Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

One pot synthesis of highly functionalized pyrimido[1, 2-b]indazoles via 6-endo-dig cyclization

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Experimental section:

All commercially available reagents were used without any further purification and the reactions were monitored by TLC. ^{1}H and ^{13}C NMR were obtained using a Bruker Avance 400 Mz spectrometer in $CDCl_3$ solvent with TMS as an internal standard. Chemical shift values (δ) were expressed in parts per million (ppm). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Melting points were measured on Elchem Microprocessor based DT apparatus using an open capillary tubes and are corrected with benzoic acid. Mass spectra were obtained by high resolution mass spectrometer. UV-vis spectrum was obtained on UV-2550, Shimadzu Corporation, Kyoto, Japan. The fluorescence spectra were obtained on Hitachi F-7000 FL spectrophotometer.

General procedure for the synthesis of 2,4-diphenylpyrimido [1,2-b] indazole 4 (a-q) via metal mediated condition:

A mixture of 1H-indazol-3-amine (1mmol) , aldehydes (1mmol) and acetylenes (1mmol) in 5 mL of toluene. Then added $CuSO_4$. $5H_2O$ (21 mol %) followed by *para* –toluene sulphonic acid (10 mol %) in the presence of nitrogen atmosphere. The mixture was refluxed at 121 ^{o}C for 8 h 30 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, evaporated the solvent and the crude was purified by column chromatography afford the product as a solid.

Experimental design & Mathematical model:

An experimental design for the series of parameters used for the synthesis of 2,4-diphenylpyrimido [1,2-*b*] indazole by two reaction methods such as metal mediated and metal free conditions. The model was built by Response Surface Methodology (RSM) with the Design – Expert Version 9.0.5.1 (State-Ease, Inc., Minneapolis, USA). Levels of selection for each variable based on the results of the preliminary studies. The three components for each reaction method, such as the catalyst loading (A1), reaction temperature (B1) and response time (C1) were utilized for metal mediated reaction.. The actual isolated yields $\mathbf{Y_1}$ was chosen to be the target or response parameter as dependent variables. The $\mathbf{X_1}$ was denoted as predicted isolated yields. Seventeen sets of experiments were performed for each both reaction methods according to Box-Behnken experimental design (BBD). The variables were tested at the three levels by associating negative sign (-1) for lower level, Zero (0) indicating the core value and plus signs (+1) for higher stages (Table 1). The quadratic polynomial equation recommended by RSM was used to predict the optimal value and examine the interaction between the response of experimental design (actual

yield) and the variables (process parameters). The general form of quadratic polynomial was as follows

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_2 + \beta_{23} X_2 X_3$$

Where β_0 is constant coefficient of the models. The regression coefficients (β_1, β_2 and β_3), (β_{11}, β_{22} and β_{33}) and (β_{12}, β_{13} and β_{23}) respectively represent linear, quadratic and interaction effects of the model estimated by multiple regression analysis.

Figure S1: The solvatochromism spectra of the compound **4a**.

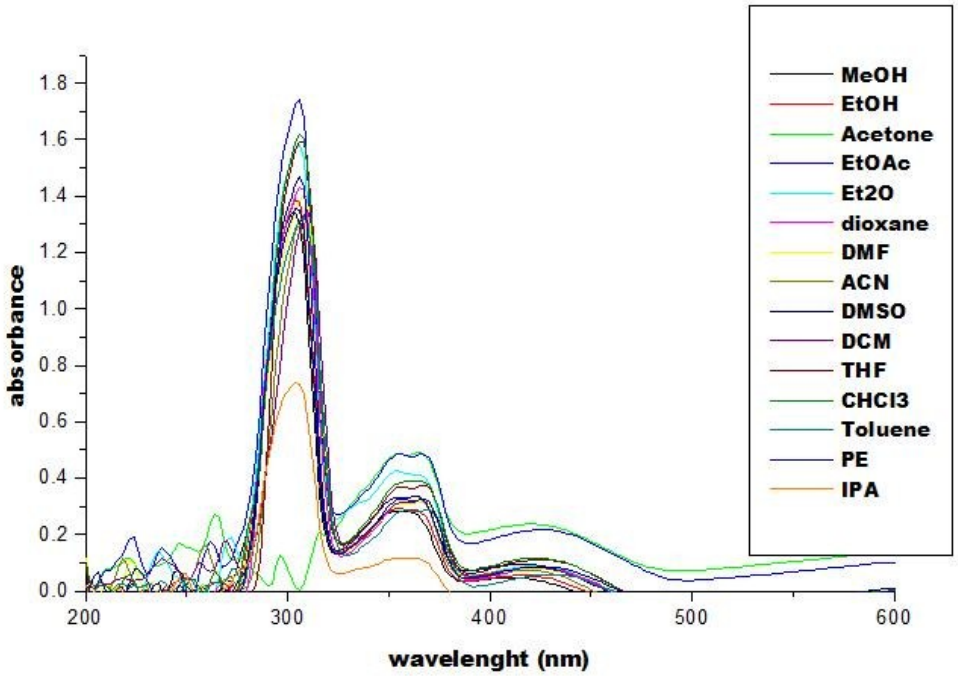


Figure S2. UV/Vis absorbance spectra of the pyrimido[1,2-*b*]indazoles 4(a-t) in ethyl acetate.

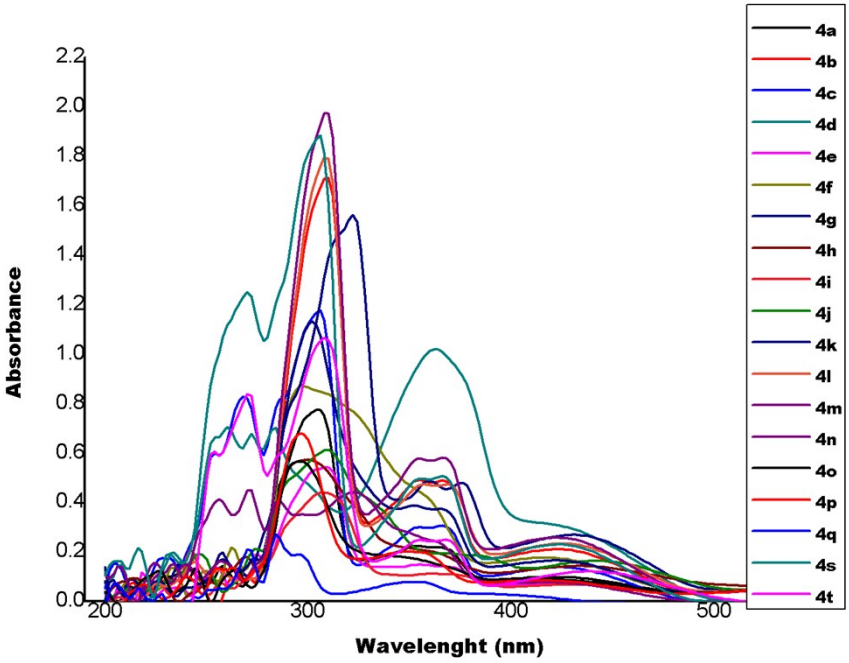
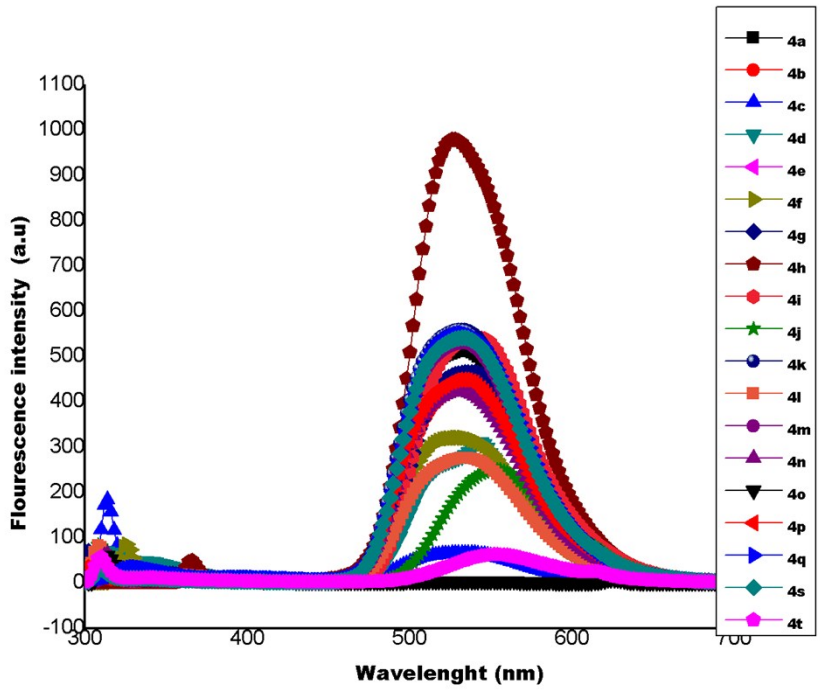
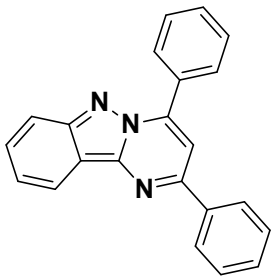


Figure S3: Fluorescence emission spectra of the pyrimido[1,2-*b*]indazoles **4(a-t)** in ethyl acetate.



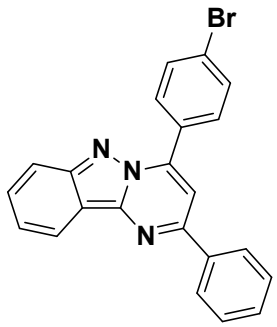
Spectral characterization of the compound 4(a-t):

2,4-diphenylpyrimido[1,2-*b*]indazole (4a)



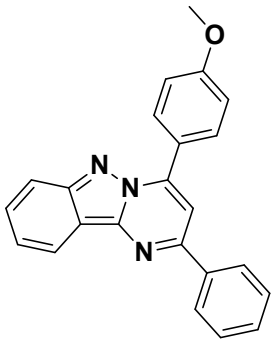
Yellow solid; Isolated yield - 90 %; mp: 154-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.2 Hz, 1H), 8.30-8.27 (m, 2H), 8.23-820 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.75 (s, 1H), 7.67-7.50 (m, 7H), 7.33-7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ108.6,113.9, 116.6, 120.7, 121.2, 127.2, 128.8, 129.0, 129.5, 129.8, 130.1, 131.1, 131.8, 137.3, 145.0, 145.3, 151.6, 152.6; HRMS: m/z calcd. for $C_{22}H_{15}N_3$ 321.1266 found 321.1256.

4-(4-bromophenyl)-2-phenylpyrimido[1,2-*b*]indazole (4b)



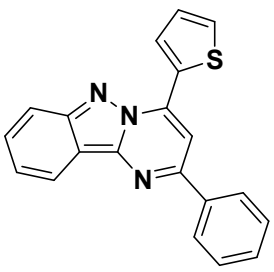
Yellow solid; Isolated yield - 89 %; mp: 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.20-8.12 (m, 4H), 7.86-7.84 (m, 1H), 7.69-7.59 (m, 7H), 7.32-7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.1, 113.9, 116.6, 120.9, 121.1, 124.7, 128.6, 128.9, 129.4, 130.0, 131.1, 131.6, 132.2, 136.2, 144.9, 145.3, 151.1, 151.6; HRMS: m/z calcd. for $C_{22}H_{14}BrN_3$ 399.0371 found 399.0370.

4-(4-methoxyphenyl)-2-phenylpyrimido[1,2-*b*]indazole (4c)



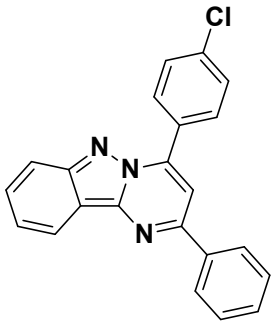
Yellow solid; Isolated yield - 85 %; mp: 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 8.15-8.10 (m, 3H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.57-7.49 (m, 5H), 7.21-7.17 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 108.1, 113.7, 114.4, 116.5, 120.4, 121.2, 128.6, 128.8, 129.5, 129.7, 129.8, 130.9, 131.9, 145.0, 145.2, 151.5, 152.4, 161.4; HRMS: m/z calcd. for $C_{23}H_{17}N_3O$ 351.1372 found 351.1371.

2-phenyl-4-(thiophen-2-yl)pyrimido[1,2-*b*]indazole (4d)



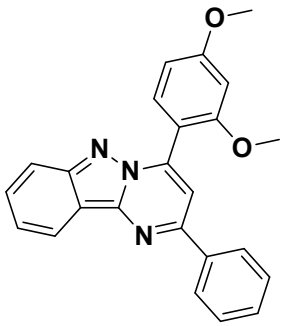
Brown solid; Isolated yield - 81 %; mp: 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.0 Hz, 1H), 8.23-8.20 (m, 2H), 7.86-7.82 (m, 2H), 7.69-7.56 (m, 6H), 7.33-7.29 (m, 1H), 7.22-7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.5, 113.6, 116.5, 120.6, 121.3, 126.8, 128.4, 128.8, 129.5, 129.9, 131.0, 131.6, 143.2, 144.6, 145.2, 148.0, 151.6; HRMS: m/z calcd. for $C_{20}H_{13}N_3S$ 327.0830 found 327.0829.

4-(4-chlorophenyl)-2-phenylpyrimido[1,2-*b*]indazole (4e)



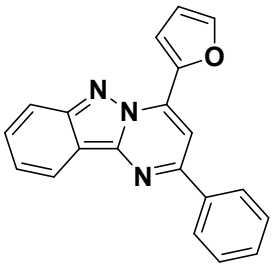
Yellow solid; Isolated yield - 89 %; mp: 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (d, *J* = 8.4 Hz, 1H), 8.23-8.19 (m, 4H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.65 (s, 1H), 7.65-7.59 (m, 4H), 7.53-7.51 (m, 2H), 7.31-7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.2, 113.2, 116.6, 120.9, 121.1, 128.4, 128.9, 129.2, 129.4, 129.9, 131.1, 131.7, 135.7, 136.3, 144.9, 145.4, 151.1, 151.6; HRMS: m/z calcd. for $C_{22}H_{14}N_3Cl$ 355.0876 found 355.0875.

4-(2,4-dimethoxyphenyl)-2-phenylpyrimido[1,2-*b*]indazole (4f)



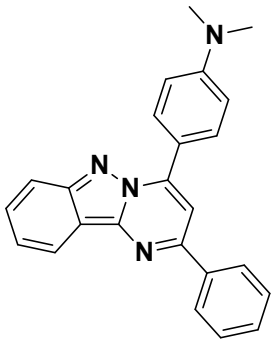
Yellow solid; Isolated yield - 87 %; mp: 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.0 Hz, 1H), 8.15-8.14 (m, 2H), 7.92 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.55-7.50 (m, 4H), 7.21-7.18 (m, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.54 (s,1H), 3.86 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.8, 99.0, 105.7, 113.0, 113.7, 116.4, 120.0, 120.1, 121.2, 128.7, 129.5, 129.6, 130.6, 132.2, 132.4, 143.8, 144.9, 151.2, 152.0, 158.8, 162.5; HRMS: m/z calcd. for $C_{24}H_{19}N_3O_2$ 381.1477 found 381.1477.

4-(furan-2-yl)-2-phenylpyrimido[1,2-*b*]indazole (4g)



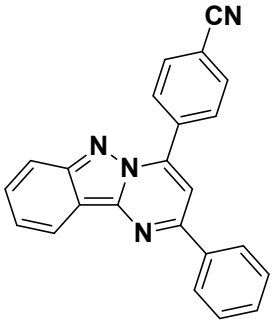
Brown solid; Isolated yield - 79 %; mp: 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 8.20-8.17 (m, 2H), 7.83-7.79 (m, 2H), 7.65-7.53 (m, 6H), 7.30-7.27 (m, 1H), 7.20-7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.5, 113.6, 116.5, 120.6, 121.3, 126.8, 128.4, 128.8, 129.5, 129.9, 131.0, 131.6, 143.2, 144.6, 145.2, 148.0, 151.6; HRMS: m/z calcd. for $C_{20}H_{13}N_3O$ 311.1059 found 311.1058.

N,N-dimethyl-4-(2-phenylpyrimido[1,2-*b*]indazol-4-yl)aniline (4h)



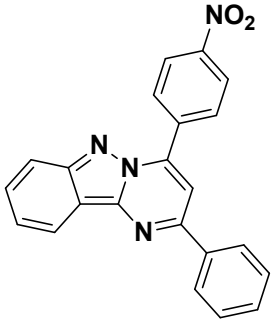
Brown solid; Isolated yield - 84 %; mp: 147-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 8.13-8.11 (m, 3H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.57-7.47 (m, 5H), 7.18-7.15 (m, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.2, 107.8, 112.1, 113.6, 116.3, 119.9, 121.3, 124.7, 128.3, 128.7, 129.4, 129.5, 130.7, 132.2, 151.5; HRMS: m/z calcd. for $C_{24}H_{20}N_4$ 364.1688 found 364.1688.

4-(2-phenylpyrimido[1,2-*b*]indazol-4-yl)benzonitrile (4i)



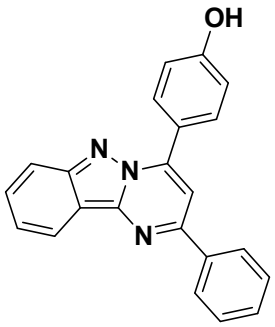
Yellow solid; Isolated yield - 78 %; mp: 252-254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.20-8.12 (m, 4H), 7.86-7.84 (m, 1H), 7.69-7.59 (m, 7H), 7.32-7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.1, 113.9, 116.6, 120.9, 121.1, 124.7, 128.6, 128.9, 129.4, 130.0, 131.1, 131.6, 132.2, 136.2, 144.9, 145.3, 151.1, 151.6; HRMS: m/z calcd. for $C_{23}H_{14}N_4$ 346.1218 found 346.1217.

4-(4-nitrophenyl)-2-phenylpyrimido[1,2-*b*]indazole (4j)



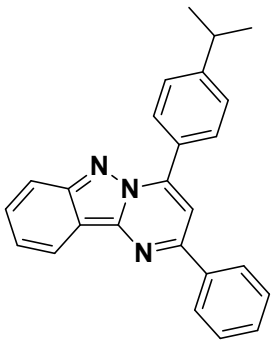
Yellow solid; Isolated yield - 75 %; mp: 272-274 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48-8.40 (m, 5H), 8.24-8.22 (m, 2H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 1H), 7.69-7.65 (m, 4H), 7.40-7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.4, 114.2, 116.9, 121., 121.5, 124.2, 127.8, 128.9, 129.5, 130.3, 131.3, 143.1, 144.9, 145.5, 148.6, 149.1, 151.8; HRMS: m/z calcd. for $C_{22}H_{14}N_4O_2$ 366.1117 found 366.1115.

4-(2-phenylpyrimido[1,2-*b*]indazol-4-yl)phenol (4k)



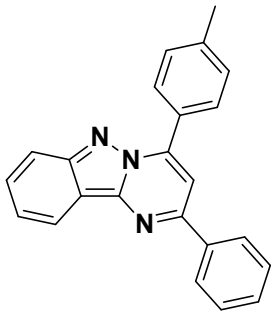
Brown solid; Isolated yield - 80 %; mp: 306-308 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.36-8.33 (m, 3H), 8.15 (s, 1H), 7.89-7.71 (m, 3H), 7.70-7.63 (m, 4H), 7.42-7.32 (m, 2H), 6.99-6.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.9, 113.0, 113.7, 116.2, 117.5, 118.2, 120.6, 120.7, 128.4, 129.8, 129.9, 130.0, 130.9, 131.2, 137.9, 144.0, 144.7, 150.6, 152.1, 157.9; HRMS: m/z calcd. for $C_{22}H_{15}N_3O$ 337.1215 found 337.1214.

4-(4-isopropylphenyl)-2-phenylpyrimido[1,2-*b*]indazole (4l)



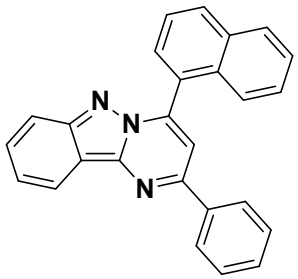
Yellow solid; Isolated yield - 87 %; mp: 156-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.22-8.19 (m, 4H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.72 (s, 1H), 7.66-7.59 (m, 4H), 7.43-7.41 (m, 2H), 7.31-7.28 (m, 1H), 3.05-2.98 (m 1H), 1.32 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 34.1, 108.5, 113.8, 116.5, 120.5, 121.2, 127.2, 128.8, 129.5, 129.8, 130.9, 131.9, 135.0, 131.9, 135.0, 145.0, 151.3, 151.5, 152.8; HRMS: m/z calcd. for $C_{25}H_{21}N_3$ 363.1735 found 363.1734.

2-phenyl-4-(p-tolyl)pyrimido[1,2-*b*]indazole (4m)



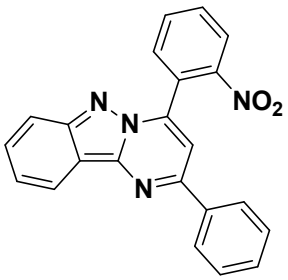
Yellow solid; Isolated yield - 90 %; mp: 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43-8.40 (m, 1H), 8.22-8.17 (m, 4H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.72 (s, 1H), 7.64-7.58 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31-7.28 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 108.4, 113.8, 116.5, 120.5, 121.2, 127.1, 128.8, 129.5, 129.8, 130.9, 131.9, 134.6, 140.4, 145.0, 145.2, 151.6, 152.7; HRMS: m/z calcd. for $C_{23}H_{17}N_3$ 335.1422 found 335.1420.

4-(naphthalen-1-yl)-2-phenylpyrimido[1,2-*b*]indazole (4n)



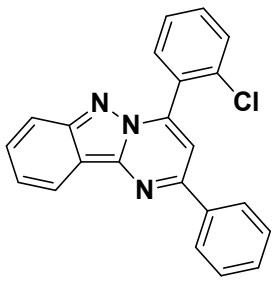
Brown solid; Isolated yield - 81 %; mp: 180-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44-8.37 (m, 2H), 8.27-8.25 (m, 2H), 8.01-7.85 (m, 4H), 7.66-7.53 (m, 8H), 7.32 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.1, 113.8, 116.6, 120.8, 121.2, 125.3, 126.2, 127.1, 128.2, 128.6, 128.8, 129.5, 129.9, 130.0, 130.9, 131.1, 131.5, 134.1, 136.4, 144.9, 151.6, 154.7; HRMS: m/z calcd. for $C_{26}H_{17}N_3$ 371.1422 found 371.1420.

4-(2-nitrophenyl)-2-phenylpyrimido[1,2-*b*]indazole (4o)



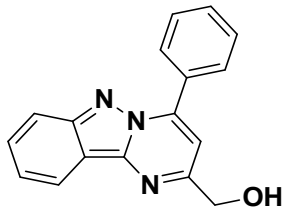
Brown solid; Isolated yield - 77 %; mp: 200-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.6 Hz, 1H), 8.22-8.19 (m, 2H), 8.04-8.01 (m, 1H), 7.89-7.85 (m, 2H), 7.76-7.75 (m, 1H), 7.66-7.61 (m, 5H), 7.41 (s, 1H), 7.33-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.6, 113.9, 116.7, 121.1, 121.3, 124.8, 128.9, 129.5, 130.1, 130.1, 131.2, 131.3, 131.5, 132.8, 133.6, 144.6, 145.3, 149.0, 150.4, 151.6 ; HRMS: m/z calcd. for $C_{22}H_{14}N_4O_2$ 366.1117 found 366.1115.

4-(2-chlorophenyl)-2-phenylpyrimido[1,2-*b*]indazole (4p)



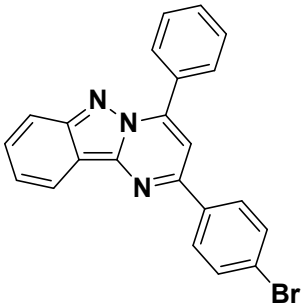
Yellow solid; Isolated yield - 70 %; mp: 198-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 8.26-8.24 (m, 2H), 7.91-7.88 (m, 2H), 7.76 (s, 1H), 7.66-7.43 (m, 7H), 7.34-7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.8, 113.9, 116.6, 120.9, 121.0, 127.4, 128.8, 129.5, 129.8, 130.4, 130.5, 131.1, 131.5, 131.8, 132.4, 137.5, 144.2, 144.9, 151.4, 152.2; HRMS: m/z calcd. for $C_{22}H_{14}N_3Cl$ 355.0876 found 355.0875.

(4-phenylpyrimido[1,2-*b*]indazol-2-yl)methanol (4q)



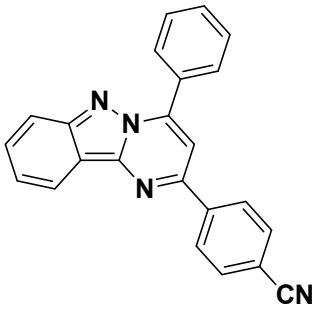
Brown solid; Isolated yield - 76 %; mp: 206-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.73 (s, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.58-7.49 (m, 3H), 7.32 (t, *J* = 8.0 Hz, 1H), 5.33 (s, 2H), 4.28 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.1, 106.0, 113.8, 116.0, 120.9, 121.3, 127.3, 129.1, 130.2, 130.3, 137.1, 144.9, 151.5, 153.2; HRMS: m/z calcd. for $C_{17}H_{13}N_3O$ 275.1059 found 275.1059.

2-(4-bromophenyl)-4-phenylpyrimido[1,2-*b*]indazole (4s)



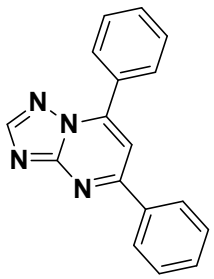
Yellow solid; Isolated yield - 76 %; mp: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.0 Hz, 1H), 8.29-8.27 (m, 2H), 8.23-8.31 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.74 (s, 1H), 7.65-7.51 (m, 6H), 7.31 (t, *J* = 7.6 Hz, 1H**);** ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.6, 113.9, 116.6, 120.7, 121.2, 127.2, 128.5, 129.0, 129.5, 129.8, 130.1, 131.0, 131.8, 137.3, 145.0, 145.3, 151.6, 152.6; HRMS: m/z calcd. for $C_{22}H_{14}BrN_3$ 399.0371 found 399.0370.

4-(4-phenylpyrimido[1,2-*b*]indazol-2-yl)benzonitrile (4t)



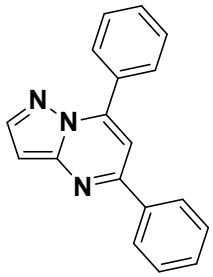
Yellow solid; Isolated yield - 76 %; mp: 232-234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.30 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.79 (s, 1H), 7.70-7.50 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 1H**);** ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.8, 114.0, 114.5, 116.5, 118.1, 121.2, 127.1, 129.1, 130.2, 130.3, 130.4, 132.5, 136.0, 136.9, 142.9, 145.0, 151.6, 152.5; HRMS: m/z calcd. for $C_{23}H_{14}N_4$ 346.1218 found 346.1218.

5,7-diphenyl-[1,2,4]triazolo[1,5-*a*]pyrimidine (4u)



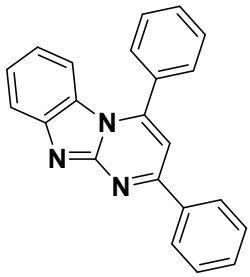
Off-White solid; Isolated yield - 65 %; mp: 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.27 (s, 2H), 8..14 (d, *J* = 5.2 Hz, 2H), 7.67-7.56 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.6, 127.8, 128.3, 128.5, 129.0, 129.1, 129.3, 130.2, 131.3, 131.8, 133.1, 136.4, 148.1, 156.3, 161.7; HRMS: m/z calcd. for $C_{17}H_{12}N_4$ 272.1062 found 272.1060.

5,7-diphenylpyrazolo[1,5-*a*]pyrimidine (4v)



Brown solid; Isolated yield - 60 %; mp: 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.06 (m, 5H), 7.58-7.46 (m, 6H), 7.35 (s, 1H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.2, 105.2, 127.3, 128.3, 128.5, 128.7, 128.9, 129.7, 130.3, 130.9, 131.5, 137.5, 145.2, 146.8, 149.9, 156.2; HRMS: m/z calcd. for $C_{18}H_{13}N_3$ 271.1109 found 272.1109.

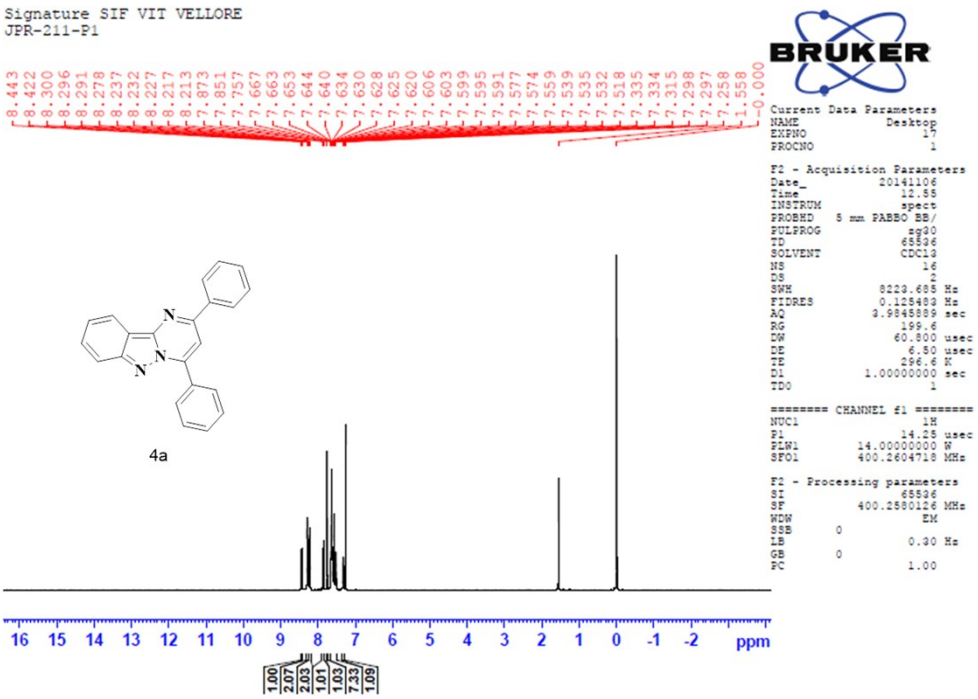
2,4-diphenylbenzo[4,5]imidazo[1,2-*a*]pyrimidine (4w)



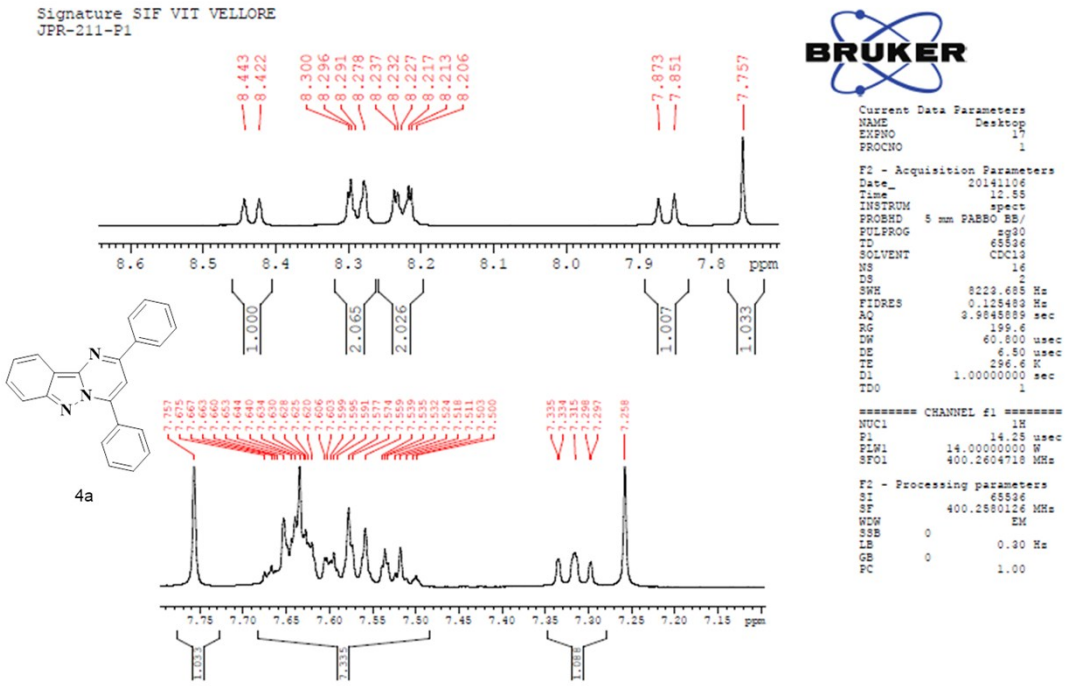
Off-White solid; Isolated yield - 35 %; mp: 276-277 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.23 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.64-7.60 (m, 4H), 7.59-7.46 (m, 4H), 7.38-7.37 (m, 2H), 7.20-7.19 (m, 1H), 6.96-6.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.2, 113.4, 119.2, 120.1, 124.9, 126.8, 127.3, 127.9, 128.4, 130.0, 130.2, 131.5, 135.6, 144.5, 148.3, 160.1 ; HRMS: m/z calcd. for $C_{22}H_{15}N_3$ 321.1266 found 321.1265.

Copies of ^{1}H NMR, ^{13}C NMR and HRMS of 4(a-t):

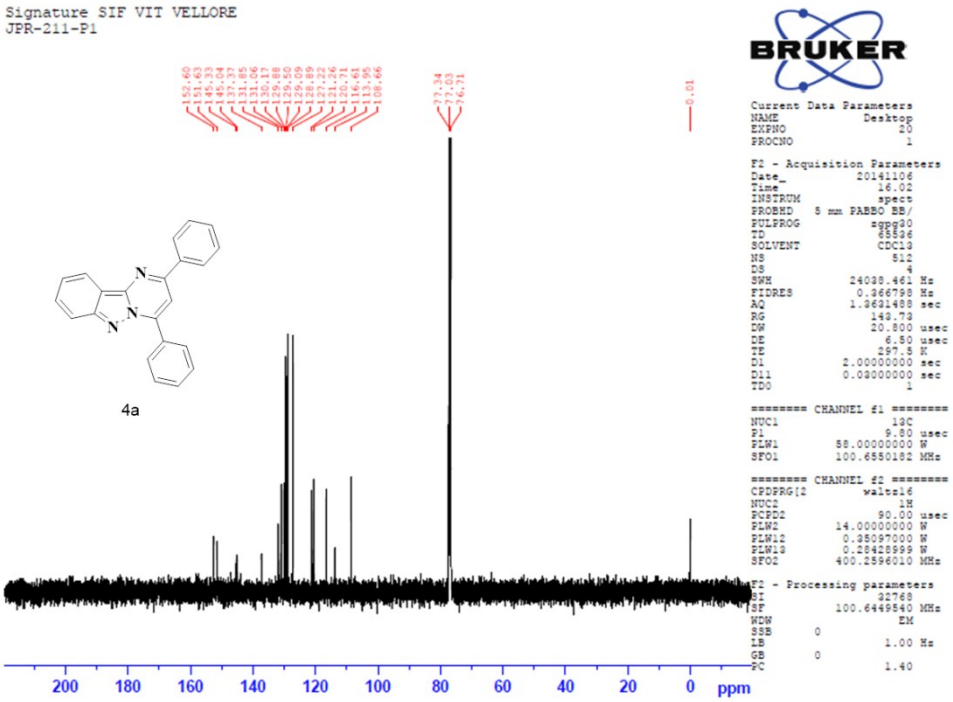
^{1}H NMR spectrum of compound (4a):



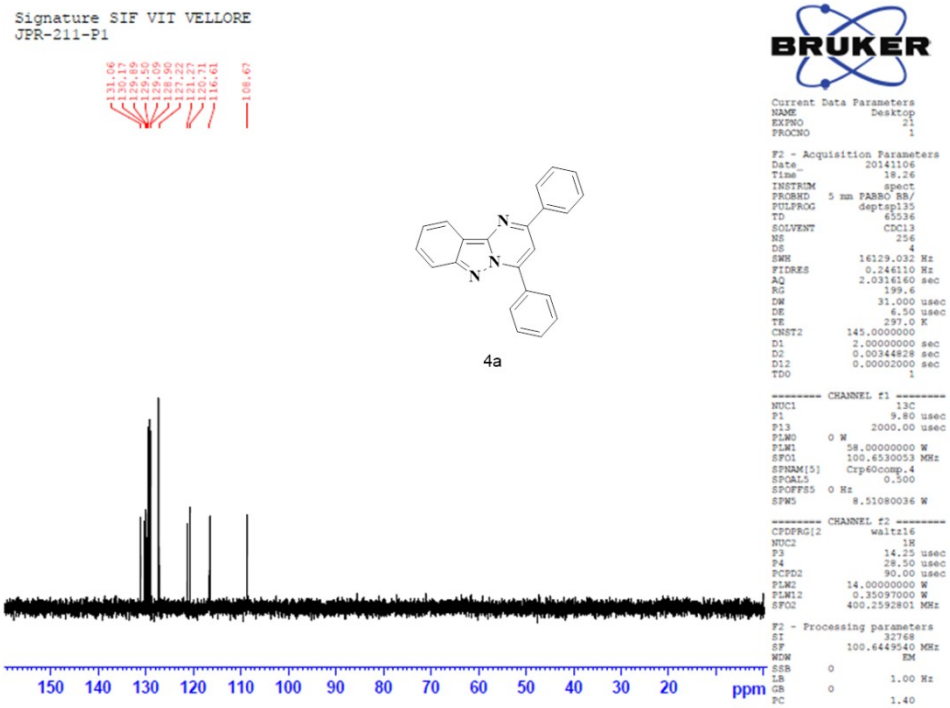
Expanded ^{1}H NMR spectrum of compound (4a):



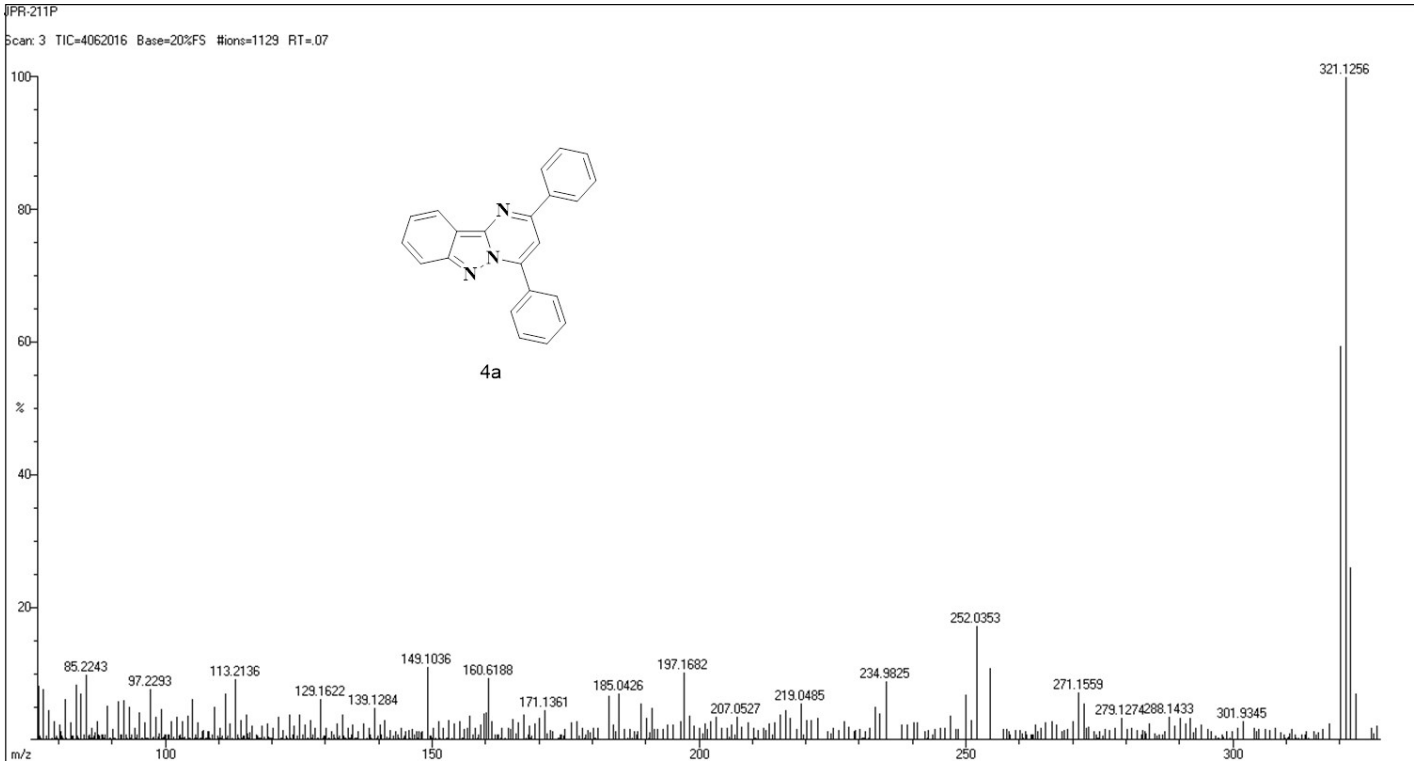
^{13}C NMR spectrum of compound (4a):



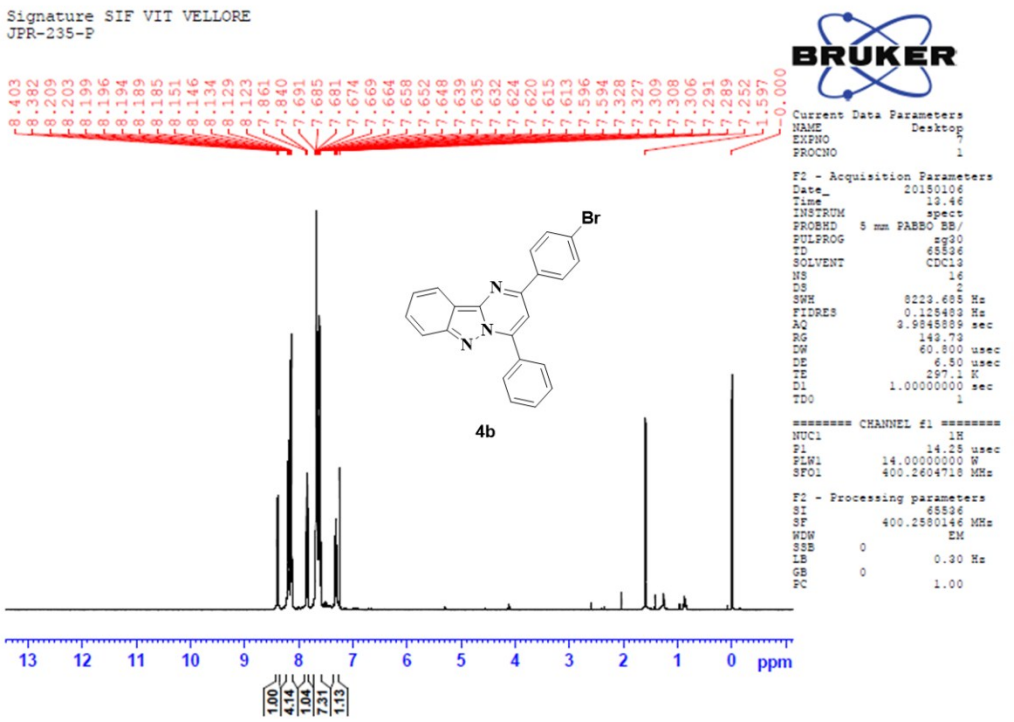
DEPT – 135 spectrum of compound (4a):



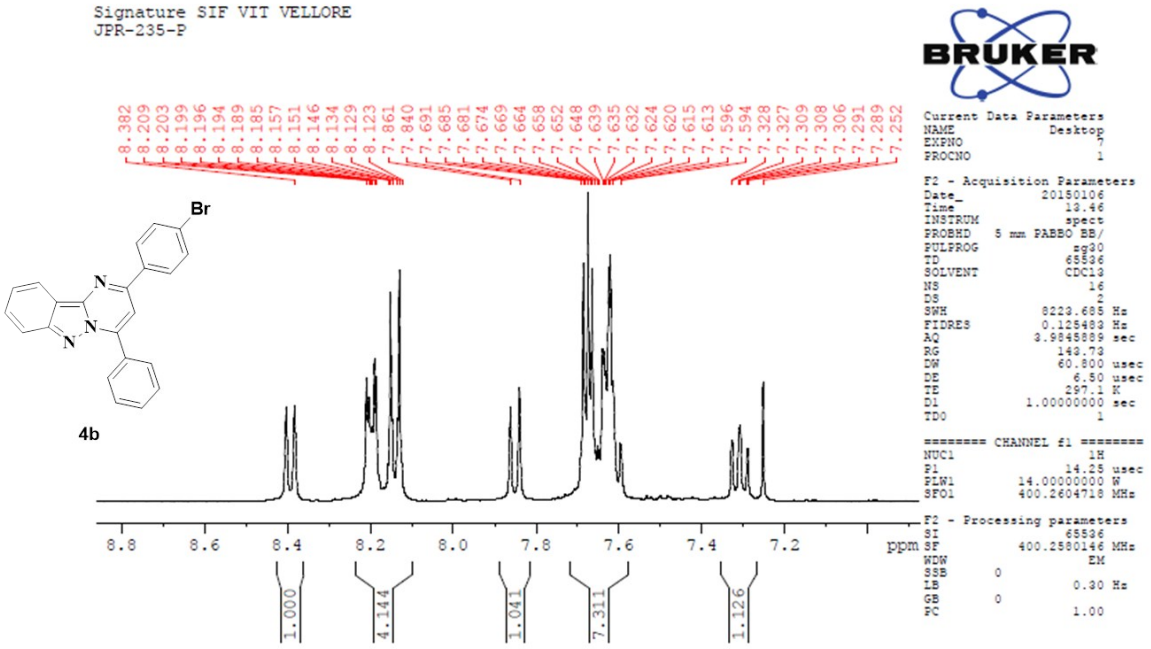
HRMS spectrum of compound (4a):



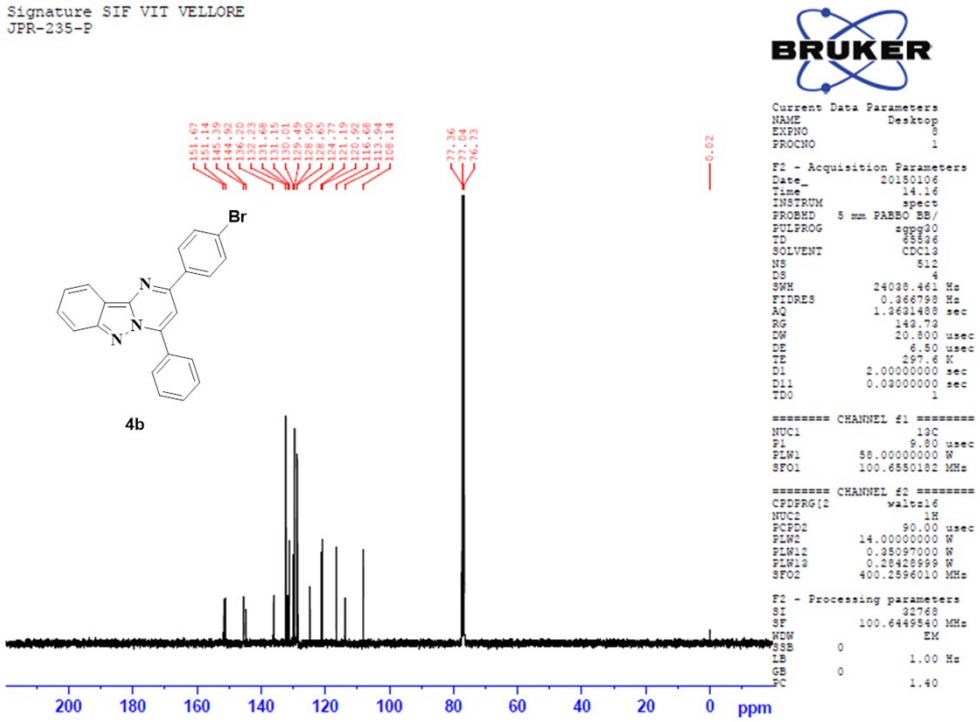
^{1}H NMR spectrum of compound (4b):



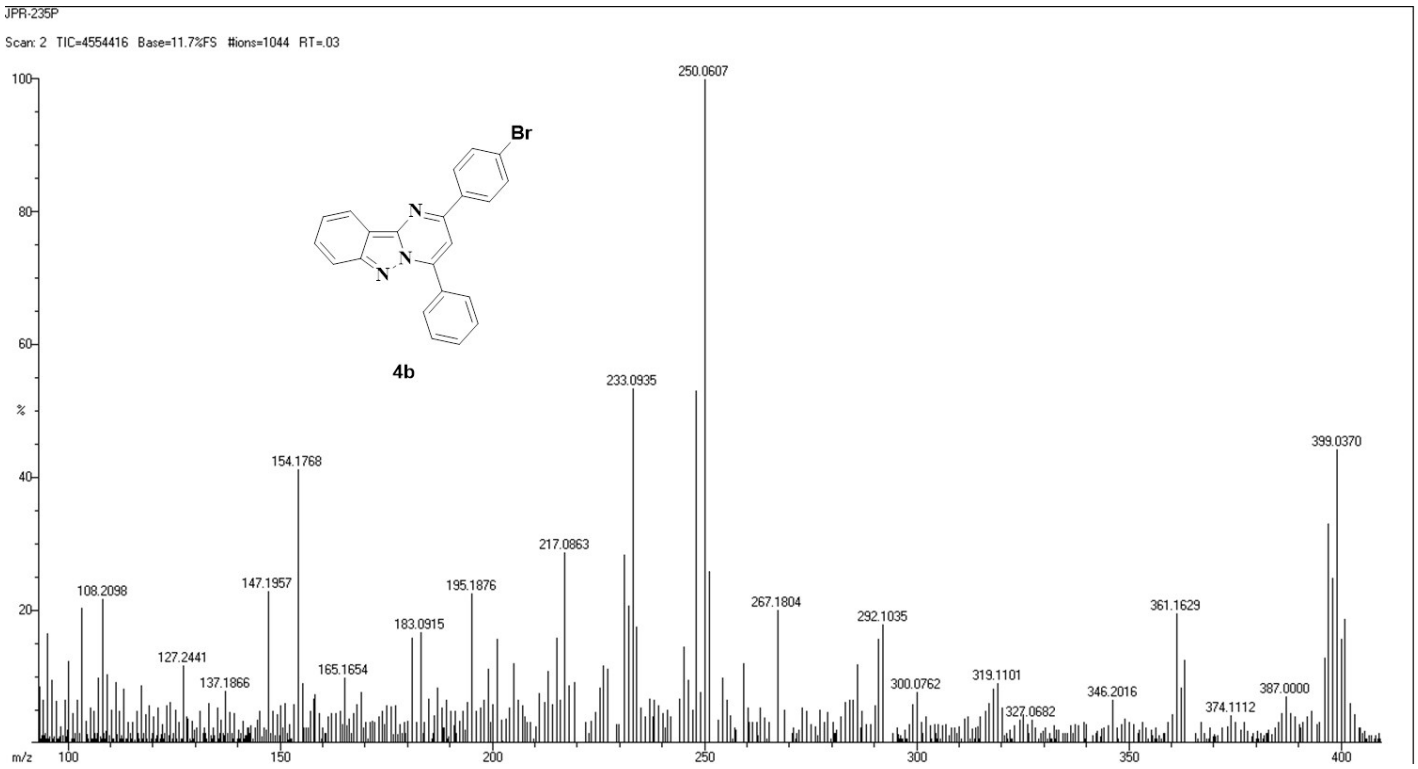
Expanded ^{1}H NMR spectrum of compound (4b):



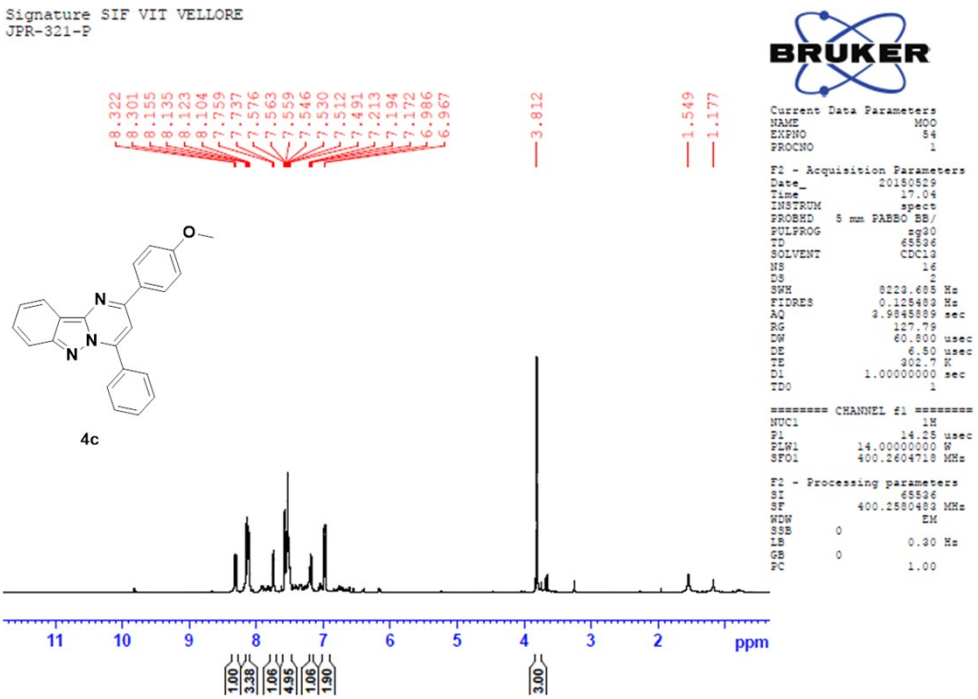
^{CN13}C NMR spectrum of compound (4b):



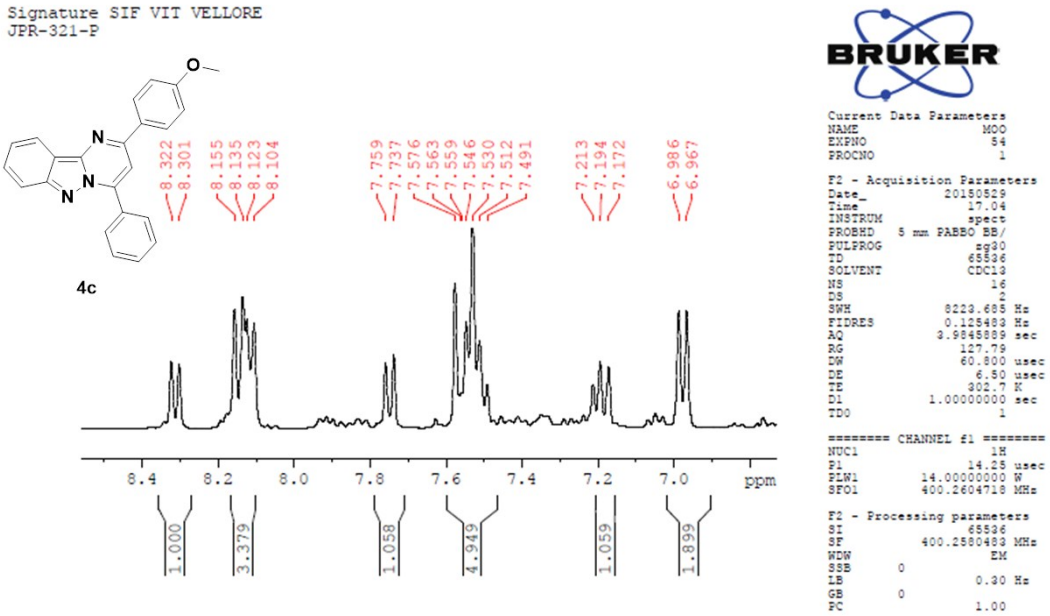
HRMS spectrum of compound (4b):



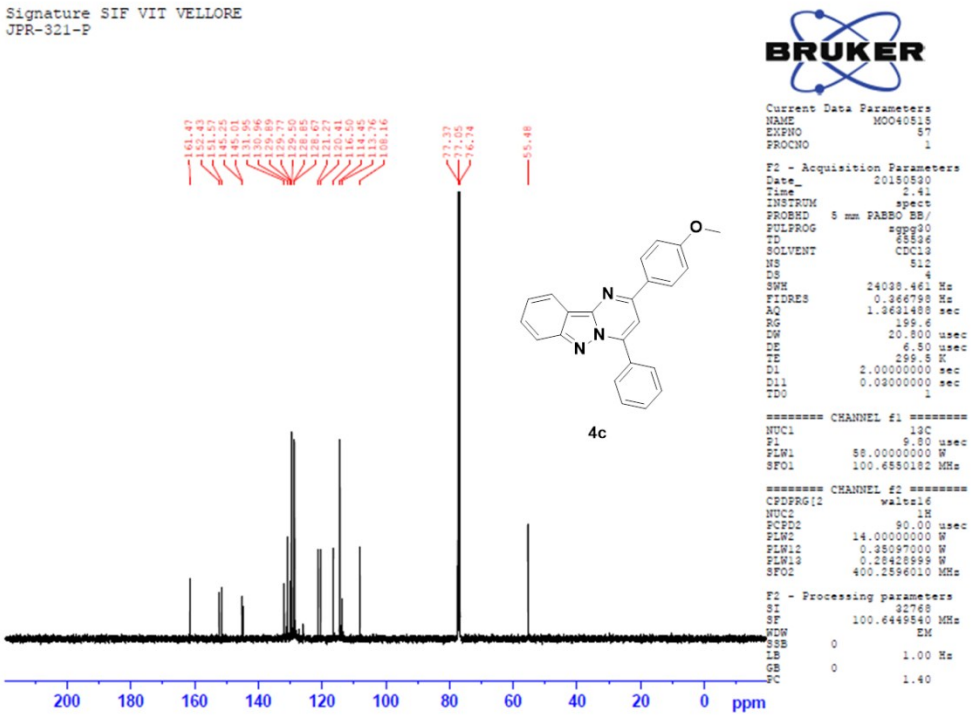
[1]H NMR spectrum of compound (4c):



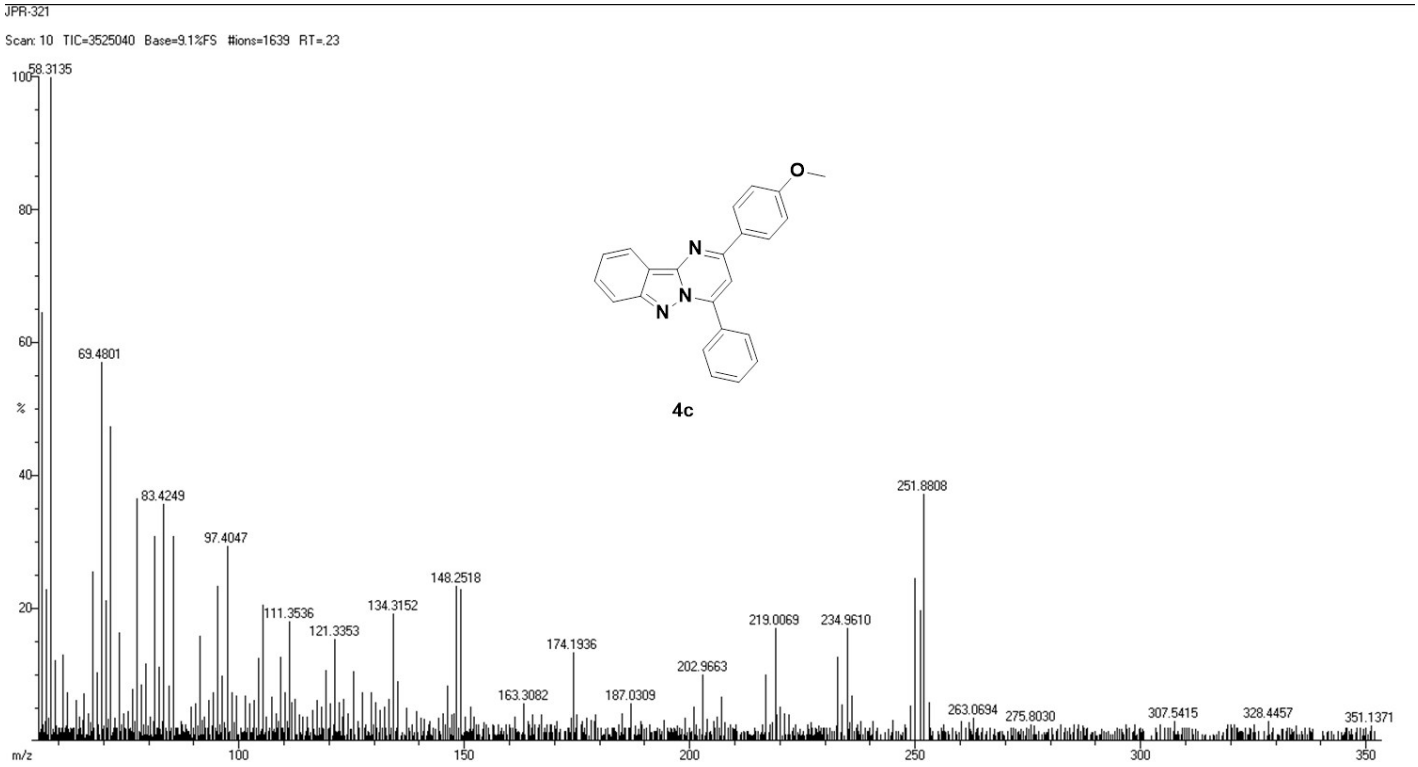
Expanded [1]H NMR spectrum of compound (4c):



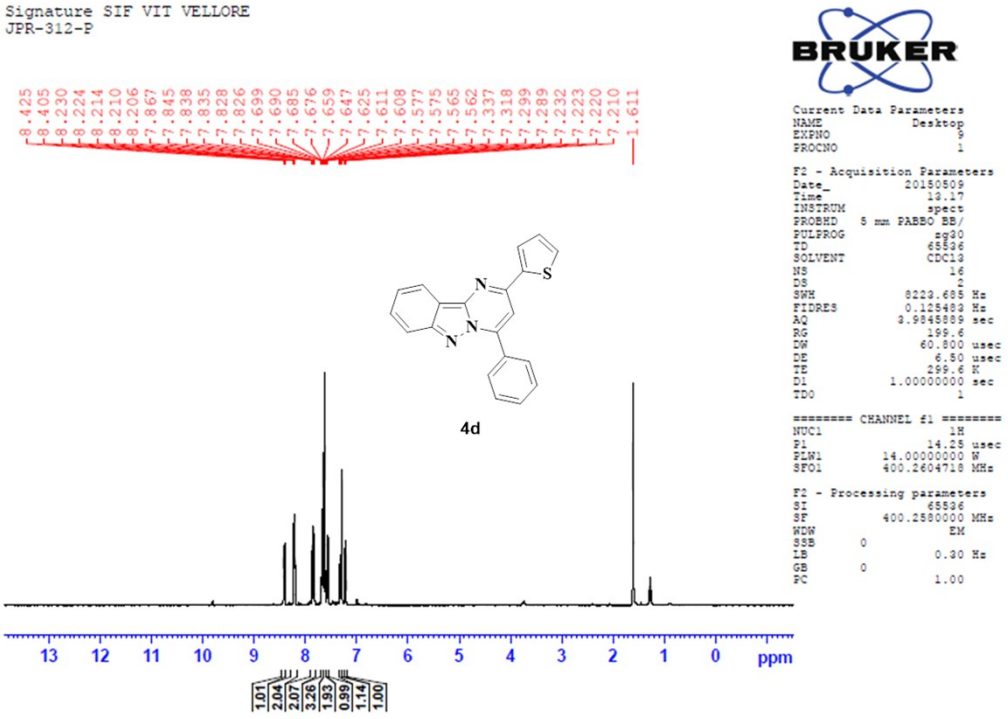
^{13}C NMR spectrum of compound (4c):



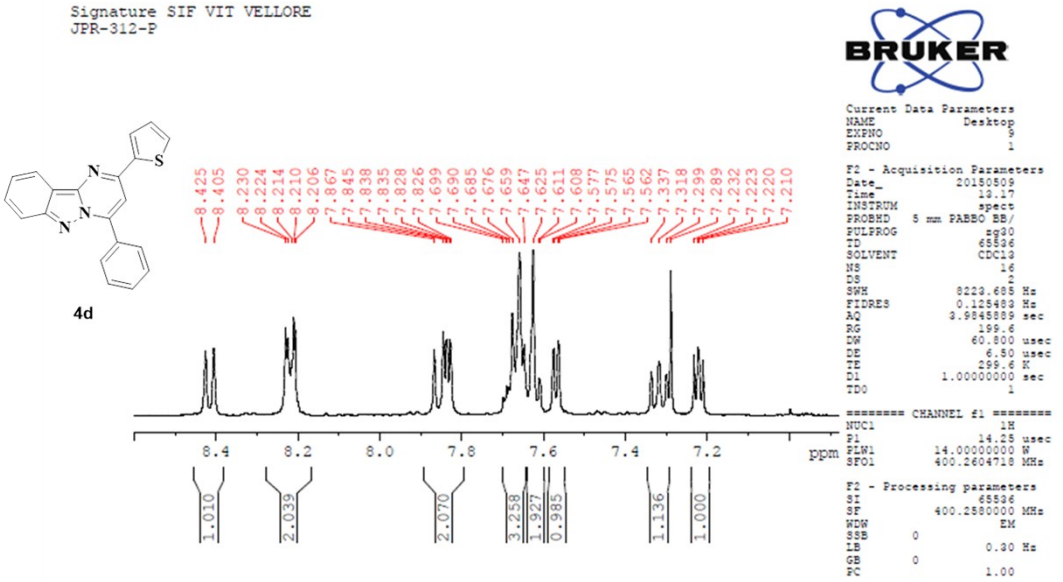
HRMS spectrum of compound (4c):



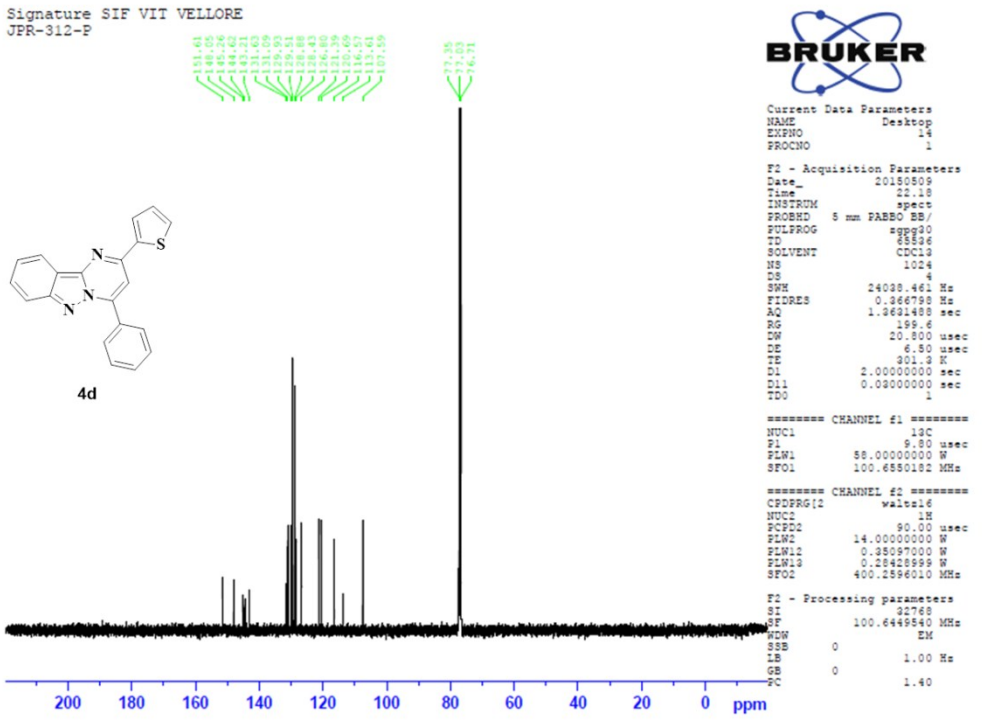
^{1}H NMR spectrum of compound (4d):



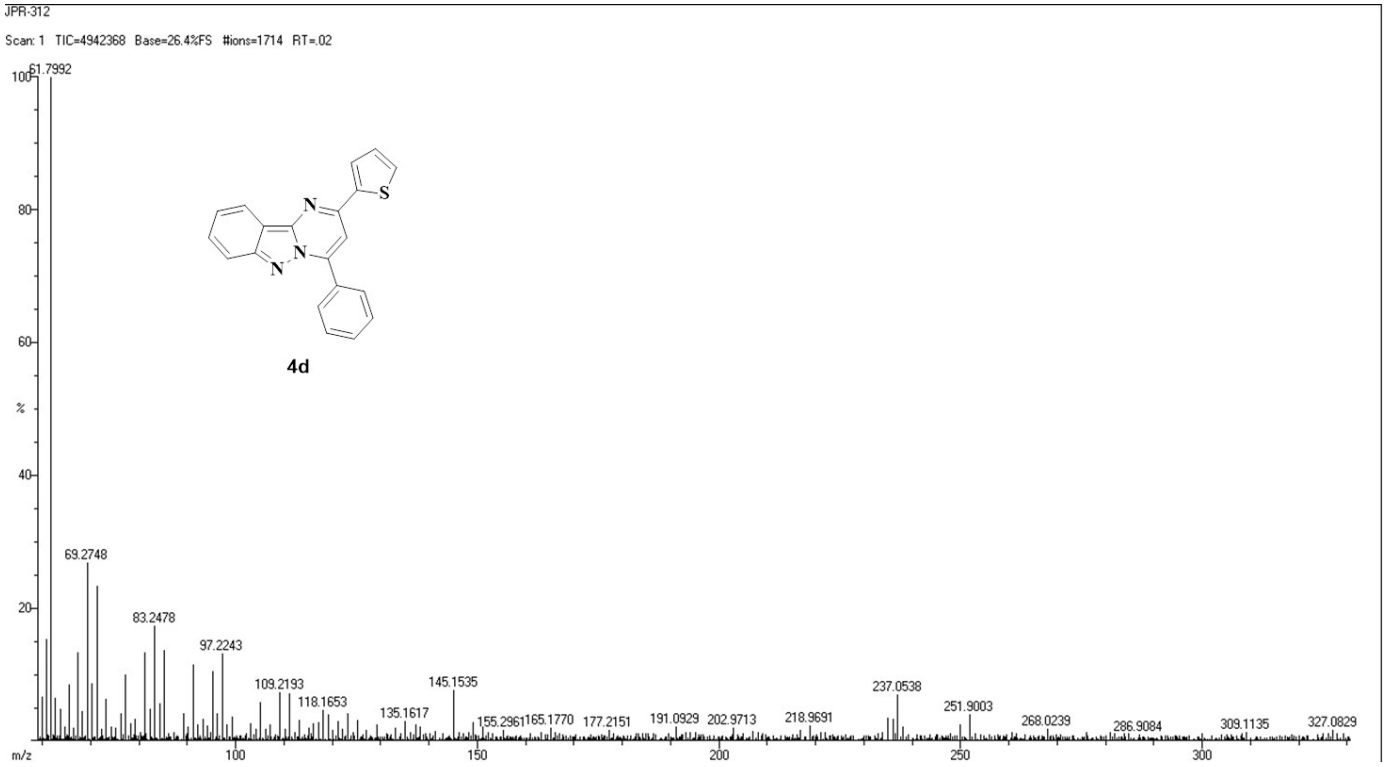
Expanded ^{1}H NMR spectrum of compound (4d):



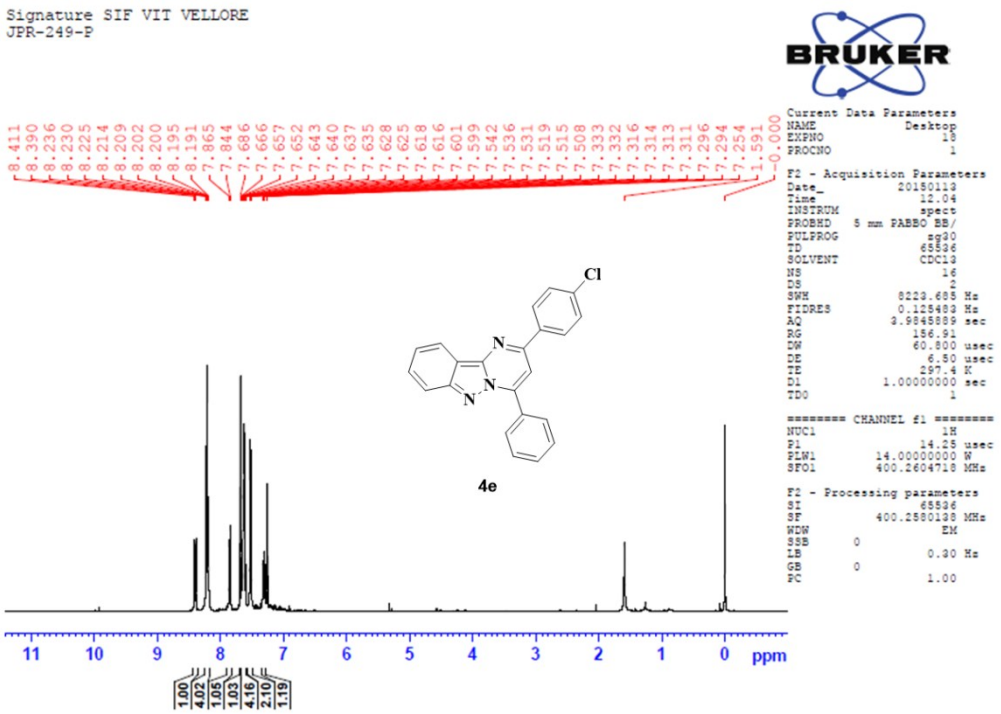
^{13}C NMR spectrum of compound (4d):



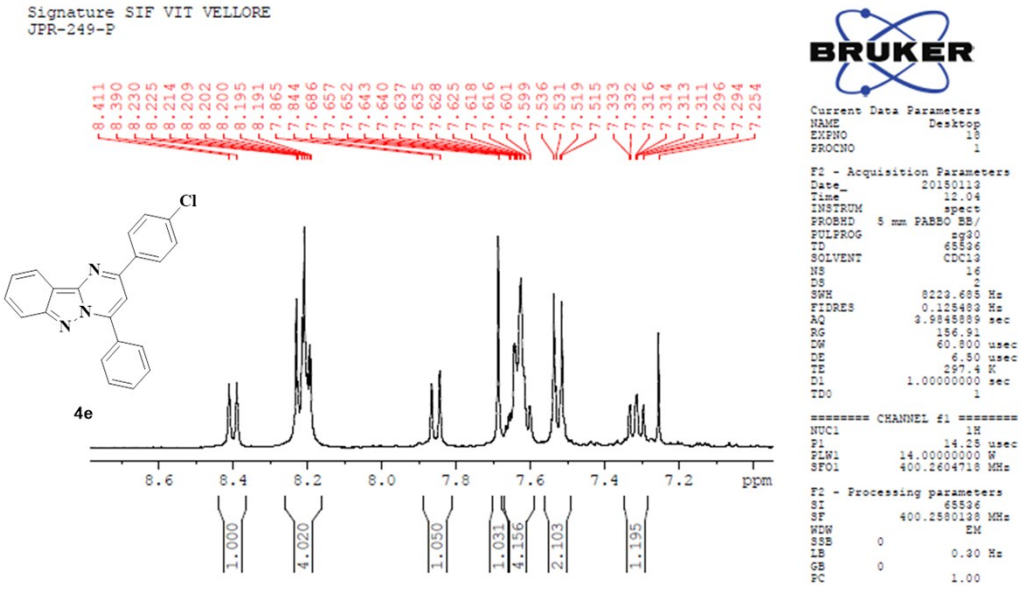
HRMS spectrum of compound (4d):



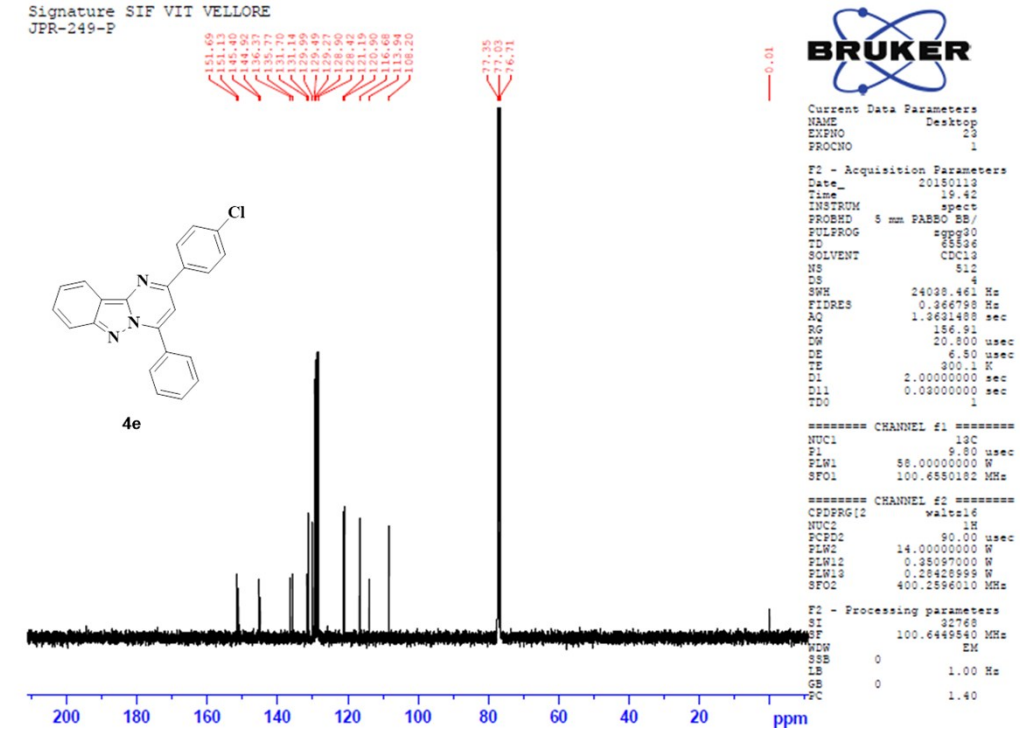
[1]H NMR spectrum of compound (4e):



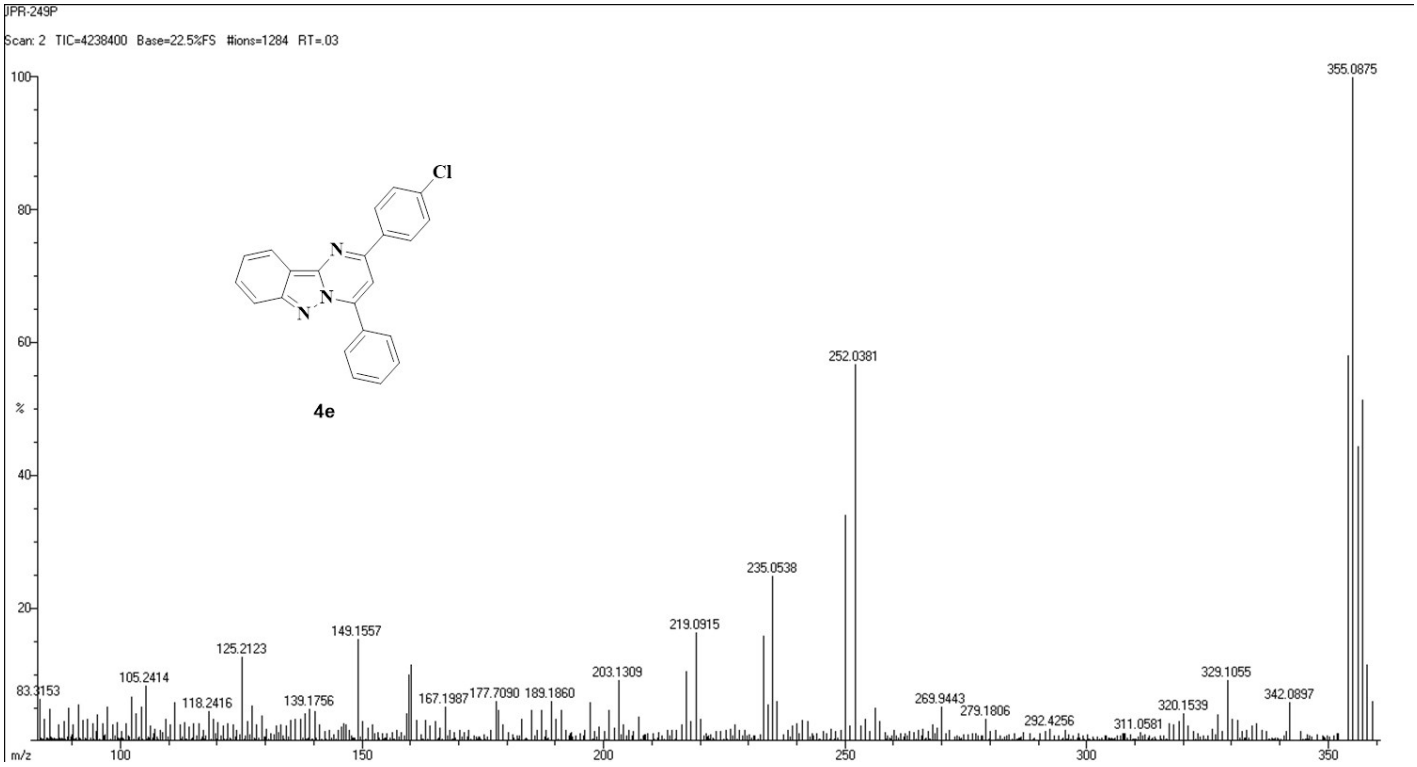
Expanded [1]H NMR spectrum of compound (4e):



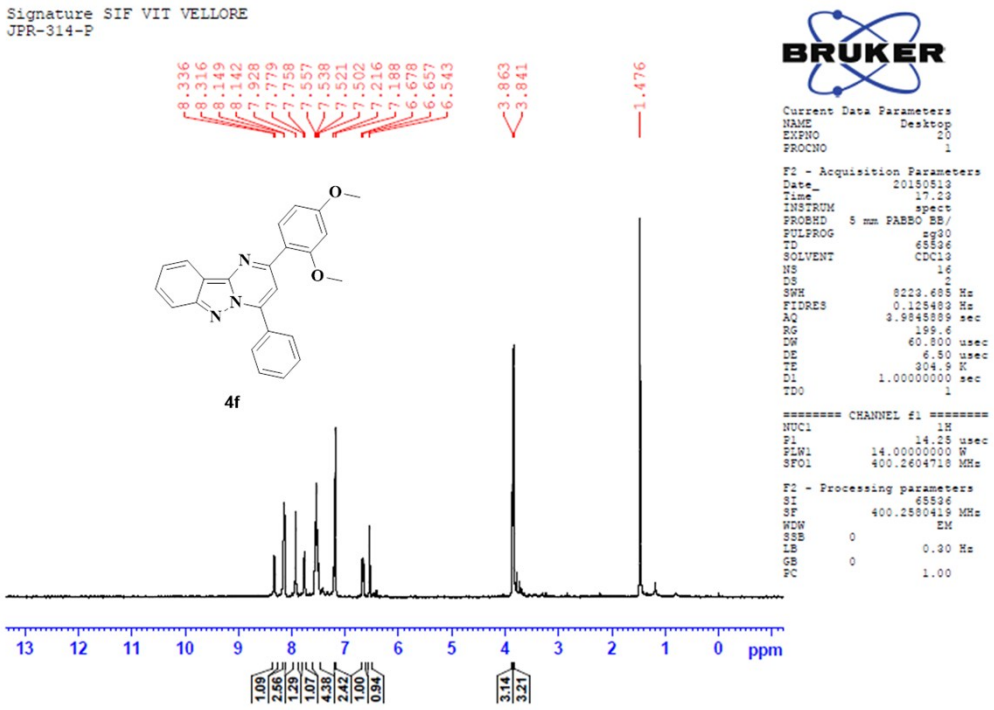
^{13}C NMR spectrum of compound (4e):



HRMS spectrum of compound (4e):



^{1}H NMR spectrum of compound (4f):

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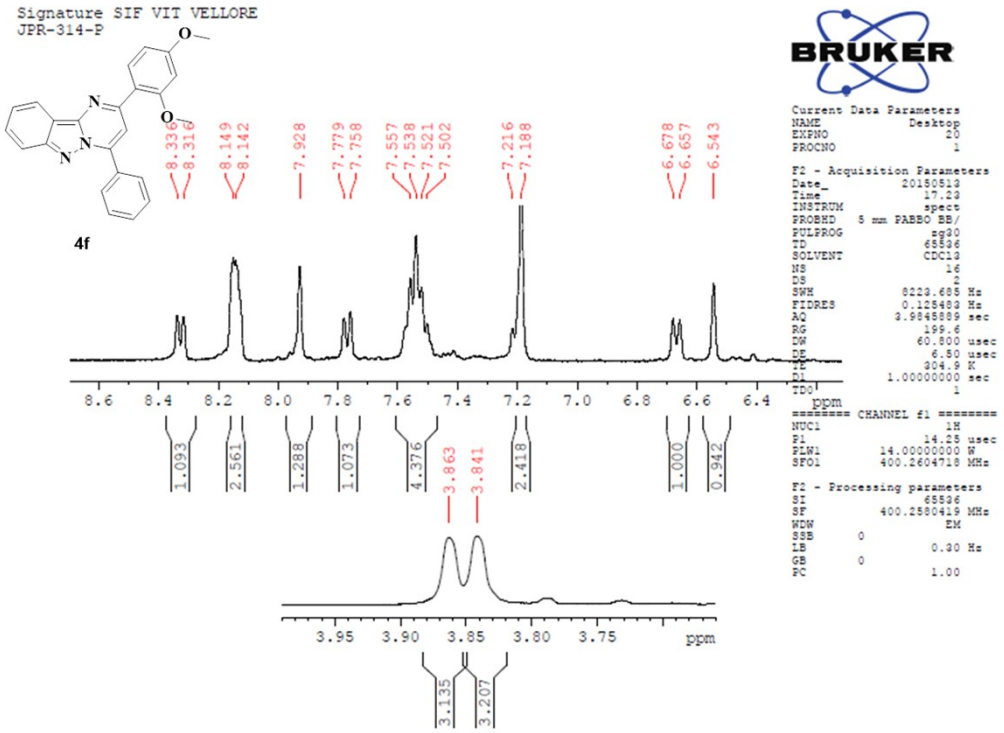
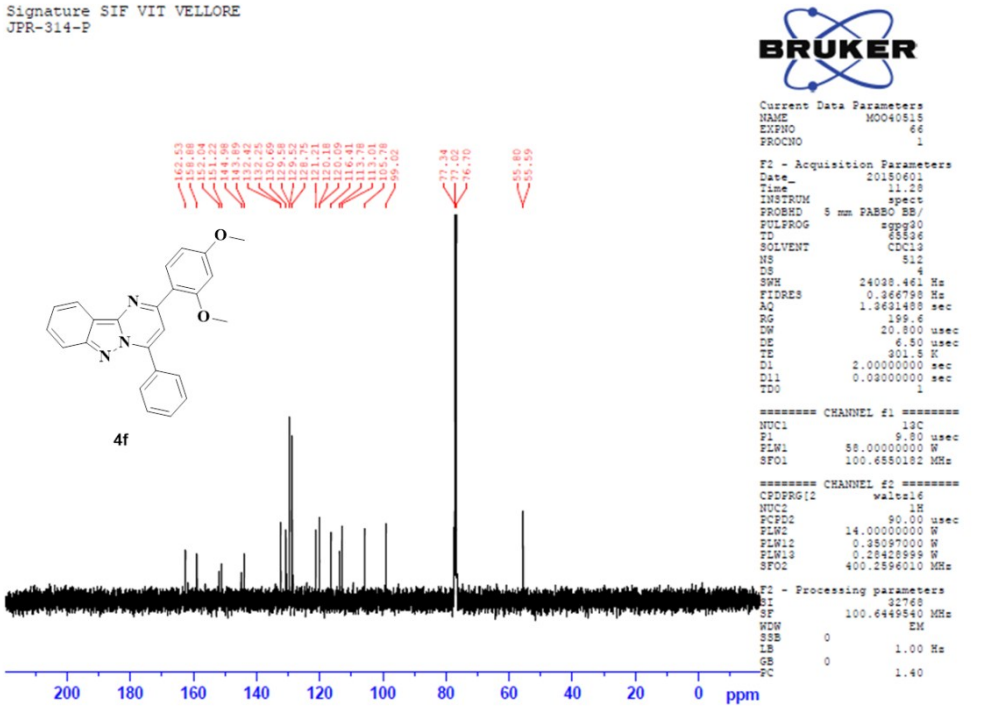
Expanded ^{1}H NMR spectrum of compound (4f):



^{13}C NMR spectrum of compound (4f):



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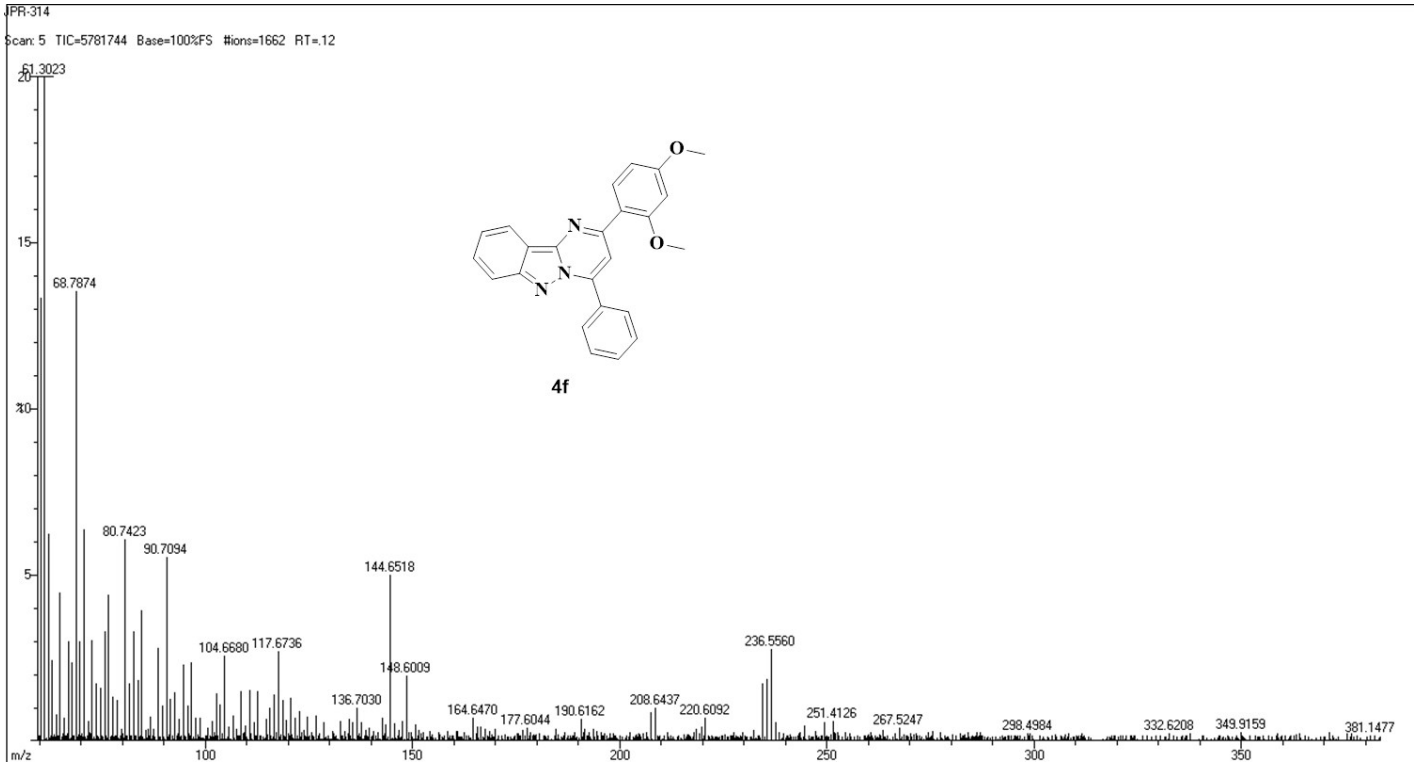

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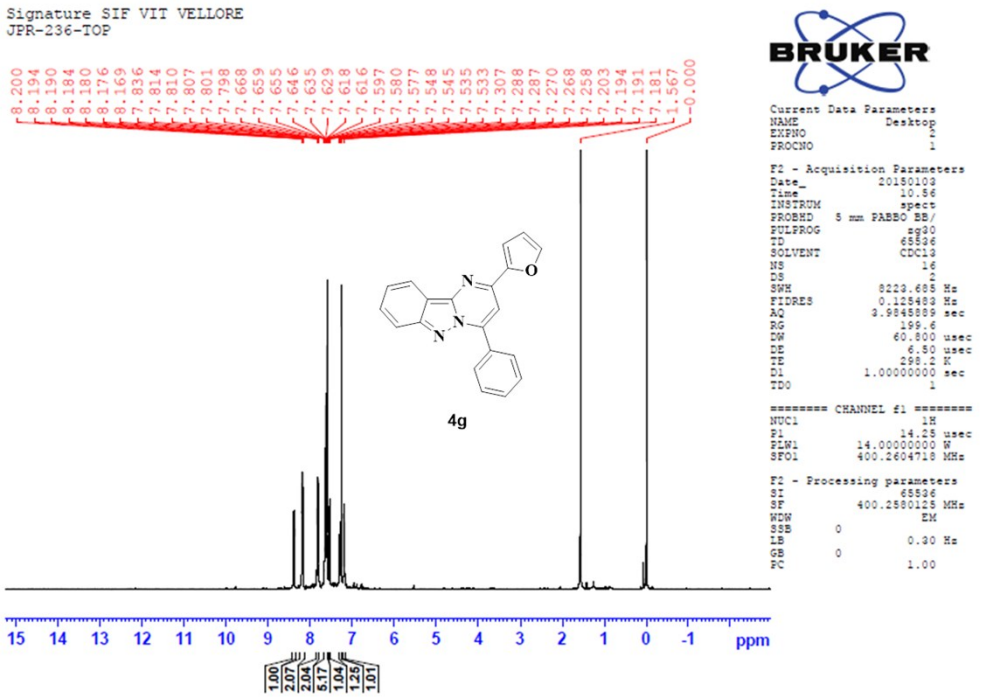
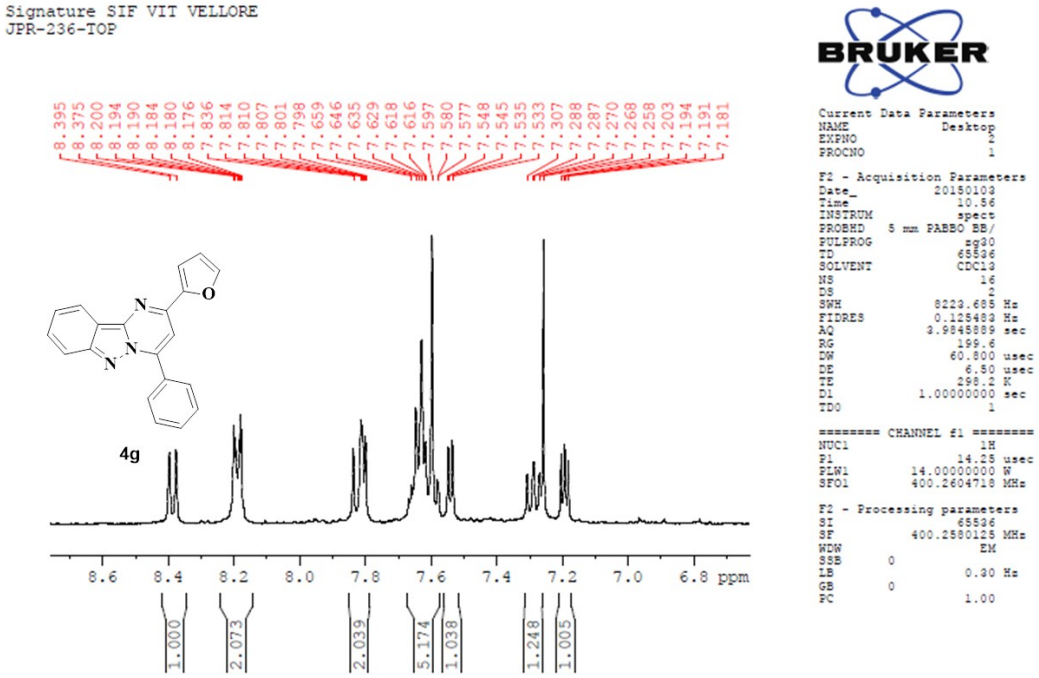
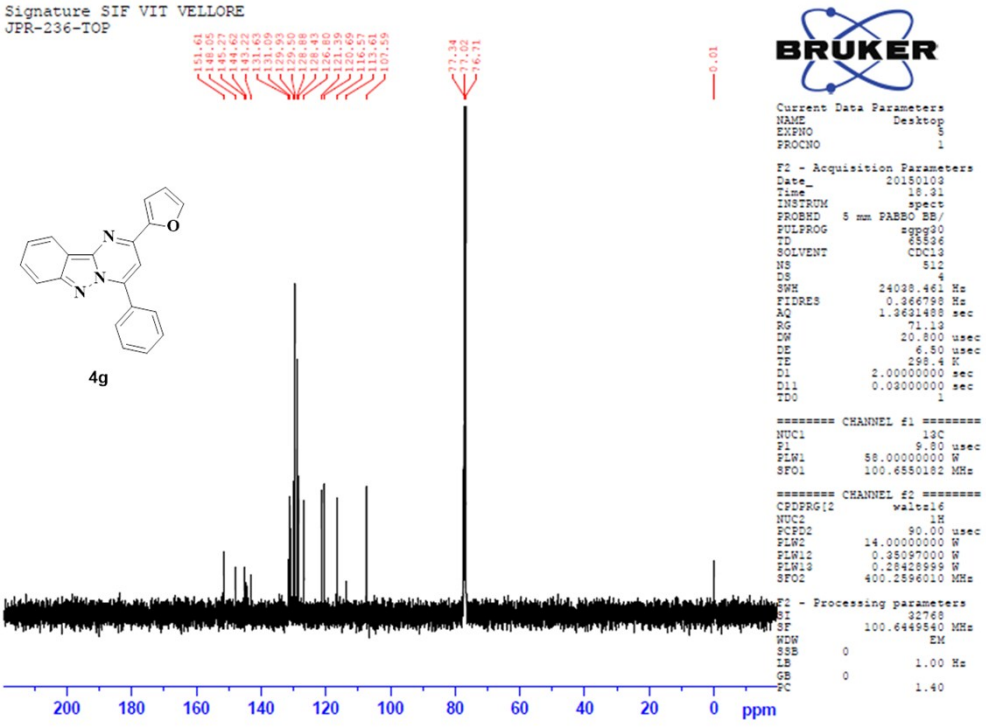


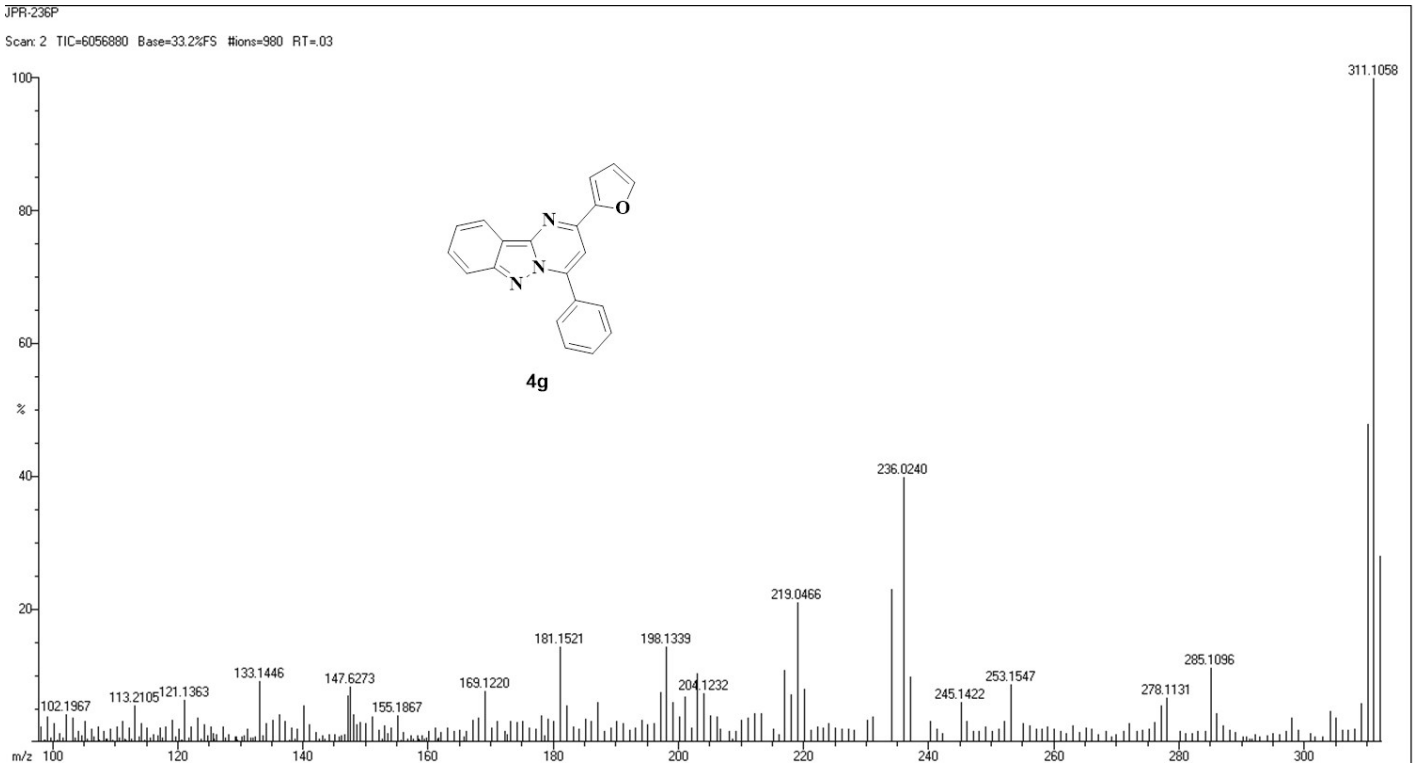
Expanded [1]H NMR spectrum of compound (4g):



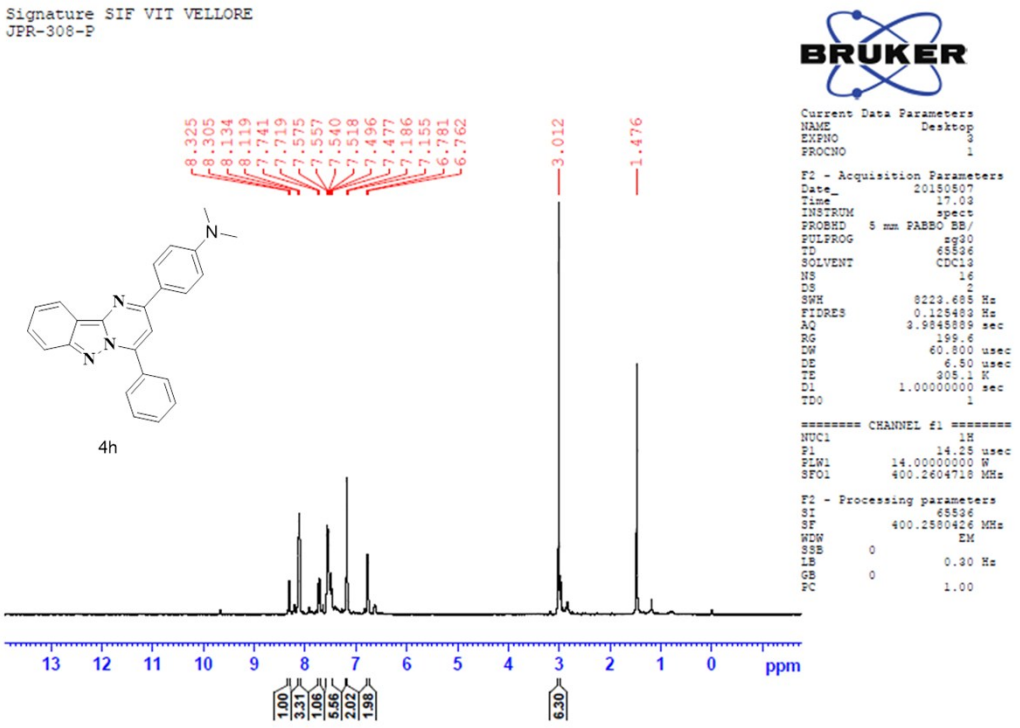
^{13}C NMR spectrum of compound (4g):



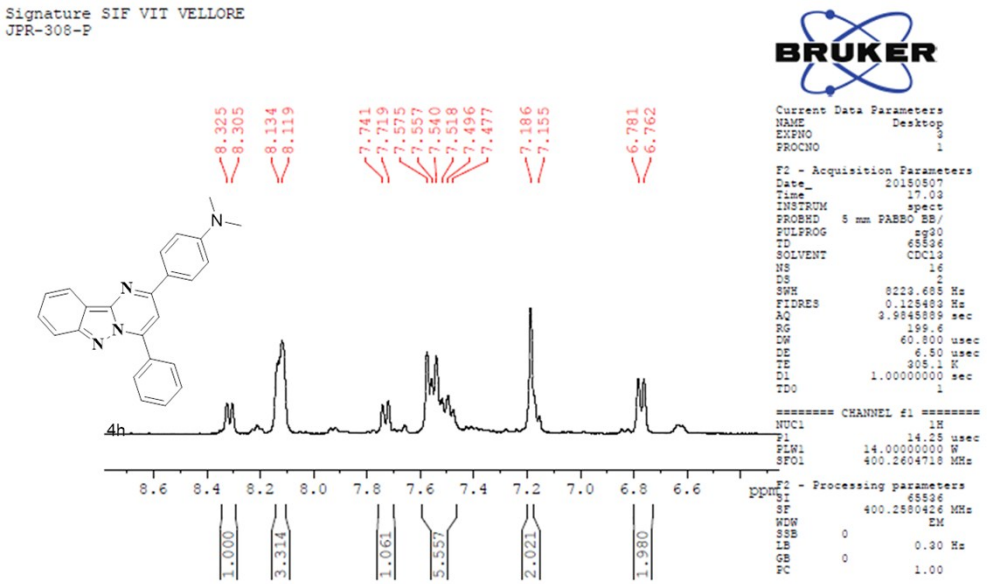
HRMS spectrum of compound (4g):



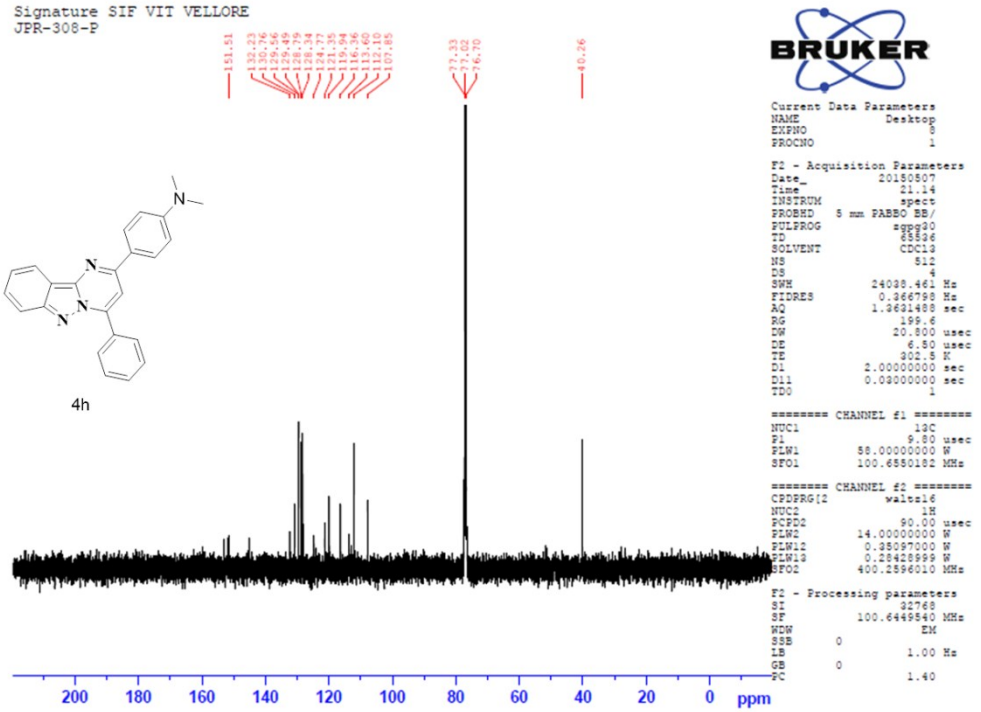
^{1}H NMR spectrum of compound (4h):



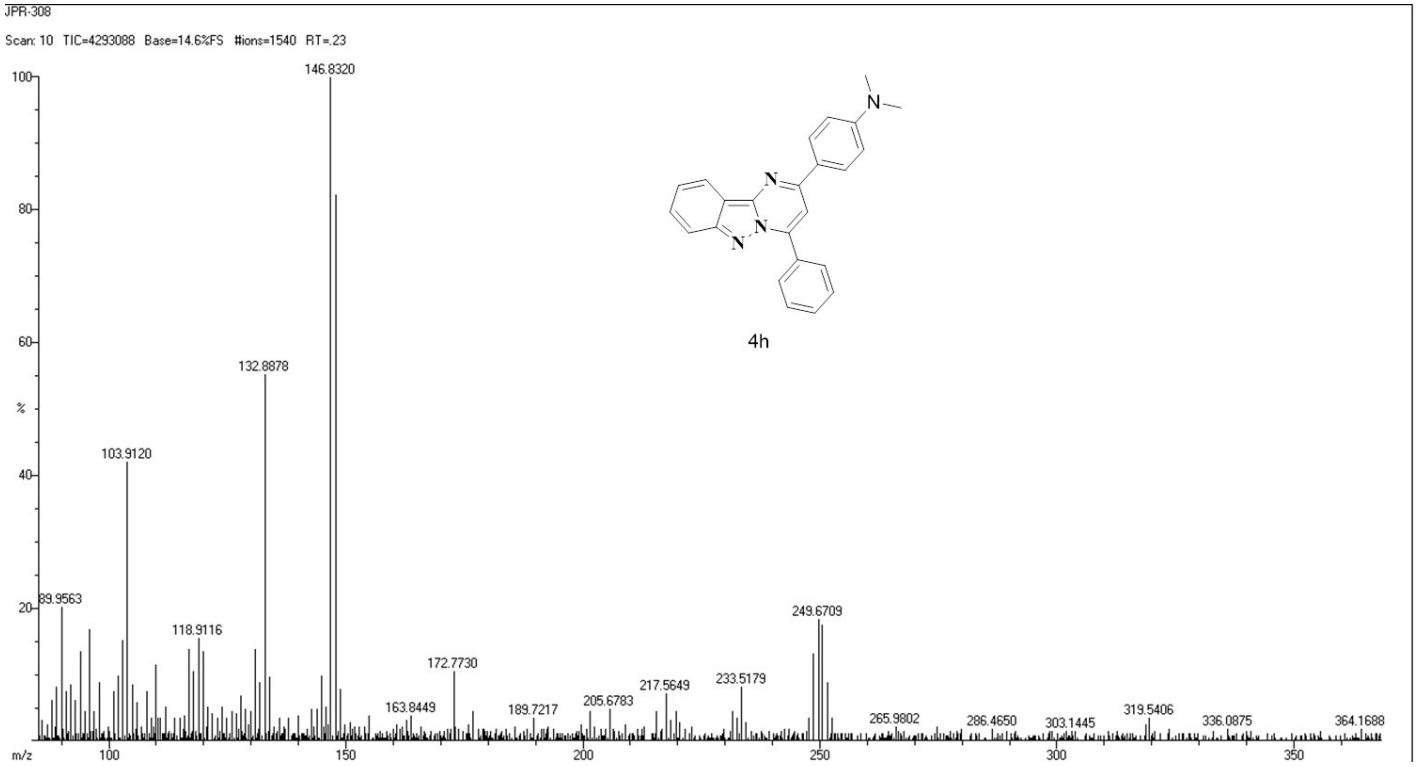
Expanded ^{1}H NMR spectrum of compound (4h):



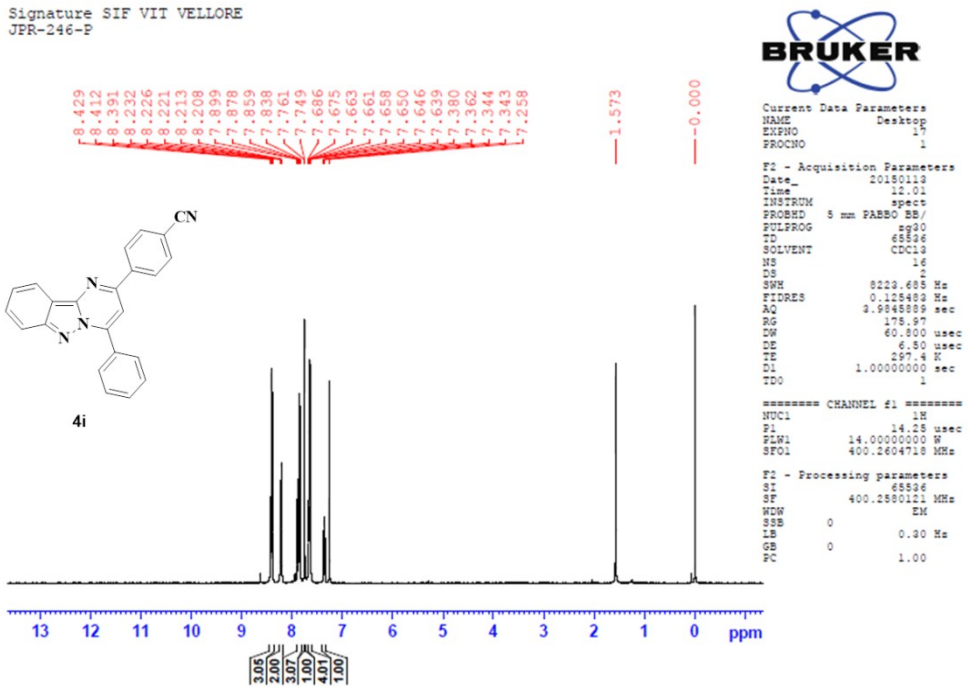
^{13}C NMR spectrum of compound (4h):



HRMS spectrum of compound (4h):



[1]H NMR spectrum of compound (4i):

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SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ             3.9845889 sec
RG                175.97
DW                60.800 usec
DE                 6.50 usec
TE                297.4 K
D1             1.00000000 sec
TD0                   1

========= CHANNEL f1 =========
NUC1                  1H
P1                 14.25 usec
PLW1        14.00000000 W
SFO1        400.2604718 MHz

F2 - Processing parameters
SI                65536
SF          400.2580121 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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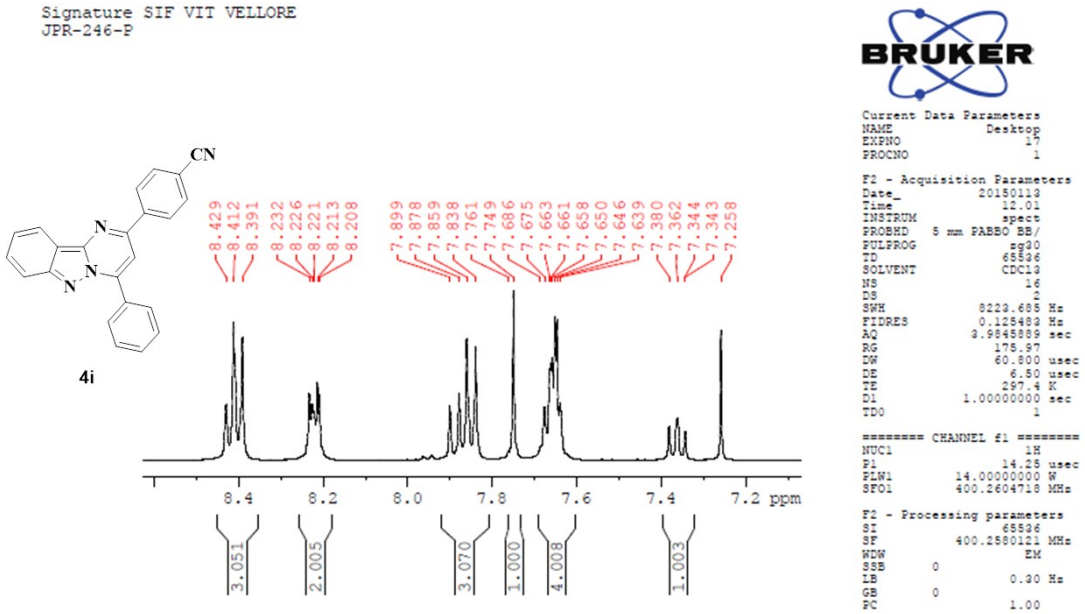
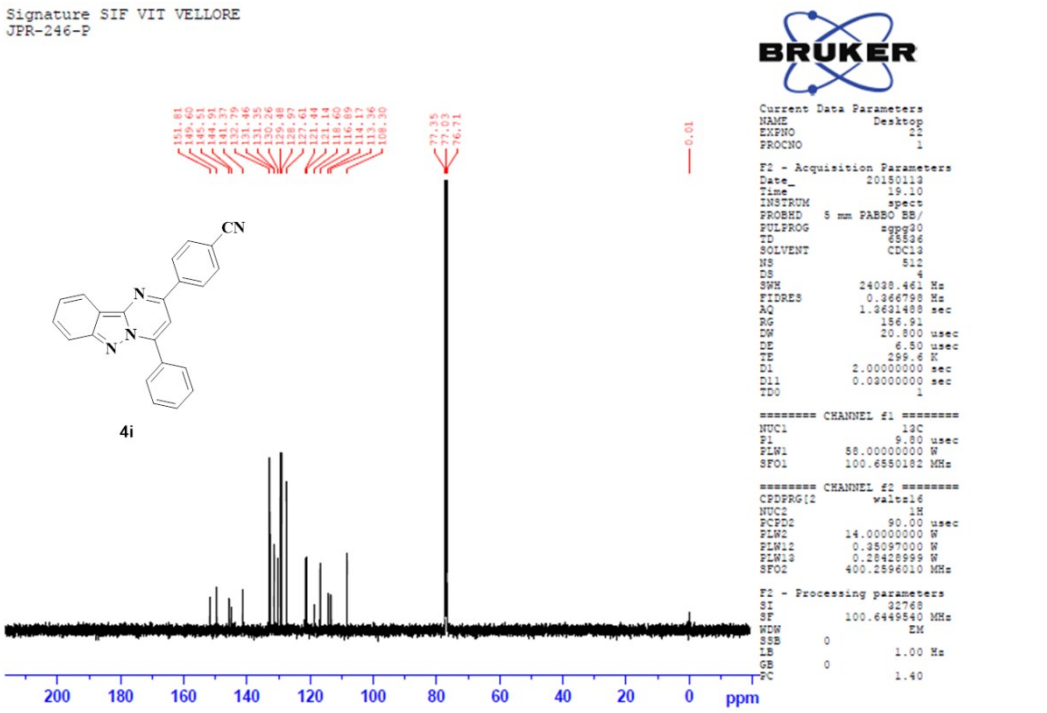
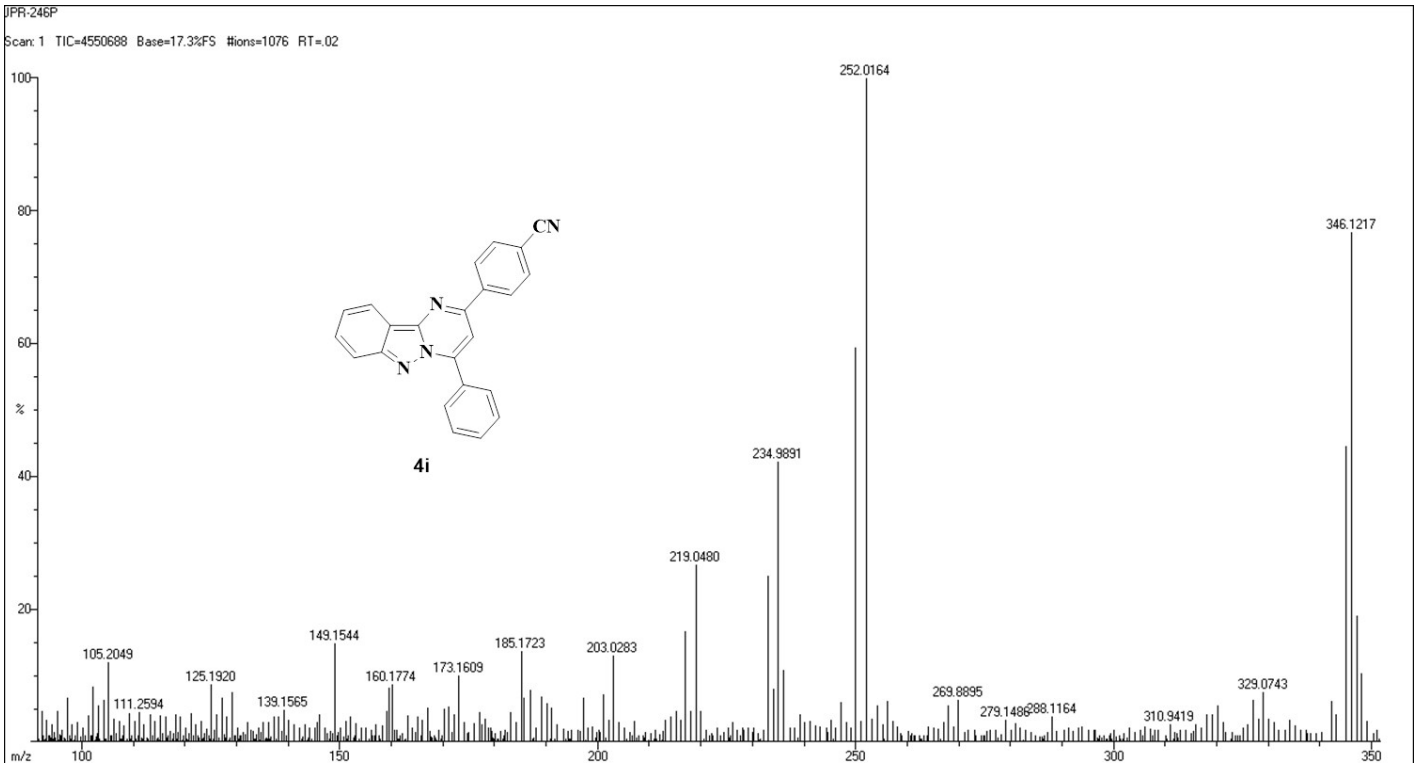
Expanded ^{1}H NMR spectrum of compound (4i):



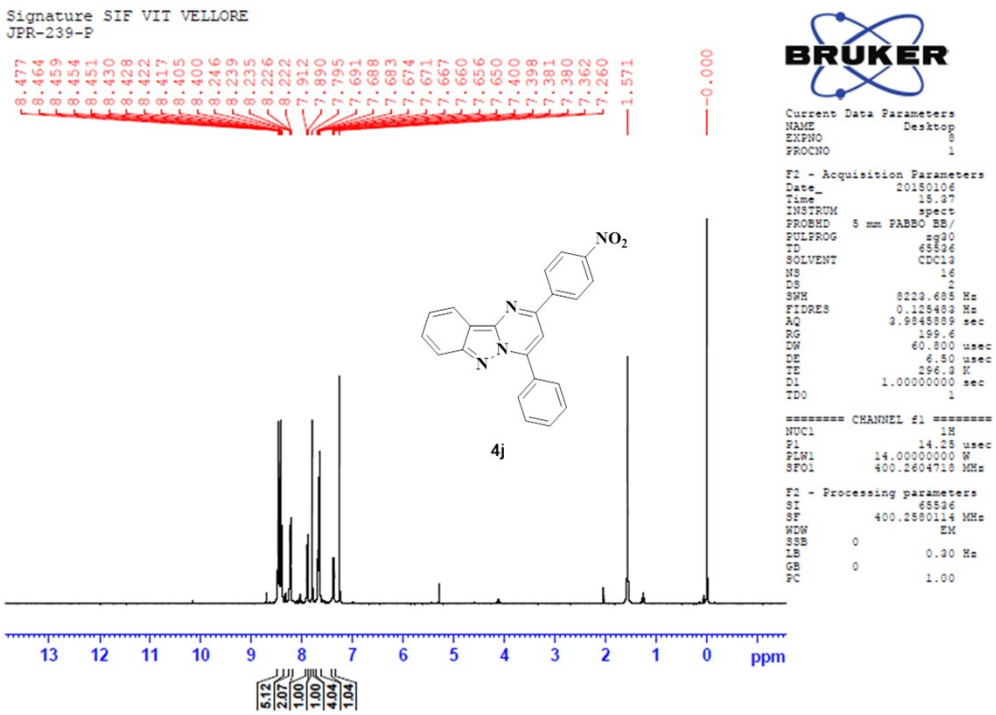
^{13}C NMR spectrum of compound (4i):



HRMS spectrum of compound (4i):



^{1}H NMR spectrum of compound (4j):



BRUKER

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Current Data Parameters
NAME                  Desktop
EXPNO                       8
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150106
Time                   15.27
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9845889 sec
RG                     199.6
DW                    60.800 usec
DE                     6.50 usec
TE                    296.3 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      1H
P1                     14.25 usec
PLW1           14.00000000 W
SFO1           400.2604718 MHz

F2 - Processing parameters
SI                        65536
SF             400.2580114 MHz
WDW                         EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
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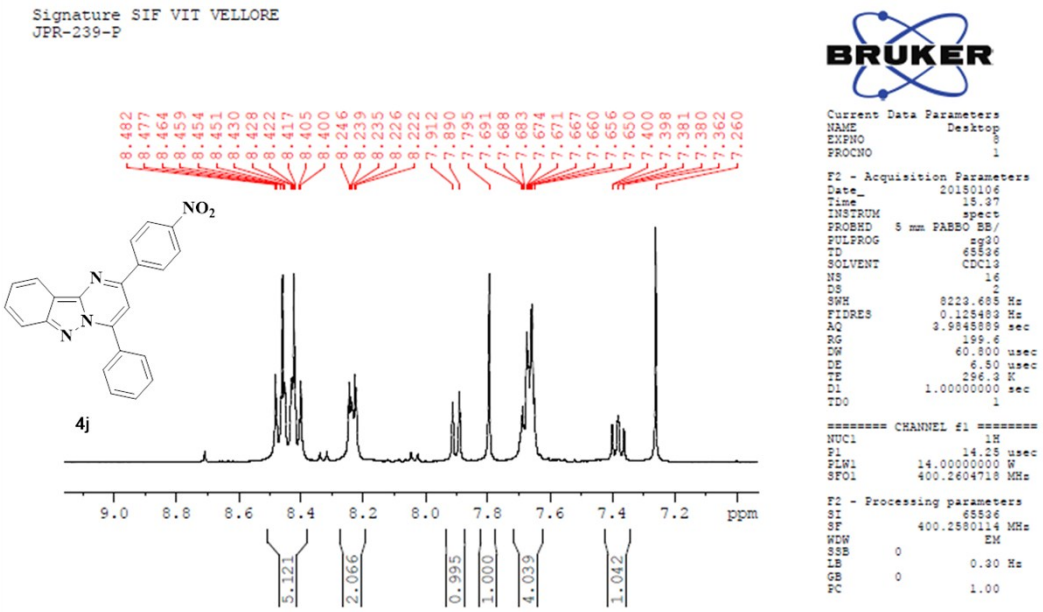
Expanded ^{1}H NMR spectrum of compound (4j):



BRUKER

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Current Data Parameters
NAME                  Desktop
EXPNO                       8
PROCNO                      1

F2 - Acquisition Parameters
Date_               20150106
Time                   15.37
INSTRUM                spect
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PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9845889 sec
RG                     199.6
DW                    60.800 usec
DE                     6.50 usec
TE                    296.3 K
D1                 1.00000000 sec
TD0                        1

========= CHANNEL f1 =========
NUC1                      1H
P1                     14.25 usec
PLW1            14.00000000 W
SFO1           400.2604718 MHz

F2 - Processing parameters
SI                     65536
SF              400.2580114 MHz
WDW                       EM
SSB                    0
LB                      0.30 Hz
GB                     0
PC                      1.00
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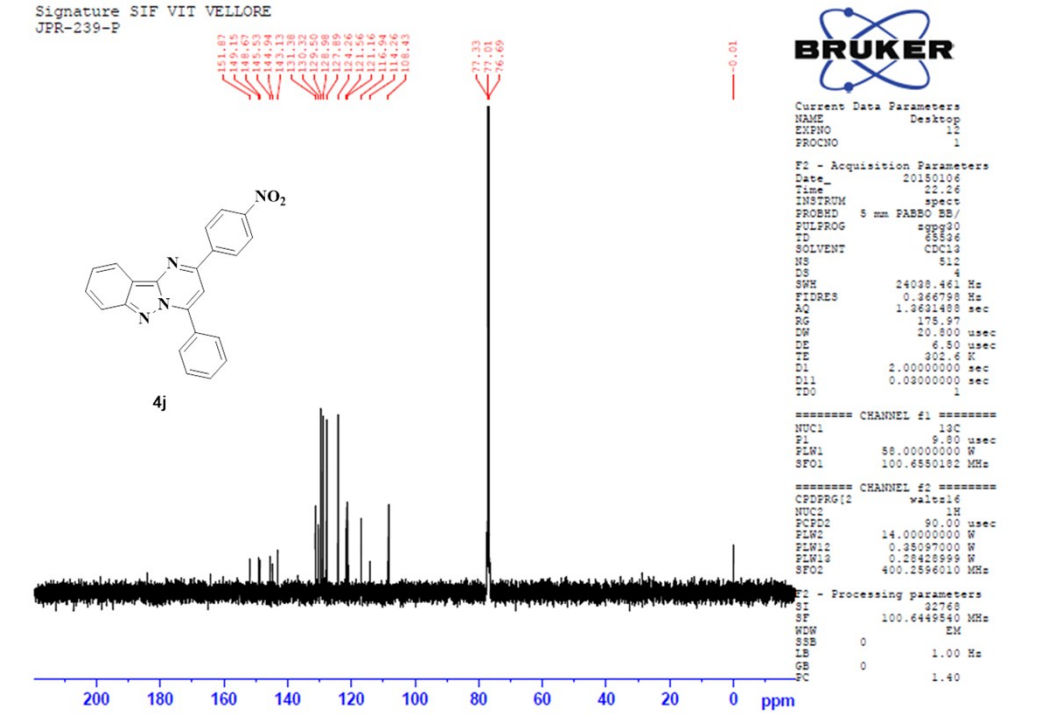
^{13}C NMR spectrum of compound (4j):



BRUKER

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Current Data Parameters
NAME                  Desktop
EXPNO                      12
PROCNO                      1

F2 - Acquisition Parameters
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Time                   22.26
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       512
DS                         4
SWH              24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                     175.97
DW                    20.800 usec
DE                     6.50 usec
TE                    302.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

========= CHANNEL f1 =========
NUC1                      13C
P1                     9.80 usec
PLW1            58.00000000 W
SFO1           100.6550182 MHz

========= CHANNEL f2 =========
CPDPRG[2             waltz16
NUC2                      1H
PCPD2                 90.00 usec
PLW2            14.00000000 W
PLW12            0.35097000 W
PLW13            0.28428999 W
SFO2           400.2596010 MHz

F2 - Processing parameters
SI                     32768
SF              100.6449540 MHz
WDW                       EM
SSB                    0
LB                      1.00 Hz
GB                     0
PC                      1.40
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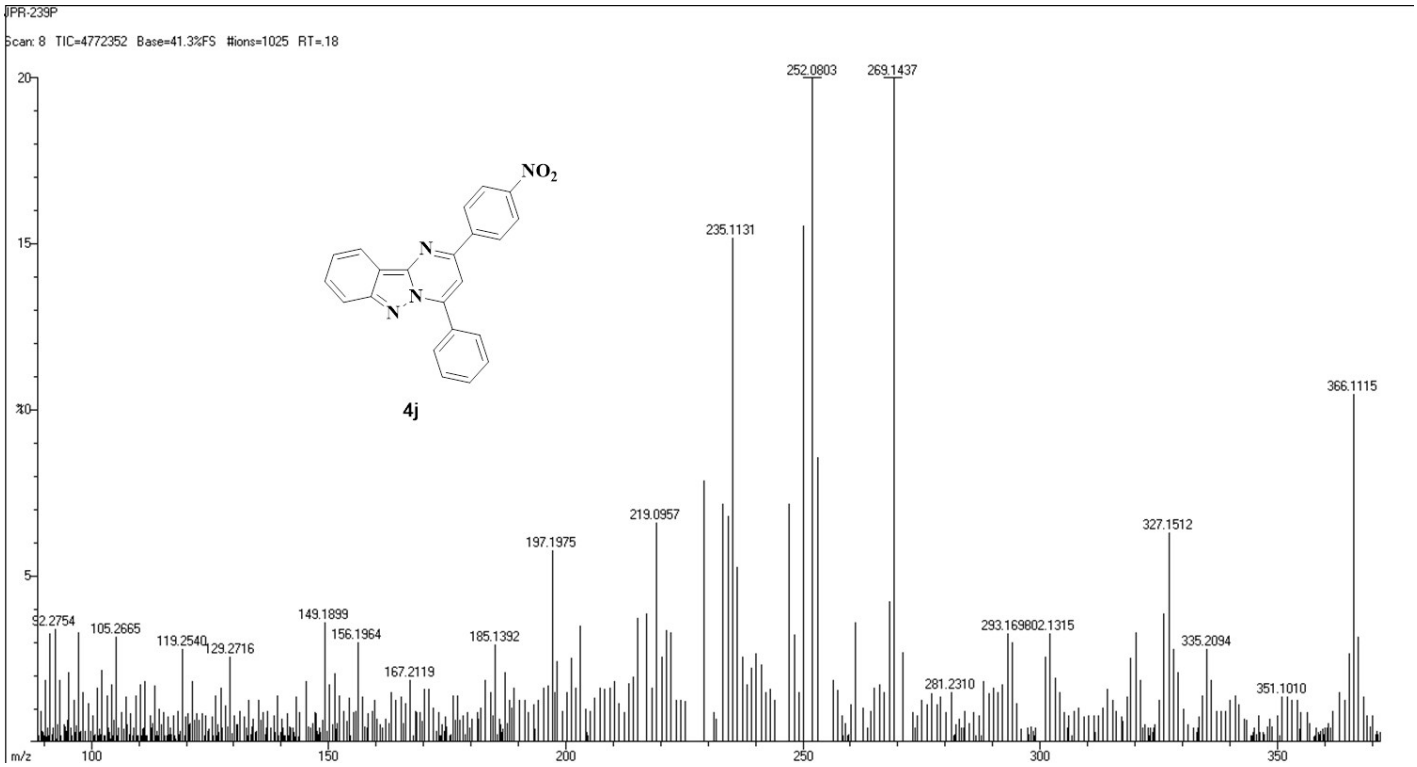
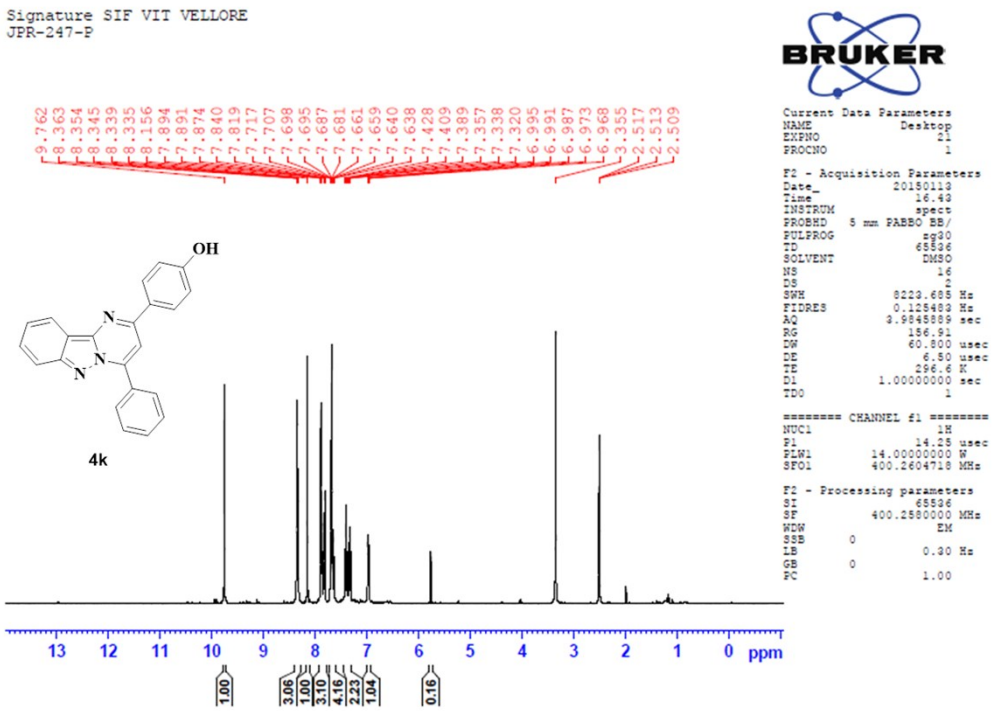
HRMS spectrum of compound (4j):



^{1}H NMR spectrum of compound (4k):

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Current Data Parameters
NAME                  Desktop
EXPNO                      21
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150113
Time_                 16.43
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                        16
DS                         2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9845889 sec
RG                    156.91
DW                   60.800 usec
DE                    6.50 usec
TE                   296.6 K
D1                1.00000000 sec
TD0                        1

========== CHANNEL f1 ==========
NUC1                      1H
P1                     14.25 usec
PLW1            14.00000000 W
SFO1            400.2604718 MHz

F2 - Processing parameters
SI                        65536
SF              400.2580000 MHz
WDW                       EM
SSB          0
LB                      0.30 Hz
GB           0
PC                      1.00
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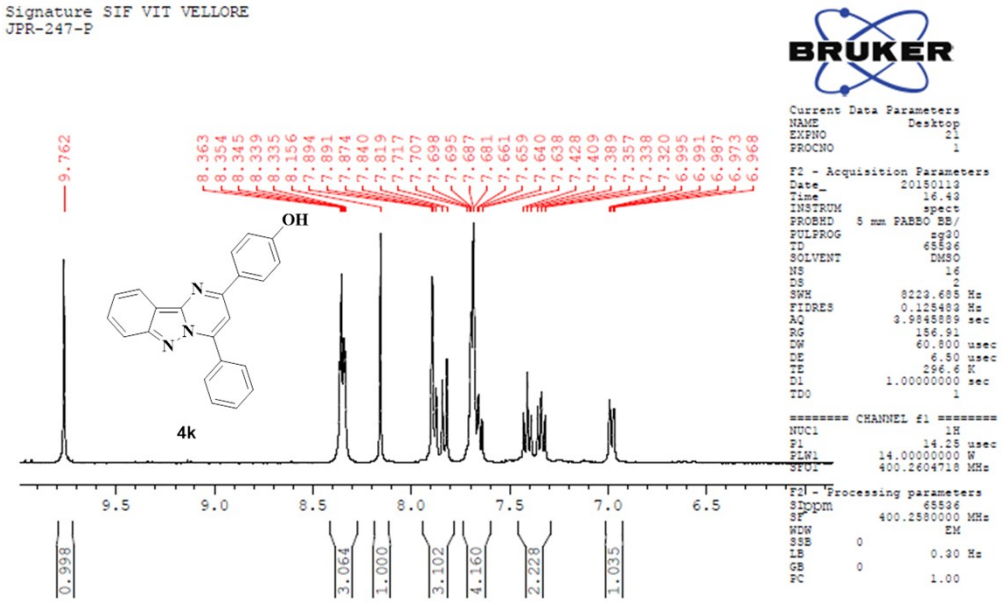
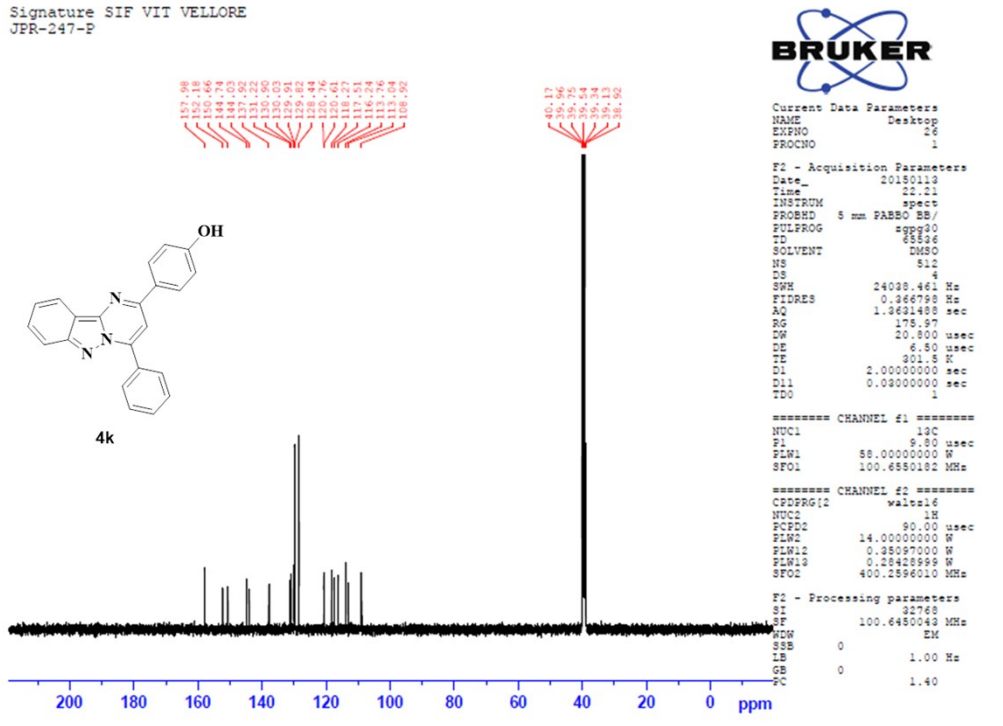
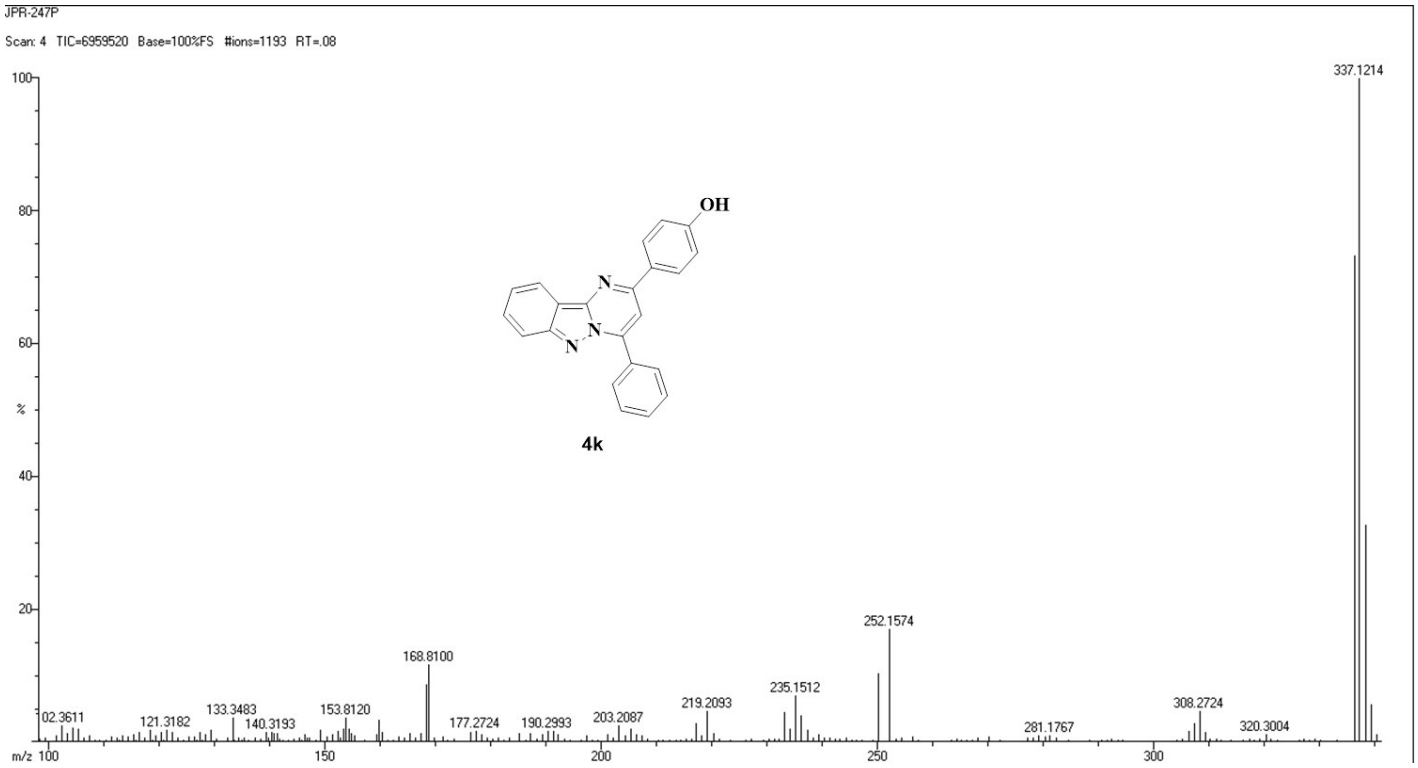
Expanded ^{1}H NMR spectrum of compound (4k):



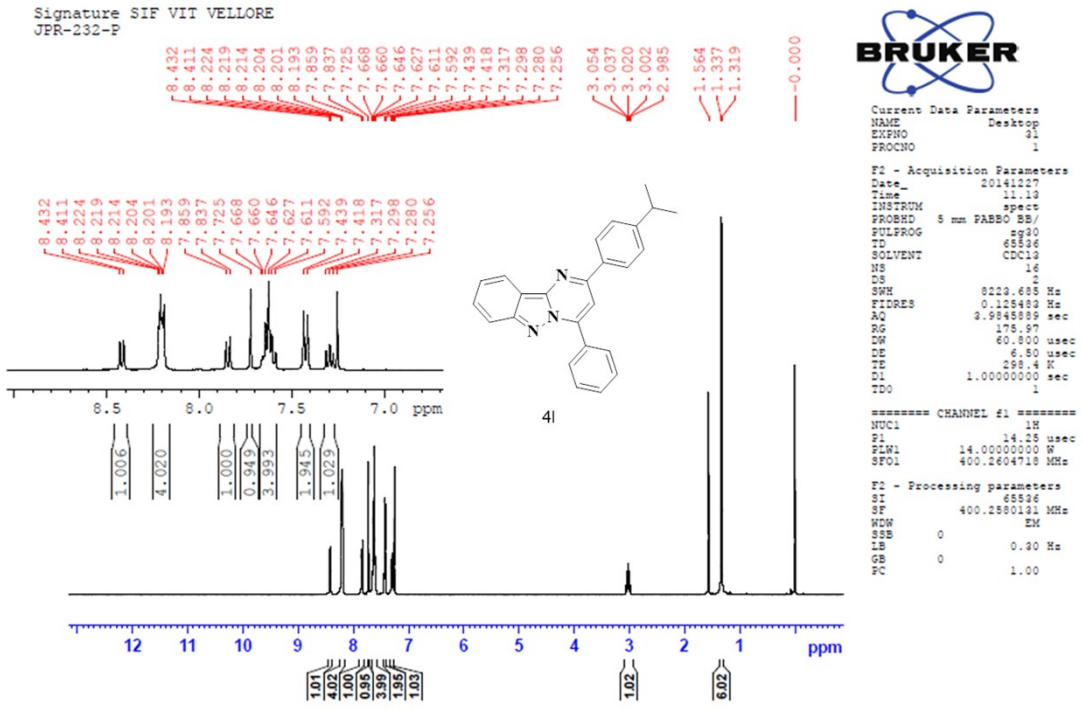
^{13}C NMR spectrum of compound (4k):



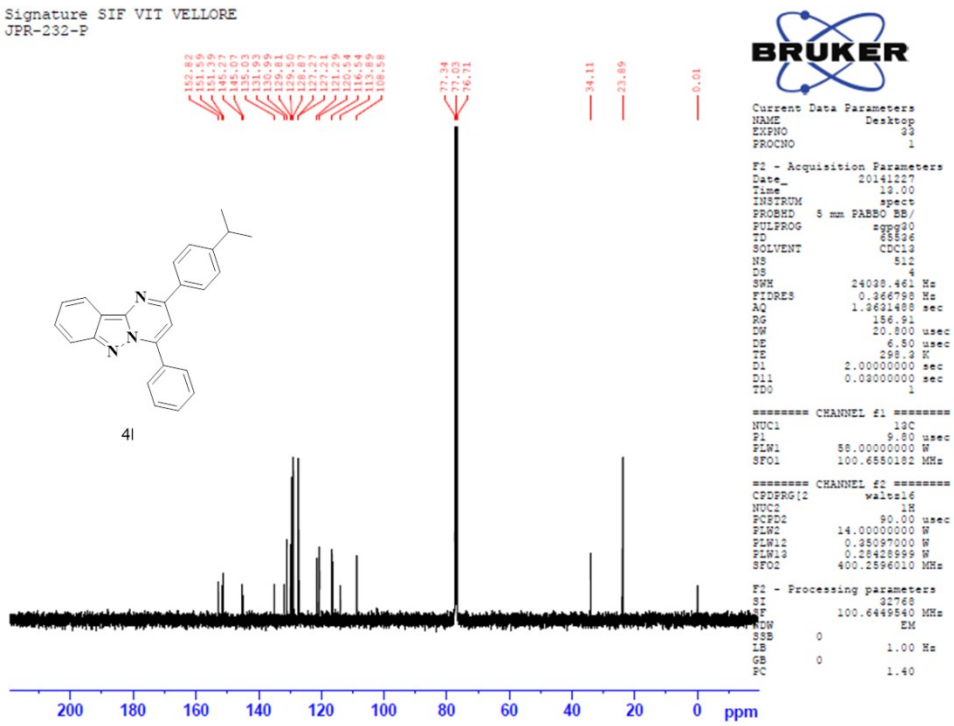
HRMS spectrum of compound (4k):



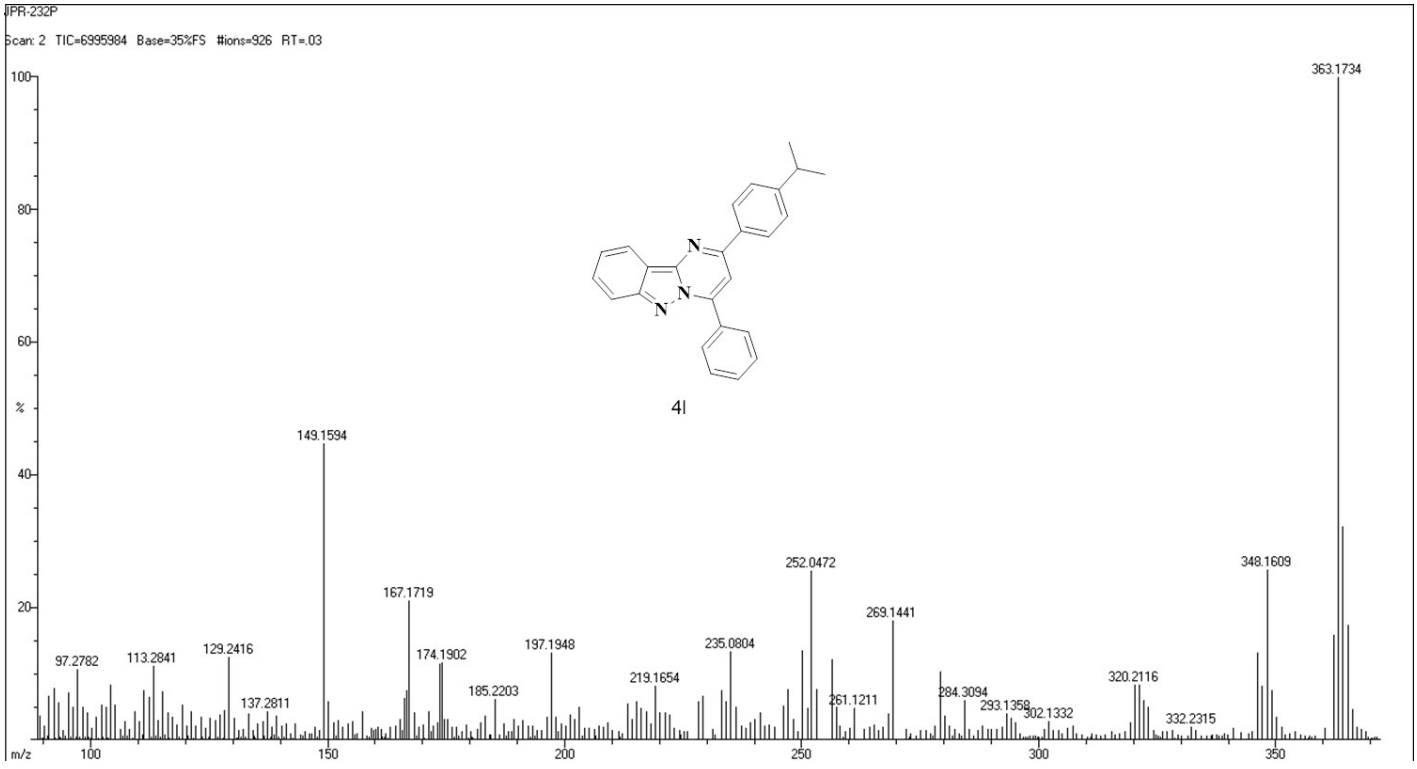
^{1}H NMR spectrum of compound (4l):



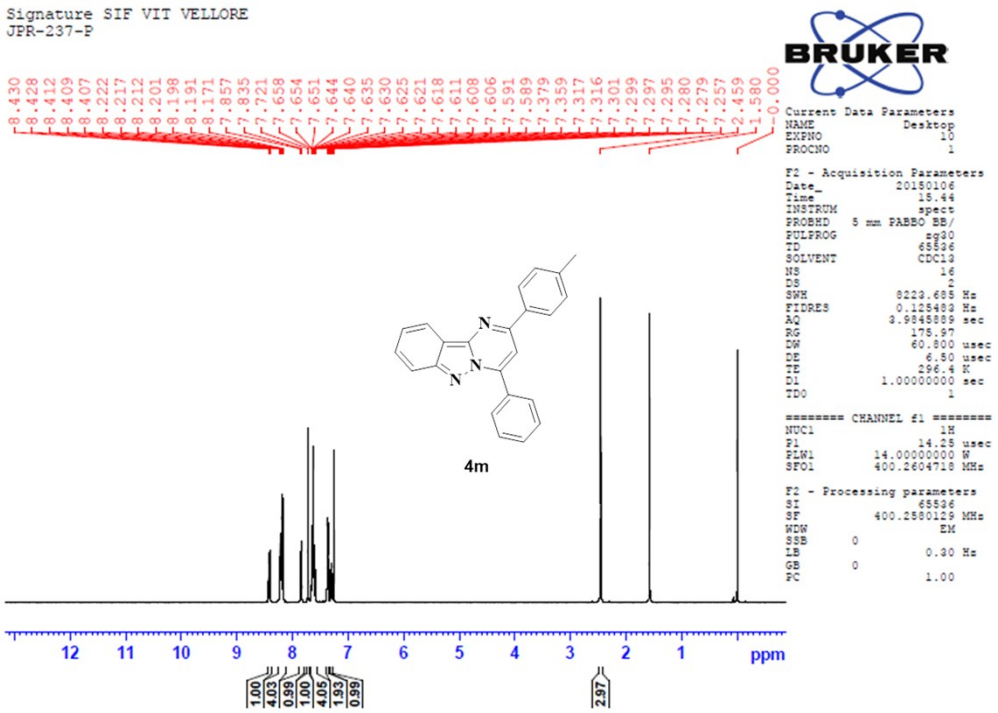
^{13}C NMR spectrum of compound (4l):



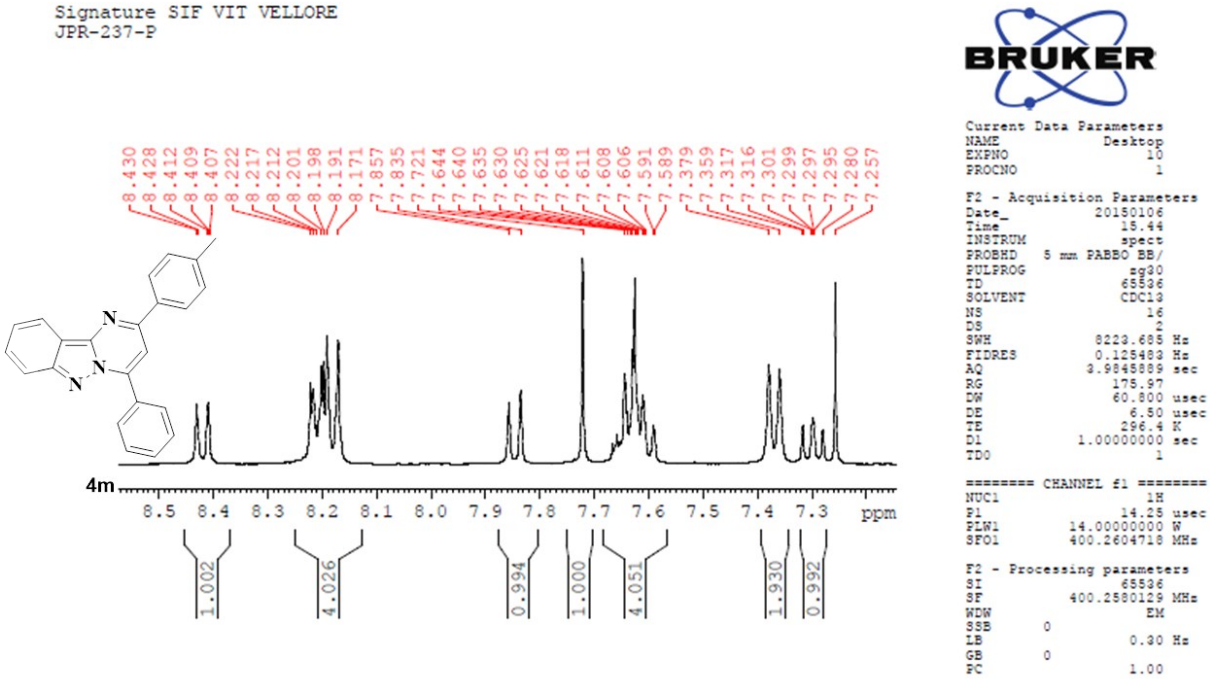
HRMS spectrum of compound (4l):



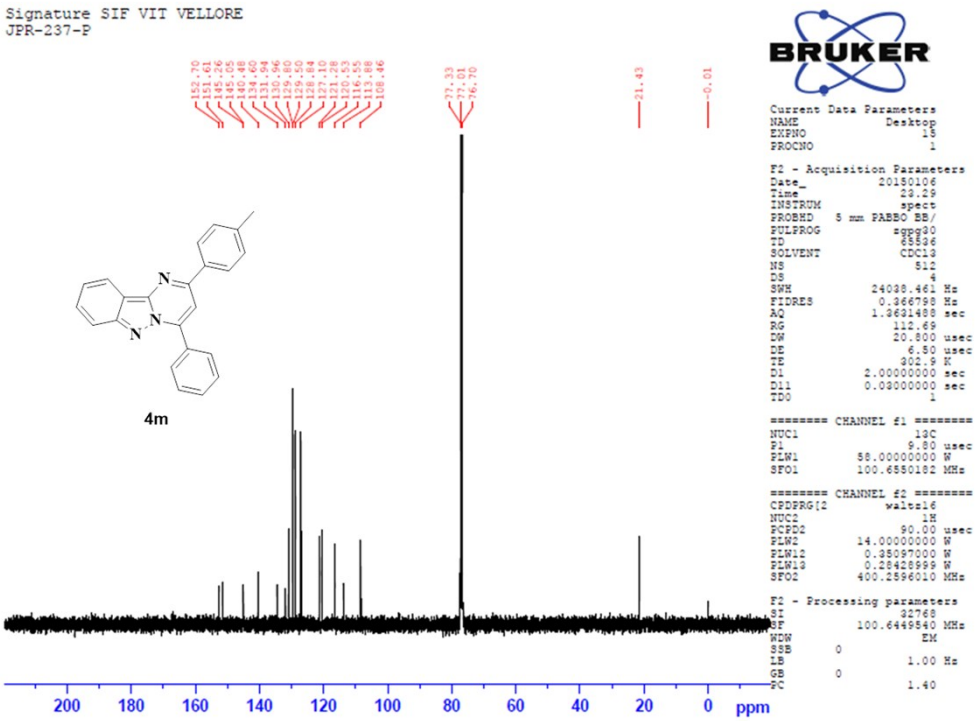
^{1}H NMR spectrum of compound (4m):



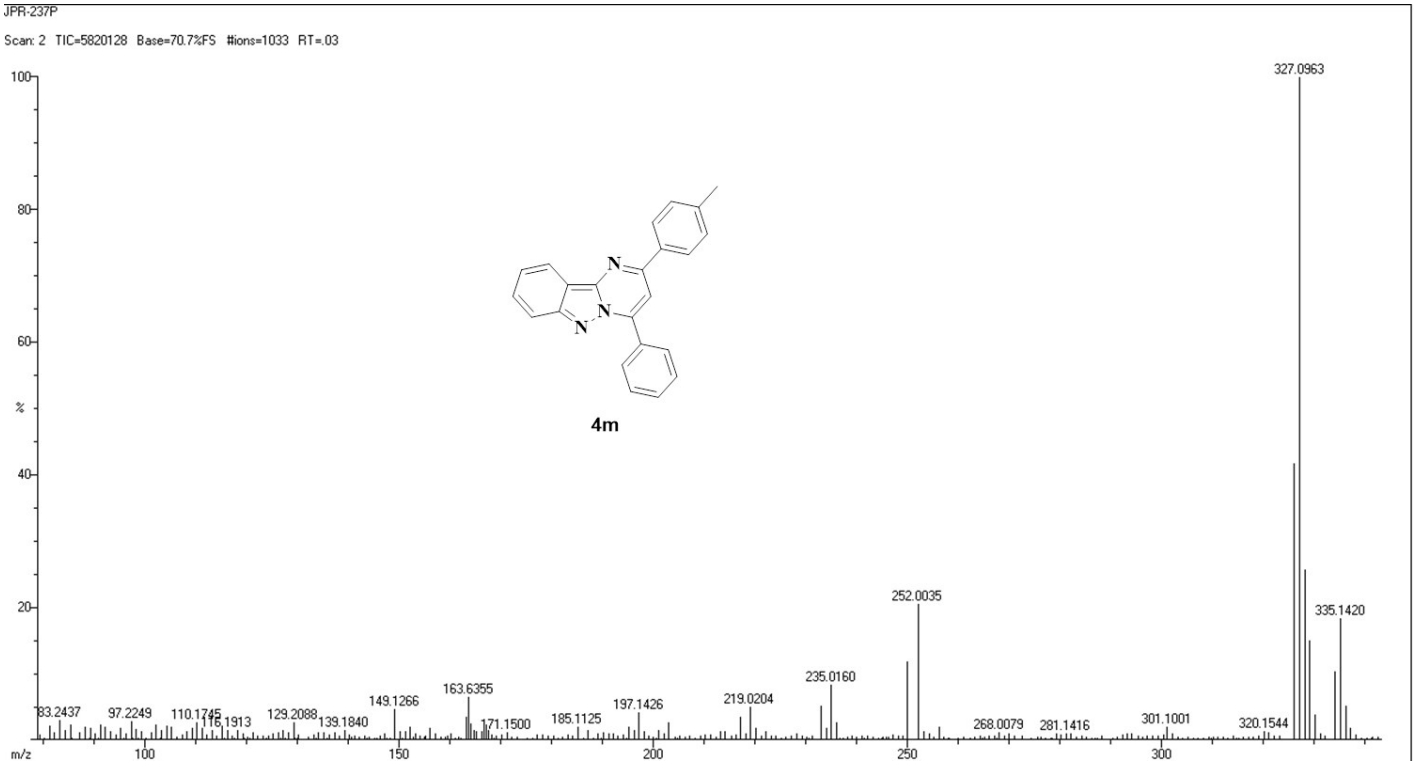
Expanded ^{1}H NMR spectrum of compound (4m):



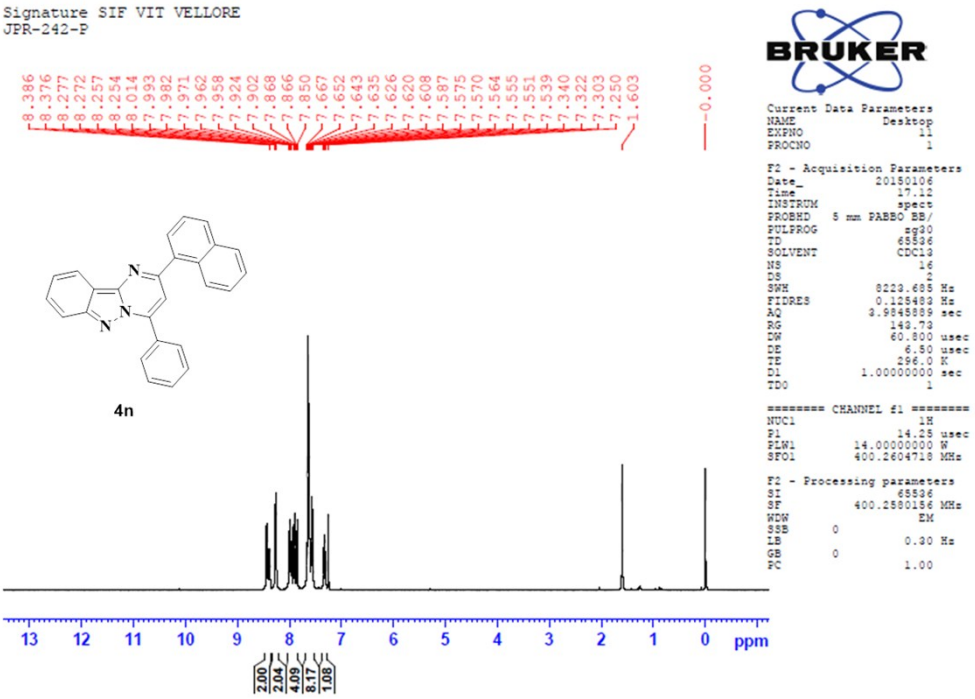
^{13}C NMR spectrum of compound (4m):



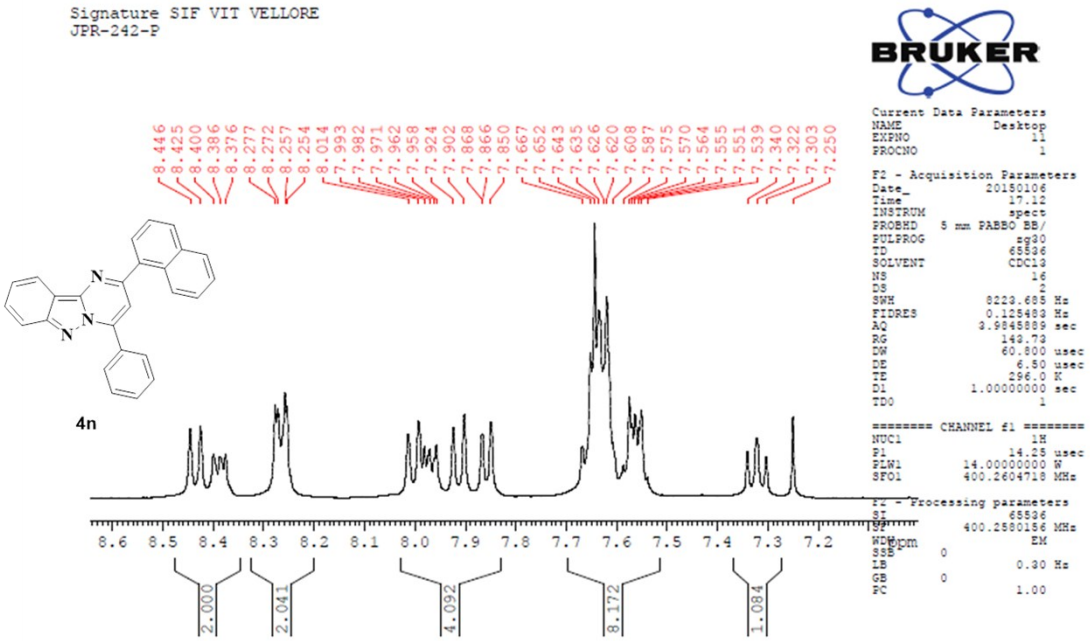
HRMS spectrum of compound (4m):



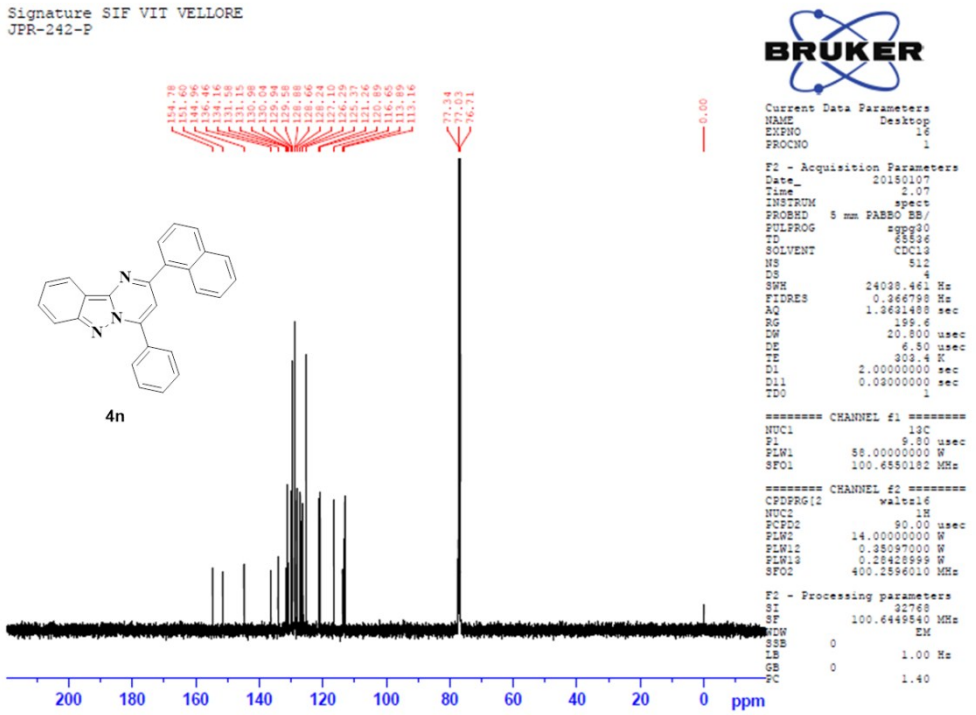
^{1}H NMR spectrum of compound (4n):



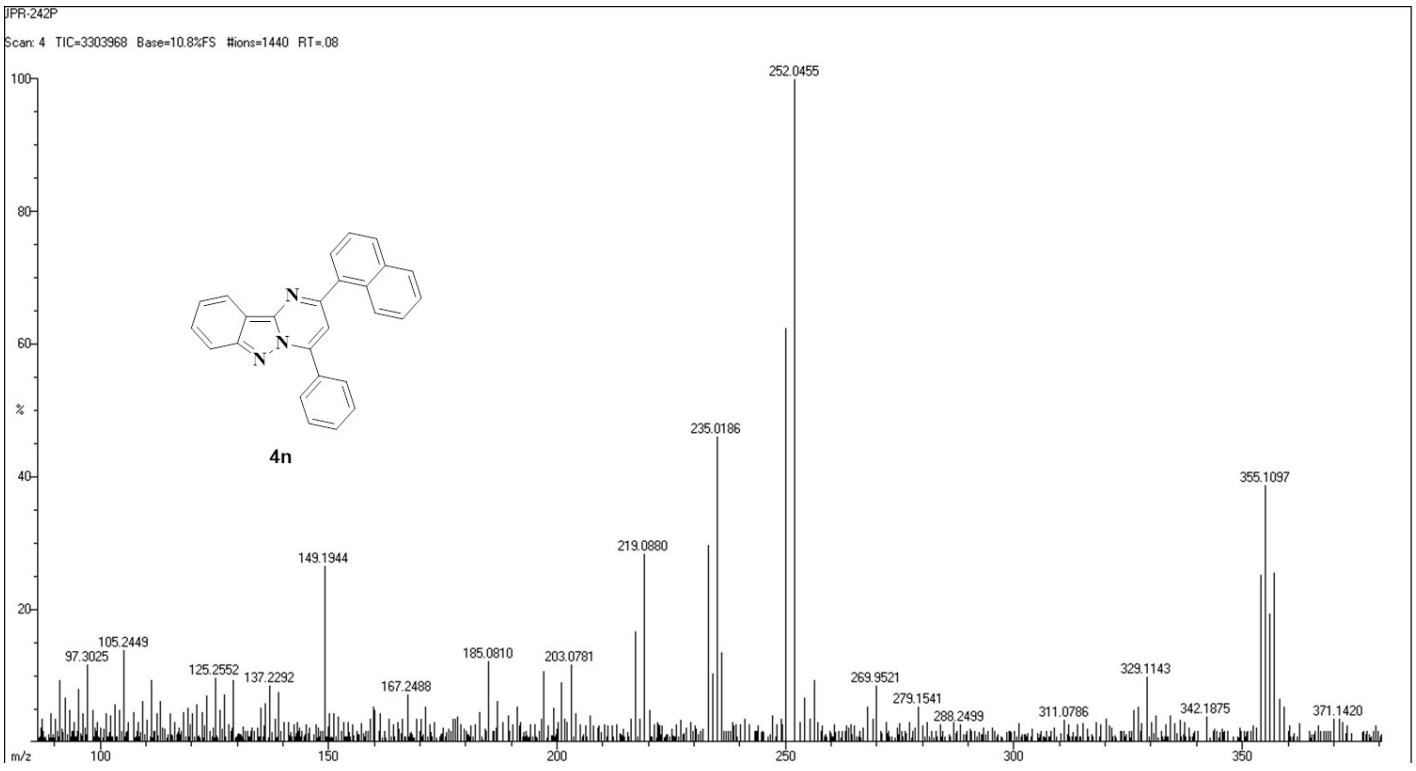
Expanded ^{1}H NMR spectrum of compound (4n):



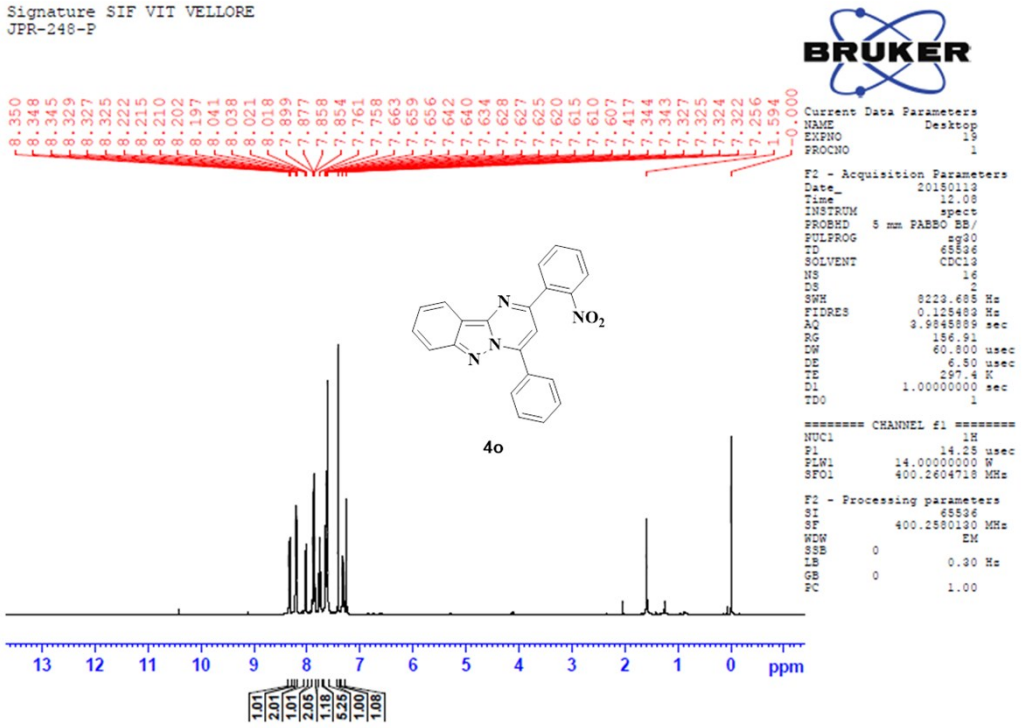
^{13}C NMR spectrum of compound (4n):



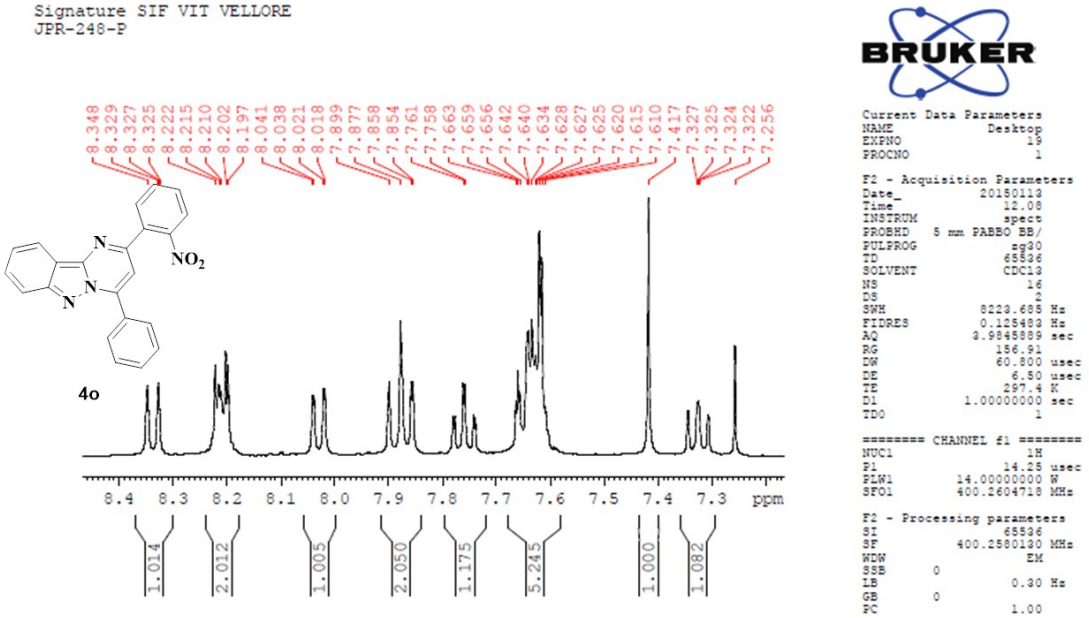
HRMS spectrum of compound (4n):



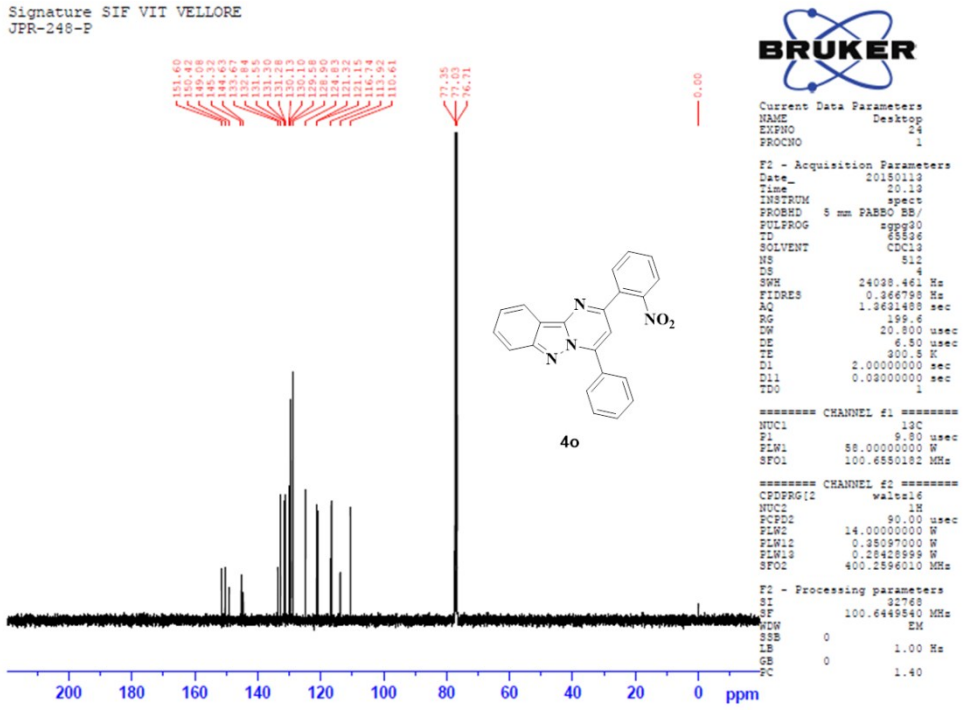
^{1}H NMR spectrum of compound (4o):



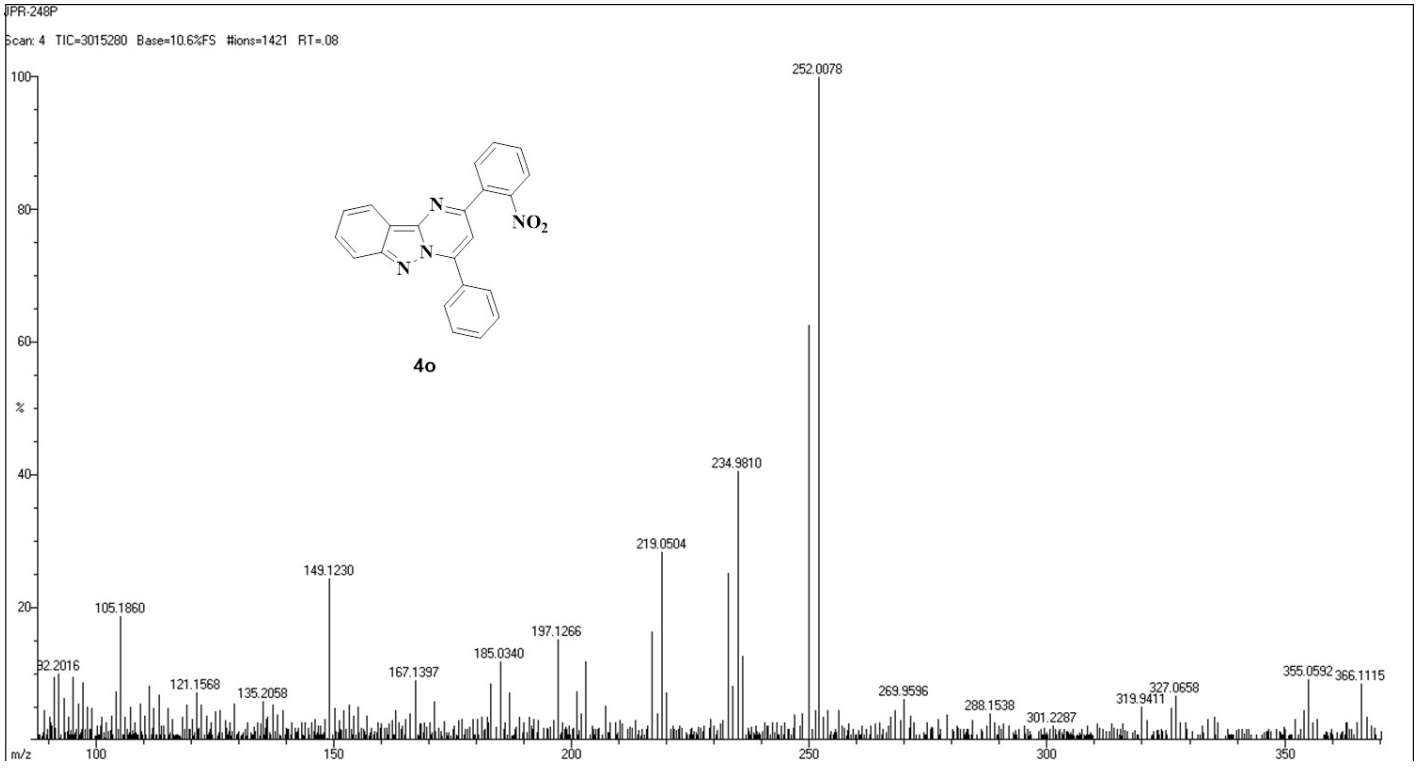
Expanded ^{1}H NMR spectrum of compound (4o):



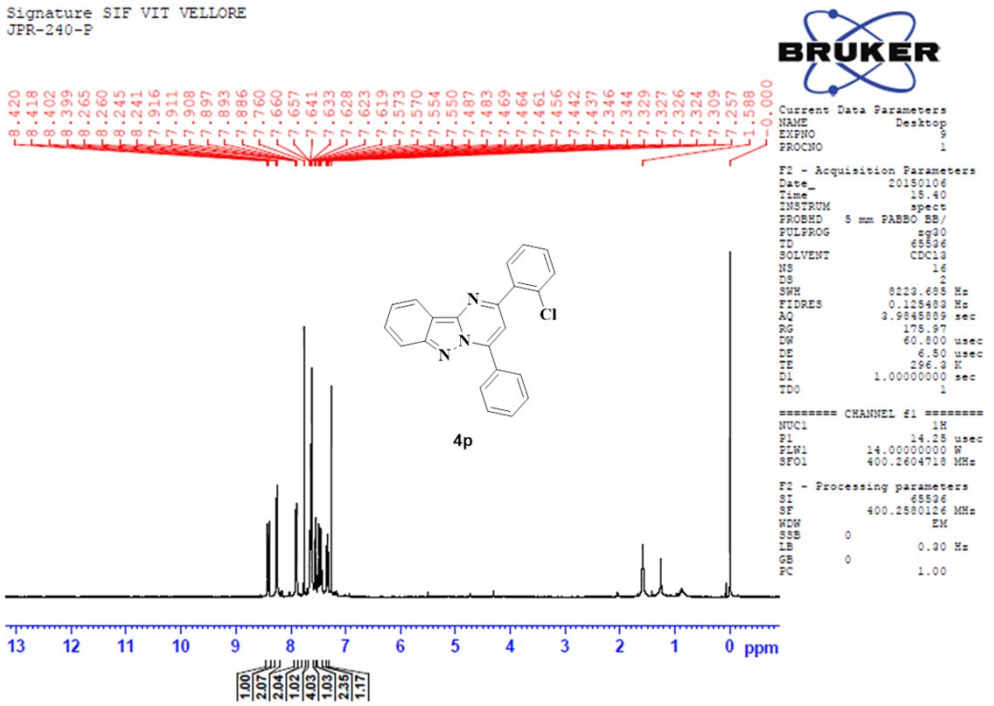
^{13}C NMR spectrum of compound (4o):



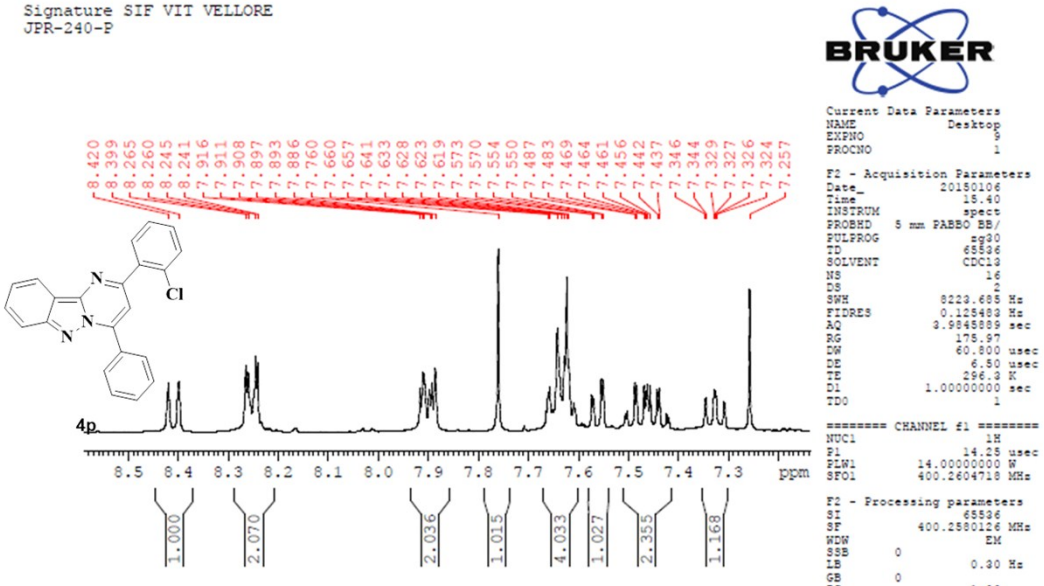
HRMS spectrum of compound (4o):



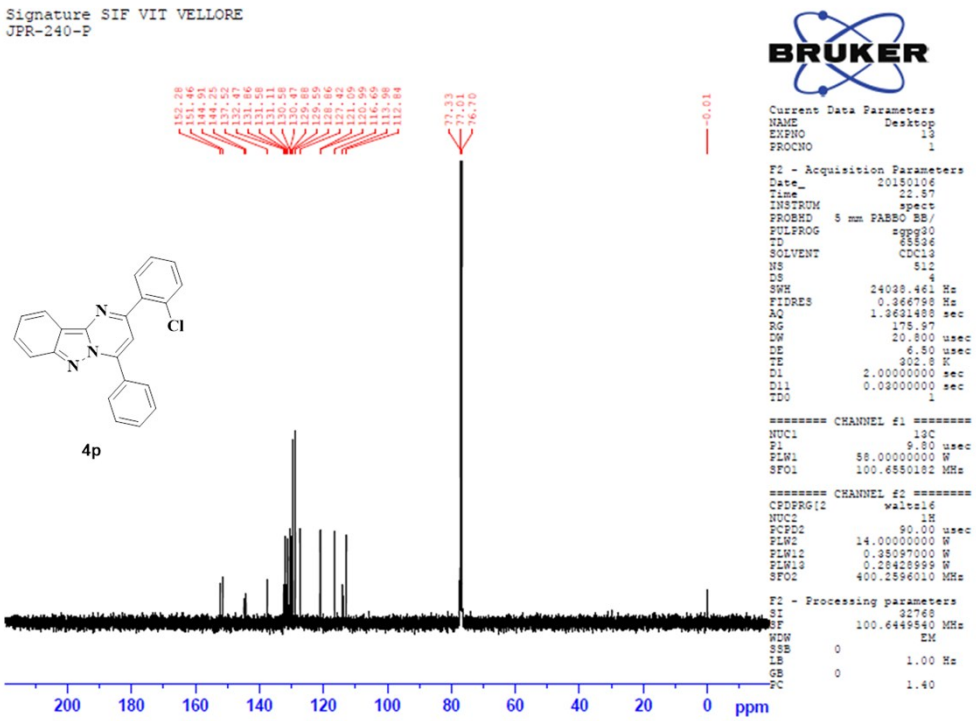
^{1}H NMR spectrum of compound (4p):



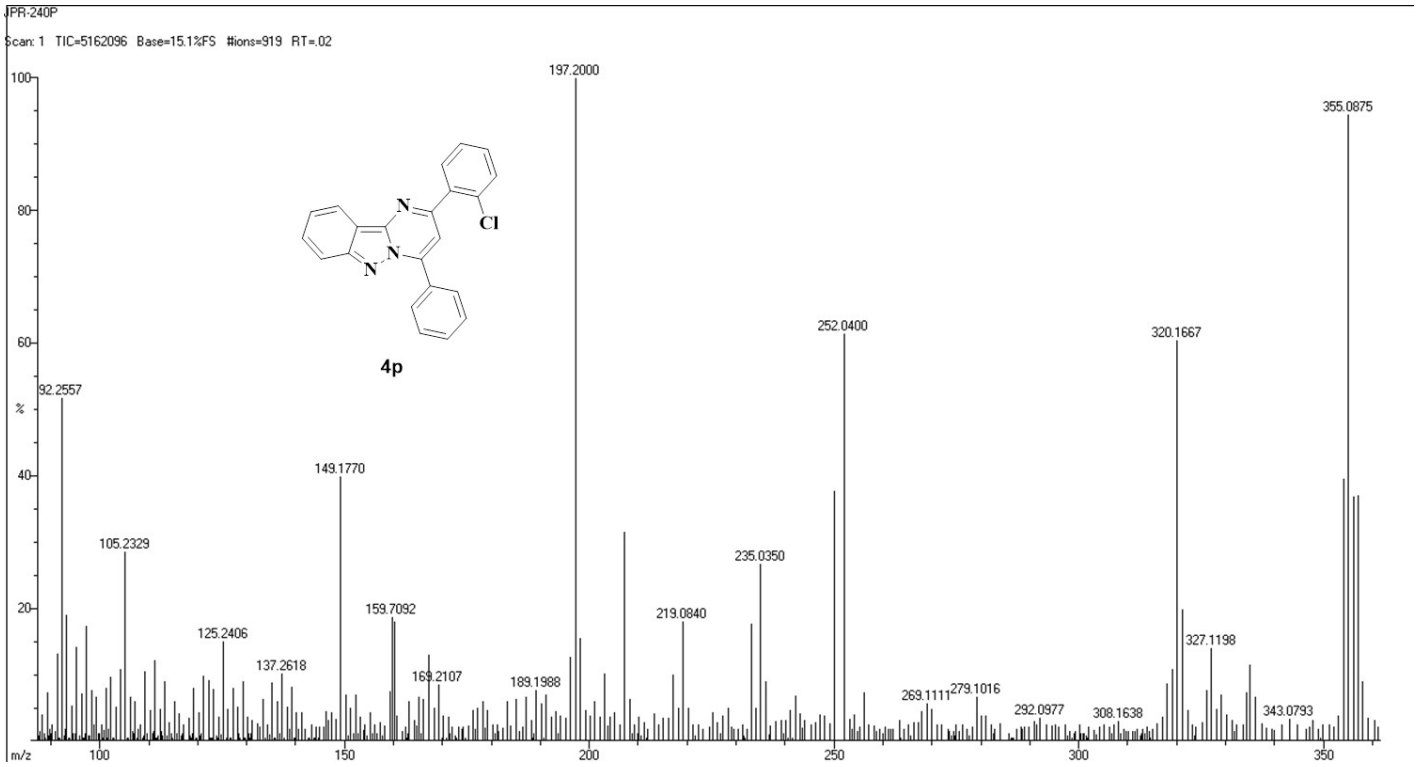
Expanded ^{1}H NMR spectrum of compound (4p):



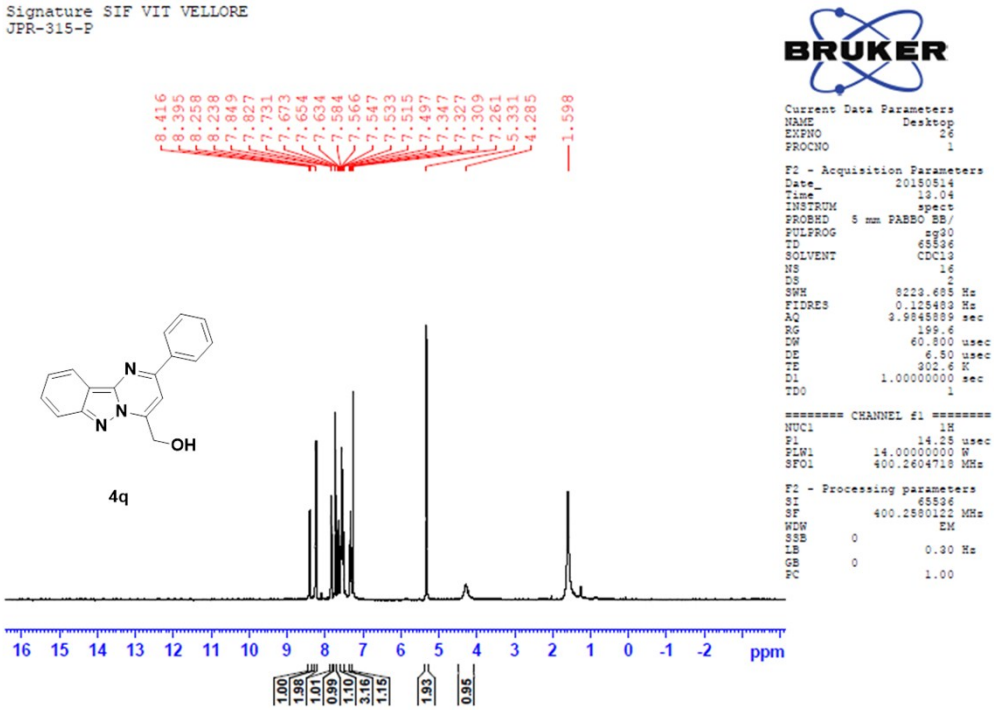
^{13}C NMR spectrum of compound (4p):



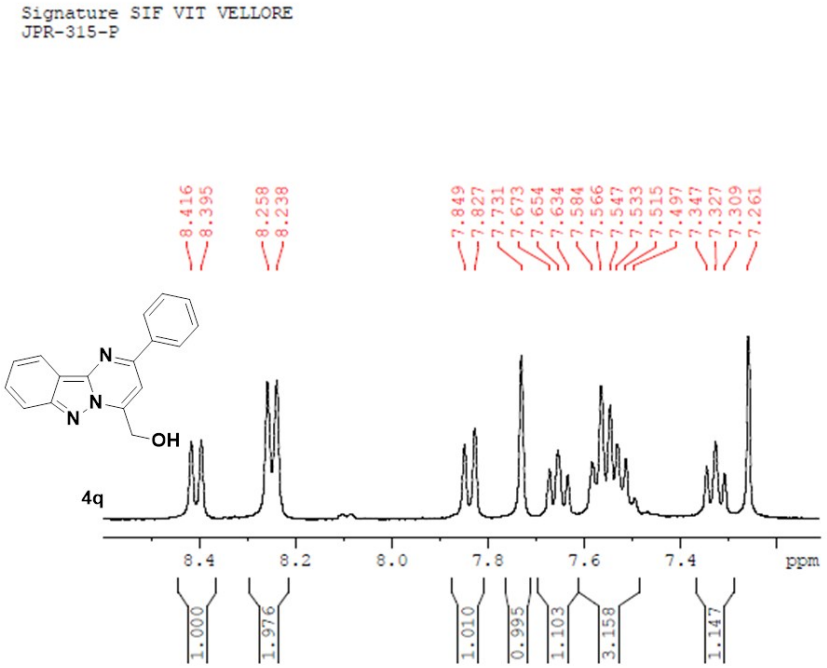
HRMS spectrum of compound (4p):

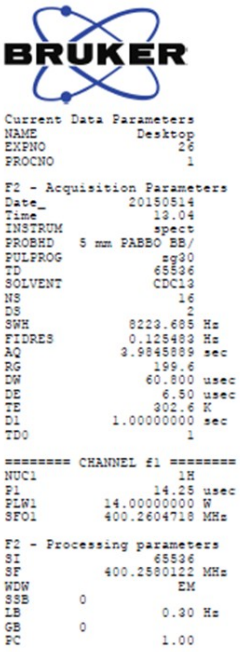


^{1}H NMR spectrum of compound (4q):

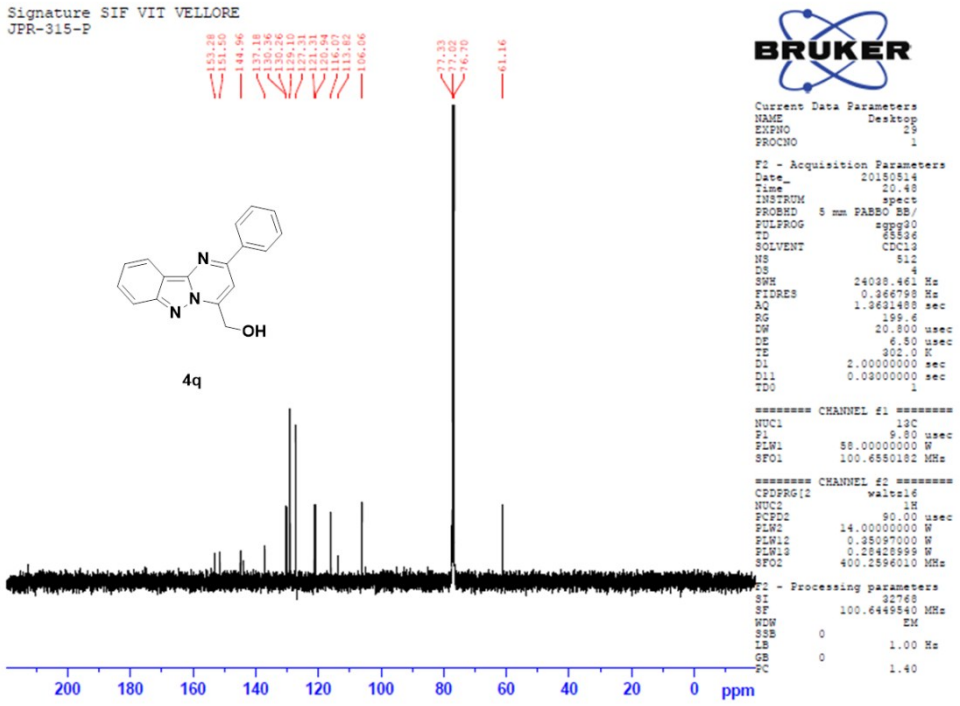


Expanded ^{1}H NMR spectrum of compound (4q):

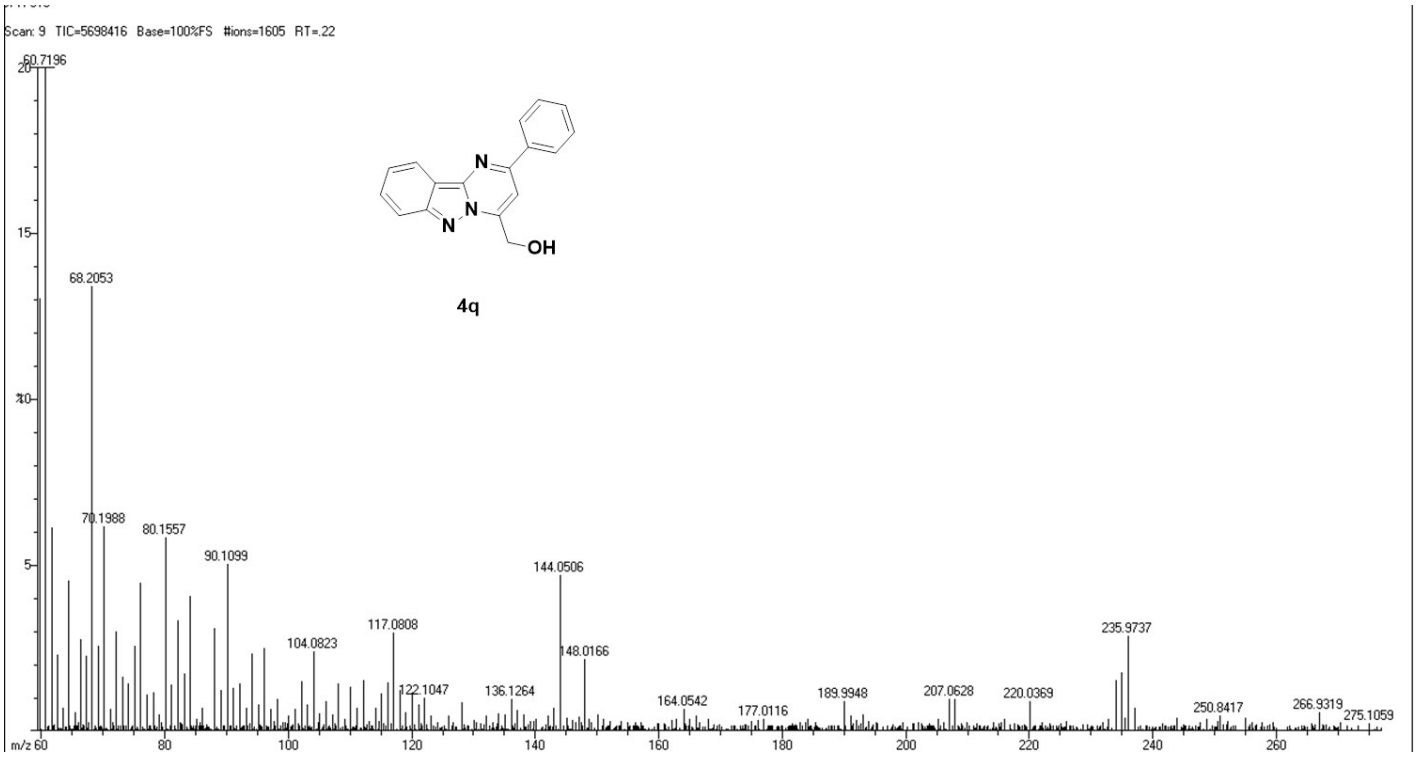




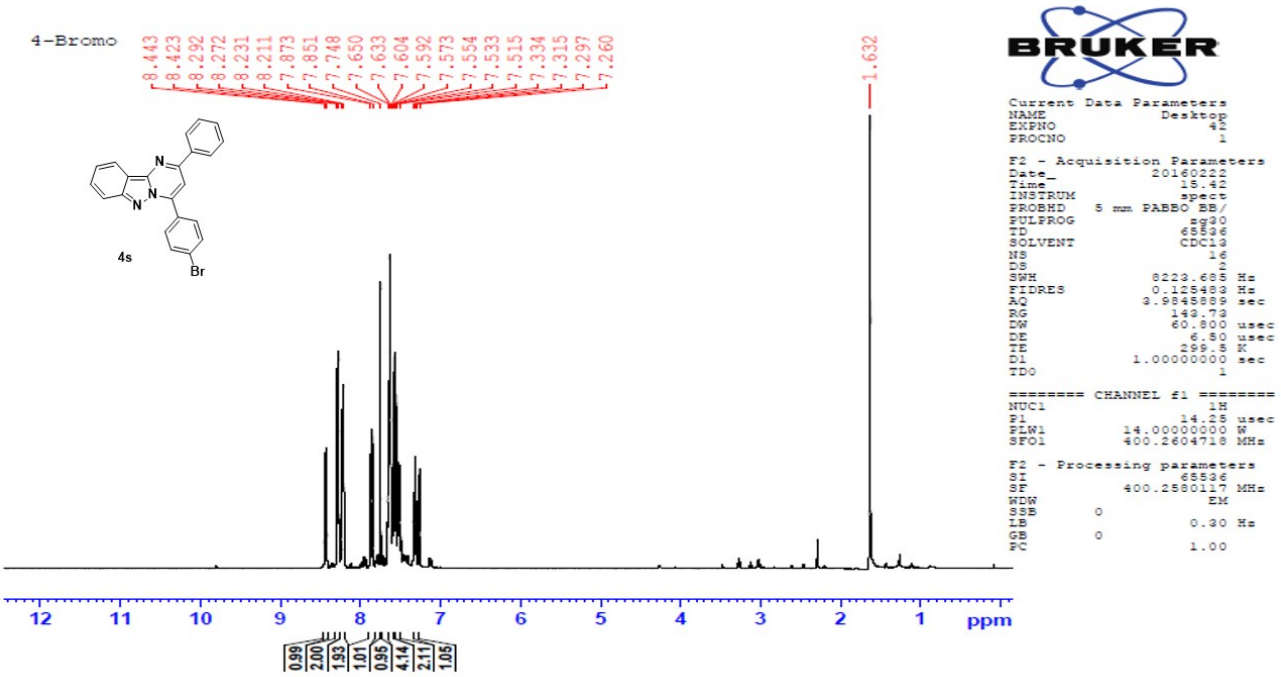
^{13}C NMR spectrum of compound (4q):



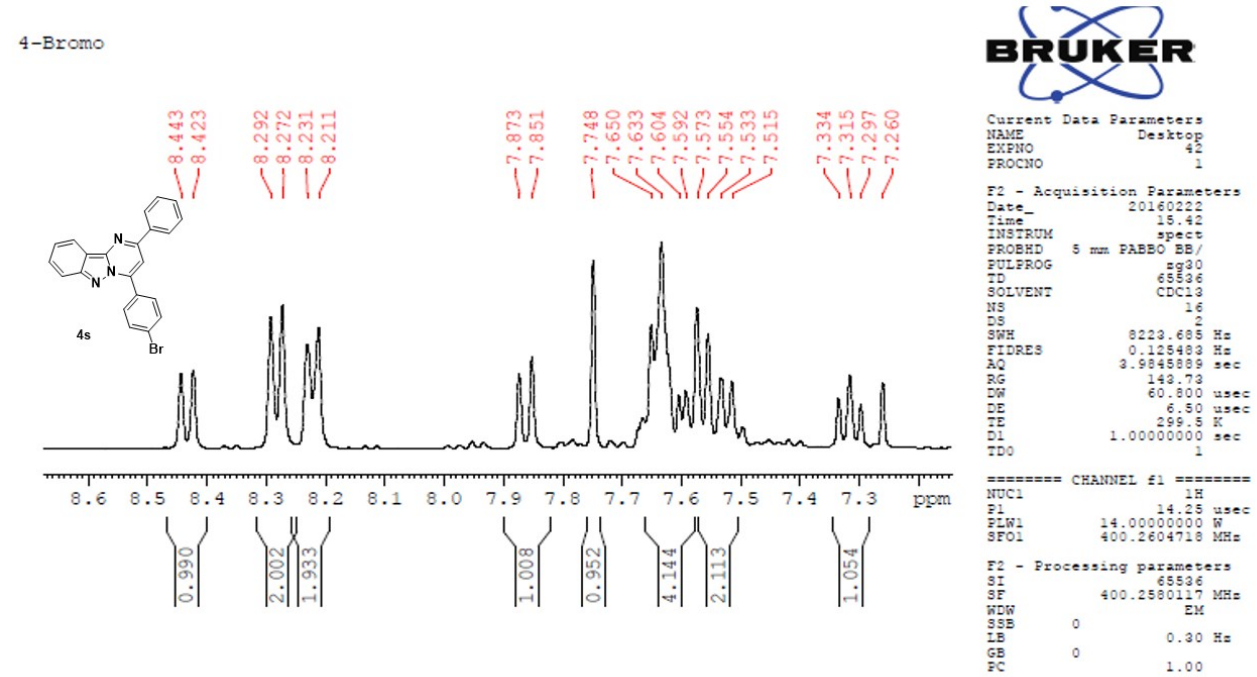
HRMS spectrum of compound (4q):



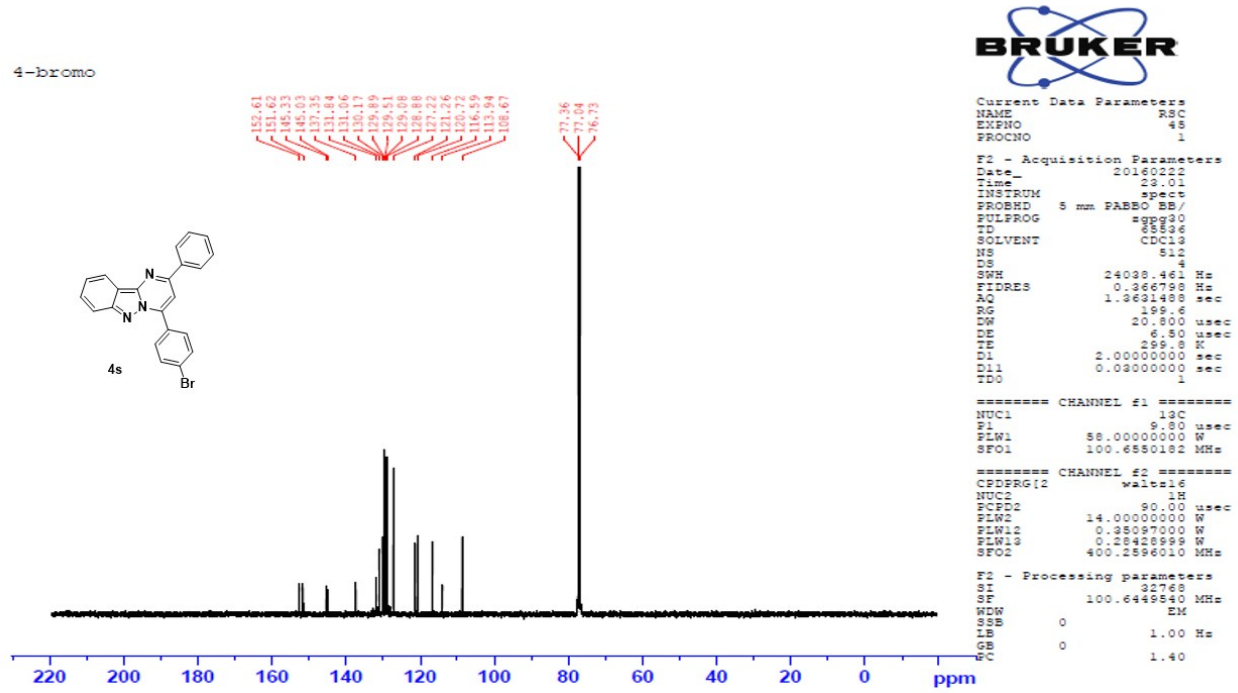
^{1}H NMR spectrum of compound (4s):



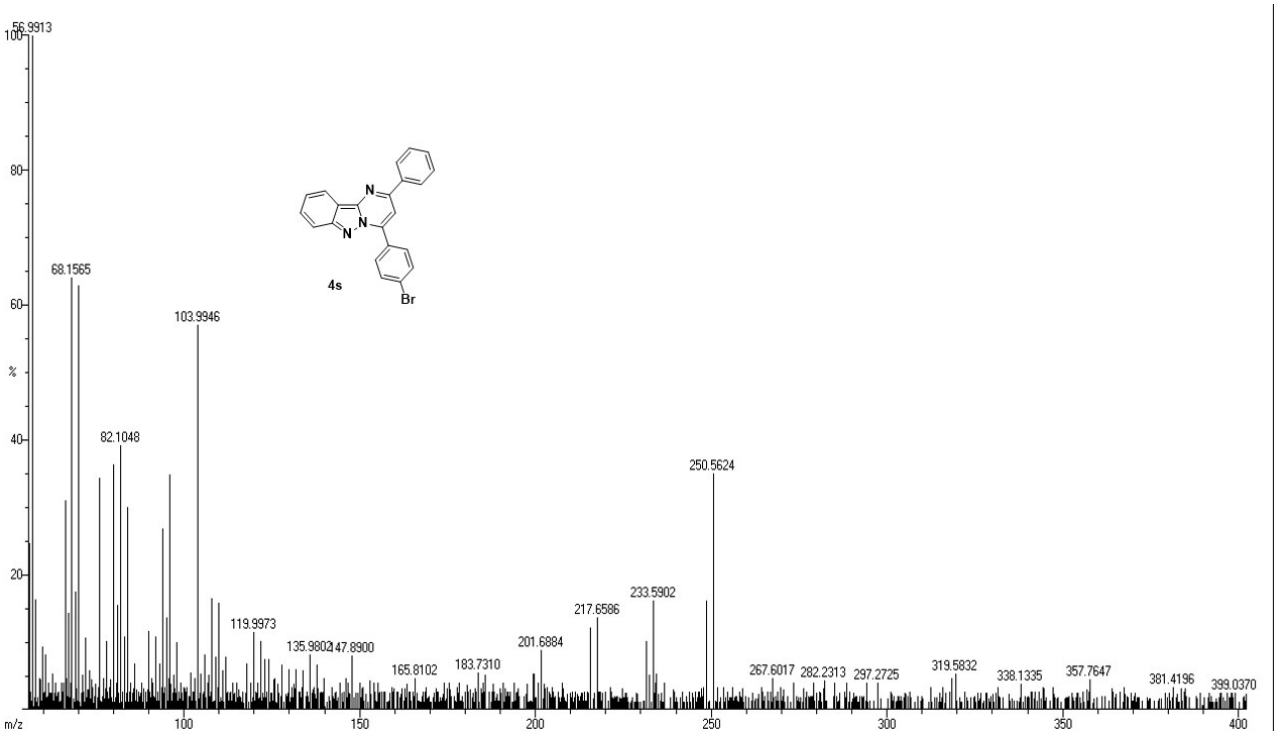
Expanded ^{1}H NMR spectrum of compound (4s):



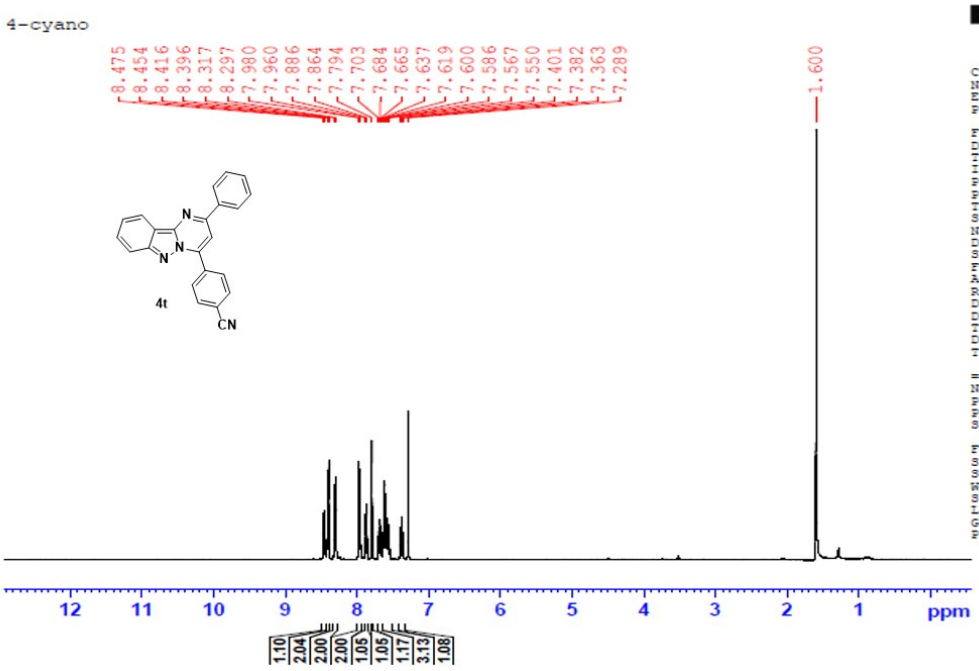
^{13}C NMR spectrum of compound (4s):

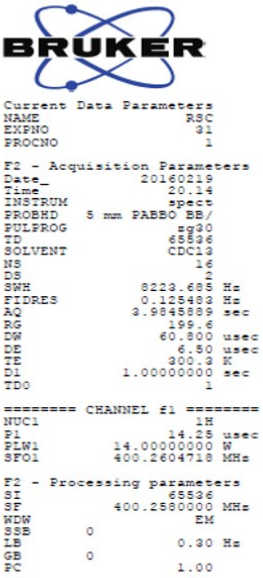


HRMS spectrum of compound (4s):

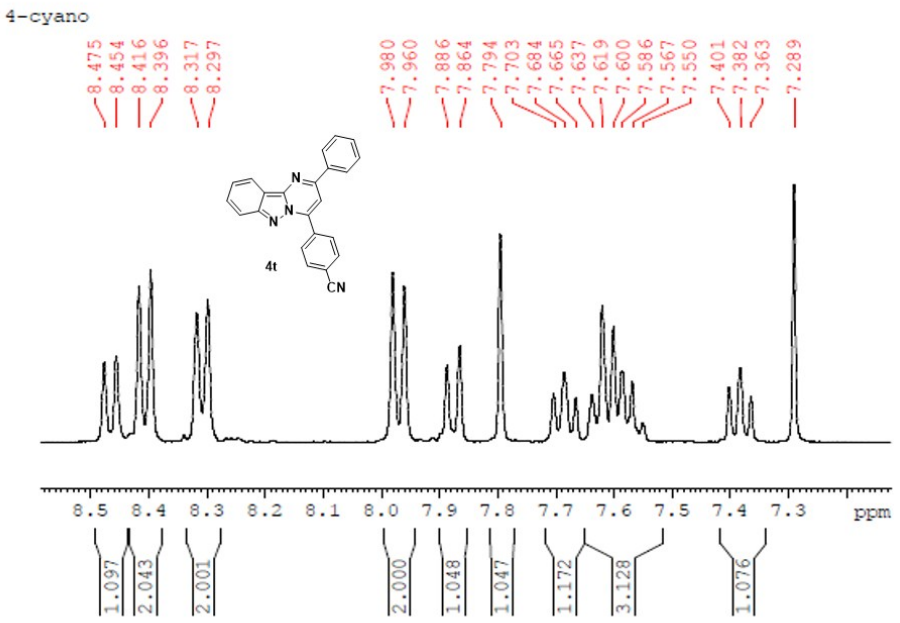


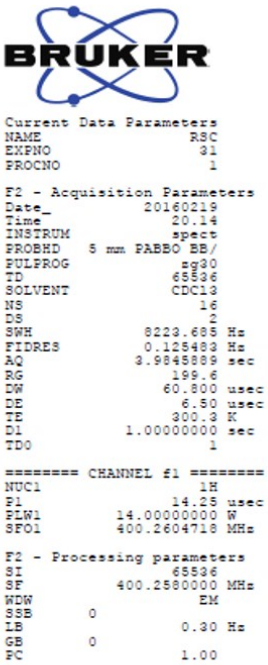
^{1}H NMR spectrum of compound (4t):



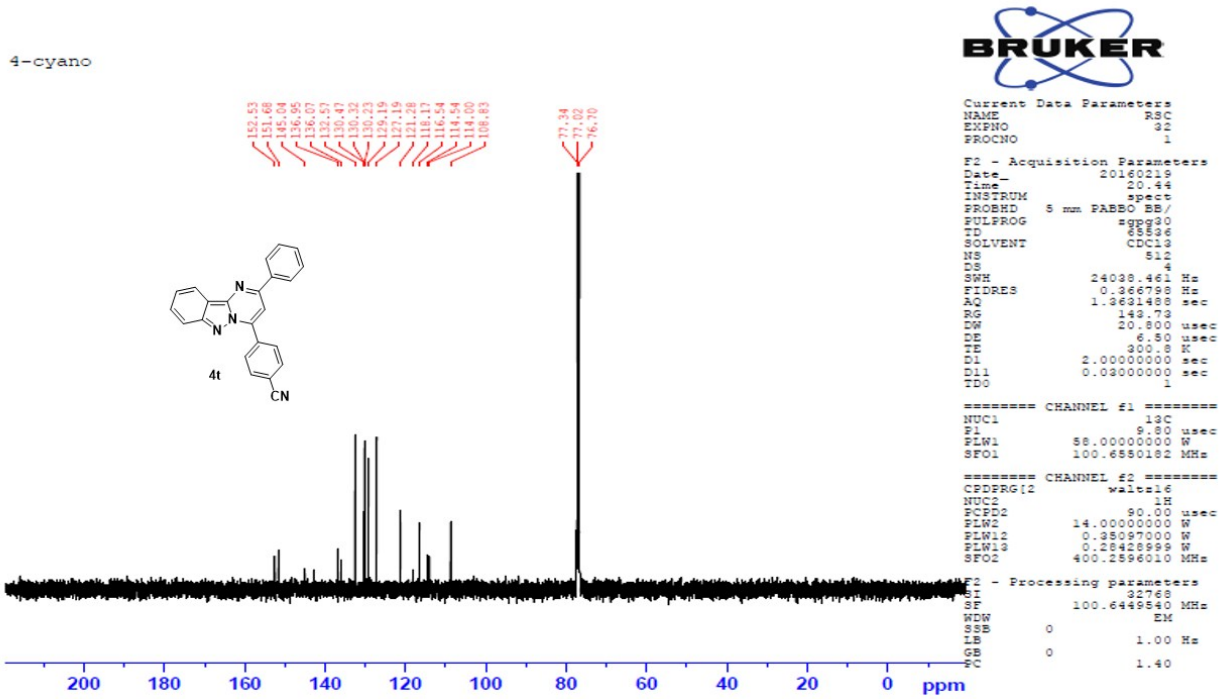


Expanded ^{1}H NMR spectrum of compound (4t):

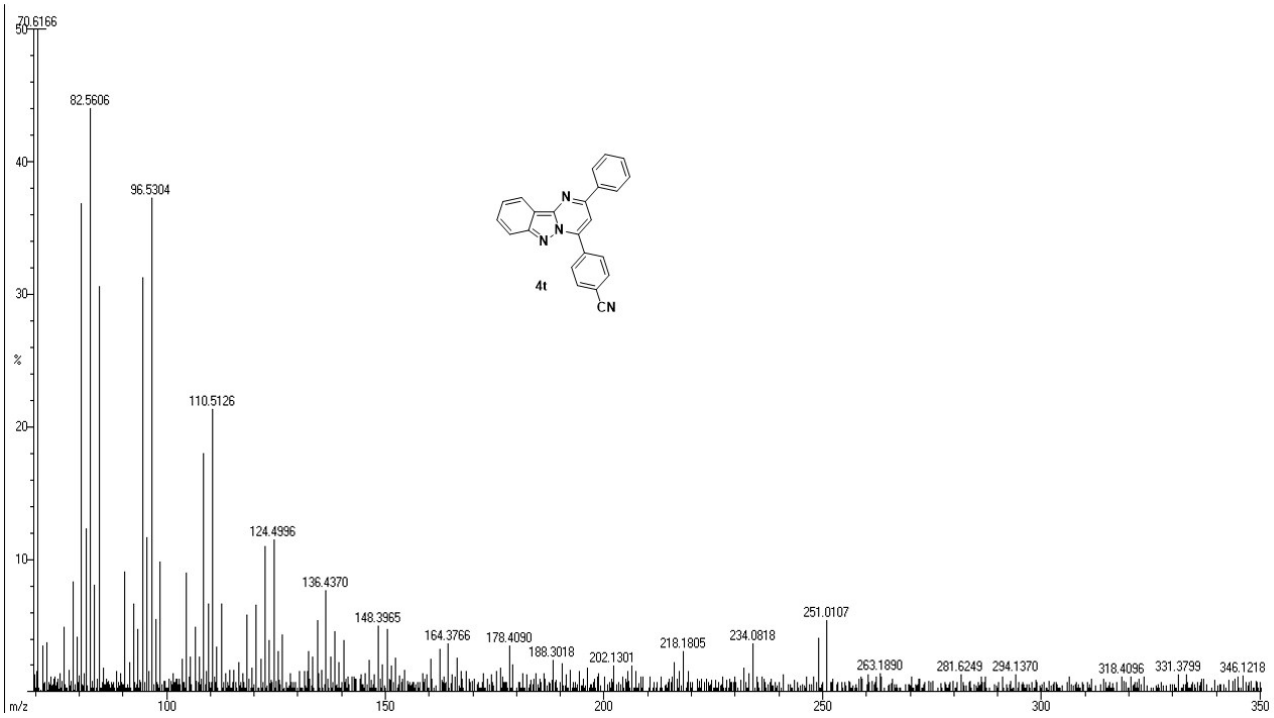




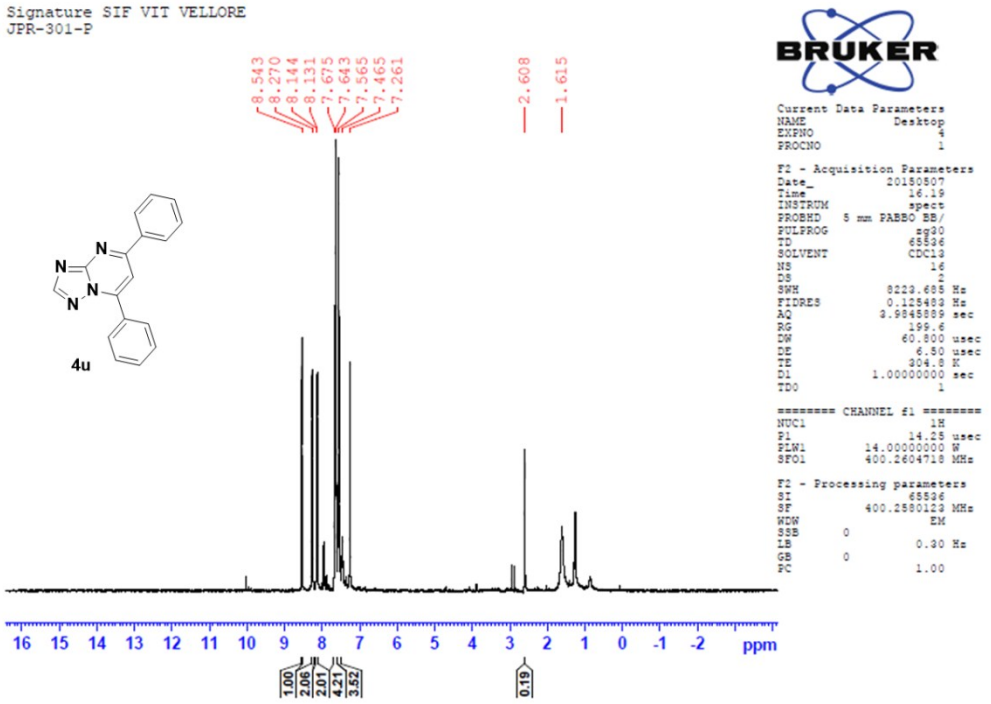
^{13}C NMR spectrum of compound (4t):



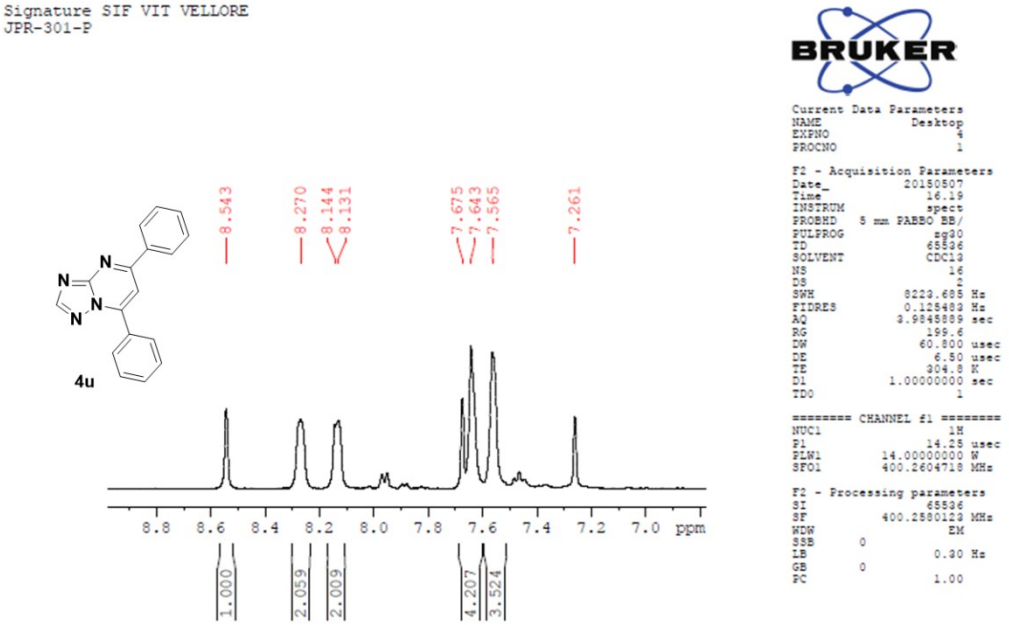
HRMS spectrum of compound (4t):



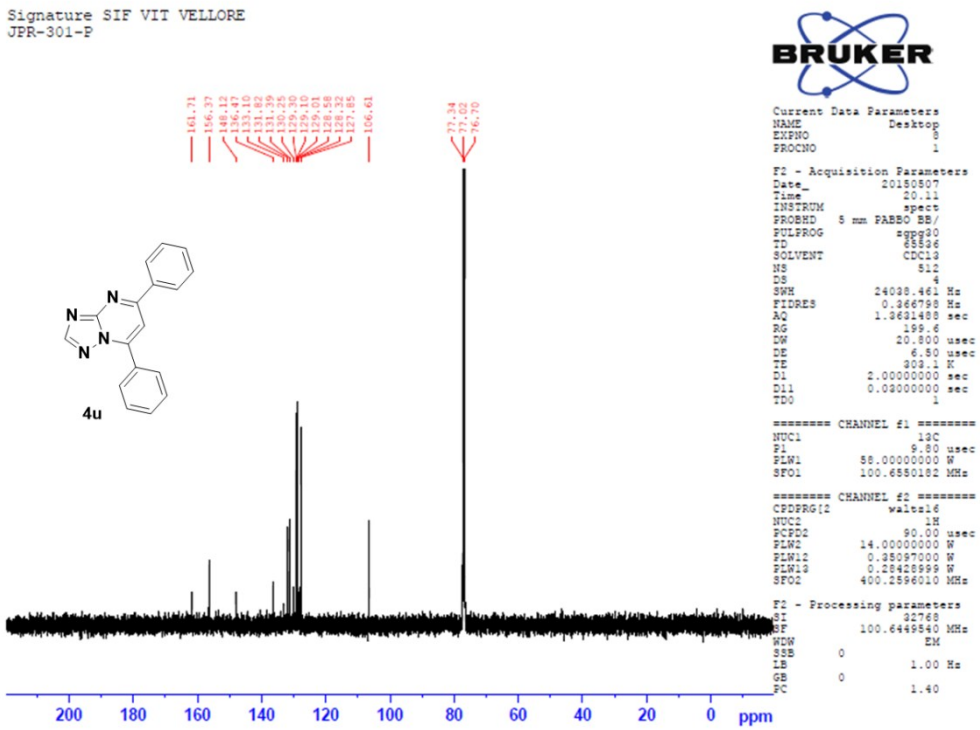
^{1}H NMR spectrum of compound (4u):



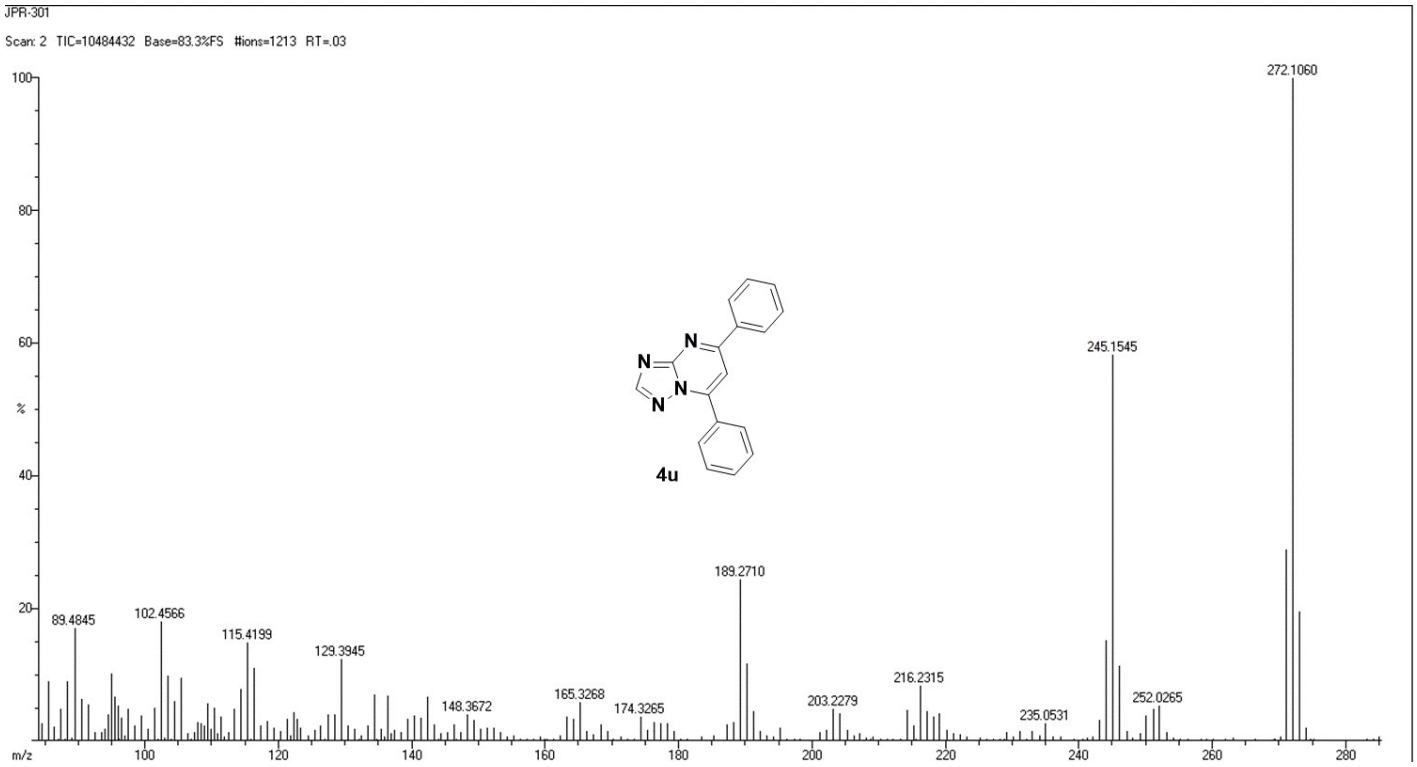
Expanded ^{1}H NMR spectrum of compound (4u):



^{13}C NMR spectrum of compound (4u):



HRMS spectrum of compound (4u):



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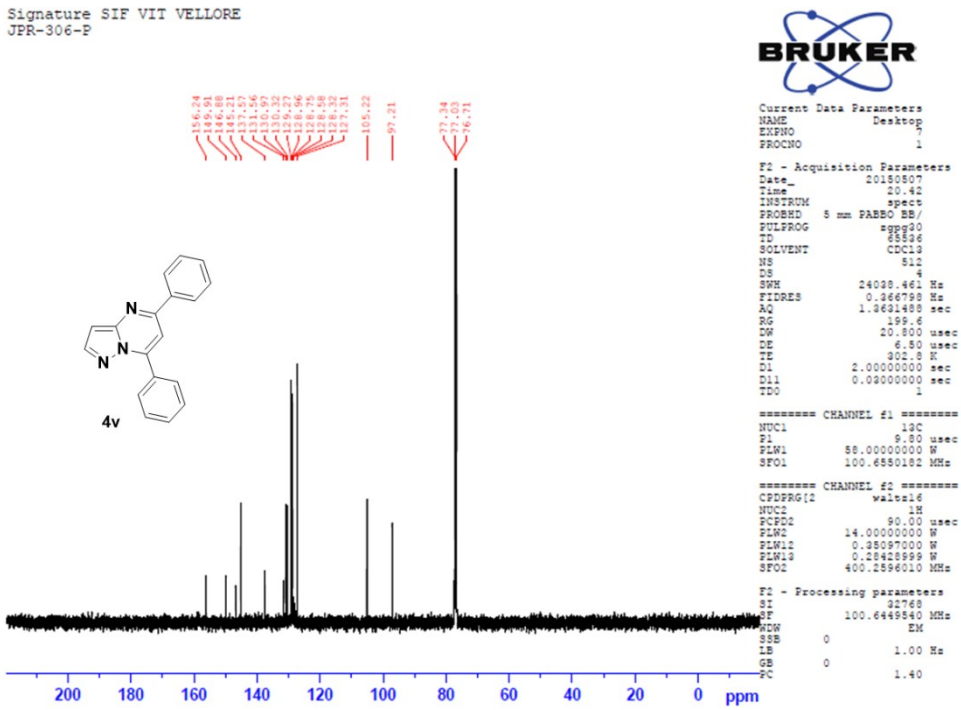
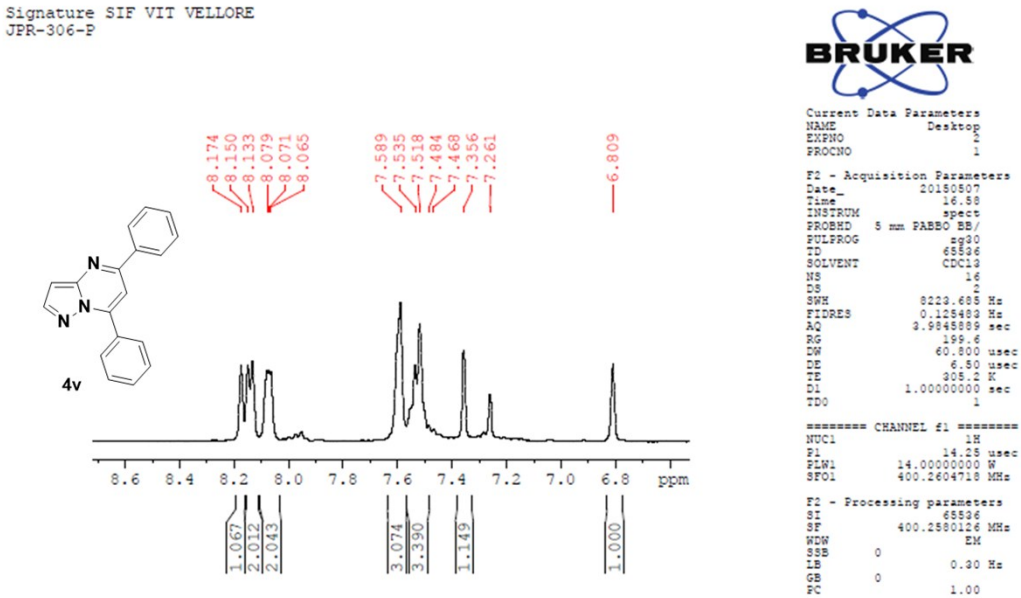
^{1}H NMR spectrum of compound (4v):

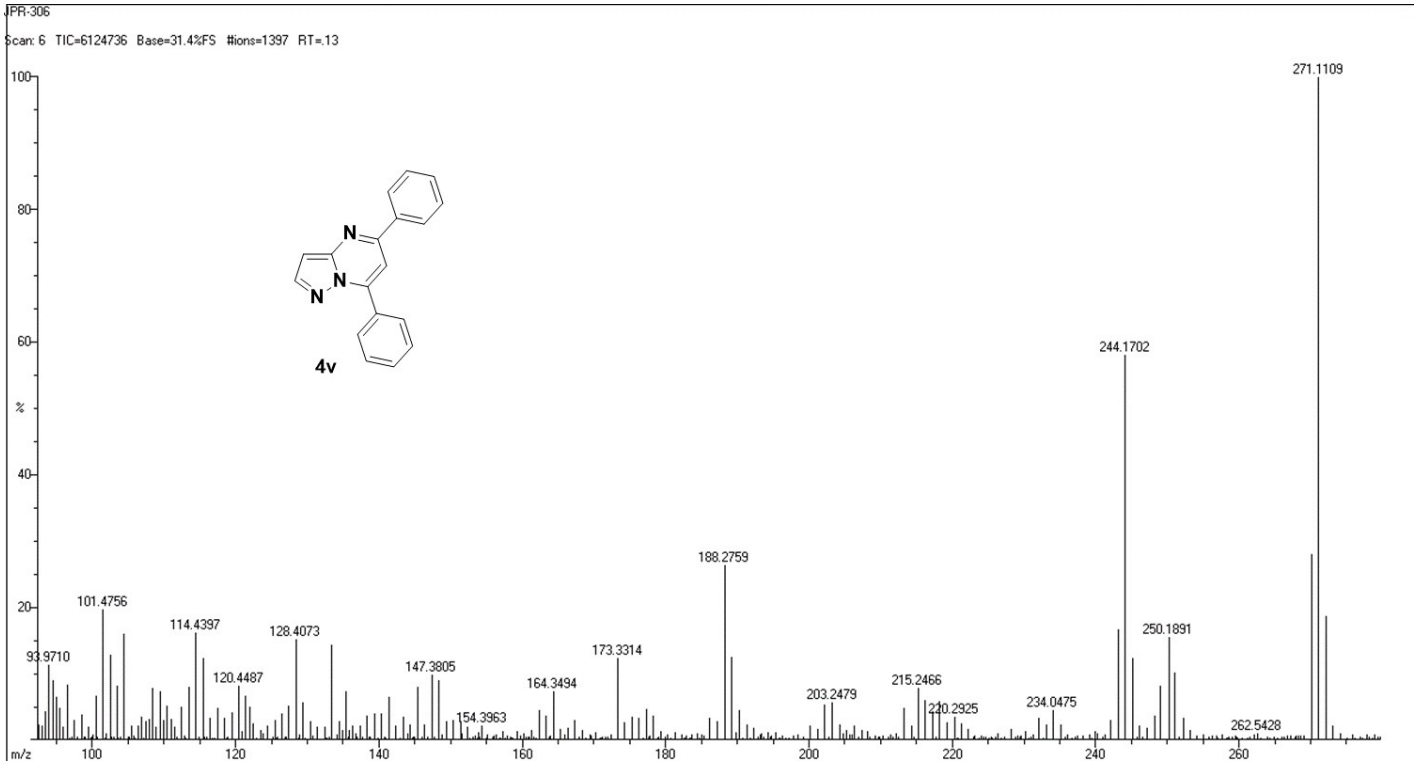


Expanded ^{1}H NMR spectrum of compound (4v):

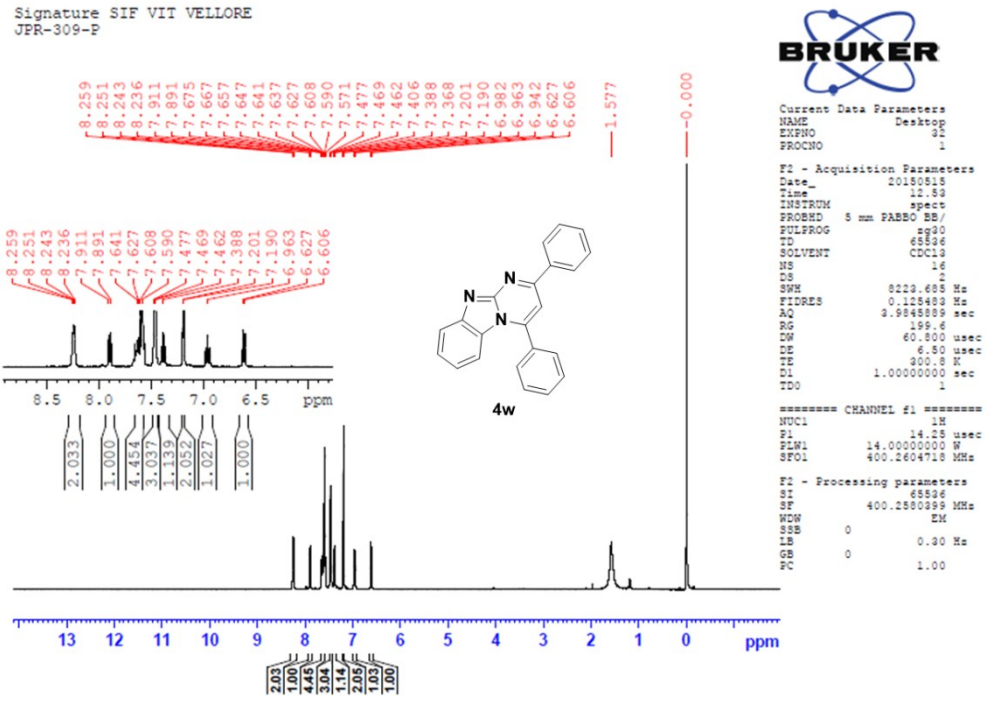


^{13}C NMR spectrum of compound (4v):

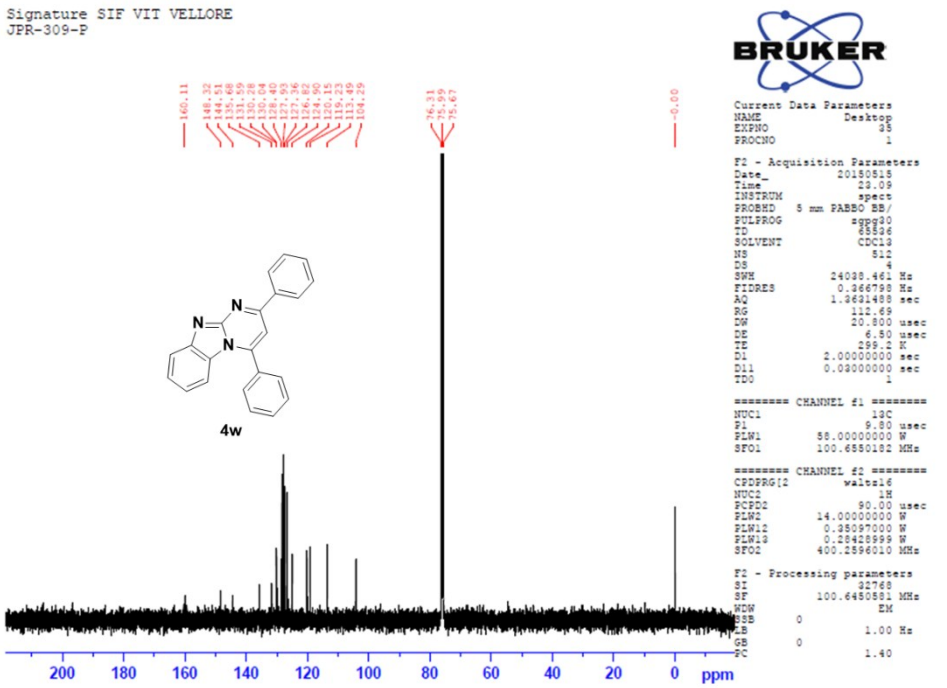
HRMS spectrum of compound (4v):



^{1}H NMR spectrum of compound (4w):



^{13}C NMR spectrum of compound (4w):



HRMS spectrum of compound (4w):