A Novel Facile Synthesis Method of *N*-Vinylpyrroles

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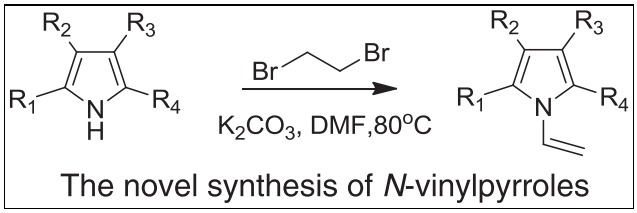

A facile and effective synthesis of *N*-vinylpyrroles had been explored. The synthetic approach was practicable for preparation of *N*-vinylpyrroles for the mild reaction conditions and readily available materials, compared with previously inaccessible *N*-vinylpyrroles with electron-withdrawing groups, especially these pyrroles bearing alkaline sensitive substitution groups.

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INTRODUCTION

Pyrrole ring system, which widely existed in nature, is a subunit of many natural products and pharmaceutical agents, such as haem, chlorophylls, and vitamin B_{12}. This structure can also be found in functional polymers and pigments. Substitutions and modifications at different positions of the five-membered hetero ring further extend number and types of its derivatives, and embedded many major applications. Many substitutions and modifications at all of its five positions of the ring system have been widely explored [1]. However, among these substitutions and modifications, the substitutions and modifications at the nitrogen atom are less studied. *N*-vinylpyrrole, a vinyl group conjugated with the hetero atom of the aromatic ring, has been only studied in a very limited fraction, mostly owing to the limited numbers of *N*-vinylpyrroles, which are available by the current synthetic method. With the increasing interests in pyrrole derivatives and their great potential in many applications, such as conductive polymers and pharmaceutical usage, more and more attention has been drawn all over the world from researchers.

N-Vinylpyrroles were first reported by Trofimov [2]. Chemistry involving *N*-vinylpyrroles was then developed in several fields, such as synthetic chemistry [3,4], structural chemistry [5], and conductive polymer chemistry [6–8]. However, restricted by the harsh reaction conditions employed in Trofimov's method, the preparations of *N*-vinylpyrroles were limited to those pyrroles with alkyl substituted on the ring carbon atoms. *N*-Vinylpyrroles with substitution groups are unstable and sensitive to strong alkaline conditions and high temperature; all these restrictions lowered the feasibility of Trofimov reaction, in which strong basic system (KOH-DMSO) was employed along with high reaction temperature and high reaction pressure (Scheme 1) [2,9]. Bogdal and Jaskot tried to prepare *N*-vinylpyrroles by employing dichoroethane as vinyl formation agent with slightly less alkaline conditions by using alcohols as solvent instead of DMSO in Trofimov reaction, but the strong base, KOH, still was used as the alkali for the reaction system. In their report, only very limited samples of *N*-vinylpyrroles were successful and with low yields [10].

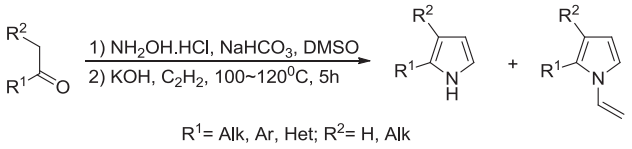
N-Vinylpyrroles with diverse functional groups other than alkyl groups are of great interest to researchers both for better understanding of their chemical and physical properties and their potential applications. Full investigation with *N*-vinylpyrroles requires mild synthetic approaches in which those sensitive functional groups, such as esters, carbonyl group and nitrile would survive.

The methods for synthesis of *N*-vinylpyrrole derivatives with mild reaction conditions had been studied for some time in our lab. A novel method had been developed to solve the difficulties in the preparation of *N*-vinylpyrroles with alkaline sensitive substitution groups. The mild reaction conditions used potassium carbonate with mild heating, and no high reaction pressure was required (Scheme 2). *N*-Vinylpyrrole derivatives with alkaline sensitive groups, such as CN, CHO, and COOEt, were synthesized [11].

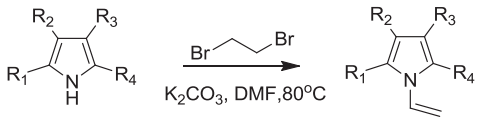
RESULTS AND DISCUSSION

Different with the Trofimov method in which the vinyl group was formed along with the pyrrole ring system, our approach took existing pyrroles as starting materials that would make the synthesis of *N*-vinylpyrroles easier.

Scheme 1. Synthesis of *N*-vinylpyrroles via Trofimov reaction.



Scheme 2. The novel synthesis of *N*-vinylpyrroles.



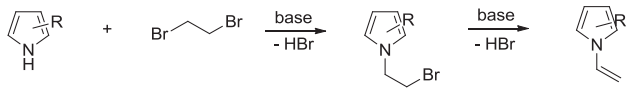
The mild *N*-vinylation reaction system involved mild base, suitable solvents, and bifunctional reactants with abilities to alkylation and elimination of its hydrogen–halogen [12]. The reaction involves a possible two-step mechanism (Scheme 3). In the first step, the bifunctional reagent, 1,2-dibromoethane, for example, under the help of K_2CO_3, alkylates the nitrogen of pyrroles, and then in the subsequent step, was eliminated by the hydrogen bromide to form the vinyl group.

Anhydrous DMSO, DMF, and THF were studied as solvents in the *N*-vinylation. It was found that DMSO interfered with the bifunctional reagents and THF led to very poor yields of the *N*-vinylpyrroles. DMF as an excellent solvent for alkylation reactions was found to be the solvent of choice, in which *N*-vinylation occurred smoothly.

1,2-Dichloroethane, 1,2-bromochloroethane, and 1,2-dibromoethane were explored as bifunctional reagents. Among them, 1,2-dibromoethane gave the best yields of *N*-vinylpyrroles, partially owing to the fact that 1,2-dibromoethane has good abilities for both alkylation and elimination. The chloride derivatives were found more difficult in *N*-alkylation than that of bromide derivative in this mild alkaline condition. 1,2-Dichloroethane required much stronger alkaline condition to react as evidenced in a previous report [10]. The use of KOH, as in Bogdal and Jaskot's study, could be harmful to these alkaline sensitive substitution groups studied in this research, and therefore, was not suitable for the *N*-vinylation of pyrroles with alkaline sensitive substitution groups, such as CN, CHO, and COOEt.

The optimum reaction temperature was 60–80°C. When it was below 60°C, the reaction went very slowly. When it was over 80°C, decomposition of the bifunctional reagents prevailed.

Scheme 3. The two steps of synthesis of *N*-vinylpyrroles.



Using the previous method, the desired alkylation of nitrogen of pyrroles, the bifunctional reagents underwent elimination of the hydrogen–halogen; a side reaction with the loss of hydrogen–halogen would take place. This decomposition of the 1,2-dihalogenethanes in the presence of base forms vinyl halide would escape from the reaction system. This was proved by the observation of formation of a large amount of gas during the *N*-vinylation. The decomposition of 1,2-dihalogenethanes occurred more rapidly when strong bases were employed and when high reaction temperatures were applied. Although the side reaction and its volatile products, vinyl bromide, for example, would not affect the *N*-vinylation of pyrroles as long as there was sufficient 1,2-dibromoethane existing in the reaction system. A suitable base for *N*-vinylation of pyrroles should assure the *N*-alkylation step taking place prior to the elimination step before the exhaustion of the 1,2-dibromoethane. The selection of a suitable base was laid to the balance of its basicity. An appropriate base should be strong enough to deprotonate the proton from pyrrole nitrogen while its ability to elimination of hydrogen–halogen of the haloethyl group should be softly allowing the sufficient reaction time for the alkylation but still making a tangible elimination subsequently. The bases studied in the exploration were Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, Cs_2CO_3, NaOH, and KOH. Potassium carbonate gave the best results among the bases studied (Table 1). The strong bases, such as NaOH and KOH, led to rapid elimination of hydrogen–halogen of the bifunctional reactants prior to their alkylation to nitrogen of pyrroles. Sodium bicarbonate and potassium bicarbonate were not reactive enough in helping the alkylation of pyrrole nitrogen. Sodium carbonate and cesium carbonate yield did not help in the formation of the desired vinyl products. The organic bases, such as Et_3N and DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) (entries 10 and 11), led to the low yields and some undissolved dark residue formed after the reaction.

Table 1

The effects of bases and 1,2-dibromoethane in synthesis of diethyl *N*-vinyl-3,4-pyrroledicarboxylate from 3,4-pyrroledicarboxylate.

Entries	Bases	Amounts of bases[a]	Amounts of 1,2-dibromoethane[a]	Yields (%)
1	K_2CO_3	1	1	9
2	K_2CO_3	5	5	16
3	K_2CO_3	10	10	33
4	K_2CO_3	15	15	32
5	NaOH	10	10	-
6	KOH	10	10	-
7	Na_2CO_3	10	10	-
8	$NaHCO_3$	10	10	-
9	Cs_2CO_3	10	10	-
10	Et_3N	10	10	11
11	DBU	10	10	17

[a]Molar ratios to 3,4-pyrroledicarboxylate

To overcome the side effects caused by the competing side reaction, which consumes the bifunctional reagents as well, excessive bifunctional reagents were needed to bring up the yield of the desired *N*-vinyl products. A 10 times in molar ratio of the bifunctional reagents vs the pyrroles was found to be necessary to achieve a reasonable yield of *N*-vinylation products. When less amount of the bifunctional reagents would be used in the reaction, it would result in poor *N*-vinylation products caused by the decomposition. However, when the molar ratios of the bifunctional reagents were over 10 times, no improvement of the yields of *N*-vinylation was found. Equal molar amount of anhydrous base to the dihalogenethanes was required in the reaction.

The *N*-vinylation reactions used take from 4 to 8 h to complete. After this improvement, the most of bifunctional reagents would be depleted out as evidenced by the cease of gas emission. Extending the reaction time beyond 8 h would not make any sense.

The reaction conditions were relatively mild that most alkaline sensitive substitution groups could survive, and a number of *N*-vinylpyrrole derivatives were able to be prepared from their corresponding pyrroles (Table 2).

As the first step, in which the *N*-vinylation was carried out, the alkylation of nitrogen of pyrroles must go prior to the elimination of hydrogen–halogen. The acidity of nitrogen proton of the pyrrole rings was crucial for the alkylation. Electron-drawing substitutions at the pyrrole ring would increase the acidity of the nitrogen protons of pyrroles, therefore, would facilitate the alkylation of pyrrole nitrogen. The electron-withdrawing groups, which promote the *N*-alkylation, include nitro, carbonyl, esters and nitrile groups. Among them, many were sensitive to alkaline owing to possible hydrolysis or condensation.

Table 2

Several *N*-vinylpyrroles obtained by the novel method from their corresponding pyrroles.

Entries	R_1	R_2	R_3	R_4	Yields (%)[a]
1	H	H	COOEt	H	-[b]
2	H	H	$COCH_3$	H	23
3	H	H	NO_2	H	56
4	H	COOEt	COOEt	H	33
5	H	p-MeOPh	COOEt	H	-[b]
6	H	p-FPh	$COCH_3$	H	8
7	H	p-MeOPh	$COCH_3$	H	30
8	H	p-BrPh	NO_2	H	33
9	H	p-MePh	NO_2	H	42
10	H	p-MeOPh	NO_2	H	48
11	H	p-FPh	NO_2	H	52
12	H	o-ClPh	NO_2	H	43
13	CN	H	H	H	35
14	H	CH_3	H	CH_3	-[b]

[a]Isolated yields
[b]No desired product formed

It was observed that the substitution groups on the pyrrole ring played important roles in the reaction (Table 2). In general, stronger electron-withdrawing groups (R_3) helped with the higher yields. The yields rose successively from COOEt, $COCH_3$ to NO_2 (entries 1–3 in Table 2) as their increased electron-withdrawing effects. The similar trend was also noticed in other trial in which disubstitutions of pyrroles were employed (entries 4–12 in Table 2).

Electron-withdrawing substitutions at α and/or β positions of pyrroles ring had similar effects for *N*-vinylation (entry 13 in Table 2). No reactions were going on with substitutions only with non-electron-withdrawing groups or electron-donating groups on the pyrrole ring (entry 14 in Table 2). To enable the *N*-vinylation, the existence of electron-withdrawing group on the pyrrole ring is necessary. The similar yields were obtained when the benzene substituted by different steric groups (entries 9–12), it was indicated that the steric effect was much less than that of electron-withdrawing effect for the reaction.

CONCLUSIONS

A facile and effective method for synthesis of *N*-vinylpyrrole derivatives with mild reaction conditions has been developed. The use of mild base instead of strong base like KOH as used in Trofimov and Bogdal's methods was noteworthy for the achievement of *N*-vinylation of alkaline sensitive pyrroles. The presence of electron-withdrawing groups at the pyrrole ring is necessary for the *N*-vinylation. The stronger the electron-withdrawing effect the substitution group brings, the easier the reaction runs. Similarly, the more electron-withdrawing groups present at the pyrrole ring, the easier the reaction is carried on and the higher reaction yield it obtained. Presumably, substitution by other electron-withdrawing groups, such as sulphonyl and trifluoromethyl groups would also help the reaction. Further exploration of functional applications of these novel *N*-vinylpyrroles would be very interesting.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were characterized by a Varian 300 MHz Spectrophotometer in $CDCl_3$ solutions, and chemical shift values are expressed in δ values (ppm) relative to tetramethylsilane (TMS) as internal standard, MS spectra were carried out on a MicroMass GCT. Reaction progress was monitored by analytical thin-layer chromatography (TLC) on precoated glass plates (Silica gel 60 F254-plate). Melting points were not corrected.

General procedure for synthesis of 1-ethenylpyrroles. To a solution of corresponding pyrroles (1 m*M*) in DMF(10 mL), K_2CO_3 (1.4 g, 10 m*M*) and 1,2-dibromoethane (2.3 g, 10 m*M*)

were added. The mixtures were stirred at 80°C under nitrogen atmosphere for 8 h, and then, were poured into 50 mL water, extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and then the solvent was removed in vacuum. The crude products were purified by column chromatography on silica gel with ethyl acetate/hexanes as eluents to afford the *N*-vinylpyrroles.

3-acetyl-1-ethenylpyrrole (2). Oil; IR (cm^{-1}, KBr): 3193, 2917, 1652, 1633, 1507, 1435, 1335. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.45 (1 H, s), 6.88 (1 H, s), 6.81 (1 H, dd, J = 9, 15.6 Hz), 6.66 (1 H, s), 5.26 (1 H, d, J = 15.6 Hz), 4.85 (1 H, d, J = 9 Hz), 2.38 (3 H, s). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 193.6, 132.6, 127.3, 123.7, 120.1, 110.7, 100.7, 21.4. MS (m/z): 134 [M^+-1]. *Anal*. Calcd. for C_8H_9NO (%): C, 71.09; H, 6.71; N, 10.36; O, 11.84. Found: C, 71.12; H, 6.78; N, 10.33.

3-nitro-1-ethenylpyrrole (3). Solid, m.p. 64 ~ 66 ^{0}C; IR (cm^{-1}, KBr): 3281, 2954, 1687, 1655, 1506, 1327. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.70 (1 H, m), 6.84 (1 H, m), 6.80 (1 H, dd, J = 9, 15.6 Hz), 6.75 (1 H, s), 5.33 (1 H, dd, J = 15.6, 2.1 Hz), 4.98 (1 H, dd, J = 9, 2.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 132.1, 119.3, 106.9, 103.0, 77.7, 77.3, 76.8. MS (m/z): 137 [M^+-1]. *Anal*. Calcd. for $C_6H_6N_2O_2$(%): C, 52.17; H, 4.38; N, 20.28; O, 23.17. Found: C, 52.20; H, 4.31; N, 20.15.

Diethyl 1-ethenylpyrrole-3,4,-dicarboxylate (4). Yellow solid, m.p. 89 ~ 91 ^{0}C; IR (cm^{-1}, KBr): 3142, 1716, 1508, 1485. ^{1}HNMR (400 MHz, $CDCl_3$), δ (ppm): 7.37 (2 H, s), 6.74 (1 H, dd, J = 15.7, 8.7 Hz), 5.31 (1 H, dd, J = 15.7, 2.0 Hz), 4.91 (1 H, dd, J = 8.8, 2.0 Hz), 4.27 (4 H, m, J = 7.2 Hz), 1.27 (6 H, t, J = 6.9 Hz); ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 163.4, 131.9, 125.0, 117.7, 102.4, 60.6, 14.5. MS (m/z): 237 [M^+]. *Anal*. Calcd. for $C_{12}H_{15}NO_4$(%): C, 60.75; H, 6.37; N, 5.90; O, 26.97. Found: C, 60.50; H, 6.99; N, 5.84.

3-acetyl-4-(4-fluorophenyl)-1-ethenyl pyrrole (6). Oil; IR (cm^{-1}, KBr): 3024, 2940, 1605, 1563, 1527, 1415, 1253, 1194. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.54 (1 H, m), 7.39 (2 H, m), 7.03 (2 H, m), 6.88 (1 H, s), 6.84 (1 H, dd, J = 9, 15.6 Hz), 5.28 (1 H, dd, J = 15.6, 2.1 Hz), 4.88 (1 H, dd, J = 9, 2.1 Hz), 2.33 (3 H, s). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 194.2, 160.9, 131.1, 128.7, 125.7, 125.3, 119.5, 119.2, 115.0, 114.7, 104.3, 28.7. MS (m/z): 229 [M^+]. *Anal*. Calcd. for $C_{14}H_{12}NOF$ (%): C, 73.35; H, 5.28; N, 6.11; O, 6.98; F, 8.29. Found: C, 83.22; H, 5.29; N, 6.05.

3-acetyl-4-(4-methoxyphenyl)- 1-ethenylpyrrole (7). Yellow solid, m.p: 113–115 ^{0}C; IR (cm^{-1}, KBr): 2925, 1716, 1648, 1516, 1246, 1179, 1079, 1034. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.45 (1 H, s), 7.35 (2 H, d, J = 8.4 Hz), 6.90 (2 H, d, J = 8.4 Hz), 6.88 (1 H, s), 6.80 (1 H, dd, J = 9, 15.6 Hz), 5.27 (1 H, d, J = 15.6 Hz), 4.86 (1 H, d, J = 9 Hz), 3.83 (3 H, s), 2.30 (3 H, s). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 198.7, 161.8, 132.0, 130.6, 125.4, 123.1, 119.8, 110.9, 110.8, 107.2, 101.1, 56.2, 27.4, . MS (m/z): 241 [M^+]. *Anal*. Calcd. for $C_{15}H_{15}NO_2$ (%): C, 74.67; H, 6.27; N, 5.81; O, 13.26. Found: C, 74.65; H, 6.32; N, 5.87.

3-nitro-4-(4-bromophenyl)- 1-ethenylpyrrole (8). Oil; IR (cm^{-1}, KBr): 3077, 2864, 1867, 1621, 1543, 1508, 1218. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.81 (1 H, m), 7.52 (1 H, d, J = 8.4 Hz), 7.31 (2 H, d, J = 8.4 Hz), 6.85 (1 H, m), 6.81 (1 H, dd, J = 9.0, 15.6 Hz), 5.42 (1 H, dd, J = 15.6, 1.5 Hz), 5.05 (1 H, dd, J = 9.0, 1.5 Hz). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 137.5, 132.1, 130.0, 128.7, 126.8, 121.4, 119.4, 117.4, 117.1, 105.2. MS (m/z): 291 [M^+]. *Anal*. Calcd. for $C_{12}H_9N_2O_2Br$ (%): C, 49.17; H, 3.09; N, 9.56; O, 10.92; Br, 27.26. Found: C, 49.08; H, 3.11; N, 9.53.

3-nitro-4-(4-methylphenyl)-1-ethenylpyrrole (9). Oil; IR (cm^{-1}, KBr): 3104, 1743, 1559, 1564, 1442, 1083. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.78 (1 H, m), 7.34 (1 H, d, J = 7.5 Hz), 7.21 (2 H, d, J = 7.5 Hz), 6.83 (1 H, m), 6.82 (1 H, dd, J = 9.0, 15.6 Hz), 5.38 (1 H, dd, J = 15.6, 1.5 Hz), 5.02 (1 H, dd, J = 9.0, 1.5 Hz), 2.37 (3 H, s). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 139.5, 135.2, 133.7, 130.6, 127.7, 125.9, 123.4, 120.7, 111.8, 108.5, 23.7. MS (m/z): 227 [M^+-1]. *Anal*. Calcd. for $C_{13}H_{12}N_2O_2$ (%): C, 68.41; H, 5.30; N, 12.27; O, 14.02. Found: C, 68.38; H, 5.28; N, 12.30.

3-nitro-4-(4-methoxyphenyl)- 1-ethenylpyrrole (10). Yellow solid, m.p: 127–128 ^{0}C; IR (cm^{-1}, KBr): 2912, 2850, 1718, 1603, 1513, 1487,1132. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.78 (1 H, m), 7.37 (2 H, d, J = 8.7 Hz), 6.93 (2 H, d, J = 8.7 Hz), 6.82 (1 H, m), 6.79 (1 H, dd, J = 9.0, 15.6 Hz), 5.38 (1 H, dd, J = 15.6, 2.1 Hz), 4.86 (1 H, dd, J = 9.0, 2.1 Hz), 3.84 (3 H, s). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 159.5, 133.9, 131.8, 130.9, 130.7, 124.0, 121.3, 117.9, 113.8, 102.9, 55.5. MS (m/z): 244 [M^+]. *Anal*. Calcd. for $C_{13}H_{12}N_2O_3$ (%): C, 63.93; H, 4.95; N, 11.47; O, 19.65. Found: C, 63.90; H, 4.98; N, 11.47.

3-nitro-4-(4-fluorophenyl)-1-ethenylpyrrole (11). Solid, m.p: 77–79 ^{0}C; IR (cm^{-1}, KBr): 2987, 2876, 1658, 1603,1576, 1446. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.80 (1 H, s), 7.41 (2 H, m,), 7.08 (2 H, m), 6.84 (1 H, s), 6.79 (1 H, dd, J = 9.0, 15.6 Hz), 5.41 (1 H, dd, J = 15.6, 2.1 Hz), 5.03 (1 H, dd, J = 9.0, 2.1 Hz). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 163.9, 161.5, 131.8, 131.3, 122.3, 121.4, 118.4, 115.4, 115.2, 103.3. MS (m/z): 232 [M^+]. *Anal*. Calcd. for $C_{12}H_9N_2O_2F$ (%): C, 62.07; H, 3.91; N, 12.06; O, 13.78; F, 8.18. Found: C, 62.10; H, 3.91; N, 12.02.

3-nitro-4-(2-chlorophenyl)- 1-ethenylpyrrole (12). Solid, m.p: 68–70 ^{0}C; IR (cm^{-1}, KBr): 2991, 2855, 1590, 1543, 1507, 1474. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.74 (1 H, d, J = 2.4 Hz), 7.44 (1 H, m), 7.38 (3 H, m), 6.88 (1 H, dd, J = 15.9, 8.7 Hz), 6.76 (1 H, d, J = 2.4 Hz), 5.29 (1 H, dd, J = 15.9, 2.1 Hz), 4.89 (1 H, dd, J = 8.7, 2.1 Hz). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm):140.2, 137.5, 132.1, 129.9, 129.5, 129.0, 127.9, 127.5, 122.8, 121.6, 115.5, 100.4. MS (m/z): 248 [M^+]. *Anal*. Calcd. for $C_{12}H_9N_2O_2Cl$ (%): C, 57.96; H, 3.65; N, 11.27; O, 12.87; Cl, 14.26. Found: C, 57.92; H, 3.66; N, 11.23.

2-cyano-1-ethenyl pyrrole (13). Oil, IR (cm^{-1}, KBr):3178, 2226, 1517, 1357, 1242. ^{1}HNMR (300 MHz, $CDCl_3$), δ (ppm): 7.16 (1 H, s), 7.04 (1 H, s), 6.86 (1 H, s), 6.28 (1 H, s), 5.40 (1 H, dd, J = 15.6, 2.1 Hz), 4.98 (1 H, dd, J = 8.8, 2.1 Hz). ^{13}CNMR (75 MHz, $CDCl_3$), δ (ppm): 129.5, 117.9, 116.8, 115.3, 105.6, 101.7. MS (m/z): 91 [M^+-27]. *Anal*. Calcd. for $C_7H_6N_2$ (%): C, 71.17; H, 5.12; N, 23.71. Found: C, 71.21; H, 5.11; N, 23.68.

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