Supplementary Material

EXPERIMENTAL SECTION

Preparation of 2-Methoxy-4-(2, 6-diphenylpyridin-4-yl) phenol 1

3.0g of 4-hydroxy-3-methoxy benzaldehyde (1.971×10^{-2} mmol; 1.0 equiv.) 4.97 g of acetophenone (4.140×10^{-2} mmol; 2.0equiv.) and 10g of NH_4OAc are dissolved (4.140×10^{-2} mmol; 1.0equiv.) in 50mL of acetic acid (4.140×10^{-2} mmol; 2.0equiv.) under refluxing condition for 3 h. to give 2-methoxy-4-(2, 6-diphenylpyridin-4-yl) phenol **1** in qualitative yield. Yield: 7.82g, (98%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 3.98 (s, 3H), 7.09 (s, 1H), 7.11-7.24 (d, 2H), 7.44 (s, 2H), 7.96-8.24 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ= 56.1, 109.7, 115.2, 116.7, 120.5, 127.1, 128.5, 129.0, 133.1, 137.1, 146.9, 150.1, 157.4; MS: m/e: 353.14; Anal. Calcd for: $C_{24}H_{19}NO_2$: C: 81.55; H: 5.38; N: 3.96; Found: C: 81.48; H: 5.30; N: 3.88.

General Procedure of *N*-Alkylation Reaction

2-methoxy-4-(2, 6-diphenylpyridin-4-yl) phenol **1** (7.158×10^{-3} mmol; 1.0 equiv.) is treated with benzyl bromide/4-nitro benzyl bromide (7.516×10^{-3} mmol; 1.05 equiv.) in the presence of 20 mL of dry acetonitrile under refluxing condition for 9-10 hours to give N-alkylated product of compound **2a/3a**.

2-Methoxy-4-(2, 6-diphenyl-l-methyl benzyl pyridiniumbromide-4-yl) phenol 2a

Yield: 3.77g, (97%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 3.94 (s, 3H), 4.52 (s, 2H), 6.08 (s, 1H), 6.96-7.12 (d, 2H), 7.39-7.51 (m, 5H) 7.49 (s, 2H), 7.76-8.01 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.0, 76.7, 110.1, 114.9, 119.8, 123.4, 127.4, 127.3, 128.4, 128.5, 129.0, 130.1, 132.5, 138.5, 139.4, 145.2, 148.4, 157.4; MS: m/e: 524.45; Anal. Calcd for: $C_{31}H_{26}BrNO_2$: C: 70.93; H: 4.95; N: 2.66; Found: C: 70.85; H: 4.87; N: 2.58.

2-Methoxy-4-(2, 6-diphenyl-l-methyl-4-nitrobenzylpyridiniumbromide-4-yl) phenol 3a

Yield: 5.44 g (98%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 3.90 (s, 3H), 4.49 (s, 2H), 6.93 (s, 1H), 7.13 (d, 2H), 7.47 (s, 2H), 7.51-7.55 (m, 4H), 7.99-8.16 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.1, 76.8, 109.0, 114.5, 115.0, 119.6, 127.3, 128.4, 128.5, 129.9, 132.6, 133.1, 138.4, 144.8, 145.3, 148.5, 151.9, 162.5; MS: m/e: 569.45; Anal. Calcd for: $C_{31}H_{25}BrN_2O_4$: C: 65.32; H: 4.39; N: 4.91; Found: C: 65.24; H: 4.31; N: 4.83.

General Procedure for Anion Exchange Reaction

Triaryl pyridinium bromide **2a/3a** (1.716×10^{-3} mmol; 1.0 equiv.) is treated with various counter anions containing inorganic salt such as $NaBF_4$, K_4PF_6, and $LiCF_3SO_3$ (1.801×10^{-3} mmol; 1.05 equiv.) in the presence of 20 mL of deionized water at room temperature with stirring for 2 hours to give anion exchange product in 92-94% yield. Both metallic bromide and triaryl pyridinium salts are soluble in water. So the separation is not easier. Under these circumstances we have used Soxhlet extraction for separation with dry THF for 1 h under refluxing condition and confirmed by aqueous $AgNO_3$.

2-Methoxy-4-(2, 6-diphenyl-l-methylbenzyl pyridinium hexafluorophosphate-4-yl) phenol 2b

Yield: 1.16g; (94%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 4.02 (s, 3H), 4.54 (s, 2H), 7.13 (s, 1H), 7.15-7.28 (d, 2H), 7.29-7.40 (m, 5H) 7.48 (s, 2H), 8.00-8.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.5, 65.0, 110.1, 115.6, 117.1, 120.9, 127.5, 127.7, 128.9, 129.0, 129.4, 130.5, 133.5, 137.5, 139.9, 147.3, 150.5, 157.8 ; MS: m/e: 563.14; Anal. Calcd for: $C_{29}H_{24}F_6NO_2P$: C: 61.79; H: 4.26; N: 2.48; Found: C: 61.71; H: 4.18; N: 2.40.

2-Methoxy-4-(2, 6-diphenyl-l-methylbenzyl pyridinium tetrafluoroborate-4-yl) phenol 2c

Yield: 1.01g; (92%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 4.01 (s, 3H), 4.53 (s, 2H), 7.12 (s, 1H), 7.14-7.27 (d, 2H), 7.28-7.39 (m, 5H) 7.47 (s, 2H), 7.99-8.27 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.4, 64.9, 110.0, 115.5, 117.0, 120.8, 127.4, 127.7, 128.8, 128.9, 129.3, 130.4, 133.5, 137.4, 139.8, 147.2, 150.4, 157.7; MS: m/e: 531.35; Anal. Calcd for: $C_{31}H_{26}BF_4NO_2$: C: 70.11; H: 4.61; N: 2.63; Found: C: 70.03; H: 4.53; N: 2.55.

2-Methoxy-4-(2, 6-diphenyl-l-methylbenzyl pyridinium trifluoromethanesulfonate-4-yl) phenol 2d

Yield: 0.95g; (80%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 4.00 (s, 3H), 4.52 (s, 2H), 7.11 (s, 1H), 7.13-7.26 (d, 2H), 7.27-7.38 (m, 5H) 7.46 (s, 2H), 7.98-8.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.3, 64.8, 109.9, 115.4, 116.9, 120.7, 127.3, 127.5, 128.7, 128.8, 129.2, 130.3, 133.3, 137.3, 139.6, 147.1, 150.3, 157.6; MS: m/e: 593.61; Anal. Calcd for: $C_{32}H_{26}F_3NO_5S$: C: 64.68; H: 4.37; N: 2.35; Found: C: 64.60; H: 4.29; N: 2.27.

2-Methoxy-4-(2, 6-diphenyl-l-methyl-4-nitrobenzyl pyridinium hexafluorophosphate-4-yl) phenol 3b

Yield: 1.25g; (87%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 4.09 (s, 3H), 4.73 (s, 2H), 7.15 (s, 1H), 7.17 (d, 2H), 7.51 (s, 2H), 7.52-7.71 (m, 4H), 8.02-8.31 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.5, 77.0, 110.3, 115.9, 117.3, 121.2, 127.7, 128.0, 129.1, 129.7, 133.7, 135.4, 137.8, 142.6, 146.4, 150.9, 158.1, 162.7; MS: m/e: 634.51; Anal. Calcd for: $C_{31}H_{25}F_6N_2O_4P$: C: 58.62; H: 3.94; N: 4.41; Found: C: 58.54; H: 3.86; N: 4.33.

2-Methoxy-4-(2, 6-diphenyl-l-methyl-4-nitrobenzyl pyridinium tetrafluoroborate-4-yl) phenol 3c

Yield: 1.12 g; (93%); Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 4.08 (s, 3H), 4.72 (s, 2H), 7.14 (s, 1H), 7.30 (d, 2H), 7.50 (s, 2H), 7.51-7.70 (m, 4H), 8.01-8.30 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.4, 63.4, 110.2, 115.8, 117.2, 121.2, 127.7, 127.9, 129.0, 129.7, 133.7, 135.3, 137.7, 142.5, 146.3, 150.8, 160.0, 162.6; MS: m/e: 576.35; Anal. Calcd for: $C_{31}H_{25}BF_4N_2O_4$: C: 66.54; H: 4.33; N: 4.85; Found: C: 64.46; H: 4.25; N: 4.77.

2-Methoxy-4-(2, 6-diphenyl-l-methyl-4-nitrobenzyl pyridinium trifluoromethanesulfonate -4-yl) phenol 3d

Yield: 1.19 g; 92%; Liquid; ^{1}H NMR (400 MHz, $CDCl_3$); δ= 4.07 (s, 3H), 4.71 (s, 2H), 7.13 (s, 1H), 7.29 (d, 2H), 7.49 (s, 2H), 7.50-7.69 (m, 4H), 8.00-8.29 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$); δ= 56.3, 63.3, 110.2, 115.7, 117.1, 121.0, 127.5, 127.8, 128.9, 129.5, 133.5, 135.2, 137.6, 142.4, 146.2, 150.7, 157.9, 162.5; MS: m/e: 638.61; Anal. Calcd for: $C_{32}H_{25}F_3N_2O_7S$: C: 60.13; H: 3.91; N: 4.28; Found: C: 60.00; H: 3.82; N: 4.30.

General Procedure for one Pot Preparation of Quinoline Derivatives

Equal molar concentration of 5, 5-dimethylcyclohexadienone (3.856×10^{-3} mmol; 1.05 equiv.), ethylacetoacetate (4.049×10^{-3} mmol; 1.05 equiv.), substituted aryl aldehyde (3.672×10^{-3} mmol; 1.0 equiv.) and NH_4OAc (4.251×10^{-2} mmol; 1.05 equiv.), in the presence of 1.053×10^{-4} mmol CH_3CN with optimized catalyst concentration of triaryl pyridinium bromide **3a** (1.053×10^{-4} mmol) for 50 minutes under refluxtion to give quinoline derivative **4(a-d)** in 80-96%

Ethyl 1, 4, 5, 6, 7, 8-hexahdro-4-(4-hydroxyphenyl)-2, 7, 7-trimethyl-5-oxoquinoline-3-carboxylate 4a

Yield: 0.5g; (91%); Mp:230-232 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ= 0.94 (s, 3H), 1.08 (s, 3H), 1.20 (t, 3H), 2.08-2.18 (m, 3H), 2.20-2.35 (m, 4H),4.07 (q, 2H), 4.98 (s, 1H), 5.62 (s, 1H), 6.65 (d, 2H), 7.16 (d, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ= 14.1, 18.1, 26.4, 29.1, 32.1, 34.7, 50.3, 104.0, 110.2, 114.4, 128.3, 138.4, 144.3, 144.3, 149.0, 155.1, 167.0, 194.3; MS: m/e: 355.43; Anal. Calcd for: $C_{21}H_{25}NO_4$: C: 70.96; H: 4.09; N: 3.94; Found: C: 70.90; H: 7.03; N: 3.93.

Ethyl 1, 4, 5, 6, 7, 8-hexahdro-4-(4-methoxyphenyl)-2, 7, 7-trimethyl-5-oxoquinoline-3-carboxylate 4b

Yield: 0.5g; (87%); Mp:203-205 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ= 0.86 (s, 3H), 1.14 (t, 3H), 1.97 (d, 1H), 2.16 (d, 1H), 2.26 (s, 3H), 2.3 (s, 1H), 2.40 (d, 1H), 3.97 (q, 2H), 4.74 (s, 1H), 6.56 (d,2H), 6.93 (d, 2H) 8.98 (s, 1H) 9.07 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ= 14.1, 18.1, 26.4, 29.1, 32.1, 34.7, 50.3, 104.0, 110.2, 114.4, 128.3, 138.4, 144.3, 144.3, 149.0, 155.1, 167.0, 194.3; MS: m/e: 385.42; Anal. Calcd for: $C_{22}H_{27}NO_5$: C: 68.55; H: 7.06; N: 3.63; Found: C: 68.49; H: 7.00; N: 3.60.

Ethyl 1, 4, 5, 6, 7, 8-hexahdro-2, 7, 7-trimethyl -5-oxo-4-phenylquinoline-3-carboxylate 4c

Yield: 0.5 g; (90 %); Mp:220-222 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6): δ= 0.94 (s, 3H), 1.08 (s, 3H), 1.19 (t, 3H), 2.14-2.33 (m, 4H), 2.38 (s, 3H), 4.05 (q, 2H), 5.05 (s, 1H), 5.78 (s, 1H), 7.08-7.31 (m, 5H);^{13}C NMR (100 MHz, DMSO-d_6): δ= 14.0, 18.0, 26.1, 29.0, 32.0, 34.3, 50.1, 104.2, 110.4, 114.2, 128.1, 138.2, 144.1, 144.6, 149.2, 155.5, 167.3, 194.1; MS: m/e: 339.43; Anal. Calcd for: $C_{21}H_{25}NO_3$: C: 74.31; H: 7.42; N: 4.13; Found: C: 74.57; H, 7.51; N, 4.06.

Ethyl 1, 4, 5, 6, 7, 8-hexahdro-2, 7, 7-trimethyl -4-(4-nitrophenyl) -5-oxoquinoline-3-carboxylate 4d

Yield: 0.5g; (85%); Mp:243-245 ^{0}C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ= 0.92 (s, 3H), 1.09 (s, 3H), 1.24 (t, 3H), 2.13-2.37 (m, 4H), 2.40 (s, 3H), 4.07 (q, 2H), 5.18 (s, 1H), 6.72 (s, 1H), 7.51 (d, 2H), 8.10 (d, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ= 14.1, 18.1, 26.4, 29.1, 32.1, 34.7, 50.3, 104.0, 110.2, 114.4, 128.3, 138.4, 144.3, 144.3, 149.0, 155.1, 167.0, 194.3; MS: m/e: 384.43; Anal. Calcd for: $C_{21}H_{24}N_2O_5$: C: 65.61; H: 6.29; N: 7.29; Found: C: 65.55; H: 6.24; N: 7.28;

Ethyl 1, 4, 5, 6, 7, 8-hexahdro-2, 7, 7-trimethyl -4-(4-nitrophenyl) -5-oxoquinoline-3-carboxylate 4e

Yield: 0.5 g; (89 %); Mp: 175-177 ^{0}C ; ^{1}H NMR (400 MHz, DMSO-d_6): δ= 0.94 (s, 3H), 1.03 (s, 3H), 1.2 (t, 3H), 2.14-2.42 (m, 4H), 4.08 (q, 2H), 5.17 (s, 1H), 6.69 (s, 1H), 7.39 (t, 1H), 7.74 (d, 1H), 8 (d, 1H), 8.14 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ= 14.0, 18.0, 26.1, 29.0, 32.0, 34.3, 50.1, 104.2, 110.4, 114.2, 128.1, 138.2, 144.1, 144.6, 149.2, 155.5, 167.3, 194.1; MS: m/e: 384.43; Anal. Calcd for: $C_{21}H_{24}N_2O_5$: C: 65.61; H: 6.29; N: 7.29; Found: C: 65.55; H: 6.24; N:7.2.

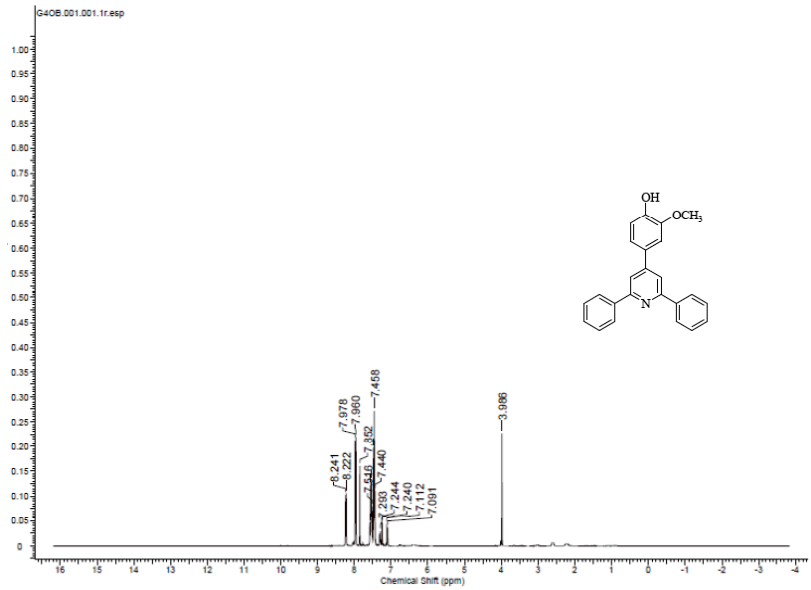

Figure 1: ^{1}H NMR Spectrum of 2-methoxy-4-(2, 6-diphenyl pyridin-4-yl) phenol **1.**

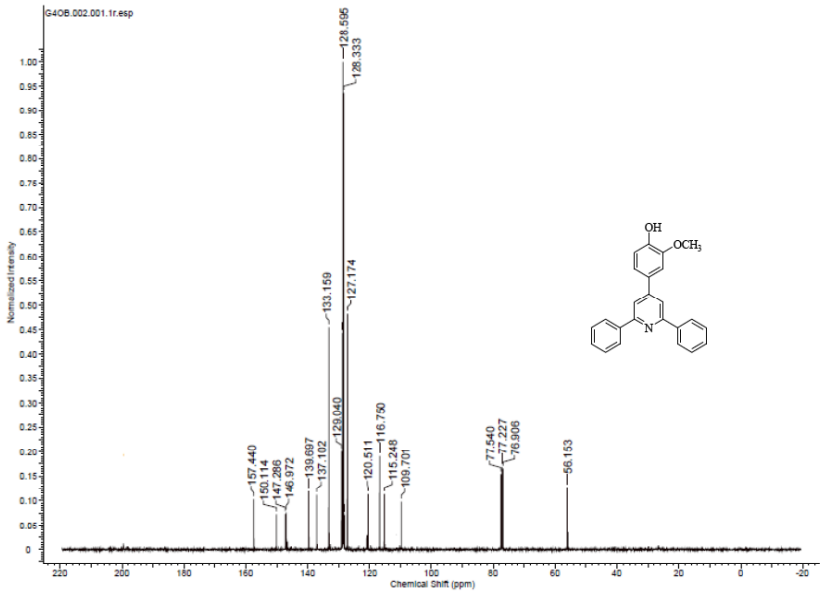

Figure 2: ^{13}C NMR Spectrum of 2-methoxy-4-(2, 6-diphenyl pyridin-4-yl) phenol **1.**

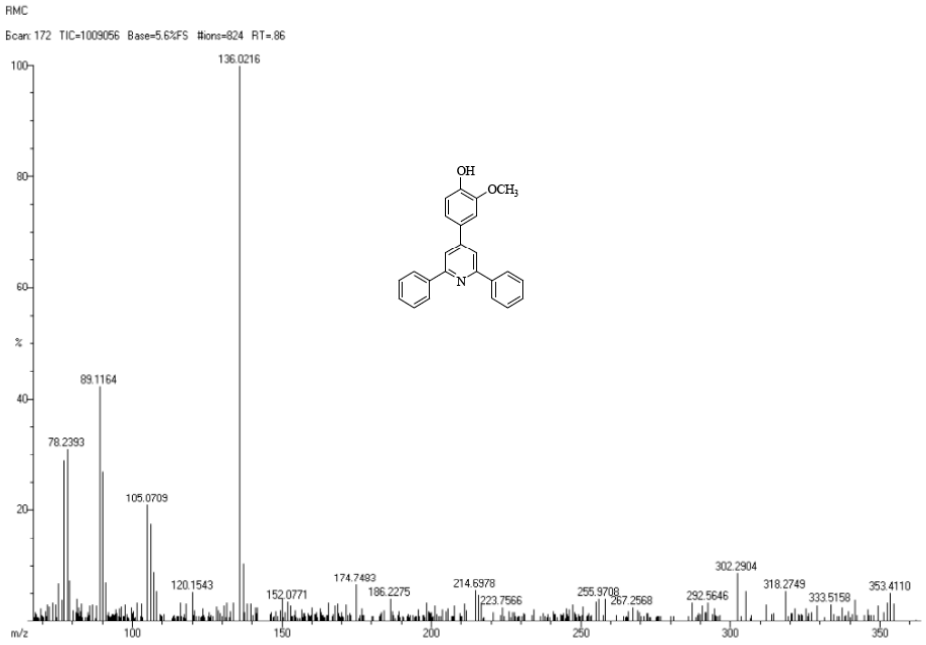

Figure 3: Mass Spectrum of 2-methoxy-4-(2, 6-diphenyl pyridin-4-yl) phenol **1.**

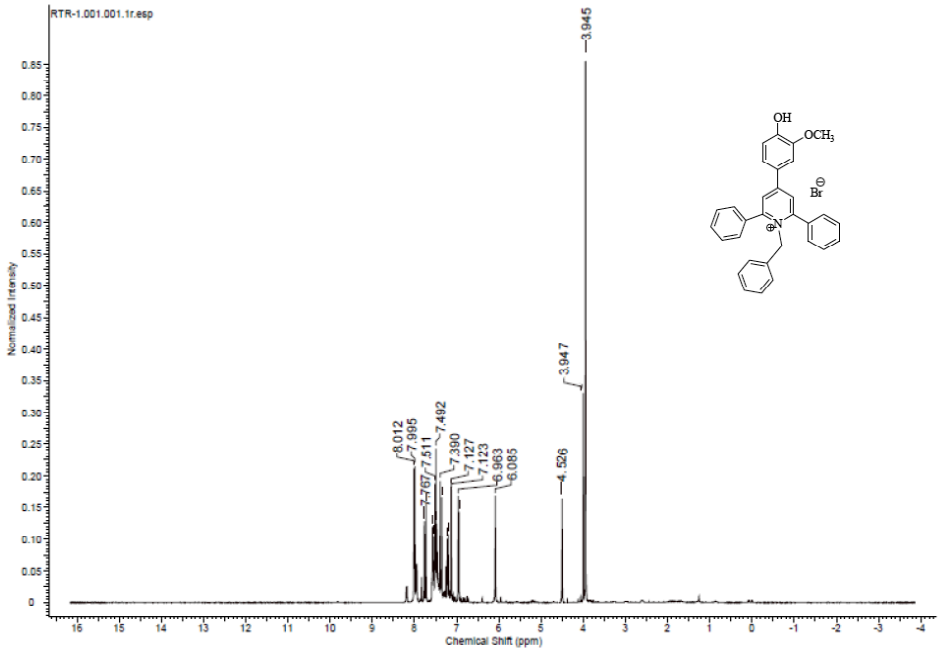

Figure 4: ^{1}H NMR Spectrum of 2-methoxy-4-(2, 6-diphenyl-l-methyl benzyl pyridiniumbromide-4-yl) phenol **2a.**

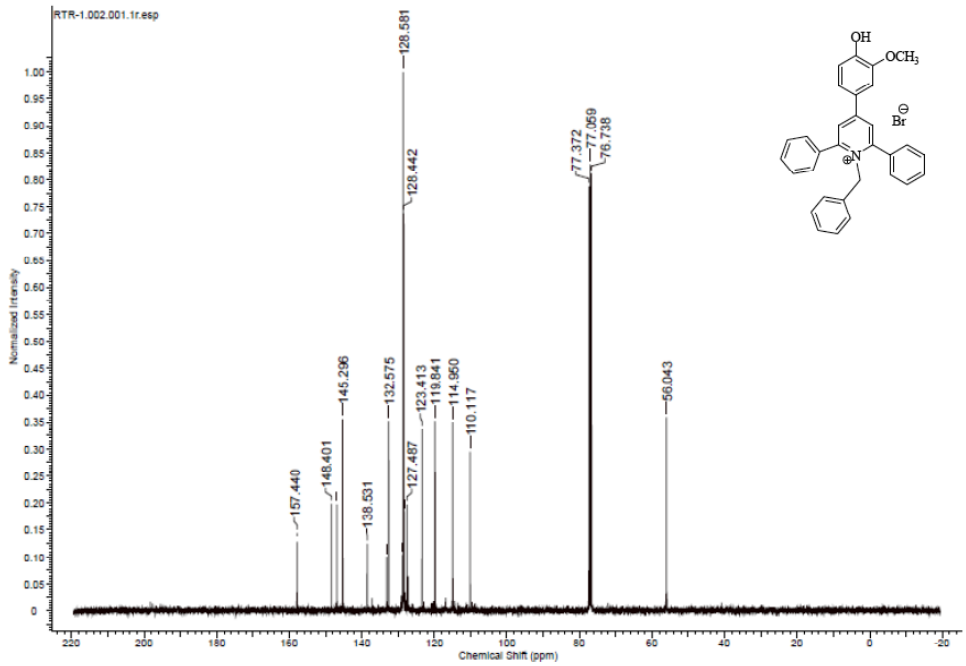

Figure 5: ^{13}C NMR Spectrum of 2-methoxy-4-(2, 6-diphenylbenzyl pyridiniumbromide-4-yl) phenol **2a.**

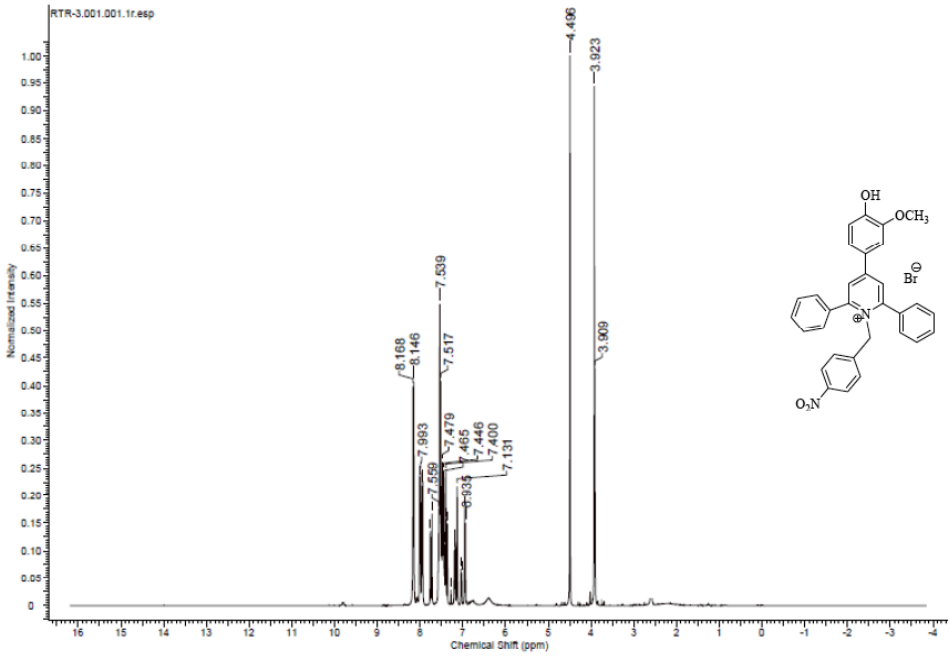

Figure 6: ^{13}C NMR Spectrum of 2-methoxy-4-(2, 6-diphenyl-l-methyl-4-nitrobenzylpyridiniumbromide-4-yl) phenol **3a.**

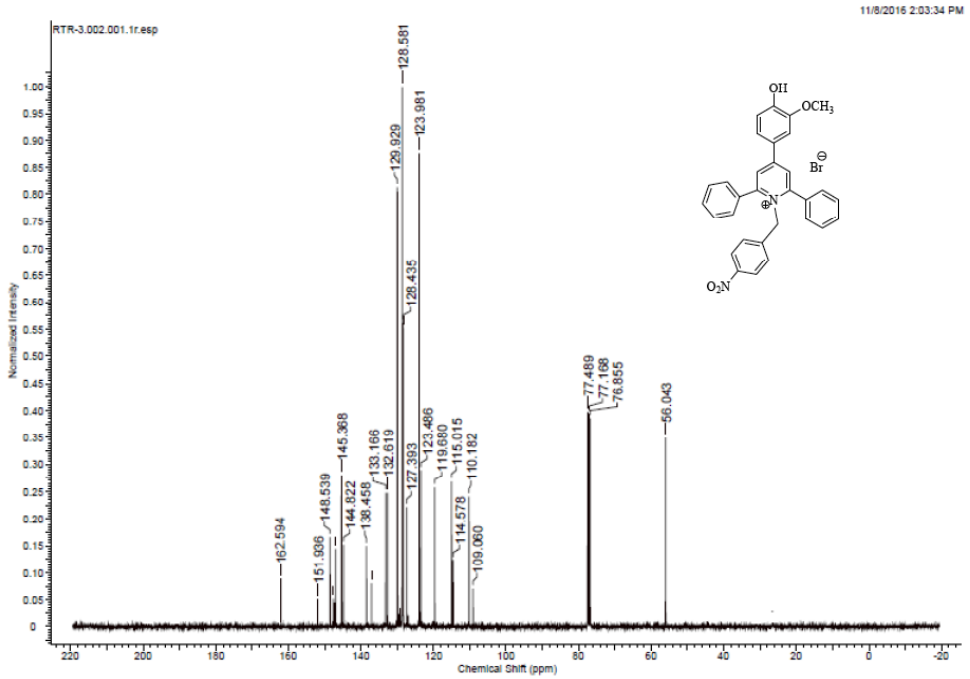

Figure 7: ^{13}C NMR Spectrum of 2-methoxy-4-(2, 6-diphenyl-l-methyl-4-nitrobenzylpyridiniumbromide-4-yl) phenol **3a.**

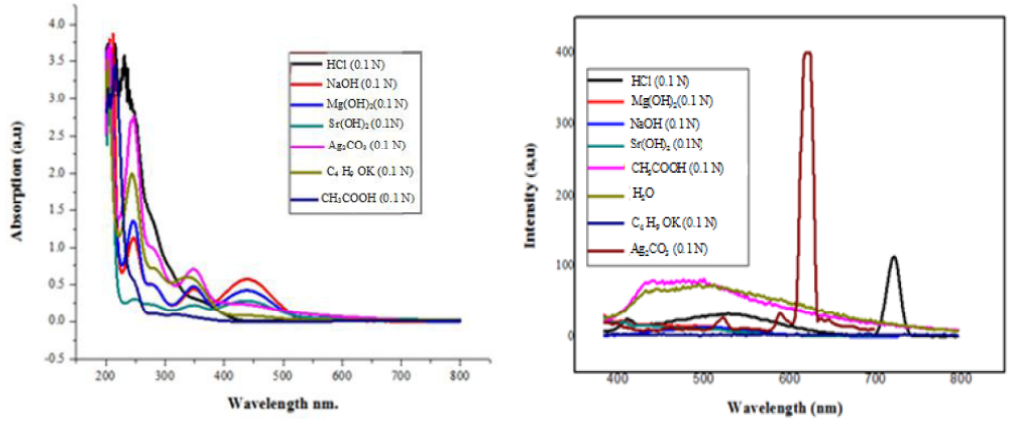

Figure 8: Absorption and emission spectrum of triaryl pyridine **3a** with different medium.