Electronic Supplementary Information (ESI) for

Synthesis of *N*-Aryl Substituted, Five- and Six- membered Azacycles using Aluminum-amide complexes

Balaji L. Korbad and Sang-Hyeup Lee*

Department of Life Chemistry, Catholic University of Daegu, Gyeongsan-si, Gyeongbuk 712-702, South Korea

E-mail: leeshh@cu.ac.kr

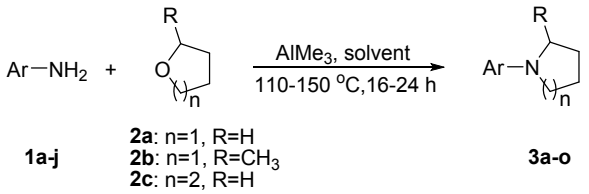
Contents

General information

All chemicals were obtained from commercial supplier and used without further purification. Anhydrous grade tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, toluene, and xylene were purchased and used out of the bottle without further purification. ***Caution!*** *Trimethylaluminum is moisture sensitive and pyrophoric, and should be handled with great care. All transfers, storage, and reactions must be performed under an anhydrous atmosphere of pure nitrogen or argon. Since methane is liberated during the reaction, the authors recommend that the reactions should be carried out using the sealed tube and behind a blast shield.* Thin layer chromatography (TLC) was carried out using Merck 60 F_{254} plates with a 0.25 mm thickness. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh) using ethyl acetate/hexanes as eluent. ^{1}H NMR (400 MHz and 600 MHz) and ^{13}C NMR (100 MHz and 150 MHz) spectra were recorded using Varian INOVA-399 (400 MHz) and Agilent VNMR (600 MHz) calibrated using tetramethylsilane as an internal reference. High resolution mass data were obtained from Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer.

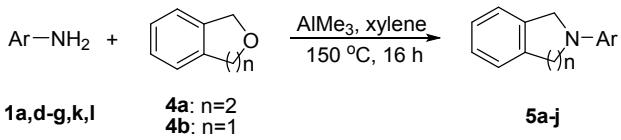
General experimental procedure:

Experimental procedure for the synthesis of azacycloalkanes 3 (Table 2)



***N*-phenylpyrrolidine (3a, entry 1):** Trimethylaluminum (0.6 mL, 2 M solution in toluene, 1.2 mmol) was added to a stirred solution of aniline (**1a**, 0.093 g, 1.0 mmol) in toluene (3 mL) at 0 °C under argon. After being stirred for 10 minute at 0 °C the resulting solution was warmed to room temperature, and stirred for 30 minutes. Then tetrahydrofuran **2a** (0.8 mL, 10.0 mmol) was added drop wise to the reaction mixture. The glass tube was then closed tightly with Teflon cap, and the resulting reaction mixture was heated to 110 °C for 16 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled to room temperature. Then the reaction was quenched by adding a mixture of THF:water (9:1, 2 mL) slowly under argon and the resulting suspension was stirred for an additional 10 minutes. Then it was filtered through the Celite@ and further eluted with THF (5 mL). The combined filtrate was concentrated under reduced pressure and purification of the crude product by column chromatography (hexane:ethyl acetate = 30:1) gave **3a** (106 mg, 0.72 mmol, 72 %) as light yellow oil.

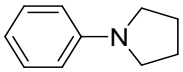
Experimental procedure for the synthesis of tetrahydroisoquinolines and isoindolines 5 (Table 3)



2-phenyl-1,2,3,4-tetrahydroisoquinoline (5a, entry 1): Trimethylaluminum (0.75 mL, 2 M solution in toluene, 1.5 mmol) was added to a stirred solution of aniline (**1a**, 0.186 g, 2.0 mmol) in xylene (4 mL) at 0 °C under argon. After being stirred for 10 minute at 0 °C the resulting solution was warmed to room temperature, and stirred for 30 minutes. Then isochroman **4a** (0.134 g, 1.0 mmol) was added to the reaction mixture at room temperature. Then glass tube was then closed tightly with Teflon cap, and the resulting reaction mixture was heated to 150 °C (bath temperature) for 16 h. The progress of the reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled to room temperature. Then the reaction was quenched by adding a mixture of THF:water (9:1, 3 mL) slowly under argon and the resulting suspension was stirred for an additional 10 minutes. Then it was filtered through the Celite@ and further eluted with THF (10 mL). The combined filtrate was concentrated under reduced pressure and purification of the crude product by column chromatography (hexane:ethyl acetate, 20:1) gave **5a** (136 mg, 0.65 mmol, 65 %) as colorless oil.

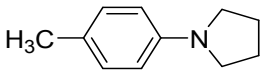
Characterization data of products:

***N*-Phenylpyrrolidine**[1] (**3a**):



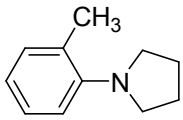
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22-2.12 (m, 4H), 3.52-3.39 (m, 4H), 6.77 (m, 2H), 6.87 (m, 1H), 7.39-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9, 47.9, 112.1, 115.8, 129.5, 148.4. HRMS (EI+): *m/z* calcd for $C_{10}H_{13}N$ $[M-H]^+$, 146.0970, found 146.0973 ($C_{10}H_{12}N^+$).

***N*-*p*-Tolylpyrrolidine**[2] (**3b**):



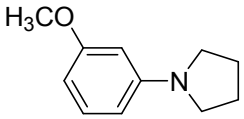
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08-2.19 (m, 4H), 2.44 (s, 3H), 3.34-3.47 (m, 4H), 6.67 (d, 2H, *J* = 8.4 MHz), 7.22 (d, 2H, *J* = 8.4 MHz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 25.8, 48.2, 112.2, 124.7, 130.0, 146.5. HRMS (EI+): *m/z* calcd for $C_{11}H_{15}N$ $[M-H]^+$, 160.1126, found 160.1126 ($C_{11}H_{14}N^+$).

***N*-*o*-Tolylpyrrolidine**[2] (**3c**):



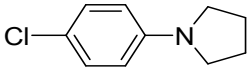
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.00-2.12 (m, 4H), 2.47 (s, 3H), 3.24-3.38 (m, 4H), 6.93-7.06 (m, 2H), 7.20-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 25.3, 51.3, 116.1, 120.6, 126.6, 129.0, 132.0, 149.7. HRMS (EI+): *m/z* calcd for $C_{11}H_{15}N$ $[M-H]^+$, 160.1126, found 160.1124 ($C_{11}H_{14}N^+$).

***N*-(3-Methoxyphenyl)pyrrolidine**[3] (**3d**):



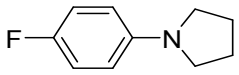
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01-2.18 (m, 4H), 3.32-3.45 (m, 4H), 3.89 (s, 3H), 6.22-6.26 (m, 1H), 6.29-6.35 (m, 1H), 6.36-6.39 (m, 1H), 7.21-7.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.8, 47.9, 55.3, 98.2, 100.8, 105.3, 130.1, 149.6, 161.1. HRMS (EI+): *m/z* calcd for $C_{11}H_{15}ON$ $[M-H]^+$, 176.1075, found 176.1072 ($C_{11}H_{14}ON^+$).

***N*-(4-Chlorophenyl) pyrrolidine**[3] (**3e**):



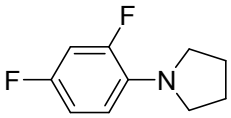
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85-2.09 (m, 4H), 3.19-3.32 (m, 4H), 6.47 (d, 2H, J = 7.2 MHz), 7.17 (d, 2H, J = 7.2 MHz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 47.9, 112.8, 120.2, 129.0, 146.7; HRMS (EI+): *m/z* calcd for $C_{10}H_{12}ClN$ $[M-H]^+$, 180.0580, found 180.0580 ($C_{10}H_{11}ClN^+$).

***N*-(4-Fluorophenyl)pyrrolidine** (**3f**):



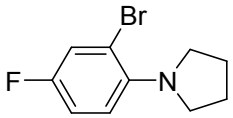
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85-2.10 (m, 4H), 3.19-3.33 (m, 4H), 6.47-6.55 (m, 2H), 6.95-7.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 48.3, 112.3 (d, J_{CF} = 7.4 Hz), 115.5 (d, J_{CF} = 21.6 Hz), 145.1(d, J_{CF} = 5.2 Hz), 155.1 (d, J_{CF} = 231.3 Hz). HRMS (EI+): *m/z* calcd for $C_{10}H_{12}FN$ $[M-H]^+$, 164.0876, found 164.0874 ($C_{10}H_{11}FN^+$).

***N*-(2,4-Difluorophenyl)pyrrolidine** (**3g**):



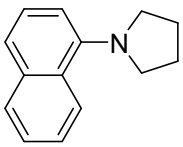
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.89-1.97 (m, 4H), 3.20-3.34 (m, 4H), 6.57-6.62 (m, 1H), 6.69-6.79 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 24.9 (d, J_{CF} = 1.7 Hz), 49.9 (d, J_{CF} = 4.6 Hz), 104.4 (dd, J_{CF} = 3.5, 26.0 Hz), 110.4 (dd, J_{CF} = 3.5, 21.9 Hz), 115.2 (dd, J_{CF} = 6.9, 9.2 Hz), 134.3 (dd, J_{CF} = 3.5, 10.3 Hz), 151.9 (dd, J_{CF} = 11.4, 243.8 Hz), 154.8 (dd, J_{CF} = 11.4, 236.9 Hz). HRMS (EI+): *m/z* calcd for $C_{10}H_{11}F_2N$ $[M-H]^+$, 182.0781, found 182.0782 ($C_{10}H_{10}F_2N^+$).

***N*-(2-Bromo-4-fluorophenyl)pyrrolidine** (**3h**):



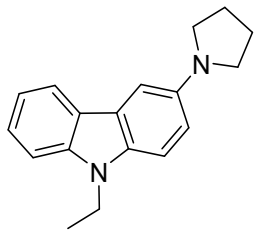
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80-1.99 (m, 4H), 3.09-3.35 (m, 4H), 6.80-6.97 (m, 2H), 7.25-7.32 (m,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 51.7, 114.5 (d, J_{CF} = 21.5 Hz), 115.1 (d, J_{CF} = 8.9 Hz), 118.7 (d, J_{CF} = 8.2 Hz), 121.3 (d, J_{CF} = 24.5 Hz), 145.6 (d, J_{CF} = 1.5 Hz), 157.1 (d, J_{CF} = 242.5 Hz); HRMS (EI+): *m/z* calcd for $C_{10}H_{11}BrFN$ $[M-H]^+$, 241.9981, found 241.9984 ($C_{10}H_{10}BrFN^+$).

***N*-(Naphthalen-1-yl)pyrrolidine**[3] (**3i**):



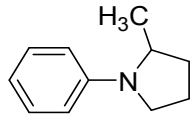
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84-2.00 (m, 4H), 3.22-3.38 (m, 4H), 6.85-6.95 (m, 1H), 7.25-7.33 (m, 1H), 7.34-7.45 (m, 3H), 7.70-7.81 (m, 1H), 8.13-8.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.2, 53.1, 111.9, 121.7, 124.7, 125.3, 126.0, 126.4, 128.7, 128.8, 135.5, 148.2. HRMS (EI+): m/*z* cacld. for $C_{14}H_{15}N$ $[M-H]^+$, 196.1126; found 196.1129 ($C_{14}H_{14}N^+$).

9-Ethyl-3-(pyrrolidin-1-yl)-9H-carbazole (**3j**):



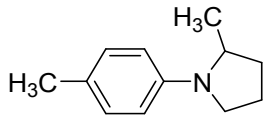
^{1}H NMR (600 MHz, $CDCl_3$): δ 1.39 (t, 3H, *J* = 7.8 Hz), 2.02-2.15 (m, 4H), 3.30-3.55 (m, 4H), 4.31 (q, 2H, *J* = 7.8 Hz), 6.88 (d, 1H, *J* = 8.4 Hz), 7.13-7.20 (m, 1H), 7.26-7.37 (m, 3H), 7.40-7.45 (m, 1H), 8. 06 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.9, 25.4, 37.5, 49.0, 102.5, 108.3, 108.9, 112.7, 117.7, 120.4, 122.9, 123.8, 125.2, 133.1, 140.4, 142.6. HRMS (EI+): m/*z)* cacld. for $C_{18}H_{20}N_2$ $[M-H]^+$, 263.1548; found 263.1551 ($C_{18}H_{19}N_2^+$).

2-Methyl-1-phenylpyrrolidine (**3k**):



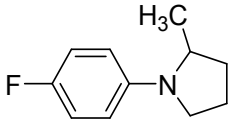
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, 3H, *J* = 6.0 Hz), 1.78-1.89 (m, 1H), 2.02-2.28 (m, 3H), 3.22-3.25 (m, 1H), 3.49-3.58 (m, 1H), 3.95-4.07 (m, 1H), 6.73 (d, 1H, *J* = 8.0 Hz), 6.79 (t, 2H, *J* = 8.0 Hz), 7.02-7.41 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 23.7, 33.5, 48.5, 53.9, 112.1, 115.5, 129.5, 147.5. HRMS (EI+): m/*z* cacld. for $C_{11}H_{15}N$ $[M]^+$, 161.1204; found 161.1207.

2-Methyl-1-(*p*-tolyl)pyrrolidine[4](**3l**)**:**



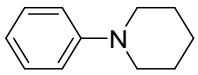
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (d, 3H, *J* = 6.0 Hz), 1.73-1.82 (m, 1H), 1.95-2.23 (m, 3H), 2.32 (s, 3H), 3.15-3.23 (m, 1H), 3.41-3.50 (m, 1H), 3.82-3.95 (m, 1H), 6.58 (d, 2H, *J* = 8.4 Hz), 7.09 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 20.5, 23.6, 33.4, 48.7, 54.0, 112.2, 124.5, 129.9, 145.6. HRMS (EI+): m/*z* cacld. for $C_{12}H_{17}N$ $[M]^+$, 175.1361; found 175.1360.

1-(4-Fluorophenyl)-2-methylpyrrolidine (**3m**):



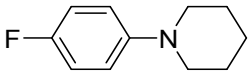
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (d, 3H, J = 6.0 Hz), 1.52-1.59 (m, 1H), 1.78-2.00 (m, 3H), 2.93-3.02 (m, 1H), 3.21-3.30 (m, 1H), 3.62-3.72 (m, 1H),6.33-6.39 (m, 2H), 6.78-6.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 23.7, 33.5, 48.9, 54.3, 112.5 (d, J_{CF} = 11.2 Hz), 115.7 (d, J_{CF} = 21.6 Hz), 144.3 (d, J_{CF} = 1.5 Hz), 154.9 (d, J_{CF} = 232.0 Hz) . HRMS (EI+): m/z cacld. for $C_{11}H_{14}FN$ $[M]^+$, 179.1110; found 179.1109.

***N*-Phenylpiperidine** (**3n**):



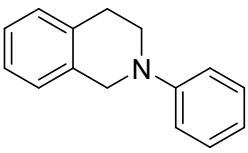
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.566 (quin, 2H, J = 5.6 Hz) 1.704 (quin, 4H, J = 5.6 Hz), 3.14 (t, 4H, J = 5.6 Hz), 6.81 (t, 1H, J = 7.6 Hz), 6.93 (d, 2H, J = 7.6 Hz), 7.20-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 26.1, 50.9, 116.7, 119.4, 129.3, 152.5. HRMS (EI+): m/z cacld. for $C_{11}H_{15}N$ $[M-H]^+$, 160.1126; found 160.1128 ($C_{11}H_{14}N^+$).

***N*-(4-Fluorophenyl)piperidine**[5] (**3o**):



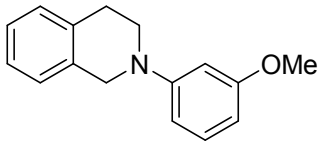
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.527 (quin, 2H, J = 5.2 Hz) 1.698 (quin, 4H, J = 5.2 Hz), 3.03 (t, 4H, J = 5.2 Hz), 6.81-6.88 (m, 2H), 6.89-6.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 26.2, 52.0,115.5 (d, J_{CF} = 21.6 Hz), 118.5 (d, J_{CF} = 7.4 Hz), 149.3 (d, J_{CF} = 2.2 Hz), 157.1 (d, J_{CF} = 236.5 Hz). HRMS (EI+): m/z cacld. for $C_{11}H_{14}FN$ $[M-H]^+$, 178.1032; found 178.1034 ($C_{11}H_{13}FN^+$).

2-Phenyl-1,2,3,4-tetrahydroisoquinoline (**5a**):



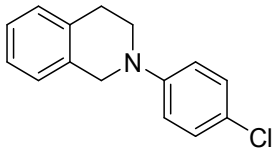
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94 (t, 2H, J = 5.6 Hz), 3.51 (t, 2H, J = 5.6 Hz), 4.37 (s, 2H), 6.75-6.85 (m, 1H), 6.88-7.20 (m, 3H), 7.06-7.19 (m, 3H),7.22-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.4, 46.8, 51.0, 115.5, 118.9, 126.3, 126.6, 126.9, 128.8, 129.5, 134.8, 135.2, 150.9. HRMS (EI+): m/z cacld. for $C_{15}H_{15}N$ $[M]^+$, 209.1204; found 209.1202.

2-(3-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (**5b**):



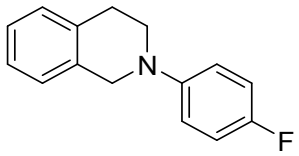
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96 (t, 2H, *J* = 5.6 Hz), 3.54 (t, 2H, *J* = 5.6 Hz), 3.78 (s, 3H), 4.39 (s, 2H), 6.38 (dd, 1H, *J* = 2.4 and 2.4 Hz), 6.50 (t, 1H, *J* = 2.4 Hz), 6.58 (dd, 1H, *J* = 2.4 and 2.4 Hz), 7.11-7.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.3, 46.6, 50.8, 55.4, 101.7, 103.5, 108.1, 126.3, 126.6, 126.8, 128.7, 130.1, 134.6, 135.1, 152.1, 160.9. HRMS (EI+): m/*z* cacld. for $C_{16}H_{17}NO$ $[M]^+$, 239.1310; found 239.1310.

2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (**5c**):



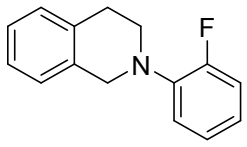
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96 (t, 2H, *J* = 5.6 Hz), 3.51 (t, 2H, *J* = 5.6 Hz), 4.36 (s, 2H), 6.79-6.91 (m, 2H), 7.08-7.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.2, 46.7, 50.9, 116.4, 123.6, 126.4, 126.7, 126.8, 128.7, 129.2, 134.3, 134.9, 149.3. HRMS (EI+): (m/*z)* cacld. for $C_{15}H_{14}ClN$ $[M-H]^+$, 242.0737; found 242.0738 ($C_{15}H_{13}ClN^+$).

2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**5d**):



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 (t, 2H, *J* = 5.6 Hz), 3.48 (t, 2H, *J* = 5.6 Hz), 4.33 (s, 2H), 6.85-7.03 (m, 4H), 7.11-7.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.3, 47.9, 52.1, 115.8 (d, J_{CF} = 21.6 Hz), 117.3, 117.4, 126.2, 126.7 (d, J_{CF} = 11.1 Hz), 128.8, 134.5, 134.7, 147.6 (d, J_{CF} = 2.2 Hz), 156.9 (d, J_{CF} = 236.5 Hz). HRMS (EI+): (m/*z)* cacld. for $C_{15}H_{14}FN$ $[M-H]^+$, 226.1032; found 226.1035 ($C_{15}H_{13}FN^+$).

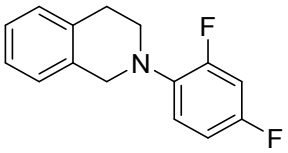
2-(2-Fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**5e**):



^{1}H NMR (600 MHz, $CDCl_3$): δ 2.95 (t, 2H, *J* = 6 Hz), 3.41 (t, 2H, *J* = 6 Hz), 4.27 (s, 2H), 6.86-6.92 (m, 1H), 6.94-7.17 (m, 7 H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ 28.9, 48.8 (d, J_{CF} = 4.6 Hz), 52.5 (d, J_{CF} = 2.4 Hz), 116.1 (d, J_{CF} = 20.7 Hz), 119.3 (d, J_{CF} = 3.5 Hz), 122.2 (d, J_{CF} = 7.9 Hz), 124.3 (d, J_{CF} = 3.5 Hz), 125.8, 126.2, 126.3, 128.8, 134.3, 134.4, 139.7 (d, J_{CF}

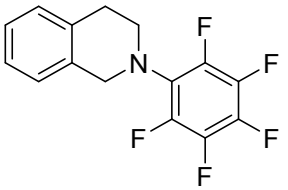
= 9.3 Hz), 155.7 (d, J_{CF} = 244.9 Hz) HRMS (EI+): m/*z* cacld. for $C_{15}H_{14}FN$ $[M]^+$, 227.1110; found 227.1107.

2-(2,4-Difluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**5f**):



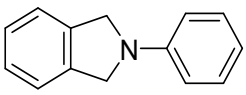
^{1}H NMR (600 MHz, $CDCl_3$): δ 2.95 (t, 2H, *J* = 6 Hz), 3.34 (t, 2H, *J* = 6 Hz), 4.21 (s, 2H), 6.73-6.84 (m, 2H), 6.90-6.96 (m, 1H), 7.04-7.08 (m, 1H), 7.10-7.17 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 28.8, 49.2 (d, J_{CF} = 3.4 Hz), 52.9 (d, J_{CF} = 2.4 Hz), 104.7 (t, J_{CF} = 24 Hz), 110.6 (dd, J_{CF} = 21.9, 3.4 Hz), 119.9 (dd, J_{CF} = 9.3, 3.5 Hz), 125.9, 126.26, 126.33, 128.7, 134.15, 134.20, 136.4 (dd, J_{CF} = 9.3, 3.5 Hz), 155.7 (dd, J_{CF} = 11.4 , 248.4 Hz), 157.7 (dd, J_{CF} = 11.6, 241.4 Hz). HRMS (EI+): m/*z* cacld. for $C_{15}H_{13}F_2N$ $[M-H]^+$, 244.0938; found 244.0940 ($C_{15}H_{13}FN^+$).

2-(Pentafluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**5g**):



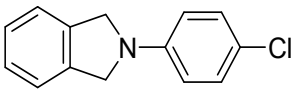
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (t, 2H, *J* = 5.6 Hz), 3.47 (t, 2H, *J* = 5.6 Hz), 4.37 (s, 2H), 6.99-7.06 (m, 1H), 7.10-7.20 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.8, 49.4, 53.1, 126.1, 126.2, 126.6, 129.4, 134.2, 134.3. HRMS (EI+): (m/*z)* cacld. for $C_{15}H_{10}F_5N$ $[M]^+$, 299.0733; found 299.0731.

2-Phenylisoindoline (**5h**):



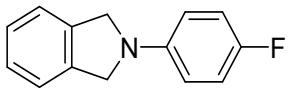
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.65 (s, 4H), 6.65-6.7 (m, 2H), 6.72-6.77 (m, 1H), 7.26-7.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 53.9, 111.8, 116.4, 122.8, 127.4, 129.6, 138.2, 147.4. HR-MS (EI+): m/*z* cacld. for $C_{14}H_{13}N$ $[M-H]^+$, 194.0970; found 194.0973 ($C_{14}H_{12}N^+$).

2-(4-Chlorophenyl)isoindoline (**5i**):



^{1}H NMR (400 MHz, $CDCl_3$): δ 4.61 (s, 4H), 6.57 (d, 2H, *J* = 8.8 Hz)), 7.23 (d, 2H, J = 8.8 Hz), 7.25-7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.1, 112.8, 121.3, 122.8, 127.5, 129.3, 137.8, 146.1. HR-MS (EI+): m/*z* cacld. for $C_{14}H_{12}ClN$ $[M-H]^+$, 228.0580; found 228.0577 ($C_{14}H_{11}ClN^+$).

2-(4-Fluorophenyl)isoindoline (**5j**):



^{1}H NMR (400 MHz, $CDCl_3$): δ 4.58 (s, 4H), 6.50-6.59 (m, 2H), 6.95-7.05 (m, 2H), 7.24-7.39 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.4, 112.2 (d, J_{CF} = 7.4 Hz), 116.1 (d, J_{CF} = 22.3 Hz), 122.7, 127.4, 138.1, 144.1 (d, J_{CF} = 1.5 Hz), 155.4 (d, J_{CF} = 232.8 Hz). HR-MS (EI+): m/*z* cacld. for $C_{14}H_{12}FN$ $[M-H]^+$, 212.0876; found 212.0878 ($C_{14}H_{11}ClN^+$).

References:

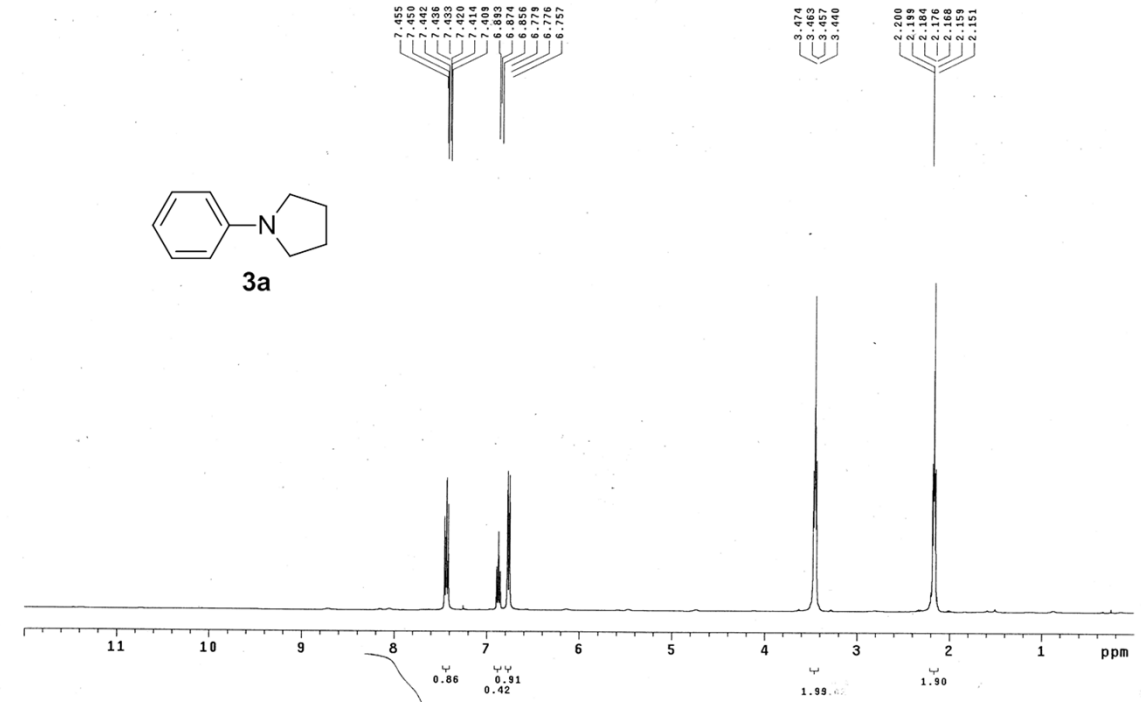
1. J. M. Flaniken, C. J. Collins, M. Lanz and B. Singaram, *Org. Lett.,* 1999, **1**, 799.
2. G. Manolikakes, A. Gavryushin and P. Knochel, *J. Org. Chem.,* 2008, **73**, 1429.
3. C.-Y. Gao and L.-M. Yang, *J. Org. Chem.,* 2008, **73**, 1624.
4. R. P. Rucker, A. M.Whittaker, H. Dang and G. Lalic, *Angew. Chem. Int. Ed.,* 2012, **51**, 3953.
5. L. Djakovitch, M. Wagner and K. Kohler, *J. Organomet. Chem.,* 1999, **592**, 225.

^{1}H NMR and ^{13}C NMR Spectra of the products

blk-002-021

File: BLK-002-021-hnmr-120614

Pulse Sequence: s2pul

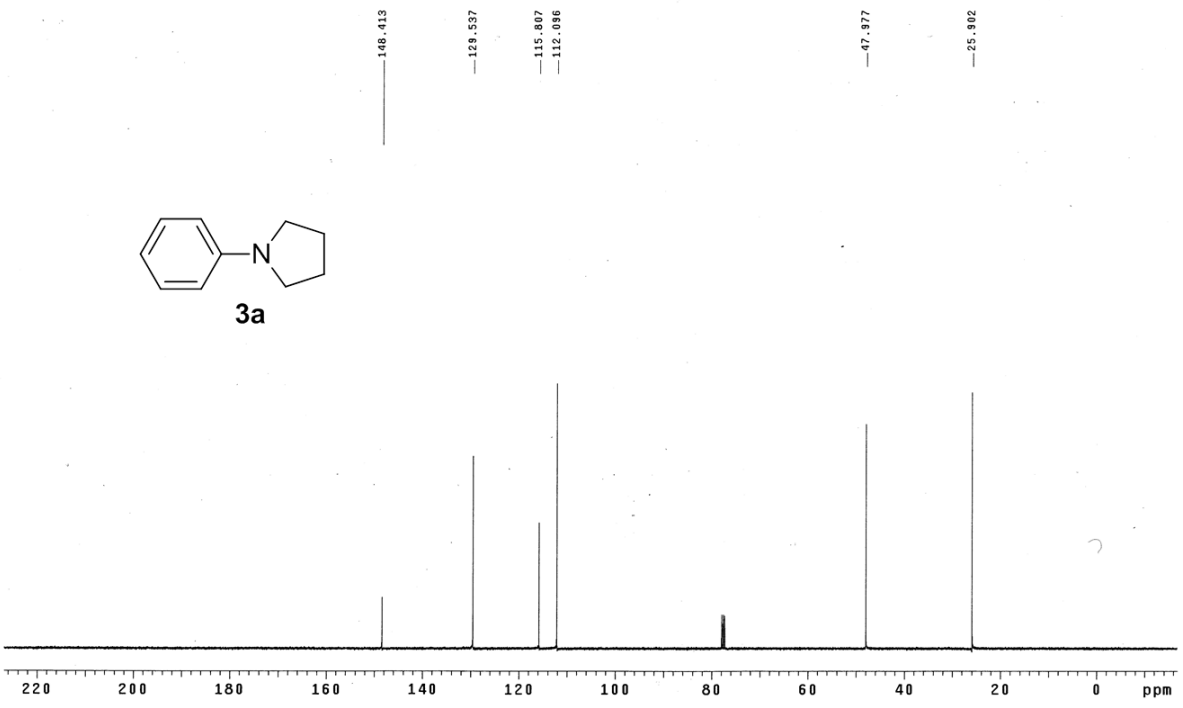


3a

blk-002-021

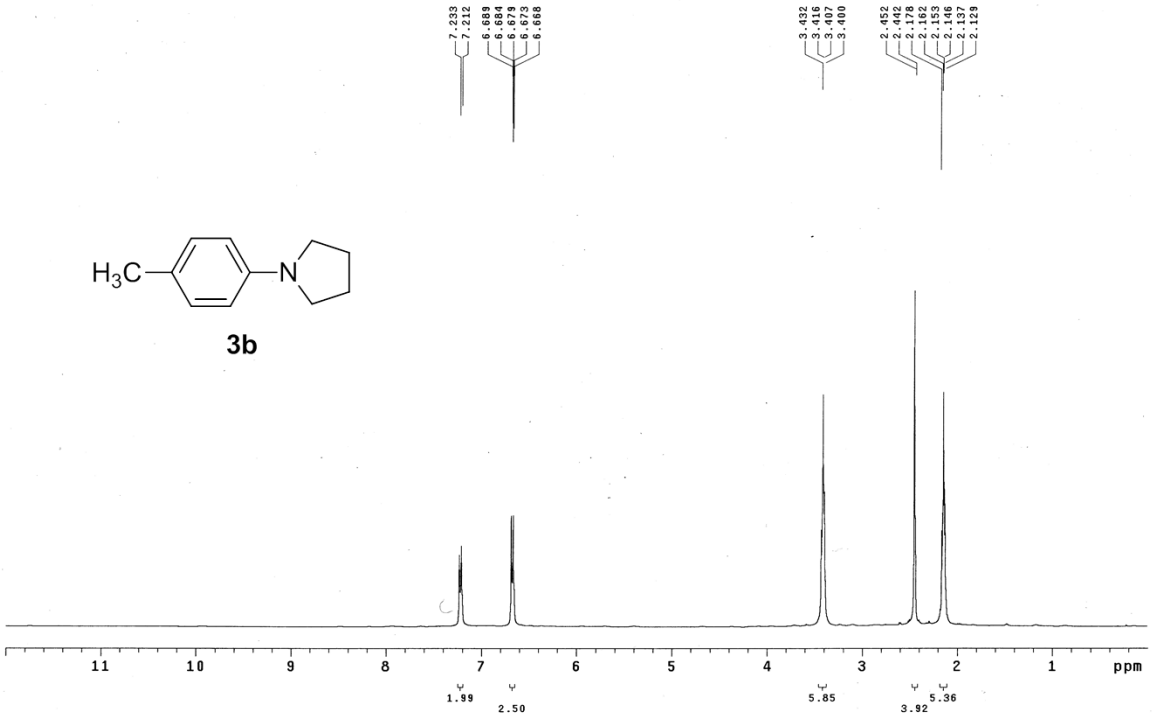
File: BLK-002-021-cnmr-120614

Pulse Sequence: s2pul



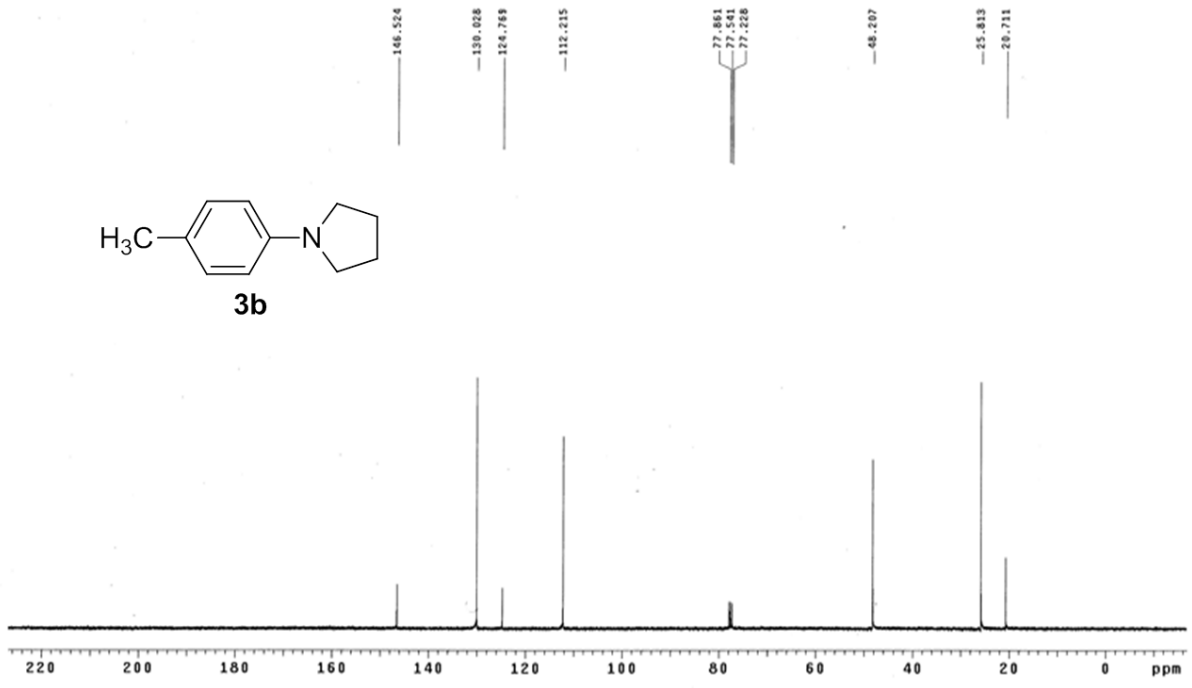
3a

blk-002-023
File: BLK-002-023-hnmr-120620
Pulse Sequence: s2pul



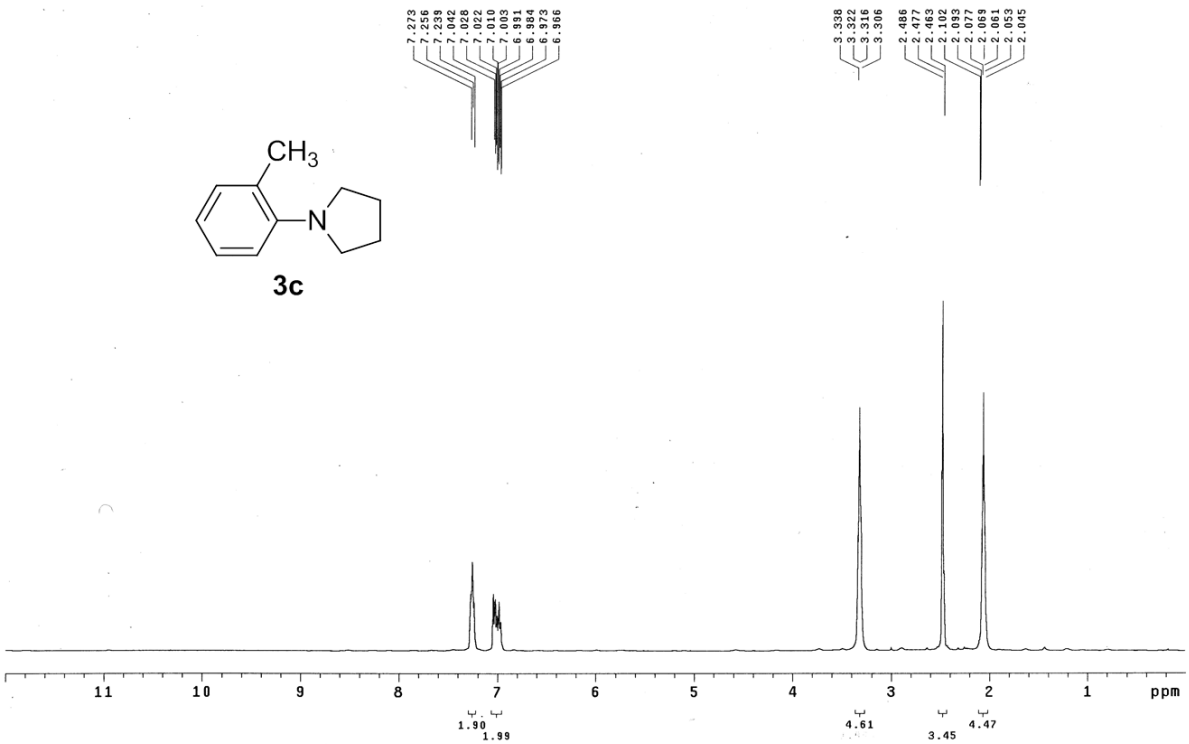
3b

blk-002-023
File: BLK-002-023-cnmr-120620
Pulse Sequence: s2pul



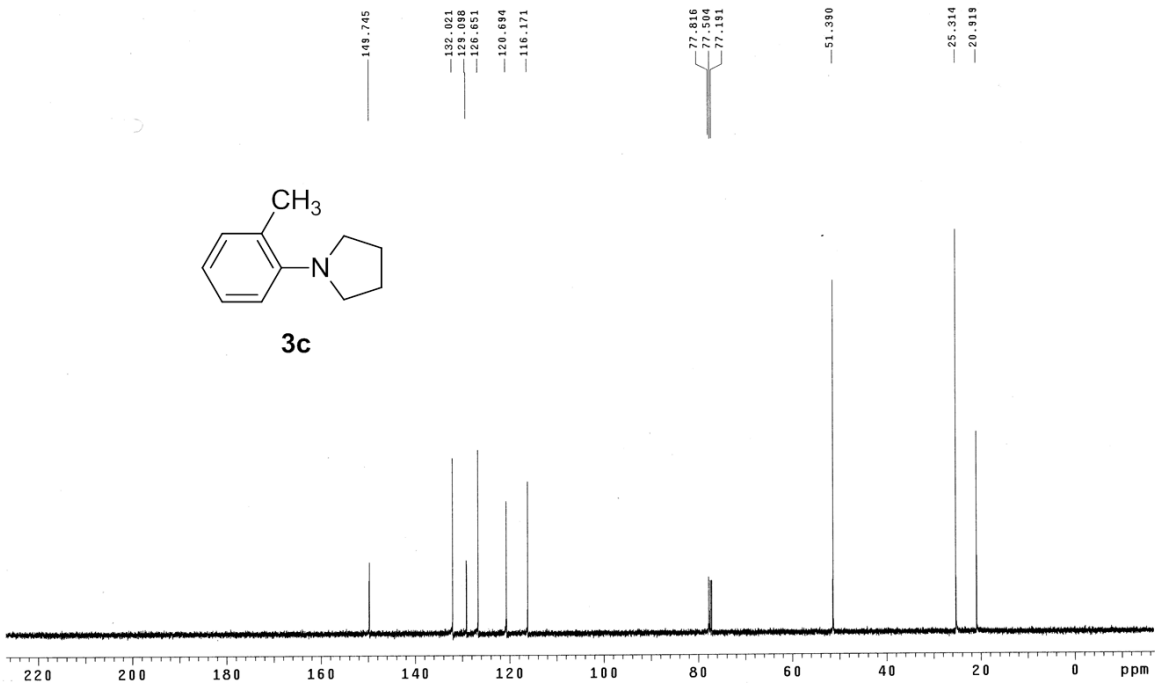
3b

blk-002-032
File: BLK-002-032-hnmr-120712
Pulse Sequence: s2pul



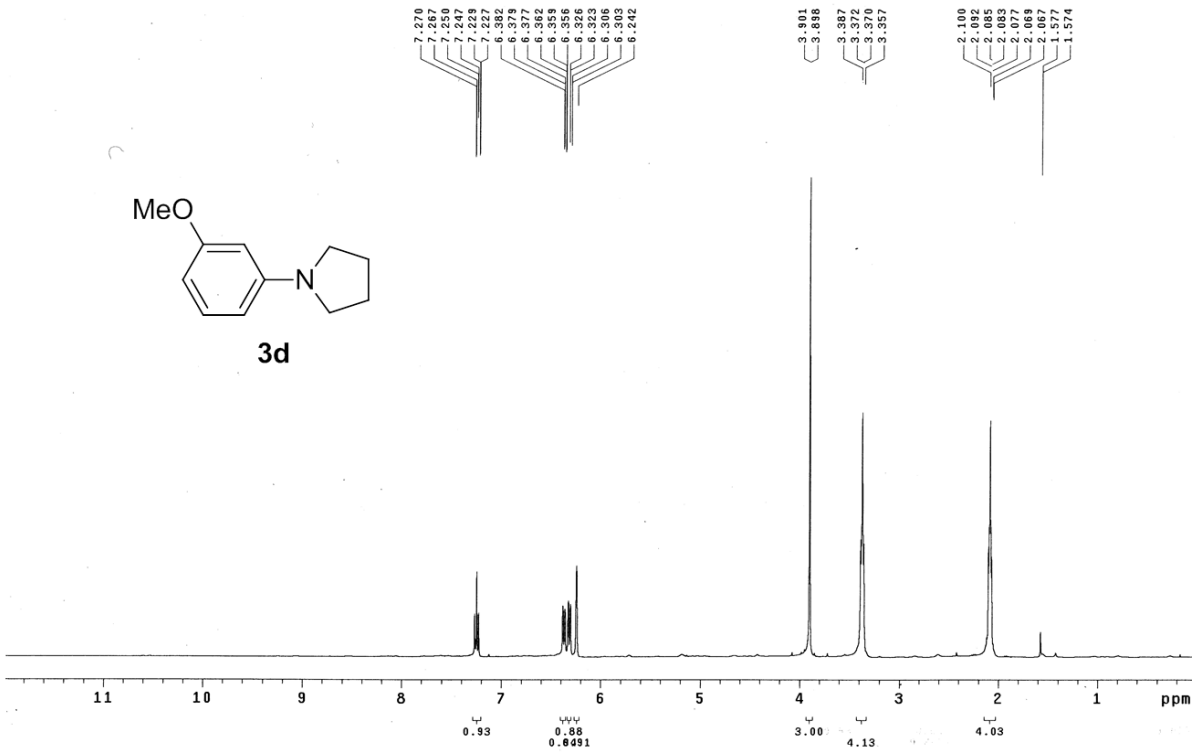
3c

blk-002-032
File: BLK-002-032-cnmr-120712
Pulse Sequence: s2pul

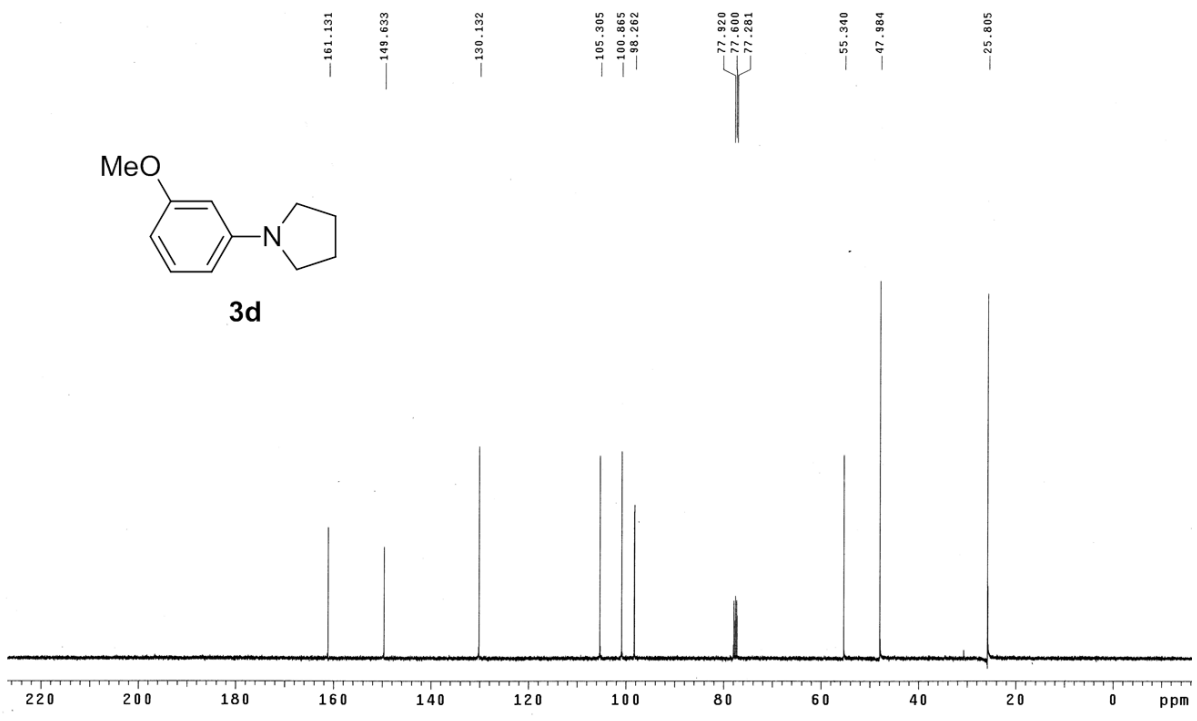


3c

blk-002-033
File: BLK-002-033-hnmr-120712
Pulse Sequence: s2pul

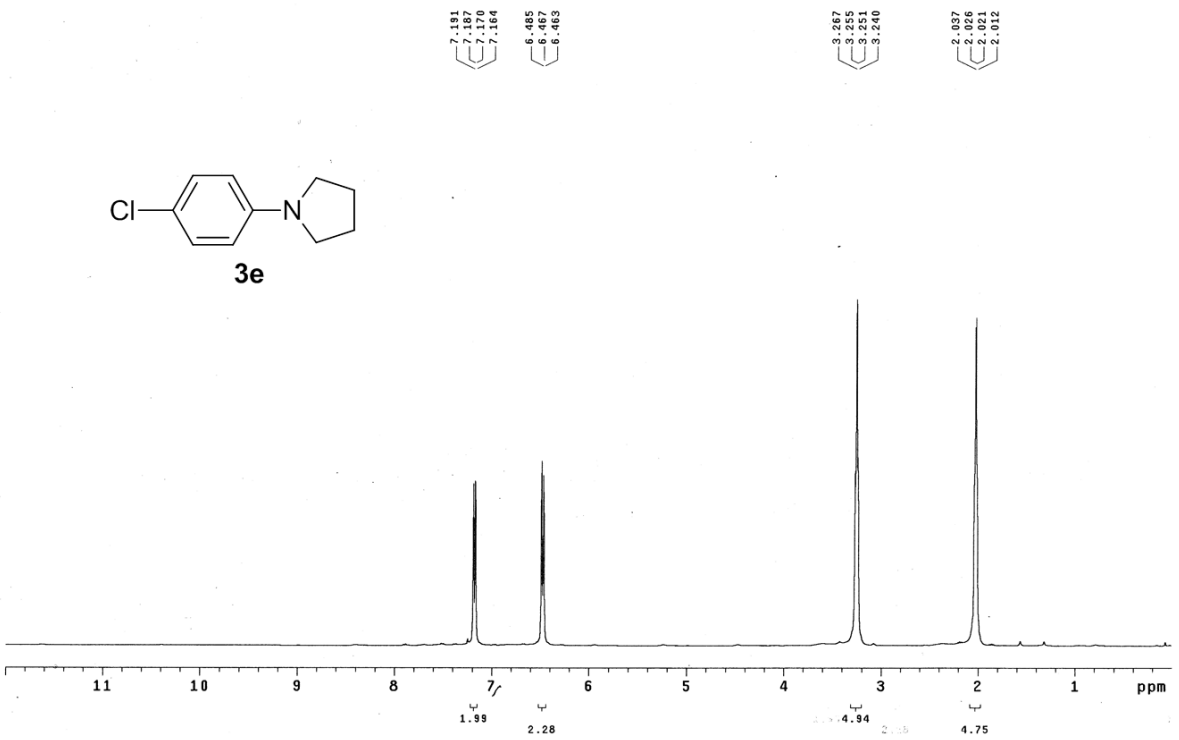


blk-002-033
File: BLK-002-033-cnmr-120712
Pulse Sequence: s2pul



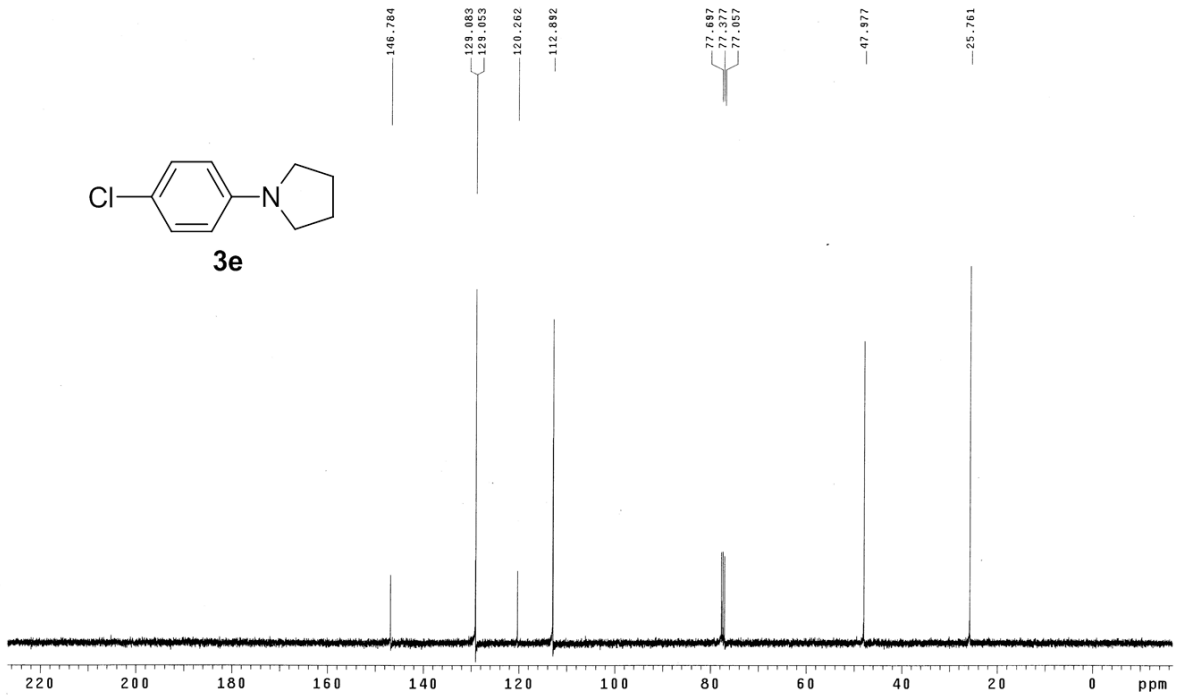
blk-002-025
File: BLK-002-025-hnmr-120621
Pulse Sequence: s2pul

3e

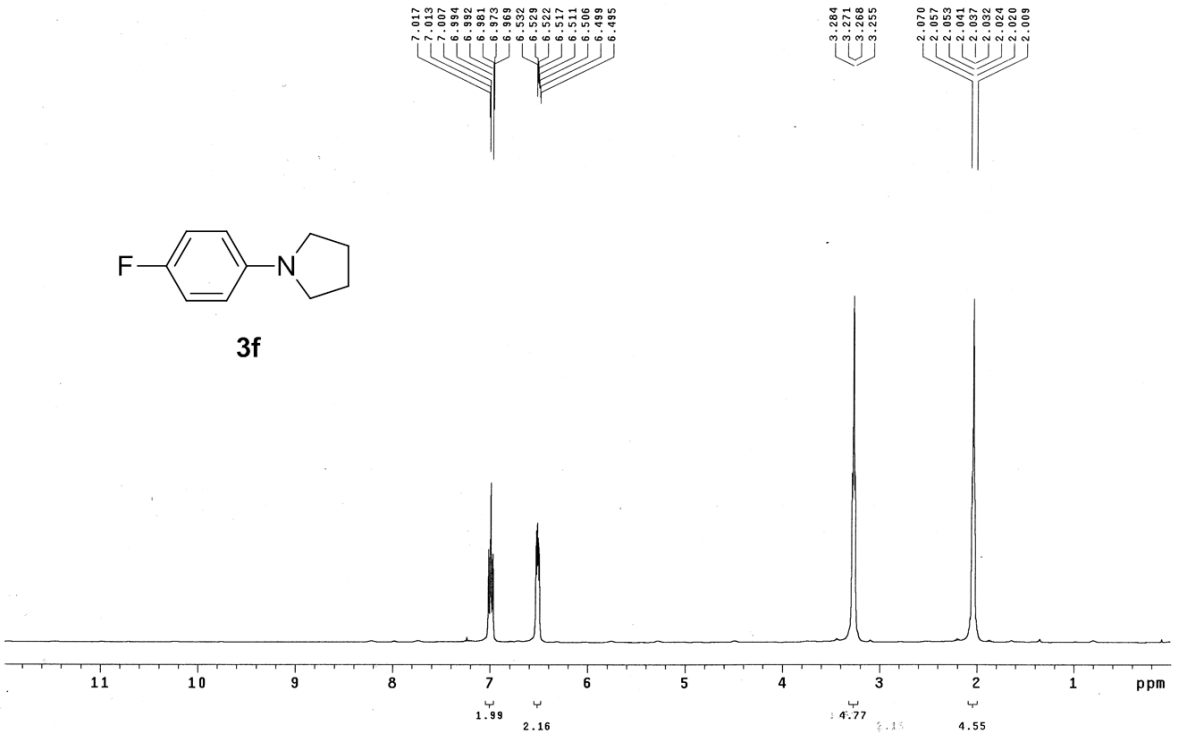


blk-002-025
File: BLK-002-025-cnmr-120621
Pulse Sequence: s2pul

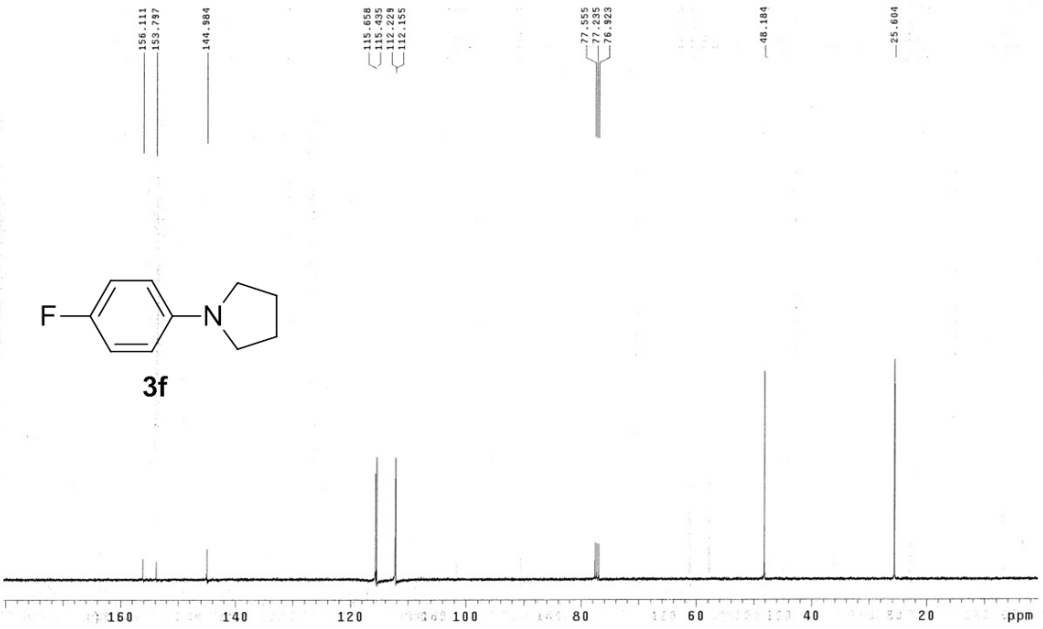
3e



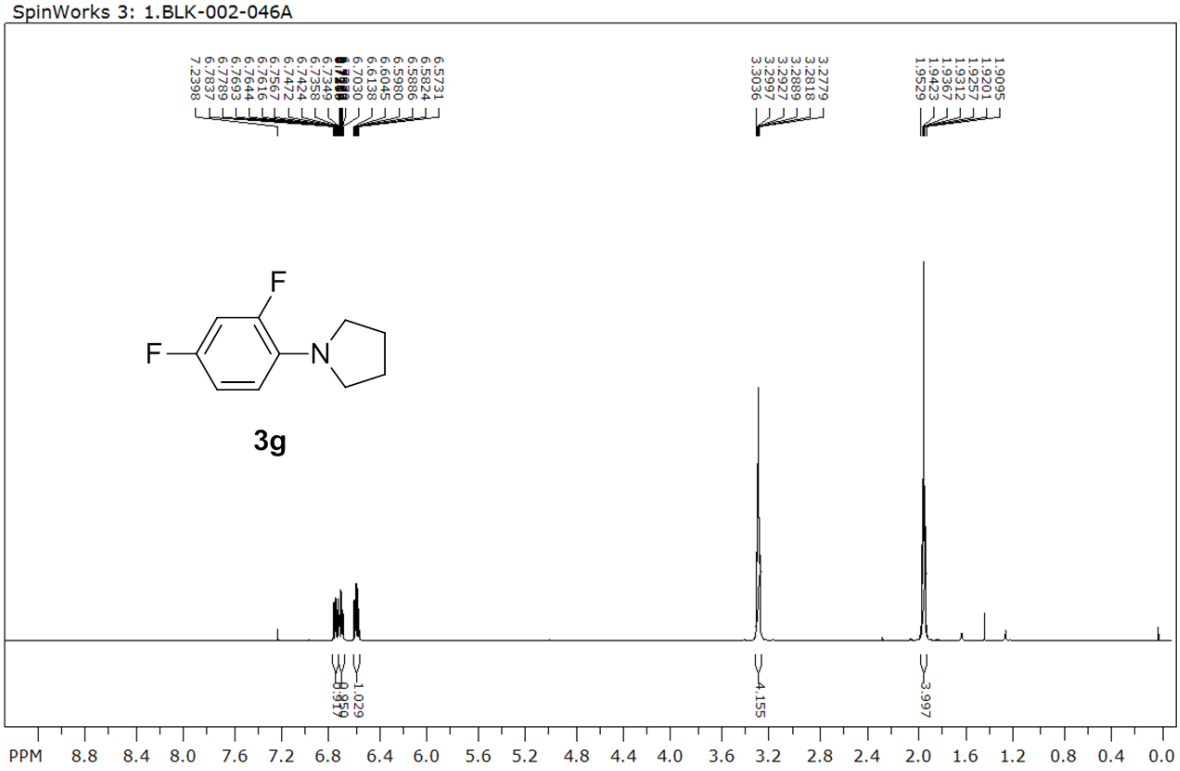
blk-002-022
File: BLK-002-022-hnmr-120620
Pulse Sequence: s2pul



blk-002-022
File: BLK-002-022-cnmr-120620
Pulse Sequence: s2pul



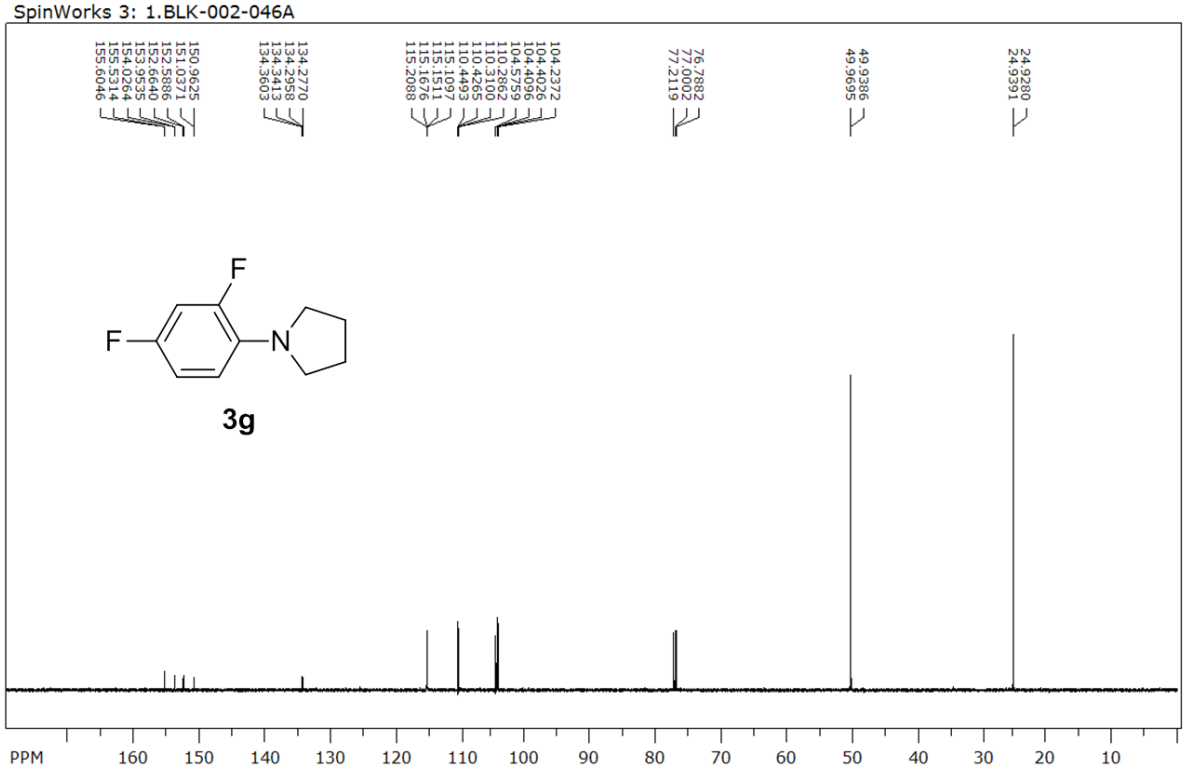
SpinWorks 3: 1.BLK-002-046A



file: ...\NMR\12sep21\1blk-002-046a.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 599.859519 MHz
time domain size: 32768 points
width: 9615.38 Hz = 16.0294 ppm = 0.293438 Hz/pt
number of scans: 4

freq. of 0 ppm: 599.855932 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 230.134 ppm/cm: 0.38365

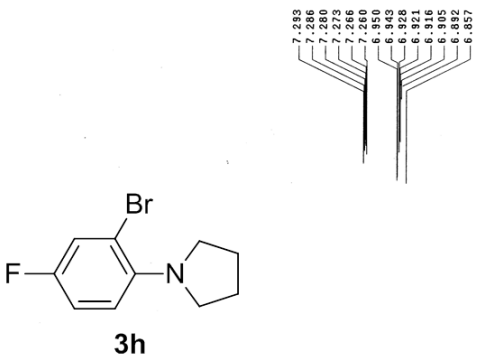
SpinWorks 3: 1.BLK-002-046A



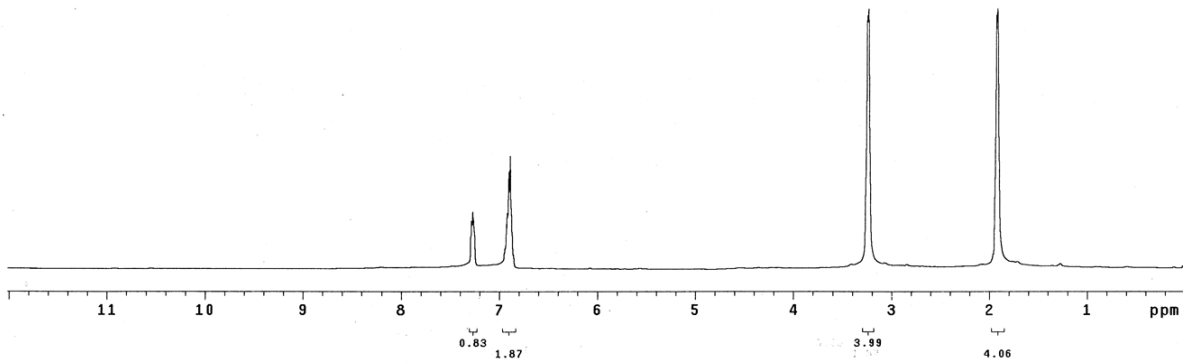
file: ...\12sep21\1blk-002-046a_13C.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 150.850483 MHz
time domain size: 65536 points
width: 37878.79 Hz = 251.1015 ppm = 0.577984 Hz/pt
number of scans: 72

freq. of 0 ppm: 150.833896 MHz
processed size: 65536 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 1086.902 ppm/cm: 7.20516

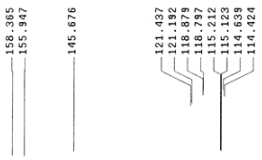
blk-002-027
File: BLK-002-027-hnmr-120622
Pulse Sequence: s2pul

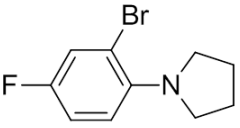


3h

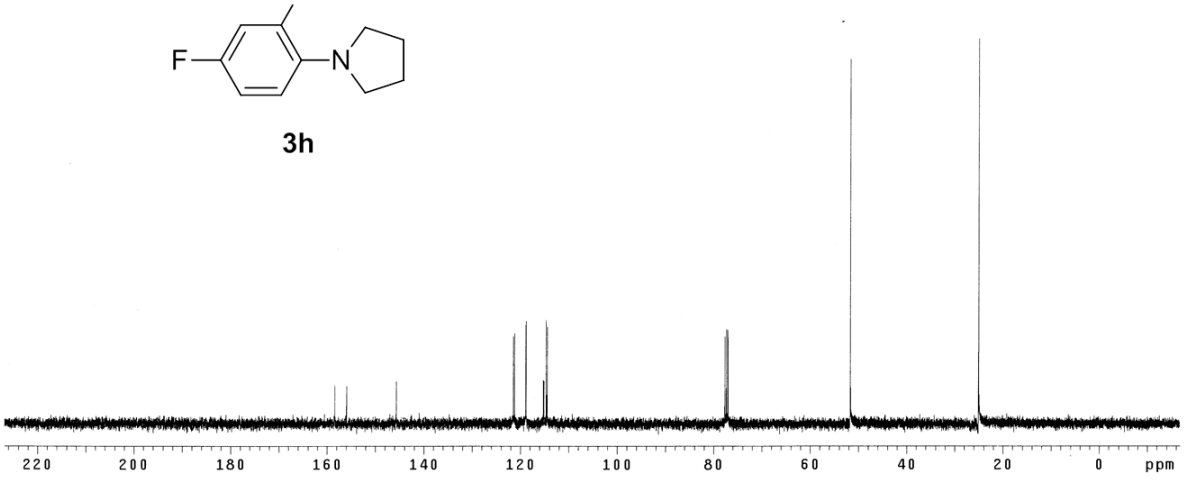


blk-002-027
File: BLK-002-027-cnmr-120622
Pulse Sequence: s2pul

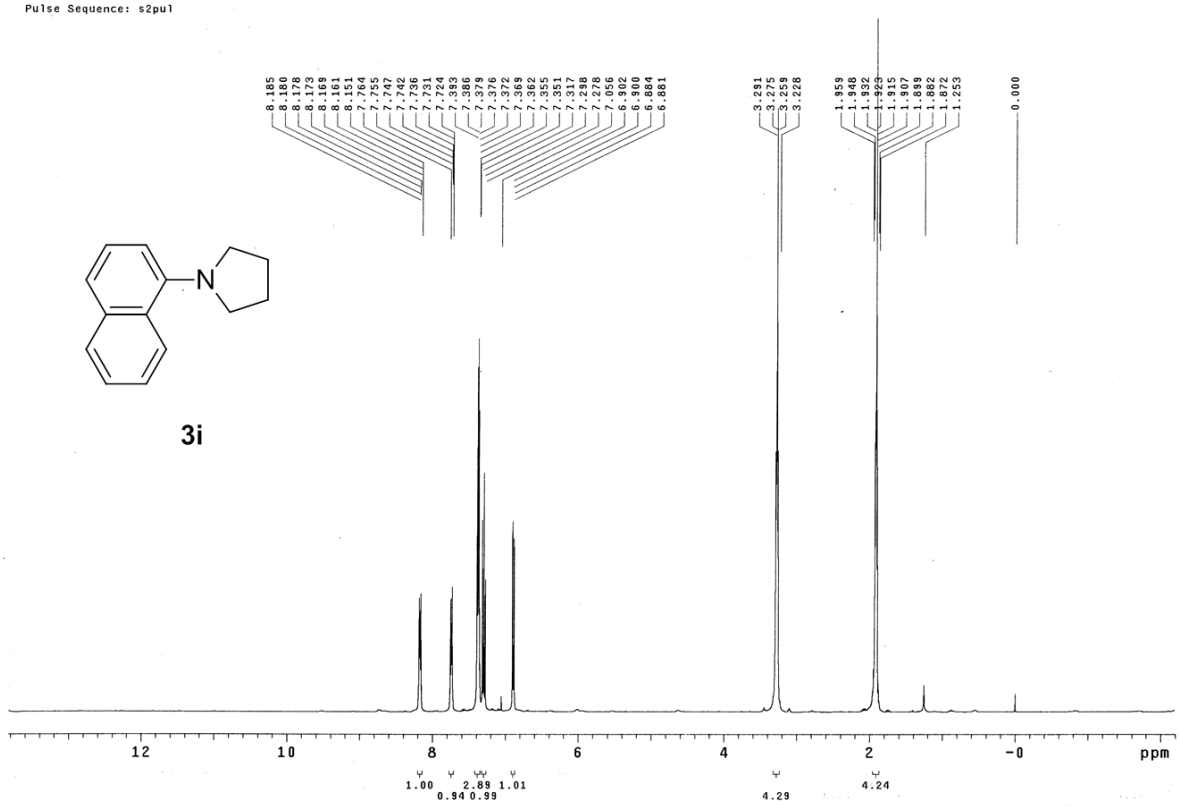




3h

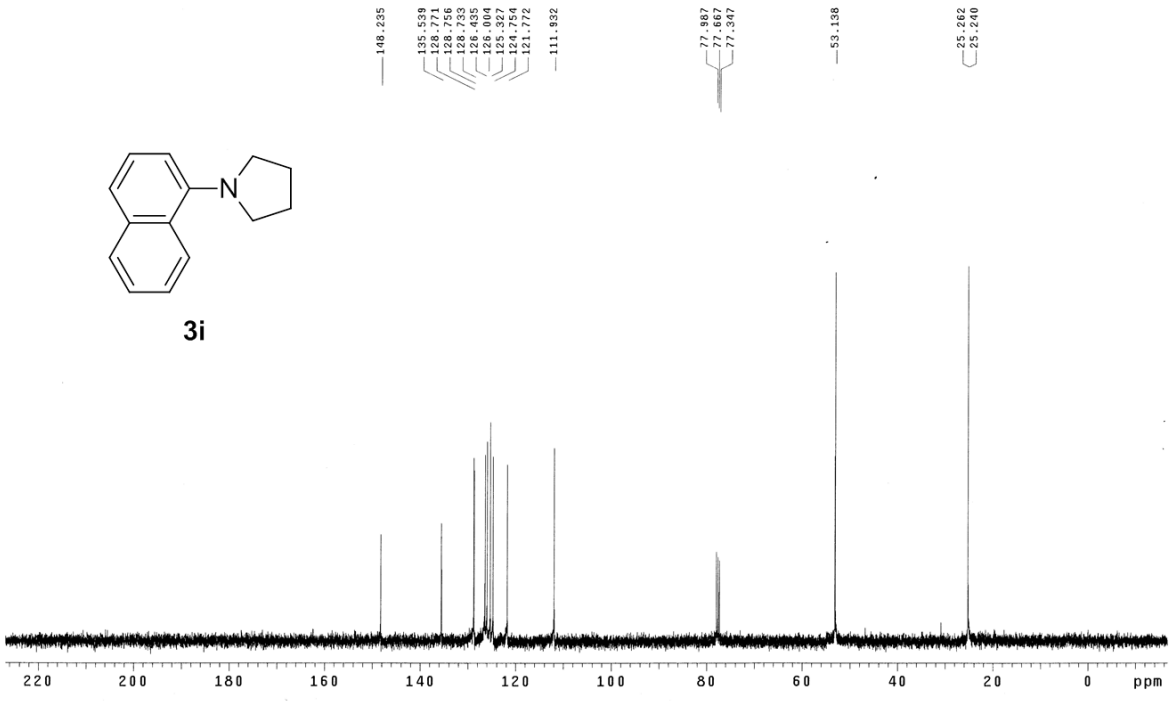


blk-002-031a
File: Proton
Pulse Sequence: s2pul



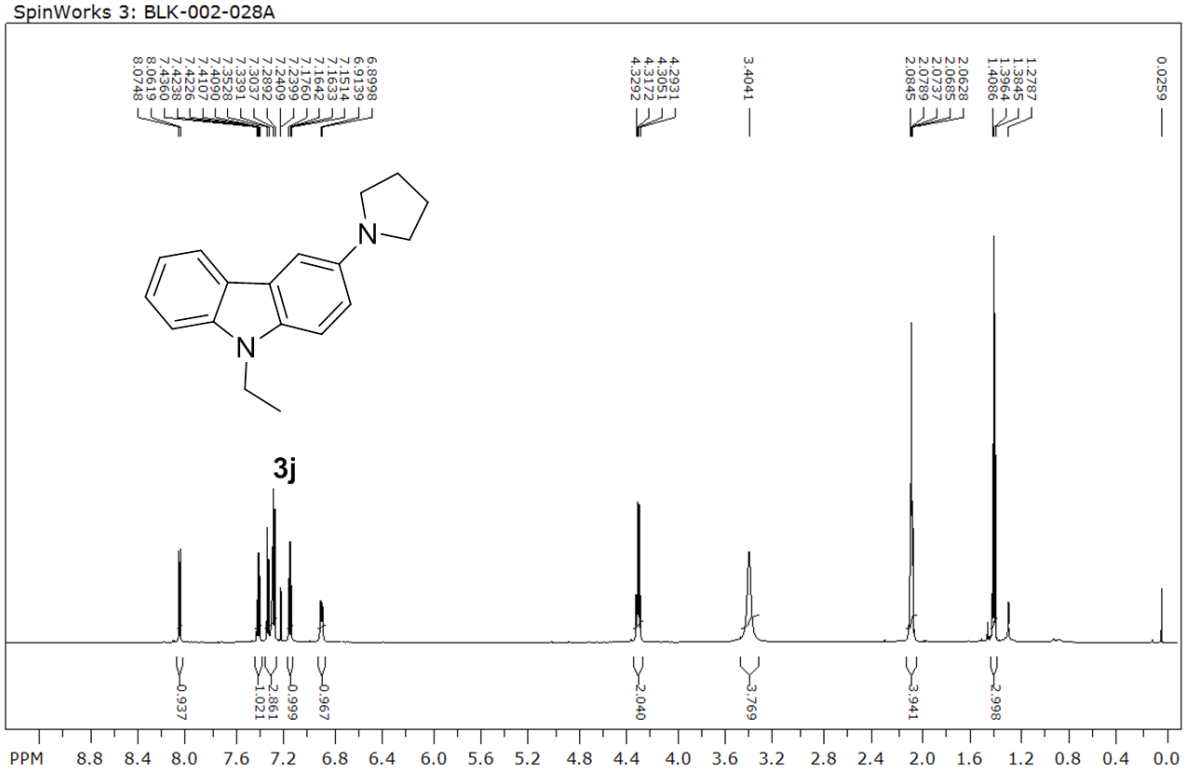
3i

blk-002-031
File: BLK-002-031-cnmr-120702
Pulse Sequence: s2pul



3i

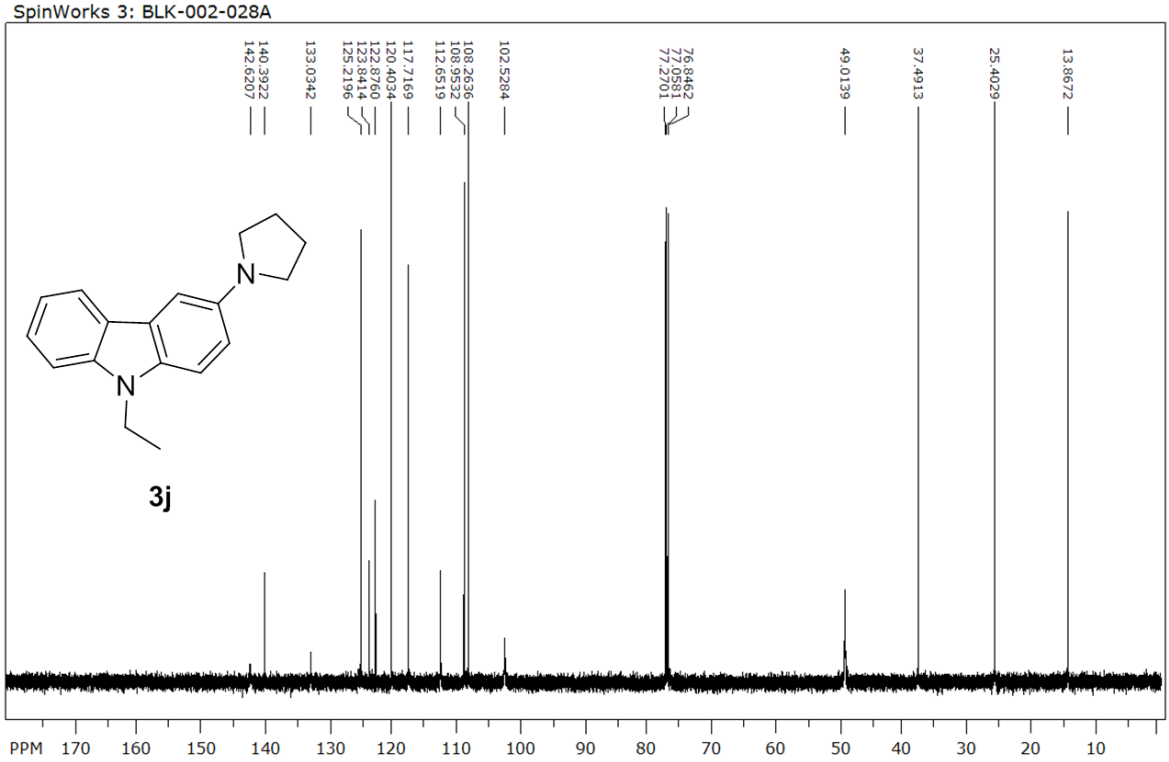
SpinWorks 3: BLK-002-028A



file: ...\NMR\12sep21\2blk-002-028a.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 599.859519 MHz
time domain size: 32768 points
width: 9615.38 Hz = 16.0294 ppm = 0.293438 Hz/pt
number of scans: 4

freq. of 0 ppm: 599.855932 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 230.134 ppm/cm: 0.38365

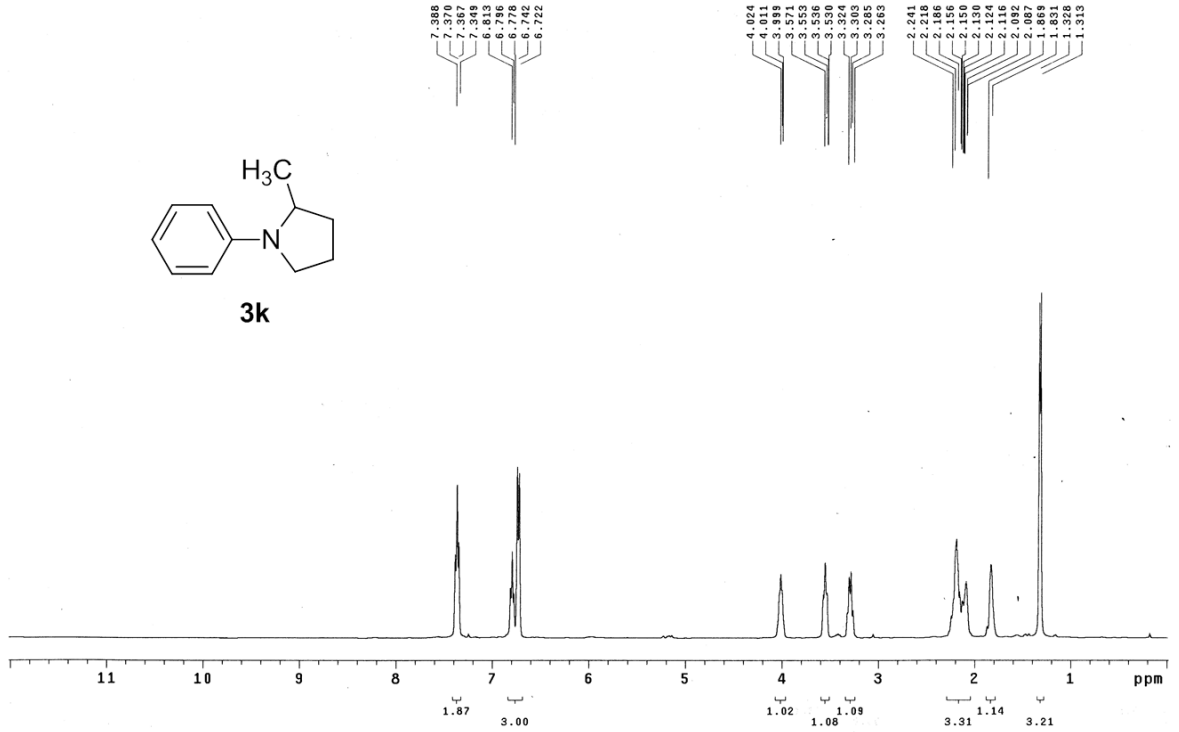
SpinWorks 3: BLK-002-028A



file: ...\12sep21\2blk-002-028a_13C.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 150.850483 MHz
time domain size: 65536 points
width: 37878.79 Hz = 251.1015 ppm = 0.577984 Hz/pt
number of scans: 288

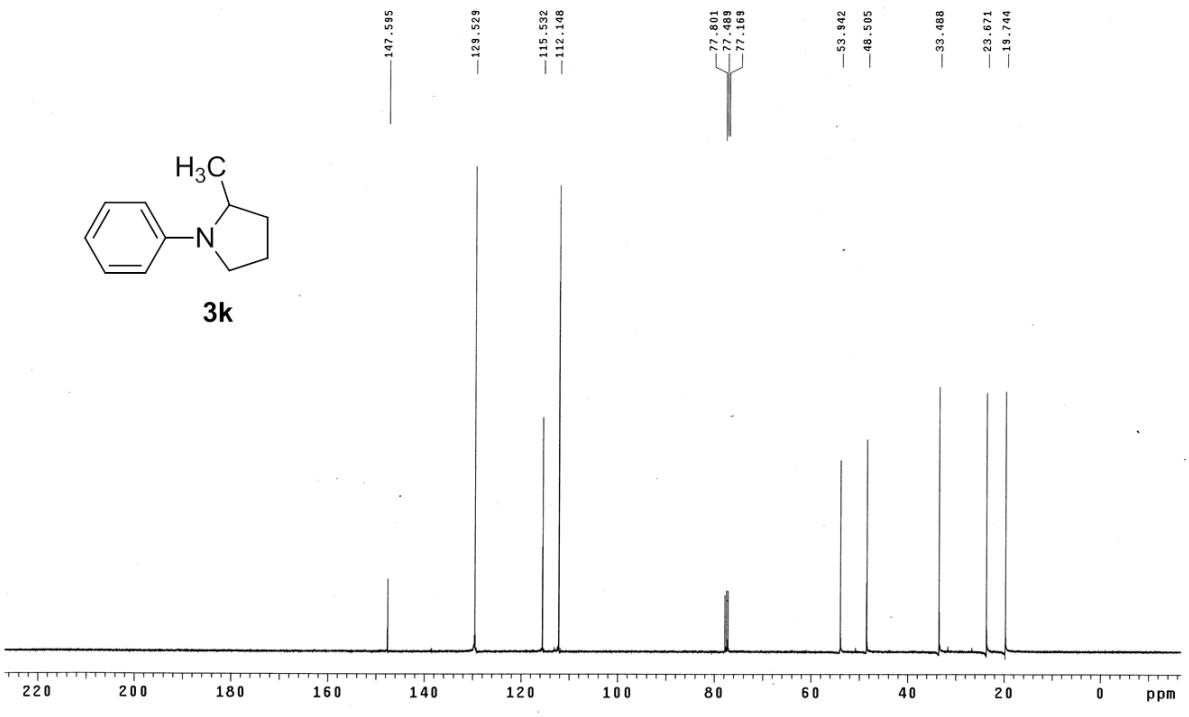
freq. of 0 ppm: 150.833891 MHz
processed size: 65536 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 1096.920 ppm/cm: 7.27157

blk-002-053a
File: BLK-002-053a-hnmr-120905
Pulse Sequence: s2pul



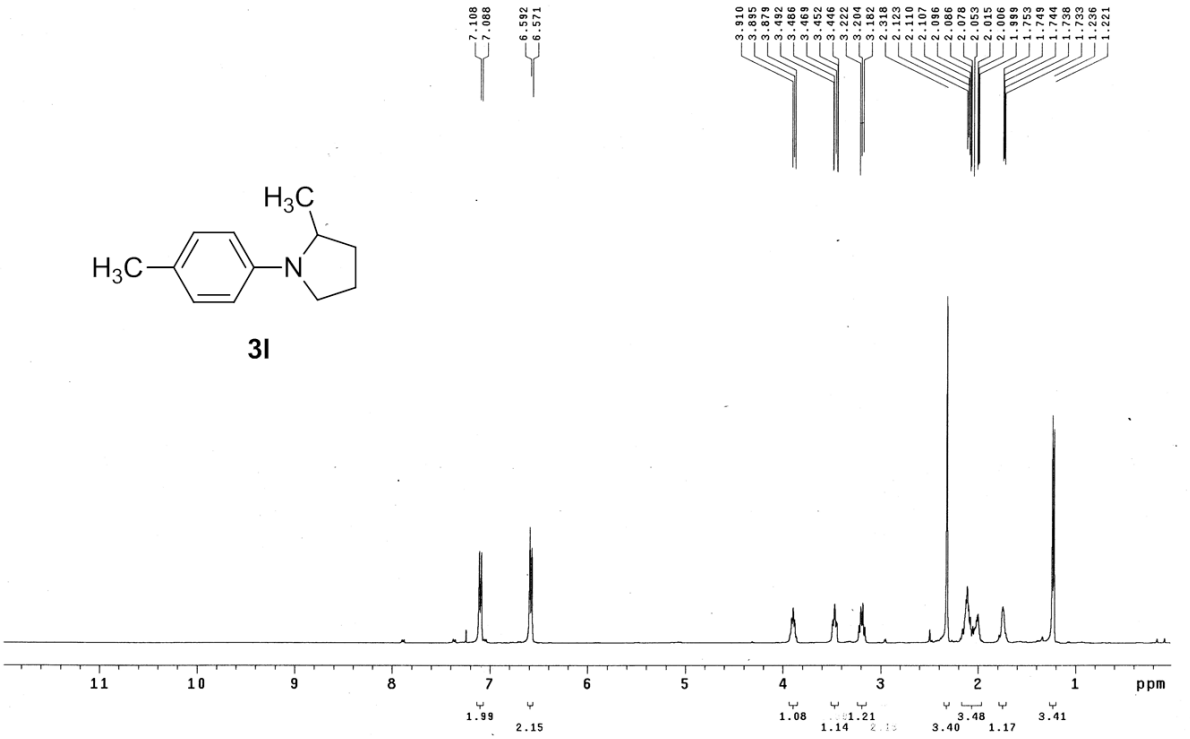
3k

blk-002-053a
File: BLK-002-053a-cnmr-120905
Pulse Sequence: s2pul



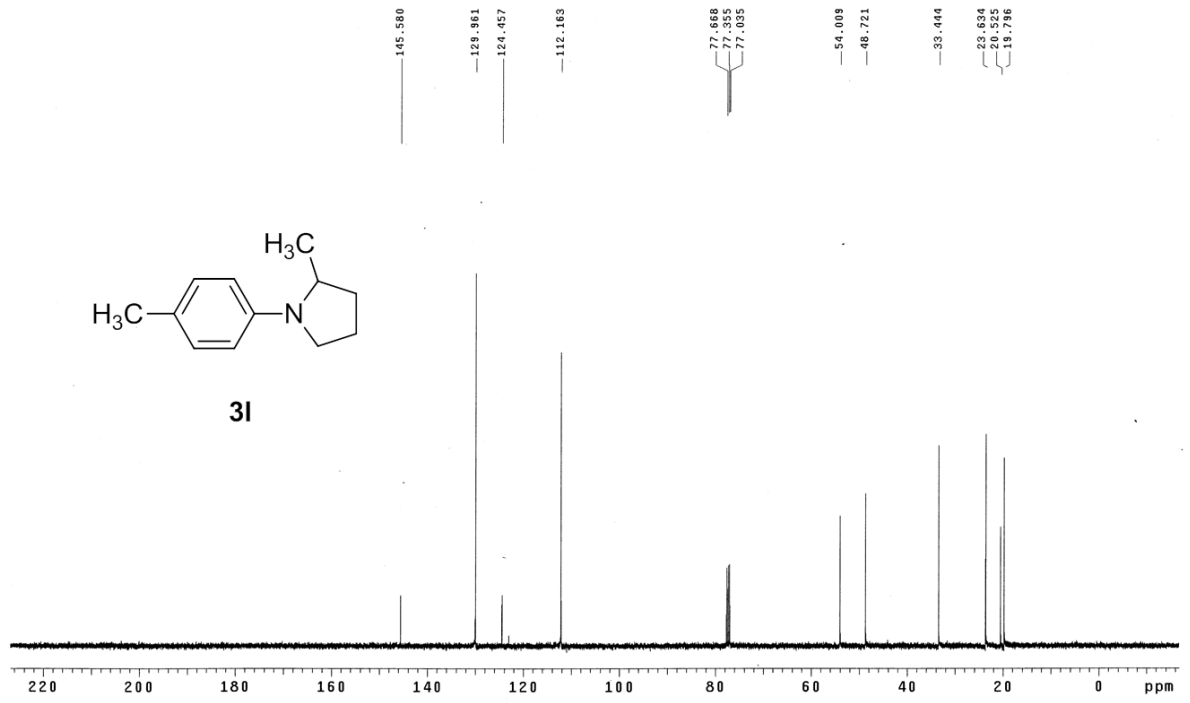
3k

blk-002-055
File: BLK-002-055-hnmr-120910
Pulse Sequence: s2pul



3l

blk-002-055
File: BLK-002-055-cnmr-120910
Pulse Sequence: s2pul

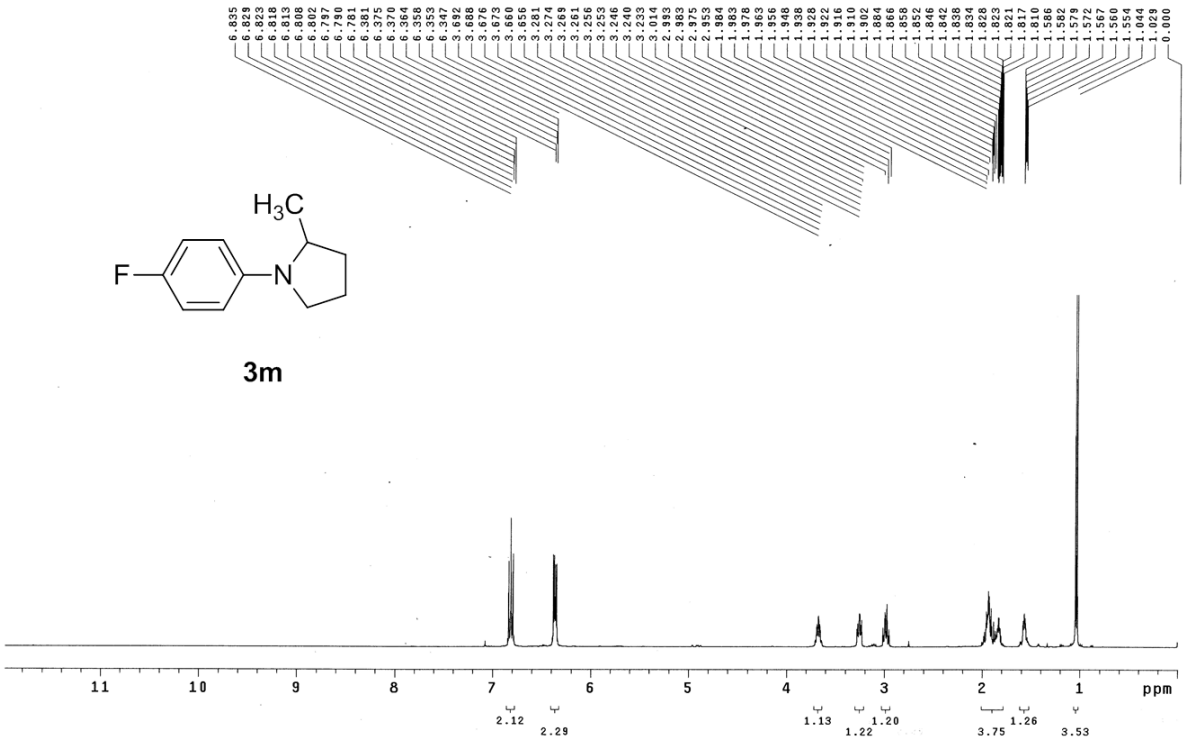


3l

blk-002-056

File: BLK-002-056-hnmr-120910

Pulse Sequence: s2pul

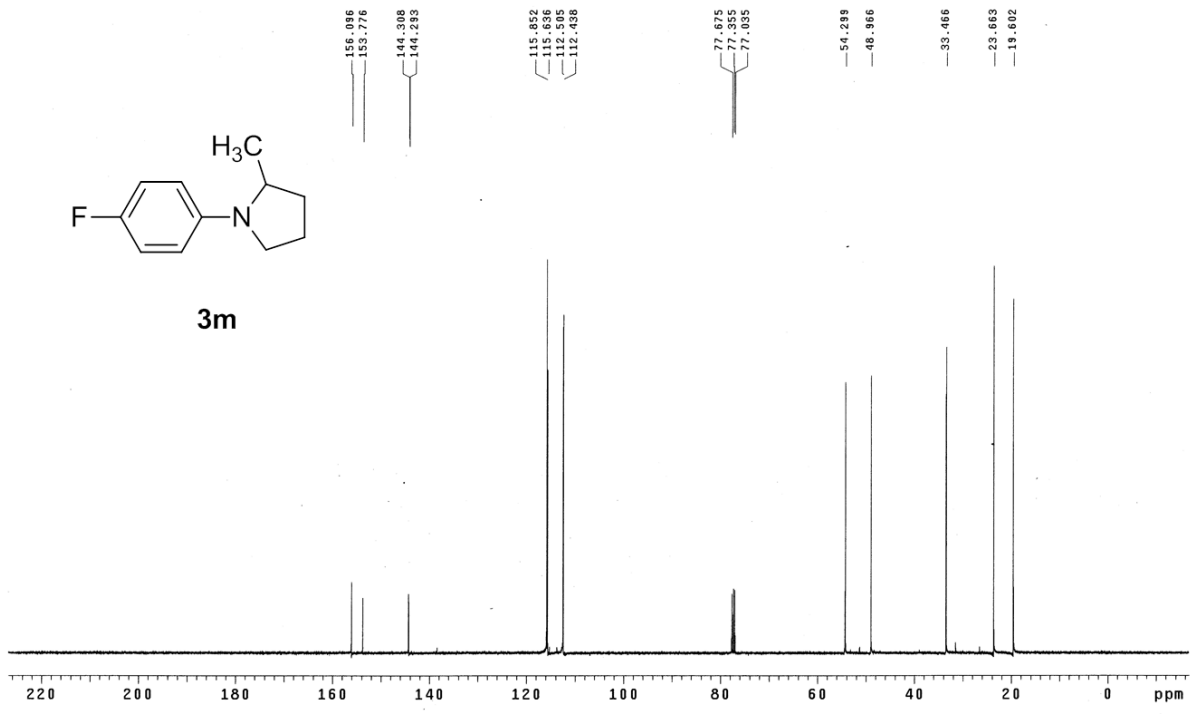


3m

blk-002-056

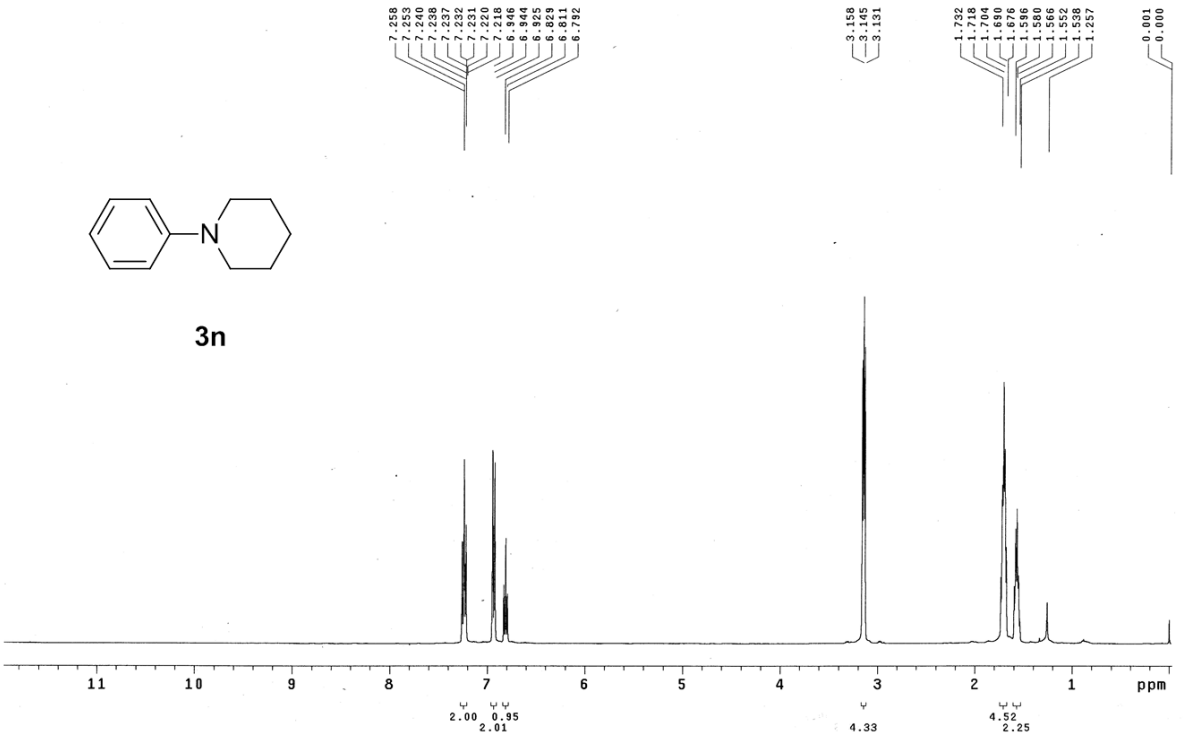
File: BLK-002-056-cnmr-120910

Pulse Sequence: s2pul



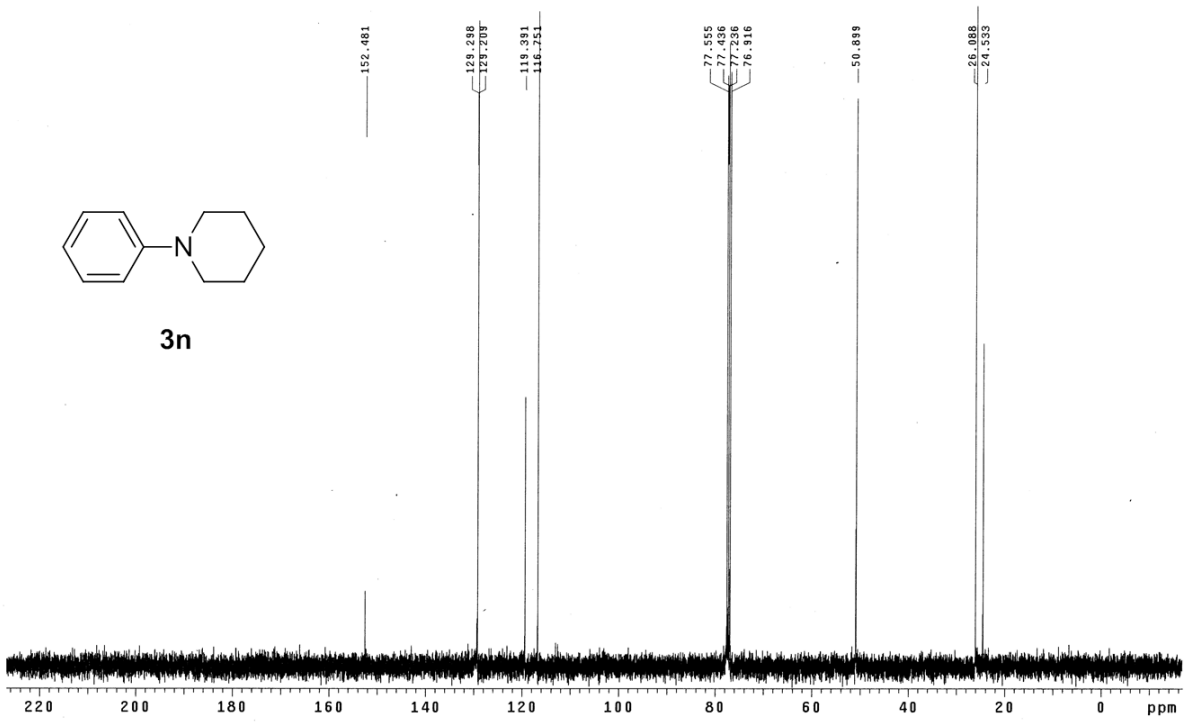
3m

blk-002-030
File: BLK-002-030-hnmr-120629
Pulse Sequence: s2pul



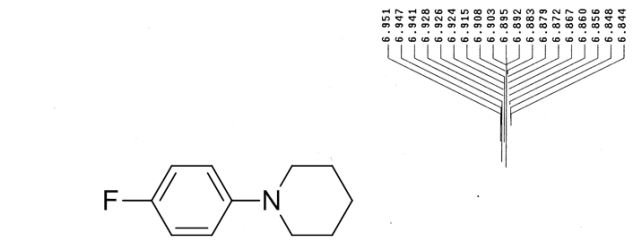
3n

blk-002-030
File: Carbon
Pulse Sequence: s2pul

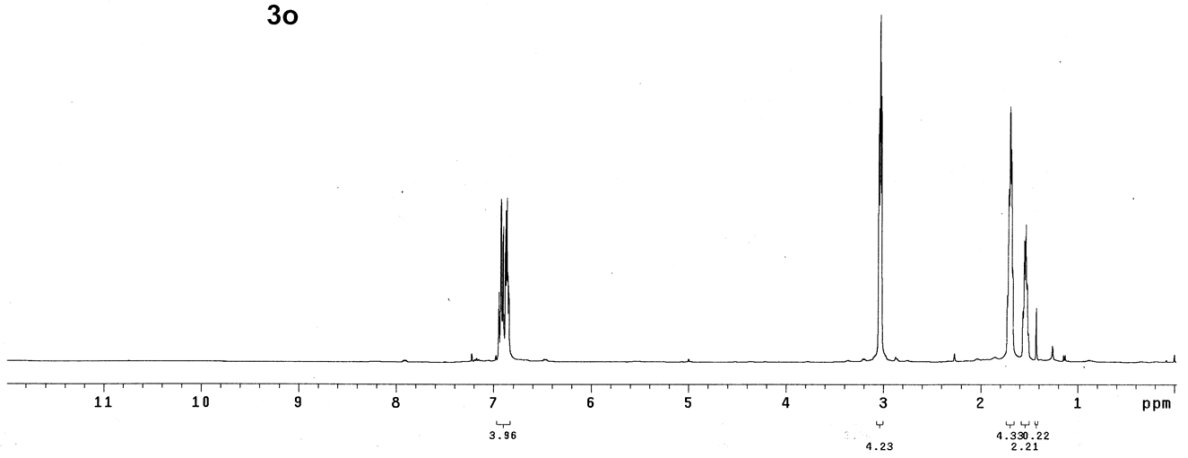


3n

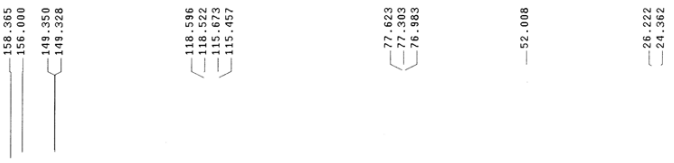
blk-002-035
File: BLK-002-035-hnmr-120713
Pulse Sequence: s2pul

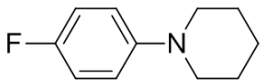


3o

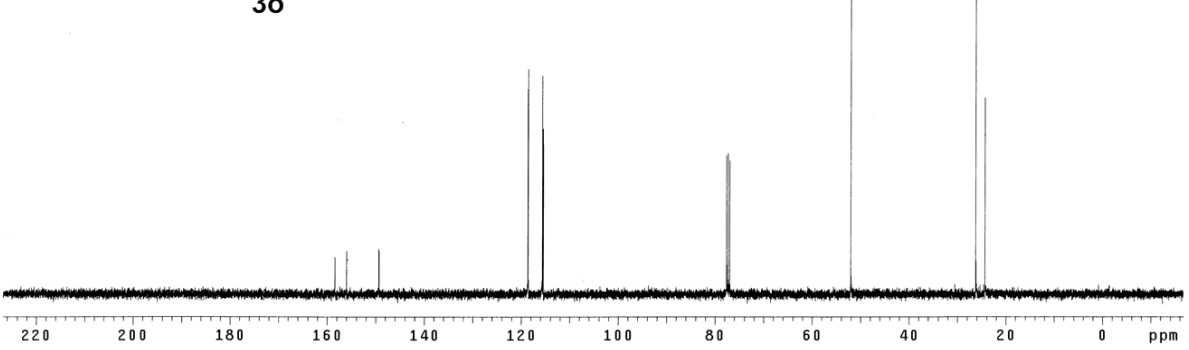


blk-002-035
File: BLK-002-035-cnmr-120713
Pulse Sequence: s2pul





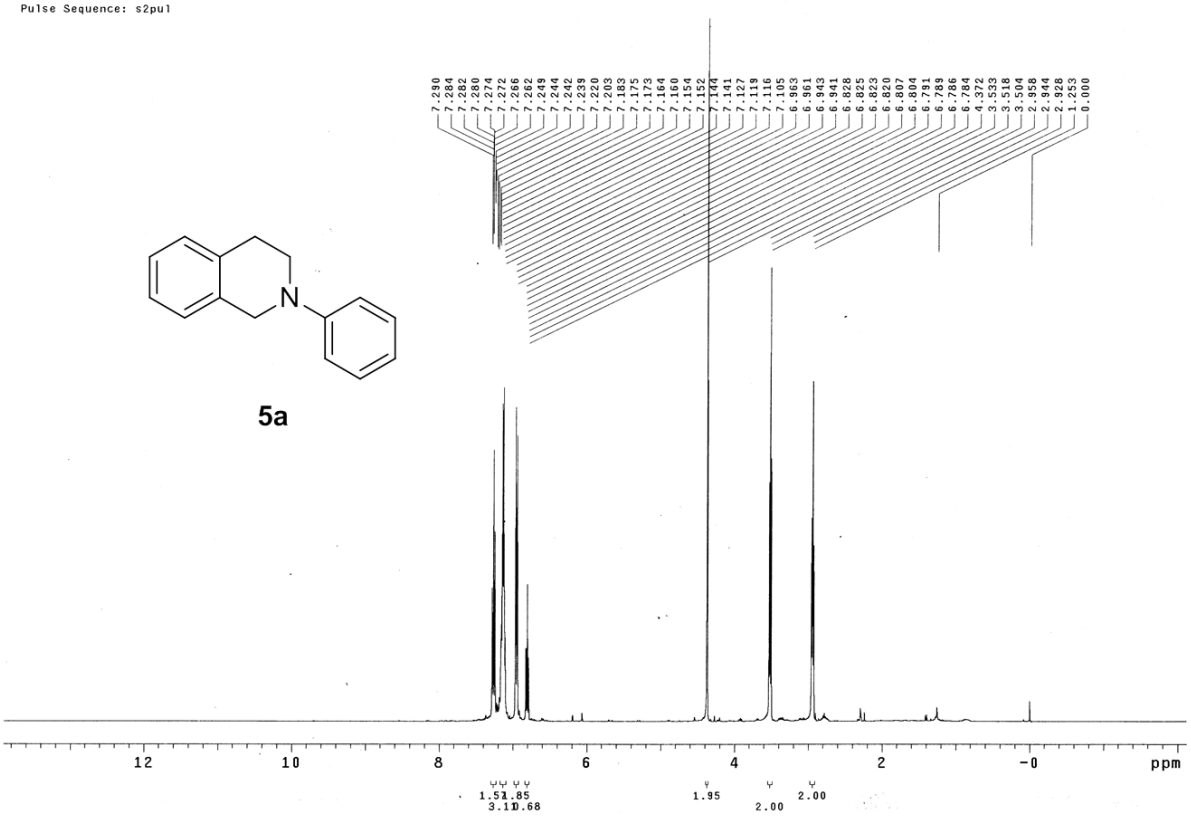
3o



blk-002-058

File: Proton

Pulse Sequence: s2pul

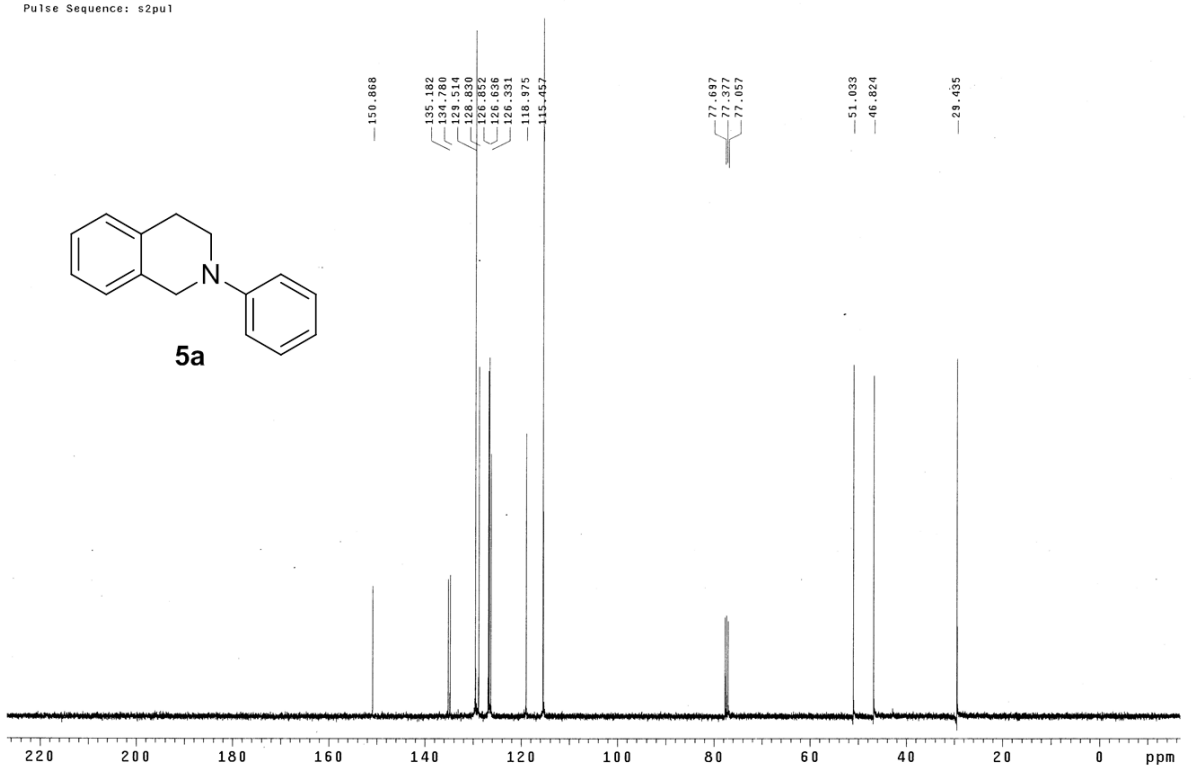


5a

blk-002-058

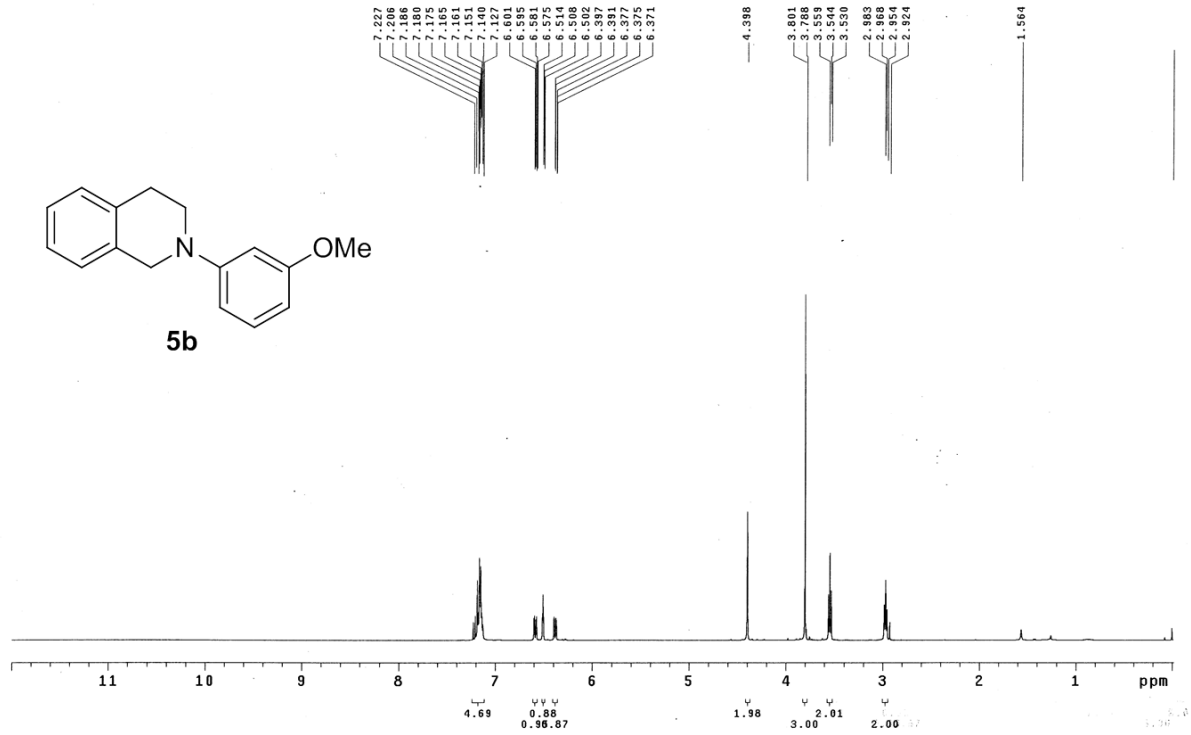
File: Carbon

Pulse Sequence: s2pul



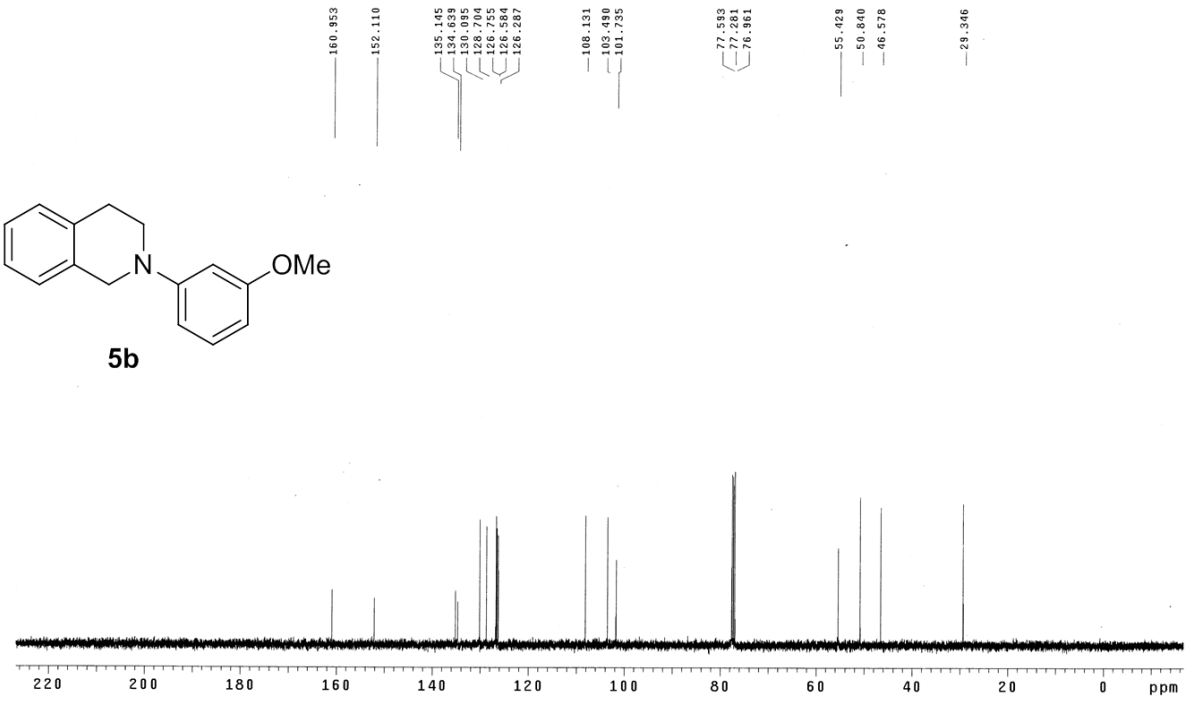
5a

blk-002-057
File: BLK-002-057-hnmr-120912
Pulse Sequence: s2pul



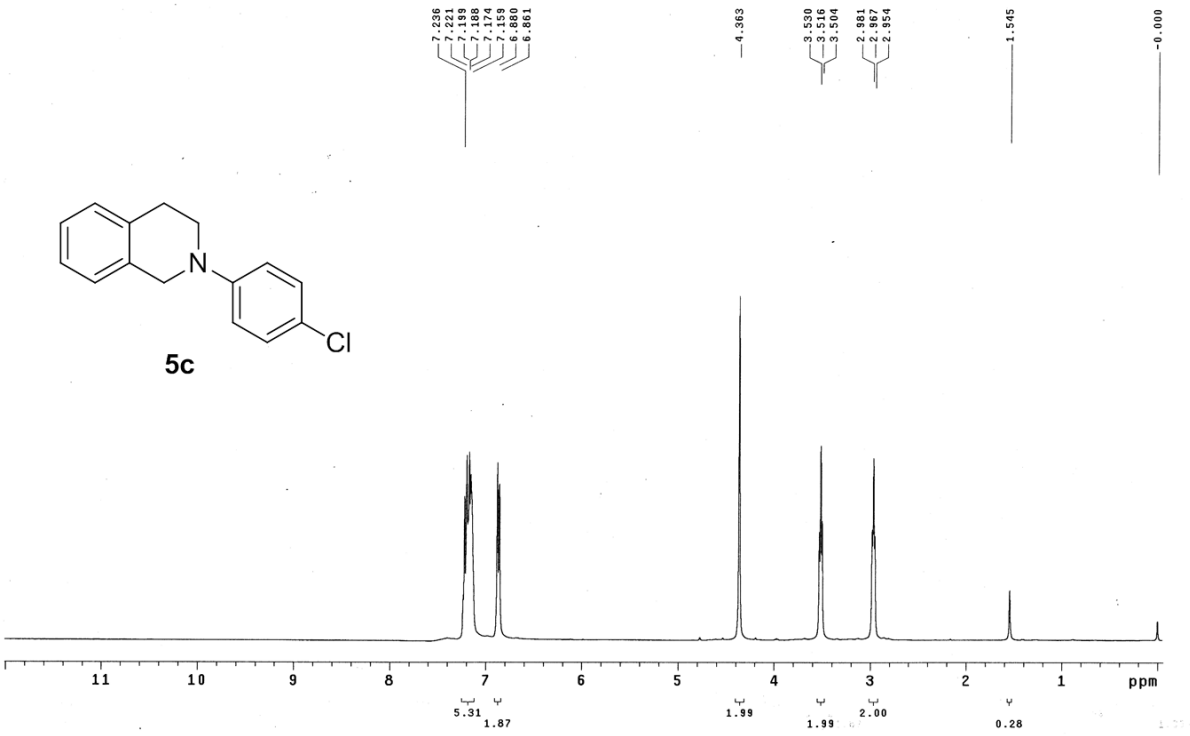
5b

blk-002-057
File: BLK-002-057-cnmr-120912
Pulse Sequence: s2pul

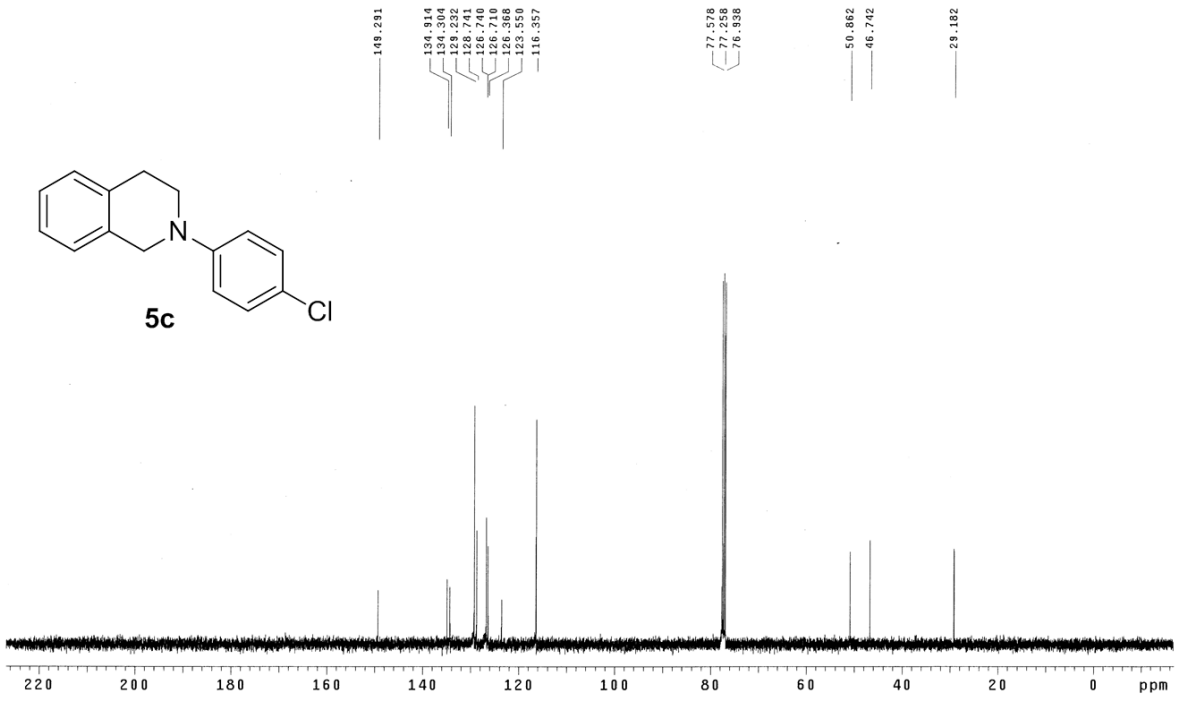


5b

blk-002-040
File: BLK-002-040-hnmr-120725
Pulse Sequence: s2pul

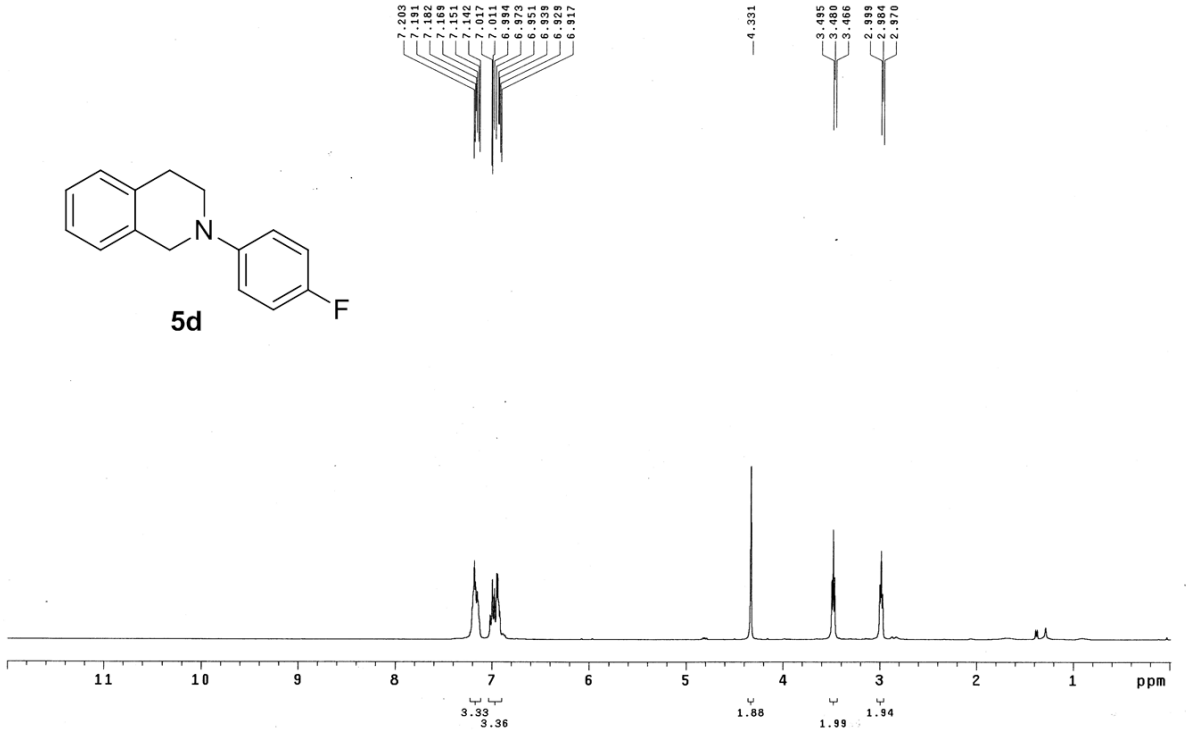


blk-002-040
File: BLK-002-040-cnmr-120725
Pulse Sequence: s2pul



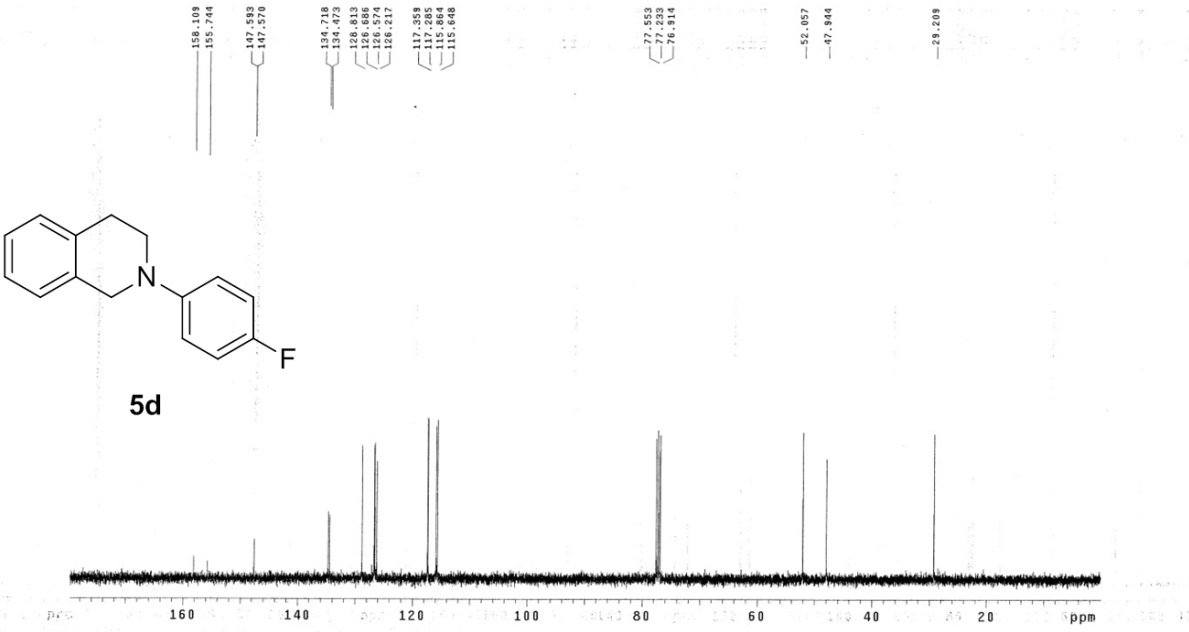
blk-002-037a
File: BLK-002-037a-hnmr-120723
Pulse Sequence: s2pul

5d



blk-002-037a
File: BLK-002-037a-cnmr-120723
Pulse Sequence: s2pul

5d



BLK-002-052A

Sample Name:

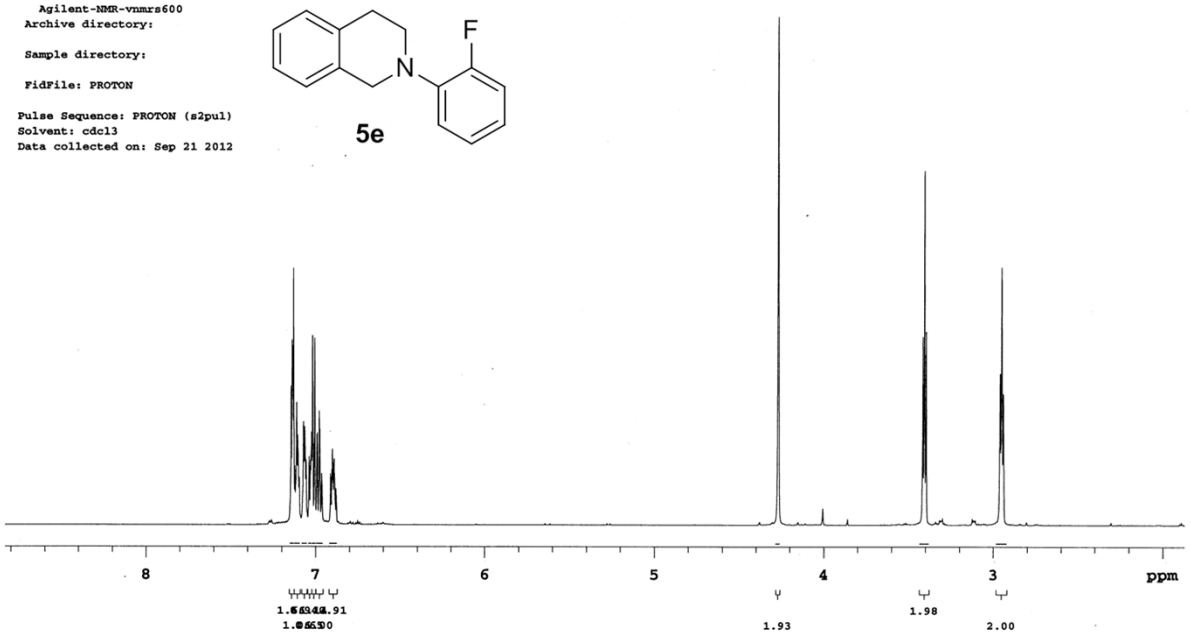
Data Collected on:
Agilent-NMR-vnmrs600
Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 21 2012

5e



BLK-002-052A

Sample Name:

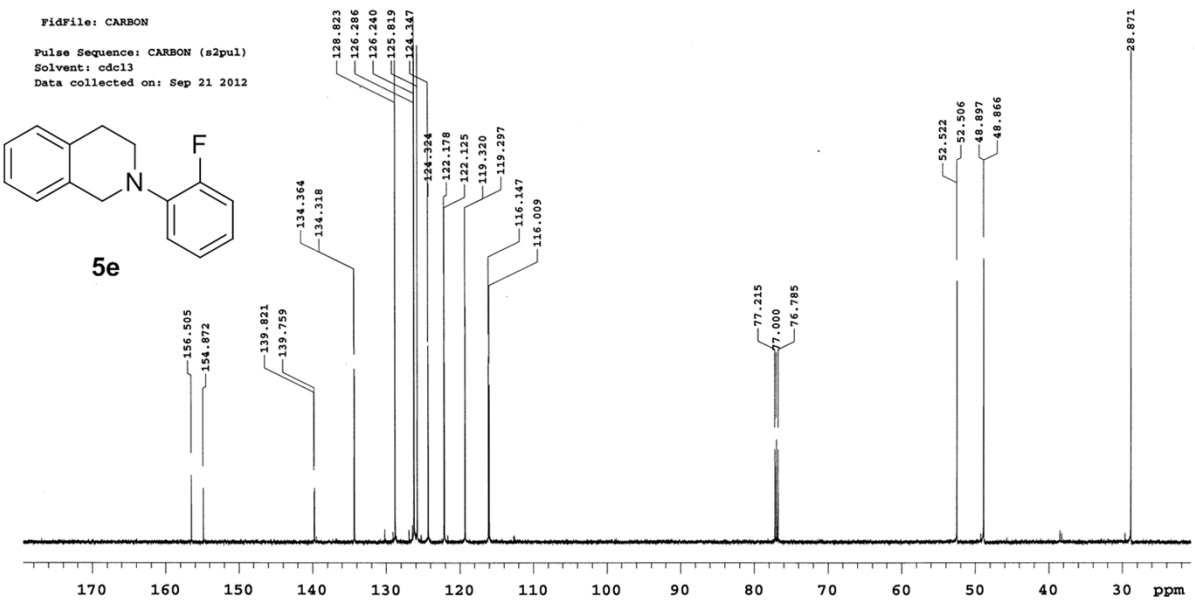
Data Collected on:
Agilent-NMR-vnmrs600
Archive directory:

Sample directory:

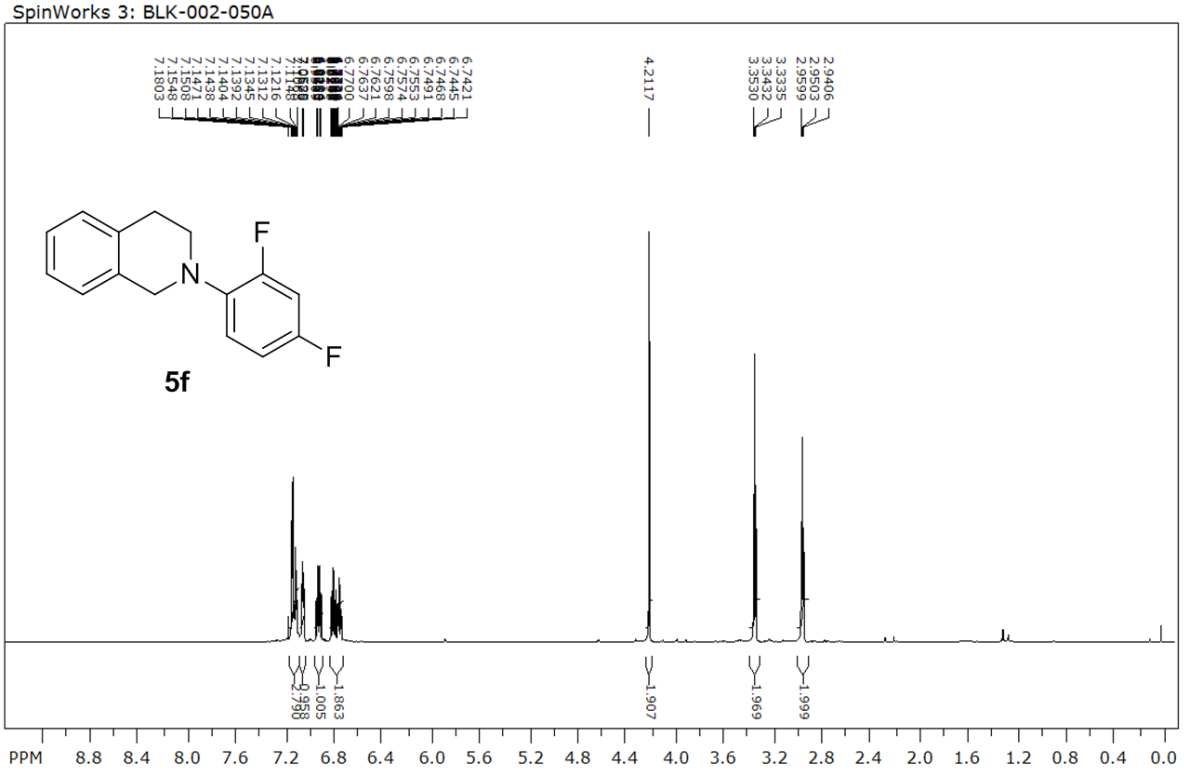
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 21 2012

5e



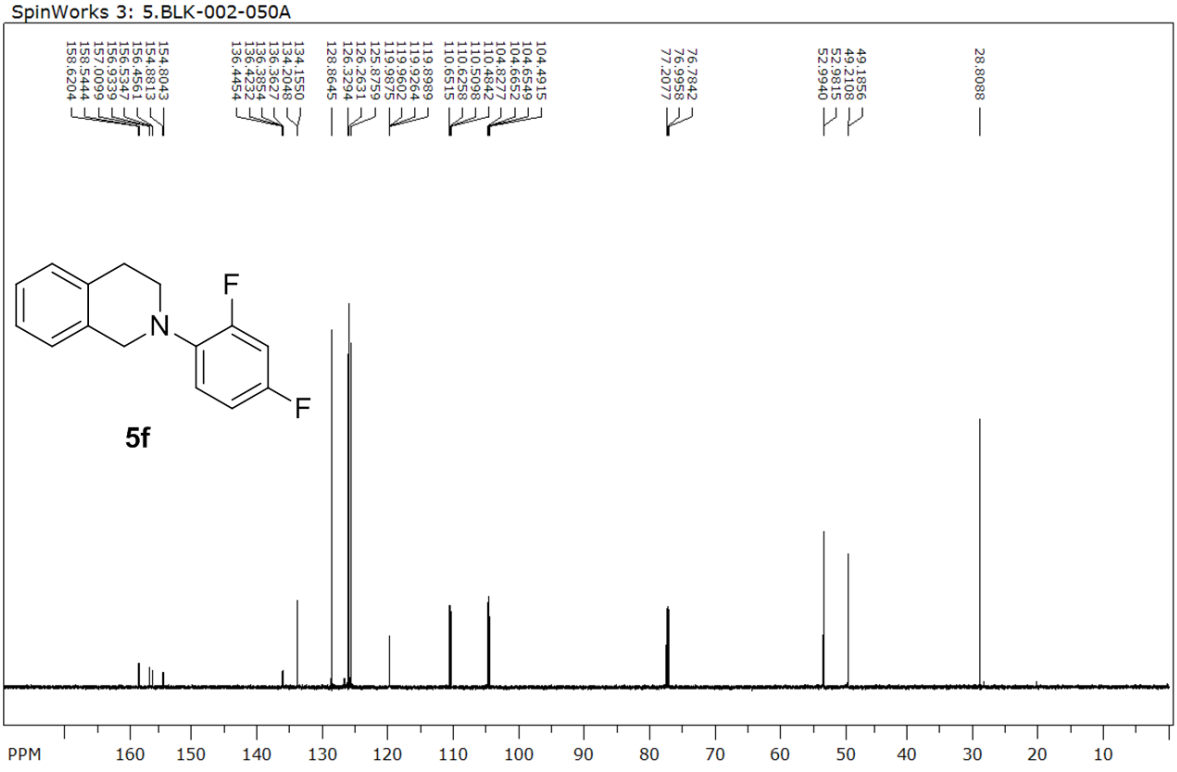
SpinWorks 3: BLK-002-050A



file: ...\NMR\12sep21\4blk-002-050a.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 599.859519 MHz
time domain size: 32768 points
width: 9615.38 Hz = 16.0294 ppm = 0.293438 Hz/pt
number of scans: 4

freq. of 0 ppm: 599.855968 MHz
processed size: 32768 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 230.769 ppm/cm: 0.38471

SpinWorks 3: 5.BLK-002-050A

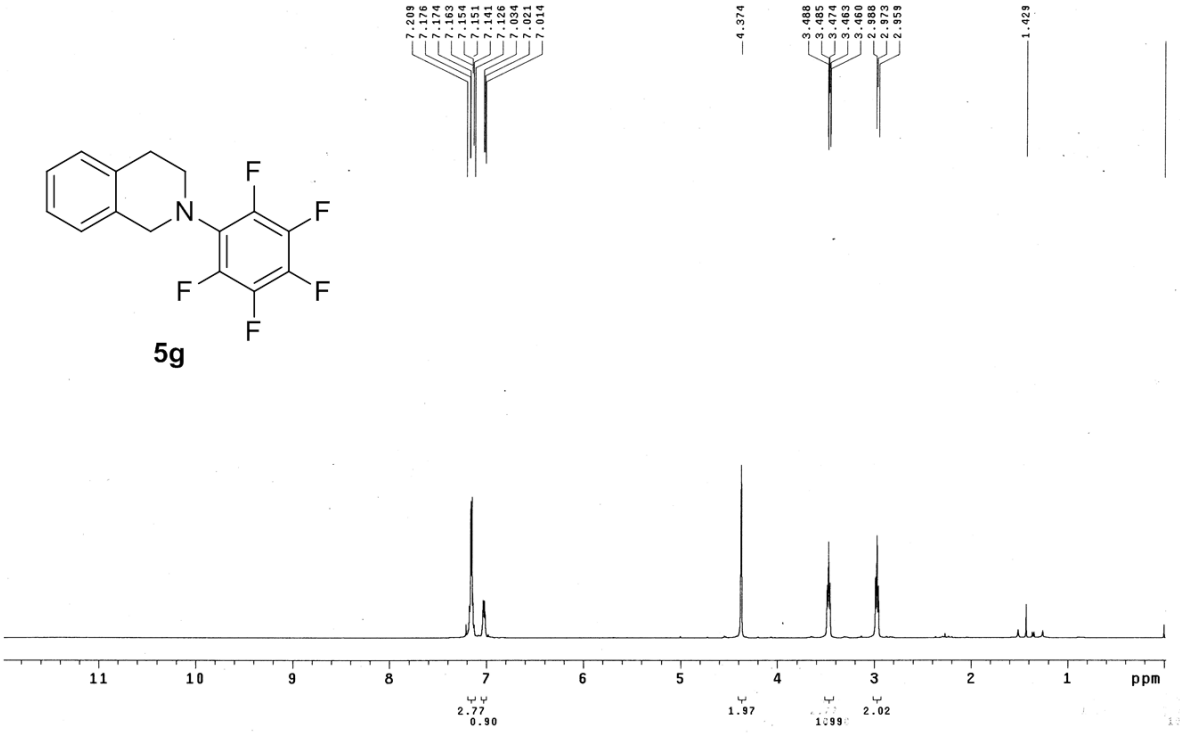


file: ...\12sep21\4blk-002-050a_13C.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 150.850483 MHz
time domain size: 65536 points
width: 37878.79 Hz = 251.1015 ppm = 0.577984 Hz/pt
number of scans: 80

freq. of 0 ppm: 150.833908 MHz
processed size: 65536 complex points
LB: 0.000 GF: 0.0000
Hz/cm: 1084.398 ppm/cm: 7.18856

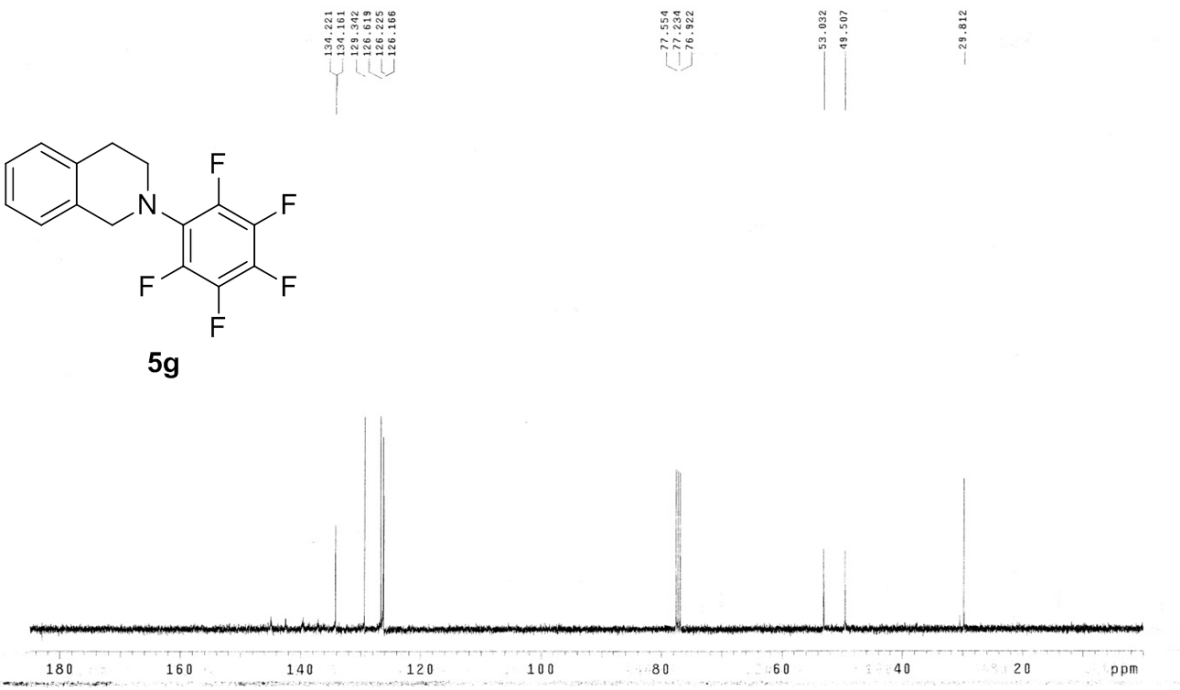
blk-002-051
File: BLK-002-051-hnmr-120821
Pulse Sequence: s2pul

5g

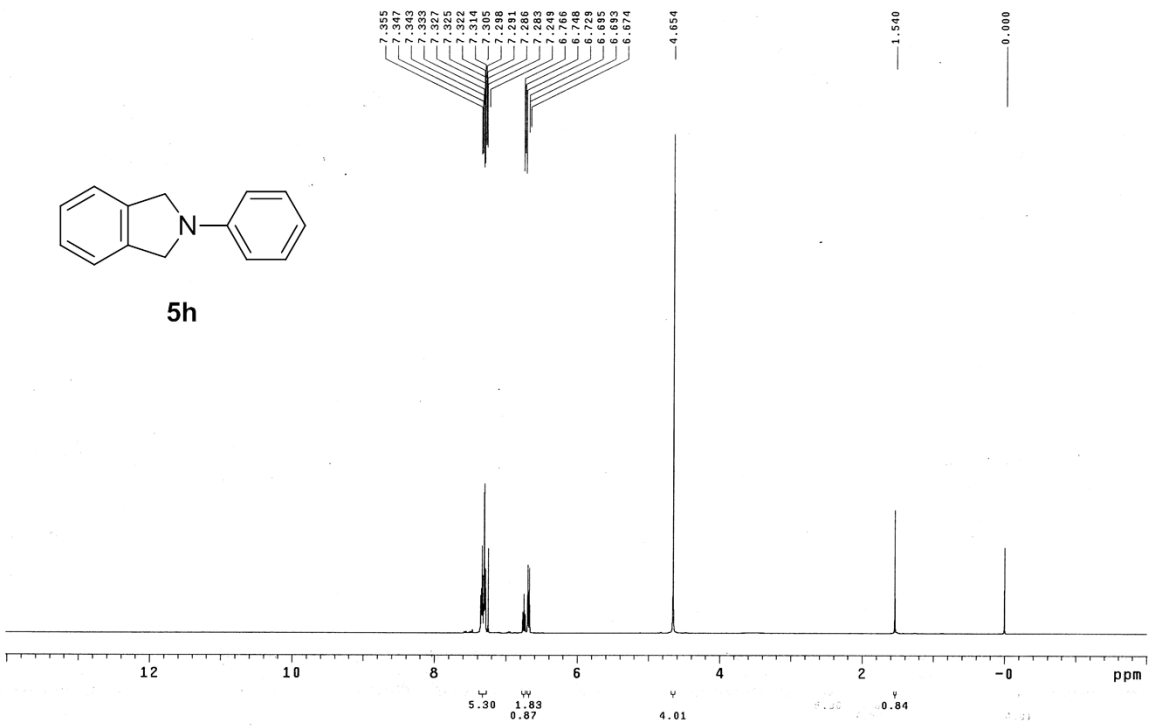


blk-002-051
File: BLK-002-051-cnmr-120821
Pulse Sequence: s2pul

5g

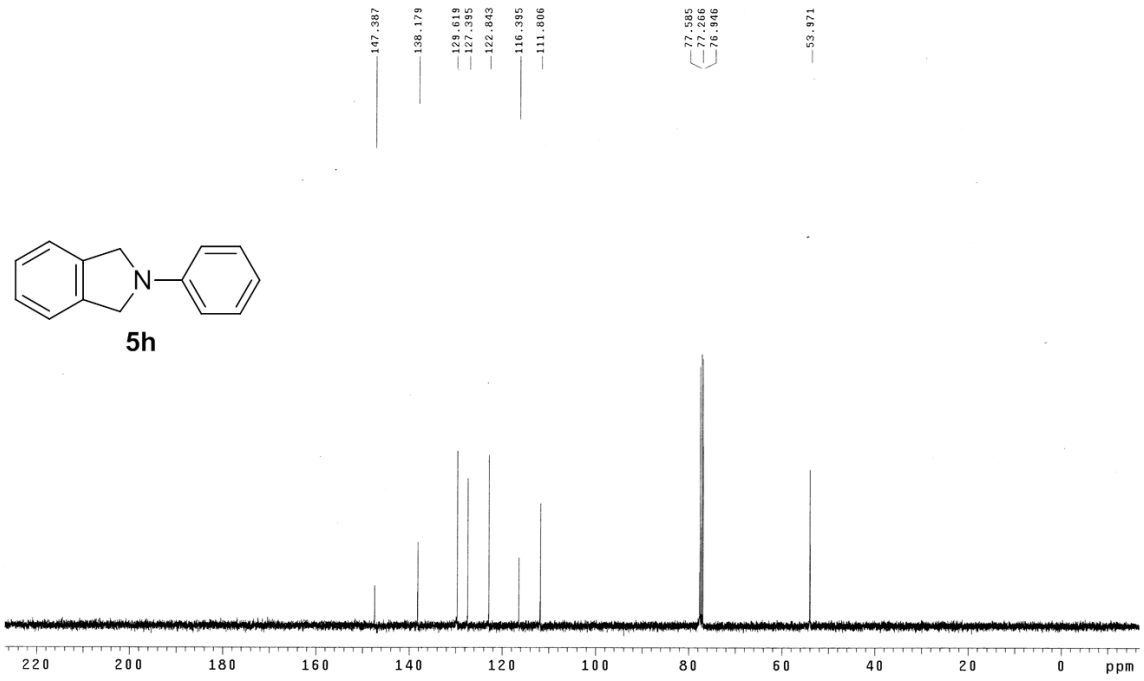


blk-002-049
File: BLK-002-049-hnmr-120810
Pulse Sequence: s2pul

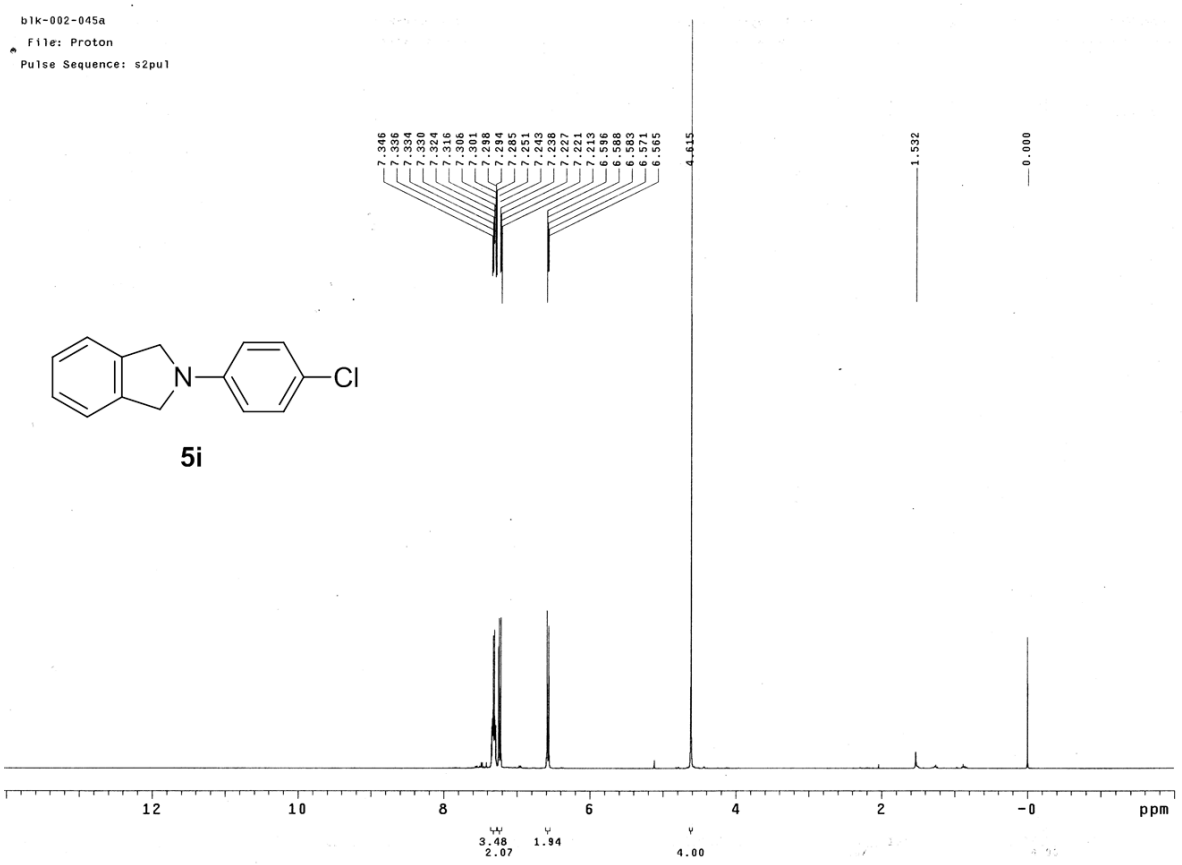


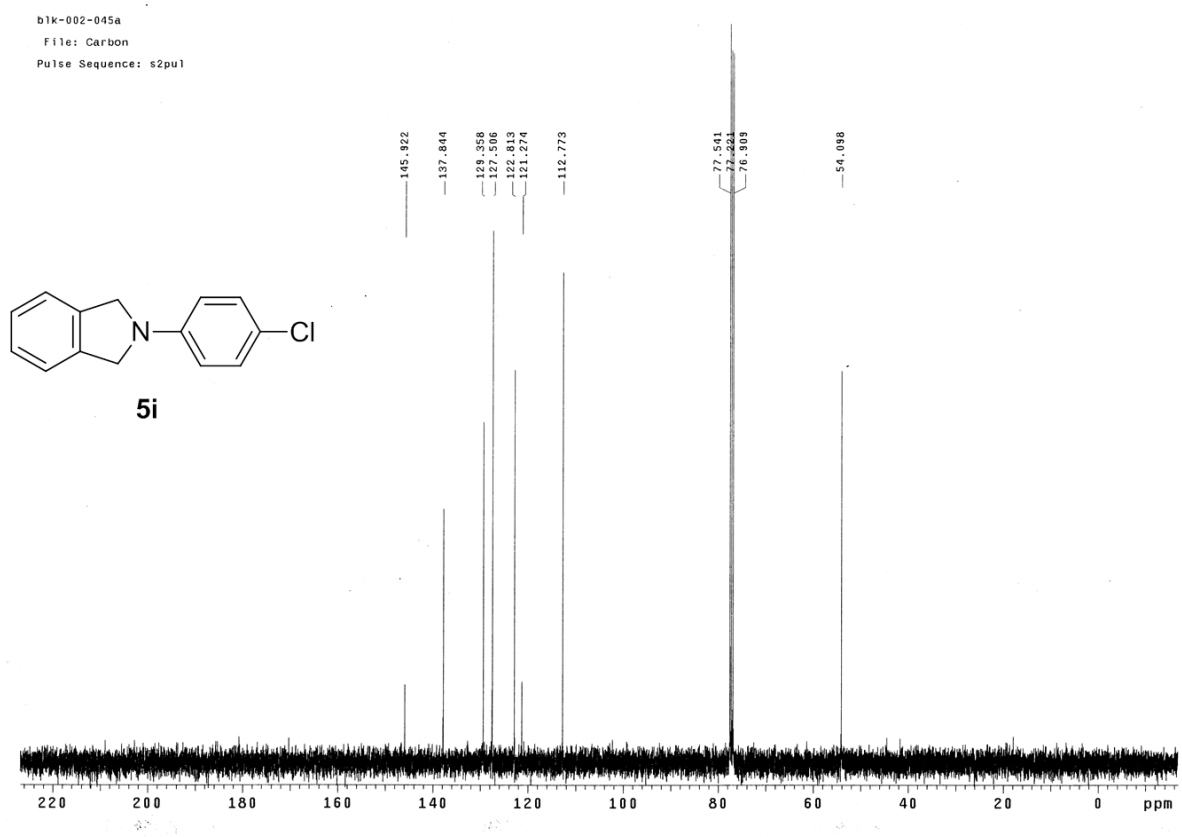
5h

blk-002-049a
File: BLK-002-049a-cnmr-120813
Pulse Sequence: s2pul

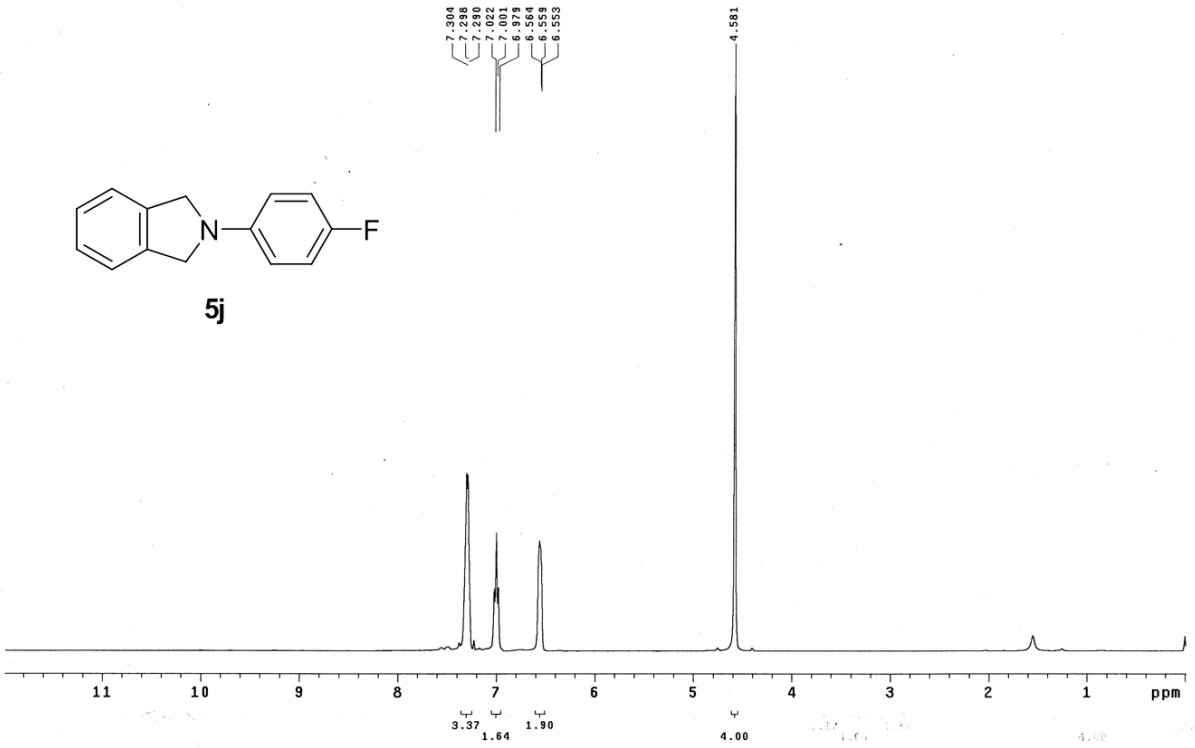


5h


blk-002-045a
File: Proton
Pulse Sequence: s2pul
7.346
7.336
7.334
7.330
7.324
7.316
7.306
7.301
7.298
7.294
7.285
7.251
7.243
7.238
7.227
7.221
7.213
6.596
6.588
6.583
6.571
6.565
4.615
1.532
0.000
N
Cl
5i
12
10
8
6
4
2
-0
ppm
3.48
2.07
1.94
4.00

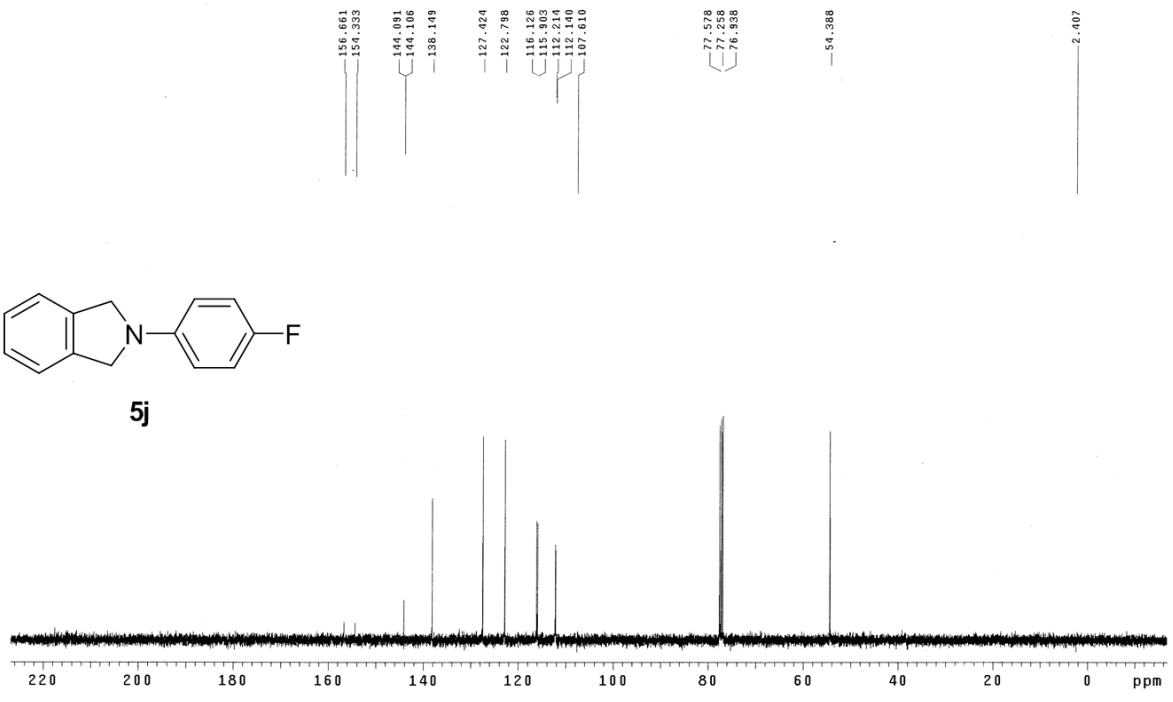

blk-002-045a
File: Carbon
Pulse Sequence: s2pul
145.922
137.844
129.358
127.506
122.813
121.274
112.773
77.541
77.221
76.909
54.098
N
Cl
5i
220
200
180
160
140
120
100
80
60
40
20
0
ppm

blk-002-039a
File: BLK-002-039a-hnmr-120806
Pulse Sequence: s2pul



5j

blk-002-039a
File: BLK-002-039a-cnmr-120806
Pulse Sequence: s2pul



5j