Notes

Synthesis of 3-Vinylpyrrole

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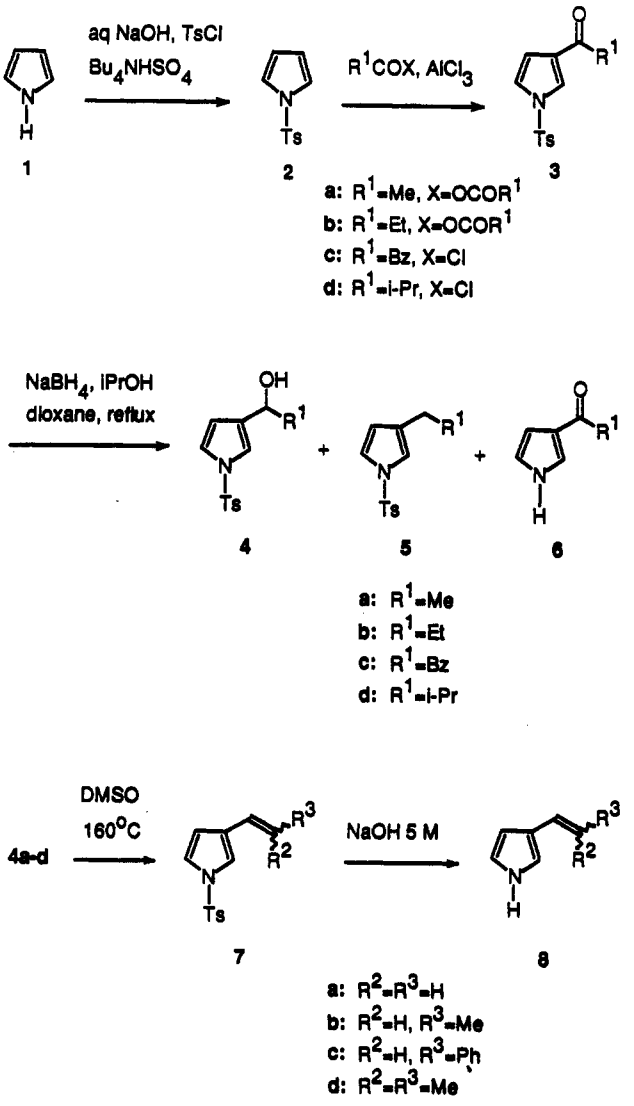
In recent years, 3-alkylpyrroles have been investigated as starting monomers for the preparation of organic conducting materials,[1] as well as precursors in porphyrin chemistry.[2] At present, simple 3-alkenylpyrroles are the subject of considerable interest. These compounds, reactive both at the exocyclic double bond and at positions 2 and 5 of the pyrrole ring, represent interesting bifunctional monomers for the synthesis of polypyrroles.[3] It is surprising that, although an ab initio molecular orbital study of the simplest member of this class, 3-vinylpyrrole, has been reported,[4] this compound has never been synthesized. Its supposed inaccessibility and/or instability is a possible explanation.[5] We report here a simple general method which leads in five steps from pyrrole to 3-ethenylpyrroles with good yield of isolated, pure product. The 3-acyl-1-tosylpyrroles, easily obtained by the procedure of Kakushima et al.,[6] were successfully used as starting material to prepare 3-vinylpyrrole **8a** and some related compounds **8b–d** (Scheme I), previously unreported in the literature.

Results and Discussion

The synthetic sequence used is shown in Scheme I. Pyrrole (1) was treated with tosyl chloride under catalytic phase-transfer conditions to give 1-tosylpyrrole (2) in high yield.[7,8] Then **2** was acetylated to afford 3-acetyl-1-tosylpyrrole (**3a**)[9] in quantitative yield using acetic anhydride and $AlCl_3$, according to the experimental conditions described by Kakushima[6] et al. for 3-acetyl-1-phenylsulfonyl)pyrrole. The partial reduction of **3a** to 3-(1-hydroxyethyl) derivative **4a** is a crucial step in the reaction sequence. Whereas some methods for the reductive deoxygenation of 3-acyl-1-(phenylsulfonyl)pyrroles

Scheme I



to 3-alkyl-1-(phenylsulfonyl)pyrroles have been described in the literature,[7,10,11] the preparation of 3-(1-hydroxyalkyl)pyrroles from acylic precursors has not been developed. After several attempts, we found that the treatment of **3a** with $NaBH_4$ and 2-propanol in boiling dioxane (molar ratio **3a**/$NaBH_4$/2-propanol = 1:0.5:1) gives the best yield of the hydroxyl derivative **4a** (Table I). When less 2-propanol was present, no reaction was observed. On the other hand, upon carrying out the reaction in pure 2-propanol, significant deprotection of the nitrogen atom occurred and the resulting N-unsubstituted 3-acetylpyrrole was recovered. The reaction is not completely chemoselective, affording **4a** along with the corresponding 3-ethyl-1-tosylpyrrole (**5a**) (20%) and traces of detosylated acyl derivative **6a**. The isolation of **4a**, as a pure yellow oil (70% yield), was accomplished by liquid chromatography on a silica gel column, eluting with chloroform–

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(1) Inagaki, T.; Hunter, M.; Yang, X. Q.; Skotheim, T. A.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 126.
(2) Smith, K. M.; Bisset, G. M. F. *J. Org. Chem.* **1979**, *44*, 2077.
(3) Kamogawa, H.; Nakata, T.; Ohori, S.; Komatsu, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1066.
(4) Kao, J.; Hinde, A. L.; Radom, L. *Nouv. J. Chim.* **1979**, *3*, 473.
(5) (a) Jones, R. A.; Marriott, M. T. P.; Rosenthal, W. P.; Arques, J. S. *J. Org. Chem.* **1980**, *45*, 4515. (b) Hosmane, R. S.; Hiremath, S. P.; Schneller, S. W. *J. Chem. Soc., Perkin Trans. 1*, **1973**, 2450.
(6) Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* **1983**, *48*, 3214.
(7) Anderson, H. J.; Loader, C. E.; Xu, R. X.; Lê, N.; Gogan, N. J.; McDonald, R.; Edwards, L. G. *Can. J. Chem.* **1985**, *63*, 896.
(8) Papadopoulos, E. P.; Haidar, N. F. *Tetrahedron Lett.* **1968**, *14*, 1721.
(9) Muratake, H.; Natsume, M. *Heterocycles* **1990**, *31*, 683.
(10) Ketcha, D. M.; Carpenter, K. P.; Atkinson, S. T.; Rajagopalan, H. R. *Synth. Commun.* **1990**, *20*, 1647.
(11) Greenhouse, R.; Ramirez, C.; Muchowski, J. M. *J. Org. Chem.* **1985**, *50*, 2961.

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Table I. Reduction of 3-Acyl-1-Tosylpyrroles 3a–d to 3-(1-Hydroxyalkyl)-1-tosylpyrroles 4a–d with $NaBH_4$ and 2-Propanol in Dioxane at Reflux

starting material		reaction	product		
entry	compd	time, h	compd	yield,[a] %	purification process (CC[b])
1	3a	6.5	4a	70	oil; $CHCl_3$–EtOAc (70:30)
2	3b	7.0	4b	67	oil; CCl_4–Et_2O (1:1)
3	3c	4.0	4c	72	solid;[c] hexane–EtOAc (2:1)
4	3d	5.5	4d	48	oil; hexane–Et_2O (2:3)

[a] Yield of pure isolated product 4 based on 3. [b] CC = Column chromatography: the stationary phase was silica gel. [c] Mp 90–92 °C.

ethyl acetate (70:30). Several attempts at the dehydration of 4a under a variety of experimental conditions[12] were unsuccessful, leading to decomposition or oligomer formation. Finally, 3-vinyl-1-tosylpyrrole (7a) was obtained by heating 4a under neutral conditions with anhydrous DMSO at 160 °C, following the procedure described by Traynelis et al. for the dehydration of benzylic alcohols.[13] The crude product was chromatographed (SiO_2; $CHCl_3$–hexane = 1:1) to obtain 7a as a colorless solid in 94% yield (Table II). In order to remove the tosyl group, 7a was submitted to heat treatment with NaOH in 2-propanol/water. The result was 3-vinylpyrrole (8a), obtained as a pale yellow oil (82% yield, Table III) by distillation at reduced pressure. Contrary to what was previously supposed,[5] 8a is stable enough to be distilled without any decomposition, easily handled at room temperature, and perfectly stable for long periods at 0 °C.

The same reaction sequence afforded 3-(1-propenyl)-pyrrole (8b), 3-(2-phenylethenyl)pyrrole (8c), and 3-(2-methyl-1-propenyl)pyrrole (8d) in good overall yield of isolated pure product (Tables I–III), respectively, from 3b–d. As observed for 3-vinylpyrrole, the compounds 8b–d are stable at 0 °C.

In one case (entry 2 in Table III), the addition of diphenylamine as a polymerization inhibitor was necessary in order to prevent the formation of oligomers during the basic hydrolysis. All the newly synthesized compounds 3b–d, 4a–d, 7a–d, and 8a–d were characterized by ^1H NMR, MS, and elemental analysis.

3-Alkyl-1-tosylpyrrole byproducts arising from the reduction step undergo no detosylation under the experimental conditions adopted. As a consequence they can be easily eliminated during the purification of the final product.

It must be noted that the sequence used for the preparation of 8a–d cannot be varied. Attempts to carry out the reduction of N-unsubstituted 3-acetylpyrrole[6] (6a) in boiling dioxane/2-propanol/$NaBH_4$ were unsuccessful, with unreacted starting substrate being recovered. On the other hand, the N-tosylated alcohols decomposed to some extent under the basic hydrolysis conditions used in the detosylation step; therefore the tosyl group must be removed after the dehydration step. This clearly indicates that the partial reduction of the 3-acyl-1-tosylpyrroles 3 to the corresponding alcohols 4 is the key step in the synthesis of the 3-ethenylpyrroles 8. The reduction of both 3-(phenylacetyl)-1-tosylpyrrole (3c) and 3-(isobutyryl)-1-tosylpyrrole (3d) affords only traces of the alkyl derivatives 5c and 5d. In these cases, 3-(phenylacetyl)-pyrrole (6c) and 3-(isobutyryl)pyrrole (6d), arising from detosylation of 3c and 3d, were recovered (15 and 28% of isolated product, respectively), along with the desired alcohols 4c and 4d.

(12) (a) Hoffman, R. V.; Bishop, R. D.; Fitch, P. M.; Hardenstein, R. *J. Org. Chem.* **1980**, *45*, 917. (b) Giner, J. L.; Margot, C.; Djerassi, C. *J. Org. Chem.* **1989**, *54*, 369. (c) Botteghi, C.; Caccia, G.; Gladiali, S.; Tatone, D. *Synth. Commun.* **1979**, *9*, 69.

(13) Traynelis, V. J.; Hergenrother, W. L.; Livingston, J. R.; Valicenti, J. A. *J. Org. Chem.* **1962**, *27*, 2377.

Conclusion

A suitable synthetic route to the 3-ethenylpyrroles has been developed, starting from readily available 3-acetyl-1-tosylpyrroles. The expected p-toluenesulfonic acid is the main byproduct of the reaction sequence, which employs inexpensive reagents and provides pure products after a simple purification process. This easy accessibility to the 3-ethenylpyrroles makes these compounds a convenient source of other 3-substituted pyrrole derivatives. Among the synthesized products, 3-vinylpyrrole 8a constitutes the most interesting substrate for experimental and theoretical investigations.

Experimental Section

All reagents were of commercial quality. Silica gel (70–230 mesh) was purchased from Merck. DMSO was refluxed and then distilled over sodium hydroxide pellets. The NH_3-saturated eluents used in the column chromatography were obtained by bubbling gaseous NH_3 into organic mixture at 0 °C. Melting points were taken using a Reichart Thermovar apparatus and were uncorrected. Microanalyses were performed at Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. ^1H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) or VXR-300 (300 MHz) spectrometers with TMS as internal standard and $CDCl_3$ as the solvent. Electron impact mass spectra were recorded on a Perkin Elmer Q-Mass 910 mass spectrometer interfaced with a Perkin Elmer 8500 gas chromatograph. 1-Tosylpyrrole (2)[7,8] and 3-acetyl-1-tosylpyrrole (3a)[6,9] were synthesized as described in the literature.

3-Acyl-1-tosylpyrroles. General Procedure. 3-Propionyl-1-tosylpyrrole (3b). The procedure of Kakushima[6] et al. was used. To a suspension of anhydrous $AlCl_3$ (46.4 g, 0.348 mol) in 750 mL of dichloromethane at 25 °C was added slowly propionic anhydride (23.0 g, 0.177 mol) and the resulting mixture was stirred for 15 min. A solution of 2 (12.0 g, 0.054 mol) in 150 mL of dichloromethane was added dropwise, and the mixture was stirred at 25 °C for 2 h. The reaction was quenched with ice and water, and the aqueous layer was extracted with additional dichloromethane (3 × 200 mL). The combined organic layers were treated with saturated $NaHCO_3$, washed with brine, dried (Na_2SO_4), and evaporated in vacuo to give a red solid. Crystallization from ether gave 3b (12.5 g, 0.045 mol, 84%) as colorless needles: mp 67–69 °C; ^1H NMR δ 7.80 (d, 2 H, J = 8.26 Hz), 7.74 (dd, 1 H, J = 1.68, 2.16 Hz, H2), 7.34 (d, 2 H, J = 8.26 Hz), 7.14 (dd, 1 H, J = 2.16, 3.31 Hz, H5), 6.68 (dd, 1 H, J = 1.68, 3.31 Hz, H4), 2.76 (q, 2 H, J = 7.34 Hz, CH_2), 2.42 (s, 3 H), 1.15 (t, 3 H, J = 7.34 Hz, CH_3); MS m/e 277 (M^+, 2.0), 248 (36.5), 155 (43.8), 91 (100), 65 (32.1), 39 (67.3). Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05. Found: C, 60.81; H, 5.53; N, 4.95.

3-(Phenylacetyl)-1-tosylpyrrole (3c). Prepared according to the general procedure except that phenylacetyl chloride (21.04 g, 0.136 mol), $AlCl_3$ (18.0 g, 0.135 mol), and 2 (10 g, 0.045 mol) were used. Yield 12.16 g (0.036 mol, 80%) of pure 3c as a yellow-orange solid (SiO_2; hexane–EtOAc = 6:4): mp 84.5–87.5 °C; ^1H NMR δ 7.78–7.75 (m, 2 H), 7.34–7.23 (m, 8 H), 7.11 (dd, 1 H, J = 2.08, 3.42 Hz, H5), 6.69 (dd, 1 H, J = 1.71, 3.42 Hz, H4), 4.02 (s, 2 H, CH_2), 2.42 (s, 3 H); MS m/e 248 (M^+ – 91, 100), 155 (56.4), 91 (66.0), 65 (21.7), 39 (30.6). Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 67.24; H, 5.05; N, 4.13. Found: C, 67.10; H, 5.02; N, 4.31.

3-(Isobutyryl)-1-tosylpyrrole (3d). Prepared according to the general procedure except that isobutyryl chloride (13.23 g, 0.124 mol), $AlCl_3$ (18.10 g, 0.135 mol), and 2 (25.00 g, 0.113 mol) were used. Yield 30.8 g (0.106 mol, 94%) of pure 3d as a colorless oil (SiO_2; hexane–Et_2O = 6:4): ^1H NMR δ 7.80 (d, 2 H, J = 8.26 Hz), 7.75 (dd, 1 H, J = 1.68, 2.13 Hz, H2), 7.34 (d, 2 H, J = 8.26 Hz), 7.14 (dd, 1 H, J = 2.13, 3.32 Hz, H5), 6.69 (dd, 1 H, J = 1.68,

Table II. Dehydration of 3-(1-Hydroxyalkyl)-1-tosylpyrroles 4a–d to 3-Ethenyl-1-tosylpyrroles 7a–d with DMSO at 160 °C

starting material			product			
entry	compd	reaction time, min	compd	yield,[a] %	mp,[b] °C	purification process
1	**4a**	30	**7a**	94	81–83	CC;[c] hexane–$CHCl_3$ (1:1)
2	**4b**	20	**7b**	69	55–56[d]	CC; hexane–$CHCl_3$ (1:1)
3	**4c**	7	**7c**	65	204–205[e]	CC; hexane–CH_2Cl_2 (1:1)
4	**4d**	60	**7d**	93	105–107	cryst; pentane–Et_2O

[a] Yield of pure isolated product 7 based on 4. [b] Uncorrected. [c] CC = Column chromatography: the stationary phase was silica gel. [d] 80:20 trans/cis mixture determined by ^1H NMR spectroscopy. [e] Pure trans isomer.

Table III. Detosylation of 3-Ethenyl-1-tosylpyrroles 7a–d to 3-Ethenylpyrroles 8a–d with 5 N NaOH

starting material				product		
entry	compd	solvent	reaction time, h	compd	yield,[a] %	purification process
1	**7a**	*i*-PrOH	8.0	**8a**	82 (54)	oil;[b] distillation
2	**7b**	*i*-PrOH[c]	9.0	**8b**	75 (35)	oil;[d] CC;[e] C_6H_6–CCl_4 (2:3)
3	**7c**	dioxane[f]	8.5	**8c**	80 (37)	solid;[g,h] CC; hexane–THF (2:1)
4	**7d**	*i*-PrOH	15.0	**8d**	73 (33)	oil;[i] distillation

[a] Yield of pure isolated product 8 based on 7. Numbers in parentheses are overall yields based on 3. [b] Bp 30 °C, 6×10^{-3} torr. [c] In the presence of diphenylamine (5% w/w) as polymerization inhibitor. [d] 80/20 trans/cis mixture determined by ^1H NMR spectroscopy. [e] CC = Column chromatography: the stationary phase was silica gel and the eluent mixture was NH_3-saturated. [f] Dioxane was used as the solvent due to the low solubility of **7c** in 2-propanol. [g] The product decomposed under mp determination conditions. [h] Pure trans isomer. [i] Bp 38–40 °C, 6×10^{-3} torr.

3.32 Hz, H4), 3.15 (h, 1 H, J = 6.88 Hz, CH), 2.42 (s, 3 H), 1.16 (d, 6 H, J = 6.88 Hz, $(CH_3)_2$); MS *m/e* 291 (M^+, 6.22), 248 (90.54), 155 (66.5), 91 (100), 65 (36.1), 41 (45.7), 39 (60.5). Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88; N, 4.81. Found: C, 61.54; H, 5.63; N, 4.73.

3-(1-Hydroxyalkyl)-1-tosylpyrroles. General Procedure. 3-(1-Hydroxyethyl)-1-tosylpyrrole (4a). To a solution of 3-acetyl-1-tosylpyrrole (**3a**) (10.0 g, 0.038 mol) in dioxane (320 mL) were added $NaBH_4$ (0.76 g, 0.020 mol) and 2-propanol (3.3 mL, 0.043 mol). The reaction suspension was refluxed for 6.5 h, and then it was cooled to room temperature, treated with 5 M aqueous ammonium chloride solution (150 mL), and extracted with Et_2O (3 × 50 mL). The combined ethereal extracts were treated with water (1000 mL), and then the aqueous phase was extracted with Et_2O (5 × 150 mL). The organic extracts were dried over anhydrous sodium sulfate, and the solvents were evaporated under reduced pressure to give a yellow-orange residue which was chromatographed on silica gel, by eluting with 70:30 chloroform/ethyl acetate to afford 3-(1-hydroxyethyl)-1-tosylpyrrole (**4a**) (7.02 g, 0.026 mol, 70% yield) as a pale yellow oil: ^1H NMR δ 7.74 (d, 2 H, J = 8.14 Hz), 7.28 (d, 2 H, J = 8.14 Hz), 7.12–7.07 (m, 2 H, H2, H5), 6.29 (dd, 1 H, J = 1.71, 3.14 Hz, H4), 4.76 (q, 1 H, J = 6.40 Hz, CH), 2.40 (s, 3 H), 2.00–1.90 (br s, 1 H, OH), 1.42 (d, 3 H, J = 6.40 Hz, CH_3); MS *m/e* 265 (M^+, 21), 250 (43.5), 155 (37.1), 132 (12.9), 91 (100), 65 (24.2). Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70; N, 5.28. Found: C, 58.73; H, 5.71; N, 5.27.

3-(1-Hydroxypropyl)-1-tosylpyrrole (4b): ^1H NMR δ 7.73 (d, 2 H, J = 8.63 Hz), 7.28 (d, 2 H, J = 8.63 Hz), 7.12–7.06 (m, 2 H, H2, H5), 6.27 (dd, 1 H, J = 1.64, 3.16 Hz, H4), 4.49 (t, 1 H, J = 6.22 Hz, CH), 2.40 (s, 3 H), 1.78–1.64 (m, 3 H, CH_2, OH), 0.88 (t, 3 H, J = 7.41 Hz, CH_3); MS *m/e* 277 (M^+, 20.8), 250 (41.7), 248 (100), 207 (10.4). Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.63; H, 5.46; N, 5.05. Found: C, 60.51; H, 5.48; N, 5.03.

3-(1-Hydroxy-2-phenylethyl)-1-tosylpyrrole (4c): ^1H NMR δ 7.71 (d, 2 H, J = 8.30 Hz), 7.28 (d, 2 H, J = 8.30 Hz), 7.26–7.20 (m, 5 H), 7.14–7.03 (m, 2 H, H2, H5), 6.29 (m, 1 H, H4), 4.79 (t, 1 H, J = 6.20 Hz, CH), 3.02–2.89 (m, 2 H, CH_2), 2.41 (s, 3 H), 2.02 (br s, 1 H, OH); MS *m/e* 323 (M^+ – 18, 24.7), 250 (41.9), 168 (100), 167 (89.7), 155 (45.3), 141 (69.3), 115 (30.0), 91 (90.2), 65 (23.0), 39 (21.3). Anal. Calcd for $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.61; N, 4.10. Found: C, 67.05; H, 5.48; N, 4.25.

3-(1-Hydroxy-2-methylpropyl)-1-tosylpyrrole (4d): ^1H NMR δ 7.73 (d, 2H, J = 8.12 Hz), 7.28 (d, 2H, J = 8.12 Hz), 7.10 (t, 1H, J = 2.20 Hz, H2), 7.06 (m, 1 H, H5), 6.25 (dd, 1 H, J = 1.72, 3.24 Hz, H4), 4.30 (d, 1 H, J = 6.22 Hz, C*H*OH), 2.40 (s, 3 H), 1.76–1.92 (m, 2 H, C*H*CH_3, OH), 0.91 (d, 3 H, J = 6.74 Hz, CH_3), 0.79 (d, 3 H, J = 6.74 Hz, CH_3); MS *m/e* 275 (M^+ – 18, 27.2), 250 (38.8), 155 (34.8), 120 (39.3), 93 (41.1), 91 (100), 65 (32.7), 51 (24.8), 41 (44.4), 39 (56.4). Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.55; H, 6.71; N, 4.69.

3-Ethenyl-1-tosylpyrroles. General Procedure. 3-Vinyl-1-tosylpyrrole (7a). 3-(1-Hydroxyethyl)-1-tosylpyrrole (**4a**) (13.5 g, 0.051 mol) and DMSO (47 mL, 0.67 mol) were stirred under a nitrogen atmosphere at 160 °C for 0.5 h. After cooling to room temperature, water was added and the mixture extracted thoroughly with Et_2O (5 × 50 mL). The combined ethereal extracts were dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure to give a residue which was chromatographed on silica gel by eluting with 1:1 chloroform/hexane to afford 3-vinyl-1-tosylpyrrole (**7a**) (11.9 g, 0.048 mol, 94% yield) as a colorless solid: mp 81–83 °C; ^1H NMR δ 7.74 (d, J = 8.60 Hz, 2 H), 7.28 (d, J = 8.60 Hz, 2 H), 7.10 (d, 2 H, J = 2.40 Hz, H2, H5), 6.49 (dd, 1 H, J = 10.80, 17.60 Hz, CHα), 6.45 (d, 1 H, J = 2.40 Hz, H4), 5.44 (dd, 1 H, J = 1.22, 17.60 Hz, CHβ cis), 5.10 (dd, 1 H, J = 1.22, 10.80 Hz, CHβ trans), 2.4 (s, 3 H); MS *m/e* 247 (M^+, 50), 155 (42.9), 135 (14.3), 91 (100), 65 (21.4), 39 (17.9). Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.14; H, 5.30; N, 5.66. Found: C, 62.95; H, 5.32; N, 5.64.

3-(1-Propenyl)-1-tosylpyrrole (7b): ^1H NMR δ 7.83–7.79 (m 2 H), 7.37–7.34 (m, 2 H), 7.16 (m, 1 H, H2), 7.05 (m, 1 H, H5), 6.46 (m, 1 H, H4), 6.27 (*trans*-**7b** d, 1 H, J = 16.00 Hz, CHα), 6.03 (*trans*-**7b** dq, 1 H, J = 6.90, 16.00 Hz, CHβ), 5.74 (*cis*-**7b** dq, 1 H, J = 7.10, 11.60 Hz, CHβ), 2.48 (s, 3 H), 1.94 (*cis*-**7b** dd, 3 H, J = 1.80, 7.10 Hz, CH_3), 1.88 (*trans*-**7b** dd, 3 H, J = 1.80, 6.90 Hz, CH_3); MS *m/e* *trans*-**7b** 261 (M^+, 45.1), 155 (27.1), 106 (43.0), 91 (100), 79 (44.4), 65 (29.2), 51 (27.1), 39 (17.4), 31 (93). Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.35; H, 5.79; N, 5.36. Found: C, 64.16; H, 5.80; N, 5.34.

3-(2-Phenylethenyl)-1-tosylpyrrole (7c): ^1H NMR δ 7.86 (d, 2 H, J = 8.45 Hz), 7.52–7.43 (m, 8 H), 7.23 (dd, 1 H, J = 2.35, 3.31 Hz, H5), 6.99 (d, 1 H, J = 16.17 Hz, CHα or CHβ), 6.88 (d, 1 H, J = 16.17 Hz, CHβ or CHα), 6.63 (dd, 1 H, J = 1.65, 3.31 Hz, H4), 2.50 (s, 3 H); MS *m/e* 323 (M^+, 23.9), 168 (100), 167 (88.8), 141 (69.8), 115 (27.7), 91 (33.2), 39 (11.7). Anal. Calcd for $C_{19}H_{17}NO_2S$: C, 70.56; H, 5.30; N, 4.33. Found: C, 70.71; H, 5.52; N, 4.18.

3-(2-Methyl-1-propenyl)-1-tosylpyrrole (7d): ^1H NMR δ 7.73 (d, 2 H, J = 8.05 Hz), 7.27 (d, 2 H, J = 8.05 Hz), 7.10–7.03 (m, 2 H, H2, H5), 6.28 (dd, 1 H, J = 1.67, 6.34 Hz, H4), 5.94 (br s, 1 H, CH), 2.40 (s, 3 H), 1.83 (s, 6 H, $(CH_3)_2$); MS *m/e* 275 (M^+, 27.2), 250 (38.8), 155 (34.8), 120 (39.3), 93 (41.1), 91 (100), 65 (32.7), 51 (24.8), 41 (44.4), 39 (56.4). Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22; N, 5.09. Found: C, 65.17; H, 6.02; N, 5.31.

3-Ethenylpyrroles. General Procedure. 3-Vinylpyrrole (8a). A mixture of 3-vinyl-1-tosylpyrrole (**7a**) (8.0 g, 0.032 mol) in 2-propanol (200 mL) was stirred with 150 mL of 5 N aqueous NaOH under reflux for 8 h. After cooling to room temperature, 2-propanol was removed at reduced pressure and the aqueous residue extracted with Et_2O (3 × 30 mL). The combined extracts were washed with water, dried over Na_2SO_4 and concentrated to

give a red-orange oil which was distilled at reduced pressure to afford 3-vinylpyrrole (**8a**) (2.44 g, 0.026 mol, 82% yield) as a yellowish oil: bp 30 °C, 6×10^{-3} torr; ^{1}H NMR δ 8.11 (br s, 1 H, NH), 6.80–6.72 (m, 2 H, H2, H5), 6.64 (dd, 1 H, J = 10.80, 17.50 Hz, CHα), 6.40 (q, 1 H, J = 2.72, 4.29 Hz, H4), 5.42 (dd, 1 H, J = 1.69, 17.50 Hz, CHβ cis), 4.97 (dd, 1 H, J = 1.69, 10.80 Hz, CHβ trans); MS m/e 93 (M^+, 100), 92 (36.7), 65 (16.8), 41 (19.0), 39 (60.0), 31 (37.0). Anal. Calcd for C_6H_7N: C, 77.58; H, 7.58; N, 15.04. Found: C, 77.35; H, 7.60; N, 14.99.

3-(1-Propenyl)pyrrole (8b). Prepared according to the general procedure except that diphenylamine (5% weight) as polymerization inhibitor was used: ^{1}H NMR δ 8.40–7.80 (br s, 1 H, NH), 6.65 (m, 2 H, H2, H5), 6.40–6.25 (*trans*-**8b** m, 2 H, H4, CHα), 5.94 (*trans*-**8b** dq, 1 H, J = 6.50, 17.10 Hz, CHβ), 1.88 (*cis*-**8b** dd, 3 H, J = 1.76, 7.09 Hz, CH_3), 1.80 (*trans*-**8b** dd, 3 H, J = 1.62, 6.50 Hz, CH_3); MS m/e *trans*-**8b** 107 (M^+, 57.9), 92 (53.9), 67 (38.2), 65 (34.4), 53 (22.8), 52 (25.9), 51 (37.6), 41 (30.4), 39 (100). Anal. Calcd for C_7H_9N: C, 78.45; H, 8.47; N, 13.08. Found: C, 78.21; H, 8.49; N, 13.04.

3-(2-Phenylethenyl)pyrrole (8c). Prepared according to the general procedure except that dioxane was used as a solvent: ^{1}H NMR δ 8.30–8.05 (br s, 1 H, NH), 7.47–6.83 (m, 8 H), 6.78 (m, 1 H, H5), 6.49 (m, 1 H, H4); MS m/e 169 (M^+, 97.1), 168 (100), 141 (29.9), 139 (17.3), 115 (31.0), 84 (24.1), 83 (23.0), 39 (18.1). Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.22. Found: C, 85.42; H, 6.37; N, 8.27.

3-(2-Methyl-1-propenyl)pyrrole (8d): ^{1}H NMR δ 8.30–7.75 (br s, 1 H, NH), 6.73–6.71 (m, 2 H, H2, H5), 6.25 (dd, 1 H, J = 2.20, 4.60 Hz, H4), 6.11 (br s, 1 H, CH), 1.89 (s, 3 H, CH_3), 1.87 (s, 3 H, CH_3); MS m/e 121 (M^+, 100), 106 (69.9), 80 (53.2), 51 (25.7), 41 (21.8), 39 (45.3). Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.18; H, 9.36; N, 11.70.