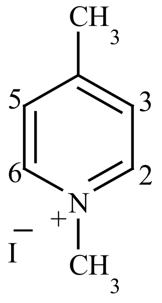
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Structural elucidation of the starting materials

3.1.1 1,4-Dimethylpyridinium iodide (B2A)

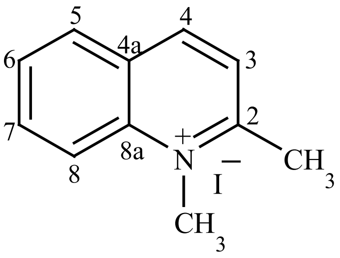


B2A

A pale yellow solid of **B2A** was received in 66% yield, mp. 140-142 °C. The UV-Vis absorption spectra (**Fig. 25**) exhibited maximum bands at 219.7 and 255.3 nm. The FT-IR spectrum (**Fig. 26**) revealed the presence of stretching vibration of C=C in aromatic ring at 1600-1500 cm^{-1}.

The ^{1}H NMR spectrum (**Fig. 27**) showed two *doublet* signals of equivalent protons H-2, H-6 and H-3, H-5 at δ9.09 (2H, J = 6.6 Hz) and δ7.92 (2H, J = 6.6 Hz) respectively. Two *singlet* signals of *N*-CH_3 and 4-CH_3 appeared at δ4.55 and δ 2.71 respectively. The possible structure of a pale yellow solid was 1,4-dimethylpyridinium iodide **(B2A)**.

3.1.2 1,2-Dimethylquinolinium iodide (B2B)



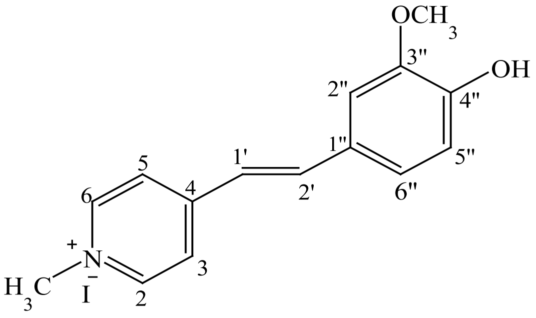
B2B

A yellow solid of B2B was obtained in 66% yield, mp. 172-174 °C. The UV-Vis absorption spectra (**Fig. 28**) showed maximum bands at 204.8, 234.5 and 316.7 nm. The FT-IR spectrum (**Fig. 29**) exhibited stretching vibration of C=C in aromatic ring at 1600-1500 cm^{-1}.

The ^1H NMR spectrum was shown in **Fig. 30**. The peak assigned to *N*-CH_3 and 2-CH_3 protons appeared at δ 4.57 (3H, *s*) and δ 3.20 (3H, *s*) respectively. Two *doublet* signals at δ 9.07 (1H, J = 8.7 Hz) and δ 8.09 (1H, J = 8.7 Hz) were assigned to H-4 and H-3 respectively. ^1H NMR spectrum also showed the signals of aromatic protons H-5 (δ 8.39), H-6 (δ 7.98), H-7 (δ 8.23) and H-8 (δ 8.55). From the above spectral data, the possible structure should be 1,2-dimethylquinolinium iodide.

3.2 Structural elucidation of the cation parts

3.2.1 4-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (B3A)



B3A

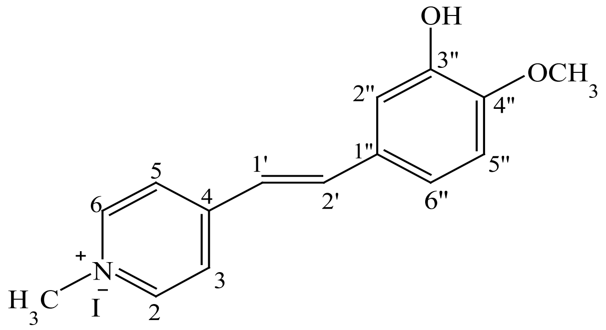
The dark brown crystal of **B3A** was prepared, mp. 267-268 °C. The UV-Vis spectrum (**Fig. 31**) showed absorption maxima at 212.6, 261.7 and 407.1 nm. The O-H stretching was observed in the FT-IR spectrum (**Fig. 32**) at 3440 cm^{-1}. The C=C stretching vibrations appeared at 1645 and 1590 cm^{-1}. Furthermore, the C-O stretching vibration was observed at 1245 cm^{-1}.

The ^{1}H NMR spectrum (**Fig. 33,** see **Table 1**) consisted of three *singlet* signals of 4-OH, *N*-CH_3 and *O*-CH_3 protons at δ 9.71 (1H), δ 4.29 (3H) and δ 3.91 (3H) respectively. Two *doublets* of H-1′ (δ 7.28, J = 16.2 Hz) and H-2′ (δ 7.87, J = 16.2 Hz) were assigned to be *trans*-disubstituted double bonds and two *doublets* at δ 8.78 (2H, J = 6.6 Hz) and δ 8.11 (2H, J = 6.6 Hz) were the signals of H-2, H-6 and H-3, H-5 respectively. Resonances of aromatic protons H-2″, H-5″ and H-6″ were also shown at δ 7.34 (*d*, J = 1.8 Hz), δ 6.87 (*d*, J = 8.1 Hz) and δ 7.19 (*dd*, J = 1.8, 8.1 Hz) respectively. The ^{13}C spectrum (**Fig. 34** and **35**, see **Table 1**) with the analysis of the DEPT experiments exhibited thirteen signals for fifteen carbons with four quaternary carbons (δ 153.48, 149.85, 148.06 and 126.67), seven methines (δ 144.50, 141.89, 123.50, 122.98, 119.51, 115.75 and 110.94) and two methyls (δ 55.86 and 46.74). HMBC correlation (**Fig. 36**, see **Table 1**) corresponded to the assigned structure. Thus, these assignments clearly support the proposed structure.

Table 1 ^{1}H, ^{13}C and HMBC of compound **B3A**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.29 (3H, *s*)	46.74	CH_3	2, 6
2	8.78 (2H, *d*, 6.6)	144.50	CH	1-CH_3, 3, 4, 6
6				1-CH_3, 2, 4, 5
3	8.11 (2H, *d*, 6.6)	122.98	CH	2, 5, 1′, 2′
5				3, 6, 1′, 2′
4		153.48	C	
1′	7.28 (1H, *d*, 16.2)	119.51	CH	3, 4, 5, 1″
2′	7.87 (1H, *d*, 16.2)	141.89	CH	4, 1′, 1″, 2″, 6″
1″		126.67	C	
2″	7.34 (1H, *d*, 1.8)	110.94	CH	2′, 1″, 3″,4″, 6″
3″		148.06	C	
3″-OCH_3	3.91 (3H, *s*)	55.86	CH_3	3″
4″		149.85	C	
4″-OH	9.71 (1H, *s*)			3″, 5″
5″	6.87 (1H, *d*, 8.1)	115.75	CH	1″, 3″, 4″, 6″
6″	7.19 (1H, *dd*, 1.8, 8.1)	123.50	CH	2′, 2″, 4″, 5″

3.2.2 4-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylpyridinium iodide (B4A)



B4A

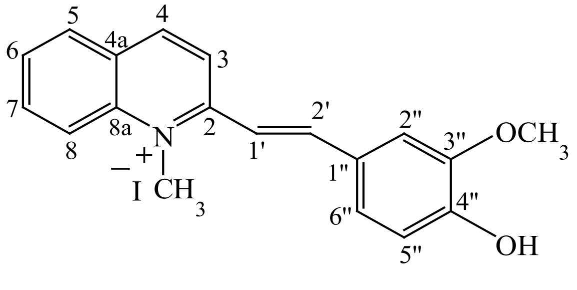
Compound **B4A** was obtained as brown crystals, mp. 230-231 °C. The UV-Vis spectrum was displayed in **Fig. 37**, with maximum absorptions at 214.4, 260.7, 275.6 and 400.7 nm. The FT-IR spectrum (**Fig. 38**) exhibited stretching vibrations of O-H (3372 cm^{-1}), C=C (1646 and 1600 cm^{-1}) and C-O (1235 cm^{-1}).

The ^{1}H NMR spectrum (**Fig. 39**, see **Table 2**) showed the presence of methyl protons at δ 4.34 (*N*-CH_3, *s*) and δ 3.93 (*O*-CH_3, *s*). The *singlet* signal of 3″-OH appeared at δ 9.27. Two *doublets* of H-1′ (δ 7.14, J = 16.2 Hz) and H-2′ (δ 7.77, J = 16.2 Hz) were assigned to be *trans*-disubstituted double bonds. Equivalent protons of *p*-disubstituted aromatic appeared as two *doublets* at δ 8.79 (2H, J = 6.6 Hz, H-2 and H-6) and δ 8.09 (2H, J = 6.6 Hz, H-3 and H-5). ^{1}H NMR spectrum also showed the signal of aromatic protons of H-2″ (δ 7.23), H-5″ (δ 6.94) and H-6″ (δ 7.17). The ^{13}C NMR and DEPT spectra (**Fig. 40** and **41**, see **Table 2**) exhibited thirteen signals for fifteen carbons with four quaternary carbons (δ 153.10, 150.23, 146.82 and 128.04), seven methines (δ 144.61, 141.35, 123.12, 121.45, 120.32, 114.04 and 111.85) and two methyls (δ 55.67 and 46.72). This assigned structure was confirmed by HMBC experiment (**Fig. 42**, see **Table 2**). These observations confirmed the structure of compound **B4A**.

Table 2 ^{1}H, ^{13}C and HMBC of compound **B4A**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.34 (3H, *s*)	46.72	CH_3	2, 6
2	8.79 (2H, *d*, 6.6)	144.61	CH	1-CH_3, 3, 4, 6
6				1-CH_3, 2, 4, 5
3	8.09 (2H, *d*, 6.6)	123.12	CH	2, 5, 1′
5				3, 6, 1′
4		153.10	C	
1′	7.14 (1H, *d*, 16.2)	120.32	CH	3, 4, 5, 1″
2′	7.77 (1H, *d*, 16.2)	141.35	CH	4, 1″, 2″, 6″
1″		128.04	C	
2″	7.23 (1H, *d*, 1.8)	114.04	CH	2′, 3″,4″
3″		146.82	C	
3″-OH	9.27 (1H, *s*)			2″, 3″, 4″
4″		150.23	C	
4″-OCH_3	3.93 (3H, *s*)	55.67	CH_3	4″
5″	6.94 (1H, *d*, 8.4)	111.85	CH	1″, 3″, 4″, 6″
6″	7.17 (1H, *dd*, 1.8, 8.4)	121.45	CH	2′, 2″, 4″

3.2.3 2-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methyl-quinolinium iodide (B3B)



B3B

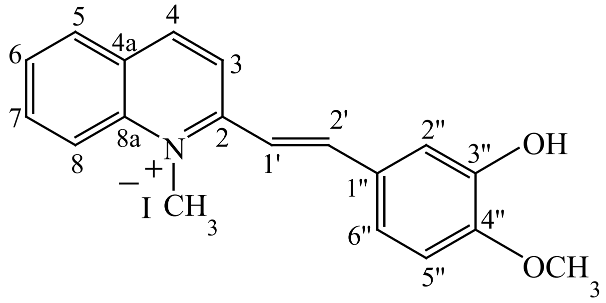
Compound **B3B** was obtained in a dark red crystal, mp. 248-250 °C. The UV-Vis spectrum (**Fig. 43**) showed maximum absorptions at 215.3, 308.9, 440.1 and 576.5 nm. The FT-IR spectrum (**Fig. 44**) exhibited stretching vibrations of O-H (3439 cm^{-1}), C=C (1609 and 1580 cm^{-1}) and C-O (1233 cm^{-1}).

The ^{1}H NMR spectrum (**Fig. 45**, see **Table 3**) showed characteristic of *trans*-disubstituted double bonds at δ 7.73 (1H, *d*, *J* = 15.6 Hz, H-1′) and δ 8.17 (1H, *d*, *J* = 15.6 Hz, H-2′).Three *singlet* signals at δ 10.02 (1H), δ 4.62 (3H) and δ 3.95 (3H) were assigned as OH, *N*-CH_3 and *O*-CH_3. Three signals of 1,2,4-trisubstituted benzene pattern at δ 7.58 (1H, *d*, *J* = 1.8 Hz), δ 6.93 (1H, *d*, *J* = 8.1 Hz) and δ 7.41 (1H, *dd*, *J* = 1.8, 8.1 Hz) were assigned to H-2″, H-5″ and H-6″ respectively. Two *doublet* signals at δ 8.94 (1H, *J* = 9.0 Hz) and δ 8.53 (1H, *J* = 9.0 Hz) were the signals of H-4 and H-3 respectively. ^{1}H NMR spectrum also showed resonances of aromatic protons H-5 (δ 8.30), H-6 (δ 7.90), H-7 (δ 8.15) and H-8 (δ 8.50). The ^{13}C NMR and DEPT spectra (**Fig. 46** and **47**, see **Table 3**) exhibited nineteen signals of six quaternary carbons (δ 161.78, 156.41, 153.34, 144.37, 132.57 and 131.68), eleven methines (δ 153.83, 148.63, 139.83, 135.19, 133.75, 130.51, 125.89, 124.03, 120.95, 120.17 and 117.11) and two methyls (δ 61.16 and 44.77). HMBC correlation (**Fig. 48**, see **Table 3**) corresponded to the assigned structure. Accordingly, compound **B3B** was proposed to be 2-[(*E*)-2′-(4″-hydroxy-3″-methoxyphenyl)ethenyl]-1-methyl-quinolinium iodide.

Table 3 ^{1}H, ^{13}C and HMBC of compound **B3B**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.62 (3H, *s*)	44.77	CH_3	2, 8a
2		161.78	C	
3	8.53 (1H, *d*, 9)	125.89	CH	2, 4a, 1′
4	8.94 (1H, *d*, 9)	148.63	CH	2, 3, 4a, 5, 8a
4a		132.57	C	
5	8.30 (1H, *dd*, 1.2, 7.5)	135.19	CH	4, 4a, 7, 8a
6	7.90 (1H, *t*, 7.5)	133.75	CH	4a, 7, 8
7	8.15 (1H, *dt*, 1.2, 7.5)	139.83	CH	5, 6, 8
8	8.50 (1H, *d*, 7.5)	124.03	CH	4a, 6, 7
8a		144.37	C	
1′	7.73 (1H, *d*, 15.6)	120.17	CH	3, 2′, 1″
2′	8.17 (1H, *d*, 15.6)	153.83	CH	2, 2″, 6″
1″		131.68	C	
2″	7.58 (1H, *d*, 1.8)	117.11	CH	2′, 3″,4″, 6″
3″		153.34	C	
3″-OCH_3	3.95 (3H, *s*)	61.16	CH_3	3″
4″		156.41	C	
4″- OH	10.02 (1H, *s*)			
5″	6.93 (1H, *d*, 8.1)	120.95	CH	1″, 3″, 4″
6″	7.41 (1H, *dd*, 1.8, 8.1)	130.51	CH	2′, 2″

3.2.4 2-[(*E*)-2′-(3″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methylquinolinium iodide (B4B)



B4B

Compound **B4B** was obtained as red-brown crystals, mp. 218-220 °C. The UV-Vis absorption bands appeared at 216.1, 306.2 and 431.3 nm. The FT-IR spectrum (**Fig. 50**) displayed stretching vibrations of O-H (3424 cm^{-1}), C=C (1612 and 1583 cm^{-1}) and C-O (1235 cm^{-1}).

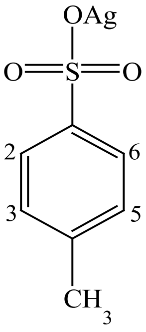
The ^{1}H NMR spectrum (**Fig. 51**, see **Table 4**) showed characteristic of *trans*-disubstituted double bonds at δ 7.69 (1H, *d*, J = 15.9 Hz, H-1′) and δ 8.09 (1H, *d*, J = 15.9 Hz, H-2′).Two *singlet* signals at δ 4.65 (3H) and δ 3.95 (3H) were assigned as *N*-CH_3 and *O*-CH_3 respectively. Three signals of 1,2,4-trisubstituted benzene pattern at δ 7.49 (1H, *d*, J = 2.1 Hz), δ 7.36 (1H, *d*, J = 8.4 Hz) and δ 7.41 (1H, *br d*, J = 8.4 Hz) were assigned to H-2″, H-5″ and H-6″ respectively. Two *doublet* signals at δ 8.95 (1H, J = 9.0 Hz) and δ 8.52 (1H, J = 9.0 Hz) were the signals of H-4 and H-3 respectively. ^{1}H NMR spectrum also further showed the signals of aromatic protons of H-5 (δ 8.32), H-6 (δ 7.93), H-7 (δ 8.18) and H-8 (δ 8.49). The ^{13}C NMR and DEPT spectra (**Fig. 52** and **53**, see **Table 4**) exhibited nineteen signals of six quaternary carbons (δ 161.62, 156.56, 152.06, 144.29, 132.86 and 132.64), eleven methines (δ 153.41, 148.93, 140.00, 135.22, 133.85, 128.45, 126.01, 123.81, 120.87, 119.87 and 116.63) and two methyls (δ 60.86 and 44.80). HMBC correlation (**Fig. 54**, see **Table 4**) corresponded to the assigned structure. Accordingly, compound **B4B** was considered to be 2-[(*E*)-2′-(3″-hydroxy-4″-methoxyphenyl)ethenyl]-1-methylquinolinium iodide.

Table 4 ^{1}H, ^{13}C and HMBC of compound **B4B**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.65 (3H, *s*)	44.80	CH_3	2, 8a
2		161.62	C	
3	8.52 (1H, *d*, 9)	126.01	CH	2, 4a, 1′
4	8.95 (1H, *d*, 9)	148.93	CH	2, 4a, 5, 8a
4a		132.64	C	
5	8.32 (1H, *d*, 7.5)	135.22	CH	4, 4a, 7, 8a
6	7.93 (1H, *t*, 7.5)	133.85	CH	4a, 7, 8
7	8.18 (1H, *dt*, 1.5, 7.5)	140.00	CH	5, 6, 8
8	8.49 (1H, *d*, 7.5)	123.81	CH	4a, 6, 7
8a		144.29	C	
1′	7.69 (1H, *d*, 15.9)	120.87	CH	3, 2′, 1″
2′	8.09 (1H, *d*, 15.9)	153.41	CH	2, 2″, 6″
1″		132.86	C	
2″	7.49 (1H, *d*, 2.1)	119.87	CH	2′, 3″,4″, 6″
3″		152.06	C	
4″		156.56	C	
4″-OCH_3	3.95 (3H, *s*)	60.86	CH_3	4″
5″	7.36 (1H, *d*, 8.4)	116.63	CH	1″, 3″, 4″
6″	7.41 (1H, *br d*, 8.4)	128.45	CH	2′, 2″, 4″

3.3 Structural elucidation of the anions counter part

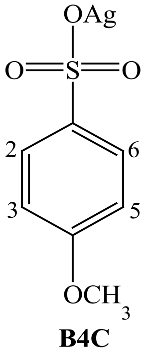
3.3.1 Silver (I) 4-methylbenzenesulfonate (B2C)



B2C

A white solid of compound **B2C** was obtained in 71% yield which decomposed at 264-266 °C. The ^{1}H NMR spectrum (**Fig.55**) showed equivalent protons of *p*-disubstituted aromatic at δ 7.74 (2H, *d*, J = 8.1 Hz, H-2, H-6) and 7.17 (2H, *d*, J = 8.1 Hz, H-3, H-5). A *singlet* signal of 4-CH_3 was observed at δ 2.38. Therefore, compound **B2C** was identified to be silver (I) 4-methylbenzenesulfonate.

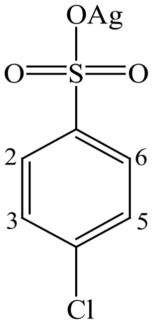
3.3.2 Silver (I) 4-methoxybenzenesulfonate (B4C)



B4C

Compound **B4C** was obtained as a white solid, decomposed at 240-242 °C. The ^{1}H NMR spectrum (**Fig. 56**) showed two *doublet* signals of H-2, H-6 and H-3, H-5 at δ7.78 (2H, J = 8.7 Hz) and δ 6.86 (2H, J = 8.7 Hz) respectively. The *singlet* signal of 4-*O*CH_3 appeared at δ 3.82 (3H). Therefore, compound **B4C** was proposed to be silver (I) 4-methoxybenzenesulfonate.

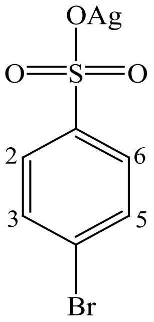
3.3.3 Silver (I) 4-chlorobenzenesulfonate (B6C)



B6C

Compound **P5C** was obtained as a white solid, decomposed at 227-229 °C. The ^{1}H NMR spectrum (**Fig. 57**) exhibited only two *doublet* signals of AA′ BB′ pattern at δ7.76 (H-2, H-6) and δ7.50 (H-3, H-5) with coupling constant of 7.8 Hz which indicated the location of Cl at C-4. Thus, compound **B6C** was assigned to be silver (I) 4-chlorobenzenesulfonate.

3.3.4 Silver (I) 4-bromobenzenesulfonate (B8C)

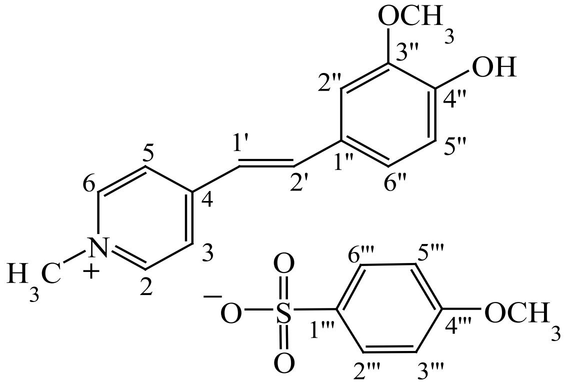


B8C

Compound **B8C** was received as a white solid, decomposed at 230-232 °C. The ^{1}H NMR spectrum (**Fig. 58**) exhibited only two *doublet*s of AA′ BB′ pattern at δ7.81 (H-2, H-6) and δ7.34 (H-3, H-5) with coupling constant of 8.4 Hz which indicated the location of Br at C-4. Accordingly, compound **B8C** was assigned as silver (I) 4-bromobenzenesulfonate.

3.4 Structural elucidation of salt formations

3.4.1 4-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methyl-pyridinium 4-methoxybenzenesulfonate (B1D)



B1D

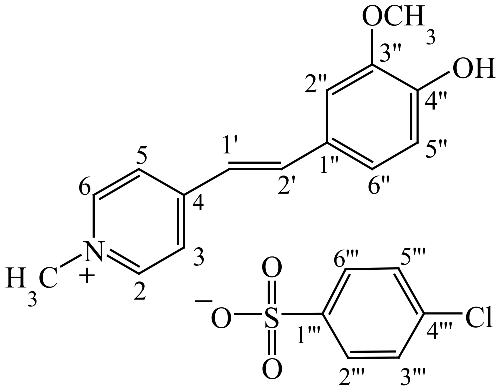
Compound **B1D** was obtained as a yellow solid, mp. 257-258 °C. The UV-Vis absorption spectra (**Fig. 59**) showed maximum bands at 219.6, 262.5 and 406.0 nm. The FT-IR spectrum (**Fig. 60**) exhibited stretching vibrations of O-H (3431 cm^{-1}), C=C (1645 and 1587 cm^{-1}), C-O (1233 cm^{-1}) and S=O in sulfonates (1185 cm^{-1}).

The ^{1}H NMR spectrum (**Fig. 61,** see **Table 5**) showed two fragments of cationic and anionic parts. The former showed characteristic of *trans*-disubstituted double bonds at δ 7.17 (1H, *d*, *J* = 15.9 Hz, H-1′) and δ 7.84 (1H, *d*, *J* = 15.9 Hz, H-2′). Two *singlet* signals at δ 4.32 (3H) and 3.95 (3H) were assigned as *N*-CH_3 and 3″-*O*-CH_3 respectively. Equivalent protons of *p*-disubstituted aromatic appeared as two *doublet* signals at δ 8.77 (2H, *J* = 6.6 Hz, H-2, H-6) and δ 8.03 (2H, *J* = 6.6 Hz, H-3, H-5). Three signals of 1,2,4-trisubstituted benzene pattern at δ 7.28 (1H, *d*, *J* = 1.8 Hz), δ 6.91 (1H, *d*, *J* = 8.4 Hz) and δ 7.16 (1H, *dd*, *J* = 1.8, 8.4 Hz) were assigned to H-2″, H-5″ and H-6″ respectively. ^{1}H NMR spectrum also showed resonances of aromatic protons of anionic part at δ 7.73 (2H, *d*, *J* = 8.4 Hz, H-2‴, H-6‴) and δ 6.84 (2H, *d*, *J* = 8.4 Hz, H-3‴, H-5‴). The *singlet* signal of 4‴-OCH_3 appeared at δ 3.80 (3H). The ^{13}C NMR (**Fig. 62** and **63,** see **Table 5**) exhibited eighteen signals for twenty two carbons with six quaternary carbons (δ 164.75, 158.66, 155.03, 153.08, 144.85 and 131.56), nine methines (δ 149.42, 147.22, 132.31, 128.61, 128.09, 124.26, 120.80, 117.75 and 115.80) and three methyls (δ 60.88, 60.11 and 51.80). The assigned structure was confirmed by HMBC experiment (**Fig. 64,** see **Table 5**). These observations confirmed the structure of compound **B1D**.

Table 5 ^{1}H, ^{13}C and HMBC of compound **B1D**

Position	δ_H, *mult*, *J* (Hz)	δ_C	DEPT	HMBC
1-CH$_3$	4.32 (3H, *s*)	51.80	CH$_3$	2, 6
2	8.77 (2H, *d*, 6.6)	149.42	CH	1-CH$_3$, 3, 4, 6
6				1-CH$_3$, 2, 4, 5
3	8.03 (2H, *d*, 6.6)	128.09	CH	2, 5, 1′, 2′
5				3, 6, 1′, 2′
4		158.66	C	
1′	7.17 (1H, *d*, 15.9)	124.26	CH	3, 4, 5, 1″
2′	7.84 (1H, *d*, 15.9)	147.22	CH	4, 1′, 2″, 6″
1″		131.56	C	
2″	7.28 (1H, *d*, 1.8)	115.80	CH	2′, 1″, 3″,4″, 6″
3″		153.08	C	
3″-OCH$_3$	3.95 (3H, *s*)	60.88	CH$_3$	3″
4″		155.03	C	
5″	6.91 (1H, *d*, 8.4)	120.80	CH	1″, 3″, 4″, 6″
6″	7.16 (1H, *dd*, 1.8, 8.4)	128.61	CH	2′, 2″, 4″, 5″
1‴		144.85	C	
2‴	7.73 (2H, *d*, 8.4)	132.31	CH	4‴, 6‴
6‴				2‴, 4‴
3‴	6.84 (2H, *d*, 8.4)	117.75	CH	1‴, 4‴, 5‴
5‴				1‴, 3‴,4‴
4‴		164.75	C	
4‴-OCH$_3$	3.80 (3H, *s*)	60.11	CH$_3$	4‴

3.4.2 4-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-chlorobenzenesulfonate (B2D)



B2D

A yellow solid of compound **B2D** was obtained in high yield (93%), mp. 232-233 °C. The UV-Vis and FT-IR spectra of **B2D** (**Fig. 65** and **66**) were closely resembled with those of compound **B1D**. ^{1}H NMR spectrum of **B2D** (**Fig. 67,** see **Table 6**) was similar to that of **B1D** except for anionic part which showed only equivalent protons of *p*-disubstituted aromatic at δ 7.74 (2H, *d*, J = 8.4 Hz, H-2‴, H-6‴) and 7.31 (2H, *d*, J = 8.4 Hz, H-3‴, H-5‴). The ^{13}C NMR and DEPT spectra data (**Fig. 68** and **69,** see **Table 6)** exhibited seventeen signals for twenty one carbons with six quaternary carbons (δ 153.80, 150.20, 148.31, 146.61, 134.09 and 126.85), nine methines (δ 144.70, 142.32, 127.86, 127.68, 123.78, 123.27, 119.63, 116.03 and 111.10) and two methyls (56.02 and 46.95). HMBC correlation (**Fig. 70,** see **Table 6**) corresponded to the assigned structure. Thus compound **B2D** was 4-[(*E*)-2′-(4″-hydroxy-3″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-chlorobenzenesulfonate.

The crystal structure of **B2D** was illustrated in **Fig. 7** and **8** which showed the tertiary structure and the packing diagram of **B2D**. The crystal and experiment data were given in **Table 7**. Bond lengths and angles were shown in **Table 8**. Compound **B2D** crystallized in centrosymmetric space group **P-1**.

Table 6 ^{1}H, ^{13}C and HMBC of compound **B2D**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.29 (3H, *s*)	46.95	CH_3	2, 6
2	8.75 (2H, *d*, 6.0)	144.70	CH	1-CH_3, 3, 4, 6
6				1-CH_3, 2, 4, 5
3	8.04 (2H, *d*, 6.0)	123.27	CH	2, 5, 1′, 2′
5				3, 6, 1′, 2′
4		153.80	C	
1′	7.18 (1H, *d*, 16.2)	119.63	CH	3, 4, 5, 1″
2′	7.80 (1H, *d*, 16.2)	142.32	CH	4, 1′, 2″, 6″
1″		126.85	C	
2″	7.29 (1H, *s*)	111.10	CH	2′, 3″,4″, 6″
3″		148.31	C	
3″-OCH_3	3.91 (3H, *s*)	56.02	CH_3	3″
4″		150.20	C	
5″	6.89 (1H, *d*, 8.1)	116.03	CH	1″, 3″, 4″, 6″
6″	7.16 (1H, *br d*, 8.1)	123.78	CH	2′, 2″, 4″, 5″
1‴		146.61	C	
2‴	7.74 (2H, *d*, 8.4)	127.68	CH	1‴, 3‴, 4‴, 6‴
6‴				1‴, 2‴, 4‴, 5‴
3‴	7.31 (2H, *d*, 8.4)	127.86	CH	1‴, 2‴, 4‴, 5‴
5‴				1‴, 3‴,4‴, 6‴
4‴		134.09	C	

Table 7 Crystal data of **B2D**.

Identification code	**B2D**
Empirical formula	$C_{15}H_{16}NO_2^{+}\cdot C_6H_4ClO_3S^{-}$
Formula weight	433.89
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.8153(16) Å α = 110.538(2)° b = 10.4218(17) Å β = 93.864(2)° c = 10.5894(17) Å γ = 97.819(2)°
Volume	997.2(3) Å^3
Z, Calculated density	2, 1.445 Mg/m^3
Absorption coefficient	0.330 mm^{-1}
F(000)	452
Crystal size	0.50 x 0.27 x 0.19 mm
Theta range for data collection	2.07 to 25.00°
Limiting indices	-11<=h<=11, -12<=k<=12, -12<=l<=12
Completeness to theta = 25.00	99.8%
Reflections collected / unique	9566/3510 [R(int) = 0.0198]
Max. and min. transmission	0.9399 and 0.8523
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3510/0/265
Goodness-of-fit on F^2	1.039
Final R indices [I>2σ(I)]	R1 = 0.0451, wR2 = 0.1213
R indices (all data)	R1 = 0.0491, wR2 = 0.1257
Largest diff. peak and hole	0.584 and -0.417 e.Å^3

Table 8 Bond lengths [Å] and angles [°] for **B2D**

Cl1-C4	1.738(2)		C4-C5	1.378(3)
S1-O1	1.413(2)		C5-C6	1.381(3)
S1-O3	1.4334(19)		C7-C8	1.388(3)
S1-O2	1.440(2)		C7-C12	1.387(3)
S1-C1	1.780(2)		C8-C9	1.379(3)
O4-C9	1.358(2)		C9-C10	1.405(3)
O5-C10	1.361(3)		C10-C11	1.375(3)
O5-C2	1.424(3)		C11-C12	1.410(3)
N1-C17	1.377(3)		C12-C13	1.457(3)
N1-C18	1.344(3)		C13-C14	1.328(3)
N1-C20	1.479(3)		C14-C15	1.457(3)
C1-C2	1.387(3)		C15-C16	1.389(3)
C1-C6	1.389(3)		C15-C19	1.399(3)
C2-C3	1.337(3)		C16-C17	1.365(3)
C3-C4	1.386(3)		C18-C19	1.365(3)
O1-S1-O3	112.70(15)		C9-C8-C7	120.11(19)
O1-S1-O2	116.47(18)		O4-C9-C8	123.57(18)
O3-S1-O2	109.96(14)	106.42	O4-C9-C10	116.63(18)
O1-S1-C1	(12)		O5-C10-C9	114.94(18)
O2-S1-C1	103.99(11)		O5-C10-C11	125.26(19)
O3-S1-C1	106.36(10)	117.87	C8-C9-C10	119.79(19)
C10-O5-C21	(17)		C10-C11-C12	120.81(19)
C17-N1-C18	119.61(18)		C11-C10-C9	119.80(19)
C17-N1-C20	119.8(2)		C7-C12-C11	118.40(19)
C18-N1-C20	120.55(19)		C7-C12-C13	119.20(19)
C2-C1-C6	120.24(19)	119.45	C11-C12-C13	122.39(19)
C2-C1-S1	(15)		C14-C13-C12	126.3(2)
C3-C2-C1	120.02(19)		C13-C14-C15	126.1(2)
C6-C1-S1	120.30(16)		C16-C15-C19	116.18(19)
C2-C3-C4	119.2(2)		C16-C15-C14	119.18(19)
C5-C4-C3	121.46(19)		C17-C16-C15	121.5(2)
C5-C4-Cl1	119.62(17)		C19-C15-C14	124.65(19)

Table 8 (Continued)

C3-C4-Cl1	118.92(17)	N1-C17-C16	120.8(2)
C4-C5-C6	119.2(2)	N1-C18-C19	121.6(2)
C5-C6-C1	119.9(2)	C18-C19-C15	120.3(2)
C12-C7-C8	121.1(2)		

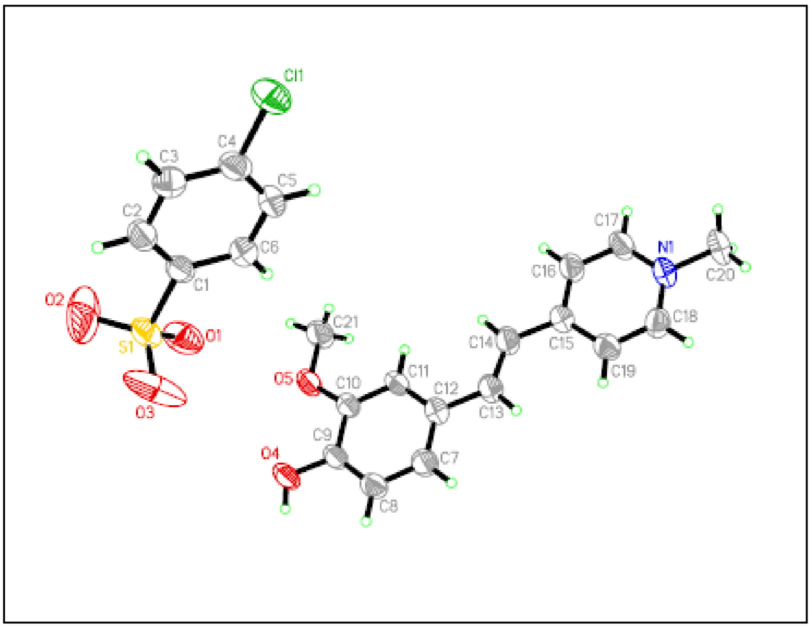


Figure 7 Structure of **B2D**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

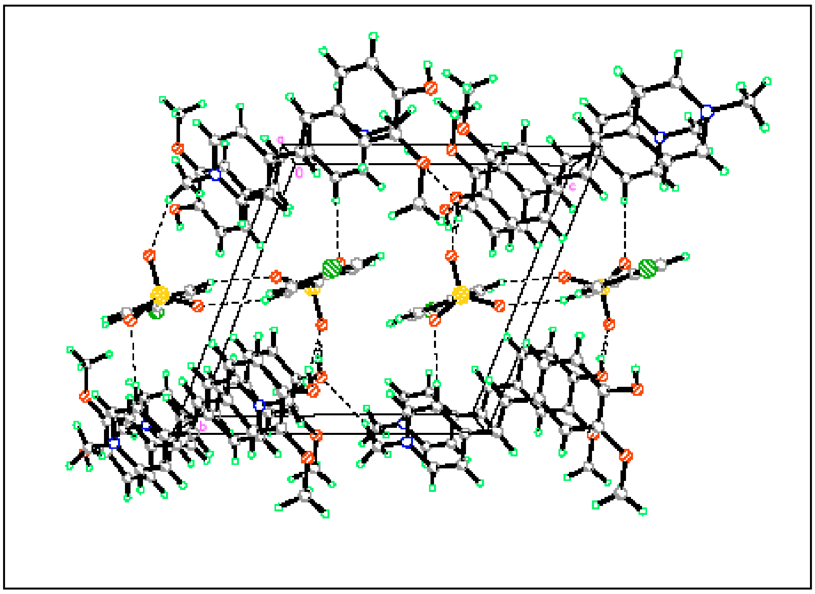
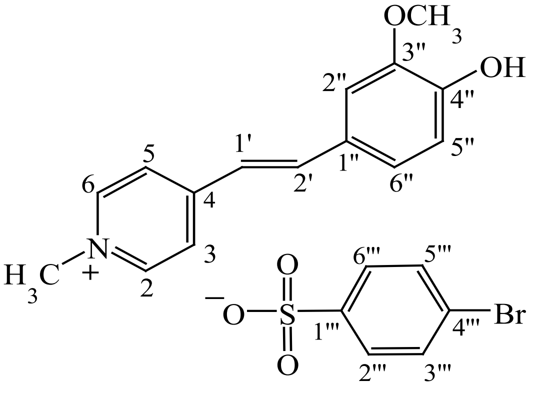


Figure 8 Packing diagram of **B2D** viewed down the *a* axis with H-bonds shown as dash lines.

3.4.3 4-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-bromobenzenesulfonate (B3D)



B3D

Compound **B3D** was obtained as a red solid, mp. 242-243 °C. The UV-Vis and FT-IR spectra of **B3D** (**Fig. 71** and **72**) were similar to those of compound **B1D**. ^{1}H NMR spectrum of **B2D** (**Fig. 73,** see **Table 9**) showed the same pattern as compound **B1D**. The difference was shown in the signal of anion part whose ^{1}H NMR spectrum showed only signals of AA′ BB′ pattern, indicating C-4‴ position of Br. The ^{13}C NMR and DEPT spectra data (**Fig. 74** and **75,** see **Table 9**) exhibited seventeen signals for twenty one carbons with six quaternary carbons (δ 153.36, 149.81, 148.04, 147.02, 126.67 and 122.02), nine methines (δ 144.54, 141.80, 130.53, 127.69, 123.42, 122.91, 119.54, 115.74 and 110.90) and two methyls (δ 55.71 and 46.63). HMBC correlation (**Fig. 76,** see **Table 9**) corresponded to the assigned structure. These assignments clearly support the proposed structure.

The crystal structure of **B3D** was illustrated in **Fig. 9** and **10** which showed the tertiary structure and the packing diagram of **B3D.** The crystal and experiment data were given in **Table 10**. Bond lengths and angles were shown in **Table 11.** Compound **B3D** crystallized out in centrosymmetric space group **P-1**.

Table 9 ^{1}H, ^{13}C and HMBC of compound **B3D**

Position	**δ_{H}, *mult*, *J* (Hz)**	**δ_{C}**	**DEPT**	**HMBC**
1-CH$_3$	4.31 (3H, *s*)	46.63	CH$_3$	2, 6
2	8.78 (2H, *d*, 6.6)	144.54	CH	1-CH$_3$, 3, 4, 6
6				1-CH$_3$, 2, 4, 5
3	8.07 (2H, *d*, 6.6)	122.91	CH	2, 5, 1′, 2′
5				3, 6, 1′, 2′
4		153.36	C	
1′	7.21 (1H, *d*, 16.2)	119.54	CH	3, 4, 5, 1″
2′	7.84 (1H, *d*, 16.2)	141.80	CH	4, 1′, 1″, 2″, 6″
1″		126.67	C	
2″	7.30 (1H, *d*, 1.8)	110.90	CH	2′, 1″, 3″,4″, 6″
3″		148.04	C	
3″-OCH$_3$	3.91 (3H, *s*)	55.71	CH$_3$	3″
4″		149.81	C	
4″ -OH	9.71 (1H, *s*)			
5″	6.90 (1H, *d*, 8.1)	115.74	CH	1″, 3″, 4″, 6″
6″	7.19 (1H, *dd*, 1.8, 8.1)	123.42	CH	2′, 2″, 4″, 5″
1‴		147.02	C	
2‴	7.68 (2H, *d*, 8.4)	127.69	CH	3‴, 4‴, 6‴
6‴				2‴, 4‴, 5‴
3‴	7.47 (2H, *d*, 8.4)	130.53	CH	1‴, 2‴, 4‴, 5‴
5‴				1‴, 3‴, 4‴,6‴
4‴		122.02	C	

Table 10 Crystal data of **B3D**.

Identification code	**B3D**
Empirical formula	$C_{15}H_{16}NO_2^{+}\cdot C_6H_4BrO_3S^{-}$
Formula weight	478.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.9319(7) Å α = 109.7100(10)°
	b = 10.3666(8) Å β = 94.1380(10)°
	c = 10.5606(8) Å γ = 98.4580(10)°
Volume	1003.79(13) Å^3
Z, Calculated density	2, 1.583 Mg/m^3
Absorption coefficient	2.185 mm^{-1}
F(000)	488
Crystal size	0.47 x 0.24 x 0.21 mm
Theta range for data collection	2.07 to 28.28°
Limiting indices	-12<=h<=11, -12<=k<=13, -14<=l<=13
Reflections collected / unique	6754 / 4118 [R(int) = 0.0148]
Completeness to theta = 25.00	92.8 %
Max. and min. transmission	0.6617 and 0.4278
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4118 / 12 / 264
Goodness-of-fit on F^2	1.040
Final R indices [I>2σ(I)]	R1 = 0.0346, wR2 = 0.0886
R indices (all data)	R1 = 0.0404, wR2 = 0.0919
Largest diff. peak and hole	0.696 and -0.421 e.Å^3

Table 11 Bond lengths [Å] and angles [°] for **B3D**

Br1-C4	1.892(2) 1.420	C4-C5	1.375(4)
S1-O2	(3)	C5-C6	1.386(3)
S1-O1	1.429(2)	C7-C12	1.380(4)
S1-O3	1.438(3)	C7-C8	1.384(4)
S1-C1	1.774(2)	C8-C9	1.376(4)
O4-C9	1.354(3)	C9-C10	1.410(3)
O5-C10	1.363(3)	C10-C11	1.368(3)
O5-C21	1.422(3)	C11-C12	1.406(4)
N1-C17	1.341(3)	C12-C13	1.453(3)
N1-C18	1.343(4)	C13-C14	1.322(4)
N1-C20	1.474(3)	C14-C15	1.455(3)
C1-C6	1.382(3)	C15-C16	1.385(4)
C1-C2	1.388(3)	C15-C19	1.400(4)
C2-C3	1.382(3)	C16-C17	1.362(4)
C3-C4	1.382(3)	C18-C19	1.361(4)
O2-S1-O1	112.76(17)	C9-C8-C7	120.2(2)
O2-S1-O3	116.3(2)	O4-C9-C8	123.8(2)
O1-S1-O3	110.35(18)	O4-C9-C10	116.8(2)
O2-S1-C1	106.19(14)	C8-C9-C10	119.4(2)
O1-S1-C1	106.50(12)	O5-C10-C11	125.7(2)
O3-S1-C1	103.78(13)	O5-C10-C9	114.4(2)
C10-O5-C21	117.6(2)	C11-C10-C9	119.8(2)
C17-N1-C18	119.3(2)	C10-C11-C12	121.0(2)
C17-N1-C20	119.7(2)	C7-C12-C11	118.3(2)
C18-N1-C20	121.0(2)	C7-C12-C13	119.0(2)
C6-C1-C2	120.4(2)	C11-C12-C13	122.6(2)
C6-C1-S1	120.25(19)	C14-C13-C12	127.0(2)
C2-C1-S1	119.32(18)	C13-C14-C15	126.1(2)
C3-C2-C1	119.7(2)	C16-C15-C19	116.0(2)
C4-C3-C2	119.2(2)	C16-C15-C14	119.6(2)
C5-C4-C3	121.6(2)	C19-C15-C14	124.4(2)
C5-C4-Br1	119.60(18)	C17-C16-C15	121.7(2)
C3-C4-Br1	118.79(19)	N1-C17-C16	120.9(3)

Table 11 (Continued)

C4-C5-C6	119.1(2)	N1-C18-C19	121.8(2)
C1-C6-C5	120.0(2)	C18-C19-C15	120.3(2)
C12-C7-C8	121.3(2)		

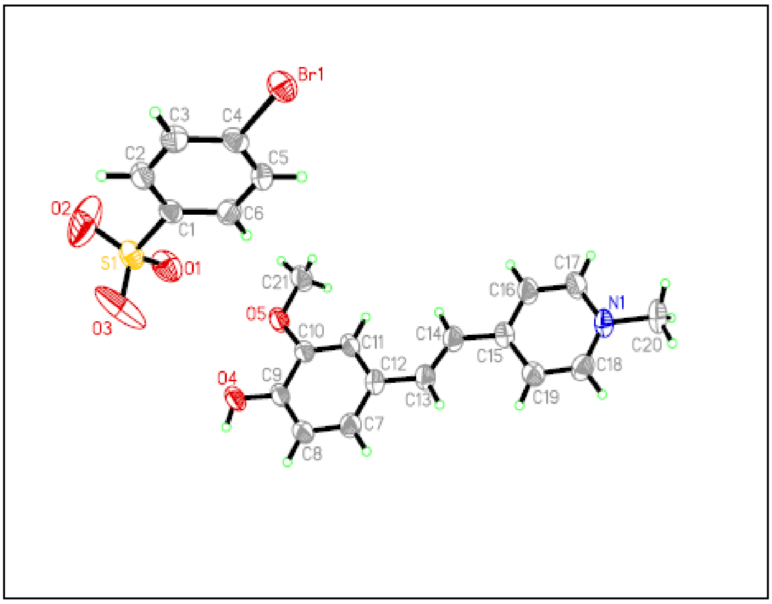


Figure 9 Structure of **B3D**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

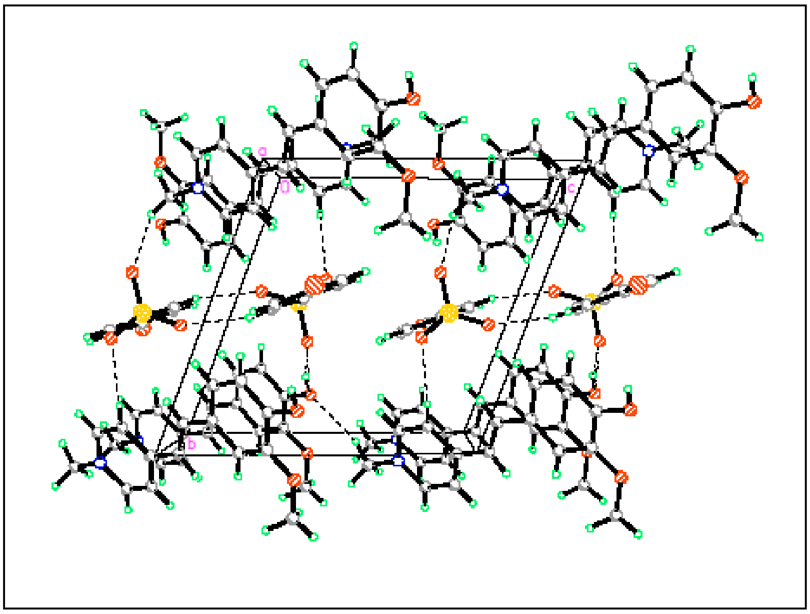
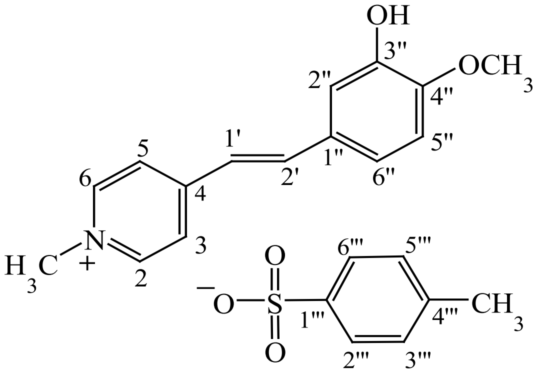


Figure 10 Packing diagram of **B3D** viewed down the *a* axis with H-bonds shown as dash lines.

3.4.4 4-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methylbenzenesulfonate (B1E)



B1E

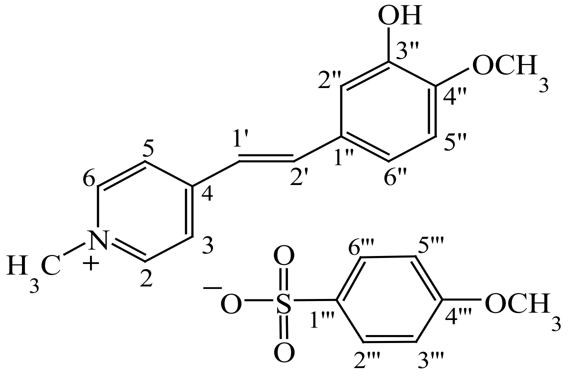
Compound **B1E** was obtained as a yellow solid, mp. 118-120 °C. The UV-Vis spectrum (**Fig. 77**) showed maximum absorptions at 212.6, 259.0 and 399.8 nm. The FT-IR spectrum (**Fig. 78**) exhibited absorption corresponding to O-H stretching at 3428 cm^{-1}, C=C stretching at 1640 and 1599 cm^{-1}, C-O stretching 1220 cm^{-1} and S=O in sulfonates stretching at 1193 cm^{-1}.

The ^{1}H NMR spectrum (**Fig.79, see Table 12**) showed two fragments of cationic and anionic parts. The former showed characteristic of *trans*-disubstituted double bonds at δ 7.17 (1H, *d*, J = 16.2 Hz, H-1′) and δ 7.80 (1H, *d*, J = 16.2 Hz, H-2′). Two *singlet* signals at δ 4.28 (3H) and 3.89 (3H) were assigned as *N*-CH$_3$ and *O*-CH$_3$ respectively. Three signals of 1,2,4-trisubstituted benzene pattern at δ 7.23 (1H, *d*, J = 1.8 Hz), δ 6.96 (1H, *d*, J = 8.4 Hz) and δ 7.16 (1H, *dd*, J = 1.8, 8.4 Hz) were assigned to H-2″, H-5″ and H-6″ respectively. Equivalent protons of *p*-disubstituted aromatic appeared as two *doublet* signals at δ 8.76 (2H, J = 6.6 Hz, H-2, H-6) and δ 8.10 (2H, J = 6.6 Hz, H-3, H-5). ^{1}H NMR spectrum also exhibited equivalent protons of *p*-disubstituted aromatic protons of anionic part at δ 7.59 (2H, *d*, J = 7.8 Hz, H-2‴, H-6‴) and δ 7.12 (2H, *d*, J = 7.8 Hz, H-3‴, H-5‴). The *singlet* signal of 4‴-CH$_3$ was also observed at δ 2.30 (3H). The ^{13}C NMR and DEPT spectra data (**Fig. 80** and **81,** see **Table 12**) exhibited eighteen signals for twenty two carbons with six quaternary carbons (δ 158.29, 155.40, 151.99, 150.06, 143.16 and 133.20), nine methines (δ 149.72, 146.57, 133.15, 130.69, 128.29, 126.67, 125.40, 119.14 and 116.87) and three methyls (δ 60.78, 51.81 and 26.01). The assigned structure was confirmed by HMBC experiment (**Fig. 82,** see **Table 12**). These spectroscopic data confirmed the structure of compound **B1E**.

Table 12 ^1H, ^{13}C and HMBC of compound **B1E**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.28 (3H, *s*)	51.81	CH_3	2, 6
2	8.76 (2H, *d*, 6.6)	149.72	CH	1-CH_3, 3, 4, 6
6				1-CH_3, 2, 4, 5
3	8.10 (2H, *d*, 6.6)	128.29	CH	2, 5, 1′
5				3, 6, 1′
4		158.29	C	
1′	7.17 (1H, *d*, 16.2)	125.40	CH	3, 4, 5, 1″
2′	7.80 (1H, *d*, 16.2)	146.57	CH	4, 1″, 2″, 6″
1″		133.20	C	
2″	7.23 (1H, *d*, 1.8)	119.14	CH	2′, 3″,4″, 6″
3″		151.99	C	
4″		155.40	C	
4″ -OCH_3	3.89 (3H, *s*)	60.78	CH_3	4″
5″	6.96 (1H, *d*, 8.4)	116.87	CH	1″, 3″, 4″, 6″
6″	7.16 (1H, *dd*, 1.8, 8.4)	126.67	CH	2′, 2″, 4″
1‴		150.06	C	
2‴	7.59 (2H, *d*, 7.8)	130.69	CH	3‴, 4‴, 6‴
6‴				2‴, 4‴, 5‴
3‴	7.12 (2H, *d*, 7.8)	133.15	CH	4‴-CH_3, 1‴, 2‴, 5‴
5‴				4‴-CH_3, 1‴, 3‴,6‴
4‴		143.16	C	
4‴-CH_3	2.30 (3H, *s*)	26.01	CH_3	3‴, 4‴, 5‴

3.4.5 4-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methoxybenzenesulfonate (B2E)



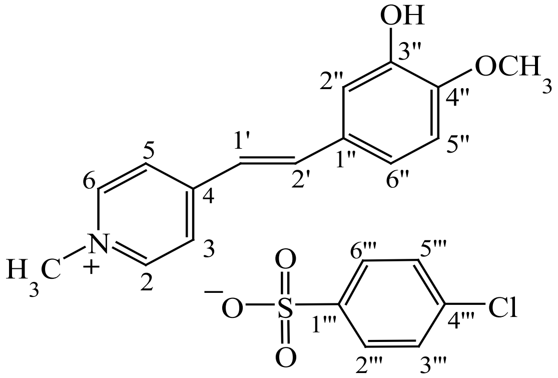
B2E

Compound **B2E** was obtained as a yellow solid, mp. 114-116 °C. The UV-Vis and FT-IR spectra of **B2E** (**Fig. 83** and **84**) were closely resembled with those of compound **B1E**. ^{1}H NMR spectrum of **B2E** (**Fig.. 85,** see **Table 13**) exhibited the same pattern as compound **B1E**. The difference was found in the signal of 4‴-OCH$_3$ which was observed at δ 3.80 (3H, *s*). The ^{13}C NMR and DEPT spectra data (**Fig. 86** and **87,** see **Table 13**) exhibited eighteen signals for twenty two carbons with six quaternary carbons (δ 164.82, 158.41, 155.43, 151.90, 144.60 and 132.85), nine methines (δ 149.46, 146.81, 132.32, 128.27, 126.80, 124.96, 118.97, 117.77 and 116.48) and three methyls (δ 60.71, 60.09 and 51.81). HMBC correlation (**Fig. 88,** see **Table 13**) corresponded to the assigned structure. Consequently, compound **B2E** is 4-[(*E*)-2′-(3″-hydroxy-4″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-methoxybenzenesulfonate.

Table 13 ^{1}H, ^{13}C and HMBC of compound **B2E**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.32 (3H, *s*)	51.81	CH_3	2, 6
2 6	8.74 (2H, *d*, 6.6)	149.46	CH	1-CH_3, 3, 4, 6 1-CH_3, 2, 4, 5
3 5	7.98 (2H, *d*, 6.6)	128.27	CH	2, 5, 1′ 3, 6, 1′
4		158.41	C	
1′	7.06 (1H, *d*, 16.2)	124.96	CH	3, 4, 5, 2′, 1″
2′	7.68 (1H, *d*, 16.2)	146.81	CH	4, 1′, 2″, 6″
1″		132.85	C	
2″	7.25 (1H, *d*, 2.1)	118.97	CH	2′, 3″,4″, 6″
3″		151.90	C	
4″		155.43	C	
4″ -OCH_3	3.92 (3H, *s*)	60.71	CH_3	4″
5″	6.91 (1H, *d*, 8.4)	116.48	CH	1″, 3″, 4″
6″	7.12 (1H, *dd*, 2.1, 8.4)	126.80	CH	2′, 2″, 4″
1‴		144.60	C	
2‴ 6‴	7.74 (2H, *d*, 8.7)	132.32	CH	1‴, 4‴, 6‴ 1‴, 2‴, 4‴
3‴ 5‴	6.83 (2H, *d*, 8.7)	117.77	CH	1‴, 4‴, 5‴ 1‴, 3‴,4‴
4‴		164.82	C	
4‴-OCH_3	3.80 (3H, *s*)	60.09	CH_3	4‴

3.4.6 4-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-chlorobenzenesulfonate (B3E)



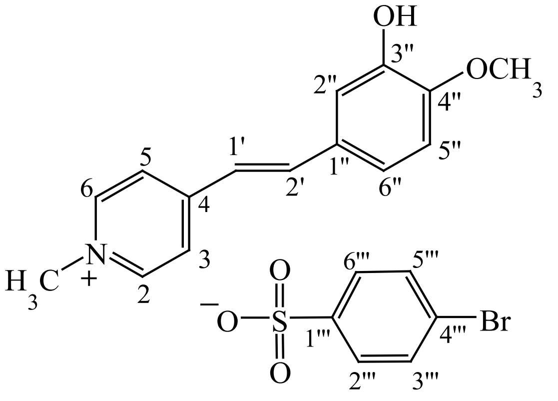
B3E

Compound **B3E** was obtained as a yellow solid, mp. 189-190 °C. The UV-Vis and FT-IR spectra of **B3E** (**Fig. 89** and **90**) were closely resembled with those of compound **B1E**. ^{1}H NMR spectrum of **B3E** (**Fig. 91,** see **Table 14**) was also similar to that of **B1E** except for the signals of anionic part which showed only signals of AA′BB′ pattern. The ^{13}C NMR and DEPT spectra data (**Fig. 92** and **93,** see **Table 14**) exhibited seventeen signals for twenty one carbons with six quaternary carbons (δ 158.44, 155.41, 151.88, 150.59, 139.15 and 132.94), nine methines (δ 149.50, 146.77, 132.70, 132.49, 128.31, 126.80, 125.09, 118.99 and 116.59) and two methyls (δ 60.73 and 51.83). The assigned structure was confirmed by HMBC experiment (**Fig. 94,** see **Table 14**). Consequently, these assignments clearly supported the proposed structure of compound **B3E**.

Table 14 ^{1}H, ^{13}C and HMBC of compound **B3E**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.28 (3H, *s*)	51.83	CH_3	2, 6
2	8.73 (2H, *d*, 6.6)	149.50	CH	1-CH_3, 3, 4, 6
6				1-CH_3, 2, 4, 5
3	8.04 (2H, *d*, 6.6)	128.31	CH	2, 5, 1′
5				3, 6, 1′
4		158.44	C	
1′	7.10 (1H, *d*, 15.9)	125.09	CH	3, 4, 5, 1″
2′	7.72 (1H, *d*, 15.9)	146.77	CH	4, 2″, 6″
1″		132.94	C	
2″	7.22 (1H, *d*, 1.8)	118.99	CH	2′, 3″,4″, 6″
3″		151.88	C	
4″		155.41	C	
4″ -OCH_3	3.88 (3H, *s*)	60.73	CH_3	4″
5″	6.91 (1H, *d*, 8.4)	116.59	CH	1″, 3″, 4″, 6″
6″	7.13 (1H, *dd*, 1.8, 8.4)	126.80	CH	2′, 2″
1‴		150.59	C	
2‴	7.74 (2H, *d*, 8.4)	132.49	CH	4‴, 6‴
6‴				2‴, 4‴
3‴	7.30 (2H, *d*, 8.4)	132.70	CH	1‴, 4‴, 5‴
5‴				1‴, 3‴,4‴
4‴		139.15	C	

3.4.7 4-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-bromobenzenesulfonate (B4E)



B4E

Compound **B4E** was obtained as a yellow solid, mp. 238-239 °C. The UV-Vis and FT-IR spectra of **B4E** (**Fig. 95** and **96**) were closely resembled those of compound **B1E**. ^{1}H NMR spectrum of **B4E** (**Fig. 97,** see **Table 15**) was similar to that of **B1E** except for the signals of anionic part which showed only equivalent protons of *p*-disubstituted aromatic at δ 7.68 (2H, *d*, J = 8.4 Hz, H-2‴, H-6‴) and 7.47 (2H, *d*, J = 8.4 Hz, H-3‴, H-5‴). The ^{13}C NMR and DEPT spectra data (**Fig. 98** and **99,** see **Table 15**) exhibited seventeen signals for twenty one carbons with six quaternary carbons (δ 152.96, 150.08, 146.88, 146.67, 127.85 and 121.82), nine methines (δ 144.43, 141.23, 130.36, 127.52, 122.95, 121.31, 120.12, 113.87 and 111.61) and two methyls (δ 55.47 and 46.50). HMBC correlation (**Fig. 100,** see **Table 15**) corresponded to the assigned structure. Therefore, compound **B4E** is 4-[(*E*)-2′-(3″-hydroxy-4″-methoxyphenyl)ethenyl]-1-methylpyridinium 4-bromobenzenesulfonate.

The crystal structure of **B4E** was illustrated in **Fig. 11** and **12** which showed the tertiary structure and the packing diagram of **B4E**. The crystal and experiment data were given in **Table 16**. Bond lengths and angles were shown in **Table 17.** Compound **B3E** crystallized in centrosymmetric space group **P-1**.

Table 15 ^1H, ^{13}C and HMBC of compound **B4E**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.30 (3H, *s*)	46.50	CH_3	2, 6
2	8.79 (2H, *d*, 6.9)	144.43	CH	1-CH_3, 3, 4, 6
6				1-CH_3, 2, 4, 5
3	8.10 (2H, *d*, 6.9)	122.95	CH	2, 5, 1′
5				3, 6, 1′
4		152.96	C	
1′	7.16 (1H, *d*, 16.2)	120.12	CH	3, 4, 5, 1″
2′	7.79 (1H, *d*, 16.2)	141.23	CH	4, 1′, 2″, 6″
1″		127.85	C	
2″	7.24 (1H, *d*, 2.1)	113.87	CH	2′,1″, 3″,4″, 6″
3″		146.67	C	
4″		150.08	C	
4″ -OCH_3	3.90 (3H, *s*)	55.47	CH_3	4″
5″	6.95 (1H, *d*, 8.4)	111.61	CH	1″, 3″, 4″
6″	7.17 (1H, *dd*, 2.1, 8.4)	121.31	CH	2′, 2″, 4″
1‴		146.88	C	
2‴	7.68 (2H, *d*, 8.4)	127.52	CH	3‴, 4‴, 6‴
6‴				2‴, 4‴, 5‴
3‴	7.47 (2H, *d*, 8.4)	130.36	CH	1‴, 2‴, 4‴, 5‴
5‴				1‴, 3‴,4‴, 6‴
4‴		121.82	C	

Table 16 Crystal data of **B4E**.

Identification code	**B4E**
Empirical formula	$C_{15}H_{16}NO_2^+ \cdot C_6H_4BrO_3S^-$
Formula weight	992.73
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.7426(7) Å α = 80.1070(10)°
	b = 9.8821(7) Å β = 73.1400(10)°
	c = 11.8356(8) Å γ = 83.2970(10)°
Volume	1071.60(13) Å^3
Z, Calculated density	1, 1.538 Mg/m^3
Absorption coefficient	2.053 mm^{-1}
F(000)	508
Crystal size	0.54 x 0.51 x 0.16 mm
Theta range for data collection	2.10 to 24.99°
Limiting indices	-11<=h<=11, -11<=k<=11, -14<=l<=12
Reflections collected / unique	5431 / 3717 [R(int) = 0.0267]
Completeness to theta = 24.99	98.4 %
Max. and min. transmission	0.7281 and 0.4024
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3717 / 0 / 286
Goodness-of-fit on F^2	1.048
Final R indices [I>2σ(I)]	R1 = 0.0432, wR2 = 0.1223
R indices (all data)	R1 = 0.0462, wR2 = 0.1254
Largest diff. peak and hole	0.594 and -0.816 e.Å^3

Table 17 Bond lengths [Å] and angles [°] for **B4E**

Br1-C4	1.890(3)	C4-C5	1.389(4)
S1-O1	1.440(2) 1.441	C5-C6	1.377(4)
S1-O2	(2) 1.445(2)	C7-C8	1.371(4)
S1-O3	1.777(2) 1.348	C7-C12	1.404(4)
S1-C1	(3) 1.369(4)	C8-C9	1.406(4)
O4-C8	1.416(4) 1.344	C9-C10	1.370(4)
O5-C9	(4) 1.338(4)	C10-C11	1.386(5)
O5-C21	1.483(4) 1.391	C11-C12	1.390(4)
N1-C17	(4) 1.390(4)	C12-C13	1.448(4)
N1-C18		C13-C14	1.326(5)
N1-C20		C14-C15	1.449(4)
C1-C2		C15-C16	1.397(4)
C1-C6		C15-C19	1.402(4)
C2-C3	1.377(4) 1.388	C16-C17	1.361(5)
C3-C4	(4)	C18-C19	1.359(5)
O1-S1-O2	112.81(16)	C5-C4-Br1	119.21(19)
O1-S1-O3	112.92(16)	C5-C6-C1	120.4(2)
O1-S1-C1	105.43(12)	C6-C5-C4	119.0(2)
O2-S1-O3	113.31(16)	C7-C8-C9	120.3(2)
O2-S1-C1	106.15(12)	C7-C12-C13	121.8(3)
O3-S1-C1	105.34(12)	C8-C7-C12	121.1(3)
O4-C8-C7	123.9(2) 115.8	C9-C10-C11	120.0(3)
O4-C8-C9	(2)	C10-C9-C8	119.4(3)
O5-C9-C10	125.6(3)	C10-C11-C12	121.9(3)
O5-C9-C8	115.0(2)	C11-C12-C7	117.4(3)
C9-O5-C21	118.7(3) 119.8	C11-C12-C13	120.8(3)
C18-N1-C17	(3) 120.5(3)	C13-C14-C15	126.5(3)
C18-N1-C20	119.6(3)	C14-C13-C12	127.6(3)
C17-N1-C20		C16-C15-C14	124.2(3)

Table 17 (Continued)

C6-C1-C2	119.9(2)	C16-C15-C19	116.0(3)
C6-C1-S1	119.64(19)	C17-C16-C15	120.9(3)
C2-C1-S1	120.50(19)	C18-C19-C15	121.0(3)
C2-C3-C4	119.1(2)	C19-C15-C14	119.8(3)
C3-C2-C1	120.3(2) 121.3	N1-C17-C16	121.1(3)
C3-C4-C5	(2) 119.4(2)	N1-C18-C19	121.2(3)
C3-C4-Br1			

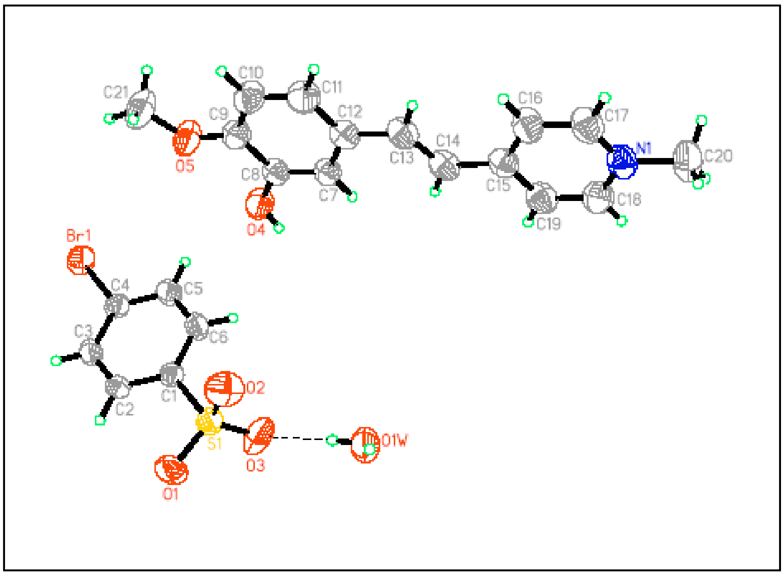


Figure 11 Structure of **B4E**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

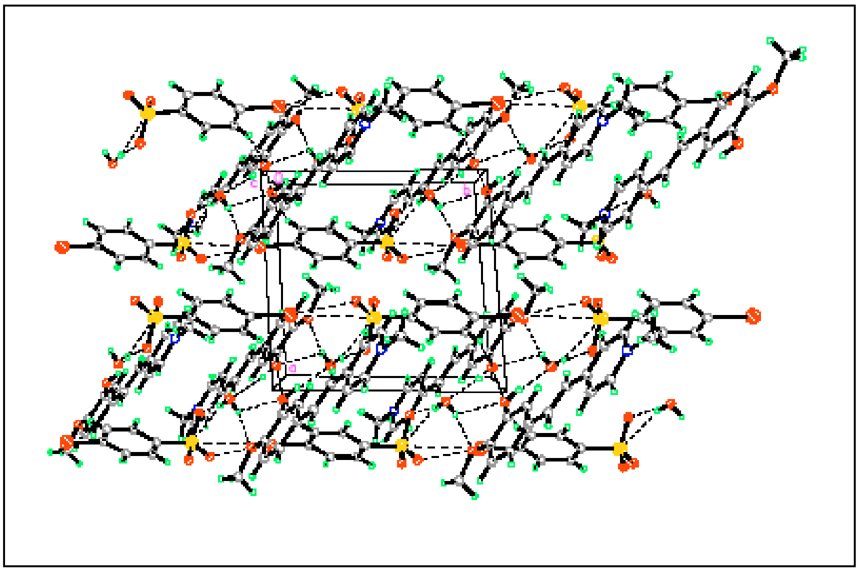
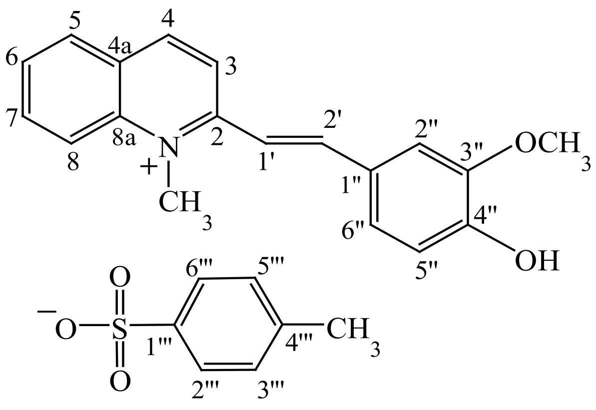


Figure 12 Packing diagram of **B4E** viewed down the *a* axis with H-bonds shown as dash lines.

3.4.8 2-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methyl-

quinolinium 4-methylbenzenesulfonate (B1F)



B1F

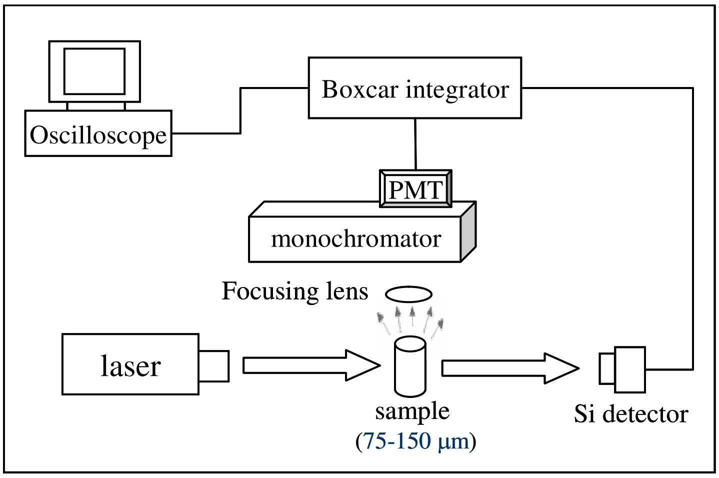
Compound **B1F** was obtained as a brown solid, mp. 263-265 °C. The UV-Vis absorption bands (**Fig. 101**) were shown at 217.0, 249.4, 308.0, 440.9 and 574.8 nm. The FT-IR spectrum (**Fig. 102**) exhibited stretching vibrations of O-H (3430 cm^{-1}), C=C (1600 and 1579 cm^{-1}), C-O (1219 cm^{-1}) and S=O in sulfonates (1190 cm^{-1}).

The ^{1}H NMR spectrum (**Fig. 103,** see **Table 18**) showed two fragments of cationic and anionic parts. The former showed characteristic of *trans*-disubstituted double bonds at δ 7.70 (1H, *d*, J = 15.6 Hz, H-1′) and δ 8.10 (1H, *d*, J = 15.6 Hz, H-2′). Two *singlet* signals at δ 4.59 (3H) and 3.97 (3H) were assigned as *N*-CH$_3$ and *O*-CH$_3$ respectively. Three signals of 1,2,4-trisubstituted benzene pattern at δ 7.53 (1H, *d*, J = 1.8 Hz), δ 6.95 (1H, *d*, J = 8.1 Hz) and δ 7.38 (1H, *dd*, J = 1.8, 8.1 Hz) were assigned to H-2″, H-5″ and H-6″ respectively. Two *doublets* of H-3 and H-4 were observed at δ 8.47 (1H, J = 9.0 Hz) and δ 8.88 (1H, J = 9.0 Hz) respectively. Resonances of aromatic protons H-5, H-6, H-7 and H-8 were also shown at δ 8.27 (*dd*, J = 1.5, 7.5 Hz), δ 7.89 (*t*, J = 7.5 Hz), δ 8.14 (*dt*, J = 1.5, 7.5 Hz) and δ 8.44 (*d*, J = 7.5 Hz) respectively. ^{1}H NMR spectrum showed signals of anionic part. Equivalent protons of *p*-disubstituted aromatic appeared as two *doublets* at δ 7.63 (2H, J = 8.1 Hz, H-2‴, H-6‴) and δ 7.11 (2H, J = 8.1 Hz, H-3‴, H-5‴). The *singlet* signal of 4‴-CH$_3$ was observed at δ 2.32 (3H). The ^{13}C NMR and DEPT spectra (**Fig.**

104 and **105,** see **Table 18**) exhibited twenty four signals for twenty six carbons with eight quaternary carbons (δ 161.79, 156.56, 153.32, 149.31, 144.33, 143.18, 132.48 and 131.48), thirteen methines (δ 154.05, 148.66, 139.89, 135.18, 133.75, 133.11, 130.69, 130.47, 125.79, 123.60, 120.93, 119.79 and 116.88) and three methyls (δ 61.08, 44.77 and 26.01). The assigned structure was confirmed by HMBC experiment (**Fig. 106,** see **Table 18**). These spectroscopic data confirmed the structure of compound **B1F**.

The crystal structure of **B1F** was illustrated in **Fig. 13** and **14** which showed the tertiary structure and the packing diagram of **B1F**. The crystal and experiment data were given in **Table 19**. Bond lengths and angles were shown in **Table 20.** Compound **B1F** crystallized in the **Pc** space group which was a noncentrosymmetric space group meaning that **B1F** exhibited SHG properties.

The SHG measurement was made in accordance with the classical powder method developed by Kurtz and Perry (Kurtz and Perry, 1968).



Nd: YAG laser of powder 8 mJ/pulse was used 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 second harmonic wave of 532 nm generated from the sample was detected by a photomultiplier as reflected light and converted into electrical signal. The converted electrical signal was displayed on an oscilloscope.

Comparison of relative SHG intensities was made with that of urea. It was found that the SHG effect of **B1F** was about 2.10 times that of urea. Furthermore, compound **B1F** showed very good stability under laser irradiation (1064 nm, 8 mJ/pulse, 8 ns, and 10 Hz) and no sign of decomposition.

Table 18 ^{1}H, ^{13}C and HMBC of compound **B1F**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.59 (3H, *s*)	44.77	CH_3	2, 8a
2		161.79	C	
3	8.47 (1H, *d*, 9)	125.79	CH	2, 4a, 1′
4	8.88 (1H, *d*, 9)	148.66	CH	2, 5, 8a
4a		132.48	C	
5	8.27 (1H, *dd*, 1.5, 7.5)	135.18	CH	4, 7, 8a
6	7.89 (1H, *t*, 7.5)	133.75	CH	4a, 8
7	8.14 (1H, *dt*, 1.5, 7.5)	139.89	CH	5, 8
8	8.44 (1H, *d*, 7.5)	123.60	CH	4a, 6
8a		144.33	C	
1′	7.70 (1H, *d*, 15.6)	119.79	CH	3, 1″
2′	8.10 (1H, *d*, 15.6)	154.05	CH	2, 2″, 6″
1″		131.48	C	
2″	7.53 (1H, *d*, 1.8)	116.88	CH	2′, 3″,4″, 6″
3″		153.32	C	
3″-OCH_3	3.97 (3H, *s*)	61.08	CH_3	3″
4″		156.56	C	
5″	6.95 (1H, *d*, 8.1)	120.93	CH	1″, 3″
6″	7.38 (1H, *dd*, 1.8, 8.1)	130.47	CH	2′, 2″
1‴		149.31	C	
2‴	7.63 (2H, *d*, 8.1)	130.69	CH	3‴, 4‴, 6‴
6‴				2‴, 4‴, 5‴

Table 18 (Continued)

Position	***δ*$_H$, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
3‴	7.11 (2H, *d*, 8.1)	133.11	CH	1‴, 4‴-CH_3, 5‴
5‴				1‴, 3‴, 4‴-CH_3
4‴		143.18	C	
4‴-CH_3	2.32 (3H, *s*)	26.01	CH_3	3‴, 4‴, 5‴

Table 19 Crystal data of **B1F**.

Identification code	**B1F**
Empirical formula	$C_{19}H_{18}NO_2^+ \; C_7H_7O_3S^-$
Formula weight	463.53
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Pc
Unit cell dimensions	a = 6.9237(5) Å α = 90°
	b = 11.1007(7) Å β = 106.507(3)°
	c = 15.1376(9) Å γ = 90°
Volume	1115.49(13) Å^3
Z, Calculated density	2, 1.380 Mg/m^3
Absorption coefficient	0.184 mm^{-1}
F(000)	488
Crystal size	0.58 x 0.23 x 0.13 mm
Theta range for data collection	1.83 to 25.00°
Limiting indices	-8<=h<=8, -9<=k<=13, -17<=l<=17
Reflections collected / unique	5512 / 3665 [R(int) = 0.0140]
Completeness to theta = 25.00	99.4 %
Max. and min. transmission	0.9764 and 0.9006
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3665 / 2 / 303

Table 19 (Continued)

Goodness-of-fit on F^2	1.057
Final R indices [I>2σ(I)]	R1 = 0.0324, wR2 = 0.0852
R indices (all data)	R1 = 0.0330, wR2 = 0.0861
Largest diff. peak and hole	0.194 and -0.177 e.Å3

Table 20 Bond lengths [Å] and angles [°] for **B1F**

S1-O3	1.443(2) 1.4353	C8-C9	1.405(3)
S1-O4	(17) 1.4502(18)	C9-C10	1.454(3)
S1-O5	1.782(2)	C10-C11	1.319(3)
S1-C20	1.393(2)	C11-C12	1.452(3)
N1-C1	1.348(2)	C12-C13	1.406(3)
N1-C9	1.478(2)	C12-C17	1.391(3)
N1-C18	1.368(2)	C13-C14	1.372(3)
O1-C14	1.340(2)	C14-C15	1.398(3)
O2-C15	1.422(3)	C15-C16	1.389(3)
O1-C19	1.402(3)	C16-C17	1.371(3)
C1-C2	1.415(3)	C20-C21	1.384(3)
C1-C6	1.376(3)	C20-C25	1.371(3)
C2-C3	1.397(4)	C21-C22	1.392(4)
C3-C4	1.354(3)	C22-C23	1.376(4)
C4-C5	1.403(3)	C23-C24	1.371(4)
C5-C6	1.404(3)	C23-C26	1.521(4)
C6-C7	1.351(3)	C24-C25	1.379(3)
C7-C8			
N1-C1-C2	122.27(17)	C7-C6-C1	118.65(17)
N1-C1-C6	118.64(16)	C7-C8-C9	121.17(18)
N1-C9-C8	118.89(17)	C8-C7-C6	120.40(17)
N1-C9-C10	119.57(17)	C8-C9-C10	121.51(17)
O1-C14-C13	126.38(18)	C10-C11-C12	126.48(19)
O1-C14-C15	113.39(17)	C11-C10-C9	124.26(18)
O2-C15-C14	122.40(18)	C13-C12-C11	119.02(17)

Table 20 (Continued)

O2-C15-C16	118.80(18)	C13-C14-C15	120.23(17)
O3-S1-O5	112.57(12)	C14-C13-C12	120.95(18)
O3-S1-C20	105.98(10)	C16-C15-C14	118.78(17)
O4-S1-O3	114.21(11)	C16-C17-C12	120.74(18)
O4-S1-O5	112.68(11)	C17-C12-C11	122.76(17)
O4-S1-C20	106.66(10)	C17-C12-C13	118.22(17)
O5-S1-C20	103.74(10)	C17-C16-C15	121.08(18)
C1-N1-C18	118.66(15)	C20-C21-C22	119.6(2)
C9-N1-C1	122.01(16)	C20-C25-C24	121.4(2)
C9-N1-C18	119.32(15)	C21-C20-S1	120.24(17)
C2-C1-C6	119.09(17)	C22-C23-C26	120.7(3)
C2-C3-C4	120.9(2) 119.7	C23-C22-C21	121.6(2)
C3-C2-C1	(2) 120.6(2)	C23-C24-C25	121.0(2)
C4-C5-C6	120.2(2) 119.41	C24-C23-C22	118.0(2)
C5-C4-C3	(18) 121.90	C24-C23-C26	121.3(3)
C5-C6-C1	(18)	C25-C20-S1	121.29(17)
C5-C6-C7		C25-C20-C21	118.5(2)

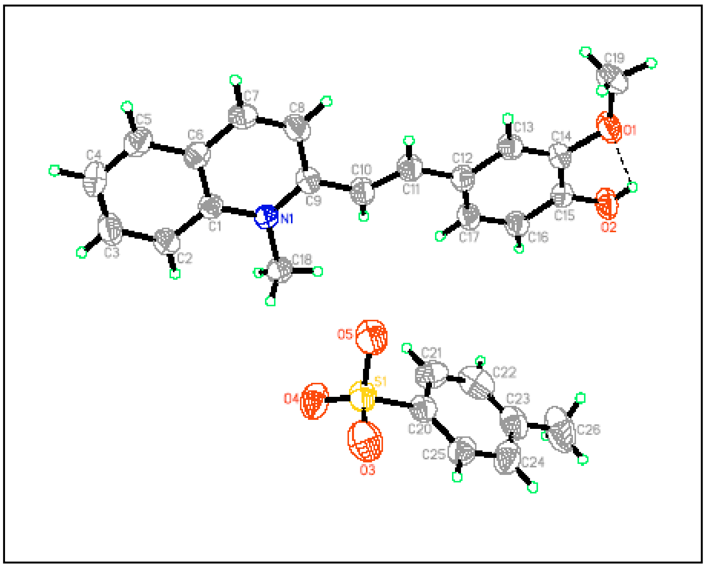


Figure 13 Structure of **B1F**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

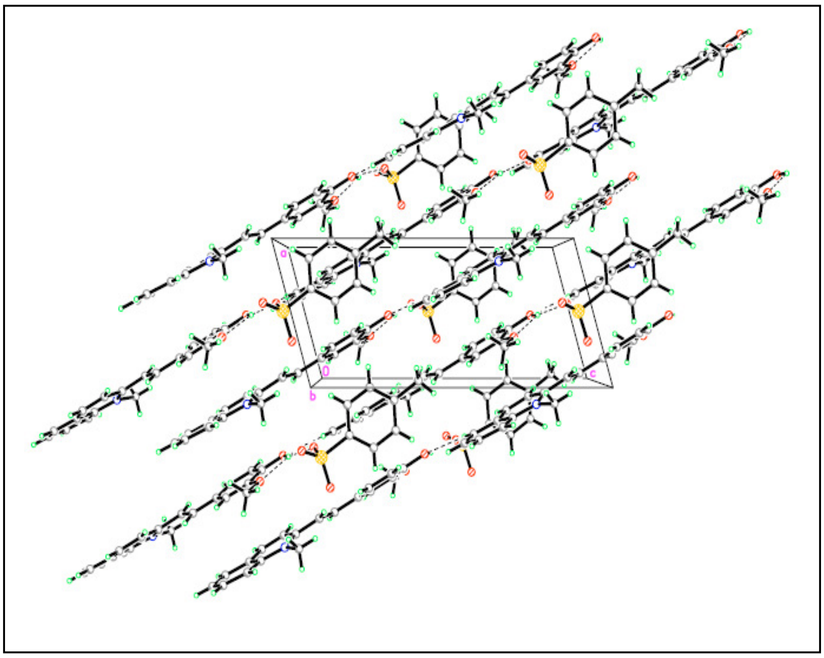
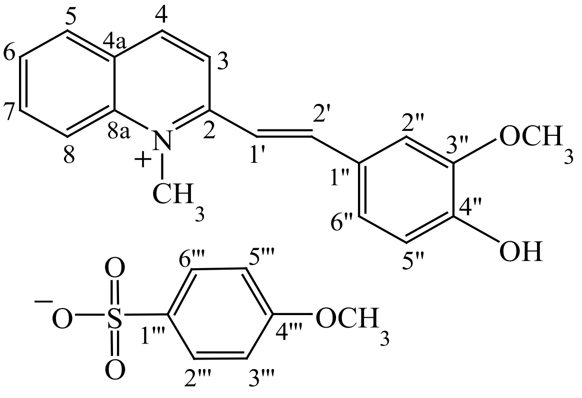


Figure 14 Packing diagram of **B1F** viewed down the *b* axis with H-bonds shown as dash lines.

3.4.9 2-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (B2F)



B2F

Compound **B2F** was obtained as a brown solid, mp. 257-259 °C. The UV-Vis and FT-IR spectra of **B2F** (**Fig. 107** and **108**) were closely resembled with those of compound **B1F**. ^{1}H NMR spectrum of **B2F** (**Fig.109,** see **Table 21**) exhibited the same pattern as compound **B1F**. The difference was found at the signal of 4‴-OCH_3 which was observed at δ 3.79 (3H, *s*). The ^{13}C NMR and DEPT spectra data (**Fig. 110** and **111, see Table 21**) exhibited twenty four signals for twenty six carbons with eight quaternary carbons (δ 164.63, 161.78, 156.60, 153.32, 145.03, 144.29, 132.49 and 131.42), thirteen methines (δ 154.09, 148.67, 139.92, 135.18, 133.76, 132.29, 130.45, 125.77, 123.60, 120.93, 119.69, 117.68 and 116.86) and three methyls (δ 61.08, 60.08 and 44.49). HMBC correlation (**Fig. 112** see **Table 21**) corresponded to the assigned structure. Consequently, compound **B2F** is 2-[(*E*)-2′-(4″-hydroxy-3″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate.

The crystal structure of **B2F** was illustrated in **Fig. 15** and **16** which showed the tertiary structure and the packing diagram of **B2F**. The crystal and experiment data were given in **Table 22**. Bond lengths and angles were shown in **Table 23.** The X-ray study showed that **B2F** crystallized in noncentrosymmetric space group, **Pc.**

The SHG efficiency of **B2F** was about 0.45 times that of urea. It was found that compound **B2F** showed very good stability under laser irradiation (1064 nm, 8 mJ/pulse, 8 ns, and 10 Hz) and no sign of decomposition.

Table 21 ^{1}H, ^{13}C and HMBC of compound **B2F**

Position	***δ_H*, *mult*, *J* (Hz)**	***δ_C***	**DEPT**	**HMBC**
1-CH_3	4.59 (3H, *s*)	44.49	CH_3	2, 8a
2		161.78	C	
3	8.45 (1H, *d*, 9)	125.77	CH	2, 4a, 1′
4	8.87 (1H, *d*, 9)	148.67	CH	2, 3, 5, 8a
4a		132.49	C	
5	8.26 (1H, *br d*, 7.2)	135.18	CH	4, 7, 8a
6	7.89 (1H, *t*, 7.2)	133.76	CH	4a, 8
7	8.14 (1H, *dt*, 1.5, 7.2)	139.92	CH	5, 6, 8
8	8.43 (1H, *d*, 7.2)	123.60	CH	4a, 6
8a		144.29	C	
1′	7.69 (1H, *d*, 15.6)	119.69	CH	3, 1″
2′	8.08 (1H, *d*, 15.6)	154.09	CH	2, 2″, 6″
1″		131.42	C	
2″	7.52 (1H, *d*, 1.8)	116.86	CH	2′, 3″,4″, 6″
3″		153.32	C	
3″-OCH_3	3.97 (3H, *s*)	61.08	CH_3	3″
4″		156.60	C	
5″	6.96 (1H, *d*, 8.4)	120.93	CH	1″, 3″, 4″
6″	7.38 (1H, *dd*, 1.8, 8.4)	130.45	CH	2′, 2″, 4″
1‴		145.03	C	

Table 21 (Continued)

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
2‴	7.69 (2H, *d*, 9.0)	132.29	CH	4‴, 6‴
6‴				2‴, 4‴
3‴	6.81 (2H, *d*, 9.0)	117.68	CH	1‴, 4‴, 5‴
5‴				1‴, 3‴, 4‴
4‴		164.63	C	
4‴-OCH_3	3.79 (3H, *s*)	60.08	CH_3	4‴

Table 22 Crystal data of **B2F**.

Identification code	**B2F**
Empirical formula	$C_{19}H_{18}NO_2^{+}\cdot C_7H_7O_4S^{-}$
Formula weight	479.53
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Pc
Unit cell dimensions	a = 10.98950(10) Å α = 90°
	b = 7.13630(10) Å β = 110.3(10)°
	c = 15.6341(2) Å γ = 90°
Volume	1149.94(2) $Å^3$
Z, Calculated density	2, 1.385 Mg/m^3
Absorption coefficient	0.185 mm^{-1}
F(000)	504
Crystal size	0.51 x 0.14 x 0.08 mm
Theta range for data collection	1.98 to 30.00°
Limiting indices	-14<=h<=15, -10<=k<=10, -21<=l<=21
Reflections collected / unique	24429 / 6583 [R(int) = 0.0299]
Completeness to theta = 30.00	100.0 %
Max. and min. transmission	0.9859 and 0.9111

Table 22 (Continued)

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6583 / 2 / 310
Goodness-of-fit on F^2	1.025
Final R indices [I>2σ(I)]	R1 = 0.0432, wR2 = 0.0982
R indices (all data)	R1 = 0.0620, wR2 = 0.1072
Largest diff. peak and hole	0.291 and -0.253 e.Å3

Table 23 Bond lengths [Å] and angles [°] for **B2F**

S1-O1	1.4360(17)	C8-C9	1.404(3)
S1-O2	1.4443(18)	C8-C13	1.402(3)
S1-O3.	1.4356(17)	C9-C10	1.371(3)
S1-C1	1.777(2) 1.369	C10-C11	1.375(4)
O4-C4	(3) 1.411(4)	C11-C12	1.372(3)
O4-C7	1.364(2) 1.379	C12-C13	1.420(3)
O5-C22	(2) 1.412(3)	C13-C14	1.410(3)
O6-C21	1.397(2) 1.349	C14-C15	1.357(3)
O6-C26	(2) 1.476(3)	C15-C16	1.403(3)
N1-C8	1.383(3) 1.383	C16-C17	1.459(2)
N1-C16	(3)	C17-C18	1.333(3)
N1-C25	1.367(4) 1.384	C18-C19	1.464(2)
C1-C2	(4) 1.383(3)	C19-C20	1.400(3)
C1-C6	1.400(3)	C19-C24	1.382(3)
C2-C3		C20-C21	1.379(2)
C3-C4		C21-C22	1.398(3)
C4-C5		C22-C23	1.380(3)
C5-C6		C23-C24	1.387(2)
O1-S1-O2	113.00(13)	C8-N1-C25	117.81(15)
O1-S1-C1	106.86(10)	C8-C13-C12	119.40(18)
O2-S1-C1	106.24(11)	C8-C13-C14	118.97(16)
O3-S1-O1	113.44(12)	C9-C10-C11	122.4(2)
O3-S1-O2	110.74(12)	C10-C9-C8	118.9(2)

Table 23 (Continued)

O3-S1-C1	105.96(9) 115.1	C11-C12-C13	119.6(2)
O4-C4-C3	(2) 124.4(2)	C12-C11-C10	119.93(18)
O4-C4-C5	121.51(17)	C13-C8-C9	119.71(16)
N1-C8-C9		C14-C13-C12	121.62(19)
N1-C8-C13	118.78(16)	C15-C14-C13	120.09(19)
N1-C16-C15	118.97(16)	C14-C15-C16	121.11(17)
N1-C16-C17	119.68(17)	C15-C16-C17	121.29(16)
O5-C22-C21	117.94(17)	C16-N1-C8	122.03(16)
O5-C22-C23	122.12(18)	C16-N1-C25	120.16(15)
O6-C21-C20	124.96(18)	C17-C18-C19	126.33(18)
O6-C21-C22	115.49(16)	C18-C17-C16	123.00(18)
C1-C6-C5	120.6(2) 120.47	C19-C24-C23	120.43(17)
C2-C1-S1	(15) 119.18(19)	C20-C19-C18	118.13(17)
C2-C1-C6	120.0(2) 120.9	C20-C21-C22	119.54(17)
C2-C3-C4	(2)	C21-O6-C26	117.64(16)
C3-C2-C1	118.5(2) 118.7	C21-C20-C19	120.68(18)
C4-O4-C7	(2)	C22-C23-C24	120.27(18)
C4-C5-C6	120.5(2) 120.24	C23-C22-C21	119.94(16)
C5-C4-C3	(16)	C24-C19-C18	122.73(17)
C6-C1-S1		C24-C19-C20	119.14(16)

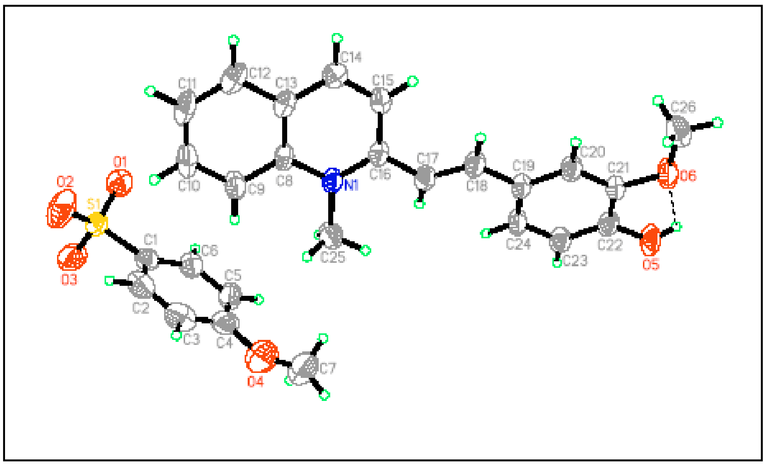


Figure 15 Structure of **B2F**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

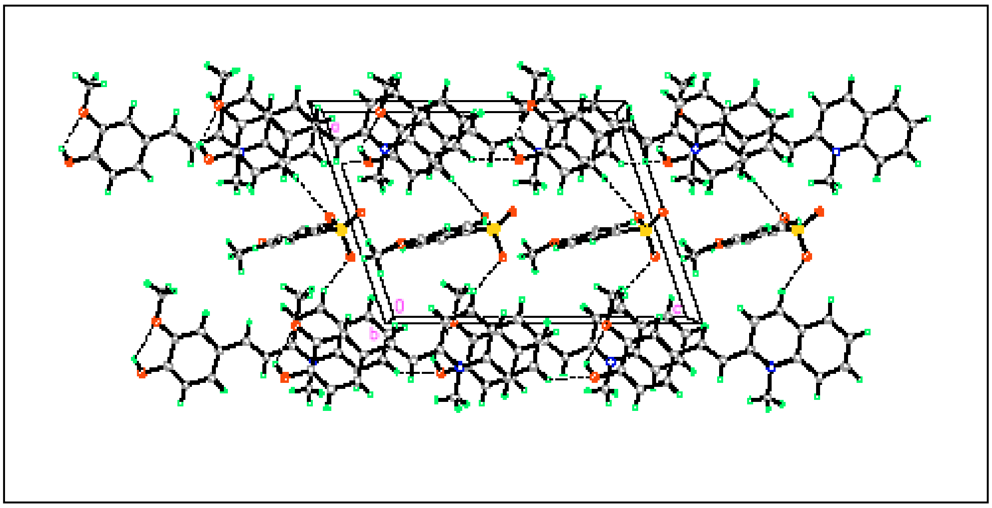
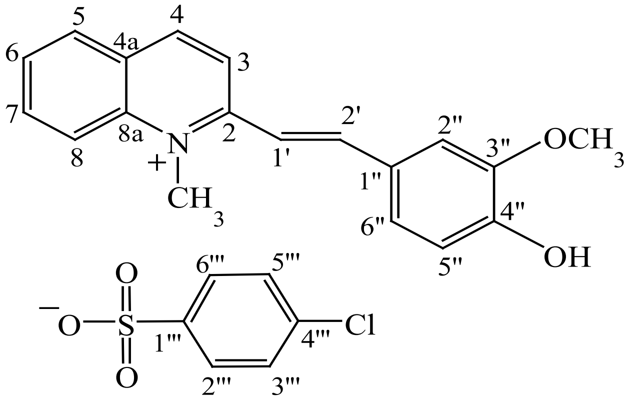


Figure 16 Packing diagram of **B2F** viewed down the *b* axis with H-bonds shown as dash lines.

3.4.10 2-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (B3F)



B3F

A brown solid of compound **B3F** was obtained in a good yield (87%), mp. 262-264°C. The UV-Vis and FT-IR spectra of **B3D** (**Fig. 113** and **114**) were closely resembled those of compound **B1F**. ^{1}H NMR spectrum of **B3F** (**Fig. 115,** see **Table 24**) was similar to that of **B1F** except for anionic part which showed only equivalent protons of *p*-disubstituted aromatic at δ 7.76 (2H, *d*, J = 8.4 Hz, H-2‴, H-6‴) and 7.27 (2H, *d*, J = 8.4 Hz, H-3‴, H-5‴). The ^{13}C NMR and DEPT spectra data (**Fig. 116** and **117** , see **Table 24)** exhibited twenty three signals for twenty five carbons with eight quaternary carbons (δ 161.76, 156.61, 153.31, 151.48, 144.30, 139.03, 132.46 and 131.37), thirteen methines (δ 154.10, 148.69, 139.96, 135.18, 133.78, 132.57, 132.46, 130.42, 125.74, 123.52, 120.93, 119.59 and 116.78) and two methyls (δ 61.06 and 44.54). HMBC correlation (**Fig. 118,** see **Table 24**) corresponded to the assigned structure. These spectroscopic data confirmed the structure of compound **B3F.**

The crystal structure of **B3F** was illustrated in **Fig. 17** and **18** which showed the tertiary structure and the packing diagram of **B3F**. The crystal and experiment data were given in **Table 25**. Bond lengths and angles were shown in **Table 26.** It was found that **B3F** crystallized in noncentrosymmetric, **Pc**, space group.

The SHG efficiency of **B3F** was about 0.50 times that of urea. It was found that compound **B3F** showed very good stability under laser irradiation (1064 nm, 8 mJ/pulse, 8 ns, and 10 Hz) and no sign of decomposition.

Table 24 ^{1}H, ^{13}C and HMBC of compound **B3F**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.59 (3H, *s*)	44.54	CH_3	2, 8a
2		161.76	C	
3	8.42 (1H, *d*, 9)	125.74	CH	2, 4a, 1′
4	8.84 (1H, *d*, 9)	148.69	CH	2, 5, 8a
4a		132.46	C	
5	8.25 (1H, *dd*, 1.5, 7.8)	135.18	CH	4, 8a
6	7.89 (1H, *t*, 7.8)	133.78	CH	4a, 8
7	8.14 (1H, *dt*, 1.5, 7.8)	139.96	CH	8
8	8.40 (1H, *d*, 7.8)	123.52	CH	4a, 6
8a		144.30	C	
1′	7.66 (1H, *d*, 15.6)	119.59	CH	3, 1″
2′	8.05 (1H, *d*, 15.6)	154.10	CH	2, 2″, 6″
1″		131.37	C	
2″	7.48 (1H, *d*, 1.8)	116.78	CH	2′, 3″,4″, 6″
3″		153.31	C	
3″-OCH_3	3.98 (3H, *s*)	61.06	CH_3	3″
4″		156.61	C	
5″	6.97 (1H, *d*, 8.1)	120.93	CH	1″, 3″, 4″
6″	7.37 (1H, *dd*, 1.8, 8.1)	130.42	CH	2″
1‴		151.48	C	

Table 24 (Continued)

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
2′′′	7.76 (2H, *d*, 8.4)	132.46	CH	4′′′, 6′′′
6′′′				2′′′, 4′′′
3′′′	7.27 (2H, *d*, 8.4)	132.57	CH	1′′′, 4′′′, 5′′′
5′′′				1′′′, 3′′′, 4′′′
4′′′		139.03	C	

Table 25 Crystal data of **B3F**.

Identification code	**B3F**
Empirical formula	$C_{19}H_{18}NO_2^{+}\cdot C_6H_4ClO_3S^{-}$
Formula weight	967.91
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Pc
Unit cell dimensions	a = 7.83860(10) Å α = 90°
	b = 6.77310(10) Å β = 108.4760(10)°
	c = 21.7096(3) Å γ = 90°
Volume	1093.19(3) Å^3
Z, Calculated density	1, 1.470 Mg/m^3
Absorption coefficient	0.310 mm^{-1}
F(000)	504
Crystal size	0.22 x 0.15 x 0.06 mm
Theta range for data collection	2.74 to 30.00°
Limiting indices	-11<=h<=11, -9<=k<=9, -30<=l<=30
Reflections collected / unique	19358 / 6151 [R(int) = 0.0406]
Completeness to theta = 30.00	99.9 %
Max. and min. transmission	0.9817 and 0.9364
Refinement method	Full-matrix least-squares on F^2

Table 25 (Continued)

Data / restraints / parameters	6151 / 2 / 321
Goodness-of-fit on F^2	1.041
Final R indices [I>2σ(I)]	R1 = 0.0389, wR2 = 0.0877
R indices (all data)	R1 = 0.0454, wR2 = 0.0923
Largest diff. peak and hole	0.494 and -0.413 e.Å^3

Table 26 Bond lengths [Å] and angles [°] for **B3F**

Cl1-C4	1.751(2)	C7-C12	1.413(3) 1.378
S1-O1	1.4694(15)	C8-C9	(3) 1.400(3)
S1-O2	1.4487(15)	C9-C10	1.374(3) 1.415
S1-O3	1.4468(15)	C10-C11	(3) 1.424(3)
S1-C1	1.778(2) 1.401	C11-C12	1.358(3) 1.420
N1-C7	(2) 1.353(2)	C12-C13	(3) 1.445(3)
N1-C15	1.477(2) 1.360	C13-C14	1.338(3) 1.459
N1-C24	(2) 1.370(2)	C14-C15	(3)
O4-C21	1.429(2) 1.395	C15-C16	1.405(3)
O5-C20	(3) 1.403(3)	C16-C17	1.400(3)
O5-C25	1.391(3) 1.382	C17-C18	1.384(3) 1.413
C1-C2	(3) 1.392(3)	C18-C19	(2) 1.388(3)
C1-C6	1.381(3)	C18-C23	1.382(3)
C2-C3	1.403(3)	C19-C20	
C3-C4		C20-C21	
C4-C5		C21-C22	
C5-C6		C22-C23	
C7-C8			
N1-C7-C8	121.76(17)	C7-C12-C11	119.70(18)
N1-C7-C12	118.77(17)	C7-C12-C13	118.64(18)
N1-C15-C14	118.78(17)	C7-N1-C24	118.18(16)
N1-C15-C16	119.21(17)	C8-C7-C12	119.46(18)
O1-S1-C1	104.99(9)	C8-C9-C10	121.3(2)
O2-S1-O1	111.78(9)	C9-C8-C7	119.61(19)

Table 26 (Continued)

O2-S1-C1	105.69(9)	C10-C11-C12	119.8(2)
O3-S1-O1	112.64(9)	C11-C10-C9	120.05(19)
O3-S1-O2	114.85(9)	C11-C12-C13	121.66(18)
O3-S1-C1	105.95(9)	C13-C14-C15	120.88(17)
O4-C21-C20	118.00(17)	C20-O5-C25	116.48(15)
O4-C21-C22	122.39(17)	C14-C15-C16	121.99(17)
O5-C20-C19	125.27(16)	C15-N1-C7	122.35(16)
O5-C20-C21	115.28(16)	C15-N1-C24	119.46(16)
C2-C1-S1	121.27(15)	C16-C17-C18	124.82(17)
C2-C1-C6	119.74(19)	C17-C16-C15	125.20(17)
C3-C2-C1	119.98(19)	C19-C18-C17	118.91(16)
C3-C4-C5	121.8(2)	C19-C20-C21	119.44(17)
C3-C4-Cl1	119.52(16)	C20-C19-C18	121.03(16)
C4-C3-C2	119.20(19)	C22-C21-C20	119.61(17)
C5-C4-Cl1	118.58(16)	C22-C23-C18	120.73(18)
C5-C6-C1	120.48(19)	C23-C18-C17	122.47(17)
C6-C1-S1	119.00(16)	C23-C18-C19	118.61(17)
C6-C5-C4	118.75(19)	C23-C22-C21	120.57(17)
C14-C13-C12	120.38(18)		

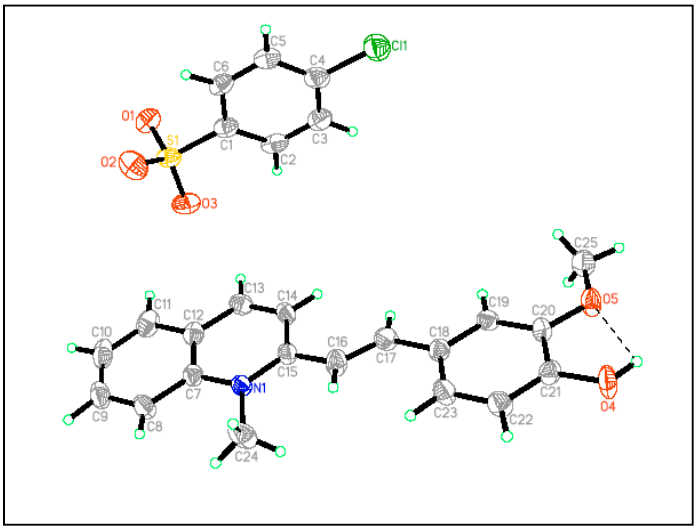


Figure 17 Structure of **B3F**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

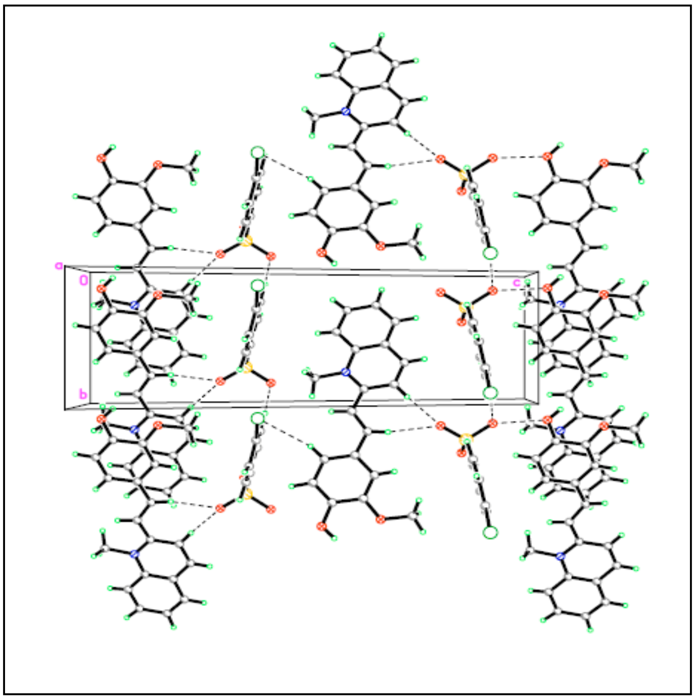
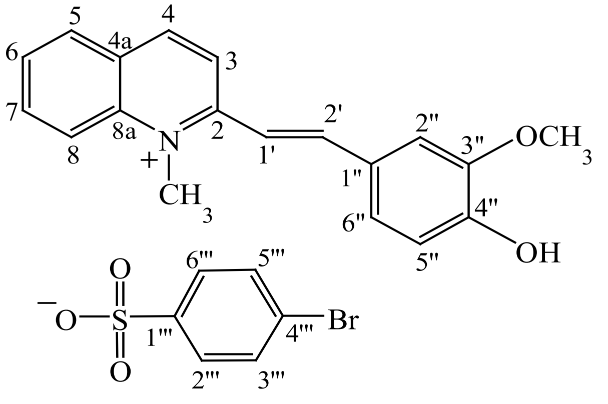


Figure 18 Packing diagram of **B3F** viewed down the *a* axis with H-bonds shown as dash lines.

3.4.11 2-[(*E*)-2′-(4″-Hydroxy-3″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-bromobenzenesulfonate (B4F)



B4F

Compound **B4F** was synthesized as a red-brown solid, mp. 288-290 °C. The UV-Vis and FT-IR spectra of **B4F** (**Fig. 119** and **120**) were similar to that of compound **B1F**. ^{1}H NMR spectrum of **B4F** (**Fig. 121,** see **Table 27**) showed the same pattern as compound **B1F**. The difference was shown in the signal of anion part whose ^{1}H NMR spectrum showed only signals of AA′ BB′ pattern, indicating C-4‴ position of Br. The ^{13}C NMR and DEPT spectra data (**Fig. 122** and **123,** see **Table 27**) exhibited twenty three signals for twenty five carbons with eight quaternary carbons (δ 161.77, 156.38, 153.36, 152.10, 144.36, 132.57, 131.68 and 127.12), thirteen methines (δ 153.78, 148.66, 139.85, 135.66, 135.19, 133.76, 132.84, 130.47, 125.87, 124.00, 120.95, 120.20 and 117.07) and two methyls (δ 61.11 and 44.69). HMBC correlation (**Fig. 124.** see **Table 27**) corresponded to the assigned structure. These assignments clearly supported the proposed structure.

The crystal structure of **B4F** was illustrated in **Fig. 19** and **20** which showed the tertiary structure and the packing diagram of **B4F**. The crystal and experiment data were given in **Table 28**. Bond lengths and angles are shown in **Table 29.** It was found that **B4F** crystallized out in noncentrosymmetric, **Pc**, space group.

The SHG efficiency of **B4F** was about 0.80 times that of urea. It was found that compound **B4F** showed very good stability under laser irradiation (1064 nm, 8 mJ/pulse, 8 ns, and 10 Hz) and no sign of decomposition.

Table 27 ^{1}H, ^{13}C and HMBC of compound **B4F**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH$_3$	4.57 (3H, *s*)	44.69	CH$_3$	2, 8a
2		161.77	C	
3	8.50 (1H, *d*, 9.0)	125.87	CH	2, 4a, 1′
4	8.93 (1H, *d*, 9.0)	148.66	CH	2, 5, 8a
4a		132.57	C	
5	8.30 (1H, *dd*, 1.5, 7.5)	135.19	CH	4, 7, 8a
6	7.90 (1H, *t*, 7.5)	133.76	CH	4a, 8
7	8.15 (1H, *t*, 7.5)	139.85	CH	6
8	8.49 (1H, *d*, 7.5)	124.00	CH	4a
8a		144.36	C	
1′	7.73 (1H, *d*, 15.6)	120.20	CH	3, 1″
2′	8.15 (1H, *d*, 15.6)	153.78	CH	2, 2″, 6″
1″		131.68	C	
2″	7.57 (1H, *d*, 1.8)	117.07	CH	3″,4″, 6″
3″		153.36	C	
3″-OCH$_3$	3.95 (3H, *s*)	61.11	CH$_3$	3″
4″		156.38	C	
5″	6.94 (1H, *d*, 8.1)	120.95	CH	1″, 3″, 4″
6″	7.41 (1H, *dd*, 1.8, 8.1)	130.47	CH	2″
1‴		152.10	C	
2‴	7.61 (2H, *d*, 8.4)	132.84	CH	4‴, 6‴
6‴				2‴, 4‴
3‴	7.48 (2H, *d*, 8.4)	135.66	CH	1‴, 4‴, 5‴
5‴				1‴, 3‴, 4‴
4‴		127.12	C	

Table 28 Crystal data of **B4F**.

Identification code	**B4F**
Empirical formula	$C_{19}H_{18}NO_2^+ \cdot C_6H_4BrO_3S^-$
Formula weight	528.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Pc
Unit cell dimensions	a = 7.942(3) Å α = 90°
	b = 6.751(2) Å β = 108.861(12)°
	c = 21.964(8) Å γ = 90°`
Volume	1114.4(7) Å^3
Z, Calculated density	2, 1.575 Mg/m^3
Absorption coefficient	1.977 mm^{-1}
F(000)	540
Crystal size	0.51 x 0.31 x 0.05 mm
Theta range for data collection	1.96 to 26.00 °
Limiting indices	-9<=h<=9, -8<=k<=6, -25<=l<=27
Reflections collected / unique	5630 / 3825 [R(int) = 0.0315]
Completeness to theta = 26.00	99.6 %
Max. and min. transmission	0.8991 and 0.4309
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3825 / 2 / 300
Goodness-of-fit on F^2	0.998
Final R indices [I>2σ(I)]	R1 = 0.0370, wR2 = 0.0881
R indices (all data)	R1 = 0.0407, wR2 = 0.0902
Largest diff. peak and hole	0.580 and -0.322 e.Å^3

Table 29 Bond lengths [Å] and angles [°] for **B4F**

Br1-C4	1.905(4)	C7-C12	1.405(5)
S1-O1	1.461(3) 1.437	C8-C9	1.374(6)
S1-O2	(3) 1.443(3)	C9-C10	1.392(7)
S1-O3	1.769(4) 1.362	C10-C11	1.363(6)
S1-C1	(4) 1.368(4)	C11-C12	1.411(5)
O4-C21	1.425(4) 1.394	C12-C13	1.414(5)
O5-C20	(4) 1.353(4)	C13-C14	1.353(5)
O5-C25	1.487(4)	C14-C15	1.416(5)
N1-C7	1.398(5) 1.398	C15-C16	1.449(5)
N1-C15	(6) 1.380(6)	C16-C17	1.320(5)
N1-C24	1.377(6) 1.395	C17-C18	1.465(5)
C1-C2	(6) 1.390(6)	C18-C19	1.409(5)
C1-C6	1.419(5)	C18-C23	1.387(5)
C2-C3		C19-C20	1.381(5)
C3-C4		C20-C21	1.408(5)
C4-C5		C21-C22	1.381(5)
C5-C6		C22-C23	1.381(5)
C7-C8			
O1-S1-C1	105.24(17)	C7-C12-C11	119.7(4)
O2-S1-O1	111.79(19)	C7-C12-C13	118.1(3)
O2-S1-O3	115.6(2)	C8-C9-C10	121.5(4)
O2-S1-C1	105.60(18)	C9-C8-C7	119.4(4)
O3-S1-O1	112.13(19)	C10-C11-C12	120.4(4)
O3-S1-C1	105.49(18)	C11-C10-C9	120.0(4)
O4-C21-C20	118.2(3) 121.9	C12-C7-C8	119.0(4)
O4-C21-C22	(3)	C13-C12-C11	122.1(4)
O5-C20-C19	125.2(3)	C13-C14-C15	121.2(3)
O5-C20-C21	115.3(3) 121.4	C14-C13-C12	120.6(3)
N1-C7-C8	(3) 119.6(3)	C14-C15-C16	121.8(3)
N1-C7-C12	118.4(3) 119.8	C15-N1-C7	122.0(3)
N1-C15-C14	(3)	C15-N1-C24	119.5(3)
N1-C15-C16		C16-C17-C18	124.9(3)

Table 29 (Continued)

O5-C20-C21	115.3(3) 121.4	C14-C13-C12	120.6(3)
N1-C7-C8	(3) 119.6(3)	C14-C15-C16	121.8(3)
N1-C7-C12	118.4(3) 119.8	C15-N1-C7	122.0(3)
N1-C15-C14	(3) 122.1(3)	C15-N1-C24	119.5(3)
N1-C15-C16	118.8(4)	C16-C17-C18	124.9(3)
C2-C1-S1	120.5(4) 119.7	C17-C16-C15	125.9(3)
C2-C1-C6	(3) 121.8(4)	C19-C18-C17	118.7(3)
C3-C2-C1	119.6(4) 118.3	C19-C20-C21	119.5(3)
C3-C4-Br1	(3)	C20-O5-C25	117.1(3)
C3-C4-C5	121.2(4) 118.0	C20-C19-C18	120.6(3)
C4-C3-C2	(4) 119.1(3)	C22-C21-C20	120.0(3)
C5-C4-Br1	118.5(3)	C22-C23-C18	121.4(3)
C5-C6-C1		C23-C18-C17	122.8(3)
C6-C5-C4		C23-C18-C19	118.4(3)
C6-C1-S1		C23-C22-C21	120.0(3)
C7-N1-C24			

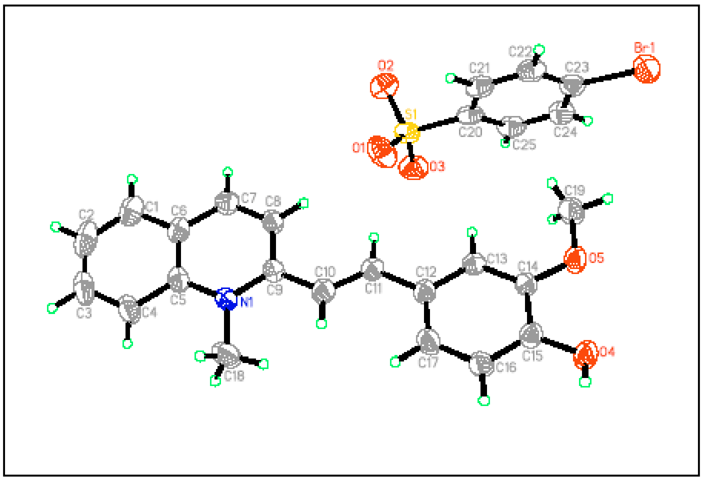


Figure 19 Structure of **B4F**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

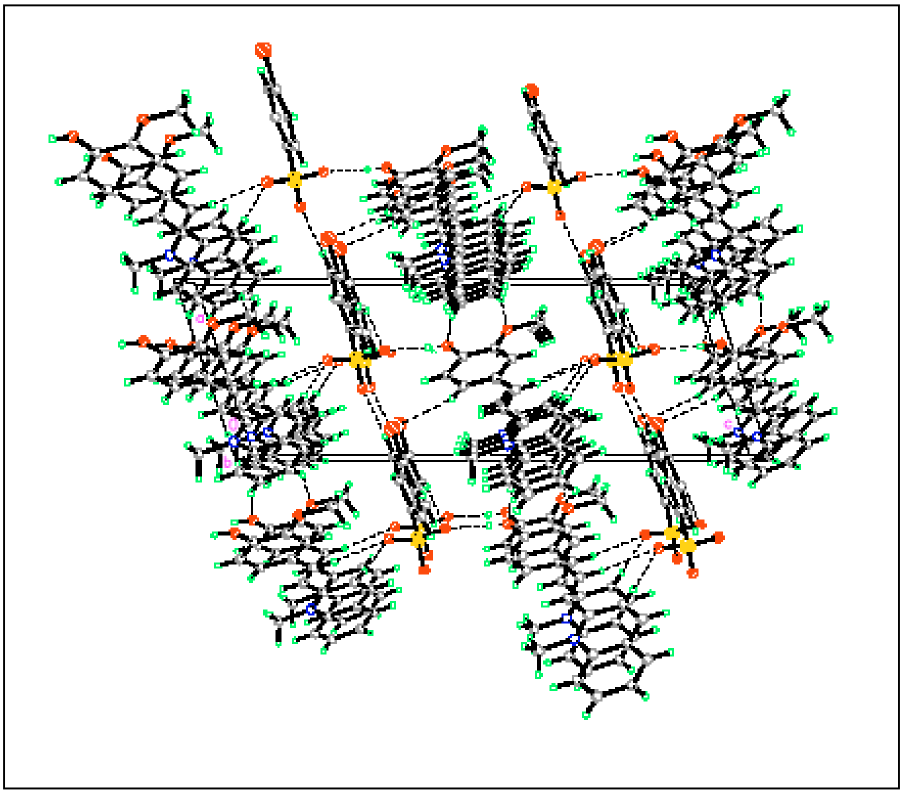
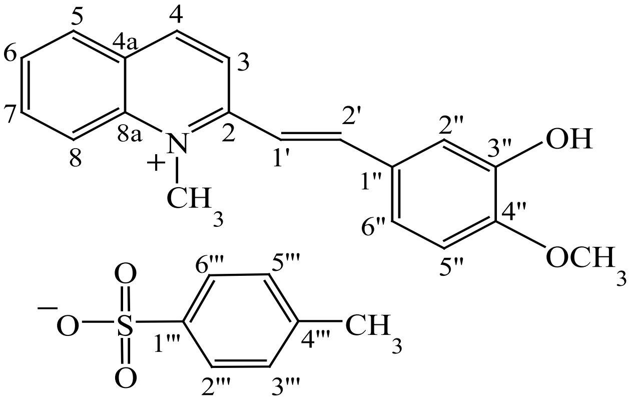


Figure 20 Packing diagram of **B4F** viewed down the *b* axis with H-bonds shown as dash lines.

3.4.12 2-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methylbenzenesulfonate (B1G)



B1G

Compound **B1G** was obtained as an orange solid, mp. 253.255 °C. The UV-Vis absorption bands (**Fig. 125**) were shown at 216.1, 252.1, 306.4 and 431.6 nm. The FT-IR spectrum (**Fig. 126**) exhibited stretching vibrations of O-H (3430 cm^{-1}), C=C (1606 and 1594 cm^{-1}), C-O (1229 cm^{-1}) and S=O in sulfonates (1176 cm^{-1}).

The ^{1}H NMR spectrum (**Fig. 127,** see **Table 30**) showed two fragments of cationic and anionic parts. The former showed characteristic of *trans*-disubstituted double bonds at δ 7.69 (1H, *d*, *J* = 15.9 Hz, H-1′) and δ 8.06 (1H, *d*, *J* = 15.9 Hz, H-2′). Two *singlet* signals at δ4.58 (3H) and 3.94 (3H) were assigned as *N*-CH$_3$ and *O*-CH$_3$ respectively. Three signals of 1,2,4-trisubstituted benzene pattern at δ7.51 (1H, *d*, *J* = 2.1 Hz), δ7.00 (1H, *d*, *J* = 8.4 Hz) and δ7.36 (1H, *dd*, *J* = 2.1, 8.4 Hz) were assigned to H-2″, H-5″ and H-6″ respectively. Two d*oublets* of H-3 and H-4 were observed at δ 8.48 (1H, *J* = 9.0 Hz) and δ 8.91 (1H, *J* = 9.0 Hz) respectively. Resonances of aromatic protons H-5, H-6, H-7 and H-8 were also shown at δ8.29 (*dd*, *J* = 1.5, 7.8 Hz), δ7.91 (*t*, *J* = 7.8 Hz), δ8.15 (*dt*, *J* = 1.5, 7.8 Hz) and δ8.46 (*d*, *J* = 7.8 Hz) respectively. ^{1}H NMR spectrum also showed signals of anionic part. Equivalent protons of *p*-disubstituted aromatic appeared as two *doublets* at δ7.63 (2H, *J* = 8.1 Hz, H-2‴, H-6‴) and δ7.11 (2H, *J* = 8.1 Hz, H-3‴, H-5‴). The singlet signal of 4‴–CH$_3$ was observed at δ 2.33 (3H). The ^{13}C NMR and DEPT spectra (**Fig. 128** and **129,** see **Table 30**) exhibited twenty four signals for twenty six carbons with eight quaternary carbons (δ 161.65, 156.61, 152.12, 149.68, 144.29, 143.19, 132.86 and 132.64), thirteen methines (δ 153.44, 148.94, 139.99, 135.21, 133.84, 133.13, 130.69, 128.50, 125.94, 123.76, 120.85, 119.78 and 116.62) and three methyls (δ 60.83, 44.73 and 26.00). The assigned structure was confirmed by HMBC experiment (**Fig. 130** see **Table 30**). These spectroscopic data confirmed the structure of compound **B1G**.

The crystal structure of **B1G** was illustrated in **Fig. 21** and **22** which showed the tertiary structure and the packing diagram of **B1G**. The crystal and experiment data were given in **Table 31**. Bond lengths and angles were shown in **Table 32.** Compound **B1G** crystallized out in centrosymmetric space group **P2(1)/c**.

Table 30 ^{1}H, ^{13}C and HMBC of compound **B1G**

Position	δ_H, *mult*, *J* (Hz)	δ_C	DEPT	HMBC
1-CH_3	4.58 (3H, *s*)	44.73	CH_3	2, 8a
2		161.65	C	
3	8.48 (1H, *d*, 9.0)	125.94	CH	2, 4a, 1′
4	8.91 (1H, *d*, 9.0)	148.94	CH	2, 4a, 5, 8a
4a		132.64	C	
5	8.29 (1H, *dd*, 1.5, 7.8)	135.21	CH	4, 7, 8a
6	7.91 (1H, *t*, 7.8)	133.84	CH	4a, 8
7	8.15 (1H, *dt*, 1.5, 7.8)	139.99	CH	5, 8
8	8.46 (1H, *d*, 7.8)	123.76	CH	4a, 6, 7
8a		144.29	C	
1′	7.69 (1H, *d*, 15.9)	120.85	CH	3, 1″
2′	8.06 (1H, *d*, 15.9)	153.44	CH	2, 2″, 6″
1″		132.86	C	
2″	7.51 (1H, *d*, 2.1)	119.78	CH	2′, 3″,4″, 6″

Table 30 (Continued)

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
3″		152.12	C	
4″		156.61	C	
4″-OCH$_3$	3.94 (3H, *s*)	60.83	CH$_3$	4″
5″	7.00 (1H, *d*, 8.4)	116.62	CH	1″, 3″, 4″
6″	7.36 (1H, *dd*, 2.1, 8.4)	128.50	CH	2′, 1″, 2″
1‴		149.68	C	
2‴	7.63 (2H, *d*, 8.1)	130.69	CH	3‴, 4‴, 6‴
6‴				2‴, 4‴, 5‴
3‴	7.11 (2H, *d*, 8.1)	133.13	CH	1‴, 2‴, 5‴, CH$_3$
5‴				1‴, 3‴, 6‴ ,CH$_3$
4‴		143.19	C	
4‴-CH$_3$	2.33 (3H, *s*)	26.00	CH$_3$	3‴, 4‴, 5‴

Table 31 Crystal data of **B1G**.

Identification code	**B1G**
Empirical formula	$C_{19}H_{18}NO_2^{+}\cdot C_7H_7O_3S^{-}$
Formula weight	463.53
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2(1)/c
Unit cell dimensions	a = 7.3382(3) Å α = 90°
	b = 21.8714(7) Å β = 100.4640 (10)°
	c = 14.0755(4) Å γ = 90°
Volume	2221.50(13) Å^3
Z, Calculated density	4, 1.386 Mg/m^3
Absorption coefficient	0.185 mm^{-1}

Table 31 (Continued)

F(000)	976
Crystal size	0.50 x 0.24 x 0.10 mm
Theta range for data collection	1.74 to 25.00°
Limiting indices	-8<=h<=8, -25<=k<=25, -16<=l<=16
Reflections collected / unique	17716 / 3896 [R(int) = 0.0248]
Completeness to theta = 25.00	99.6 %
Max. and min. transmission	0.9826 and 0.9131
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3896 / 0 / 301
Goodness-of-fit on F^2	1.039
Final R indices [I>2σ(I)]	R1 = 0.0409, wR2 = 0.0984
R indices (all data)	R1 = 0.0538, wR2 = 0.1067
Largest diff. peak and hole	0.290 and -0.239 e.Å^3

Table 32 Bond lengths [Å] and angles [°] for **B1G**

S1-O1	1.4600(15)	C8-C9	1.383(3)
S1-O2	1.4453(17)	C8-C13	1.391(3)
S1-O3	1.4402(17)	C9-C10	1.384(3)
S1-C3	1.780(2)	C10-C11	1.404(3)
O4-C10	1.363(2)	C11-C12	1.371(3)
O4-C25	1.425(3)	C12-C13	1.402(3)
O5-C11	1.362(2)	C13-C14	1.452(3)
N1-C16	1.339(3)	C14-C15	1.324(3)
N1-C20	1.412(3)	C15-C16	1.452(3)
N1-C26	1.461(3)	C16-C17	1.429(3)
C1-C2	1.383(3) 1.379	C17-C18	1.349(3)
C1-C6	(3)	C18-C19	1.403(3)
C2-C3	1.381(3)	C19-C20	1.410(3)
C3-C4	1.378(3)	C19-C24	1.422(3)

Table 32 (Continued)

C4-C5	1.388(3)	C20-C21	1.383(3)
C5-C6	1.383(3)	C21-C22	1.357(3)
C6-C7	1.507(3)	C23-C24	1.358(4)
C22-C23	1.387(3)		
O1-S1-C3	104.74(9)	O5-C11-C12	122.85(18)
O2-S1-O1	111.25(10)	O5-C11-C10	117.05(18)
O2-S1-C3	106.91(9)	C12-C11-C10	120.10(18)
O3-S1-O2	114.56(11)	C11-C12-C13	121.34(18)
O3-S1-O1	112.80(10)	C8-C13-C12	117.95(18)
O3-S1-C3	105.76(10)	C8-C13-C14	120.03(18)
C10-O4-C25	117.98(17)	C12-C13-C14	122.02(18)
C16-N1-C20	122.49(17)	C15-C14-C13	125.9(2)
C16-N1-C26	120.29(17)	C14-C15-C16	124.9(2)
C20-N1-C26	117.21(17)	N1-C16-C17	118.9(2)
C6-C1-C2	121.0(2) 120.5	N1-C16-C15	119.73(19)
C3-C2-C1	(2) 119.2(2)	C17-C16-C15	121.3(2)
C4-C3-C2	120.51(16)	C18-C17-C16	120.0(2)
C4-C3-S1	120.34(17)	C17-C18-C19	121.6(2)
C2-C3-S1	119.9(2) 121.2	C18-C19-C20	118.7(2)
C3-C4-C5	(2) 118.2(2)	C18-C19-C24	122.7(2)
C6-C5-C4	120.7(2) 121.2	C20-C19-C24	118.6(2)
C1-C6-C5	(2) 121.06(19)	C21-C20-C19	120.04(19)
C1-C6-C7	120.55(19)	C21-C20-N1	121.80(19)
C5-C6-C7	125.23(18)	C19-C20-N1	118.1(2)
C9-C8-C13	115.78(18)	C22-C21-C20	119.5(2)
C8-C9-C10	118.98(19)	C21-C22-C23	122.0(2)
O4-C10-C9		C24-C23-C22	119.9(2)
O4-C10-C11		C23-C24-C19	119.9(2)
C9-C10-C11			

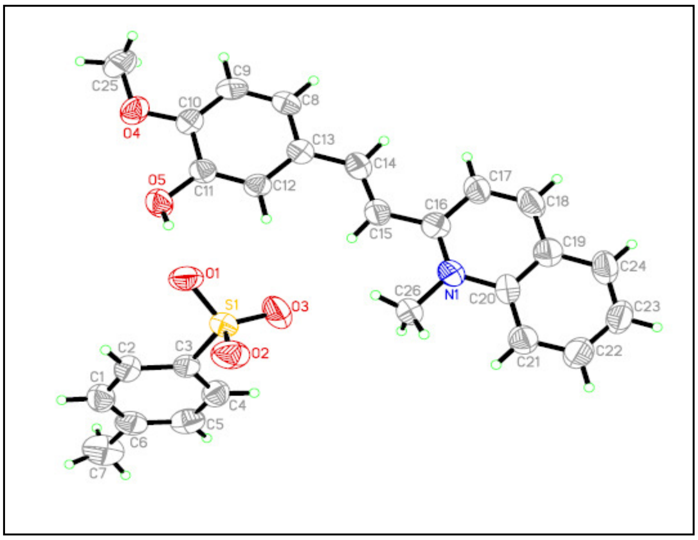


Figure 21 Structure of **B1G**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

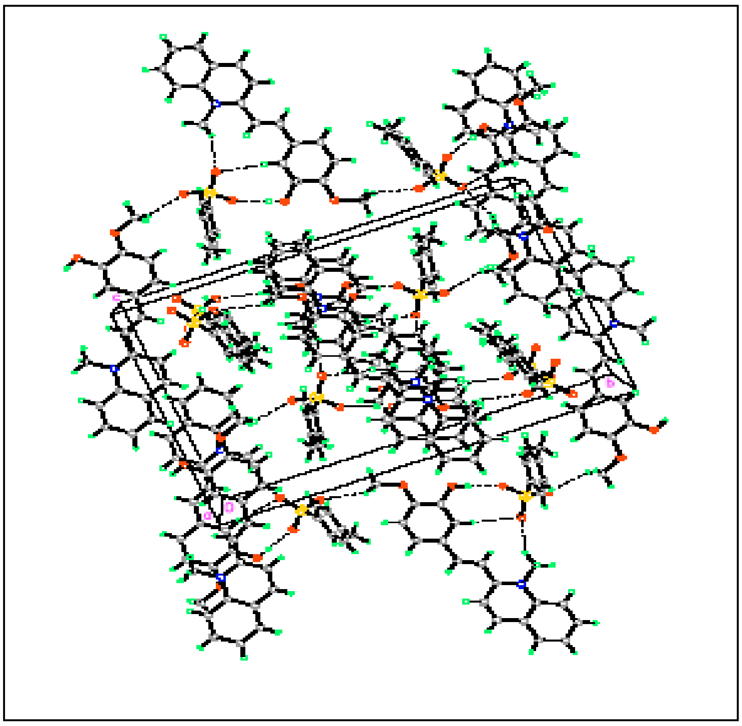
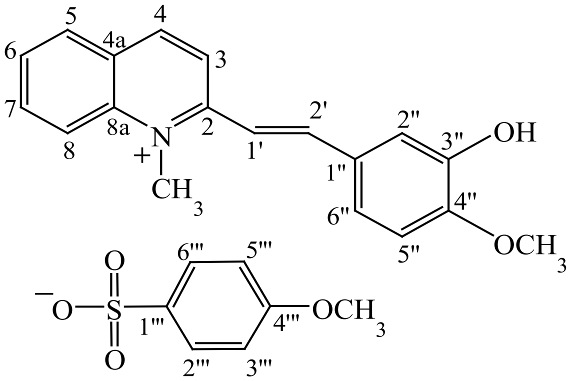


Figure 22 Packing diagram of **B1G** viewed down the *b* axis with H-bonds shown as dash lines.

3.4.13 2-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (B2G)



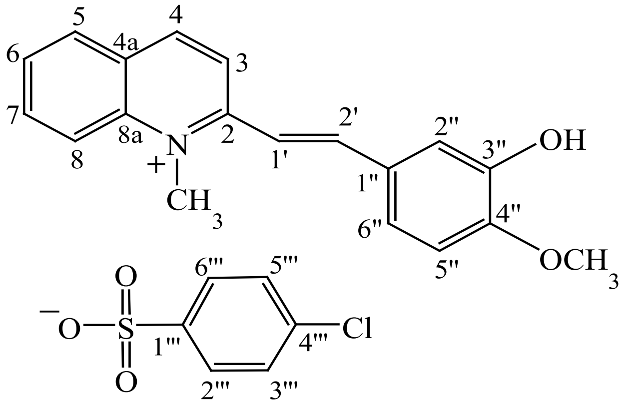
B2G

Compound **B2G** was obtained as an orange solid, mp. 223-225 °C. The UV-Vis and FT-IR spectra of **B2G** (**Fig. 131** and **132**) were closely resembled with those of compound **B1G**. ^{1}H NMR spectrum (**Fig. 133,** see **Table 33**) exhibited the same pattern as compound **B1G**. The difference was found in the signal of 4‴-OCH$_3$ which was observed at δ3.75 (3H, *s*). The ^{13}C NMR and DEPT spectra data (**Fig. 134** and **135,** see **Table 33**) exhibited twenty three signals for twenty six carbons with eight quaternary carbons (δ 159.34, 156.34, 151.27, 146.89, 140.48, 139.11, 127.88 and 127.47), thirteen methines (δ 147.90, 143.58, 134.66, 130.00, 128.61, 127.06, 123.16, 120.79, 118.95, 116.10, 114.88, 112.66 and 111.71) and two methyls (δ55.04 and 40.10). HMBC correlation (**Fig. 136,** see **Table 33**) corresponded to the assigned structure. Consequently, compound **B2G** is 2-[(*E*)-2′-(3″-hydroxy-4″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate.

Table 33 ^{1}H, ^{13}C and HMBC of compound **B2G**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.53 (3H, *s*)	40.10	CH_3	2, 8a
2		156.34	C	
3	8.51 (1H, *d*, 9.0)	120.79	CH	2, 4a, 1′
4	8.93 (1H, *d*, 9.0)	143.58	CH	2, 3, 4a, 5, 8a
4a		127.47	C	
5	8.29 (1H, *dd*, 1.5, 7.8)	130.00	CH	4, 4a, 7, 8a
6	7.89 (1H, *t*, 7.8)	128.61	CH	4a, 7, 8
7	8.13 (1H, *dt*, 1.5, 7.8)	134.66	CH	5, 6, 8
8	8.48 (1H, *d*, 7.8)	118.95	CH	4a, 6, 7, 8a
8a		139.11	C	
1′	7.67 (1H, *d*, 15.6)	116.10	CH	3, 2′, 1″
2′	8.10 (1H, *d*, 15.6)	147.90	CH	2, 1″, 2″, 6″
1″		127.88	C	
2″	7.50 (1H, *d*, 2.1)	114.88	CH	2′, 3″,4″, 6″
3″		146.89	C	
4″		151.27	C	
4″-OCH_3	3.87 (3H, *s*)	55.69	CH_3	4″
5″	7.00 (1H, *d*, 8.4)	111.71	CH	1″, 3″, 4″
6″	7.37 (1H, *dd*, 2.1, 8.4)	123.16	CH	2′, 2″
1‴		140.48	C	
2‴	7.59 (2H, *d*, 8.7)	127.06	CH	1‴, 3‴, 4‴, 6‴
6‴				1‴, 2‴, 4‴, 5‴
3‴	6.83 (2H, *d*, 8.7)	112.66	CH	1‴, 4‴, 5‴
5‴				1‴, 3‴, 4‴
4‴		159.34	C	
4‴-OCH_3	3.75 (3H, *s*)	55.04	CH_3	4‴

3.4.14 2-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (B3G)



B3G

An orange solid of compound **B3G** was obtained in a high yield (90%), mp. 262-264°C. The UV-Vis and FT-IR spectra of **B3D** (**Fig. 137** and **138**) were closely resembled with those of compound **B1F**. ^{1}H NMR spectrum (**Fig. 139,** see **Table 34**) was similar to that of **B1G** except for anionic part which showed only equivalent protons of *p*-disubstituted aromatic at δ 7.72 (2H, *d*, *J* = 8.4 Hz, H-2‴, H-6‴) and 7.32 (2H, *d*, *J* = 8.4 Hz, H-3‴, H-5‴). The ^{13}C NMR and DEPT spectra data (**Fig. 140** and **141,** see **Table 34**) exhibited twenty three signals for twenty five carbons with eight quaternary carbons (δ 161.65, 156.61, 152.10, 151.41, 144.29, 138.90, 132.86 and 132.65), thirteen methines (δ 153.40, 148.96, 140.01, 135.22, 133.86, 132.65, 132.50, 128.48, 125.95, 123.70, 120.87, 119.80 and 116.64) and two methyls (δ 60.85 and 44.69). HMBC correlation (**Fig. 142,** see **Table 34**) corresponded to the assigned structure. Thus compound **B3G** was 2-[(*E*)-2′-(3″-hydroxy-4″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate.

The crystal structure of **B3G** was illustrated in **Fig. 23** and **24** which showed the tertiary structure and the packing diagram of **B3G**. The crystal and experiment data were given in **Table 35**. Bond lengths and angles were shown in **Table 36.** Compound **B3G** crystallized out in the $P2_12_12_1$ space group which was a noncentrosymmetric space group meaning that **B3G** exhibited nonlinear optical properties.

Comparison of relative SHG intensities was made with that of urea. It was found that the SHG effect of **B3G** was about 0.85 times that of urea. In addition, compound **B3G** showed very good stability under laser irradiation (1064 nm, 8 mJ/pulse, 8 ns, and 10 Hz) and no sign of decomposition.

Table 34 ^{1}H, ^{13}C and HMBC of compound **B3G**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.58 (3H, *s*)	44.69	CH_3	2, 8a
2		161.65	C	
3	8.48 (1H, *d*, 9.0)	125.95	CH	2, 4a, 1′
4	8.92 (1H, *d*, 9.0)	148.96	CH	2, 5, 8a
4a		132.65	C	
5	8.29 (1H, *d*, 7.5)	135.22	CH	4, 7, 8a
6	7.91 (1H, *t*, 7.5)	133.86	CH	4a, 8
7	8.16 (1H, *br t*, 7.5)	140.01	CH	8
8	8.46 (1H, *d*, 7.5)	123.70	CH	4a, 6
8a		144.29	C	
1′	7.68 (1H, *d*, 15.6)	120.87	CH	3, 1″
2′	8.05 (1H, *d*, 15.6)	153.40	CH	2, 2″, 6″
1″		132.86	C	
2″	7.48 (1H, *d*, 1.8)	119.80	CH	2′, 3″,4″, 6″
3″		152.10	C	
3″ -OH	9.38 (1H, *s*)			2″, 3″,4″
4″		156.61	C	
4″-OCH_3	3.94 (3H, *s*)	60.85	CH_3	4″
5″	7.00 (1H, *d*, 8.4)	116.64	CH	1″, 3″, 4″

Table 34 (Continued)

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
6″	7.36 (1H, *dd*, 1.8, 8.4)	128.48	CH	2′, 2″
1‴		151.41	C	
2‴	7.72 (2H, *d*, 8.4)	132.50	CH	3‴, 4‴, 6‴
6‴				2‴, 4‴, 5‴
3‴	7.32 (2H, *d*, 8.4)	132.65	CH	1‴, 2‴, 4‴, 5‴
5‴				1‴, 3‴, 4‴, 6‴
4‴		138.90	C	

Table 35 Crystal data of **B3G**.

Identification code	**B3G**
Empirical formula	$C_{19}H_{18}NO_2^{+}\cdot C_6H_4ClO_3S^{-}$
Formula weight	483.95
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.95030(10) Å α = 90°
	b = 15.6916(2) Å β = 90°
	c = 20.4365(3) Å γ = 90°
Volume	2228.83(5) $Å^3$
Z, Calculated density	4, 1.442 Mg/m^3
Absorption coefficient	0.304 mm^{-1}
F(000)	1008
Crystal size	0.51 x 0.31 x 0.31 mm
Theta range for data collection	1.64 to 30.06°
Limiting indices	-9<=h<=9, -22<=k<=20, -24<=l<=28
Reflections collected / unique	28163 / 6533 [R(int) = 0.0295]

Table 35 (Continued)

Completeness to theta = 30.06	99.9 %
Max. and min. transmission	0.9103 and 0.8599
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6533 / 2 / 301
Goodness-of-fit on F^2	1.036
Final R indices [I>2σ(I)]	R1 = 0.0435, wR2 = 0.1010
R indices (all data)	R1 = 0.0612, wR2 = 0.1104
Largest diff. peak and hole	0.302 and -0.361 e.Å^3

Table 36 Bond lengths [Å] and angles [°] for **B3G**

S1-O3	1.4293(17)	C1-C2	1.398(3)
S1-O4	1.4385(18)	C1-C6	1.410(3)
S1-O5	1.4631(16)	C2-C3	1.377(3)
S1-C20	1.7708(19)	C3-C4	1.382(4)
Cl1-C23	1.742(2)	C4-C5	1.372(4)
O1-C16	1.364(2)	C5-C6	1.411(3)
O2-C15	1.364(3)	C6-C7	1.399(3)
O2-C18	1.421(3)	C7-C8	1.356(3)
N1-C9	1.343(3)	C8-C9	1.416(3)
N1-C1	1.404(2)	C9-C10	1.461(3)
N1-C19	1.481(3)	C10-C11	1.325(3)
C11-C12	1.453(3)	C20-C25	1.377(3)
C12-C13	1.382(3)	C20-C21	1.383(3)
C12-C17	1.407(3)	C21-C22	1.378(3)
C13-C14	1.387(3)	C22-C23	1.368(4)
C14-C15	1.379(3)	C23-C24	1.369(3)
C15-C16	1.405(3)	C24-C25	1.379(3)
C16-C17	1.374(3)		

Table 36 (Continued)

O1-C16-C15	116.62(18)	C7-C6-C5	122.8(2)
O1-C16-C17	123.34(18)	C7-C8-C9	120.5(2)
O2-C15-C14	125.69(19)	C8-C7-C6	121.4(2)
O2-C15-C16	114.99(18)	C8-C9-C10	120.7(2)
O3-S1-O4	113.57(13)	C9-N1-C1	122.37(16)
O3-S1-O5	112.73(11)	C9-N1-C19	120.82(16)
O4-S1-O5	112.90(11)	C10-C11-C12	127.12(19)
O3-S1-C20	106.40(10)	C11-C10-C9	124.89(19)
O4-S1-C20	106.30(10)	C12-C13-C14	121.2(2)
O5-S1-C20	104.02(9)	C13-C12-C11	119.93(19)
N1-C1-C6	118.75(19)	C13-C12-C17	118.34(19)
N1-C9-C8	118.60(19)	C14-C15-C16	119.32(19)
N1-C9-C10	120.70(17)	C15-O2-C18	117.12(18)
C1-N1-C19	116.80(17)	C15-C14-C13	120.3(2)
C1-C6-C5	118.9(2)	C16-C17-C12	120.79(18)
C2-C1-N1	121.60(18)	C17-C12-C11	121.73(18)
C2-C1-C6	119.65(19)	C17-C16-C15	120.04(18)
C2-C3-C4	121.6(2)	C20-C25-C24	120.52(18)
C3-C2-C1	119.5(2)	C21-C20-S1	120.14(16)
C4-C5-C6	120.6(2)	C22-C21-C20	119.7(2)
C5-C4-C3	119.7(2)	C22-C23-Cl1	119.34(18)
C7-C6-C1	118.27(19)	C22-C23-C24	121.9(2)
C23-C22-C21	119.36(19)	C25-C20-S1	119.92(14)
C24-C23-Cl1	118.7(2)	C25-C20-C21	119.94(19)

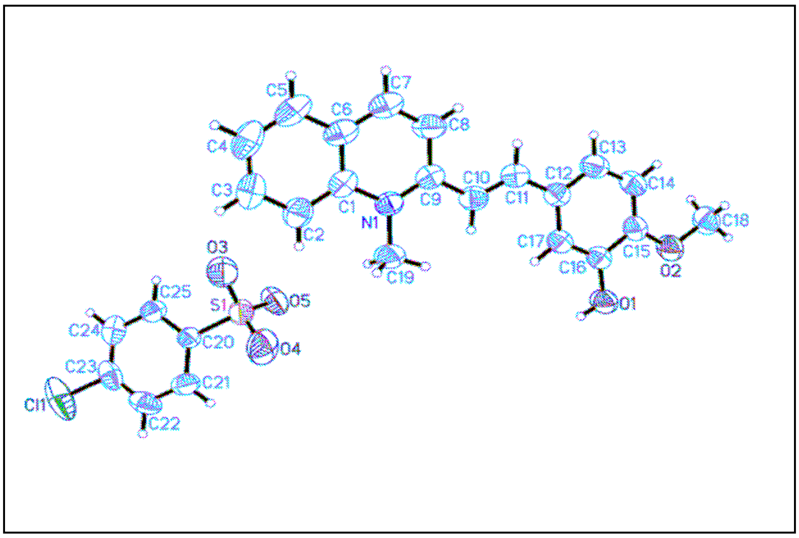


Figure 23 Structure of **B3G**, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

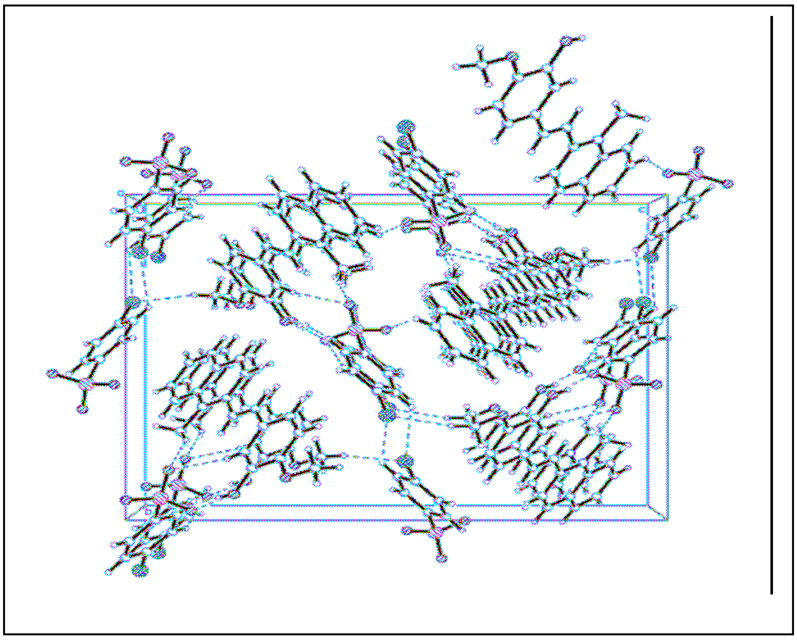
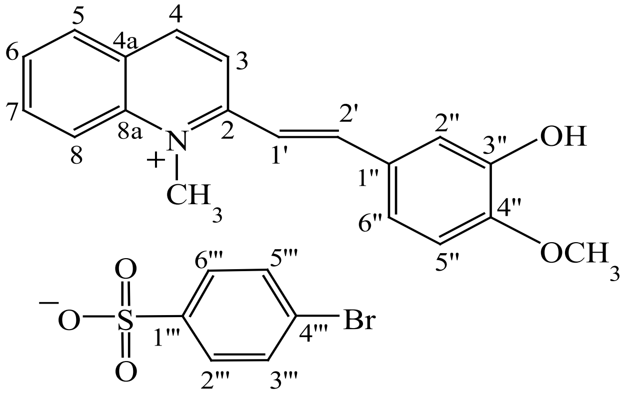


Figure 24 Packing diagram of **B3G** viewed down the *c* axis with H-bonds shown as dash lines.

3.4.15 2-[(*E*)-2′-(3″-Hydroxy-4″-methoxyphenyl)ethenyl]-1-methylquinolinium 4-bromobenzenesulfonate (B4G)



B4G

An orange product of compound **B4G** was obtained in 92% yield, mp. 263-265 °C. The UV-Vis and FT-IR spectra of **B4F** (**Fig. 143** and **144**) were similar to that of compound **B1G**. ^{1}H NMR spectrum of **B4G** (**Fig. 145,** see **Table 37**) showed the same pattern as compound **B1G**. The difference appeared in the signal of anion part whose ^{1}H NMR spectrum showed only signals of AA′ BB′ pattern, indicating C-4‴. position of Br. The ^{13}C NMR and DEPT spectra data (**Fig. 146** and **147,** see **Table 27**) exhibited twenty two signals for twenty five carbons with seven quaternary carbons (δ 156.44, 151.35, 146.93, 139.16, 127.88, 127.51 and 121.97), thirteen methines (δ 148.04, 143.69, 134.75, 130.51, 130.05, 128.66, 127.69, 123.19, 120.84, 118.89, 116.03, 114.90 and 111.68) and two methyls (δ 55.73 and 39.58). HMBC correlation (**Fig. 148,** see **Table 37**) corresponded to the assigned structure. These assignments clearly supported the proposed structure.

Table 37 ^{1}H, ^{13}C and HMBC of compound **B4G**

Position	**δ_H, *mult*, *J* (Hz)**	**δ_C**	**DEPT**	**HMBC**
1-CH_3	4.55 (3H, *s*)	39.58	CH_3	2, 8a
2		156.44	C	
3	8.51 (1H, *d*, 8.7)	120.84	CH	2, 4a, 1′
4	8.94 (1H, *d*, 8.7)	143.69	CH	2, 3, 4a, 5, 8a
4a		127.51	C	
5	8.30 (1H, *dd*, 1.2, 7.8)	130.05	CH	4, 4a, 7, 8a
6	7.90 (1H, *t*, 7.8)	128.66	CH	4a, 7, 8
7	8.15 (1H, *m*)	134.75	CH	5, 6, 8
8	8.48 (1H, *d*, 7.8)	118.89	CH	4a, 6, 8a
8a		139.16	C	
1′	7.68 (1H, *d*, 15.9)	116.03	CH	3, 1″
2′	8.09 (1H, *d*, 15.9)	148.04	CH	2, 2″, 6″
1″		127.88	C	
2″	7.48 (1H, *d*, 2.1)	114.90	CH	2′, 3″,4″, 6″
3″		146.93	C	
4″		151.35	C	
4″-OCH_3	3.90 (3H, *s*)	55.73	CH_3	4″
5″	7.02 (1H, *d*, 8.4)	111.68	CH	1″, 3″, 4″
6″	7.38 (1H, *dd*, 2.1, 8.4)	123.19	CH	2′, 2″
1‴		146.93	C	
2‴	7.61 (2H, *d*, 8.4)	127.69	CH	1‴, 3‴, 4‴, 6‴
6‴				1‴, 2‴, 4‴, 5‴
3‴	7.47 (2H, *d*, 8.4)	130.51	CH	1‴, 2‴, 4‴, 5‴
5‴				1‴, 3‴, 4‴, 6‴