Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Neutral and Cationic Pyridylbutadienes: Solvatochromism and Fluorescence Response with Sodium Cholate

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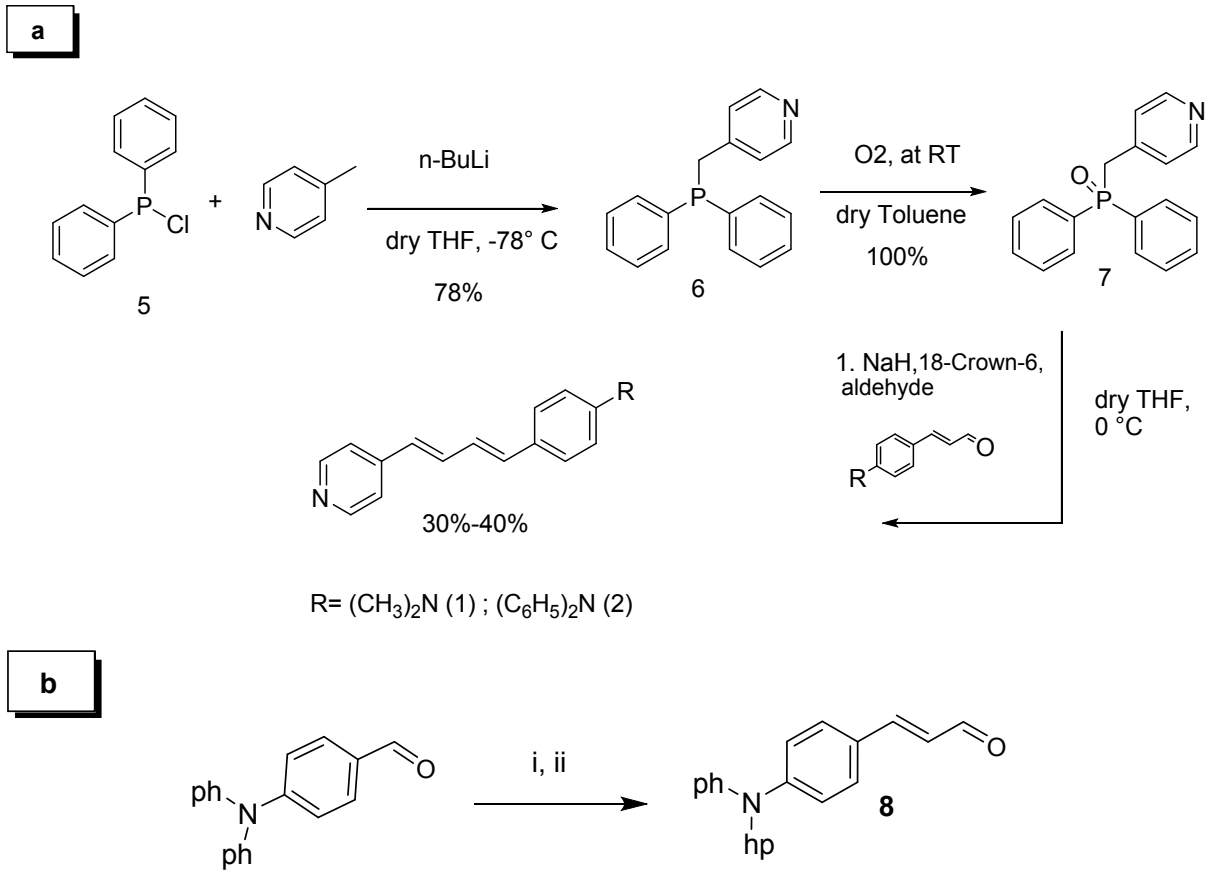
Electronic Supporting Information

14th July 2015



Scheme S1:(a) A general method for the preparation of diene (**1**) and (**2**). (b) procedure for the synthesis of intermediate: b) (i) 1,3-dioxan-2-yl-tributylphosphonium bromide, NaH, 18-crown-6, dry THF, RT, 24h. (ii) 10% HCl, THF at RT, 1h.

Experimental procedure of scheme S1: The synthetic scheme for the preparation of dienes (**1**) & (**2**) is given in scheme 1. In a typical procedure[1], a mixture of diphenyl (4-picolyl)phosphane oxide[2] (1 equiv), NaH (2.5 equiv), 18-crown-6 (0.5 equiv) was stirred in 40 mL of dry THF at 0°C. After 30 min of stirring, 4-substituted cinnamaldehyde (1 equiv) in dry THF was added drop wise and allowed to stir for 10 h at room temperature. The reaction mixture was then filtered over celitepadand the desired product was purified by column chromatography using neutral silica gel using 30-40%ethylacetate /petroleum ether.

N,N-dimethyl-4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl)aniline (**1**): Brown solid, ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.50-8.49 (d, 2H), δ 7.36-7.34 (d, 2H), δ 7.26-7.24 (d, 2H), δ 7.14-7.09 (dd, 1H, J=15.5 Hz), δ 6.80-6.68 (m, 4H), δ 6.47-6.44 (d, 1H, J=15.5 Hz), δ 2.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 150.56, 149.89, 136.54, 134.68, 128.03, 126.95, 123.93, 120.42, 112.29, 40.34 [ESI] $[M+1]^+$251.1356.

N,N-diphenyl-4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl)aniline (**2**): Yellow solid, ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.51-8.50 (d, 2H), δ 7.32-7.26 (m, 8H), δ 7.14-7.09 (m, 5H), δ 7.05-7.00 (m, 4H), δ 6.86-6.80 (m, 1H, J=15.5 Hz), δ 6.73-6.70 (d, 1H, J=15.5 Hz), δ 6.53-6.49 (d, 1H, J=15.5 Hz); ^{13}C NMR ($CDCl_3$, 125MHz, ppm) δ 149.96, δ 148.06, δ 147.36, δ 144.9, δ 135.56, δ 134.06, δ 130.58, δ 129.36, δ 128.58, δ 127.65, δ 126.39, δ 124.81, δ 123.39, δ 123.02, 120.54. HRMS [ESI] $[M+1]^+$ 375.1390.

Procedure for (E)-3-(4-(diphenylamino)phenyl)acrylaldehyde (8): The reported procedure[3] shown in scheme S1b. A mixture of aldehyde (1.83 mmol), 1,3-dioxan-2-yl-tributylphosphonium bromide (3.60 mmol) in anhydrous THF was taken in single necked RB flask. The sodium hydride (5.21 mmol)was added with a catalytic amount of 18-crown-6 and stirred the reaction mixture for 22 h at room temperature. The reaction mixture was quenched with water (25 ml) and extracted with diethylether (3x25ml). The organic layer combined and concentrated under vacuum to afford oil. The resulting product dissolved in THF and added 10% HCl, left the reaction mixture on stirring for 1 hour at room temperature. The solution was extracted by DCM and dried the organic layer over Na_2SO_4 and concentrated under vacuum to give yellow solid.

(E)-3-(4-(diphenylamino)phenyl)acrylaldehyde (**8**), yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 9.64-9.62 (d, 1H), δ 7.40-7.37 (m,3H), δ 7.32-7.26 (m, 4H), δ 7.15-7.11(m, 6H), δ 7.01-7.00 (d, 2H), δ 6.60-6.56 (m, *J* = 15.5 Hz, 1H).

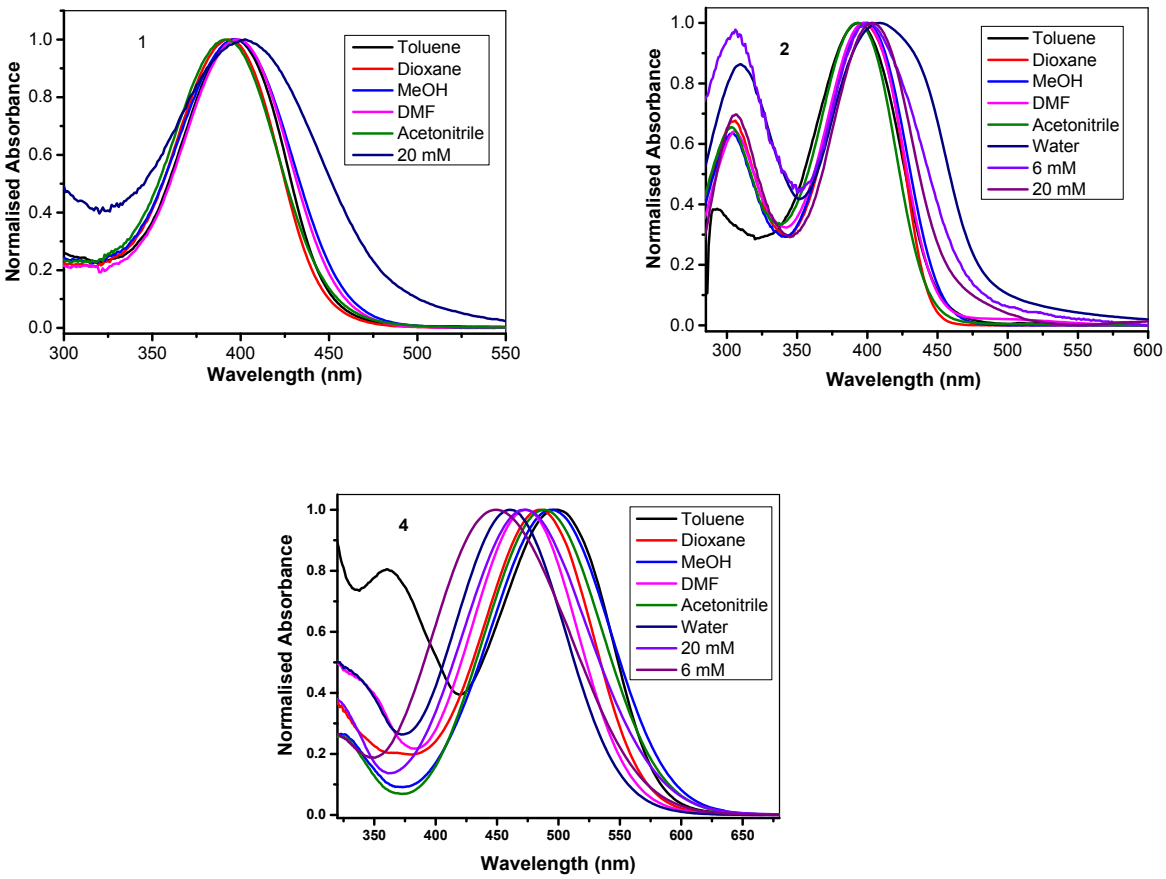


Figure S1. UV-Vis absorption spectra of (**1**), (**2**) and (**4**), in homogeneous organic solvents, water and sodium cholate media. Clean absorption spectra for diene (**1**) in water and at 6mM cholate concentrations could not be obtained.

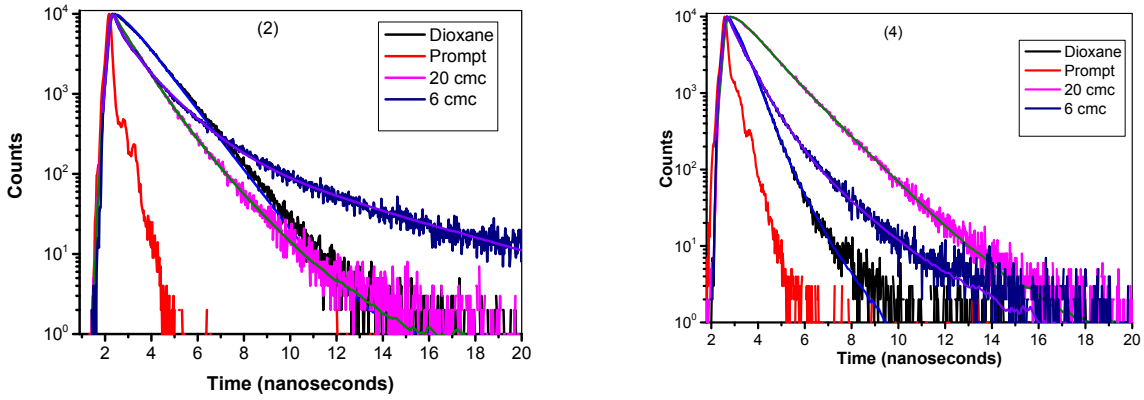
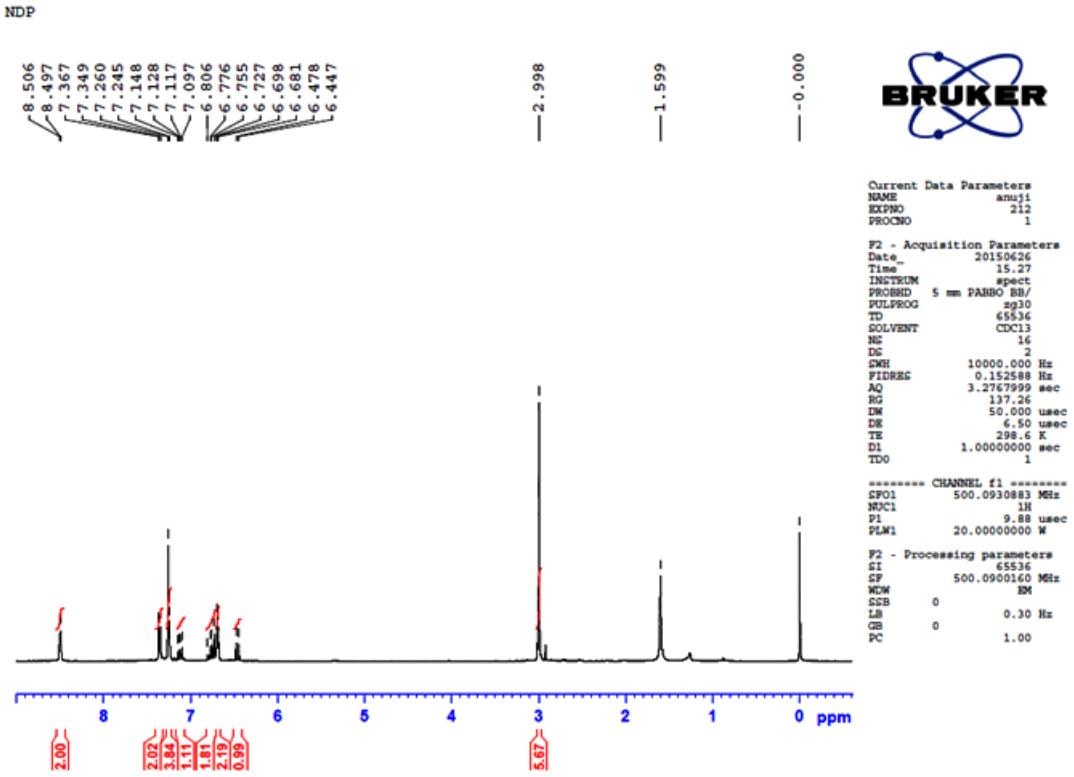
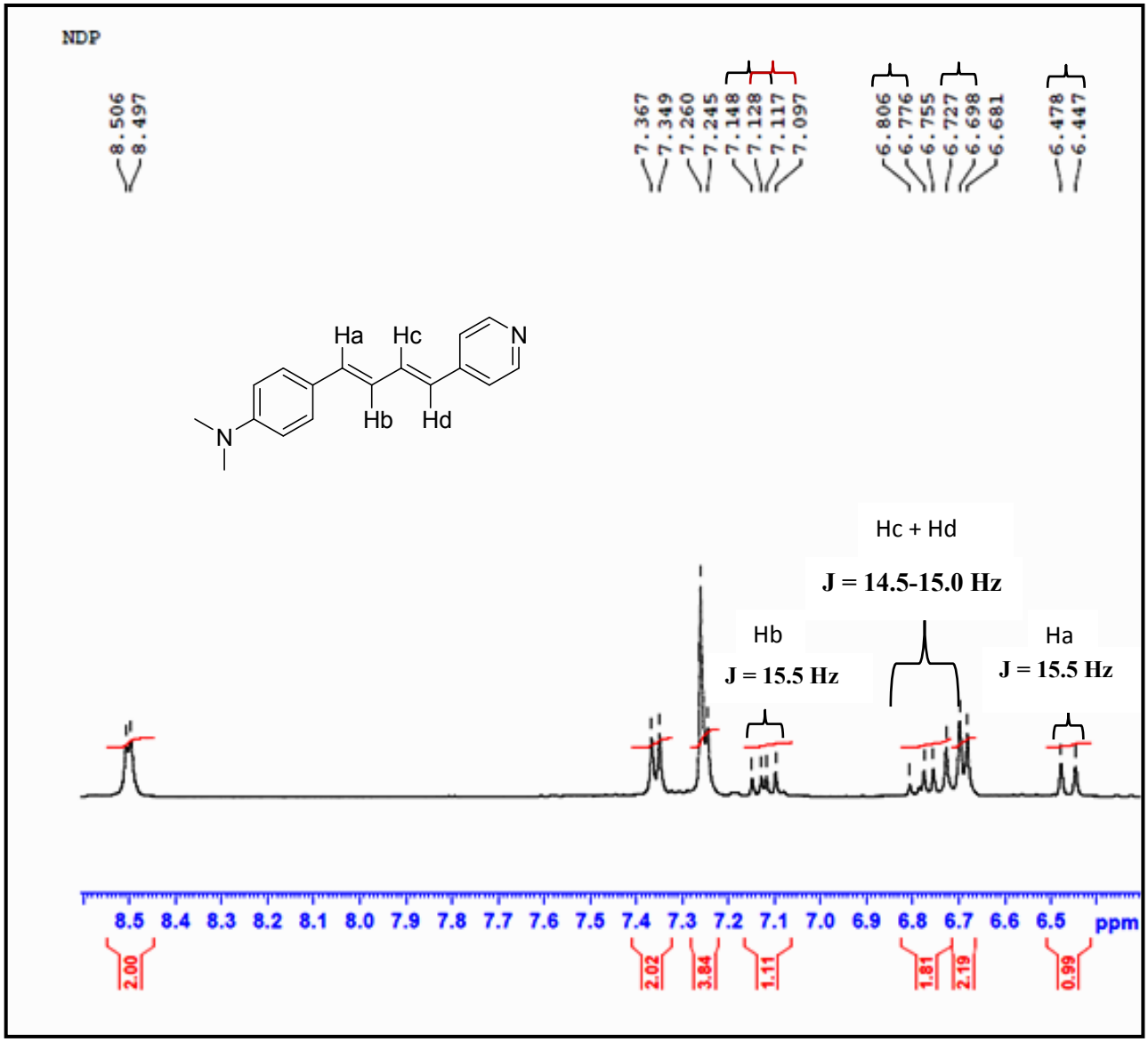


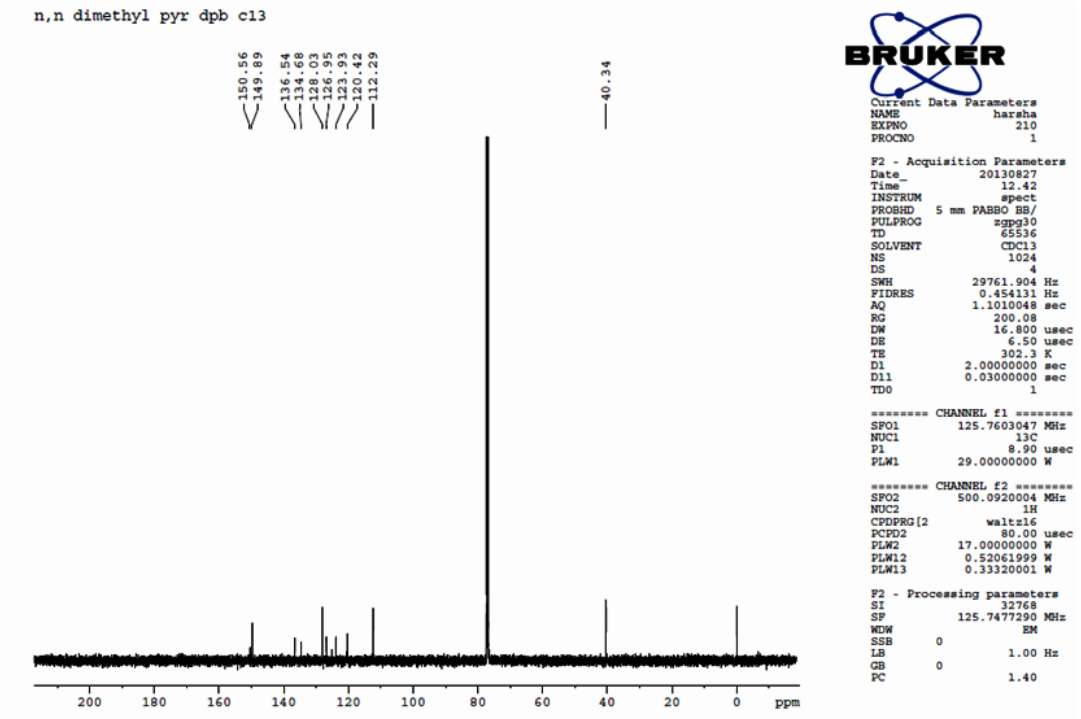
Figure S2. Life-time decay profile in dioxane, 6mM and 20mM of aqueous NaC of (**2**) and (**4**) excited at 405 and 445nm respectively.

^{1}H ,^{13}C NMR and Mass spectra of N,N-dimethyl-4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl)aniline (**1**)



^{1}H ,^{13}C NMR and Mass spectra of N,N-dimethyl-4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl)aniline (**1**): Expansion of aromatic region.

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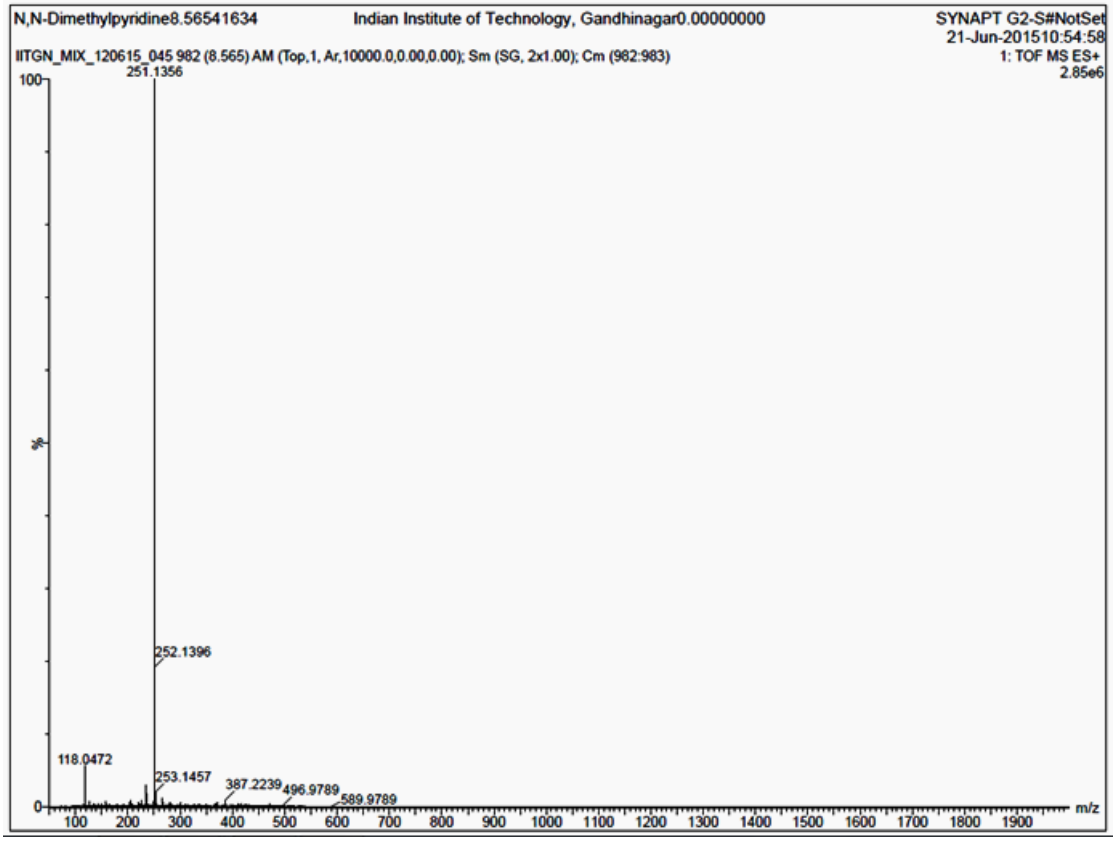
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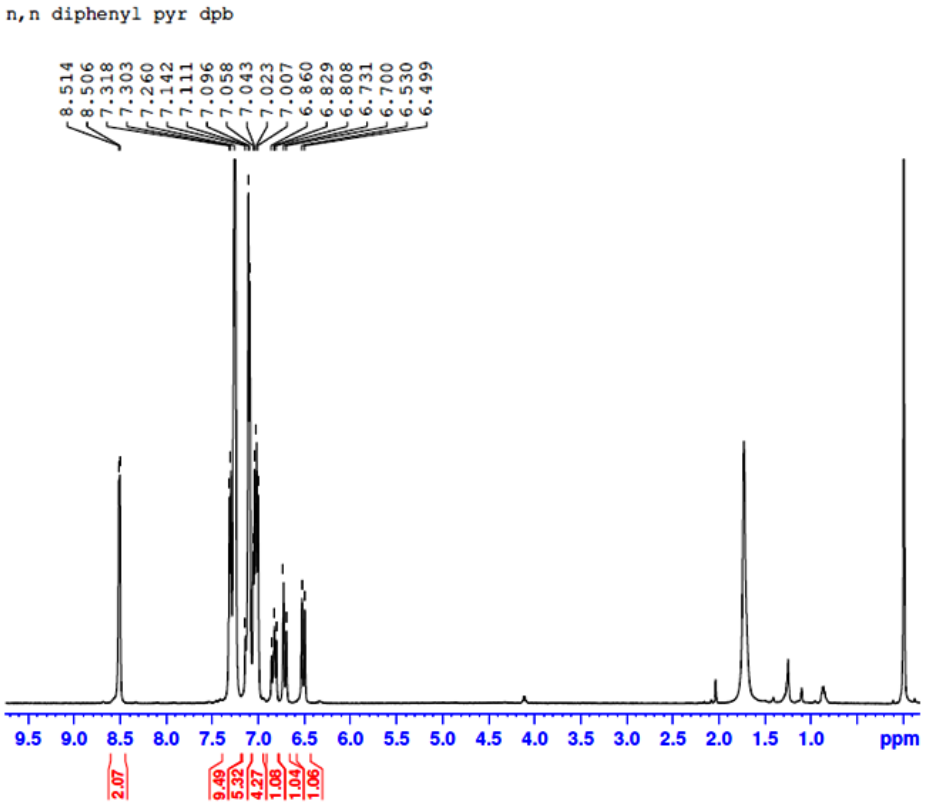
m/z

^{1}H ,^{13}C NMR and Mass spectra of N,N-diphenyl-4-((1E,3E)-4-(pyridin-4-yl)buta-1,3-dienyl)aniline (**2**)



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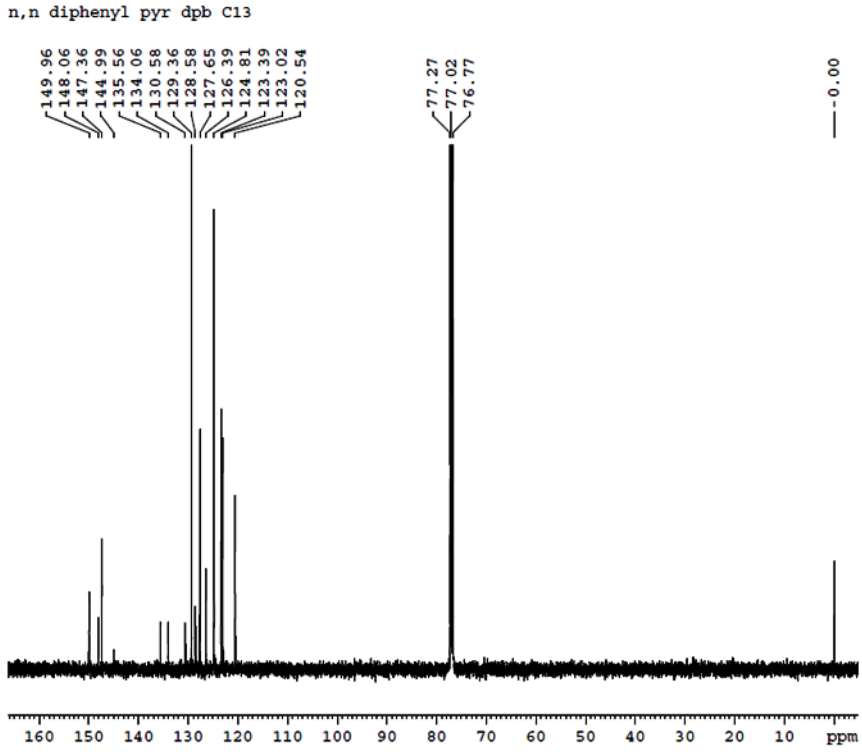

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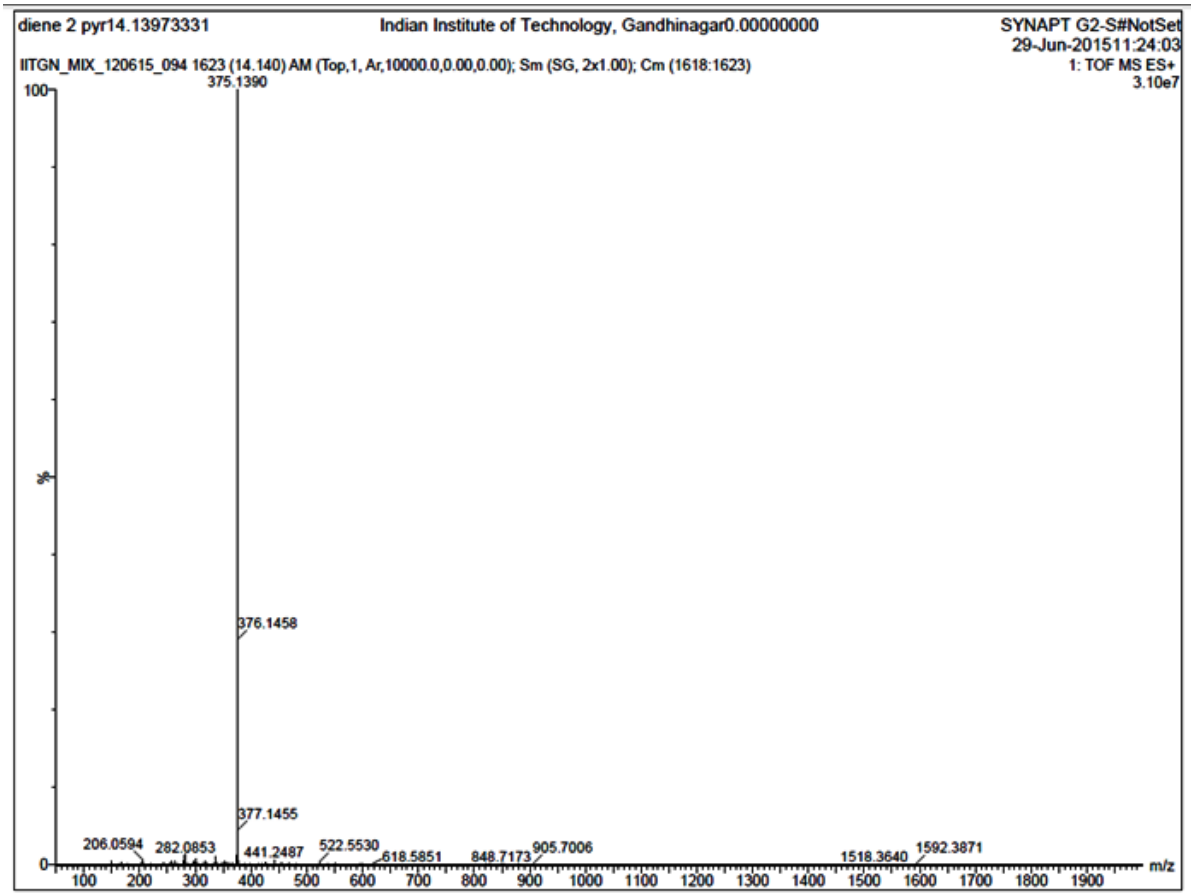
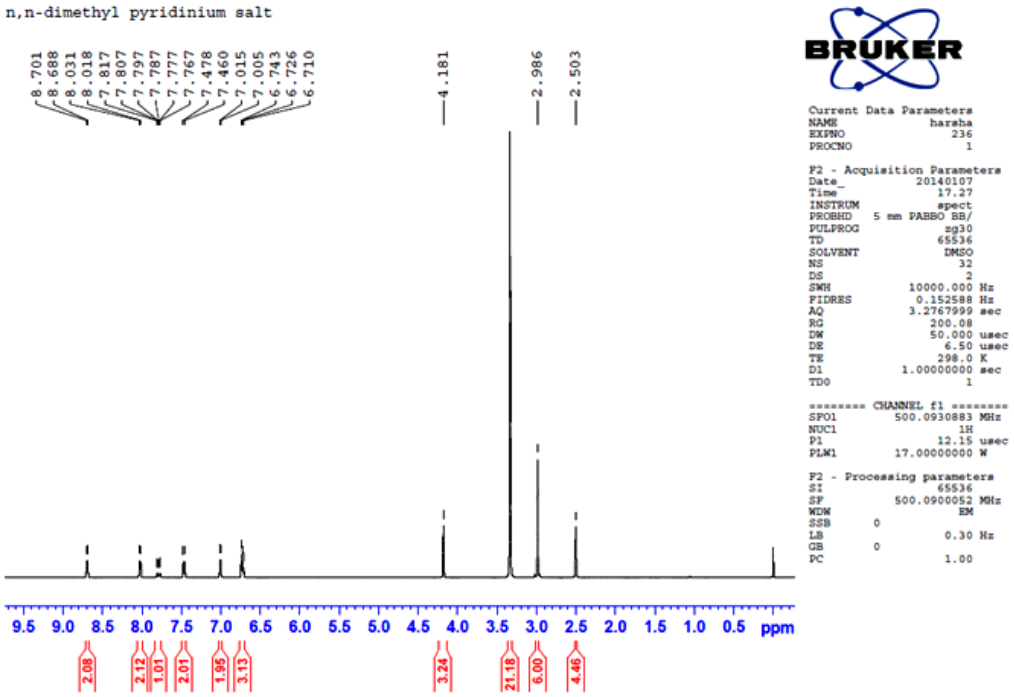
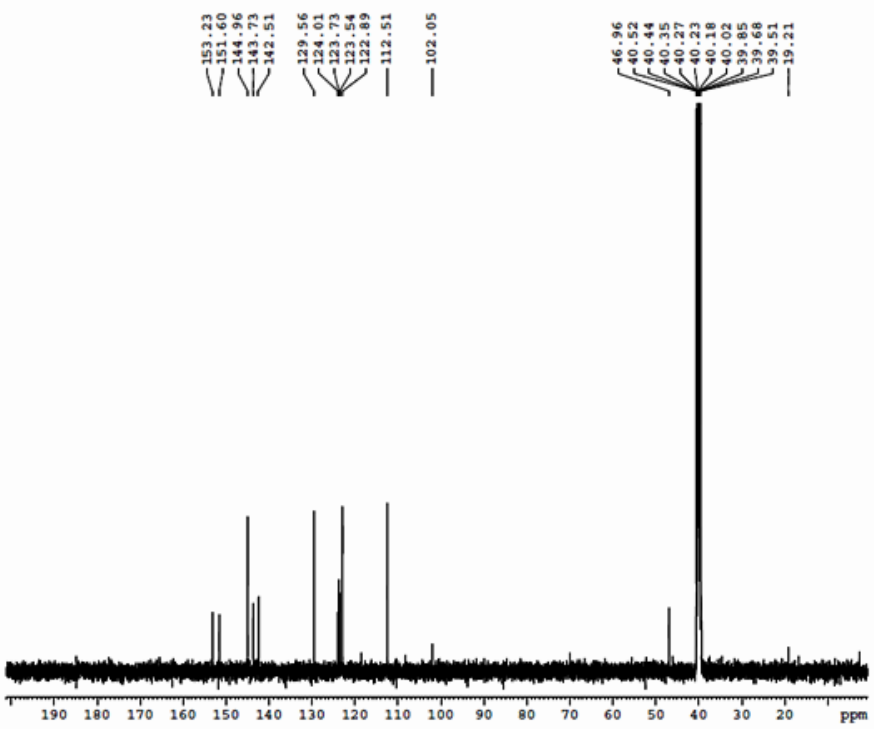


$^{1}H,^{13}C$ NMR and Mass spectra of 4-((1E,3E)-4-(4-(dimethylamino)phenyl)buta-1,3-dienyl)-1-methylpyridinium (**3**)



n,n-dimethyl pyridinium salt



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NUC1 13C
P1 8.90 usec
PLW1 29.00000000 W

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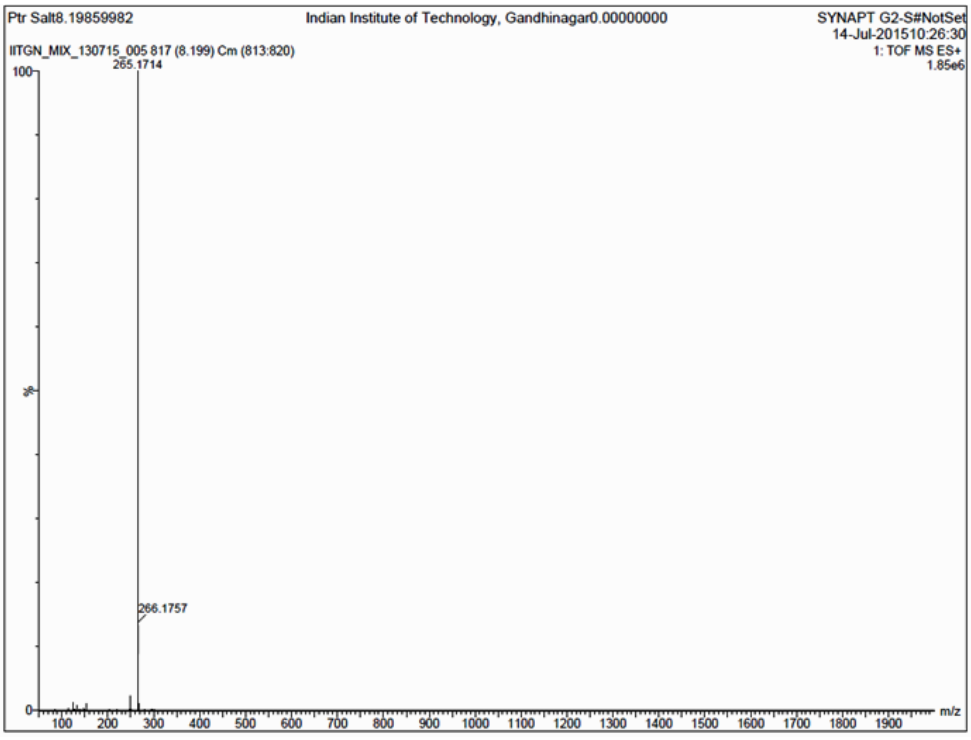
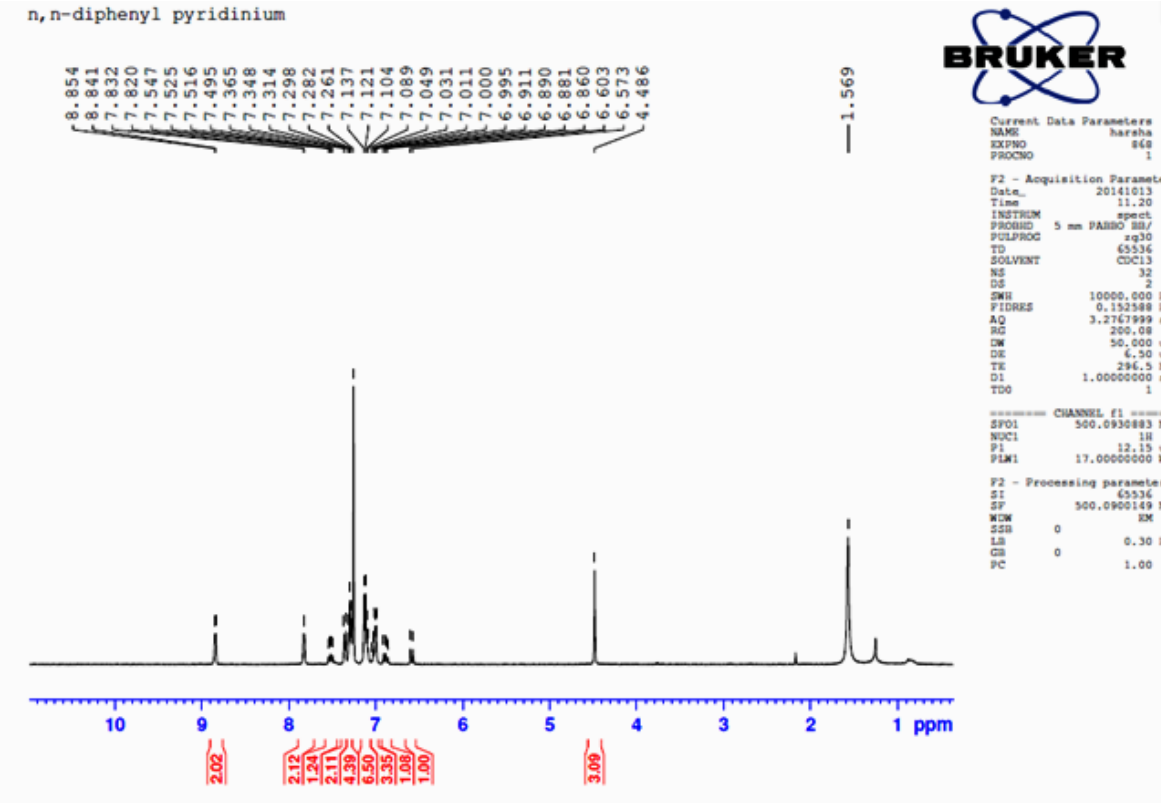
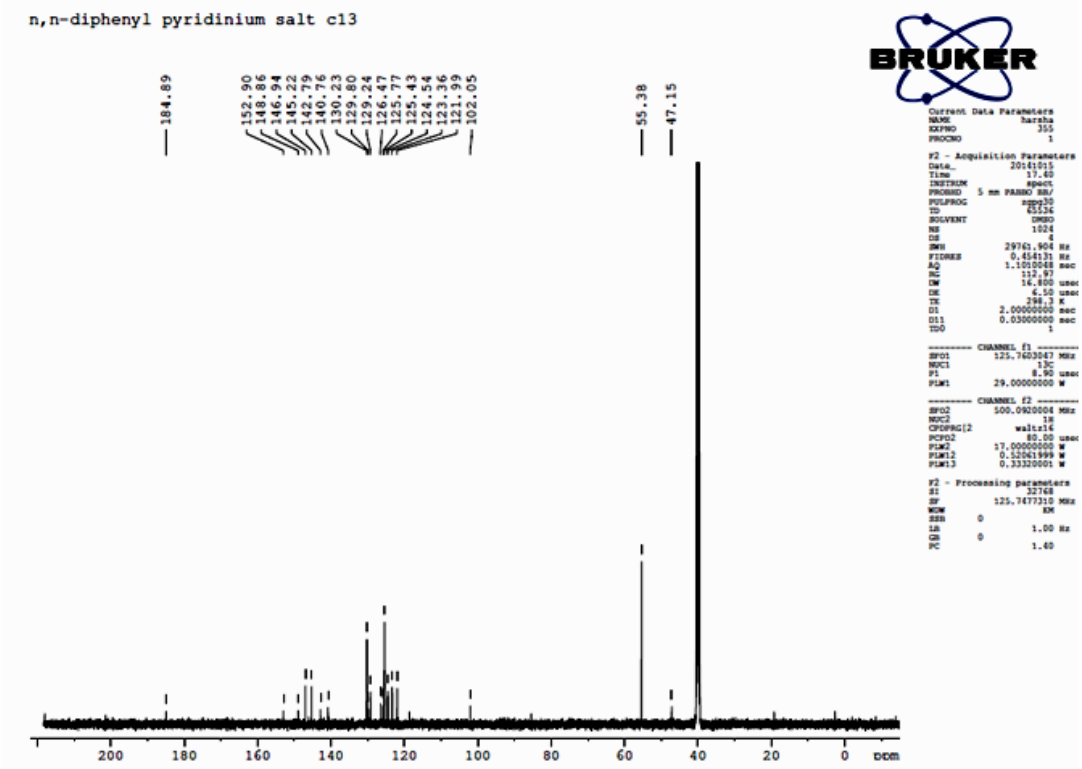
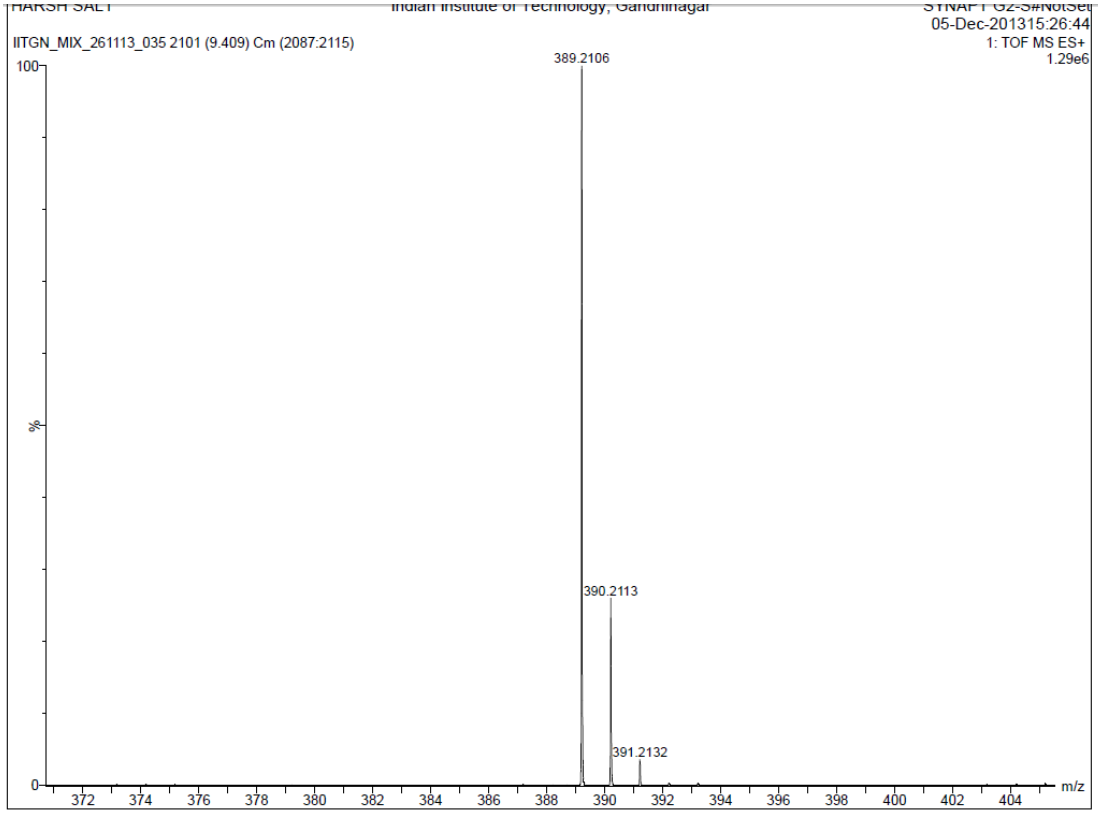


^{1}H ,^{13}C NMR and Massspectra of 4-((1E,3E)-4-(4-(diphenylamino)phenyl)buta-1,3-dienyl)-1-methylpyridinium iodide (**4**)







References

1. N. S. S. Kumar, S. Varghese, N. P. Rath and S. Das, Solid State Optical Properties of 4-Alkoxy-pyridine Butadiene Derivatives: Reversible Thermal Switching of Luminescence, *The Journal of Physical Chemistry C*, 2008, **112**, 8429-8437.
2. K. K. K. Fernando Hung-Low, John Brannon Gary, Effect of anion and ligand ratio in self-assembled silver(I) complexes of 4-(diphenylphosphinomethyl)pyridine and their derivatives with bipyridine ligands, *Inorganica Chimica Acta*, 2009, **362**, 426-436.
3. B. J. Coe, J. Fielden, S. P. Foxon, M. Helliwell, B. S. Brunschwig, I. Asselberghs, K. Clays, J. Olesiak, K. Matczyszyn and M. Samoc, Quadratic and Cubic Nonlinear Optical Properties of Salts of Diquat-Based Chromophores with Diphenylamino Substituents, *The Journal of Physical Chemistry A*, 2010, **114**, 12028-12041.