Supporting Information

Copper-Catalyzed Conversion of Aryl and Heteroaryl Bromides into the Corresponding Chlorides

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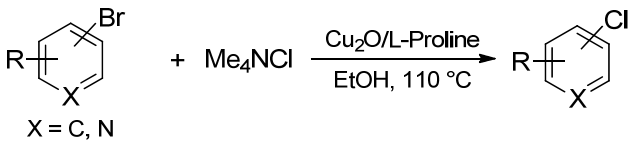
1. General Information

Solvents were dried and degassed before use by standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or a Bruker Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (δ) from TMS, and the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. IR spectrum was recorded on a NEXUS FT-IR spectrometer. High resolution mass spectrum was recorded on a Q-TOF mass spectrometry. GC analysis was performed on an Agilent Technologies T820A GC system. The products were separated on a 30 m length by 0.320 mm id, HP-5. Nitrogen was employed as the carrier gas, with a constant column flow of 0.8 mL/min. The injector temperature was held constant at 250 ºC. The GC oven temperature program was as follows: start from 60 ºC, ramp 20 ºC/min to 140 ºC, ramp 5 ºC/min to 180 ºC, and then ramp 25 ºC/min to 300 ºC, hold for 3 min. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light or iodoplatinate reagent. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh). The starting materials **1a**–**1p** and **3a**–**3g** are commercially available.

2. General Procedure for Aryl and Heteroaryl Bromide-Chloride Exchange Reaction

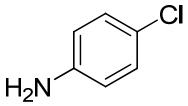
A Schlenk tube was charged with Cu_2O (7.2 mg, 10 mol%), L-proline (11.5 mg, 20 mol%), aryl (or heteroaryl) bromide (**1** or **3**, 0.50 mmol), tetramethylammonium chloride (Me_4NCl) (110 mg, 1.00 mmol), and EtOH (2.0 mL) under nitrogen atmosphere. The Schlenk tube was sealed with a teflon valve, and then the reaction mixture was stirred at 110 °C for a period (the reaction progress was monitored by GC analysis). After the reaction was completed, GC yield of high volatile product was determined using an appropriate internal standard (chlorobenzene or 1-chloro-4-methylbenzene) or the solvent was removed under reduced pressure. The residue obtained was purified via silica gel chromatography (eluent: petroleum ether/ethyl acetate = 10/1) to afford aryl chlorides **2a**–2**p** or heteroaryl chlorides **4a**–**4g**.



Scheme S1. Cu(I)-Catalyzed Aryl and Heteroaryl Bromide-Chloride Exchange Reaction.

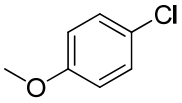
3. Characterization Data

4-Chloroaniline (2c)[1]



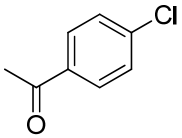
Yield: 94%, 60.0 mg, pale yellow solid. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7. 09 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 8.6 Hz, 2H), 3.64 (bs, 2H).

1-Chloro-4-methoxybenzene (2d)[2]



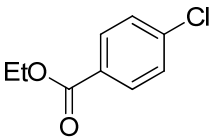
Yield: 80%, 57.0 mg, colorless oil. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.24 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H).

1-(4-Chlorophenyl)ethanone (2e)[2]



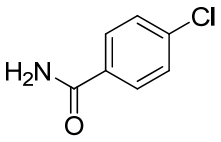
Yield: 86%, 66.5 mg, colorless oil. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.90 (d, J = 8.6 Hz, 2H), 7.44 (dd, J = 8.6 Hz, 2H). 2.59 (s, 3H).

Ethyl 4-chlorobenzoate (2f)[3]



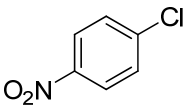
Yield: 86%, 79.4 mg, colorless oil. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 4.37 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H).

4-Chlorobenzamide (2g)[2]



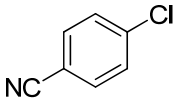
Yield: 98%, 76.2 mg, colorless crystal. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 5.95 (bs, 2H).

1-Chloro-4-nitrobenzene (2h)[3]



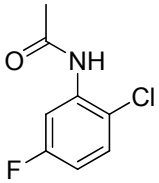
Yield: 88%, 69 mg, white solid. ^{1}H NMR (400 MHz, CDC1$_3$) δ 8.19 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H).

4-Chlorobenzonitrile (2i)[4]



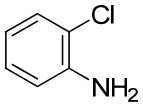
Yield: 65%, 44.7 mg, white solid. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.62–7.59 (m, 2H), 7.49-7.46 (m, 2H).

***N*-(2-chloro-4-fluorophenyl)acetamide (2m)[5]**



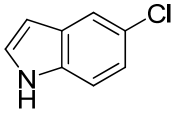
Yield: 92%, 86.3 mg, white solid, mp. 76–78 °C. ^{1}H NMR (400 MHz, CDC1$_3$) δ 8.23–8.20 (m, 1H), 7.63 (bs, 1H), 7.10 (dd, J = 8.0, 2.8 Hz, 1H), 7.00−6.95 (m, 1H), 2.22 (s, 3H).

2-Chloroaniline (2n)[6]



Yield: 97%, 62 mg, light yellow oil. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.20 (dd, J = 7.9, 1.1 Hz, 1H), 7.02−6.98 (m, 1H), 6.67−6.61 (m, 2H), 3.97 (bs, 2H).

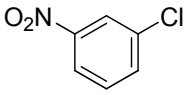
5-Chloroindole (2o)[7]



Yield: 98%, 74.3 mg, white solid. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.92 (bs ,1H), 7.50 (d, J =

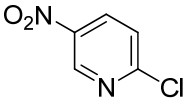
1.2 Hz, 1H), 7.12−7.02 (m, 3H), 6.37−6.36 (m, 1H).

1-Chloro-3-nitrobenzene (2p)[2]



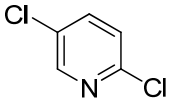
Yield: 93%, 73.3 mg, pale yellow crystal. ^{1}H NMR (400 MHz, CDC1$_3$) δ 8.24 (dd, J = 2.0, 2.0 Hz, 1H), 8.15−8.12 (m, 1H), 7.70−7.67 (m, 1H), 7.51 (dd, J = 8.2, 8.2 Hz,, 1H).

2 -Chloro-5-nitropyridine (4b)[8]



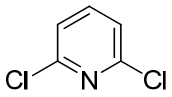
Yield: 52%, 41.2 mg, colorless crystal. ^{1}H NMR (400 MHz, CDC1$_3$) δ 9.25 (d, J = 2.8 Hz, 1H), 8.45 (dd, J = 8.7, 2.8 Hz ,1H), 7.55 (d, J = 8.7 Hz, 1H).

2,5-Dichloropyridine (4c)[9]



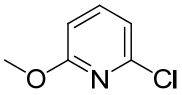
Yield: 81%, 59.9 mg, colorless crystal. ^{1}H NMR (400 MHz, CDC1$_3$) δ 8.28 (d, J = 2.5 Hz, 1H), 7.56 (dd, J = 8.5, 2.5 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H).

2,6-Dichloropyridine (4d)[9]



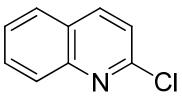
Yield: 75%, 55.5 mg, colorless crystal. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.63 (dd, J = 8.0, 8.0 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H).

2-Chloro-6-methoxypyridine (4e)[10]



Yield: 70%. 50.1 mg, colorless oil. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.52–7.48 (m, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 3.93 (d, J = 1.2 Hz, 3H).

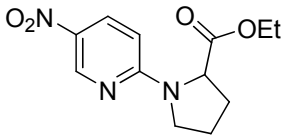
2-Chloroquinoline (4g)[11]



Yield: 98%, 80.2 mg, white solid. ^{1}H NMR (400 MHz, CDC1$_3$) δ 7.89 (dd, J = 14.0, 8.6 Hz,

2H), 7.64–7.56 (m, 2H), 7.39 (dd, J = 8.0, 7.0 Hz, 1H), 7.20 (d, J = 8.6 Hz,1H).

Ethyl 1-(5-nitropyridin-2-yl)pyrrolidine-2-carboxylate (5)



Yield: 11%, 14.6 mg, yellow oil. ^{1}H NMR (400 MHz, CDC1$_3$) δ 8.93 (s, 1H), 8.14 (dd, J = 9.3, 2.6 Hz, 1H), 6.32 (d, J = 7.5 Hz, 1H), 4.63 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.63 –3.49 (m, 2H), 2.30–2.26 (m, 2H), 2.12–2.05 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDC1$_3$) δ 172.6, 158.6, 146.6, 135.6, 132.8, 105.5, 61.4, 60.4, 47.9, 30.1, 24.2, 14.3. IR(neat) 3081, 2980, 2876, 2604, 1741, 1598, 1573, 1517, 1493, 1464, 1430, 1372, 1333, 1293, 1205, 1182, 1117, 1095, 1051, 1027, 998, 916, 885, 818, 766, 724, 709, 546 cm^{-1}. HRMS(EI) calsd for $C_{12}H_{15}N_3O_4$: 288.0960 $[M+Na]^+$; found: 288.0959.

4. References

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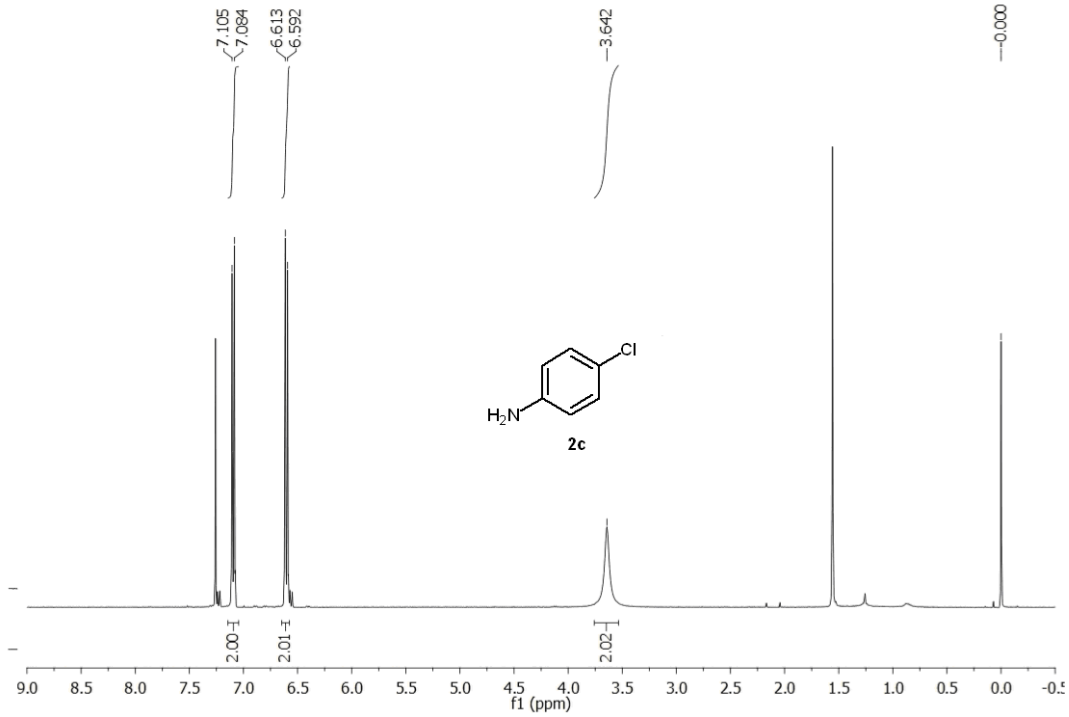
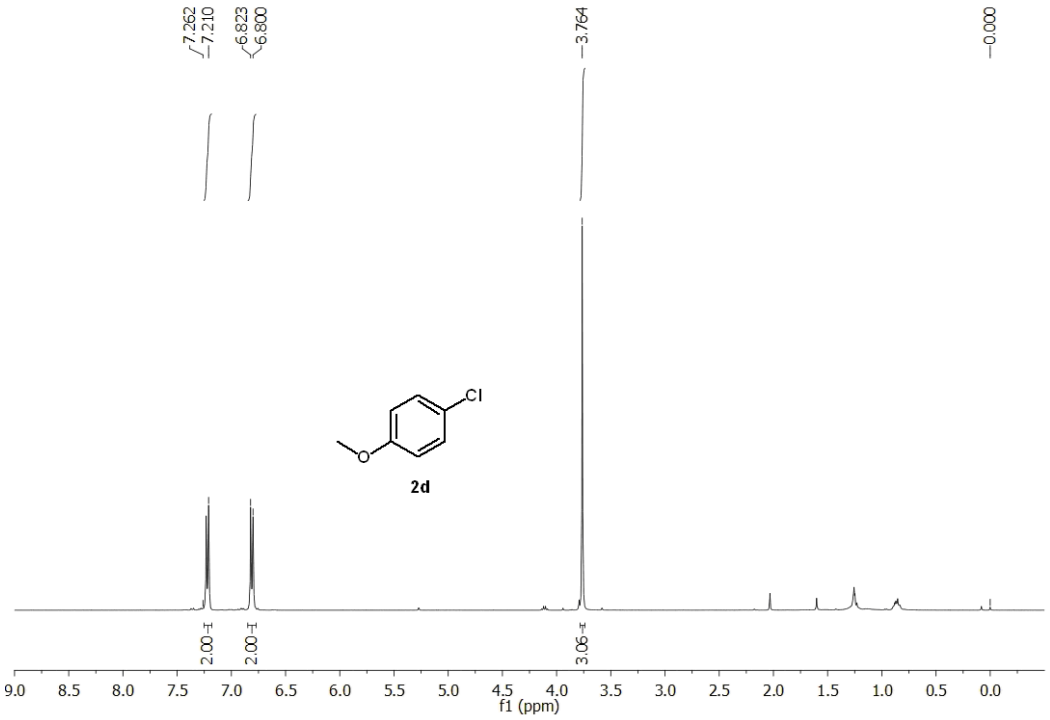
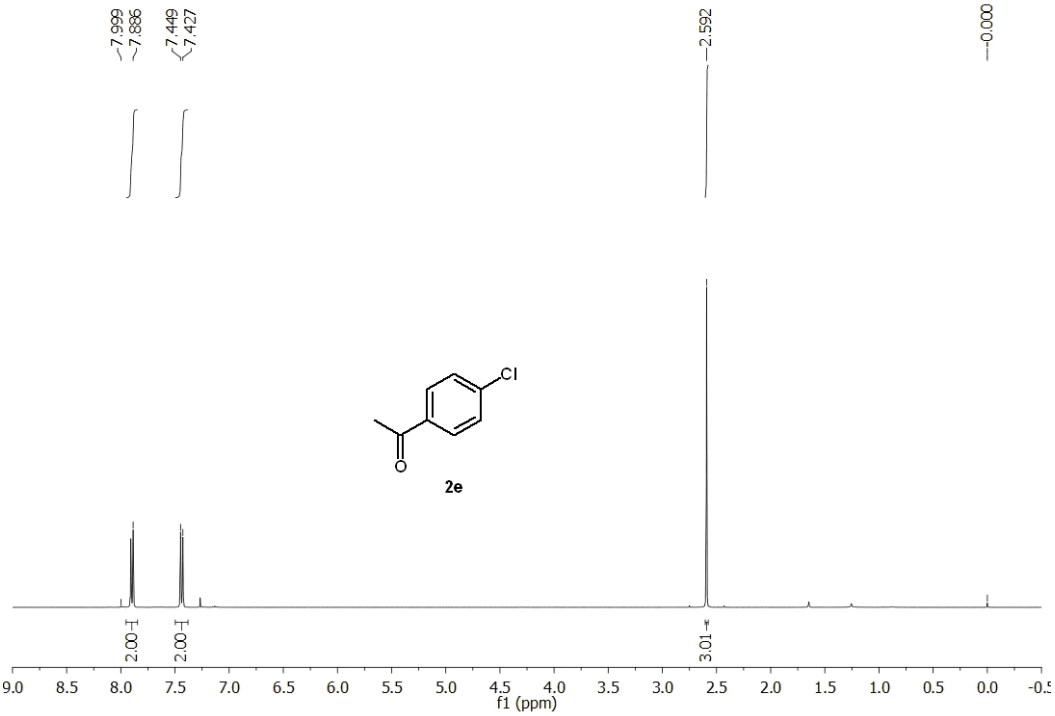
5. Copies of ^{1}H and ^{13}C NMR Spectra



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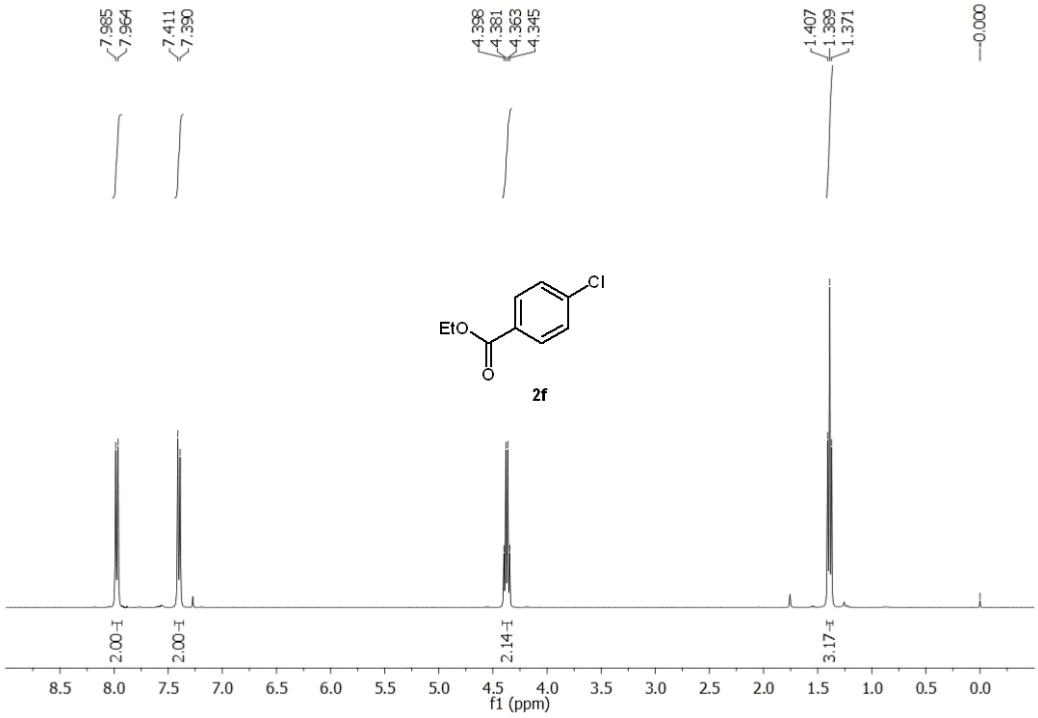
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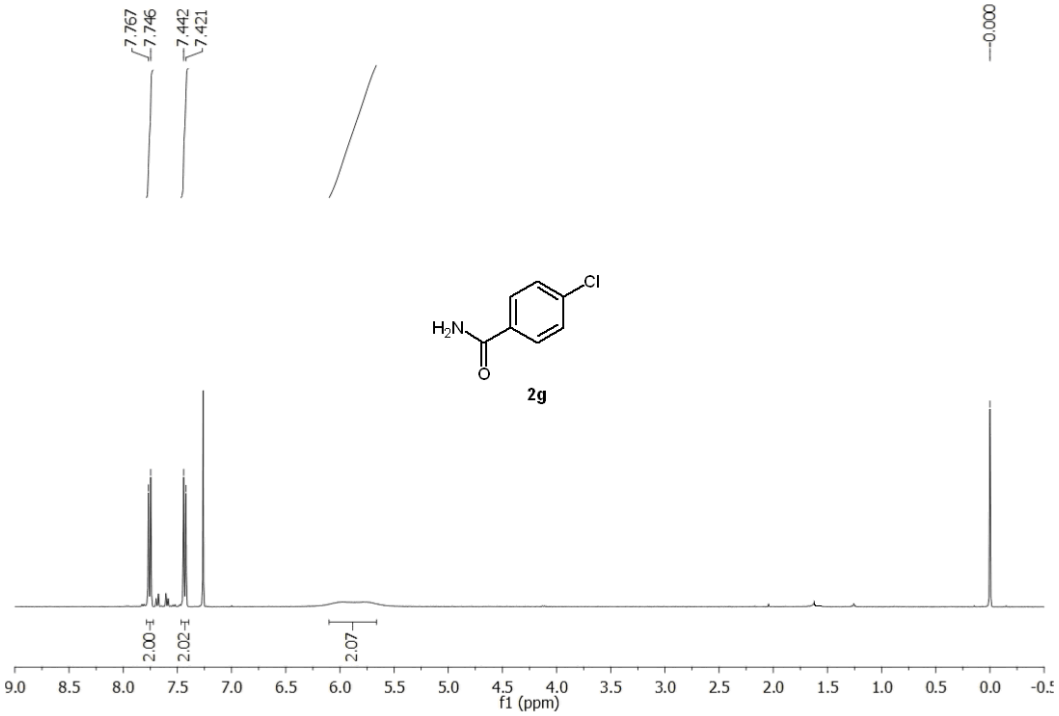
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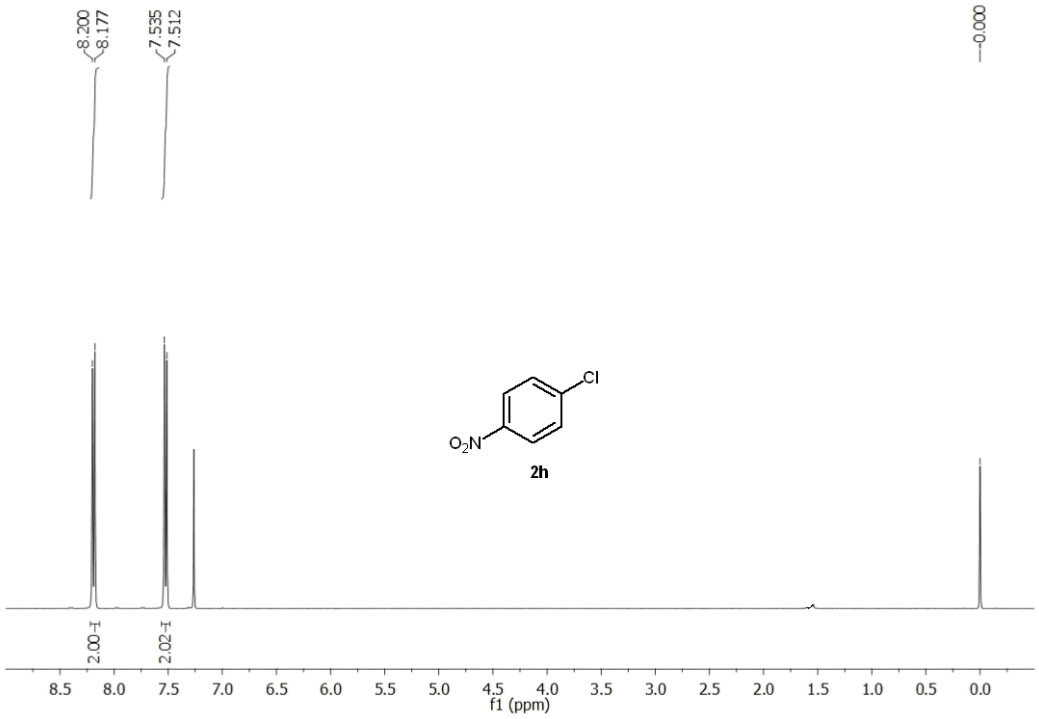
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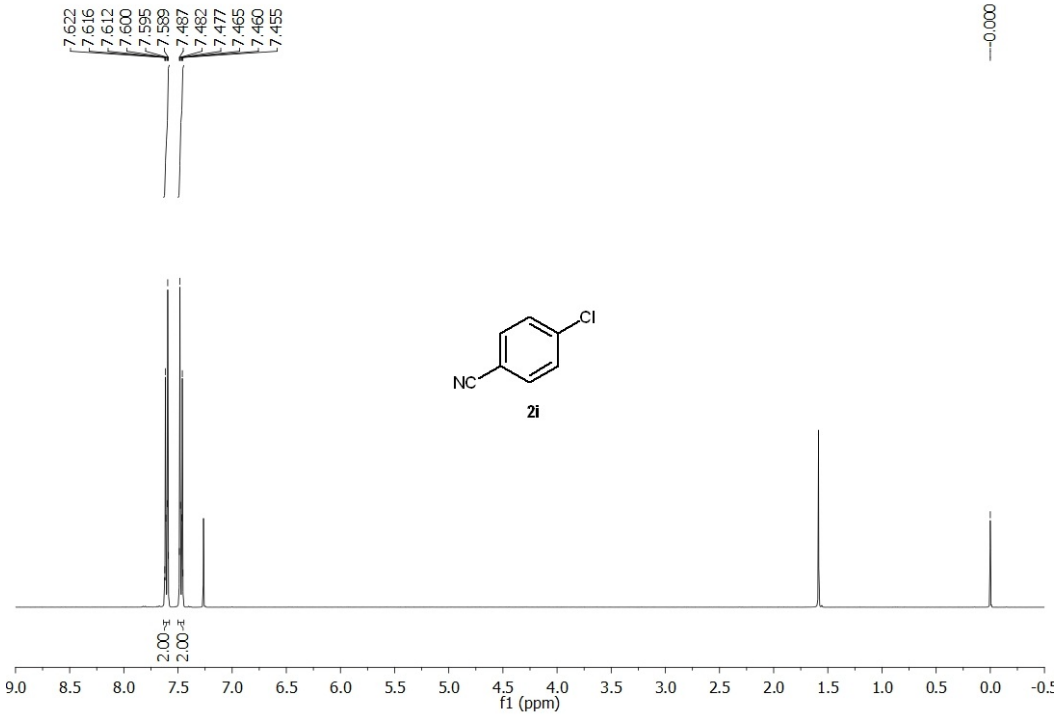
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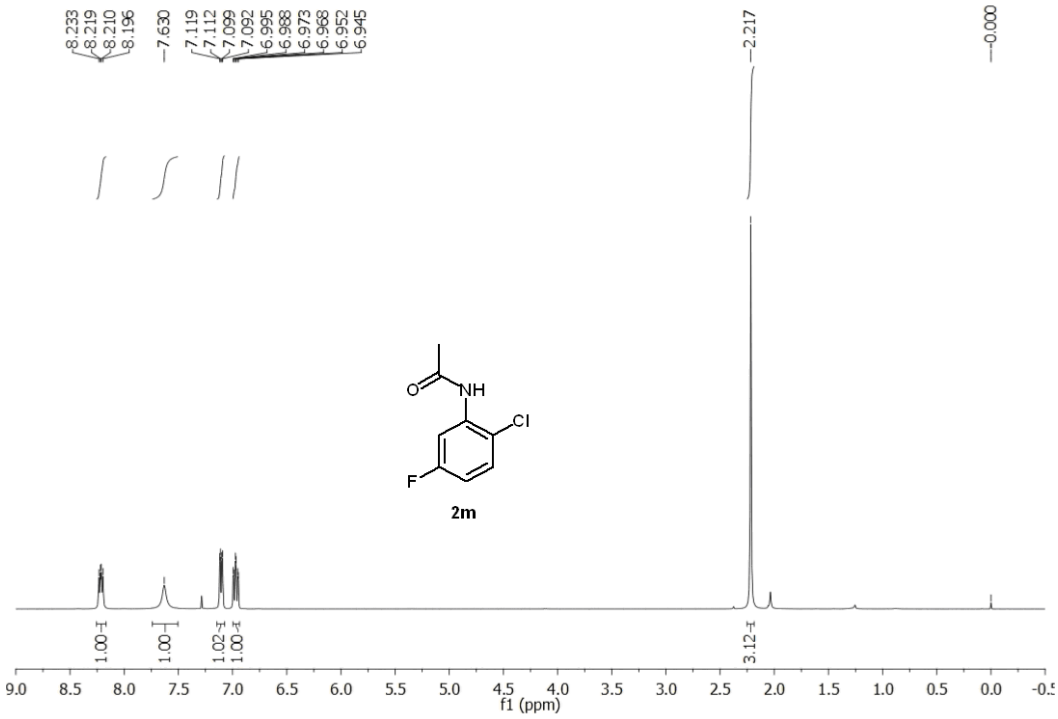
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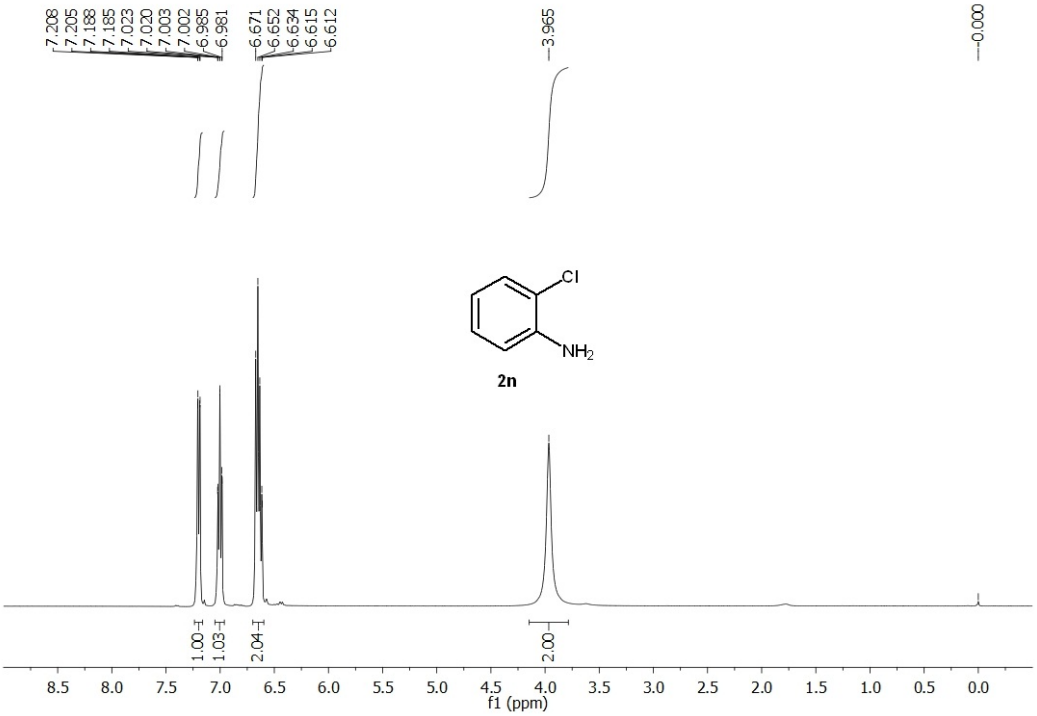
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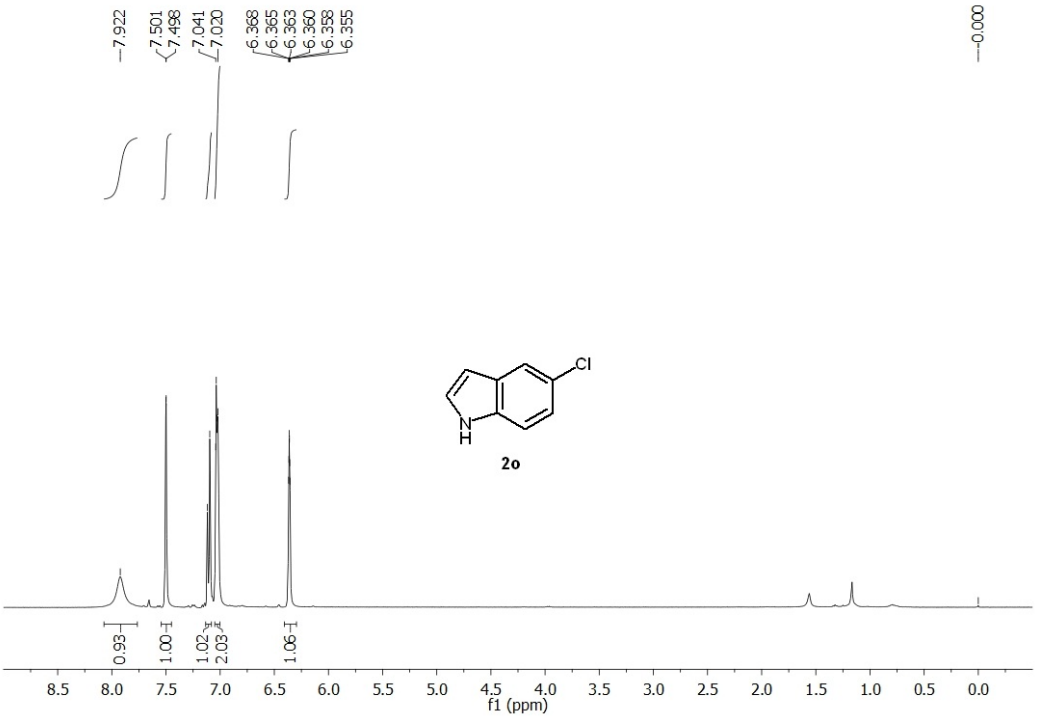
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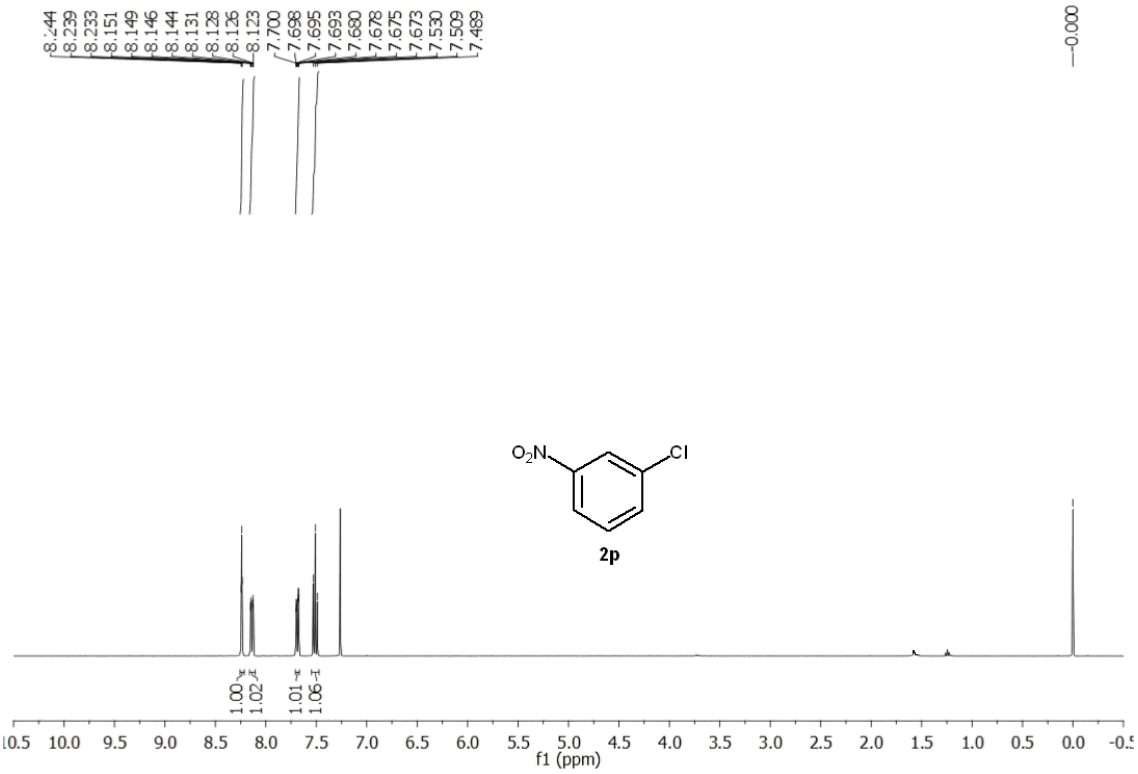
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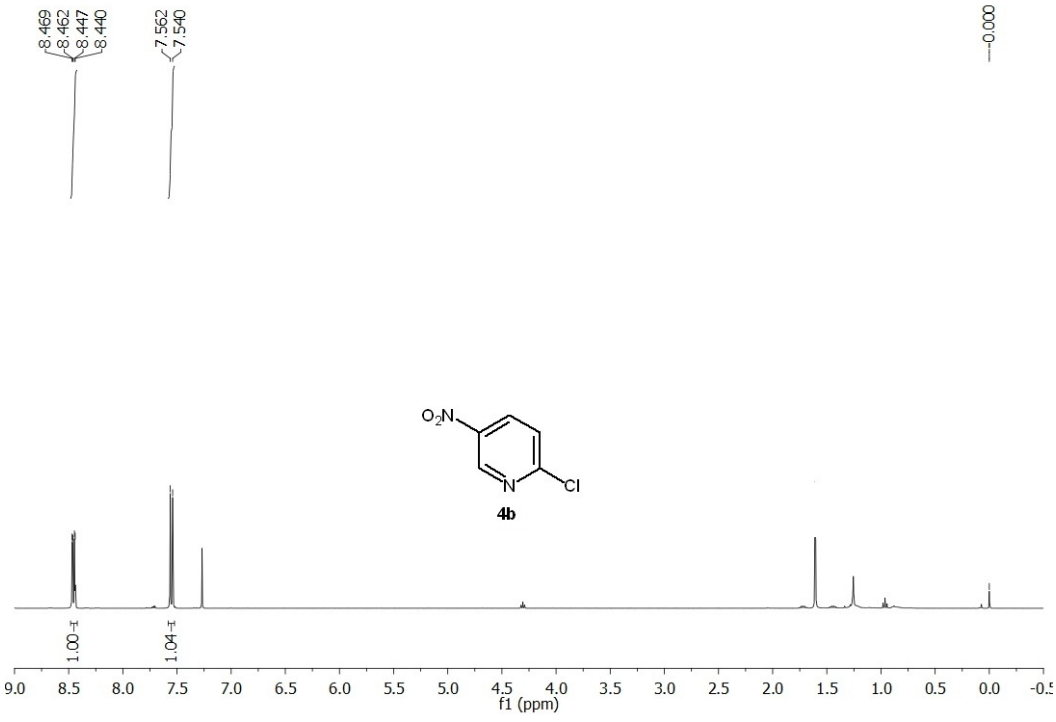
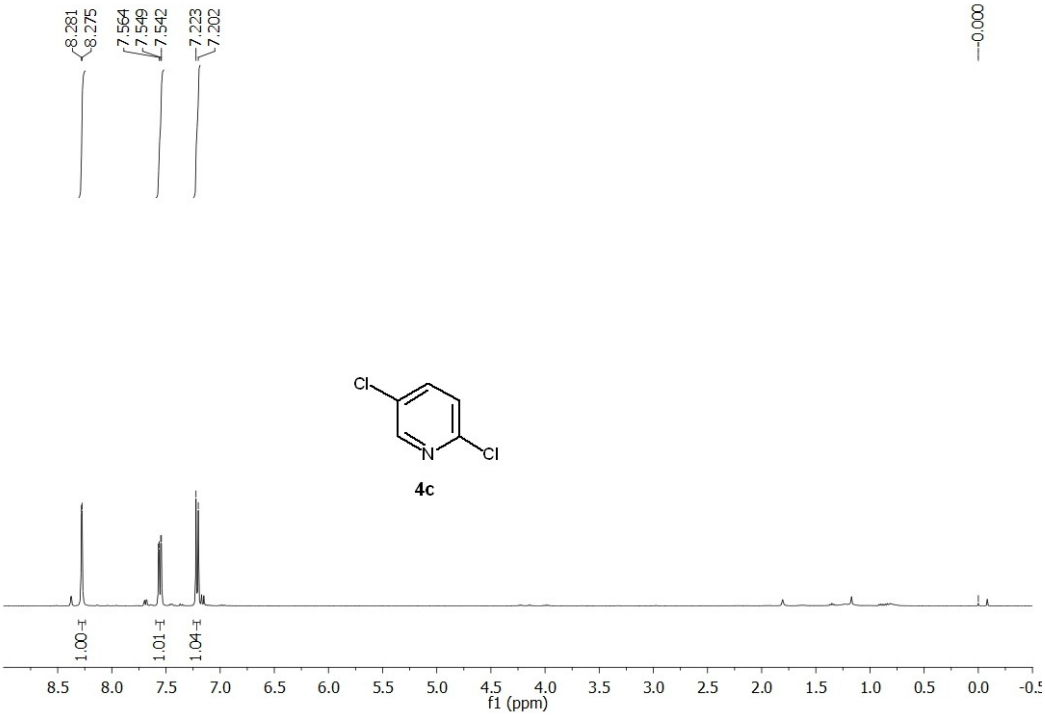
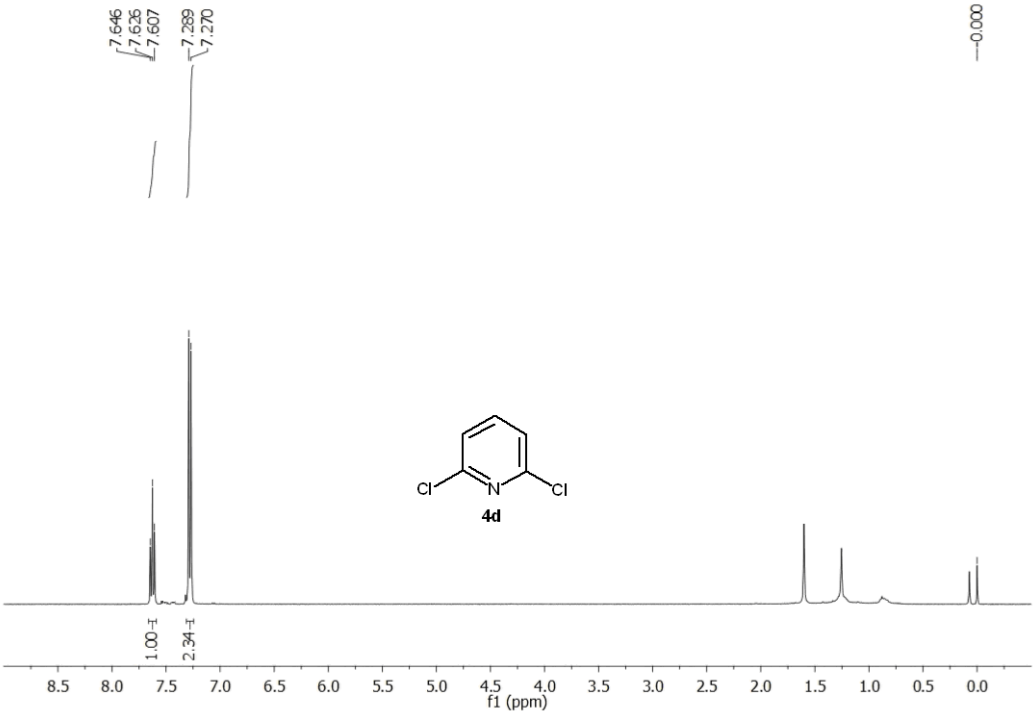
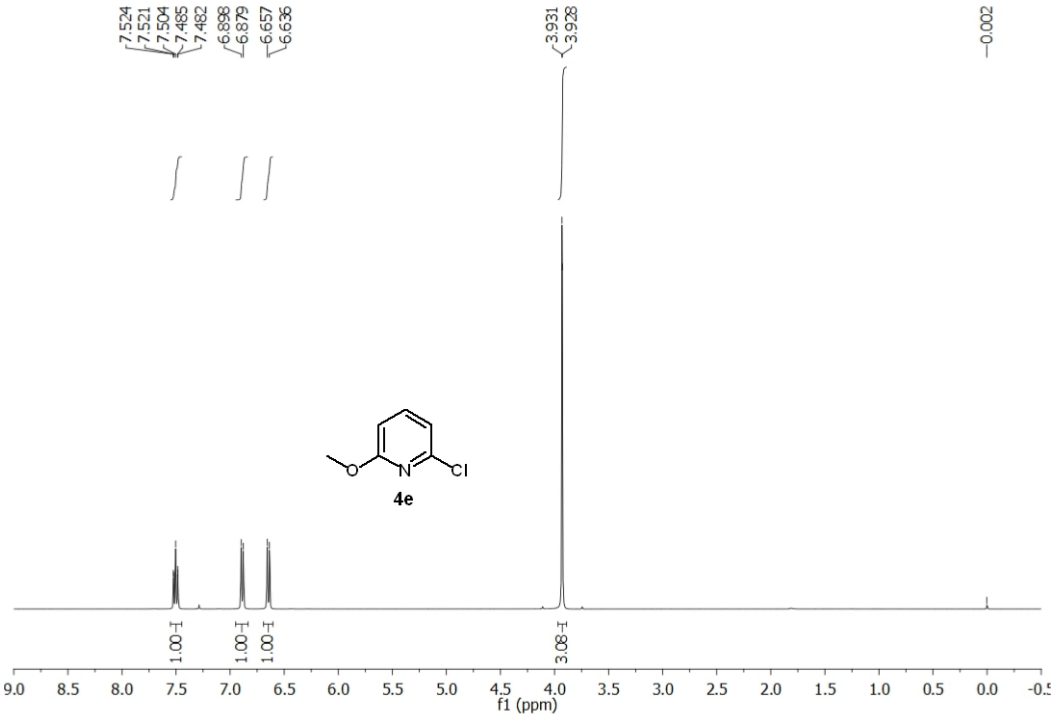
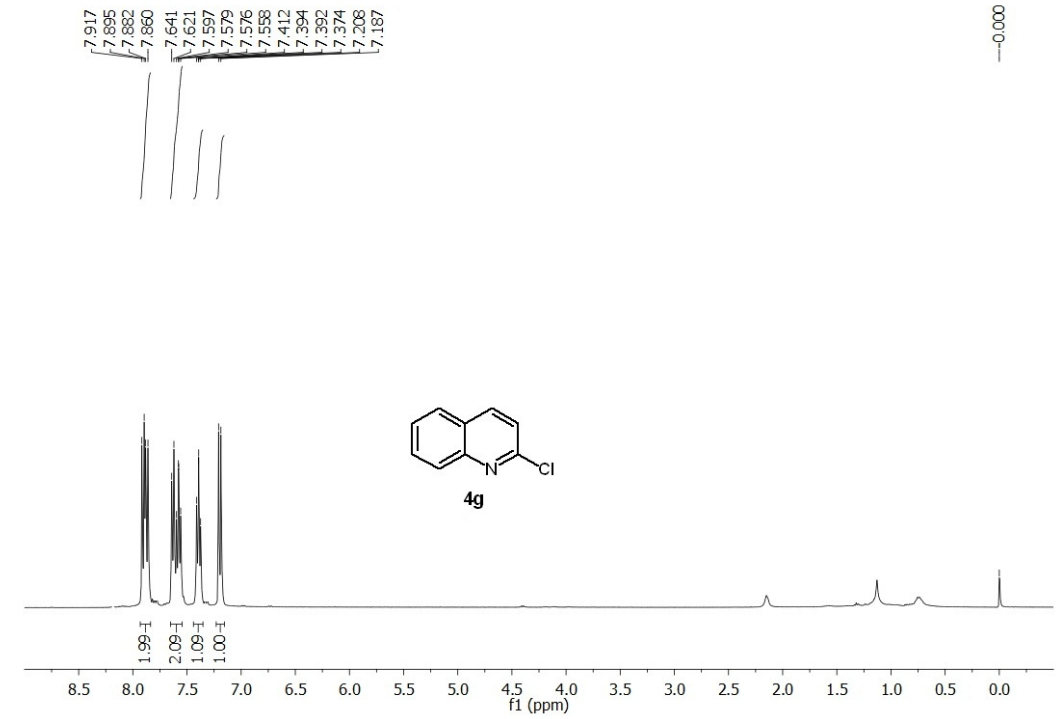
0.000
O2N
Cl
2p
1.00
1.02
1.01
1.06
f1 (ppm)

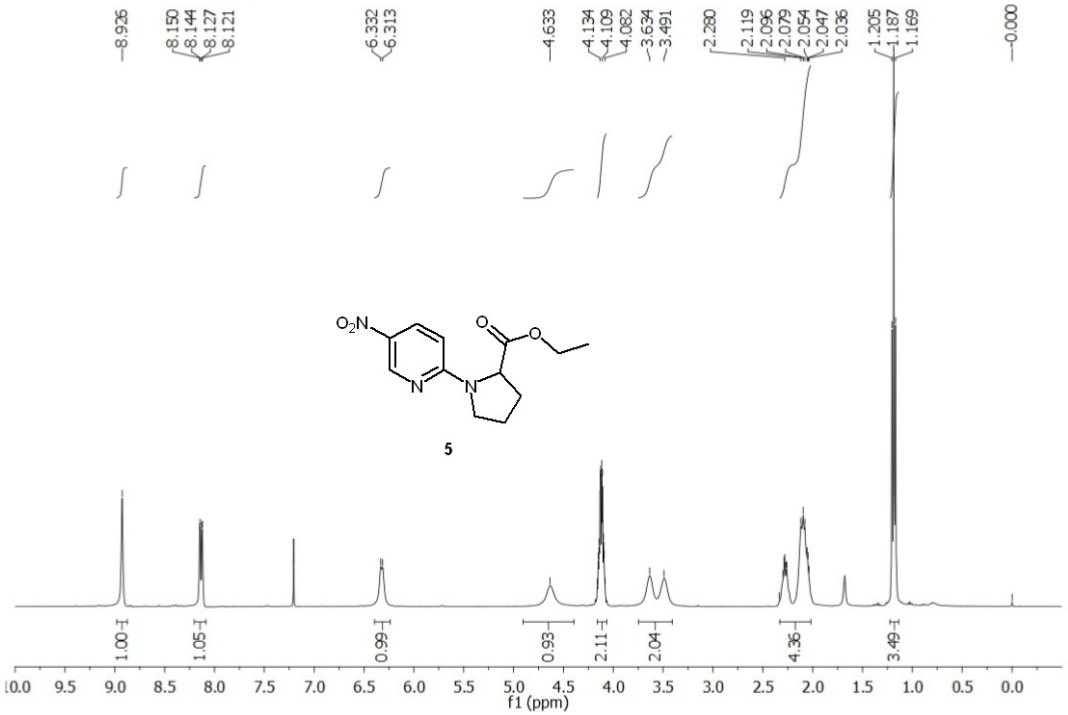

8.469
8.462
8.447
8.440
7.562
7.540
0.000
O2N
N
Cl
4b
1.00
1.04
f1 (ppm)


8.281
8.275
7.564
7.549
7.542
7.223
7.202
0.000
Cl
N
Cl
4c
1.00
1.01
1.04
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)

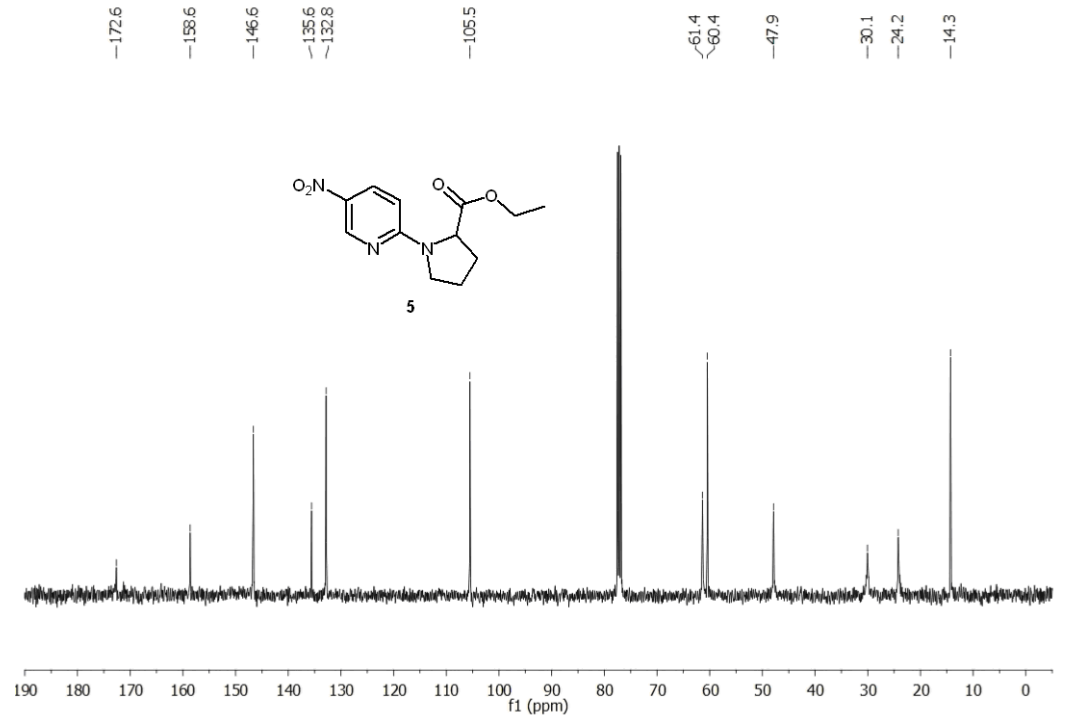

7.646
7.626
7.607
7.289
7.270
0.000
Cl
N
Cl
4d
1.00
2.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.524
7.521
7.504
7.485
7.482
6.898
6.879
6.657
6.636
3.931
3.928
0.002
4e
1.00
1.00
1.00
3.08
f1 (ppm)


7.917
7.895
7.882
7.860
7.641
7.621
7.597
7.579
7.576
7.558
7.412
7.394
7.392
7.374
7.208
7.187
0.000
4g
1.99
2.09
1.09
1.00
f1 (ppm)


8.926
8.150
8.144
8.127
8.121
6.332
6.313
4.633
4.134
4.109
4.082
3.634
3.491
2.280
2.119
2.096
2.079
2.054
2.047
2.036
1.205
1.187
1.169
0.000
1.00
1.05
0.99
0.93
2.11
2.04
4.36
3.49
f1 (ppm)

5


172.6
158.6
146.6
135.6
132.8
105.5
61.4
60.4
47.9
30.1
24.2
14.3
f1 (ppm)

5