A Convenient Preparation of 1-Vinylpyridinium Salts

Olegas Eicher-Lorka,* Gytis K.Kupetis, Laimute Rastenyté, Algirdas Matijoška

Institute of Chemistry, Akademijos 7, 2600 Vilnius, Lithuania

E-mail: lorka@takas.lt

Received 1 April 1999; revised 30 June 1999

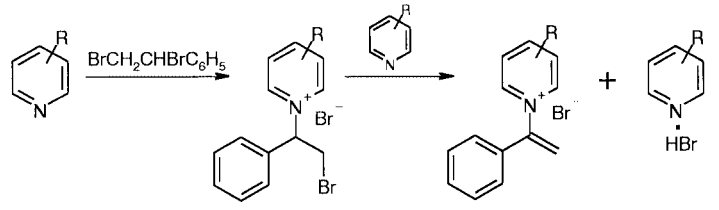
Abstract: Alkylation of various substituted pyridines with 1,2-dibromo- or 1,2,3-tribromoalkanes provides a new simple route to the corresponding 1-vinylpyridinium salts. It was established that a correlation, similar to pyridine's quaternization reaction, exists between the reaction time and the product yield and the electronic nature of the substituents in the pyridine ring. The synthesis of 1,1'-vinylenebis-pyridinium salt that is the representative of the new type of quaternary pyridines is described.

Key words: pyridines, alkylation, 1,2-dibromides, 1-vinylpyridinium salts, bromine, esters, condensation

1-Vinylpyridinium salts are known as potential monomers for the cationic quaternary polyelectrolytes[1] and for the new photochromic polymers,[2] but despite their potential importance and theoretical interest, they have not been thoroughly investigated. They are generally prepared by the dehydrohalogenation of 1-(2-halogenalkyl or 2-halogenalkylaryl)pyridinium salts. Ag_2O[1] or, most often, NaOH[3,4] was used as the dehydrohalogenating reagent. 1-(2-Arylvinyl)pyridinium salts are prepared from 1-(2-hydroxy-2-arylethyl)pyridinium salts via intermediate formation of acetylated[5] or benzoylated[6] derivatives. In 1973, Relles[7] described a general synthesis of 1-(1-arylvinyl)pyridinium salts from pyridine, acetophenone and thionyl chloride. However, this method could not be applied to pyridine derivatives containing functional groups sensitive to thionyl chloride (e.g., NH_2, OH, CO_2R, etc.).

We now report on a new efficient synthesis method of the preparation of the substituted 1-(1-phenylvinyl)pyridinium salts, based on addition of 1,2-dibromo-1-phenylethane to various pyridines, where pyridine derivatives are both the alkylation substrate and the dehydrohalogenating agent at the same time (Scheme 1). A correlation, similar to pyridine's quaternization reaction, exists between the reaction time and the product yield and the electronic nature of the substituents in the pyridine ring. Thus, electron-donating groups tend to accelerate the rate of reaction (compounds **3a–e**), while electron-withdrawing groups cause a reduction in the reaction rate (compounds **3f–m**, Scheme 1). These results, combined with the fact that only compounds **3** and **4** were produced in the typical procedure, suggest that the quaternization reaction occurred more slowly than the elimination reaction. Only at low temperatures and with the excess of dibromide, a small amount of compound **2** was produced. For ease of isolation, some of the vinyl-pyridinium bromides were converted to vinylpyridinium perchlorates (see experimental).

In contrast to the above reaction, where secondary bromine atom was the first to react under the influence of the phenyl group and where elimination was faster than qua-

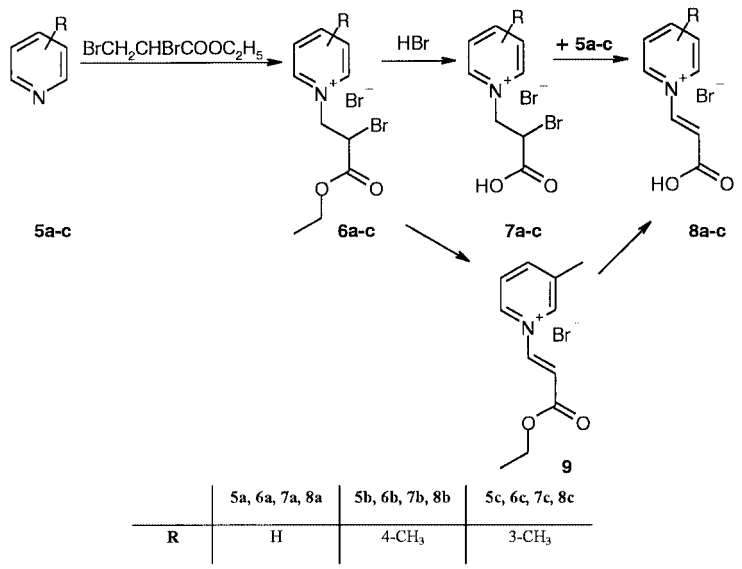


1a-m **2** **3a-m** **4**

	3a	3b	3c	3d	3e	3f	3g
R	H	4-CH_3	3-CH_3	4-$CH_2C_6H_5$	3-$CH_2C_6H_5$	4-COC_6H_5	4-styryl
Yield, %	84	82	82	80	72	64	47
Reaction time, h	6	5	11	5	10	18	15

	3h	3i	3j	3k	3l	3m	
R	4-(4-pyridyl)	3-$COOC_2H_5$	3-COOH	4-NH_2	3-Br	3,5-diBr	
Yield, %	31	38	92 (from **3i**)	20	35	10	
Reaction time, h	18	22	10	20	40	100	

Scheme 1

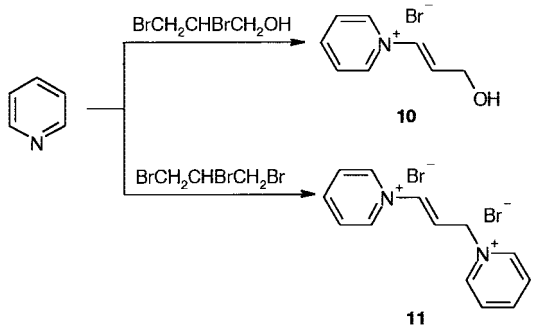


	5a, 6a, 7a, 8a	5b, 6b, 7b, 8b	5c, 6c, 7c, 8c
R	H	4-CH_3	3-CH_3

Scheme 2

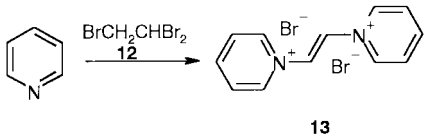
ternization, the primary bromine atom was the first to react in the reaction of various picolines and pyridine **5a–c** with ethyl 2,3-dibromopropionate, and the reaction was halted at the first stage to afford bromoalkyl esters **6a–c** in good yields. Unsaturated acids **8a–c** were synthesized by a two-step process by first hydrolysing the esters **6a–c** with 46% HBr to **7a–c** and then dehydrohalogenation with corresponding pyridines. Only 3-methylpyridinium unsaturated ester **9** was prepared by direct dehydrohalogenation of bromoalkyl ester **6c,** other unsaturated esters were unstable (Scheme 2). It was observed that an exchange reaction takes place if compounds with pyridine rings different from that of substrate pyridine ring were used as the dehydrohalogenating agent. This reaction yielded a mixture of two unsaturated quaternary pyridine acids. This phenomenon is currently under investigation and will be published elsewhere.

Reaction of pyridine with 2,3-dibromopropan-1-ol or with 1,2,3-tribomopropane gave only unsaturated compounds **10**,**11** respectively (Scheme 3). ^{1}H NMR spectra indicated a clean formation of the (*E*)-derivatives **8–11** attested by a 14 Hz coupling constant between the CH=CH group protons.



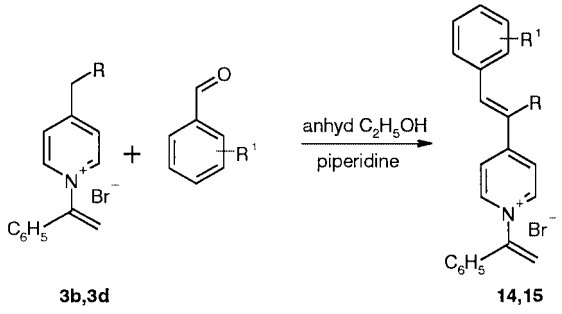
Scheme 3

Treatment of 1,1,2-tribromoethane (**12**) with an excess of pyridine for 20 hours at 70°C in the absence of a solvent gave compound **13** in 32% yield (Scheme 4). This particular type of quaternary pyridine derivatives was unknown previously.



Scheme 4

Compounds **3b** and **3d** (Scheme 1) with acidic methylene groups are unstable and they readily decompose during the workup and purification process. Thus, they were condensed with benzaldehydes without any purification to afford 1-(1-phenylvinyl)stilbazolium salts **14** and **15** respectively (Scheme 5).



	3b	3d	14	15
R	H	C_6H_5	H	C_6H_5
R^1	H	H	2-OH	4-$N(CH_3)_2$

Scheme 5

The structures of all products were determined on the basis of their ^1H and ^{13}C NMR spectra and confirmed by IR, mass spectra and elemental analyses.

In conclusion, a short and efficient synthesis of various 1-vinylpyridinium salts was realized. This procedure, which is based on the reaction of various substituted 1,2-dibromoalkynes with substituted pyridines can also be recommended for the synthesis of other *N*-vinyl heterocycles.

Melting points are uncorrected. ^1H NMR spectra were recorded on a Hitachi R-22 spectrometer (90 MHz) in CD_3OD with TMS as an internal standard. ^{13}C NMR spectra were recorded on a Bruker AC-300 (50.32 MHz) in DMSO-d_6 with TMS as an internal standard. Mass spectra were performed on a Kratos MS-30 (70 eV). IR spectra were recorded as KBr pellets using a FT-IR spectrophotometer Bomem MB (Hartman and Braun, Canada). Elemental analyses were performed by the Analytical Laboratory of the Chemistry faculty of the University of Vilnius. The course of reaction and the purity of products were followed by TLC analysis using Silufol UV-254 (Cavalier, Praha) plates, eluent: acetone/$CHCl_3$/EtOH/H_2O (12:10:6:1 v/v). 1,2-Dibromo-2-phenylethane, ethyl 2,3-dibromopropionate, 2,3-dibromopropan-1-ol, 1,2,3-tribromopropane and pyridines are commercially available and were used without further purification.

Exchange of the Br-Anion in Pyridinium Salts by ClO_4-Perchlorate Anion; General Procedure

64.5% Aq $HClO_4$ (1 mL) was added to appropriate pyridinium salt (10 mmol) and was diluted with H_2O (5 mL). The separated solid was filtered and was recrystallized from H_2O.

1-(2-Bromo-1-phenylethyl)pyridinium Perchlorate (2)

Pyridine (3.9 g, 4 mL, 50 mmol) was added to a solution of 1,2-dibromo-2-phenylethane (26.4 g, 100 mmol) in MeCN (50 mL). The mixture was stirred for 18 h at 50°C. The solvent was removed in vacuo and the residue neutralized with satd aq Na_2CO_3 solution and dissolved in acetone. After filtration of NaBr and removal of the solvent, the residue was treated with 64.5% $HClO_4$ (5 mL) and **3a**•ClO_4^- formed was filtered. The solvent was removed from filtrate in vacuo and the residue was purified by column chromatography on silica gel (MeCN/EtOH, 3:1) to give **2** (1.8 g, 10%) as very hydroscopic material.

^1H NMR (90 MHz, CD_3OD): δ = 4.31, 4.93 (dd, ^2J = 10 Hz, ^3J = 5Hz, 2 H, CH_2Br), 6.8 (dd, ^3J =9 Hz, ^3J = 5 Hz, 1 H, CH), 7.67–7.84 (m, 5 H_{arom}), 8.13 (t, *J* = 7 Hz, 2 H, Py^+ 3,5-H), 8.67 (t, *J* = 7 Hz, 1 H, Py^+ 4-H), 9.67 (d, 2 H, *J* = 7 Hz, Py^+ 2,6-H).

1,1,2-Tribromoethane (12)

A solution of Br_2 (8 g, 50 mmol) in $CHCl_3$ (5 mL) was added dropwise at –10°C to a stirred solution of vinyl bromide (5.35 g, 50 mmol) in $CHCl_3$ (10 mL) over a period of 3 h. The solution was kept at r.t. for 12 h, the solvent was evaporated and the residue was distilled in vacuo to give **12** (11.6 g, 87%) as colorless liquid; bp 77–78°C/14 Torr (Lit.[8] bp 73.1°C/10 Torr).

^1H NMR (90 MHz, CD_3OD): δ = 3.96 (d, *J* = 6 Hz, 2 H, CH_2), 5.82 (t, 1 H, CH).

1-(1-Phenylvinyl)pyridinium Bromides 3a–m; General Procedure

1,2-Dibromo-1-phenylethane (3.96 g, 15 mmol) was added to a solution of **1a–m** (31 mmol) in MeCN (15mL). The mixture was refluxed for 5–100 h. The solvent was evaporated and the residue was neutralized with satd aq Na_2CO_3 solution and was dissolved in acetone. After filtration of NaBr and removal of the solvent, the product was purified by crystallization or was treated with $HClO_4$.

1-(1-Phenylvinyl)pyridinium Perchlorate (3a)

After the reaction of **1a** (2.45 g, 2.5 mL) with 1,2-dibromo-1-phenylethane (4.0 g) for 6 h and treatment with $HClO_4$ followed by recrystallization from H_2O, pure **3a**•ClO_4 was obtained as sand-coloured crystals; yield: 3.55 g (84%); mp 129–130°C.

IR (KBr): ν = 1624 (C=N^+), 1094 cm^{-1} (ClO_4^-).

^1H NMR (90 MHz, CD_3OD): δ = 8.91 (d, 2 H, *J* = 7 Hz, Py^+ 2,6-H), 8.69 (t, *J* =7 Hz, 1 H, Py^+ 4-H), 8.13 (t, 2 H, *J* = 7 Hz, Py^+ 3,5-H), 7.49 – 7.11 (m, 5 H_{arom}), 6.11 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.89 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

^{13}C NMR: δ = 149.60 (=C), 148.06 (Py^+ 4 C), 144.86 (Py^+ 2,6-C), 133.05, 131.44, 129.87 (C_{arom}), 128.83 (Py^+ 3,5-C), 127.16 (C_{arom}), 116.52 ($=CH_2$).

MS (EI): *m*/*z* (%) = 182 (13), 105 (100), 103 (10), 79 (54), 77 (55), 52 (28), 39 (8).

Anal. Calcd for $C_{13}H_{12}ClNO_4$: C, 55.43; H, 4.29; N, 4.97. Found C, 55.25; H 4.39; N 4.81.

^1H NMR and MS data are in accordance with literature.[7]

4-Methyl-1-(1-phenylvinyl)pyridinium Bromide (3b)

Reaction of **1b** (2.89 g, 3 mL) with 1,2-dibromo-2-phenylethane (4.0 g) for 5 h afforded **3b** in 82% yield (determined by ^1H NMR of the crude reaction mixture). The product was used for further reaction without any purification.

^1H NMR (90 MHz, CD_3OD): δ = 8.67 (d, 2 H, *J* = 7 Hz, Py^+ 2,6-H), 7.93 (d, 2 H, *J* = 7 Hz, Py^+ 3,5-H), 7.49 – 7.09 (m, 5 H_{arom}), 6.07 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.80 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5), 2.64 (s, 3 H, CH_3).

3-Methyl-1-(1-phenylvinyl)pyridinium Perchlorate (3c)

After the reaction of **1c** (2.89 g, 3 mL) with 1,2-dibromo-1-phenylethane (4.0 g) for 11 h and treatment with $HClO_4$ followed by recrystallization from H_2O gave pure **3c**•ClO_4 as sand-coloured crystals; yield: 3.64 g (82%); mp 153–154°C.

IR (KBr): ν = 1625 (C=N^+), 1096 cm^{-1} (ClO_4^-).

^1H NMR (90 MHz, CD_3OD): δ = 8.84 (s, 1 H, Py^+ 2-H), 8.71 (d, 1 H, *J* = 7 Hz, Py^+ 6-H), 8.49 (d, 1 H, *J* = 7 Hz, Py^+ 4-H), 8.00 (t, *J* = 7 Hz, 1 H, Py^+ 5-H), 7.49–7.11 (m, 5 H_{arom}), 6.13 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.86 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5), 2.56 (s, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 196 (100), 103 (63), 94 (58), 93 (48), 77 (52), 65 (12), 51 (26), 39 (13).

Anal. Calcd for $C_{14}H_{14}ClNO_4$: C, 56.86; H, 4.77; N, 4.74. Found C, 56.73; H 4.83; N 4.69.

4-Benzyl-1-(1-phenylvinyl)pyridinium Bromide (3d)

Reaction of **1d** (5.25 g) with 1,2-dibromo-1-phenylethane (4.0 g) for 5 h gave **3d** in 64% yield (determined by ^1H NMR of the crude reaction mixture). Product was used for further reaction without any purification.

^1H NMR (90 MHz, CD_3OD): δ = 8.73 (d, 2 H, *J* = 7 Hz, Py^+ 2,6-H), 7.92 (d, 2 H, *J* = 7 Hz, Py^+ 3,5-H), 7.42–7.04 (m, 10 H_{arom}), 6.04 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.79 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5), 4.07 (s, 2 H, CH_2).

MS (EI): *m*/*z* (%) = 259 (41), 156 (100), 103 (33), 80 (12), 77 (13), 50 (27), 39 (5).

3-Benzyl-1-(1-phenylvinyl)pyridinium Perchlorate (3e)

After the reaction of **1e** (5.25 g) with 1,2-dibromo-1-phenylethane (4.0 g) for 10 h and treatment with $HClO_4$ followed by recrystallization from H_2O gave pure **3e**•ClO_4 as sand-coloured crystals; yield: 4.02 g (72%); mp 76–77°C.

IR (KBr): ν = 1618 (C=N$^+$), 1088 cm^{-1} (ClO_4^-).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.87 (s, 1 H, Py$^+$ 2-H), 8.71 (d, 1 H, *J* = 7 Hz, Py$^+$ 6-H), 8.46 (d, 1 H, *J* = 7 Hz, Py$^+$ 4-H), 8.00 (t, *J* = 7 Hz, 1 H, Py$^+$ 5-H), 7.44–7.02 (m, 10 H_{arom}), 6.09 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.87 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5), 4.22 (s, 2 H, CH_2).

MS (EI): *m*/*z* (%) = 272 (8), 168 (100), 105 (47), 91 (15), 77 (23), 51 (15), 39 (8).

Anal. Calcd for $C_{20}H_{18}ClNO_4$: C, 64.61; H, 4.88; N, 3.77. Found C, 64.21; H 4.96; N 3.70.

4-Benzoyl-1-(1-phenylvinyl)pyridinium Bromide (3f)
Reaction of **1f** (5.68 g) with 1,2-dibromo-1-phenylethane (4.0 g) for 18 h and recrystallization of the product from MeCN gave pure **3f** as yellow crystals; yield: 3.52 g (64%); mp 179–180°C.

IR (KBr): ν = 1632 (C=N$^+$), 1670 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.09 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 8.24 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 7.95 – 7.31 (m, 10 H_{arom}), 6.15 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 6.00 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

MS (EI): *m*/*z* (%) = 286 (33), 184 (72), 105 (89), 103 (80), 77 (100), 51 (39), 39 (5).

Anal. Calcd for $C_{20}H_{16}BrNO$: C, 65.59; H, 4.40; N, 3.82. Found C, 65.31; H 4.51; N 3.60.

4-(2-Phenyl-1-ethenyl)-1-(1-phenylvinyl)pyridinium Bromide (3g)
Reaction of **1g** (5.62 g) with 1,2-dibromo-1-phenylethane (4.0 g) for 15 h and recrystallization of the product from H_2O gave pure **3g** as yellow crystals; yield: 2.57 g (47%); mp 239.5–240.5°C.

IR (KBr): ν = 1615 cm^{-1} (C=N$^+$).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.69 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 8.18 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 7.98 (d, 1 H, *J* = 16 Hz, =C*H*–C_6H_5), 7.78–7.60 (m, 5 H_{arom}), 7.53–7.31 (m, 5 H_{arom}), 7.40 (d, 1 H, *J* = 16 Hz, =C*H*–Py$^+$), 6.04 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.82 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

MS (EI): *m*/*z* (%) = 284 (82), 180 (100), 103 (39), 81 (10), 80 (20), 79 (14), 77 (32), 51 (13), 39 (6).

Anal. Calcd for $C_{21}H_{18}BrN$: C, 69.24; H, 4.98; N, 3.85. Found C, 69.02; H 5.10; N 3.71.

1-(1-Phenylvinyl)-4-(4-pyridyl)pyridinium Bromide (3h)
Reaction of **1h** (5.96 g) with 1,2-dibromo-1-phenylethane (4.0 g) for 18 h and recrystallization of the product from MeCN afforded pure **3h** as sand-coloured crystals; yield: 1.58 g (31%); mp 102–104°C.

IR (KBr): ν = 1629 cm^{-1} (C=N$^+$).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.04 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 8.61 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 8.01 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 7.96 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 7.26 (s, 5 H_{arom}), 6.16 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.93 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

MS (EI): *m*/*z* (%) = 259 (41), 156 (100), 103 (33), 80 (12), 77 (13), 50 (27), 39 (5).

Anal. Calcd for $C_{18}H_{15}BrN_2$: C, 63.73; H, 4.46; N, 8.26. Found C, 63.69; H 4.57; N 8.10.

3-Ethoxycarbonyl-1-(1-phenylvinyl)pyridinium Bromide (3i)
Reaction of **1i** (4.69 g, 4.23 mL) with 1,2-dibromo-1-phenylethane (4.0 g) for 22 h and recrystallization from MeCN gave pure **3i** as sand-coloured crystals; yield:1.91 g (38%); mp 162–163°C.

IR (KBr): ν = 1610 (C=N$^+$), 1710 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.44 (s, 1 H, Py$^+$ 2 H), 9.26 (d, 1 H, *J* = 7 Hz, Py$^+$ 6-H), 9.18 (d, 1 H, *J* = 7 Hz, Py$^+$ 4-H), 8.38 (t, *J* = 7 Hz, 1 H, Py$^+$ 5-H), 7.44 (s, 5 H_{arom}), 6.29 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 6.04 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5), 4.47 (q, *J* = 7 Hz, 2 H, CH_2), 1.31 (t, *J* = 7 Hz, 3 H, CH_3).

MS (EI): *m*/*z* (%) = 254 (56), 226 (53), 182 (15), 152 (40), 124 (52), 103 (100), 77 (50), 51 (20), 39 (6).

Anal. Calcd for $C_{16}H_{16}BrNO_2$: C, 57.50; H, 4.83; N, 4.19. Found C, 57.35; H 4.99; N 4.00.

3-Carboxy-1-(1-phenylvinyl)pyridinium Bromide (3j)
A solution of **3i** (5.01 g, 15 mmol) in aq 46.8% HBr (6 mL) was stirred at 60°C for 10 h. The solvent was evaporated in vacuo and the residue was washed with acetone (2 × 10 mL). The product was further purified by recrystallization from MeCN to give pure **3j** as white crystals; yield: 4.23 g (92%); mp 223–224°C (dec.).

IR (KBr): ν = 1623 (C=N$^+$), 1717 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.13 (s, 1 H, Py$^+$ 2-H), 9.03 (d, 1 H, *J* = 7 Hz, Py$^+$ 6-H), 8.96 (d, 1 H, *J* = 7 Hz, Py$^+$ 4-H), 8.22 (t, *J* = 7 Hz, 1 H, Py$^+$ 5-H), 7.13 (s, 5 H_{arom}), 6.15 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.86 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

MS (EI): *m*/*z* (%) = 227 (72), 123 (54), 105 (67), 103 (100), 80 (31), 77 (64), 51 (40), 39 (12).

Anal. Calcd for $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.57. Found C, 54.89; H 4.02; N 4.37.

4-Amino-1-(1-phenylvinyl)pyridinium Bromide (3k)
Reaction of **1k** (2.92 g) with 1,2-dibromo-1-phenylethane (4.0 g) for 20 h and recrystallization of the product from MeCN gave pure **3k** as sand-coloured crystals; yield: 0.83 g (20%); mp 178–180° C.

IR (KBr): ν = 1626 cm^{-1} (C=N$^+$).

^{1}H NMR (90 MHz, CD_3OD): δ = 7.73 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 7.40–7.03 (m, 5 H_{arom}), 6.91 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 5.68 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.42 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

MS (EI): *m*/*z* (%) = 196 (100), 103 (85), 94 (77), 80 (49), 77 (36), 67 (18), 51 (14), 39 (10).

Anal. Calcd for $C_{13}H_{13}BrN_2$: C, 56.34; H, 4.73; N, 10.11. Found C, 56.22; H 4.89; N 10.08.

3-Bromo-1-(1-phenylvinyl)pyridinium Bromide (3l)
Reaction of **1l** (4.90 g,) with 1,2-dibromo-1-phenylethane (4.0 g) for 40 h and recrystallization of the product from MeCN gave pure **3 l** as sand-coloured crystals; yield: 1.79 g (35%); mp 95–96°C.

IR (KBr): ν = 1613 cm^{-1} (C=N$^+$).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.36 (s, 1 H, Py$^+$ 2-H), 8.98 (d, 1 H, *J* = 7 Hz, Py$^+$ 6-H), 8.87 (d, 1 H, *J* = 7 Hz, Py$^+$ 4-H), 8.07 (t, J= 7 Hz, 1 H, Py$^+$ 5-H), 7.36 (s, 5 H_{arom}), 6.11 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.87 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

MS (EI): *m*/*z* (%) = 260 (19), 181 (10), 157 (79), 103 (100), 78 (62), 51 (42), 39 (9).

Anal. Calcd for $C_{13}H_{11}Br_2N$: C, 45.78; H, 3.25; N, 4.11. Found C, 45.66; H 3.35; N 4.00.

3,5-Dibromo-1-(1-phenylvinyl)pyridinium Bromide (3m)
Reaction of **1m** (7.34 g) with 1,2-dibromo-1-phenylethane (4.0 g) for 100 h and recrystallization of the product from MeCN gave pure **3m** as sand-coloured crystals; yield: 0.63 g (10%); mp >250°C (dec.).

IR (KBr): ν = 1600 cm^{-1} (C=N$^+$).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.36 (s, 2 H, Py$^+$ 2,6-H), 9.20 (s, 1 H, Py$^+$ 4-H), 7.40 (s, 5 H_{arom}), 6.26 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.98 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5).

MS (EI): *m*/*z* (%) = 339 (6), 237 (17), 156 (100), 105 (23), 103 (12), 77 (10), 50 (6), 38 (4).

Anal. Calcd for $C_{13}H_{10}Br_3N$: C, 37.18; H, 2.40; N, 3.34. Found C, 37.01; H 2.56; N 3.33.

1-(2-Bromo-2-ethoxycarbonylethyl)pyridinium Bromides 6a–c; General Procedure

Ethyl 2,3-dibromopropionate (2.60 g, 10 mmol) was added to a solution of **5a–c** (12 mmol) in MeCN (5 mL). The mixture was stirred for 5–22 h at the appropriate temperature (see below). The solvent was evaporated in vacuo and the residue was washed with benzene (2 × 10 mL).

1-(2-Bromo-2-ethoxycarbonylethyl)pyridinium Perchlorate (6a)

After the reaction of **5a** (0.95 g, 1 mL) with ethyl 2,3-dibromopropionate (2.60 g, 1.5 mL) for 6 h at 21°C and treatment with $HClO_4$ followed by recrystallization from EtOH pure **6a**•ClO_4 was obtained as white crystals; yield: 2.90 g (81%); mp 75–76°C.

IR (KBr): ν = 1625 (C=N$^+$), 1717 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.96 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 8.62 (t, *J* = 7 Hz, 1 H, Py$^+$ 4-H), 8.02 (t, *J* = 7 Hz, 2 H, Py$^+$ 3,5-H), 5.36–4.80 (m, 3 H, C*H*$_2$C*H*Br), 4.04 (q, *J* = 7 Hz, 2 H, C*H*$_2$CH$_3$), 1.20 (t, *J* = 7 Hz, 3 H, CH_3).

^{13}C NMR: δ = 167.00 (C=O), 146.84 (Py$^+$ 4-C), 145.70 (Py$^+$ 2,6-C), 127.96 (Py$^+$ 3,5-C), 62.53 (*C*H$_2$CHBr), 61.18 (*C*H$_2$CH$_3$), 43.19 (CHBr), 13.70 (CH_3).

MS (EI): *m*/*z* (%) = 178 (6), 152 (11), 105 (21), 80 (40), 79 (100), 71 (10), 52 (42), 45 (8), 39 (5).

Anal. Calcd for $C_{10}H_{13}BrClNO_6$: C, 33.50; H, 3.65; N, 3.91. Found C, 33.33; H 3.78; N 3.80.

1-(2-Bromo-2-ethoxycarbonylethyl)-4-methylpyridinium Bromide (6b)

Reaction of **5b** (1.12 g, 1,2 mL) with ethyl 2,3-dibromopropionate (2.60 g, 1.5 mL) for 5 h at 21°C and recrystallization from acetone gave pure **6b** as white crystals; yield: 2.08 g (59%); mp 123–124°C.

IR (KBr): ν = 1620 (C=N$^+$), 1710 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.69 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 7.84 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 5.29–4.71 (m, 3 H, C*H*$_2$C*H*Br), 4.18 (q, *J* = 7 Hz, 2 H, C*H*$_2$CH$_3$), 2.60 (s, 3 H, CH_3), 1.18 (t, *J* = 7 Hz, 3 H, CH$_2$C*H*$_3$).

^{13}C NMR: δ = 166.54 (C=O), 159.89 (Py$^+$ 4-C), 144.56 (Py$^+$ 2,6-C), 128.01 (Py$^+$ 3,5-C), 62.00 (*C*H$_2$CHBr), 59.92 (*C*H$_2$CH$_3$), 42.94 (CHBr), 21.57 (CH_3), 13.51 (CH$_2$*C*H$_3$).

MS (EI): *m*/*z* (%) = 191 (100), 163 (92), 146 (25), 117 (25), 93 (31), 80 (12), 65 (11), 39 (13).

Anal. Calcd for $C_{11}H_{15}Br_2NO_2$: C, 37.42; H, 4.28; N, 3.97. Found C, 37.39; H 4.33; N 3.88.

1-(2-Bromo-2-ethoxycarbonylethyl)-3-methylpyridinium Bromide (6c)

Reaction of **5c** (1.12 g, 1.2 mL) with ethyl 2,3-dibromopropionate (2.60 g, 1.5 mL) for 22 h at 15°C and recrystallization of the product from MeCN gave pure **6c** as white crystals; yield: 1.66 g (47%); mp 128–129°C.

IR (KBr): ν = 1638 (C=N$^+$), 1727 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.67 (s, 1 H, Py$^+$ 2-H), 8.62 (d, 1 H, *J* = 7 Hz, Py$^+$ 6-H), 8.31 (d, 1 H, *J* = 7 Hz, Py$^+$ 4-H), 7.82 (dd, 1 H, Py$^+$ 5-H), 5.36 – 4.67 (m, 3 H, C*H*$_2$C*H*Br), 4.11 (q, *J* = 7 Hz, 2 H, C*H*$_2$CH$_3$), 2.49 (s, 3 H, CH_3), 1.40 (t, *J* = 7 Hz, 3 H, CH$_2$C*H*$_3$).

^{13}C NMR: δ = 166.98 (C = O), 147.10 (Py$^+$ 2-C), 145.15 (Py$^+$ 6-C), 142.95 (Py$^+$ 4-C), 138.79 (Py$^+$ 3-C), 127.10 (Py$^+$ 5-C), 62.40 (*C*H$_2$CHBr), 61.38 (*C*H$_2$CH$_3$), 43.21 (CHBr), 17.86 (CH_3), 13.71 (CH$_2$*C*H$_3$).

MS (EI): *m*/*z* (%) = 192 (30), 164 (34), 133 (30), 93 (100), 80 (11), 65 (16), 39 (15).

Anal. Calcd for $C_{11}H_{15}Br_2NO_2$: C, 37.42; H, 4.28; N, 3.97. Found C, 37.33; H 4.35; N 3.87.

1-(2-Bromo-2-carboxyethyl)pyridinium Bromides 7a–c; General Procedure

A solution of **6a–c** (10 mmol) in aq 46.8% HBr (5 mL) was stirred at 60°C for 10 h. The solvent was evaporated in vacuo and the residue was washed with acetone (2 × 10 mL).

1-(2-Bromo-2-carboxyethyl)pyridinium Bromide (7a)

Reaction of **6a** (3.59 g) with aq 46.8% HBr (5 mL) and recrystallization of the product from EtOH gave pure **7a** as white crystals; yield: 2.89 g (93%); mp 162–163°C.

IR (KBr): ν = 1620 (C=N$^+$), 1700 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.89 (d, 2 H, *J* = 7Hz, Py$^+$ 2,6-H), 8.51 (t, *J* = 7 Hz, 1 H, Py$^+$ 4-H), 8.00 (t, *J* = 7 Hz, 2 H, Py$^+$ 3,5-H), 5.67 – 4.71 (m, 3 H, C*H*$_2$C*H*Br).

^{13}C NMR: δ = 168.09 (C=O), 146.85 (Py$^+$ 4-C), 145.72 (Py$^+$ 2,6-C), 127.91 (Py$^+$ 3,5-C), 61.28 (*C*H$_2$CHBr), 44.04 (CHBr).

MS (EI): *m*/*z* (%) = 150 (19), 133 (9), 105 (15), 80 (32), 79 (100), 52 (30), 39 (3).

Anal. Calcd for $C_8H_9Br_2NO_2$: C, 30.90; H, 2.92; N, 4.50. Found C, 30.89; H 3.01; N 4.40.

1-(2-Bromo-2-carboxyethyl)-4-methylpyridinium Bromide (7b)

Reaction of **6b** (3.53 g) with aq 46.8% HBr (5 mL) and recrystallization of the product from MeCN gave pure **7b** as white crystals; yield: 2.99 g (92%); mp 107–108°C.

IR (KBr): ν = 1615 (C=N$^+$), 1710 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.82 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 7.87 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 5.33–4.80 (m, 3 H, C*H*$_2$C*H*Br), 2.62 (s, 3 H, CH_3).

^{13}C NMR: δ = 168.01 (C=O), 160.02 (Py$^+$ 4-C), 144.62 (Py$^+$ 2,6-C), 128.16 (Py$^+$ 3,5-C), 60.49 (*C*H$_2$CHBr), 43.95 (CHBr), 21.74 (CH_3).

MS (EI): *m*/*z* (%) = 163 (10), 152 (35), 133 (8), 105 (12), 93 (100), 80 (60), 79 (53), 71 (14), 65 (40), 51 (17), 39 (19).

Anal. Calcd for $C_9H_{11}Br_2NO_2$: C, 33.26; H, 3.41; N, 4.31. Found C, 33.22; H 3.41; N 4.28.

1-(2-Bromo-2-carboxyethyl)-3-methylpyridinium Bromide (7c)

Reaction of **6c** (3.53 g) with aq 46.8% HBr (5 mL) and recrystallization of the product from EtOH gave pure **7c** as white crystals; yield: 2.89 g (89%); mp 185.5–186.5°C.

IR (KBr): ν = 1625 (C=N$^+$), 1739 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.89 (s, 1 H, Py$^+$ 2-H), 8.82 (d, 1 H, *J* = 7 Hz, Py$^+$ 6-H), 8.40 (d, 1 H, *J* = 7 Hz, Py$^+$ 4-H), 7.82 (dd, J = 7Hz, 1 H, Py$^+$ 5-H), 5.31–4.73 (m, 3 H, C*H*$_2$C*H*Br), 2.49 (s, 3 H, CH_3).

^{13}C NMR: δ = 168.35 (C=O), 147.11 (Py$^+$ 2-C), 145.15 (Py$^+$ 6-C), 142.97 (Py$^+$ 4-C), 138.88 (Py$^+$ 3-C), 127.16 (Py$^+$ 5-C), 61.20 (*C*H$_2$CHBr), 44.15 (CHBr), 17.95 (CH_3).

MS (EI): *m*/*z* (%) = 150 (39), 133 (9), 93 (100), 80 (51), 66 (50), 53 (10), 39 (19).

Anal. Calcd for $C_9H_{11}Br_2NO_2$: C, 33.26; H, 3.41; N, 4.31. Found C, 33.16; H 3.56; N 4.20.

1-[(*E*)-2-Carboxy-1-ethenyl]pyridinium Bromides 8a–c; General Procedure

Corresponding pyridine **5a–c** (30 mmol) was added to a solution of **7a–c** (15 mmol) in EtOH (25 mL) and refluxed for 7 h. After evaporation to dryness, the residue was washed with acetone (2 × 10 mL).

1-[(*E*)-2-Carboxy-1-ethenyl])pyridinium Bromide (8a)

Reaction of pyridine **5a** (2.37 g, 2.4 mL) with **7a** (4.67 g) and recrystallization of the product from propan-2-ol gave pure **8a** as pale lilac crystals; yield: 1.17 g (34%); mp 188–189°C (dec.).

IR (KBr): ν = 1610 (C=N$^+$), 1640 (C=C), 1695 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.17 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 8.62 (t, J = 7 Hz, 1 H, Py$^+$ 4-H), 8.27 (d, *J* = 14 Hz, 1 H, =CHPy$^+$), 8.11 (t, J = 7 Hz, 2 H, Py$^+$ 3,5-H), 6.91 (d, *J* = 14 Hz, 1 H, =CHCO$_2$H).

^{13}C NMR: δ = 164.73 (C=O), 148.56 (=*C*HPy$^+$), 145.63 (Py$^+$ 4-C), 142.99 (Py$^+$ 2,6-C), 128.08 (Py$^+$ 3,5-C), 120.68 (=*C*HCO$_2$H).

MS (EI): *m*/*z* (%) = 150 (4), 80 (27), 79 (100), 70 (10), 52 (55), 39 (8).

Anal. Calcd for $C_8H_8BrNO_2$: C, 41.17; H, 3.50; N, 6.09. Found C, 41.59; H 3.60; N 6.00.

1-[(*E*)-2-Carboxy-1-ethenyl]-4-methylpyridinium Bromide (8b)

Reaction of **5b** (2.79 g, 2.9 mL) with **7b** (4.88 g) and recrystallization of the product from acetone/H_2O (30:1) gave pure **8b** as pale lilac crystals; yield: 1.50 g (41%); mp 155–156°C (dec.).

IR (KBr): ν = 1615 (C=N$^+$), 1640 (C=C), 1705 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.98 (d, 2 H, *J* = 7 Hz, Py$^+$ 2,6-H), 8.22 (d, 1 H, *J* = 14 Hz, =CHPy$^+$), 7.93 (d, 2 H, *J* = 7 Hz, Py$^+$ 3,5-H), 6.84 (d, 1 H, *J* = 14 Hz, =CHCO$_2$H), 2.67 (s, 3 H, CH$_3$).

^{13}C NMR: δ = 165.22 (C=O), 160.66 (Py$^+$ 4-C), 141.86 (=*C*HPy$^+$), 141.15 (Py$^+$ 2,6-C), 128.30 (=*C*HCO$_2$H), 127.57 (Py$^+$ 3,5-C), 21.73 (CH$_3$).

MS (EI): *m*/*z* (%) = 163 (2), 93 (100), 80 (21), 65 (21), 51 (12), 39 (26).

Anal. Calc for $C_9H_{10}BrNO_2$: C, 44.29; H, 4.13; N, 5.74. Found C, 44.13; H 4.18; N 5.70.

1-[(*E*)-2-Carboxy-1-ethenyl]-3-methylpyridinium Bromide (8c)

Reaction of **5c** (2.79 g, 2.9 mL) with **7c** (4.88 g) and recrystallization from EtOH gave pure **8c** as white crystals; yield: 2.53 g (69%); mp 190–191°C (dec.).

IR (KBr): ν = 1621 (C=N$^+$), 1659 (C=C), 1714 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.09 (s, 1 H, Py$^+$ 2-H), 8.98 (d,*J* = 7 Hz, 1 H, Py$^+$ 6-H), 8.46 (d, 1 H, *J* = 7 Hz, Py$^+$ 4-H), 8.20 (d, *J* = 14 Hz, 1 H, =CH–Py$^+$), 7.96 (dd, *J* = 7Hz, 1 H, Py$^+$ 5-H), 6.90 (d, 1 H, *J* = 14 Hz, =CHCO$_2$H), 2.51 (s, 3 H, CH$_3$).

^{13}C NMR: δ = 165.12 (C=O), 149.00 (=*C*H–Py$^+$), 142.86 (Py$^+$2-C), 142.03 (Py$^+$ 6-C), 140.74 (Py$^+$ 4-C), 138.89 (Py$^+$ 3-C), 127.30 (Py$^+$ 5-C), 120.38 (=*C*HCO$_2$H), 17.89 (CH$_3$).

MS (EI): *m*/*z* (%) = 164 (4), 93 (100), 80 (29), 66 (48), 51 (8), 39 (27).

Anal. Calcd for $C_9H_{10}BrNO_2$: C, 44.29; H, 4.13; N, 5.74. Found C, 44.10; H 4.25; N 5.59.

1-[(*E*)-2-Ethoxycarbonyl-1-ethenyl]-3-methylpyridinium Bromide (9):

3-Methylpyridine (2.79 g, 2.9 mL, 30 mmol) was added to a solution of **6c** (5.30 g, 15 mmol) in EtOH (25 mL) and stirred for 48 h at 50°C. After evaporation to dryness, the residue was washed with acetone (2 × 10 mL). The product was further purified by recrystallization from MeCN to give pure **9** as sand-coloured crystals; yield: 2.25 g (55%); mp 185–186°C (dec.).

IR (KBr): ν = 1618 (C=N$^+$), 1652 (C=C), 1716 cm^{-1} (C=O).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.16 (s, 1 H, Py$^+$ 2-H), 9.07 (d, *J* = 7 Hz, 1 H, *J* = 7 Hz, Py$^+$ 6-H), 8.51 (d, *J* = 7 Hz 1 H, Py$^+$ 4-H), 8.29 (d, *J* = 14 Hz, 1 H, =CH–Py$^+$), 8.00 (t, *J* = 7 Hz, 1 H, Py$^+$ 5-H), 7.00 (d, *J* = 14 Hz, 1 H, =CHCO$_2$), 4.16 (q, *J* = 7 Hz, 2 H, C*H*$_2$CH$_3$), 2.53 (s, 3 H, CH$_3$), 1.22 (t, *J* = 7 Hz, 3 H, CH$_2$*CH*$_3$).

^{13}C NMR: δ = 163.73 (C=O), 149.10 (=*C*H–Py$^+$), 143.19 (Py$^+$ 2-C), 142.01 (Py$^+$ 6-C), 140.79 (Py$^+$ 4-C), 138.74 (Py$^+$ 3-C), 127.19 (Py$^+$ 5-C), 119.04 (=*C*HCO$_2$), 61.32 (*C*H$_2$CH$_3$), 17.75 (CH$_3$), 13.97 (CH$_2$*C*H$_3$).

MS (EI): *m*/*z* (%) = 192 (21), 164 (24), 135 (20), 108 (39), 93 (100), 80 (7), 66 (18), 51 (5), 39 (16).

Anal. Calcd for $C_{11}H_{14}BrNO_2$: C, 48.55; H, 5.19; N, 5.15. Found C, 48.38; H 5.28; N 5.09.

1-[(*E*)-3-Hydroxyprop-1-en-1-yl]pyridinium Bromide (10)

Adapting the general procedure for the preparation of **3a–m**, pyridine (2.45 g, 2.5 mL, 31 mmol) and 2,3-dibromopropan-1-ol (3.27 g, 1.6 mL, 15 mmol) were reacted to give **10**; sand-coloured crystals; yield: 1.43 g (44%); mp 156–157°C (MeCN).

IR (KBr): ν = 1088 (C–C–O), 1624 cm^{-1} (C=N$^+$).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.00 (d, *J* = 7 Hz, 2 H, Py$^+$ 2,6-H), 8.49 (t, *J* =7 Hz, 1 H, Py$^+$ 4-H), 8.00 (t, *J* = 7 Hz, 2 H, Py$^+$ 3,5-H), 7.44 (dt, ^3J = 14Hz, ^4J = 2 Hz,1 H =C*H*–Py$^+$), 6.78 (dt, ^3J = 14Hz, ^4J = 2 Hz, 1 H =C*H*CH$_2$), 4.27 (dd, ^3J = 4 Hz, ^4J = 2 Hz,2 H, C*H*$_2$OH).

^{13}C NMR: δ = 146.20 (Py$^+$ 4-C), 142.02 (Py$^+$ 2,6-C), 133.18 (=*C*H–Py$^+$), 129.95 (=*C*HCH$_2$), 127.98 (Py$^+$ 3,5-C), 58.36 (CH$_2$OH).

MS (EI): *m*/*z* (%) = 136 (8), 117 (7), 105 (6), 80 (29), 79 (100), 52 (21), 39 (7).

Anal. Calcd for $C_8H_{10}BrNO$: C, 44.47; H, 4.66; N, 6.48. Found C, 44.33; H 4.77; N 6.41.

1-[(*E*)-3-(Pyridinium-1-yl)prop-1-en-1-yl]pyridinium Dibromide (11)

Prepared by reacting pyridine (3.64 g, 3.7 mL, 46 mmol) and 1,2,3-tribromopropane (4.20 g, 2.65 mL, 15 mmol) as desribed for **10**. The product was treated with $HClO_4$ and further purified by recrystallization from MeCN to give pure **11** as sand-coloured crystals; yield: 2.47 g (46%); mp 218–219°C (dec.).

IR (KBr): ν = 1624 (C=N$^+$), 1680 (C=C).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.24–9.04 (m, 4 H, Py$^+$ 2,6-H), 8.71–8.44 (m, 2 H, Py$^+$ 4-H), 8.09 (br d t, 4 H, Py$^+$ 3,5-H), 7.96 (d, *J* = 14 Hz, 1 H, =C*H*–Py$^+$), 7.11 (dt, 1 H, ^3J = 14 Hz, ^4J = 6.5 Hz, 1 H =C*H*CH$_2$), 5.62 (d, ^3J = 6.5 Hz, 2 H, CH$_2$).

^{13}C NMR: δ = 147.57, 146.38 (Py$^+$ 4-C), 145.10, 142.51 (Py$^+$ 2,6-C), 136.39 (=*C*H–Py$^+$), 128.29, 128.07 (Py$^+$ 3,5-C), 124.38 (=*C*HCH$_2$), 58.46 (CH$_2$).

MS (EI): *m*/*z* (%) = 79 (100), 50 (25), 39 (8).

Anal. Calcd for $C_{13}H_{14}Br_2N_2$: C, 43.61; H, 3.94; N, 7.82. Found C, 43.53; H 4.05; N 7.79.

1-[2-(Pyridinium-1-yl)-1-ethenyl]pyridinium Dibromide (13)

A mixture of pyridine (1.3 mL, 16 mmol) and 1,1,2-tribromoethane (0.5 mL, 5 mmol) was heated at 70°C for 22 h. The mixture was left in the freezer overnight. The solid was filtered and recrystallized from EtOH to give **13** (550 mg, 32%) as lilac crystals; mp >250 °C (dec.).

IR (KBr): ν = 1625 cm^{-1} (C=N^+).

^{1}H NMR (90 MHz, CD_3OD): δ = 9.12 (d, *J* = 7 Hz, 4 H, Py^+ 2,6-H), 8.67 (t, *J* = 7 Hz, 2 H, Py^+ 4 H), 8.63 (s, 2 H, =CH), 8.14 (t, J = 7 Hz, 4 H, Py^+ 3,5-H).

^{13}C NMR: δ = 150.26 (Py^+ 4 C), 144.90 (Py^+ 2,6-C), 134.79 (=*C*H–Py^+), 129.89 (Py^+ 3,5-C).

MS (EI): *m*/*z* (%) = 181 (12), 154 (4), 82 (100), 79 (98), 52 (35), 39 (6).

Anal. Calcd for $C_{12}H_{12}Br_2N_2$: C, 41.89; H, 3.52; N, 8.14. Found C, 41.77; H 3.62; N 8.02.

4-[2-(2-Hydroxyphenyl)-1-ethenyl]-1-(1-phenylvinyl)pyridinium Bromide (14)

Piperidine (0.3 mL) was added to a solution of **3b** (2.3 g of the crude product) and 2-hydroxybenzaldehyde (0.74 g, 6 mmol) in anhyd EtOH (5 mL). The mixture was refluxed for 3 h. H_2O (30 mL) was added to the solution and was left overnight at r.t. The precipitate was filtered and was purified by crystallization from EtOH to give **14** (0.67 g, 35%) as yellow solid; mp 214–216 °C (dec.).

IR (KBr): ν = 1618 cm^{-1} (C=N^+).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.62 (d, *J* = 7 Hz, 2 H, Py^+ 2,6-H), 8.09 (d, *J* = 7 Hz,2 H, Py^+ 3,5-H), 7.98 – 6.56 (m, 9 H_{arom} and CH=CH), 6.16 (d, *J* = 3 Hz, 1 H, =CH *trans* to C_6H_5), 5.82 (d, *J* = 3 Hz,1 H, =CH *cis* to C_6H_5).

^{13}C NMR: δ = 157.31 (2-OHC_6H_4, 2-C), 155.48 (Py^+ 4-C), 147.68 (CH_2=*C*), 143.57 (Py^+ 2,6-C), 138.60 (C_6H_5, 1-C), 132.80 (=*C*HPhOH), 131.81 (2-OHC_6H_4, 1-C), 130.21 (2-OHC_6H_4, 4-C), 129.01 (C_6H_5, 4-C), 128.97 (C_6H_5, 3,5-C), 126.39 (C_6H_5, 2,6-C), 123.53 (Py^+ 3,5-C), 122.34 (2-OHC_6H_4, 6-C), 121.65 (=*C*H–Py), 119.24 (2-OHC_6H_4, 5-C), 116.40 (2-OHC_6H4, 3-C), 115.78 (C=*C*H_2).

MS (EI): *m*/*z* (%) = 299 (11), 195 (90), 167 (20), 103 (72), 93 (100), 77 (41), 65 (10), 51 (10), 39 (13).

Anal. Calcd for $C_{21}H_{18}BrNO$: C, 66.33; H, 4.77; N, 3.68. Found C, 66.20; H 4.88; N 3.56.

4-[2-(4-Dimethylaminophenyl)-1-phenyl-1-ethenyl]-1-(1-phenylvinyl)pyridinium Bromide (15)

Piperidine (0.3 mL) was added to a solution of **3d** (3.2 g of the crude product) and 4-dimethylaminobenzaldehyde (0.9 g, 6 mmol) in anhyd EtOH (5 mL). The mixture was refluxed for 4 h. H_2O (30 mL) was added to the mixture and left overnight at r.t. The precipitate was filtered, dried and washed with hot hexane (2 × 20 mL). The residue was extracted with benzene (3 × 20 mL). The precipitate which was formed after the addition of hexane (20 mL) to the benzene solution was collected by filtration and gave **15** (0.68 g, 28%) as metallic violet crystals; mp 155–160°C (dec.).

IR (KBr): ν = 1616 cm^{-1} (C=N^+).

^{1}H NMR (90 MHz, CD_3OD): δ = 8.31 (d, 2 H, *J* = 7 Hz, Py^+ 2,6-H), 7.89 (s, 1 H, C=C*H*), 7.70 (d, 2 H, *J* = 7 Hz, Py^+ 3,5-H), 7.58–6.24 (m, 14 H_{arom}), 5.91 (d, 1 H, *J* = 3 Hz, =CH *trans* to C_6H_5), 5.69 (d, 1 H, *J* = 3 Hz, =CH *cis* to C_6H_5), 2.82 (s, 6 H, CH_3).

^{13}C NMR: δ = 159.98 (C_{arom}), 158.12 (Py^+ 4-C), 151.13 (CH=*C*Ph), 147.53 (CH_2=*C*), 142.76 (Py^+ 2,6-C), 141.36, 137.42, 133.34, 129.94, 129.59, 128.96, 128.33, 126.36, 122.20, 111.05 (C_{arom}), 132.80 (=*C*HPh), 115.41 (C=*C*H_2), 39.92 (CH_3).

MS (EI): *m*/*z* (%) = 403 (1), 300 (83), 285 (61), 271 (40), 228 (18), 174 (82), 168 (73), 105 (100), 103 (81), 91 (43), 80 (40), 77 (99), 63 (23), 51 (63), 39 (20).

Anal. Calcd for $C_{29}H_{27}BrN_2$: C, 72.05; H, 5.63; N, 5.79. Found C, 71.88; H 5.79; N 5.60.

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Article Identifier:
1437-210X,E;1999,0,12,2131,2137,ftx,en;Z03099SS.pdf