Electronic Supporting Information (ESI)

Metal-free oxidative cyclization of acetophenones with diamines: A facile access to phenylpyridines

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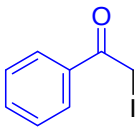
SECTION S1. EXPERIMENTAL PROCEDURES AND SPECTRAL DATA

S1.1. Chemistry protocols

General. All chemicals were obtained from Sigma-Aldrich Company and used as received. ^{1}H, ^{13}C and DEPT NMR spectra were recorded on Brucker-Avance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm; CD_3OD, 3.31 ppm). The carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$, 77.16 ppm; CD_3OD, 49.0). ESI-MS and HRMS spectra were recorded on Agilent 1100 LC-Q-TOF and HRMS-6540-UHD machines. IR spectra were recorded on Perkin-Elmer IR spectrophotometer. Melting points were recorded on digital melting point apparatus. HPLC analysis was done on Shimadzu HPLC system (model: LC-6AD) equipped with a PDA detector (model: SPD-M20A) using Enable C_{18} G (5µm, 4.6 × 250 mm) column. Mobile phase used was ACN: Water (90:10) isocratic elution at flow rate of 1ml/min.

Procedure for synthesis of 2-iodo-1-phenylethanone (V):[1] To the solution of acetophenone **1a** (1 equiv.) in ethanol was added CuO(II) (20 mol%) and iodine (20 mol%) and reaction mixture was heated at 80 ^{o}C for 2 hrs. After completion of the reaction, solvent was evaporated. Ethyl acetate and water was added to reacton mixture and organic layer was separated, dried over anhydrous sodium sulphate and concentarted in vacuo to get crude product. The crude residue was purified over silica gel column chromatography (EtOAc/hexane) to get product **V**.

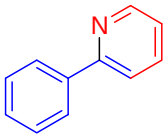


V

2-Iodo-1-phenylethanone (V): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.60-7.58 (m, 1H), 7.58-7.45 (m, 2H), 4.35 (s, 2H); GC-MS: *m/z* (EI) 246 (M^{+}, 100), 127 (65), 106 (125).

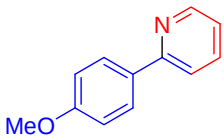
Procedure for synthesis of 2-phenylpyridines 3a-t and 3-phenylpyridines 5a-b: To a solution of acetophenones **1a-t** or phenylacetones **4a-b** (1 equiv.) in 2 mL of DMSO was added 8 mol% iodine, 10 µl of HCl and 3 equiv of 1,3-diaminopropane (**2**) and resulting mixture was stirred at 80 ^{o}C under oxygen atmosphere for 4 hrs. After completion of the reaction, iodine was quenched with sodium thiosulphate solution. Ethyl acetate was added to the reaction mixture and organic layer was separated, dried over anhydrous sodium sulphate and concentrated over vacuo rotavapor to get crude product. The crude residue was chromatographed on a silica gel column (#100-200) using EtOAc/hexane as eluent to get titled products **3a-t** and **5a-b**.

2-Phenylpyridine (3a):



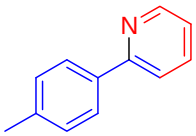
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68-8.67 (m, 1H), 7.99-7.97 (m, 2H), 7.69-7.68 (m, 2H), 7.47-7.37 (m, 3H), 7.20- 7.16 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 149.7, 139.4, 136.8, 129, 128.8, 126.9, 122.1, 120.6; IR ($CHCl_3$): ν_{max} 3086, 3062, 3036, 3007, 2921, 1954, 1766, 1586, 1580, 1565, 1468, 1449, 1425, 1293, 1269, 1152, 1060, 1039, 1020 cm^{-1}; GC-MS: *m/z* (EI) 157 (M+H, 100), 254 (31), 157 (15); HR-ESIMS: *m/z* 156.0806 calcd for $C_{11}H_9N + H^+$ (156.0808).

2-(4-Methoxyphenyl) pyridine (3b):



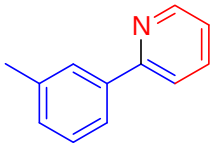
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.0 Hz, 1H), 7.96-7.94 (m, 2H), 7.71-7.67 (m, 2H), 7.18- 7.01 (m, 1H), 7.01-6.99 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 157.1, 149.5, 136.7, 132, 128.4, 128.2, 121.4, 119.8, 114.1, 114.0, 55.4; IR ($CHCl_3$): ν_{max} 3356, 3052, 3005, 2956, 2926, 2852, 2837, 1608, 1589, 1515, 1466, 1434, 1305, 1270, 1248, 1176, 1039, 1024 cm^{-1}; GC-MS: *m/z* (EI) 185 (M^+, 100), 170 (15), 142 (39), 115 (8); HR-ESIMS: *m/z* 186.0917 calcd for $C_{12}H_{12}NO+H^+$ (186.0913).

2-(p-Tolyl) pyridine (3c):



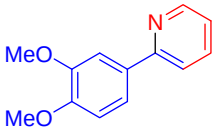
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4.8 Hz, 1H), 7.90 (d, *J* = 8 Hz, 2H), 7.72-7.71 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.18 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 149.6, 139, 136.7, 136.6, 129.5, 126.8, 121.8, 120.3, 21.3; IR ($CHCl_3$): ν_{max} 3747, 3584, 3348, 2922, 2852, 2359, 1729, 1588, 1464, 1018 cm^{-1}; GC-MS: *m/z* (EI) 169 (M^+, 100), 154 (9), 115 (8); HR-ESIMS: *m/z* 170.0964 calcd for $C_{12}H_{25}N+H^+$ (170.0965).

2-(m-Tolyl) pyridine (3d):



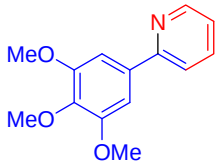
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 4 Hz, 1H), 7.90 (d, *J* = 8 Hz, 2H), 7.71-7.70 (m, 2H), 7.29-7.26 (m, 2H), 7.20-7.19 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 149.6, 138.9, 136.7, 136.6, 129.5, 126.8, 121.8, 120.3, 21.3; IR ($CHCl_3$): ν_{max} 3371, 3051, 3007, 2923, 2854, 1614, 1588, 1563, 1467, 1433, 1298, 1266, 1185, 1094, 1016cm^{-1}; GC-MS: *m/z* (EI) 169 (M^+, 100), 154 (8), 139 (5), 127 (3), 115 (8); HR-ESIMS: *m/z* 170.0962 calcd for $C_{12}H_{11}N+H^+$ (170.0964).

2-(3, 4-Dimethoxyphenyl) pyridine (3e):



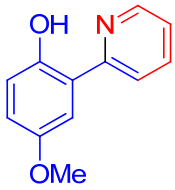
White solid; m.p. 75-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4 Hz, 1H), 7.71-7.68 (m, 3H), 7.56- 7.49 (m, 1H), 7.19-7.16 (m, 1H), 6.96 (d, *J* = 8 Hz, 1H), 3.99 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 150.0, 149.5, 149.3, 136.6, 132.4, 121.5, 119.9, 119.3, 111.2, 110.0, 55.98, 55.96; IR ($CHCl_3$): ν_{max} 3584, 3384, 3082, 3003, 2956, 2932, 2837, 1726, 1584, 1564, 1519, 1466, 1433, 1405, 1254, 1066, 1026 cm^{-1}; GC-MS: *m/z* (EI) 215 (M^+, 100), 200 (27), 172 (37), 144 (22), 129 (31), 117 (6), 102 (11); HR-ESIMS: *m/z* 216.1023 calcd for $[C_{13}H_{13}NO_2+H]^+$ (216.1019).

2-(3, 4, 5-Trimethoxyphenyl) pyridine (3f):



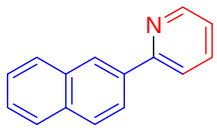
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68-8.67 (m, 1H), 7.77-7.69 (m, 3H), 7.26-7.20 (m, 2H), 3.96 (s, 6H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156, 152.5, 148.5, 138, 135.7, 134, 121, 119.3, 103.1, 59.9, 55.2; IR ($CHCl_3$): ν_{max} 3355, 2923, 2851, 1585, 1565, 1469, 1407, 1127, 1017 cm^{-1}; GC-MS: *m/z* (EI) 245 (M^+, 100), 230 (64), 202 (38), 187 (40), 172 (51), 130 (20), 116 (32); HR-ESIMS: *m/z* 246.1136 calcd for $[C_{14}H_{15}NO_3+H]^+$ (246.1125).

4-Methoxy-2-(pyridin-2-yl) phenol (3g):



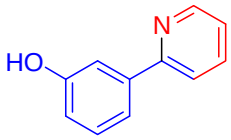
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 4 Hz, 1H), 7.87-7.82 (m, 2H), 7.31-7.23 (m, 2H), 6.98-6.91 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 154.1, 152.1, 146.0, 137.8, 121.6, 119.1, 118.8, 117.9, 111.0, 56.0; IR ($CHCl_3$): ν_{max} 3585, 2925, 2850, 1725, 1595, 1564, 1493, 1463, 1420, 1287, 1225, 1178, 1159, 1057, 1041 cm^{-1}; ESI-MS: *m/z* 202.04 $[M+H]^+$; HR-ESIMS: *m/z* 202.0868 calcd for $[C_{12}H_{12}NO_2+H]^+$ (202.0863).

2-(Naphthalen-2-yl) pyridine (3h):



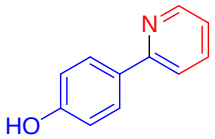
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80-8.78 (m, 1H), 8.09-8.07 (m, 1H), 7.92-7.90 (m, 2H), 7.83-7.79 (m, 1H), 7.59-7.48 (m, 5H), 7.34-7.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 147.7, 136.7, 134.6, 132.1, 129.3, 127.1, 126.5, 125.6, 124.6, 124, 123.8, 123.5, 123.2, 120.2; IR ($CHCl_3$): ν_{max} 3049, 3008, 2924, 2853, 1587, 1563, 1472, 1438, 1425, 1251, 1189, 1092, 1046 cm^{-1}; GC-MS: *m/z* (EI) 205 (M^+, 100), 178 (6); HR-ESIMS: *m/z* 206.0952 calcd for $[C_{15}H_{12}N+H]^+$ (206.0964).

3-(Pyridin-2-yl) phenol (3i):



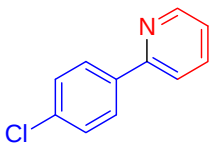
Yellow solid; m.p. 150-155 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67-8.66 (m, 1H), 7.79-7.66 (m, 2H), 7.56-7.55 (m, 1H), 7.45-7.41 (m, 1H), 7.32-7.23 (m, 2H), 6.90-6.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 156.9, 149.2, 140.5, 137.3, 130, 122.4, 121.4, 119, 116.6, 114.4; IR ($CHCl_3$): ν_{max} 3850, 3745, 3306, 2924, 2852, 1728, 1586, 1565, 1456, 1428, 1312, 1281, 1210, 1154, 1020 cm^{-1}; GC-MS: *m/z* (EI) 171 (M^+, 100), 143 (52), 117 (68); HR-ESIMS: *m/z* 172.0755 calcd for $C_{11}H_9NO+H^+$ (172.0757).

4-(Pyridin-2-yl) phenol (3j):



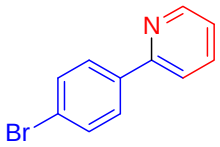
White solid; HPLC: 95% (t_R = 3.22 min); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62-8.61 (m, 1H), 7.77-7.73 (m, 3H), 7.65 (d, *J* = 8 Hz, 1H), 7.22-7.20 (m, 1H), 6.80 (d, *J* = 4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$ + CD_3OD): δ 159.5, 159, 150.3, 138.6, 132.1, 129.8, 129.7, 122.8, 121.9, 117, 116.9; IR ($CHCl_3$): ν_{max} 3585, 3333, 2921, 2851, 1595, 1564, 1518, 1470, 1443, 1268, 1237, 1173, 1020 cm^{-1}; ESI-MS: *m/z* 172.18 $[M+H]^+$.

2-(4-Chlorophenyl) pyridine (3k):



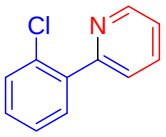
Yellow solid; m.p. 47-51 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 4 Hz, 1H), 7.95 (d, *J* = 8 Hz, 2H), 7.76-7.69 (m, 2H), 7.46 (d, *J* = 12 Hz, 2H), 7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 149.7, 137.8, 136.8, 135.1, 128.9, 128.2, 122.3, 120.3; IR ($CHCl_3$): ν_{max} 3584, 3357, 2922, 2851, 1588, 1464, 1434, 1398, 1089, 1012 cm^{-1}; GC-MS: *m/z* (EI) 189 (M^+, 100), 127 (34), 102 (5); HR-ESIMS: *m/z* 190.0411 calcd for $C_{11}H_8ClN+H^+$ (190.0418).

2-(4-Bromophenyl) pyridine (3l):



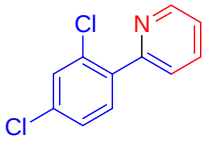
Yellow solid; m.p. 60-65 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.68 (m, 1H), 7.88-7.86 (m, 2H), 7.75 (m, 1H), 7.70-7.69 (m, 1H), 7.61-7.59 (m, 2H), 7.26-7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 149.8, 138.3, 136.8, 131.9, 128.5, 123.4, 122.4, 120.3; IR ($CHCl_3$): ν_{max} 3584, 3050, 3007, 2923, 2851, 1586, 1560, 1464, 1433, 1289, 1100, 1030 cm^{-1}; GC-MS: *m/z* (EI) 233 (M^+, 100), 155 (10), 127 (20); HR-ESIMS: *m/z* 233.9913 calcd for $C_{11}H_9BrN+H^+$ (233.9913).

2-(2-Chlorophenyl) pyridine (3m):



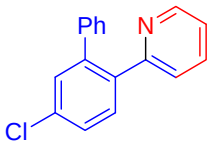
Yellow oil; HPLC: 85% (t_R = 4.17 min); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.75-8.73 (m, 1H), 7.81-7.76 (m, 1H), 7.68-7.65 (m, 1H), 7.62-7.60 (m, 1H), 7.50-7.48 (m, 1H), 7.38-7.30 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 149.5, 139.1, 136, 132.2, 131.6, 130.1, 130, 127, 125, 122.5; IR ($CHCl_3$): ν_{max} 3584, 3356, 2923, 2852, 1652, 1615, 1429, 1321, 1219, 1156, 1020 cm^{-1}; ESI-MS: *m/z* 190.00 $[M+H]^+$; HR-ESIMS: *m/z* 190.0410 calcd for $[C_{11}H_8ClN+H]^+$ (190.0418).

2-(2, 4-Dichlorophenyl) pyridine (3n):



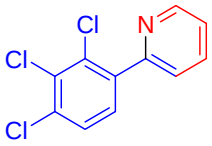
Yellow solid; m.p. 80-85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74-8.72 (m, 1H), 7.78-7.76 (m, 1H), 7.66-7.64 (m, 1H), 7.58-7.56 (m, 1H), 7.51 (d, *J* = 4 Hz, 1H), 7.38-7.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ154.4, 148.2, 136.1, 134.6, 133.4, 131.5, 131, 128.5, 126, 123.4, 121.3; IR ($CHCl_3$): ν_{max} 3584, 3360, 3069, 2957, 2926, 2854, 1726, 1593, 1571, 1460, 1432, 1376, 1287, 1105, 1084, 1051 cm^{-1}; GC-MS: *m/z* (EI) 224 (M^+, 100), 190 (25), 153 (16), 126 (10); HR-ESIMS: *m/z* 224.0029 calcd for $[C_{11}H_7Cl_2N+H]^+$ (224.0028).

2-(5-Chloro-[1, 1'-biphenyl]-2-yl) pyridine (3o):



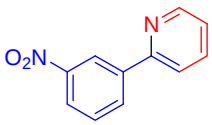
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (dd, *J* = 2, 4.8 Hz, 1H), 7.73(dd, *J* = 1.6, 7.6 Hz, 1H), 7.35-7.28 (m, 6H), 7.20-7.15 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 148.5, 139.6, 138.7, 138.6, 136.1, 134, 131.3, 129.5, 128.5, 128.1, 127.4, 122.3; IR ($CHCl_3$): ν_{max} 3584, 3352, 3057, 3852, 2924, 1724, 1579, 1596, 1579, 1443, 1419, 1091, 1073, 1012 cm^{-1}; GC-MS: *m/z* (EI) 265 (M^+, 100), 228 (41), 202 (8), 114 (13); HR-ESIMS: *m/z* 266.0735 calcd for $C_{17}H_{12}ClN+H^+$ (266.0731).

2-(2, 3, 4-Trichlorophenyl) pyridine (3p):



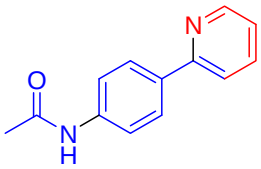
White solid; m.p. 75-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4 Hz, 1H), 7.81-7.77 (m, 1H), 7.61 (d, *J* = 8 Hz, 1H), 7.50-7.42 (m, 2H), 7.34-7.32 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156, 149.7, 139.7, 136.1, 134.2, 132.5, 132.4, 129.5, 128.4, 124.8, 123; IR ($CHCl_3$): ν_{max} 3584, 3356, 3055, 2924, 2853, 1726, 1649, 1588, 1568, 1445, 1429, 1359, 1286, 1153, 1020 cm^{-1}; GC-MS: *m/z* (EI) 256 (M^+, 100), 222 (37), 186 (77), 152 (26), 111 (32); HR-ESIMS: *m/z* 257.9636 calcd for $[C_{11}H_8Cl_3N+H]^+$ (257.9639).

2-(3-Nitrophenyl)pyridine (3q):



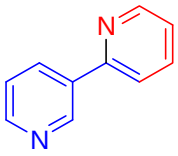
Yellow solid; m.p. 120-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97-8.96 (m, 1H), 8.56-8.53 (m, 1H), 8.34- 8.31 (m, 1H), 7.99-7.97 (m, 1H), 7.89-7.87 (m, 1H), 7.74-7.70 (m, 2H), 7.54-7.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 148.9, 140.6, 138.5, 132.9, 130.9, 129.9, 128.9, 124, 121.8, 120; IR ($CHCl_3$): ν_{max} 3584, 3352, 2925, 2853, 1723, 1592, 1531, 1347, 1281, 1072, 1020 cm^{-1}; ESI-MS: *m/z* 201.1 $[M+H]^+$.

N-(4-(Pyridin-2-yl) phenyl) acetamide (3r):



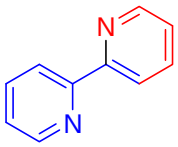
Yellow solid; m.p. 155- 160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4 Hz, 1H), 7.94 (d, *J* = 8 Hz, 2H), 7.75-7.71 (m, 1H), 7.69 (d, *J* = 4 Hz, 1H), 7.63 (d, *J* = 8 Hz, 2H), 7.22-7.19 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$ + CD_3OD): δ 170.2, 157, 148.8, 139.5, 137.7, 134.3, 127.5, 122.1, 121.1, 119.9, 23.6; IR ($CHCl_3$): ν_{max} 3584, 3300, 2923, 2852, 1668, 1600, 1536, 1467, 1404, 1371, 1317, 1153, 1018 cm^{-1}; ESI-MS: *m/z* 213.1 $[M+H]^+$; HR-ESIMS: *m/z* 213.0997 calcd for $[C_{13}H_{12}N_2+H]^+$ (213.1022).

2, 3'-Bipyridine (3s):



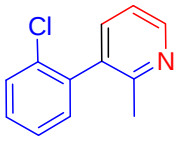
Yellow oil; HPLC: 92% (t_R = 3.83 min); ^{1}H NMR (400 MHz, CD_3OD): δ 9.17-9.16 (m, 1H), 8.70-8.69 (m, 1H), 8.62 (d, *J* = 4 Hz, 1H), 8.45-8.42 (m, 1H), 7.96-7.95 (m, 2H), 7.60-7.56 (m, 1H), 7.46-7.42 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 154.2, 149.5, 148.9, 147.2, 137.7, 135.3, 135.1, 124, 123.2, 121.2; IR ($CHCl_3$): ν_{max} 3584, 3348, 1925, 2853, 1723, 1587, 1460, 1433, 1282, 1017 cm^{-1}; GC-MS: *m/z* (EI) 156 (M^+, 100), 130 (30), 104 (10); HR-ESIMS: *m/z* 157.0758 calcd for $[C_{10}H_8N_2+H]^+$ (157.0760).

2, 2'-Bipyridine (3t):



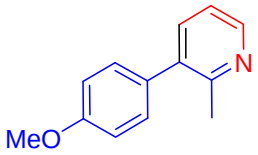
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69-8.68 (m, 2H), 8.41-8.39 (m, 2H), 7.84-7.80 (m, 2H), 7.32-7.29 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2, 149.2, 136.9, 123.7, 121.1; IR ($CHCl_3$): ν_{max} 3410, 3055, 3008, 2978, 1965, 1801, 1581, 1559, 1455, 1418, 1252, 1215, 1090, 1040, 1068 cm^{-1}; GC-MS: *m/z* (EI) 156 (M^+, 100), 128 (12), 102 (5); HR-ESIMS: *m/z* 157.0753 calcd for $[C_{10}H_8N_2+H]^+$ (157.0760).

3-(2-Chlorophenyl)-2-methylpyridine (5a):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55- 8.53 (m, 1H), 7.50-7.46 (m, 2H), 7.46-7.32 (m, 3H), 7.23-7.18 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 150, 139.9, 138.6, 135.9, 134.8, 132.3, 131.1, 130.7, 128.3, 122.2, 24.2; IR ($CHCl_3$): ν_{max} 3583, 3382, 2921, 2850, 1649, 1627, 1569, 1434, 1262, 1125, 1076, 1035, 1005 cm^{-1}; GC-MS: *m/z* (EI) 203 (M^+, 100), 139 (12), 126 (10), 115 (6); HR-ESIMS: *m/z* 204.0580 calcd for $[C_{12}H_{10}ClN+H]^+$ (204.0575).

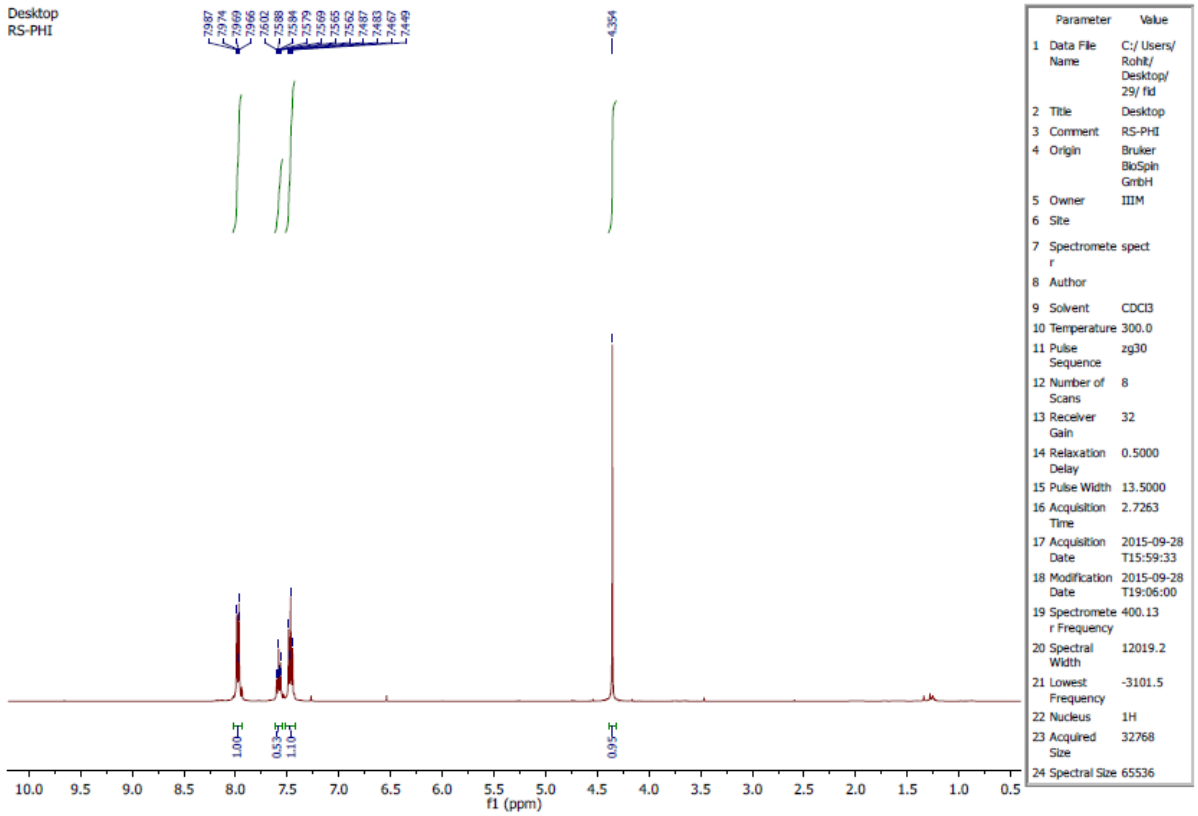
3-(4-Methoxyphenyl)-2-methylpyridine (5b):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47-8.46 (m, 1H), 7.51-7.48 (m, 1H), 7.25-7.23 (m, 2H), 7.16-6.99 (m, 1H), 6.98-6.95 (m, 2H), 3.85 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159, 155.9, 147.6, 137.2, 136.7, 132.2, 130.1, 121, 113.8, 56.3, 23.4; GC-MS: *m/z* (EI) 199 (M^+, 100), 154 (10).

SECTION S2. Scanned copies of ^{1}H, ^{13}C and DEPT135 NMR spectras of all compounds

S2.1. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-phenylpyridine (**3a**)



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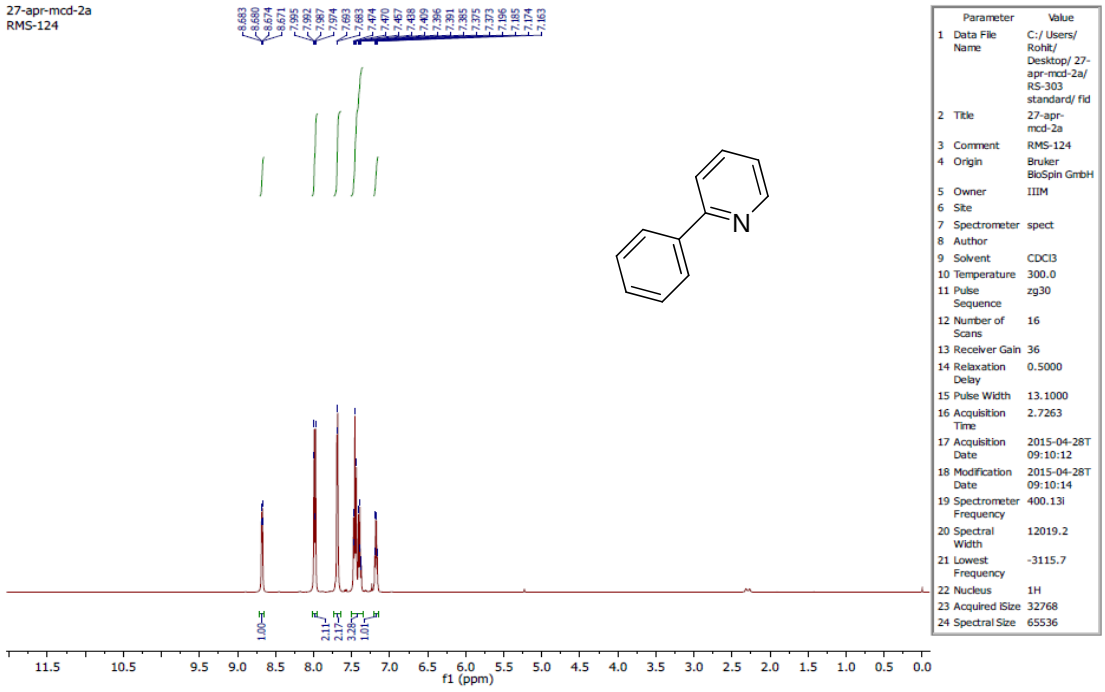
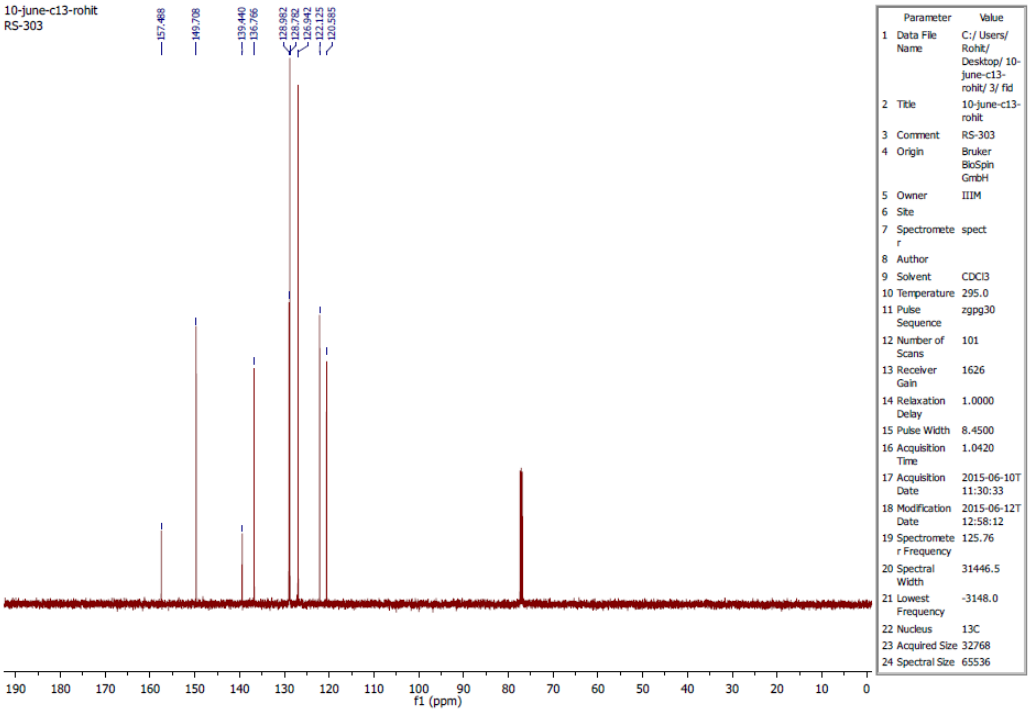
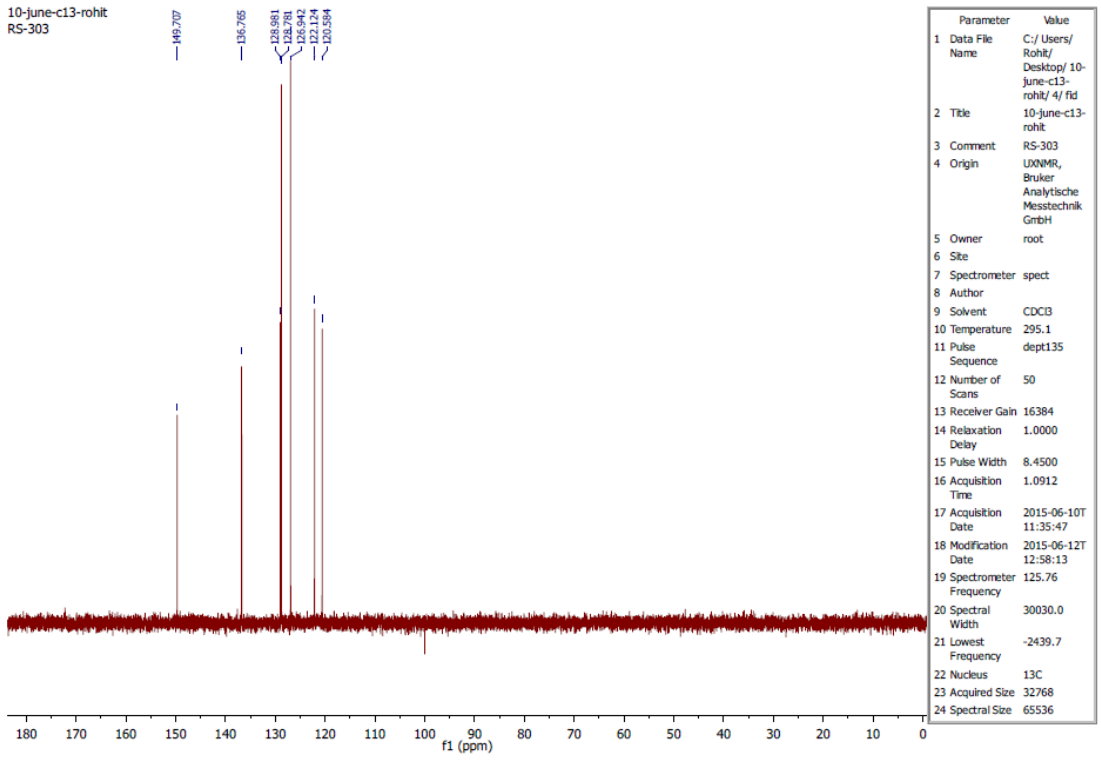
5	Owner	IIIM
6	Site	
7	Spectrometer	spect r
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zg30
12	Number of Scans	8
13	Receiver Gain	32
14	Relaxation Delay	0.5000
15	Pulse Width	13.5000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-09-28 T15:59:33
18	Modification Date	2015-09-28 T19:06:00
19	Spectrometer Frequency	400.13
20	Spectral Width	12019.2
21	Lowest Frequency	-3101.5
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

S2.2. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-phenylpyridine (**3a**)







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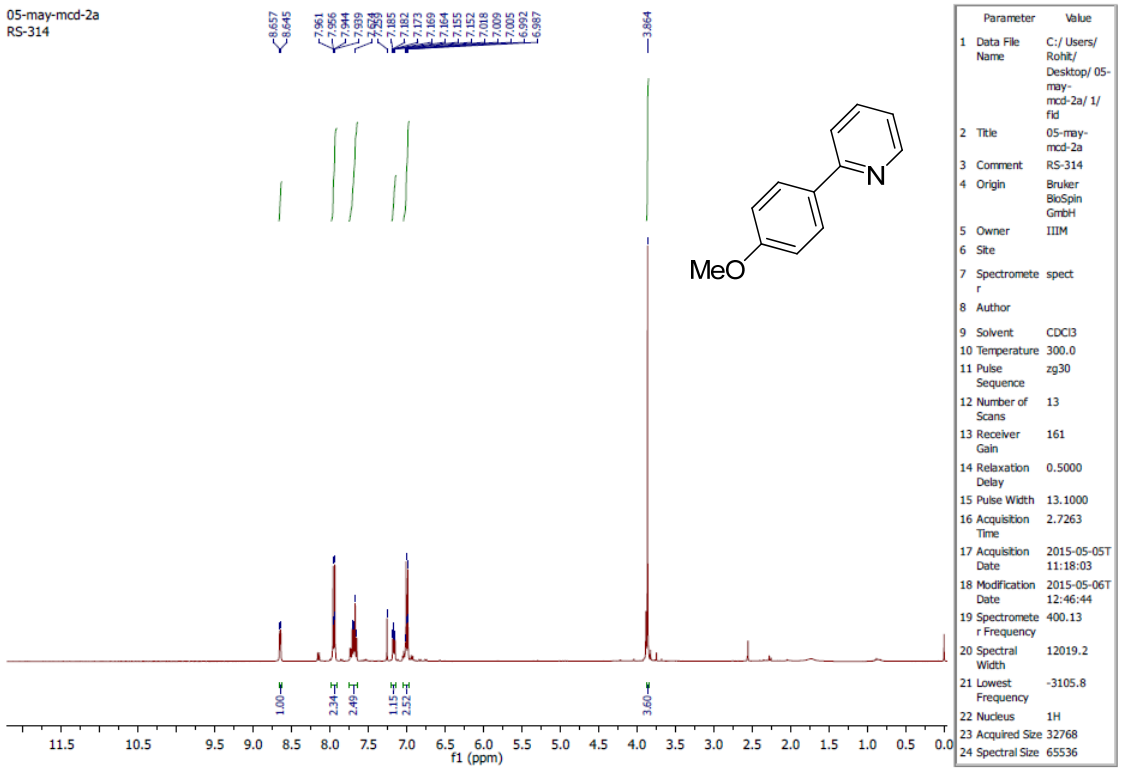
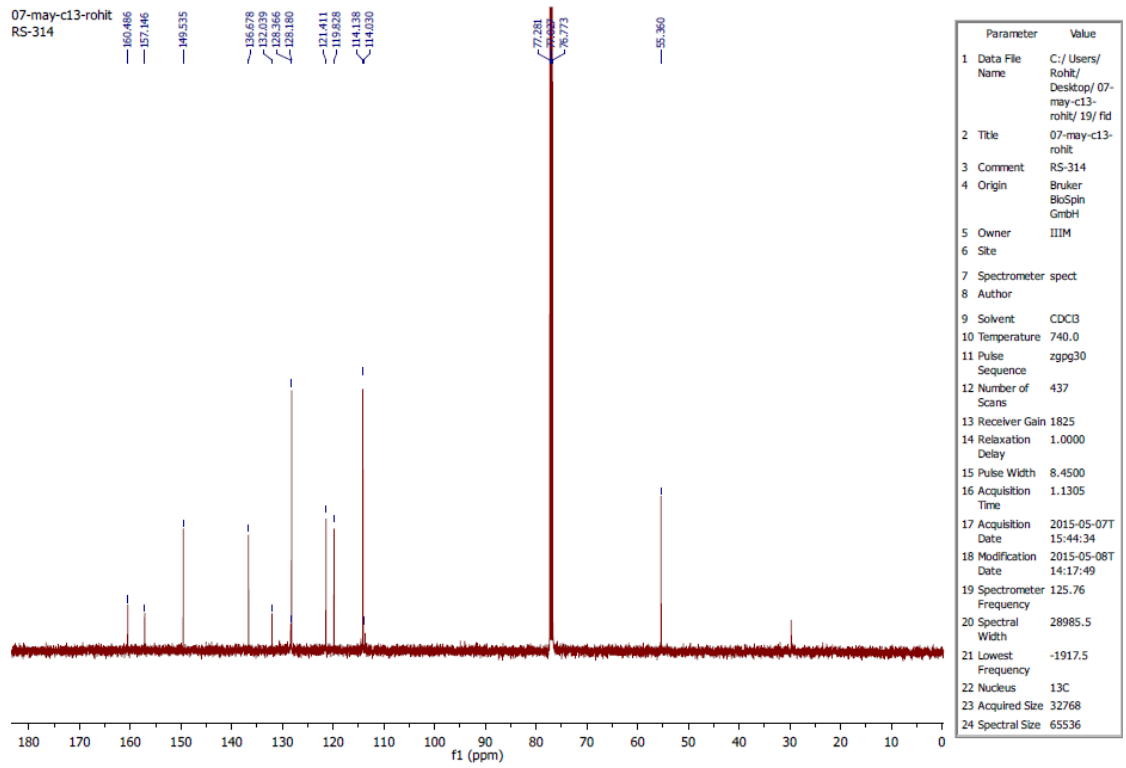
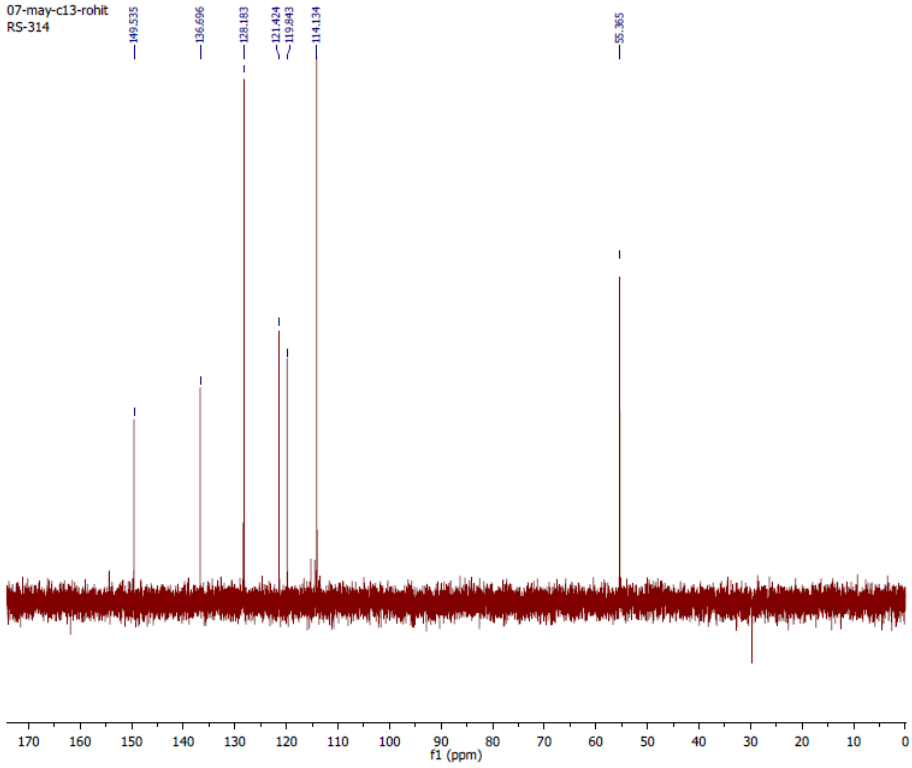
3	Comment	RS-303
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.1
11	Pulse Sequence	dept135
12	Number of Scans	50
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-06-10T 11:35:47
18	Modification Date	2015-06-12T 12:58:13
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.3. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(4-methoxyphenyl) pyridine (**3b**)







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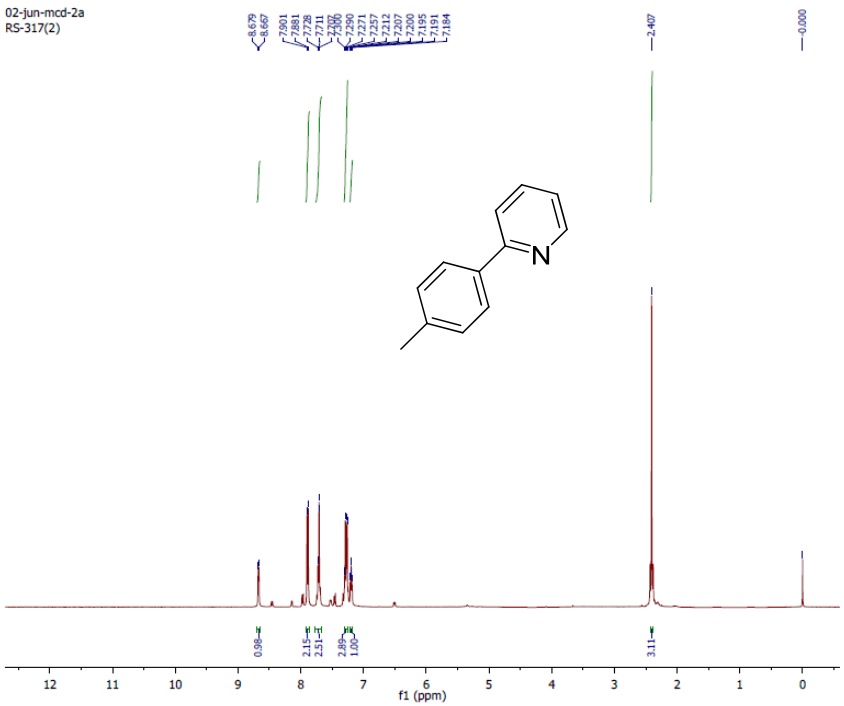
2	Title	07-may-c13-rohit
3	Comment	RS-314
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	740.0
11	Pulse Sequence	dept135
12	Number of Scans	177
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-05-07T 17:37:49
18	Modification Date	2015-05-08T 14:17:50
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.4. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(p-tolyl) pyridine (**3c**)



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1	Data File Name	C:/ Users/ Rohit/ Desktop/ 02-jun-mcd-2a/ 3/ fid
2	Title	02-jun-mcd-2a
3	Comment	RS-317(2)
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect r
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zg30
12	Number of Scans	8
13	Receiver Gain	161
14	Relaxation Delay	0.5000
15	Pulse Width	13.1000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-06-02 T13:43:18
18	Modification Date	2015-06-03 T12:06:44
19	Spectrometer Frequency	400.13
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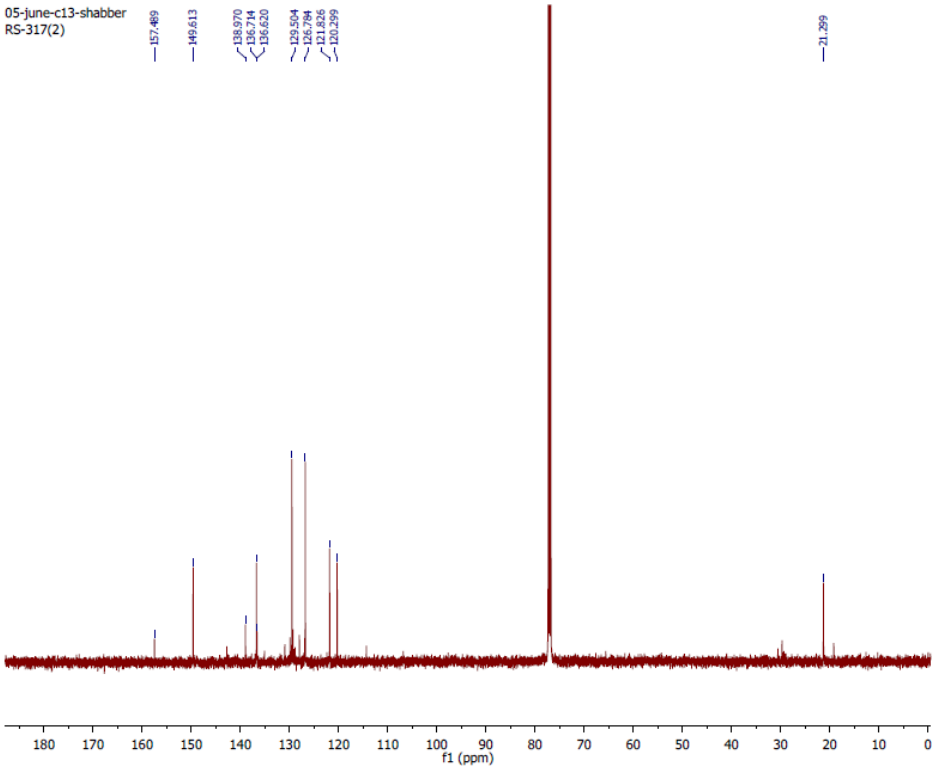
21	Lowest Frequency	-3106.8
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



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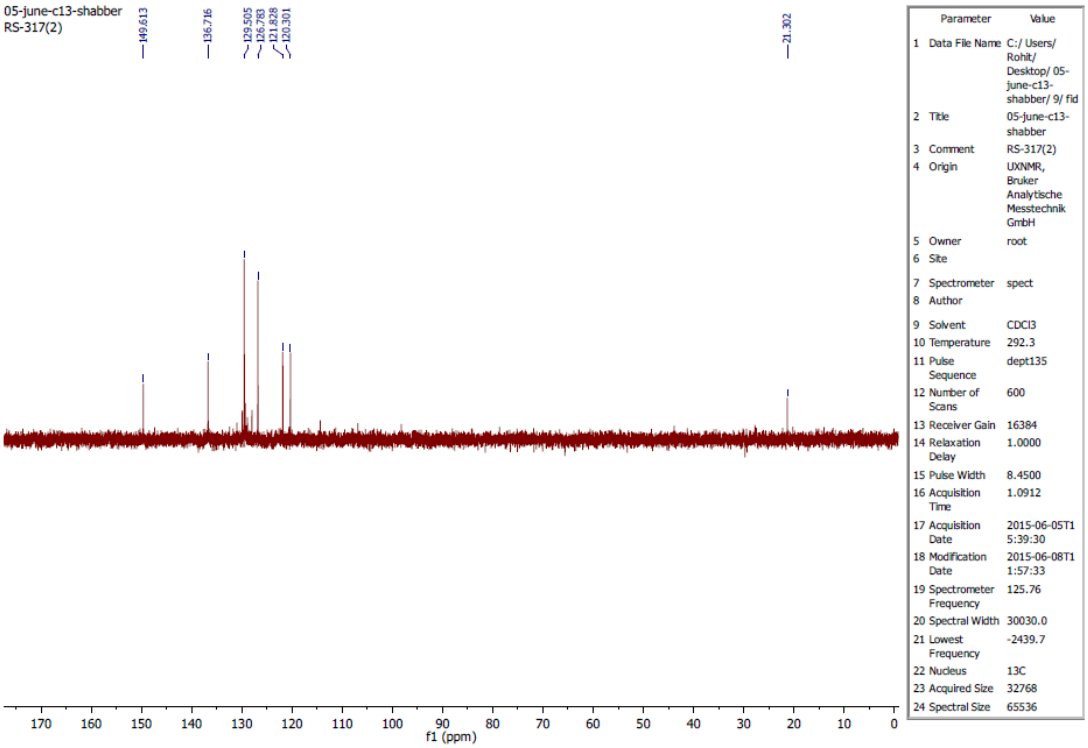
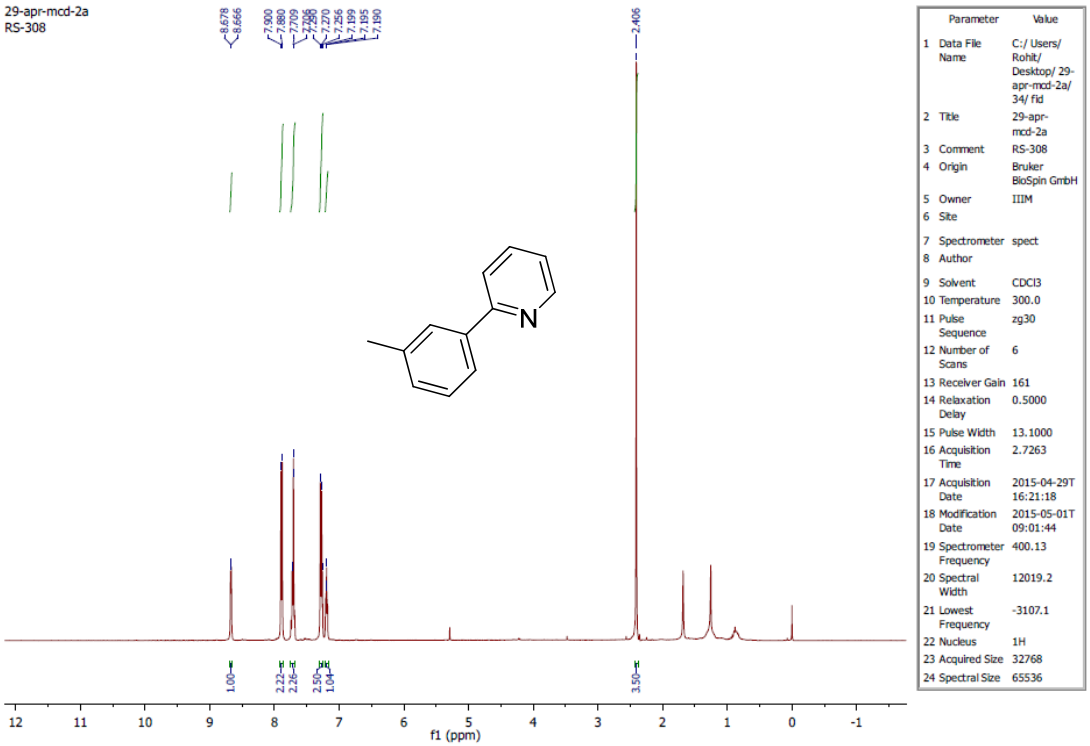
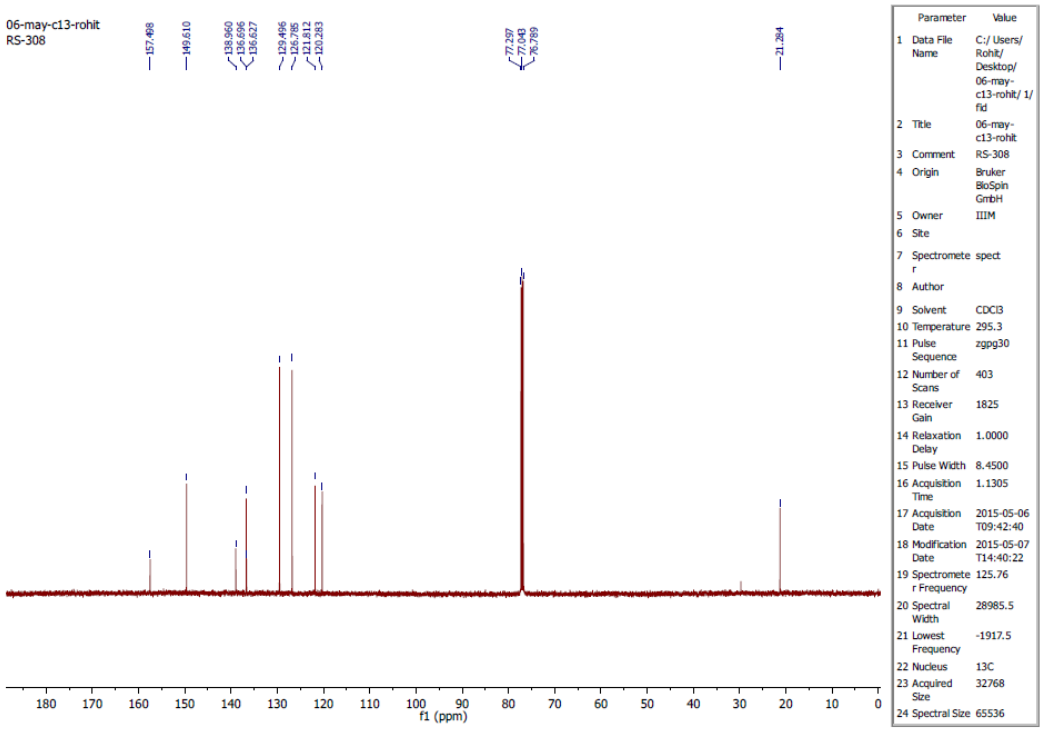
2	Title	05-june-c13-shabber
3	Comment	RS-317(2)
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.1
11	Pulse Sequence	zgpg30
12	Number of Scans	1200
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-06-05T 14:36:17
18	Modification Date	2015-06-08T 11:57:28
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



S2.5. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(m-tolyl) pyridine **(3d)**





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3	Comment	RS-308
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.3
11	Pulse Sequence	zgpg30
12	Number of Scans	403
13	Receiver Gain	1825
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15	Pulse Width	8.4500
16	Acquisition Time	1.1305
17	Acquisition Date	2015-05-06 T09:42:40
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19	Spectrometer Frequency	125.76
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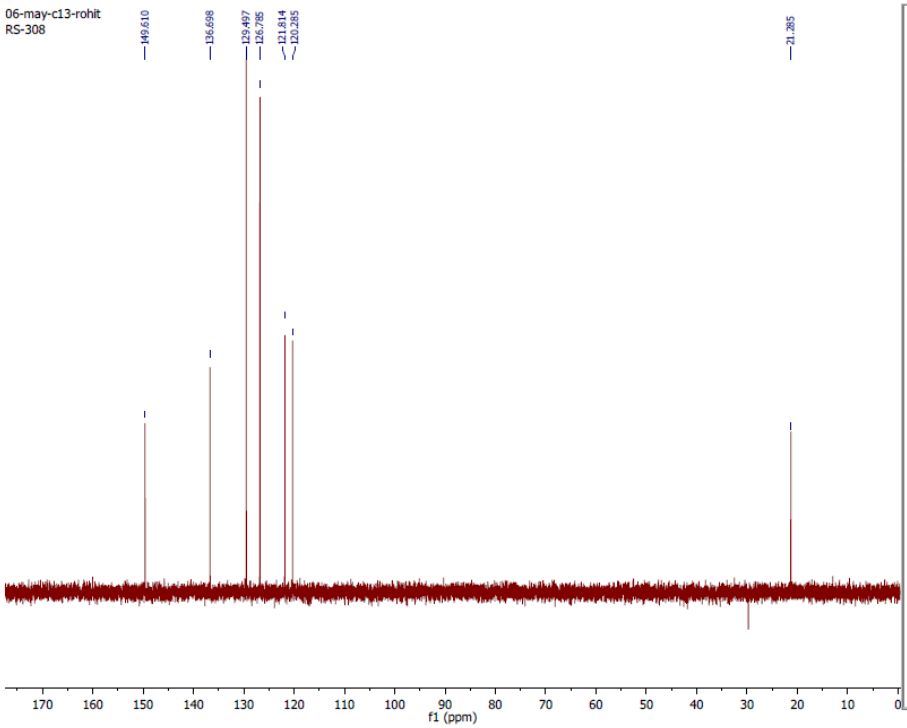
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



	Parameter	Value
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2	Title	06-may-c13-rohit
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4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.1
11	Pulse Sequence	dept135
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13	Receiver Gain	16384
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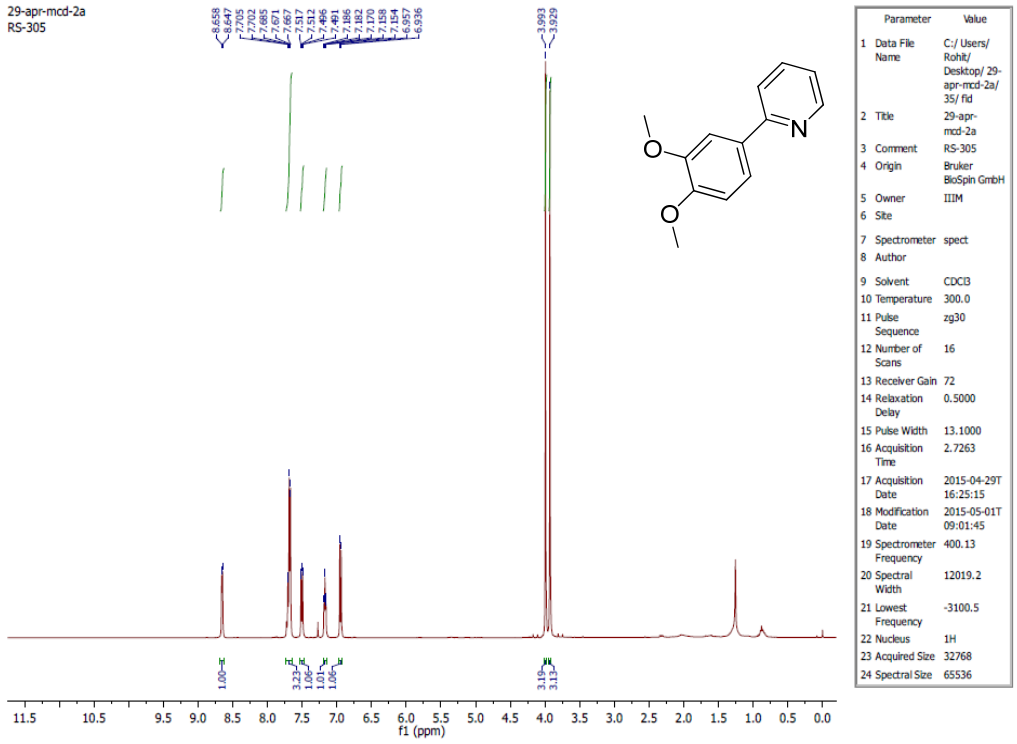
20	Spectral Width	31446.5
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.6. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(3,4-dimethoxyphenyl)pyridine (**3e**)



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5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
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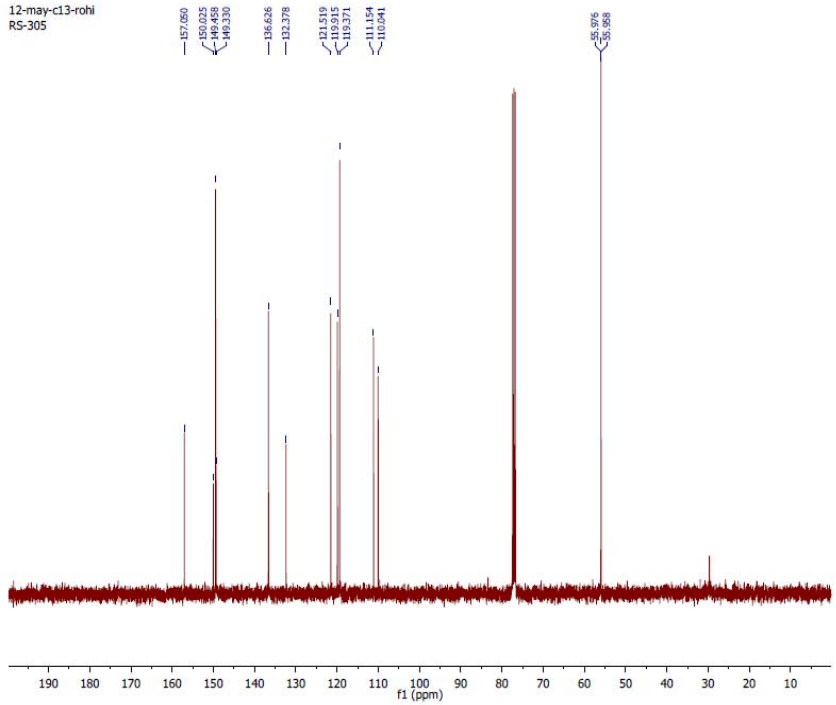
17	Acquisition Date	2015-04-29T 16:25:15
18	Modification Date	2015-05-01T 09:01:45
19	Spectrometer Frequency	400.13
20	Spectral Width	12019.2
21	Lowest Frequency	-3100.5
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



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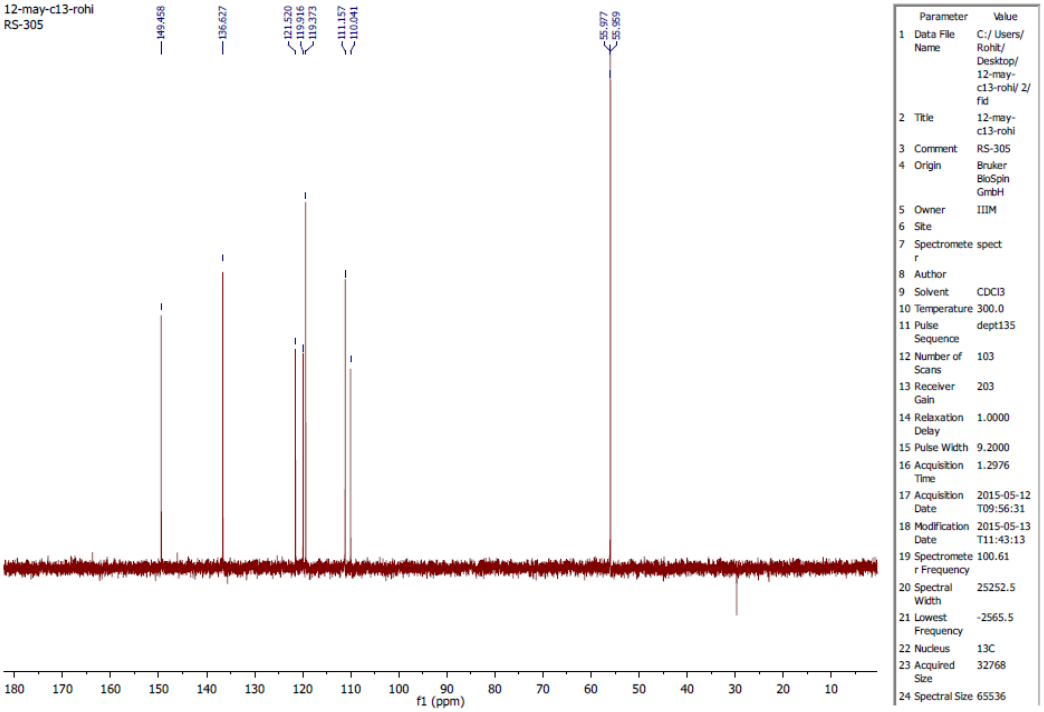
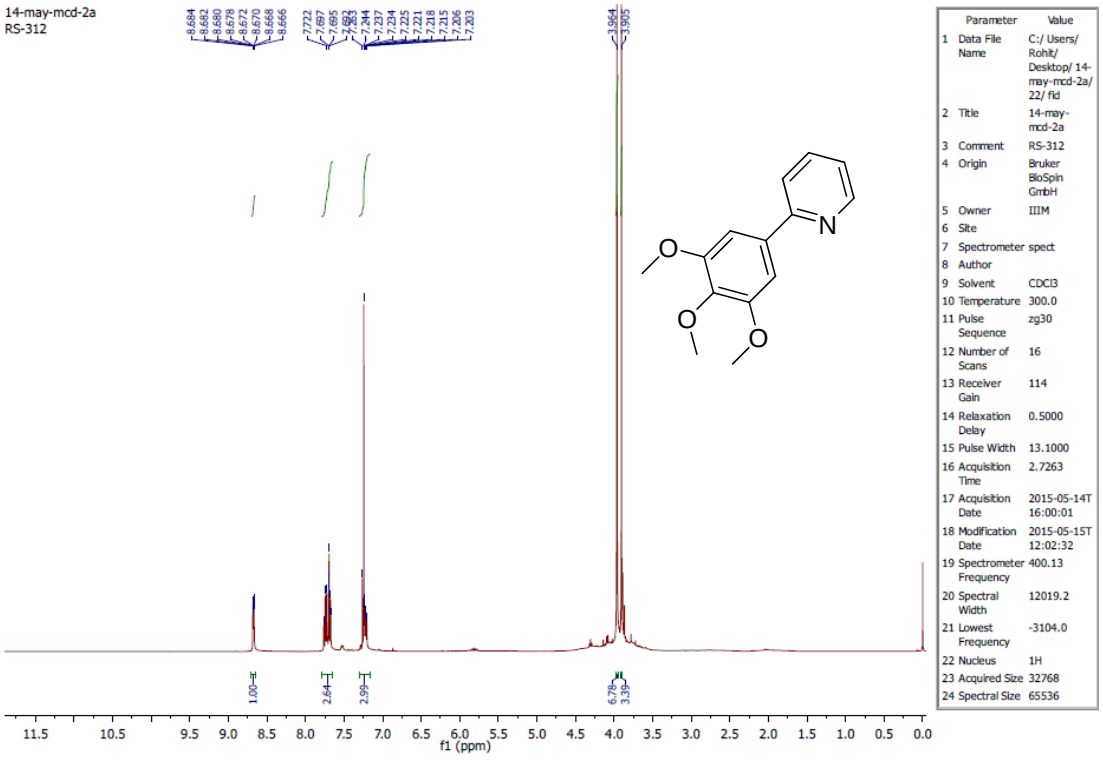
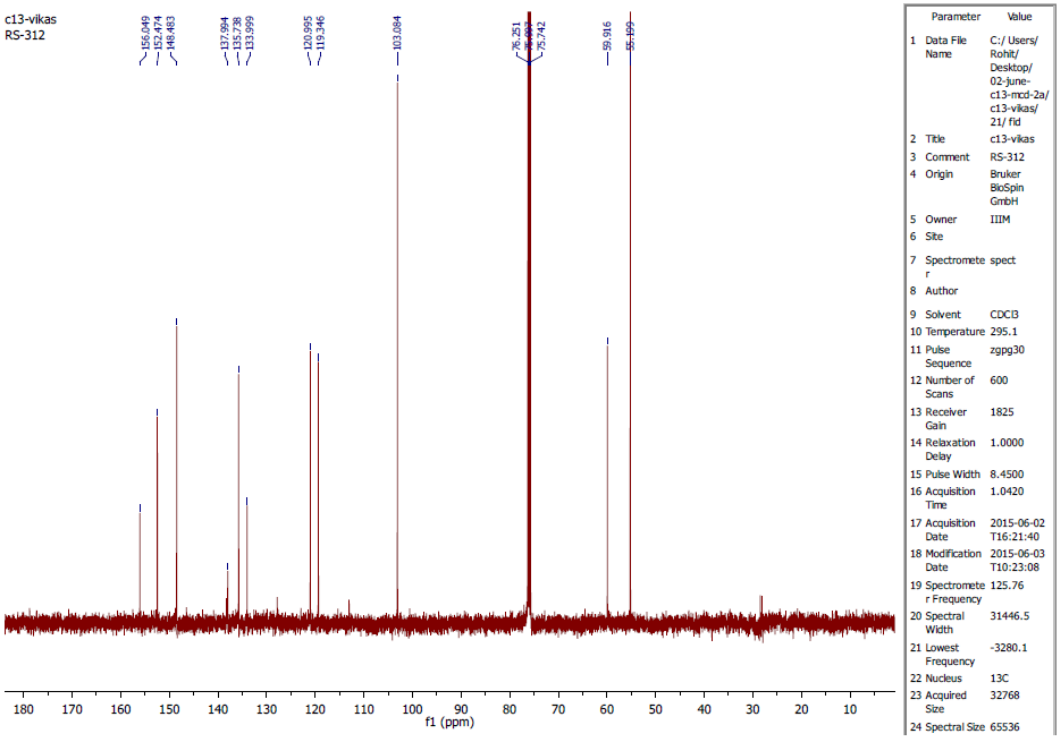
21	Lowest Frequency	-2565.5
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



S2.7. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(3, 4, 5-trimethoxyphenyl) pyridine (**3f**)





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5	Owner	IIIM
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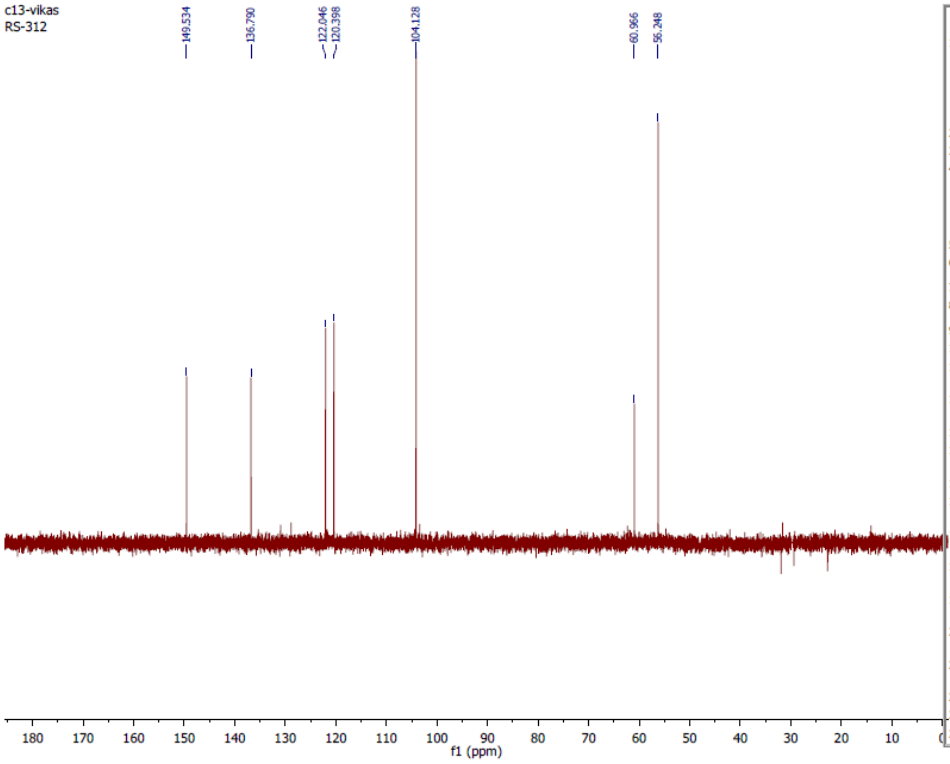
7	Spectrometer	spect r
8	Author	
9	Solvent	CDCl3
10	Temperature	295.1
11	Pulse Sequence	zgpg30
12	Number of Scans	600
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-06-02 T16:21:40
18	Modification Date	2015-06-03 T10:23:08
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3280.1
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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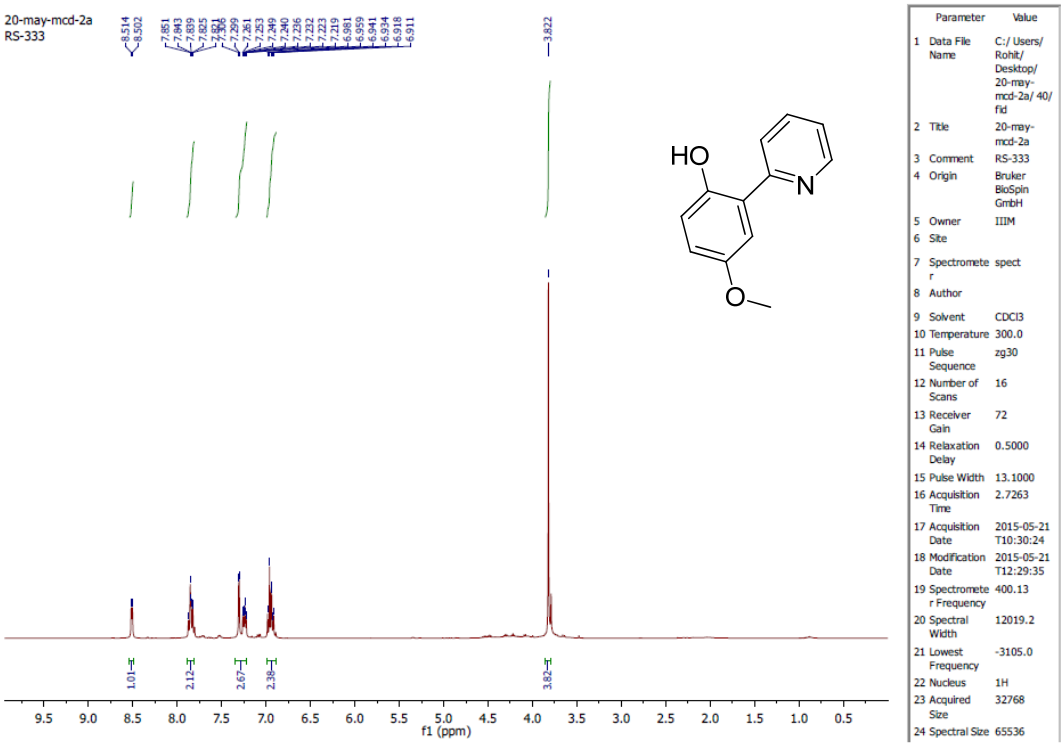
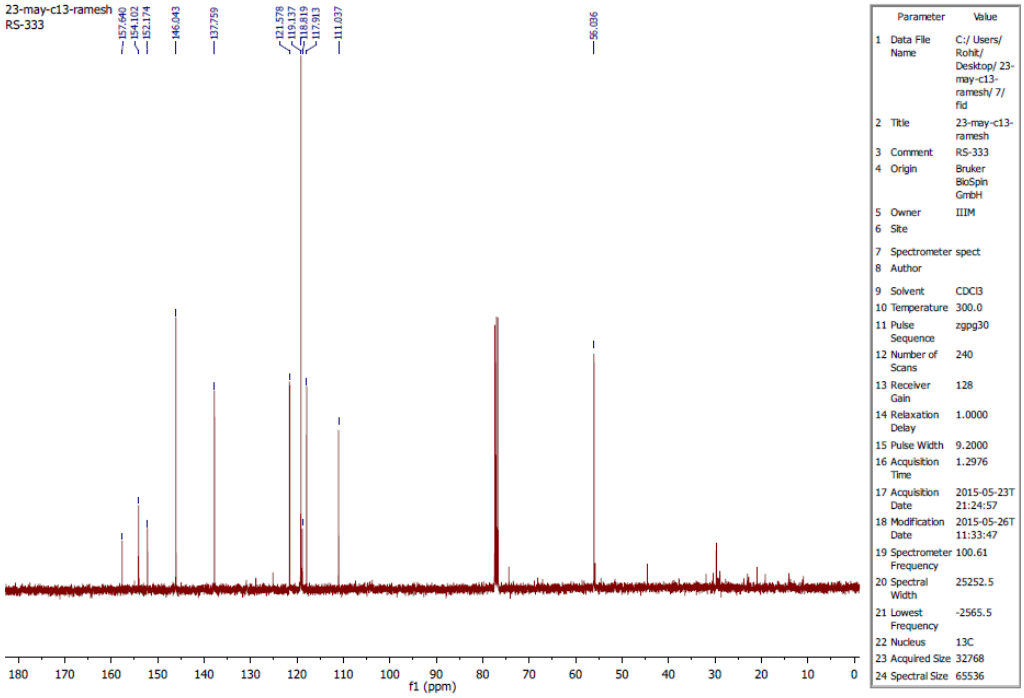
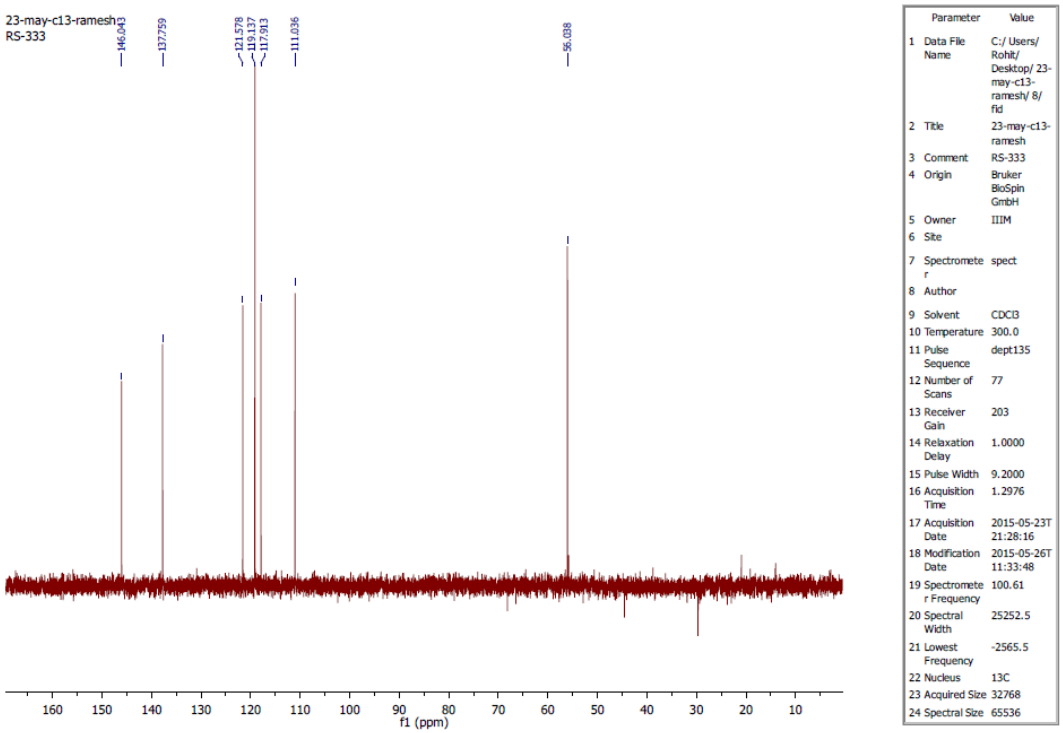
3	Comment	RS-312
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.1
11	Pulse Sequence	dept135
12	Number of Scans	300
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-06-02T 16:32:43
18	Modification Date	2015-06-03T 10:23:09
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

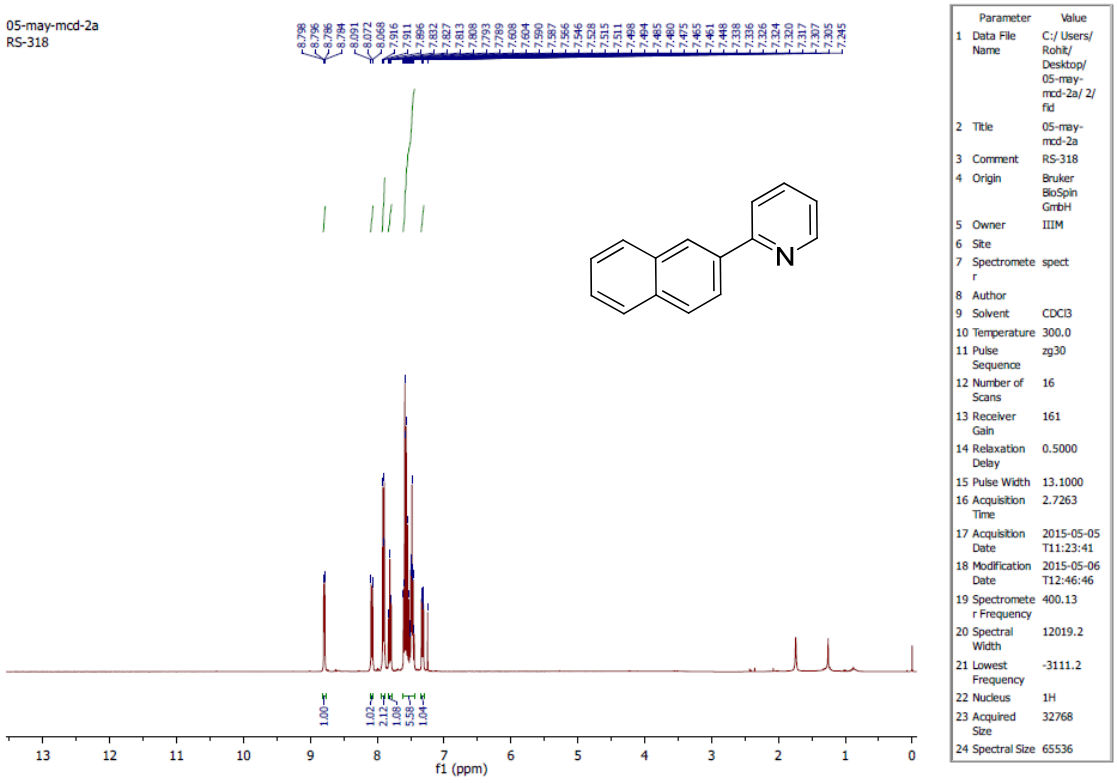
S2.8. ^{1}H, ^{13}C and DEPT135 NMR spectra of 4-methoxy-2-(pyridin-2-yl) phenol (**3g**)

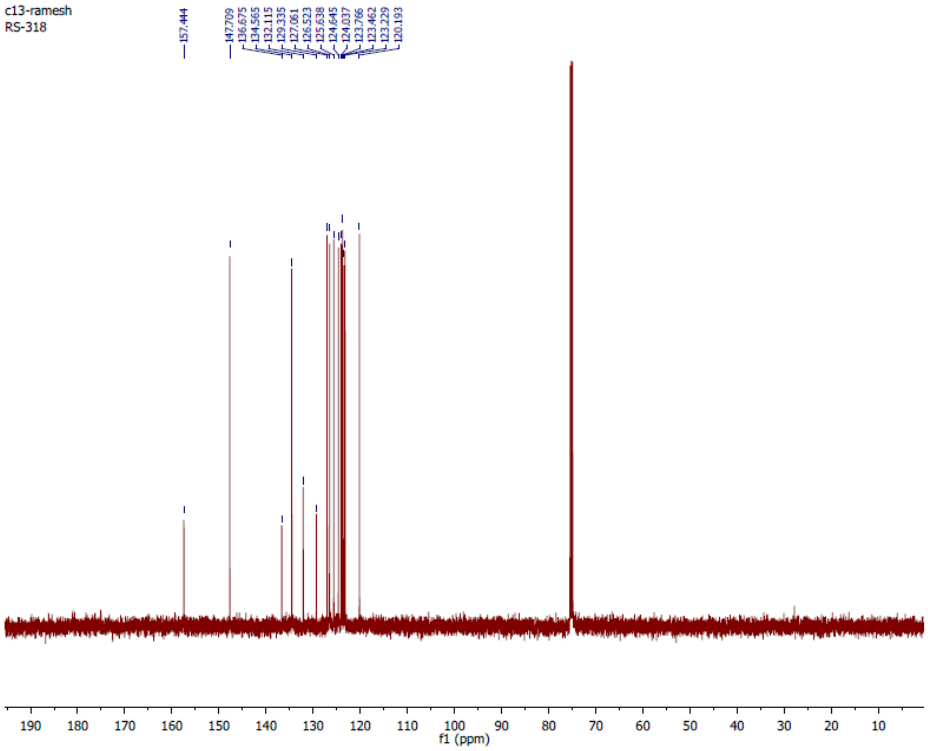






S2.9. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(naphthalen-2-yl) pyridine (**3h**)





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5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
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11	Pulse Sequence	zgpg30
12	Number of Scans	503
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.1305
17	Acquisition Date	2015-05-12T 15:15:48
18	Modification Date	2015-05-13T 10:36:43
19	Spectrometer Frequency	125.76
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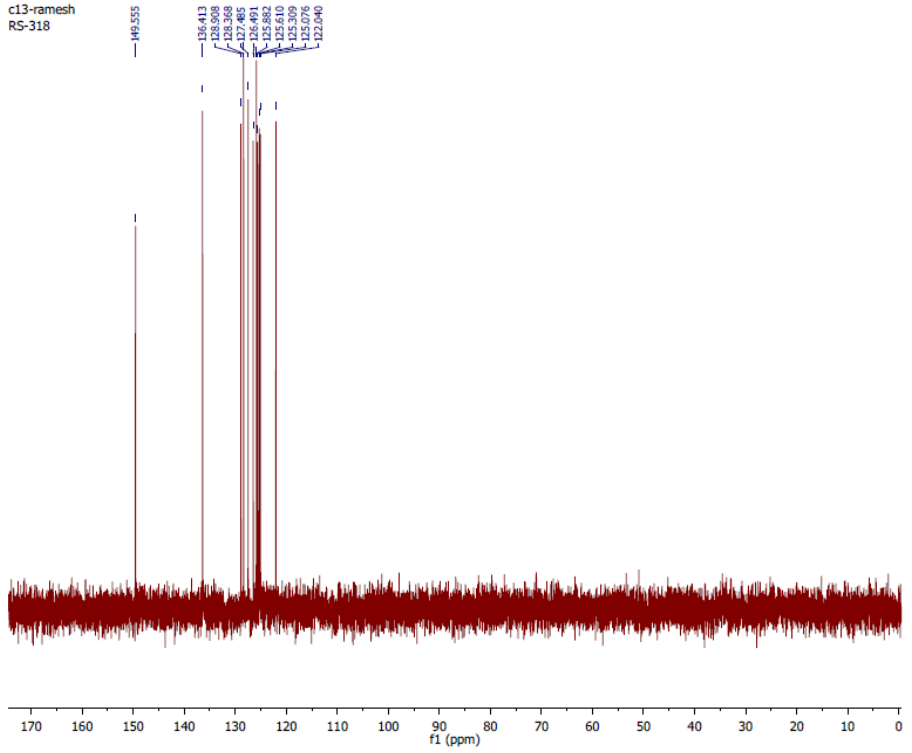
21	Lowest Frequency	-2149.5
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	685.5
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12	Number of Scans	195
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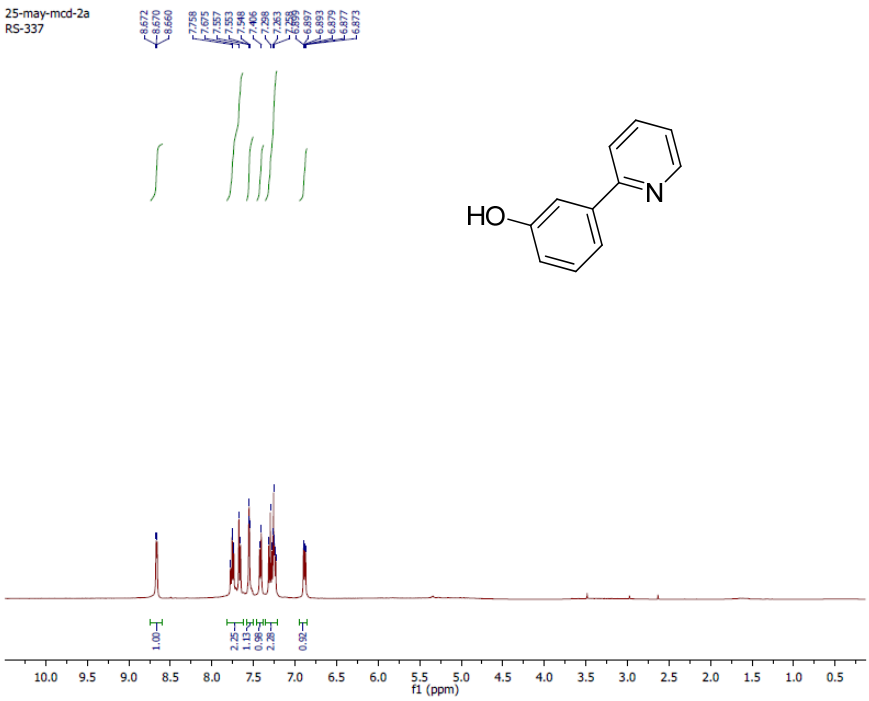
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-05-12T1 5:40:56
18	Modification Date	2015-05-13T1 0:36:45
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.10. ^{1}H, ^{13}C and DEPT135 NMR spectra of 3-(pyridin-2-yl) phenol (**3i**)



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6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zg30
12	Number of Scans	8
13	Receiver Gain	90
14	Relaxation Delay	0.5000
15	Pulse Width	13.1000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-05-25 T16:18:04
18	Modification Date	2015-05-26 T15:16:43
19	Spectrometer Frequency	400.13
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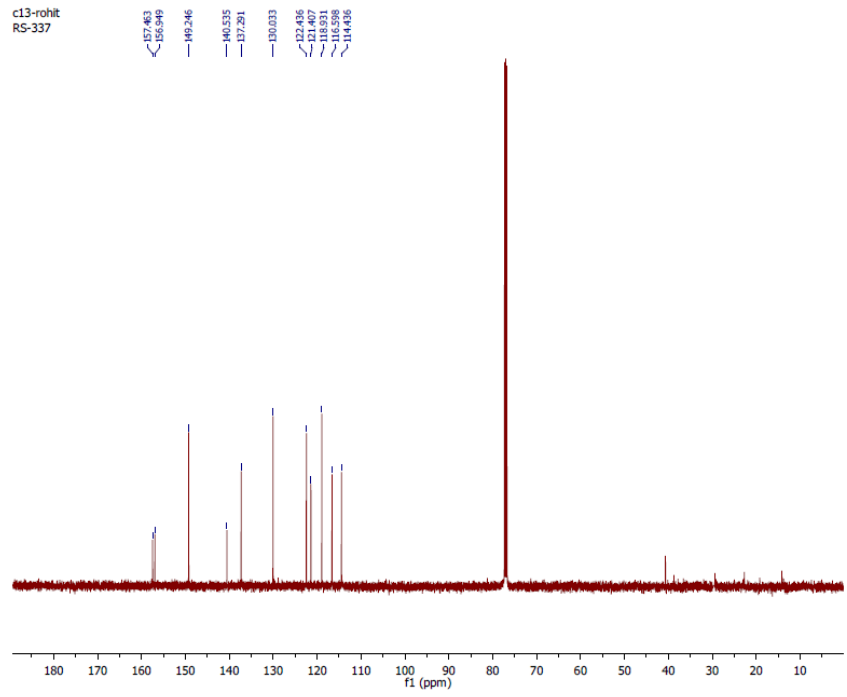
21	Lowest Frequency	-3106.1
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



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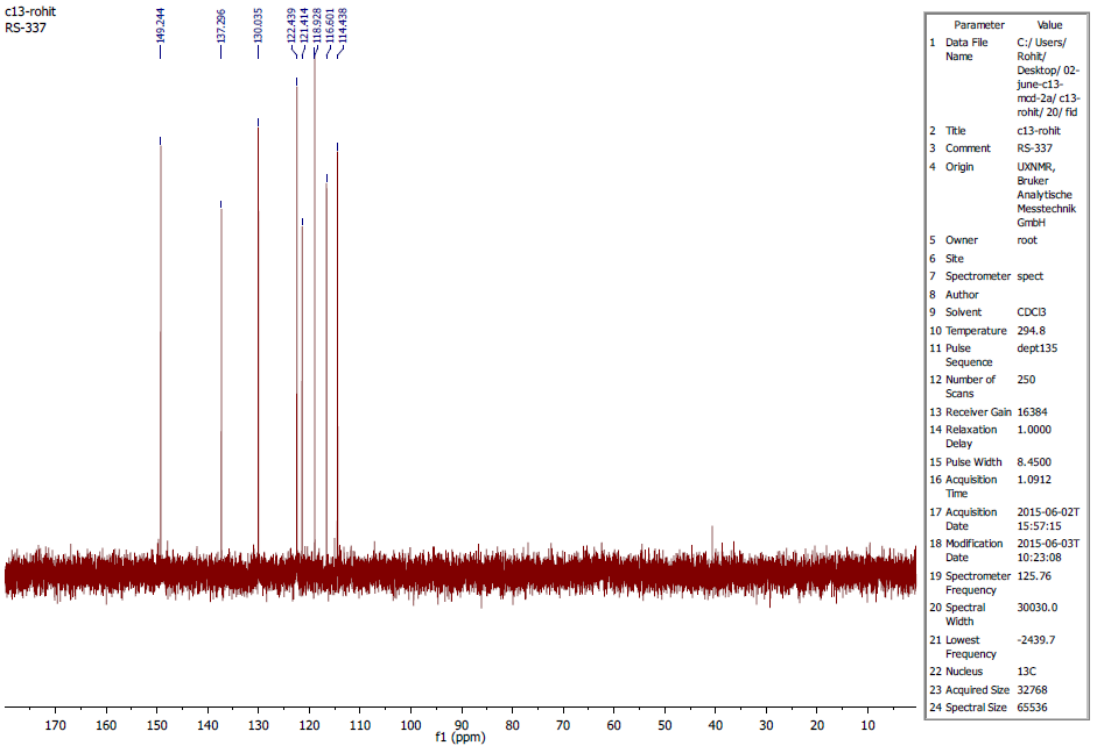
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	295.0
11	Pulse Sequence	zgpg30
12	Number of Scans	633
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-06-02 T15:27:19
18	Modification Date	2015-06-03 T10:23:06
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
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11	Pulse Sequence	dept135
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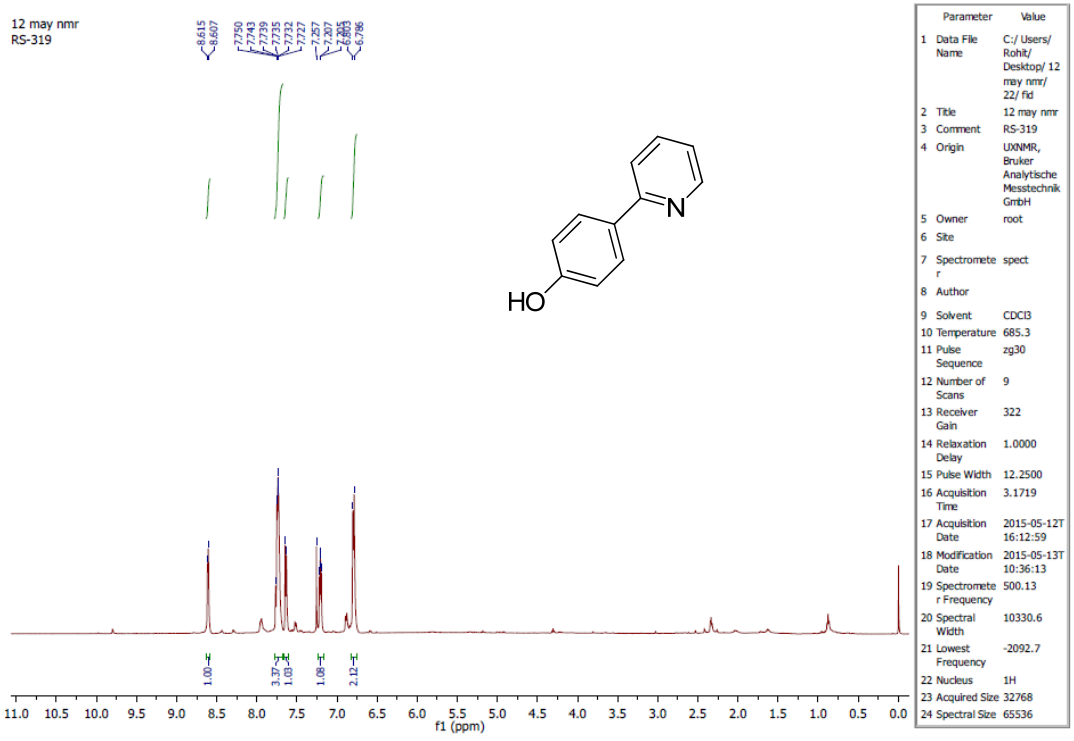
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-06-02T 15:57:15
18	Modification Date	2015-06-03T 10:23:08
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.11. ^{1}H, ^{13}C, DEPT135 NMR and HPLC spectra of 4-(pyridin-2-yl) phenol (**3j**)



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6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	685.3
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12	Number of Scans	9
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17	Acquisition Date	2015-05-12T 16:12:59
18	Modification Date	2015-05-13T 10:36:13
19	Spectrometer Frequency	500.13
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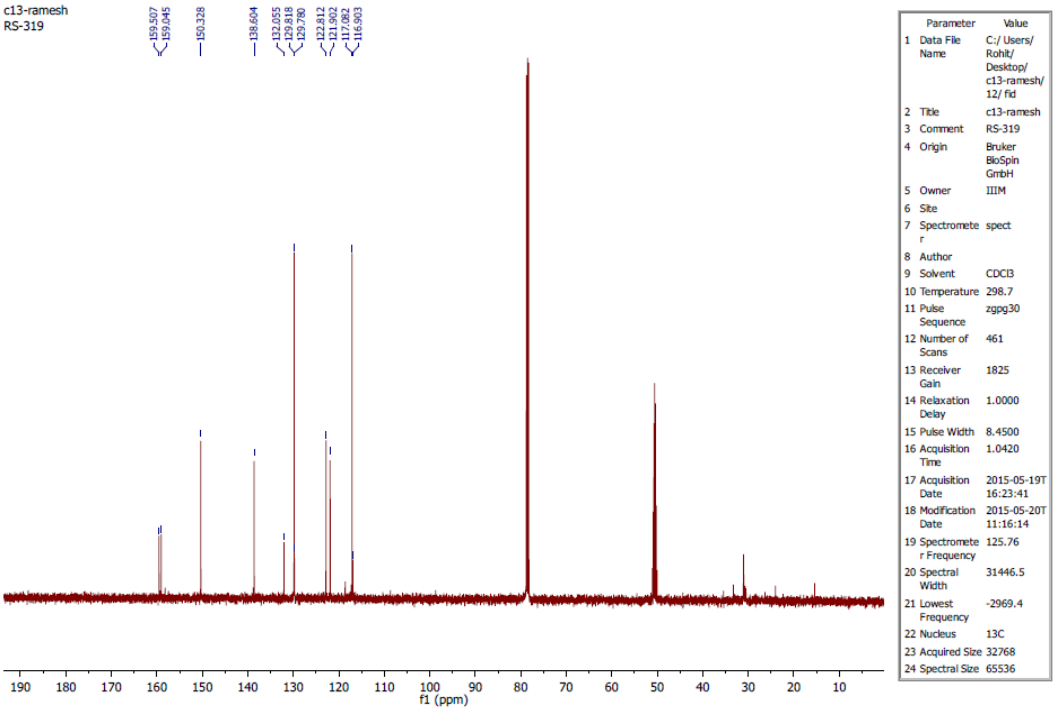
21	Lowest Frequency	-2092.7
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



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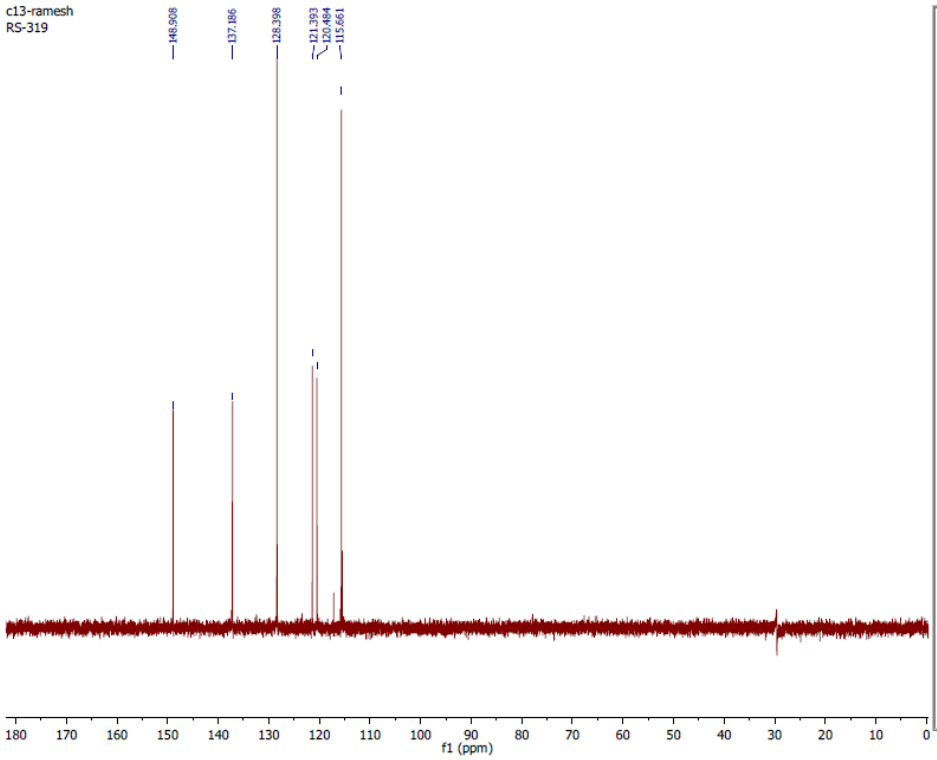
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.7
11	Pulse Sequence	zgpg30
12	Number of Scans	461
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-05-19T 16:23:41
18	Modification Date	2015-05-20T 11:16:14
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-2969.4
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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1	Data File Name	C:/ Users/ Rohit/ Desktop/ c13-ramesh/ 13/ fid
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3	Comment	RS-319
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	298.7
11	Pulse Sequence	dept135
12	Number of Scans	318
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-05-19T 16:46:34
18	Modification Date	2015-05-20T 11:16:15
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: Rs-319		
Sample ID	: Rs-319		
Data Filename	: Rs-319		
Method Filename	: 2-phenylpyridine.lcm		
Batch Filename	:		
Vial #	: 1-2	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 05-10-2015 11:03:36	Acquired by	: System Administrator
Date Processed	: 05-10-2015 11:27:22	Processed by	: System Administrator

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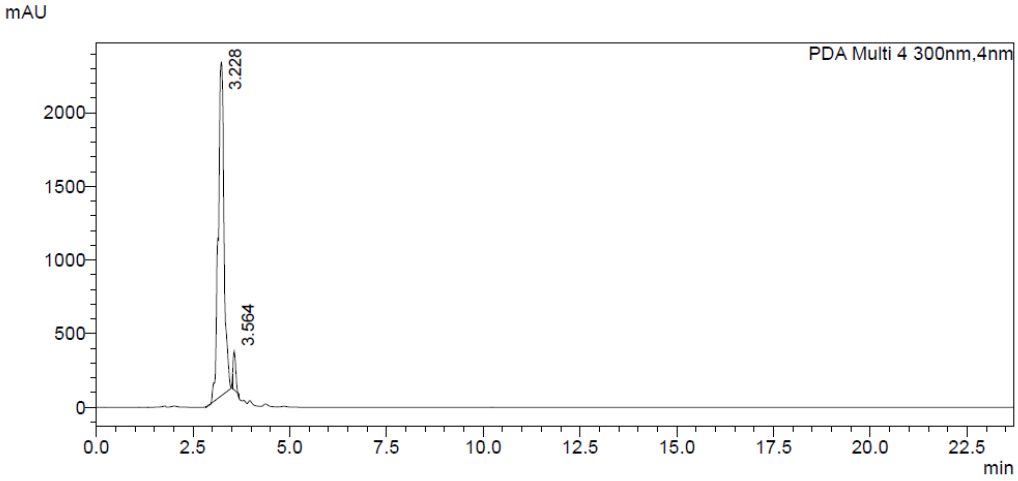

<Peak Table>

PDA Ch4 300nm

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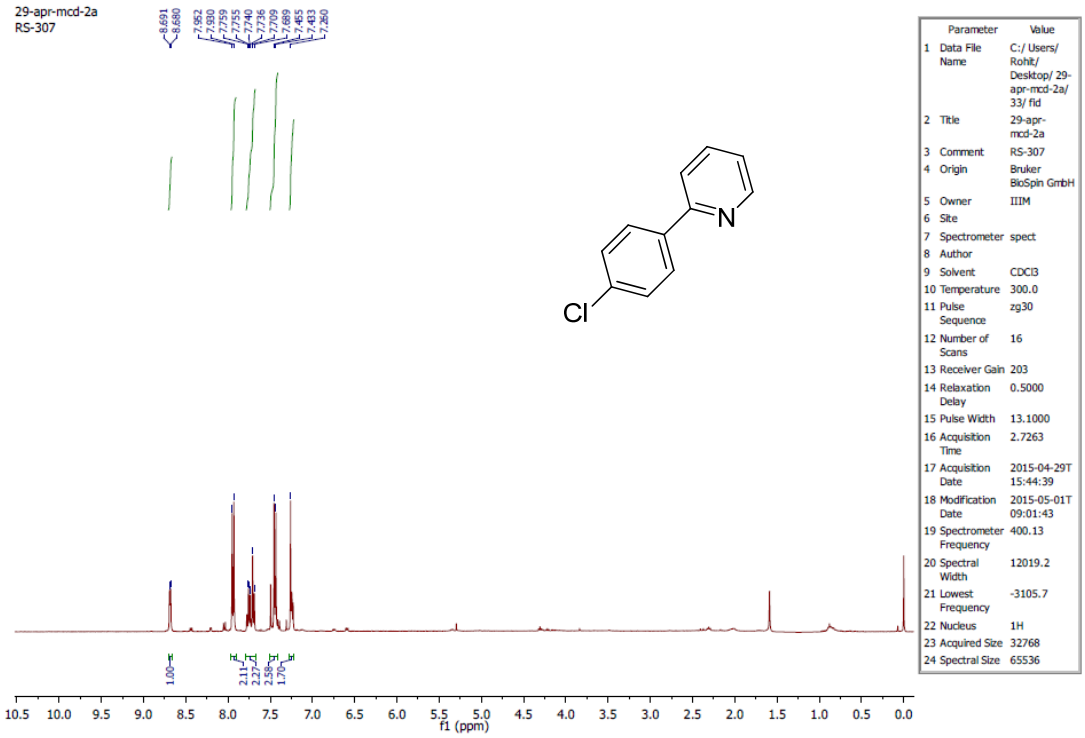
2	3.564	1156005	263802	3.520	3.680	4.613
Total		25061485	2526652			100.000

S2.12. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(4-chlorophenyl) pyridine (**3k**)



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5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
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11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	203
14	Relaxation Delay	0.5000
15	Pulse Width	13.1000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-04-29T 15:44:39
18	Modification Date	2015-05-01T 09:01:43
19	Spectrometer Frequency	400.13
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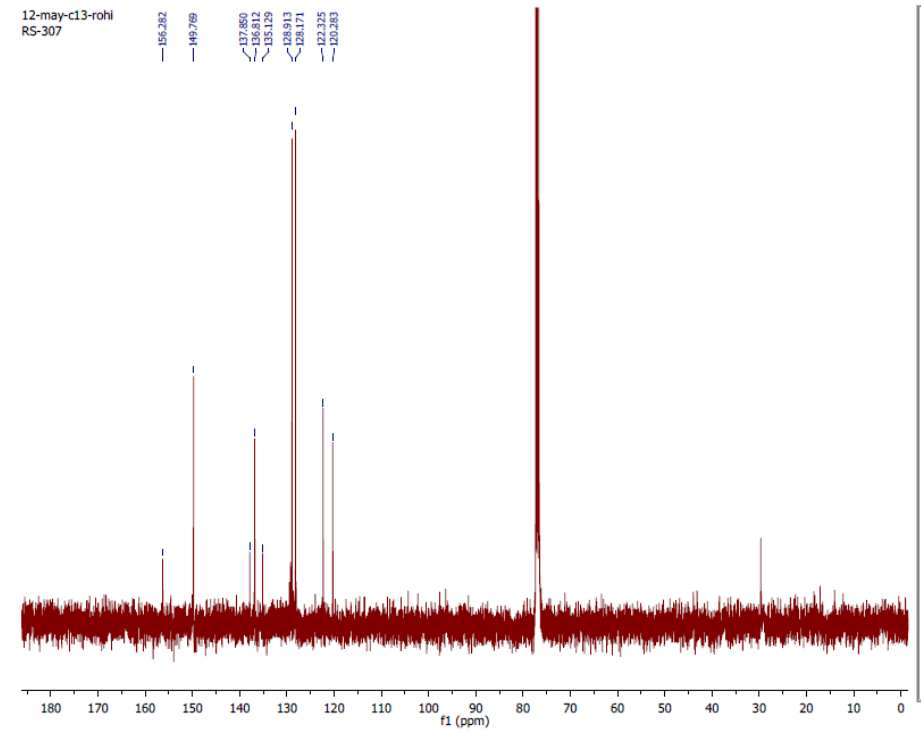
21	Lowest Frequency	-3105.7
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



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5	Owner	IIIM
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7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgpg30
12	Number of Scans	1600
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	9.2000
16	Acquisition Time	1.2976
17	Acquisition Date	2015-05-12T 13:25:08
18	Modification Date	2015-05-13T 11:43:14
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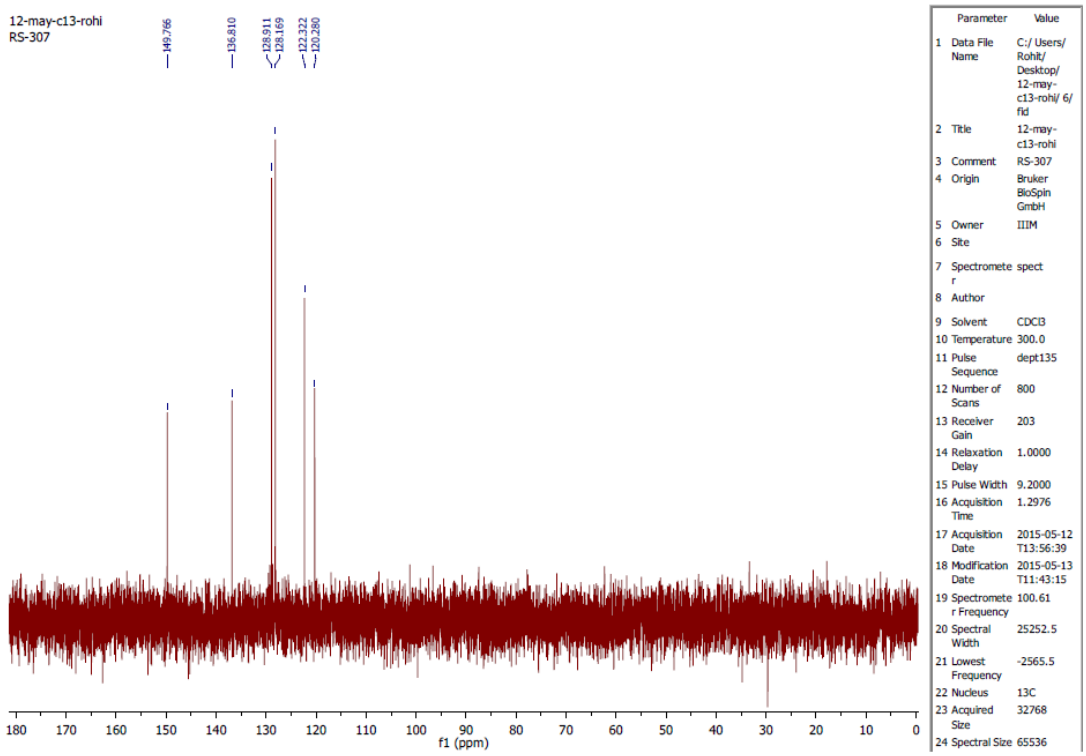
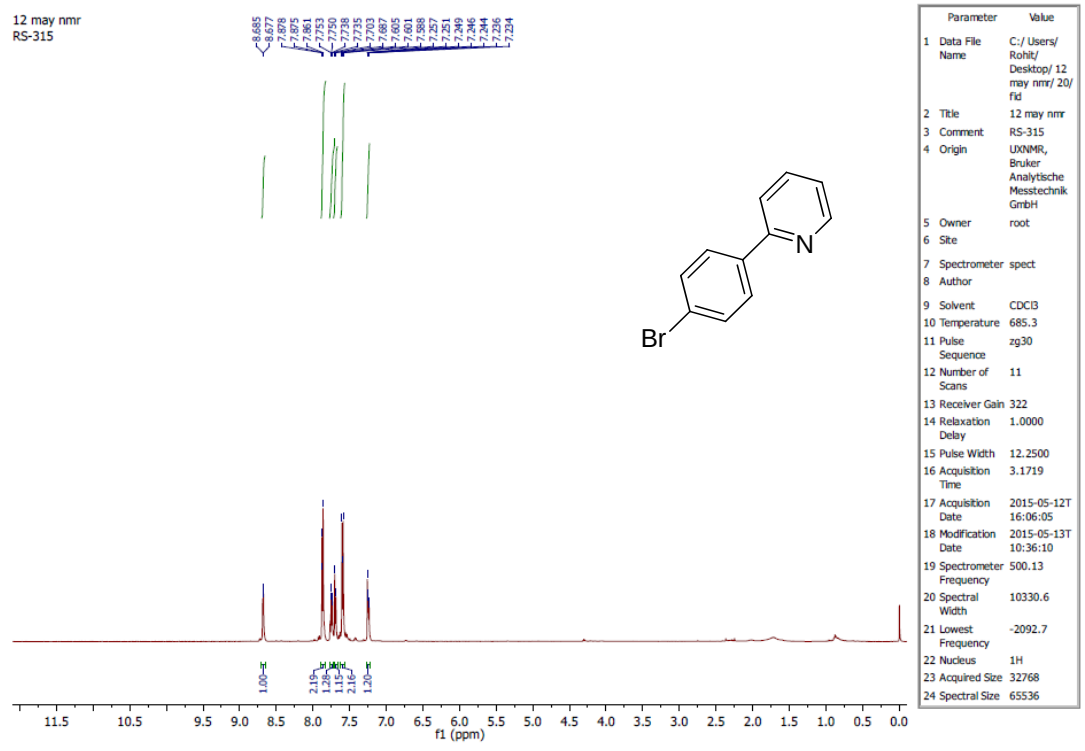
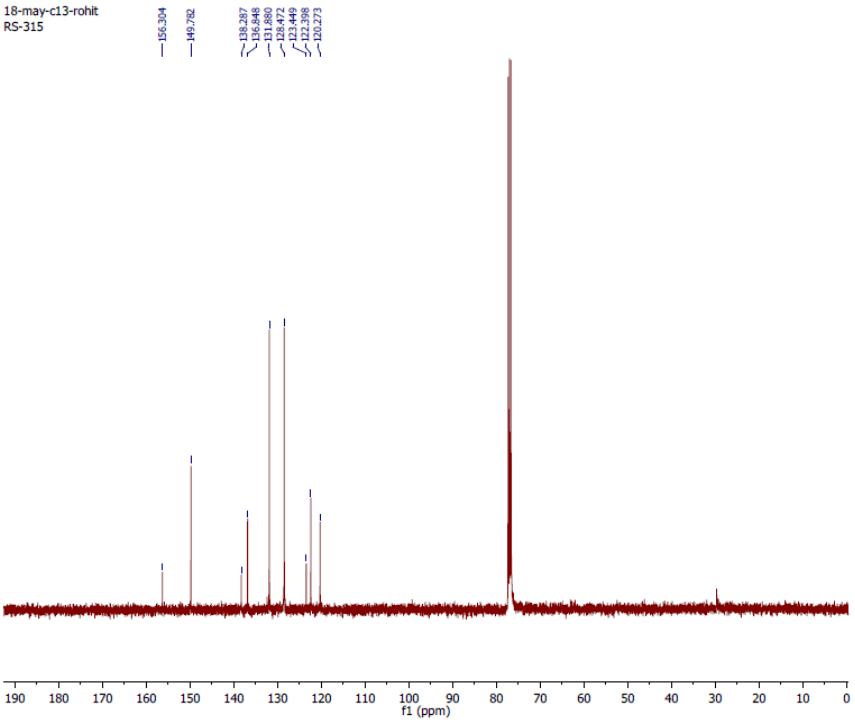
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



S2.13. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(4-bromophenyl) pyridine **(3l)**





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12	Number of Scans	863
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14	Relaxation Delay	1.0000
15	Pulse Width	9.2000
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17	Acquisition Date	2015-05-19T 09:14:41
18	Modification Date	2015-05-19T 18:12:13
19	Spectrometer Frequency	100.61
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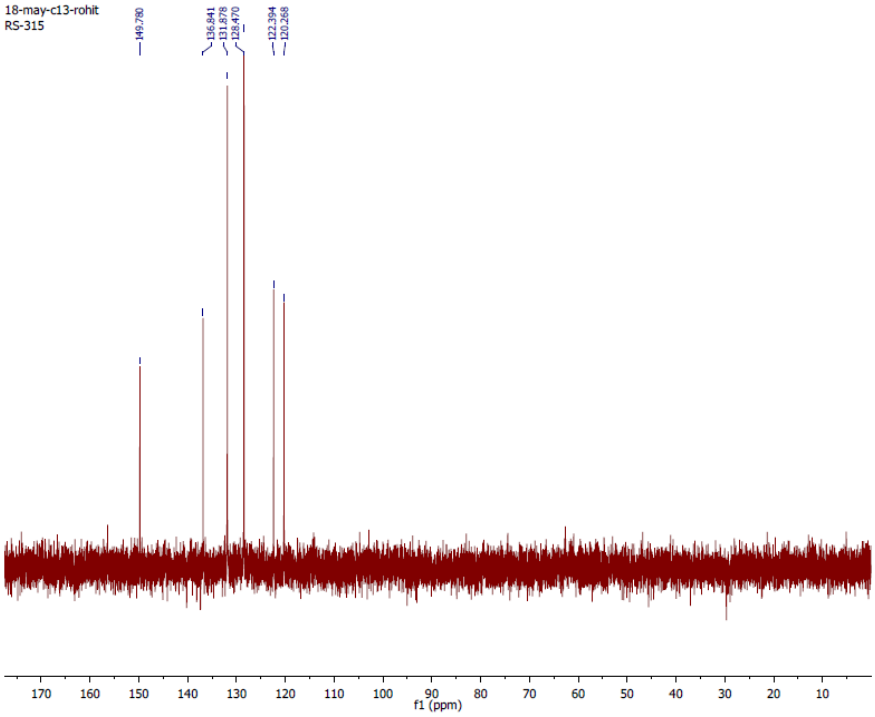
21	Lowest Frequency	-2565.5
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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5	Owner	IIIM
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7	Spectrometer	spect
8	Author	
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12	Number of Scans	270
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14	Relaxation Delay	1.0000
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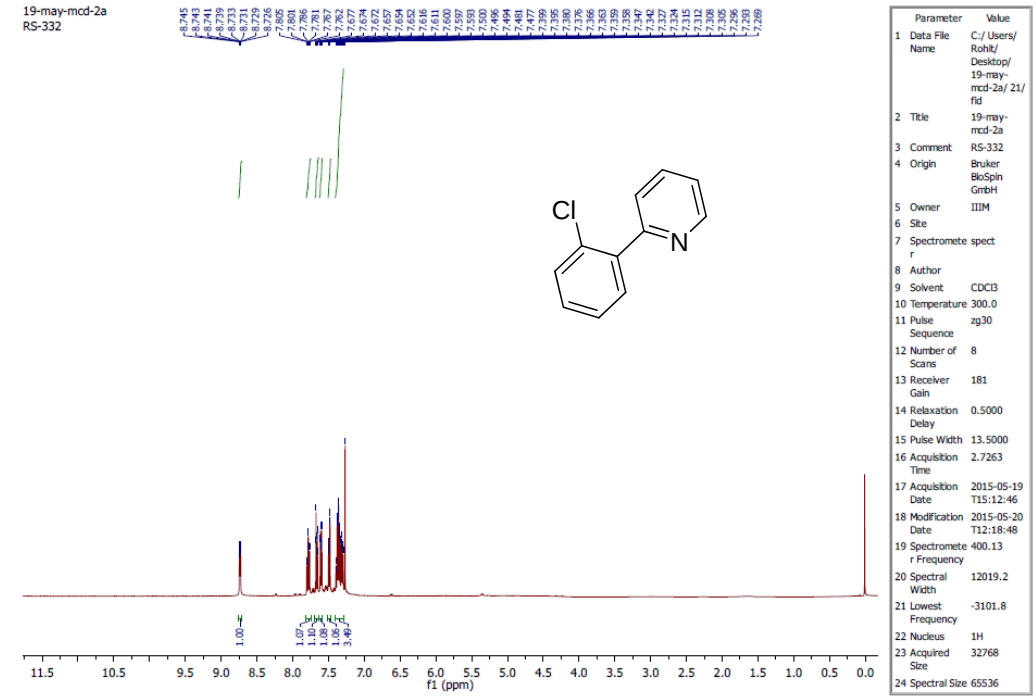
19	Spectrometer Frequency	100.61
20	Spectral Width	25252.5
21	Lowest Frequency	-2565.5
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.14. ^{1}H, ^{13}C, DEPT135 NMR and HPLC spectra of 2-(2-chlorophenyl) pyridine (**3m**)



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7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zg30
12	Number of Scans	8
13	Receiver Gain	181
14	Relaxation Delay	0.5000
15	Pulse Width	13.5000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-05-19 T15:12:46
18	Modification Date	2015-05-20 T12:18:48
19	Spectrometer Frequency	400.13
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21	Lowest Frequency	-3101.8
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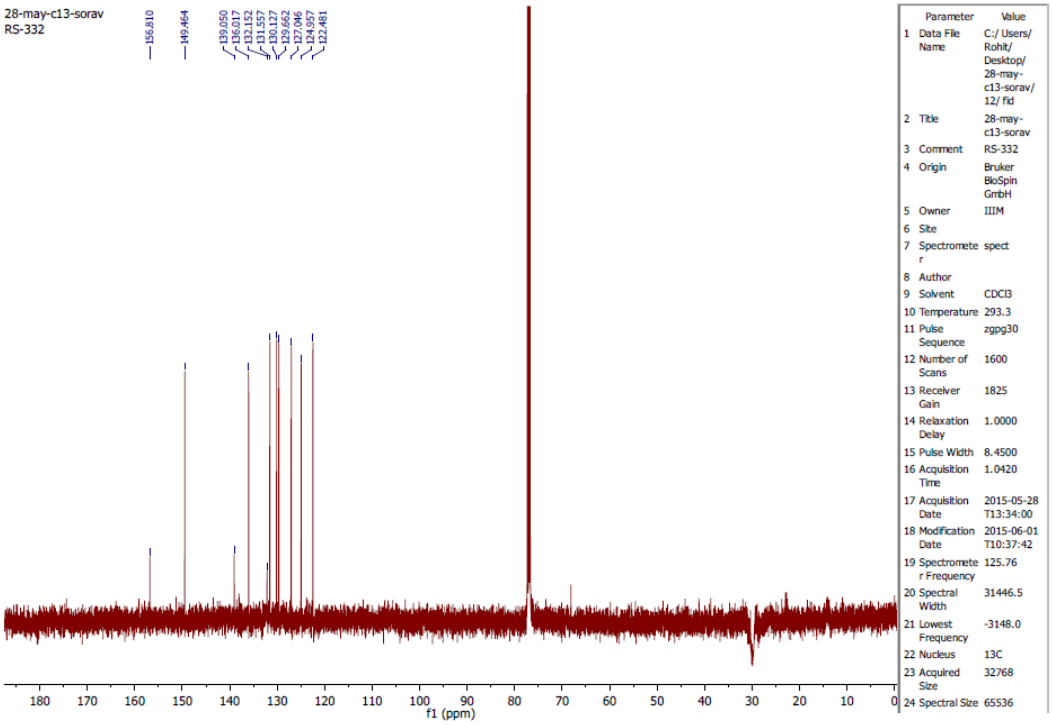
23	Acquired Size	32768
24	Spectral Size	65536



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7	Spectrometer	spect
8	Author	
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12	Number of Scans	1600
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14	Relaxation Delay	1.0000
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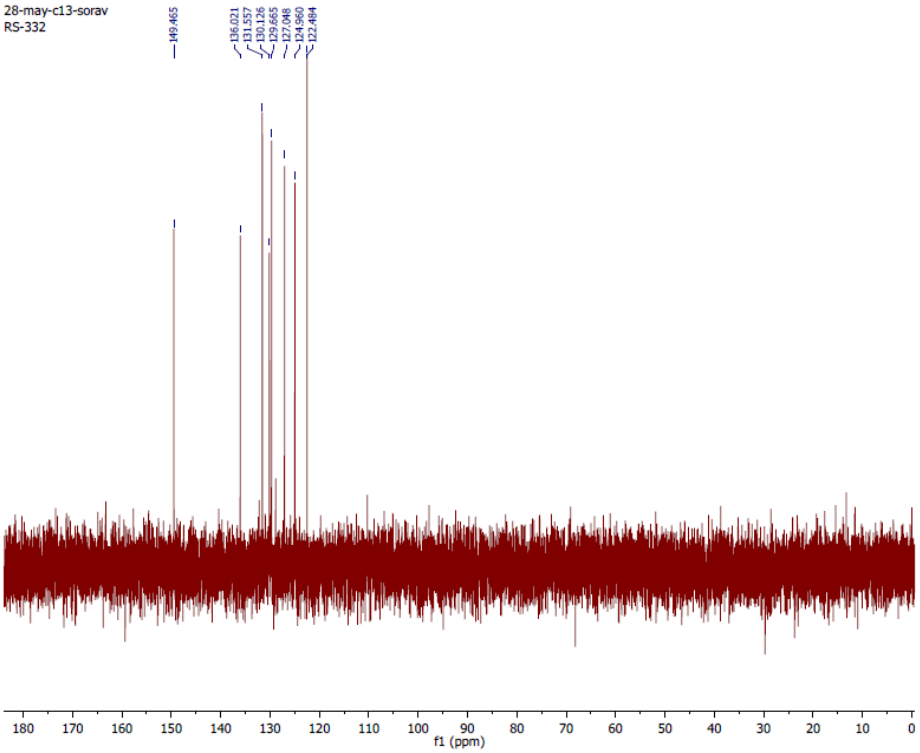
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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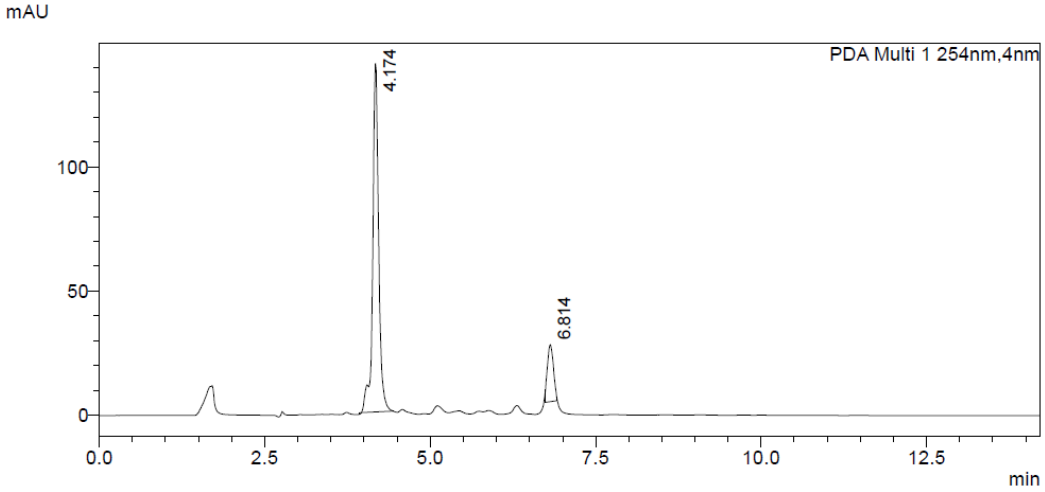
1	Data File Name	C:/ Users/ Rohit/ Desktop/ 28-may-c13-sorav/ 13/ fid
2	Title	28-may-c13-sorav
3	Comment	RS-332
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.9
11	Pulse Sequence	dept135
12	Number of Scans	800
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-05-28T 14:02:50
18	Modification Date	2015-06-01T 10:37:42
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: Rs-332		
Sample ID	: Rs-332		
Data Filename	: RS-332.lcd		
Method Filename	: 2-phenylpyridine.lcm		
Batch Filename	:		
Vial #	: 1-4	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 05-10-2015 11:48:59	Acquired by	: System Administrator
Date Processed	: 05-10-2015 12:03:15	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

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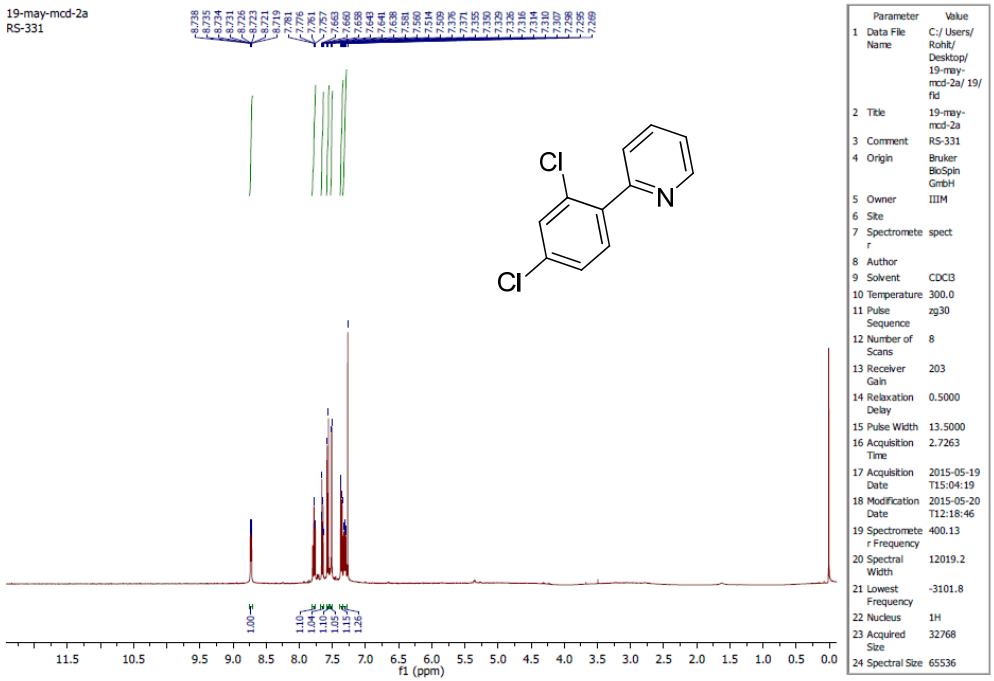
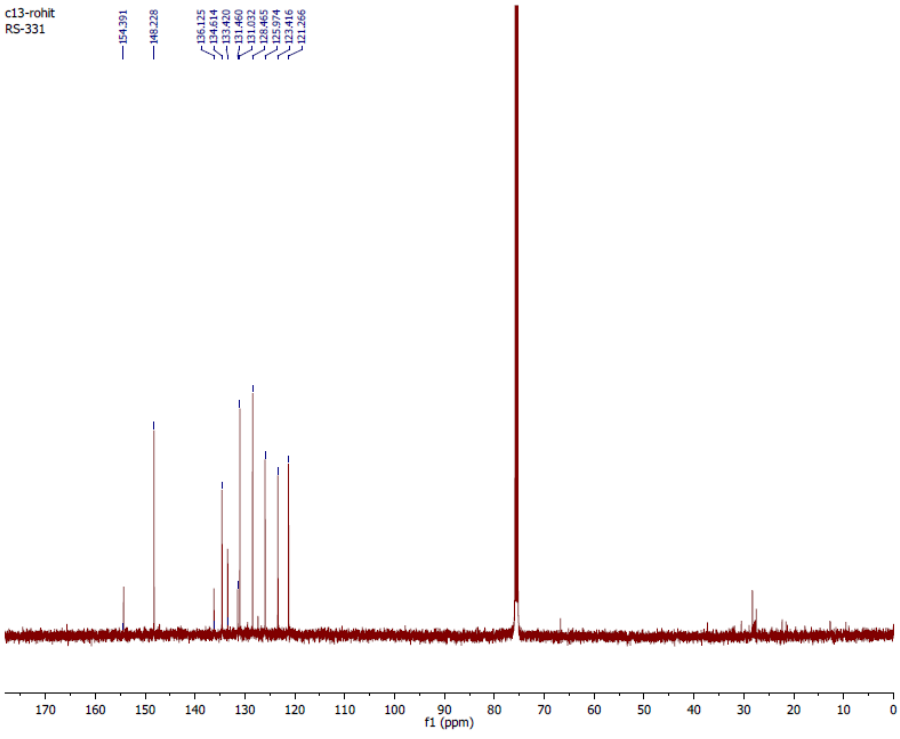
2	6.814	6.741	6.912	14.233	14.043
Total				100.000	100.000

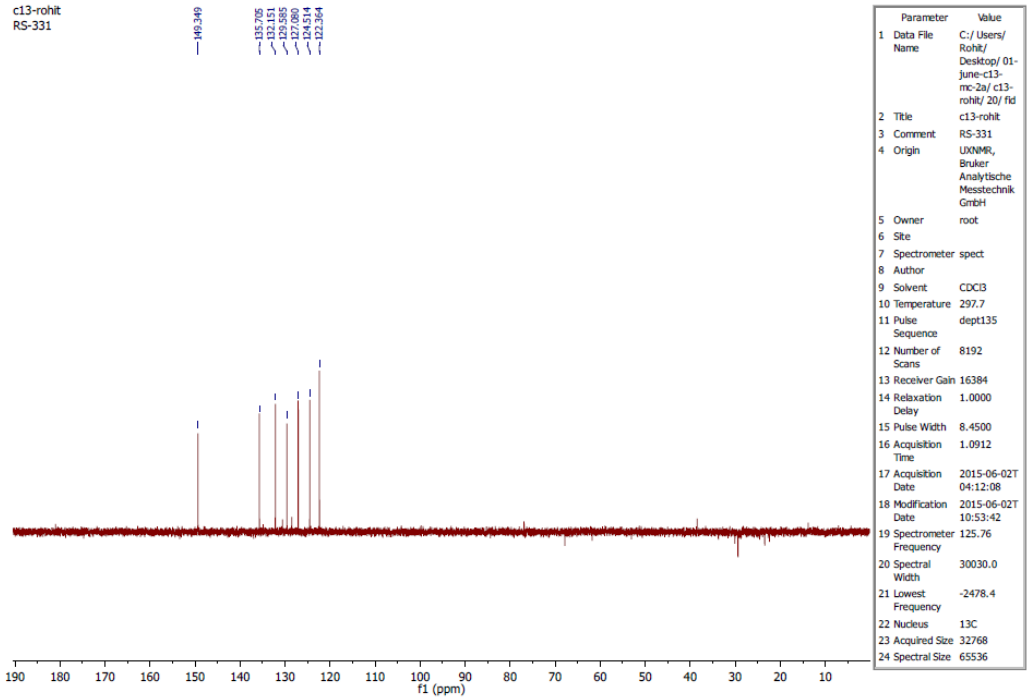
S2.15. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(5-chloro-[1, 1'-biphenyl]-2-yl) pyridine (**3n**)



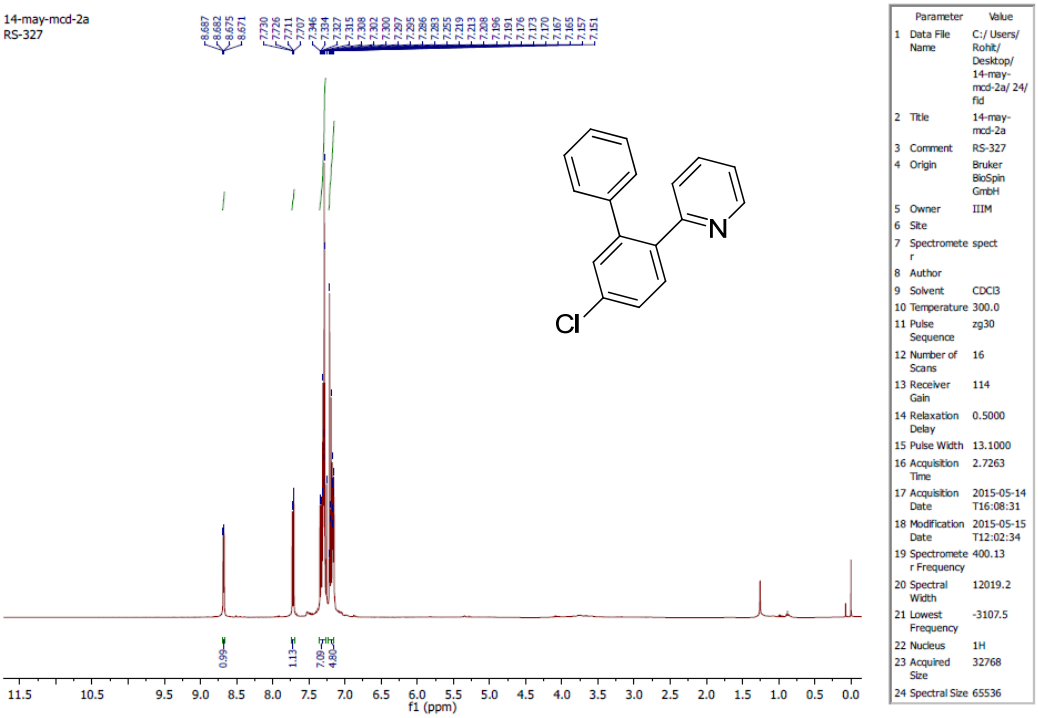
	Parameter	Value
1	Data File Name	C:/ Users/ Rohit/ Desktop/ 19-may-mcd-2a/ 19/ fid
2	Title	19-may-mcd-2a
3	Comment	RS-331
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zg30
12	Number of Scans	8
13	Receiver Gain	203
14	Relaxation Delay	0.5000
15	Pulse Width	13.5000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-05-19 T15:04:19
18	Modification Date	2015-05-20 T12:18:46
19	Spectrometer Frequency	400.13
20	Spectral Width	12019.2
21	Lowest Frequency	-3101.8
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

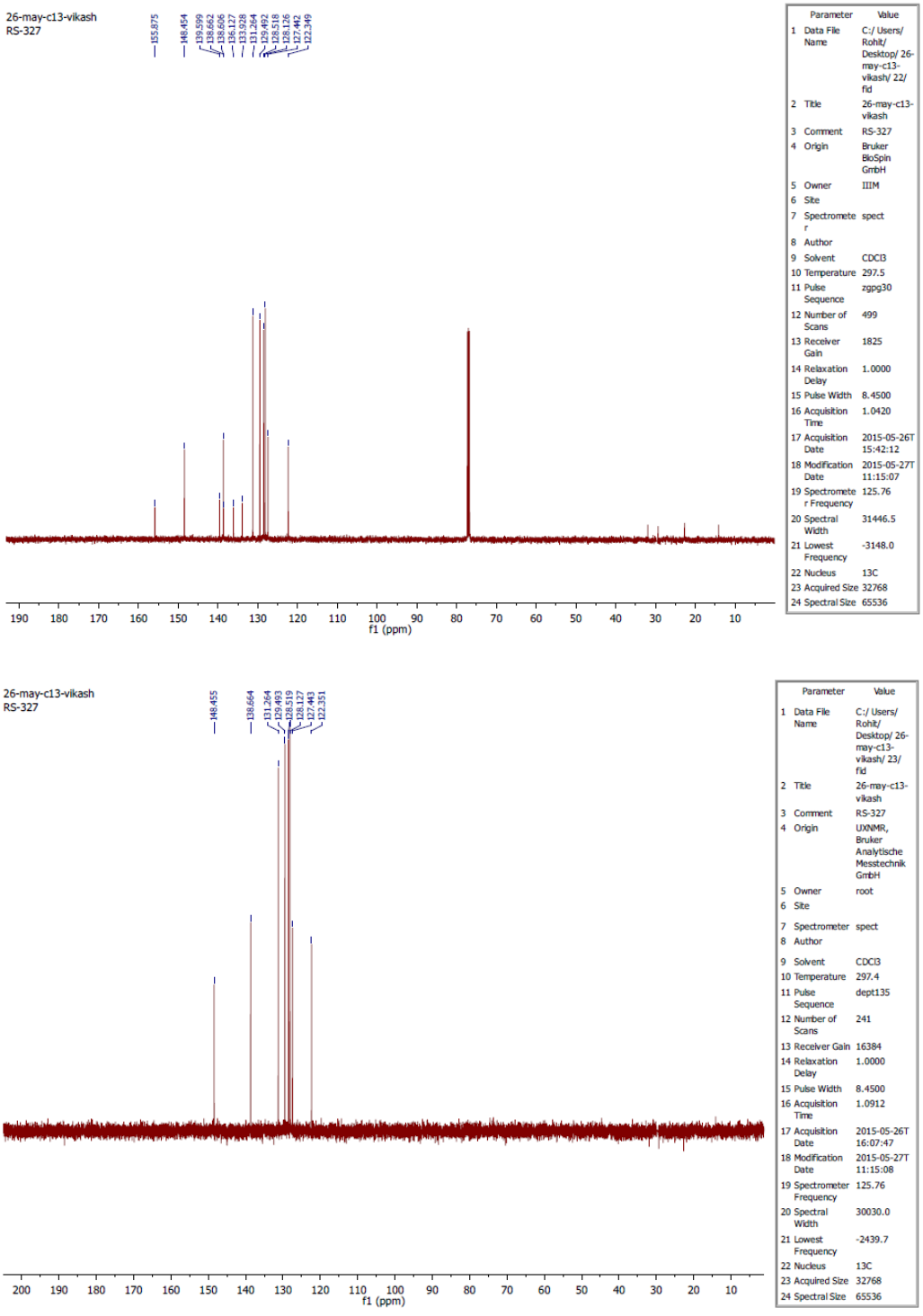


	Parameter	Value
1	Data File Name	C:/ Users/ Rohit/ Desktop/ 01-june-c13-mc-2a/ c13-rohit/ 19/ fid
2	Title	c13-rohit
3	Comment	RS-331
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.7
11	Pulse Sequence	zgpg30
12	Number of Scans	10240
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-06-01T 17:26:27
18	Modification Date	2015-06-02T 10:53:41
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3327.8
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



S2.16. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(5-chloro-[1, 1'-biphenyl]-2-yl) pyridine (**3o**)

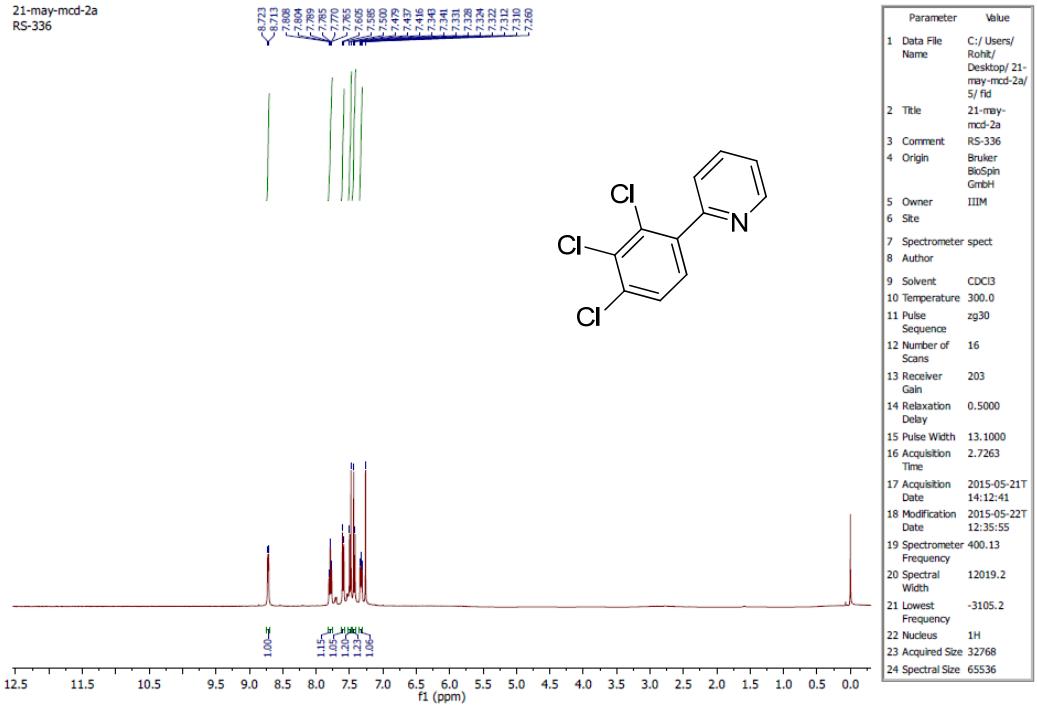


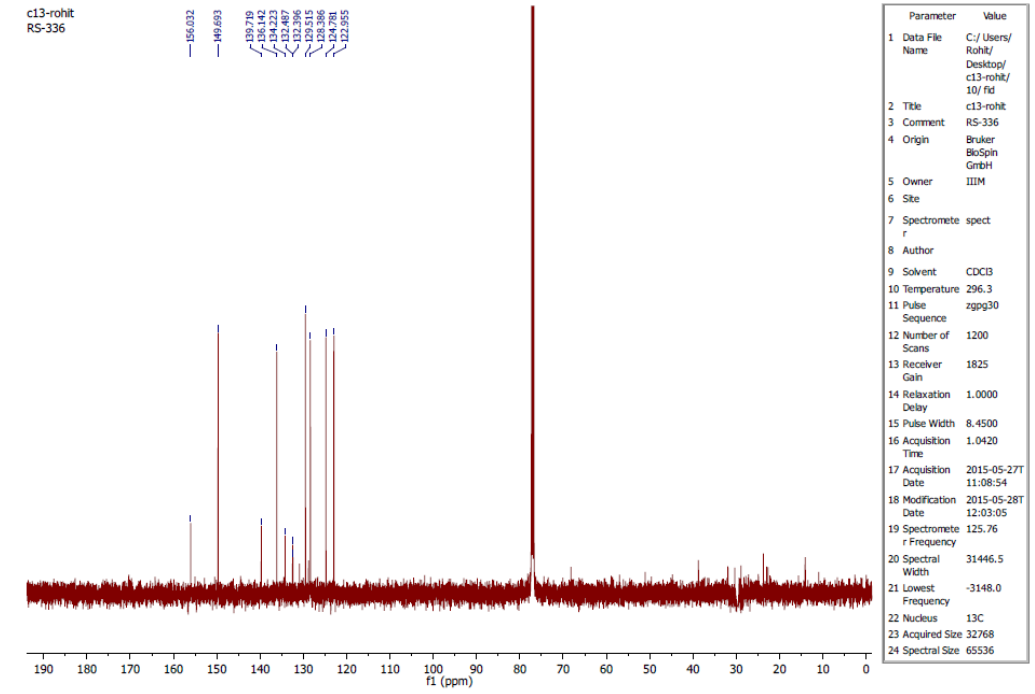


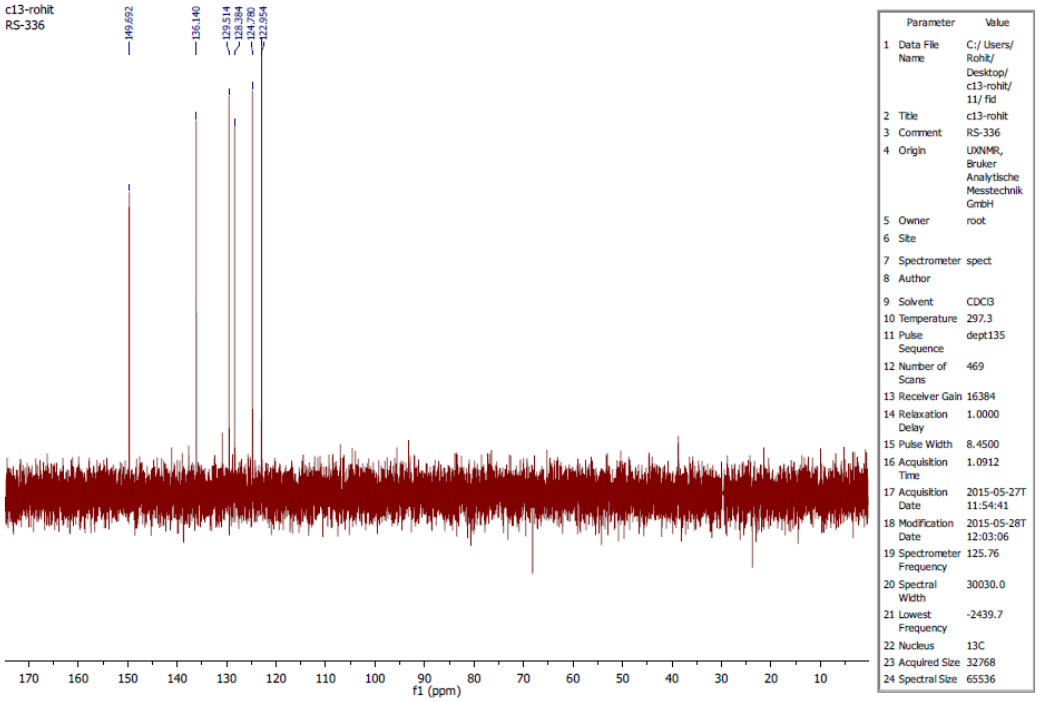
	Parameter	Value
1	Data File Name	C:/ Users/ Rohit/ Desktop/ 26-may-c13-vikash/ 22/ fid
2	Title	26-may-c13-vikash
3	Comment	RS-327
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.5
11	Pulse Sequence	zgpg30
12	Number of Scans	499
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-05-26T 15:42:12
18	Modification Date	2015-05-27T 11:15:07
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

	Parameter	Value
1	Data File Name	C:/ Users/ Rohit/ Desktop/ 26-may-c13-vikash/ 23/ fid
2	Title	26-may-c13-vikash
3	Comment	RS-327
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.4
11	Pulse Sequence	dept135
12	Number of Scans	241
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-05-26T 16:07:47
18	Modification Date	2015-05-27T 11:15:08
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.17. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(2, 3, 4-trichlorophenyl) pyridine (**3p**)


21-may-mcd-2a
RS-336
8.723
8.713
7.808
7.804
7.789
7.785
7.770
7.765
7.605
7.585
7.500
7.479
7.437
7.416
7.343
7.341
7.331
7.328
7.324
7.322
7.312
7.310
7.260
Cl
Cl
Cl
N
1.00
1.15
1.05
1.20
1.23
1.06
12.5
11.5
10.5
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
0.0
f1 (ppm)
Parameter Value
1 Data File Name C:/ Users/ Rohit/ Desktop/ 21-may-mcd-2a/ 5/ fid
2 Title 21-may-mcd-2a
3 Comment RS-336
4 Origin Bruker BioSpin GmbH
5 Owner IIIM
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 300.0
11 Pulse Sequence zg30
12 Number of Scans 16
13 Receiver Gain 203
14 Relaxation Delay 0.5000
15 Pulse Width 13.1000
16 Acquisition Time 2.7263
17 Acquisition Date 2015-05-21T 14:12:41
18 Modification Date 2015-05-22T 12:35:55
19 Spectrometer Frequency 400.13
20 Spectral Width 12019.2
21 Lowest Frequency -3105.2
22 Nucleus 1H
23 Acquired Size 32768
24 Spectral Size 65536


c13-rohit
RS-336
156.032
149.693
139.719
136.142
134.223
132.396
129.515
128.386
124.781
122.955
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Parameter Value
1 Data File Name C:/ Users/ Rohit/ Desktop/ c13-rohit/ 10/ fid
2 Title c13-rohit
3 Comment RS-336
4 Origin Bruker BioSpin GmbH
5 Owner IIIM
6 Site
7 Spectrometer spect
8 Author
9 Solvent CDCl3
10 Temperature 296.3
11 Pulse Sequence zgpg30
12 Number of Scans 1200
13 Receiver Gain 1825
14 Relaxation Delay 1.0000
15 Pulse Width 8.4500
16 Acquisition Time 1.0420
17 Acquisition Date 2015-05-27T 11:08:54
18 Modification Date 2015-05-28T 12:03:05
19 Spectrometer Frequency 125.76
20 Spectral Width 31446.5
21 Lowest Frequency -3148.0
22 Nucleus 13C
23 Acquired Size 32768
24 Spectral Size 65536



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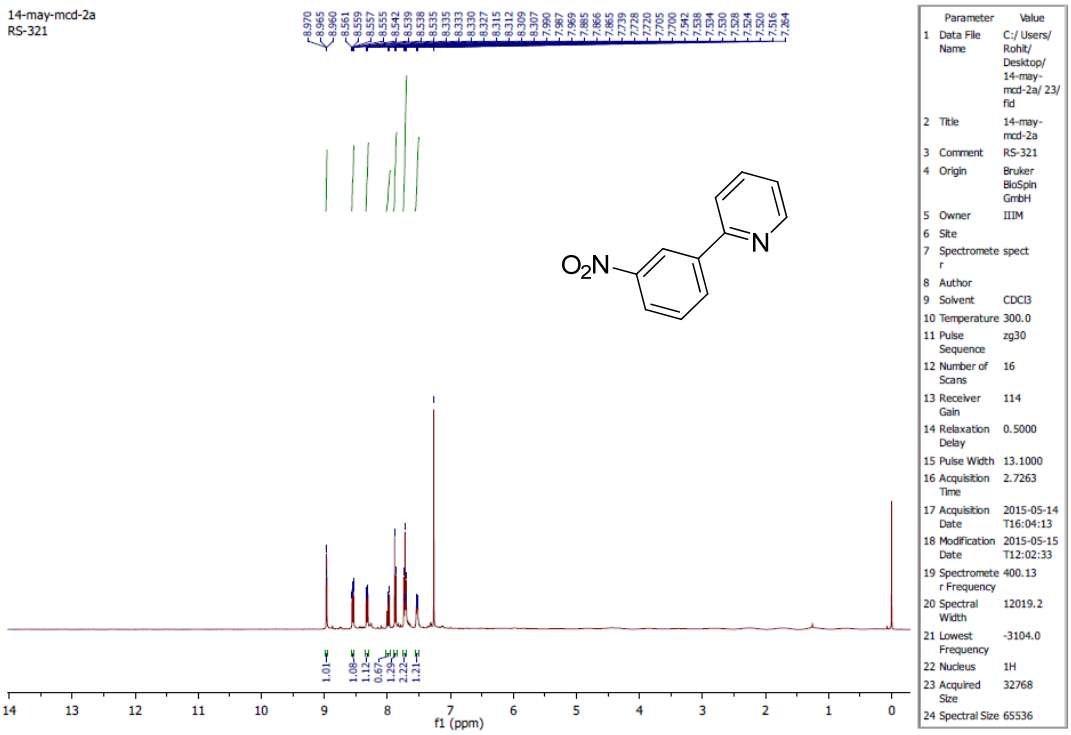
2	Title	c13-rohit
3	Comment	RS-336
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	297.3
11	Pulse Sequence	dept135
12	Number of Scans	469
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-05-27T 11:54:41
18	Modification Date	2015-05-28T 12:03:06
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.18. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2-(3-nitrophenyl) pyridine (**3q**)



	Parameter	Value
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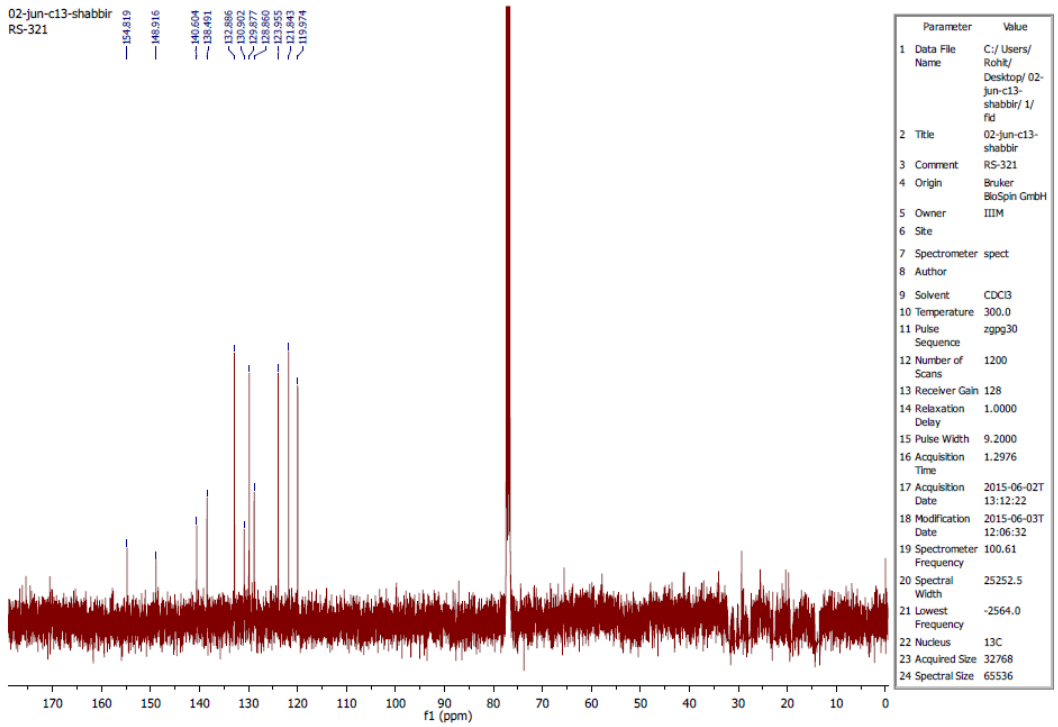
2	Title	14-may-mcd-2a
3	Comment	RS-321
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect r
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zg30
12	Number of Scans	16
13	Receiver Gain	114
14	Relaxation Delay	0.5000
15	Pulse Width	13.1000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-05-14 T16:04:13
18	Modification Date	2015-05-15 T12:02:33
19	Spectrometer Frequency	400.13
20	Spectral Width	12019.2
21	Lowest Frequency	-3104.0
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



	Parameter	Value
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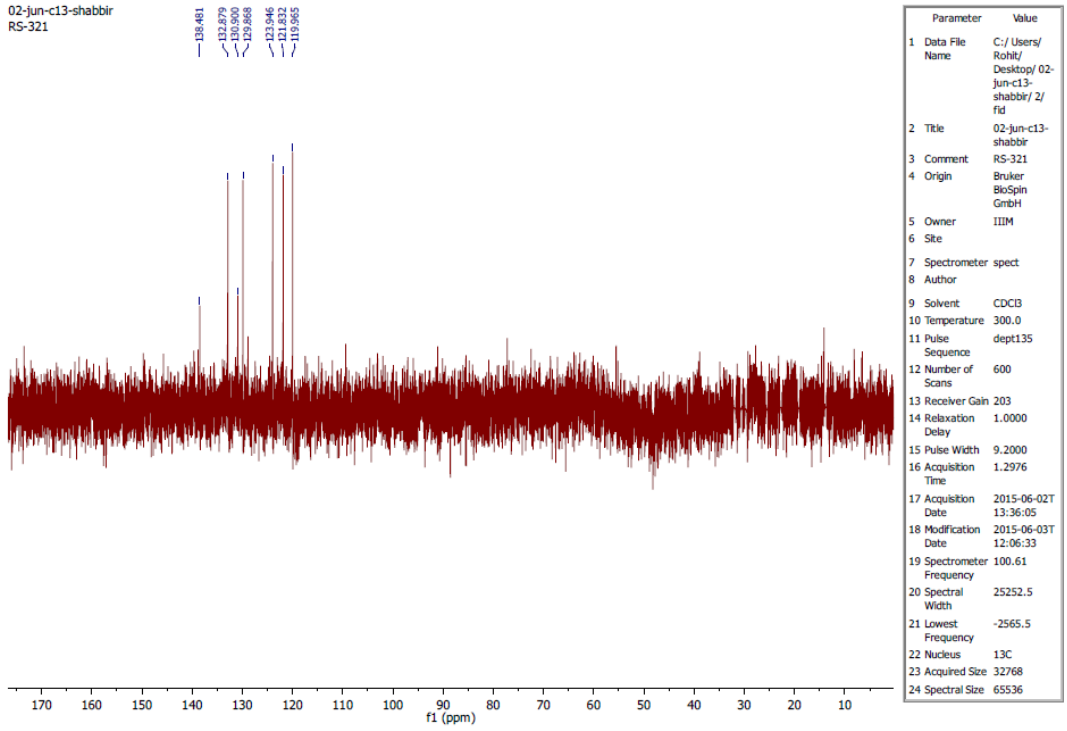
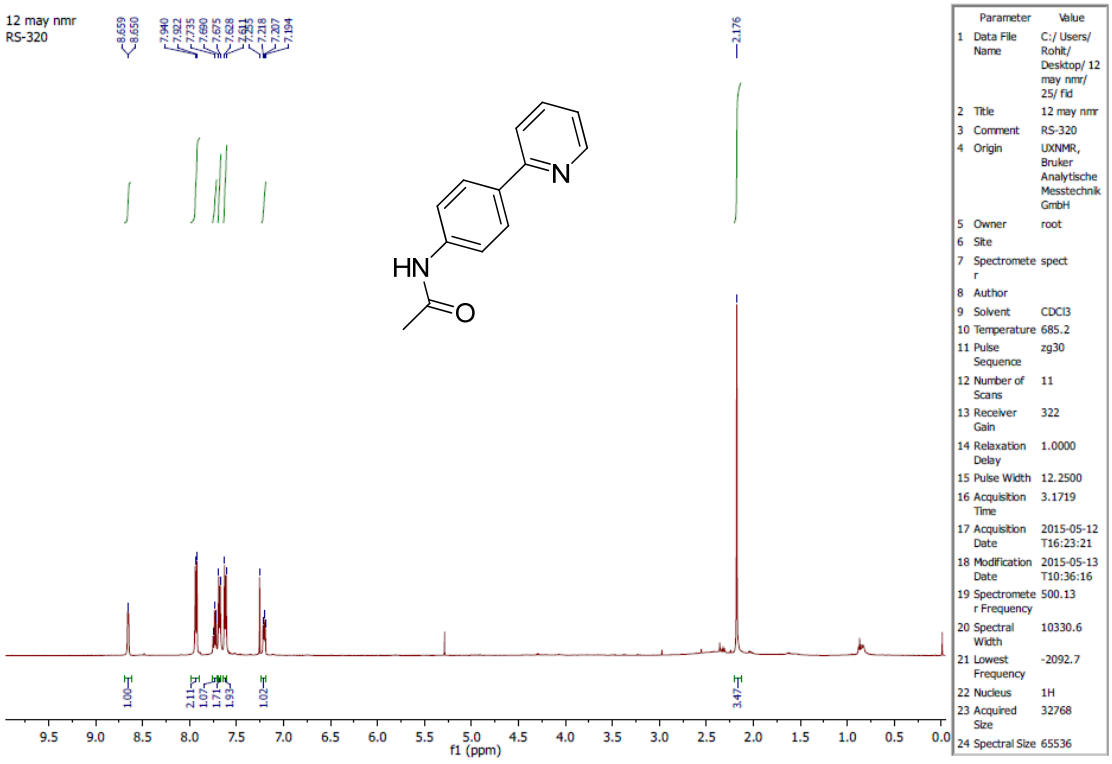
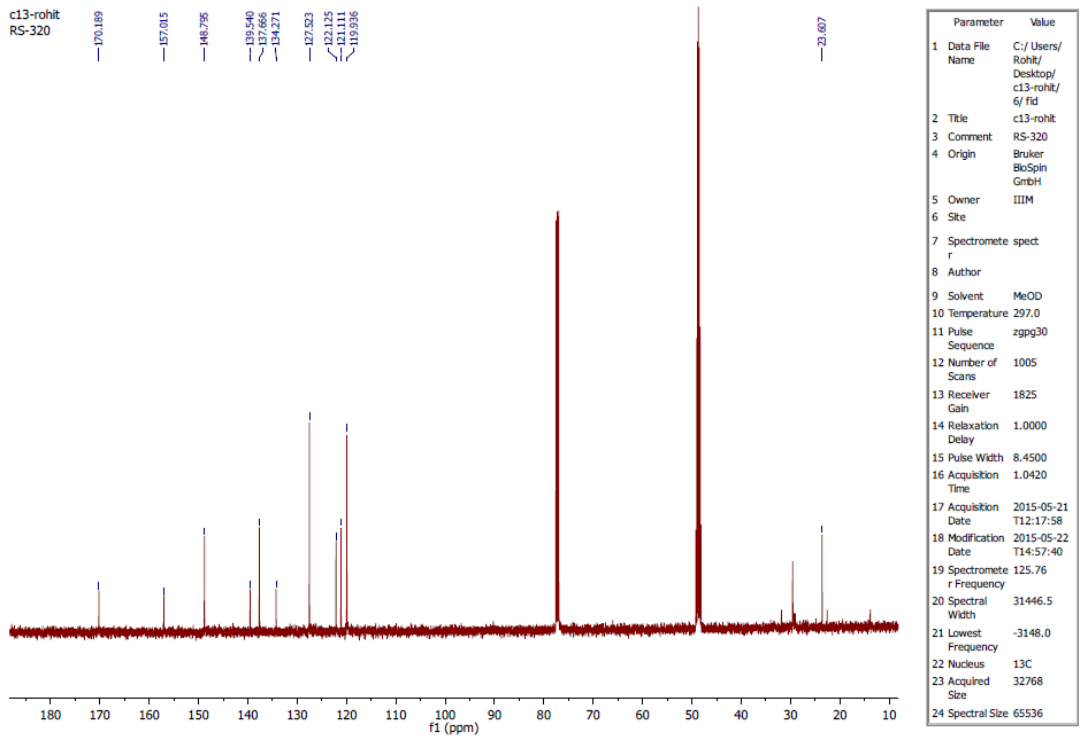
2	Title	02-jun-c13-shabbir
3	Comment	RS-321
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgpg30
12	Number of Scans	1200
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	9.2000
16	Acquisition Time	1.2976
17	Acquisition Date	2015-06-02T 13:12:22
18	Modification Date	2015-06-03T 12:06:32
19	Spectrometer Frequency	100.61
20	Spectral Width	25252.5
21	Lowest Frequency	-2564.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



S2.19. ^{1}H, ^{13}C and DEPT135 NMR spectra of N-(4-(pyridin-2-yl) phenyl) acetamide (**3r**)





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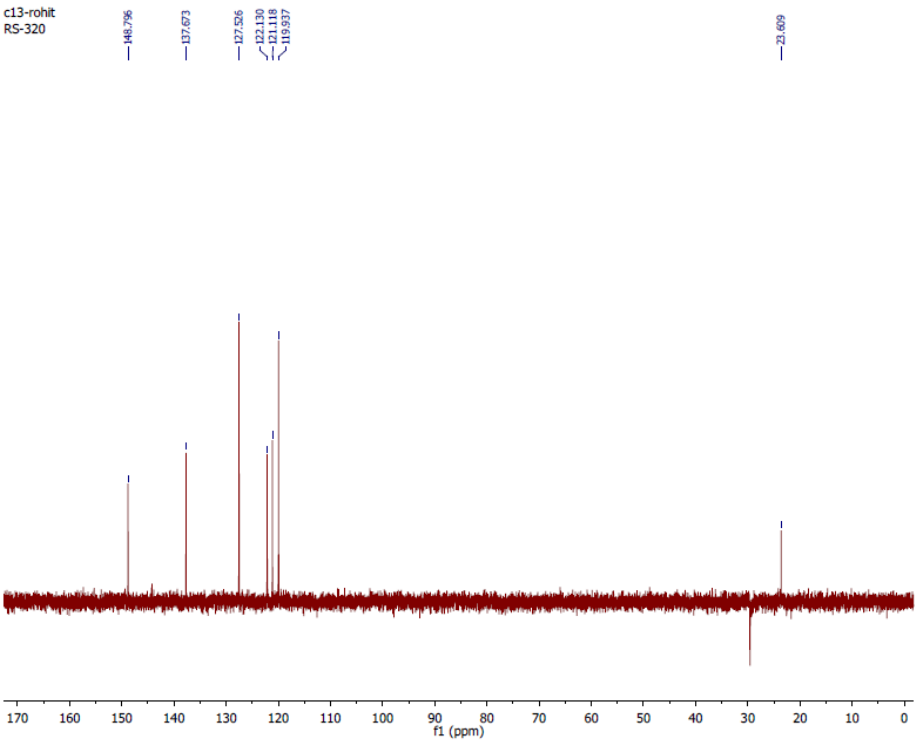
2	Title	c13-rohit
3	Comment	RS-320
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	MeOD
10	Temperature	297.0
11	Pulse Sequence	zgpg30
12	Number of Scans	1005
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-05-21 T12:17:58
18	Modification Date	2015-05-22 T14:57:40
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-3148.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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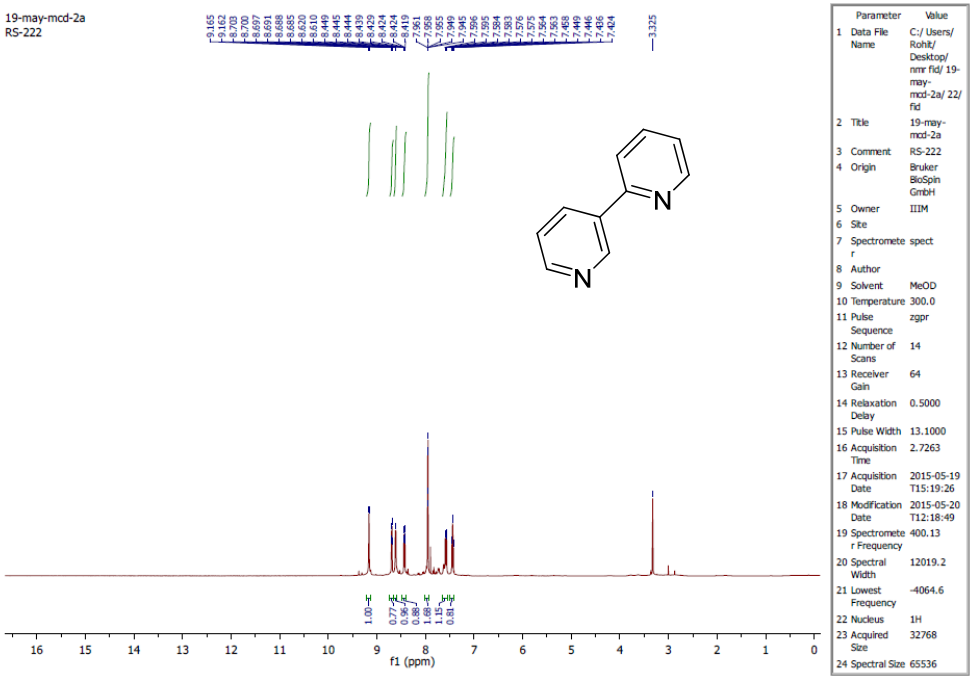
1	Data File Name	C:/ Users/ Rohit/ Desktop/ c13-rohit/ 7/ fid
2	Title	c13-rohit
3	Comment	RS-320
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	MeOD
10	Temperature	296.8
11	Pulse Sequence	dept135
12	Number of Scans	448
13	Receiver Gain	16384
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0912
17	Acquisition Date	2015-05-21T 12:44:49
18	Modification Date	2015-05-22T 14:57:40
19	Spectrometer Frequency	125.76
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.20. ^{1}H, ^{13}C, DEPT135 and HPLC NMR spectra of 2, 3'-bipyridine (**3s**)



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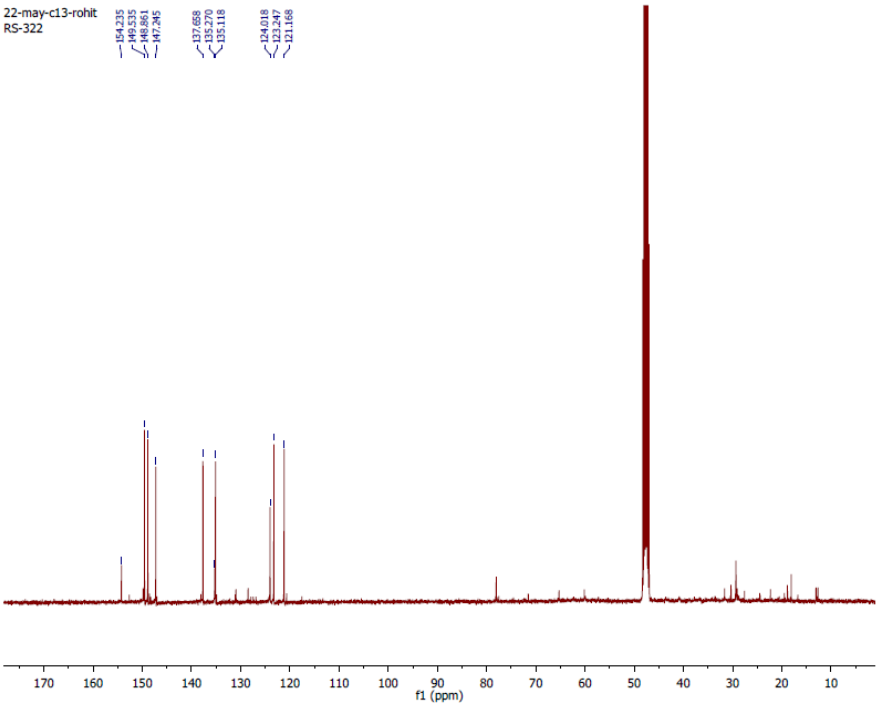
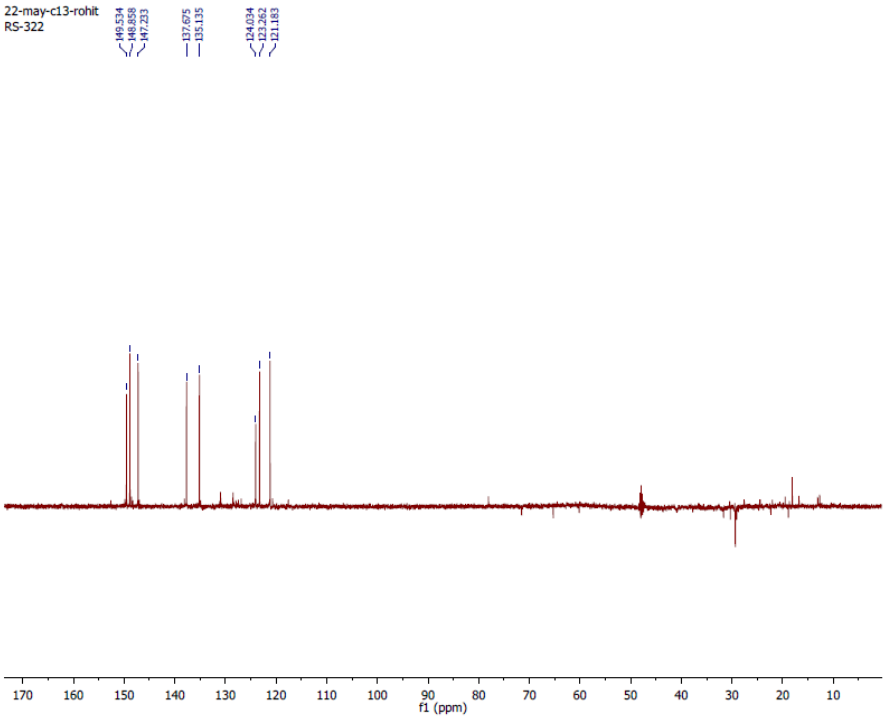
2	Title	19-may-mcd-2a
3	Comment	RS-222
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect r
8	Author	
9	Solvent	MeOD
10	Temperature	300.0
11	Pulse Sequence	zgpr
12	Number of Scans	14
13	Receiver Gain	64
14	Relaxation Delay	0.5000
15	Pulse Width	13.1000
16	Acquisition Time	2.7263
17	Acquisition Date	2015-05-19 T15:19:26
18	Modification Date	2015-05-20 T12:18:49
19	Spectrometer Frequency	400.13
20	Spectral Width	12019.2
21	Lowest Frequency	-4064.6
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536



	Parameter	Value
1	Data File Name	C:/ Users/ Rohit/ Desktop/ 22-may-c13-rohit/ 43/ fid
2	Title	22-may-c13-rohit
3	Comment	RS-322
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect r
8	Author	
9	Solvent	MeOD
10	Temperature	300.0
11	Pulse Sequence	zgpg30
12	Number of Scans	10240
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	9.2000
16	Acquisition Time	1.2976
17	Acquisition Date	2015-05-23 T00:59:18
18	Modification Date	2015-05-26 T18:40:37
19	Spectrometer Frequency	100.61
20	Spectral Width	25252.5
21	Lowest Frequency	-2565.5
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



	Parameter	Value
1	Data File Name	C:/ Users/ Rohit/ Desktop/ 22-may-c13-rohit/ 44/ fid
2	Title	22-may-c13-rohit
3	Comment	RS-322
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	MeOD
10	Temperature	300.0
11	Pulse Sequence	dept135
12	Number of Scans	8192
13	Receiver Gain	203
14	Relaxation Delay	1.0000
15	Pulse Width	9.2000
16	Acquisition Time	1.2976
17	Acquisition Date	2015-05-23 T06:19:14
18	Modification Date	2015-05-26 T18:40:38
19	Spectrometer Frequency	100.61
20	Spectral Width	25252.5
21	Lowest Frequency	-2565.5
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

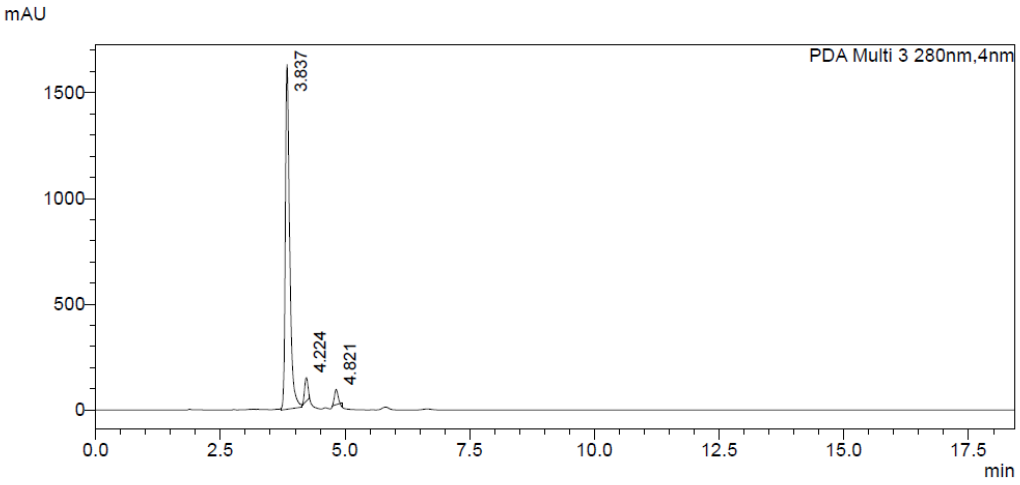
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: Rs-322		
Sample ID	: Rs-322		
Data Filename	: RS-322.lcd		
Method Filename	: 2-phenylpyridine.lcm		
Batch Filename	:		
Vial #	: 1-3	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 05-10-2015 11:29:27	Acquired by	: System Administrator
Date Processed	: 05-10-2015 11:47:55	Processed by	: System Administrator

<Chromatogram>

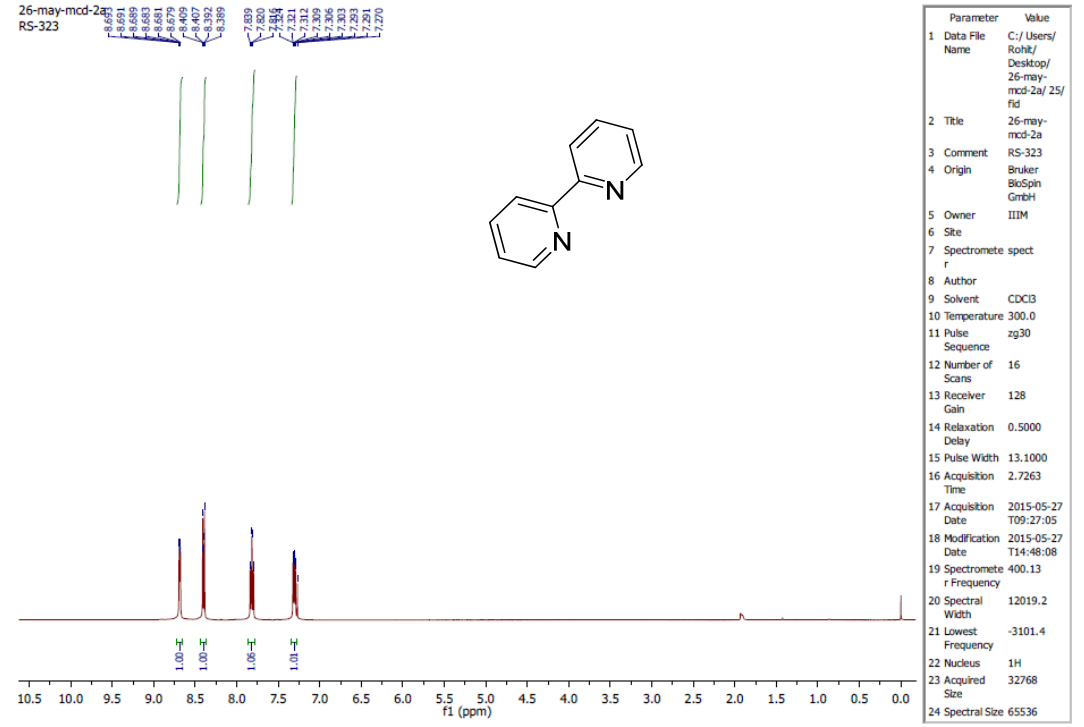


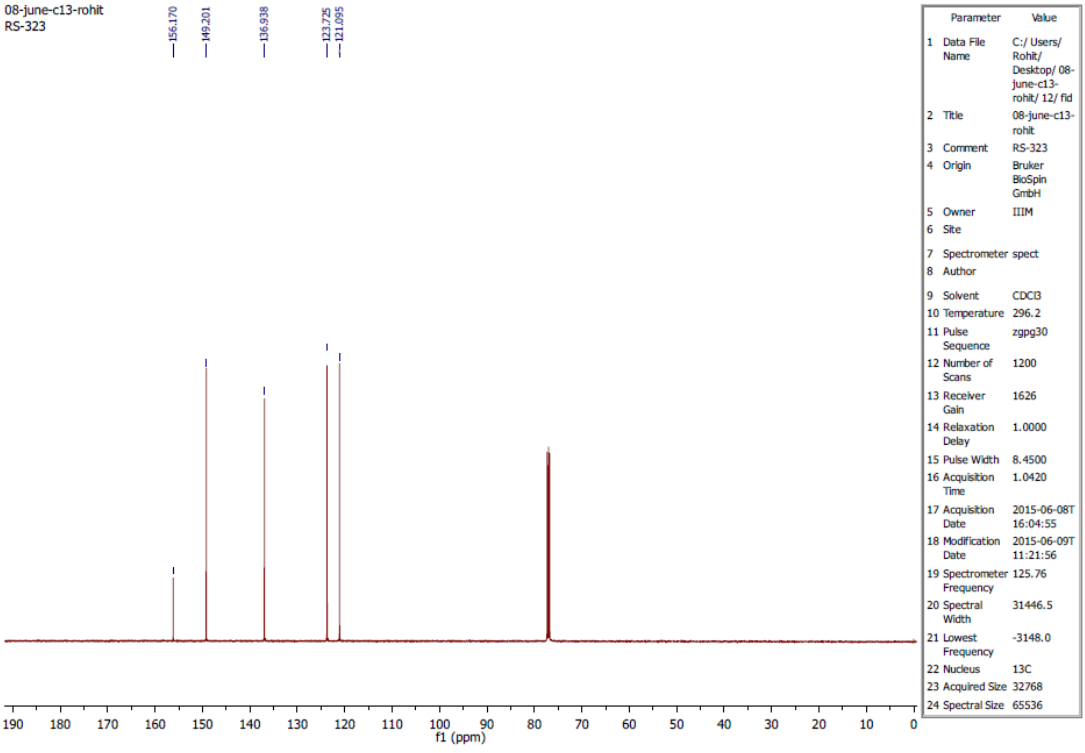
<Peak Table>

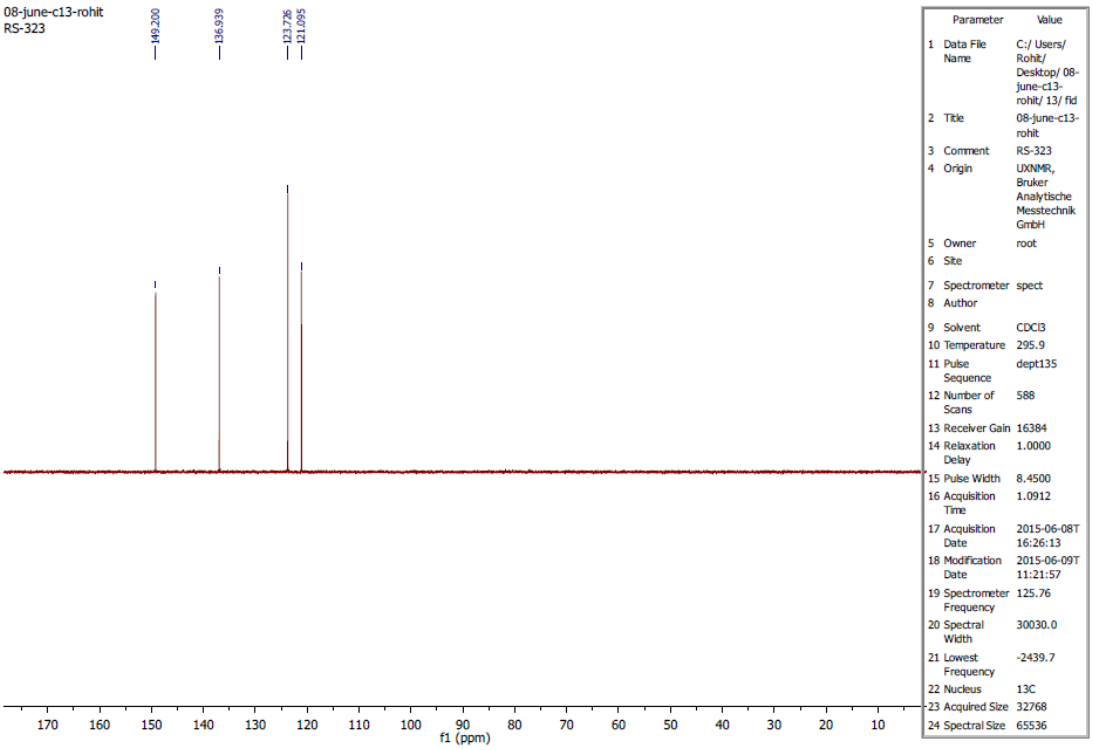
PDA Ch3 280nm

Peak#	Ret. Time	Peak Start	Peak End	Area%
1	3.837	3.712	4.128	92.313
2	4.224	4.149	4.277	4.679
3	4.821	4.747	4.939	3.009
Total				100.000

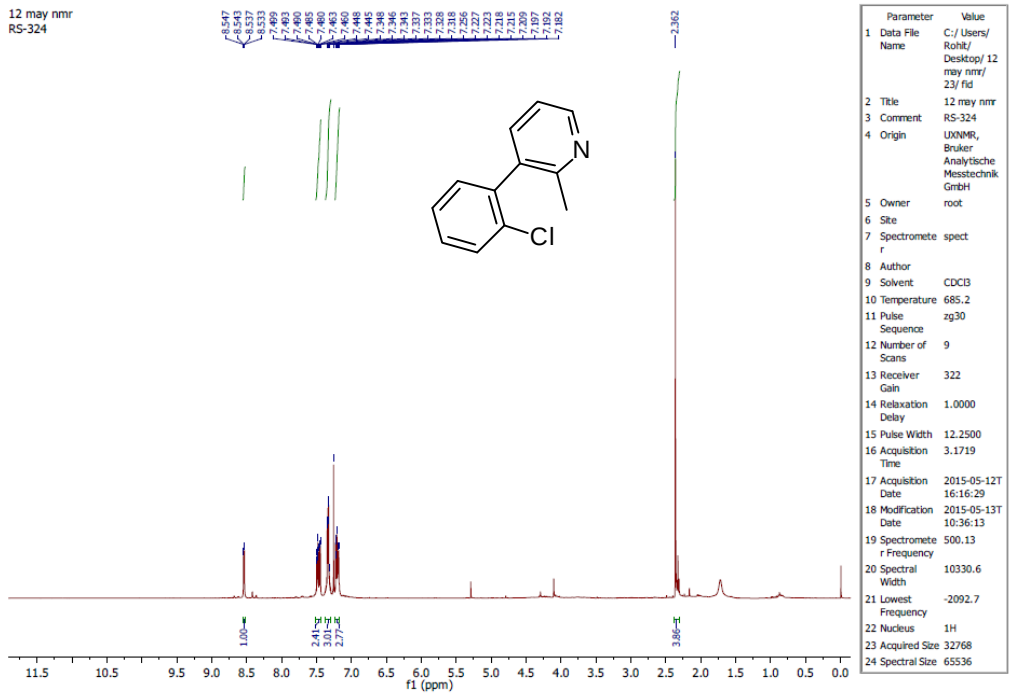
S2.21. ^{1}H, ^{13}C and DEPT135 NMR spectra of 2, 2'-bipyridine (**3t**)

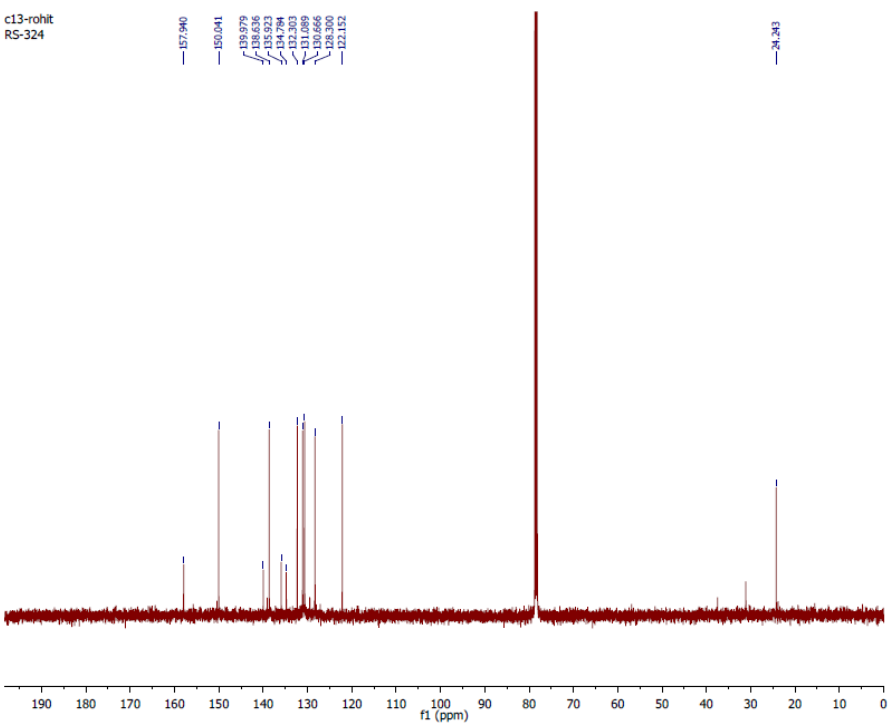






S2.22. ^{1}H, ^{13}C and DEPT135 NMR spectra of 3-(2-chlorophenyl)-2-methylpyridine (**5a**)





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3	Comment	RS-324
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5	Owner	IIIM
6	Site	
7	Spectrometer	spect r
8	Author	
9	Solvent	CDCl3
10	Temperature	298.7
11	Pulse Sequence	zgpg30
12	Number of Scans	1200
13	Receiver Gain	1825
14	Relaxation Delay	1.0000
15	Pulse Width	8.4500
16	Acquisition Time	1.0420
17	Acquisition Date	2015-05-19 T15:16:58
18	Modification Date	2015-05-20 T11:15:35
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-2969.4
22	Nucleus	13C
23	Acquired Size	32768
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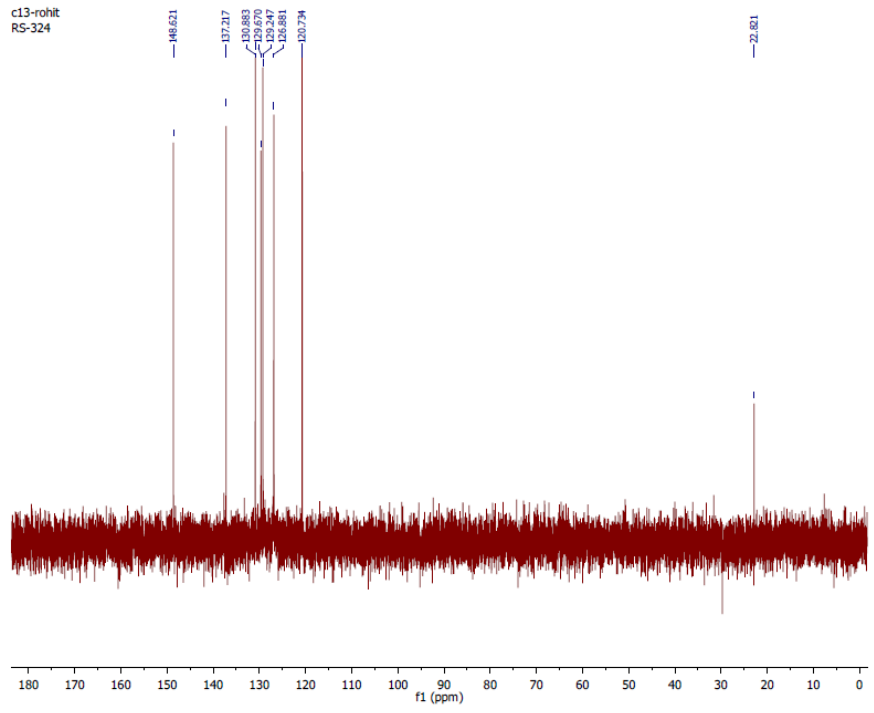

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6	Site	
7	Spectrometer	spect r
8	Author	
9	Solvent	CDCl3
10	Temperature	298.7
11	Pulse Sequence	dept135
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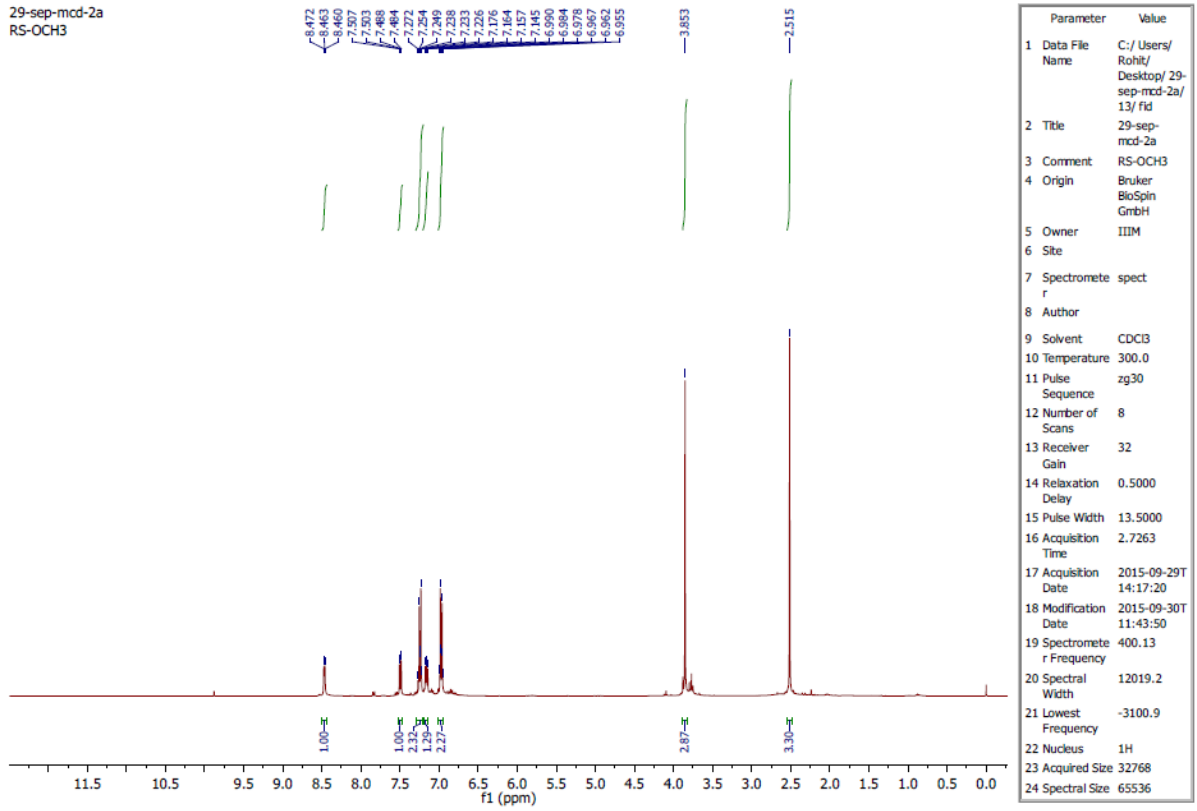
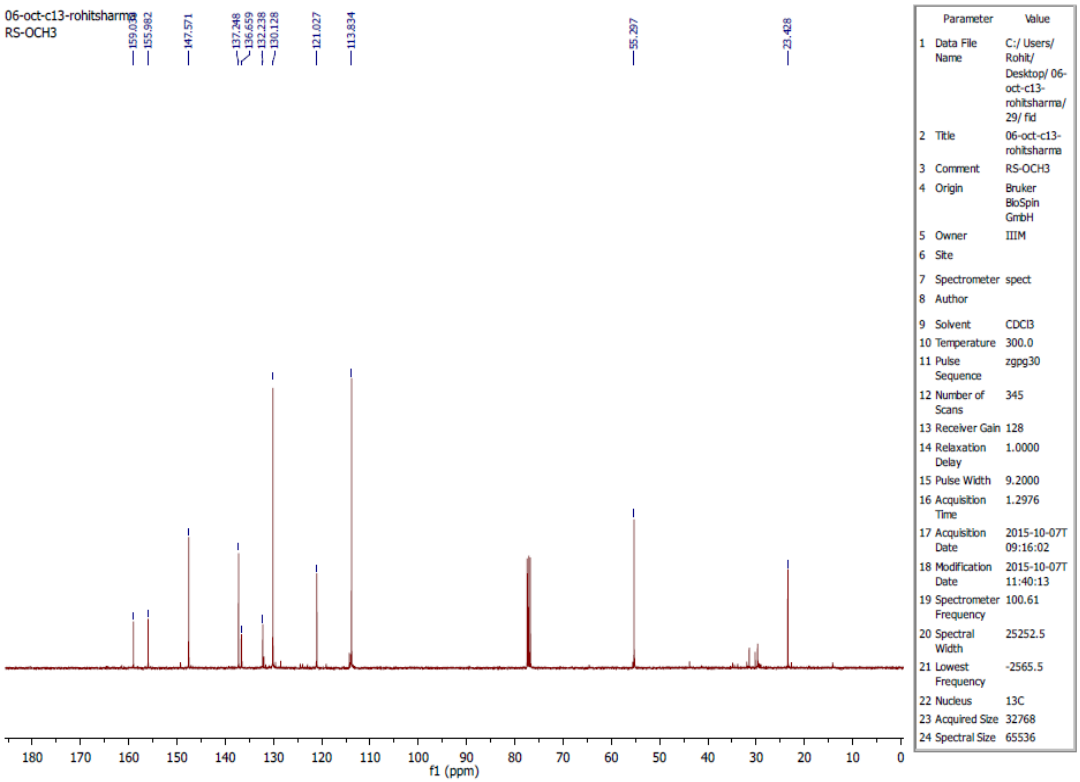
20	Spectral Width	30030.0
21	Lowest Frequency	-2439.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

S2.23. ^{1}H, ^{13}C and DEPT135 NMR spectra of 3-(4-methoxyphenyl)-2-methylpyridine (**5b**)





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3	Comment	RS-OCH3
4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgpg30
12	Number of Scans	345
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	9.2000
16	Acquisition Time	1.2976
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19	Spectrometer Frequency	100.61
20	Spectral Width	25252.5
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22	Nucleus	13C
23	Acquired Size	32768
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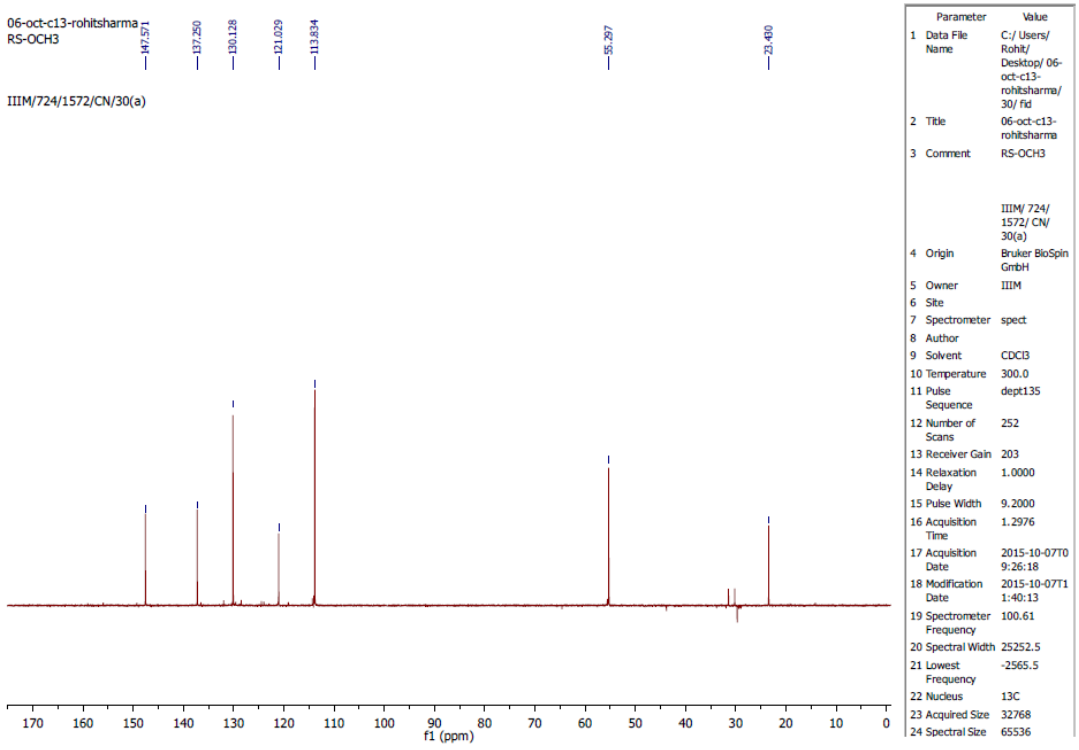

	Parameter	Value
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4	Origin	Bruker BioSpin GmbH
5	Owner	IIIM
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	dept135
12	Number of Scans	252
13	Receiver Gain	203
14	Relaxation Delay	1.0000
15	Pulse Width	9.2000
16	Acquisition Time	1.2976
17	Acquisition Date	2015-10-07T0 9:26:18
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19	Spectrometer Frequency	100.61
20	Spectral Width	25252.5
21	Lowest Frequency	-2565.5
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

SECTION S3. COMPUTATIONAL DETAILS

S3.1. General information

Geometry optimization of all reactants, intermediates, final compound and their corresponding tautomers and conformers have been carried out using Gaussian09 suite of programs.[2] Density Functional B3LYP/6-311+G(d,p)[3] method was utilized to carry out geometry optimization.

Table S1. List of energy values for all the optimized geometries calculated at B3LYP/6 311+G(d,p) level.

Entry no.	Gibbs Free Energy (Hartrees)
1a	-479.331513
2a	-384.897263
3a	-229.801182
I	-538.231196
II	-556.930420
II-C	-556.920318
II-H_2O Complex	-633.370361
II-H_2O-TS	-633.331615
III	-567.723857
IV	-491.282498
V	-395.685998
VI	-549.021117
VIII	-567.717338
VIII-C	-567.706931
VIII-H_2O Complex	-644.156604
VIII-H_2O-TS	-644.125050
IX	-556.928510
X	-480.487101
NH_3	-56.566443
O_2	-150.324188
H_2O	-76.454816
HI	-12.001929
I_2	-22.794938

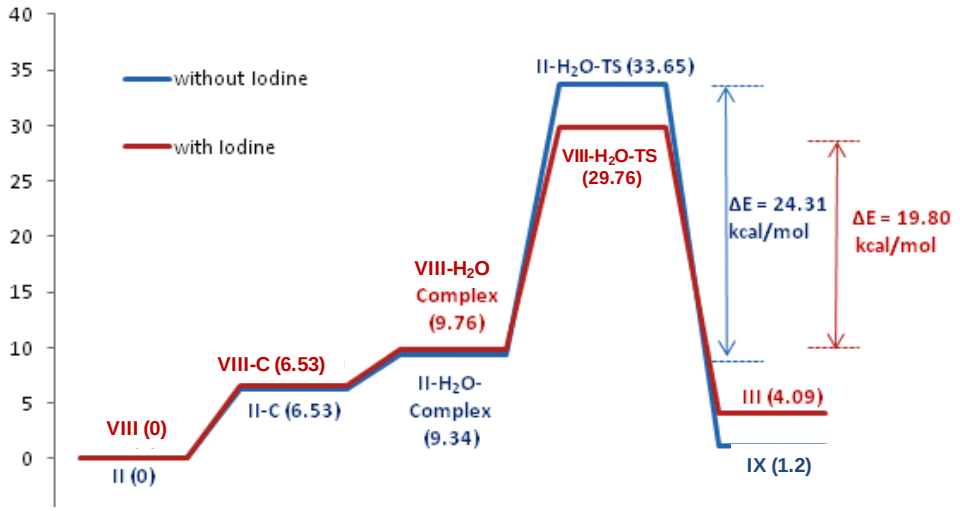


Figure S1. Potential energy surface diagrams of pathway 1 (without I_2) and pathway 3 (with I_2). y axis is showing relative energy values in kcal/mol. All energy differences are taken from the most stable tautomer **VIII**.

S3.2 Cartesian coordinates of optimized geometries

1a

0 1

C	-3.53601800	-0.02648000	0.01027700
C	-2.81076300	-1.19546200	0.24050000
C	-1.42008400	-1.17314100	0.22811200
C	-0.72480000	0.02229600	-0.00492400
C	-1.46455600	1.18960500	-0.24224100
C	-2.85685000	1.16536900	-0.23533600
H	-4.62005600	-0.04522100	0.01693700
H	-3.33087700	-2.12800600	0.42976000
H	-0.85151100	-2.07847900	0.39660100
H	-0.95658400	2.12179900	-0.45976600
H	-3.41068000	2.07696900	-0.43028000
C	0.76287700	0.02461300	-0.00165400
C	1.50301000	1.18815200	0.26223700
C	2.89088200	1.13134600	0.24492200
C	2.70258700	-1.19234100	-0.25542400
C	3.51399700	-0.08381900	-0.02458500
N	1.37035600	-1.14951500	-0.24609700
H	3.47655400	2.02100000	0.44864100
H	4.59307600	-0.17600400	-0.04840800
H	3.14510700	-2.16377100	-0.45995900

H	1.00079600	2.11748300	0.49786100

2a

0 1

C	-2.59038500	0.11447400	0.00000400
C	-1.82101600	1.27642500	-0.00001600
C	-0.43059100	1.19137100	-0.00002300
C	0.20445300	-0.05768000	-0.00000400
C	-0.57995700	-1.21974300	0.00001700
C	-1.96662200	-1.13473600	0.00002000
H	-3.67269100	0.18124300	0.00000600
H	-2.30281800	2.24755300	-0.00002900
H	0.15389700	2.10337400	-0.00004100
H	-0.07728100	-2.17917000	0.00003100
H	-2.56421100	-2.03935300	0.00003700
C	1.69881900	-0.20441700	-0.00000700
O	2.21337200	-1.30703900	-0.00004000
C	2.55853800	1.04628600	0.00003800
H	2.35532300	1.66056700	-0.88200400
H	2.35534700	1.66049000	0.88214000
H	3.60602500	0.74972100	0.00001200

3a

0 1

C	-1.27558100	0.49571100	0.05244900
H	-1.30075000	1.24966500	-0.74164300
H	-1.25398600	1.04367800	1.00896300
C	-0.00001800	-0.33560300	-0.08221700
H	-0.00039700	-1.11803900	0.68996500
H	0.00037100	-0.84847100	-1.04762900
C	1.27566500	0.49547100	0.05326900
H	1.25391400	1.04252300	1.01041100
H	1.30054500	1.25043200	-0.73993400
N	-2.46565200	-0.35022500	-0.10440500
N	2.46556900	-0.34994800	-0.10462500
H	3.31458000	0.20441700	-0.07619100
H	2.52708500	-1.03089700	0.64609300
H	-3.31459100	0.20437800	-0.07540100
H	-2.52658400	-1.02994700	0.64757400

I

0 1

C	-3.22655900	-1.80260400	0.11663200
C	-2.87351900	-1.11152700	1.27458400
C	-1.99514700	-0.03199200	1.20533100
C	-1.44219900	0.35975200	-0.01961000
C	-1.80246600	-0.34101100	-1.17653900

C	-2.69166200	-1.41190500	-1.10976200
H	-3.91474900	-2.63860900	0.16953000
H	-3.28386600	-1.41079300	2.23264800
H	-1.72803900	0.50158200	2.11131100
H	-1.38828100	-0.04185300	-2.13332600
H	-2.96501000	-1.94163500	-2.01562200
C	-0.50761200	1.53868100	-0.09385900
C	-1.13547500	2.88344600	0.18868300
H	-1.94232800	3.08626000	-0.52354900
H	-1.58692300	2.90043900	1.18615600
H	-0.38076700	3.66642200	0.11928700
C	1.42344000	0.23510100	-0.63047600
H	0.82181400	-0.64946900	-0.38417800
H	1.64238700	0.19058500	-1.70537500
C	2.74368300	0.20236700	0.14676400
H	3.31015000	1.11009100	-0.09059000
H	2.54033200	0.23045400	1.22168600
C	3.58568900	-1.03301800	-0.16906000
H	3.77060100	-1.07452900	-1.25559500
H	3.02310800	-1.93680900	0.08898700
N	0.73188900	1.49351600	-0.38205300
N	4.81754200	-1.03619600	0.62986900
H	5.36265100	-1.87439200	0.45832000
H	5.40387400	-0.24272100	0.38947900

II

0 1

C	-4.16467600	-0.96517000	-0.03179100
C	-4.01721200	0.41839400	-0.04373800
C	-2.74416100	0.98781200	-0.03036800
C	-1.59633200	0.18373100	-0.00282300
C	-1.76140300	-1.21077400	0.00965900
C	-3.02890600	-1.77764200	-0.00556000
H	-5.15390800	-1.40885400	-0.04380400
H	-4.89141900	1.05944900	-0.06373800
H	-2.65932600	2.06711300	-0.03975500
H	-0.87538600	-1.83169000	0.03003900
H	-3.13498200	-2.85684400	0.00211800
C	-0.21996000	0.77317100	0.01344800
C	-0.10717900	2.28272200	-0.07543300
H	-0.60500300	2.65622600	-0.97442600
H	-0.59593300	2.75268100	0.78318000
H	0.92745300	2.61744300	-0.09581600
C	2.14221300	0.44058200	0.12872000
H	2.35525100	1.11039800	-0.71436300
H	2.33277100	1.01362400	1.04740300
C	3.10093000	-0.75892500	0.06886400
H	2.82330000	-1.45255200	0.87293900

H	3.00949200	-1.28485300	-0.88305300
C	4.53491100	-0.35198400	0.28720000
H	4.73063100	0.18474600	1.24388400
N	0.76616900	-0.03374600	0.10758000
O	5.44306600	-0.56527000	-0.47834200

II-C

0 1

C	3.83829100	0.34101900	-0.53844800
C	3.04976500	1.39467300	-0.07843700
C	1.73918400	1.16415000	0.33175900
C	1.19644900	-0.12688300	0.29472900
C	1.99546300	-1.17897000	-0.17604300
C	3.30644500	-0.94654100	-0.58552000
H	4.85775600	0.52228200	-0.85979600
H	3.45156900	2.40138600	-0.04947100
H	1.12050000	1.98843600	0.66589200
H	1.59521200	-2.18632100	-0.19345000
H	3.91513100	-1.77355200	-0.93411800
C	-0.20349800	-0.37408900	0.74529300
C	-0.66674200	0.15591000	1.89493000
H	-1.67385600	0.00211600	2.25588600
H	-0.00272300	0.72612400	2.52784400
C	-2.34273200	-1.46481400	0.03747400
H	-2.56110800	-2.45803500	-0.36556500
H	-2.59549500	-1.50351200	1.09879300
C	-3.24716900	-0.45072500	-0.70547100
H	-3.01979100	-0.44581600	-1.77513500
H	-4.28667900	-0.78617800	-0.58328200
C	-3.18208500	0.97087000	-0.19905200
H	-3.43562500	1.10865500	0.87336500
N	-0.91814300	-1.23071600	-0.09141800
O	-2.90873600	1.92259800	-0.88877300
H	-0.56823100	-1.26894600	-1.03813700

II-H_2O Complex

0 1

C	3.85528800	0.49349300	0.15665300
C	3.15071300	0.11703000	1.29927500
C	1.85977400	-0.39412500	1.19108400
C	1.25229500	-0.54384100	-0.06257300
C	1.96552100	-0.15255800	-1.20449200
C	3.25699300	0.35744000	-1.09520900
H	4.86026600	0.89164800	0.24119200
H	3.60291600	0.23003400	2.27847000
H	1.30620400	-0.66433000	2.08246700
H	1.51038400	-0.26985600	-2.18083000

H	3.79909900	0.64266800	-1.99015600
C	-0.12187800	-1.11181100	-0.17999200
C	-0.48305900	-2.19451200	0.54213900
H	-1.46610700	-2.64190000	0.49307100
H	0.24584500	-2.69203600	1.16517700
C	-2.32490700	-0.77220700	-1.26284300
H	-2.62503500	-0.57502200	-2.29573000
H	-2.47153700	-1.83893000	-1.09415800
C	-3.28271500	0.06644000	-0.35589900
H	-3.30701400	1.09431400	-0.72456600
H	-4.28807300	-0.36212400	-0.44056000
C	-2.88522800	0.09858000	1.09419400
H	-3.13685300	-0.78886400	1.70531400
N	-0.92049800	-0.46176100	-1.11860200
O	-2.31055800	1.03728800	1.60781600
H	-0.70713400	0.52679200	-1.22360100
H	-1.39950200	2.24297500	0.36430900
O	-1.02002700	2.52958200	-0.48513300
H	-0.29206800	3.11842600	-0.26566600

II-H_2O-TS

0 1

C	-3.66217600	0.00487200	0.42033300
C	-3.00148700	-1.15262900	0.00793800
C	-1.63334900	-1.28854300	0.20927500
C	-0.90798400	-0.24743800	0.80851400
C	-1.57608600	0.92072600	1.20871300
C	-2.94837400	1.03995300	1.02334300
H	-4.73153100	0.10091200	0.26983200
H	-3.55264400	-1.94740700	-0.48092800
H	-1.11015800	-2.16139700	-0.15903000
H	-1.02091300	1.71876100	1.68747400
H	-3.46058200	1.93804600	1.34825800
C	0.53908400	-0.36605700	1.00339900
C	1.23863800	-1.65625200	1.21816900
H	1.85172200	-1.64517300	2.12639300
H	0.54139300	-2.48816400	1.28005200
C	2.75600700	0.55593200	0.88877200
H	3.17959300	1.48318500	0.50886100
H	3.00510900	0.48046600	1.95135800
C	3.28523400	-0.68464000	0.11942400
H	3.64024200	-0.38588700	-0.86651500
H	4.12638100	-1.10157700	0.68216500
C	2.17982700	-1.74775200	-0.07923800
H	2.63039200	-2.75113000	-0.04778700
N	1.29613600	0.67610400	0.78793700

O	1.45509100	-1.57665800	-1.23108000
H	0.96833900	1.30114200	0.01917000
H	1.27371800	-0.42306100	-1.53184800
O	1.06505300	0.78602900	-1.67695200
H	1.08040000	1.06829100	-2.59378300

III

0 1

C	-4.41364700	-0.34418600	0.20297000
C	-4.01798200	0.52495800	-0.81517200
C	-2.69735200	0.94637900	-0.90202900
C	-1.73926600	0.50617400	0.02442800
C	-2.14704300	-0.37233900	1.03665200
C	-3.47372700	-0.78945000	1.12779700
H	-5.44446700	-0.67323800	0.27118900
H	-4.74178500	0.87199100	-1.54416300
H	-2.38290600	1.62411600	-1.68485600
H	-1.44135700	-0.74354600	1.76846300
H	-3.76851900	-1.46564800	1.92219000
C	-0.33120700	1.00004100	-0.09479300
C	0.75974000	0.30265700	0.69110300
C	2.02469300	1.15157900	0.85348000
H	0.41650200	-0.01219700	1.67094100
C	1.20395900	2.59651600	-1.02716100
C	2.39314700	1.80144600	-0.47531600
H	1.32278400	2.76452500	-2.10221500
H	3.25982900	2.45374700	-0.34251900
N	-0.12053700	2.02466000	-0.83102000
O	1.80107700	2.10717700	1.89728200
H	1.13643900	2.74619000	1.61560700
H	2.83989900	0.53101800	1.22354700
H	2.67838100	1.01433100	-1.17778300
H	1.16916000	3.60527200	-0.59349000
I	1.24572200	-1.65451400	-0.26641100

IV

0 1

C	-4.27671400	-0.83807600	0.08043400
C	-4.08064700	0.39980300	-0.53479600
C	-2.82471000	0.99210800	-0.53221000
C	-1.73362700	0.36314400	0.08879500
C	-1.94251000	-0.87996800	0.70069200
C	-3.20314300	-1.47496100	0.69545400
H	-5.25728900	-1.30073400	0.07793200
H	-4.91108700	0.90393600	-1.01651000
H	-2.66365100	1.95168300	-1.00553400
H	-1.12467700	-1.41364000	1.16677300

H	-3.34064100	-2.44019000	1.16946600
C	-0.40393400	1.04756800	0.08762900
C	0.72102900	0.46965200	0.90894000
C	1.77082300	1.44348800	1.26128900
C	0.96262500	2.87418200	-0.56524400
C	1.89537200	2.57477500	0.56541700
H	1.47000200	2.68548300	-1.52577700
H	2.66737100	3.29952100	0.80280300
N	-0.28346800	2.13343900	-0.57726200
H	2.43398400	1.19861100	2.08302700
H	0.71283700	3.94127000	-0.58576800
H	0.37545300	-0.10952200	1.75700300
I	1.70404900	-1.23548700	-0.29096200

V

0 1

C	3.86135900	-1.11731900	-0.19110200
C	2.76259300	-1.64357600	0.48547800
C	1.62413700	-0.86570400	0.67807000
C	1.57413600	0.44868900	0.19485200
C	2.68576000	0.96826300	-0.48477100
C	3.82047900	0.19091400	-0.67691400
H	4.74686300	-1.72478800	-0.34107000
H	2.79018200	-2.66003300	0.86062500
H	0.77644800	-1.29822800	1.19394400
H	2.63617100	1.98557100	-0.85253600
H	4.67397900	0.60105700	-1.20447400
C	0.39095400	1.34356600	0.38561500
O	0.39974100	2.49754800	0.00166800
C	-0.84168100	0.82645300	1.10636800
H	-0.62727300	0.18097100	1.95285100
H	-1.45974300	1.66843500	1.39799300
I	-2.11322600	-0.37058700	-0.22653300

VI

0 1

C	3.43356900	-3.18863700	0.19603000
C	2.87784400	-2.60995500	1.33581600
C	1.79250800	-1.74321300	1.22242800
C	1.26006100	-1.43582300	-0.03475500
C	1.82106300	-2.02308800	-1.17441800
C	2.90217800	-2.89457300	-1.05872100
H	4.27570500	-3.86537900	0.28510100
H	3.28801900	-2.83309300	2.31429800
H	1.36475200	-1.29429600	2.11267200
H	1.41193300	-1.79425200	-2.15267900
H	3.32942000	-3.34280800	-1.94873900

C	0.08247400	-0.50063700	-0.15789600
C	-1.22155400	-1.20735900	0.13624100
H	-1.38353300	-2.01730600	-0.57487900
H	-1.20807400	-1.63742300	1.13722500
C	1.37970200	1.40716400	-0.74896500
H	2.26430800	0.77921900	-0.58149900
H	1.36581800	1.67913800	-1.81169000
C	1.47310000	2.68539800	0.09164400
H	0.56015900	3.27098500	-0.06301400
H	1.50666200	2.42836900	1.15481200
C	2.69930300	3.52873300	-0.25592100
H	2.67660700	3.77054300	-1.33166200
H	3.60866200	2.94274900	-0.08403600
N	0.12371000	0.72326700	-0.47664900
N	2.76840100	4.71498800	0.60555700
H	3.60627200	5.25523800	0.41807800
H	1.97421600	5.32602000	0.44126800
I	-3.01673900	0.02182000	0.04667000

VIII

0 1

C	3.65415000	-2.84981400	0.14908200
C	3.02113600	-2.38450500	1.30036300
C	1.87588100	-1.59730400	1.19958100
C	1.36130100	-1.25485900	-0.05604700
C	2.00072800	-1.72710900	-1.20794400
C	3.14090700	-2.52127400	-1.10459800
H	4.54294400	-3.46516500	0.22844200
H	3.41788000	-2.63394900	2.27788500
H	1.38825500	-1.23700600	2.09923500
H	1.60547400	-1.47128700	-2.18520500
H	3.62856800	-2.88169700	-2.00327200
C	0.12272700	-0.40271000	-0.16558100
C	-1.13565200	-1.19994500	0.08921600
H	-1.24385500	-1.98430700	-0.65986000
H	-1.09582900	-1.67568000	1.06847200
C	1.29091000	1.60545000	-0.67948600
H	2.21693300	1.04302700	-0.51121500
H	1.27701600	1.91657600	-1.73124500
C	1.26491000	2.85971000	0.21109100
H	0.28915400	3.34503400	0.08033000
H	1.38028500	2.60134900	1.26556700
C	2.33057000	3.85126800	-0.18112000
H	2.31520400	4.15603100	-1.25232900
N	0.08139200	0.83100900	-0.44939100

O	3.15620300	4.31377500	0.56662400
I	-3.00201500	-0.08138900	0.04921900

VIII-C

0 1

C	2.81934800	2.89244700	0.59213700
C	2.06189700	2.20648700	1.54035100
C	0.98378300	1.42033200	1.14049800
C	0.65348700	1.31542700	-0.21440200
C	1.41012300	2.01435100	-1.16170600
C	2.49231900	2.79449300	-0.75941200
H	3.66074900	3.50054500	0.90490700
H	2.30966800	2.28225300	2.59305000
H	0.39319500	0.88727200	1.87624300
H	1.15769000	1.93233600	-2.21286500
H	3.08102800	3.32208000	-1.50148400
C	-0.53170400	0.51362400	-0.64202300
C	-0.59906800	-0.82857700	-0.57741100
H	-1.45896000	-1.39944000	-0.88728600
C	-2.90892900	0.83963700	-1.39306200
H	-3.35417600	1.47460900	-2.16379400
H	-2.86473300	-0.16557100	-1.81701500
C	-3.84225600	0.87605000	-0.15728900
H	-3.92684500	1.89662900	0.22564800
H	-4.83910200	0.55338200	-0.48803400
C	-3.43674700	-0.02746200	0.98336500
H	-3.38545800	-1.11057900	0.74243000
N	-1.55742300	1.31088800	-1.15657600
O	-3.20255800	0.36100300	2.10159100
H	-1.48986200	2.27927100	-0.87733500
I	0.99293800	-2.10599800	-0.02297100

VIII-H_2O Complex

0 1

C	0.51163700	3.96899500	0.30863100
C	0.51593800	2.99425100	1.30550500
C	0.21782100	1.67029200	0.99250100
C	-0.09054400	1.30704000	-0.32262600
C	-0.10773800	2.29301500	-1.31618300
C	0.19949900	3.61519700	-1.00310800
H	0.74935900	4.99834300	0.55291200
H	0.75192400	3.26408700	2.32883300
H	0.21767800	0.91444300	1.76827500
H	-0.35135700	2.01621500	-2.33525600
H	0.19683200	4.36766700	-1.78378300
C	-0.45089400	-0.10064800	-0.66320400
C	0.36364300	-1.15888500	-0.47211800

H	0.08994000	-2.17173400	-0.71640700
C	-2.34452400	-1.47580800	-1.52228500
H	-3.02372600	-1.34736800	-2.36914300
H	-1.58357500	-2.18838800	-1.84103400
C	-3.20158000	-2.06380100	-0.35368600
H	-4.11344500	-1.47061500	-0.25727000
H	-3.47489300	-3.09123800	-0.61935300
C	-2.50519300	-2.06750000	0.97967900
H	-1.78594900	-2.88594000	1.17276300
N	-1.71685500	-0.20306800	-1.24201500
O	-2.69521500	-1.22290600	1.83143500
H	-2.36596500	0.51148300	-0.92051500
H	-3.52043900	0.44229700	1.20291400
O	-3.80485900	1.08995500	0.53414200
H	-3.79789400	1.94666200	0.97107900
I	2.40342800	-1.07007000	0.09465700

VIII-H_2O-TS

0 1

C	-3.70126300	0.02062500	0.55536000
C	-3.08320900	-1.14896000	0.11222900
C	-1.70689600	-1.29942100	0.22515400
C	-0.92977100	-0.26605300	0.77144200
C	-1.55901400	0.91124300	1.20912000
C	-2.93751400	1.04935800	1.10558700
H	-4.77657600	0.12982200	0.47177200
H	-3.67438600	-1.94095300	-0.33202700
H	-1.22796400	-2.18793900	-0.16516200
H	-0.96511700	1.69984500	1.65510200
H	-3.41660500	1.95522700	1.45797500
C	0.52675900	-0.38740200	0.88049200
C	1.22568100	-1.69441700	1.05304200
H	0.53955100	-2.52455700	0.94680400
C	2.72969600	0.63377200	0.80689300
H	3.09982300	1.54297700	0.33858500
H	2.94635100	0.68078500	1.87669500
C	3.36997600	-0.63222500	0.19009400
H	3.81255000	-0.39622300	-0.77843000
H	4.16262000	-0.98363500	0.85456500
C	2.32541500	-1.73452600	-0.04136600
H	2.81041300	-2.71729700	-0.01430400
N	1.26723100	0.66447800	0.66736500
O	1.61305700	-1.57996600	-1.22863500
H	0.93863300	1.26577200	-0.13376500
H	1.41289000	-0.47988300	-1.55376100
O	1.11469400	0.75229200	-1.74969300
H	1.27002100	1.09149800	-2.63384400
I	1.88182100	-1.96343100	3.18717100

IX

0 1

C	3.96097800	-0.27193200	0.18577200
C	3.37590800	0.98319900	0.36848800
C	2.00463400	1.14502800	0.22212100
C	1.18224300	0.05329500	-0.10203000
C	1.78103300	-1.20085500	-0.28127100
C	3.15948300	-1.36104300	-0.14284400
H	5.03198500	-0.39716300	0.29932600
H	3.99361500	1.83652500	0.62598200
H	1.54187500	2.11460500	0.35380400
H	1.18206900	-2.06282600	-0.54703300
H	3.60351000	-2.33875300	-0.29279900
C	-0.28428700	0.26544600	-0.26663100
C	-1.24311500	-0.91019400	-0.31988400
C	-2.49187900	-0.68047500	0.56283100
H	-1.58438800	-1.00734700	-1.36106400
C	-2.16950800	1.60160200	-0.53513200
C	-2.93226500	0.79871400	0.52983700
H	-2.42545700	2.66105000	-0.47393600
H	-4.01116700	0.85214700	0.35874700
N	-0.72495500	1.46222600	-0.38368700
O	-3.53463200	-1.59066000	0.20072500
H	-3.80334500	-1.41040700	-0.70723100
H	-2.24979500	-0.96517900	1.58775000
H	-2.74462900	1.25953800	1.50353800
H	-2.46060100	1.26858800	-1.54352100
H	-0.78127000	-1.85778700	-0.05109300

X

0 1

C	-3.60997700	0.02601700	0.09781600
C	-2.93341300	-1.17937000	-0.10063400
C	-1.54579900	-1.20139200	-0.16884300
C	-0.80446700	-0.01629400	-0.04945300
C	-1.49350100	1.18751900	0.14901100
C	-2.88537800	1.20789600	0.22668500
H	-4.69288500	0.04176800	0.15095300
H	-3.49187500	-2.10331400	-0.20333800
H	-1.00996300	-2.13071200	-0.31414300
H	-0.94661200	2.11551700	0.26604100
H	-3.40100400	2.14770900	0.38989000
C	0.68519500	-0.06361900	-0.11586500
C	1.43279000	1.17254700	-0.45082000
C	2.74119300	1.24705100	-0.18076900
C	2.73003400	-1.21866000	-0.01017100

C	3.43024200	0.06498900	0.44391800
H	3.09423800	-2.07972600	0.55467000
H	4.48921900	0.03387600	0.17234500
N	1.27253500	-1.18408300	0.10751000
H	3.30190200	2.15431300	-0.38360000
H	3.39273700	0.15685000	1.53950400
H	2.96876000	-1.41193100	-1.06768800
H	0.90621100	2.00413900	-0.90245300

SECTION S4. Effect of HCl loading on product yield

The effect of the variation in loading of HCl quantity along with amount of 1,3-diaminopropane (**2**) was studied, and results are shown in Figure S2.

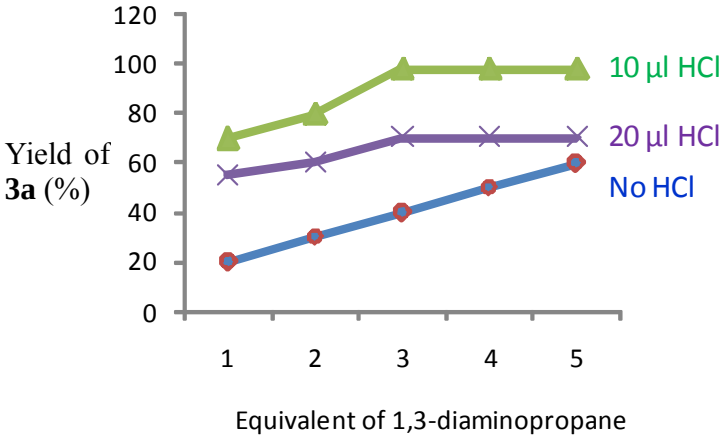


Figure S2. Effect of HCl loading on product yield.

SECTION S5. The gram-scale reaction

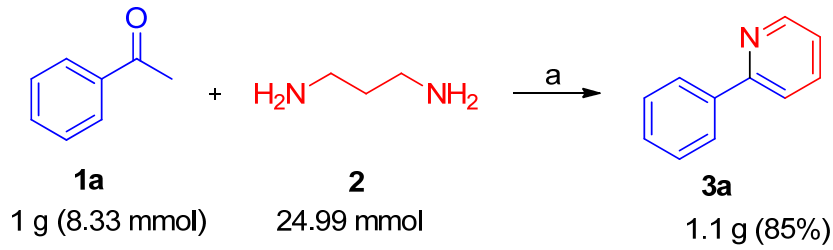
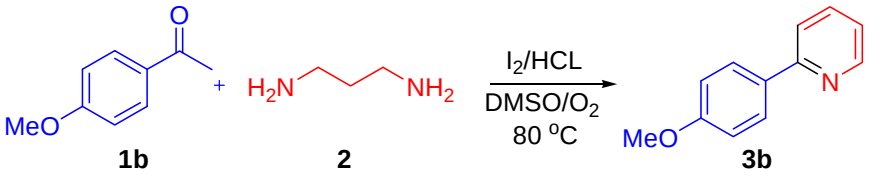


Figure S3. The gram-scale reaction for synthesis of **3a**. Reagents and conditions: (a) **1a** (1g, 8.33 mmol), **2** (24.99 mmol), I_2 (8 mol%), HCl (100 µl), DMSO (15 mL), 80 °C, 4 h, 85%.

SECTION S6. LC-ESI-MS based mechanistic studies for synthesis of 2-(4-methoxyphenyl) pyridine (3b). In order to further support experimentally the most plausible pathway 3, a LCMS study of the reaction mixture was performed, in order to trap possible reaction intermediates using the model reaction of 4-methoxyacetophenone (**1b**) with diamine **2** under optimized condition. After 2 hrs of reaction time, LCMS analysis of reaction mixture was performed.

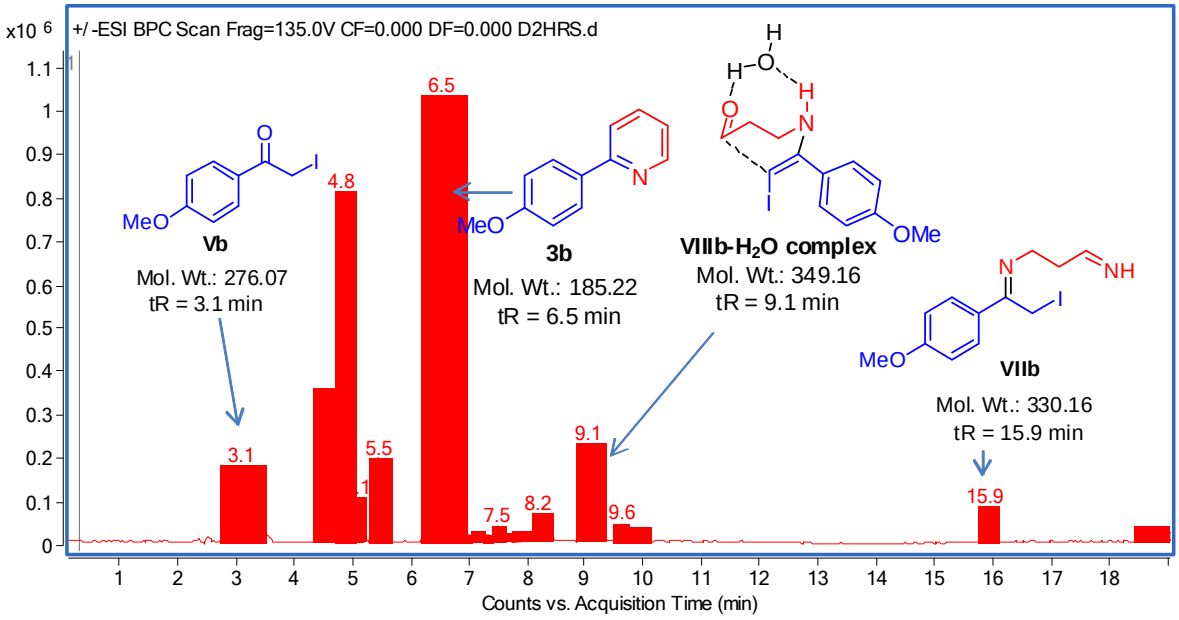


1b **2** **3b**

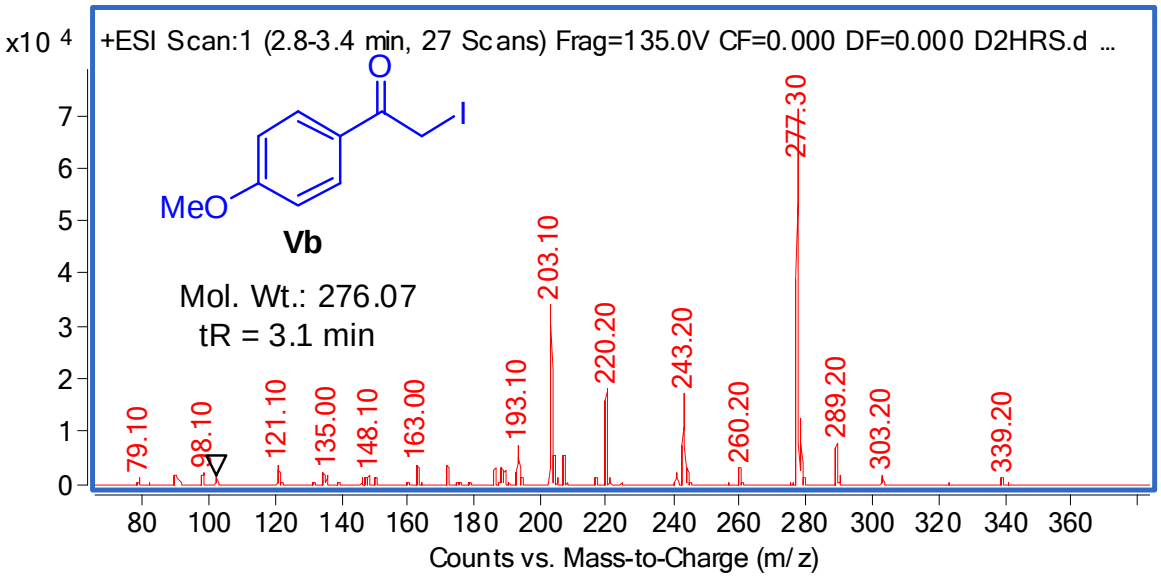
LC-ESI-MS/MS analysis was carried out on Agilent Triple-Quad LC-MS/MS system (model 6410). Liquid chromatography analyses were carried out using an Agilent 1260 Infinity (Agilent, USA) quaternary pump equipped with an autosampler, column heater and online degasser. A Chromolith C_{18} (Merck, Germany) column (4.6 x 100 mm) was used at 30 °C temperature and the injection volume was 10 µl. The elution was carried out with binary solvent system consisting of water (solvent A) and acetonitrile (solvent B) at a constant flow-rate of 0.5 ml/min. The gradient elution was used, as depicted in Table S2. The LCMS chromatogram and MS spectras are shown in Figure S3.

Table S2. Gradient details used in LC-ESI-MS/MS analysis

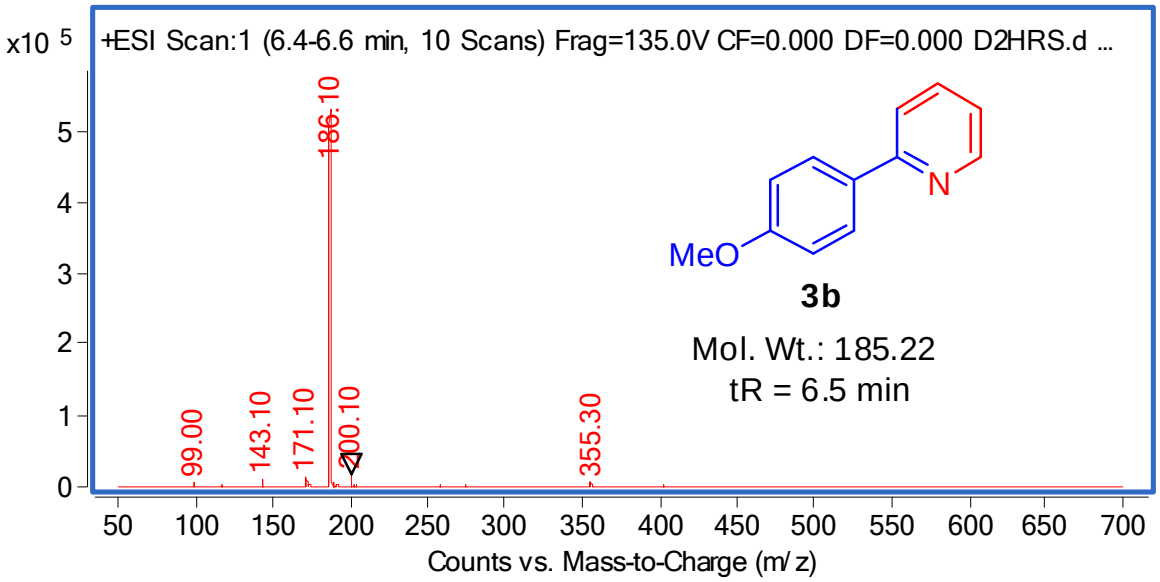
Time (min)	0	10	15	17	20
% B (ACN)	10	70	70	10	10


x10 6
+/ -ESI BPC Scan Frag=135.0V CF=0.000 DF=0.000 D2HRS.d
Vb
Mol. Wt.: 276.07
tR = 3.1 min
3b
Mol. Wt.: 185.22
tR = 6.5 min
VIIIb-H2O complex
Mol. Wt.: 349.16
tR = 9.1 min
VIIb
Mol. Wt.: 330.16
tR = 15.9 min
Counts vs. Acquisition Time (min)

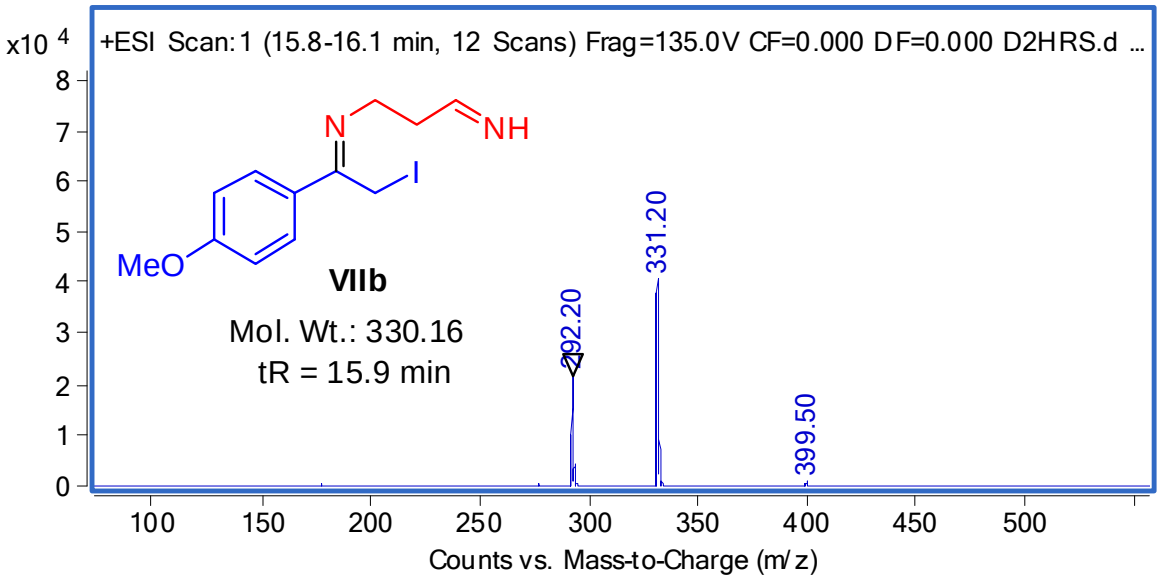
(a)


x10 4
+ESI Scan:1 (2.8-3.4 min, 27 Scans) Frag=135.0V CF=0.000 DF=0.000 D2HRS.d ...
Vb
Mol. Wt.: 276.07
tR = 3.1 min
Counts vs. Mass-to-Charge (m/z)

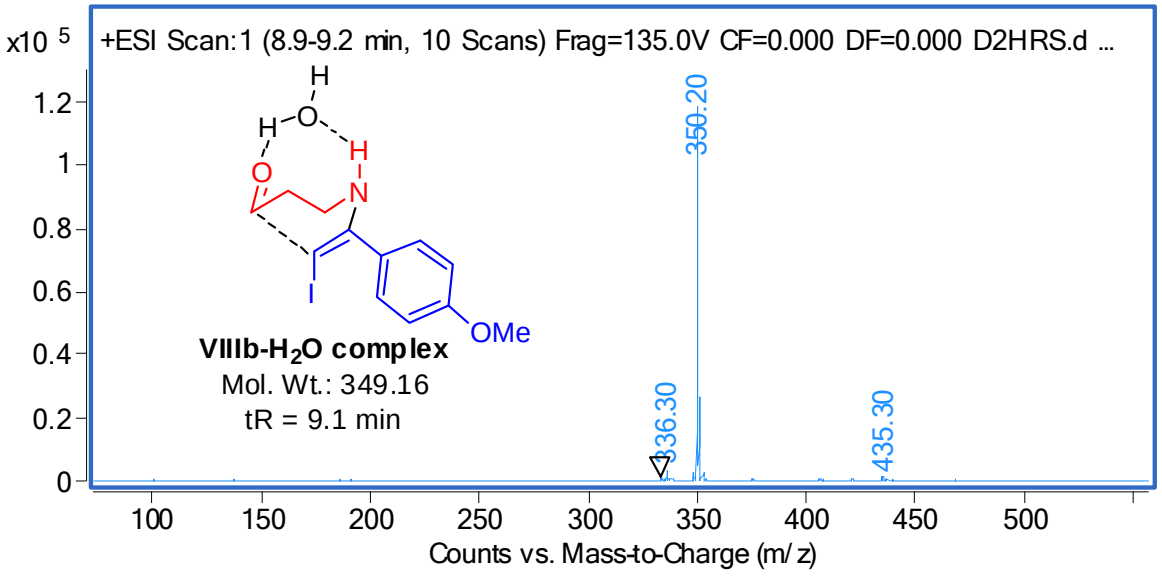
(b)


x10 5
+ESI Scan:1 (6.4-6.6 min, 10 Scans) Frag=135.0V CF=0.000 DF=0.000 D2HRS.d ...
186.10
99.00
143.10
171.10
200.10
355.30
MeO
N
3b
Mol. Wt.: 185.22
tR = 6.5 min
Counts vs. Mass-to-Charge (m/z)

(c)


x10 4
+ESI Scan:1 (15.8-16.1 min, 12 Scans) Frag=135.0V CF=0.000 DF=0.000 D2HRS.d ...
N
NH
I
MeO
VIIb
Mol. Wt.: 330.16
tR = 15.9 min
292.20
331.20
399.50
Counts vs. Mass-to-Charge (m/z)

(d)



(e)

Figure S4. Experimental evidence to support reaction mechanism pathway 3: LCMS analysis of reaction mixture after 2 hrs. (a). LC chromatogram of a reaction mixture; (b) MS spectrum of peak at t_R 3.1 min; (c) MS spectrum of peak at t_R 6.5 min; (d) MS spectrum of peak at t_R 15.9 min; (e) MS spectrum of peak at t_R 9.1 min.

<u>SECTION S7</u>. Synthesis of intermediate α-iodoacetophenone V and further its reaction with diamine 2 to produce 2-phenylpyridine 3a

The procedure for synthesis of intermediate **V** has been provided in section S1. Next, the intermediate **V** was reacted with diamine **2** using the similar procedure as described for synthesis of 2-phenylpyridines **3a-t** in section S1.

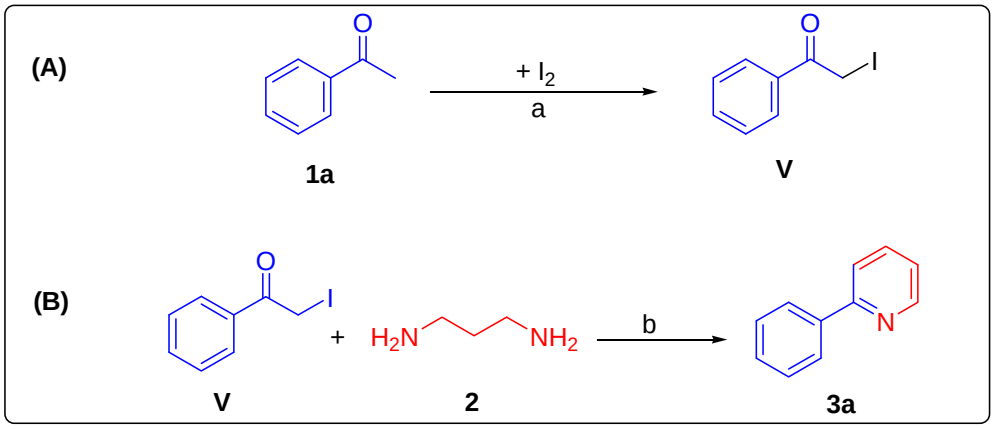


Figure S5. Experimental evidence to support reaction mechanism pathway 3: Synthesis of intermediate **V** and further its reaction with diamine **2** to produce 2-phenylpyridine **3a**

A. Synthesis of intermediate α-iodoacetophenone **V.** Reagents and conditions: (a) CuO/ I_2, EtOH, 80 °C, 2 h, 75%;

B. Reaction of α-iodoacetophenone **V** with diamine **2** produces product **3a**. (b) α-iodoacetophenone **V** (1 equiv.), 1,3-diaminopropane (3 equiv.), I_2 (8 mol%), HCl (10 µl), DMSO (2 mL), 80 °C, O_2, 4 h, 95%.

SECTION S8. References associated with ESI

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