41.

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