

## CHAPTER 2

### EXPERIMENT

#### *2.1 Instruments and chemicals*

##### **2.1.1 Instruments**

Melting point was measured on an Electrothermal melting point apparatus. Ultraviolet (UV) absorption spectra were measured using a SPECORD S 100 (Analytikjena) spectrophotometer with methanol as solvent and principle bands ( $\lambda_{\max}$ ) were recorded as wavelengths (nm) and  $\log \epsilon$ . Infrared spectra were recorded on a FTS 165 FT-IR spectrophotometer (KBr pellets) and major bands ( $\nu$ ) were recorded in wave numbers ( $\text{cm}^{-1}$ ). Proton nuclear magnetic resonance spectra were recorded on FT-NMR Bruker Ultra Shield<sup>TM</sup> 300 MHz. Spectra were recorded as  $\delta$  value in ppm downfield from TMS (internal standard  $\delta$  0.00) and using deuteriochloroform mixed with hexadeutero-dimethyl sulphoxide as solvents. Single crystal X-ray diffraction measurements were collected using a Bruker Apex2 CCD diffractometer with a graphite monochromated Mo K $\alpha$  radiation at a detector distance of 5 cm and with APEX2 software. The collected data were reduced using *SAINTE* program, and the empirical absorption corrections were performed using *SADABS* program. The structures were solved by direct methods and refined by least-squares using the *SHELXTL* software package. The SHG measurements were done at Department of Studies in Physics, Mangalore University, Mangalagangothri, Mangalore, India. The SHG measurements were made in accordance with the classical powder method developed by Kurtz and Perry (1968) using DCR-11-type Nd: YAG laser with pulse energy of 8 mJ/pulse as a source. A fundamental wave with a pulse width of 8 ns, repetition frequency 10 Hz, and a wavelength 1064 nm was applied to the upgraded microcrystalline powder samples which were densely loaded in glass capillaries. The SHG wave generated from the samples was detected by a photomultiplier tube (Hamamatsu-R 2059) and converted into electrical signal.

The converted electrical signal was displayed on an oscilloscope (Tektronix-TDS 3000B) and the signal amplitude in volts indicates the SHG efficiency of the sample. Urea crystals ground into identical size were used as the reference material. The yields were reported as percentage of crude products.

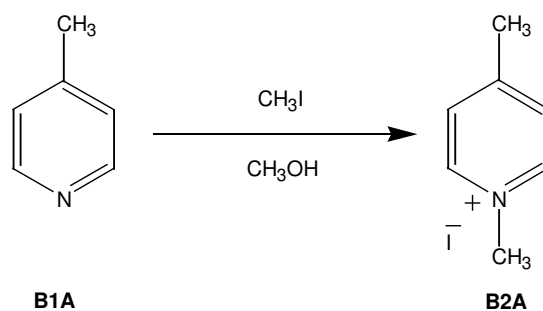
### 2.1.2 Chemicals

All chemicals used in this study are AR grade and used without further purification.

- 1) 4-Picoline from Fluka Chemica, Switzerland
- 2) 2-Methylquinoline from Fluka Chemica, Switzerland
- 3) 4-Hydroxy-3-methoxybenzaldehyde (vanillin) from Sigma Chemica, USA
- 4) 3-Hydroxy-4-methoxybenzaldehyde (isovanillin) from Sigma Chemica, USA
- 5) Piperidine from Fluka Chemica, Switzerland
- 6) *p*-Toluenesulfonic acid monohydrate from Fluka Chemica, Switzerland
- 7) 4-Methoxybenzenesulfonyl chloride from Fluka Chemica, Switzerland
- 8) 4-Chlorobenzenesulfonyl chloride from Fluka Chemica, Switzerland
- 9) 4-Bromobenzenesulfonyl chloride from Fluka Chemica, Switzerland
- 10) Silver nitrate from Merck, Germany
- 11) Methyl iodide from Riedel-de Haën, Germany
- 12) Sodium hydroxide from Lab-Scan, Ireland
- 13) Ethanol from Merck, Germany
- 14) Methanol from Merck, Germany
- 15) Dichloromethane from Merck, Germany
- 16) Diethyl ether from Merck, Germany

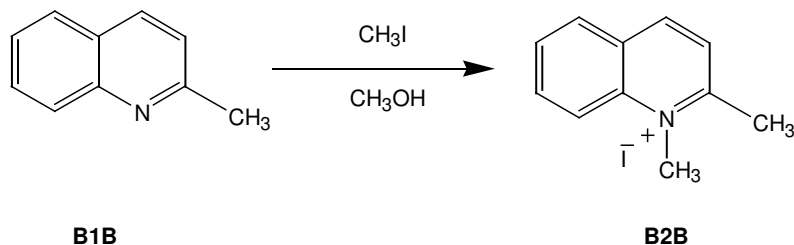
## 2.2 Synthesis of the starting materials

### 2.2.1 1,4-Dimethylpyridinium iodide (B2A)



Methyl iodide (6.45 ml, 0.10 mol) was added dropwise to a stirred solution of 4-picoline (**B1A**) (10.00 ml, 0.10 mol) in cold methanol (15 ml) at 7 °C under nitrogen atmosphere for 1 hr and then refluxing for 1 hr. The mixture was cooled in an ice bath and the obtained crystalline solid was filtered, washed with cold methanol and dried in vacuum to give a pale yellow solid of 1,4-dimethylpyridinium iodide (**B2A**) (15.50 g, 66%), mp. 140-142 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 219.7 (3.78), 255.3 (3.16), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 1600-1500 (C=C stretching), <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-*d*<sub>6</sub>) ( $\delta$  ppm) (300 MHz): 9.13 (2H, *d*, *J* = 6.3 Hz), 7.88 (2H, *d*, *J* = 6.3 Hz), 4.62 (3H, *s*), 2.69 (3H, *s*).

### 2.2.2 1,2-Dimethylquinolinium iodide (B2B)

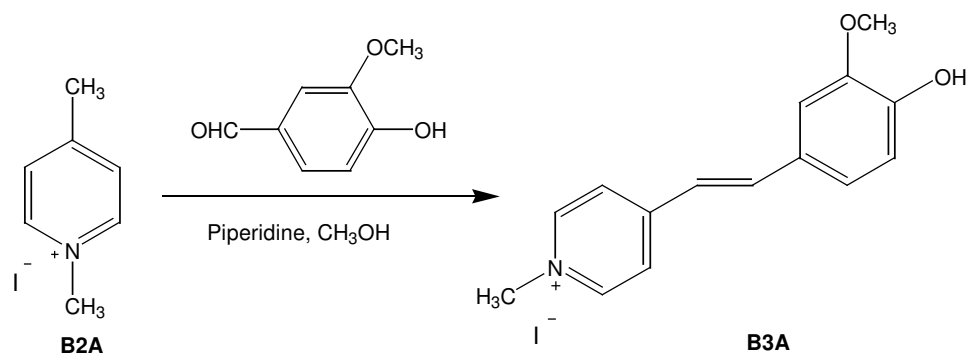


1,2-dimethylquinolinium iodide (**B2B**) was prepared to be employed as starting material for the syntheses of related products. Methyl iodide (4.65 ml, 0.07 mol) was added dropwise to a stirred solution of 2-methylquinoline (quinaldine, **B1B**)

(10.00 ml, 0.07 mol) in cold methanol (15 ml) at 7 °C under nitrogen atmosphere for 1 hr and then refluxing for an additional 2 hrs. The mixture was cooled and the precipitated solid was filtered, washed with cold methanol and dried to give yellow solid of **(B2B)** (14.00 g, 66%), mp. 182-184 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log  $\epsilon$ ): 234.5 (3.47), 316.7 (2.90); FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 1600-1500 (C=C stretching), <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-*d*<sub>6</sub>) ( $\delta$  ppm) (300 MHz): 9.07 (1H, *d*, *J* = 8.7 Hz), 8.55 (1H, *d*, *J* = 8.1 Hz), 8.39 (1H, *dd*, *J* = 1.5, 8.1 Hz), 8.23 (1H, *dt*, *J* = 1.5, 8.1 Hz), 8.09 (1H, *d*, *J* = 8.7 Hz), 7.98 (1H, *t*, *J* = 8.1 Hz), 4.57 (3H, *s*), 3.20 (3H, *s*).

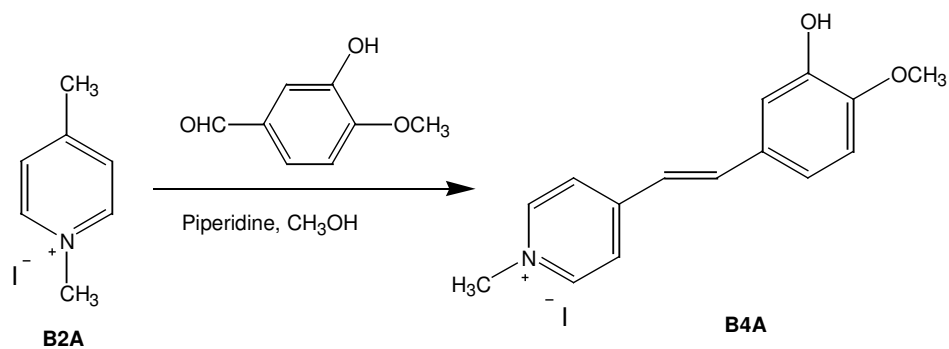
### 2.3 Synthesis of the cations part

#### 2.3.1 4-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (**B3A**)



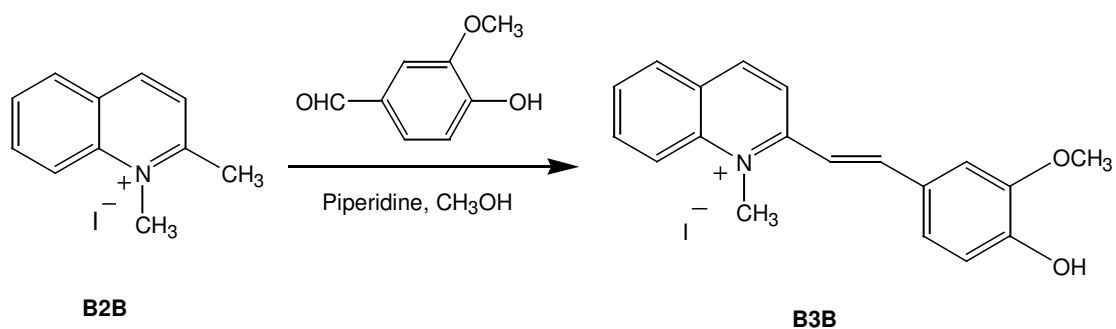
The mixture of 1,4-dimethylpyridinium iodide (3.00 g, 12.80 mmol), vanillin (1.95 g, 12.82 mmol) and piperidine (1.25 ml, 12.65 mmol) in methanol was refluxed under nitrogen atmosphere for 2 hrs. The solid formed was filtered off, washed with diethyl ether and re-crystallized from methanol to give dark brown crystals of 4-[(*E*)-2-(4-hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (**B3A**) (3.52 g, 75%), mp. 267-268 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log  $\epsilon$ ): 212.6 (4.12), 261.7 (3.69), 407.1 (4.16), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3440 (O-H stretching), 1645, 1590 (C=C stretching), 1245 (C-O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 1**).

### 2.3.2 4-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (**B4A**)



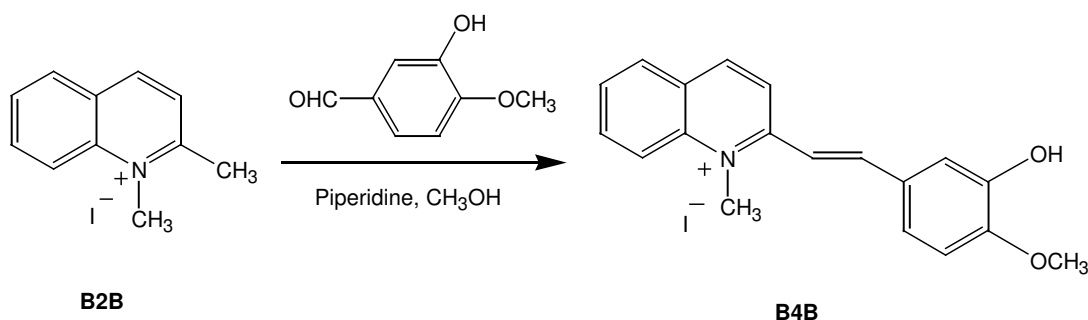
A solution of isovanillin (1.96 g, 12.86 mmol) in methanol (10 ml) was added to a stirred solution of 1,4-dimethylpyridinium iodide (**B2A**) (2.98 g, 12.68 mmol) in methanol (10 ml) in the presence of piperidine (1.25 ml, 12.65 mmol). The mixture was refluxed for 3 hrs under nitrogen atmosphere. The solid formed was filtered, washed with diethyl ether and crystallized from methanol to give brown crystals of **B4A** (3.99 g, 85%), mp. 230-231 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 214.4 (4.08), 260.7 (3.57), 275.6 (3.55), 400.7 (4.11), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3372 (O-H stretching), 1646, 1600 (C=C stretching), 1235 (C-O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 2**).

### 2.3.3 2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (**B3B**)



2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (**B3B**) was prepared to be employed as cationic part by refluxing a stirred solution of 1,2-dimethylquinolinium iodide (2.98 g, 10.05 mmol), vanillin (1.60 g, 10.05 mmol) and piperidine (1.00 ml, 10.00 mmol) in methanol (25 ml) for 3 hrs under nitrogen atmosphere. The solid was filtered, washed with diethyl ether and crystallized from methanol to give dark red crystals of **B3B** (3.00 g, 68%), mp. 248-250 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 215.3 (3.59), 308.9 (3.02), 440.1 (3.54), 576.5 (3.19), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3439 (O-H stretching), 1609, 1580 (C=C stretching), 1233 (C-O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 3**).

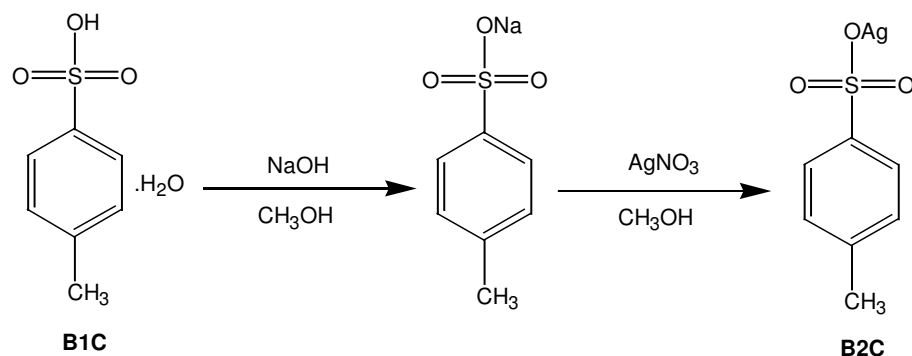
### 2.3.4 2-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (**B4B**)



2-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (**B4B**) was prepared by condensation of 1,2-dimethylquinolinium iodide (**B2B**) (3.00 g, 10.05 mmol) and isovanillin (1.60 g, 10.05 mmol) in the presence of piperidine (1.00 ml, 10.00 mmol) as a catalyst. The reaction mixture was refluxed for 2 hrs under nitrogen atmosphere. The solid formed was filtered, washed with diethyl ether and recrystallized from methanol to give red-brown crystals of **B4B** (2.80 g, 64%), mp. 218-220 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 216.1 (4.12), 306.2 (3.59), 431.3 (4.06), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3424 (O-H stretching), 1612, 1583 (C=C stretching), 1235 (C-O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° ( see **Table 4**).

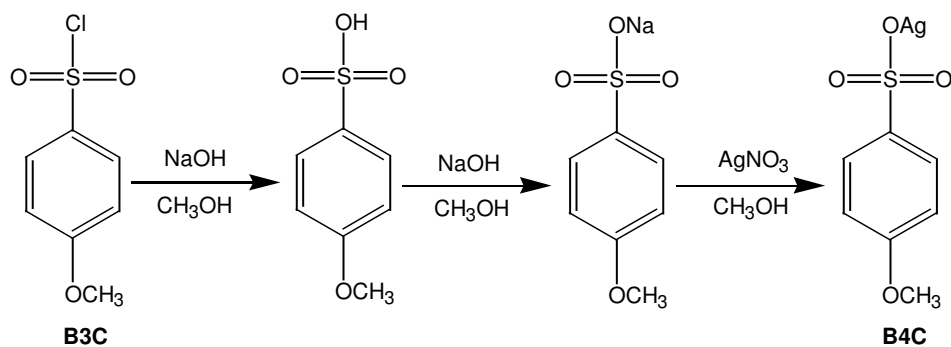
## 2.4 Synthesis of the anions counter part

### 2.4.1 Silver (I) 4-methylbenzenesulfonate (B2C)



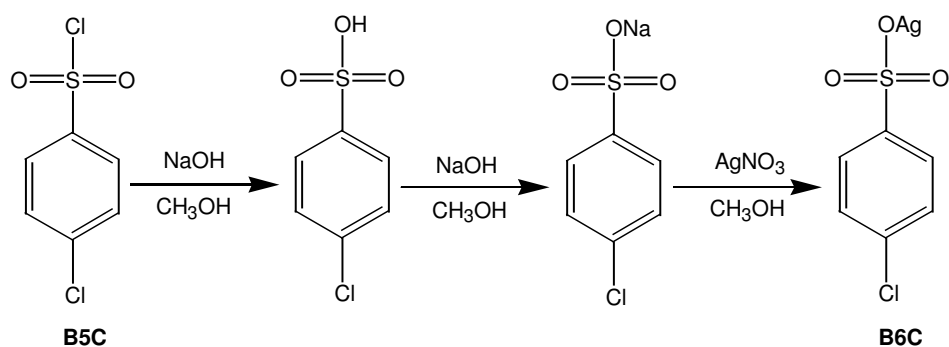
A solution of 4-methylbenzenesulfonic acid monohydrate (**B1C**) (5.00 g, 26.30 mmol) in hot methanol was added to a stirred solution of sodium hydroxide (1.05 g, 26.30 mmol) in hot methanol, followed by addition of a solution of silver nitrate (4.47 g, 26.30 mmol) in hot methanol. A solution mixed with a solid was obtained which was filtered. The white crystalline solid of **B2C** (5.20 g, 71%) was collected after allowing the filtrate to stand in air for a few days, mp. 264-266 °C (decomp.), <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-*d*<sub>6</sub>) ( $\delta$  ppm) (300 MHz): 7.74 (2H, *d*, *J* = 8.1 Hz), 7.17 (2H, *d*, *J* = 8.1 Hz), 2.38 (1H, *s*).

### 2.4.2 Silver (I) 4-methoxybenzenesulfonate (B4C)



Silver (I) 4-methoxybenzenesulfonate (**B4C**) was prepared by mixing a solution of 4-methoxybenzenesulfonyl chloride (**B3C**) (5.00 g, 24.20 mmol) and sodium hydroxide (0.97 g, 24.25 mmol) in hot methanol. A colorless solution mixed with a white solid of sodium chloride was obtained. The mixture was worked up by addition of water and extraction with dichloromethane. The dichloromethane part was evaporated and the resulting residue was dissolved in methanol, followed by addition of the solution of sodium hydroxide (0.96 g, 24.00 mmol) in hot methanol and a solution of silver nitrate (4.10 g, 24.14 mmol) in hot methanol. The colorless solution mixed with a solid of sodium nitrate was obtained, which was filtered and discarded. Compound **B4C** (4.53 g, 63%) was obtained after allowing the resulting filtrate to stand in air for a few days, mp. 240-242 °C (decomp.),  $^1\text{H NMR}$  ( $\text{CDCl}_3 + \text{DMSO-}d_6$ ) ( $\delta$  ppm) (300 MHz): 7.78 (2H, *d*,  $J = 8.7$ ), 6.86 (2H, *d*,  $J = 8.7$  Hz), 3.82 (1H, *s*).

### 2.4.3 Silver (I) 4-chlorobenzenesulfonate (**B6C**)

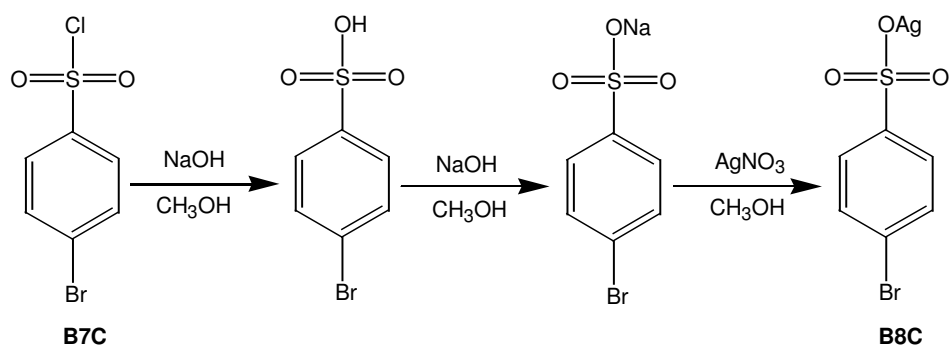


Silver (I) 4-chlorobenzenesulfonate (**B6C**) was prepared to be employed as anionic part by mixing a solution (1:1 molar ratio) of 4-chlorobenzenesulfonyl chloride (**B5C**) (5.00 g, 19.57 mmol) and sodium hydroxide (0.78 g, 19.57 mmol) in hot methanol. A colorless solution mixed with a white solid of sodium chloride was obtained. The mixture was worked up by addition of water and extraction with dichloromethane. The dichloromethane part was evaporated and dissolved in methanol, followed by addition of the solution of sodium hydroxide



(0.77 g, 19.32 mmol) in hot methanol and a solution of silver nitrate (3.32 g, 19.57 mmol) in hot methanol. The colorless solution mixed with a solid of sodium nitrate was obtained, which was filtered and discarded. Compound **B4C** (4.56 g, 68%) was obtained after allowing the resulting filtrate to stand in air for a few days, mp. 227-229 °C (decomp.),  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-}d_6$ ) ( $\delta$  ppm) (300 MHz): 7.76 (2H, *d*,  $J = 7.8$  Hz), 7.50 (2H, *d*,  $J = 7.8$  Hz).

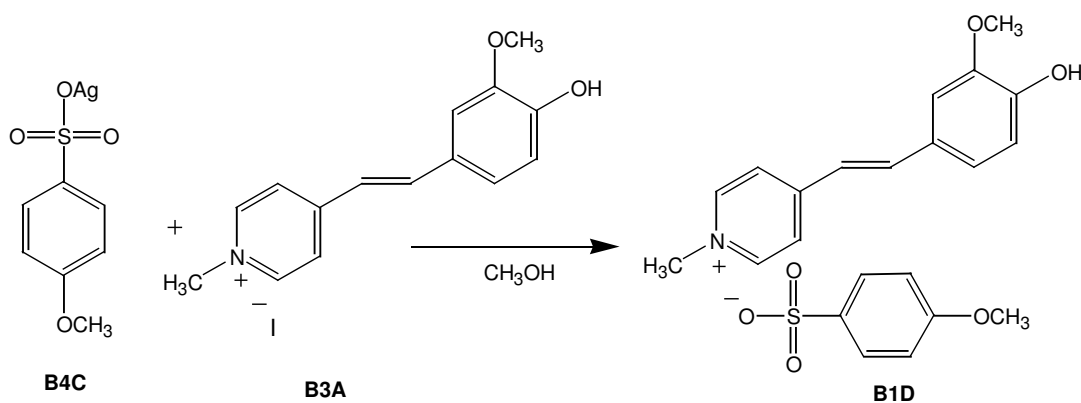
#### 2.4.4 Silver (I) 4-bromobenzenesulfonate (**B8C**)



Silver (I) 4-bromobenzenesulfonate (**B8C**) was synthesized by mixing a solution of 4-bromobenzenesulfonyl chloride (**B7C**) (5.00 g, 23.69 mmol) and sodium hydroxide (0.95 g, 23.69 mmol) in hot methanol. A colorless solution mixed with a white solid of sodium chloride was obtained. The mixture was worked up by addition of water and extraction with dichloromethane. The dichloromethane part was evaporated and dissolved in methanol, followed by addition of the solution of sodium hydroxide (0.96 g, 23.64 mmol) in hot methanol and a solution of silver nitrate (4.00 g, 23.57 mmol) in hot methanol. The colorless solution mixed with a solid of sodium nitrate was obtained, which was filtered and discarded. Compound **B4C** (4.36 g, 61%) was obtained after allowing the resulting filtrate to stand in air for a few days, mp. 230-232 °C decomposed,  $^1\text{H}$  NMR ( $\text{CDCl}_3 + \text{DMSO-}d_6$ ) ( $\delta$  ppm) (300 MHz): 7.81 (2H, *d*,  $J = 8.4$ ), 7.34 (2H, *d*,  $J = 8.4$  Hz).

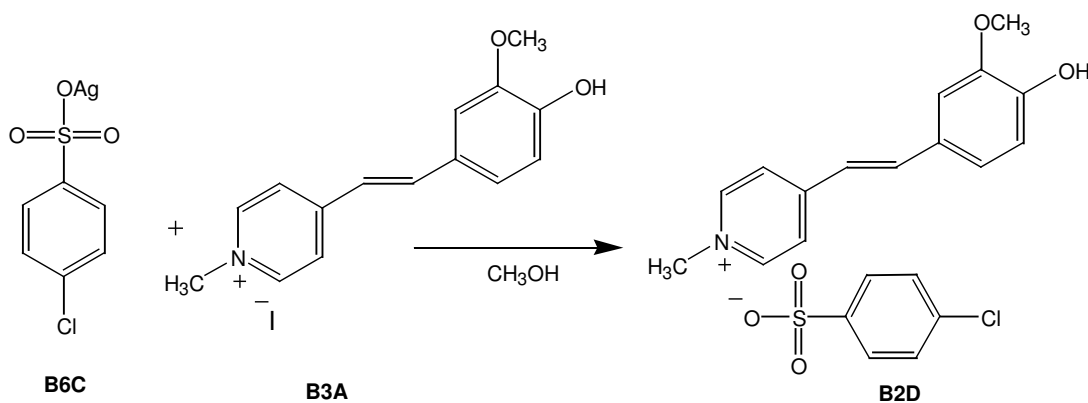
## 2.5 Salt formation

### 2.5.1 4-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methoxybenzenesulfonate (**B1D**)



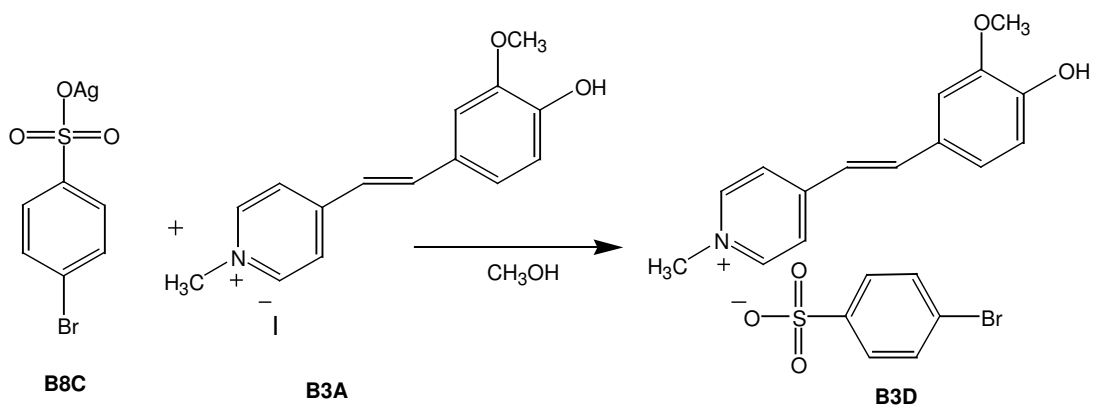
4-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methoxybenzenesulfonate (**B1D**) was synthesized by addition of a solution of silver (I) 4-methoxybenzenesulfonate (0.20 g, 0.68 mmol) in hot methanol (35 ml) to a solution of compound **B3A** (0.25 g, 0.68 mmol) in hot methanol (45 ml). Upon addition a yellow solid of silver iodide was immediately formed which was removed by filtration and the yellow filtrate was evaporated under reduced pressure to yield a yellow solid (0.25 g, 86%). The yellow solid was recrystallized from methanol to give yellow crystals of compound **B1D**, mp. 257-258 °C, UV-Vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ ): 219.6 (4.04), 262.5 (3.58), 406.0 (3.99), FT-IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3431 (O-H stretching), 1645, 1587 (C=C stretching), 1233 (C-O stretching), 1185 (S=O stretching),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT 135° (see **Table 5**).

### 2.5.2 4-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium 4-chlorobenzenesulfonate (**B2D**)



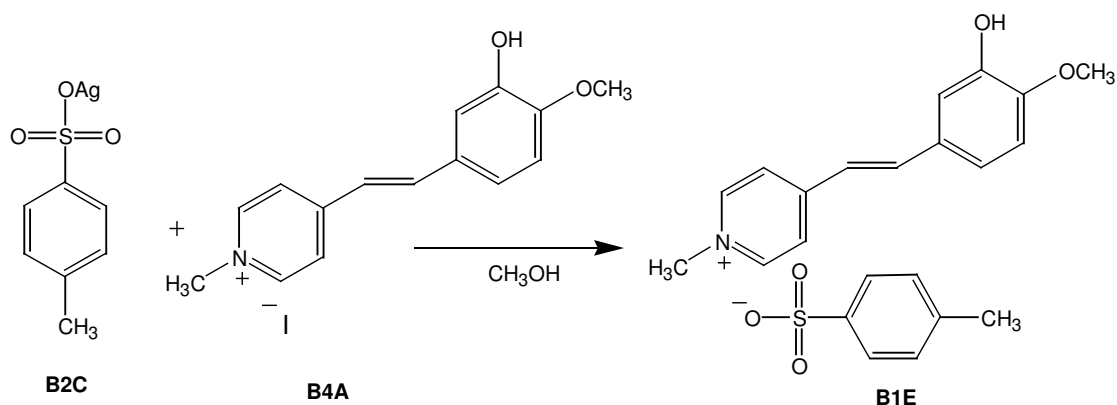
A solution of **B3A** (0.25 g, 0.67 mmol) in hot methanol (50 ml) was added dropwise to a stirred solution of 4-chlorobenzenesulfonate (**B6C**) (0.20 g, 0.67 mmol) in hot methanol (55 ml). The mixture turned yellow and cloudy immediately. After stirring for 0.5 hr, the precipitate of silver iodide was filtered off and the filtrate was evaporated to give a yellow solid of compound **B2D** (0.27 g, 93%). Brown single crystals suitable for X-ray analysis of **B2D** were obtained after crystallization from methanol at room temperature for several days (mp. 232-233 °C), UV-Vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ ): 206.2 (3.36), 260.8 (2.81), 405.7 (3.30), FT-IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3431 (O-H stretching), 1642, 1587 (C=C stretching), 1233 (C-O stretching), 1177 (S=O stretching),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT 135° (see **Table 6**).

### 2.5.3 4-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium 4-bromobenzenesulfonate (**B3D**)



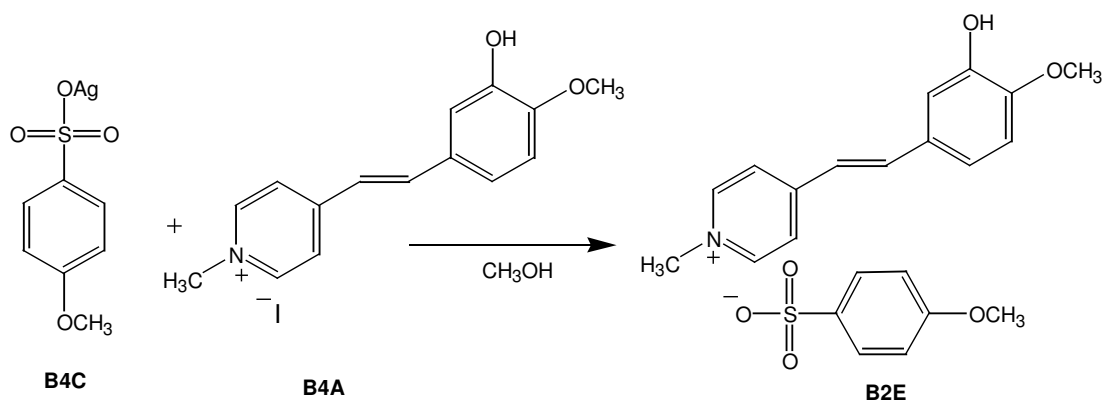
The 4-[(*E*)-2-(4-hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (**B3A**) (0.22 g, 0.59 mmol) was dissolved in 40 ml methanol, upon heating was added a solution of silver (I) 4-bromobenzenesulfonate (**B8C**) (0.20 g, 0.59 mmol) in hot methanol (50 ml). The mixture yielded a yellow solid of silver iodide immediately. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting red solution was evaporated to yield a red solid (0.25 g, 90%). The red solid was dissolved in methanol and ethanol (1:1) to give red single crystals of **B3D**, after allowing the resulting solution to stand in ambient temperature for several days (mp. 242-243°C), UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 208.3 (4.04), 262.5 (3.64), 406.8 (4.12), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3428 (O-H stretching), 1643, 1588 (C=C stretching), 1221 (C-O stretching), 1185 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 9**).

### 2.5.4 4-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methylbenzenesulfonate (**B1E**)



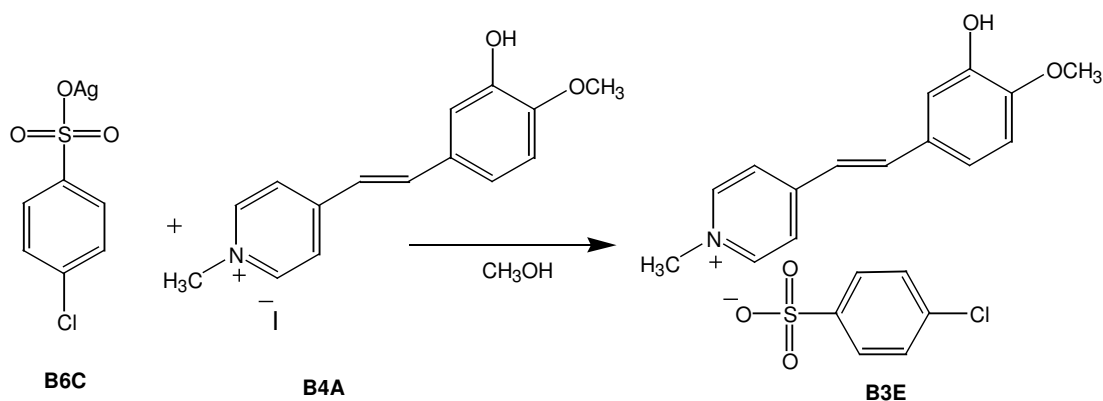
A 0.26 g (0.70 mmol) solution of 4-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (**B4A**) in hot methanol (50 ml) was mixed with 0.20 g (0.72 mmol) of silver (I) 4-methylbenzenesulfonate (**B2C**) in hot methanol (25 ml). The mixture turned yellow and cloudy immediately. After stirring for 25 min, the precipitate of silver iodide was filtered and the filtrate was evaporated to give a yellow solid of 4-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methylbenzenesulfonate (**B1E**) (0.27 g, 91%). The yellow product was recrystallized in methanol to give yellow crystal of **B1E**: mp. 118-120 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log  $\epsilon$ ): 212.6 (4.04), 259.0 (3.55), 399.8 (4.07), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3428 (O-H stretching), 1640, 1599 (C=C stretching), 1220 (C-O stretching), 1193 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 12**).

**2.5.5 4-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methoxybenzenesulfonate (B2E)**



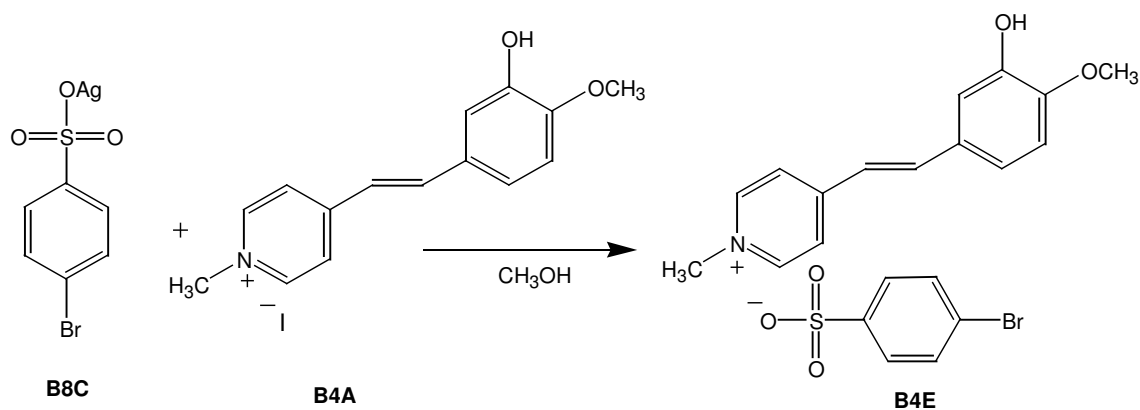
4-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methoxybenzenesulfonate (**B2E**) was synthesized by addition of a solution of silver (I) 4-methoxybenzenesulfonate (0.20 g, 0.68 mmol) in hot methanol (25 ml) to a solution of compound **B4A** (0.25 g, 0.68 mmol) in hot methanol (60 ml). Upon addition, a yellow solid of silver iodide was immediately formed which was removed by filtration and the yellow filtrate was evaporated under reduced pressure to yield a yellow solid (0.28 g, 95%). The yellow solid was recrystallized in methanol to give yellow crystal of compound **B2E**, mp. 114-116 °C, UV-Vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ ): 223.3 (4.24), 269.5 (3.66), 401.2 (4.10), FT-IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3437 (O-H stretching), 1633, 1598 (C=C stretching), 1221 (C-O stretching), 1188 (S=O stretching),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT 135° (see **Table 13**).

### 2.5.6 4-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium 4-chlorobenzenesulfonate (**B3E**)



**B3E** was synthesized by a simple method. A solution of **B4A** (0.24 g, 0.65 mmol) in hot methanol (60 ml) was added dropwise to a stirred solution of 4-chlorobenzenesulfonate (**B6C**) (0.19 g, 0.65 mmol) in hot methanol (45 ml). The mixture turned yellow and cloudy immediately. After stirring for 0.5 hr, the precipitate of silver iodide was filtered off and the filtrate was evaporated to give a yellow solid of compound **B3E** (0.25 g, 88%). The yellow solid was recrystallized in methanol to give yellow crystal of compound **B3E**, mp. 189-190 °C, UV-Vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ ): 210.0 (4.35), 260.8 (3.74), 273.9 (3.70), 400.7 (4.22), FT-IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3439 (O-H stretching), 1642, 1613 (C=C stretching), 1229 (C-O stretching), 1182 (S=O stretching),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT 135° (see **Table 14**).

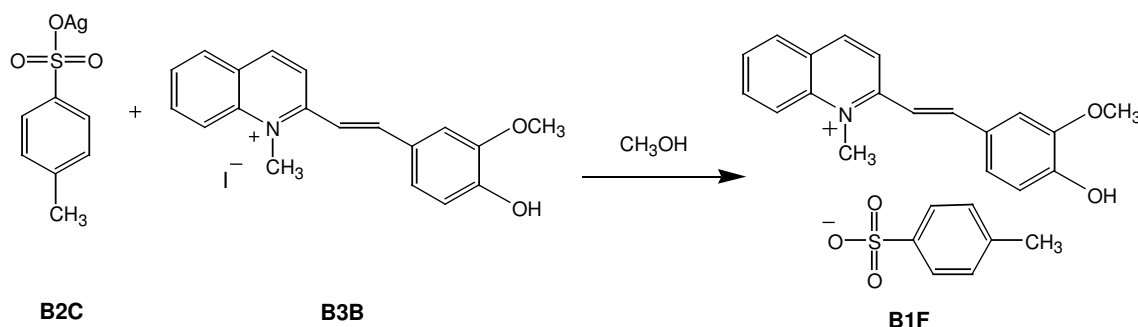
### 2.5.7 4-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium 4-bromobenzenesulfonate (**B4E**)



The 4-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (**B4A**) (0.21 g, 0.58 mmol) was dissolved in 45 ml of methanol, upon heating was added a solution of silver (I) 4-bromobenzenesulfonate (**B8C**) (0.20 g, 0.58 mmol) in hot methanol (40 ml). The mixture yielded a yellow solid of silver iodide immediately. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting red solution was evaporated to yield a red solid (0.27 g, 94%). The red solid was dissolved in methanol and ethanol (1:1) to give yellow single crystals of **B4E**, after allowing the resulting solution to stand in ambient temperature for several days (mp. 238-239°C), UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log $\epsilon$ ): 212.7 (4.08), 259.9 (3.62), 373.9 (3.60), 399.8 (4.15), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3340 (O-H stretching), 1612, 1591 (C=C stretching), 1237 (C-O stretching), 1189 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 15**).

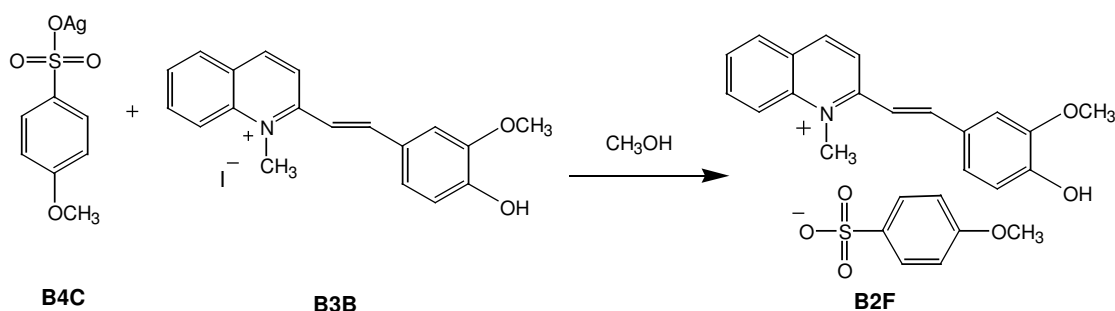


### 2.5.8 2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methylbenzenesulfonate (**B1F**)



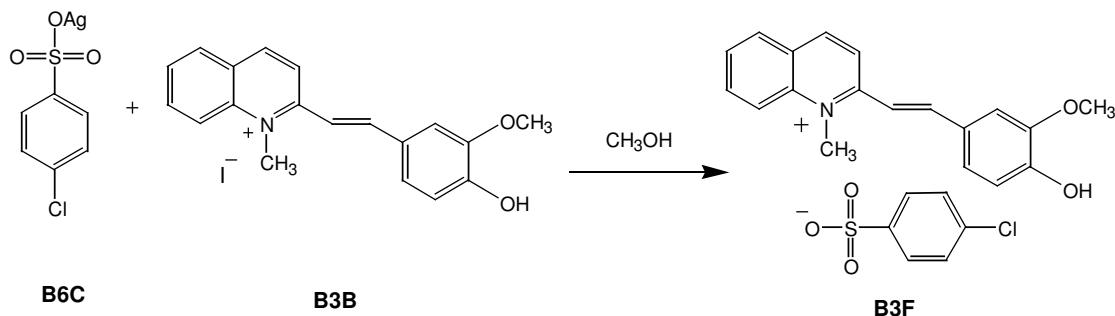
A 0.30 g (0.72 mmol) solution of 2-[(*E*)-2-(4-hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium iodide in hot methanol (150 ml) was mixed with 0.20 g (0.72 mmol) of silver (I) 4-methylbenzenesulfonate in hot methanol (30 ml). The mixture turned dark-red and cloudy immediately. After stirring for 30 min, the precipitate of silver iodide was filtered and the filtrate was evaporated to give a brown solid (0.31 g, 92%). Brown single crystals of **B1F** suitable for X-ray data collection were obtained after recrystallization from methanol after several days at ambient temperature (mp. 263-265 °C), UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 217.0 (4.21), 249.4 (3.82), 308.0 (3.70), 440.9 (4.21), 574.8 (3.59), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3430 (O-H stretching), 1600, 1579 (C=C stretching), 1219 (C-O stretching), 1190 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 18**).

### 2.5.9 2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (**B2F**)



2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (**B2F**), was synthesized by addition of a solution of silver (I) 4-methoxybenzenesulfonate (0.20 g, 0.68 mmol) in hot methanol (35 ml) to a solution of compound **B3B** (0.28 g, 0.67 mmol) in hot methanol (165 ml). Upon addition a yellow solid of silver iodide was immediately formed which was removed by filtration and the red filtrate was evaporated under reduced pressure to yield a brown solid (0.28 g, 85%). The brown solid was recrystallized in methanol to give brown single crystal of compound **B2F**, mp. 257-259 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log  $\epsilon$ ): 224.9 (4.33), 254.6 (3.98), 308.0 (3.86), 440.9 (4.37), 574.8 (3.74), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3432 (O-H stretching), 1600, 1581 (C=C stretching), 1220 (C-O stretching), 1189 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 21**).

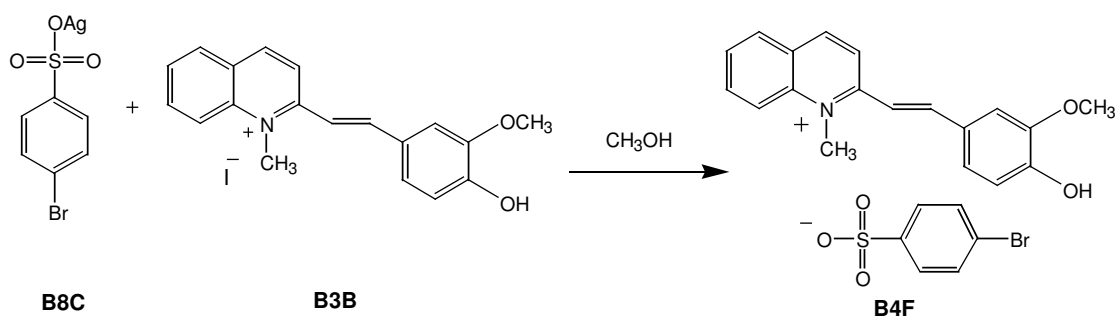
#### 2.5.10 2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (**B3F**)



**B3F** was synthesized by a simple method. A solution of **B3B** (0.28 g, 0.67mmol) in hot methanol (155 ml) was added dropwise to a stirred solution of 4-chlorobenzenesulfonate (**B6C**) (0.21 g, 0.68 mmol) in hot methanol (50 ml). The mixture turned red and cloudy immediately. After stirring for 0.5 hr, the precipitate of silver iodide was filtered off and the filtrate was evaporated to give a brown solid (0.28 g, 87%) which was further recrystallized in methanol to give orange crystals of 2-[(*E*)-2-(4-hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (**B3F**): mp. 262-264 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log  $\epsilon$ ): 220.5 (4.32), 252.9 (3.90), 310.6 (3.76), 440.1 (4.26), 574.8 (3.94), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>):

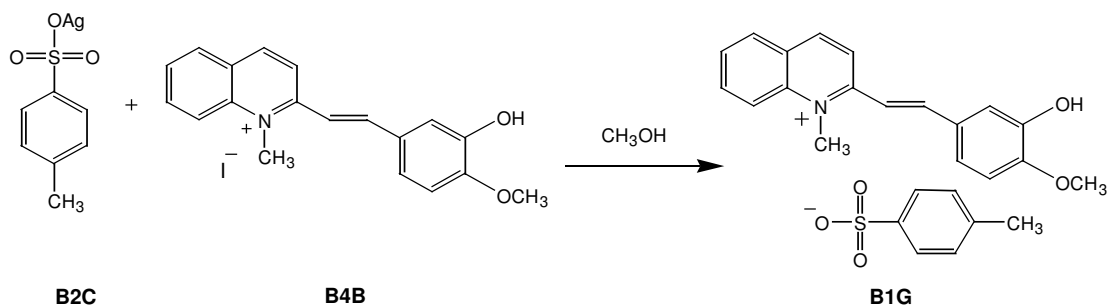
3432 (O-H stretching), 1608, 1584 (C=C stretching), 1240 (C-O stretching), 1189 (S=O stretching),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT 135° (see **Table 24**).

### 2.5.11 2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium 4-bromobenzenesulfonate (**B4F**)



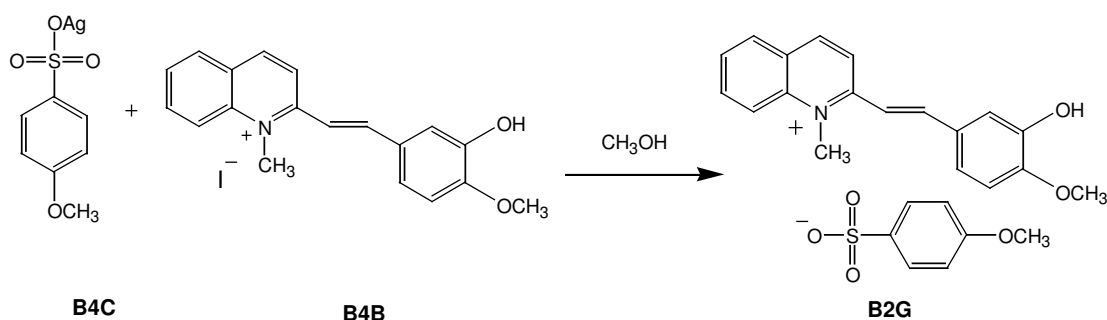
The 2-[(*E*)-2-(4-hydroxy-3-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (**B3B**) (0.25 g, 0.58 mmol) was dissolved in 165 ml methanol, upon heating was added a solution of silver (I) 4-bromobenzenesulfonate (**B8C**) (0.20 g, 0.58 mmol) in hot methanol (45 ml). The mixture yielded a yellow solid of silver iodide immediately. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated to yield a dark-red solid (0.28 g, 89%). The dark-red solid was dissolved in methanol to give red single crystals of **B4F**, after allowing the resulting solution to stand in ambient temperature for several days (mp. 288-290°C), UV-Vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon$ ): 220.5 (4.24), 252.9 (3.86), 309.0 (3.74), 440.4 (4.23), 574.4 (3.65), FT-IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3436 (O-H stretching), 1608, 1584 (C=C stretching), 1240 (C-O stretching), 1189 (S=O stretching),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT 135° (see **Table 27**).

### 2.5.12 2-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methylbenzenesulfonate (**B1G**)



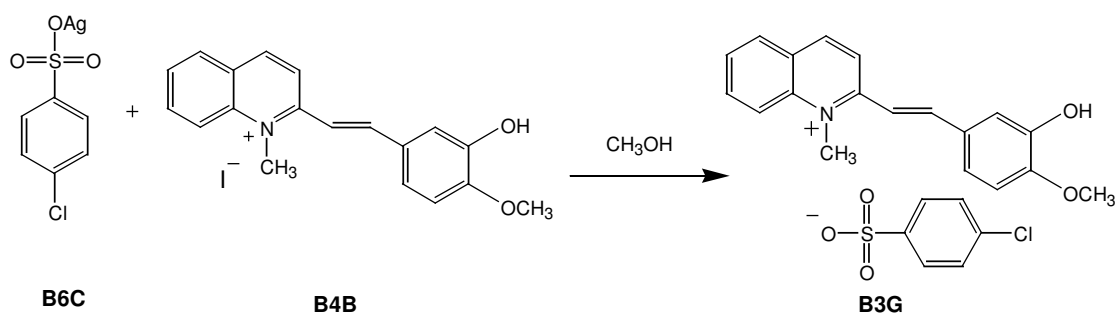
A 0.30 g (0.72 mmol) solution of 2-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium iodide in hot methanol (50 ml) was mixed with 0.20 g (0.72 mmol) of silver (I) 4-methylbenzenesulfonate in hot methanol (30 ml). The mixture turned orange and cloudy immediately. After stirring for 45 min, the precipitate of silver iodide was filtered and the filtrate was evaporated to give an orange solid (0.32 g, 95%). Colorless single crystals of **B1G** suitable for X-ray data collection were obtained by recrystallization in methanol and dichloromethane (1:1) after several days at ambient temperature (mp. 253-255 °C), UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 216.1 (4.18), 252.1 (3.81), 306.4 (3.70), 431.6 (4.17), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3430 (O-H stretching), 1606, 1594 (C=C stretching), 1229 (C-O stretching), 1176 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 30**).

### 2.5.13 2-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (**B2G**)



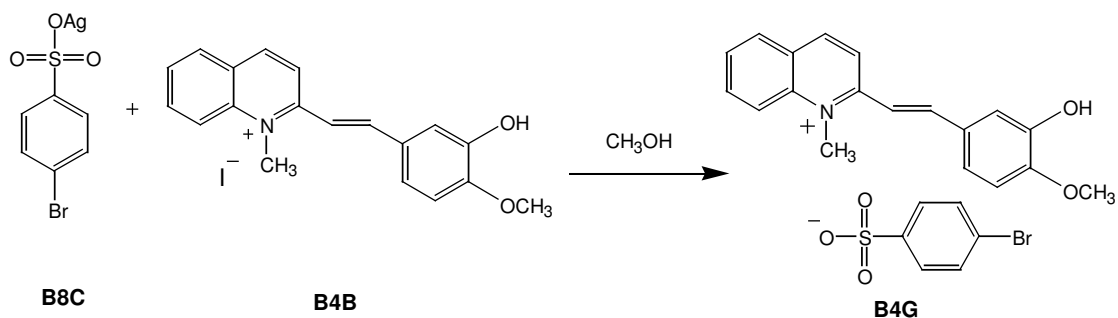
2-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (**B2G**), was synthesized by addition of a solution of silver (I) 4-methoxybenzenesulfonate (0.20 g, 0.68 mmol) in hot methanol (40 ml) to a solution of compound **B4B** (0.29 g, 0.69 mmol) in hot methanol (55 ml). Upon addition a yellow solid of silver iodide was immediately formed which was removed by filtration and the filtrate was evaporated under reduced pressure to yield an orange powder (0.27 g, 82%), mp. 223-225 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log  $\epsilon$ ): 218.8 (4.00), 251.1 (3.60), 306.2 (3.49), 431.3 (3.96), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3436 (O-H stretching), 1600, 1588 (C=C stretching), 1240 (C-O stretching), 1173 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 33**).

#### 2.5.14 2-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (**B3G**)



**B3G** was synthesized by a simple method. A solution of **B4B** (0.28 g, 0.67 mmol) in hot methanol (45 ml) was added dropwise to a stirred solution of 4-chlorobenzenesulfonate (**B6C**) (0.20 g, 0.67 mmol) in hot methanol (50 ml). The mixture turned orange and cloudy immediately. After stirring for 0.5 hr, the precipitate of silver iodide was filtered off and the filtrate was evaporated to give orange solids (0.29 g, 90%) which was further recrystallized in methanol to give orange single crystals of 2-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (**B3G**): mp. 262-264 °C, UV-Vis (CH<sub>3</sub>OH)  $\lambda_{\max}$  (nm) (log  $\epsilon$ ): 223.1 (4.04), 253.8 (3.70), 306.2 (3.58), 430.4 (4.06), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3432 (O-H stretching), 1600, 1592 (C=C stretching), 1236 (C-O stretching), 1189 (S=O stretching), <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT 135° (see **Table 34**).

**2.5.15 2-[(*E*)-2-(3-Hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium 4-bromobenzenesulfonate (B4G)**



The 2-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (**B4B**) (0.24 g, 0.58 mmol) was dissolved in 45 ml methanol, upon heating was added a solution of silver (I) 4-bromobenzenesulfonate (**B8C**) (0.21 g, 0.61 mmol) in hot methanol (45 ml). The mixture yielded a yellow solid of silver iodide immediately. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated to yield an orange solid (0.30 g, 92%): mp. 263-265°C), UV-Vis ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm) (log  $\epsilon$ ): 218.8 (4.15), 255.5 (3.75), 305.4 (3.65), 431.3 (4.12), FT-IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3421 (O-H stretching), 1600, 1595 (C=C stretching), 1237 (C-O stretching), 1190 (S=O stretching),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT 135° (see **Table 35**).