Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A rearrangement involving solid state melt reaction for the synthesis of multifunctional tetrasubstituted olefins

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General Information:

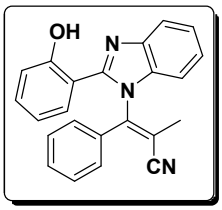
All reagents were procured from commercial sources and utilized without further purification. Solvents were distilled prior to use. Silica gel used for Column chromatography purification as stationary phase. FTIR-Nicolet iS10 spectrophotometer using for IR spectral studies. ^{1}H NMR (300 & 400 MHz) and ^{13}C NMR (75 & 100 MHz) were recorded on a Bruker spectrometer using $CDCl_3$ as solvent and TMS as an internal standard; chemical shifts are reported in δ (ppm). Mass spectra were recorded on a Agilent 1200 LC/MS-6110 mass spectrometer. Melting points are uncorrected. Thin-layer chromatography (TLC) was performed using glass plates coated with silica gel (ACME, 254F). Spots were visualized using UV lamp and iodine vapour.

Experimental Section

Typical experimental procedure for the synthesis of compounds (5a-q)

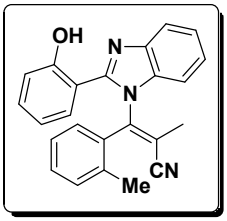
A mixture of (*E*)-2-((2-Formylphenoxy)methyl)-3-phenylacrylonitrile (**1a**, 1mmol), and *o*-phenylenediamine (**4**, 1 mmol) was placed in a round bottom flask and melted at 160 ºC for 1 h. After completion of the reaction as indicated by TLC, the crude reaction mass was purified by column chromatography on silica gel (60-120 mesh), using ethylacetate : hexanes (0.5 : 9.5) to afford **5a** as a colourless solid in 84% yield.

(*E*)-3-(2-(2-Hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methyl-3-phenylacrylonitrile (5a)



Yield : 84%; M. P : 162-164 °C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : *δ* 1.81 (s, 3H), 6.80 (t, *J*=7.5 Hz, 1H), 7.06 (t, *J*=7.5 Hz, 2H), 7.25-7.45 (m, 6H), 7.52 (d, *J*=7.2 Hz, 2H), 7.63 (d, *J*=7.8 Hz, 1H), 7.84 (d, *J*=7.8 Hz, 1H), 13.03 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.29, 108.53, 110.35, 111.86, 118.32, 118.74, 118.95, 119.38, 124.26, 124.73, 125.74, 128.22, 129.26, 131.64, 132.33, 133.03, 134.13, 140.52, 148.43, 150.75, 159.13; IR (KBr) : 1625, 3030, 3246, 3414 cm^{-1}; **HRMS** calculated for $C_{23}H_{18}N_3O$ $[M+H]^+$ 352.1450, found 352.1451.

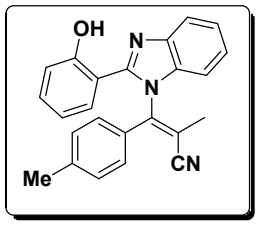
(*E*)-3-(2-(2-Hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methyl-3-*o*-tolylacrylonitrile (5b)



Yield : 80%; M. P : 161-163 °C; Reaction time : 1h; ^{1}H NMR (400 MHz, $CDCl_3$) : *δ* 1.86 (s, 3H), 2.33 (s, 3H), 6.85 (t, *J*=1.2Hz, 1H), 6.89 (d, *J*=0.8Hz, 1H), 7.0-7.34 (m, 7H), 7.35 (d, *J*=1.2Hz, 2H), 7.37 (d, *J*=0.8Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 17.17, 19.42, 109.19, 109.69, 111.06, 117.07,

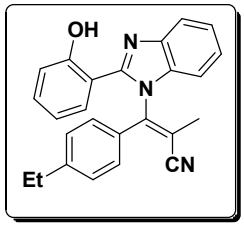
117.29, 117.58, 118.29, 122.97, 123.42, 124.93, 125.10, 128.82, 129.88, 130.82, 131.08, 131.44, 133.02, 136.44, 139.36, 146.79, 149.64, 157.53; IR (KBr) : 1621, 3010, 3236, 3434cm^{-1}, **HRMS** calculated for $C_{24}H_{20}N_3O$ $[M+H]^+$ 366.1606, found 366.1595.

(*E*)-3-(2-(2-Hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methyl-3-*p*-tolylacrylonitrile (5c)



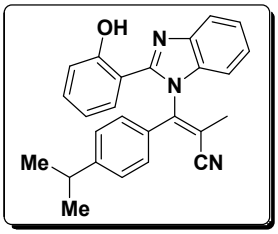
Yield: 85%; M. P : 162-164°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.76 (s, 3H), 2.33 (s, 3H), 6.79 (t, *J*=7.5Hz, 1H), 7.04-7.43 (m, 10H), 7.64 (q, *J*=1.2Hz, 1H), 7.82 (d, *J*=8.1Hz, 1H), 13.08 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.16, 21.50, 107.40, 110.41, 111.90, 118.30, 118.94, 118.97, 119.32, 124.19, 124.68, 125.79, 128.15, 129.98, 130.23, 132.28, 134.16, 140.49, 142.37, 148.46, 150.74, 159.15; IR (KBr) : 1620, 3037, 3240, 3419cm^{-1}; **HRMS** calculated for $C_{24}H_{20}N_3O$ $[M+H]^+$ 366.1606, found 366.1589.

(*E*)-3-(4-Ethylphenyl)-3-(2-(2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methylacrylo nitrile (5d)



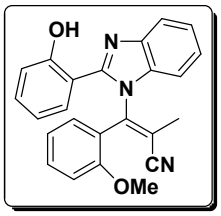
Yield : 84%; M. P : 163-165°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.20 (t, *J*=7.5 Hz, 3H), 1.76 (s, 3H), 2.64 (q, *J*=7.5 Hz, 2H), 6.8 (t, *J*=7.5Hz, 1H), 7.04-7.47 (m, 9H), 7.64 (d, *J*=7.8Hz, 1H), 7.83 (d, *J*=7.8Hz 1H), 13.11 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.93, 18.15, 28.74, 107.41, 110.41, 111.90, 118.29, 118.96, 119.29, 124.17, 124.65, 125.74, 128.22, 128.79, 130.37, 132.26, 134.15, 140.47, 148.48, 150.71, 159.15; IR (KBr) : 1635, 3043, 3231, 3434cm^{-1}; **HRMS** calculated for $C_{25}H_{22}N_3O$ $[M+H]^+$ 380.1763, found 380.1746.

(*E*)-3-(2-(2-Hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-(4-isopropylphenyl)-2-methyl acrylonitrile (5e)



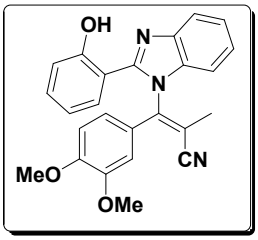
Yield : 83%; M. P : 161-163°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.20 (d, *J*=6.9 Hz, 6H), 1.74 (s, 3H), 2.89 (sep, *J*=6.9 Hz, 1H), 6.78-6.83 (m, 1H), 7.04 (m, 2H), 7.21-7.63 (m, 7H), 7.66 (d, *J* = 1.5 Hz, 1H), 7.82 (d, *J* = 7.8Hz, 1H), 13.01 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.13, 23.55, 34.05, 107.48, 110.44, 111.93, 118.31, 118.99, 119.28, 124.16, 124.65, 125.73, 127.41, 128.25, 130.46, 132.27, 134.16, 140.48, 148.46, 150.71, 153.02, 159.18; IR (KBr) : 1621, 3043, 3231, 3440cm^{-1}; **HRMS** calculated for $C_{26}H_{24}N_3O$ $[M+H]^+$ 394.1919, found 394.1907.

(*E*)-3-(2-(2-Hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-(2-methoxyphenyl)-2-methyl acrylonitrile (5f)



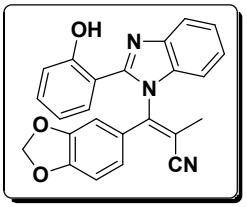
Yield : 82%; M. P : 164-166°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.89 (s, 3H), 3.79 (s, 3H), 6.80-6.92 (m, 2H), 7.03 (t, J = 6 Hz, 1H), 7.17 (d, J = 7.5 Hz, 2H),7.30-7.37 (m, 5H), 7.80 (d, J=7.8Hz 1H), 7.88 (d, J=7.8Hz 1H), 12.78 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.00, 55.21, 110.67, 111.13, 111.85, 112.41, 117.92, 118.41, 118.53, 119.19, 120.76, 122.42, 123.90, 124.41, 126.71, 130.20, 132.03, 132.77, 134.44, 140.37, 144.85, 150.89, 157.43, 159.00; IR (KBr) : 1622, 3023, 3239, 3419cm^{-1}; **HRMS** calculated for $C_{24}H_{20}N_3O_2$ $[M+H]^+$ 382.1556, found 382.1543.

(*E*)-3-(3,4-Dimethoxyphenyl)-3-(2-(2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methyl acrylonitrile (5g)



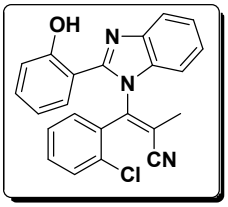
Yield : 81%; M. P : 168-170°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.74 (s, 3H), 3.83 (s, 3H), 3.85 (s, 3H), 6.74-6.87 (m, 3H), 7.09 (t, J=9.3Hz, 2H), 7.26-7.41 (m, 5H), 7.60 (d, J=8.1Hz, 1H), 7.82 (d, 7.8Hz 1H), 12.90 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.09, 55.98, 56.15, 105.71, 110.44, 110.82, 111.25, 111.89, 118.32, 118.95, 119.30, 121.95, 124.20, 124.67, 125.41, 125.76, 132.30, 134.24, 140.46, 148.13, 149.23, 150.87, 151.89, 159.13; IR (KBr) : 1622, 3038, 3240, 3412cm^{-1}; **HRMS** calculated for $C_{25}H_{22}N_3O_3$ $[M+H]^+$ 412.1661, found 412.1688.

(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-3-(2-(2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methylacrylonitrile (5h)



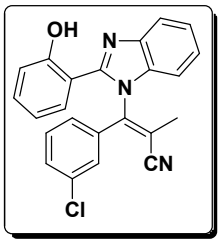
Yield : 80%; M. P : 171-173°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.75 (s, 3H), 5.98 (s, 2H), 6.75-6.96 (m, 2H), 7.04-7.12 (m, 4H), 7.29-7.60 (m, 3H), 7.62 (d, J = 1.2 Hz, 1H), 7.83 (d, J = 7.8Hz, 1H), 13.04 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.16, 102.05, 106.52, 107.97, 108.87, 110.35, 111.83, 118.33, 118.96, 119.37, 123.73, 124.26, 124.74, 125.75, 126.89, 132.32, 134.08, 140.45, 147.85, 148.50, 150.50, 150.68, 159.15; IR (KBr) : 1618, 3024, 3236, 3427cm^{-1}; **HRMS** calculated for $C_{24}H_{18}N_3O_3$ $[M+H]^+$ 396.1348, found 396.1351.

(*E*)-3-(2-Chlorophenyl)-3-(2-(2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methylacrylonitrile (5i)



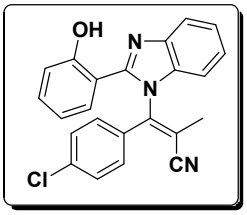
Yield : 82%; M. P : 160-162°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.12 (s, 3H), 7.09-7.25 (m, 2H), 7.33 (t, J = 7.5Hz, 1H), 7.44-7.58 (m, 4H), 7.82 (t, J = 7.8Hz, 3H), 7.98(d, J = 7.2Hz, 1H), 8.13 (d, J = 6.9Hz, 1H), 12.76 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.09, 110.64, 111.82, 112.58, 117.13, 118.37, 118.62, 119.12, 123.64, 124.15, 125.51, 126.73, 126.80, 130.70, 131.01, 131.34, 131.77, 133.19, 133.99, 140.48, 144.68, 150.48, 158.42; IR (KBr) : 1631, 3050, 3237, 3434cm^{-1}; **HRMS** calculated for $C_{23}H_{17}ClN_3O$ $[M+H]^+$ 386.1060, found 386.1054.

(*E*)-3-(3-Chlorophenyl)-3-(2-(2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methylacrylo nitrile (5j)



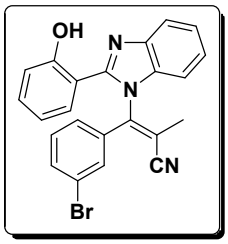
Yield : 80%; M. P : 161-163°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.72 (s, 3H), 6.70 (t, J=7.5Hz, 1H),7.02 (q, J=8.4Hz, 2H), 7.16-7.50 (m, 8H), 7.75 (d, J=7.8Hz, 1H), 12.84 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.39, 110.08, 110.19, 111.71, 118.25, 118.47, 119.04, 119.55, 124.46, 124.93, 125.55, 126.47, 128.04, 130.55, 131.74, 132.51, 133.94, 134.81, 135.43, 140.58, 146.92, 150.62, 159.13; IR (KBr) : 1623, 3036, 3241, 3419cm^{-1}; **HRMS** calculated for $C_{23}H_{17}ClN_3O$ $[M+H]^+$ 386.1060, found 386.1055.

(*E*)-3-(4-Chlorophenyl)-3-(2-(2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methylacrylo nitrile (5k)



Yield : 84%; M. P : 158-160°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.82 (s, 3H), 6.82 (q, J=7.2Hz, 1H), 7.09(q, J=8.4Hz, 2H), 7.25-7.57 (m, 8H), 7.83 (d, 7.8Hz, 1H), 12.87 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.32, 109.06, 110.18, 111.74, 118.44, 118.48, 119.00, 119.53, 124.43, 124.88, 125.59, 129.48, 129.61, 131.48, 132.47, 133.97, 137.87, 140.57, 147.31, 150.68, 159.14. IR (KBr) : 1630, 3040, 3251, 3431cm^{-1}; **HRMS** calculated for $C_{23}H_{17}ClN_3O$ $[M+H]^+$ 386.1060, found 386.1056.

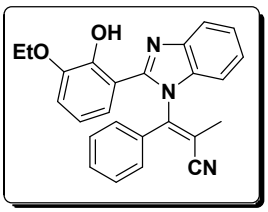
(*E*)-3-(3-Bromophenyl)-3-(2-(2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methylacrylo nitrile (5l)



Yield : 83%; M. P : 166-168°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.80 (s, 3H), 6.81-6.87 (m, 1H), 7.04-7.12(m, 2H), 7.22-7.85 (m, 9H), 12.89 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.36, 29.70, 110.11, 110.19, 111.70, 118.21, 118.47, 119.04, 119.55, 123.36, 124.45, 124.92, 125.52, 126.90, 130.73, 130.89, 132.50, 133.92, 134.66, 135.03, 140.59,

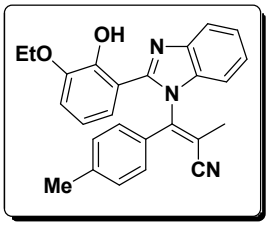
146.80, 150.62, 159.12; IR (KBr) : 1631, 3029, 3237, 3434cm^{-1} ; **HRMS** calculated for $C_{23}H_{17}BrN_3O$ $[M+H]^+$ 430.0555, found 430.0559.

(*E*)-3-(2-(3-Ethoxy-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methyl-3-phenylacrylo nitrile (5m)



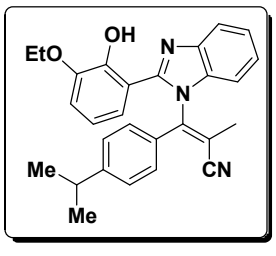
Yield : 83%; M. P : 159-161°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.50 (t, *J*=6.9 Hz, 3H), 1.79 (s, 3H), 4.13 (q, *J*=6.9 Hz, 2H), 6.75 (t, *J*=8.1Hz, 1H),6.92 (d, *J*=7.8Hz, 1H), 7.04 (d, *J*=8.1, 1H), 7.23-7.52 (m, 9H), 7.83 (d, J=7.8, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.86, 18.29, 64.63, 108.36, 110.38, 112.27, 115.22, 117.71, 118.55, 118.80, 119.45, 124.18, 124.66, 128.24, 129.18, 131.52, 133.14, 134.10, 140.57, 148.45, 149.46, 150.99; IR (KBr) : 1620, 3031, 3243, 3434cm^{-1}; **HRMS** calculated for $C_{25}H_{22}N_3O_2$ $[M+H]^+$ 396.1712, found 396.1703.

(*E*)-3-(2-(3-Ethoxy-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methyl-3-*p*-tolylacrylo nitrile (5n)



Yield: 83%; M. P : 163-165°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.50 (t, *J*=6.9 Hz, 3H), 1.75 (s, 3H), 2.34 (s, 3H), 4.13 (q, *J*=6.9 Hz, 2H), 6.74 (t, *J*=8.1Hz, 1H), 6. 92 (d, *J*=7.5Hz, 1H), 7.04 (d, *J*=7.8Hz, 1H), 7.14-7.42 (m, 7H), 7.82 (d, *J*=7.8Hz, 1H), 13.11 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.87, 18.15, 21.47, 64.62, 107.25, 110.42, 112.26, 115.21, 117.70, 118.49, 119.02, 119.38, 124.11, 124.60, 128.17, 129.91, 130.31, 134.12, 140.51, 142.24, 148.48, 149.53, 150.98; IR (KBr) : 1630, 3021, 3236, 3432cm^{-1}; **HRMS** calculated for $C_{26}H_{24}N_3O_2$ $[M+H]^+$ 410.1869, found 410.1870

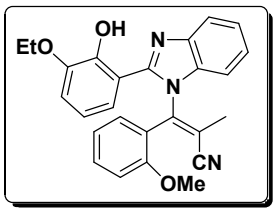
(*E*)-3-(2-(3-Ethoxy-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-(4-isopropylphenyl)-2-methylacrylonitrile (5o)



Yield : 81%; M. P : 160-162°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.20 (d, *J*=6.9 Hz, 6H), 1.49 (t, *J*=6.9 Hz, 3H), 1.73 (s, 3H), 2.88 (sep, *J*=6.9 Hz, 1H), 4.12 (q, *J*=6.9 Hz, 2H), 6.74 (d, *J*=8.1Hz, 1H), 6.92 (d, *J*=7.8Hz, 1H), 7.03 (d, J=8.1Hz, 1H), 7.20- 7.47 (m,7H), 7.81(d, *J*=8.1Hz 1H), 13.11 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.89, 18.13, 23.55, 34.03, 64.64, 107.36, 110.47, 112.30, 115.27, 117.70, 118.55, 119.05, 119.33,

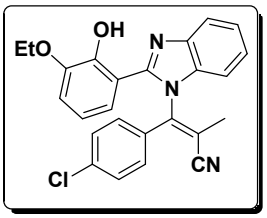
124.11, 124.60, 127.33, 128.28, 130.58, 134.13, 140.50, 148.47, 148.48, 149.58, 150.97, 152.88; IR (KBr) : 1632, 3041, 3239, 3430cm^{-1}; **HRMS** calculated for $C_{28}H_{28}N_3O_2$ $[M+H]^+$ 438.2182, found 438.2167.

(*E*)-3-(2-(3-Ethoxy-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-3-(2-methoxyphenyl)-2-methylacrylonitrile (5p)



Yield : 79%; M. P : 162-164°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.48 (t, J = 6.9 Hz, 3H), 1.88 (s, 3H), 3.75 (s, 3H), 4.12 (q, J = 6.9 Hz, 2H), 6.71-6.92 (m, 3H), 7.05(d, J=7.5Hz, 2H), 7.15 (d, J=7.8Hz 1H), 7.34 (d, J=7.8Hz 3H), 7.44 (d, J=8.1Hz, 1H), 7.8 (d, J=7.8Hz 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.89, 18.00, 55.19, 64.63, 110.73, 110.92, 111.79, 112.86, 115.12, 118.10, 118.50, 118.71, 119.26, 120.68, 122.51, 123.80, 124.33, 130.31, 132.67, 134.43, 140.42, 144.96, 148.17, 149.35, 151.06, 157.44; IR (KBr) : 1622, 3036, 3241, 3429cm^{-1}; **HRMS** calculated for $C_{26}H_{24}N_3O_3$ $[M+H]^+$ 426.1818, found 426.1817.

(*E*)-3-(4-Chlorophenyl)-3-(2-(3-ethoxy-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-1-yl)-2-methylacrylonitrile (5q)



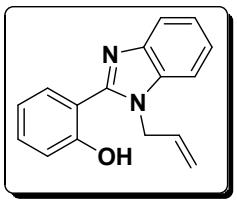
Yield : 79%; M. P : 159-161°C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.50 (t, J=6.9 Hz, 3H), 1.82 (s, 3H), 4.13 (q, J=6.9 Hz, 2H), 6.73 (t, J = 8.1 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 7.04 (d, J = 7.8Hz, 1H), 7.14 (d, J = 8.1Hz, 1H), 7.26-7.43 (m, 7H), 7.84 (d, J = 8.1H z, 1H), 12.66 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.85, 18.33, 64.64, 108.78, 110.20, 112.21, 115.24, 117.62, 118.56, 118.65, 119.63, 124.33, 124.79, 129.51, 131.61, 133.96, 137.74, 140.68, 147.35, 148.48, 149.35, 150.92; IR (KBr) : 1631, 3045, 3240, 3429cm^{-1}; **HRMS** calculated for $C_{25}H_{21}ClN_3O_2$ $[M+H]^+$ 430.1322, found 430.1320.

Typical experimental procedure for the synthesis of compounds (8a-e)

A mixture of 2-(allyloxy)benzaldehyde (**7a**, 1mmol), and *o*-phenylenediamine (**4**, 1 mmol) was placed in a round bottom flask and melted at 160 ºC for 1 h. After completion of the reaction as indicated by TLC, The crude reaction mass was purified by column chromatography on silica

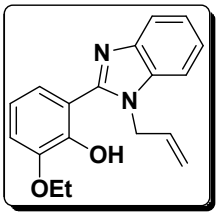
gel (Acme 60-120 mesh), using ethylacetate : hexanes (0.5 : 9.5) to afford **8a** as a colourless semi-solid in 84% yield.

2-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)phenol (8a)



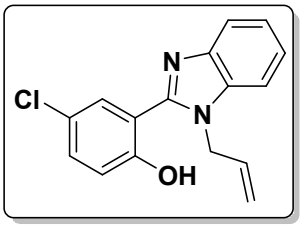
Yield : 84%; Semi-solid; Reaction time: 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 3.37 (d, J = 6 Hz, 2H), 5.11 (m, 2H), 6.06 – 6.16 (m, 1H), 6.92 (t, J = 7.6 Hz, 1H), 7.27 – 7.53 (m, 7H), 7.63 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 34.20, 111.60, 115.71, 116.07, 118.10, 118.63, 122.51, 123.34, 124.22, 129.20, 132.17, 132.54, 136.58, 137.44, 151.71, 156.94; IR (KBr) : 1607, 3015, 3226, 3406 cm^{-1}; **HRMS** calculated for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1184, found 251.1175.

2-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-6-ethoxyphenol (8b)



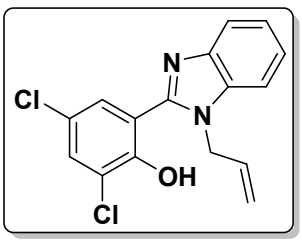
Yield : 83%; Reaction time: 1h; Semi-solid; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.47 (t, J = 6.9 Hz, 3H), 3.32 (d, J = 6.0 Hz, 2H), 4.15 (q, J = 6.9 Hz, 2H), 5.06 (t, J=9.6Hz, 2H), 5.86–5.99 (m, 1H), 6.77 (s, 1H), 7.27 (q, J=3.9Hz 4H), 7.63 (q, J=3.3Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.88, 39.82, 64.85, 112.68, 115.28, 116.04, 116.91, 117.14, 117.28, 120.03, 123.18, 125.55, 126.36, 130.97, 137.32, 146.37, 147.75, 151.11; IR (KBr) : 1616, 3024, 3231, 3401 cm^{-1}; **HRMS** calculated for $C_{18}H_{19}N_2O_2$ $[M+H]^+$ 295.1447, found 295.1443.

2-(1-allyl-1H-benzo[d]imidazol-2-yl)-4-chlorophenol (8c)



Yield : 82%; M.P. : 185-187, Reaction time: 1h; Solid; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 3.58 (d, J = 5.6 Hz, 2H), 5.23 (t, J = 6.4 Hz, 2H), 6.08 – 6.17 (m, 1H), 7.36 (d, J=8.1Hz, 4H), 7.59-7.68 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 34.13, 112.78, 112.90, 116.64, 117.86, 119.79, 122.30, 123.44, 123.69, 127.90, 131.15, 131.65, 132.90, 135.83, 150.70, 155.56 ; IR (KBr) : 1623, 3020, 3224, 3412 cm^{-1}; **HRMS** calculated for $C_{16}H_{14}ClN_2O$ $[M+H]^+$ 285.0795, found 285.0790.

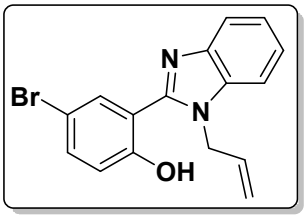
2-(1-allyl-1H-benzo[d]imidazol-2-yl)-4,6-dichlorophenol (8d)



Yield : 81%; M.P. : 188-190, Reaction time: 1h; Solid; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 3.50 (d, J = 6.8 Hz, 2H), 5.12 - 5.18 (m, 2H), 5.99 - 6.09 (m, 1H), 7.19 (d, J = 0.9Hz, 1H), 7.32(q, J = 2.1 Hz, 2H), 7.48 (d, J = 1.5Hz, 1H), 7.62 (q, J = 2.1Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 34.16, 112.66, 116.71, 120.04, 122.20, 123.92, 124.03, 125.03, 131.43,

131.90, 132.48, 135.79, 139.34, 150.49, 155.59 ; IR (KBr) : 1624, 3017, 3242, 3412 cm^{-1}; **HRMS** calculated for $C_{16}H_{13}Cl_2N_2O$ $[M+H]^+$ 319.0405, found 319.0404.

2-(1-allyl-1H-benzo[d]imidazol-2-yl)-4-bromophenol (8e)



Yield : 86%; M.P. : 174-177, Reaction time: 1h; Solid; ^1H NMR (300 MHz, $CDCl_3$) : δ 3.50 (d, J = 6.4 Hz, 2H), 5.12 – 5.15 (m, 2H), 6.02 – 6.06 (m, 1H), 6.68 (q, J = 2.7Hz, 1H), 6.74-6.79 (m, 1H), 7.30 (q, J = 2.4Hz, 2H), 7.43 (d, J = 2.1 Hz, 1H), 7.62 (d, J = 1.8Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 34.10, 110.48, 112.88, 113.39, 113.45, 116.66, 117.92, 119.81, 125.17, 131.72, 131.91, 132.89, 134.52, 135.84, 150.53, 156.12; IR (KBr) : 1628, 3014, 3240, 3422 cm^{-1}; **HRMS** calculated for $C_{16}H_{14}BrN_2O$ $[M+H]^+$ 329.0290, found 329.0289.

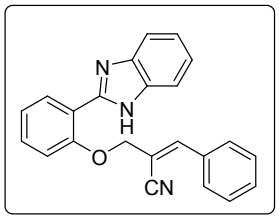
Typical experimental procedure for the synthesis of intermediates (5a)

A mixture of (*E*)-2-((2-Formylphenoxy)methyl)-3-phenylacrylonitrile (**1a**, 1mmol), and *o*-phenylenediamine (**4**, 1 mmol) was placed in a round bottom flask and melted at 160 ºC for 20 minutes. The crude reaction mass was purified by column chromatography on silica gel (100-200 mesh), using ethylacetate : hexanes (3.5 : 6.5) to afford intermediate **5a** as a yellow liquid.

Typical experimental procedure for the synthesis of intermediate (5b)

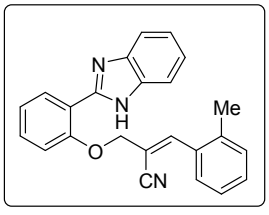
A mixture of (E)-2-((2-formylphenoxy)methyl)-3-(o-tolyl)acrylonitrile (**1b**, 1mmol), and *o*-phenylenediamine (**4**, 1 mmol) was placed in a round bottom flask and melted at 160 ºC for 20 minutes. The crude reaction mass was purified by column chromatography on silica gel (100-200 mesh), using ethylacetate : hexanes (5 : 5) to afford intermediate **5b** as a red liquid.

(E)-2-((2-(1H-benzo[d]imidazol-2-yl)phenoxy)methyl)-3-phenylacrylonitrile (Intermediate of 5a)



Reaction time : 20 min; liquid; ^1H NMR (400 MHz, $CDCl_3$) : δ 4.98 (s, 2H), 7.02 (d, J = 8.4 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.24-7.28 (m, 3H), 7.40 (q, J = 1.6 Hz, 1H), 7.46-7.49 (m, 3H), 7.67 (t, J = 2.4 Hz, 2H), 7.80-7.83 (m, 2H); 8.57(t, J = 1.6 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) : δ70.54, 105.79, 112.65, 118.17, 118.74, 122.94, 123.02, 129.29, 129.42, 131.00, 131.37, 131.70, 132.32, 146.85, 149.04, 154.87. **HRMS** calculated for $C_{23}H_{17}N_3O$ $[M+H]^+$ 352.1451, found 352.1445.

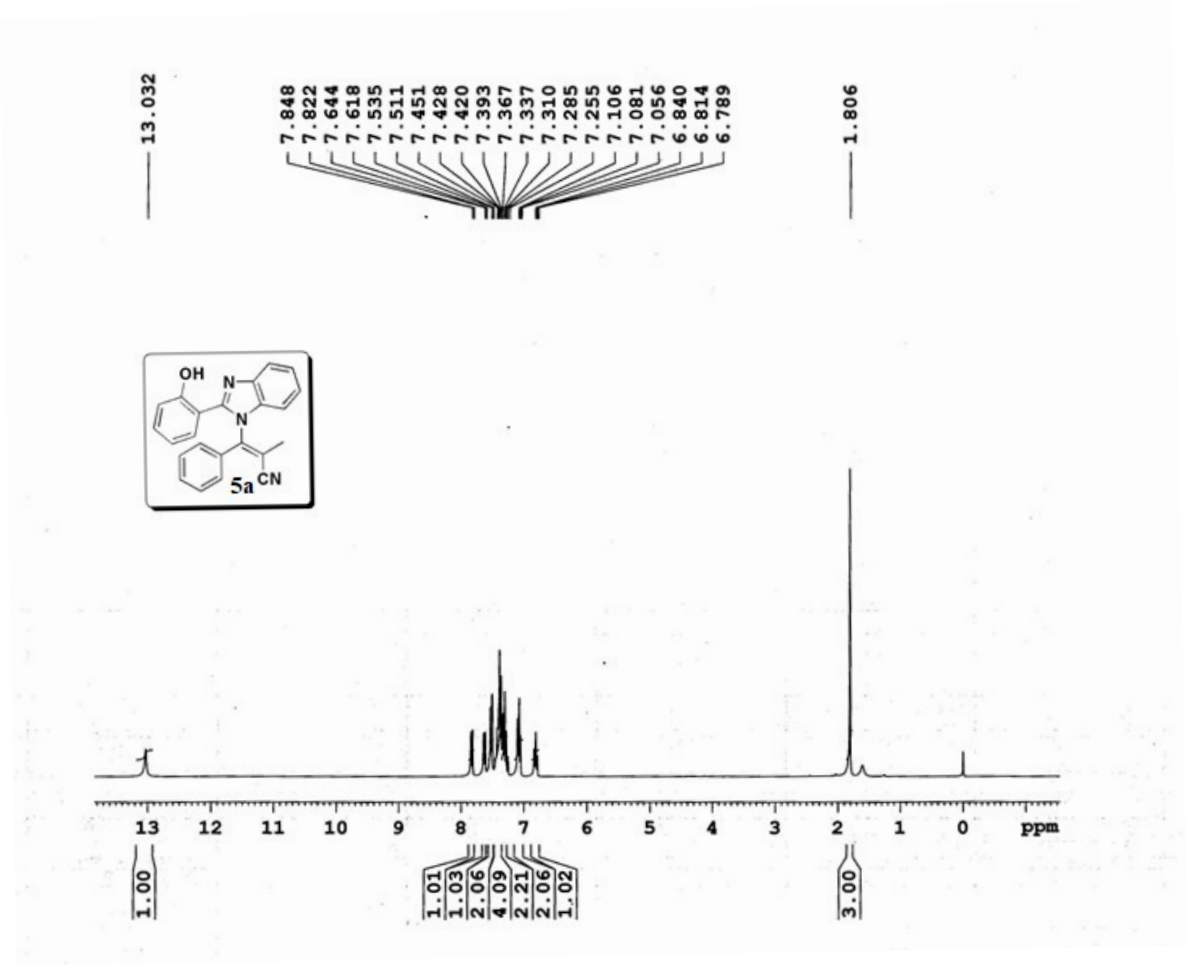
(E)-2-((2-(1H-benzo[d]imidazol-2-yl)phenoxy)methyl)-3-phenylacrylonitrile (Intermediate of 5b)

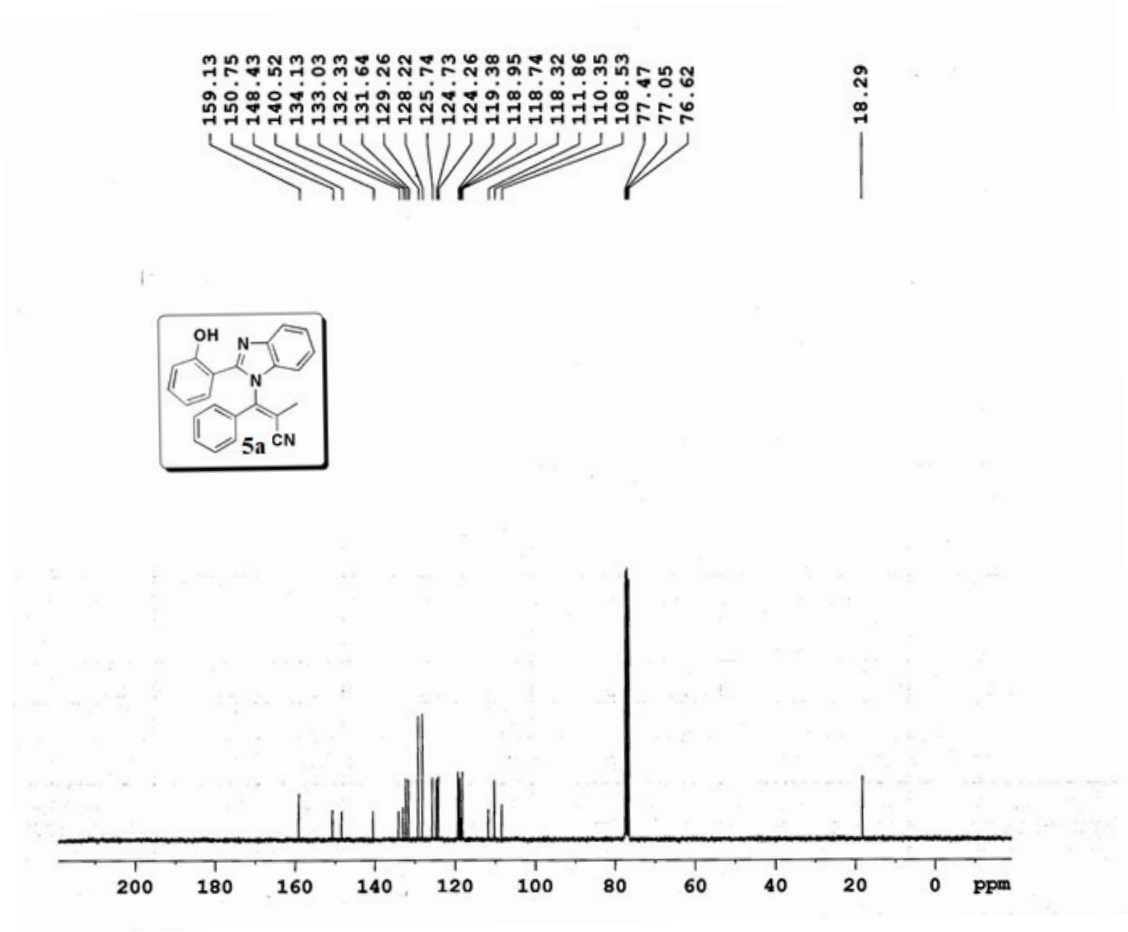


Reaction time : 20 min; liquid; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.29 (s, 3H), 4.99 (s, 2H), 7.02 (d, J = 8.4 Hz,1H), 7.18-7.25 (m, 4H), 7.30-7.51 (m, 4H), 7.40 (q, J = 1.6 Hz, 1H), 7.67 (s, 2H), 7.92 (d, J = 7.6 Hz, 1H), 8.58 (q, J = 1.6Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : 19.84, 70.18, 107.89, 112.66, 117.97, 118.90, 122.85, 122.99, 126.71, 128.01, 130.86, 131.00, 131.25, 131.60, 137.65, 145.56, 149.05, 154.76.

HRMS calculated for $C_{24}H_{19}N_3O$ $[M+H]^+$ 366.1607, found 366.1601.

^{1}H, ^{13}C NMR and Mass spectra for compounds **5a-q**

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140.52
134.13
133.03
132.33
131.64
129.26
128.22
125.74
124.73
124.26
119.38
118.95
118.74
118.32
111.86
110.35
108.53
77.47
77.05
76.62
18.29
OH
N
N
CN
5a
200
180
160
140
120
100
80
60
40
20
0
ppm

Sample Name	PVKT-17	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
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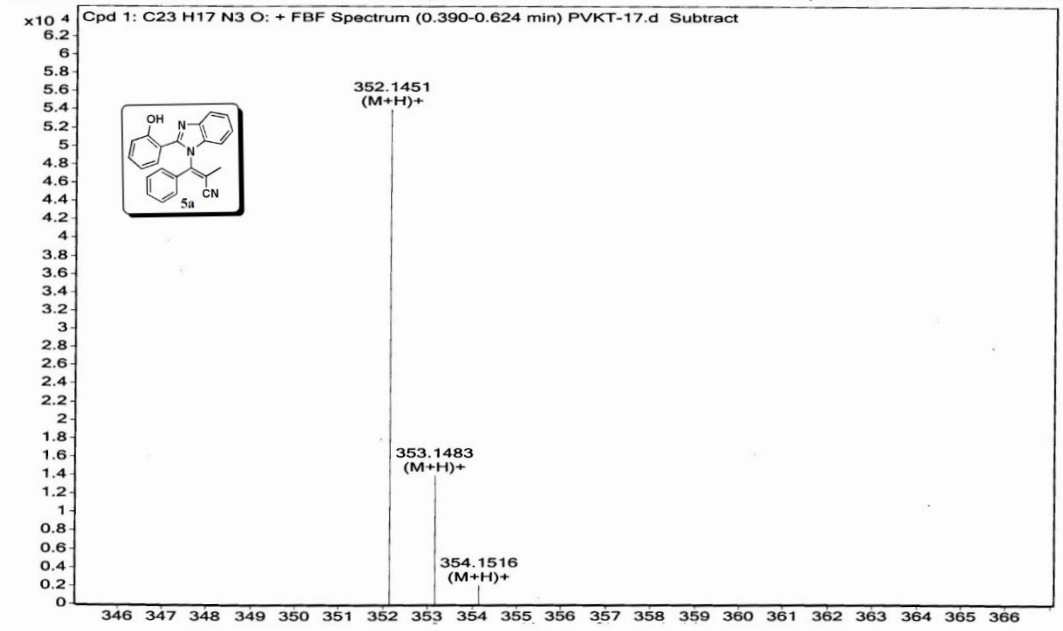

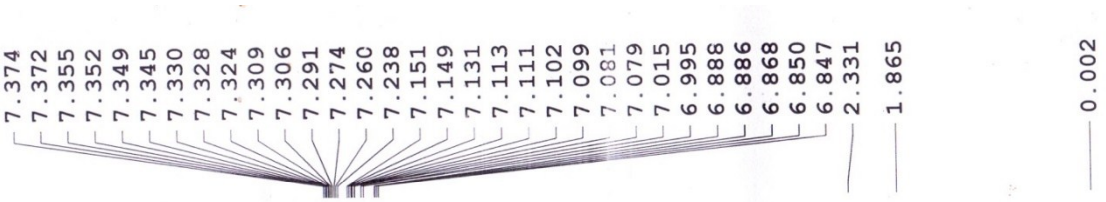
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7.372
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7.345
7.330
7.328
7.324
7.309
7.306
7.291
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7.260
7.238
7.151
7.149
7.131
7.113
7.111
7.102
7.099
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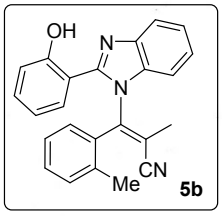
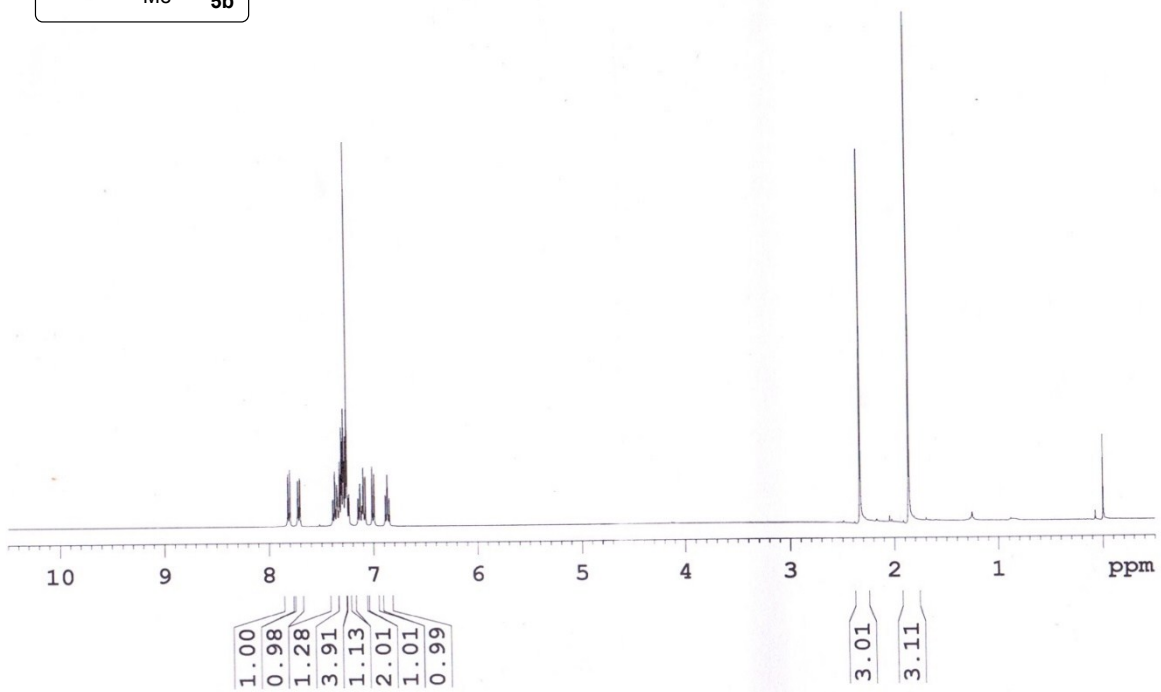
6.850
6.847
2.331
1.865
0.002


OH
N
N
Me
CN
5b


10
9
8
7
6
5
4
3
2
1
ppm
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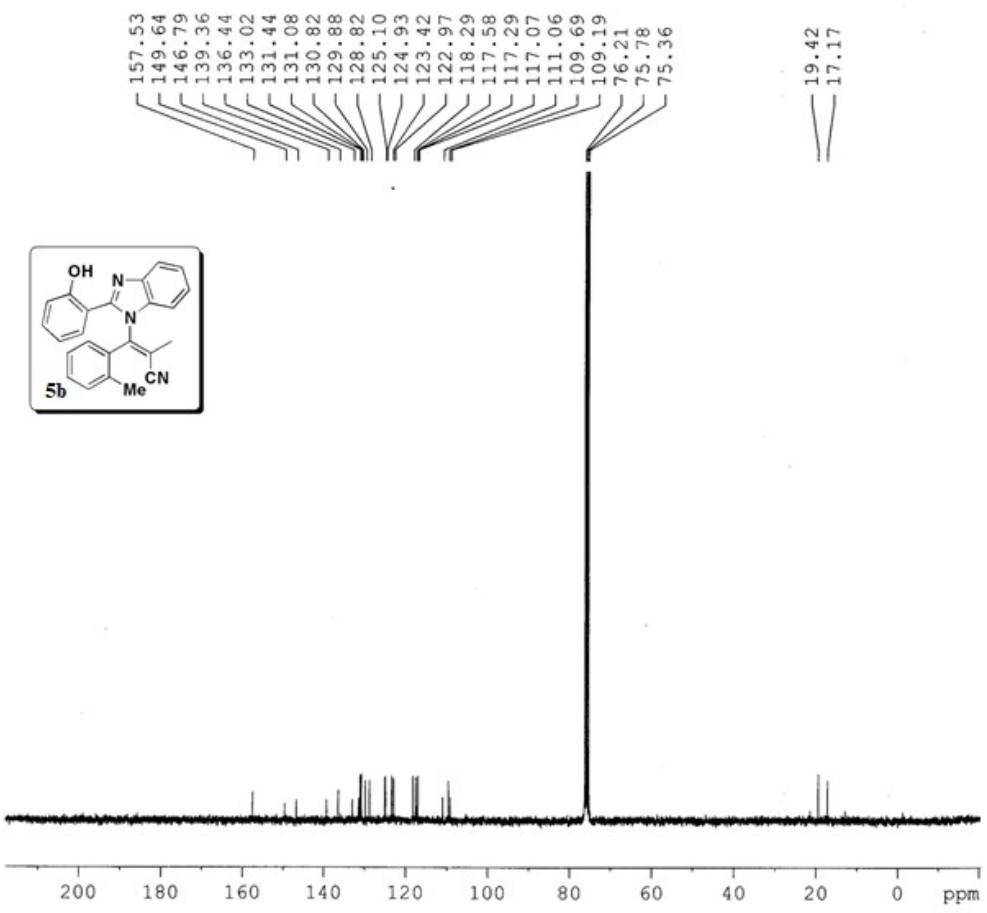
1.28
3.91
1.13
2.01
1.01
0.99
3.01
3.11


157.53
149.64
146.79
139.36
136.44
133.02
131.44
131.08
130.82
129.88
128.82
125.10
124.93
123.42
122.97
118.29
117.58
117.29
117.07
111.06
109.69
109.19
76.21
75.78
75.36
19.42
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Me
5b
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0
ppm

Sample Name	PVKT-8	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
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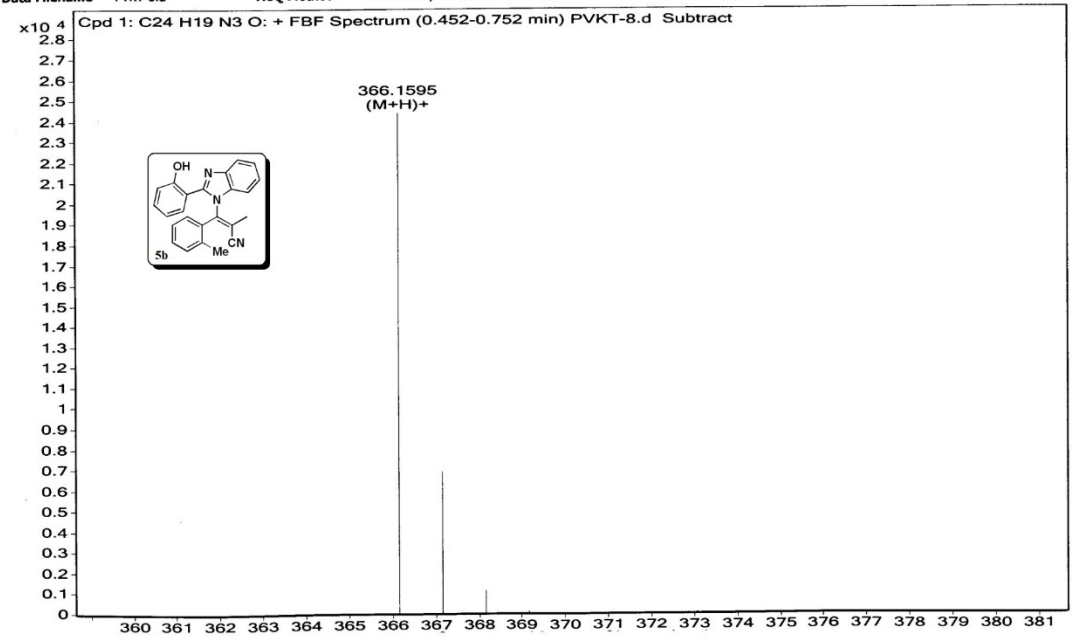

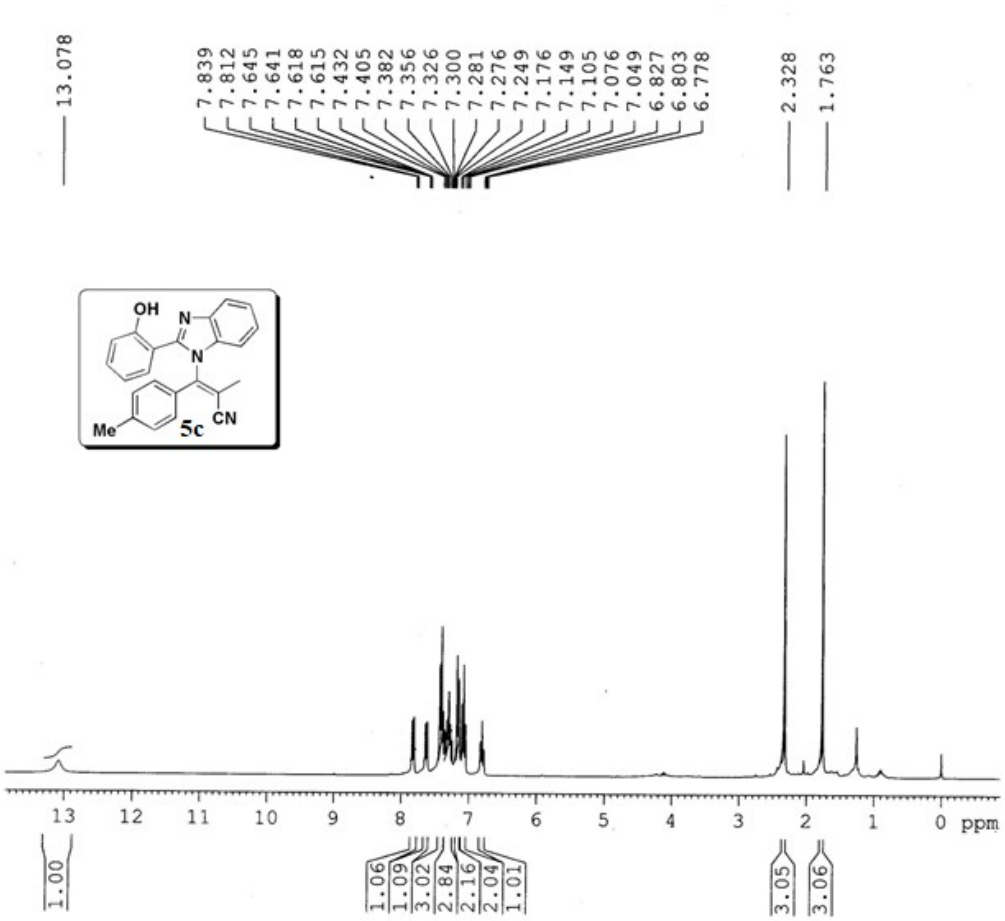
13.078
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7.645
7.641
7.618
7.615
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7.356
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7.249
7.176
7.149
7.105
7.076
7.049
6.827
6.803
6.778
2.328
1.763
OH
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N
Me
CN
5c
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12
11
10
9
8
7
6
5
4
3
2
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1.09
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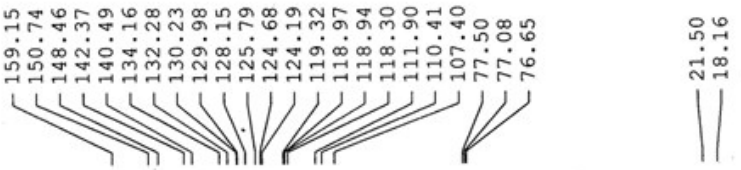
2.16
2.04
1.01
3.05
3.06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132.28
130.23
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125.79
124.68
124.19
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118.94
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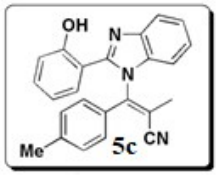
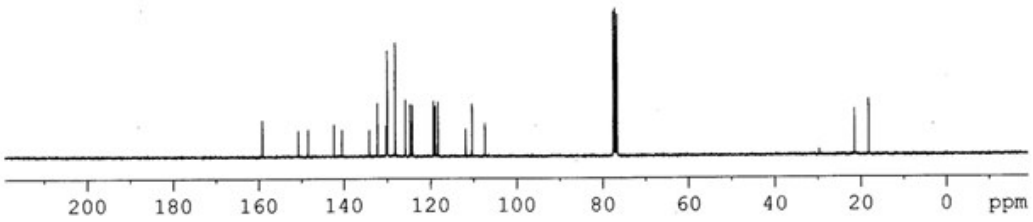
111.90
110.41
107.40
77.50
77.08
76.65
21.50
18.16


OH
N
N
Me
5c
CN


200
180
160
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120
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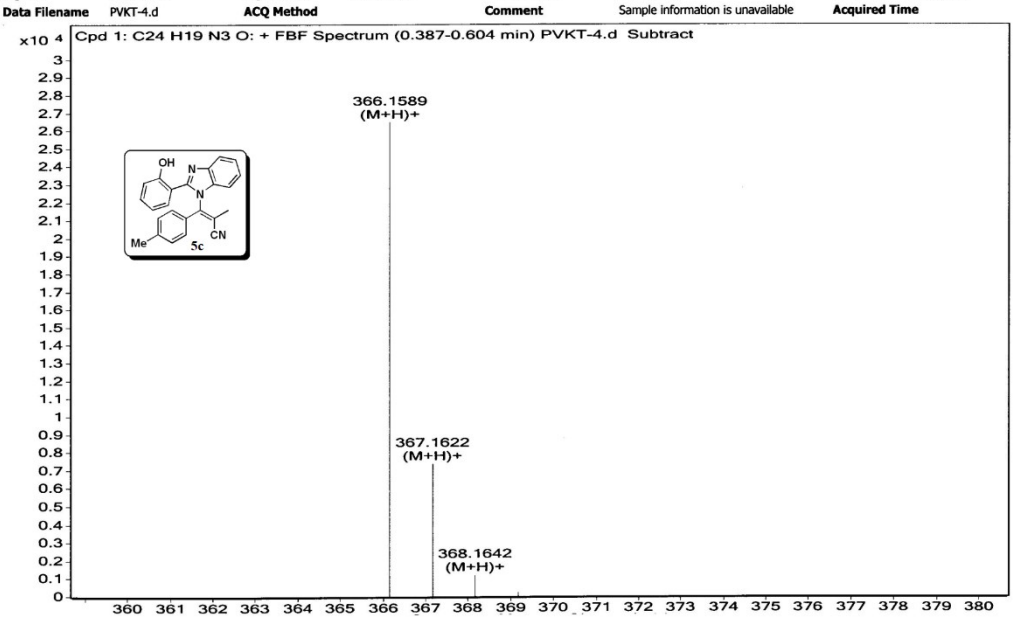
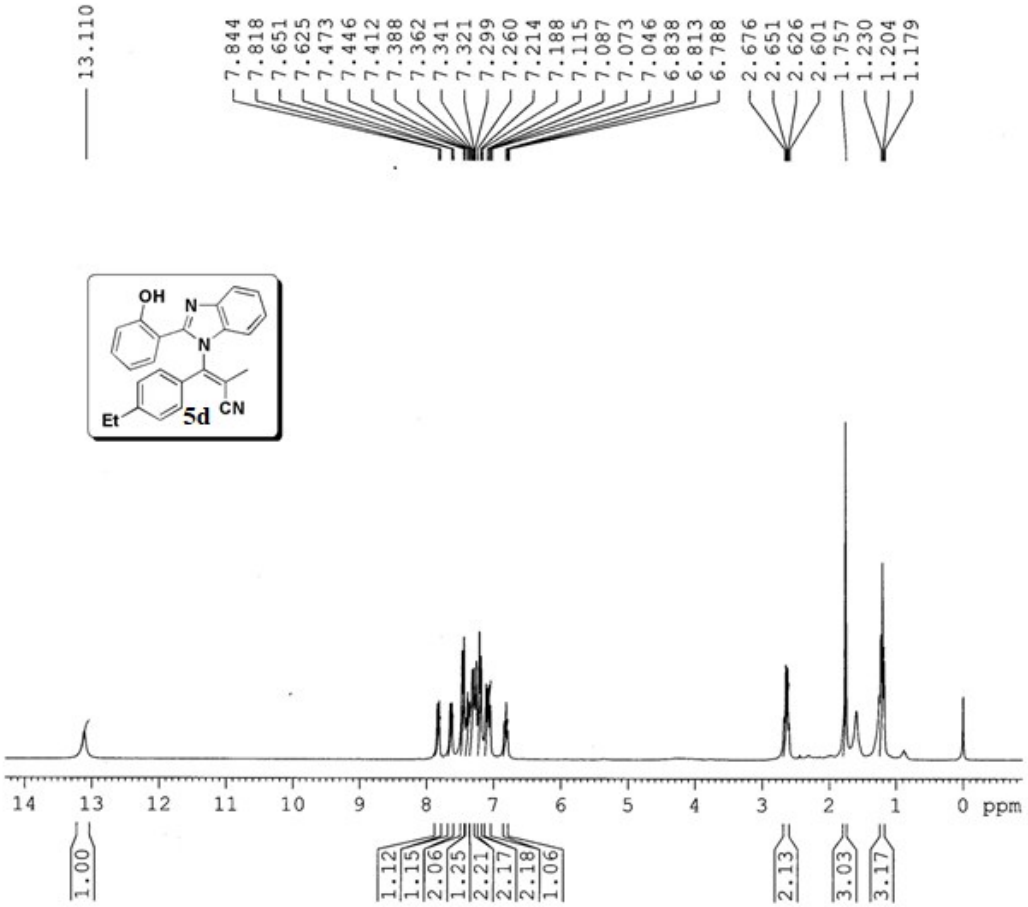
80
60
40
20
0
ppm

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Success
Data Filename	PVKT-4.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable




13.110
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7.188
7.115
7.087
7.073
7.046
6.838
6.813
6.788
2.676
2.651
2.626
2.601
1.757
1.230
1.204
1.179
OH
N
N
Et
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CN
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13
12
11
10
9
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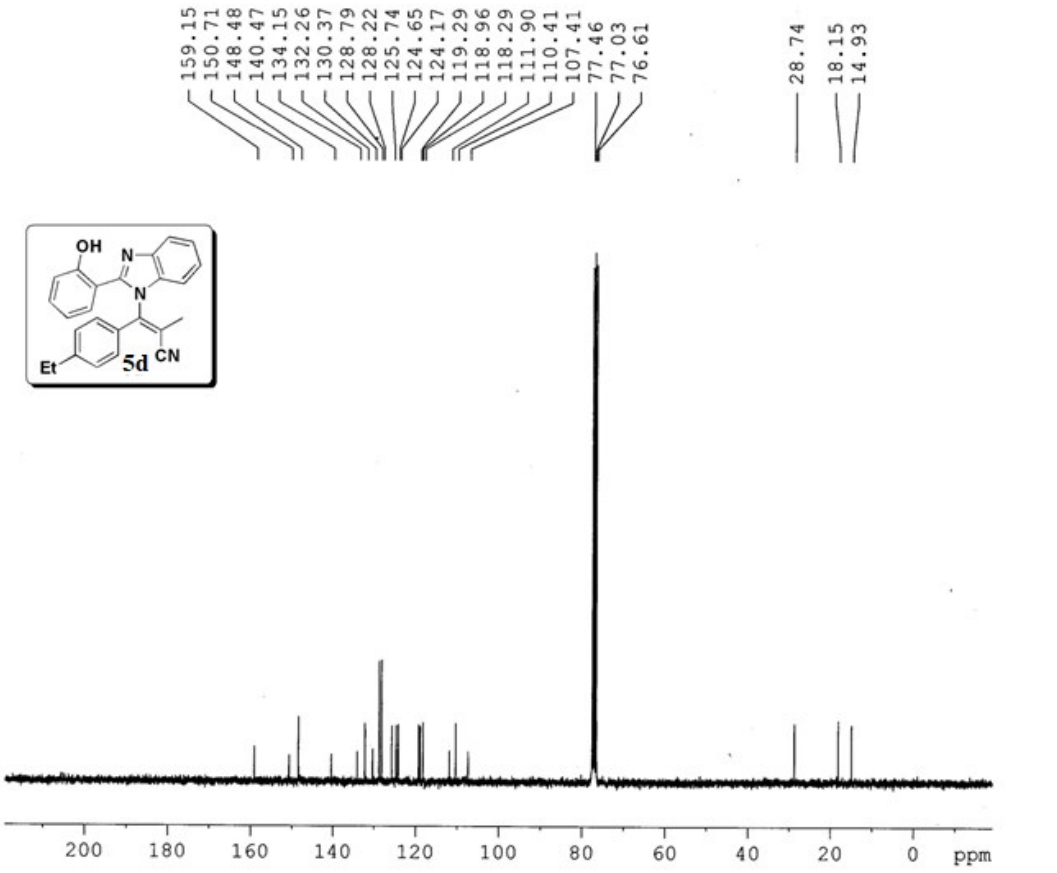
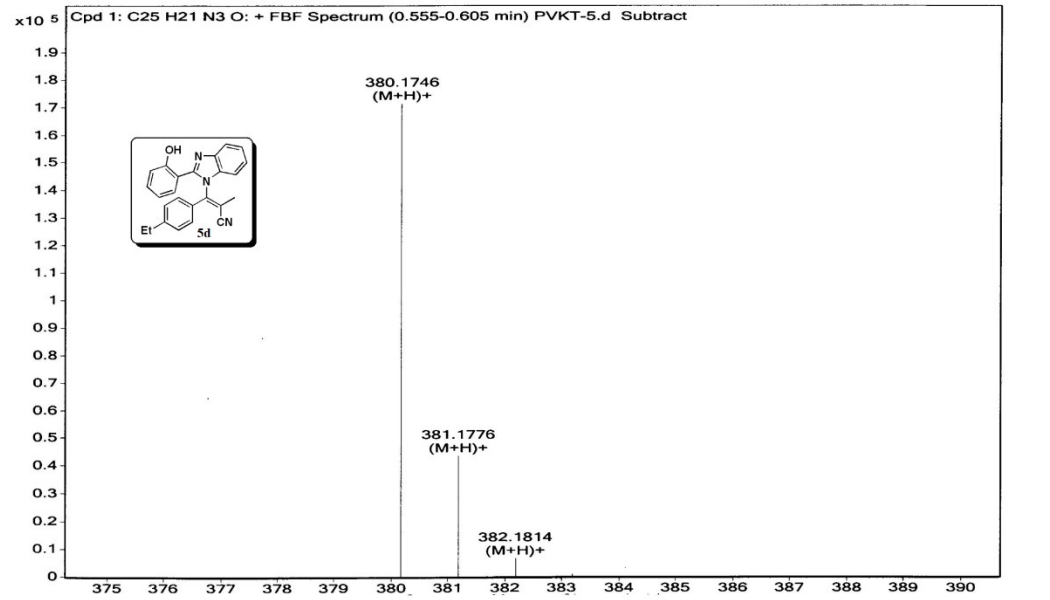
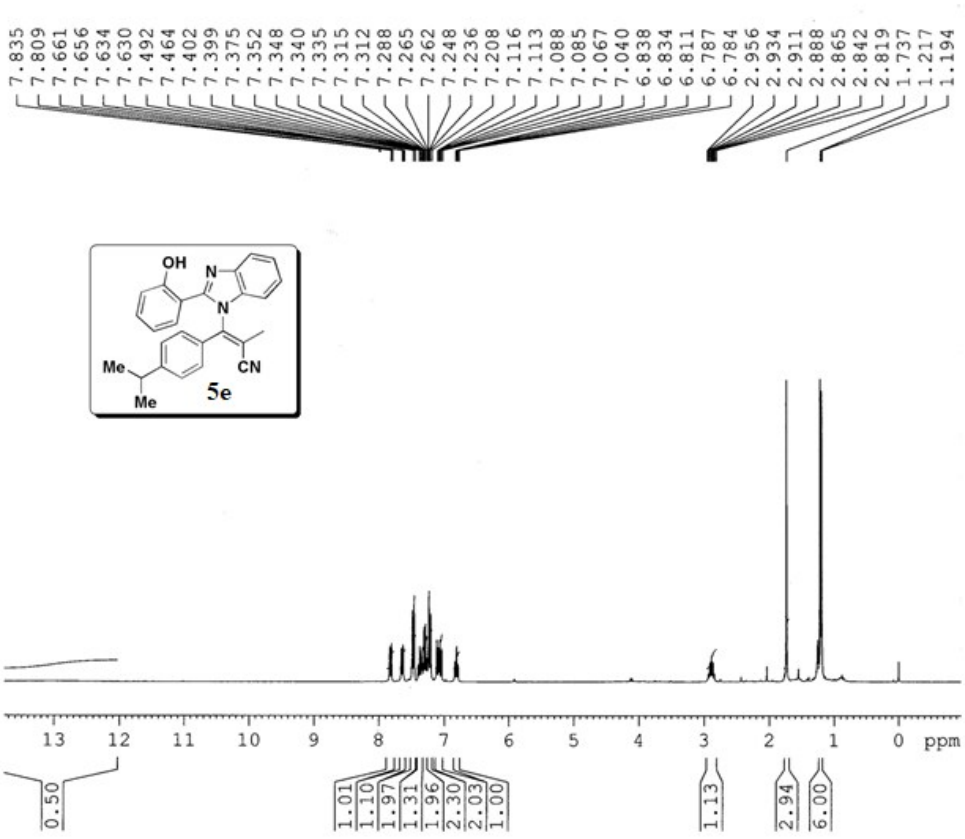
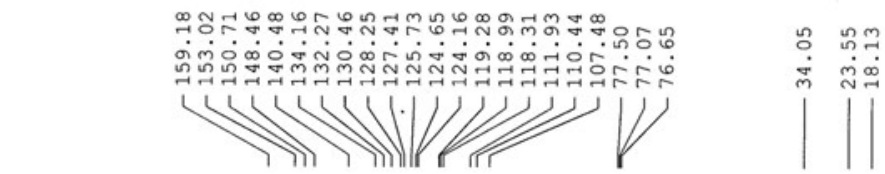
7
6
5
4
3
2
1
0 ppm
1.00
1.12
1.15
2.06
1.25
2.21
2.17
2.18
1.06
2.13
3.03
3.17

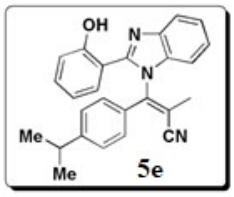


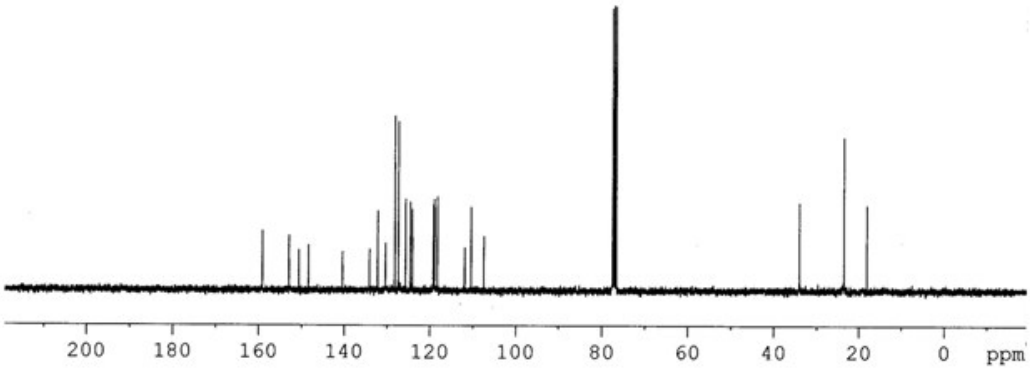
Sample Name	PVKT-5	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-5.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-379.1685	**Acquired Time**	13-02-2015 14:44:19



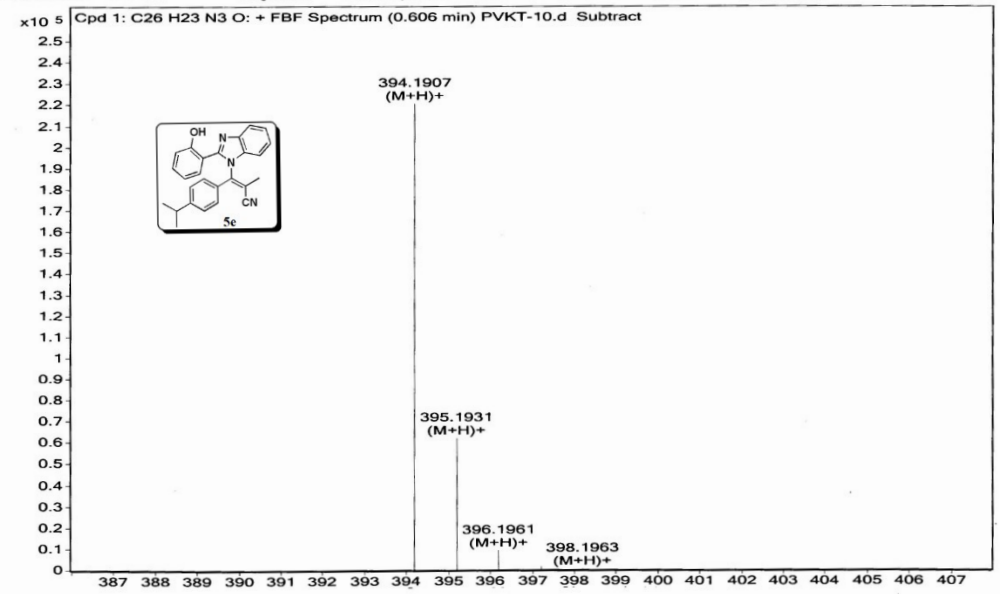

7.835
7.809
7.661
7.656
7.634
7.630
7.492
7.464
7.402
7.399
7.375
7.352
7.348
7.340
7.335
7.315
7.312
7.288
7.265
7.262
7.248
7.236
7.208
7.116
7.113
7.088
7.085
7.067
7.040
6.838
6.834
6.811
6.787
6.784
2.956
2.934
2.911
2.888
2.865
2.842
2.819
1.737
1.217
1.194
OH
N
N
Me
Me
CN
5e
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.50
1.01
1.10
1.97
1.31
1.96
2.30
2.03
1.00
1.13
2.94
6.00

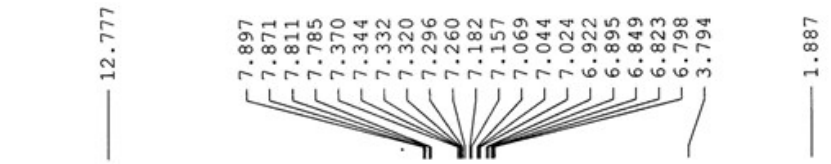

159.18
153.02
150.71
148.46
140.48
134.16
132.27
130.46
128.25
127.41
125.73
124.65
124.16
119.28
118.99
118.31
111.93
110.44
107.48
77.50
77.07
76.65
34.05
23.55
18.13

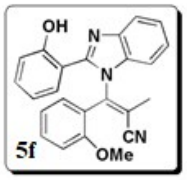

OH
N
N
Me
Me
CN
5e

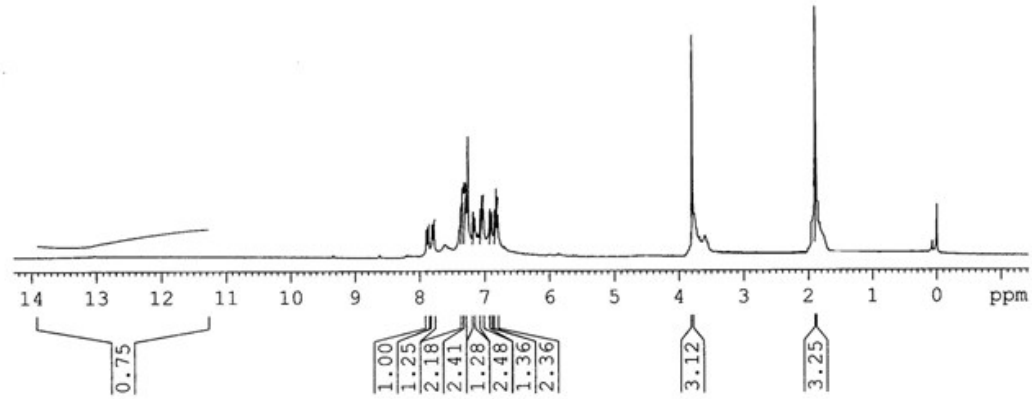

200
180
160
140
120
100
80
60
40
20
0
ppm

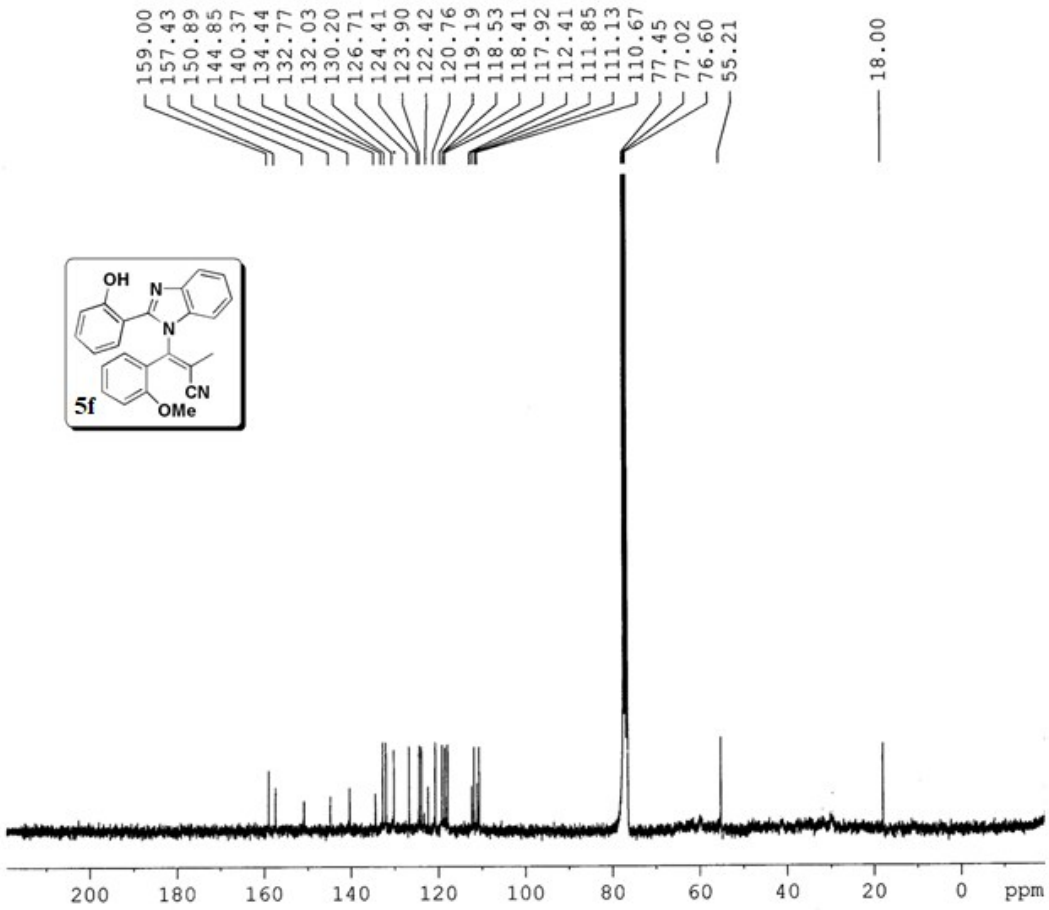
Sample Name	PVKT-10	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-10.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-393.1841	**Acquired Time**	13-02-2015 14:30:55



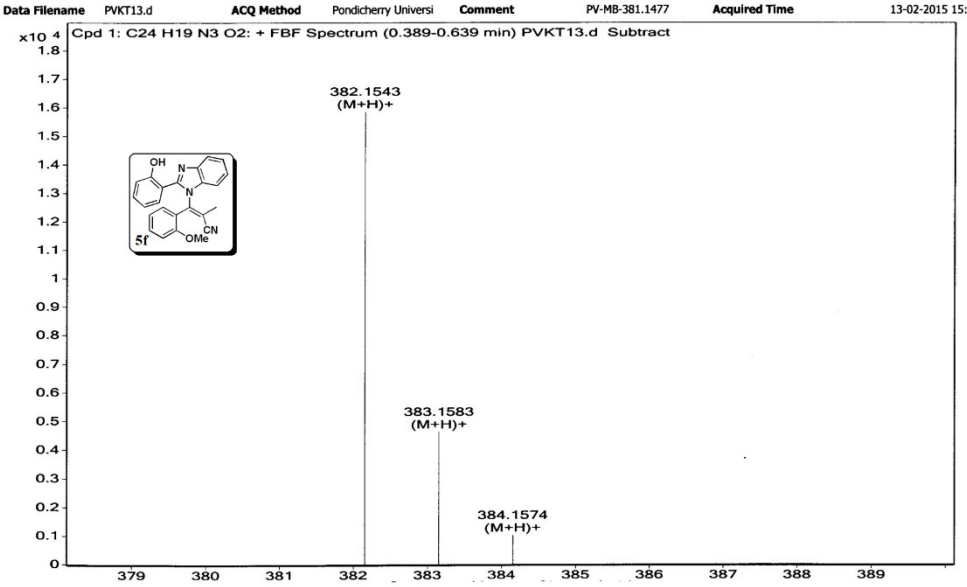

12.777
7.897
7.871
7.811
7.785
7.370
7.344
7.332
7.320
7.296
7.260
7.182
7.157
7.069
7.044
7.024
6.922
6.895
6.849
6.823
6.798
3.794
1.887

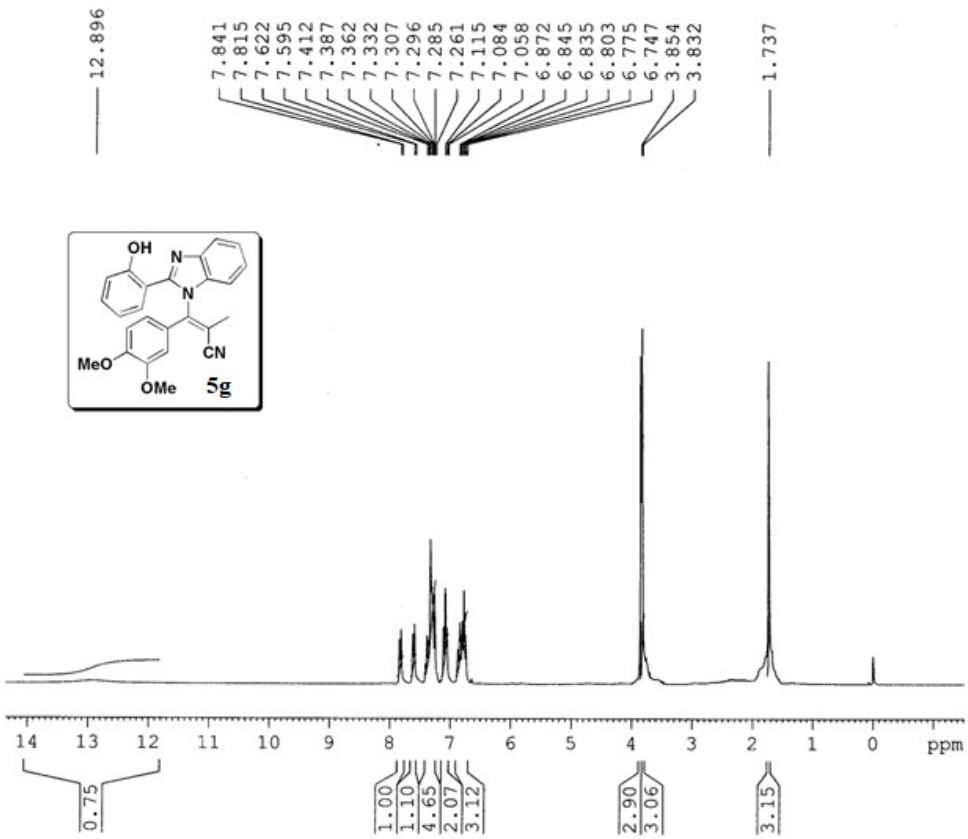

OH
N
N
CN
OMe
5f

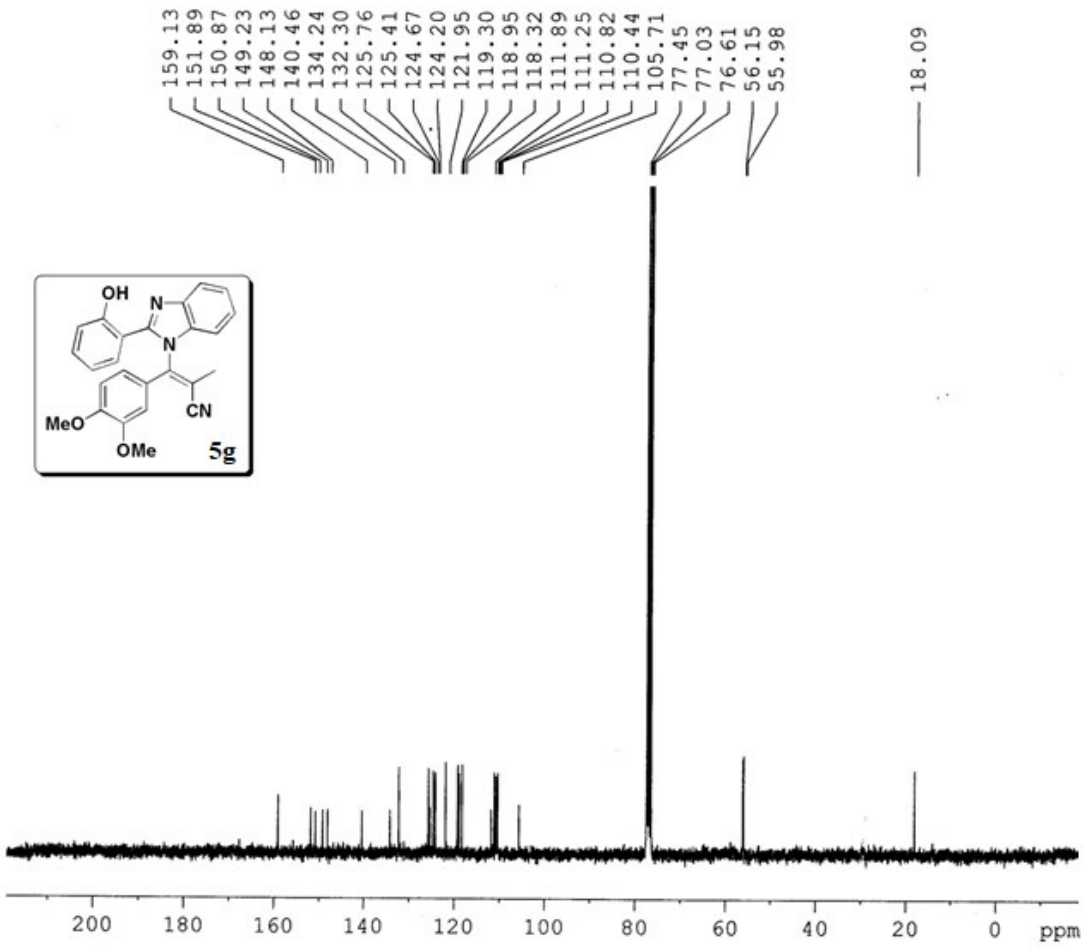

14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.75
1.00
1.25
2.18
2.41
1.28
2.48
1.36
2.36
3.12
3.25



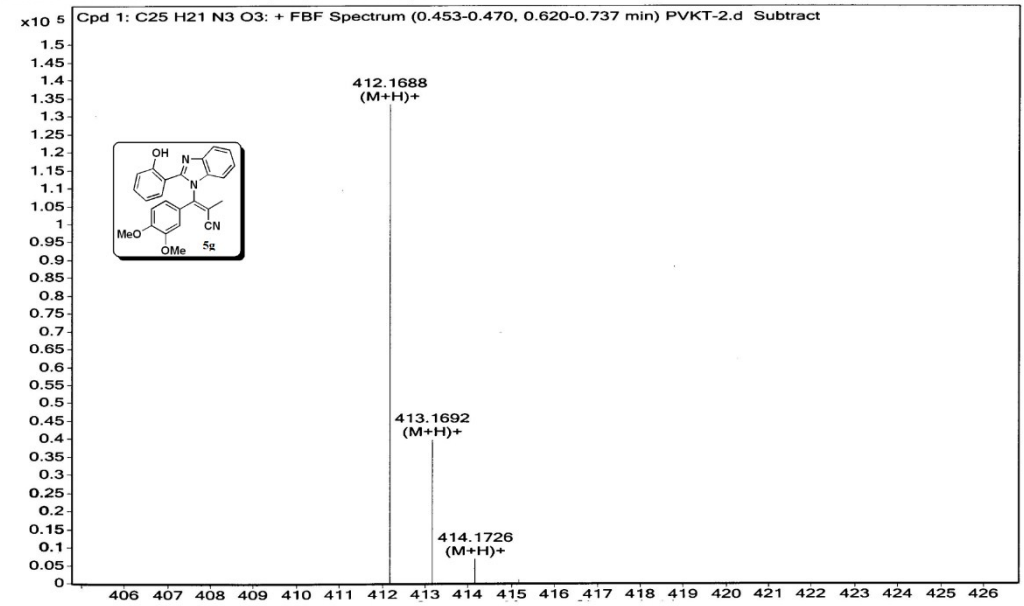
Sample Name	PVKT-13	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT13.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-381.1477	**Acquired Time**	13-02-2015 15:07:25

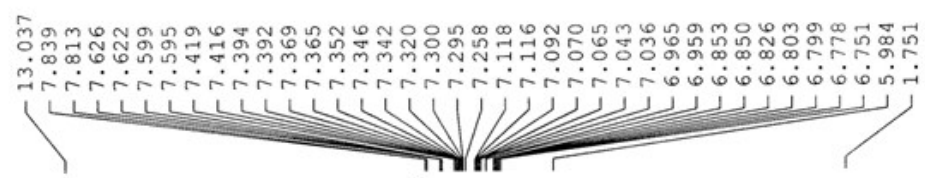


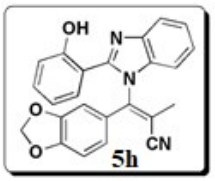

12.896
7.841
7.815
7.622
7.595
7.412
7.387
7.362
7.332
7.307
7.296
7.285
7.261
7.115
7.084
7.058
6.872
6.845
6.835
6.803
6.775
6.747
3.854
3.832
1.737
OH
N
N
CN
MeO
OMe
5g
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.75
1.00
1.10
4.65
2.07
3.12
2.90
3.06
3.15

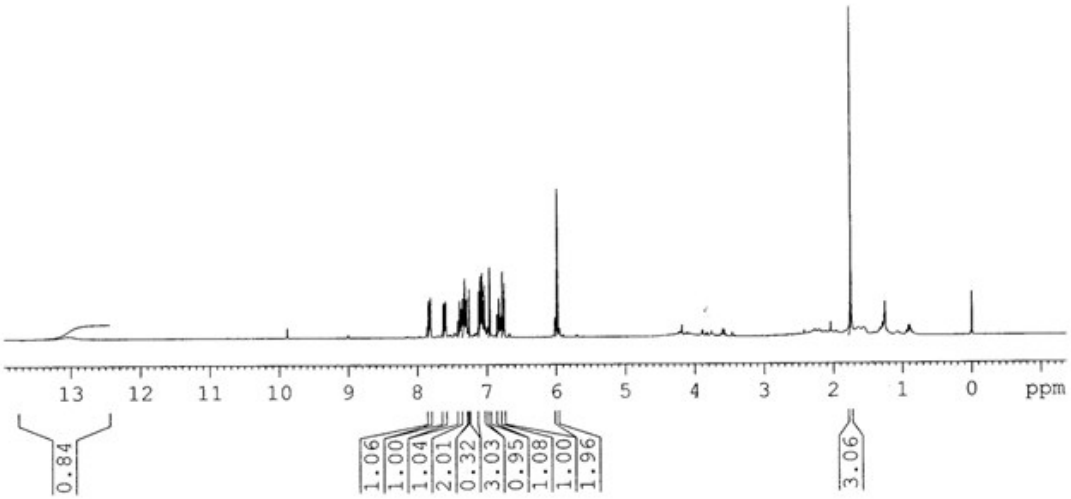

159.13
151.89
150.87
149.23
148.13
140.46
134.24
132.30
125.76
125.41
124.67
124.20
121.95
119.30
118.95
118.32
111.89
111.25
110.82
110.44
105.71
77.45
77.03
76.61
56.15
55.98
18.09
OH
N
N
CN
MeO
OMe
5g
200
180
160
140
120
100
80
60
40
20
0
ppm

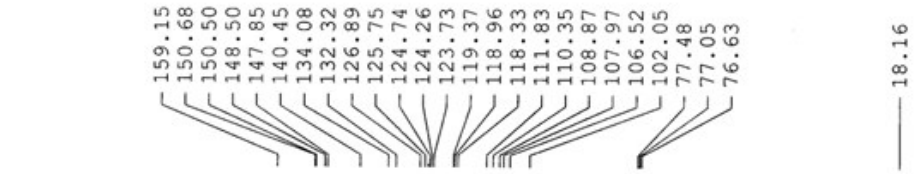
Sample Name	PVKT-2	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-2.d	**ACQ Method**	Pondicherry Universi	**Comment**	MS-MB-411.1583	**Acquired Time**	20-03-2015 11:34:32

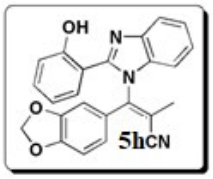


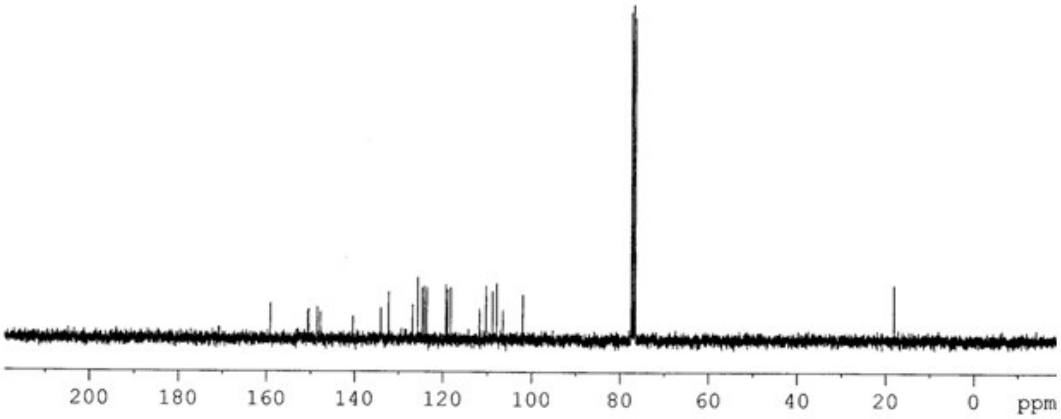

13.037
7.839
7.813
7.626
7.622
7.599
7.595
7.419
7.416
7.394
7.392
7.369
7.365
7.352
7.346
7.342
7.320
7.300
7.295
7.258
7.118
7.116
7.092
7.070
7.065
7.043
7.036
6.965
6.959
6.853
6.850
6.826
6.803
6.799
6.778
6.751
5.984
1.751


OH
N
N
O
O
CN
5h

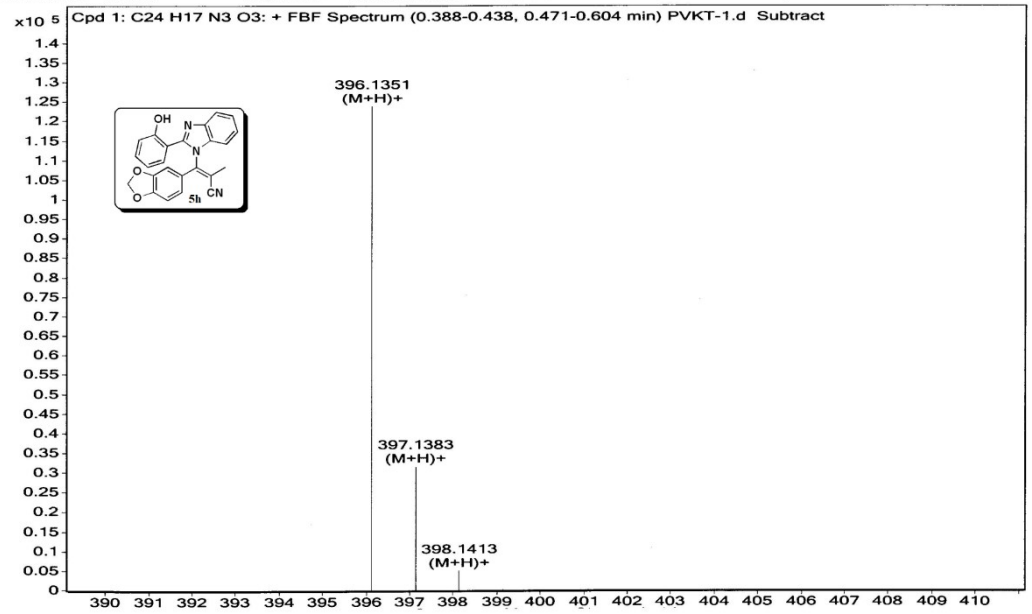

13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.84
1.06
1.00
1.04
2.01
0.32
3.03
0.95
1.08
1.00
1.96
3.06

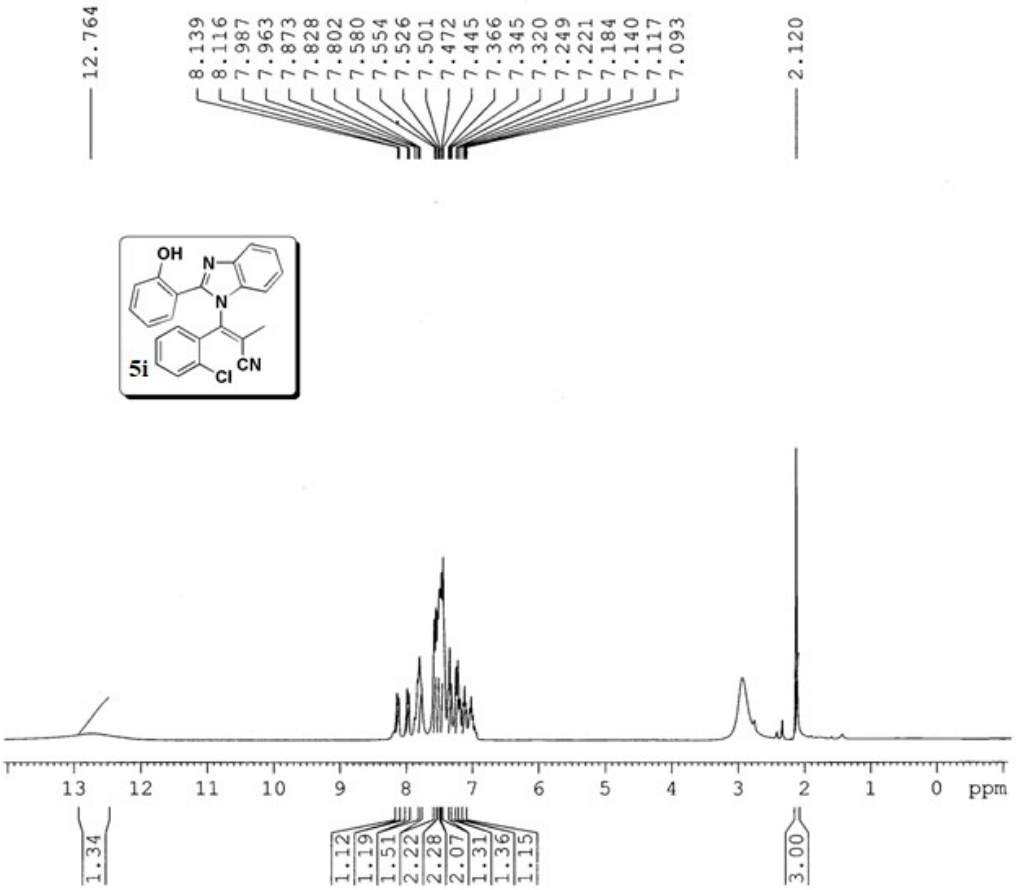

159.15
150.68
150.50
148.50
147.85
140.45
134.08
132.32
126.89
125.75
124.74
124.26
123.73
119.37
118.96
118.33
111.83
110.35
108.87
107.97
106.52
102.05
77.48
77.05
76.63
18.16

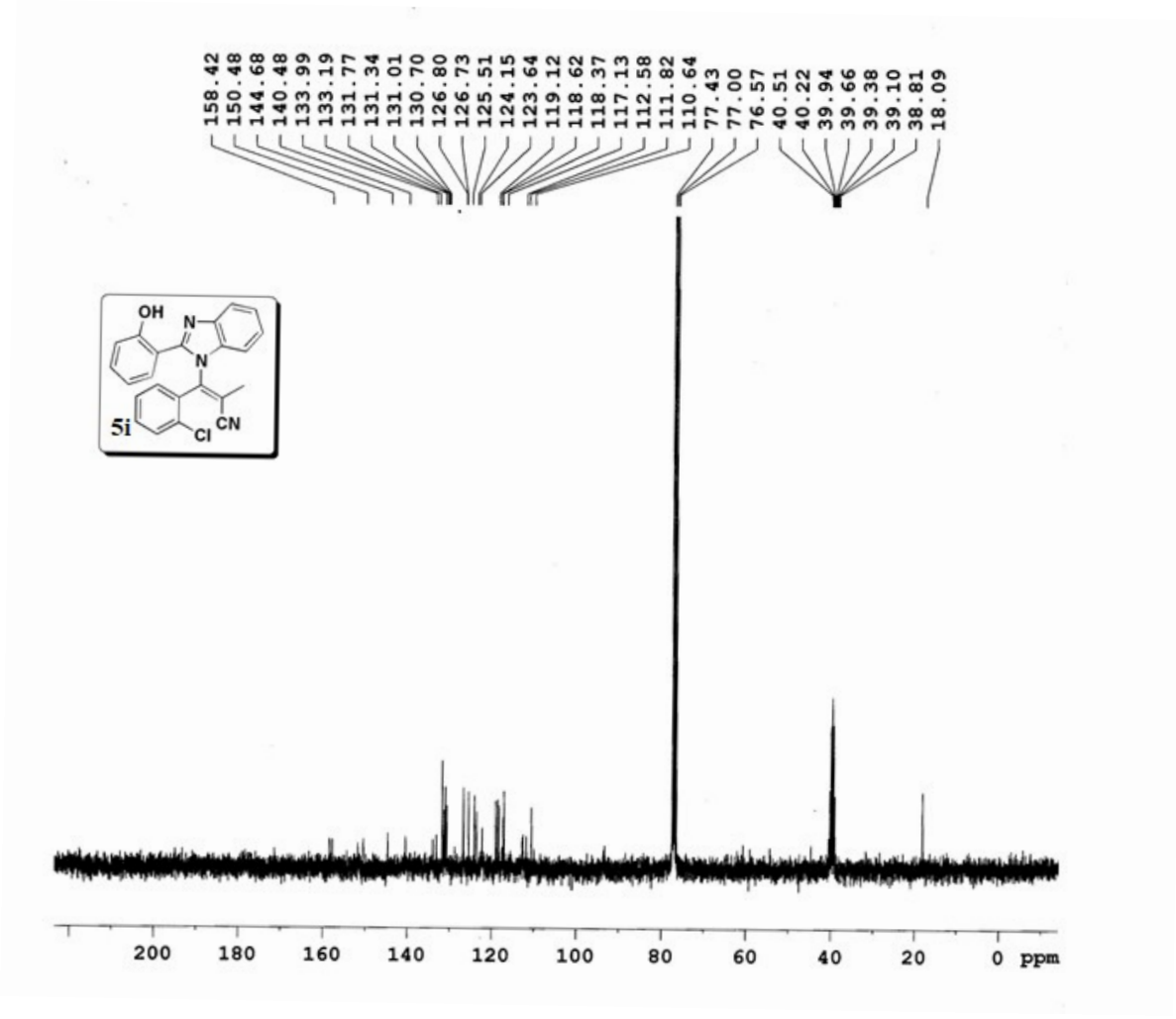

OH
N
N
O
O
5hCN


200
180
160
140
120
100
80
60
40
20
0
ppm

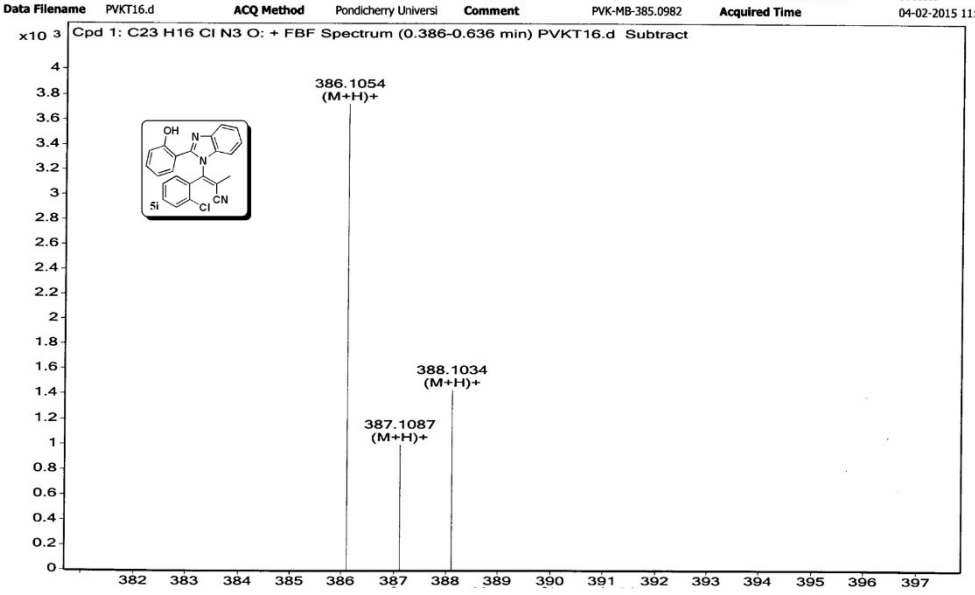
Sample Name	PVKT-1	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-1.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-395.1270	**Acquired Time**	09-02-2015 12:28:03

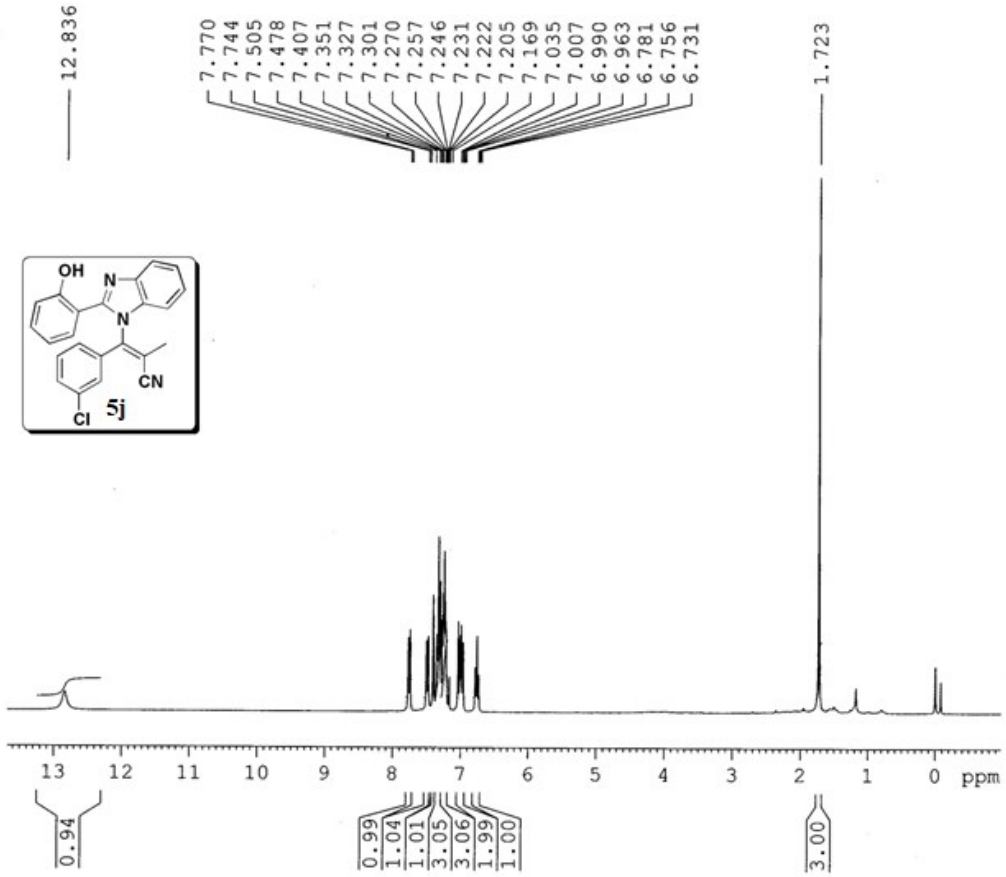


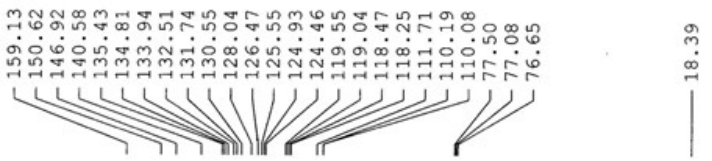

12.764
8.139
8.116
7.987
7.963
7.873
7.828
7.802
7.580
7.554
7.526
7.501
7.472
7.445
7.366
7.345
7.320
7.249
7.221
7.184
7.140
7.117
7.093
2.120
OH
N
N
CN
Cl
5i
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.34
1.12
1.19
1.51
2.22
2.28
2.07
1.31
1.36
1.15
3.00

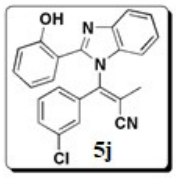


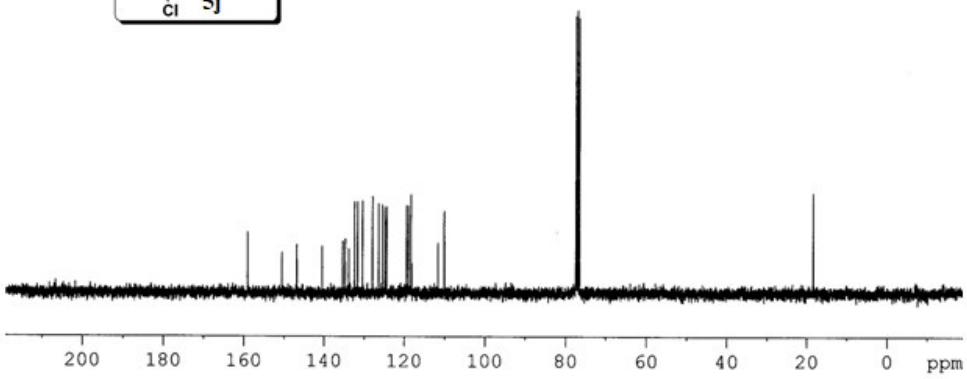
Sample Name	PVKT16	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT16.d	**ACQ Method**	Pondicherry Universi	**Comment**	PVK-MB-385.0982	**Acquired Time**	04-02-2015 11:23:14



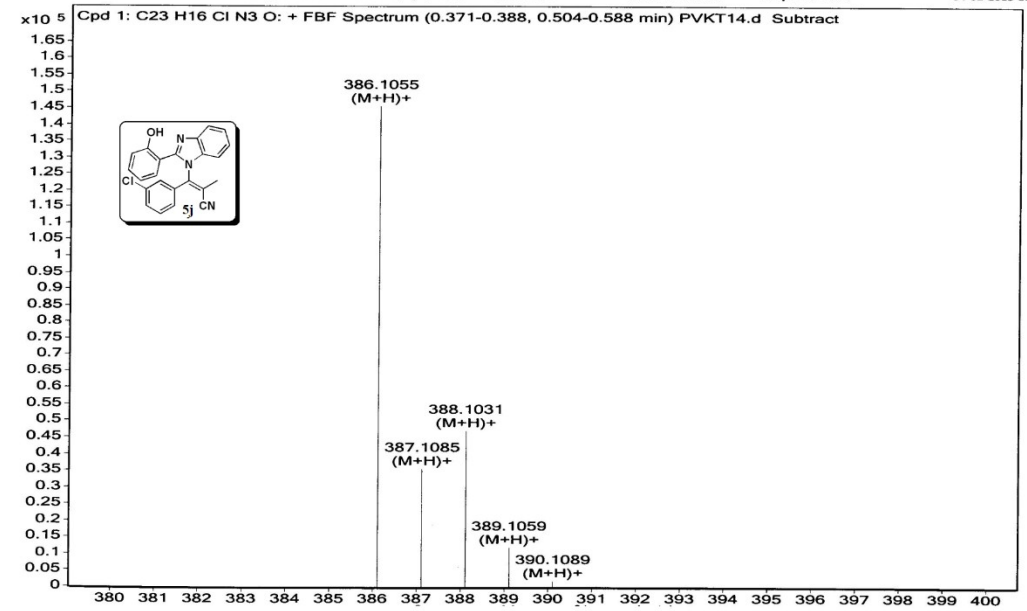

12.836
7.770
7.744
7.505
7.478
7.407
7.351
7.327
7.301
7.270
7.257
7.246
7.231
7.222
7.205
7.169
7.035
7.007
6.990
6.963
6.781
6.756
6.731
1.723
OH
N
N
CN
Cl
5j
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
0.99
1.04
1.01
3.05
3.06
1.99
1.00
3.00

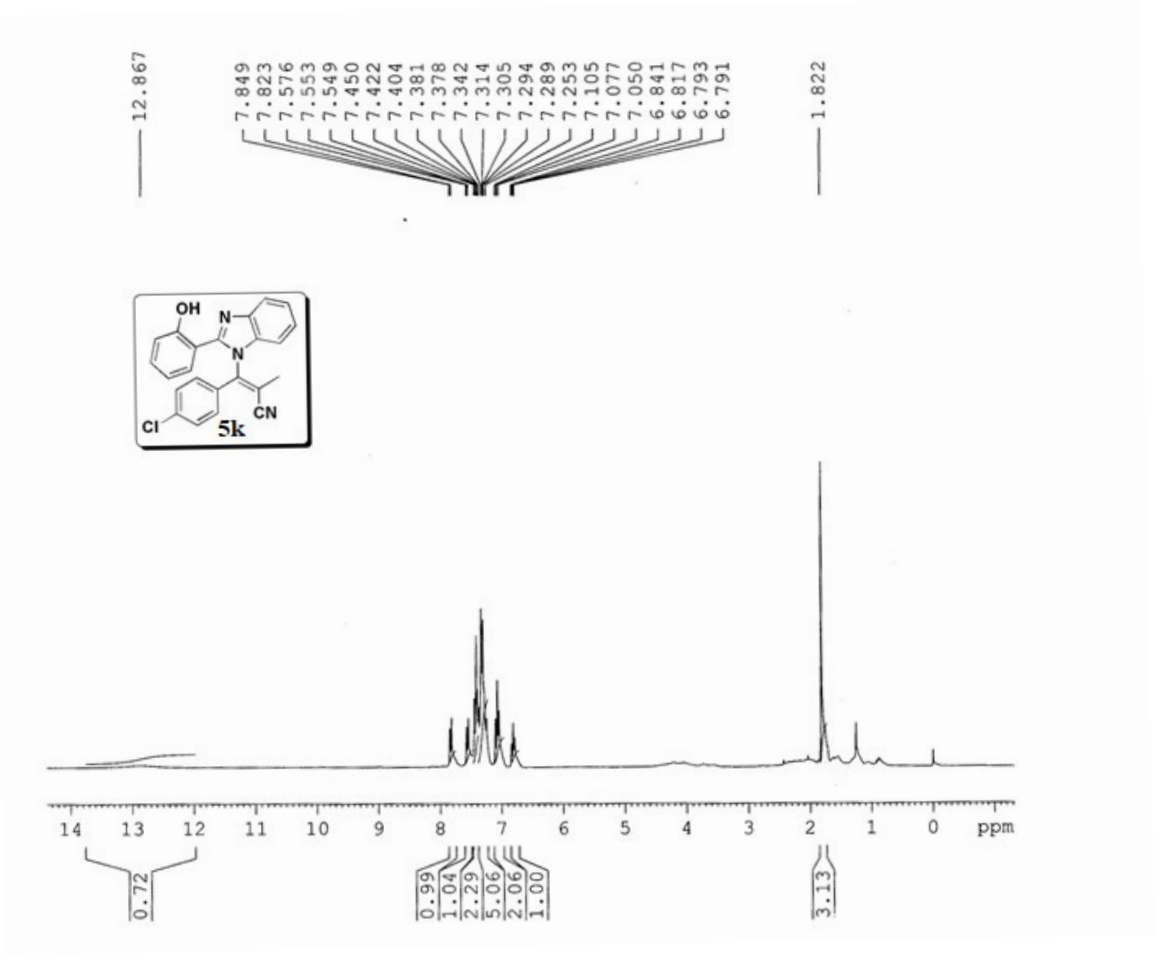


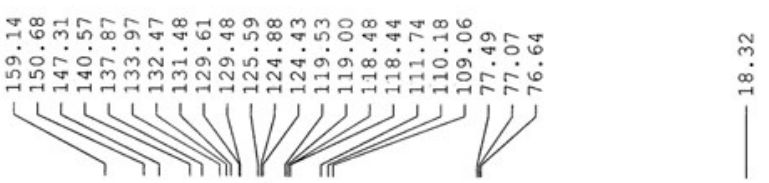


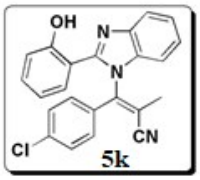


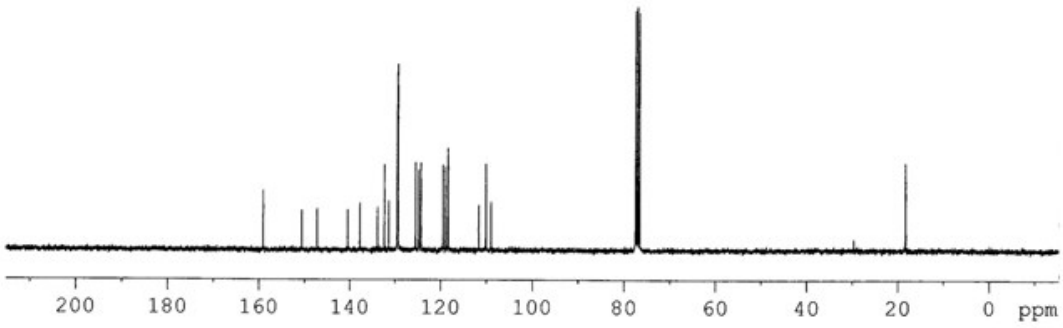
Sample Name	PVKT14	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT14.d	**ACQ Method**	Pondicherry Universi	**Comment**	PVK-MB-385.0982	**Acquired Time**	04-02-2015 11:26:22



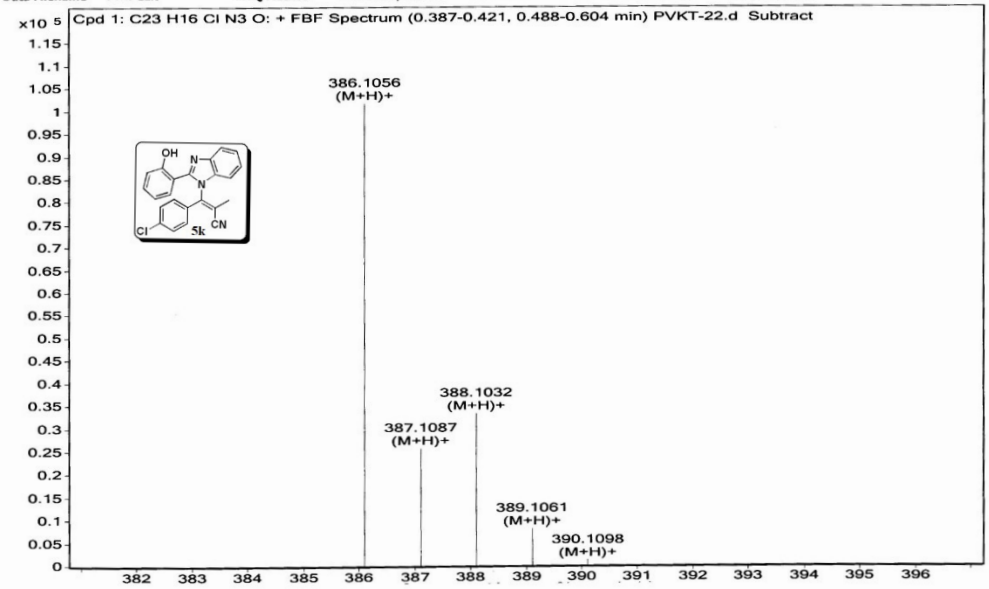

12.867
7.849
7.823
7.576
7.553
7.549
7.450
7.422
7.404
7.381
7.378
7.342
7.314
7.305
7.294
7.289
7.253
7.105
7.077
7.050
6.841
6.817
6.793
6.791
1.822
OH
N
N
CN
Cl
5k
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.72
0.99
1.04
2.29
5.06
2.06
1.00
3.13

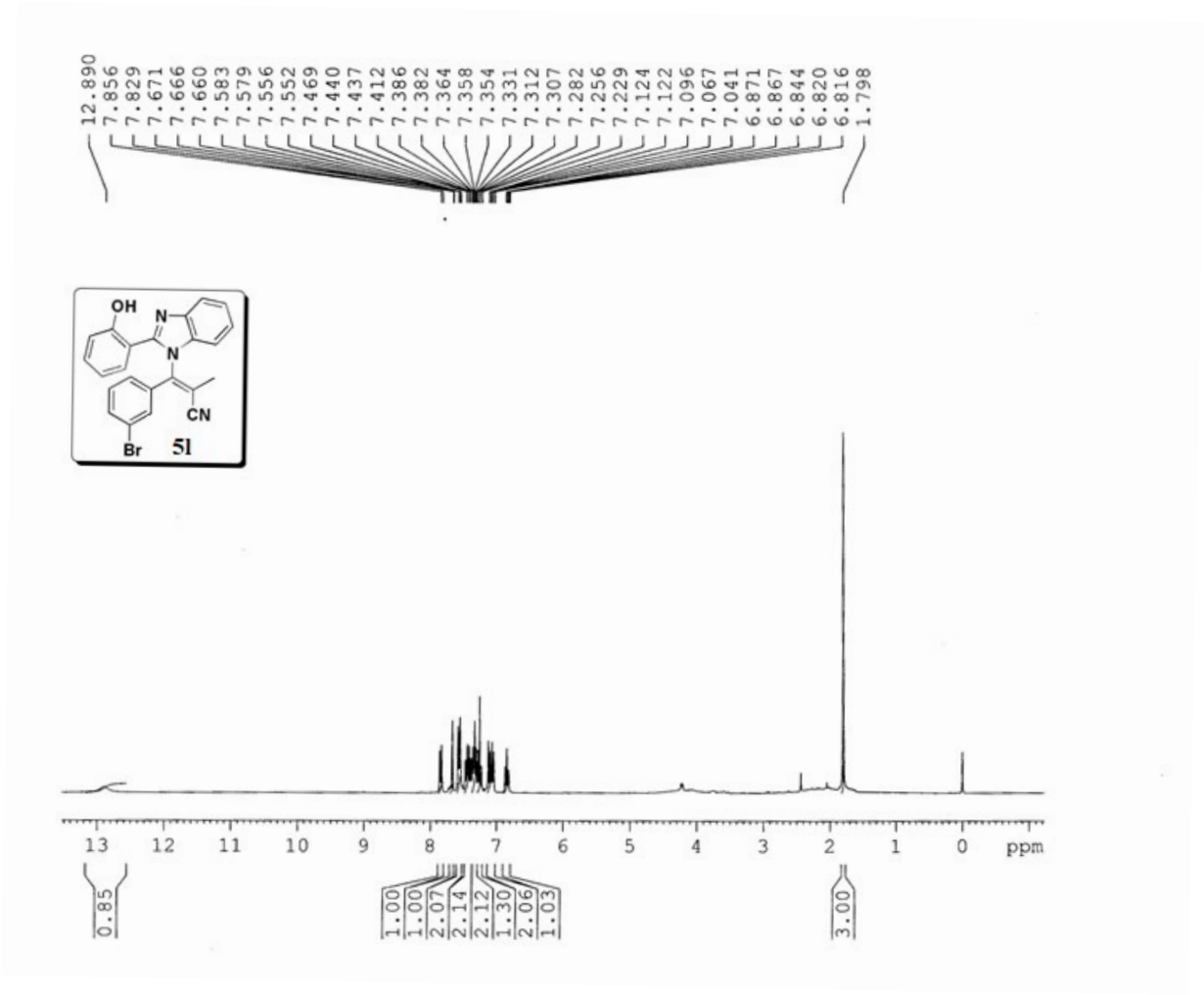

159.14
150.68
147.31
140.57
137.87
133.97
132.47
131.48
129.61
129.48
125.59
124.88
124.43
119.53
119.00
118.48
118.44
111.74
110.18
109.06
77.49
77.07
76.64
18.32

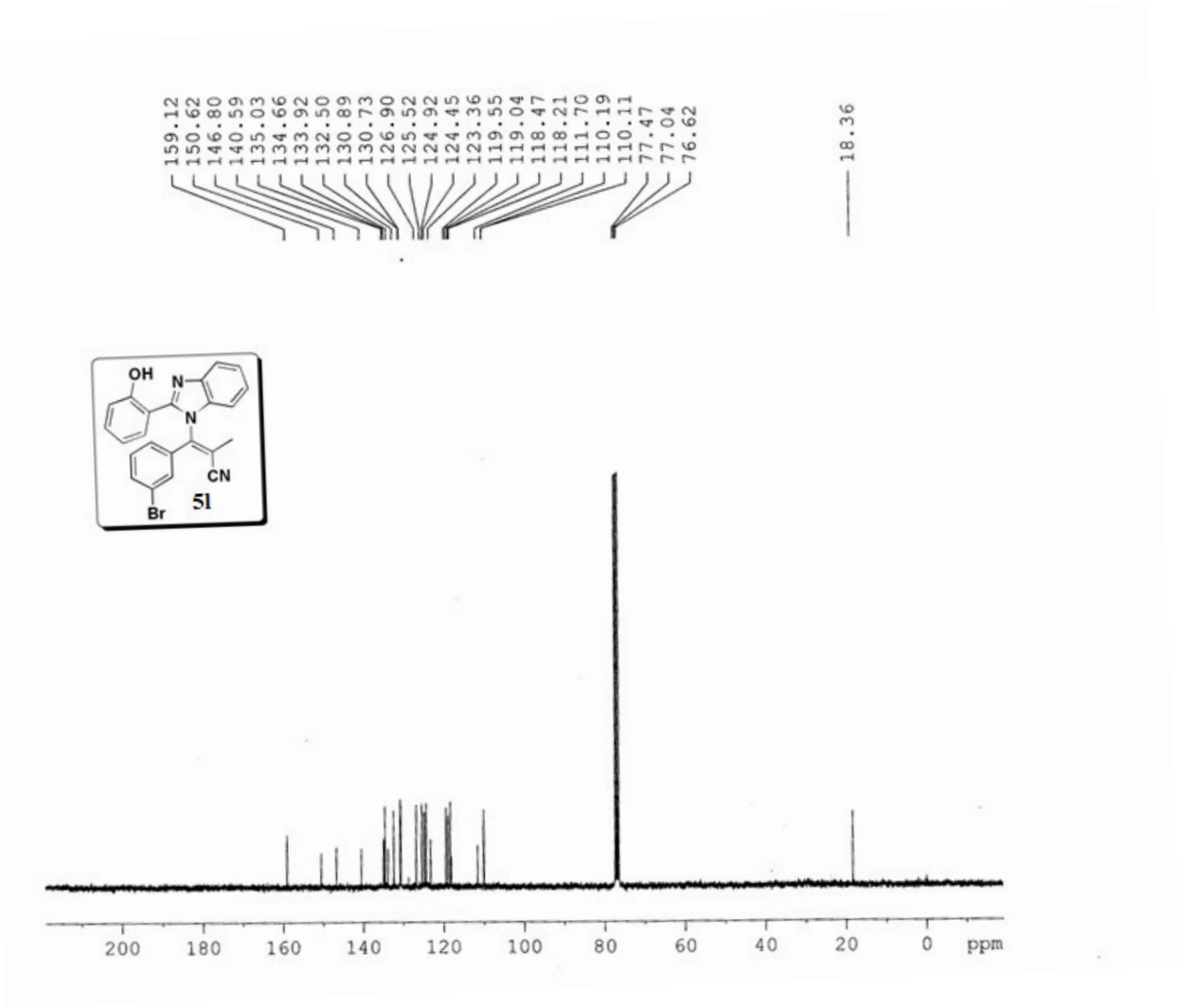

OH
N
N
CN
Cl
5k


200
180
160
140
120
100
80
60
40
20
0
ppm

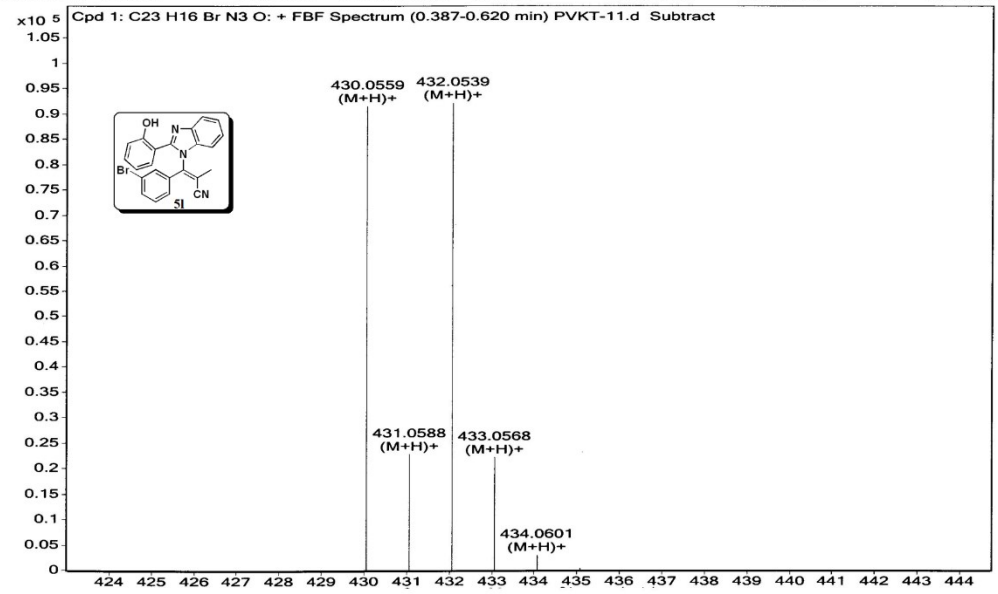
Sample Name	PVKT-22	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-22.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-385.0982	**Acquired Time**	25-02-2015 11:14:47

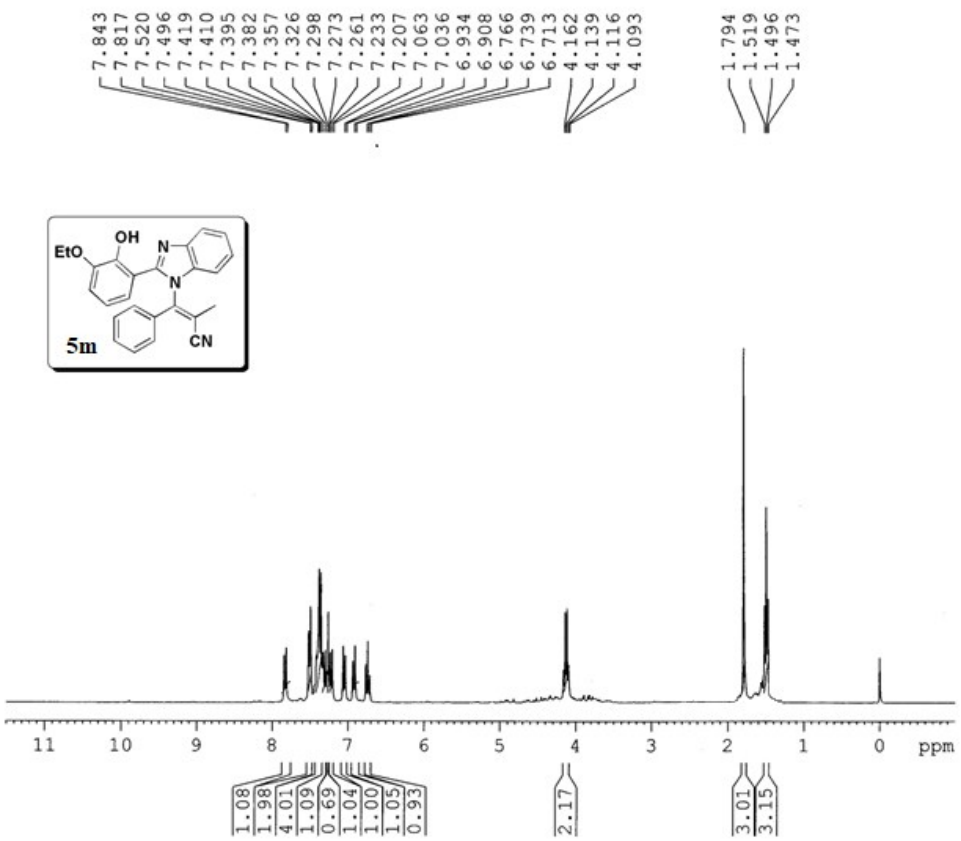


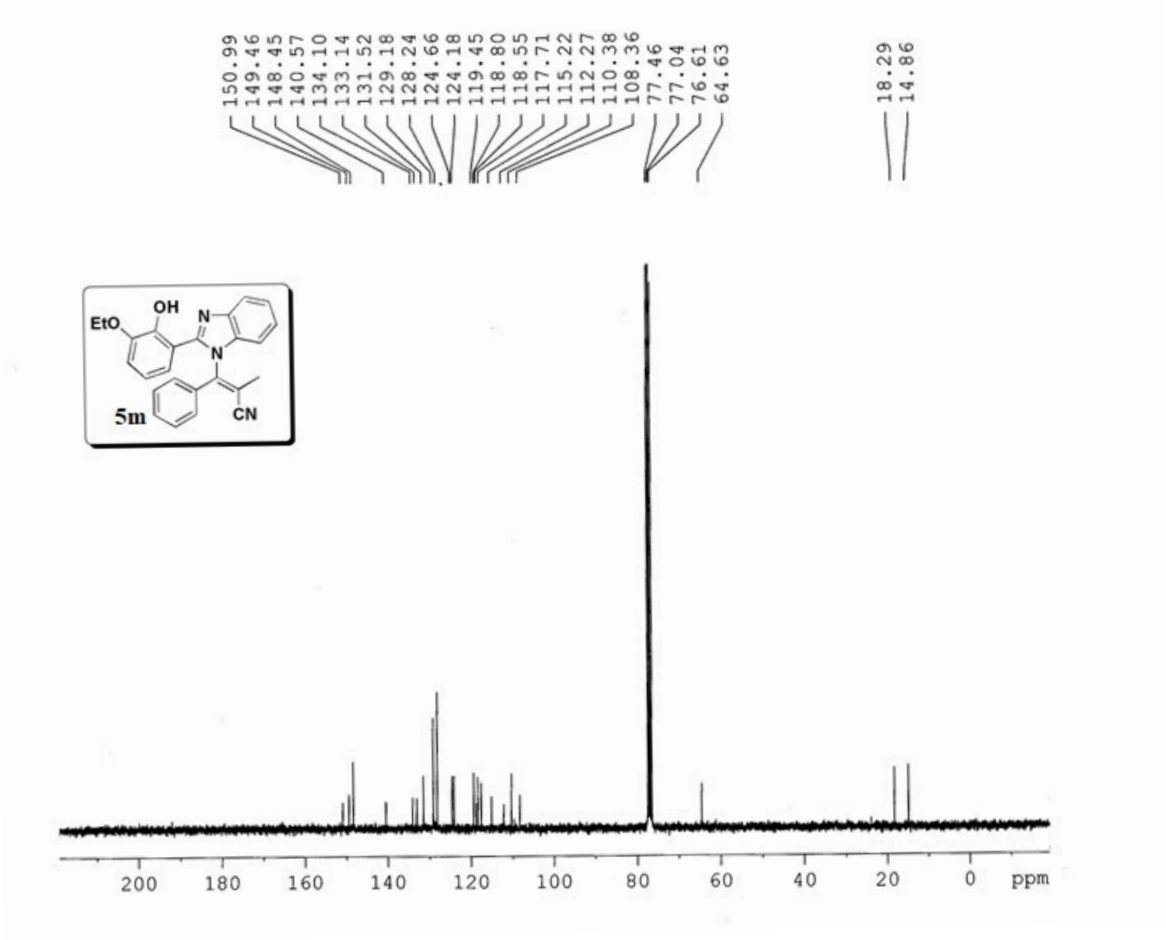

12.890
7.856
7.829
7.671
7.666
7.660
7.583
7.579
7.556
7.552
7.469
7.440
7.437
7.412
7.386
7.382
7.364
7.358
7.354
7.331
7.312
7.307
7.282
7.256
7.229
7.124
7.122
7.096
7.067
7.041
6.871
6.867
6.844
6.820
6.816
1.798
OH
N
N
CN
Br
5l
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.85
1.00
1.00
2.07
2.14
2.12
1.30
2.06
1.03
3.00


159.12
150.62
146.80
140.59
135.03
134.66
133.92
132.50
130.89
130.73
126.90
125.52
124.92
124.45
123.36
119.55
119.04
118.47
118.21
111.70
110.19
110.11
77.47
77.04
76.62
18.36
OH
N
N
CN
Br
51
200
180
160
140
120
100
80
60
40
20
0
ppm

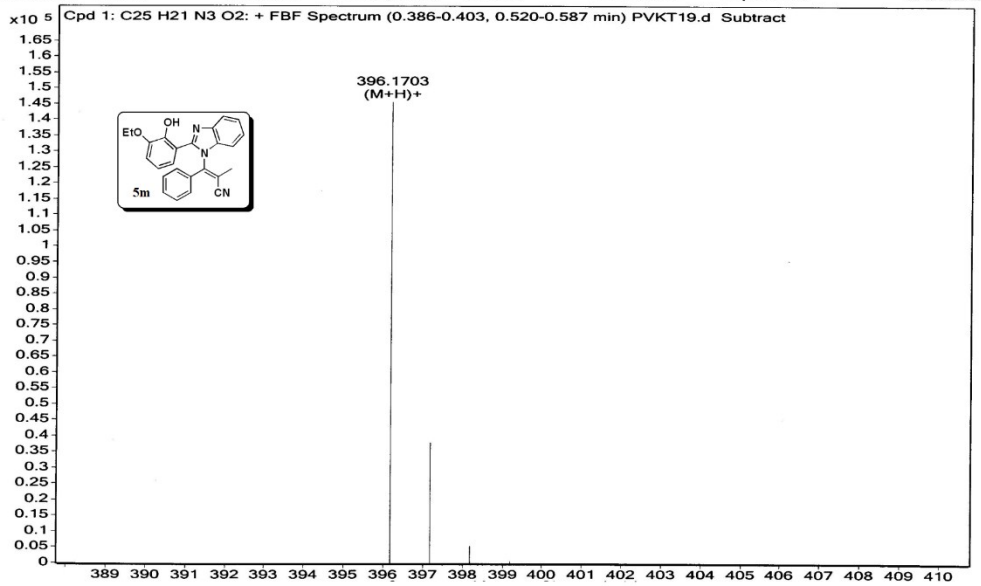
Sample Name	PVKT-11	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-11.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-429.0477	**Acquired Time**	09-02-2015 12:21:40

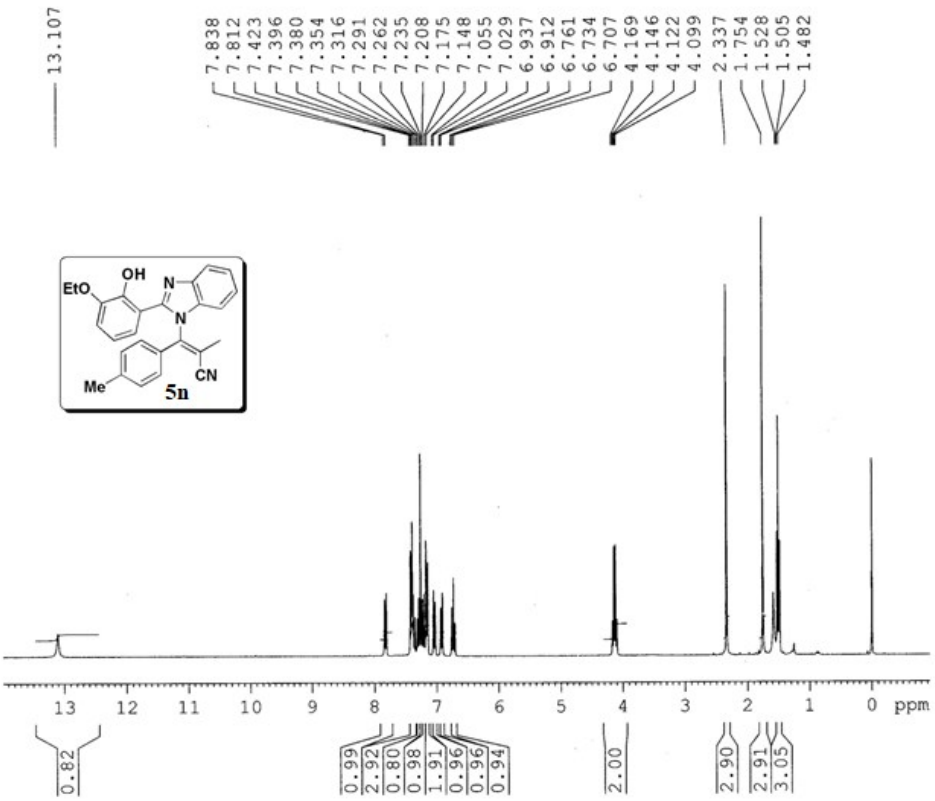


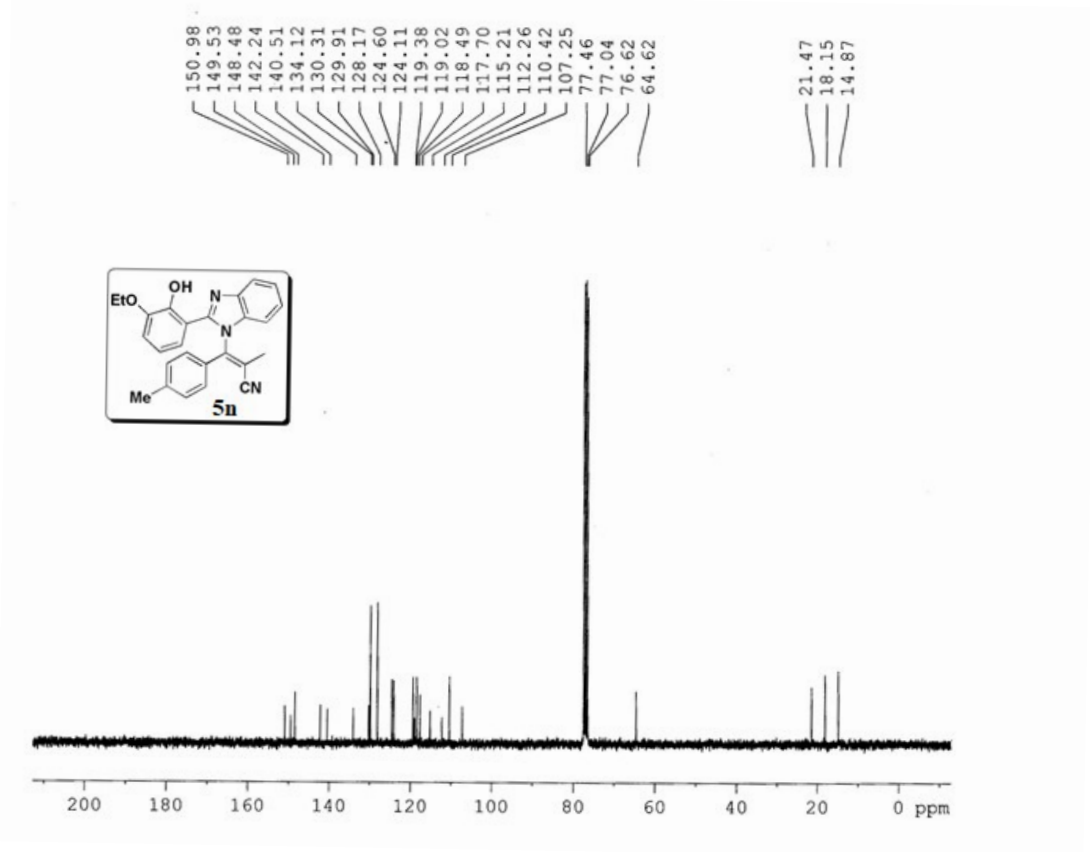

7.843
7.817
7.520
7.496
7.419
7.410
7.395
7.382
7.357
7.326
7.298
7.273
7.261
7.233
7.207
7.063
7.036
6.934
6.908
6.766
6.739
6.713
4.162
4.139
4.116
4.093
1.794
1.519
1.496
1.473
EtO
OH
N
N
CN
5m
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.08
1.98
4.01
1.09
0.69
1.04
1.00
1.05
0.93
2.17
3.01
3.15



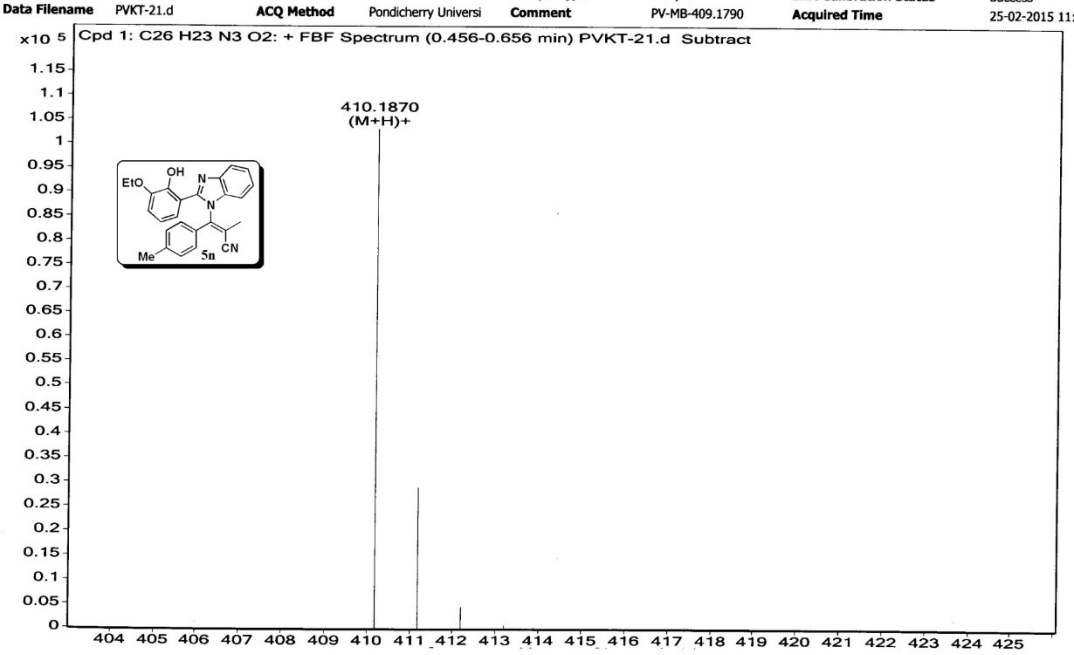
Sample Name	PVKT-19	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT19.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-395.1634	**Acquired Time**	13-02-2015 15:10:47

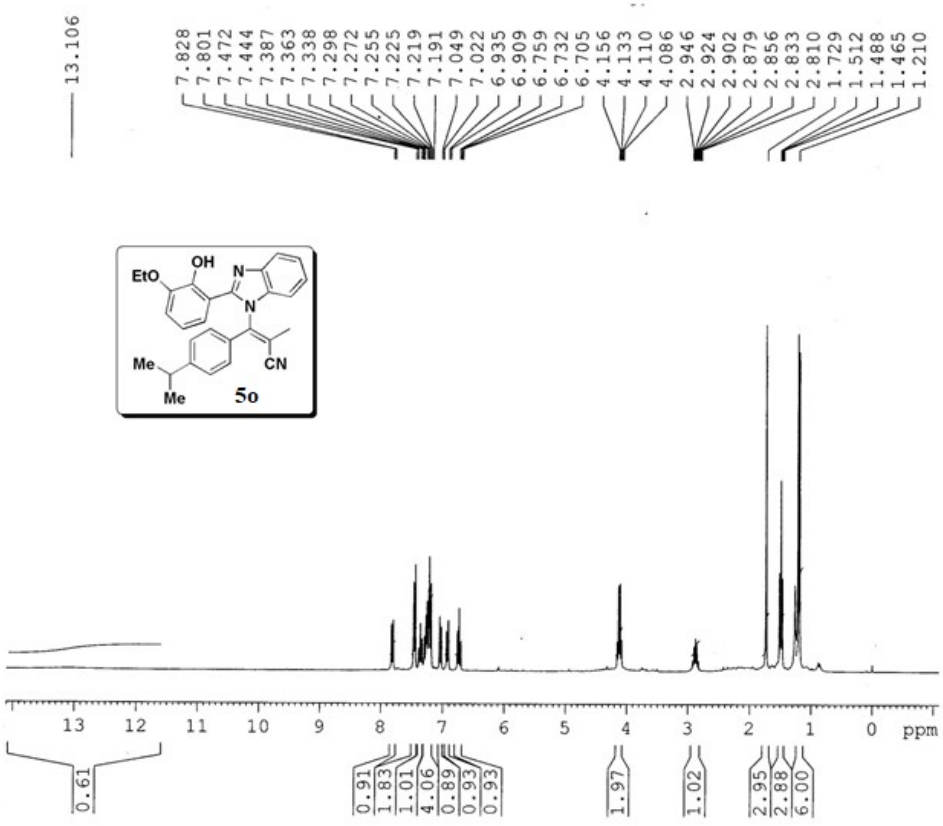


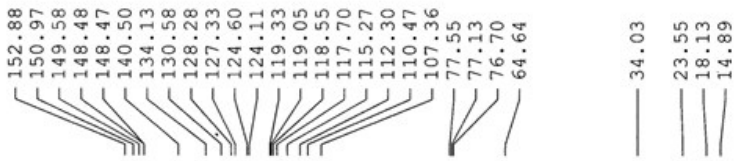

13.107
7.838
7.812
7.423
7.396
7.380
7.354
7.316
7.291
7.262
7.235
7.208
7.175
7.148
7.055
7.029
6.937
6.912
6.761
6.734
6.707
4.169
4.146
4.122
4.099
2.337
1.754
1.528
1.505
1.482
EtO
OH
N
N
Me
CN
5n
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.82
0.99
2.92
0.80
0.98
1.91
0.96
0.96
0.94
2.00
2.90
2.91
3.05

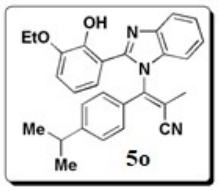


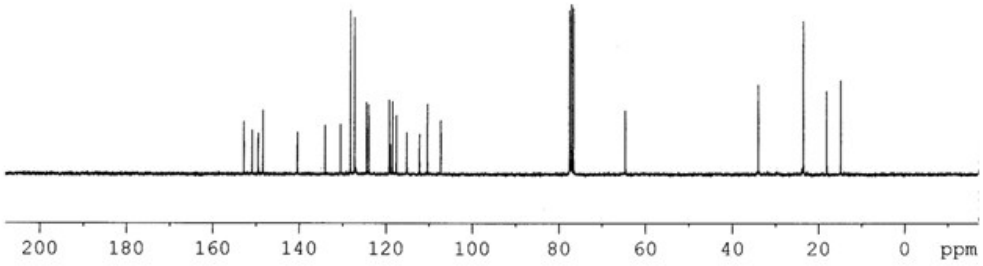
Sample Name	PVKT-21	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-21.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-409.1790	**Acquired Time**	25-02-2015 11:24:24



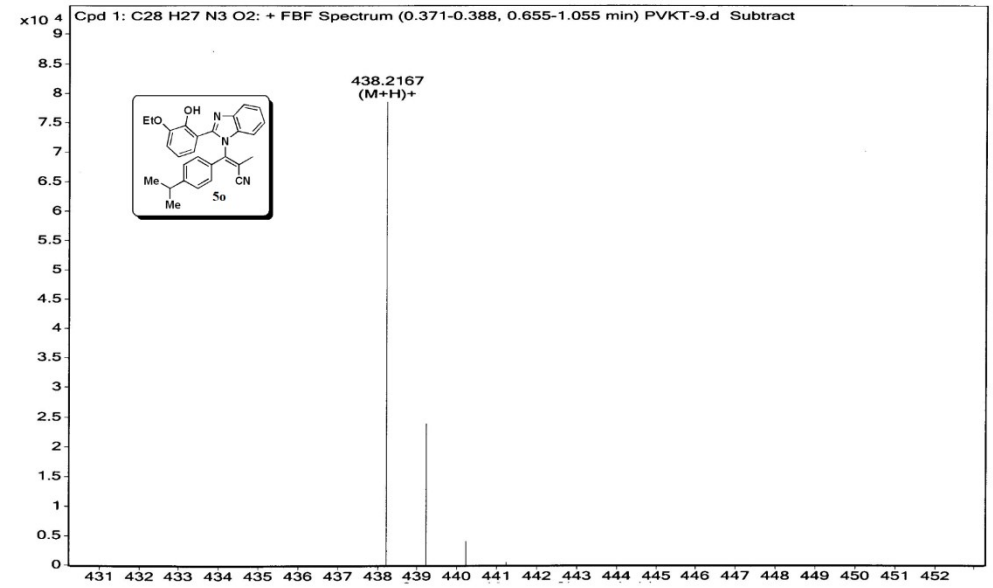

13.106
7.828
7.801
7.472
7.444
7.387
7.363
7.338
7.298
7.272
7.255
7.225
7.219
7.191
7.049
7.022
6.935
6.909
6.759
6.732
6.705
4.156
4.133
4.110
4.086
2.946
2.924
2.902
2.879
2.856
2.833
2.810
1.729
1.512
1.488
1.465
1.210
EtO
OH
N
N
Me
Me
CN
5o
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.61
0.91
1.83
1.01
4.06
0.89
0.93
0.93
1.97
1.02
2.95
2.88
6.00

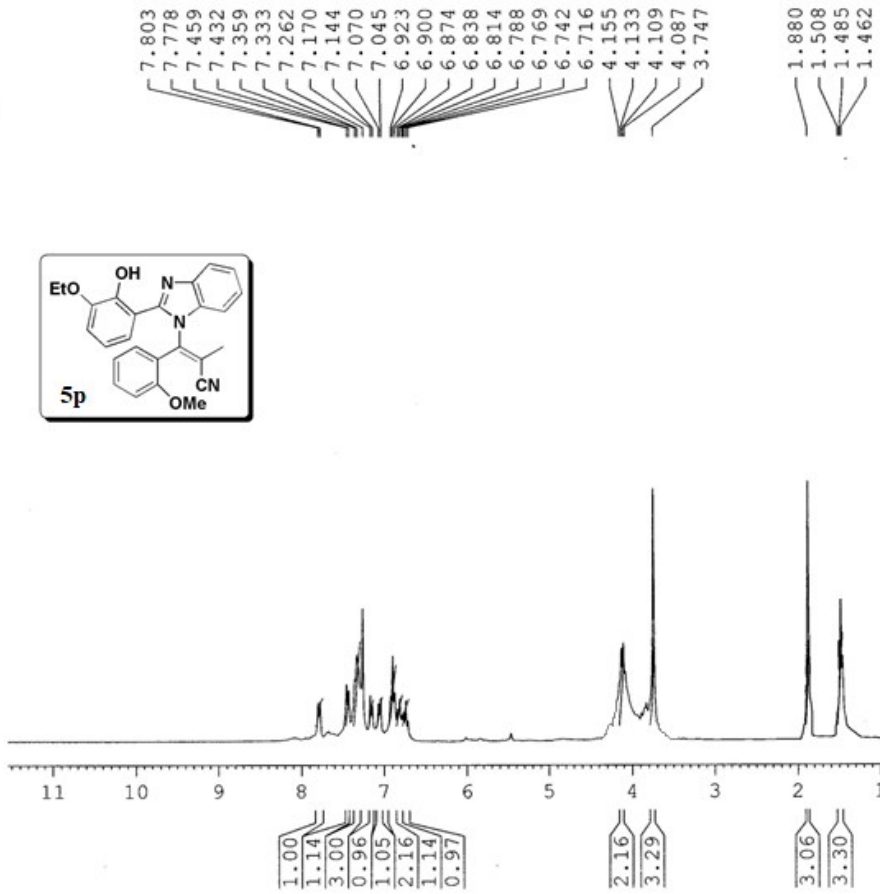


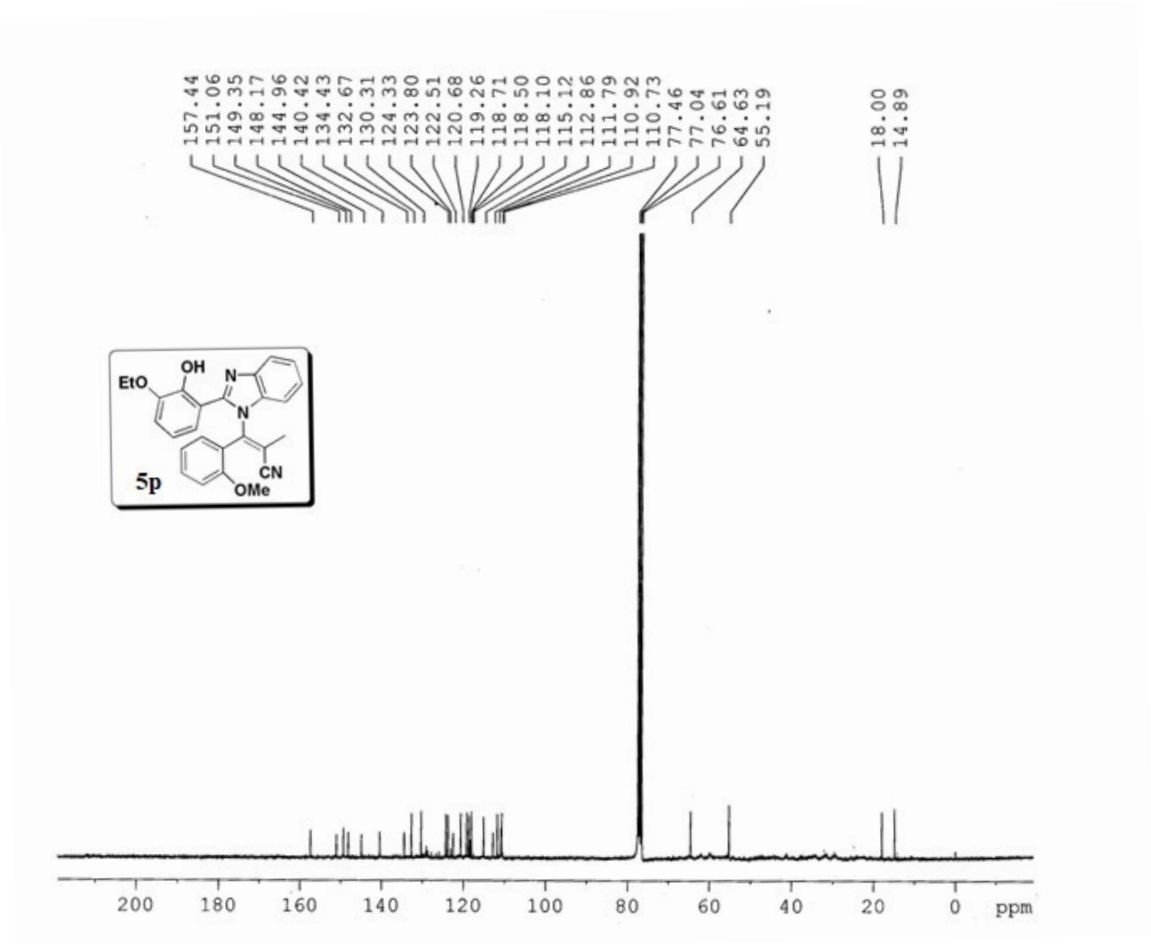




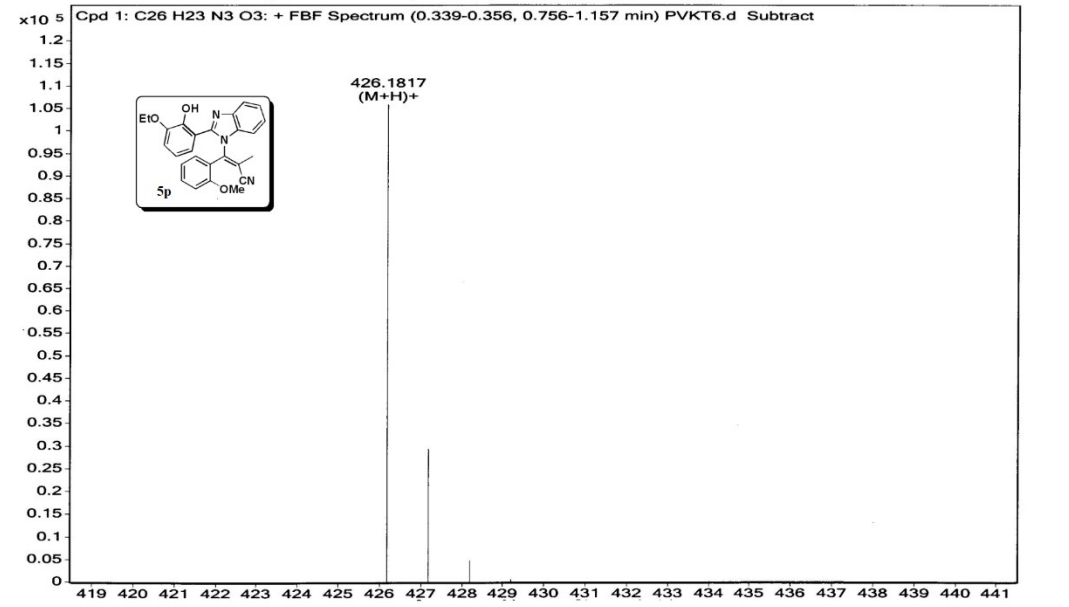
Sample Name	PVKT-9	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-9.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-437.2103	**Acquired Time**	13-02-2015 12:17:13

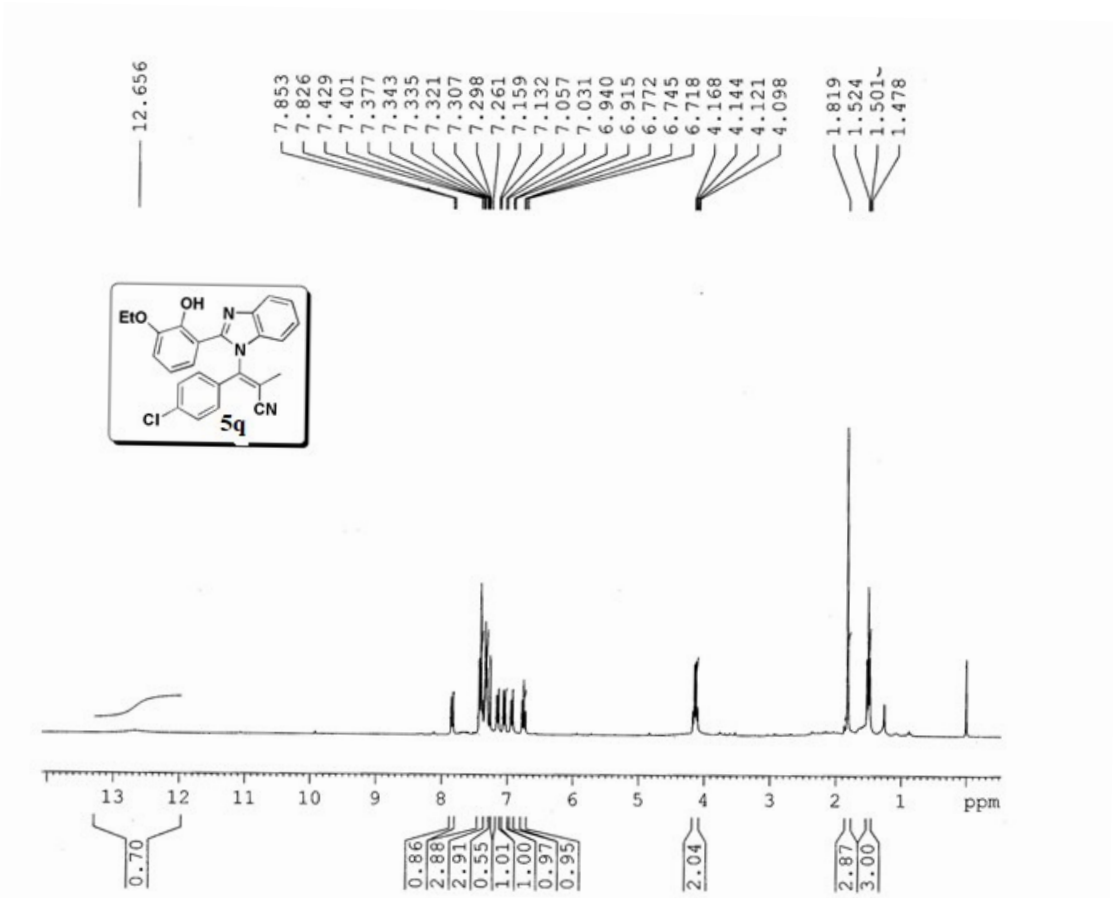


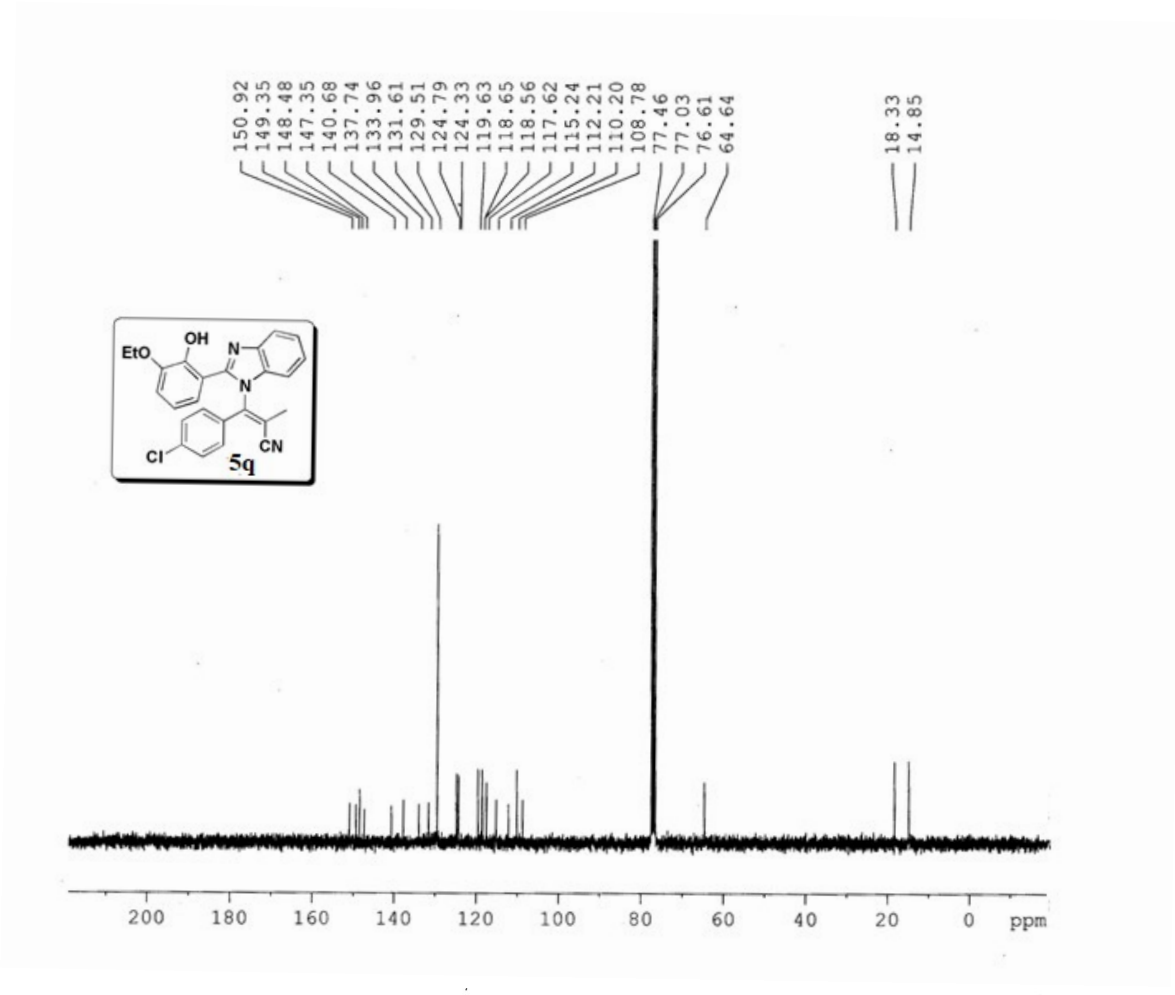

7.803
7.778
7.459
7.432
7.359
7.333
7.262
7.170
7.144
7.070
7.045
6.923
6.900
6.874
6.838
6.814
6.788
6.769
6.742
6.716
4.155
4.133
4.109
4.087
3.747
1.880
1.508
1.485
1.462
EtO
OH
N
N
CN
OMe
5p
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.14
3.00
0.96
1.05
2.16
1.14
0.97
2.16
3.29
3.06
3.30



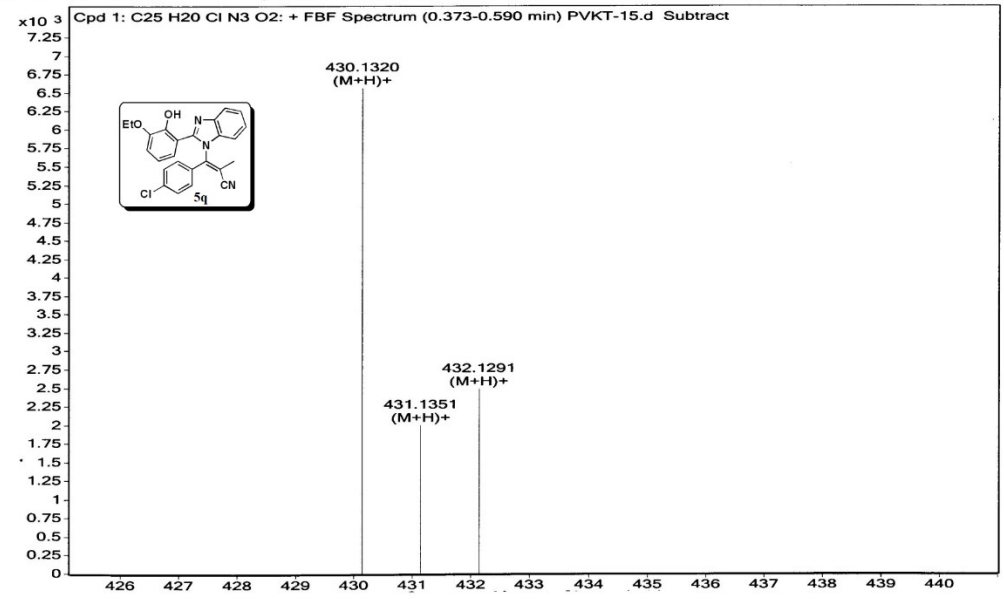
Sample Name	PVKT-6	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT6.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-425.1739	**Acquired Time**	09-02-2015 12:18:26



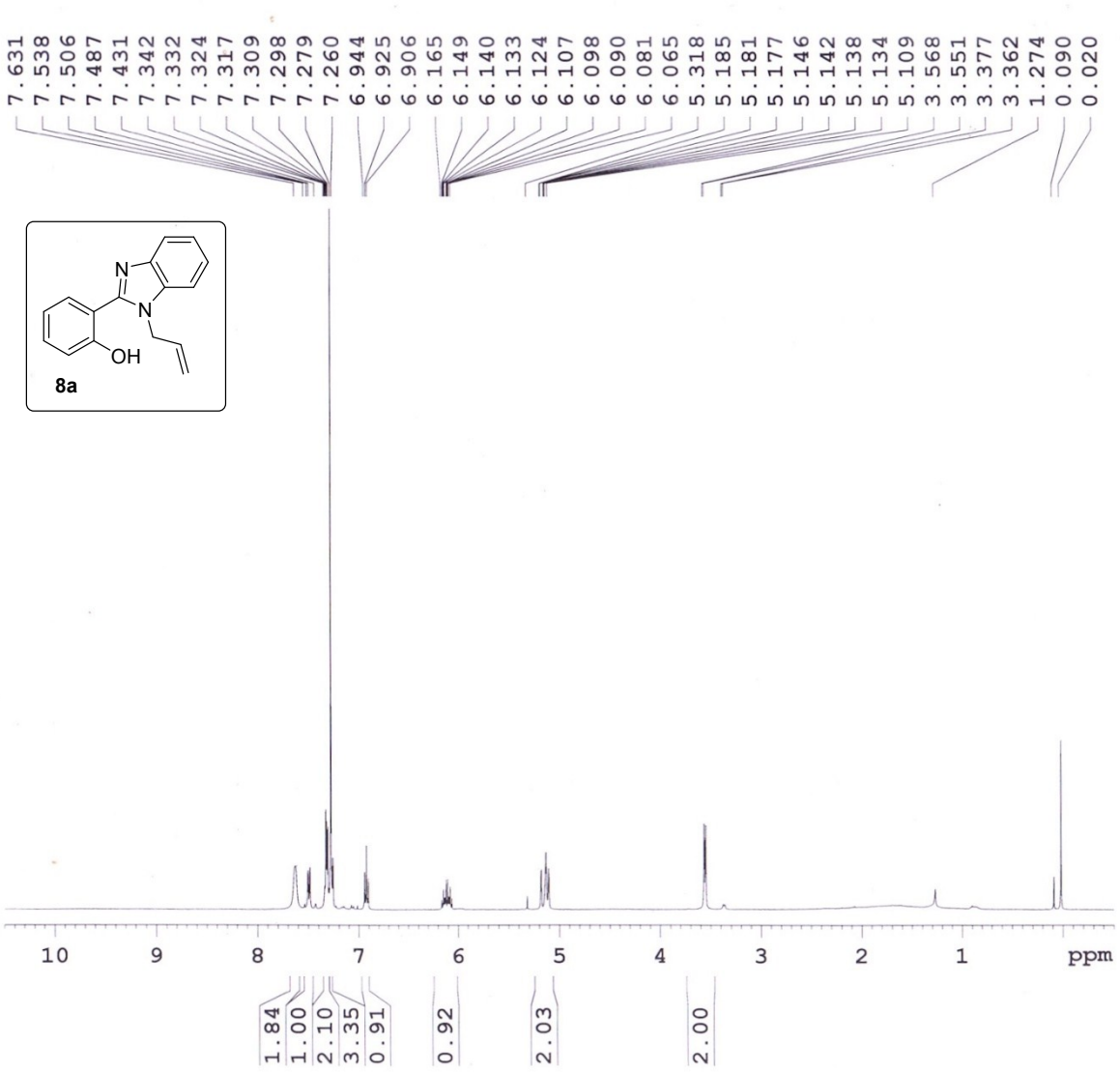

12.656
7.853
7.826
7.429
7.401
7.377
7.343
7.335
7.321
7.307
7.298
7.261
7.159
7.132
7.057
7.031
6.940
6.915
6.772
6.745
6.718
4.168
4.144
4.121
4.098
1.819
1.524
1.501
1.478
EtO
OH
N
N
Cl
CN
5q
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.70
0.86
2.88
2.91
0.55
1.01
1.00
0.97
0.95
2.04
2.87
3.00

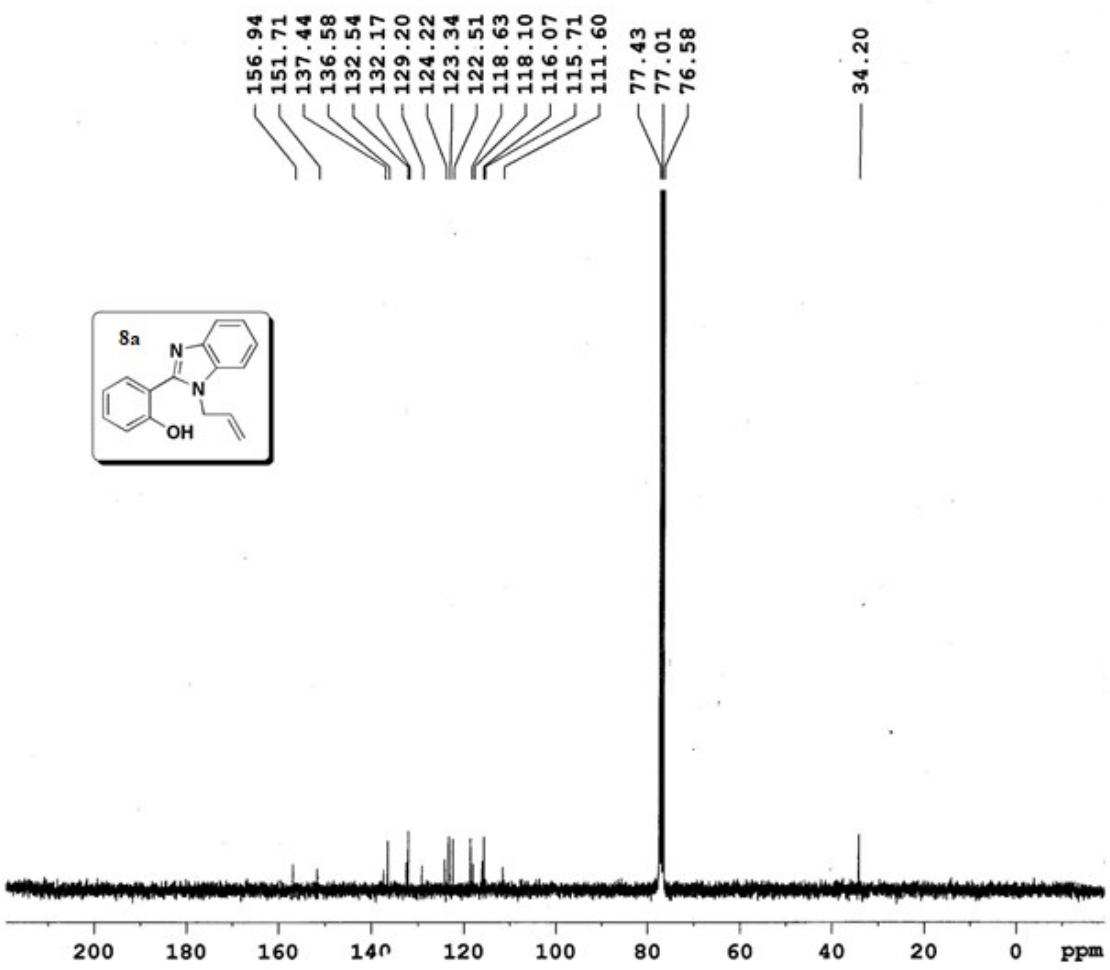


Sample Name	PVKT-15	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT-15.d	**ACQ Method**	Pondicherry Universi	**Comment**	PV-MB-429.1244	**Acquired Time**	09-02-2015 12:24:26

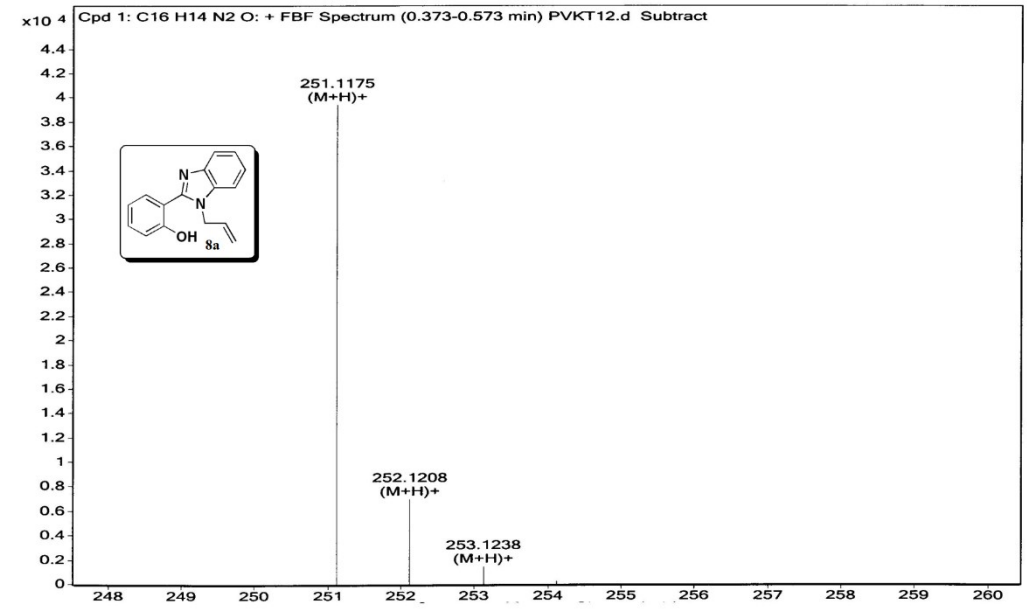


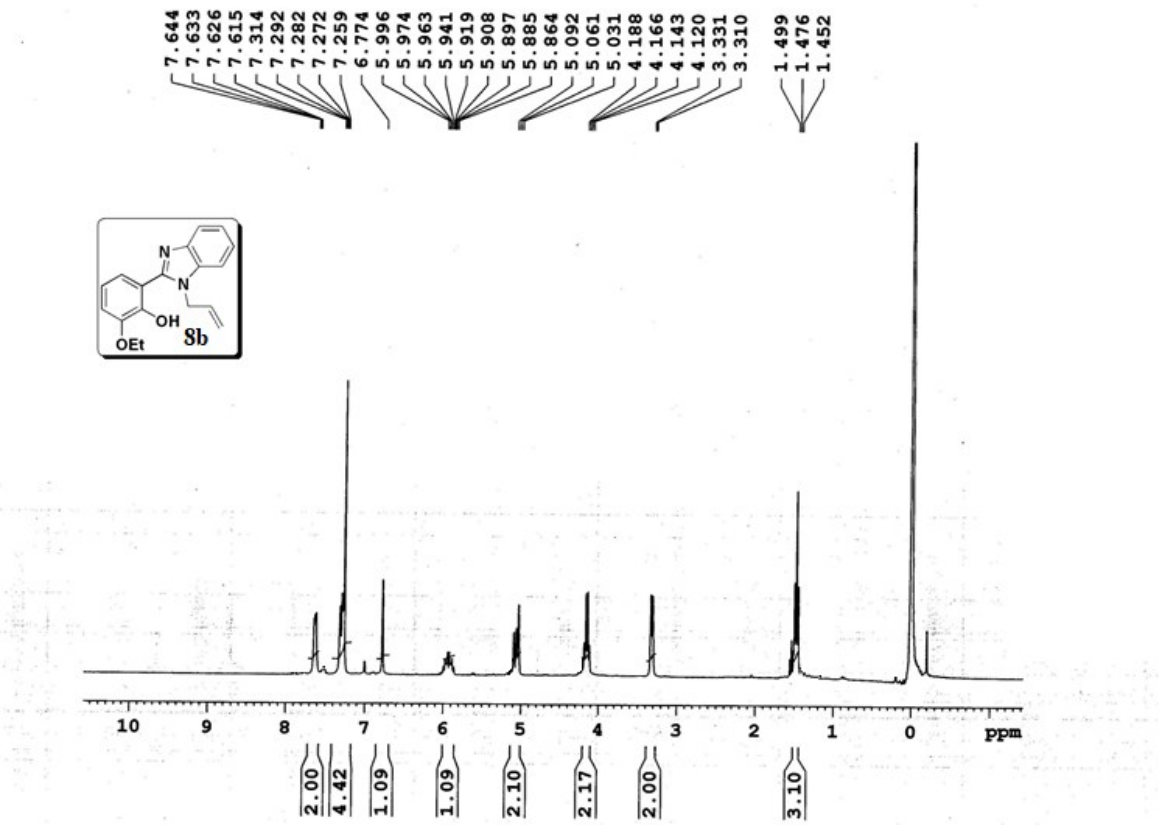
^{1}H, ^{13}C NMR and Mass spectra for compounds **8a-e**

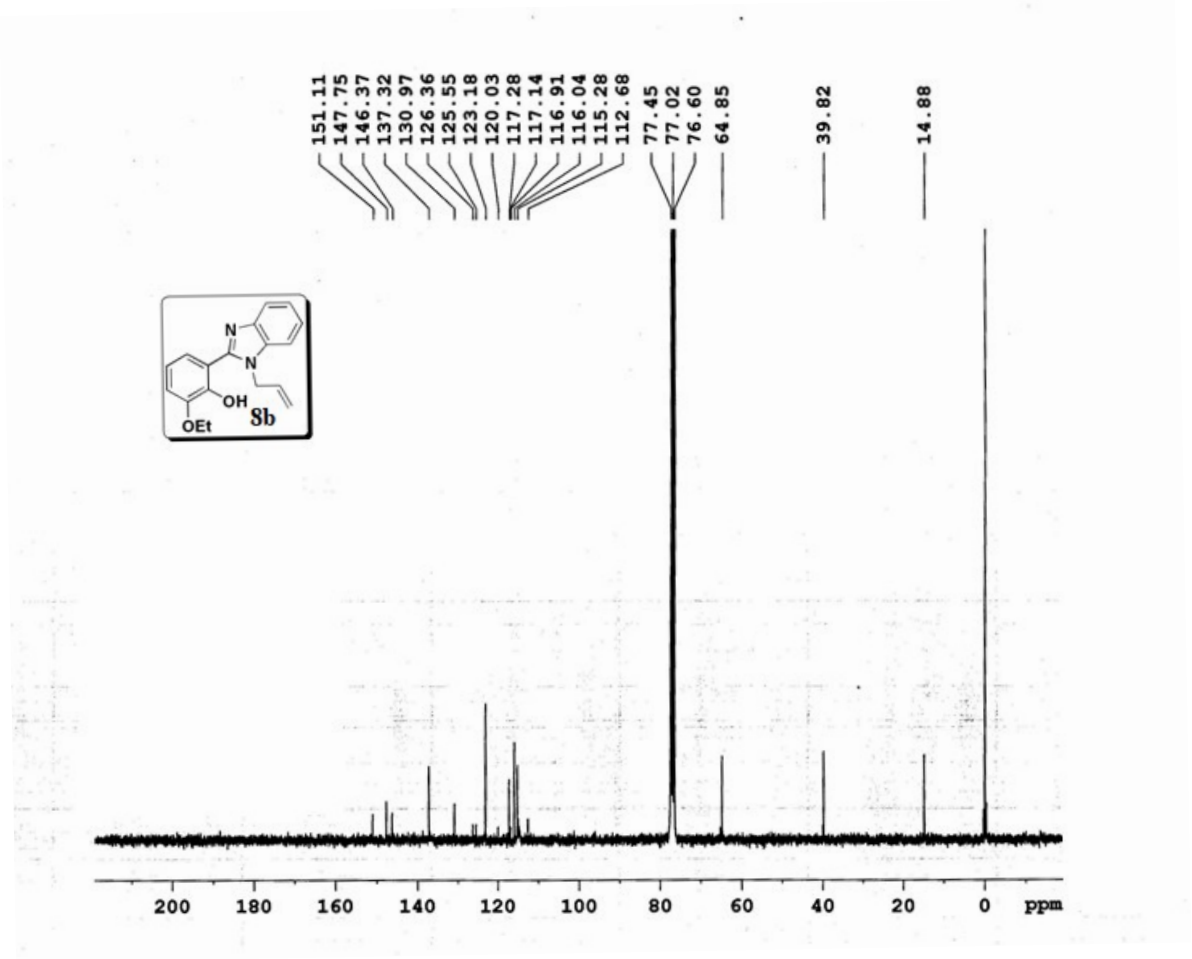

7.631
7.538
7.506
7.487
7.431
7.342
7.332
7.324
7.317
7.309
7.298
7.279
7.260
6.944
6.925
6.906
6.165
6.149
6.140
6.133
6.124
6.107
6.098
6.090
6.081
6.065
5.318
5.185
5.181
5.177
5.146
5.142
5.138
5.134
5.109
3.568
3.551
3.377
3.362
1.274
0.090
0.020
N
N
OH
8a
10
9
8
7
6
5
4
3
2
1
ppm
1.84
1.00
2.10
3.35
0.91
0.92
2.03
2.00

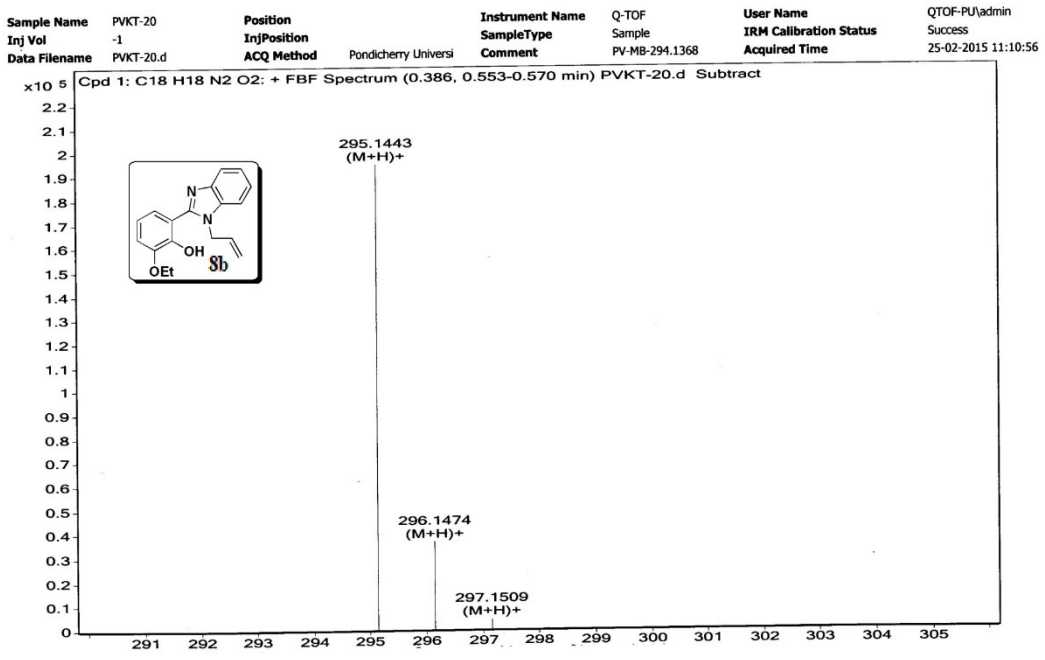

156.94
151.71
137.44
136.58
132.54
132.17
129.20
124.22
123.34
122.51
118.63
118.10
116.07
115.71
111.60
77.43
77.01
76.58
34.20
8a
N
N
OH
200
180
160
140
120
100
80
60
40
20
0
ppm

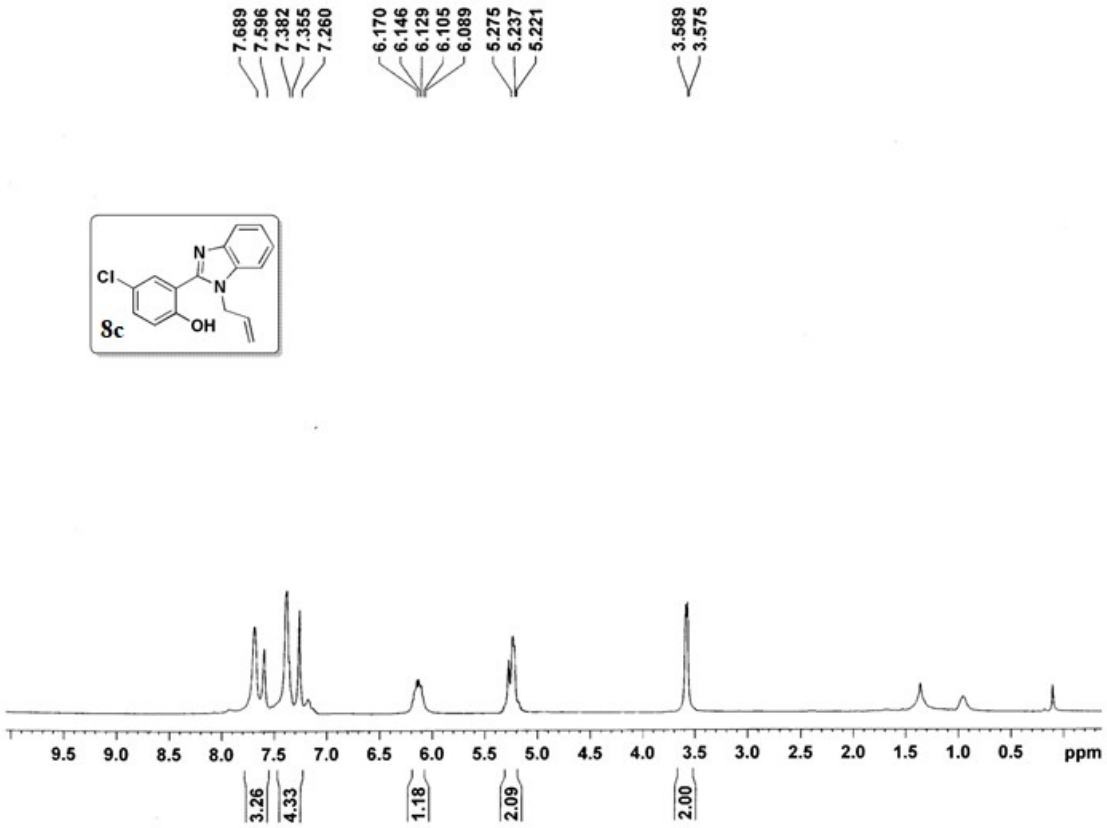
Sample Name	PVKT12	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	PVKT12.d	**ACQ Method**	Pondicherry Universi	**Comment**	PVK-MB-250.1106	**Acquired Time**	04-02-2015 11:30:40

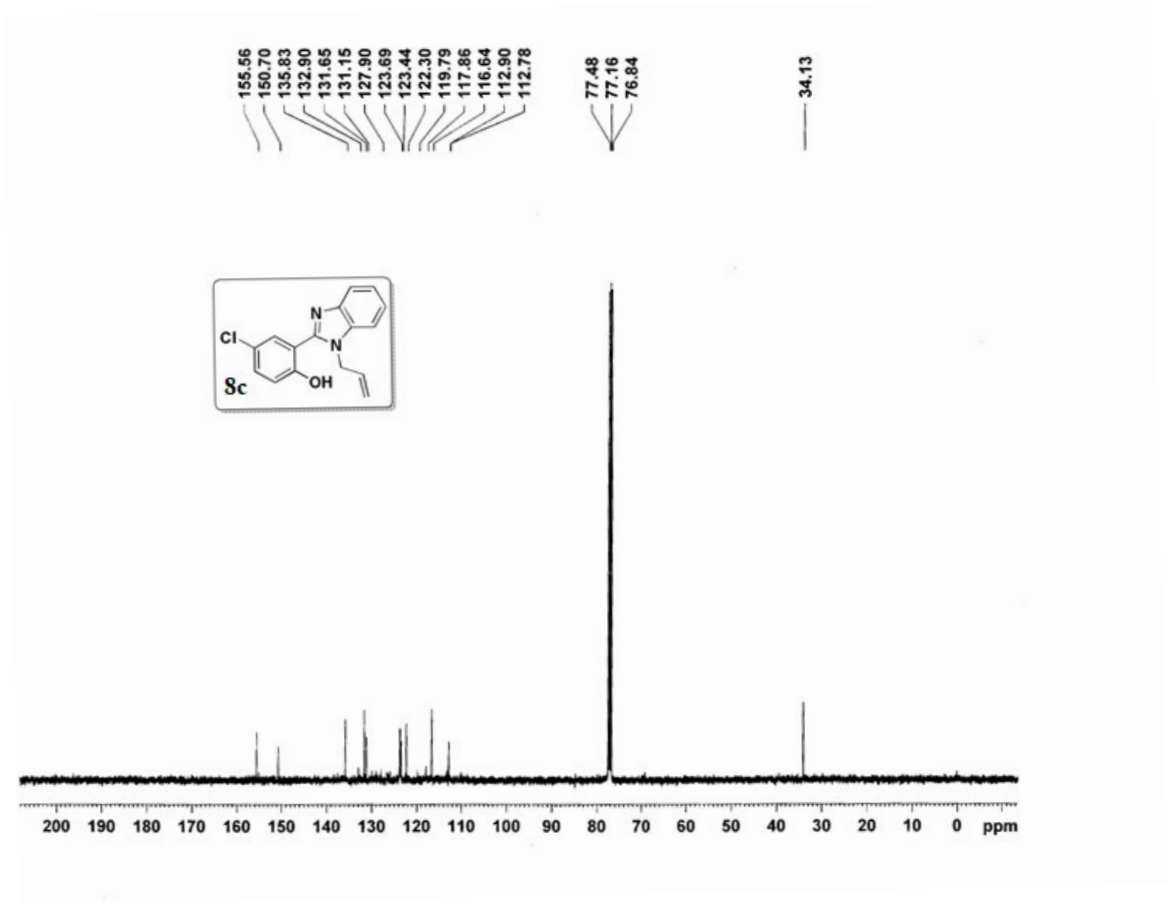



7.644
7.633
7.626
7.615
7.314
7.292
7.282
7.272
7.259
6.774
5.996
5.974
5.963
5.941
5.919
5.908
5.897
5.885
5.864
5.092
5.061
5.031
4.188
4.166
4.143
4.120
3.331
3.310
1.499
1.476
1.452
N
N
OH
OEt
8b
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.42
1.09
1.09
2.10
2.17
2.00
3.10

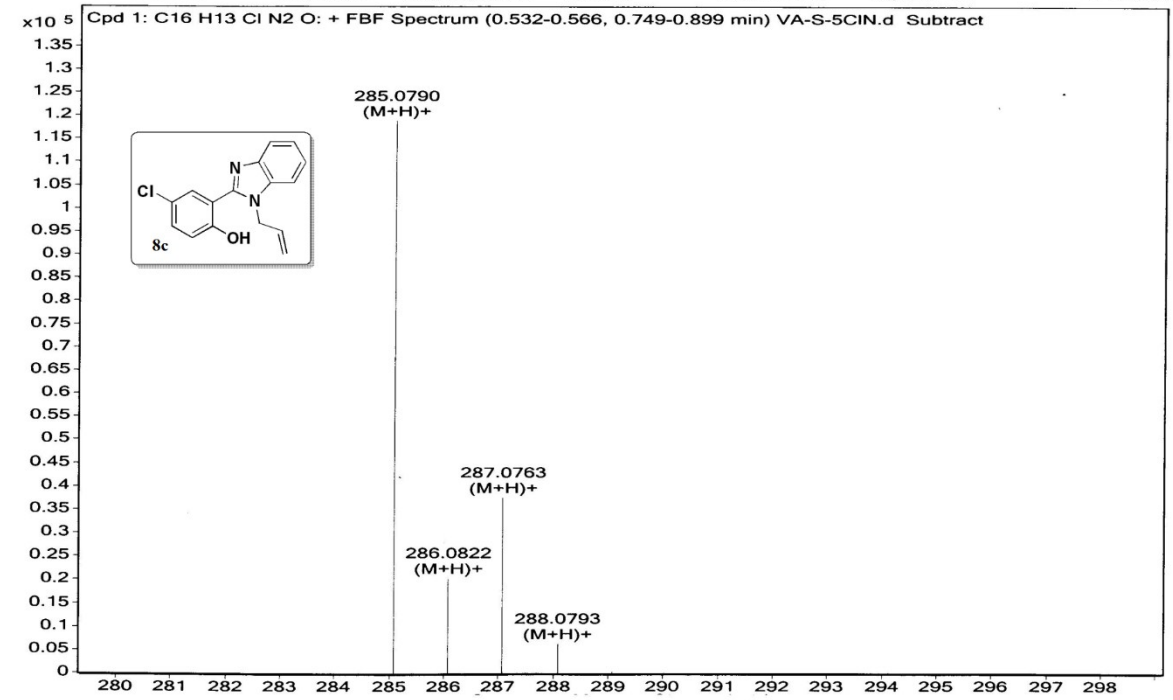

151.11
147.75
146.37
137.32
130.97
126.36
125.55
123.18
120.03
117.28
117.14
116.91
116.04
115.28
112.68
77.45
77.02
76.60
64.85
39.82
14.88
N
N
OH
OEt
Sb
200
180
160
140
120
100
80
60
40
20
0
ppm

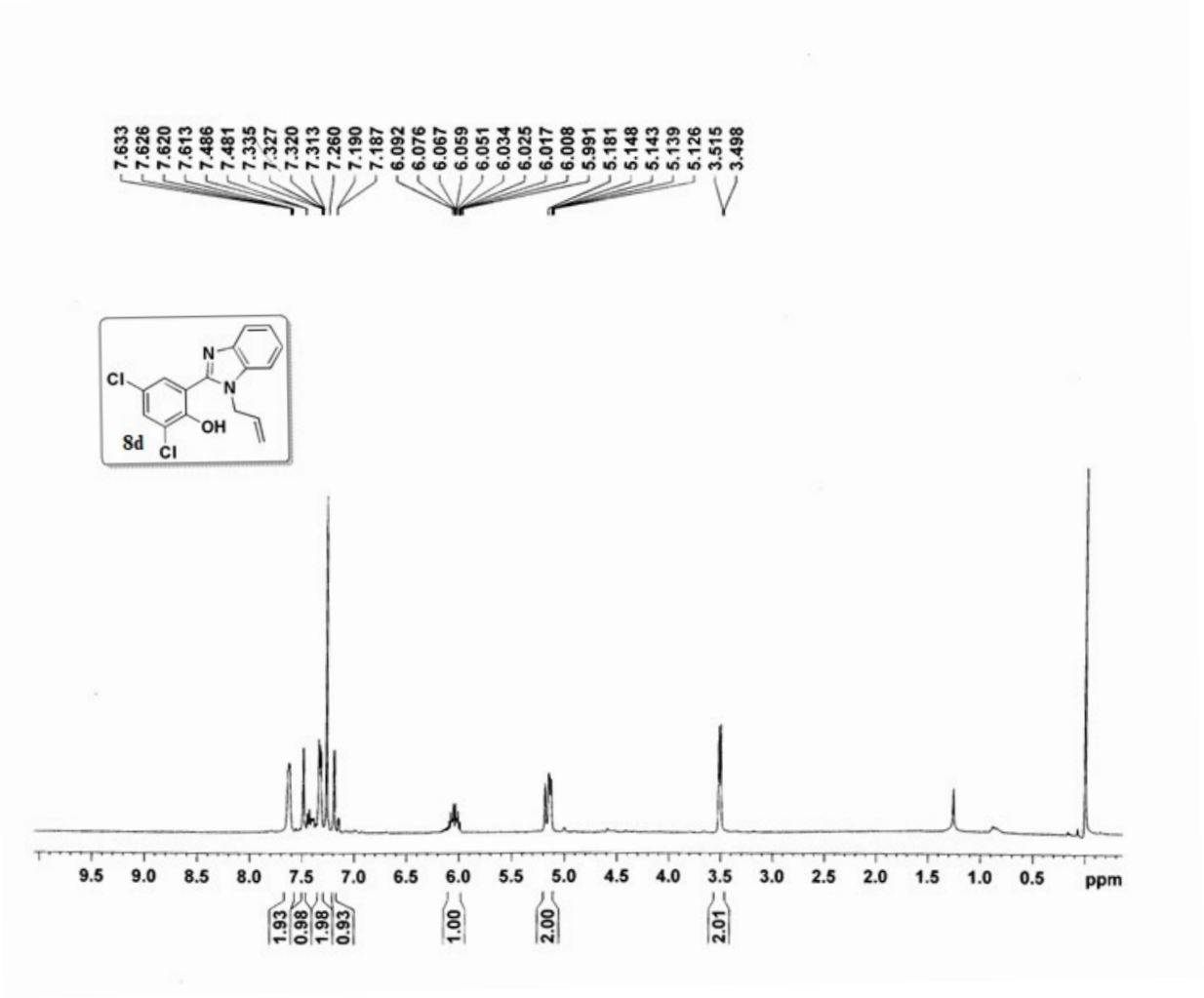

Sample Name PVKT-20
Inj Vol -1
Data Filename PVKT-20.d
Position
InjPosition
ACQ Method Pondicherry Universi
Instrument Name Q-TOF
SampleType Sample
Comment PV-MB-294.1368
User Name QTOF-PU\admin
IRM Calibration Status Success
Acquired Time 25-02-2015 11:10:56
Cpd 1: C18 H18 N2 O2: + FBF Spectrum (0.386, 0.553-0.570 min) PVKT-20.d Subtract
x10 5
295.1443
(M+H)+
296.1474
(M+H)+
297.1509
(M+H)+
N
N
OH
OEt
Sb
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305

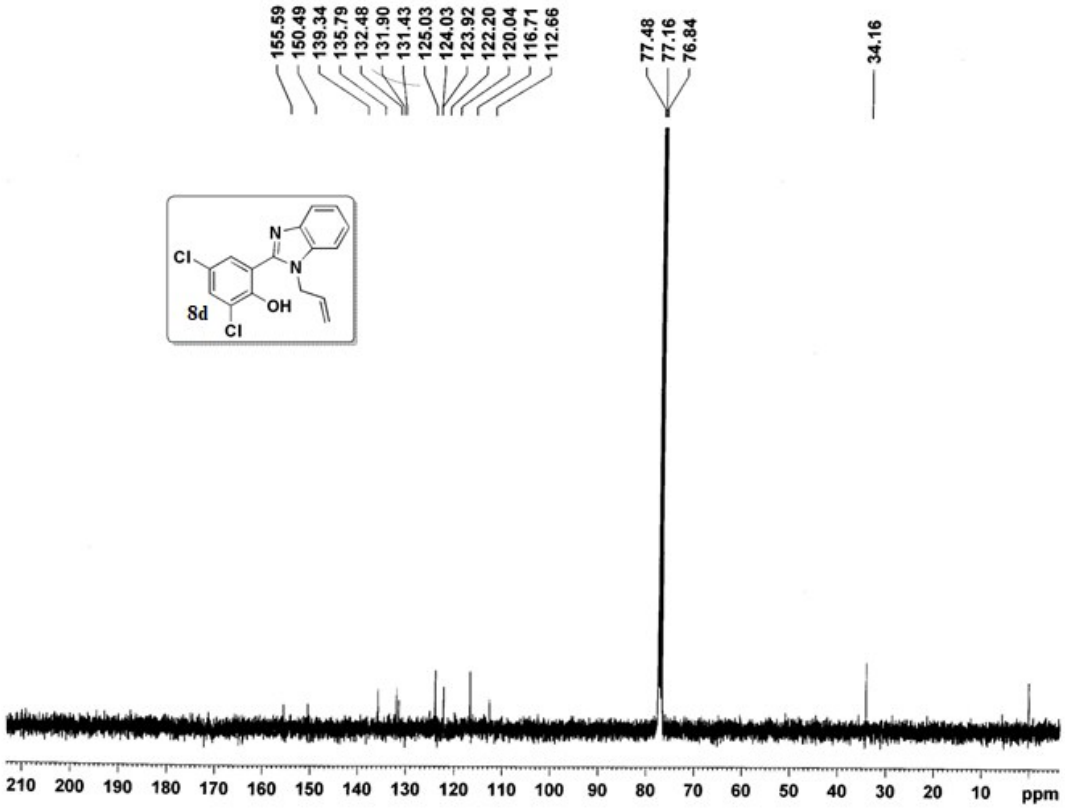

7.689
7.596
7.382
7.355
7.260
6.170
6.146
6.129
6.105
6.089
5.275
5.237
5.221
3.589
3.575
Cl
N
N
OH
8c
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.26
4.33
1.18
2.09
2.00


155.56
150.70
135.83
132.90
131.65
131.15
127.90
123.69
123.44
122.30
119.79
117.86
116.64
112.90
112.78
77.48
77.16
76.84
34.13
Cl
N
N
OH
8c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

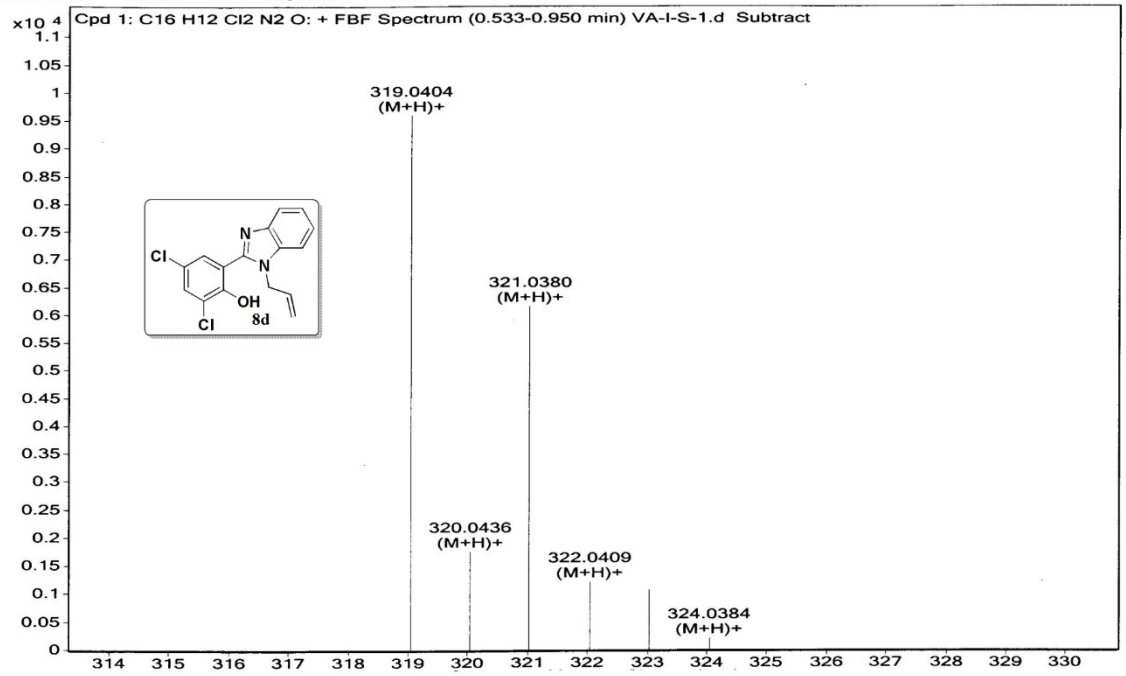
Sample Name	VA-S-5Cl	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	VA-S-5ClN.d	**ACQ Method**	Pondicherry Universi	**Comment**	MSK-MB-284.0716	**Acquired Time**	27-08-2015 12:53:28

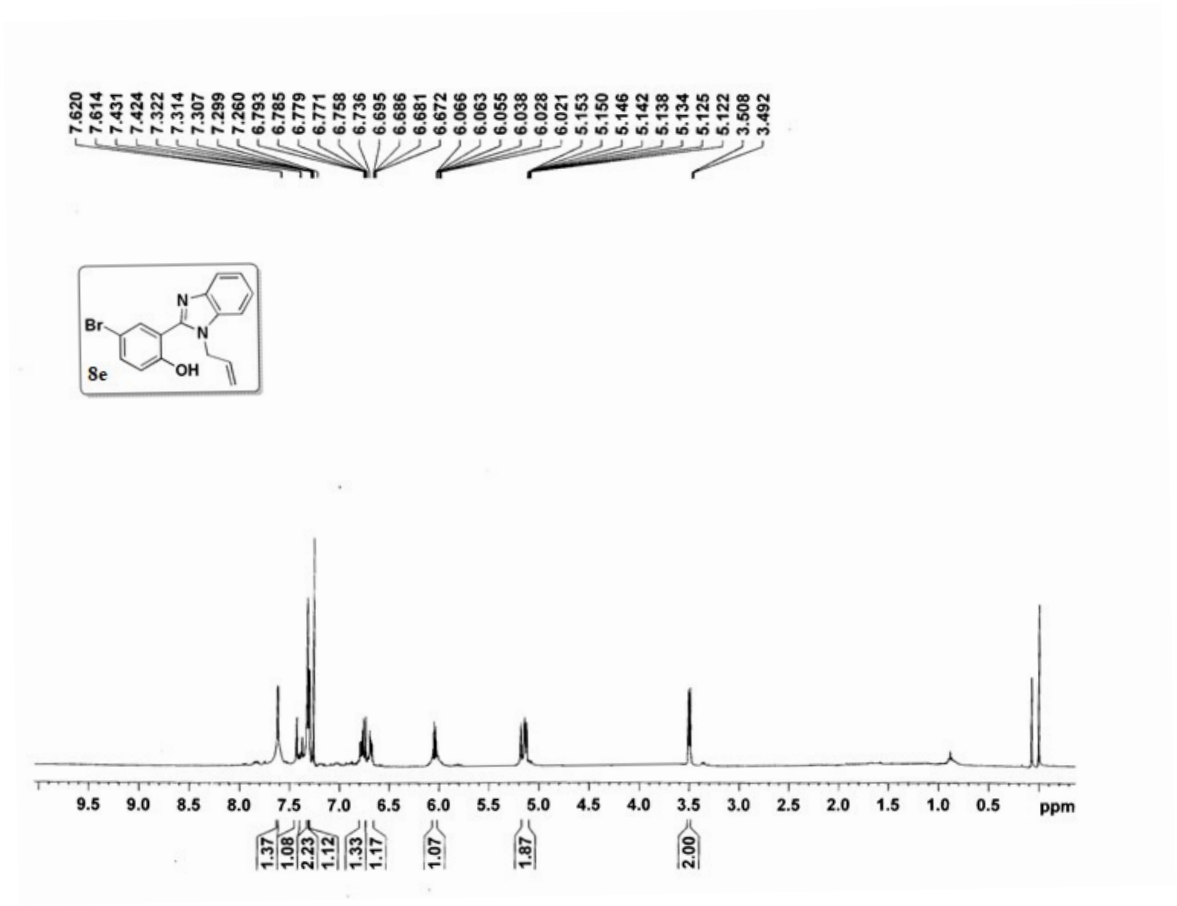


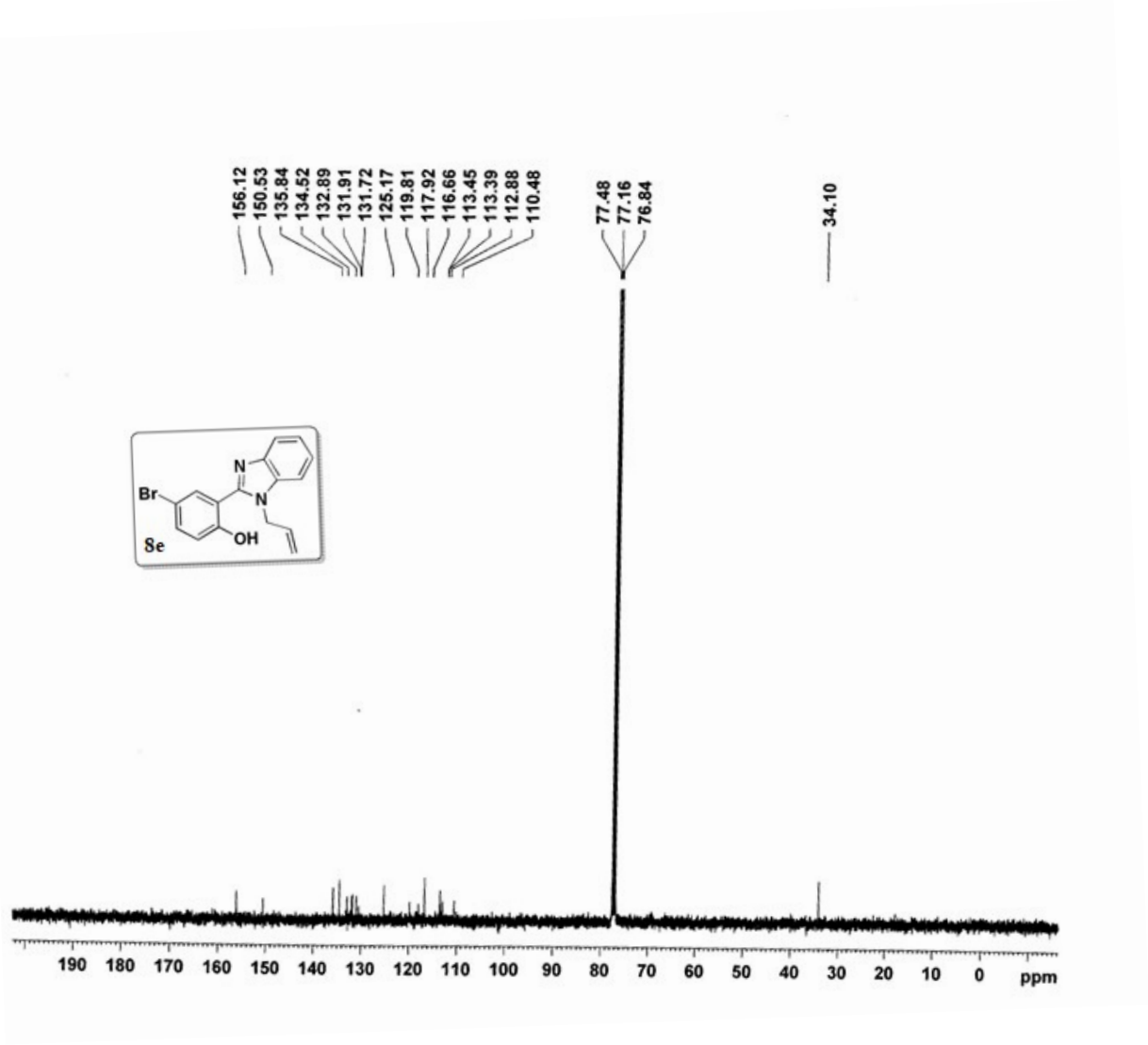

7.633
7.626
7.620
7.613
7.486
7.481
7.335
7.327
7.320
7.313
7.260
7.190
7.187
6.092
6.076
6.067
6.059
6.051
6.034
6.025
6.017
6.008
5.991
5.181
5.148
5.143
5.139
5.126
3.515
3.498
Cl
N
N
OH
8d
Cl
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.93
0.98
1.98
0.93
1.00
2.00
2.01


155.59
150.49
139.34
135.79
132.48
131.90
131.43
125.03
124.03
123.92
122.20
120.04
116.71
112.66
77.48
77.16
76.84
34.16
N
N
Cl
OH
Cl
8d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

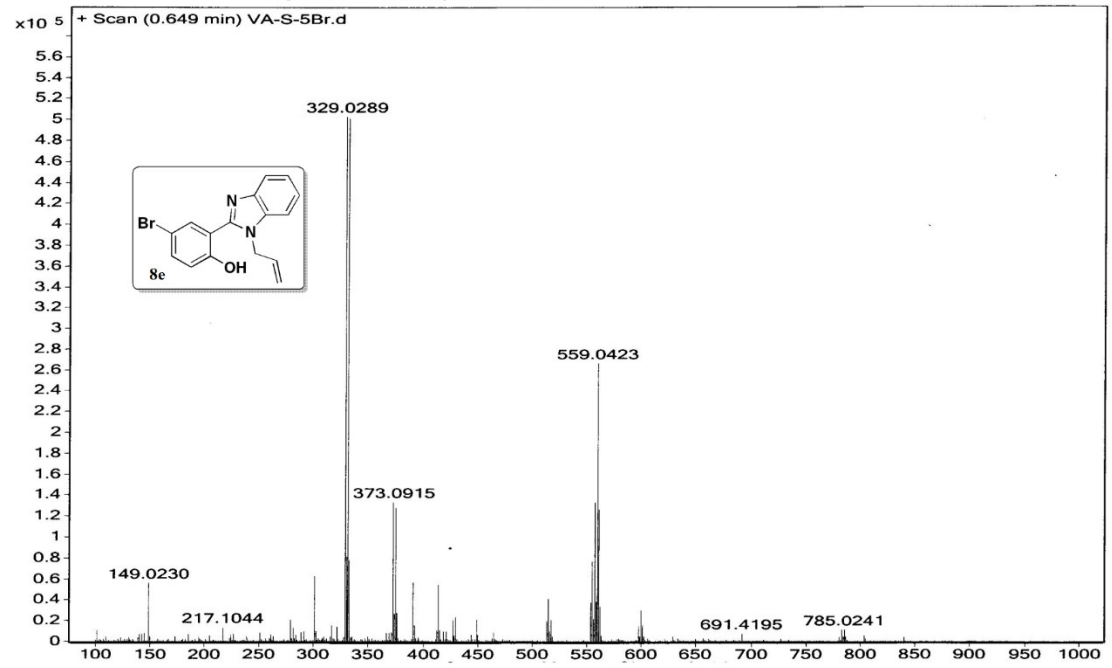
Sample Name	VA-I-S-1	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	VA-I-S-1.d	**ACQ Method**	Pondicherry Universi	**Comment**	VA-MB-UNK	**Acquired Time**	25-08-2015 10:56:22



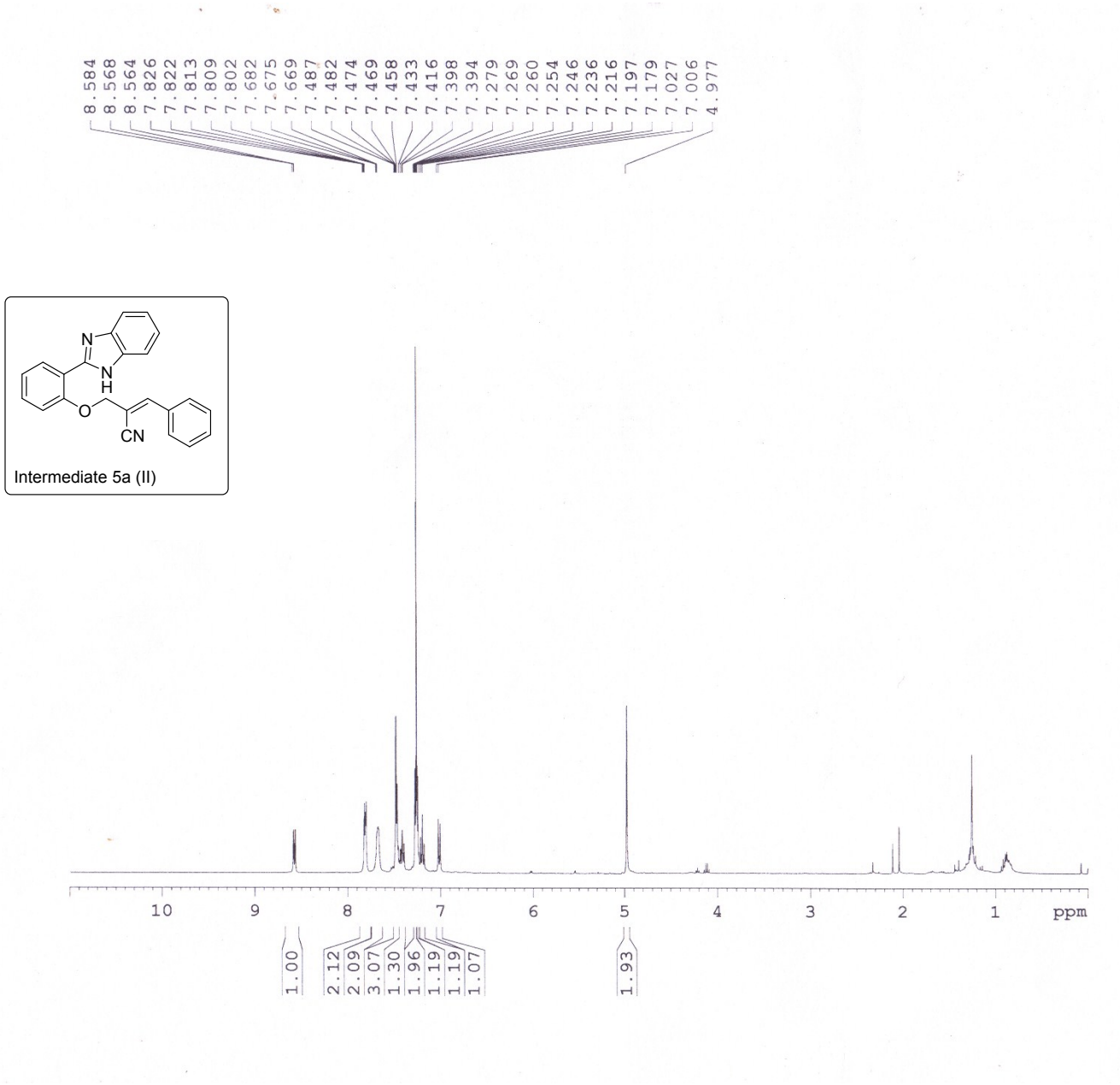

7.620
7.614
7.431
7.424
7.322
7.314
7.307
7.299
7.260
6.793
6.785
6.779
6.771
6.758
6.736
6.695
6.686
6.681
6.672
6.066
6.063
6.055
6.038
6.028
6.021
5.153
5.150
5.146
5.142
5.138
5.134
5.125
5.122
3.508
3.492
N
Br
N
Se
OH
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.37
1.08
2.23
1.12
1.33
1.17
1.07
1.87
2.00


156.12
150.53
135.84
134.52
132.89
131.91
131.72
125.17
119.81
117.92
116.66
113.45
113.39
112.88
110.48
77.48
77.16
76.84
34.10
N
N
Br
OH
Se
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

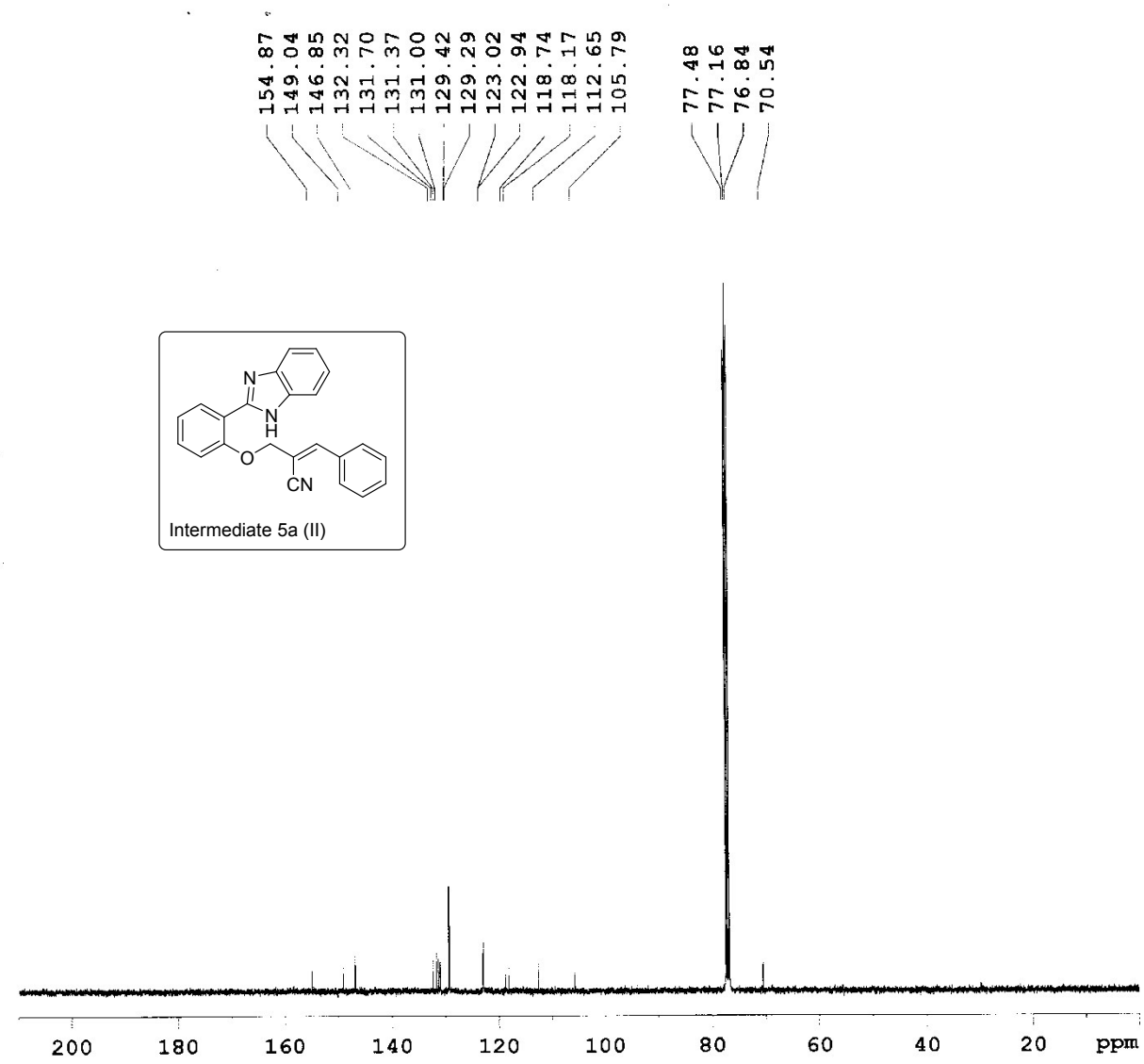
Sample Name	VA-S-5Br	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	VA-S-5Br.d	**ACQ Method**	Pondicherry Universi	**Comment**	MSK-MB-328.0211	**Acquired Time**	27-08-2015 12:36:54



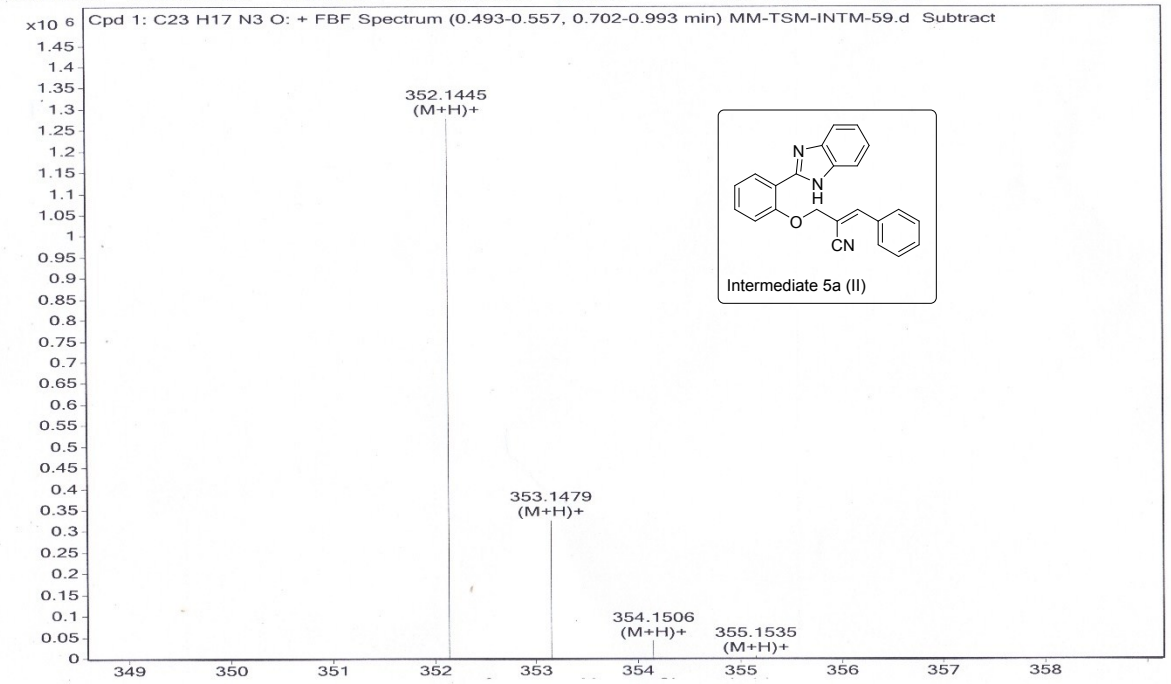
^{1}H NMR of intermediate (5a)



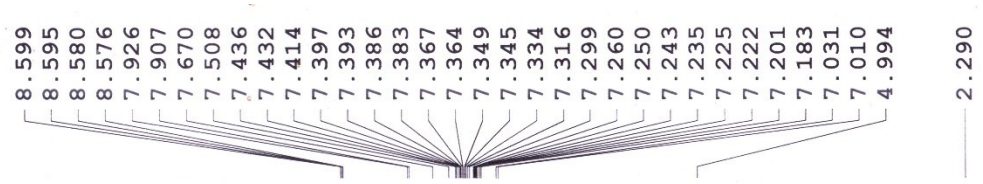
^{13}C NMR of intermediate 5a (II)

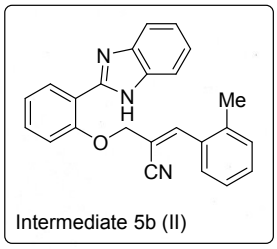


Sample Name	MM-TSM-INTM-59	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	MM-TSM-INTM-59.d	**ACQ Method**	Pondicherry Universi	**Comment**	MM-MB-351.1372	**Acquired Time**	22-04-2019 13:11:57

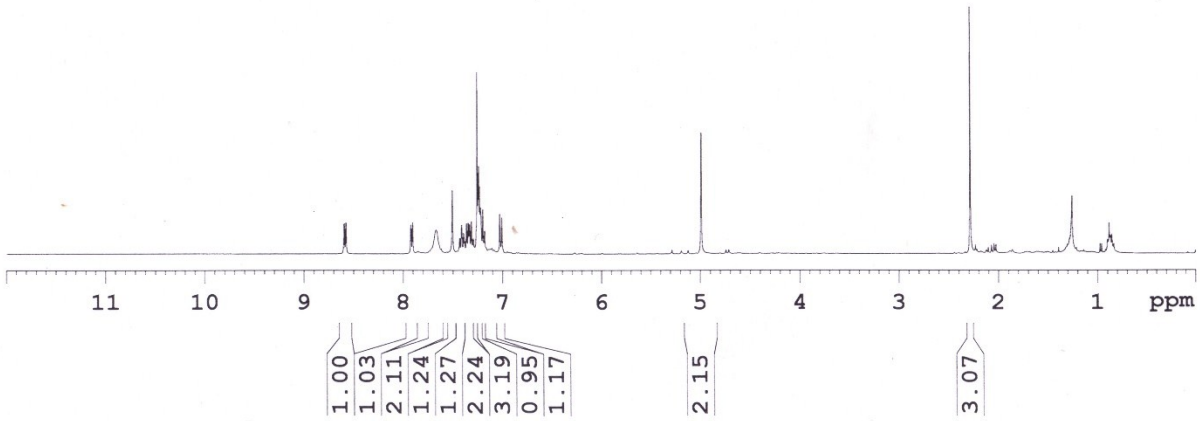


^{1}H NMR of intermediate 5b (II)

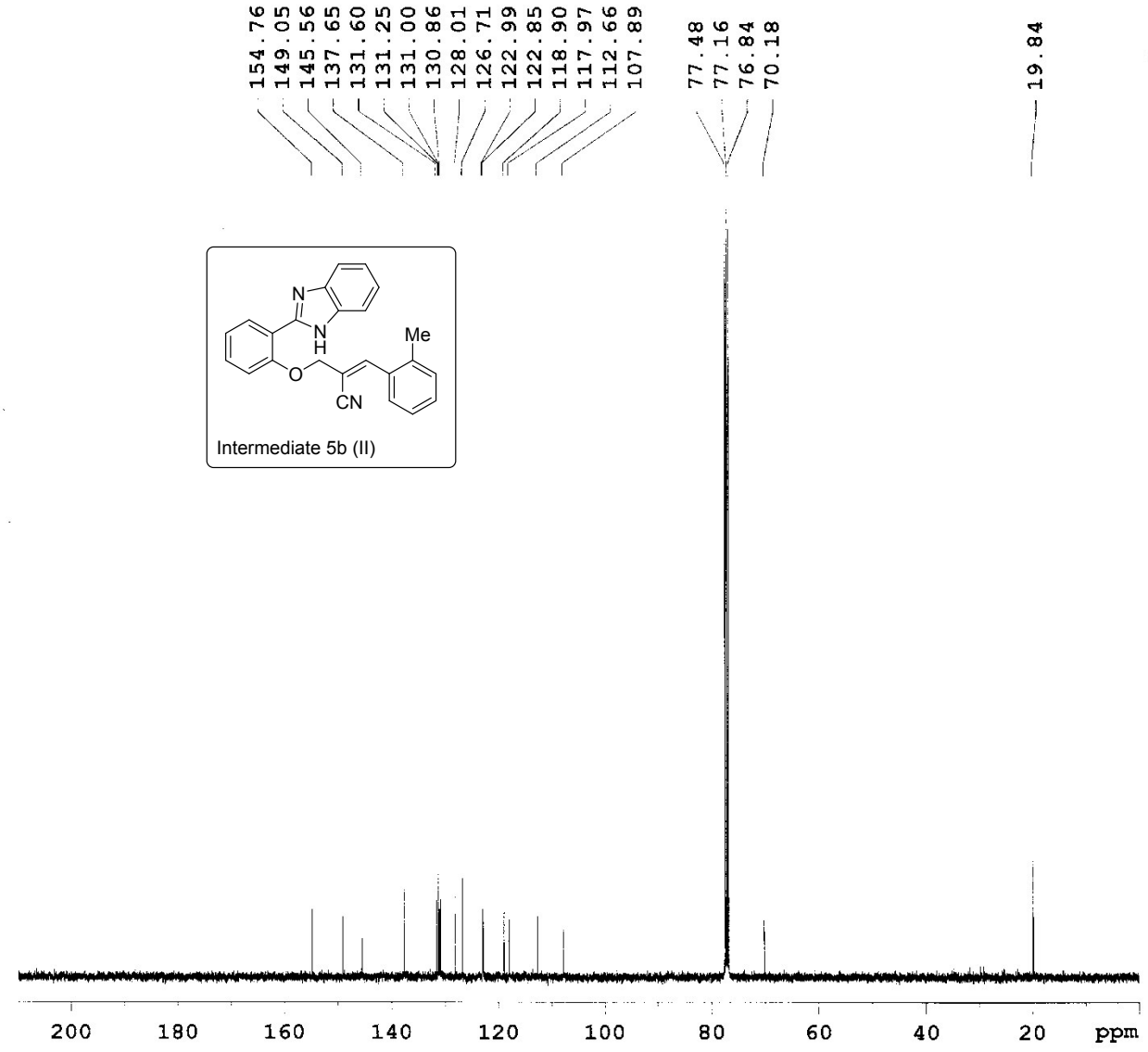




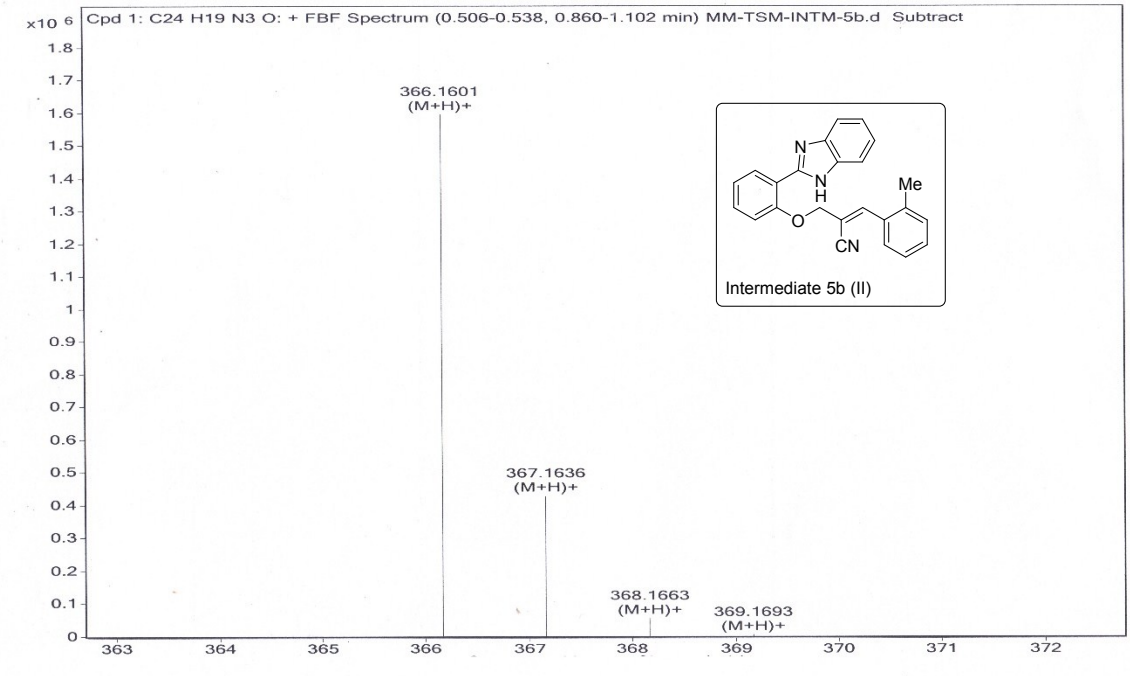
Intermediate 5b (II)



^{13}C NMR of intermediate 5b (II)



Sample Name	MM-TSM-INTM-5b	**Position**		**Instrument Name**	Q-TOF	**User Name**	QTOF-PU\admin
Inj Vol	-1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	MM-TSM-INTM-5b.d	**ACQ Method**	Pondicherry Universi	**Comment**	MM-MB-365.1528	**Acquired Time**	22-04-2019 13:15:57



Crystal Structure of **5a**

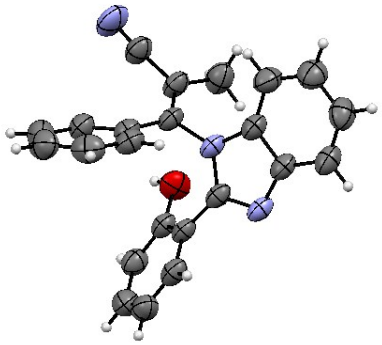


Table 1 Crystal data and structure refinement for 5a.

Identification code	MB-MN-688-S
Empirical formula	$C_{13}H_{14}N_2O_{0.07}$
Formula weight	199.40
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	20.4023(13)
b/Å	16.0765(13)
c/Å	11.2547(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3691.5(4)
Z	14
ρ_{calc}g/cm^3	1.256
μ/mm^{-1}	0.076
F(000)	1492.0
Crystal size/mm^3	0.36 × 0.34 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.956 to 58.36
Index ranges	$-27 \leq h \leq 16$, $-20 \leq k \leq 18$, $-13 \leq l \leq 15$
Reflections collected	10778
Independent reflections	6348 [R_{int} = 0.0335, R_{sigma} = 0.0538]
Data/restraints/parameters	6348/1/491
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0495, wR_2 = 0.0987
Final R indexes [all data]	R_1 = 0.0945, wR_2 = 0.1219
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15
Flack parameter	-0.1(10)