Copper-catalyzed Aromatic C—H Bond Halogenation with Lithium Halide under Aerobic Conditions

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Supporting Information

Table of Contents **Page**

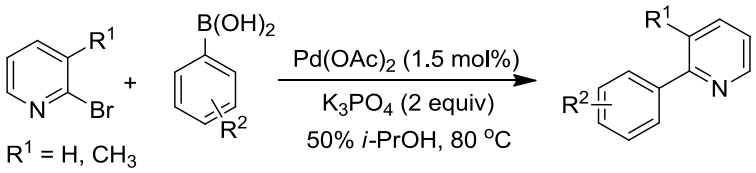
I	General procedure	*S*1
II	Preparation and characterization of starting materials	*S2- S7*
III	General procedure for the Cu-catalyzed halogenation	*S8-19*
IV	References	*S20*
V	Spectra data of NMR	*S21-S43*

I. General Procedure

All experiments were carried out under an oxygen atmosphere unless otherwise noted. Reactions were monitored using thin-layer chromatography (TLC). All solvents were dried and distilled before use according to the standard methods. Substrates **1a, 1k, 1w** and **1x** are commercially avaible. Other Substrates **1b-1j**,[1] **1l-1q**,[1] and **1r-1v**[2] were synthesized according to the reported methods. ^{1}H and ^{13}C NMR spectra were obtained on a Mercury Plus-400 at 400 and 100 MHz, respectively. Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector. Infrared spectra were recorded on an AVATAR 370 spectrometer.

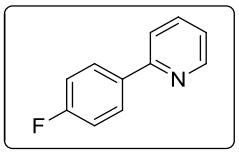
II. Preparation and Characterization of Starting Materials

(i) General procedure for the preparation of arylpyridine substrates through Suzuki-coupling reaction: [1]



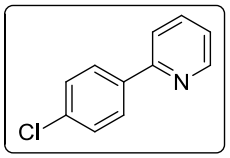
A mixture of heteroaryl bromide (4 mmol), phenylboronic acid (6 mmol), $Pd(OAc)_2$ (1.5 mol%), $K_3PO_4 \cdot 7H_2O$ (8 mmol) and 50% isopropanol (40 mL) was stirred at 80 °C under oxygen. After the reaction finished, the mixture was added to brine (10 mL) and extracted four times with ethylacetate (4 × 15 mL), the solvent was evaporated under reduced pressure and the product was isolated by short column chromatography.

(4-Fluorophenyl)pyridine (1b)[4]



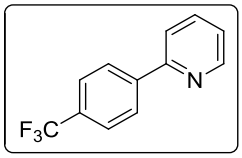
White solid, m.p. 39-41 °C, yield: 94%. ^{1}H NMR (400 MH z, $CDCl_3$) δ 7.14-7.18 (t, *J* = 8.8 Hz, 2H), 7.22-7.25 (m, 1 H), 7.68 (dd, *J* = 0.8, 7.6Hz, 1H), 7.75 (dt, *J* = 0.8, 8.0 H z, 1H), 7.96-8.00 (m, 2H), 8.67-8.69 (m,1H);IR (KBr): 1667, 1589, 1462, 1153 cm^{-1}; MS (ESI) m/z: 174 $(M+1)^+$

2-(4-Chlorophenyl)pyridine (1c)[5]



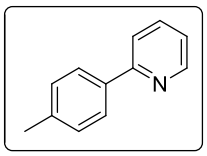
White solid, m.p. 48-49 °C, yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.25 (m, 1H), 7.44-7.46 (m, 2H), 7.69-7.71 (m, 1H), 7.74-7.78 (m, 1H), 7.93-7.95 (m, 2H), 8.68-8.70 (m, 1H); IR (KBr): 3046, 1666, 1586, 1462, 1154, 1086 cm^{-1}; MS (ESI) m/z: 190 $[(M+1)^+$ (^{35}Cl)], 192 $[(M+1)^+$ (^{37}Cl)].

2-(4-(Trifluoromethyl)phenyl)pyridine (1d)[6]



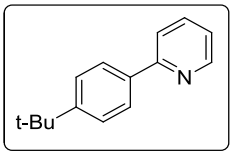
White solid, m.p. 72-74 °C, yield: 32%. ^{1}H NMR (400 M Hz, $CDCl_3$) δ 7.28-7.32 (m, 1H), 7.72 (s, 1H), 7.74-7.75 (m, 1H), 7.77-7.82 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.7 2-8.74 (m, 1H); IR (KBr): 3056, 2963, 1614, 1587, 1156, 1013 cm^{-1}; MS (ESI) m/z: 224 $(M+1)^+$.

2-(p-Tolyl)pyridine (1e)[7]



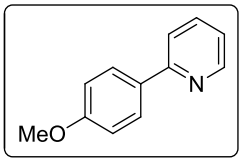
Yellow oil, yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.20-7.22(m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.69-7.74 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 8.67-8.68 (m, 1H); IR (K Br): 2920, 1588, 1467, 1152 cm^{-1}; MS (ESI) m/z:170 $(M+1)^+$.

2-(4-(tert-Butyl)phenyl)pyridine (1f)[8]



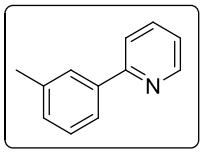
Yellow oil, yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 9H), 7.18-7.22(m, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.71-7.73 (m, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.67-8.68 (m, 1H); IR (KBr): 2962, 1609, 1587, 1466, 1153 cm^{-1}; MS (ESI) m/z: 212 $(M+1)^+$.

2-(4-Methoxyphenyl)pyridine (1g)[9]



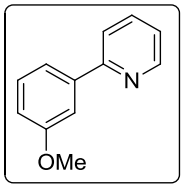
White solid, m.p. 53-54 °C, yield: 82%; ^{1}H NMR (400 M Hz, $CDCl_3$) δ 3.87 (s, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.16 -7.19 (m, 1H), 7.66-7.74 (m, 2H), 7.95(d, *J* = 8.8 Hz, 2H), 8.64-8.66 (m, 1H); IR (KBr): 3046, 2920, 1589, 1462, 10 96 cm^{-1}; MS (ESI) m/z: 186 $(M+1)^+$.

2-(m-Tolyl)pyridine (1h)[5]



Yellow oil, yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.18-7.24(m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.68-7.7 5 (m, 3H), 7.83 (s, 1H), 8.67-8.68(m, 1H); IR (KBr): 2920, 1615, 1590, 1460 cm^{-1}; MS (ESI) m/z: 170 $(M+1)^+$.

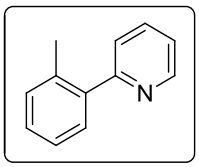
2-(3-Methoxyphenyl)pyridine (1i)[10]



Colorless oil, yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.96-6.99 (m, 1H), 7.21-7.24 (m, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.53-7.55 (m, 1H), 7.59 (s, 1H), 7.70-7.75 (m, 2H),

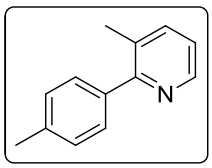
8.68-8.70 (m, 1H); IR (KBr): ν 2920, 1614, 1560, 1503, 1156 cm^{-1}; MS (ESI) m/z: 186 $(M+1)^+$.

2-(o-Tolyl)pyridine (1j)[11]



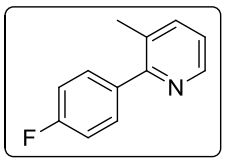
Yellow oil, yield: 71%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 7.22-7.25(m, 2H), 7.27-7.30 (m, 2H), 7.39-7.41 (m, 2 H), 7.74 (dt, *J* = 1.6, 7.6 Hz, 1H),8.69-8.70 (m, 1H); IR (KBr): ν 3060, 2958, 1605, 1586, 1562, 1470, 1425, 795, 751, 728, 620 cm^{-1}; MS (ESI) m/z: 170 $(M+1)^+$.

3-Methyl-2-(p-tolyl)pyridine (1l)[12]



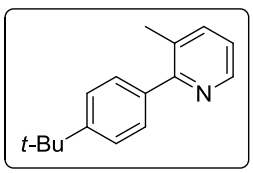
Colorless oil, yield: 80%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.41 (s,3H), 7.16 (dd, *J* = 4.8, 7.6 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* =8.0 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 8.51-8.52 (m, 1H); IR (KBr): 2926, 1768, 1624, 1188 cm^{-1}; MS (ESI) m/z: 184 $(M+1)^+$.

2-(4-Fluorophenyl)-3-methylpyridine (1m)



Yellow oil, yield: 52%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.52-7.47 (m , 2H), 7.17 (dd, *J* = 4.8, 7.6 Hz, 1H), 7.14-7.10 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, J_{C-F} = 245.5 Hz, 1C), 157.5, 146.9, 146.7, 138.6, 136.4 (d, J_{C-F} = 2.7 Hz, 1C), 130.6 (d, J_{C-F} = 7.8 Hz, 1C), 122.1, 115.0 (d, J_{C-F} = 21.3 Hz, 1C), 20.0; IR (KBr): ν 2962, 2918, 1637, 1384, 1260, 800, 609, 513 cm^{-1}; MS (EI) m/z: 187 (M^+), 186 $(M-1)^+$, 185, 166, 159, 133, 92; HRMS (EI) Calcd for $C_{12}H_{10}FN$: 187.0797, Found: 187.0793.

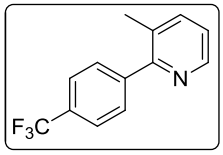
2-(4-(*tert*-Butyl)phenyl)-3-methylpyridine (1n)



Colorless oil, yield: 80%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.46 (s , 4H), 7.15 (dd, *J* = 4.8, 7.6 Hz, 1H), 2.38 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 150.8, 146.9, 138.4, 137.7, 130.7, 128.6, 125.0, 121.8, 34.6, 31.3, 20.1; IR (KBr): ν 2962, 1584, 1573, 1468, 1446, 1424, 841, 789 cm^{-1};

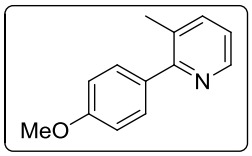
MS (EI) m/z: 225 (M^+) , 224 $(M-1)^+$, 210, 195, 181, 168; HRMS (EI) Calcd for $C_{16}H_{19}N$: 225.1517, Found: 225.1515.

3-Methyl-2-(4-(trifluoromethyl)phenyl)pyridine (1o)



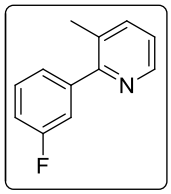
Colorless oil, yield: 24%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 4.8, 7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ □157.1, 147.2, 144.0, 138.7, 130.9, 130.0 (q, J_{C-F} = 31.9 Hz, 1C), 129.3, 125.1, 124.2 (q, J_{C-F} = 270.4 Hz, 1C), 122.7, 19.9; IR (KBr): ν 1674, 1405, 1325, 1163, 1124, 850 cm^{-1}; MS (EI) m/z: 237 (M^+) , 236 $(M-1)^+$, 218, 216, 167, 166; HRMS (EI) Calcd for $C_{13}H_{10}F_3N$: 237.0765, Found: 237.0762.

2-(4-Methoxyphenyl)-3-methylpyridine (1p)[13]



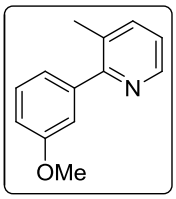
Yellow oil, yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.49 (d , *J* = 8.4 Hz, 2H), 7.14 (dd, *J* = 4.8, 7.6 Hz, 1H), 6.97 (d , *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 2.37 (s, 3H); IR (KBr): ν 2956, 1610, 1580, 1514, 1447, 1422, 1247, 837, 791, 773, 591 cm^{-1}; MS (EI) m/z: 199 (M^+) , 198 $(M-1)^+$, 183, 154.

2-(3-Fluorophenyl)-3-methylpyridine (1h)



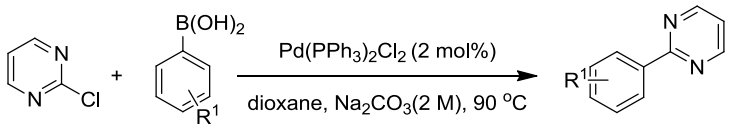
Yellow oil, yield: 44%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.59-7.57 (m, 1H), 7.41 (dt, *J* = 6.0, 8.0 Hz, 1H), 7.30 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.26-7.22 (m, 1H), 7.19 (dd, *J* = 4.8, 7.6 Hz, 1H), 7.09 (dt, *J* = 2.8, 8.8 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ □162.6 (d, J_{C-F} = 244.4 Hz, 1C), 157.3, 147.0, 142.9 (d, J_{C-F} = 7.6 Hz, 1C), 138.6, 130.8, 129.6 (d, J_{C-F} = 8.3 Hz, 1C), 124.7, 122.5, 116.0 (d, J_{C-F} = 21.9 Hz, 1C), 114.8 (d, J_{C-F} = 20.9 Hz, 1C), 19.9; IR (KBr): ν 2975, 1613, 1583, 1567, 1486, 1455, 1433, 1273, 1258, 891, 787, 766 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{11}FN$ $(M+H)^+$: 188.0876, Found:188.0900.

2-(3-Methoxyphenyl)-3-methylpyridine (1q)



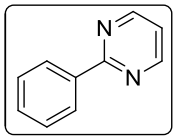
Yellow oil, yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.8 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 4.8, 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 2.4 Hz, 1H), 6.94 (dd, *J* = 2.4, 8.4 Hz, 1H), 3.85 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 158.8, 147.1, 142.2, 138.7, 131.1, 129.2, 122.4, 121.6, 114.5, 114.1, 55.5, 20.3; IR (KBr): ν 2936, 1582, 1488, 1459, 1427, 1287, 1229, 879, 788, 766, 701 cm^{-1}; HRMS (EI) Calcd for $C_{13}H_{14}NO$ $(M+H)^{+}$: 200.1075; Found: 200.1082.

(ii) General procedure for the preparation of arylpyrimidine substrates through Suzuki-coupling reaction[2]



To a round-bottom flask was added 2-chloropyrimidine (2.0 mmol), arylboronic acid (1.2-2.5 equiv), $PdCl_2(PPh_3)_2$ (1.0-4.0 mol%) and Na_2CO_3 (2 M, 5 mL) in dioxane (5 mL). The reaction mixture was heated to 90 °C until the 2-chloropyrimidine was consumed completely (monitored by TLC). The heterogeneous aqueous was concentrated under reduced pressure and the residue was diluted with EtOAc (30 mL), washed by H_2O (30 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (eluant: PE / EtOAc) to afford the arylpyrimidines.

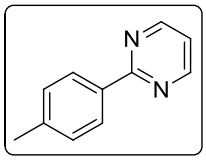
2-Phenylpyrimidine (1r)[2]



White solid, 36-38 °C, yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ

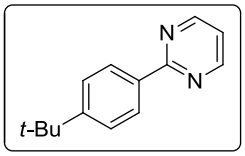
8.82 (d, *J* = 4.8 Hz, 2H), 8.45-8.43 (m, 2H), 7.51-7.48 (m, 3H), 7.20 (t, *J* = 4.8 Hz, 1H); IR (KBr): ν 2960, 1677, 1626, 1583, 1543, 825, 809, 689, 639, 615, 553 cm^{-1}; MS (EI) m/z: 156 (M^+) , 155 $(M-1)^+$, 129, 103, 76.

2-(p-Tolyl)pyrimidine (1s) [2]



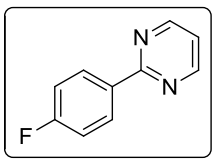
White solid, 86-88°C, yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.16 (t, *J* = 4.8 Hz, 1H), 2.42 (s, 3H); IR (KBr): ν 2918, 1609, 1574, 1564, 1412, 1179, 785, 628, 545 cm^{-1}; MS (EI) m/z: 170 (M^+) , 169 $(M-1)^+$, 117, 89, 75.

2-(4-(*tert*-Butyl)phenyl)pyrimidine (1t)



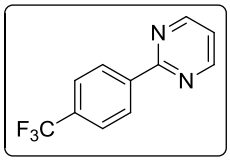
White solid, 46-48 °C, yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.0 Hz, 2H), 8.38-8.34 (m, 2H), 7.53-7.50 (m, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 157.2, 157.1, 154.1, 134.8, 127.9, 125.5, 118.7, 34.8, 31.2; IR (KBr): ν 2969, 1606, 1568, 1551, 1417, 808, 800, 575 cm^{-1}; MS (EI) m/z: 212 (M^+), 211 $(M-1)^+$, 197, 169; HRMS (EI) Calcd for $C_{14}H_{16}N_2$: 212.1313, Found: 212.1315.

2-(4-Fluorophenyl)pyrimidine (1u) [2]



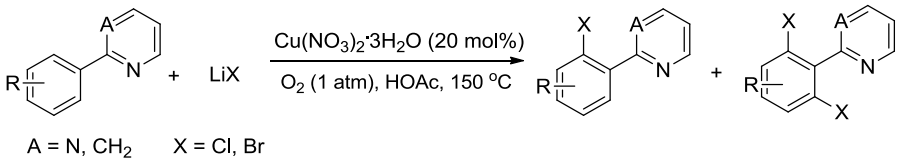
White solid, 61-62 °C, yield: 40%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.47-8.43 (m, 2H), 7.19-7.14 (m, 3H); IR (KBr): ν 2923, 1603, 1565, 1419, 1215, 794, 581 cm^{-1}; MS (EI) m/z: 175 $(M+1)^+$.

2-(4-(Trifluoromethyl)phenyl)pyrimidine (1v) [2]



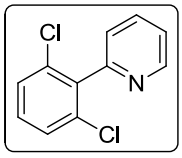
White solid, 104-105 °C, yield: 23%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 4.8 Hz, 2H), 8.56 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* =8.4 Hz, 2H), 7.26 (t, *J* = 4.8 Hz, 1H); IR (KBr): ν 2929, 1617, 1560, 1426, 1316, 864, 804, 793, 734, 599 cm^{-1}; MS (ESI) m/z: 225 $(M+1)^+$.

III. General Procedure for the Cu-Catalyzed Halogenation



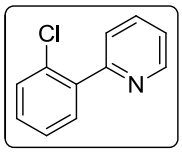
In a sealed tube, a solution of heterocycle (0.3 mmol), LiX (X = Cl, Br) (0.9 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (15 mg, 0.06 mmol) in HOAc (2 mL) under O_2 (1 atm) was stirred at 150 °C. Reactions were monitored by thin-layer chromatography (TLC). When the starting material disappeared, the mixture was neutralized with $NaHCO_3$ (saturated solution) and extracted with EtOAc (3 x 15 mL). The extract was washed with brine (2 x 15 mL) and dried over Na_2SO_4. After evaporation, the residue was purified via chromatography on silica gel with petroleum ether/Et_2O (2/1 (v/v)) to provide the corresponding product.

2-(2,6-dichlorophenyl)pyridine(3a)[14]



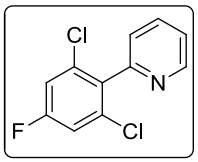
Yellow oil, yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.28 (m, 1H), 7.34-7.37 (m, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.82 (td, *J* = 2.0, 8.0 Hz, 1H), 8.76-8.75 (m, 1H); IR (KBr): ν 3054, 1593, 1560, 1427, 1191, 1116, 773, 747 cm^{-1}; MS (EI) m/z: 227 [M^+ ($^{37}Cl^{37}Cl$)], 225 [$(M-1)^+$ ($^{37}Cl^{35}Cl$)], 223 [M^+ ($^{35}Cl^{35}Cl$)], 190, 188, 161, 153, 152.

2-(2-chlorophenyl)pyridine(2a)[14]



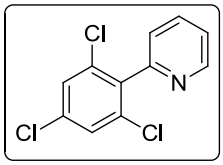
Yellow oil, yield: 3%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.32 (m, 1H), 7.32-7.39 (m, 2H), 7.48 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.60 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.77 (td, *J* = 1.6, 7.6 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 1H); IR (KBr): ν 3057, 1585, 1459, 1422, 1035, 750 cm^{-1}; MS (EI) m/z: 191 [M^+ (^{37}Cl)] (19.72), 189 [M^+ (^{35}Cl)] (51.25), 188, 154, 127, 77, 51.

2-(2,6-Dichloro-4-fluorophenyl)pyridine (3b)



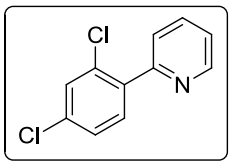
Yellow oil, yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76-8.74 (m, 1H), 7.82 (td, *J* = 1.2 , 7.6, 1H), 7.35 (ddd , *J* = 1.6 , 4.8 , 7.6 Hz, 1H), 7.32 (td, *J* = 1.2 , 7.6 Hz, 1H), 7.18 (d, *J* =8.0 Hz , 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (q, $^{1}J_{C-F}$ = 251.5 Hz), 154.7, 149.7, 136.5, 135.4 (q, $^{3}J_{C-F}$ = 11.4 Hz), 134.9 (q, $^{4}J_{C-F}$ = 3.7 Hz) , 125.2, 123.1, 115.8 (q, $^{2}J_{C-F}$ = 24.3 Hz); IR (KBr): ν 2925, 1599, 1573, 1449, 1426, 1392, 941, 855, 810, 787, 566 cm^{-1}; MS (EI) m/z: 245 [M^+ (^{37}Cl^{37}Cl)] (3.12), 243 [M^+ (^{37}Cl^{35}Cl)] (18.47), 241 [M^+ (^{35}Cl^{35}Cl)] (29.10), 208.0, 206.0, 171.0; HRMS (EI) Calcd for $C_{11}H_6Cl_2(^{35}Cl)FN$: 240.9861, Found: 240.9865.

2-(2,4,6-Trichlorophenyl)pyridine (3c)



White solid, m.p.: 100-101 °C, yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.8 Hz, 1H), 7.81 (td, *J* = 1.6, 7.6 Hz, 1H), 7.42 (s, 2H), 7.35-7.29 (m, 1H), 7.31 (dt, *J* =1.2, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 149.7, 137.0, 136.5, 135.2, 134.7, 128.1, 125.0, 123.2; IR (KBr): ν 3039, 3003, 1590, 1539, 1422, 1371, 1107, 780, 745, 575 cm^{-1}; MS (EI) m/z: 263 [M^+ (^{37}Cl^{37}Cl^{37}Cl)] (1.03), 261 [M^+ (^{37}Cl ^{37}Cl^{35}Cl)] (8.54), 259 [M^+ (^{37}Cl ^{35}Cl^{35}Cl)] (27.34), 257 [M^+ (^{35}Cl ^{35}Cl^{35}Cl)] (29.32), 224, 222, 189, 187; HRMS (EI) Calcd for $C_{11}H_6Cl_3(^{35}Cl)N$: 256.9566, Found: 256.9571.

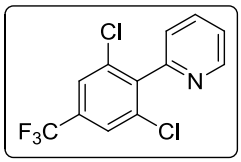
2-(2,4-Dichlorophenyl)pyridine (2c)



White solid, m.p. 75-76 °C, yield: 9%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73-8.71 (m, 1H), 7.77 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.36 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.31 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7, 149.7, 137.7, 135.9, 134.8, 132.8, 132.4, 129.8, 127.4, 124.8, 122.6; IR (KBr): ν 3069, 2924, 1592, 1571, 1459, 1376, 818, 778, 744 cm^{-1}; MS (EI) m/z: 223 [M^+ (^{35}Cl^{35}Cl)] (49.72), 225 [M^+ (^{35}Cl^{37}Cl)] (31.31), 227 [M^+ (^{37}Cl^{37}Cl)] (5.07), 190, 188, 153, 74; HRMS (EI) Calcd for $C_{11}H_7Cl_2(^{35}Cl)N$:

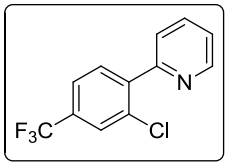
222.9956, Found: 222.9954.

2-(2,6-Dichloro-4-(trifluoromethyl)phenyl)pyridine (3d)[15]



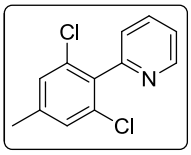
Colorless oil, yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$): 8.77 (d, *J* = 4.8 Hz, 1H), 7.79 (td, *J* = 2.0 ,7.6 Hz, 1H), 7.68 (s, 2H), 7.38 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 1H), 7.34 (d, *J* = 7.6, 1H); IR (KBr): 3054, 2928, 1587, 1568, 1560, 1485, 1428, 880, 857, 814, 787, 747, 738, 486 cm^{-1}; MS (EI) m/z: 291 [M^+ ($^{35}Cl^{35}Cl$)] (24.03), 293 [M^+ ($^{35}Cl^{37}Cl$)] (14.29), 295 [M^+ ($^{37}Cl^{37}Cl$)] (2.26), 238.0 ,236.0, 221.0, 152.1.

2-(2-Chloro-4-(trifluoromethyl)phenyl)pyridine (2d) [15]



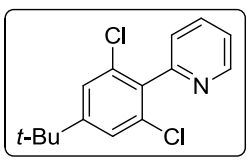
White solid, m.p. 42-43 ^{o}C, yield: 3%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.8 Hz, 1H), 7.81 (td, *J* = 2.0, 7.6 Hz, 1H), 7.76 (s , 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.38 (ddd, *J* = 1.2, 4.8, 7.6 Hz, 1H); IR (KBr): ν 1590, 1465, 1434, 1391, 1338, 887, 861, 833, 783 cm^{-1}; MS (EI) m/z: 259 [M^+ (^{37}Cl)] (13.65), 257 [M^+ (^{35}Cl)] (43.92), 223, 222, 191, 91, 71.

2-(2,6-Dichloro-4-methylphenyl)pyridine (3e) [15]



Yellow oil, yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (td, *J* = 1.6, 4.4 Hz, 1H), 7.79 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.34-7.31 (m, 2H), 7.23 (s, 2H), 2.37 (s, 3H); IR (KBr): ν 2923, 1600, 1566, 1453, 1390, 849, 801, 782, 745, 578 cm^{-1}; MS (EI) m/z: 237 [M^+ ($^{35}Cl^{35}Cl$)] (31.23), 239 [M^+ ($^{35}Cl^{37}Cl$)] (19.40), 241 [M^+ ($^{37}Cl^{37}Cl$)] (3.17), 204, 202, 167, 139.

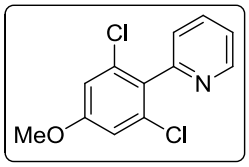
2-(4-(tert-Butyl)-2,6-dichlorophenyl)pyridine (3f)



Yellow solid, m.p. 64-66 ^{o}C, yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75-8.73 (m, 1H), 7.79 (td, *J* = 1.6 ,7.6 Hz, 1H), 7.40 (s, 2H), 7.34-7.30 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 153.8, 149.5, 136.2, 135.4, 134.0, 125.4, 125.0, 122.7, 34.9, 30.9; IR

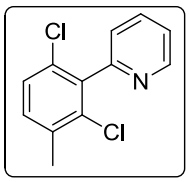
(KBr): ν 2965, 1597, 1567, 1542, 1454, 1426, 1379, 1262, 803, 746, 588 cm^{-1}; MS (EI) m/z: 283 [M^+ ($^{37}Cl^{37}Cl$)] (2.18), 281 [M^+ ($^{35}Cl^{37}Cl$)] (13.0), 279 [M^+ ($^{35}Cl^{35}Cl$)] (19.69), 264, 236, 236, 228, 192, 115, 78; HRMS (EI) Calcd for $C_{15}H_{15}Cl_2N$: 279.0582, Found:279.0581.

2-(2,6-Dichloro-4-methoxyphenyl)pyridine (3g) [15]



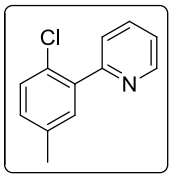
White solid, m.p. 65-67 ^oC, yield: 46%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.75-8.73 (m, 1H), 7.78 (td, *J* = 1.6 ,7.6 Hz, 1H), 7.33-7.30 (m, 2H), 6.96 (s, 2H), 3.83 (s, 3H); IR (KBr): ν 2942, 1602, 1554, 1462, 1425, 1397, 833, 787, 747, 570 cm^{-1}; MS (EI) m/z: 257 [M^+ ($^{37}Cl^{37}Cl$)] (4.67), 255 [M^+ ($^{35}Cl^{37}Cl$)] (28.89), 253 [M^+ ($^{35}Cl^{35}Cl$)] (47.67), 219, 218, 203, 175, 140, 78.

2-(2,6-Dichloro-3-methylphenyl)pyridine (3h)



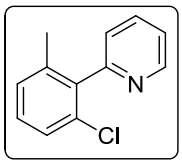
Yellow oil, yield: 25%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.76-8.74 (m, 1H), 7.81 (td, *J* = 2.0, 8.0 Hz, 1H), 7.35-7.30 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 149.6, 149.5, 137.3, 136.0, 131.1, 129.3, 129.2, 126.6, 125.1, 122.5, 21.1; IR (KBr): ν 2924, 1593, 1566, 1445, 1428, 1382, 810, 773, 747, 692, 581 cm^{-1}; MS (EI) m/z: 241 [M^+ ($^{37}Cl^{37}Cl$)] (2.38), 239 [M^+ ($^{35}Cl^{37}Cl$)] (15.25), 237 [M^+ ($^{35}Cl^{35}Cl$)] (25.67), 204, 202, 167, 139, 83; HRMS (EI) Calcd for $C_{12}H_9Cl_2N$: 237.0112, Found: 237.0113.

2-(2-Chloro-5-methylphenyl)pyridine (2h)[16]



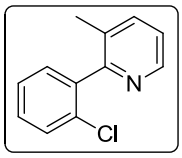
Yellow oil, yield: 58%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.72-8.70 (m, 1H), 7.75 (td, *J* = 2.0, 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28-7.25 (m, 1H), 7.13 (dd, *J* = 2.0, 8.0 Hz, 1H), 2.37 (s, 3H); IR (KBr): ν 2924, 2855, 1587, 1565, 1457, 1428, 1383, 812, 787, 747, 692, 581 cm^{-1}; MS (EI) m/z: 202 [$(M-1)^+$ (^{35}Cl)] (100.0), 204 [$(M-1)^+$ (^{37}Cl)] (23.06), 167, 166, 139, 87, 74.

2-(2-chloro-6-methylphenyl)pyridine (2j)[15]



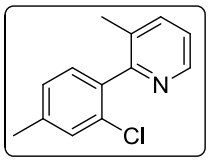
Colorless oil, yield: 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74-8.73 (m, 1H), 7.79 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.32-7.29 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.19-7.17 (m, 1H), 2.09 (s, 3H); IR (KBr): ν 2956, 2925, 1596, 1586, 1566, 1453, 1422, 860, 787, 774, 749, 669, 530 cm^{-1}; MS (EI) m/z: 204 [$(M-1)^+$ (^{37}Cl)] (31.13), 202 [$(M-1)^+$ (^{35}Cl)] (100.0), 191, 167, 166, 139, 76.

2-(2-Chlorophenyl)-3-methylpyridine (2k)[15]



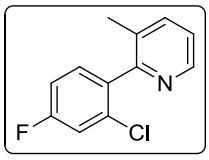
Colorless oil, yield: 57%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52-8.51 (m, 1H), 7.59-7.56 (m, 1H), 7.47-7.44 (m, 1H), 7.36-7.29 (m , 3H), 7.23 (dd, *J* = 4.8 , 7.6 Hz, 1H), 2.16 (s, 3H); IR (KBr): ν 3054, 2926 1596, 1570, 1445, 1431, 792, 777, 756, 738, 622 cm^{-1}; MS (EI) m/z: 205 [M^+ (^{37}Cl)] (15.37), 203 [M^+ (^{35}Cl)] (50.23), 202, 204, 168, 167, 75.

2-(2-Chloro-4-methylphenyl)-3-methylpyridine (2l)



Yellow oil , yield: 62%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51-8.50 (m, 1H), 7.59-7.57 (m, 1H), 7.29 (s, 1H), 7.24-7.14 (m , 3H), 2.39 (s, 3H), 2.16(s, 3H); ^{13}C NMR (100 MHz, CDCl3): 157.0, 146.4, 139.6, 137.9, 136.3, 132.4, 132.3, 130.1, 129.8, 127.7, 122.8, 21.0, 18.9; IR (KBr): ν 2924, 1610, 1583, 1571, 1445, 1425, 1081, 874, 824, 791, 588 cm^{-1}; MS (EI) m/z: 219 [M^+ (^{37}Cl)] (16.36), 217 [M^+ (^{35}Cl)] (52.08), 216, 218, 182, 167, 152, 77; HRMS (EI) Calcd for $C_{13}H_{12}ClN$: 217.0658, Found: 217.0656.

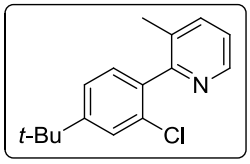
2-(2-Chloro-4-fluorophenyl)-3-methylpyridine (2m)



Yellow oil, yield: 61%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52-8.51 (m, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.31-7.21 (m, 3H), 7.02 (dt , *J* = 2.4, 8.4 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^{1}J_{C-F}$ = 248.5 Hz, 1C), 156.2, 146.8, 137.8, 135.7 (d, $^{4}J_{C-F}$ = 3.3 Hz, 1C), 133.6 (d, $^{3}J_{C-F}$ = 10.1 Hz, 1C), 132.3, 131.5 (d, $^{3}J_{C-F}$ = 8.8 Hz, 1C), 123.0, 116.7 (d,

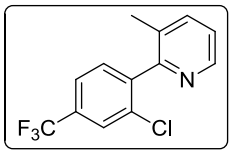
$^{2}J_{C\text{-}F}$ = 24.6 Hz, 1C), 114.2 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz, 1C), 18.7; IR (KBr): ν 2925, 1600, 1574, 1496, 1446, 1424, 1384, 898, 858, 791, 579 cm^{-1}; MS (EI) m/z: 223 [M^{+} (^{37}Cl)] (15.91), 221 [M^{+} (^{35}Cl)] (56.02), 222 [$(M-1)^{+}$ (^{37}Cl)] (30.12), 220 [$(M-1)^{+}$ (^{35}Cl)] (100), 186, 185, 157, 75; HRMS (EI) Calcd for $C_{12}H_8ClFN$ [$(M+H)^{+}$ (^{35}Cl)]: 222.0486, Found: 222.0453.

2-(4-(*tert*-Butyl)-2-chlorophenyl)-3-methylpyridine (2n)



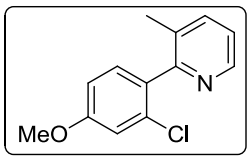
Yellow oil, yield: 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 4.8 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.35 (dd , *J* =1.6, 8.0 Hz, 1H), 7.23 (d , *J* = 8.0 Hz, 1H), 7.20 (dd , *J* = 4.8, 7.6 Hz, 1H), 2.18 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 153.2, 146.9, 137.8, 136.8, 132.6, 132.5, 130.2, 126.7, 124.3, 122.9, 35.0, 31.4, 19.1; IR (KBr): ν 2962, 1606, 1570, 1445, 1385, 868, 832, 790, 632, 573 cm^{-1}; MS (EI) m/z: 259 [M^{+} (^{35}Cl)] (25.5), 261 [M^{+} (^{37}Cl)] (7.84), 246, 244, 216, 167, 92; HRMS (EI) Calcd for $C_{16}H_{18}ClN$: 259.1128, Found: 259.1127.

2-(2-Chloro-4-(trifluoromethyl)phenyl)-3-methylpyridine (2o)



Yellow oil, yield: 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (dd, *J* = 1.2, 4.8 Hz, 1H), 7.75 (s, 1H), 7.64-7.62 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.27 (dd , *J* = 4.8, 8.0 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7, 146.9, 143.1, 137.9, 133.6, 132.0, 131.8 (q, $^{2}J_{C\text{-}F}$ =33.0 Hz), 131.2, 126.6, 124.5 (q, $^{1}J_{C\text{-}F}$ = 270.8 Hz), 123.7, 123.3, 18.6; IR (KBr): ν 2929, 1572, 1448, 1388, 1323, 1132, 888, 845, 792, 721, 481 cm^{-1}; MS (EI) m/z: 273 [M^{+} (^{37}Cl)] (15.36), 271 [M^{+} (^{35}Cl)] (46.53), 270, 272, 236, 235, 167, 166; HRMS (EI) Calcd for $C_{13}H_9ClNF_3$: 271.0376, Found: 271.0377.

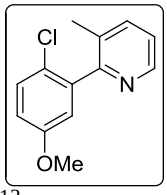
2-(2-Chloro-4-methoxyphenyl)-3-methylpyridine (2p)[17]



Yellow oil, yield: 52%; ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 4.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.27 (dd, *J* = 4.8, 7.6

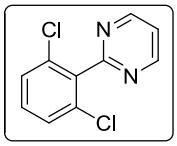
Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.90 (dd , *J* = 2.4, 8.4 Hz, 1H), 3.84 (s, 3H), 2.17 (s, 3H); IR (KBr): ν 2931, 1607, 1503, 1424, 1287, 792, 592, 571 cm^{-1}; MS (EI) m/z: 233 [M^+ (^{35}Cl)] (68.05), 235 [M^+ (^{37}Cl)] (17.42), 232, 234, 199, 198, 183, 154, 127.

2-(2-Chloro-5-methoxyphenyl)-3-methylpyridine (2q)



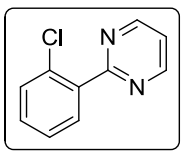
Yellow oil, yield: 72%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.8 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.24-7.20 (m, 2H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 3.84 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 160.1, 157.3, 146.9, 137.9, 133.6, 132.7, 132.3, 131.2, 122.9, 114.9, 113.3, 55.8, 19.1; IR (KBr): ν 3049, 2930, 1607, 1503, 1424, 1287, 879, 792, 592 cm^{-1}; MS (EI) m/z: 235 [M^+(^{37}Cl)] (19.51), 233 [M^+ (^{35}Cl)] (68.20), 232, 217, 198, 183, 155, 154, 77; HRMS (EI) Calcd for $C_{13}H_{12}ClNO$: 233.0607, Found: 233.0608.

2-(2,6-Dichlorophenyl)pyrimidine (3r)[2]



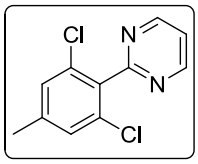
White solid, m.p.: 128-130 °C, yield: 39%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 4.8 Hz, 2H), 7.43-7.27 (m, 4H); IR (KBr): ν 2922, 1588, 1562, 1467, 1429, 1407, 781, 737, 558 cm^{-1}; MS (EI) m/z: 228 [M^+ ($^{37}Cl^{37}Cl$)] (4.39), 226 [M^+ ($^{37}Cl^{35}Cl$)] (27.54), 224 [M^+ ($^{35}Cl^{35}Cl$)] (46.25), 191, 189, 173, 171, 136, 75.

2-(2-Chlorophenyl)pyrimidine (2r) [2]



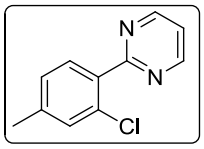
Yellow oil, yield: 58%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 1.2, 4.8 Hz, 2H), 7.75-7.73 (m, 1H), 7.52-7.50 (m , 1H), 7.41-7.37 (m, 2H), 7.29 (t, *J* = 4.8 Hz,1H); IR (KBr): ν 1595, 1566, 1441, 1413, 1037, 817, 754, 696, 631 cm^{-1}; MS (EI) m/z: 192 [M^+ (^{37}Cl)] (22.8), 190 [M^+ (^{35}Cl)] (100.0), 156, 155, 139, 137, 102, 75.

2-(2,6-Dichloro-4-methylphenyl)pyrimidine (3s) [2]



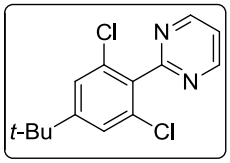
White solid, m.p.: 119-121 ^{o}C, yield: 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 5.2 Hz, 2H), 7.34 (t, *J* = 4.8 Hz, 1H), 7.23 (s, 2H), 2.37 (s, 3H); IR (KBr): ν 2924, 1600, 1557, 1410, 853, 792, 736, 576 cm^{-1}; MS (EI) m/z: 242 [M^+ ($^{37}Cl^{37}Cl$)] (4.7), 240 [M^+ ($^{37}Cl^{35}Cl$)] (32.3), 238 [M^+ ($^{35}Cl^{35}Cl$)] (62.2), 205, 203, 187, 185, 150, 114.

2-(2-Chloro-4-methylphenyl)pyrimidine (2s) [2]



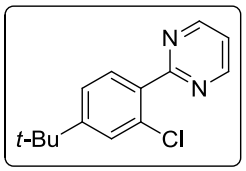
Colorless oil, yield: 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.8 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.33 (s, 1H), 7.25 (t, *J* = 4.8 Hz, 1H), 7.19-7.17 (m, 1H); IR (KBr): ν 2924, 1673, 1607, 1563, 1415, 802, 742, 633 cm^{-1}; MS (EI) m/z: 206 [M^+ (^{37}Cl)] (22.1), 204 [M^+ (^{35}Cl)] (100.0), 169, 151, 116, 89, 63.

2-(4-(*tert*-Butyl)-2,6-dichlorophenyl)pyrimidine (3t)



White solid, m.p.: 154-156 ^{o}C, yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.8 Hz, 2H), 7.40 (s, 2H), 7.34 (t, *J* = 4.8 Hz, 1H), 134 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 157.3, 154.3, 134.5, 133.3, 125.3, 119.9, 35.0, 30.9; IR (KBr): ν 2965, 1600, 1559, 1534, 1413, 1379, 870, 799, 584 cm^{-1}; MS (EI) m/z: 284 [M^+ ($^{37}Cl^{37}Cl$)] (1.71), 282 [M^+ ($^{37}Cl^{35}Cl$)] (8.82), 280 [M^+ ($^{35}Cl^{35}Cl$)] (13.07), 267, 265, 237, 225, 183, 141, 115; HRMS (EI) Calcd for $C_{14}H_{14}Cl_2N_2$: 280.0534, Found: 280.0532.

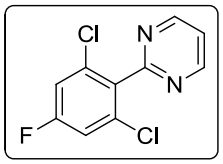
2-(4-(tert-Butyl)-2-chlorophenyl)pyrimidine (2t)



Yellow solid, m.p.: 154-156 ^{o}C, yield: 22%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (d, *J* = 4.8 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.27 (t, *J* = 4.8 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 157.0, 154.2, 134.6, 132.2, 131.3, 127.6, 124.0, 119.1, 34.8, 31.0; IR (KBr): ν 2965, 1601, 1559, 1413, 1379, 870, 1262, 799, 653, 584 cm^{-1}; MS (EI) m/z: 248 [M^+ (^{37}Cl)] (6.91), 246 [M^+ (^{35}Cl)] (20.24), 233, 231, 216, 203, 63; HRMS (EI) Calcd for $C_{14}H_{15}ClN_2$: 246.0924,

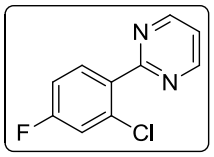
Found: 246.0932.

2-(2,6-Dichloro-4-fluorophenyl)pyrimidine (3u) [2]



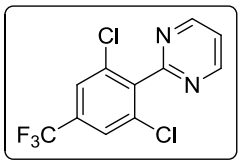
White solid, m.p.: 98-100 °C, yield: 33%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, J = 4.8 Hz, 2H), 7.37 (t, J = 4.8 Hz, 1H), 7.19 (d, J_{F-H} = 8.0 Hz, 2H); IR (KBr): ν 3091, 1598, 1559, 1409, 1396, 942, 858, 804, 578 cm^{-1}; MS (EI) m/z: 246 [M^+ (^{37}Cl^{37}Cl)] (6.36), 244 [M^+ (^{37}Cl^{35}Cl)] (44.55), 242 [M^+ (^{35}Cl^{35}Cl)] (83.40), 209, 207, 191, 189, 154.

2-(2-Chloro-4-fluorophenyl)pyrimidine (2u) [2]



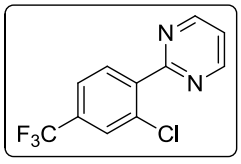
White solid, m.p.: 101-103 °C, yield: 33%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (d, J = 4.8 Hz, 2H), 7.78 (dd, J = 6.4, 8.8 Hz, 1H), 7.31-7.25 (m, 2H), 7.10 (td, J = 2.4, 8.4 Hz, 1H); IR (KBr): ν 2922, 1597, 1558, 1418, 1384, 902, 883, 793, 581 cm^{-1}; MS (EI) m/z: 210 [M^+ (^{37}Cl)] (25.19), 208 [M^+ (^{35}Cl)] (100.00), 173, 157, 155, 120, 75.

2-(2,6-Dichloro-4-(trifluoromethyl)phenyl)pyrimidine (3v) [2]



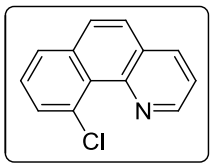
White solid, m.p.: 106-108 °C, yield: 64%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (d, J = 5.2 Hz, 2H), 7.69 (s, 2H), 7.40 (t, J = 4.8 Hz, 1H); IR (KBr): ν 2924, 1564, 1415, 1400, 1164, 1135, 873, 798, 664 cm^{-1}; MS (EI) m/z: 296 [M^+ (^{37}Cl^{37}Cl)] (4.28), 294 [M^+ (^{37}Cl^{35}Cl)] (28.07), 292 [M^+ (^{35}Cl^{35}Cl)] (48.62), 259, 257, 241, 239, 204, 75.

2-(2-Chloro-4-(trifluoromethyl)phenyl)pyrimidine (2v) [2]



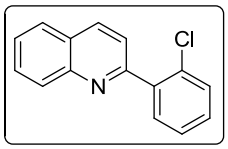
Colorless oil, yield: 36%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (d, J = 4.8 Hz, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 4.8 Hz, 1H); IR (KBr): ν 1567, 1559, 1421, 1318, 1180, 1122, 841, 806, 709 cm^{-1}; MS (EI) m/z: 258 [M^+ (^{37}Cl)] (6.53), 256 [M^+ (^{35}Cl)] (6.40), 243, 236, 241, 215, 213, 186, 143.

10-Chlorobenzo[*h*]quinoline (2w)[15]



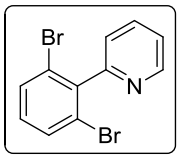
White solid, m.p.: 81-82 ^{o}C, yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (dd, *J* = 2.0, 4.4 Hz, 1H), 8.13 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.80 (t, *J* = 6.0 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.55-7.51 (m, 2H); IR (KBr): ν 3043, 1622, 1590, 1553, 1493, 1437, 925, 833, 714, 646 cm^{-1}; MS (EI) m/z: 215 [M^{+}(^{37}Cl)](22.8), 213 [M^{+} (^{35}Cl)] (100.0), 178, 177, 150, 75.

2-(2-Chlorophenyl)quinoline (2x)[14]



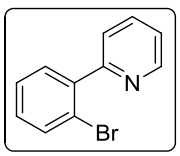
White solid, m.p.: 73-75 ^{o}C, yield: 27%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.77-7.73 (m, 2H), 7.71-7.69 (m , 1H), 7.60-7.58 (m, 1H), 7.53-7.50 (m, 1H), 7.42-7.38 (m, 2H); IR (KBr): ν 3059, 1598, 1503, 1436, 1312, 1038, 831, 761 cm^{-1}; MS (EI) m/z: 241 [M^{+}(^{37}Cl)](10.99), 239 [M^{+} (^{35}Cl)] (38.88), 204, 203, 176, 151, 102, 75.

2-(2,6-Dibromophenyl)pyridine (5a) [15]



White solid, m.p.: 120-130 ^{o}C, yield: 27%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.8 Hz, 1H), 7.82 (td, *J* = 2.0, 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.37-7.30 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 1H); IR (KBr): ν 1562, 1467, 1407, 1130, 781 cm^{-1}; MS (ESI) m/z: 316 [(M+H $^{+}$) (^{81}Br^{81}Br)], 314 [(M+H $^{+}$) (^{79}Br ^{81}Br)], 312 [(M+H $^{+}$) (^{79}Br^{79}Br)].

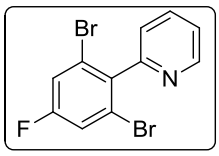
2-(2-Bromophenyl)pyridine (4a) [15]



Yellow oil, yield: 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72-8.70 (m, 1H), 7.76 (td, *J* = 2.0, 7.6 Hz, 1H), 7.67 (dd , *J* = 1.2, 8.0 Hz, 1H), 7.59 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.53 (dd, *J* = 1.2, 7.2 Hz, 1H), 7.39 (td, *J* = 1.2, 7.2 Hz, 1H), 7.31-7.23 (m, 2H); IR (KBr): ν 3053, 1592, 1583, 1458, 1420, 1016, 750 cm^{-1}; MS (EI) m/z: 235 [M^{+} (^{81}Br)] (23.53), 233 [M^{+} (^{79}Br)] (24.63), 232,

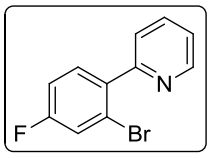
154, 127, 77, 43.

2-(2,6-Dibromo-4-fluorophenyl)pyridine (5b)



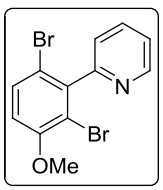
White solid, m.p.: 64-65 ^{o}C, yield: 51%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, J = 4.8 Hz, 1H), 7.80 (td, J = 1.6, 8.0 Hz, 1H), 7.40 (d, J_{F-H} = 7.6 Hz, 2H), 7.35 (ddd, J =1.6, 4.8, 7.6 Hz, 1H) , 7.28 (d, J = 7.6, Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, $^{1}J_{C-F}$ = 253.7 Hz, 1C), 158.2, 149.8, 138.6, 136.8, 125.1, 124.0 (d, $^{3}J_{C-F}$ = 10.1 Hz, 1C), 123.4, 119.7 (d, $^{2}J_{C-F}$ = 23.9 Hz, 1C); IR (KBr): ν 1594, 1562, 1446, 1423, 910, 856, 745, 566 cm^{-1}; MS (EI) m/z: 333 [M^+ (^{81}Br^{81}Br)] (10.66), 331 [M^+ (^{79}Br ^{81}Br)] (24.26), 329 [M^+ (^{79}Br^{79}Br)] (12.22), 252, 250, 171, 144, 118; HRMS (EI) Calcd for $C_{11}H_6Br_2FN$: 328.8851, Found: 328.8848.

2-(2-Bromo-4-fluorophenyl)pyridine (4b)



Colorless oil, yield: 7%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, J = 4.8 Hz, 1H), 7.76 (td , J = 2.0, 8.0 Hz 1H), 7.58 (d , J = 8.0 Hz, 1H), 7.53 (dd, J = 6.0, 8.4Hz, 1H), 7.42 (dd, J = 2.8, 8.4Hz, 1H), 7.30 (ddd, J =1.2, 4.8, 7.6 Hz, 1H), 7.13 (td, J = 2.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^{1}J_{C-F}$ = 250.3 Hz), 157.2, 149.3, 137.3 (d, $^{4}J_{C-F}$ = 3.0 Hz, 1C), 136.0, 132.5 (d, $^{3}J_{C-F}$ = 8.5 Hz, 1C), 124.8, 122.5, 121.9 (d, $^{3}J_{C-F}$ = 9.7 Hz, 1C), 120.3 (d, $^{2}J_{C-F}$ = 24.3 Hz, 1C), 114.7 (d, $^{2}J_{C-F}$ = 20.9 Hz, 1C); IR (KBr): ν 1651, 1589, 1568, 1456, 1429, 1370, 1098, 797, 777, 744 cm^{-1}; HRMS (ESI) Calcd for ($C_{11}H_7BrFN$+H^+): 251.9824, Found: 251.9820.

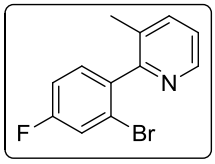
2-(2,6-Dibromo-3-methoxyphenyl)pyridine (5i)



Yellow solid, m.p.: 104-105 ^{o}C, yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72-8.71 (m, 1H), 8.77 (td, J = 1.6, 7.6 Hz, 1H), δ 7.54 (d, J = 8.8 Hz, 1H), 7.31 (ddd, J = 1.2, 4.8, 7.6 Hz, 1H), 7.25 (d, J = 7.6, Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 155.9, 150.0, 143.1, 136.7, 132.2, 124.8, 123.2, 114.1, 144.0, 113.0, 56.9; IR (KBr): ν

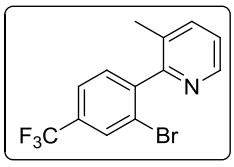
2964, 1557, 1452, 1294, 1091, 801 cm^{-1}; MS (EI) m/z: 345 [M^+ ($^{81}Br^{81}Br$)] (15.03), 343 [M^+ (^{81}Br ^{79}Br)] (34.00), 341 [M^+ ($^{79}Br^{79}Br$)] (16.08), 264, 262, 247, 221, 140, 113; HRMS (EI) Calcd for $C_{12}H_9Br_2NO$: 340.9051, Found: 340.9054.

2-(2-Bromo-4-fluorophenyl)-3-methylpyridine (4m)



Yellow oil, yield: 30%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.52-8.51 (m, 1H), 7.61-7.60 (m, 1H), 7.40 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.29-7.23 (m, 2H), 7.12 (td, *J* = 2.4, 8.4 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, $^1J_{C-F}$ = 249.6 Hz, 1C), 157.6, 146.7, 138.2, 137.9, 137.7, 132.1, 131.2 (d, $^3J_{C-F}$ = 8.5 Hz, 1C), 123.1, 119.8 (d, $^2J_{C-F}$ = 24.3 Hz, 1C), 114.7 (d, $^2J_{C-F}$ = 21.9 Hz, 1C), 18.9; IR (KBr): ν 2925, 2854, 1601, 1581, 1494, 1446, 1384, 909, 877, 859, 733, 592 cm^{-1}; MS (EI) m/z: 267 [M^+ (^{81}Br)] (16.04), 265 [M^+ (^{79}Br)] (17.64), 186, 185, 166, 157, 93, 75; HRMS (EI) Calcd for $C_{12}H_9BrFN$: 264.9902, Found: 264.9906.

2-(2-Bromo-4-(trifluoromethyl)phenyl)-3-methylpyridine (4o)



Colorless oil, yield: 46%; ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* =4.8 Hz, 1H), 7.93 (s, 1H), 7.67-7.61 (m 2H), 7.42 (d, *J* =8.0 Hz, 1H), 7.28 (dd, *J* = 4.8, 7.6, Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 147.1, 145.3, 138.3, 131.9, 131.8 (q, $^2J_{C-F}$ = 32.9 Hz, 1C), 131.0, 129.9, 123.3 (q, $^1J_{C-F}$ = 270.9 Hz, 1C), 124.6, 123.7, 123.2, 19.0; IR (KBr): ν 2926, 1321, 1131, 1080, 792 cm^{-1}; MS (EI) m/z: 317 [M^+ (^{81}Br)](17.46), 315 [M^+ (^{79}Br)](16.94), 237, 236, 216, 167, 139, 75; HRMS (EI) Calcd for $C_{13}H_9BrF_3N$: 314.9870, Found: 314.9876.

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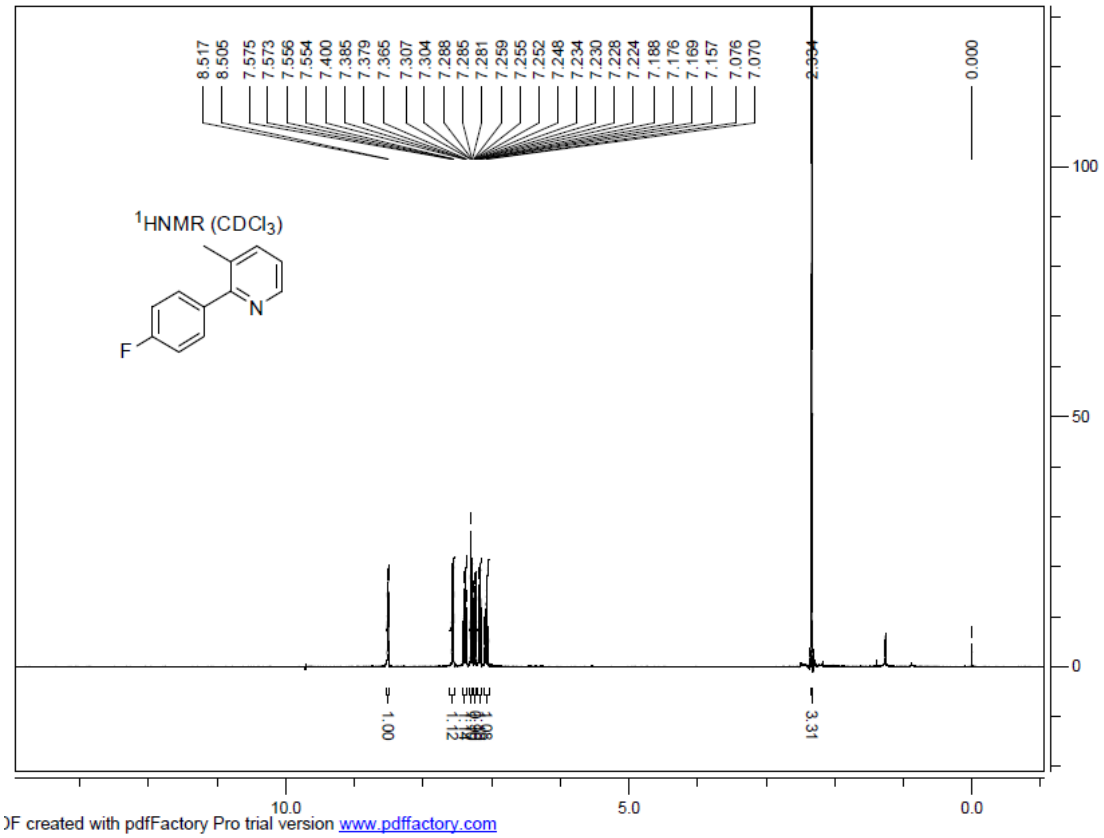
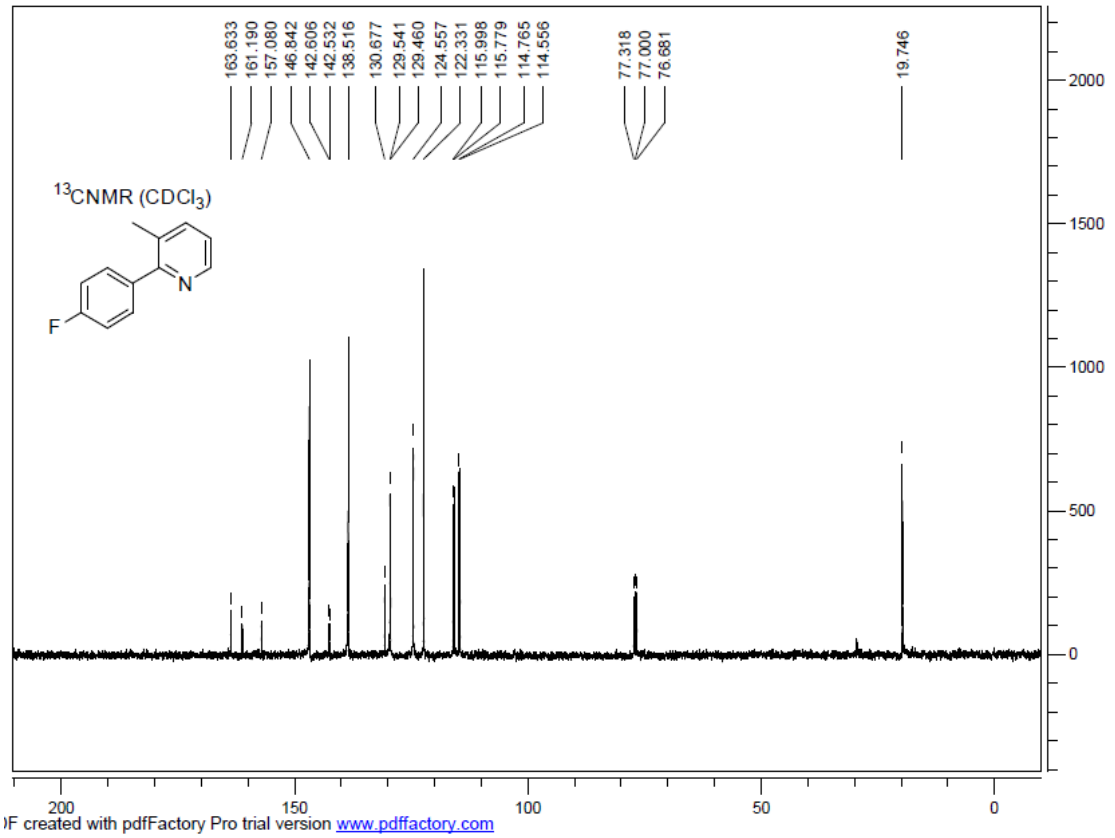
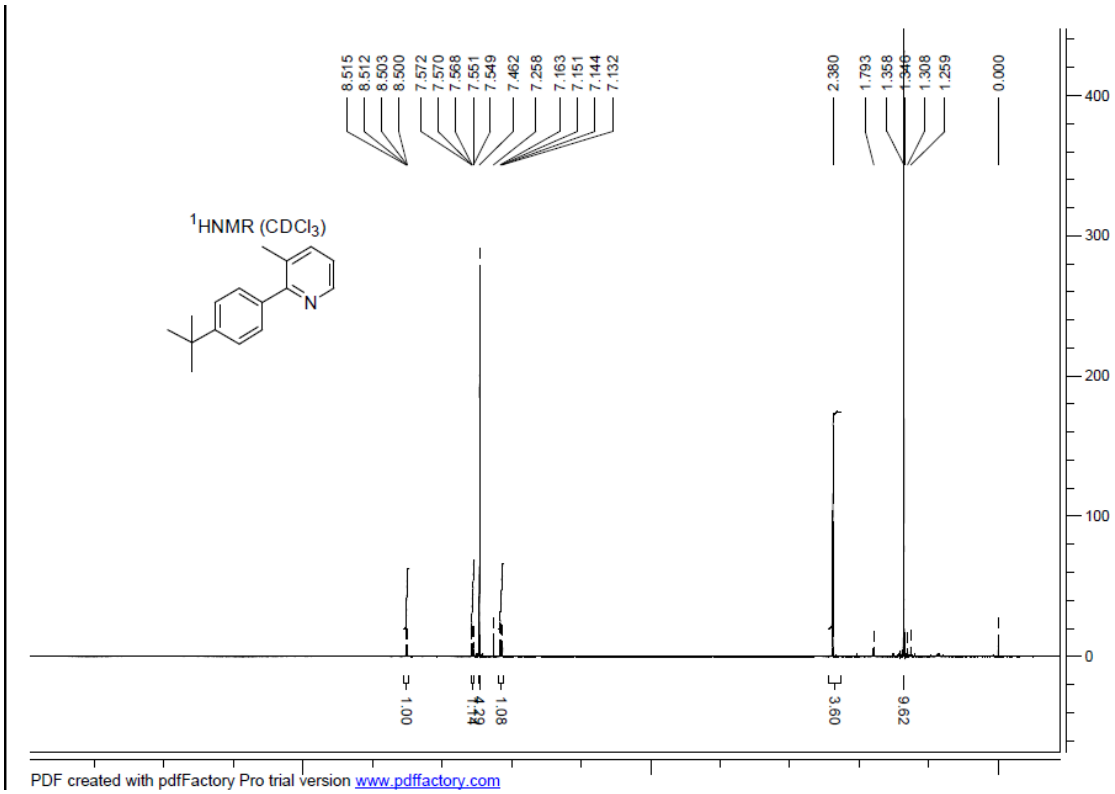
V Spectra data of NMR

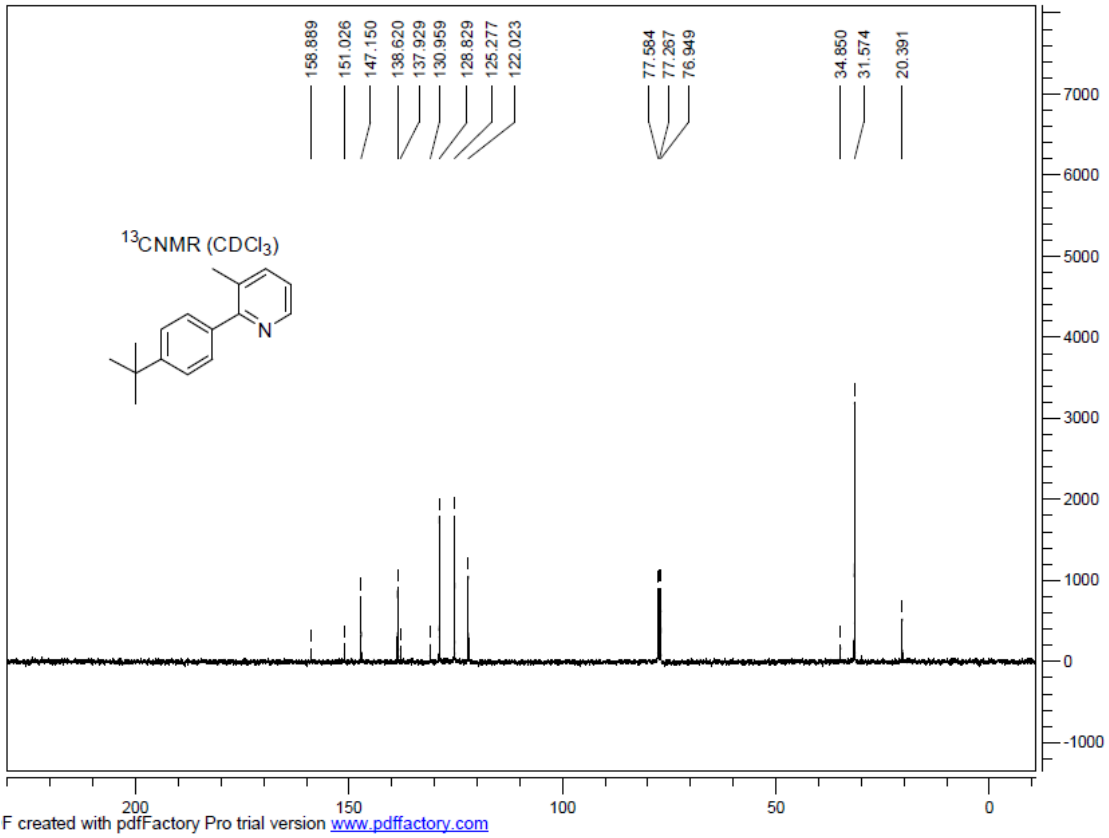
NMR spectra of compound **1m**



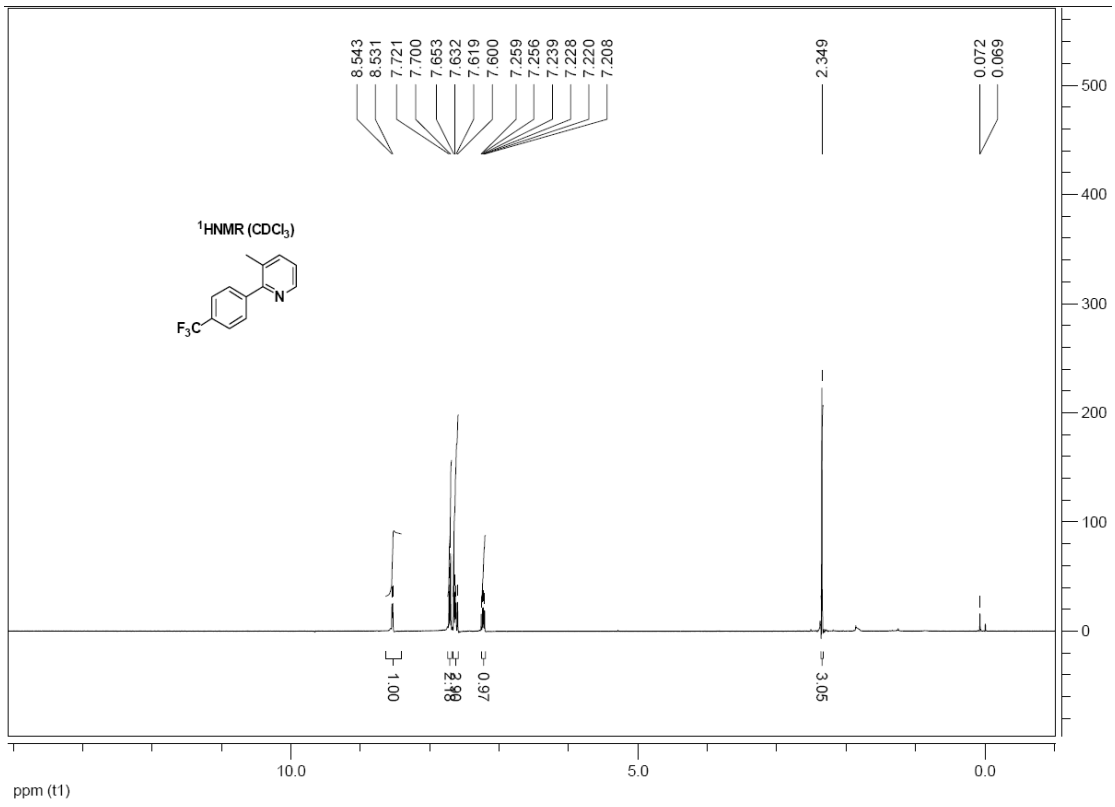


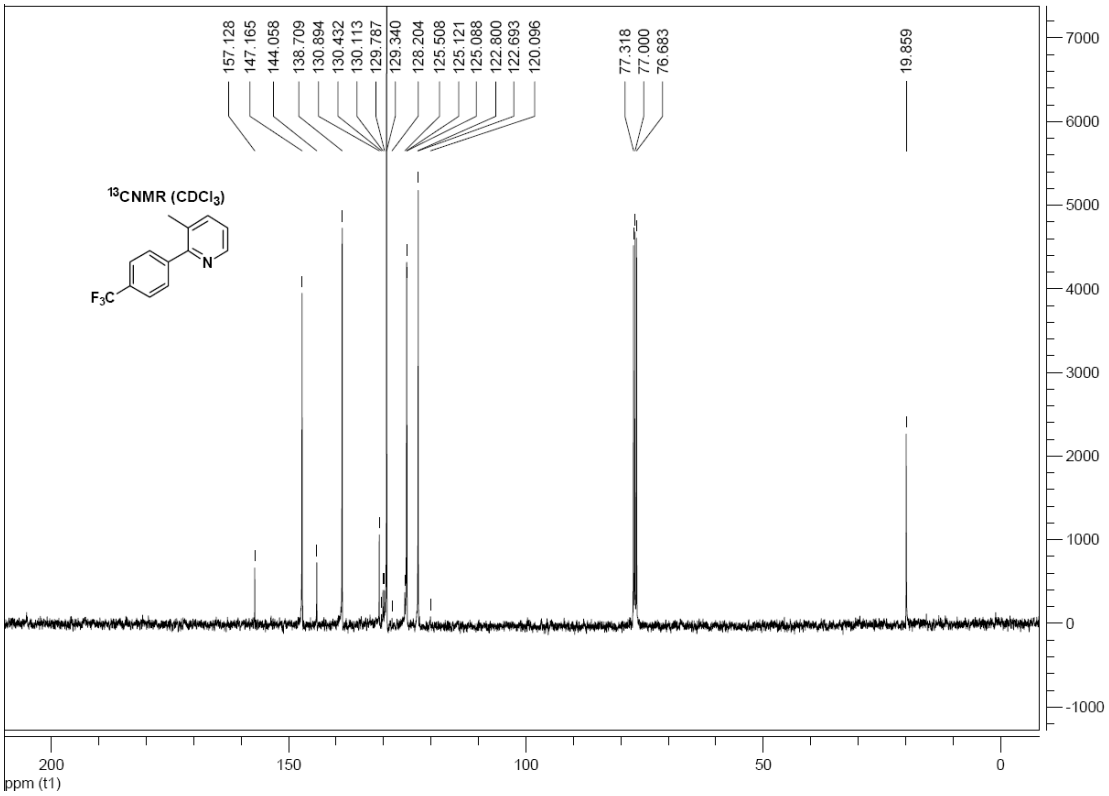
NMR spectra of compound **1n**



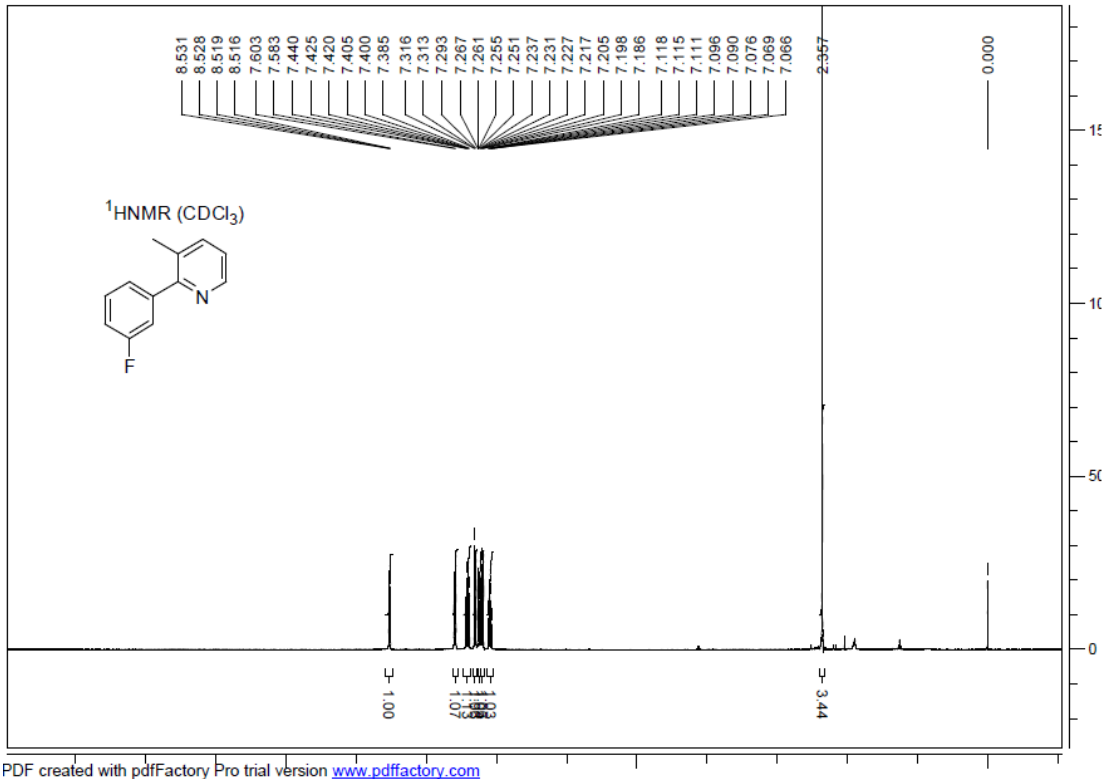


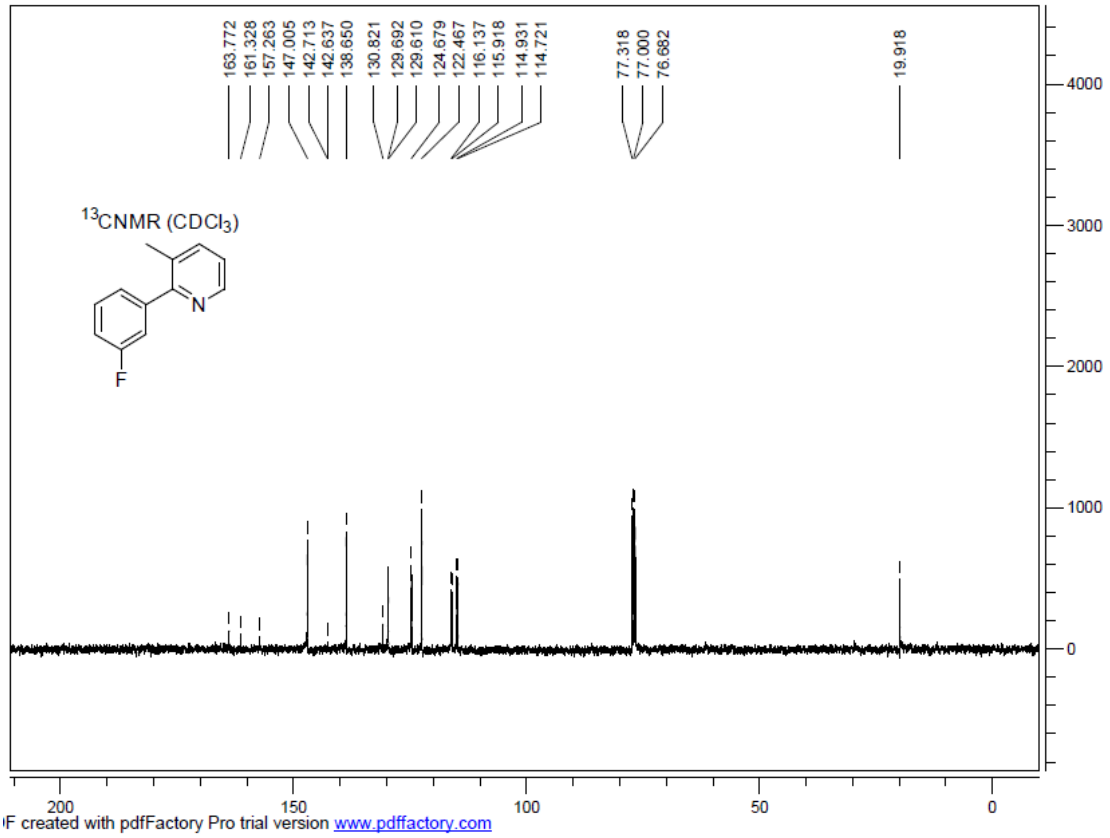
NMR spectra of compound **1o**



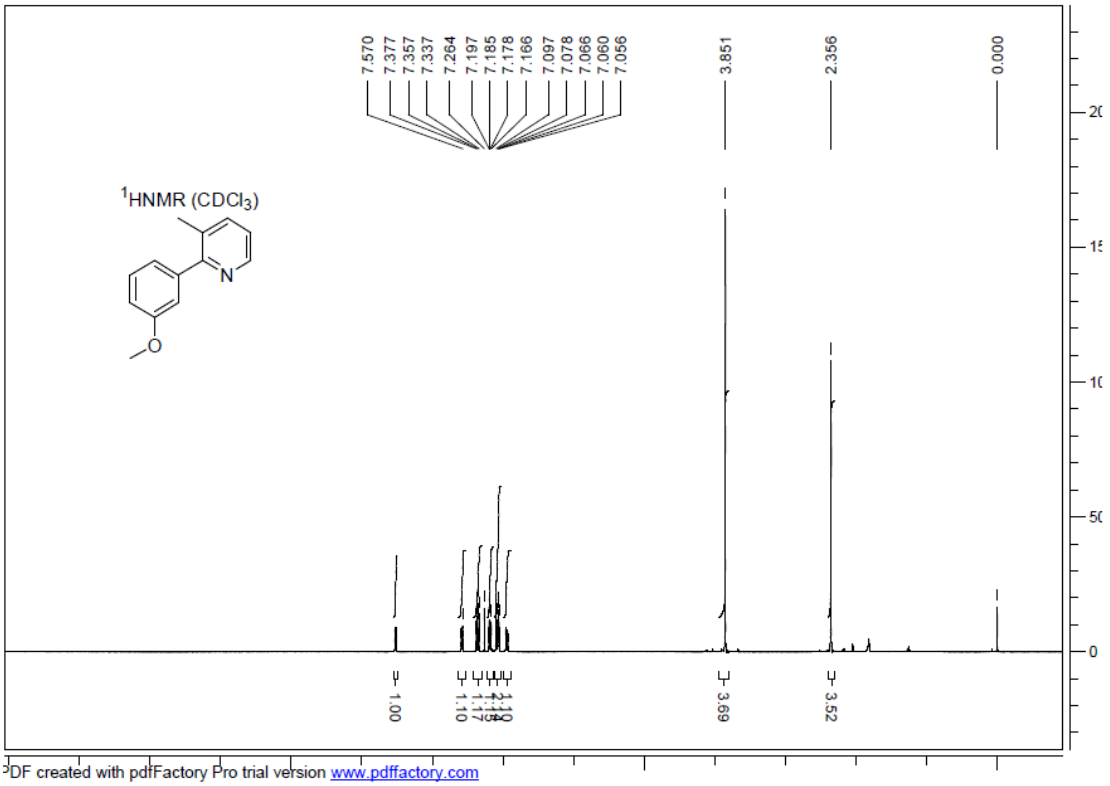


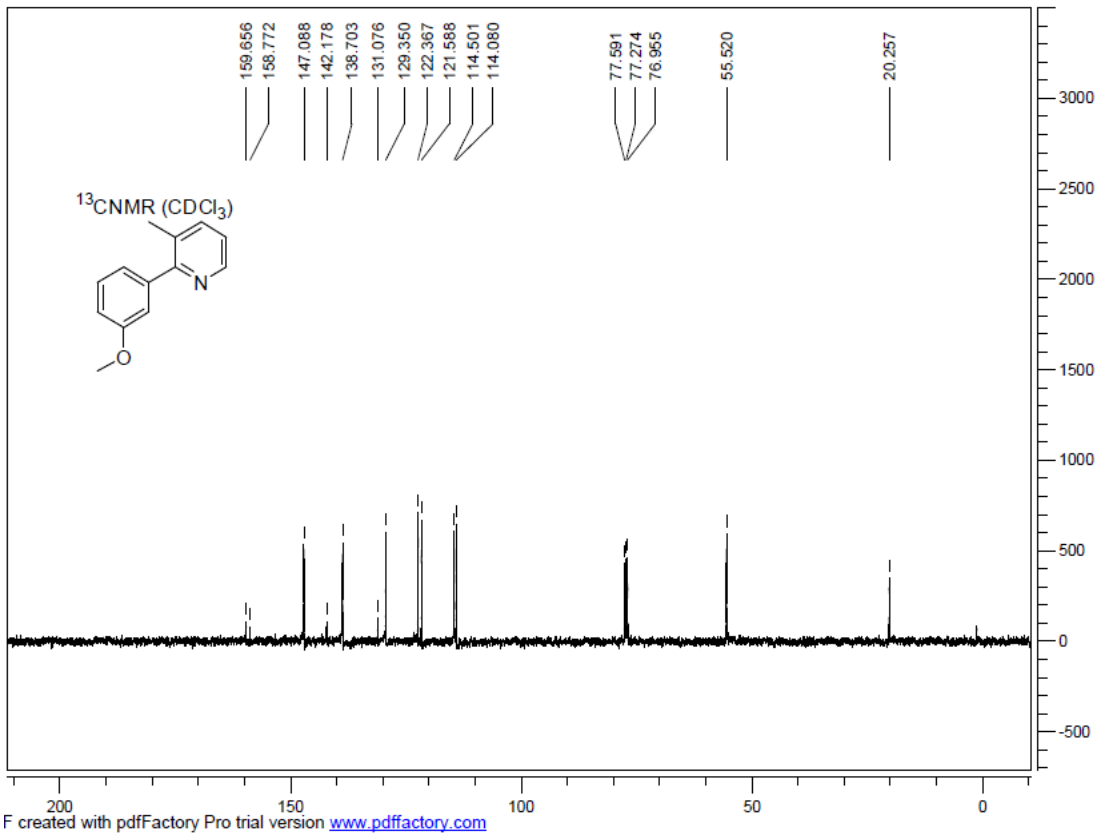
NMR spectra of compound **1h**



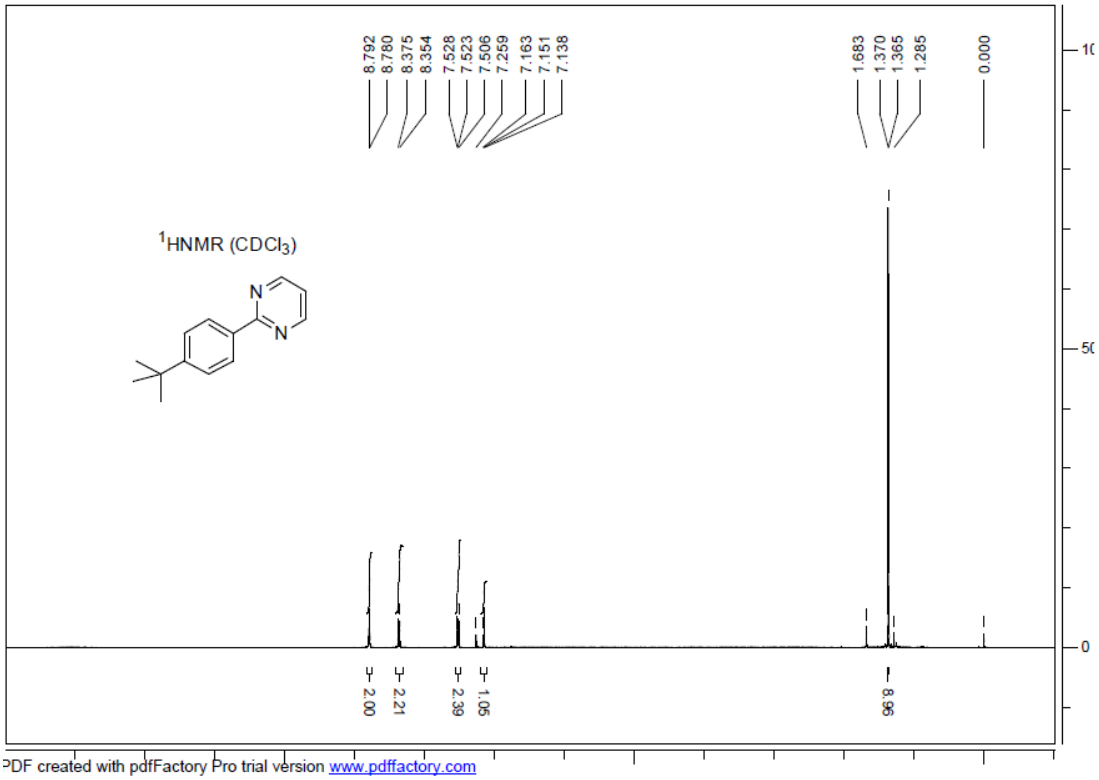


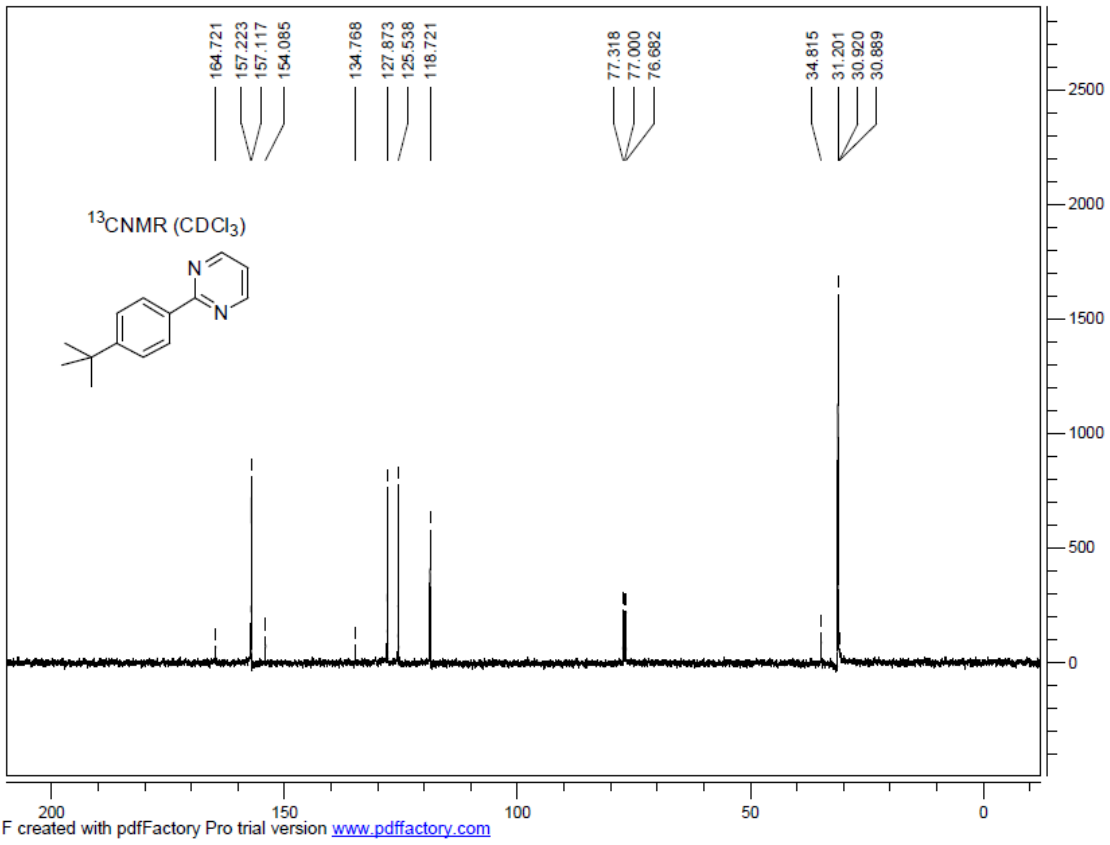
NMR spectra of compound **1r**



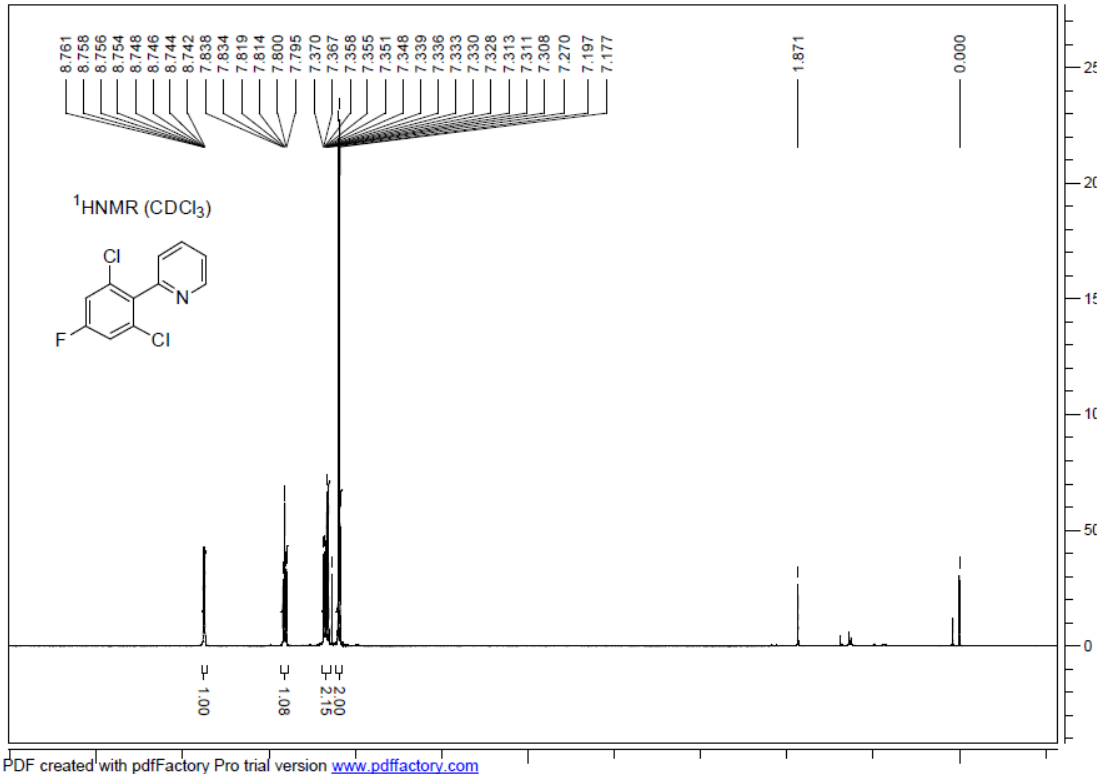


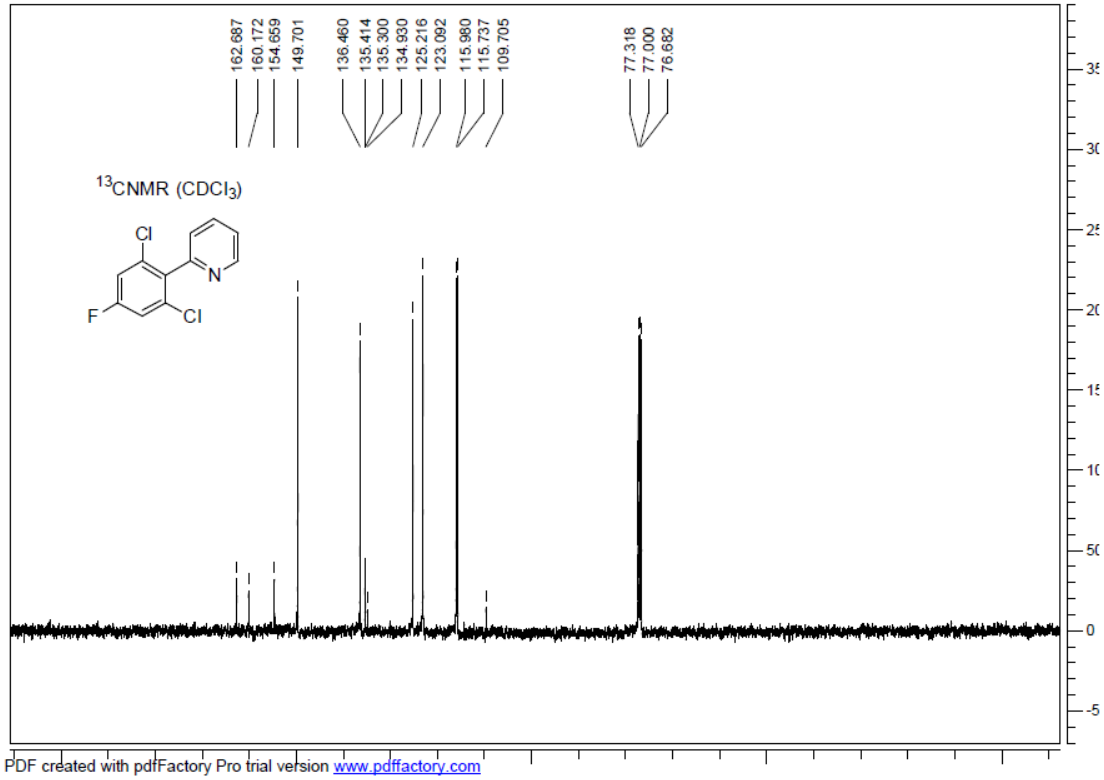
NMR spectra of compound **1t**



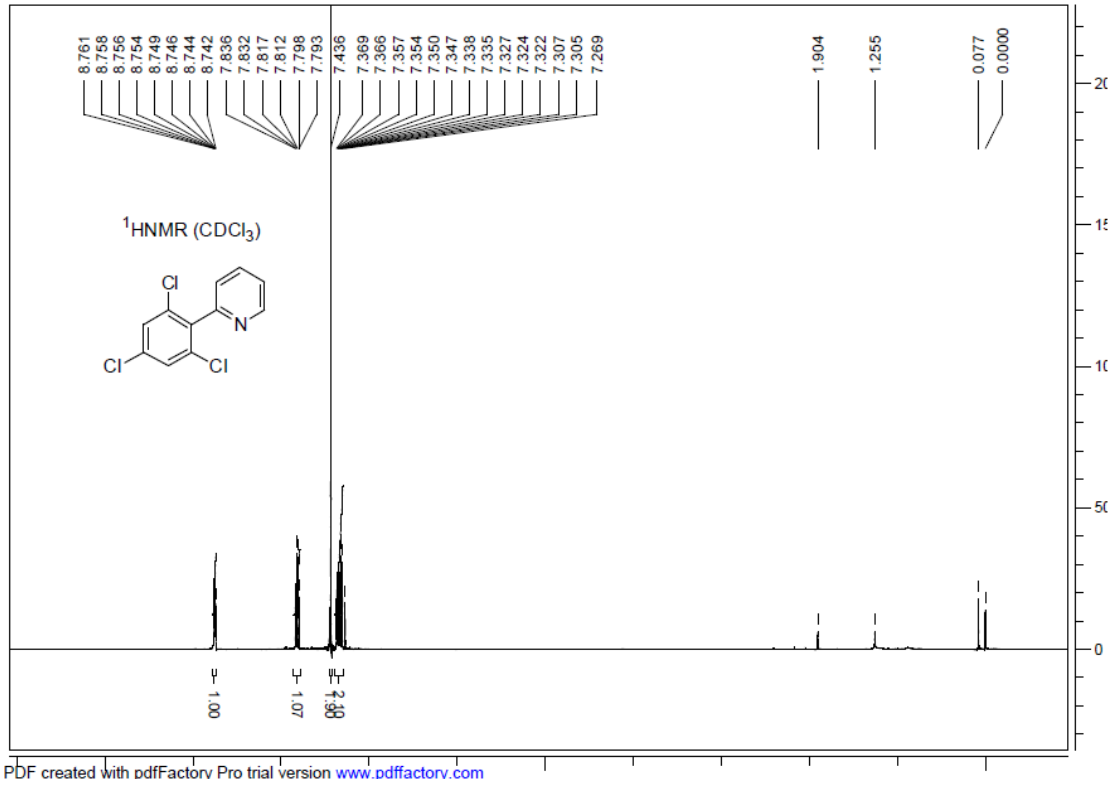


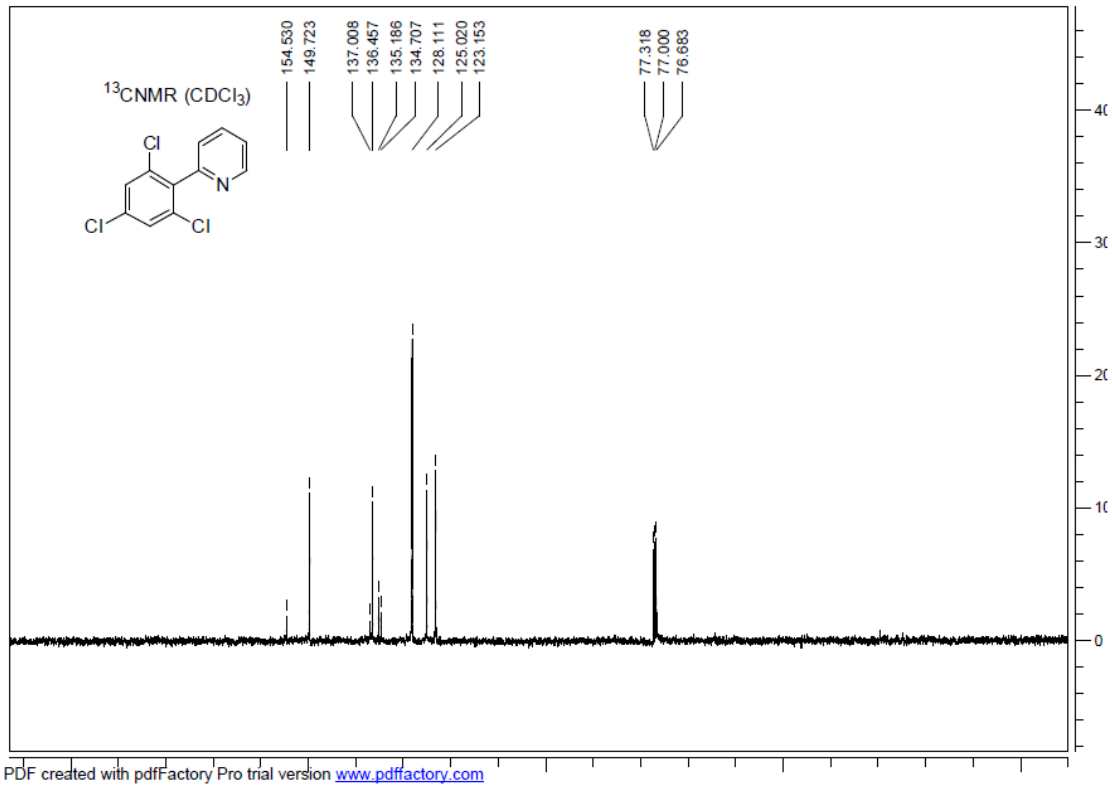
NMR spectra of compound **3b**



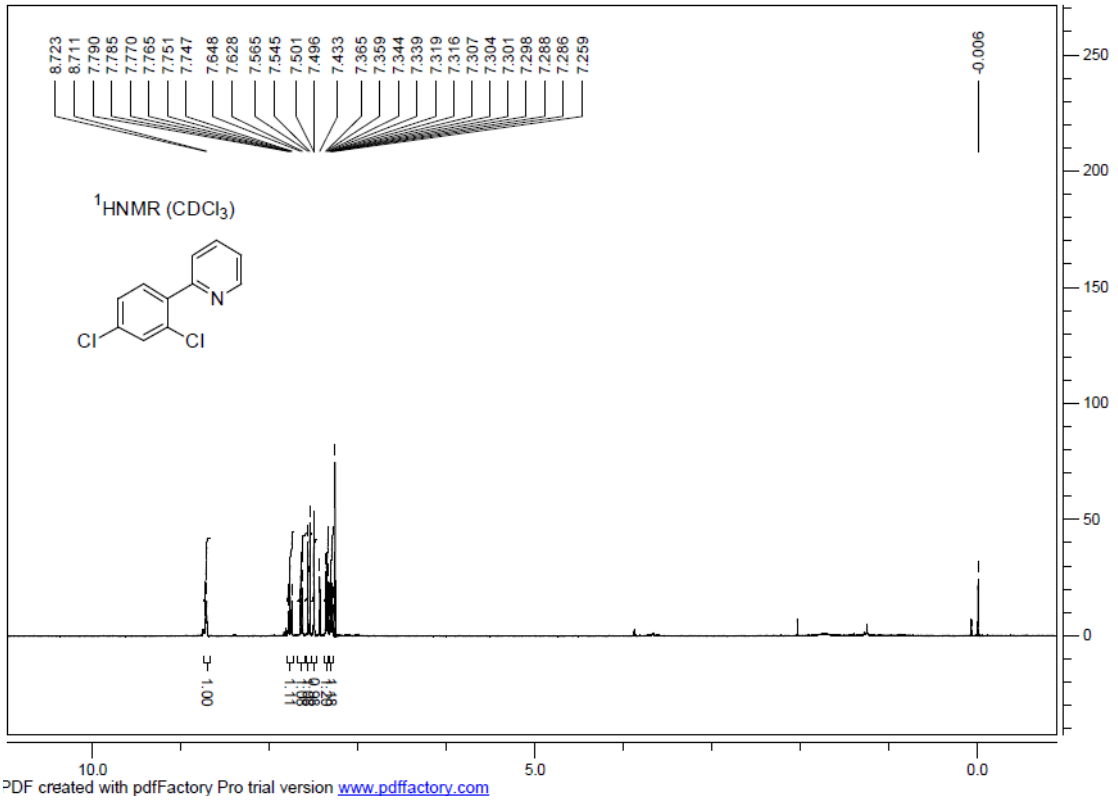


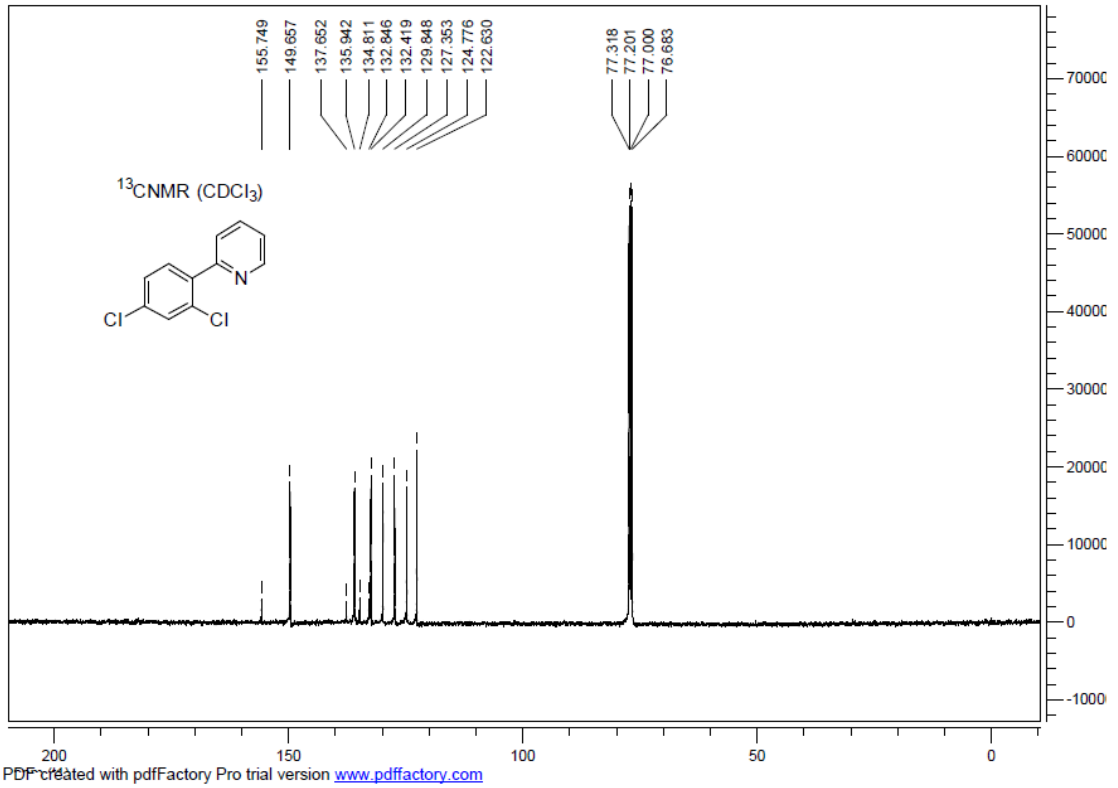
NMR spectra of compound **3c**



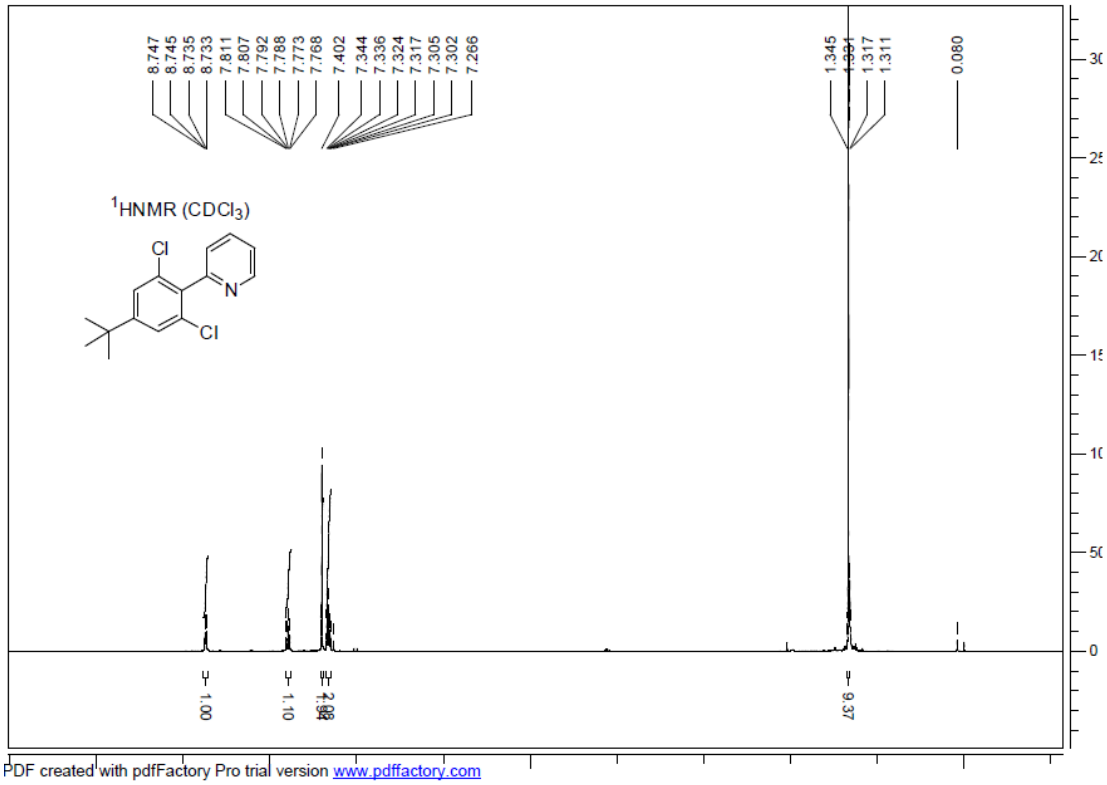


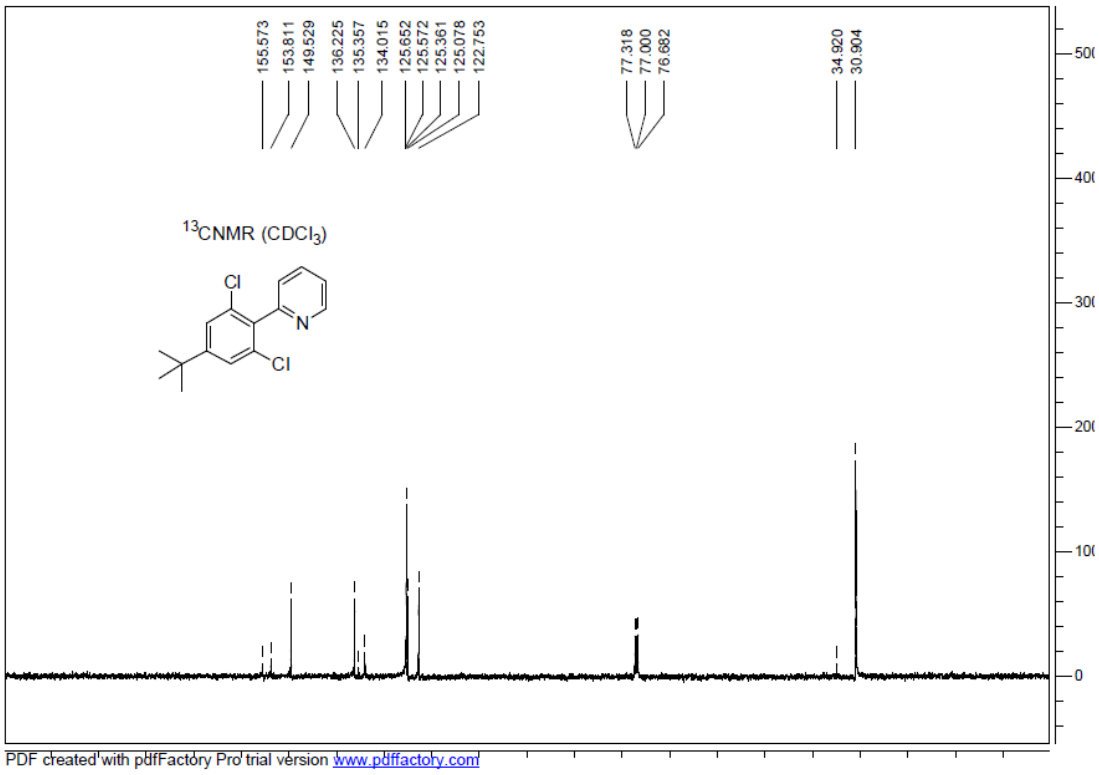
NMR spectra of compound **2c**



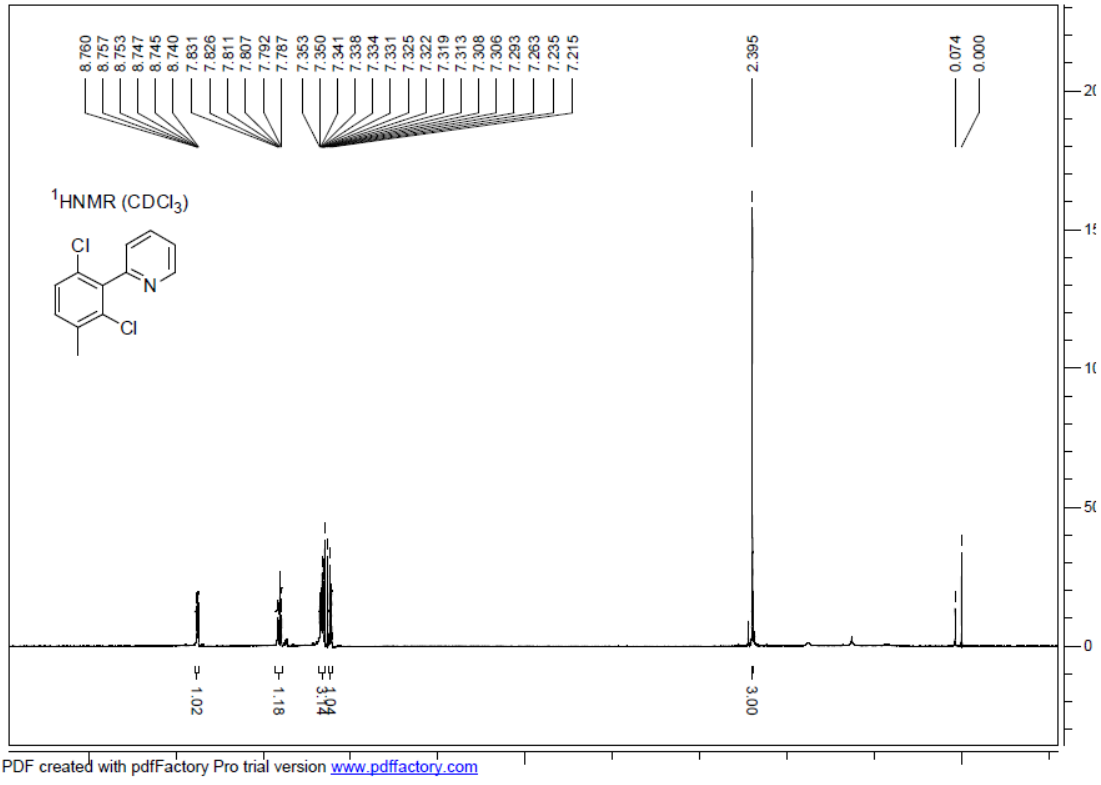


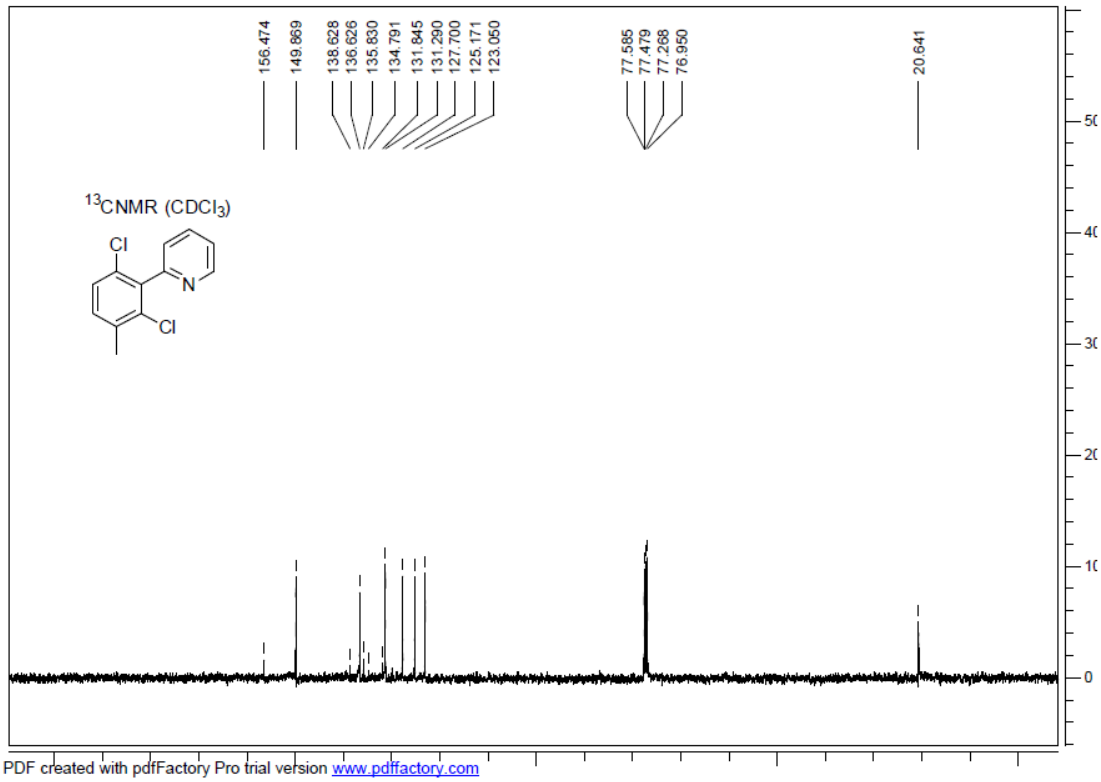
NMR spectra of compound **3f**



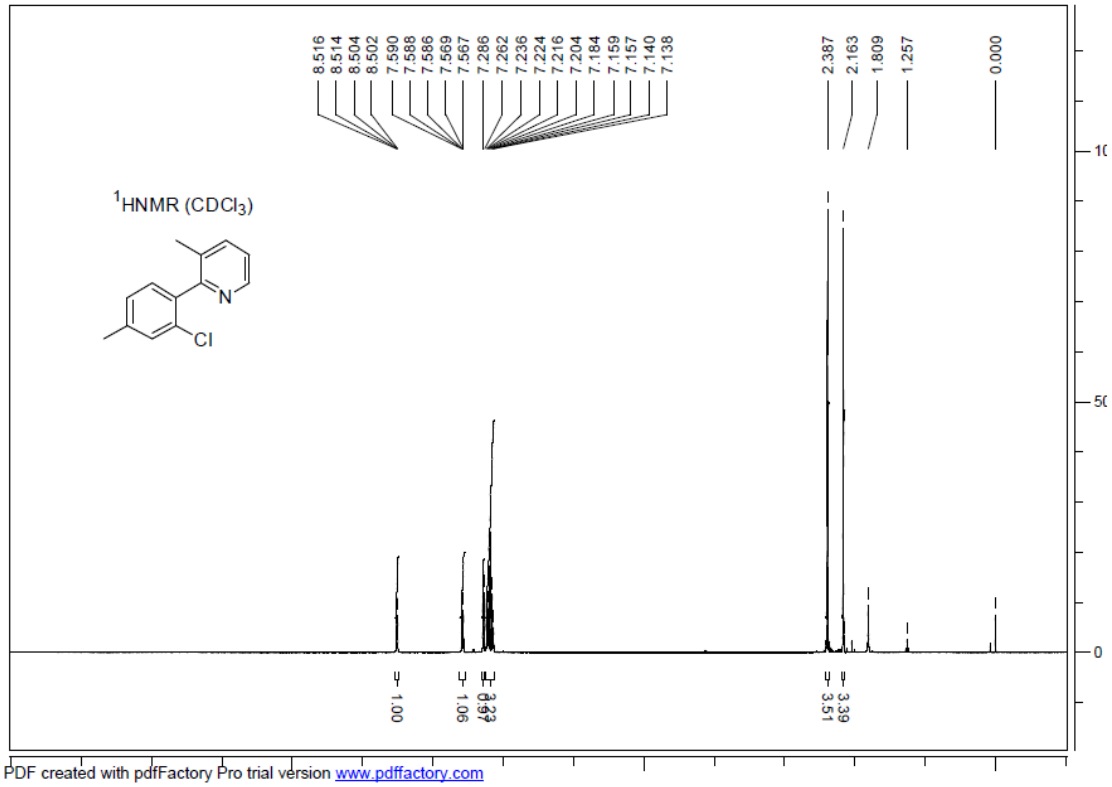


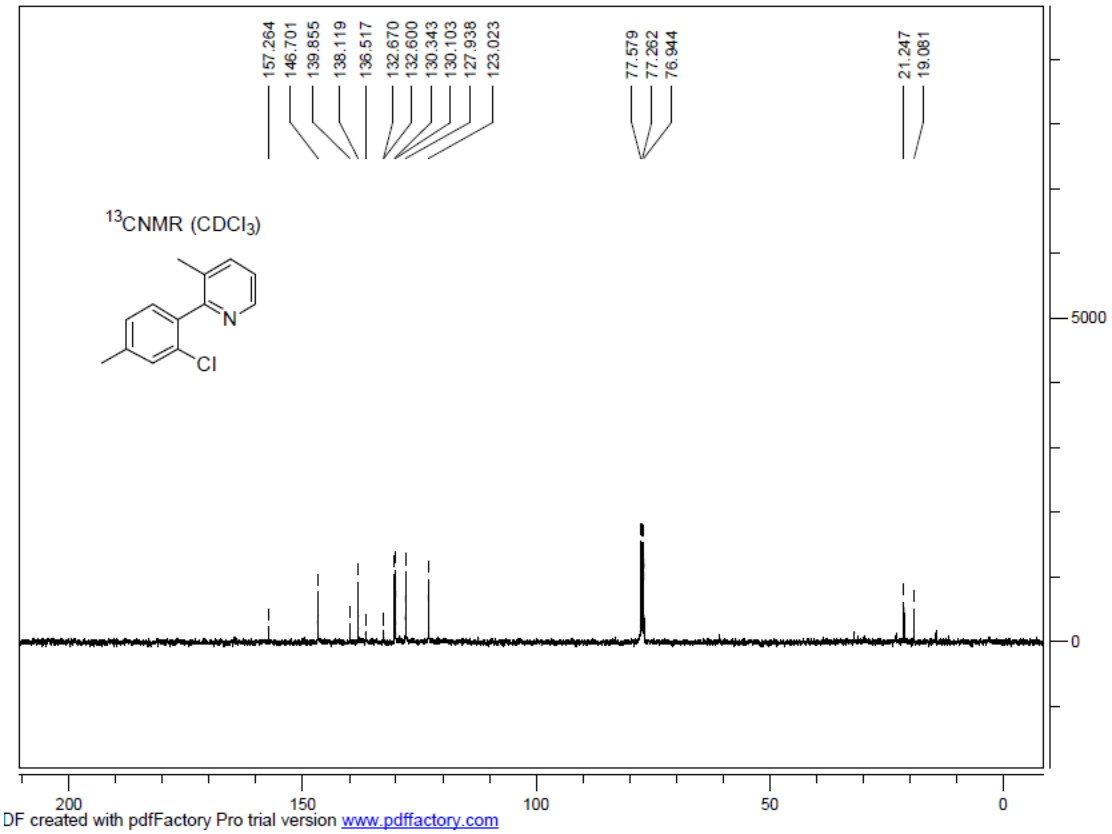
NMR spectra of compound **3h**



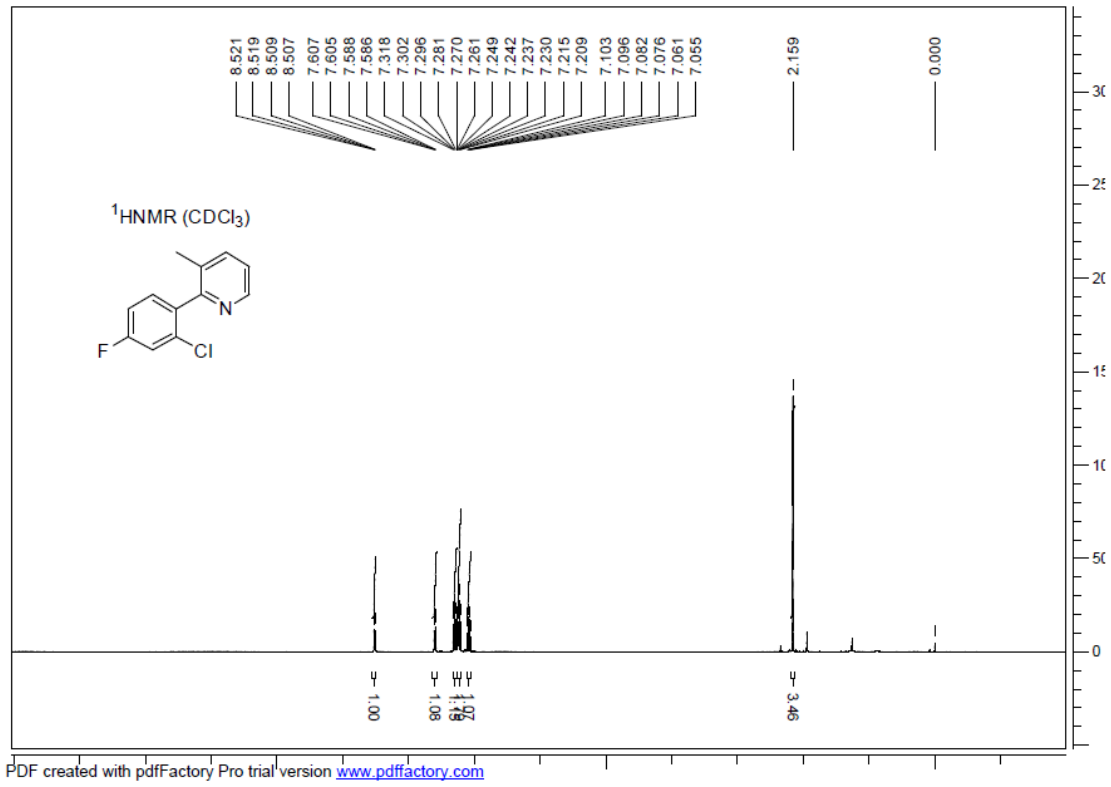


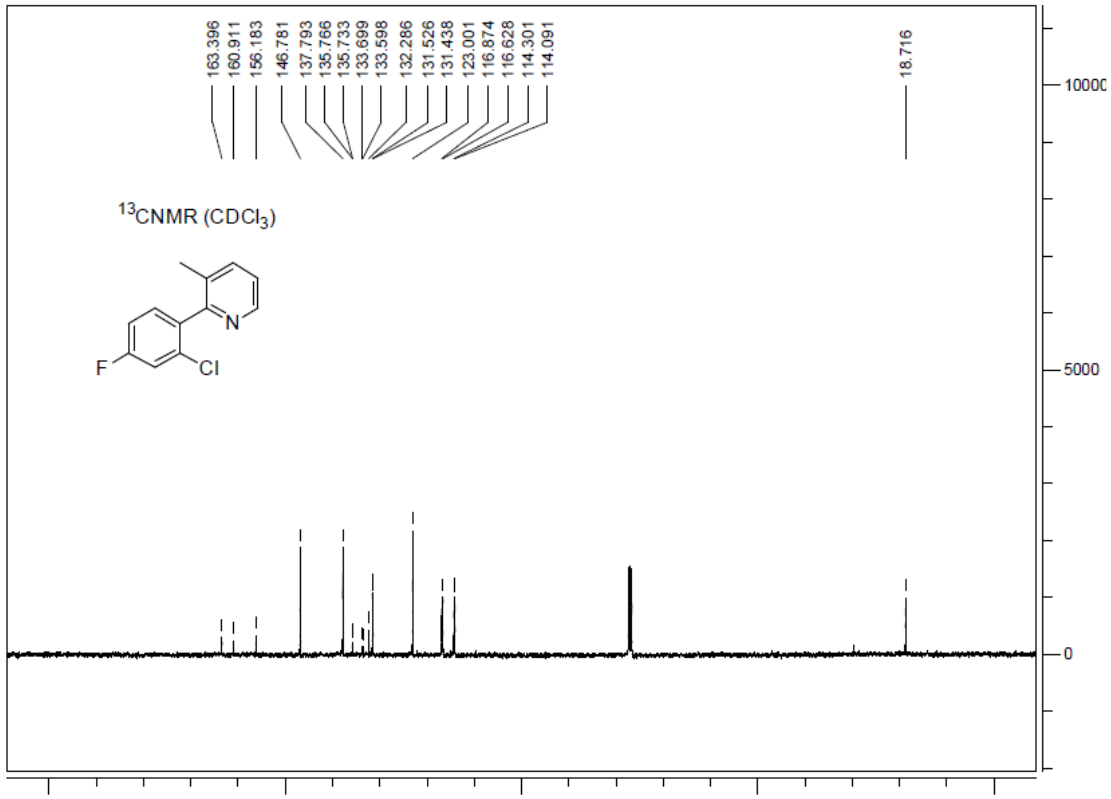
NMR spectra of compound **2l**



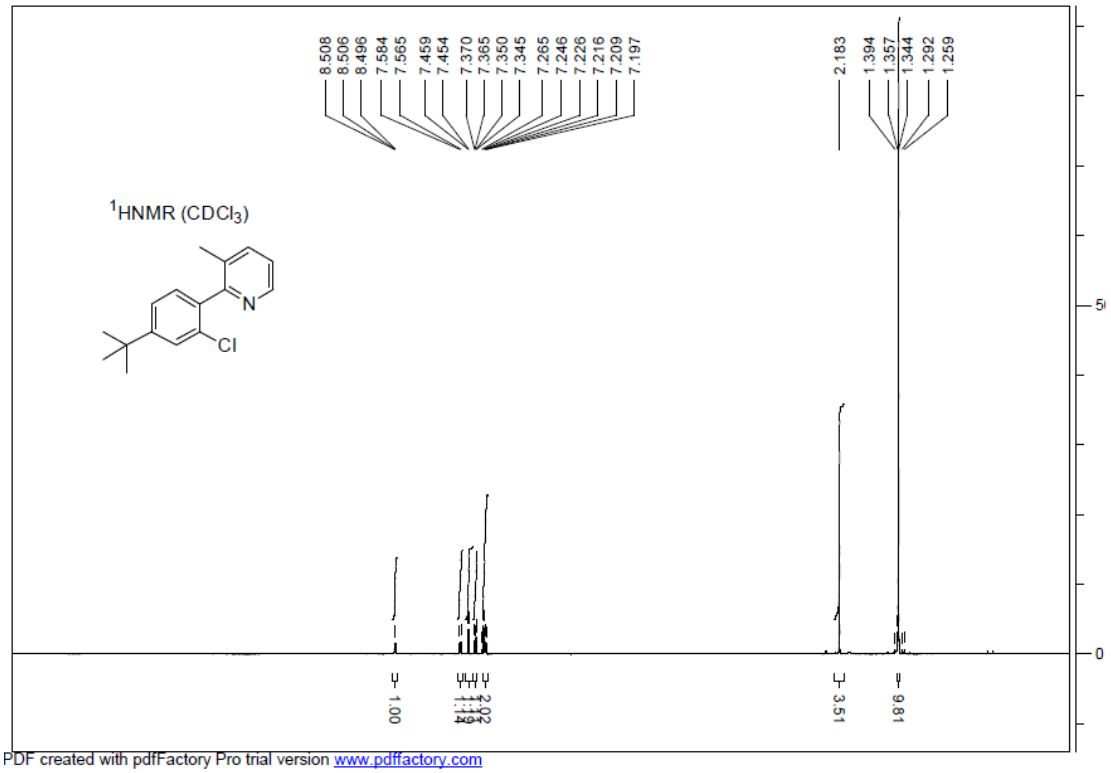


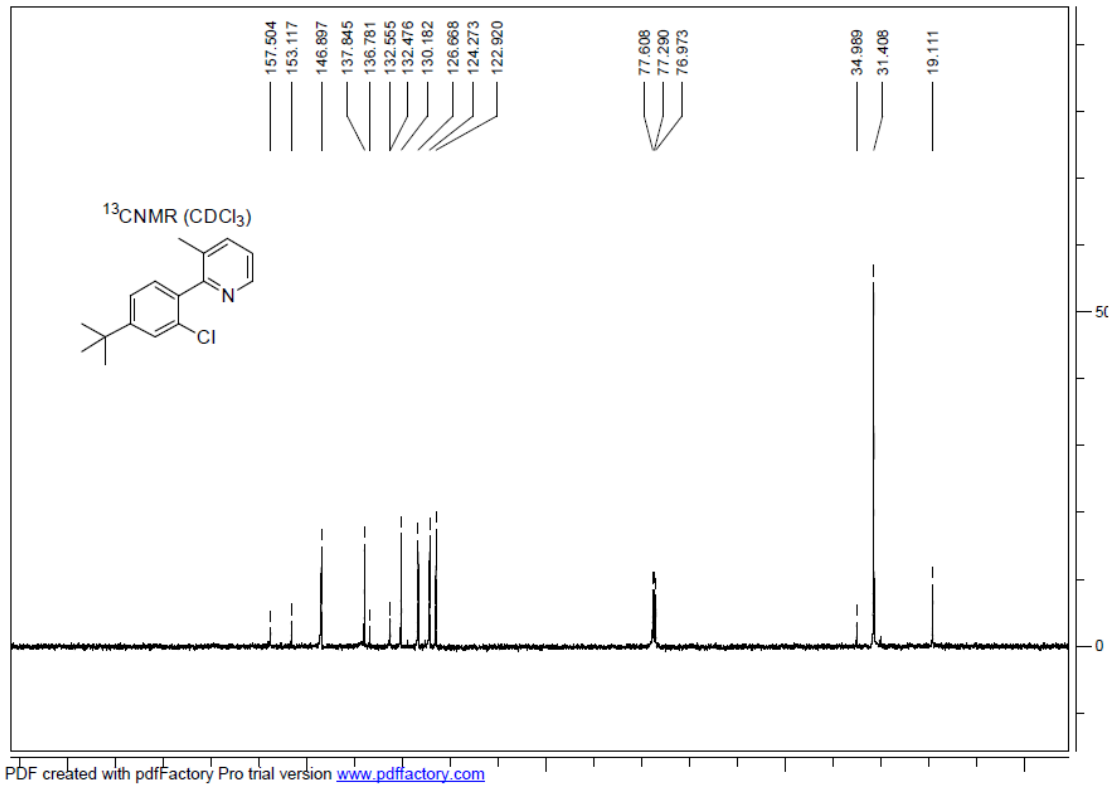
NMR spectra of compound **2m**



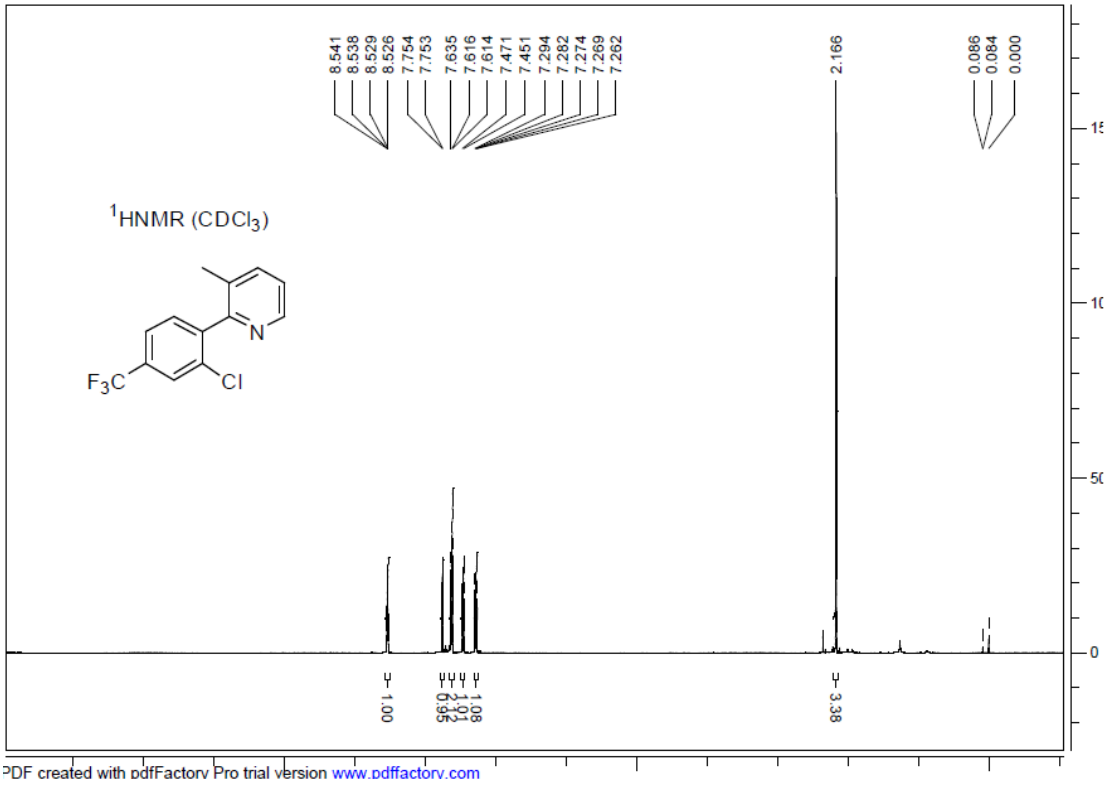


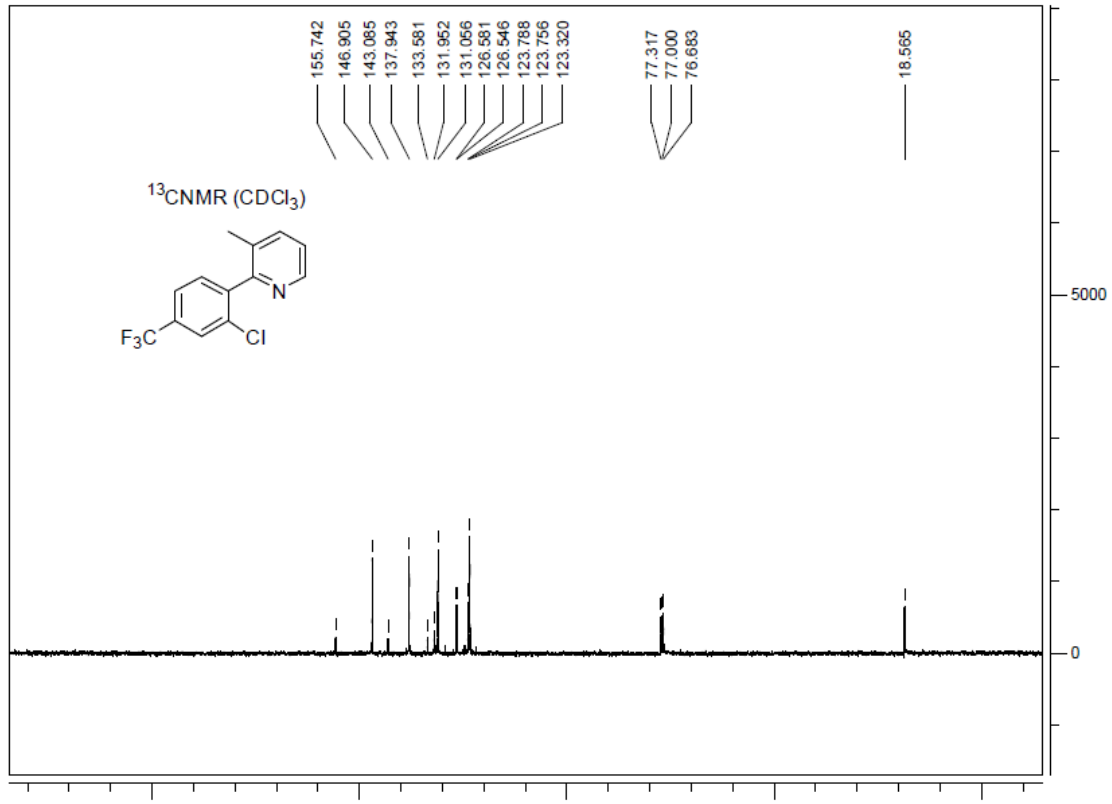
NMR spectra of compound **2n**



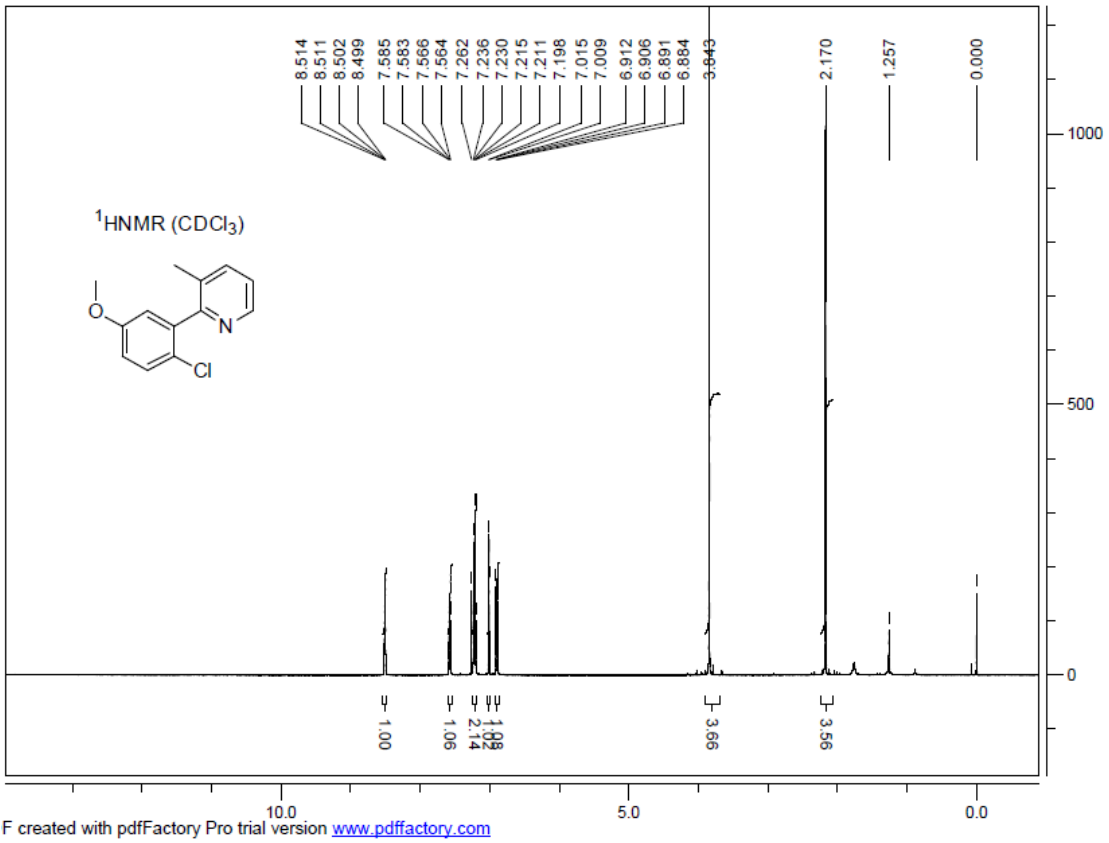


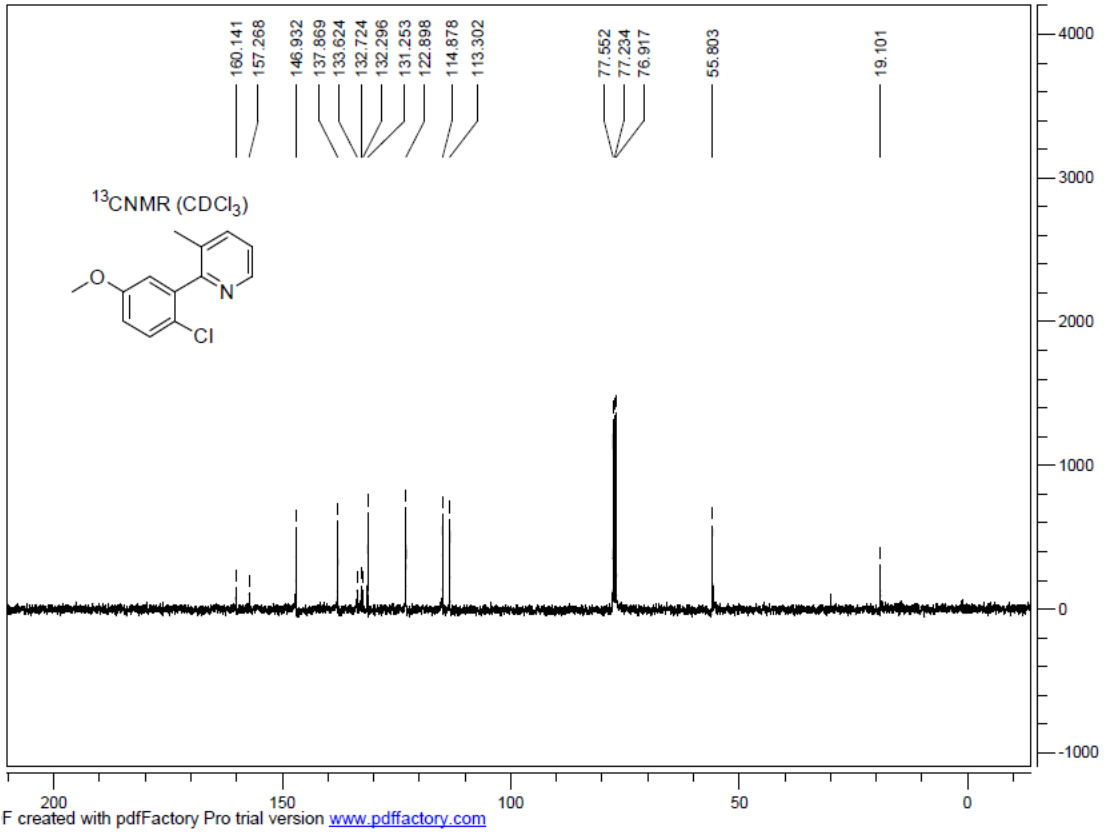
NMR spectra of compound **2o**



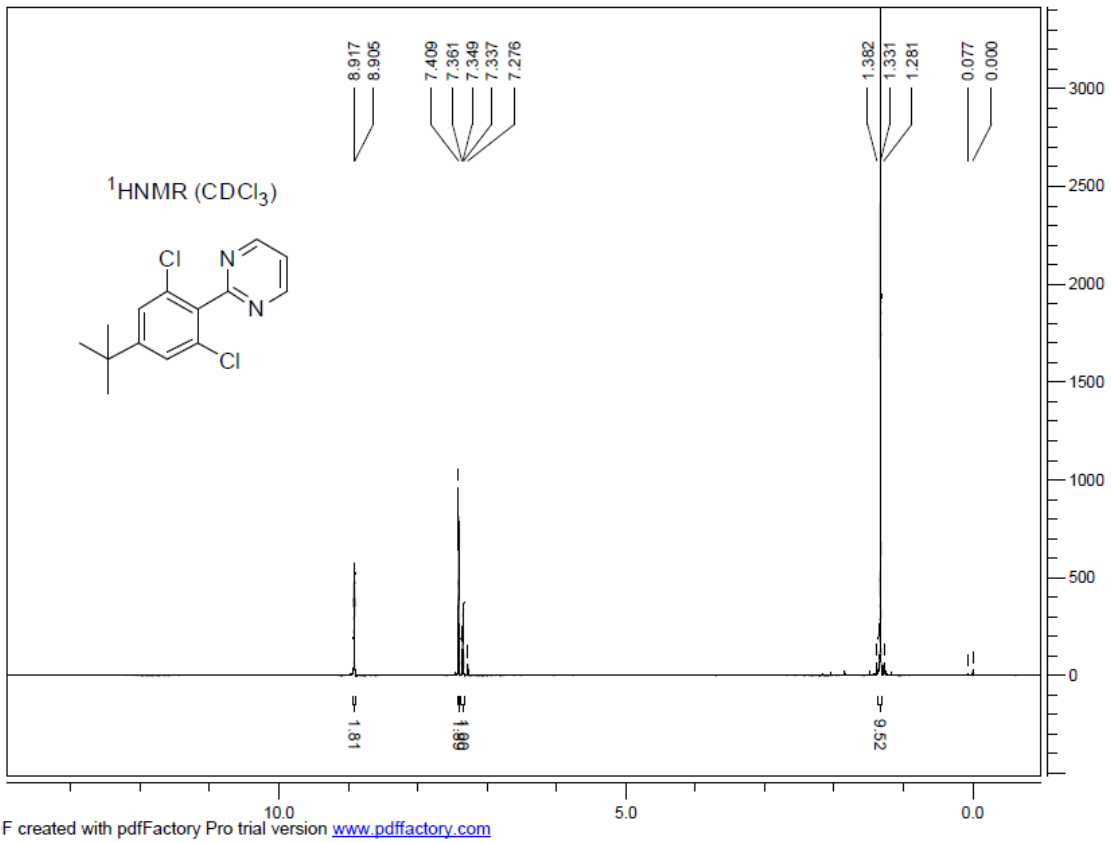


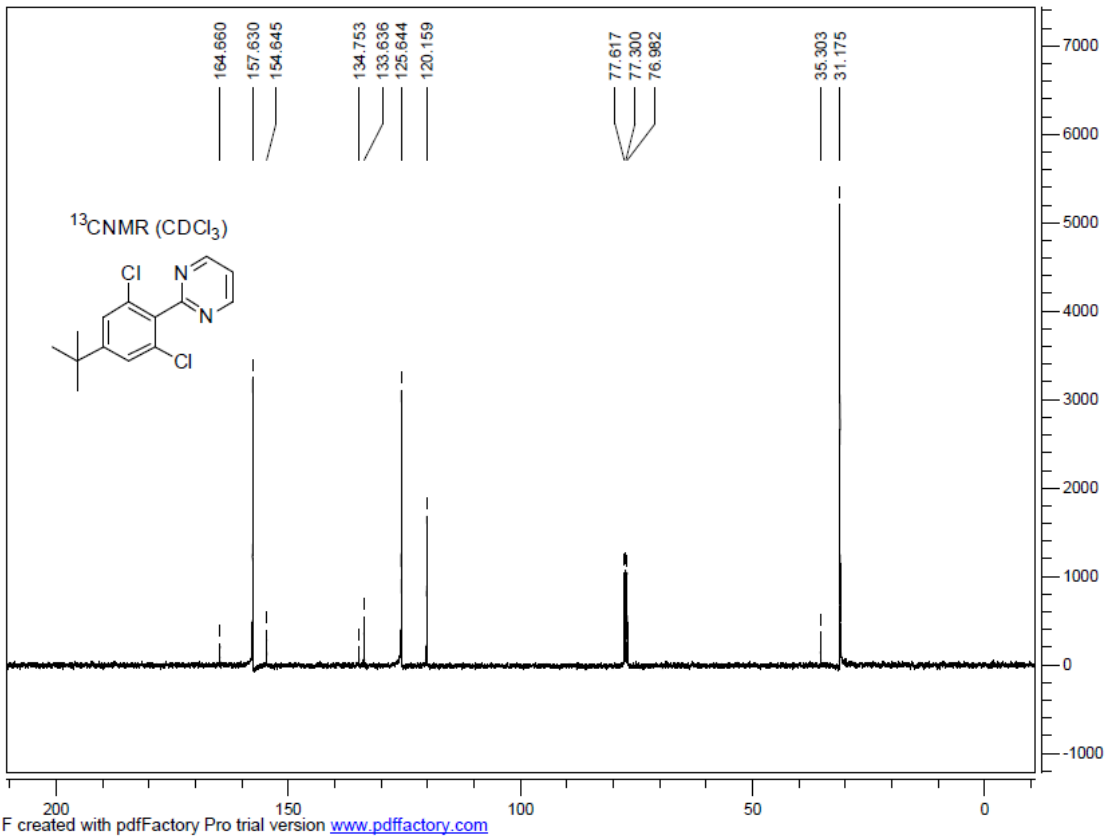
NMR spectra of compound **2q**



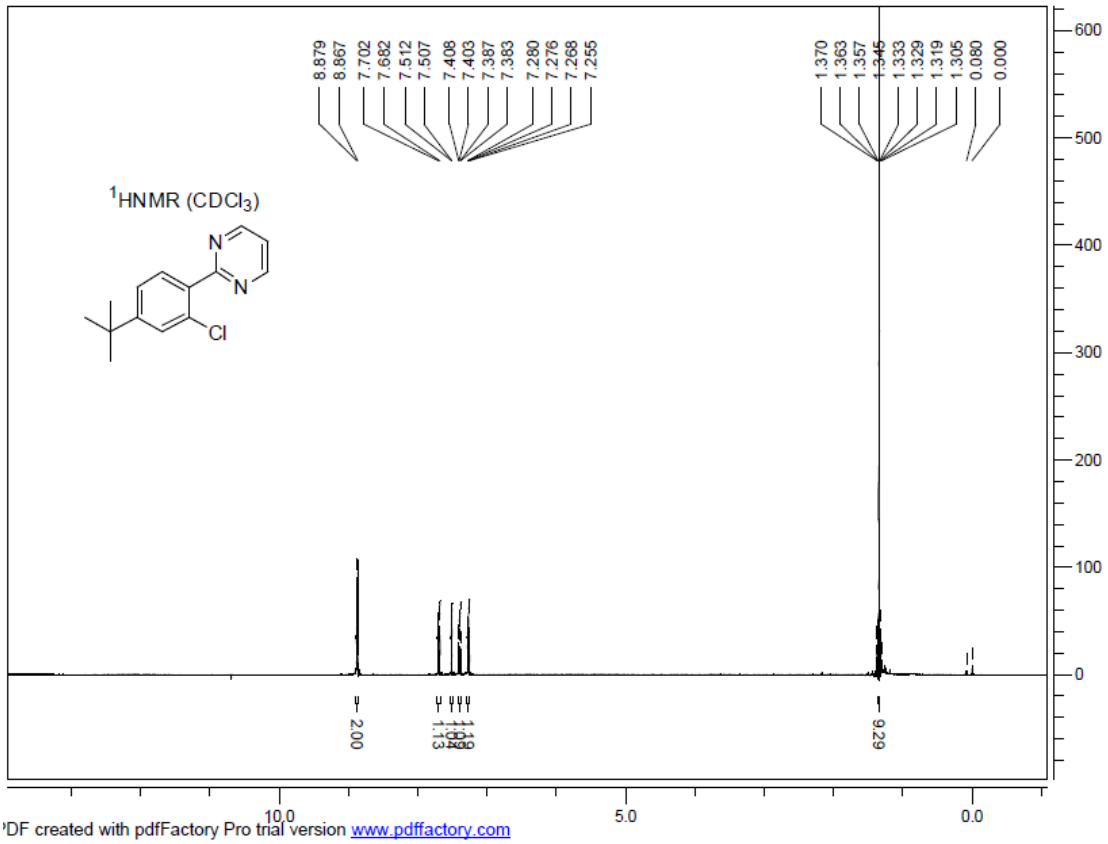


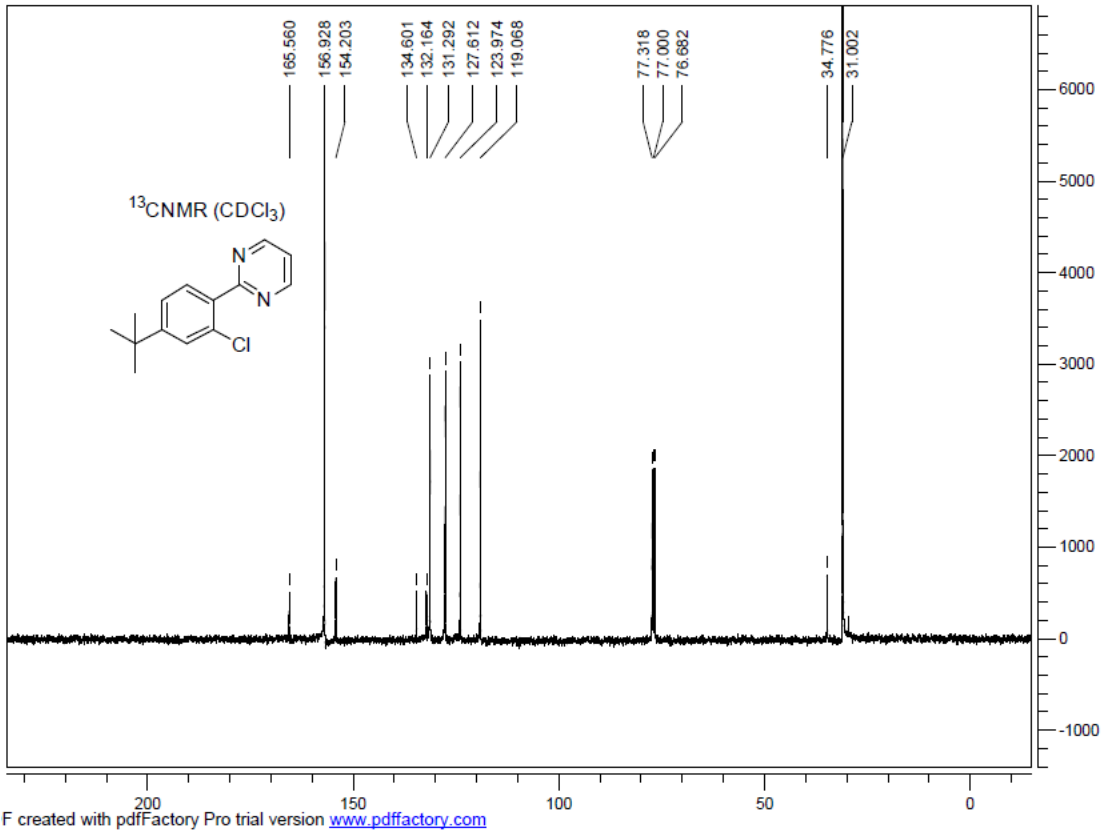
NMR spectra of compound **3t**



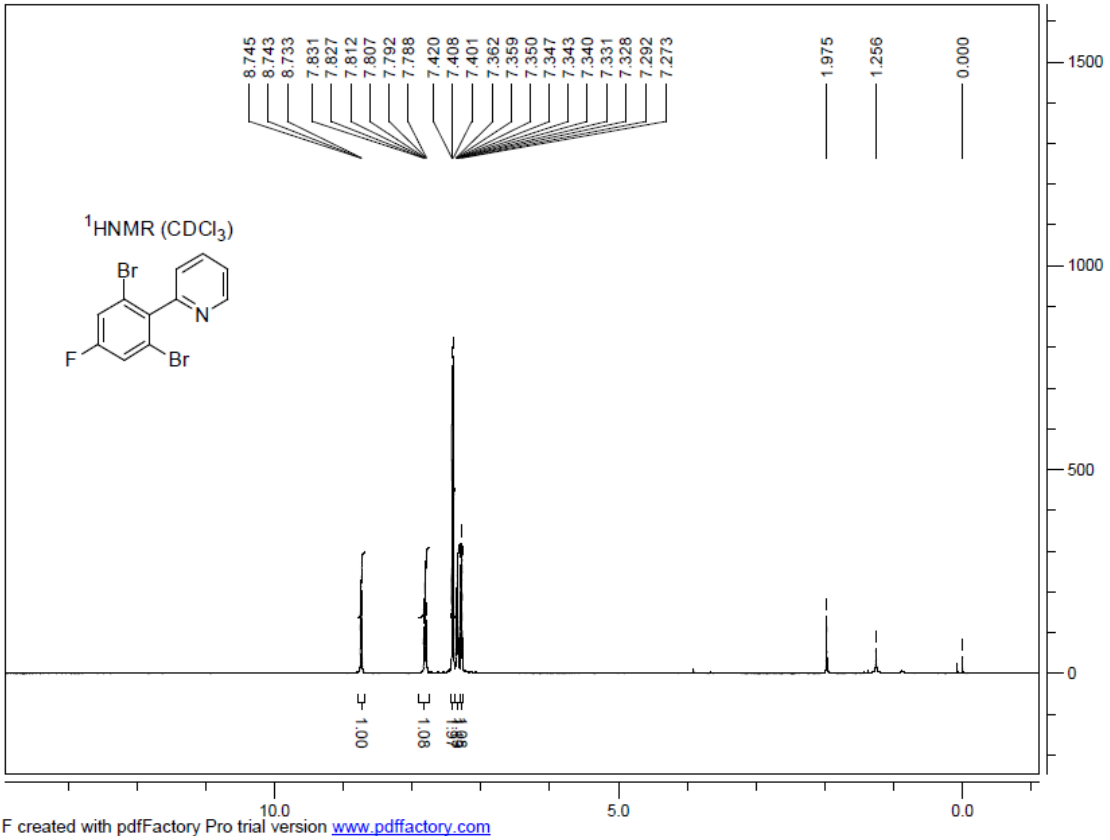


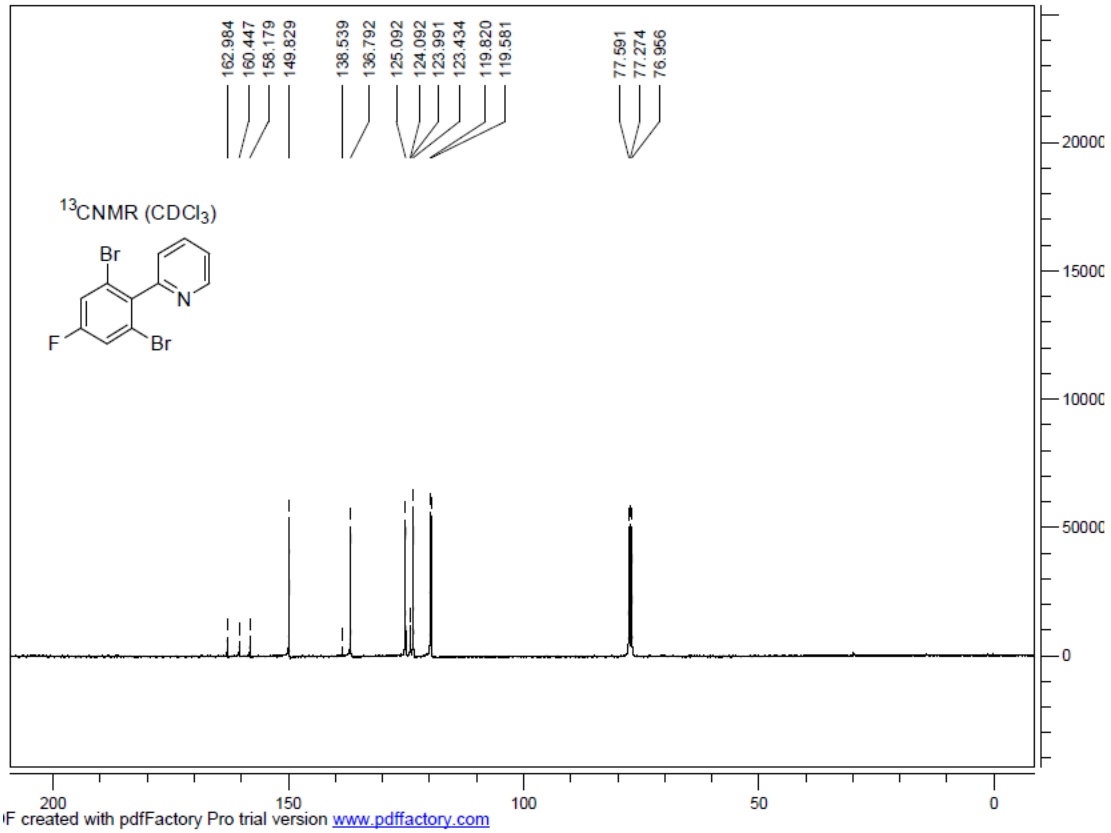
NMR spectra of compound **2u**



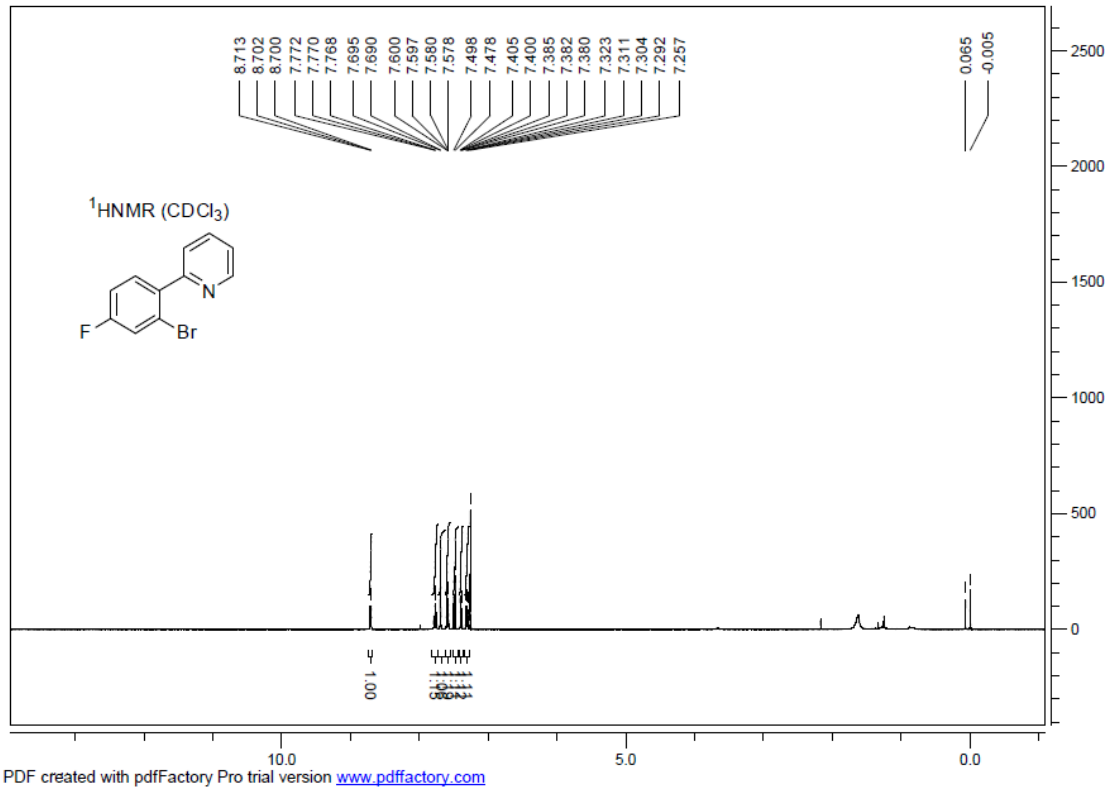


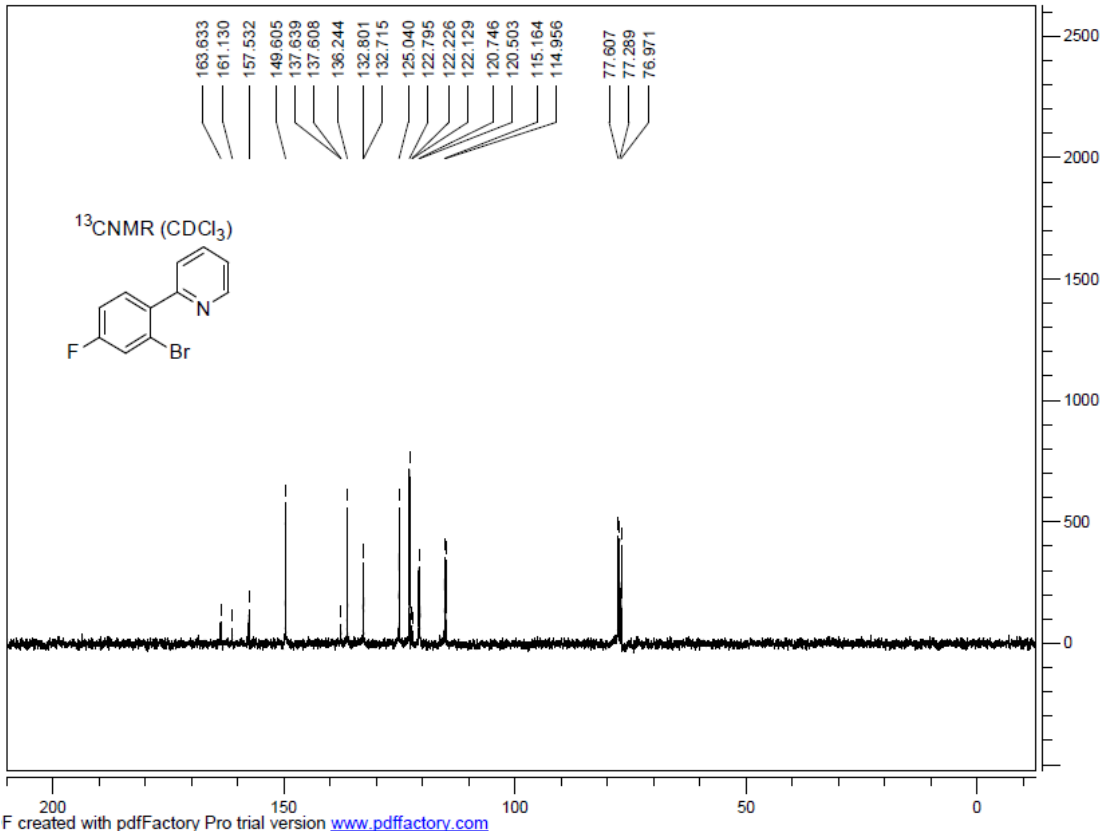
NMR spectra of compound **5b**



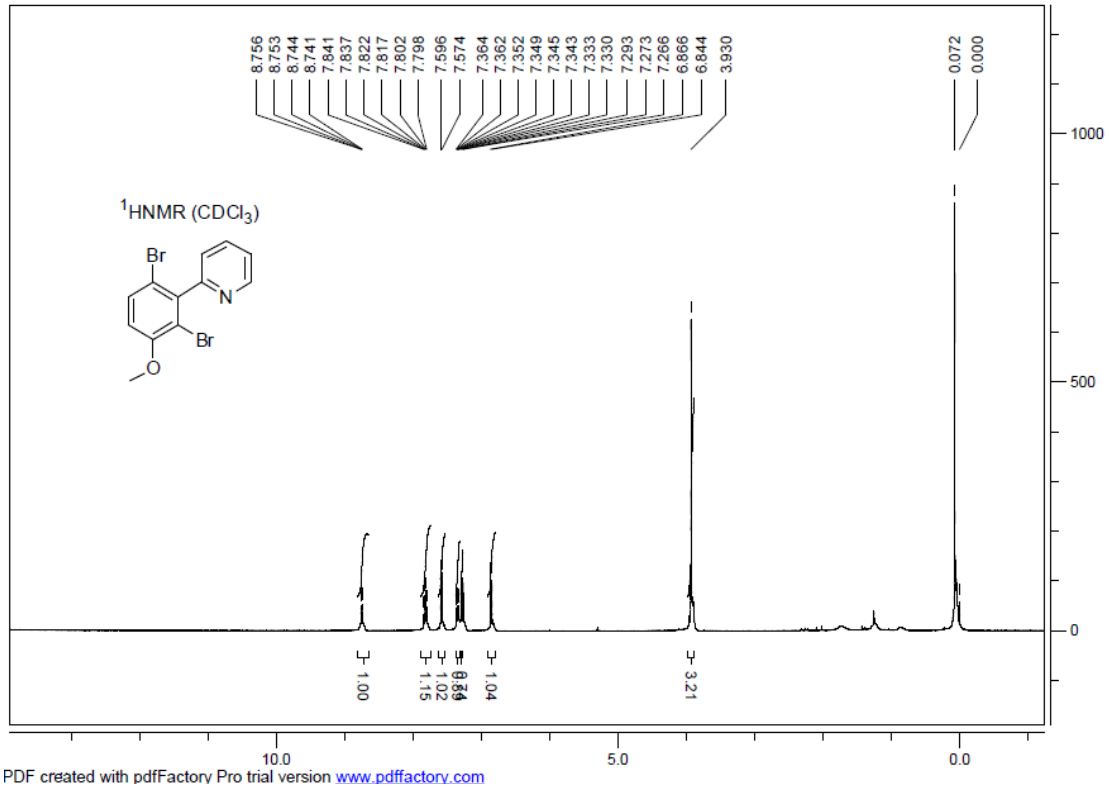


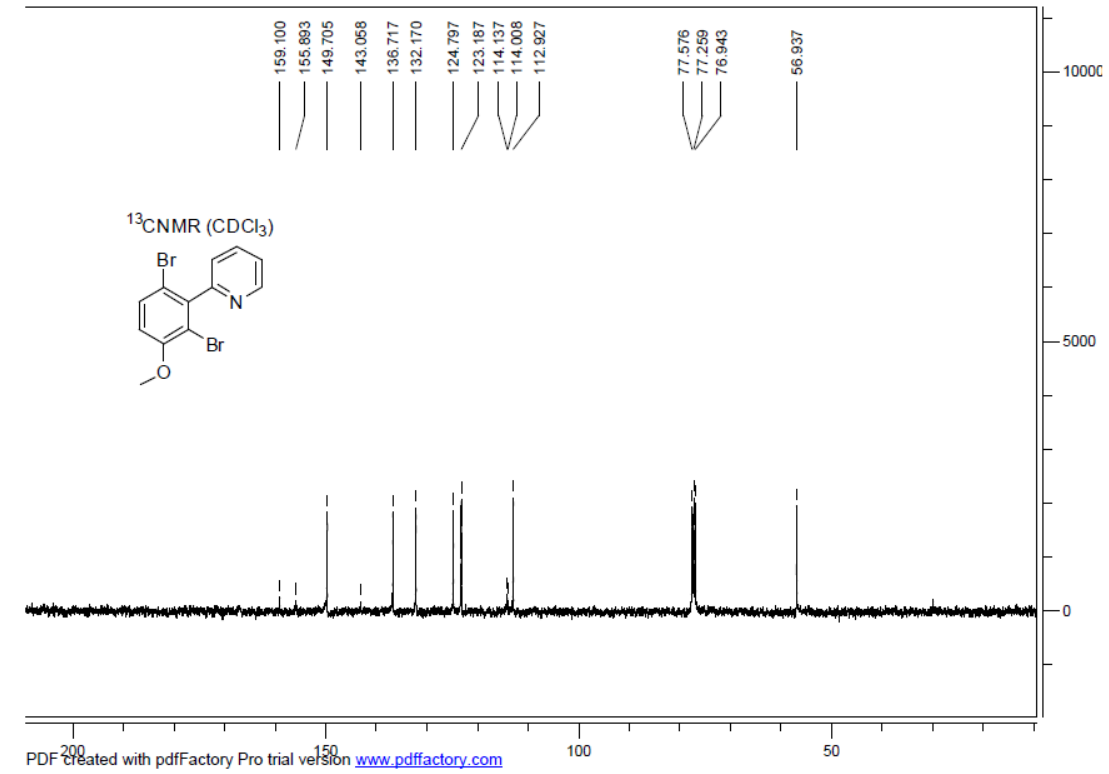
NMR spectra of compound **4b**



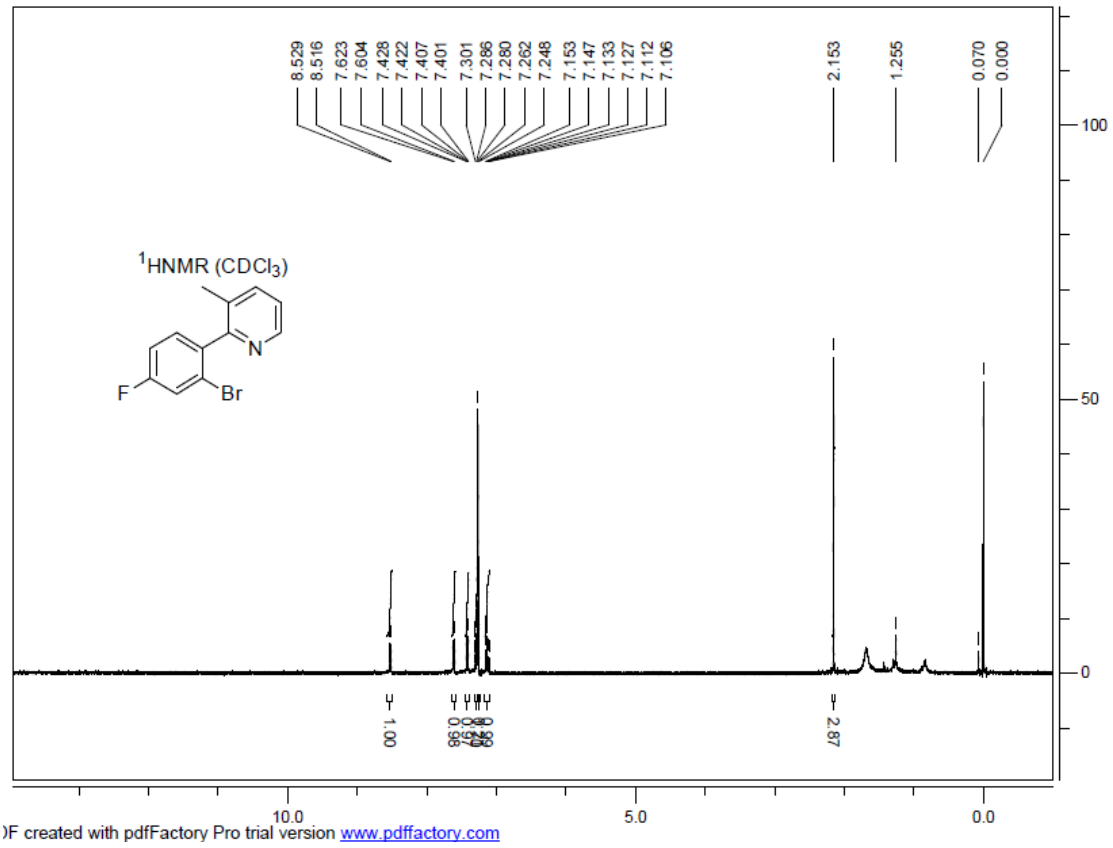


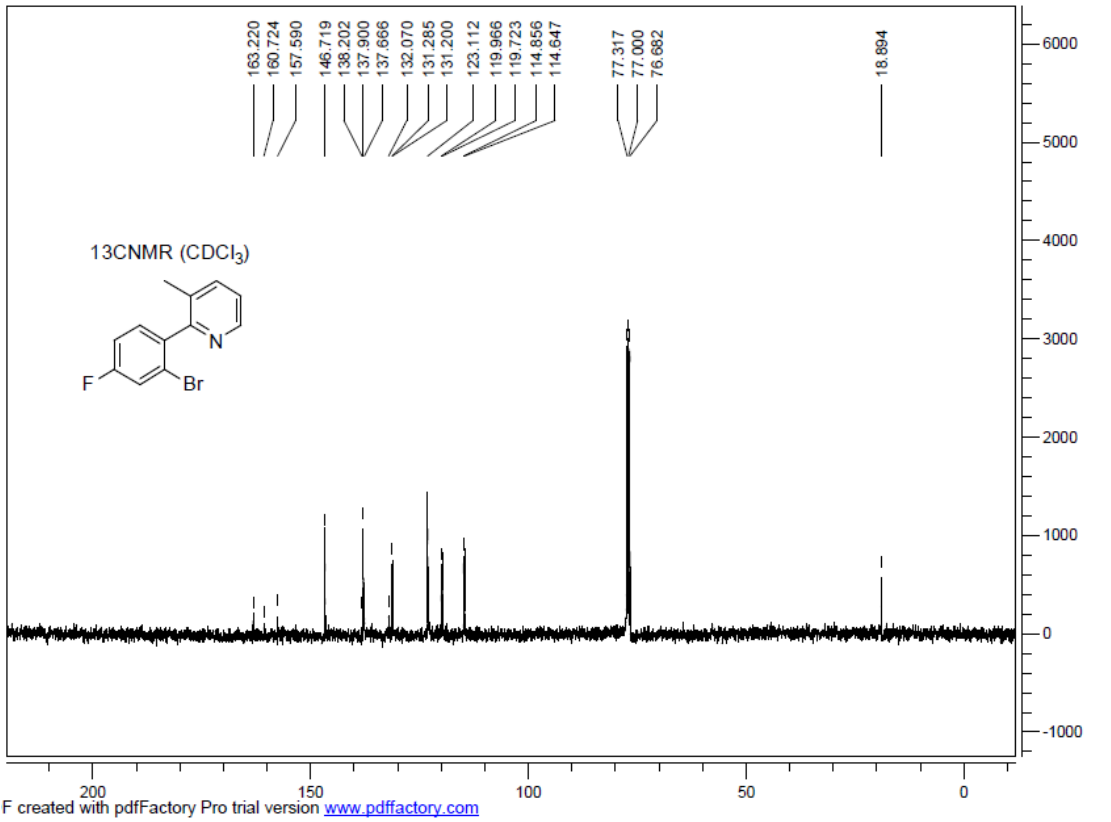
NMR spectra of compound **5i**





NMR spectra of compound **4m**





NMR spectra of compound **4o**